Total Synthesis of (±)-Cylindricine C

Guillaume Lapointe,[†] Kurt Schenk,[‡] and Philippe Renaud*,[†]

Departement für Chemie und Biochemie, Universität Berne Freiestrasse 3, CH-3012 Bern, Switzerland, and École Polytechnique Fédérale de Lausanne, Laboratoire de Cristallographie, Le Cubotron – Dorigny, CH-1015 Lausanne, Switzerland

philippe.renaud@ioc.unibe.ch

Supporting information

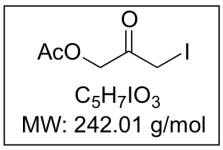
Section A: General Information

All reactions were performed under a nitrogen atmosphere, heat-gun dried glassware were used and standard precautions against moisture were taken. Silica gel 60 Å (40-60 μm) from SDS was used for flash column chromatography unless otherwise stated. Deactivated silica gel was prepared by adding 20% weight of hexamethyldisilazane (HMDS) to a suspension of silica gel in diethyl ether. After sonication for 5 minutes, the resulting mixture was used to wet pack a chromatography column. The column was then washed successively with diethyl ether, 50% diethyl ether/pentane, and finally the desired solvent before loading the sample. Reactions were monitored by thin-layer chromatography (TLC) carried out on Silicycle silica gel 60 F_{254} plates. Yields refer to chromatographically and spectroscopically pure compounds. Melting points are uncorrected. Commercial reagents were used as received. Solvents for reactions (distilled THF, Et_2O, benzene, toluene and CH_2Cl_2) were filtered over columns of dried alumina under a positive pressure of argon. Solvents for extraction and flash column chromatography were of technical grade and were distillated prior to use.

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-300 spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C at 22 ºC unless otherwise stated. Some ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE II-400 (^{1}H: 400MHz; ^{13}C 100MHz) spectrometer by the NMR group of Professor Bigler at the University of Bern. Chemical shift data are reported in units of δ (ppm) using as the internal standard residual $CHCl_3$ (δ = 7.26 for ^{1}H NMR spectra and δ = 77.0 for ^{13}C NMR spectra). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad) for ^{1}H spectra. Coupling constants, *J*, are reported in Hz. Infrared spectra were recorded on a Jasco FT-IR-460 Plus spectrometer equipped with a Specac MKII Golden Gate Single Reflection Diamond ATR System and is reported in wave numbers (cm^{-1}). Low and high- resolution mass spectra were recorded on a Waters Micromass Autospec Q mass spectrometer in EI mode at 70 eV. GC-MS: Finnigan Trace GC 2000 gas chromatograph equipped with an autosampler and a Trace MS mass selective detector. GC: CE instruments HRGC series 8532 using MN *optima d-3*, ID 0.25 mM, 30m. Melting points were measured on a Büchi Melting point B-545 apparatus.

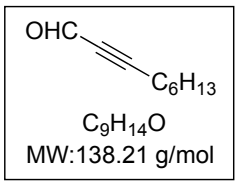
Caution: Since organic azides are capable of exploding, it is strongly recommended to apply standard safety rules and to use a safety shield.

Section B: Synthesis of compounds



1-Acetoxy-3-iodoacetone (**5**). To a stirred solution of sodium iodide (5.21 g, 35.0 mmol) in acetone (60 mL) was added the 1-acetoxy-3-chloroacetone (4.50 g, 30.0 mmol) as a solution in acetone (10 mL) at room temperature. *The reaction mixture has to be protected from light.* The solution is stirred for 12 h and water (60 mL) is then added. The mixture was extracted with Et_2O (3 x 100 mL), washed with brine (100 mL), dried on Na_2SO_4, filtered, and concentrated under reduced pressure.

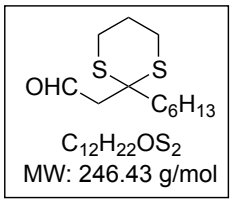
Purification by flash column chromatography (pentane/Et_2O 70:30) afforded **5** as a yellow oil (6.53 g, 90%). Physical and spectral data were in accordance with those reported in the literature.[1] *In order to avoid decomposition, the pure product was freezed at -20 °C, protected from light.* ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.93 (s, 2H), 3.86 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.75, 169.85, 64.76, 20.29, 0.71.



Non-2-ynal (**6**). To a solution of 1-octyne (7.35 mL, 50.0 mmol) and lithium bromide (5.20 g, 60.0 mmol) in THF (250 mL) at –78 ºC was added *n*-butyllithium (2.5 M in hexanes, 21.0 mL, 52.5 mmol). The reaction mixture was stirred at this temperature for 1 h. Then, DMF (20.0 mL, 250 mmol) was added and the resultant solution was slowly warmed to rt overnight. An NH_4Cl saturated aqueous solution (100 mL) and Et_2O (300 mL) was poured into the reaction mixture, the phases were separated, and the aqueous phase was extracted with Et_2O (2 x 200 mL). The combined organic extracts were washed with brine (250 mL), dried on Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (pentane/Et_2O 95:5) afforded a pale yellow oil (6.62 g, 96%). Spectral data were in accordance with those reported in the literature.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.18 (s, 1H), 2.41 (td, *J* = 7.1, 0.6 Hz, 2H), 1.66-1.54 (m, 2H), 1.48-1.35 (m, 2H), 1.35-1.24 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 176.86, 99.00, 81.56, 31.02, 28.33, 27.37, 22.28, 18.92, 13.78. IR (neat) 2953, 2929, 2858, 2199, 1668, 1136. MS

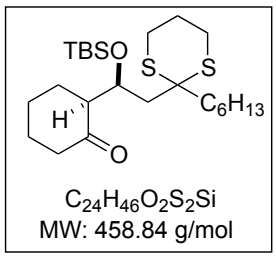
1) Clark, E. R.; Howes, J. G. B. *J. Chem. Soc.* **1956**, 1152.
2) Prakesch, M.; Grée, D.; Grée, R. *Tetrahedron* **2003**, *59*. 8833.

(EI, 70ev) *m/z* (%) 123 (7), 109 (36), 95 (39), 81 (57), 79 (41), 68 (49), 67 (73), 59 (51), 55 (52), 43 (100). HRMS (ESI) for $C_9H_{14}ONa$ calcd 161.0942, found 161.0937.



$C_{12}H_{22}OS_2$
MW: 246.43 g/mol

[2-Hexyl-[1,3]dithiane-2-yl]-acetaldehyde (**7**). 1,3-Propanedithiol (4.7 mL, 47 mmol) and NaOMe (3.05 g, 56.4 mmol) were added to non-2-ynal **6** (6.50 g, 47.0 mmol) in MeOH (310 mL) and CH_2Cl_2 (60 mL) at – 10 ºC. The reaction mixture was stirred at this temperature for 3 h. After this time the reaction was treated with NH_4Cl saturated aqueous solution (250 mL) and Et_2O (300 mL) was poured into the mixture. The phases were then separated, and the aqueous phase was extracted with Et_2O (3 x 200 mL). The combined organic extracts were washed with brine (250 mL), dried on Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (pentane/Et_2O 95:5) afforded a pale yellow oil (11.47 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.77 (t, *J* = 2.9 Hz, 1H), 2.97-2.76 (m, 6H), 2.11-1.86 (m, 4H), 1.57-1.45 (m, 2H), 1.37-1.24 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.72, 50.04, 49.23, 40.35, 31.47, 29.25, 26.14 (2C), 24.66, 23.91, 22.47, 13.96. IR (neat) 2928, 2855, 1716, 1423, 1277, 1050, 907. MS (EI, 70ev) *m/z* (%) 246 (M, 35), 203 (41), 161 (83), 133 (45), 107 (50), 74 (100). HRMS (ESI) for $C_{12}H_{22}ONaS_2$ calcd 269.1009, found 269.1012.

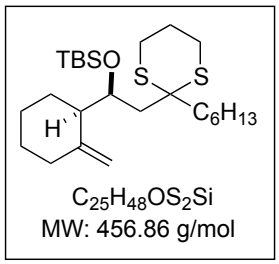


$C_{24}H_{46}O_2S_2Si$
MW: 458.84 g/mol

(S)-2-((S*)-1-((tert-Butyldimethylsilyl)oxy)-2-(2-hexyl-1,3-dithian-2-yl)ethyl)cyclohexanone* (**8**). To a solution of diisopropylamine (6.6 mL, 47 mmol) in THF (185 mL) was added at 0 ºC *n*-butyllithium (2.5 M in hexanes, 18.8 mL, 47.0 mmol). The mixture was stirred at this temperature for 0.5 h, and afterward cooled to – 78 ºC. Cyclohexanone (4.9 mL, 47 mmol) was then added, and the reaction mixture was further stirred at – 78 ˚C for 1 h. The aldehyde **7** (10.50 g, 42.60 mmol) in THF (15 mL) was injected slowly in the solution, and after stirring for 5 minute at – 78 ºC an NH_4Cl aqueous solution (100 mL) and Et_2O (200 mL) were poured into the reaction mixture. The phases were then separated, and the aqueous phase was extracted with Et_2O (3 x 200 mL). The combined organic extracts were washed with brine (250 mL), dried on Na_2SO_4, filtered and concentrated under reduced pressure. Purification by passing through a

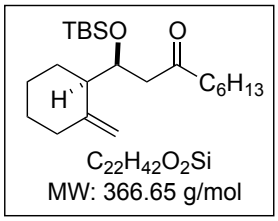
short silica pad (pentane/Et_2O 75:25) afforded a colorless oil that was directly used in the next step.

To the aldol product in DMF (21 mL) was added DMAP (0.26 g, 2.1 mmol), imidazole (4.38 g, 64.4 mmol) and TBSCl (9.70 g, 64.4 mmol). The reaction mixture was then stirred at rt for 48 h. NH_4Cl aqueous solution (50 mL) and Et_2O (100 mL) was then poured into the reaction. The phases were separated, and the aqueous phase was extracted with Et_2O (3 x 100 mL). The combined organic extracts were washed with brine (200 mL), dried on Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (pentane/Et_2O 95:5) afforded an amorphous white solid (16.81 g, 86%, *anti/syn* 94:6). The diastereoisomers were not separated. *anti*-**8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.68-4.60 (m, 1H), 3.42 (ddd, *J* = 14.3, 11.8, 2.6 Hz, 1H), 2.95 (ddd, *J* = 14.3, 11.8, 2.6 Hz, 1H), 2.79-2.46 (m, 3H), 2.44-2.24 (m, 4H), 2.17-2.03 (m, 2H), 2.03-1.77 (m, 5H), 1.75-1.46 (m, 3H), 1.38-1.19 (m, 6H), 0.97-0.81 (m, 5H), 0.89 (s, 9H), 0.12 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 211.94, 69.31, 57.44, 53.78, 42.48, 40.73, 39.65, 31.84, 29.63, 27.26, 26.78, 26.62, 25.99 (3C), 25.86, 25.46, 25.26, 24.01, 22.64, 18.06, 14.05, -3.33, -4.45. *anti/syn*-**21**: IR (neat) 2949, 2929, 2853, 1707, 1254, 1100, 1053, 835. MS (EI, 70ev) *m/z* (%) 458 (M, 1), 401 (5), 241 (8), 203 (100), 183 (69), 155 (8), 75 (28), 73 (52). HRMS (ESI) for $C_{24}H_{46}O_2NaSiS_2$ calcd 481.2606, found 481.2614.



tert-Butyl((S)-2-(2-hexyl-1,3-dithian-2-yl)-1-((R*)-2-methylenecyclohexyl)ethoxy)dimethylsilane* (**9**). To methyltriphenylphosphonium bromide (17.5 g, 49.0 mmol) in Et_2O (120 mL) was added at 0 ºC potassium *tert*-butoxide (5.50 g, 49.0 mmol). The reaction mixture was stirred at rt for 1 h, and ketone **8** (18.72 g, 40.80 mmol) in Et_2O (120 mL) was slowly added to the reaction mixture. The solution was stirred for another 2.5 h and diluted with pentane (500 mL). The solution was filtered over a silica pad, and the silica was further washed with a mixture of Et_2O/pentane (20/80). The solvent was then removed under reduced pressure, and further purification by flash column chromatography (pentane/Et_2O 95:5) afforded **9** as a yellow oil (17.71 g, 95%, 1 diastereoisomer observed). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.84 (d, *J* = 1.3 Hz, 1H), 4.79 (d, *J* = 1.3 Hz, 1H), 4.37 (dt, *J* = 7.5, 2.9 Hz, 1H), 2.86-2.70 (m, 4H), 2.34 (dd, *J* = 15.0, 3.3 Hz, 1H), 2.31-2.17 (m, 1H), 2.05-1.70 (m, 8H), 1.53-1.43 (m, 1H), 1.39-

1.22 (m, 10H), 0.93-0.84 (m, 5H), 0.89 (s, 9H), 0.13 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.06, 107.36, 71.21, 53.52, 49.90, 42.01, 39.43, 37.59, 31.90, 29.59, 28.53, 28.26, 26.43, 26.39, 26.29, 26.10 (3C), 25.30, 24.68, 22.68, 18.22, 14.07, -3.32, -4.41. IR (neat) 2927, 2854, 1462, 1048, 833. MS (EI, 70ev) *m/z* (%) 419 (4), 345 (22), 275 (35), 239 (22), 207 (22), 203 (100), 181 (19), 165 (15), 133 (15), 73 (71). HRMS (ESI) for $C_{25}H_{48}ONaSiS_2$ calcd 479.2800, found 479.2794.

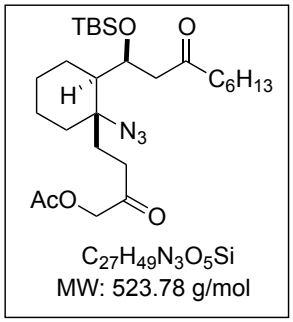


(S)-1-((tert-Butyldimethylsilyl)oxy)-1-((R*)-2-methylene cyclohexyl)nonan-3-one* (**4**). To alkene **9** (2.28 g, 5.00 mmol) and sodium bicarbonate (2.52 g, 30.0 mmol) in acetone/ H_2O (390/18 mL) was added portionwise at 0 ºC iodide (3.81 g, 15.0 mmol). The reaction mixture was stirred at 0 ºC for 1 h, and then a 10% $Na_2S_2O_3$ aqueous solution (50 mL), water (100 mL) and Et_2O (300 mL) were poured into the reaction. The phases were separated, and the aqueous phase was extracted with Et_2O (3 x 250 mL). The combined organic extracts were washed with brine (400 mL), dried on Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (pentane) afforded **4** as a colorless oil (1.43 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.72 (s, 1H), 4.59-4.53 (m, 1H), 4.51 (s, 1H), 2.66-2.56 (m, 2H), 2.41 (td, *J* = 7.2, 1.8 Hz, 2H), 2.24 (dt, *J* = 13.5, 3.9 Hz, 1H), 2.14-1.97 (m, 2H), 1.94-1.84 (m, 1H), 1.80-1.65 (m, 2H), 1.60-1.52 (m, 1H), 1.42-1.23 (m, 9H), 0.94-0.81 (m, 4H), 0.89 (s, 9H), 0.05 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 210.08, 149.36, 107.21, 69.28, 48.91, 47.06, 44.50, 36.49, 31.59, 28.87, 28.32, 28.11, 25.82 (3C), 25.42, 23.50, 22.47, 17.93, 13.98, -4.74, -4.86. IR (neat) 2927, 2855, 1715, 1462, 1254, 1056, 835. MS (EI, 70ev) *m/z* (%) 309 (5), 271 (21), 217 (55), 213 (74), 183 (20), 133 (33), 113 (100), 85 (34), 75 (74). HRMS (ESI) for $C_{22}H_{42}O_2NaSi$ calcd 389.2851, found 389.2850.

Tin-mediated radical carboazidation: Di-*tert*-butylhyponitrite (35 mg, 0.20 mmol) was added in one portion to a solution of **4** (734 mg, 2.00 mmol), 1-acetoxy-3-iodoacetone **5** (532 mg, 2.20 mmol), hexabutyldistannane (1.2 ml, 2.4 mmol) and 3-$PySO_2N_3$ (1.1 g, 6.0 mmol) in benzene (4 mL). The solution was warmed to 70 ºC for 3 h and the crude mixture was directly purified by flash column chromatography

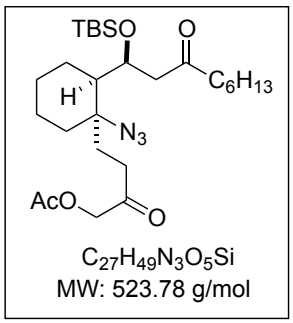
(pentane/Et_2O 80/20) using 10% KF/ 90% silica gel as stationary phase. Colorless oil (785 mg, 75%, *trans/cis* 7:3).

Et_3B-mediated radical carboazidation: A 2 M solution of Et_3B in EtOH (2 mL, 4 mmol) was added over 2 h at rt to a open-flask, vigorously stirred mixture of **4** (367 mg, 1.00 mmol), **5** (266 mg, 1.10 mmol) and 3-$PySO_2N_3$ (0.55 g, 3.0 mmol) in H_2O/EtOH (0.5/0.5 mL). *The needle should be immersed into the reaction mixture in order to avoid a direct contact of Et_3B drops with air.* After 1 h of extra stirring, Et_2O (10 mL) and water (5 mL) were added and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 10 mL) and the combined organic extracts were washed with H_2O (20 mL), brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane/Et_2O 80/20). Colorless oil (0.31 g, 59%, *trans/cis* 7:3).



$C_{27}H_{49}N_3O_5Si$
MW: 523.78 g/mol

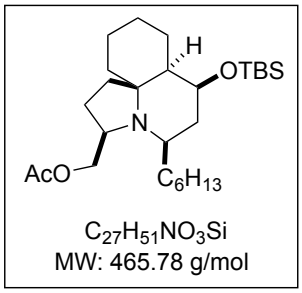
4-((1S,2R*)-1-Azido-2-((S*)-1-((tert-butyldimethylsilyl)oxy)-3-oxononyl)cyclohexyl)-2-oxobutyl acetate* (*trans*-**3**). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.68 (dt, *J* = 16.7 Hz, 1H), 4.60 (d, *J* = 16.7 Hz, 1H), 4.54-4.47 (m, 1H), 2.64-2.59 (m, 2H), 2.58-2.44 (m, 1H), 2.39 (td, *J* = 7.2, 2.8 Hz, 2H), 2.37-2.30 (m, 1H), 2.16 (s, 3H), 2.00-1.62 (m, 7H), 1.61-1.35 (m, 4H), 1.35-1.21 (m, 8H), 0.94-0.79 (m, 3H), 0.84 (s, 9H), 0.10 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 209.18, 203.19, 170.17, 68.59, 67.87, 65.75, 51.35, 48.14, 44.18, 33.66, 33.23, 31.57, 28.85, 25.83 (3C), 25.68, 25.05, 24.86, 23.37, 22.50, 22.46, 20.41, 17.91, 13.98, -4.72, -4.93. IR (neat) 2930, 2853, 2094, 1752, 1734, 1714, 1374, 1247, 1230, 1050, 910, 836. HRMS (ESI) for $C_{27}H_{49}N_3O_5NaSi$ calcd 546.3339, found 546.3355.



$C_{27}H_{49}N_3O_5Si$
MW: 523.78 g/mol

4-((1R,2R*)-1-Azido-2-((S*)-1-((tert-butyldimethylsilyl) oxy)-3-oxononyl)cyclohexyl)-2-oxobutyl acetate* (*cis*-**3**). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.69 (s, 2H), 4.48 (dt, *J* = 9.0, 2.3 Hz, 1H), 2.79 (dd, *J* = 16.5, 2.1 Hz, 1H), 2.63-2.31 (m, 5H), 2.18 (s, 3H), 2.16-1.80 (m, 5H), 1.70-1.13 (m, 14H), 0.93-0.79 (m, 3H), 0.83 (s, 9H), 0.05 (s, 3H), -0.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 209.84, 202.43, 170.17, 67.89, 66.66, 64.26, 50.74, 46.10, 44.58, 34.58, 33.38, 32.17, 31.58, 28.86, 25.77, 25.71 (3C), 23.41, 22.46, 22.12, 20.98, 20.41, 17.86, 13.98, -4.75, -4.77. IR

(neat) 2950, 2929, 2856, 2097, 1756, 1737, 1713, 1374, 1255, 1229, 1059, 837. HRMS (ESI) for $C_{27}H_{50}N_3O_5Si$ calcd 524.3514, found 524.3519.

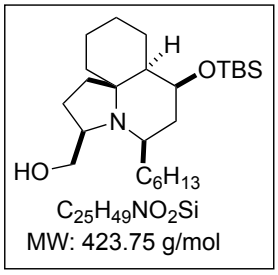


$C_{27}H_{51}NO_3Si$
MW: 465.78 g/mol

((3R,5R*,7S*,7aR*,11aS*)-7-((tert-Butyldimethylsilyl)oxy)-5-hexyldecahydro-1H-pyrrolo[2,1-j]quinolin-3-yl)methyl acetate* (**12**). **Reductive amination with Raney nickel**: Raney nickel (50% slurry in water, 4 g) was added to a solution of the *trans*-**3** (1.3 g, 2.5 mmol) in 5 mL ethyl acetate. The mixture was then pressurized under hydrogen (40 bar) and allowed to react at room temperature for 96 h. After completion, the mixture was filtered through Celite®, washed with EtOAc (5 mL), and a 1:9 MeOH/CH_2Cl_2 solution (5 mL). The combined organic extracts were dried on Na_2SO_4, and concentrated under reduced pressure to afford crude amine **11.** ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.77-4.69 (m, 1H), 4.67-4.62 (m, 1H), 4.09 (dd, *J* = 10.7, 5.0 Hz, 1H), 4.00 (dd, *J* = 10.7, 6.7 Hz, 1H), 3.51-3.40 (m, 1H), 2.63-2.51 (dd, *J* = 15.0, 9.2 Hz, 1H), 2.45-2.34 (m, 3H), 2.11-2.04 (m, 1H), 2.07 (s, 3H), 1.87-1.01 (m, 22H), 0.91-0.77 (m, 3H), 0.82 (s, 9H), 0.04 (s, 3H), -0.02 (s, 3H). ^{3}C NMR (75 MHz, $CDCl_3$) δ = 210.59, 171.04, 69.25, 68.47, 63.57, 54.68, 52.74, 47.45, 44.68, 43.92, 31.61, 29.69, 28.88, 28.55, 26.46, 25.79, 25.77, 24.10, 23.33, 22.46, 20.92, 17.89, 13.98, -4.42, -4.71. To the crude **11** in dichloroethane (25 mL) was added AcOH (0.5 mL) and $NaBH(OAc)_3$ (2.1 g, 10 mmol). The reaction was stirred for 18 h, after which it was treated with NaOH 1N (50 mL) and diluted with Et_2O (100 mL). The phases were separated and the aqueous phase was extracted with Et_2O (5 x 25 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The product was purified by flash column chromatography using HMDS pre-treated silica gel. (pentane/Et_2O 90/10). Colorless crystal (0.84 g, 72%, 1 diastereoisomer observed by ^{1}H NMR). m.p. 63.4-65.4 ºC.

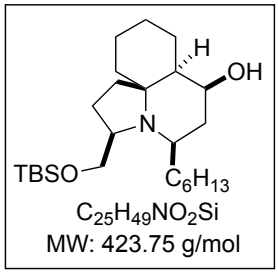
Reduction with Stannous chloride: Stannous chloride (0.21 g, 1.1 mmol) in acetonitrile (4 mL) was added to a mixture of thiophenol (0.45 mL, 4.4 mmol), triethylamine (0.46 mL, 3.3 mmol) and *trans*-**3** (385 mg, 0.730 mmol) in acetonitrile (3 mL). The reaction mixture was stirred at room temperature for 3 h, after which AcOH (1 mL) and $NaBH(OAc)_3$ (1.2 g, 5.5 mmol) were added. The reaction was further stirred for 24 h, after which it was treated with NaOH 1N (5 mL) and diluted

with Et_2O (20 mL). The phases were separated and the aqueous phase was extracted with Et_2O (5 x 25 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The product was purified by flash column chromatography using HMDS pre-treated silica gel. (pentane/Et_2O 90/10). Colorless crystal (246 mg, 72%, 1 diastereoisomer observed by ^1H NMR). m.p. 63.4-65.4 ºC. ^1H NMR (300 MHz, $CDCl_3$) δ = 4.45 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.07 (d, *J* = 10.5 Hz, 1H), 4.03 (d, *J* = 10.5 Hz, 1H), 3.45-3.35 (m, 1H), 2.99 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.45-2.32 (m, 1H), 2.12-2.01 (m, 1H), 2.03 (s, 3H), 1.84-1.59 (m, 6H), 1.53-1.21 (m, 17H), 0.94-0.83 (m, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.80, 71.66, 66.56, 63.64, 58.88, 50.05, 46.79, 42.01, 39.61, 32.92, 31.92, 29.39, 28.34, 27.90, 27.03, 26.97, 26.04 (3C), 25.80, 24.84, 22.66, 21.03, 18.24, 14.09, -4.29, -5.11. IR (neat) 2958, 2925, 2855, 1740, 1230, 1033, 835. HRMS (ESI) for $C_{27}H_{52}NO_3Si$ calcd 466.3711, found 466.3707.



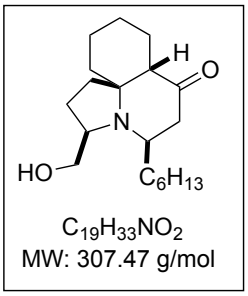
$C_{25}H_{49}NO_2Si$
MW: 423.75 g/mol

((3R,5R*,7S*,7aR*,11aS*)-7-((tert-Butyldimethylsilyl)oxy)5-hexyldecahydro-1H-pyrrolo[2,1-j]quinolin-3-yl)methanol* (**13**). To acetate **12** (1.15 g, 2.47 mmol) in methanol (25 mL) was added K_2CO_3 (0.41 g, 3.0 mmol). The reaction mixture was stirred at room temperature for 12 h. The mixture was then poured into water (50 mL) and Et_2O (100 mL), the phases were separated, and the aqueous phase was washed with Et_2O (5 x 25 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The product was pure after extraction. Colorless oil (1.04 g, 99%). ^1H NMR (300 MHz, $CDCl_3$) δ = 4.07 (d, *J* = 10.9 Hz, 1H), 3.88 (ddd, *J* = 10.9, 5.6, 3.7 Hz, 1H), 3.56 (ddd, *J* = 11.9, 8.9, 2.8 Hz, 1H), 3.44-3.36 (m, 1H), 3.09-2.98 (m, 1H), 2.76 (dd, *J* = 8.9, 3.7 Hz, 1H), 2.29 (dd, *J* = 19.7, 11.9 Hz, 1H), 2.12 (ddd, *J* = 14.4, 9.6, 4.5 Hz, 1H), 1.88-1.60 (m, 6H), 1.51-1.20 (m, 17H), 0.96-0.84 (m, 3H), 0.91 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 72.27, 66.02, 63.76, 61.74, 50.10, 47.06, 41.89, 39.10, 33.04, 31.90, 29.67, 29.43, 28.26, 27.98, 27.01, 27.00, 26.04 (3C), 24.80, 22.67, 18.34, 14.09, -4.47, -4.85. IR (neat) 3382 (br), 2955, 2925, 2855, 1469, 1254, 1036, 835. HRMS (ESI) for $C_{25}H_{50}NO_2Si$ calcd 424.3605, found 424.3597.



$C_{25}H_{49}NO_2Si$
MW: 423.75 g/mol

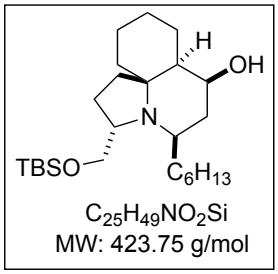
(3R,5R*,7S*,7aR*,11aS*)-3-(((tert-Butyldimethylsilyl)oxy)methyl)-5-hexyldecahydro-1H-pyrrolo[2,1-j]quinolin-7-ol* (**26**). To a solution of **25** (0.11 g, 0.26 mmol) in THF (2.6 mL) was added TBAF (1M in THF, 0.29 mL, 0.29 mmol) at 0 ºC. The reaction mixture was stirred at room temperature for 16 h, after which the mixture was poured into water (10 mL) and Et_2O (10 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (5 x 10 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting diol was purified on a short pad of HMDS pre-treated silica gel (Et_2O), and used directly in the next step. To this diol in DMF (0.5 mL) was added DMAP (1 mg, 0.01 mmol), imidazole (22 mg, 0.32 mmol) and TBSCl (48 mg, 0.32 mmol). The reaction mixture was then stirred at rt for 24 h. $NaHCO_3$ Aqueous solution (2 mL) and Et_2O (5 mL) were then poured into the reaction mixture. The phases were then separated and the aqueous phase was extracted with Et_2O (5 x 5 mL). The combined organic extracts were dried on Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (pentane/Et_2O 80:20) afforded a white solid (91 mg, 83%). m.p. 115.9-117.0 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.99-3.90 (m, 1H), 3.90 (dd, *J* = 10.5, 5.4 Hz, 1H), 3.60 (dd, *J* = 10.5, 3.1 Hz, 1H), 3.40 (m, 1H), 3.03 (m, 1H), 2.78 (d, *J* = 7.1 Hz, 1H), 2.23-2.11 (m, 2H), 1.88-1.20 (m, 23H), 0.97-0.82 (m, 3H), 0.91 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 71.35, 66.69, 64.00, 61.28, 50.07, 47.14, 41.60, 39.04, 33.20, 31.89, 29.96, 29.43, 27.93, 27.56, 27.05, 26.77, 26.13 (3C), 24.92, 22.66, 18.64, 14.09, -5.13, -5.38. IR (neat) 3158 (br), 2952, 2925, 2853, 1461, 1250, 1057, 867, 836. HRMS (ESI) for $C_{25}H_{50}NO_2Si$ calcd 424.3605, found 424.3605.



$C_{19}H_{33}NO_2$
MW: 307.47 g/mol

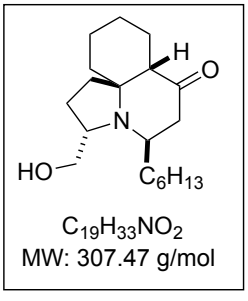
13-Epicylindricine C (**28**). To a solution of **26** (68 mg, 0.16 mmol) in CH_2Cl_2 (3.2 mL) was added at 0 ˚C MS 3Å (70 mg), TPAP (28 mg, 0.08 mmol) and NMO (26 mg, 0.19 mmol). The reaction mixture was stirred at room temperature for 24 h, after which pentane (2 mL) was added. The mixture was purified on a short pad of HMDS pre-treated silica gel (pentane/Et_2O 75:25), and used directly in the next step. To this ketone in THF (2.5 mL) was added

TBAF (1M in THF, 0.3 mL, 0.3 mmol) at 0 ºC. The reaction mixture was stirred at room temperature for 8 h, after which time it was poured into water (10 mL) and CH_2Cl_2 (10 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (5 x 10 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane/Et_2O 70:30) affording a colorless oil (43 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.59 (dd, *J* = 10.3, 3.5 Hz, 1H), 3.45 (d, *J* = 10.3 Hz, 1H), 3.28-3.11 (m, 2H), 3.00 (s, 1H), 2.48 (dd, *J* = 15.5, 3.5 Hz, 1H), 2.32 (s, 1H), 2.28-2.09 (m, 3H), 1.98 (dd, *J* = 15.5, 10.3 Hz, 1H), 1.83-1.75 (m, 1H), 1.75-1.63 (m, 2H), 1.56-1.08 (m, 16H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 210.45, 67.40, 66.68, 57.97, 57.09, 52.88, 46.93, 36.08, 33.87, 31.73, 29.62, 29.44, 25.81, 25.33, 23.53, 23.14, 22.52, 21.33, 14.00. IR (neat) 3438 (br), 2928, 2860, 1704, 1455, 1038. HRMS (ESI) for $C_{19}H_{34}NO_2$ calcd 308.2584, found 308.2589.



(3S,5R*,7S*,7aR*,11aS*)-3-(((tert-Butyldimethylsilyl)oxy)methyl)-5-hexyldecahydro-1H-pyrrolo[2,1-j]quinolin-7-ol* (**15**). To a stirred solution of alcohol **13** (74.0 mg, 0.175 mmol) in acetone (1.75 mL) at 0 ºC was added Jones reagent (0.15 mL of a 5M solution, 0.70 mmol) via syringe. After 1 h at rt, water (5 mL) and CH_2Cl_2 (5 mL) were added and the aqueous layer was neutralized to pH 6-7 using a phosphate buffer. The phases were separated and the aqueous layer was extracted with CH_2Cl_2 (6 x 10 mL). The organic layers were combined, dried on Na_2SO_4 and passed through a short plug of neutral alumina, washing with 10% MeOH in CH_2Cl_2 (10 mL). Concentration under reduced pressure gave the acid, which was dissolved in MeOH (4.5 mL) at rt and concentrated H_2SO_4 (0.5 mL) was added. After heating under reflux for 48 h, the reaction mixture was cooled, treated with saturated aqueous $NaHCO_3$ (20 mL) and extracted with CH_2Cl_2 (6 x 15 mL). The organic layers were combined, dried on Na_2SO_4 and concentrated under reduced pressure. The crude ester was dissolved in MeOH (7 mL) and sodium methoxide (49 mg, 0.90 mmol) was added. After heating under reflux for 48 h, the reaction mixture was cooled and treated with water (20 mL), CH_2Cl_2 (20 mL) was added, the phases were separated and the aqueous layer

extracted with CH_2Cl_2 (6 x 20 mL). The organic layers were combined, dried on Na_2SO_4 and concentrated under reduced pressure. The crude product was diluted in Et_2O (5 mL) at 0 ºC and $LiAlH_4$ (0.44 mL, 0.44 mmol) was added. The reaction mixture was stirred for 15 minutes, NaOH 1M (0.1 mL) was poured into the mixture and the suspension was further stirred for 10 minutes. Na_2SO_4 solid was added, and the mixture was passed through a short plug of neutral alumina, washing with 10% MeOH in CH_2Cl_2 (10 mL). Concentration under reduced pressure gave the diol, which was diluted in DMF (0.7 mL). DMAP (1 mg, 0.01 mmol), imidazole (16 mg, 0.23 mmol) and TBSCl (35 mg, 0.23 mmol) were then added. The reaction mixture was stirred at rt for 24 h. $NaHCO_3$ aqueous saturated solution (2 mL) and Et_2O (5 mL) were then poured into the solution. The phases were separated and the aqueous phase was extracted with Et_2O (5 x 5 mL). The combined organic extracts were dried on Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (pentane/Et_2O 80:20) afforded a white solid (41 mg, 55%). m.p. 53.0-57.0 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.10-3.99 (m, 1H), 3.73 (d, *J* = 5.1 Hz, 1H), 3.25-3.15 (m, 2H), 2.99-2.86 (m, 1H), 2.14-1.94 (m, 3H), 1.84-1.72 (m, 2H), 1.72-1.14 (m, 21H), 0.91-0.85 (m, 3H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 70.82, 70.15, 67.06, 60.12, 53.28, 43.65, 41.92, 33.80, 33.61, 31.83, 30.59, 29.57, 28.79, 27.67, 26.57, 26.07, 26.02 (3C), 24.40, 22.61, 18.38, 14.06, -5.18, -5.23. IR (neat) 3403 (br), 2955, 2926, 2856, 1462, 1254, 1112, 1080, 835. HRMS (ESI) for $C_{25}H_{50}NO_2Si$ calcd 424.3605, found 424.3605.



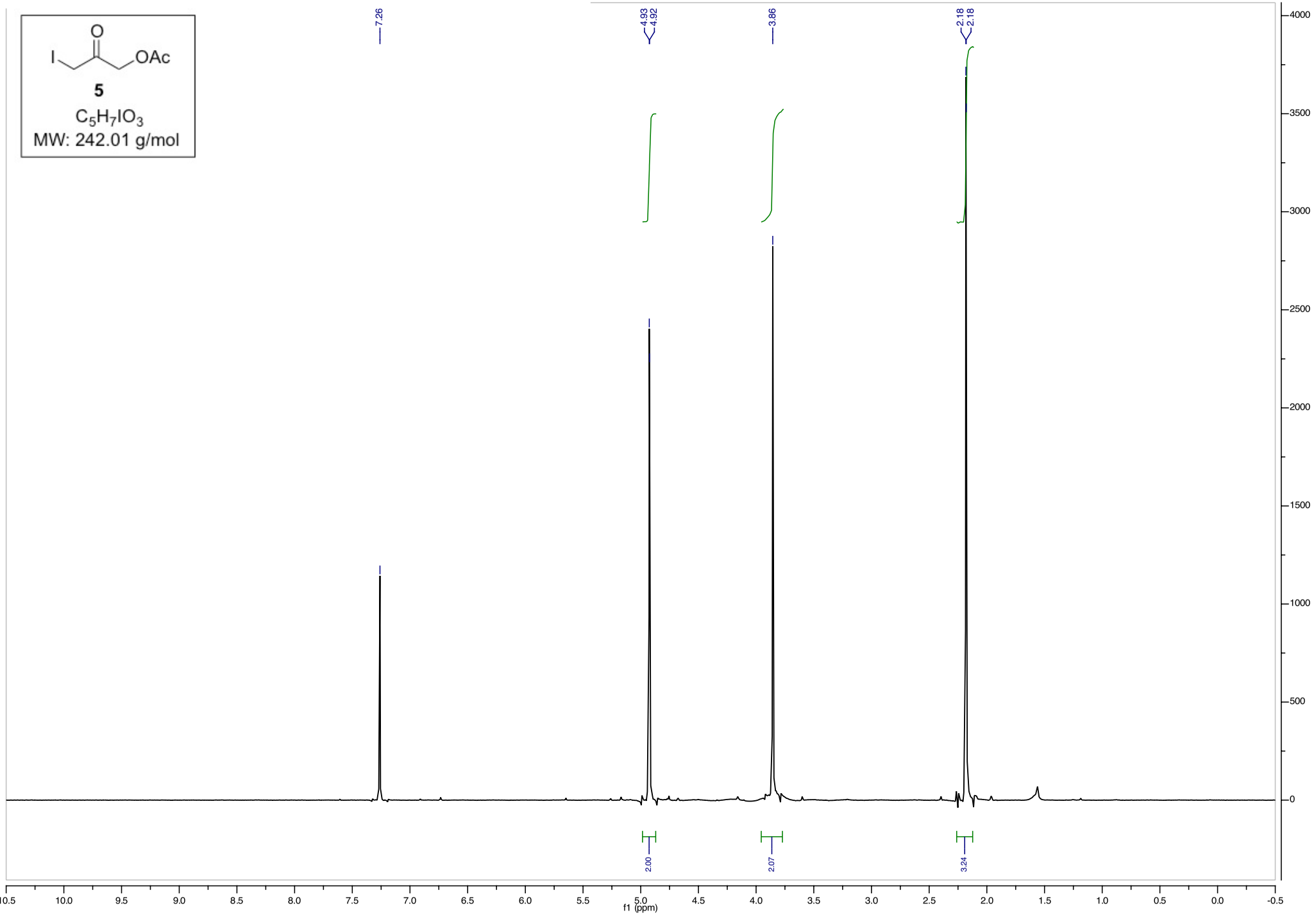
$C_{19}H_{33}NO_2$
MW: 307.47 g/mol

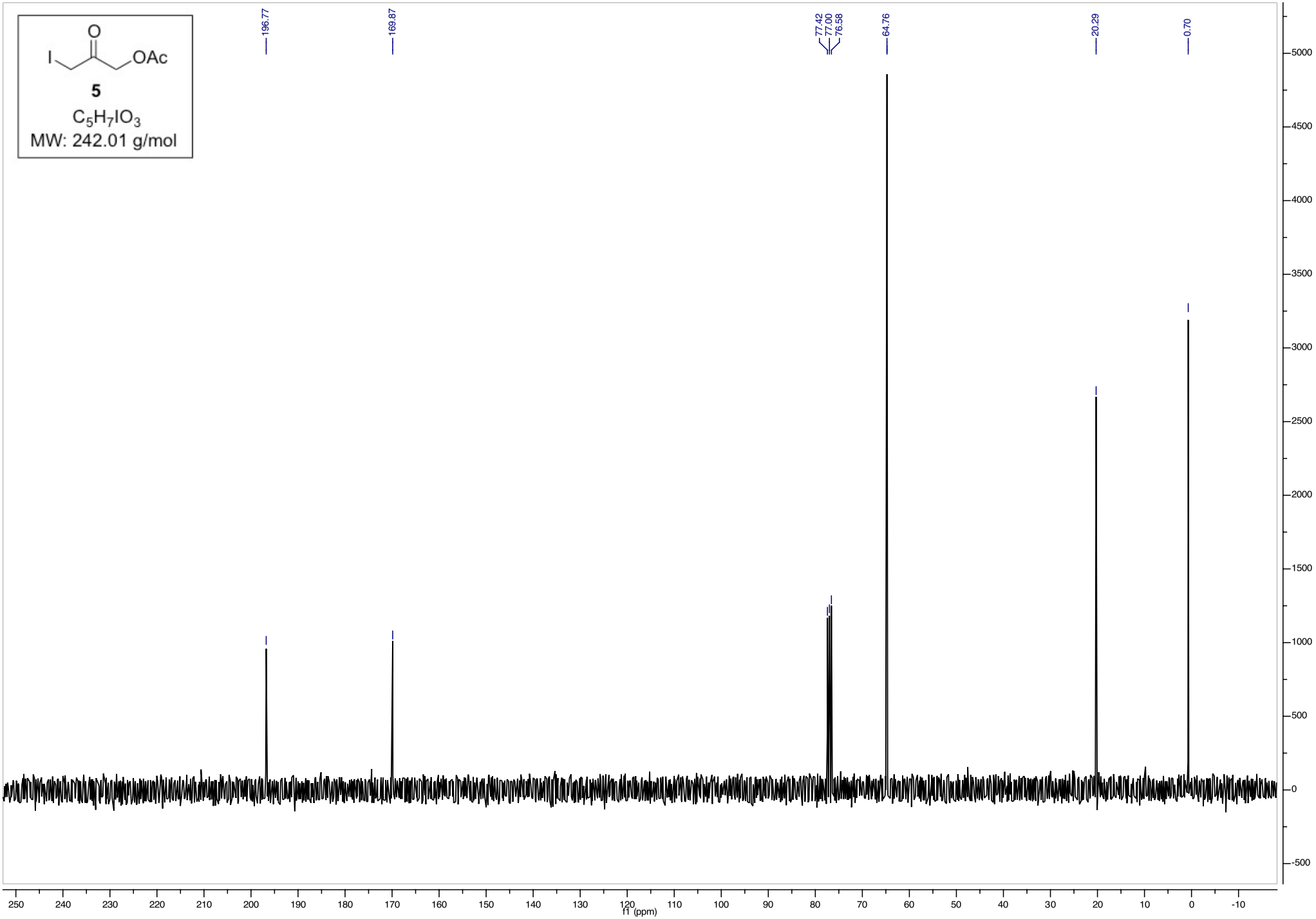
Cylindricine C (**1**). To a solution of **15** (32 mg, 75 μmol) in CH_2Cl_2 (1.5 mL) was added at 0 ºC MS 3Å (30 mg), TPAP (13 mg, 38 μmol) and NMO (12 mg, 90 μmol). The reaction mixture was stirred at room temperature for 24 h, after which pentane (2 mL) was added. The mixture was passed through a short pad of HMDS pre-treated silica gel (pentane/Et_2O 75:25), and used directly in the next step. To this ketone in THF (2 mL) was added TBAF (1M in THF, 0.23 mL, 0.23 mmol) at 0 ºC. The reaction mixture was stirred at room temperature for 8 h, after which it was poured into water (5 mL) and CH_2Cl_2 (5 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (5 x 5 mL). The combined organic extracts were dried over Na_2SO_4, filtered and

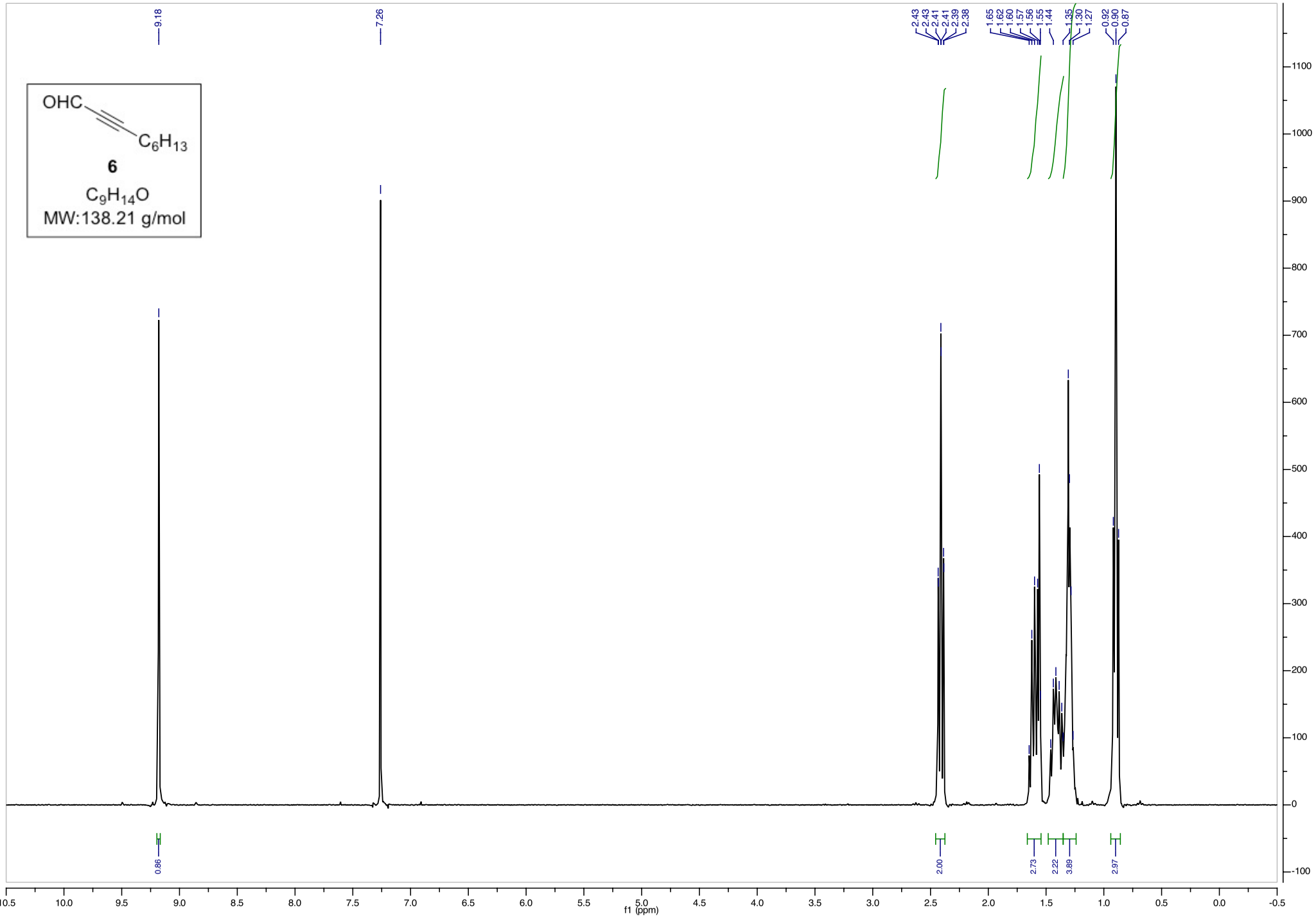
concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane/Et_2O 70:30) affording **1** as a colorless oil (22 mg, 96%). Spectral data were in accordance with those reported in the literature.[3] ^1H NMR (300 MHz, $CDCl_3$) δ = 3.58-3.47 (m, 2H), 3.46-3.39 (m, 1H), 3.33-3.21 (m, 1H), 2.88 (s, 1H), 2.36-2.17 (m, 4H), 2.11 (dd, *J* = 11.8, 7.9 Hz, 1H), 1.89-1.76 (m, 1H), 1.75-1.55 (m, 4H), 1.53-1.17 (m, 15H), 0.86 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 210.39, 70.63, 66.36, 56.57, 55.30, 50.28, 42.52, 36.40, 35.90, 35.18, 31.67, 29.25, 28.65, 27.08, 24.26, 22.71, 22.53, 21.84, 13.99. IR (neat) 3433 (br), 2928, 2858, 1702, 1448, 1331, 1025. HRMS (ESI) for $C_{19}H_{34}NO_2$ calcd 308.2584, found 308.2587.

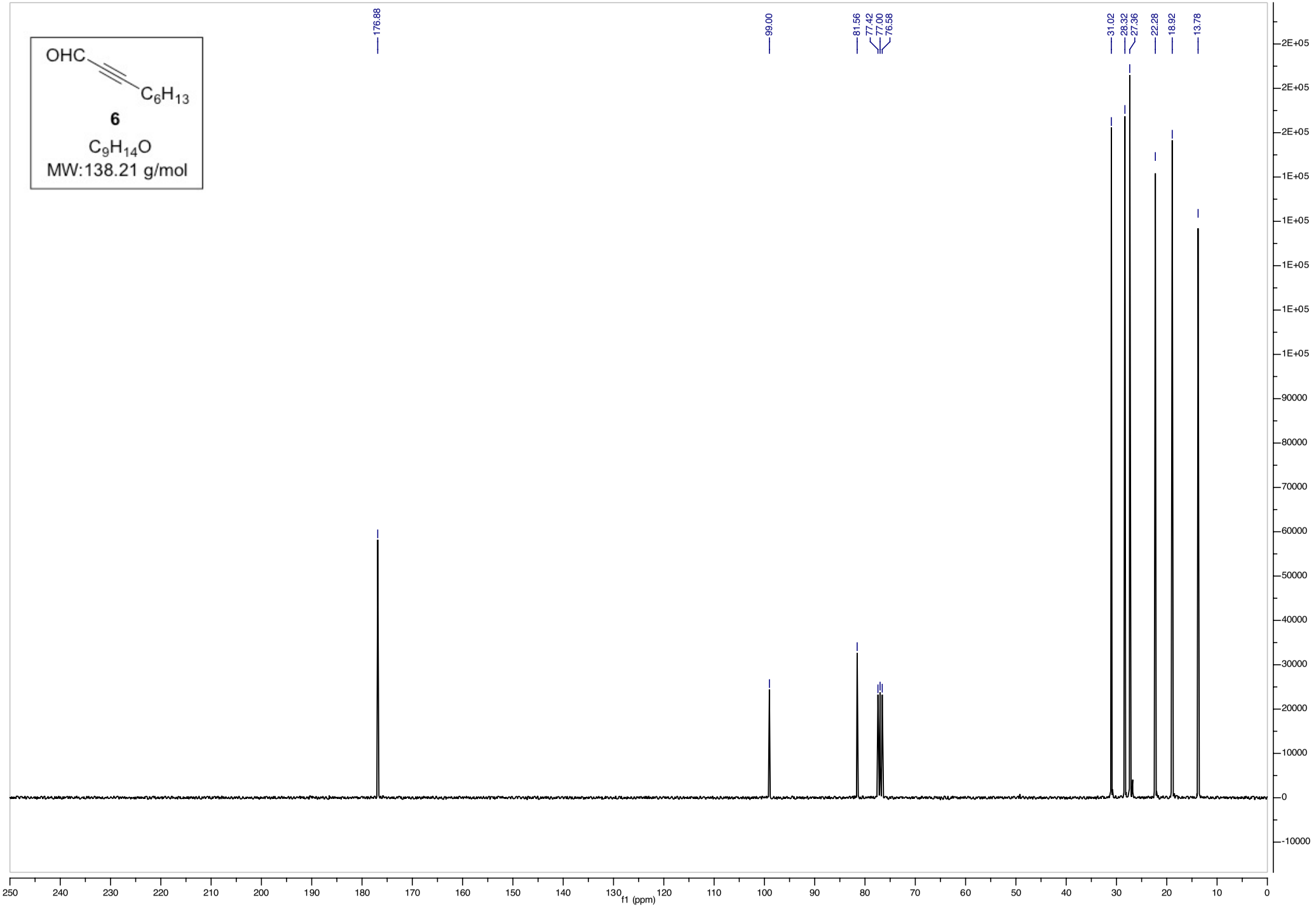
3) Abe, H.; Aoyagi, S.; Kibayashi, C. *J. Am. Chem. Soc.* **2005**, *127*, 1473.

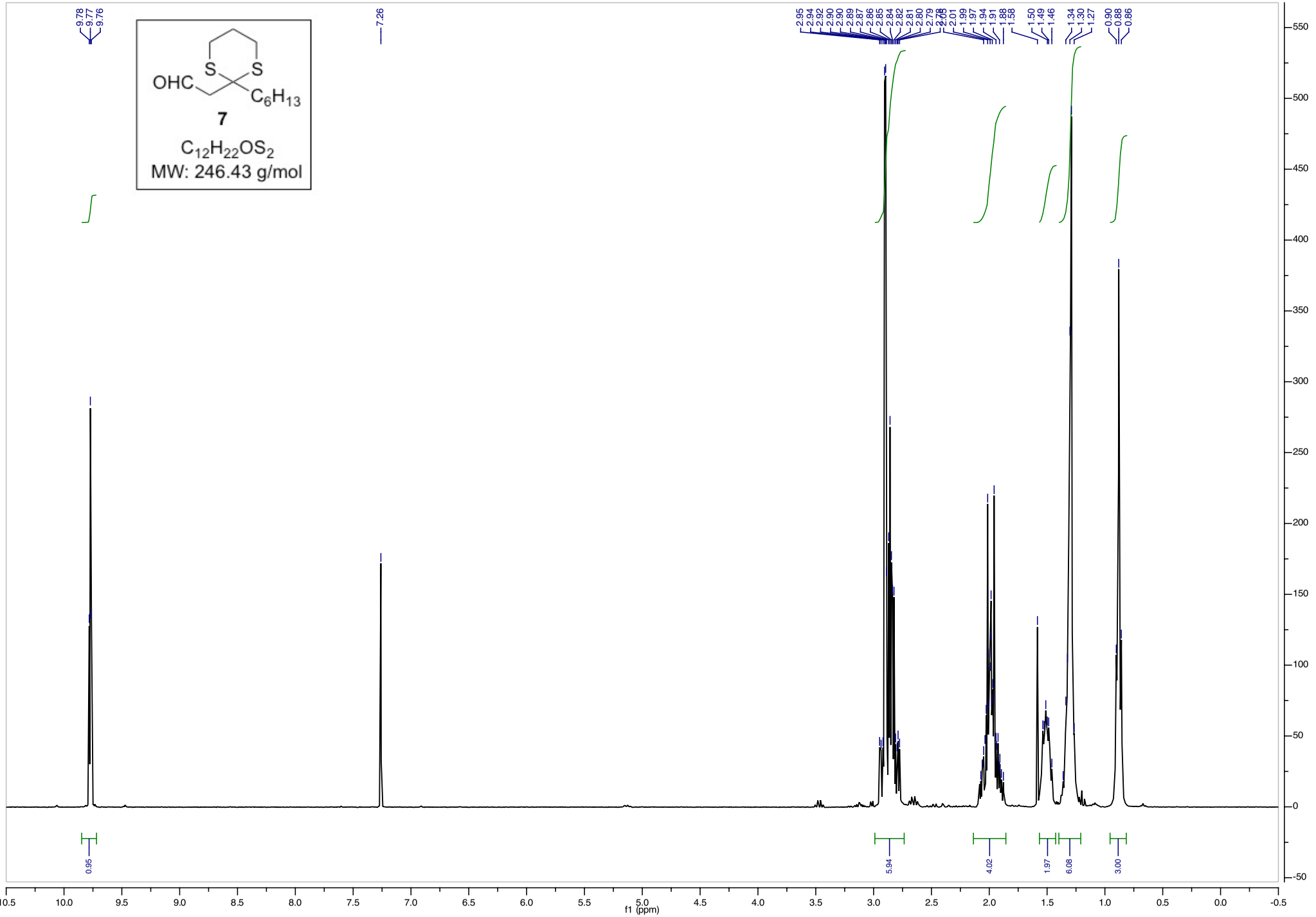
Section C: 1H and 13C NMR Spectra of the Synthesized Compounds

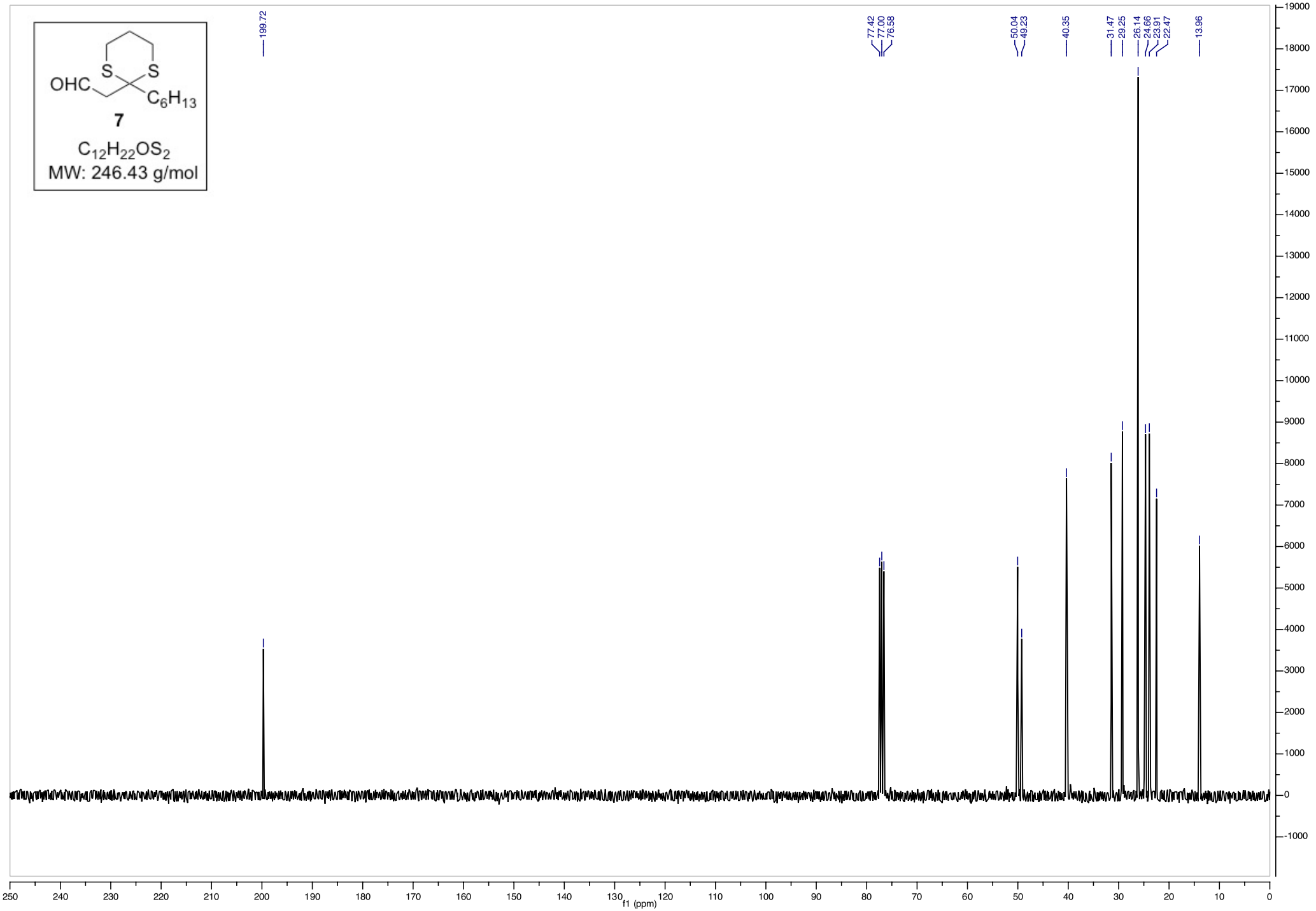


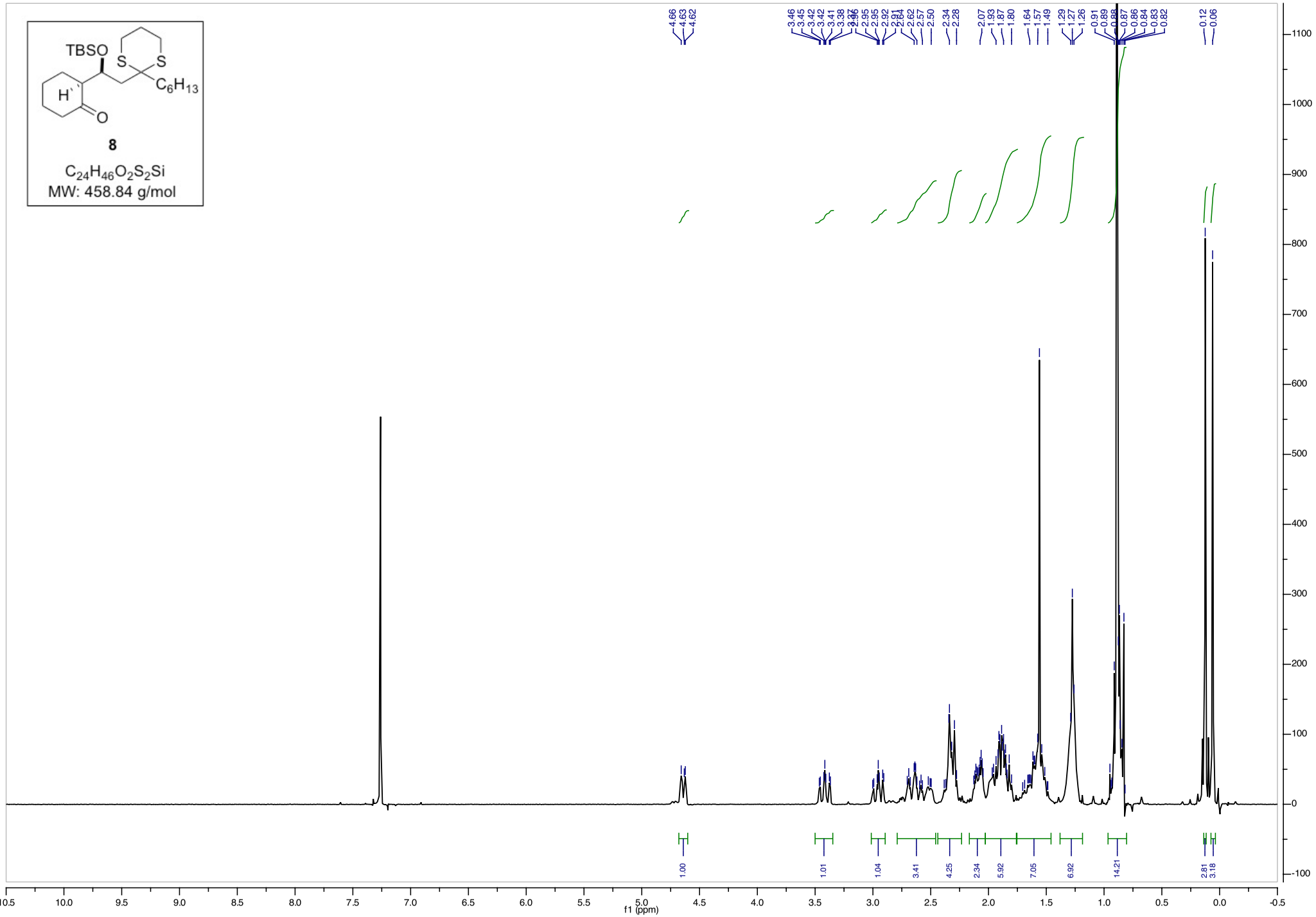

O
I
OAc
5
C5H7IO3
MW: 242.01 g/mol
196.77
169.87
77.42
77.00
76.58
64.76
20.29
0.70
f1 (ppm)

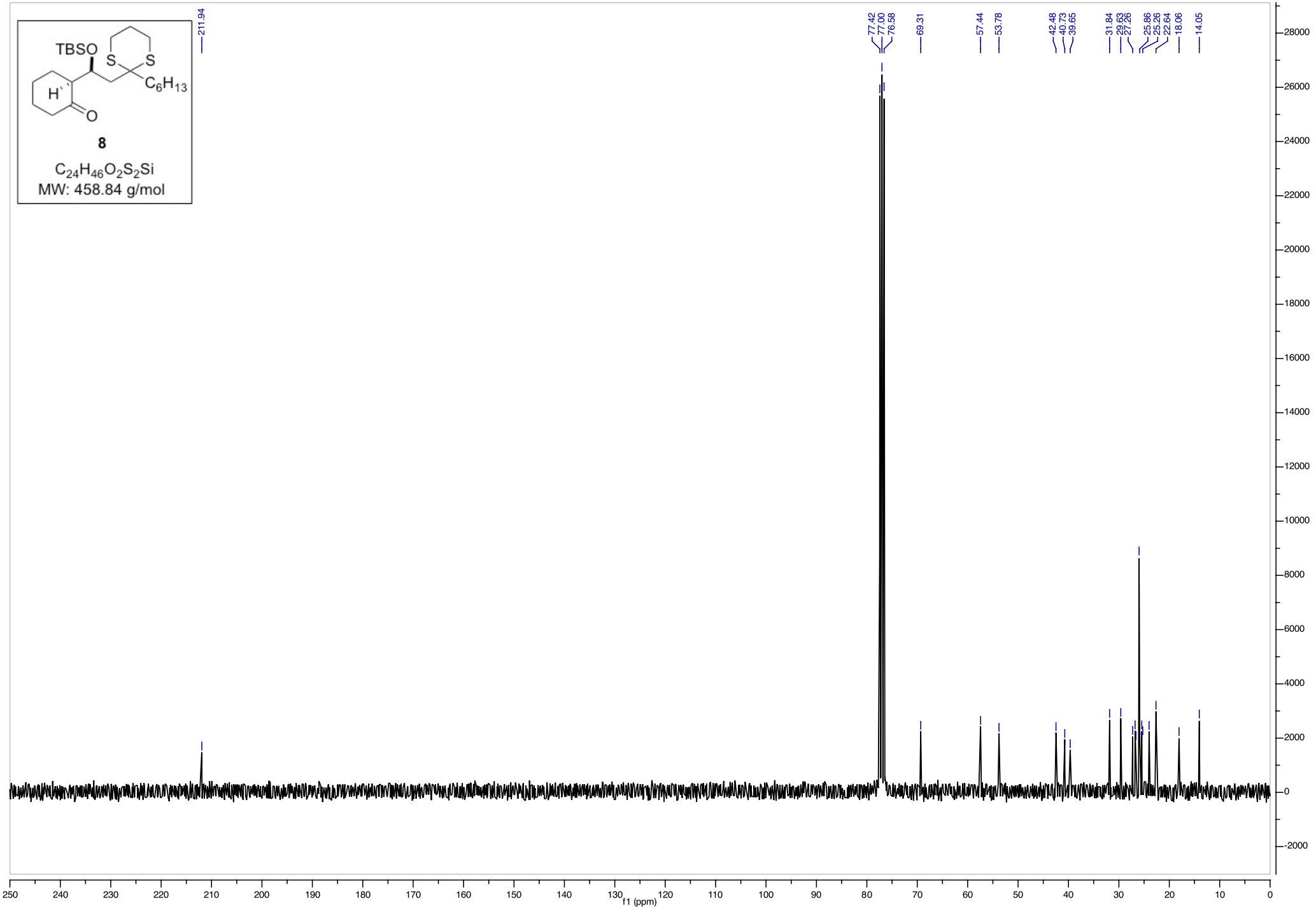

OHC
C6H13
6
C9H14O
MW:138.21 g/mol
9.18
7.26
2.43
2.43
2.41
2.41
2.39
2.38
1.65
1.62
1.60
1.57
1.56
1.55
1.44
1.35
1.30
1.27
0.92
0.90
0.87
0.86
2.00
2.73
2.22
3.89
2.97
f1 (ppm)

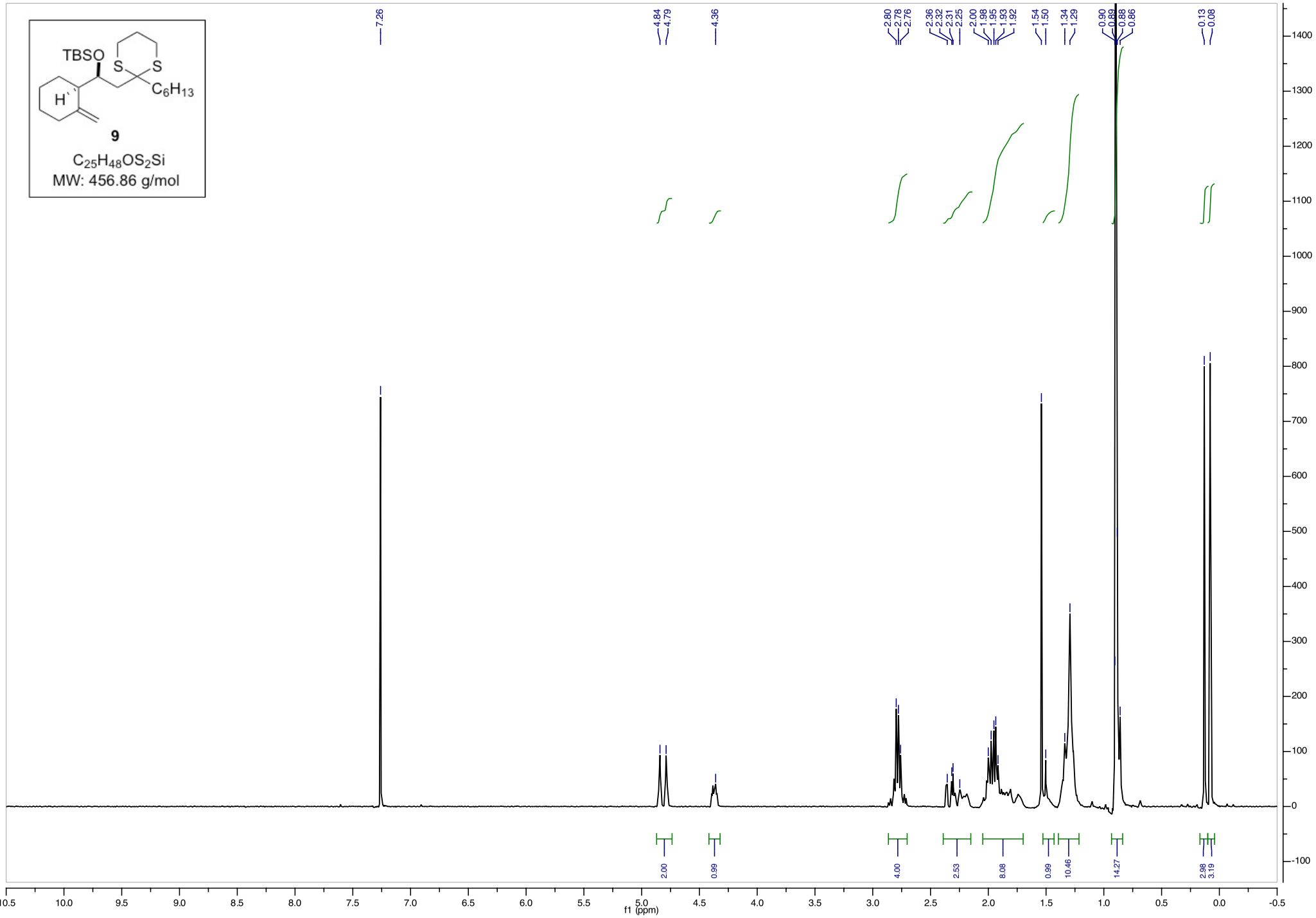

OHC
C6H13
6
C9H14O
MW:138.21 g/mol
176.88
99.00
81.56
77.42
77.00
76.58
31.02
28.32
27.36
22.28
18.92
13.78
f1 (ppm)

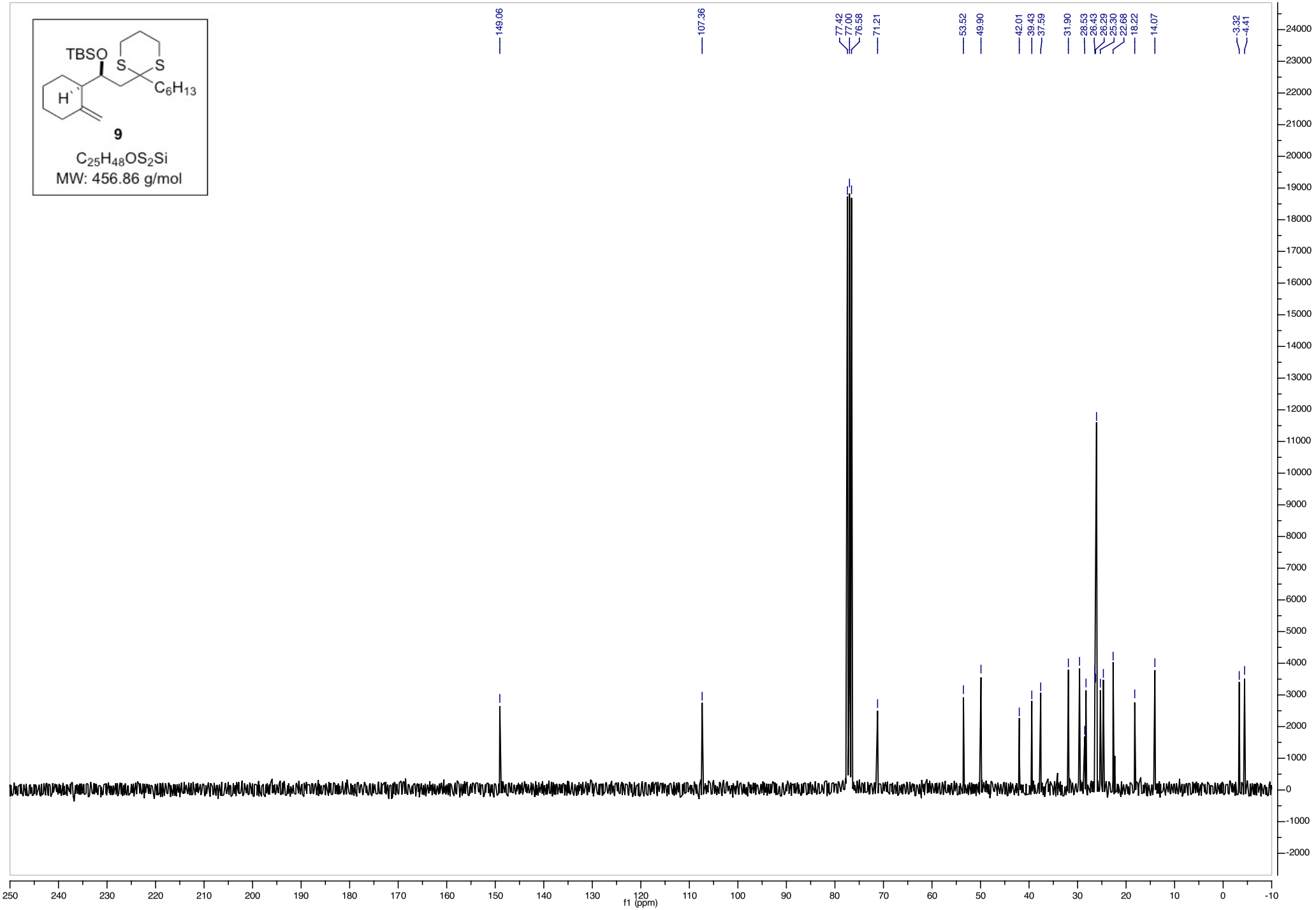

9.78
9.77
9.76
7.26
2.95
2.94
2.92
2.90
2.90
2.89
2.87
2.86
2.85
2.84
2.82
2.81
2.80
2.79
2.08
2.01
1.99
1.97
1.94
1.91
1.88
1.58
1.50
1.49
1.46
1.34
1.30
1.27
0.90
0.88
0.86
OHC
S
S
C6H13
7
C12H22OS2
MW: 246.43 g/mol
0.95
5.94
4.02
1.97
6.08
3.00
f1 (ppm)

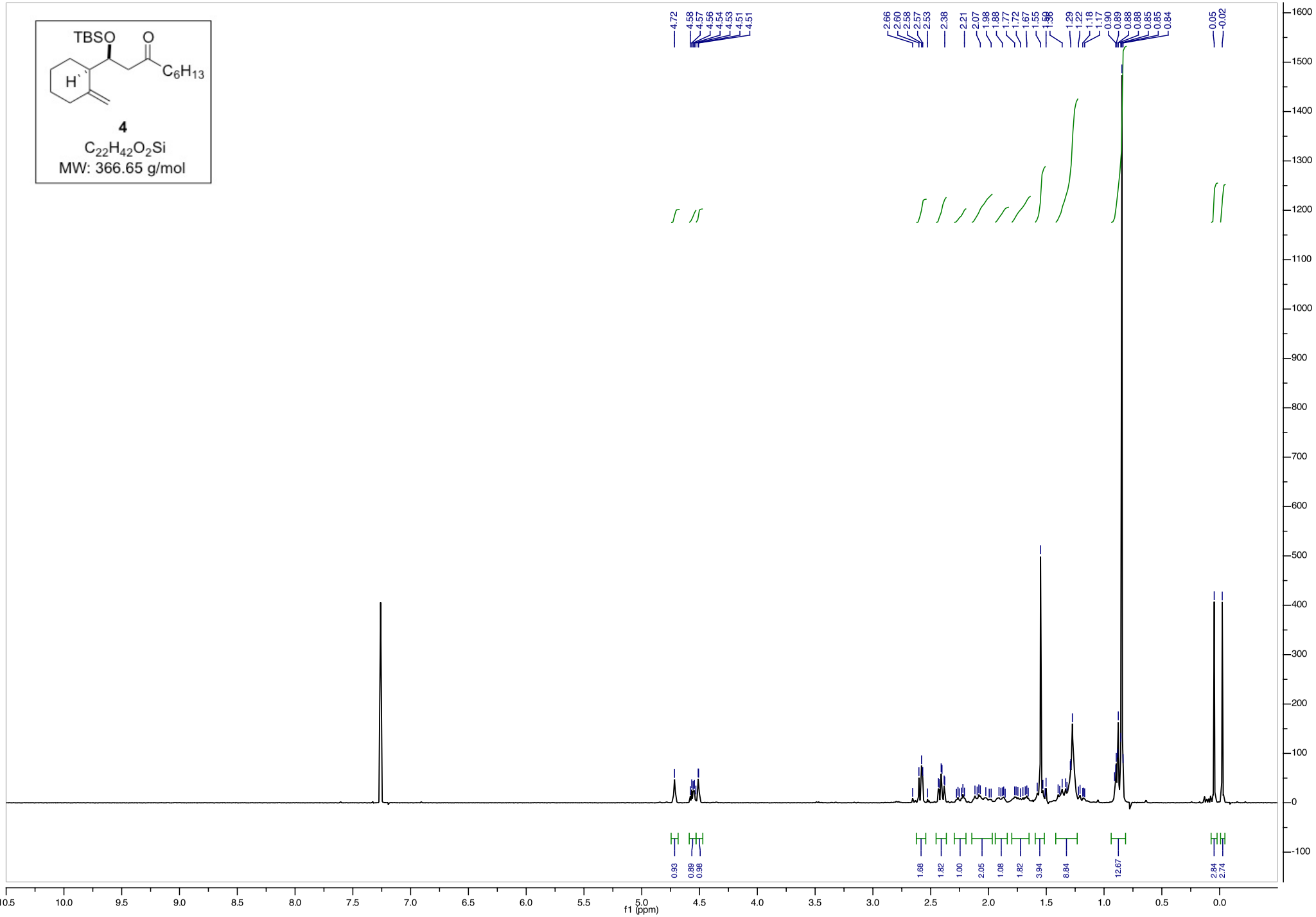

OHC
S
S
C_6H_{13}
7
$C_{12}H_{22}OS_2$
MW: 246.43 g/mol
199.72
77.42
77.00
76.58
50.04
49.23
40.35
31.47
29.25
26.14
24.66
23.91
22.47
13.96
f1 (ppm)

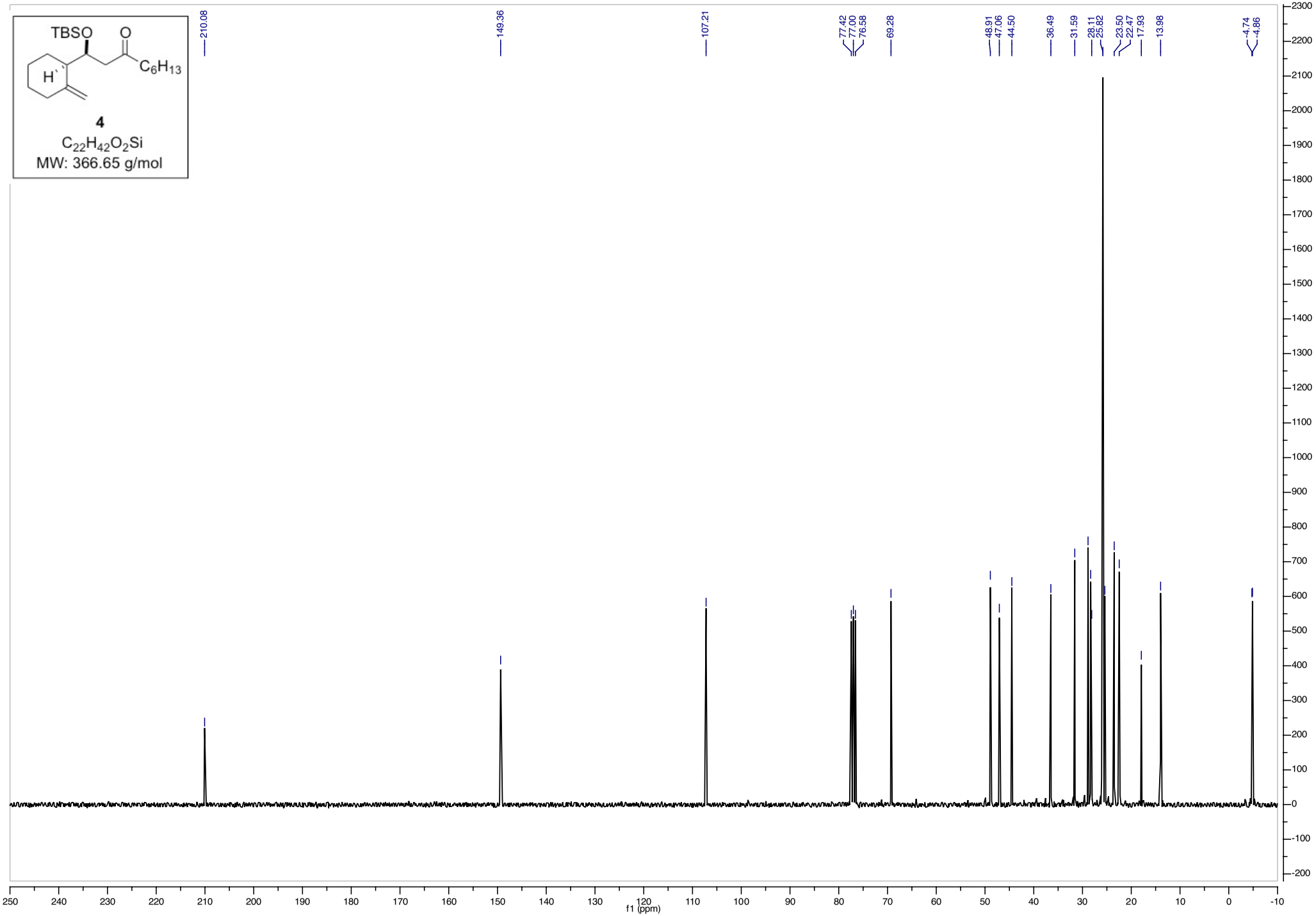

TBSO
S
S
C_6H_{13}
H
O
8
$C_{24}H_{46}O_2S_2Si$
MW: 458.84 g/mol
4.66 4.63 4.62
3.46 3.45 3.42 3.42 3.41 3.38 2.96 2.95 2.95 2.92 2.91 2.84 2.62 2.57 2.50 2.34 2.28
2.07 1.93 1.87 1.80 1.64 1.57 1.49 1.29 1.27 1.26 0.91 0.89 0.88 0.87 0.86 0.84 0.83 0.82
0.12 0.06
1.00 1.01 1.04 3.41 4.25 2.34 5.92 7.05 6.92 14.21 2.81 3.18
f1 (ppm)

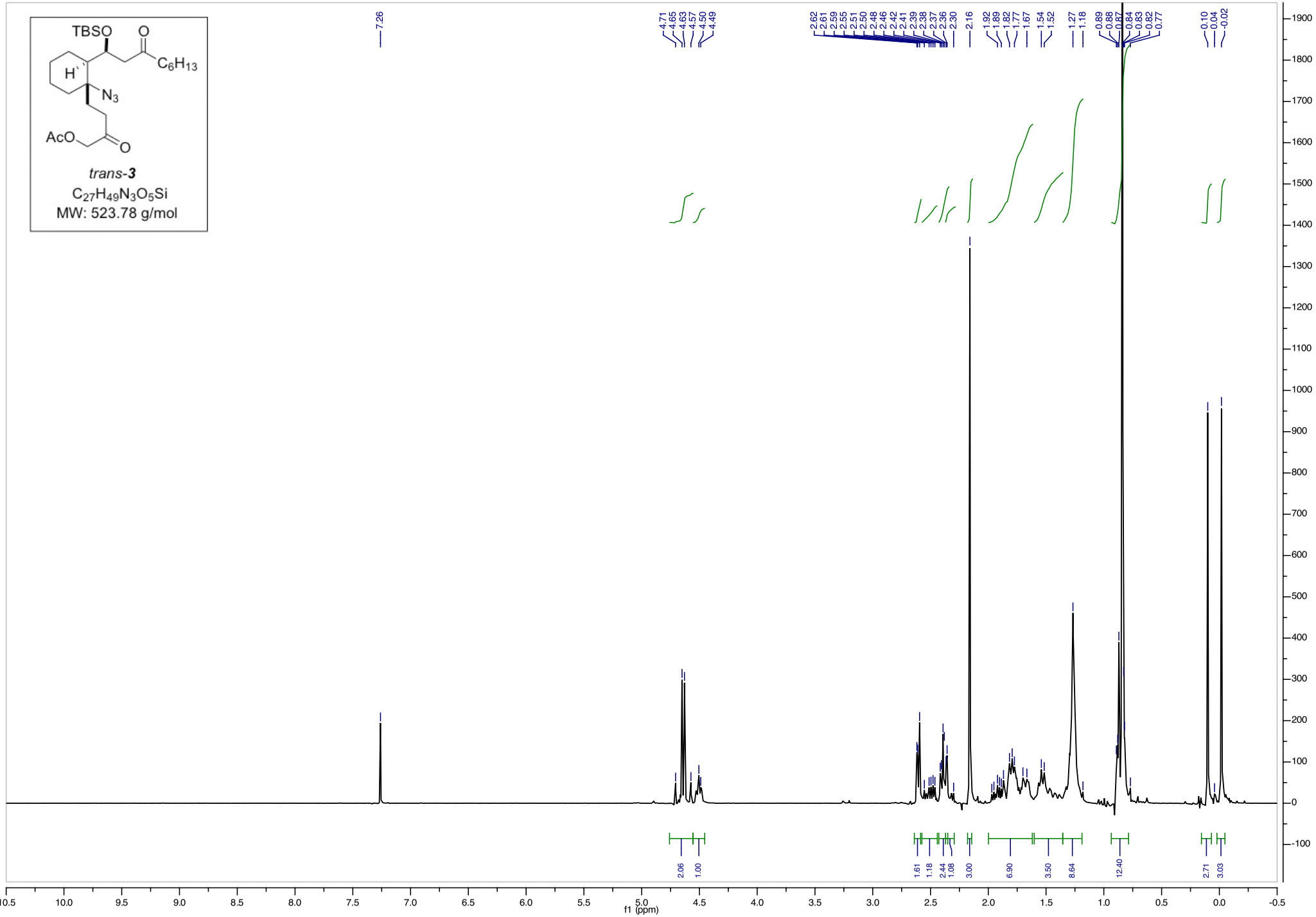

TBSO
S
S
C_6H_{13}
H
O
8
$C_{24}H_{46}O_2S_2Si$
MW: 458.84 g/mol
211.94
77.42
77.00
76.58
69.31
57.44
53.78
42.48
40.73
39.65
31.84
29.63
27.26
25.86
25.26
22.64
18.06
14.05
f1 (ppm)

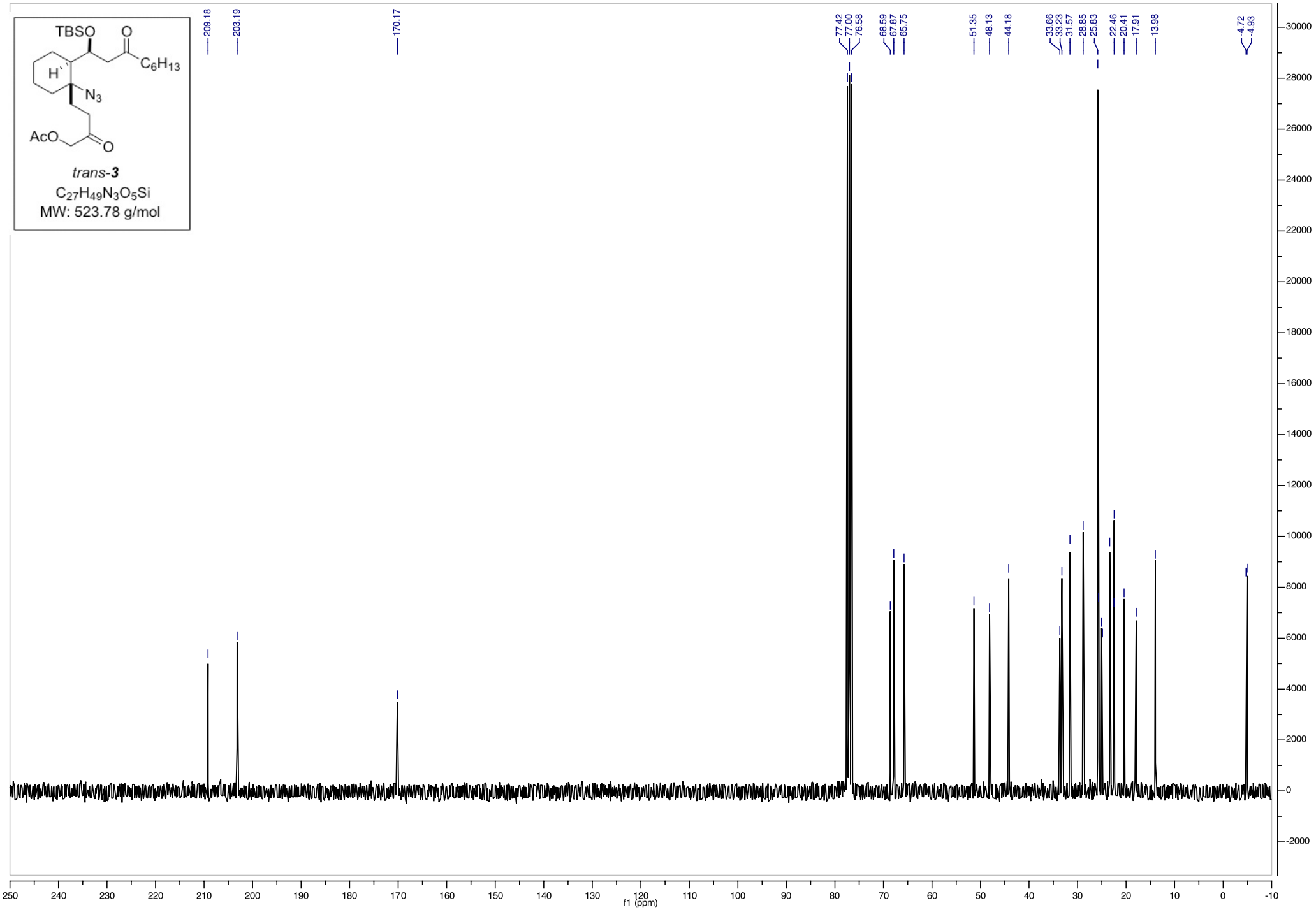

TBSO
S
S
C_6H_{13}
H
9
$C_{25}H_{48}OS_2Si$
MW: 456.86 g/mol
7.26
4.84
4.79
4.36
2.80
2.78
2.76
2.36
2.32
2.31
2.25
2.00
1.98
1.95
1.93
1.92
1.54
1.50
1.34
1.29
0.90
0.89
0.88
0.86
0.13
0.08
2.00
0.99
4.00
2.53
8.08
0.99
10.46
14.27
2.98
3.19
f1 (ppm)

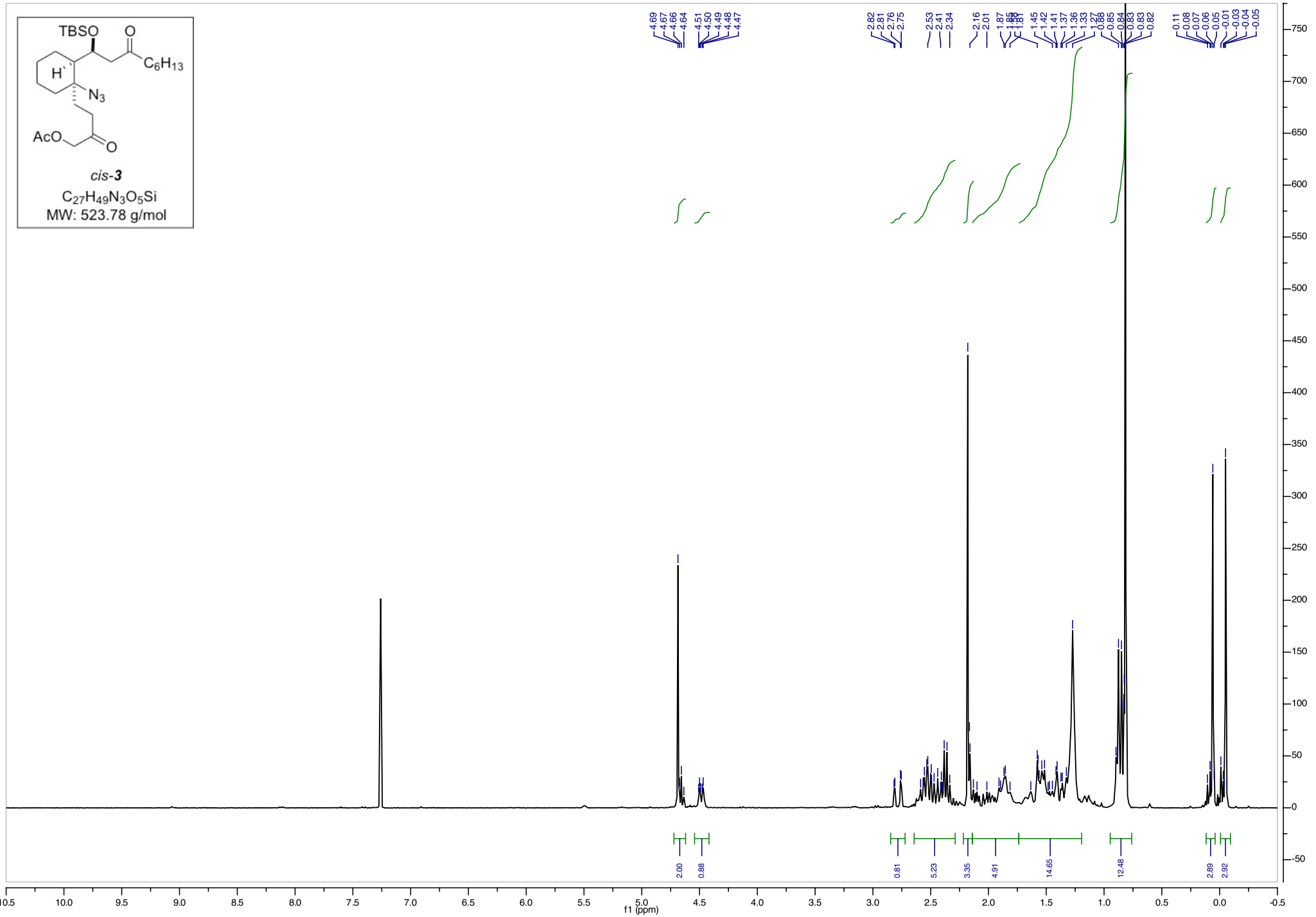

TBSO
S
S
C_6H_{13}
H
9
$C_{25}H_{48}OS_2Si$
MW: 456.86 g/mol
149.06
107.36
77.42
77.00
76.58
71.21
53.52
49.90
42.01
39.43
37.59
31.90
28.53
26.43
26.29
25.30
22.68
18.22
14.07
-3.32
-4.41
f1 (ppm)

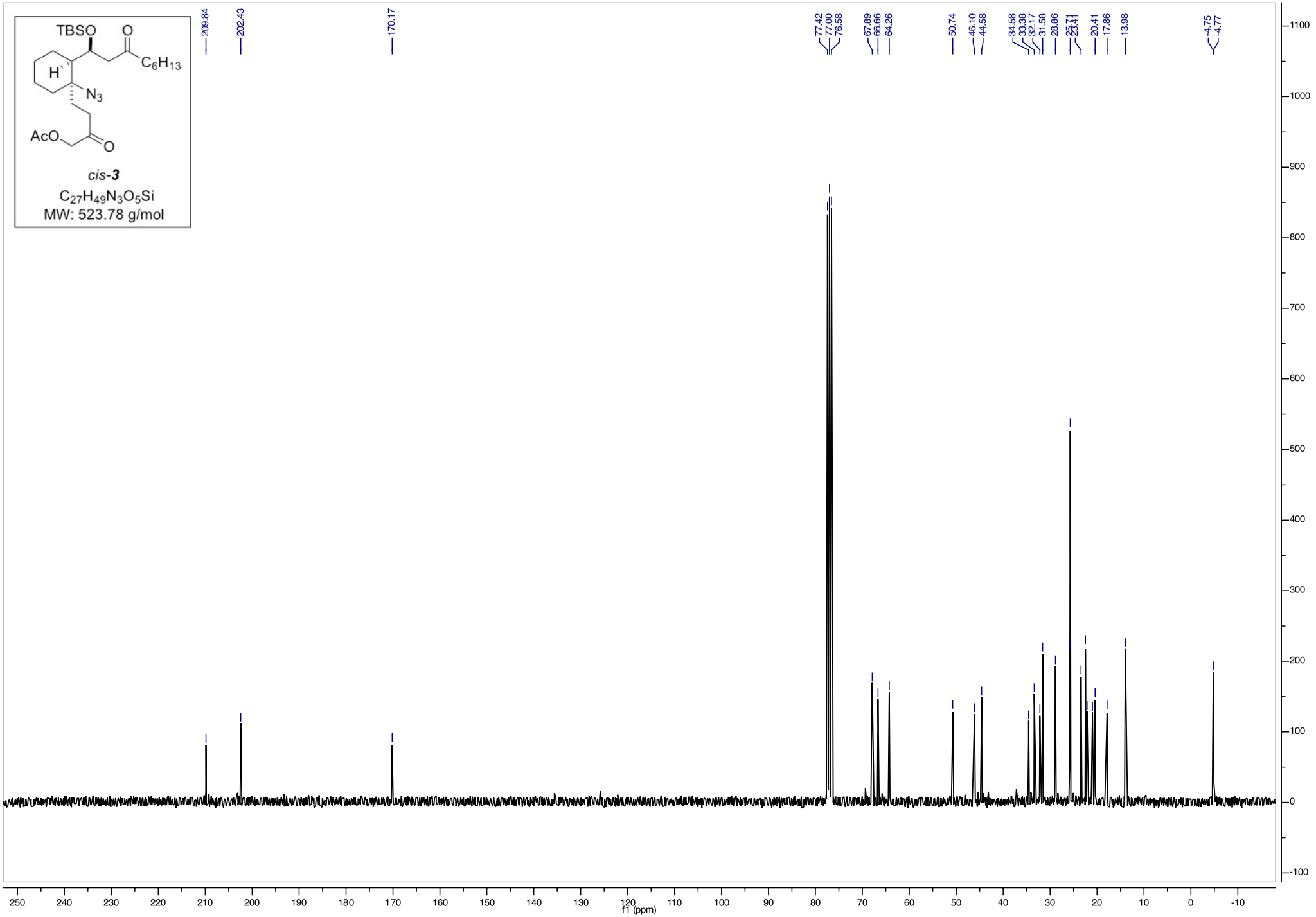

TBSO
O
C_6H_{13}
H
4
$C_{22}H_{42}O_2Si$
MW: 366.65 g/mol
4.72
4.58
4.57
4.56
4.54
4.53
4.51
4.51
2.66
2.60
2.58
2.57
2.53
2.38
2.21
2.07
1.98
1.88
1.77
1.72
1.67
1.55
1.29
1.22
1.18
1.17
0.90
0.89
0.88
0.88
0.85
0.85
0.84
0.05
-0.02
0.93
0.89
0.98
1.68
1.82
1.00
2.05
1.08
1.82
3.94
8.84
12.67
2.84
2.74
f1 (ppm)

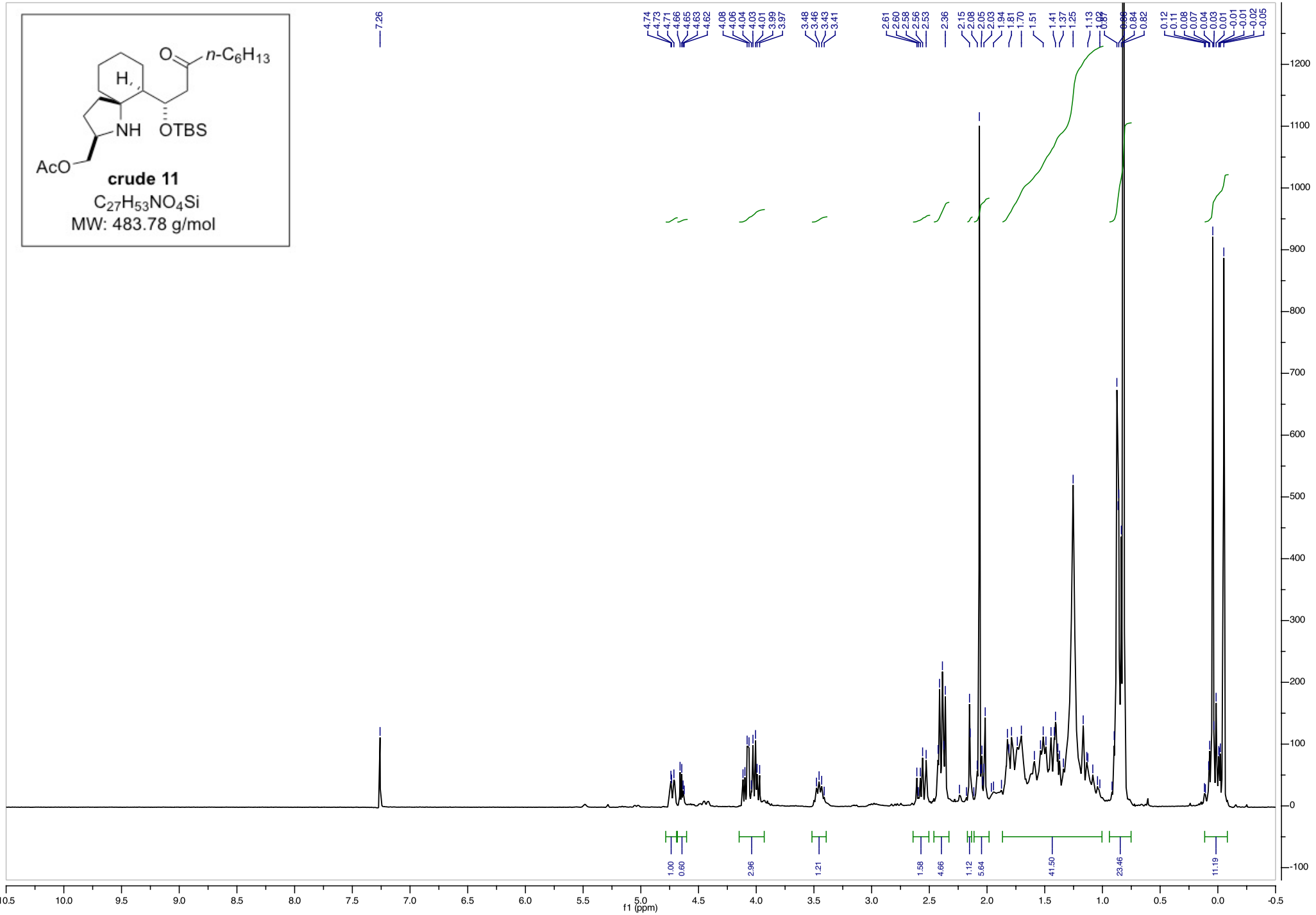

TBSO
O
C_6H_{13}
H
4
$C_{22}H_{42}O_2Si$
MW: 366.65 g/mol
210.08
149.36
107.21
77.42
77.00
76.58
69.28
48.91
47.06
44.50
36.49
31.59
28.11
25.82
23.50
22.47
17.93
13.98
-4.74
-4.86
f1 (ppm)

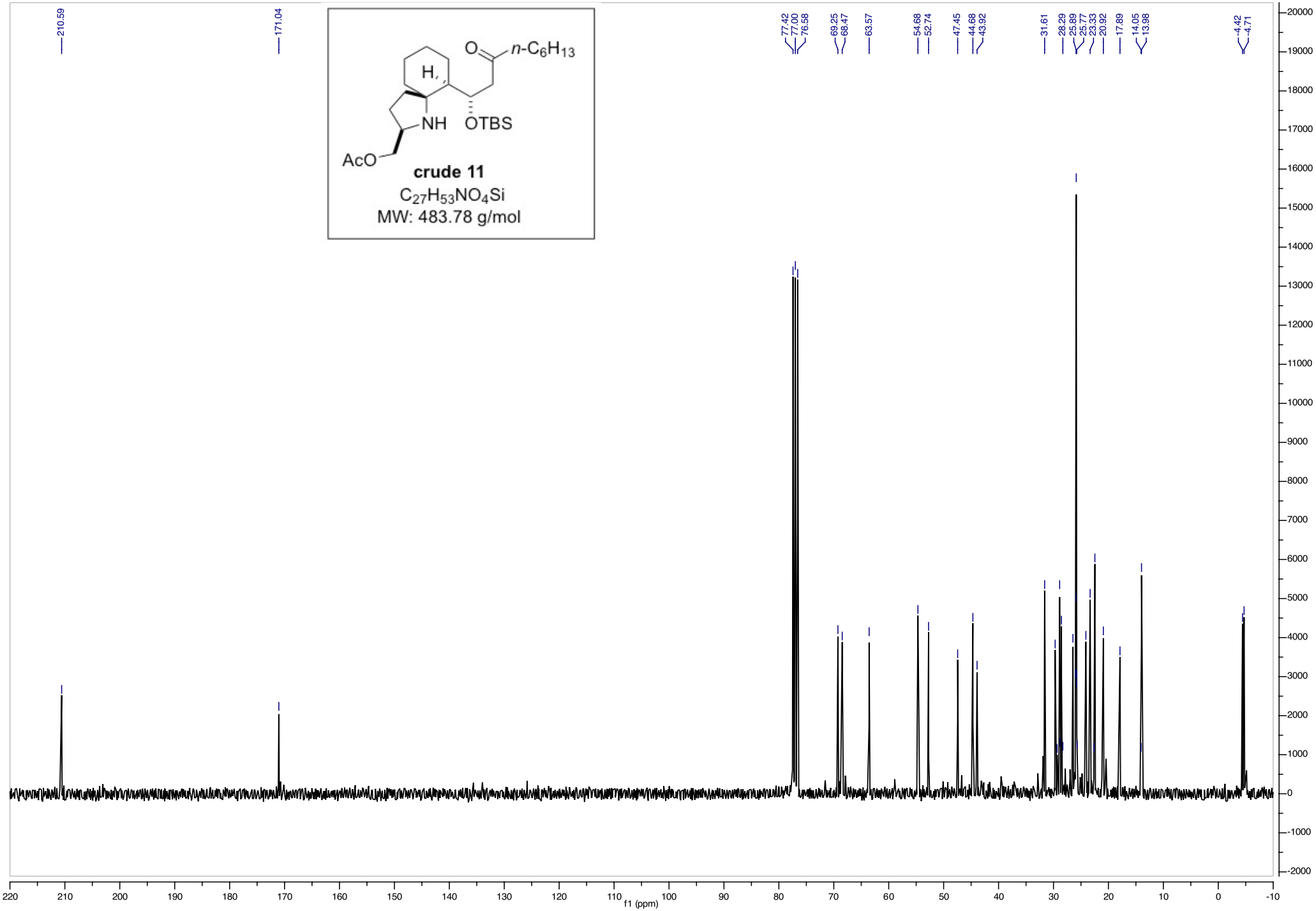

TBSO
O
C6H13
H
N3
AcO
O
trans-3
C27H49N3O5Si
MW: 523.78 g/mol
7.26
4.71
4.65
4.63
4.57
4.50
4.49
2.62
2.61
2.59
2.55
2.51
2.50
2.48
2.46
2.42
2.41
2.39
2.38
2.37
2.36
2.30
2.16
1.92
1.89
1.82
1.77
1.67
1.54
1.52
1.27
1.18
0.89
0.88
0.87
0.84
0.83
0.82
0.77
0.10
0.04
-0.02
2.06
1.00
1.61
1.18
2.44
1.08
3.00
6.90
3.50
8.64
12.40
2.71
3.03
f1 (ppm)

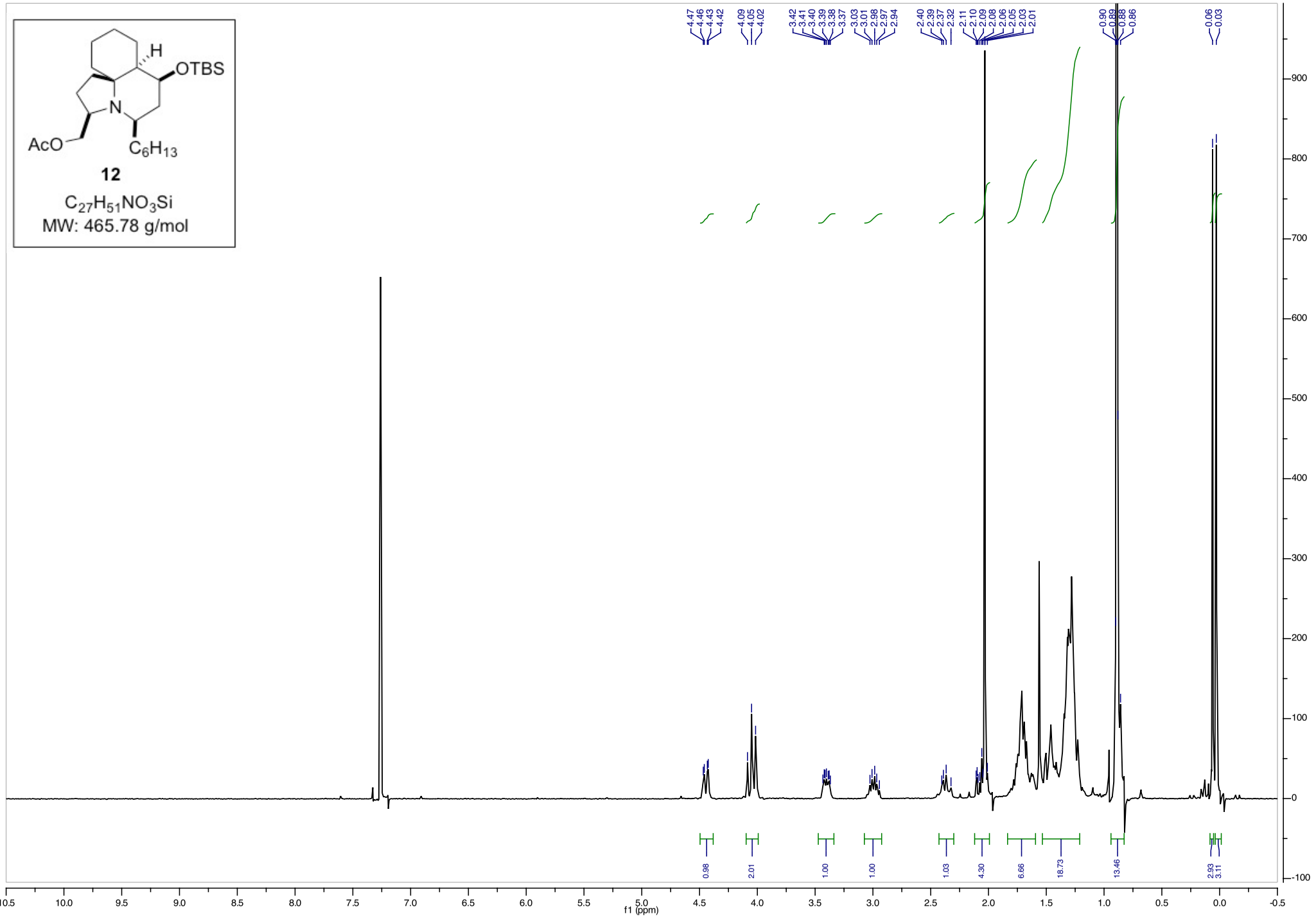

TBSO
O
C_6H_{13}
H
N_3
AcO
O
trans-**3**
$C_{27}H_{49}N_3O_5Si$
MW: 523.78 g/mol
209.18
203.19
170.17
77.42
77.00
76.58
68.59
67.87
65.75
51.35
48.13
44.18
33.66
33.23
31.57
28.85
25.83
22.46
20.41
17.91
13.98
-4.72
-4.93
f1 (ppm)

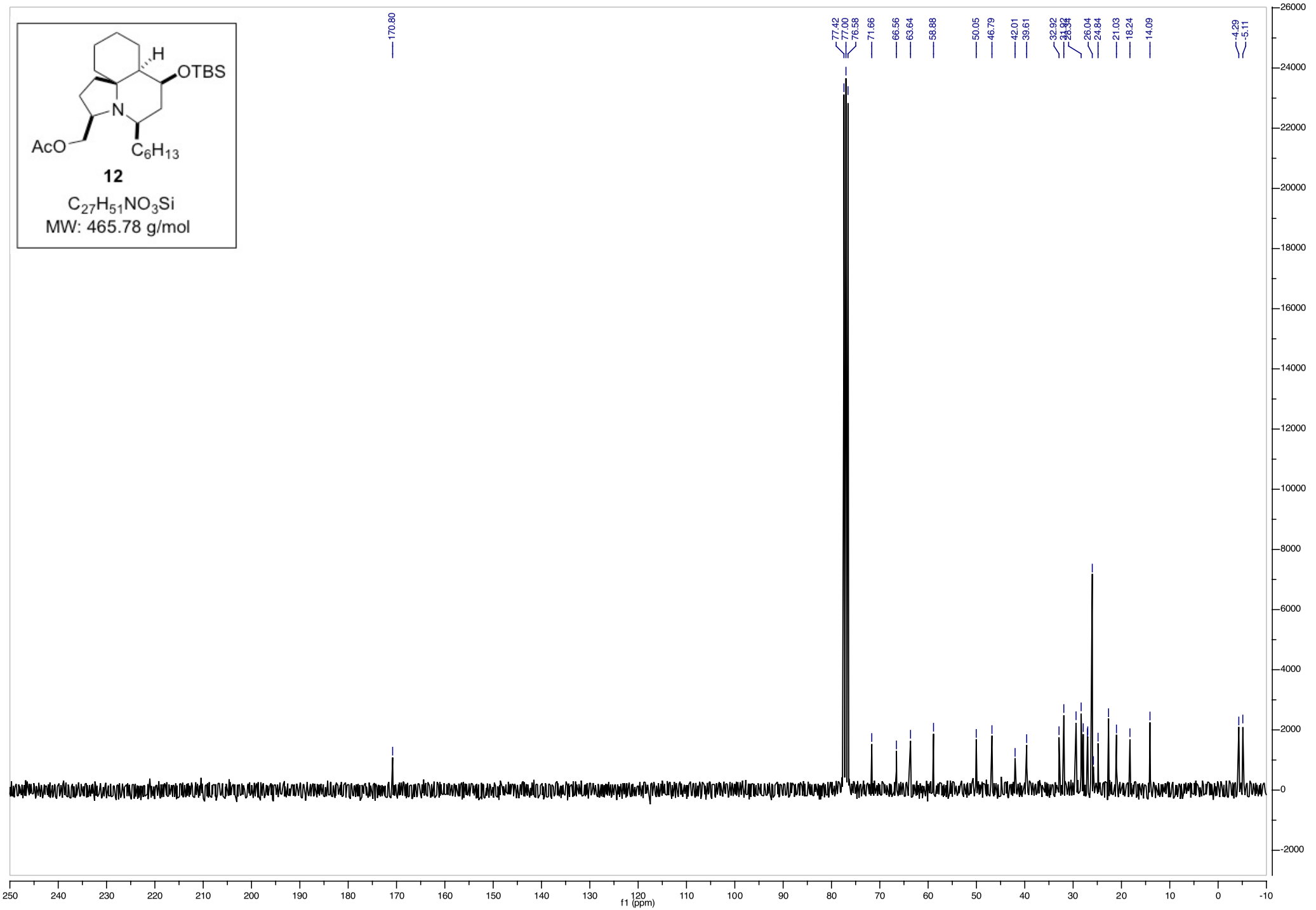

TBSO
O
C_6H_{13}
H
N_3
AcO
O
cis-3
$C_{27}H_{49}N_3O_5Si$
MW: 523.78 g/mol
f1 (ppm)

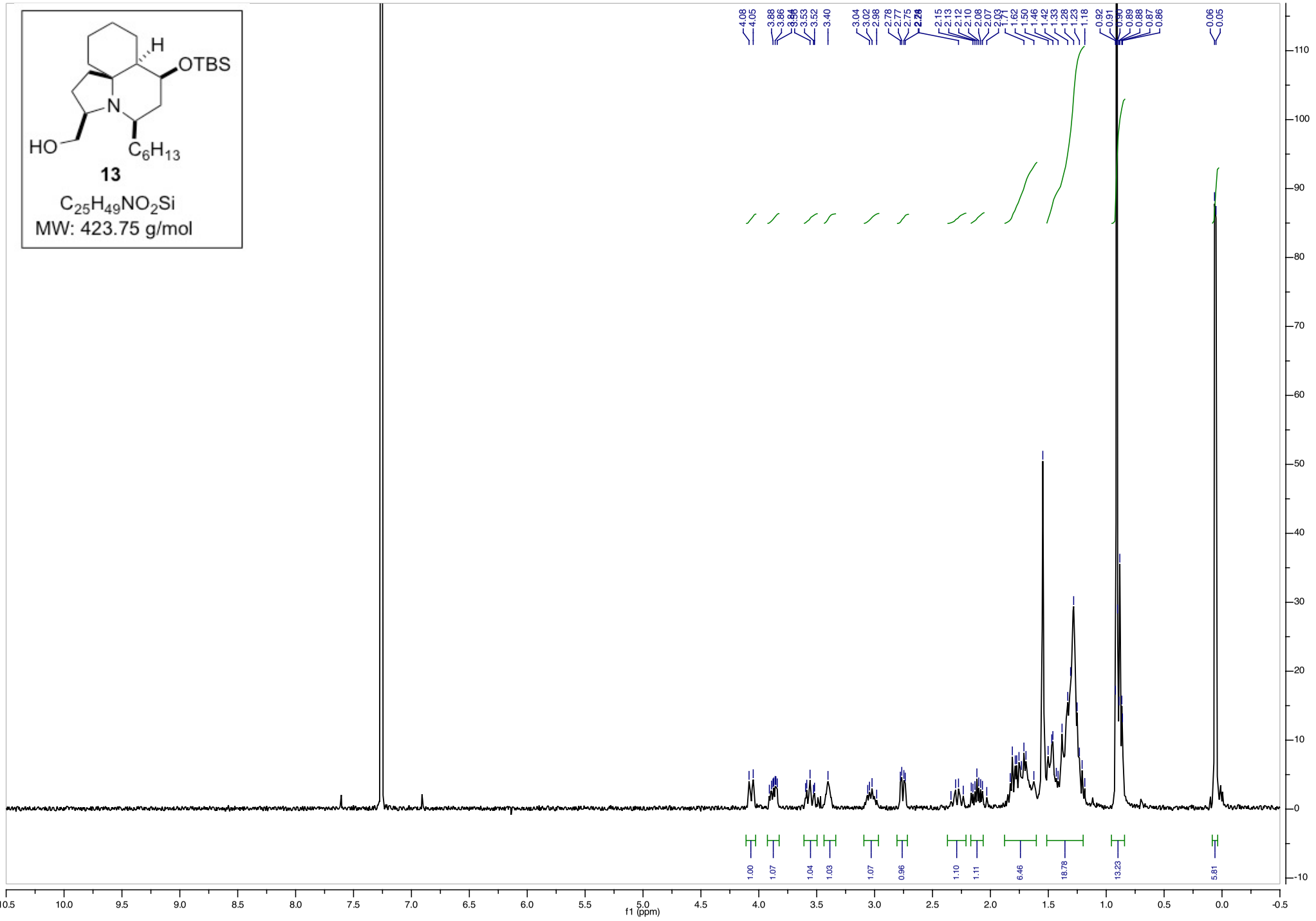

TBSO
O
C6H13
H
N3
AcO
O
cis-3
C27H49N3O5Si
MW: 523.78 g/mol
209.84
202.43
170.17
77.42
77.00
76.58
67.89
66.66
64.26
50.74
46.10
44.58
34.58
33.38
32.17
31.58
28.86
25.71
23.41
20.41
17.86
13.98
-4.75
-4.77
f1 (ppm)

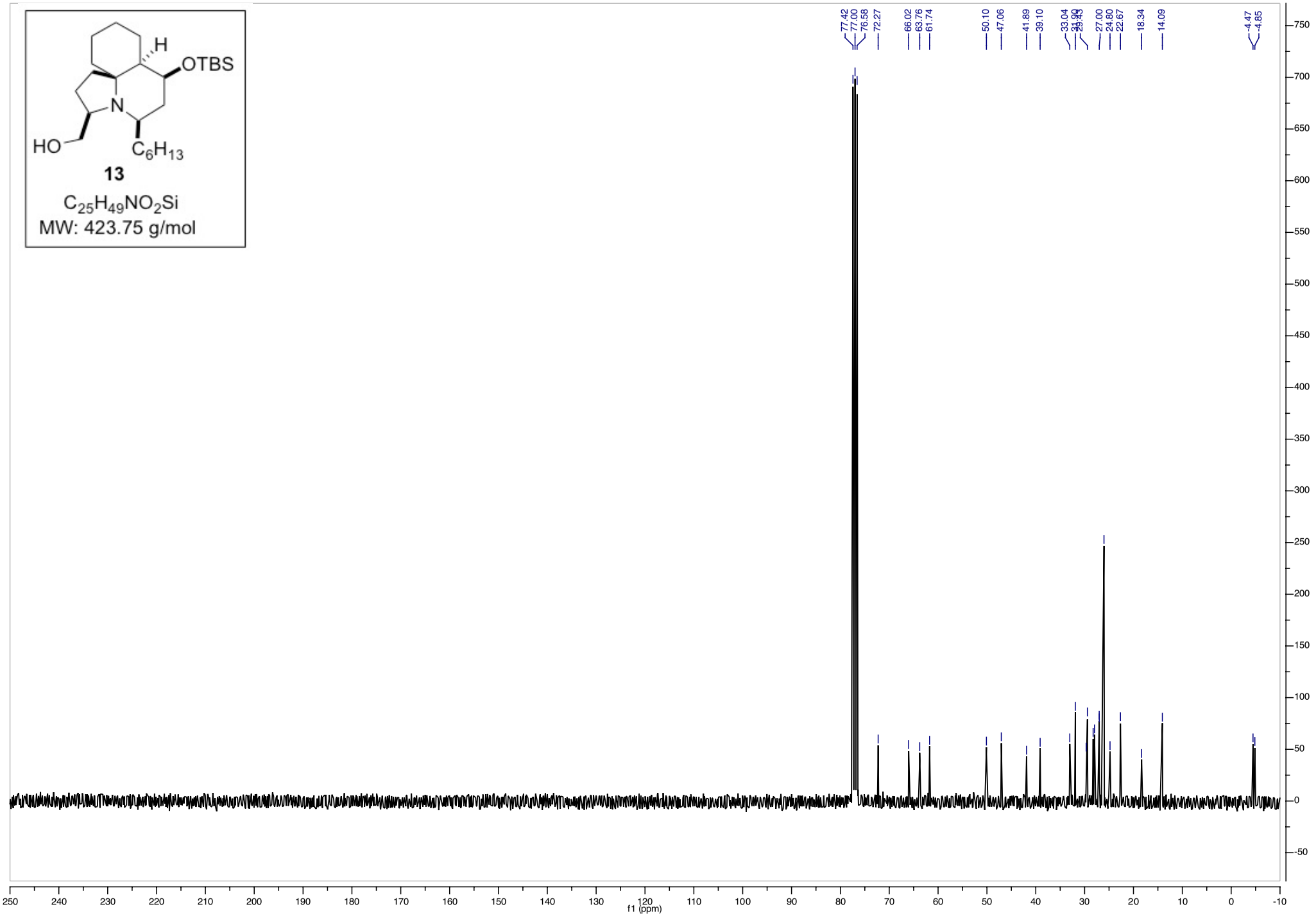

O
n-C6H13
H
NH
OTBS
AcO
crude 11
C27H53NO4Si
MW: 483.78 g/mol
f1 (ppm)

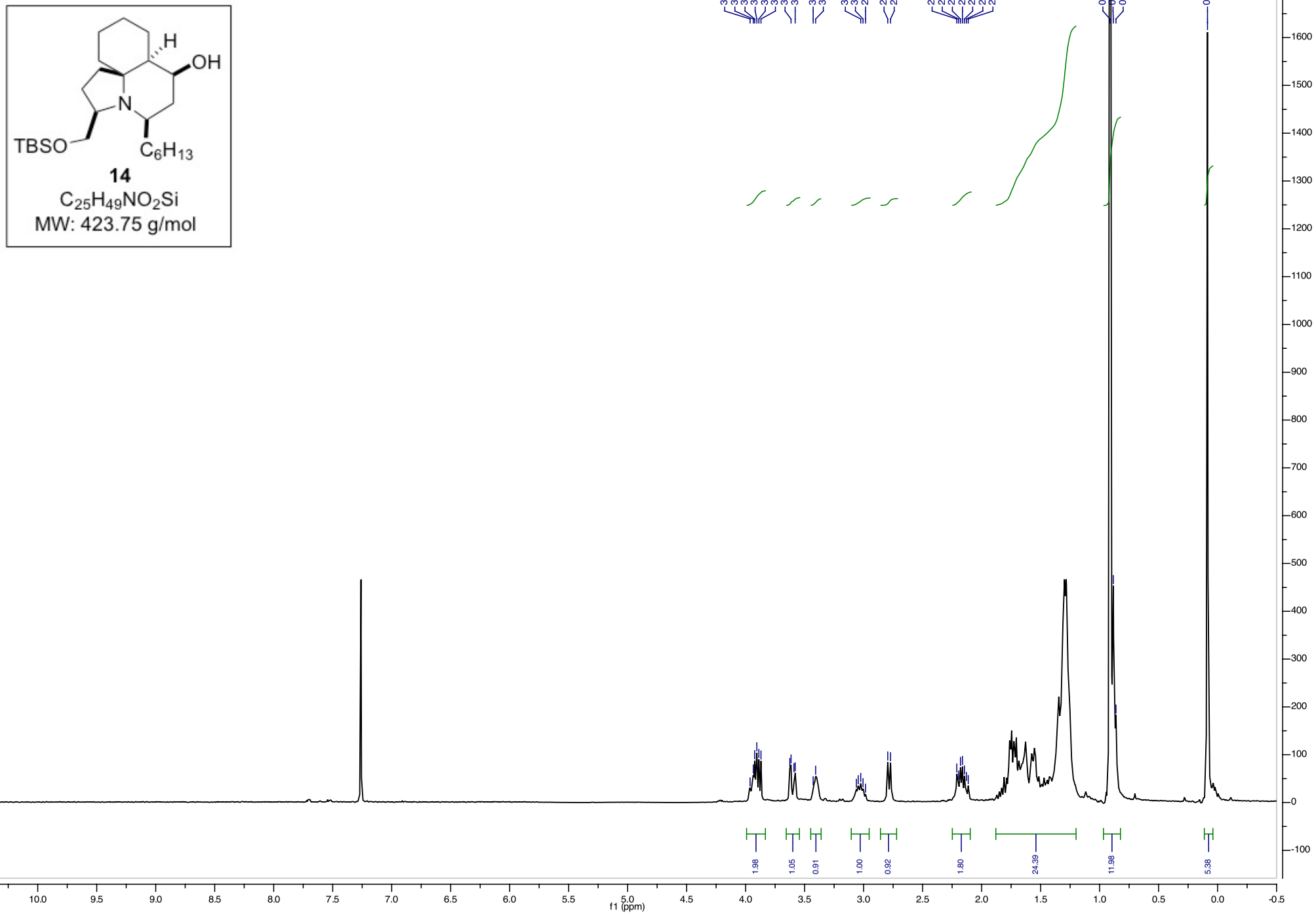

210.59
171.04
77.42
77.00
76.58
69.25
68.47
63.57
54.68
52.74
47.45
44.68
43.92
31.61
28.29
25.89
25.77
23.33
20.92
17.89
14.05
13.98
-4.42
-4.71
O
n-C6H13
H
NH
OTBS
AcO
crude 11
C27H53NO4Si
MW: 483.78 g/mol
f1 (ppm)

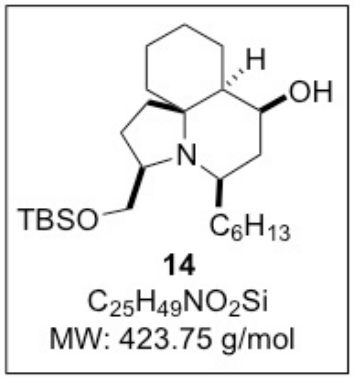

H
OTBS
N
AcO
C6H13
12
C27H51NO3Si
MW: 465.78 g/mol
4.47 4.46 4.43 4.42
4.09 4.05 4.02
3.42 3.41 3.40 3.39 3.38 3.37
3.03 3.01 2.98 2.97 2.94
2.40 2.39 2.37 2.32
2.11 2.10 2.09 2.08 2.06 2.05 2.03 2.01
0.90 0.89 0.88 0.86
0.06 0.03
0.98 2.01 1.00 1.00 1.03 4.30 6.66 18.73 13.46 2.93 3.11
f1 (ppm)


H
OTBS
N
AcO
C6H13
12
C27H51NO3Si
MW: 465.78 g/mol
170.80
77.42
77.00
76.58
71.66
66.56
63.64
58.88
50.05
46.79
42.01
39.61
32.92
31.92
28.34
26.04
24.84
21.03
18.24
14.09
-4.29
-5.11
f1 (ppm)


H
OTBS
N
HO
C_6H_{13}
13
$C_{25}H_{49}NO_2Si$
MW: 423.75 g/mol
f1 (ppm)


H
OTBS
N
HO
C_6H_{13}
13
$C_{25}H_{49}NO_2Si$
MW: 423.75 g/mol
77.42
77.00
76.58
72.27
66.02
63.76
61.74
50.10
47.06
41.89
39.10
33.04
31.90
29.43
27.00
24.80
22.67
18.34
14.09
-4.47
-4.85
f1 (ppm)


H
OH
N
TBSO
C_6H_{13}
14
$C_{25}H_{49}NO_2Si$
MW: 423.75 g/mol
3.96
3.94
3.92
3.91
3.89
3.87
3.62
3.58
3.43
3.41
3.02
3.01
2.98
2.80
2.77
2.21
2.20
2.18
2.16
2.15
2.13
2.11
0.91
0.88
0.86
0.09
1.98
1.05
0.91
1.00
0.92
1.80
24.39
11.98
5.38
f1 (ppm)



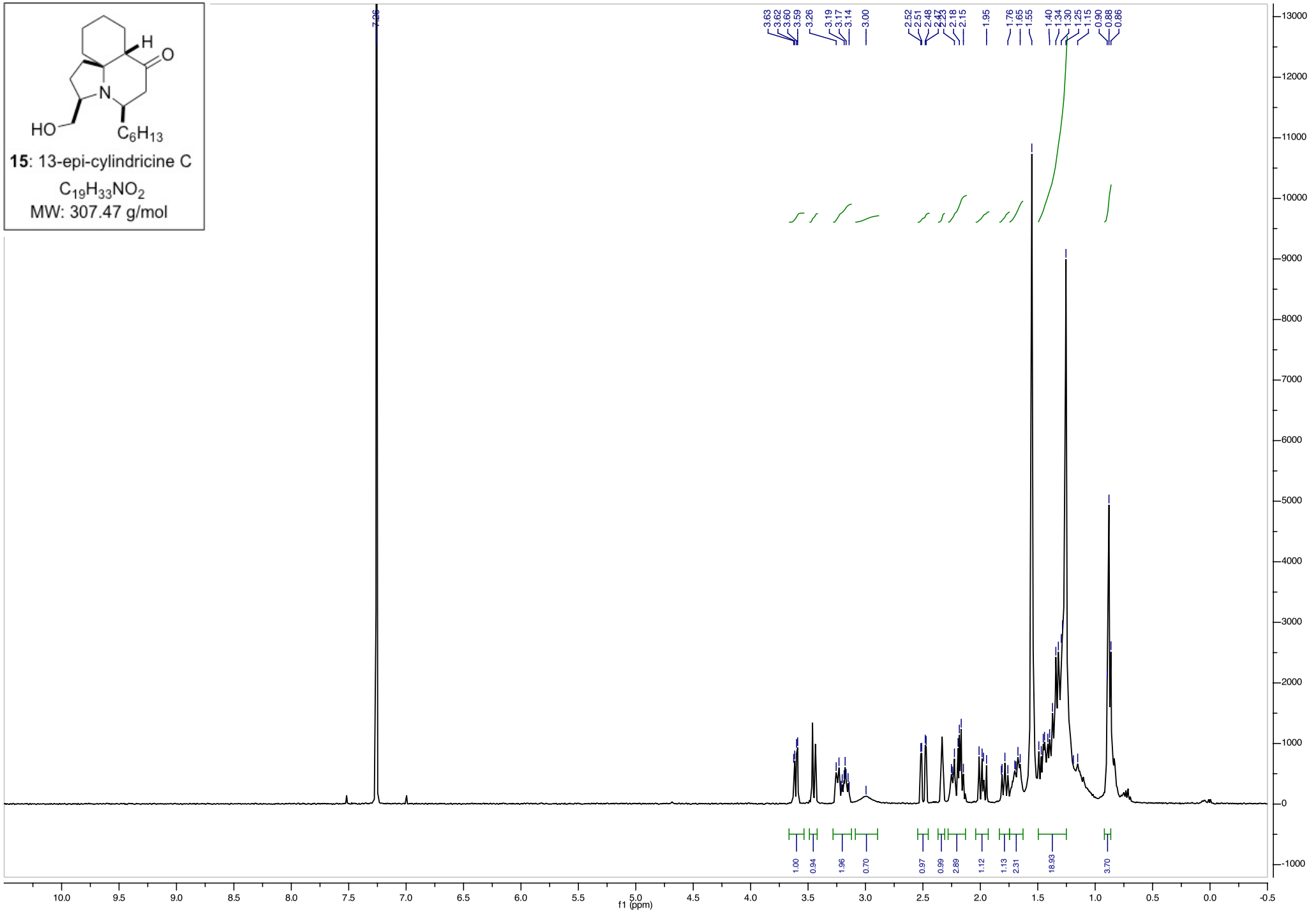
14

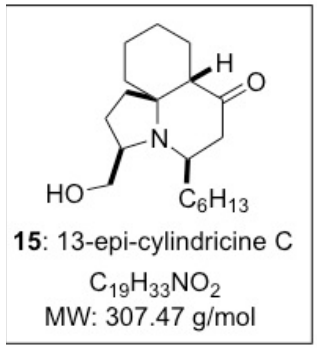
$C_{25}H_{49}NO_2Si$

MW: 423.75 g/mol

77.42
76.58
71.35
66.69
64.00
61.28
50.07
47.14
41.60
39.04
31.89
27.56
27.05
26.77
26.13
24.92
22.66
18.64
14.09
-5.13
-5.38

f1 (ppm)

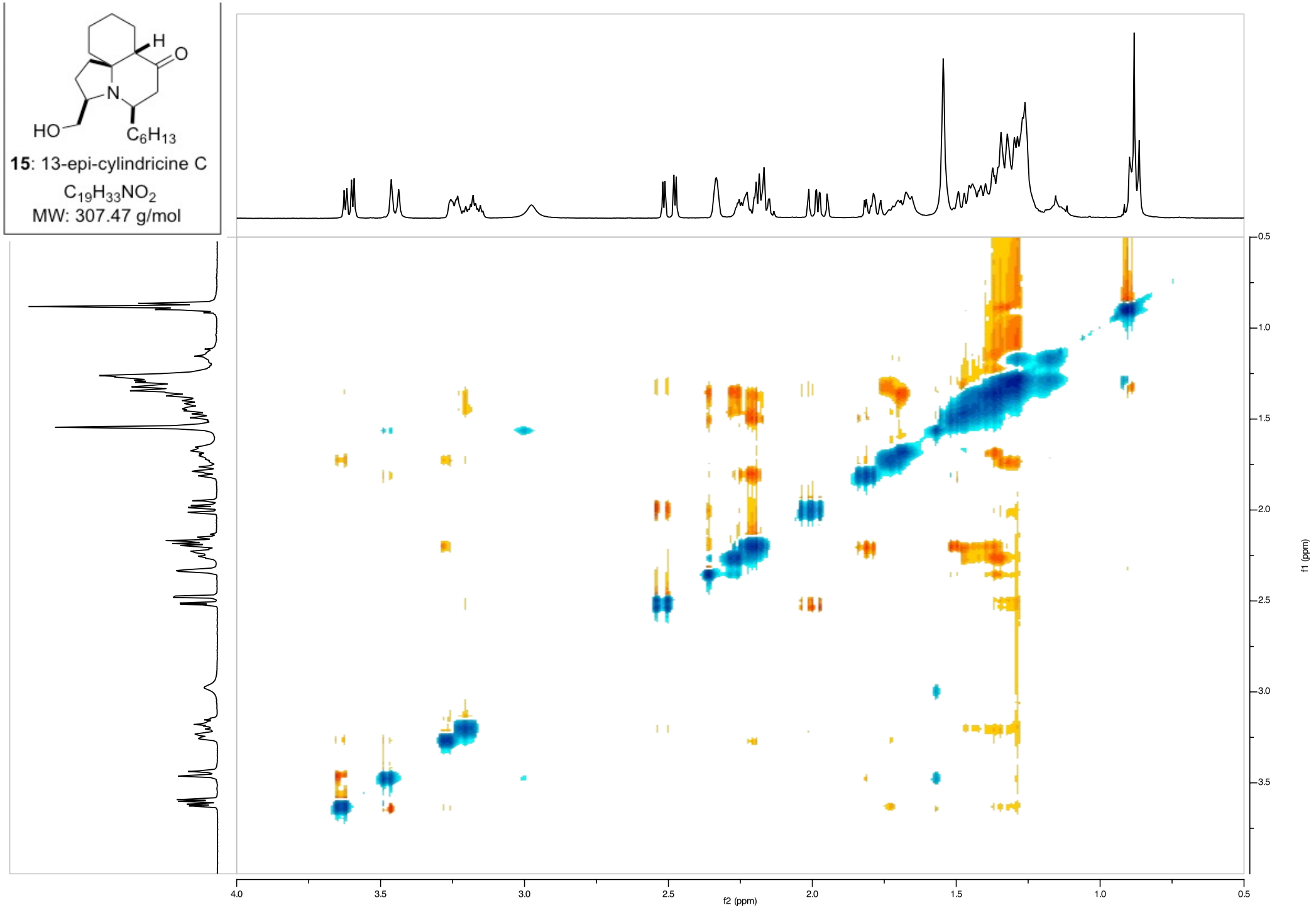

H
O
N
HO
C_6H_{13}
15: 13-epi-cylindricine C
$C_{19}H_{33}NO_2$
MW: 307.47 g/mol
7.26
3.63
3.62
3.60
3.59
3.26
3.19
3.17
3.14
3.00
2.52
2.51
2.48
2.47
2.23
2.18
2.15
1.95
1.76
1.65
1.55
1.40
1.34
1.30
1.25
1.15
0.90
0.88
0.86
1.00
0.94
1.96
0.70
0.97
0.99
2.89
1.12
1.13
2.31
18.93
3.70
f1 (ppm)

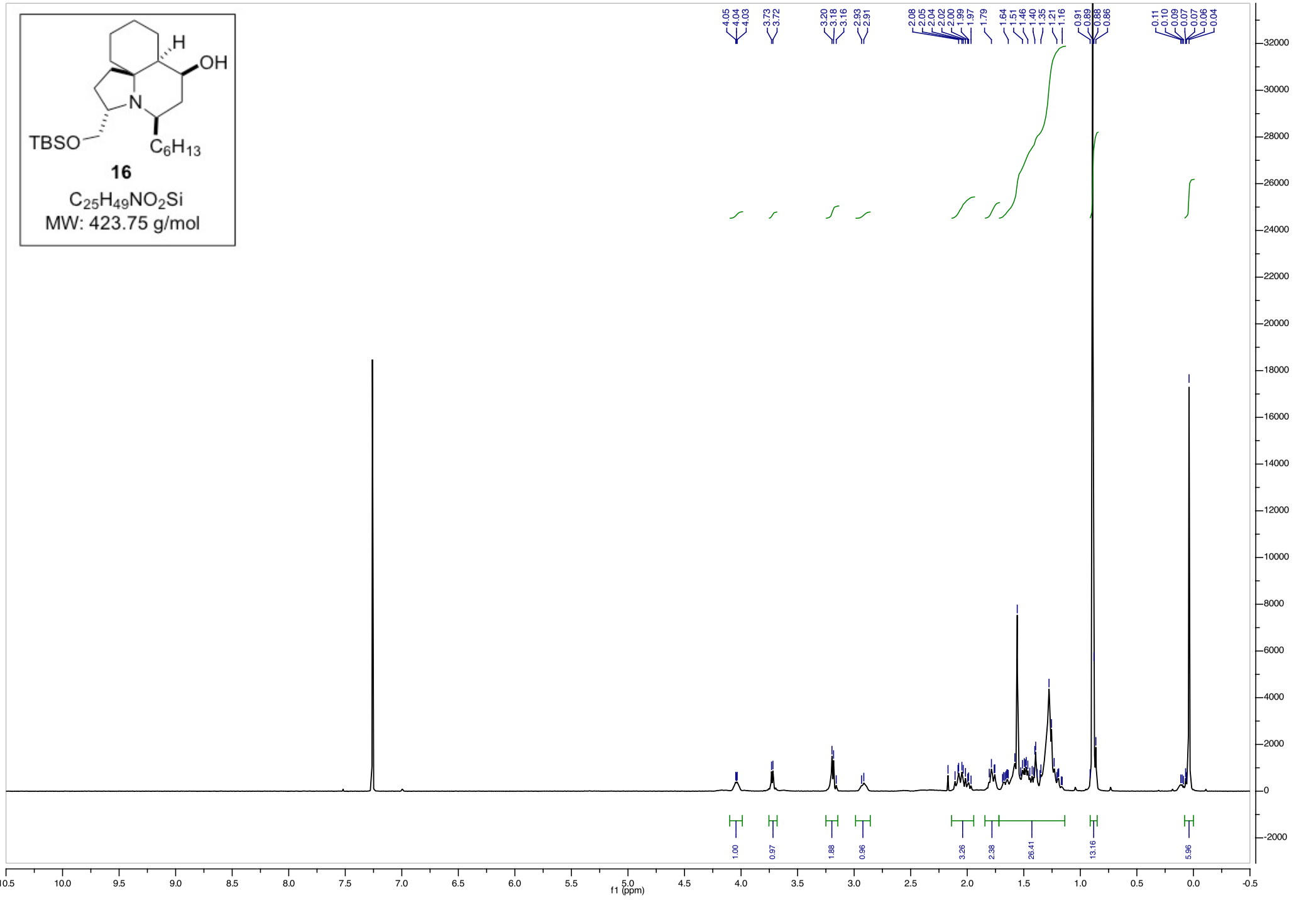


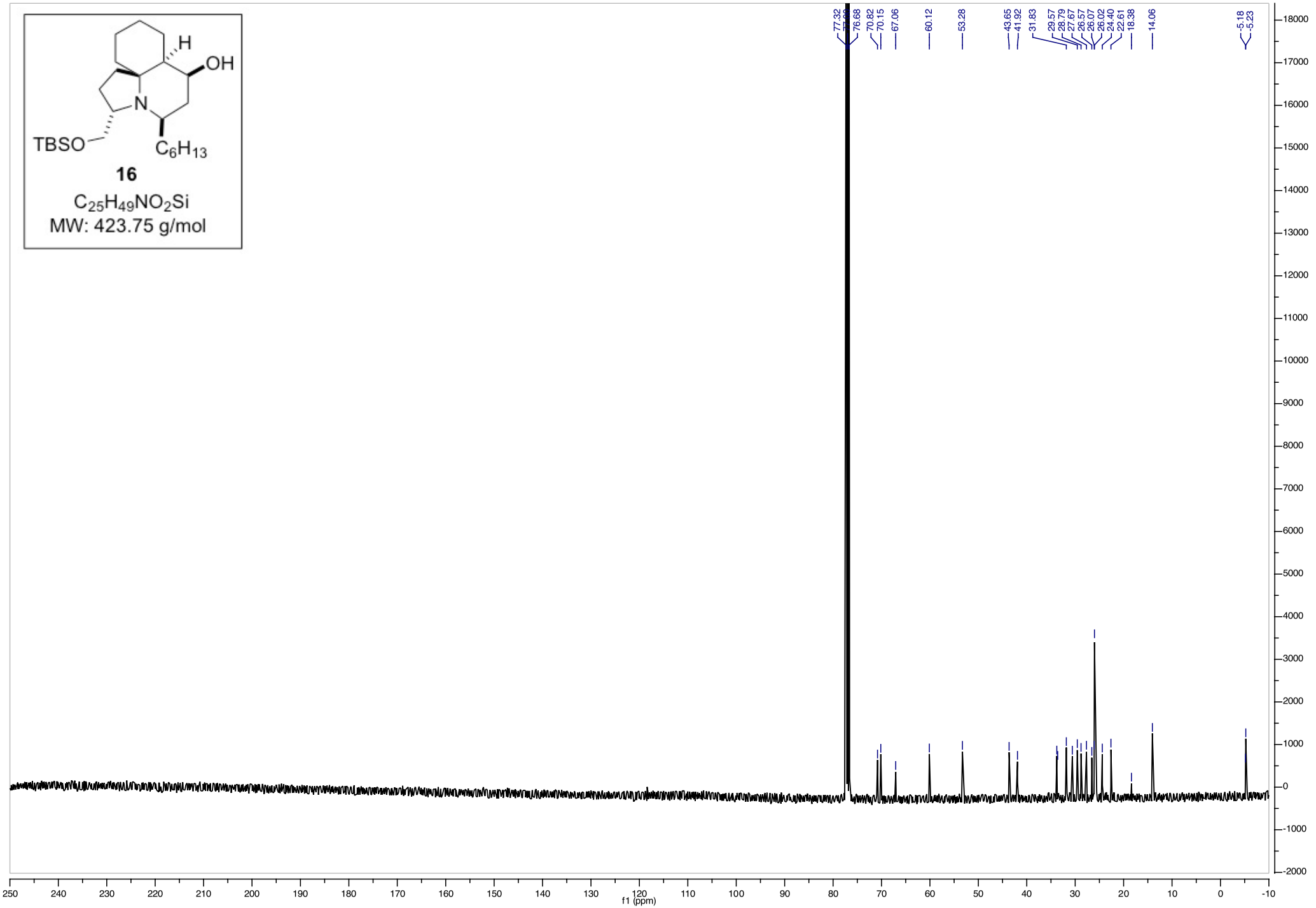
15: 13-epi-cylindricine C

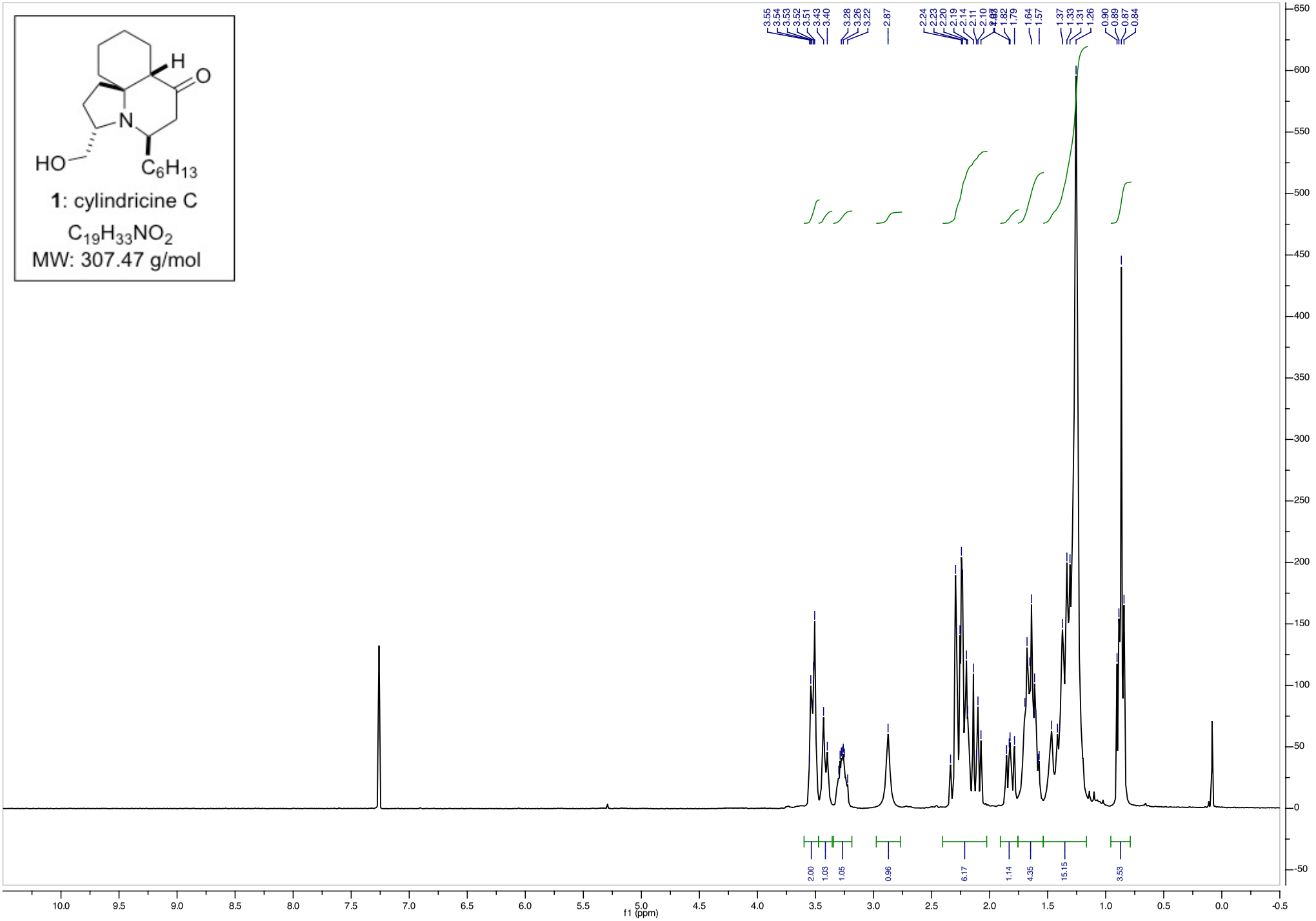
$C_{19}H_{33}NO_2$

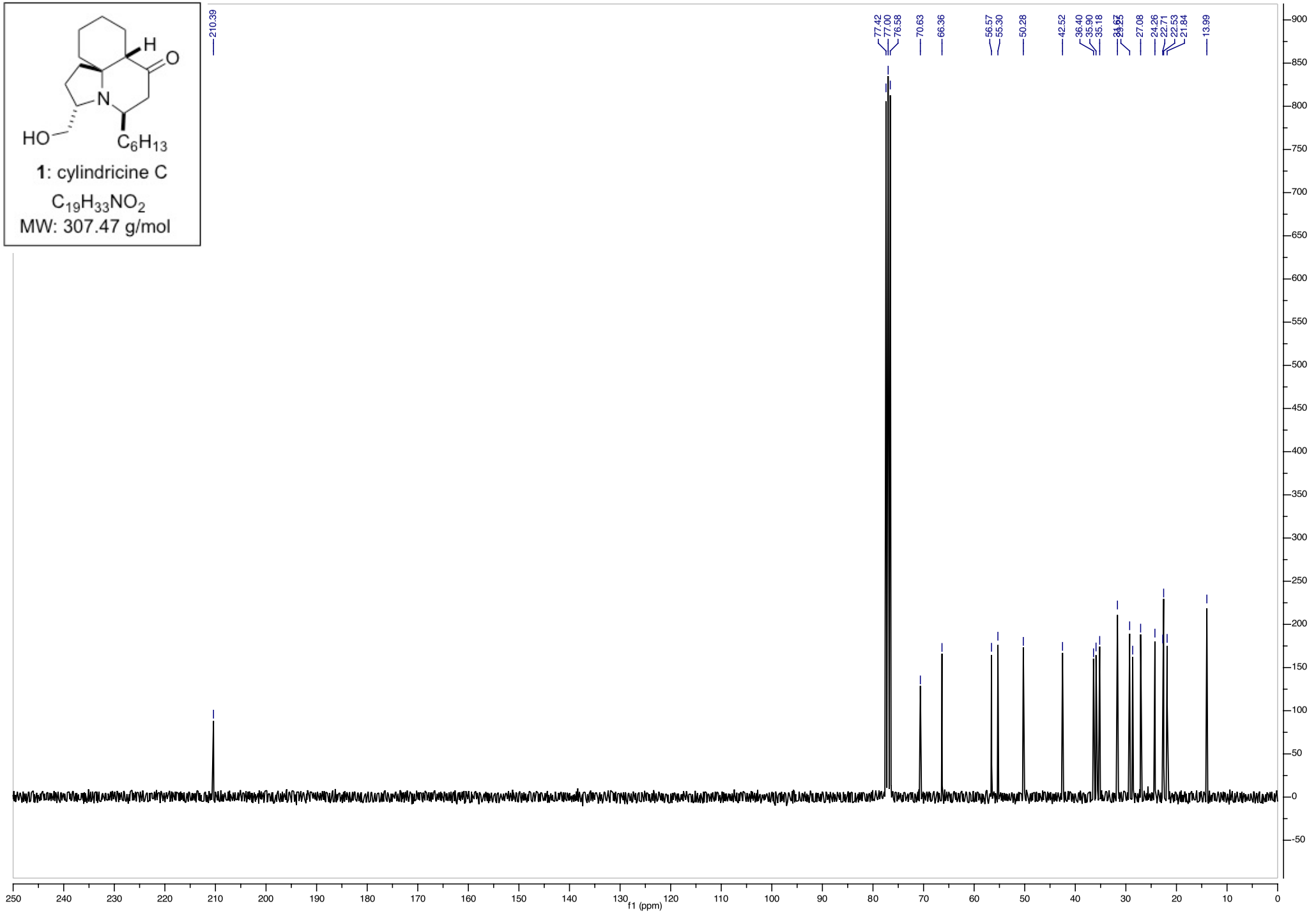
MW: 307.47 g/mol


H
O
N
HO
C_6H_{13}
15: 13-epi-cylindricine C
$C_{19}H_{33}NO_2$
MW: 307.47 g/mol
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
f1 (ppm)


TBSO
OH
H
N
C_6H_{13}
16
$C_{25}H_{49}NO_2Si$
MW: 423.75 g/mol
4.05 4.04 4.03 3.73 3.72 3.20 3.18 3.16 2.93 2.91 2.08 2.05 2.04 2.02 2.00 1.99 1.97 1.79 1.64 1.51 1.46 1.40 1.35 1.21 1.16 0.91 0.89 0.88 0.86 0.11 0.10 0.09 0.07 0.07 0.06 0.04
1.00 0.97 1.88 0.96 3.26 2.38 26.41 13.16 5.96
f1 (ppm)


H
OH
N
TBSO
C6H13
16
C25H49NO2Si
MW: 423.75 g/mol
77.32
76.68
70.82
70.15
67.06
60.12
53.28
43.65
41.92
31.83
29.57
28.79
27.67
26.57
26.07
26.02
24.40
22.61
18.38
14.06
-5.18
-5.23
f1 (ppm)


HO
H
O
N
C_6H_{13}
1: cylindricine C
$C_{19}H_{33}NO_2$
MW: 307.47 g/mol
3.55
3.54
3.53
3.52
3.51
3.43
3.40
3.28
3.26
3.22
2.87
2.24
2.23
2.20
2.19
2.14
2.11
2.10
1.82
1.79
1.64
1.57
1.37
1.33
1.31
1.26
0.90
0.89
0.87
0.84
2.00
1.03
1.05
0.96
6.17
1.14
4.35
15.15
3.53
f1 (ppm)


1: cylindricine C
C19H33NO2
MW: 307.47 g/mol
210.39
77.42
77.00
76.58
70.63
66.36
56.57
55.30
50.28
42.52
36.40
35.90
35.18
27.08
24.26
22.71
22.53
21.84
13.99
f1 (ppm)