SUPPORTING INFORMATION

Total Synthesis of (±)-Lycojaponicumin D and Lycodoline-Type *Lycopodium* Alkaloids

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General

All moisture or oxygen-sensitive reactions were carried out under an argon atmosphere in oven flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: THF (Na), CH_2Cl_2 (CaH_2), toluene (Na), Et_3N (CaH_2), CH_3CN (CaH_2), EtOH (Mg). All reactions were monitored by thin-layer chromatography (TLC) on silica gel F_{254} plates using UV light as visualizing agent (if applicable), and a solution of phosphomolybdic acid (50 g/L) in EtOH followed by heating as developing agents. The products were purified by flash column chromatography on silica gel (200−300 meshes) from the Anhui Liangchen silicon material company in China.

^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, $(CD_3)_2CO$ or CD_3OD solution on a Varian Mercury-300 MHz instrument, Bruker AM 400 MHz instrument or Varian AS 600 MHz instrument. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent ($CDCl_3$ (7.27 ppm), $(CD_3)_2CO$ (2.05 ppm), CD_3OD (3.31 ppm) or tetramethylsilane (0.00 ppm)) as internal reference for ^1H NMR and the deuterated solvent ($CDCl_3$ (77.00 ppm), $(CD_3)_2CO$ (29.84 ppm), CD_3OD (49.00 ppm) or tetramethylsilane (0.00 ppm)) as internal standard for ^{13}C NMR. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet.

The high-resolution mass spectral analysis (HRMS) data were measured on Thermo Fisher Orbitrap Elite Mass Spectrometer by means of the ESI technique.

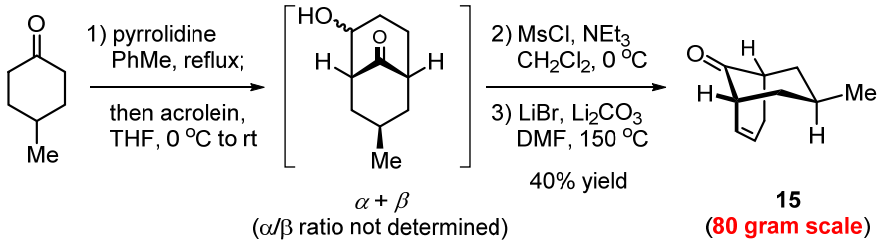
The IR spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer.

The X-ray single-crystal determination was performed on an Agilent SuperNova single crystal X-ray diffractometer.

The melting points were measured on an X–4 microscopic melting point apparatus without calibration (BeijingTech Instrument Co., LTD).

1. Synthesis of Precursors for Tandem Oxidative Dehydrogenation/*Oxa*-Michael Reaction

1.1. Compound 15



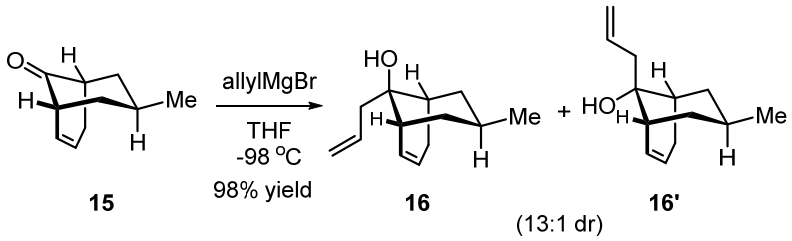
To a 2-L round-bottomed flask containing 4-methylcyclohexanone (158.2 g, 1.410 mol) in toluene (600 mL) was added pyrrolidine (217 mL, 2.63 mol). The reaction mixture was refluxed with the removal of water for 18 h. After removal of toluene and unconverted pyrrolidine under reduced pressure, the residue was dissolved in THF (1000 mL), and acrolein (122.5 mL, 1.837 mol) was added dropwise at 0 °C in an argon atmosphere. The resulting mixture was stirred at ambient temperature for 2 h. The aqueous 2*N* HCl was added until the pH of the solution is 1~2. After stirring for 30 min, EtOAc (200 mL) was added. The organic phase was separated, and the aqueous layer was extracted with EtOAc (3 × 100 mL). The organic extracts were combined, washed with water (1 × 200 mL) and brine (1 × 200 mL), dried with Na_2SO_4. The solvent was removed under reduced pressure and the crude product was used in the next reaction without further purification.

To a stirred solution of the crude product obtained above, Et_3N (413 mL, 2.97 mol) in dry CH_2Cl_2 (1000 mL) was added a solution of methanesulfonyl chloride (120.3 mL, 1.55 mol) in dry CH_2Cl_2 (200 mL) dropwise over 1 h at 0 °C. The resulting solution was stirred at 0 °C for 2 h, quenched with saturated NH_4Cl. The organic phase was separated, washed with 2*N* HCl and brine, dried over Na_2SO_4. Evaporation of solvent gave yellow oil, and the crude product was used for the next reaction without purification.

A solution of the crude product obtained above, LiBr (491 g, 5.65 mol) and Li_2CO_3 (626 g, 8.48 mol) in DMF (1500 mL) was stirred at 150 °C (bath temperature) for 1.5 h. The reaction mixture was allowed to cool to the ambient temperature and then filtered under reduced pressure. The filtrate was poured into water (500 mL) and extracted with Et_2O (4 × 150 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The pale yellow oil was obtained, which was purified by column chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 30:1) to afford the enone **15** (84.9 g, 0.566 mol, 40% yield, three steps) as a light yellow liquid.

15: R_f = 0.39 (silica, petroleum ether/EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.86 (dt, J = 9.5, 3.3Hz, 1H), 5.62−5.55 (m, 1H), 2.77−2.68 (m, 2H), 2.53−2.49 (m, 1H), 2.45 (dd, J = 18.5, 3.3 Hz, 1H), 2.36−2.21 (m, 1H), 1.92−1.83 (m, 2H), 1.59−1.46 (m, 2H), 0.90 ppm (d, J = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 216.9, 129.5, 127.9, 47.2, 45.0, 44.9, 41.2, 37.1, 23.3, 20.2 ppm; **IR**: $\bar{\nu}$ = 3422, 2926, 2371, 1731, 1458, 1225, 1088, 694 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{10}H_{15}O$, $[M+H]^+$: 151.1117; found: 151.1119.

1.2. Compound 16



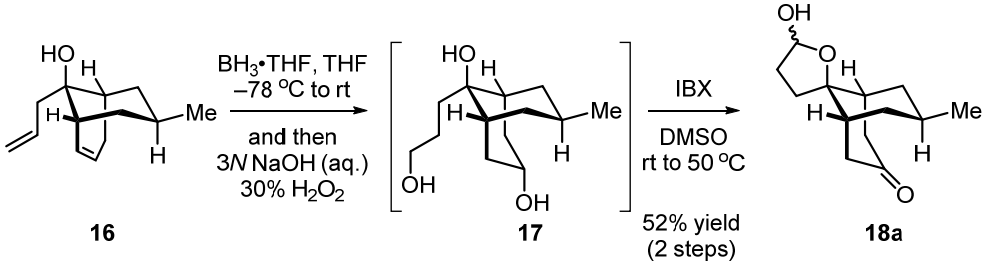
Allylmagnesium bromide (1212 mL, 0.606 mol, 0.50 M solution in THF) was added dropwise to the solution of enone **15** (18.2 g, 0.121 mol) in THF (200 mL) at −98 °C (MeOH/N_2(l) bath). The resulting mixture was stirred at −98 °C for 1 h. After warmed to ambient temperature, the reaction was quenched with saturated NH_4Cl (200 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (3×200 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 30:1) to afford **16** (20.961 g, 0.109 mol, 91% yield) as a light yellow liquid and **16'** (1.60 g, 8.33 mmol, 7 % yield) as a light yellow liquid.

16: R_f = 0.46 (silica, petroleum ether/EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.97−5.85 (m, 1H), 5.71 (dt, J = 9.7, 3.3 Hz, 1H), 5.57 (m, 1H), 5.14 (d, J = 8.4 Hz, 1H), 5.11 (d, J = 16.9 Hz, 1H), 2.40−2.25 (m, 3H), 2.11 (d, J = 2.8 Hz, 1H), 2.00 (dd, J = 19.0, 3.6 Hz, 1H), 1.83−1.71 (m, 2H), 1.62 (qd, J = 11.9, 3.8 Hz, 2H), 1.64 (s, 1H), 1.30 (t, J = 13.5 Hz, 2H), 0.85 ppm (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 134.1, 129.1, 127.8, 118.8, 71.8, 43.1, 40.4, 38.1, 36.7, 32.8, 32.7, 22.5, 21.7 ppm; **IR**: $\bar{\nu}$ = 3458, 2914, 1638, 1456, 1141, 1373, 999, 915, 727 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{13}H_{20}ONa$, [M+Na]$^+$: 215.1406; found: 215.1405.

16': R_f = 0.37 (silica, petroleum ether/EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.05−5.92 (m, 2H), 5.62−5.55 (m, 1H), 5.14 (dd, J = 12.9, 1.3 Hz, 2H), 2.49 (qd, J = 20.2, 7.2 Hz, 2H), 2,47 (t, J = 6.9 Hz, 1H), 2.23 (s, 1H), 1.92 (brd, J = 18.7 Hz, 2H), 1.86−1.75 (m, 1H), 1.56−1.32 (m, 4H), 0.88 ppm (d, J = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 134.0, 130.2, 128.1, 117.5, 72.3, 40.7, 40.6, 39.9, 36.8, 34.9, 31.3, 22.1, 21.5 ppm; **IR**: $\bar{\nu}$ = 3579, 3472, 2916, 1639, 1459, 1376, 1148, 1000, 910 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{13}H_{20}ONa$, [M+Na]$^+$: 215.1406; found: 215.1409.

1.3. Compound 18a and X-Ray Crystallography of 17

1.3.1. Compound 18a



To a solution of **16** (9.615 g, 50 mmol) in dry THF (150 mL) was added the BH_3•THF complex (Across, 250 mL of 1.0 M, 0.25 mol) dropwise at −78 °C. The resulting mixture was stirred at −78 °C for 24 h, and stirred at ambient temperature for another 24 h. 3N sodium hydroxide

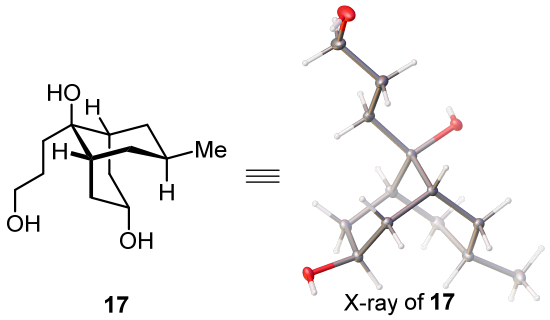
(250 mL, 0.75 mol) was slowly dripped into the reaction mixture at 0 °C, and 30% hydrogen peroxide (250 mL) was subsequently added dropwise. The reaction mixture was stirred at ambient temperature for 24 h, and extracted with *n*-butylalcohol (4 × 100 mL). After removal of *n*-butylalcohol under reduced pressure, the residue was dissolved in DMSO (1000 mL), and 2-iodoxybenzoic acid (IBX, 70.0 g, 0.250 mol) was added. The reaction mixture was stirred at 50 °C and constantly monitored by TLC until complete consumption of the starting material was observed. The reaction mixture was cooled to ambient temperature and quenched with saturated $NaHCO_3$ (200 mL) and $Na_2S_2O_3$ (200 mL), diluted with EtOAc (200 mL). The organic phase was separated, and the aqueous layer was extracted with EtOAc (3 × 200 mL). The organic layers were combined, washed with saturated $NaHCO_3$, saturated $Na_2S_2O_3$, water, brine, and dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 3/1) to afford **18a** (**mp** 164−167 °C, 5.850 g, 26.1 mmol, 52% yield, two steps) as a white solid.

17: (white solid, **mp** 173−176 °C): $\boldsymbol{R_f}$ = 0.42 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.38−4.24 (m, 1H), 3.59 (t, J = 6.5 Hz, 2H), 1.97−1.88 (m, 2H), 1.81−1.69 (m, 9H), 1.67−1.56 (m, 2H), 1.44 (d, J = 5.5 Hz, 2H), 0.89 ppm (d, J = 4.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 73.1, 66.4, 63.7, 39.42, 39.36, 36.9, 35.7, 28.8, 26.6, 23.9 ppm; **IR**: $\bar{\nu}$ = 3306, 2954, 2925, 1456, 1384, 1057, 1035, 994, 734 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{13}H_{24}O_3Na$, $[M+Na]^+$: 251.1618; found: 251.1620.

18a: $\boldsymbol{R_f}$ = 0.29 (silica, petroleum ether/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.58 (s, 1H), 2.65−2.53 (m, 3H), 2.47−2.38(m, 2H), 2.25−2.19 (m, 1H), 2.17−2.02 (m, 4H), 2.01−1.96 (m, 1H), 1.83 (td, J = 13.1, 4.0 Hz, 1H), 1.74 (td, J = 12.5, 3.8 Hz, 1H), 1.64−1.44 (m, 3H), 0.88 ppm (d, J = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 211.4, 98.1, 84.6, 45.9, 45.6, 41.2, 38.6, 37.3, 36.8, 33.2, 32.4, 22.7, 22.2 ppm; **IR**: $\bar{\nu}$ = 3047, 2931, 2872, 1701, 1461, 1206, 1036, 994 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{13}H_{20}O_3Na$, $[M+Na]^+$: 247.1305; found: 247.1307.

1.3.2. X-Ray Crystallography of 17

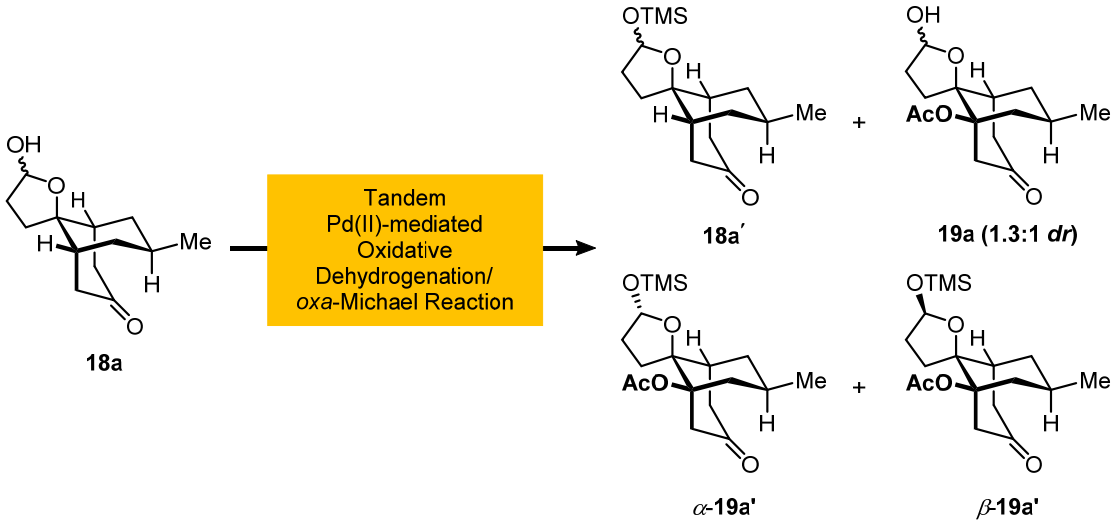
The single crystal of **17**, which was obtained through one recrystallization from a mixed solvent of CH_2Cl_2 and MeOH, was used for the determination of its relative configurations via X-ray crystallographic analysis. The crystal structure and the X-ray crystallographic data of **17** (CCDC 1539340) were described as follows:



Crystal data and structure refinement for compound 17

Identification code	Compound **17**
Empirical formula	$C_{13}H_{26}O_4$
Formula weight	246.34
Temperature/K	292.84(10)
Crystal system	trigonal
Space group	P-3
a/Å	19.4673(6)
b/Å	19.4673(6)
c/Å	6.5368(3)
α/°	90.00
β/°	90.00
γ/°	120.00
Volume/Å^3	2145.39(14)
Z	2
ρ_{calc}g/cm^3	1.144
μ/mm^{-1}	0.083
F(000)	816.0
Crystal size/mm^3	0.41 × 0.37 × 0.35
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.68 to 52.04
Index ranges	$-21 \le h \le 23$, $-22 \le k \le 24$, $-8 \le l \le 4$
Reflections collected	4625
Independent reflections	2804 [R_{int} = 0.0205, R_{sigma} = 0.0491]
Data/restraints/parameters	2804/3/166
Goodness-of-fit on F^2	1.552
Final R indexes [I>=2σ (I)]	R_1 = 0.1229, wR_2 = 0.3895
Final R indexes [all data]	R_1 = 0.1495, wR_2 = 0.4197
Largest diff. peak/hole / e Å^{-3}	3.61/-0.28

2. Study of the Tandem Oxidative Dehydrogenation/*Oxa*-Michael Reaction



2.1. General Produce of Oxidative Dehydrogenation/*Oxa*-Michael Reaction

To a stirred solution of **18a** in the solvent was added the base (3.0 equiv) and chlorotrimethyhilane (3.0 equiv) or TMSOTf (3.0 equiv). The reaction was constantly monitored by TLC until complete consumption of starting material was observed, and then quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic extracts were combined, washed with brine, dried over Na_2SO_4. The solvent was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel.

To a solution of the silyl enol ether obtained above in freshly distilled acetonitrile was added palladium(II) acetate, freshly prepared according to the reported procedure[1] and other additive. The reaction mixture was stirred for 24 h, and filtered through a short silica gel column with EtOAc. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel.

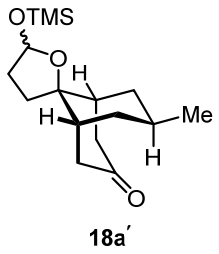
2.2. Detail of the Screening of Optimum Conditions

Table SI-1. Optimum Conditions Screened for the Key Tandem Reaction

Entry	Conditions	Yield[a][%]				
		19a	α-19a'	β-19a'	19a+19a'	18a'
1	1. TMSOTf, NEt_3, CH_2Cl_2, 0 °C 2. $Pd(OAc)_2$, CH_3CN, 60 °C	6	8	5	19	20
2	1. KHMDS, TMSCl, THF, 0 °C 2. $Pd(OAc)_2$, CH_3CN, 60 °C	17	23	12	52	25
3	1. LDA, TMSCl, THF, −78 °C 2. $Pd(OAc)_2$, CH_3CN, 60 °C	17	24	12	53	26
4	1. LDA, TMSCl, THF, −78 °C 2. $Pd(OAc)_2$, CH_3CN, 30 °C	12	13	9	38	30
5	1. LDA, TMSCl, THF, −78 °C 2. $Pd(OAc)_2$, Na_2CO_3, CH_3CN, 60 °C	15	22	11	48	28

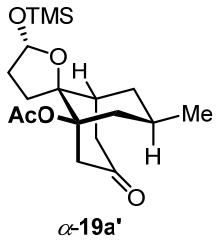
[a]Yield of isolated product.

2.3. Spectroscopic Data for the Products of 18a', α-19a', β-19a' and 19a



18a'

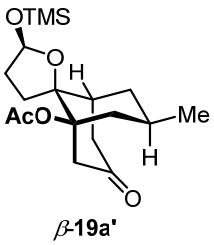
18a': R_f = 0.50 (silica, petroleum ether/EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.46 (s, 1H), 2.57 (dd, J = 18.5, 6.5 Hz, 2H), 2.42−2.32 (m, 2H), 2.14−2.09 (m, 1H), 2.08−1.98 (m, 3H), 1.95−1.87 (m, 2H), 1.82 (td, J = 12.3, 3.8 Hz, 1H), 1.72 (td, J = 12.0, 3.6 Hz, 1H), 1.57−1.37 (m, 3H), 0.84 (d, J = 6.1 Hz, 3H), 0.13 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 211.7, 97.9, 83.7, 45.9, 45.5, 41.0, 38.4, 37.2, 36.7, 34.7, 32.2, 22.7, 22.3, 0.21 ppm; **IR**: $\bar{\nu}$ = 3398, 2951, 1710, 1457, 1251, 1198, 1016, 985, 842 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{28}O_3SiNa$, $[M+Na]^+$: 319.1700; found: 319.1702.



α-19a'

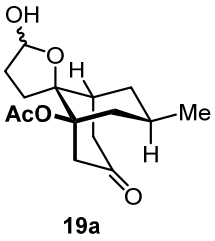
α-19a': R_f = 0.37 (silica, petroleum ether/EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.62 (d, J = 4.1 Hz, 1H), 3.71 (dd, J = 17.7, 2.6 Hz, 1H), 2.68−2.58 (m, 2H), 2.55 (dd, J = 12.3, 1.2 Hz, 1H), 2.40 (dt, J = 17.8, 2.0 Hz, 1H), 2.33−2.23 (m, 2H), 2.22−2.12 (m, 1H), 2.10−2.03 (m, 1H), 1.97 (s, 3H), 1.95−1.88 (m, 1H), 1.88−1.79 (m, 1H), 1.75 (td, J = 12.3, 1.8 Hz, 1H), 1.63−1.49 (m, 1H), 1.42 (dq, J = 13.1, 2.0 Hz, 1H), 0.91 (d, J = 6.2 Hz, 3H), 0.17 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.3, 169.6, 99.0, 85.9, 84.3, 49.9, 44.7, 42.2, 38.8, 36.4, 36.2, 30.5, 25.5, 22.3, 21.9, 0.3 ppm; **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 5.59 (d, J = 4.3 Hz, 1H), 3.67 (dd, J = 17.7, 2.6 Hz, 1H), 2.64−2.56 (m, 2H), 2.52 (dd, J = 12.3, 2.9 Hz, 1H), 2.36 (brd, J = 17.8, 2.0 Hz, 1H), 2.29−2.20 (m, 2H), 2.18−2.11 (m, 1H), 2.06−1.99 (m, 1H), 1.94 (s, 3H), 1.91−1.86 (m, 1H), 1.85−1.77 (m, 1H), 1.72 (td, J = 12.5, 1.4 Hz, 1H), 1.56−1.46 (m, 1H), 1.41−1.36 (m, 1H), 0.88 (d, J = 6.2 Hz, 3H), 0.14 ppm (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 208.1, 169.5, 99.0, 85.9, 84.2, 49.8, 44.7, 42.1, 38.7, 36.4, 36.1, 30.4, 25.5, 22.2, 21.9, 0.2 ppm; **IR**: $\bar{\nu}$ = 3400, 2957, 2373, 1736, 1717, 1251, 1098, 1032, 734 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{18}H_{30}O_5SiNa$, $[M+Na]^+$: 377.1755; found: 377.1758.

The relative configuration of **α-19a'** was determined according to the 2D NOESY (see S72–S73).



β-19a'

β-19a': R_f = 0.30 (silica, petroleum ether/EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.53 (dd, J = 5.0, 2.8 Hz, 1H), 3.74 (dd, J = 17.5, 2.5 Hz, 1H), 2.65−2.43 (m, 4H), 2.36 (dt, J = 18.2, 1.8 Hz, 1H), 2.19−2.08 (m, 1H), 2.07−1.94 (m, 2H), 2.02 (s, 3H), 1.84−1.73 (m, 3H), 1.62−1.48 (m, 1H), 1.41−1.34 (m, 1H), 0.90 (d, J = 6.2 Hz, 3H), 0.17 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.1, 170.0, 98.4, 85.8, 82.3, 49.7, 44.7, 39.3, 39.0, 35.9, 34.8, 27.8, 25.5, 22.4, 22.0, 0.3 ppm; **IR**: $\bar{\nu}$ = 3407, 2957, 1731, 1459, 1368, 1250, 1024, 842 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{18}H_{30}O_5SiNa$, $[M+Na]^+$: 377.1755; found: 377.1760.



19a

19a: (1.3:1 dr), R_f = 0.30 (silica, petroleum ether/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.69 (d, J = 4.2 Hz, 1.3H, ,major), 5.50 (dd, J = 8.0, 4.5 Hz, 1H, minor), 3.80 (dd, J = 17.4, 2.4 Hz, 1H, minor), 3.72 (dd, J = 17.7, 2.6 Hz, 1.3 H, major), 2.93 (d, J = 8.3 Hz, 0.9H, minor), 2.70−2.53 (m, 9.7H, major+minor), 2.47−2.28 (m, 7.1H, major+minor), 2.26−2.16 (m, 2.3H, major+minor), 2.15−2.09 (m, 3.8H, major+minor), 2.09−2.01 (m, 3.7H,

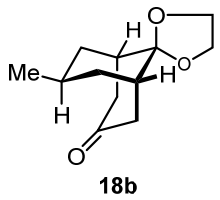
major+minor), 2.06 (s, 3H, minor), 2.01−1.90 (m, 1.7H, major), 1.98 (s, 3.9H, major), 1.87−1.71 (m, 5.9H, major+minor), 1.68−1.50 (m, 5H, major+minor), 1.48−1.36 (m, 3.5H, major+minor), 0.94−0.90 ppm (d, J = 6.2 Hz, 6.9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.9 (major), 207.4 (minor), 169.6 (major), 168.9 (minor), 99.1 (major), 98.6 (minor), 86.6 (major), 86.5 (minor), 84.1 (major), 83.1 (minor), 49.9 (major), 49.5 (minor), 44.9 (minor), 44.7 (major), 42.5 (major), 39.5 (minor), 38.8 (major), 38.6 (minor), 36.4 (major), 35.6 (minor), 34.4 (major), 34.2 (minor), 30.4 (major+minor), 26.4 (minor), 25.5 (major), 22.3 (major), 22.2 (minor), 21.84 (major), 21.76 (minor) ppm; **IR**: $\bar{\nu}$ = 3434, 2955, 2929, 1711, 1459, 1369, 1252, 1028, 734 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{15}H_{22}O_5Na$, $[M+Na]^+$: 305.1359; found: 305.1363.

3. Scope of Tandem Oxidative Dehydrogenation/*Oxa*-Michael Reaction

3.1. Preparation of the Substrates 18b−18h

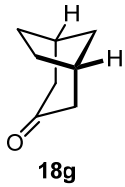
3.1.1 Synthesis of 18b, 18g and 18h

The substrates **18b,**[2] **18g,**[3] and **18h**[4] were synthesized according to the reported procedures.



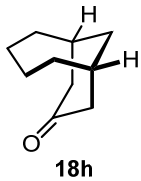
18b

18b: (colorless solid, **mp** 50−52 °C): R_f = 0.36 (silica, petroleum ether/EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.94 (s, 4H), 2.76 (dd, J = 17.5, 6.4 Hz, 2H), 2.23 (brd, J = 17.1 Hz, 2H), 2.03 (d, J = 4.4 Hz, 2H), 1.53 (td, J = 12.5, 2.4 Hz, 5H), 0.78 ppm (d, J = 5.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 211.4, 108.7, 64.5, 64.2, 44.8, 38.2, 37.8, 22.6, 21.6 ppm; **IR**: $\bar{\nu}$ = 3396, 2921, 1708, 1456, 1259, 1127, 1078, 1018 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{12}H_{18}O_3Na$, $[M+Na]^+$: 233.1148; found: 233.1151.



18g

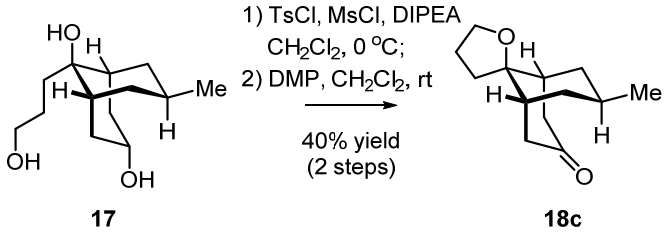
18g: (acicular crystal, **mp** 100−110 °C): R_f = 0.37 (silica, petroleum ether/EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.51 (d, J = 2.8 Hz, 2H), 2.40 (d, J = 15.8 Hz, 2H), 2.29 (d, J = 16.6 Hz, 2H), 1.84−1.67 (m, 4H), 1.51 ppm (dd, J = 8.1, 4.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.7, 50.3, 37.8, 35.2, 29.3 ppm; **IR**: $\bar{\nu}$ = 3407, 2944, 1711, 1451, 1417, 1350, 1223, 1077, 992 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_8H_{13}O$, $[M+H]^+$: 125.0961; found: 125.0960.



18h

18h: (white solid, **mp** 131−135 °C): R_f = 0.58 (silica, petroleum ether/EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 2.63 (s, 2H), 2.51 (dd, J = 14.3, 7.6 Hz, 2H), 2.19 (d, J = 14.4 Hz, 2H), 2.00 (dt, J = 14.4, 5.4 Hz, 1H), 1.84 (dd, J = 14.4, 1.9 Hz, 1H), 1.79−1.69 (m, 2H), 1.57−1.34 ppm (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 213.3, 48.4, 35.1, 34.6, 31.2, 25.9 ppm; **IR**: $\bar{\nu}$ = 3398, 2921, 1712, 1457, 1416, 1238, 1115, 734 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{10}H_{17}O$, $[M+H]^+$: 153.1274; found: 153.1273.

3.1.2. Synthesis of 18c

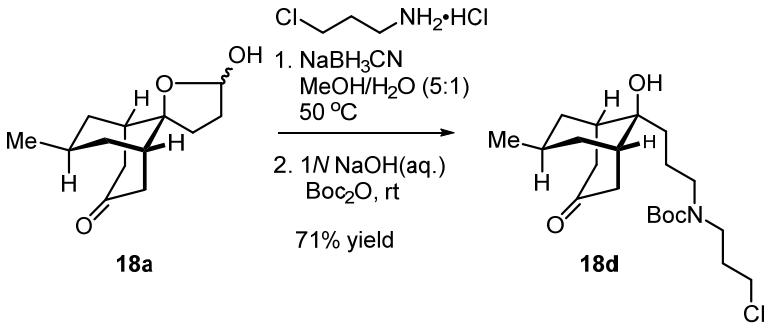


To a solution of triol **17** (2.283 g, 10.0 mmol) in CH_2Cl_2 (100 mL) was added Hünig's base (DIPEA, 0.52 mL, 50.0 mmol) and *p*-toluenesulfonyl chloride (2.288 g, 12.0 mmol) at 0 °C. After stirring for 0.5 h, the methanesulfonyl chloride was added to the above mentioned solution. The reaction mixture was stirred at at ambient temperature for another 2 h, quenched with saturated NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4. The solvent was concentrated in vacuo, and the crude compound was directly used in the next step without further purification.

To a 250 mL round bottom flask equipped with the crude product obtained above was added Dess–Martin periodinane (DMP, 2.969 g, 7.0 mmol) and CH_2Cl_2 (100 mL). The resulting mixture was stirred at ambient temperature for 3 h, quenched with saturated $NaHCO_3$ and saturated $Na_2S_2O_3$. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 30 mL). The organic layers were combined, washed with brine, dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 4:1) to afford **18c** (830 mg, 3.99 mmol, 40% yield) as a colorless liquid.

18c: R_f = 0.68 (silica, petroleum ether/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.87 (t, J = 6.5 Hz, 2H), 2.57 (dd, J = 18.0, 5.9 Hz, 2H), 2.41 (brd, J = 17.6 Hz, 2H), 2.06−1.93 (m, 6H), 1.76 (td, J = 12.8, 2.9 Hz, 2H), 1.61−1.50 (m, 1H), 1.46 (brd, J = 13.9 Hz, 2H), 0.86 ppm (d, J = 6.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 211.9, 82.3, 66.4, 45.7, 38.3, 36.9, 34.5, 25.6, 22.8, 22.2 ppm; **IR**: $\bar{\nu}$ = 3395， 2949， 1706， 1456， 1408， 1174， 1071， 903 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{13}H_{20}O_2Na$, $[M+Na]^+$: 231.1356; found: 231.1357.

3.1.3. Synthesis of 18d



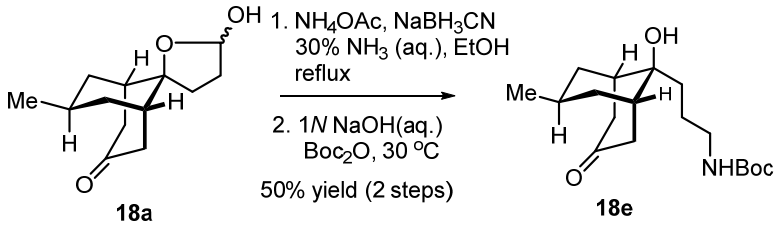
To a solution of lactol **18a** (65.0 mg, 0.290 mmol) in methanol (5.0 mL) and water (1.0 mL) was added 3-chloropropylamine hydrochloride (188.2 mg, 1.450 mmol) and sodium cyanoborohydride ($NaBH_3CN$, 36.4 mg, 0.580 mmol). The reaction mixture was stirred at 50 °C for 20 h, quenched with saturated $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4. The solvent was concentrated in vacuo, and the crude compound was directly used in the next step without further purification.

To a 10 mL round bottom flask equipped with the crude product obtained above was added Boc_2O (316.2 mg, 1.449 mmol) and 1N NaOH (aq.) (6.0 mL). The resulting mixture was stirred at ambient temperature for 10 h, extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were combined, washed with saturated $NaHCO_3$ and brine, dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 4:1) to afford **18d** (82.8 mg, 0.206 mmol, 71% yield (based on impure material containing residual CH_2Cl_2)) as white foam.

18d: R_f = 0.41 (silica, petroleum ether/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.56 (t, J = 6.3 Hz, 2H), 3.34 (t, J = 6.9 Hz, 2H), 3.33−3.18 (m, 2H), 2.57 (dd, J = 18.6, 6.3 Hz, 2H), 2.38 (brd, J = 18.4 Hz, 2H), 2.09−1.97 (m, 4H), 1.86−1.67 (m, 6H), 1.66−1.51 (m, 2H), 1.46 (s, 11H), 0.89 ppm (d, J = 6.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 211.5, 115.6, 79.7, 71.1, 53.3, 47.5, 44.7, 42.3, 38.3, 36.3, 34.3, 31.5, 28.3, 22.9, 22.1, 21.2 ppm; **IR**: $\bar{\nu}$ = 3445, 2928, 1705, 1478,

1418, 1288, 1161, 1124, 734 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{21}H_{36}ClNO_4Na$, $[M+Na]^+$: 424.2225; found: 424.2227.

3.1.4. Synthesis of 18e



To a solution of lactol **18a** (1.122 g, 5.00 mmol) in a saturated solution of NH_4OAc in EtOH (100 mL) was added sodium cyanoborohydride ($NaBH_3CN$, 942.6 mg, 15.00 mmol), and 30% aqueous NH_3 (50 mL). The reaction mixture was refluxed for 18 h, cooled to ambient temperature, and quenched with saturated $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4. The solvent was concentrated in vacuo and the crude compound was directly used in the next step without further purification.

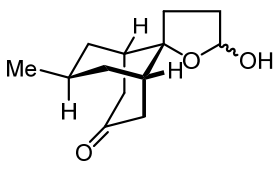
To a 10 mL round bottom flask was equipped with the crude product obtained above was added Boc_2O (3.274 g, 15.0 mmol) and 1*N* NaOH (aq.) (150 mL). The resulting mixture was stirred at ambient temperature for 10 h, extracted with CH_2Cl_2 (3 × 30 mL). The organic layers were combined, washed with brine, dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 2:1) to afford **18e** (813.6 mg, 2.502 mmol, 50% yield (based on impure material containing residual CH_2Cl_2)) as a white foam.

18e: R_f = 0.35 (silica, petroleum ether/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.22 (s, 2H), 2.52 (dd, *J* = 18.4, 5.9 Hz, 2H), 2.33 (brd, *J* = 18.3 Hz, 2H), 2.01 (s, 2H), 1.76 (t, *J* = 12.0 Hz, 3H), 1.67 (s, 4H), 1.56−1.46 (m, 1H), 1.40 (s, 9H), 0.85 ppm (d, *J* = 6.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 211.7, 155.8, 79.5, 71.2, 53.4, 47.4, 44.7, 38.3, 36.3, 28.4, 28.3, 23.0, 22.1 ppm; **IR**: $\bar{\nu}$ = 3372, 2927, 1695, 1518, 1456, 1366, 1253, 1169, 737 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{18}H_{31}NO_4Na$, $[M+Na]^+$: 348.2145; found: 348.2148.

3.1.5. Synthesis of 18f

3.1.5.1. Synthesis of C12 epimer of 18a.

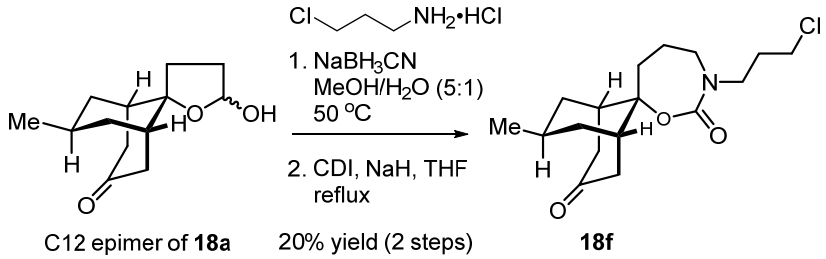
The compound C12 epimer of **18a** was prepared from **16'** by using the procedure same to the above-mentioned synthesis of compound **18a** (please see S3).



C12 epimer of **18a**

C12 epimer of **18a**: (white solid, **mp** 106−108 °C): R_f = 0.57 (silica, petroleum ether/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.59 (s, 1H), 2.95 (ddd, *J* = 29.8, 16.7, 6.2 Hz, 2H), 2.49 (s, 1H), 2.27 (t, *J* = 17.8 Hz, 3H), 2.13−1.96 (m, 5H), 1.69 (brd, *J* = 13.6 Hz, 2H), 1.63−1.52 (m, 1H), 1.39 (t, *J* = 13.1 Hz, 2H), 0.85 ppm (d, *J* = 6.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 213.3, 98.2, 85.4, 44.7, 44.0, 42.3, 39.7, 39.6, 39.2, 33.5, 31.6, 22.7, 22.0 ppm; **IR**: $\bar{\nu}$ = 3405, 2920, 1703, 1459, 1376, 1260, 1114, 1017 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{13}H_{20}O_3Na$, $[M+Na]^+$: 247.1305; found: 247.1308.

3.1.5.2. Synthesis of 18f

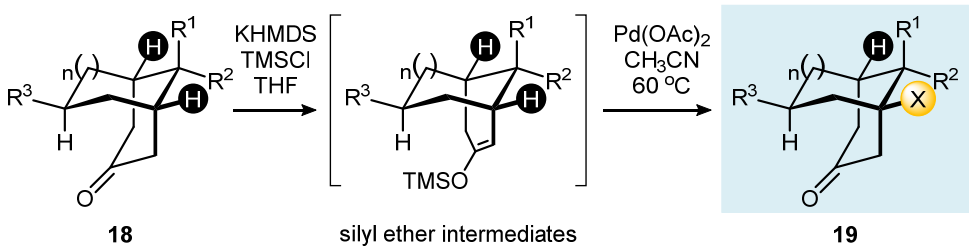


To a solution of C12 epimer of **18a** (3.929 g, 17.5 mmol) in methanol (150 mL) and water (30 mL) was added 3-chloropropylamine hydrochloride (11.387 g, 87.6 mmol), and sodium cyanoborohydride ($NaBH_3CN$, 3.303 g, 52.6 mmol). The reaction mixture was stirred at 50 °C for 20 h, and quenched with saturated $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine, dried in Na_2SO_4. The solvent was concentrated in vacuo and the crude compound was directly used in the next step without further purification.

To a solution of the crude product obtained above in THF (300 mL) was added NaH (2.520 g, 105.0 mmol) and *N,N'*-carbonyldiimidazole (CDI, 14.188 g, 87.5 mmol). The reaction mixture was refluxed for 7 h, and cooled to ambient temperature. The solution was diluted with EtOAc (200 mL) and washed with saturated $NaHCO_3$ and brine. The organic phase was dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel ($V_{\text{petroleum ether}}/V_{\text{EtOAc}}$ 3:1) to afford **18f** (1.147 g, 3.51 mmol, 20% yield) as a white foam.

18f: $\boldsymbol{R_f}$ = 0.55 (silica, petroleum ether/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.57 (t, J = 6.4 Hz, 2H), 3.47 (t, J = 7.0 Hz, 2H), 3.39 (t, J = 6.3 Hz, 2H), 3.20 (dd, J = 17.4, 6.1 Hz, 2H), 2.38 (s, 2H), 2.24 (d, J = 17.3 Hz, 2H), 2.10−2.02 (m, 4H), 1.77 (quint, J = 6.2 Hz, 2H), 1.69−1.58 (m, 3H), 1.48−1.36 (m, 2H), 0.85 ppm (d, J = 5.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.2, 156.7, 82.8, 47.6, 47.3, 43.8, 42.3, 38.25, 38.21, 30.9, 30.7, 22.7, 21.8, 20.8 ppm; **IR**: $\bar{\nu}$ = 3487, 2922, 1700, 1473, 1414, 1216, 1027, 913 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{17}H_{26}NO_3ClNa$, $[M+Na]^+$: 350.1493; found: 350.1496.

3.2. General Procedure for the Key Tandem Reaction



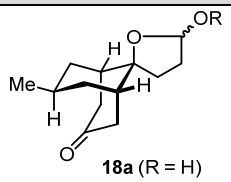
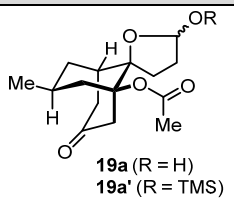
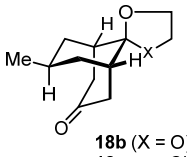
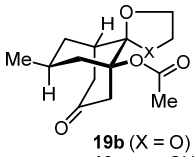
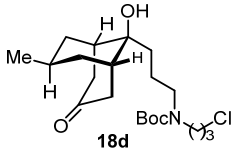
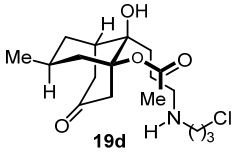
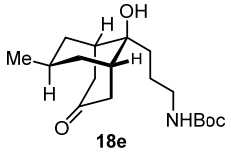
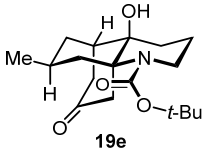
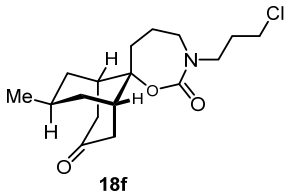
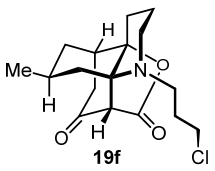
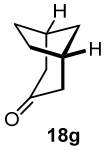
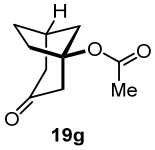
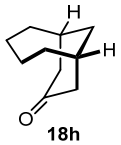
To a stirred solution of **18** in THF was added dropwise Potassium bis(trimethylsilyl)amide (3.0 equiv, 0.7 *M* in THF) at −78 °C. After 15 min chlorotrimethyhilane (TMSCl, 3.0 equiv) was added, and the reaction mixture was stirred at −78 °C for 1 h. After warmed to ambient temperature, the reaction was quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and

concentrated in vacuo. The crude product was purified by short column chromatography on silica gel.

To a solution of the silyl enol ether obtained above in freshly distilled acetonitrile was added palladium(II) acetate, which was freshly prepared according to the reported procedure.[1] The reaction mixture was stirred for 24 h, and filtered through a short silica gel column with EtOAc. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel.

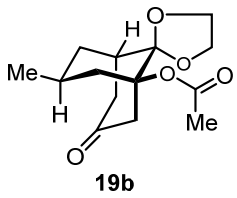
3.2.1. Generality of the Key Tandem Reaction

Table SI-2. Reactivity of the tandem reaction

entry	substrates	products	yield (%)[b,c]
1	 **18a** (R = H)	 **19a** (R = H) **19a'** (R = TMS) (**19a**/**19a'** = 1:2)	52 (70)
2	 **18b** (X = O)	 **19b** (X = O)	35 (41)
3	**18c** (X = CH_2)	**19c** (X = CH_2)	39 (51)
4	 **18d**	 **19d**	46[d]
5	 **18e**	 **19e**	22 (39)
6	 **18f**	 **19f**	46 (62)[e]
7	 **18g**	 **19g**	13[f]
8	 **18h**	 **19h**	59

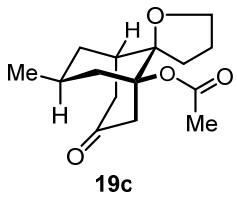
[a]Unless otherwise noted, reactions of TMS enol ethers of **18a–h**, which were individually obtained in the presence of KHMDS (3.0 equiv) and TMSCl (3.0 equiv) in THF at 0 °C (for **18a**) or at –78 °C (for **18b–h**), were performed with freshly prepared $Pd(OAc)_2$ (1.5 equiv) in freshly distilled CH_3CN at 60 °C. [b]Overall yield of the isolated product starting from the ketone. [c]The yield based on the recovered starting material was given in parentheses. [d]Followed by the deprotection of *N*-Boc using CF_3CO_2H. [e]The structure of 19f was established by X-ray crystallographic analysis. [f]With the remaining starting material (ca. 10%), another structurally undetermined major byproduct was isolated.

3.3. Spectroscopic Data for the Products 19b−19h



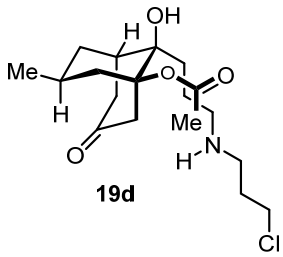
19b

19b: (35% yield, colorless solid, **mp** 130−135 °C): $\boldsymbol{R_f}$ = 0.72 (silica, petroleum ether/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.20 (d, J = 8.2 Hz, 2H), 4.06 (s, 2H), 3.59 (d, J = 16.6 Hz, 1H), 2.88 (d, J = 16.8 Hz, 2H), 2.69 (d, J = 9.0 Hz, 1H), 2.29 (d, J = 17.2 Hz, 1H), 2.12 (s, 1H), 1.99 (s, 3H), 1.61 (s, 3H), 1.53 (d, J = 9.9 Hz, 1H), 0.89 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.3, 169.4, 108.6, 83.5, 66.6, 66.3, 49.0, 44.3, 40.6, 39.0, 37.4, 25.2, 22.4, 21.5 ppm; **IR**: $\bar{\nu}$ = 3404, 2928, 1734, 1713, 1370, 1245, 1129, 1035 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{14}H_{20}O_5Na$, $[M+Na]^+$: 291.1203; found: 291.1205.



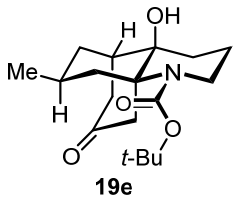
19c

19c: (39% yield,colorless solid): $\boldsymbol{R_f}$ = 0.56 (silica, petroleum ether/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.99−3.92 (m, 1H), 3.91−3.84 (m, 1H), 3.67 (dd, J = 17.5, 2.4 Hz, 1H), 2.63−2.48 (m, 3H), 2.40-2.25 (m, 2H), 2.07-2.02 (m, 2H), 1.99-1.88 (m, 1H), 1.95 (s, 3H), 1.86−1.77 (m, 1H), 1.77-1.67 (m, 2H), 1.56-1.41 (m, 1H), 1.39−1.29 (m, 1H), 0.86 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.4, 169.7, 84.4, 84.2, 68.6, 49.6, 44.8, 39.4, 39.0, 35.9, 31.2, 26.7, 25.4, 22.2, 21.7 ppm; **IR**: $\bar{\nu}$ = 3403， 2953， 1732， 1458， 1369， 1248， 1071， 1026 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{15}H_{22}O_4Na$, $[M+Na]^+$: 289.1410; found: 289.1411.



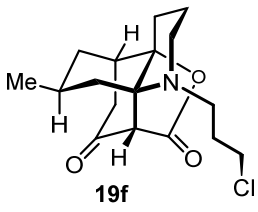
19d

19d: (46% yield (based on impure material containing residual CH_2Cl_2), white foam): $\boldsymbol{R_f}$ = 0.27 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.61 (t, J = 6.4 Hz, 2H), 3.51 (dd, J = 18.2, 1.9 Hz, 1H), 2.85−2.72 (m, 3H), 2.70−2.61 (m, 2H), 2.49 (dd, J = 18.4, 6.7 Hz, 1H), 2.30 (brd, J = 17.9 Hz, 2H), 2.23 (s, 1H), 2.02 (s, 3H), 2.01−1.79 (m, 6H), 1.78−1.60 (m, 2H), 1.58−1.43 (m, 1H), 1.32 (brd, J = 13.3 Hz, 1H), 0.90 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.5, 170.3, 85.9, 72.5, 49.8, 49.7, 46.4, 43.8, 42.8, 39.0, 36.5, 35.2, 32.3, 31.5, 25.6, 22.5, 22.2, 21.8 ppm; **IR**: $\bar{\nu}$ = 3392, 2957, 1704, 1458, 1372, 1264, 1025, 738 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{18}H_{31}ClNO_4$, $[M+H]^+$: 360.1936; found: 360.1942.



19e

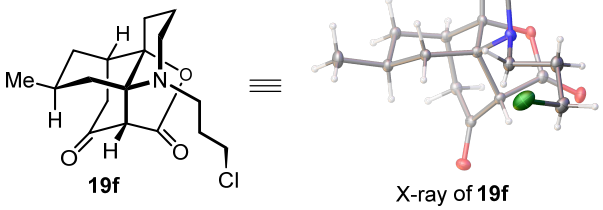
19e: (22% yield, white foam): $\boldsymbol{R_f}$ = 0.33 (silica, petroleum ether/EtOAc 2:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 4.01 (dt, J = 14.3, 4.4 Hz, 1H), 3.13 (ddd, J = 13.7, 11.2, 4.2 Hz, 1H), 2.95 (dd, J = 17.9, 2.2 Hz, 1H), 2.89 (dd, J = 13.4, 4.1 Hz, 1H), 2.79 (dd, J = 17.8, 1.2 Hz, 1H), 2.65 (dd, J = 17.9, 6.5 Hz, 1H), 2.37 (d, J = 18.0 Hz, 1H), 2.24 (s, 1H), 2.11−1.95 (m, 3H), 1.88 (td, J = 13.1, 4.1 Hz, 1H), 1.76−1.67 (m, 2H), 1.62−1.53 (m, 2H), 1.44 (s, 9H), 1.36 (dt, J = 13.2, 2.2 Hz, 1H), 0.92 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 209.9, 156.7, 80.5, 70.4, 62.6, 46.0, 44.4, 42.1, 40.8, 40.5, 35.3, 30.6, 28.4, 25.0, 22.4, 20.1 ppm; **IR**: $\bar{\nu}$ = 3451, 2928, 1702, 1458, 1388, 1366, 1250, 1160 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{18}H_{29}NO_4Na$, $[M+Na]^+$: 346.1989; found: 346.1992.



19f

19f: (46% yield, colorless solid, **mp** 167−170 °C): R_f = 0.70 (silica, petroleum ether/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.57 (s, 1H), 3.54 (dd, J = 7.1, 5.0 Hz, 2H), 2.93 (dd, J = 17.0, 7.9 Hz, 1H), 2.75−2.63 (m, 2H), 2.56−2.50 (m, 1H), 2.41−2.28 (m, 2H), 2.18 (dt, J = 13.5, 4.6 Hz, 1H), 2.06−1.91 (m, 3H), 1.90−1.83 (m, 1H), 1.83−1.59 (m, 5H), 1.52−1.38 (m, 2H), 0.93 ppm (d, J = 5.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 201.8, 171.2, 85.5, 68.4, 68.1, 45.5, 44.2, 43.1, 42.5, 40.2, 37.4, 30.8, 28.7, 26.2, 24.0, 22.0, 20.3 ppm; **IR**: $\tilde{\nu}$ = 3414, 2952, 1770, 1716, 1456, 1231, 1113, 1088, 963 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{17}H_{25}NO_3Cl$, $[M+H]^+$: 326.1517; found: 326.1522.

The single crystal of **19f**, which was obtained through one recrystallization from a mixed solvent of petroleum ether and EtOAc, was used for the determination of its relative configurations via X-ray crystallographic analysis. The crystal structure and the X-ray crystallographic data of **19f** (CCDC 1539341) were described as follows:



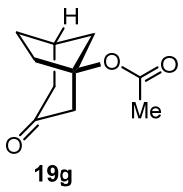
19f

X-ray of **19f**

Crystal data and structure refinement for compound 19f

Identification code	Compound **19f**
Empirical formula	$C_{17}H_{24}ClNO_3$
Formula weight	325.82
Temperature/K	294.06(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.5513(3)
b/Å	13.8572(5)
c/Å	10.2194(3)
α/°	90.00
β/°	103.624(3)
γ/°	90.00
Volume/Å^3	1589.79(9)
Z	4
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	0.253
F(000)	696.0
Crystal size/mm^3	0.27 × 0.25 × 0.24

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.76 to 52.04
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 15, -12 ≤ l ≤ 11
Reflections collected	6189
Independent reflections	3128 [R_{int} = 0.0294, R_{sigma} = 0.0464]
Data/restraints/parameters	3128/0/200
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0505, wR_2 = 0.1071
Final R indexes [all data]	R_1 = 0.0769, wR_2 = 0.1257
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.57



19g

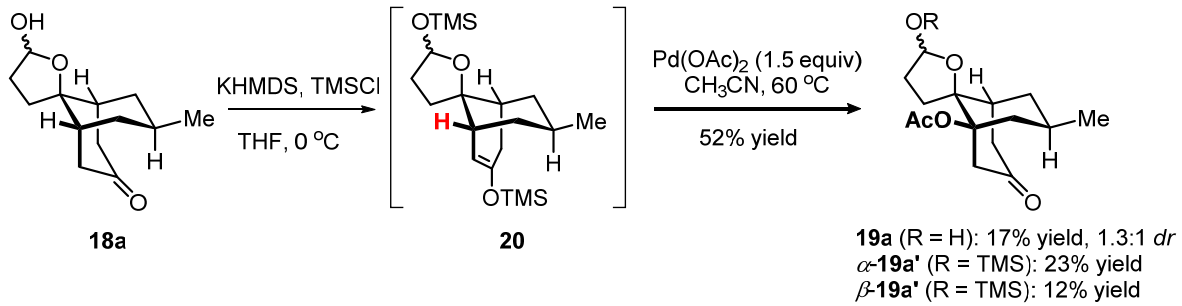
19g: (13% yield, colorless liquid): $\boldsymbol{R_f}$ = 0.14 (silica, petroleum ether/EtOAc 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 30.2 (dd, J = 15.6, 2.8 Hz, 1H), 2.89 (dt, J = 15.5, 2.3 Hz, 1H), 2.49 (s, 1H), 2.41−2.26 (m, 3H), 2.14−1.87 (m, 4H), 2.01 (s, 3H), 1.47−1.37 ppm (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.5, 170.2, 84.8, 53.3, 48.7, 41.5, 34.4, 31.6, 27.6, 21.8 ppm; **IR**: $\bar{\nu}$ = 3413, 2953, 1736, 1369, 1240, 1210, 1071, 1022 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{10}H_{14}O_3Na$, $[M+Na]^+$: 205.0835; found: 205.0836.

19h

19h: (59% yield, pale yellow liquid): $\boldsymbol{R_f}$ = 0.16 (silica, petroleum ether/EtOAc 10:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 5.55 (s, 1H), 2.48−2.03 (m, 7H), 1.94−1.76 (m, 2H), 1.60−1.33 (m, 2H), 1.26−1.03 ppm (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 199.8, 165.1, 123.0, 45.5, 37.3, 35.3, 32.0, 29.2, 28.6, 23.9 ppm; **IR**: $\bar{\nu}$ = 3422, 2927, 2860, 1720, 1659, 1446, 1244, 1024 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{10}H_{15}O$, $[M+H]^+$: 151.1117; found: 151.1119.

4. Total Synthesis of (±)-Lycodoline

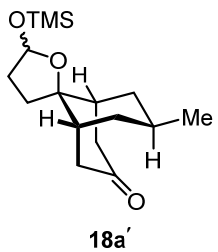
4.1. Compound 19a + 19a'



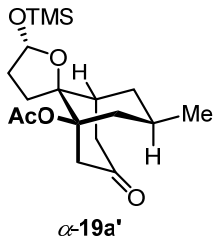
To a stirred solution of **18a** (2.243 g, 10.0 mmol) in THF (150 mL) was added dropwise Potassium bis(trimethylsilyl)amide (KHMDS, 42.8 mL, 30.0 mmol, 0.7 *M* in THF) over 15 min at 0 °C. After 15 min chlorotrimethyhilane (3.8 mL, 30.0 mmol) was added, and the reaction mixture was stirred at 0 °C for 2 h. After warmed to ambient temperature, the reaction was quenched with saturated $NaHCO_3$ (50 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (4 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by short column chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 60:1).

Or to a stirred solution of **18a** (2.243 g, 10.0 mmol) in THF (150 mL) was added dropwise lithium diisopropylamide (LDA, 15.0 mL, 30.0 mmol, 2.0 *M* in THF) over 5 min at −78 °C. After 15 min chlorotrimethyhilane (3.8 mL, 30.0 mmol) was added, and the reaction mixture was stirred at −78 °C for 2 h. After warmed to ambient temperature, the reaction was quenched with saturated $NaHCO_3$ (50 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (4 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by short column chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 60:1).

To a solution of the silyl enol ether obtained above in freshly distilled acetonitrile (260 mL) was added palladium(II) acetate (2.694 g, 12.0 mmol), which was freshly prepared according to the reported procedure.[1] The reaction mixture was stirred at 60 °C for 24 h, and filtered through a short silica gel column with EtOAc. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 10:1 to 2:1) to give the products **19a** (480.0 mg, 1.70 mmol, 17% yield, 1.3:1 dr) as a yellow liquid, ***α*-19a'** (815.1 mg, 2.30 mmol, 23% yield) as a colorless liquid, ***β*-19a'** (425.4 mg, 1.20 mmol, 12% yield) as a colourless liquid as well as **18a'** (770.1 mg, 2.60 mmol, 26% yield) as a yellow liquid.



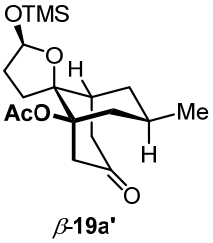
18a': R_f = 0.50 (silica, petroleum ether/EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.46 (s, 1H), 2.57 (dd, J = 18.5, 6.5 Hz, 2H), 2.42−2.32 (m, 2H), 2.14−2.09 (m, 1H), 2.08−1.98 (m, 3H), 1.95−1.87 (m, 2H), 1.82 (td, J = 12.3, 3.8 Hz, 1H), 1.72 (td, J = 12.0, 3.6 Hz, 1H), 1.57−1.37 (m, 3H), 0.84 (d, J = 6.1 Hz, 3H), 0.13 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 211.7, 97.9, 83.7, 45.9, 45.5, 41.0, 38.4, 37.2, 36.7, 34.7, 32.2, 22.7, 22.3, 0.21 ppm; **IR**: $\tilde{\nu}$ = 3398, 2951, 1710, 1457, 1251, 1198, 1016, 985, 842 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{28}O_3SiNa$, $[M+Na]^+$: 319.1700; found: 319.1702.



α-19a'

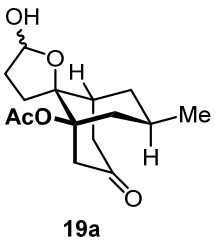
α-19a': R_f = 0.37 (silica, petroleum ether/EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.62 (d, J = 4.1 Hz, 1H), 3.71 (dd, J = 17.7, 2.6 Hz, 1H), 2.68−2.58 (m, 2H), 2.55 (dd, J = 12.3, 1.2 Hz, 1H), 2.40 (dt, J = 17.8, 2.0 Hz, 1H), 2.33−2.23 (m, 2H), 2.22−2.12 (m, 1H), 2.10−2.03 (m, 1H), 1.97 (s, 3H), 1.95−1.88 (m, 1H), 1.88−1.79 (m, 1H), 1.75 (td, J = 12.3, 1.8 Hz, 1H), 1.63−1.49 (m, 1H), 1.42 (dq, J = 13.1, 2.0 Hz, 1H), 0.91 (d, J = 6.2 Hz, 3H), 0.17 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.3, 169.6, 99.0, 85.9, 84.3, 49.9, 44.7, 42.2, 38.8, 36.4, 36.2, 30.5, 25.5, 22.3, 21.9, 0.3 ppm; **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 5.59 (d, J = 4.3 Hz, 1H), 3.67 (dd, J = 17.7, 2.6 Hz, 1H), 2.64−2.56 (m, 2H), 2.52 (dd, J = 12.3, 2.9 Hz, 1H), 2.36 (brd, J = 17.8, 2.0 Hz, 1H), 2.29−2.20 (m, 2H), 2.18−2.11 (m, 1H), 2.06−1.99 (m, 1H), 1.94 (s, 3H), 1.91−1.86 (m, 1H), 1.85−1.77 (m, 1H), 1.72 (td, J = 12.5, 1.4 Hz, 1H), 1.56−1.46 (m, 1H), 1.41−1.36 (m, 1H), 0.88 (d, J = 6.2 Hz, 3H), 0.14 ppm (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 208.1, 169.5, 99.0, 85.9, 84.2, 49.8, 44.7, 42.1, 38.7, 36.4, 36.1, 30.4, 25.5, 22.2, 21.9, 0.2 ppm; **IR**: $\bar{\nu}$ = 3400, 2957, 2373, 1736, 1717, 1251, 1098, 1032, 734 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{18}H_{30}O_5SiNa$, $[M+Na]^+$: 377.1755; found: 377.1758.

The relative configuration of **α-19a'** was determined according to the 2D NOESY (see S72–S73).



β-19a'

β-19a': R_f = 0.30 (silica, petroleum ether/EtOAc 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.53 (dd, J = 5.0, 2.8 Hz, 1H), 3.74 (dd, J = 17.5, 2.5 Hz, 1H), 2.65−2.43 (m, 4H), 2.36 (dt, J = 18.2, 1.8 Hz, 1H), 2.19−2.08 (m, 1H), 2.07−1.94 (m, 2H), 2.02 (s, 3H), 1.84−1.73 (m, 3H), 1.62−1.48 (m, 1H), 1.41−1.34 (m, 1H), 0.90 (d, J = 6.2 Hz, 3H), 0.17 ppm (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.1, 170.0, 98.4, 85.8, 82.3, 49.7, 44.7, 39.3, 39.0, 35.9, 34.8, 27.8, 25.5, 22.4, 22.0, 0.3 ppm; **IR**: $\bar{\nu}$ = 3407, 2957, 1731, 1459, 1368, 1250, 1024, 842 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{18}H_{30}O_5SiNa$, $[M+Na]^+$: 377.1755; found: 377.1760.

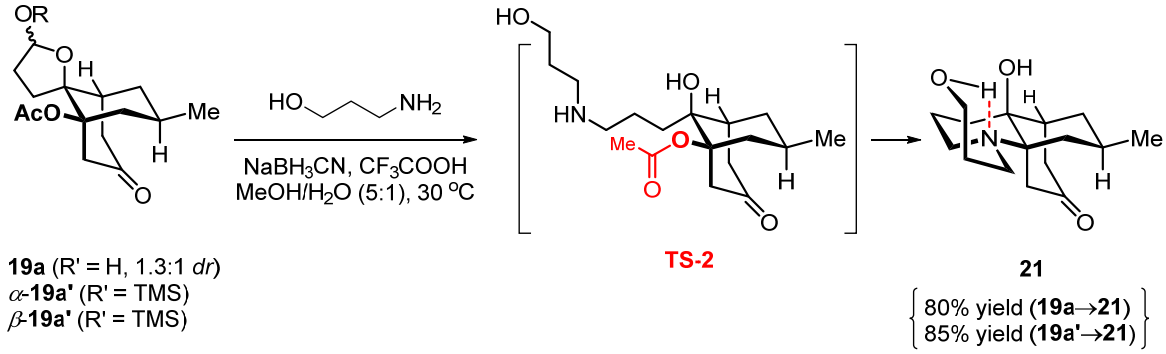


19a

19a: (1.3:1 dr), R_f = 0.30 (silica, petroleum ether/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.69 (d, J = 4.2 Hz, 1.3H, ,major), 5.50 (dd, J = 8.0, 4.5 Hz, 1H, minor), 3.80 (dd, J = 17.4, 2.4 Hz, 1H, minor), 3.72 (dd, J = 17.7, 2.6 Hz, 1.3 H, major), 2.93 (d, J = 8.3 Hz, 0.9H, minor), 2.70−2.53 (m, 9.7H, major+minor), 2.47−2.28 (m, 7.1H, major+minor), 2.26−2.16 (m, 2.3H, major+minor), 2.15−2.09 (m, 3.8H, major+minor), 2.09−2.01 (m, 3.7H, major+minor), 2.06 (s, 3H, minor), 2.01−1.90 (m, 1.7H, major), 1.98 (s, 3.9H, major), 1.87−1.71 (m, 5.9H, major+minor), 1.68−1.50 (m, 5H, major+minor), 1.48−1.36 (m, 3.5H, major+minor), 0.94−0.90 ppm (d, J = 6.2 Hz, 6.9H, major+minor); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.9 (major), 207.4 (minor), 169.6 (major), 168.9 (minor), 99.1 (major), 98.6 (minor), 86.6 (major), 86.5 (minor), 84.1 (major), 83.1 (minor), 49.9 (major), 49.5 (minor), 44.9 (minor), 44.7 (major), 42.5 (major), 39.5 (minor), 38.8 (major), 38.6 (minor), 36.4 (major), 35.6 (minor), 34.4 (major), 34.2 (minor), 30.4 (major+minor), 26.4 (minor), 25.5 (major), 22.3 (major), 22.2 (minor), 21.84 (major), 21.76 (minor) ppm; **IR**: $\bar{\nu}$ = 3434, 2955, 2929, 1711, 1459, 1369, 1252, 1028, 734 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{15}H_{22}O_5Na$, $[M+Na]^+$: 305.1359; found: 305.1363.

4.2. Compound 21 and Its X-Ray Crystallography

4.2.1. Synthesis of Compound 21



19a (R' = H, 1.3:1 *dr*)
α-**19a'** (R' = TMS)
β-**19a'** (R' = TMS)

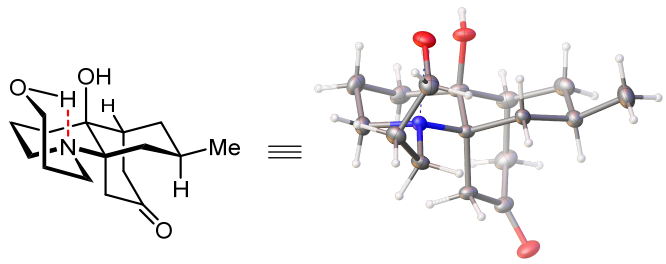
To a stirred solution of lactol (*α*-**19a'** + *β*-**19a'**) (1.773 g, 5.0 mmol) in methanol (120 mL) and water (24.0 mL) was added 3-aminopropanol (1.878 g, 25.0 mmol), sodium cyanoborohydride ($NaBH_3CN$, 1.414 g, 15.0 mmol) and TFA (1.1 mL, 15.0 mmol). The reaction mixture was stirred at 30 °C for 20 h, and quenched with saturated $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (4 × 80 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 500:10:1) to give the diol **21** (1.195 g, 4.25 mmol, 85% yield, **mp** 145−148 °C) as a white powder.

Following the procedures as mentioned above, **19a** could also generate the diol **21** in 80% yield.

21: R_f = 0.29 (silica, CH_2Cl_2/MeOH 5:1); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 3.75 (t, J = 5.8 Hz), 2.96−2.89 (m, 2H), 2.88 (dd, J = 17.3, 1.2 Hz, 1H), 2.83 (s, 1H), 2.62 (dd, J = 17.8, 6.6 Hz, 1H), 2.44−2.34 (m, 2H), 2.23 (dd, J = 17.3, 2.2 Hz, 1H), 2.13−2.07 (m, 2H), 2.05−1.95 (m, 2H), 1.91 (td, J = 12.6, 4.1 Hz, 1H), 1.82−1.74 (m, 2H), 1.67−1.62 (m, 1H), 1.61−1.55 (m, 2H), 1.52 (dd, J = 12.3, 2.0 Hz, 1H), 1.51−1.47 (m, 1H), 1.36 (brd, J = 13.2 Hz, 1H), 0.93 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 211.4, 69.2, 62.4, 60.9, 46.1, 46.0, 44.6, 41.2, 40.7, 39.8, 35.3, 30.7, 30.4, 24.9, 22.5, 20.7 ppm; **IR**: $\tilde{\nu}$ = 3438, 2932, 1702, 1457, 1269, 1227, 1069, 736 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{28}NO_3$, $[M+H]^+$: 282.2064; found: 282.2061.

4.2.2. X-Ray Crystallography of Compound 21

The single crystal of **21**, which was obtained through one recrystallization from a mixed solvent of *n*-hexane and CH_2Cl_2, was used for the determination of its relative configurations via X-ray crystallographic analysis. The crystal structure and the X-ray crystallographic data of **21** (CCDC 1539342) were described as follows:



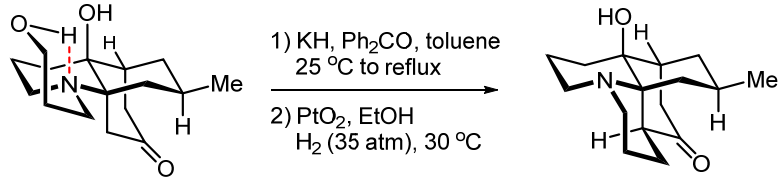
21 X-ray of **21**

Crystal data and structure refinement for compound 21

Identification code	Compound **21**
Empirical formula	$C_{16}H_{27}NO_3$
Formula weight	281.39
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.4770(9)
b/Å	8.3561(3)
c/Å	15.4163(8)
α/°	90.00
β/°	106.701(7)
γ/°	90.00
Volume/Å^3	1539.48(15)
Z	4
ρ_{calc}g/cm^3	1.214
μ/mm^{-1}	0.083
F(000)	616.0
Crystal size/mm^3	0.37 × 0.34 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.82 to 52.04
Index ranges	-15 ≤ h ≤ 15, -5 ≤ k ≤ 10, -19 ≤ l ≤ 16
Reflections collected	6004
Independent reflections	3035 [R_{int} = 0.0284, R_{sigma} = 0.0471]
Data/restraints/parameters	3035/0/184
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.1105
Final R indexes [all data]	R_1 = 0.0821, wR_2 = 0.1288
Largest diff. peak/hole / e Å^{-3}	0.17/-0.18

4.3. (±)-Lycodoline and Its X-Ray Crystallography

4.3.1. Synthesis of (±)-Lycodoline



21 75% yield (2 steps) (±)-Lycodoline (**2**)

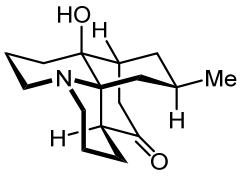
To a suspension of potassium hydride (KH, 1.534 g, 38.36 mmol, prepared by washing 4.50 g of 30% KH in mineral oil with three portions of diethyl ether) in toluene (10.0 mL) was added diol **21** (1.542 g, 5.48 mmol) under argon. After stirring for 30 min at 25 °C, benzophenone (9.986 g, 54.80 mmol) was added and the resulting mixture refluxed for 17 h. The resulting brown suspension was allowed to cool to ambient temperature, diluted with diethyl ether (6 mL), and extracted with aqueous 5% HCl (aq.) (3 × 10 mL). The aqueous extracts were neutralized with solid K_2CO_3 and extracted with CH_2Cl_2 (4 × 15 mL). The organic extracts were combined, washed with brine, dried by Na_2SO_4. The solvent was removed under reduced pressure and the crude product was directly used in the next reaction without further purification.

To a solution of the crude enone product obtained above in anhydrous ethanol (110 mL) was added platinum dioxide (165.2 mg), and the resulting mixture was stirred under hydrogen atmosphere (50 atm) until uptake ceased at 30 °C for 15 h. The catalyst was removed by filtration and the solvent evaporated. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 500:10:1) to give (±)-lycodoline (**2**) (1.077g, 4.09 mmol, 75% yield, **mp** 180−184 °C) as a pale yellow powder.

(±)-Lycodoline (**2**): $\boldsymbol{R_f}$ = 0.55 (silica, CH_2Cl_2/MeOH 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.28−3.16 (m, 2H), 2.99−2.91 (m, 2H), 2.64−2.54 (m, 2H), 2.45 (dd, J = 14.6, 5.3 Hz, 1H), 2.33 (dd, J = 16.7, 1.6 Hz, 1H), 2.26 (d, J = 9.2 Hz, 1H), 2.19−2.01 (m, 4H), 2.00−1.81(m, 2H), 1.75−1.56 (m, 2H), 1.50 (d, J = 11.7 Hz, 1H), 1.46−1.31 (m, 4H), 0.88 ppm (d, J = 5.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.4, 69.5, 61.5, 46.2, 46.1, 44.3, 43.2, 40.6, 36.0, 35.6, 30.2, 24.3, 22.6, 20.7, 19.6, 17.7 ppm; **IR**: $\bar{\nu}$ = 3438, 2945, 1701, 1457, 1301, 1124, 1099, 1073 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_2$, $[M+H]^+$: 264.1958; found: 264.1954.

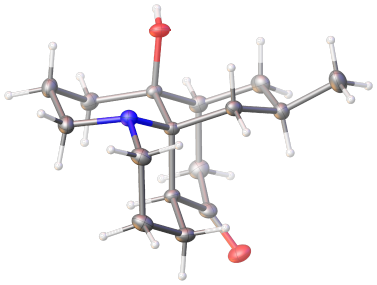
4.3.2. X-Ray Crystallography of (±)-Lycodoline

The single crystal of (±)-lycodoline (**2**), which was obtained through one recrystallization from a mixed solvent of CH_2Cl_2, was used for the determination of its relative configurations via X-ray crystallographic analysis. The crystal structure and the X-ray crystallographic data of (±)-lycodoline (**2**) (CCDC 1539343) were described as follows:



(±)-Lycodoline (**2**)

≡



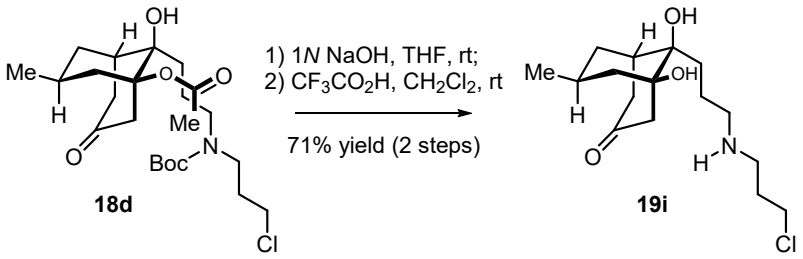
X-ray of **2**

Crystal data and structure refinement for (±)-lycodoline (2)

Identification code	(±)-Lycodoline (**2**)
Empirical formula	$C_{16}H_{25}NO_2$
Formula weight	263.37
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.8530(9)
b/Å	7.9767(5)
c/Å	16.4717(16)
α/°	90.00
β/°	107.414(10)
γ/°	90.00
Volume/Å^3	1360.6(2)
Z	4
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	0.084
F(000)	576.0
Crystal size/mm^3	0.25 × 0.22 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.28 to 52.04
Index ranges	$-9 \le h \le 13$, $-9 \le k \le 8$, $-20 \le l \le 10$
Reflections collected	4803
Independent reflections	2675 [R_{int} = 0.0528, R_{sigma} = 0.1029]
Data/restraints/parameters	2675/0/174
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0682, wR_2 = 0.1487
Final R indexes [all data]	R_1 = 0.1407, wR_2 = 0.1979
Largest diff. peak/hole / e Å^{-3}	0.18/-0.18

5. Study the Aminolysis of Bridgehead Tertiary Alcohol Ester

5.1. The Preparation of Substrate 19i

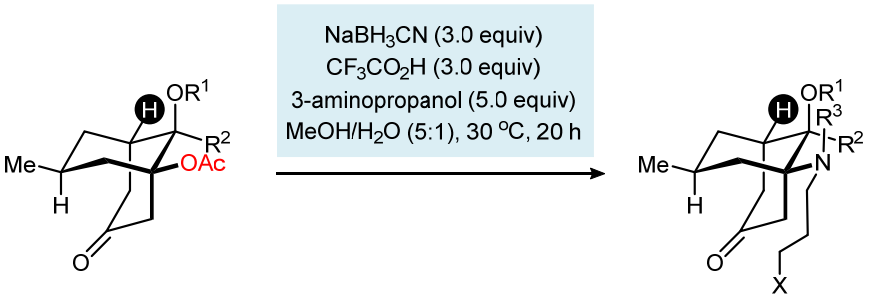


To a solution of **18d** (138.0 mg, 0.30 mmol) in THF (20 mL) was added 1*N* NaOH (2.0 mL). The reaction mixture was stirred at ambient temperature for 5 h, and quenched with saturated $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4. The solvent was concentrated in vacuo and the crude compound was directly used in the next step without further purification.

To a 25 mL round bottom flask was equipped with the crude product obtained above was added CF_3CO_2H (1.0 mL) and CH_2Cl_2 (10 mL). The resulting mixture was stirred at ambient temperature for 6 h, extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were combined, washed with brine, dried by Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 250:5:1) to afford **19i** (67.7 mg, 0.213 mmol, 71% yield) as a white foam.

19i: R_f = 0.41 (silica, CH_2Cl_2/MeOH 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.30 (s, 0.5H), 3.63 (t, J = 6.3 Hz, 2H), 2.97−2.87 (m, 1H), 2.87−2.80 (m, 1H), 2.79−2.70 (m, 1H), 2.69−2.52 (m, 3H), 2.47 (dd, J = 18.2, 6.6 Hz, 1H), 2.33 (brd, J = 18.2 Hz, 1H), 2.21 (s, 1H), 2.06−1.95 (m, 4H), 1.85−1.74 (m, 3H), 1.69−1.59 (m, 1H), 1.56−1.44 (m, 2H), 1.38−1.31 (m, 1H), 0.89ppm (d, J = 5.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 210.4, 73.7, 72.3, 51.3, 49.8, 46.3, 45.7, 45.0, 42.8, 37.0, 35.4, 32.1, 31.6, 25.9, 22.4, 21.9 ppm; **IR**: $\tilde{\nu}$ = 3425， 2930， 1701， 1456， 1308，1221，1109， 1029， 732 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{29}ClNO_3$, $[M+H]^+$: 318.1830; found: 318.1831.

5.2. General Procedure for the Aminolysis Reaction

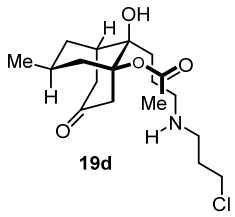
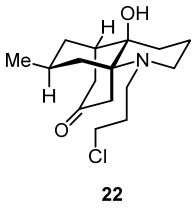
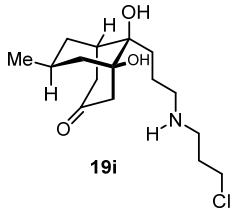
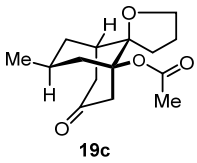


To a stirred solution of the substrate in methanol and water was added 3-aminopropanol (5.0 equiv), sodium cyanoborohydride ($NaBH_3CN$, 3.0 equiv) and CF_3COOH (TFA, 3.0 equiv). The reaction mixture was stirred at 30 °C for 20 h, and quenched with saturated $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over

Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel.

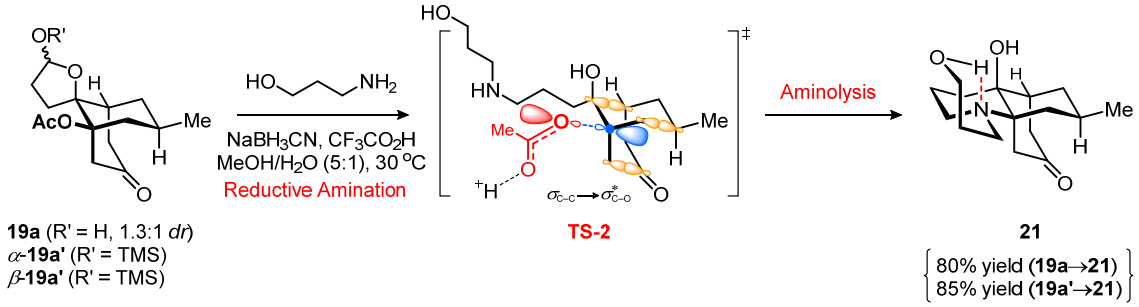
5.3. Controlled Experiments of the Aminolysis Reaction

Table SI-3. Reactivity of the aminolysis reaction

Entry	Substrate	Product	Yield[a]
1	 **19d**	 **22**	80%
2	 **19i**	No reaction	
3	 **19c**	No reaction	

[a] Isolated yield.

When conducted the substrate **19d** under the general procedure, the aza-annulation product **22** was generated in 80% yield (entry 1 of Supplementary Table 3). Instead of the bridgehead acetate group with hydroxyl, the **19i** was treated with 3-aminopropanol, $NaBH_3CN$ and TFA (entry 2), but the aza-annulation product could not be observed, meaning the bridgehead acetate group is crucial for the bridgehead C−O bond cleavage under the mild conditions. Compared with the intramolecular aminolysis of bridgehead tertiary alcohol ester, conducting the compound **19c** under the conditions mentioned above (entry 3), we just obtained the starting material.



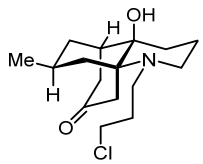
19a (R' = H, 1.3:1 *dr*)
α-**19a'** (R' = TMS)
β-**19a'** (R' = TMS)

21

80% yield (**19a**→**21**)
85% yield (**19a'**→**21**)

According the results obtained above, this unusual transformation might undergo a subsequent intramolecular bridgehead aminolysis after the initial reductive amination, wherein acid-promoted direct aminolysis of bridgehead tertiary alcohol ester might proceed through the transition state **TS-2** due to the intrinsic leaving ability of bridgehead acetate group, which was partially accelerated by the favorable hyperconjugate effect in the [3.3.1] bicycle system.

Spectroscopic Data for the Products 22

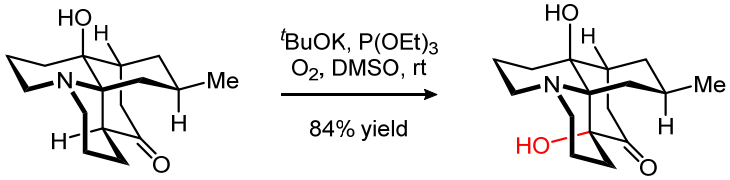


22

22: R_f = 0.38 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.58 (t, J = 6.3 Hz, 2H), 3.33 (s, 1H), 2.96−2.85 (m, 2H), 2.77 (brd, J = 13.1 Hz, 1H), 2.60 (dd, J = 17.8, 6.6 Hz, 1H), 2.51−2.41 (m, 1H), 2.36 (brd, J = 17.9 Hz, 1H), 2.22 (dd, J = 17.3, 1.8 Hz, 1H), 2.14−2.02 (m, 2H), 2.01−1.77 (m, 5H), 1.70 (dd, J = 12.3, 4.2 Hz, 1H), 1.66−1.60 (m, 1H), 1.59−1.51 (m, 1H), 1.51 −1.37 (m, 2H), 1.36−1.29 (m, 1H), 0.91 ppm (d, J = 6.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 211.4, 69.0, 60.9, 46.3, 44.9, 44.6, 42.8, 41.6, 40.9, 39.1, 35.2, 32.0, 30.5, 24.8, 22.5, 20.8 ppm; **IR**: $\tilde{\nu}$ = 3488, 2929, 1702, 1457, 1307, 1264, 1122, 1082, 737 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{27}ClNO_2$, $[M+H]^+$: 300.1725; found: 300.1716.

6. Bioinspired Total Synthesis of (±)-Lycojaponicumin D

6.1. Synthesis of (±)-Lycoposerramine G

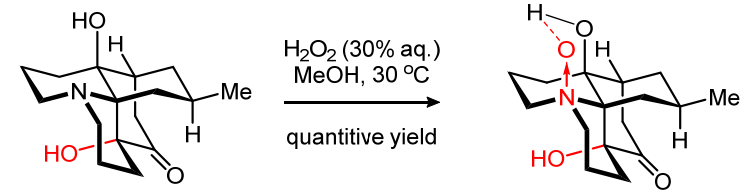


(±)-Lycodoline (**2**) (±)-Lycoposerramine G (**5**)

^{t}BuOK (80.8 mg, 0.72 mmol), $P(OEt)_3$ (1.0 mL, 6.0 mmol), (±)-lycodoline (**2**) (158.0 mg, 0.60 mmol) and dimethyl sulfoxide (12.0 mL) were added to a 50 mL Schlenk tube. The resulting mixture was stirred at ambient temperature under oxygen atmosphere (balloon pressure) for 24 h. The solution was then diluted with saturated $NaHCO_3$ (20 mL). The aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 125:5:1) to give (±)-lycoposerramine G (**5**) (140.7 mg, 0.504mmol, 84% yield (based on impure material containing residual CH_2Cl_2), **mp** 220−223 °C) as a white solid.

(±)-Lycoposerramine G (**5**): R_f = 0.63 (silica, CH_2Cl_2/MeOH 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.02 (ddd, J = 13.1, 11.0, 4.5 Hz, 1H), 3.39−3.26 (m, 2H), 3.18 (s, 1H), 2.92 (td, J = 13.1, 5.2 Hz, 1H), 2.62−2.54 (m, 2H), 2.51 (s, 1H), 2.37−1.95 (m, 7H), 1.74 (brd, J = 13.8 Hz, 2H), 1.57 (t, J = 13.1 Hz, 1H), 1.49−1.34 (m, 4H), 0.85 ppm (d, J = 5.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 208.8, 78.5, 70.1, 61.5, 48.6, 46.0, 40.6, 40.5, 38.4, 35.3, 31.1, 27.5, 24.3, 22.8, 19.9, 15.4 ppm; **IR**: $\bar{\nu}$ = 3398, 2924, 1708, 1458, 1301, 1103, 1073, 1024 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_3$, $[M+H]^+$: 280.1907; found: 280.1911.

6.2. Synthesis of (±)-Miyoshianine A



(±)-Lycoposerramine G (**5**) (±)-Miyoshianine A (**4**)
((±)-Lycoposerramine F)

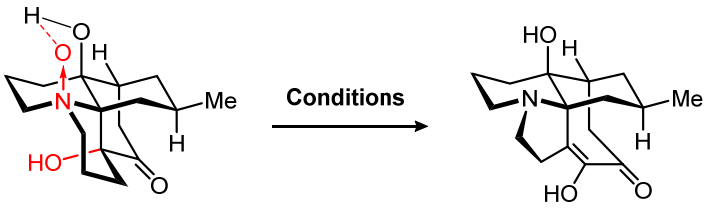
To a solution of (±)-lycoposerramine G (**5**) (139.7 mg, 0.50 mmol) in methanol (15.0 mL) was added 30% hydrogen peroxide (3.0 mL). The reaction mixture was stirred at 30 °C for 20 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 500:10:1) to give (±)-miyoshianine A (**4**) (147.2 mg, 0.499 mmol, >99% yield, **mp** 212−215 °C) as a white solid.

(±)-Miyoshianine A (**4**): R_f = 0.26 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (400 MHz, CD_3OD): δ = 5.00 (td, J = 12.7, 4.0 Hz, 1H), 3.63 (td, J = 13.8, 4.0 Hz, 1H), 3.38−3.33 (m, 1H), 3.11−2.98 (m, 3H), 2.79−2.64 (m, 2H), 2.29−1.99 (m, 5H), 1.95 (dd, J = 13.8, 4.9 Hz, 1H), 1.90−1.80 (m, 2H),

1.79−1.61 (m, 2H), 1.46−1.34 (m, 2H), 0.95 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD): δ = 207.2, 78.9, 75.0, 73.7, 64.93, 64.86, 42.5, 41.0, 36.1, 33.4, 32.0, 25.7, 25.5, 23.2, 19.2, 17.4 ppm; **IR**: $\tilde{\nu}$ = 3408, 2956, 2128, 1708, 1639, 1457, 1022, 578 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_4$, $[M+H]^+$: 296.1856; found: 296.1861.

6.3. Synthesis of (±)-Lycojaponicumin D and Its X-Ray Crystallography

6.3.1. Attempts to Optimize the Tandem Fragmentation/Mannich Reaction



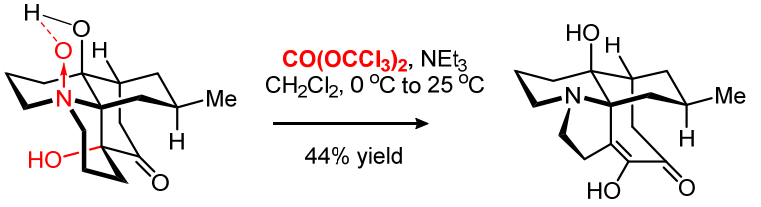
(±)-Miyoshianine A (**4**)
((±)-Lycoposerramine F)

(±)-Lycojaponicumin D (**1**)

Entry	Conditions	Results[a]
1	Ac_2O, NEt_3, CH_2Cl_2, −78 °C	no reaction
2	$(CF_3CO)_2O$, CH_2Cl_2, 0 °C	undetermined byproducts
3	$(CF_3CO)_2O$, NEt_3, CH_2Cl_2, −40 °C	undetermined byproducts
4	$(CF_3CO)_2O$, ^{t}BuOK, THF, rt	undetermined byproducts
5	$(CF_3CO)_2O$, CF_3COOH, 0 °C	no reaction
6	$(CF_3SO_2)_2O$, CH_2Cl_2, 0 °C	no reaction
7	TsCl, CH_2Cl_2, rt	no reaction
8	TsCl, ^{t}BuOK/^{t}BuOH, 60 °C	no reaction
9	TsCl, ^{t}BuOK, THF, 50 °C	SM recovered partially
10	Et_2AlCl, CH_2Cl_2, 0 °C to rt	SM recovered partially
11	Me_3Al, THF, reflux	no reaction
12	$(COCl)_2$, NEt_3, CH_2Cl_2, 0 °C to rt	SM disappeared, no desired product
13	$CO(OCCl_3)_2$, NEt_3, CH_2Cl_2, 0 °C to rt	44% yield
14	$CO(OCCl_3)_2$, pyridine, CH_2Cl_2, 0 °C to rt	SM disappeared, no desired product

[a] SM: Starting material.

6.3.2. Synthesis of (±)-Lycojaponicumin D



(±)-Miyoshianine A (**4**)
((±)-Lycoposerramine F)

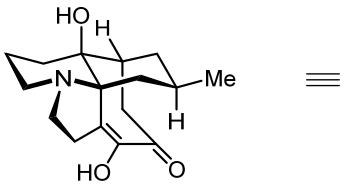
(±)-Lycojaponicumin D (**1**)

The solution of triphosgene (29.7 mg, 0.10 mmol) in dry CH_2Cl_2 (0.5 mL) was added dropwise to a stirred solution of (±)-miyoshianine A (**4**) (59.1 mg, 0.20 mmol) and NEt_3 (139 μL, 1.0 mmol) in dry CH_2Cl_2 (4.0 mL) at 0 °C under argon. The resulting mixture was warmed to 25 °C, stirred at this temperature for 20 h, and quenched with saturated $NaHCO_3$ (5 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 5 mL). The organic extracts were combined, washed with brine, dried in Na_2SO_4, concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 200:10:1) to give (±)-lycojaponicumin D (**1**) (24.4 mg, 0.0880 mmol, 44% yield, **mp** 182−185 °C) as a white powder.

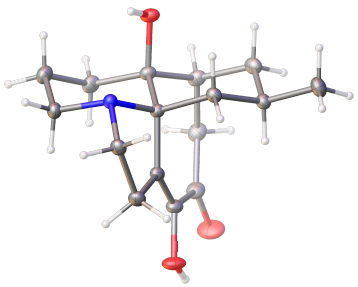
(±)-Lycojaponicumin D (**1**): R_f = 0.24 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (600 MHz, $(CD_3)_2CO$): δ = 6.99 (s, 0.32 H), 3.38 (s, 0.47 H), 3.18−3.12 (m, 1H), 3.10−3.03 (m, 1H), 2.88 (dd, J = 18.4, 5.2 Hz, 1H), 2.72−2.62 (m, 3H), 2.56 (ddd, J = 19.1, 7.6, 1.5 Hz, 1H), 2.38 (ddd, J = 13.2, 11.8, 3.3 Hz, 1H), 2.07 (qt, J = 13.2, 4.0 Hz, 1H), 2.01−1.91 (m, 2H), 1.80 (td, J = 12.9, 4.1 Hz, 1H), 1.63 (t, J = 12.1 Hz, 1H), 1.50 (brd, J = 13.5 Hz, 1H), 1.44 (brd, J = 12.4 Hz, 1H), 1.41−1.34 (m, 3H), 0.86 ppm (d, J = 6.4 Hz, 3H); **^{13}C NMR** (150 MHz, $(CD_3)_2CO$): δ = 196.3, 144.3, 133.7, 74.4, 71.1, 51.8, 49.9, 43.5, 42.4, 38.5, 36.9, 33.1, 29.8, 26.1, 22.0, 21.2 ppm; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.66 (s, 1H), 3.24−3.07 (m, 2H), 2.90−2.59 (m, 5H), 2.39 (td, J = 13.1, 3.5 Hz, 1H), 2.12−1.89 (m, 3H), 1.76 (td, J = 12.9, 4.2 Hz, 1H), 1.67−1.55 (m, 2H), 1.50−1.36 (m, 4H), 0.90 ppm (d, J = 5.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 195.8, 143.1, 133.4, 73.7, 70.7, 51.1, 49.4, 42.6, 41.0, 37.8, 36.0, 32.0, 29.2, 25.1, 21.6, 20.5 ppm; **IR**: $\bar{\nu}$ = 3401, 2953, 1622, 1456, 1354, 1264, 1132, 908, 736 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{24}NO_3$, $[M+H]^+$: 278.1751; found: 278.1754.

6.3.3. X-Ray Crystallography of (±)-Lycojaponicumin D

The single crystal of (±)-lycojaponicumin D (**1**), which was obtained through one recrystallization from a mixed solvent of CH_2Cl_2 and acetone, was used for the determination of its relative configurations via X-ray crystallographic analysis. The crystal structure and the X-ray crystallographic data of (±)-lycojaponicumin D (**1**) (CCDC 1539344) were described as follows:



(±)-Lycojaponicumin D (**1**)



X-ray of **1**

Crystal data and structure refinement for (±)-lycojaponicumin D (1)

Identification code	(±)-Lycojaponicumin D (**1**)
Empirical formula	$C_{16}H_{23}NO_3$
Formula weight	277.35
Temperature/K	293.8(3)
Crystal system	triclinic
Space group	P-1
a/Å	8.499(3)
b/Å	9.1139(17)
c/Å	10.798(3)
α/°	91.404(18)
β/°	104.88(2)
γ/°	116.48(2)
Volume/Å^3	714.2(3)
Z	2
ρ_{calc}g/cm^3	1.290
μ/mm^{-1}	0.088
F(000)	300.0
Crystal size/mm^3	0.25 × 0.22 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.9 to 52.04
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 11, -13 ≤ l ≤ 11
Reflections collected	4522
Independent reflections	2817 [R_{int} = 0.0311, R_{sigma} = 0.0651]
Data/restraints/parameters	2817/0/184
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0590, wR_2 = 0.1238
Final R indexes [all data]	R_1 = 0.1005, wR_2 = 0.1542
Largest diff. peak/hole / e Å^{-3}	0.20/-0.19

6.3.3. Comparison of ^{13}C NMR Data for Synthetic and Natural (±)-Lycojaponicumin D

The ^{1}H and ^{13}C NMR spectra for our synthetic (±)-lycojaponicumin D in $(CD_3)_2CO$ are in good agreement with those of isolated natural (±)-lycojaponicumin D in $(CD_3)_2CO$. For detailed spectral comparisons, please see the below.

Figure SI-1. Comparison of ^{1}H NMR Spectra of Lycojaponicumin D

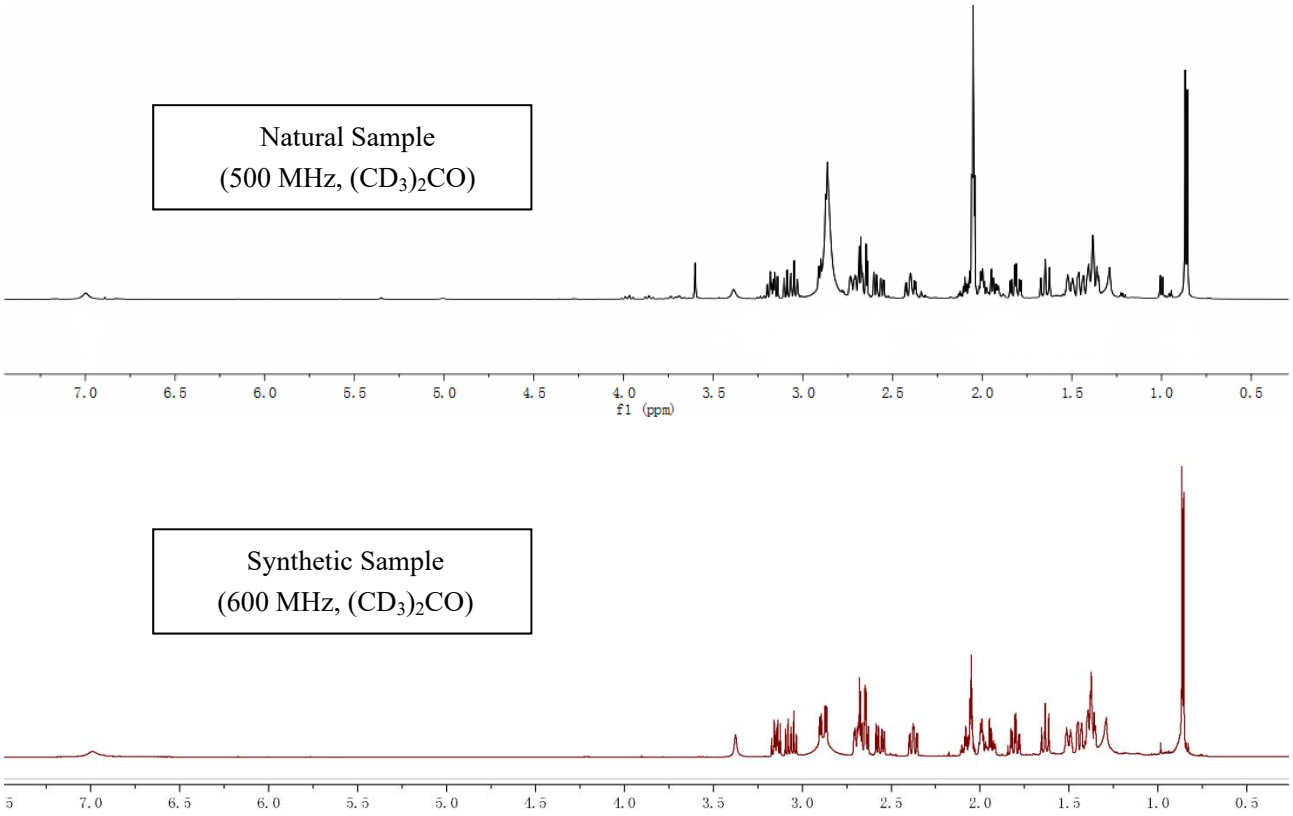


Figure SI-2. Comparison of ^{13}C NMR Spectra of Lycojaponicumin D

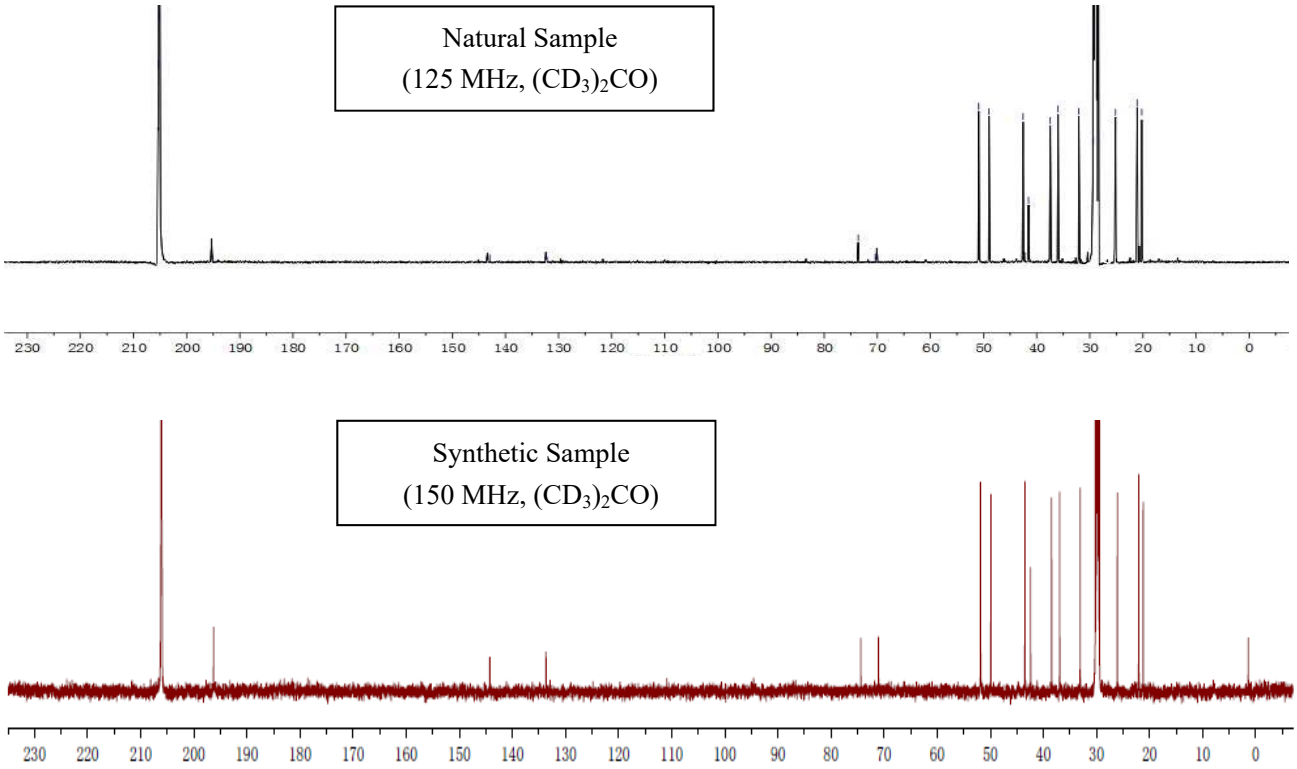


Table SI-4. Comparison of ^{13}C NMR Spectral Data of Lycojaponicumin D

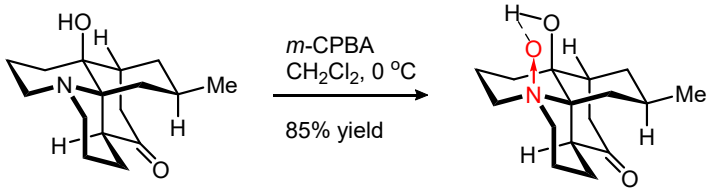
Natural Lycojaponicumin D (125 MHz, $(CD_3)_2CO$)[a]	Synthetic Lycojaponicumin D (150 MHz, $(CD_3)_2CO$)	Δδ (ppm)
20.21	21.21	−1.0
21.10	22.05	−0.95
25.16	26.07	−0.91
28.77	29.78	−1.01
32.07	33.07	−1.0
35.97	36.93	−0.96
37.45	38.46	−1.01
41.53	42.42	−0.89
42.56	43.49	−0.93
48.96	49.90	−0.94
50.91	51.84	−0.93
70.39	71.06	−0.67
73.59	74.39	−0.80
132.30	133.68	−1.38
142.94	144.27	−1.33
195.13	196.30	−1.17

[a]The spectral data from *Org. Lett.* **2012**, *14*, 5688.

In addition, the spectroscopic analysis of our synthetic (±)-lycojaponicumin D was also performed in $CDCl_3$. The related ^{13}C NMR spectral data of our synthetic sample are consistent to those of the natural sample. However, the partial deviation of ^{1}H NMR spectra in $CDCl_3$ was observed. The reason for such deviation could not be concluded at this stage.

7. Synthesis of Lycodoline-Type *Lycopodium* Alkaloids

7.1. Synthesis of (±)-Obscurumine A



(±)-Lycodoline (**2**) (±)-Obscurumine A (**6**)

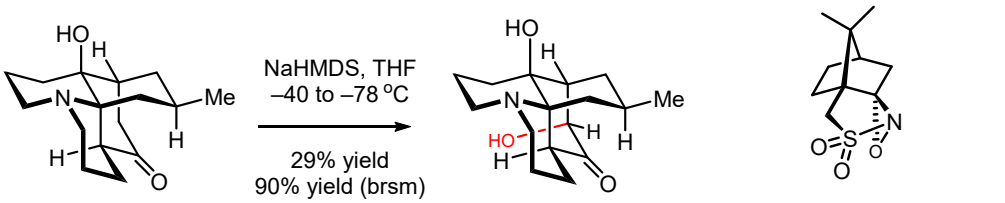
To a solution of (±)-lycodoline (**2**) (8.4 mg, 0.032 mmol) in CH_2Cl_2 (2.0 mL) was added 3-chloroperoxybenzoic acid (*m*-CPBA, 7.1 mg, 0.035 mmol). The reaction mixture was stirred at 0 °C for 1.5 h, and then quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 5 mL). The organic extracts were combined, washed with brine, dried in Na_2SO_4, concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 500:10:1) to give (±)-obscurumine A (**6**) (7.6 mg, 0.027 mmol, 85% yield, **mp** 214−218 °C) as a white solid.

(±)-Obscurumine A (**6**): R_f = 0.23 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (600 MHz, CD_3OD): δ = 4.31 (tt, J = 13.2, 3.8 Hz, 1H), 3.62 (td, J = 13.8, 4.9 Hz, 1H), 3.30−3.27 (m, 1H), 2.98 (dd, J = 12.9, 4.7 Hz, 1H), 2.92 (dd, J = 13.5, 4.5 Hz, 1H), 2.83−2.73 (m, 2H), 2.56−2.45 (m, 2H), 2.36 (dd, J = 17.0, 1.5 Hz, 1H), 2.15−2.10 (m, 1H), 2.08 (dd, J = 13.4, 4.4 Hz, 1H), 2.04−1.87 (m, 5H), 1.81 (brd, J = 14.4 Hz, 1H), 1.73−1.63 (m, 1H), 1.53 (brd, J = 13.8 Hz, 1H), 1.51−1.45 (m, 1H), 1.40−1.35 (m, 1H), 0.97 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (150 MHz, CD_3OD): δ = 209.2, 74.6, 73.1, 64.3, 60.8, 50.6, 44.8, 42.5, 36.4, 30.6, 30.3, 25.9, 22.8, 22.1, 18.7, 17.4 ppm; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.03 (t, J = 12.7 Hz, 1H), 3.60 (td, J = 13.5, 4.1 Hz, 1H), 3.10−2.99 (m, 2H), 2.92 (brd, J = 12.6 Hz, 1H), 2.84 (brd, J = 12.7 Hz, 1H), 2.77 (d, J = 13.2 Hz, 1H), 2.62 (dd, J = 17.0, 6.1 Hz, 1H), 2.43 (d, J = 17.1 Hz, 1H), 2.27−2.05 (m, 4H), 1.96−1.61 (m, 6H), 1.54−1.40 (m, 1H), 1.32 (brd, J = 12.8 Hz, 1H), 0.96 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 207.1, 72.7, 70.9, 63.2, 59.7, 49.9, 44.1, 41.2, 35.2, 29.6, 24.7, 22.4, 21.4, 17.8, 16.4 ppm; **IR**: $\bar{\nu}$ = 3403, 2925, 2372, 1705, 1458, 1265, 1144, 1097, 735 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_3$, $[M+H]^+$: 280.1907; found: 280.1905.

The spectroscopic data (^{1}H NMR, ^{13}C NMR in CD_3OD) of the synthetic product were in good agreement with those of the natural product.

7.2. Synthesis of (±)-Serratezomine C and Its X-Ray Crystallography

7.2.1. Synthesis of (±)-Serratezomine C



(±)-Lycodoline (**2**) (±)-Serratezomine C (**7**) (*1S*)-(+)-(Camphorylsulfonyl) Oxaziridine

To a solution of (±)-lycodoline (**2**) (13.2 mg, 0.050 mmol) in dry THF (1.0 mL) was added sodium hexamethyldisilazide (NaHMDS, 75 μL, 2.0 *M* in THF) at −78 °C. The resulting mixture was warmed to −40 °C, stirred at this temperature for 10 min, and cooled to −78 °C. A solution of (*1S*)-(+)-10-(camphorsulfonyl)oxaziridine (34.4 mg, 0.15 mmol) in THF (0.50 mL) was added dropwise to this reaction mixture, which was stirred for another 20 min. The reaction was quenched with Et_3N (28 μL, 0.20 mmol) at −78 °C and added a drop of HOAc. The resulting mixture was taken up in CH_2Cl_2 (10 mL), which was washed with saturated $NaHCO_3$, brine, and dried over Na_2SO_4. The solvent was concentrated in vacuo and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 500:10:1) to give (±)-serratezomine C (**7**) (4.0 mg, 0.014 mmol, 29% yield, 90 % brsm, **mp** 221−223 °C) as a pale yellow solid and (±)-lycodoline (**2**) (9.0 mg, 0.034 mmol).

(±)-Serratezomine C (**7**): $\boldsymbol{R_f}$ = 0.20 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (600 MHz, CD_3OD): δ = 3.83 (d, J = 2.0 Hz, 1H), 3.34 (td, J = 13.0, 3.2 Hz, 1H), 3.23 (td, J = 14.0, 3.9 Hz, 1H), 2.77 (td, J = 14.4, 4.6 Hz, 1H), 2.57 (brd, J = 7.8 Hz, 1H), 2.45 (dd, J = 14.3, 4.7 Hz, 1H), 2.25−2.21 (m, 2H), 2.20−1.94 (m, 4H), 1.65−1.53 (m, 3H), 1.46 (brd, J = 14.7 Hz, 1H), 1.40 (brd, J = 2.4 Hz, 1H), 1.37−1.23 (m, 3H), 0.86 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (150 MHz, CD_3OD): δ = 213.7, 79.2, 70.5, 64.2, 49.5, 47.8, 47.2, 41.0, 35.9, 34.4, 33.3, 26.2, 23.2, 21.6, 20.6, 18.7 ppm; **IR**: $\bar{\nu}$ = 3402, 2923, 2853, 1707, 1458, 1267, 1099, 1046 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_3$, $[M+H]^+$: 280.1907; found: 280.1903

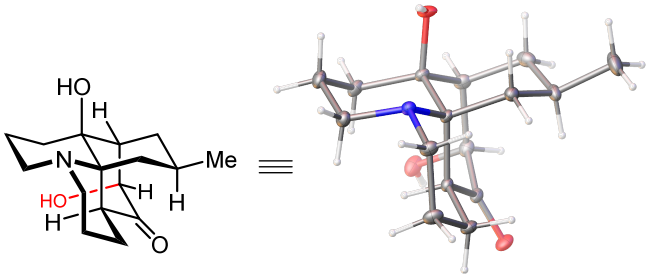
The ^{1}H and ^{13}C NMR data for (±)-Serratezomine C•TFA salt as shown below.

(±)-Serratezomine C•TFA: **^{1}H NMR** (600 MHz, CD_3OD): δ = 5.49 (s, 1H), 3.93 (d, J = 1.83 Hz, 1H), 3.92 (td, J = 13.4, 3.7 Hz, 1H), 3.69 (dd, J = 12.0, 3.3 Hz, 1H), 3.55 (td, J = 13.8, 4.0 Hz, 1H), 3.05 (dd, J = 13.1, 4.8 Hz, 1H), 2.98 (td, J = 14.6, 4.4 Hz, 1H), 2.87 (dd, J = 13.6, 5.0 Hz, 1H), 2.43 (qt, J = 13.8, 4.6 Hz, 1H), 2.32 (dd, J = 12.6, 4.9 Hz, 1H), 2.14−2.08 (m, 2H), 2.06−1.98 (m, 2H), 1.87 (brd, J = 15.1 Hz, 1H), 1.83−1.77 (m, 2H), 1.73 (ddd, J = 26.1, 13.7, 4.9 Hz, 1H), 1.62 (brd, J = 15.2 Hz, 1H), 1.44 (brd, J = 13.4 Hz, 1H), 1.41−1.33 (m, 1H), 0.93 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (150 MHz, CD_3OD): δ = 208.2, 78.1, 69.8, 68.5, 49.1, 48.4, 47.8, 42.1, 34.1, 33.6, 31.2, 26.4, 22.7, 19.7, 18.8, 18.2 ppm.

7.2.2. X-Ray Crystallography of (±)-Serratezomine C

The single crystal of (±)-serratezomine C (**7**), which was obtained through one

recrystallization from a mixed solvent of CH_2Cl_2 and MeOH, was used for the determination of its relative configurations via X-ray crystallographic analysis. The crystal structure and the X-ray crystallographic data of (±)-serratezomine C (**7**) (CCDC 1539345) were described as follows:



Serratezomine C (**7**) X-ray of **7**

Crystal data and structure refinement for (±)-serratezomine C (7)

Identification code	(±)-Serratezomine C (**7**)
Empirical formula	$C_{16}H_{25}NO_3$
Formula weight	279.37
Temperature/K	293.18(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3508(9)
b/Å	7.8777(4)
c/Å	15.0955(14)
α/°	90.00
β/°	102.872(8)
γ/°	90.00
Volume/Å^3	1431.82(19)
Z	4
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	0.088
F(000)	608.0
Crystal size/mm^3	0.28 × 0.25 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.76 to 52.04
Index ranges	-14 ≤ h ≤ 15, -9 ≤ k ≤ 9, -18 ≤ l ≤ 10
Reflections collected	5403
Independent reflections	2815 [R_{int} = 0.0583, R_{sigma} = 0.1061]
Data/restraints/parameters	2815/0/184
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0686, wR_2 = 0.1414
Final R indexes [all data]	R_1 = 0.1386, wR_2 = 0.1969
Largest diff. peak/hole / e Å^{-3}	0.20/-0.20

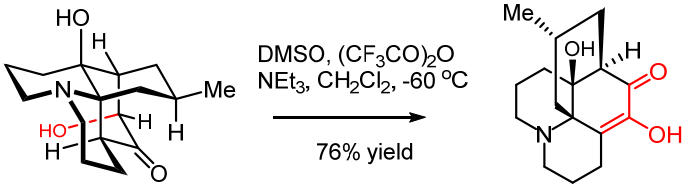
7.2.3. Comparison of ^{13}C NMR Data for Synthetic and Natural Serratezomine C

Table SI-5. Comparison of ^{13}C NMR Spectral Data of Serratezomine C

Natural Serratezomine C (125 MHz, CD_3OD)[a]	Synthetic Serratezomine C (150 MHz, CD_3OD)	Δδ (ppm)
18.59	18.66	−0.07
	20.57	
21.36[b]		
	21.61	
22.33[c]		
23.11	23.19	−0.08
26.24	26.23	+0.01
33.05	33.32	−0.27
34.26	34.36	−0.10
35.66	35.86	−0.20
41.23	41.02	+0.21
47.30	47.22	+0.08
47.89	47.81	+0.08
49.42	49.47	−0.05
64.68[c]	64.16	+0.52
70.40	70.45	−0.05
79.10	79.22	−0.12
213.00[c]	213.70	−0.70

[a]The spectral data from *J. Org. Chem.* **2000**, *65*, 6241. [b]Wrong assignment. [c]Not observed in ^{13}C NMR spectrum, published on *J. Org. Chem.* **2000**, *65*, 6241.

7.3. Synthesis of (±)-Huperzine O

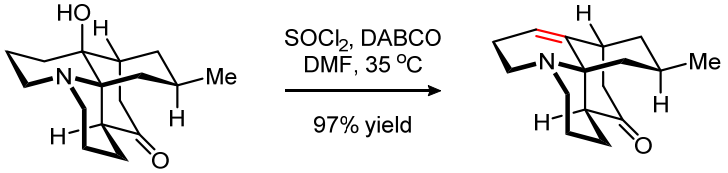


(±)-Serratezomine C (**7**) (±)-Huperzine O (**8**)

$(CF_3CO)_2O$ (10 µL, 0.072 mmol) was added dropwise to a stirred solution of dimethyl sulfoxide (DMSO, 6.1 µL, 1.4 mmol) in dry CH_2Cl_2 (2.0 mL) at −60 °C under argon. The resulting colourless, clear solution was stirred at –60 °C for 10 min, and a solution of (±)-serratezomine C (**7**) (4.1 mg, 0.015 mmol) in CH_2Cl_2 (0.50 mL) was added dropwise. The reaction solution was stirred at –60 °C for 1.5 h and NEt_3 (20 µL, 0.14 mmol) was added dropwise. The light yellow reaction mixture was stirred at −60 °C for another 1.5 h, warmed to ambient temperature, quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 5 mL). The combined organic extracts were washed with brine, dried by Na_2SO_4, contracted under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 125:5:1) to give (±)-huperzine O (**8**) (3.1 mg, 0.011 mmol, 76% yield, **mp** 243−249 °C) as a white solid.

(±)-Huperzine O (**8**): R_f = 0.29 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.07 (s, 1H), 3.41 (td, J = 13.7, 4.1 Hz, 1H), 3.03 (td, J = 12.2, 2.5 Hz, 1H), 2.96 (dd, J = 17.5, 6.5 Hz, 1H), 2.82 (s, 1H), 2.69 (dd, J = 14.6, 5.7 Hz, 1H), 2.61−2.53 (m, 2H), 2.33−2.23(m, 1H), 2.18−2.06 (m, 1H), 2.03 (dd, J = 12.7, 4.6 Hz, 1H), 1.96−1.74 (m, 3H), 1.64−1.55 (m, 3H), 1.46−1.35 (m, 3H), 0.95 ppm (d, J = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 195.7, 144.7, 130.0, 70.5, 61.8, 53.3, 48.6, 45.7, 34.2, 32.4, 30.5, 25.1, 21.5, 21.1, 19.8, 15.6 ppm; **IR**: $\bar{\nu}$ = 3406, 2924, 2373, 1666, 1458, 1270, 1196, 1092, 1070 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{24}NO_3$, $[M+H]^+$: 278.1751; found: 278.1753.

7.4. Synthesis of (±)-Anhydrolycodoline



(±)-Lycodoline (**2**) (±)-Anhydrolycodoline (**9**)

To a solution of (±)-lycodoline (**2**) (26.3 mg, 0.10 mmol) in DMF (5.0 mL) was added thionyl chloride ($SOCl_2$, 15 μL, 0.21 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO, 56.1 mg, 0.50 mmol). The reaction mixture was stirred at 35 °C for 15 h, and then quenched with saturated $NaHCO_3$. The aqueous layer was extracted with EtOAc (4 × 5 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 500:10:1) to give (±)-anhydrolycodoline (**9**) (23.8 mg, 0.097 mmol, 97 % yield) as a white foam.

(±)-Anhydrolycodoline (**9**): R_f = 0.68 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.60 (t, J = 3.9 Hz, 1H), 3.06 (td, J = 12.7, 3.7 Hz, 1H), 2.86−2.77 (m, 2H), 2.76−2.67 (m, 1H), 2.64−2.52 (m, 3H), 2.39 (d, J = 15.5 Hz, 1H), 2.36 (dd, J = 12.9, 3.8 Hz, 1H), 2.32−2.24 (m, 1H), 2.23−2.12 (m, 1H), 2.11−2.02 (m, 1H), 1.76 (dt, J = 12.9, 2.3 Hz, 1H), 1.65−1.51 (m, 3H), 1.33−1.24 (m, 2H), 1.12 (t, J = 12.6 Hz, 1H), 0.85 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 212.0, 142.7, 116.6, 59.2, 54.2, 47.64, 47.57, 45.1, 43.7, 40.4, 37.0, 26.2, 25.1, 23.0, 22.4, 19.5 ppm; **IR**: $\bar{\nu}$ = 3374, 2920, 1704, 1457, 1259, 1111, 1022, 801 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{24}NO$, $[M+H]^+$: 246.1852; found: 246.1857.

To confirm its structure, (±)-anhydrolycodoline•TFA salt was additionally prepared. Its ^{1}H and ^{13}C NMR spectral data are consistent with those previously reported by Olafsdottir (*Phytochemistry* **2010**, *71*, 149).[5] It should be noted that some unknown contaminants could be observed in the NMR spectra of anhydrolycodoline•TFA in CD_3OD. The inseparable contaminants might result from the chemical instability of anhydrolycodoline in acid conditions (For an early note on the chemical instability of anhydrolycodoline, see: Ayer, W. A.; Iverach, G. G. *Can. J. Chem.* **1964**, *42*, 2514).[6]

The ^{1}H and ^{13}C NMR data for (±)-anhydrolycodoline•TFA salt as shown below.

(±)-Anhydrolycodoline•TFA: **^{1}H NMR** (400 MHz, CD_3OD): δ = 5.9 (d, J = 6.0 Hz, 1H), 3.86 (td, J = 12.3, 4.5 Hz, 1H), 3.76 (td, J = 13.4, 4.9 Hz, 1H), 3.52−3.39 (m, 1H), 3.27 (d, J = 5.8 Hz, 1H), 3.25−3.15 (m, 2H), 3.00 (t, J = 3.4 Hz, 1H), 2.84−2.61 (m, 3H), 2.49 (d, J = 16.1 Hz, 1H), 2.46−2.39 (m, 1H), 2.14−2.04 (m, 1H), 1.97−1.83 (m, 3H), 1.75−1.64 (m, 2H), 1.36 (dd, J = 12.7, 3.8 Hz, 1H), 1.25 (t, J = 13.2 Hz, 1H), 0.96 ppm (d, J = 6.2 Hz, 3H); **^{13}C NMR** (100 MHz, CD_3OD): δ = 208.3, 140.3, 117.8, 64.2, 53.0, 49.6, 48.8, 45.9, 42.1, 40.4, 40.3, 26.3, 23.6, 22.1, 19.6, 18.8 ppm.

For ^{13}C NMR comparison of synthetic anhydrolycodoline•TFA salt with natural one, see below:

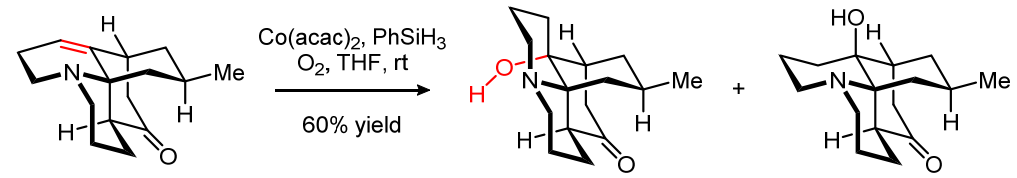
Table SI-6. Comparison of ^{13}C NMR Data for Anhydrolycodoline•TFA salt

Natural Anhydrolycodoline•TFA salt (100 MHz, CD_3OD)[a]	Synthetic Anhydrolycodoline•TFA salt (100 MHz, CD_3OD)	Δδ (ppm)
18.8	18.8	0
19.6	19.6	0
22.1	22.1	0
23.7	23.6	+0.1
26.4	26.3	+0.1
40.3	40.26	0
40.4	40.35	+0.05
42.2	42.1	+0.1
46.0	45.9	+0.1
48.9	48.8	+0.1
49.7	49.6	+0.1
53.1	53.0	+0.1
64.2	64.2	0
117.9	117.8	+0.1
140.3	140.3	0
208.3	208.3	0

[a]The spectral data from *Phytochemistry* **2010**, *71*, 149.

7.5. Synthesis of (±)-12-Epilycodoline and Its X-Ray Crystallography

7.5.1. Synthesis of (±)-12-Epilycodoline



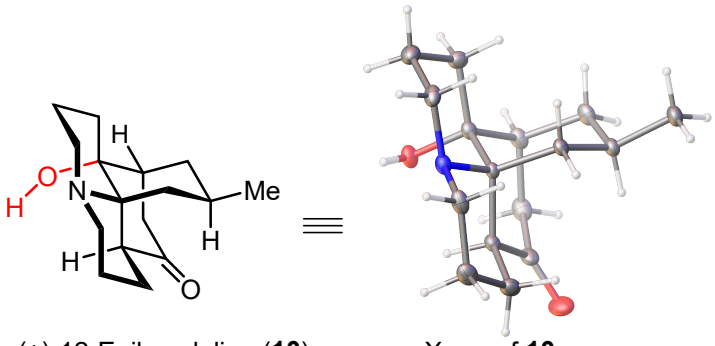
(±)-Anhydrolycodoline (**9**) (±)-12-Epilycodoline (**10**) (43% yield) (±)-Lycodoline (**2**) (17% yield)

To a solution of (±)-anhydrolycodoline (**9**) (61.3 mg, 0.25 mmol) in anhydrous THF (4.0 mL) was added cobalt(II) acetylacetonate ($Co(acac)_2$, 77.1 mg, 0.30 mmol) and phenylsilane ($PhSiH_3$, 153 μL, 1.243 mmol). The resulting mixture was stirred at ambient temperature under oxygen atmosphere (balloon pressure) for 24 h. The solution was then diluted with saturated $NaHCO_3$ (5 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (EtOAc/MeOH/NH_3•H_2O 125:5:1) to give (±)-12-epilycocoline (**10**) (28.3 mg, 0.108 mmol, 43% yield, **mp** 125−128 °C) as a white solid and (±)-lycodoline (**2**) (11.2 mg, 0.043 mmol, 17% yield).

(±)-12-Epilycodoline (**10**): $\boldsymbol{R_f}$ = 0.33 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 3.48 (s, 1H), 3.09 (dd, J = 16.4, 6.4 Hz, 1H), 2.80 (brd, J = 12.3 Hz, 1H), 2.61−2.39 (m, 4H), 2.23−1.89 (m, 5H), 1.83−1.65 (m, 3H), 1.59−1.34 (m, 7H), 0.89 ppm (d, J = 3.5 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 211.9, 70.1, 62.3, 52.1, 48.6, 47.8, 43.8, 40.7, 37.3, 30.1, 25.5, 25.0, 24.5, 22.6, 20.8, 18.5 ppm; **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 3.48 (s, 1H), 3.09 (dd, J = 15.8, 6.3 Hz, 1H), 2.79 (dd, J = 12.1, 2.7 Hz, 1H), 2.54 (td, J = 12.6, 3.5 Hz, 1H), 2.49 (td, J = 12.4, 3.3 Hz, 1H), 2.46−2.41 (m, 2H), 2.20−2.13 (m, 3H), 2.07 (brd, J = 14.0 Hz, 1H), 2.03−1.93 (m, 1H), 1.78 (brd, J = 12.9 Hz, 1H), 1.73−1.68 (m, 1H), 1.67−1.62 (m, 1H), 1.58−1.43 (m, 6H), 1.37 (ddd, J = 26.2, 13.6, 4.2 Hz, 1H), 0.89 ppm (d, J = 5.6 Hz, 3H); **IR**: $\bar{\nu}$ = 3448, 2924, 1697, 1262, 1105, 1071, 1014, 803 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_2$, $[M+H]^+$: 264.1958; found: 264.1952.

7.5.2. X-Ray Crystallography of (±)-12−Epilycodoline

The single crystal of (±)-12-epilycocoline (**10**), which was obtained through one recrystallization from a mixed solvent of CH_2Cl_2 and *n*-hexane, was used for the determination of its relative configurations via X-ray crystallographic analysis. The crystal structure and the X-ray crystallographic data of (±)-12-epilycocoline (**10**) (CCDC 1539346) were described as follows:



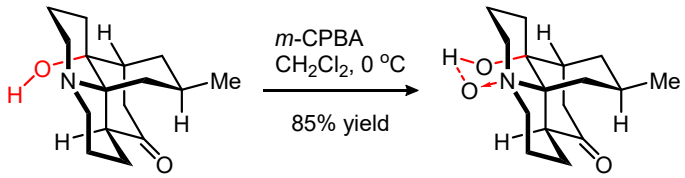
(±)-12-Epilycodoline (**10**) X-ray of **10**

Crystal data and structure refinement for (±)-12-epilycodoline (10)

Identification code	(±)-12-Epilycodoline (**10**)
Empirical formula	$C_{16}H_{25}NO_2$
Formula weight	263.37
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.0578(8)
b/Å	8.8764(5)
c/Å	14.6334(12)
α/°	90.00
β/°	98.677(7)
γ/°	90.00
Volume/Å^3	1419.87(17)
Z	4
ρ_{calc}g/cm^3	1.232
μ/mm^{-1}	0.080
F(000)	576.0
Crystal size/mm^3	0.21 × 0.15 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.78 to 52.04
Index ranges	-13 ≤ h ≤ 10, -6 ≤ k ≤ 10, -18 ≤ l ≤ 14
Reflections collected	4909
Independent reflections	2792 [R_{int} = 0.0320, R_{sigma} = 0.0524]
Data/restraints/parameters	2792/0/174
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0680, wR_2 = 0.1582
Final R indexes [all data]	R_1 = 0.1059, wR_2 = 0.1883
Largest diff. peak/hole / e Å^{-3}	0.33/-0.16

7.6. Synthesis of (±)-12-Epilycodoline *N*-Oxide

7.6.1. Synthesis of (±)-12-Epilycodoline *N*-Oxide



(±)-12-Epilycodoline (**10**) (±)-12-Epilycodoline *N*-Oxide (**11**)

To a solution of the (±)-12-epilycodoline (**10**) (27.9 mg, 0.106 mmol) in CH_2Cl_2 (2.0 mL) was added 3-chloroperbenzoic acid (*m*-CPBA, 22.1 mg, 0.128 mmol). The resulting mixture was stirred at 0 °C for 1.5 h, and then quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 5 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 500:10:1) to give (±)-12-epilycodoline *N*-oxide (**11**) (25.1 mg, 0.090 mmol, 85% yield, **mp** 195−200 °C) as a colorless solid.

(±)-12-Epilycodoline *N*-Oxide (**11**): R_f = 0.51 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 4.29 (d, J = 11.7 Hz, 1H), 3.49 (t, J = 12.3 Hz, 1H), 3.42−3.24 (m, 2H), 3.13−2.93 (m, 2H), 2.74 (dd, J = 11.2, 4.2 Hz, 1H), 2.61−2.42 (m, 1H), 2.35−2.09 (m, 5H), 1.78−1.42 (m, 9H), 0.93 ppm (d, J = 4.2 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 211.5, 73.1, 71.4, 61.4, 61.0, 45.5, 43.4, 42.2, 36.9, 34.7, 29.8, 25.9, 22.4, 19.2, 17.2, 16.6 ppm; **IR**: $\bar{\nu}$ = 3377, 2962, 1696, 1474, 1261, 1099, 1024, 801 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_3$, $[M+H]^+$: 280.1907; found: 280.1902.

7.6.2. Comparison of ^{13}C NMR Data for 12-Epilycodoline *N*-Oxide

Table SI-7. Comparison of ^{13}C NMR Spectral Data for 12-Epilycodoline *N*-Oxide

Original Report on 12-Epilycodoline *N*-Oxide (100 MHz, $CDCl_3$)[a]	Synthetic 12-Epilycodoline *N*-Oxide (75 MHz, $CDCl_3$)	Δδ (ppm)
16.4	16.6	−0.2
17.8	17.2	+0.6
21.4	19.2	+2.2
22.5	22.4	+0.3
24.7	25.9	−1.2
29.6	29.8	−0.3
29.6	34.7	−5.1
35.2	36.9	−1.7
41.2	42.2	−1.0
44.1	43.4	+0.7
49.9	45.5	+4.4
59.7	61.0	−1.3
63.2	61.4	+1.8
71.0	71.4	−0.4
72.8	73.1	−0.3
207.0	211.5	−4.5

[a]The spectral data from *Helv. Chim. Acta* **2004**, *87*, 1963.

7.6.3. Comparison of ^{13}C NMR Spectral Data for 12-Epilycodoline *N*-Oxide and Obscurumine A

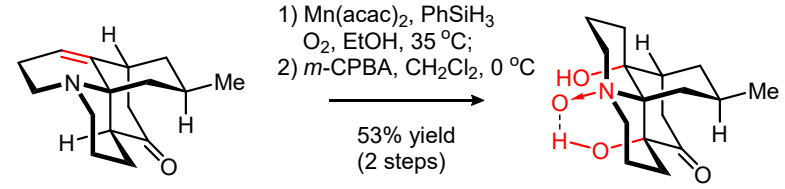
Table SI-8. Comparison of ^{13}C NMR Spectral Data for 12-Epilycodoline *N*-Oxide and Obscurumine A

Original Report on 12-Epilycodoline *N*-Oxide (100 MHz, $CDCl_3$)[a]	Synthetic Obscurumine (100 MHz, $CDCl_3$)	Δδ (ppm)
16.4	16.4	0
17.8	17.8	0
21.4	21.4	0
22.5	22.4	+0.1
24.7	24.7	0
29.6	29.6	0
29.6	29.6	0
35.2	35.2	0
41.2	41.2	0
44.1	44.1	0
49.9	49.9	0
59.7	59.7	0
63.2	63.2	0
71.0	70.9	+0.1
72.8	72.7	+0.1
207.0	207.1	−0.1

[a]The spectral data from *Helv. Chim. Acta* **2004**, *87*, 1963.

By ^{13}C NMR comparison of original report on the natural (±)-12-epilycodoline *N*-oxide with our synthetic (±)-12-epilycodoline *N*-oxide, two notes are described as follows: **1)** The ^{13}C NMR data of the synthetic product is different from the natural 12-epilycodoline *N*-oxide isolated by Zhu (*Helv. Chim. Acta.* **2004**, *87*, 1963),[7] Thasana (*Tetrahedron* **2014**, *70*, 8017),[8] and Zhao (*Nat. Prod. Bioprospect.* **2014**, *4*, 213).[9] **2)** The ^{13}C NMR data in $CDCl_3$ of the natural 12-epilycodoline *N*-oxide previously claimed by Zhu are matched with those of natural obscurumine A.

7.7. Synthesis of (±)-4-Hydroxy-12-Epilycodoline *N*-Oxide



(±)-Anhydrolycodoline (**9**)

(±)-4-Hydeoxy-12-Epilycodoline *N*-Oxide (**12**)

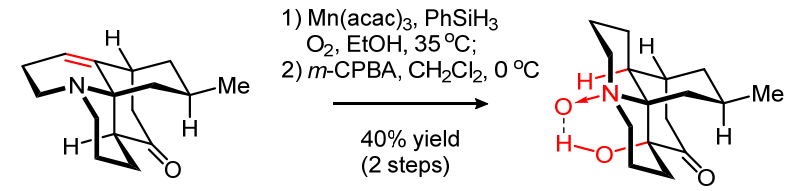
To a solution of (±)-anhydrolycodoline (**9**) (20.1 mg, 0.0819 mmol) in anhydrous EtOH (2.0 mL) was added manganese(II) acetylacetonate ($Mn(acac)_2$, 92.9 mg, 0.367 mmol) and phenylsilane ($PhSiH_3$, 70 μL, 0.57 mmol). The reaction mixture was stirred at 35 °C under oxygen atmosphere (balloon pressure) for 16 h. The solution was then diluted with saturated $NaHCO_3$ (5 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was directly used in the next reaction without further purification.

To a solution of the crude product obtained above in CH_2Cl_2 (2.0 mL) was added 3-chloroperbenzoic acid (*m*-CPBA, 18.8 mg, 0.0815 mmol). The reaction mixture was stirred at 0 °C for 1.5 h, and then quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 5 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 500:10:1) to give (±)-4-hydroxy-12-epilycodoline *N*-oxide (**12**) (12.8 mg, 0.0434 mmol, 53% yield) as a white solid.

(±)-4-hydroxy-12-epilycodoline *N*-oxide (**12**): R_f = 0.46 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.11 (s, 0.7H), 3.93 (dd, J = 14.9, 5.1 Hz, 1H), 3.55 (t, J = 12.6 Hz, 2H), 3.12−2.75 (m, 4H), 2.40−2.26 (m, 1H), 2.25−1.97 (m, 4H), 1.97−1.64 (m, 7H), 1.63−1.47 (m, 2H), 0.92 ppm (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 206.5, 78.5, 73.1, 69.4, 63.0, 62.4, 42.4, 40.2, 37.8, 36.1, 30.7, 25.5, 25.0, 22.6, 16.4, 15.8 ppm; **IR**: $\bar{\nu}$ = 3386， 2962， 1715， 1457， 1412， 1261， 1101， 1028， 802 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_4$, $[M+H]^+$: 296.1856; found: 296.1856.

7.8. Synthesis of (±)-12-*epi*-Flabelliformine *N*-Oxide and Its X-Ray Crystallography

7.8.1. Synthesis of (±)-12-*epi*-Flabelliformine *N*-Oxide



(±)-Anhydrolycodoline (**9**)

(±)-12-*epi*-Flabelliformine *N*-Oxide (**14**)

To a solution of (±)-anhydrolycodoline (**9**) (40.0 mg, 0.1630 mmol) in anhydrous EtOH (4.0 mL) was added manganese(III) acetylacetonate ($Mn(acac)_3$, 185.8 mg, 0.734 mmol) and phenylsilane ($PhSiH_3$, 141 μL, 1.14 mmol). The reaction mixture was stirred at 35 °C under oxygen

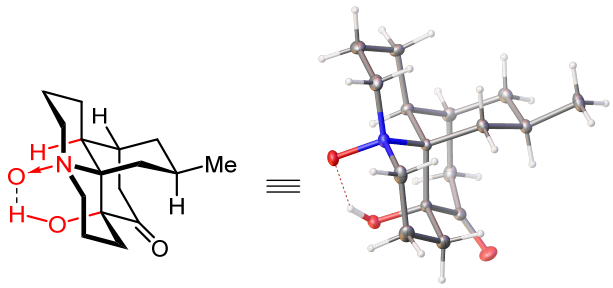
atmosphere (balloon pressure) for 16 h. The solution was then diluted with saturated $NaHCO_3$ (5 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was directly used in the next reaction without further purification.

To a solution of the crude product obtained above in CH_2Cl_2 (2.0 mL) was added 3-chloroperbenzoic acid (*m*-CPBA, 30.7 mg, 0.178 mmol). The reaction mixture was stirred at 0 °C for 1.5 h, and then quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 5 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 500:10:1) to give (±)-12-*epi*-flabelliformine *N*-oxide (**14**) (18.2 mg, 0.0652 mmol, 40% yield, **mp** 197−200 °C) as a white solid.

(±)-12-*epi*-Flabelliformine *N*-Oxide (**14**): $\boldsymbol{R_f}$ = 0.44 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 12.75 (s, 1H), 3.59−3.34 (m, 4H), 3.00 (dd, J = 11.9, 5.3 Hz, 1H), 2.94−2.67 (m, 3H), 2.20 (dd, J = 15.4, 2.0 Hz, 1H), 2.20 (t, J = 3.3 Hz, 1H), 2.01 (dd, J = 14.5, 4.2 Hz, 1H), 1.93−1.83 (m, 2H), 1.83−1.73 (m, 3H), 1.71−1.57 (m, 3H), 1.46 (d, J = 3.1 Hz, 1H), 1.44 (s, 1H), 0.92 ppm (d, J = 5.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 206.8, 77.7, 70.4, 61.8, 61.1, 43.7, 34.9, 33.32, 33.28, 30.6, 25.1, 24.3, 23.2, 22.3, 19.6, 16.0 ppm; **IR**: $\bar{\nu}$ = 3384, 2929, 1714, 1458, 1254, 1102, 939, 734 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_3$, $[M+H]^+$: 280.1907; found: 280.1910.

7.8.2. X−Ray Crystallography of (±)-12-*epi*-Flabelliformine *N*-Oxide

The single crystal of (±)-12-*epi*-flabelliformine *N*-oxide (**14**), which was obtained through one recrystallization from a mixed solvent of *n*-hexane and EtOAc, was used for the determination of its relative configurations via X-ray crystallographic analysis. The crystal structure and the X-ray crystallographic data of (±)-12-*epi*-flabelliformine *N*-oxide (**14**) (CCDC 1539347) were described as follows:



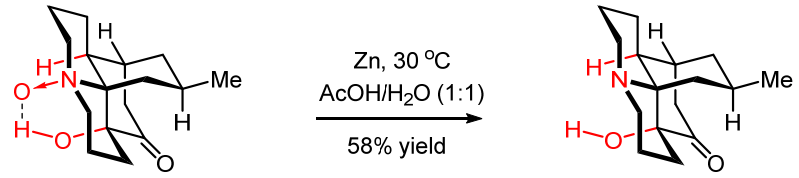
(±)-12-*epi*-Flabelliformine *N*-Oxide (**14**)

X-ray of **14**

Crystal data and structure refinement for (±)-12-epi-flabelliformine *N*-oxide (14)

Identification code	12-*epi*-Flabelliformine *N*-Oxide (**14**)
Empirical formula	$C_{16}H_{25}NO_3$
Formula weight	279.37
Temperature/K	295.37(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.6488(8)
b/Å	9.1105(5)
c/Å	10.2100(6)
α/°	90.00
β/°	100.967(7)
γ/°	90.00
Volume/Å^3	698.49(9)
Z	2
ρ_{calc}g/cm^3	1.328
μ/mm^{-1}	0.091
F(000)	304.0
Crystal size/mm^3	0.13 × 0.07 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.04 to 52.04
Index ranges	$-9 \le h \le 8$, $-7 \le k \le 11$, $-6 \le l \le 12$
Reflections collected	2473
Independent reflections	1962 [R_{int} = 0.0225, R_{sigma} = 0.0564]
Data/restraints/parameters	1962/1/183
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0499, wR_2 = 0.1008
Final R indexes [all data]	R_1 = 0.0721, wR_2 = 0.1146
Largest diff. peak/hole / e Å^{-3}	0.18/-0.17
Flack parameter	0(2)

7.9. Synthesis of (±)-12-*epi*-Flabelliformine



(±)-12-*epi*-Flabelliformine *N*-Oxide (**14**)

(±)-12-*epi*-Flabelliformine (**13**)

To a solution of (±)-12-*epi*-flabelliformine *N*-oxide (**14**) (11.0 mg, 0.0394 mmol) in 3 mL of AcOH/H_2O (1:1) was added zinc powder (12.9 mg, 0.197 mmol). The resulting mixture was stirred at 30 °C for 15 h. The solution was then neutralized with solid K_2CO_3 and extracted with CH_2Cl_2 (4 × 15 mL). The organic layers were combined, washed with brine, dried over Na_2SO_4. The solvent was removed under reduced pressured and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH/NH_3•H_2O 200:10:1) to give (±)-12-*epi*-flabelliformine (**13**) (6.0 mg, 0.023 mmol, 58% yield, **mp** 215-218 °C) as a white solid and recovered (±)-12-*epi*-flabelliformine *N*-oxide (**14**) (3.9 mg, 0.014 mmol).

(±)-12-*epi*-Flabelliformine (**13**): R_f = 0.21 (silica, CH_2Cl_2/MeOH 10:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.35 (s, 1H), 3.08 (ddd, J = 15.6, 6.5, 0.8 Hz, 1H), 2.66−2.44 (m, 3H), 2.39 (brd, J = 5.5 Hz, 1H), 2.34−2.30 (m, 1H), 2.27 (dd, J = 15.6, 1.8 Hz, 1H), 2.11−2.05 (m, 1H), 1.95−1.83 (m, 2H), 1.79 (d, J = 9.9 Hz, 1H), 1.75−1.69 (m, 1H), 1.69−1.55 (m, 4H), 1.50−1.32 (m, 5H), 0.87 ppm (d, J = 5.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 210.6, 74.7, 61.1, 48.7, 46.8, 45.1, 36.8, 36.5, 34.9, 25.9, 25.3, 24.7, 24.3, 23.8, 23.1, 19.7 ppm; **IR**: $\tilde{\nu}$ = 3339, 2935, 1710, 1666, 1452, 1245, 1135, 907, 732 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{16}H_{26}NO_3$, $[M+H]^+$: 264.1958; found: 264.1949.

8. Preliminary Study of the Biogenetic Transformation from Lycodoline to Fawcettimine

8.1. Screening of Conditions for Aza-Semipinacol Rearrangement

(±)-lycodoline (**2**) (±)-fawcettimine (**3**)

Entry	Conditions	Results[a]
1	HCl (conc.)	RSM
2	<40% HBr (aq.), AcOH, 60 °C	RSM
3	45% w/v HBr (in AcOH), 110 °C	elimination byproduct[b]
4	CF_3CH_2OH, 250 °C	RSM
5	$(CF_3)_2CHOH$, 200 °C	RSM
6	$B(OH)_3$, 250 °C	elimination byproduct[b]
7	Et_2AlCl, CH_2Cl_2, 35 °C	RSM
8	Me_3Al, CH_2Cl_2, 35 °C	RSM
9	BF_3•Et_2O, CH_2Cl_2, rt	RSM
10	^{t}BuOK, MsCl, THF, 35 °C	decomposed
11	^{t}BuLi, MsCl, THF, 0 °C	RSM
12	KH, MsCl, THF, 0 °C	RSM
13	KH, TFAA, THF, 60 °C	RSM
14	KH, triphosgene, THF, rt	RSM
15	KH, phenylphosphonic dichloride, THF, rt	decomposed
16	$(COCl)_2$, DABCO, CH_2Cl_2, 35 °C	elimination byproduct[c]
17	NaH, $SOCl_2$, CH_2Cl_2, 35 °C	elimination byproduct[c]

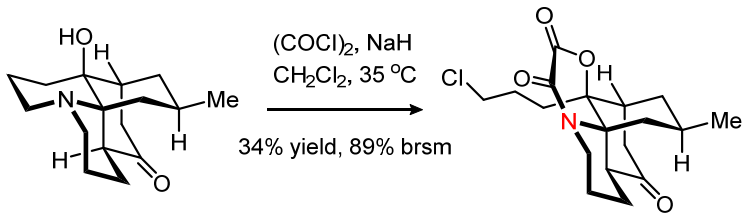
[a]RSM: recovered starting material. [b]The starting material disappeared completely, and the major elimination product, anhydrolycodoline, was obtained. [c]With the partial recovery of starting material, the main elimination product, anhydrolycodoline, was isolated.

From the results obtained above, when treating lycodoline with a series of Brønsted and Lewis acids, no desired rearrangement product was detected, partially showing the negative influence of the decreased migratory aptitude of C–C bond adjacent to electronically deactivated aliphatic amine moiety of lycodoline under acidic conditions.

Besides, *in situ* introduction of the hydroxyl leaving group by using various electrophilic reagents (e.g., acyl, sulfonyl and phosphoryl chlorides, and anhydrides) were also performed under basic conditions, and disappointedly there was still no positive result for the proposed aza-semipinacol rearrangement. This non-rearrangeable transformation might give a clue that electronic deactivation of conformationally rigid convex nitrogen atom of lycodoline, competitively caused by reaction with electrophilic reagents being used for installing an oxygen leaving group, might to some extent retard the proposed aza-semipinacol rearrangement.

8.2. Compound 23 and Its X-Ray Crystallography

8.2.1. Synthesis of Compound 23



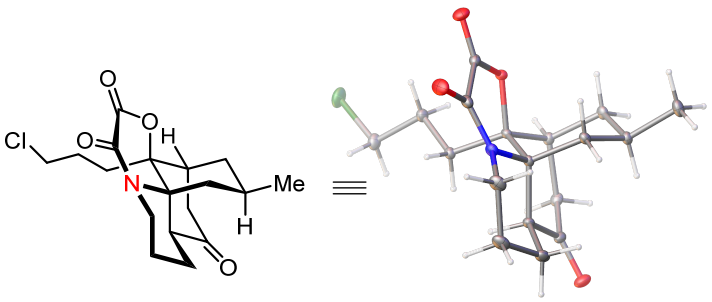
(±)-Lycodoline (**2**) **23**

To a solution of (±)-lycodoline (**2**) (26.3 mg, 0.10 mmol) in CH_2Cl_2 (2.0 mL) was added oxalyl chloride ($(COCl)_2$, 18 μL, 0.21 mmol) and NaH (12.1 mg, 0.50 mmol). The reaction mixture was stirred at 35 °C for 15 h, and then quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 5 mL). The combined organic layers were washed with brine, dired in Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel ($V_{\text{petroleum ether}}$ /V_{EtOAc} 2:1) to afford **23** (12.0 mg, 0.034 mmol, 34% yield, 89% brsm, **mp** 287−289 °C) as a white solid and (±)-lycodoline (**2**) (16.3 mg, 0.062 mmol).

23: R_f = 0.56 (silica, petroleum ether/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.17 (dt, J = 14.4, 3.6 Hz, 1H), 3.75 (dt, J = 10.9, 5.0 Hz, 1H), 3.50 (ddd, J = 11.0, 9.9, 3.9 Hz, 1H), 3.15−3.06 (m, 1H), 2.74 (dd, J = 17.4, 6.5 Hz, 1H), 2.68−2.61 (m, 2H), 2.52 (dd, J = 17.5, 1.2 Hz, 1H), 2.49−2.37 (m, 2H), 2.31 (ddd, J = 14.7, 12.1, 4.9 Hz, 1H), 2.25−2.16 (m, 1H), 2.16−2.05 (m, 1H), 2.05−1.87 (m, 2H), 1.81 (td, J = 13.5, 3.1 Hz, 1H), 1.68−1.49 (m, 4H), 1.34−1.23 (m, 1H), 0.90 ppm (d, J = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 204.9, 155.6, 154.0, 82.3, 60.8, 51.1, 44.7, 43.7, 38.9, 38.3, 34.9, 34.8, 29.6, 25.8, 24.3, 22.4, 21.5, 17.2 ppm; **IR**: $\bar{\nu}$ = 3477, 2925, 1747, 1674, 1415, 1286, 1211, 1032, 799 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{18}H_{24}NO_4ClNa$, $[M+Na]^+$: 376.1286; found: 376.1292.

8.2.2. X-Ray Crystallography of 23

The single crystal of **23**, which was obtained through one recrystallization from a mixed solvent of *n*-hexane and EtOAc, was used for the determination of its relative configurations via X-ray crystallographic analysis. The crystal structure and the X-ray crystallographic data of **23** (CCDC 1539348) were described as follows:



23 X-ray of **23**

Crystal data and structure refinement for compound 23

Identification code	Compound **23**
Empirical formula	$C_{18}H_{24}ClNO_4$
Formula weight	353.83
Temperature/K	294.09(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.4830(3)
b/Å	13.0673(7)
c/Å	17.5715(8)
α/°	90.00
β/°	91.061(4)
γ/°	90.00
Volume/Å^3	1717.89(14)
Z	4
ρ_{calc}g/cm^3	1.368
μ/mm^{-1}	0.244
F(000)	752.0
Crystal size/mm^3	0.27 × 0.25 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.66 to 52.04
Index ranges	$-9 \le h \le 8$, $-8 \le k \le 16$, $-21 \le l \le 17$
Reflections collected	6549
Independent reflections	3380 [R_{int} = 0.0339, R_{sigma} = 0.0645]
Data/restraints/parameters	3380/0/218
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0593, wR_2 = 0.1189
Final R indexes [all data]	R_1 = 0.1072, wR_2 = 0.1508
Largest diff. peak/hole / e Å^{-3}	0.21/-0.34

9. References

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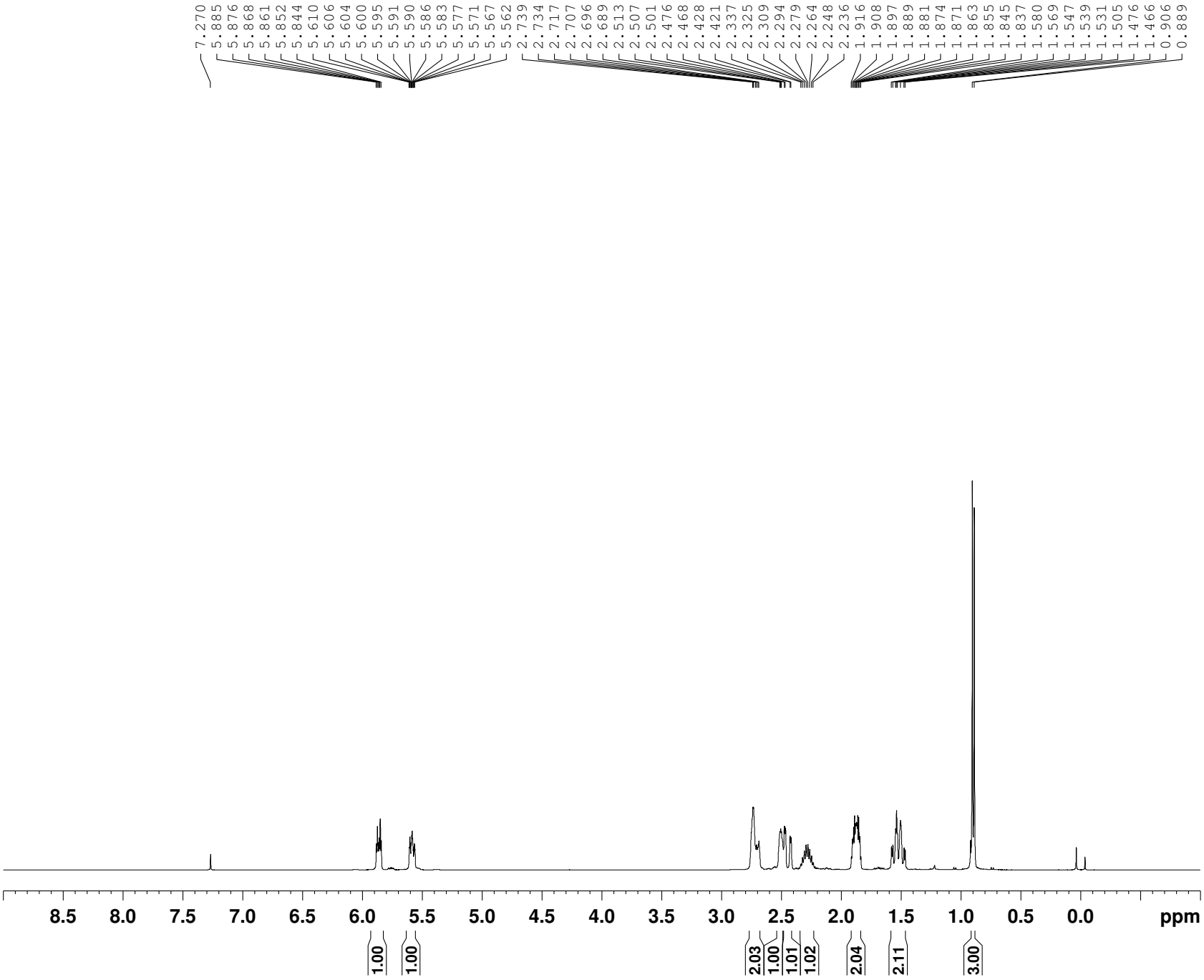


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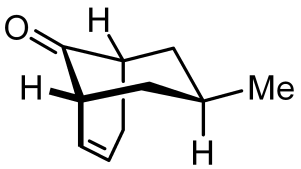

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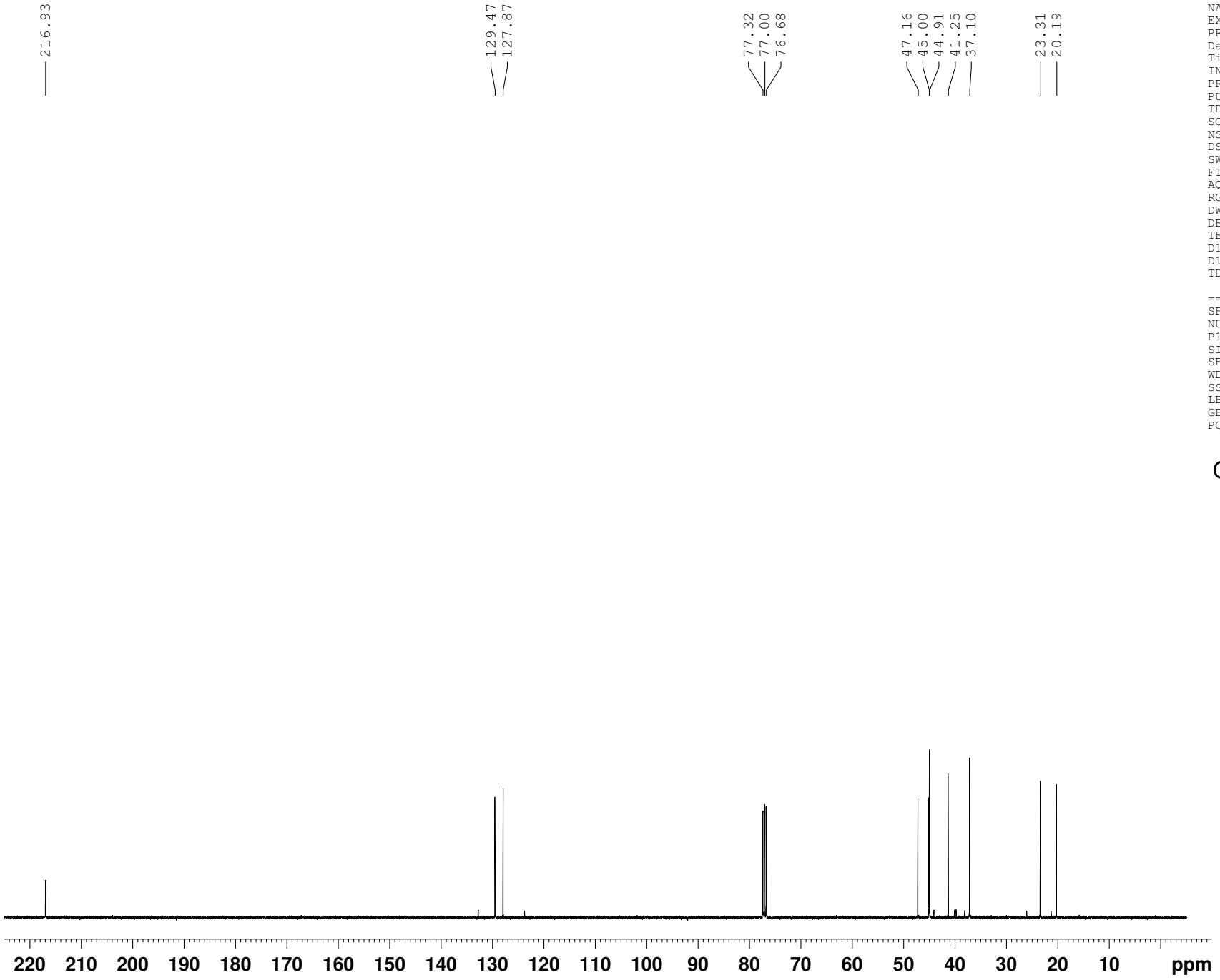


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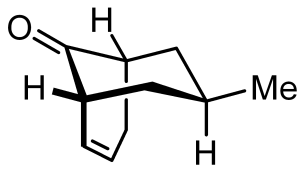

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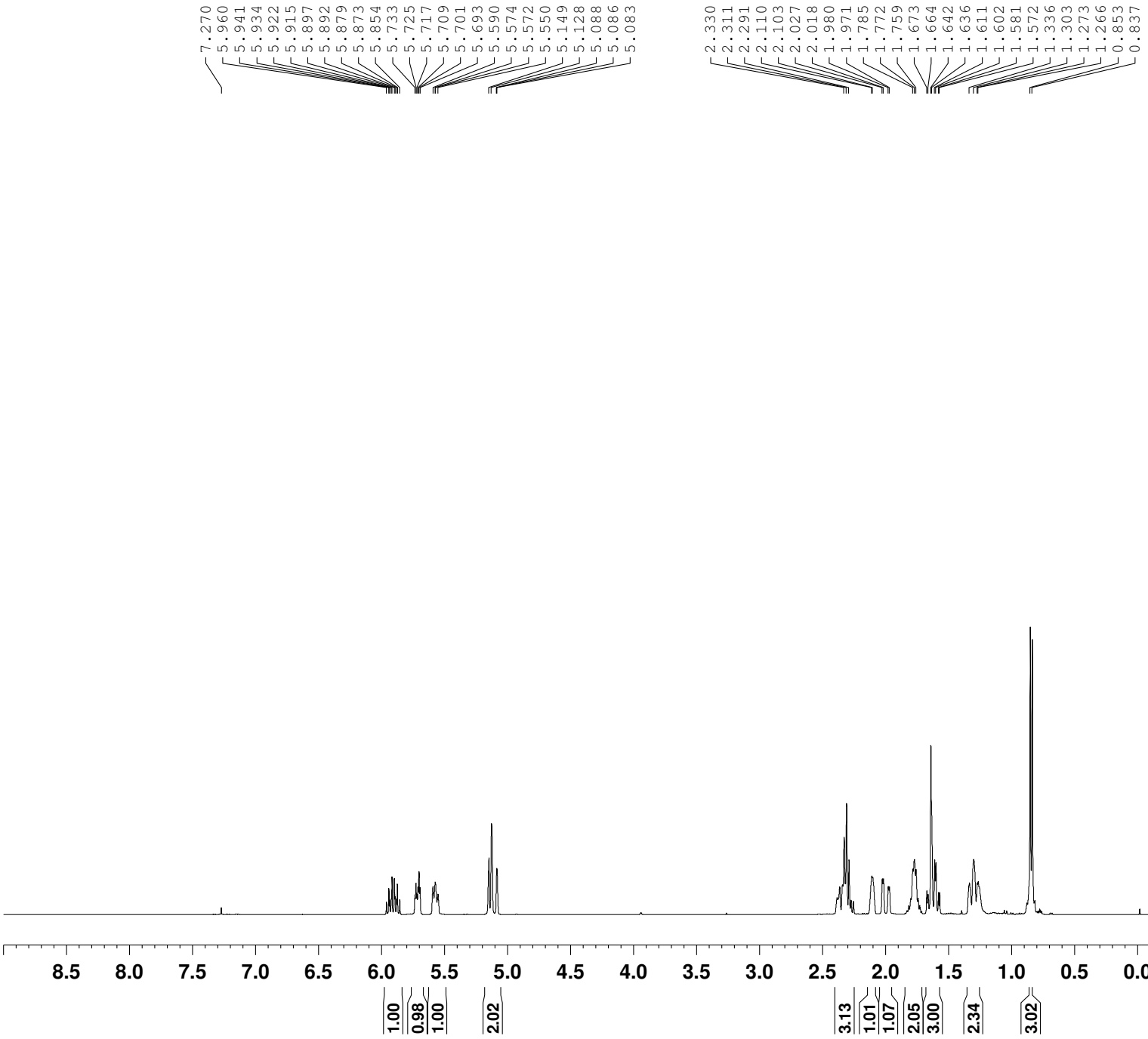


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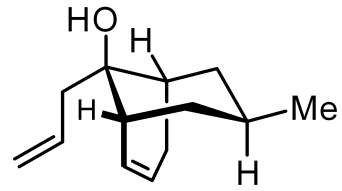

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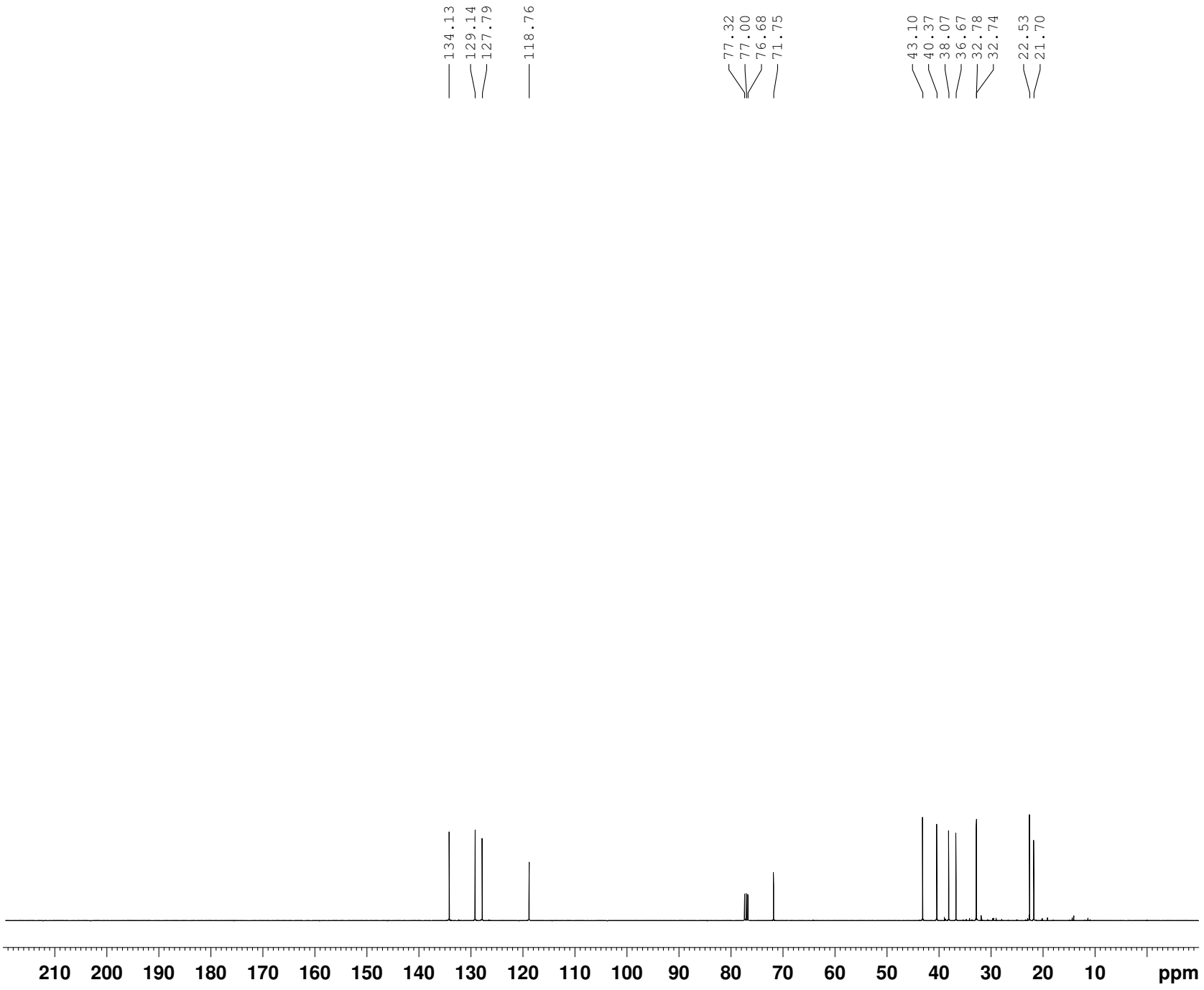


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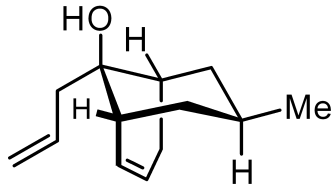

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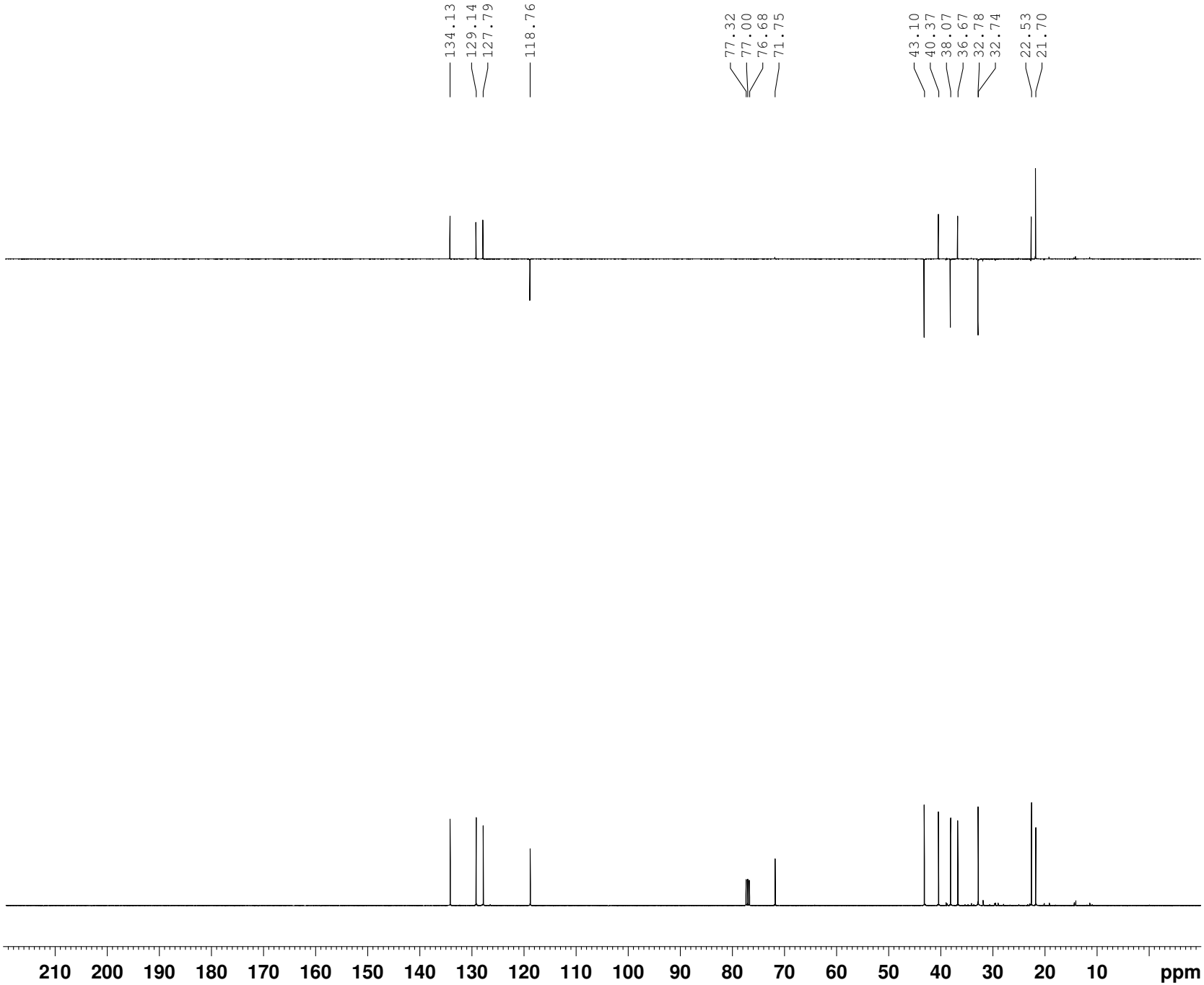

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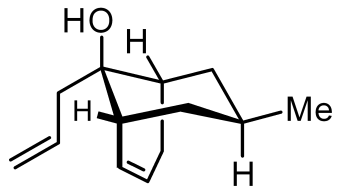

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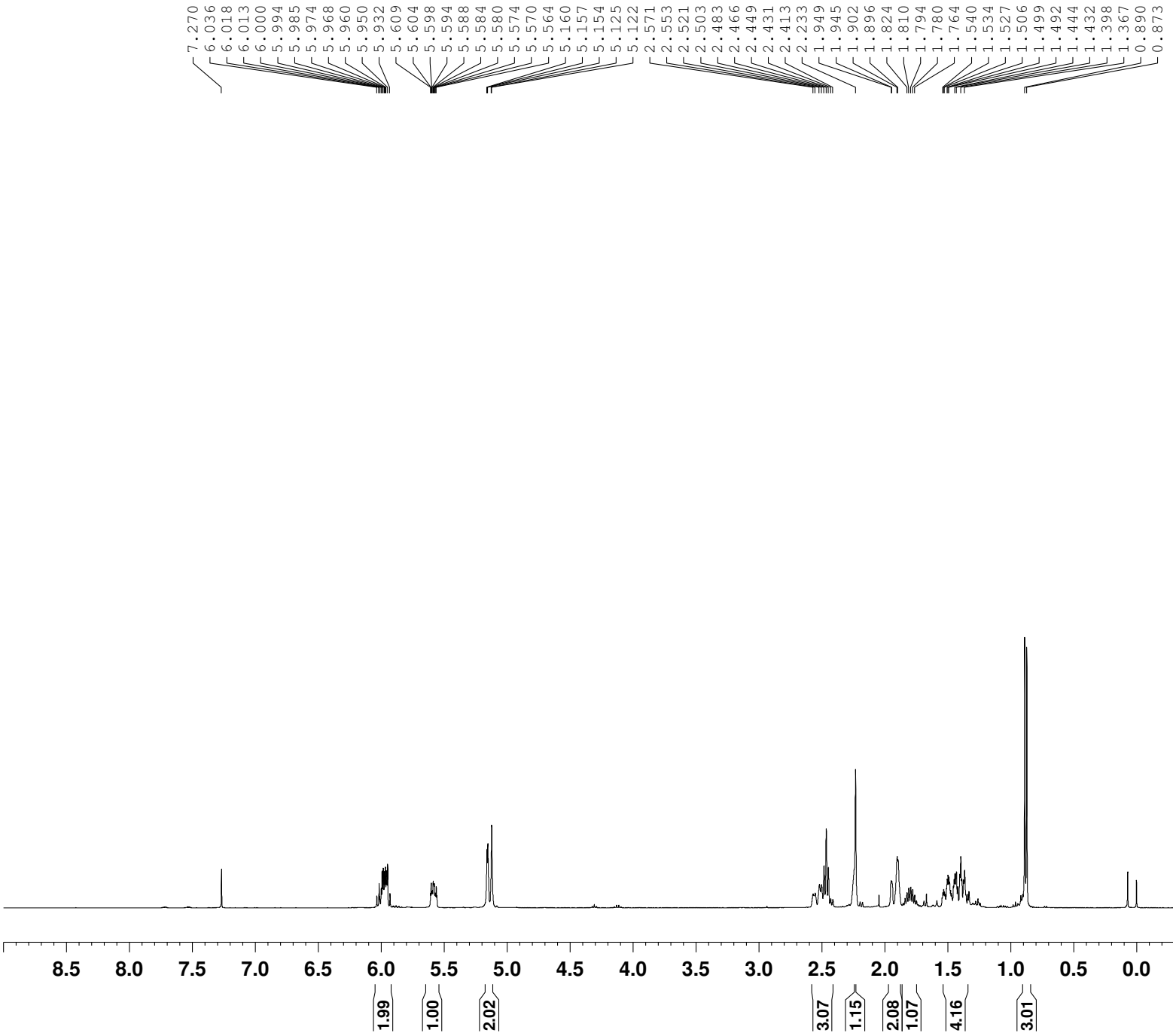


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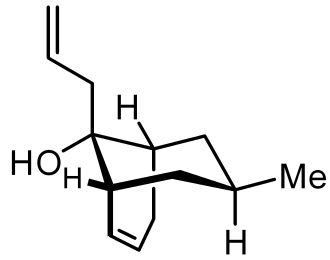
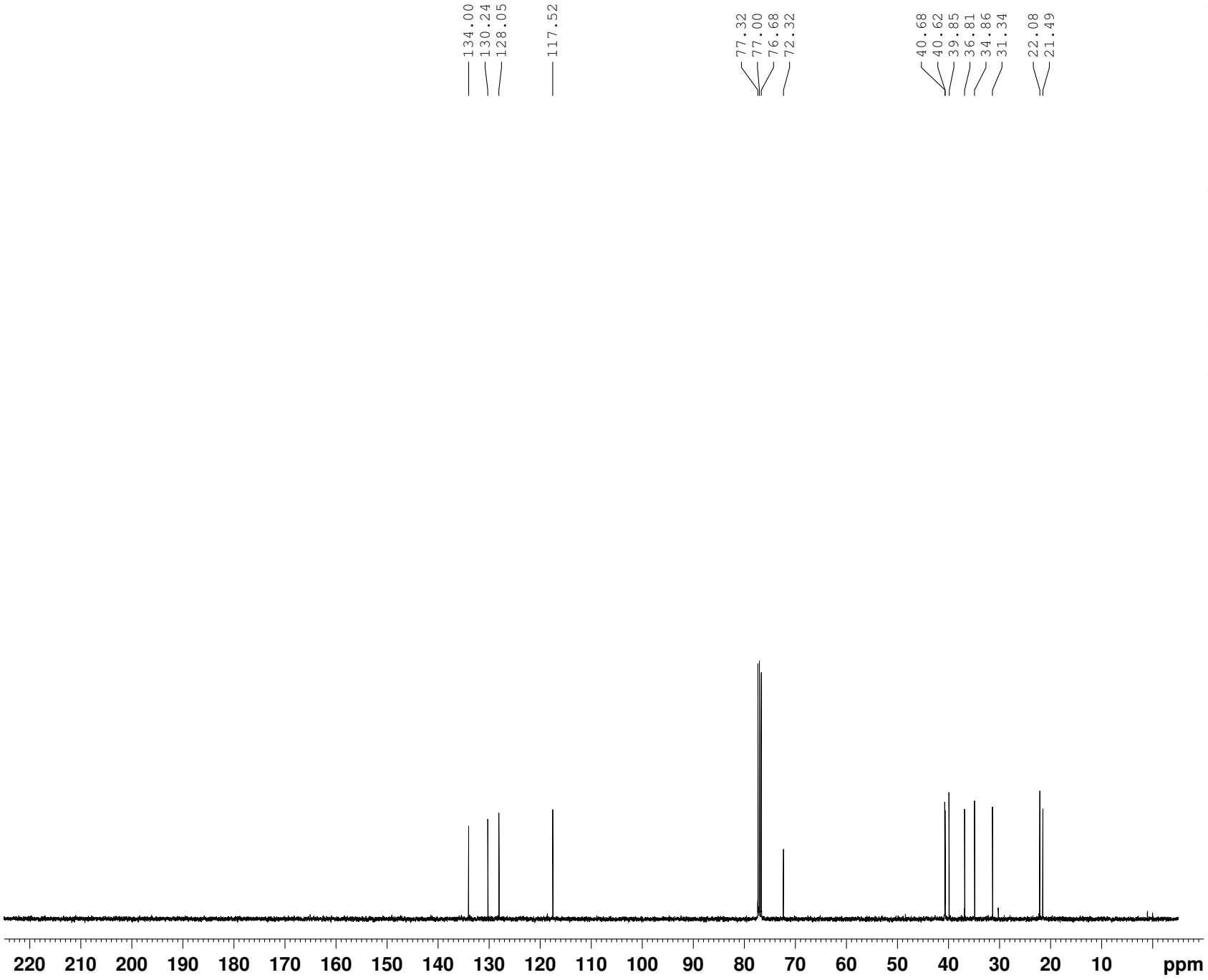
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   114
DW                62.400 usec
DE                 6.50 usec
TE                292.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.79 usec
SI                 65536
SF           400.1300059 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

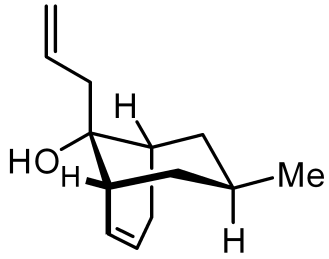


16'

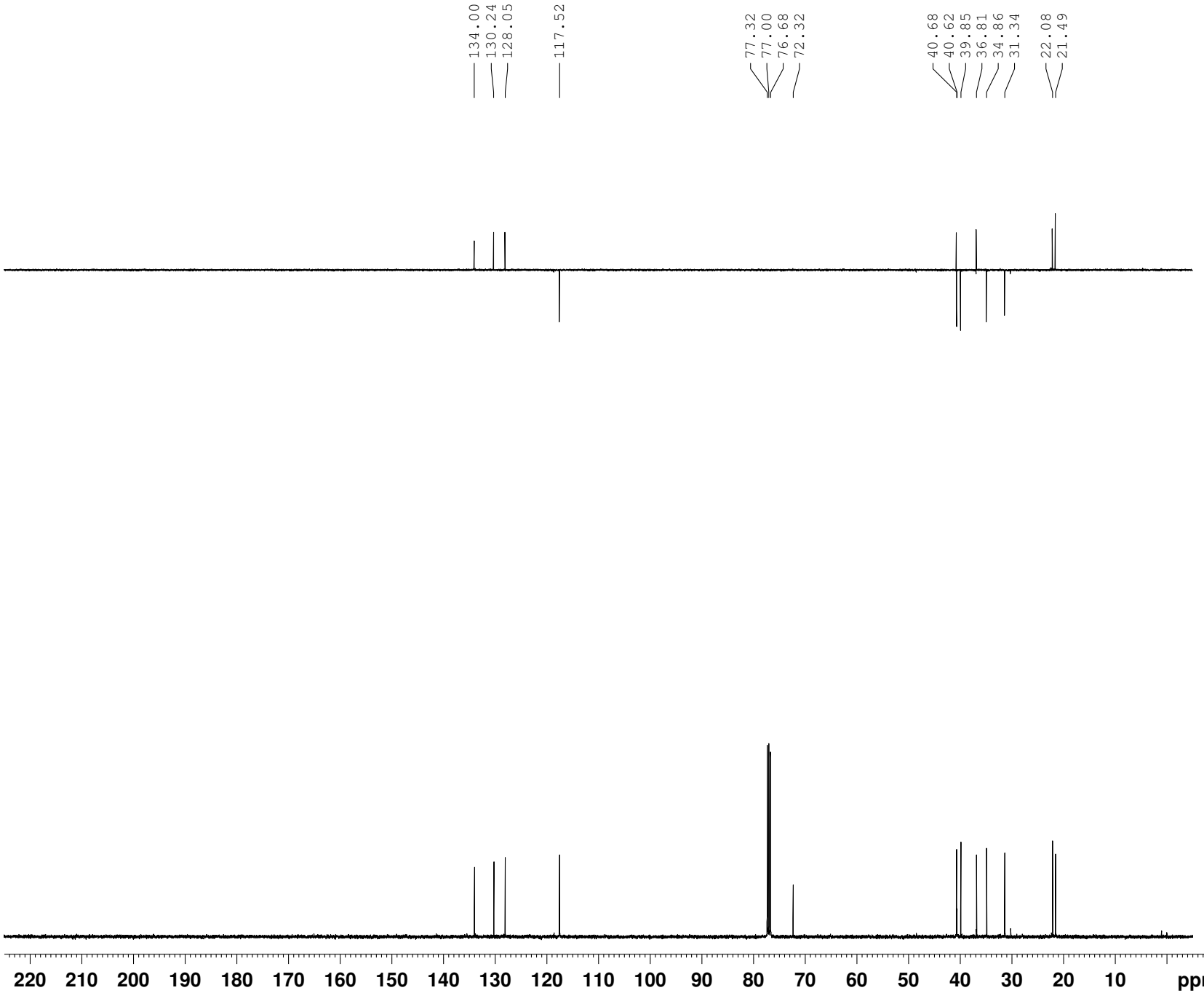



```
NAME        zxh-epidiene
EXPNO                 21
PROCNO                 1
Date_           20160228
Time                9.52
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    2
SWH           23148.148 Hz
FIDRES         0.353213 Hz
AQ            1.4156276 sec
RG                 1030
DW               21.600 usec
DE                6.50 usec
TE               294.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

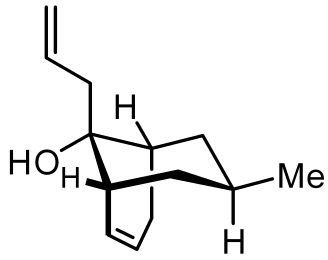
======== CHANNEL f1 ========
SFO1        100.6238364 MHz
NUC1                13C
P1                12.00 usec
SI                32768
SF          100.6127722 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



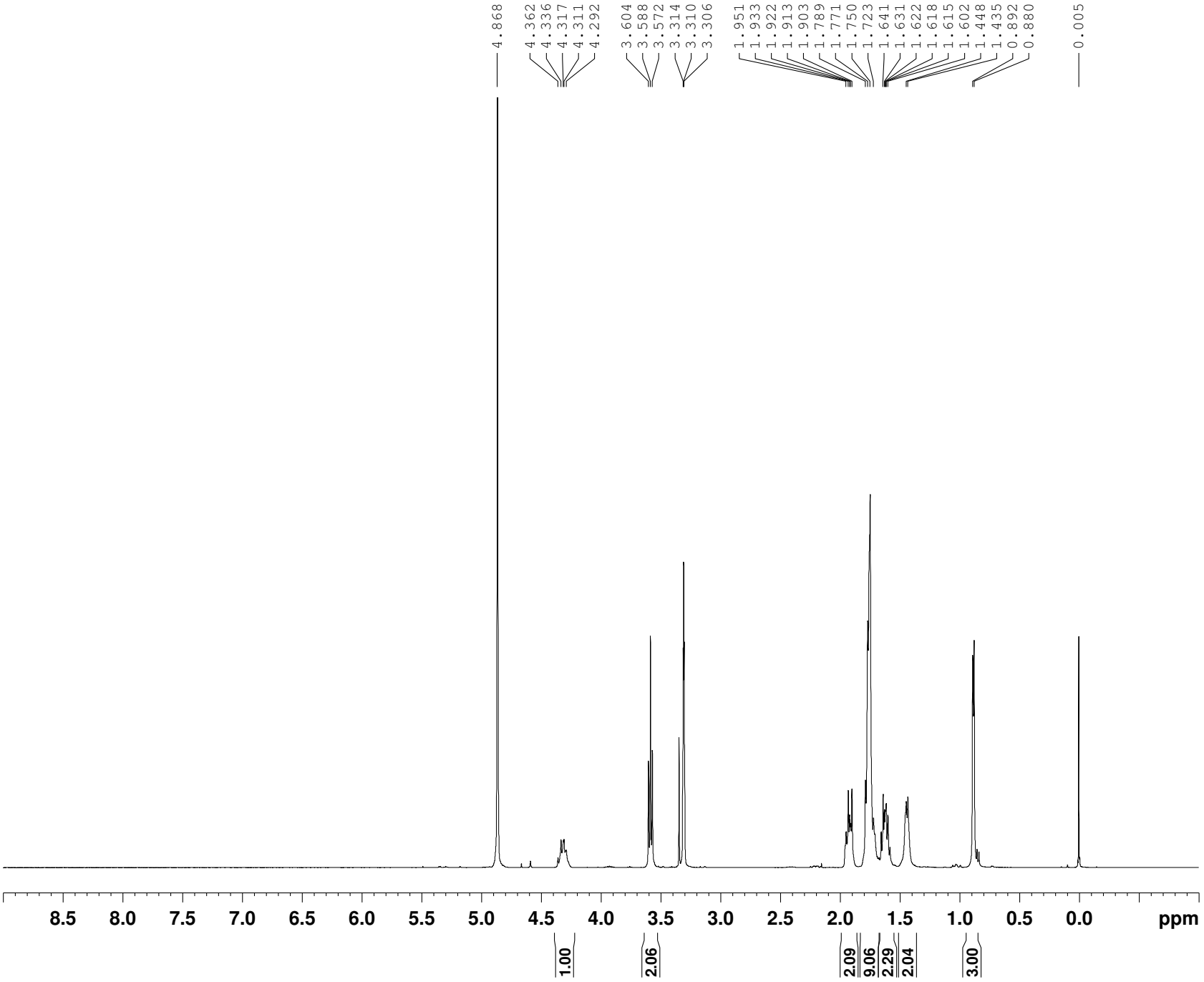
16'



NAME	zxh-epidiene
EXPNO	22
PROCNO	1
Date_	20160228
Time	9.58
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	deptsp135
TD	65536
SOLVENT	CDCl3
NS	100
DS	4
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	2050
DW	21.600 usec
DE	6.50 usec
TE	293.7 K
CNST2	145.0000000
D1	2.00000000 sec
D2	0.00344828 sec
D12	0.00002000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6238364 MHz
NUC1	13C
P1	12.00 usec
P13	2000.00 usec
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

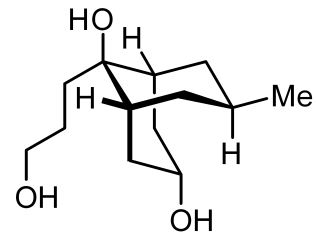


16'

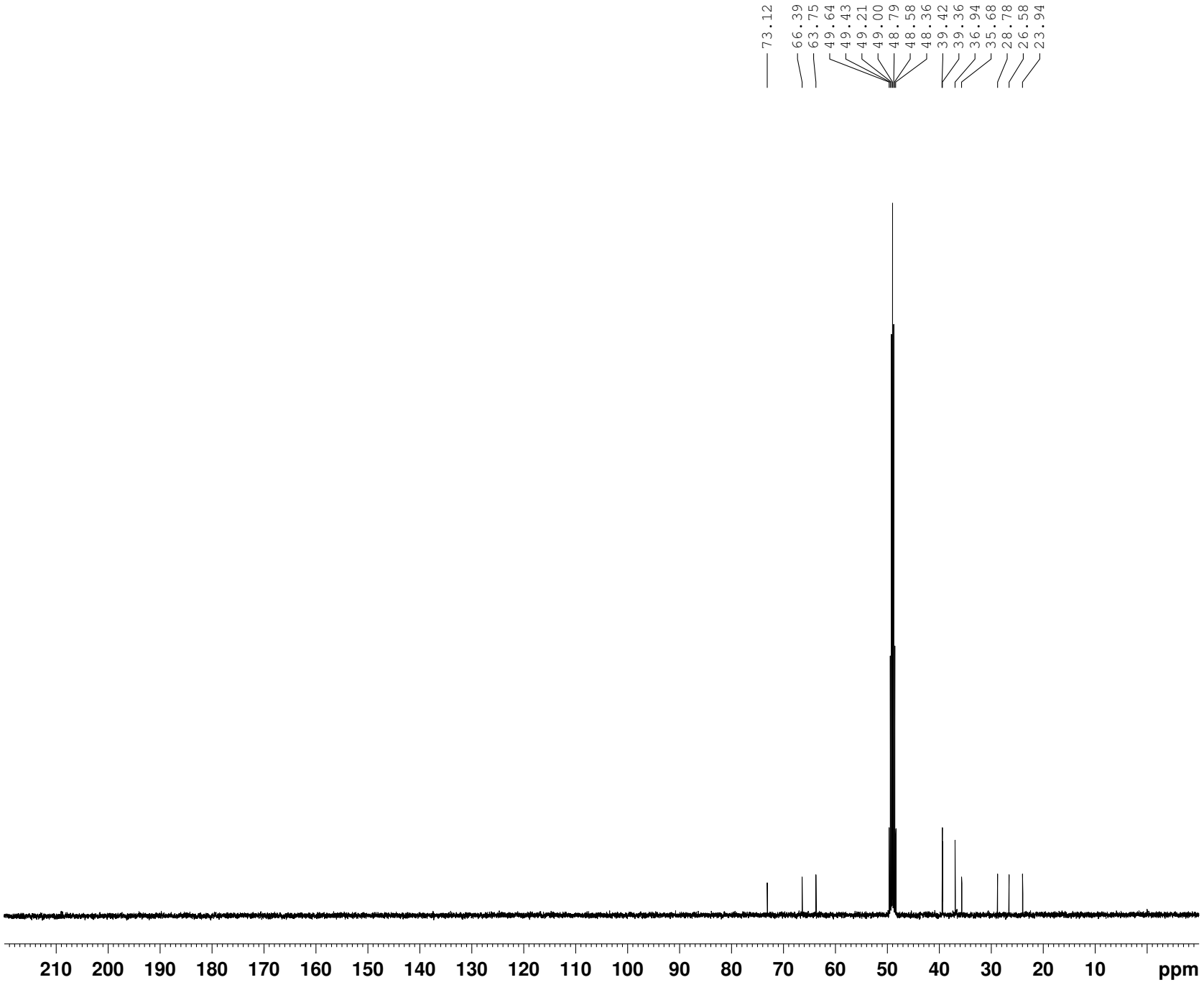



```
NAME            zxh-1772
EXPNO                 10
PROCNO                 1
Date_           20150317
Time               17.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ            4.0894966 sec
RG                   181
DW                62.400 usec
DE                 6.50 usec
TE                294.0 K
D1           1.00000000 sec
TD0                    1

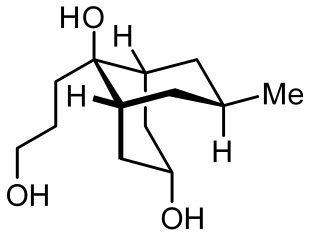
======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                   1H
P1                 11.60 usec
SI                 65536
SF          400.1300077 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



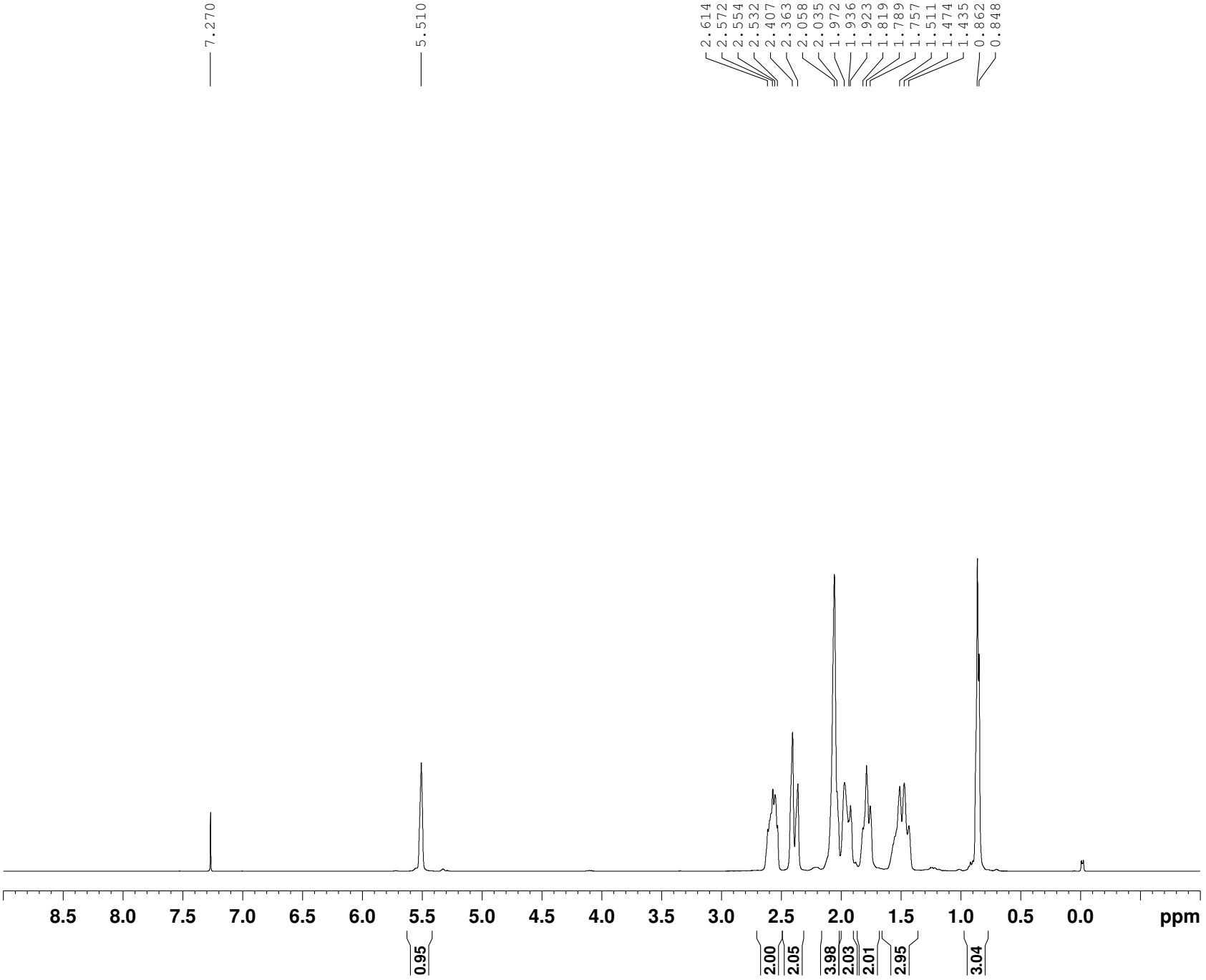
17



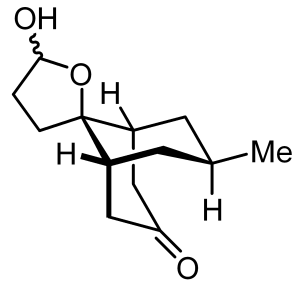
NAME	zxh-1772
EXPNO	11
PROCNO	1
Date_	20150317
Time	18.00
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	MeOD
NS	160
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	294.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.45 usec
SI	32768
SF	100.6126271 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



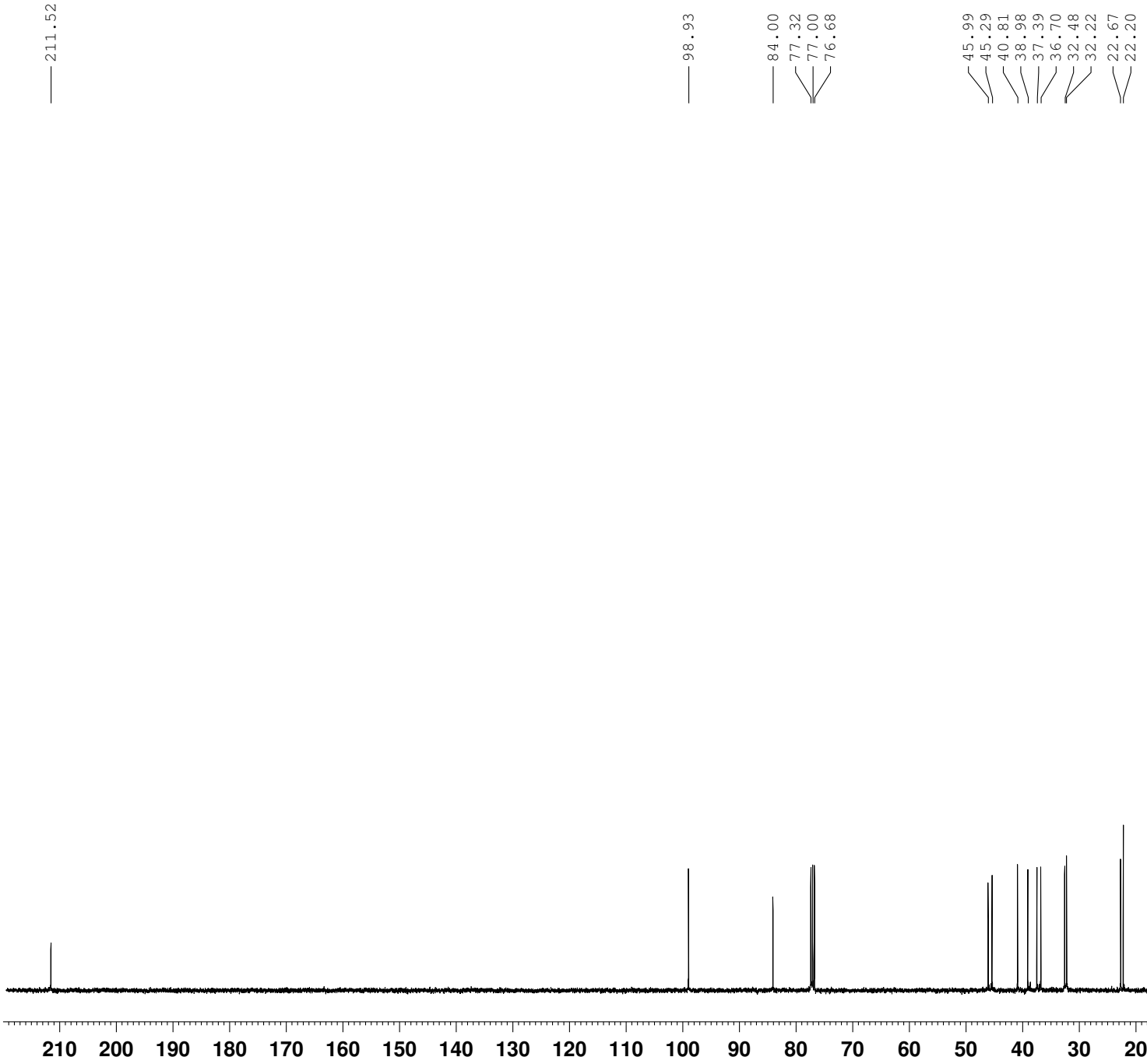
17



NAME	zxh-2381
EXPNO	10
PROCNO	1
Date_	20170312
Time	14.15
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDC13
NS	8
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	90.5
DW	62.400 usec
DE	6.50 usec
TE	292.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.92 usec
SI	65536
SF	400.1300055 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

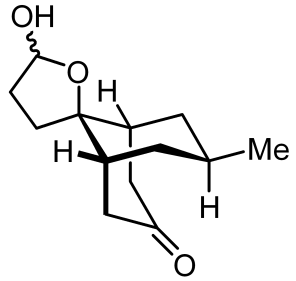


18a

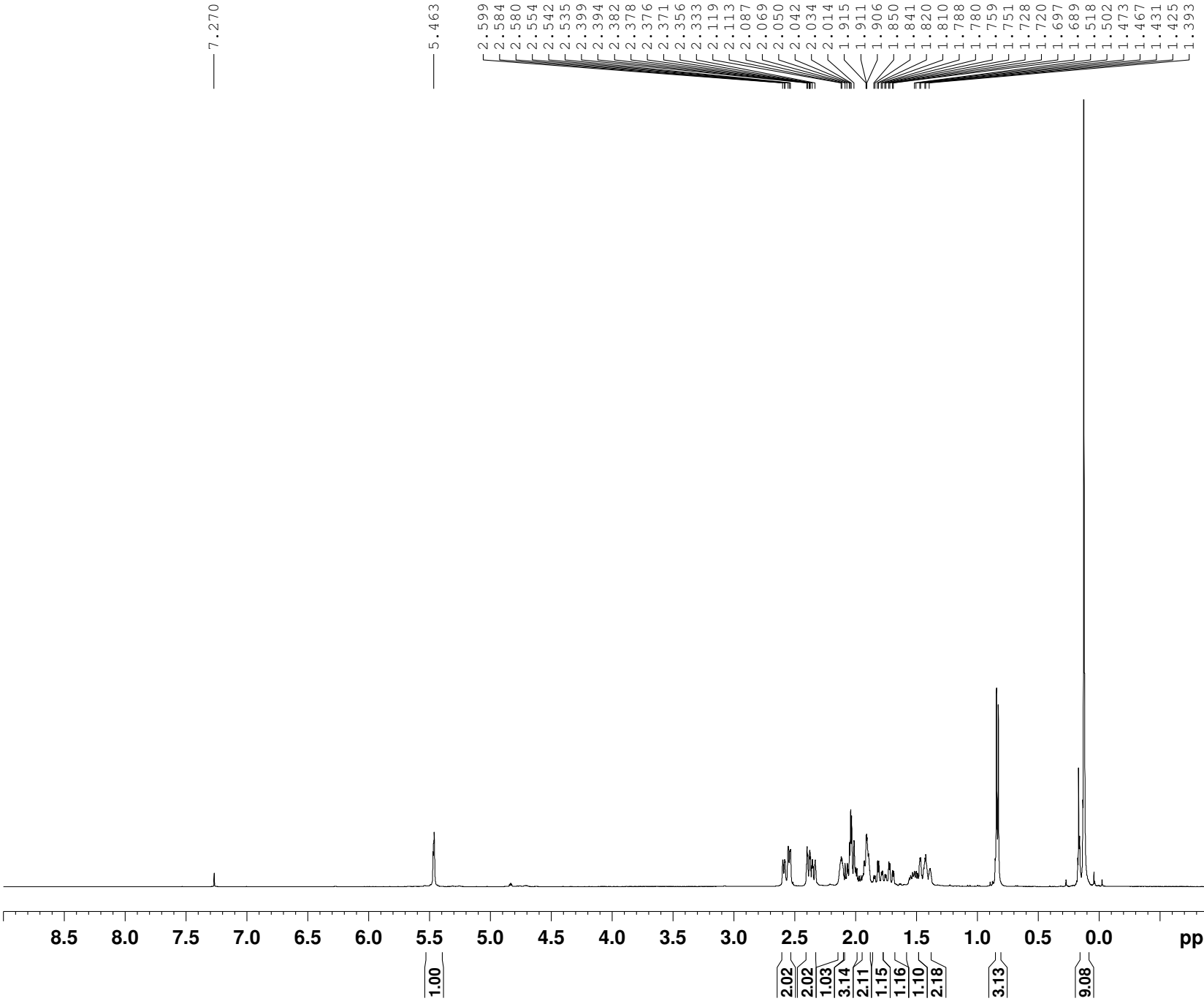



```
NAME            zxh-2381
EXPNO                 11
PROCNO                 1
Date_           20170312
Time               14.27
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                292.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                  13C
P1                 14.70 usec
SI                 32768
SF          100.6127758 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

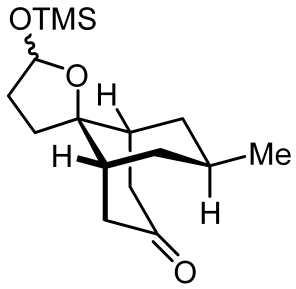


18a

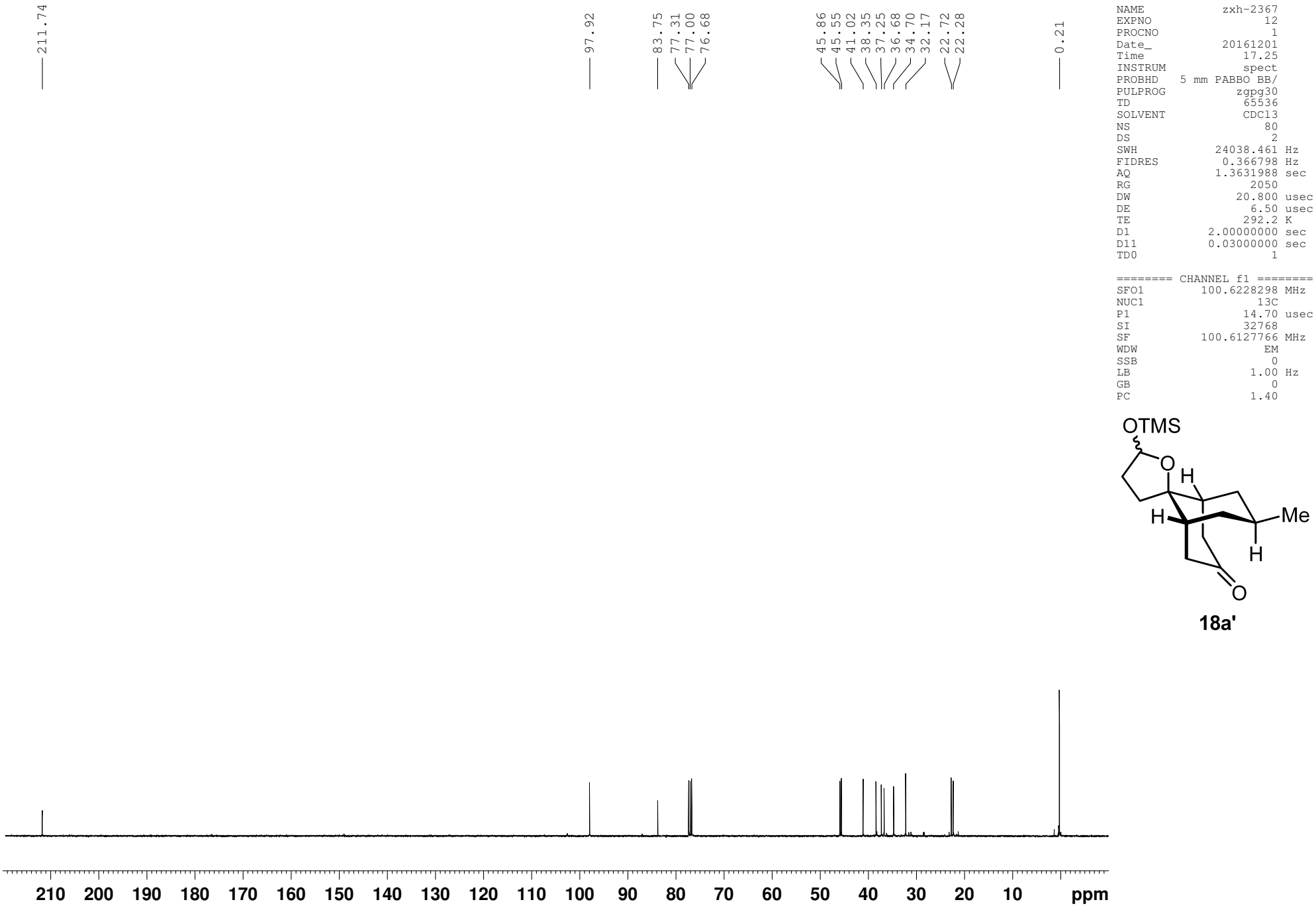


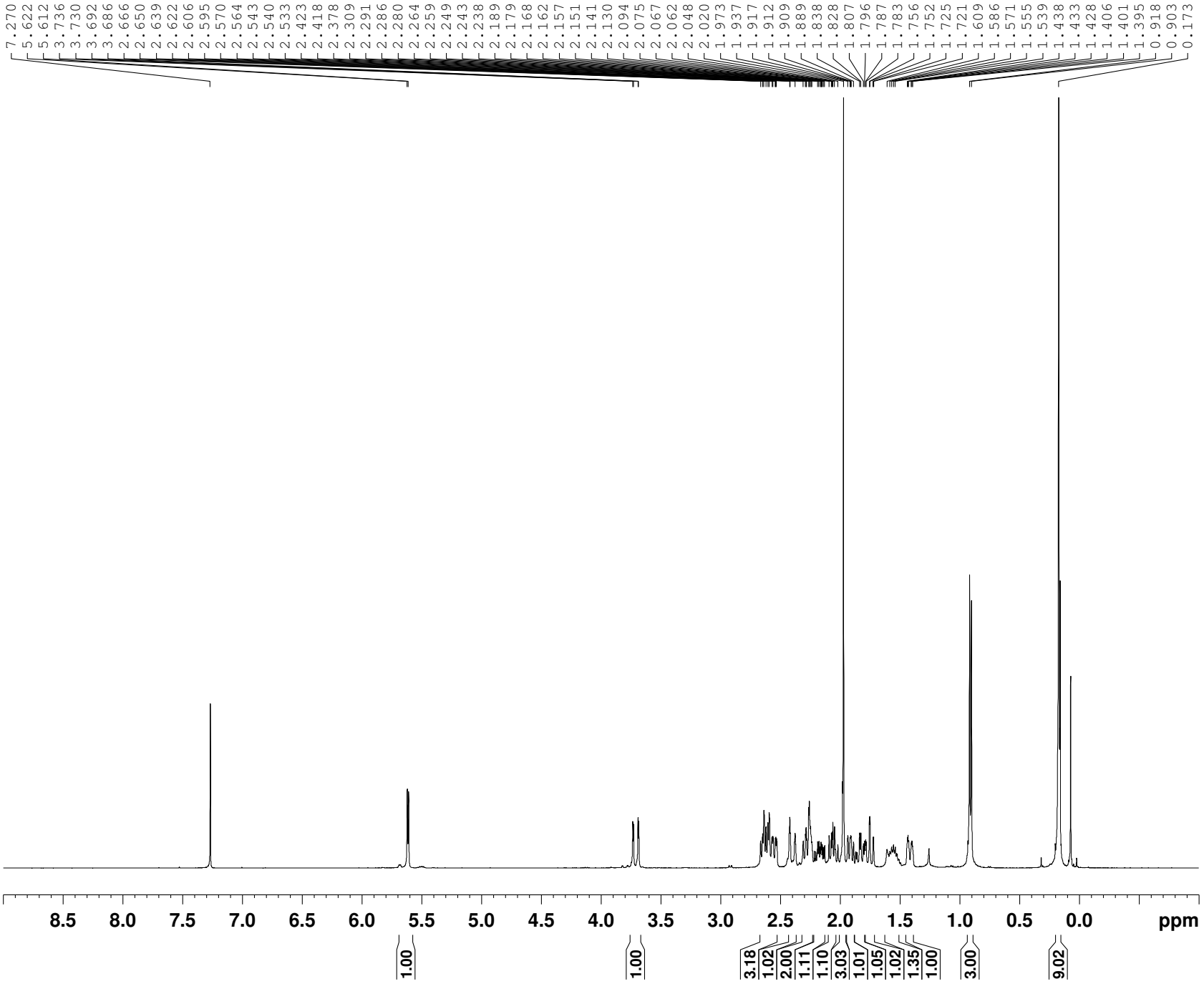

```
NAME            zxh-2367
EXPNO                 10
PROCNO                 1
Date_           20161201
Time               17.19
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     4
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                    32
DW                62.400 usec
DE                 6.50 usec
TE                291.6 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                 65536
SF           400.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



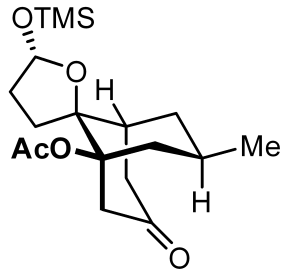
18a'


211.74
97.92
83.75
77.31
77.00
76.68
45.86
45.55
41.02
38.35
37.25
36.68
34.70
32.17
22.72
22.28
0.21
NAME zxh-2367
EXPNO 12
PROCNO 1
Date_ 20161201
Time 17.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 80
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 292.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 14.70 usec
SI 32768
SF 100.6127766 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OTMS
O
H
H
Me
H
O
18a'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

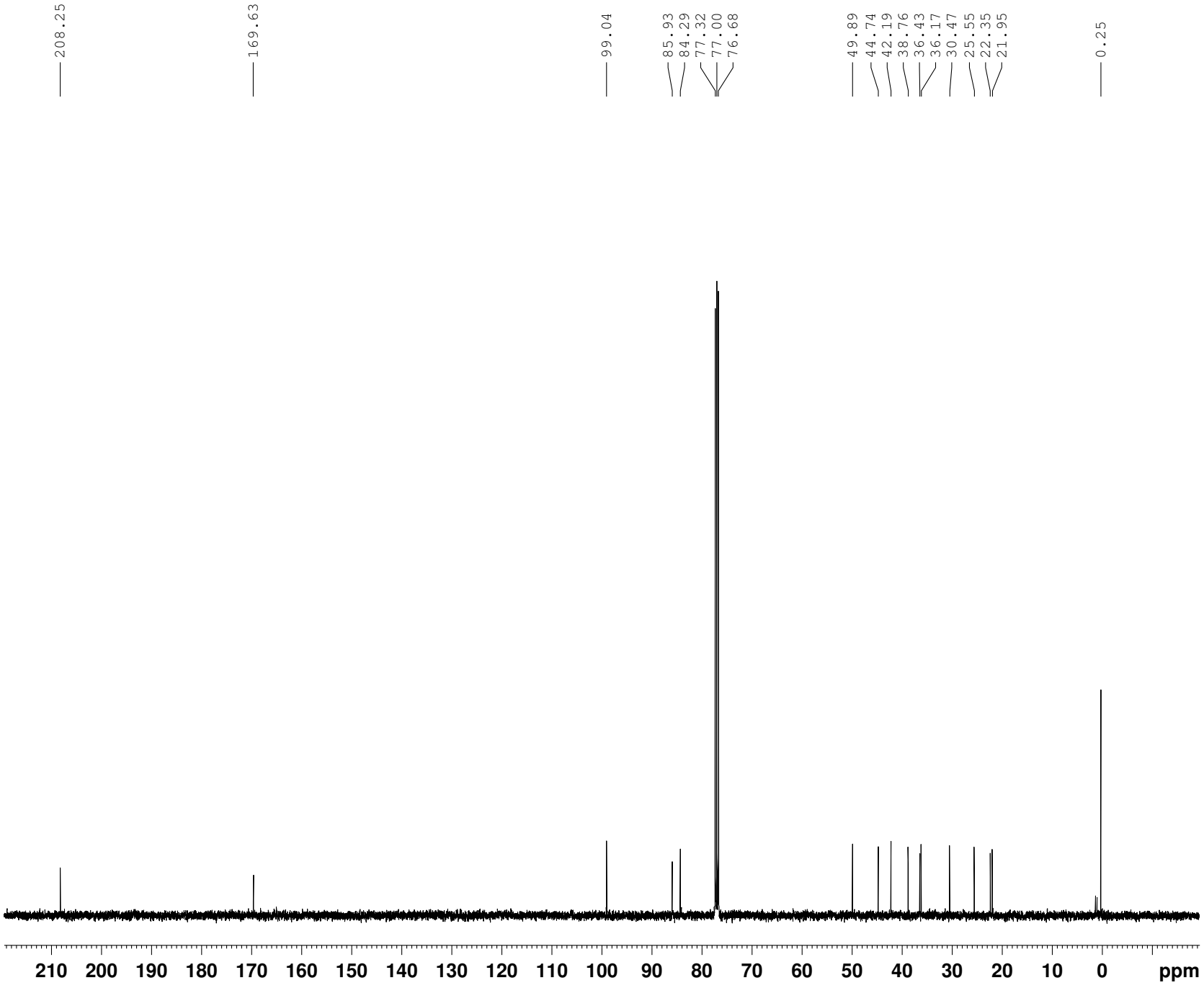



```
NAME        zxh-2236-1(400M)
EXPNO                    10
PROCNO                    1
Date_              20160301
Time                   9.07
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ              4.0894966 sec
RG                      203
DW                 62.400 usec
DE                  6.50 usec
TE                  294.3 K
D1             1.00000000 sec
TD0                       1

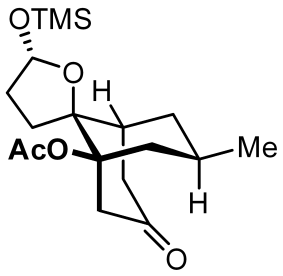
======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                    1H
P1                  10.79 usec
SI                    65536
SF            400.1300058 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```



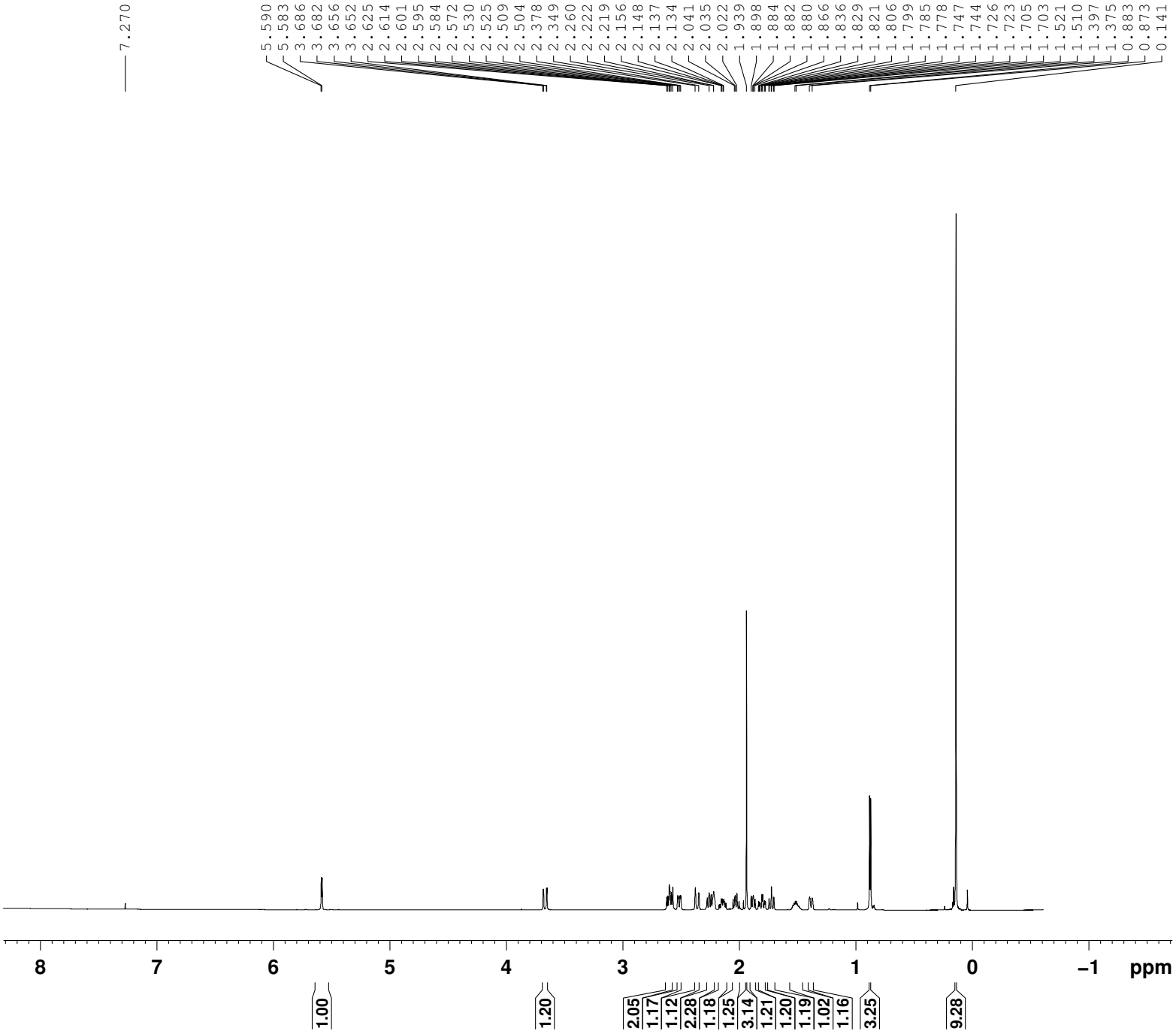
α-**19a'**



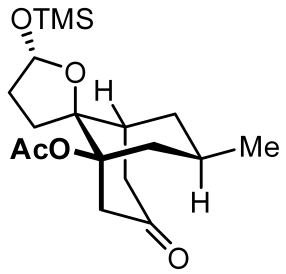
NAME	zxh-2236-1
EXPNO	11
PROCNO	1
Date_	20160301
Time	9.23
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	260
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	912
DW	20.800 usec
DE	6.50 usec
TE	295.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	12.00 usec
SI	32768
SF	100.6127707 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



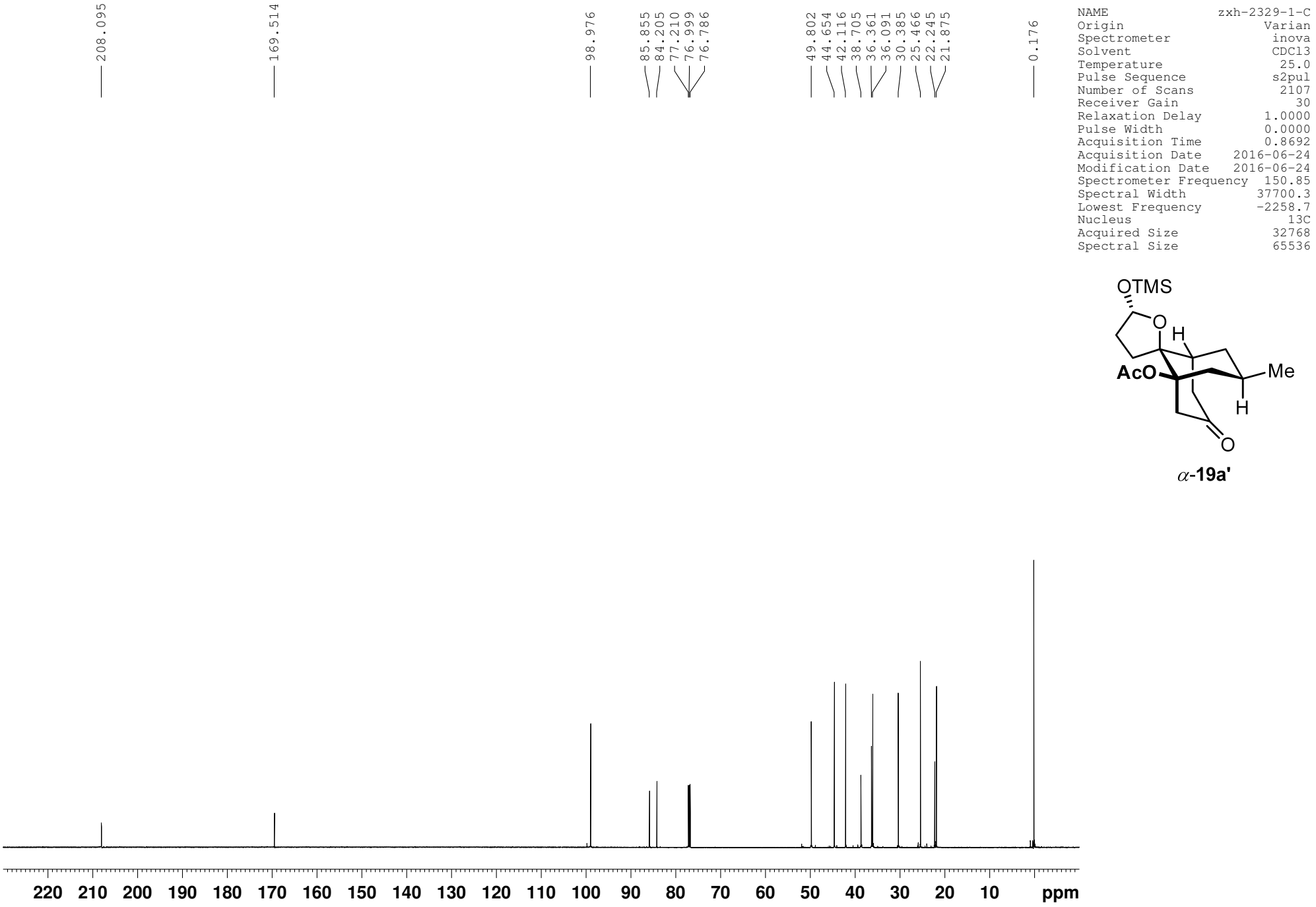
α-**19a'**



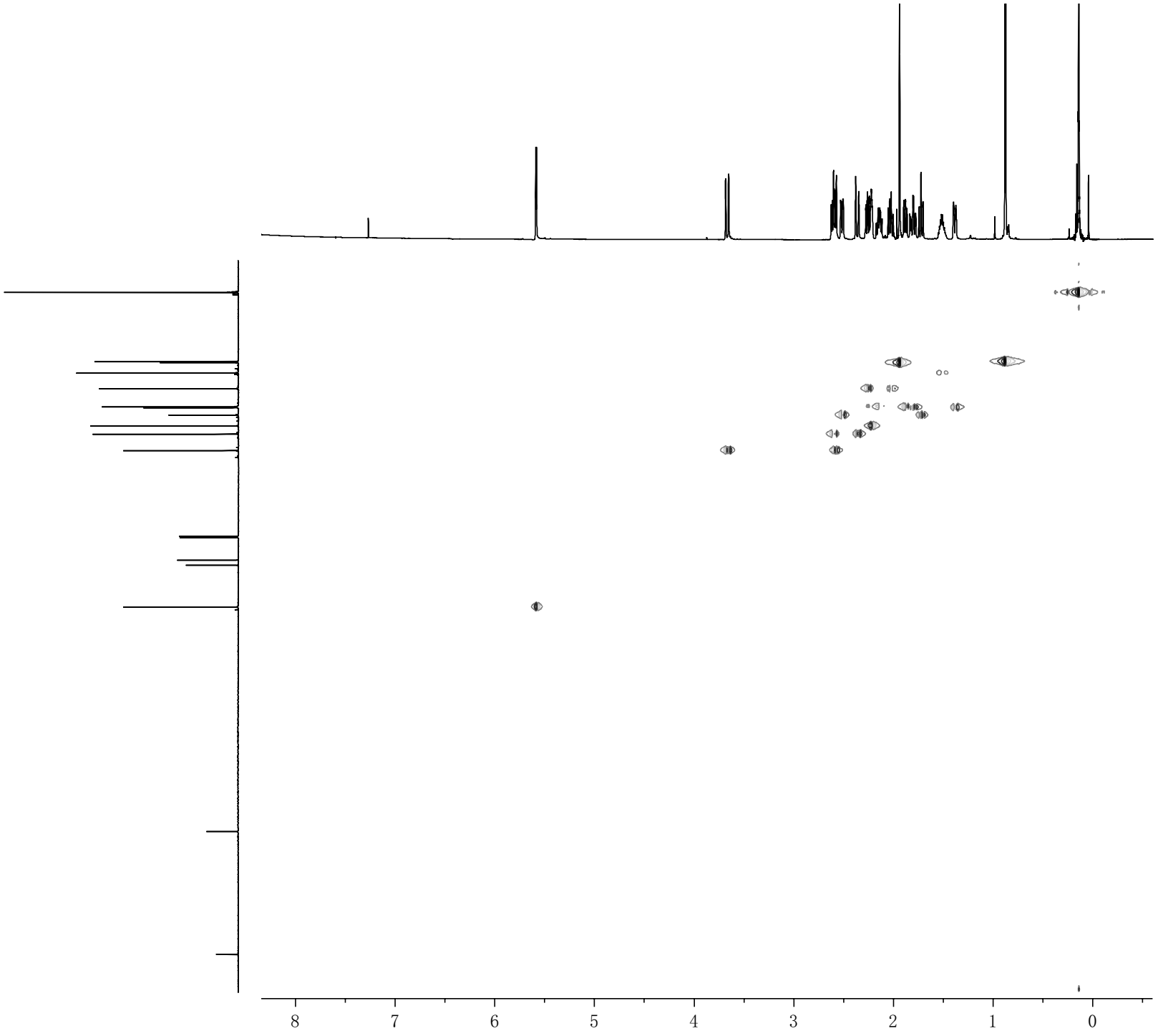
NAME	zxh-2329-1-H
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	18
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.5249
Acquisition Date	2016-06-24
Modification Date	2016-06-24
Spectrometer Frequency	599.85
Spectral Width	5372.0
Lowest Frequency	-373.8
Nucleus	1H
Acquired Size	8192
Spectral Size	16384



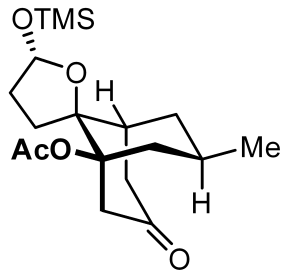
α-**19a'**


208.095
169.514
98.976
85.855
84.205
77.210
76.999
76.786
49.802
44.654
42.116
38.705
36.361
36.091
30.385
25.466
22.245
21.875
0.176
NAME zxh-2329-1-C
Origin Varian
Spectrometer inova
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Number of Scans 2107
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 0.8692
Acquisition Date 2016-06-24
Modification Date 2016-06-24
Spectrometer Frequency 150.85
Spectral Width 37700.3
Lowest Frequency -2258.7
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
OTMS
O
H
AcO
Me
H
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

α-**19a'**



NAME	zxh-2329-1-QC
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	gHSQCAD
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.1500
Acquisition Date	2016-06-24
Modification Date	2016-06-24
Spectrometer Frequency	(599.85, 150.85)
Spectral Width	(5372.0, 34692.1)
Lowest Frequency	(-373.8, -1508.8)
Nucleus	(1H, 13C)
Acquired Size	(806, 128)
Spectral Size	(1024, 1024)



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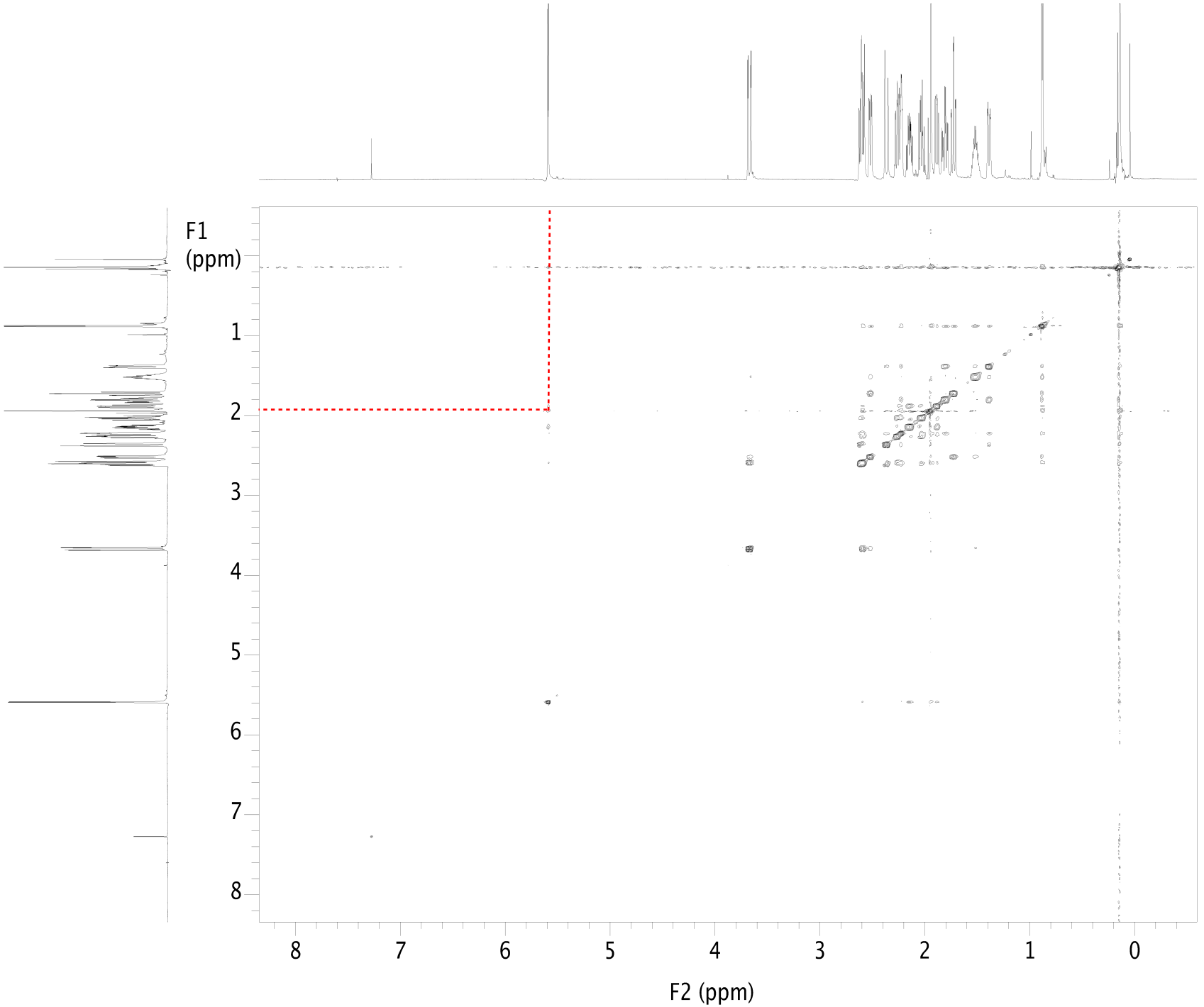
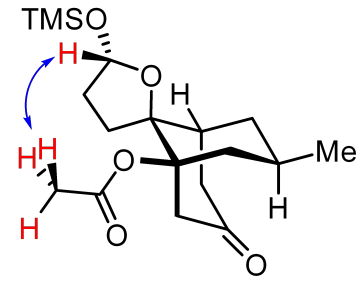
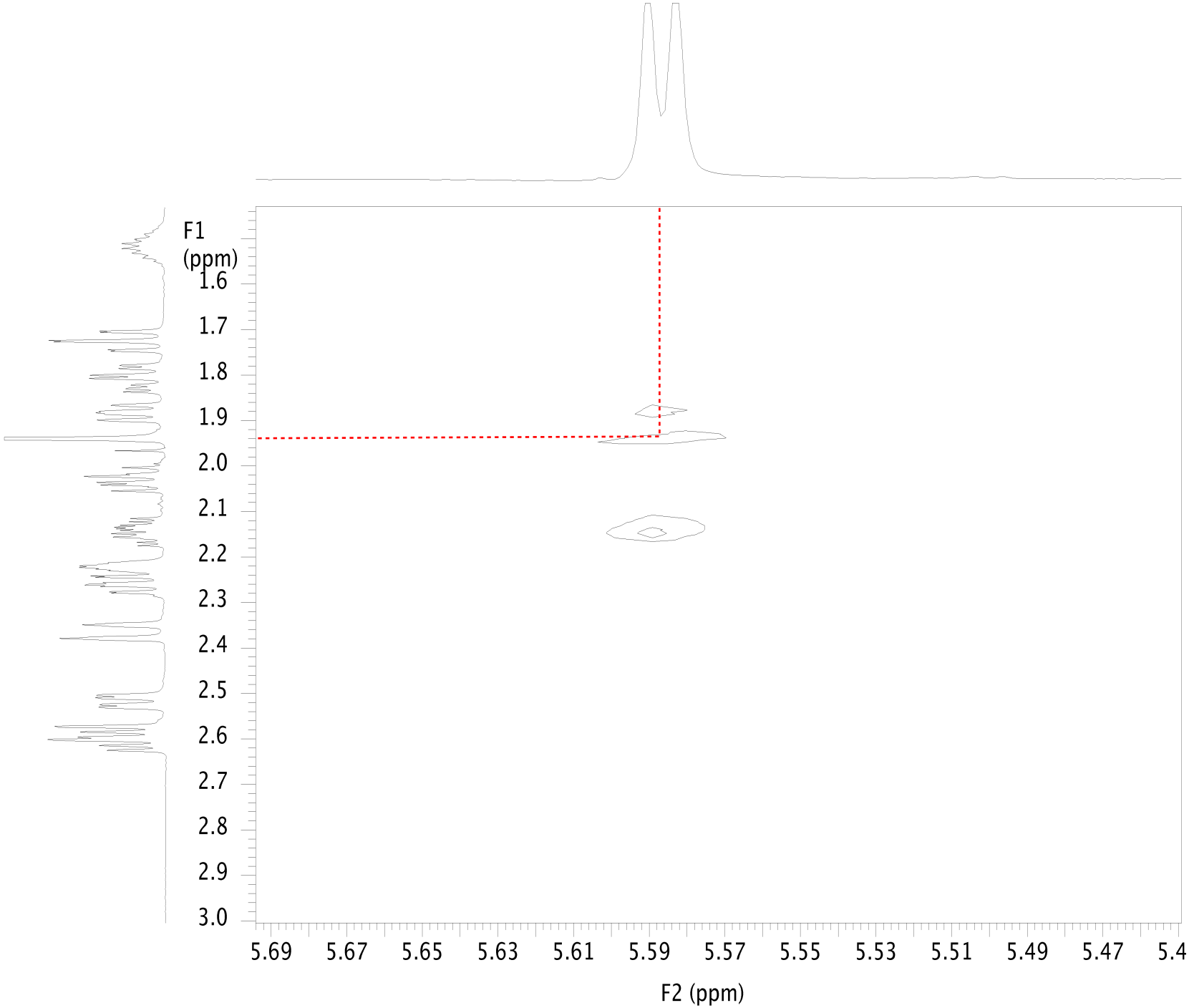


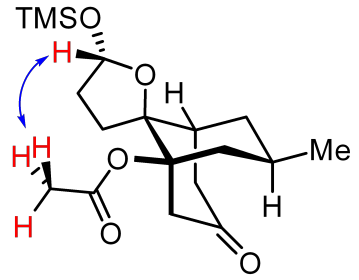
NAME	zxh-2329-1-NOESY
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	NOESY
Number of Scans	4
Receiver Gain	18
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	0.1500
Acquisition Date	2016-06-24
Modification Date	2016-06-24
Spectrometer Frequency	(599.85, 599.85)
Spectral Width	(5372.0, 5372.0)
Lowest Frequency	(-373.8, -373.8)
Nucleus	(1H, 1H)
Acquired Size	(806, 200)
Spectral Size	(1024, 1024)



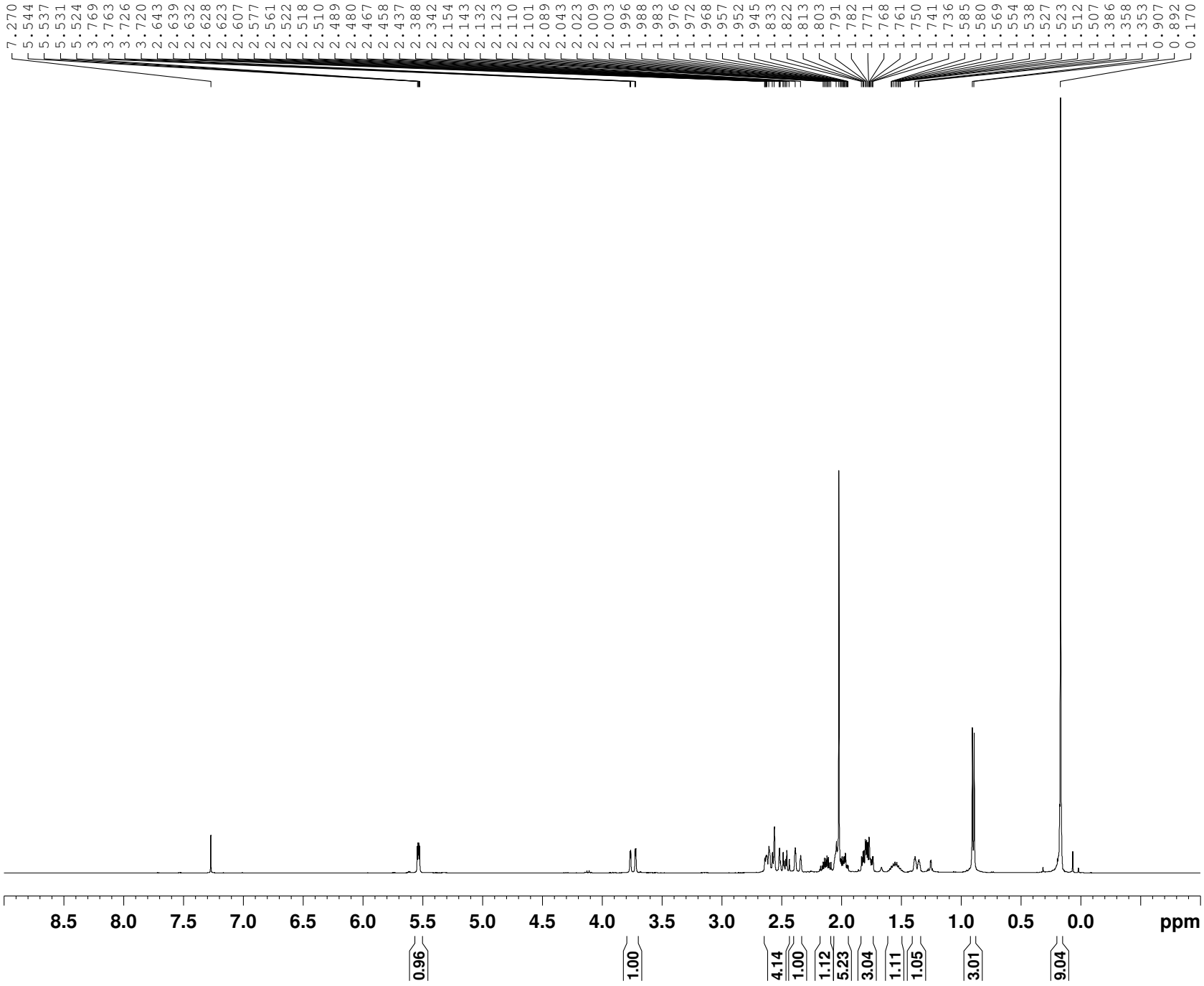
α-19a'



NAME	zxh-2329-1-NOESY
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	NOESY
Number of Scans	4
Receiver Gain	18
Relaxation Delay	2.0000
Pulse Width	0.0000
Acquisition Time	0.1500
Acquisition Date	2016-06-24
Modification Date	2016-06-24
Spectrometer Frequency	(599.85, 599.85)
Spectral Width	(5372.0, 5372.0)
Lowest Frequency	(-373.8, -373.8)
Nucleus	(1H, 1H)
Acquired Size	(806, 200)
Spectral Size	(1024, 1024)

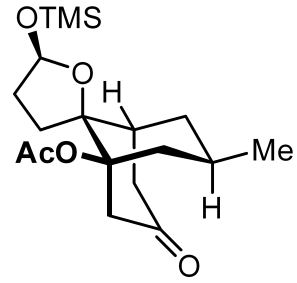


α-19a'

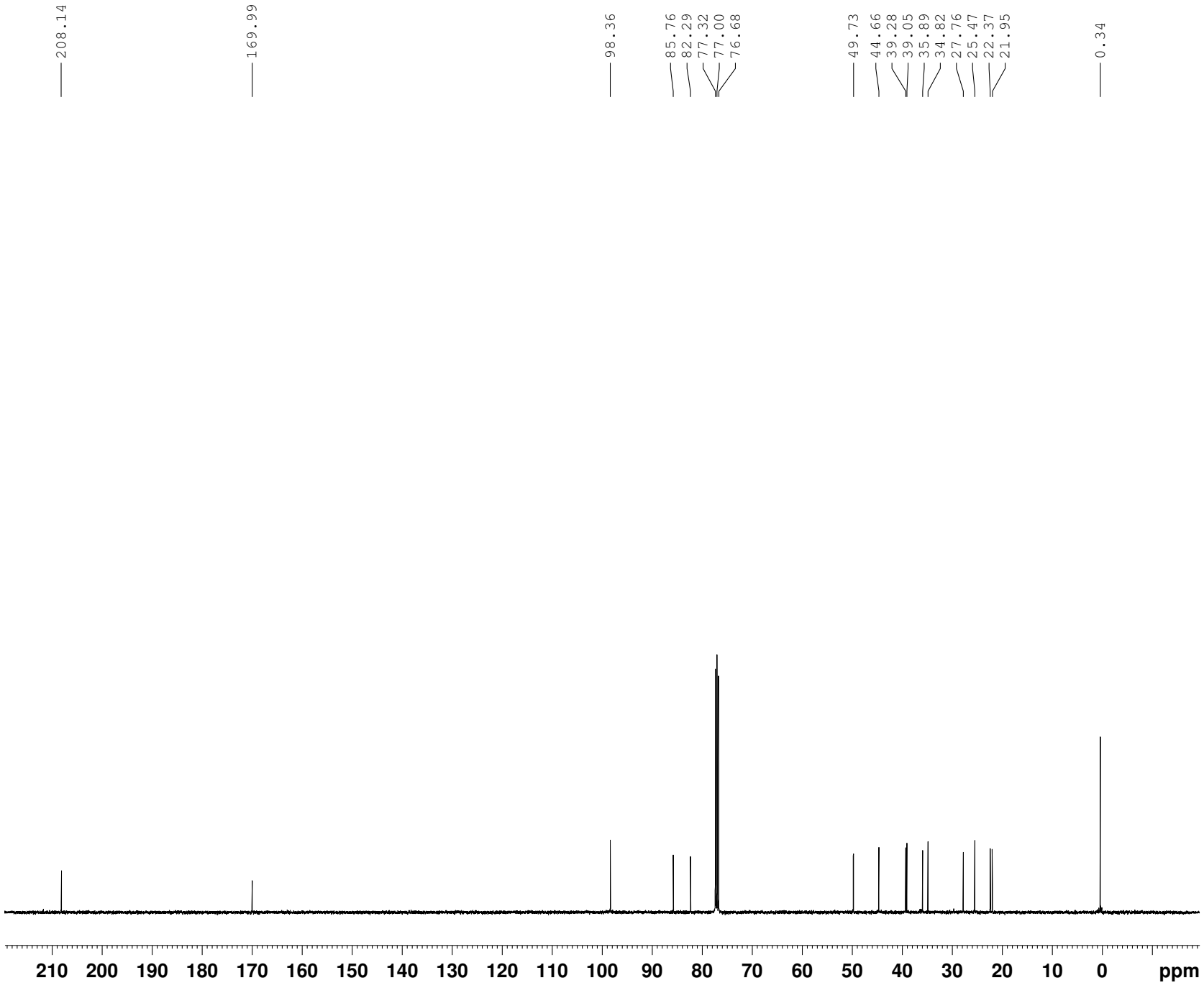



```
NAME          zxh-2236-2
EXPNO                 10
PROCNO                 1
Date_           20160301
Time                8.31
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   128
DW                62.400 usec
DE                 6.50 usec
TE                294.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.79 usec
SI                 65536
SF           400.1300058 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

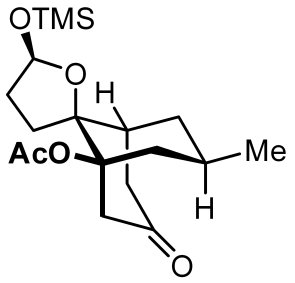


β-19a'

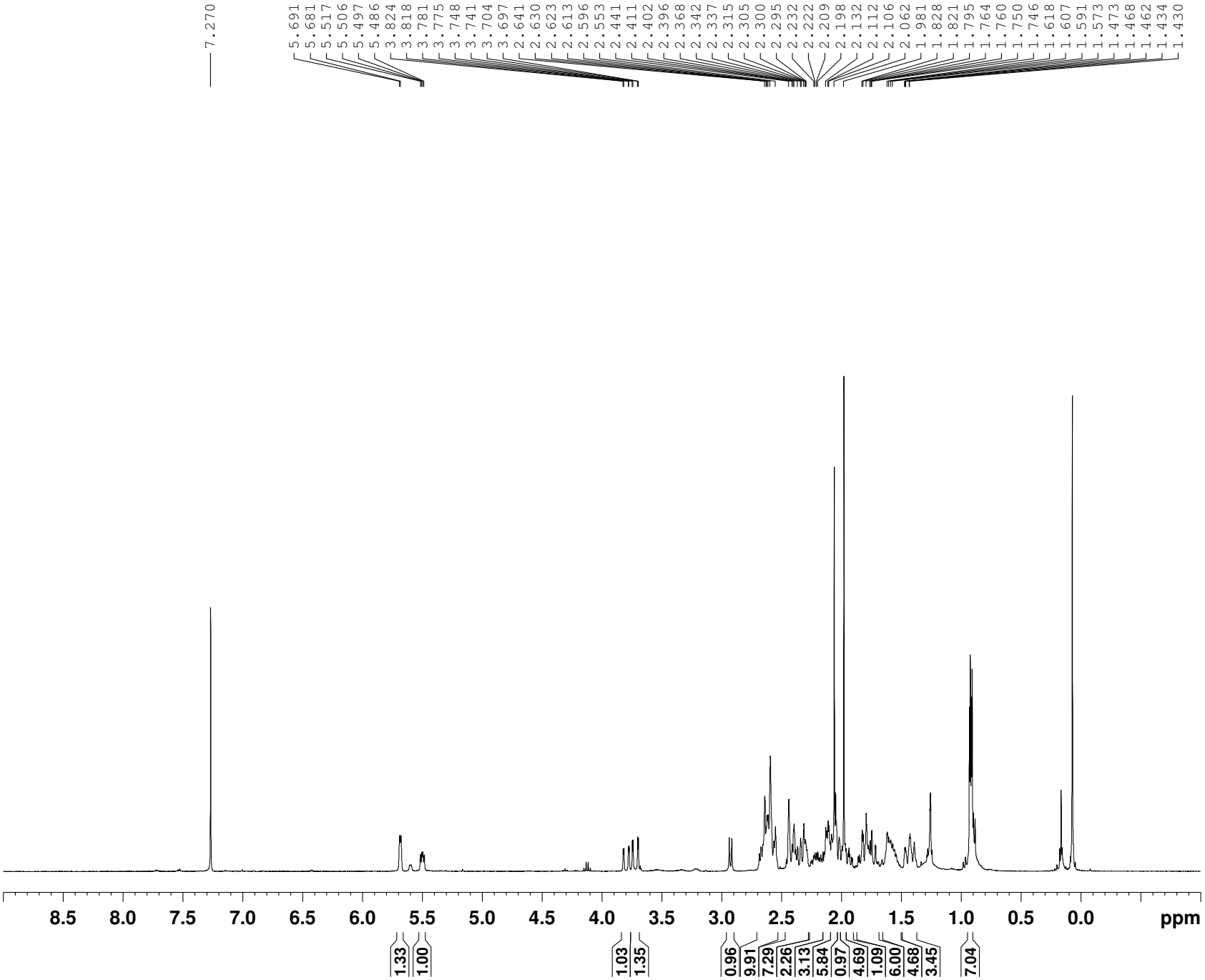


NAME	zxh-2236-2
EXPNO	11
PROCNO	1
Date_	20160301
Time	9.02
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	500
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	1030
DW	20.800 usec
DE	6.50 usec
TE	295.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	12.00 usec
SI	32768
SF	100.6127714 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

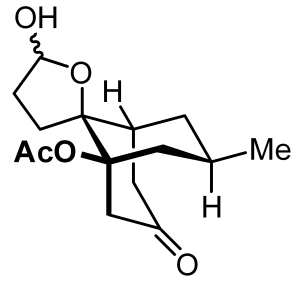


***β*-19a'**

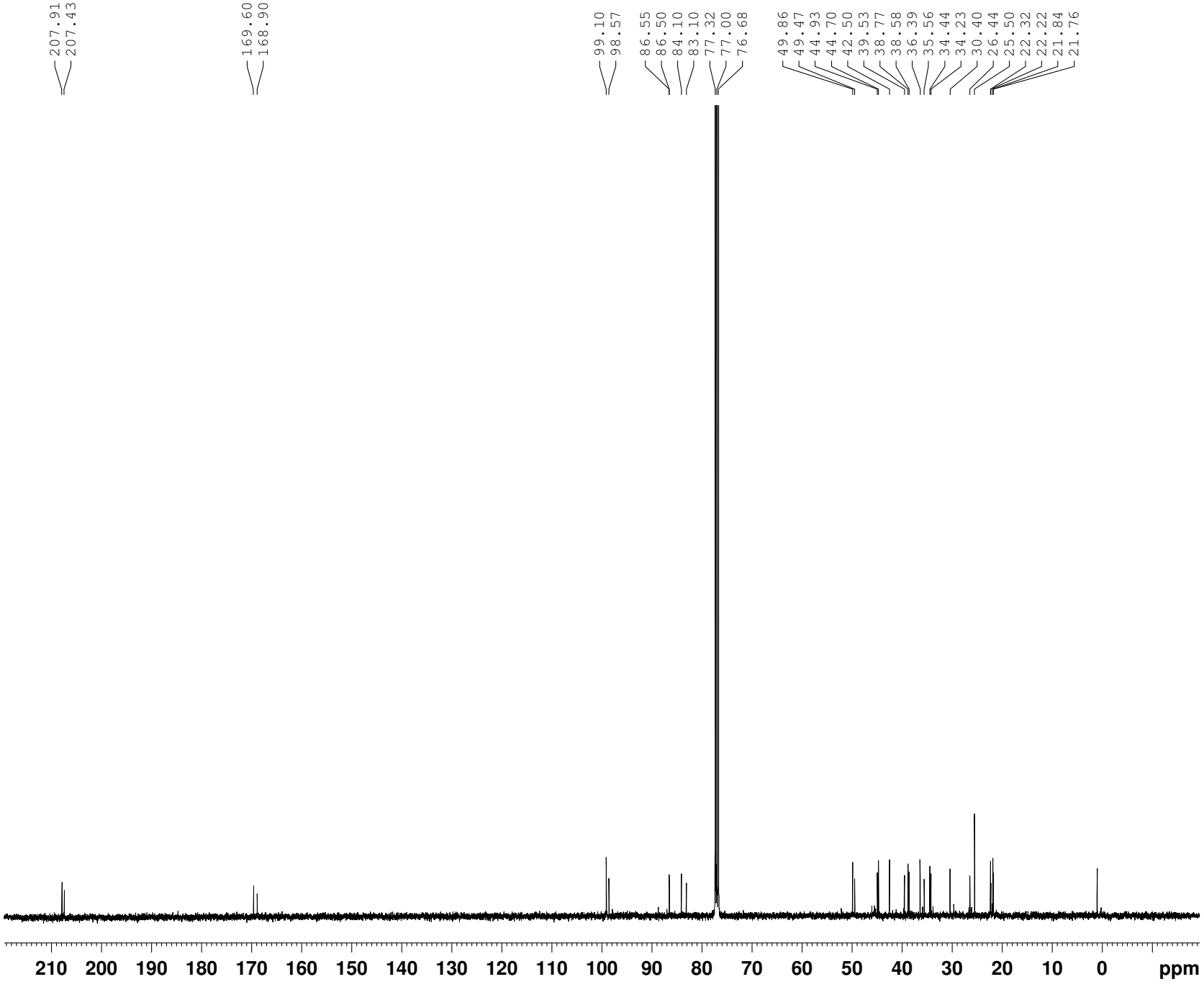


NAME	zxh-2236-3
EXPNO	10
PROCNO	1
Date_	20160301
Time	7.39
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	228
DW	62.400 usec
DE	6.50 usec
TE	294.2 K
D1	1.00000000 sec
TD0	1

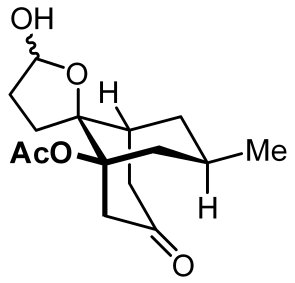
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.92 usec
SI	65536
SF	400.1300058 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



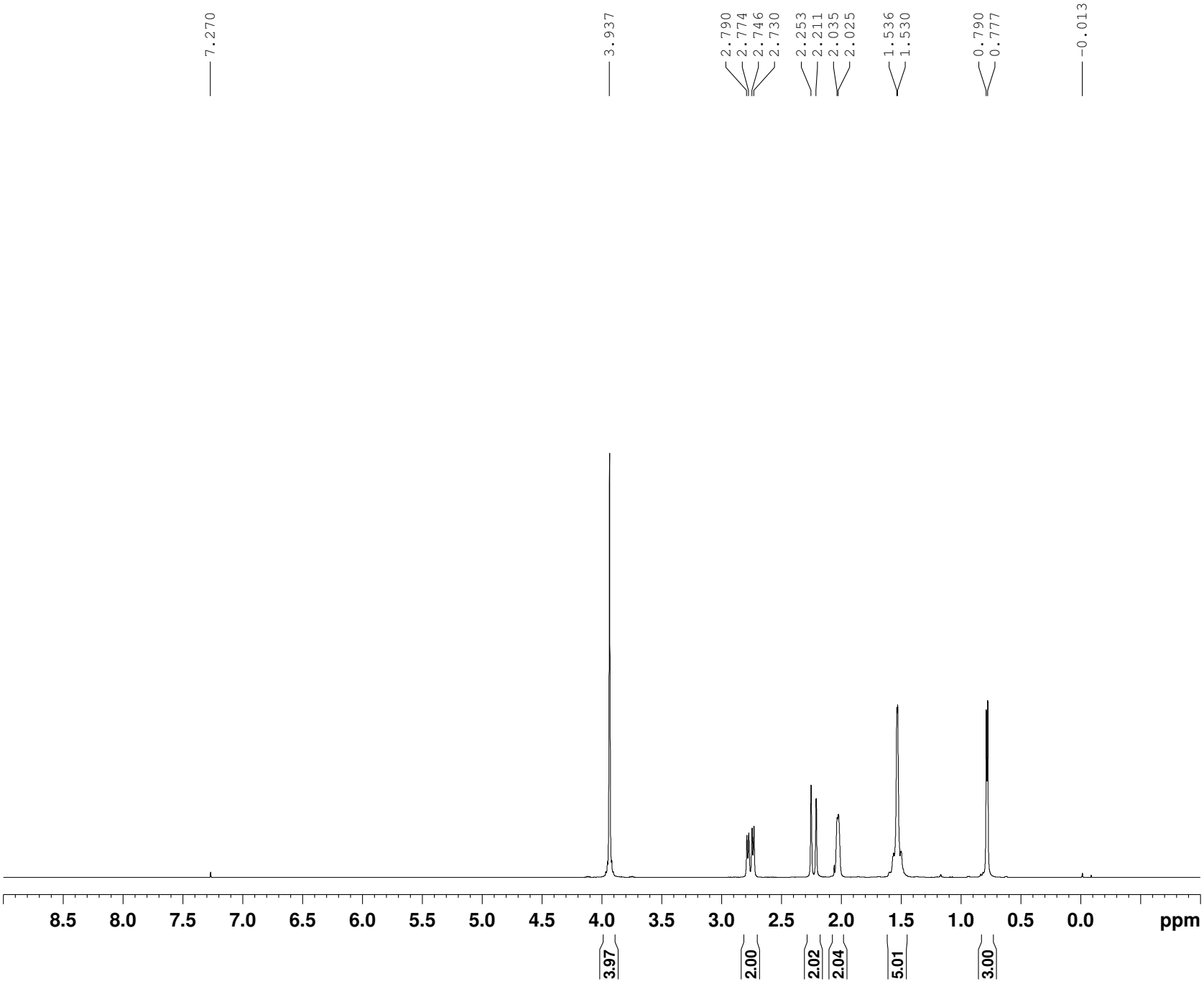
19a (1.3:1 *dr*)



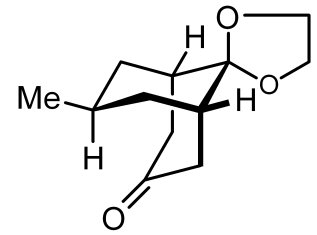
NAME	zxh-2236-3
EXPNO	12
PROCNO	1
Date_	20160301
Time	8.49
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1200
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	295.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127707 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



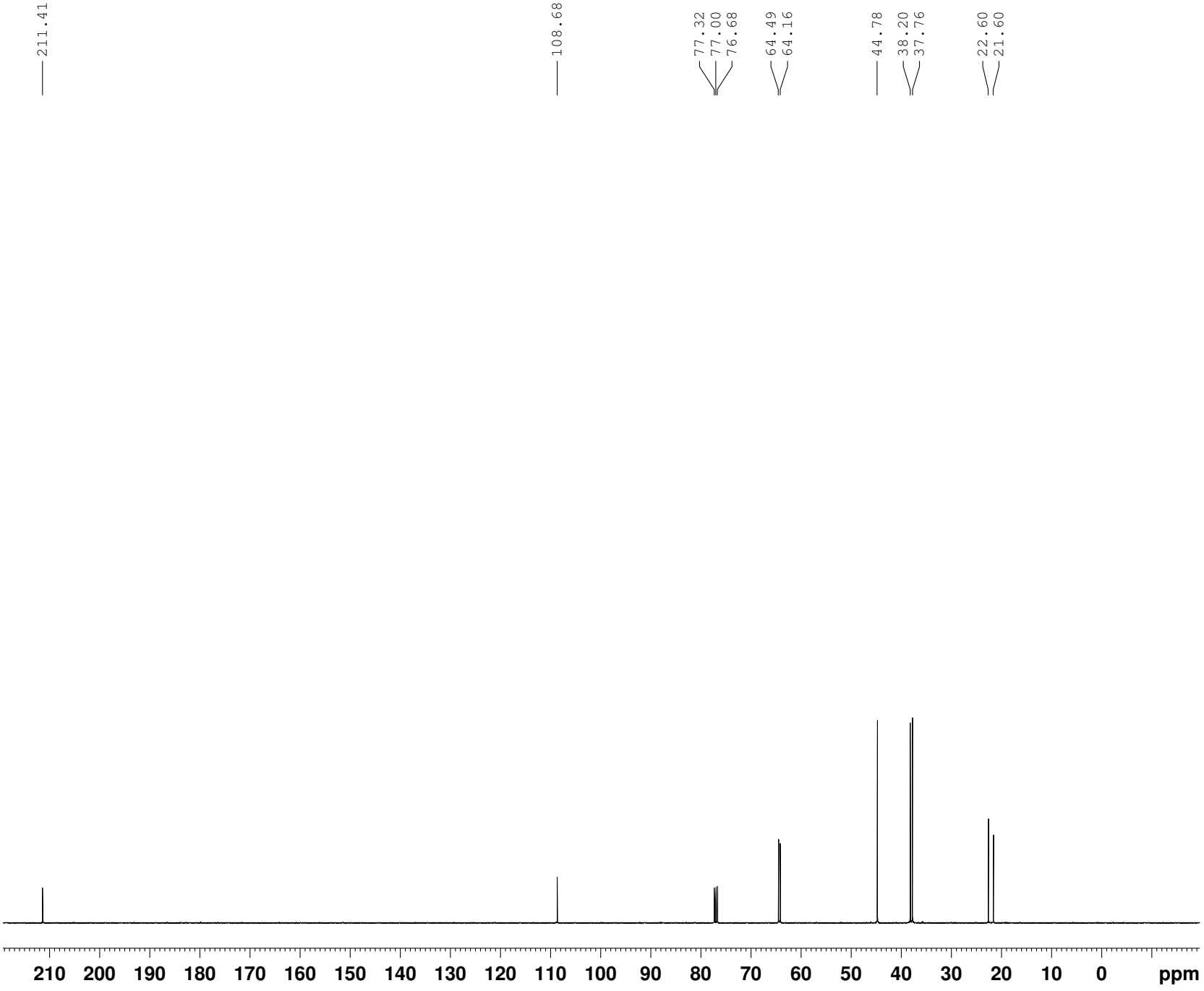
19a (1.3:1 *dr*)



NAME	zxh-2358
EXPNO	10
PROCNO	1
Date_	20160902
Time	17.09
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	32
DW	62.400 usec
DE	6.50 usec
TE	297.9 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.92 usec
SI	65536
SF	400.1300052 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

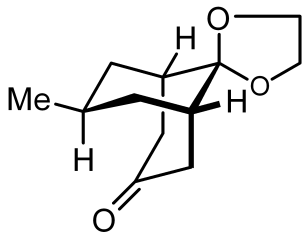


18b

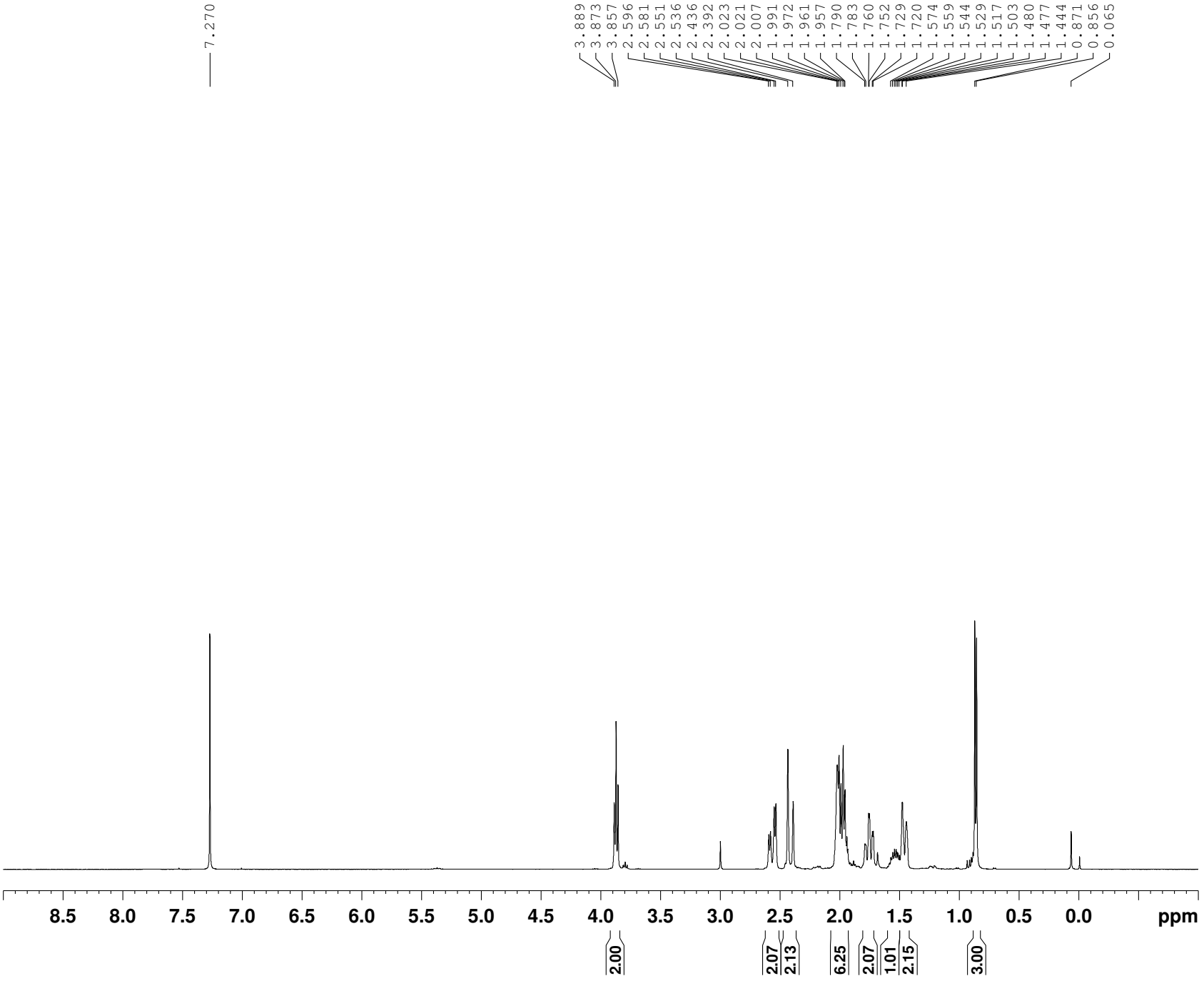


NAME	zxh-2358
EXPNO	11
PROCNO	1
Date_	20160902
Time	17.16
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	100
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	1030
DW	20.800 usec
DE	6.50 usec
TE	298.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

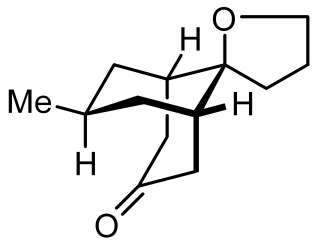
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127810 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



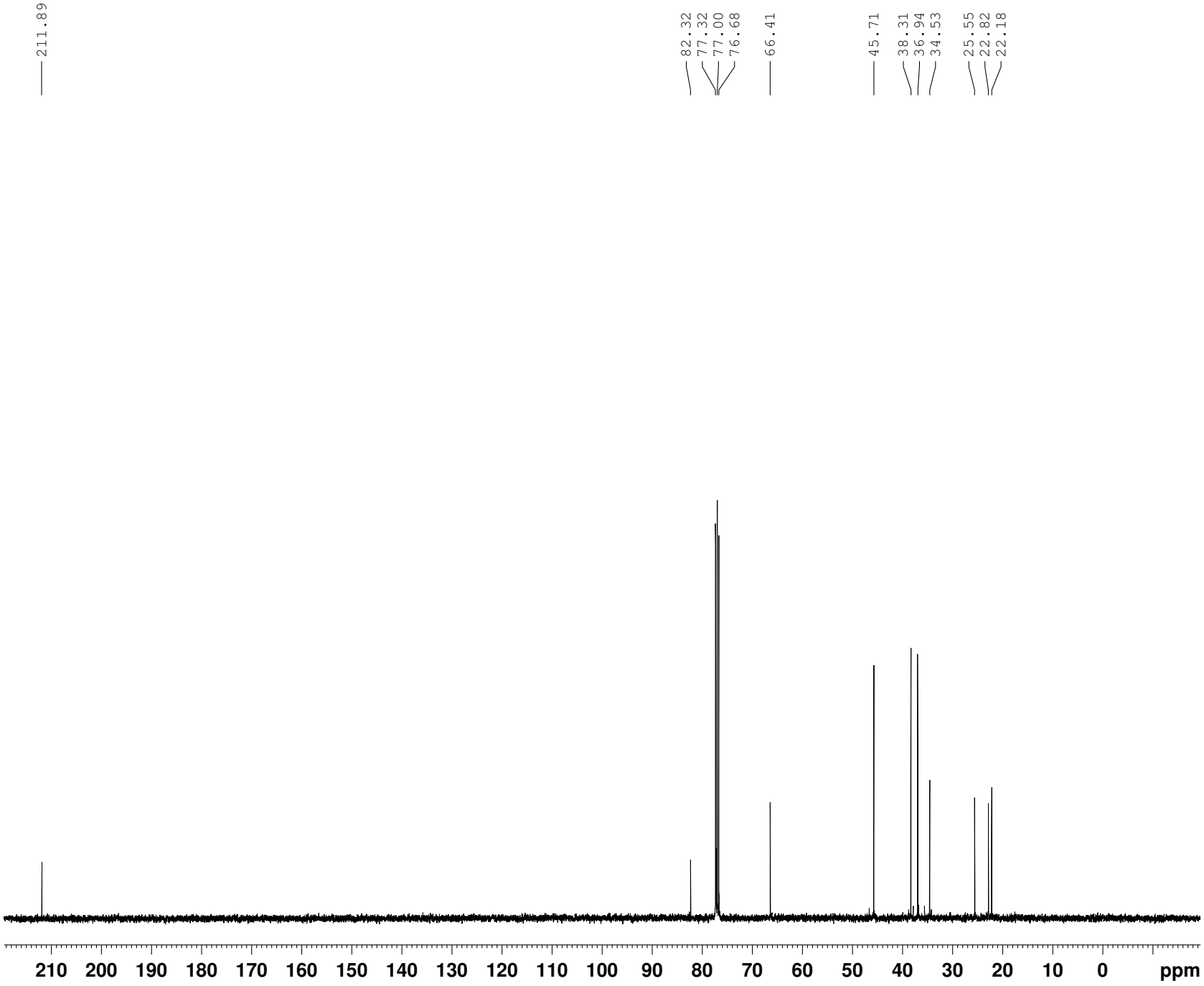
18b



NAME	zxh-2398
EXPNO	24
PROCNO	1
Date_	20170301
Time	7.50
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	144
DW	62.400 usec
DE	6.50 usec
TE	291.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.92 usec
SI	65536
SF	400.1300059 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

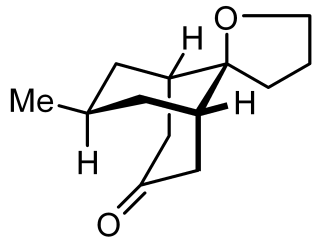


18c

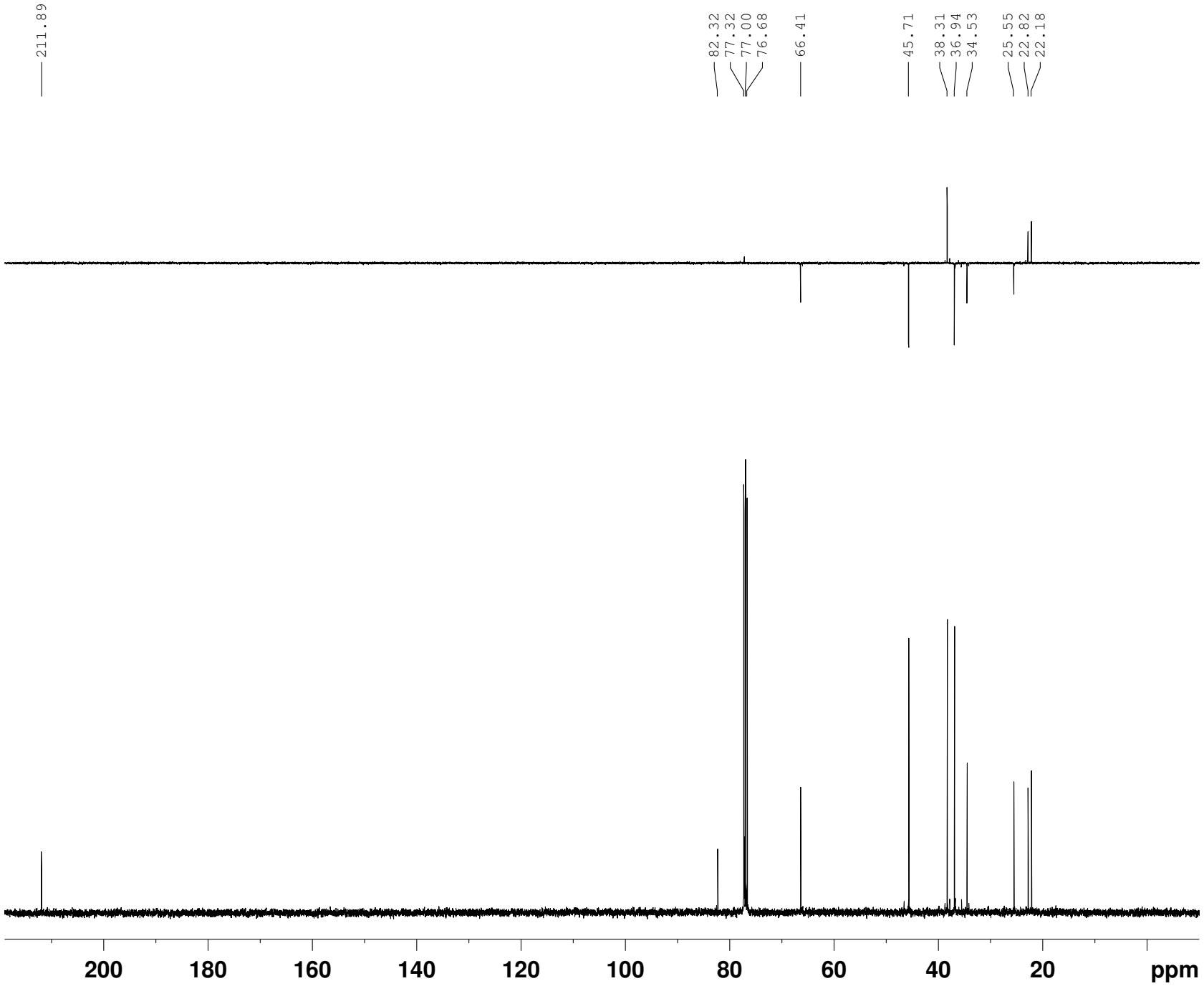


NAME	zxh-2398
EXPNO	25
PROCNO	1
Date_	20170301
Time	8.02
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	200
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	292.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127729 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

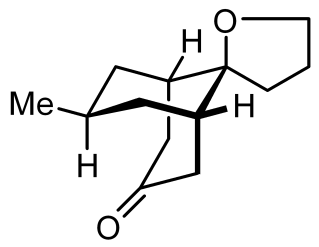


18c

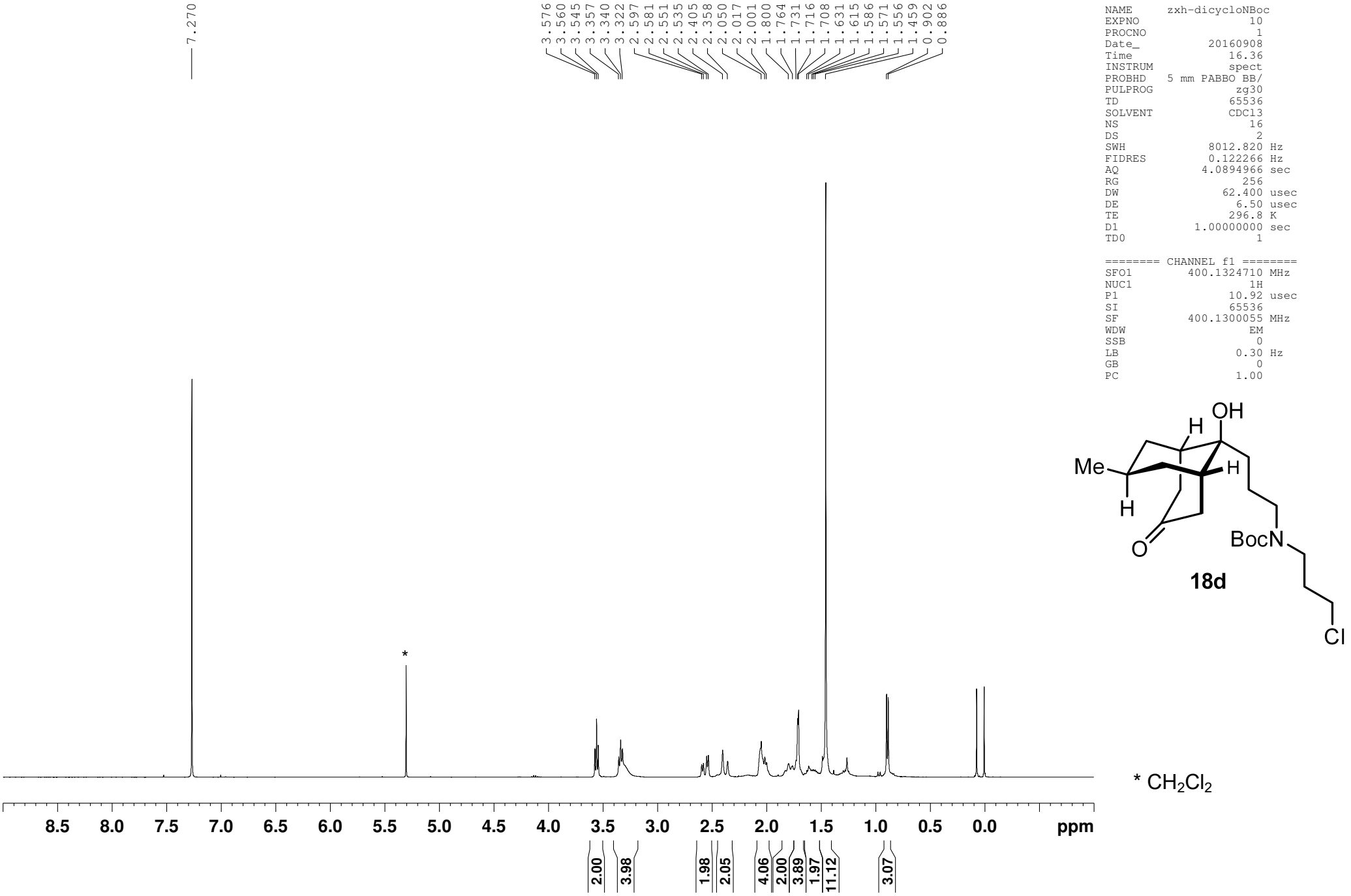


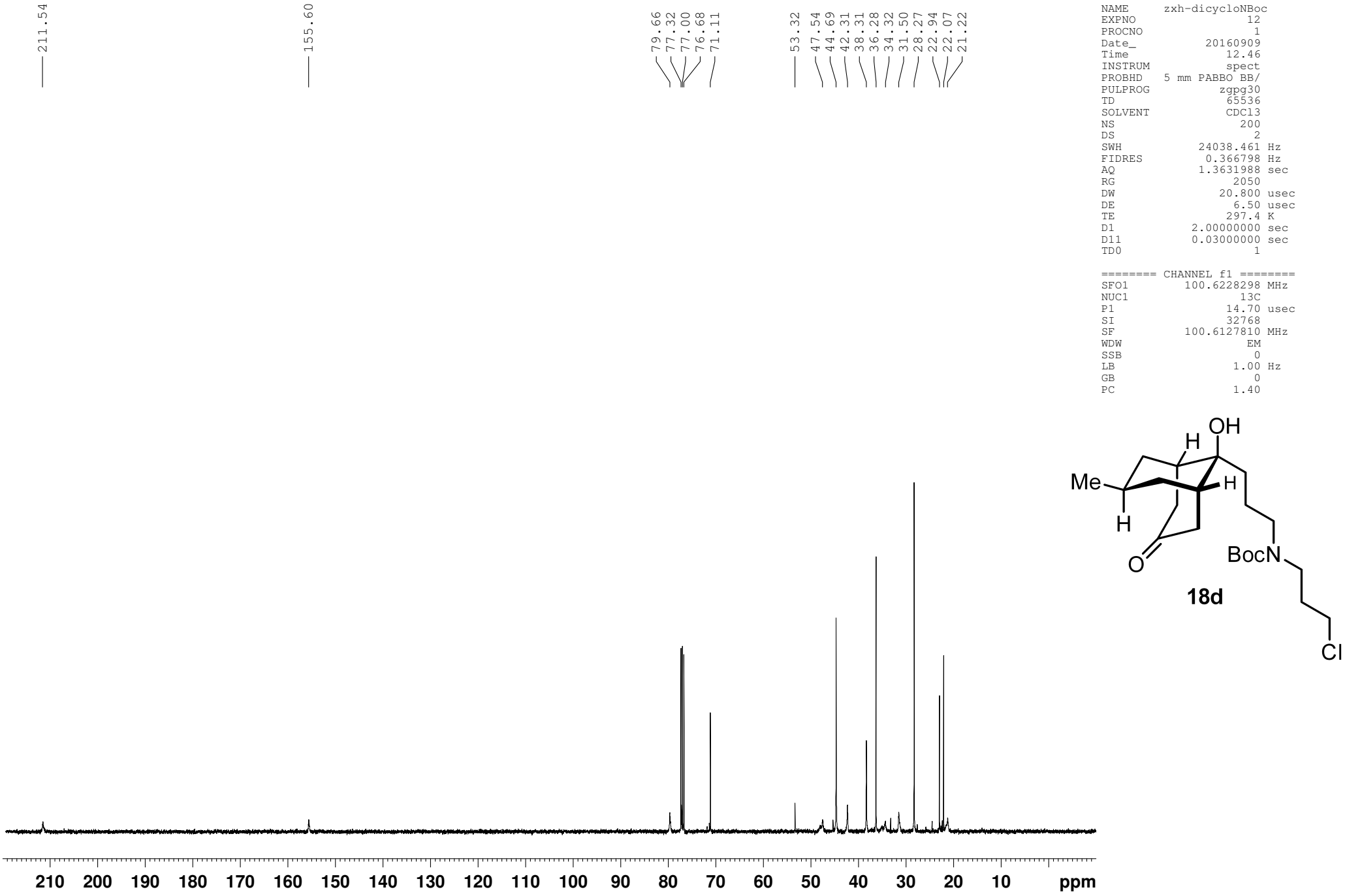

```
NAME            zxh-2398
EXPNO                 26
PROCNO                 1
Date_           20170301
Time                8.08
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG        deptsp135
TD                 65536
SOLVENT            CDCl3
NS                   100
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  1820
DW                20.800 usec
DE                 6.50 usec
TE                291.5 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                 14.70 usec
P13              2000.00 usec
SI                 32768
SF            100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



18c

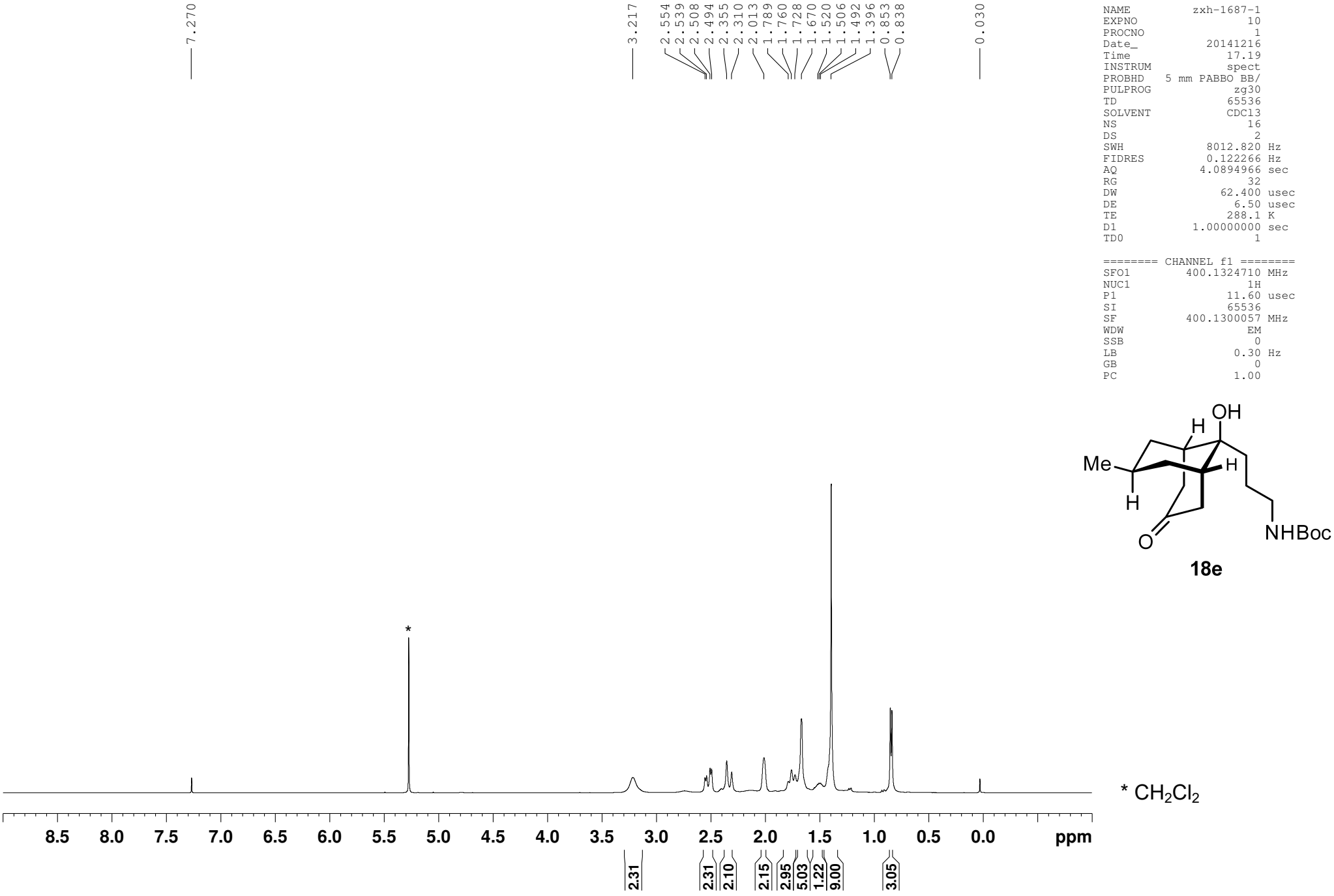

7.270
3.576
3.560
3.545
3.357
3.340
3.322
2.597
2.581
2.551
2.535
2.405
2.358
2.050
2.017
2.001
1.800
1.764
1.731
1.716
1.708
1.631
1.615
1.586
1.571
1.556
1.459
0.902
0.886
NAME zxh-dicycloNBoc
EXPNO 10
PROCNO 1
Date_ 20160908
Time 16.36
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 256
DW 62.400 usec
DE 6.50 usec
TE 296.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.92 usec
SI 65536
SF 400.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
H
Me
H
H
O
BocN
Cl
18d
*
* CH2Cl2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
3.98
1.98
2.05
4.06
2.00
3.89
1.97
11.12
3.07

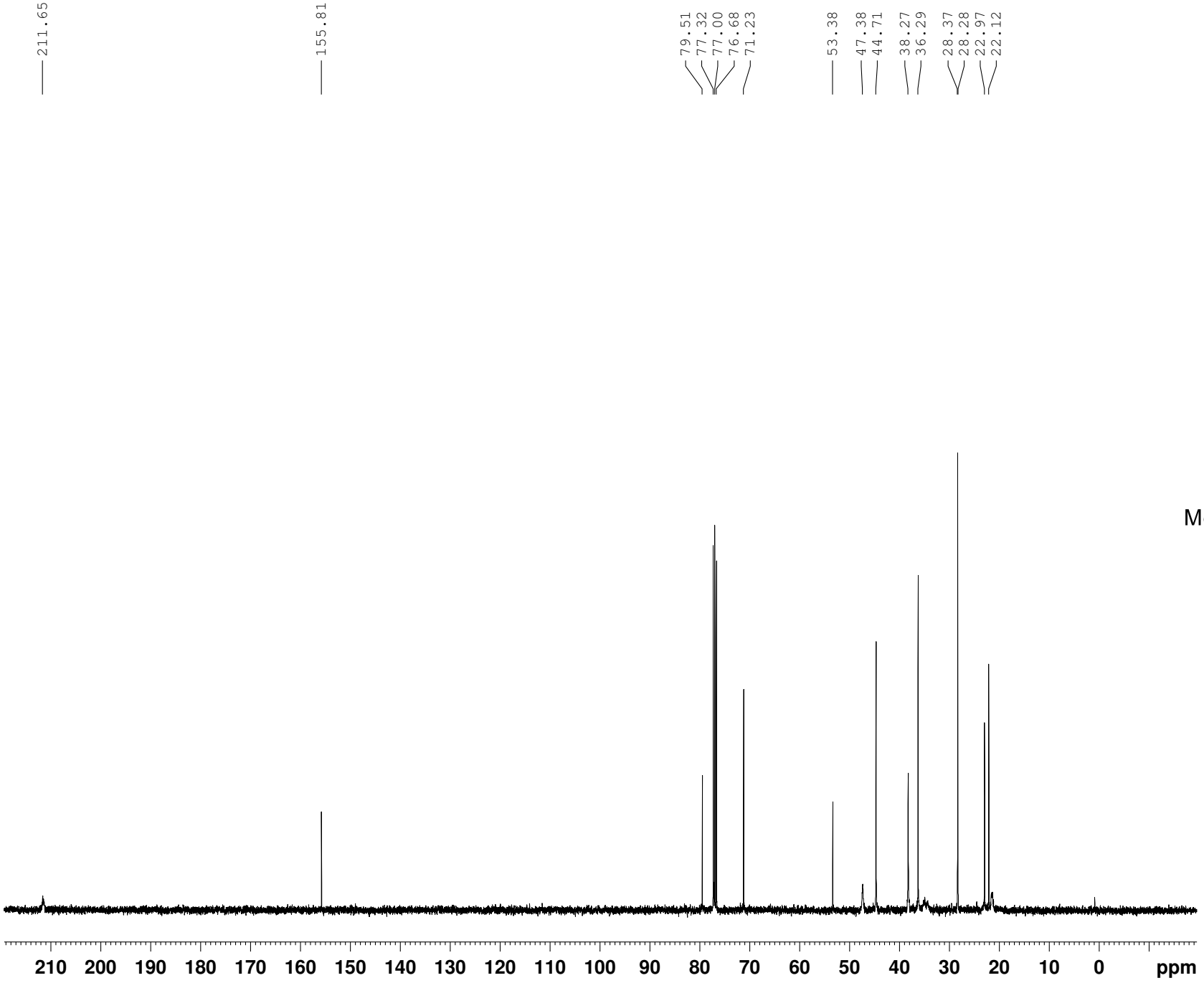



```
NAME      zxh-dicycloNBoc
EXPNO                 12
PROCNO                 1
Date_           20160909
Time               12.46
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                   200
DS                     2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                297.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                14.70 usec
SI                32768
SF          100.6127810 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

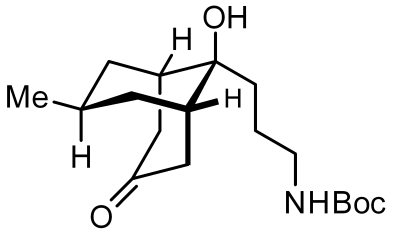

18d


7.270
3.217
2.554
2.539
2.508
2.494
2.355
2.310
2.013
1.789
1.760
1.728
1.670
1.520
1.506
1.492
1.396
0.853
0.838
0.030
NAME zxh-1687-1
EXPNO 10
PROCNO 1
Date_ 20141216
Time 17.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 32
DW 62.400 usec
DE 6.50 usec
TE 288.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 11.60 usec
SI 65536
SF 400.1300057 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
H
Me
H
H
O
NHBoc
18e
*
* CH2Cl2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.31 2.31 2.10 2.15 2.95 5.03 1.22 9.00 3.05

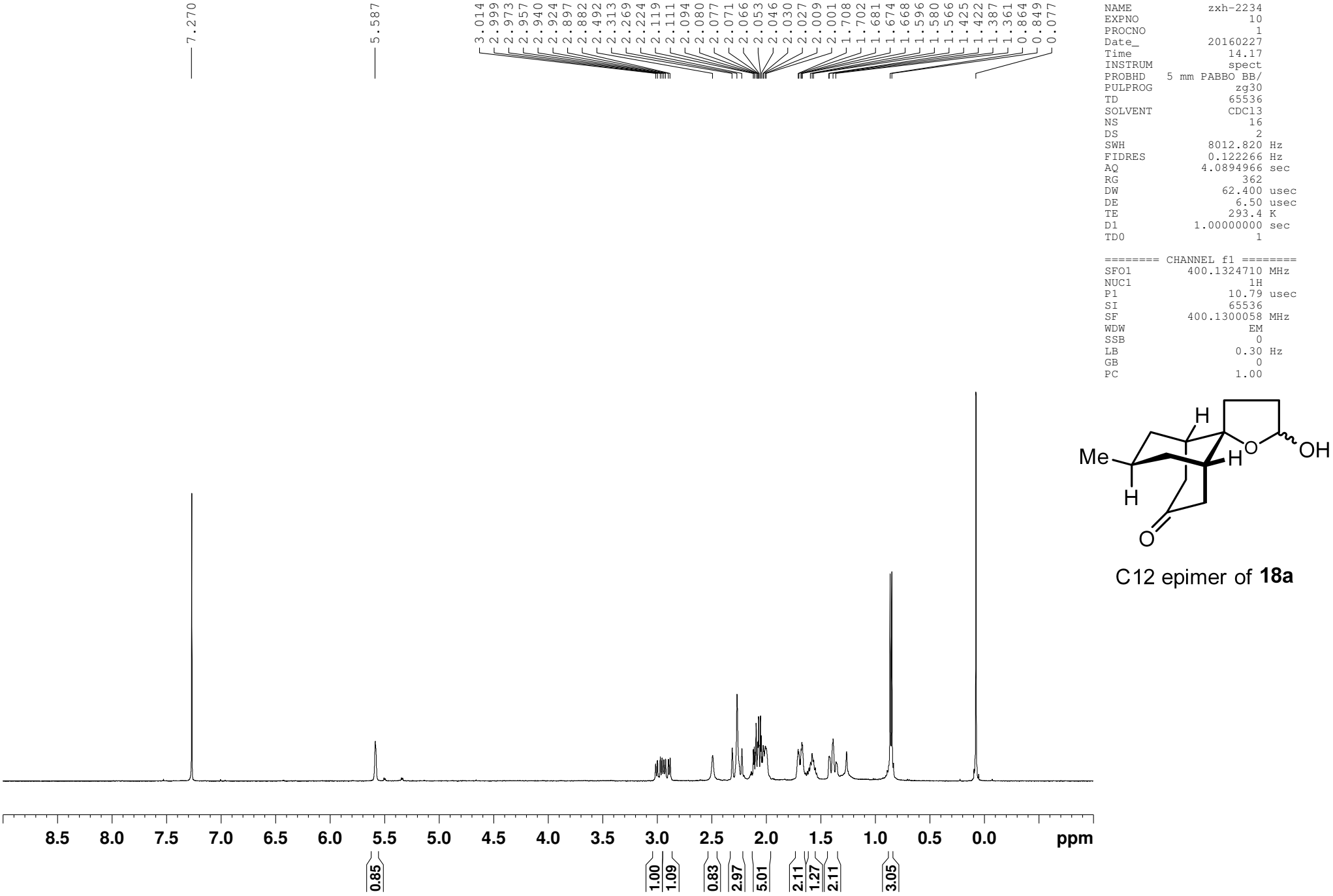


NAME	zxh-1687-1
EXPNO	11
PROCNO	1
Date_	20141216
Time	17.27
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	128
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	1030
DW	20.800 usec
DE	6.50 usec
TE	289.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.45 usec
SI	32768
SF	100.6127802 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

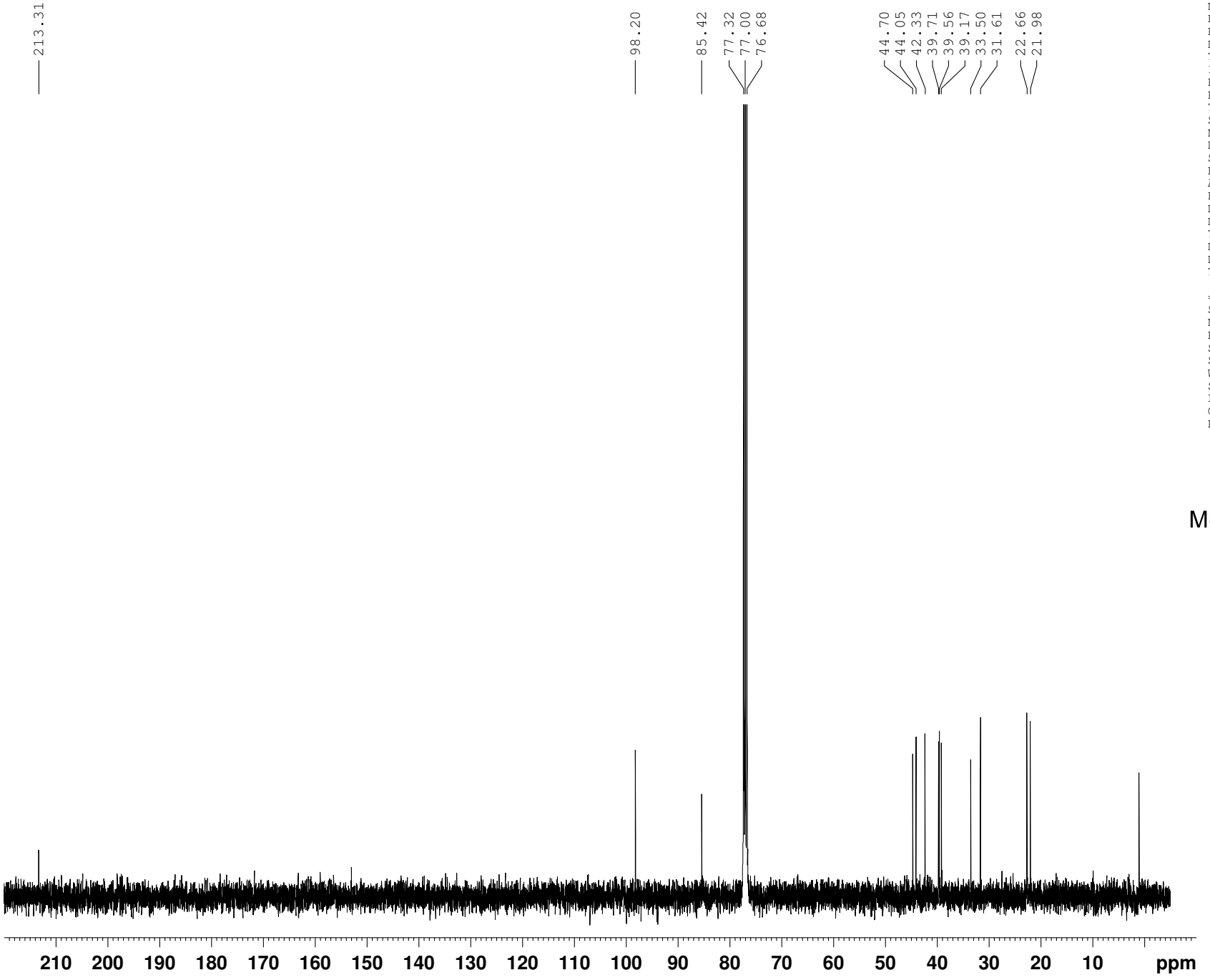


18e

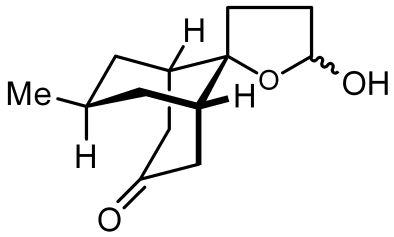


NAME	zxh-2234
EXPNO	10
PROCNO	1
Date_	20160227
Time	14.17
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDC13
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	362
DW	62.400 usec
DE	6.50 usec
TE	293.4 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.79 usec
SI	65536
SF	400.1300058 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

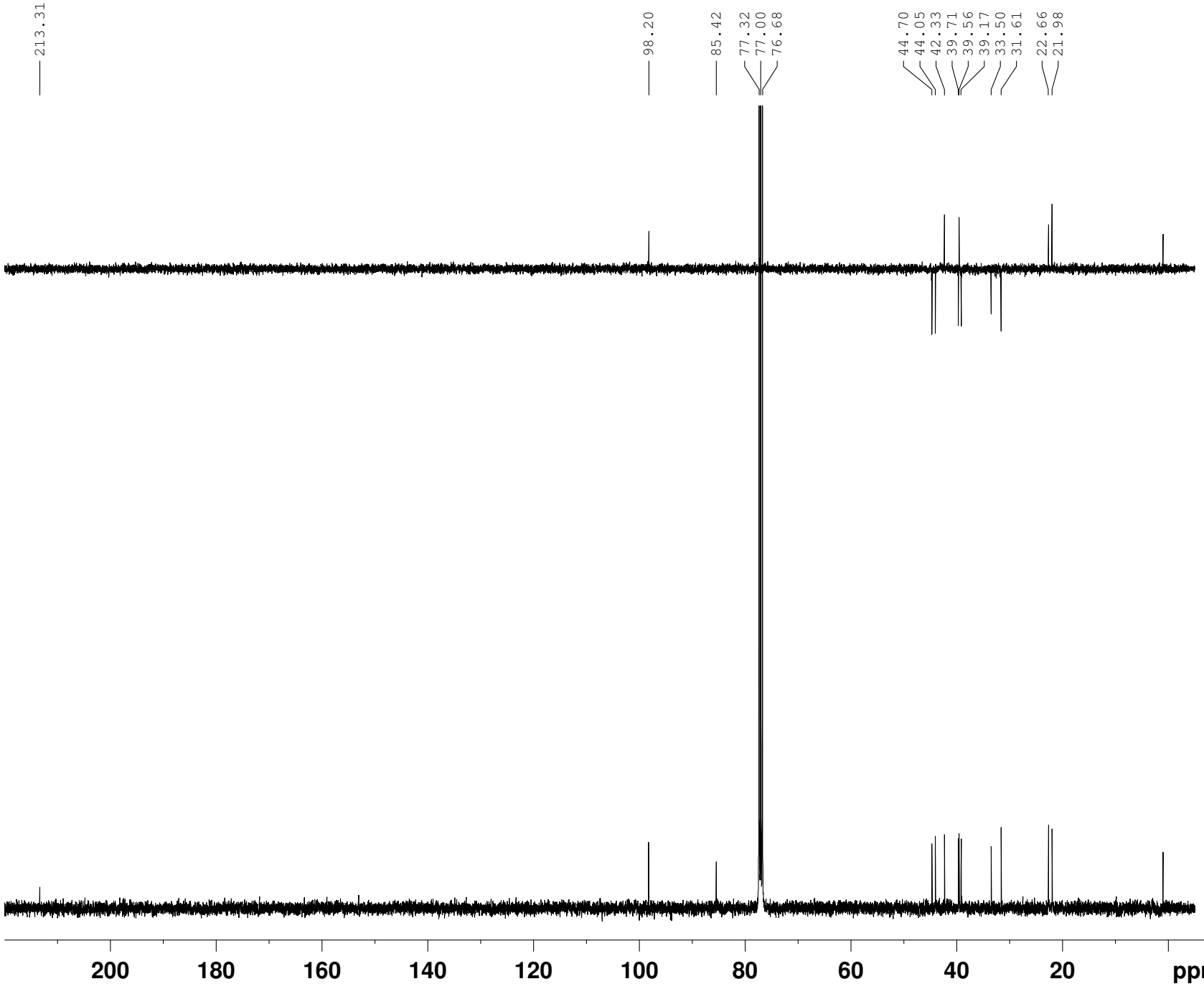
C12 epimer of **18a**



NAME	zxh-2234
EXPNO	11
PROCNO	1
Date_	20160227
Time	15.28
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1200
DS	2
SWH	23148.148 Hz
FIDRES	0.353213 Hz
AQ	1.4156276 sec
RG	812
DW	21.600 usec
DE	6.50 usec
TE	295.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6238364 MHz
NUC1	13C
P1	12.00 usec
SI	32768
SF	100.6127701 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

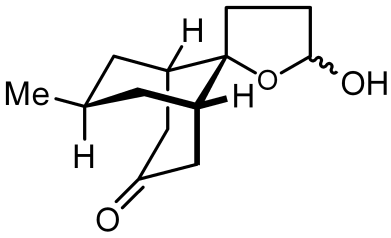


C12 epimer of **18a**

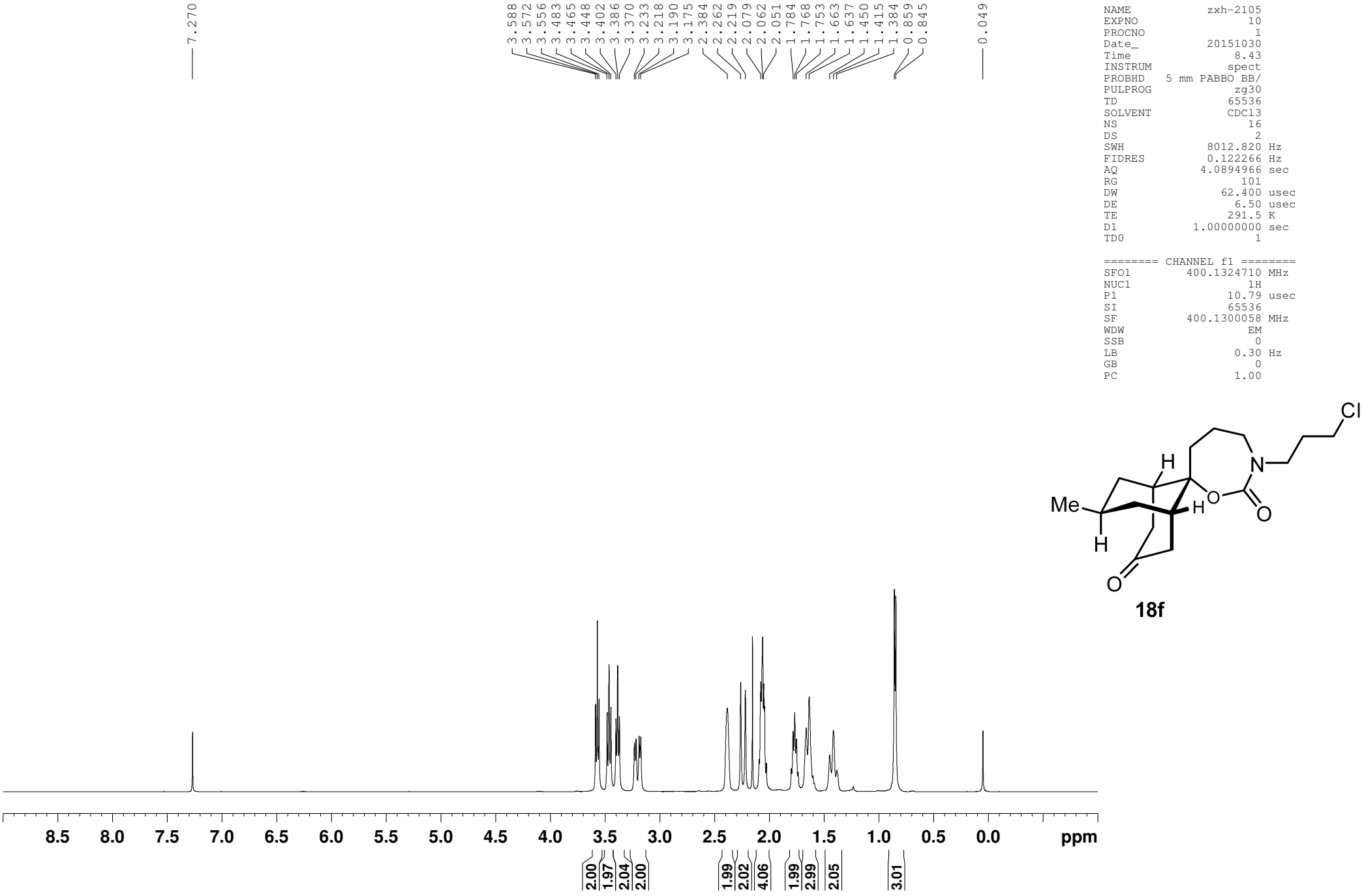


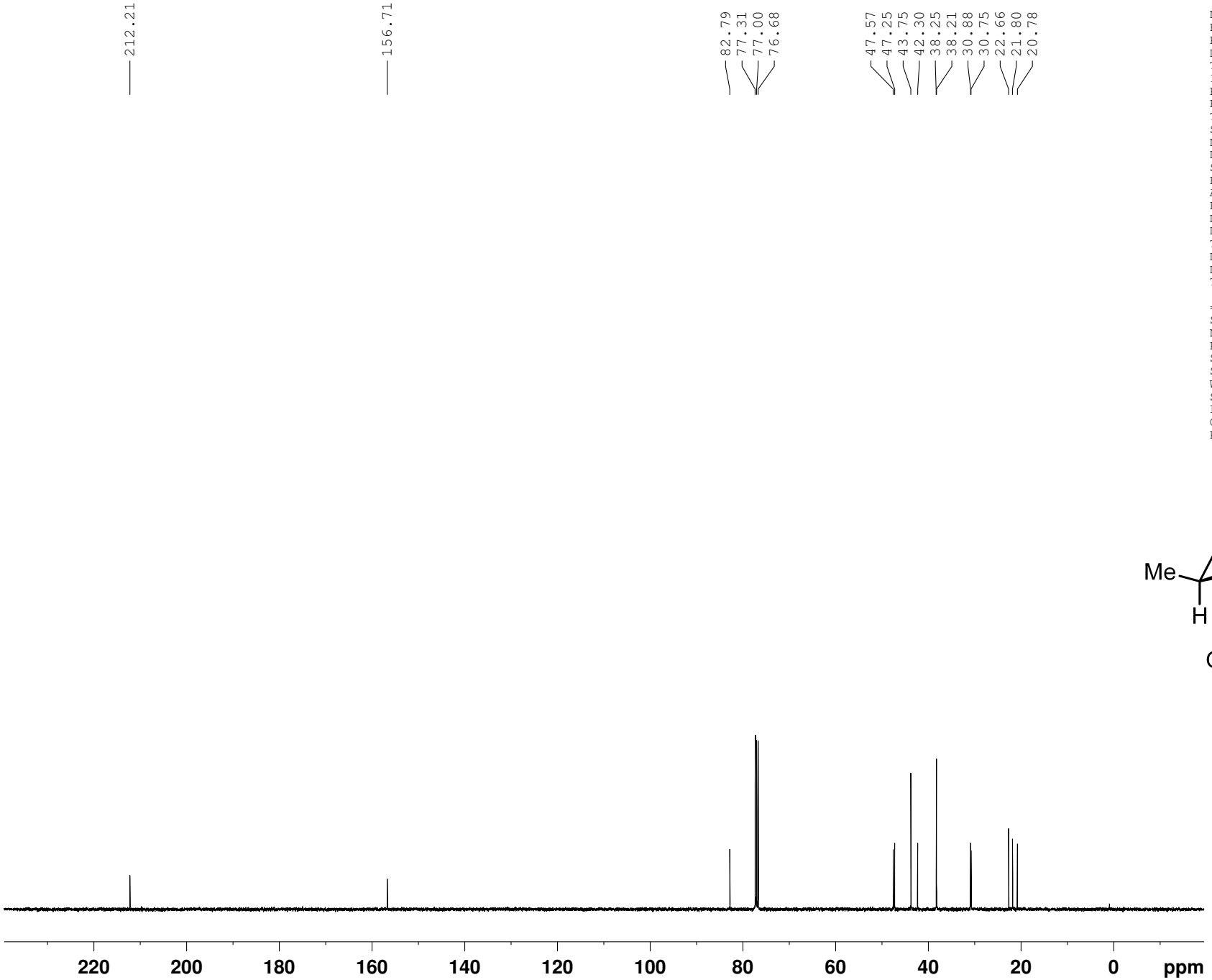

```
NAME            zxh-2234
EXPNO                 12
PROCNO                 1
Date_           20160227
Time               16.03
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG        deptsp135
TD                 65536
SOLVENT             CDC13
NS                    600
DS                      4
SWH             23148.148 Hz
FIDRES          0.353213 Hz
AQ              1.4156276 sec
RG                   2050
DW                 21.600 usec
DE                  6.50 usec
TE                 295.2 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6238364 MHz
NUC1                  13C
P1                 12.00 usec
P13              2000.00 usec
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



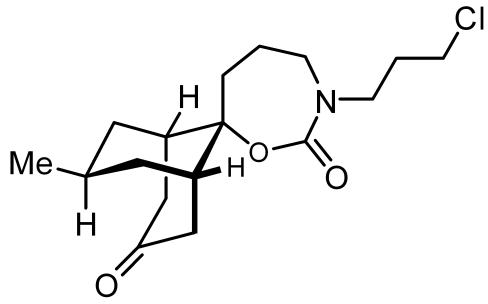
C12 epimer of **18a**


7.270
3.588
3.572
3.556
3.483
3.465
3.448
3.402
3.386
3.370
3.233
3.218
3.190
3.175
2.384
2.262
2.219
2.079
2.062
2.051
1.784
1.768
1.753
1.663
1.637
1.450
1.415
1.384
0.859
0.845
0.049
NAME zxh-2105
EXPNO 10
PROCNO 1
Date_ 20151030
Time 8.43
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 101
DW 62.400 usec
DE 6.50 usec
TE 291.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.79 usec
SI 65536
SF 400.1300058 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Cl
N
H
O
O
Me
H
O
18f
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
1.97
2.04
2.00
1.99
2.02
4.06
1.99
2.99
2.05
3.01

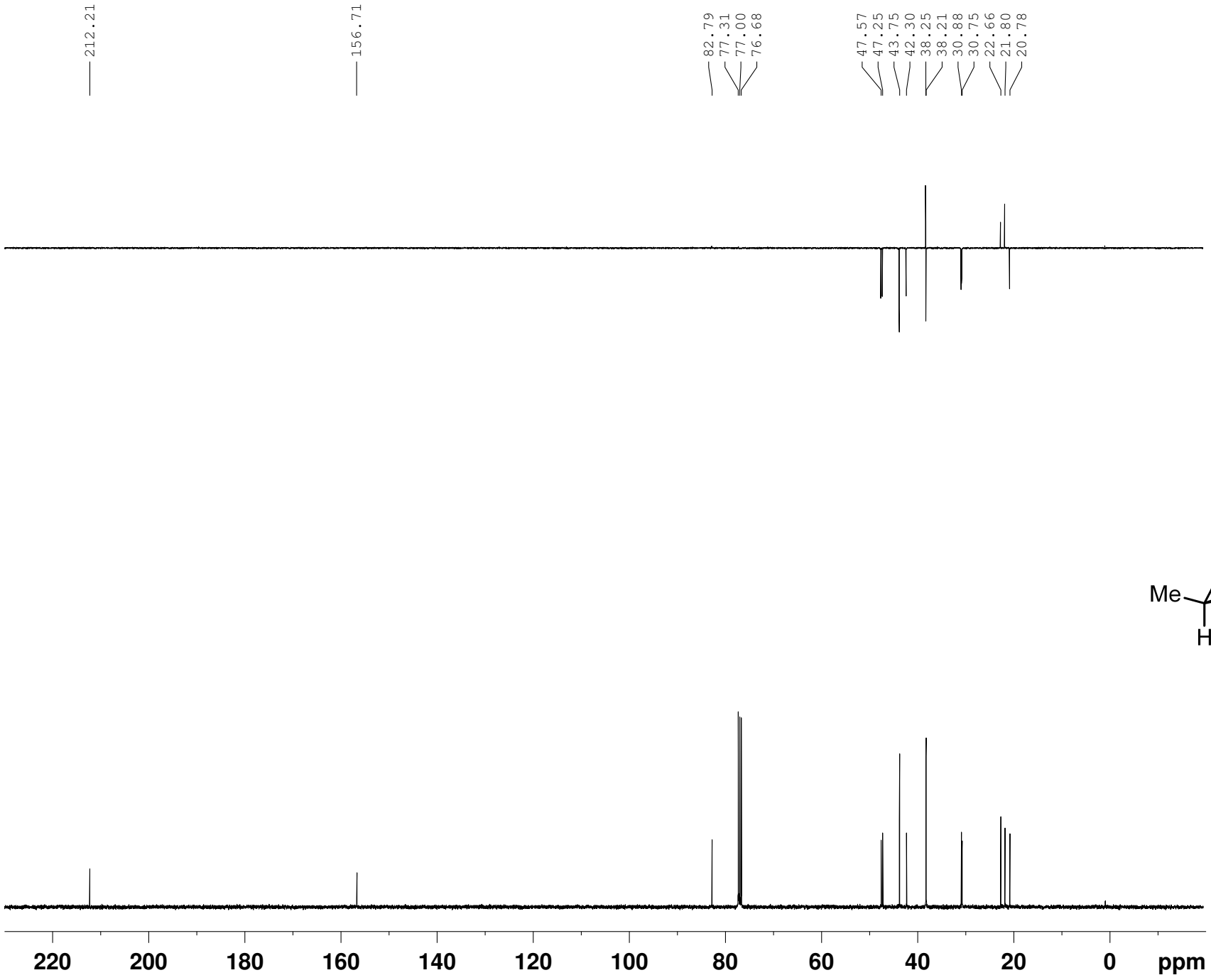



```
NAME            zxh-2105
EXPNO                 11
PROCNO                 1
Date_           20151030
Time                8.56
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     2
SWH          26041.666 Hz
FIDRES        0.397364 Hz
AQ            1.2583412 sec
RG                  2050
DW                19.200 usec
DE                 6.50 usec
TE                292.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6238364 MHz
NUC1                13C
P1                12.00 usec
SI                 32768
SF          100.6127772 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

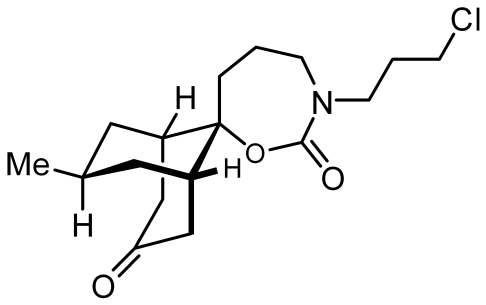


18f

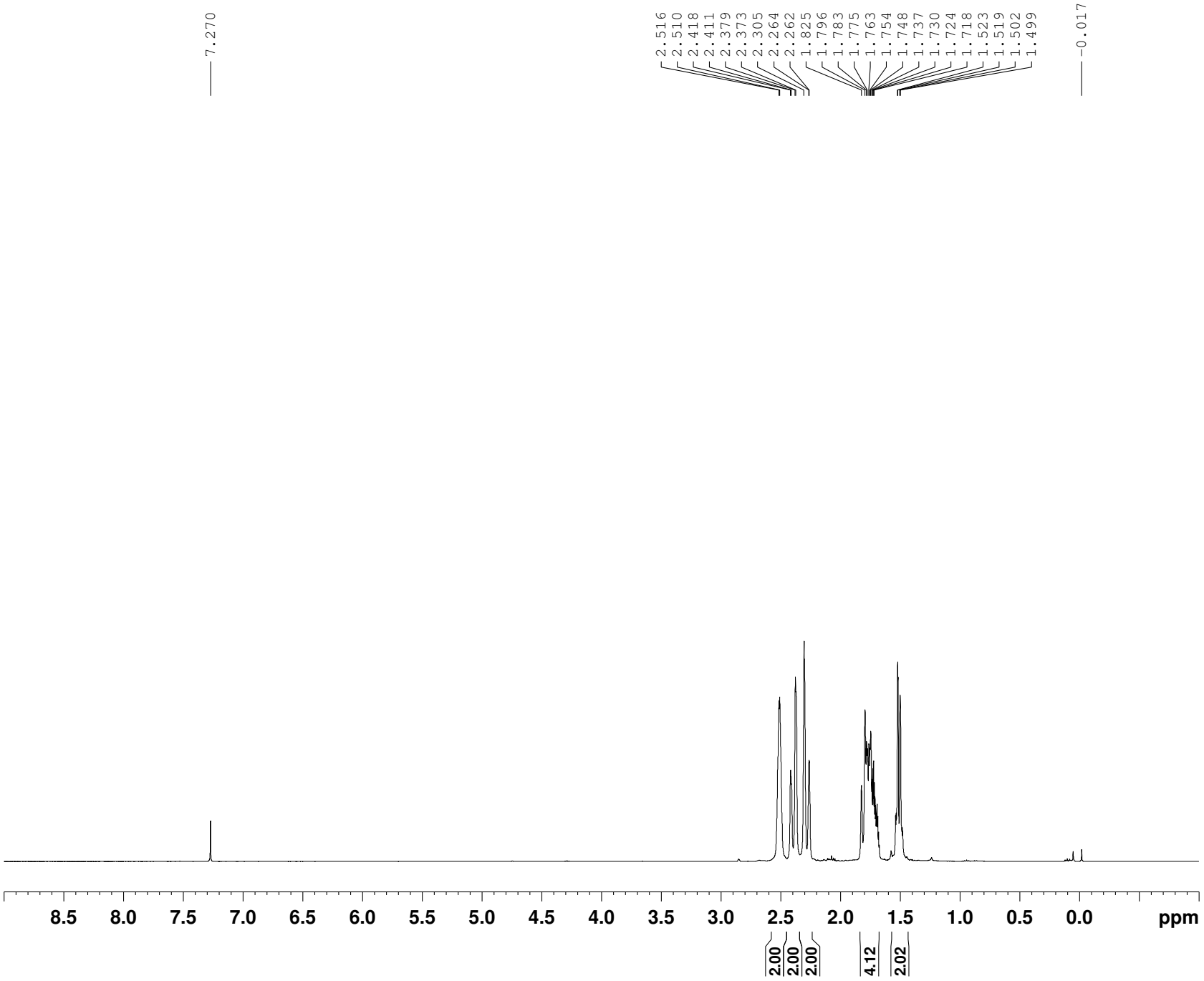



```
NAME            zxh-2105
EXPNO                 12
PROCNO                 1
Date_           20151030
Time                9.03
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG       deptsp135
TD                65536
SOLVENT           CDCl3
NS                  100
DS                    4
SWH           26041.666 Hz
FIDRES         0.397364 Hz
AQ             1.2583412 sec
RG                 2050
DW               19.200 usec
DE                6.50 usec
TE                291.7 K
CNST2        145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6238364 MHz
NUC1                13C
P1                12.00 usec
P13             2000.00 usec
SI                32768
SF          100.6127690 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

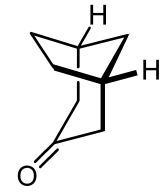


18f

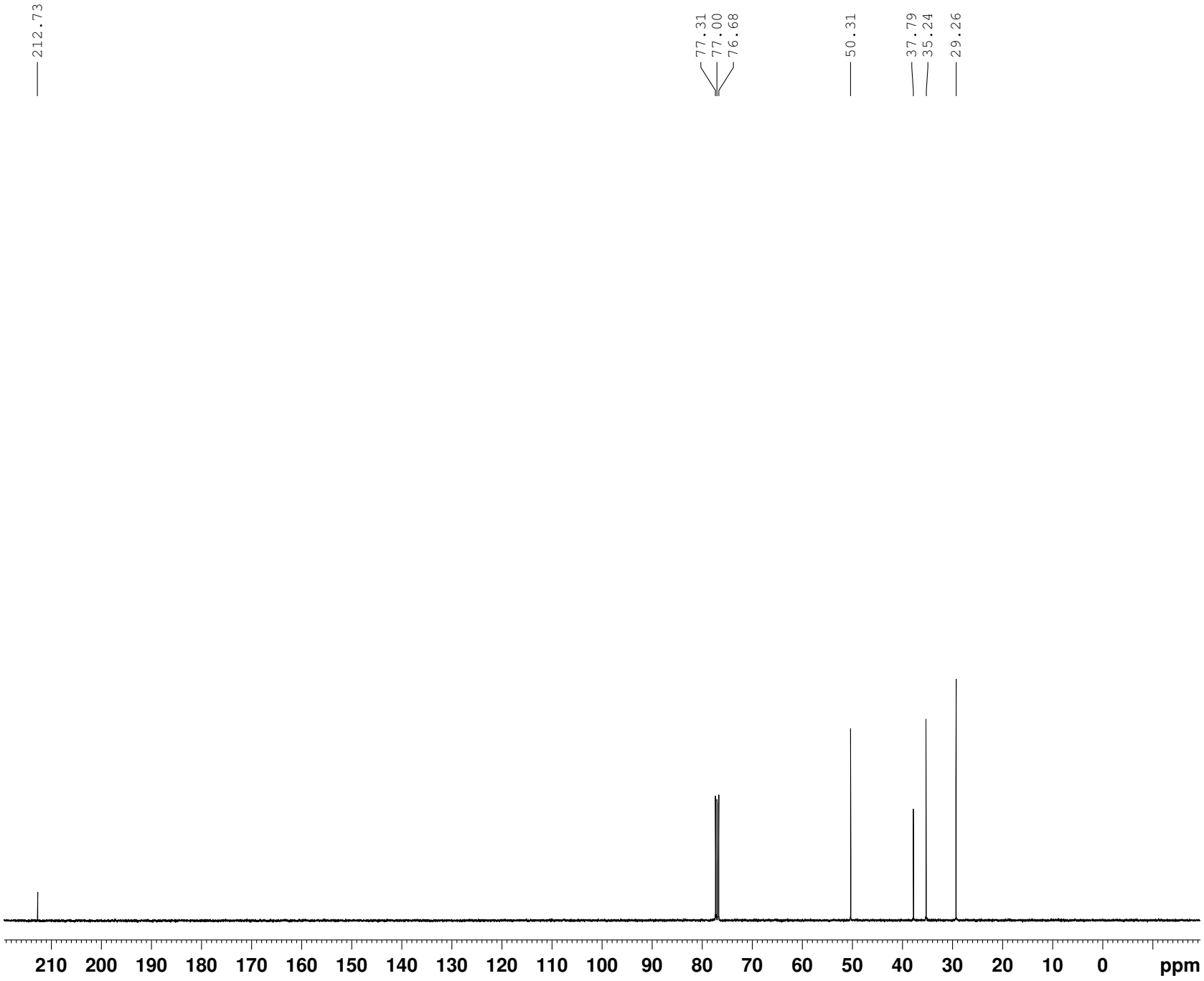


NAME	zxh-2323-1
EXPNO	10
PROCNO	1
Date_	20160526
Time	13.50
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	114
DW	62.400 usec
DE	6.50 usec
TE	294.4 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.92 usec
SI	65536
SF	400.1300055 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

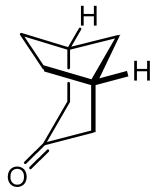


18g

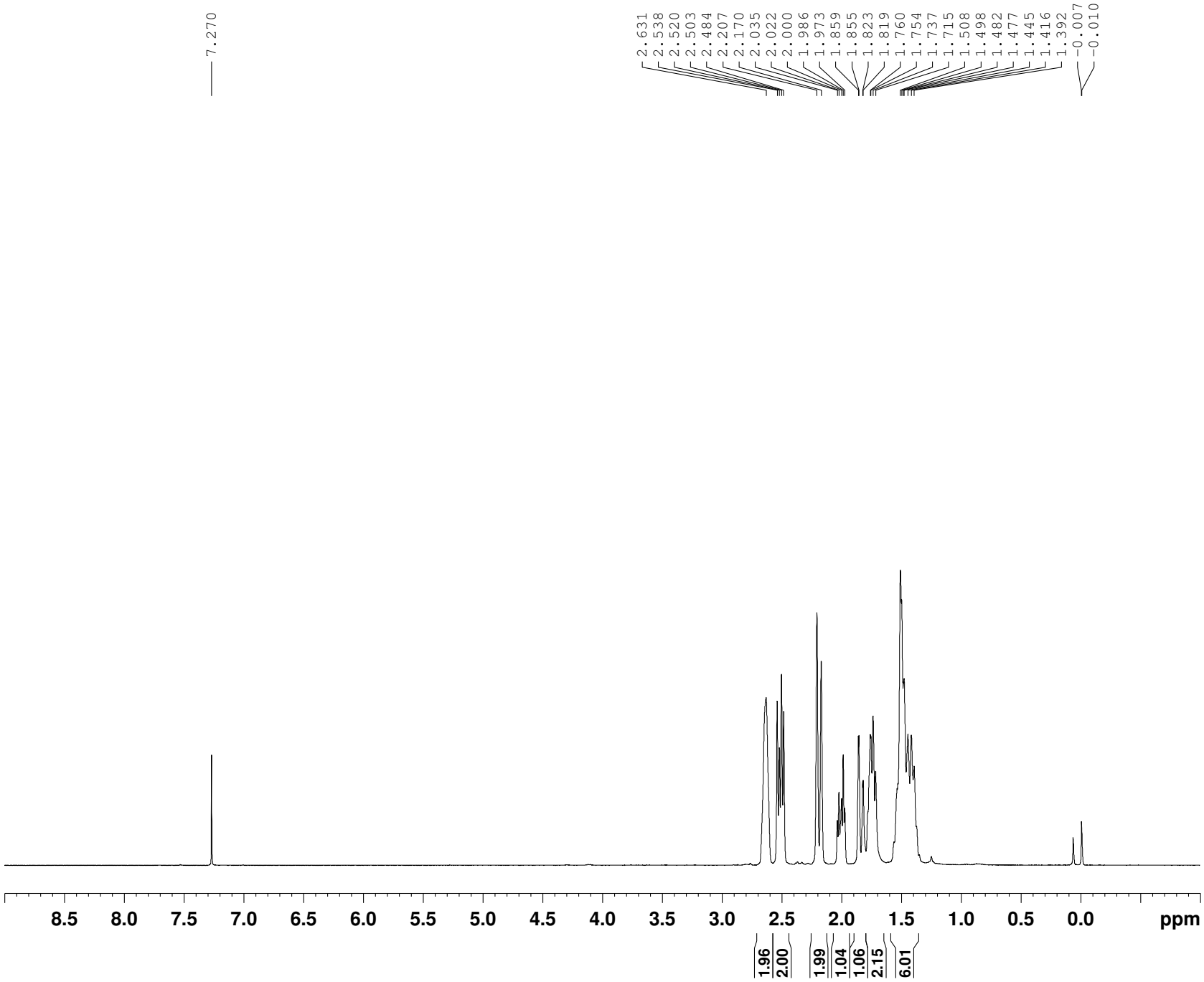



```
NAME          zxh-2323-1
EXPNO                 11
PROCNO                 1
Date_           20160526
Time               14.03
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 1030
DW               20.800 usec
DE                6.50 usec
TE               295.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                14.70 usec
SI                32768
SF          100.6127744 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

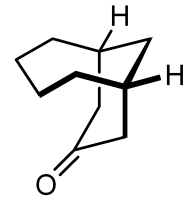


18g

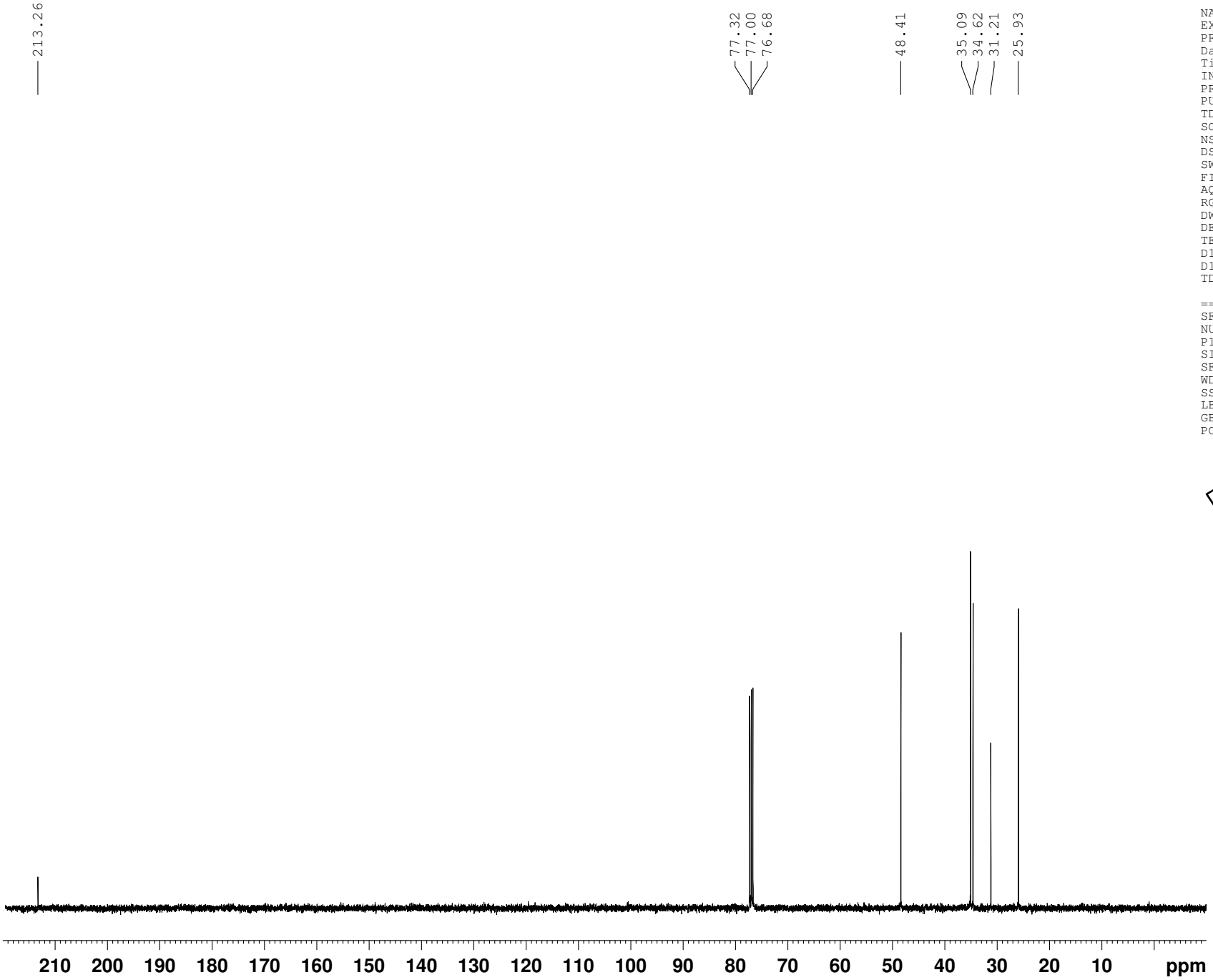


NAME	zxh-2332
EXPNO	10
PROCNO	1
Date_	20160623
Time	17.23
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	4
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	128
DW	62.400 usec
DE	6.50 usec
TE	298.2 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.92 usec
SI	65536
SF	400.1300057 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

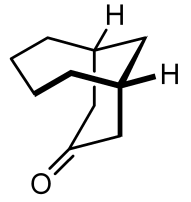


18h

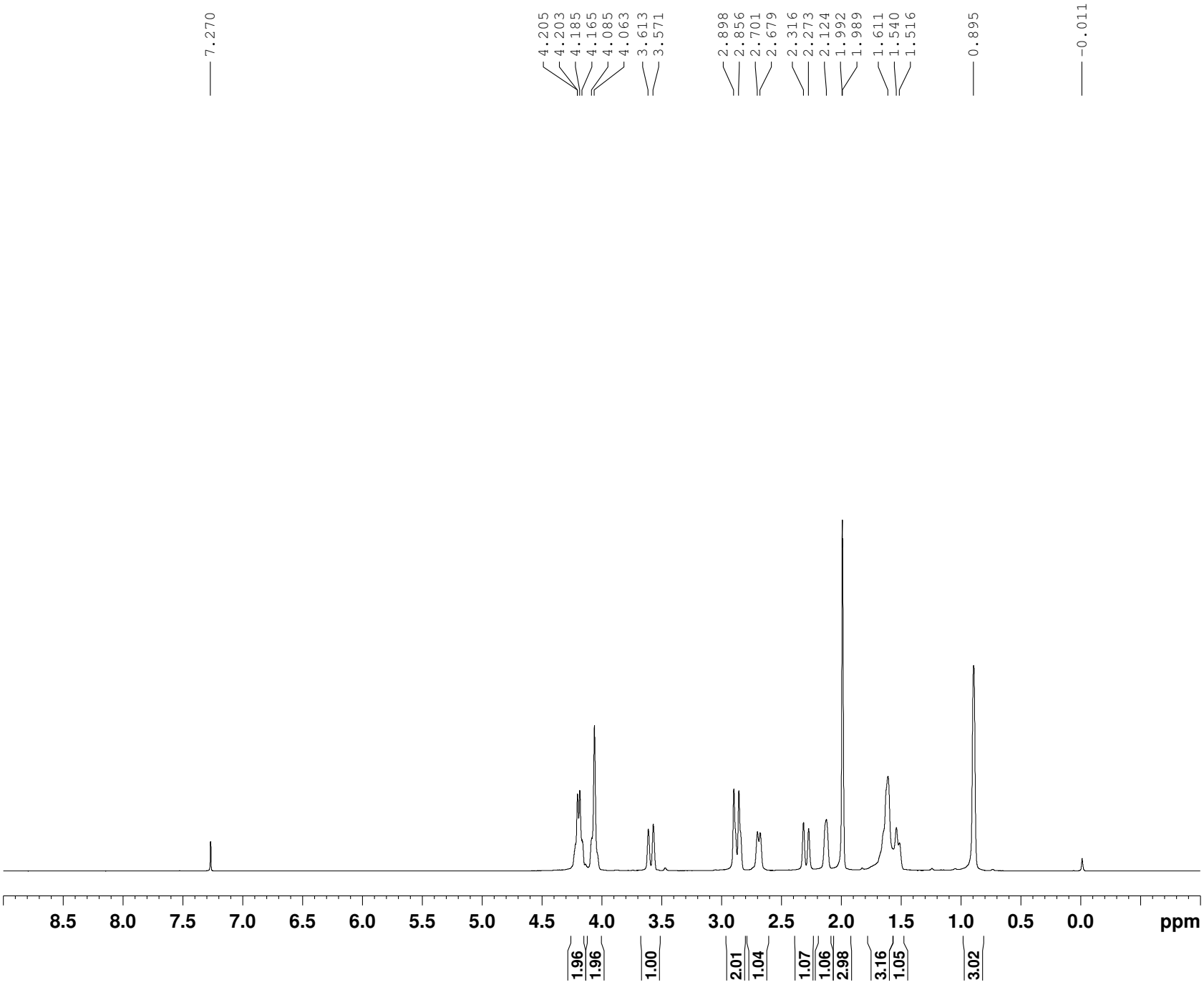



```
NAME            zxh-2332
EXPNO                 11
PROCNO                 1
Date_           20160623
Time                17.30
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    100
DS                      2
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   1030
DW                 20.800 usec
DE                  6.50 usec
TE                298.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                 14.70 usec
SI                 32768
SF           100.6127714 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

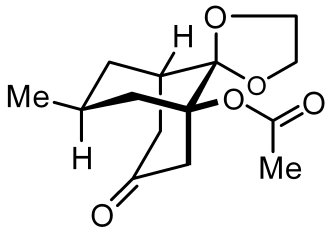


18h

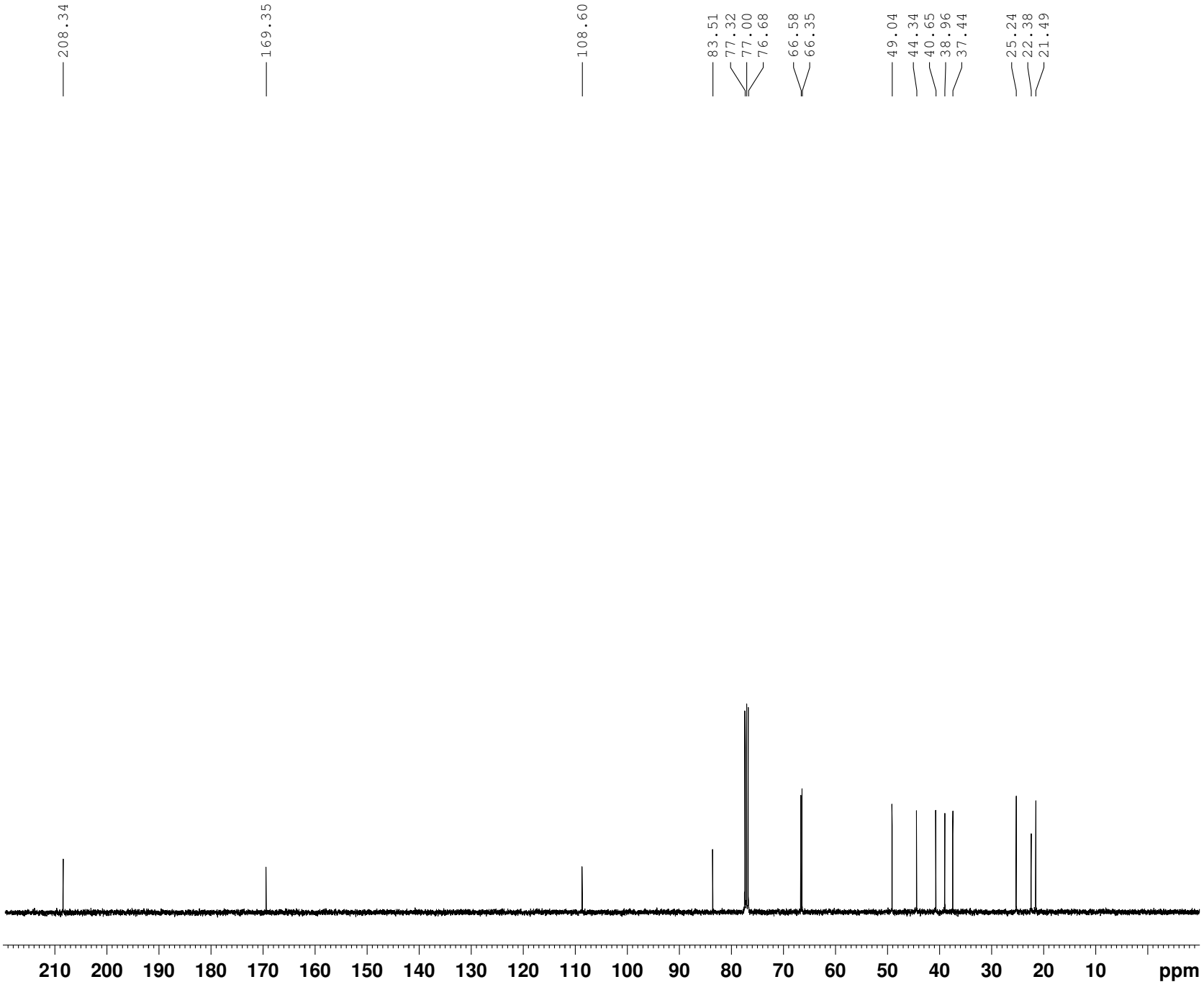



```
NAME          zxh-2362-1
EXPNO                 10
PROCNO                 1
Date_           20160907
Time                8.46
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                   128
DW                62.400 usec
DE                 6.50 usec
TE                296.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                   1H
P1                 10.79 usec
SI                 65536
SF          400.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

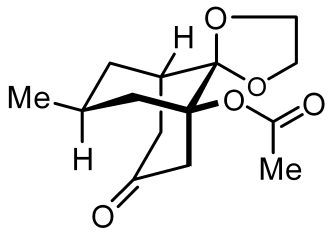


19b

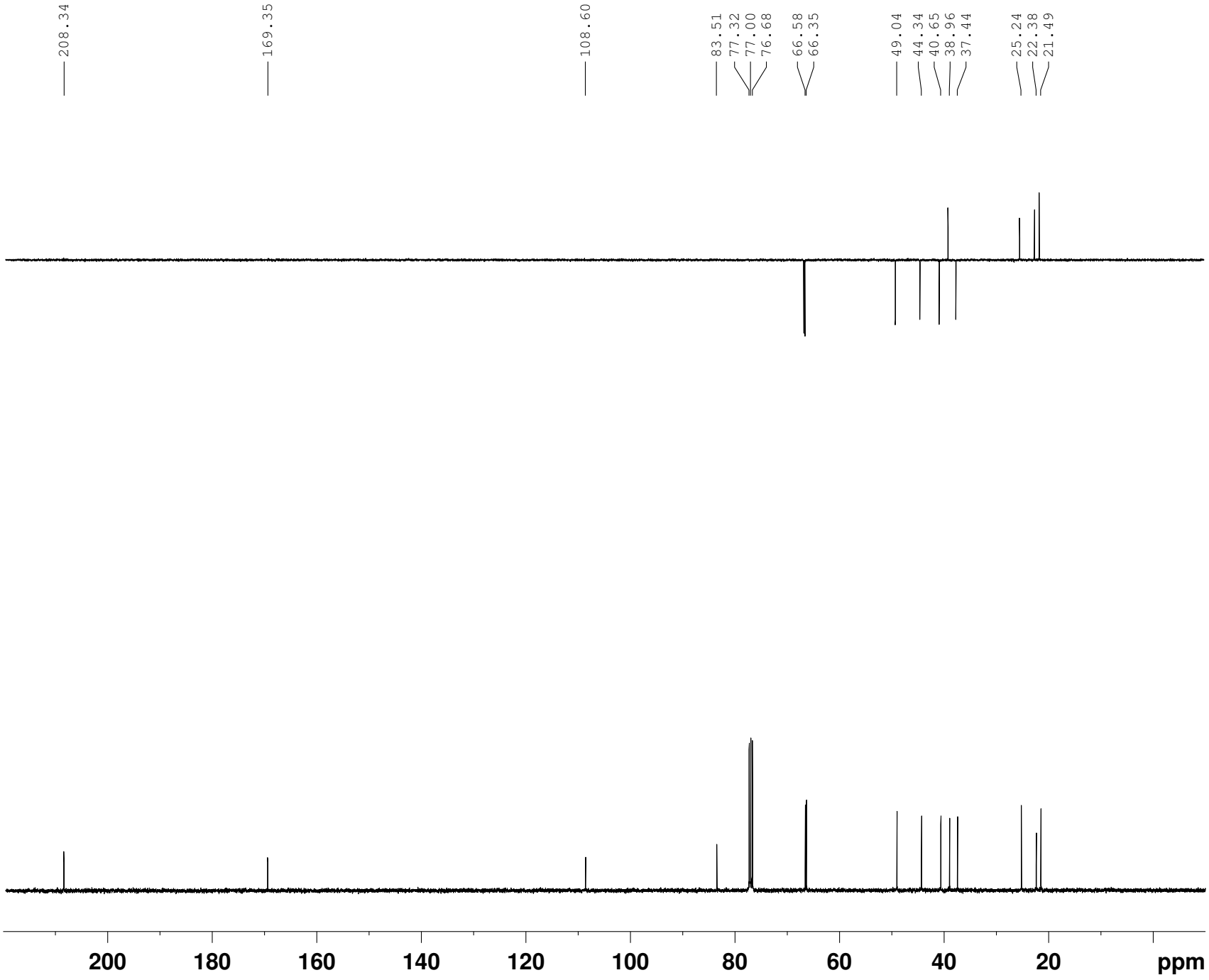


NAME	zxh-2362-1
EXPNO	11
PROCNO	1
Date_	20160907
Time	8.58
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	200
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	297.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	12.00 usec
SI	32768
SF	100.6127722 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

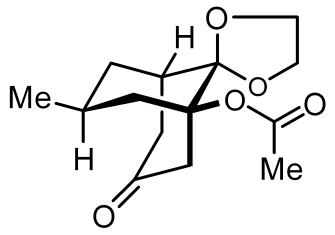


19b

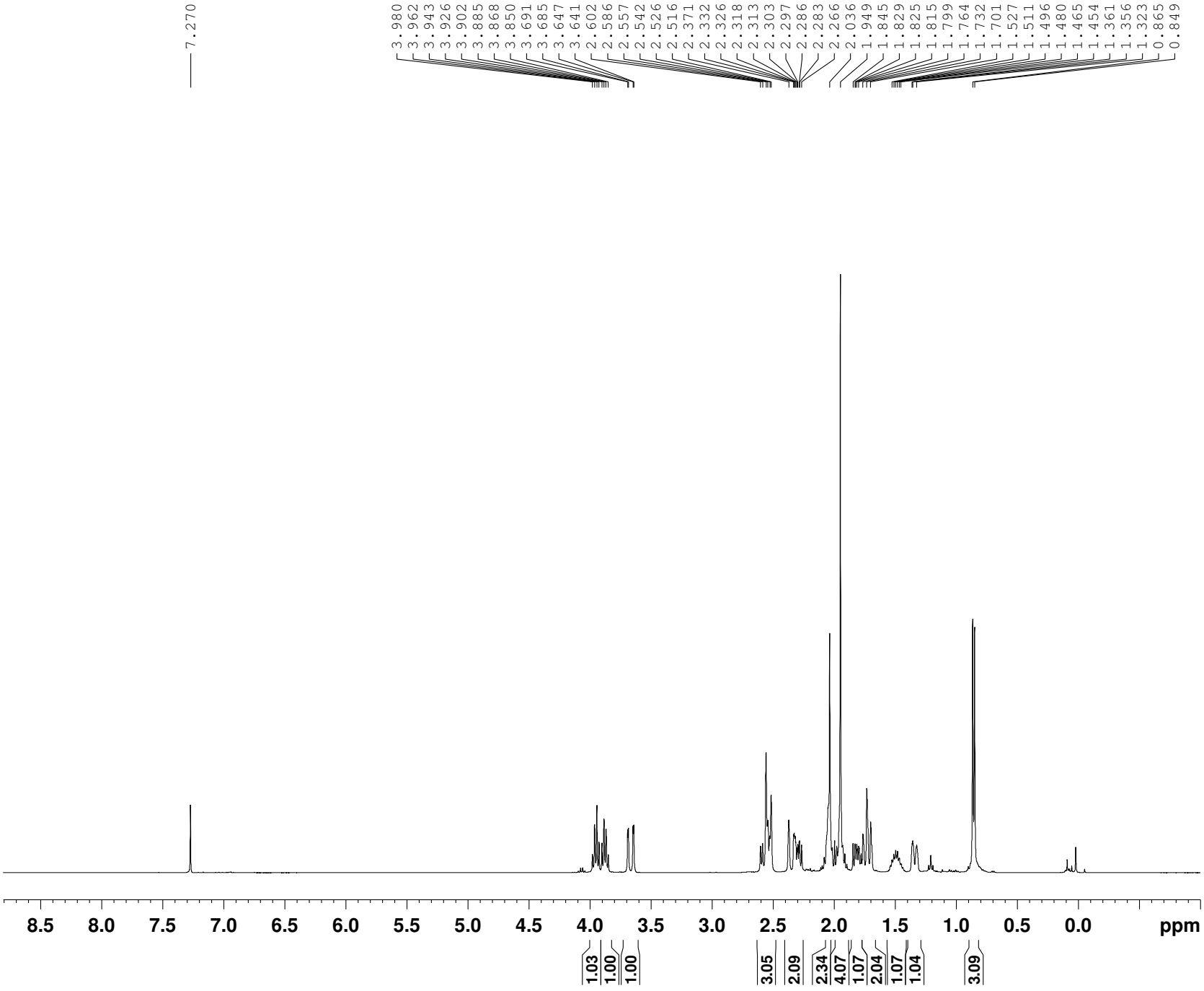



```
NAME          zxh-2362-1
EXPNO                 12
PROCNO                 1
Date_           20160907
Time                9.05
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG        deptsp135
TD                 65536
SOLVENT            CDCl3
NS                   100
DS                     4
SWH            24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                297.3 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                 13C
P1                 12.00 usec
P13              2000.00 usec
SI                 32768
SF            100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

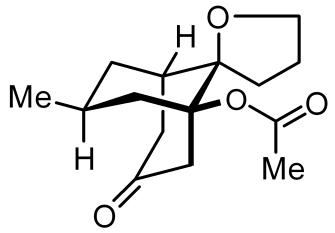


19b




```
NAME          zxh-2402-1
EXPNO                 10
PROCNO                 1
Date_           20170302
Time               17.12
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                    32
DW                62.400 usec
DE                 6.50 usec
TE                292.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                 65536
SF           400.1300055 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



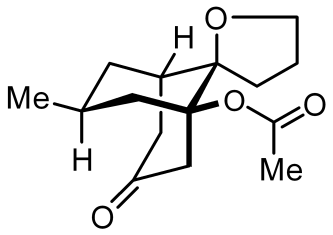
19c

208.36
169.69
84.40
84.18
77.32
77.00
76.68
68.63
49.62
44.82
39.41
39.01
35.86
31.18
26.65
25.38
22.23
21.70

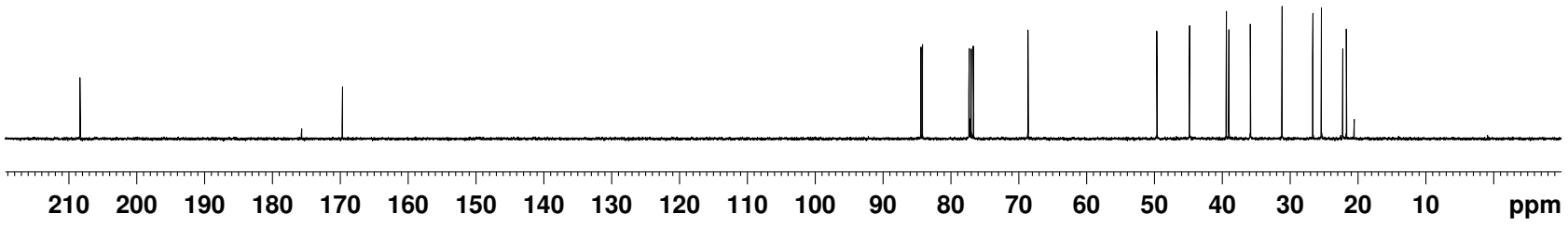
NAME	zxh-2402-1
EXPNO	11
PROCNO	1
Date_	20170302
Time	17.18
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	100
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	293.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

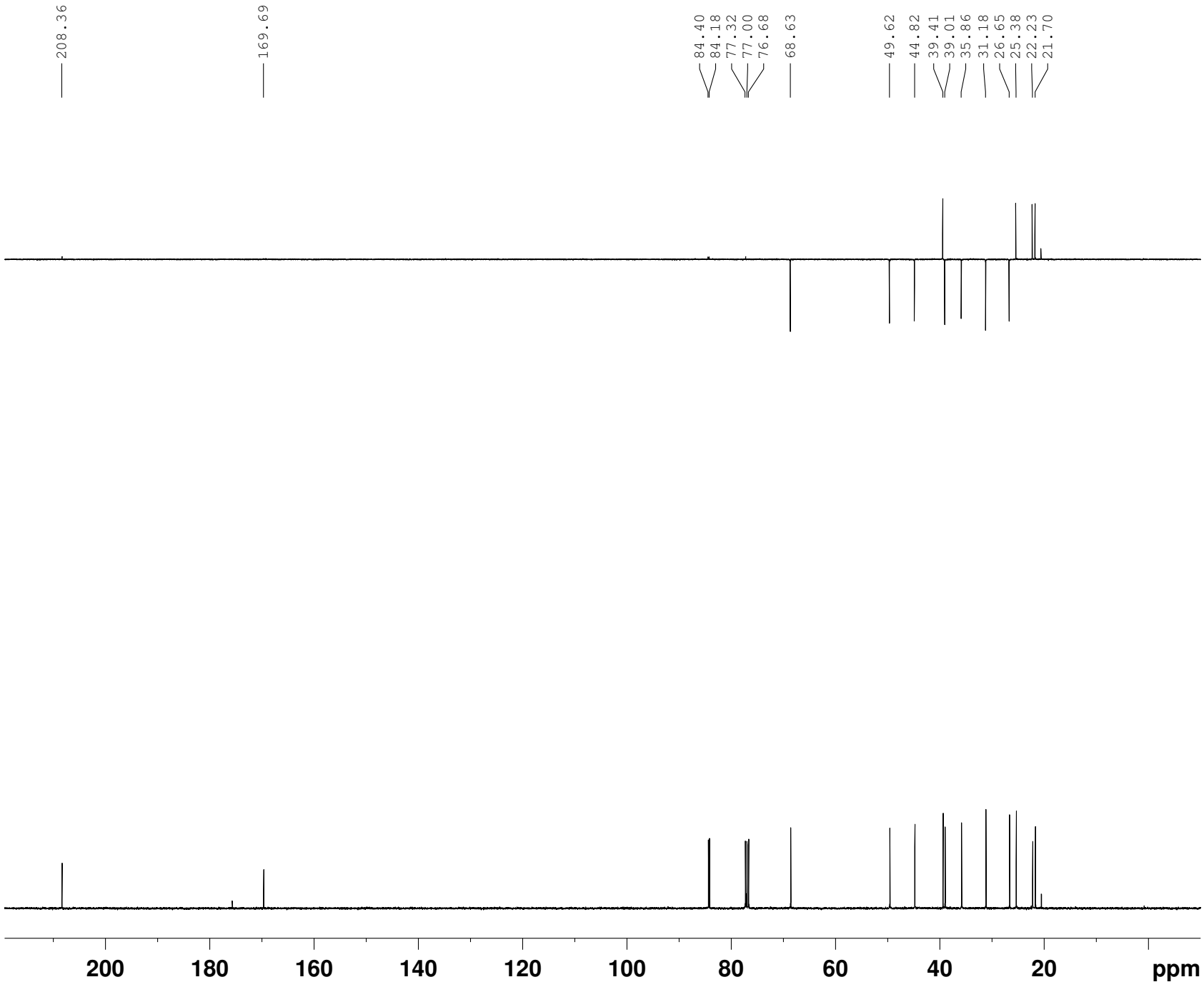
======== CHANNEL f1 ========

SFO1	100.6228298 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127802 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



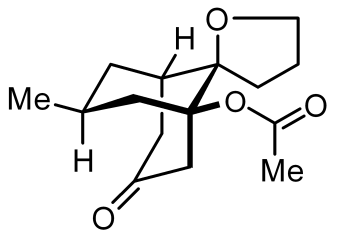
19c



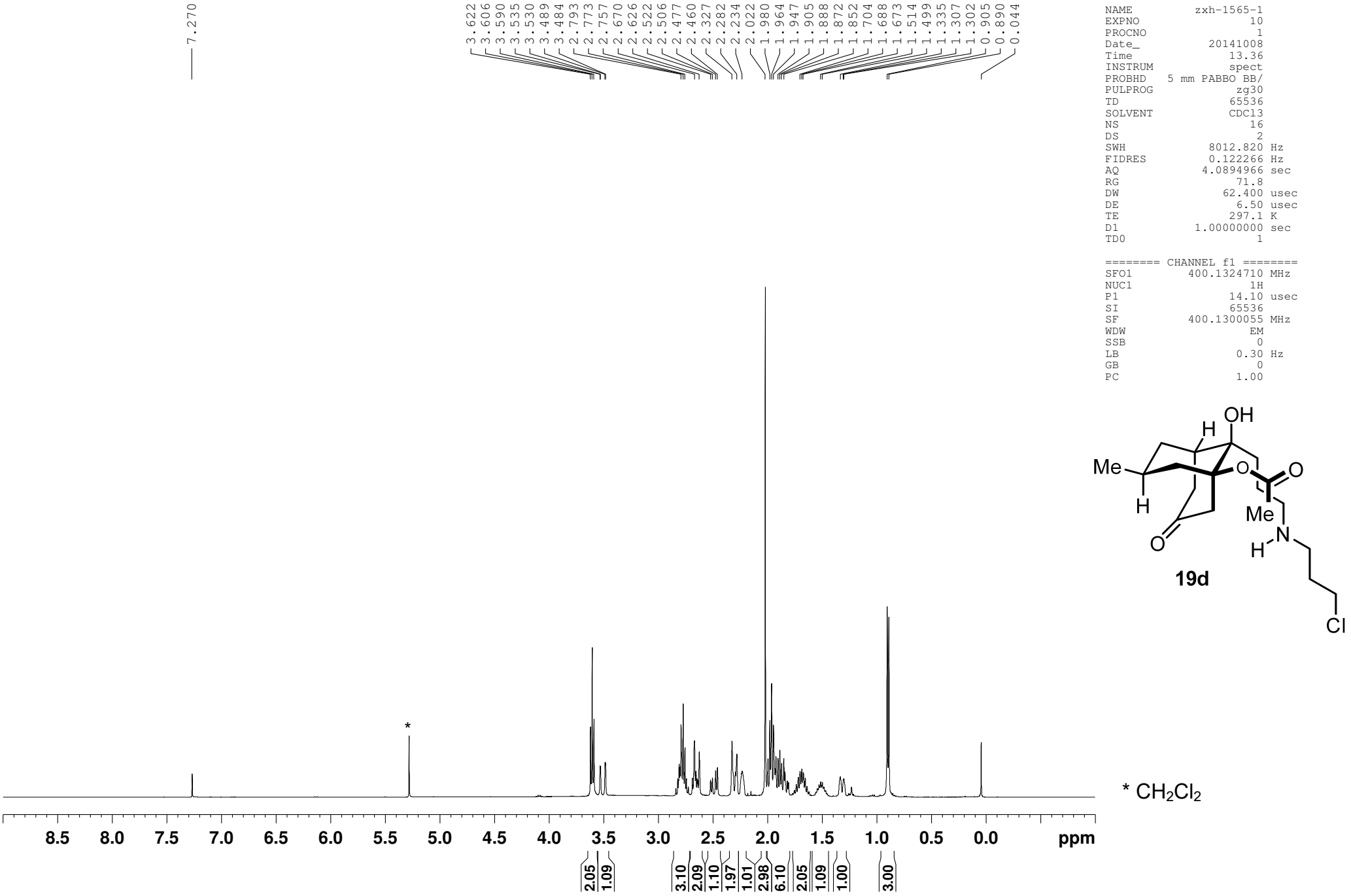



```
NAME          zxh-2402-1
EXPNO                 12
PROCNO                 1
Date_           20170302
Time               17.22
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG        deptsp135
TD                 65536
SOLVENT            CDCl3
NS                    50
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  1820
DW                20.800 usec
DE                 6.50 usec
TE                292.6 K
CNST2         145.0000000
D1              2.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                13C
P1                14.70 usec
P13             2000.00 usec
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



19c

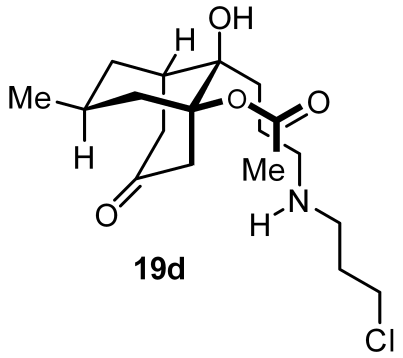

7.270
3.622
3.606
3.590
3.535
3.530
3.489
3.484
2.793
2.773
2.757
2.670
2.626
2.522
2.506
2.477
2.460
2.327
2.282
2.234
2.022
1.980
1.964
1.947
1.905
1.888
1.872
1.852
1.704
1.688
1.673
1.514
1.499
1.335
1.307
1.302
0.905
0.890
0.044
NAME zxh-1565-1
EXPNO 10
PROCNO 1
Date_ 20141008
Time 13.36
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 71.8
DW 62.400 usec
DE 6.50 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300055 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
H
Me
O
O
H
Me
N
H
O
Cl
19d
*
* CH2Cl2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.05
1.09
3.10
2.09
1.10
1.97
1.01
2.98
6.10
2.05
1.09
1.00
3.00

208.55
170.33
85.94
77.32
77.00
76.68
72.49
49.81
49.74
46.39
43.85
42.80
38.98
36.53
35.20
32.30
31.54
25.64
22.53
22.25
21.76

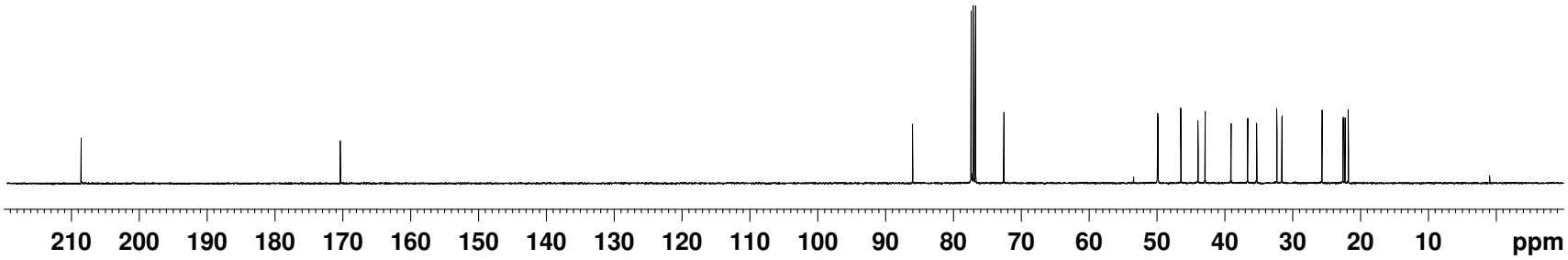
NAME	zxh-1565-1
EXPNO	11
PROCNO	1
Date_	20141008
Time	14.23
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	800
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	1030
DW	20.800 usec
DE	6.50 usec
TE	298.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

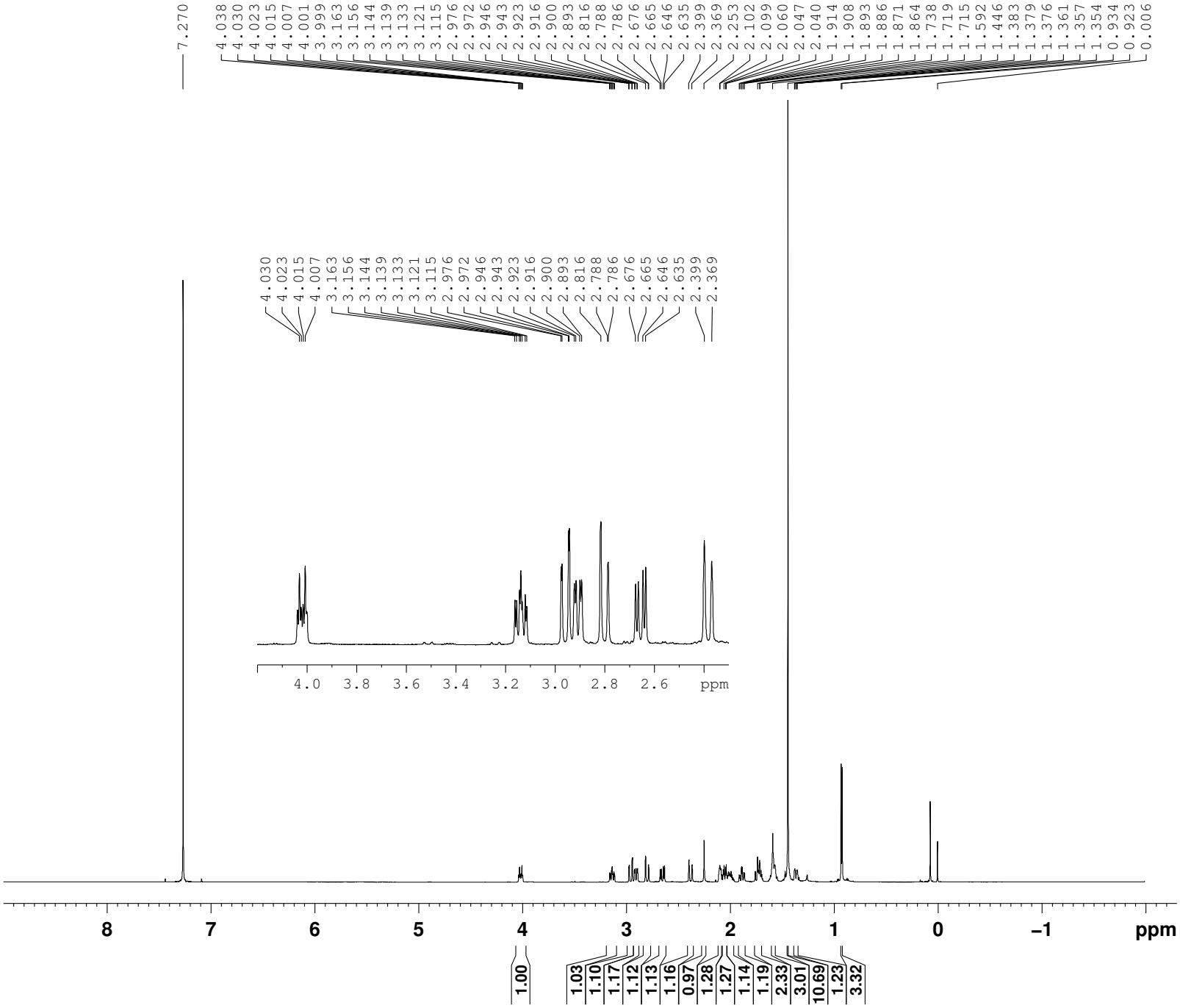
======== CHANNEL f1 ========

SFO1	100.6228298 MHz
NUC1	13C
P1	12.00 usec
SI	32768
SF	100.6127751 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

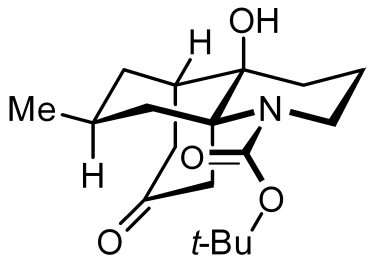


19d



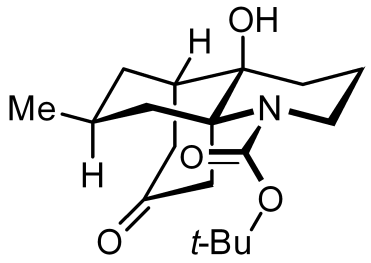


Title	zxh-2085-H
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	32
Receiver Gain	36
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.7070
Acquisition Date	2016-06-21
Modification Date	2016-06-21
Spectrometer Frequency	599.85
Spectral Width	9598.1
Lowest Frequency	-1200.0
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

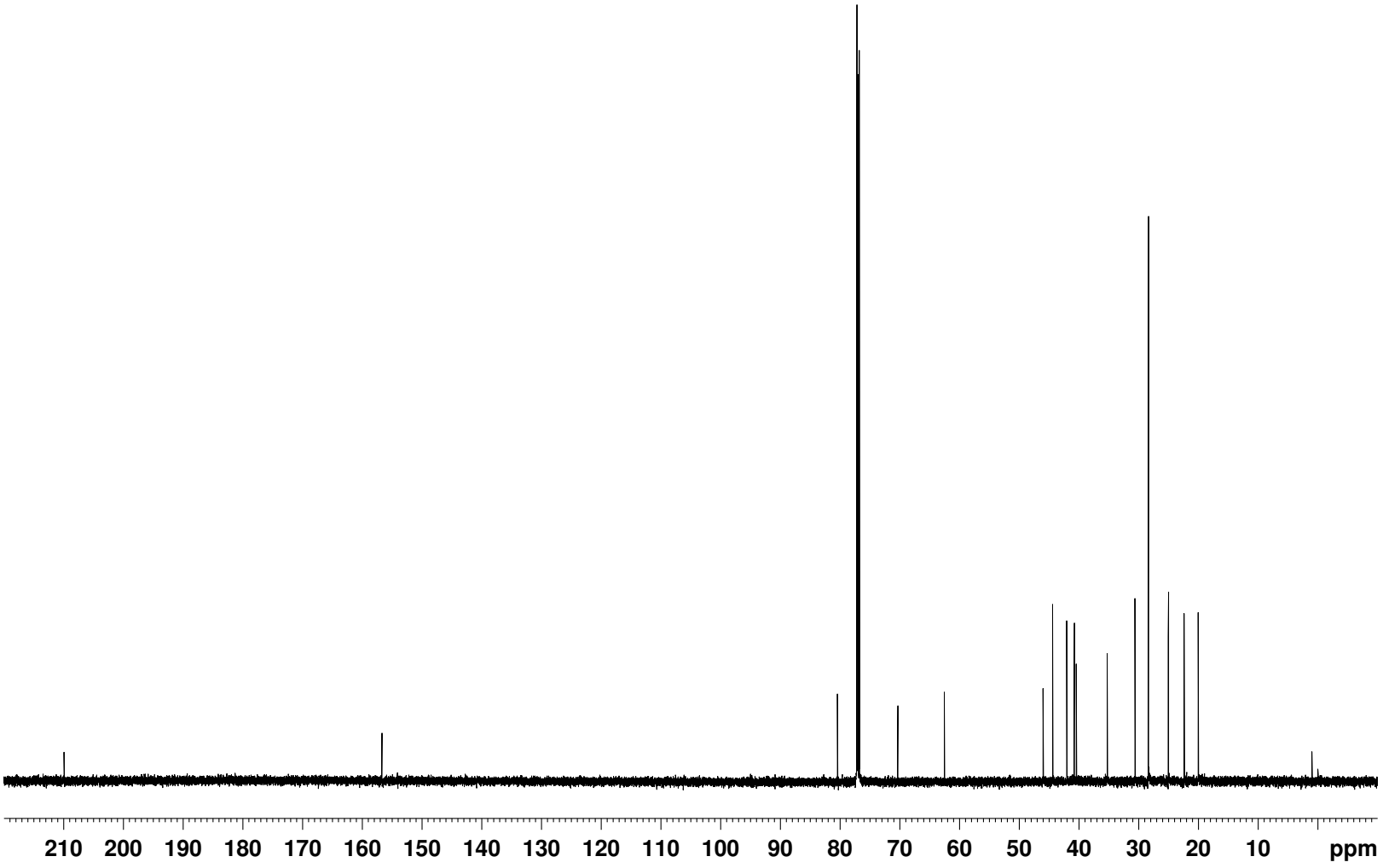


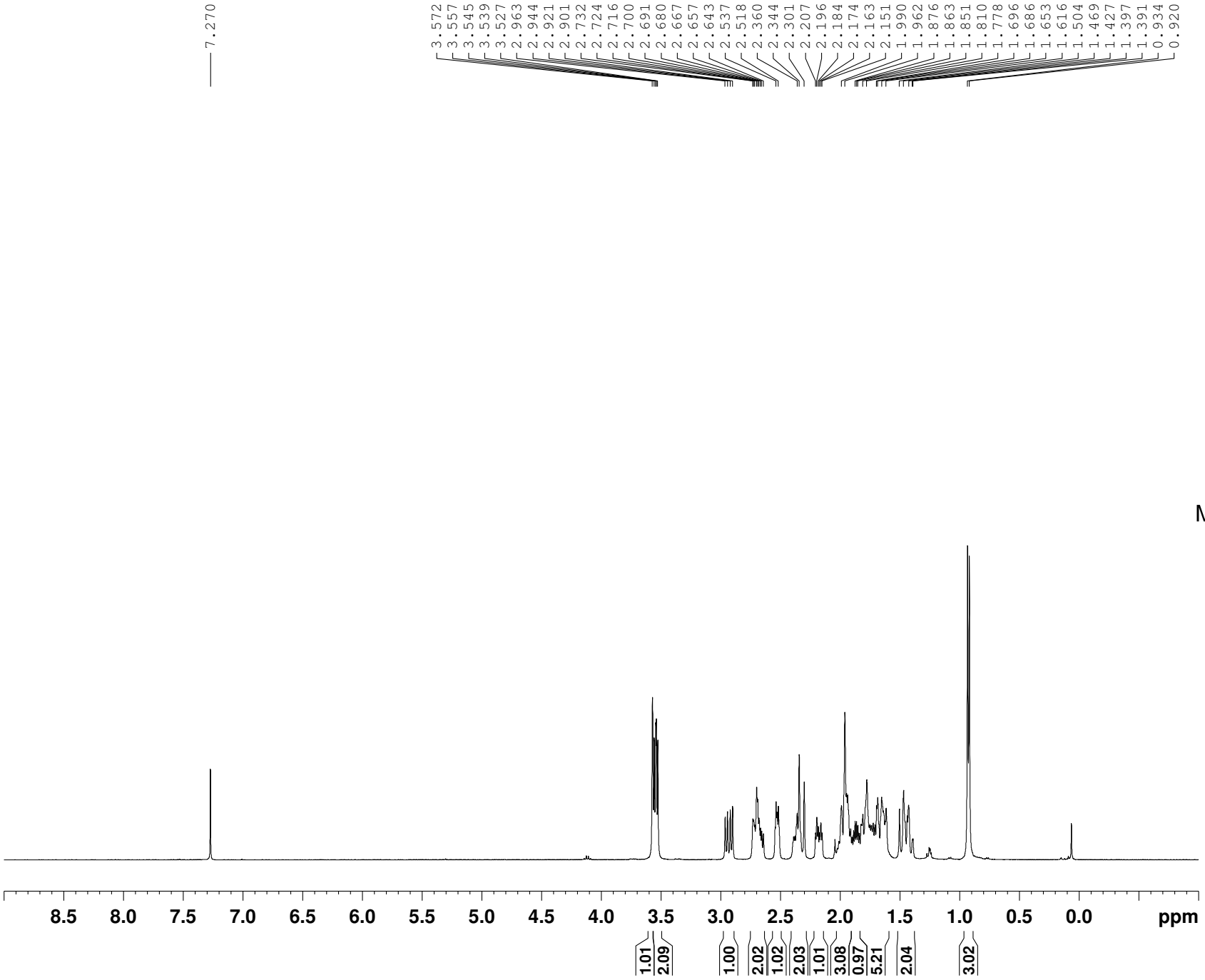
19e

Title	zxh-2085-C
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	1594
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.8692
Acquisition Date	2016-06-21
Modification Date	2016-06-21
Spectrometer Frequency	150.85
Spectral Width	37700.3
Lowest Frequency	-2258.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



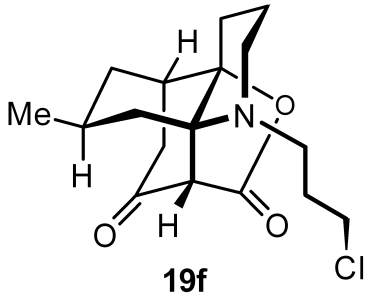
19e



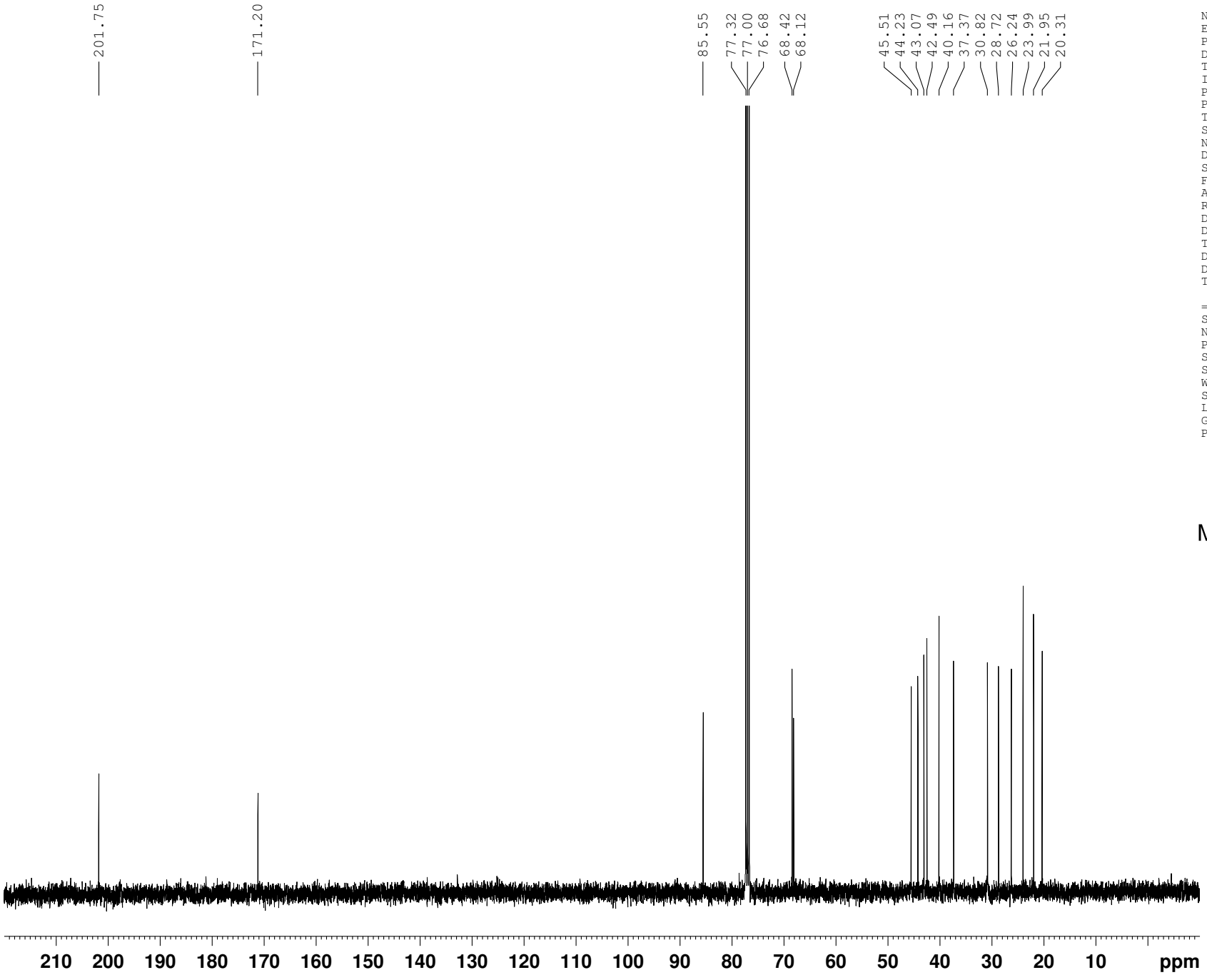



```
NAME            zxh-2176
EXPNO                 10
PROCNO                 1
Date_           20151215
Time               17.03
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     4
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   144
DW                62.400 usec
DE                 6.50 usec
TE                289.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                 65536
SF           400.1300058 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

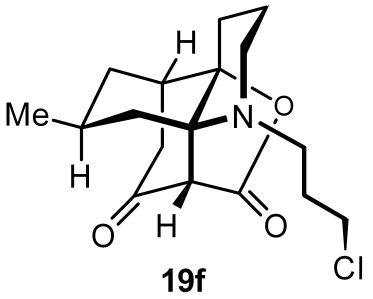


19f



NAME	zxh-2176
EXPNO	11
PROCNO	1
Date_	20151215
Time	17.15
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	200
DS	2
SWH	26041.666 Hz
FIDRES	0.397364 Hz
AQ	1.2583412 sec
RG	2050
DW	19.200 usec
DE	6.50 usec
TE	290.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	100.6238364 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127748 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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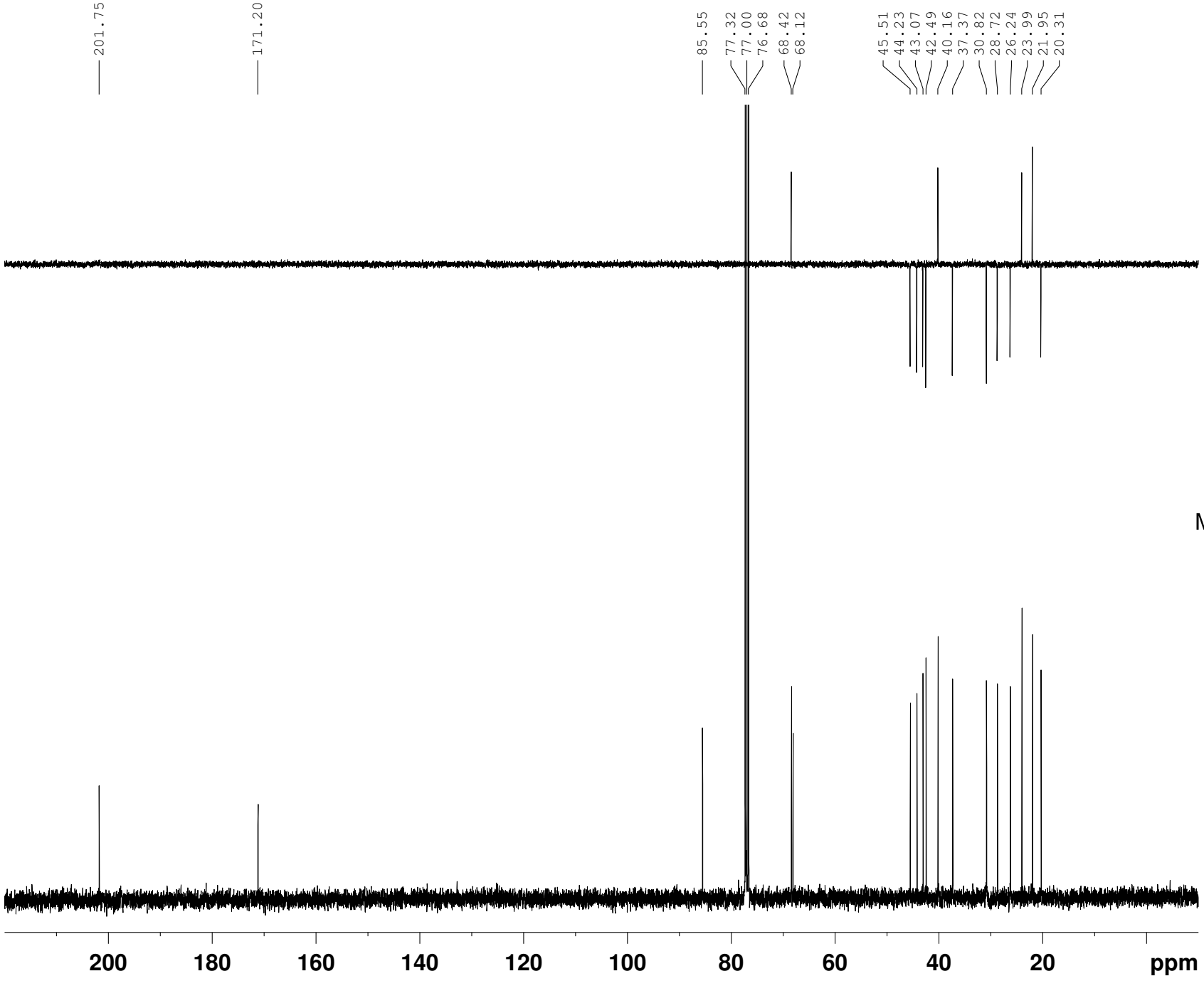
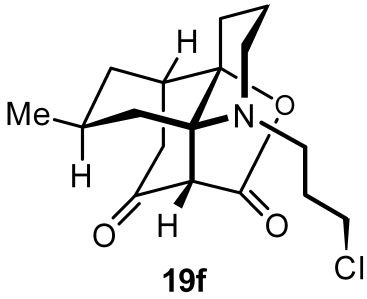



```
NAME            zxh-2176
EXPNO                 11
PROCNO                 1
Date_           20151215
Time               17.15
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    2
SWH           26041.666 Hz
FIDRES         0.397364 Hz
AQ            1.2583412 sec
RG                 2050
DW               19.200 usec
DE                6.50 usec
TE               290.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6238364 MHz
NUC1                13C
P1                14.70 usec
SI                32768
SF          100.6127748 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



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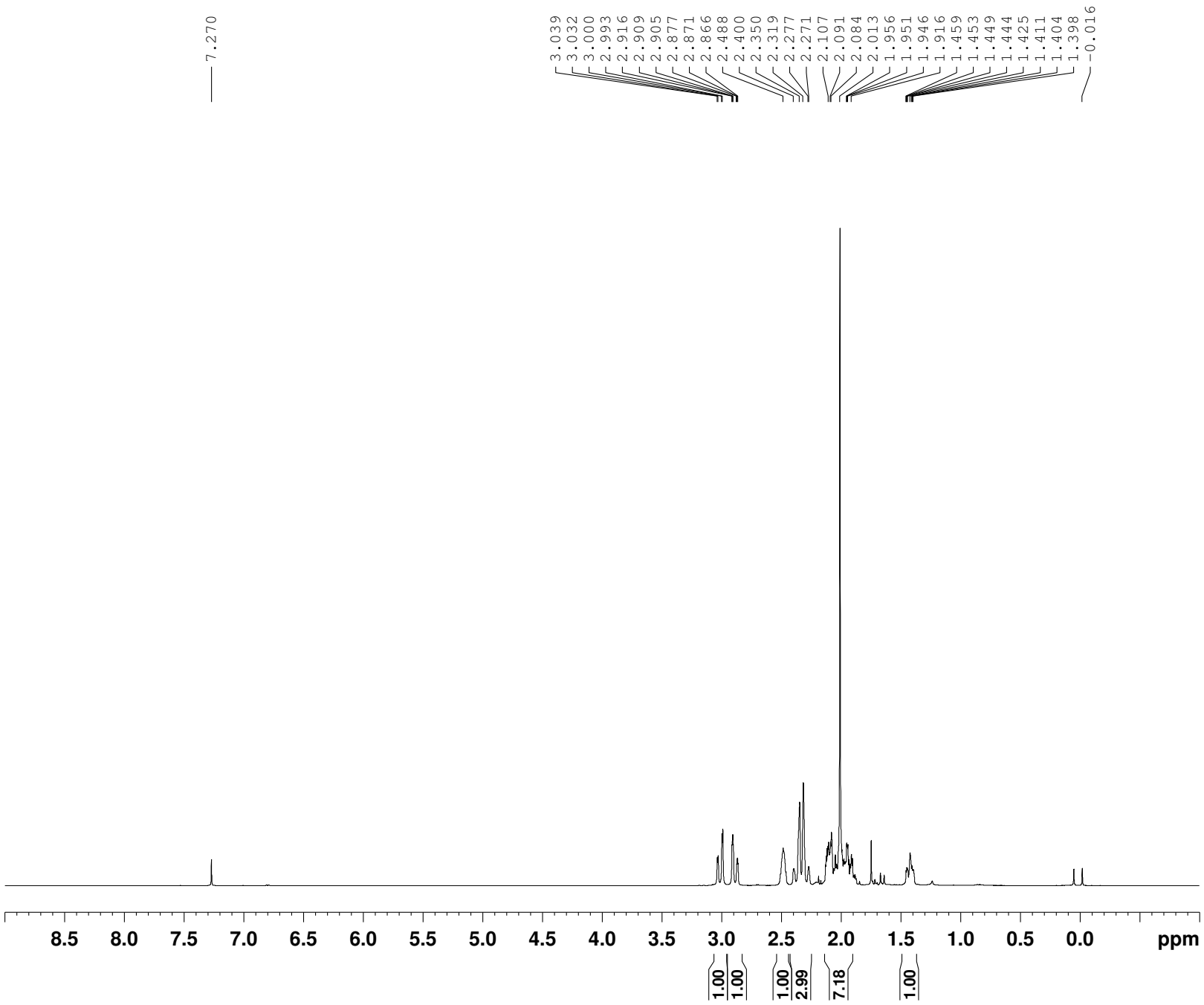
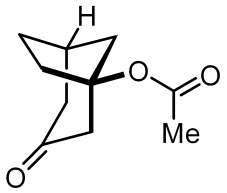



```
NAME          zxh-2326-2
EXPNO                 10
PROCNO                 1
Date_           20160528
Time               23.32
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   144
DW                62.400 usec
DE                 6.50 usec
TE                294.7 K
D1           1.00000000 sec
TD0                    1

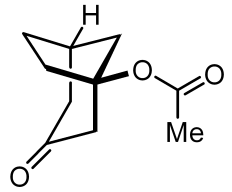
======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.79 usec
SI                 65536
SF           400.1300054 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



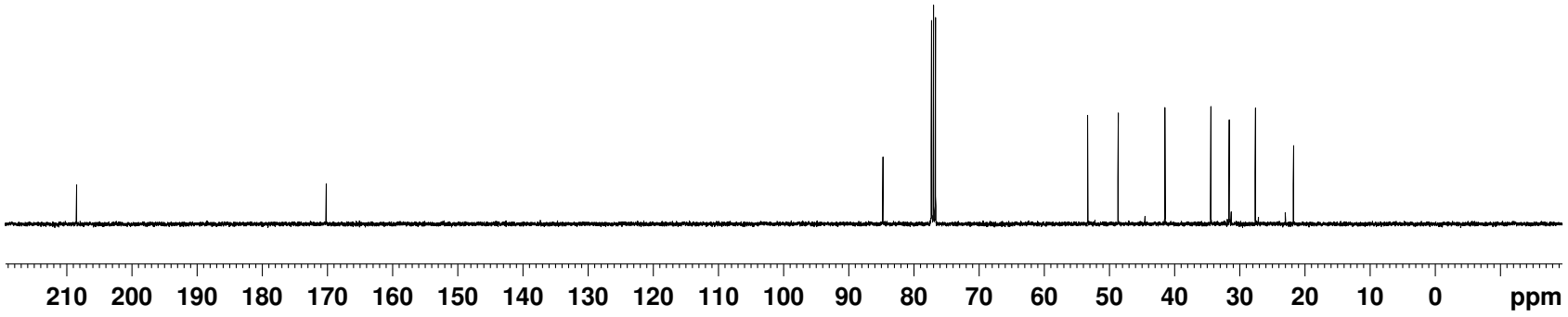
19g

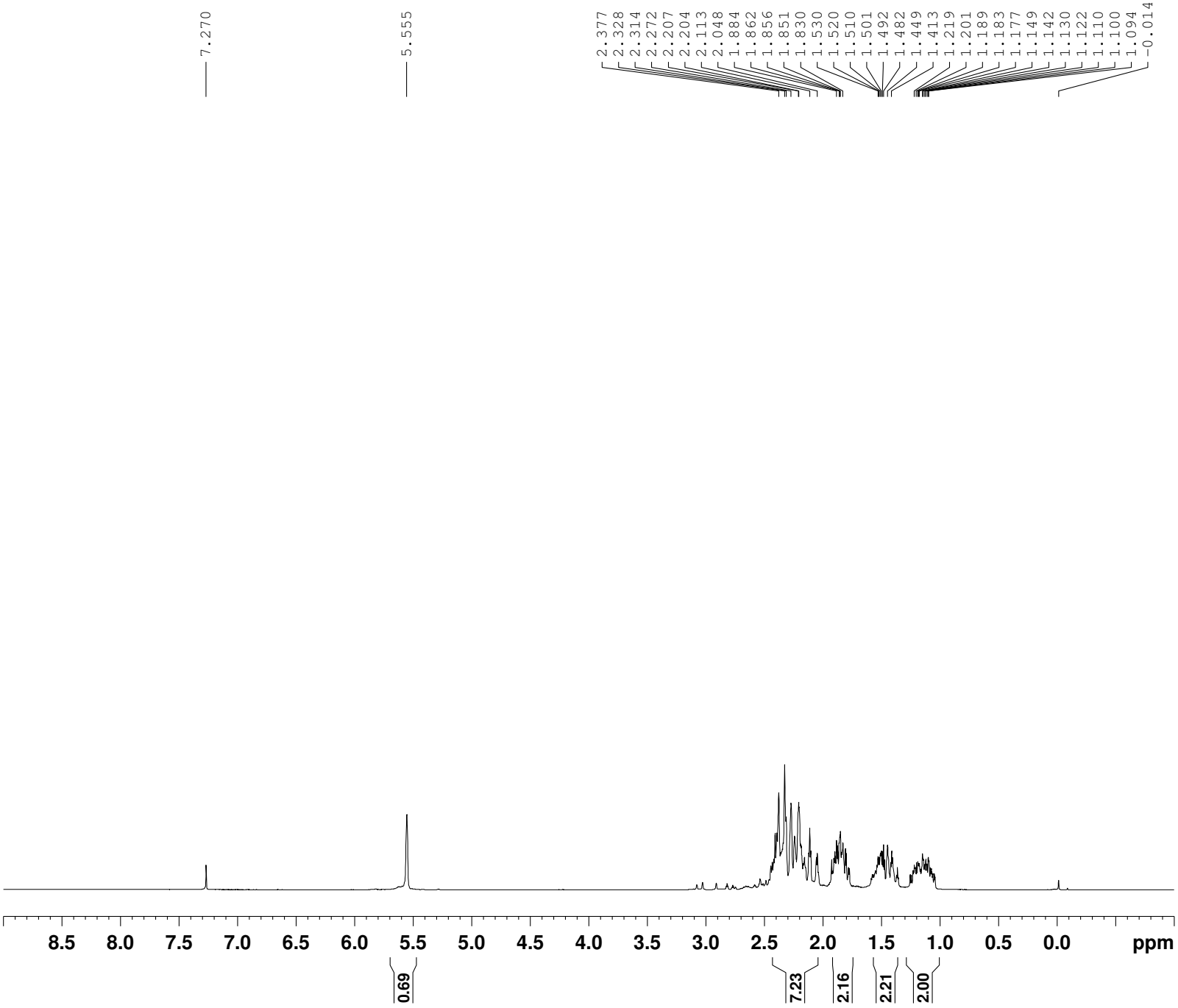

```
NAME          zxh-2326-2
EXPNO                 11
PROCNO                 1
Date_           20160528
Time               23.43
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  150
DS                    2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 2050
DW               20.800 usec
DE                6.50 usec
TE               295.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                12.00 usec
SI                32768
SF          100.6127736 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

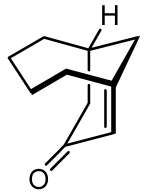


19g



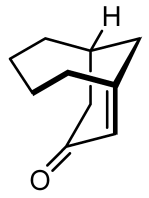


Title	zxh-2334-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Spectrometer	mercury
Author	fanchuan
Solvent	CDCl3
Temperature	3.0
Pulse Sequence	s2pul
Number of Scans	4
Receiver Gain	0
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.9971
Acquisition Date	2016-06-24
Modification Date	2016-06-24
Spectrometer Frequency	300.08
Spectral Width	4803.1
Lowest Frequency	-601.1
Nucleus	1H
Acquired Size	9592
Spectral Size	32768

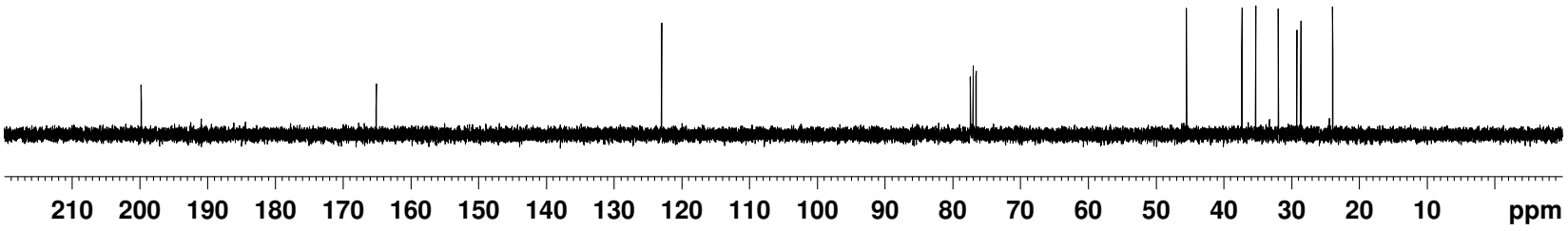


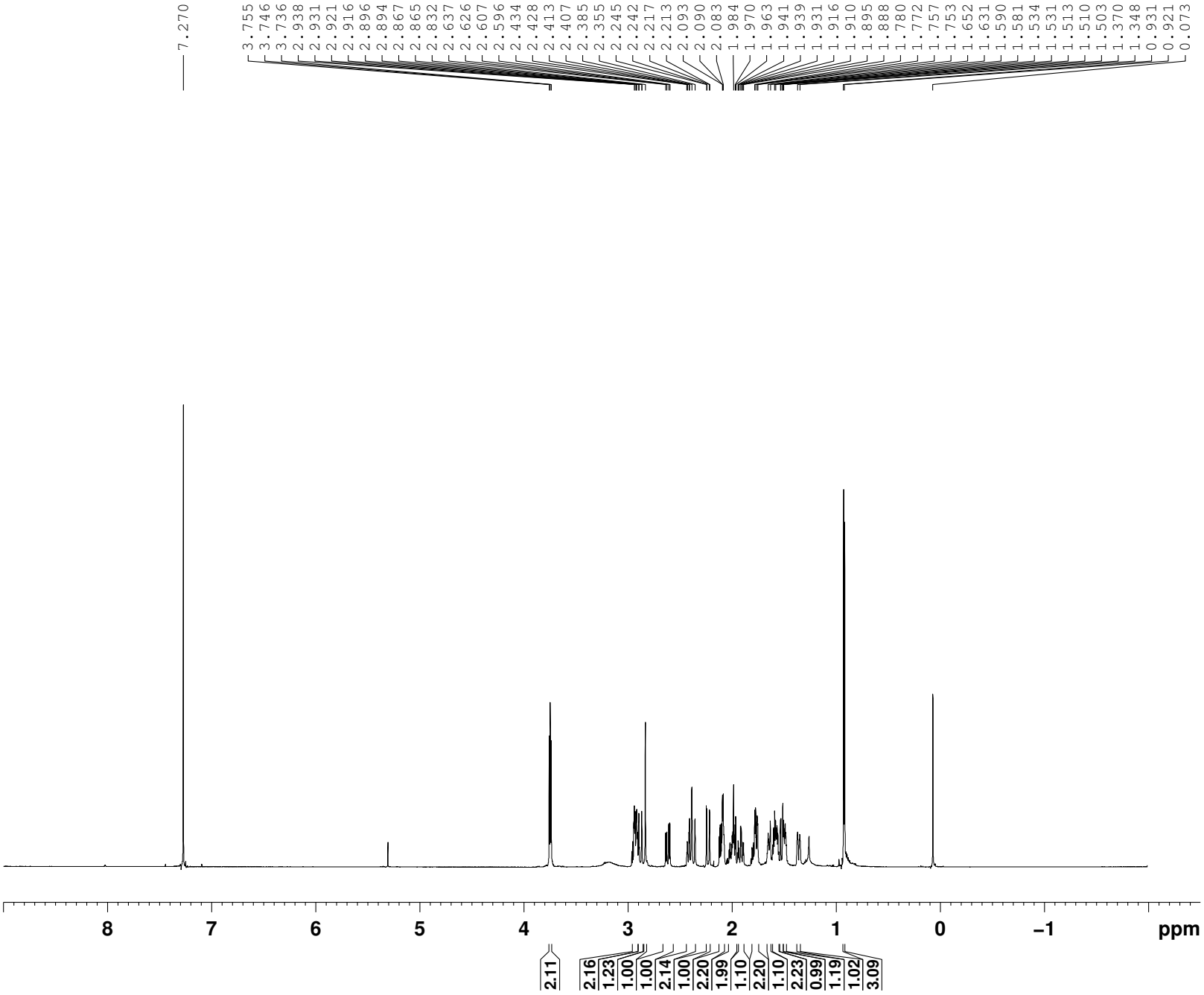
19h

Title	zxh-2334-C
Comment	13C OBSERVE
Origin	Varian
Spectrometer	mercury
Author	fanchuan
Solvent	CDCl3
Temperature	3.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	20
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.8150
Acquisition Date	2016-06-24
Modification Date	2016-06-24
Spectrometer Frequency	75.46
Spectral Width	18867.9
Lowest Frequency	-1134.1
Nucleus	13C
Acquired Size	34246
Spectral Size	131072

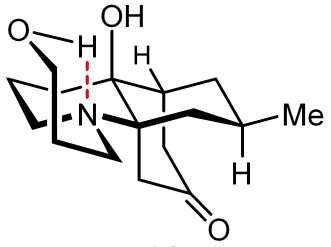


19h





Title	zxh-1709-H
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
PulseSequence	s2pul
NumberofScans	8
ReceiverGain	30
RelaxationDelay	1.0000
PulseWidth	0.0000
AcquisitionTime	1.7070
AcquisitionDate	2015-01-07
ModificationDate	2015-01-07
SpectrometerFrequency	599.85
SpectralWidth	9598.1
LowestFrequency	-1200.0
Nucleus	1H
AcquiredSize	16384
SpectralSize	32768

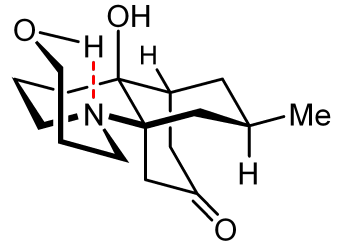


21

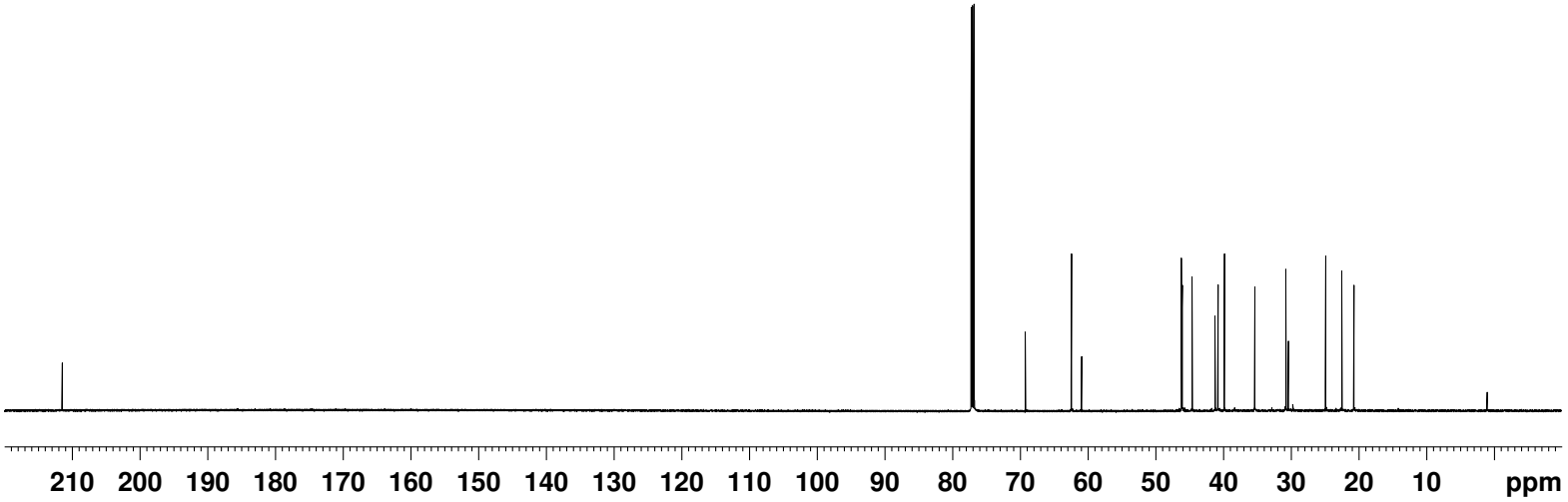
211.408

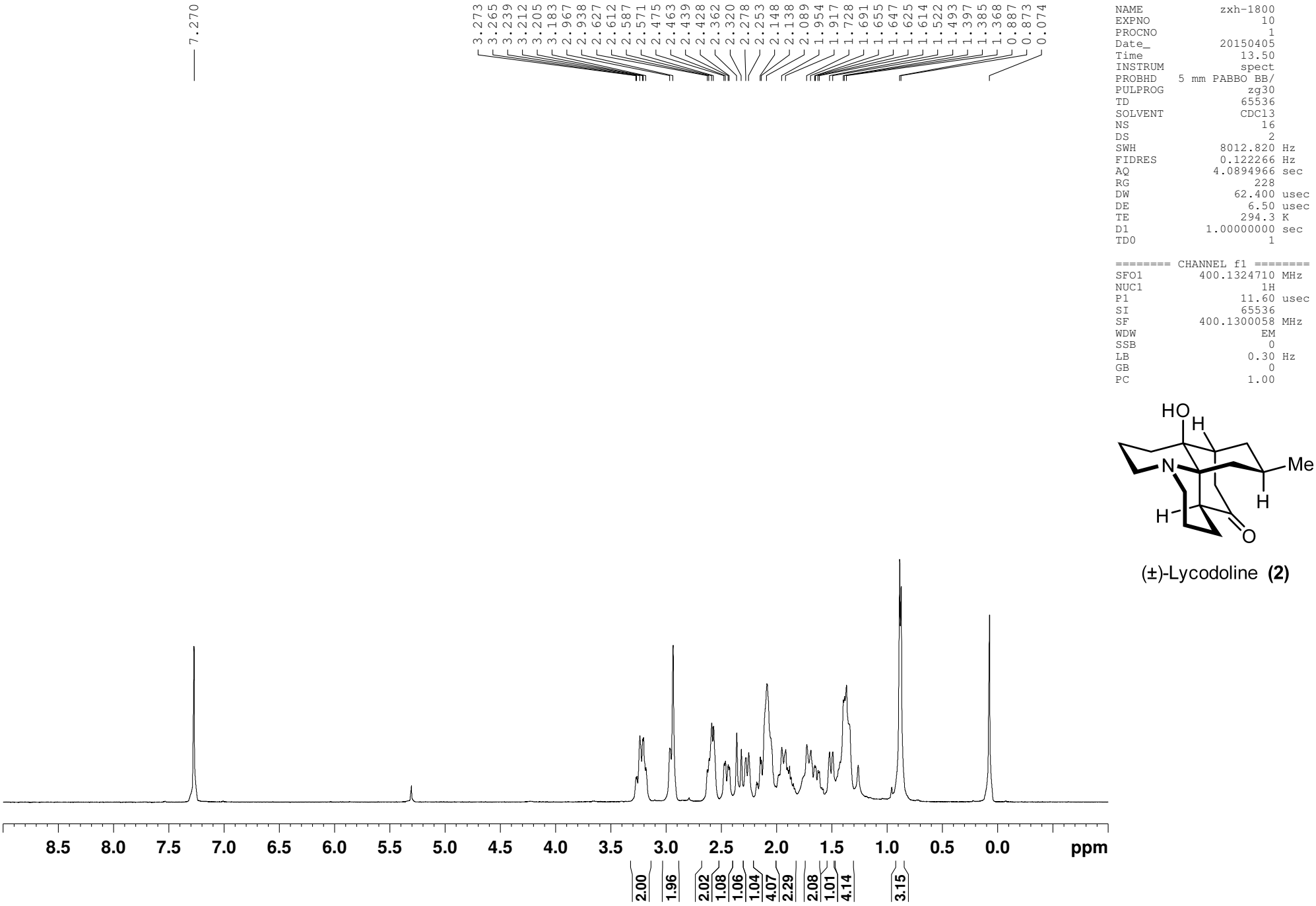
77.210
76.999
76.787
69.200
62.412
60.913
46.137
46.043
44.592
41.174
40.740
39.799
35.308
30.737
30.358
24.863
22.472
20.674

Title	zxh-1709-C
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	15000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.8692
Acquisition Date	2015-01-07
Modification Date	2015-01-07
Spectrometer Frequency	150.85
Spectral Width	3700.3
Lowest Frequency	-2258.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

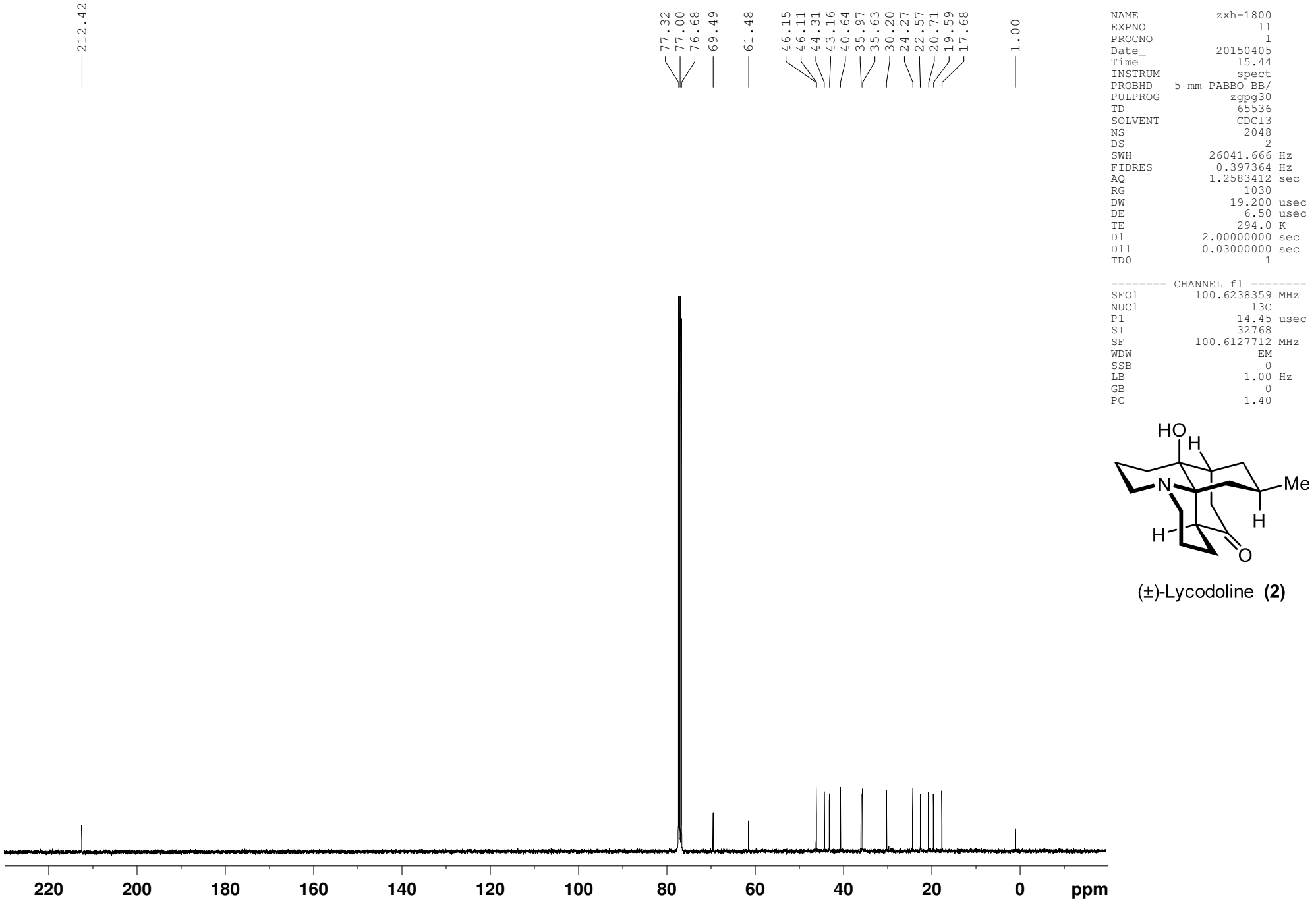


21





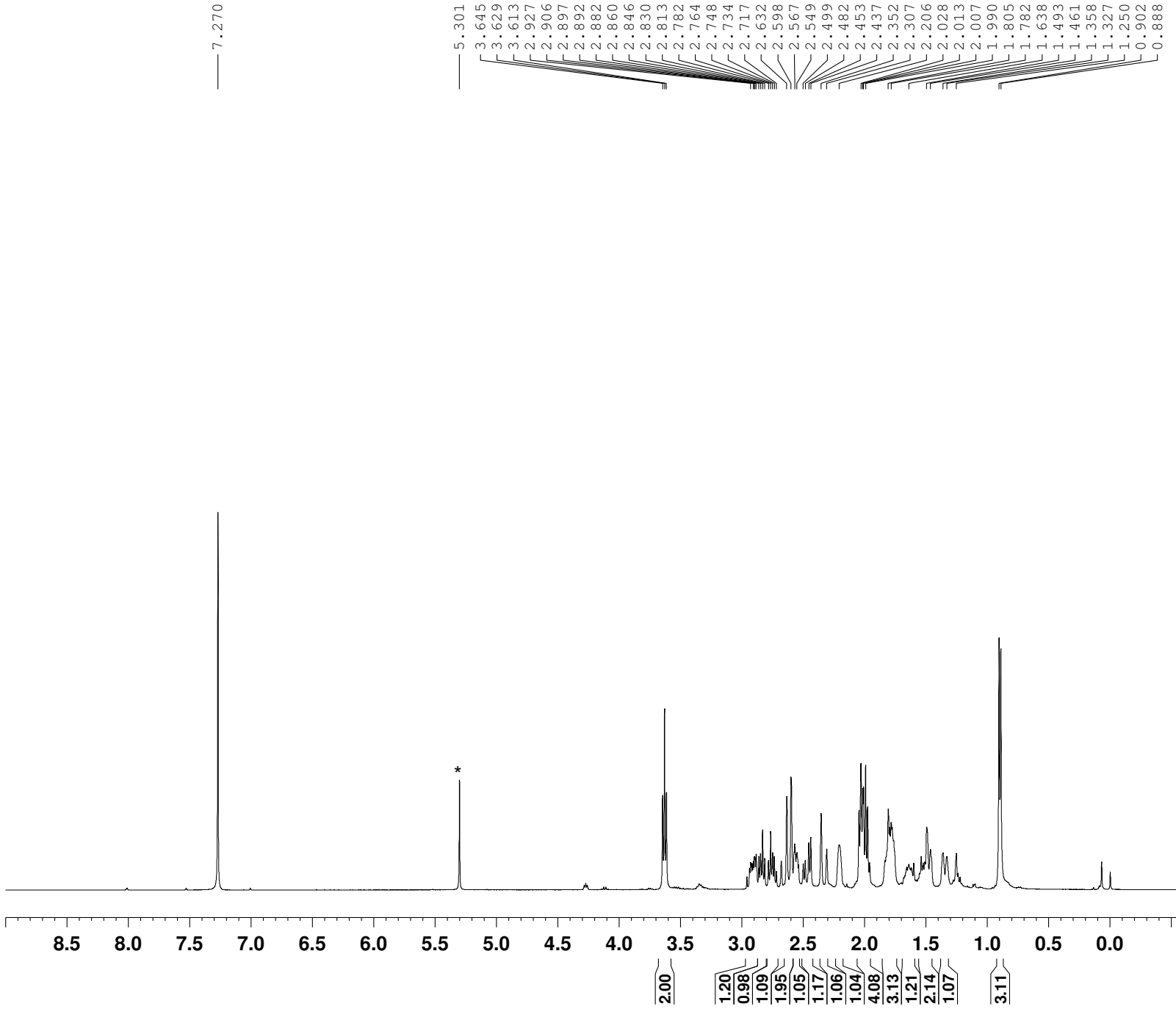
(±)-Lycodoline **(2)**



NAME	zxh-1800
EXPNO	11
PROCNO	1
Date_	20150405
Time	15.44
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2048
DS	2
SWH	26041.666 Hz
FIDRES	0.397364 Hz
AQ	1.2583412 sec
RG	1030
DW	19.200 usec
DE	6.50 usec
TE	294.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

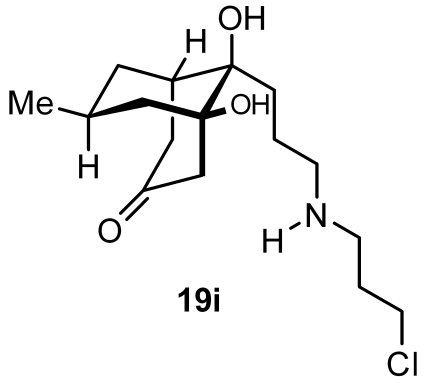
======== CHANNEL f1 ========	
SFO1	100.6238359 MHz
NUC1	13C
P1	14.45 usec
SI	32768
SF	100.6127712 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

(±)-Lycodoline **(2)**



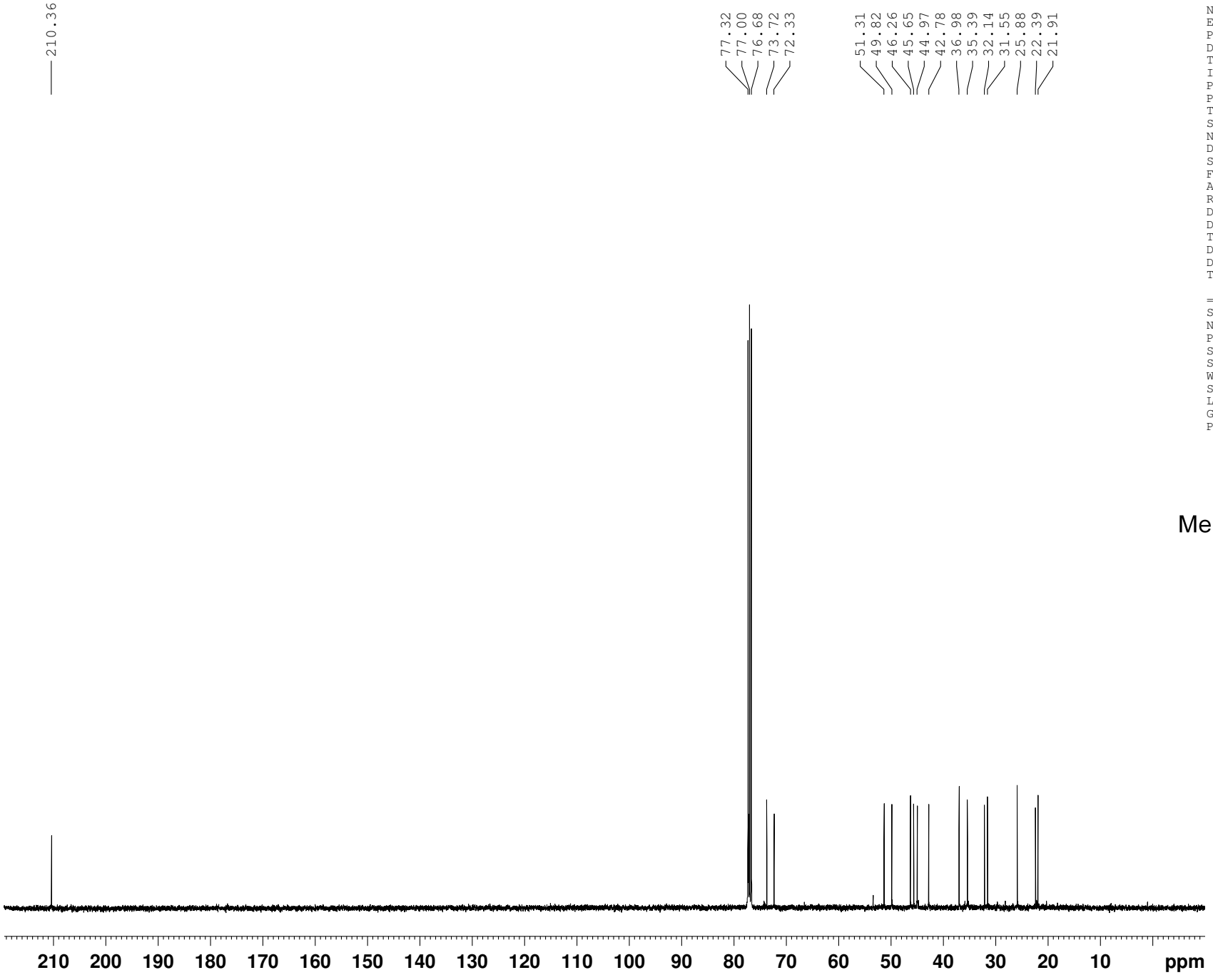

```
NAME            zxh-2405
EXPNO                 11
PROCNO                 1
Date_           20170306
Time               17.22
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   144
DW                62.400 usec
DE                 6.50 usec
TE                292.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                  1H
P1                 10.92 usec
SI                 65536
SF            400.1300058 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



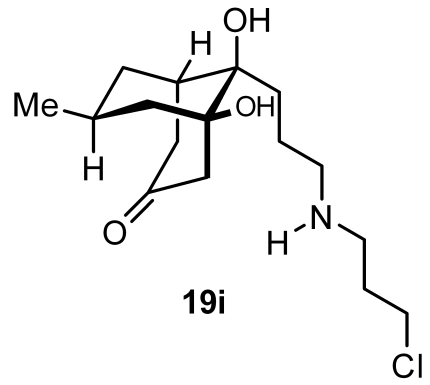
19i

* CH_2Cl_2

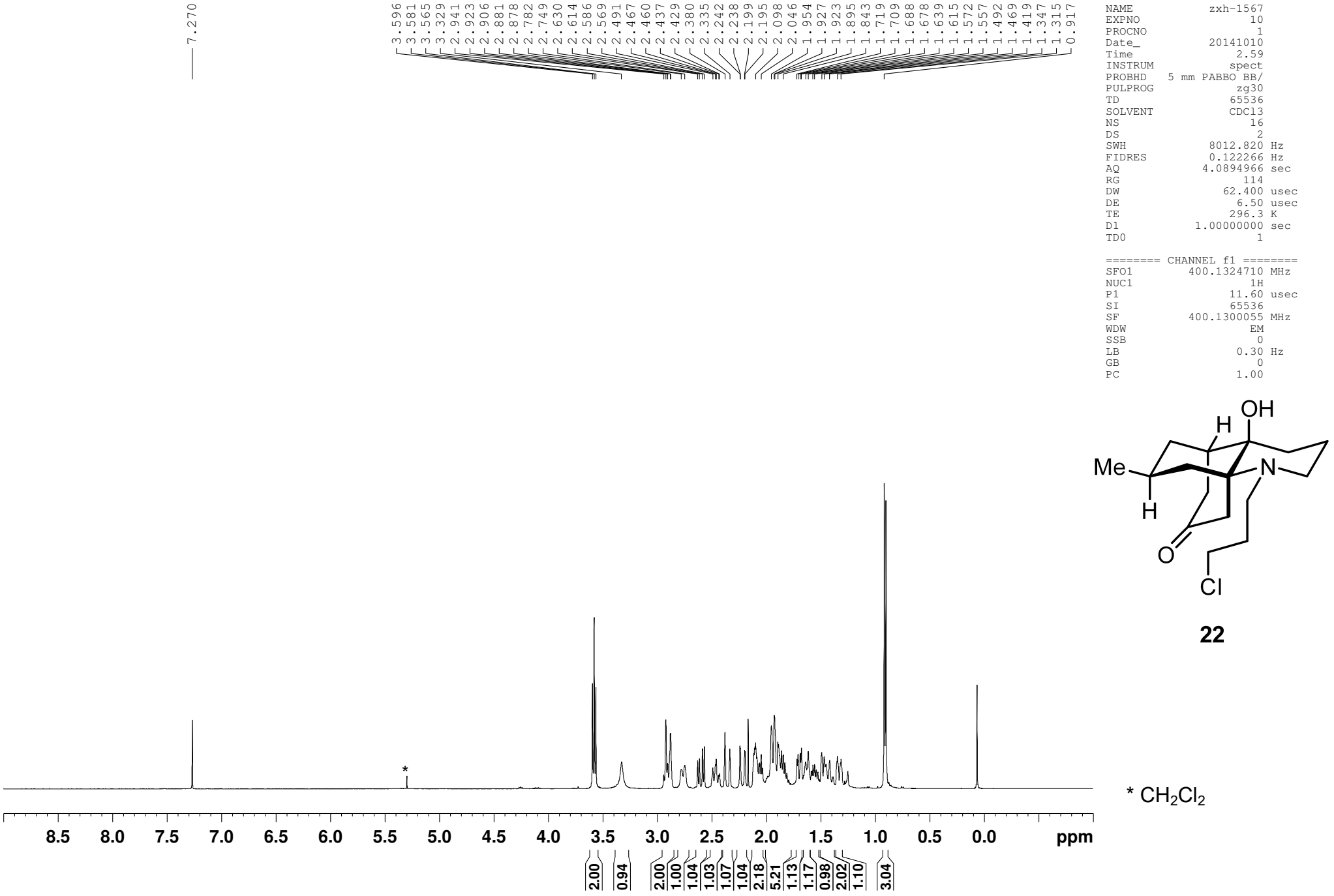



```
NAME            zxh-2405
EXPNO                 10
PROCNO                 1
Date_           20170306
Time               17.20
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   600
DS                     2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG                  1820
DW                20.800 usec
DE                 6.50 usec
TE                292.7 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                  13C
P1                14.70 usec
SI                 32768
SF          100.6127736 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  1.40
```



19i

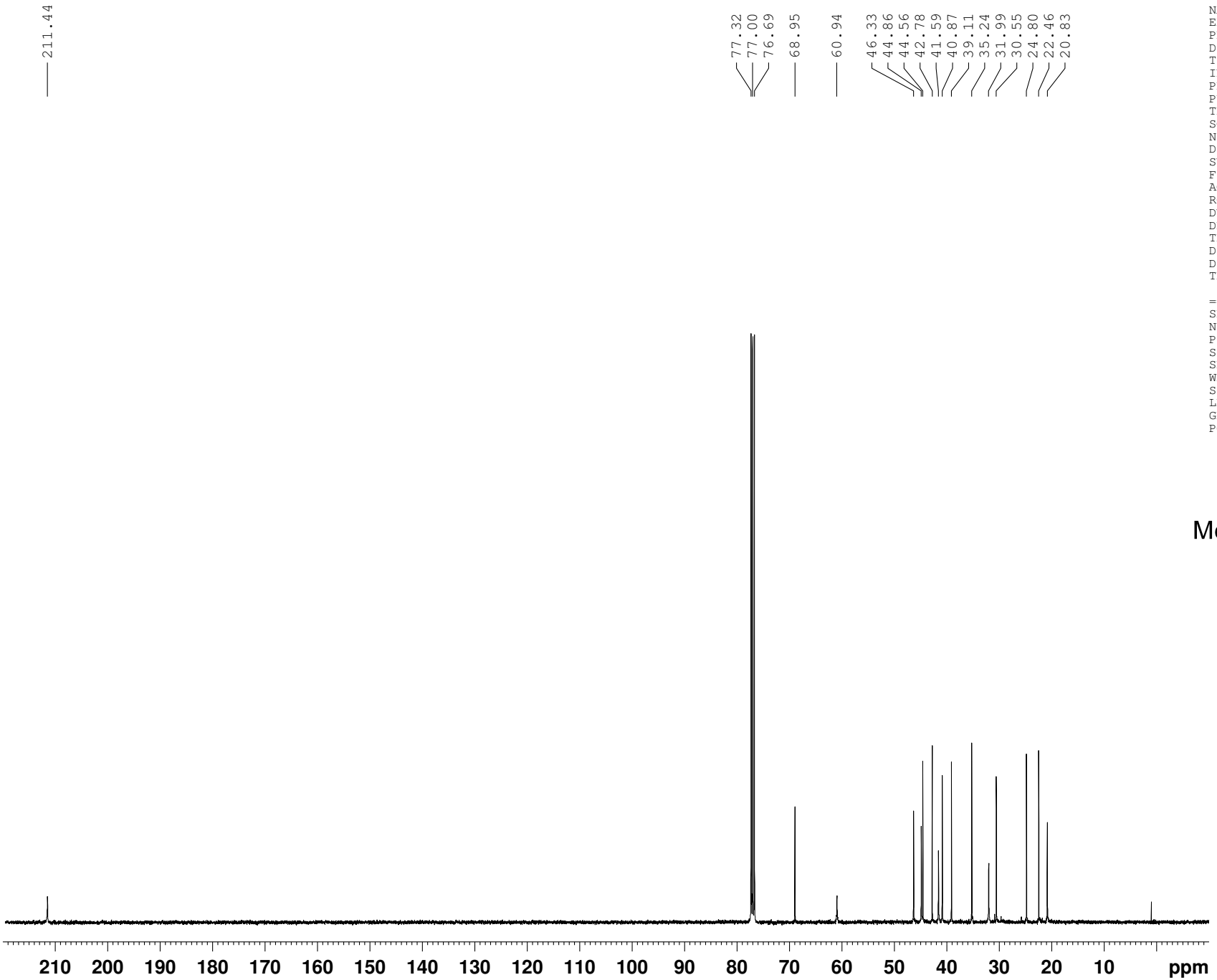



```
NAME            zxh-1567
EXPNO                 10
PROCNO                 1
Date_           20141010
Time                2.59
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   114
DW                62.400 usec
DE                 6.50 usec
TE                296.3 K
D1           1.00000000 sec
TD0                    1

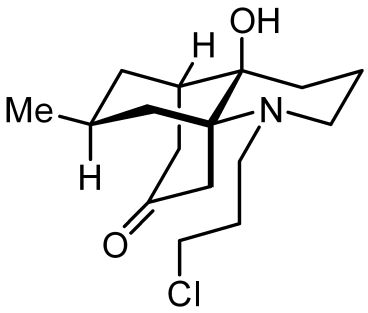
======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 11.60 usec
SI                 65536
SF           400.1300055 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                  1.00
```


22

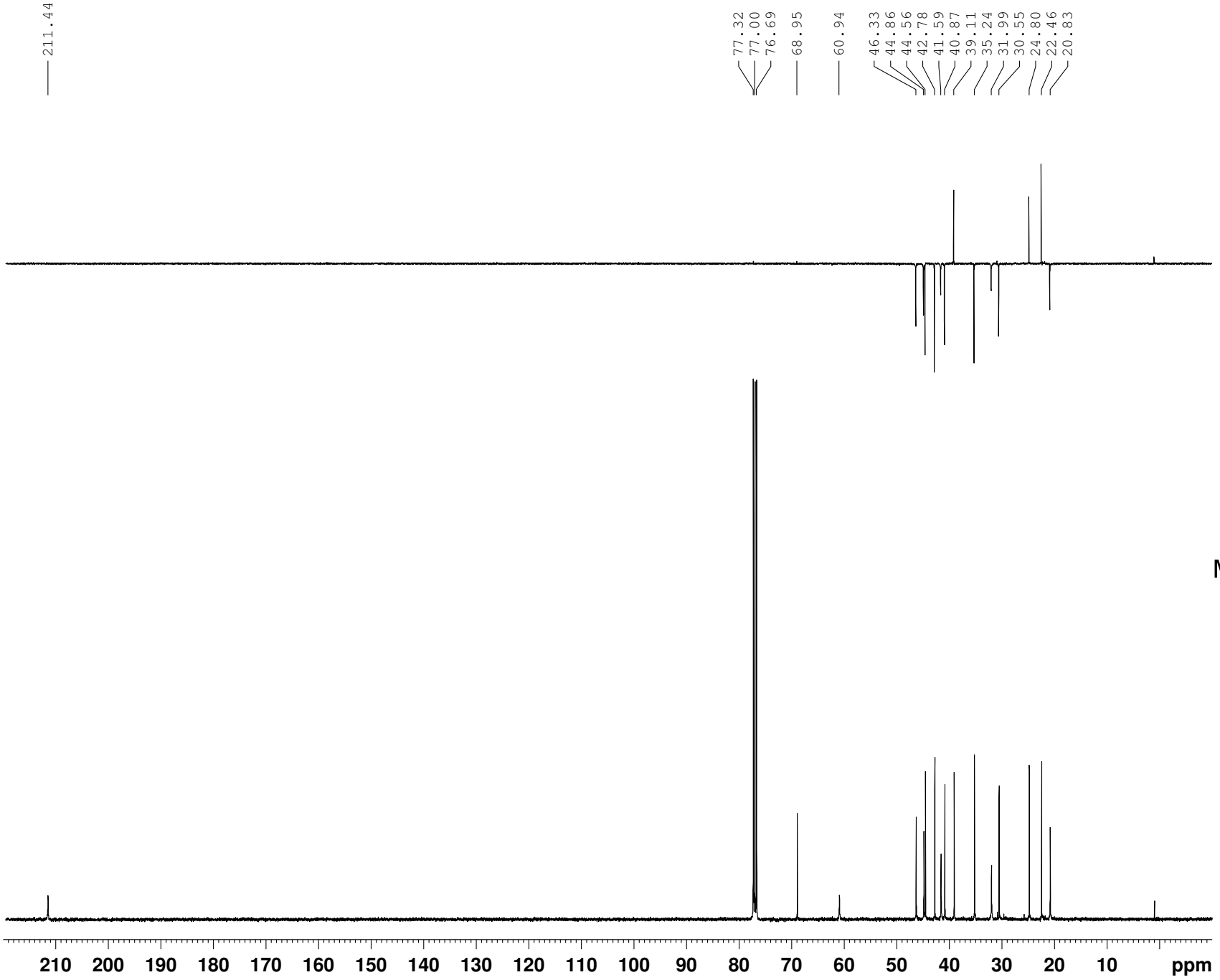
* CH_2Cl_2



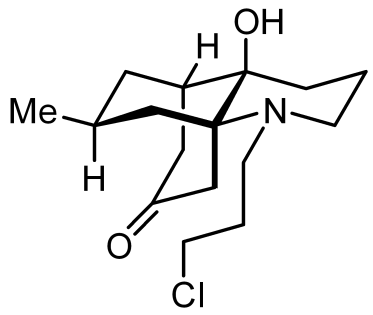
NAME	zxh-1567
EXPNO	11
PROCNO	1
Date_	20141010
Time	6.03
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	3200
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	297.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.45 usec
SI	32768
SF	100.6127714 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



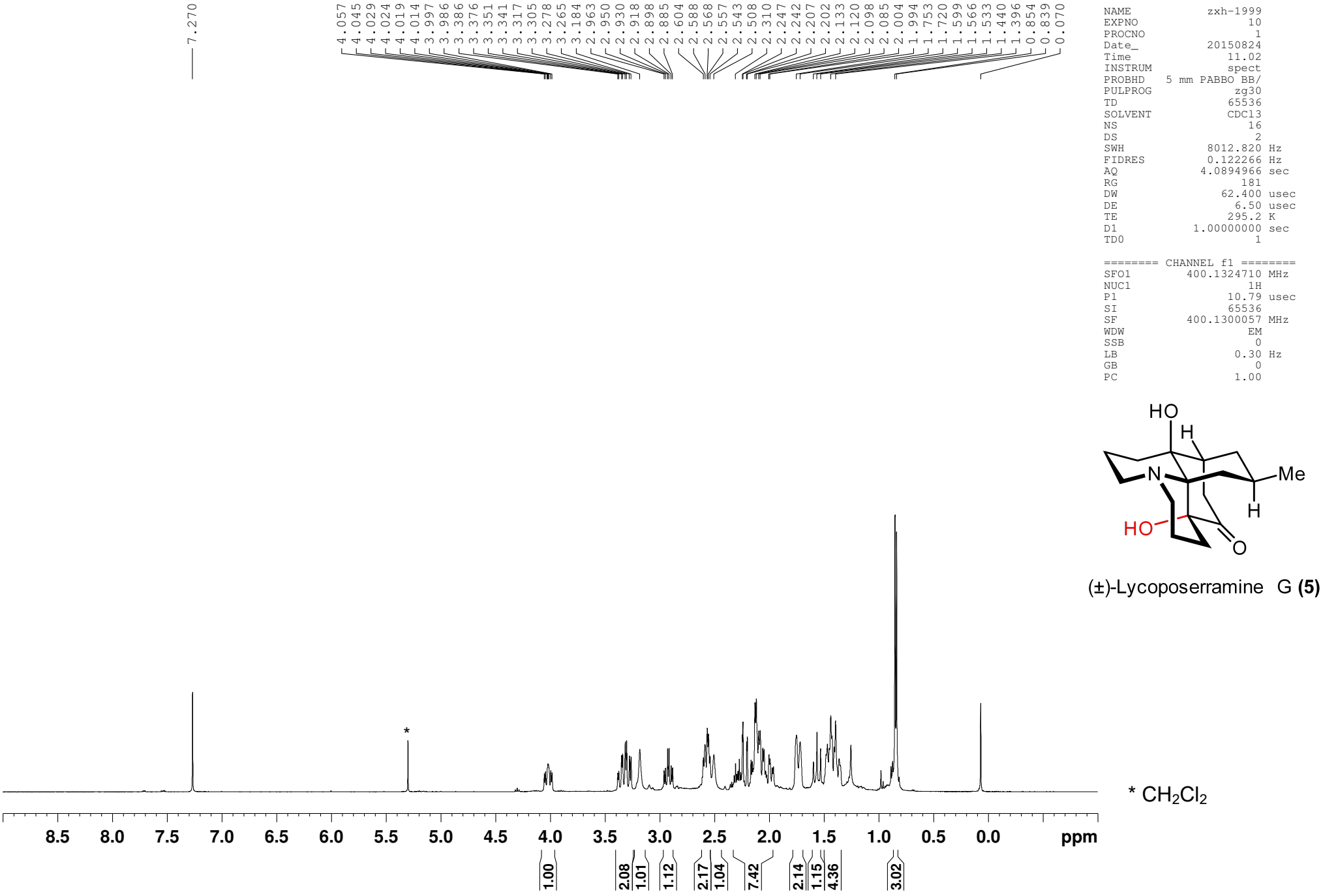
22

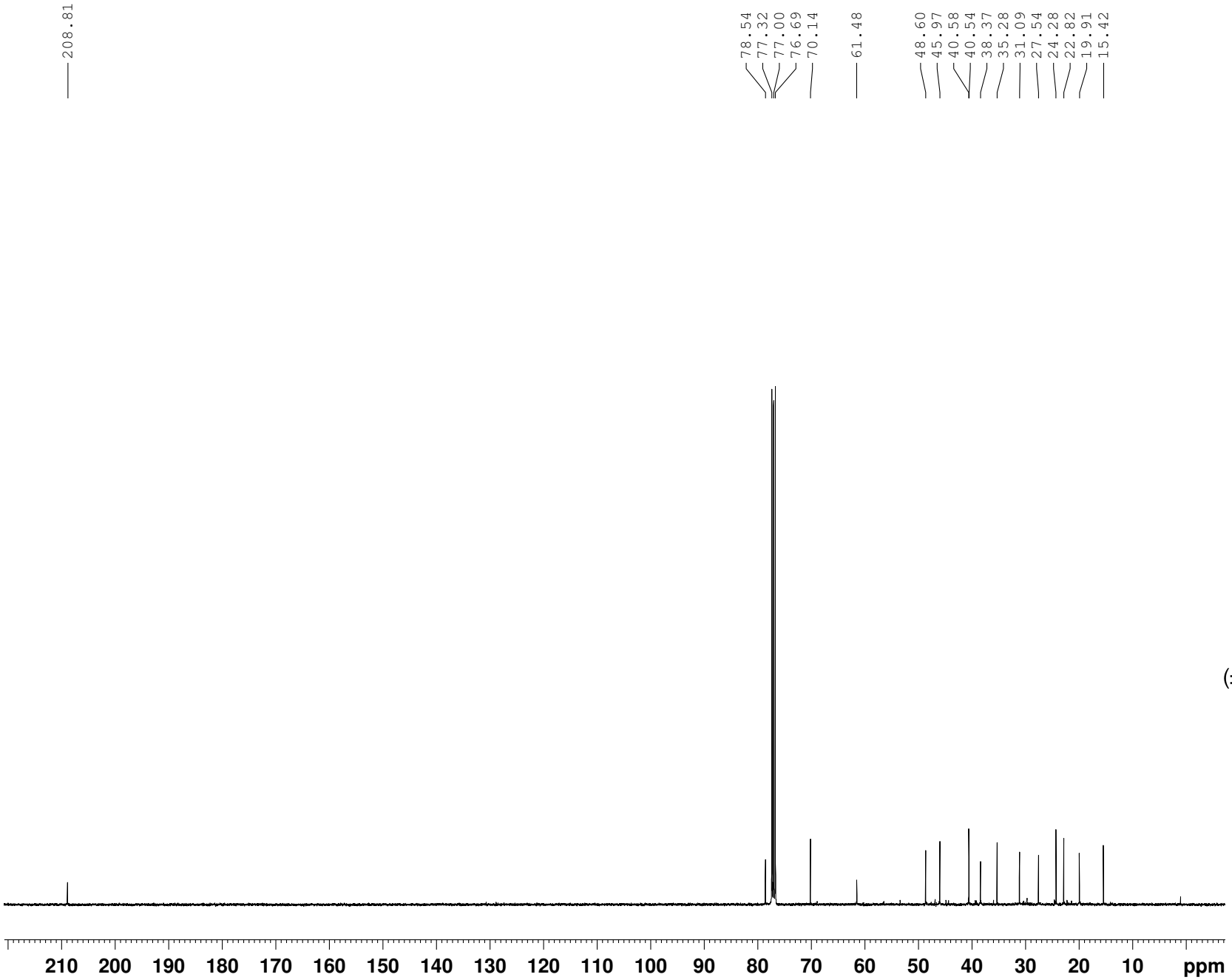


NAME	zxh-1567
EXPNO	12
PROCNO	1
Date_	20141010
Time	7.12
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	deptsp135
TD	65536
SOLVENT	CDCl3
NS	1200
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	296.7 K
CNST2	145.0000000
D1	2.00000000 sec
D2	0.00344828 sec
D12	0.00002000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.45 usec
P13	2000.00 usec
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



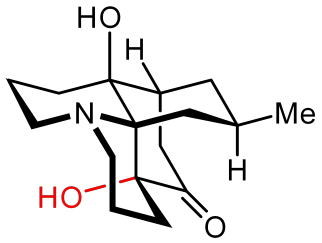
22


7.270
4.057
4.045
4.029
4.024
4.019
4.014
3.997
3.986
3.386
3.376
3.351
3.341
3.317
3.305
3.278
3.265
3.184
2.963
2.950
2.930
2.918
2.898
2.885
2.604
2.588
2.568
2.557
2.543
2.508
2.310
2.247
2.242
2.207
2.202
2.133
2.120
2.098
2.085
2.004
1.994
1.753
1.720
1.599
1.566
1.533
1.440
1.396
0.854
0.839
0.070
NAME zxh-1999
EXPNO 10
PROCNO 1
Date_ 20150824
Time 11.02
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 181
DW 62.400 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.79 usec
SI 65536
SF 400.1300057 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HO
H
N
Me
H
HO
O
(±)-Lycoposerramine G (5)
*
* CH2Cl2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.08
1.01
1.12
2.17
1.04
7.42
2.14
1.15
4.36
3.02

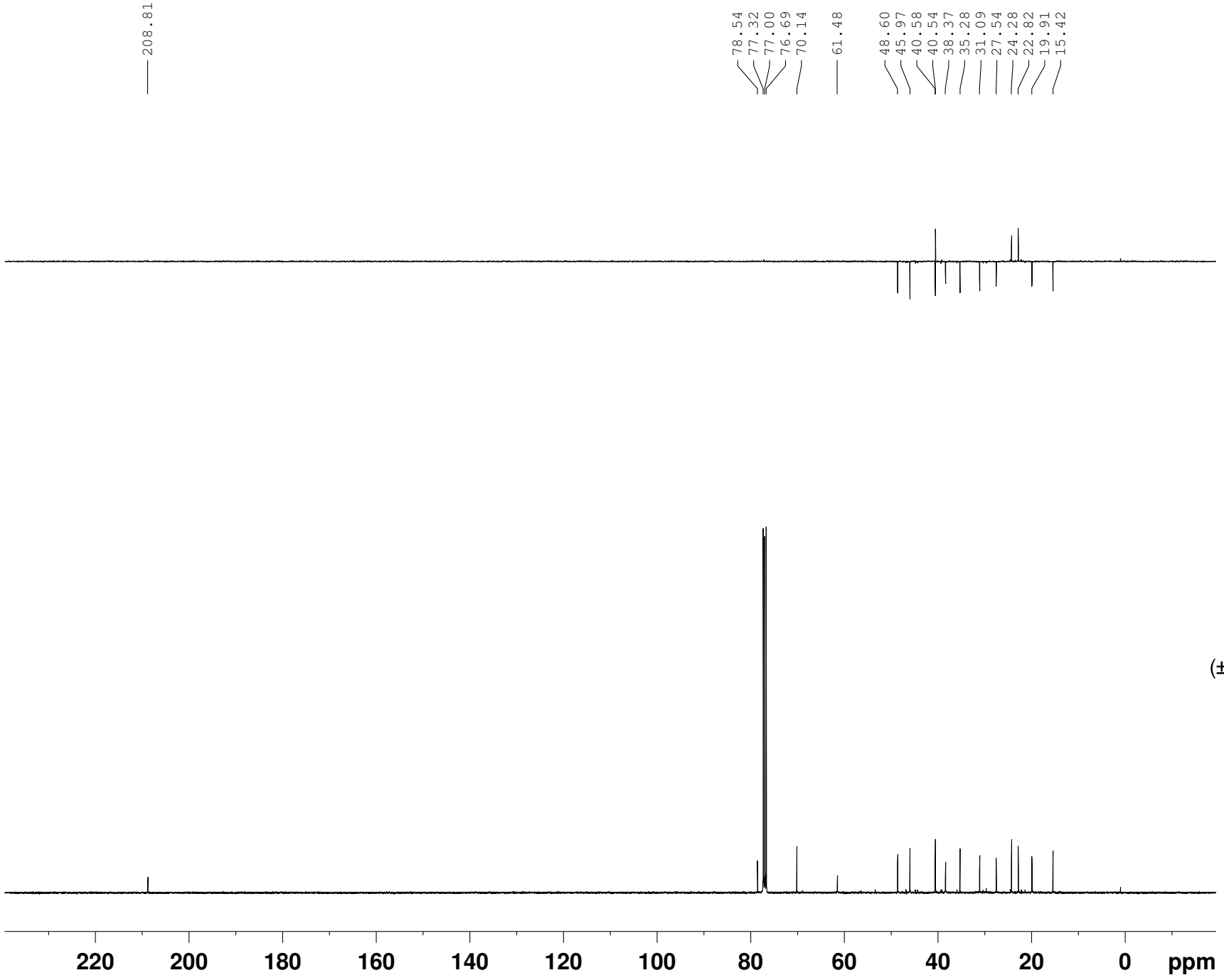



```
NAME            zxh-1999
EXPNO                 11
PROCNO                 1
Date_           20150824
Time               13.50
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  3000
DS                     2
SWH          26041.666 Hz
FIDRES        0.397364 Hz
AQ            1.2583412 sec
RG                  2050
DW               19.200 usec
DE                6.50 usec
TE                298.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

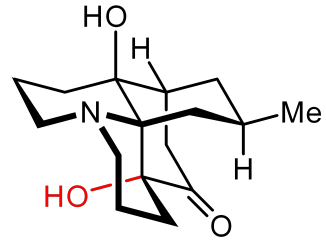
======== CHANNEL f1 ========
SFO1       100.6238364 MHz
NUC1               13C
P1              12.00 usec
SI                 32768
SF         100.6127701 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



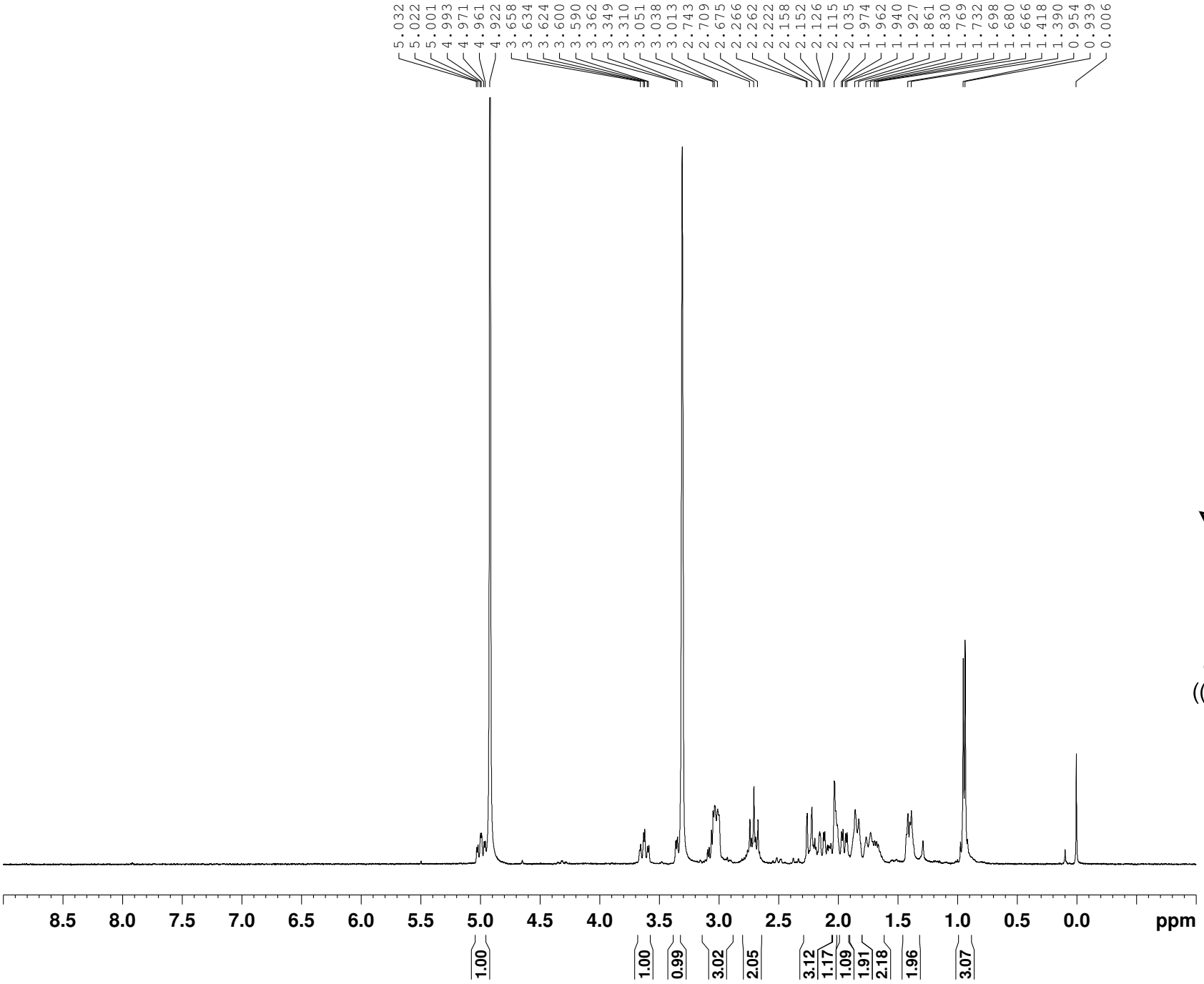
(±)-Lycoposerramine G **(5)**



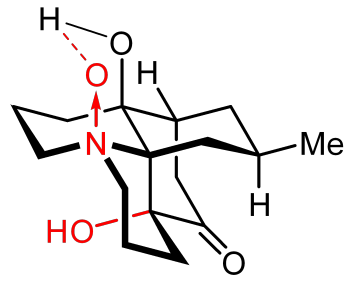
NAME	zxh-1999
EXPNO	12
PROCNO	1
Date_	20150824
Time	15.14
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	deptsp135
TD	65536
SOLVENT	CDCl3
NS	1500
DS	4
SWH	26041.666 Hz
FIDRES	0.397364 Hz
AQ	1.2583412 sec
RG	2050
DW	19.200 usec
DE	6.50 usec
TE	298.4 K
CNST2	145.0000000
D1	2.00000000 sec
D2	0.00344828 sec
D12	0.00002000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6238364 MHz
NUC1	13C
P1	12.00 usec
P13	2000.00 usec
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



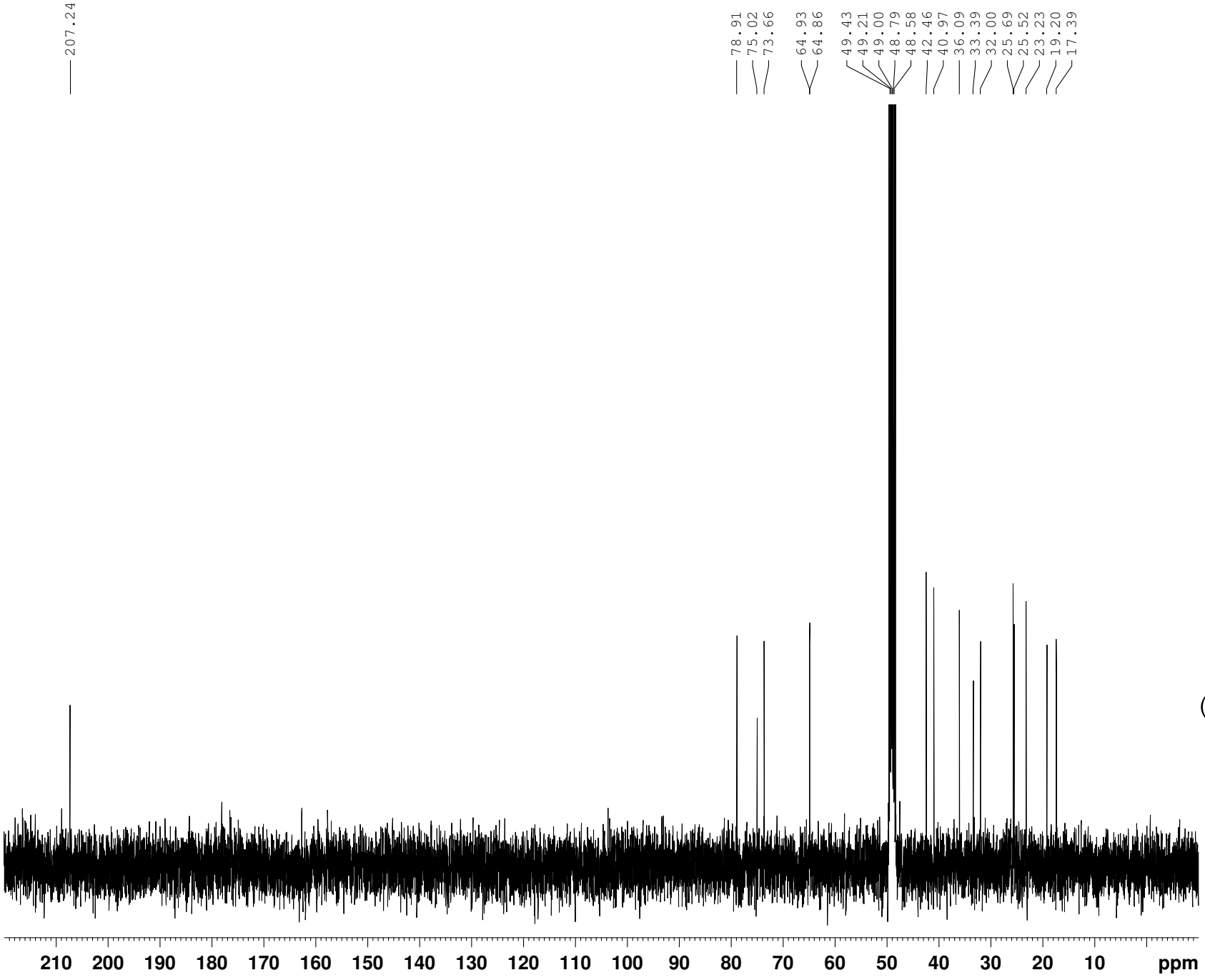
(±)-Lycoposerramine G **(5)**



NAME	zxh-N,O
EXPNO	10
PROCNO	1
Date_	20151205
Time	8.33
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	MeOD
NS	32
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	362
DW	62.400 usec
DE	6.50 usec
TE	288.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.79 usec
SI	65536
SF	400.1300077 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

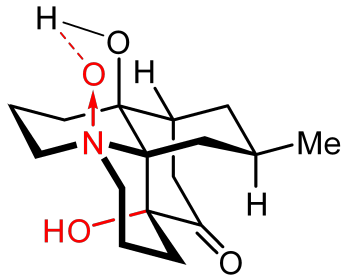


(±)-Miyoshianine A (**4**)
((±)-Lycoposerramine F)

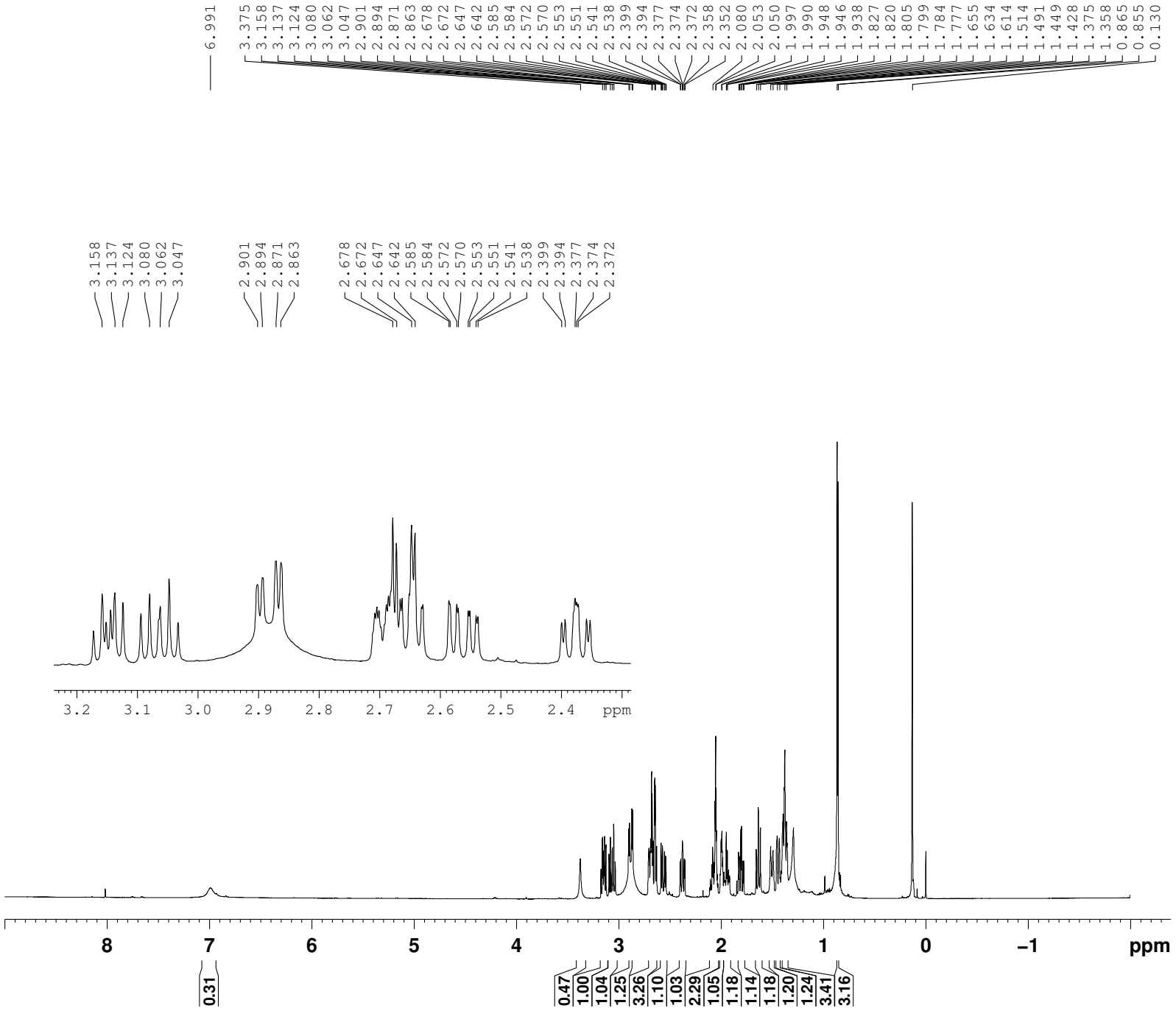



```
NAME              zxh-N,O
EXPNO                  32
PROCNO                  1
Date_            20160103
Time                10.29
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT              MeOD
NS                   2083
DS                      2
SWH            26041.666 Hz
FIDRES          0.397364 Hz
AQ              1.2583412 sec
RG                   2050
DW                19.200 usec
DE                 6.50 usec
TE                286.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

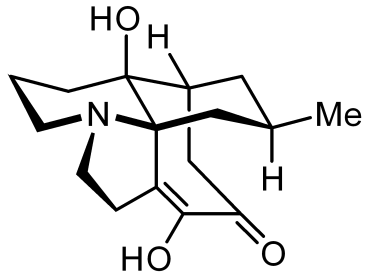
======== CHANNEL f1 ========
SFO1         100.6238364 MHz
NUC1                  13C
P1                 14.70 usec
SI                 32768
SF           100.6126269 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



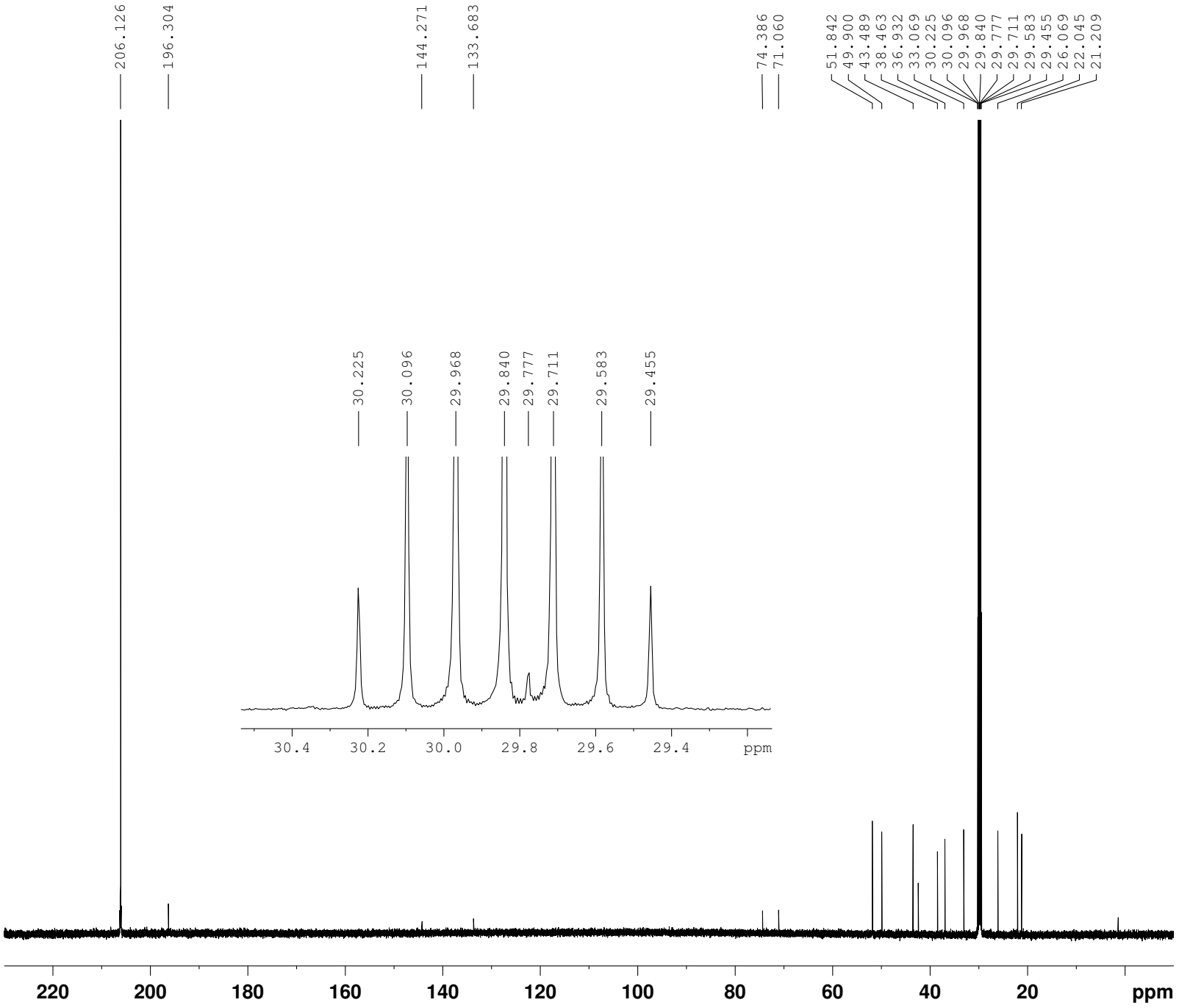
(±)-Miyoshianine A (**4**)
((±)-Lycoposerramine F)



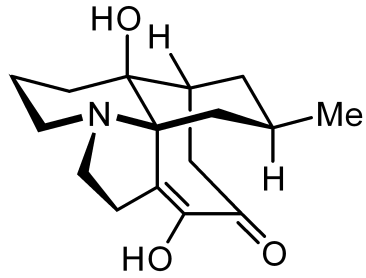
Title	zxh-2313-H
Origin	Varian
Spectrometer	inova
Solvent	Acetone-d6
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.7070
Acquisition Date	2016-05-30
Modification Date	2016-05-30
Spectrometer Frequency	599.85
Spectral Width	9598.1
Lowest Frequency	−1200.0
Nucleus	1H
Acquired Size	16384
Spectral Size	32768



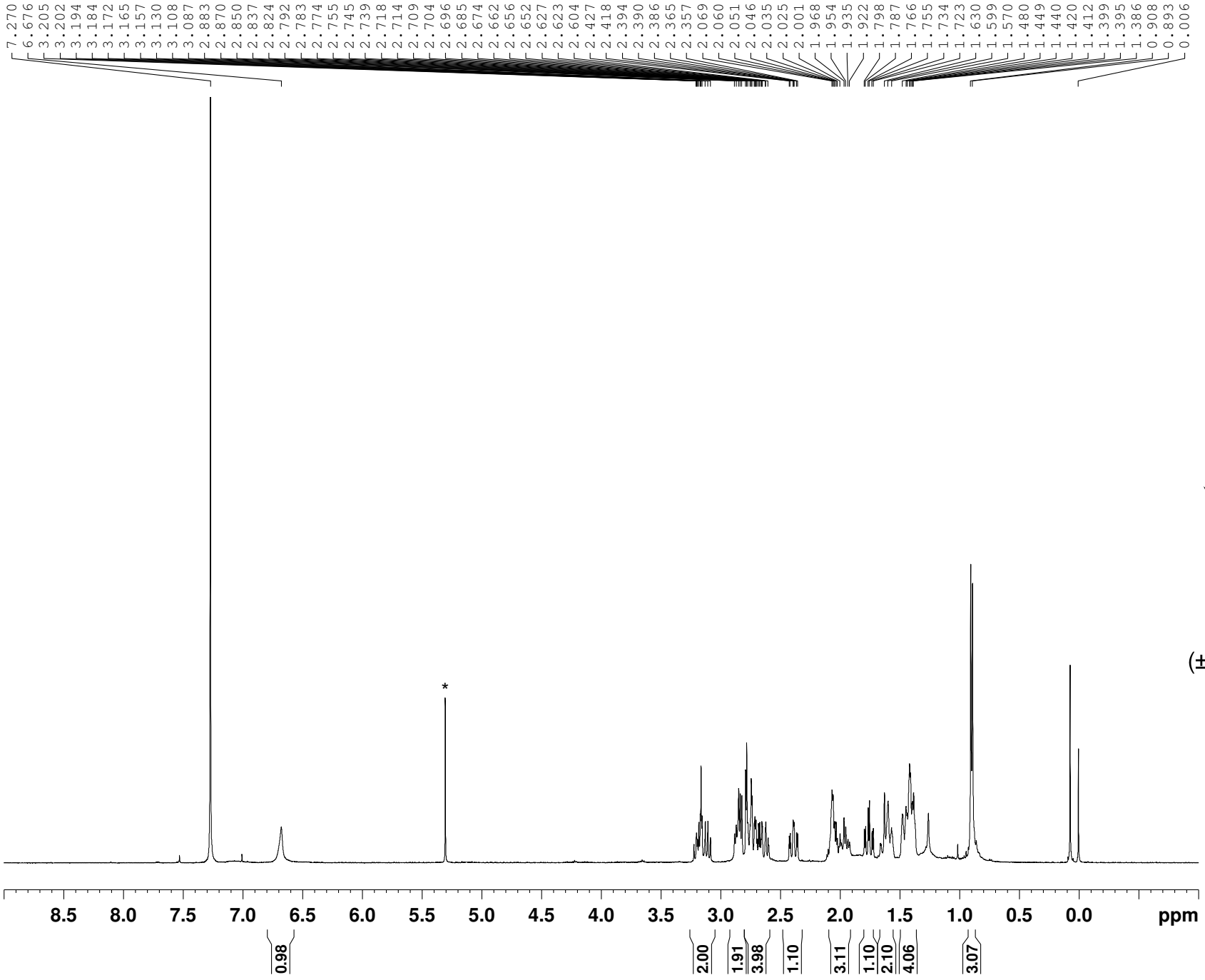
(±)-Lycojaponicumin D (**1**)
($(CD_3)_2O$)



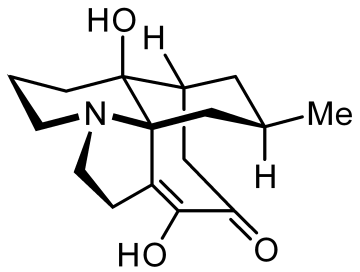
Title	zxh-2313-C
Origin	Varian
Spectrometer	inova
Solvent	Acetone-d6
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	2625
Receiver Gain	24
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	0.8692
Acquisition Date	2016-05-30
Modification Date	2016-05-30
Spectrometer Frequency	150.85
Spectral Width	37700.3
Lowest Frequency	-2126.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



(±)-Lycojaponicumin D (**1**)
($(CD_3)_2O$)

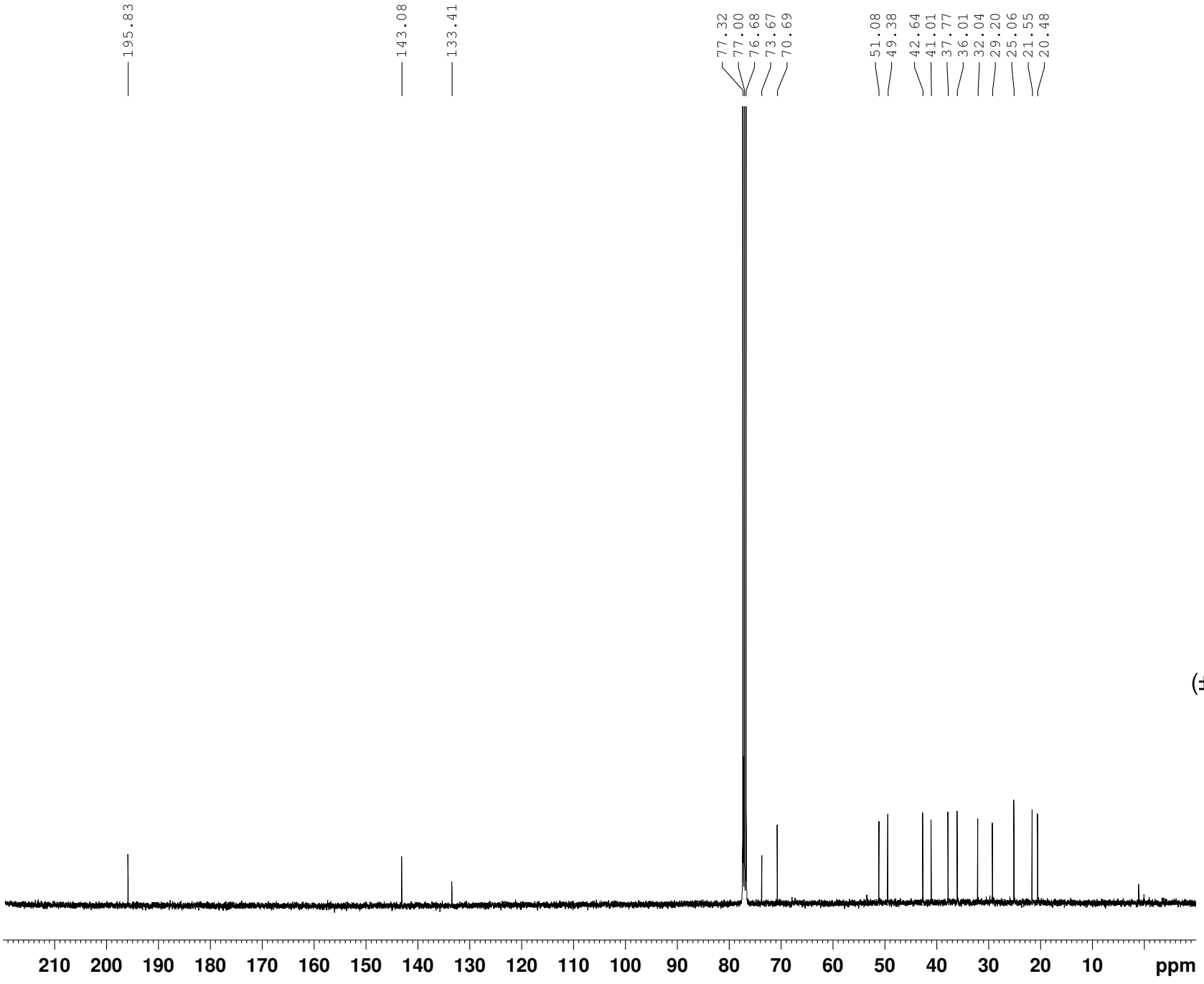


NAME	zxh-2313
EXPNO	10
PROCNO	1
Date_	20160513
Time	0.08
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	287
DW	62.400 usec
DE	6.50 usec
TE	295.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.92 usec
SI	65536
SF	400.1300057 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

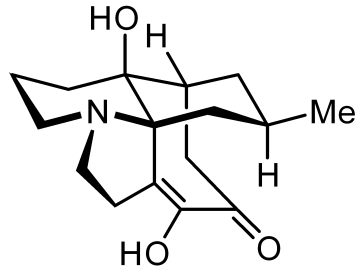


(±)-Lycojaponicumin D (**1**)
($CDCl_3$)

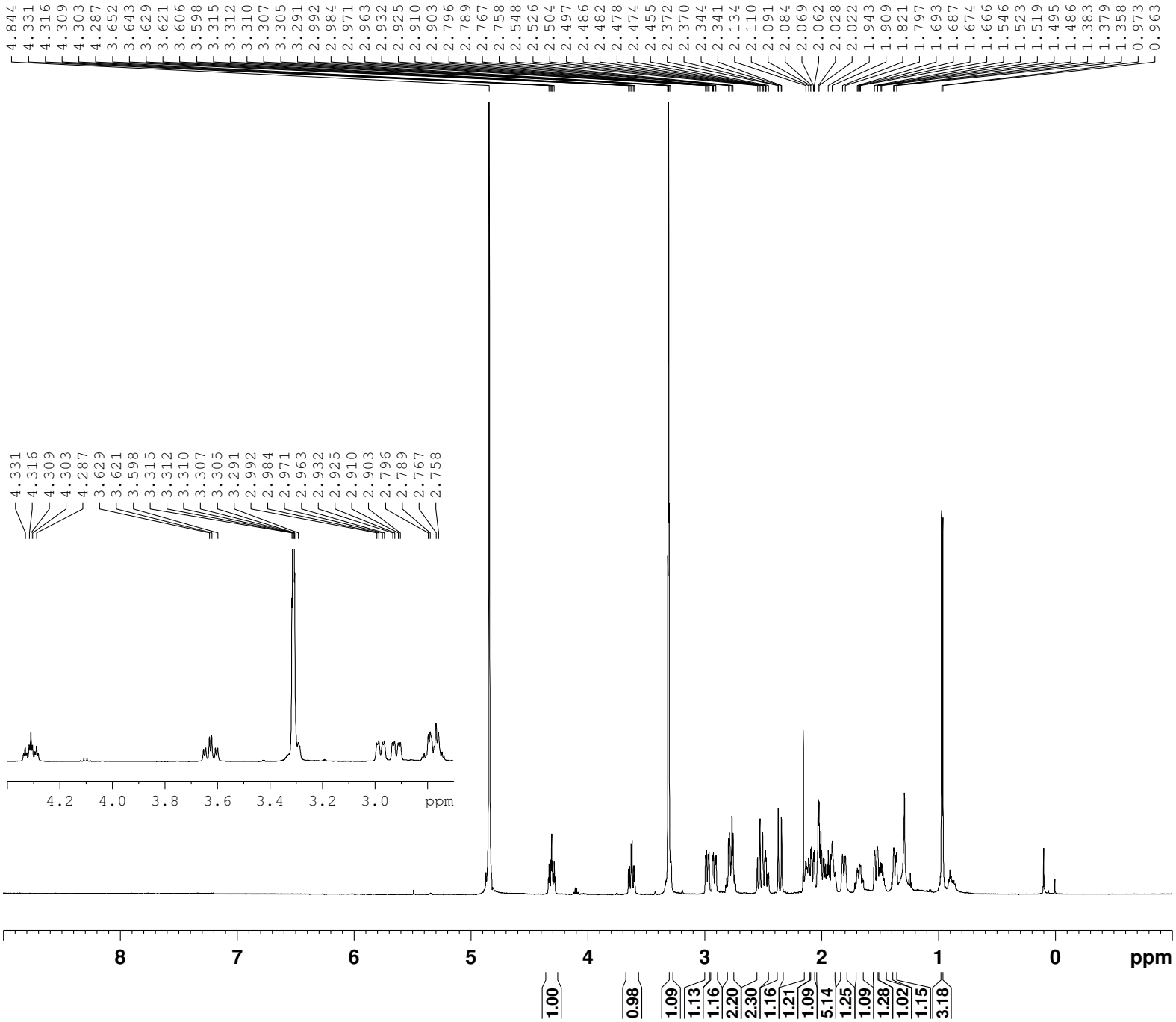
* CH_2Cl_2



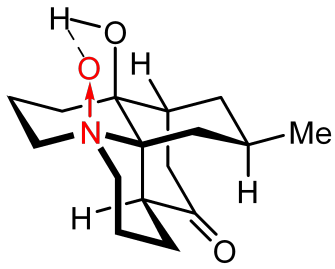
NAME	zxh-2313
EXPNO	13
PROCNO	1
Date_	20160516
Time	4.07
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	4200
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	812
DW	20.800 usec
DE	6.50 usec
TE	295.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127707 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



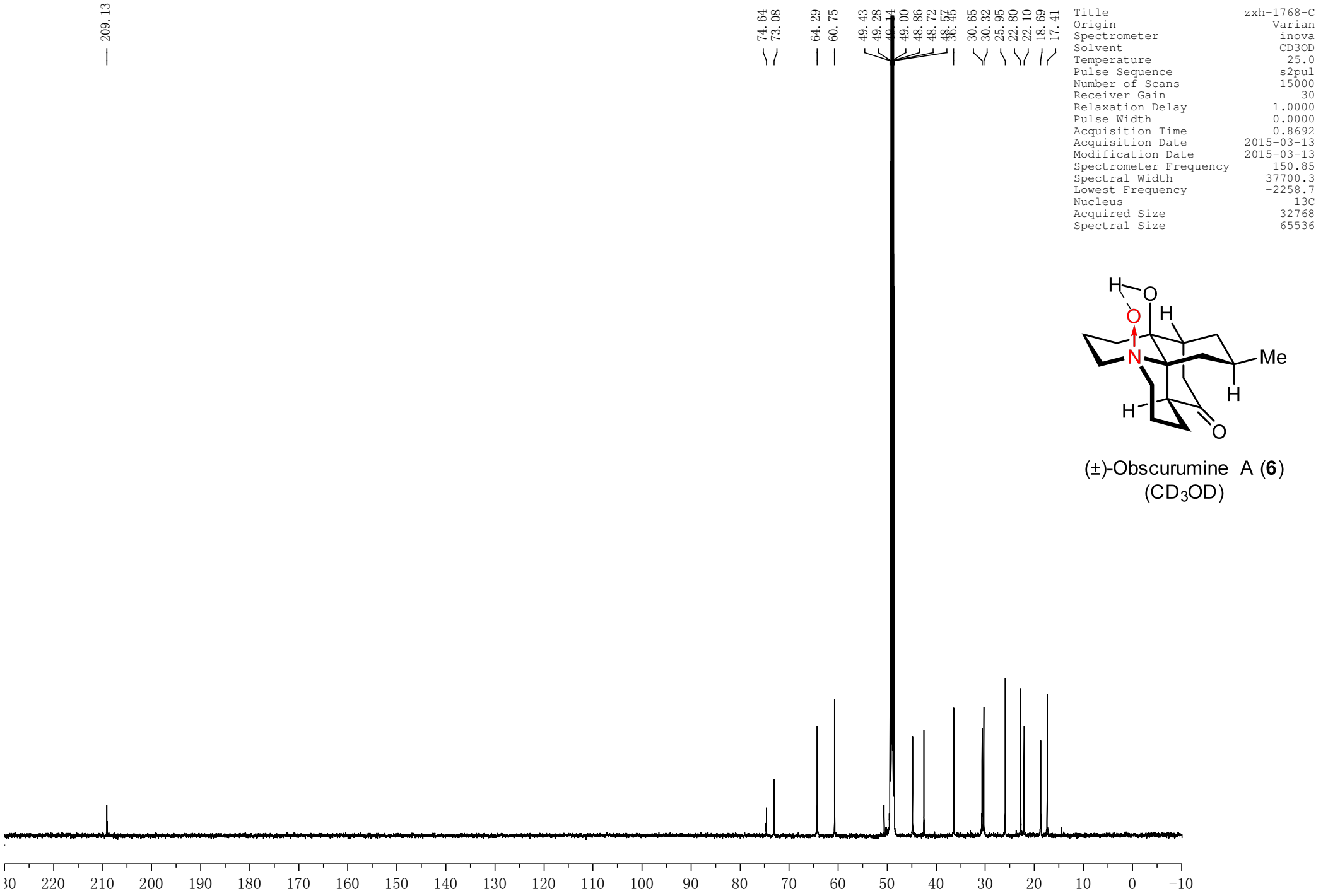
(±)-Lycojaponicumin D (**1**)
($CDCl_3$)

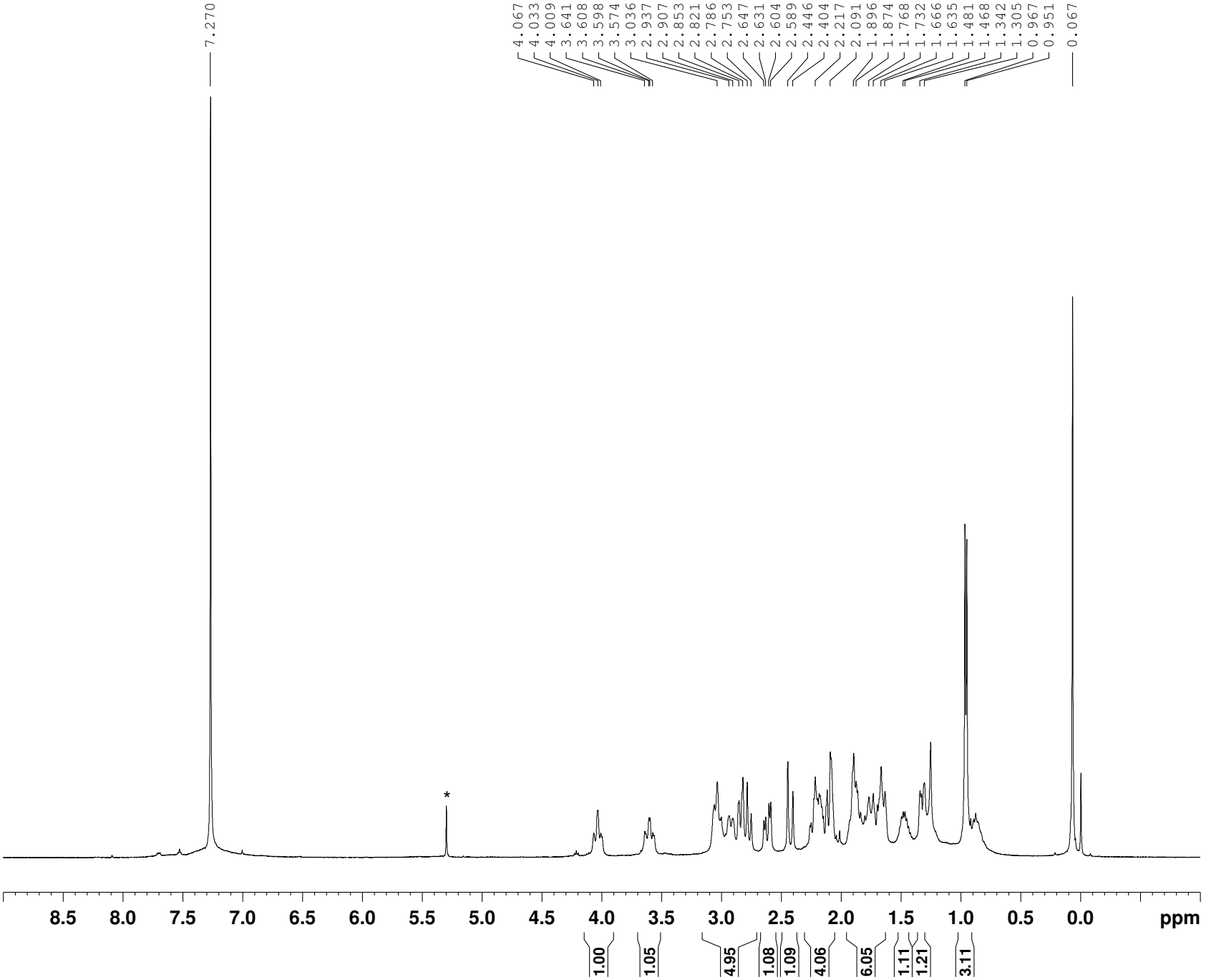


Title	zxh-1768-H
Origin	Varian
Spectrometer	inova
Solvent	CD3OD
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	64
Receiver Gain	10
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.7070
Acquisition Date	2015-03-12
Modification Date	2015-03-12
Spectrometer Frequency	599.85
Spectral Width	9598.1
Lowest Frequency	-1199.8
Nucleus	1H
Acquired Size	16384
Spectral Size	32768



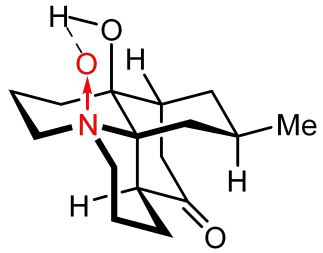
(±)-Obscurumine A (**6**)
(CD_3OD)


209.13
74.64
73.08
64.29
60.75
49.43
49.28
49.00
48.86
48.72
30.65
30.32
25.95
22.80
22.10
18.69
17.41
Title zxh-1768-C
Origin Varian
Spectrometer inova
Solvent CD3OD
Temperature 25.0
Pulse Sequence s2pul
Number of Scans 15000
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 0.8692
Acquisition Date 2015-03-13
Modification Date 2015-03-13
Spectrometer Frequency 150.85
Spectral Width 37700.3
Lowest Frequency -2258.7
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
H
O
O
H
N
Me
H
H
O
(±)-Obscurumine A (6)
(CD3OD)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



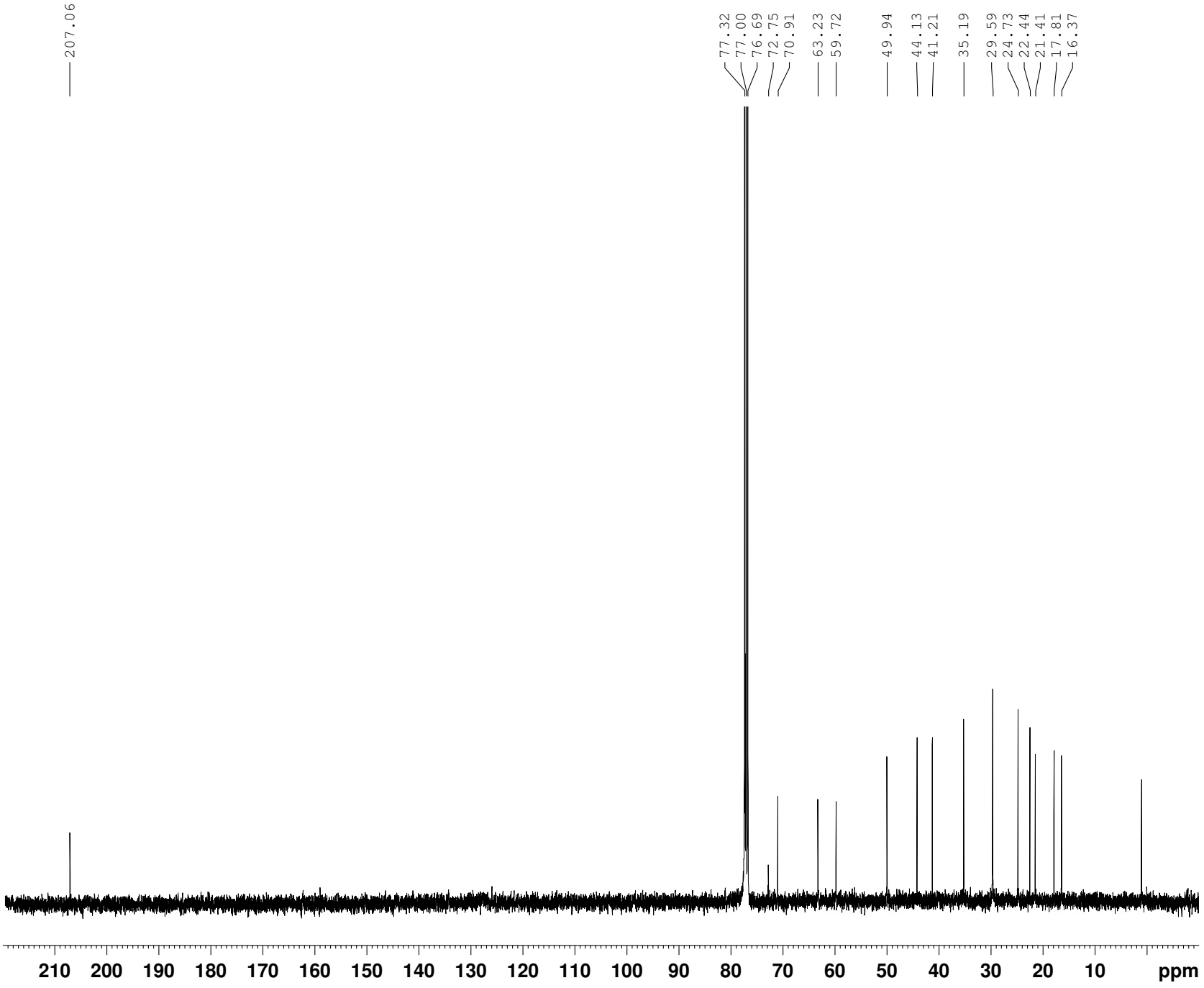

```
NAME        zxh-2314-2-H
EXPNO                 11
PROCNO                 1
Date_           20160510
Time               10.37
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   203
DW                62.400 usec
DE                 6.50 usec
TE                295.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.79 usec
SI                 65536
SF           400.1300056 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



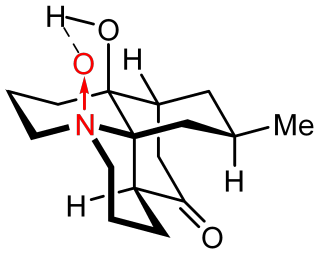
(±)-Obscurumine A (**6**)
($CDCl_3$)

* CH_2Cl_2

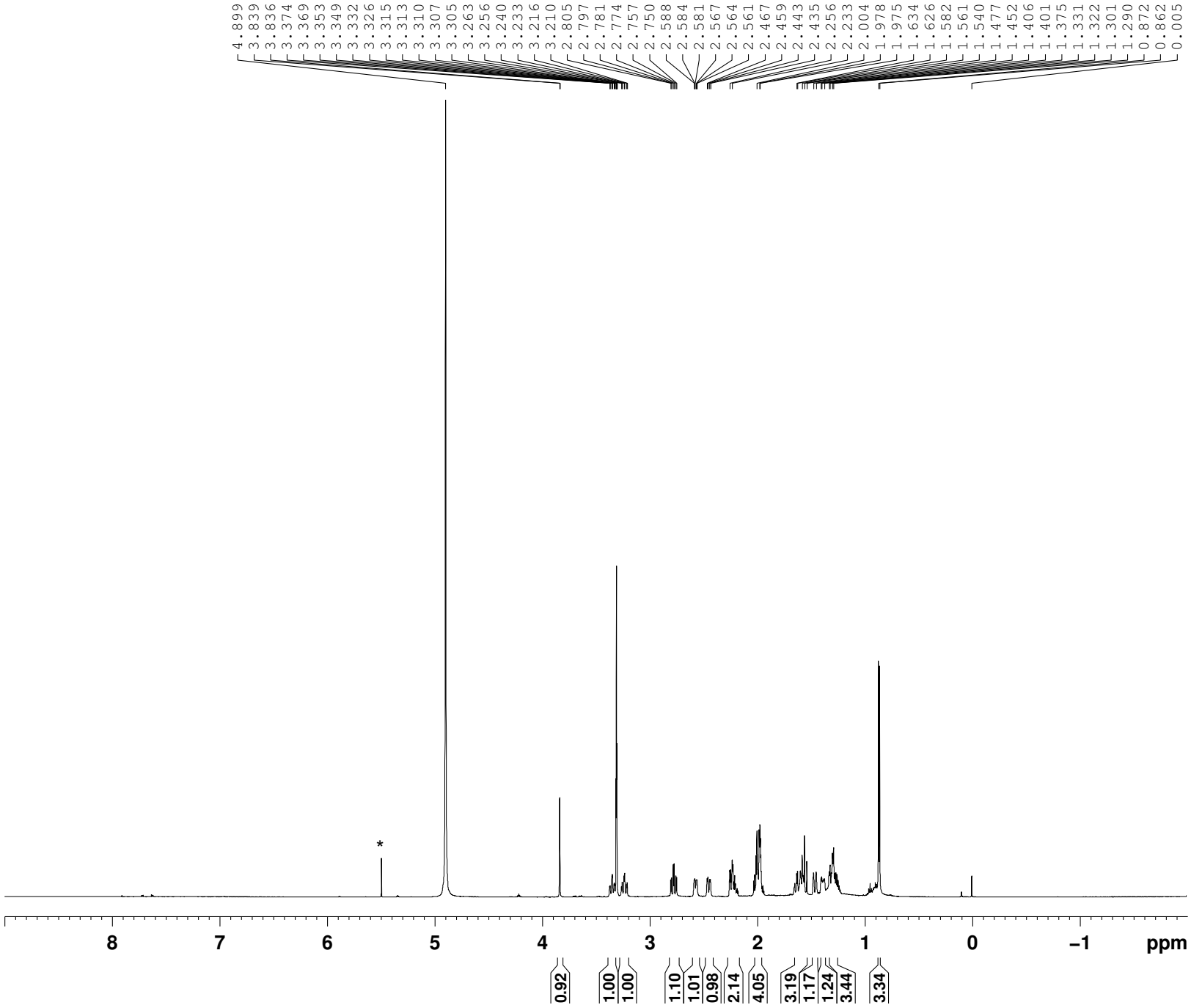



```
NAME          zxh-2314-2-C
EXPNO                   10
PROCNO                   1
Date_             20160510
Time                 17.29
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    900
DS                      2
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   1030
DW                 20.800 usec
DE                  6.50 usec
TE                 297.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

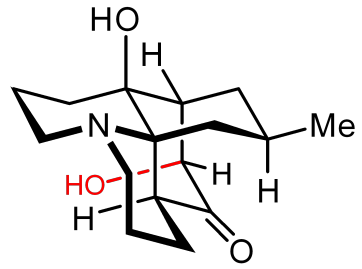
======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                 14.70 usec
SI                 32768
SF            100.6127707 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



(±)-Obscurumine A (**6**)
($CDCl_3$)

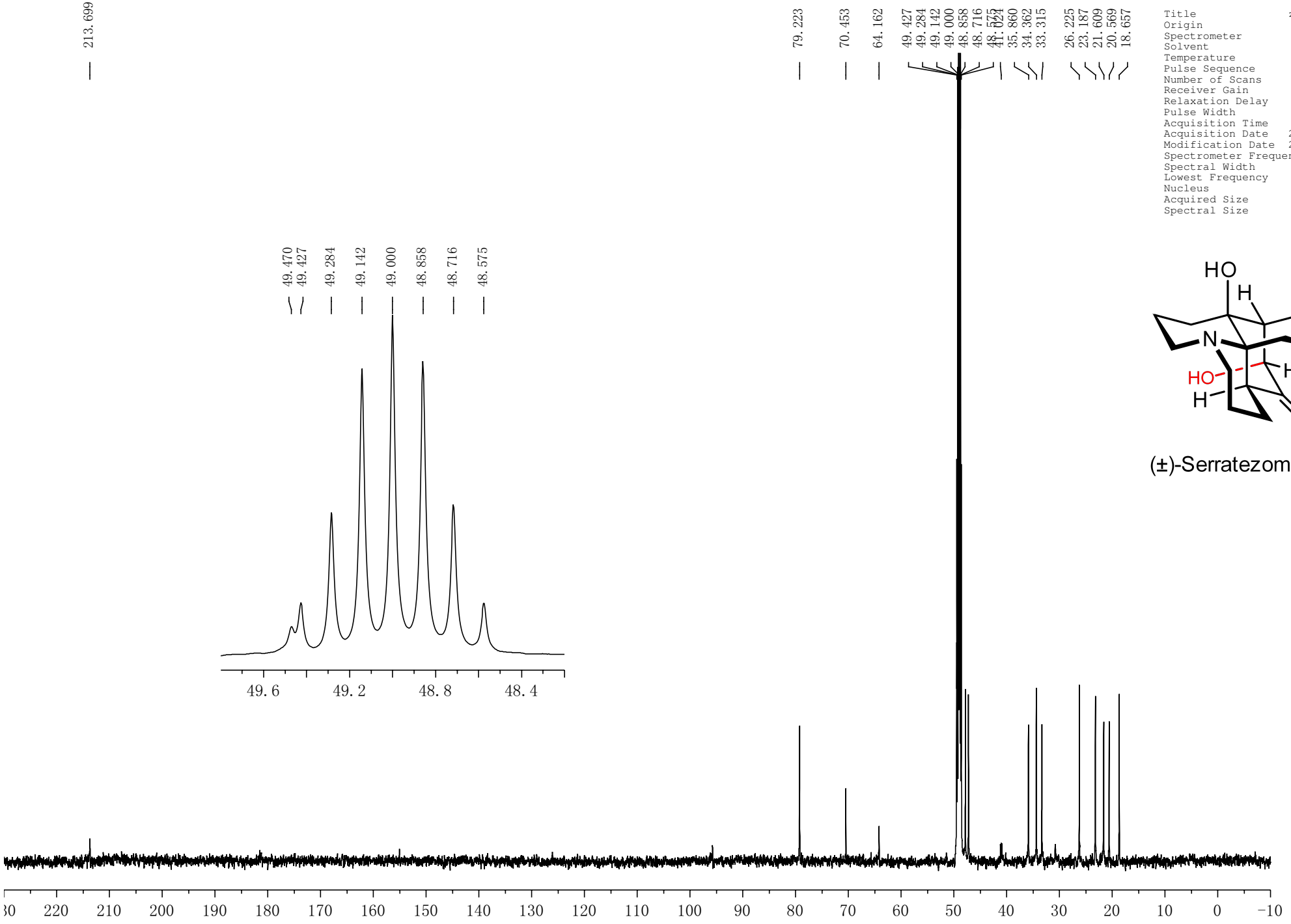


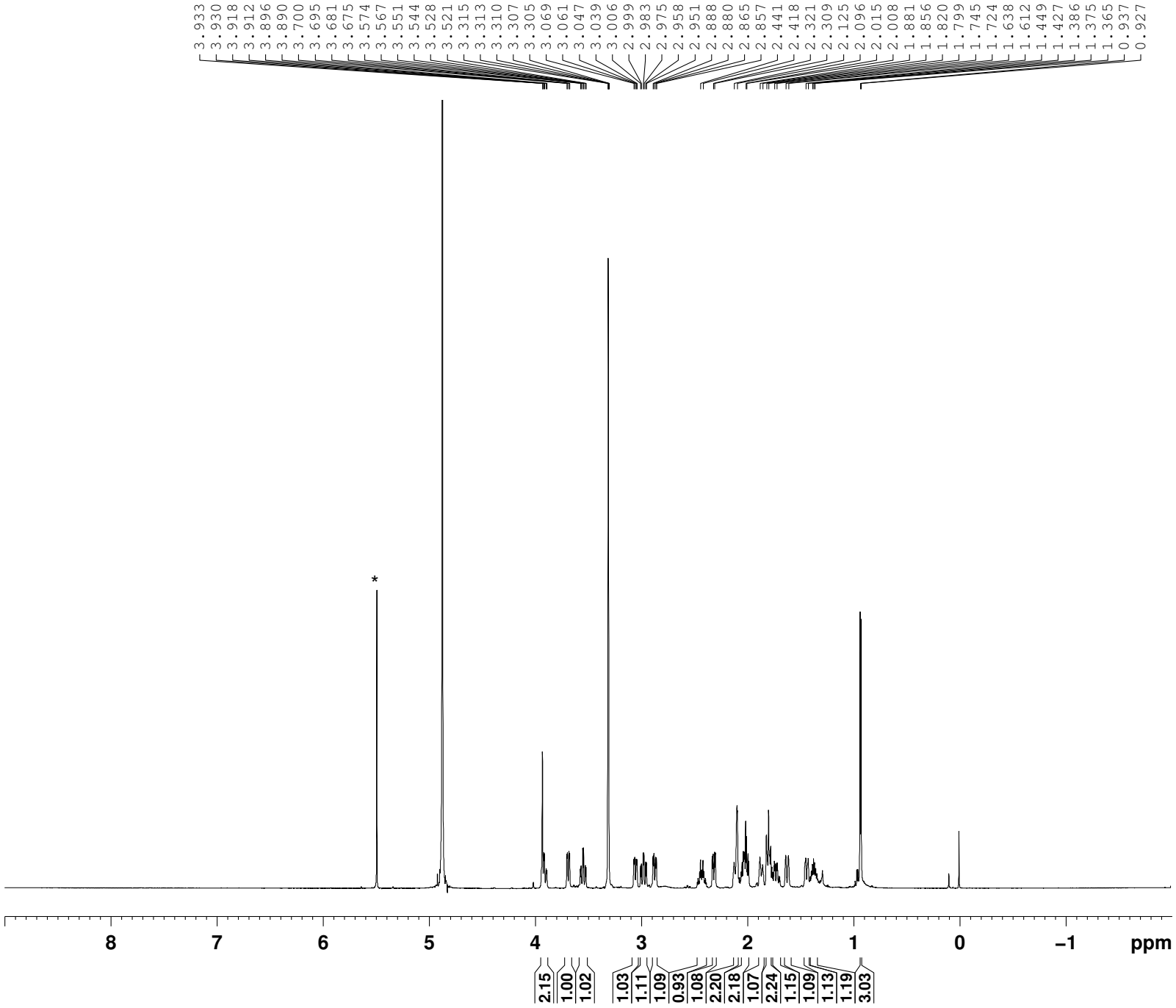
Title	zxh-1854-H
Origin	Varian
Spectrometer	inova
Solvent	CD3OD
Temperature	23.0
Pulse Sequence	s2pul
Number of Scans	32
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.7070
Acquisition Date	2015-05-11
Modification Date	2015-05-11
Spectrometer Frequency	599.85
Spectral Width	9598.1
Lowest Frequency	-1199.9
Nucleus	1H
Acquired Size	16384
Spectral Size	32768



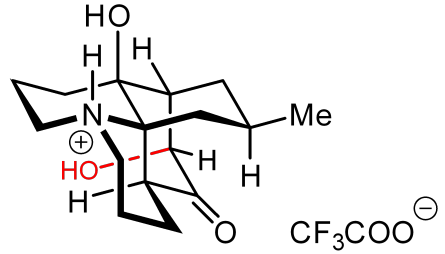
(±)-Serratezomine C (**7**)

* CH_2Cl_2


213.699
79.223
70.453
64.162
49.427
49.284
49.142
49.000
48.858
48.716
48.575
41.024
35.860
34.362
33.315
26.225
23.187
21.609
20.569
18.657
Title zxh-1854-C
Origin Varian
Spectrometer invoa
Solvent CD3OD
Temperature 23.0
Pulse Sequence s2pul
Number of Scans 5813
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 0.8692
Acquisition Date 2015-05-11
Modification Date 2015-05-11
Spectrometer Frequency 150.85
Spectral Width 37700.3
Lowest Frequency -2043.5
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
49.470
49.427
49.284
49.142
49.000
48.858
48.716
48.575
49.6
49.2
48.8
48.4
HO
H
N
Me
HO
H
H
H
O
(±)-Serratezomine C (7)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

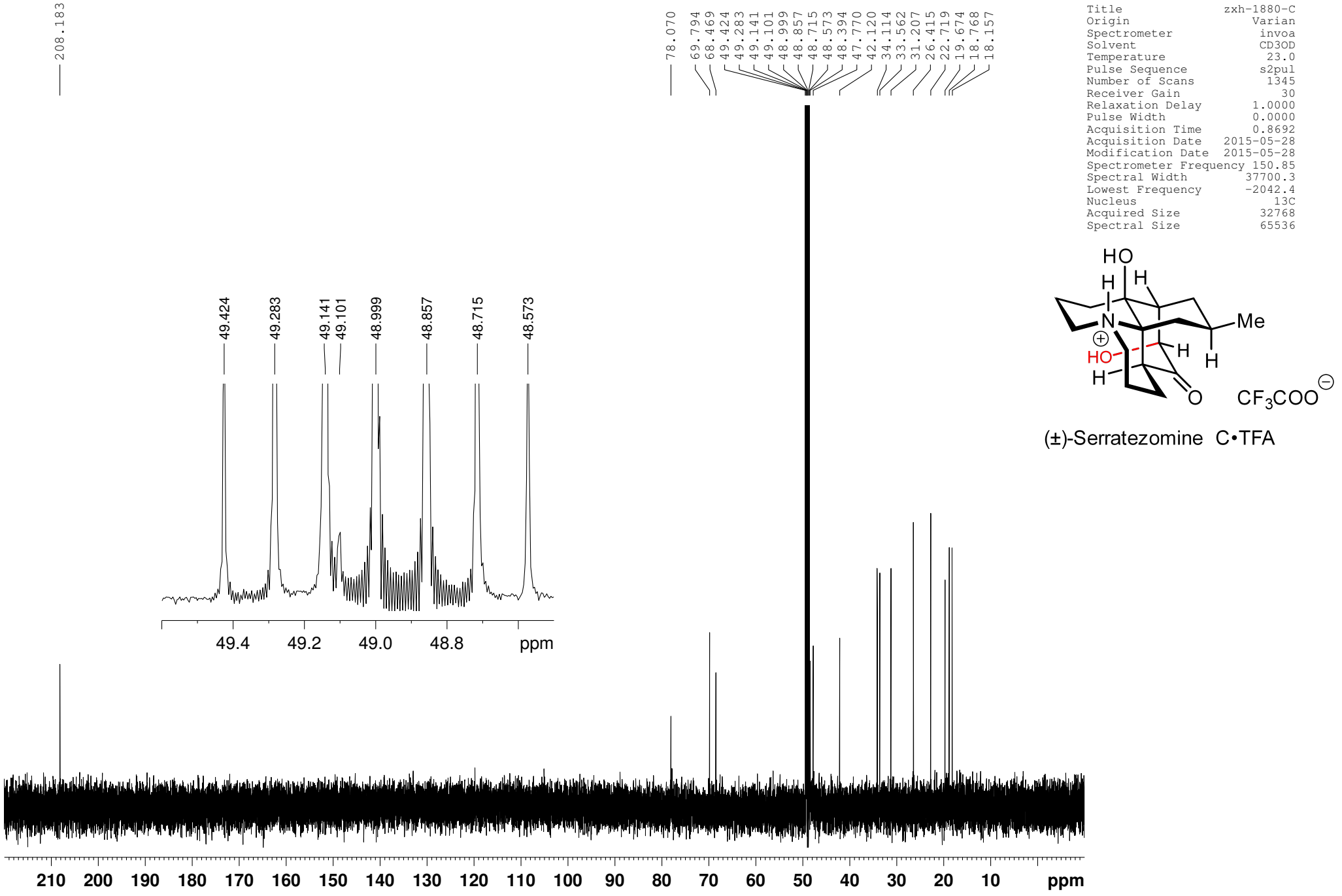


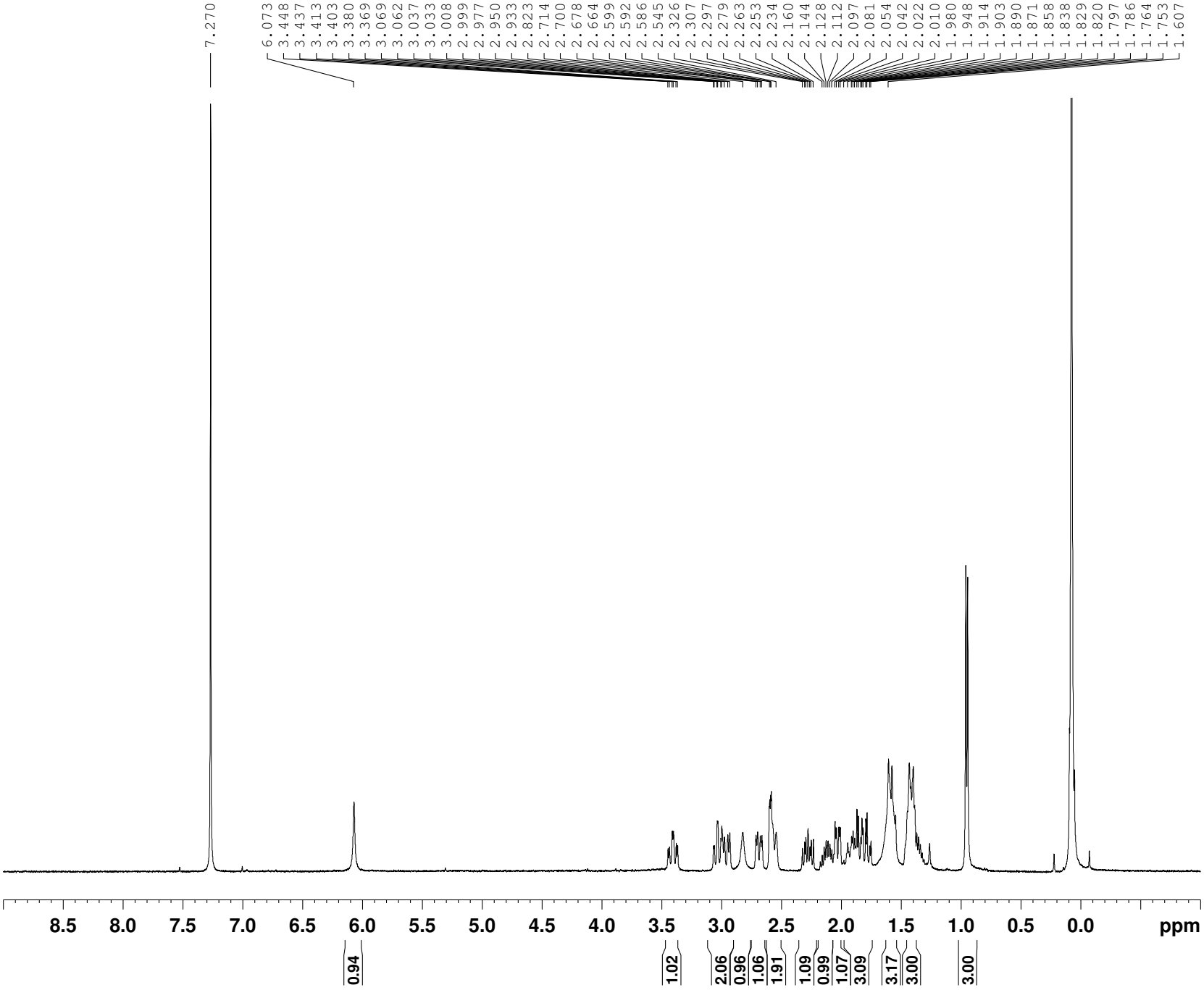
Title	zxh-1880-H
Origin	Varian
Spectrometer	invoa
Solvent	CD3OD
Temperature	23.0
Pulse Sequence	s2pul
Number of Scans	64
Receiver Gain	40
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.7070
Acquisition Date	2015-05-28
Modification Date	2015-05-28
Spectrometer Frequency	599.85
Spectral Width	9598.1
Lowest Frequency	-1199.9
Nucleus	1H
Acquired Size	16384
Spectral Size	32768



(±)-Serratezomine C•TFA

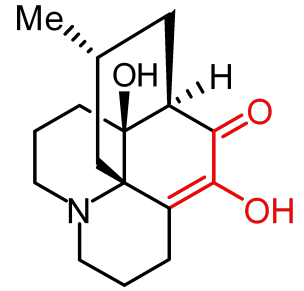
* CH_2Cl_2


208.183
78.070
69.794
68.469
49.424
49.283
49.141
49.101
48.999
48.857
48.715
48.573
48.394
47.770
42.120
34.114
33.562
31.207
26.415
22.719
19.674
18.768
18.157
Title zxh-1880-C
Origin Varian
Spectrometer invoa
Solvent CD3OD
Temperature 23.0
Pulse Sequence s2pul
Number of Scans 1345
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 0.8692
Acquisition Date 2015-05-28
Modification Date 2015-05-28
Spectrometer Frequency 150.85
Spectral Width 37700.3
Lowest Frequency -2042.4
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
HO
H
H
N
Me
HO
H
H
H
O
CF3COO
(±)-Serratezomine C•TFA
49.4
49.2
49.0
48.8
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

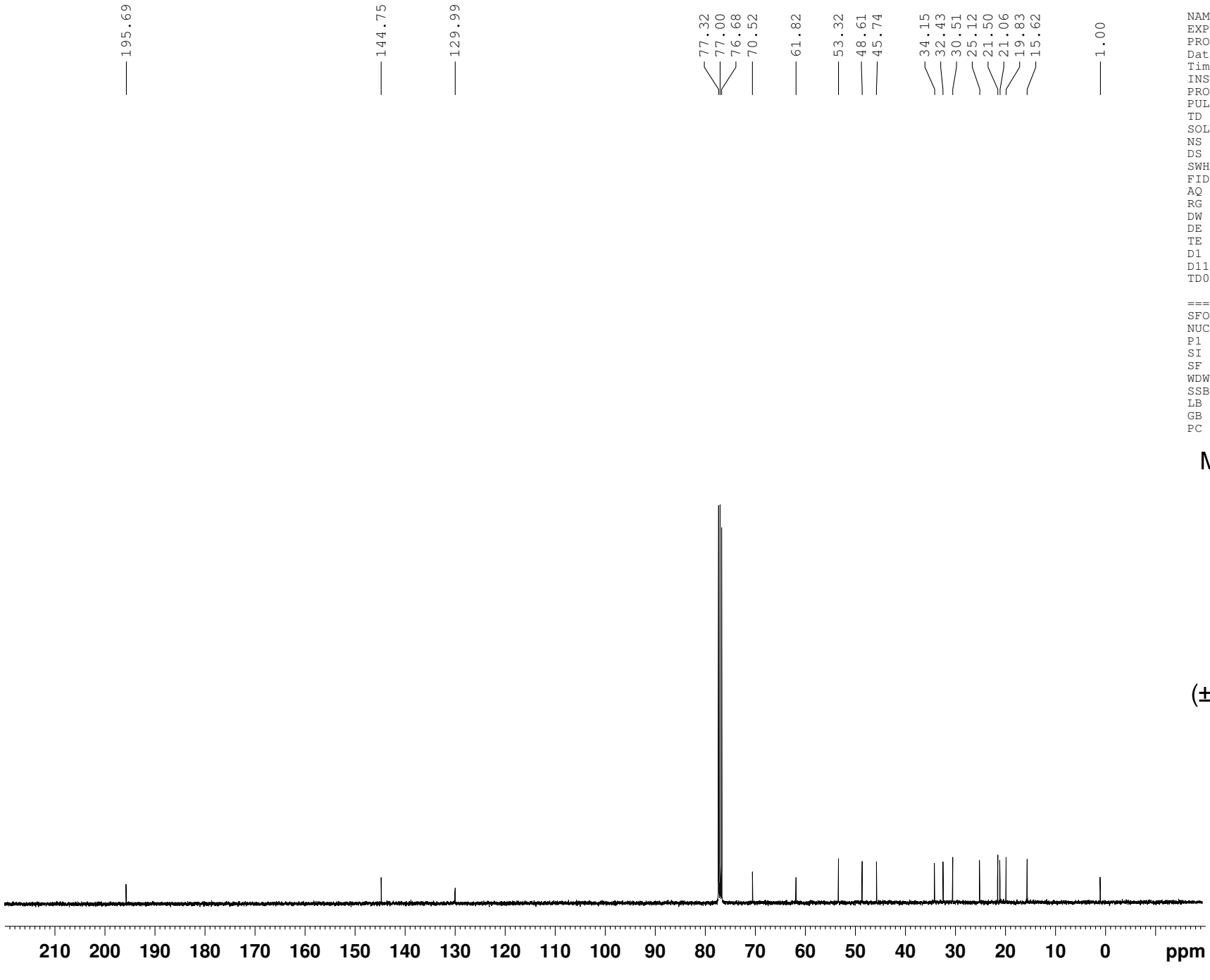



```
NAME          zxh-1883-1
EXPNO                 20
PROCNO                 1
Date_           20150529
Time               16.39
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                   362
DW                62.400 usec
DE                 6.50 usec
TE                295.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                 65536
SF           400.1300056 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



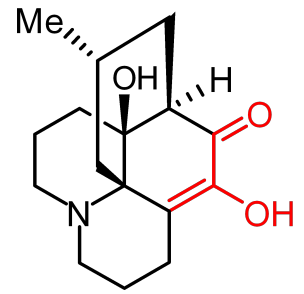
(±)-Huperzine O (**8**)



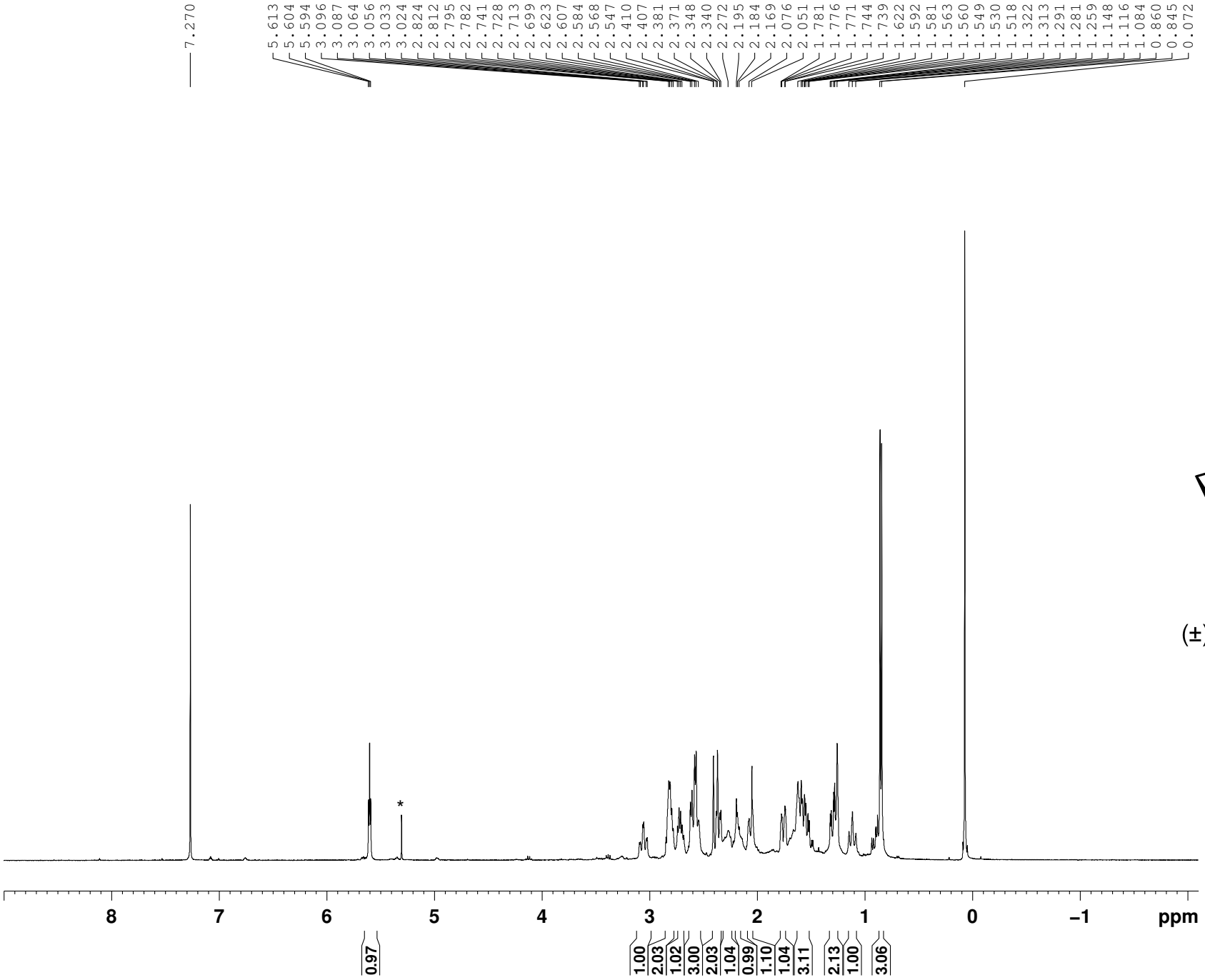
NAME	zxh-1883-1
EXPNO	14
PROCNO	1
Date_	20150528
Time	15.00
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	800
DS	2
SWH	26041.666 Hz
FIDRES	0.397364 Hz
AQ	1.2583412 sec
RG	645
DW	19.200 usec
DE	6.50 usec
TE	294.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

SFO1	100.6238364 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127709 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

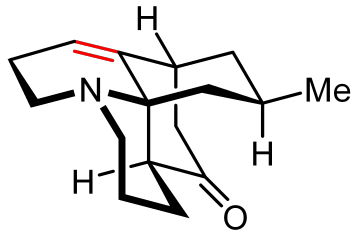


(±)-Huperzine O (**8**)



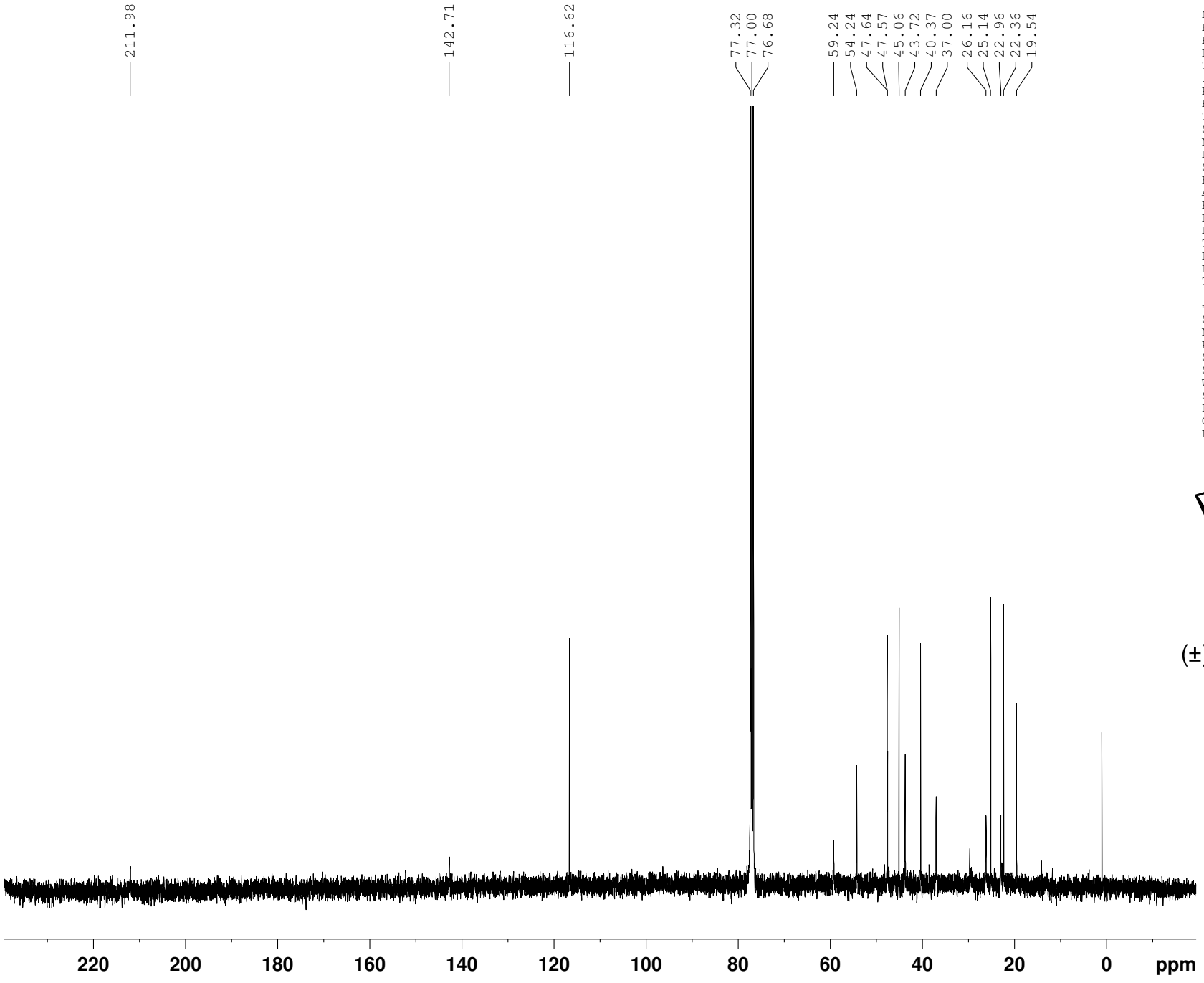

```
NAME          zxh-2175-1
EXPNO                 10
PROCNO                 1
Date_           20151210
Time                4.52
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ            4.0894966 sec
RG                   228
DW                62.400 usec
DE                 6.50 usec
TE                291.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                 65536
SF          400.1300054 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



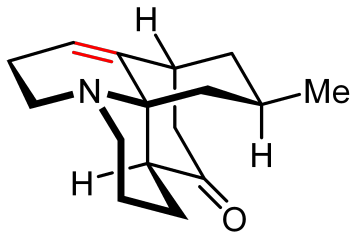
(±)-Anhydrolycodoline (**9**)

* CH_2Cl_2

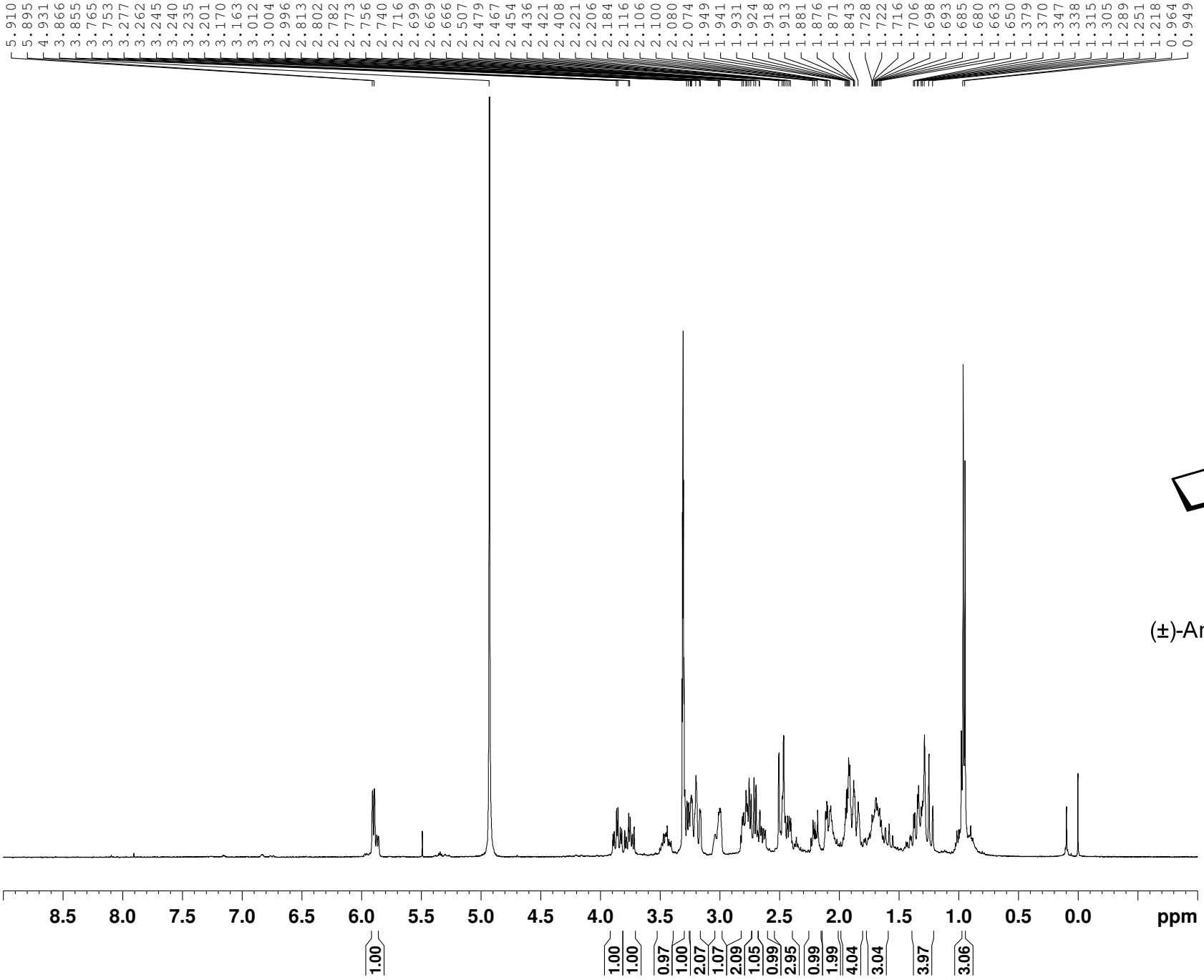



```
NAME          zxh-2175-1
EXPNO                 11
PROCNO                 1
Date_           20151210
Time                8.07
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 3500
DS                    2
SWH           26041.666 Hz
FIDRES         0.397364 Hz
AQ             1.2583412 sec
RG                 2050
DW               19.200 usec
DE                6.50 usec
TE                291.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6238364 MHz
NUC1               13C
P1               14.70 usec
SI                32768
SF          100.6127717 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

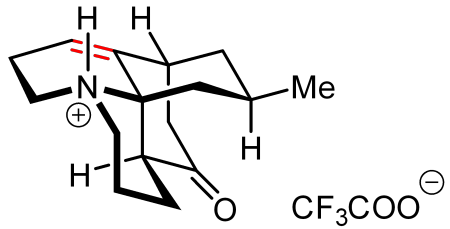


(±)-Anhydrolycodoline (**9**)

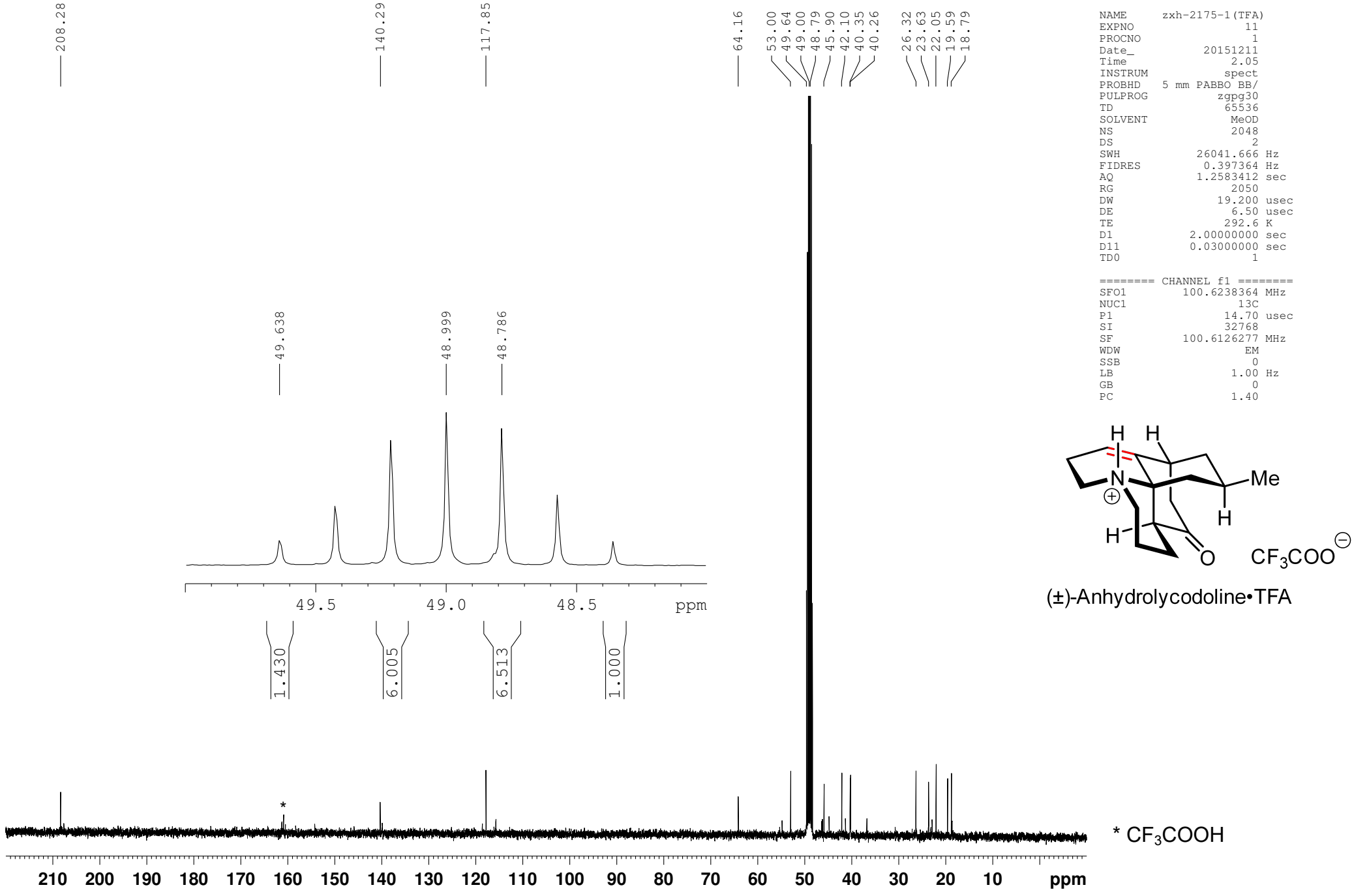



```
NAME      zxh-2175-1(TFA)
EXPNO                  10
PROCNO                  1
Date_            20151211
Time                0.12
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                   256
DW                62.400 usec
DE                 6.50 usec
TE                291.7 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                  1H
P1                 10.92 usec
SI                 65536
SF            400.1300078 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



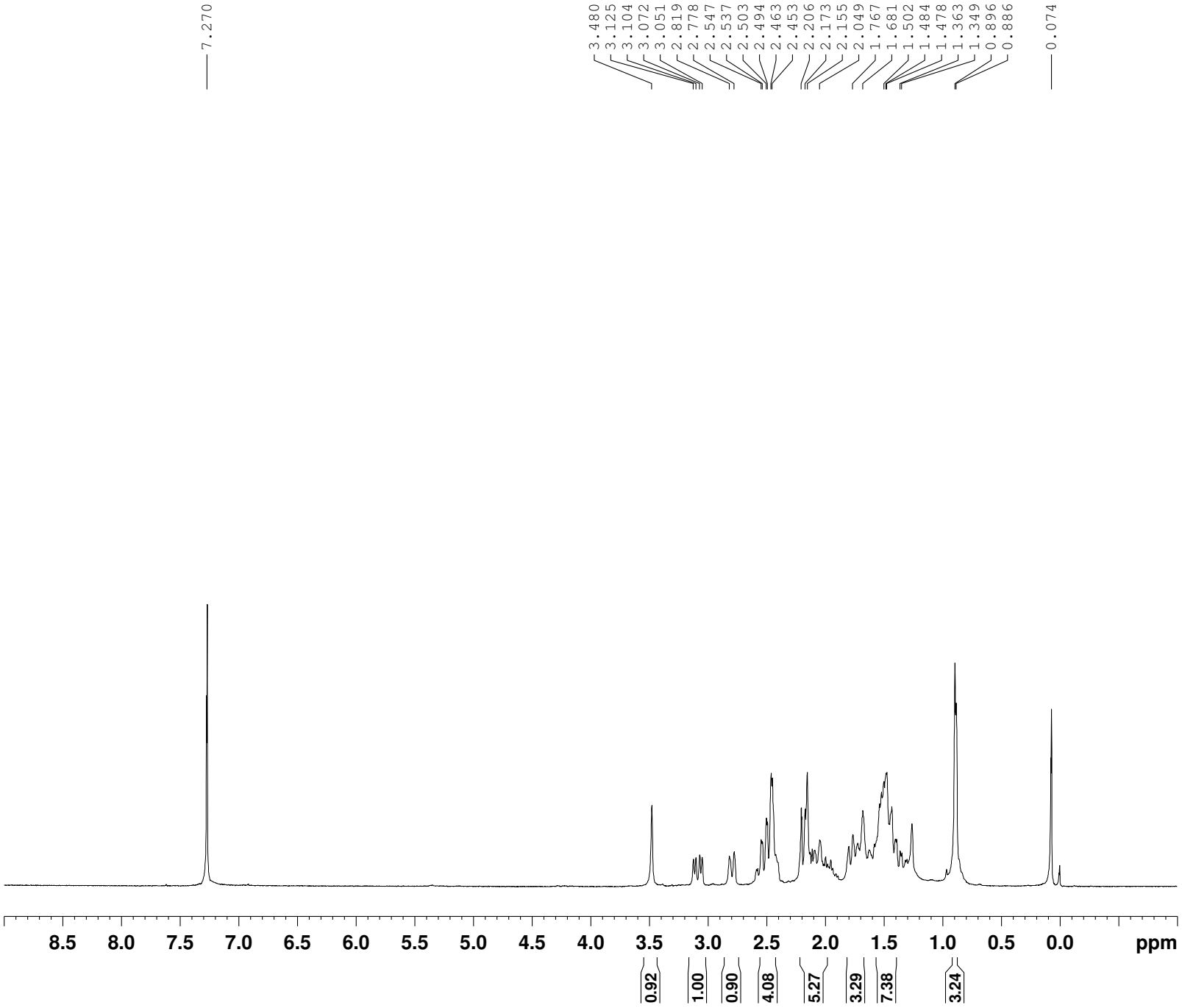
(±)-Anhydrolycodoline•TFA



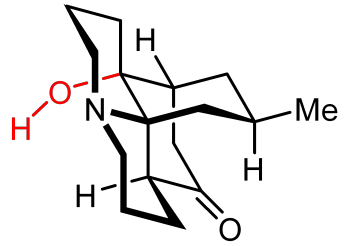
NAME	zxh-2175-1(TFA)
EXPNO	11
PROCNO	1
Date_	20151211
Time	2.05
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	MeOD
NS	2048
DS	2
SWH	26041.666 Hz
FIDRES	0.397364 Hz
AQ	1.2583412 sec
RG	2050
DW	19.200 usec
DE	6.50 usec
TE	292.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6238364 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6126277 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

(±)-Anhydrolycodoline•TFA

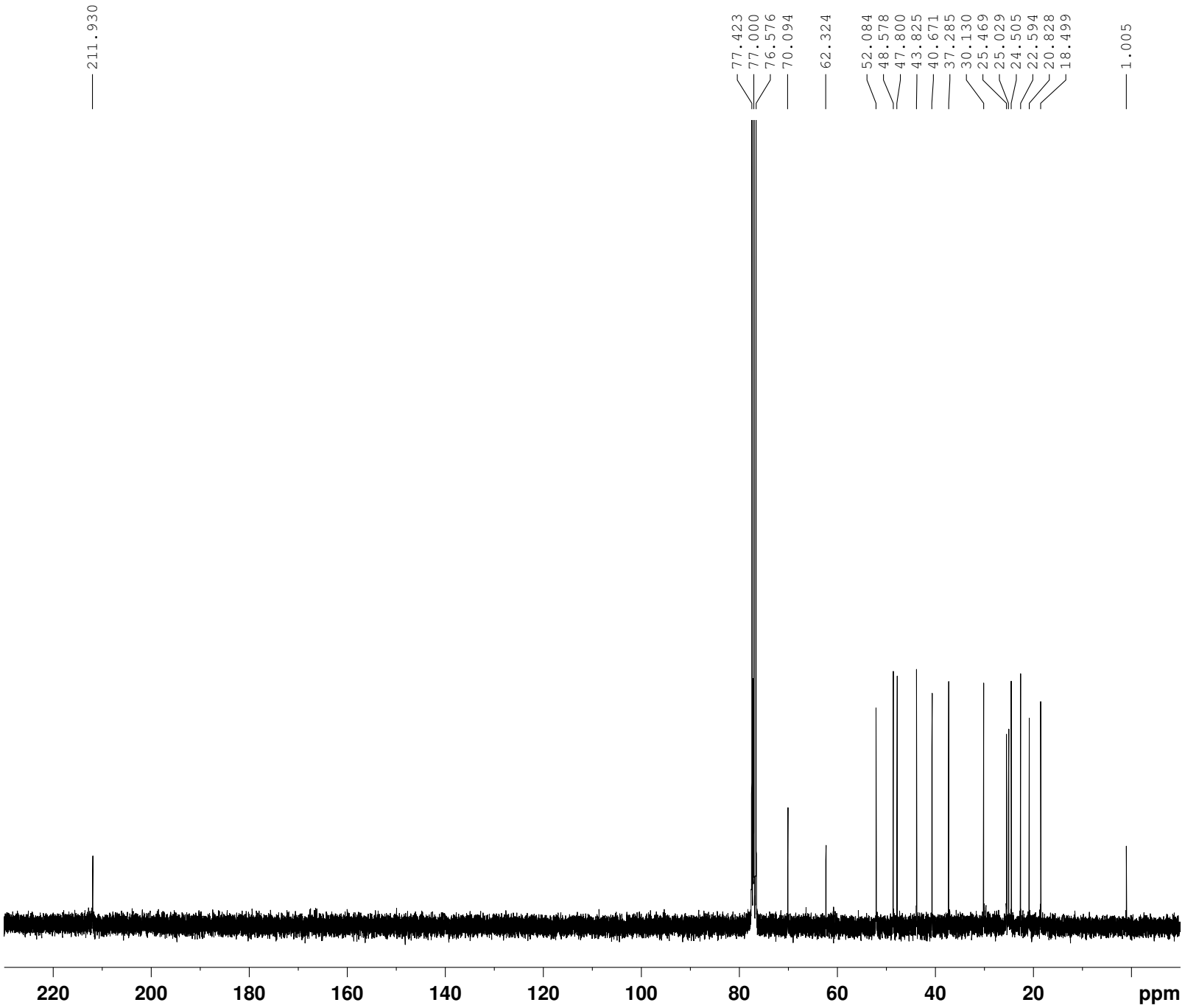
* CF_3COOH



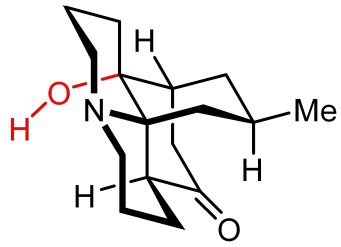
Title	zxh-2315-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Spectrometer	mercury
Author	fanchuan
Solvent	CDCl3
Temperature	3.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	20
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.9971
Acquisition Date	2016-05-12
Modification Date	2016-05-12
Spectrometer Frequency	300.08
Spectral Width	4803.1
Lowest Frequency	-601.1
Nucleus	1H
Acquired Size	9592
Spectral Size	32768



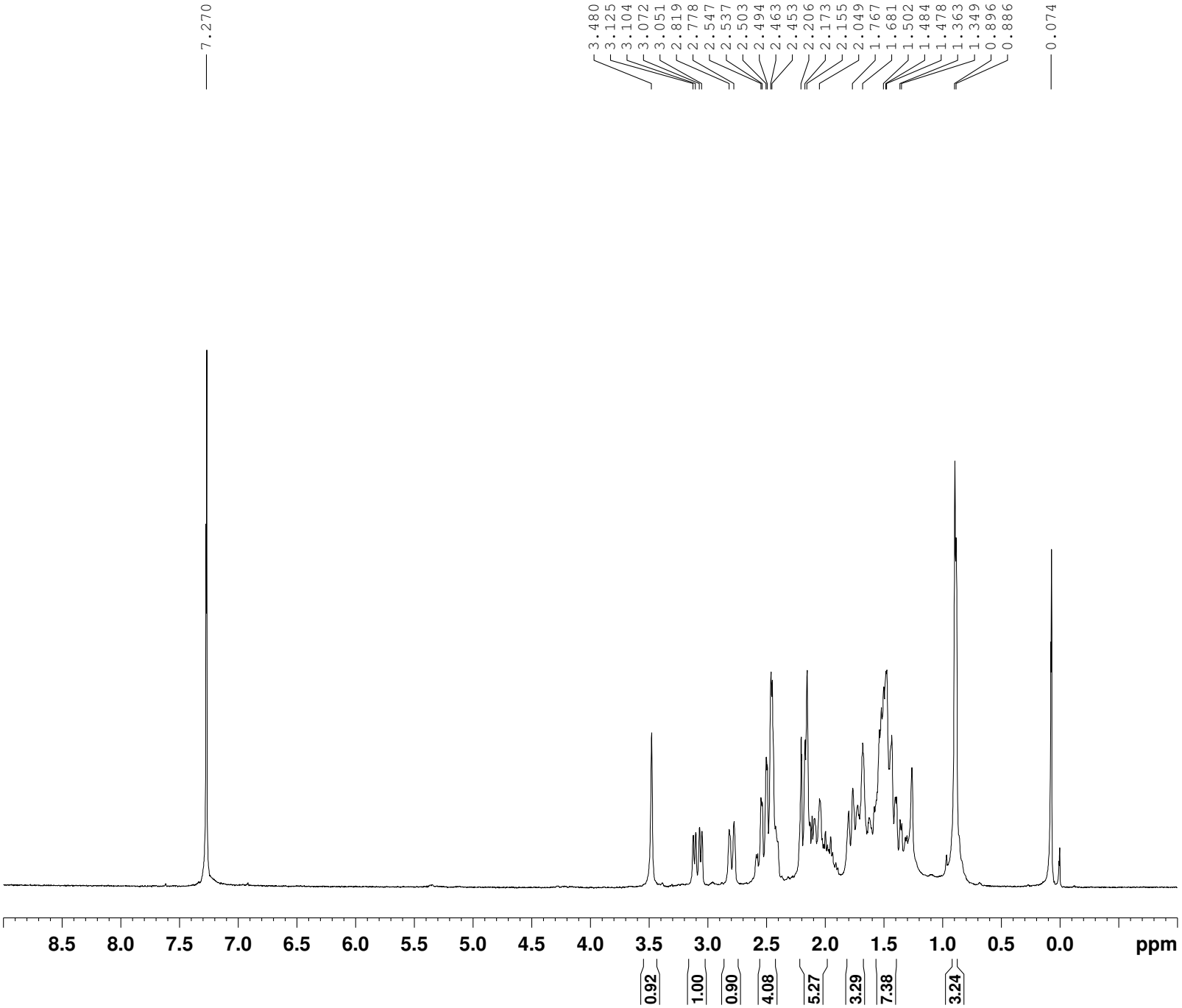
(±)-12-Epilycodoline (**10**)



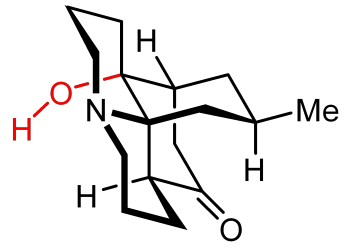
Title	zxh-2315-C
Comment	13C OBSERVE
Origin	Varian
Spectrometer	mercury
Author	fanchuan
Solvent	CDCl3
Temperature	3.0
Pulse Sequence	s2pul
Number of Scans	9024
Receiver Gain	20
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.8150
Acquisition Date	2016-05-12
Modification Date	2016-05-12
Spectrometer Frequency	75.46
Spectral Width	18867.9
Lowest Frequency	-1127.4
Nucleus	13C
Acquired Size	34246
Spectral Size	131072



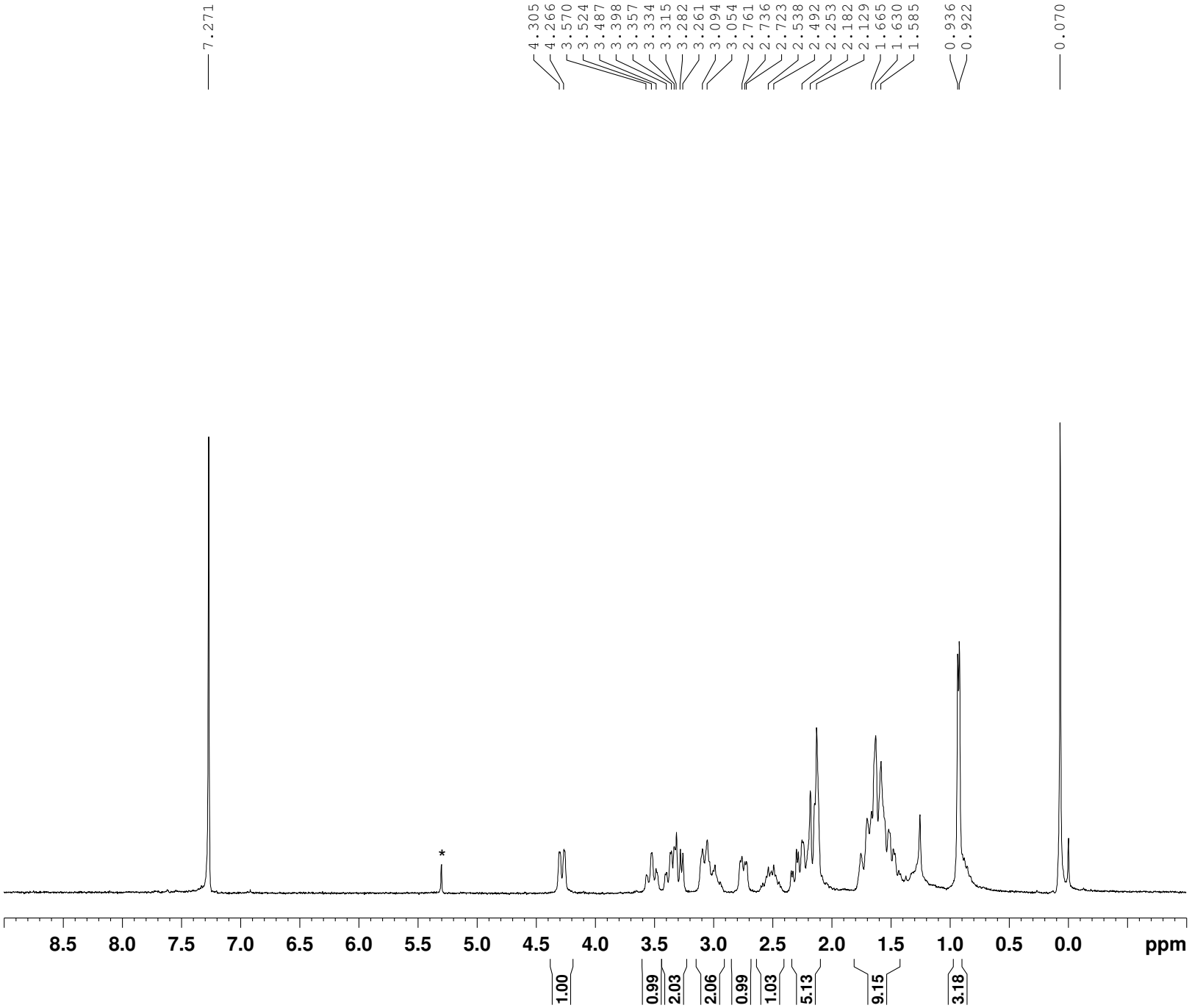
(±)-12-Epilycodoline (**10**)



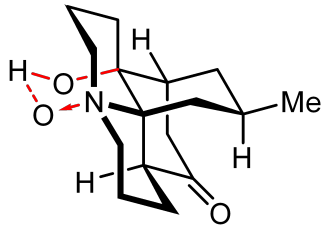
Title	zxh-2315-H
Origin	Varian
Spectrometer	inova
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.7070
Acquisition Date	2016-05-12
Modification Date	2016-05-12
Spectrometer Frequency	599.85
Spectral Width	9598.1
Lowest Frequency	-1200.0
Nucleus	1H
Acquired Size	16384
Spectral Size	32768



(±)-12-Epilycodoline (**10**)

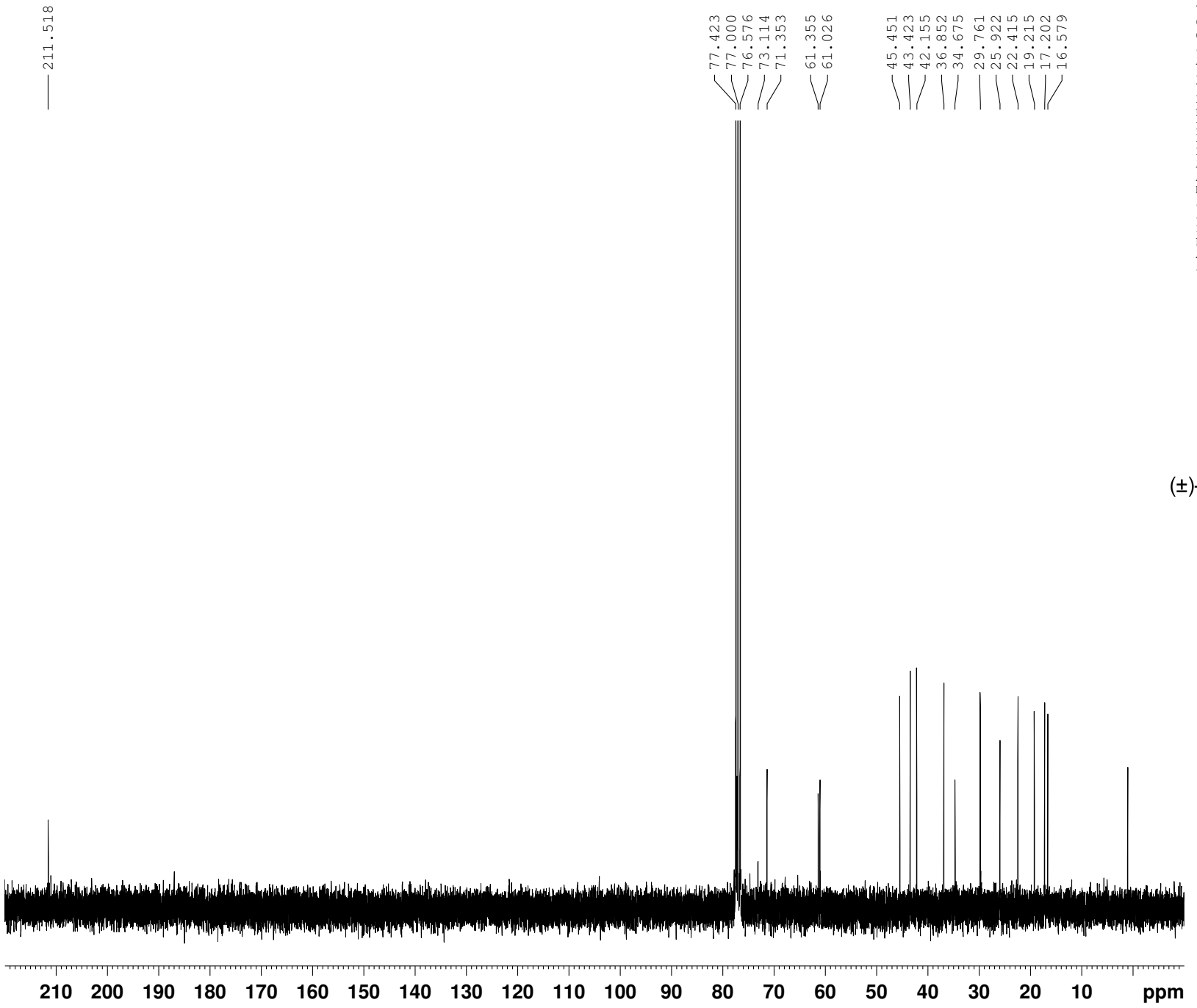


Title	zxh-2289-H
Comment	STANDARD 1H OBSERVE
Origin	Varian
Spectrometer	mercury
Author	fanchuan
Solvent	CDCl3
Temperature	3.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	20
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.9971
Acquisition Date	2016-04-20
Modification Date	2016-04-20
Spectrometer Frequency	300.08
Spectral Width	4803.1
Lowest Frequency	-601.1
Nucleus	1H
Acquired Size	9592
Spectral Size	32768

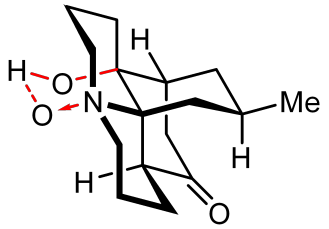


(±)-12-Epilycodoline *N*-Oxide (**11**)
(proposed structure)

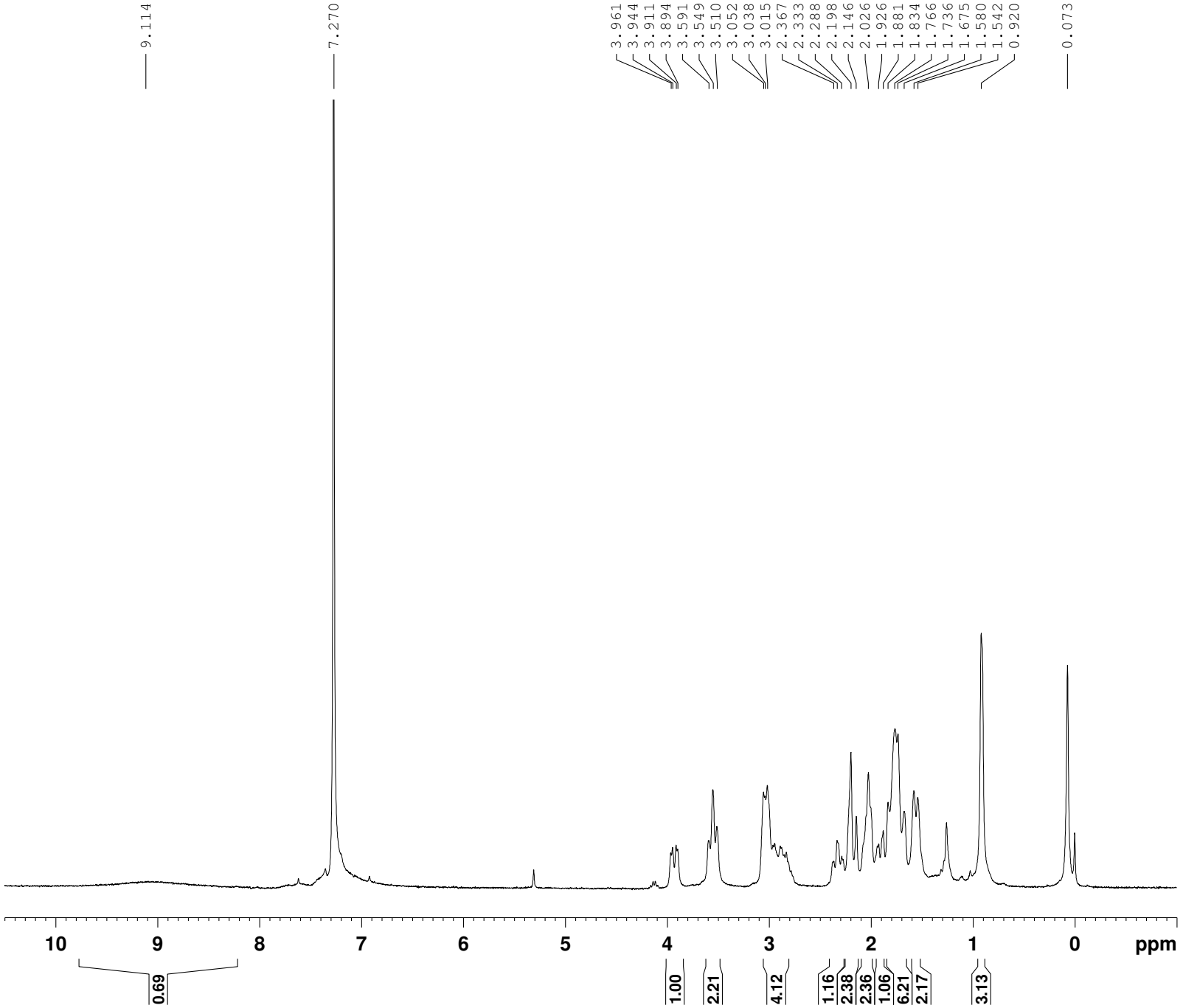
* CH_2Cl_2



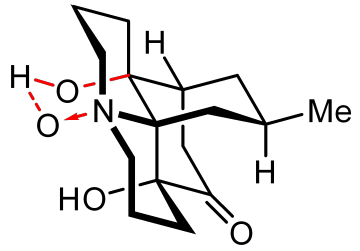
Title	zxh-2289-C
Comment	13C OBSERVE
Origin	Varian
Spectrometer	mercury
Author	fanchuan
Solvent	CDCl3
Temperature	3.0
Pulse Sequence	s2pul
Number of Scans	4000
Receiver Gain	20
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.8150
Acquisition Date	2016-04-21
Modification Date	2016-04-21
Spectrometer Frequency	75.46
Spectral Width	18867.9
Lowest Frequency	-1134.1
Nucleus	13C
Acquired Size	34246
Spectral Size	131072



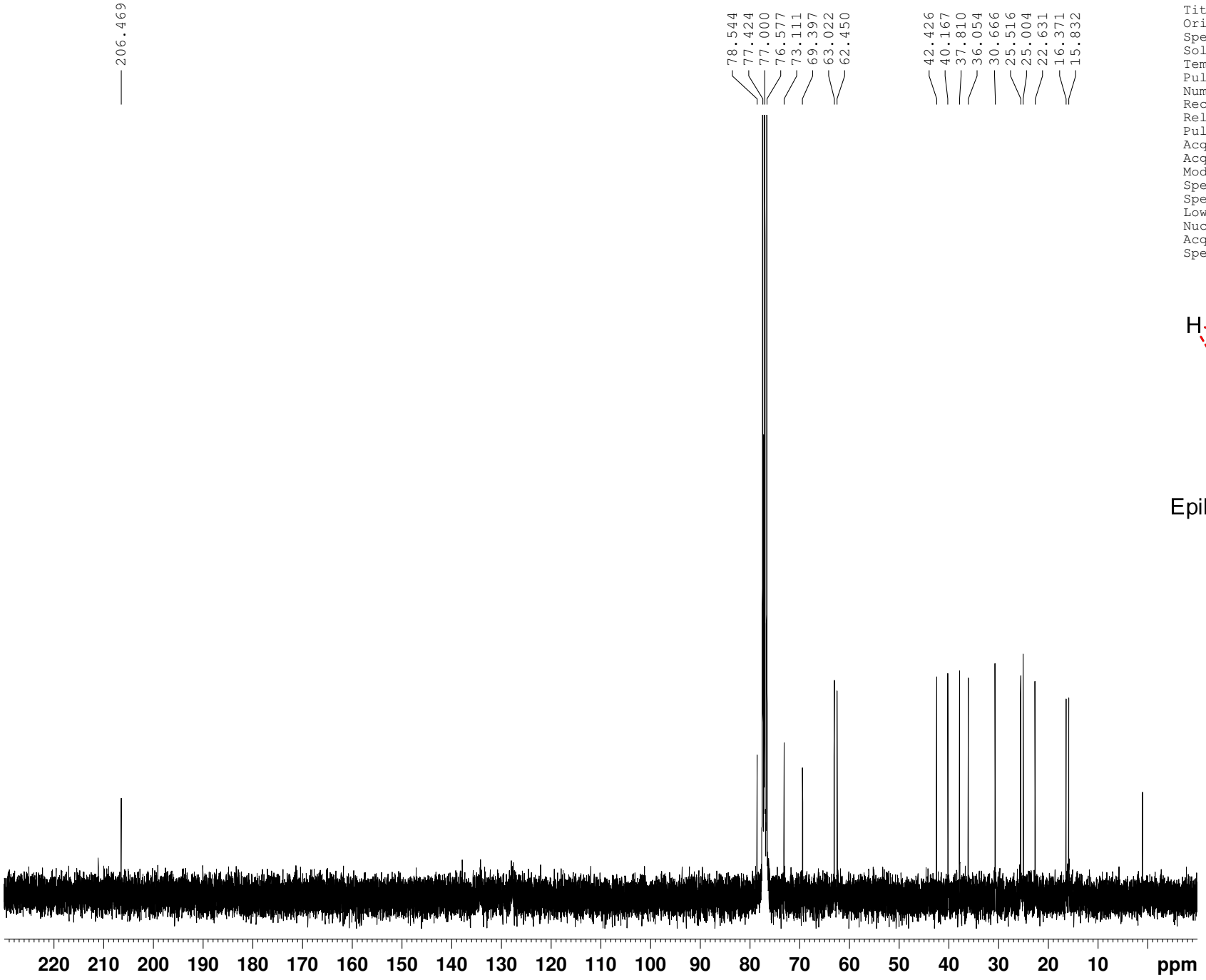
(±)-12-Epilycodoline *N*-Oxide (**11**)
(proposed structure)



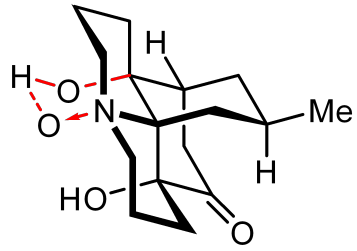
Title	zxh-2397-H
Origin	Varian
Spectrometer	mercury
Solvent	CDCl3
Temperature	3.0
Pulse Sequence	s2pul
Number of Scans	8
Receiver Gain	20
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.9971
Acquisition Date	2017-02-28
Modification Date	2017-02-28
Spectrometer Frequency	300.08
Spectral Width	4803.1
Lowest Frequency	-601.1
Nucleus	1H
Acquired Size	9592
Spectral Size	32768



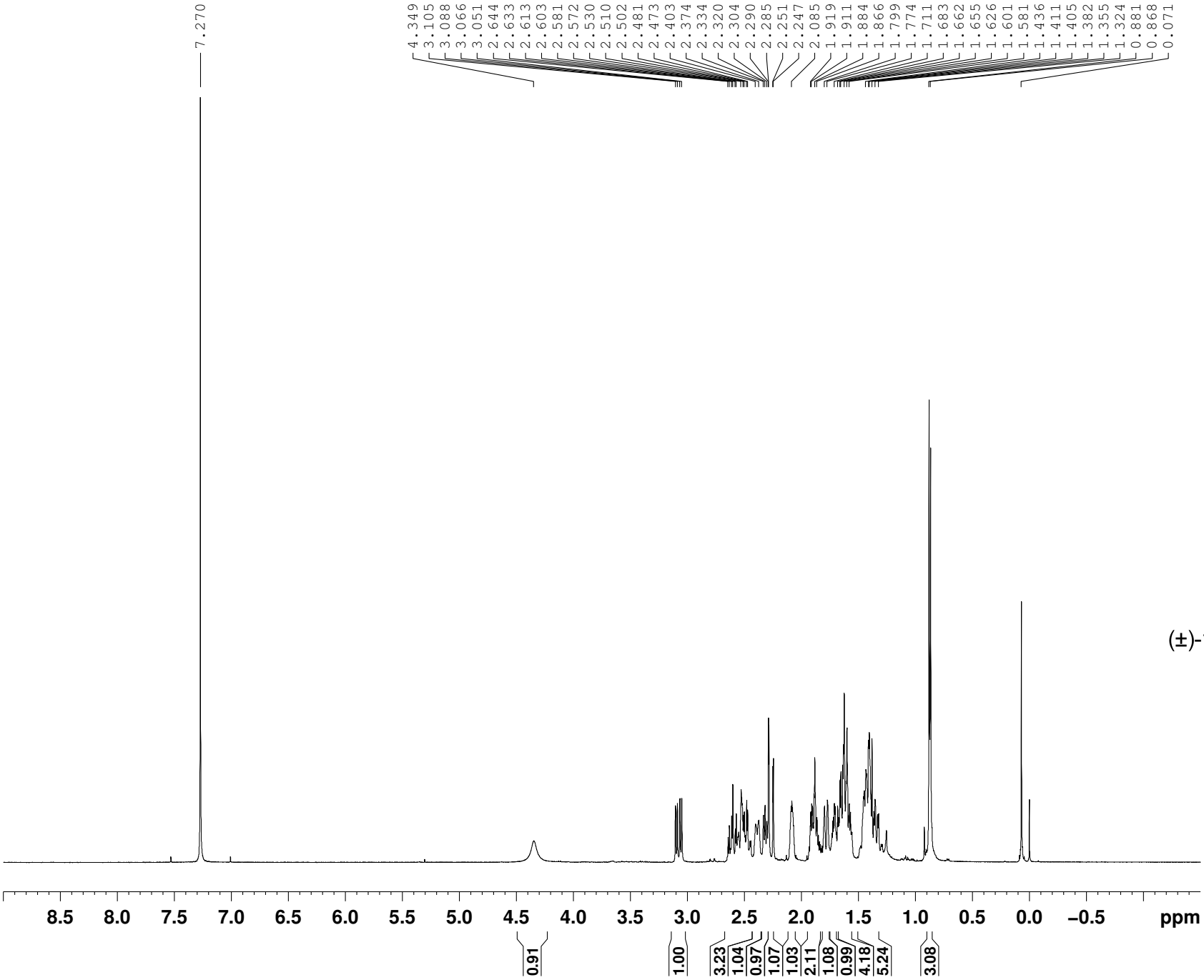
(±)-4-Hydroxy-12-Epilycodoline *N*-Oxide (**12**)



Title	zxh-2397-C
Origin	Varian
Spectrometer	mercury
Solvent	CDCl3
Temperature	3.0
Pulse Sequence	s2pul
Number of Scans	7784
Receiver Gain	20
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.8150
Acquisition Date	2017-02-28
Modification Date	2017-02-28
Spectrometer Frequency	75.46
Spectral Width	18867.9
Lowest Frequency	-1134.1
Nucleus	13C
Acquired Size	34246
Spectral Size	131072

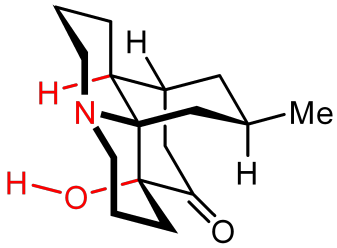


(±)-4-Hydroxy-12-Epilycodoline *N*-Oxide (**12**)

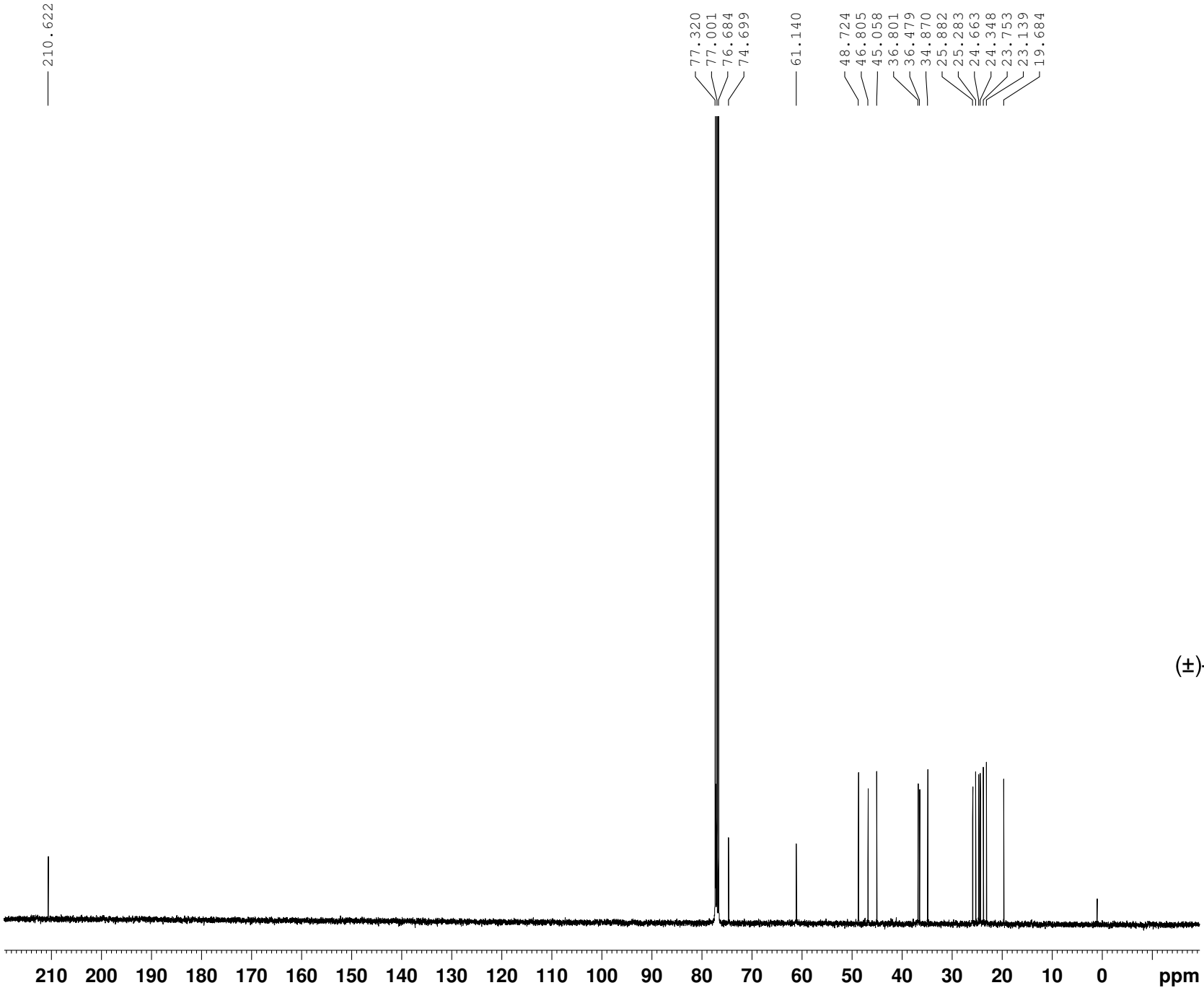


NAME	zxh-2376-2
EXPNO	11
PROCNO	1
Date_	20170120
Time	0.40
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	228
DW	62.400 usec
DE	6.50 usec
TE	364.1 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	400.1324710 MHz
NUC1	1H
P1	10.92 usec
SI	65536
SF	400.1300057 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	15.00

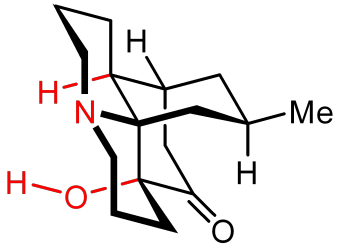


(±)-12-*epi*-Flabelliformine (**13**)

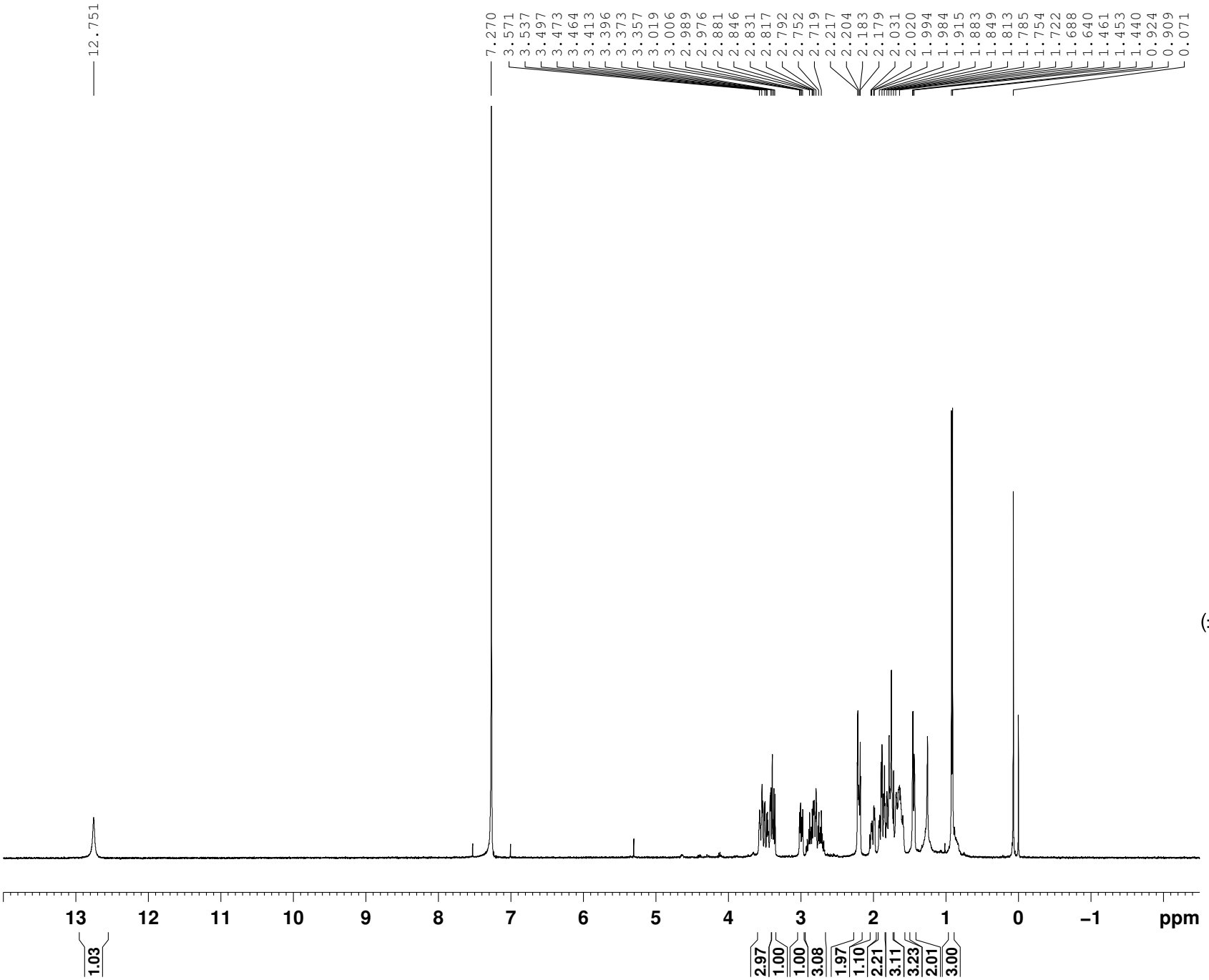



```
NAME            zxh2376-2
EXPNO                  12
PROCNO                  1
Date_            20170120
Time                3.32
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  3000
DS                     2
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                   912
DW                20.800 usec
DE                 6.50 usec
TE                293.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6228298 MHz
NUC1                13C
P1                14.70 usec
SI                32768
SF          100.6127722 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

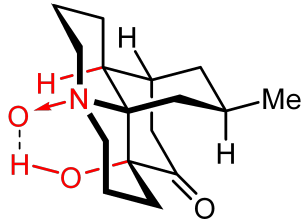


(±)-12-*epi*-Flabelliformine (**13**)

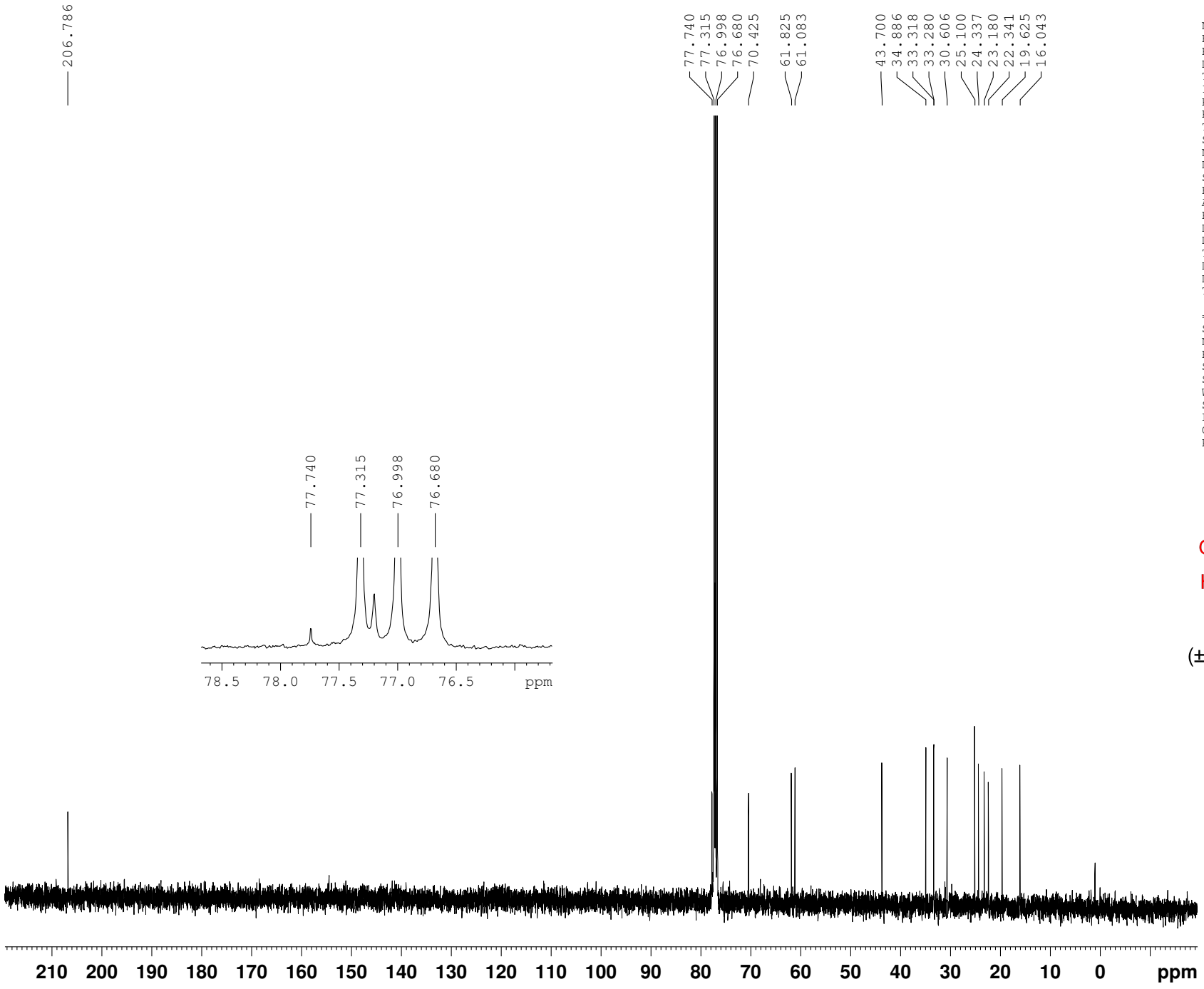



```
NAME          zxh-2376-1
EXPNO                 10
PROCNO                 1
Date_           20170120
Time                8.35
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG                   456
DW                62.400 usec
DE                 6.50 usec
TE                290.2 K
D1          1.00000000 sec
TD0                    1

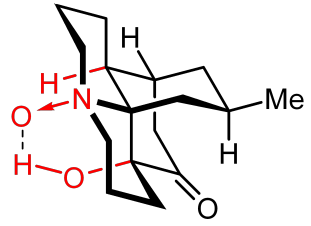
======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                   1H
P1                 10.79 usec
SI                 65536
SF          400.1300059 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



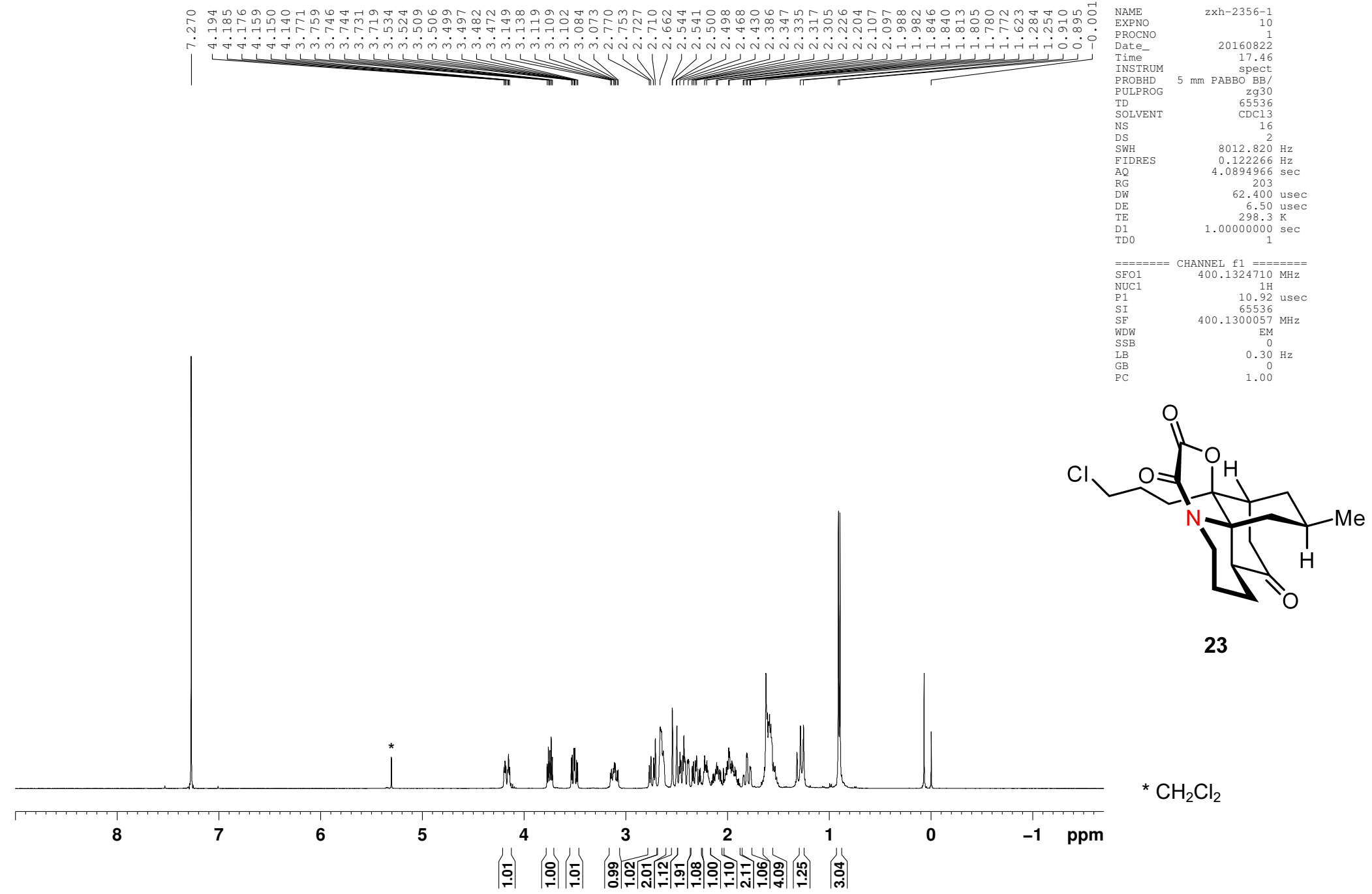
(±)-12-*epi*-Flabelliformine *N*-Oxide (**14**)

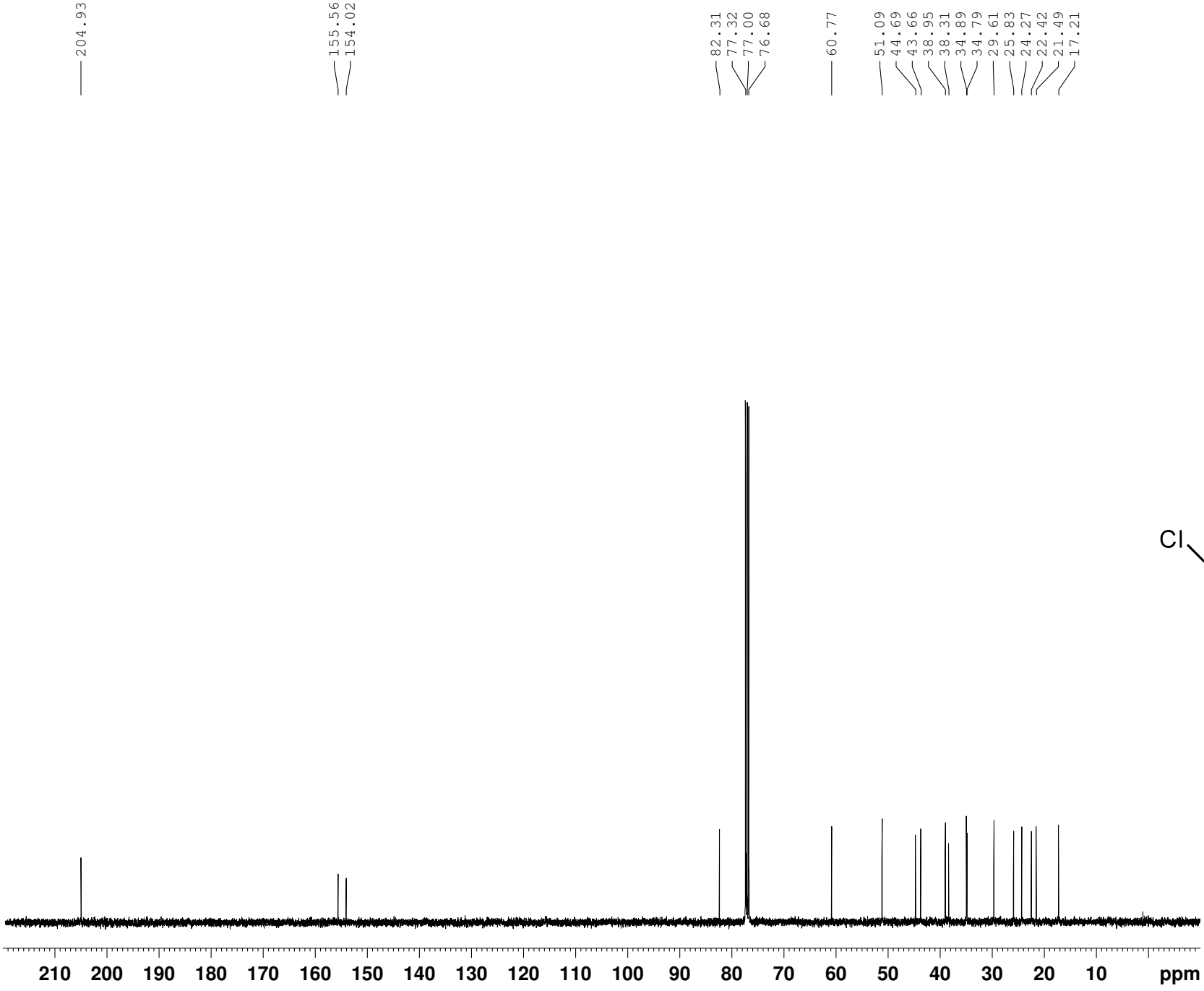


NAME	zxh2376-1
EXPNO	11
PROCNO	1
Date_	20170120
Time	10.00
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1477
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	290.7 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	12.00 usec
SI	32768
SF	100.6127729 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



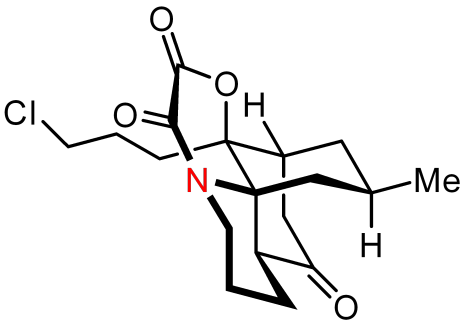
(±)-12-*epi*-Flabelliformine *N*-Oxide (**14**)


7.270
4.194
4.185
4.176
4.159
4.150
4.140
3.771
3.759
3.746
3.744
3.731
3.719
3.534
3.524
3.509
3.506
3.499
3.497
3.482
3.472
3.149
3.138
3.119
3.109
3.102
3.084
3.073
2.770
2.753
2.727
2.710
2.662
2.544
2.541
2.500
2.498
2.468
2.430
2.386
2.347
2.335
2.317
2.305
2.226
2.204
2.107
2.097
1.988
1.982
1.846
1.840
1.813
1.805
1.780
1.772
1.623
1.284
1.254
0.910
0.895
-0.001
NAME zxh-2356-1
EXPNO 10
PROCNO 1
Date_ 20160822
Time 17.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 203
DW 62.400 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.92 usec
SI 65536
SF 400.1300057 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
O
H
Cl
O
N
Me
H
O
23
*
* CH2Cl2
8
7
6
5
4
3
2
1
0
−1
ppm
1.01
1.00
1.01
0.99
1.02
2.01
1.12
1.91
1.08
1.00
1.10
2.11
1.06
4.09
1.25
3.04



NAME	zxh-2356-1
EXPNO	11
PROCNO	1
Date_	20160822
Time	18.08
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	360
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	1620
DW	20.800 usec
DE	6.50 usec
TE	298.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127707 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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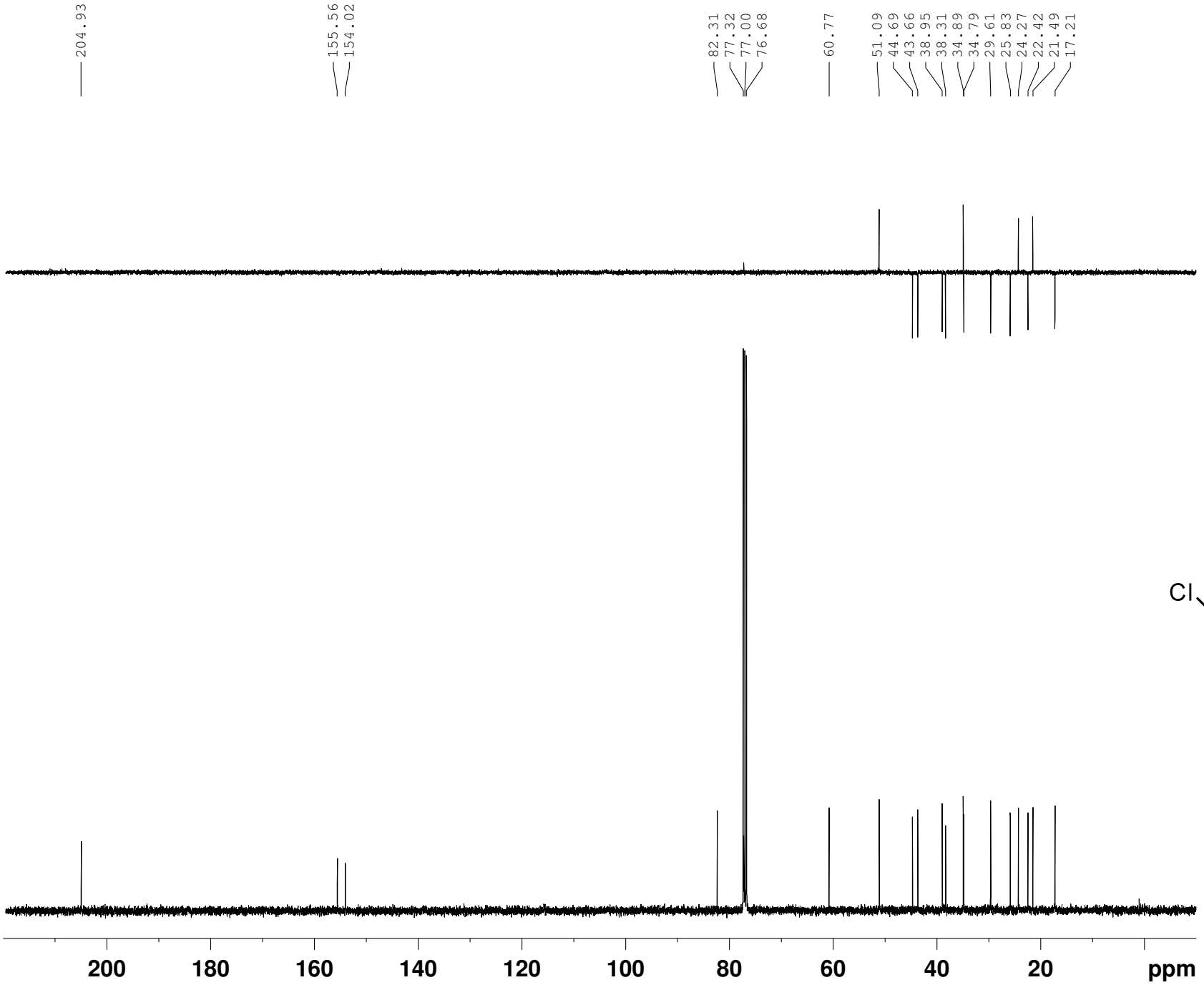
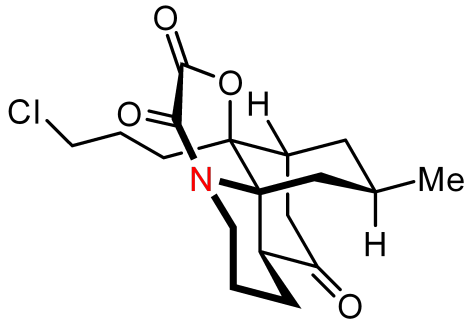



```
NAME          zxh-2356-1
EXPNO                 12
PROCNO                 1
Date_           20160822
Time               18.17
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG       deptsp135
TD                65536
SOLVENT           CDCl3
NS                  150
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 2050
DW                20.800 usec
DE                 6.50 usec
TE                298.4 K
CNST2        145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228298 MHz
NUC1                 13C
P1                14.70 usec
P13             2000.00 usec
SI                32768
SF           100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



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