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Supporting Information

Total Synthesis of an Exceptional Brominated 4-Pyrone Derivative of Algal Origin: An Exercise in Gold Catalysis and Alkyne Metathesis

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Crystallographic Information

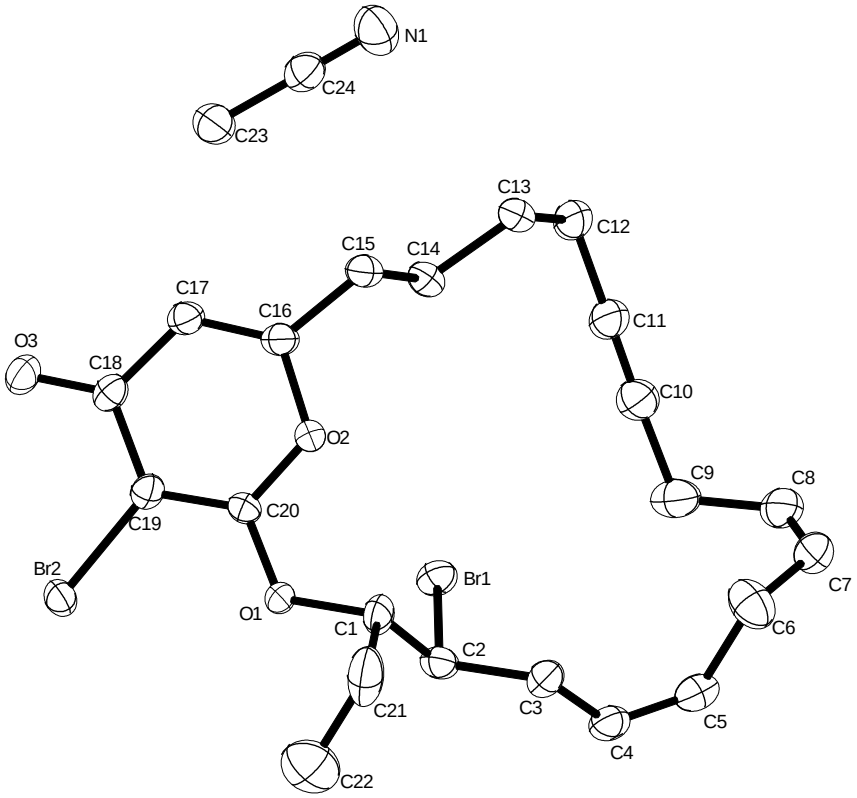


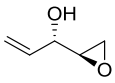
Figure S-1. Structure of compound ***syn*-1** in the solid state.

CCDC 1038629 contains the supporting crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray Crystal Structure Analysis of compound 1: $C_{24}H_{29}Br_2NO_3$, M_r = 539.30 g · mol^{-1}, colorless plate, crystal size 0.25 x 0.07 x 0.05 mm, orthorhombic, space group $P2_12_12_1$, a = 4.7865(4) Å, b = 20.3783(16) Å, c = 24.3411(19) Å, V = 2374.2(3) Å^3, T = 100 K, Z = 4, D_{calc} = 1.509 g · cm^3, λ = 1.54178 Å, $\mu(Cu\text{-}K_\alpha)$ = 4.525 mm^{-1}; empirical absorption correction (T_{min} = 0.25, T_{max} = 0.84), Bruker AXS X8 Proteum diffractometer, 2.828 < θ < 67.738°, 63947 measured reflections, 4285 independent reflections, 4199 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.033 [$I > 2\sigma(I)$], wR_2 = 0.089, 273 parameters, absolute structure parameter = –0.009(7), H atoms riding, S = 1.064, residual electron density 1.0 / –0.9 e Å^{-3}.

General. All reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2, MeCN (CaH_2), hexane, toluene (Na/K), MeOH (Mg), DMF (MS 4 Å). Flash chromatography: Merck silica gel 60 (40–63 μm) or Florisil (60-100 mesh). NMR: Spectra were recorded on a Bruker DPX 300, AV 400, AV 500 or AVIII 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.2$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; C_6D_6: $\delta_C \equiv 128.1$ ppm; residual C_6D_5H: $\delta_H \equiv 7.16$ ppm). Where indicated, the signal assignments are unambiguous; the numbering scheme is arbitrary and shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygpqf* and *cosydqtp*); HSQC (*hsqcedetgpsisp2.2*) optimized for $^1J_{C,H}$ = 145 Hz; HMBC (*hmbcetgpl3nd*) for correlations via $^nJ_{C,H}$; HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms; NOESY (noesygpph). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Unless stated otherwise, all commercial compounds (Fluka, Acros, Aldrich) were used as received.

Compound 8. A suspension of powdered MS 4 Å (2.00 g) in CH_2Cl_2 (60 mL) was stirred



–35 °C for 10 min before titanium tetraisopropoxide (1.76 mL, 5.94 mmol, 10 mol%) and (+)-diisopropyl L-tartrate (1.62 mL, 7.73 mmol, 0.13 equiv) were added. Stirring was continued for 3 h at –35 °C before 1,4-pentadien-3-ol (5.78 mL, 59.4 mmol) was slowly introduced, followed by cumene hydroperoxide (17.6 mL, 119 mmol). The mixture was stirred for 38 h at –35 °C before the reaction was quenched with saturated aqueous Na_2SO_4 (5 mL). The mixture was diluted with *tert*-butyl methyl ether (50 mL) and the suspension was stirred for 3 h before the resulting slurry was filtered through a pad of Celite. The filtrate was concentrated and excess 2-phenyl-2-propanol and cumene hydroperoxide were removed by flash chromatography (SiO_2, hexanes/*tert*-butyl methyl ether = 5:1) to give the desired epoxide as a colorless oil (4.87 g, 82%). $[\alpha]_D^{25}$ = +68.8 (c = 0.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83 (ddd, 1H, J = 17.2, 10.5, 6.2 Hz), 5.38 (dt, 1H, J = 17.2, 1.3 Hz), 5.25 (dt, 1H, J = 10.5, 1.3 Hz), 4.34 – 4.28 (m, 1H), 3.08 (dt, 1H, J = 4.0, 3.0 Hz), 2.79 (dd, 1H, J = 5.0, 3.0 Hz), 2.74 (dd, 1H, J = 5.0, 4.0 Hz), 2.23 ppm (d, 1H, J = 3.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 117.7, 70.3, 54.0, 43.6 ppm; IR (film): $\tilde{\nu}$ = 3417, 2997, 1427, 1251, 1024, 972, 930, 885, 832, 793, 756 cm^{-1}; MS (EI): *m/z* (%) 69 (22), 57 (100), 55 (24), 43 (29), 31 (18), 29 (55), 27 (29); HRMS (CI): *m/z*: calcd. for $C_5H_9O_2$ [$M+H^+$]: 101.0603, found: 101.0602. The spectral data are in good agreement with those previously reported in the literature.[1]

[1] S. Singh, P. J. Guiry, *J. Org. Chem.* **2009**, *74*, 5758.

Compound S1. TBSCl (6.96 g, 46.2 mmol) was added at 0 °C to a solution of compound **8** (4.20 g, 42.0 mmol) and imidazole (6.00 g, 88.2 mmol) in DMF (42 mL). After stirring for 1 h at 0 °C, the mixture was diluted with *tert*-butyl methyl ether (300 mL) and washed with water (4 × 100 mL) and brine (1 × 100 mL). The organic phase was dried over Na_2SO_4 and concentrated, and the residue was purified by flash chromatography (SiO_2, hexanes/*tert*-butyl methyl ether = 10:1) to give the title compound as a colorless oil (8.09 g, 90%). $[\alpha]_D^{25}$ = +1.90 (c = 0.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88 (ddd, 1H, *J* = 17.2, 10.4, 5.5 Hz), 5.32 (dt, 1H, *J* = 17.2, 1.5 Hz), 5.18 (dt, 1H, *J* = 10.4, 1.5 Hz), 4.12 (ddt, 1H, *J* = 5.5, 4.0, 1.5 Hz), 2.94 (td, 1H, *J* = 3.9, 3.1 Hz), 2.70 – 2.69 m, 2H), 0.89 (s, 9H), 0.06 (s, 3H), 0.05 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.6, 116.0, 72.6, 54.6, 44.4, 25.9 (3C), 18.4, −4.6, −4.7 ppm; IR (film): $\tilde{\nu}$ = 2956, 2930, 2857, 1472, 1250, 1119, 1079, 1033, 1000, 926, 834, 774, 673 cm^{-1}; MS (EI): *m/z* (%) 171 (11), 157 (18), 127 (100), 101 (32), 75 (71), 59 (23), 45 (13); HRMS (ESI+): *m/z*: calcd. for $C_{11}H_{22}NaO_2Si$ [$M+Na^+$]: 237.1281, found: 237.1283.

Compound 9. A mixture of compound **S1** (8.00 g, 37.3 mmol) and palladium on charcoal (10% Pd, 400 mg) in EtOAc (80 mL) was vigorously stirred under H_2 atmosphere for 2 h. The suspension was filtered through a pad of Celite and the filtrate was concentrated. The residue was distilled in a Kugelrohr apparatus (90–105 °C, 9 mbar) to give the title compound as a colorless oil (7.65 g, 95%). $[\alpha]_D^{25}$ = +13.0 (c = 0.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.51 (dt, 1H, *J* = 6.6 Hz), 2.86 (ddd, 1H, *J* = 4.6, 3.9, 2.6 Hz), 2.69 (dd, 1H, *J* = 5.5, 3.9 Hz), 2.65 (dd, 1H, *J* = 5.0, 2.6 Hz), 1.71 – 1.49 (m, 2H), 0.96 (t, 3H, *J* = 7.5 Hz), 0.88 (s, 9H), 0.04 (s, 3H), 0.04 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 72.5, 54.6, 44.9, 28.3, 26.0 (3C), 18.3, 9.4, −4.3, −4.7 ppm; IR (film): $\tilde{\nu}$ = 2957, 2930, 2857, 1463, 1251, 1110, 1074, 1017, 994, 833, 773 cm^{-1}; MS (EI): *m/z* (%)173 (4), 159 (29), 129 (44), 117 (33), 101 (48), 89 (11), 75 (100), 59 (22); HRMS (ESI+): *m/z*: calcd. for $C_{11}H_{24}NaO_2Si$ [$M+Na^+$]: 239.1438, found: 239.1438. The ^{1}H NMR data are in good agreement with those previously reported in the literature.[2]

Compound S2. A solution of propargyl alcohol (30.0 mL, 515 mmol) and *p*-TsOH·H_2O (98.0 mg, 0.515 mmol, 0.10 mol%) in ethyl vinyl ether (74 mL) was stirred for 5 h at 0 °C. The reaction was quenched with saturated aqueous Na_2CO_3 (10 mL). Excess Na_2CO_3 was then added before the mixture was passed through a glass filter. Evaporation of the filtrate followed by distillation of the residue in a Vigreux column (bp 58 – 64 °C, 50 mbar) gave the title compound as a colorless oil (55.6 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.85 (q, 1H, *J* = 5.4 Hz), 4.20 (d, 2H, *J* = 2.4 Hz), 3.65 (dq, 2H, *J* = 9.4, 7.1 Hz), 3.51 (dq, 1H, *J* = 9.4, 7.1 Hz), 2.39 (t, 1H, *J* = 2.4 Hz), 1.33 (d, 3H, *J* = 5.4 Hz), 1.20 ppm (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 98.8, 80.2, 73.9, 60.9, 52.6, 19.8,

[2] C. Barry, J. Cherian, I. Choi, T. Keller, U. Manjunatha, A. Nayyar, H. H. Young, PCT Patent WO 2011087995 A2, 2011.

15.4 ppm; IR (film): $\tilde{\nu}$ = 2979, 2933, 2900, 1445, 1385, 1339, 1267, 1128, 1084, 1052, 1036, 991, 946, 927, 852, 823, 659, 631, 500 cm^{-1}; MS (EI): *m/z* (%) 113 (87), 85 (29), 83 (95), 73 (100), 57 (31), 55 (33), 45 (99), 43 (94),39 (95), 29 (61); HRMS (CI): *m/z*: calcd. for $C_7H_{13}O_2$ [$M+H^+$]: 129.0916, found: 129.0915. The NMR data are in good agreement with those previously reported in the literature.[3,4]

Compound 11. EtMgBr (3.0 M in Et_2O, 39.6 mL, 119 mmol) was diluted with THF (120 mL) and the solution warmed to 45 °C. 3-(1-Ethoxyethoxy)prop-1-yne **S2** (15.0 mL, 110 mmol) was added dropwise at this temperature. After stirring for 0.5 h, CuCl (546 mg, 5.51 mmol, 5 mol%) was introduced and the mixture stirred at 50 °C for 0.5 h. A toluene solution of propargyl bromide (80%, 14.1 mL, 127 mmol) was then added dropwise, the temperature was raised to 60 °C and stirring continued for 1.5 h. For work up, the mixture was cooled to ambient temperature and then poured into a solution of KCN (1.94 g) and NH_4Cl (14.8 g) in water (97.8 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (3 x), and the combined extracts were washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by distillation (bp 53 – 55 °C, 0.07 mbar) to give the title compound as a pale yellow oil (12.4 g, 68%). *This product is very sensitive to air and must be stored under argon in a freezer*. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.82 (q, 1H, *J* = 5.4 Hz), 4.18 (dt, 2H, *J* = 2.2, 1.1 Hz), 3.64 (dq, 1H, *J* = 9.4, 7.1 Hz), 3.50 (dq, 1H, *J* = 9.4, 7.1 Hz), 3.21 – 3.18 (m, 2H), 2.05 (t, 1H, *J* = 2.8 Hz), 1.31 (d, 3H, *J* = 5.4 Hz), 1.19 ppm (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 98.7, 79.2, 77.9, 77.2, 69.1, 60.8, 53.1, 19.8, 15.4, 9.8 ppm; IR (film): $\tilde{\nu}$ = 3295, 2979, 2900, 1445, 1385, 1338, 1311, 1124, 1083, 1053, 1028, 979, 945, 927, 854 cm^{-1}; MS (EI): *m/z* (%) 151 (20), 121 (25), 93 (10), 77 (100), 73 (53), 65 (7), 51 (39), 45 (57); HRMS (CI): *m/z*: calcd. for $C_{10}H_{15}O_2$ [$M+H^+$]: 167.1072, found: 167.1073.

Compound 12. *n*-BuLi (1.6 M in hexanes, 2.60 mL, 4.16 mmol) was added dropwise to a solution of the skipped diyne **11** (691 mg, 4.16 mmol) in THF (40 mL) at –78 °C. After stirring for 0.5 h at that temperature, $BF_3{\cdot}OEt_2$ (513 µL, 4.16 mmol) was slowly introduced. After stirring for 5 min, a solution of the epoxide **9** (300 mg, 1.39 mmol) in THF (4 mL) was added and stirring continued for 0.5 h at –78 °C. For work up, the solution was poured into saturated aqueous $NaHCO_3$ (40 mL) and the mixture extracted with *tert*-butyl methyl ether (3 x). The combined extracts were washed with water and brine, dried over Na_2SO_4, and concentrated, and the crude product was purified by flash chromatography (SiO_2, hexane/EtOAc = 10:1 containing 1% Et_3N) to give the title compound as a yellow oil (381 mg, 72%). $[\alpha]_D^{25}$ = +16.4 (c = 1.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.82 (q, 1H, *J* = 5.3 Hz), 4.18 (q, 2H, *J* =

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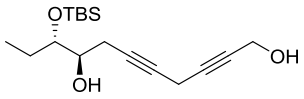
3 A. J. Poss, R. K. Belter, *J. Org. Chem.* **1987**, *52*, 4810.

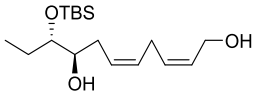
4 A. Mames, S. Stecko, P. Mikołajczyk, M. Soluch, B. Furman, M. Chmielewski, *J. Org. Chem.* **2010**, *75*, 7580.

2.2 Hz), 3.73 – 3.59 (m, 3H), 3.50 (dq, 1H, *J* = 9.4, 7.1 Hz), 3.19 (tt, 2H, *J* = 2.2, 2.2 Hz), 2.40 – 2.35 (m, 2H), 2.17 (br s, 1H), 1.63 – 1.40 (m, 2H), 1.32 (d, 3H, *J* = 5.3 Hz), 1.19 (t, 3H, *J* = 7.1 Hz), 0.90 (t, 3H, *J* = 7.4 Hz), 0.89 (s, 9H), 0.07 (s, 3H), 0.07 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 98.7, 80.3, 76.6, 75.9, 75.2, 72.1, 60.7, 53.1, 46.3, 26.0 (3C), 24.7, 22.8, 19.8, 18.2, 15.4, 10.1, 9.4, −4.3, −4.4 ppm; IR (film): $\tilde{\nu}$ = 3481, 2930, 2858, 1463, 1384, 1253, 1128, 1084, 1055, 1030, 1004, 928, 834, 774, 668 cm^{-1}; MS (EI): *m/z* (%)279 (13), 235 (21), 173 (61), 145 (24), 115 (9), 91 (7), 73 (100), 45 (26); HRMS (ESI+): *m/z*: calcd. for $C_{21}H_{38}NaO_4Si$ [$M+Na^+$]: 405.2432, found: 405.2428.

Compound S3. A solution of compound **12** (775 mg, 2.03 mmol) and pyridinium *p*-toluenesulfonate (509 mg, 2.03 mmol) in MeOH (100 mL) was stirred for 1 h at ambient temperature before saturated aqueous $NaHCO_3$ was added. The mixture was concentrated to remove the MeOH prior to extraction with EtOAc (3 x). The combined extracts were washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash chromatography (SiO_2, hexane/EtOAc = 2:1 containing 1% Et_3N) to give the title compound as a yellow oil (615 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.25 (t, 2H, *J* = 2.2 Hz), 3.74 – 3.64 (m, 2H), 3.20 (tt, 2H, *J* = 2.3, 2.3 Hz), 2.41 – 2.36 (m, 2H), 1.64 – 1.39 (m, 2H), 0.91 (t, 3H, *J* = 7.5 Hz), 0.89 (s, 9H), 0.08 (s, 3H), 0.08 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 80.5, 78.7, 77.6, 75.8, 75.2, 72.2, 51.4, 26.0 (3C), 24.6, 22.8, 18.2, 10.1, 9.5, −4.3, −4.4 ppm; IR (film): $\tilde{\nu}$ = 3361, 2929, 2857, 1463, 1252, 1068, 1003, 834, 773, 668 cm^{-1}; MS (EI): *m/z* (%): 235 (21), 187 (11), 174 (14), 173 (100), 145 (53), 133 (14), 117 (19), 115 (27), 105 (13), 91 (16), 77 (12), 75 (98), 73 (82), 57 (23); HRMS (ESI+): *m/z*: calcd. for $C_{17}H_{30}O_3SiNa$ [$M+Na^+$]: 333.1854, found: 333.1856.



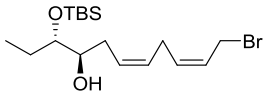
Compound S4. A solution of $NaBH_4$ (1 M in EtOH, 495 µL, 0.495 mmol, 25 mol%) was added to a solution of $Ni(OAc)_2 \cdot 4H_2O$ (138 mg, 0.495 mmol, 25 mol%) in EtOH (0.7 mL). After the evolution of hydrogen had ceased, the resulting black suspension was cooled to –78 °C and the flask was filled with hydrogen gas. 1,2-Ethylenediamine (106 µL, 1.58 mmol) and a solution of the skipped diyne **S3** (615 mg, 1.98 mmol) were added and the mixture was allowed to reach ambient temperature. After stirring for 7 h, the mixture was diluted with EtOAc. The resulting suspension was filtered through a pad of Celite and the filtrate was concentrated. The residue was purified by flash chromatography (SiO_2, hexane/EtOAc = 3:1 containing 1% Et_3N) to give the title compound as a pale yellow oil (489 mg, 79%).[5] $[\alpha]_D^{25}$ = +2.2 (c = 1.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.70 – 5.60 (m, 1H), 5.59 – 5.43 (m, 3H), 4.27 – 4.21 (m, 1H), 4.17 – 4.08 (m, 1H), 3.65 – 3.54 (m, 2H), 2.99 – 2.92 (m, 1H), 2.84 – 2.74 (m, 1H), 2.32 – 2.16 (m, 2H), 2.05 (br s, 2H), 1.64 – 1.40 (m, 2H), 0.90 (t, 3H, *J* = 7.4 Hz), 0.90 (s, 9H), 0.07 (s, 3H), 0.07 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.7, 130.2, 128.8, 126.6,



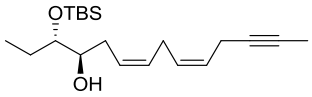
[5] Contains ~22% of the C9-C10 *trans*-isomer.

76.1, 73.8, 58.4, 30.3, 26.1, 26.0 (3C), 24.3, 18.2, 9.9, −4.2, −4.3 ppm; IR (film): $\tilde{\nu}$ = 3361, 2929, 2857, 1463, 1253, 1082, 1004, 834, 773, 755, 666 cm^{-1}; MS (EI): *m/z* (%) 239 (12), 187 (21), 173 (80), 145 (60), 133 (43), 115 (17), 93 (50), 75 (100), 67 (13), 57 (20), 41 (13); HRMS (ESI+): *m/z*: calcd. for $C_{17}H_{34}NaO_3Si$ [$M+Na^+$]: 337.2169, found: 337.2166.

Compound *syn*-13. A solution of PPh_3 (84.3 mg, 0.322 mmol) in CH_2Cl_2 (1.5 mL) was added at 0 °C to a solution of compound **S4** (77.8 mg, 0.247 mmol) and CBr_4 (107 mg, 0.322 mmol) in CH_2Cl_2 (3.5 mL). After stirring for 0.5 h at 0 °C, the reaction was quenched with saturated aqueous NH_4Cl and the mixture was extracted with *tert*-butyl methyl ether. The combined extracts were washed with water and brine, dried over Na_2SO_4, and concentrated, and the crude material was purified by flash chromatography (SiO_2, hexane/EtOAc = 20:1) to give the title compound as a colorless oil (85.3 mg, 91%). $[\alpha]_D^{25}$ = −3.4 (c = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.76 (dtt, 1H, J = 10.4, 8.4, 1.7 Hz), 5.61 – 5.47 (m, 3H), 4.01 (dd, 2H, *J* = 8.3, 1.0 Hz), 3.66 – 3.57 (m, 2H), 2.92 (t, 2H, *J* = 6.6 Hz), 2.31 – 2.14 (m, 2H), 2.06 (br d, 1H, *J* = 3.5 Hz), 1.64 – 1.40 (m, 2H), 0.92 (t, 3H, *J* = 7.5 Hz), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.7, 128.9, 127.4, 125.8, 76.3, 73.9, 30.1, 27.0, 26.0 (3C), 25.6, 24.1, 18.3, 10.1, −4.2, −4.3 ppm; IR (film): $\tilde{\nu}$ = 3567, 2930, 2857, 1463, 1253, 1077, 1004, 834, 774, 754, 668 cm^{-1}; HRMS (ESI+): *m/z*: calcd. for $C_{17}H_{33}BrNaO_2Si$ [$M+Na^+$]: 399.1326, found: 399.1329.

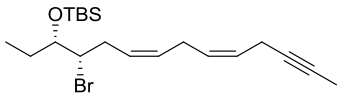


Compound *syn*-14. A suspension of CuI (38 mg, 0.20 mmol) in THF (10 mL) was added to a solution of 1-propynylmagnesium bromide (0.5 M in THF, 2.38 mL, 1.19 mmol) at −15 °C. After stirring for 0.5 h at −15 °C, a solution of bromide **13** (150 mg, 0.397 mmol) in THF (4 mL) was slowly introduced and stirring was continued for 5 h at −10 °C. The reaction was quenched with saturated aqueous NH_4Cl and the mixture was warmed to ambient temperature before it was extracted with *tert*-butyl methyl ether (3 x). The combined extracts were washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash chromatography (SiO_2, hexane/EtOAc = 30:1) to give the title compound as a colorless oil (108 mg, 81%). For characterization purposes, an aliquot was purified by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 30 mm; 35 °C, 74 bar, 35 mL/min, MeOH/H_2O = 85/15). $[\alpha]_D^{20}$ = +2.5 (*c* = 0.50, $CHCl_3$), ^{1}H NMR (600 MHz, C_6D_6): δ = 5.56 (dtt, 1H, *J* = 10.4, 7.0, 1.7 Hz), 5.50 (dtt, 1H, *J* = 10.7, 7.0, 1.4 Hz), 5.49 (dtt, 1H, *J* = 10.7, 6.9, 1.3 Hz), 5.41 (dtt, 1H, *J* = 10.5, 7.3, 1.7 Hz), 3.58 (dt, 1H, *J* = 8.5, 4.3 Hz), 3.54 (dt, 1H, *J* = 7.3, 4.2 Hz), 2.91 (ddqt, 2H, *J* = 7.0, 2.6, 1.9, 0.8 Hz), 2.79 (bt, 2H, *J* = 6.7 Hz), 2.34 – 2.23 (m, 2H), 1.77 (br s, 1H), 1.64 (dq, 1H, *J* = 13.9, 7.4 Hz), 1.55 (t, 3H, *J* = 2.6 Hz), 1.40 (ddq, 1H, *J* = 14.0, 7.4, 4.3 Hz), 0.96 (s, 9H), 0.91 (t, 3H, *J* 7.5 Hz), 0.07 (s, 3H), 0.06 ppm (s, 3H); ^{13}C NMR (150 MHz, C_6D_6): δ = 130.2, 129.2, 127.0, 126.1, 77.6, 76.8, 75.7, 73.9, 30.6, 26.1 (3C), 26.0, 25.1, 18.4, 17.7, 10.1, 3.4, −4.2, −4.3 ppm; IR (film): $\tilde{\nu}$ = 2956, 2928, 2857,



1463, 1388, 1361, 1253, 1080, 1005, 939, 909, 834, 792, 774, 730, 671 cm^{-1}; MS (pos. ESI) *m/z* (%): 359 ($M+Na^+$, 100); HRMS (ESI): *m/z*: calcd. for $C_{20}H_{36}O_2SiNa$ [M^++Na]: 359.2377, found 359.2377.

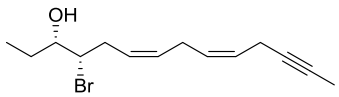
Compound *syn*-15. PPh_3 (1.96 g, 7.49 mmol) was added at 0 °C to a solution of alcohol **14**



(630 mg, 1.87 mmol) in toluene (62 mL) and the resulting mixture was stirred for 10 min before CBr_4 (2.48 g, 7.49 mmol) was introduced. After stirring for another 10 min, the flask was placed into a pre-heated oil bath (65 °C) and stirring continued for 1 h. After cooling to ambient temperature, the pale yellow suspension was filtered through a pad of Celite, which was carefully rinsed with pentane/EtOAc (20:1). The combined filtrates were concentrated and the residue purified by flash chromatography (SiO_2, pentane/EtOAc = 200:1) to yield the title bromide as a pale yellow oil (445 mg, 60%).[6] *The material is very unstable and can only be stored under Ar at −20°C for a few days*. For characterization purposes, an aliquot was purified by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 30 mm; 25 °C, 61 bar, 35 mL/min, 210 nm, MeOH/H_2O = 95/5). $[\alpha]_D^{20}$ = −16.2 (*c* = 1.01, $CHCl_3$); ^{1}H NMR (600 MHz, C_6D_6): δ = 5.56 (ddt, 1H, *J* = 10.4, 7.0, 1.7 Hz), 5.53 (dddt, 1H, *J* = 10.7, 7.6, 6.2, 1.4 Hz), 5.47 (ddt, 1H, *J* = 10.7, 7.0, 1.4 Hz), 5.39 (ddt, 1H, *J* = 10.5, 7.2, 1.7 Hz), 3.93 (dt, 1H, *J* = 10.1, 3.5 Hz), 3.63 (ddd, 1H, *J* = 7.7, 4.6, 3.3 Hz), 2.90 (ddqt, 2H, *J* = 7.0, 2.6, 1.9, 0.7 Hz), 2.78 (dq, 1H, *J* = 16.0, 7.1 Hz), 2.75 (dq, 1H, *J* = 16.0, 7.1 Hz); 2.69 (dddd, 1H, *J* = 15.5, 6.4, 3.6, 1.6 Hz), 2.61 (dddd, 1H, *J* = 15.2, 9.9, 7.5, 1.2 Hz), 1.89 (ddq, 1H, *J* = 13.6, 7.5, 4.6 Hz), 1.54 (t, 3H, *J* = 2.6 Hz), 1.44 (dq, 1H, *J* = 13.7, 7.5 Hz), 0.95 (s, 9H), 0.81 (t, 3H, J = 7.4 Hz), 0.00 (s, 3H), −0.01 ppm (s, 3H); ^{13}C NMR (150 MHz, C_6D_6): δ = 130.1, 128.9, 127.5, 126.3, 77.5, 76.7, 75.8, 59.4, 31.7, 26.3, 26.1, 26.0 (3C), 18.3, 17.7, 10.5, 3.4, −4.2, −4.3 ppm; IR (film): $\tilde{\nu}$ = 2956, 2929, 2857, 1462, 1382, 1361, 1254, 1094, 1048, 1005, 834, 794, 774, 726, 671 cm^{-1}; MS (pos. ESI) *m/z* (%): 421 ($M+Na^+$, 100); HRMS (ESI): *m/z*: calcd. for $C_{20}H_{35}OBrSiNa$ [M^++Na]: 421.1536, found 421.1533.

For an unambiguous assignment of the NMR data, see Table S-1

Compound *syn*-16. In a Teflon vial, a solution of compound **15** (432 mg, 1.08 mmol) in THF

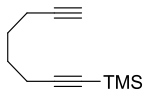


(18 mL) was cooled to 0 °C before HF·pyridine (70% HF, 3.41 mL, 37.8 mmol) was slowly added. The resulting mixture was stirred for 5 h at 0 °C before it was diluted with ethyl acetate (10 mL) and H_2O (5 mL). Next, a sat. aq. solution of $NaHCO_3$ was added until the evolution of gas ceased. The mixture was then extracted with EtOAc, the combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography (SiO_2, pentane/EtOAc = 15:1) to yield the title compound as a colorless oil

[6] 11% of the elimination product and ca. 12% of a *trans*-isomer were detected.

(371 mg, 83%).[7] *The material is very unstable and should be immediately used in the next step*. For characterization purposes, an aliquot was purified by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 30 mm; 35 °C, 70 bar, 35 mL/min, 210 nm, MeOH/H_2O = 75/25). $[\alpha]_D^{20}$ = −18.6 (*c* = 0.56, $CHCl_3$); ^{1}H NMR (600 MHz, C_6D_6): δ = 5.53 (dtt, 1H, *J* = 10.5, 7.0, 1.7 Hz), 5.42 (dtt, 1H, *J* = 10.7, 7.3, 1.6 Hz), 5.34 (dtt, 1H *J* = 10.4, 7.3, 1.7 Hz), 5.30 (dtt, 1H, *J* = 10.7, 7.3, 1.7 Hz), 3.73 (ddd, 1H, *J* = 7.9, 6.3, 2.9 Hz), 3.10 (m, 1H), 2.88 (ddqt, 2H, *J* = 7.0, 2.6, 1.8, 0.8 Hz), 2.70 (m, 2H), 2.60 (dddt, 1H, *J* = 15.0, 7.3, 6.3, 1.5 Hz), 2.56 (dddt, 1H, *J* = 15.0, 7.9, 7.2, 1.5 Hz), 1.55 (t, 3H, *J* = 2.6 Hz), 1.38 (dq, 1H, *J* = 13.7, 7.4 Hz), 1.35 – 1.33 (m, 1H), 1.30 (ddq, 1H, *J* = 13.7, 7.4, 4.7 Hz), 0.79 ppm (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (150 MHz, C_6D_6): δ = 130.6, 128.8, 126.8, 126.2, 77.6, 75.8, 74.2, 63.3, 34.0, 29.1, 26.0, 17.7, 10.2, 3.4 ppm; IR (film): $\tilde{\nu}$ = 3436, 3020, 2964, 2920, 1710, 1424, 1375, 1222, 1112, 1059, 969, 792, 681, 535, 482 cm^{-1}; MS (EI) *m/z* (%): 187 (11), 147 (17), 145 (23), 133 (24), 132 (10), 131 (42), 129 (10), 121 (18), 119 (34), 118 (15), 117 (40), 115 (11), 107 (14), 106 (12), 105 (86), 93 (29), 92 (24), 91 (100), 85 (40), 81 (16), 79 (55), 78 (13), 77 (40), 69 (19), 67 (24), 65 (14), 59 (32), 57 (85), 55 (22), 53 (20), 43 (12), 41 (39), 39 (17), 29 (20); HRMS (ESI): *m/z*: calcd. for $C_{14}H_{21}OBrNa$ [M^++Na]: 307.0667, found 307.0668.

Compound 20. A solution of LiHMDS was prepared by dropwise addition of *n*-BuLi (1.6 M in hexanes, 60.8 mL, 97.2 mmol) to a stirred solution of hexamethyldisilazane (20.3 mL, 97.2 mmol) in THF (50 mL) at –78 °C. Once the addition was complete, the mixture was stirred at 0 °C for 0.5 h prior to use.

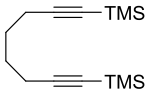


The LiHMDS solution was cooled to –78 °C before it was transferred via cannula to a solution of 1,7-octadiyne (12.9 mL, 97.2 mmol) in THF (135 mL) at –78 °C. After stirring for 0.5 h, chlorotrimethylsilane (12.3 mL, 97.2 mmol) was added dropwise. The mixture was stirred for 10 min before it was allowed to reach ambient temperature. After stirring for 2 h, the reaction was quenched with water (200 mL). The mixture was extracted with pentane (3 x) and the combined extracts were successively washed with HCl (1 M, 200 mL), water (200 mL), and brine (100 mL) before they were dried over $MgSO_4$ and concentrated. Distillation of the crude product (Vigreux column, bp 75 – 78.5 °C, 7 mbar) gave the title compound as a colorless oil (9.10 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 – 2.18 (m, 4H), 1.94 (t, 1H, *J* = 2.7 Hz), 1.67 – 1.59 (m, 4H), 0.14 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.0, 84.9, 84.3, 68.6, 27.7, 27.6, 19.5, 18.1, 0.3 ppm (3C); IR (film): $\tilde{\nu}$ = 3305, 2949, 2174, 1249, 837, 758, 697 cm^{-1}; MS (EI): *m/z* (%) 163 (47), 145 (16), 135 (72), 119 (10), 109 (20), 95 (14), 83 (33),73 (93), 69 (12), 59 (100), 55 (12), 43 (25); HRMS (EI): *m/z*: calcd. for $C_{11}H_{19}Si$ [M+H^+]: 179.1256, found:

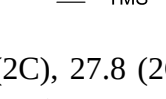
[7] The material contains ca.15% of a *trans*-isomer as a by-product.

179.1254. The ^{1}H NMR data are in good agreement with those previously reported in the literature.[8,9]

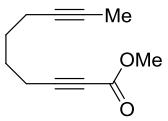
The remainder of the distillation was re-distilled in a Kugelrohr apparatus (100–120 °C, 0.09 mbar) to give the corresponding disilylated product (4.07 g, 17%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 – 2.18 (m, 4H), 1.65 – 1.56 (m, 4H), 0.13 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.1 (2C), 84.8 (2C), 27.8 (2C), 19.5 (2C), 0.3 ppm (2C); IR (film): $\tilde{\nu}$ = 2957, 2174, 1248, 835, 757, 697 cm^{-1}; MS (EI): *m/z* (%) 162 (29), 147 (13), 73 (100), 67 (4), 59 (21); HRMS (EI): *m/z*: calcd. for $C_{14}H_{26}Si_2$ [M^+]: 250.1573, found: 250.1571. The NMR data are in good agreement with those previously reported in the literature.[10]



Compound S5. *n*-BuLi (1.6 M in hexanes, 39.9 mL, 63.9 mmol) was added dropwise to a solution of compound **20** (7.60 g, 42.6 mmol) in THF (200 mL) at –78 °C. After stirring for 1 h, iodomethane (5.30 mL, 85.2 mmol) was slowly introduced, the mixture was allowed to warm to ambient temperature while stirring was continued for 2 h. For work up, the reaction was quenched with water at 0 °C and the mixture was extracted with pentane (3 x). The combined extracts were washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by distillation (bp 119 – 125 °C, 20 mbar) to give the title compound as a colorless oil (7.42 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (t, 2H, *J* = 6.9 Hz), 2.17 – 2.10 (m, 2H), 1.76 (t, 3H, *J* = 2.5 Hz), 1.65 – 1.51 (m, 4H), 0.13 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.3, 84.7, 78.9, 75.8, 28.3, 27.9, 19.6, 18.4, 3.6, 0.3 ppm (3C); IR (film): $\tilde{\nu}$ = 2946, 2174, 1248, 837, 758, 697 cm^{-1}; MS (EI): *m/z* (%) 177 (18), 149 (21), 135 (11), 118 (17), 97 (16), 83 (13), 73 (100), 67 (6), 59 (40), 43 (10); HRMS (CI): *m/z*: calcd. for $C_{12}H_{21}Si$ [M+H^+]: 193.1413, found: 193.1411. The ^{1}H NMR data are in good agreement with those previously reported in the literature.[8]



Compound 21. MeLi (1.6 M in ether, 23.7 mL, 37.9 mmol) was added dropwise to a solution of **S5** (3.65 g, 19.0 mmol) in THF (73 mL) at –78 °C. After stirring for 10 min, the mixture was stirred at 0 °C for an additional 6 h. After cooling to –78 °C, methyl chloroformate (3.70 mL, 47.9 mmol) was slowly added, the mixture was stirred for 0.5 h at this temperature and for 10 min at 0 °C. The reaction was then quenched with saturated aqueous $NaHCO_3$ (50 mL) and the mixture was extracted with *tert*-butyl methyl ether (3 x). The combined extracts were washed with water and brine, dried over Na_2SO_4, and concentrated, and the crude product purified by flash chromatography (SiO_2, hexanes/EtOAc = 20:1) to give the title compound as a colorless oil (2.90 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3H), 2.34 (t, 2H, *J* = 7.0 Hz), 2.18 – 2.10 (m, 2H), 1.75 (t,



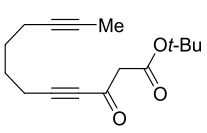
[8] J. Gierlich, G. A. Burley, P. Gramlich, D. M. Hammond, T. Carell, *Org. Lett.* **2006**, *8*, 3639.

[9] B. M. Trost, M. T. Rudd, *Org. Lett.* **2003**, *5*, 4599.

[10] S. M. Yousaf, M. F. Farona, R. J. Shively, W. J. Youngs, *J. Organomet. Chem.* **1989**, *363*, 281.

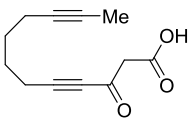
3H, J = 2.4 Hz), 1.72 – 1.62 (m, 2H), 1.62 – 1.52 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 89.5, 78.4, 76.2, 73.1, 52.6, 28.0, 26.7, 18.3, 18.3, 3.5 ppm; IR (film): $\tilde{\nu}$ = 2951, 2235, 1712, 1434, 1248, 1076, 751 cm^{-1}; MS (EI): *m/z* (%) 177 (15), 163 (14), 149 (15), 135 (22), 131 (6), 119 (53), 117 (54), 105 (23), 91 (100), 79 (59), 66 (31), 59 (13), 53 (57), 41 (48), 27 (33); HRMS (CI): *m/z*: calcd. for $C_{11}H_{15}O_2$ [$M+H^+$]: 179.1072, found: 179.1074. The ^{1}H NMR and IR data are in good agreement to those previously reported in the literature.[11]

Compound S6. *n*-BuLi (1.6 M in hexanes, 6.57 mL, 10.5 mmol) was added to a solution of diisopropylamine (1.48 mL, 10.5 mmol) in THF (15 mL) at –78 °C and the resulting mixture was stirred at 0 °C for 5 min prior to use.



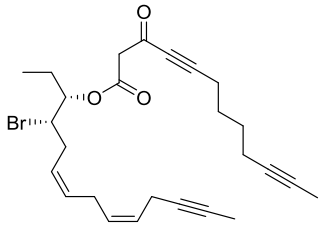
The resulting LDA solution was cooled to –78 °C before neat *t*-butyl acetate (1.41 mL, 10.5 mmol) was added. After stirring for 0.5 h, a solution of **21** (950 mg, 5.33 mmol) in THF (15 mL) was added dropwise and the mixture was stirred for 2 h at –78 °C before it was carefully poured into saturated aqueous NH_4Cl (5 mL). The mixture was extracted with *tert*-butyl methyl ether (3 x) and the combined extracts were washed with water and brine before they were dried over Na_2SO_4 and concentrated, keeping the temperature below 30°C. The residue was purified by flash chromatography (SiO_2, hexanes/EtOAc = 20:1) to give the title compound as yellow oil (166 mg, 87%). *The compound must be kept in a freezer under Ar to avoid decomposition.* ^{1}H NMR (400 MHz, $CDCl_3$, mixture of keto/enol tautomers): δ = 12.01 (s, 0.18H), 5.20 (s, 0.18), 3.45 (s, 1.38), 2.43 – 2.35 (m, 2H), 2.20 – 2.11 (m, 2H), 1.77 (br s, 3H), 1.74 – 1.64 (m, 2H), 1.64 – 1.53 (m, 2H), 1.47 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.6, 165.5, 98.0, 95.9, 82.3, 78.4, 76.3, 52.9, 28.4, 28.1 (3C), 26.8, 18.8, 18.3, 3.6 ppm; IR (film): $\tilde{\nu}$ = 2933, 2213, 1732, 1677, 1610, 1393, 1368, 1323, 1254, 1135, 956, 837, 732 cm^{-1}; MS (EI): *m/z* (%) 205 (13), 189 (14), 177 (37), 161 (15), 146 (32), 119 (21), 91 (25), 57 (100), 53 (11), 41 (28), 29 (11); HRMS (ESI+): *m/z*: calcd. for $C_{16}H_{22}NaO_3$ [$M+Na^+$]: 285.1461, found: 285.1461.

Compound 22. A solution of **S6** (1.00 g, 3.81 mmol) and trifluoroacetic acid (5.0 mL) in CH_2Cl_2 (5 mL) was stirred for 0.5 h. All volatile materials were distilled off and the remaining brown oil was purified by flash chromatography (SiO_2, hexanes/EtOAc = 5:1 → EtOAc) to give the title compound as a pale brown solid (777 mg, 99%). *This product has to be used without delay as it gradually decomposes even if stored at −20 °C.* ^{1}H NMR (400 MHz, $CDCl_3$, mixture of keto/enol tautomers): δ = 11.56 (br s, 0.33H), 5.32 (s, 0.33H), 3.63 (s, 1.28H), 2.42 (t, 2H, J = 6.9 Hz), 2.20 – 2.11 (m, 2H), 1.76 (t, 3H, J = 2.5 Hz), 1.74 – 1.63 (m, 2H), 1.63 – 1.52 ppm (m, 2H); IR (film): $\tilde{\nu}$ = 2936, 2214, 1650, 1574, 1455, 1252, 1183, 1040, 965, 901, 804, 721, 689 cm^{-1}; MS (EI): *m/z* (%) 161 (18), 147 (50), 119 (51), 105 (17), 91 (66), 77 (26), 65 (16), 53 (35), 43 (100), 27 (23); HRMS (ESI−): *m/z*: calcd. for $C_{12}H_{13}O_3$ [$(M-H)^-$]: 205.0870, found: 205.0872.

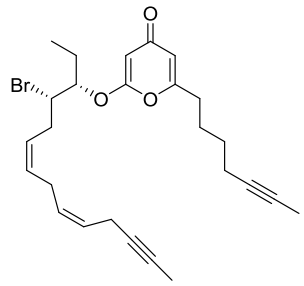


[11] P. Bhatarah, E. H. Smith, *J. Chem. Soc., Perkin Trans. 1* **1992**, 2163.

Compound *syn*-23. A solution of acid **22** (298 mg, 1.45 mmol) in CH_2Cl_2 (16 mL) was added at 0 °C to a solution of alcohol **16** (165 mg, 0.58 mmol) in CH_2Cl_2 (16 mL). DCC (298 mg, 1.45 mmol) was then introduced, followed by DMAP (21 mg, 30 mol%). The mixture was stirred at 0°C for 0.5 h before it was diluted with *tert*-butyl methyl ether. The resulting suspension was filtered through a pad of Celite and the filtrate was concentrated. The residue was triturated with a mixture of hexanes/*tert*-butyl methyl ether (2:1) and the resulting suspension was filtered through a pad of Celite. After evaporation of the filtrate, the residue was purified by flash chromatography (SiO_2, hexanes/EtOAc = 10:1 → 5:1) to give the highly unstable title compound as a yellow oil, which was directly used in the next step without further purification (208 mg, 76%, mixture of keto/enol tautomers). $[\alpha]_D^{20} = -13.2$ (c = 0.55, $CHCl_3$). MS (pos. ESI) *m/z* (%): 495 (M+Na, 100); HRMS (ESI): *m/z*: calcd. for $C_{26}H_{33}O_3BrNa$ [M^++Na]: 495.1507, found 495.1505.



Compound *syn*-25. [(SPhos)Au]NTf_2 (6.2 mg, 7.0 μmol, 3 mol%)[12] was added to a solution of the β-keto ester **23** (110 mg, 0.23 mmol) in MeCN/AcOH (5:1, 7.7 mL). The mixture was stirred for 38 h at ambient temperature before it was concentrated. The residue was purified by flash chromatography (SiO_2, hexanes/ EtOAc = 1:1 → EtOAc) to give the title compound as a colorless oil (105 mg, 97%). For characterization purposes, an aliquot was purified by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 30 mm; 25 °C, 75 bar, 35 mL/min, 244 nm, MeOH/H_2O = 85/15). $[\alpha]_D^{20} = -41.9$ (c = 0.44, $CHCl_3$); ^{1}H NMR (600 MHz, C_6D_6): δ = 5.95 (dt, 1H, J = 1.8, 0.7 Hz), 5.63 (d, 1H, J = 1.9 Hz), 5.52 (dtt, 1H, J = 10.5, 7.0, 1.7 Hz), 5.41 (dtt, 1H, J = 10.7, 7.4, 1.6 Hz), 5.28 (dtt, 1H, J = 10.5, 7.3, 1.8 Hz), 5.22 (dtt, 1H, J = 10.7, 7.1, 1.7 Hz), 4.01 (ddd, 1H, J = 7.2, 5.8, 3.5 Hz), 3.75 (ddd, 1H, J = 8.2, 5.9, 3.5 Hz), 2.84 (ddqt, 2H, J = 7.0, 1.8, 2.6, 0.8 Hz), 2.64 (dt, 1H, J = 15.8, 7.4 Hz), 2.60 (dt, 1H, J = 15.8, 7.3 Hz), 2.52 – 2.47 (m, 2H), 1.91 (tq, 2H, J = 7.0, 2.6 Hz), 1.85 (dd, 2H, J = 7.4, 0.7 Hz), 1.61 (ddq, 1H, J = 14.2, 5.8, 7.5 Hz), 1.56 (t, 3H, J = 2.5 Hz), 1.55 (t, 3H, J = 2.6 Hz), 1.52 (dq, 1H, J = 14.2, 7.3 Hz), 1.38 – 1.32 (m, 2H), 1.21 – 1.16 (m, 2H), 0.81 ppm (t, 3H, J = 7.5 Hz); ^{13}C NMR (150 MHz, C_6D_6): δ = 180.9, 166.8, 164.8, 131.2, 128.4, 126.4, 125.8, 112.8, 92.0, 82.5, 78.7, 77.4, 76.2, 75.9, 54.3, 32.8, 32.3, 28.4, 25.9, 25.8, 24.7, 18.7, 17.6, 9.4, 3.4, 3.4 ppm; IR (film): $\tilde{\nu}$ = 2919, 1659, 1577, 1404, 1240, 1157, 928, 858, 679 cm^{-1}; MS (EI) *m/z* (%): 393 (23), 208 (13), 207 (100), 187 (32), 165 (25), 159 (16), 147 (16), 146 (12), 145 (47), 143 (12), 135 (11), 132 (16), 131 (60), 129 (13), 123 (11), 119 (24), 118 (11), 117 (40), 111 (24), 109 (11), 107 (18), 106 (10), 105 (57), 95 (31), 93 (36), 92 (13), 91 (64), 81 (45), 80 (12), 79 (51), 77 (20), 69 (20), 55 (29), 53



[12] A. Leyva, A. Corma, *J. Org. Chem*. **2009**, *74*, 2067-2074.

(11), 43 (13), 41 (24); HRMS (ESI): *m/z*: calcd. for $C_{26}H_{33}O_3BrNa$ [M^++Na]: 495.1507, found 495.1505.

Compound *syn*-27. Activated MS 5 Å (powder, 440 mg) was added to a solution of diyne **25** (30.0 mg, 63.0 µmol) in toluene (60 mL) and the resulting suspension was stirred for 0.5 h before a solution of the molybdenum alkylidyne complex **26** (3.3 mg, 3.2 µmol, 5 mol%)[13] in toluene (0.05 mL) was added. After stirring for 2 h at rt, the suspension was filtered through a pad of Celite which was thoroughly rinsed with acetone. The combined filtrates were concentrated and the residue was purified by flash chromatography (SiO_2, EtOAc → EtOAc/acetone = 1:1) to give the title compound as a colorless oil (21.7 mg, 82%). An aliquot was purified by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 20 mm; 35 °C, 55 bar, 25 mL/min, 240 nm, MeCN/H_2O = 60/40). $[\alpha]_D^{20}$ = −42.1 (*c* = 1.05, $CHCl_3$), ^{1}H NMR (600 MHz, C_6D_6): δ = 5.87 (d, 1H, *J* = 1.8 Hz), 5.51 (d, 1H, *J* = 1.8 Hz), 5.48 – 5.45 (m, 1H), 5.46 – 5.42 (m, 1H), 5.33 (dtt, 1H, *J* = 10.3, 6.9, 1.3 Hz), 5.20 (dtt, 1H, *J* = 10.7, 7.3, 1.7 Hz), 3.75 (td, 1H, *J* = 6.8, 2.6 Hz), 3.63 (ddd, 1H, *J* = 9.5, 4.9, 2.6 Hz), 2.83 (dddt, 1H, *J* = 17.4, 8.0, 1.4, 2.1 Hz), 2.79 (dt, 1H, *J* = 16.3, 7.4 Hz), 2.73 (dt, 1H, *J* = 16.3, 6.9 Hz), 2.68 – 2.64 (m, 1H), 2.54 (dddt, 1H, *J* = 15.1, 9.5, 7.2, 1.6 Hz), 2.44 (dddt, 1H, *J* = 15.1, 7.3, 4.9, 1.6 Hz), 1.93 – 1.87 (m, 3H), 1.67 (dt, 1H, *J* = 14.2, 7.8 Hz), 1.65 – 1.55 (m, 2H), 1.44 – 1.37 (m, 2H), 1.09 – 0.99 (m, 2H), 0.55 ppm (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, C_6D_6): δ = 180.3, 166.7, 164.5, 131.0, 129.9, 126.0, 125.2, 113.1, 91.5, 82.1, 79.3, 79.2, 54.4, 33.1, 32.6, 27.6, 26.2, 26.0, 24.9, 18.6, 17.3, 9.5 ppm; MS (pos. ESI) *m/z* (%): 441 (*M*+Na^+, 100); HRMS (ESI): *m/z*: calcd. for $C_{22}H_{27}O_3BrNa$ [M^++Na]: 441.1037, found 441.1036.

For an unambiguous assignment of the NMR data, see Table S-2

Compound *syn*-1. N-Bromosuccinimide (4.2 mg, 2.4 µmol) was added in solid form to a solution of compound **27** (11 mg, 2.6 µmol) in THF (1.1 mL) at 0 °C. The resulting pale yellow solution was immediately warmed to ambient temperature and the reaction closely monitored by thin layer chromatography (pentane/EtOAc = 1:1). After complete consumption of the starting material, the mixture was diluted with pentane and filtered through a pad of Celite, which was carefully rinsned with pentane/EtOAc (1:1). The combined filtrates were concentrated and the residue was purified by flash chromatography (SiO_2, pentane/EtOAc = 1:1 → EtOAc 100%) to give the title compound as a colorless solid (5.3 mg, 40%). Crystals suitable for X-ray diffraction were grown form MeCN. An analytically pure sample was obtained by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 20 mm; 35 °C, 50 bar, 20 mL/min, 264 nm, MeCN/H_2O = 60/40).

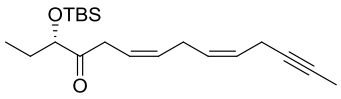
[13] J. Heppekausen, R. Stade, A. Kondoh, G. Seidel, R. Goddard, A. Fürstner, *Chem. Eur. J.* **2012**, *18*, 10281-10299.

M.p. = 105 – 108 °C; $[\alpha]_D^{20}$ = −13.8 (*c* = 0.25, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.13 (s, 1H), 5.67 (dddt, 1H, *J* = 10.7, 7.6, 7.1, 1.4 Hz), 5.55 (dtt, 1H, *J* = 10.7, 7.1, 1.6 Hz), 5.51 – 5.45 (m, 2H), 4.80 (ddd, 1H, *J* = 7.4, 5.4, 4.6 Hz), 4.14 (ddd, 1H, *J* = 8.3, 5.5, 4.6 Hz), 2.91 – 2.88 (m, 2H), 2.90 – 2.78 (m, 2H), 2.73 (dddd, 1H, *J* = 15.1, 7.2, 5.4, 1.5 Hz), 2.72 (dddd, 1H, *J* = 15.2, 8.3, 7.0, 1.5 Hz), 2.56 (ddd, 1H, *J* = 14.7, 8.5, 6.4 Hz), 2.53 (ddd, 1H, *J* = 14.6, 8.4, 6.9 Hz), 2.26 – 2.24 (m, 2H), 1.96 (ddq, 1H, *J* = 14.3, 5.4, 7.5 Hz), 1.92 (dq, 1H, *J* = 14.3, 7.3 Hz), 1.83 (dtt, 1H, *J* = 13.9, 8.5, 6.8 Hz), 1.79 (dtt, 1H, *J* = 13.7, 8.5, 6.8 Hz), 1.57 – 1.52 (m, 2H), 1.03 ppm (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.8, 163.1, 162.0, 130.8, 129.4, 125.9, 125.0, 111.8, 92.2, 84.6, 79.2, 79.0, 55.1, 33.6, 32.7, 27.8, 26.5, 26.4, 26.1, 18.6, 17.4, 9.7 ppm; IR (film): $\tilde{\nu}$ = 2926, 1659, 1573, 1459, 1379, 1324, 1262, 1157, 1091, 1013, 975, 918 cm^{-1}; MS (EI) *m/z* (%): 506 (32), 505 (82), 420 (13), 419 (25), 417 (26), 338 (12), 337 (17), 235 (19), 219 (29), 217 (28), 206 (21), 199 (20), 197 (20), 195 (21), 185 (38), 181 (23), 173 (25), 171 (59), 169 (34), 159 (25), 157 (44), 145 (44), 143 (58), 141 (27), 133 (33), 131 (62), 129 (87), 119 (32), 117 (81), 115 (29), 105 (57), 97 (22), 95 (33), 93 (38), 91 (100), 81 (42), 80 (14), 79 (58), 69 (25), 67 (50), 55 (40); HRMS (ESI): *m/z*: calcd. for $C_{22}H_{26}O_3Br_2Na$ [M^++Na]: 519.0138, found 519.0141.

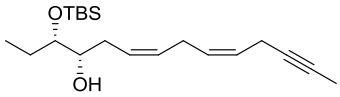
For an unambiguous assignment of the NMR data and a comparison with those of the natural product, see Tables S-3 and S-4

Synthesis of the anti-Isomer

Compound S7. A solution of Dess-Martin periodinane (265 mg, 0.624 mmol) in CH_2Cl_2 (0.5 mL) was added to a solution of alcohol **16** (140 mg, 0.416 mmol) in CH_2Cl_2 (8.7 mL) at 0 °C. The mixture was stirred for 10 min at 0°C and for 2 h at ambient temperature before the reaction was quenched with saturated aqueous $NaHCO_3$ and saturated aqueous Na_2SO_3 (1:1, 2 mL). The resulting slurry was vigorously stirred for 5 min before the aqueous phase was extracted (3x) with EtOAc. The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The resulting ketone (138 mg, 99%) was immediately used in the next step without further purification.



Compound S8. A solution of ketone **S7** (138 mg, 0.413 mmol) in toluene (8.0 mL) was added to a solution of (*S*)-(–)-1-methyl,3,3-diphenyl-tetrahydro-pyrrolo(1,2-*c*)(1,3,2)oxazaborole ((*S*)-CBS reagent, 343 mg, 1.24 mmol)[14] in toluene (1.8 mL). After cooling to −78 °C a solution of catecholborane (149 mg, 1.24 mmol)[15] in toluene (3 mL) was added via syringe pump over the course of 5 h. Once the addition was complete, the mixture was stirred for 12 h

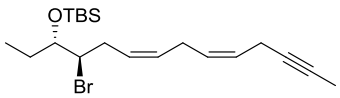


[14] E. J. Corey, C. Helal, *Angew. Chem*. **1998**, *110*, 2092; *Angew. Chem. Int. Ed.* **1998**, *37*, 1986.

[15] For the modified procedure using catecholborane as hydride source to allow for CBS-reductions in the presence of alkynes, see: a) A. Fürstner, M. Bindl, L. Jean, *Angew. Chem. Int. Ed.* **2007**, *46*,

at −78 °C. The reaction was then quenched with MeOH (2 mL) at this temperature and the resulting slurry stirred at ambient temperature for 1 h. The mixture was washed twice with NaOH (0.2 M, 3.0 mL) and the aqueous layers were extracted with EtOAc (3 x). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated, and the crude product was purified by flash chromatography (SiO_2, pentane/EtOAc = 50:1 → pentane/EtOAc = 30:1) to yield the title alcohol as a colorless oil (112 mg, 81%). An analytically pure sample was obtained by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 30 mm; 35 °C, 70 bar, 35 mL/min, 210 nm, MeOH/H_2O = 85/15). $[\alpha]_D^{20}$ = −2.4 (*c* = 0.40, $CHCl_3$). ^{1}H NMR (600 MHz, C_6D_6): δ = 5.61 (dtt, 1H, *J* = 10.8, 7.3, 1.6 Hz), 5.57 (dtt, 1H, *J* = 10.5, 7.0, 1.8 Hz), 5.50 (dtt, 1H, *J* = 10.8, 7.3, 1.6 Hz), 5.43 (dtt, 1H, *J* = 10.5, 7.2, 1.7 Hz), 3.54 (dt, 1H, *J* = 8.5, 4.1 Hz), 3.45 (dt, 1H, *J* = 5.8, 4.1 Hz), 2.92 (ddqt, 2H, *J* = 6.2, 2.6, 1.8, 0.8 Hz), 2.89 – 2.77 (m, 2H), 2.31 – 2.27 (m, 1H), 2.25 – 2.20 (m, 1H), 1.97 (br s, 1H), 1.67 (dq, 1H, *J* = 7.7, 6.0 Hz), 1.55 (t, 3H, *J* = 2.6 Hz), 1.44 – 1.37 (m, 1H), 0.94 (s, 9H), 0.86 (t, 3H, *J* = 7.5 Hz), 0.04 (s, 3H), 0.03 ppm (s, 3H); ^{13}C NMR (150 MHz, C_6D_6): δ = 129.6, 129.2, 127.2, 126.1, 77.6, 76.5, 75.7, 72.8, 32.0, 26.6, 26.1, 26.1 (3C), 18.4, 17.7, 9.8, 3.4, −4.1, −4.4 ppm; IR (film): $\tilde{\nu}$ = 2955, 2929, 2884, 2857, 1463, 1389, 1361, 1254, 1056, 1005, 939, 834, 774, 676 cm^{-1}; MS (EI) *m/z* (%): 336 (1), 279 (8), 203 (25), 187 (44), 174 (14), 173 (91), 145 (32), 134 (11), 133 (100), 131 (23), 119 (13), 117 (28), 115 (36), 93 (12), 91 (13), 75 (70), 73 (60); HRMS (ESI): *m/z*: calcd. for $C_{20}H_{36}OSiNa$ [M^++Na]: 359.2377, found 359.2377.

Compound S9. PPh_3 (341 mg, 1.30 mmol) was added to a solution of alcohol **S8** (97 mg, 0.288 mmol) in toluene (11 mL) at 0 °C and the resulting mixture was stirred for 10 min before CBr_4 (431 mg, 1.30 mmol) was introduced. After stirring for another 10 min, the flask was placed into a pre-heated oil bath (65 °C) and the mixture stirred at this temperature for 1 h. For work up, the mixture was cooled to ambient temperature before it was filtered through a pad of Celite which was carefully rinsed with pentane/EtOAc (20:1). The combined filtrates were concentrated and the residue was purified by flash chromatography (SiO_2, pentane/EtOAc = 200:1) to yield the title bromide as a pale yellow oil (64 mg, 55%).[16] *The material is very unstable and can be stored under Ar at −20°C only for a few days.* An analytically pure sample was obtained by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 20 mm; 35 °C, 53 bar, 20 mL/min, 210 nm, MeOH/H_2O = 95/5). $[\alpha]_D^{20}$ = +9.0 (*c* = 0.30, $CHCl_3$). ^{1}H NMR (600 MHz, C_6D_6): δ = 5.56 (dtt, 1H, *J* = 10.5, 7.1, 1.7 Hz), 5.51 (dtt, 1H, *J* = 10.7, 6.7, 1.6 Hz), 5.46 (dtt, 1H, *J* = 10.7, 7.0, 1.3 Hz), 5.39 (dtt, 1H, *J* = 10.5, 7.3, 1.7 Hz), 3.95 (ddd, 1H, *J* = 9.5, 4.7, 4.3 Hz), 3.72 (dt, 1H, *J* = 5.2, 4.7 Hz),



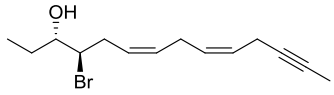
9275; b) M. Bindl, L. Jean, J. Herrmann, R. Müller, A. Fürstner, *Chem. Eur. J.* **2009**, *15*, 12310-12319.

[16] The material contains ca.11% of elimination byproduct and ca. 20% of *trans*-isomerized byproduct.

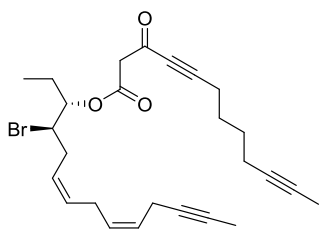
2.90 (ddqt, 2H, *J* = 7.0, 1.8, 2.6, 0.8 Hz), 2.76 – 2.73 (m, 2H), 2.68 (dddd, 1H, *J* = 15.3, 6.8, 4.2, 1.3 Hz), 2.56 (dddd, 1H, *J* = 15.5, 9.5, 6.8, 1.2 Hz), 1.80 (ddq, 1H, *J* = 14.0, 6.2, 7.4 Hz), 1.54 (t, 3H, *J* = 2.6 Hz), 1.43 (ddq, 1H, *J* = 14.0, 4.6, 7.4 Hz), 0.99 (s, 9H), 0.82 (t, 3H, *J* = 7.5 Hz), 0.10 (s, 3H), 0.03 ppm (s, 3H); ^{13}C NMR (150 MHz, C_6D_6): δ = 130.0, 128.9, 127.4, 126.3, 77.5, 76.7, 75.8, 59.5, 32.3, 27.5, 26.1 (3C), 26.0, 18.4, 17.7, 9.1, 3.4, −4.2, −4.3 ppm; IR (film): $\tilde{\nu}$ = 2959, 2928, 2856, 1462, 1258, 1091, 1014, 836, 794, 777, 674 cm^{-1}; MS (EI) *m/z* (%): 319 (11), 197 (70), 195 (71), 187 (24), 173 (39), 159 (38), 145 (41), 139 (38), 137 (37), 135 (2), 133 (56), 131 (59), 119 (21), 117 (38), 115 (43), 107 (12), 93 (30), 91 (71), 79 (36), 75 (68), 73 (100), 67 (26), 55 (28); HRMS (ESI): *m/z*: calcd. for $C_{20}H_{35}OBrSiNa$ [M^++Na]: 421.1535, found 421.1533.

For an unambiguous assignment of the NMR data, see Table S-5

Compound S10. HF·pyridine (70% HF, 0.20 mL, 2.22 mmol) was added dropwise to a solution of bromide **S9** (47 mg, 0.12 mmol) in THF (1.0 mL) at 0 °C. The mixture was then stirred at ambient temperature for 4 h before it was cooled to 0 °C and diluted with EtOAc and H_2O. Saturated aqueous $NaHCO_3$ was added until the evolution of gas ceased. The mixture was extracted with EtOAc, the combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated, and the crude material was purified by flash chromatography (SiO_2, pentane/EtOAc = 15:1) to yield the title alcohol as a colorless oil (18.5 mg, 55%). $[\alpha]_D^{20}$ = +19.2 (*c* = 0.10, $CHCl_3$). ^{1}H NMR (600 MHz, C_6D_6): δ = 5.55 (dtt, 1H, *J* = 10.5, 7.0, 1.7 Hz), 5.45 – 5.39 (m, 2H), 5.35 (dtt, 1H, *J* = 10.5, 7.3, 1.8 Hz), 3.79 (dt, 1H, *J* = 9.4, 4.3 Hz), 3.35 (dt, 1H, *J* = 8.7, 4.3 Hz), 2.88 – 2.85 (m, 2H), 2.69 – 2.66 (m, 2H), 2.56 – 2.51 (m, 1H), 2.46 – 2.42 (m, 1H), 1.54 (t, 3H, *J* = 2.7 Hz), 1.41 – 1.40 (m, 1H), 1.38 – 1.35 (m, 2H), 0.82 ppm (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (150 MHz, C_6D_6): δ = 130.1, 128.9, 127.1, 126.2, 77.5, 75.9, 75.8, 62.5, 31.6, 27.0, 26.0, 17.7, 10.4, 3.4 ppm; IR (film): $\tilde{\nu}$ = 2963, 2923, 2359, 1738, 1670, 1456, 1259, 1013, 705, 681, 561, 432 cm^{-1}; MS (EI) *m/z* (%): 187 (11), 147 (17), 145 (23), 133 (24), 132 (10), 131 (42), 121 (18), 119 (34), 118 (15), 117 (40), 115 (11), 107 (14), 106 (12), 105 (86), 93 (29), 91 (100), 85 (40), 81 (16), 79 (55), 77 (40), 59 (32), 57 (85), 41 (39); HRMS (ESI): *m/z*: calcd. for $C_{14}H_{21}OBrNa$ [M^++Na]: 307.0669, found 307.0668.

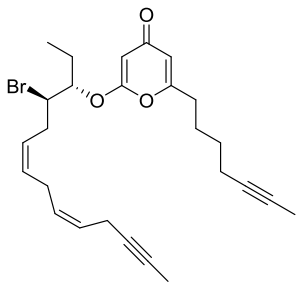


Compound *anti*-23. A solution of carboxylic acid **22** (16 mg, 77 μmol) in CH_2Cl_2 (0.6 mL) was added at 0 °C to a solution of alcohol **S10** (10 mg, 35 μmol) in CH_2Cl_2 (1 mL). DCC (16 mg, 77 μmol) was then introduced at this temperature, followed after 5 min by DMAP (1.3 mg, 11 μmol, 30 mol%). The mixture was stirred for 15 min at 0°C before it was diluted with *tert*-butyl methyl ether (3 mL). The resulting suspension was filtered through a pad of Celite and the filtrate was concentrated. The residue was triturated with a mixture of hexanes/*tert*-butyl methyl ether



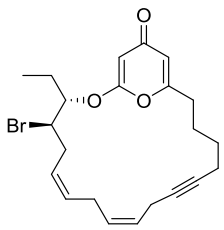
(2:1) and the resulting suspension filtered through a pad of Celite. Evaporation of the filtrate followed by purification of the residue by flash chromatography (SiO_2, hexanes/EtOAc = 15:1 → 13:1) gave the highly unstable title compound as yellow oil which was directly used in the next step without further purification (13 mg, 78%), mixture of keto/enol tautomers).

Compound *anti*-25. $AuSPhosNTf_2$ (0.4 mg, 0.7 μmol, 3 mol%)[12] was added to a solution of



***anti*-23** (10 mg, 21 μmol) in MeCN/AcOH (5:1, 1.5 mL). The mixture was stirred for 38 h before all volatile materials were evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes/ EtOAc = 1:1 → EtOAc) gave the title compound as a colorless oil (8.4 mg, 84%). An analytically pure sample was obtained by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 20 mm; 35 °C, 55 bar, 20 mL/min, 228 nm, MeCN/H_2O = 60/40). $[\alpha]_D^{20}$ = +13.6 (*c* = 0.09, $CHCl_3$). ^{1}H NMR (600 MHz, C_6D_6): δ = 5.92 (d, 1H, *J* = 1.8 Hz), 5.59 (d, 1H, *J* = 1.8 Hz), 5.55 (dtt, 1H, *J* = 10.5, 6.9, 1.7 Hz), 5.42 (dtt, 1H, *J* = 10.7, 7.3, 1.4 Hz), 5.31 (dtt, 1H, *J* = 10.5, 7.3, 1.7 Hz), 5.27 (dtt, 1H, *J* = 10.7, 7.2, 1.8 Hz), 4.09 (ddd, 1H, *J* = 9.1, 5.2, 3.6 Hz), 3.85 (dt, 1H, *J* = 8.5, 5.2 Hz), 2.86 (ddqt, 1H, *J* = 7.0, 1.6, 2.5, 0.7 Hz), 2.64 – 2.59 (m, 2H), 2.48 – 2.37 (m, 2H), 1.92 (tq, 2H, *J* = 7.2, 2.6 Hz), 1.84 – 1.81 (m, 2H), 1.58 – 1.56 (m, 2H), 1.57 (t, 3H, *J* = 2.5 Hz), 1.56 (t, 3H, *J* = 2.7 Hz), 1.35 – 1.31 (m, 2H), 1.20 – 1.16 (m, 2H), 0.68 ppm (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (150 MHz, C_6D_6): δ = 180.4, 166.4, 164.4, 131.2, 128.5, 126.4, 125.7, 112.9, 92.1, 82.7, 78.7, 77.3, 76.2, 76.0, 53.9, 32.3, 32.2, 28.4, 26.0, 25.8, 24.5, 18.7, 17.7, 9.1, 3.4, 3.4 ppm; IR (film): $\tilde{\nu}$ = 3359, 2920, 2851, 1661, 1632, 1578, 1411, 1247, 1086, 859, 800, 700 cm^{-1}; MS (pos. ESI) *m/z* (%): 495 (M+Na^+, 100); HRMS (ESI): *m/z*: calcd. for $C_{26}H_{33}O_3BrNa$ [M^++Na]: 495.1506, found 495.1505.

Compound *anti*-27. Activated MS 5 Å powder (70 mg) was added to a solution of ***anti*-25**

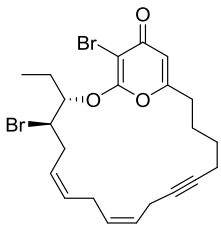


(6.0 mg, 13 μmol) in toluene (7 mL) and the resulting suspension was stirred for 0.5 h before a solution of the molybdenum alkylidyne complex **26** (0.7 mg, 0.6 μmol, 5 mol%)[13] in toluene (0.05 mL) was introduced. After stirring for 2 h, the suspension was filtered through a pad of Celite, which was thoroughly rinsed with EtOAc. The combined filtrates were concentrated and the residued purified by flash chromatography (SiO_2, EtOAc → EtOAc/acetone = 1:1) to remove Ph_3SiOH. The material was further purified by preparative HPLC (UFLC SHIMADZU; Kromasil 100-5C18, 150 x 20 mm; 35 °C, 55 bar, 20 mL/min, 240 nm, MeCN/H_2O = 60/40) to yield the title compound as a colorless oil (4.4 mg, 80%). $[\alpha]_D^{20}$ = −7.5 (*c* = 0.17, $CHCl_3$). ^{1}H NMR (600 MHz, C_6D_6): δ = 5.88 (d, 1H, *J* = 1.8 Hz), 5.55 (d, 1H, *J* = 1.8 Hz), 5.48 (dtt, 1H, *J* = 10.3, 7.3, 1.7 Hz), 5.46 (dtt, 1H, *J* = 10.6, 7.1, 1.5 Hz), 5.37 (dtt, 1H, *J* = 10.6, 7.6, 1.7 Hz), 5.35 (dtt, 1H, *J* = 10.3, 7.1, 1.4 Hz), 4.14 (td, 1H, *J* = 6.7, 4.0 Hz), 3.70 (ddd, 1H, *J* = 10.8, 5.0, 4.0 Hz), 2.79 – 2.76 (m,

4H), 2.58 – 2.53 (m, 1H), 2.50 – 2.45 (m, 1H), 1.93 (tt, 2H, *J* = 6.5, 2.3 Hz), 1.83 (ddd, 1H, *J* = 14.7, 9.2, 5.7 Hz), 1.74 – 1.69 (m, 1H), 1.61 – 1.54 (m, 1H), 1.49 – 1.43 (m, 2H), 1.39 – 1.34 (m, 1H), 1.07 – 1.01 (m, 2H), 0.63 ppm (t, 3H, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, C_6D_6): δ = 180.3, 166.4, 164.2, 131.0, 129.9, 125.8, 125.3, 113.2, 92.2, 83.0, 79.3, 79.2, 53.6, 32.6, 31.9, 27.7, 26.2, 26.0, 24.6, 18.6, 17.3, 8.5 ppm; IR (film): $\tilde{\nu}$ = 2922, 2852, 1663, 1630, 1584, 1399, 1241, 1158, 928 cm^{-1}; MS (pos. ESI) *m*/*z* (%): 443 (*M*+Na$^+$, 100); HRMS (ESI): *m/z*: calcd. for $C_{22}H_{27}O_3BrNa$ [*M*$^+$+Na]: 441.1037, found 441.1036.

For an unambiguous assignment of the NMR data, see Table S-6

Compound *anti*-1. *N*-Bromosuccinimide (1.3 mg, 7.3 µmol) was added in one portion to a solution of ***anti*-27** (3.4 mg, 8.1 µmol) in THF (0.4 mL) at 0 °C. The colorless solution was stirred at ambient temperature and the reaction closely monitored by thin layer chromatography (pentane/EtOAc = 1:1). After complete consumption of the starting material, the mixture was diluted with pentane and filtered through a pad of Celite, which was carefully rinsed with pentane/EtOAc (1:1). The combined filtrates were concentrated and the residue purified by flash chromatography (SiO_2, pentane/EtOAc = 1:1 → EtOAc 100%) to give the title compound (1.6 mg, 40%) as a colorless solid. $[\alpha]_D^{20}$ = +18.0 (*c* = 0.10, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.13 (s, 1H), 5.68 (dtt, 1H, *J* = 10.7, 7.4, 1.6 Hz), 5.54 – 5.48 (m, 2H), 5.45 (dddt, 1H, *J* = 10.7, 8.0, 6.2, 1.7 Hz), 4.86 (td, 1H, *J* = 7.1, 3.6 Hz), 4.15 (ddd, 1H, *J* = 9.1, 7.1, 4.8 Hz), 2.95 (ddt, 1H, *J* = 17.1, 6.5, 2.3 Hz), 2.91 – 2.87 (m, 2H), 2.83 (ddt, 1H, *J* = 17.1, 5.9, 2.5 Hz), 2.77 (ddddt, 1H, *J* = 15.2, 6.1, 4.9, 1.8, 0.9 Hz), 2.66 (dddd, 1H, *J* = 15.2, 9.1, 8.0, 1.4 Hz), 2.59 (ddd, 1H, *J* = 14.6, 9.3, 6.1 Hz), 2.51 (ddd, 1H, *J* = 14.7, 9.3, 6.3 Hz), 2.27 – 2.24 (m, 2H), 2.06 (dq, 1H, *J* = 14.9, 7.4 Hz), 2.05 (ddq, 1H, *J* = 14.8, 3.7, 7.4 Hz), 1.86 – 1.75 (m, 2H), 1.58 – 1.55 (m, 2H), 1.07 ppm (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 175.6, 163.3, 161.7, 131.1, 129.9, 125.6, 125.0, 111.7, 92.3, 84.6, 79.2, 79.1, 53.8, 33.4, 33.0, 28.0, 26.6, 26.1, 25.6, 18.6, 17.1, 9.3 ppm; IR (film): $\tilde{\nu}$ = 2921, 2851, 1659, 1633, 1575, 1468, 1376, 1261, 1090, 800 cm^{-1}; MS (pos. ESI) *m*/*z* (%): 521 (*M*+Na$^+$, 100); HRMS (ESI): *m/z*: calcd. for $C_{22}H_{26}O_3Br_2Na$ [*M*$^+$+Na]: 519.0140, found 519.0141.



For an unambiguous assignment of the NMR data and a comparison with those of the natural product, see Tables S-7 and S-8

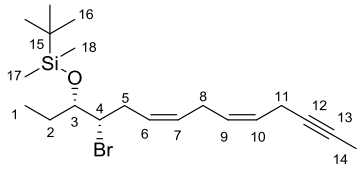


Table S-1: ^{1}H and ^{13}C data of bromide ***syn*-15**; numbering scheme as shown in the Insert.

	^{1}H NMR (C_6D_6, 600 MHz)					^{13}C NMR (C_6D_6, 150 MHz)	
No.	δ (ppm)	Integral	Splitting	COSY	J (Hz)	δ (ppm)	HMBC
1	0.81	3H	t	2a, 2b	7.4	10.5	2a, 2b, 3
2a	1.89	1H	ddq	1, 2b, 3	13.6, 4.6, 7.5	26.3	1, 3, 4
2b	1.44	1H	dq	1, 2a, 3	13.7, 7.5		
3	3.63	1H	ddd	2a, 2b, 4	7.7, 4.6, 3.3	76.7	1, 2a, 2b, 4, 5a, 5b
4	3.93	1H	dt	3, 5a, 5b	10.1, 3.5		2a, 2b, 5a, 5b, 6
5a	2.69	1H	dddd	4, 5b, 6	15.5, 6.4, 3.6, 1.6	31.7	3, 4, 6, 7
5b	2.61	1H	dddd	4, 5a, 6	15.2, 9.9, 7.5, 1.2		
6	5.53	1H	dddt	5a, 5b, 7	10.7, 7.6, 6.2, 1.4	127.5	4, 5a, 5b, 7, 8a, 8b
7	5.47	1H	ddt	6, 8a, 8b	10.7, 7.0, 1.4	130.1	5a, 5b, 6, 8a, 8b, 9
8a	2.78	1H	dq	7, 8b, 9	16.0, 7.1	26.1	6, 7, 9, 10, 11
8b	2.75	1H	dq	7, 8a, 9	16.0, 7.1		
9	5.39	1H	dtt	8a, 8b, 10, 11	10.5, 7.2, 1.7	128.9	7, 8a, 8b, 10, 11
10	5.56	1H	dtt	9, 11	10.4, 7.0, 1.7	126.3	8a, 8b, 9, 11, 14
11	2.90	2H	ddqt	9, 10, 14	7.0, 1.9, 2.6, 0.7	17.7	8a, 8b, 9, 10, 14
12	-	-	-	-	-	77.5	9, 10, 11, 14
13	-	-	-	-	-	75.8	11, 14
14	1.54	3H	t	11	2.6	3.4	-
15	-	-	-	-	-	18.3	16, 17, 18
16	0.95	9H	s	-	-	26.0	-
17	0.00	3H	s	-	-	−4.2	18
18	−0.01	3H	s	-	-	−4.3	17

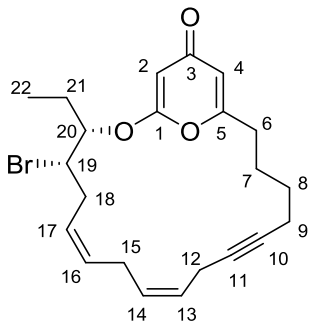


Table S-2: ^{1}H and ^{13}C data of ***syn*-27**; numbering scheme as shown in the Insert.

	^{1}H NMR (C_6D_6, 600 MHz)					^{13}C NMR (C_6D_6, 150 MHz)	
No.	δ (ppm)	Integral	Splitting	COSY	J (Hz)	δ (ppm)	HMBC
1	-	-	-	-	-	166.7	2, 20
2	5.51	1H	d	4	1.8	91.5	4
3	-	-	-	-	-	180.3	2, 4
4	5.87	1H	d	2	1.8	113.1	2, 6a, 6b
5	-	-	-	-	-	164.5	4, 6a, 6b
6a	1.93 – 1.87	1H	m	6b, 7	-	32.6	4, 7, 8
6b	1.67	1H	dt	6a, 7	14.2, 7.8		
7	1.44 – 1.37	2H	m	6a, 6b, 8	-	26.2	6a, 6b, 8, 9
8	1.09 – 0.99	2H	m	7, 9	-	27.6	6a, 6b, 7, 9
9	1.90 – 1.87	2H	m	8, 12a, 12b	-	18.6	7, 8
10	-	-	-	-	-	79.3	8, 9
11	-	-	-	-	-	79.2	12a, 12b, 13, 14
12a	2.83	1H	dddt	9, 12b, 13	17.4, 8.0, 1.4, 2.1	17.3	9, 13, 14
12b	2.68 – 2.64	1H	m	9, 12a, 13	-		
13	5.48 – 5.45	1H	m	12a, 12b, 14	-	125.2	9, 12a, 12b, 14, 15a, 15b
14	5.33	1H	dtt	13, 15a, 15b	10.3, 6.9, 1.3	129.9	12a, 12b, 13, 15a, 15b
15a	2.79	1H	dt	14, 15b, 16	16.3, 7.4	26.0	13, 14, 16, 17
15b	2.73	1H	dt	14, 15a, 16	16.3, 6.9		
16	5.46 – 5.42	1H	m	15a, 15b, 17	-	131.0	14, 15a, 15b, 17, 18a, 18b
17	5.20	1H	dtt	15a, 15b, 16, 18a, 18b	10.7, 7.3, 1.7	126.0	15a, 15b, 16, 18a, 18b, 19
18a	2.54	1H	dddt	17, 19	15.1, 9.5, 7.2, 1.6	33.1	16, 17, 19, 20
18b	2.44	1H	dddt	17, 19	15.1, 7.3, 4.9, 1.6		
19	3.63	1H	ddd	18a, 18b, 20	9.5, 4.9, 2.6	54.4	17, 18a, 18b, 20, 21
20	3.75	1H	td	19, 21	6.8, 2.6	82.1	18a, 18b, 19, 21, 22
21	1.65 – 1.55	2H	m	20, 22	-	24.9	19, 20, 22
22	0.55	3H	t	21	7.5	9.5	20, 21

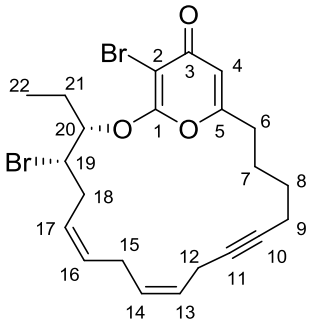


Table S-3: ^{1}H and ^{13}C data of synthetic ***syn*-1**; numbering scheme as shown in the Insert.

	^{1}H NMR ($CDCl_3$, 600 MHz)					^{13}C NMR ($CDCl_3$, 150 MHz)	
No.	δ (ppm)	Integral	Splitting	COSY	J (Hz)	δ (ppm)	HMBC
1	-	-	-	-	-	162.0	20
2	-	-	-	-	-	92.2	4
3	-	-	-	-	-	175.8	4
4	6.13	1H	s	-	-	111.8	6a, 6b
5	-	-	-	-	-	163.1	4, 6a, 6b, 7a, 7b
6a	2.56	1H	ddd	6b, 7a, 7b	14.7, 8.5, 6.4	32.7	4, 7a, 7b, 8
6b	2.53	1H	ddd	6a, 7a, 7b	14.6, 8.4, 6.9		
7a	1.83	1H	dtt	6a, 6b, 7b, 8	13.9, 8.5, 6.8	26.4	4, 6a, 6b, 8, 9
7b	1.79	1H	dtt	6a, 6b, 7a, 8	13.7, 8.5, 6.8		
8	1.57 – 1.52	2H	m	7a, 7b, 9	-	27.8	6a, 6b, 7a, 7b, 9
9	2.26 – 2.24	2H	m	8, 12	-	18.6	7a, 7b, 8
10	-	-	-	-	-	79.2	8, 9, 12
11	-	-	-	-	-	79.0	9, 12, 13
12	2.91 – 2.88	2H	m	9, 13	-	17.4	13, 14
13	5.51 – 5.45	1H	m	12	-	125.0	12, 15
14	5.51 – 5.45	1H	m	15	-	129.4	12, 15, 16
15	2.90 – 2.78	2H	m	14, 16, 17	-	26.1	13, 14, 16, 17
16	5.67	1H	dddt	15, 17, 18a, 18b	10.7, 7.6, 7.1, 1.4	130.8	14, 15, 17, 18a, 18b
17	5.55	1H	dtt	15, 16, 18a, 18b	10.7, 7.1, 1.6	125.9	15, 16, 18a, 18b, 19
18a	2.73	1H	dddd	16, 17, 18b, 19	15.1, 7.2, 5.4, 1.5	33.6	16, 17, 19, 20
18b	2.72	1H	dddd	16, 17, 18a, 19	15.2, 8.3, 7.0, 1.5		
19	4.14	1H	ddd	18a, 18b, 20	8.3, 5.5, 4.6	55.1	17, 18a, 18b, 21a, 21b
20	4.90	1H	ddd	19, 21a, 21b	7.4, 5.4, 4.6	84.6	18a, 18b, 19, 21a, 21b, 22
21a	1.96	1H	ddq	20, 22	14.3, 5.4, 7.5	26.5	19, 20, 22
21b	1.92	1H	dq	20, 22	14.3, 7.3		
22	1.03	3H	t	21a, 21b	7.4	9.7	20, 21a, 21b

Table S-4: Comparison of ^{1}H and ^{13}C data of synthetic ***syn*-1** with those of the natural product; numbering scheme as shown in the insert above.

# (lit.)	# (reassigned)[1)]	natural XX ($CDCl_3$)[1),2)]		synthetic XX (syn, $CDCl_3$)[3)]		Δ (δ(XX)-δ(lit.))		XX (C_6D_6)[4)]	Δ (δ(XX)-δ(lit.))
		^{1}H	^{13}C	^{1}H	^{13}C	Δ ^{1}H	Δ ^{13}C	^{1}H	Δ ^{1}H
5	1	–	161,6	–	162,0	–	0,4	–	–
2	2	–	91,8	–	92,2	–	0,4	–	–
3	3	–	175,4	–	175,8	–	0,4	–	–
4	4	6,10	111,2	6,13	111,8	0,03	0,6	5,80	-0,30
1	5	–	162,9	–	163,1	–	0,2	–	–
18	6	2,58	32,3	2,56 2,53	32,7	-0,02 -0,05	0,4	1,68	-0,90
7	7	1,88	26,1	1,83 1,79	26,4	-0,05 -0,09	0,3	1,29	-0,59
8	8	1,60	27,5	1,55	27,8	-0,05	0,3	1,00	-0,60
12	9	2,22	18,2	2,25	18,6	0,03	0,4	1,91	-0,31
10	10	–	78,8	–	79,2	–	0,4	–	–
11	11	–	78,5	–	79,0	–	0,5	–	–
21	12	2,88	17,0	2,90	17,4	0,02	0,4	2,71	-0,17
14	13	5,40	124,6	5,47	125,0	0,07	0,4	5,31	-0,09
17	14	5,40	128,9	5,47	129,4	0,07	0,5	5,39	-0,01
15	15	2,88	25,7	2,85	26,1	-0,03	0,4	2,61	-0,27
13	16	5,40	130,3	5,67	130,8	0,27	0,5	5,47	0,07
16	17	5,40	125,5	5,55	125,9	0,15	0,4	5,47	0,07
6	18	2,72	33,2	2,73 2,72	33,6	0,01 0,00	0,4	2,48	-0,24
19	19	4,14	54,9	4,14	55,1	0,00	0,2	3,81	-0,33
20	20	4,90	84,2	4,80	84,6	-0,10	0,4	4,47	-0,43
12	21	1,92	26,1	1,96 1,92	26,5	0,04 0,00	0,4	1,53	-0,39
22	22	1,00	9,3	1,03	9,7	0,03	0,4	0,69	-0,31

[1)] 1H and ^{13}C NMR shifts were reassigned according to 2D experiments .

[2)] Source of data: R. Kazlauskas, P. T. Murphy, R. J. Wells, A. J. Blackman, *Aust. J. Chem* . **1982**, *35* , 113.

[3)] Experiments were run on a 600 MHz/150 MHz NMR machine accordingly, 298 K.

[4)] For comparison a ^{1}H NMR spectrum of **XX** was measured in C_6D_6.

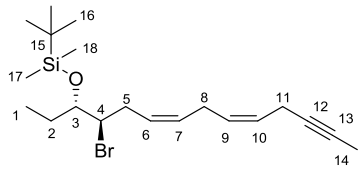


Table S-5: ^{1}H and ^{13}C data of ***anti*-15**; numbering scheme as shown in the Insert.

^{1}H NMR (C_6D_6, 600 MHz)						^{13}C NMR (C_6D_6, 150 MHz)	
No.	δ (ppm)	Integral	Splitting	COSY	J (Hz)	δ (ppm)	HMBC
1	0.82	3H	t	2a, 2b	7.5	9.1	2a, 2b, 3
2a	1.80	1H	ddq	1, 2b, 3	14.0, 6.2, 7.4	27.5	1, 3, 4
2b	1.43	1H	ddq	1, 2a, 3	14.0, 4.6, 7.4		
3	3.72	1H	dt	2a, 2b, 4	6.2, 4.7	76.7	1, 2a, 2b, 4
4	3.95	1H	ddd	3, 5a, 5b	9.5, 4.7, 4.3	59.5	2a, 2b, 5a, 5b, 6
5a	2.68	1H	dddd	4, 5b, 6	15.3, 6.8, 4.2, 1.3	32.3	3, 4, 6, 7
5b	2.56	1H	dddd	4, 5a, 6	15.5, 9.5, 6.8, 1.2		
6	5.51	1H	dtt	5a, 5b, 7	10.7, 6.7, 1.4	127.4	4, 5a, 5b, 7, 8
7	5.46	1H	dtt	6, 8	10.7, 7.0, 1.3	130.0	5a, 5b, 6, 8, 9
8	2.76 – 2.73	2H	m	7, 9	-	26.0	7, 9, 10, 11
9	5.39	1H	dtt	8, 10, 11	10.5, 7.3, 1.7	128.9	7, 8, 10, 11
10	5.56	1H	dtt	9, 11	10.5, 7.1, 1.7	126.3	8, 9, 11
11	2.88	2H	ddqt	9, 10, 14	7.0, 1.8, 2.6, 0.8	17.7	8, 9, 10, 14
12	-	-	-	-	-	77.5	9, 10, 11, 14
13	-	-	-	-	-	75.8	11, 14
14	1.54	3H	t	11	2.6	3.4	-
15	-	-	-	-	-	18.4	16, 17, 18
16	0.99	9H	s	-	-	26.1	-
17	0.10	3H	s	-	-	−4.2	18
18	0.03	3H	s	-	-	−4.3	17

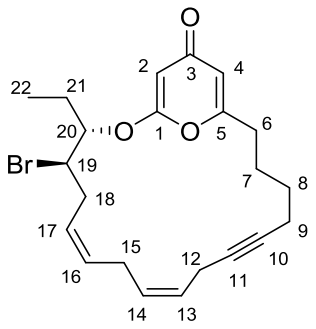


Table S-6: ^{1}H and ^{13}C data of ***anti*-27**; numbering scheme as shown in the Insert.

^{1}H NMR (C_6D_6, 600 MHz)						^{13}C NMR (C_6D_6, 150 MHz)	
No.	δ (ppm)	Integral	Splitting	COSY	J (Hz)	δ (ppm)	HMBC
1	-	-	-	-	-	166.4	2, 20
2	5.55	1H	d	4	1.8	92.2	4
3	-	-	-	-	-	180.3	2, 4
4	5.88	1H	d	2	1.8	113.2	2, 6a, 6b
5	-	-	-	-	-	164.2	4, 6a, 6b
6a	1.83	1H	ddd	6b, 7	14.7, 9.2, 5.7	31.9	4, 7, 8
6b	1.74 – 1.69	1H	m	6a, 7	-		
7a	1.49 – 1.43	1H	m	6a, 6b, 8	-	26.2	6a, 6b, 8, 9
7b	1.39 – 1-43	1H	m				
8	1.07 – 1.01	2H	m	7, 9	-	27.7	6a, 6b, 7, 9
9	1.93	2H	tt	8, 12a, 12b	6.5, 2.3	18.6	7, 8
10	-	-	-	-	-	79.3	8, 9
11	-	-	-	-	-	79.2	12a, 12b, 13, 14
12	2.79 – 2.76	2H	m	9, 12b, 13	-	17.3	9, 13, 14
13	5.48	1H	dtt	12a, 12b, 14	10.3, 7.3, 1.7	125.3	9, 12a, 12b, 14, 15a, 15b
14	5.35	1H	dtt	13, 15a, 15b	10.3, 7.1, 1.4	129.9	12a, 12b, 13, 15a, 15b
15	2.79 – 2.76	2H	m	14, 15b, 16	-	26.0	13, 14, 16, 17
16	5.37	1H	dtt	15a, 15b, 17	10.6, 7.6, 1.7	131.0	14, 15a, 15b, 17, 18a, 18b
17	5.46	1H	dtt	15a, 15b, 16, 18a, 18b	10.6, 7.1, 1.5	125.8	15a, 15b, 16, 18a, 18b, 19
18a	2.58 – 2.53	1H	m	17, 19	-	32.6	16, 17, 19, 20
18b	2.50 – 2.45	1H	m	17, 19	-		
19	3.70	1H	ddd	18a, 18b, 20	10.8, 5.0, 4.0	53.6	17, 18a, 18b, 20, 21
20	4.14	1H	td	19, 21	6.7, 4.0	83.0	18a, 18b, 19, 21, 22
21a	1.61 – 1.54	1H	m	20, 22	-	24.6	19, 20, 22
21b	1.49 – 1.43	1H	m	20, 22	-		
22	0.63	3H	t	21	7.8	8.5	20, 21

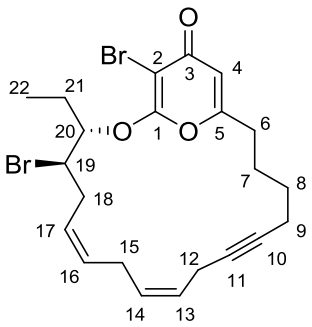


Table S-7: ^{1}H and ^{13}C data of ***anti*-1**; numbering scheme as shown in the Insert.

^{1}H NMR ($CDCl_3$, 600 MHz)						^{13}C NMR ($CDCl_3$, 150 MHz)	
No.	δ (ppm)	Integral	Splitting	COSY	J (Hz)	δ (ppm)	HMBC
1	-	-	-	-	-	161.7	20
2	-	-	-	-	-	92.3	4
3	-	-	-	-	-	175.6	4
4	6.13	1H	s	-	-	111.7	6a, 6b
5	-	-	-	-	-	163.3	4, 6a, 6b, 7
6a	2.59	1H	ddd	6b, 7	14.6, 9.3, 6.1	33.0	4, 7, 8
6b	2.51	1H	ddd	6a, 7	14.7, 9.3, 6.3		
7	1.86 – 1.75	2H	m	6a, 6b, 8	-	26.6	6a, 6b, 8, 9
8	1.58 – 1.55	2H	m	7, 9	-	28.0	6a, 6b, 7, 9
9	2.27 – 2.24	2H	m	8, 12	-	18.6	7, 8
10	-	-	-	-	-	79.2	8, 9, 12
11	-	-	-	-	-	79.1	9, 12
12a	2.95	1H	ddt	9, 12b, 13	17.1, 6.5, 2.3	17.1	13, 14
12b	2.83	1H	ddt	9, 12a, 13	17.1, 5.9, 2.5		
13	5.54 – 5.48	1H	m	12a, 12b	-	125.0	12a, 12b, 15
14	5.54 – 5.48	1H	m	15	-	129.9	13, 15
15	2.91 – 2.87	2H	m	14, 16	-	26.1	13, 14, 17
16	5.68	1H	dtt	15, 17	10.7, 7.4, 1.6	131.1	13, 15, 18a, 18b
17	5.45	1H	dddt	16, 18a, 18b	10.7, 8.0, 6.2, 1.7	125.6	15, 18a, 18b, 19
18a	2.77	1H	ddddt	17, 18b, 19	15.2, 6.1, 4.9, 1.8, 0.9	33.4	16, 17, 20
18b	2.66	1H	dddd	17, 18a, 19	15.2, 9.1, 8.0, 1.4		
19	4.15	1H	ddd	18a, 18b, 20	9.1, 7.1, 4.8	55.8	18a, 18b, 21a, 21b
20	4.86	1H	td	19, 21a, 21b	7.1, 3.6	84.6	18a, 18b, 19, 21a, 21b, 22
21a	2.06	1H	dq	20, 22	14.9, 7.4	25.6	19, 20, 22
21b	2.05	1H	ddq	20, 22	14.8, 3.7, 7.4		
22	1.05	3H	t	21a, 21b	7.4	9.3	20, 21a, 21b

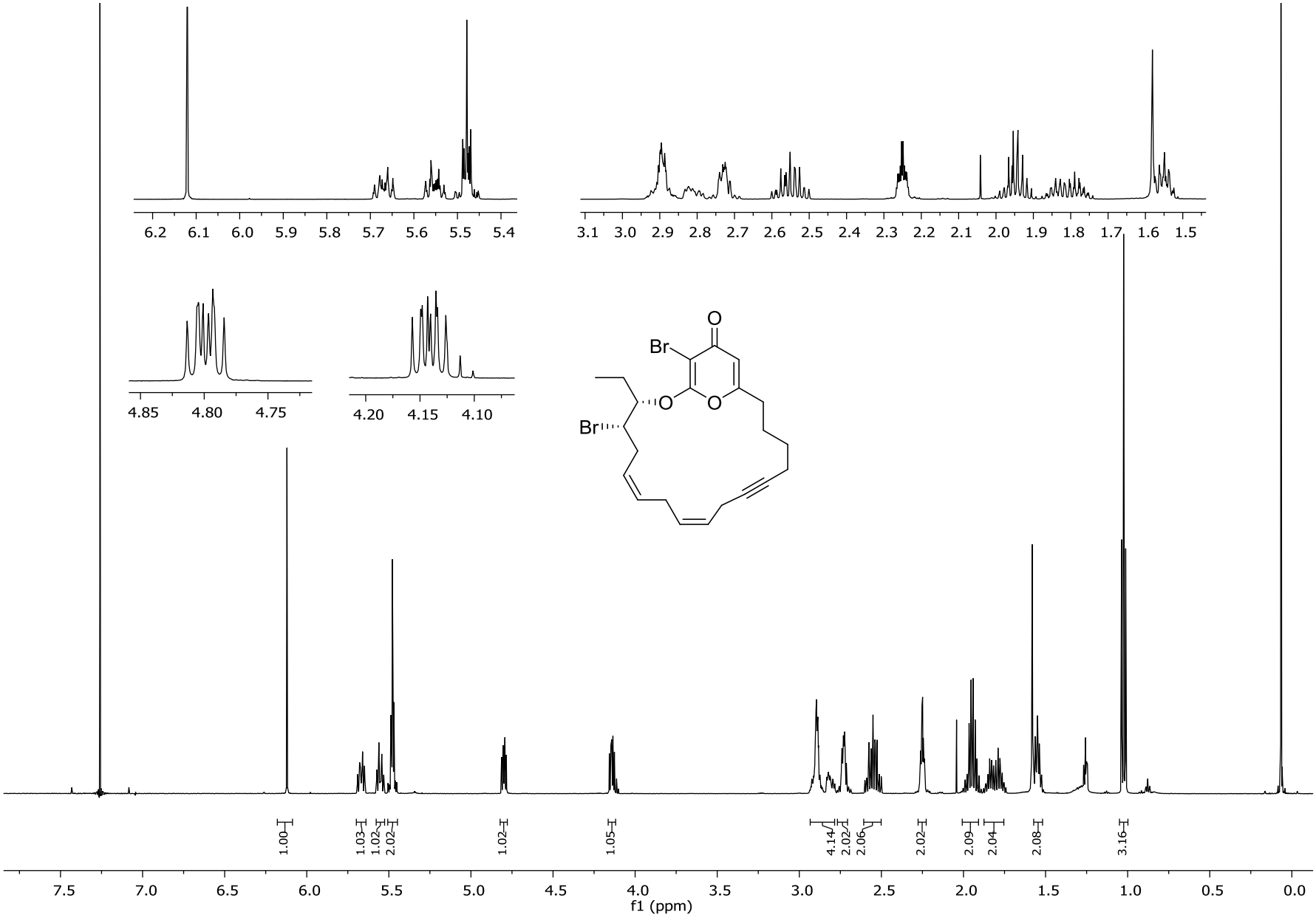
Table S-8: Comparison of ^{1}H and ^{13}C data of synthetic ***anti*-1** with those of the natural product; numbering scheme as shown in the insert above.

# (lit.)	# (reassigned)*	natural XX ($CDCl_3$)*		synthetic XX (anti, $CDCl_3$)		Δ (δ(XX)-δ(lit.))	
		^{1}H	^{13}C	^{1}H	^{13}C	Δ ^{1}H	Δ ^{13}C
5	1	–	161,6	–	161,7	–	0,1
2	2	–	91,8	–	92,3	–	0,5
3	3	–	175,4	–	175,6	–	0,2
4	4	6,10	111,2	6,13	111,7	0,03	0,5
1	5	–	162,9	–	163,3	–	0,4
18	6	2,58	32,3	2,59 2,51	33,0	0,01 -0,07	0,7
7	7	1,88	26,1	1,82 1,79	26,6	-0,06 -0,09	0,5
8	8	1,60	27,5	1,56	28,0	-0,04	0,5
12	9	2,22	18,2	2,26	18,6	0,04	0,4
10	10	–	78,8	–	79,2	–	0,4
11	11	–	78,5	–	79,1	–	0,6
21	12	2,88	17,0	2,95	17,1	0,07	0,1
14	13	5,40	124,6	5,51	125,0	0,11	0,4
17	14	5,40	128,9	5,51	129,9	0,11	1,0
15	15	2,88	25,7	2,89	26,1	0,01	0,4
13	16	5,40	130,3	5,68	131,1	0,28	0,8
16	17	5,40	125,5	5,45	125,6	0,05	0,1
6	18	2,72	33,2	2,77 2,66	33,4	0,05 -0,06	0,2
19	19	4,14	54,9	4,15	55,8	0,01	0,9
20	20	4,90	84,2	4,86	84,6	-0,04	0,4
12	21	1,92	26,1	2,06 2,05	25,6	0,14 0,13	-0,5
22	22	1,00	9,3	1,05	9,7	0,05	0,4

[1)] 1H and ^{13}C NMR shifts were reassigned according to 2D experiments .

[2)] Source of data: R. Kazlauskas, P. T. Murphy, R. J. Wells, A. J. Blackman, *Aust. J. Chem* . **1982**, *35* , 113.

[3)] Experiments were run on a 600 MHz NMR machine, 298 K.


6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4
3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5
4.85 4.80 4.75
4.20 4.15 4.10
O
Br
O
O
Br
1.00
1.03
1.02
2.02
1.02
1.05
4.14
2.02
2.06
2.02
2.09
2.04
2.08
3.16
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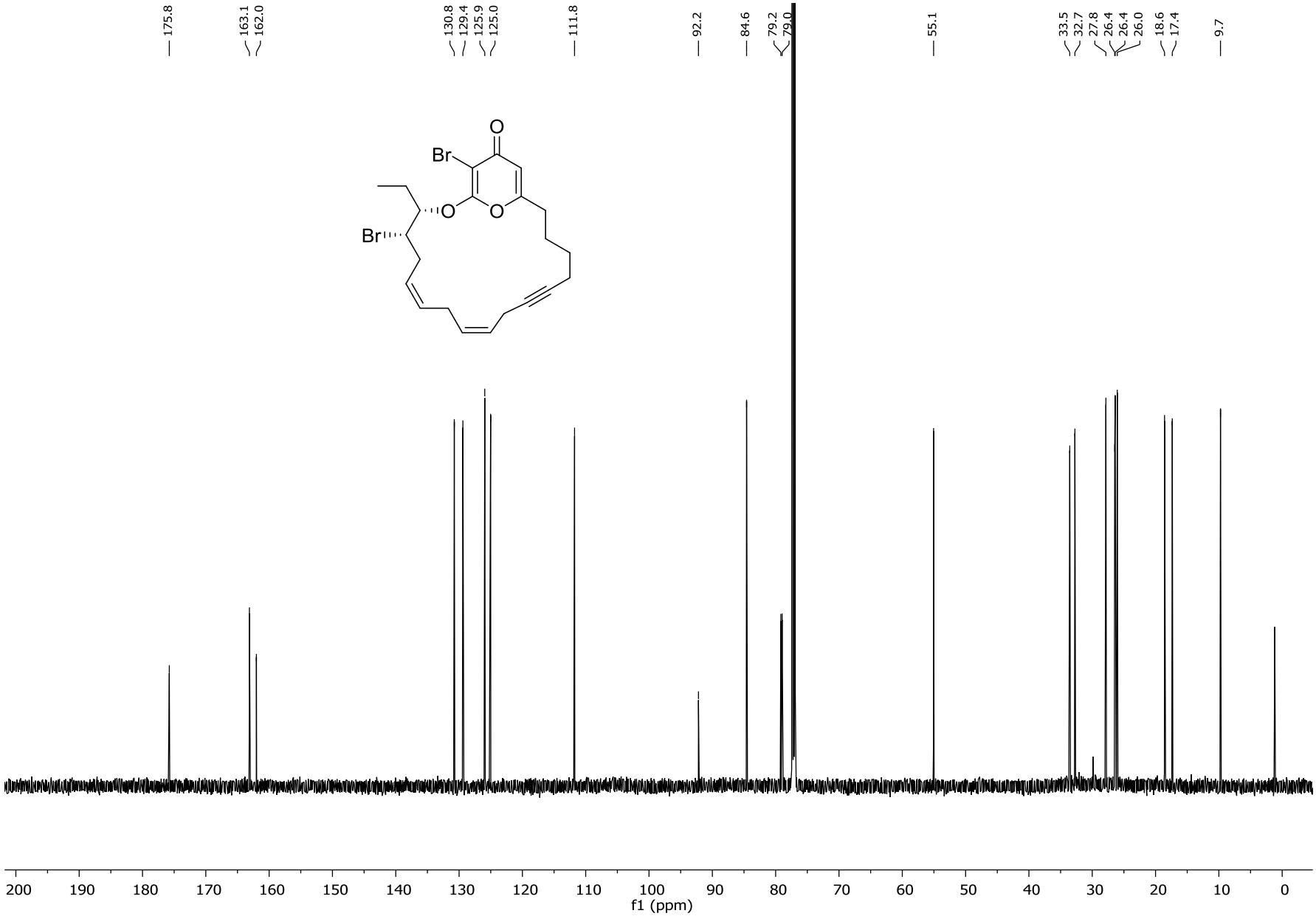
f1 (ppm)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125.0
111.8
92.2
84.6
79.2
79.0
55.1
33.5
32.7
27.8
26.4
26.4
26.0
18.6
17.4
9.7
Br
O
O
O
Br
200
190
180
170
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150
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130
120
110
100
90
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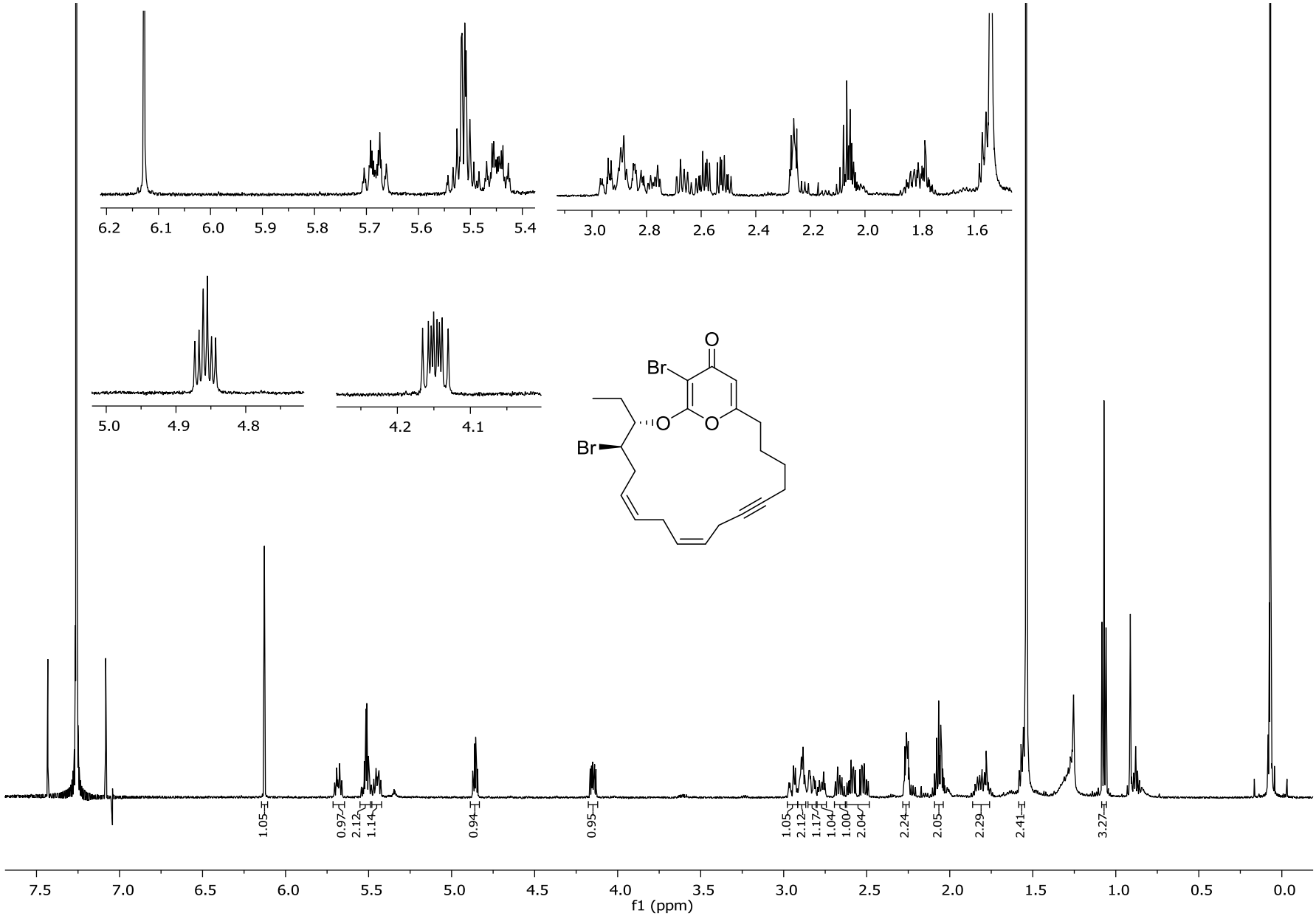
60
50
40
30
20
10
0
f1 (ppm)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3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
5.0 4.9 4.8
4.2 4.1
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Br
O
O
Br
1.05
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2.12
1.14
0.94
0.95
1.05
2.12
1.17
1.04
1.00
2.04
2.24
2.05
2.29
2.41
3.27
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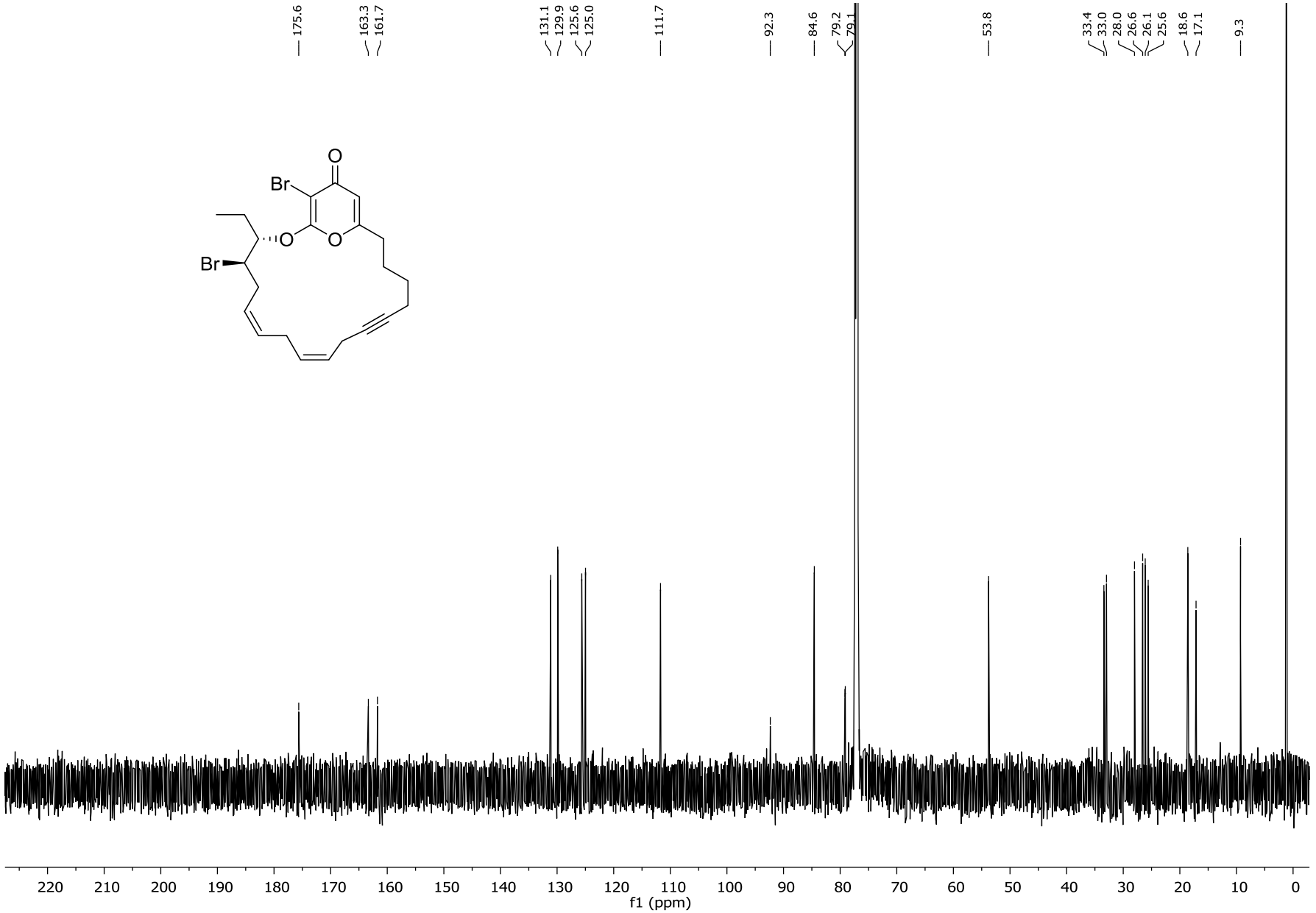
f1 (ppm)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161.7
131.1
129.9
125.6
125.0
111.7
92.3
84.6
79.2
79.1
53.8
33.4
33.0
28.0
26.6
26.1
25.6
18.6
17.1
9.3
O
Br
O
O
Br
220
210
200
190
180
170
160
150
140
130
120
110
100
90
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60
50
40
30
20
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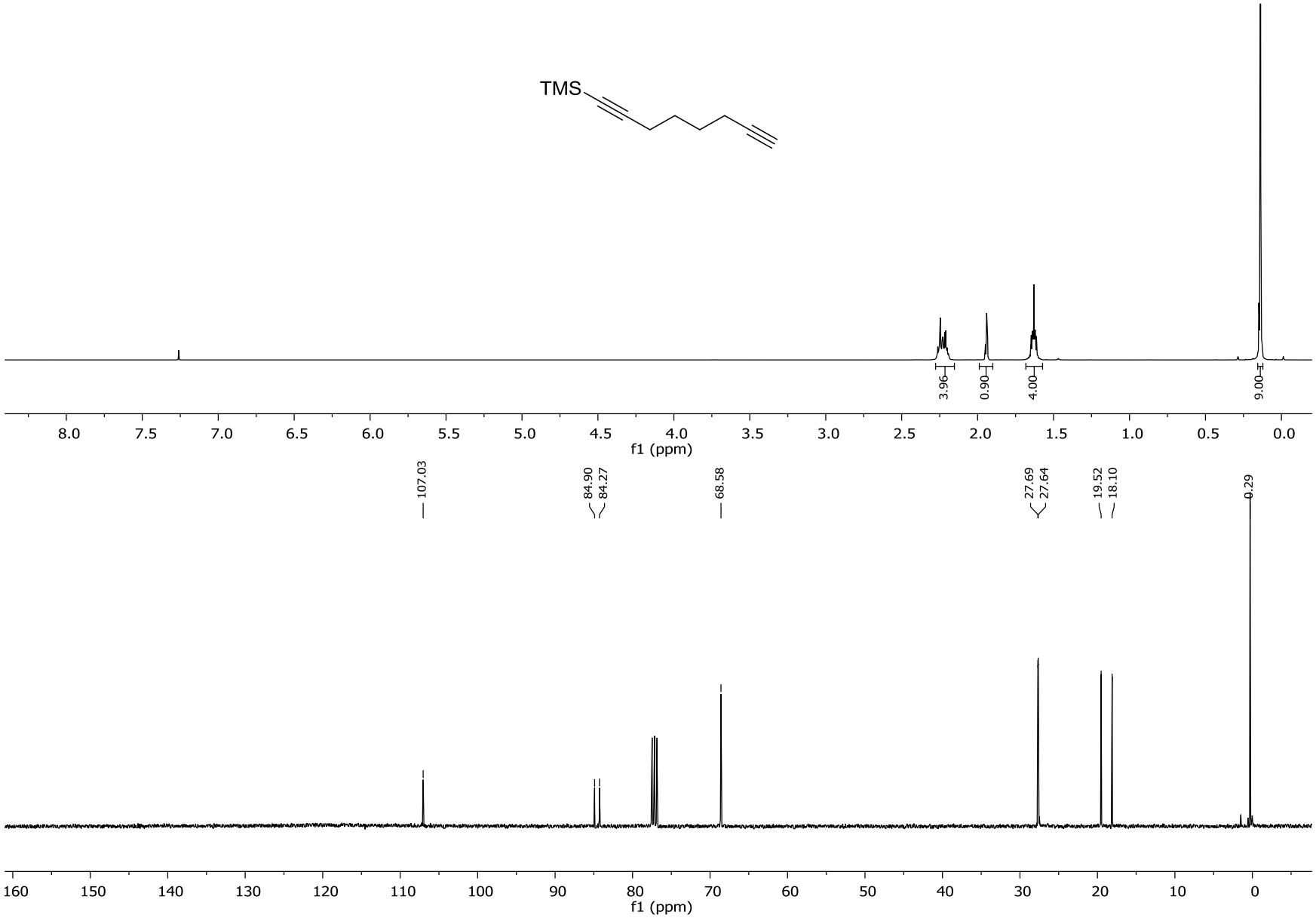
0
f1 (ppm)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9.00
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
107.03
84.90
84.27
68.58
27.69
27.64
19.52
18.10
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110
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90
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70
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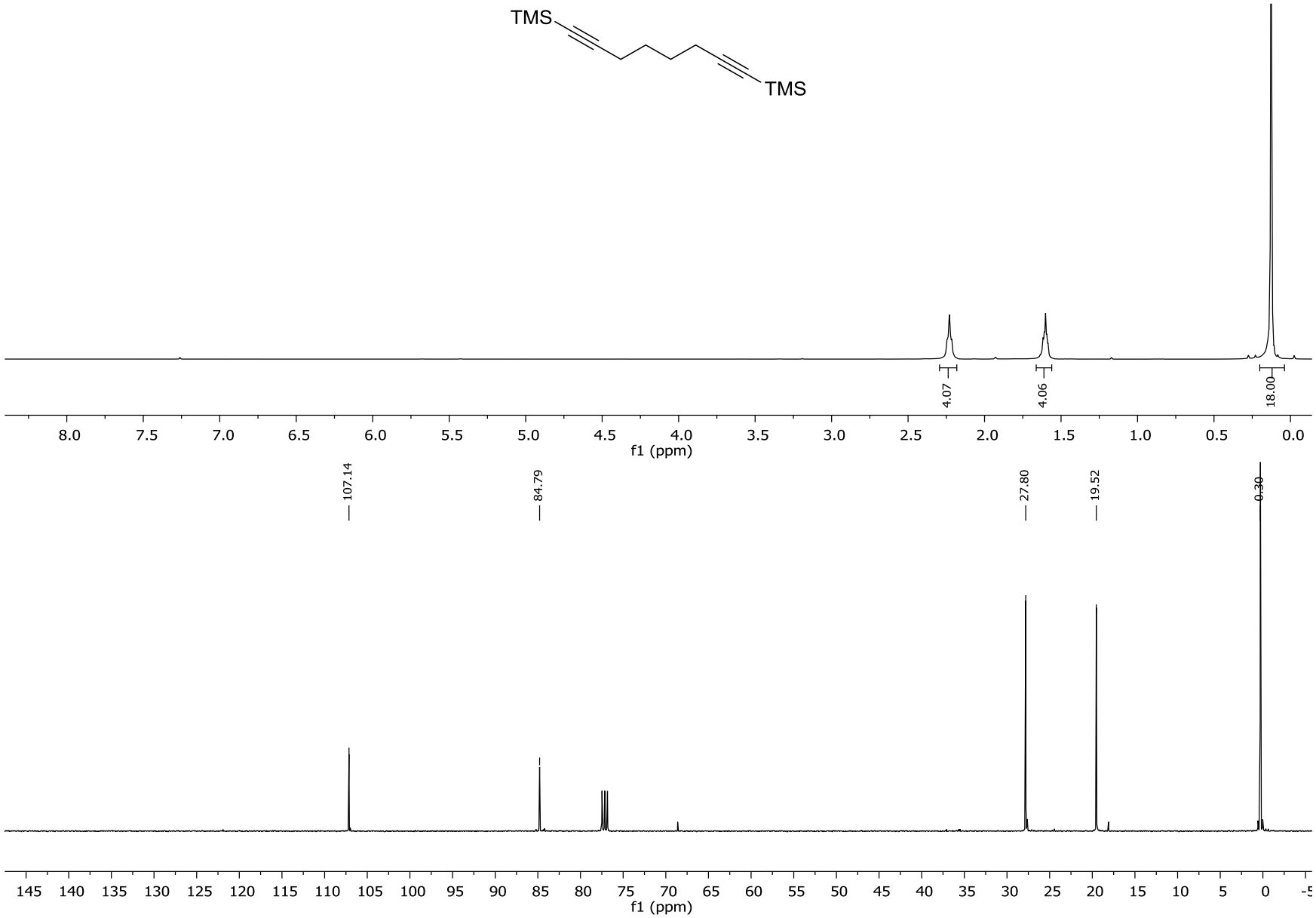
50
40
30
20
10
0
f1 (ppm)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6.0
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
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84.79
27.80
19.52
0.30
145
140
135
130
125
120
115
110
105
100
95
90
85
80
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65
60
55
50
45
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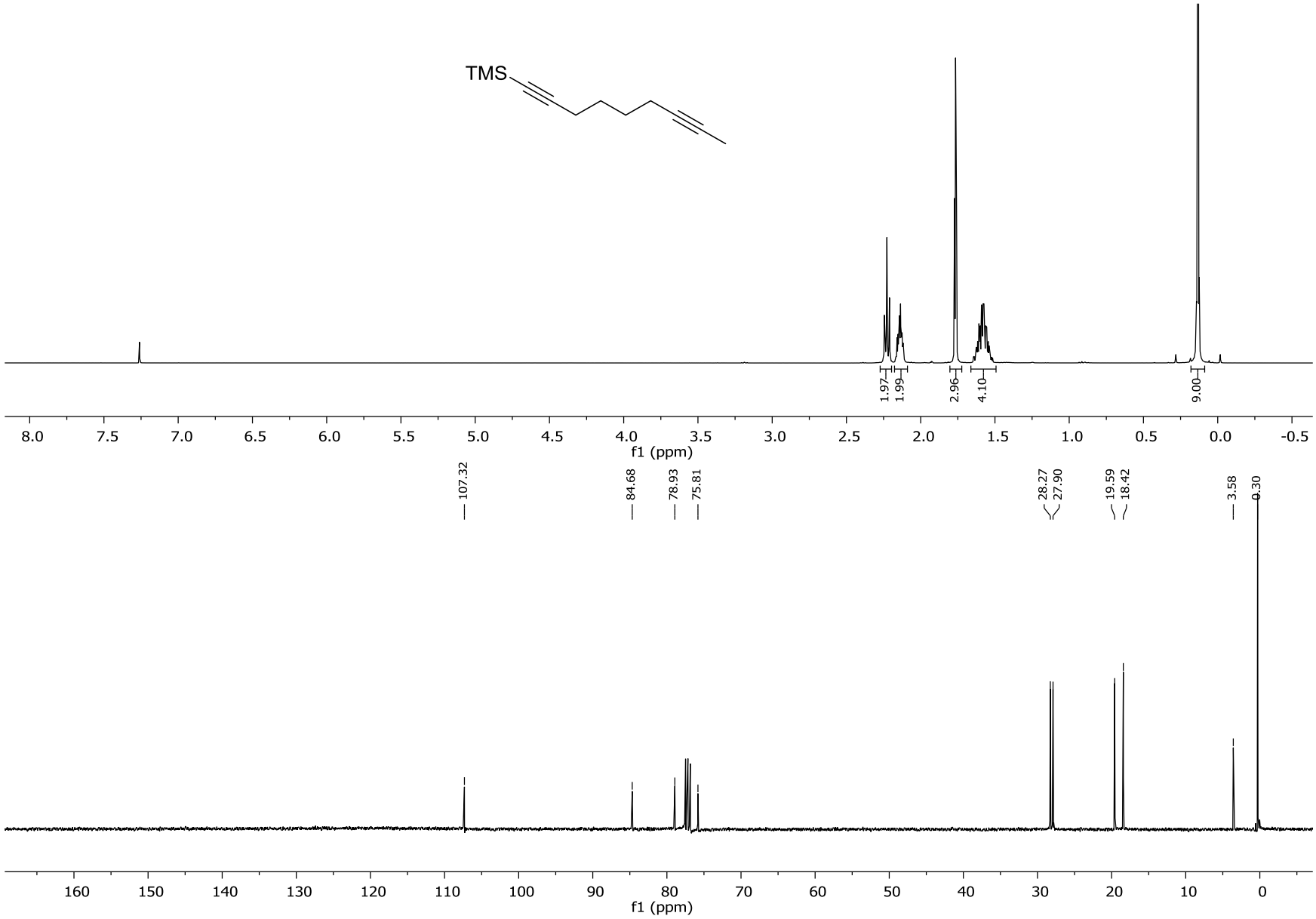
35
30
25
20
15
10
5
0
f1 (ppm)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2.96
4.10
9.00
f1 (ppm)
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78.93
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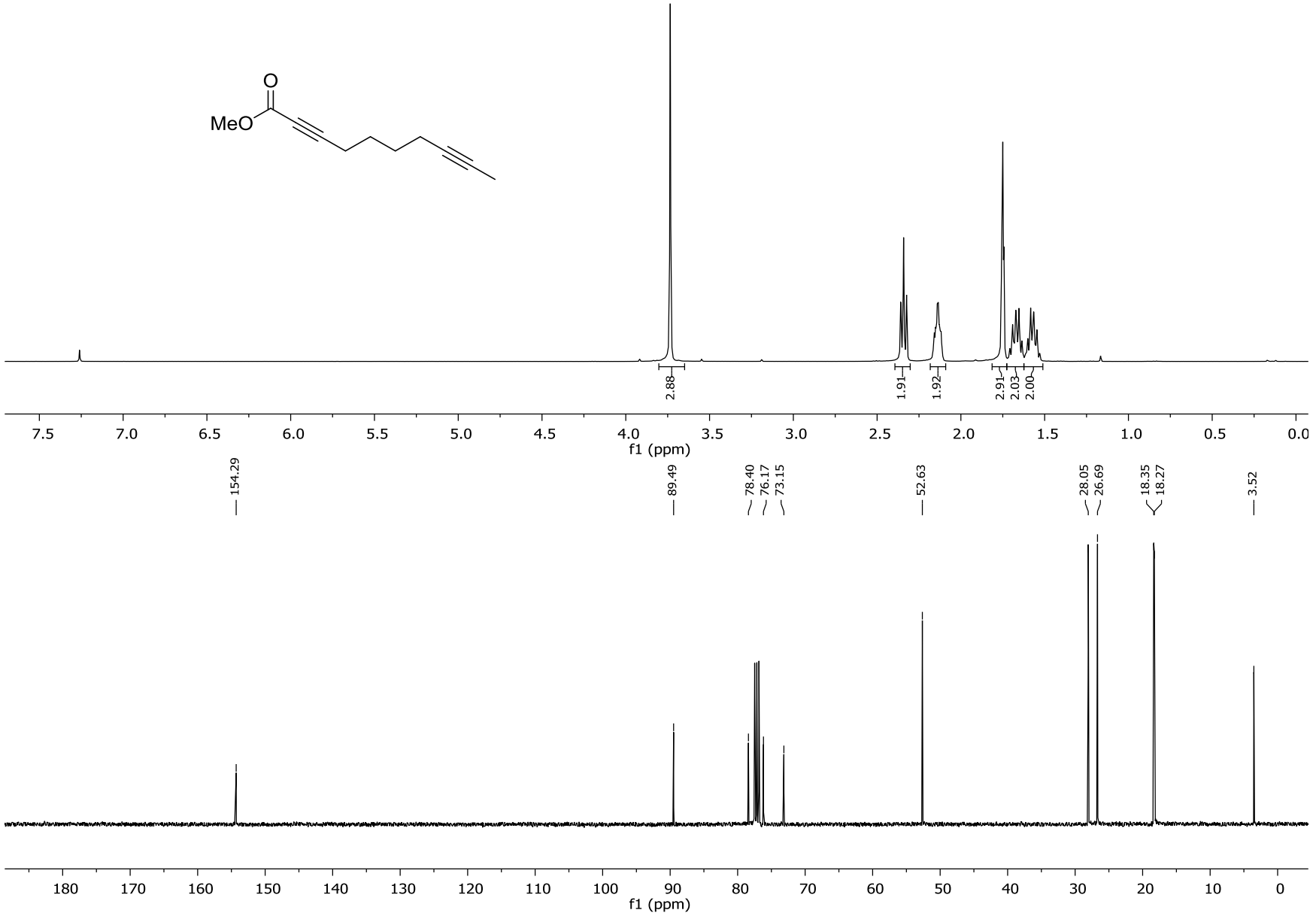
27.90
19.59
18.42
3.58
0.30
f1 (ppm)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MeO
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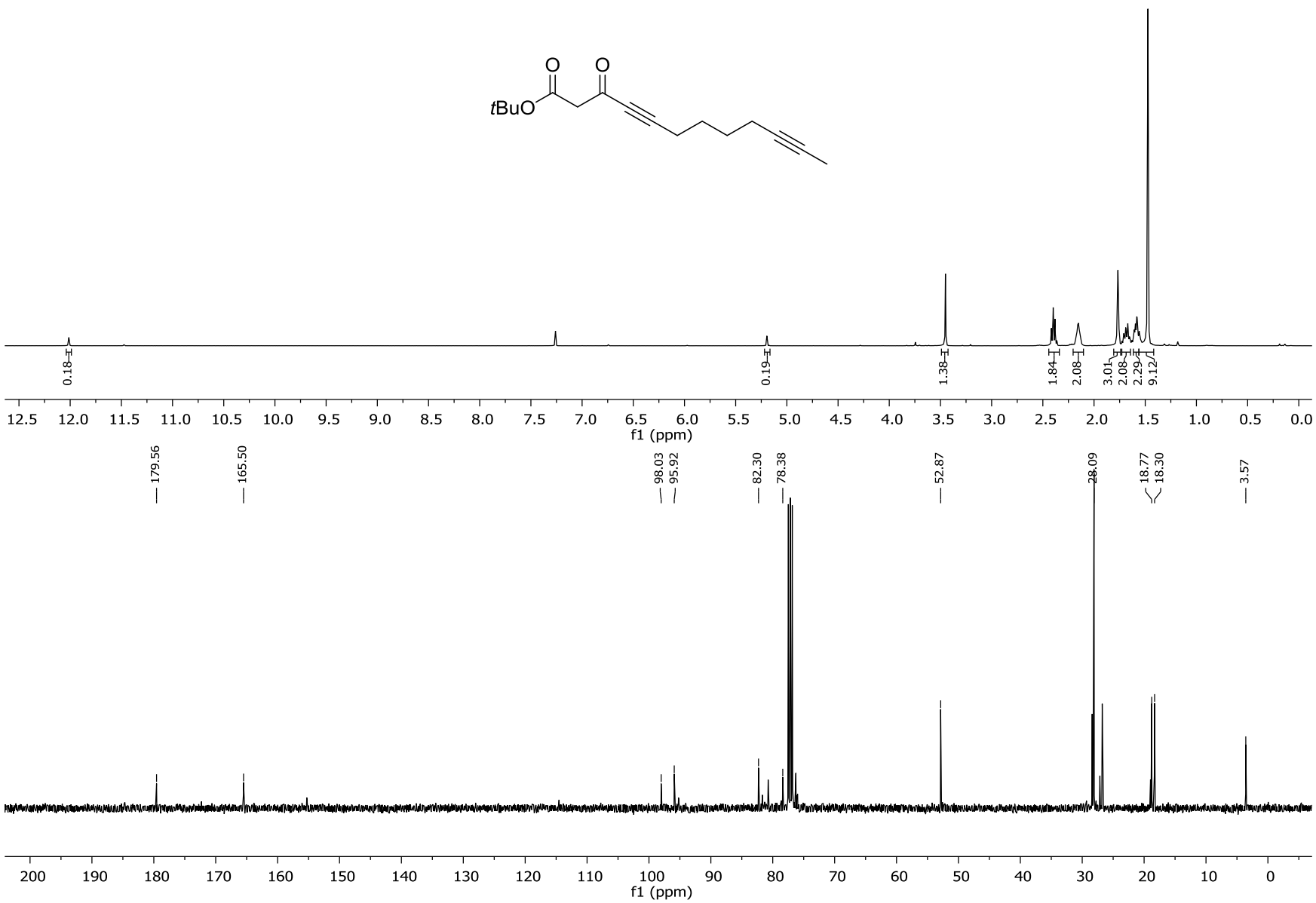
1.91
1.92
2.91
2.03
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
154.29
89.49
78.40
76.17
73.15
52.63
28.05
26.69
18.35
18.27
3.52
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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O
tBuO
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0.19
1.38
1.84
2.08
3.01
2.08
2.29
9.12
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f1 (ppm)
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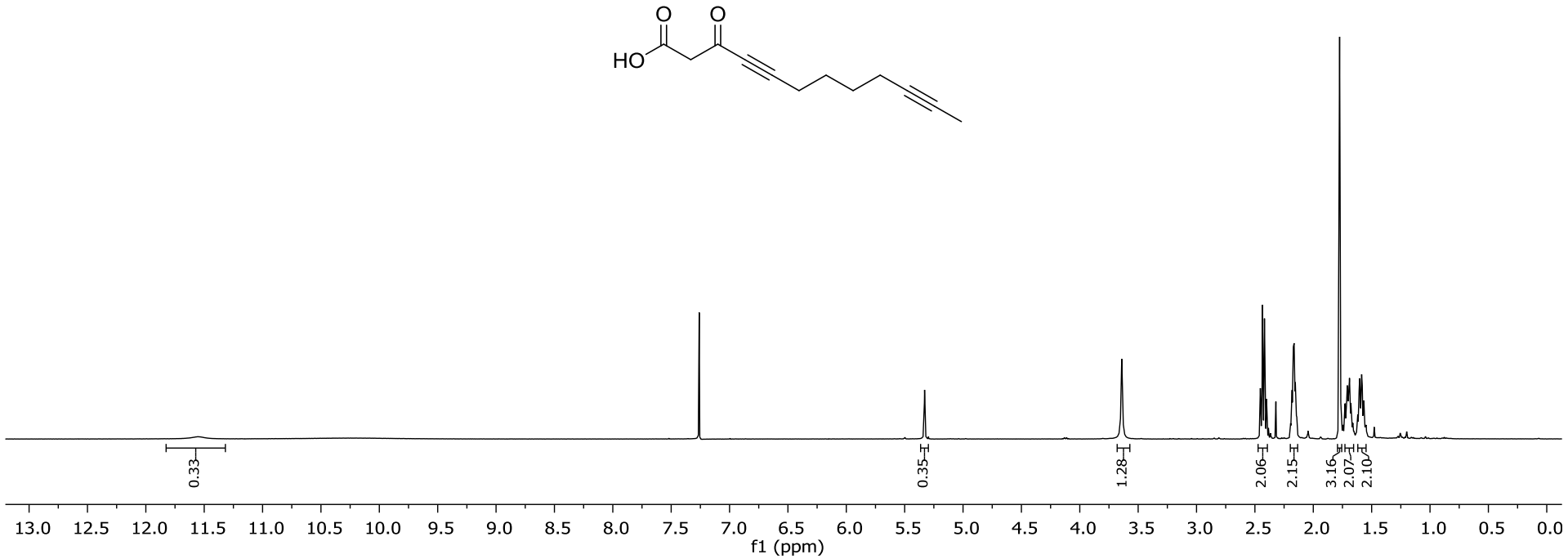
165.50
98.03
95.92
82.30
78.38
52.87
28.09
18.77
18.30
3.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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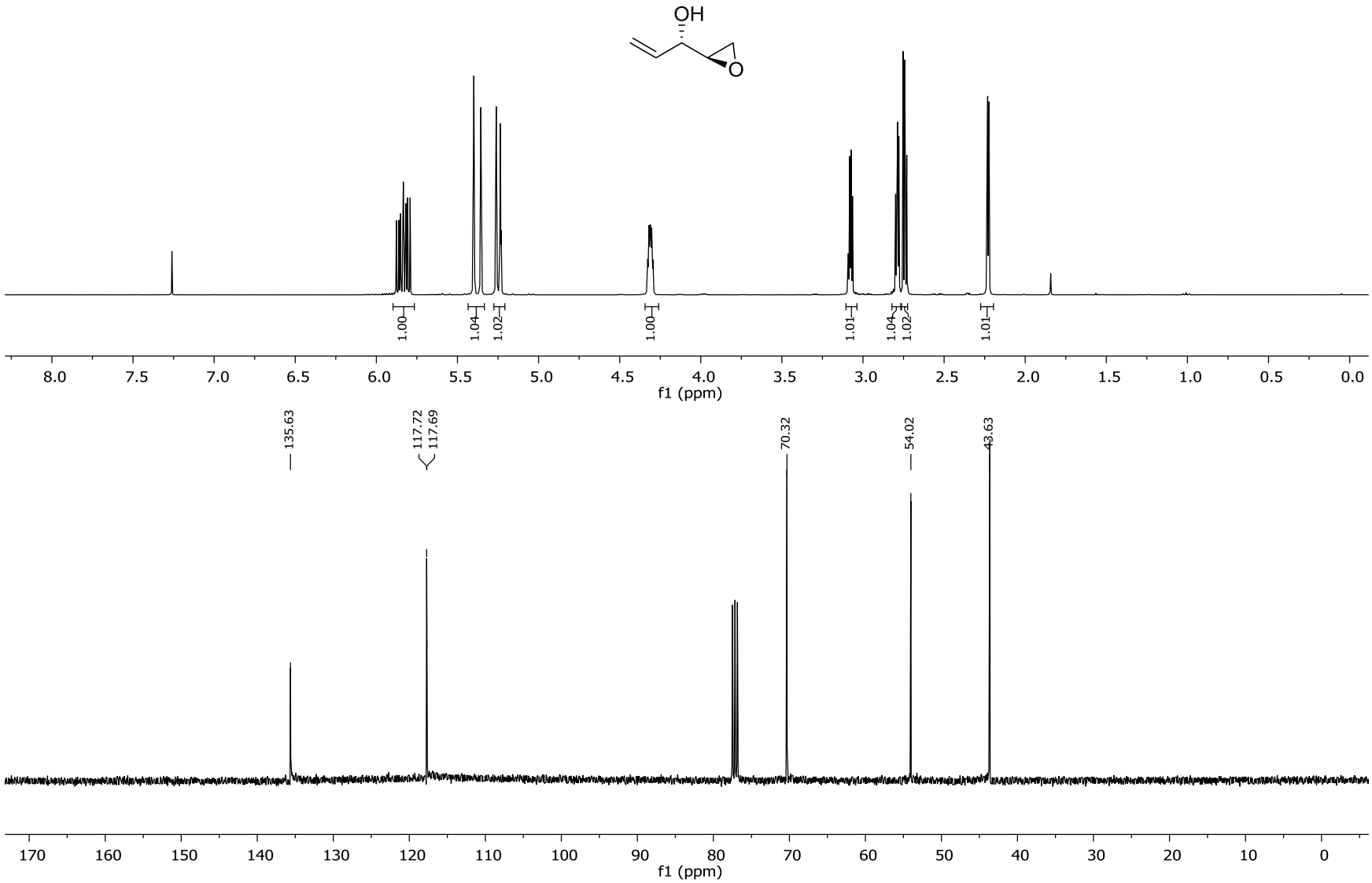
0.35
1.28
2.06
2.15
3.16
2.07
2.10
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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1.00
1.01
1.04
1.02
1.01
8.0
7.5
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6.5
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
f1 (ppm)
135.63
117.72
117.69
70.32
54.02
43.63
170
160
150
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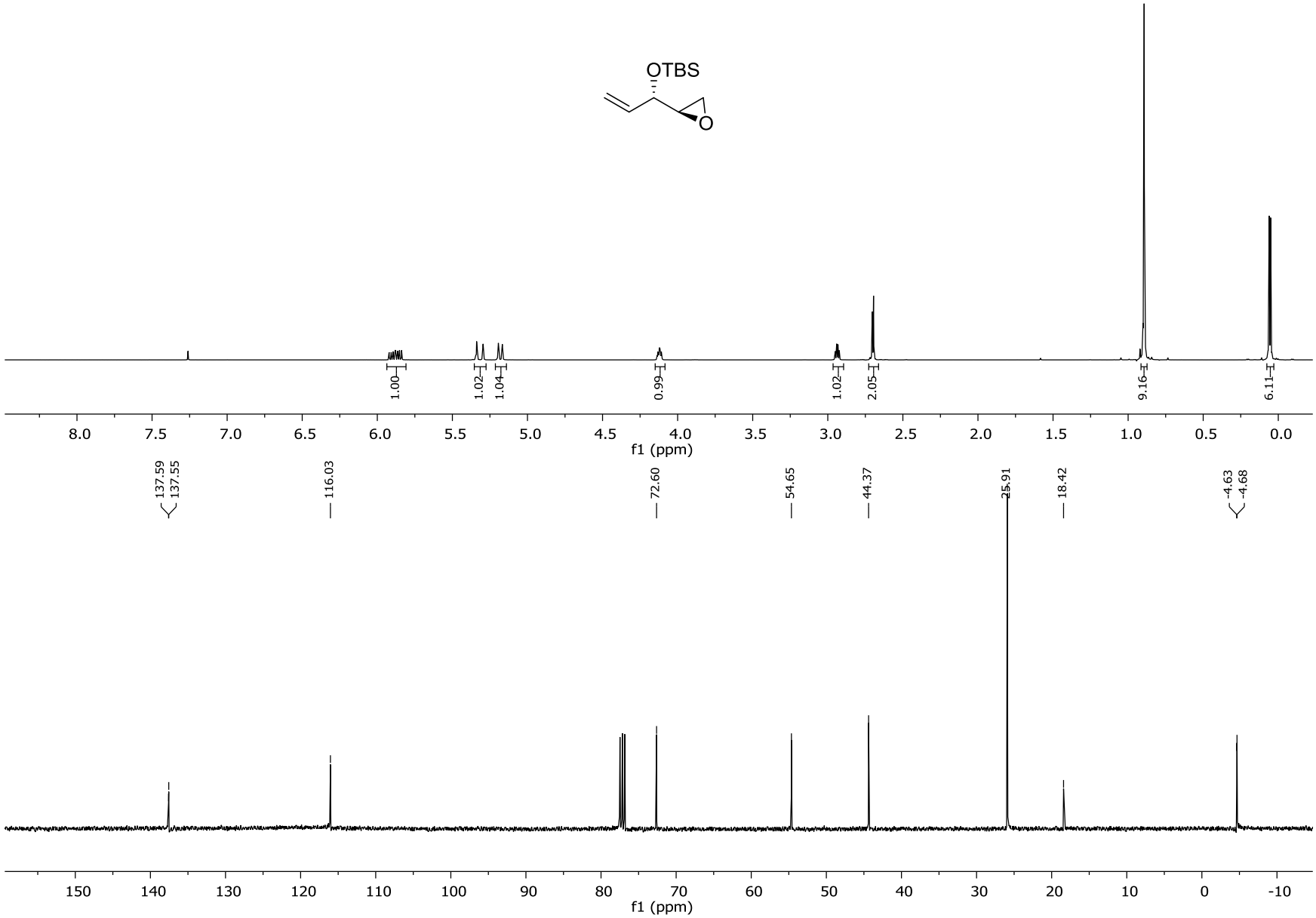
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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1.02
2.05
9.16
6.11
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72.60
54.65
44.37
25.91
18.42
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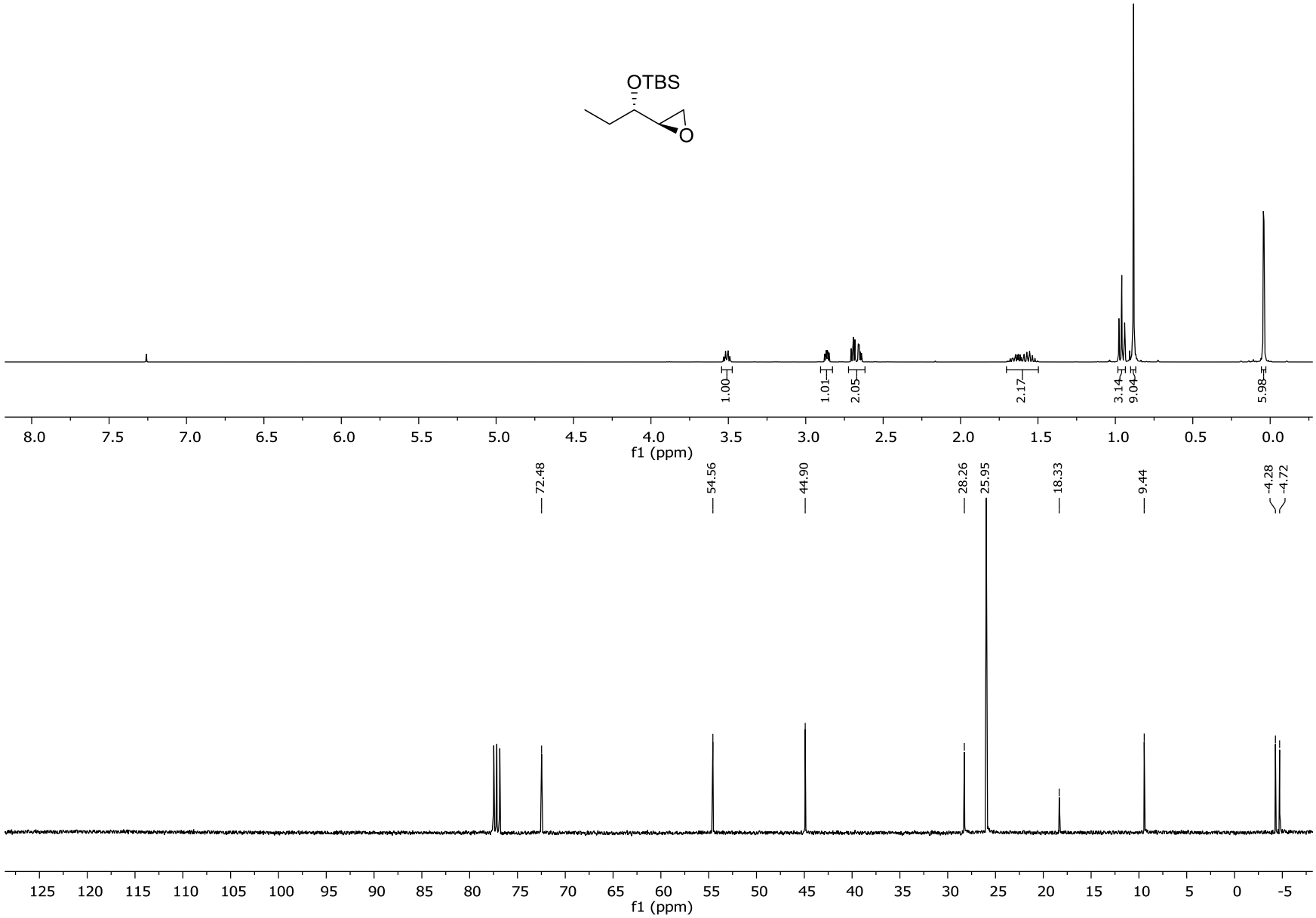
f1 (ppm)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9.44
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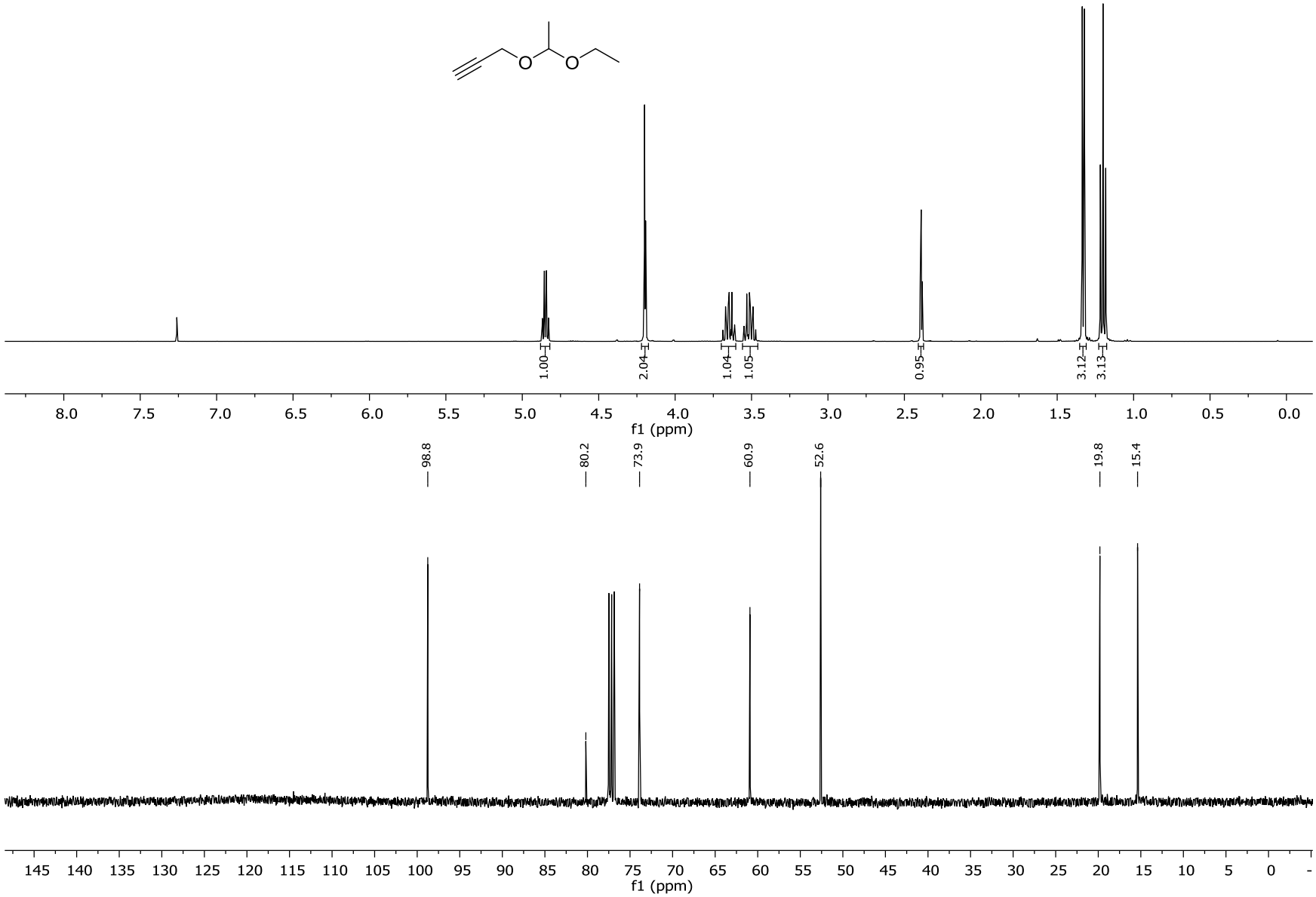
-4.72
f1 (ppm)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O
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1.04
1.05
0.95
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3.13
8.0
7.5
7.0
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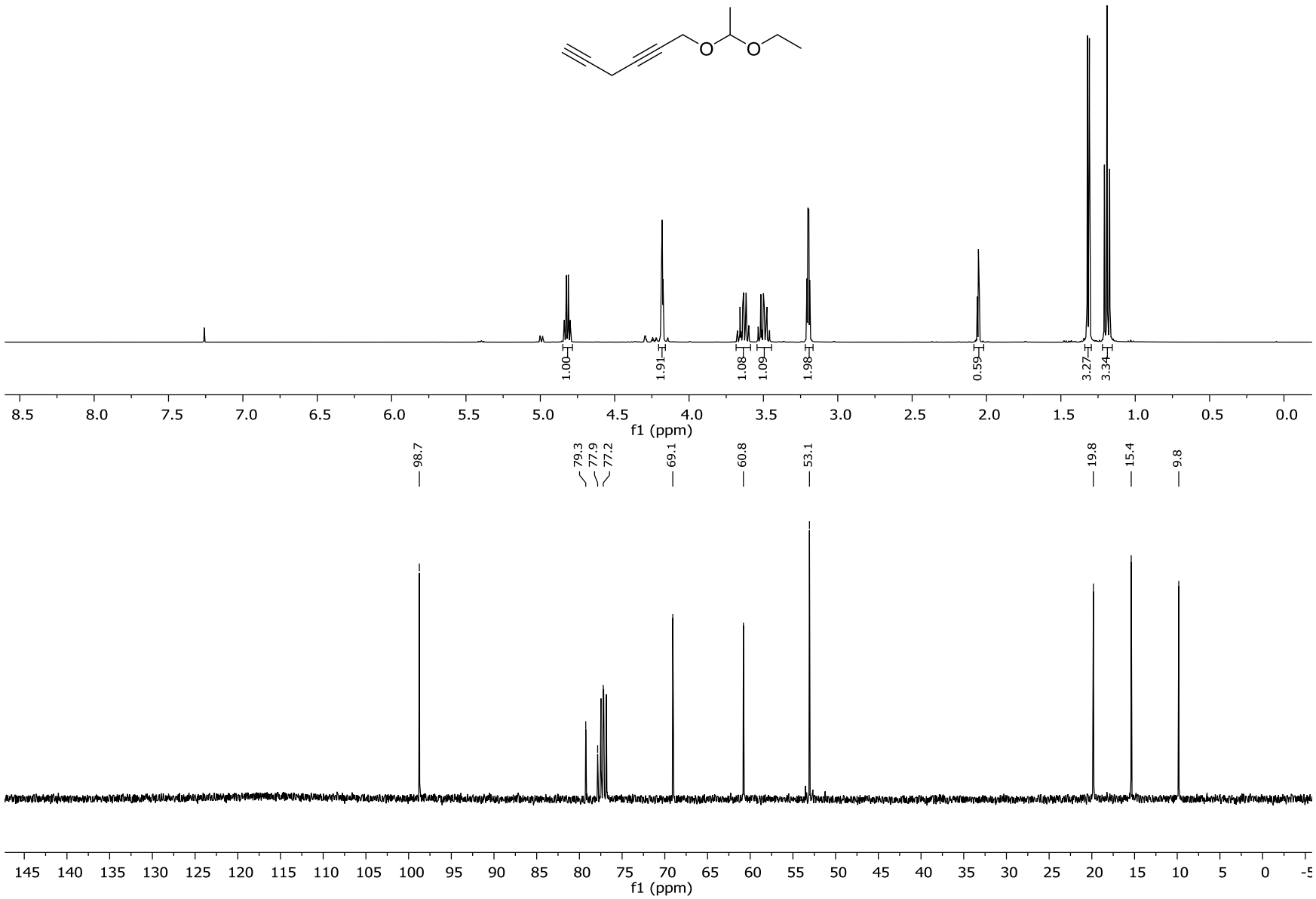
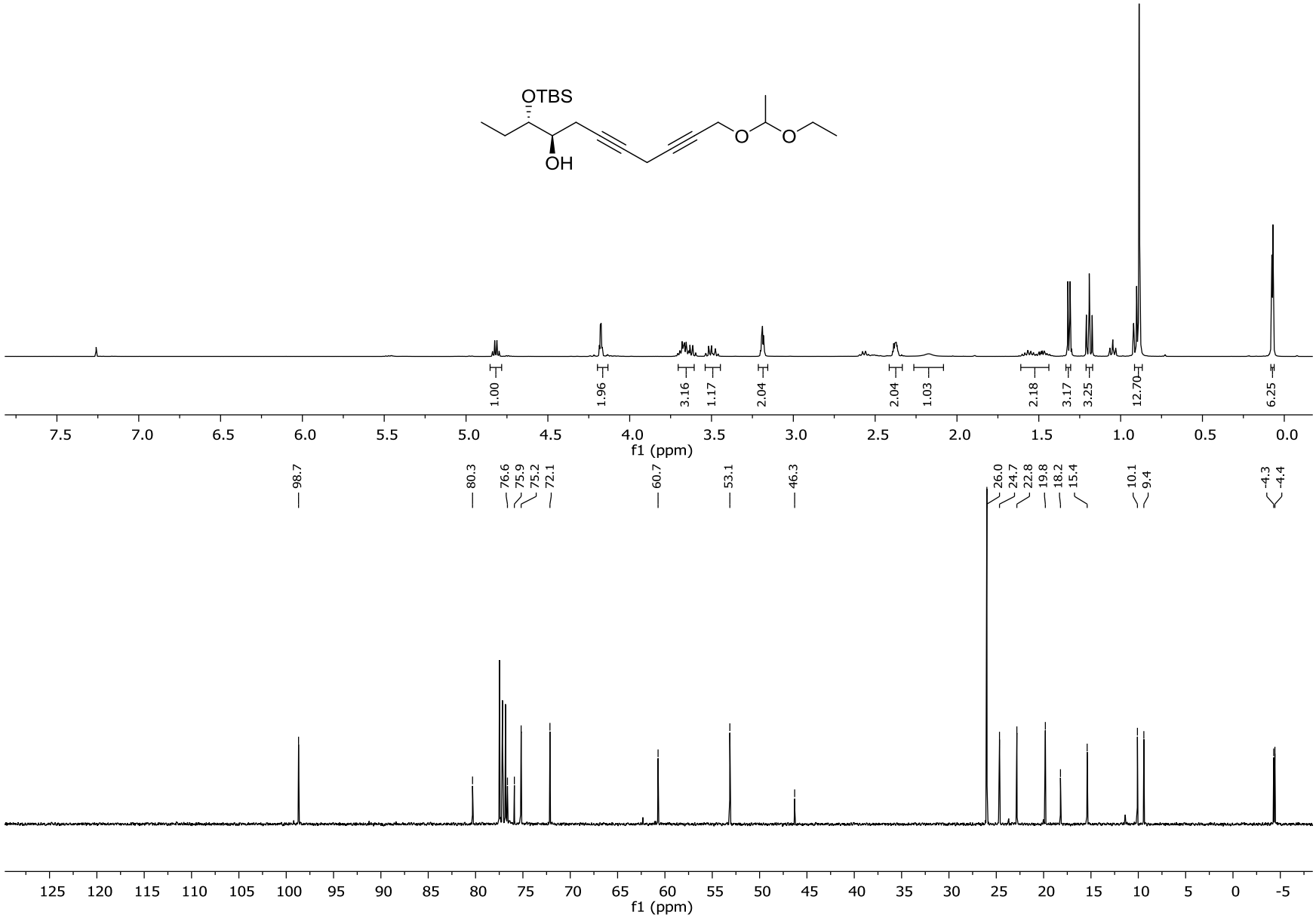
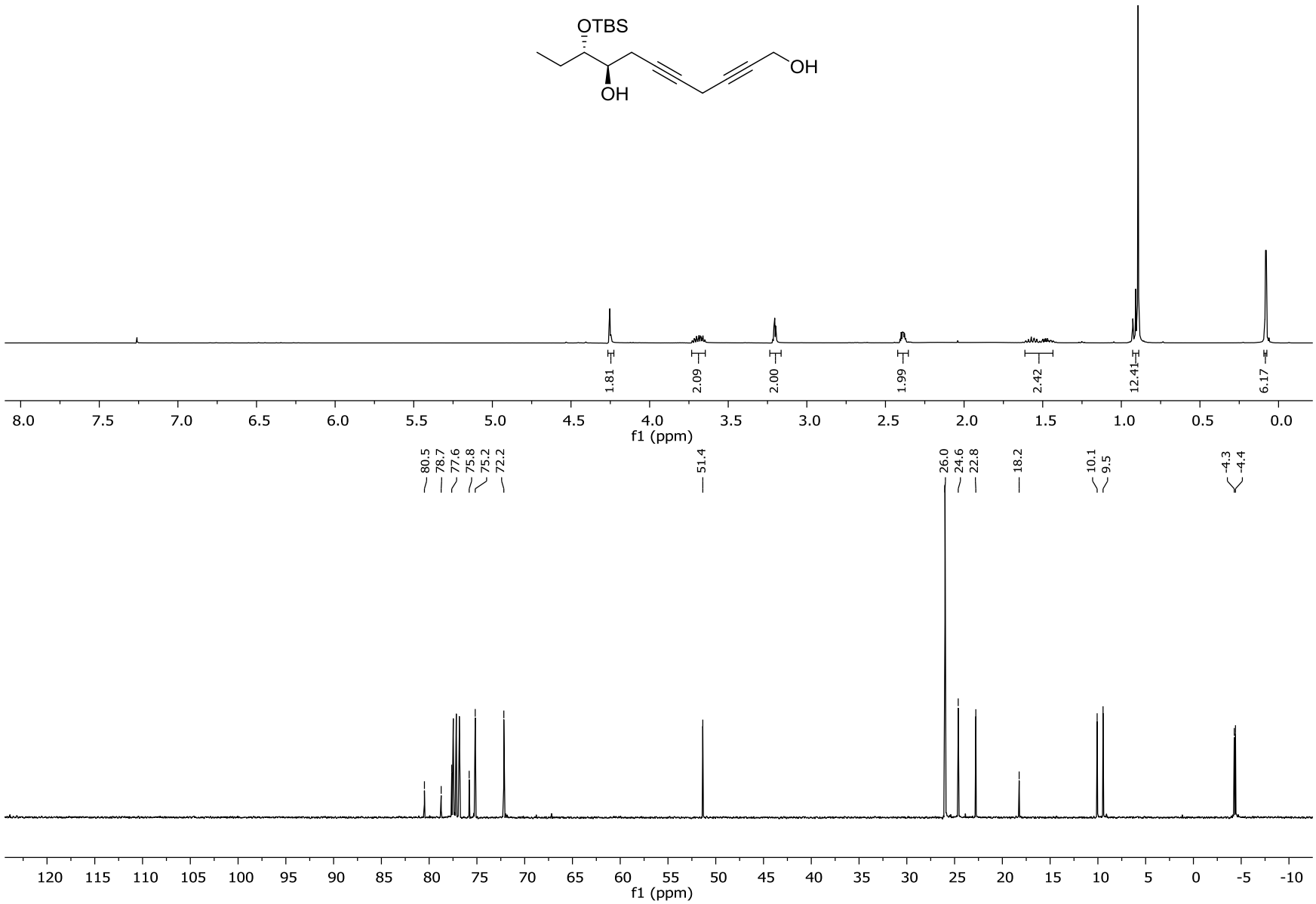
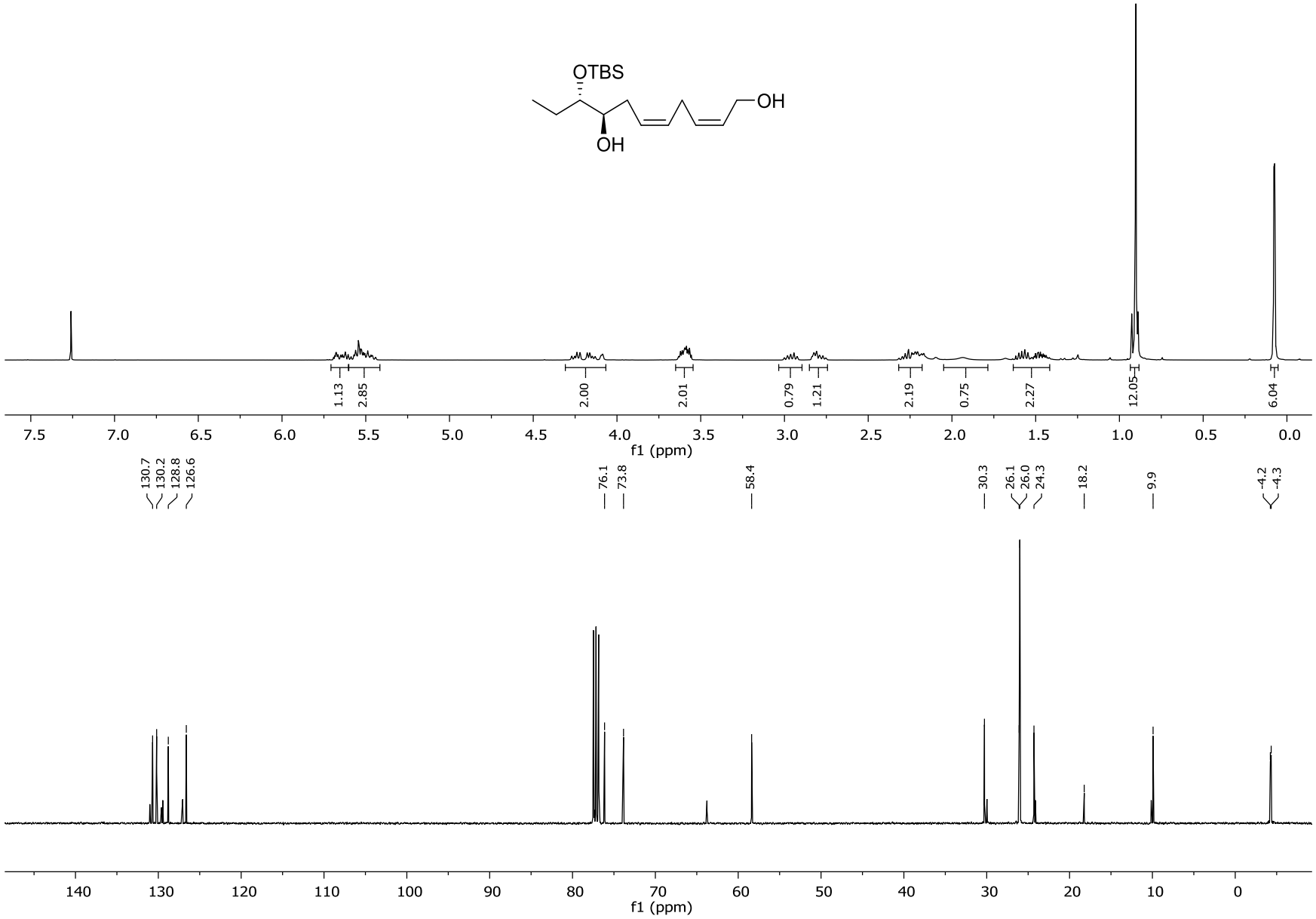
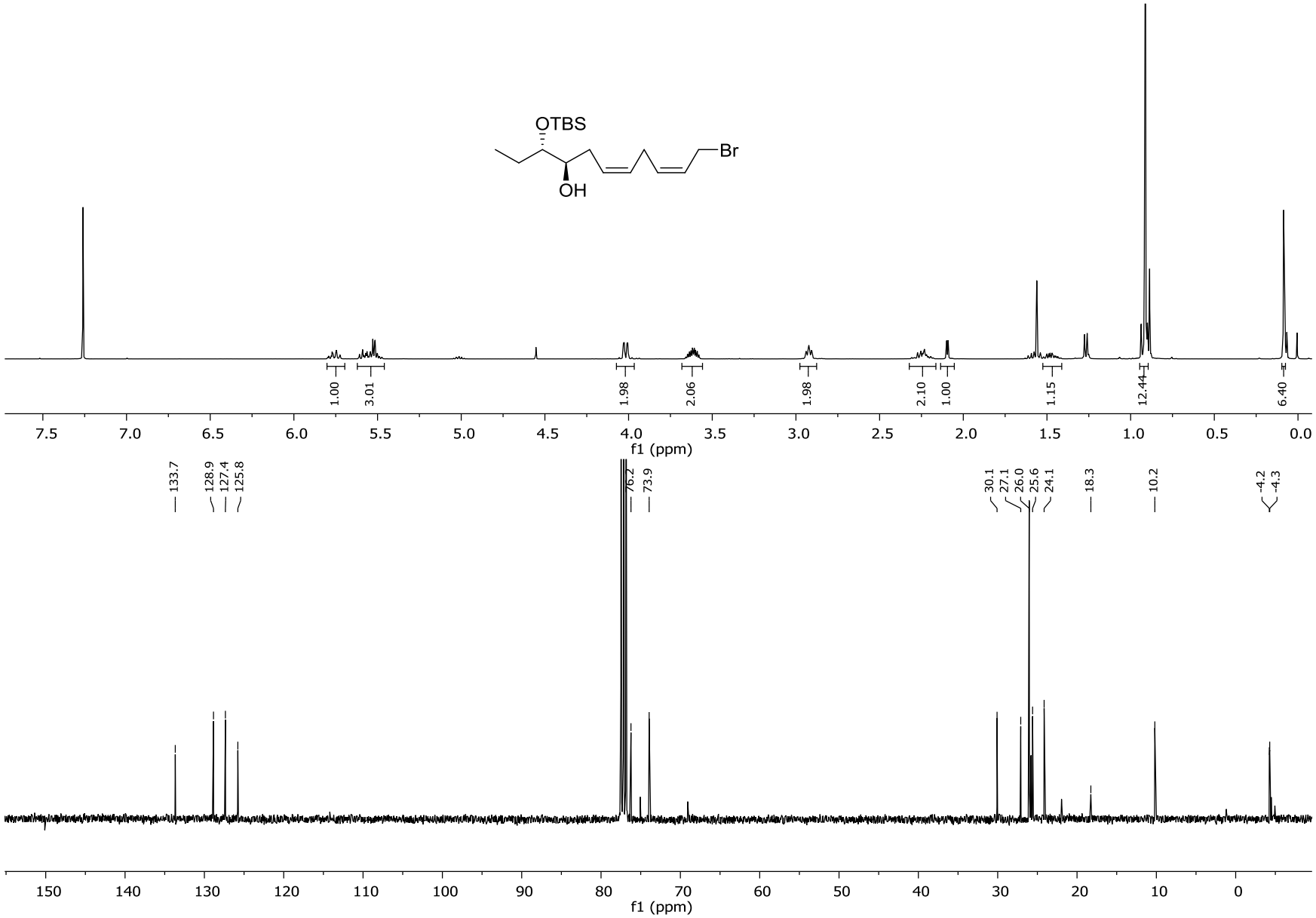
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
98.8
80.2
73.9
60.9
52.6
19.8
15.4
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-
f1 (ppm)

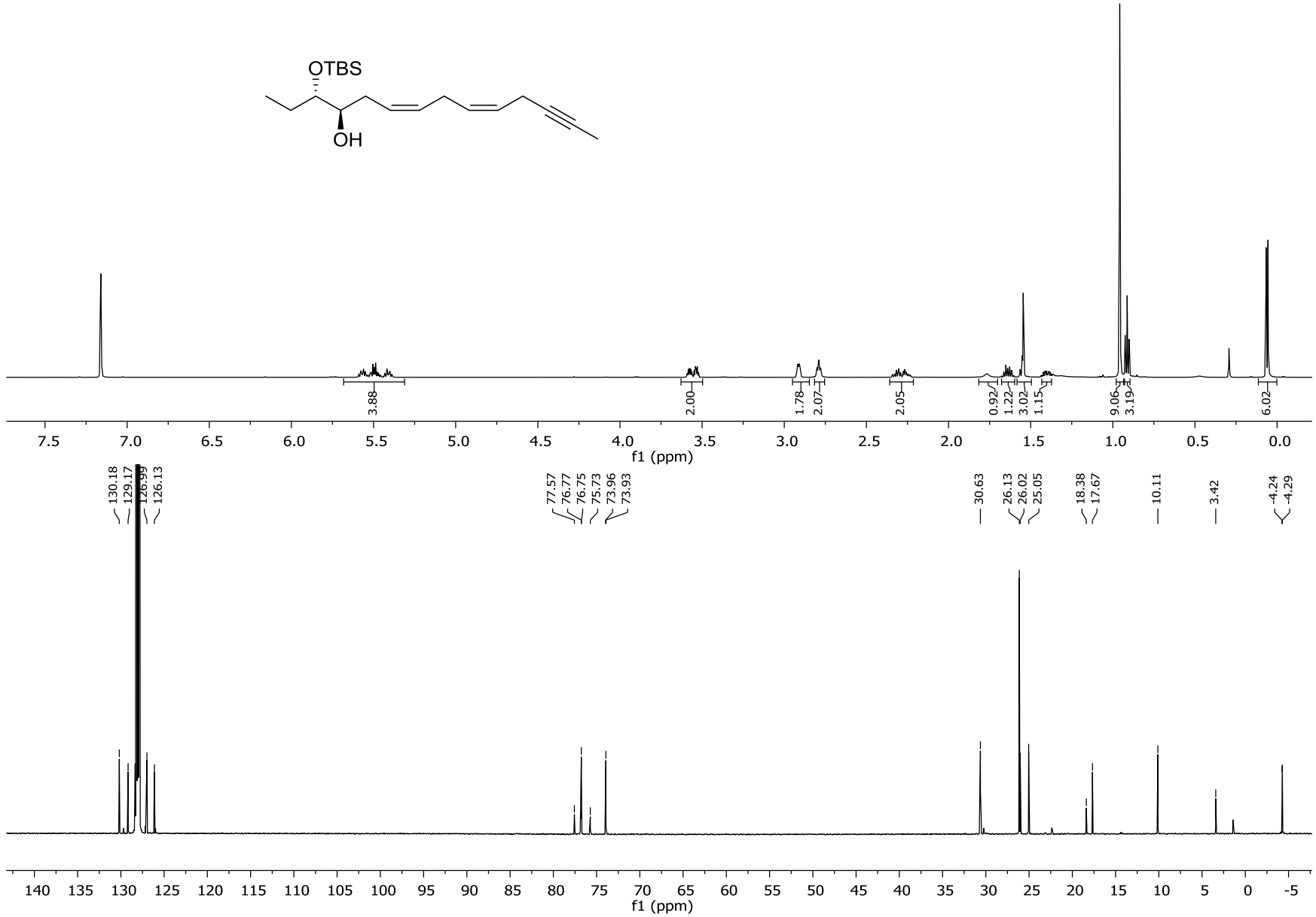

O
O
1.00
1.91
1.08
1.09
1.98
0.59
3.27
3.34
f1 (ppm)
98.7
79.3
77.9
77.2
69.1
60.8
53.1
19.8
15.4
9.8
f1 (ppm)

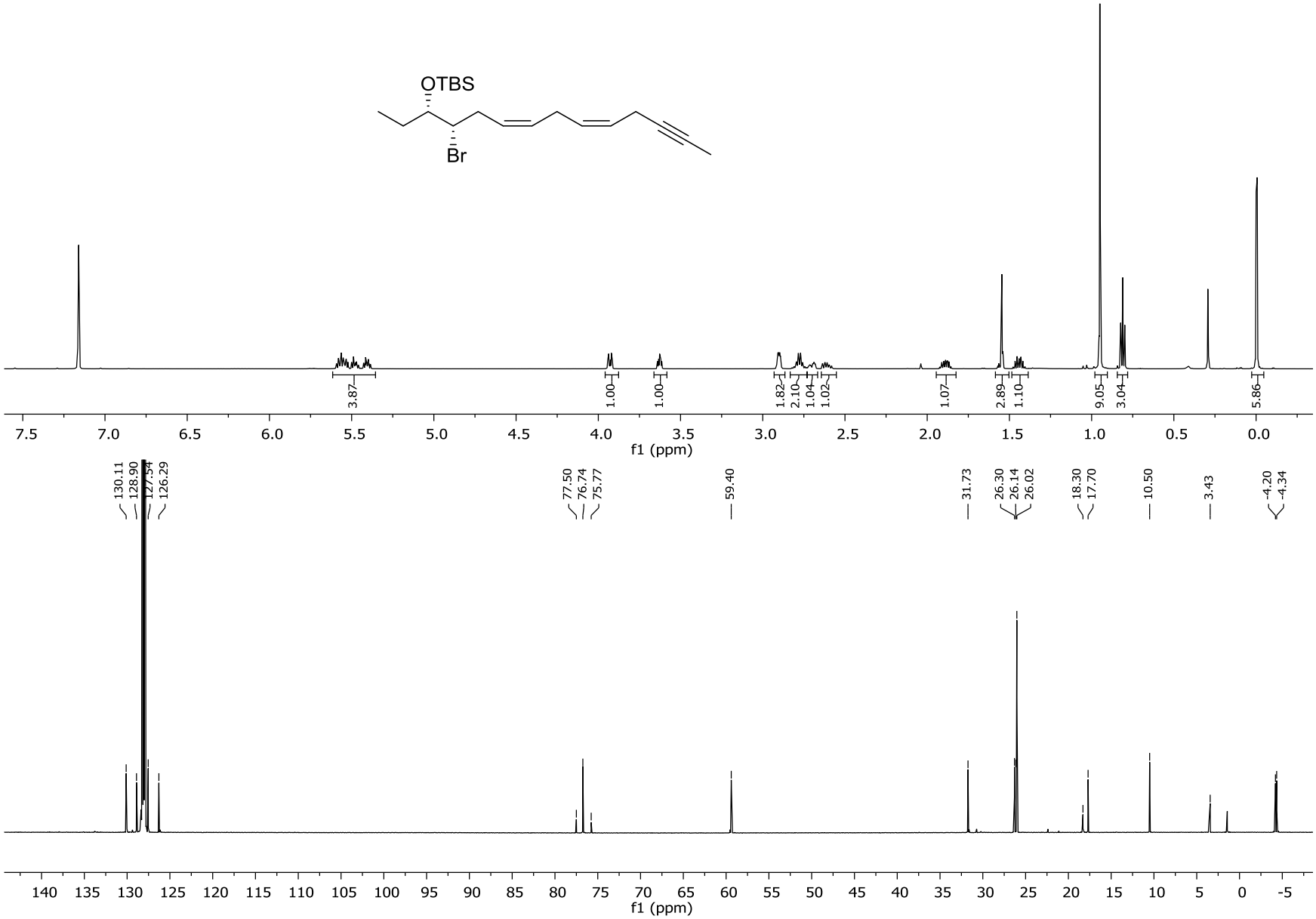

OTBS
OH
O
O
1.00
1.96
3.16
1.17
2.04
2.04
1.03
2.18
3.17
3.25
12.70
6.25
f1 (ppm)
98.7
80.3
76.6
75.9
75.2
72.1
60.7
53.1
46.3
26.0
24.7
22.8
19.8
18.2
15.4
10.1
9.4
-4.3
-4.4
f1 (ppm)

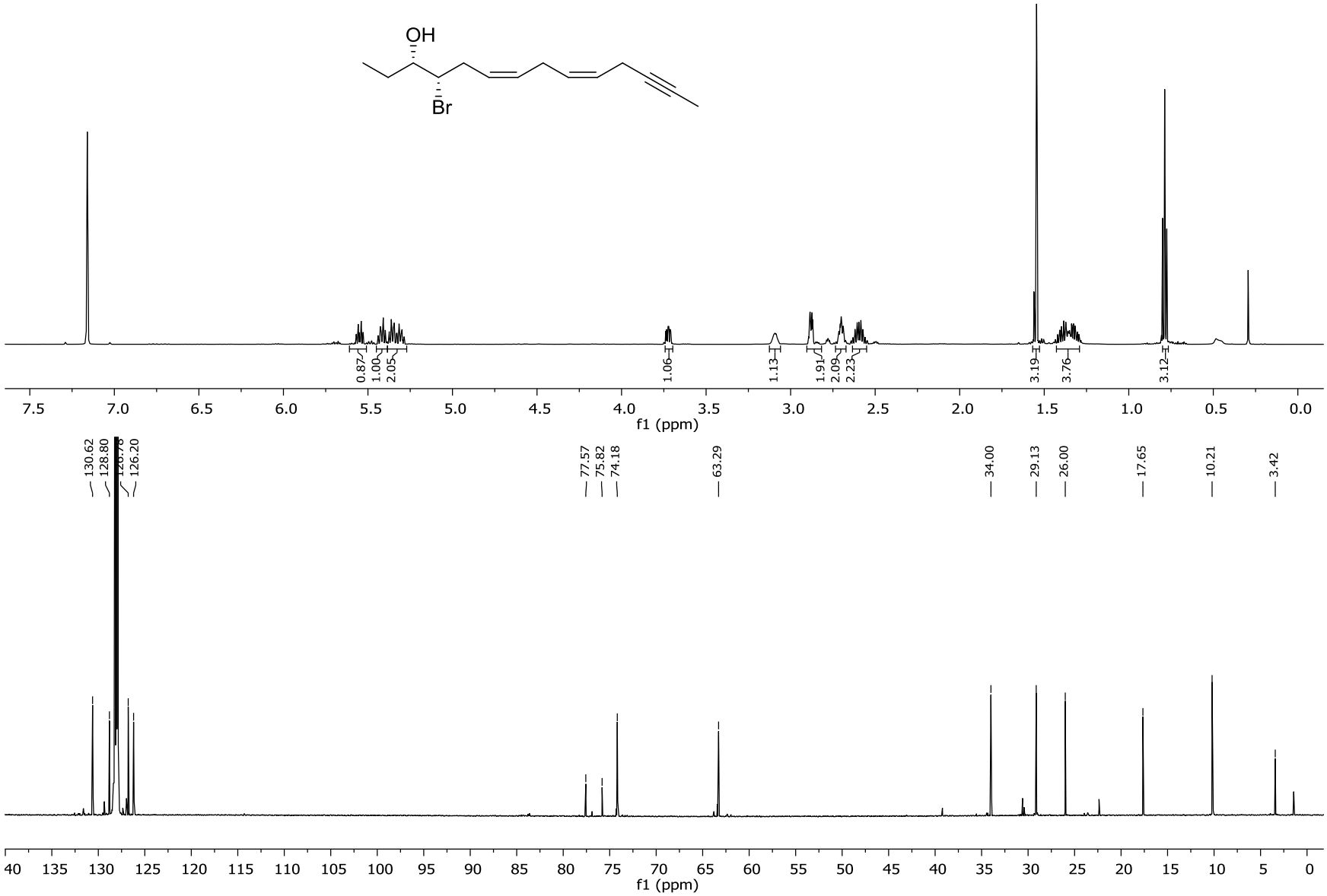

OTBS
OH
OH
1.81
2.09
2.00
1.99
2.42
12.41
6.17
f1 (ppm)
80.5
78.7
77.6
75.8
75.2
72.2
51.4
26.0
24.6
22.8
18.2
10.1
9.5
-4.3
-4.4
f1 (ppm)

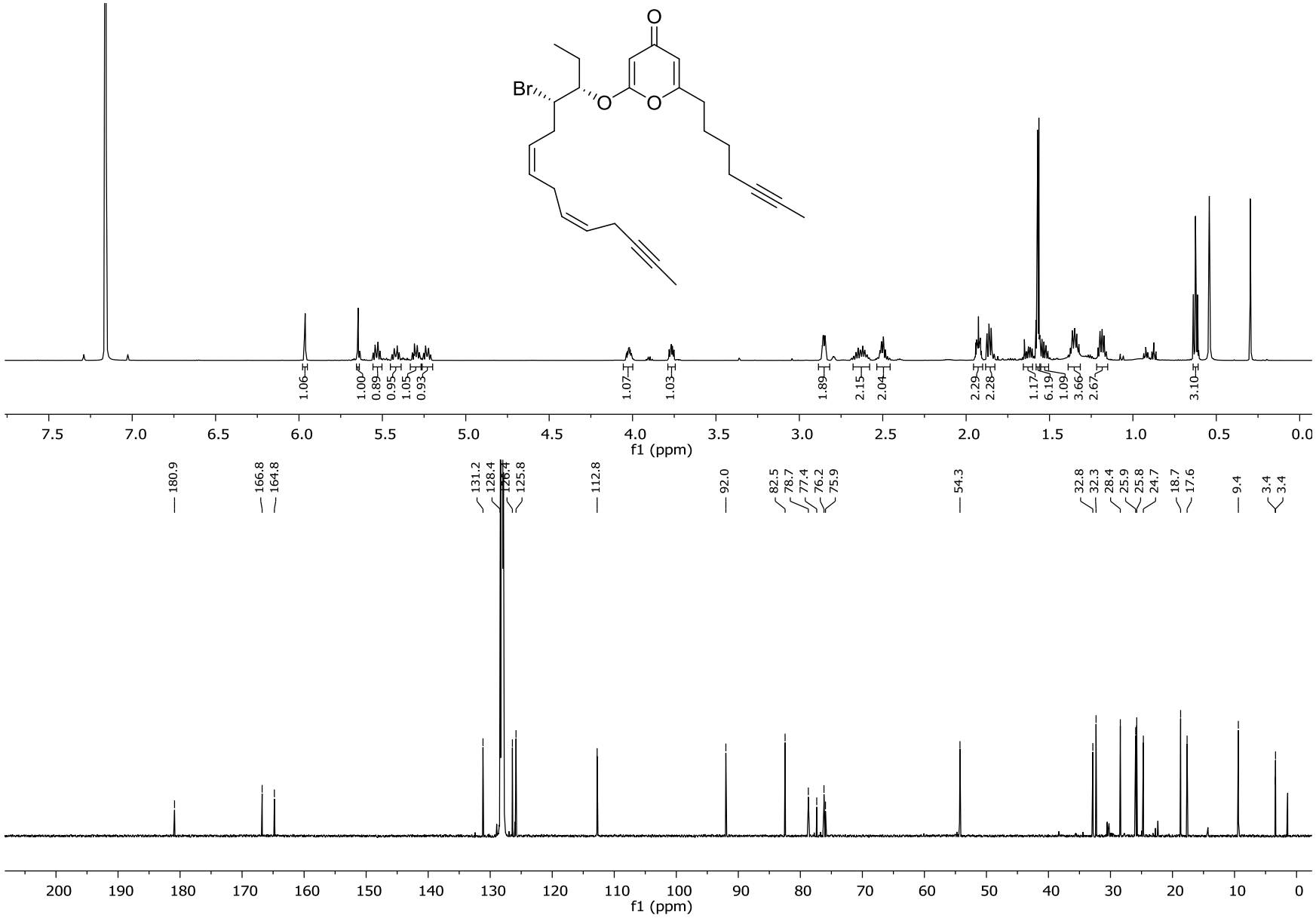

OTBS
OH
OH
1.13
2.85
2.00
2.01
0.79
1.21
2.19
0.75
2.27
12.05
6.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
130.7
130.2
128.8
126.6
76.1
73.8
58.4
30.3
26.1
26.0
24.3
18.2
9.9
-4.2
-4.3
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

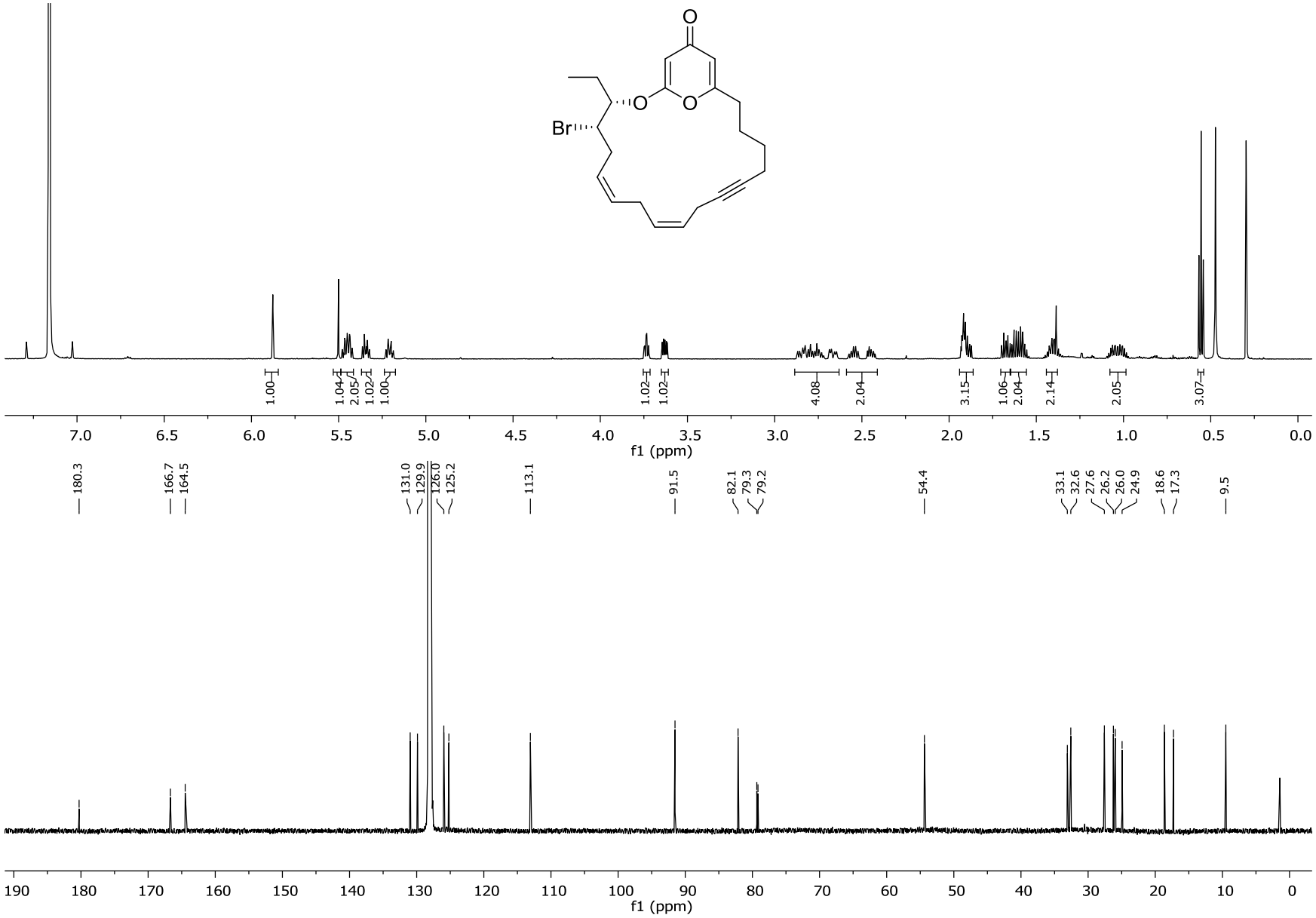

OTBS
Br
OH
1.00
3.01
1.98
2.06
1.98
2.10
1.00
1.15
12.44
6.40
f1 (ppm)
133.7
128.9
127.4
125.8
76.2
73.9
30.1
27.1
26.0
25.6
24.1
18.3
10.2
-4.2
-4.3
f1 (ppm)

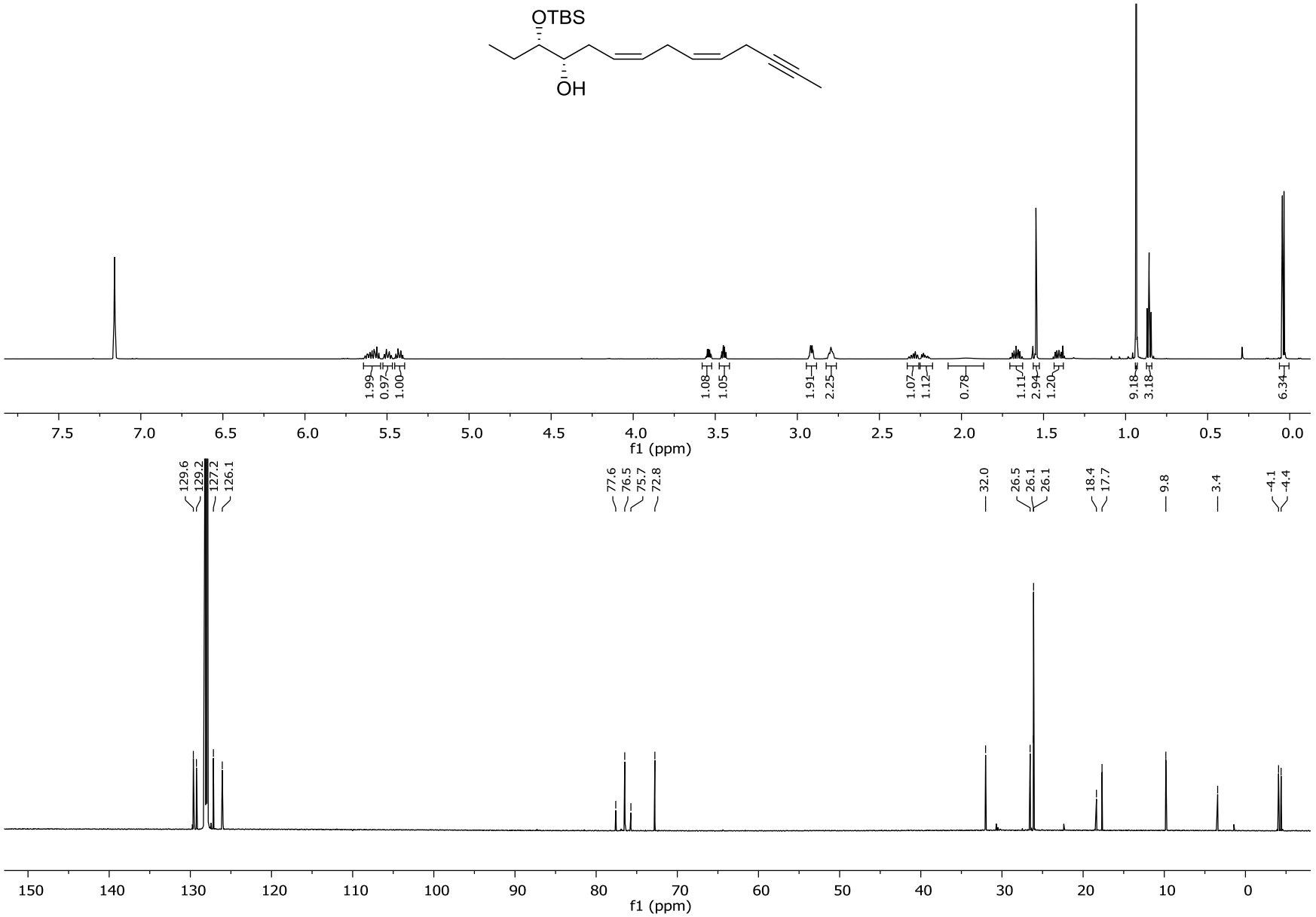

OTBS
OH
3.88
2.00
1.78
2.07
2.05
0.92
1.22
3.02
1.15
9.06
3.19
6.02
f1 (ppm)
130.18
129.17
126.99
126.13
77.57
76.77
76.75
75.73
73.96
73.93
30.63
26.13
26.02
25.05
18.38
17.67
10.11
3.42
-4.24
-4.29
f1 (ppm)

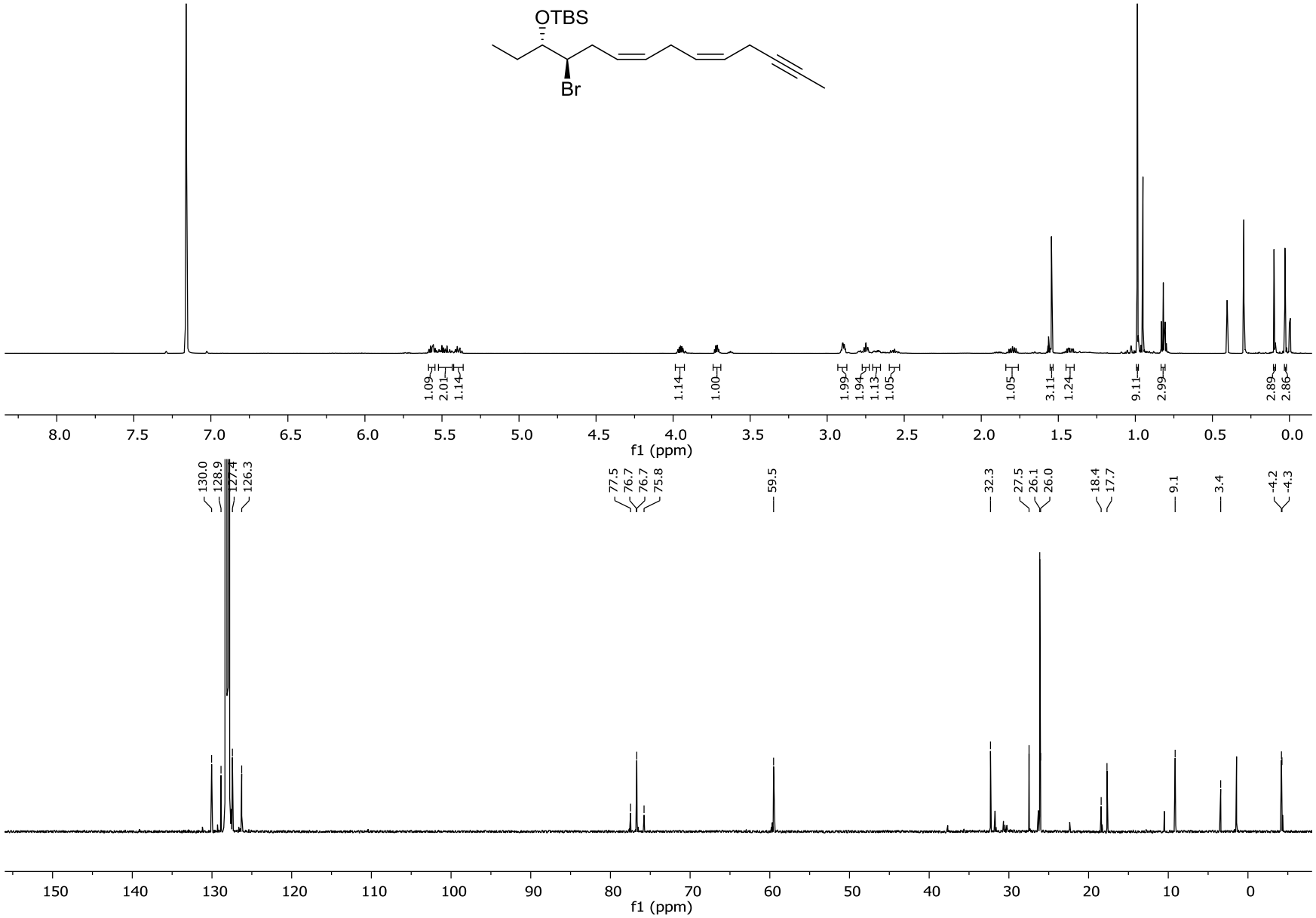

OTBS
Br
3.87
1.00
1.00
1.82
2.10
1.04
1.02
1.07
2.89
1.10
9.05
3.04
5.86
f1 (ppm)
130.11
128.90
127.54
126.29
77.50
76.74
75.77
59.40
31.73
26.30
26.14
26.02
18.30
17.70
10.50
3.43
-4.20
-4.34
f1 (ppm)

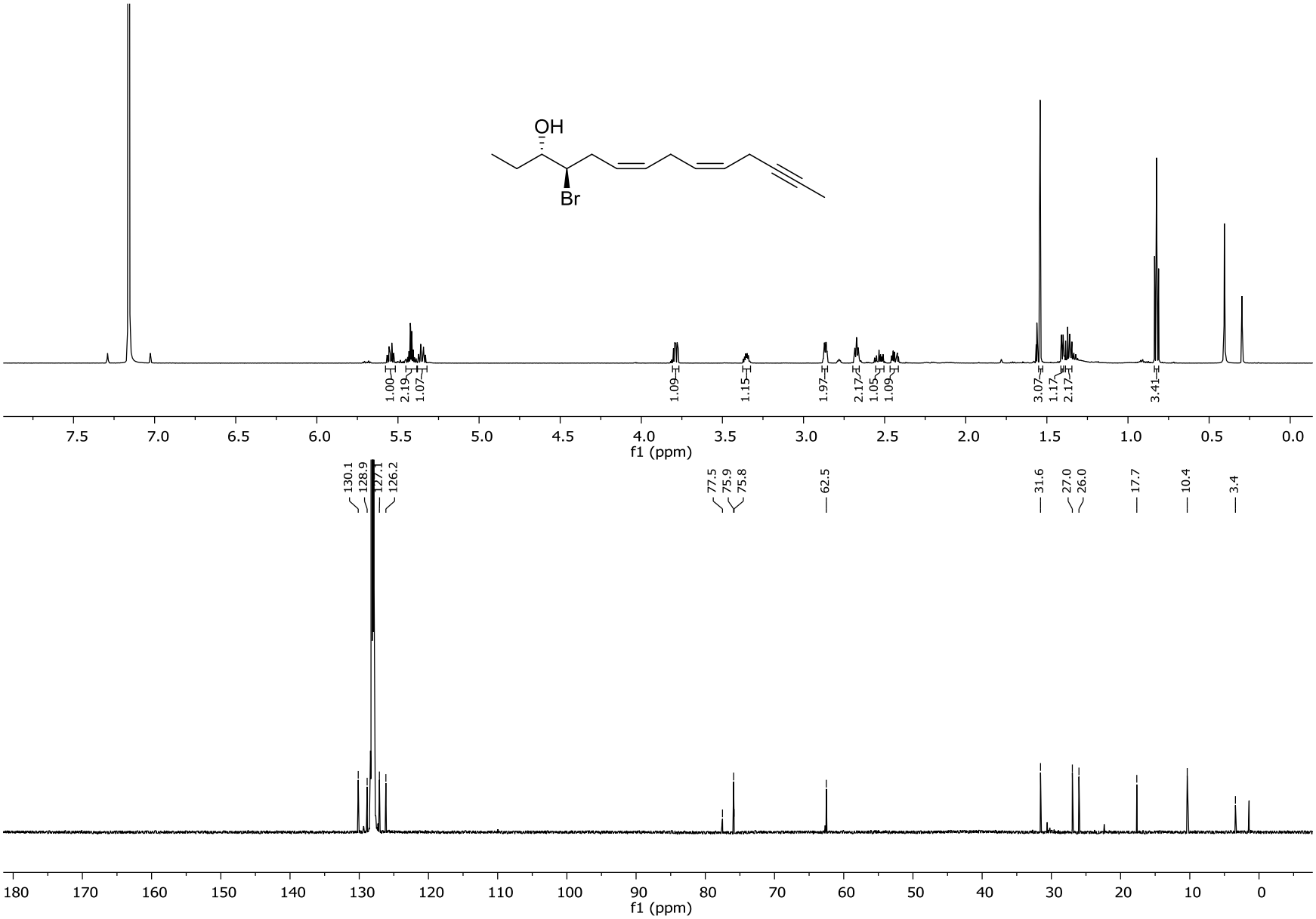

OH
Br
0.87
1.00
2.05
1.06
1.13
1.91
2.09
2.23
3.19
3.76
3.12
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
130.62
128.80
126.78
126.20
77.57
75.82
74.18
63.29
34.00
29.13
26.00
17.65
10.21
3.42
40 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

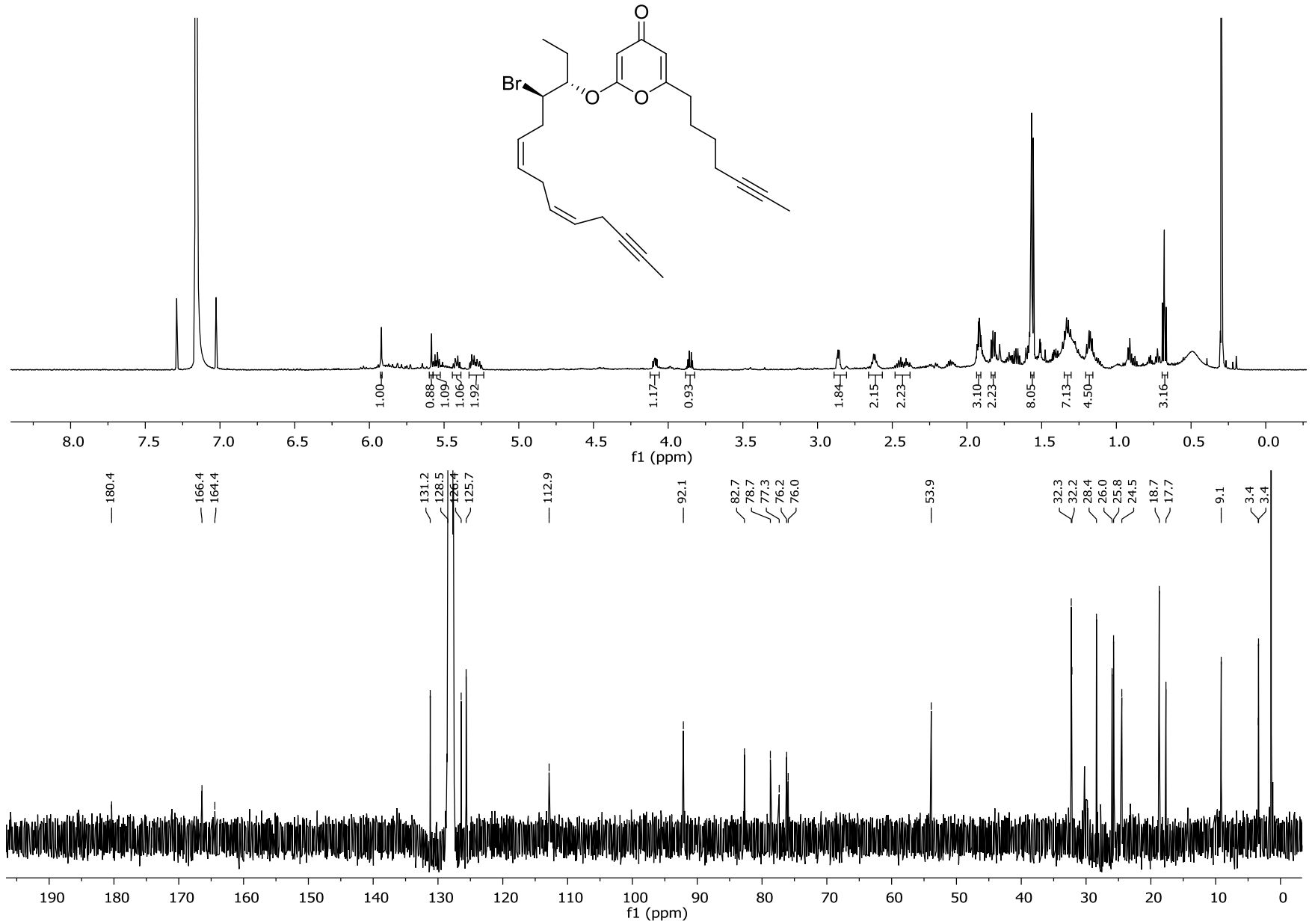

Br
O
O
O
1.06
1.00
0.89
0.95
1.05
0.93
1.07
1.03
1.89
2.15
2.04
2.29
2.28
1.17
6.19
1.09
3.66
2.67
3.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
180.9
166.8
164.8
131.2
128.4
126.4
125.8
112.8
92.0
82.5
78.7
77.4
76.2
75.9
54.3
32.8
32.3
28.4
25.9
25.8
24.7
18.7
17.6
9.4
3.4
3.4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

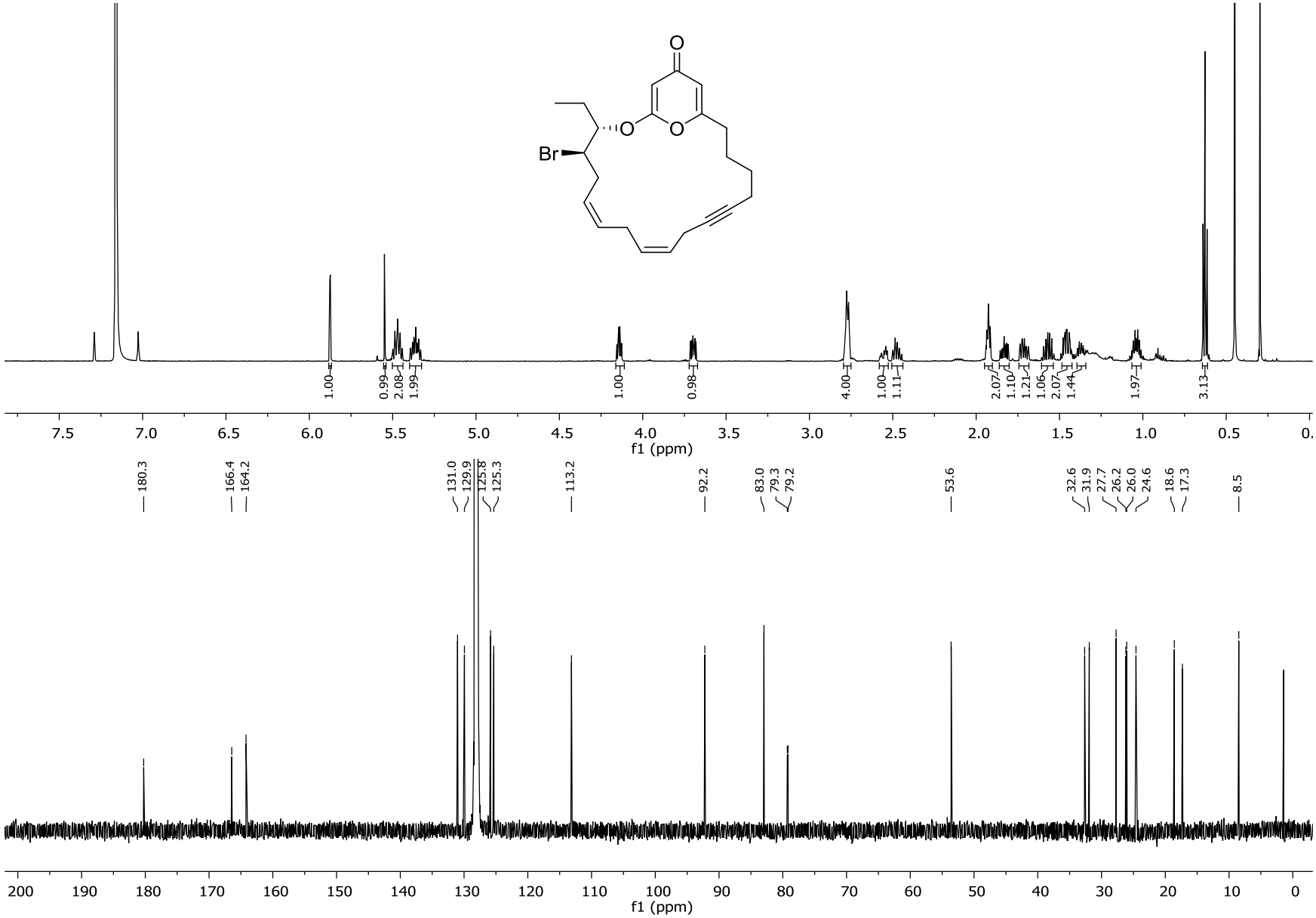

O
O
O
Br
1.00
1.04
2.05
1.02
1.00
1.02
1.02
4.08
2.04
3.15
1.06
2.04
2.14
2.05
3.07
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
180.3
166.7
164.5
131.0
129.9
126.0
125.2
113.1
91.5
82.1
79.3
79.2
54.4
33.1
32.6
27.6
26.2
26.0
24.9
18.6
17.3
9.5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OTBS
OH
1.99
0.97
1.00
1.08
1.05
1.91
2.25
1.07
1.12
0.78
1.11
2.94
1.20
9.18
3.18
6.34
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
f1 (ppm)
129.6
129.2
127.2
126.1
77.6
76.5
75.7
72.8
32.0
26.5
26.1
26.1
18.4
17.7
9.8
3.4
-4.1
-4.4
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OTBS
Br
1.09
2.01
1.14
1.14
1.00
1.99
1.94
1.13
1.05
1.05
3.11
1.24
9.11
2.99
2.89
2.86
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
f1 (ppm)
130.0
128.9
127.4
126.3
77.5
76.7
76.7
75.8
59.5
32.3
27.5
26.1
26.0
18.4
17.7
9.1
3.4
-4.2
-4.3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
Br
1.00
2.19
1.07
1.09
1.15
1.97
2.17
1.05
1.09
3.07
1.17
2.17
3.41
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
f1 (ppm)
130.1
128.9
127.1
126.2
77.5
75.9
75.8
62.5
31.6
27.0
26.0
17.7
10.4
3.4
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
O
O
O
1.00
0.88
1.09
1.06
1.92
1.17
0.93
1.84
2.15
2.23
3.10
2.23
8.05
7.13
4.50
3.16
f1 (ppm)
180.4
166.4
164.4
131.2
128.5
126.4
125.7
112.9
92.1
82.7
78.7
77.3
76.2
76.0
53.9
32.3
32.2
28.4
26.0
25.8
24.5
18.7
17.7
9.1
3.4
3.4
f1 (ppm)


O
O
O
Br
1.00
0.99
2.08
1.99
1.00
0.98
4.00
1.00
1.11
2.07
1.10
1.21
1.06
2.07
1.44
1.97
3.13
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
f1 (ppm)
180.3
166.4
164.2
131.0
129.9
125.8
125.3
113.2
92.2
83.0
79.3
79.2
53.6
32.6
31.9
27.7
26.2
26.0
24.6
18.6
17.3
8.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)