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Supporting Information

Formal Total Synthesis of Kendomycin by Way of Alkyne Metathesis/Gold Catalysis

Laura Hoffmeister, Peter Persich, and Alois Fürstner*[a]

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SUPPORTING INFORMATION

Formal Total Synthesis of Kendomycin

by Way of Alkyne Metathesis/Gold Catalysis

Laura Hoffmeister, Peter Persich, and Alois Fürstner*

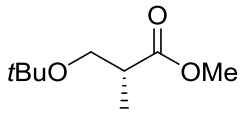
Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

email: fuerstner@kofo.mpg.de

General. All reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2, MeCN (CaH_2), hexane, toluene (Na/K), MeOH (Mg), DMF (MS 4Å), DMSO (distilled over CaH_2, stored over MS 4Å). Flash chromatography: Merck silica gel 60 (40–63 μm) or Florisil (60-100 mesh). NMR: Spectra were recorded on 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 ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.24$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual ^1H: $\delta_H \equiv 5.32$ ppm; C_6D_6: $\delta_C \equiv 128.0$ ppm; residual C_6D_5H: $\delta_H \equiv 7.15$ ppm, [D_6]-DMSO: $\delta_C \equiv 39.52$ ppm, residual $CD_2HS(O)CD_3$: $\delta_H \equiv 2.50$ 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 commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

The Polyketide Segment

Compound S-1: Isobutene was bubbled through a solution of (*R*)-Roche ester (**18**) (4.67 mL, 42.3 mmol) and conc. H_2SO_4 (1 mL, 4.23 mmol) in CH_2Cl_2 (200 mL) at ambient temperature for 4.5 h. For work-up, sat. aq. $NaHCO_3$ was carefully added and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and evaporated to give the title compound as a colorless oil (6.76 g, 92%) which was used without further purification. $[\alpha]_D^{20} = -13.7°$ (c = 0.75, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3H), 3.55 (dd, J = 8.6, 7.1 Hz, 1H), 3.34 (dd, J = 8.6, 6.3 Hz, 1H), 2.69-2.60 (m, 1H), 1.15 (s, 9H), 1.15 ppm (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.9, 73.0, 64.0, 51.6, 40.9, 27.6, 14.2 ppm; IR (film): $\tilde{\nu}$ = 2975, 1739, 1458, 1435, 1363, 1194, 1174, 1083, 1059, 1022, 880 cm^{-1}; MS (EI): *m*/*z* (%): 159 (13), 117 (40), 102 (5), 101 (100), 88 (36), 87 (14), 85 (18), 73 (15), 69 (13), 59 (62), 57 (89), 56 (11), 55 (7), 43 (8), 41 (34), 39 (9), 29 (5); HRMS (ESI): *m*/*z* calcd. for $C_9H_{18}O_3Na$:



197.1148 [*M*+Na^+]; found: 197.1149. The spectral data are in accordance with those reported in the literature.[1]

Compound S-2: A solution of ester S-**1** (6.70 g, 38.4 mmol) in THF (100 mL) was added dropwise to a suspension of $LiAlH_4$ (2.92 g, 77.0 mmol) in THF (300 mL) at −78 °C. The mixture was then stirred at 0 °C for 1 h before the reaction was carefully quenched with water (3 mL). An aqueous solution of NaOH (15% *v*/*v*, 3 mL) and again water (9 mL) were added. The resulting mixture was stirred for 1 h at ambient temperature before the organic layer was dried over $MgSO_4$. The solvents were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 10/1 → 6/1) to give alcohol **S-2** as a colorless oil (4.50 g, 80%). $[\alpha]_D^{20} = -18.3°$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62 (ddd, *J* = 10.7, 3.7, 1.2 Hz, 1H), 3.54 (dd, *J* = 10.7, 8.1 Hz, 1H), 3.50 (ddd, *J* = 8.6, 4.3, 1.1 Hz, 1H), 3.27 (t, *J* = 8.6 Hz, 1H), 3.07 (br s, 1H), 2.04-1.91 (m, 1H), 1.19 (s, 9H), 0.83 ppm (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 73.4, 69.3, 68.2, 35.7, 27.5, 13.6 ppm; IR (film): $\tilde{\nu}$ = 3414, 2973, 2910, 2874, 1475, 1389, 1362, 1234, 1196, 1078, 1022, 1037, 991, 879 cm^{-1}; MS (EI): *m*/*z* (%): 131 (19), 89 (23), 73 (9), 71 (6), 59 (98), 58 (8), 57 (100), 56 (38), 55 (25), 43 (15), 42 (10), 41 (35), 39 (11), 31 (9), 29 (13); HRMS (CI): *m*/*z* calcd. for $C_8H_{19}O_2$: 147.1385 [*M*+H^+]; found: 147.1386. The analytical and spectral data are in accordance with those reported in the literature.[2]

Compound 19: PPh_3 (26.5 g, 90.5 mmol), imidazole (6.16 g, 90.5 mmol), and iodine (23.0 g, 90.5 mmol) were successively added to a solution of alcohol **S-2** (7.35 g, 50.2 mmol) in Et_2O/MeCN (2:1, 360 mL) at 0 °C. The resulting suspension was stirred for 1 h at ambient temperature before it was filtered. The residue was rinsed with the same solvent and the combined filtrates were evaporated. The crude product was dissolved in pentane and water, and the aqueous layer extracted with pentane. The combined extracts were dried over $MgSO_4$ and evaporated. The residue was purified by distillation in vacuum (5 mbar, 78 °C) to give iodide **19** as colorless oil (11.3 g, 88%). $[\alpha]_D^{20} = -15.5°$ (*c* = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.35-3.27 (m, 2H), 3.23 (dd, *J* = 8.6, 4.9 Hz, 1H), 3.13 (dd, *J* = 8.6, 7.9 Hz, 1H), 1.69-1.56 (m, 1H), 1.18 (s, 9H), 0.96 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 72.8, 65.6, 35.5, 27.8, 18.0, 15.2 ppm; IR (film): $\tilde{\nu}$ = 2971, 2931, 2899, 2869, 1474, 1390, 1362, 1249, 1234, 1196, 1082, 1022, 884 cm^{-1}; MS (EI): *m*/*z* (%): 256 (4), 241 (17), 200 (2), 183 (23), 155 (2), 129 (3), 88 (2), 87 (42), 73 (2), 59 (14), 58 (5), 57 (100), 56 (10), 55 (35), 43 (3), 42 (2), 41 (20), 39 (6), 29 (6); HRMS (EI): *m*/*z* calcd. for $C_8H_{17}OI$: 256.0324 [M^+]; found: 256.0325. The analytical and spectral data are in accordance with those reported in the literature.[3]

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1 M. Sunagawa, Y. Nozaki, A. Sasaki, H. Matsumura, EP 229384 A2 19870722, **1987**.

2 N. Cohen, W. F. Eichel, R. J. Lopresti, C. Neukom, G. Saucy, *J. Org. Chem.* **1976**, *41*, 3505-3511.

3 C. Spino, M. Allan, *Can. J. Chem.* **2004**, *82*, 177-184.

Compound S-3: Diisopropylamine (10.6 mL, 75.5 mmol) was added to a suspension of LiCl (9.70 g, 228 mmol) in THF (70 mL) before *n*BuLi (1.6 M in hexane, 44.5 mL, 71.2 mmol) was introduced at 0 °C. After stirring for 15 min at this temperature the mixture was cooled to −78 °C and a solution of amide **25** (8.54 g, 38.6 mmol)[4] in THF (70 mL) was slowly added. The mixture was stirred for 1 h at −78 °C, for 15 min at 0 °C and for 5 min at ambient temperature. A solution of iodide **19** (4.63 g, 18.1 mmol) in THF (70 mL) was then added at 0 °C and stirring continued for 2 d at ambient temperature before the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was extracted with *tert*-butyl methyl ether and the combined extracts were dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 2/1) to give amide **S-3** as a colorless oil (6.09 g, 96%). $[\alpha]_D^{20} = -70.2°$ (*c* = 1.24, $CHCl_3$); ^{1}H NMR (600 MHz, two rotamers, DMSO-d_6): δ = 7.38-7.28 (m, 8H, 2 *rot*.), 7.27 (tt, *J* = 7.1, 1.6 Hz, 1H, 1 *rot*.), 7.22 (tt, *J* = 6.9, 1.9 Hz, 1H, 1 *rot*.), 5.46 (d, *J* = 3.7 Hz, 1H, 1 *rot*.), 5.31 (d, *J* = 4.4 Hz, 1H, 1 *rot*.), 4.77-4.66 (m, 1H, 1 *rot*.), 4.57 (dd, *J* = 7.5, 4.6 Hz, 1H, 1 *rot*.), 4.52 (dd, *J* = 8.3, 3.7 Hz, 1H, 1 *rot*.), 3.95 (qd, *J* = 7.3, 6.8 Hz, 1H, 1 *rot*.), 3.14 (dd, *J* = 8.7, 5.4 Hz, 1H, 1 *rot*.), 3.11 (dd, *J* = 8.6, 6.2 Hz, 1H, 1 *rot*.), 3.09 (dd, *J* = 8.7, 5.8 Hz, 1H, 1 *rot*.), 3.02 (dd, *J* = 8.8, 6.4 Hz, 1H, 1 *rot*.), 2.89-2.84 (m, 1H, 1 *rot*.), 2.87 (s, 3H, 1 *rot*.), 2.78-2.72 (m, 1H, 1 *rot*.), 2.75 (s, 3H, 1 *rot*.), 1.59-1.52 (m, 1H, 1 *rot*.), 1.50-1.43 (m, 1H, 1 *rot*.), 1.42-1.29 (m, 3H, 2 *rot*.), 1.27-1.22 (m, 1H, 1 *rot*.), 1.13 (s, 9H, 1 *rot*.), 1.09 (s, 9H, 1 *rot*.), 0.93 (d, *J* = 6.8 Hz, 3H, 1 *rot*.), 0.91 (d, *J* = 6.8 Hz, 3H, 1 *rot*.), 0.88 (d, *J* = 7.0 Hz, 3H, 1 *rot*.), 0.82 (d, *J* = 6.6 Hz, 3H, 1 *rot*.), 0.80 (d, *J* = 6.8 Hz, 3H, 1 *rot*.), 0.79 ppm (d, *J* = 6.6 Hz, 3H, 1 *rot*.); ^{13}C NMR (150 MHz, two rotamers, DMSO-d_6): δ = 176.1, 175.8, 143.6, 143.6, 128.1, 127.8, 127.3, 126.9, 126.9, 126.6, 73.8, 73.6, 71.7, 71.6, 66.6, 66.4, 57.0, 53.0, 37.9, 37.1, 32.8, 32.2, 31.5, 30.9, 29.8, 27.4, 27.3, 26.9, 17.7, 17.4, 17.4, 17.2, 15.5, 14.0 ppm; IR (film): $\tilde{\nu}$ = 3370, 2971, 2932, 2872, 1616, 1453, 1361, 1197, 1078, 1051, 1022, 753, 700 cm^{-1}; MS (EI): *m*/*z* (%): 274 (11), 242 (7), 216 (27), 148 (25), 147 (25), 146 (11), 130 (6), 129 (57), 128 (8), 118 (5), 117 (8), 115 (5), 114 (5), 111 (18), 105 (5), 91 (8), 83 (19), 69 (21), 59 (7), 58 (100), 57 (24), 56 (11), 55 (11), 43 (8), 42 (6), 41 (13); HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{35}NO_3Na$: 372.2509 [M+Na^+]; found: 372.2509.

Compound 20: *n*BuLi (1.6 M in hexane, 42.0 mL, 67.2 mmol) was added dropwise to a solution of diisopropylamine (10.2 mL, 72.2 mmol) in THF (75 mL) at −78 °C. The mixture was stirred for 10 min at this temperature and for 10 min at 0 °C before $BH_3{\cdot}NH_3$ (90 % *w*/*w*, 2.75 g, 80.2 mmol) was introduced. After stirring for 1.5 h at ambient temperature, a solution of amide **S-3** (6.02 g, 17.2 mmol) in THF (100 mL) was added dropwise at 0 °C and stirring was continued for 2.5 h at ambient

[4] A. G. Myers, B. H. Yang, H. Chen, L. McKinstry, D. J. Kopecky, J. L. Gleason, *J. Am. Chem. Soc.* **1997**, *119*, 6496-6511.

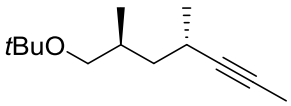
temperature before the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was extracted with *tert*-butyl methyl ether and the combined extracts were dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 10/1) to give the title alcohol as a colorless oil (3.12 g, 96%). $[\alpha]_D^{20} = -30.5°$ (c = 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.45 (d, J = 6.6 Hz, 2H), 3.15 (d, J = 6.6 Hz, 2H), 1.88-1.67 (m, 2H), 1.37-1.24 (m, 1H), 1.21-1.06 (m, 1H), 1.18 (s, 9H), 0.88 ppm (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 72.8, 68.9, 68.0, 37.9, 33.3, 30.8, 27.7, 17.8, 16.7 ppm; IR (film): $\tilde{\nu}$ = 3370, 2972, 2924, 2873, 1461, 1390, 1361, 1234, 1197, 1082, 1038, 1022, 884 cm^{-1}; MS (EI): *m*/*z* (%): 131 (9), 115 (12), 113 (12), 101 (5), 97 (25), 95 (6), 85 (5), 84 (9), 83 (10), 69 (13), 59 (18), 58 (11), 57 (100), 56 (21), 55 (38), 43 (12), 42 (6), 41 (21); HRMS (CI): *m*/*z* calcd. for $C_{11}H_{25}O_2$: 189.1854 [M+H$^+$]; found: 189.1856.

Compound S-4: MS 4Å (7.6 g) was added to a solution of NMO (2.89 g, 24.7 mmol) in CH_2Cl_2 (25 mL). After stirring for 30 min at ambient temperature, the solution was cooled to 0 °C and TPAP (288 mg, 0.82 mmol) and a solution of alcohol **20** (3.10 g, 16.4 mmol) in CH_2Cl_2 (25 mL) were successively introduced. The mixture was stirred for 10 min at this temperature and for 30 min at ambient temperature before it was filtered through a pad of Celite which was carefully rinsed with CH_2Cl_2. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 20/1) to give the title aldehyde as a yellow oil (2.20 g, 72%). $[\alpha]_D^{20} = +2.1°$ (c = 0.68, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.63 (d, J = 1.4 Hz, 1H), 3.16 (d, J = 6.0 Hz, 2H), 2.52-2.39 (m, 1H), 1.80-1.67 (m, 1H), 1.50 (ddd, J = 13.8 , 8.3, 5.8 Hz, 1H), 1.42 (ddd, J = 13.8, 8.4, 5.5 Hz, 1H), 1.16 (s, 9H), 1.07 (d, J = 7.0 Hz, 3H), 0.89 ppm (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.6, 72.5, 67.2, 44.3, 34.6, 31.6, 27.6, 17.0, 13.5 ppm; IR (film): $\tilde{\nu}$ = 3972, 2933, 2875, 1725, 1708, 1460, 1392, 1362, 1234, 1197, 1080, 1021, 882 cm^{-1}; MS (EI): *m*/*z* (%): 130 (10), 129 (14), 114 (12), 113 (21), 112 (5), 111 (5), 95 (16), 83 (7), 71 (12), 69 (5), 59 (12), 58 (28), 57 (100), 56 (9), 55 (15), 43 (26), 41 (19); HRMS (CI): *m*/*z* calcd. for $C_{11}H_{23}O_2$: 187.1698 [M+H$^+$]; found: 187.1699.

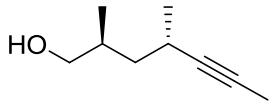
Compound S-5: Zinc powder (1.48 g, 22.6 mmol), CBr_4 (7.30 g, 22.0 mmol) and PPh_3 (5.93 g, 22.6 mmol) were suspended in CH_2Cl_2 (70 mL) and the resulting mixture was stirred for 14 h before a solution of aldehyde **S-4** (2.10 g, 11.3 mmol) in CH_2Cl_2 (25 mL) was added. After stirring for another 1.5 h, the mixture was diluted with hexane and filtered, the combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 1/0 → 30/1) to give the title compound as a colorless oil (2.63 g, 68%). $[\alpha]_D^{20}$ = +5.3° (c = 0.72, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.20 (d, J = 9.4 Hz, 1H), 3.20 (dd, J = 8.6, 5.5 Hz, 1H), 3.10 (dd, J = 8.6, 6.9 Hz, 1H), 2.62-2.49 (m, 1H), 1.70-1.60 (m, 1H), 1.41 (ddd, J = 13.6, 6.8, 6.8 Hz, 1H), 1.20-1.10 (m, 1H), 1.17 (s, 9H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 87.1,

72.4, 66.8, 40.2, 36.2, 31.8, 27.7, 19.2, 17.7 ppm; IR (film): $\tilde{\nu}$ = 2971, 2929, 2872, 1455, 1391, 1361, 1197, 1081, 1064, 1021, 883, 871 cm^{-1}; MS (EI): *m*/*z* (%): 215 (4), 213 (8), 211 (4), 133 (3), 131 (3), 125 (6), 108 (2), 107 (5), 71 (10), 59 (9), 58 (5), 57 (100), 55 (3), 53 (2), 43 (2), 41 (11), 39 (2), 29 (2), 28 (2); HRMS (CI): *m*/*z* calcd. for $C_{12}H_{23}OBr_2$: 341.0116 [M+H^+]; found: 341.0116.

Compound 21: *n*BuLi (1.6 M in hexane, 10.6 mL, 17.4 mmol) was added dropwise to a solution of dibromide **S-5** (2.59 g, 7.57 mmol) in THF (25 mL) at –78 °C. After stirring for 1.5 h at this temperature and for 30 min at ambient temperature, MeI (1.27 mL, 20.4 mmol) was introduced and stirring continued for 20 h before the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was extracted with *tert*-butyl methyl ether and the combined extracts were dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 1/0 → 50/1) to give the title alkyne as a colorless oil (1.47 g, 99%). $[\alpha]_D^{20}$ = +26.5° (*c* = 0.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.24 (dd, *J* = 8.7, 5.2 Hz, 1H), 3.08 (dd, *J* = 8.7, 6.7 Hz, 1H), 2.52-2.40 (m, 1H), 1.88-1.78 (m, 1H), 1.78 (d, *J* = 2.2 Hz, 3H), 1.42 (ddd, *J* = 13.4, 6.8, 6.8 Hz, 1H), 1.26 (ddd, *J* = 13.2, 7.4, 7.5 Hz, 1H), 1.16 (s, 9H), 1.10 (d, *J* = 6.8 Hz, 3H), 0.91 ppm (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 84.5, 75.4, 72.4, 66.7, 41.7, 32.1, 27.7, 23.8, 21.6, 17.9, 3.7 ppm; IR (film): $\tilde{\nu}$ = 2971, 2920, 2872, 1455, 1390, 1361, 1234, 1197, 1079, 1059, 1017, 883, 874 cm^{-1}; MS (EI): *m*/*z* (%): 140 (9), 125 (7), 123 (14), 109 (5), 107 (12), 98 (43), 95 (10), 93 (6), 91 (5), 83 (12), 82 (23), 81 (30), 79 (9), 71 (10), 69 (12), 67 (27), 65 (6), 59 (5), 58 (6), 57 (100), 55 (8), 43 (7), 41 (22), 39 (5); HRMS (CI): *m*/*z* calcd. for $C_{13}H_{25}O$: 197.1905 [M+H^+]; found: 197.1904.

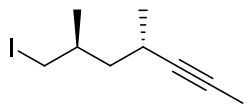


Compound S-6: Trifluoroacetic acid (5.2 mL, 67 mmol) was added to a solution of *tert*-butylether **21** (1.32 g, 6.72 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred for 17 h at ambient temperature before sat. aq. Na_2CO_3 was slowly introduced. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were dried over $MgSO_4$ and evaporated. The residue was dissolved in MeOH/H_2O (2:1, 30 mL) and KOH (754 mg, 13.4 mmol) was added. The mixture was stirred for 1 h before the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was extracted with *tert*-butyl methyl ether and the combined extracts were dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 1/0 → 10/1) to give the title alcohol as a pale yellow oil (825 mg, 88%). $[\alpha]_D^{20}$ = +21.7° (*c* = 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 (dd, *J* = 10.7, 5.5 Hz, 1H), 3.46 (dd, *J* = 10.7, 6.1 Hz, 1H), 2.55-2.43 (m, 1H), 1.92-1.82 (m, 1H), 1.78 (d, *J* = 2.3 Hz, 3H), 1.47 (br s, 1H), 1.42 (ddd, *J* = 13.5, 6.1, 7.4 Hz, 1H), 1.33 (ddd, *J* = 13.5, 8.8, 6.3 Hz, 1H), 1.12 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 84.1, 75.9, 67.7, 41.0, 33.7, 23.6, 21.7, 17.4, 3.6 ppm; IR (film): $\tilde{\nu}$ = 3324, 2965,

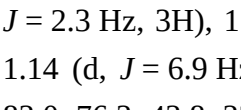


2919, 2873, 1453, 1375, 1335, 1042, 999, 978, 948 cm^{-1}; MS (EI): *m*/*z* (%): 125 (9), 109 (6), 107 (17), 98 (20), 93 (7), 91 (17), 83 (24), 82 (92), 81 (8), 80 (12), 79 (26), 77 (12), 71 (7), 69 (22), 68 (8), 67 (100), 66 (6), 65 (20), 58 (6), 57 (8), 55 (27), 53 (17), 51 (5), 43 (24), 41 (57), 39 (26), 31 (14), 29 (10), 27 (9); HRMS (CI): *m*/*z* calcd. for $C_9H_{17}O$: 141.1279 [M+H^+]; found: 141.1278.

Compound 22: PPh_3 (1.73 g, 6.60 mmol), imidazole (450 mg, 6.60 mmol) and iodine (1.68 g, 6.60 mmol) were successively added to a solution of alcohol **S-6** (840 mg, 6.00 mmol) in Et_2O/MeCN (2:1, 60 mL) at 0 °C. The resulting mixture was stirred for 1 h at ambient temperature before pentane was added. The resulting precipitate was filtered off and the combined filtrates were evaporated. The residue was purified by flash chromatography (hexanes) to give iodide **22** as a colorless oil (1.43 g, 95%). $[\alpha]_D^{20}$ = +51.4° (*c* = 1.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30 (dd, *J* = 9.7, 3.9 Hz, 1H), 3.25 (dd, *J* = 9.7, 5.3 Hz, 1H), 2.49-2.32 (m, 1H), 1.78 (d, *J* = 2.3 Hz, 3H), 1.68-1.54 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 1H), 1.33 (dd, *J* = 6.5, 1.5 Hz, 1H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.98 ppm (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 83.0, 76.3, 43.8, 32.1, 23.6, 21.8, 21.5, 18.4, 3.6 ppm; IR (film): $\tilde{\nu}$ = 2963, 2919, 2871, 1454, 1376, 1316, 1226, 1194, 1155, 909, 796, 733 cm^{-1}; MS (EI): *m*/*z* (%): 250 (6), 169 (5), 124 (10), 123 (61), 109 (8), 107 (16), 95 (25), 93 (12), 91 (13), 82 (12), 81 (100), 80 (6), 79 (32), 77 (10), 69 (10), 68 (8), 67 (86), 66 (7), 65 (25), 57 (13), 55 (20), 53 (12), 43 (8), 41 (36), 39 (12); HRMS (EI): *m*/*z* calcd. for $C_9H_{15}I$: 250.0218 [M^+]; found: 250.0219.



(*S*)-4-Methylhept-5-ynal (5). The compound was prepared as described in the literature (1.54 g, 96%, 90% ee).[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.77 (s, 1H), 2.65 –2.50 (m, 2H), 2.44 – 2.41 (m, 1H), 1.81 – 1.73 (m, 1H), 1.76 (s, 3H), 1.63 (tdd, 1H, *J* = 14.3, 8.2, 6.2 Hz), 1.12 ppm (d, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz. $CDCl_3$): δ = 202.0, 82.1, 76.5, 41.6, 29.0, 25.2, 21.0, 3.0 ppm; IR (film): $\tilde{\nu}$ = 2971, 2922, 1723, 1454, 1376, 1335, 1259, 1021, 800 cm^{-1}; MS (EI) *m/z* (%): 96 (10), 82 (100), 81 (25), 80 (42), 79 (62), 77 (18), 67 (63), 65 (29), 55 (14), 53 (18), 41 (43), 39 (24); HRMS (ESI): *m/z*: calcd. for $C_8H_{13}O_1$ [M^++H]: 125.0965, found 125.0966.

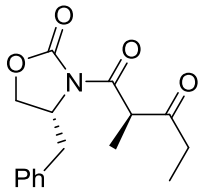


(*R*)-4-Benzyl-3-((*2R,3S*)-3-hydroxy-2-methylpentanoyl)oxazolidin-2-one (S-7). Bu_2BOTf (1.0 M in CH_2Cl_2, 29.4 mL, 29.4 mmol) was added via syringe over 10 min to a solution of (*R*)-4-benzyl-3-propionyloxazolidin-2-one (5.80 g, 24.9 mmol) in CH_2Cl_2 (47 mL) at −78 °C. Et_3N (4.49 mL, 32.4 mmol) was then added dropwise over a period of 15 min before the mixture was briefly allowed to warm to ambient temperature. After cooling to 0 °C,

[5] A. Fürstner, D. De Souza, L. Turet, M. D. B. Fenster, L. Parra-Rapado, C. Wirtz, R. Mynott, C. W. Lehmann, *Chem. Eur. J.* **2007**, *13*, 115-134.

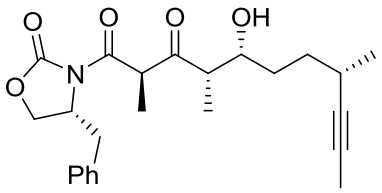
freshly distilled propanal (2.35 mL, 32.4 mmol) was slowly introduced and stirring continued for another 3.5 h before the reaction was quenched with H_2O (28 mL), MeOH (74 mL) and H_2O_2 (28 mL, 30% *w/w*). The mixture was stirred for 2.5 h and then concentrated to a slurry which was extracted with EtOAc (3 x 90 mL). The combined organic layers were dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (SiO_2, pentane/EtOAc, 7/3) to afford the title compound as a white solid (6.66 g, 92%). $[\alpha]_D^{23}$ = −36.5 (*c* = 1.07, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.19 (m, 3H), 7.14 – 7.12 (m, 2H), 4.64 (ddt, 1H, *J* = 9.4, 7.4, 3.3 Hz), 4.18 – 4.10 (m, 2H), 3.79 (ddd, 1H, *J* = 8.1, 5.1, 2.8 Hz), 3.72 (qd, 1H, *J* = 7.0, 2.7 Hz), 3.18 (dd, 1H, *J* = 13.4, 3.4 Hz), 2.79 (s, 1H), 2.72 (dd, 1H, *J* = 13.4, 9.4 Hz), 1.56 – 1.40 (m, 2H), 1.18 (d, 3H, *J* = 7.0 Hz), 0.91 ppm (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.2, 155.7, 134.7, 129.1 (2C), 128.6 (2C), 127.1, 72.7, 65.9, 54.8, 41.3, 37.5, 26.4, 10.1, 9.9 ppm; IR (film): $\tilde{\nu}$ = 3524, 2975, 2937, 2880, 1755, 1697, 1478, 1456, 1373, 1346, 1326, 1264, 1208, 1185, 1115, 1098, 1069, 1055, 983, 969, 928, 764, 750, 706, 696 cm^{-1}; MS (EI) *m/z* (%): 291 (42), 273 (17), 245 (12), 244 (74), 233 (38), 178 (63), 158 (15), 142 (13), 134 (36), 133 (23), 118 (16), 117 (68), 116 (33), 115 (70), 97 (33), 96 (11), 92 (27), 91 (57), 86 (100), 85 (11), 69 (27), 65 (14), 59 (23), 57 (38), 56 (17), 45 (14), 42 (14), 41 (13), 31 (16), 29 (16); HRMS (ESI): *m/z*: calcd. for $C_{16}H_{21}NO_4Na$ [M^++Na]: 314.1362, found 314.1363. The analytical and spectroscopic data are in agreement with those reported in the literature.[6]

(*R*)-1-((*R*)-4-Benzyl-2-oxooxazolidin-3-yl)-2-methylpentane-1,3-dione (12). Compound **S-7** (5.49 g, 18.8 mmol) was dissolved in CH_2Cl_2/DMSO (108 mL, 1:1) and the solution cooled to −15 °C before Et_3N (8.03 mL, 57.1 mmol) was added in one portion. Next, a solution of SO_3·pyridine (9.09 g, 57.1 mmol) in DMSO (81 mL) was added very slowly via a dropping funnel. Once the addition was complete, the mixture was stirred for 3 h. For workup, aq. $KHSO_4$ (1 M, 250 mL) was added and the slurry extracted with Et_2O (3 x 200 mL), the combined organic layers were washed with sat. aq. $NaHCO_3$ (40 mL) and brine, dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (SiO_2, pentane/*tert*-butyl methyl ether, 1/1) to afford the title compound as a crystalline white solid (4.55 g, 83%). $[\alpha]_D^{23}$ = −129 (*c* = 1.38, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.27 (m, 3H), 7.20 – 7.16 (m, 2H), 4.73 (ddt, 1H, *J* = 9.5, 7.8, 3.2 Hz), 4.60 (q, 1H, *J* = 7.3 Hz), 4.26 – 4.13 (m, 2H), 3.30 (dd, 1H, *J* = 13.4, 3.6 Hz), 2.77 (dd, 1H, *J* = 13.4, 9.5 Hz), 2.64 (dq, 2H, J = 11.0, 7.3 Hz), 1.43 (d, 3H, *J* = 7.3 Hz), 1.06 ppm (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.0, 170.1, 153.8, 135.1, 129.3 (2C), 128.9 (2C), 127.3, 66.4, 55.2, 52.6, 37.9, 34.0, 12.8, 7.5 ppm; IR (film): $\tilde{\nu}$ = 2981, 1766, 1713, 1696, 1451, 1386, 1352, 1337, 1280, 1247, 1223, 1215, 1179, 1120, 1070, 1049, 994, 958, 908, 763, 750, 705,



[6] a) D. A. Evans, J. Bartroli, T. L. Shih, *J. Am. Chem. Soc.* **1981**, *103*, 2127-2129; b) J. R. Gage, D. A. Evans, *Org. Synth.* **1989**, *68*, 83-91.

686 cm^{-1}; MS (EI) *m/z* (%): 289 (20), 260 (32), 233 (20), 178 (12), 142 (29), 134 (21), 133 (18), 117 (59), 116 (21), 113 (51), 91 (28), 57 (100), 56 (15), 29 (22); HRMS (ESI): *m/z*: calcd. for $C_{16}H_{19}NO_4Na$ [M^++Na]: 312.1205, found 312.1206. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

(*2R,4S,5R,8S*)-1-((*R*)-4-Benzyl-2-oxooxazolidin-3-yl)-5-hydroxy-2,4,8-trimethylundec-9-yne-1,3-dione (13). 

$Sn(OTf)_2$ (4.36 g, 10.5 mmol) was dispersed in CH_2Cl_2 (20 mL) and the suspension cooled to −20 °C. Upon addition of Et_3N (1.46 mL, 10.5 mmol) the white suspension turned pale yellow. A solution of compound **12** (2.86 g, 9.89 mmol) in CH_2Cl_2 (10 mL) was added dropwise and the resulting mixture stirred for 1 h at −20 °C before it was cooled to −78 °C. A solution of aldehyde **5** (766 mg, 6.18 mmol) in CH_2Cl_2 (10 mL) was slowly introduced. Once TLC control indicated complete conversion, the mixture was diluted with CH_2Cl_2 (100 mL), poured into a pre-cooled (0 °C) aq. solution of $NaHSO_4$ (1 M, 150 mL) and vigorously stirred for 20 min. The mixture was extracted with CH_2Cl_2 (3 x 100 mL), the combined organic layers were washed with sat. aq. $NaHCO_3$, dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (SiO_2, pentane/*tert*-butyl methyl ether, 1/1) to afford the title compound as white sticky oil (1.46 g, 57%).[8] $[\alpha]_D^{23}$ = −48.0 (*c* = 1.00, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.32 (m, 2H), 7.30 – 7.28 (m, 1H), 7.21 – 7.19 (m, 2H), 4.87 (q, 1H, *J* = 7.3 Hz), 4.76 (ddt, 1H, *J* = 9.7, 8.0, 3.1 Hz), 4.27 (t, 1H, *J* = 8.0 Hz), 4.19 (dd, 1H, *J* = 9.1, 2.9 Hz), 3.94 (ddd, 1H, *J* = 9.0, 4.1, 2.7 Hz), 3.31 (dd, 1H, *J* = 13.4, 3.4 Hz), 2.83 – 2.76 (m, 2H), 2.49 (br, 1H), 2.44 – 2.39 (m, 1H), 1.78 (d, 3H, *J* = 2.3 Hz), 1.72 – 1.66 (m, 1H), 1.60 – 1.52 (m, 1H), 1.49 (d, 3H, *J* = 7.3 Hz), 1.47 – 1.40 (m, 2H), 1.25 (d, 3H, *J* = 7.2 Hz), 1.14 ppm (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.1, 170.3, 153.6, 135.0, 129.4 (2C), 129.0 (2C), 127.4, 83.3, 76.0, 70.9, 66.5, 55.3, 51.9, 48.4, 37.9, 33.4, 31.6, 25.6, 21.4, 12.9, 10.0, 3.5 ppm; IR (film): $\tilde{\nu}$ = 2970, 2940, 1775, 1711, 1690, 1454, 1357, 1289, 1212, 1115, 1077, 1049, 998, 923, 761, 742, 702 cm^{-1}; MS (EI) *m/z* (%): 344 (13), 289 (34), 260 (53), 233 (46), 178 (56), 177 (11), 167 (25), 142 (12), 135 (12), 134 (34), 133 (23), 125 (16), 123 (15), 118 (10), 117 (62), 116 (17), 113 (17), 112 (100), 107 (11), 93 (11), 92 (29), 91 (45), 86 (24), 83 (26), 82 (15), 80 (16), 79 (13), 67 (18), 65 (10), 56 (24), 55 (32); HRMS (ESI): *m/z*: calcd. for $C_{24}H_{31}NO_5Na$ [M^++Na]: 436.2098, found 436.2094. The analytical and spectroscopic data are in agreement with those reported in the literature.[9]

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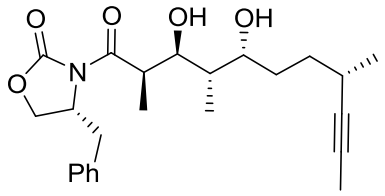
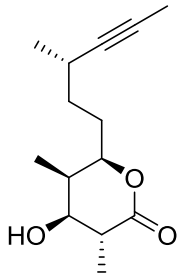
[7] D. A. Evans, H. P. Ng, J. S. Clark, D. L. Rieger, *Tetrahedron* **1992**, *48*, 2127-2142.

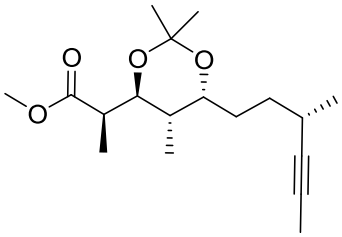
[8] D. A. Evans, J. S. Clark, R. Metternich, V. J. Novack, G. S. Sheppard, *J. Am. Chem. Soc.* **1990**, *112*, 866-868.

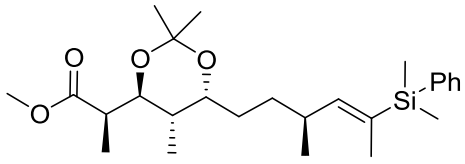
[9] Y. Yuan, H. Men, C. Lee, *J. Am. Chem. Soc*. **2004**, *126*, 14720-14721.

(*R*)-4-Benzyl-3-((*2R,3S,4S,5R,8S*)-3,5-dihydroxy-2,4,8-trimethylundec-9-ynoyl)-oxazolidin-2-one (S-8).  A solution of aldol **13** (1.46 g, 3.53 mmol) in MeCN (44 mL) was added via a dropping funnel to a solution of $Me_4NBH(OAc)_3$ (4.64 g, 17.7 mmol) in MeCN (70 mL) and HOAc (39 mL) at −50 °C. The solution was allowed to slowly warm to −10 °C. After stirring for 1 h the mixture was poured into a mixture of Rochelle salt (350 mL) and CH_2Cl_2 (350 mL) (1:1) at 0 °C. Sat. aq. $NaHCO_3$ followed by solid $NaHCO_3$ were successively added under vigorous stirring until gas evolution ceased. The biphasic mixture was extracted with CH_2Cl_2 (4 x 200 mL, the last batch was stirred with the aqueous layer for 5 min). The combined organic phases were washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (SiO_2, pentane/EtOAc, 1/1) to afford the title compound as white foam (1.16 g, 80%). $[\alpha]_D^{23}$ = −5.0 (*c* = 0.93, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.28 (m, 3H), 7.21 – 7.19 (m, 2H), 4.71 (ddt, 1H, *J* = 9.4, 7.6, 3.2 Hz), 4.27 – 4.19 (m, 2H), 4.00 (dd, 1H, *J* = 9.1, 2.5 Hz), 3.90 (qd, 1H, *J* = 7.0, 2.5 Hz), 3.82 (dt, 1H, *J* = 9.7, 2.8 Hz), 3.65 (br, 1H), 3.25 (dd, 1H, *J* = 13.4, 3.4 Hz), 2.80 (dd, 1H, *J* = 13.4, 9.4 Hz), 2.47 – 2.35 (m, 1H), 1.87 (dqd, 1H, *J* = 9.4, 7.1, 2.5 Hz), 1.78 (d, 3H, *J* = 2.3 Hz), 1.70 – 1.42 (m, 5H), 1.28 (d, 3H, *J* = 7.0 Hz), 1.14 (d, 3H, *J* = 7.0 Hz), 0.87 ppm (d, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 152.5, 134.6, 129.1 (2C), 128.6 (2C), 127.1, 83.3, 75.6, 73.4, 73.2, 65.9, 54.7, 39.2, 38.9, 37.5, 33.6, 30.2, 25.4, 21.1, 11.4, 9.8, 3.2 ppm; IR (film): $\tilde{\nu}$ = 2970, 2919, 1779, 1697, 1455, 1387, 1210, 1106, 1045, 1015, 972, 762, 702 cm^{-1}; MS (pos. ESI) *m*/*z* (%): 438 (M+Na, 100); HRMS (ESI): *m*/*z*: calcd. for $C_{24}H_{33}NO_5Na$ [M^++Na]: 438. 2254, found 438.2251. The analytical and spectroscopic data are in agreement with those reported in the literature.[9]

(*3R,4S,5R,6R*)-4-Hydroxy-3,5-dimethyl-6-((*S*)-3-methylhex-4-yn-1-yl)tetrahydro-2*H*-pyran-2-one (14).  H_2O_2 (0.85 mL, 30% *w*/*w*) and LiOH (143 mg, 3.41 mmol) were subsequently added to a solution of diol **S-8** (878 mg, 2.13 mmol) in THF/H_2O (21 mL, 3:1) at 0 °C. The mixture was stirred at ambient temperature for 2 h until complete consumption of the substrate was observed by TLC. For workup the mixture was acidified with HCl (1 M, 2 mL) and stirred for 5 min before the aq. phase was extracted with Et_2O (3 x 60 mL). The combined organic phases were dried over $MgSO_4$ and evaporated, and the residue purified by flash chromatography (SiO_2, pentane/EtOAc, 7/3 → 1/1) to afford the title compound as a colorless oil (512 mg, 99%). $[\alpha]_D^{23}$ = +95.2 (*c* = 0.75, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (ddd, 1H, *J* = 8.7, 5.0, 2.4 Hz), 3.36 (dd, 1H, *J* = 10.4, 4.3 Hz), 2.47 – 2.35 (m, 2H), 2.16 (br, 1H), 1.98 (dddd, 1H, *J* = 13.1, 10.2, 8.6, 4.4 Hz), 1.72 – 1.58 (m, 2H), 1.68 (d, 3H, *J* = 2.4 Hz), 1.52 – 1.33 (m, 2H), 1.47 (d, 3H, *J* = 7.1 Hz), 1.22 (d, 3H, *J* = 6.9 Hz), 0.81 ppm (d, 3H, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 83.6, 79.4, 76.8, 74.0, 40.4, 37.8, 33.4, 30.6, 26.3, 21.9, 14.7, 4.7,

3.6 ppm; IR (film): $\tilde{\nu}$ = 2941, 1766, 1713, 1696, 1475, 1464, 1451, 1386, 1353, 1337, 1280, 1247, 1223, 1214, 1179, 1120, 1085, 1070, 1049, 1032, 994, 973, 958, 908, 857, 825, 763, 750, 705, 686 cm^{-1}; MS (EI) *m/z* (%): 152 (11), 151 (45), 147 (11), 137 (10), 136 (17), 135 (23), 133 (11), 131 (12), 130 (12), 125 (50), 124 (17), 123 (35), 122 (12), 121 (40), 119 (20), 113 (49), 112 (16), 111 (10), 109 (56), 108 (31), 107 (81), 106 (12), 105 (34), 103 (15), 98 (42), 97 (21), 96 (32), 95 (48), 94 (17), 93 (74), 91 (53), 87 (16), 86 (12), 85 (77), 83 (22), 82 (81), 81 (49), 80 (93), 79 (90), 77 (31), 69 (43), 68 (26), 67 (100), 66 (15), 65 (28), 59 (13), 58 (35), 57 (69), 56 (31), 55 (72), 53 (27), 44 (19), 43 (44), 41 (67), 39 (27), 29 (21); HRMS (ESI): *m/z*: calcd. for $C_{14}H_{22}NO_3Na$ [M^++Na]: 261.1459, found 261.1461. The analytical and spectroscopic data are in agreement with those reported in the literature.[9]

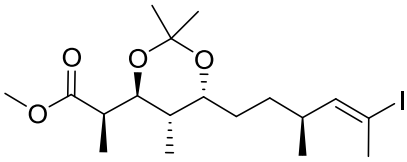
Methyl (*R*)-2-((*4S,5S,6R*)-2,2,5-trimethyl-6-((*S*)-3-methylhex-4-yn-1-yl)-1,3-dioxan-4-yl)propanoate (15).  CSA (49 mg, 0.21 mmol, 10 mol%) was added to a solution of lactone **14** (512 mg, 2.11 mmol) in 2,2-dimethoxypropane (26 mL) and the resulting solution was stirred at ambient temperature overnight. The mixture was diluted with Et_2O (50 mL), carefully neutralized with sat. aq. $NaHCO_3$ and extracted with Et_2O (3 x 50 mL). The combined extracts were washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (SiO_2, pentane/Et_2O, 7/3) to afford the title compound as colorless oil (589 mg, 90%).[10] $[\alpha]_D^{20}$ = −1.86 (*c* = 0.59, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (dt, 1H, *J* = 9.4, 4.4 Hz), 3.69 (s, 3H), 3.63 (dd, 1H, *J* = 7.7, 5.0 Hz), 2.60 – 2.54 (m, 1H), 2.43 – 2.37 (m, 1H), 1.87 – 1.82 (m, 1H), 1.79 (d, 3H, *J* = 2.3 Hz), 1.62 – 1.49 (m, 2H), 1.44 – 1.35 (m, 2H), 1.31 (s, 3H), 1.29 (s, 3H), 1.20 (d, 3H, *J* = 7.0 Hz), 1.13 (d, 3H, *J* = 6.9 Hz), 0.84 ppm (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.6, 100.2, 83.2, 75.4, 75.0, 68.7, 51.3, 42.6, 36.5, 33.0, 27.8, 25.3, 24.6, 23.3, 20.9, 11.7, 11.1, 3.2 ppm; IR (film): $\tilde{\nu}$ = 2983, 2937, 2877, 1738, 1456, 1434, 1379, 1224, 1198, 1166, 1126, 1090, 1018, 985, 954, 876, 855, 838 cm^{-1}; MS (pos. ESI) *m/z* (%): 333 (M+Na, 100); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{30}NO_4Na$ [M^++Na]: 333.2037, found 333.2036.

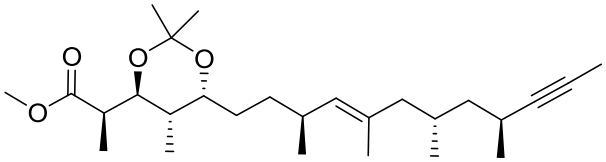
Methyl (*R*)-2-((*4S,5S,6R*)-6-((*S,E*)-5-(dimethyl(phenyl)silyl)-3-methylhex-4-en-1-yl)-2,2,5-trimethyl-1,3-dioxan-4-yl)propanoate (16).  A solution of freshly prepared $LiSiMe_2Ph$ (6.70 mL, 2.01 mmol)[11] in THF (5.1 mL) was added to CuCN (180 mg, 2.01 mmol) in a Schlenk flask at 0 °C. After stirring for 30 min, the mixture was cooled to −78 °C before a solution of alkyne **15** (406 mg, 1.34 mmol) in THF (1 mL) was slowly added. Stirring was continued for 30 min at this

[10] a) T. Magauer, H. J. Martin, J. Mulzer, *Angew. Chem.* **2009**, *121*, 6148-6152; *Angew. Chem. Int. Ed*. **2009**, *48*, 6032-6036; b) T. Magauer, H. J. Martin, J. Mulzer, *Chem. Eur. J*. **2010**, *16*, 507-519.

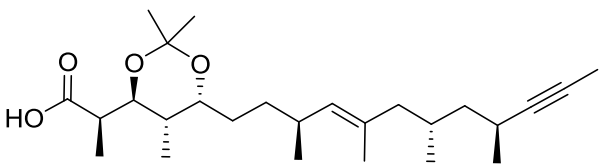
[11] I. Fleming, T. W. Newton, F. Roessler, *J. Chem. Soc. Perkin Trans. 1* **1981**, 2527-2532.

temperature before the mixture was allowed to reach 0 °C. For work up, sat. aq. NH_4Cl (20 mL) was introduced, the biphasic system was extracted CH_2Cl_2 (3 x 50 mL), and the combined organic layers were dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (SiO_2, pentane/EtOAc, 1/0 → 30/1) to afford the title compound as colorless oil (557 mg, 93%). $[\alpha]_D^{23}$ = −18.0 (*c* = 0.52, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.47 (m, 2H), 7.34 – 7.32 (m, 3H), 5.58 (d, 1H, *J* = 9.4 Hz), 3.74 – 3.69 (m, 1H), 3.69 (s, 3H), 3.62 (dd, 1H, *J* = 7.8, 5.0 Hz), 2.63 – 2.53 (m, 2H), 1.84 – 1.75 (m, 1H), 1.64 (d, 3H, *J* = 1.7 Hz), 1.47 – 1.34 (m, 2H), 1.31 (s, 3H), 1.30 (s, 3H), 1.28 – 1.25 (m, 2H), 1.19 (d, 3H, *J* = 6.9 Hz), 0.95 (d, 3H, *J* = 6.6 Hz), 0.81 (d, 3H, *J* = 6.8 Hz), 0.32 s, 3H), 0.31 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.1, 147.8, 139.1, 134.1 (2C), 132.2, 128.9, 127.8 (2C), 100.7, 75.5, 69.4, 51.8, 43.1, 36.9, 33.3, 32.5, 28.5, 25.2, 23.8, 20.8, 15.1, 12.1, 11.6, −3.1, −3.3 ppm; IR (film): $\tilde{\nu}$ = 2986, 2953, 1739, 1618, 1456, 1428, 1379, 1320, 1290, 1247, 1224, 1200, 1173, 1200, 1173, 1109, 1055, 1020, 999, 985, 968, 956, 926, 880, 831, 811, 772, 746, 729, 699 cm^{-1}; MS (EI) *m/z* (%): 245 (14), 137 (23), 136 (14), 135 (100), 128 (19), 127 (13), 121 (13), 75 (11), 73 (15); HRMS (ESI): *m/z*: calcd. for $C_{26}H_{42}O_4SiNa$ [M^++Na]: 469.2748, found 469.2745.

Methyl (*R*)-2-((*4S,5S,6R*)-6-((*S,E*)-5-iodo-3-methylhex-4-en-1-yl)-2,2,5-trimethyl-1,3-dioxan-4-yl)propanoate (17). 
At 0 °C, a solution of alkenyl silane **16** (472 mg, 1.06 mmol) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) (11 mL) was treated with 2,6-lutidine (0.50 mL, 4.3 mmol). N-iodosuccinimde (358 mg, 1.59 mmol) was then added in one portion and the resulting mixture was stirred for 30 min at 0 °C. Sat. aq. $Na_2S_2O_5$ (30 mL) was introduced, the mixture was extracted with CH_2Cl_2 (3 x 50 mL), and the combined organic phases were dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (SiO_2, pentane/EtOAc, 1/0 → 20/1) to afford the title compound as colorless oil (458 mg, 97%). $[\alpha]_D^{23}$ = +11.5 (*c* = 1.08, $CHCl_3$), ^{1}H NMR (400 MHz, C_6D_6): δ = 5.97 (d, 1H, *J* = 10.0 Hz), 3.80 (dd, 1H, *J* = 7.7, 4.8 Hz), 3.67 (dt, 1H, *J* = 9.1, 4.2 Hz), 3.38 (s, 3H), 2.49 (qd, 1H, J = 6.9, 4.4 Hz), 2.20 – 2.15 (m, 1H), 2.14 (s, 3H), 1.75 – 1.66 (m, 1H), 1.45 – 1.32 (m, 2H), 1.34 (s, 3H), 1.29 (d, 3H, *J* = 6.7 Hz), 1.29 (s, 3H), 1.13 – 1.00 (m, 2H), 0.75 (d, 3H, *J* = 6.8 Hz), 0.75 ppm (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, C_6D_6): δ = 174.2, 147.4, 100.7, 92.9, 75.8, 69.3, 51.3, 43.4, 37.7, 35.8, 33.4, 28.6, 27.8, 25.3, 23.9, 20.3, 12.3, 11.8 ppm; IR (film): $\tilde{\nu}$ = 2984, 2946, 1737, 1635, 1456, 1434, 1378, 1358, 1325, 1290, 1224, 1198, 1169, 1135, 1090, 1035, 1019, 986, 955, 878, 858, 839, 808, 765, 699 cm^{-1}; MS (EI) *m/z* (%): 380 (31), 293 (14), 253 (43), 235 (17), 208 (31), 195 (51), 183 (15), 175 (13), 147 (16), 137 (28), 129 (31), 128 (100), 125 (69), 113 (34), 107 (21), 97 (39), 96 (11), 95 (37), 83 (23), 82 (11), 81 (49), 79 (11), 69 (80), 68 (26), 67 (40), 59 (34), 55 (42), 53 (12), 43 (46), 41 (43), 29 (12); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{31}O_4INa$ [M^++Na]: 461.1160, found 461.1160.

Methyl (*R*)-2-((4S,5S,6R)-2,2,5-trimethyl-6-((*3S,7S,9S,E*)-3,5,7,9-tetramethyldodec-4-en-10-yn-1-yl)-1,3-dioxan-4-yl)propanoate (23). 

tert-BuLi (1.7 M in pentane, 2.64 mL, 4.48 mmol) was added to a solution of alkyl iodide **22** (560 mg, 2.24 mmol) in Et_2O (6.6 mL) and the resulting mixture was cooled to −78 °C. After stirring for 5 min, 9-MeO-9-BBN (1 M in THF, 5.39 mL, 5.39 mmol) was introduced and the mixture diluted with THF (6.6 mL). After additional 10 min, the mixture was allowed to reach ambient temperature over 1 h. Next aq. K_3PO_4 (3 M, 0.87 mL, 2.61 mmol) and a solution of alkenyl iodide **17** (394 mg, 0.897 mmol) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (64 mg, 0.09 mmol, 10 mol%) in DMF (9 mL) were successively added and stirring was continued for 1 h. The reaction was quenched with sat. aq. NH_4Cl and the mixture extracted with *tert*-butyl methyl ether (3 x 50 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (SiO_2, pentane/EtOAc, 1/0 → 30/1) to afford the title compound as colorless oil (388 mg, quant.). $[\alpha]_D^{20}$ = +0.94 (*c* = 1.00, CH_2Cl_2), ^{1}H NMR (600 MHz, C_6D_6): δ = 5.00 (d, 1H, *J* = 9.4 Hz), 3.84 (dd, 1H, *J* = 7.3, 4.8 Hz), 3.80 (dt, 1H, *J* = 9.6, 4.4 Hz), 3.38 (s, 3H), 2.55 – 2.49 (m, 2H), 2.44 – 2.37 (m, 1H); 2.14 (dd, 1H, *J* = 13.0, 5.3 Hz), 1.99 – 1.93 (m, 1H), 1.81 – 1.76 (m, 1H), 1.67 (dd, 1H, *J* = 13.0, 9.0 Hz), 1.64 (d, 3H, *J* = 1.4 Hz), 1.63 – 1.57 (m, 1H), 1.59 (d, 3H, *J* = 2.4 Hz), 1.50 – 1.42 (m, 2H), 1.36 (s, 3H), 1.34 (s, 3H), 1.33 – 1.27 (m, 2H), 1.31 (d, 3H, *J* = 7.0 Hz), 1.24 – 1.18 (m, 1H), 1.16 (d, 3H, *J* = 6.8 Hz), 1.02 (d, 3H, *J* = 6.6 Hz), 0.90 (d, 3H, *J* = 6.6 Hz), 0.84 ppm (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (150 MHz, C_6D_6): δ = 174.2, 133.3, 132.8, 100.7, 84.2, 75.8, 75.7, 69.5, 51.1, 47.5, 45.3, 43.3, 37.3, 34.5, 32.8, 29.1, 29.1, 25.2, 24.2, 23.8, 21.9, 21.7, 20.2, 16.2, 12.3, 11.7, 3.4 ppm; IR (film): $\tilde{\nu}$ = 2952, 2920, 1740, 1455, 1435, 1379, 1328, 1291, 1225, 1196, 1167, 1087, 1056, 1020, 955, 877, 837, 809, 756 cm^{-1}; MS (EI) *m/z* (%): 434 (17), 376 (28), 289 (31), 249 (16), 248 (57), 233 (24), 219 (10), 206 (20), 205 (97), 191 (21), 189 (44), 183 (27), 177 (15), 164 (15), 163 (37), 159 (36), 150 (18), 149 (44), 147 (28), 135 (34), 134 (16), 133 (24), 129 (17), 128 (34), 127 (58), 126 (77), 125 (12), 124 (15), 123 (57), 122 (27), 121 (100), 120 (14), 119 (35), 113 (13), 107 (48), 105 (16), 97 (11), 95 (32), 93 (19), 83 (11), 69 (70), 59 (25), 55 (22), 43 (32); HRMS (ESI): *m/z*: calcd. for $C_{27}H_{46}NO_4Na$ [M^++Na]: 457.3294, found 457.3297.

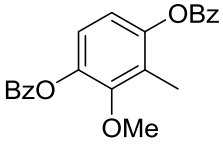
(*R*)-2-((*4S,5S,6R*)-2,2,5-Trimethyl-6-((*3S,7S,9S,E*)-3,5,7,9-tetramethyldodec-4-en-10-yn-1-yl)-1,3-dioxan-4-yl)propanoic acid (24). 

Ester **23** (356 mg, 0.81 mmol) was dissolved in a mixture of THF/MeOH/H_2O (10 mL, 2:2:1). After addition of LiOH (195 mg, 8.1 mmol) the solution was stirred for 16 h. CH_2Cl_2 (15 mL) was then added and the biphasic system was acidified by dropwise addition of aq. HCl (1 M). The phases were separated and the aq. phase was extracted with CH_2Cl_2 (3 x

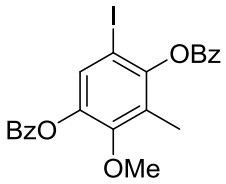
25 mL). The combined organic layers were dried over $MgSO_4$ and evaporated. The residue was dried by azeotropic distillation with toluene (3 x 5 mL) to afford the title compound as colorless sticky oil which was used without further purification (307 mg, 90%). $[\alpha]_D^{23}$ = −0.20 (*c* = 1.0, CH_2Cl_2), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.0 (br, 1H), 4.86 (d, 1H, *J* = 8.3 Hz), 3.74 – 3.65 (m, 2H), 2.60 (dq, 1H, *J* = 7.0, 3.7 Hz), 2.48 – 2.42 (m, 1H), 2.38 – 2.31 (m, 1H), 2.05 (dd, 1H, = 12.8, 5.0 Hz), 1.83 – 1.72 (m, 2H), 1.78 (d, 3H, *J* = 2.4 Hz), 1.68 – 1.60 (m, 1H), 1.56 (d, 3H, *J* = 1.3 Hz), 1.48 – 1.39 (m, 1H), 1.32 (s, 3H), 1.31 (s, 3H), 1.30 – 1.22 (m, 5H), 1.20 (d, 3H, *J* = 7.0 Hz), 1.09 (d, 3H, *J* = 6.8 Hz), 0.92 (d, 3H, *J* = 6.6 Hz), 0.84 (d, 3H, *J* = 6.6 Hz), 0.80 ppm (d, 3H, *J* = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.1, 132.3, 132.2, 100.5, 83.8, 74.9, 74.8, 69.1, 47.0, 44.5, 42.4, 36.2, 33.4, 31.9, 28.3, 28.0, 24.6, 23.4, 23.3, 21.0, 21.0, 19.5, 15.7, 11.8, 10.6, 3.1 ppm; IR (film): $\tilde{\nu}$ = 2953, 2919, 1708, 1455, 1379, 1225, 1166, 1087, 1019, 968, 928, 909, 877 cm^{-1}; MS (EI) *m/z* (%): 362 (11), 289 (26), 248 (19), 233 (12), 227 (11), 220 (13), 205 (17), 203 (10), 191 (16), 177 (12), 175 (12), 169 (23), 164 (15), 163 (24), 161 (18), 151 (30), 150 (21), 149 (40), 147 (29), 137 (16), 136 (10), 135 (34), 134 (11), 133 (32), 127 (39), 126 (100), 125 (16), 124 (13), 123 (51), 122 (27), 121 (62), 120 (12), 119 (28), 114 (22), 111 (11), 110 (12), 109 (66), 108 (21), 107 (60), 105 (12), 97 (18), 96 (14), 95 (46), 93 (26), 91 (12), 85 (15), 83 (24), 82 (26), 81 (37), 79 (15), 69 (88), 68 (13), 67 (66), 59 (63), 57 (15), 55 (48), 43 (49), 41 (48); HRMS (ESI): *m/z*: calcd. for $C_{26}H_{44}NO_4Na$ [M^++Na]: 443.3137, found 43.3132.

The Aromatic Segments

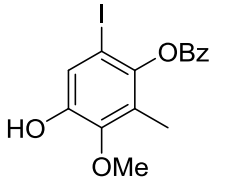
Compound 28: Benzoyl chloride (3.25 mL, 29.9 mmol) and NEt_3 (5.53 mL, 39.9 mmol) were added to a solution of 2-methoxy-3,6-dihydroxytoluene (**27**) (2.05 g, 13.3 mmol) in THF (50 mL) at 0 °C. After stirring for 3 h at ambient temperature, sat. aq. NH_4Cl and *tert*-butyl methyl ether were introduced. The aqueous layer was extracted with *tert*-butyl methyl ether and the combined extracts were dried over $MgSO_4$ and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 20/1 → 6/1) to give the title compound as a pale yellow solid (4.28 g, 89%). M.p. = 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27-8.22 (m, 4H), 7.69-7.64 (m, 2H), 7.57-7.51 (m, 4H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 2.21 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 164.9, 151.1, 147.9, 142.0, 133.9, 133.8, 130.4, 130.3, 129.4, 129.4, 128.8 (2C), 126.1, 120.9, 117.9, 61.2, 10.1 ppm; IR (film): $\tilde{\nu}$ = 1731, 1599, 1476, 1449, 1267, 1212, 1082, 1055, 1023, 1004, 975, 793, 706, 674 cm^{-1}; MS (EI): *m/z* (%): 363 (4), 362 (18), 106 (7), 105 (100), 78 (1), 77 (21), 51 (3); HRMS (ESI): *m/z* calcd. for $C_{22}H_{18}O_5Na$: 385.1046 [M+Na^+]; found: 385.1045.



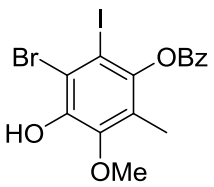
Compound S-9: NIS (2.69 g, 11.9 mmol) and conc. H_2SO_4 (0.2 mL) were added to a solution of **28** (2.88 g, 7.95 mmol) in HOAc (20 mL). After stirring for 1.5 h at ambient temperature, a second portion of NIS (2.69 g, 11.9 mmol) was introduced and stirring continued for 1 h before an aqueous solution of NaOH (15 % *v*/*v*) and *tert*-butyl methyl ether were slowly added. The aqueous layer was extracted with *tert*-butyl methyl ether and the combined extracts were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 30/1 → 6/1) to give the title compound as a white solid (3.64 g, 94%). M.p. = 152-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31-8.27 (m, 2H), 8.25-8.20 (m, 2H), 7.72-7.64 (m, 2H), 7.60-7.51 (m, 5H), 3.80 (s, 3H), 2.22 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.6, 163.8, 151.4, 148.7, 142.5, 134.1, 134.0, 130.6, 130.4, 130.3, 129.0, 129.0, 128.9 (2C), 127.5, 83.7, 61.3, 11.3 ppm; IR (film): $\tilde{\nu}$ = 1732, 1600, 1470, 1540, 1256, 1219, 1192, 1175, 1083, 1056, 1024, 884, 796, 702, 684 cm^{-1}; MS (EI): *m*/*z* (%): 489 (4), 488 (15), 362 (1), 361 (4), 106 (7), 105 (100), 78 (1), 77 (21), 51 (3); HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{17}O_5INa$: 511.0013 [*M*+Na$^+$]; found: 511.0013.



Compound 29: A solution of KOH (836 mg, 14.9 mmol) in MeOH (4 mL) was added to a suspension of diester **S-9** (3.64 g, 7.45 mmol) in MeOH (40 mL). After stirring for 1 h, sat. aq. NH_4Cl was introduced and the mixture was acidified by dropwise addition of conc. HCl. The aqueous layer was extracted with *tert*-butyl methyl ether and the combined extracts were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 10/1 → 6/1) to give the title compound as a pale yellow solid (2.28 g, 80%). M.p. = 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29-8.25 (m, 2H), 7.67 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.58-7.50 (m, 2H), 7.33 (s, 1H), 5.58 (s, 1H), 3.81 (s, 3H), 2.18 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 147.7, 146.2, 143.7, 134.0, 130.6, 129.2, 128.8, 125.6, 122.4, 84.8, 61.2, 22.3 ppm; IR (film): $\tilde{\nu}$ = 3380, 1729, 1584, 1470, 1450, 1425, 1238, 1190, 1165, 1089, 1054, 1024, 982, 838, 792, 752, 702, 684 cm^{-1}; MS (EI): *m*/*z* (%): 385 (3), 384 (17), 179 (1), 257 (3), 197 (1), 152 (1), 137 (1), 124 (1), 106 (8), 105 (100), 81 (1), 78 (1), 77 (21), 76 (1), 67 (3), 53 (2), 51 (4), 50 (1); HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{13}O_4INa$: 406.9751 [*M*+Na$^+$]; found: 406.9750.

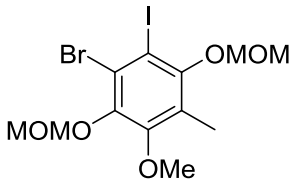


Compound S-10: NBS (1.15 g, 6.47 mmol) was added to solution of alcohol **29** (2.26 g, 5.88 mmol) in MeCN (35 mL) at –10 °C. After stirring for 30 min at this temperature, sat. aq. $Na_2S_2O_3$ and *tert*-butyl methyl ether were introduced and the aqueous layer was extracted with *tert*-butyl methyl ether. The combined extracts were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 10/1 → 6/1) to give bromide **S-10** as an orange solid (1.33 g, 49%). M.p. = 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29-8.24 (m, 2H), 7.68 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.58-7.52 (m, 2H), 5.90 (s, 1H),

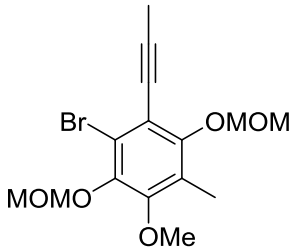


3.86 (s, 3H), 2.15 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.1, 146.4, 145.3, 144.6, 134.1, 130.7, 129.1, 128.9, 125.5, 114.7, 93.6, 61.2, 11.4 ppm; IR (film): $\tilde{\nu}$ = 3356, 1715, 1450, 1409, 1262, 1249, 1232, 1175, 1091, 1059, 1021, 1000, 908, 822, 710, 698, 685 cm^{-1}; MS (EI): *m*/*z* (%): 465 (1), 464 (8), 463 (1), 462 (8), 337 (2), 335 (2), 213 (1), 179 (1), 106 (7), 105 (100), 83 (1), 79 (1), 78 (2), 77 (19), 67 (2), 51 (49); HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{12}O_4IBrNa$: 484.8856 [*M*+Na$^+$]; found: 484.8855.

Compound S-11: A solution of DIBAl-H (1 M in CH_2Cl_2, 8.24 mL, 8.24 mmol) was added to a solution of benzoate **S-10** (1.09 g, 2.35 mmol) in CH_2Cl_2 (25 mL) at –78 °C. The mixture was stirred for 30 min at this temperature before ethyl acetate (3 mL) was slowly added. After warming to ambient temperature water (1.13 mL) and an aqueous solution of NaOH (15 % *v*/*v*, 0.33 mL) were introduced and the organic phase was dried over Na_2SO_4. The solvents were evaporated and the residue was dissolved in acetone (25 mL). After the addition of DBU (1.23 mL, 8.24 mmol) and MOMCl (0.63 mL, 7.24 mmol) the resulting mixture was stirred for 2 h before the reaction was quenched with pH 7 phosphate buffer. The aqueous layer was extracted with *tert*-butyl methyl ether and the combined extracts were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 30/1 → 20/1) to give compound **S-11** as an orange oil (643 mg, 61 % over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.13 (s, 2H), 5.01 (s, 2H), 3.80 (s, 3H), 3.66 (s, 3H), 3.66 (s, 3H), 2.25 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2, 153.0, 145.3, 127.0, 123.0, 100.3, 99.3, 95.7, 60.5, 58.4, 58.2, 11.4 ppm; IR (film): $\tilde{\nu}$ = 2935, 2827, 1447, 1421, 1370, 1206, 1155, 1091, 1062, 1021, 1000, 984, 922, 894 cm^{-1}; MS (EI): *m*/*z* (%): 448 (7), 447 (1), 368 (1), 367 (9), 335 (1), 322 (2), 321 (3), 294 (1), 275 (1), 273 (1), 263 (1), 195 (5), 46 (2), 45 (100); HRMS (ESI): *m*/*z* calcd. for $C_{12}H_{16}O_5IBrNa$: 468.9118 [*M*+Na$^+$]; found: 468.9118.



Compound 31: A solution of 1-propynylmagnesium bromide (0.5 M in THF, 1.36 mL, 0.68 mmol) was added to a solution of $ZnBr_2$ (152 mg, 0.68 mmol) in THF (9 mL). After stirring for 15 min, the suspension was filtered and one half of the filtrate was added to a solution of iodide **S-11** (50 mg, 0.11 mmol) and $Pd(PPh_3)_4$ (26 mg, 0.022 mmol) in THF (1.5 mL). After stirring for 1 h at 75 °C in a closed vessel the second half of the filtrate and a second portion of $Pd(PPh_3)_4$ (26 mg, 0.022 mmol) were added and stirring was continued for 1 h at 75 °C. After reaching ambient temperature, the mixture was passed through a plug of silica which was rinsed with *tert*-butyl methyl ether. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 30/1 → 20/1) to give the title compound as an orange oil (33 mg, 82%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.14 (s, 2H), 5.11 (s, 2H), 3.80 (s, 3H), 3.65 (s, 3H), 3.61 (s, 3H), 2.18 (s, 3H), 2.13 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9,

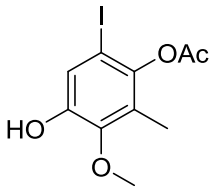


152.3, 144.7, 126.2, 118.8, 116.9, 99.7, 99.2, 94.4, 75.4, 60.7, 58.3, 57.8, 10.3, 4.9 ppm; IR (film): $\tilde{\nu}$ = 2937, 2829, 1456, 1423, 1405, 1377, 1344, 1156, 1062, 1020, 1002, 956, 923 cm^{-1}; MS (EI): *m/z* (%): 360 (5), 358 (5), 285 (6), 283 (7), 249 (23), 219 (6), 189 (5), 175 (9), 91 (6), 45 (100); HRMS (ESI): *m/z* calcd. for $C_{15}H_{19}O_5BrNa$: 381.0308 [M+Na^+]; found: 381.0306.

2-Methoxy-3-methyl-1,4-phenylene diacetate (42). Et_3N (11.2 mL, 81.1 mmol) was added to a solution of compound **27** (2.50 g, 16.2 mmol) in THF (125 mL) at −78 °C. Next, acetyl chloride (2.36 mL, 33.3 mmol) was added via a dropping funnel. Once the addition was complete, the mixture was allowed to reach 0 °C over the course of 1 h. The reaction was carefully quenched with sat. aq. $NaHCO_3$ (100 mL) and H_2O (50 mL) and the mixture was extracted with *tert*-butyl methyl ether (3 x 200 mL). The organic phases were dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (SiO_2, pentane/EtOAc, 7/3) to afford the title compound as pale yellow oil (3.47 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (d, 1H, *J* = 8.7 Hz), 6.79 (d, 1H, *J* = 8.7 Hz), 3.74 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.09 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 168.6, 150.3, 147.2, 141.2, 125.2, 120.1, 117.2, 60.4, 20.3, 20.3, 9.5 ppm; IR (film): $\tilde{\nu}$ = 1757, 1613, 1583, 1477, 1420, 1370, 1276, 1237, 1210, 1180, 1145, 1073, 1027, 1008, 980, 916, 897, 829, 797, 739, 657 cm^{-1}; MS (EI) *m/z* (%): 196 (15), 154 (100), 139 (22), 43 (19); HRMS (ESI): *m/z*: calcd. for $C_{12}H_{14}O_5Na$ [M^++Na]: 261.0737, found 261.0733. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

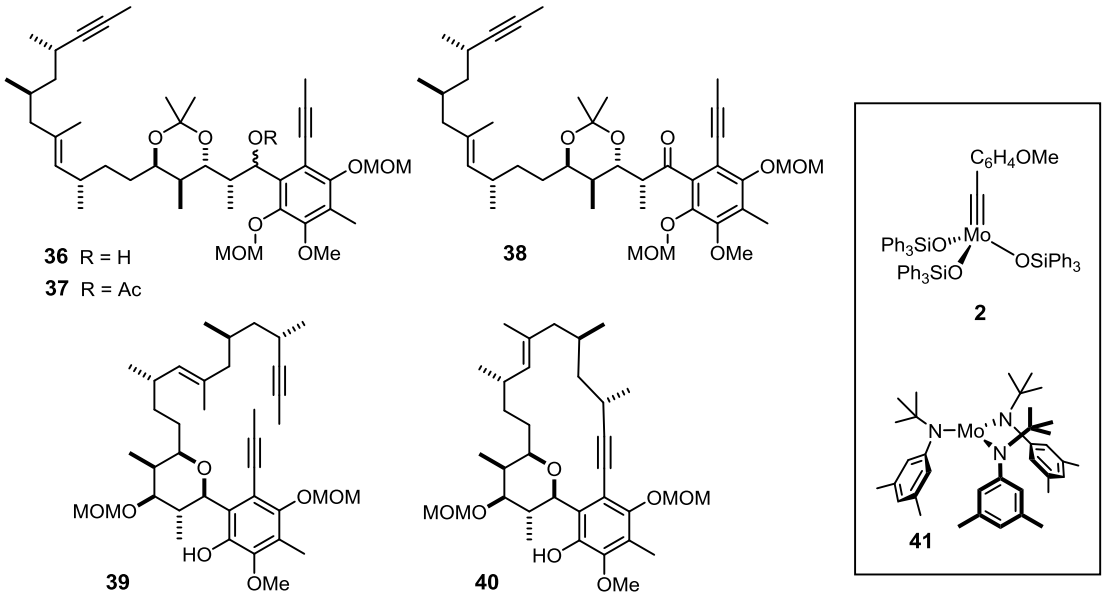
5-Iodo-2-methoxy-3-methyl-1,4-phenylene diacetate (S-12). N-iodosuccinimide (2.88 g, 12.8 mmol) was added in one portion to a solution of diacetate **42** (2.74 g, 7.53 mmol) in acetic acid (23 mL) and conc. H_2SO_4 (0.32 mL, 5.9 mmol, 50 mol%). The orange solution was stirred for 3 h before it was carefully diluted with H_2O (50 mL). The aq. mixture was extracted with EtOAc (3 x 70 mL), the combined extracts were evaporated and the residue was purified by flash chromatography (SiO_2, pentane/EtOAc, 4/1) to afford the title compound as yellow solid (2.73 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (s, 1H), 3.75 (s, 3H), 2.37 (s, 3H), 2.31 (3H), 2.13 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 167.5, 150.6, 148.1, 141.7, 129.6, 126.7, 83.2, 60.6, 20.6, 20.3, 10.7 ppm; IR (film): $\tilde{\nu}$ = 2941, 1763, 1468, 1423, 1408, 1367, 1285, 1228, 1166, 1086, 1031, 1007, 992, 919, 894, 872, 800, 681 cm^{-1}; MS (EI) *m/z* (%): 364 (14), 322 (23), 280 (100), 265 (20), 43 (26); HRMS (ESI): *m/z*: calcd. for $C_{12}H_{13}O_5Na$ [M^++Na]: 386.9689, found 386.9700. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

[12] K. B. Bahnck, S. D. Rychnovsky, *J. Am. Chem. Soc*. **2008**, *130*, 13177-13181.



4-Hydroxy-6-iodo-3-methoxy-2-methylphenyl acetate (43). K_2CO_3 (1.52 g, 11.0 mmol) in H_2O (5 mL) were added to a stirred solution of iodide **S-12** (1.00 g, 2.75 mmol) in MeOH (40 mL) at 0 °C. Stirring was continued for 3 h at ambient temperature before the reaction was quenched with sat. aq. NH_4Cl (25 mL). The mixture was extracted with EtOAc (3 x 100 mL), the combined organic phases were dried over Na_2SO_4 and evaporated to afford the title compound as sticky yellow oil which was used without further purification (859 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (s, 1H), 5.56 (s, 1H), 3.77 (s, 3H), 2.36 (s, 3H), 2.14 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 147.7, 146.1, 143.6, 125.4, 122.4, 84.8, 61.2, 21.1, 11.2 ppm; IR (film): $\tilde{\nu}$ = 1753, 1712, 1581, 1472, 1423, 1368, 1336, 1284, 1180, 1079, 1030, 1008, 989, 917, 873, 847, 794, 757, 727, 707, 668 cm^{-1}; MS (EI) *m/z* (%): 322 (15), 280 (100), 265 (40); HRMS (ESI): *m/z*: calcd. for $C_{10}H_{11}O_4INa$ [M^++Na]: 344.9597, found 344.9594.

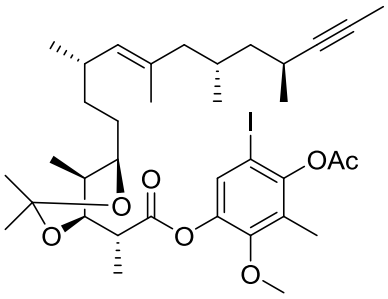
Table S1. Representative attempts at forming the macrocyclic frame of kendomycin starting from overcrowded diyne substrates comprising an *ortho,ortho'*-disubstituted arylalkyne subunit ("Route A").



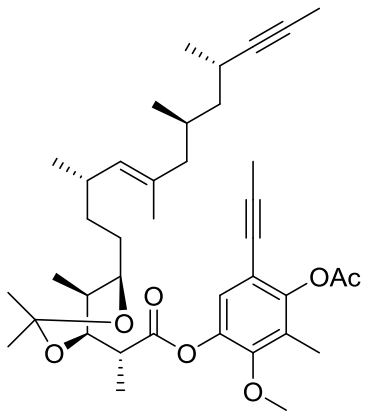
Entry	Substrate	Catalyst (mol%)	c (M)	T (°C)	t (h)	Outcome
1	**36**	**2** (25)	0.0005	80	3	no reaction[a]
2		**2** (50)	0.001	120	5	decomposition[b]
3	**37**	**2** (25)	0.001	120	5	dimer (66%)[c]
4	**38**	**2** (25)	0.001	80	1.5	no reaction[a]
5			0.002	120	4	dimer (53%)[c]
6		**41** (100)	0.002	120	14	decomposition
7	**39**	**41** (50)	0.001	120	19	decomposition
8		**2** (50)	0.001	120	15	**40** (37%)
9		**2** (2 x 30)	0.0001	120	72	**40** (≤ 62%)[d]

[a] the substrate was recovered; [b] elimination of the alcohol as the prevalent decomposition pathway; [c] refers to self-metathesis of the aliphatic alkyne; [d] as discussed in the text, the outcome was highly variable, with the single best result being 62%

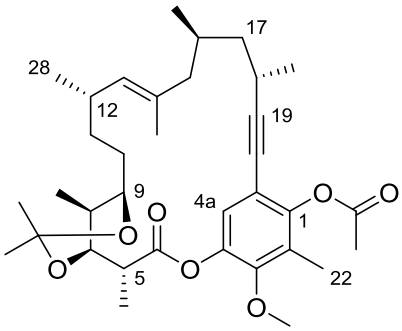
Completion of the Synthesis

4-Acetoxy-5-iodo-2-methoxy-3-methylphenyl (*2R*)-2-((4R,5S)-2,2,5-trimethyl-6-((*3S,7S,9S,E*)-3,5,7,9-tetramethyldodec-4-en-10-yn-1-yl)-1,3-dioxan-4-yl)propanoate (44).  EDCI·HCl (102 mg, 0.50 mmol) was added at 0 °C to a solution of acid **24** (219 mg, 0.500 mmol), phenol **43** (178 mg, 0.550 mmol) and DMAP (21 mg, 0.17 mmol) in CH_2Cl_2 (1 mL). Stirring was continued overnight at ambient temperature. The mixture was filtered through a pad of cotton and SiO_2, the filtrate was evaporated and the crude material purified by flash chromatography (SiO_2, pentane/EtOAc, 1/0 → 10/1) to afford the title compound as colorless oil (279 mg, 77%). $[\alpha]_D^{20}$ = −6.4 (*c* = 0.50, CH_2Cl_2), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (s, 1H), 4.88 (d, 1H, *J* = 9.3 Hz), 3.82 – 3.75 (m, 2H), 3.74 (s, 3H), 2.83 (qd, 1H, *J* = 7.0, 4.1 Hz), 2.48 – 2.40 (m, 1H), 2.38 – 2.32 (m, 1H), 2.36 (s, 3H), 2.13 (s, 3H), 2.06 (dd, 1H, *J* = 13.0, 5.1 Hz), 1.94 – 1.87 (m, 1H), 1.83 – 1.74 (m, 1H), 1.78 (d, 3H, *J* = 2.2 Hz), 1.67 – 1.61 (m, 1H), 1.57 (d, 3H, *J* = 1.1 Hz), 1.49 – 1.40 (m, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 1.33 (s, 3H), 1.31 – 1.23 (m, 5H), 1.09 (d, 3H, *J* = 6.8 Hz), 0.93 (d, 3H, *J* = 6.6 Hz), 0.90 (s, 3H, *J* = 6.8 Hz), 0.81 ppm (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.5, 168.0, 151.2, 148.4, 142.3, 132.8, 132.6, 130.0, 127.1, 100.7, 84.3, 83.6, 75.4, 75.3, 69.4, 61.1, 47.4, 45.0, 43.0, 36.6, 33.9, 32.4, 28.8, 28.6, 25.2, 24.0, 23.7, 21.5, 21.5, 21.0, 20.0, 16.2, 12.3, 11.3, 11.2, 3.6 ppm; IR (film): $\tilde{\nu}$ = 2952, 2920, 1768, 1468, 1426, 1370, 1328, 1286, 1224, 1182, 1086, 1019, 968, 916, 873, 800, 753, 666 cm^{-1}; MS (EI) *m/z* (%): 418 (22), 403 (11), 345 (26), 322 (59), 280 (100), 195 (18), 191 (19), 189 (10), 163 (11), 151 (31), 147 (10), 137 (12), 135 (29), 123 (32), 121 (35), 109 (49), 107 (32), 97 (10), 96 (40), 95 (32), 93 (12), 83 (23), 81 (20), 69 (60), 67 (28), 55 (20), 43 (36), 41 (16); HRMS (ESI): *m/z*: calcd. for $C_{36}H_{53}O_7INa$ [M^++Na]: 747.2729, found 747.2728.

Diyne 45. Trimethylborate (110 μL, 0.969 mmol) was added to a slurry of propynyl sodium (60 mg, 0.97 mmol) in THF (6.4 mL). The mixture was stirred for 10 min to form a clear solution. *t*BuXPhos (33 mg, 77 μmol, 20 mol%), $PdCl_2(PPh_3)_2$ (27 mg, 39 μmol, 10 mol%) and compound **44** (279 mg, 0.386 mmol) were added. The resulting mixture was degassed by bubbling argon through it via needle for 10 min before the reaction vessel was sealed and heated to reflux temperature for 2 h. The black mixture was filtered through a pad of Celite, the filtrate was evaporated and the brown residue subjected to flash chromatography (SiO_2, pentane/EtOAc, 1/0 → 10/1) to afford the title compound as



colorless oil (192 mg, 78%). $[\alpha]_D^{20}$ = −5.1 (*c* = 0.57, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.96 (s, 1H), 4.88 (d, 1H, *J* = 9.5 Hz), 3.80 (dd, 1H, *J* = 7.5, 4.4 Hz), 3.76 (dt, 1H, *J* = 8.5, 4.6 Hz), 3.75 (s, 3H), 2.83 (dq, 1H, *J* = 7.1, 4.4 Hz), 2.46 – 2.43 (m, 1H), 2.39 – 2.34 (m, 1H), 2.34 (s, 3H), 2.09 (s, 3H), 2.06 (dd, 1H, *J* = 13.0, 5.3 Hz), 2.02 (s, 3H), 1.91 (ddq, 1H, *J* = 7.4, 6.8, 4.6 Hz), 1.81 – 1.76 (m, 1H), 1.79 (d, 3H, *J* = 2.3 Hz), 1.64 (ddd, 1H, *J* = 13.0, 8.9, 0.7 Hz), 1.58 (d, 3H, *J* = 1.1 Hz), 1.49 – 1.43 (m, 1H), 1.36 (s, 3H), 1.35 (d, 3H, *J* = 7.0 Hz), 1.33 (s, 3H), 1.32 – 1.25 (m, 5H), 1.10 (d, 3H, *J* = 6.8 Hz), 0.93 (d, 3H, *J* = 6.6 Hz), 0.90 (d, 3H, *J* = 6.8 Hz), 0.82 ppm (d, 3H, *J* = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.6, 168.6, 150.5, 148.8, 141.4, 132.9, 132.7, 126.2, 124.2, 114.1, 100.8, 90.4, 84.8, 75.4, 75.4, 74.3, 69.5, 61.2, 47.5, 45.0, 43.2, 36.8, 34.0, 32.5, 28.8, 28.7, 25.3, 24.1, 23.8, 21.5, 21.5, 20.7, 20.0, 16.2, 12.4, 11.5, 10.2, 4.6, 3.6 ppm; IR (film): $\tilde{\nu}$ = 2919, 2280, 1768, 1481, 1455, 1379, 1341, 1330, 1247, 1225, 1207, 1186, 1108, 1074, 1022, 966, 912, 879, 812, 739, 703 cm^{-1}; MS (EI) *m/z* (%): 330 (19), 235 (12), 234 (70), 193 (14), 192 (100), 151 (13), 149 (12), 135 (14), 123 (14), 121 (17), 109 (24), 107 (16), 95 (16), 83 (11), 69 (28), 67 (15), 55 (11), 43 (13); HRMS (ESI): *m/z*: calcd. for $C_{39}H_{56}O_7Na$ [M^++Na]: 659.3924, found 659.3918.

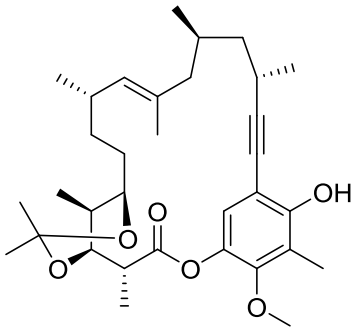


Cycloalkyne 46. Activated MS 5Å powder (370 mg, 2 mg/μmol) was dispersed in freshly distilled toluene (93 mL) under argon in a flame-dried Schlenk flask. A solution of diyne **45** (120 mg, 0.185 mmol, azeotropically dried with toluene (3 x 3 mL)) in toluene (1 mL) was added and the mixture stirred for 30 min before complex **2** (in 250 μL toluene)[13] was introduced (9.4 mg, 9.3 μmol, 5 mol%). The resulting pale orange slurry was stirred at ambient temperature for 1 h. For work up, the mixture was filtered through a pad of SiO_2 which was rinsed with EtOAc. The filtrate was evaporated and the residue was purified by flash chromatography (SiO_2, pentane/EtOAc, 20/1) to afford the title compound as colorless sticky oil (102 mg, 95%). As the material contained traces of silanol impurities, an aliquot was purified by HPLC (150 mm, Kromasil, Ø 30 mm, MeOH/H_2O = 90:10, 35 mL/min, 308 K, 6.3 MPa) for characterization purposes. The impurity could be removed by flash chromatography after the next transformation. $[\alpha]_D^{23}$ = +2.3 (*c* = 0.57, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.86 (s, 1H), 4.93 (d, 1H, *J* = 9.0 Hz), 3.91 (td, 1H, *J* = 7.1, 3.6 Hz), 3.76 (s, 3H), 3.51 (dd, 1H, *J* = 7.9, 5.3 Hz), 3.07 (dq, 1H– 2.79 (m, 1H), 2.48 – 2.43 (m, 1H), 2.34 (s, 3H), 2.13 – 2.10 (m, 1H), 2.10 (s, 3H), 1.99 – 1.94 (m, 1H), 1.92 (ddq, 1H, *J* = 6.8, 5.3, 3.5 Hz), 1.66 (d, 3H, *J* = 0.8 Hz), 1.52 (dd, 1H, *J* = 14.0, 9.8 Hz), 1.47 – 1.42 (m, 2H), 1.41 – 1.39 (m, 1H), 1.39 (s, 6H), 1.38 (d, 3H, *J* = 7.0 Hz), 1.34 – 1.24 (m, 3H), 1.22 (d, 3H, *J* = 6.8 Hz), 0.96 (d, 3H, *J* = 6.7 Hz), 0.95 (d, 3H, *J* = 6.8 Hz), 0.92 ppm (d, 3H, *J* = 6.6 Hz);

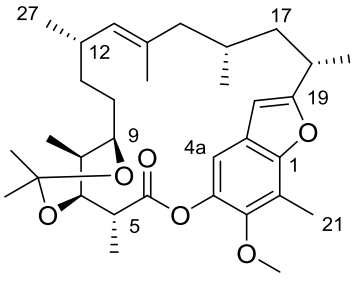
[13] J. Heppekausen, R. Stade, A. Kondoh, G. Seidel, R. Goddard, A. Fürstner, *Chem. Eur. J.* **2012**, *18*, 10281-10299.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.5, 168.5, 150.7, 148.2, 141.0, 133.3, 131.1, 126.3, 124.7, 114.3, 100.5, 99.2, 78.2, 76.3, 68.7, 61.1, 44.6, 44.5, 44.4, 35.5, 32.5, 31.6, 30.1, 27.1, 25.9, 25.3, 24.7, 21.5, 21.2, 20.7, 20.4, 18.3, 15.1, 13.0, 10.2 ppm; IR (film): $\tilde{\nu}$ = 2930, 1767, 1589, 1482, 1456, 1428, 1371, 1318, 1247, 1224, 1207, 1186, 1116, 1065, 997, 934, 851, 740, 709, 699 cm^{-1}; MS (pos. ESI) *m/z* (%): 605 (M+Na, 100); HRMS (ESI): *m/z*: calcd. for $C_{35}H_{50}O_7Na$ [M^++Na]: 605.3453, found 605.3449.

Compound S-13. K_2CO_3 (47 mg, 0.34 mmol) in H_2O (200 µL) were added to a solution of cycloalkyne **46** (100 mg, 0.172 mmol) in MeOH (8.6 mL) at 0 °C. The mixture was stirred for 1.5 h at this temperature before it was filtered through a pad of SiO_2 that was rinsed with EtOAc. The filtrate was evaporated and the residue purified by flash chromatography (SiO_2, pentane/EtOAc, 1/0 → 10/1) to afford the title compound as colorless oil (73 mg, 86%). $[\alpha]_D^{20}$ = −31.8 (*c* = 1.71, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.73 (s, 1H), 5.69 (s, 1H), 4.95 (d, 1H, *J* = 9.0 Hz), 3.90 (td, 1H, *J* = 7.4, 3.5 Hz), 3.75 (s, 3H), 3.53 (dd, 1H, *J* = 7.7, 5.1 Hz), 3.07 (dq, 1H, *J* = 7.1, 6.9 Hz), 2.92 – 2.84 (m, 1H), 2.48 – 2.40 (m, 1H), 2.18 (s, 3H), 2.18 – 2.15 (m, 1H), 2.01 – 1.97 (m, 1H), 1.95 – 1.90 (m, 1H), 1.66 (d, 3H, *J* = 1.3 Hz), 1.52 – 1.41 (m, 4H), 1.39 (s, 6H), 1.37 (d, 3H, *J* = 7.1 Hz), 1.34 – 1.28 (m, 2H), 1.26 (d, 3H, *J* = 6.9 Hz), 1.24 – 1.20 (m, 1H), 0.97 – 0.93 pm (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.1, 153.2, 151.4, 136.6, 133.1, 131.0, 122.8, 118.9, 105.5, 101.9, 100.4, 78.3, 75.3, 68.7, 61.0, 44.4, 44.4, 44.1, 34.9, 32.5, 31.7, 30.0, 27.3, 26.0, 25.5, 24.8, 21.7, 21.2, 20.4, 18.5, 15.0, 13.0, 9.5 ppm; IR (film): $\tilde{\nu}$ = 2931, 1756, 1713, 1483, 1454, 1423, 1377, 1317, 1251, 1220, 1159, 1111, 1095, 1023, 998, 881, 861, 798, 755, 663 cm^{-1}; MS (pos. ESI) *m/z* (%): 563 (M+Na, 100); HRMS (ESI): *m/z*: calcd. for $C_{33}H_{48}O_6Na$ [M^++Na]: 563.3346, found 563.3343.

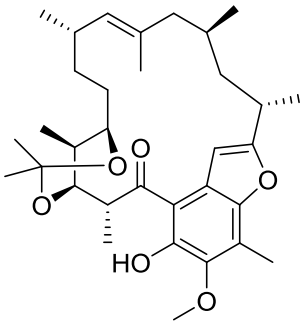


Benzofuran 47. A solution of freshly prepared [JohnphosAu]OTs (8.7 mg, 13 µmol, 10 mol%) in CH_2Cl_2 (100 µL) was added to a solution of phenol **S-13** (70 mg, 0.13 mmol) in CH_2Cl_2 (1.3 mL). After stirring for 14 h, the mixture was filtered through a pad of SiO_2. Evaporation of the filtrate and purification of the residue by flash chromatography (SiO_2, pentane/EtOAc, 1/0 → 9/1) afforded the title compound as pale yellow oil that was further subjected to HPLC purification to remove trace impurities derived from the phosphine ligand (63 mg, 79%). $[\alpha]_D^{20}$ = −27.1 (*c* = 0.35, CH_2Cl_2), ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.04 (s, 1H), 6.20 (s, 1H), 4.42 (d, 1H, *J* = 9.1 Hz), 3.80 (s, 3H), 3.77 (ddd, 1H, *J* = 9.4, 5.4, 3.4 Hz), 3.58 (dd, 1H, *J* = 9.9, 9.9 Hz), 3.14 – 3.10 (m, 1H), 3.05 (dq, 1H, *J* = 7.1, 4.5 Hz), 2.45 (s, 3H), 2.25 – 2.20 (m, 1H), 1.98 (d, 1H, *J* = 15.6 Hz), 1.91 (ddq, 1H, *J* = 6.9, 5.4, 3.4 Hz), 1.61 – 1.55 (m, 1H), 1.51 (s, 3H), 1.49 – 1.45 (m, 1H), 1.44 (s, 3H),



1.43 – 1.41 (m, 1H), 1.41 (s, 3H), 1.38 (d, 3H, *J* = 6.9 Hz), 1.35 – 1.33 (m, 1H), 1.33 (d, 3H, *J* = 7.1 Hz), 1.31 – 1.25 (m, 2H), 1.00 – 0.94 (m, 1H), 0.91 – 0.84 (m, 1H), 0.89 (d, 3H, *J* = 6.9 Hz), 0.82 (d, 3H, *J* = 6.4 Hz), 0.79 ppm (d, 3H, *J* = 6.7 Hz); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.8, 163.0, 151.6, 146.8, 140.4, 131.5, 129.4, 123.7, 115.7, 110.1, 102.9, 100.8, 78.4, 69.7, 61.7, 44.1, 42.8, 42.5, 33.8, 33.7, 32.3, 31.6, 28.3, 28.1, 26.9, 24.5, 21.6, 20.2, 19.2, 19.1, 14.4, 13.1, 9.4 ppm; IR (film): $\tilde{\nu}$ = 2930, 2872, 1758, 1604, 1456, 1417, 1377, 1324, 1226, 1194, 1108, 1024, 1002, 931, 861 cm^{-1}; MS (pos. ESI) *m/z* (%): 563 (M+Na, 100); HRMS (ESI): *m/z*: calcd. for $C_{33}H_{48}O_6Na$ [M^++Na]: 563.3346, found 563.3343. The analytical and spectroscopic data are in agreement with those reported in the literature.[10]

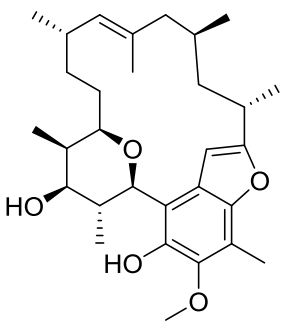
Photo-Fries Product 48. In a quartz tube (30 cm x 1.2 cm) a solution of benzofuran **47**



(37 mg, 0.068 mmol) in cyclohexane (15 mL) was degassed by bubbling argon through it via canula for 30 min. The quartz tube was then sealed and positioned directly next to a quartz photo reactor (double-walled vessel with water cooling at high flow). A Heraeus 125 W high pressure mercury gas lamp was put inside the quartz apparatus. The inner void containing the lamp was filled with argon and sealed with a plug of cotton to avoid ozone formation. The stirred pale yellow solution was irradiated for 3-5 h causing a color change to deep yellow. The solvent was removed and the crude material was purified by flash chromatography (SiO_2, pentane/EtOAc, 9/1) to afford ketone **48** as bright yellow oil (31 mg, 85%). $[\alpha]_D^{23}$ = −50.4 (*c* = 0.30, CH_2Cl_2), ^{1}H NMR (500 MHz, $CDCl_3$): δ = 13.74 (s, 1H), 6.77 (s, 1H), 4.67 (d, 1H, *J* = 9.4 Hz), 3.90 (s, 3H), 3.89 – 3.82 (m, 2H), 3.60 (dd, 1H, *J* = 8.7, 6.7 Hz), 3.12 – 3.05 (m, 1H), 2.52 – 2.46 (m, 1H), 2.50 (s, 3H), 2.30 (d, 1H, *J* = 14.5 Hz), 1.84 – 1.78 (m, 1H), 1.70 (d, 3H, *J* = 1.3 Hz), 1.60 (td, 1H, *J* = 6.9, 4.2 Hz), 1.49 (dd, 1H, *J* = 5.0, 0.4 Hz), 1.47 – 1.44 (m, 2H), 1.43 – 1.30 (m, 1H), 1.39 – 1.18 (m, 2H), 1.37 (s, 3H), 1.36 (d, 3H, *J* = 6.0 Hz), 1.35 (s, 3H), 1.34 (d, 3H, *J* = 6.3 Hz), 1.18 – 1.10 (m, 1H), 0.83 (d, 3H, *J* = 6.7 Hz), 0.82 (d, 3H, *J* = 6.2 Hz), 0.71 ppm (d, 3H, *J* = 6.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 208.1, 163.7, 156.3, 147.2, 143.5, 132.5, 129.2, 125.2, 121.9, 110.6, 103.8, 100.3, 78.2, 68.4, 60.6, 47.2, 43.8, 43.6, 37.0, 32.1, 31.7, 31.2, 30.2, 26.9, 25.9, 24.4, 21.5, 20.9, 20.0, 19.5, 15.7, 12.5, 10.0 ppm; IR (film): $\tilde{\nu}$ = 2928, 1612, 1454, 1401, 1378, 1311, 1263, 1226, 1162, 1084, 1014, 991, 939, 809, 722 cm^{-1}; MS (pos. ESI) *m/z* (%): 563 (M+Na, 100); HRMS (ESI): *m/z*: calcd. for $C_{33}H_{48}O_6Na$ [M^++Na]: 563.3347, found 563.3343. The analytical and spectroscopic data are in agreement with those reported in the literature.[10]

Tetrahydropyran 49. $NaBH_4$ (4.9 mg, 0.13 mmol) was added in one portion to a solution of ketone **48** (17 mg, 32 μmol) in MeOH (0.64 mL), causing an immediate color change from yellow to colorless. After 10 min, the reaction was quenched by the dropwise addition of aq. HCl (0.5 M, 0.33 mL) and stirring was continued for 5 min. The mixture was extracted with

CH_2Cl_2 (3 x 120 mL), and the combined organic phases were dried over $MgSO_4$ and evaporated.



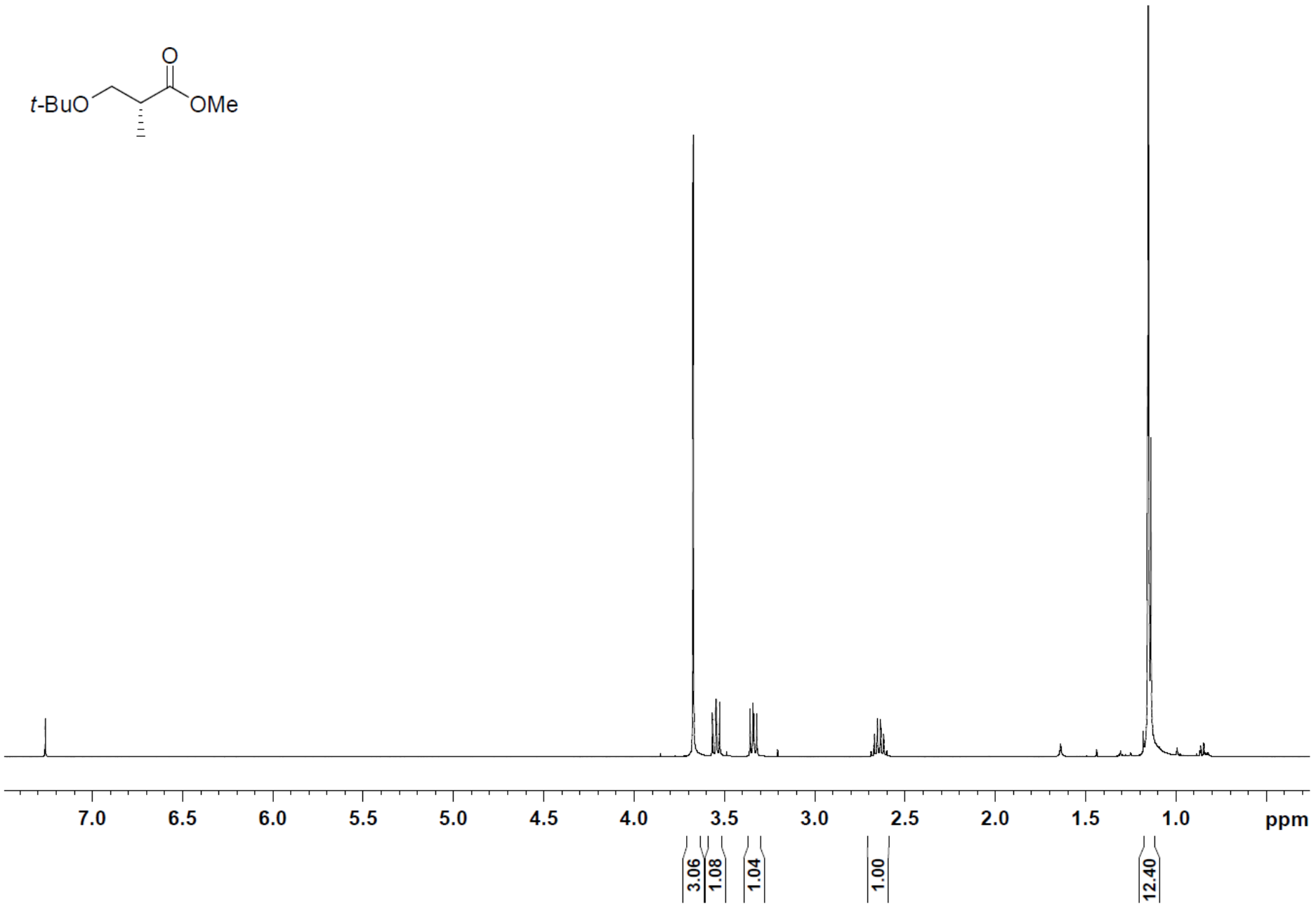
The residue was dissolved in MeOH (0.2 mL) and treated with four drops of HCl (2 M). The mixture was stirred overnight before it was diluted with H_2O (5 mL) and extracted with EtOAc (3 x 15 mL). The combined organic phases were dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (SiO_2, pentane/EtOAc, 3/2) to afford tetrahydropyran **49** as colorless oil (89%). $[\alpha]_D^{23}$ = +16.3 (*c* = 0.17, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.55 (s, 1H), 5.53 (s, 1H), 4.60 (d, 1H, *J* = 9.8– 3.62 (m, 1H), 3.44 (ddd, 1H, *J* = 11.3, 2.3, 1.5 Hz), 3.11 – 3.03 (m, 1H), 2.46 – 2.43 (m, 1H), 2.45 (s, 3H), 2.25 – 2.19 (m, 1H), 1.93 – 1.88 (m, 1H), 1.84 – 1.76 (m, 1H), 1.62 (s, 3H), 1.61 – 1.56 (m, 1H), 1.51 (d, 1H, *J* = 5.3 Hz), 1.48 – 1.41 (m, 2H), 1.38 (d, 3H, *J* = 6.9 Hz), 1.33 – 1.18 (m, 5H), 1.03 (d, 3H, *J* = 6.8 Hz), 0.90 (d, 3H, *J* = 6.6 Hz), 0.81 (d, 3H, *J* = 6.6 Hz), 0.76 ppm (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.7, 148.2, 141.7, 141.5, 131.5, 129.0, 122.2, 115.7, 112.5, 104.8, 77.8, 77.4, 77.3, 61.4, 43.8, 41.8, 39.6, 38.7, 33.7, 32.5, 31.5, 31.2, 27.5, 21.8, 21.0, 19.6, 18.7, 12.8, 9.4, 6.6 ppm; IR (film): $\tilde{\nu}$ = 2925, 1454, 1404, 1383, 1324, 1216, 1106, 1055, 998, 974, 922, 852, 808 cm^{-1}; MS (EI) *m/z* (%): 485 (32), 484 (100), 466 (18), 456 (17), 245 (29); HRMS (ESI): *m/z*: calcd. for $C_{30}H_{44}O_5Na$ [M^++Na]: 507.3082, found 507.3081. The analytical and spectroscopic data are in agreement with those reported in the literature.[10]

Table S2. Analysis of the ^{1}H and ^{13}C NMR data of cycloalkyne **46**; numbering scheme as shown in the Insert in the Experimental Part.

	^{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	-	-	-	-	-	148.2	4a, 21, 22
2	-	-	-	-	-	126.3	22
3	-	-	-	-	-	150.7	4a, 22, 23
4	-	-	-	-	-	141.0	4a, 22
5	--	-	-	-	-	172.5	6, 7, 24
6	3.07	1H	dq	7, 24	7.9, 7.0	44.6	7, 8, 24
7	3.51	1H	dd	8, 24	7.9, 5.3	78.2	6, 8, 24, 27
8	1.92	1H	ddq	7, 9, 27	6.8, 5.3, 3.5	35.5	6, 7, 10, 27
9	3.91	1H	td	8, 10a, 10b	7.1, 3.6	68.7	7, 10, 11, 27
10	1.47 – 1.39	2H	m	9, 11a, 11b	-	27.1	9, 11, 12
11	1.34 – 1.24	2H	m	10, 11b, 12	-	32.5	9, 10, 12, 13, 28, 29
12	2.48 – 2.43	1H	m	11, 13, 28	-	31.6	10, 11, 13, 28, 29
13	4.93	1H	d	12, 15a, 29	9.0	131.1	12, 14, 15, 29
14	-	-	-	-	-	133.3	12, 15, 29
15a	2.13 – 2.10	1H	m	13, 15b, 16	-	44.4	13, 17, 29, 30
15b	1.52	1H	dd	15a, 16	14.0, 9.8	44.4	
16	1.99 – 1.94	1H	m	15a, 15b, 17a, 17b, 30	-	30.1	15, 17, 18, 30
17a	1.41 – 1.39	1H	m	16, 17b, 18	-	44.5	15, 18, 30, 31
17b	1.34 – 1.24	1H	m	16, 17a, 18	-		
18	2.85 – 2.79	1H	m	17a, 17b, 31	-	24.7	17, 31
19	-	-	-	-	-	99.2	17, 18, 31
20	-	-	-	-	-	76.3	4a, 17, 18, 22
21	2.34	3H	s	-	-	20.7	-
22	2.10	3H	s	4a	-	10.2	-
23	3.76	3H	s	-	-	61.1	-
24	1.38	3H	d	6	7.0	15.1	6, 7
25	-	-	-	-	-	100.5	7, 9, 26a, 26b
26a	1.39	6H	s	-	-	25.9	26b
26b				-	-	25.3	26a
27	0.95	3H	d	8	6.8	13.0	7, 8, 9
28	0.96	3H	d	12	6.7	20.4	11, 12, 13, 29
29	1.66	3H	d	13	0.8	18.3	13, 15
30	0.92	3H	d	16	6.6	21.2	15, 17
31	1.22	3H	d	18	6.8	21.5	17, 18

Table S3. Analysis of the ^{1}H and ^{13}C NMR data of benzofuran **47**; numbering scheme as shown in the Insert in the Experimental Part.

^{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	-	-	-	-	-	151.6	4a, 20, 21
2	-	-	-	-	-	115.7	4a, 21
3	-	-	-	-	-	146.8	4a, 21, 22
4	-	-	-	-	-	140.4	4a
5	-	-	-	-	-	172.8	5, 6, 23
6	3.05	1H	dq	7, 23	7,1, 4.5	44.1	7, 8, 23
7	3.58	1H	dd	5, 8	9.9, 9.9	78.4	6, 8, 9, 23, 26
8	1.91	1H	ddq	7, 9, 26	6.9, 5.4, 3.4	33.7	6, 7, 9, 10, 26
9	3.77	1H	ddd	8, 10a, 10b	9.4, 5.4, 3.4	69.7	7, 10, 11, 26
10a	1.43 – 1-41	1H	m	9, 10b, 11a, 11b	-	28.1	9, 11, 12
10b	1.31 – 1.25	1H	m	9, 10a, 11a, 11b	-		
11a	1.00 – 0.94	1H	m	10a, 10b, 11b, 12	-	33.8	9, 10, 12, 13, 27
11b	0.91 – 0.84	1H	m	10a, 10b, 11a, 12	-		
12	2.25 – 2.20	1H	m	11a, 11b, 13, 27	-	32.3	10, 11, 13, 27, 28
13	4.42	1H	d	12, 15a, 28	9.1	129.4	11, 12, 15, 27, 28
14	-	-	-	-	-	131.5	12, 15, 28
15a	1.98	1H	d	13, 15b, 16, 28	15.6	42.5	13, 17, 28, 29
15b	1.35 – 1.33	1H	m	15a, 16	-		
16	1.31 – 1.27	1H	m	15a, 15b, 17a, 17b, 29	-	28.3	15, 17, 18, 29
17a	1.61 – 1.55	1H	m	16, 17b, 18	-	42.8	15, 18, 29, 30
17b	1.49 – 1.45	1H	m	16, 17a, 18	-		
18	3.14 – 3.10	1H	m	17a, 17b, 30	-	31.6	17, 20, 30
19	-	-	-	-	-	163.0	4a, 17, 18, 20, 30
20	6.20	1H	s	-	-	102.9	4a, 18
21	2.45	3H	s	4a	-	9.4	20
22	3.80	3H	s	-	-	61.7	21
23	1.33	3H	d	6	7.1	14.4	6, 7
24	-	-	-	-	-	100.8	7, 9, 25a, 25b
25a	1.44	3H	s	-	-	26.9	25b
25b	1.41	3H	s	-	-	24.5	25a
26	0.89	3H	d	8	6.9	13.1	7, 8, 9
27	0.79	3H	d	12	6.7	20.2	11, 12, 13
28	1.51	3H	s	13, 15a	-	19.1	13, 15
29	0.82	3H	d	16	6.4	21.6	15, 17
30	1.39	3H	d	18	6.9	19.2	18, 20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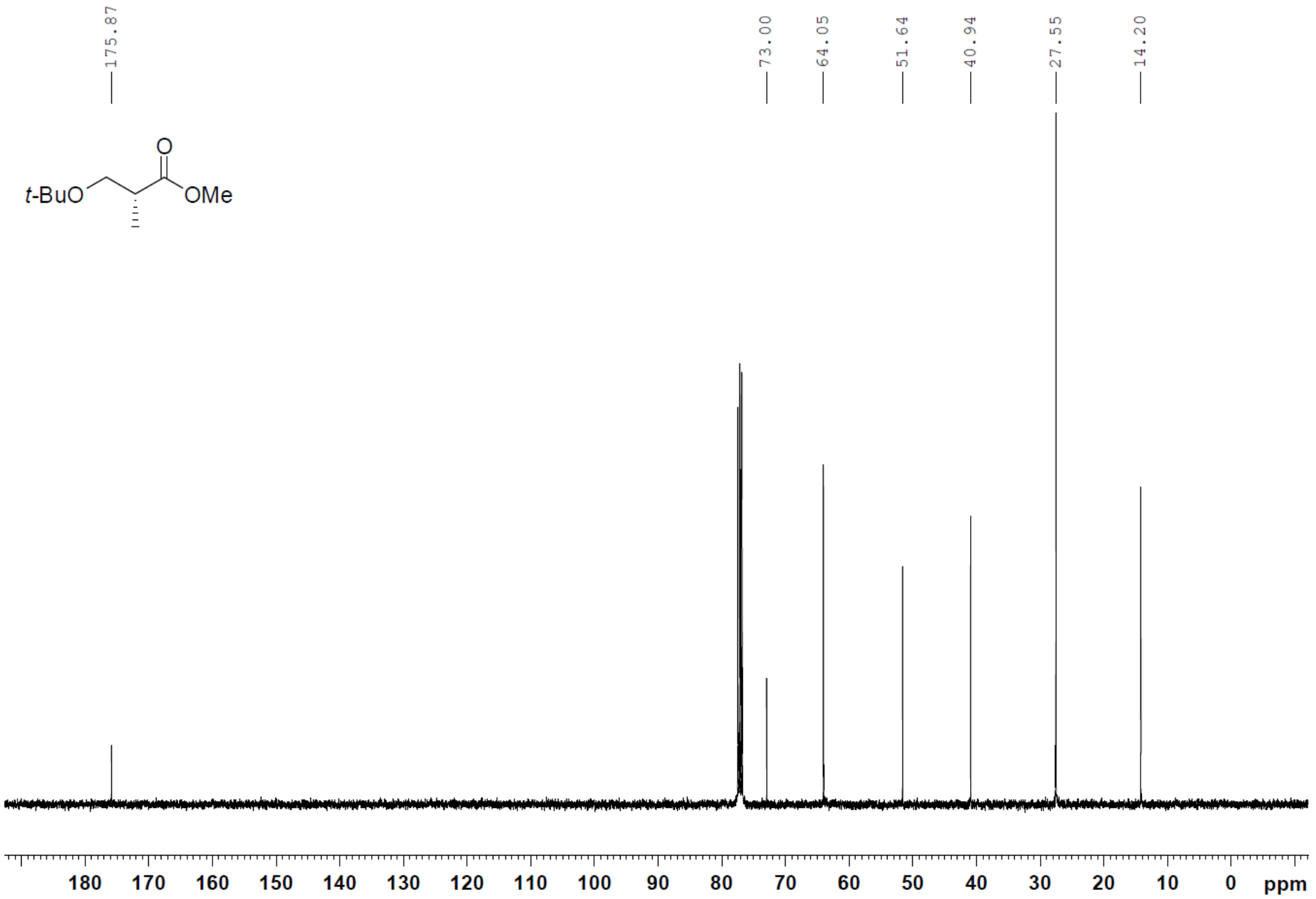
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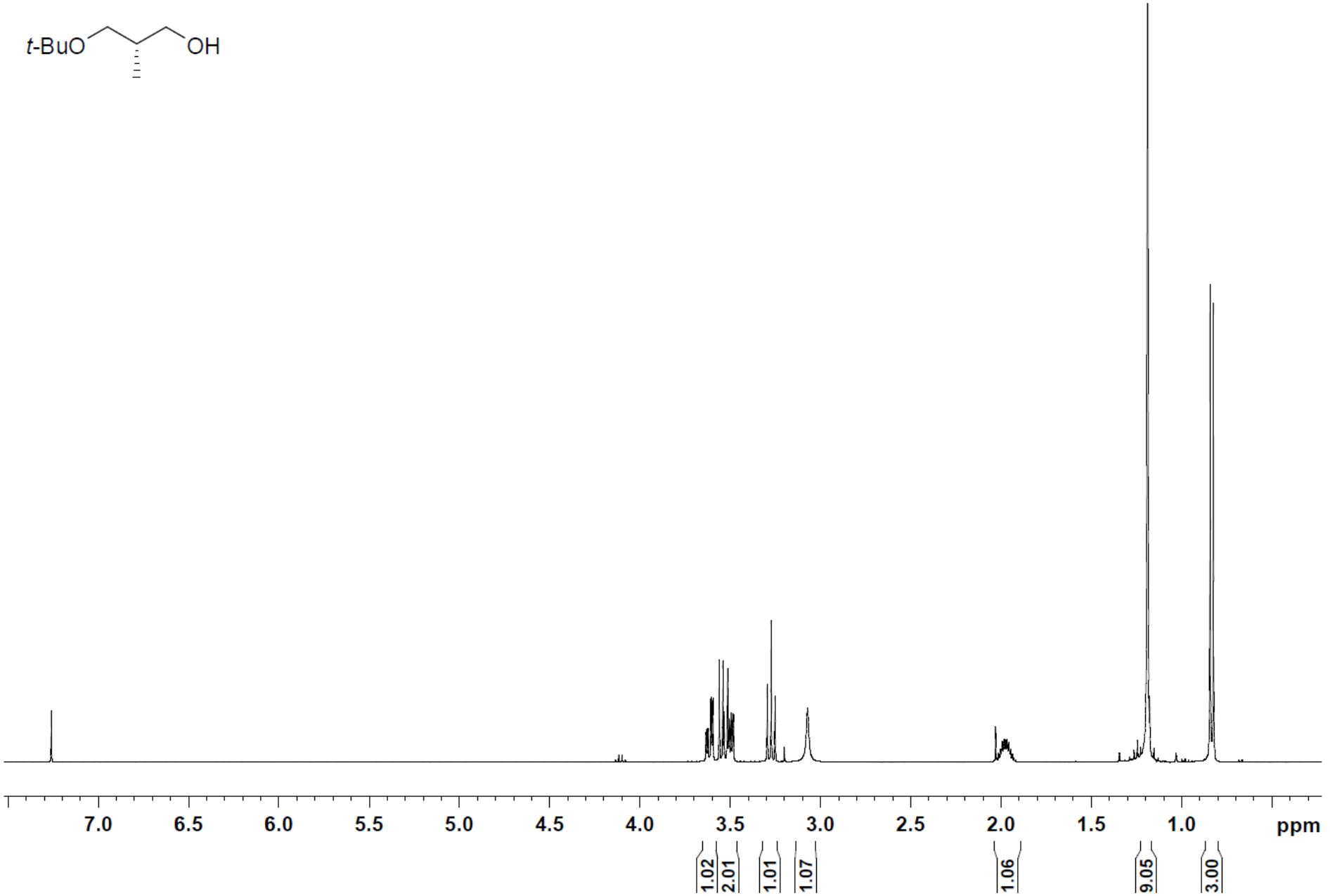
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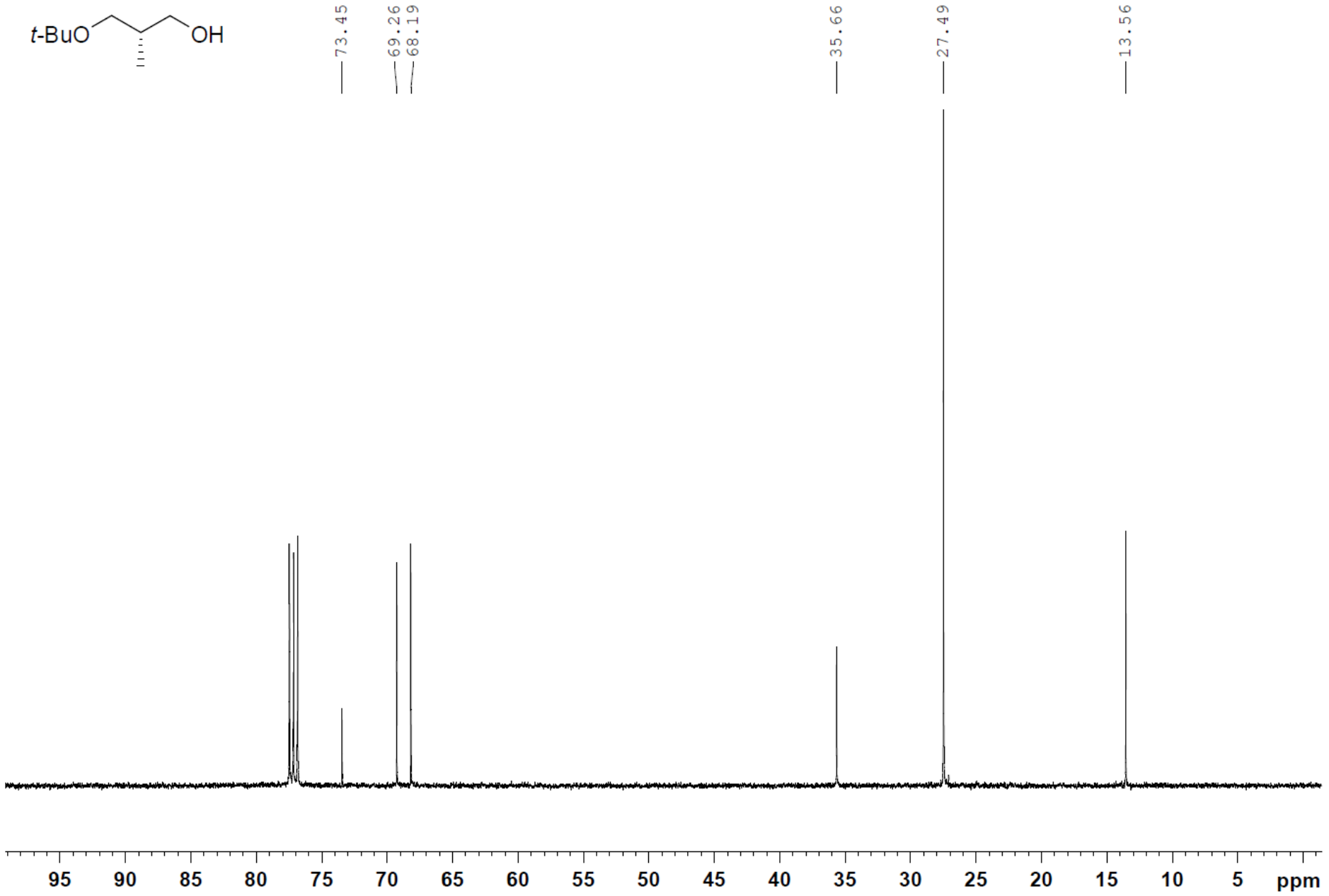
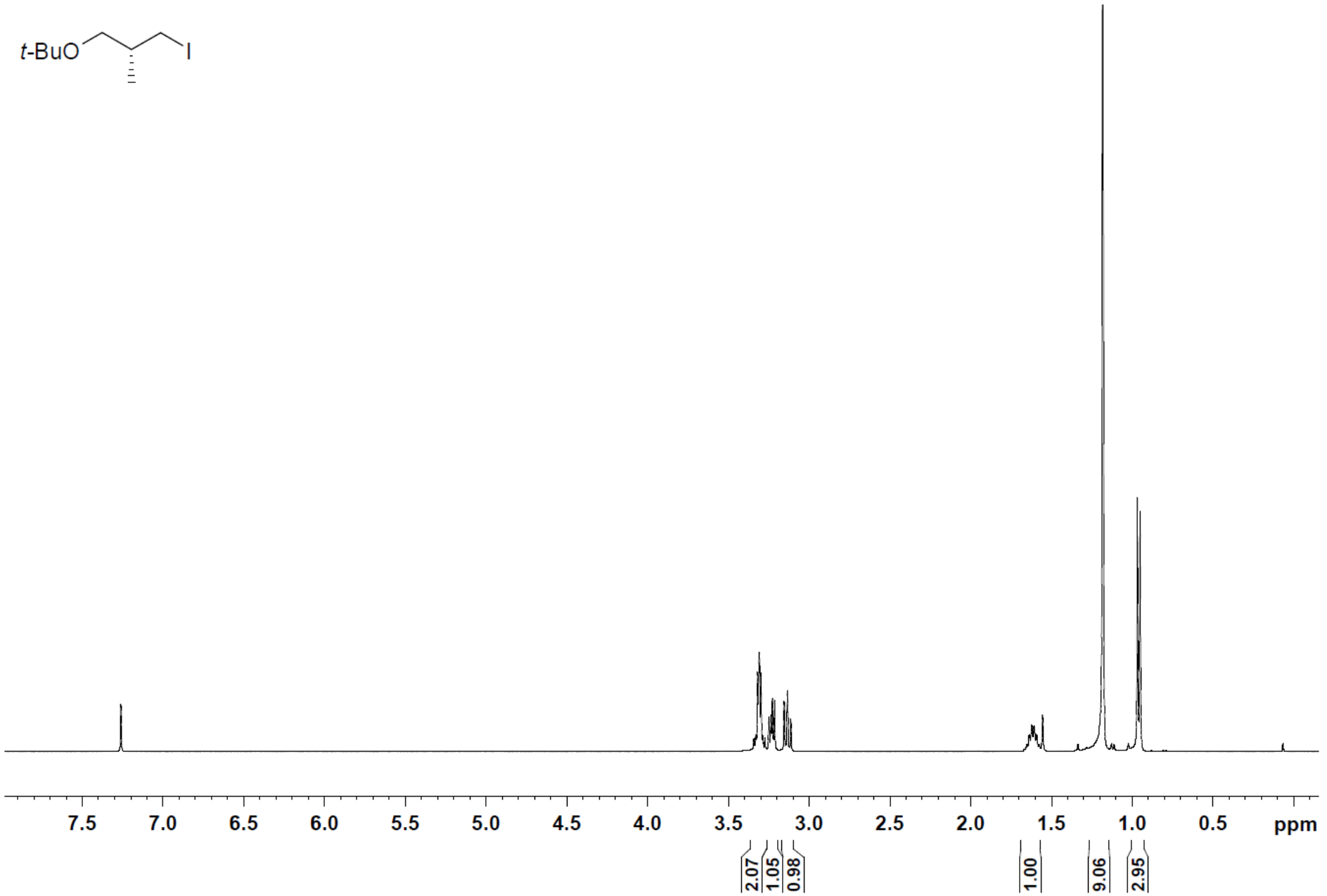
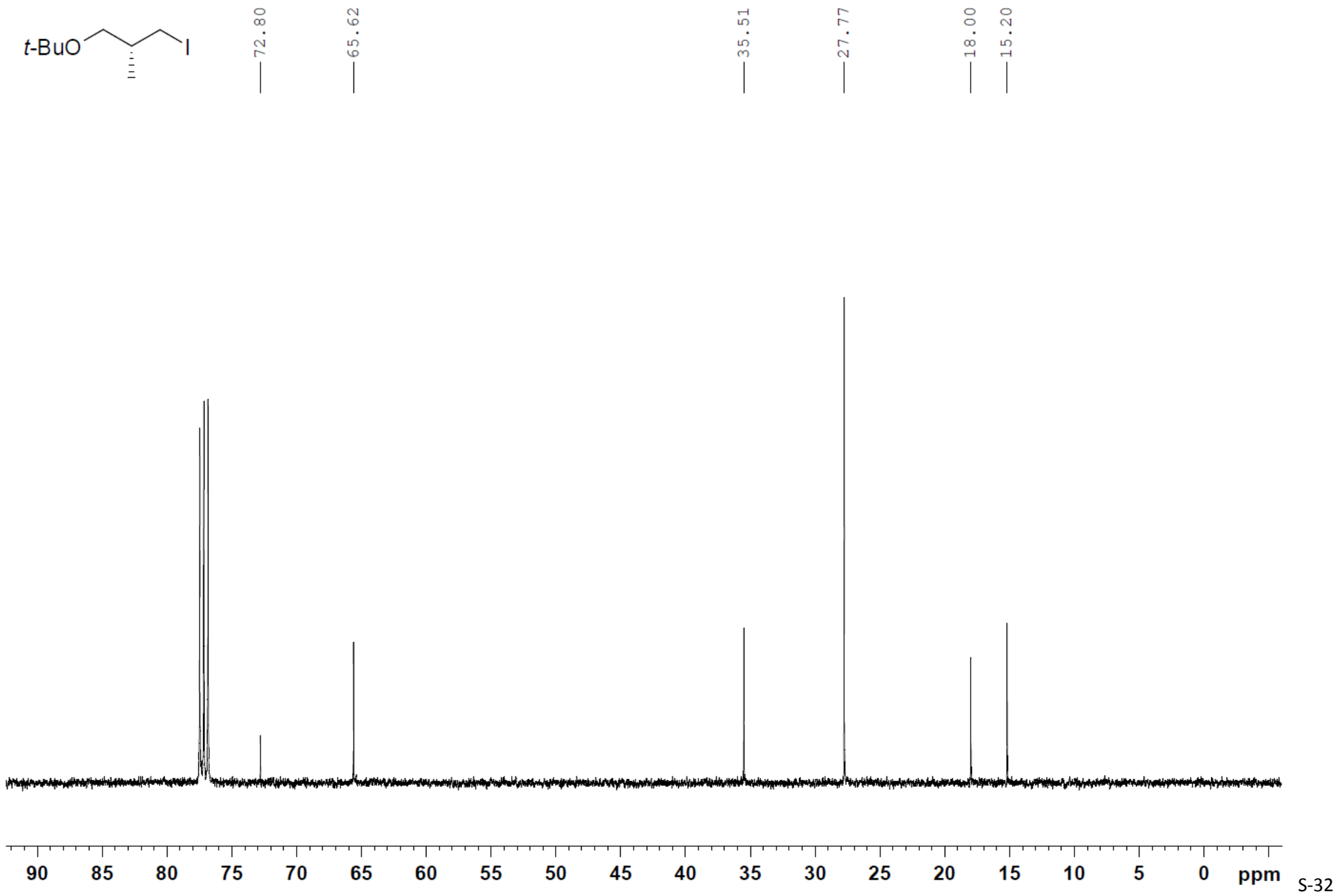
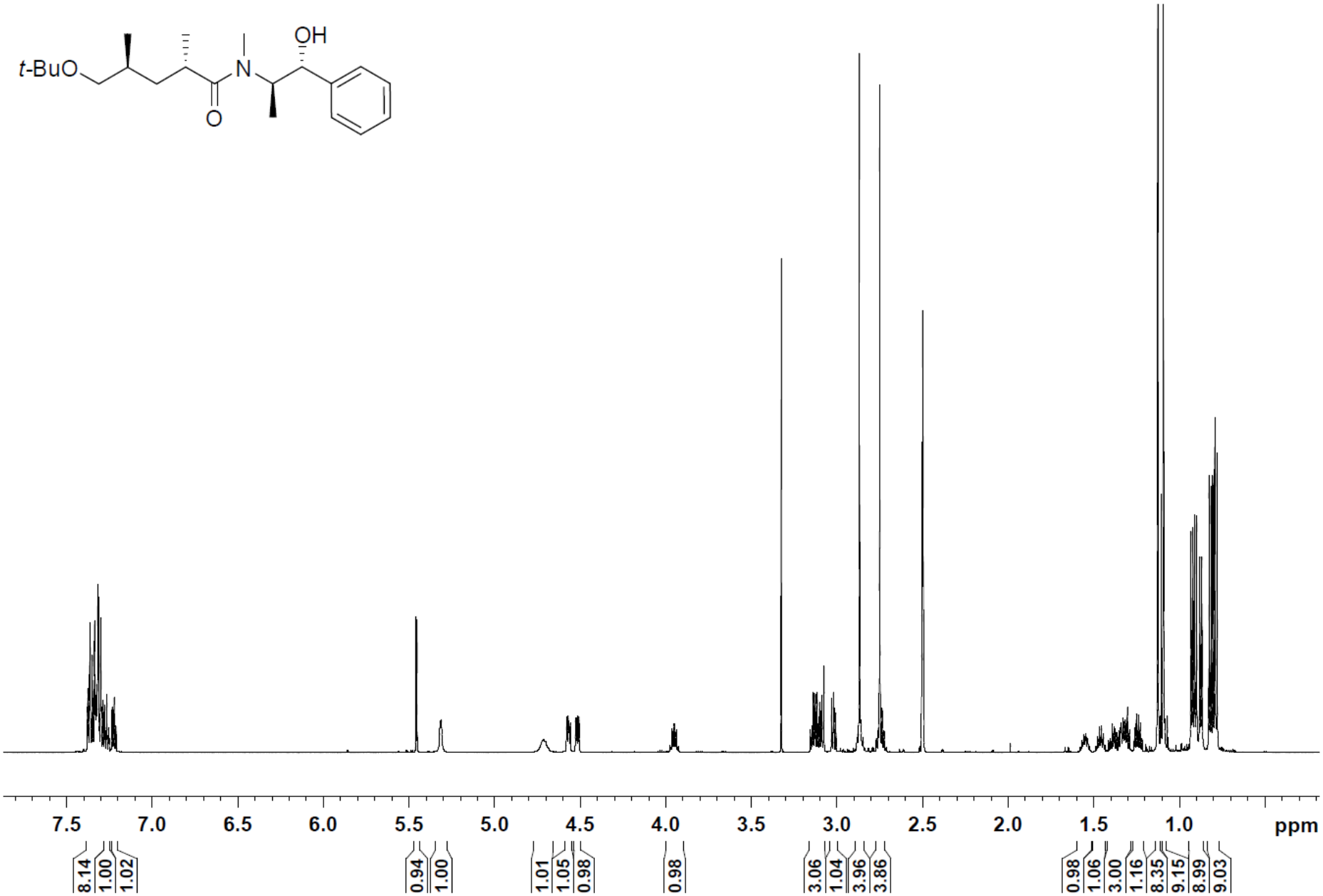
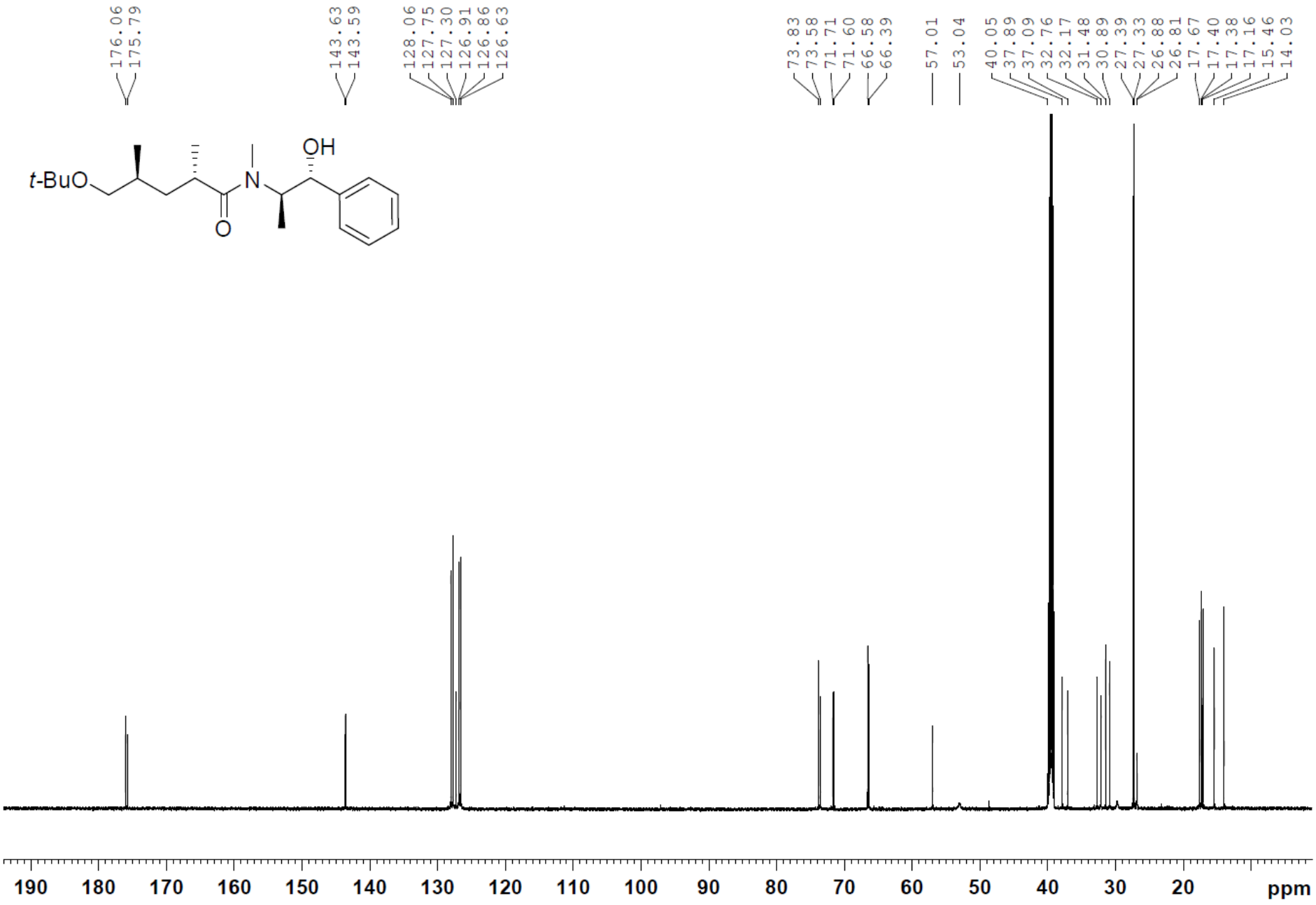
9.05
3.00

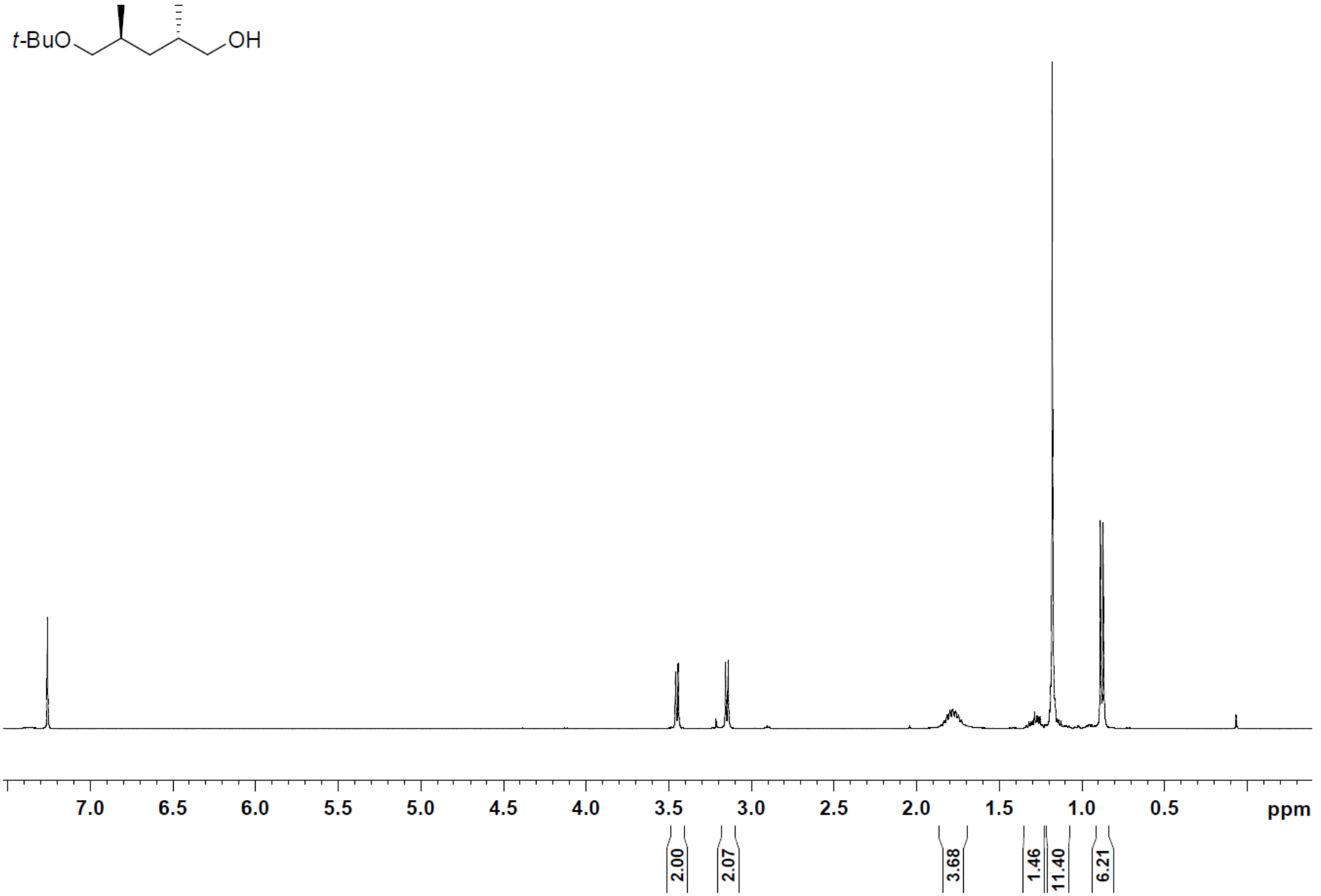

t-BuO
OH
73.45
69.26
68.19
35.66
27.49
13.56
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
ppm

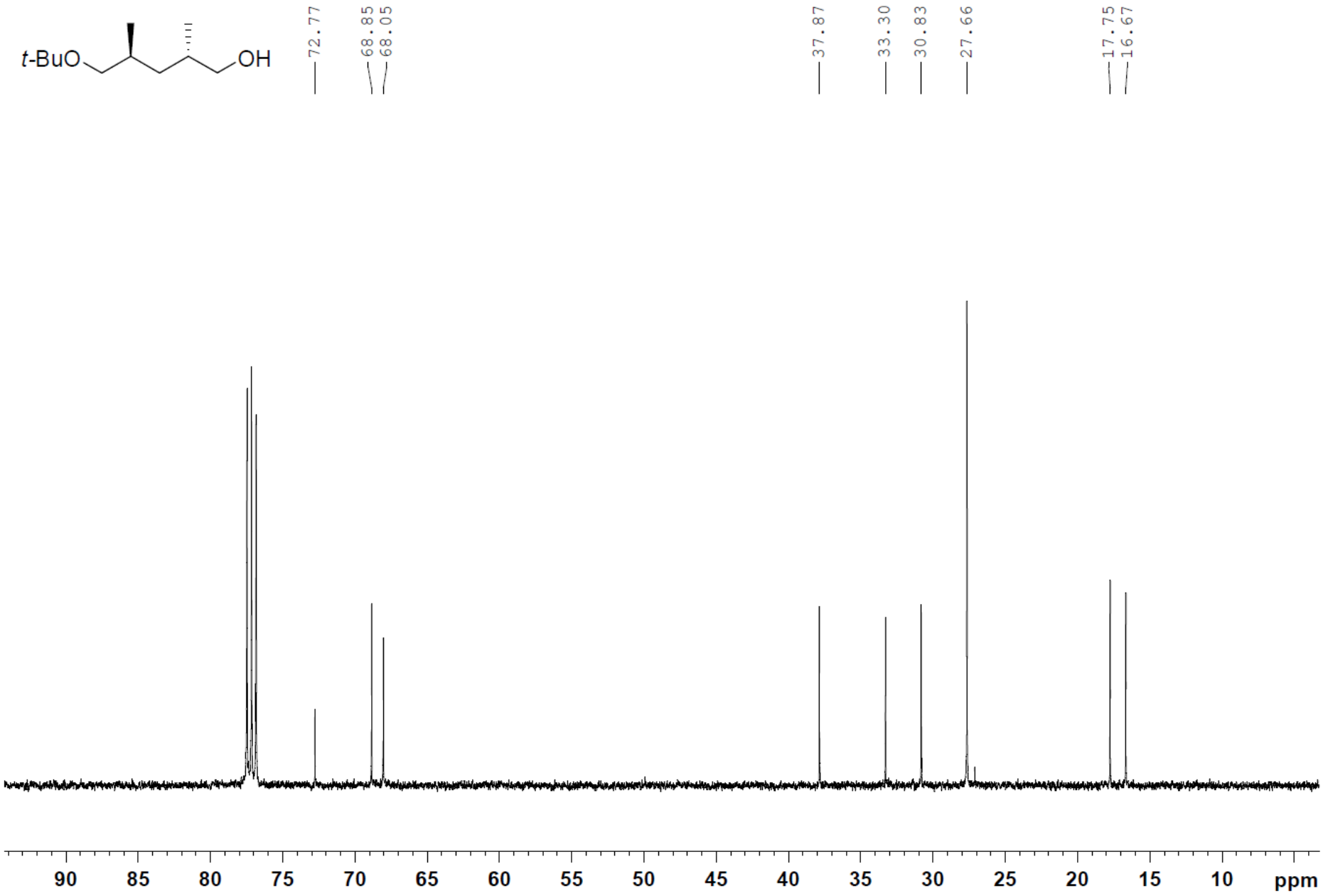

t-BuO
I
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.07
1.05
0.98
1.00
9.06
2.95

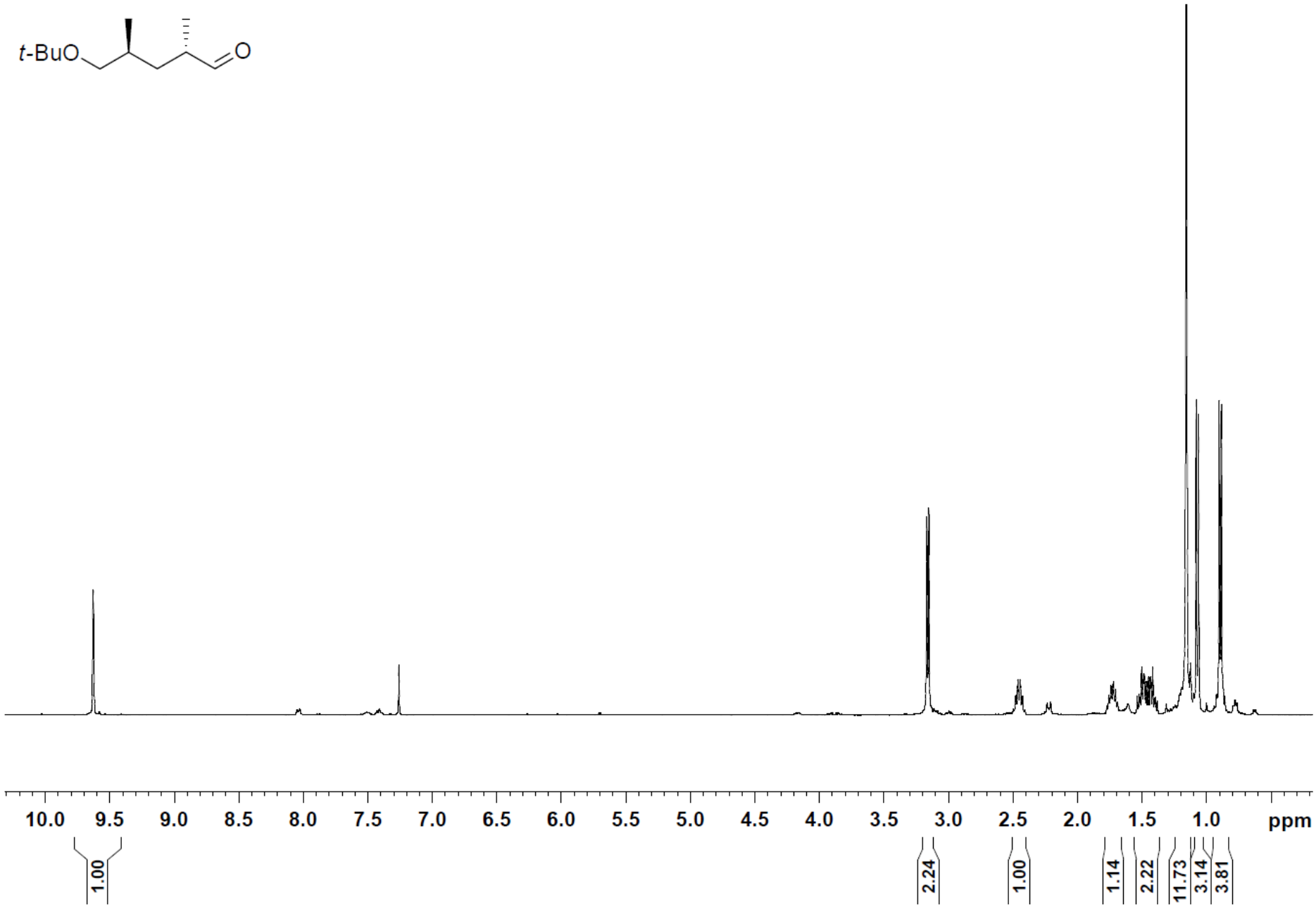

t-BuO
I
72.80
65.62
35.51
27.77
18.00
15.20
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
ppm

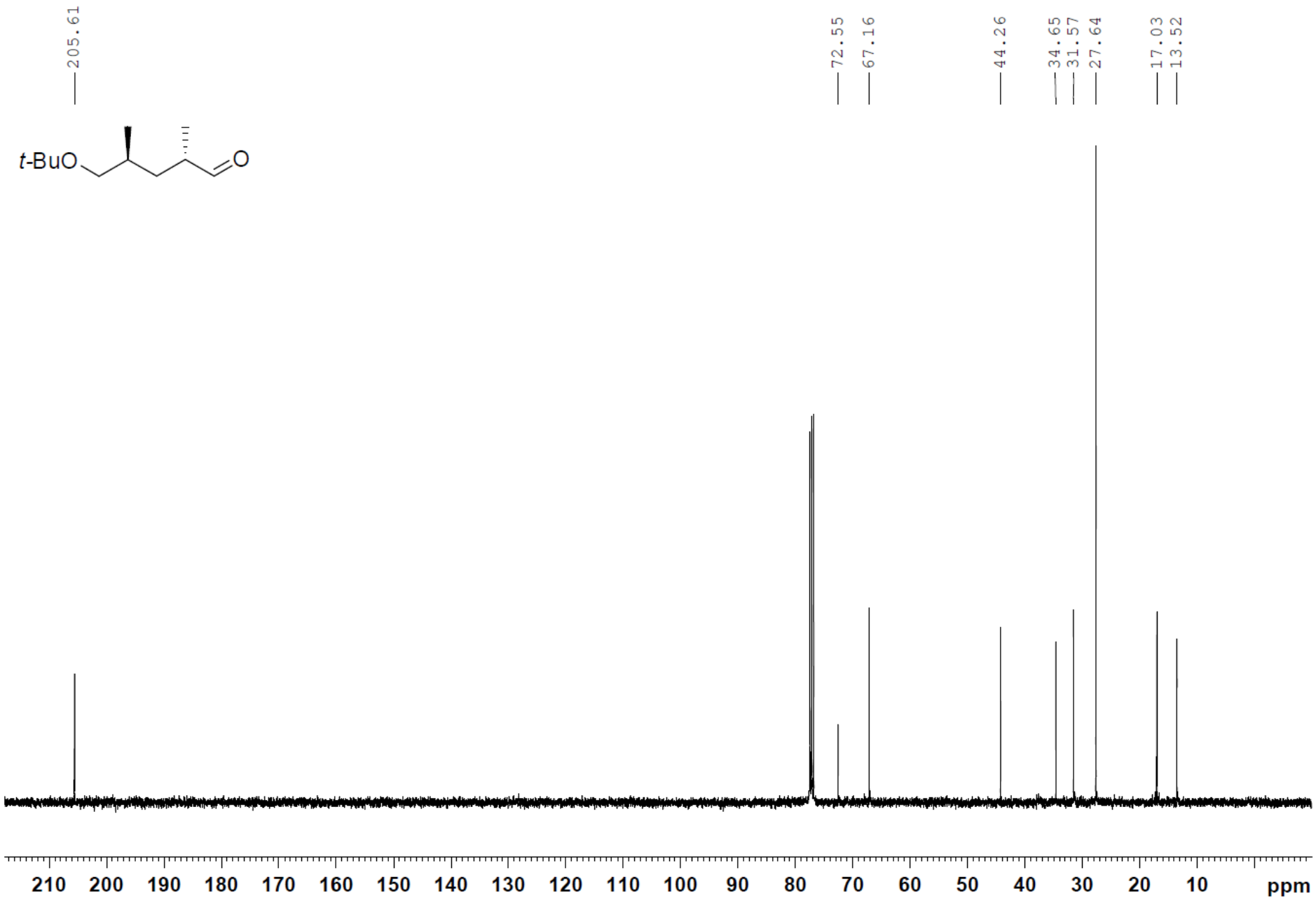

t-BuO
N
OH
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
8.14
1.00
1.02
0.94
1.00
1.01
1.05
0.98
0.98
3.06
1.04
3.96
3.86
0.98
1.06
3.00
1.16
8.35
9.15
8.99
9.03

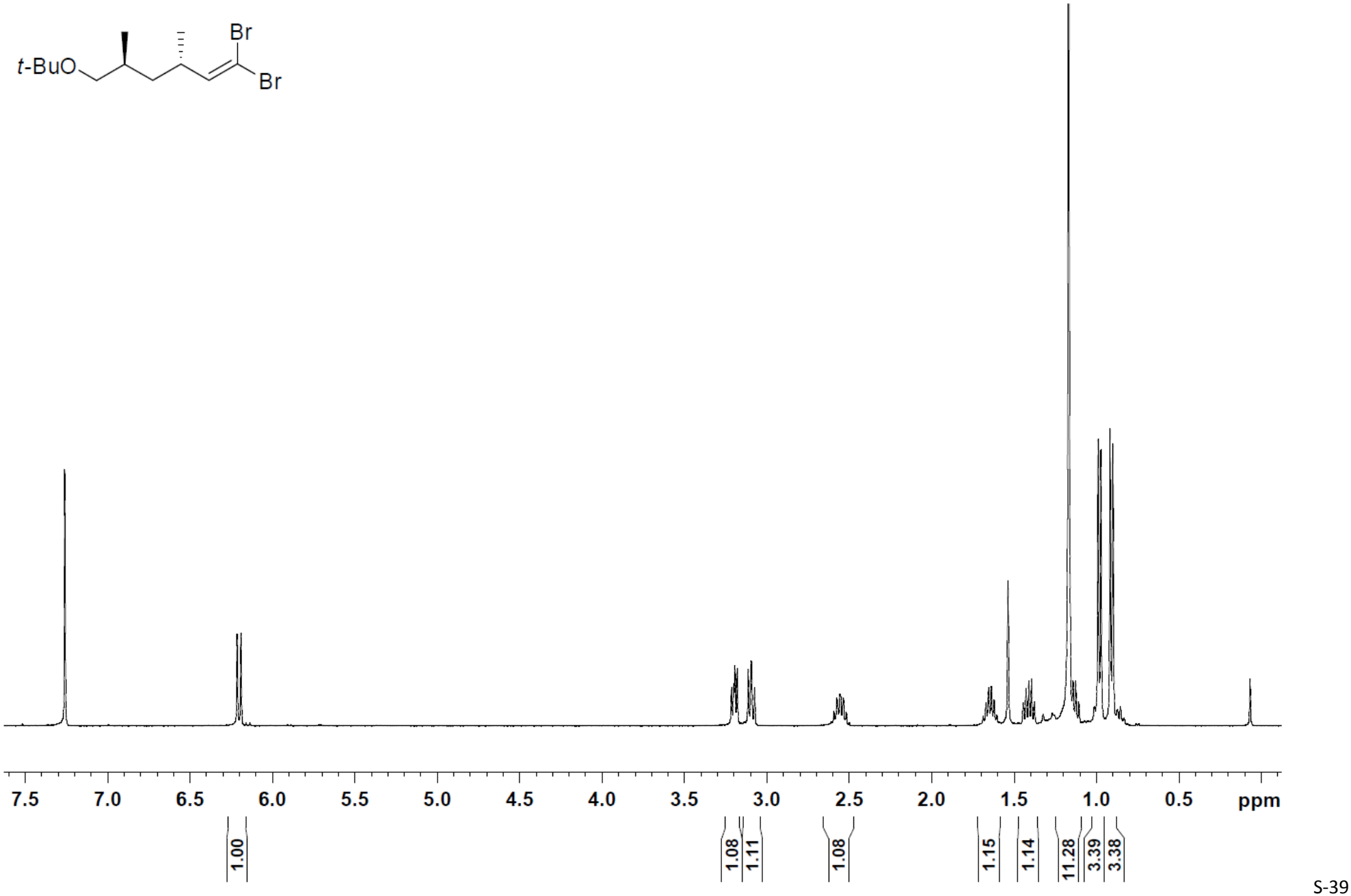

176.06
175.79
143.63
143.59
128.06
127.75
127.30
126.91
126.86
126.63
73.83
73.58
71.71
71.60
66.58
66.39
57.01
53.04
40.05
37.89
37.09
32.76
32.17
31.48
30.89
27.39
27.33
26.88
26.81
17.67
17.40
17.38
17.16
15.46
14.03
t-BuO
N
OH
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

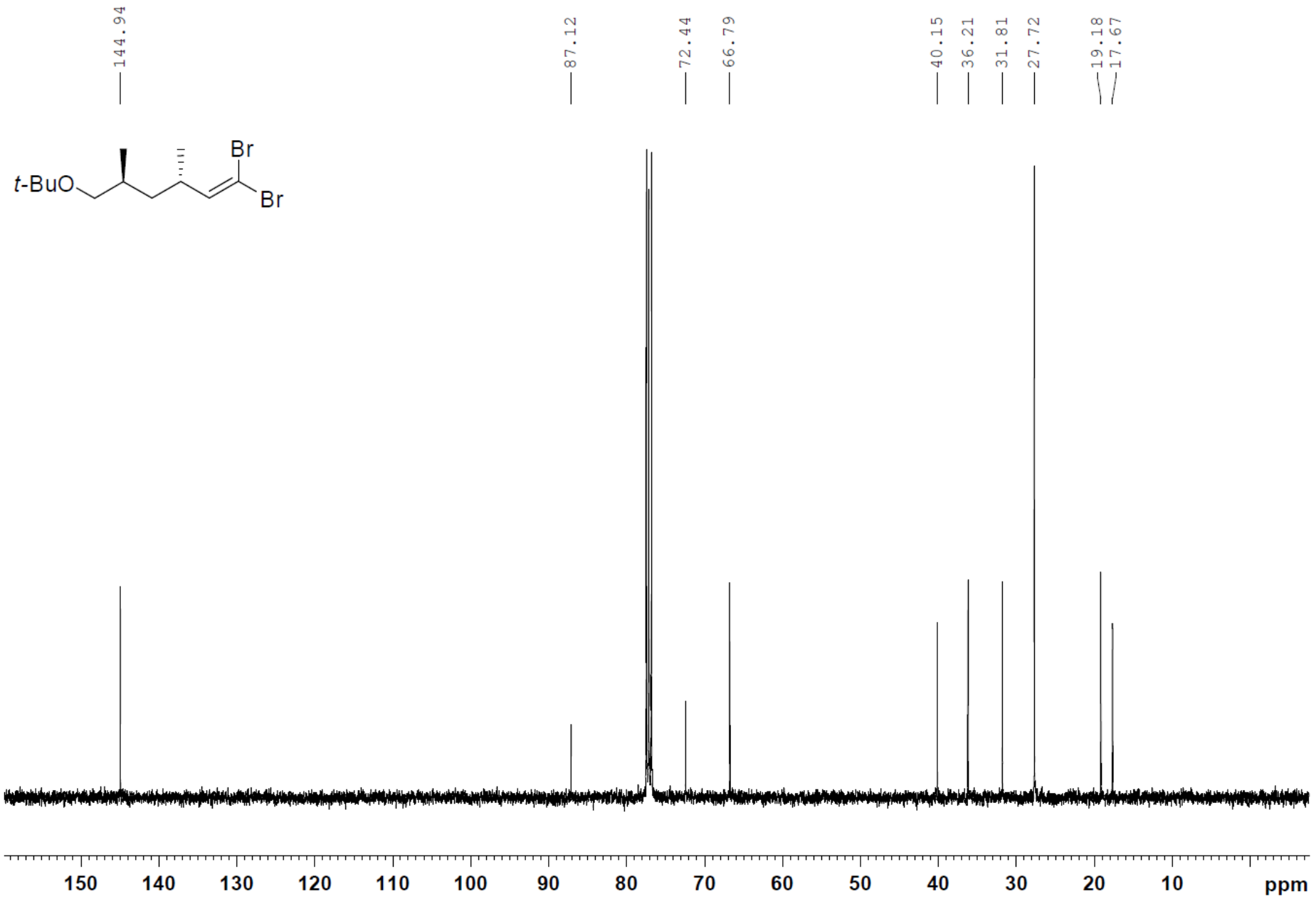

t-BuO
OH
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.07
3.68
1.46
11.40
6.21

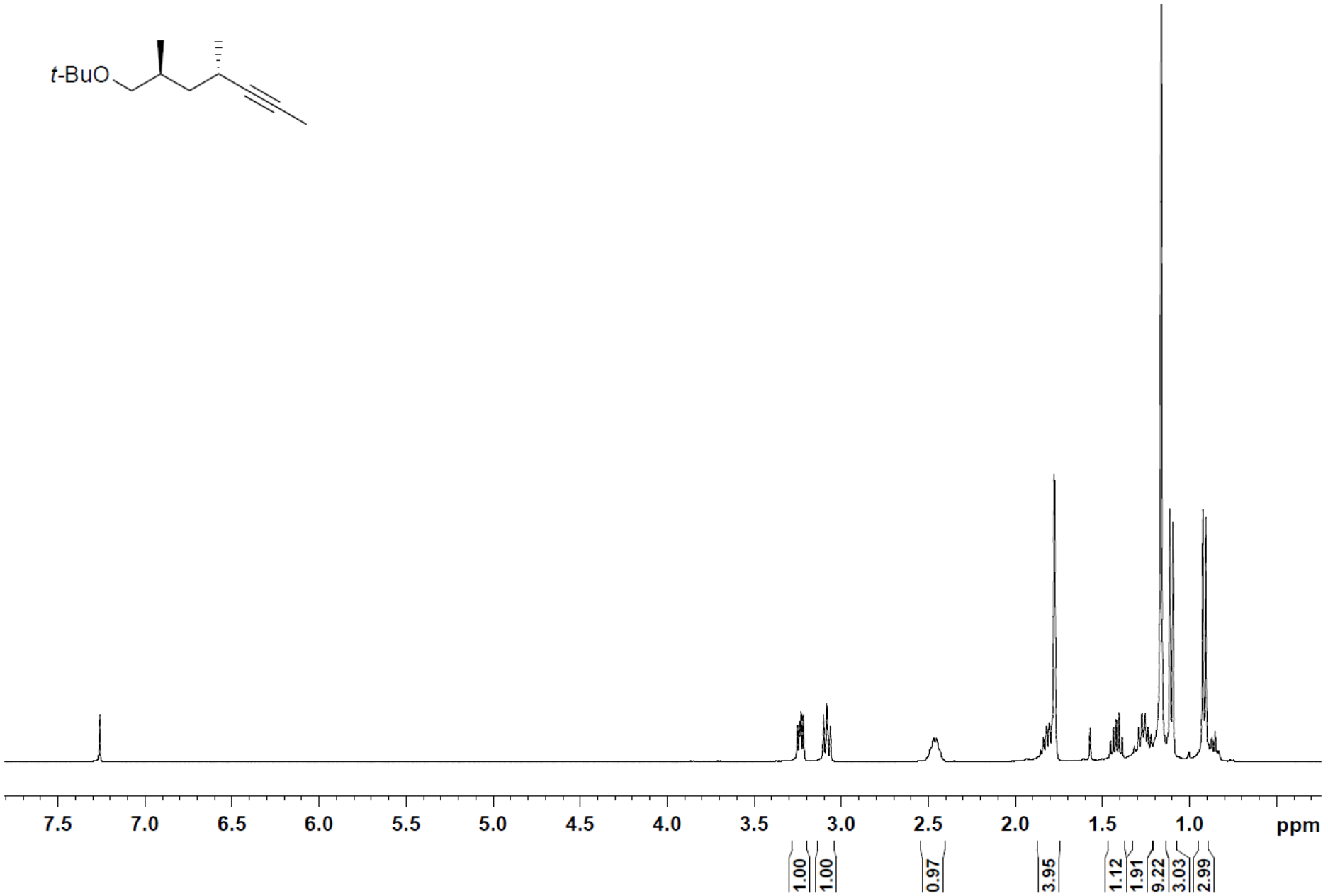

t-BuO
OH
72.77
68.85
68.05
37.87
33.30
30.83
27.66
17.75
16.67
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
ppm

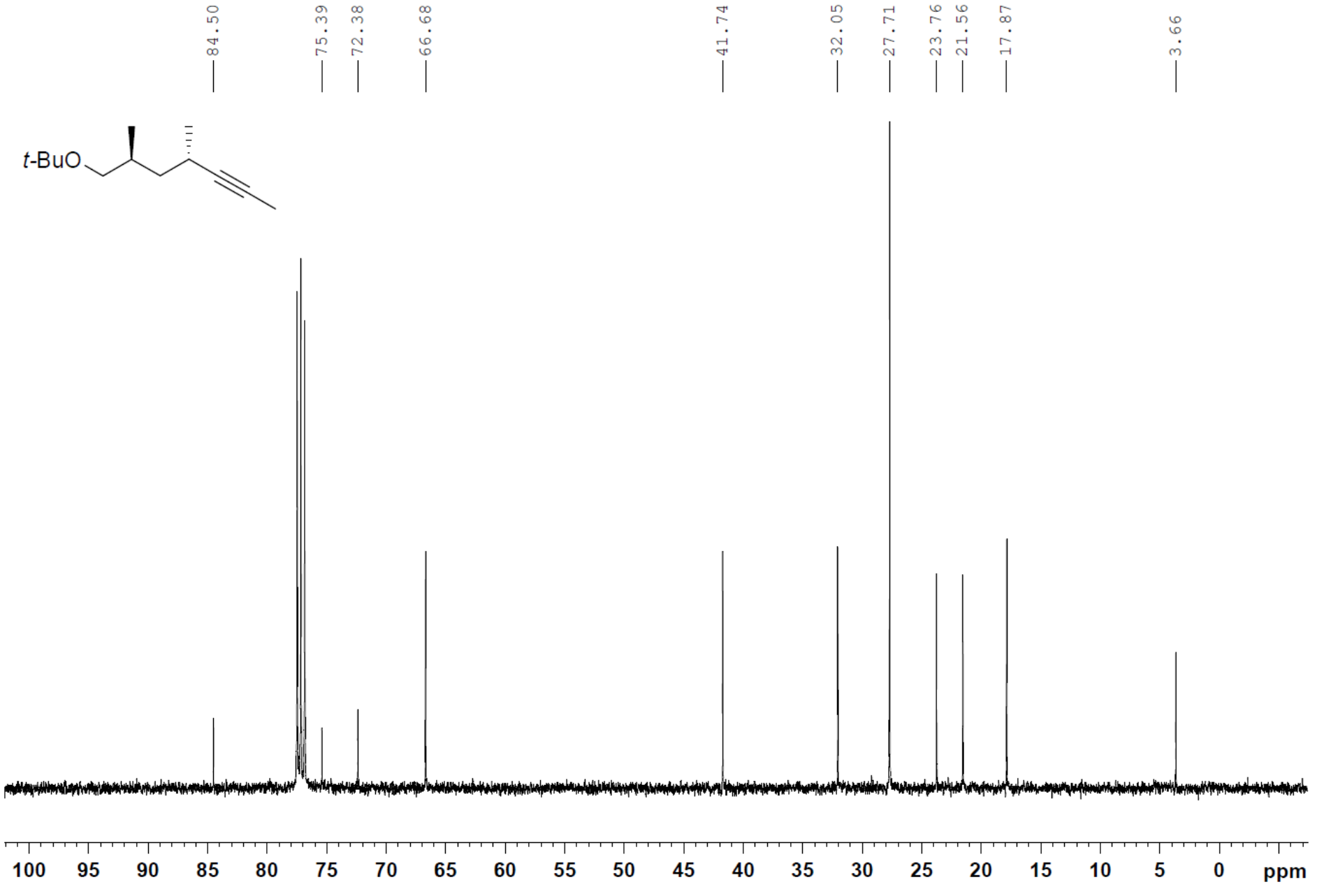

t-BuO
O
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
2.24
1.00
1.14
2.22
11.73
3.14
3.81

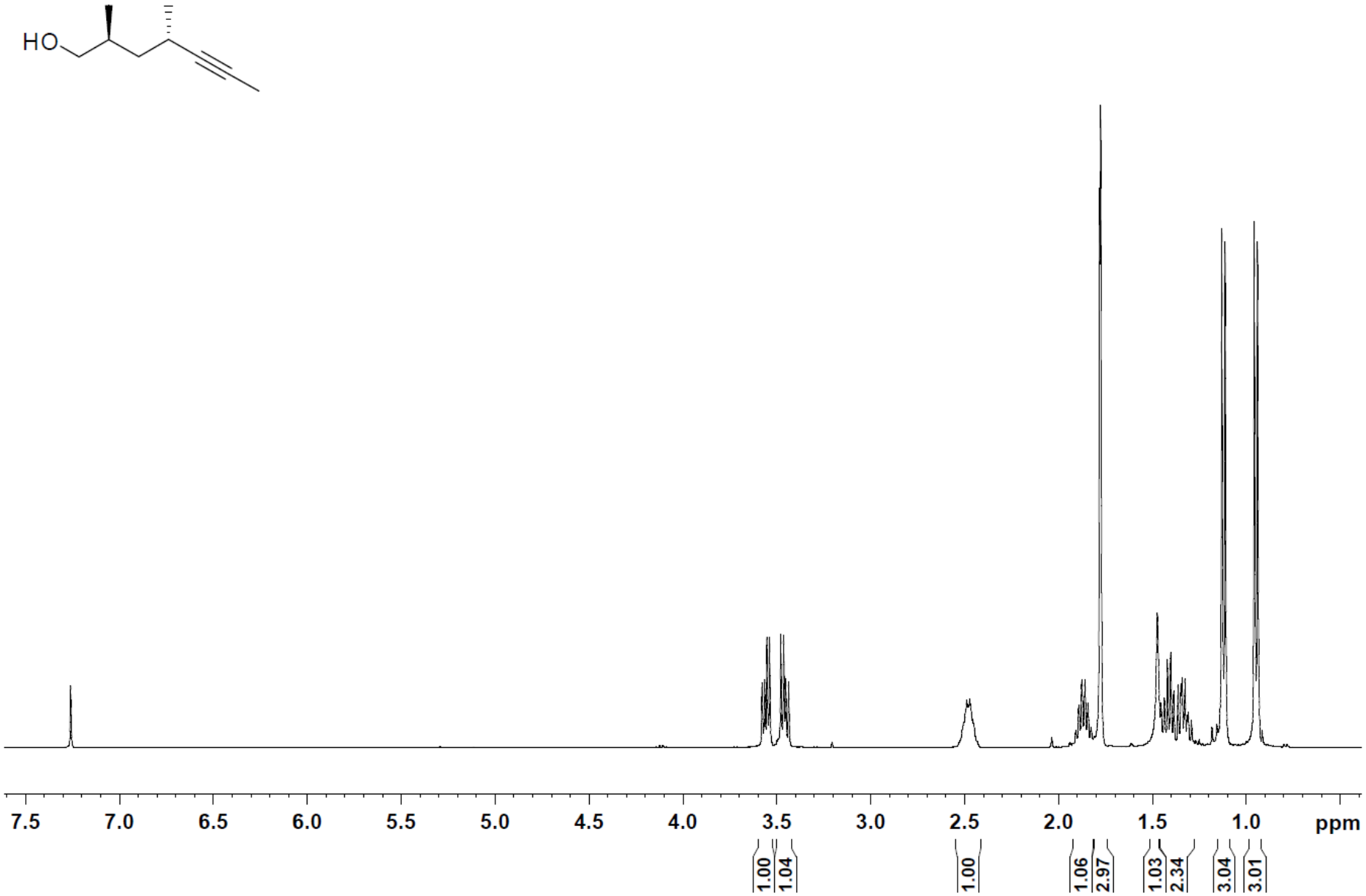

205.61
72.55
67.16
44.26
34.65
31.57
27.64
17.03
13.52
t-BuO
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

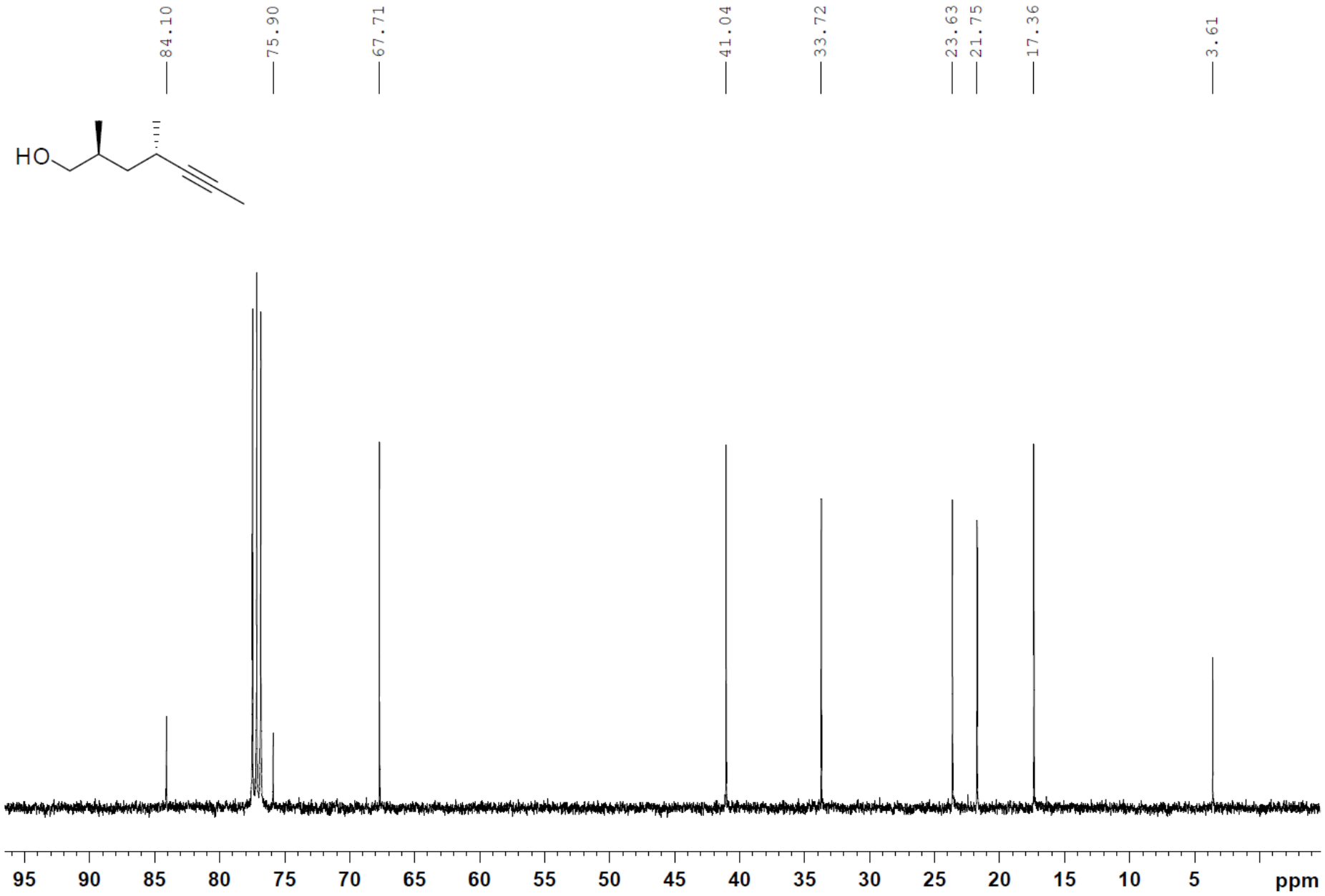

t-BuO
Br
Br
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.08
1.11
1.08
1.15
1.14
11.28
3.39
3.38

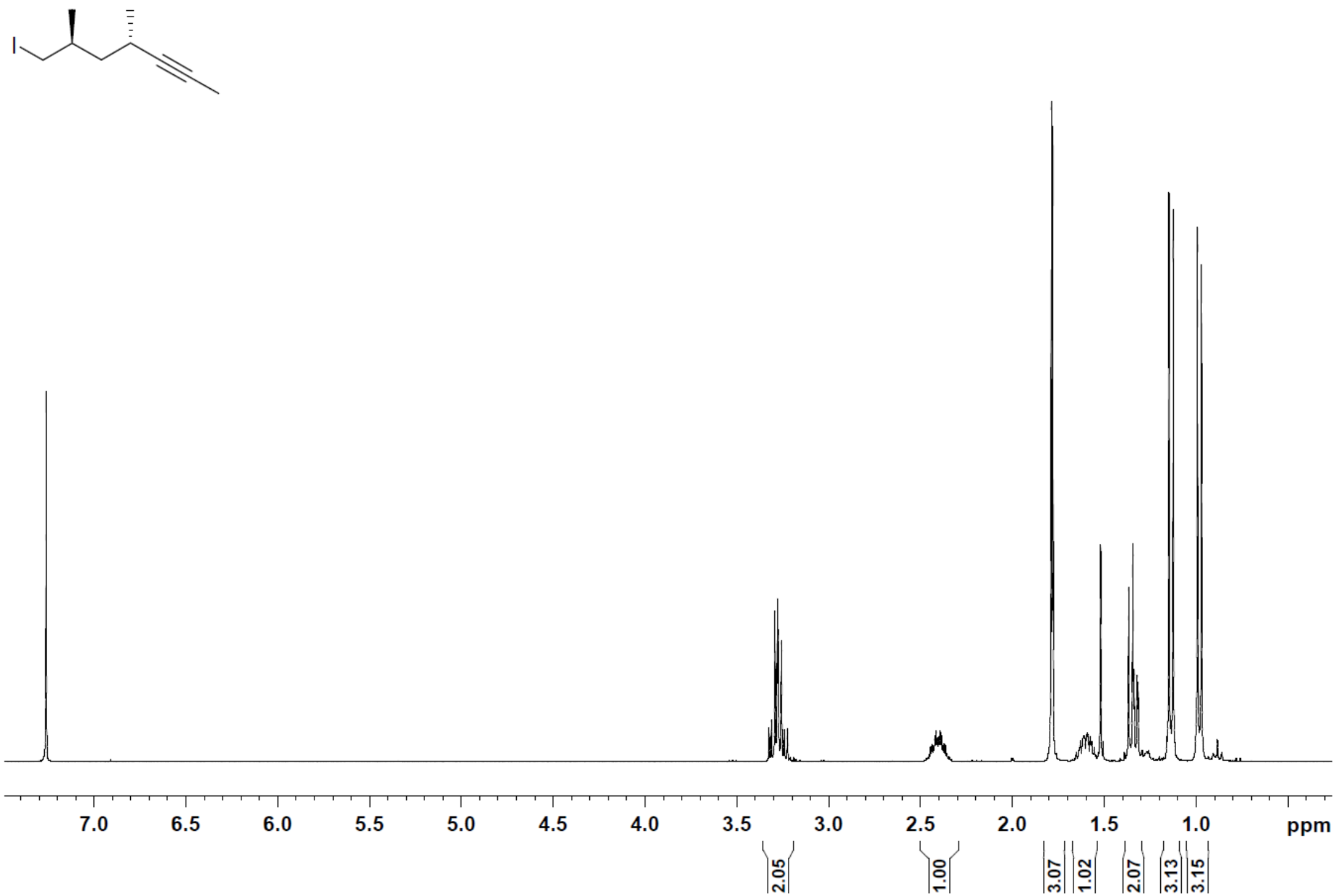

144.94
87.12
72.44
66.79
40.15
36.21
31.81
27.72
19.18
17.67
t-BuO
Br
Br
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

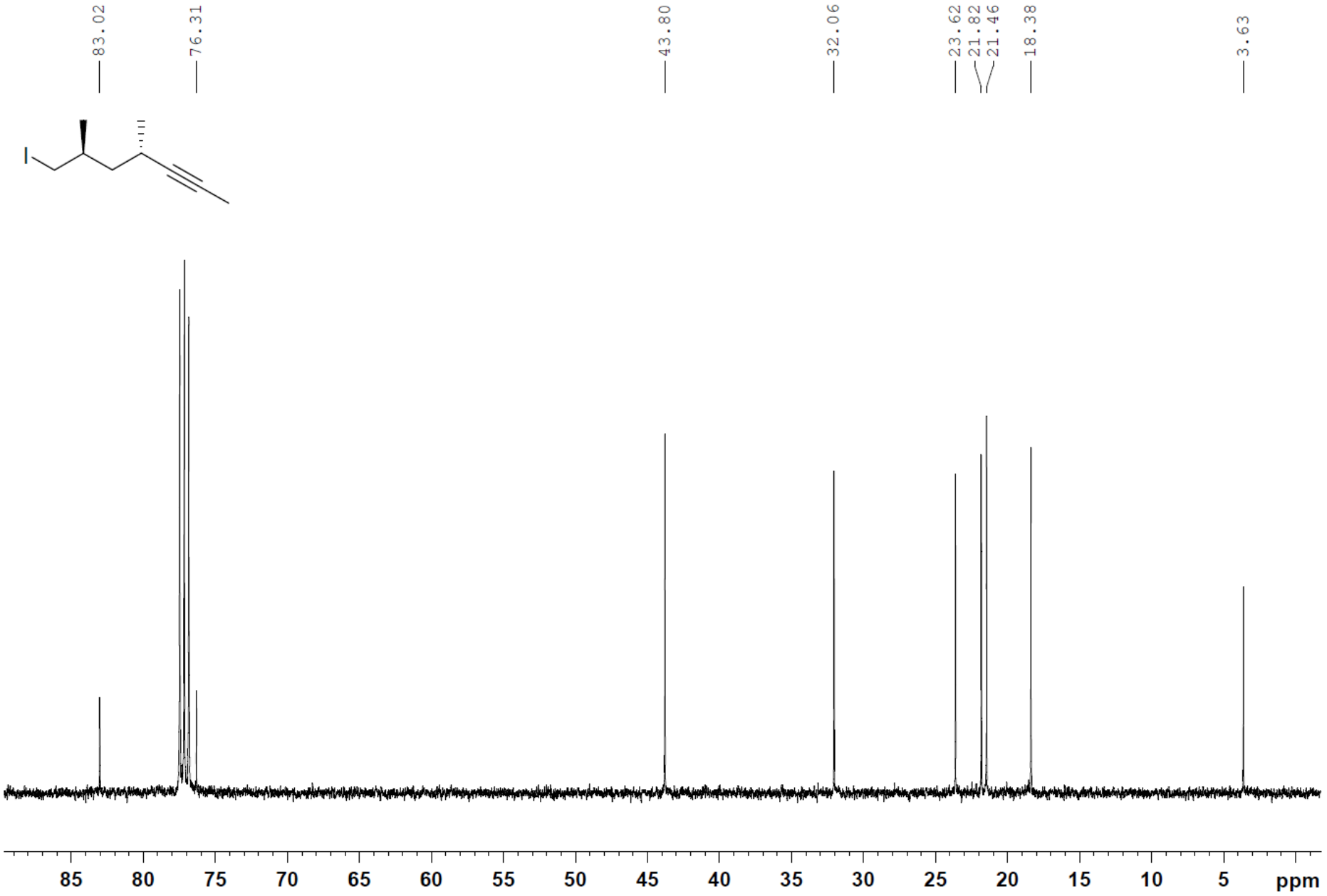

t-BuO
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
0.97
3.95
1.12
1.91
9.22
3.03
2.99

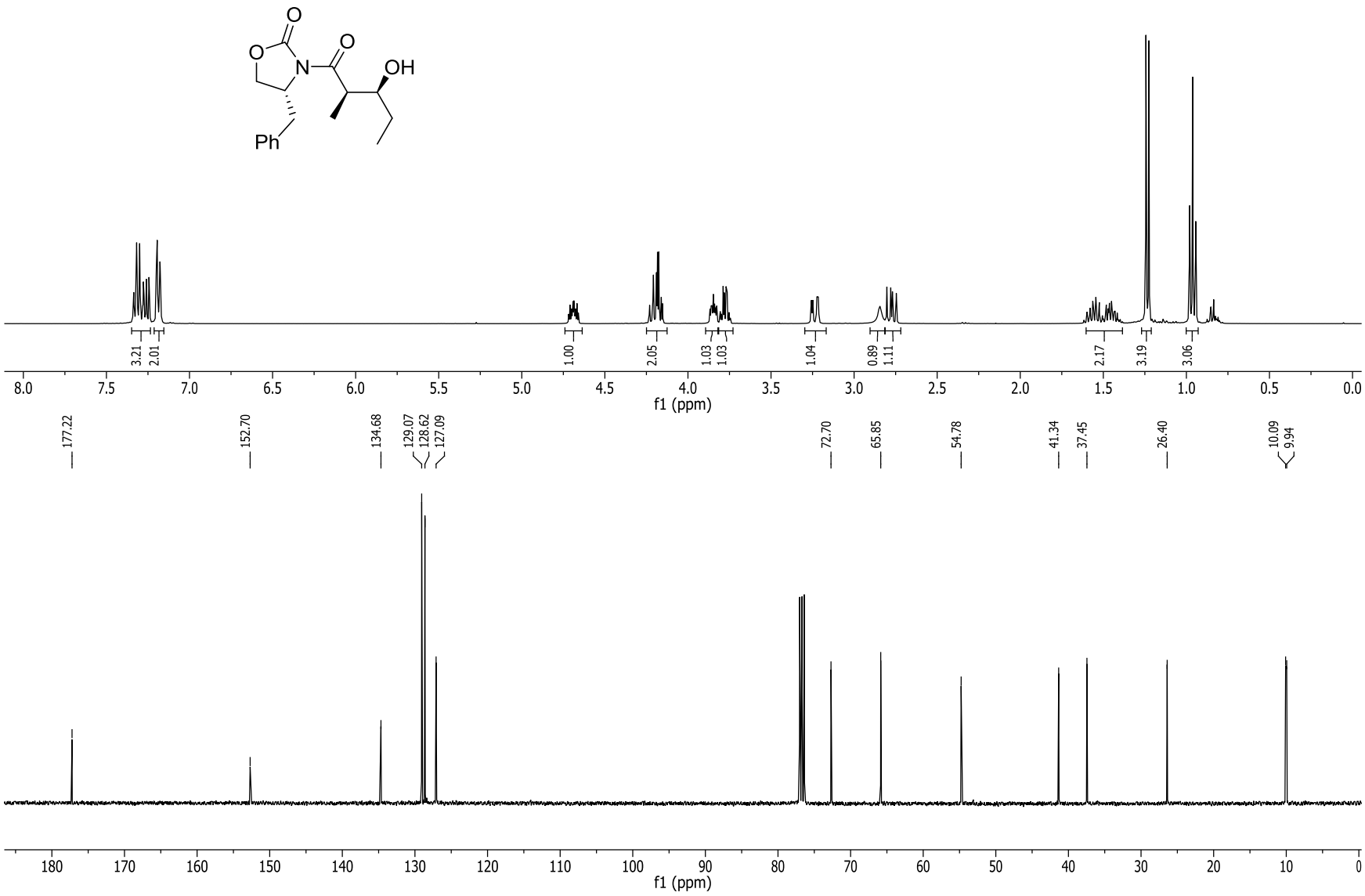

84.50
75.39
72.38
66.68
41.74
32.05
27.71
23.76
21.56
17.87
3.66
t-BuO
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
ppm

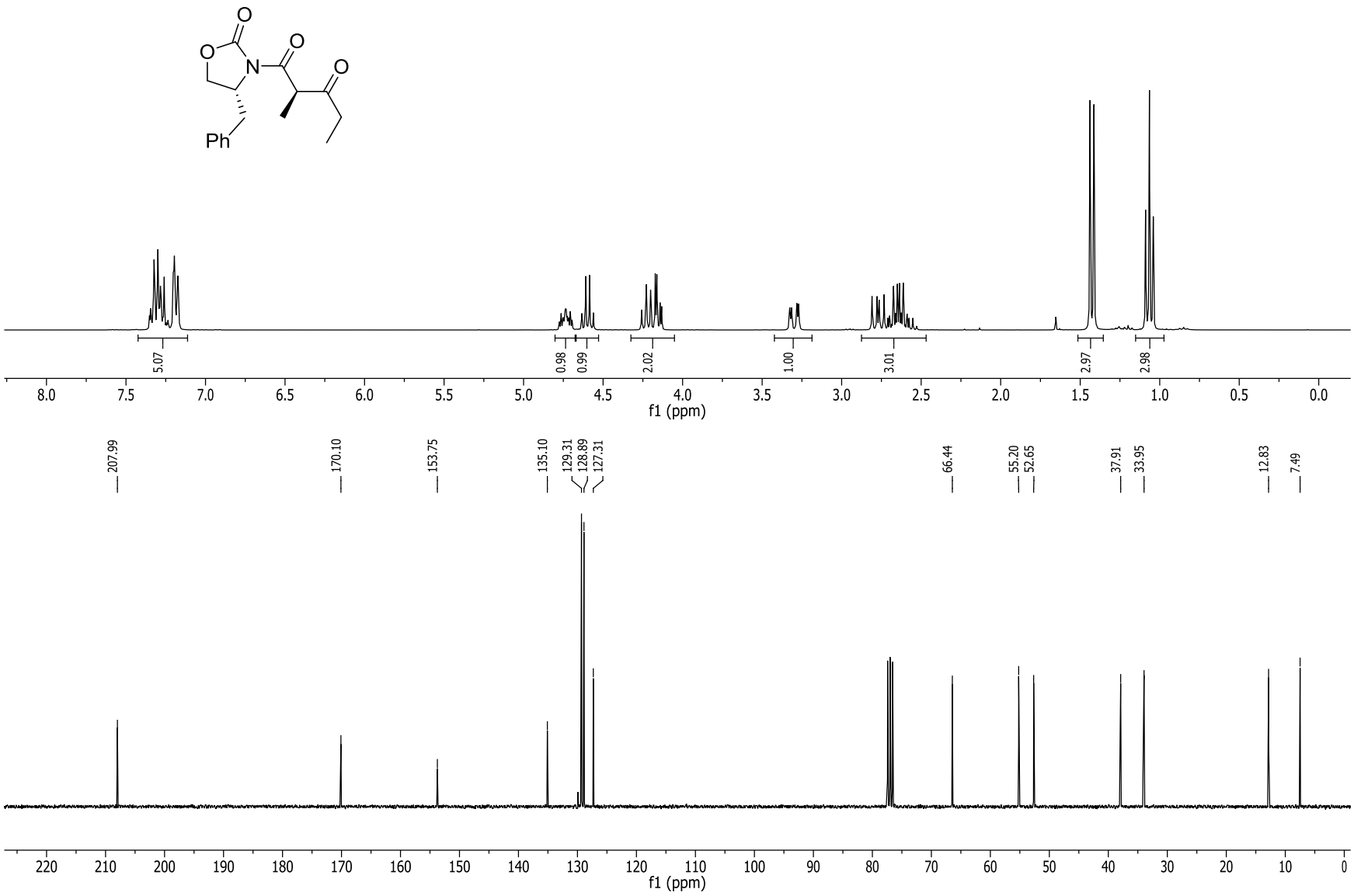

HO
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.04
1.00
1.06
2.97
1.03
2.34
3.04
3.01

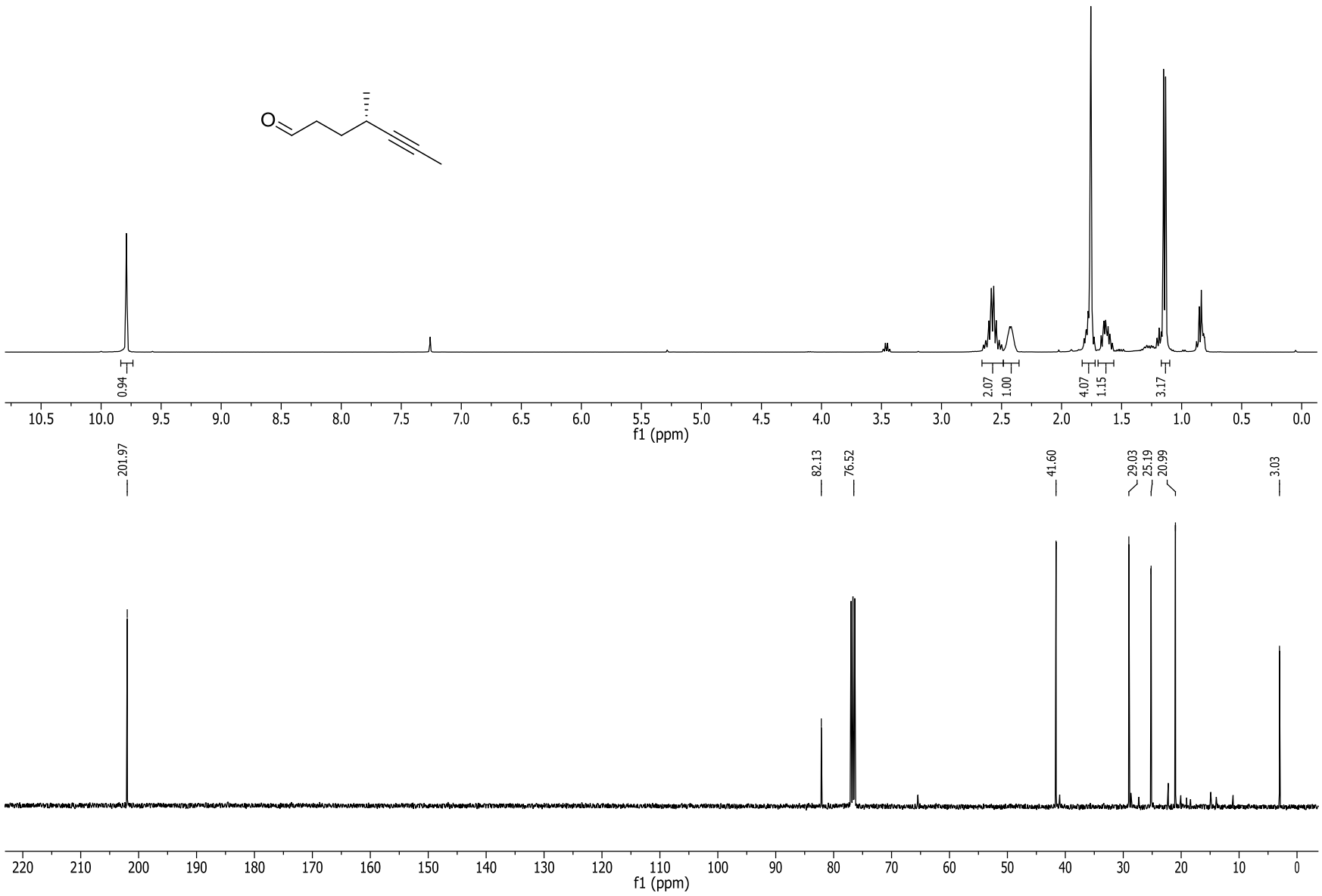

84.10
75.90
67.71
41.04
33.72
23.63
21.75
17.36
3.61
HO
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
ppm

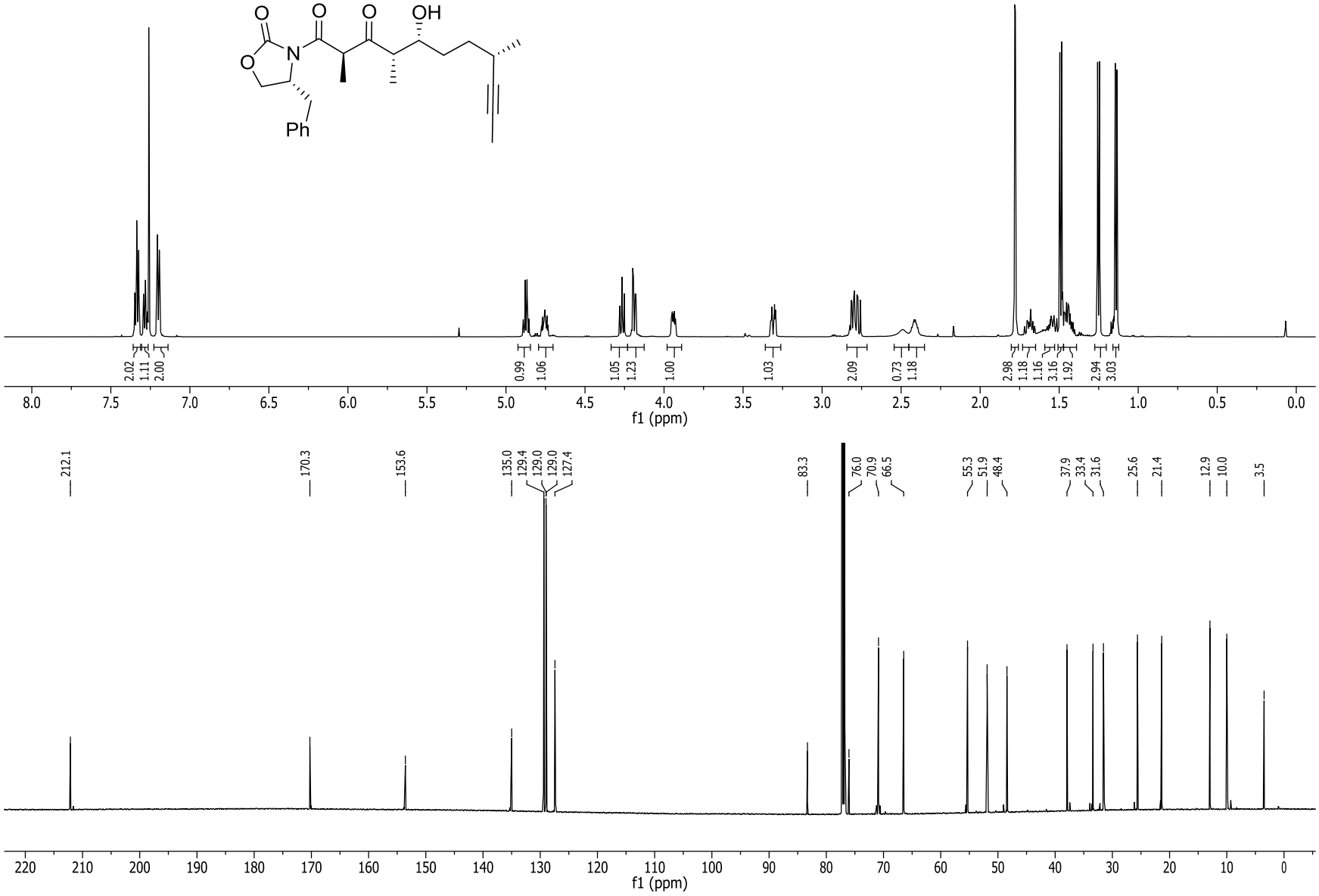

I
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.05
1.00
3.07
1.02
2.07
3.13
3.15

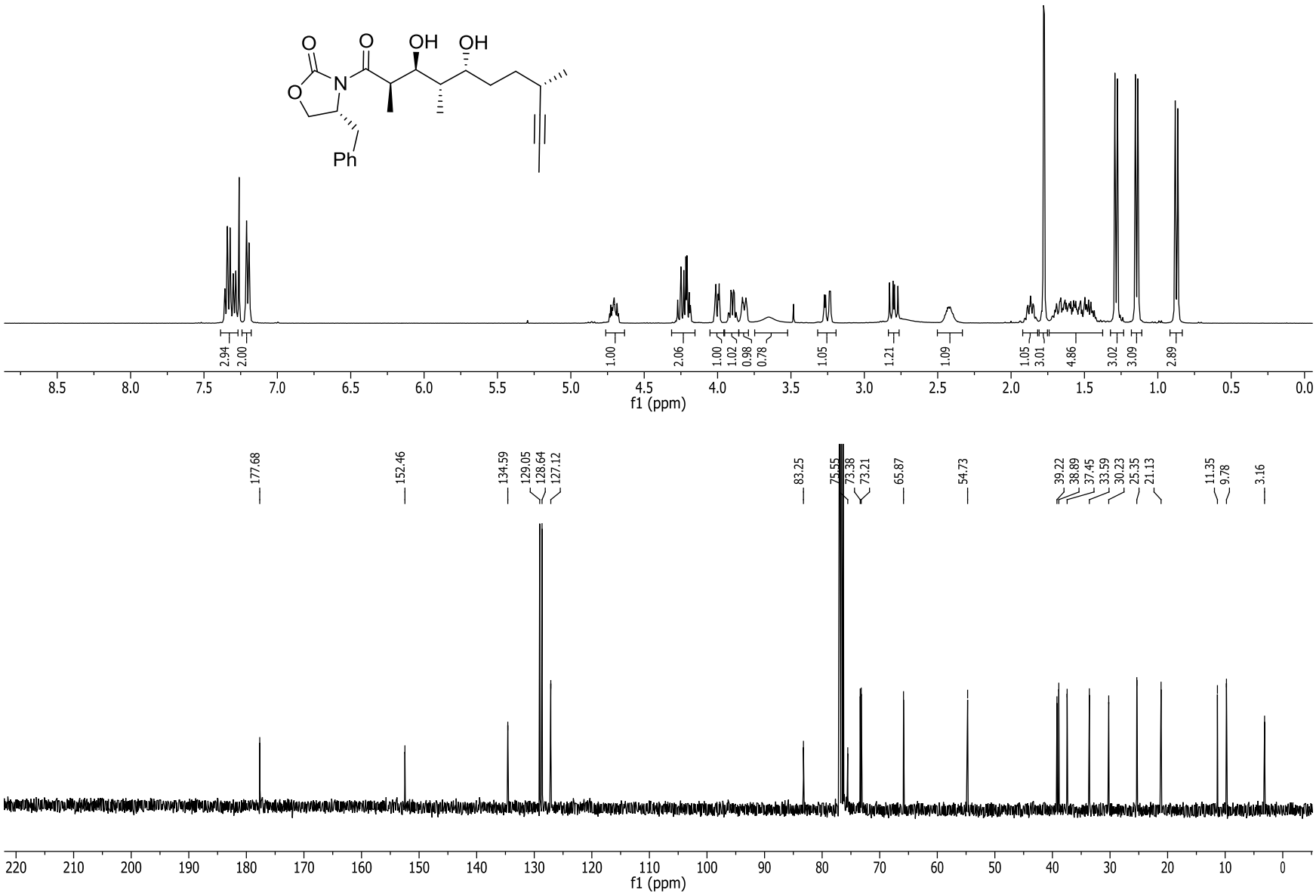

83.02
76.31
43.80
32.06
23.62
21.82
21.46
18.38
3.63
I
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
ppm

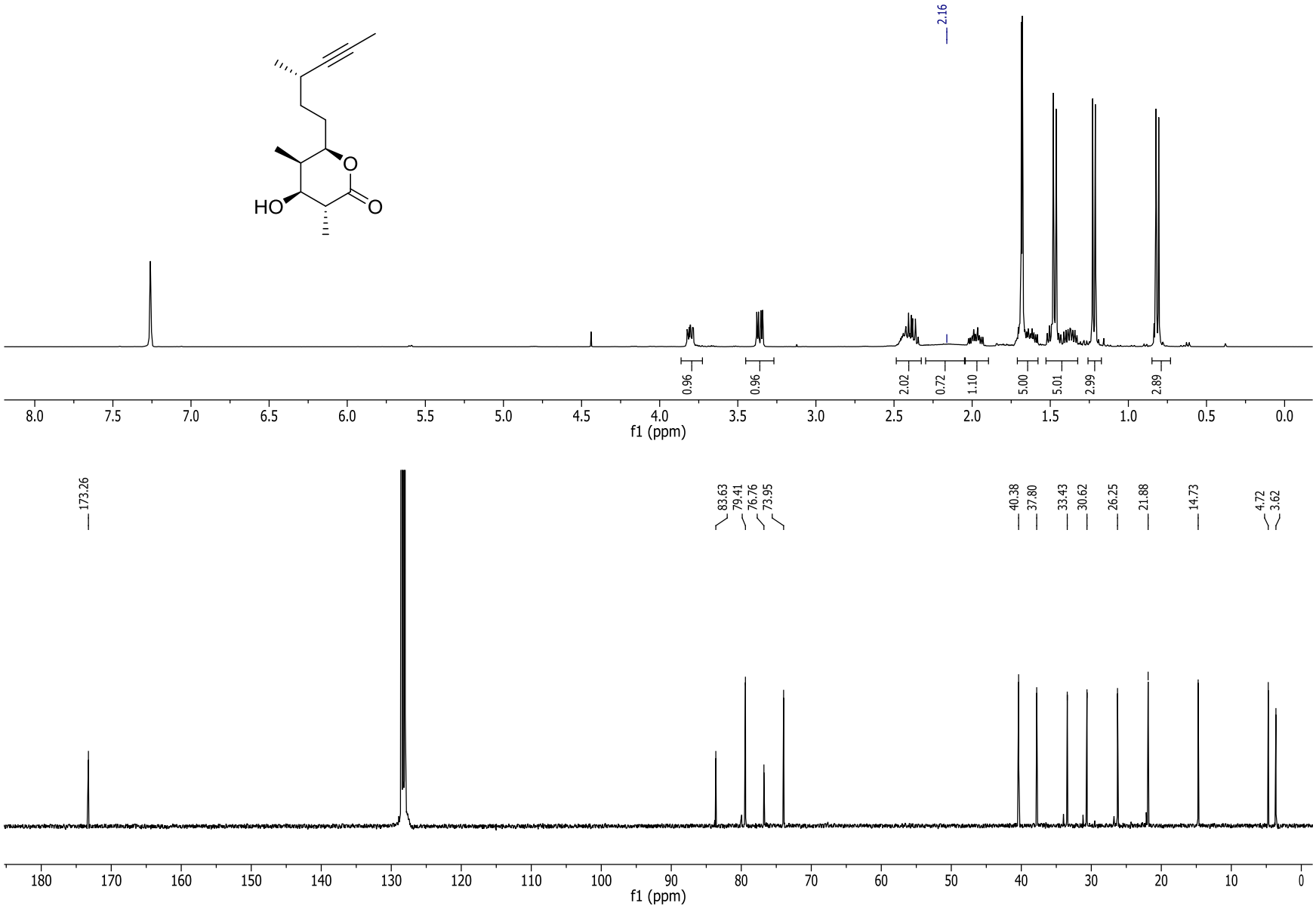

O
O
N
O
OH
Ph
3.21
2.01
1.00
2.05
1.03
1.03
1.04
0.89
1.11
2.17
3.19
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
177.22
152.70
134.68
129.07
128.62
127.09
72.70
65.85
54.78
41.34
37.45
26.40
10.09
9.94
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

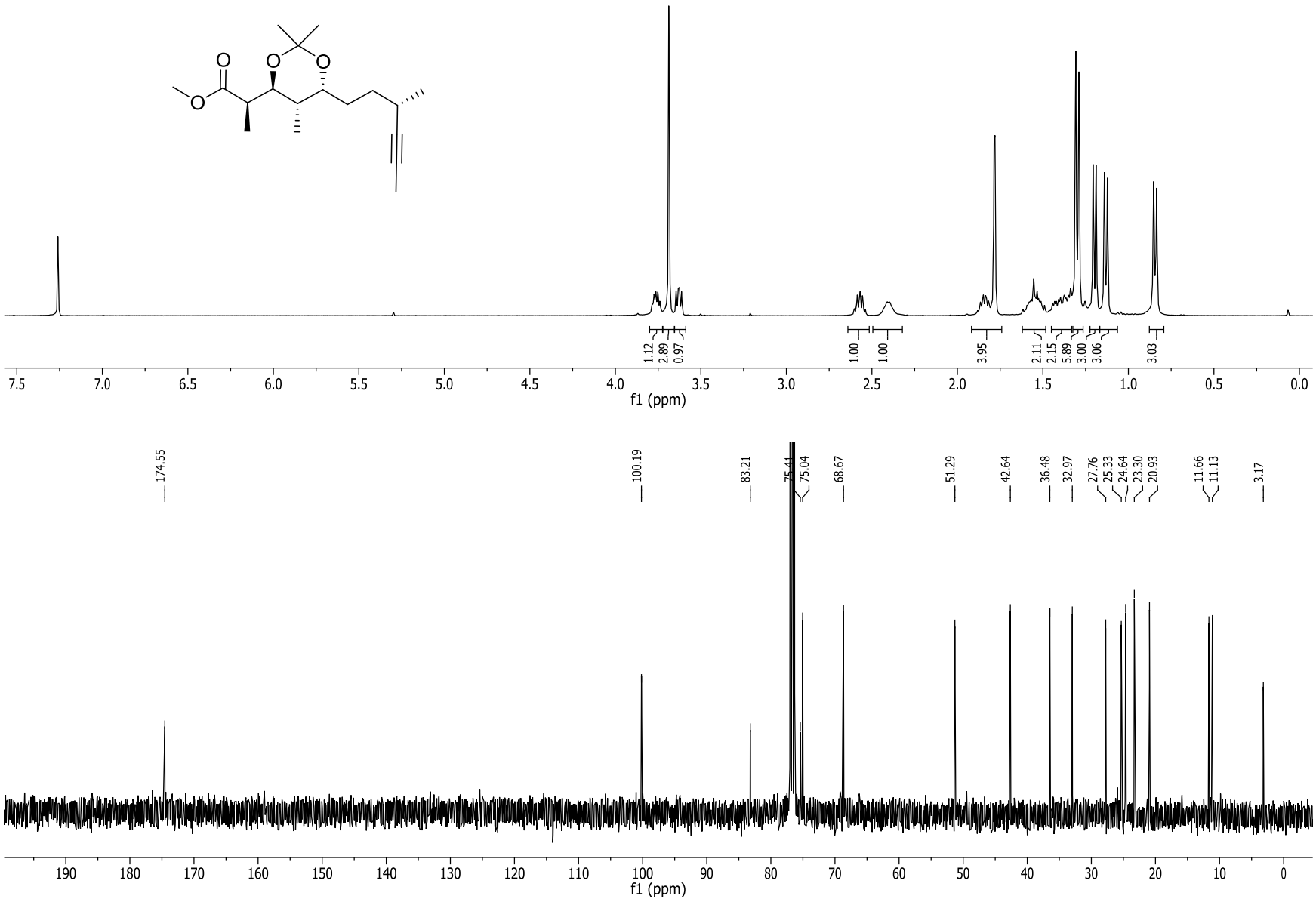

O
O
N
O
O
Ph
5.07
0.98
0.99
2.02
1.00
3.01
2.97
2.98
f1 (ppm)
207.99
170.10
153.75
135.10
129.31
128.89
127.31
66.44
55.20
52.65
37.91
33.95
12.83
7.49
f1 (ppm)

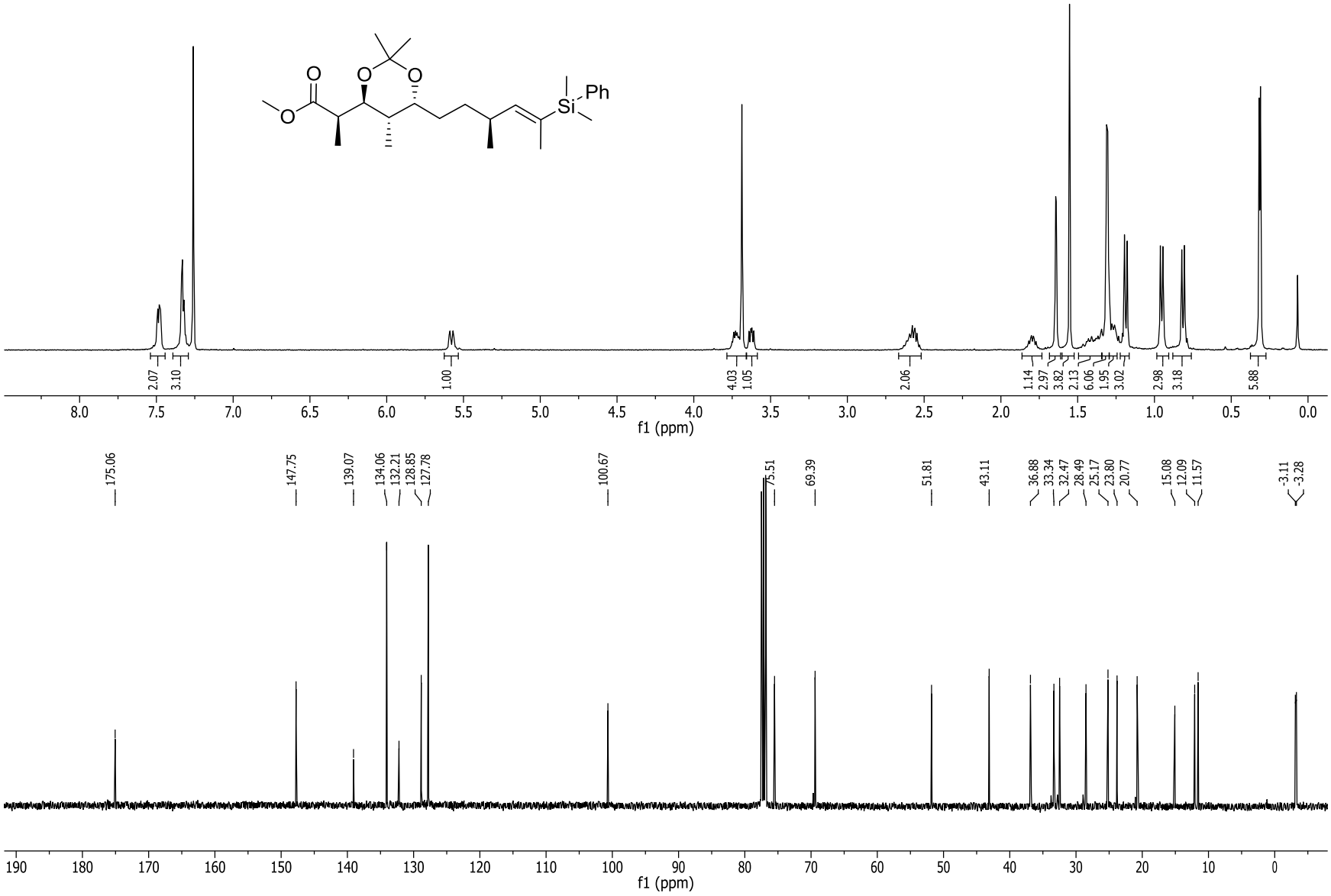

O
0.94
2.07
1.00
4.07
1.15
3.17
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
201.97
82.13
76.52
41.60
29.03
25.19
20.99
3.03
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

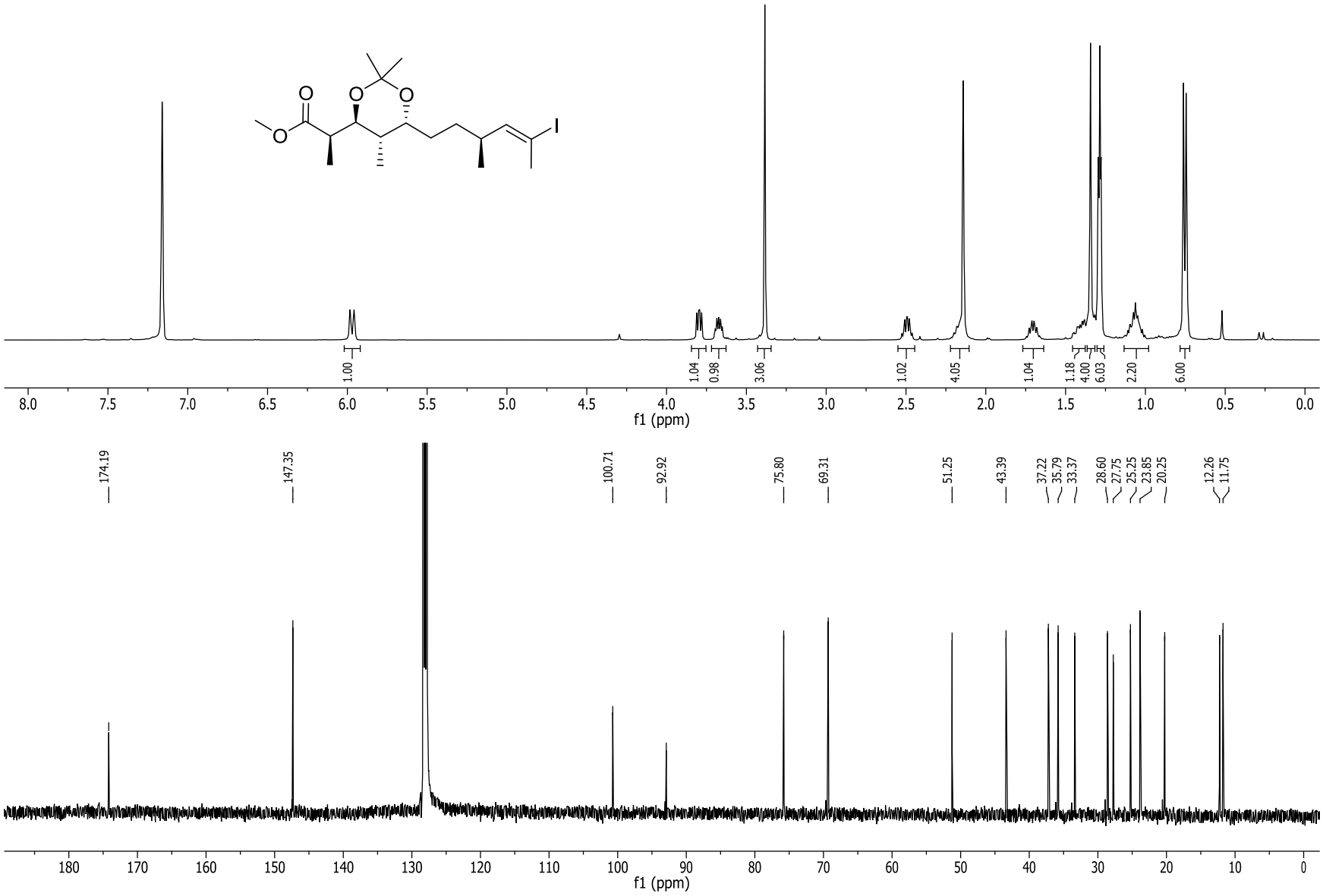

O
O
O
OH
N
O
Ph
2.02
1.11
2.00
0.99
1.06
1.05
1.23
1.00
1.03
2.09
0.73
1.18
2.98
1.18
1.16
3.16
1.92
2.94
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
212.1
170.3
153.6
135.0
129.4
129.0
129.0
127.4
83.3
76.0
70.9
66.5
55.3
51.9
48.4
37.9
33.4
31.6
25.6
21.4
12.9
10.0
3.5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

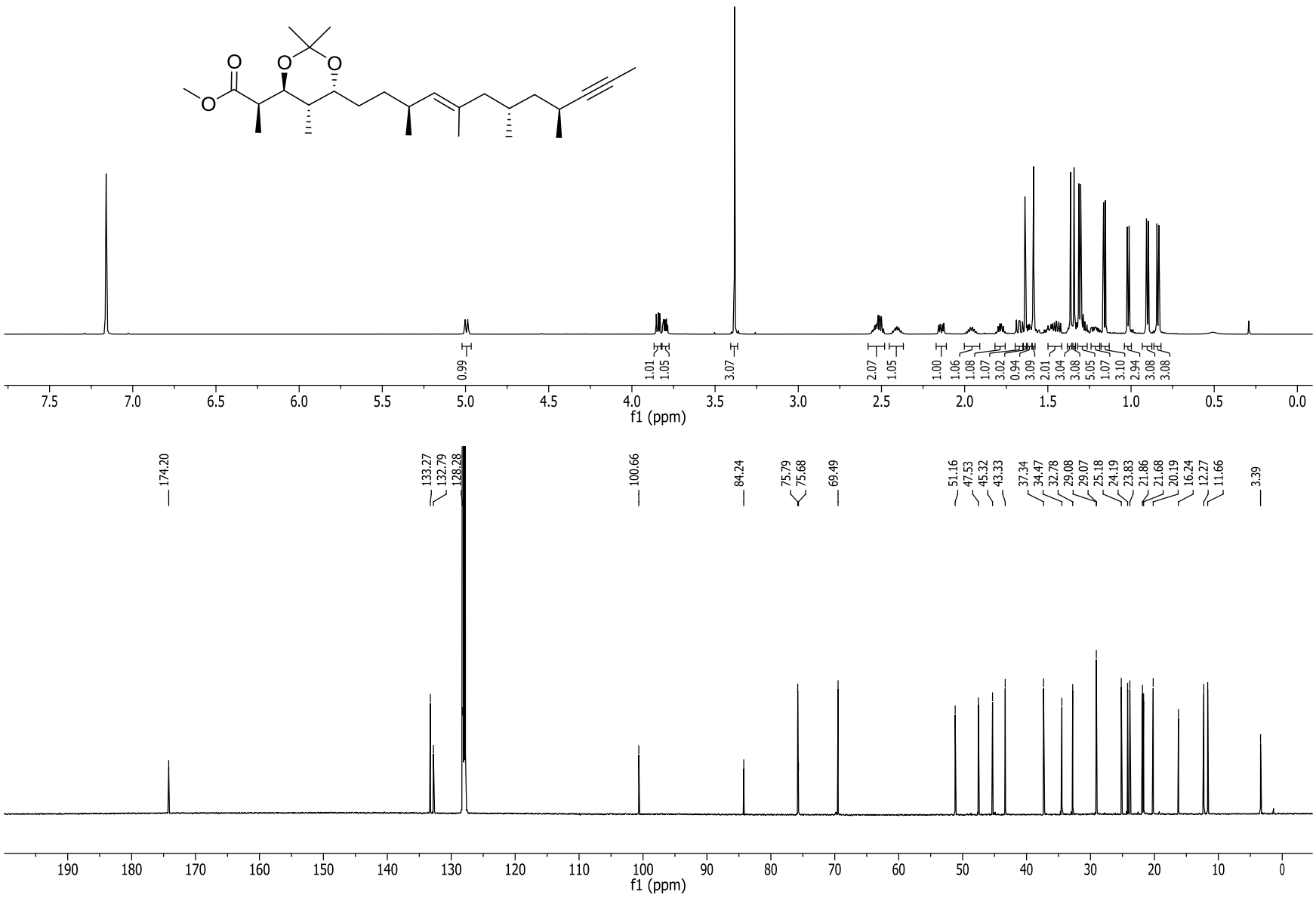

O
O
OH
OH
N
O
Ph
2.94
2.00
1.00
2.06
1.00
1.02
0.98
0.78
1.05
1.21
1.09
1.05
3.01
4.86
3.02
3.09
2.89
f1 (ppm)
177.68
152.46
134.59
129.05
128.64
127.12
83.25
75.55
73.38
73.21
65.87
54.73
39.22
38.89
37.45
33.59
30.23
25.35
21.13
11.35
9.78
3.16
f1 (ppm)

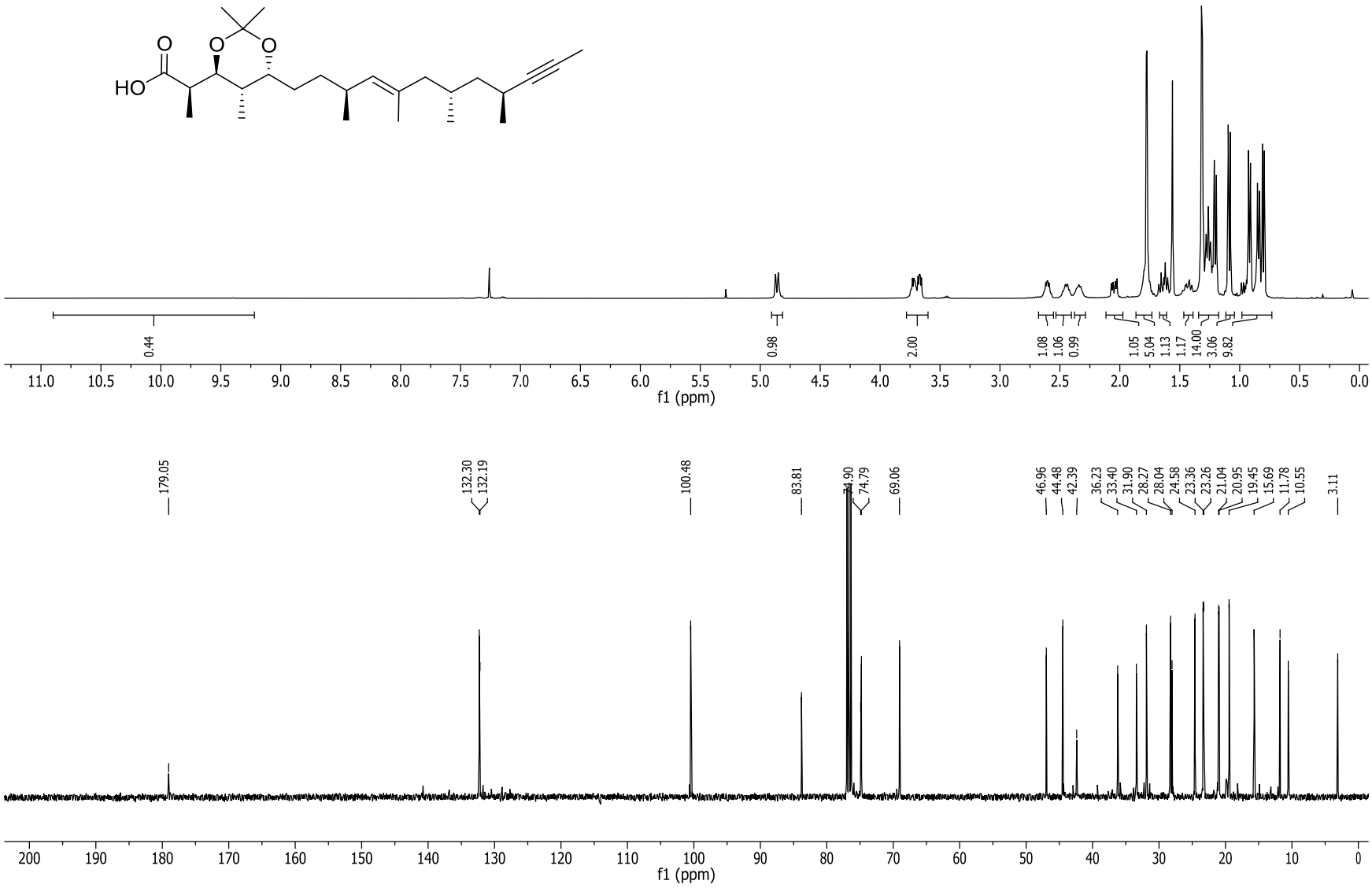

HO
O
O
2.16
0.96
0.96
2.02
0.72
1.10
5.00
5.01
2.99
2.89
f1 (ppm)
173.26
83.63
79.41
76.76
73.95
40.38
37.80
33.43
30.62
26.25
21.88
14.73
4.72
3.62
f1 (ppm)

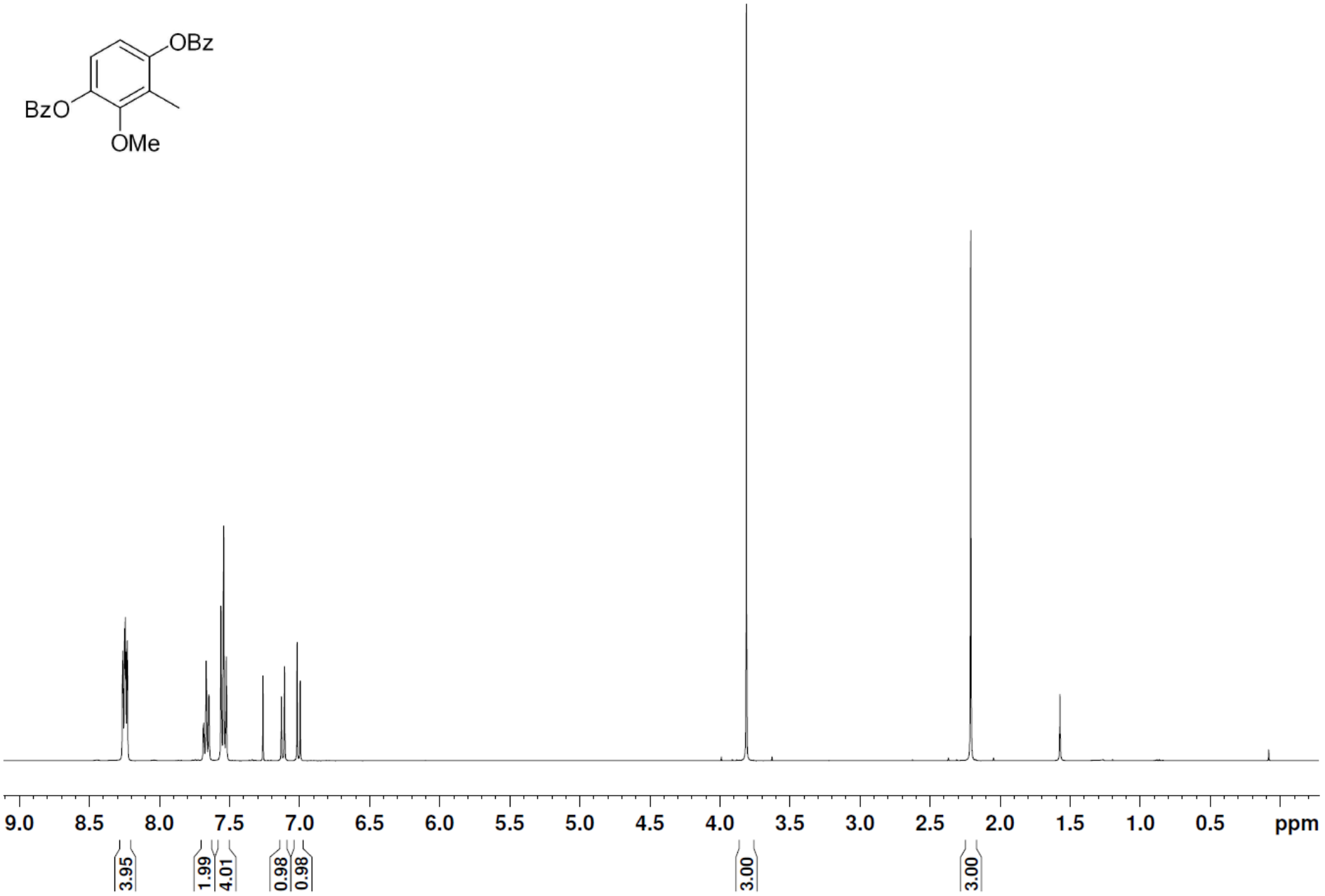

1.12
2.89
0.97
1.00
1.00
3.95
2.11
2.15
5.89
3.00
3.06
3.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
174.55
100.19
83.21
75.41
75.04
68.67
51.29
42.64
36.48
32.97
27.76
25.33
24.64
23.30
20.93
11.66
11.13
3.17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

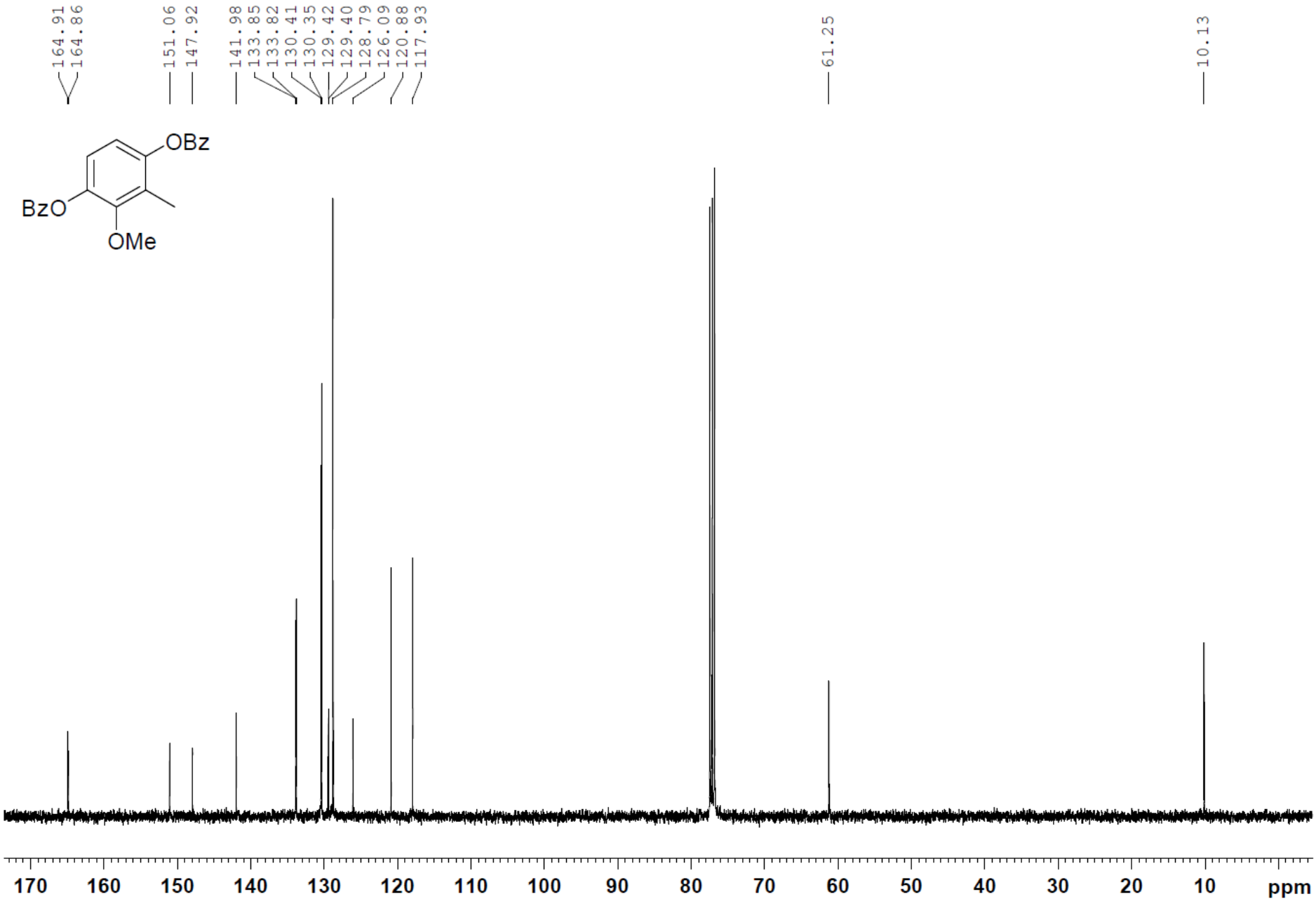

O
O
O
O
Si
Ph
2.07
3.10
1.00
4.03
1.05
2.06
1.14
2.97
3.82
2.13
6.06
1.95
3.02
2.98
3.18
5.88
f1 (ppm)
175.06
147.75
139.07
134.06
132.21
128.85
127.78
100.67
75.51
69.39
51.81
43.11
36.88
33.34
32.47
28.49
25.17
23.80
20.77
15.08
12.09
11.57
-3.11
-3.28
f1 (ppm)

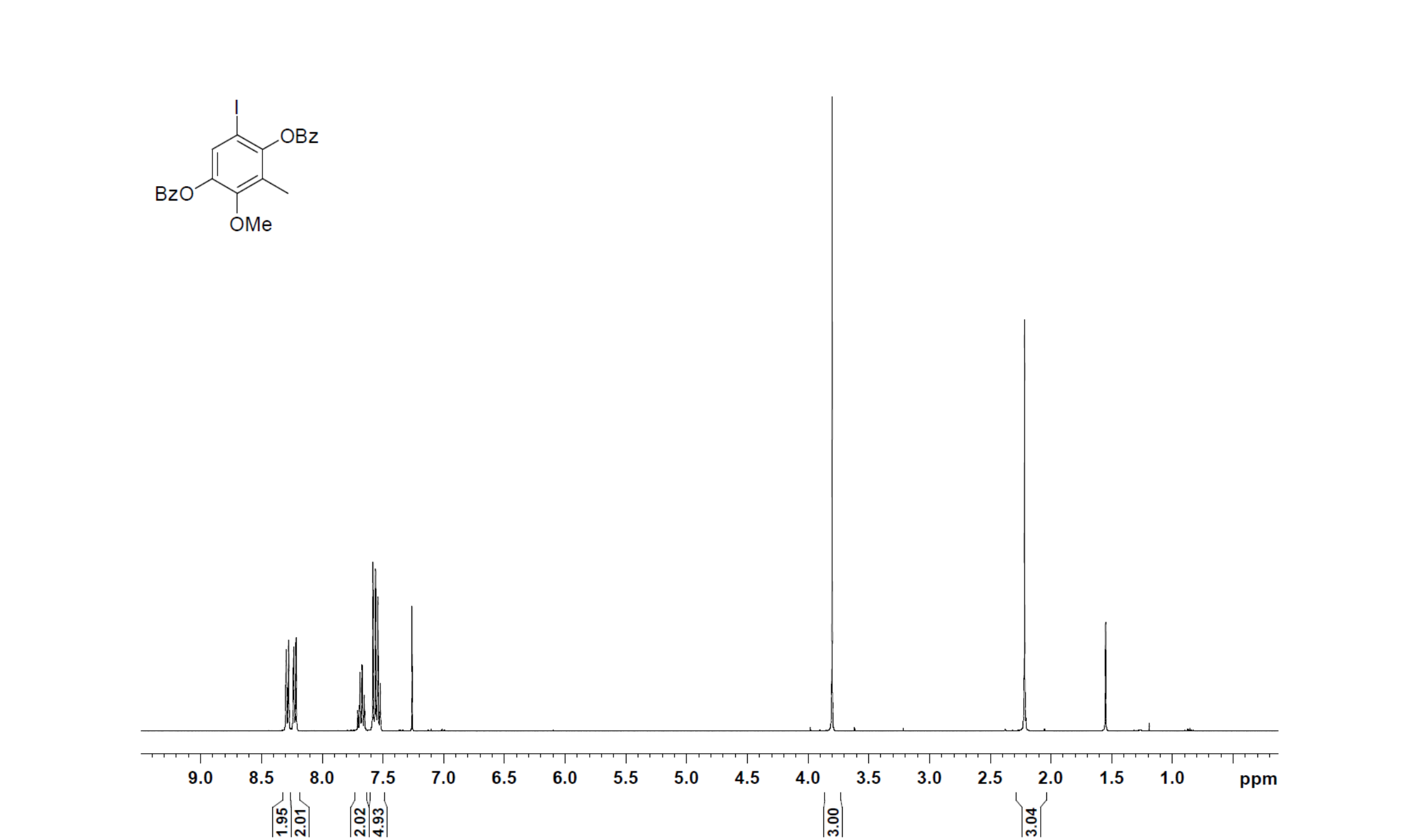

O
O
O
O
I
1.00
1.04
0.98
3.06
1.02
4.05
1.04
1.18
4.00
6.03
2.20
6.00
f1 (ppm)
174.19
147.35
100.71
92.92
75.80
69.31
51.25
43.39
37.22
35.79
33.37
28.60
27.75
25.25
23.85
20.25
12.26
11.75
f1 (ppm)

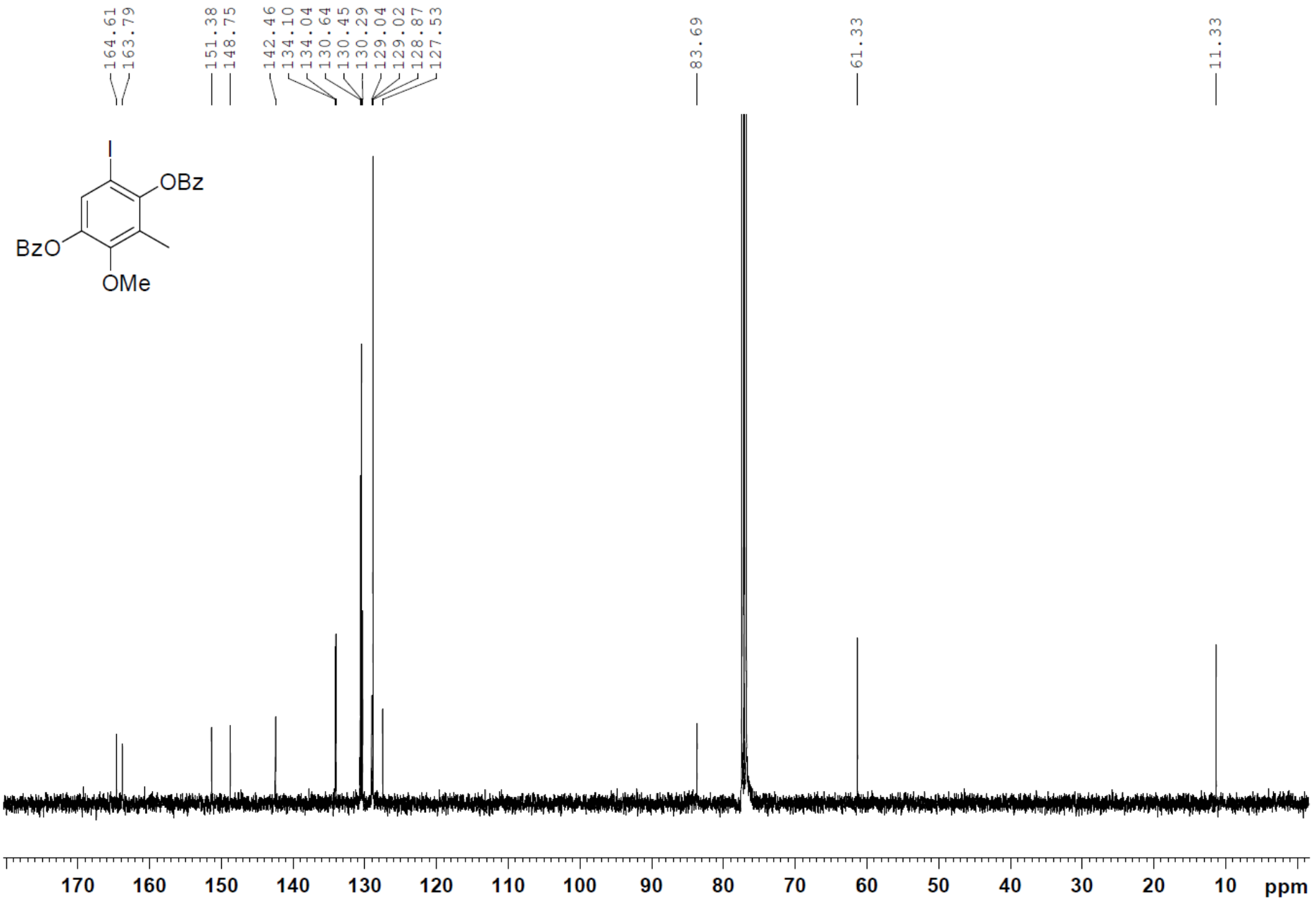

0.99
1.01
1.05
3.07
2.07
1.05
1.00
1.06
1.08
1.07
3.02
0.94
3.09
2.01
3.04
3.08
5.05
1.07
3.10
2.94
3.08
3.08
f1 (ppm)
174.20
133.27
132.79
128.28
100.66
84.24
75.79
75.68
69.49
51.16
47.53
45.32
43.33
37.34
34.47
32.78
29.08
29.07
25.18
24.19
23.83
21.86
21.68
20.19
16.24
12.27
11.66
3.39
f1 (ppm)

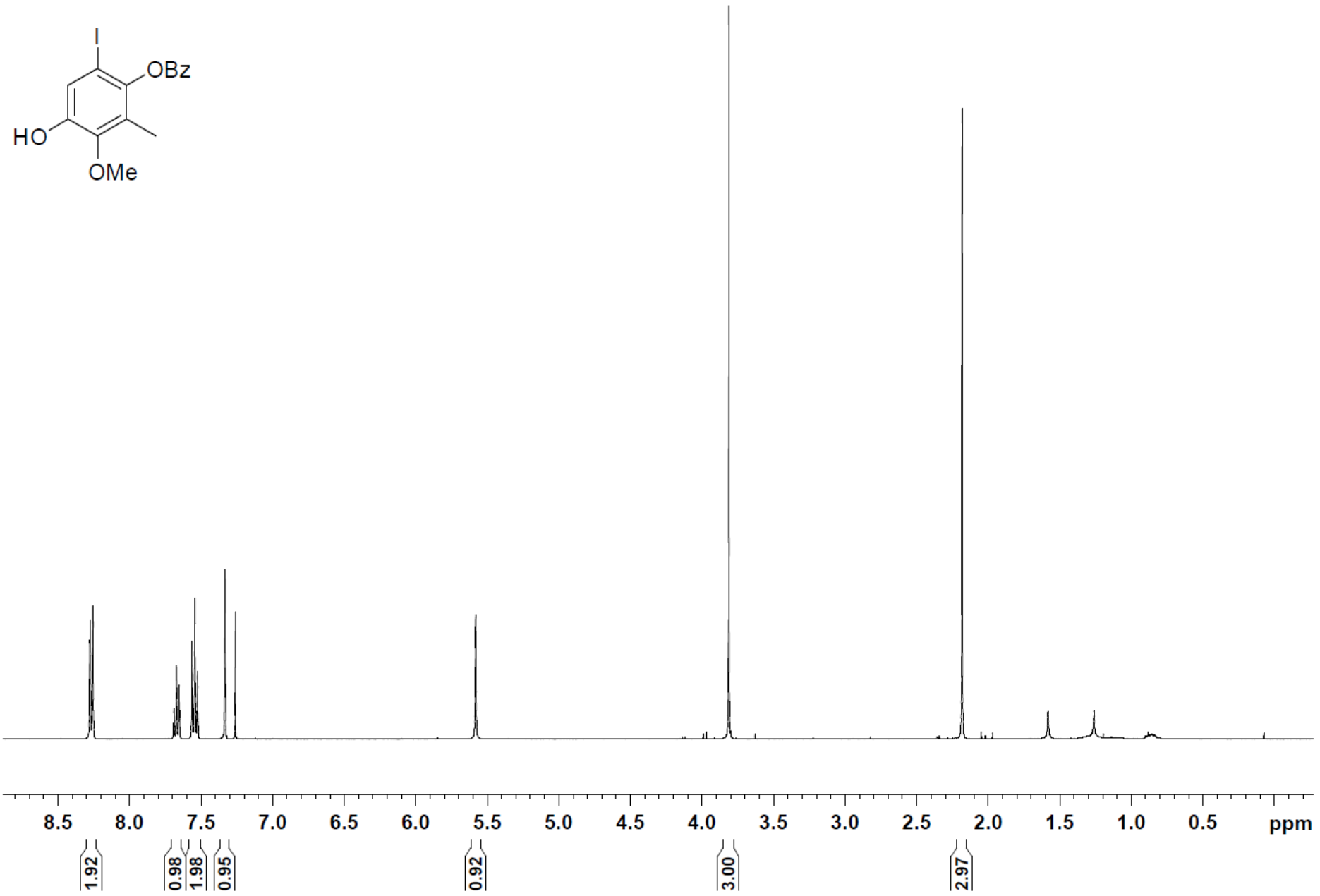

HO
O
O
O
0.44
0.98
2.00
1.08
1.06
0.99
1.05
5.04
1.13
1.17
14.00
3.06
9.82
f1 (ppm)
179.05
132.30
132.19
100.48
83.81
74.90
74.79
69.06
46.96
44.48
42.39
36.23
33.40
31.90
28.27
28.04
24.58
23.36
23.26
21.04
20.95
19.45
15.69
11.78
10.55
3.11
f1 (ppm)

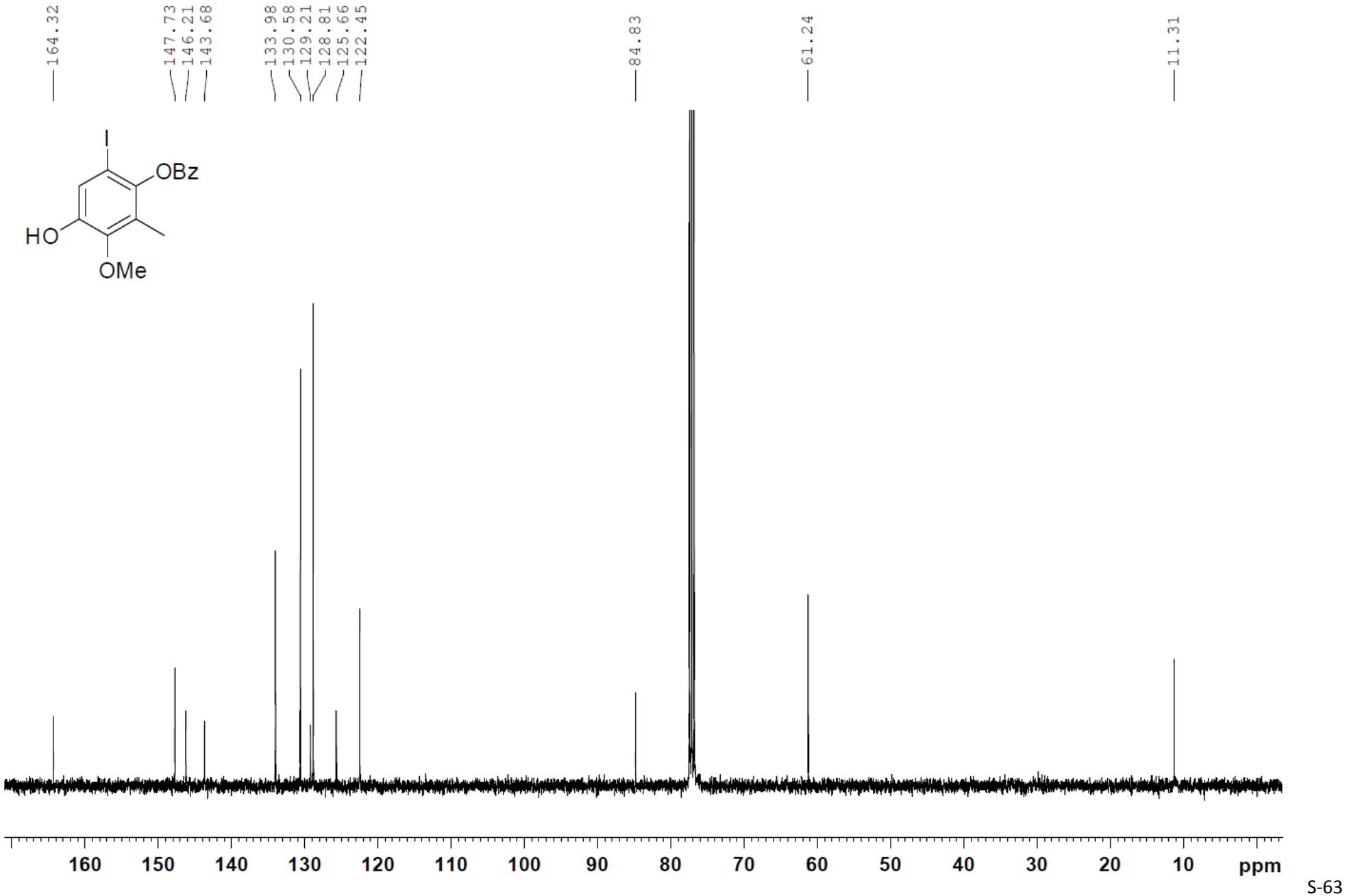

OBz
BzO
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.95
1.99
4.01
0.98
0.98
3.00
3.00

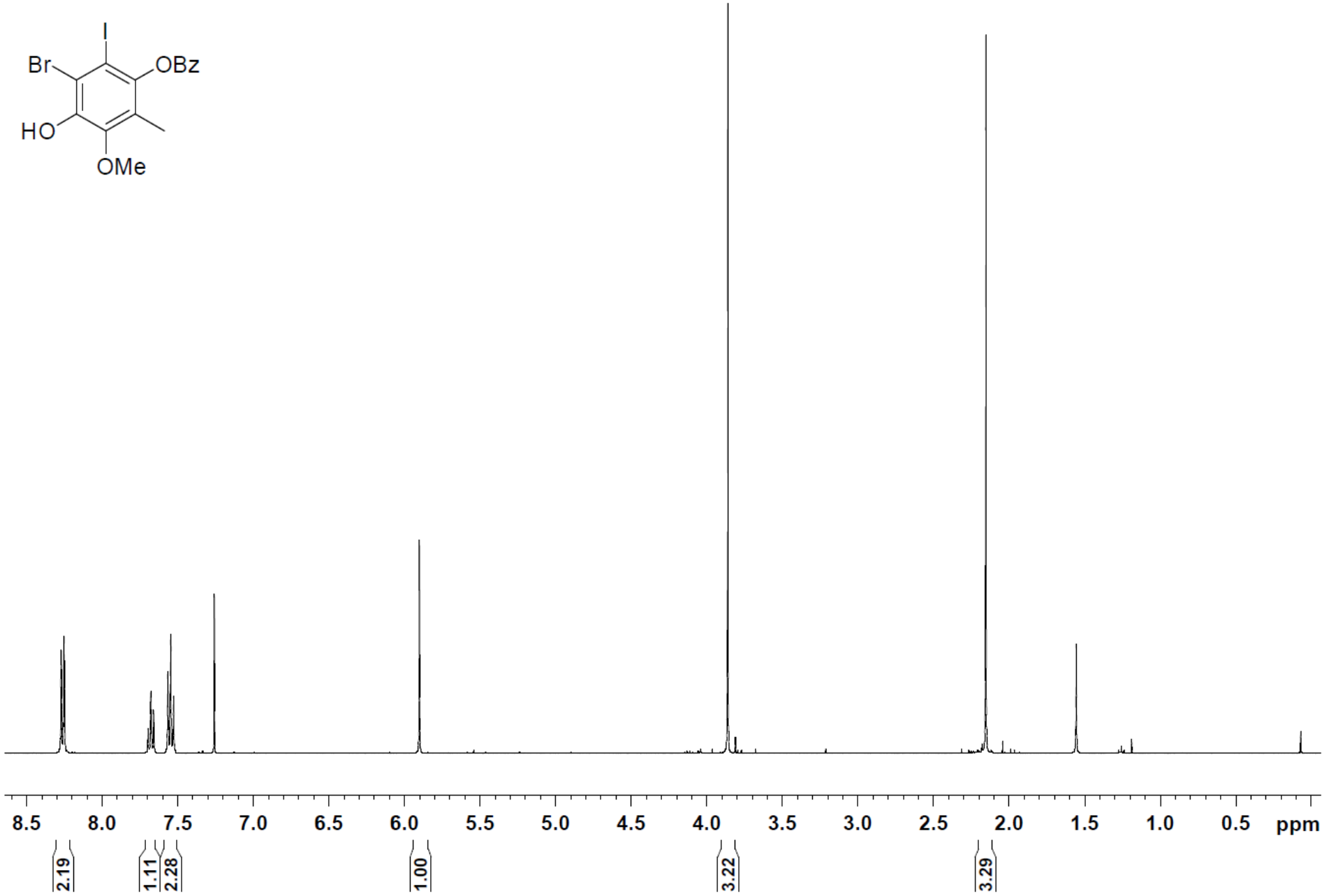

164.91
164.86
151.06
147.92
141.98
133.85
133.82
130.41
130.35
129.42
129.40
128.79
126.09
120.88
117.93
61.25
10.13
OBz
BzO
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

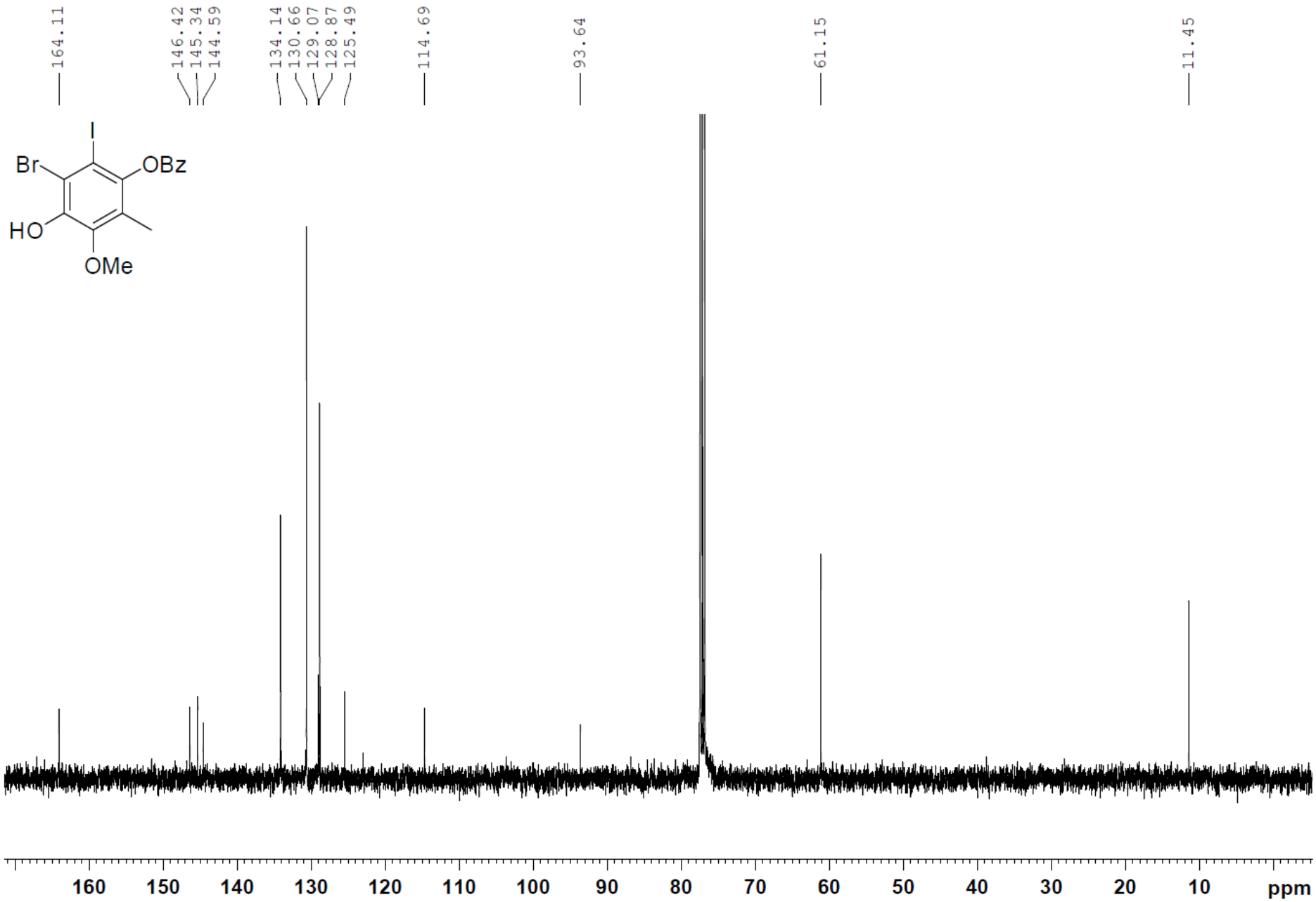

I
OBz
BzO
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.95
2.01
2.02
4.93
3.00
3.04

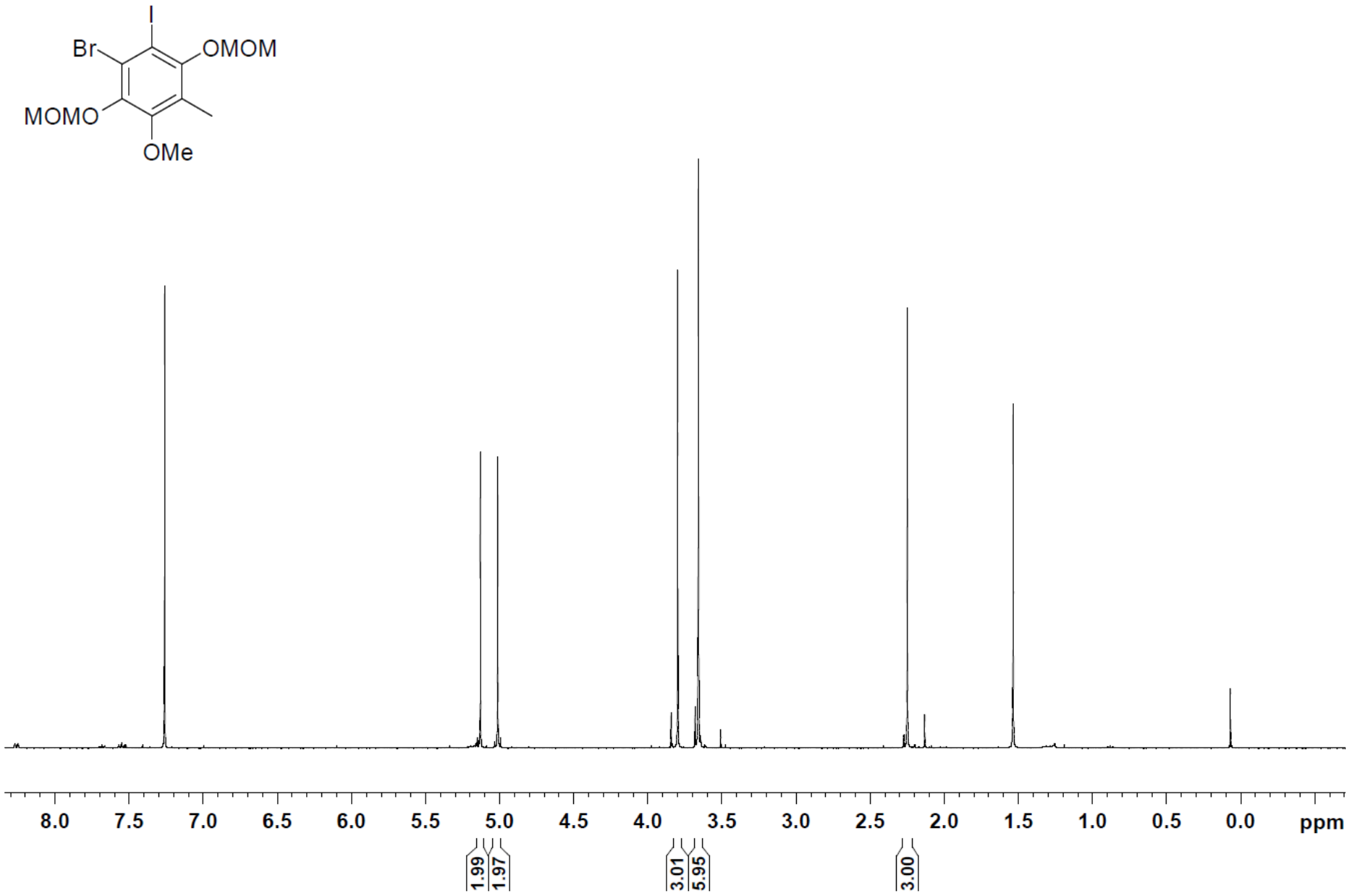

164.61
163.79
151.38
148.75
142.46
134.10
134.04
130.64
130.45
130.29
129.04
129.02
128.87
127.53
83.69
61.33
11.33
I
OBz
BzO
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

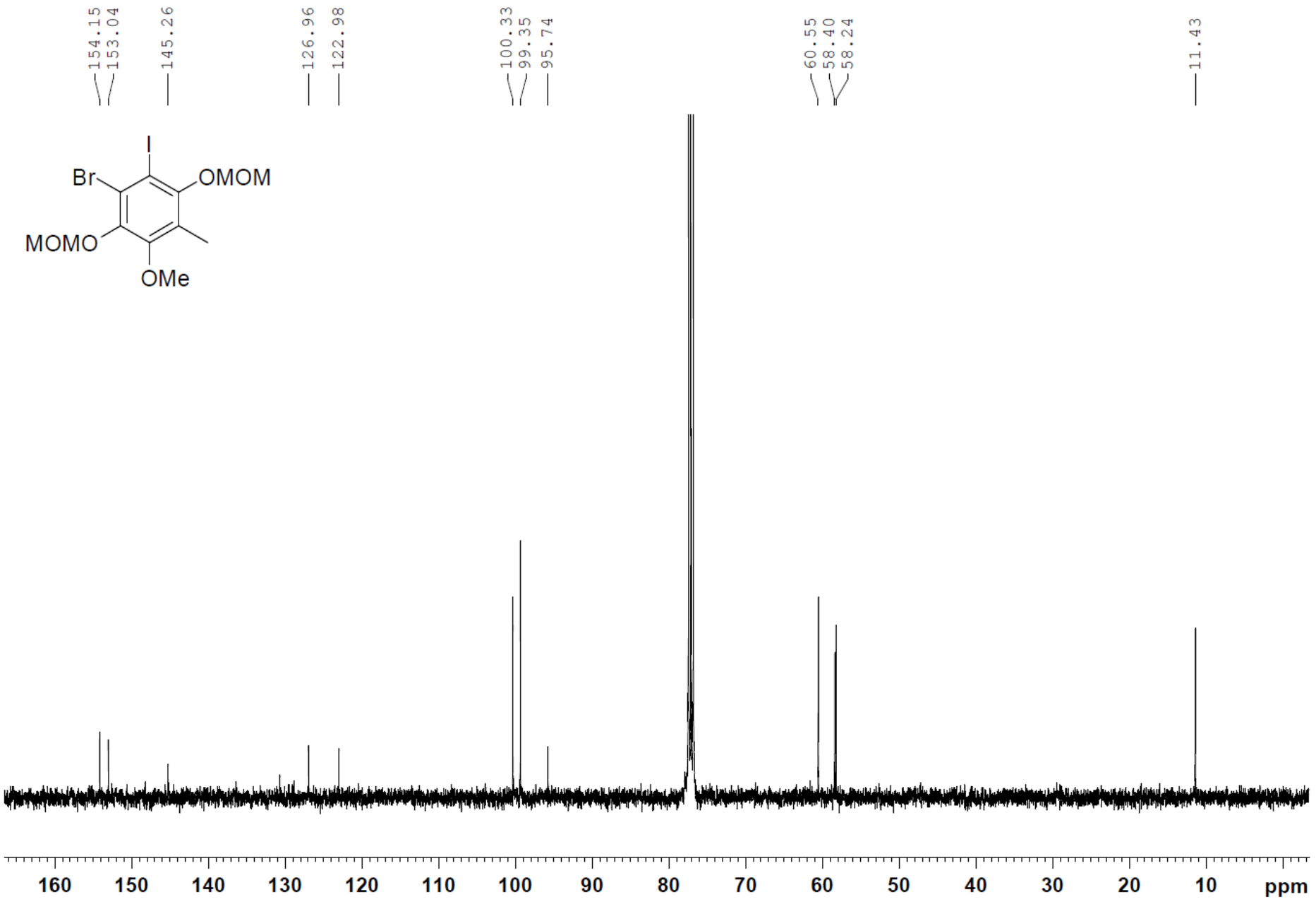

I
OBz
HO
OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.92
0.98
1.98
0.95
0.92
3.00
2.97

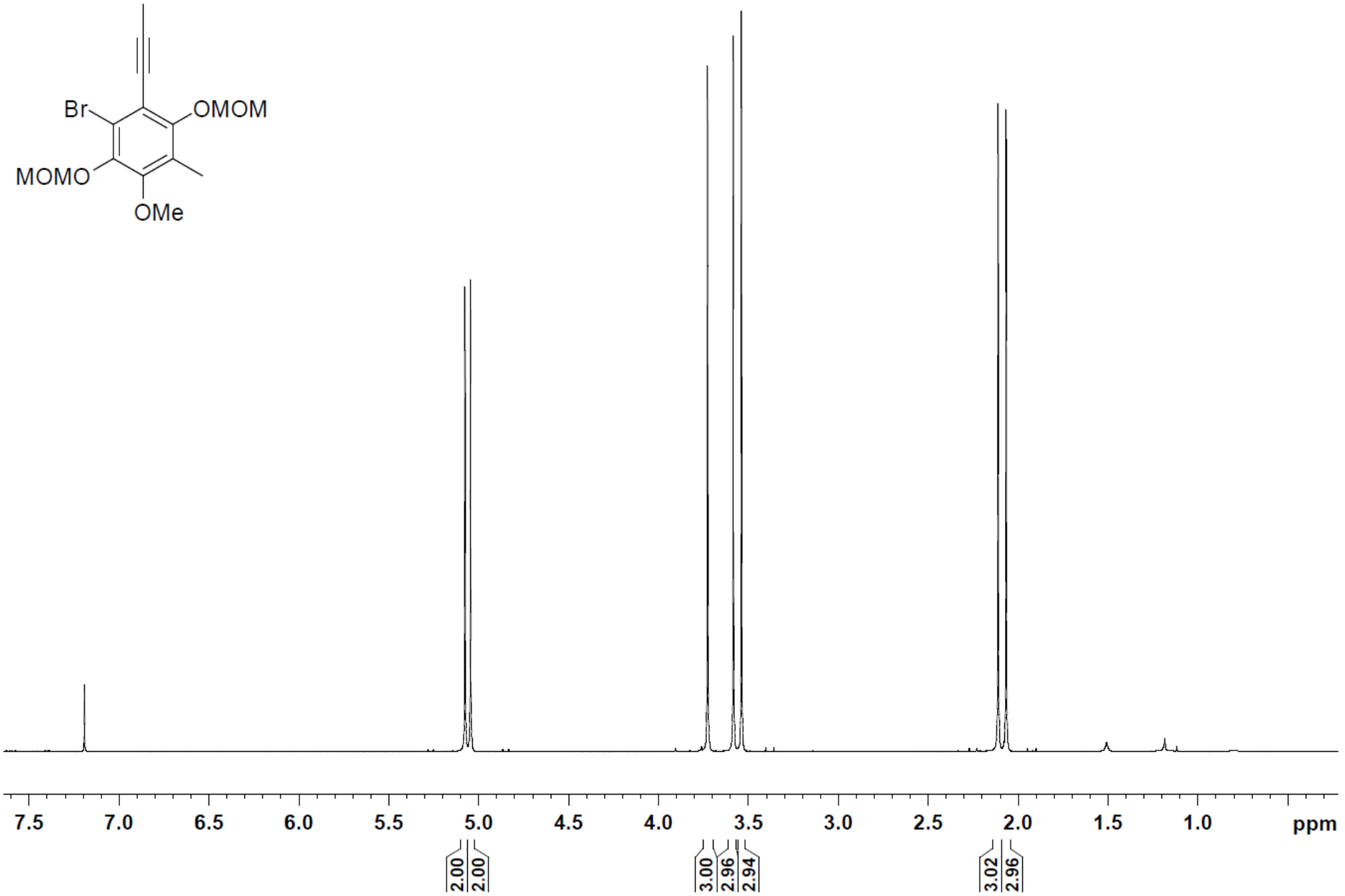

164.32
147.73
146.21
143.68
133.98
130.58
129.21
128.81
125.66
122.45
84.83
61.24
11.31
I
OBz
HO
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

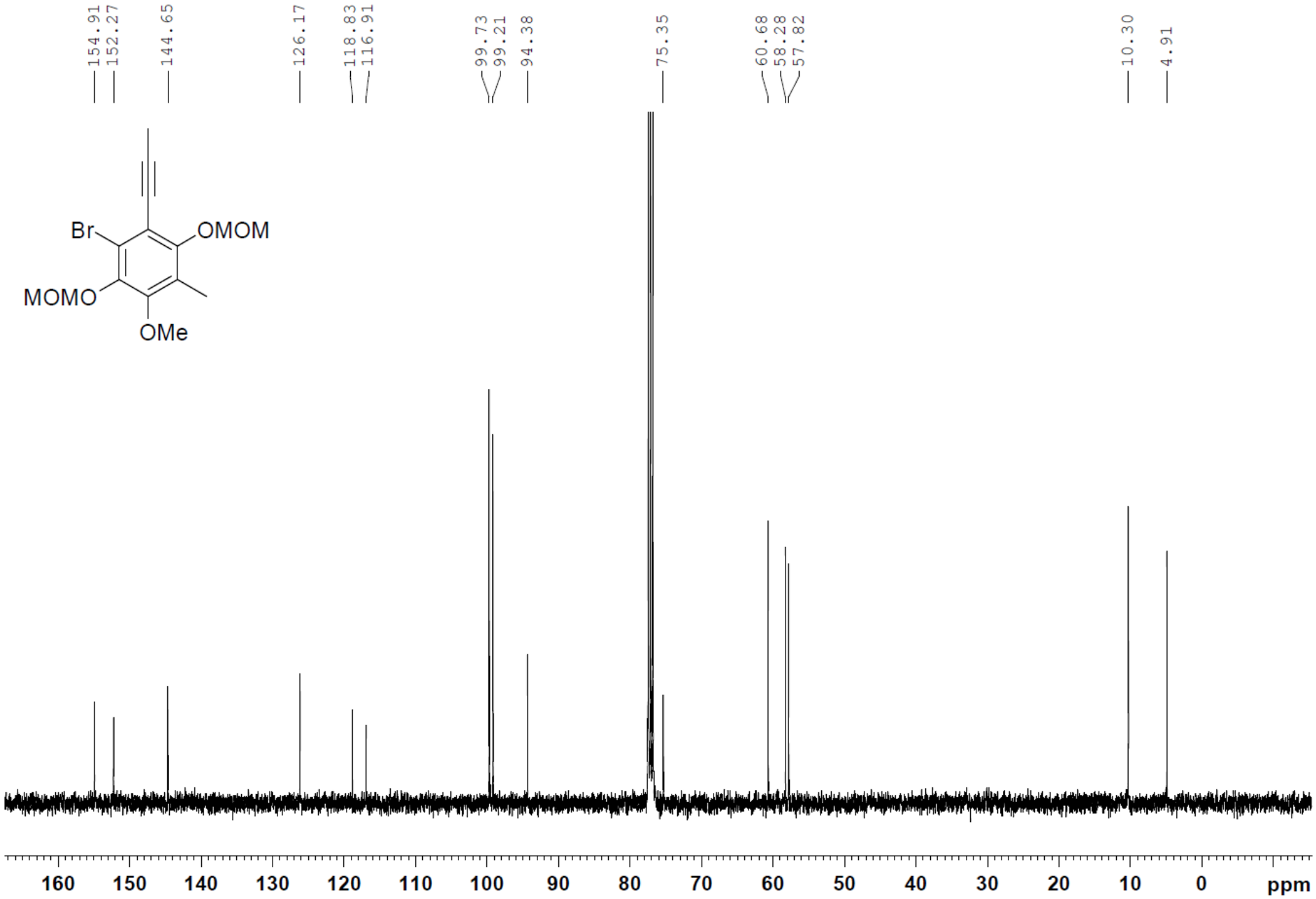

I
Br
OBz
HO
OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.19
1.11
2.28
1.00
3.22
3.29

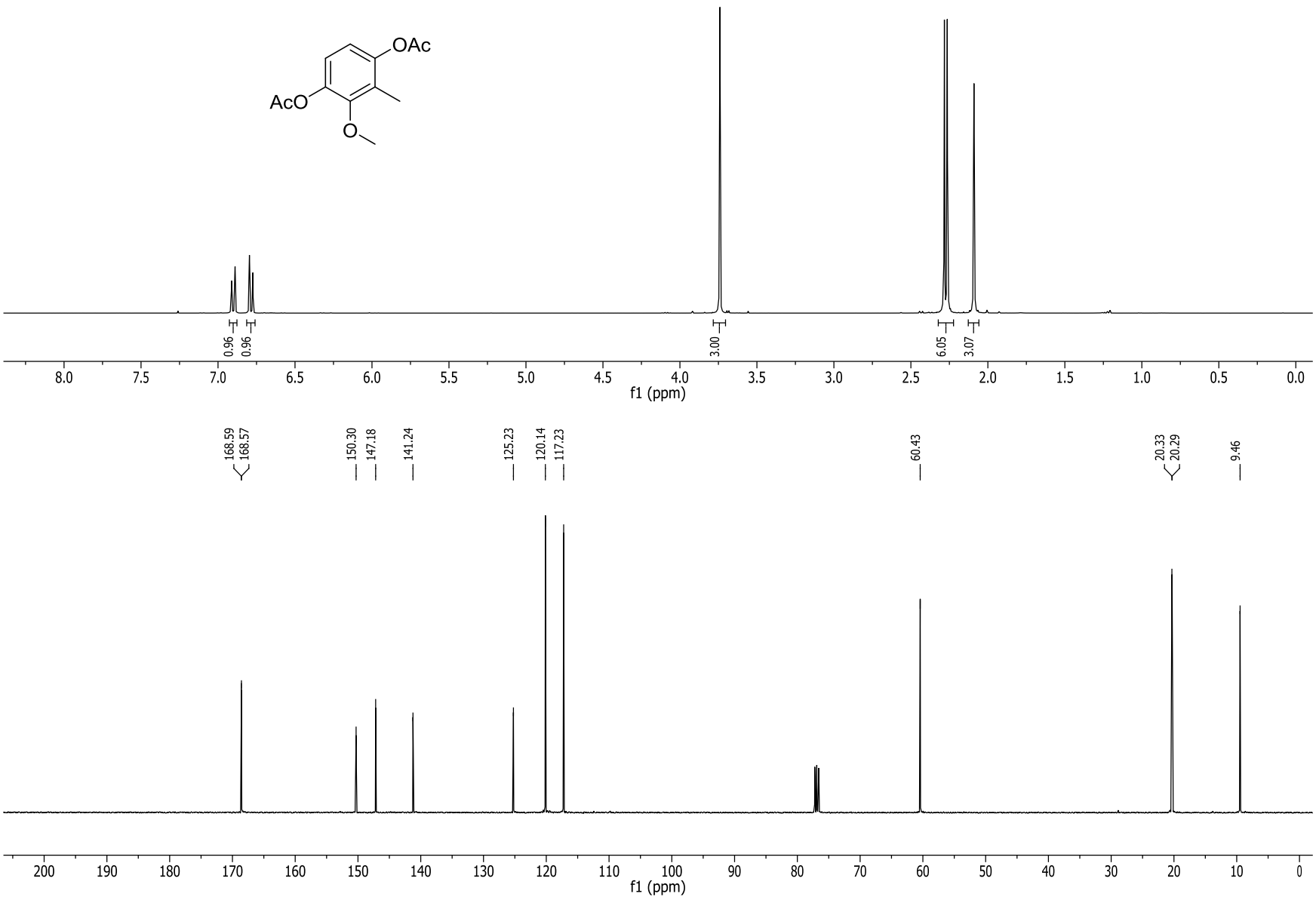

164.11
146.42
145.34
144.59
134.14
130.66
129.07
128.87
125.49
114.69
93.64
61.15
11.45
I
Br
OBz
HO
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

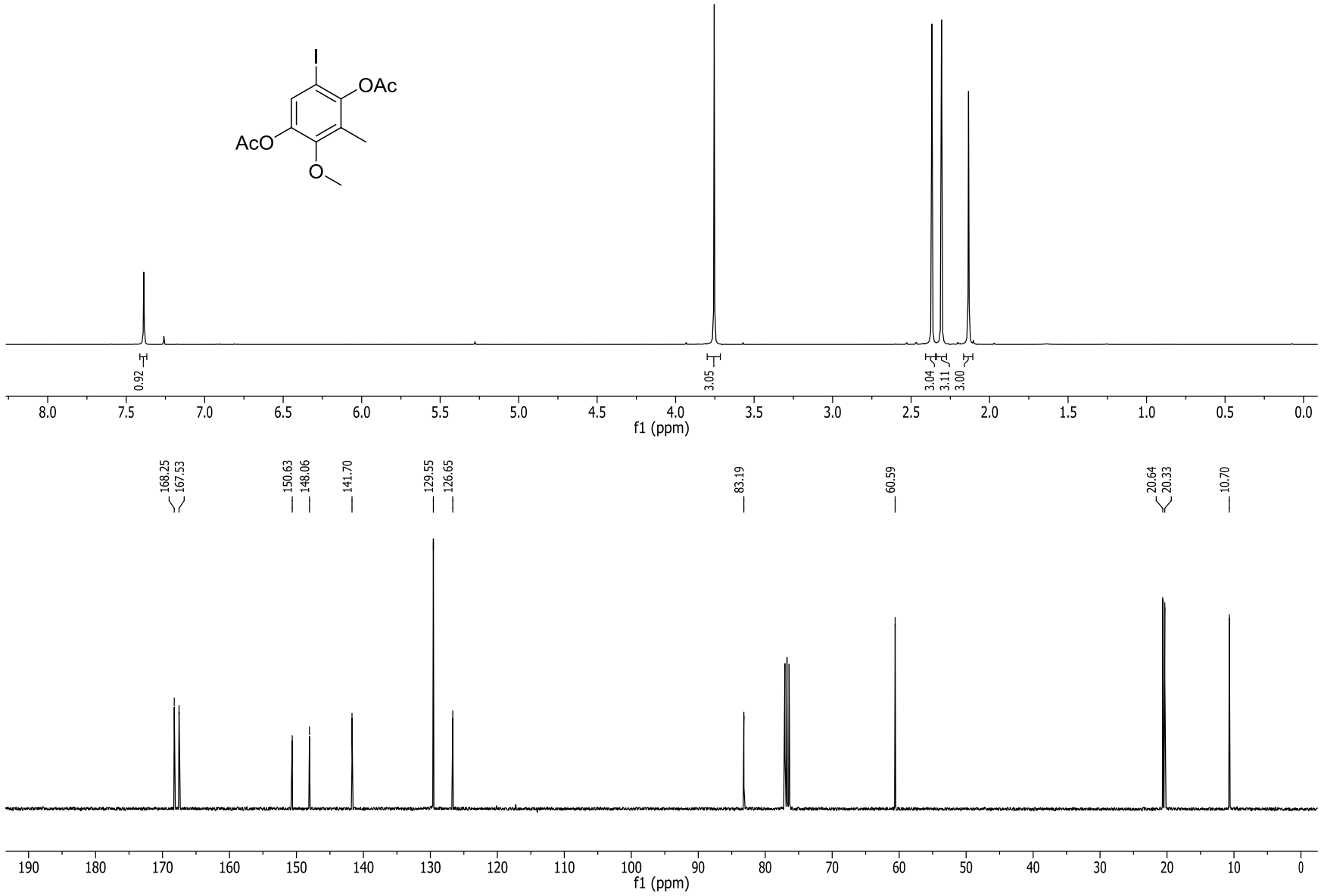

I
Br
OMOM
MOMO
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.99
1.97
3.01
5.95
3.00

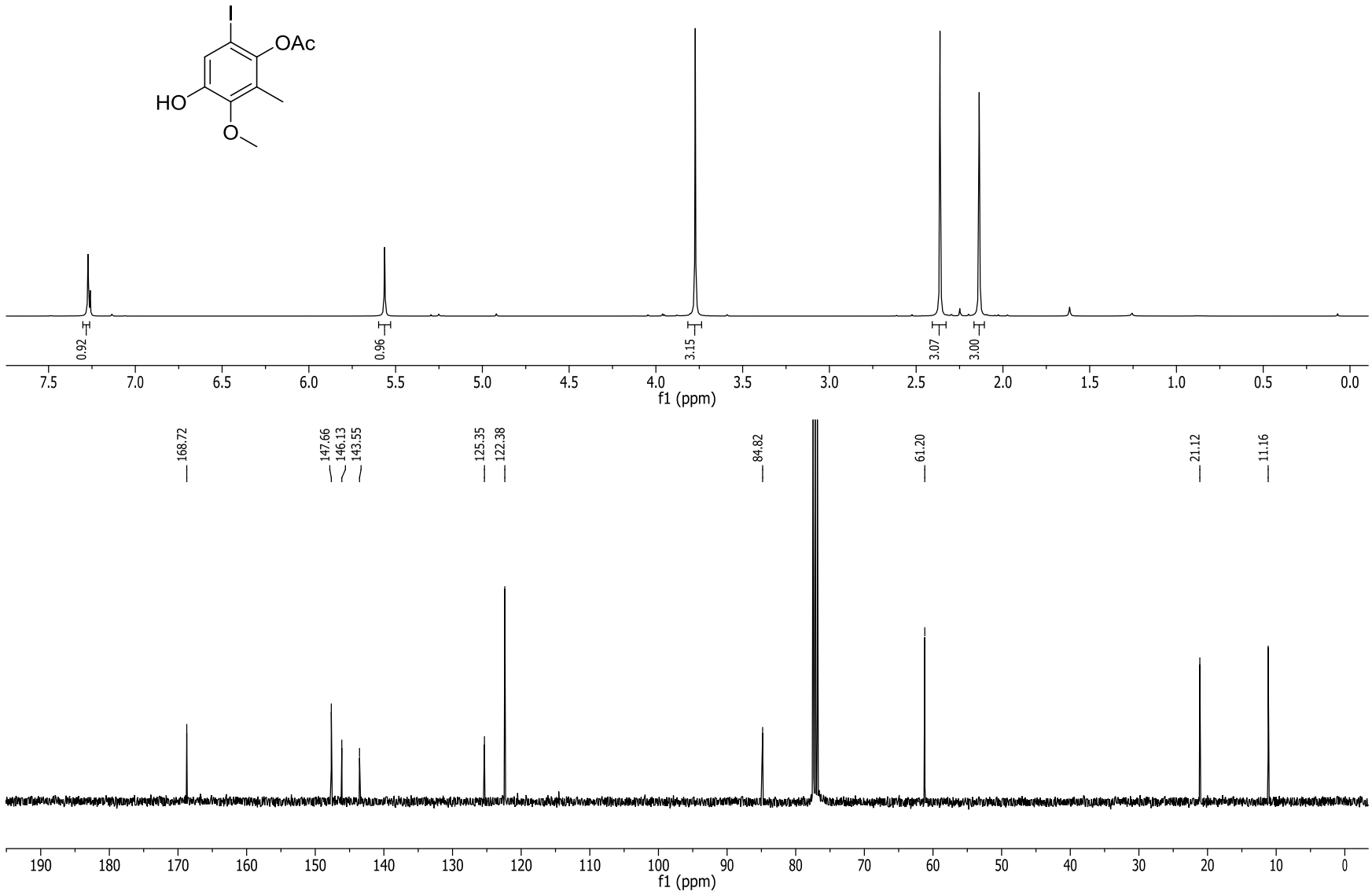

154.15
153.04
145.26
126.96
122.98
100.33
99.35
95.74
60.55
58.40
58.24
11.43
I
Br
OMOM
MOMO
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

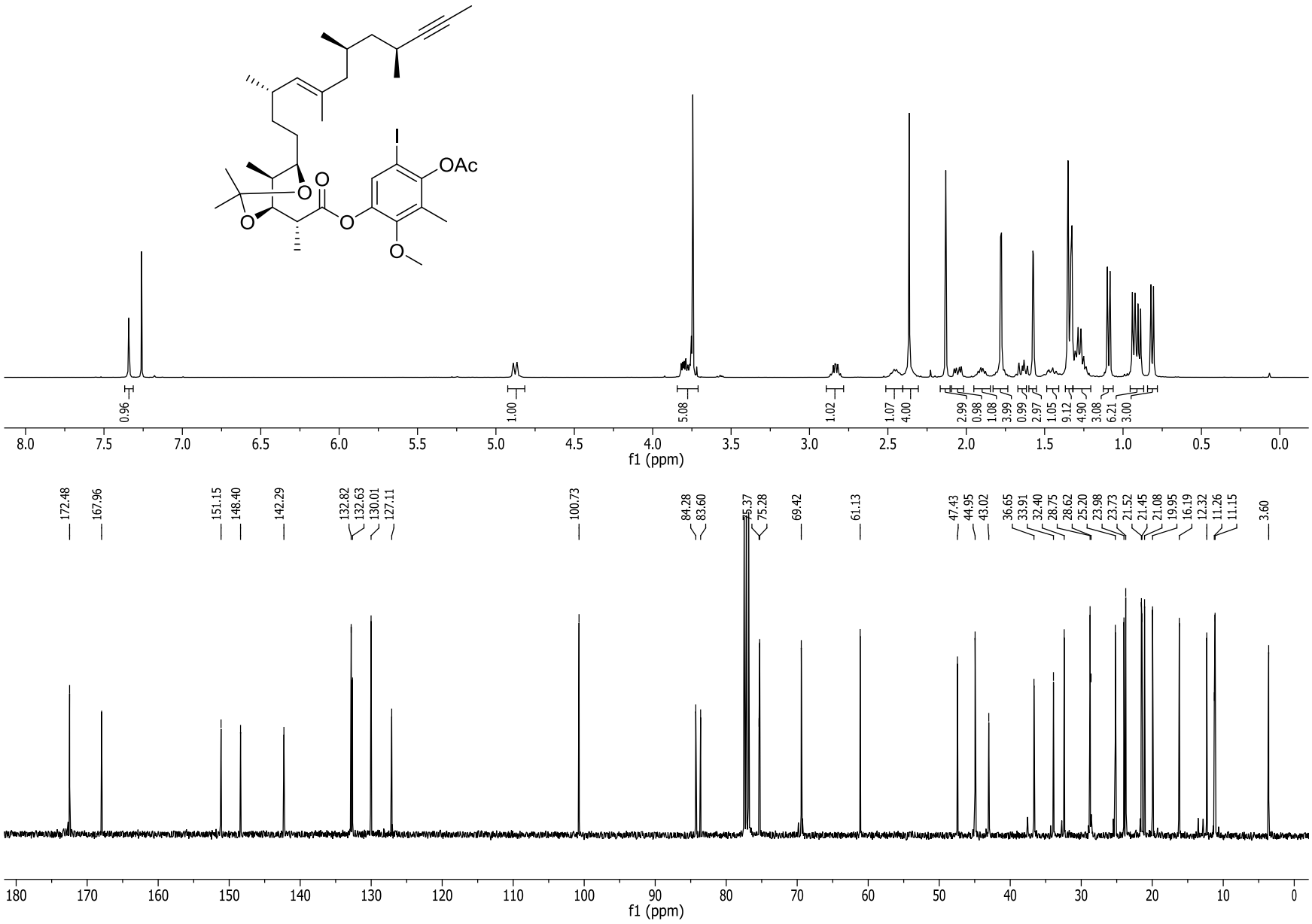

Br
OMOM
MOMO
OMe
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.00
3.00
2.96
2.94
3.02
2.96

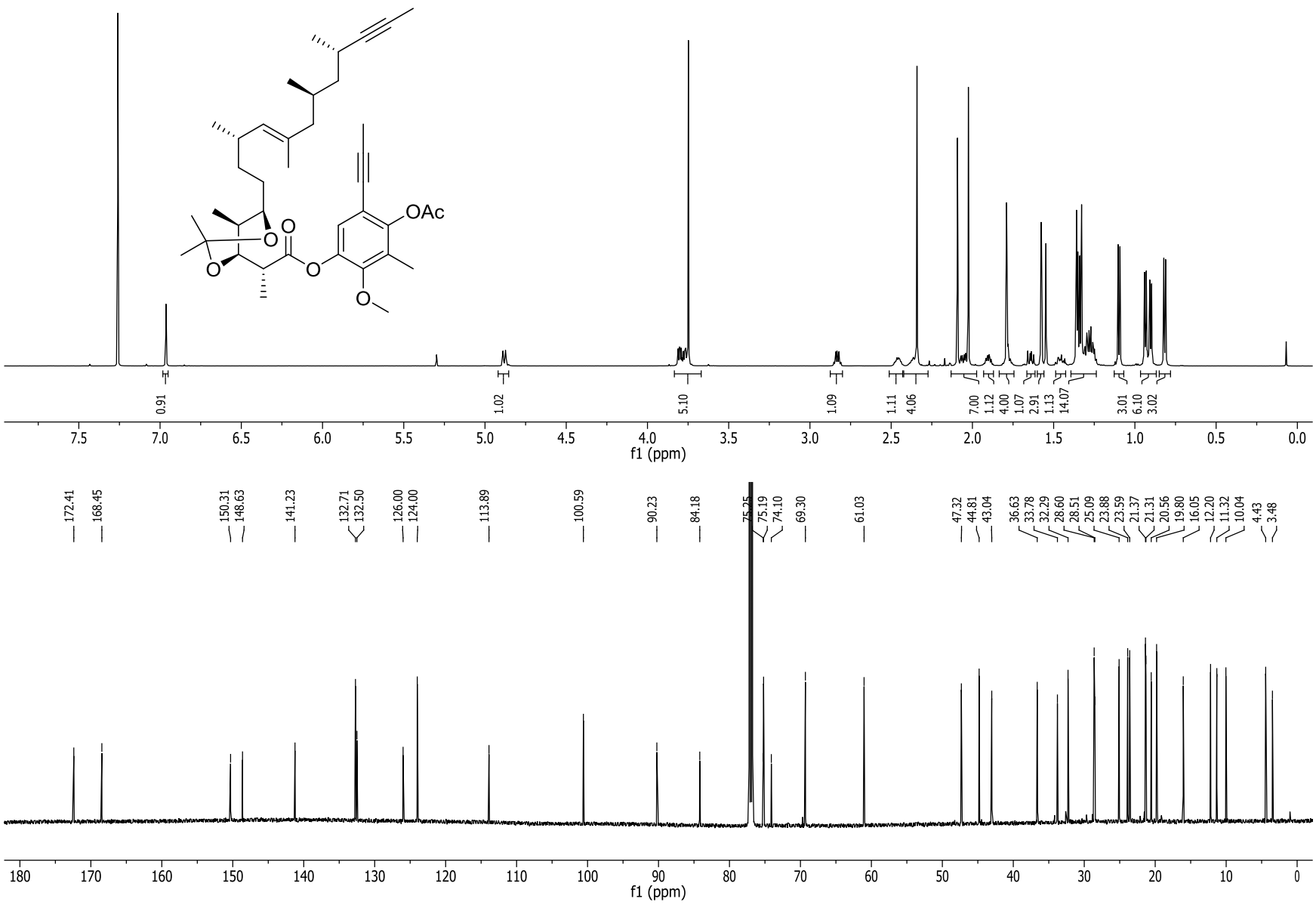

154.91
152.27
144.65
126.17
118.83
116.91
99.73
99.21
94.38
75.35
60.68
58.28
57.82
10.30
4.91
Br
OMOM
MOMO
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

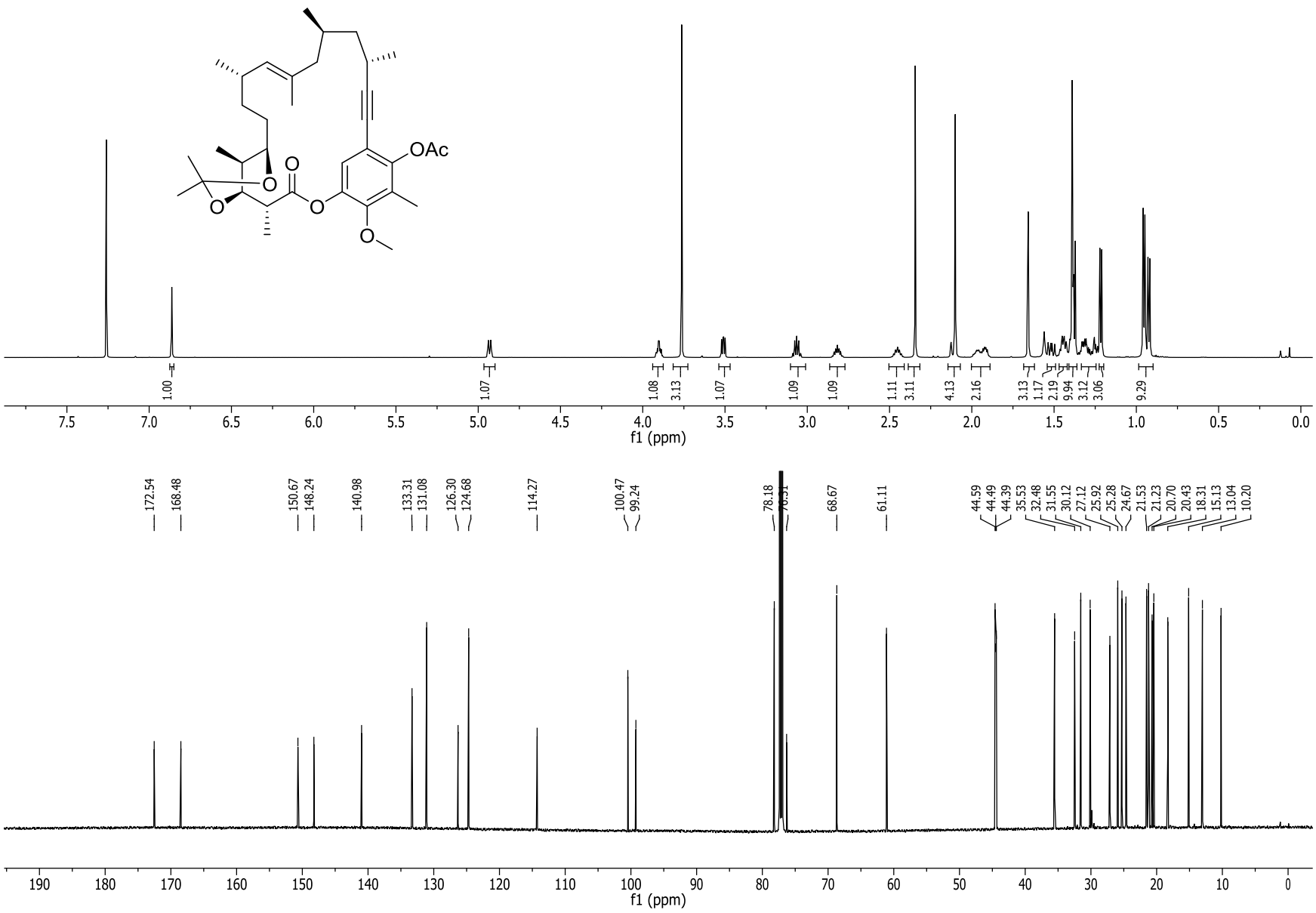

OAc
AcO
O
0.96
0.96
3.00
6.05
3.07
f1 (ppm)
168.59
168.57
150.30
147.18
141.24
125.23
120.14
117.23
60.43
20.33
20.29
9.46
f1 (ppm)

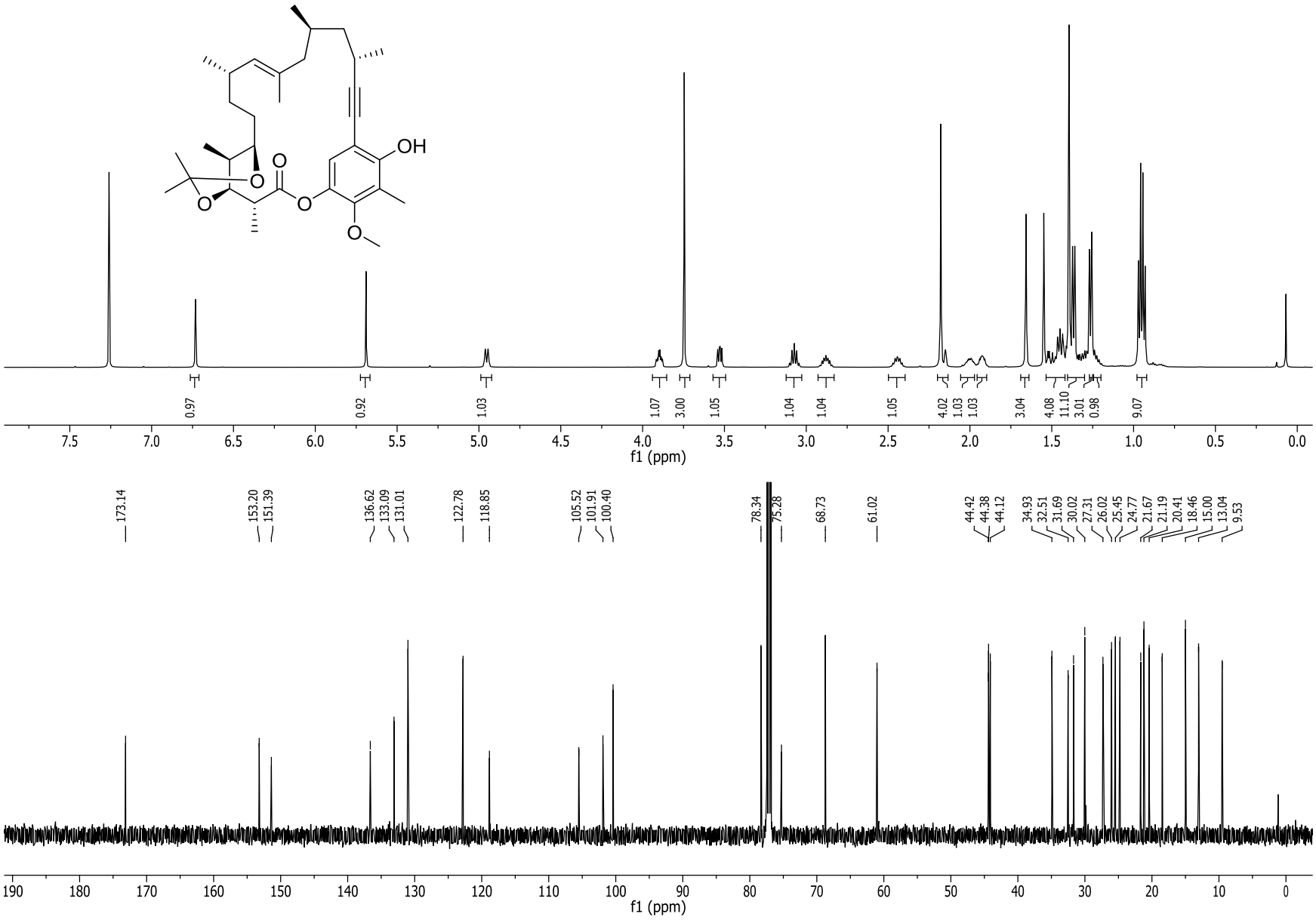

I
OAc
AcO
O
0.92
3.05
3.04
3.11
3.00
f1 (ppm)
168.25
167.53
150.63
148.06
141.70
129.55
126.65
83.19
60.59
20.64
20.33
10.70
f1 (ppm)

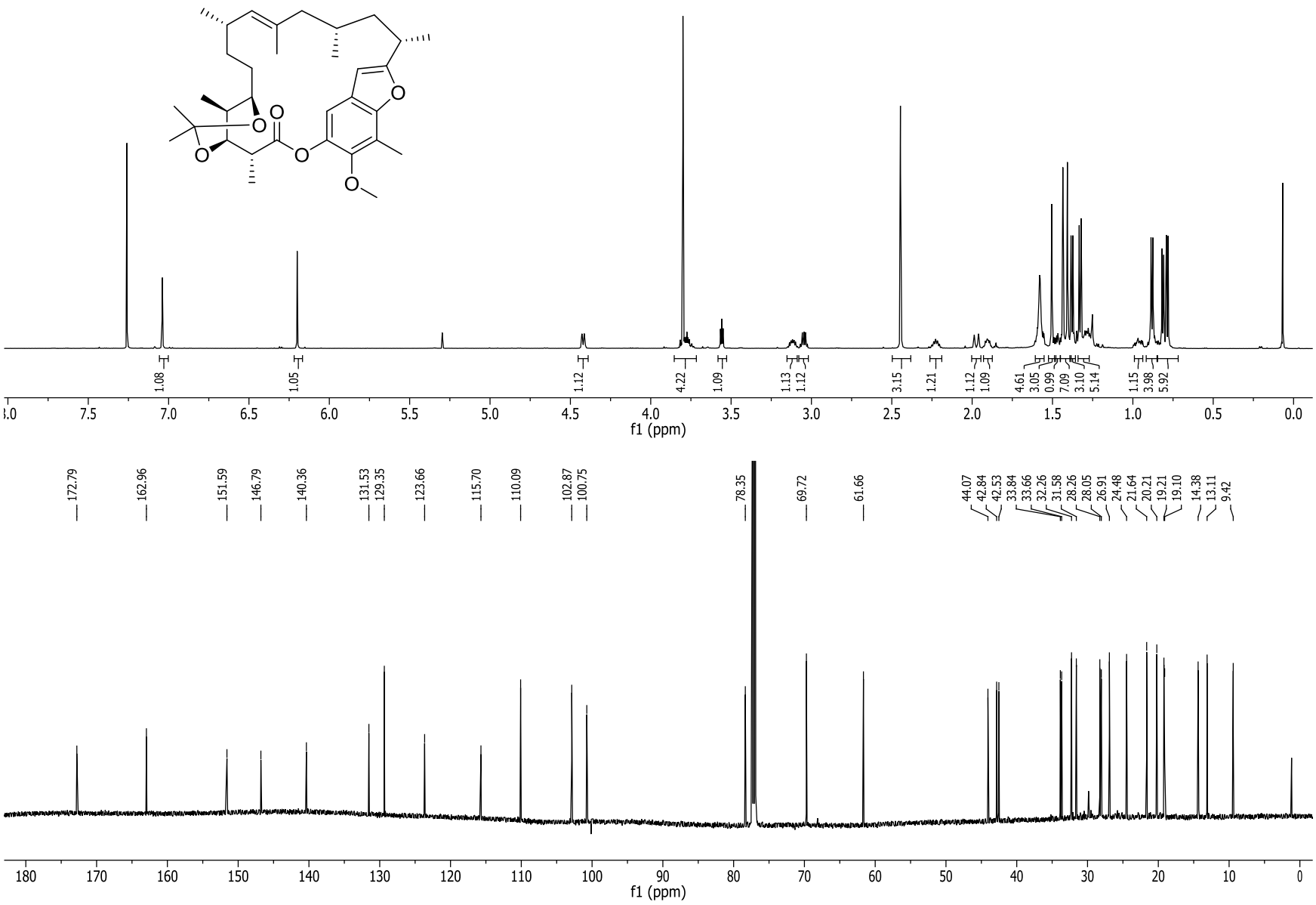

I
OAc
HO
O
0.92
0.96
3.15
3.07
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
168.72
147.66
146.13
143.55
125.35
122.38
84.82
61.20
21.12
11.16
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

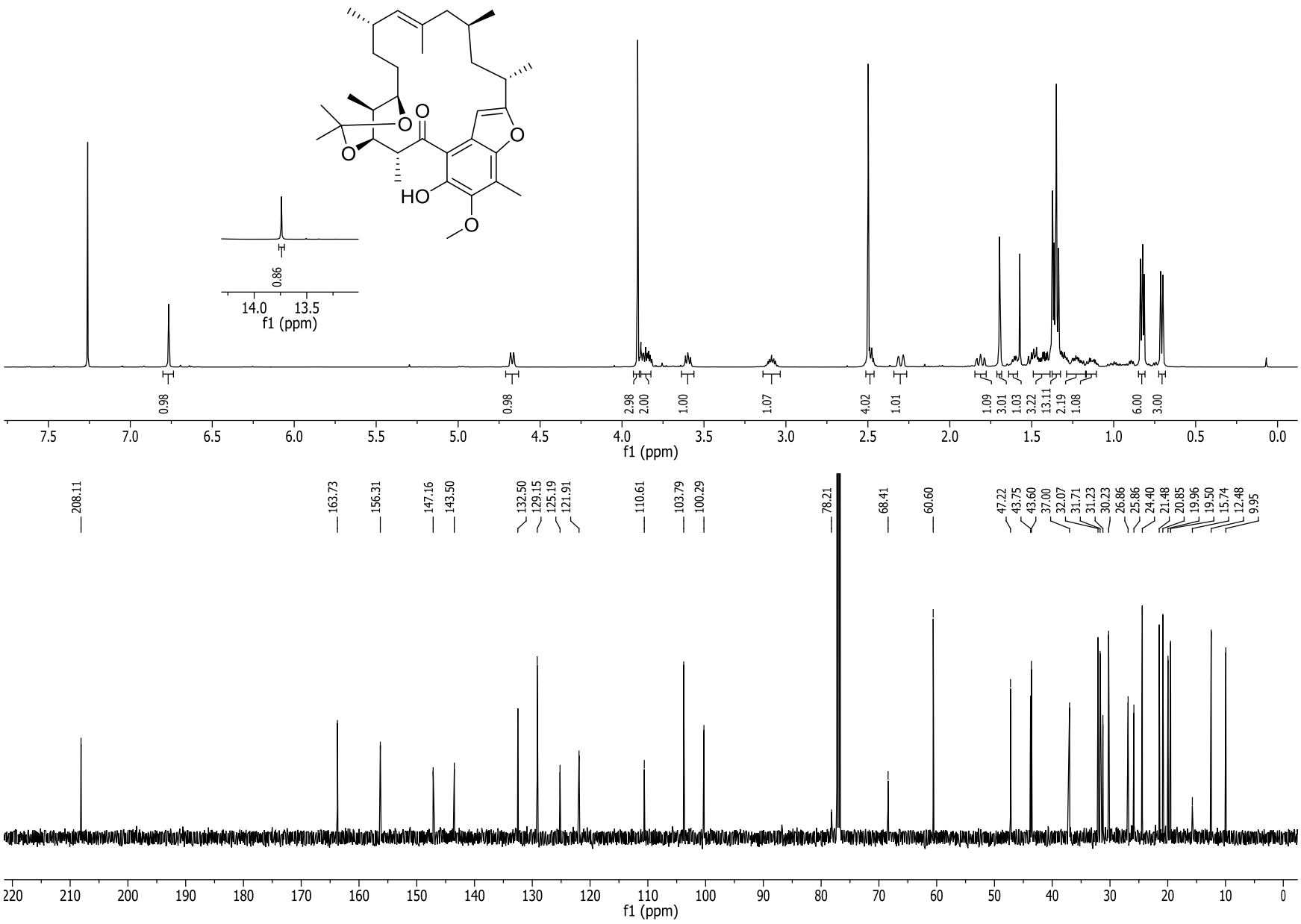

OAc
I
O
O
O
O
O
0.96
1.00
5.08
1.02
1.07
4.00
2.99
0.98
1.08
3.99
0.99
2.97
1.05
9.12
4.90
3.08
6.21
3.00
f1 (ppm)
172.48
167.96
151.15
148.40
142.29
132.82
132.63
130.01
127.11
100.73
84.28
83.60
75.37
75.28
69.42
61.13
47.43
44.95
43.02
36.65
33.91
32.40
28.75
28.62
25.20
23.98
23.73
21.52
21.45
21.08
19.95
16.19
12.32
11.26
11.15
3.60
f1 (ppm)

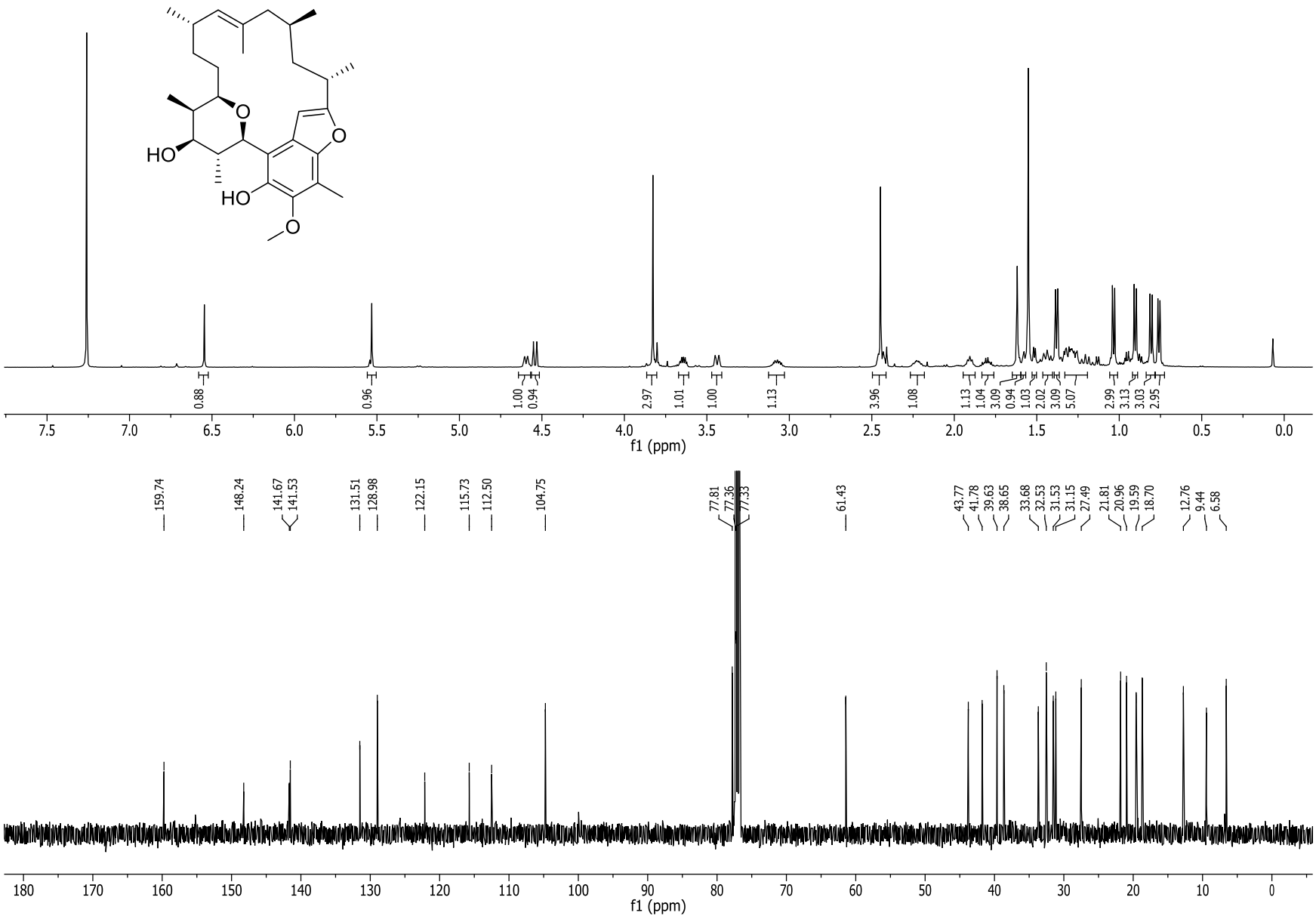

OAc
O
O
O
O
O
0.91
1.02
5.10
1.09
1.11
4.06
7.00
1.12
4.00
1.07
2.91
1.13
14.07
3.01
6.10
3.02
f1 (ppm)
172.41
168.45
150.31
148.63
141.23
132.71
132.50
126.00
124.00
113.89
100.59
90.23
84.18
75.25
75.19
74.10
69.30
61.03
47.32
44.81
43.04
36.63
33.78
32.29
28.60
28.51
25.09
23.88
23.59
21.37
21.31
20.56
19.80
16.05
12.20
11.32
10.04
4.43
3.48
f1 (ppm)


OAc
O
O
O
O
O
1.00
1.07
1.08
3.13
1.07
1.09
1.09
1.11
3.11
4.13
2.16
3.13
1.17
2.19
9.94
3.12
3.06
9.29
f1 (ppm)
172.54
168.48
150.67
148.24
140.98
133.31
131.08
126.30
124.68
114.27
100.47
99.24
78.18
76.51
68.67
61.11
44.59
44.49
44.39
35.53
32.48
31.55
30.12
27.12
25.92
25.28
24.67
21.53
21.23
20.70
20.43
18.31
15.13
13.04
10.20
f1 (ppm)


OH
O
O
O
O
O
0.97
0.92
1.03
1.07
3.00
1.05
1.04
1.04
1.05
4.02
1.03
1.03
3.04
4.08
11.10
3.01
0.98
9.07
f1 (ppm)
173.14
153.20
151.39
136.62
133.09
131.01
122.78
118.85
105.52
101.91
100.40
78.34
75.28
68.73
61.02
44.42
44.38
44.12
34.93
32.51
31.69
30.02
27.31
26.02
25.45
24.77
21.67
21.19
20.41
18.46
15.00
13.04
9.53
f1 (ppm)


1.08
1.05
1.12
4.22
1.09
1.13
1.12
3.15
1.21
1.12
1.09
4.61
3.05
0.99
7.09
3.10
5.14
1.15
3.98
5.92
f1 (ppm)
172.79
162.96
151.59
146.79
140.36
131.53
129.35
123.66
115.70
110.09
102.87
100.75
78.35
69.72
61.66
44.07
42.84
42.53
33.84
33.66
32.26
31.58
28.26
28.05
26.91
24.48
21.64
20.21
19.21
19.10
14.38
13.11
9.42
f1 (ppm)


O
O
O
O
HO
O
0.86
14.0
13.5
f1 (ppm)
0.98
0.98
2.98
2.00
1.00
1.07
4.02
1.01
1.09
3.01
1.03
3.22
13.11
2.19
1.08
6.00
3.00
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)
208.11
163.73
156.31
147.16
143.50
132.50
129.15
125.19
121.91
110.61
103.79
100.29
78.21
68.41
60.60
47.22
43.75
43.60
37.00
32.07
31.71
31.23
30.23
26.86
25.86
24.40
21.48
20.85
19.96
19.50
15.74
12.48
9.95
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
O
O
HO
O
0.88
0.96
1.00
0.94
2.97
1.01
1.00
1.13
3.96
1.08
1.13
1.04
3.09
0.94
1.03
2.02
3.09
5.07
2.99
3.13
3.03
2.95
f1 (ppm)
159.74
148.24
141.67
141.53
131.51
128.98
122.15
115.73
112.50
104.75
77.81
77.36
77.33
61.43
43.77
41.78
39.63
38.65
33.68
32.53
31.53
31.15
27.49
21.81
20.96
19.59
18.70
12.76
9.44
6.58
f1 (ppm)