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Supporting Information

Increasing the Structural Span of Alkyne Metathesis

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Additional Crystallographic Information

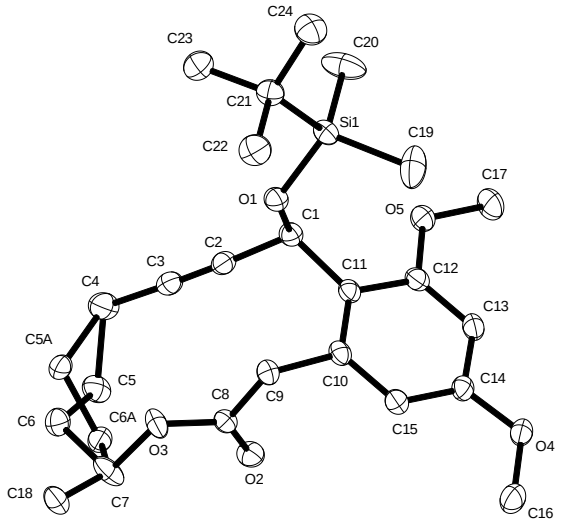


Figure S1. Structure of compound **33** in the solid state, showing the disorder of the C4-C6 region within the aliphatic chain.

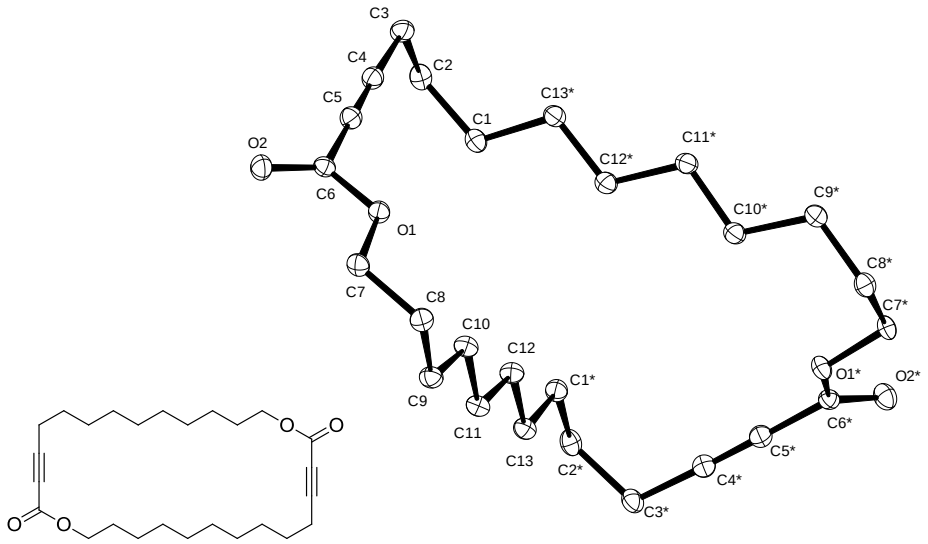


Figure S2. Structure of the head-to-tail cyclodimer formed as a minor by-product upon metathesis of alkynoate **48a**.

X-ray Crystal Structure Analysis of Compound 33: $C_{24}H_{36}O_5Si$, M_r = 432.62 g · mol^{-1}, colorless block, crystal size 0.403 x 0.161 x 0.119 mm, orthorhombic, space group $P2_12_12_1$, a = 7.8769(7) Å, b = 10.6641(10) Å, c = 28.818(3) Å, V = 2420.8(4) Å^3, T = 100 K, Z = 4, D_{calc} = 1.187 g · cm^3, λ = 1.54178 Å, μ(Cu-K_α) = 1.102 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.72, T_{max} = 0.88), Bruker AXS X8 Proteum diffractometer, 3.07 < θ < 67.11, 105639 measured reflections, 4259 independent

reflections, 4228 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.024 [$I > 2\sigma(I)$], wR_2 = 0.065, absolute structure parameter = 0.015(18), 297 parameters, H atoms riding, S = 1.047, residual electron density +0.2 / -0.2 e Å^{-3}.

X-ray Crystal Structure Analysis of Compound 25: $C_{17}H_{28}O_4$, M_r = 296.39 g · mol^{-1}, colorless block, crystal size 0.25 x 0.23 x 0.11 mm, monoclinic, space group $P2_1/n$, a = 8.5595(7) Å, b = 9.7342(7) Å, c = 20.3518(14) Å, β = 100.851(7)°, V = 1665.4(2) Å^3, T = 100 K, Z = 4, D_{calc} = 1.182 g · cm^3, λ = 0.71073 Å, $\mu(Mo\text{-}K_\alpha)$ = 0.082 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.97, T_{max} = 0.99), Nonius KappaCCD diffractometer, 2.80 < θ < 33.06, 29258 measured reflections, 6281 independent reflections, 4672 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.067 [$I > 2\sigma(I)$], wR_2 = 0.179, extinction coefficient = 0.0084(13), 190 parameters, H atoms riding, S = 1.067, residual electron density +1.1 / -0.4 e Å^{-3}.

X-ray Crystal Structure Analysis of Compound 39: $C_{32}H_{48}O_4$, M_r = 496.70 g · mol^{-1}, colorless block, crystal size 0.25 x 0.06 x 0.06 mm, orthorhombic, space group $P2_12_12$, a = 13.0760(8) Å Å, b = 23.4954(13) Å, c = 4.8287(3) Å, V = 1483.50(15) Å^3, T = 100 K, Z = 2, D_{calc} = 1.112 g · cm^3, λ = 1.54178 Å, $\mu(Cu\text{-}K_\alpha)$ = 0.556 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.90, T_{max} = 0.97), Bruker AXS X8 Proteum diffractometer, 3.76 < θ < 61.15, 18776 measured reflections, 2120 independent reflections, 1323 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.054 [$I > 2\sigma(I)$], wR_2 = 0.129, absolute structure parameter = –0.1(5), extinction coefficient = 0.0220(16), 165 parameters, H atoms riding, S = 0.931, residual electron density +0.2 / -0.2 e Å^{-3}.

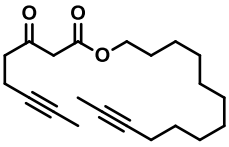
X-ray Crystal Structure Analysis of the Cyclodimer (Figure S2): $C_{26}H_{40}O_4$, M_r = 416.58 g · mol^{-1}, colorless block, crystal size 0.20 x 0.14 x 0.06 mm, monoclinic, space group $P2/n$, a = 9.1055(15) Å, b = 5.2069(9) Å, c = 24.954(4) Å, β = 93.551(3)°, V = 1180.8(3) Å^3, T = 100 K, Z = 2, D_{calc} = 1.172 g · cm^3, λ = 0.71073 Å, $\mu(Mo\text{-}K_\alpha)$ = 0.077 mm^{-1}, Semi-empirical absorption correction (T_{min} = 0.99, T_{max} = 1.00), Bruker-AXS APEX-II diffractometer, 1.635 < θ < 31.632, 32308 measured reflections, 3979 independent reflections, 3412 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.051 [$I > 2\sigma(I)$], wR_2 = 0.149, 136 parameters, H atoms riding, S = 1.218, residual electron density +0.4 / -0.3 e Å^{-3}.

CCDC 936549 (**33**), 936550 (**25**), 936551 (**39**) and 944741 (cyclodimer, Figure S2) contain the supporting crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

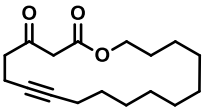
General. All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O, CH_2Cl_2, hexane, toluene (Na/K), MeOH (Mg). Flash chromatography (FC): Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker PX 300, AMX 300, AV 400, or AV 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 $CDCl_3$: $\delta_H \equiv 7.26$ ppm; [D_6]-acetone: $\delta_C \equiv 205.87$ ppm; residual $(CH_3)_2CO$ in [D_6]-acetone: $\delta_H \equiv 2.09$ ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (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. DBU was dried over CaH_2, whereas the molecular sieves were dried by heating (280°C, sand bath) in vacuo (10^{-3} mbar) overnight.

Model Studies

Compound 8. CsF (152 mg, 1.00 mmol) was added to a solution of ester **7** (1.68 g, 10.0 mmol)[1] and tridec-11-yn-1-ol (2.45 g, 12.5 mmol) in toluene and the resulting suspension was stirred at reflux temperature for 18 h. For work up, the mixture was allowed to cool before it was filtered through a silica pad, which was rinsed with EtOAc. The combined filtrates were evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 9:1) to give ester **8** as a colorless syrup (2.75 g, 83%). The product partly exists in enolized form. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (t, *J* = 6.8 Hz, 2H), 3.45 (s, 2H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.40 (tq, *J* = 7.6, 2.5 Hz, 2H), 2.10 (tq, *J* = 7.2 Hz, 2.5 Hz, 2H), 1.77 (t, *J* = 2.5 Hz, 3H), 1.74 (t, *J* = 2.5 Hz, 3H), 1.67 - 1.59 (m, 2H), 1.50 - 1.41 (m, 2H), 1.38 - 1.23 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.1, 167.0, 79.4, 77.1, 76.4, 75.3, 65.6, 49.2, 42.2, 29.4 (2C), 29.2, 29.1, 29.0, 28.9, 28.5, 25.8, 18.7, 13.2, 3.4 (2C); IR (film): $\tilde{\nu}$ = 2915, 2850, 1738, 1704, 1469, 1434, 1411, 1371, 1332, 1281, 1253, 1191, 1133, 1087, 1040, 1020, 985, 970, 923, 787, 755, 721 cm^{-1}; MS (EI): *m/z* (%): 332 (2) $[M]^+$, 317 (5), 161 (9), 154 (12), 153 (25), 147 (12), 137 (14), 134 (10), 133 (15), 121 (17), 120 (19), 119 (20), 110 (17), 109 (26), 108 (18), 107 (18), 95 (69), 94 (11), 93 (22), 83 (10), 81 (46), 80 (11), 79 (27), 69 (44), 68 (45), 67 (100), 66 (25), 65 (13), 55 (74), 54 (14), 53 (30), 43 (34), 42 (11), 41 (72), 39 (13), 29 (13), 27 (10); HRMS (EI): *m/z*: calcd for $C_{21}H_{32}O_3$: 332.2351; found: 332.2352.



Cycloalkyne 9. Et_3N (83 µL, 600 µmol) was added to a solution of compound **8** (166 mg, 500 µmol) in CH_2Cl_2 (2 mL), followed by slow addition of TMSCl (70 µL, 550 µmol). The resulting mixture was stirred overnight before all volatile materials were pumped off in vacuum (10^{-3} mbar). The residue was dissolved in toluene (250 mL), MS 5Å (1 g) was added and the resulting suspension stirred for 10 min before a solution of



[1] S. Trudeau, P. Deslongschamps, *J. Org. Chem*. **2004**, *69*, 832-838.

complex **2**·Et_2O (27.1 mg, 25 µmol) in toluene (1 mL) was introduced. After stirring for 16 h at 80°C, additional catalyst (27.1 mg, 25 µmol) in toluene (1 mL) was added and stirring continued for another 4 h at 80°C.[2] The mixture was then filtered through a pad of silica, the filtrate was evaporated, and the residue purified by flash chromatography (hexanes/acetone, 15:1) to furnish cycloalkyne **9** as a colorless solid (125 mg, 90%). The product partly exists in enolized form. Mp = 40-41 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (t, *J* = 5.8 Hz, 2H), 3.44 (s, 2H), 2.78 - 2.73 (m, 2H), 2.45 - 2.39 (m, 2H), 2.17 - 2.13 (m, 2H), 1.71 - 1.62 (m, 2H), 1.47 - 1.37 (m, 6H), 1.37 - 1.29 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 167.0, 81.1, 78.5, 65.4, 49.9, 41.9, 28.1, 27.6 (2C), 27.4, 27.3, 27.0, 26.7, 25.3, 18.3, 13.3; IR (film): $\tilde{\nu}$ = 2966, 2924, 2852, 1742, 1713, 1689, 1469, 1443, 1428, 1402, 1391, 1367, 1336, 1312, 1269, 1240, 1203, 1144, 1125, 1080, 1038, 1018, 995, 978, 955, 929, 914, 892, 868, 816, 784, 726, 704 cm^{-1}; MS (EI): *m/z* (%): 278 (39) $[M]^+$, 250 (9), 234 (17), 193 (10), 176 (10), 165 (32), 153 (38), 152 (48), 149 (39), 139 (30), 135 (27), 121 (24), 119 (20), 109 (68), 108 (26), 107 (61), 105 (20), 96 (23), 95 (27), 94 (42), 93 (43), 91 (39), 87 (20), 81 (43), 80 (32), 79 (73), 77 (32), 69 (47), 67 (60), 65 (24), 55 (96), 53 (24), 43 (47), 42 (22), 41 (100), 39 (25), 29 (30); HRMS (ESI+): *m/z*: calcd for $C_{17}H_{26}O_3$+Na: 301.1774; found: 301.1775.

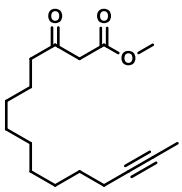
Compound 11. $AgNTf_2$ (10.7 mg, 27.5 µmol) was added to a solution of Ph_3PAuCl (15.0 mg, 30.3 µmol) in CH_2Cl_2 (0.9 mL) and the resulting suspension stirred for 15 min before the precipitate was allowed to settle. The supernatant was transferred via canula into a solution of cycloalkyne **9** (153 mg, 550 µmol) in CH_2Cl_2 (1.8 mL). The resulting mixture was stirred for 16 h before it was passed through a pad consisting of a layer of silica and a layer of Celite. The filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 3:1) to give the title compound as a colorless solid (149 mg, 97%). Mp = 69-70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (t, *J* = 5.5 Hz, 2H), 2.42 (t, *J* = 6.7 Hz, 2H), 2.38 (t, *J* = 6.1 Hz, 2H), 2.29 - 2.23 (m, 2H), 2.04 - 1.96 (m, 2H), 1.73 - 1.66 (m, 2H), 1.59 - 1.50 (m, 2H), 1.46 - 1.22 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 167.4, 163.2, 133.3, 64.0, 37.0, 35.0, 29.0, 27.4, 27.3, 25.7, 25.3, 24.7, 24.3, 23.9, 22.1, 21.9; IR (film): $\tilde{\nu}$ = 3526, 3317, 2927, 2906, 2852, 2683, 1715, 1667, 1617, 1460, 1440, 1433, 1420, 1385, 1368, 1345, 1328, 1302, 1268, 1239, 1206, 1185, 1170, 1153, 1145, 1104, 1070, 1062, 1040, 1028, 965, 948, 925, 897, 880, 802, 775, 762, 734, 703, 694 cm^{-1}; MS (EI): *m/z* (%): 278 (9) $[M]^+$, 163 (7), 149 (12), 136 (10), 110 (8), 79 (18), 77 (11), 69 (12), 67 (18), 66 (10), 55 (100), 53 (19), 43 (30), 42 (19), 41 (98), 39 (25), 29 (38), 27 (26); HRMS (ESI+): *m/z*: calcd for $C_{17}H_{26}O_3$ +Na: 301.1774; found: 301.1772.

Compound 12. TMSCl (98 µL, 770 µmol) and DDQ (175 mg, 770 µmol) were added at –20°C to a solution of compound **11** (195 mg, 700 µmol) in MeCN (2.8 mL) in a pressure tube, which was tightly closed. The mixture was allowed to reach ambient temperature overnight before it was stirred for 6 h at 90°C. After cooling to ambient temperature, the mixture was diluted with acetone until all insoluble materials had

[2] Since the substrate and the product could not be distinguished by TLC, the second crop was added to ensure that no trace of starting material remained; no attempt was made to check whether this replenishing is actually necessary.

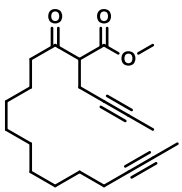
dissolved, and the resulting solution was adsorped onto silica. The loaded silica was added on top of a flash column loaded with silica and the product was eluted with hexane/EtOAc (15:1 → 6:1) to give product **12** as a colorless solid (92.5 mg, 48%, 67% brsm) and recovered starting material (54.0 mg, 28%). Mp = 73-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.26 (s, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 6.83 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.74 (dd, *J* = 7.6, 1.1 Hz, 1H), 4.44 - 4.41 (m, 2H), 2.88 - 2.82 (m, 2H), 1.84 - 1.76 (m, 2H), 1.63 - 1.32 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1, 162.4, 146.1, 134.0, 122.4, 115.4, 112.3, 66.1, 36.5, 31.2, 27.3, 27.0, 26.5, 26.2, 23.6, 23.1, 22.9; IR (film): $\tilde{\nu}$ = 2941, 2915, 2899, 2846, 1952, 1868, 1652, 1606, 1572, 1470, 1441, 1388, 1373, 1342, 1310, 1292, 1256, 1241, 1213, 1204, 1164, 1141, 1124, 1101, 1071, 1048, 1030, 1019, 976, 936, 910, 885, 863, 815, 802, 789, 769, 756, 712 cm^{-1}; MS (EI): *m/z* (%): 277 (20), 276 (100) [M]$^+$, 258 (20), 240 (10), 211 (11), 197 (14), 173 (18), 162 (27), 161 (37), 160 (16), 152 (53), 148 (28), 147 (51), 146 (32), 135 (16), 134 (65), 107 (14), 105 (19), 91 (13), 77 (16), 55 (27), 41 (34); HRMS (ESI+): *m/z*: calcd for $C_{17}H_{24}O_3$ +Na: 299.1618; found: 299.1617.

Methyl 3-oxo-13-pentadecynoate (S1). Methyl acetoacetate (581 mg, 5.00 mmol) was slowly added



at 0°C to a suspension of NaH (132 mg, 5.50 mmol) in THF (10 mL). Once the additon of gas had ceased, *n*-BuLi (1.6 M in hexane, 3.28 mL, 5.25 mmol) was introduced and stirring continued for 15 min at 0°C before 11-bromo-2-undecyne (1.21 g, 5.25 mmol) was added. After stirring for 16 h at ambient temperature, the reaction was quenched with aq. HCl (1 M). The aqueous layer was extracted with Et_2O, the combined extracts were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (pentane/Et_2O, 7:1) to give the title compound as a colorless solid (701 mg, 53%). Mp = 39-40 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.72 (s, 3H), 3.43 (s, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 2.09 (tq, *J* = 7.2, 2.6 Hz, 2H), 1.76 (t, J = 2.6 Hz, 3H), 1.61 - 1.53 (m, 2H), 1.48 - 1.39 (m, 2H), 1.38 - 1.22 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.7, 167.6, 79.3, 75.3, 52.3, 49.0, 43.0, 29.2 (2C), 29.0 (2C), 28.9, 28.8, 23.4, 18.7, 3.4; IR (film): $\tilde{\nu}$ = 2934, 2916, 2848, 1743, 1708, 1469, 1438, 1406 1379, 1370, 1356, 1336, 1317, 1274, 1257, 1232, 1198, 1159, 1110, 1089, 1072, 1011, 1002, 983, 949, 896, 861, 833, 718, 657 cm^{-1}; MS (EI): *m/z* (%): 266 (2) [M]$^+$, 235 (5), 199 (10), 175 (6), 174 (7), 150 (6), 149 (6), 138 (5), 135 (9), 129 (32), 121 (14), 116 (63), 109 (21), 101 (37), 97 (15), 95 (52), 93 (19), 84 (17), 81 (41), 79 (23), 74 (23), 69 (44), 68 (100), 67 (44), 59 (25), 55 (60), 53 (22), 43 (35), 41 (45), 29 (15); HRMS (ESI+): *m/z*: calcd for $C_{16}H_{26}O_3$+Na: 289.1774; found: 289.1775.

Compound 14. A solution of compound **S1** (559 mg, 2.10 mmol) in THF (4 mL) was slowly added at



0°C to a suspension of NaH (50.4 mg, 2.10 mmol) in THF (4.2 mL). After stirring for 30 min at this temperature, 1-bromo-2-butyne (190 µl, 2.10 mmol) was introduced and the resulting mixture stirred for 16 h at ambient temperature. The reaction was quenched with aq. HCl (1 M). The aqueous layer was extracted with Et_2O, the combined extracts were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexane/EtOAc, 12:1) to give the title compound as a colorless solid (428 mg, 64%). Mp = 40-41 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.71 (s, 3H), 3.64 (t, *J* = 7.6 Hz, 1H), 2.66 - 2.47 (m, 4H), 2.08 (tq, *J* = 7.2, 2.5 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H), 1.71 (t, *J* = 2.5 Hz, 3H), 1.61 - 1.57

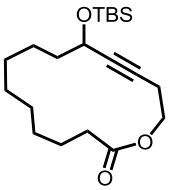
(m, 2H), 1.48 - 1.39 (m, 2H), 1.37 - 1.22 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.0, 168.9, 79.3, 77.7, 75.3, 75.0, 57.8, 52.5, 42.6, 29.3 (2C), 29.1, 29.0, 28.9, 28.8, 23.3, 18.7, 180, 3.4 (2C); IR (film): $\tilde{\nu}$ = = 3010, 2920, 2849, 1735, 1707, 1649, 1616, 1463, 1454, 1439, 1431, 1401, 1370, 1354, 1341, 1301, 1284, 1272, 1263, 1238, 1225, 1180, 1113, 1100, 1083, 1025, 1001, 972, 923, 867, 833, 812, 726, 656 cm^{-1}; MS (EI): *m/z* (%): 318 (8) [M]$^+$, 287 (8), 286 (6), 259 (11), 193 (9), 175 (6), 168 (7), 161 (8), 153 (6), 147 (13), 133 (11), 126 (11), 125 (100), 121 (10), 120 (11), 119 (12), 109 (19), 108 (15), 107 (11), 95 (47), 93 (13), 81 (31), 79 (14), 69 (20), 68 (11), 67 (33), 55 (52), 53 (22), 43 (16), 41 (30); HRMS (ESI+): *m/z*: calcd for $C_{20}H_{30}O_3$ +Na: 341.2087; found: 341.2087.

Cycloalkyne 15. NEt_3 (166 µL, 1.20 mmol) was added to a solution of compound **14** (319 mg, 1.00 mmol) in CH_2Cl_2 (4 mL), followed by slow addition of TMSCl (140 µL, 1.20 mmol). The resulting mixture was stirred overnight before all volatile materials were pumped off in vacuum (10^{-3} mbar). The residue was dissolved in toluene (200 mL), MS 5Å (2 g) was added and the resulting suspension stirred for 10 min before a solution of complex **2**·Et_2O (54.3 mg, 50 µmol) in toluene (2 mL) was introduced. After stirring for 16 h at 80°C, additional catalyst (54.3 mg, 50 µmol) in toluene (2 mL) was added and stirring continued for another 6 h at 80°C.[2] The mixture was then filtered through a pad of silica, the filtrate was evaporated, and the residue purified by flash chromatography (hexanes/acetone, 10:1) to furnish cycloalkyne **15** as a colorless solid (173 mg, 66%). Mp = 38-39 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 3H), 3.77 (dd, *J* = 12.0, 3.0 Hz, 1H), 2.95 (ddt, *J* = 16.7, 12.0, 2.4 Hz, 1H), 2.74 - 2.69 (m, 2H), 2.55 (ddt, *J* = 2.3, 3.0, 16.7 Hz, 1H), 2.25 - 2.09 (m, 2H), 1.92 - 1.81 (m, 1H), 1.62 - 1.50 (m, 1H), 1.46 - 1.22 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.0, 168.6, 81.6, 76.7, 57.0, 52.6, 41.7, 26.9, 26.1, 25.9, 25.1, 25.0, 24.7, 22.3, 17.8, 17.7; IR (film): $\tilde{\nu}$ = 2929, 2858, 1745, 1716, 1457, 1434, 1404, 1342, 1266, 1211, 1192, 1169, 1107, 1078, 1021, 911, 858, 758, 709, 672 cm^{-1}; MS (EI): *m/z* (%): 264 (11) [M]$^+$, 233 (17), 205 (52), 187 (25), 177 (17), 162 (32), 147 (25), 137 (59), 133 (34), 121 (37), 119 (45), 107 (39), 105 (36), 95 (42), 94 (39), 93 (48), 91 (53), 81 (58), 80 (32), 79 (78), 77 (36), 69 (33), 67 (68), 66 (28), 65 (30), 59 (25), 55 (95), 53 (27), 43 (35), 41 (100), 29 (34); HRMS (ESI+): *m/z*: calcd for $C_{16}H_{24}O_3$ +Na: 287.1618; found: 287.1616.

Furan (16). $AuCl_3$ (12.1 mg, 40.0 µmol) was added to a solution of cycloalkyne **15** (150 mg, 566 µmol) in MeOH (3.0 mL) and the resulting mixture was stirred in a closed vessel at 70°C for 24 h. After reaching ambinet temperature, the mixture was adsorped on silica which was loaded on top of a flash column filled with silica. The product was eluted with pentanes/Et_2O (30:1) to give furan **16** as a colorless oil (100 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.23 (s, 1H), 3.79 (s, 3H), 3.01 - 2.96 (m, 2H), 2.63 - 2.59 (m, 2H), 1.77 - 1.70 (m, 2H), 1.69 - 1.62 (m, 2H), 1.37 - 1.18 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 162.0, 154.5, 113.5, 106.2, 51.1, 27.0, 26.9, 26.7, 26.6 (2C), 26.1, 26.0, 25.9, 25.8, 25.5; IR (film): $\tilde{\nu}$ = 2927, 2858, 1716, 1613, 1574, 1459, 1437, 1392, 1338, 1300, 1281, 1206, 1151, 1092, 1064, 1027, 956, 806, 777, 700 cm^{-1}; MS (EI): *m/z* (%): *m/z* (%): 265 (18), 264 (100) [M]$^+$, 249 (5), 233 (23), 232 (12), 221 (5), 205 (23), 204 (16), 203 (6), 189 (5), 187 (14), 186 (8), 179 (7), 168 (5), 166 (8), 165 (22), 154 (7), 153 (15), 152

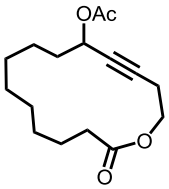
(26), 147 (5), 135 (5), 122 (6), 121 (5), 94 (8), 55 (9), 41 (10), 29 (6); HRMS (ESI+): *m/z*: calcd for $C_{16}H_{24}O_3$+Na: 287.1618; found: 287.1618.

Representative Alkyne Metathesis Reaction of a Propargyl Alcohol Derivative (Table 1, entry 1). A stock solution of complex **2**·Et_2O (0.01 M in toluene, 0.50 mL, 5.0 µmol) was added to a solution of diyne **17a** (0.020 g, 0.050 mmol) in toluene (2.5 mL), containing activated MS 5Å powder (300 mg). The suspension was stirred overnight at ambient temperature before it was filtered, the filtrate was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 10:1) to give product **18a** as a colorless oil (12.1 mg, 69%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.40-4.32 (m, 1H), 4.19-4.07 (m, 2H), 2.64-2.50 (m, 2H), 2.42-2.32 (m, 2H), 1.74-1.50 (m, 4H), 1.50-1.20 (m, 10H), 0.87 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.2, 82.5, 81.5, 63.5, 63.2, 38.1, 33.3, 27.1, 26.8, 26.1, 25.9, 25.7, 24.9, 22.7, 19.2, 18.3, –4.6, –4.9; IR (film): $\tilde{\nu}$ = 2929, 2858, 1737, 1462, 1386, 1339, 1250, 1176, 1104, 1074, 1006, 938, 836, 777, 665 cm^{-1}; MS (EI): *m/z* (%): 337 (2), 295 (100), 265 (2), 225 (4), 185 (2), 155 (2), 127 (4), 105 (3), 91 (3), 75 (13), 55 (2), 41 (1); HRMS (ESI+): *m/z*: calcd for $C_{20}H_{36}O_3SiNa$: 375.2326 $[M+Na]^+$; found: 375.2328.

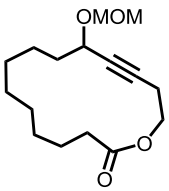


Small amounts of a ***cyclic dimer*** were also isolated, which analyzed as follows: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (t, *J* = 6.4 Hz, 2H), 4.20-4.09 (m, 4H), 2.60-2.47 (m, 4H), 2.31 (t, *J* = 7.5 Hz, 4H), 1.70-1.56 (m, 8H), 1.48-1.22 (m, 20H), 0.90 (s, 18H), 0.11 (s, 6H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6, 83.3, 80.4, 63.1, 62.2, 38.9, 34.4, 29.5, 29.4, 29.3, 29.2, 25.8, 25.2, 25.1, 19.3, 18.3, –4.5, –5.0; MS (EI): *m/z* (%): 689 (2), 647 (100), 629 (1), 555 (1), 515 (4), 423 (3), 347 (6), 295 (20), 277 (5), 243 (6), 185 (4), 93 (5), 73 (24), 55 (4); HRMS (ESI+): *m/z*: calcd for $C_{40}H_{72}O_6Si_2Na$: 727.4760 $[M+Na]^+$; found: 727.4757.

Cycloalkyne 18b: Prepared analogously as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.38-5.32 (m, 1H), 4.14 (t, *J* = 5.2 Hz, 2H), 2.62-2.49 (m, 2H), 2.40-2.34 (m, 2H), 2.04 (s, 3H), 1.75-1.60 (m, 4H), 1.54-1.20 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.1, 170.0, 83.3, 78.4, 64.7, 62.9, 33.9, 33.2, 26.9, 26.8, 26.0, 25.7, 24.9, 22.5, 21.1, 19.2; IR (film): $\tilde{\nu}$ = 2931, 2860, 1735, 1458, 1372, 1350, 1233, 1178, 1104, 1020, 971 cm^{-1}; MS (EI): *m/z* (%): 280 (9) $[M]^+$, 238 (8), 220 (7), 192 (4), 179 (3), 163 (2), 151 (5), 137 (16), 123 (14), 96 (100), 91 (19), 79 (18), 67 (15), 55 (39), 43 (94); HRMS (ESI+): *m/z*: calcd for $C_{16}H_{24}O_4Na$: 303.1567 $[M+Na]^+$; found: 303.1566.

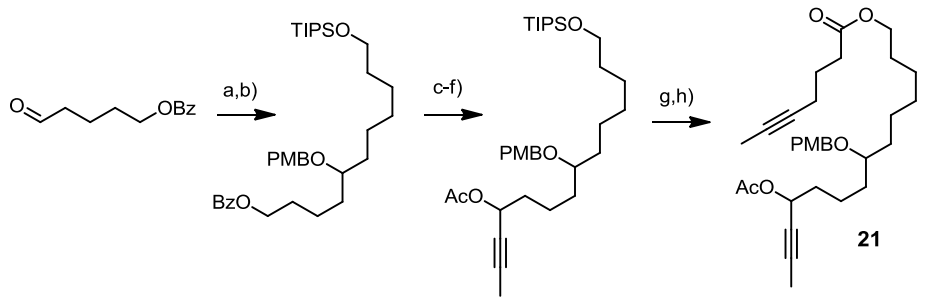


Cycloalkyne 18c: Prepared analogously as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.89 (d, *J* = 6.7 Hz, 1H), 4.57 (d, *J* = 6.7 Hz, 1H), 4.39-4.30 (m, 1H), 4.20-4.07 (m, 2H), 3.35 (s, 3H), 2.65-2.53 (m, 2H), 2.43-2.30 (m, 2H), 1.80-1.55 (m, 4H), 1.50-1.20 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.2, 94.0, 83.3, 79.5, 66.1, 63.0, 55.5, 34.8, 33.3, 27.0, 26.8, 26.1, 25.7, 24.9, 22.7, 19.2; IR (film): $\tilde{\nu}$ = 2931, 2860, 1734, 1458, 1384, 1343, 1213, 1149, 1100, 1033, 947, 919 cm^{-1}; MS (EI): *m/z* (%): 282 (< 1) $[M]^+$, 252 (1), 237 (2), 221 (5), 169 (3), 151 (4), 139 (6), 126 (7), 107 (7), 96 (14), 80 (9), 67 (9), 55 (17), 45 (100), 41 (14); HRMS (ESI+): *m/z*: calcd for $C_{16}H_{26}O_4Na$: 305.1723 $[M+Na]^+$; found: 305.1721.



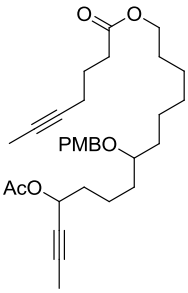
Compound 18d (R = H). *p*-TsOH·H_2O (5.7 mg, 0.030 mmol) was added to a solution of cycloalkyne **18a** (13 mg, 0.037 mmol) in MeOH (1.5 mL). The resulting mixture was stirred for 40 min before the reaction was quenched with H_2O. The product was extracted with a mixture of hexanes and EtOAc and the organic layer was dried over Na_2SO_4 and evaporated. Purification of the residue by flash chromatography (hexane/EtOAc, 4:1) provided the title compound as a colorless oil (8.2 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.45-4.35 (m, 1H), 4.21-4.08 (m, 2H), 2.66-2.52 (m, 2H), 2.44-2.30 (m, 2H), 1.78 (brs, 1H), 1.73-1.55 (m, 4H), 1.50-1.20 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.1, 82.6, 82.0, 63.0, 62.9, 37.1, 33.4, 27.0, 26.8, 26.1, 25.8, 24.9, 22.7, 19.2; IR (film): $\tilde{\nu}$ = 3421, 2931, 2859, 1733, 1457, 1385, 1340, 1232, 1176, 1100, 1030 cm^{-1}; MS (EI): *m/z* (%): 238 (< 1) $[M]^+$, 220 (10), 209 (2), 191 (5), 181 (4), 163 (9), 149 (9), 137 (12), 123 (23), 109 (25), 96 (75), 81 (100), 73 (15), 67 (28), 55 (87), 41 (70), 29 (24); HRMS (ESI$^+$): *m/z*: calcd for $C_{14}H_{22}O_3Na$: 261.1461 $[M+Na]^+$; found: 261.1459.

Enone 20. Complex **19** (1.4 mg, 1.8 µmol) and 10-camphorsulfonic acid (0.7 mg, 3.0 µmol) were added to a solution of compound **18d** (4.2 mg, 0.018 mmol) in THF (1.5 mL). The solution was stirred for 10 min before $In(OTf)_3$ (1.0 mg, 1.8 µmol) was introduced and the resulting mixture stirred under reflux for 3 h. After cooling to room temperature, the mixture was passed through a short plug of silica, the filtrate was evaporated, and the residue purified by flash chromatography (hexane/EtOAc, 4:1) to provide enone **20** as a colorless oil (3.3 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.76 (dt, *J* = 15.8, 6.8 Hz, 1H), 6.22 (d, *J* = 15.8 Hz, 1H), 4.27 (t, *J* = 5.4 Hz, 2H), 2.62-2.55 (m, 2H), 2.48 (t, *J* = 6.8 Hz, 2H), 2.34-2.29 (m, 2H), 1.70-1.55 (m, 4H), 1.40-1.16 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 173.9, 143.6, 131.6, 62.3, 40.4, 34.0, 31.7, 27.1, 26.9, 26.6, 26.4, 24.9, 24.6; IR (film): $\tilde{\nu}$ = 2932, 2856, 1732, 1694, 1668, 1629, 1459, 1348, 1255, 1169, 1052, 977 cm^{-1}; MS (EI): *m/z* (%): 238 (23) $[M]^+$, 220 (3), 210 (2), 192 (3), 180 (2), 165 (1), 151 (2), 137 (8), 124 (38), 109 (9), 96 (100), 84 (17), 81 (75), 69 (9), 55 (44), 41 (34), 29 (10); HRMS (ESI$^+$): *m/z*: calcd for $C_{14}H_{22}O_3Na$: 261.1461 $[M+Na]^+$; found: 261.1461.

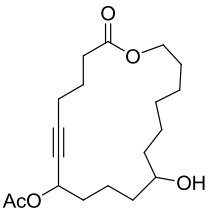


Scheme S1. Preparation of compound **21**: a) 6-(Tri-isopropylsilyloxy)hexylmagnesium bromide, THF, −78°C, 55%; b) PMBOC(=NH)CCl_3, $Sc(OTf)_3$ (10 mol%), toluene, 64%; c) K_2CO_3, MeOH, 71%; d) Dess-Martin periodinane, CH_2Cl_2, 72%; e) propynylmagnesium bromide, THF, 75%; f) Ac_2O, Et_3N, DMAP (10 mol%), CH_2Cl_2, 89%; g) trifluoromethansulfonic acid, aq. THF, 90%; h) 5-hexynoic acid, DCC, DMAP (5 mol%), CH_2Cl_2, 0°C → RT, 71%; DCC = dicyclohexylcarbodiimide; DMAP = 4-dimethylaminopyridine; PMP = *p*-methoxybenzyl; Tf = trifluoromethanesulfonyl

Compound 21. DCC (105 mg, 0.517 mmol) was added to a solution of 5-heptynoic acid (65 mg, 0.517 mmol), 14-hydroxy-8-((4-methoxybenzyl)oxy)tetradec-2-yn-4-yl acetate (190 mg, 0.47 mmol) and DMAP (5.7 mg, 0,047 mmol) in CH_2Cl_2 (4.7 mL) at 0°C. The mixture was stirred at room temperature for 5 hours before the precipitated urea was filtered off and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2 (4 mL) and the resulting solution washed with HCl (0.5 M, 2 x 2 mL) and aq. sat. $NaHCO_3$ (2 x 2 mL). After drying over Na_2SO_4, the solvent was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 15:1 → 10:1) to yield the title compound as a colorless oil (170 mg, 71%, mixture of diastereomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.34-5.29 (m, 1H), 4.42 (s, 2H), 4.05 (t, *J* = 6.7 Hz, 2H), 3.79 (s, 3H), 3.37-3.32 (m, 1H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.21-2.16 (m, 2H), 2.06 (s, 3H), 1.83 (d, *J* = 2.1 Hz, 3H), 1.83-1.21 (m, 21 H); ^{13}C NMR (100 MHz, $CDCl_3$, resolved signals of diastereomers): δ =173.6, 170.3, 159.3, 131.3, 129.5, 129.5, 113.9, 81.9, 78.5, 78.4, 78.2, 77.0, 76.6, 70.7, 64.7, 64.6, 55.5, 35.3, 35.3, 34.0, 34.0, 33.6, 33.5, 33.4, 29.7, 28.8, 26.1, 25.5, 25.4, 24.5, 21.3, 21.1, 21.1, 18.4. 3.8, 3.6; IR (film): $\tilde{\nu}$ = 2935, 2859, 1735, 1612, 1513, 1457, 1370, 1302, 1237, 1171, 1034, 819 cm^{-1}; MS (EI) *m/z* (%): 452 (4.97), 391 (0.47), 121 (100); HRMS (ESI): *m/z*: calcd. for $C_{31}H_{44}NaO_6$ [M^++Na]: 535.3030, found: 535.3037



Compound 22. Powdered molecular sieves (MS 5Å, 120 mg) was added to a solution of compound **21** (120 mg, 0.234 mmol) in toluene (115 mL), and the resulting mixture was stirred at 80 °C for 15 min. Catalyst **1** (Ar = *p*MeOC$_6$H$_4$-) (26 mg, 0.0234 mmol) was introduced and stirring continued at 80 °C for 15 h. To ensure total conversion, additional catalyst **1** (Ar = *p*MeOC$_6$H$_4$-) (5.2 mg, 0.0047 mmol) was added and the mixture stirred for an additional hour at the same temperature. The mixture was filtrated through a pad of silica which was rinsed with ethyl acetate. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexane/EtOAc, 10:1) to yield the title compound as a viscous oil (100 mg, 95%, mixture of diastereomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.40-5.36 (m, 1H), 4.70 (d, *J* = 11.3 Hz, 1H), 4.37 (d, *J* = 11.3 Hz, 1H), 4.18-4.06 (m, 2H), 3.80 (s, 3H), 3.39-3.30 (m, 1H), 2.40-2.39 (m, 2H), 2.28 (dt, *J* = 7.2, 1.9 Hz, 2H), 2.07 (d, *J* = 1.3, 3H), 1.85 (quint, *J* = 7.5, 2H), 1.72-1.25 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$, resolved signals of diastereomers): δ = 173.1, 170.2, 170.1, 159.3, 131.3, 129.4, 129.4, 113.9, 85.7, 85.7, 70.5, 70.4, 64.8, 64.7, 64.3, 55.5, 34.9, 34.8, 33.9, 33.8, 32.9, 32.8, 32.5, 32.5, 28.1, 28.0, 25.2, 24.6, 24.5, 24.5, 21.4, 20.6, 20.4, 18.5; IR (film): $\tilde{\nu}$ = 2934, 2858, 1734, 1513, 1238, 1096 cm^{-1}; MS (EI) *m/z* (%): 398 (6.25), 337 (0.72), 121 (100); HRMS (ESI): *m/z*: calcd. for $C_{27}H_{38}NaO_6$ [M^++Na]: 481.2571, found: 481.2563.



Compound 22b. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (513 mg, 1.05 mmol) was added to a solution of compound **22a** (100 mg, 0.21 mmol) in a biphasic mixture CH_2Cl_2 (20 mL) and phosphate buffer (pH 7, 20 mL). The mixture was stirred for 70 min before it was diluted with CH_2Cl_2 (20 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (2 x 50 mL), the aqueous phase was

extracted with CH_2Cl_2 (3 x 20 mL), the combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexane/EtOAc, 3:1) to yield the corresponding alcohol as a colorless syrup (69 mg, 97%, mixture of diastereomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41-5.35 (m, 1H), 4.18-4.07 (m, 2H), 3.67-3.65 (m, 1H), 2.42 (dt, *J* = 8.0, 1.6 Hz, 2H), 2.29 (dt, *J* = 7.12, 2.16 Hz, 2H), 2.06 (s, 3H), 1.85 (quint, *J* = 7.4 Hz, 2H), 1.75-1.35 (m, 16H), 1.24 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, resolved ignals of diastereomers): δ = 173.1, 170.2, 170.1, 85.8, 85.7, 78.4, 78.3, 71.4, 71.3, 64.7, 64.6, 64.3, 64.2, 37.2, 37.2, 34.8, 34.8, 34.6, 33.8, 33.7, 28.0, 27.9, 26.7, 27.6, 25.0, 24.4, 24.3, 24.2, 21.3, 21.3, 20.8, 20.518.5, 18.4; IR (film): $\tilde{\nu}$ = 3466, 2934, 2860, 1734, 1458, 1372, 1234, 1167, 1020 cm^{-1}; MS (EI) *m/z* (%): 296 (11.3), 278 (8.89), 43 (100); HRMS (ESI): *m/z*: calcd. for $C_{19}H_{30}NaO_5$ [M^++Na]: 361.1985, found: 361.1981.

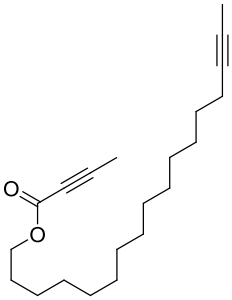
Compound 24. $Ph_3PAuNTf_2$ (14 µL of a 0.05 M stock solution in CH_2Cl_2, 0.0007 mmol) was added to a solution of compound **22b** (5 mg, 0.0147 mmol) in CH_2Cl_2 (0.7 mL). The mixture was stirred for 1 hour 45 minutes before it was filtered through a pad of Celite. The filtrate was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 10:1) to yield the title compound as a viscous oil (4.5 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.22 (d, *J* = 8.2 Hz, 1H), 4.44 (dt, *J* = 11.2, 3.1 Hz, 1H), 3.94-3.88 (m, 2H), 3.40-3.34 (m, 1H), 2.49 (ddd, *J* = 14.7, 8.7, 7.8 Hz, 1H), 2.43-2.28 (m, 3H), 2.11 (s, 3H), 1.88-1.17 (m, 18H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.9, 169.5, 151.7, 120.5, 75.6, 73.6, 62.7, 35.5, 33.1, 32.2, 31.9, 28.9, 27.3, 25.9, 25.2, 24.7, 23.8, 22.1, 21.2; IR (film): $\tilde{\nu}$ = 2932, 2838, 1765, 1732, 1368, 12100, 1074, 1024, 910 cm^{-1}; MS (EI) *m/z* (%): 296 (17.5), 279 (39.75), 43 (100); HRMS (ESI): *m/z*: calcd. for $C_{19}H_{30}NaO_5$ [M^++Na]: 361.1985, found: 361.1982.

Compound 25. $Ph_3PAuNTf_2$ (47 µL from a 0.05 M stock solution in CH_2Cl_2, 0.00235 mmol) was added to a solution of compound **22b** (16 mg, 0.047 mmol) in CH_2Cl_2 (2.1 ml). The mixture was stirred for 90 min before K_2CO_3 (19.5 mg, 0.141 mmol) and MeOH (1 mL) were introduced. After stirring for additional 45 minutes, the mixture was washed with sat. aq. NH_4Cl (2 mL) and extracted with CH_2Cl_2 (2 x 2 mL). The combined extracts were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexane/EtOAc, 9:1) to yield the title compound as a white solid (10. 8 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.41-4.1 (m, 2H), 3.73 (tt, *J* = 10.8, 4.4 Hz, 1H), 3.28-3.23 (m, 1H), 2.64-2.48 (m, 3H), 2.38 (7, *J* = 6.2 Hz, 2H), 7.42 (dd, *J* = 13.8, 2.5 Hz, 1H), 1.94-1.11 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.9, 173.7, 77.2, 75.5, 63.2, 50.2, 42.2, 35.7, 33.9, 31.9, 31.7, 27.7, 27.1, 25.2, 25.0, 23.8, 18.9; IR (film): $\tilde{\nu}$ = 2924, 2854, 1733, 1458, 1375, 1254, 1200, 1157, 1081, 1013, 721 cm^{-1}; MS (EI) *m/z* (%): 115 (77.3), 41 (100); HRMS (ESI): *m/z*: calcd. for $C_{17}H_{28}NaO_4$ [M^++Na]: 319.1879, found: 319.1881.

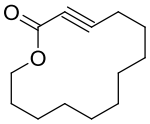
11-Tridecynyl but-2-ynoate (48a). Triphenylphosphine (786 mg, 3 mmol) and diisopropyl azodicarboxylate (0.6 mL, 3 mmol) were successively added to a solution of 11-tridecyn-1-ol (300 mg, 1.5 mmol) and 2-butynoic acid (193 mg, 3 mmol) in toluene (20 mL) at 0°C. The ice bath was removed and the solution stirred

at room temperature for 1.5 h. For work up, the solvent was evaporated and the residue was purified by flash chromatography (hexane/EtOAc, 40:1 → 30:1) to afford the title compound as a colorless oil (361 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.14 (t, *J* = 6.8 Hz 2H), 2.11 (tq, *J* = 7.0, 2.6 Hz, 2H), 1.98 (s, 3H), 1.78 (t, *J* = 2.6 Hz, 3H), 1.65 (quint, *J* = 6.8 Hz, 2H), 1.46 (quint, *J* = 7.0 Hz, 2H), 1.38-1.25 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1, 85.5, 79.6, 75.5, 72.8, 66.2, 29.6, 29.4, 29.4, 29.3, 29.1, 28.6, 26.0, 19.0, 4.0, 3.7; IR (film): $\tilde{\nu}$ = 2924, 2855, 2243, 1708, 1248, 1073, 751 cm^{-1}; MS (EI) *m/z* (%): 137 (16), 135 (11), 121 (14), 111 (11), 109 (12), 108 (11) 107 (23), 96 (10), 95 (38), 94 (19), 93 (38), 85 (33), 82 (15), 81 (43), 80 (15), 79 (39), 69 (26), 68 (57), 67 (100), 66 (13); 55 (47), 54 (17), 53 (20), 43 (14), 41 (43), 39 (22), 29 (11); HRMS (ESI): *m/z*: calcd. for $C_{17}H_{26}O_2Na$ [M^++Na]: 285.1822, found 285.1825.

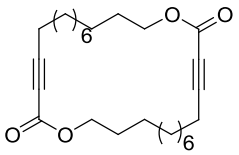
15-Heptadecynyl but-2-ynoate (48b). Prepared analogously as a white solid (361 mg, 88%). Mp 43.8-44.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (t, *J* = 6.8 Hz, 2H), 2.11-2.05 (m, 2H), 1.97 (s, 3H), 1.75 (t, *J* = 2.4 Hz, 3H), 1.64 (quint, *J* = 7.6 Hz, 2H), 1.48-1.22 (m, 22H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 85.4, 79.6, 75.4, 72.7, 66.1, 29.8, 29.7, 29.6, 29.4, 29.3, 29.1, 28.9, 28.6, 28.4, 26.0, 21.8, 18.9, 3.9, 3.6; IR (film): $\tilde{\nu}$ = 2915, 2847, 2242, 1703, 1460, 1260, 1076, 754, 724 cm^{-1}; MS (EI) *m/z* (%): 318 (1), 151 (17), 139 (12), 138 (21), 137 (26), 135 (15), 124 (13), 121 (21), 109 (30), 108 (17), 107 (28), 97 (16), 96 (21), 95 (74), 94 (24), 93 (37), 85 (51), 83 (22), 82 (23), 81 (61), 80 (18), 79 (32), 69 (38), 68 (82), 67 (100), 66 (10), 57 (11), 55 (73), 84 (23), 53 (19), 43 (26), 41 (52), 39 (17), 29 (12); HRMS (ESI): *m/z*: calcd. for $C_{21}H_{34}O_2Na$ [M^++Na]: 341.2451, found 341.2451.



Representative Procedure for the RCAM of Alkynoates. Preparation of Compound 49a. A mixture comprising compound **48a** (20 mg, 0.07 mmol) and powdered molecular sieves (MS 5 Å, 400 mg) in toluene (70 mL) was stirred at ambient temperature for 30 min before complex **1** (5 mg, 0.0004 mmol) was added. The mixture was stirred at 80 °C for 2 h, cooled to ambient temperature, filtered through a plug of silica gel that was carefully rinsed with hexane:ethyl acetate (1:1). The combined filtrates were evaporated and the residue was purified by flash chromatography (hexane/EtOAc, 50:1 → 30:1) to give product **49a** as a colorless oil (10 mg, 66%), which analysed as follows: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.17 (t, *J* = 6.2 Hz, 2H), 2.36 (t, *J* = 6.6 Hz, 2H), 1.67 (tt, *J* = 6.6, 6.0 Hz, 2H), 1.61-1.54 (m, 2H), 1.49-1.29 ppm (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 89.7, 73.7, 66.1, 29.2, 29.2, 29.1, 29.0, 28.6, 28.4, 27.4, 26.0, 18.8 ppm; IR (film): $\tilde{\nu}$ = 2922, 2852, 2232, 1712, 1254, 1080, 753 cm^{-1}; MS (EI) *m/z* (%): 208 (5), 149 (10), 136 (12), 135 (27), 123 (12), 122 (23), 121 (43), 119 (13), 109 (12), 108 (29), 107 (47), 105 (12), 97 (18), 95 (31), 94 (25), 93 (51), 91 (24), 82 (19), 81 (67), 80 (25), 79 (100), 77 (20), 71 (12), 69 (16), 68 (77), 67 (53), 66 (49), 55 (66), 54 (10), 53 (27), 43 (22), 41 (78), 39 (33), 29 (19), 27 (18); HRMS (ESI): *m/z*: calcd. for $C_{13}H_{20}O_2Na$ [M^++Na]: 231.1357, found 231.1355.

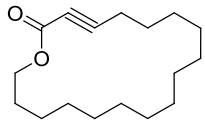


In addition, a small amount of a second product was isolated as a white solid, which turned out to be

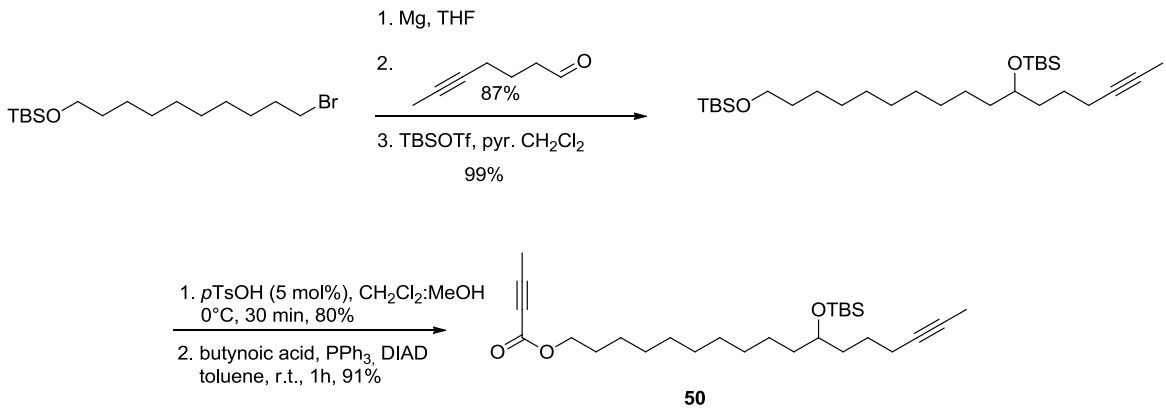


the corresponding cyclic dimer (3.8 mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.17 (t, *J* = 6.2 Hz, 4H), 2.36 (t, *J* = 6.7 Hz, 4H), 1.67 (tt, *J* = 6.7, 6.2 Hz, 4H), 1.61-1.55 (m, 4H), 1.47-1.29 (m, 24H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 89.7, 73.6, 66.1, 29.2, 29.2, 29.1, 29.0, 28.6, 28.4, 27.4, 26.0, 18.8 ppm; IR (film): $\tilde{\nu}$ = 2922, 2852, 2236, 1718, 1253, 1079, 753 cm^{-1}; MS (EI) *m/z* (%): 417 (5), 416 (16), 227 (15), 191 (19), 190 (27), 163 (17), 162 (17), 161 (15), 149 (18), 148 (16), 147 (20), 135 (19), 133 (19), 122 (31), 119 (21), 109 (15), 108 (18), 107 (35), 105 (22), 95 (36), 94 (21), 93 (56), 91 (37), 83 (16), 81 (62), 80 (23), 79 (81), 77 (27), 69 (53), 97 (95), 57 (16), 53 (26), 52 (16), 44 (28), 43 (49), 41 (86), 29 (24); HRMS (ESI): *m/z*: calcd. for $C_{26}H_{40}O_4Na$ [M^++Na]: 439.2818, found 439.2819. See **Figure S2** for a confirmation of this assignment by X-ray diffraction.

Compound 49b. Prepared analogously as a white solid (36 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.21 (t, *J* = 5.3 Hz, 2H), 2.38 (t, *J* = 5.9 Hz, 2H), 1.66-1.60 (m, 2H), 1.53-1.23 ppm (m, 22H); ^{13}C NMR

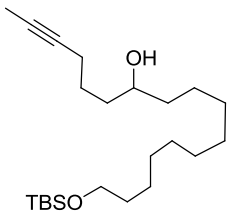


(100 MHz, $CDCl_3$): δ = 154.3, 89.2, 74.1, 65.8, 28.7, 28.3, 28.2, 27.8, 27.3, 27.1, 26.9, 26.8, 26.6, 24.5, 18.6 ppm; IR (film): $\tilde{\nu}$ = 2925, 2856, 2235, 1711, 1460, 1244, 1078, 751cm^{-1}; MS (EI) *m/z* (%): 264 (3), 165 (28), 140 (27), 138 (39), 126 (26), 124 (26), 121 (27), 109 (23), 107 (28), 95 (49), 94 (26), 93 (46), 86 (21), 83 (27), 82 (28), 81 (67), 80 (32), 79 (54), 69 (46), 68 (24), 67 (67), 66 (29), 55 (100), 53 (20), 43 (40), 41 (100), 29 (31); HRMS (ESI): *m/z*: calcd. for $C_{17}H_{28}O_2Na$ [M^++Na]: 287.1983, found 287.1982.



Scheme S2. Preparation of compound **50**

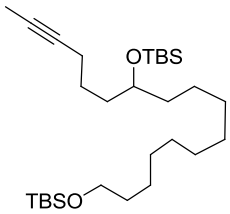
Compound S2. ((10-Bromodecyl)oxy)(*tert*-butyl)dimethylsilane (780 mg, 2.2 mmol) was dropwise



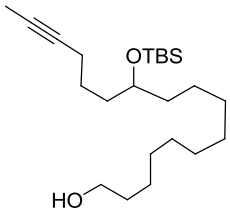
added to a suspension of pre-activated magnesium (264 mg, 11 mmol, activated 2 times on treatment with dichloroethane, 40 µL) in THF (5 mL). The suspension was stirred for 1 h at ambient temperature before it was added to a solution of 5-heptynal (200 mg, 1.8 mmol) in THF (5 mL) at 0°C. The mixture was slowly warmed to room temperature and stirred 1 h before the reaction was quenched with sat. aq. NH_4Cl and Et_2O. The aqueous phase was extracted with Et_2O (3x), the

combined organic layers were washed with brine and dried over Na_2SO_4, all volatile materials were evaporated and the residue was purified by flash chromatography (hexane/EtOAc, 9:1) to afford the title compound as a colorless oil (600 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.61-3.56 (m, 2H, overlap), 3.57 (t, *J* = 6.3 Hz, 2H, overlap), 2.16-2.11 (m, 2H), 1.75 (t, *J* = 2.5 Hz, 3H), 1.58-1.39 (m, 10H), 1.30-1.23 (m, 14H), 0.87 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.2, 75.9, 71.7, 63.5, 37.7, 36.7, 33.0, 29.9, 29.8, 29.7, 29.6, 26.0, 25.9, 25.8, 25.3, 18.9, 15.5, 3.6, –5.1; IR (film): $\tilde{\nu}$ = 3339, 2926, 2854, 1462, 1387, 1361, 1254, 1097, 833, 773 cm^{-1}; MS (EI) *m/z* (%): 325 (24), 135 (17), 123 (11), 121 (15), 111 (13), 109 (41), 107 (17), 95 (100), 93 (21), 81 (53), 79 (10), 75 (65), 73 (14), 67 (30); HRMS (ESI): *m/z*: calcd. for $C_{23}H_{46}O_2SiNa$ [M^++Na]: 405.3162, found: 305.3159.

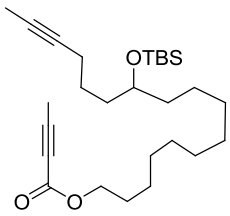
Compound S3. Pyridine (253 µL, 3.1 mmol) and TBSOTf (434 µL, 2.4 mmol) were successively added to a solution of the above alcohol (600 mg, 1.87 mmol) in dichloromethane (4 mL) at 0°C. After 10 min, the mixture was warmed at room temperature and stirred for 1 h before dichloromethane and sat. aq. NH_4Cl were added. The aqueous phase was extracted with Et_2O (3x), the combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexane/EtOAc, 30:1) to afford the title compound as a colorless oil (544 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69-3.62 (m, 1H, overlap), 3.60 (t, *J* = 6.6 Hz, 2H, overlap), 2.15-2.09 (m, 2H), 1.77 (t, *J* = 2.5 Hz, 3H), 1.55-1.24 (m, 24H), 0.90 (s, 9H), 0.89 (s, 9H), 0.05 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.5, 75.7, 72.2, 63.6, 37.3, 36.4, 33.1, 30.1, 29.8, 29.8, 29.7, 26.2, 26.2, 26.0, 25.6, 25.0, 19.1, 3.6, –4.2, –5.1; IR (film): $\tilde{\nu}$ = 2927, 2855, 1471, 1462, 1253, 1097, 832, 772 cm^{-1}; MS (EI) *m/z* (%): 440 (14), 439 (38), 307 (11), 233 (13), 191 (15), 149 (20), 147 (20), 135 (19), 121 (16), 109 (16), 107 (13), 95 (41), 93 (39), 81 (19), 75 (100), 73 (36), 67 (10); HRMS (ESI): *m/z*: calcd. for $C_{29}H_{60}O_2Si_2Na$[M^++Na]: 519.4023, found: 519.4024.



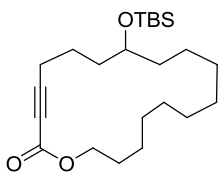
Compound S4. *p*-TsOH (5.5 mg, 0.029 mmol) was added to a solution of compound **S3** (290 mg, 0.58 mmol) in CH_2Cl_2/MeOH (1:1, 6 mL) at 0°C. After stirring for 45 min at that temperature, the reaction was quenched with sat. aq. $NaHCO_3$, the aqueous phase was extracted three times with ethyl acetate, the combined extracts were dried over Na_2SO_4 and evaporated. Purification of the residue by flash chromatography (hexane/EtOAc, 15:1) afforded the title compound as a colorless oil (161 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67-3.54 (m, 1H, overlap), 3.63 (t, *J* = 6.6 Hz, 2H, overlap), 2.13-2.09 (m, 2H), 1.77 (t, *J* = 2.5 Hz, 3H), 1.60-1.24 (m, 25H), 0.88 (s, 9H), 0.04 (2, 3H), 0.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.5, 75.7, 72.2, 63.3, 37.3, 36.4, 33.0, 30.0, 29.8, 29.8, 29.8, 29.6, 26.2, 26.0, 25.5, 25.0, 19.1, 18.4, 3.7, –4.2; IR (film): $\tilde{\nu}$ = 3347, 2926, 2854, 1462, 1373, 1360, 1253, 1057, 1005, 834, 772 cm^{-1}; MS (EI) *m/z* (%): 325 (12), 301 (11), 149 (10), 135 (18), 123 (12), 121 (16), 109 (39), 107 (18), 95 (98), 93 (43), 109 (39), 107 (18), 95 (98), 93 (43), 83 (11), 81 (53), 75 (100), 73 (44), 69 (18), 67 (23), 55 (21); HRMS (ESI): *m/z*: calcd. for $C_{23}H_{46}O_2SiNa$ [M^++Na]: 405.3157, found: 405.3159.



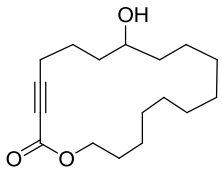
Compound 50. Ph_3P (46 mg, 0.18 mmol) and DIAD (35 µL, 0.178 mmol) were added to a solution of alcohol **S4** (60 mg, 0.16 mmol) and 2-butynoic acid (21 mg, 0.24 mmol) in toluene (8 mL) at 0°C. The reaction was stirred at room temperature for 1 h before the solvent was evaporated. The residue was purified by flash chromatography (hexane/EtOAc, 30:1) to afford product **50** as a colorless oil (65 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.14 (t, *J* = 6.8 Hz, 2H), 3.69-3.62 (m, 1H), 2.15-2.08 (m, 2H), 1.98 (s, 3H), 1.77 (s, *J* = 2.6 Hz, 3H), 1.66 (quint., *J* = 6.9 Hz, 2H), 1.59-1.21 (m, 22H), 0.89 (s, 9H), 0.04 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.1, 85.4, 79.4, 75.7, 72.8, 72.2, 66.2, 37.3, 36.4, 30.0, 29.8, 29.7, 29.7, 29.4, 28.6, 26.1, 26.0, 25.5, 25.0, 19.1, 18.4, 4.0, 3.6, –4.2; IR (film): $\tilde{\nu}$ = 2927, 2855, 2244, 1712, 1463, 1253, 1072, 835, 773 cm^{-1}; MS (EI) *m/z* (%): 392 (24), 391 (72), 367 (14), 159 (23), 149 (11), 142 (15), 141 (100), 97 (14), 95 (41), 93 (21), 81 (21), 75 (58), 73 (28), 69 (12), 67 (24), 55 (15); HRMS (ESI): *m/z*: calcd. for $C_{27}H_{48}O_3SiNa$ [M^++Na]: 471.3265, found: 471.3269.



Compound 51. A solution of compound **50** (60 mg, 0.13 mmol) containing powdered molecular sieves (MS 5 Å, 800 mg) in toluene (130 mL) was stirred at ambient temperature for 30 min before complex **1** (9 mg, 0.007 mmol) was added. The mixture was stirred at 80 °C for 2 h before it was passed through a short pad of silica that was carefully rinsed with hexane/ethyl acetate (1:1). The filtrate was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 40:1 → 30:1) to afford the title compound as a colorless oil (41 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20 (t, *J* = 5.3 Hz, 2H), 3.71-3.65 (m, 1H), 2.41-2.35 (m, 2H), 1.80-1.25 (m, 22H), 0.87 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2, 88.1, 74.1, 71.9, 65.8, 37.7, 34.4, 29.3, 28.5, 28.1, 27.6, 27.0, 26.3, 26.1, 24.5, 24.2, 23.1, 18.7, 18.3, –4.1, –4.5; IR (film): $\tilde{\nu}$ = 2929, 2856, 2236, 1713, 1462, 1247, 1081, 835, 774 cm^{-1}; MS (EI) *m/z* (%): 338 (26), 337 (100), 319 (42), 79 (10), 75 (40), 73 (21), 55 (10); HRMS (ESI): *m/z*: calcd. for $C_{23}H_{42}O_3SiNa$ [M^++Na]: 417.2798, found: 417.2795.



Compound 52. *p*-TsOH (2 mg, 0.01 mmol) was added to a solution of compound **51** (39 mg, 0.1 mmol) in MeOH (1 mL) at 0°C and the resulting mixture stirred at ambient temperature for 2 h before it was quenched with sat. aq. $NaHCO_3$. The methanol was partially removed under vacuum, the residue was extracted three times with ethyl acetate. The combined extracts were dried over Na_2SO_4 and evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 8:1) to afford the title compound as a colorless oil (21 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.21 (t, *J* = 5.4 Hz, 2H), 3.75-3.66 (m, 1H), 2.48 (ddd, *J* = 17.5, 8.1, 4.3 Hz, 1H), 2.38 (ddd, *J* = 17.5, 8.1, 4.2 Hz, 1H), 1.92-1.84 (m, 1H), 1.81-1.71 (m, 1H), 1.67-1.55 (m, 4H), 1.50-2.28 (m, 16H), 1.24 (br *s*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 88.7, 74.3, 71.1, 65.9, 37.7, 34.1, 28.9, 28.2, 28.1, 27.6, 27.0, 26.3, 24.4, 24.3, 22.9, 18.4; IR (film): $\tilde{\nu}$ = 3404, 2930, 2870, 2236, 1712, 1250, 1080 cm^{-1}; MS (EI) *m/z* (%): 280 (2), 141 (20), 123 (100), 122 (31), 113 (53), 95 (52), 84 (40), 83 (28), 81 (36), 79 (32), 69 (42), 68 (25), 67 (42), 66 (49), 55 (78), 43 (36), 41 (74), 26 (26); HRMS (ESI): *m/z*: calcd. for $C_{17}H_{28}O_3Na$ [M^++Na]: 303.1929, found: 303.1931.



Compound 53. A freshly prepared solution of $AuCl_3$ in anhydrous MeOH (0.01 M, 150 µL, 2 mol%) was added to compound **52** (21 mg, 0.075 mmol) at 0°C. The mixture was stirred at ambient temperature for 40 min before it was diluted with pentane/Et_2O (4:1) and sat. aq. $NaHCO_3$. The aqueous phase was extracted with Et_2O and the combined organic layers were washed with water, brine and dried over Na_2SO_4. The solvent was evaporated and the residue purified by flash chromatography (pentane/Et_2O, 8:1; the silica was deactivated with pentane/Et_2O/NEt_3, 8:2:1 prior to use) to afford the title compound as a colorless oil (22 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.43 (ddd, *J* = 10.7, 6.3, 4.5 Hz, 1H), 3.80 (ddd, *J* = 10.7, 6.6, 4.1 Hz, 1H), 3.47 (ddt, *J* = 11.5, 9.3, 2.2 Hz, 1H), 3.22 (s, 3H), 2.92 (d, *J* = 12.9 Hz, 1H), 2.18 (d, *J* = 12.9 Hz, 1H), 2.11 (td, *J* = 13.0, 4.6 Hz, 1H), 1.86-1.69 (m, 2H), 1.62-1.15 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 98.4, 71.4, 64.6, 47.7, 42.2, 35.6, 32.1, 30.8, 28.4, 27.3, 26.9, 26.4, 25.8, 24.3, 24.1, 23.1, 19.2; IR (film): $\tilde{\nu}$ = 2932, 2860, 1734, 1459, 1384, 1350, 1326, 1228, 1209, 1098, 1054, 1043, 1021, 964, 947, 851 cm^{-1}; MS (EI) *m/z* (%): 312 (5), 281 (24), 194 (32), 166 (13), 119 (100), 117 (15), 116 (14), 110 (14), 109 (11), 101 (17), 96 (25), 95 (17), 83 (13), 82 (29), 81 (22), 69 (17), 68 (16), 67 (20), 55 (30), 54 (12), 43 (14), 41 (31); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{32}O_4Na$ [M^++Na]: 325.2194, found: 325.2193.

Representative Procedure for Alkyne Dimerization. Preparation of 1,2-Bis(dimethyl(phenyl)-silyl)ethyne: A suspension containing dimethyl(phenyl)(prop-1-yn-1-yl)silane (174 mg, 1 mmol), complex **1** (21 mg, 0.02 mmol, 2 mol%) and powdered MS 5Å (2 g) in toluene (5 mL) was stirred for 2 h at ambient temperature. The mixture was then filtered through a pad of silica, the filtrate was evaporated, and the residue purified by flash chromatography (pentane/EtOAc, 98:2) to give the title compound as a colorless oil (137 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.70 (m, 4H), 7.44-7.40 (m, 6H), 0.50 (m, 12H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.9 (2C), 133.9 (4C), 129.6 (2C), 128.0 (4C), 113.8 (2C), –0.7 (4C); IR (film): $\tilde{\nu}$ = 3069, 3050, 3021, 2960, 1606, 1508, 1428, 1249, 1113, 825, 779 cm^{-1}; MS (EI) *m/z* (%): 294 (35) [M+], 279 (100), 221 (18), 135 (29), 105 (14); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{22}Si_2$: 294.1260; found: 294.1259. The analytical and spectroscopic data are in agreement with those reported in the literature.[3]

1,2-Bis(diphenylphosphino)ethyne. Prepared analogously as a colorless solid (103 mg, 52%). Mp = 71-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67-7.60 (m, 8H), 7.38-7.33 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.8 (m, 4C), 132.8 (m, 8C), 129.3 (4C), 128.8 (m, 8C), 107.0 (m, 4C); ^{31}P NMR (162 MHz, $CDCl_3$)): δ = –31.1; IR (film): $\tilde{\nu}$ = 3055, 1585, 1571, 1478, 1432, 1308, 1090, 1067, 1025, 998, 814, cm^{-1}; MS (EI) *m/z* (%): 394 (100) [M+], 209 (87), 185 (48), 183 (52), 165 (11), 107 (10), 77 (8); HRMS (ESI): *m/z*: calcd. for $C_{26}H_{20}P_2$: 394.1040; found: 394.1042. The analytical and spectroscopic data are in agreement with those reported in the literature.[4]

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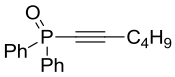
[3] A. Naka, M. Ishikawa *Organometallics* **2000**, *19*, 4921-4924.

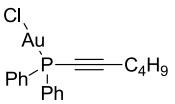
[4] O. Ekkert, G. Kehr, R. Fröhlich, G. Erker *J. Am. Chem. Soc.* **2011**, *133*, 4610-4616.

Representative Procedure for Alkyne Cross Metathesis. Preparation of Hex-1-yn-1-yldimethyl(phenyl)silane: A suspension containing dimethyl(phenyl)(prop-1-yn-1-yl)silane (174 mg, 1 mmol), 5-decyne (270 µL, 1.5 mmol), complex **1** (21 mg, 0.02 mmol, 2 mol%) and powdered MS 5Å (1 g) in toluene (5 mL) was stirred for 2h at ambient temperature. The mixture was then filtered through a pad of silica, the filtrate was evaporated, and the residue purified by flash chromatography (pentane) to give the title compound as a colorless oil (154 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.61 (m, 2H), 7.39-7.36 (m, 3H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.60-1.50 (m, 2H), 1.50-1.39 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9, 133.8 (2C), 129.3, 127.9 (2C), 109.8, 82.3, 30.8, 22.1, 19.8, 13.7, –0.4; IR (film): $\tilde{\nu}$ = 3069, 2958, 2932, 2873, 2173, 1428, 1248, 1114, 834, 825, 778 cm^{-1}; MS (EI) *m/z* (%): 216 (5) [M+], 201 (100), 174 (19), 159 (9), 145 (11), 105 (7), 43 (8); HRMS (ESI): *m/z*: calcd. for $C_{14}H_{20}Si$: 216.1334; found: 216.1333.

Hex-1-yn-1-yldiphenylphosphine. Prepared analogously as a pale yellow oil, (210 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.63 (m, 4H), 7.42-7.31 (m, 6H), 2.49 (dt, *J* = 7.1, 1.4 Hz, 2H), 1.71-1.60 (m, 2H), 1.57-1.47 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.3 (d, *J* = 7 Hz, 2C), 132.5 (d, *J* = 21 Hz, 4C), 128.9 (2C), 128.6 (d, *J* = 8 Hz, 4C), 110.6 (d, *J* = 4 Hz), 75.8 (d, *J* = 2 Hz), 30.8, 22.2, 20.3, 13.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ = –31.3; IR (film): $\tilde{\nu}$ = 3054, 2957, 2929, 2870, 2178, 1585, 1478, 1434, 1323, 1209, 1095, 1025 cm^{-1}; MS (EI) *m/z* (%): 266 (100) [M+], 237 (9), 224 (22), 209 (14), 178 (21), 145 (12), 115 (13), 91 (15); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{19}P$: 226.1224; found: 226.1223.



Hex-1-yn-1-yldiphenylphosphine oxide. Prepared analogously as a colorless solid (189 mg, 67%). Mp = 61-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.76 (m, 4H), 7.53-7.47 (m, 2H), 7.47-7.40 (m, 4H), 2.44 (dt, *J* = 7.1, 3.5 Hz, 2H), 1.65-1.55 (m, 2H), 1.49-1.38 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.6 (d, *J* = 121 Hz, 2C), 132.0 (d, *J* = 3 Hz, 2C), 130.9 (d, *J* = 11 Hz, 4C), 128.6 (d, *J* = 13 Hz, 4C), 109.8 (d, *J* = 30 Hz), 75.0 (d, *J* = 175 Hz), 29.6 (d, *J* = 1 Hz), 22.0, 19.5 (d, *J* = 3 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.4; IR (film): $\tilde{\nu}$ = 3056, 2958, 2931, 2871, 2190, 1590, 1437, 1202, 1119, 1105, 1069, 1027 957, 861 cm^{-1}; MS (EI) *m/z* (%): 282 (21) [M+], 254 (32), 240 (33), 201 (100), 115 (12), 77 (21), 51 (8); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{19}OP$: 282.1174; found: 282.1172.



(Hex-1-yn-1-yldiphenylphosphine)gold chloride. Prepared analogously as a colorless solid (46 mg, 92%). Mp = 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.70 (m, 4H), 7.54-7.43 (m, 6H), 2.51 (dt, *J* = 7.1, 3.4 Hz, 2H), 1.69-1.58 (m, 2H), 1.51-1.38 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.0 (d, *J* = 16 Hz, 4C), 132.2 (d, *J* = 3 Hz, 2C), 129.7 (d, *J* = 71 Hz, 2C), 129.4 (d, *J* = 13 Hz, 4C), 114.8 (d, *J* = 21 Hz), 69.2 (d, *J* = 123 Hz), 29.9, 22.1, 20.1 (d, *J* = 3 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$)): δ = 3.8; IR (film): $\tilde{\nu}$ = 2953, 2935, 2869, 2196, 1478, 1435, 1309, 1102, 983, 846 cm^{-1}; Elemental analysis (%) calcd for $C_{18}H_{20}AuClP$: C 43.26, H 4.03, Cl 7.09, P 6.20; found: C 43.70, H 3.83, Cl 7.01, P 6.01.

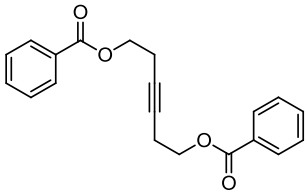
Representative Procedure for Ring Opening Alkyne Metathesis. Preparation of Bis(4-(dimethyl(phenyl)silyl)but-3-yn-1-yl) adipate: A suspension containing dimethyl(phenyl)(prop-1-yn-1-yl)silane (105 mg, 0.6 mmol), 1,8-dioxacyclotetradec-11-yne-2,7-dione (45 mg, 0.2 mmol), complex **1** (17 mg, 0.01 mmol, 5 mol%) and powdered MS 5Å (400 mg) in toluene (5 mL) was stirred for 24 h at 60°C. The mixture was then filtered through a pad of silica, the filtrate was evaporated, and the residue purified by flash chromatography (pentane/EtOAc, 95:5) to give the title compound as a colorless oil (80 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.58 (m, 4H), 7.41-7.35 (m, 6H), 4.21 (t, *J* = 6.9 Hz, 4H), 2.62 (t, *J* = 6.9 Hz, 4H), 2.35-2.30 (m, 4H), 1.69-1.63 (m, 4H), 0.40 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1 (2C), 137.2 (2C), 133.7 (4C), 129.5 (2C), 128.0 (4C), 104.3 (2C), 84.6 (2C), 62.2 (2C), 33.8 (2C), 24.4 (2C), 20.6 (2C), –0.7 (4C); IR (film): $\tilde{\nu}$ = 3069, 2959, 2179, 1735, 1428, 1248, 1165, 1115, 902, 836, 820, 779 cm^{-1}; MS (EI) *m/z* (%): 518 (3) [M+], 441 (17), 315 (5), 239 (6), 171 (12), 159 (100), 135 (42); HRMS (ESI): *m/z*: calcd. for $C_{30}H_{38}O_4Si_2$ + Na: 541.2201; found: 541.2199.

Bis(4-(diphenylphosphino)but-3-yn-1-yl) adipate. Prepared analogously as a pale yellow oil (44 mg, 36%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64-7.54 (m, 8H), 7.37-7.29 (m, 12H), 4.26 (t, *J* = 6.8 Hz, 4H), 2.78 (dt, *J* = 6.8, 1.5 Hz, 4H), 2.33-2.27 (m, 4H), 1.66-1.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1 (2C), 136.6 (d, *J* = 6 Hz, 4C), 132,6 (d, *J* = 21 Hz, 8C), 129.1 (4C), 128.7 (d, *J* = 7 Hz, 8C), 105.3 (d, *J* = 3 Hz, 2C), 78.4 (d, *J* = 6 Hz, 2C), 62.1, (2C), 33.8 (2C), 24.4 (2C), 21.0 (2C); ^{31}P NMR (162 MHz, $CDCl_3$)): δ = –33.3; IR (film): $\tilde{\nu}$ = 3053, 2956, 2185, 1732, 1478, 1434, 1163, 1136, 1067, 1024, 910 cm^{-1}; MS (EI) *m/z* (%): 618 (3) [M+], 443 (20), 382 (44), 236 (100), 221 (35), 133 (22); HRMS (ESI): *m/z*: calcd. for $C_{36}H_{36}O_4P_2$ + Na: 641.1981; found: 641.1987.

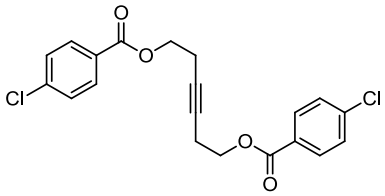
Representative Procedure for the Metathesis of Terminal Alkynes. Preparation of Hex-3-yne-1,6-diyl bis(4-methoxybenzoate): A suspension containing but-3-yn-1-yl 4-methoxybenzoate (102 mg, 0.5 mmol), powdered MS 5Å (2 g) and MS 4Å (1 g) in toluene (22 mL) was stirred for 5 min at ambient temperature before a solution of complex **1** (5 mg, 5 µmmol, 1 mol%) in toluene (2 mL) was added. The mixture was stirred for 1 h before it was filtered through a pad of Celite. The filtrate was evaporated and the residue purified by flash chromatography on alumina (toluene/EtOAc, 100:0 → 8:2) to give the title compound as a colorless solid (77 mg, 81%). Mp = 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.8 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 4H), 4.35 (t, *J* = 6.7 Hz, 4H), 3.85 (s, 6H), 2.62 (t, *J* = 6.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2 (2C), 163.5 (2C), 131.8 (4C), 122.6 (2C), 113.7 (4C), 77.7 (2C), 62.9 (2C), 55.5 (2C), 19.5 (2C); IR (film): $\tilde{\nu}$ = 3006, 2958, 2897, 2839, 1706, 1604, 1509, 1459, 1315, 1254, 1116, 1103, 1024, 984, 840 cm^{-1}; MS (EI) *m/z* (%): 382 (8) [M$^+$], 230 (5), 152 (100), 135

(80), 92 (6), 77 (10); HRMS (ESI): *m/z*: calcd. for $C_{22}H_{22}O_6$ + Na: 405.1309; found: 405.1308. The analytical and spectroscopic data are in agreement with those reported in the literature. [5]

Hex-3-yne-1,6-diyl dibenzoate. Prepared analogously as a colorless solid (64 mg, 79%). Mp = 73-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.3 Hz, 4H), 7.55 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.42 (dd, *J* = 7.3, 7.3 Hz, 4H), 4.39 (t, *J* = 6.5 Hz, 4H), 2.64 (t, *J* = 6.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4 (2C), 133.1 (2C), 130.2 (2C), 129.7 (4C), 128.5 (4C), 77.7 (2C), 63.2 (2C), 19.5 (2C); IR (film): $\tilde{\nu}$ = 2981, 2927, 1715, 1600, 1472, 1453, 1270, 1183, 1121, 1022, 978, 850 cm^{-1}; MS (EI) *m/z* (%): 322 (1) [M$^+$], 200 (20), 105 (98), 78 (100), 51 (7); HRMS (ESI): *m/z*: calcd. for $C_{20}H_{18}O_4$ + Na: 345.1097; found: 345.1099. The analytical and spectroscopic data are in agreement with those reported in the literature.[6]



Hex-3-yne-1,6-diyl bis(4-chlorobenzoate). Prepared analogously as a colorless solid (73 mg, 75%). Mp = 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.5 Hz, 4H), 7.38 (d, *J* = 8.5 Hz, 4H), 4.37 (t, *J* = 6.7 Hz, 4H), 2.63 (t, *J* = 6.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6 (2C), 139.7 (2C), 131.1 (4C), 128.9 (4C), 128.6 (2C), 77.6 (2C), 67.4 (2C), 19.5 (2C); IR (film): $\tilde{\nu}$ = 2962, 2920, 2850, 1703, 1591, 1489, 1402, 1296, 1264, 1120, 1106, 1016, 976, 855, 753cm^{-1}; MS (EI) *m/z* (%): 413.3 [M + Na]+, 331.1 (1); HRMS (ESI): *m/z*: calcd. for $C_{20}H_{16}Cl_2O_4$ + Na: 413.0318; found: 413.0316. The analytical and spectroscopic data are in agreement with those reported in the literature. [5]



1,6-Bis(benzyloxy)hex-3-yne. Prepared analogously as a colorless oil (58 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.27 (m, 10H), 4.55 (s, 4H), 3.57 (t, *J* = 7.0 Hz, 4H), 2.49 (t, *J* = 7.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3 (2C), 128.5 (4C) 127.8 (4C), 127.8(2C), 78.1(2C), 73.0 (2C), 68.8 (2C), 20.3 (2C); IR (film): $\tilde{\nu}$ = 3029, 2911, 2859, 1495, 1453, 1362, 1204, 1095, 1028, 820 cm^{-1}; MS (EI) *m/z* (%): 203 (2), 173 (5), 159 (4), 129 (3), 105 (8), 91 (100), 77 (15), 65 (14); HRMS (ESI): *m/z*: calcd. for $C_{20}H_{22}O_2$ + Na: 317.1512; found: 317.1509. The analytical and spectroscopic data are in agreement with those reported in the literature.[5]

1,6-Bis((tetrahydro-2H-pyran-2-yl)oxy)hex-3-yne. Prepared analogously as a pale yellow oil (58 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.63 (t, *J* = 3.3 Hz, 2H), 3.92-3.83 (m, 2H), 3.82-3.74 (m, 2H), 3.56-3.46 (m, 4H), 2.45 (t, *J* = 7.1 Hz, 4H), 1.90-1.77 (m, 2H), 1.76-1.66 (m, 2H), 1.63-1.46 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 98.9 (2C), 78.0 (2C), 66.2 (2C), 62.3 (2C), 30.7 (2C), 25.6 (2C), 20.4 (2C), 19.6 (2C); IR (film): $\tilde{\nu}$ = 2939, 2870, 1440, 1352, 1200, 1134, 1120, 1068, 1032, 970, 906, 869, 814 cm^{-1}; MS (EI) *m/z* (%): 197 (2), 153 (3), 125 (5), 101 (6), 85

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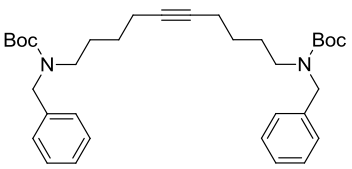
[5] B. Haberlag, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, *Angew. Chem.* **2012**, *124*, 13195-13199; *Angew. Chem. Int. Ed.* **2012**, *51*, 13019-13022.

[6] B. Haberlag, X. Wu, K. Brandhorst, J. Grunenberg, C. G. Daniliuc, P. G. Jones, M. Tamm, *Chem. Eur. J.* **2010**, *16*, 8868-8877.

(100), 79 (5), 67 (12), 55 (13), 41 (14); HRMS (ESI): *m/z*: calcd. for $C_{16}H_{26}O_4$ + Na: 305.1723; found: 305.1725.

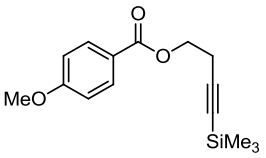
2,2,3,3,12,12,13,13-Octamethyl-4,11-dioxa-3,12-disilatetradec-7-yne. Prepared analogously as a yellow oil, (57 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (t, *J* = 7.2 Hz, 4H), 2.36 (t, *J* = 7.2 Hz, 4H), 0.90 (s, 18H), 0.07 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 78.3 (2C), 62.5 (2C), 26.1 (6C), 23.3 (2C), 18.5 (2C), -5.12 (4C); IR (film): $\tilde{\nu}$ = 2954, 2929, 2857, 1472, 1361, 1253, 1097, 1058, 1006, 915, 334, 774 cm^{-1}; MS (EI) *m/z* (%): 327 (5), 285 (100), 255 (5), 189 (11), 155 (45), 147 (35), 115 (12), 89 (23), 73 (80); HRMS (ESI): *m/z*: calcd. for $C_{18}H_{38}O_2Si_2$ + Na: 365.2303; found: 365.2303.

N,N'-(Dec-5-yne-1,10-diyl)bis(N-benzyl-4-methylbenzenesulfonamide). Prepared analogously as a white solid; (69 mg, 42%); M. p. = 91-93°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 4H), 7.34-7.24 (m, 14H), 4.30 (s, 4H), 3.09 (t, *J* = 7.3 Hz, 4H), 2.44 (s, 6H), 1.94 (t, *J* = 6.6 Hz, 4H), 1.46-1.36 (m, 4H), 1.31-1.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3 (2C), 137.2 (2C), 136.6 (2C), 129.8 (4C), 128.7 (4C), 128.4 (4C), 127.9 (2C), 127.3 (4C), 79.9 (2C), 52.1 (2C), 47.8 (2C), 27.3 (2C), 26.1 (2C), 21.6 (2C), 18.3 (2C); IR (film): $\tilde{\nu}$ = 3034, 2942, 2865, 1599, 1494, 1455, 1323, 1309, 1149, 1087, 1025, 934, 813 cm^{-1}; MS (EI) *m/z* (%): 656 (1) [M$^+$], 501 (50), 345 (2), 300 (22), 274 (14), 155 (4), 91 (100); HRMS (ESI): *m/z*: calcd. for $C_{38}H_{44}N_2O_4S_2$ + Na: 679.2635; found: 679.2643.



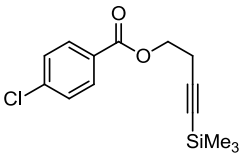
Di-*tert*-butyl dec-5-yne-1,10-diylbis(benzylcarbamate). Prepared analogously as a colorless oil, (116 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.26 (m, 4H), 7.25-7.18 (m, 6H), 4.41 (bs, 4H), 3.20 and 3.12 (bs, rotamers, 4H), 2.11 (t, *J* = 6.0 Hz, 4H), 1.66-1.36 (m, 26H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 and 155.7 (2C, rotamers), 138.6 (2C), 128.5 (4C), 127.7 (2C), 127.1 (4C), 80.1 (2C), 79.6 (2C), 50.4 and 49.8 (2C, rotamers), 46.0 (2C), 28.5 (6C), 27.3 (2C), 26.4 (2C), 18.5 (2C); MS (EI) *m/z* (%): 548 (1) [M+], 448 (27), 392 (51), 375 (16), 347 (12), 257 (40), 200 (18), 146 (39), 120 (34), 106 (30), 91 (100), 57 (87); HRMS (ESI): *m/z*: calcd. for $C_{34}H_{48}N_2O_4$ + H: 549.3687; found: 549.3690.

Representative Procedure for the Cross Metathesis of Terminal Alkynes. Preparation of 4-(Trimethylsilyl)but-3-yn-1-yl 4-methoxybenzoate: A suspension containing but-3-yn-1-yl 4-methoxybenzoate (102 mg, 0.5 mmol), trimethyl(prop-1-yn-1-yl)silane (148 µL, 2 mmol), powdered MS 5Å (2 g) and MS 4Å (1 g) in toluene (22 mL) was stirred for 5 min before a solution of complex **1** (5 mg, 5 µmmol, 1 mol%) in toluene (2 mL) was added. After stirring for 1 h, the mixture was filtered through a pad of Celite and the filtrate was evaporated. Purification of the residue by flash chromatography over alumina (toluene/EtOAc, 100:0 → 95:5) afforded the cross metathesis product as a colorless oil

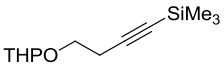


(133 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 4.38 (t, *J* = 7.0 Hz, 2H), 3.86 (s, 3H), 2.68 (t, *J* = 7.0 Hz, 2H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 163.6, 131.8 (2C), 122.7, 113.7 (2C), 102.5, 86.7, 62.5, 55.6, 20.7, 0.1 (3C); IR (film): $\tilde{\nu}$ = 2960, 2901, 2840, 2179, 1713, 1606, 1511, 1248, 1166, 1100, 1029, 842 cm^{-1}; MS (EI) *m/z* (%): 276 (8) [M+], 261 (8), 231 (6), 209 (6), 189 (8), 165 (7), 152 (100), 135 (85), 107 (6), 92 (8), 77 (10); HRMS (ESI): *m/z*: calcd. for $C_{15}H_{20}O_3Si$ + Na: 299.1074; found: 299.1076.

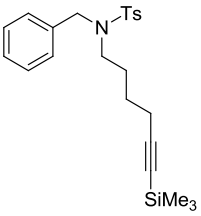
4-(Trimethylsilyl)but-3-yn-1-yl 4-chlorobenzoate. Prepared analogously as a yellow syrup, (132 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 4.41 (t, *J* = 6.9 Hz, 2H), 2.69 (t, *J* = 6.9 Hz, 2H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 139.7, 131.2 (2C), 128.9 (2C), 128.7, 102.2, 87.0, 63.0, 20.6, 0.11 (3C); IR (film): $\tilde{\nu}$ = 2961, 2852, 2179, 1722, 1595, 1488, 1402, 1266, 1249, 1103, 1091, 1015, 838 cm^{-1}; MS (EI) *m/z* (%): 265 (18), 235 (15), 213 (18), 193 (12), 169 (12), 141 (31), 139 (100), 124 (82), 111 (49), 109 (79), 75 (20); HRMS (ESI): *m/z*: calcd. for $C_{14}H_{17}ClO_2Si$ + Na: 303.0579; found: 303.0576.



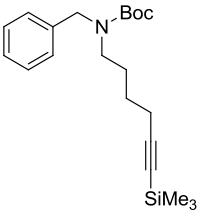
Trimethyl(4-((tetrahydro-2*H*-pyran-2-yl)oxy)but-1-yn-1-yl)silane. Prepared analogously as a colorless oil, (99 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.66 (t, *J* = 3.2 Hz, 1H), 3.92-3.86 (m, 1H), 3.85-3.77 (m, 1H), 3.58-3.47 (m, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.89-1.77 (m, 1H), 1.75-1.66 (m, 1H), 1.64-1.46 (m, 4H); 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 104.1, 98.7, 85.7, 65.7, 62.2, 30.7, 25.6, 21.5, 19.4, 0.2 (3C); IR (film): $\tilde{\nu}$ = 2942, 2873, 2178, 1441, 1352, 1258, 1200, 1122, 1032, 907, 836, 815, 759 cm^{-1}; MS (EI) *m/z* (%): 173 (5), 127 (28), 109 (10), 99 (15), 85 (10), 75 (50), 55 (19); HRMS (ESI): *m/z*: calcd. for $C_{12}H_{22}O_2Si$ + Na: 249.1281; found: 249.1280. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]



N-Benzyl-4-methyl-N-(6-(trimethylsilyl)hex-5-yn-1-yl)benzenesulfonamide. Prepared analogously as a colorless oil, (188 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.1 Hz, 2H), 7.33-7.23 (m, 7H), 4.30 (s, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 2.04 (t, *J* = 6.9 Hz, 2H), 1.48-1.37 (m, 2H), 1.36-1.26 (m, 2H), 0.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 137.2, 136.6, 129.8 (2C), 128.7 (2C), 128.4 (2C), 127.9, 127.3 (2C), 106.9, 84.9, 52.0, 47.6, 27.2, 25.7, 21.6, 19.4, 0.3 (3C); IR (film): $\tilde{\nu}$ = 3031, 2956, 2866, 2172, 1599, 1495, 1455, 1338, 1248, 1156, 1089, 1023, 840, 758 cm^{-1}; MS (EI) *m/z* (%): 398 (11), 322 (2), 300 (35), 274 (14), 258 (27), 184 (5), 149 (3), 91 (100), 73 (9); HRMS (ESI): *m/z*: calcd. for $C_{23}H_{31}NO_2SSi$ + Na: 436.1737; found: 436.1741.



***tert*-Butyl benzyl(6-(trimethylsilyl)hex-5-yn-1-yl)carbamate**. Prepared analogously as a colorless oil, (167 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.27 (m, 2H), 7.26-7.18 (m, 3H), 4.43 (bs, 2H), 3.21 and 3.13 (bs, rotamers, 2H),

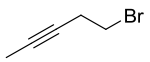


[7] H. J. Bestmann, T. Zeibig, O. Vostrowsky *Synthesis* **1990**, 1039-1047.

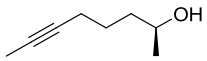
2.20 (t, J = 6.9 Hz, 2H), 1.66-1.37 (m, 13H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 and 155.7 (1C, rotamers), 138.5, 128.5 (2C), 127.8, 127.2 (2C), 107.1, 84.8, 79.7, 50.4 and 49.8 (1C, rotamers), 45.9, 28.5 (3C), 27.2, 25.9, 19.7, 0.3 (3C); IR (film): $\tilde{\nu}$ = 2960, 2932, 2861, 2174, 1691, 1454, 1414, 1365, 1248, 1156, 1117, 1028, 834 cm^{-1}; MS (EI) *m/z* (%): 359 (2) [M$^+$], 303 (11), 288 (29), 258 (16), 212 (13), 190 (32), 186 (22), 168 (17), 146 (24), 120 (30), 91 (100), 73 (28), 57 (70); HRMS (ESI): *m/z*: calcd. for $C_{21}H_{33}NO_2Si$ + Na: 382.2173; found: 382.2170.

Total Synthesis of Dehydrocurvularin

Compound S5: CBr_4 (27.0 g, 81.5 mmol) and PPh_3 (21.4 g, 81.5 mmol) were added in several portions to a stirred solution of pent-3-yn-1-ol (4.57 g, 54.3 mmol) in CH_2Cl_2 (160 mL) at 0 °C. The mixture was stirred at ambient temperature for 1 h and at reflux temperature for 2 h. The solvent was evaporated and the residue suspended in pentane, which was also evaporated. The remaining white solid was suspended in pentane/Et_2O (90:10), the suspension was filtered and the solid carefully rinsed with the same solvent. The combined filtrates were evaporated and the residue was purified by flash chromatography (pentane/Et_2O, 100/0 → 95/5) to give product **S5** as a colorless oil (7.10 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.41 (t, J = 7.4 Hz, 2H), 2.69 (tq, J = 7.4, 2.5 Hz, 2H), 1.79 (t, J = 2.5, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 78.0 (C), 76.2 (C), 30.4 (CH_2), 23.4 (CH_2), 3.6 (CH_3); IR (film): $\tilde{\nu}$ = 2968, 2920, 2854, 1436, 1334, 1271, 1212 cm^{-1}; MS (EI): *m/z* (%): 148 (26), 146 (26), 68 (5), 67 (100), 66 (17), 65 (20), 63 (7), 53 (19), 51 (10), 50 (6), 41 (61), 39 (41), 38 (6), 27 (15); HRMS (EI): *m/z:* calcd for C_5H_7Br [M]$^+$: 145.9731; found 145.9730.



Compound S6: A solution of bromide **S5** (1.00 g, 6.8 mmol) in THF (4 mL) was added dropwise to a suspension of activated magnesium[8] (230 mg, 9.5 mmol) in THF (6 mL) at 0 °C. The mixture was stirred for 20 min at ambient temperature before it was cooled to −78 °C. CuCN (61 mg, 0.68 mmol) and (*S*)-propylene oxide (0.24 mL, 3.4 mmol) were added and the resulting mixture was allowed to reach ambient temperature overnight. The reaction was quenched with sat. aq. NH_4Cl and diluted with *tert*-butyl methyl ether and water. The aqueous layer was extracted with *tert*-butyl methyl ether, the combined organic phases were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 94/6 → 90/10) to afford product **S6** as a colorless oil (450 mg, 97%). $[\alpha]_D^{20}$ = +10.4° (c = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86-3.78 (m, 1H), 2.19-2.12 (m, 2H) 1.77 (t, J = 2.7, 3H), 1.64-1.46 (m, 5H), 1.35 (br s, 1H), 1.20 (d, J = 6.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.1 (C), 75.9 (C), 67.9 (CH), 38.6 (CH_2), 25.4 (CH_2), 23.7 (CH_3), 18.8 (CH_2), 3.6 (CH_3); IR (film): $\tilde{\nu}$ = 3357, 2964, 2920, 2862, 1455, 1435, 1373, 1332, 1127, 1084, 1044, 990, 944, 862 cm^{-1}; MS (EI): *m/z* (%): 111 (30), 109 (5), 108 (5), 107 (5), 97 (5), 94 (9), 93 (99), 91 (17), 84 (91), 83 (10), 81 (14), 79 (24), 77 (22), 71 (45), 69 (5), 68 (21), 67 (66),



[8] E. Bartmann, B. Bogdanović, N. Janke, S. Liao, K. Schlichte, B. Spliethoff, J. Treber, U. Westeppe, U. Wilczok, *Chem. Ber.* **1990**, *123*, 1517-1528.

66 (100), 65 (17), 58 (6), 57 (11), 55 (33), 54 (44), 53 (29), 52 (8), 51 (11), 50 (5), 45 (83), 43 (50), 42 (5), 41 (35), 40 (8), 39 (33), 29 (14), 27 (30); HRMS (CI): *m/z* calcd for $C_8H_{15}O$+H $[M+H]^+$: 127.1123; found 127.1122.

Compound 31: Ac_2O (0.78 mL, 8.24 mmol), DMAP (101 mg, 0.82 mmol) and NEt_3 (1.71 mL, 12.4 mmol) were added to a stirred solution of alcohol **S6** (520 mg, 4.12 mmol) in CH_2Cl_2 (15 mL). After stirring for 1.5 h, the reaction was quenched with water and the mixture diluted with *tert*-butyl methyl ether. The aqueous layer was extracted with *tert*-butyl methyl ether and the combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 100/0 → 98/2) to furnish product **31** as a colorless oil (679 mg, 98%). $[\alpha]_D^{20}$ = +1.2° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.90 (tq, *J* = 6.3, 6.3 Hz, 1H), 2.17-2.10 (m, 2H), 2.02 (s, 3H), 1.77 (t, *J* = 2.5, 3H), 1.69-1.57 (m, 2H), 1.54-1.41 (m, 2H), 1.21 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9 (C), 78.8 (C), 76.0 (C), 70.7 (CH), 35.2 (CH_2), 25.1 (CH_2), 21.5 (CH_3), 20.1 (CH_3), 18.7 (CH_2), 3.6 (CH_3); IR (film): $\tilde{\nu}$ = 2978, 2940, 2921, 2866, 1733, 1436, 1371, 1238, 1132, 1083, 1043, 1017, 953 cm^{-1}; MS (EI): *m/z* (%): 126 (22), 111 (15), 108 (14), 94 (5), 93 (77), 91 (11), 87 (5), 84 (7), 79 (15), 77 (9), 71 (8), 67 (9), 66 (67), 55 (19), 53 (9), 43 (100), 41 (9), 39 (6), 27 (7); HRMS (CI): *m/z* calcd for $C_{10}H_{17}O_2$+H $[M+H]^+$: 169.1229; found 169.1227.

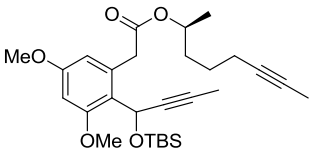
Compound S7: A solution of 1-propynylmagnesium bromide (0.5 M in THF, 6.2 mL, 3.10 mmol) was added dropwise to a stirred solution of aldehyde **29** (600 mg, 2.45 mmol)[9] in THF (4.5 mL) at 0 °C. After stirring at ambient temperature overnight, the reaction was quenched with sat. aq. NH_4Cl and *tert*-butyl methyl ether. 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, 90/10 → 85/15) to give product **S7** as a colorless solid (649 mg, 93%). Mp = 90-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.68 (d, *J* = 2.4 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 5.81 (dq, *J* = 11.1, 2.3 Hz, 1H), 3.89 (s, 3H), 3.80 (d, *J* = 11.1 Hz, 1H), 3.77 (s, 3H), 1.82 (d, *J* = 2.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3 (C), 159.1 (C), 123.1 (C), 122.3 (C), 109.7 (CH), 99.7 (CH), 80.7 (C), 79.1 (C), 62.9 (CH), 56.3 (CH_3), 55.8 (CH_3), 4.0 (CH_3); IR (film): $\tilde{\nu}$ = 3529, 3090, 2972, 2943, 2839, 1595, 1566, 1482, 1465, 1451, 1433, 1409, 1302, 1209, 1177, 1143, 1125, 1029, 1005, 947, 832, 811, 795, 721 cm^{-1}; MS (EI): *m/z* (%): 286 (8), 284 (8), 271 (13), 169 (17), 255 (6), 253 (7), 218 (7), 206 (13), 205 (100), 190 (14), 162 (11), 161 (7), 147 (7), 67 (7), 63 (5), 39 (7); HRMS (ESI): *m/z* calcd for $C_{12}H_{13}O_3BrNa$ $[M+Na]^+$: 306.9940; found 306.9938.

Compound 30: Imidazole (402 mg, 5.9 mmol) and TBSCl (1.07 g, 7.1 mmol) were added to a stirred solution of alcohol **S7** (1.35 g, 4.9 mmol) in DMF (4 mL) at 0 °C. After stirring at ambient temperature for 4 h, the reaction was quenched with water and the mixture diluted with *tert*-butyl methyl ether. The aqueous layer was extracted

[9] S. A. Snyder, T. C. Sherwood, A. G. Ross, *Angew. Chem.* **2010**, *122*, 5272-5276; *Angew. Chem. Int. Ed.* **2010**, *49*, 5146-5150.

with *tert*-butyl methyl ether and the combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 98/2 → 96/4) to give product **30** as a colorless oil (1.92 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.71 (d, *J* = 2.5 Hz, 1H), 6.39 (d, *J* = 2.5 Hz, 1H), 6.08 (q, *J* = 2.3 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 1.81 (d, *J* = 2.3 Hz, 3H), 0.86 (s, 9H), 0.09 (s, 3H), –0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1 (2 C), 124.2 (C), 122.8 (C), 110.4 (CH), 98.9 (CH), 79.8 (C), 79.5 (C), 56.2 (CH), 56.2 (CH_3), 55.7 (CH_3), 26.0 (CH_3), 18.4 (C), 4.1 (CH_3), –4.5 (CH_3), –4.7 (CH_3); IR (film): $\tilde{\nu}$ = 2955, 2929, 2855, 1598, 1567, 1460, 1434, 1410, 1300, 1286, 1249, 1214, 1199, 1155, 1126, 1060, 1035, 1004, 938, 831, 812, 773 cm^{-1}; MS (EI): *m/z* (%): 344 (16), 343 (80), 342 (16), 341 (77), 270 (13), 269 (98), 268 (13), 267 (100), 217 (4), 215 (5), 188 (7), 173 (8), 145 (5), 115 (7), 102 (5), 97 (9), 75 (11), 73 (15), 53 (7), 41 (5); HRMS (ESI): *m/z* calcd for $C_{18}H_{27}O_3BrSiNa$ $[M+Na]^+$: 421.0805; found 421.0805.

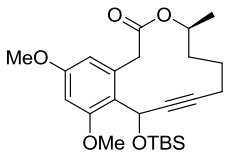
Compound 32: A solution of TMPZnCl·LiCl (1.0 M in THF, 2.8 mL, 2.8 mmol)[10] was added dropwise to a stirred solution of acetate **31** (316 mg, 1.9 mmol) in THF (6 mL). The mixture was stirred for 20 min at ambient temperature before $Pd(OAc)_2$ (22 mg, 0.095 mmol), SPhos (78 mg, 0.19 mmol) and a solution of bromide **30** (760 mg, 1.9 mmol) in THF (5 mL) were successively added. The resulting mixture was heated to 50 °C for 3 h, before the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 98/2 → 95/5) to afford product **32** as a pale orange oil (566 mg, 62%, mixture of diastereomers). $[\alpha]_D^{20}$ = +3.3° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.42 (d, *J* = 2.5 Hz, 1H, 1 *dia.*), 6.41 (d, *J* = 2.5 Hz, 1H, 1 *dia.*), 6.31 (d, *J* = 2.3 Hz, 2H, 2 *dia.*), 6.09 (q, *J* = 2.2 Hz, 2H, 2 *dia.*), 4.99-4.89 (m, 2H, 2 *dia.*), 4.18 (d, *J* = 16.7 Hz, 1H, 1 *dia.*), 4.17 (d, *J* = 16.8 Hz, 1H, 1 *dia.*), 4.07 (d, *J* = 16.7 Hz, 1H, 1 *dia.*), 4.06 (d, *J* = 16.8 Hz, 1H, 1 *dia.*), 3.77 (s, 6H, 2 *dia.*), 3.76 (s, 6H, 2 *dia.*), 2.15-2.07 (m, 4H, 2 *dia.*), 1.77 (d, *J* = 2.3 Hz, 3H, 1 *dia.,* overlap), 1.77 (d, *J* = 2.3 Hz, 3H, 1 *dia.*, overlap), 1.75 (t, *J* = 2.5 Hz, 6H, 2 *dia.*), 1.72-1.58 (m, 4H, 2 *dia.*), 1.58-1.41 (m, 4H, 2 *dia.*), 1.22 (d, *J* = 6.0 Hz, 6H, 2 *dia.*), 0.85 (s, 18H, 2 *dia.*), 0.07 (s, 6H, 2 *dia.*), -0.06 (s, 6H, 2 *dia.*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.9 (C), 171.9 (C), 159.8 (C, 2 *dia.*), 156.5 (C, 2 *dia.*), 136.8 (C), 136.8 (C), 122.4 (C, 2 *dia.*), 107.6 (CH), 107.6 (CH), 97.2 (CH, 2 *dia.*), 80.5 (C), 80.4 (C), 78.9 (C, 2 *dia.*), 75.9 (C, 2 *dia.*), 70.8 (CH), 70.8 (CH), 56.6 (CH_3), 55.9 (CH_3, 2 *dia.*), 55.3 (CH_3), 38.4 (CH_2), 38.3,(CH_2), 35.4 (CH_2), 35.3 (CH_2), 26.0 (CH_3, 2 *dia.*), 25.1 (CH_2, 2 *dia.*), 20.1 (CH_3, 2 *dia.*), 18.8 (CH_2, 2 *dia.*), 18.3 (C, 2 *dia.*), 4.0 (CH_3, 2 *dia.*), 3.6 (CH_3, 2 *dia.*), -4.9 (CH_3, 2 *dia.*), -4.9 (CH_3, 2 *dia.*); IR (film): $\tilde{\nu}$ = 2929, 2856, 1728, 1604, 1462, 1427, 1360, 1302, 1250, 1203, 1166, 1148, 1129, 1080, 1030, 1003, 858, 834, 775 cm^{-1}; MS (EI): *m/z* (%): 486 (1), 431 (5), 430 (16), 429 (51), 361 (12), 323 (7), 322 (24), 321 (100), 307 (4), 305 (9), 304 (15), 303 (64), 281 (10), 277 (14), 262 (6), 261 (10), 253 (6), 248 (7), 247 (40), 246 (6), 245 (7), 229 (19), 203 (6), 202 (7), 201 (14), 188 (7), 187 (10), 159 (11), 144 (6), 128 (6), 116 (5), 115 (7), 109 (19), 81 (11), 75 (22), 73 (18), 67 (25), 66 (6), 57 (14), 55 (15), 53



[10] S. Duez, S. Bernhardt, J. Heppekausen, F. F. Fleming, P. Knochel, *Org. Lett.* **2011**, *13*, 1690-1693.

(10), 43 (13), 41 (17), 29 (7); HRMS (ESI): *m/z* calcd for $C_{28}H_{42}O_5SiNa$ $[M+Na]^+$: 509.2694; found 509.2699.

Compound 33: A two-neck flask with a reflux condenser was charged with diyne **32** (155 mg, 0.32 mmol) in degassed toluene (35 mL) under Ar. Complex **6** (100 mg, 0.16 mmol)[11] and degassed abs. CH_2Cl_2 (0.51 mL, 7.95 mmol) were added and the mixture was stirred at reflux temperature for 18 h. After cooling, the mixture was passed through a pad of silica, which was carefully rinsed with ethyl acetate. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 98/2 → 93/7) to give product **33** as a colorless solid (109 mg, 79%). For analytical reasons an aliquot of the sample was re-subjected to flash chromatography to afford analytically pure samples of both diastereomers, which analyzed as follows:



First diastereomer: $[\alpha]_D^{20}$ = –53.2° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.32 (d, *J* = 2.5 Hz, 1H), 6.29 (d, *J* = 2.5 Hz, 1H), 6.11-6.09 (m, 1H), 5.03-4.93 (m, 1H), 4.86 (d, *J* = 17.1 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.46 (d, *J* = 17.1 Hz, 1H), 2.36-2.27 (m, 1H), 2.10-2.00 (m, 1H), 1.80-1.64 (m, 2H), 1.56-1.39 (m, 2H), 1.04 (d, *J* = 6.3 Hz, 3H), 0.84 (s, 9H), 0.09 (s, 3H), -0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.1 (C), 159.7 (C), 156.5 (C), 137.4 (C), 122.7 (C), 108.2 (CH), 96.9 (CH), 85.2 (C), 81.8 (C), 71.5 (CH), 56.5 (CH), 55.8 (CH_3), 55.4 (CH_3), 39.6 (CH_2), 34.9 (CH_2), 25.9 (CH_3), 23.9 (CH_2), 20.4 (CH_2), 20.2 (CH_3), 18.3 (C), –4.8 (CH_3), –5.0 (CH_3); IR (film): $\tilde{\nu}$ = 2932, 2856, 1717, 1604, 1462, 1426, 1360, 1322, 1250, 1204, 1147, 1131, 1083, 1057, 1027, 1003, 856, 834, 775 cm^{-1}; MS (EI): *m/z* (%): 377 (7), 376 (27), 375 (100), 358 (7), 357 (26), 302 (9), 301 (41), 283 (15), 282 (5), 281 (27), 259 (8), 257 (6), 255 (13), 253 (6), 243 (5), 242 (5), 231 (19), 205 (5), 204 (5), 201 (6), 191 (5), 179 (5), 175 (5), 109 (5), 105 (9), 75 (17), 73 (16); HRMS (ESI): *m/z* calcd for $C_{24}H_{36}O_5SiNa$ $[M+Na]^+$: 455.2224; found 455.2224.

Second diastereomer: Mp = 147-148 °C; $[\alpha]_D^{20}$ = –46.5° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45 (d, *J* = 2.5 Hz, 1H), 6.34 (d, *J* = 2.5 Hz, 1H), 6.10 (t, *J* = 1.5 Hz, 1H), 5.12-5.04 (m, 1H), 4.69 (d, *J* = 16.7 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.36 (d, *J* = 16.7 Hz, 1H), 2.39-2.29 (m, 1H), 2.14-2.04 (m, 1H), 1.95-1.85 (m, 1H), 1.77-1.60 (m, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 0.87 (s, 9H), 0.13 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7 (C), 159.8 (C), 156.6 (C), 136.6 (C), 121.9 (C), 109.8 (CH), 97.5 (CH), 86.2 (C), 81.6 (C), 70.9 (CH), 56.4 (CH), 55.8 (CH_3), 55.4 (CH_3), 38.5 (CH_2), 34.0 (CH_2), 26.0 (CH_3), 21.9 (CH_2), 20.2 (CH_2), 19.4 (CH_3), 18.3 (C), –4.8 (CH_3), –4.8 (CH_3); IR (film): $\tilde{\nu}$ = 2950, 2932, 2856, 1726, 1606, 1460, 1427, 1356, 1304, 1275, 1247, 1202, 1185, 1168, 1147, 1129, 1083, 1064, 1043, 1020, 1002, 942, 857, 836, 773 cm^{-1}; MS (EI): *m/z* (%): 377 (8), 376 (27), 375 (100), 357 (16), 302 (16), 301 (73), 283 (14), 281 (18), 259 (15), 257 (6), 255 (11), 253 (5), 243 (6), 241 (5), 232 (5), 231 (32), 217 (6), 207 (5), 205 (5), 204 (5), 201 (7), 179 (5), 175 (5), 115 (5), 109 (5), 105 (6), 75 (17), 73 (18), 69 (6), 57 (5), 55 (6), 41 (7); HRMS (ESI): *m/z* calcd for $C_{24}H_{36}O_5SiNa$ $[M+Na]^+$: 455.2224; found 455.2220.

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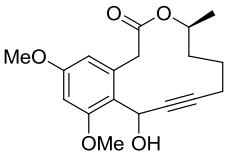
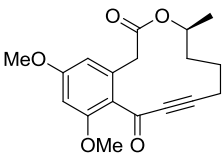
[11] A. Fürstner, C. Mathes, C. W. Lehmann, *J. Am. Chem. Soc.* **1999**, *121*, 9453-9454.



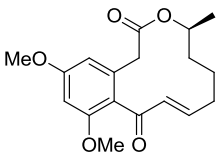
Compound S8: H_2O (31 µL, 1.7 mmol) and TASF (235 mg, 0.85 mmol) were added to a stirred solution of compound **33** (74 mg, 0.17 mmol) in DMF (2.5 mL). After stirring for 2.5 h, the reaction was quenched with aqueous pH 7 buffer and the mixture diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate and the combined extracts were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 90/10 → 80/20) to give product **S8** as a colorless foam (52 mg, 97%, 2 diastereomers). $[\alpha]_D^{20} = -9.1°$ (*c* = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.43 (d, *J* = 2.4 Hz, 2H, 2 *dia.*), 6.38 (d, *J* = 2.4 Hz, 1H, 1 *dia.*), 6.27 (d, *J* = 2.4 Hz, 1H, 1 *dia.*), 6.20-6.14 (m, 1H, 1 *dia.*), 5.94 (dt, *J* = 8.2, 2.0 Hz, 1H, 1 *dia.*), 5.14-5.04 (m, 2H, 2 *dia.*), 4.58 (d, *J* = 16.6 Hz, 1H, 1 *dia.*), 4.12 (d, *J* = 17.9 Hz, 1H, 1 *dia.*), 3.85 (d, *J* = 17.9 Hz, 1H, 1 *dia.*), 3.84 (s, 3H, 1 *dia.*), 3.81 (s, 3H, 1 *dia.*), 3.79 (s, 3H, 1 *dia.*), 3.79 (s, 3H, 1 *dia.*), 3.49 (d, *J* = 9.0 Hz, 1H, 1 *dia.*), 3.45 (d, *J* = 16.9 Hz, 1H, 1 *dia.*), 2.46-2.36 (m, 1H, 1 *dia.*), 2.35-2.29 (m, 2H, 1 *dia.*), 2.11-2.07 (m, 1H, 1 *dia.*), 2.07-2.00 (m, 1H, 1 *dia.*), 1.98-1.88 (m, 1H, 1 *dia.*), 1.88-1.77 (m, 1H, 1 *dia.*), 1.77-1.70 (m, 1H, 1 *dia.*), 1.70-1.56 (m, 4H, 2 *dia.*), 1.24 (d, *J* = 6.4 Hz, 3H, 1 *dia.*, overlap), 1.24 (d, *J* = 6.4 Hz, 3H, 1 *dia.*, overlap); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.7 (C), 172.3 (C), 160.3 (C), 160.1 (C), 158.8 (C), 157.6 (C), 136.3. (C), 134.8 (C), 120.9 (C), 120.2 (C), 110.0 (CH), 109.1 (CH), 98.1 (CH), 97.9 (CH), 88.3 (C), 88.0 (C), 82.1 (C), 80.5 (C), 72.6 (CH), 71.1 (CH), 57.1 (CH), 56.5 (CH), 56.2 (CH_3), 55.9 (CH_3), 55.5 (CH_3), 55.4 (CH_3), 42.0 (CH_2), 39.2 (CH_2), 33.6 (CH_2), 33.4 (CH_2), 23.6 (CH_2), 21.7 (CH_2), 20.1 (CH_3), 20.0 (CH_3), 19.3 (CH_2), 19.3 (CH_3); IR (film): $\tilde{\nu}$ = 3479, 2935, 2839, 1714, 1603, 1454, 1426, 1306, 1202, 1144, 1082, 1052, 980, 949, 833, 729 cm^{-1}; MS (EI): *m/z* (%): 319 (10), 318 (49), 303 (21), 302 (20), 301 (100), 300 (24), 275 (51), 273 (32), 272 (16), 271 (10), 259 (40), 257 (25), 247 (20), 243 (21), 241 (26), 233 (38), 231 (54), 229 (32), 220 (21), 219 (21), 218 (37), 217 (97), 207 (38), 205 (63), 204 (33), 203 (30), 202 (30), 201 (51), 196 (21), 191 (58), 189 (38), 187 (25), 179 (38), 178 (25), 175 (36), 165 (22), 161 (22), 152 (28), 151 (32), 128 (30), 121 (20), 115 (49), 91 (26), 77 (34), 55 (35), 43 (38), 41 (32), 39 (20), 29 (22); HRMS (ESI): *m/z* calcd for $C_{18}H_{22}O_5Na$ $[M+Na]^+$: 341.1359; found 341.1359.

Compound 34: MnO_2 (316 mg, 3.6 mmol) was added in several portions over a period of 2 h to a stirred solution of alcohol **S8** (58 mg, 0.18 mmol) in CH_2Cl_2 (1.5 mL). Stirring was continued for 30 min before the mixture was passed through a pad of silica, which was carefully rinsed with *tert*-butyl methyl ether. The combined filtrates were evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 85/15 → 50/50) to give product **34** as a yellowish solid (44 mg, 77%). Mp = 117-119 °C; $[\alpha]_D^{20} = -116°$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.42 (d, *J* = 2.3 Hz, 1H), 6.40 (d, *J* = 2.3 Hz, 1H), 5.16-5.07 (m, 1H), 3.91 (d, *J* = 16.4 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.53 (d, *J* = 16.4 Hz, 1H), 2.55 (ddd, *J* = 17.5, 8.5, 2.9 Hz, 1H), 2.41 (ddd, *J* = 17.5, 8.8, 2,8 Hz, 1H), 1.99-1.89 (m, 1H), 1.88-1.77 (m, 1H), 1.76-1.62 (m, 2H), 1.25 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.9 (C), 171.2 (C), 162.2 (2), 159.1 (C), 135.0 (C), 122.7 (C), 108.6 (CH), 98.4 (CH), 98.0 (C), 83.5 (C), 71.7 (CH), 56.2 (CH_3), 55.6 (CH_3), 40.0 (CH_2), 33.9 (CH_2), 21.6 (CH_2), 20.5 (CH_2), 19.5 (CH_3); IR (film): $\tilde{\nu}$ = 2978, 2923, 2847, 2219, 2185, 1723, 1636, 1600, 1455, 1442, 1422, 1365, 1319, 1250, 1213, 1199, 1159, 1142, 1086, 1066, 1044, 981, 961, 902, 883, 858, 847, 816, 785, 743, 716 cm^{-1}; MS

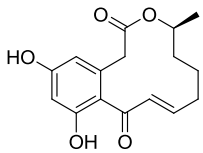


(EI): *m/z* (%): 317 (20), 316 (100), 300 (12), 299 (63), 245 (11), 244 (10), 230 (10), 229 (12), 215 (14), 189 (10), 178 (16), 128 (13), 115 (26), 91 (10), 77 (14); HRMS (ESI): *m/z* calcd for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1203; found 339.1202.

Compound 35: $CrCl_2$ (57 mg, 0.46 mmol) was added to a stirred solution of compound **34** (21.0 mg, 0.066 mmol) in degassed THF/H_2O (1:1, 1.5 mL). After 3.5 h, a second portion of $CrCl_2$ (25 mg, 0.20 mmol) was introduced and stirring continued for 1 h. The reaction was quenched with H_2O and *tert*-butyl methyl ether, the organic layer was washed with H_2O, dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 90/10 → 85/15) to give product ***E*-35** as a colorless foam (14.9 mg, 71%) together with (*Z*)-isomer ***Z*-35** (1.4 mg, 7%). $[\alpha]_D^{20} = -58.0°$ (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.50-6.39 (m, 1H, overlap), 6.49 (d, *J* = 2.0 Hz, 1H, overlap), 6.42 (d, *J* = 2.0 Hz, 1H, overlap), 6.27 (d, *J* = 15.9 Hz, 1H) 4.95-4.84 (m, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.40 (d, *J* = 15.1 Hz, 1H), 3.36 (d, *J* = 15.1 Hz, 1H), 2.39-2.29 (m, 1H), 2.24-2.13 (m, 1H), 1.94-1.75 (m, 2H), 1.54-1.39 (m, 2H), 1.16 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.6 (C), 170.7 (C), 161.1 (C), 157.4 (C), 156.6 (CH), 133.4 (CH), 133.0 (C), 122.7 (C), 106.7 (CH), 98.1 (CH), 73.1 (CH), 56.0 (CH_3), 55.6 (CH_3), 39.7 (CH_2), 34.4 (CH_2), 34.2 (CH_2), 24.6 (CH_2), 20.5 (CH_3); IR (film): $\tilde{\nu}$ = 2937, 2841, 1722, 1650, 1602, 1582, 1455, 1422, 1310, 1271, 1200, 1156, 1080, 1053, 1039, 974, 949, 913, 833, 728 cm^{-1}; MS (EI): *m/z* (%): 319 (20), 318 (100), 301 (17), 275 (19), 259 (5), 248 (5), 246 (8), 231 (9), 223 (16), 218 (9), 217 (15), 206 (5), 205 (26), 204 (15), 195 (16), 192 (6), 191 (8), 189 (8), 179 (5), 178 (26), 177 (6), 176 (8), 175 (6), 161 (7), 135 (5), 115 (5), 77 (5), 55 (8), 41 (7); HRMS (ESI): *m/z* calcd for $C_{18}H_{22}O_5Na$ $[M+Na]^+$: 341.1359; found 341.1362.



α,β-Dehydrocurvularin (27): A suspension of aluminum powder (61 mg, 2.26 mmol) and I_2 (381 mg, 1.50 mmol) in toluene (1 mL) was stirred at 90 °C for 20 min. After cooling to ambient temperature, the mixture was allowed to settle and the solution transferred to a stirred solution of compound **35** (24 mg, 0.075 mmol) and TBAI (5.5 mg, 0.015 mmol) in toluene (1 mL) at 0 °C. The resulting mixture was stirred for 20 min at 0 °C, before the reaction was quenched with sat. aq. $Na_2S_2O_3$. Ethyl acetate and sat. aq. Rochelle´s salt were added and the biphasic mixture was vigorously stirred for 10 min. The aqueous layer was extracted with ethyl acetate and the combined organic phases were dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 80/20 → 65/35) to give product **27** as yellowish plates (13 mg, 60%). Mp = 209-211 °C [12] (218-220 °C, ref.[13]); $[\alpha]_D^{20}$ = –65.5° (*c* = 0.9, EtOH) ($[\alpha]_D^{20}$ = –64.1°, ref.[13]); ^{1}H NMR (600 MHz, [D_6]-acetone): δ = 12.41 (s, 1H), 9.27 (s, 1H), 6.80 (dt, *J* = 15.4, 1.4 Hz, 1H), 6.59 (ddd, *J* = 15.4, 9.1, 4.5 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 6.31 (d, *J* = 2.4 Hz, 1H), 4.76-4.70 (m, 1H), 4.10 (d, *J* = 17.8 Hz, 1H), 3.63 (d, *J* = 17.8 Hz, 1H), 2.47-2.41 (m, 1H), 2.39-2.32 (m, 1H), 2.03-1.97 (m, 1H), 1.89-1.82 (m, 1H), 1.71-1.59 (m, 2H), 1.19 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, [D_6]-acetone): δ = 197.2 (C), 171.8 (C), 166.0 (C), 163.0 (C), 149.6 (CH), 139.5



[12] The material turned dark brown at 160-165 °C.

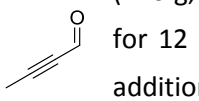
[13] M. Vurro, A. Evidente, A. Andolfi, M. C. Zonno, F. Giordano, A. Motta, *Plant Sci.* **1998**, *138*, 67-79.

C, 132.5 (CH), 115.5 (C), 113.7 (CH), 102.8 (CH), 72.8 (CH), 43.7 (CH_2), 34.6 (CH_2), 33.1 (CH_2), 24.9 (CH_2), 20.2 (CH_3); IR (film): $\tilde{\nu}$ = 3348, 2979, 2927, 1699, 1621, 1579, 1441, 1367, 1332, 1306, 1233, 1199, 1174, 159, 1139, 1120, 1069, 1048, 1027, 1011, 984, 837, 780, 682 cm^{-1}; MS (EI): *m/z* (%):291 (18), 290 (100), 218 (12), 205 (10), 203 (54), 192 (10), 190 (20), 189 (11), 177 (27), 176 (17), 175 (23), 167 (20), 166 (14), 164 (16), 163 (15), 161 (15), 150 (26), 147 (13), 121 (10), 115 (10), 81 (18), 77 (10), 69 (23), 67 (11), 65 (11), 55 (19), 53 (11), 43 (10), 41 (17), 39 (15); HRMS (ESI): *m/z* calcd for $C_{16}H_{18}O_5Na$ $[M+Na]^+$: 313.1046; found 313.1044.

Total Synthesis of (–)-A26771B

But-2-ynal (S9). 2-Butynol (10 mL, 132 mmol) was added to a vigorously stirred suspension of MnO_2 (120 g, 1.4 mol) in Et_2O (100 mL) at 0°C and stirring was continued at ambient temperature for 12 h. Additional MnO_2 (30 g, 350 mmol) was then added and the mixture stirred for additional 4 h. After filtration through a pad of Celite and careful evaporation of the filtrate at < 40°C bath temperature, the residue was distilled under vacuum to afford the title compound as a pale yellow liquid (2.2 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.13 (br s, 1H), 2.05 ppm (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.1, 95.2, 80.9, 4.1 ppm; IR (film): $\tilde{\nu}$ = 3981, 1691, 1242 cm^{-1}. The analytical and spectroscopic data are in agreement with those reported in the literature.[14]

***tert*-Butyl-3-hydroxyhex-4-ynoate (S10).** *n*BuLi (24 mL, 38.3 mmol, 1.6 M in hexane) was added dropwise to a solution of (^{i}Pr)$_2$NH (5.4 mL, 38.3 mmol) in THF (65 mL) at –78 °C over the course of 1 h and the resulting mixture was stirred for an additional hour. A solution of *tert*-butyl acetate (5.2 mL, 28.3 mmol) in THF (25 mL) was added dropwise and the mixture stirred for 1 h before a solution of but-2-ynal **S9** (2.2 g, 31.9 mmol) in THF (30 mL) was slowly added. The mixture was stirred for 1 h at that temperature before the reaction was quenched with MeOH (5 mL). The crude material was washed with aq. sat. NH_4Cl, the aqueous phase was extracted with Et_2O (3x), and the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 9:1) to afford the title compound as a colorless oil (4.8 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.68-4.63 (m, 1H), 3.10 (br s, 1H), 2.62 (s, 1H), 2.60 (d, *J* = 0.7 Hz, 1H), 1.82 (d, *J* = 2.2 Hz, 3H), 1.57 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 81.6, 81.2, 78.6, 59.1, 43.2, 28.1, 3.5; IR (film): $\tilde{\nu}$ = 3449, 2979, 2923, 1728, 1367, 1255, 1149, 1050, 1012, 845, 732 cm^{-1}; MS (EI) *m/z* (%): 57 (15), 56 (54), 55 (22), 41 (100), 40 (19), 369 (51); HRMS (ESI): *m/z*: calcd. for $C_{10}H_{16}O_3Na$ [M^++Na]: 207.0990, found 207.0992.



***tert*-Butyl-3-(benzoyloxy)hex-4-ynoate (S11).** Benzoyl chloride (2.8 mL, 24 mmol) was added dropwise to a solution of *tert*-butyl-3-hydroxyhex-4-ynoate **S10** (2.7 g, 14.6 mmol) in dichloromethane (20 mL) and pyridine (10 mL) at 0 °C. The mixture was stirred

[14] H. J. Bestmann, K. H. Koschatzky, W. Schätzke, J. Süss, O. Vostrowsky, *Liebigs Ann. Chem.* **1981**, 1705-1720.

at room temperature for 6 h before the reaction was quenched with aq. sat. NH_4Cl. The aqueous phase was extracted with dichloromethane (3x), the combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography (hexane/EtOAc, 19:1) to afford the title compound as a colorless oil (4.1 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, 2H, *J* = 8.4, 1.3 Hz), 7.56 (tt, 1H, *J* = 7.5, 1.3 Hz), 7.43 (t, 2H, *J* = 8.0 Hz), 5.89 (ddq, 1H, *J* = 8.6, 5.6, 2.1 Hz), 2.90 (dd, 1H, *J* = 15.4, 8.5 Hz), 2.78 (dd, 1H, *J* = 15.5, 5.6 Hz), 1.83 (d, 3H, *J* = 2.2 Hz), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 165.5, 133.3, 129.9, 129.8, 128.5, 82.7, 81.5, 75.9, 61.7, 42.1, 28.2, 3.9 ppm; IR (film): $\tilde{\nu}$ = 3015, 2978, 2924, 1724, 1452, 1367, 1264, 1147, 1095, 1098, 1025, 997, 709 cm^{-1}; MS (EI) *m/z* (%): 288 (0.2), 187 (15), 105 (100), 93 (14), 77 (22), 57 (24); HRMS (ESI): *m/z*: calcd. for $C_{17}H_{20}O_4Na$ [M^++Na]: 331.1256, found 331.1254.

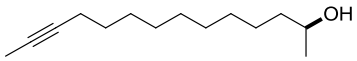
3-(Benzoyloxy)hex-4-ynoic acid (S12). Trifluoroacetic acid (3.2 mL, 43 mmol) was added to a solution of *tert*-butyl ester **S11** (2.5 g, 8.6 mmol) in dichloromethane (85 mL) at 0 °C and the mixture was stirred for 12 h at ambient temperature. Aq. sat. $NaHCO_3$ was added until a neutral pH was reached, the layers were separated and the aqueous phase was extracted with dichloromethane (3x). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated, and the residue was purified with flash chromatography (hexane/ethyl acetate, 7:3 → 6:4, 1% of HOAc) to afford the title compound as a white solid (2.0 g, 99%). mp = 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.97 (br s, 1H), 8.03 (dd, 2H, *J* = 8.3, 1.2 Hz), 7.60 (tt, 1H, *J* = 7.5, 1.4 Hz), 7.43 (dd, 2H, *J* = 8.2, 7.4 Hz), 5.92 (ddq, 1H, *J* = 7.6, 5.5, 2.1 Hz), 3.01 (dd, 1H, *J* = 16.4, 8.1 Hz), 2.93 (dd, 1H, *J* = 16.3, 5.5 Hz), 1.83 (d, 3H, *J* = 2.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.0, 165.5, 133.5, 130.1, 129.8, 128.6, 83.2, 75.5, 61.0, 40.3, 3.9; IR (film): $\tilde{\nu}$ = 3064, 2923, 2632, 1712, 1451, 1417, 1265, 1176, 1156, 1096, 1069, 1026, 997, 707 cm^{-1}; MS (EI) *m/z* (%): 233 (0.1), 232 (0.2), 187 (12), 122 (49), 105 (100), 77 (48), 66 (13), 65 (10), 51 (22), 39 (21); HRMS (ESI): *m/z*: calcd. for $C_{13}H_{12}O_4Na$ [M^++Na]: 255.0626, found 255.0628.

11-Bromo-2-undecyn (S13). Tf_2O (4.2 mL, 25.2 mmol) was added to a solution of 7-bromoheptanol (4.4 g, 20.5 mmol) in dichloromethane (80 mL) and pyridine (2 mL, 25.2 mmol) at 0°C and the resulting mixture was stirred for 30 min at this temperature and for 15 minutes at RT. For work up, the mixture was diluted with hexane (80 mL) and filtered through a pad of Celite. The filtrate was evaporated and the residue dissolved in THF (80 mL). Next, a suspension of propinyl lithium (1.0 g, 22 mmol) in THF (20 mL + 20 mL to rinse) was added via cannula at −78 °C and the mixture stirred for 20 minutes at that temperature before it was allowed to reach 0 °C. After stirring for 1 h, the reaction was quenched with aq. sat. NH_4Cl, the layers were separated and the aqueous phase was extracted with EtOAc (3x). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated, and the residue was purified by flash chromatography (hexane/EtOAc, 15:1) to afford the title compound as a colorless liquid (3.3 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (t, 2H, *J* = 6.8 Hz), 2.11 (tq, 2H, *J* = 7.0, 2.6 Hz), 1.85 (quint, 2H, *J* = 7.6 Hz), 1.77 (t, 3H, *J* = 2.6 Hz), 1.49-1.27 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.5, 75.6, 33.2, 29.2, 29.2, 29.0, 28.9, 28.3, 18.9, 3.7; IR (film): $\tilde{\nu}$ = 2929, 2855, 1462, 1436, 1268, 1247, 724 cm^{-1}. MS (EI) *m/z* (%): 233 (0.04), 232 (0.4), 231 (0.06), 230 (0.21), 135 (10.3), 109 (31), 107 (12), 96 (20), 95

(100), 93 (25), 91 (10), 82 (16), 81 (63), 79 (38), 77 (11), 69 (20), 68 (50), 67 (90), 55 (74), 54 (40), 53 (30), 43 (16), 41 (59), 39 (28), 27 (15). HRMS (ESI): *m/z*: calcd. for $C_{11}H_{19}Br$+H [M^++H]: 230.0670, found 230.0670.

HRMS (ESI): *m/z*: calcd. for $C_{27}H_{48}O_3SiNa$ [M^++Na]: 471.3265, found: 471.3269.

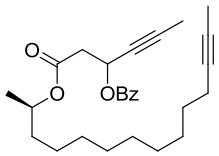
(*S*)-1-Methyl-11-tridecynol (*ent*-37). 11-Bromo-2-undecyne (2.8 g, 12.4 mmol) was added dropwise



to a suspension of Mg (1.5 g, 62 mmol, pre-activated with 2 x 50 µL of dichloroethane) in THF (15 mL) at room temperature and the resulting mixture stirred for 4 h. The suspension was transferred via cannula into a solution of (*S*)-propenoxide (840 µL, 12 mmol) and CuI (228 mg, 1.2 mmol) in THF (30 mL) at –78°C. The mixture was stirred for 10 h while slowly reaching ambient temperature before it was quenched with aq. sat. NH_4Cl and ethyl acetate. The aqueous phase was extracted with EtOAc (3x), the combined organic layers were dried over Na_2SO_4, the solvent was evaporated, and the residue was purified by flash chromatography (hexane/EtOAc, 9:1) to afford the title compound as a colorless oil (1.9 g, 79%). $[\alpha]_D^{20}$ = + 6.8 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (m, 1H), 2.11 (dq, 2H, *J* = 6.9, 2.6 Hz), 1.78 (t, 3H, *J* = 2.6 Hz), 1.50-1.29 (m, 17H), 1.18 (d, 3H, *J* = 6.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.6, 75.5, 68.4, 39.6, 29.9, 29.8, 29.7, 29.4, 29.3, 29.1, 26.0, 23.7, 19.0, 3.7; IR (film): $\tilde{\nu}$ = 3340, 2968, 2920, 2854, 1727, 1462, 1373, 1289, 1125, 1071, 933, 843, 721 cm^{-1}; MS (EI) *m/z* (%): 210 (0.03), 135 (22), 121 (28), 109 (24), 108 (18), 107 (25), 96 (19), 95 (89), 94 (25), 93 (47), 83 (13), 82 (24), 81 (88), 80 (11), 79 (50), 71 (13), 69 (38), 68 (85), 67 (93), 57 (15), 55 (100.00), 57 (23), 53 (25), 45 (98), 43 (39), 41 (68), 39 (17), 29 (20), 27 (13); HRMS (ESI): *m/z*: calcd. for $C_{14}H_{27}O$+H [M^++H]: 211.2060, found: 211.2062.

The enantiomer (**37**) was prepared analogously in 84% yield from (*R*)-propenoxide; $[\alpha]_D^{20}$ = + 7.0 (c = 0.8, $CHCl_3$)

Compound 40. Ph_3P (2.0 g, 7.8 mmol) and DIAD (1.5 mL, 7.8 mmol) were added to a solution of 1-



methyl-11-tridecynol *ent*-**37** (1.6 g, 6.5 mmol) and 3-(benzoyloxy)hex-4-ynoic acid **S9** (1.5 g, 7 mmol) in toluene (80 mL) at 0 °C. The mixture was stirred at ambient temperature for 1 h before the solvent was evaporated. The residue was purified by flash chromatography (hexane/EtOAc, 20:1) to afford the title compound as a colorless syrup (2.8 g, 98%, diastereomeric mixture). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, 2H, *J* = 7.4), 7.55 (tt, 1H, *J* = 7.3, 1.6 Hz), 7.42 (t, 2H, *J* = 7.8 Hz), 5.94-5.91 (m, 1H), 4.92 (m, 1H), 2.99 (ddd, 1H, *J* = 15.6, 8.5, 1.9 Hz), 2.84 (dd, 1H, *J* = 15.5, 5.5 Hz), 2.13-2.07 (m, 2H), 1.83 (d, 3H, *J* = 2.1 Hz), 1.78 (tt, 3H, *J* = 2.6, 0.9 Hz), 1.55-1.13 (m, 19H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9 (2 *dia.*), 165.4 (*2 dia.*), 133.4 (*2 dia.*), 130.0 (*2 dia.*), 128.6 (*2 dia.*), 128.6 (2 *dia.*), 82.9 (2 *dia.*), 79.6 (*2 dia.*), 75.9 (2 *dia.*), 75.5 (*2 dia.*), 72.0 (*2 dia.*), 61.6 (*1 dia.*), 61.6 (*1 dia.*), 41.2 (*1 dia.*), 41.2 (*1 dia.*), 36.1 (*2 dia.*), 29.7 (*1 dia.*), 29.6 (*1 dia.*), 29.6 (*1 dia.*), 29.6 (*1 dia.*), 29.4 (*1 dia.*), 29.3 (*1 dia.*), 29.3 (*2 dia.*), 29.1 (*2 dia.*), 25.6 (*1 dia.*), 25.5 (*1 dia.*), 20.1 (*1 dia.*), 20.1 (*1 dia.*), 14.4 (*2 dia.*), 3.9 (*2 dia.*), 3.7 (*2 dia.*); IR (film): $\tilde{\nu}$ = 2927, 2855, 1730, 1452, 1377, 1266, 1176, 1105, 1096, 1069 1026, 998, 711 cm$^-$

[1]; MS (EI) *m/z* (%): 424 (0.9), 187 (10), 111 (11), 105 (100), 95 (11), 93 (15), 77 (13), 67 (9), 55 (12), 41 (8); HRMS (ESI): *m/z*: calcd. for $C_{27}H_{36}O_4Na$ [M^++Na]: 447.2505; found: 447.2506.

Compound 41. Catalyst **2** (120 mg, 0.09 mmol) was added to a suspension of compound **40** (800 mg, 1.8 mmol) and powdered MS 5Å (12 g) in toluene (1.5 L) at ambient temperature. The suspension was stirred at 80 °C for 3 h before it was cooled to ambient temperature and filtered through a plug of silica, which was carefully rinsed with hexane/ethyl acetate (1:1). The combined filtrates were evaporated and the residue purified by flash chromatography (hexane/EtOAc, 30:1) to yield the title compound as a viscous oil (630 mg, 95%, 2 diastereomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.05 (m, 4H, 2 *dia.*), 7.56 (t, 2H, *J* = 7.4 Hz, *2 dia.*), 7.44 (d, 2H, *J* = 7.7 Hz, *1 dia.*), 7.42 (d, 2H, *J* = 7.6 Hz, *1 dia.*), 5.98-5.93 (m, 2H, *2 dia.*), 5.12-5.06 (m, 1H, *1 dia.*), 5.02 (dq, 1H, *J* = 7.1, 6.2 Hz, *1 dia.*), 2.99-2.88 (m, 3H, *2 dia.*), 2.84 (dd, 1H, *J* = 14.1, 9.6 Hz, *1 dia.*), 2.35-2.19 (m, 4H, *2 dia.*), 1.78-1.61 (m, 2H, *2 dia.*), 1.52-1.13 (m, 30H, *2 dia.*), 1.24 (d, 3H, *J* = 6.2 Hz, *1 dia.*), 1.22 (d, 3H, *J* = 6.4 Hz, *1 dia.*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1 (*1 dia.*), 168.2 (*1 dia.*), 165.6 (*1 dia.*), 165.4 (*1 dia.*), 133.5 (*1 dia.*), 133.4 (*1 dia.*), 130.1 (1 *dia.*), 130.0 (*1 dia.*), 128.6 (*2 dia.*), 128.6, (*2 dia.*), 87.7 (*1 dia.*), 87.0 (*1 dia.*), 77.5 (*1 dia.*), 76.6 (*1 dia.*), 71.3 (*1 dia.*), 70.7 (*1 dia.*), 61.8 (*1 dia.*), 61.7 (*1 dia.*), 41.6 (*1 dia.*), 40.5 (*1 dia.*), 35.6 (*1 dia.*), 35.5 (*1 dia.*), 27.5 (*2 dia.*), 27.1 (*1 dia.*), 27.1 (*1 dia.*), 27.0 (*1 dia.*), 27.0 (*1 dia.*), 26.8 (*1 dia.*), 26.7 (*1 dia.*), 26.7 (*2 dia.*), 26.6 (*1 dia.*), 26.5 (*1 dia.*), 26.3 (*1 dia.*), 26.1 (*1 dia.*), 24.5 (*1 dia.*), 24.3 (*1 dia.*), 20.5 (*1 dia.*), 20.4 (*1 dia.*), 18.4 (*1 dia.*), 18.3 (*1 dia.*); IR (film): $\tilde{\nu}$ = 2976, 2931, 2858, 1724, 1452, 1290, 1265, 1250, 1175, 1096, 1103, 1069, 1026, 711 cm^{-1}; MS (EI) *m/z* (%): 370 (0.3), 106 (8), 105 (100), 77 (16), 55 (7), 43 (5), 41 (9); HRMS (ESI): *m/z*: calcd. for $C_{23}H_{30}NaO_4$ [M^++Na]: 393.2035, found: 393.2036.

Compound 43. Commercial Lindlar catalyst (85 mg) and quinoline (85 µL) were added to a solution of compound **7** (630 mg, 1.7 mmol) in hexane (85 mL). The suspension was stirred under H_2 (1 atm.) for 2 h before it was filtered through a pad of silica, which was rinsed with hexane/ethyl acetate (1:1). The combined filtrates were evaporated and the residue was purified by flash chromatography (hexane:EtOAc, 35:1) to afford the title compound as a colorless oil (630 mg, 99%, mixture of 2 diastereomers). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-8.00 (m, 4H, *2 dia.*), 7.54-7.50 (m, 2H, *2 dia.*), 7.41 (t, 4H, *J* = 7.8 Hz, *2 dia.*), 6.29 (tdd, 1H, *J* = 10.2, 3.3, 0.7 Hz, *1 dia.*), 6.22 (tdd, 1H, *J* = 9.3, 4.2, 0.6 Hz, *1 dia.*), 5.70 (dtd, 1H, *J* = 10.3, 6.4, 0.5 Hz, *1 dia.*), 5.63 (dt, 1H, *J* = 10.3, 6.4 Hz, *1 dia.*), 5.48-5.40 (m, 2H, *2 dia.*), 4.94-4.91 (m, 1H, *1 dia.*), 4.90-4.83 (m, 1H, *1 dia.*), 2.89 (dd, 1H, *J* = 11.9, 10.3 Hz, *1 dia.*), 2.85 (dd, 1H, *J* = 9.7, 8.7 Hz, *1 dia.*), 2.61-2.57 (m, 3H, *2 dia.*), 2.52-2.43 (m, 1H, *1 dia.*), 2.16-2.08 (m, 1H, *1 dia.*), 2.03-1.96 (m, 1H, *1 dia.*), 1.64-1.31 (m, 32H, *2 dia.*), 1.22 (d, 3H, *J* = 6.3 Hz, 1 *dia.*), 1.02 (d, 3H, *J* = 6.2 Hz, *1 dia.*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9 (*1 dia.*), 169.3 (*1 dia.*), 165.7 (*1 dia.*), 165.7 (*1 dia.*), 135.2 (*1 dia.*), 135.0 (*1 dia.*), 133.1 (*1 dia.*), 133.0 (*1 dia.*), 130.7 (*1 dia.*), 130.5 (*1 dia.*), 129.9 (*1 dia.*), 129.7 (*1 dia.*), 128.5 (*1 dia.*), 128.5 (*1 dia.*), 127.4 (*1 dia.*), 127.0 (*1 dia.*), 72.3 (*1 dia.*), 71.5 (*1 dia.*), 68.3 (*1 dia.*), 68.0 (*1 dia.*), 41.8 (*1 dia.*), 41.1 (*1 dia.*), 34.9 (*1 dia.*), 34.4 (*1 dia.*), 27.7 (*1 dia.*), 27.6, 27.6 (*1 dia.*), 27.4 (*1 dia.*), 27.1 (*1 dia.*), 27.1 (*1 dia.*), 27.0 (*1 dia.*), 27.0 (*1 dia.*), 26.9 (*1 dia.*), 26.9 (*1 dia.*), 26.5 (*1 dia.*), 26.4 (*1 dia.*), 23.2 (*1 dia.*), 22.9 (*1 dia.*), 23.2 (*1 dia.*), 22.9 (*1 dia.*), 20.1 (*1 dia.*), 20.0 (*1 dia.*); IR (film): $\tilde{\nu}$ = 2980, 2928, 2857,

1724, 1451, 1272, 1175, 1108, 1068, 1024, 711 cm^{-1}; MS (EI) *m/z* (%): 372 (6), 267 (22), 105 (100), 77 (17), 55 (11), 41 (11); HRMS (ESI): *m/z*: calcd. for $C_{23}H_{32}NaO_4$ [M^++Na]: 395.2190, found: 395.2193.

Compound 44. DBU (1.3 mL) was added to a solution of compound **43** (630 mg, 1.7 mmol) in toluene (34 mL) at 0°C. The reaction was stirred for 6 h at ambient temperature before the solvent was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 35:1) to afford the title compound as a colorless oil (413 mg, 97%). $[\alpha]_D^{20}$ = –17.0 (c = 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (ddd, 1H, *J* = 15.3, 11.6, 0.8 Hz), 6.15 (t, 1H, *J* = 11.2 Hz), 5.88 (dt, 1H, *J* = 10.8, 6.5 Hz), 5.80 (d, 1H, *J* = 15.4 Hz), 4.83 (m, 1H), 2.59-2.49 (m, 1H), 2.03-1.94 (m, 1H), 1.62-1.55 (m, 2H), 1.52-1.16 (m, 14H), 1.28 (d, 3H, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 141.0, 138.8, 127.2, 122.1, 71.9, 35.6, 27.7, 27.7, 27.3, 27.3, 26.8, 26.6 26.3, 23.4, 20.6 ppm. IR (film): $\tilde{\nu}$ = 2928, 2857, 1710, 459, 1257, 1122, 993 cm^{-1}; MS (EI) *m/z* (%): 250 (16), 152 (10), 149 (12), 136 (10), 135 (20), 133 (11), 124 (15), 123 (18), 122 (12), 121 (25), 119 (11), 110 (23), 109 (31), 108 (17), 107 (30), 99 (17), 97 (40), 96 (48), 95 (62), 94 (34), 93 (30), 91 (19), 83 (25), 82 (57), 81 (100), 80 (50), 77 (22), 69 (31), 68 (38), 67 (75), 66 (34), 65 (15), 57 (11), 55 (68), 54 (25), 53 (23), 43 (26), 41 (57), 39 (18), 29 (14). HRMS (ESI): *m/z*: calcd. for $C_{16}H_{26}O_2Na$ [M^++Na]: 273.1827, found 273.1825. The spectroscopic data are in agreement with those reported in the literature.[15]

Compound 45. AD-mix β (800 mg), $NaHCO_3$ (143 mg, 0.52 mmol), methanesulfonamide (55 mg, 0.58 mmol) and $K_2OsO_4{\cdot}2H_2O$ (15 mg, 0.04 mmol) were successively added to a solution of compound **10** (150 mg, 0.58 mmol) in *t*BuOH/H_2O (10 mL, 1:1) at 0 °C. The suspension was stirred for 18 h before the reaction was quenched with aq. sat. Na_2SO_3 and EtOAc. The aqueous phase was extracted with EtOAc (3x), the combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 3:2 → 1:1) to afford the title compound as a white solid (133 mg, 81%); dr > 95:5 (HPLC, 150 mm YMC-Pack ODS-A, 5 µm, 12 nm, 4.5 mm, MeOH:H_2O = 65:35, 0.8 mL/min, 308 K, 13.8 MPa, 220 nm, $t_{R\ (major)}$ = 21.1 min, $t_{R\ (minor)}$ = 22.3 min). $[\alpha]_D^{20}$ = –40.5 (c = 0.5 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (dd, 1H, *J* = 15.9, 5.4 Hz), 6.09 (dd, 1H, *J* = 15.9, 1.7 Hz), 5.04-4.99 (m, 1H), 4.51-4.48 (m, 1H), 3.74-3.71 (m, 1H), 2.22 (br s, 2H), 1.66-1.14 (m, 18H), 1.26 (d, 3H, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 145.4, 123.0, 74.3, 74.2, 71.5, 35.8, 29.9, 28.0, 27.8, 27.4, 26.3, 26.3, 24.0, 23.4, 20.7; IR (film): $\tilde{\nu}$ = 3423, 2928, 2857, 1716, 1458, 1271, 1171, 1128, 1072, 984 cm^{-1}; MS (EI) *m/z* (%): 284 (0.5), 102 (100.00), 84 (35), 55 (15), 43 (11), 41 (15); HRMS (ESI): *m/z*: calcd. for $C_{16}H_{28}O_4Na$ [M^++Na]: 307.1881, found: 307.1880.

Compound 46. *p*-TsOH (99 mg, 0.52 mmol) and TEMPO (82 mg, 0.52 mmol) were added to a solution of diol **45** (75 mg, 0.26 mmol) in dichloromethane at 0°C. The mixture was stirred for 5 h at room temperature before the solvent was evaporated. The residue was purified by flash chromatography (hexanes:EtOAc, 7:1 to 5:1) to give a beige solid that was recrystallized from hexane to afford the title compound as a white

[15] T. Fuijisawa, N. Okada, M. Takeuchi, T. Sato. *Chem. Lett.* **1983**, *12*, 1271-1272.

crystalline material (46 mg, 62%). Mp = 83-84°C, [mp = 84-85 °C, cf. ref.[16]]; $[\alpha]_D^{20}$ = +22.1 (c = 0.7 $CHCl_3$), [$[\alpha]_D^{20}$ = + 22.4 (c = 1.0, $CHCl_3$), cf. ref.[16]]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, 1H, *J* = 15.9 Hz), 6.79 (d, 1H, *J* =15.9 Hz), 5.20-5.13 (m, 1H), 4.53 (t, 1H, *J* = 4.4 Hz), 3.45 (br s, 1H), 1.86-1.81 (m, 1H), 1.76-1.68 (m, 1H), 1.55-1.46 (m, 3H), 1.37-1.07 (m, 11H), 1.30 (d, 3H, *J* = 6.3 Hz), 1.01-093 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.6, 165.2, 135.1, 132.7, 76.6, 72.9, 34.4, 31.3, 28.3, 27.5, 27.3, 27.0, 23.6, 20.9, 19.9; IR (film): $\tilde{\nu}$ = 3491, 2926, 2856, 1714, 1697, 1458, 1354, 1282. 1187, 1128, 1057, 978 cm^{-1}; MS (EI) *m/z* (%): 282 (0.8), 100 (100), 82 (15), 55 (20), 43 (13), 41 (18). HRMS (ESI): *m/z*: calcd. for $C_{16}H_{26}O_4Na$ [M^++Na]: 305.1724, found 305.1724. The analytical and spectroscopic data are in agreement with those reported in the literature.[16]

(–)-A26771B (36). Succinic anhydride (365 mg, 0.035 mmol) and DMAP (24 mg, 0.02 mmol) were added to a solution of compound **12** (50 mg, 0.018 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The mixture was stirred for 18 h at room temperature before the solvent was evaporated and the residue was purified by flash chromatography ($CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH (95:5)) to afford the title compound as a white solid (55 mg, 71%). Mp = 122-123; [mp = 121-122 °C, ref.[16]; Mp = 125-126 °C, ref.[17]; Mp = 124-125 °C, ref.[18]]; $[\alpha]_D^{20}$ = –14.3 (c = 2.0 MeOH), $[\alpha]_D^{20}$ = –13.9 (c = 0.28, MeOH); ($[\alpha]_D^{20}$ = –13.2 (c = 0.19, MeOH), ref.[3]); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, 1H, *J* = 15.7 Hz), 6.76 (d, 1H, *J* = 15.7 Hz), 5.33 (t, 1H, *J* = 5.7 Hz), 5.18-5.11 (m, 1H), 2.79-2.73 (m, 4H), 1.97-1.83 (m, 2H), 1.74-1.66 (m, 1H), 1.60-1.50 (m, 1H), 1.48-1.10 (m, 14H), 1.29 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 177.3, 171.6, 165.0, 135.4, 132.7, 78.1, 72.8, 34.7, 29.0, 28.9, 28.8, 28.2, 27.4, 27.3, 27.1, 23.7, 22.4, 20.0; IR (film): $\tilde{\nu}$ = 2928, 2857, 1740, 1700, 1379, 1357, 1300, 1197, 1163 cm^{-1}; MS (EI) *m/z* (%): 282 (16), 181 (18), 112 (13), 111 (12), 100 (100), 99 (42), 98 (25), 95 (16), 83 (19), 82 (24), 81 (15), 69 (16), 67 (14), 56 (31), 55 (71), 43 (30), 42 (12), 41 (42), 28 (31). HRMS (ESI): *m/z*: calcd. for $C_{20}H_{30}O_7Na$ [M^++Na]: 405.1882, found 405.1884. The analytical and spectroscopic data are in agreement with those reported in the literature.[15,16,17,18]

Compound 42. DBU (113 µL, 0.76 mmol) was added to a solution of alkyne **41** (0.38 mmol) in toluene (4 mL) at 0 °C. The mixture was stirred overnight at ambient temperature before the solvent was evaporated. The residue was purified by flash chromatography (hexane/EtOAc, 40:1 → 30:1) and then by HPLC (50 mm Zorbax Eclipse C18, 1.8 µm, 3 mm, MeOH:H_2O, 90:1, 0.65 mL/min, 308 K, 25.2 MPa, λ = 220 nm) in order to separate *E*-**42** from small amounts of Z-**42.**

Major Isomer *E*-42: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74 (dt, 1H, *J* = 15.9, 2.3 Hz), 6.14 (d, 1H, *J* = 15.8 Hz), 5.03-4.95 (m, 1H), 2.39 (td, 2H, *J* = 6.5, 2.2 Hz), 1.61-1.50 (m, 4H), 1.42-1.37 (m, 2H), 1.33-1.26 (m, 10H), 1.23 (d, 3H, *J* = 6.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 130.1, 126.0, 100.8, 78.4, 71.5, 36.2, 29.6, 29.5, 29.3, 28.6, 28.3, 25.2, 20.4, 19.9; IR (film): $\tilde{\nu}$ = 2976, 2929, 2855, 1714, 1714,

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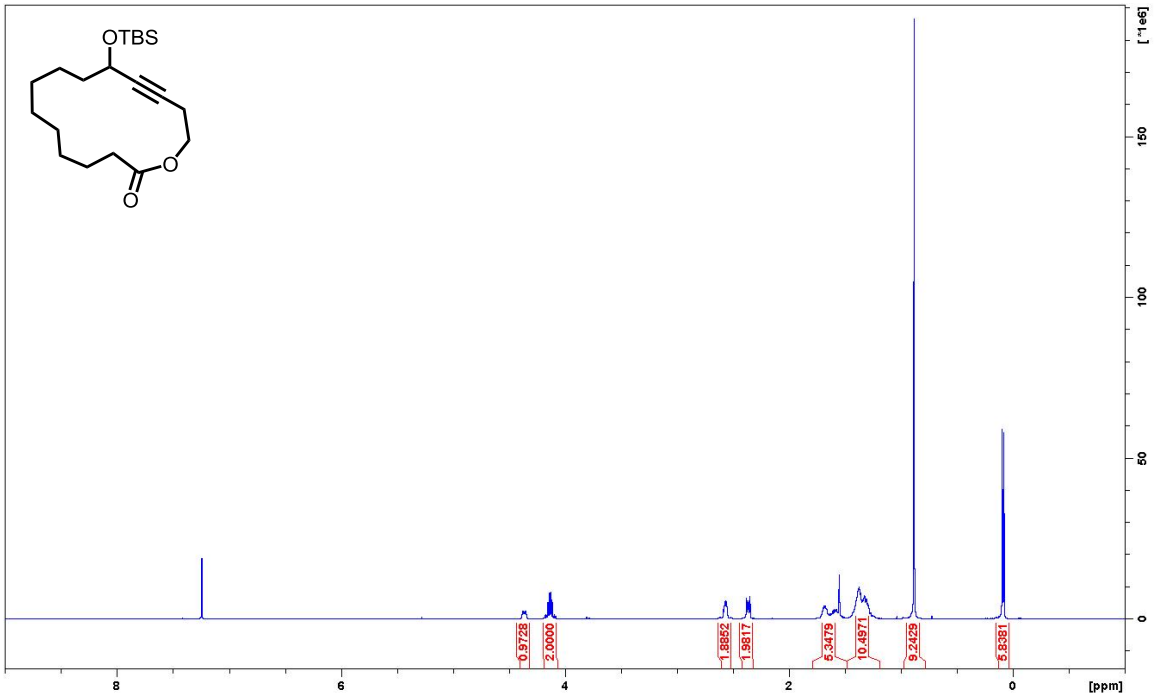
16 J. Gebauer, S. Blechert, *J. Org. Chem.* **2006**, *71*, 2021-2025.
17 K. Tatsuta, Y. Amemiya, Y. Kanemura, M. Kinoshita, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3248-3253.
18 K. H. Michel, P. V. Demarco, R. Nagarajan, *J. Antibiot.* **1977**, *30*, 571-575.

1615, 1462, 1297, 1280, 1254, 1178, 1157, 961, 859 cm^{-1}; MS (EI) *m/z* (%): 248 (23), 151 (53), 147 (35), 133 (54), 121 (29), 120 (23), 119 (65), 117 (16), 110 (23), 108 (24), 107 (43), 106 (26), 95 (22), 94 (100), 93 (50), 92 (56), 91 (93), 81 (35), 80 (87), 79 (77), 78 (30), 77 (43), 67 (45), 66 (34), 65 (44), 64 (36), 63 (33), 55 (26), 51 (22), 43 (21), 41 (67), 39 (35), 29 (24); HRMS (ESI): *m/z*: calcd. for $C_{16}H_{24}NaO_2$ [M^++Na]: 271.1668, found: 271.1668.

Minor Isomer *Z*-42: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.05 (br s, 2H), 5.28-5.21 (m, 1H), 2.53 (ddd, 1H, *J* = 17.4, 6.5, 4.5 Hz), 2.33 (ddd, 1H, *J* = 17.5, 8.9, 4.1 Hz), 1.58-1.16 (m, 16H), 1.24 (d, 3H, *J* = 6.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 128.3, 122.5, 102.4, 68.5, 35.6, 27.2, 26.8, 26.7, 26.1, 25.9, 24.4, 20.3, 19.4; IR (film): $\tilde{\nu}$ = 2980, 2928, 2857, 1271, 1601, 1459, 1407, 1223, 1185, 1129 cm^{-1}; HRMS (ESI): *m/z*: calcd. for $C_{16}H_{24}NaO_2$ [M^++Na]: 271.1668, found 271.1670.

Compound 38. (*E*)-Hex-2-en-4-ynoic acid (200 mg, 0.75 mmol), DMAP (232 mg, 1.9 mmol) and EDCI (364 mg, 1.9 mmol) were successively added to a solution of alcohol **37** (219 mg, 1.9 mmol) in dichloromethane (10 mL) at 0°C. The mixture was stirred 1 h at ambient temperature before the reaction was quenched with aq. sat. NH_4Cl. The layers were separated and the aqueous phase extracted with *tert*-butyl methyl ether (3x). The combined organic layers were dried over Na_2SO_4 and the solvent evaporated. Flash chromatography of the residue (hexane:EtOAc, 9:1) gave the title compound as a colorless oil (239 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.69 (dq, 1H, *J* = 16.0, 2.3 Hz), 6.12 (d, 1H, *J* = 16.0 Hz), 4.96 (sext, 1H, *J* = 6.3 Hz), 2.13-2.08 (m, 2H), 2.20 (d, 3H, *J* = 2.2 Hz), 1.78 (t, 3H, *J* = 2.4 Hz), 1.64-1.42 (m, 4H), 1.36-1.20 (m, 12H), 1.23 (d, 3H, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, CDCl3): δ = 166.0, 130.2, 125.9, 96.2, 79.6, 77.4, 75.5, 71.6, 36.1, 29.7, 29.6, 29.3, 29.1, 25.6, 20.2, 18.9, 4.9, 3.7; IR (film): $\tilde{\nu}$ = 2980, 2928, 2855, 1712, 1621, 1461, 1301, 1267, 1181, 1165, 1129, 961 cm^{-1}; MS (EI) *m/z* (%): 302 (1), 177 (12), 163 (13), 119 (12), 111 (62), 95 (14), 93 (100=, 81 (14), 68 (12), 67 (15), 65 (15), 55 (20), 41 (14), 39 (11). HRMS (ESI): *m/z*: calcd. for $C_{20}H_{30}NaO_2$ [M^++Na]: 325.2136, found 325.2138.

Cyclodimer 39. Complex **1** (22 mg, 0.033 mmol) was added to a suspension of compound **38** (100 mg, 0.33 mmol) and powdered MS 5Å (1 g) in toluene (80 mL) and the resulting mixture was stirred at 80 °C for 3 h. The suspension was filtered through a pad of silica which was rinsed with hexane/EtOAc (1:1). The combined filtrates were evaporated and the residue purified by flash chromatography (hexane/EtOAc, 50:1 → 40:1) to yield the title compound as a white solid (68 mg, 83%). $[\alpha]_D^{20}$ = –27.4 (c = 0.9 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.74 (d, 2H, *J* = 15.8 Hz), 6.14 (d, 2H, *J* = 15.9 Hz), 4.99 (m, 2H), 2.39 (m, 4H), 1-63-1.23 (m, 32H), 1.23 (d, 6H, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 130.1, 126.0, 100.8, 78.4, 71.5, 36.2, 29.6, 29.4, 29.3, 28.6, 28.6, 25.2, 20.4, 19.9; IR (film): $\tilde{\nu}$ = 2930, 2861, 1699, 1620, 1305, 1189, 1163, 1130, 971 cm^{-1}; (EI) *m/z* (%): 497 (31), 496 (81), 451 (23), 343 (21), 325 (23), 249 (31), 148 (100), 231 (26), 230 (40), 205 (37), 203 (44), 201 (20), 231 (26), 230 (40), 205 (37), 203 (44), 201 (20), 191 (42), 187 (20), 177 (29), 173 (22), 159 (20), 151 (24), 147 (27), 133 (62), 131 (35), 123 (25), 121 (33), 118 (72), 117 (28), 107 (37), 105 (79), 95 (34), 92 (49), 91 (94), 81 (59), 79 (90), 78 (22), 77 (31), 67 (65), 65 (30), 55 (92), 41 (42); HRMS (ESI): *m/z*: calcd. for $C_{32}H_{48}NaO_4$ [M^++Na]: 519.3444, found 519.3445.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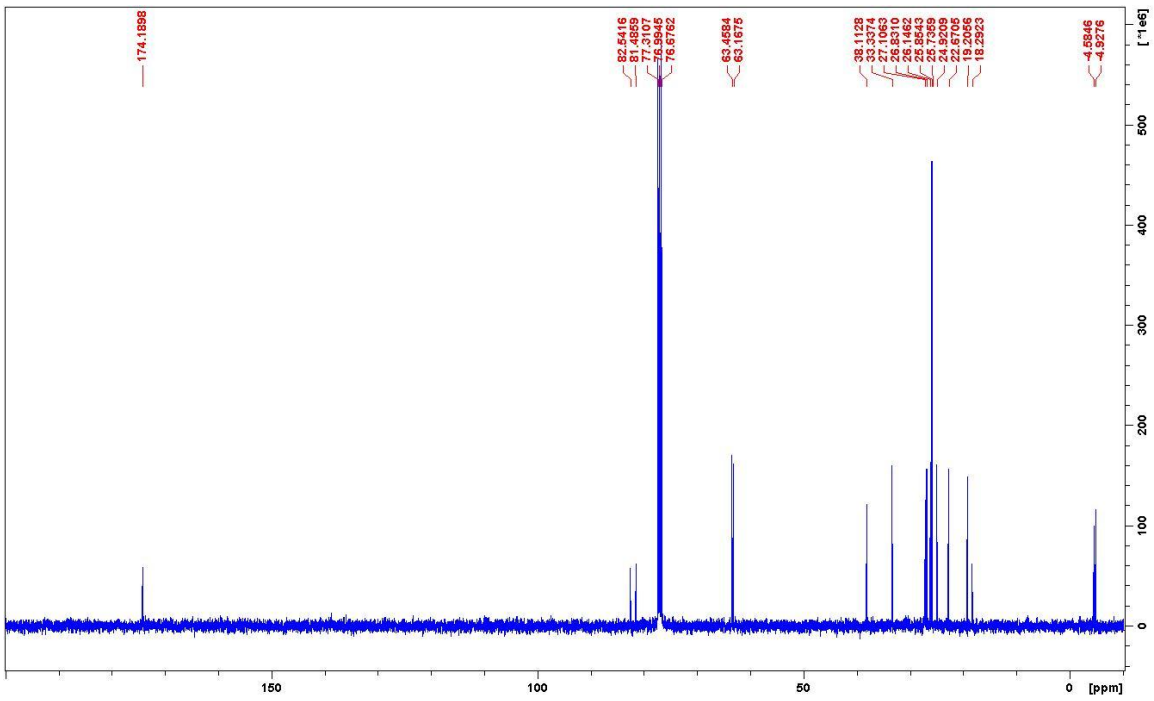
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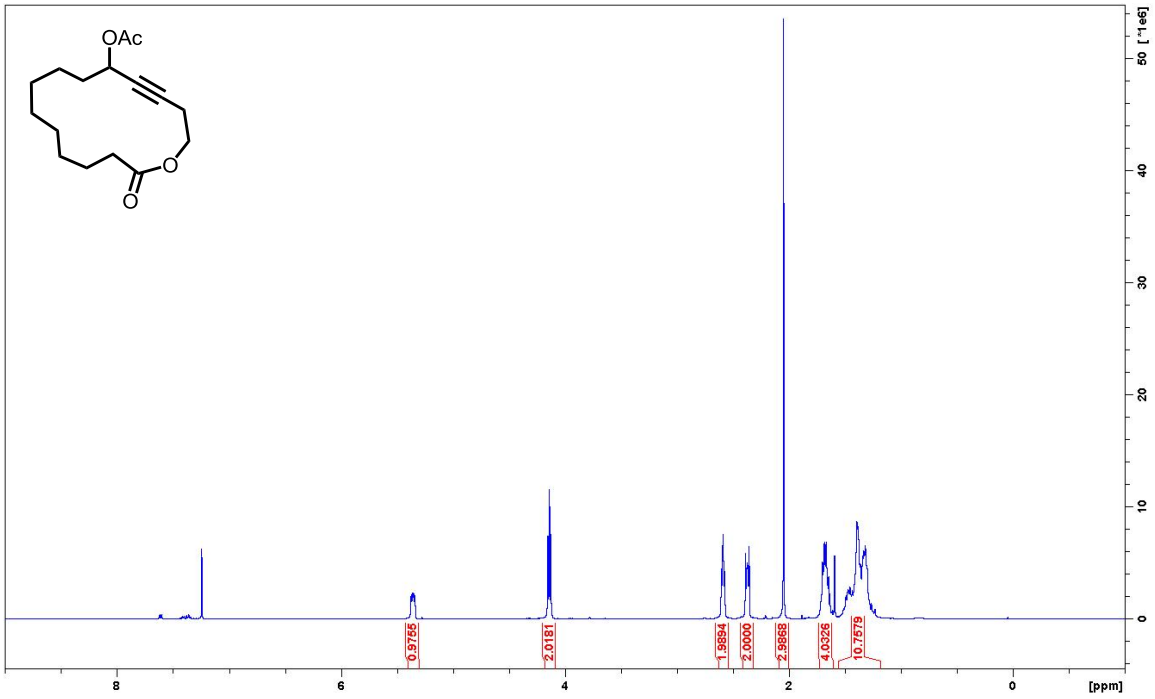
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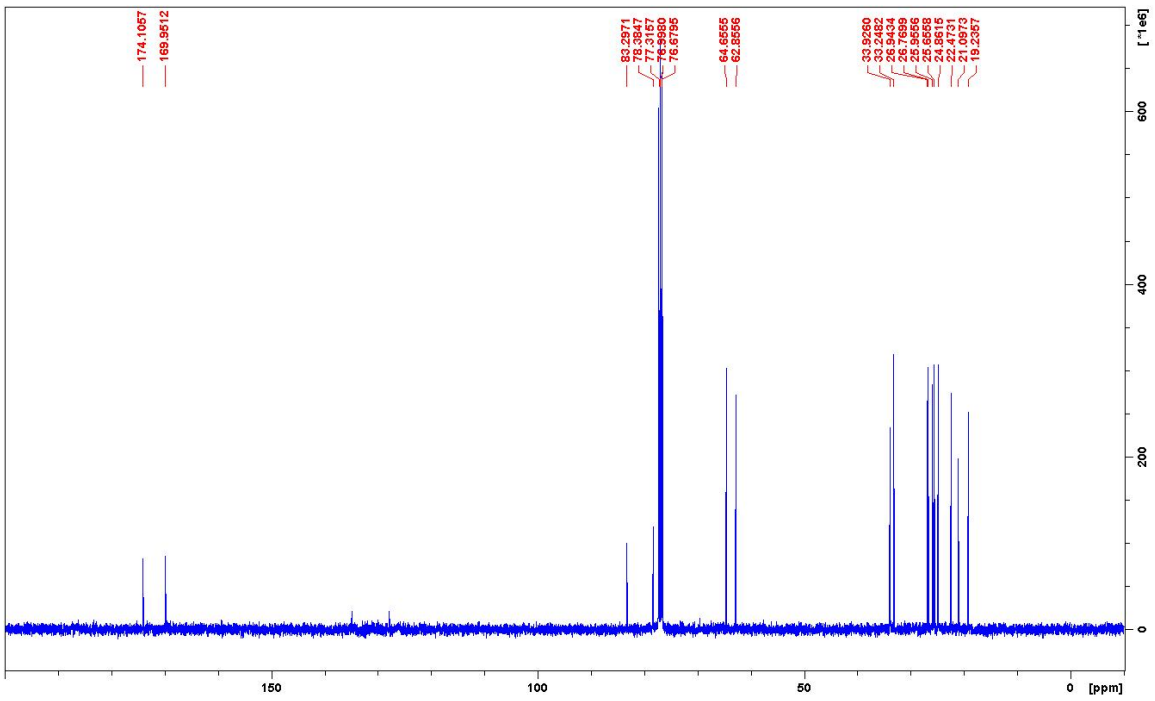
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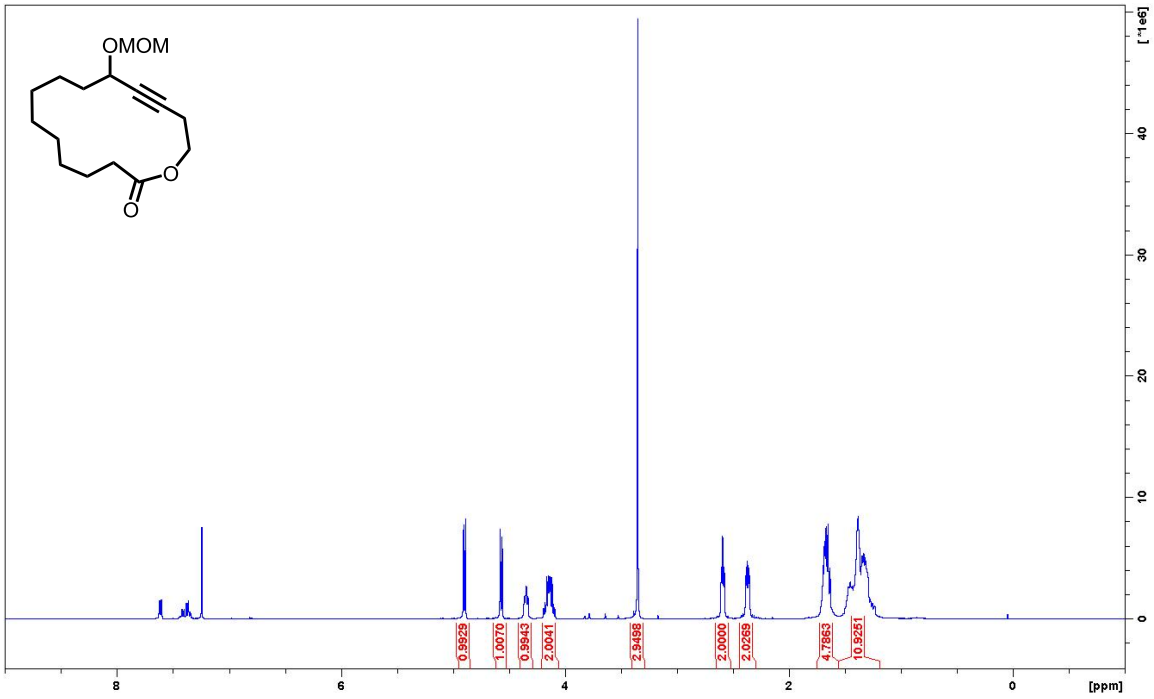
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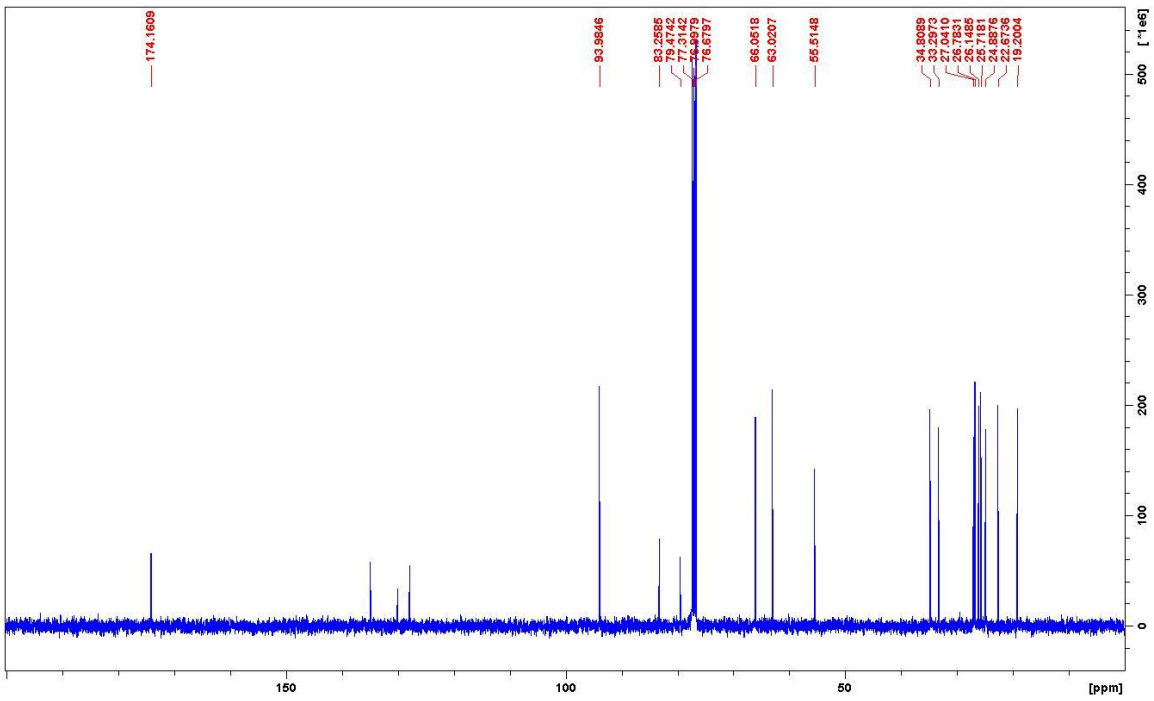
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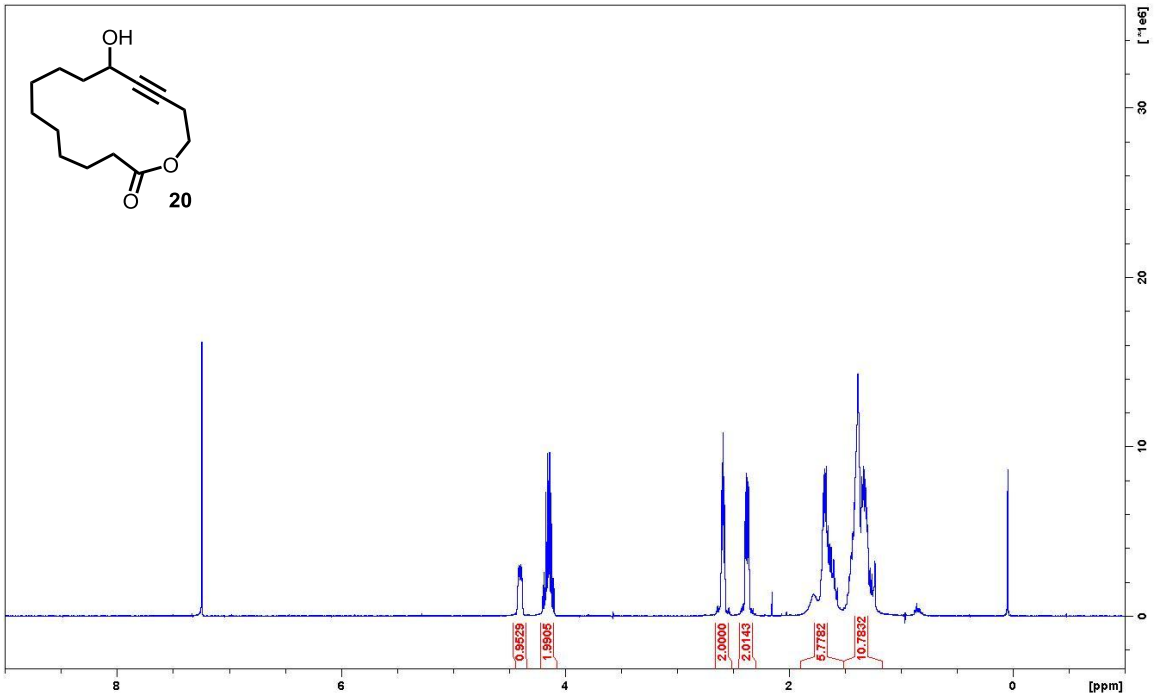
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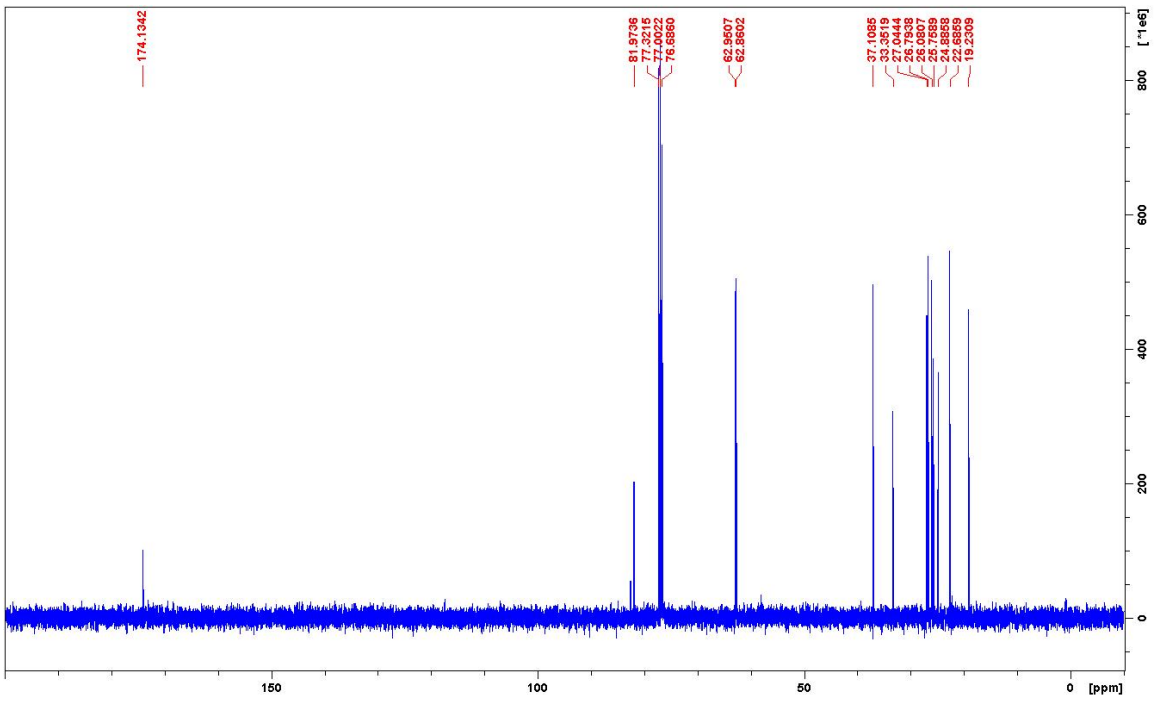
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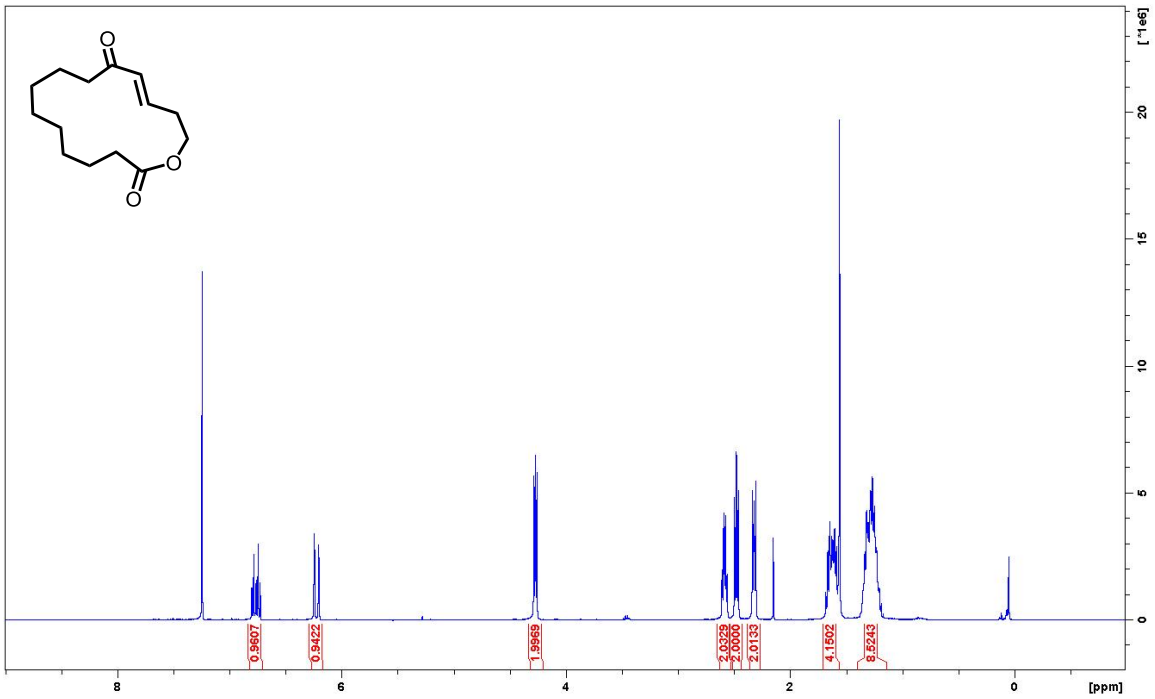
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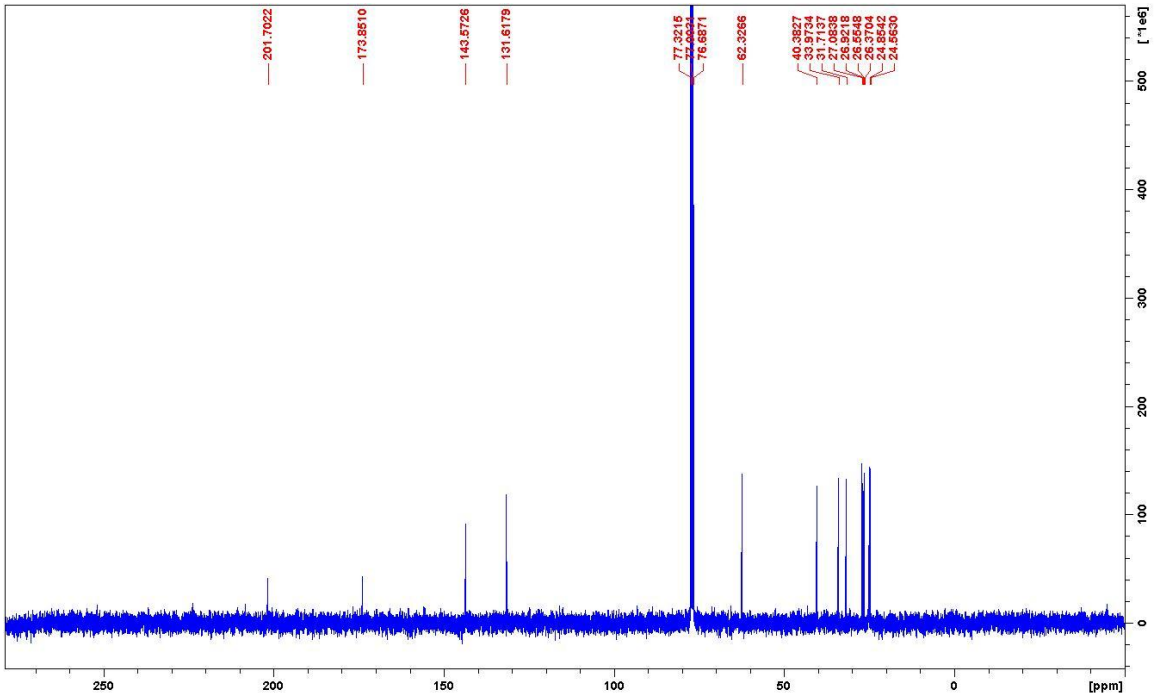
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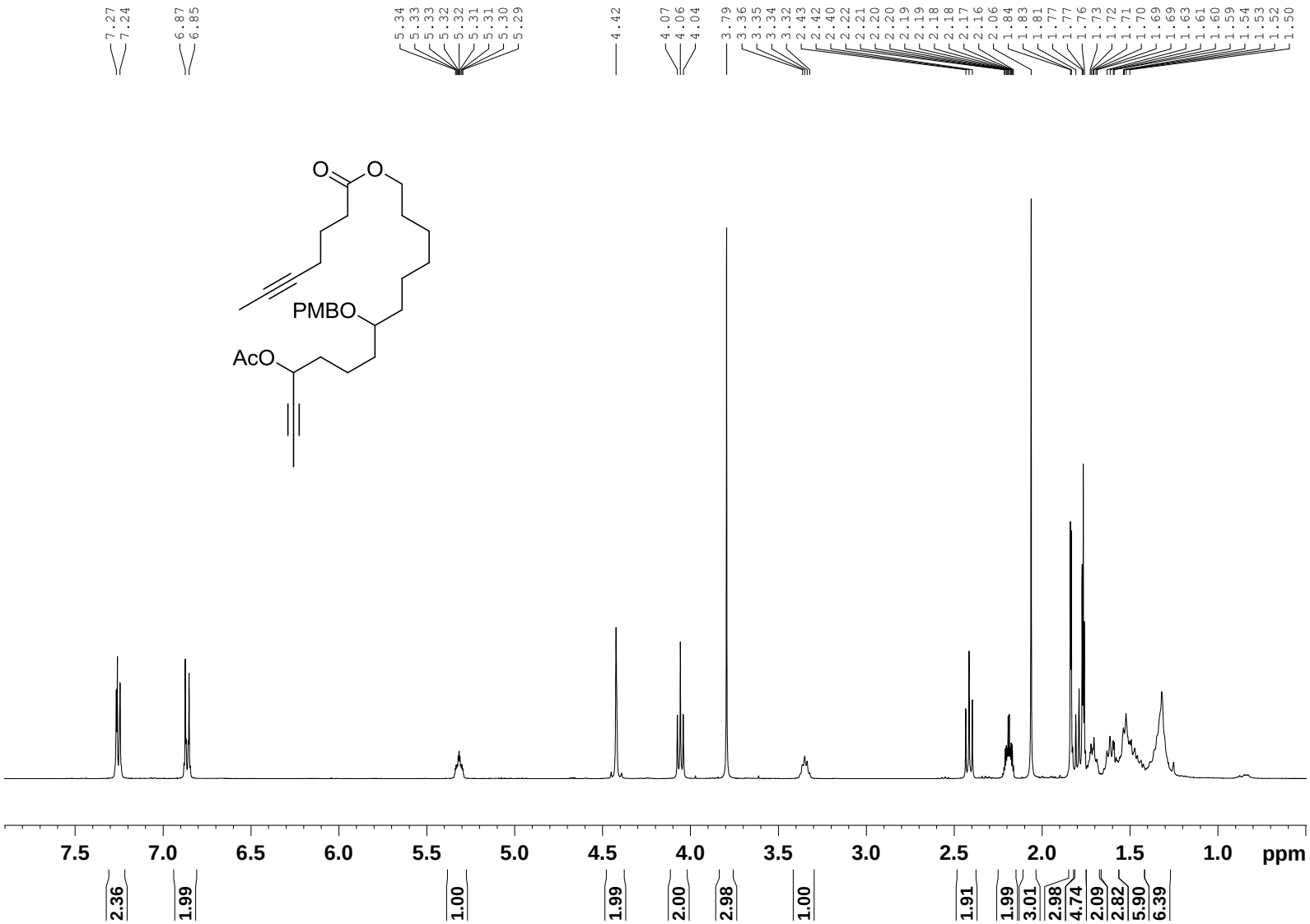

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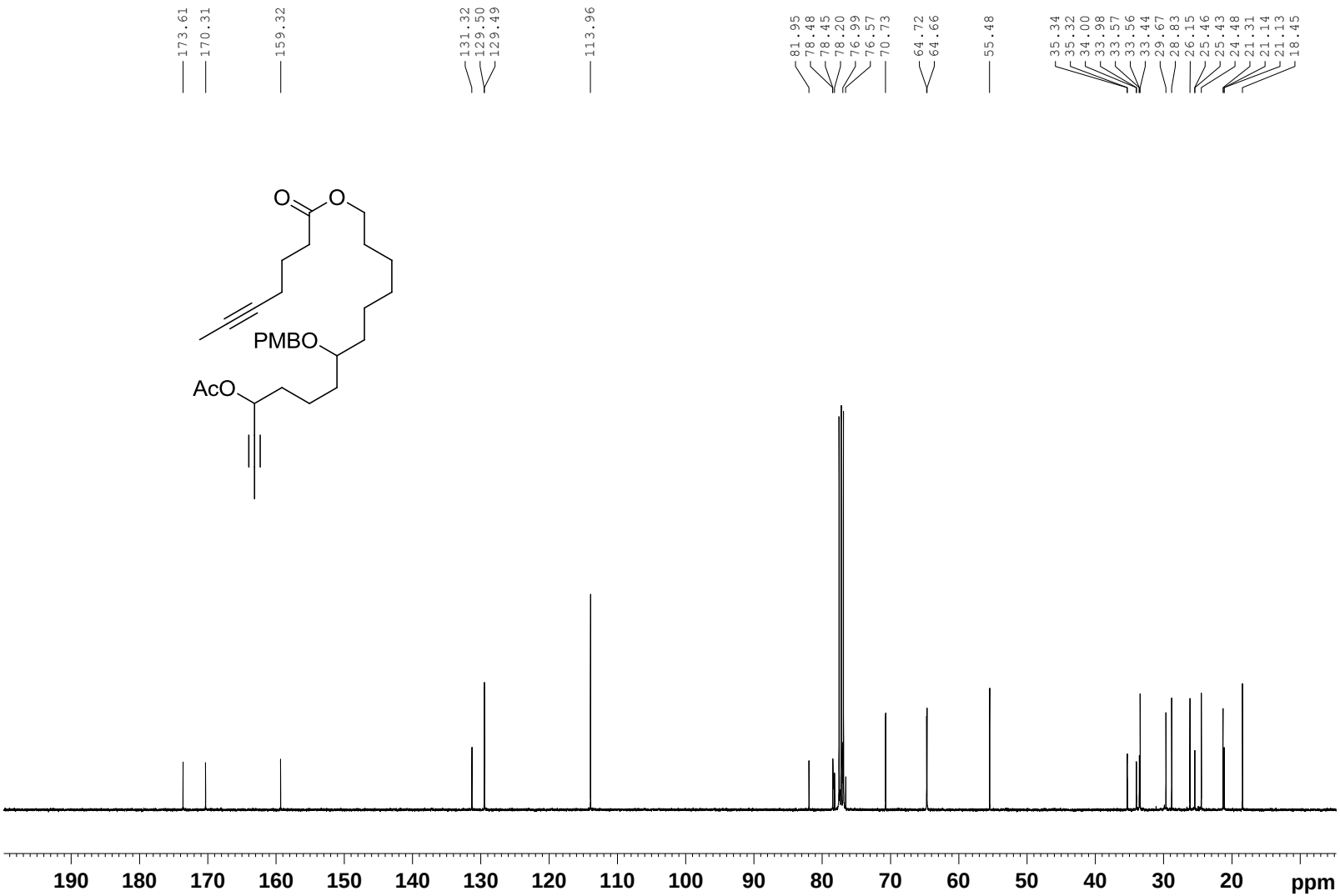

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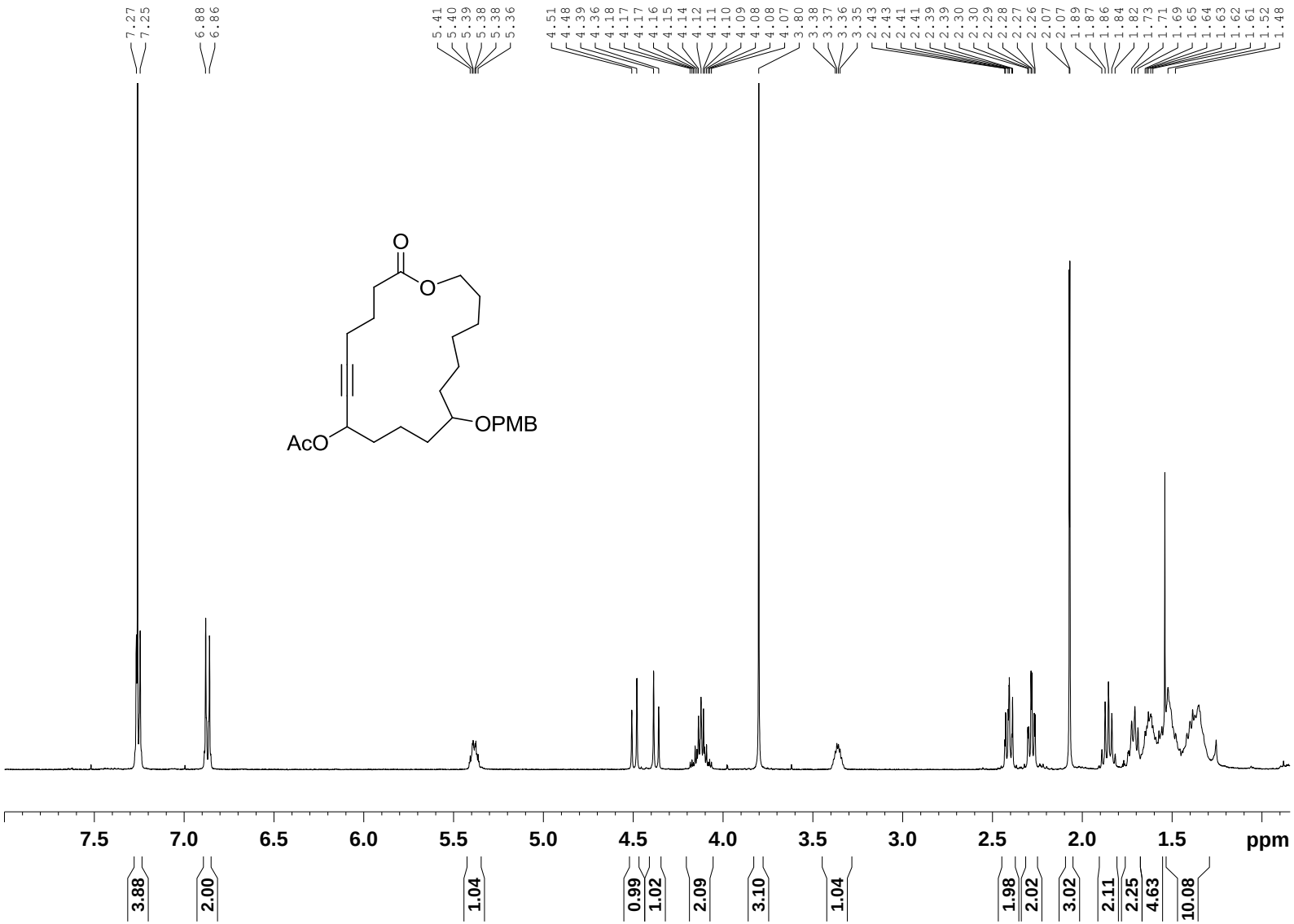

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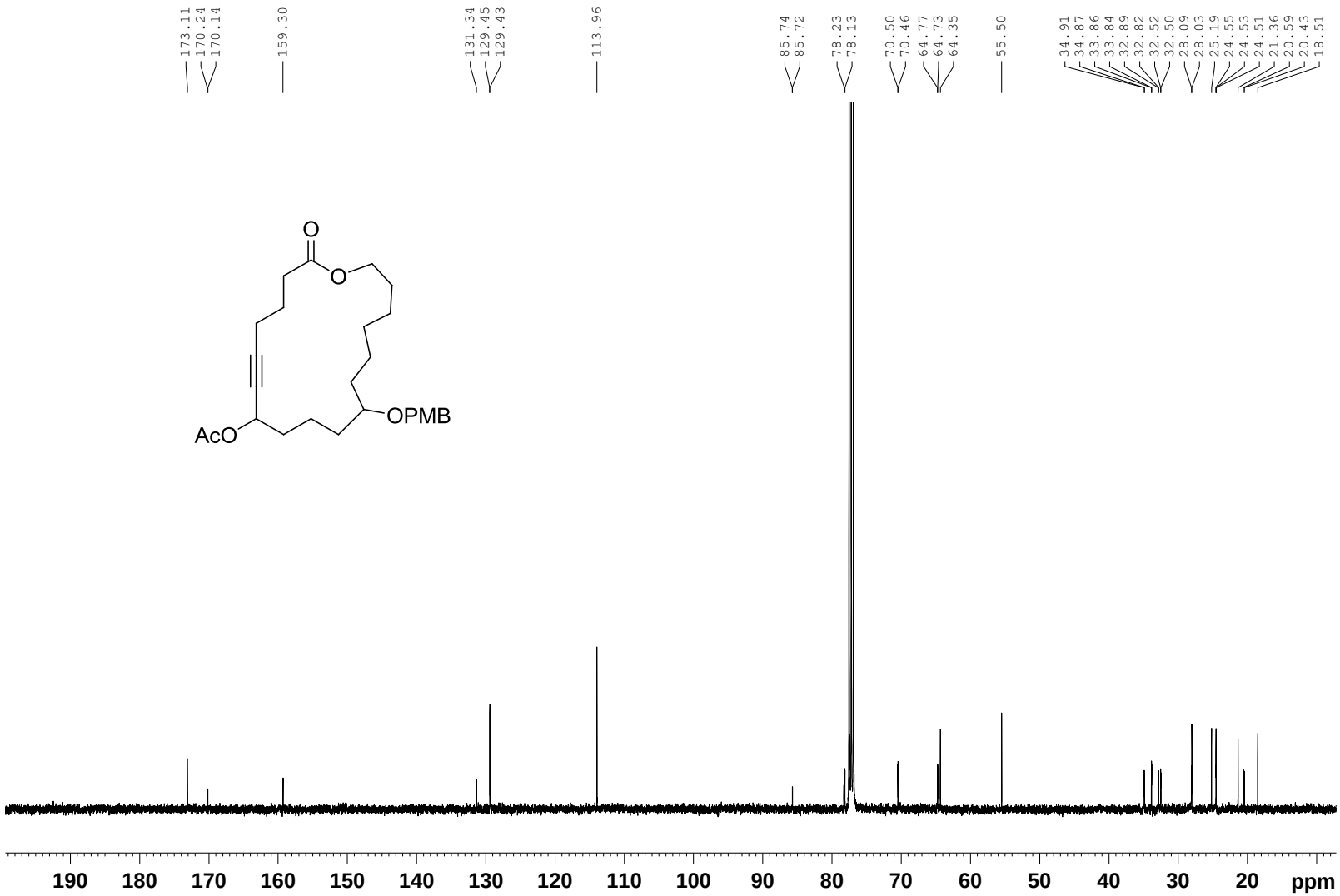
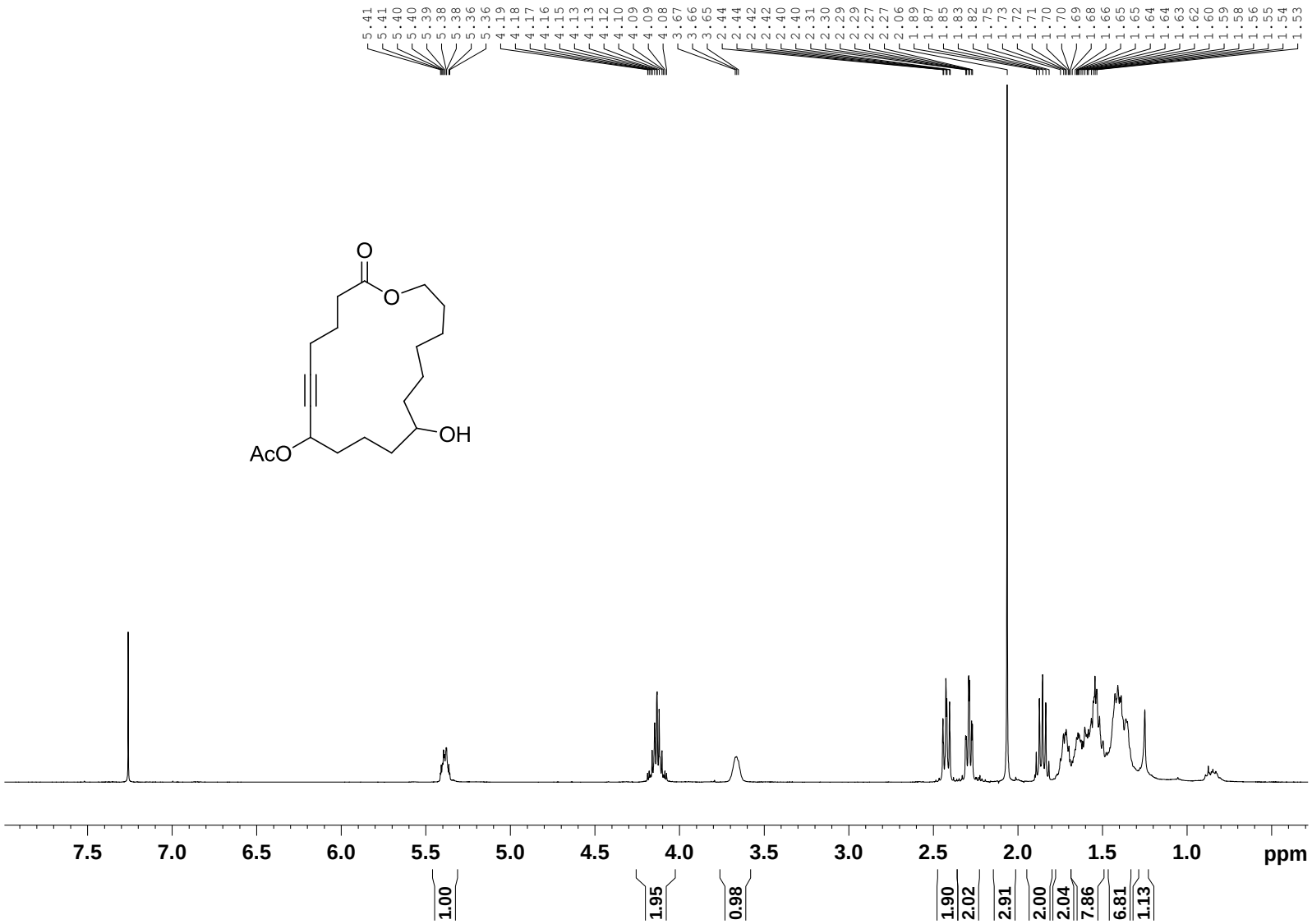
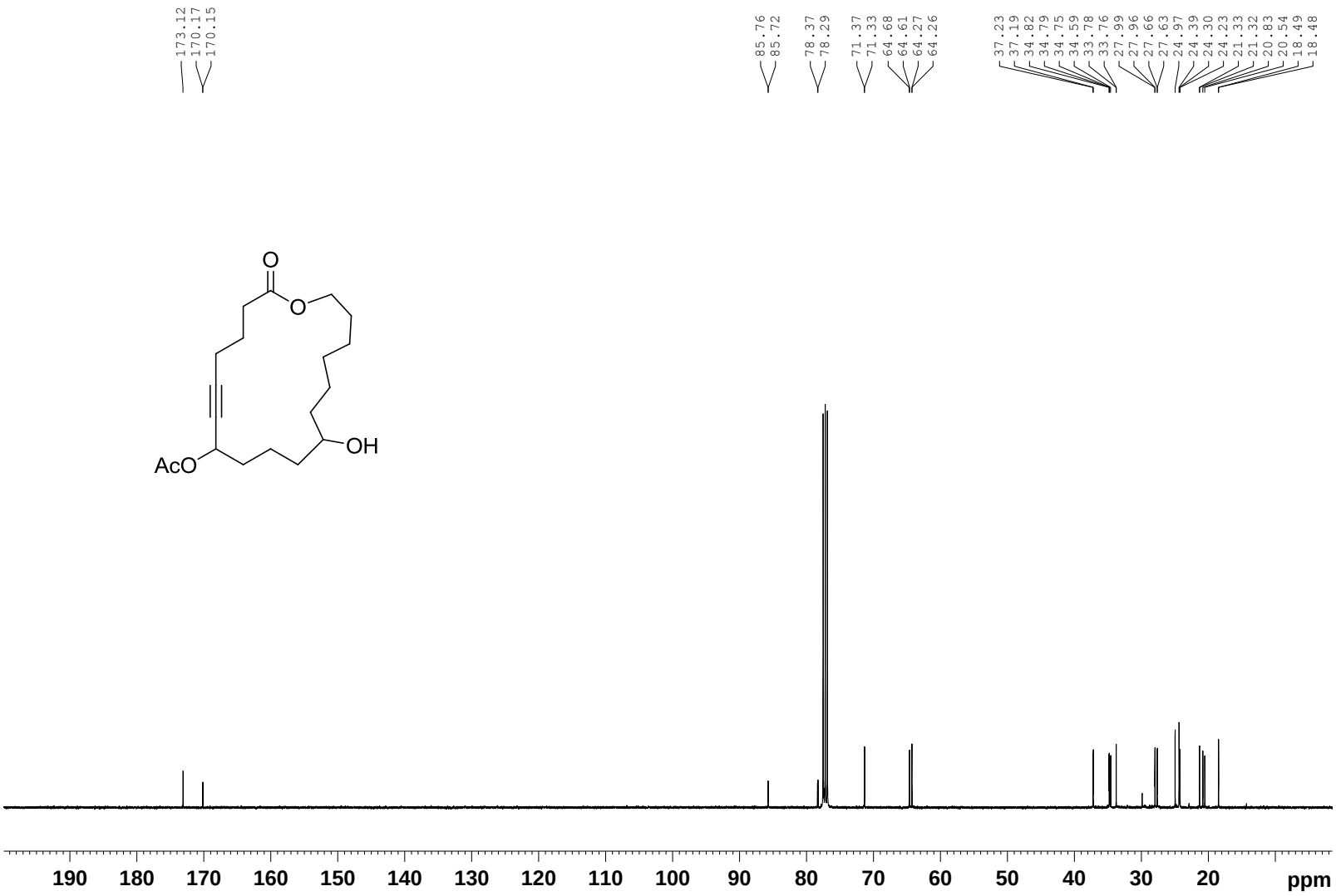


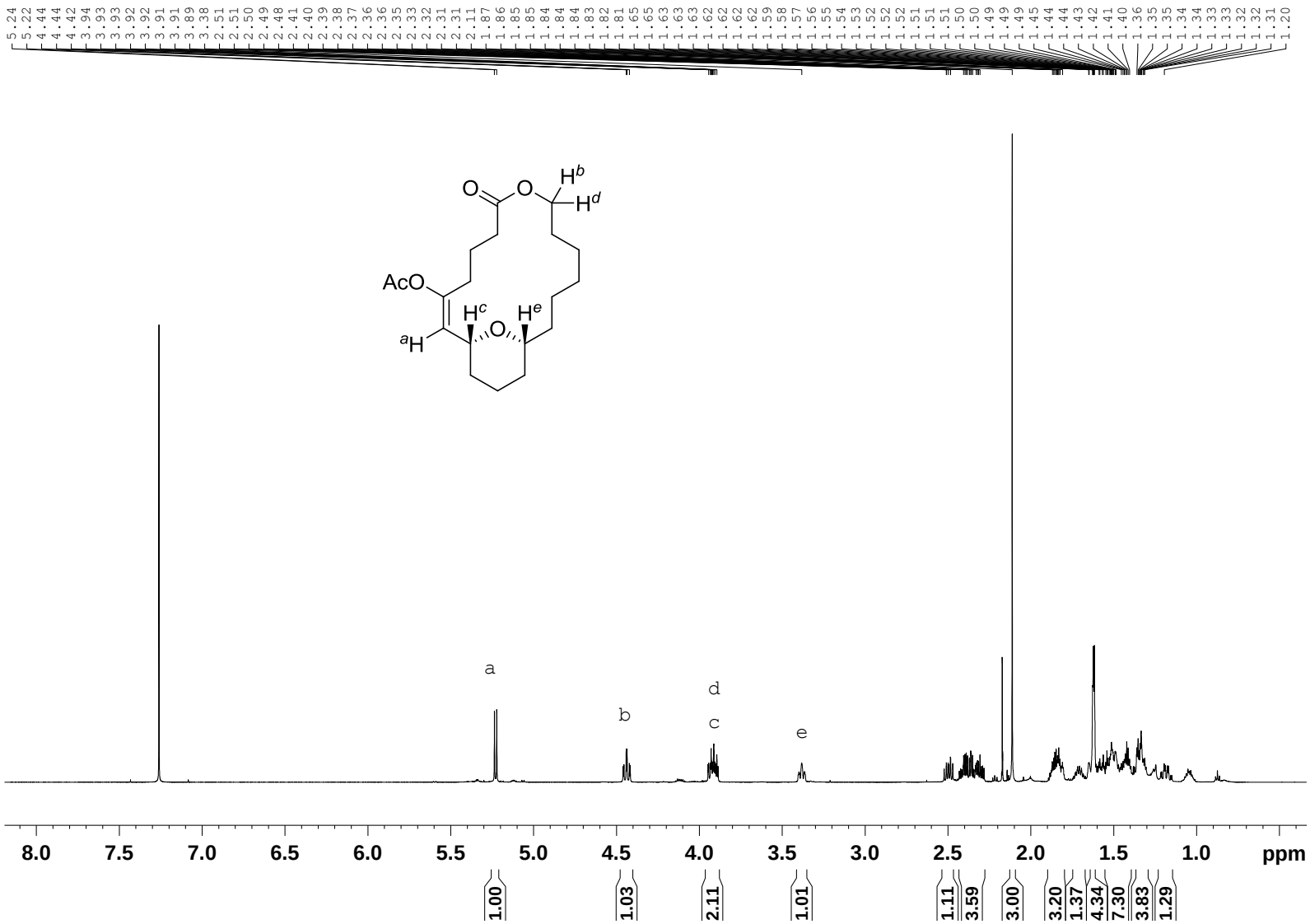
^{1}H NMR (400 MHz, $CDCl_3$)



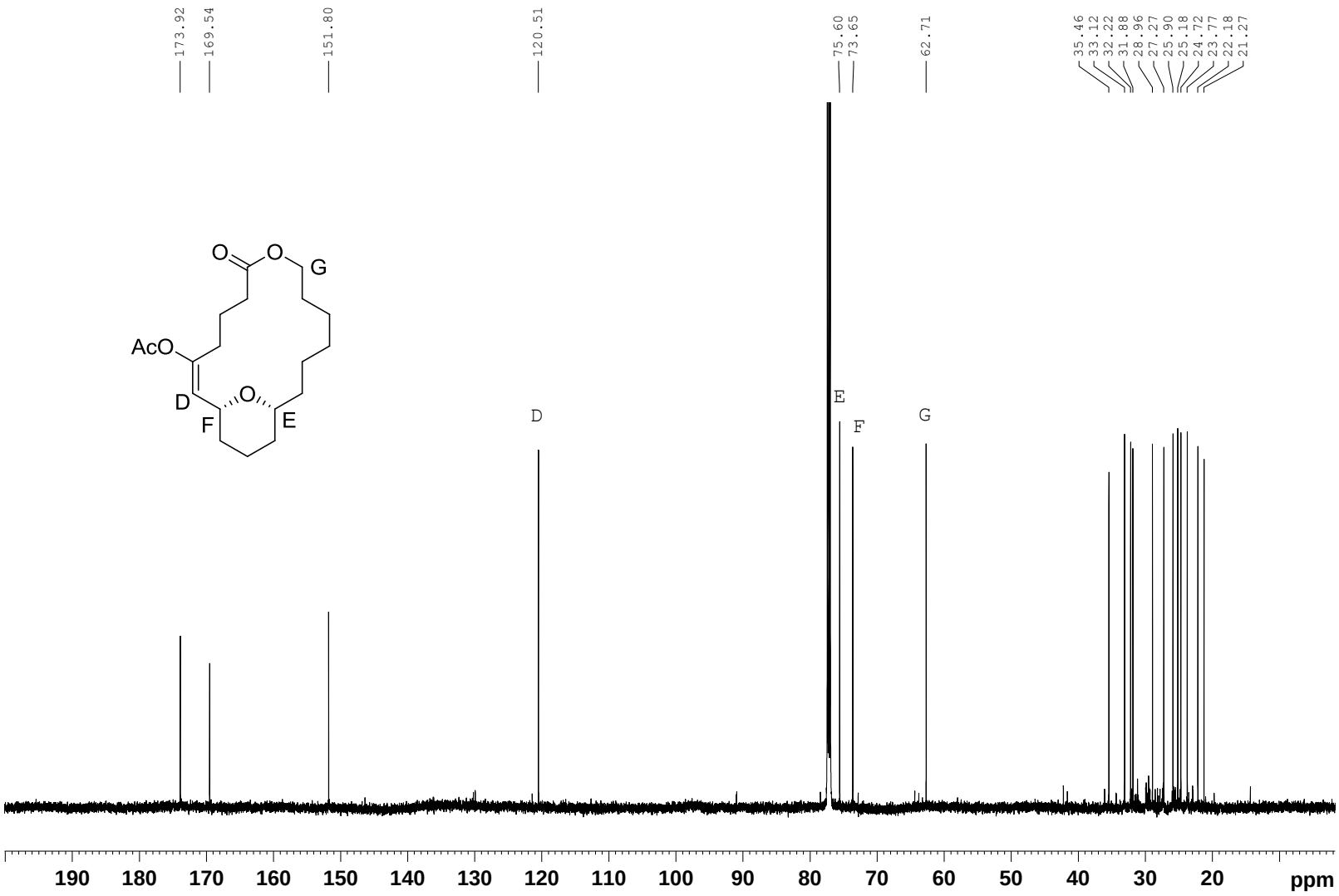
^{13}C NMR (100 MHz, $CDCl_3$)



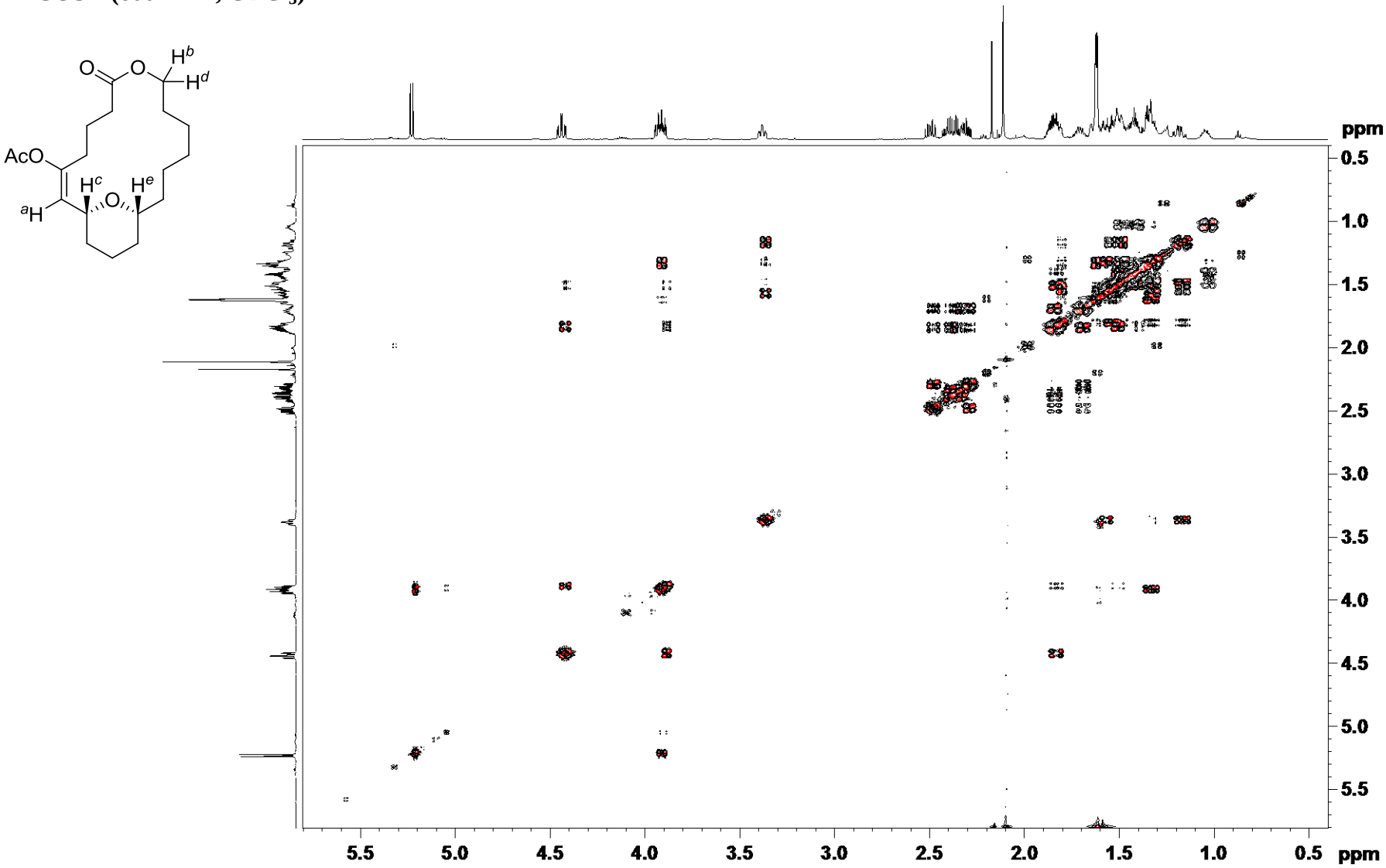
^{1}H NMR (600 MHz, $CDCl_3$)



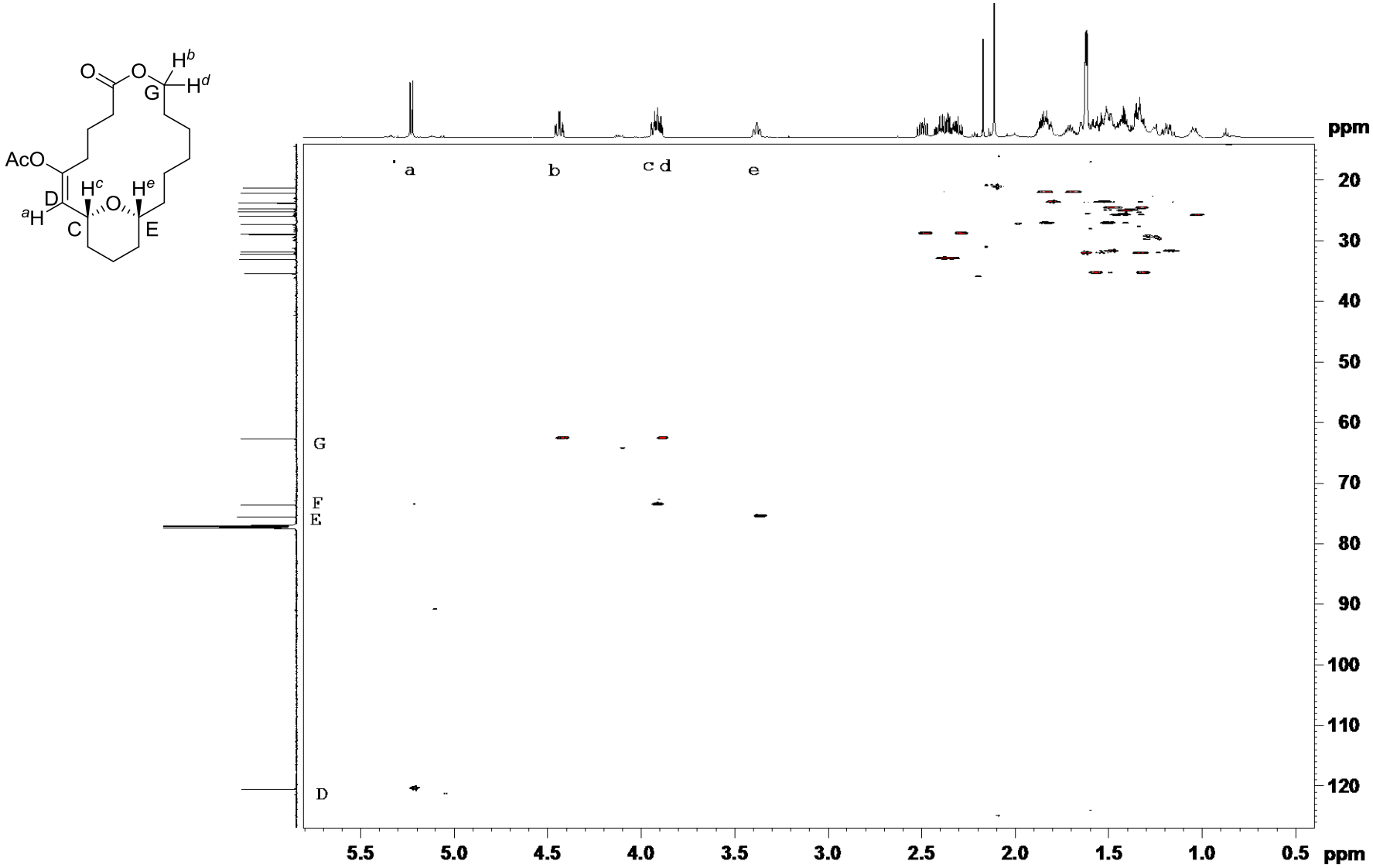
^{13}C NMR (150 MHz, $CDCl_3$)



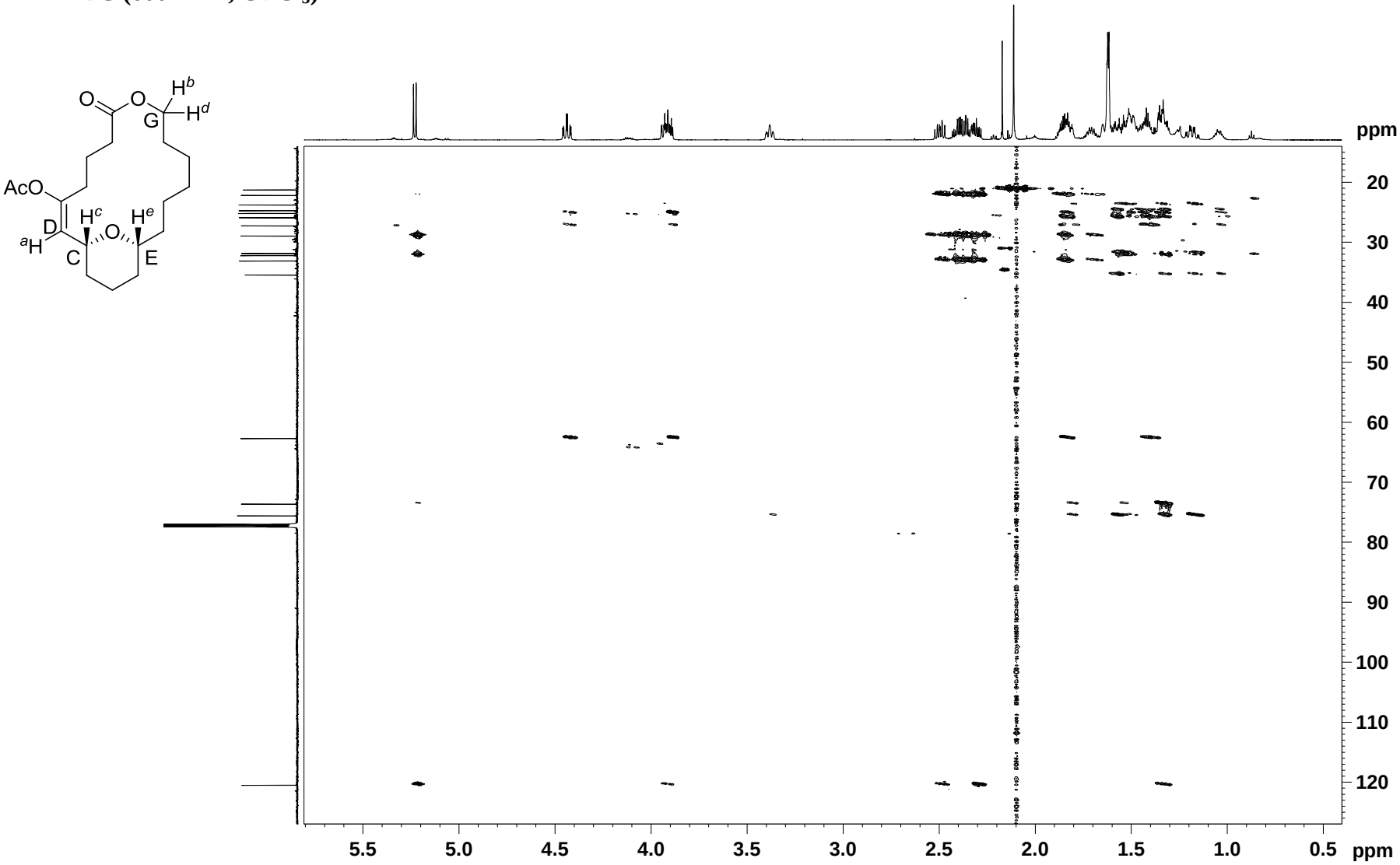
COSY (600 MHz, $CDCl_3$)



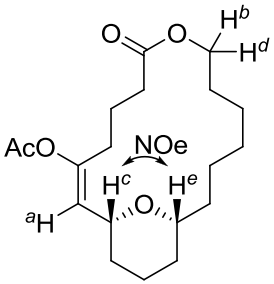
HSQC (600 MHz, $CDCl_3$)

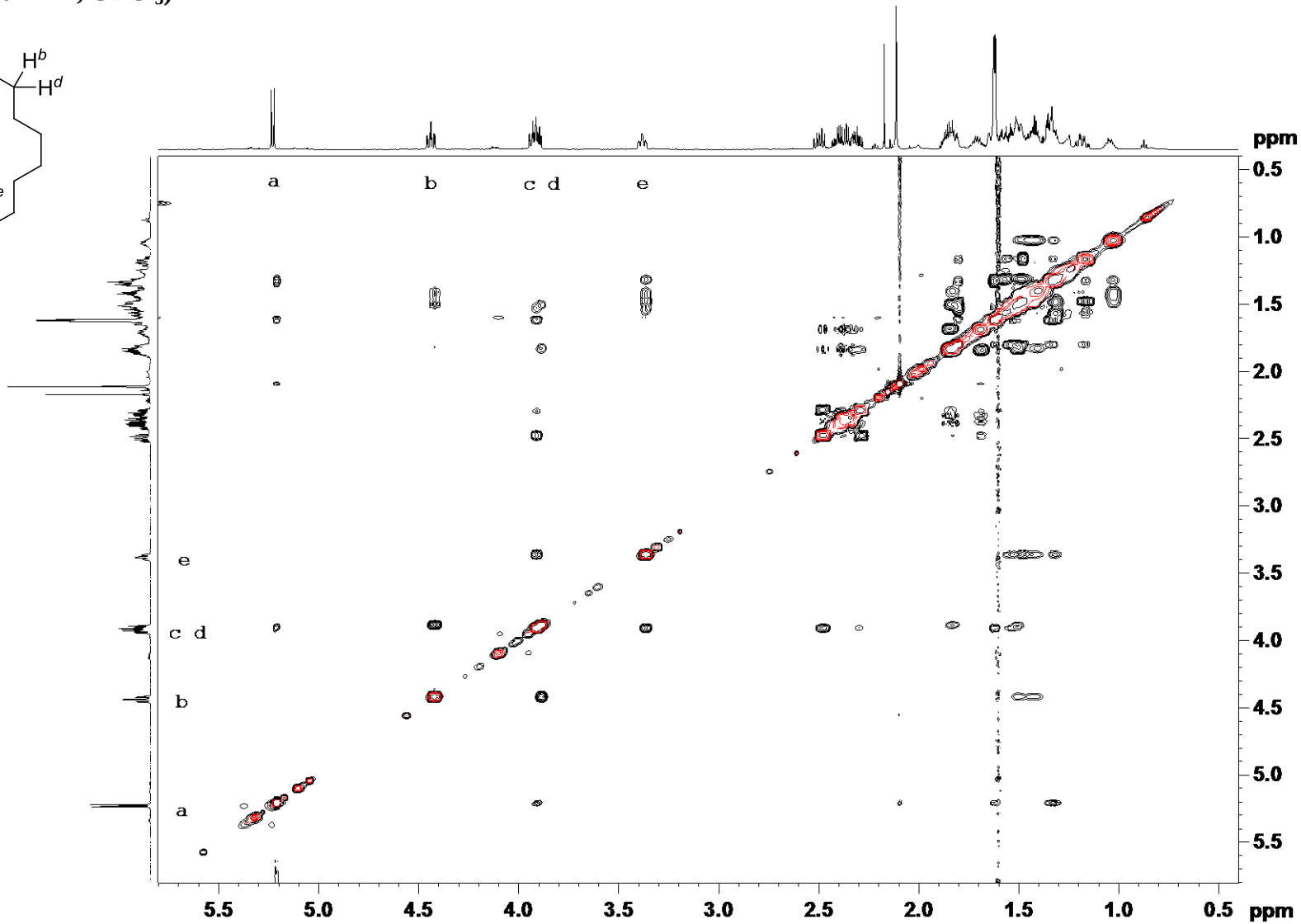


HMBC (600 MHz, $CDCl_3$)

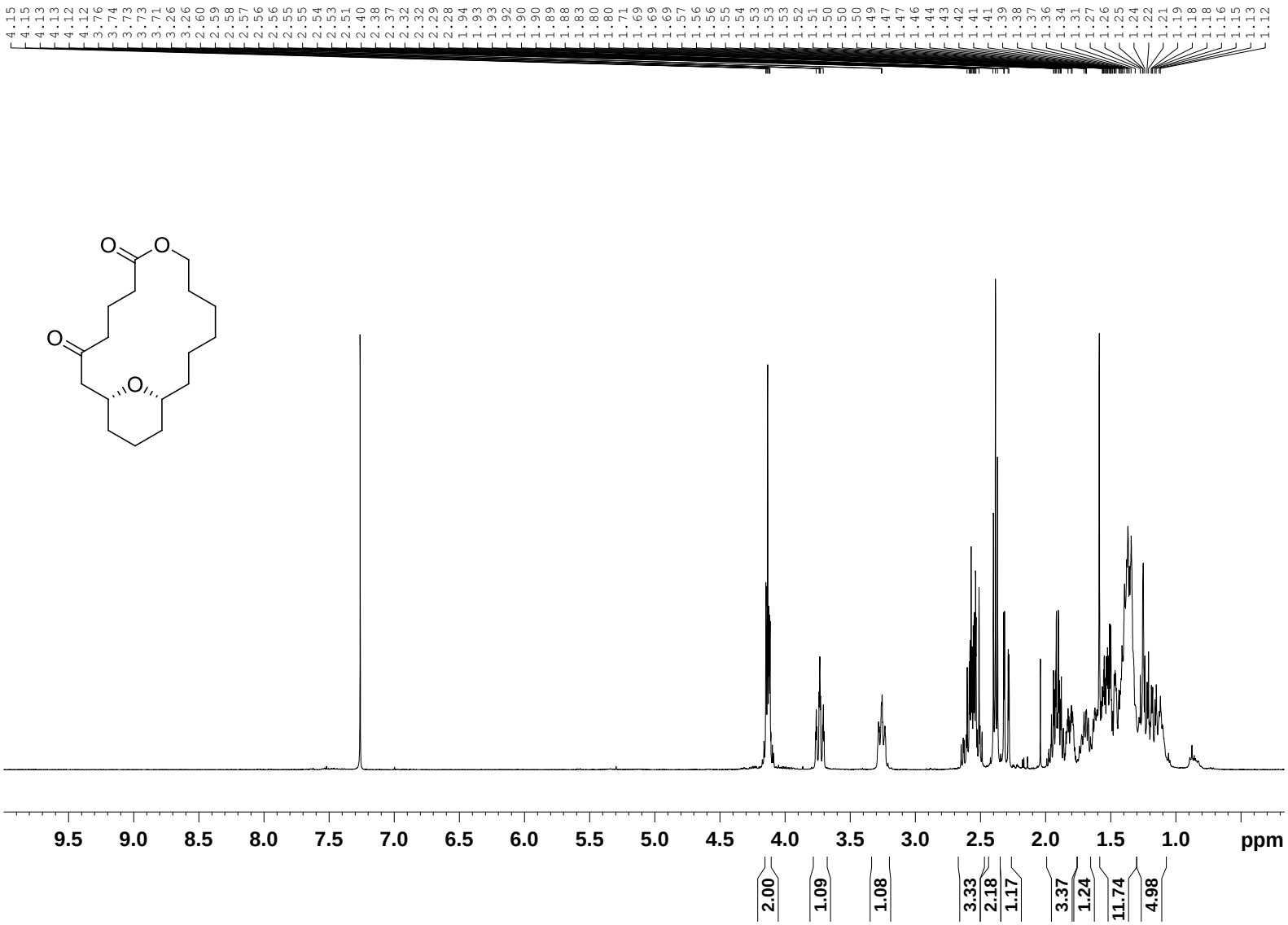


NOESY (600 MHz, $CDCl_3$)

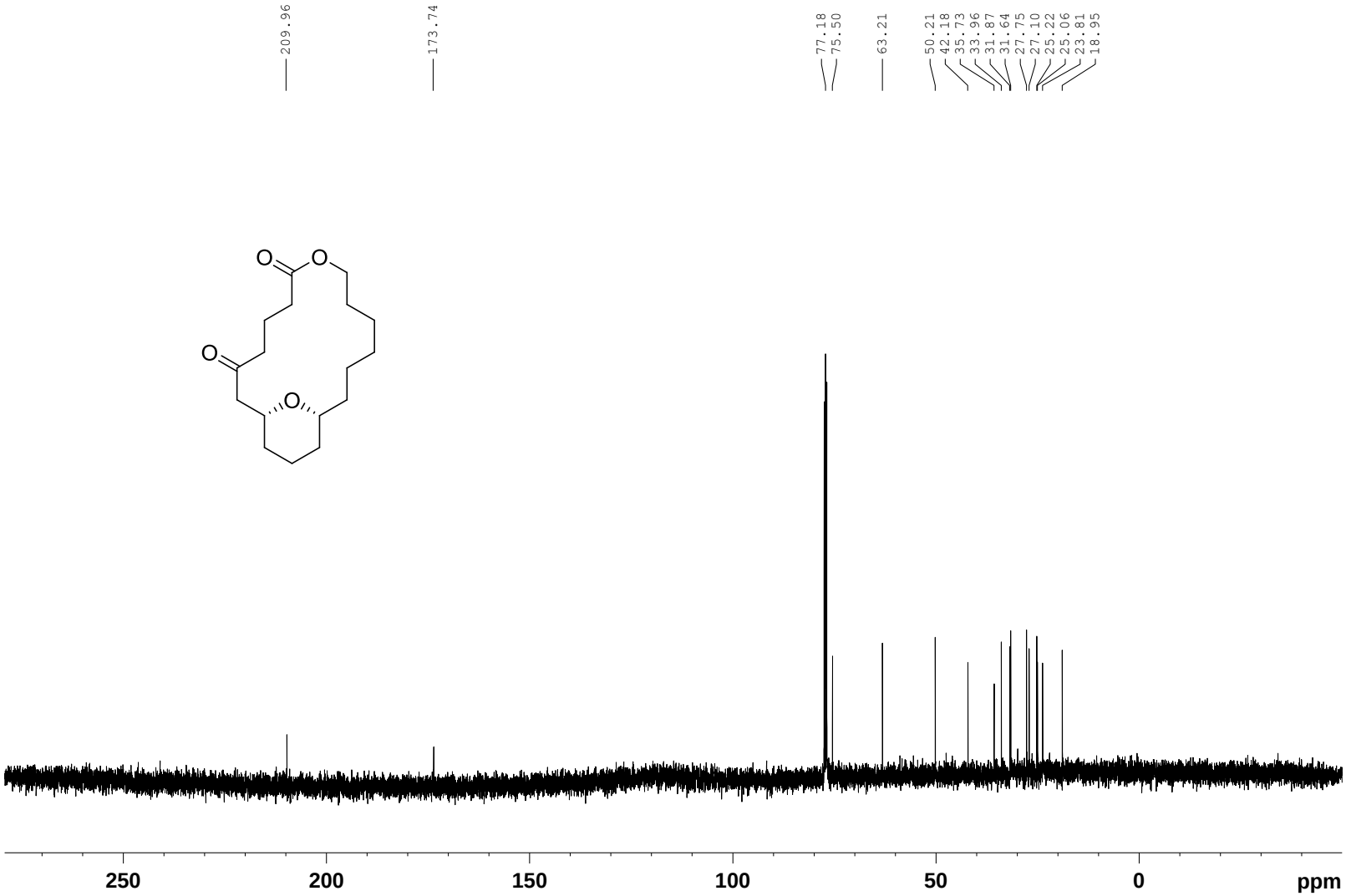




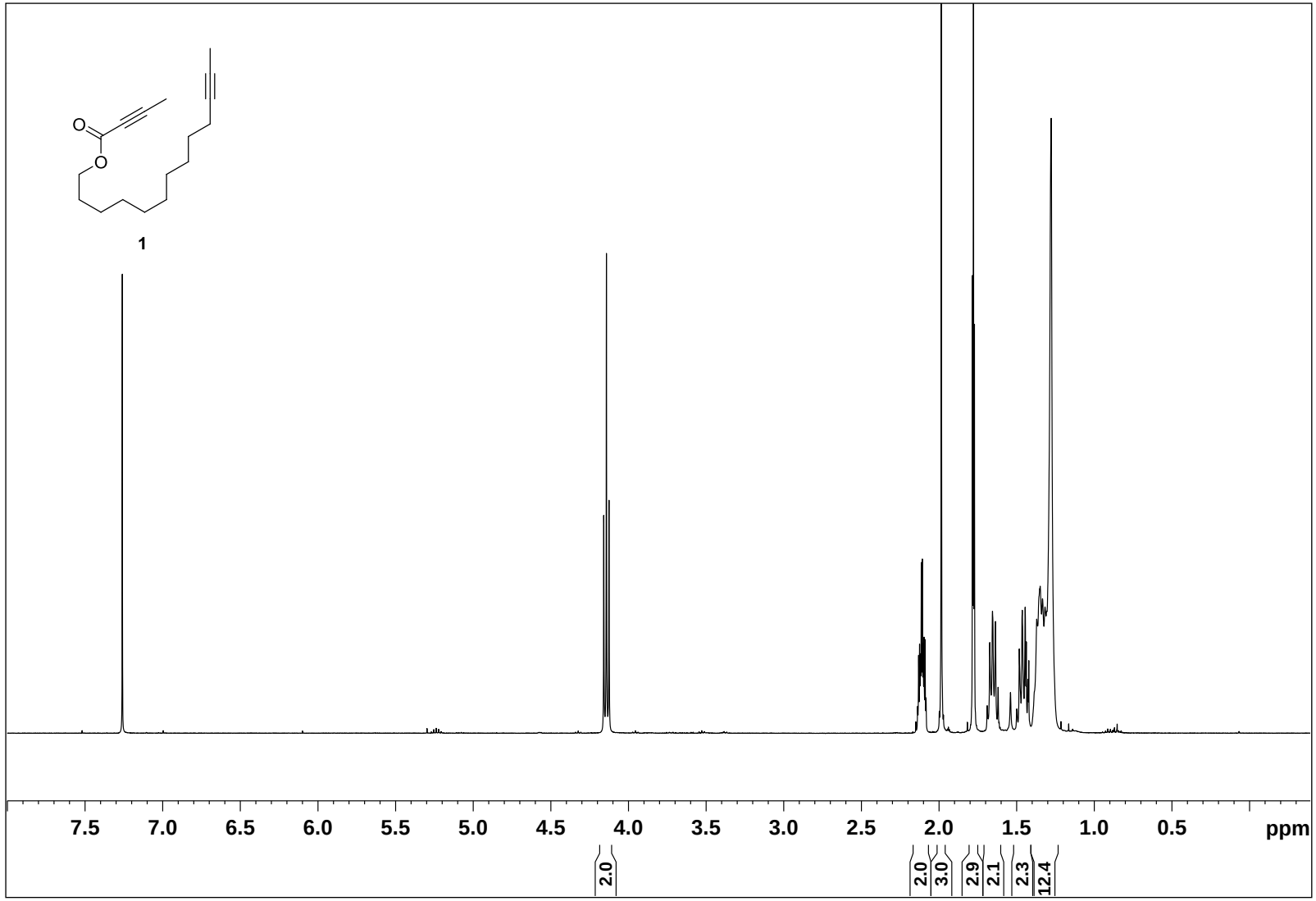
^{1}H NMR (600 MHz, $CDCl_3$)



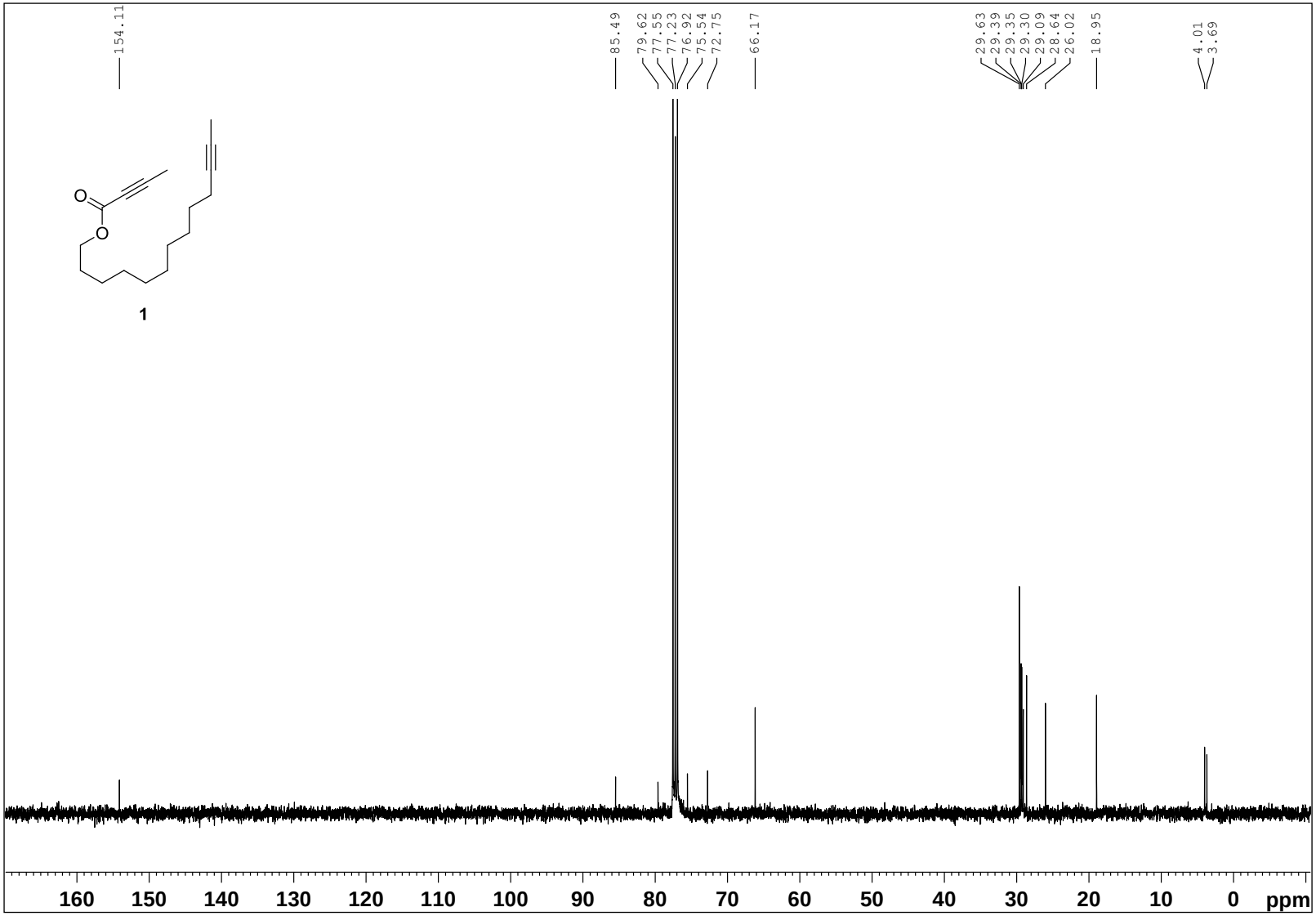
^{13}C NMR (100 MHz, $CDCl_3$)



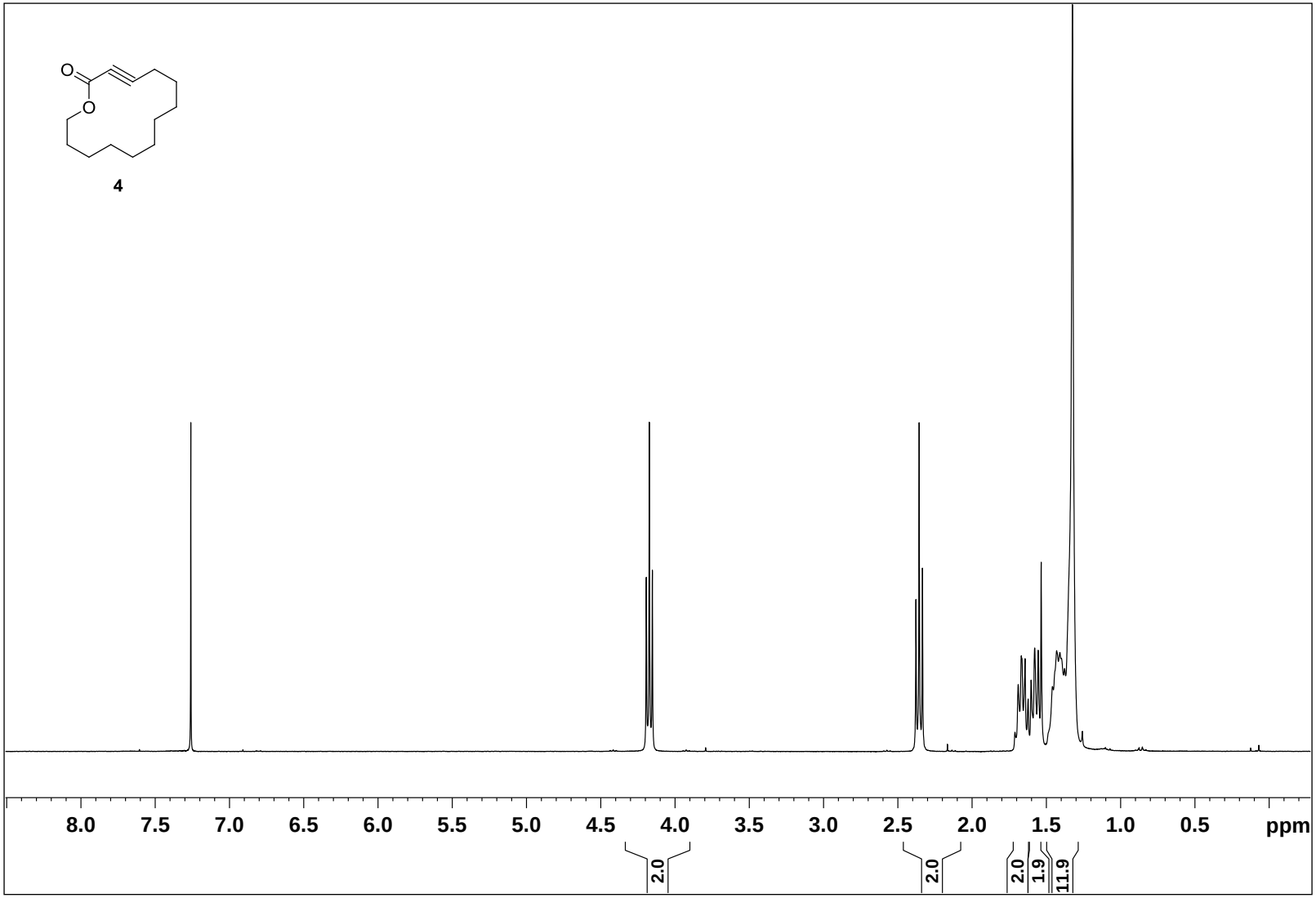
^{1}H NMR (400 MHz, $CDCl_3$)



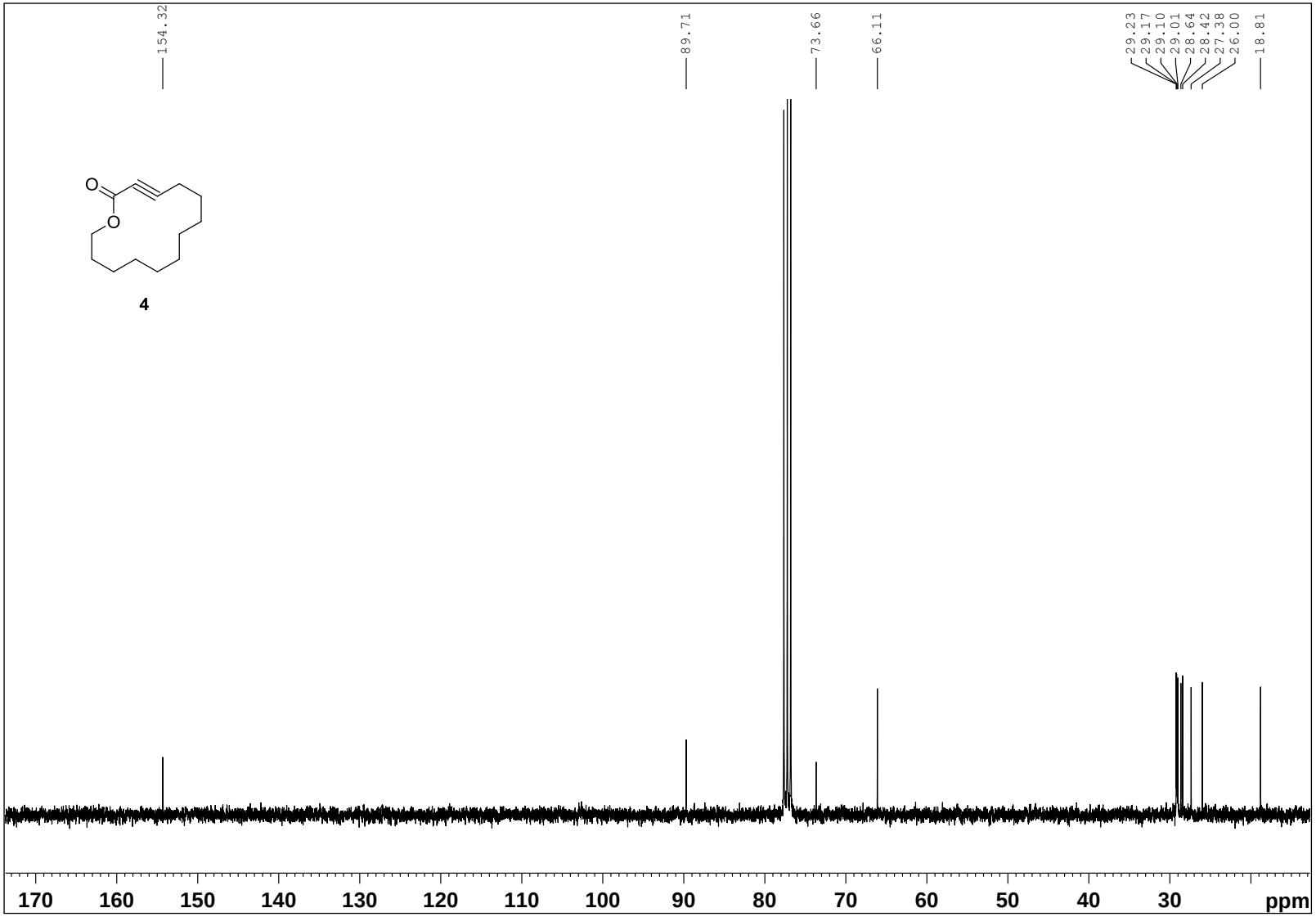
^{13}C NMR (100 MHz, $CDCl_3$)



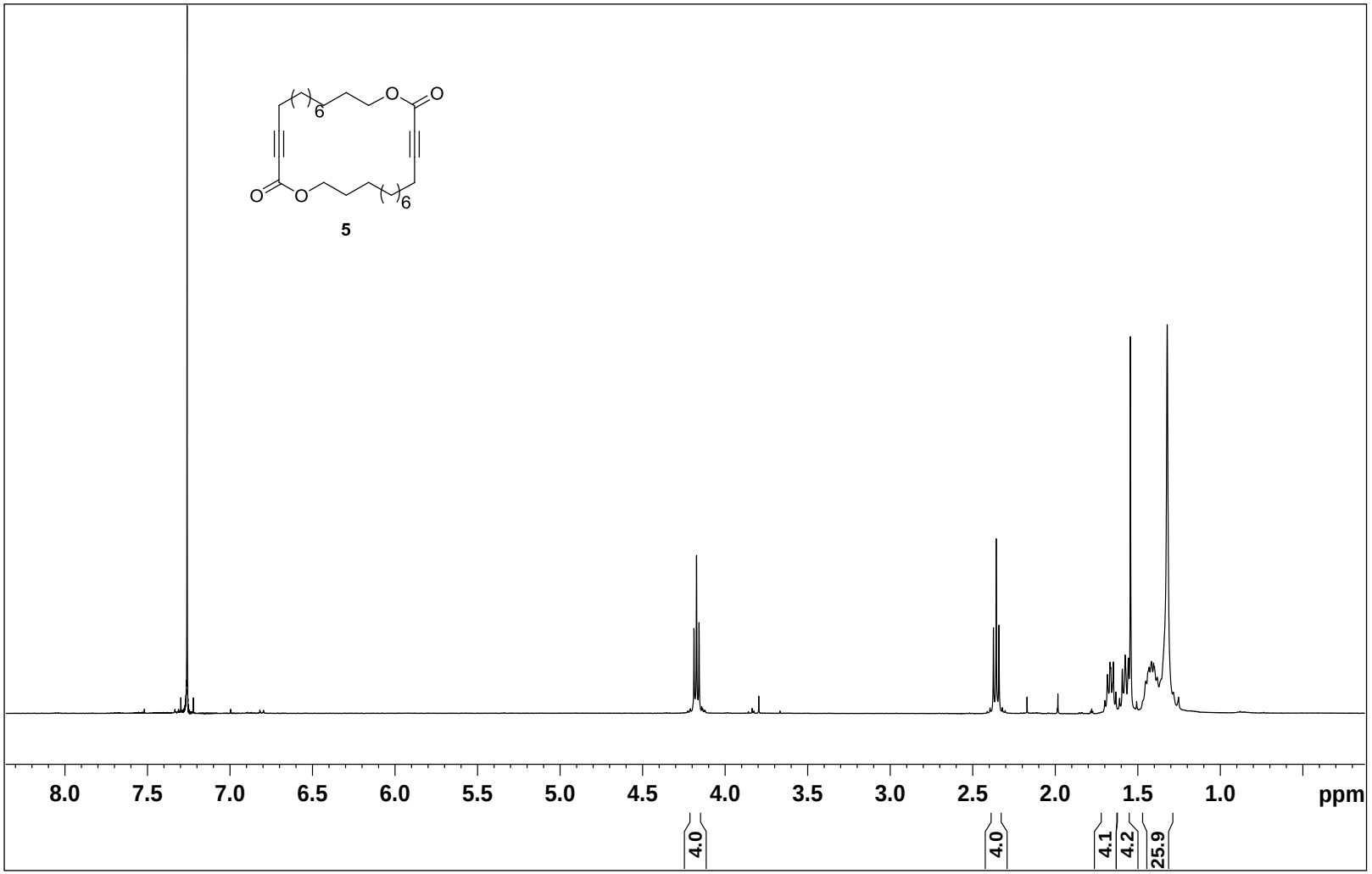
^{1}H NMR (400 MHz, $CDCl_3$)



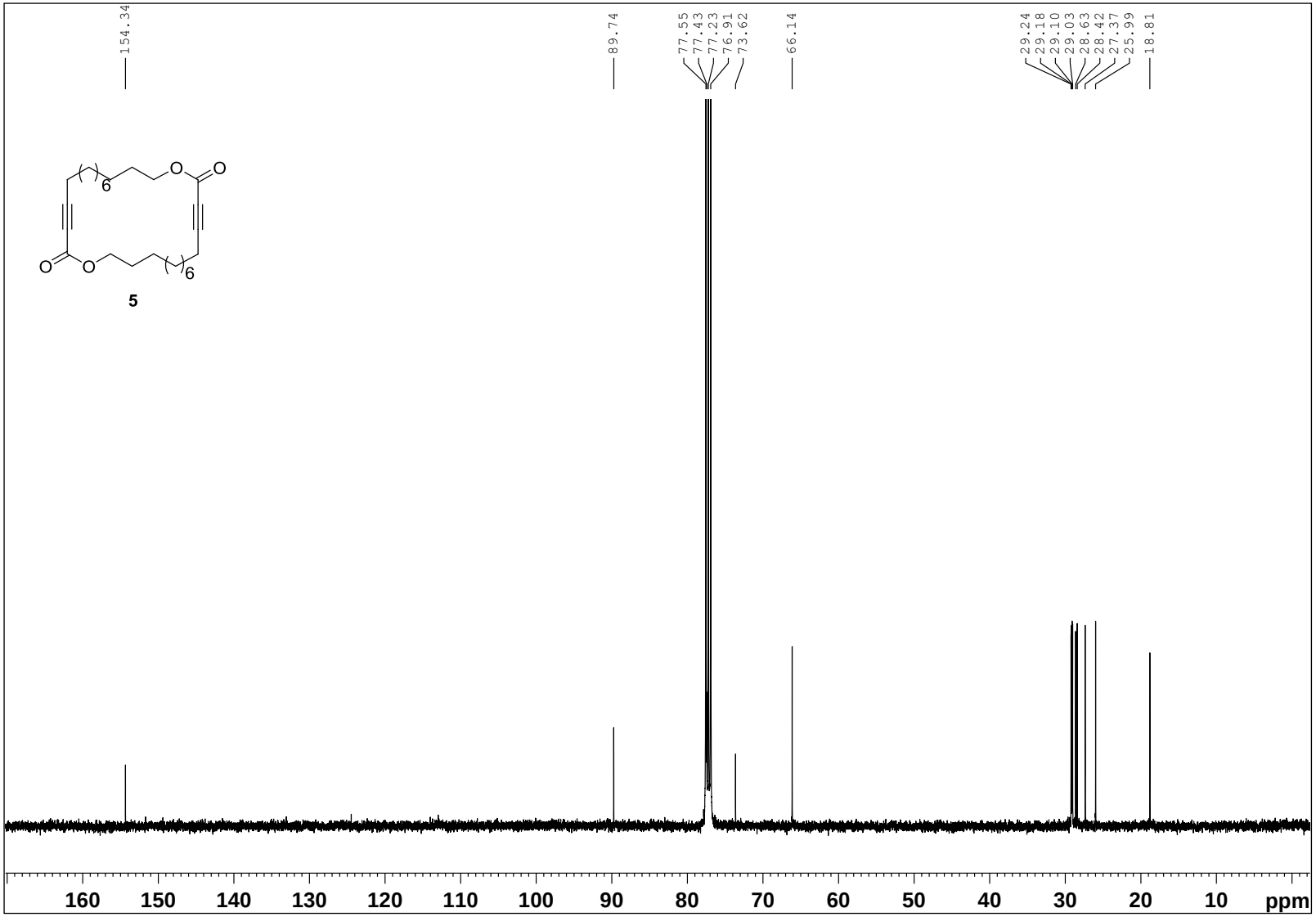
^{13}C NMR (100 MHz, $CDCl_3$)



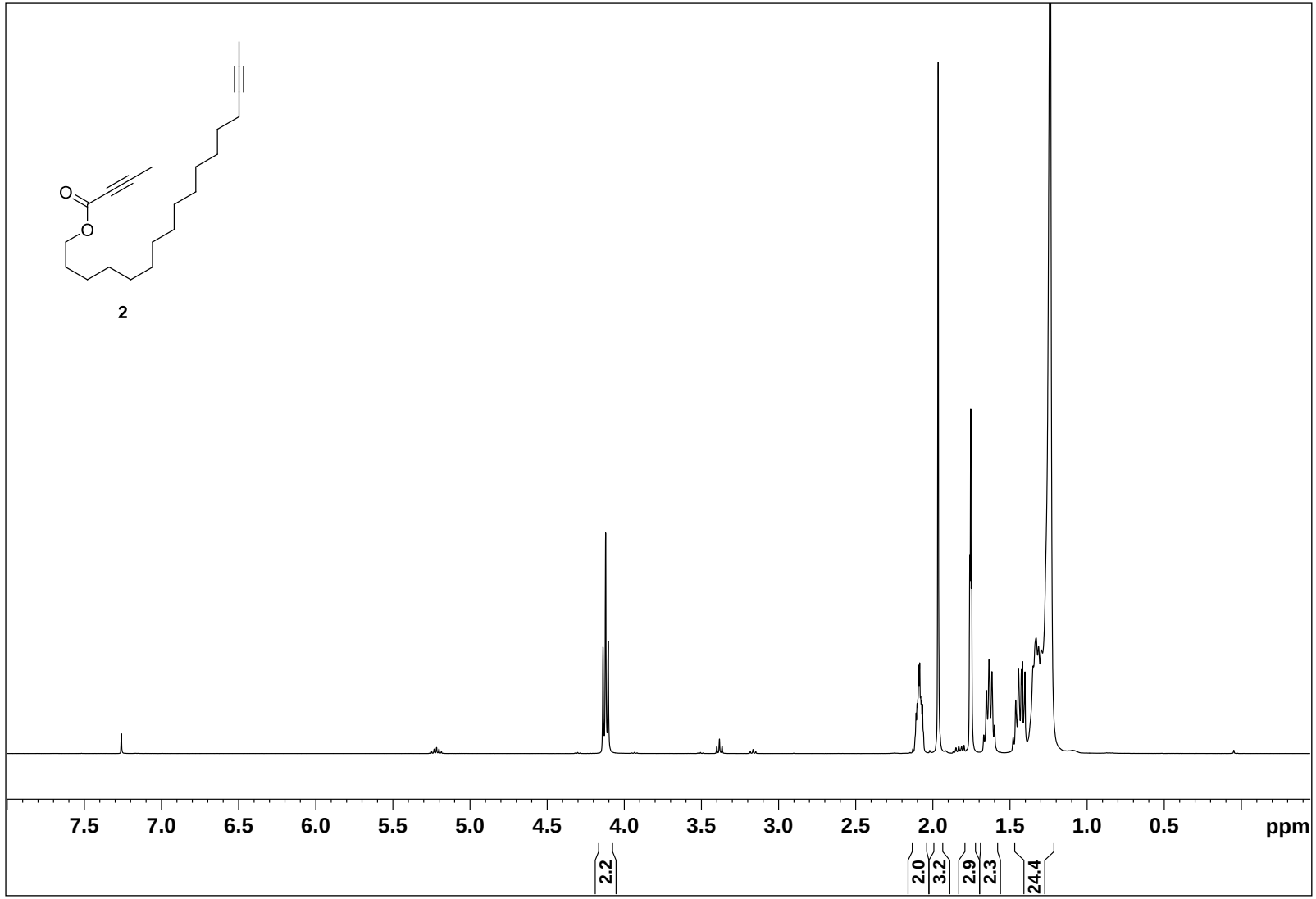
^{1}H NMR (400 MHz, $CDCl_3$) of Head-to-Tail Cyclodimer



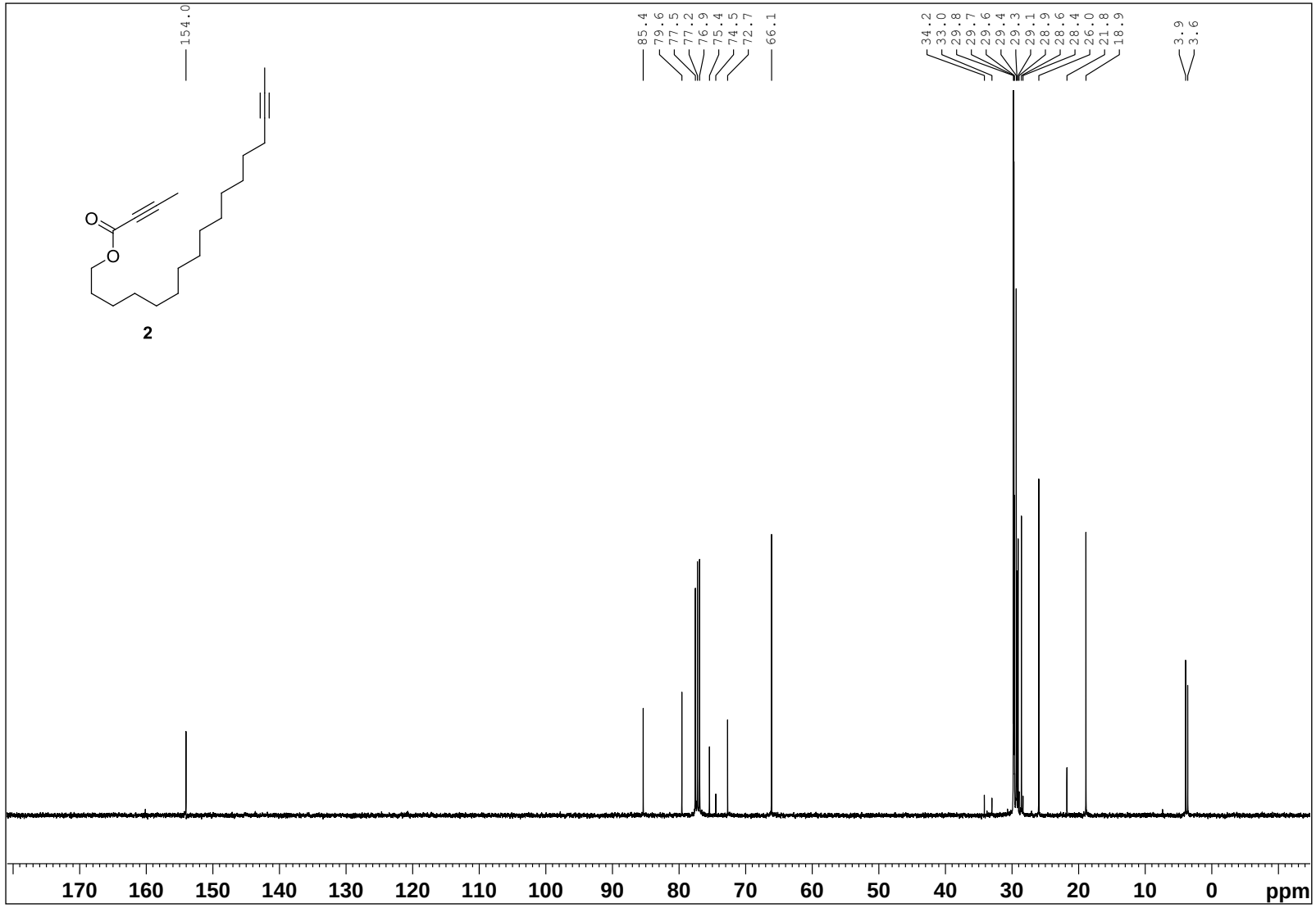
^{13}C NMR (100 MHz, $CDCl_3$) of Head-to-Tail Cyclodimer



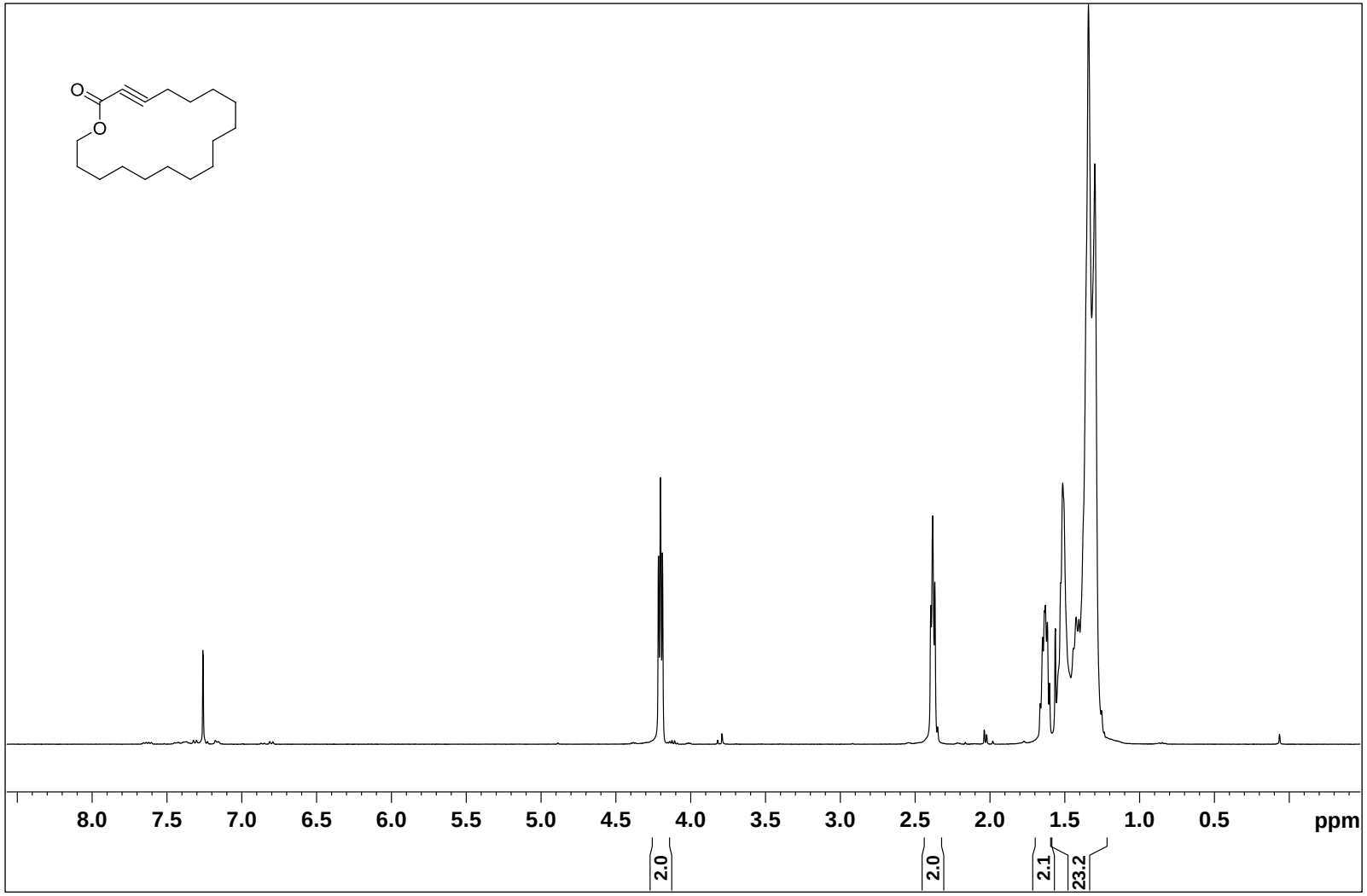
^{1}H NMR (400 MHz, $CDCl_3$) of 15-Heptadecynyl bu-2-ynoate (2)



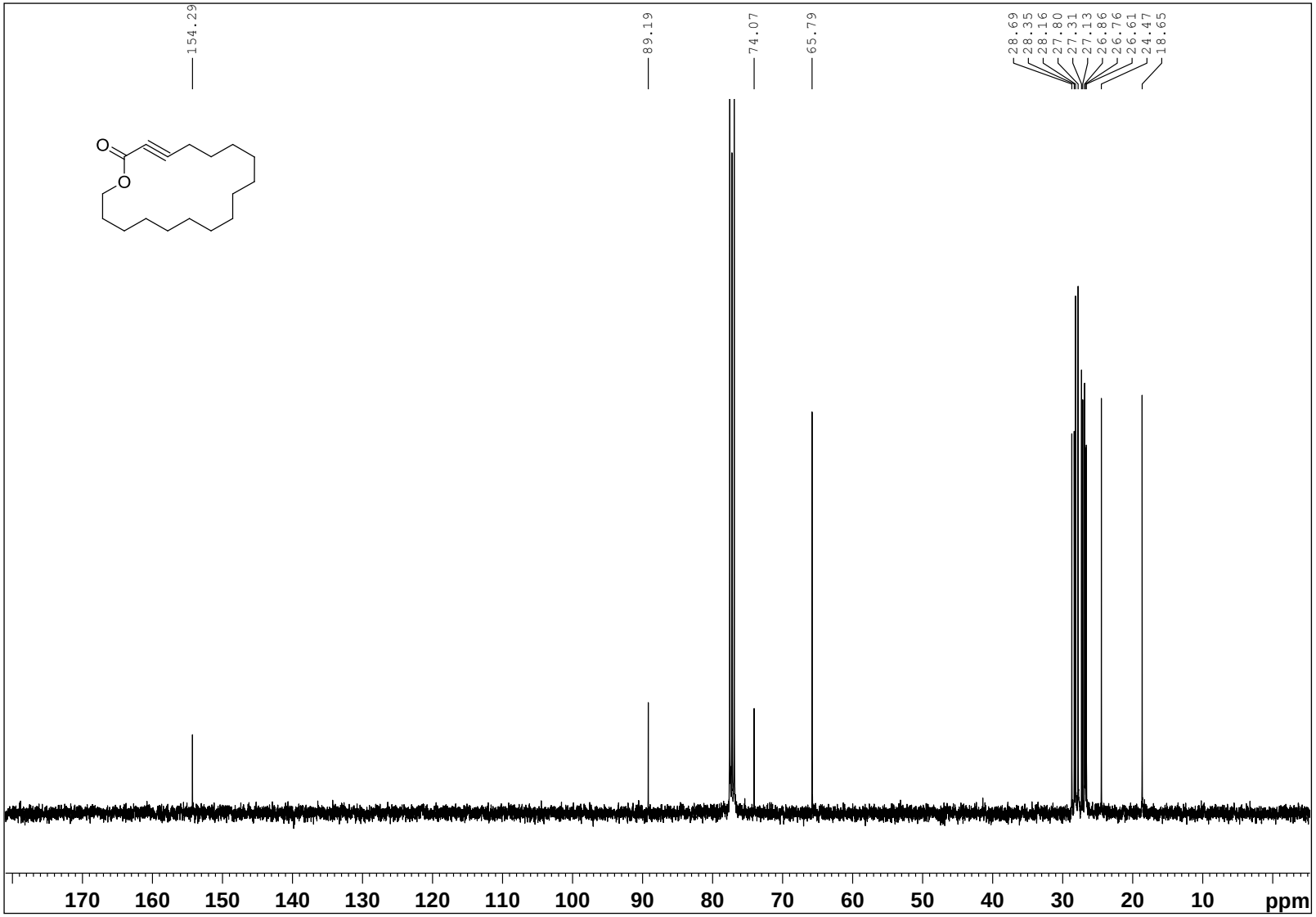
^{13}C NMR (100 MHz, $CDCl_3$)



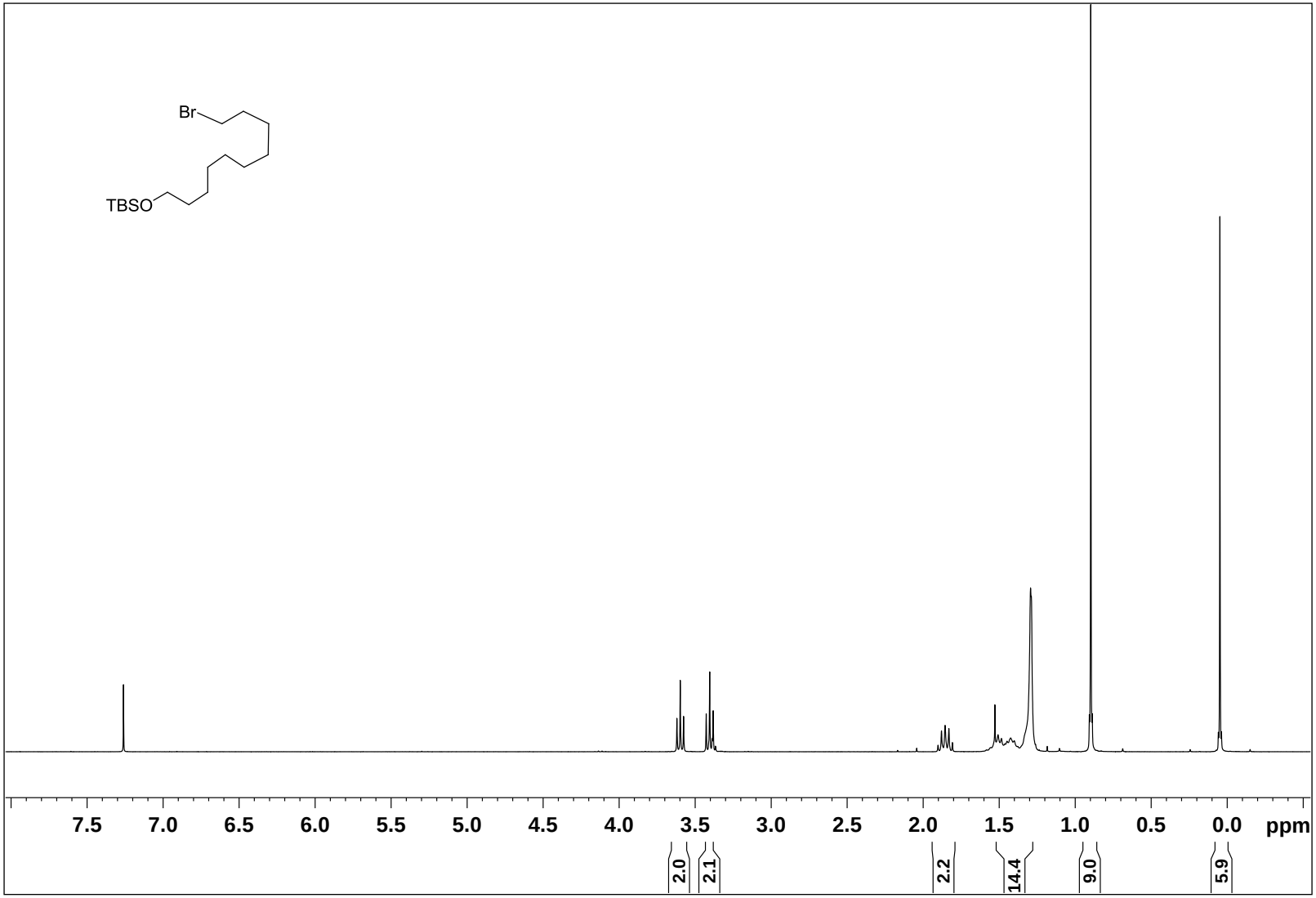
^{1}H NMR (400 MHz, $CDCl_3$).



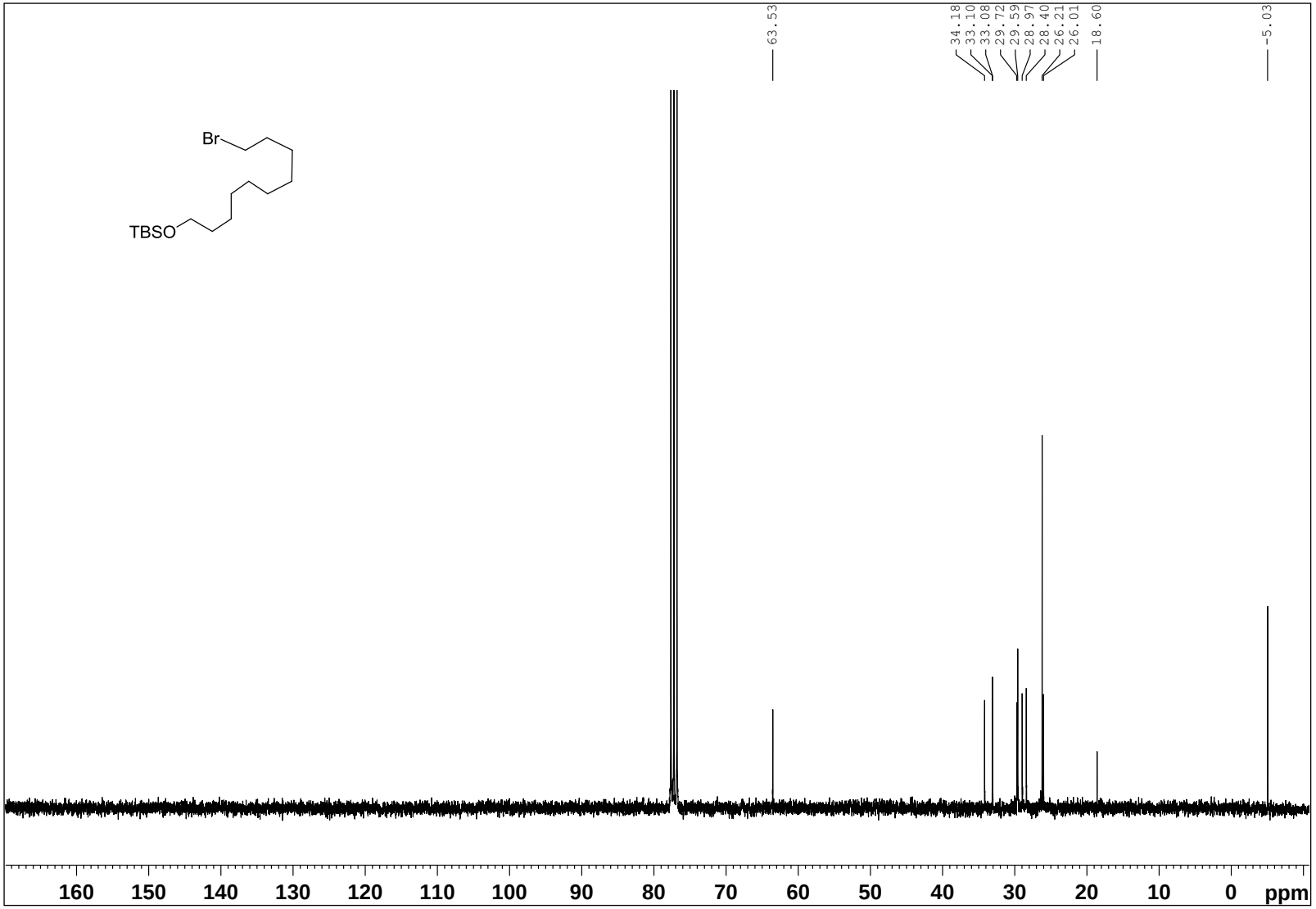
^{13}C NMR (100 MHz, $CDCl_3$)



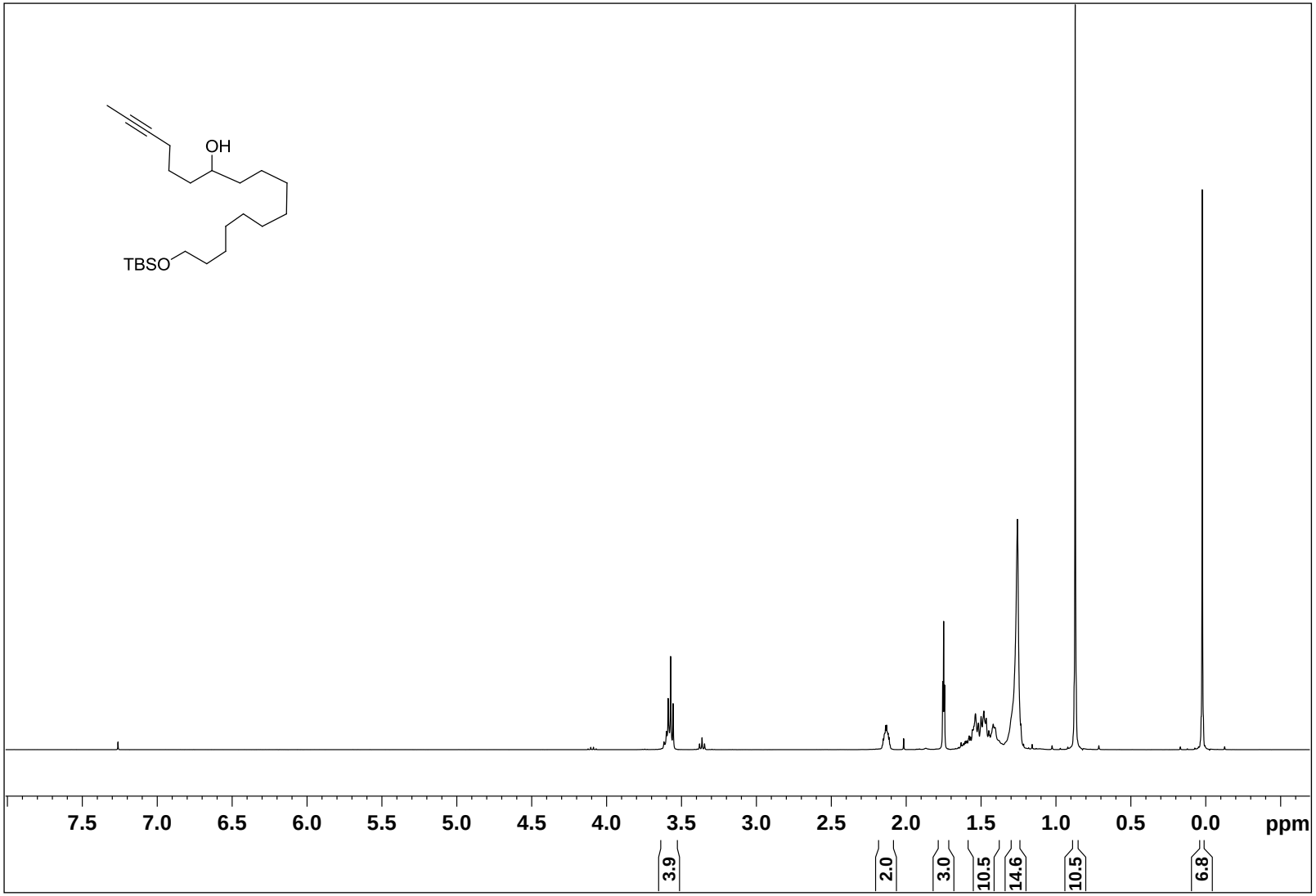
^{1}H NMR (300 MHz, $CDCl_3$) of (10-Bromodecyloxy)(*tert*-butyl)dimethylsilane



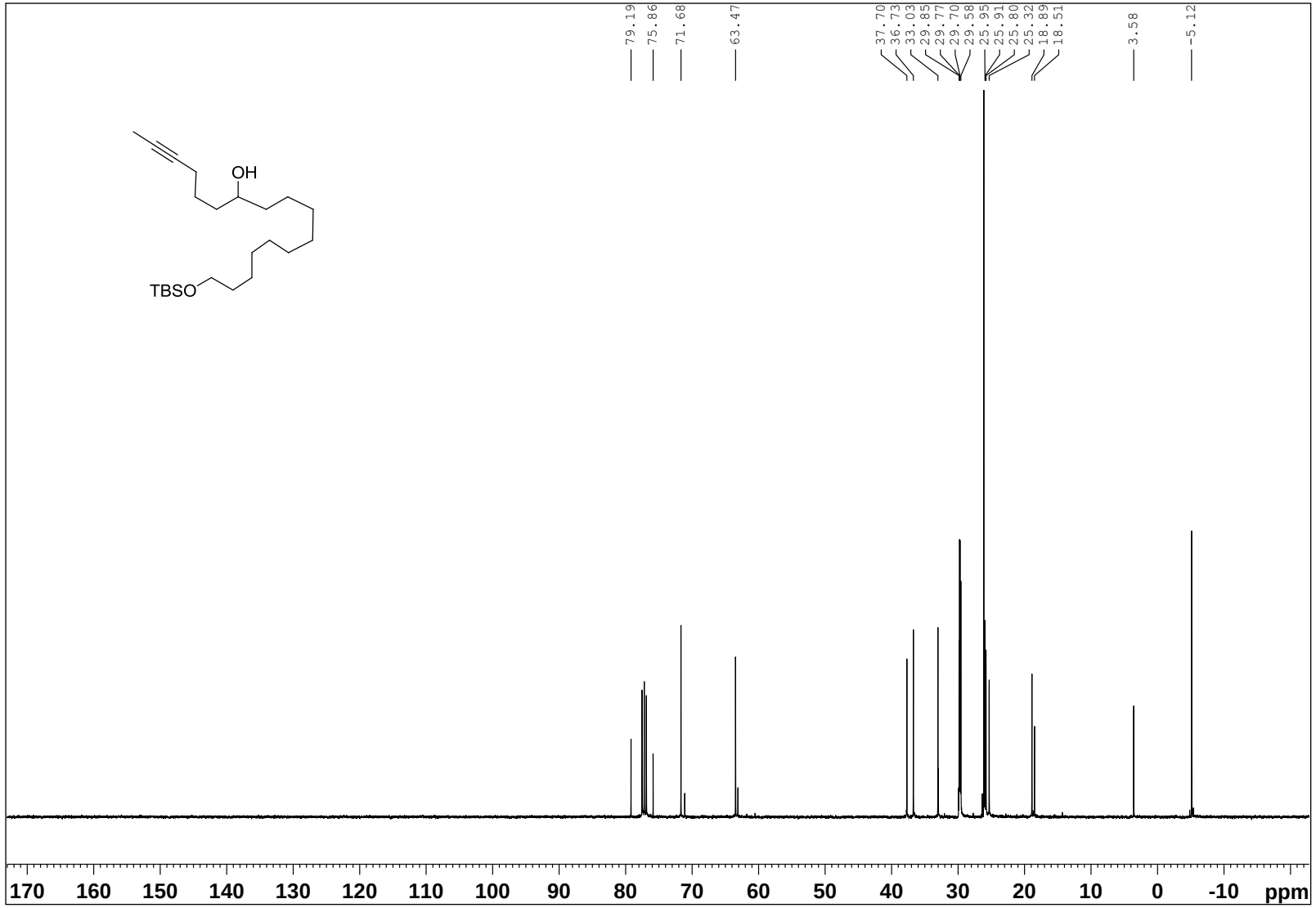
^{13}C NMR (75 MHz, $CDCl_3$) of (10-Bromodecyloxy)(*tert*-butyl)dimethylsilane



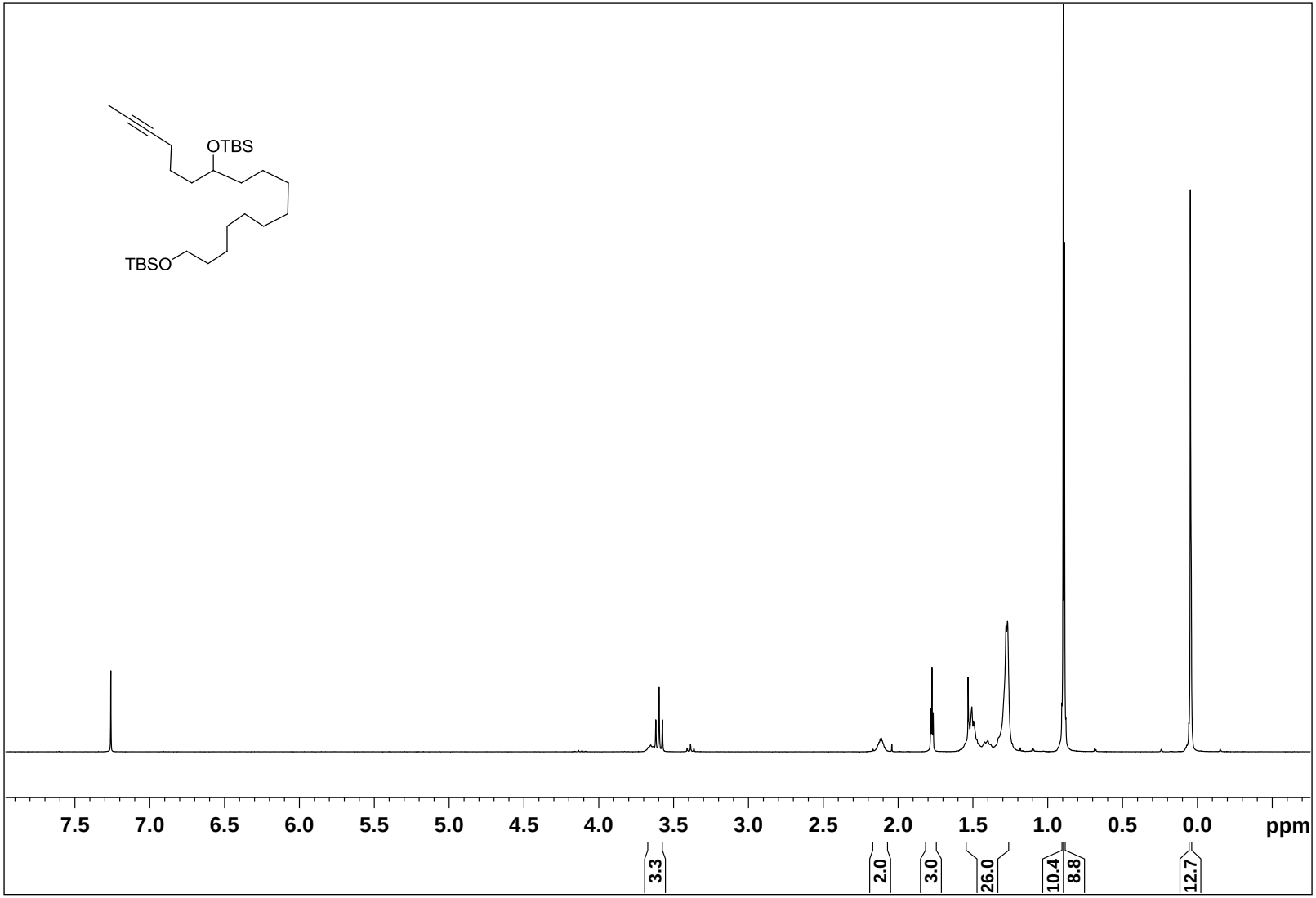
^{1}H NMR (400 MHz, $CDCl_3$)



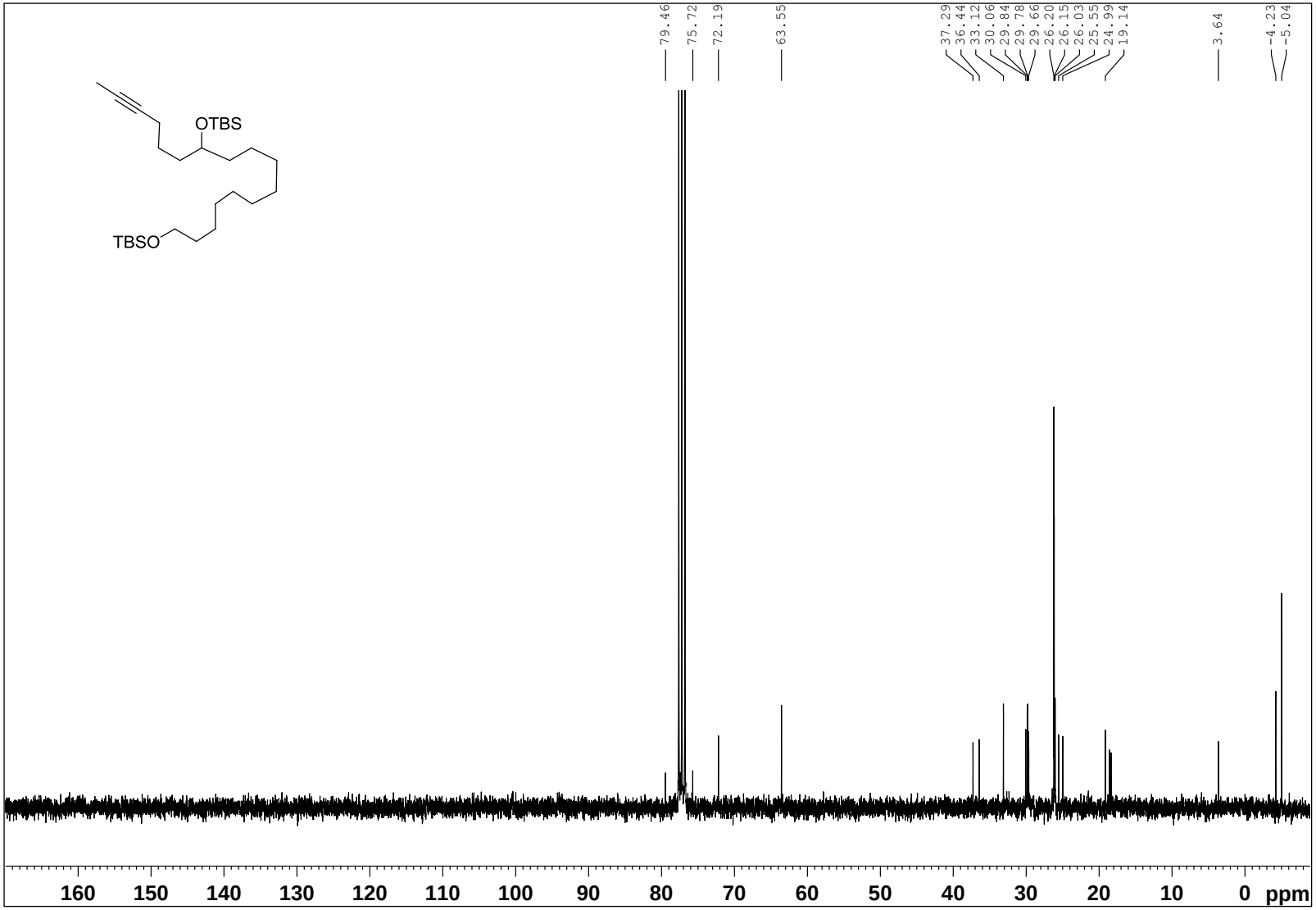
^{13}C NMR (100 MHz, $CDCl_3$)



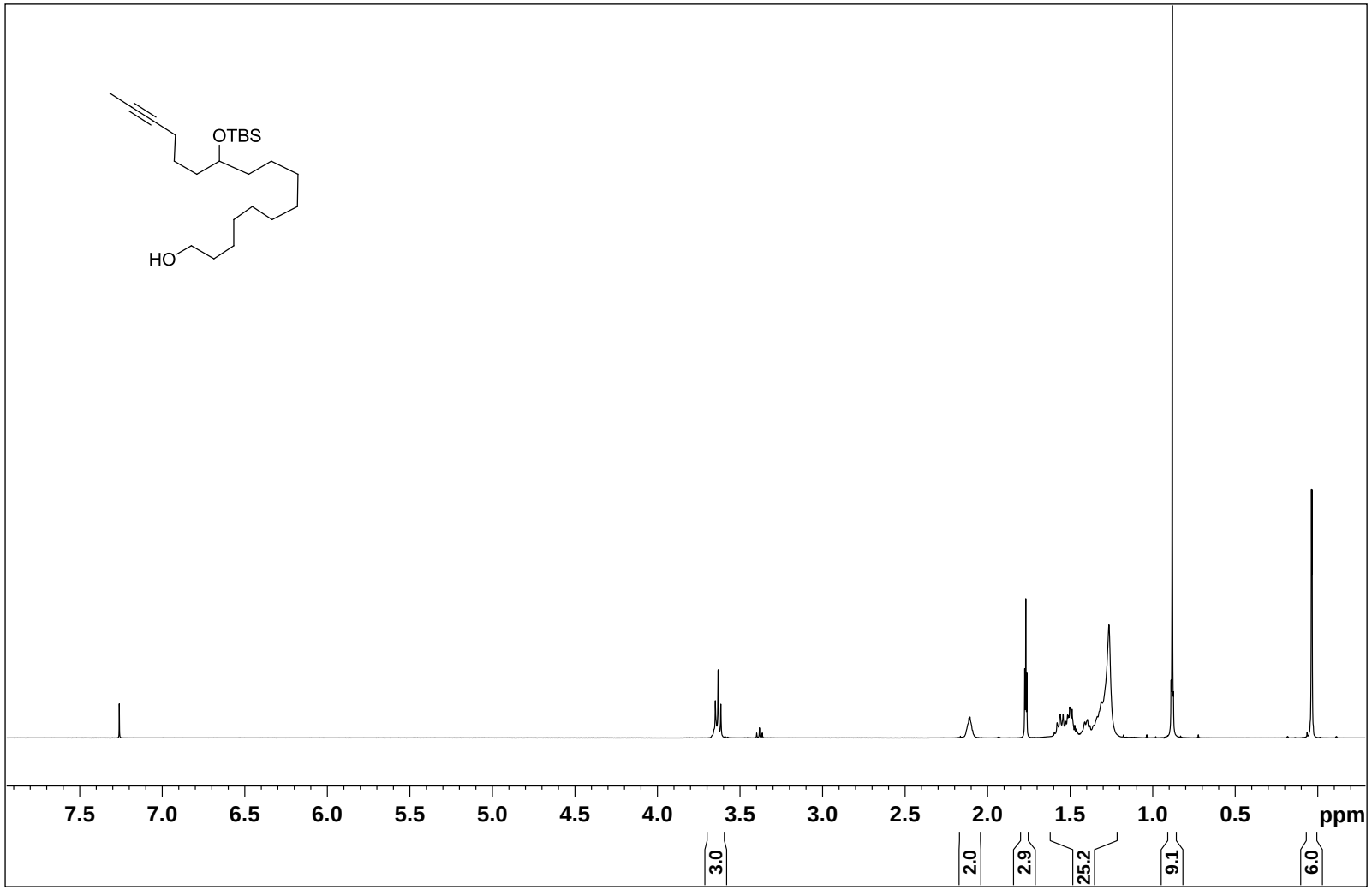
^{1}H NMR (400 MHz, $CDCl_3$)



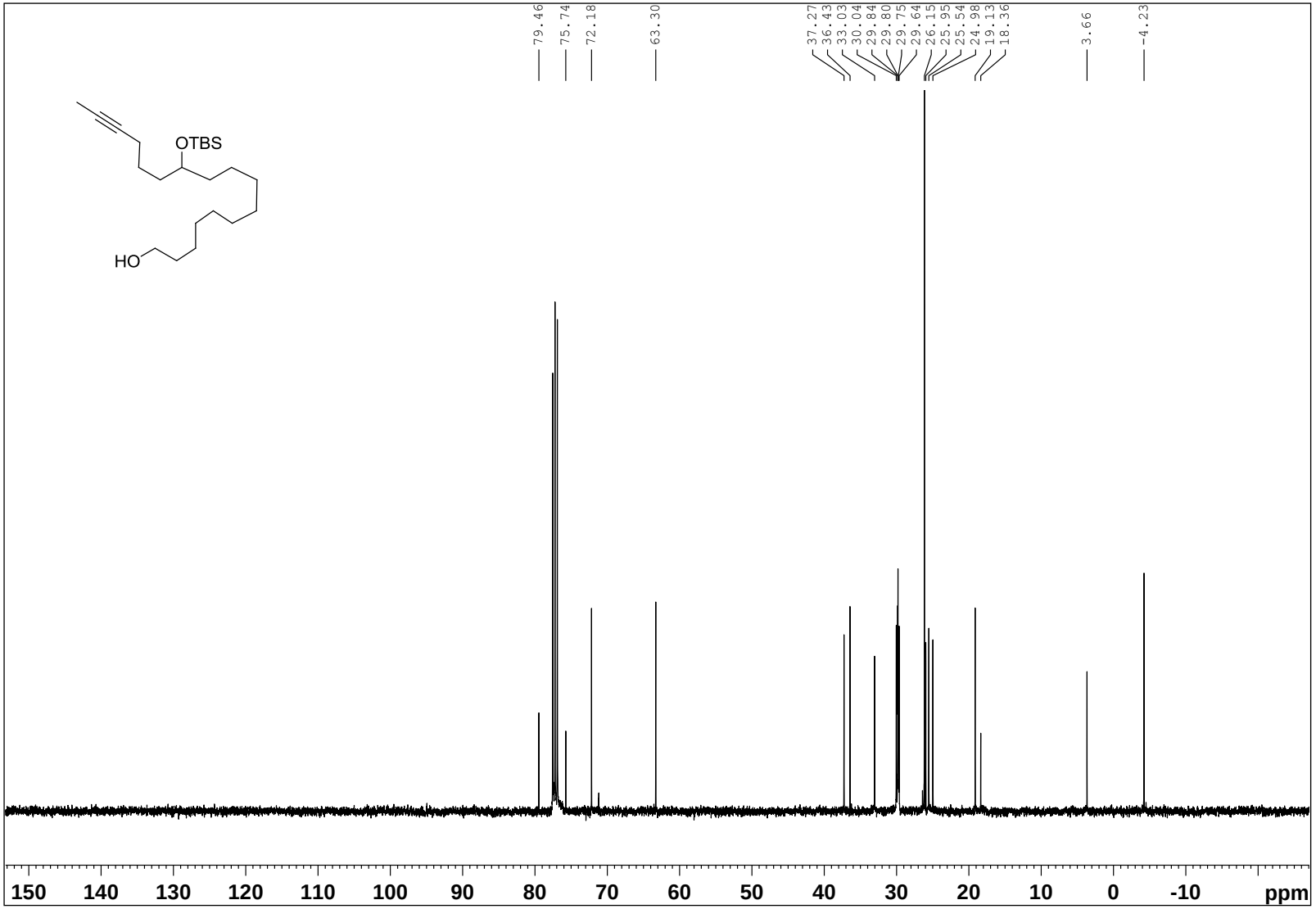
^{13}C NMR (100 MHz, $CDCl_3$)



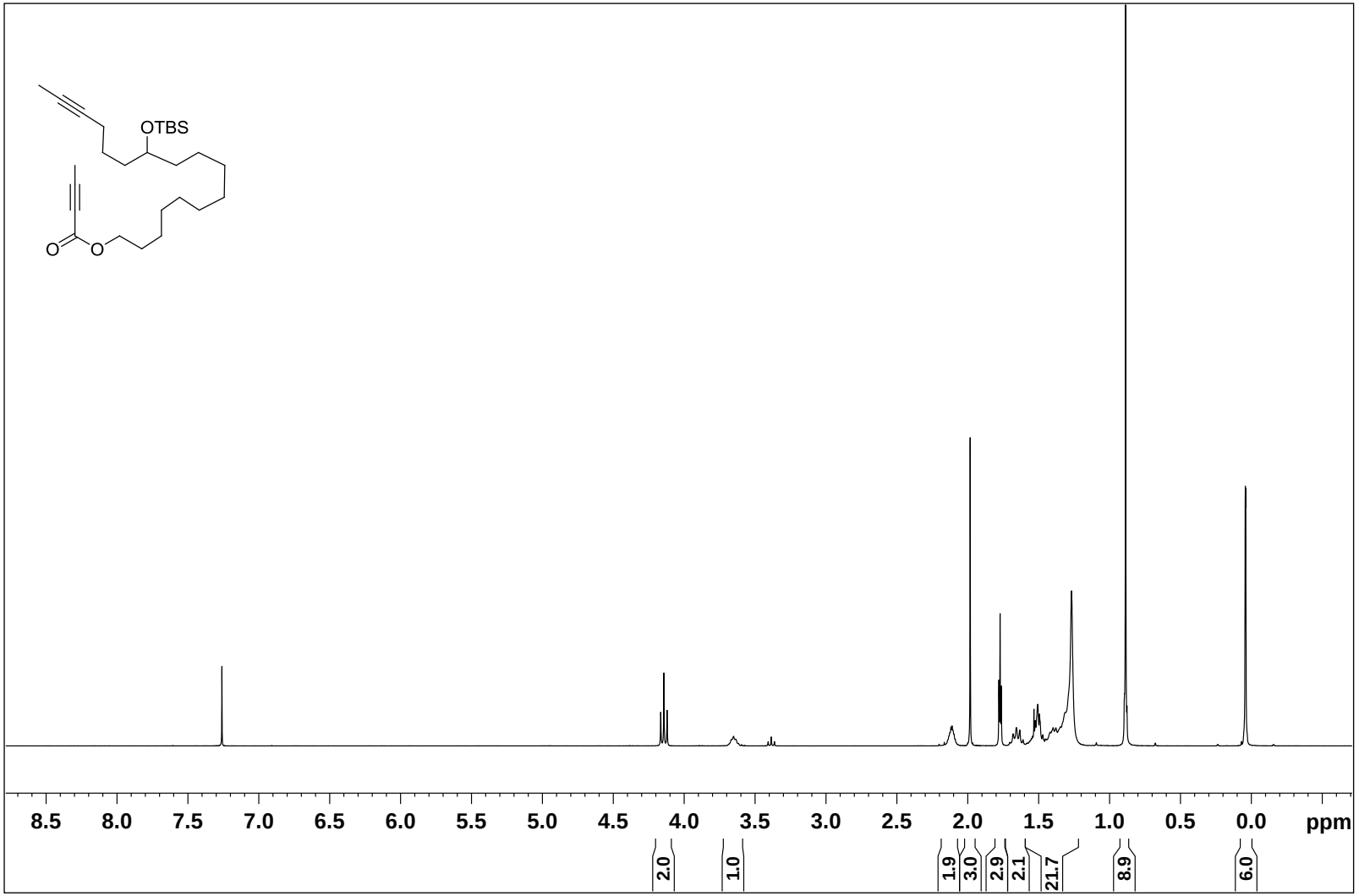
^{1}H NMR (400 MHz, $CDCl_3$)



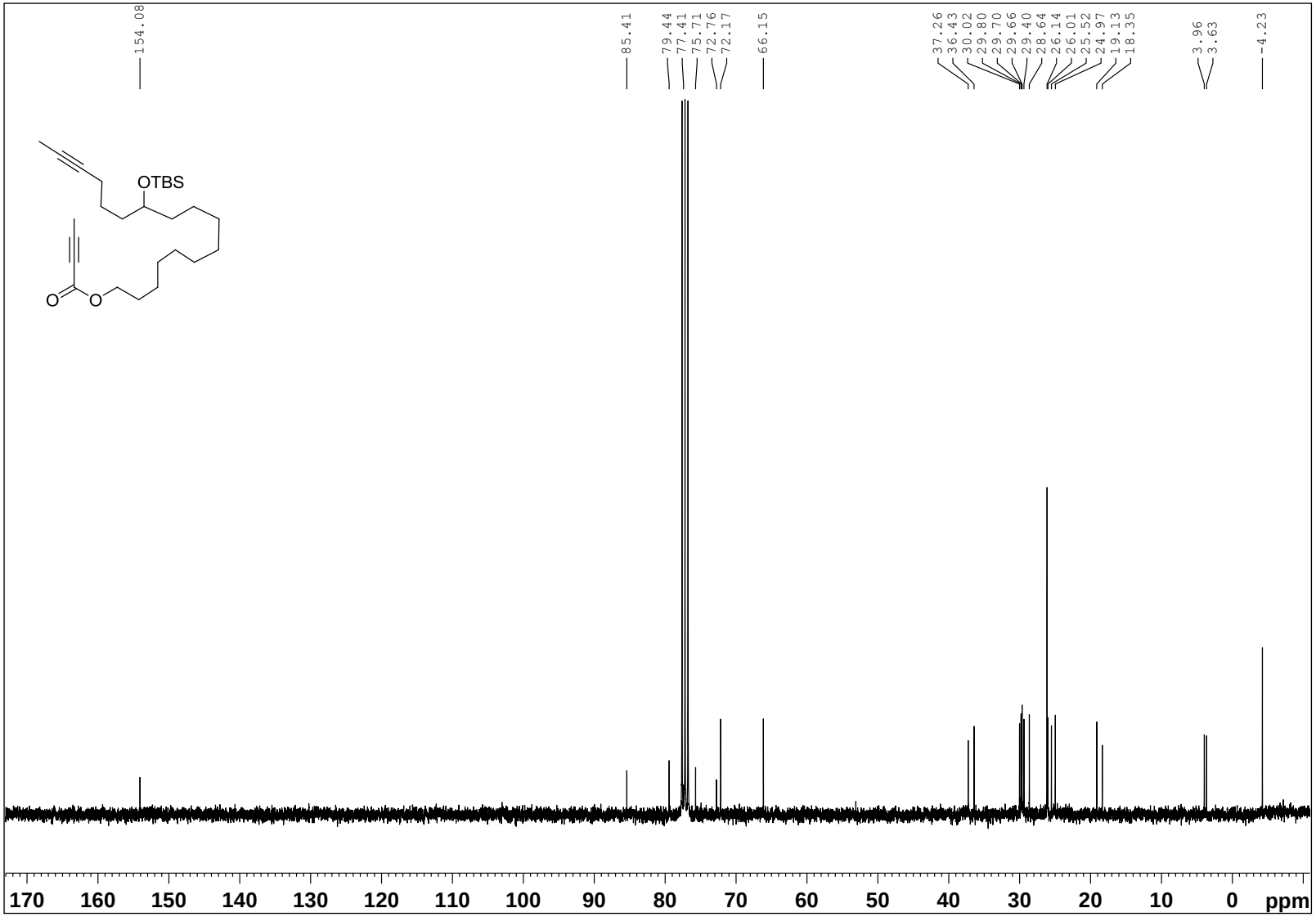
^{13}C NMR (100 MHz, $CDCl_3$)



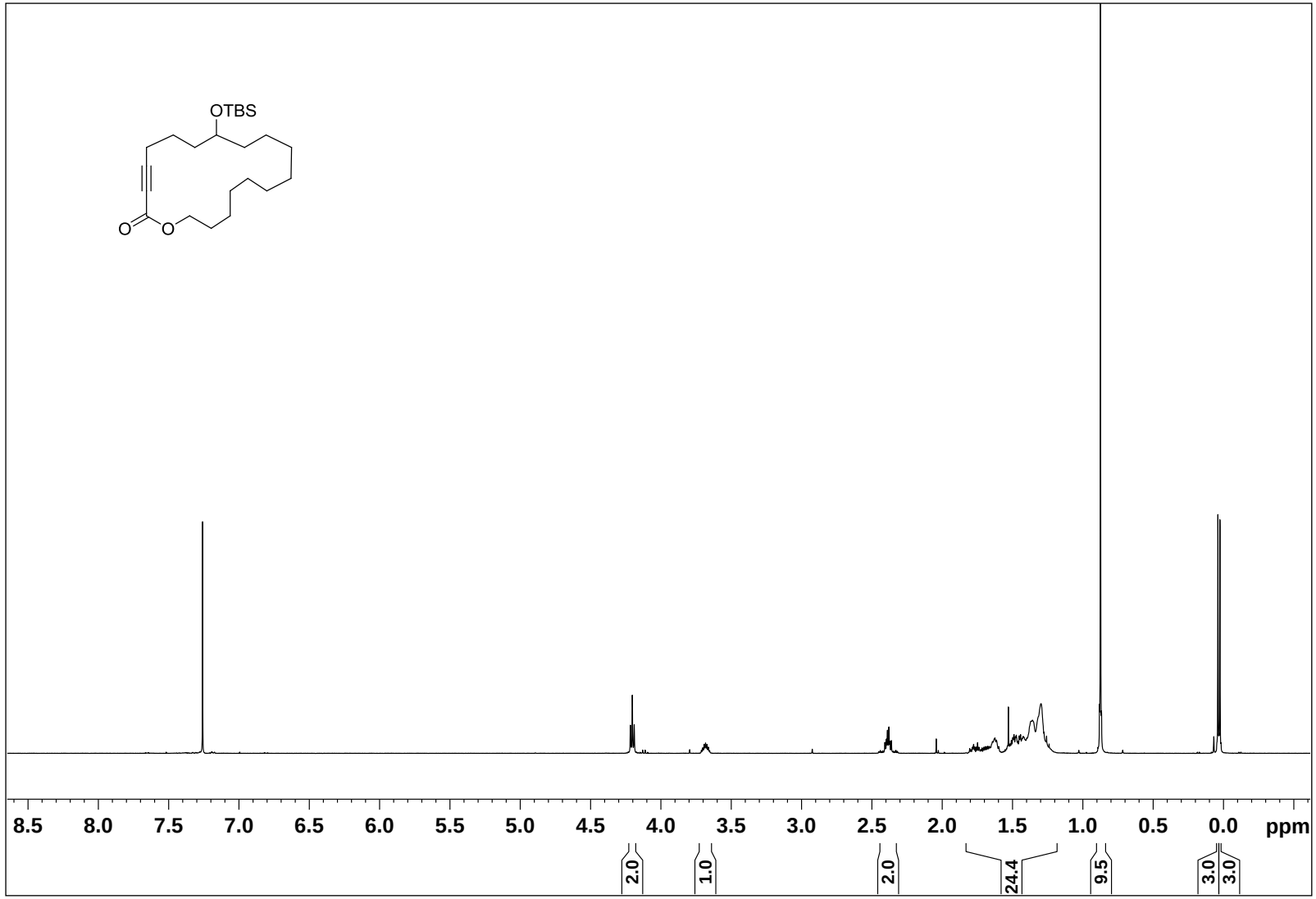
^{1}H NMR (300 MHz, $CDCl_3$)



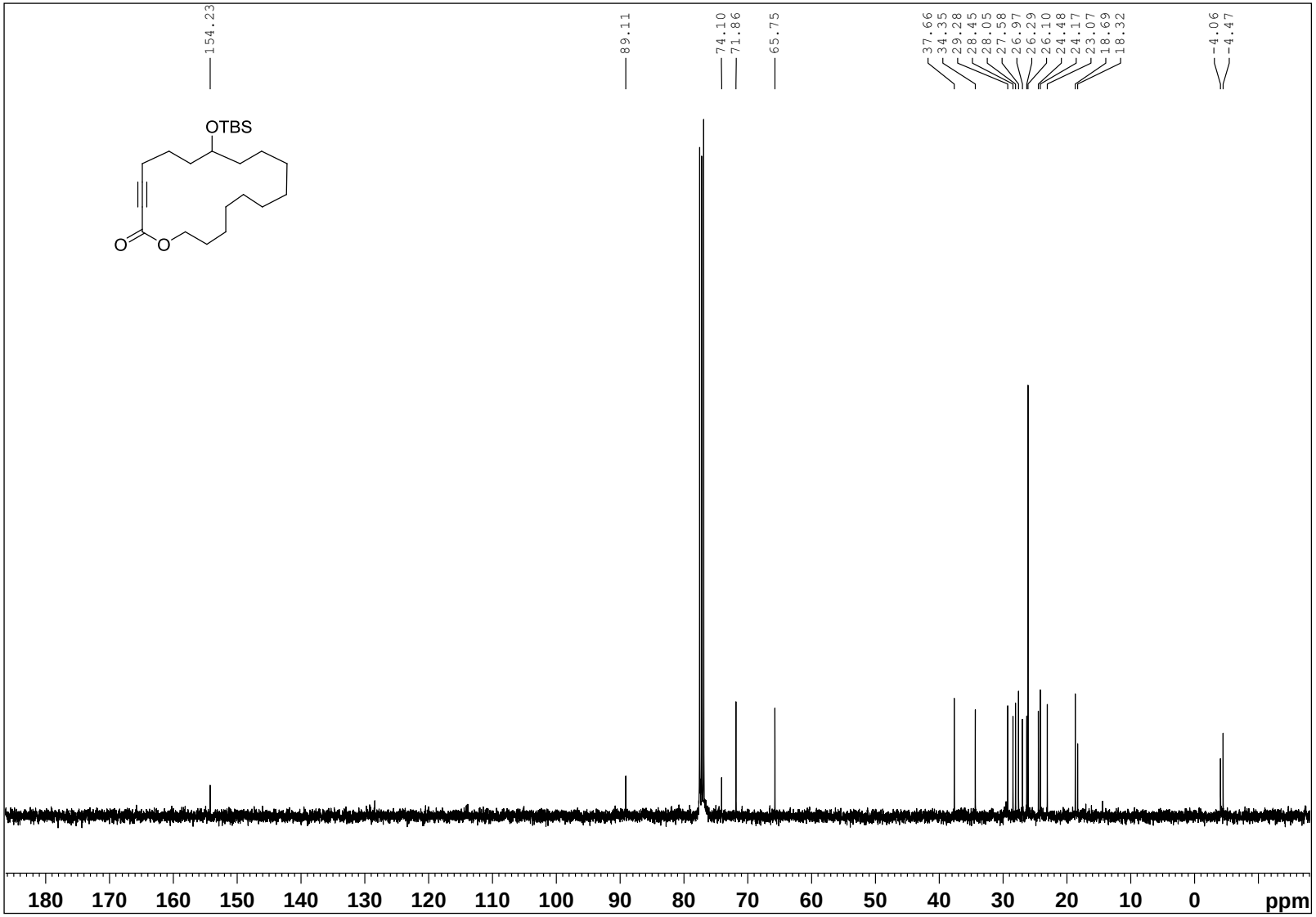
^{13}C NMR (100 MHz, $CDCl_3$)



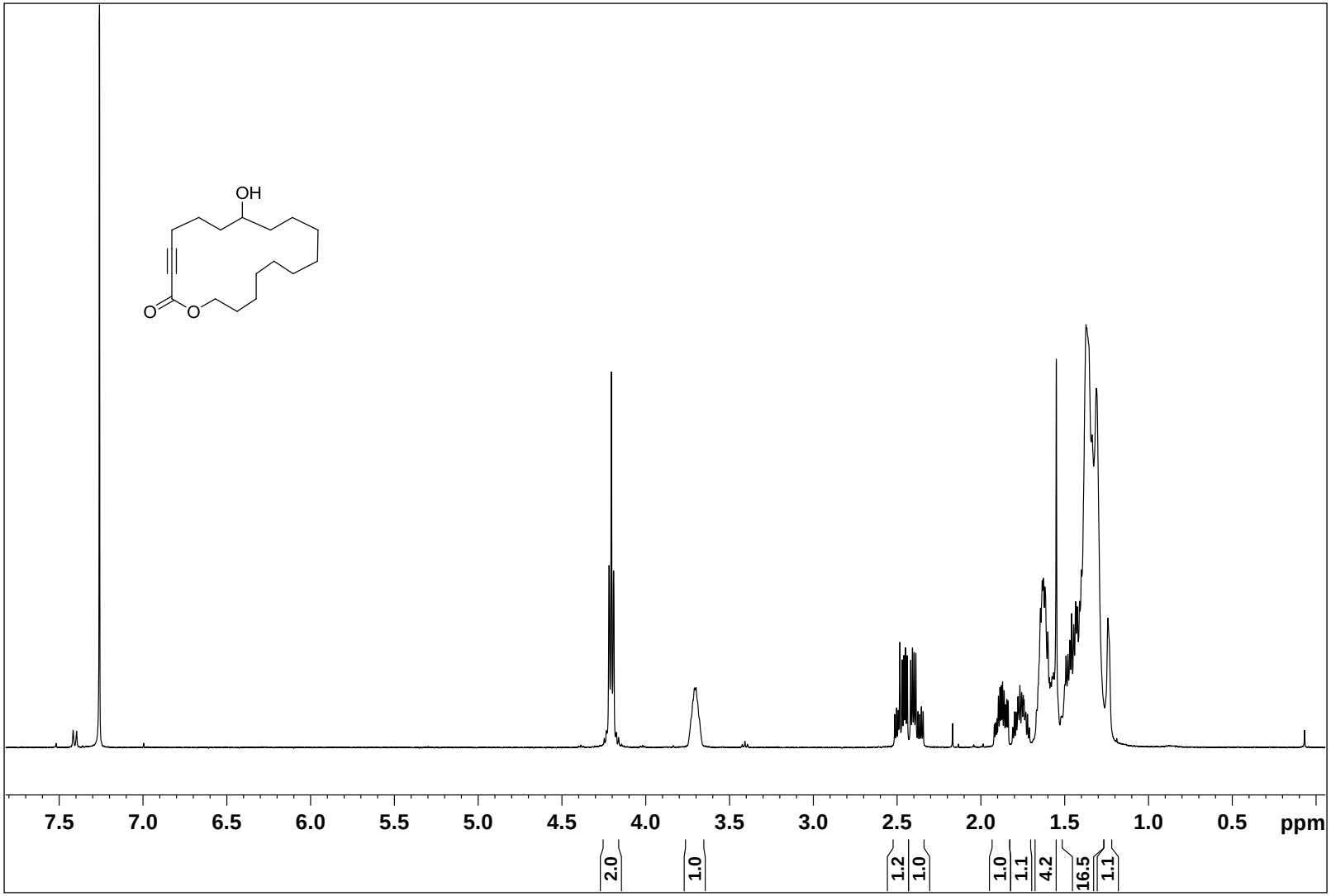
^{1}H NMR (400 MHz, $CDCl_3$)



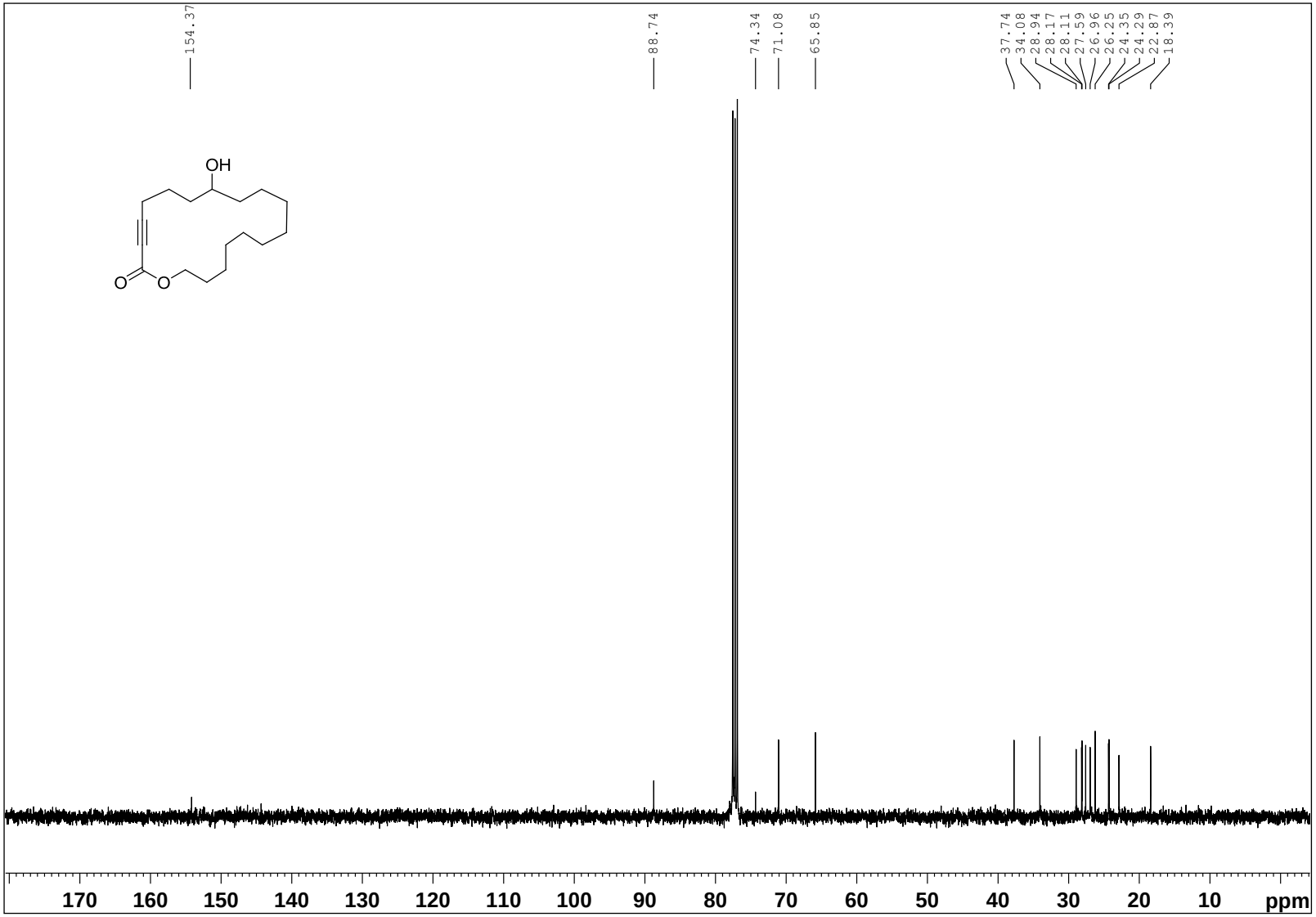
^{13}C NMR (100 MHz, $CDCl_3$)



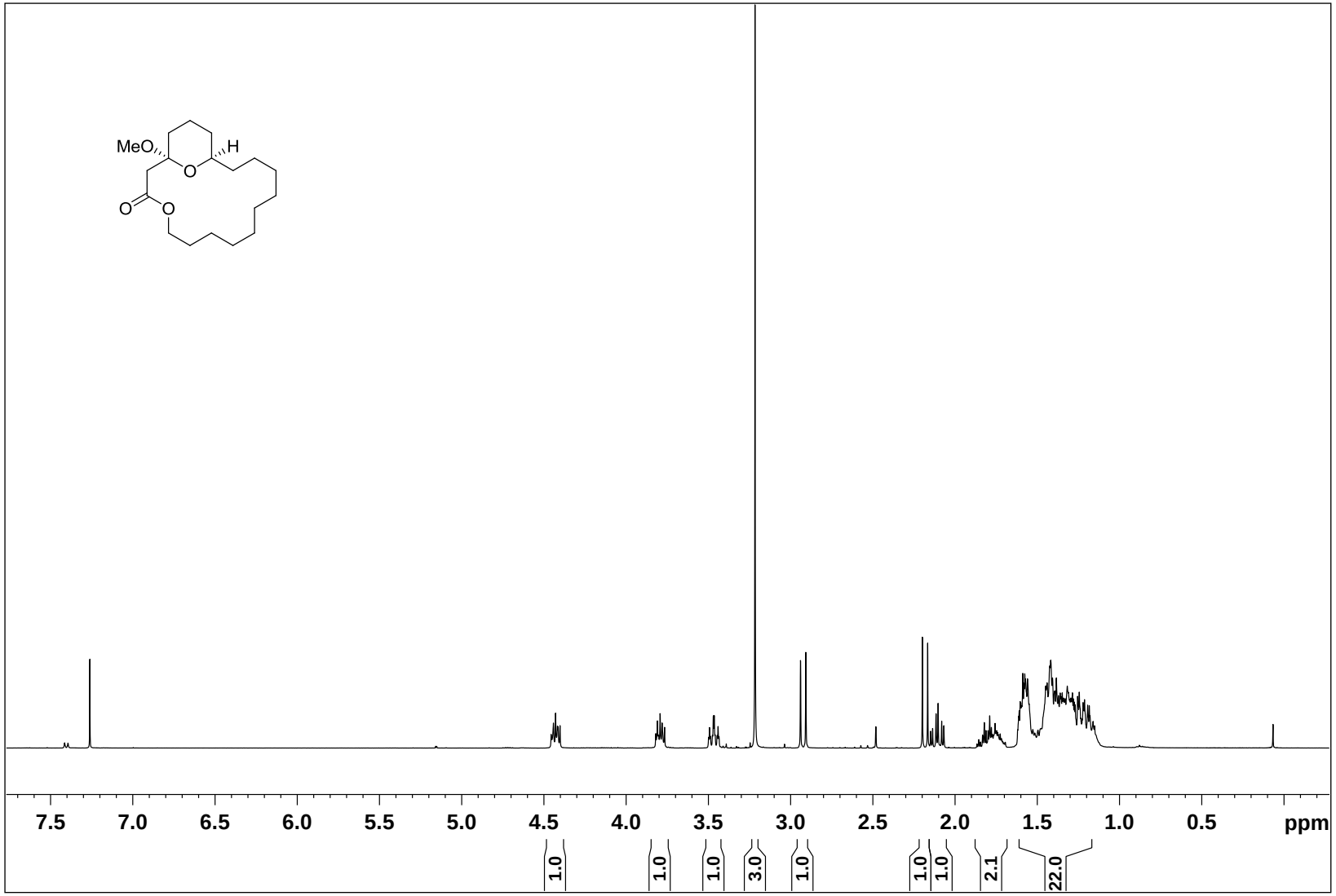
^{1}H NMR (400 MHz, $CDCl_3$)



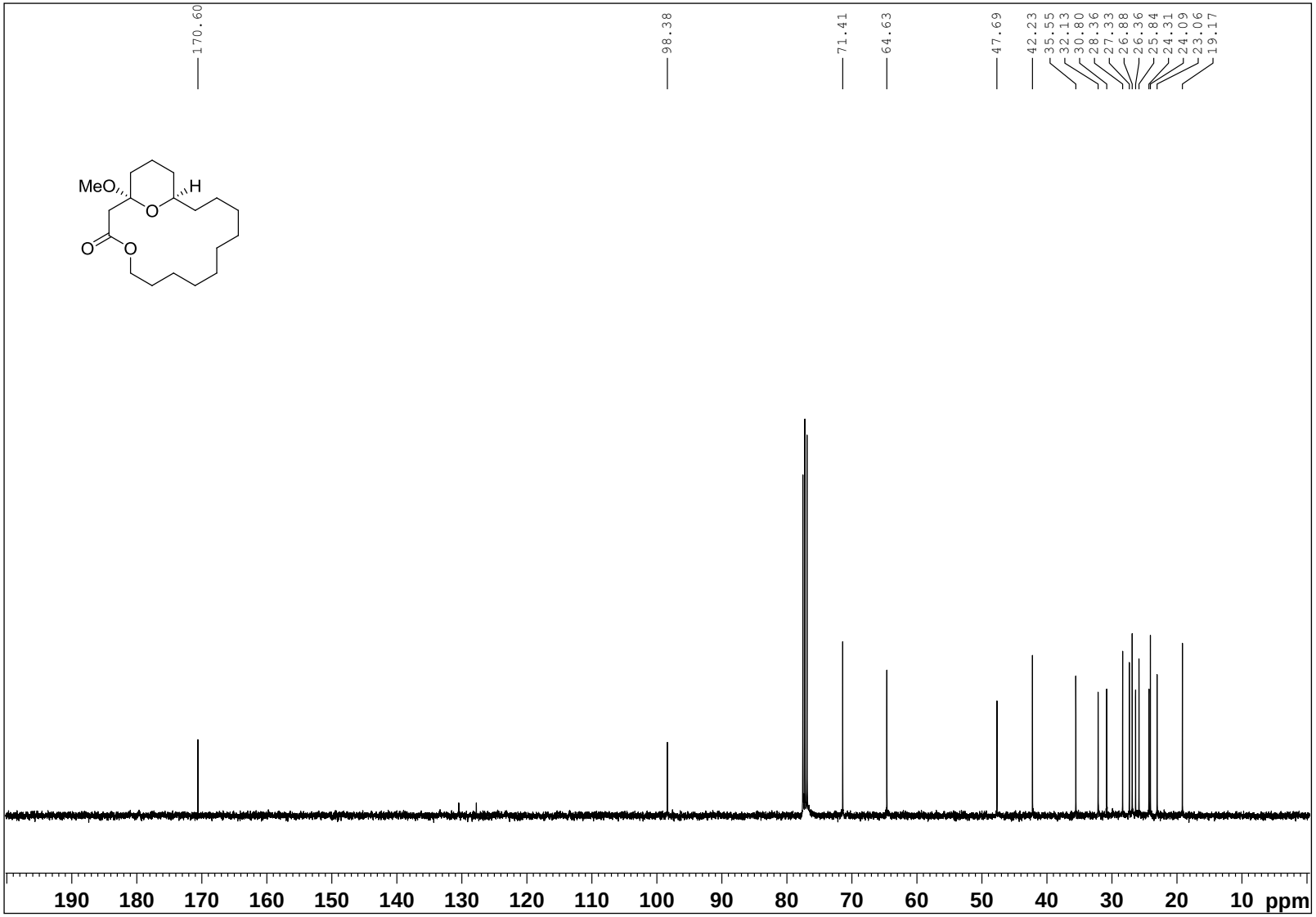
^{13}C NMR (100 MHz, $CDCl_3$)



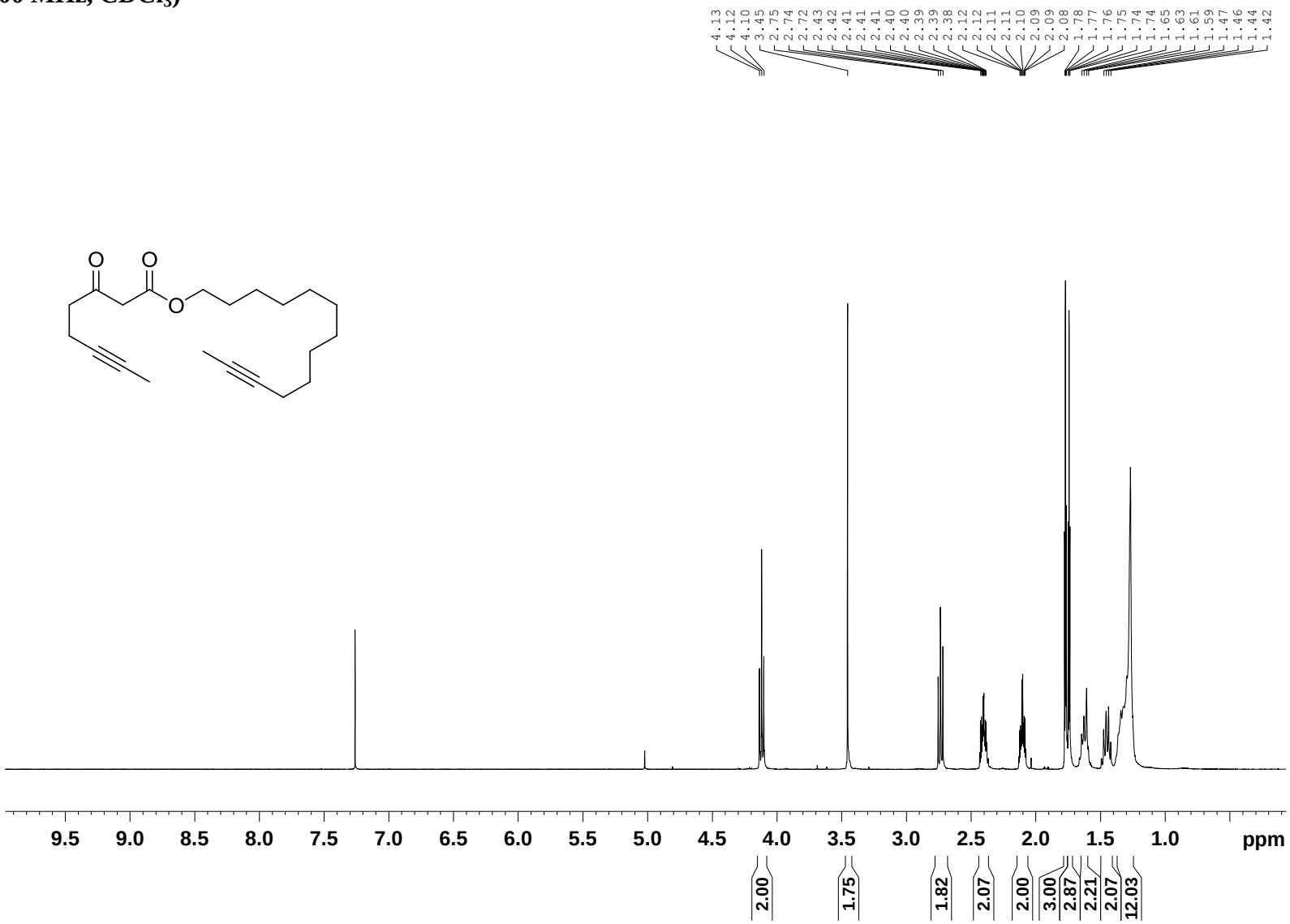
^{1}H NMR (400 MHz, $CDCl_3$)



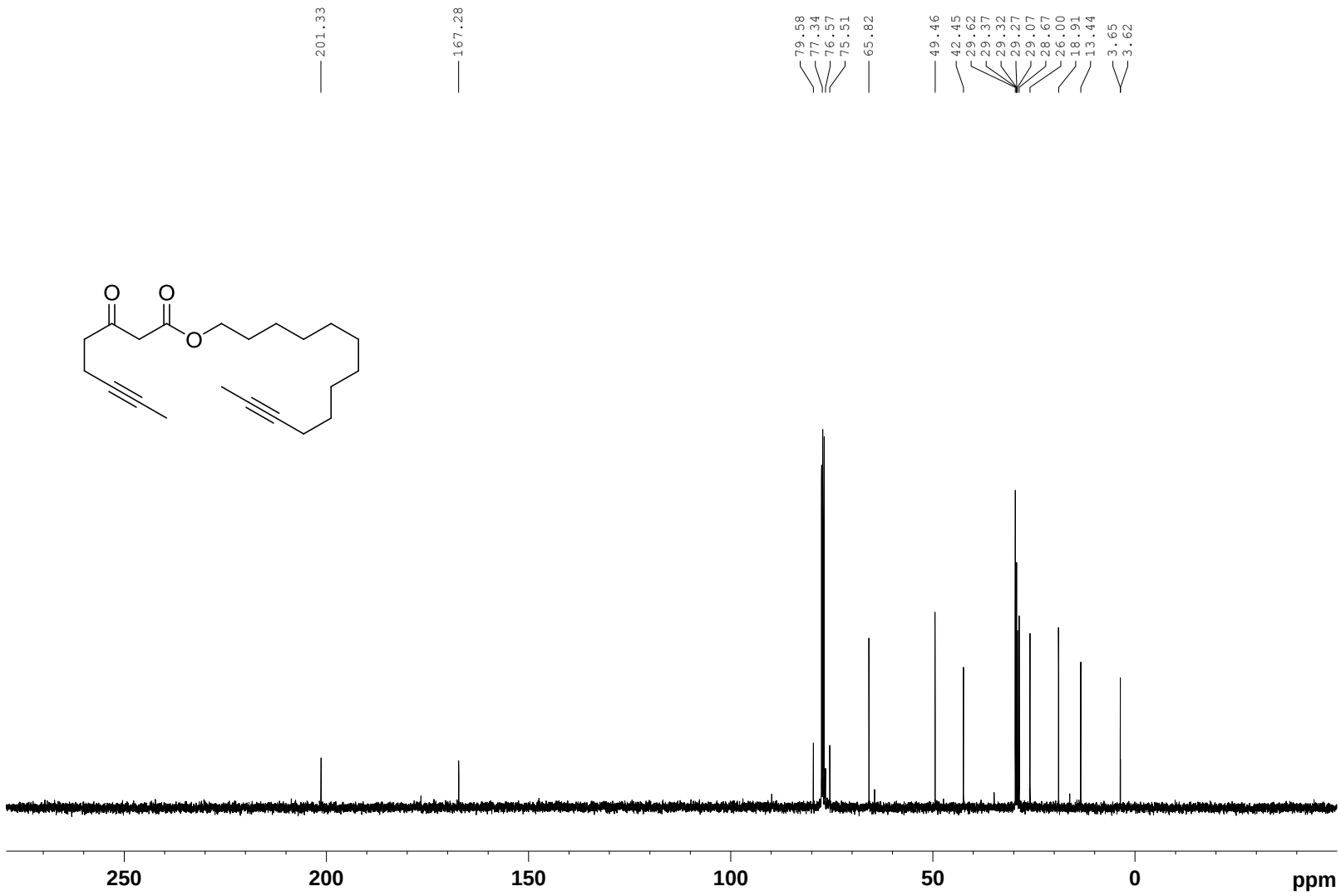
^{13}C NMR (100 MHz, $CDCl_3$)



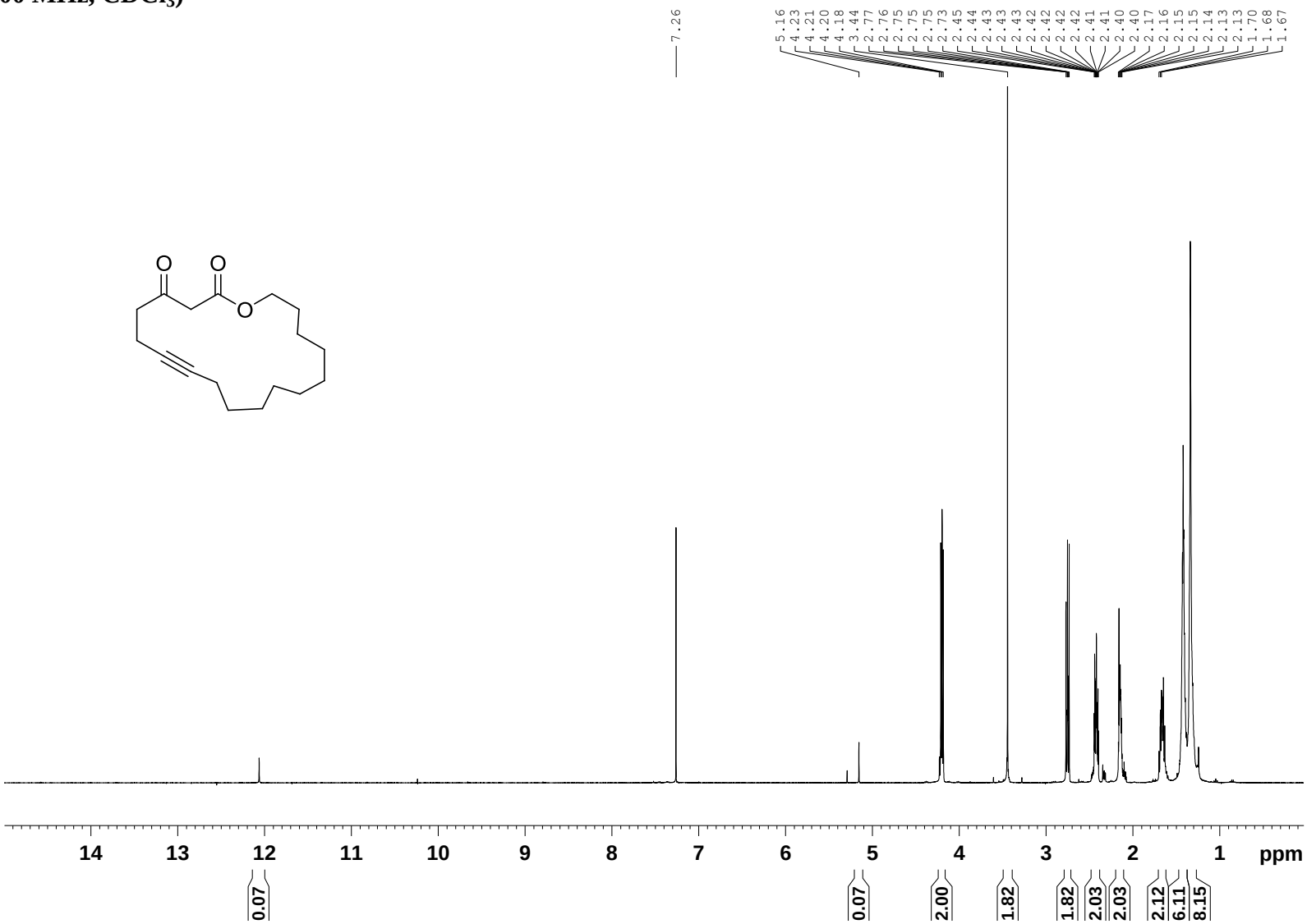
^{1}H NMR (400 MHz, $CDCl_3$)



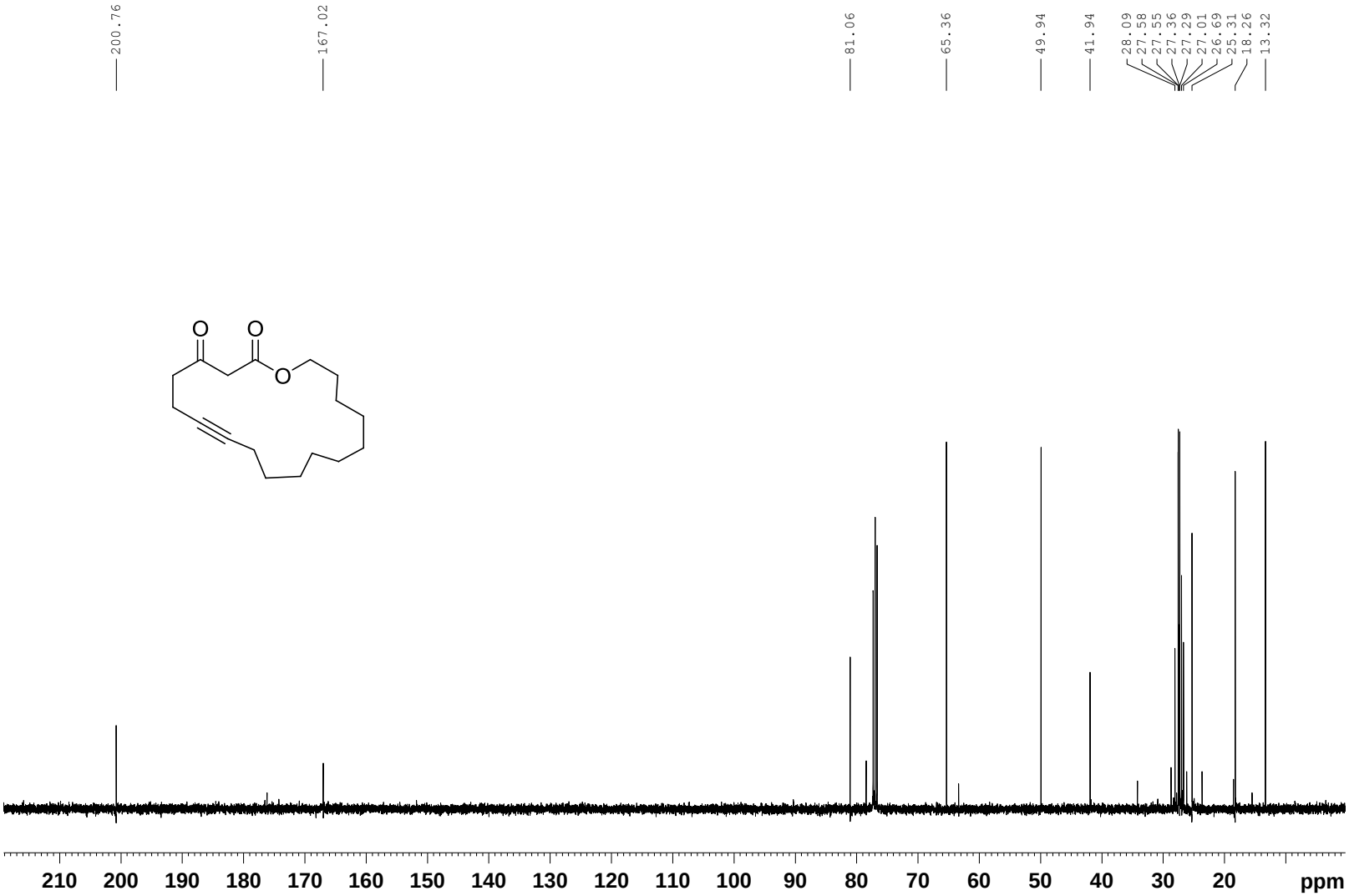
^{13}C NMR (100 MHz, $CDCl_3$)



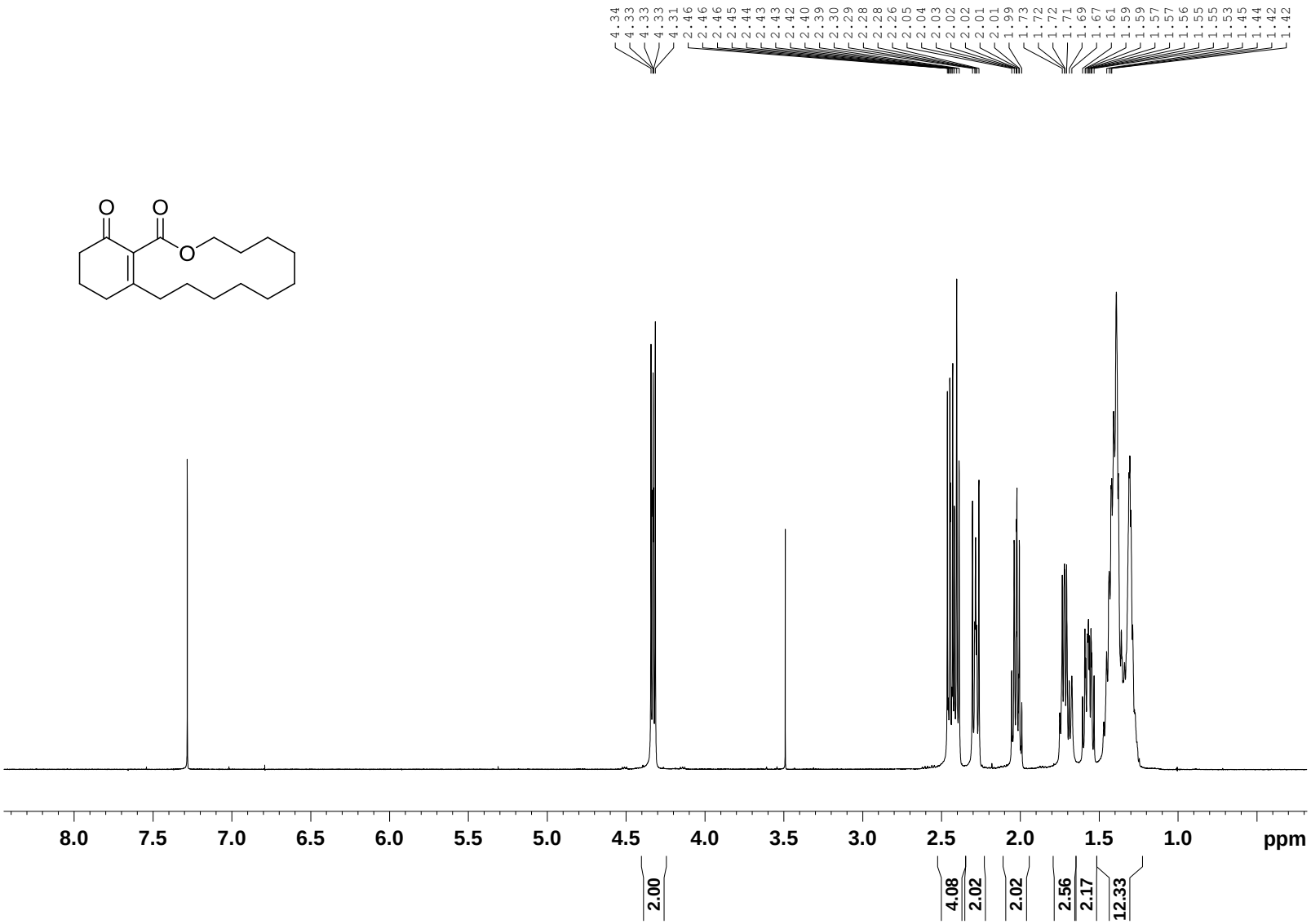
^{1}H NMR (400 MHz, $CDCl_3$)



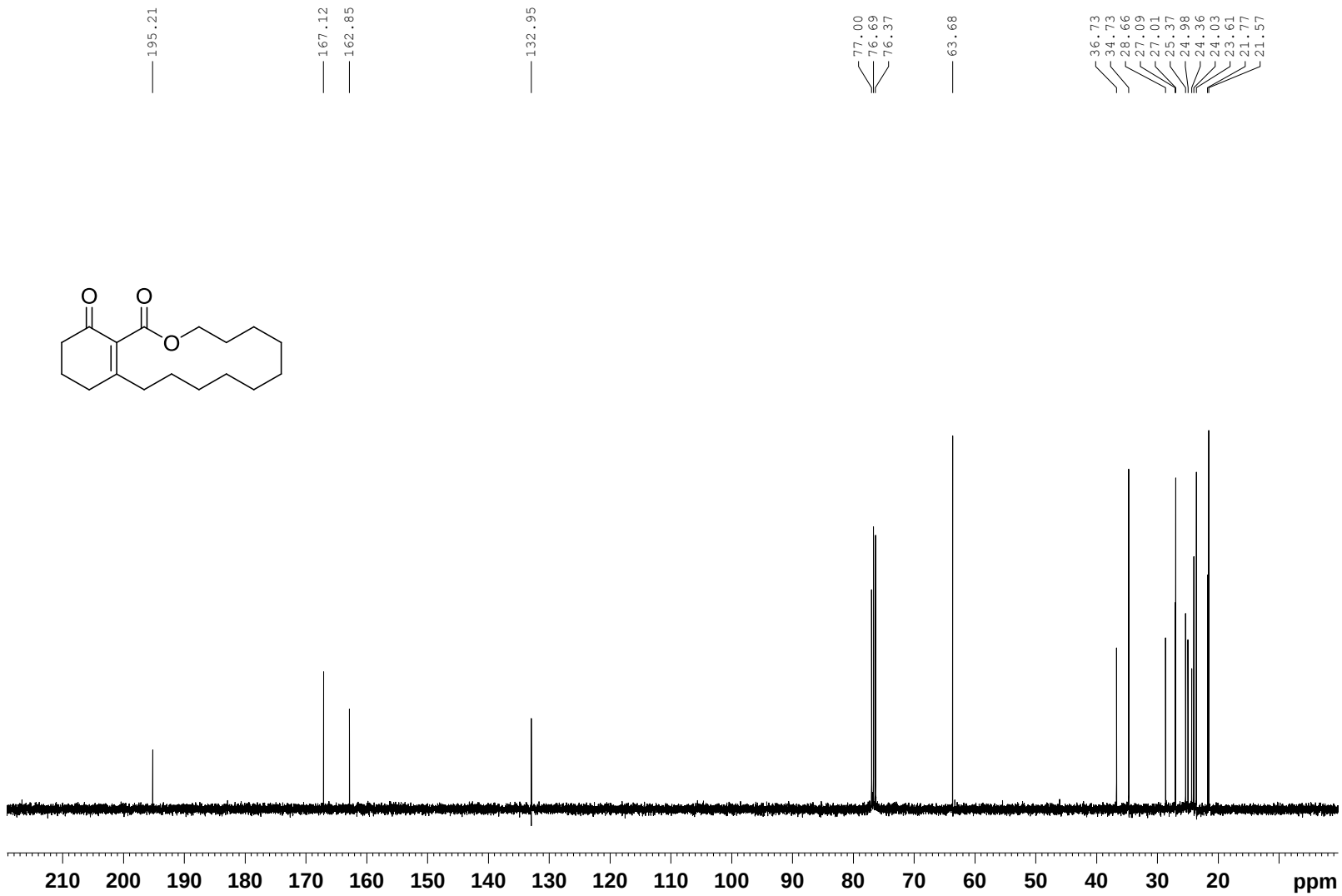
^{13}C NMR (100 MHz, $CDCl_3$)



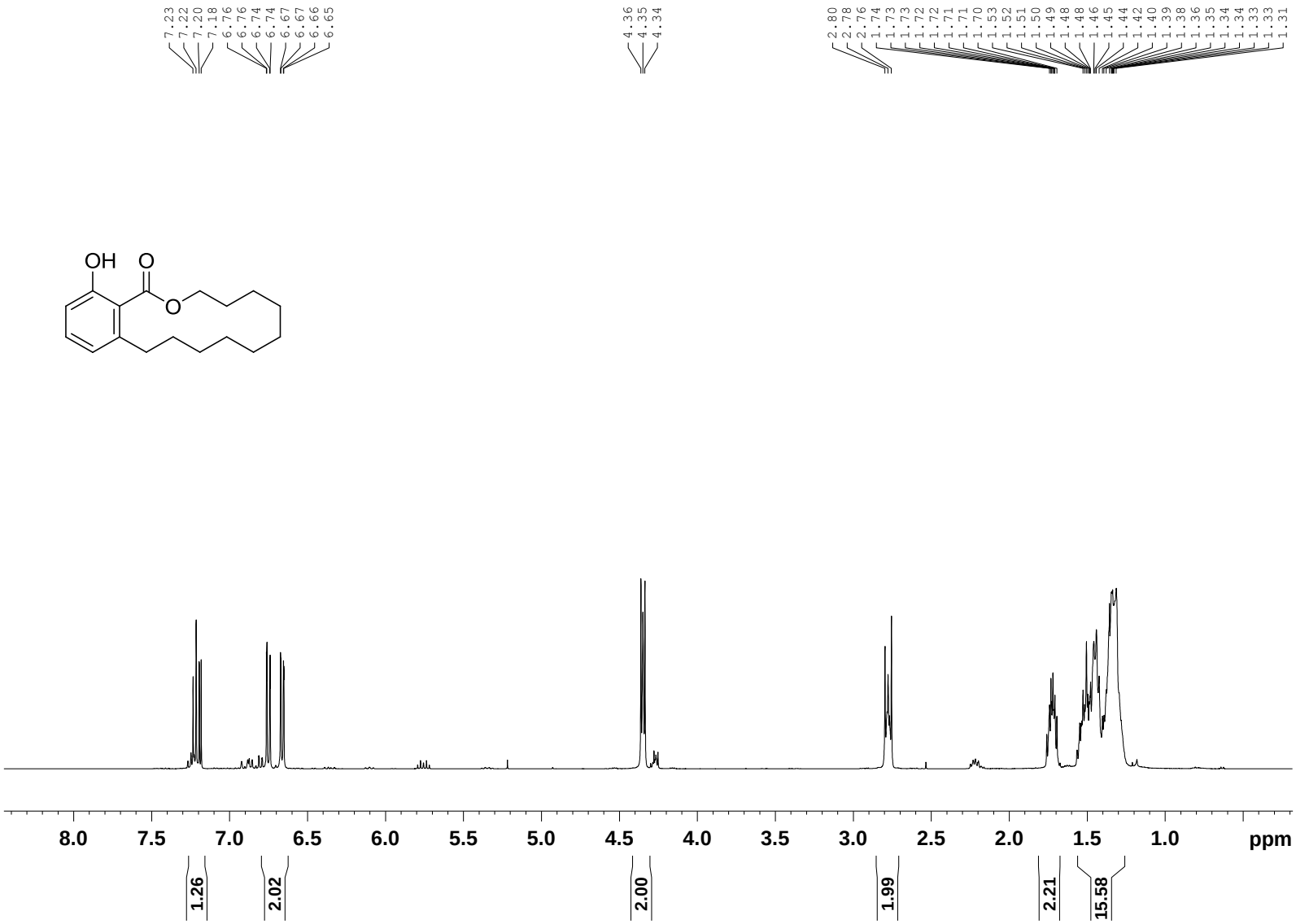
^{1}H NMR (400 MHz, $CDCl_3$)



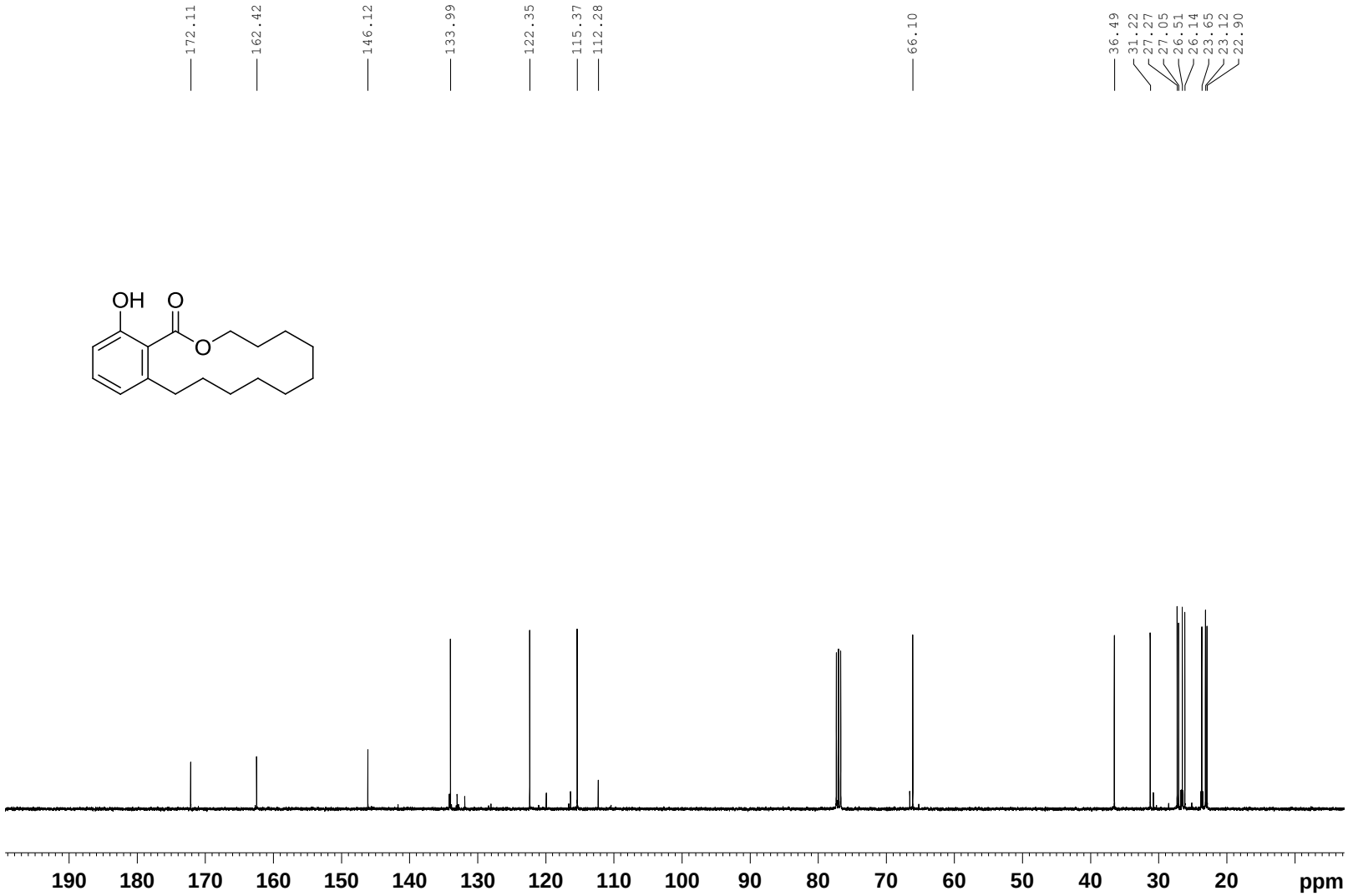
^{13}C NMR (100 MHz, $CDCl_3$)



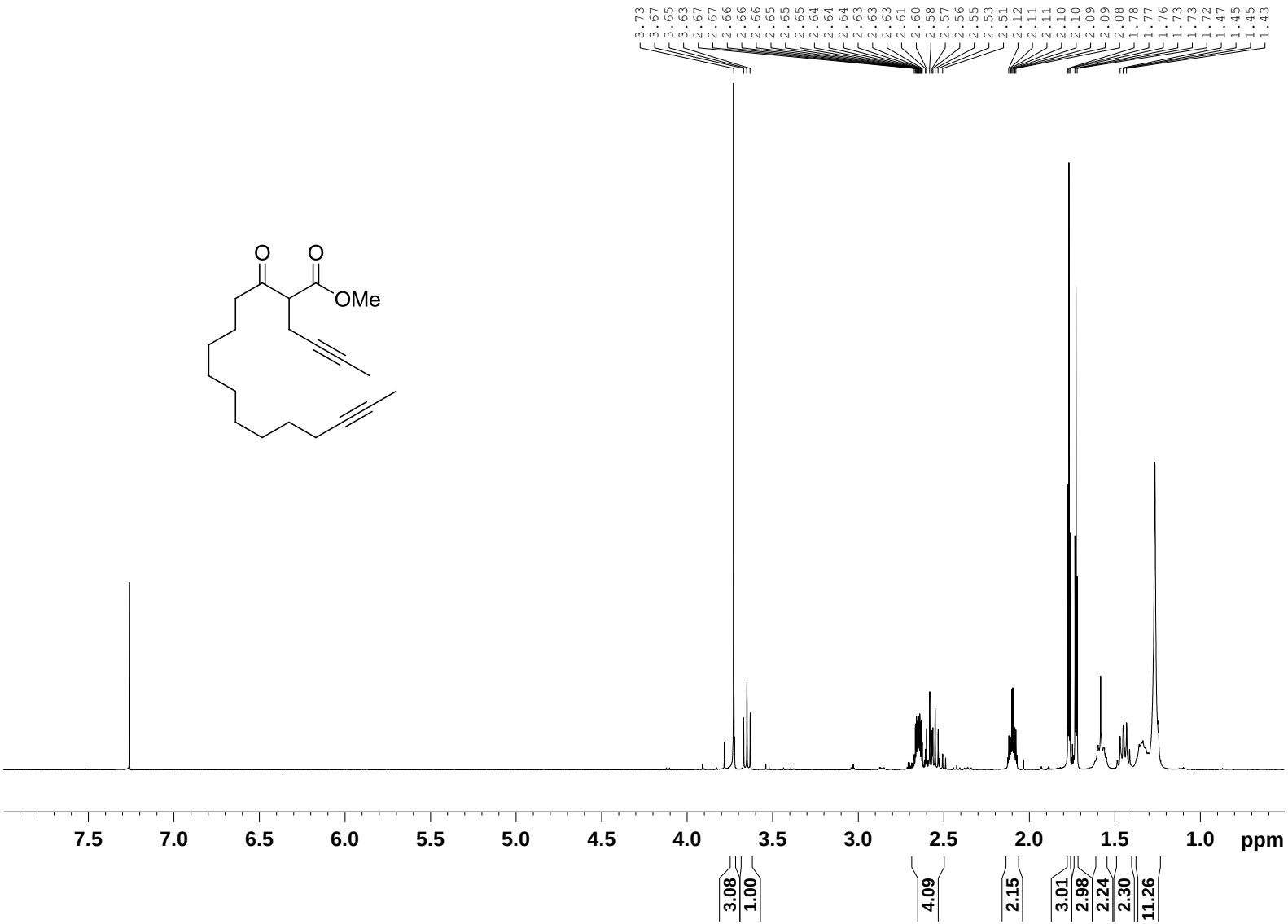
^{1}H NMR (400 MHz, $CDCl_3$)



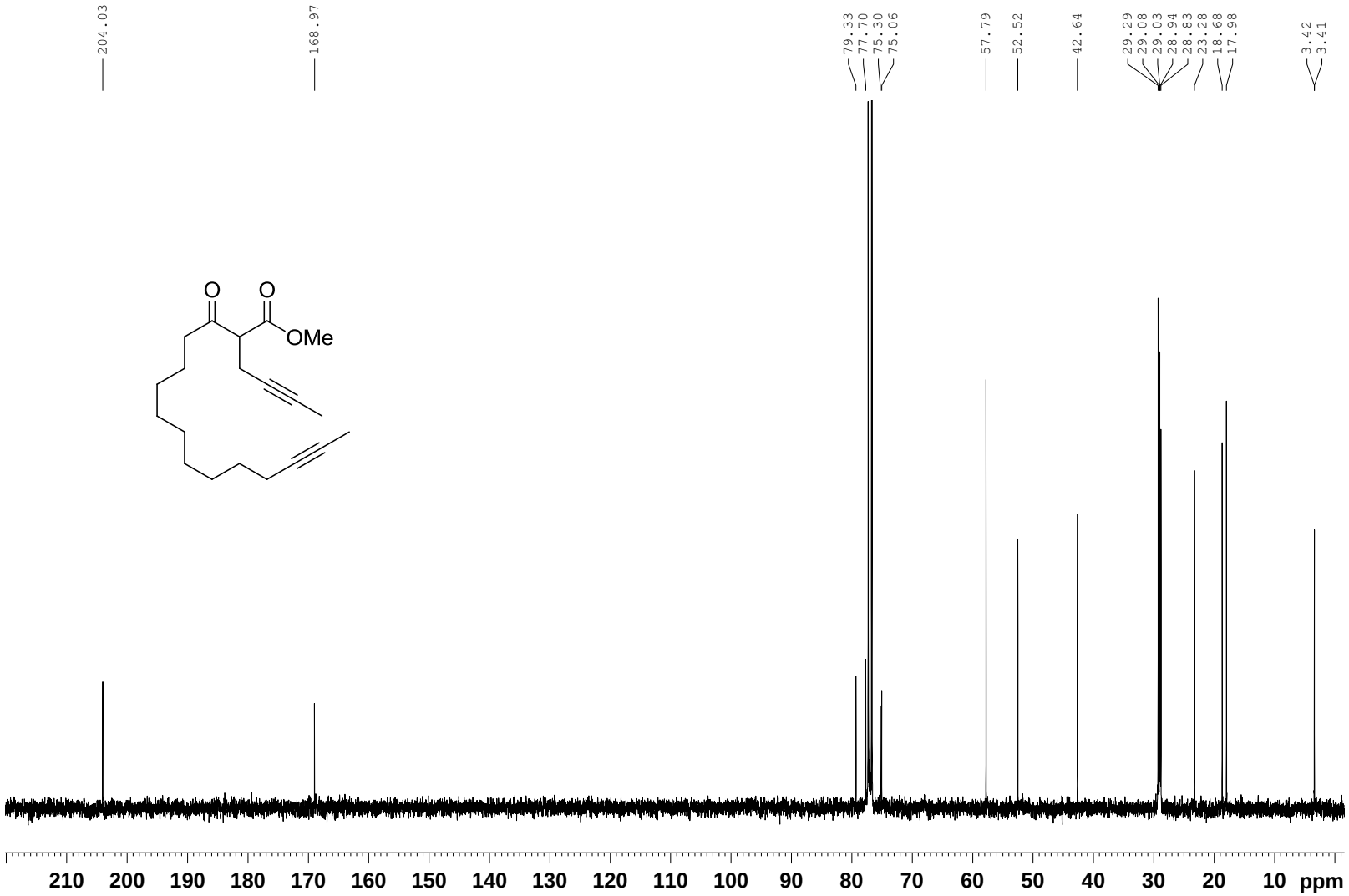
^{13}C NMR (100 MHz, $CDCl_3$)



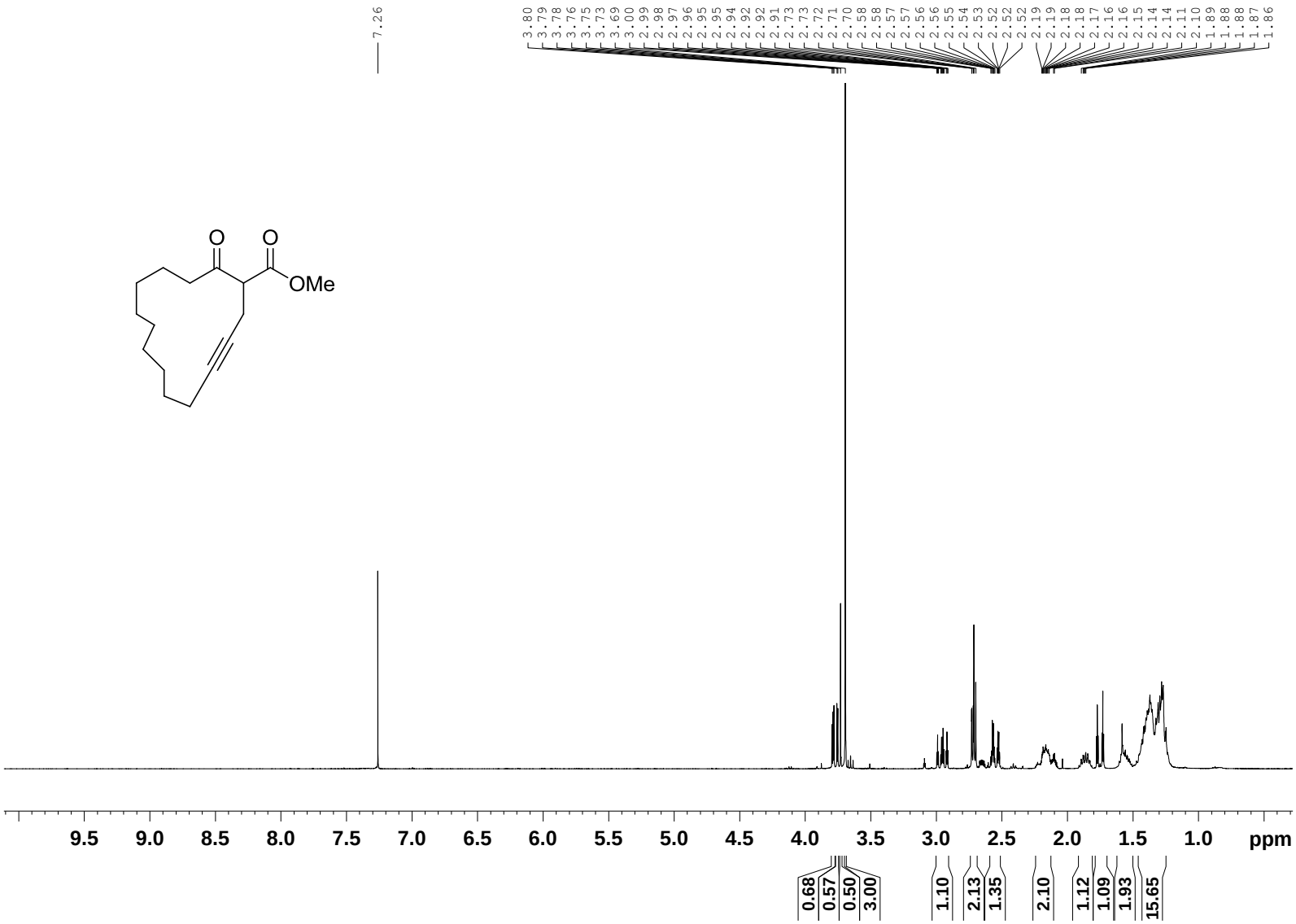
^{1}H NMR (400 MHz, $CDCl_3$)



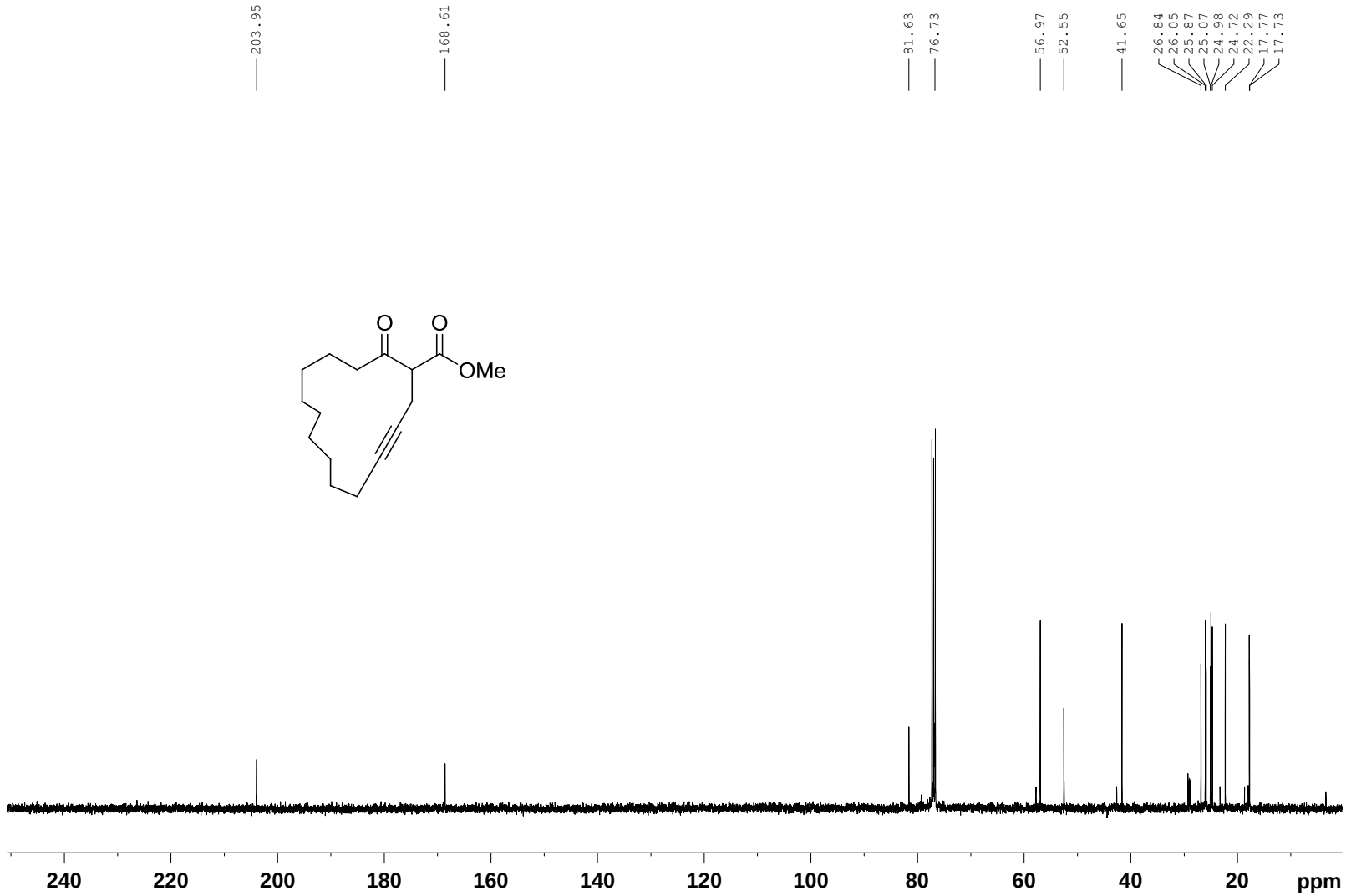
^{13}C NMR (100 MHz, $CDCl_3$)



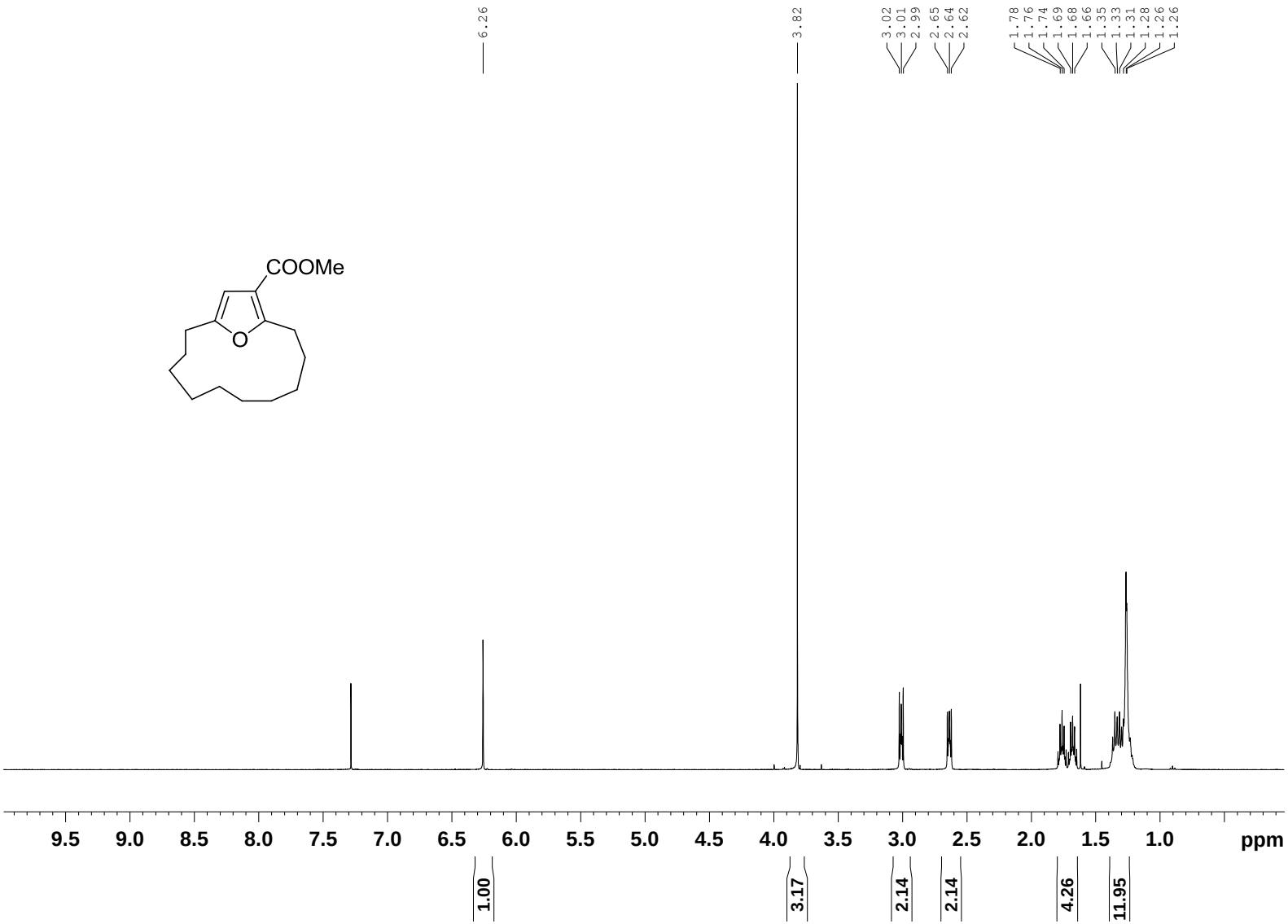
^{1}H NMR (400 MHz, $CDCl_3$)



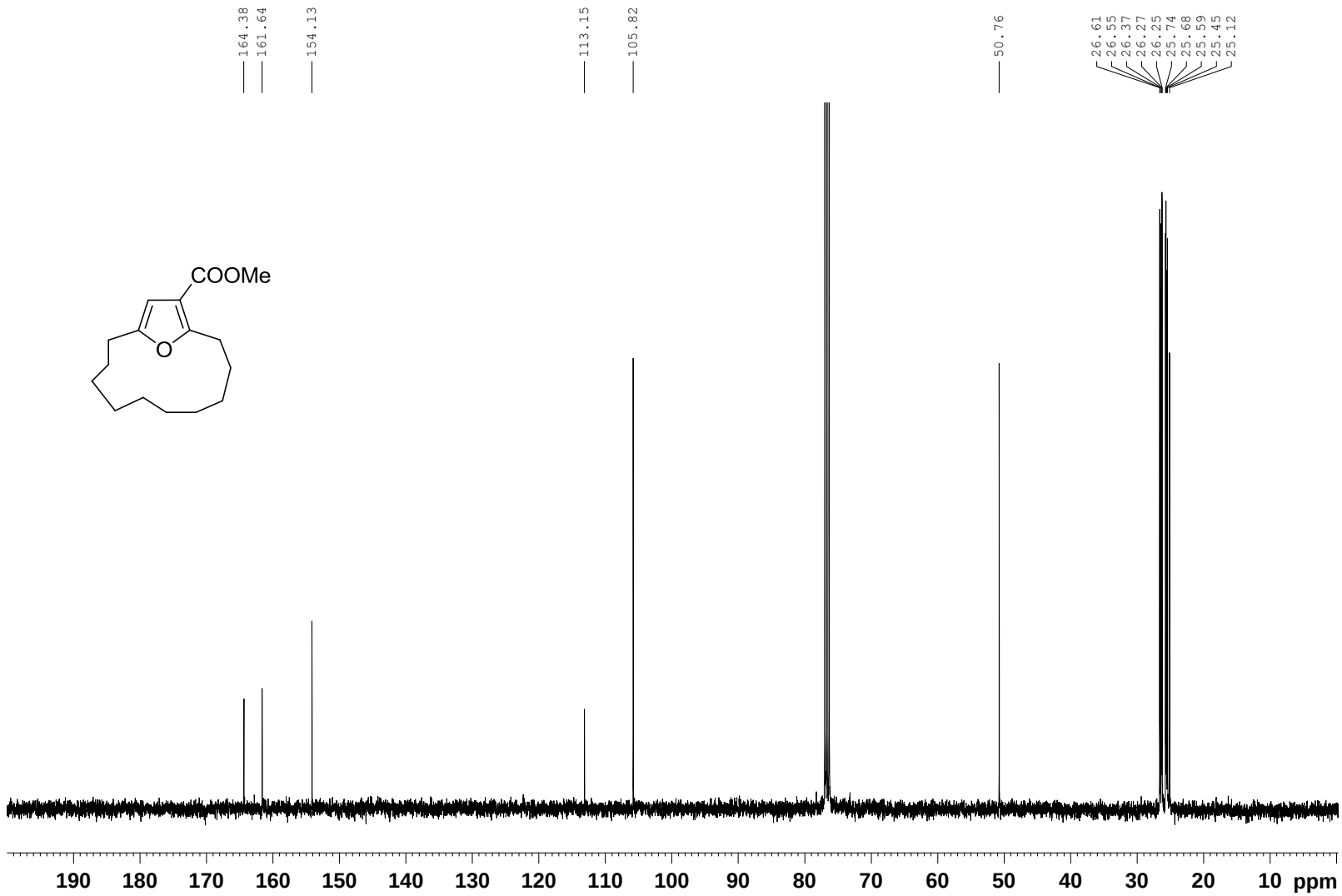
^{13}C NMR (100 MHz, $CDCl_3$)



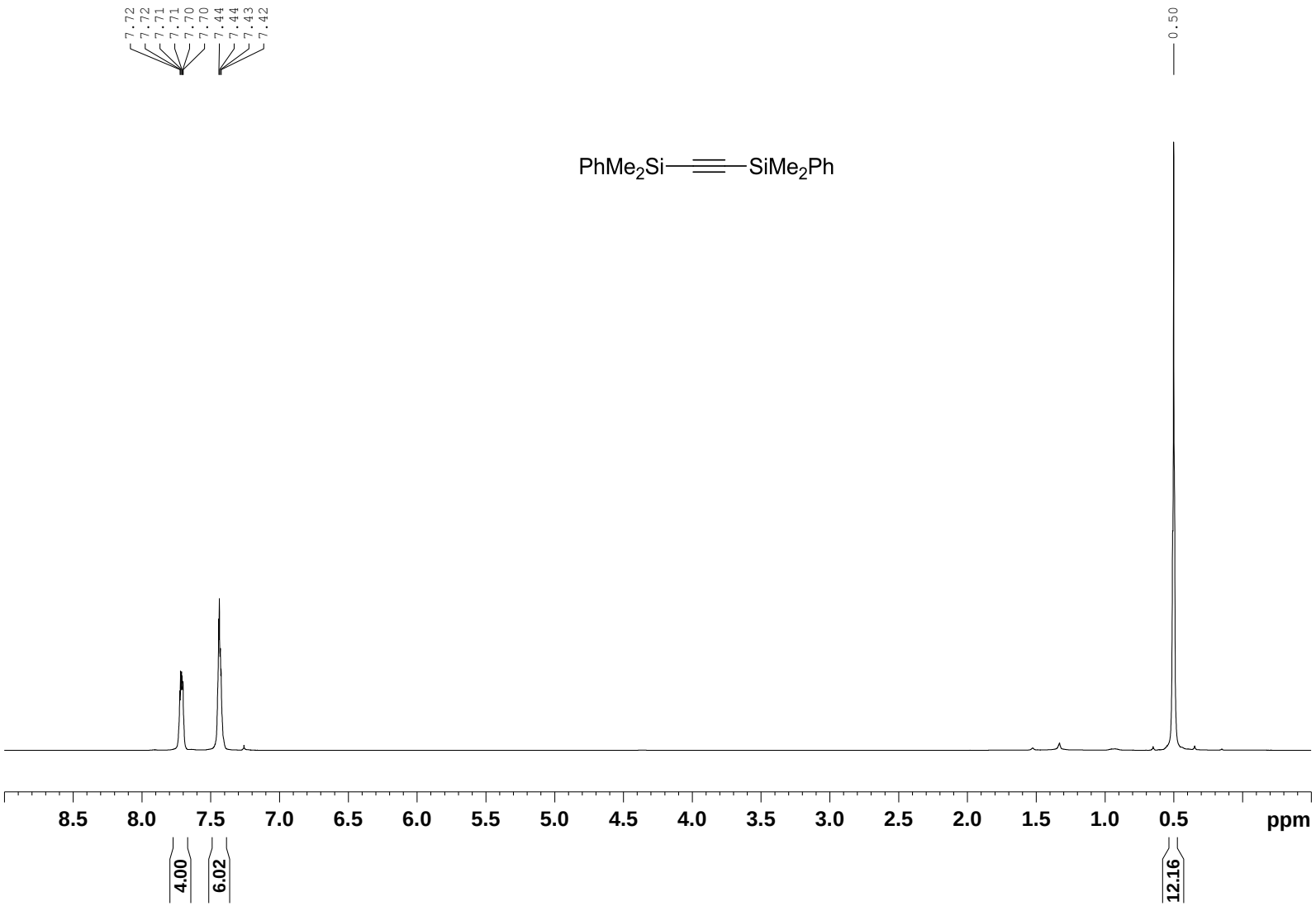
^{1}H NMR (400 MHz, $CDCl_3$)



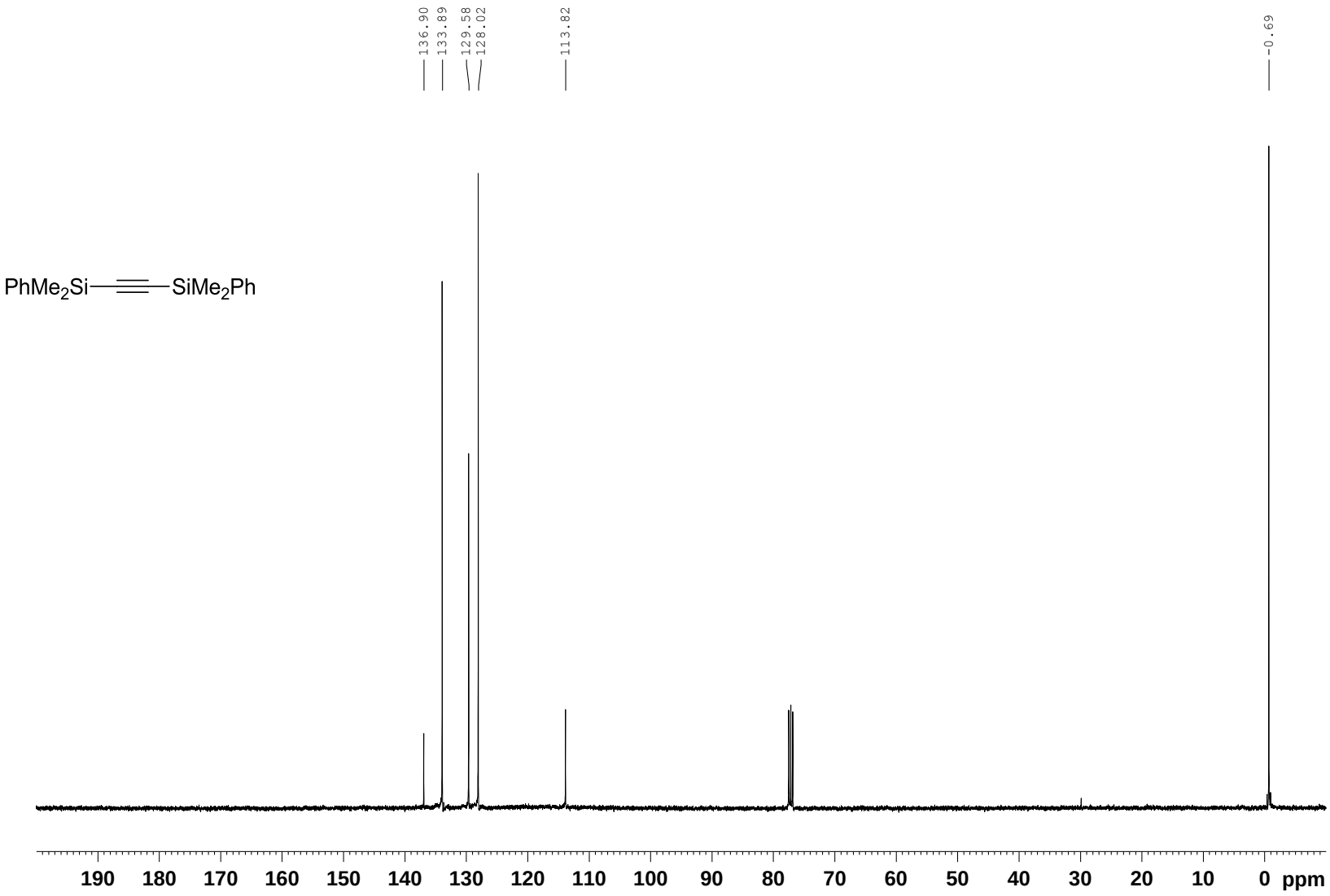
^{13}C NMR (100 MHz, $CDCl_3$)



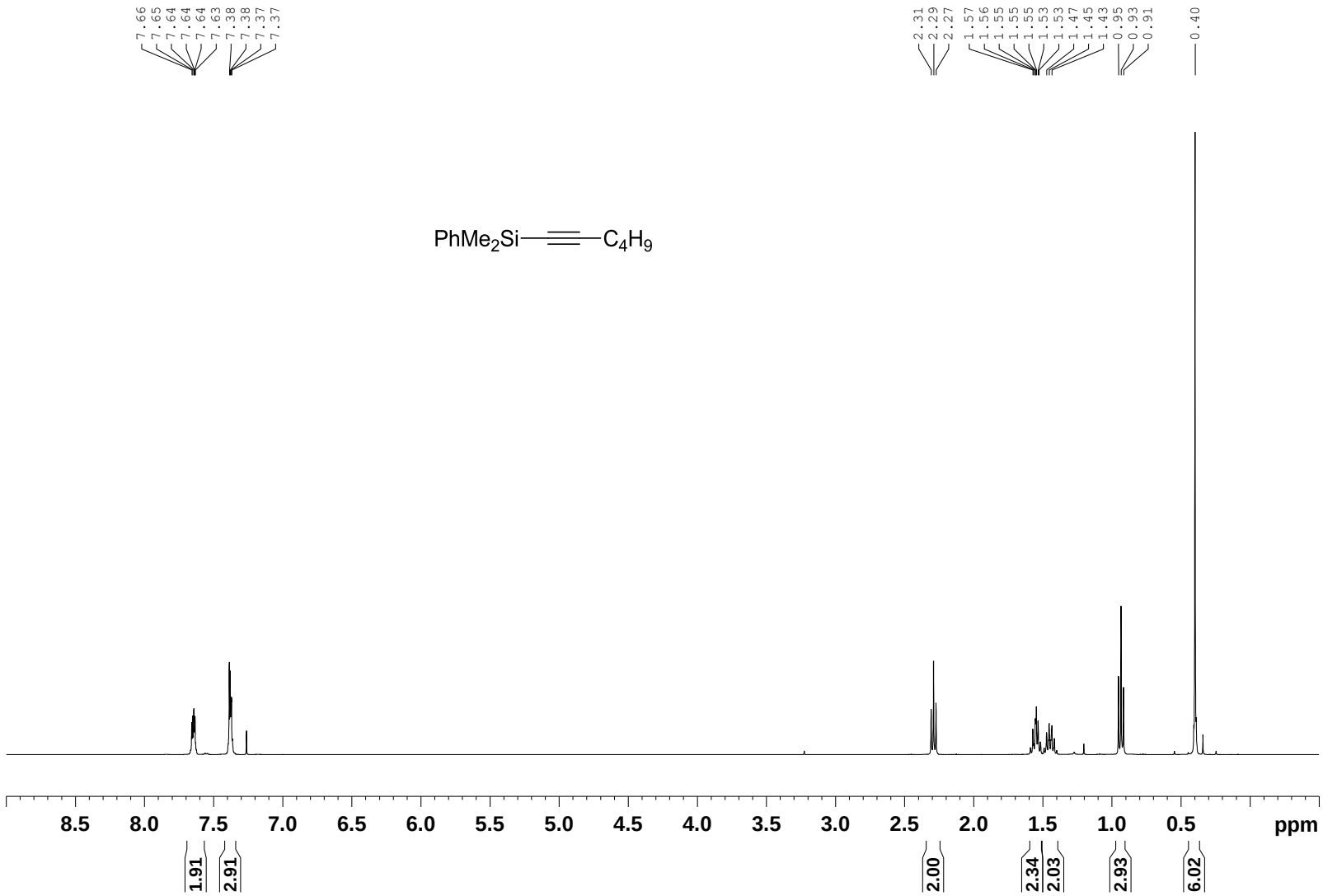
^{1}H NMR (400 MHz, $CDCl_3$)



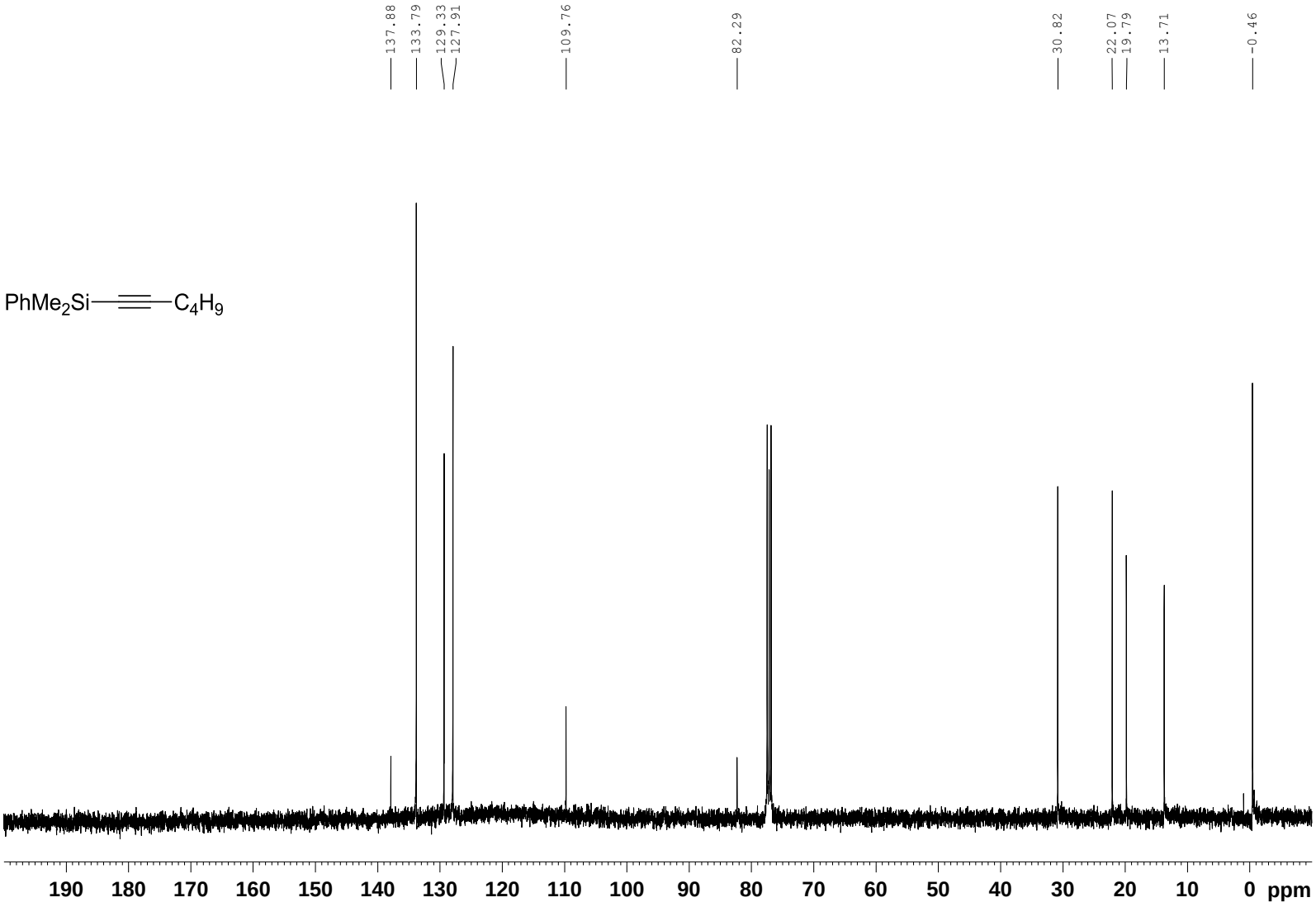
^{13}C NMR (100 MHz, $CDCl_3$)



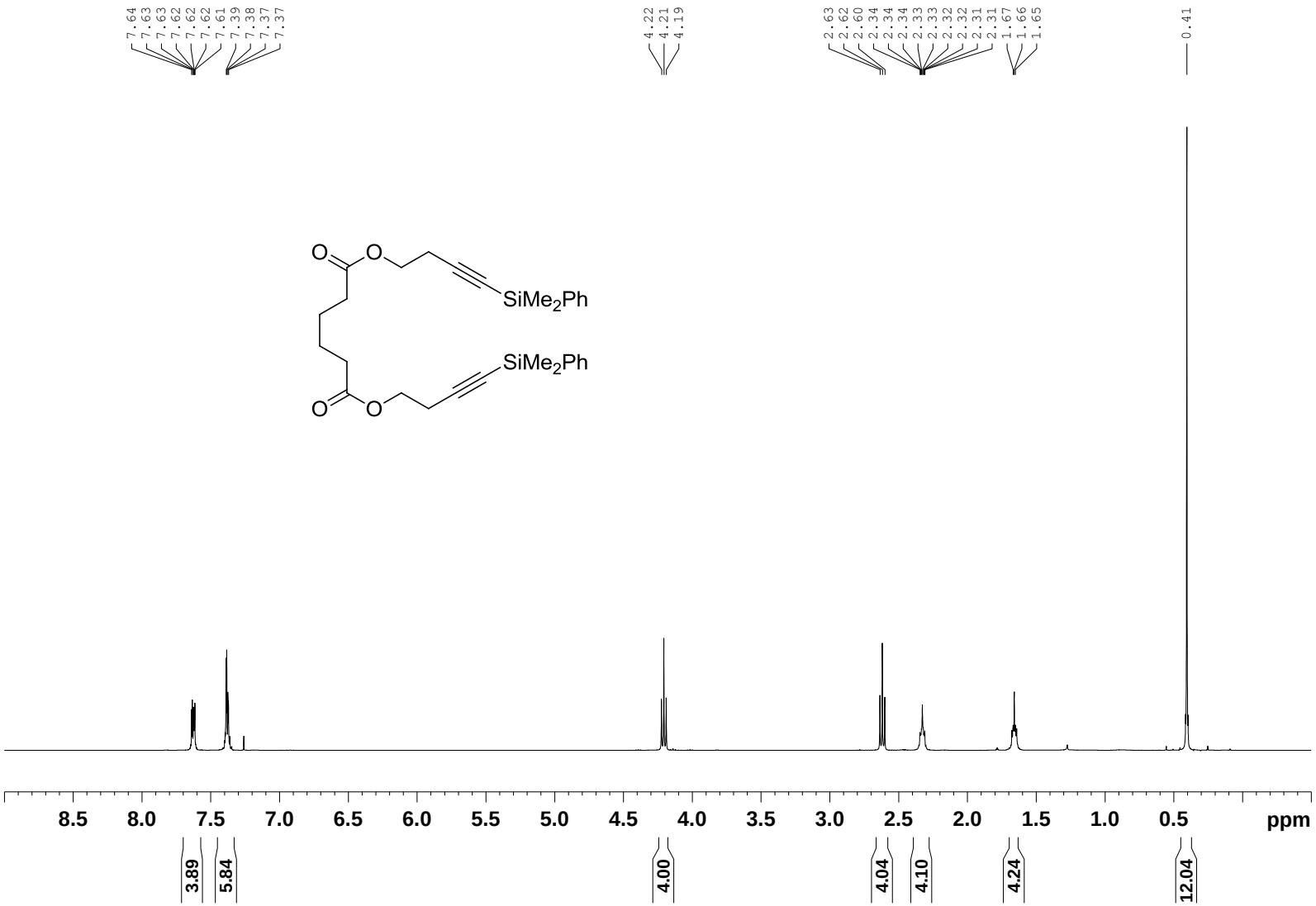
^{1}H NMR (400 MHz, $CDCl_3$)



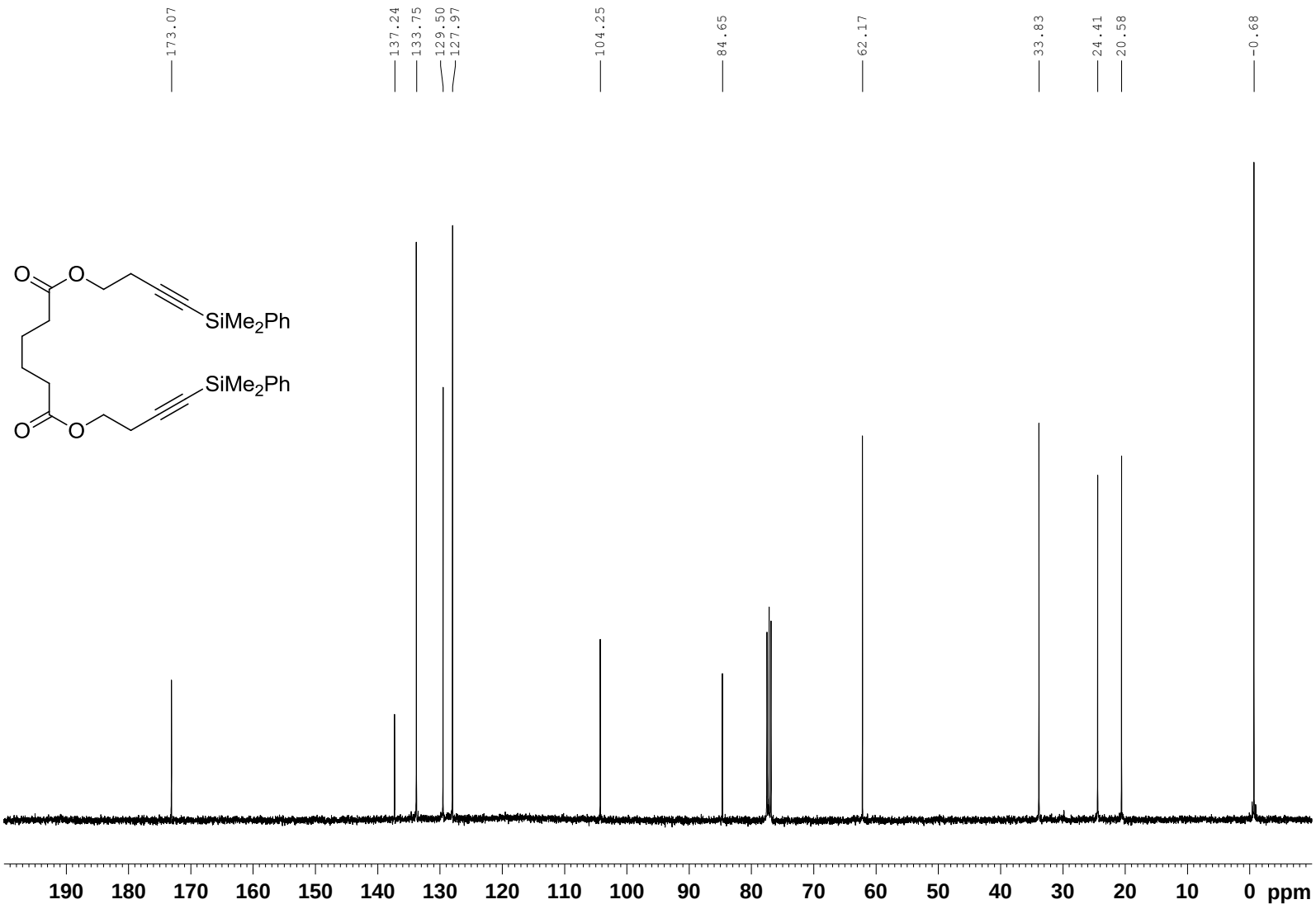
^{13}C NMR (100 MHz, $CDCl_3$)



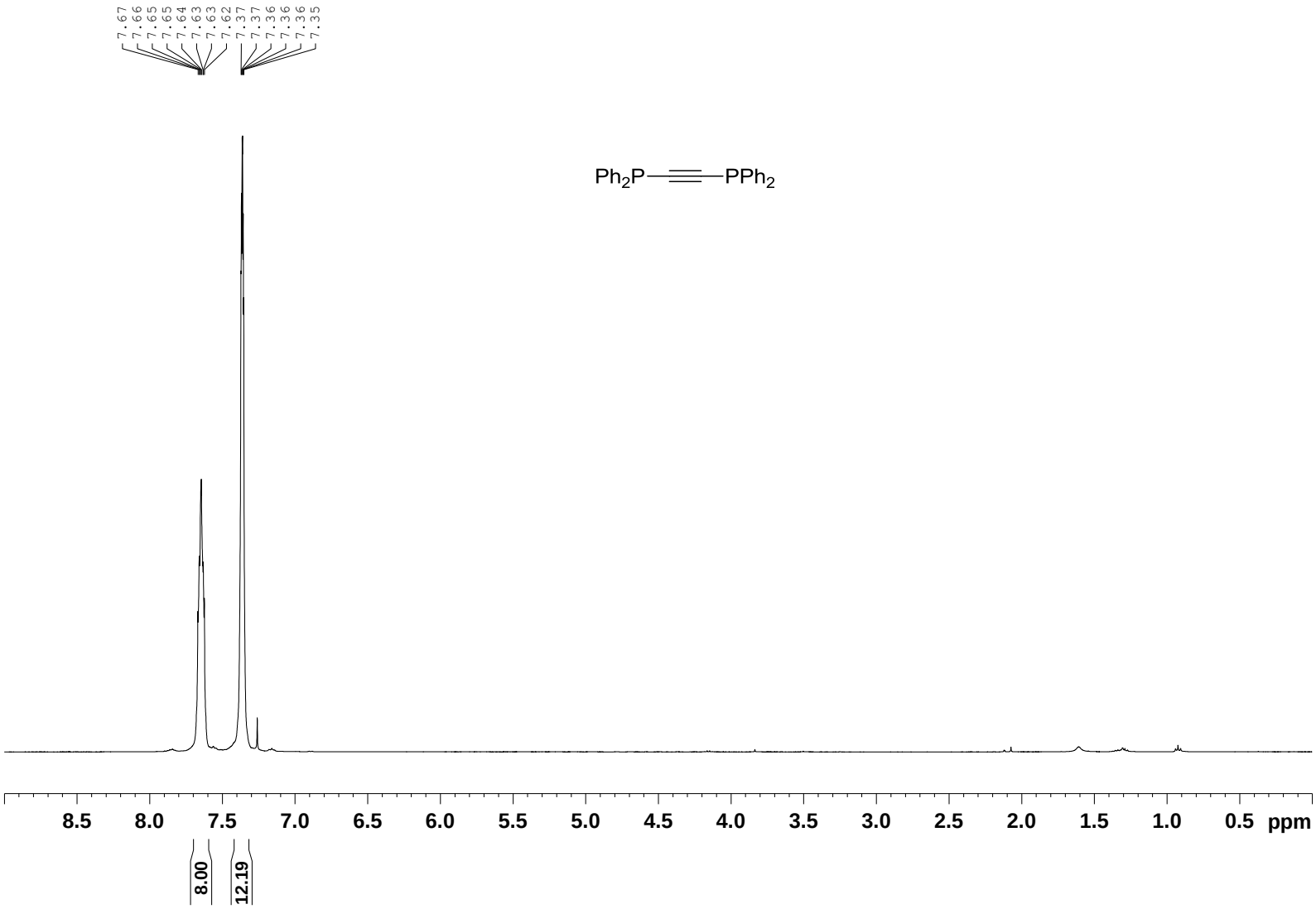
^{1}H NMR (400 MHz, $CDCl_3$)



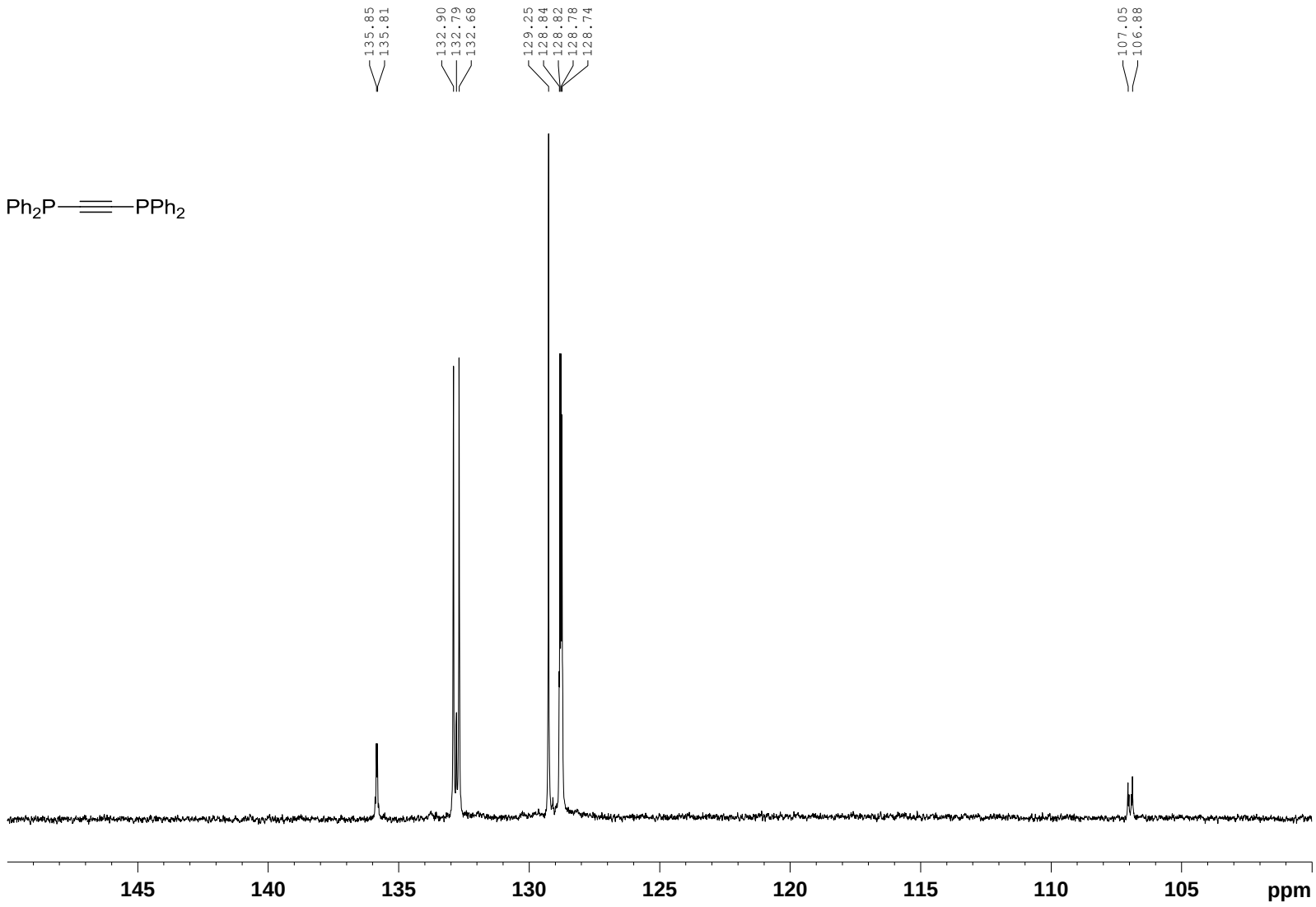
^{13}C NMR (100 MHz, $CDCl_3$)



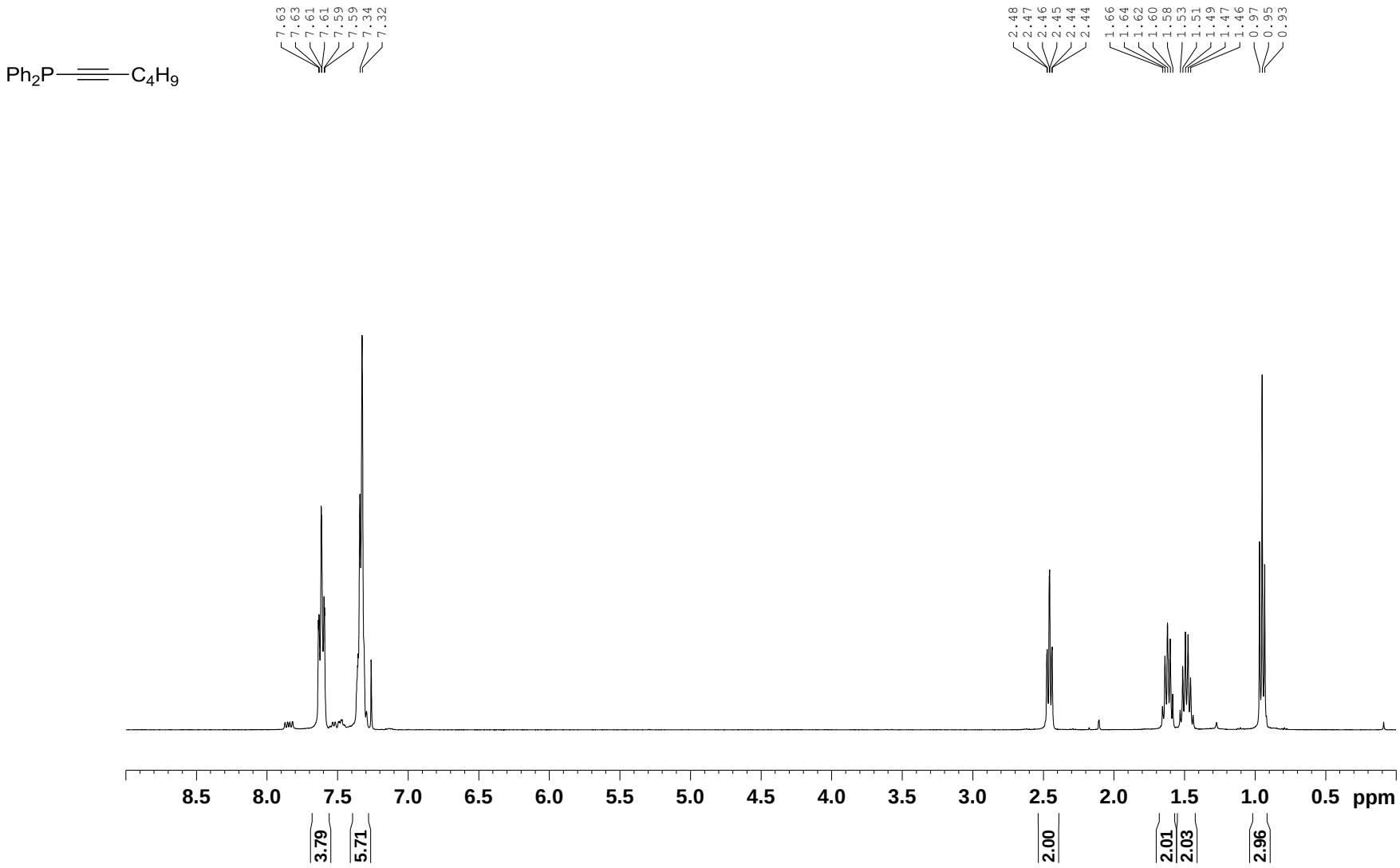
^{1}H NMR (400 MHz, $CDCl_3$)



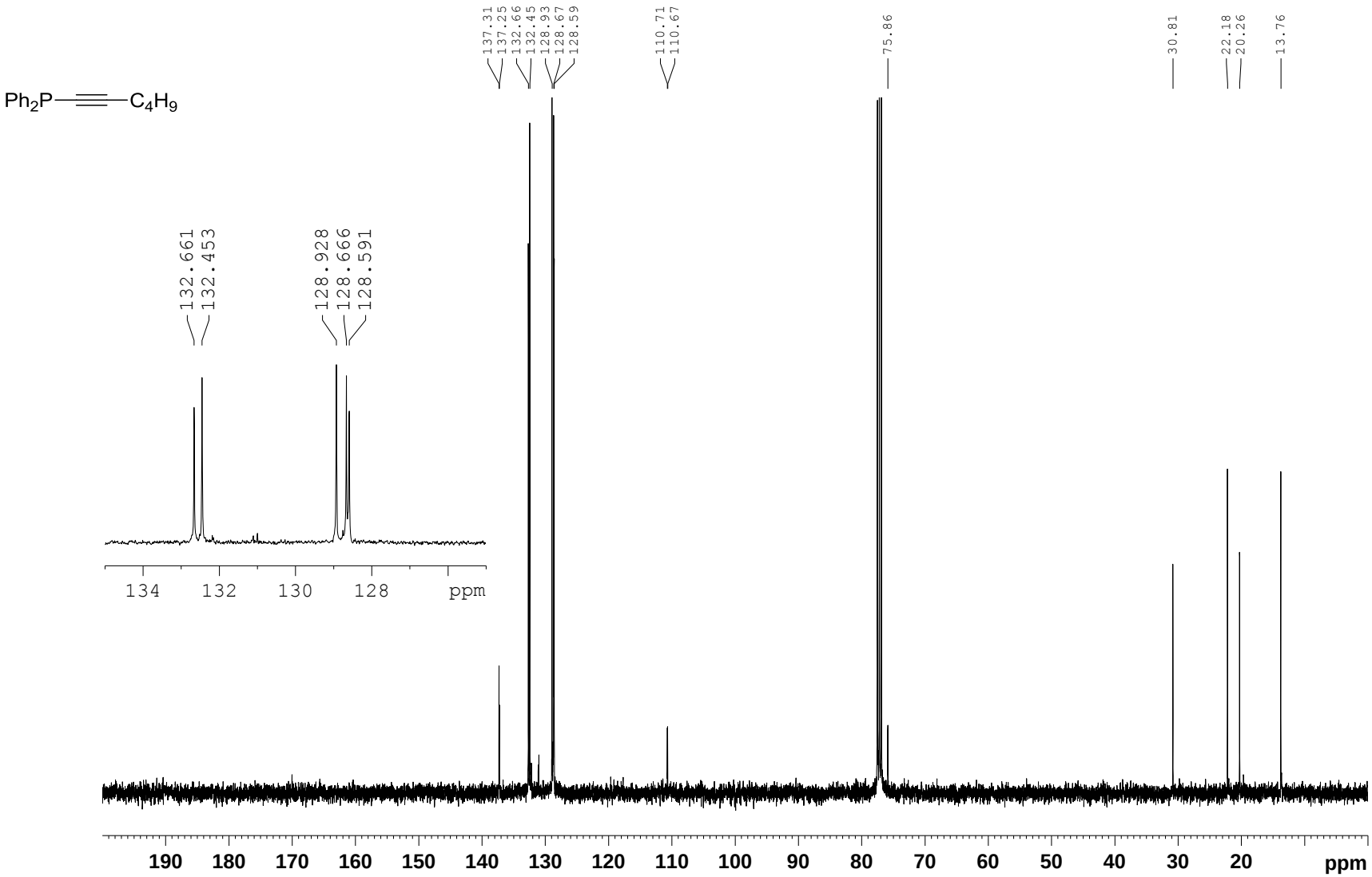
^{13}C NMR (100 MHz, $CDCl_3$)



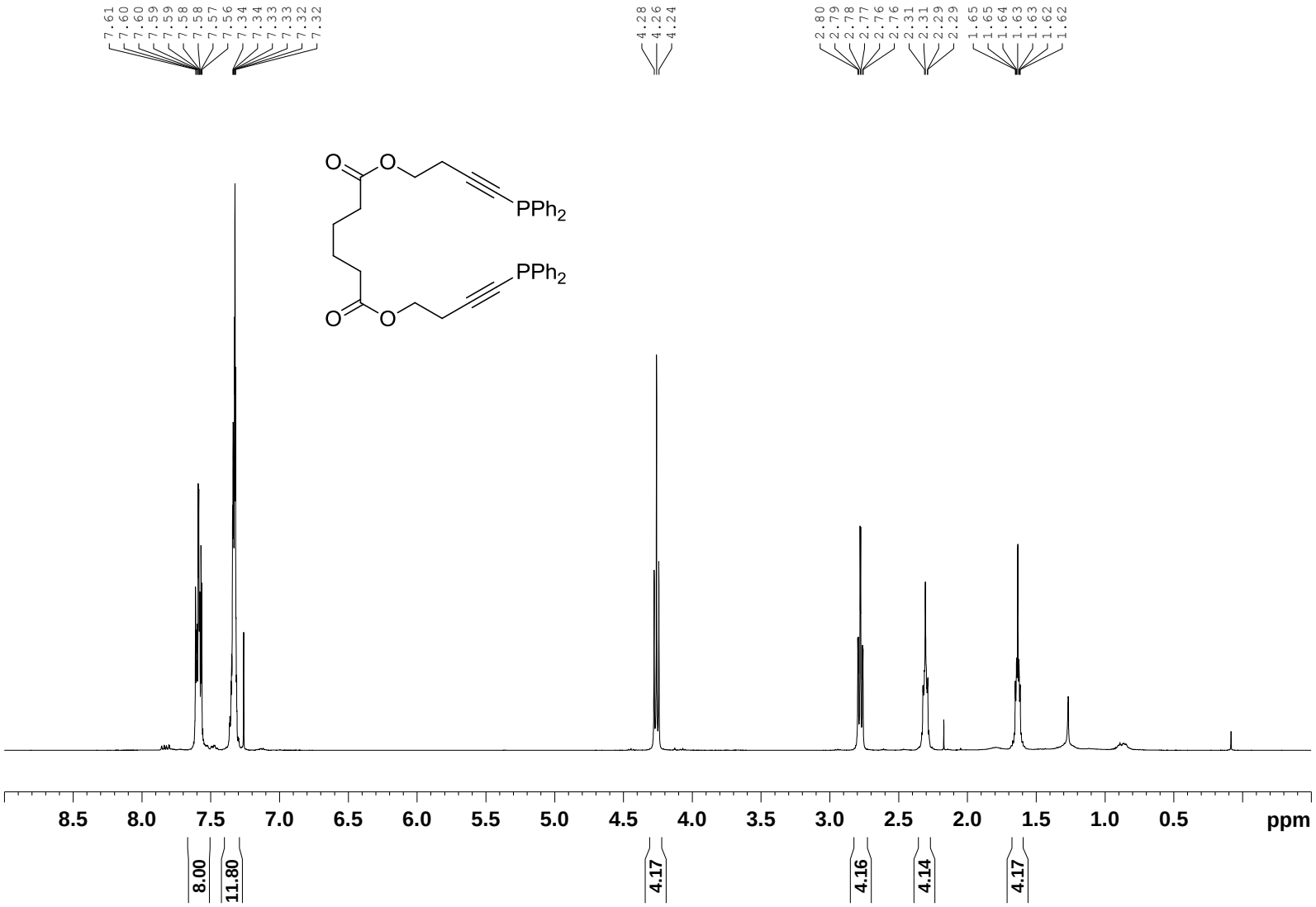
^{1}H NMR (400 MHz, $CDCl_3$) (contains traces of the corresponding phosphine oxide formed during work up)



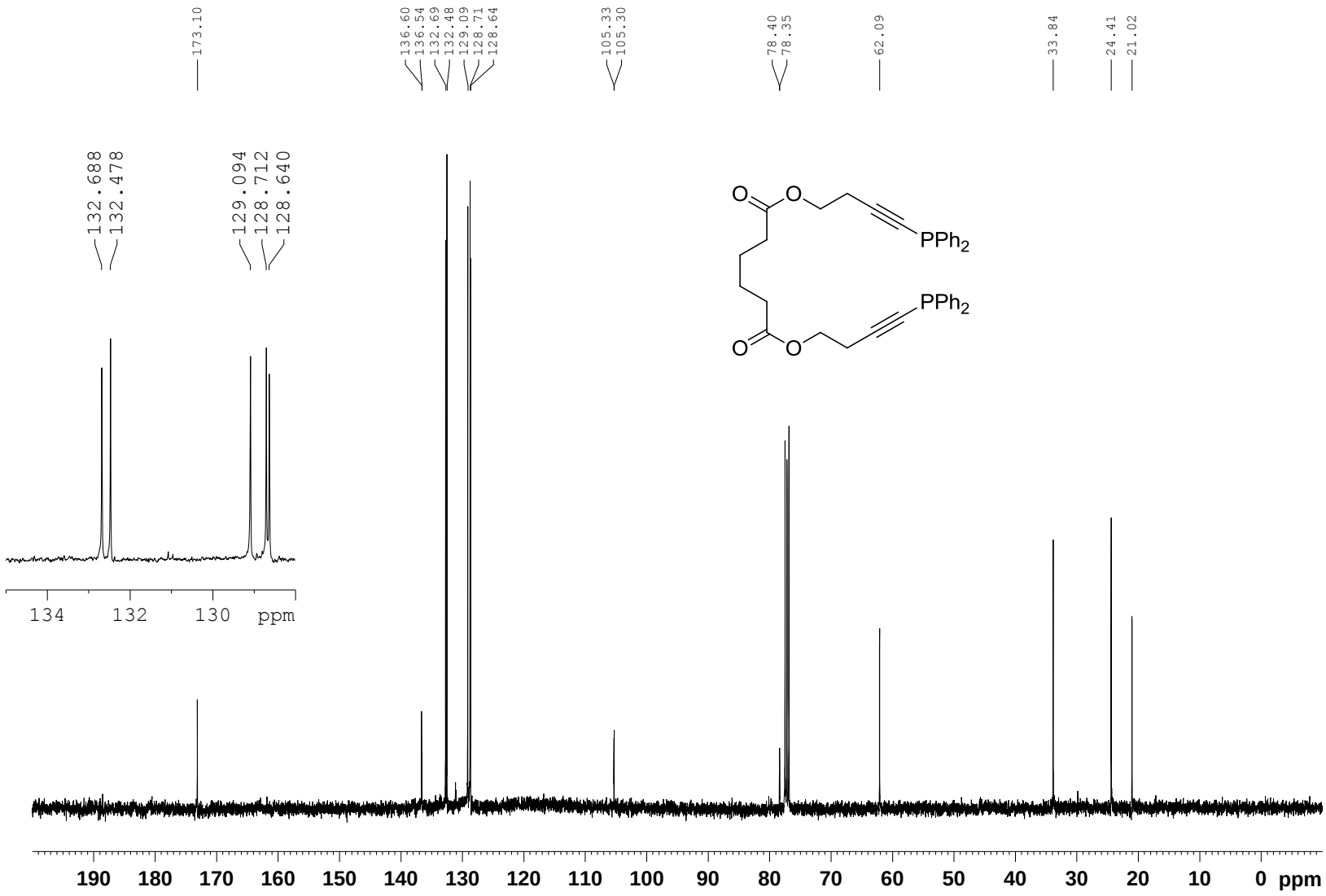
^{13}C NMR (100 MHz, $CDCl_3$) (contains traces of the corresponding phosphine oxide formed during work up)



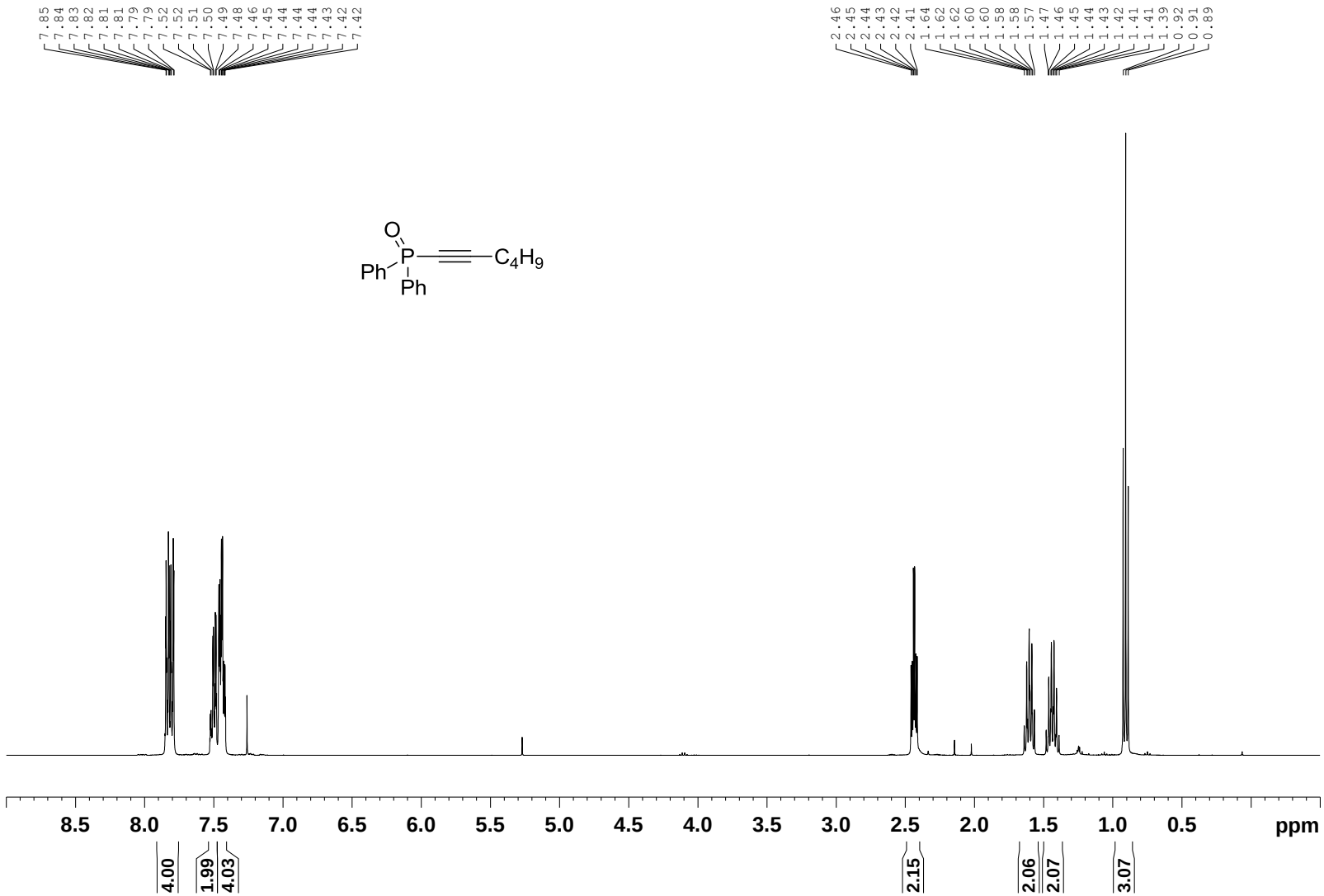
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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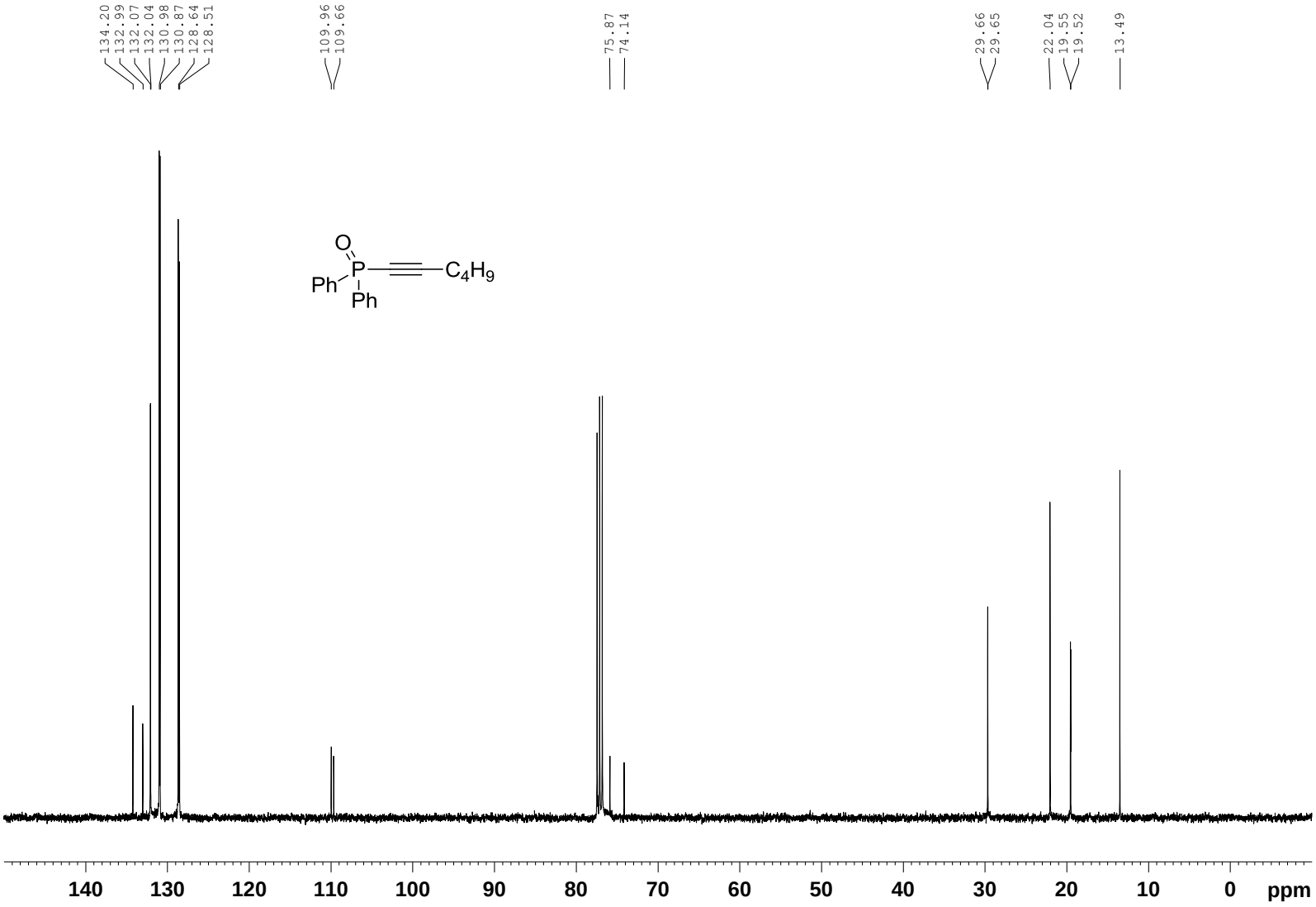

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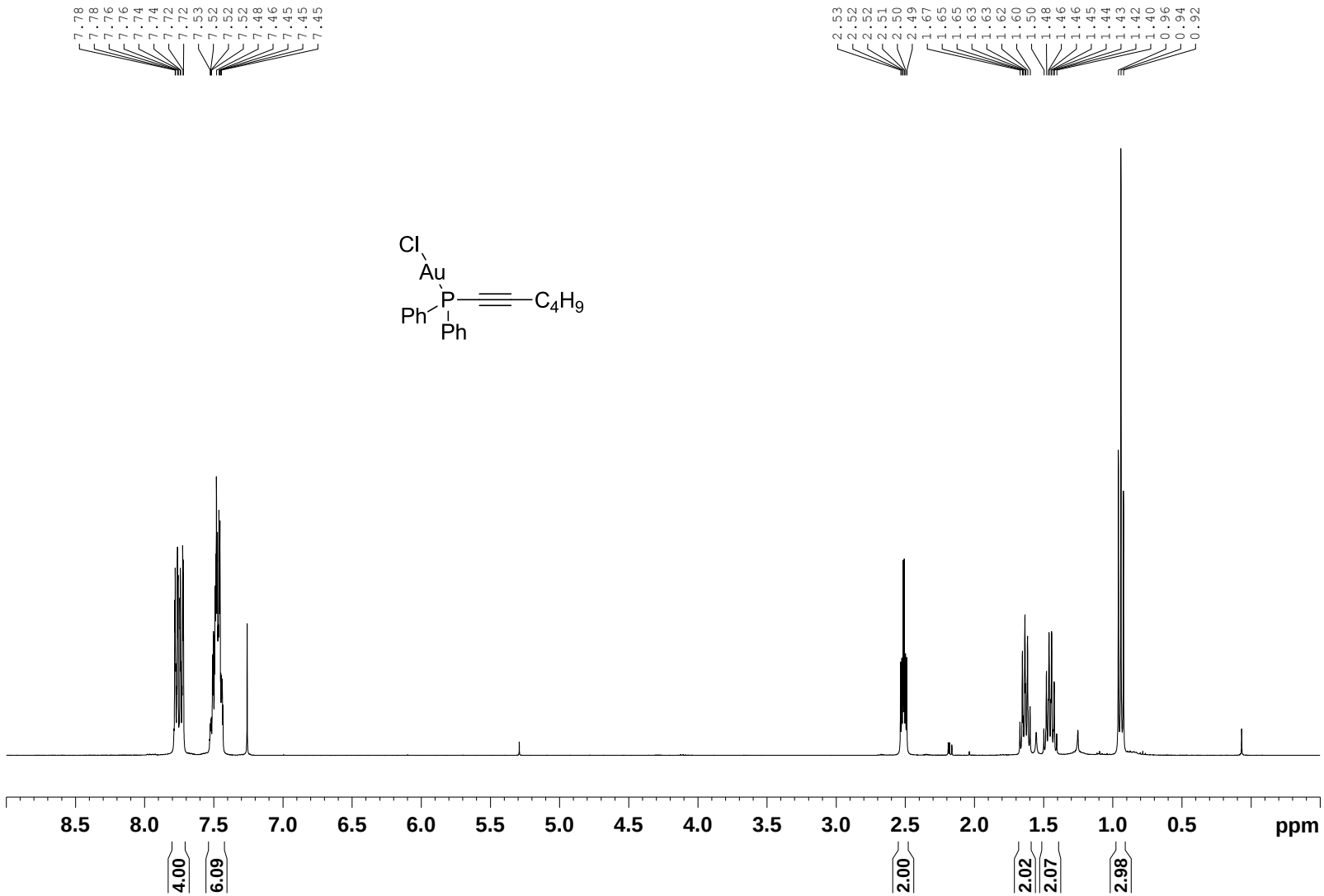

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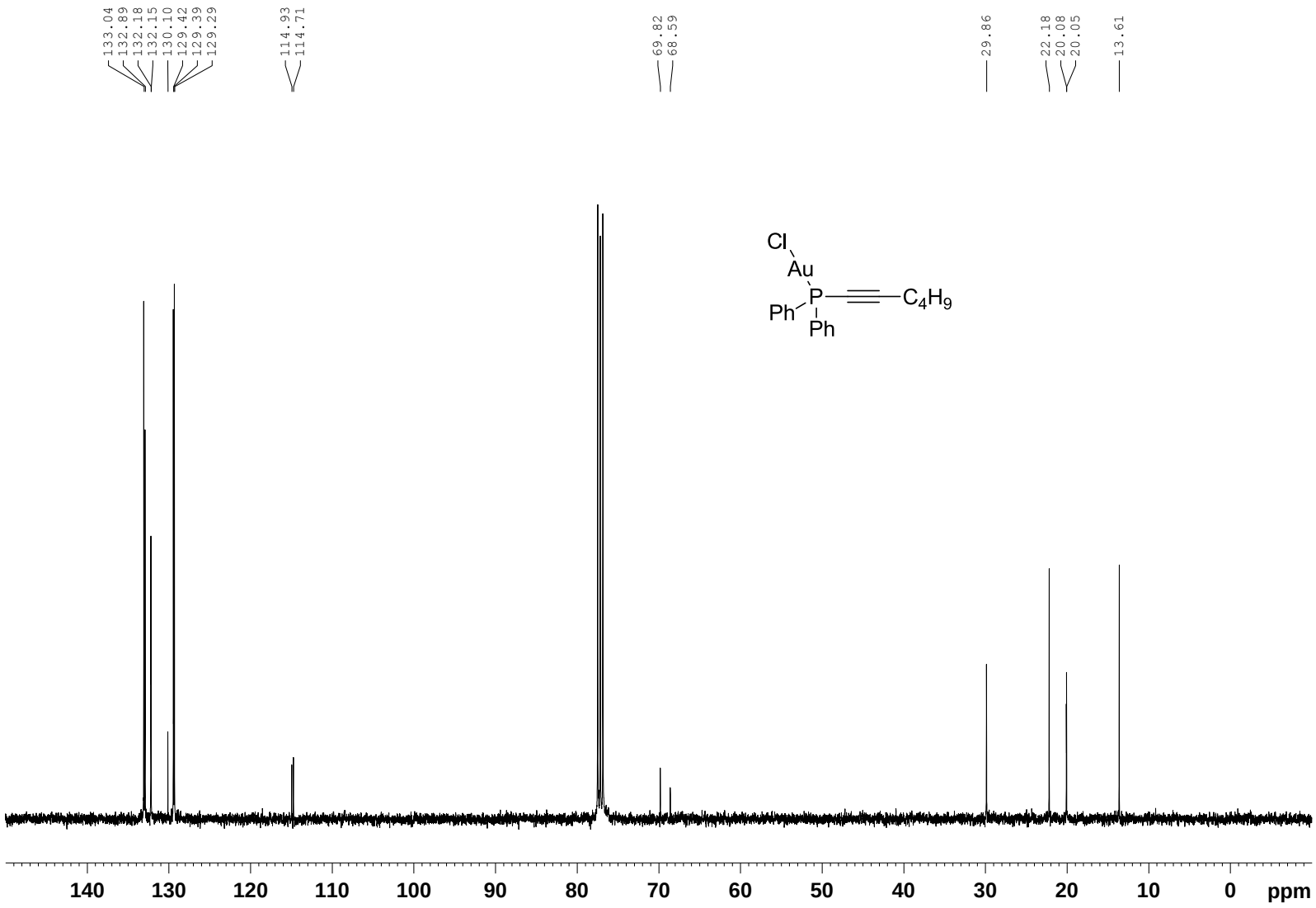

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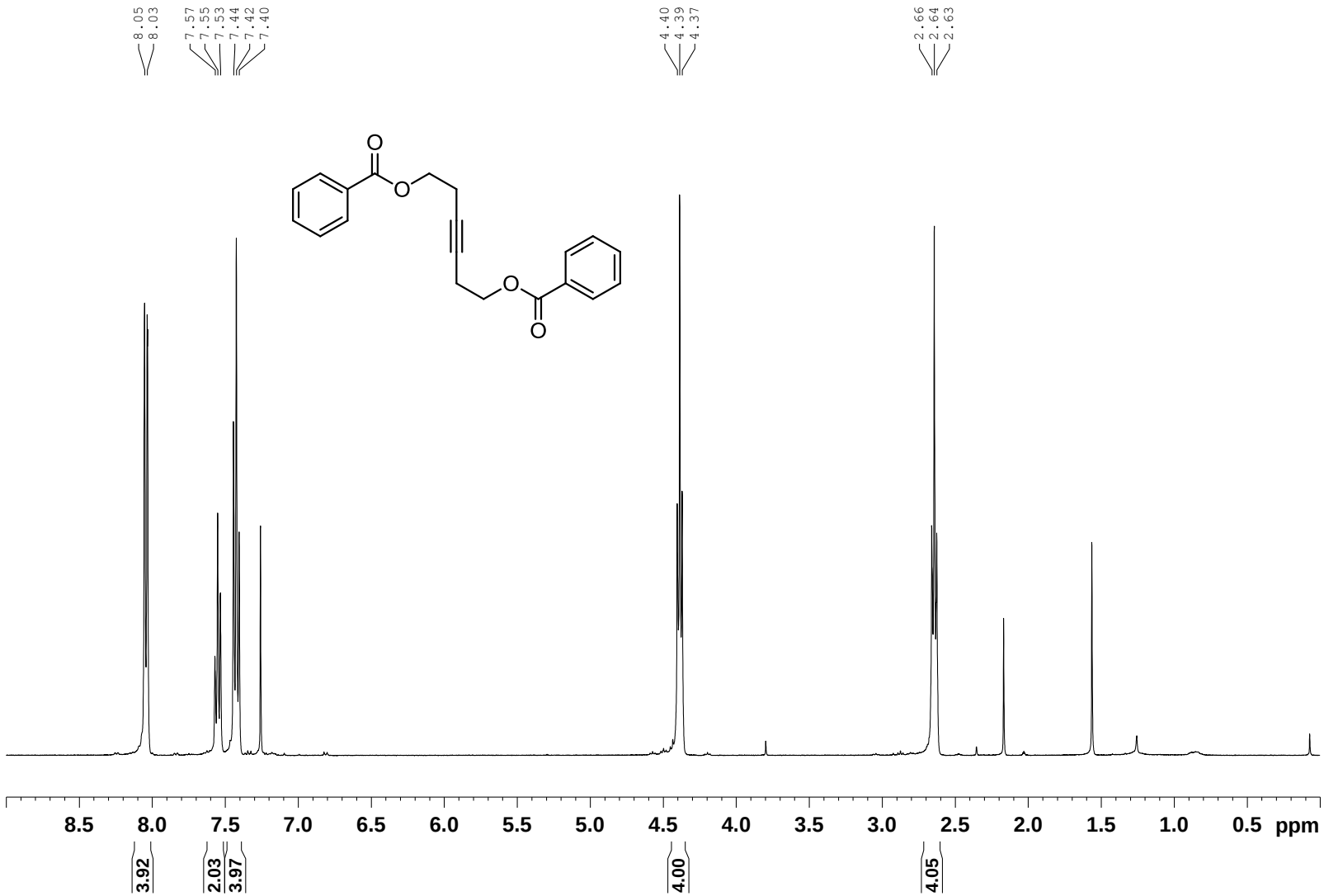

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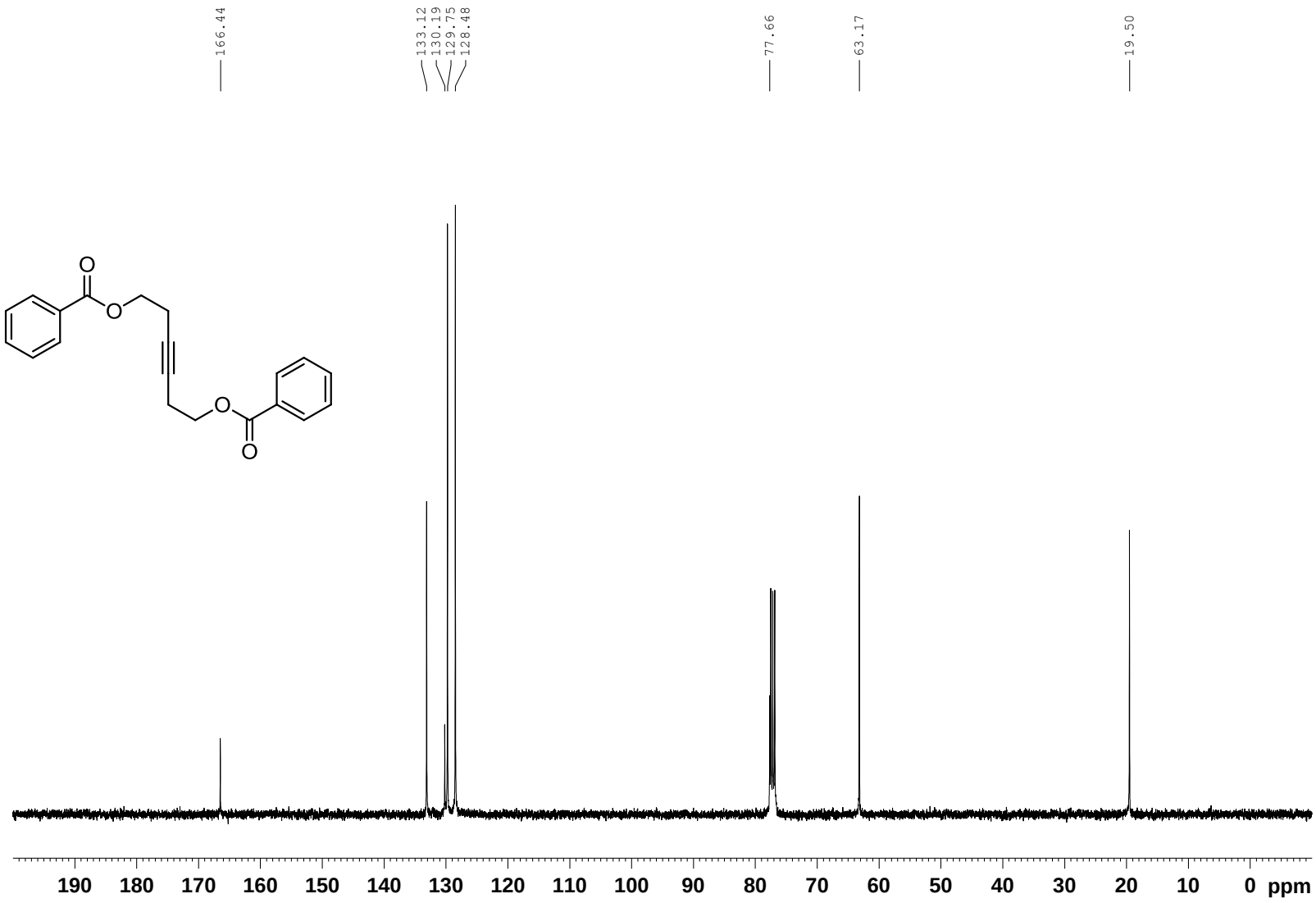

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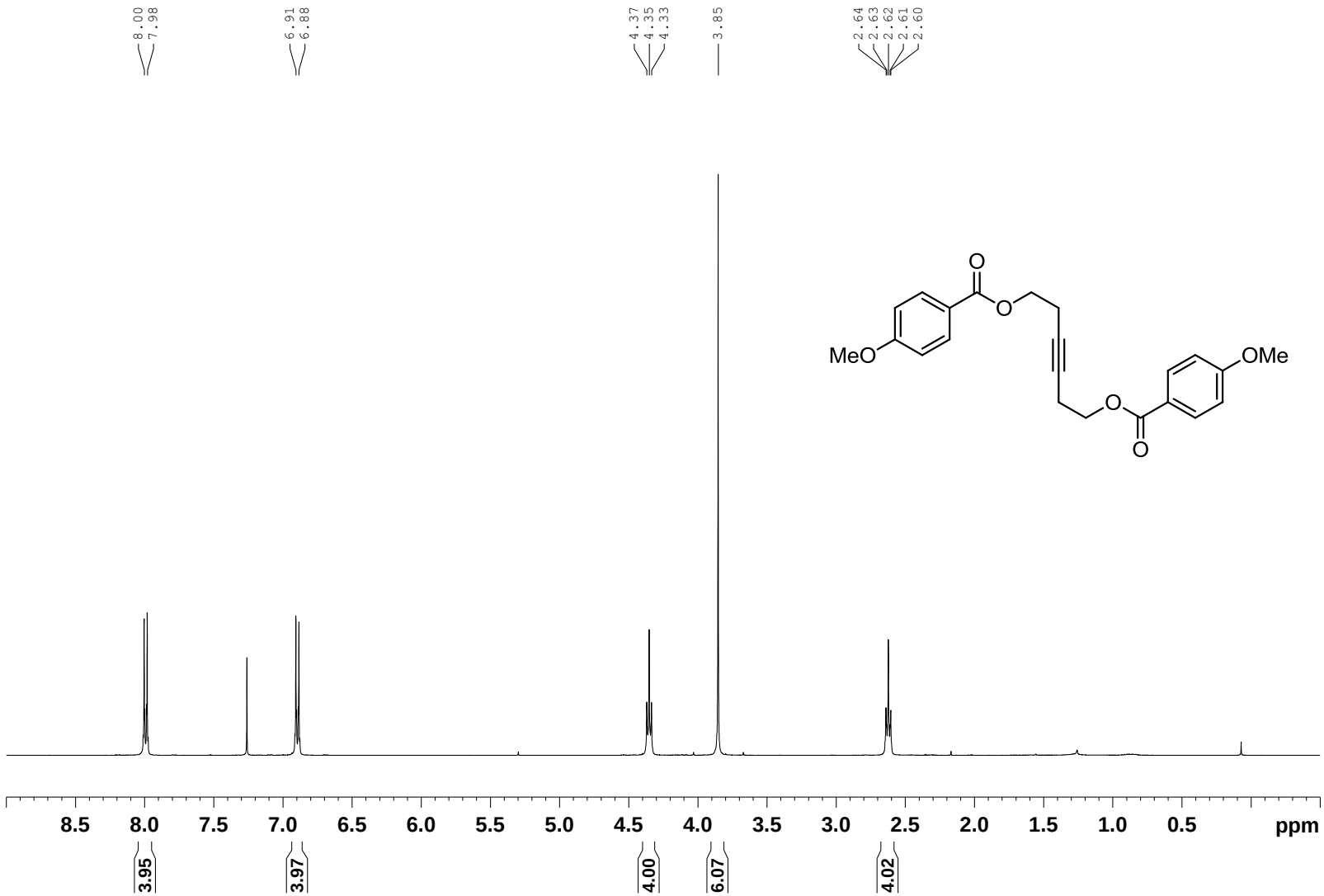

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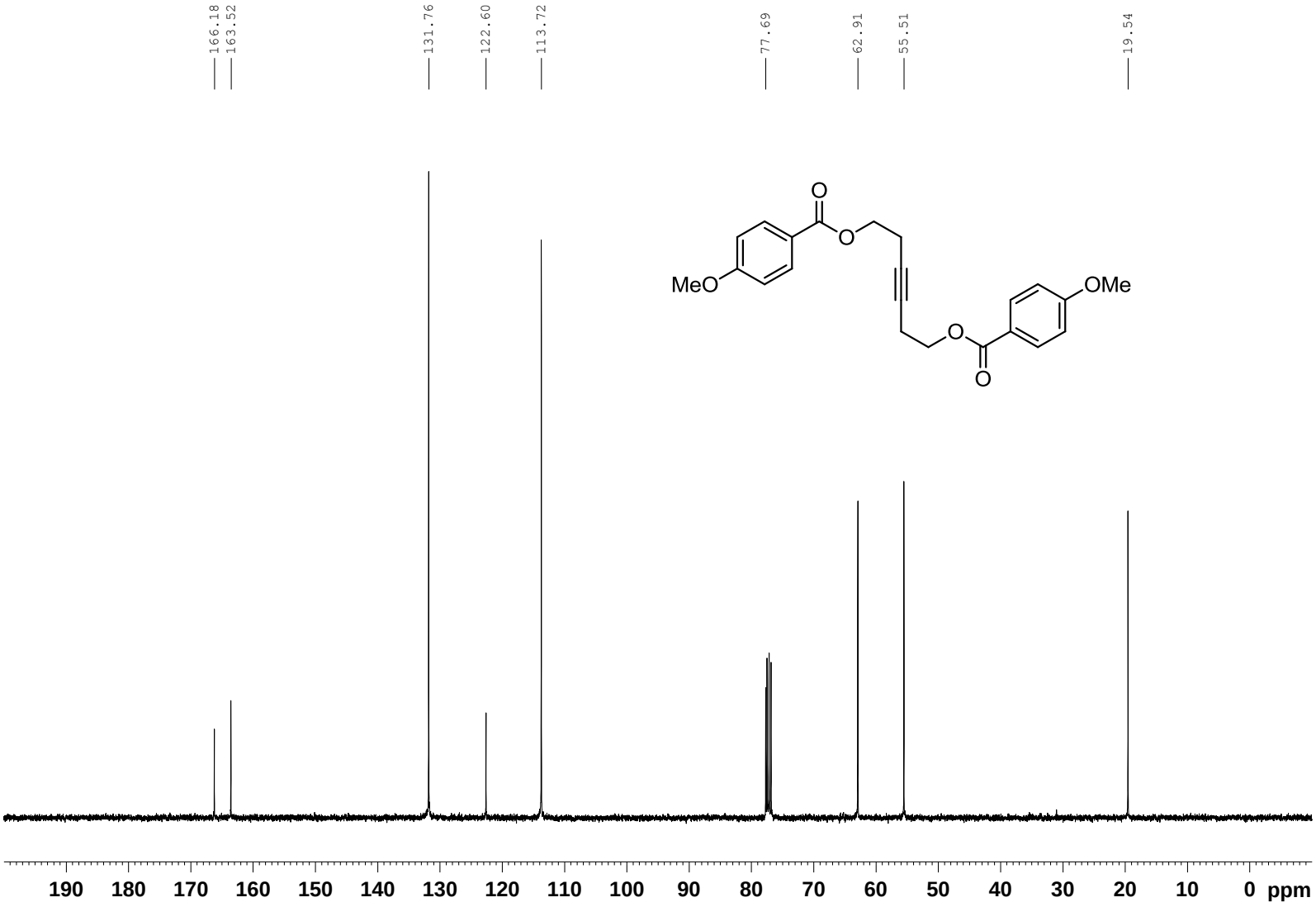

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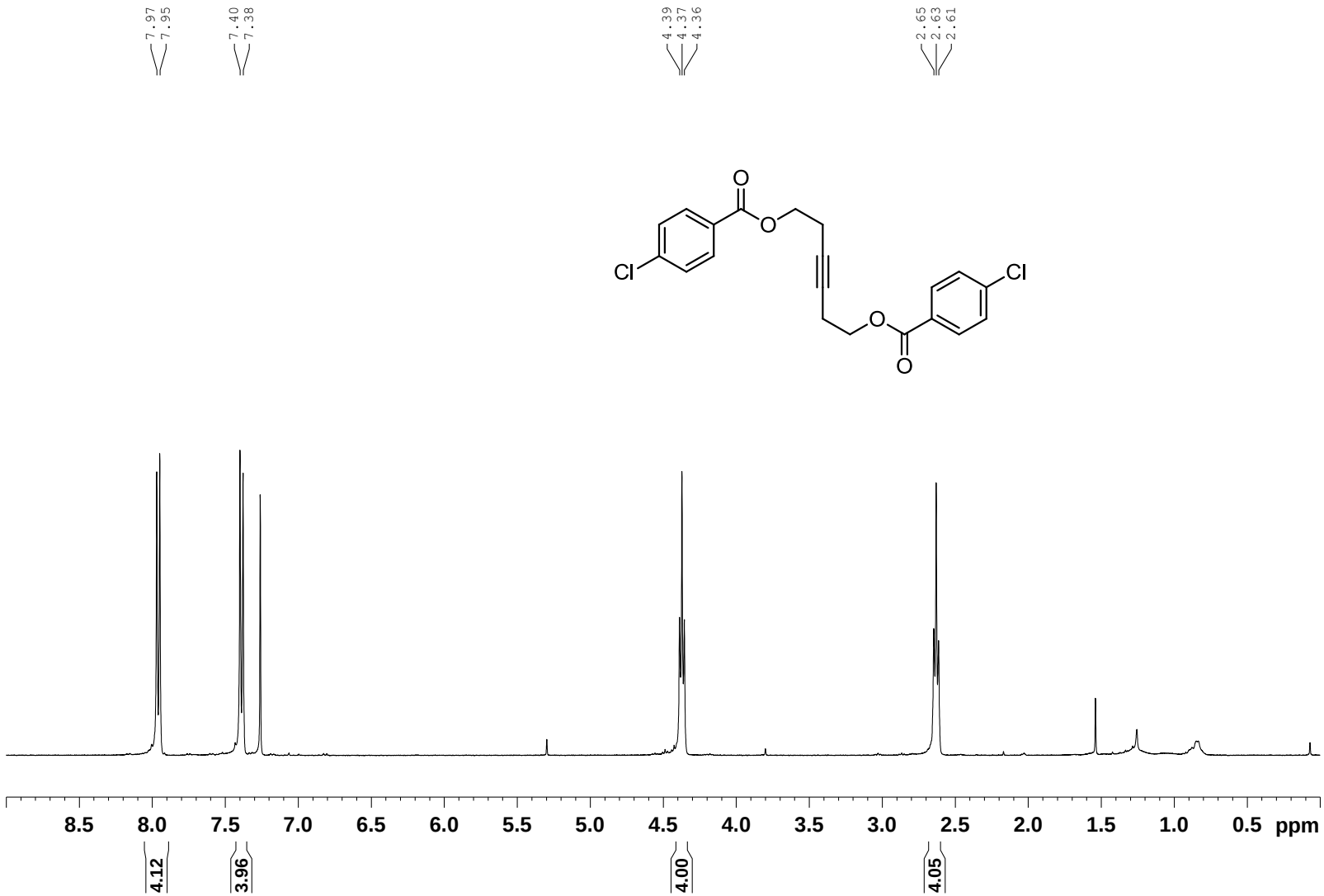

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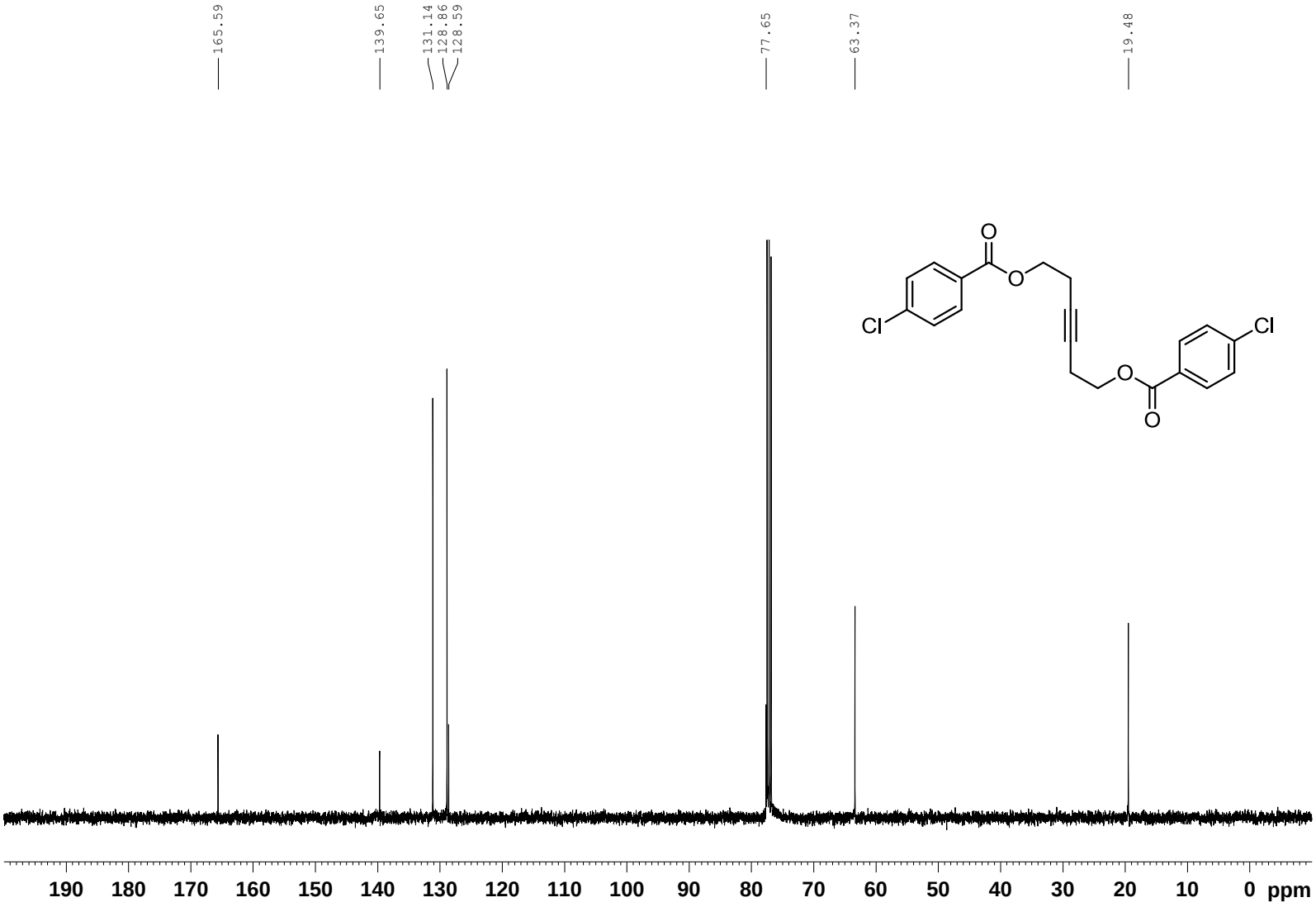

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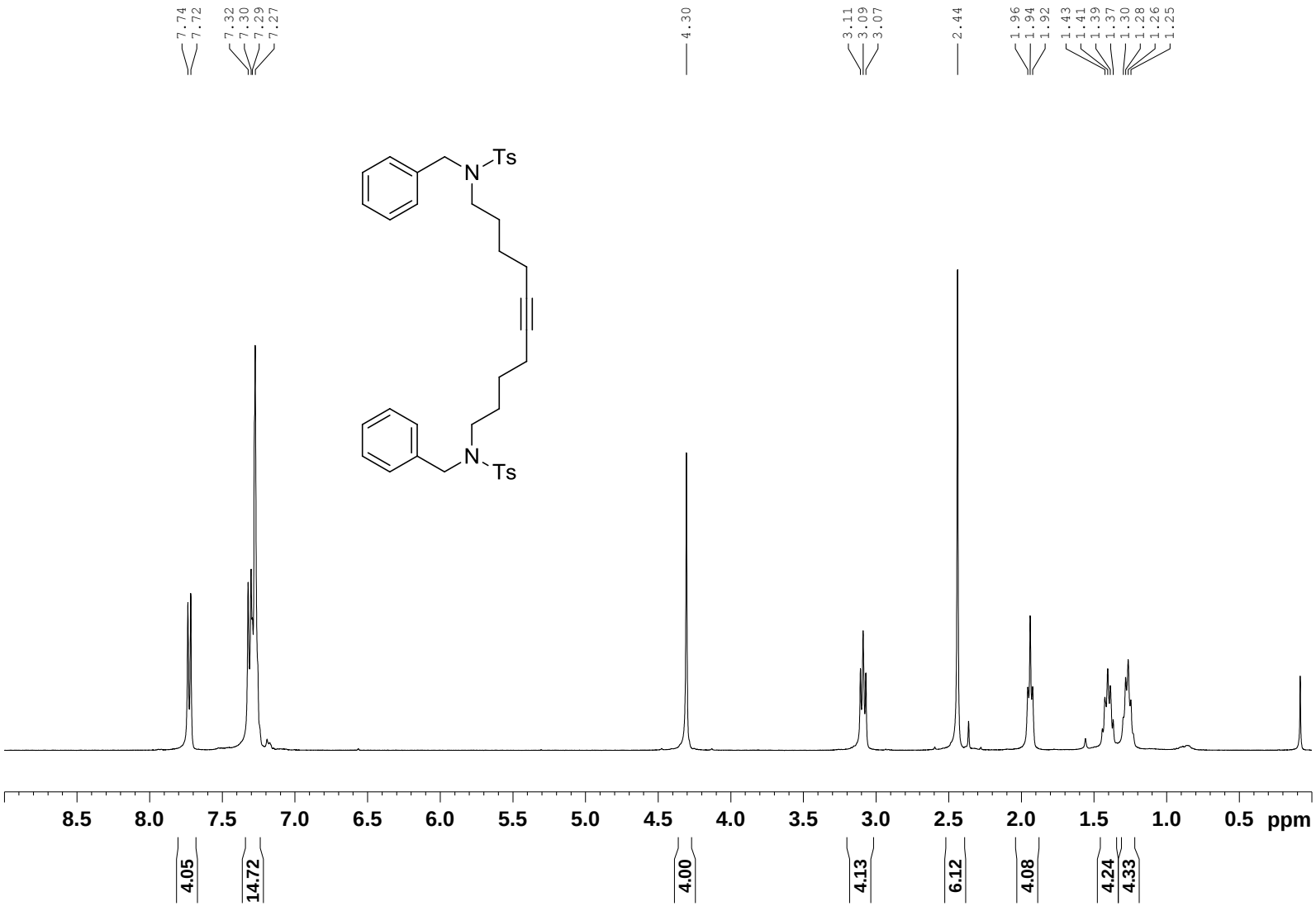

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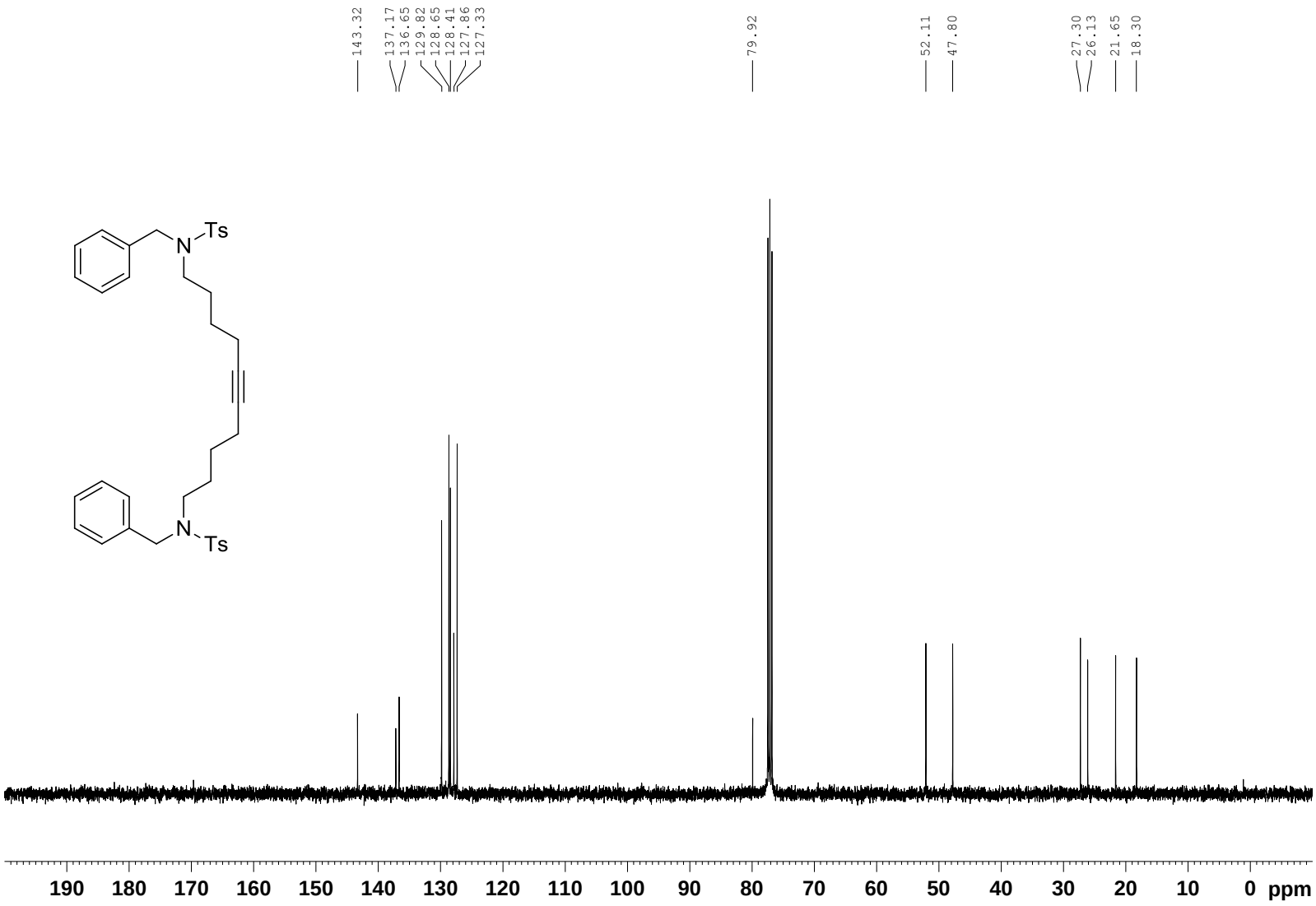

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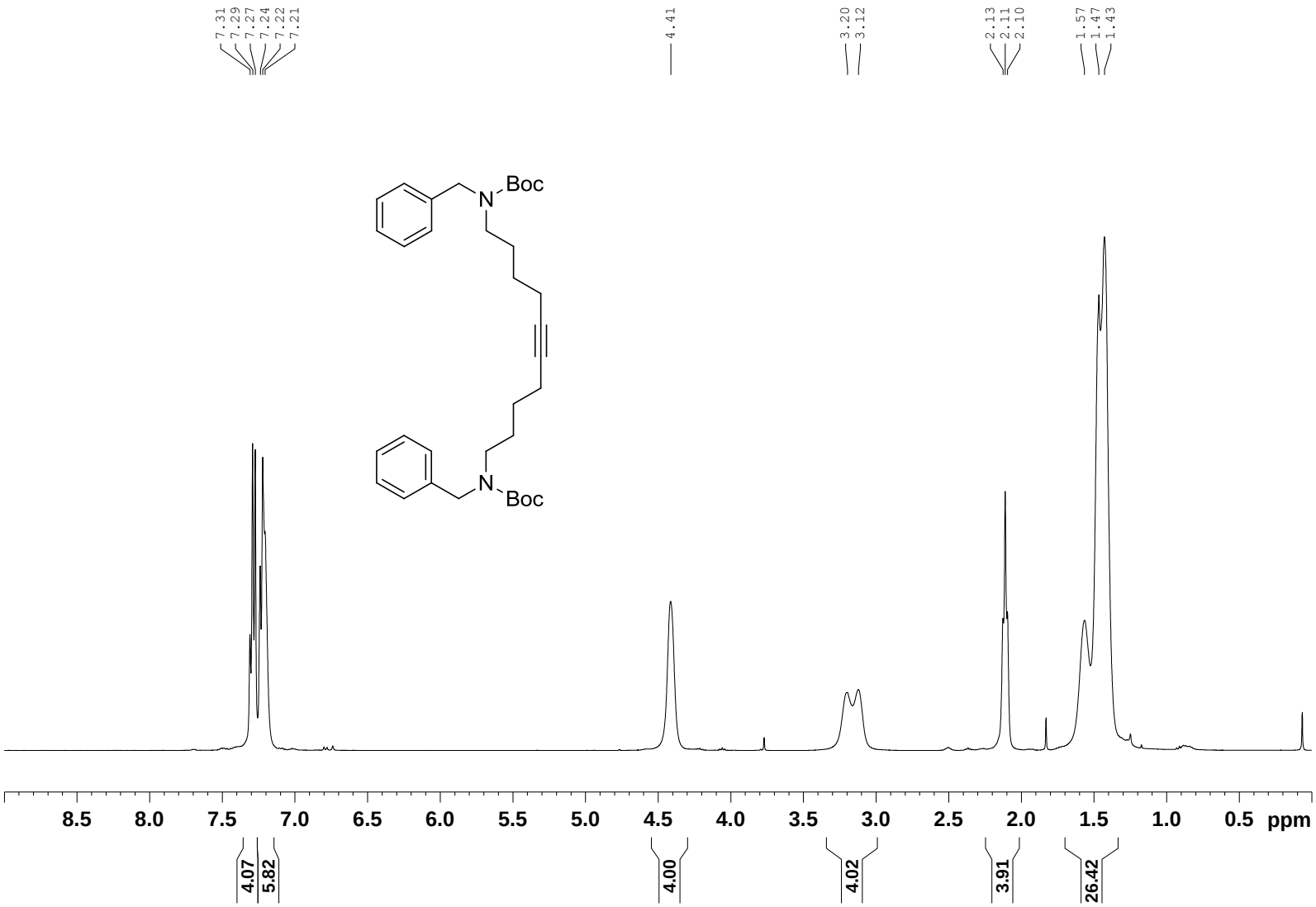

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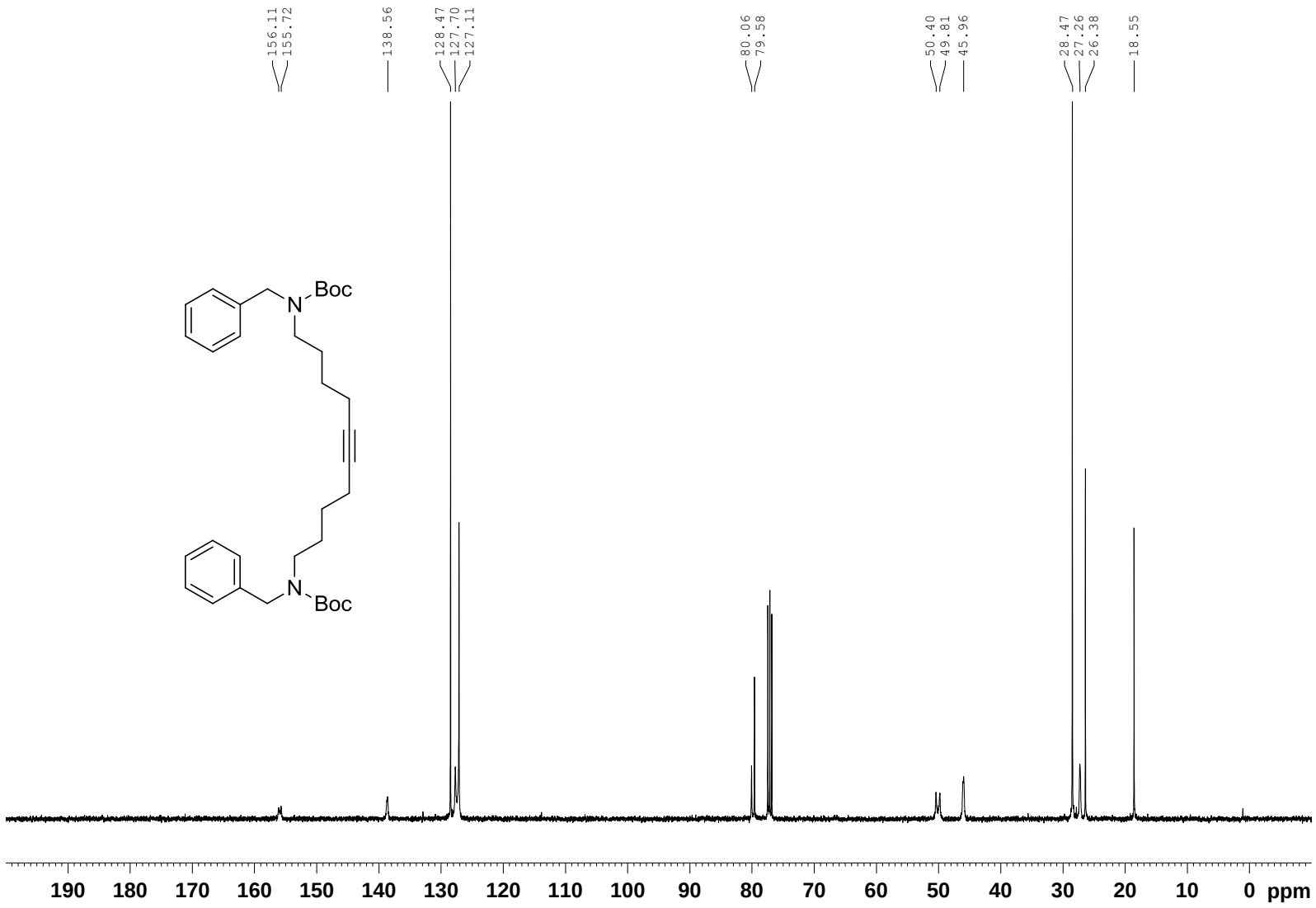

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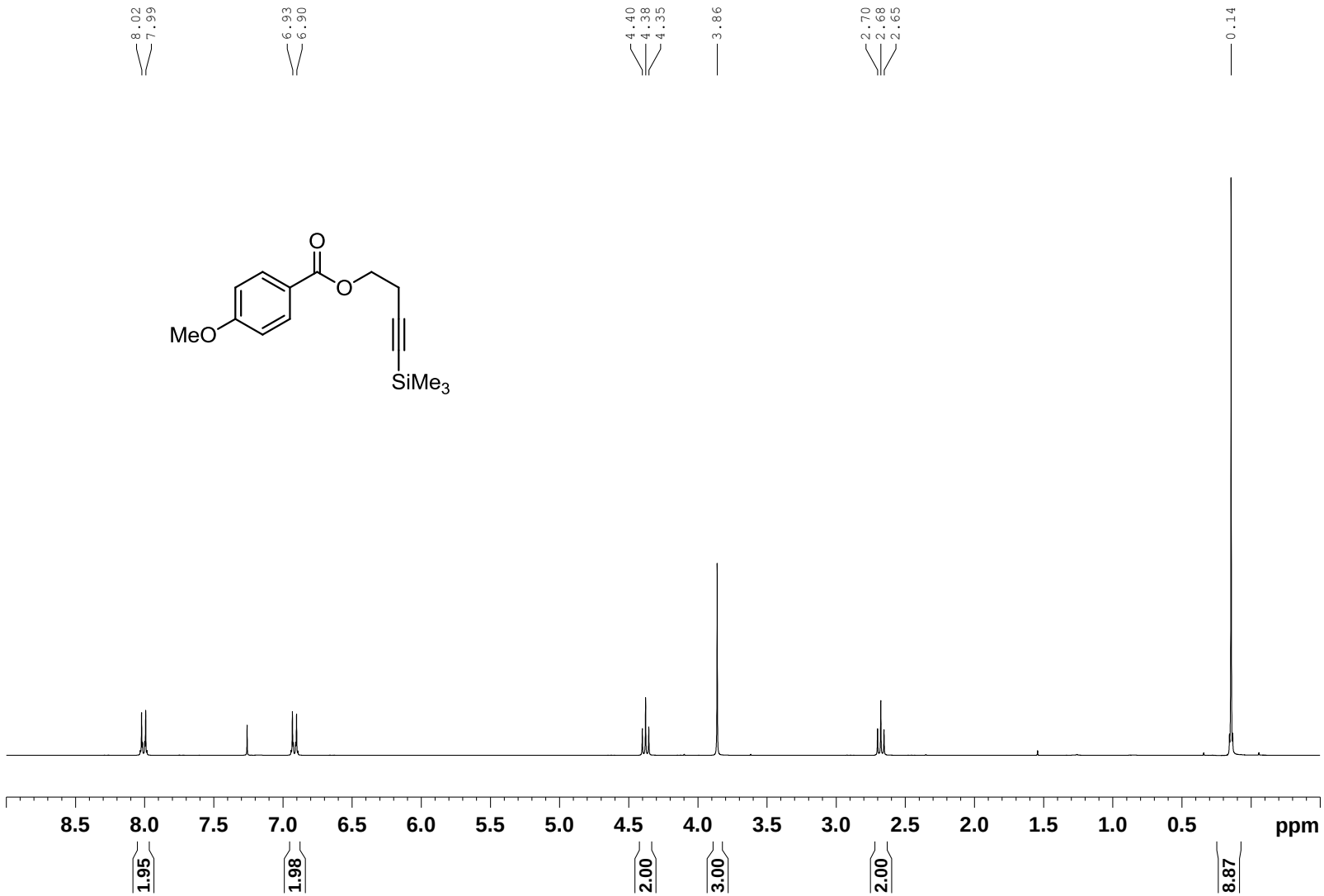
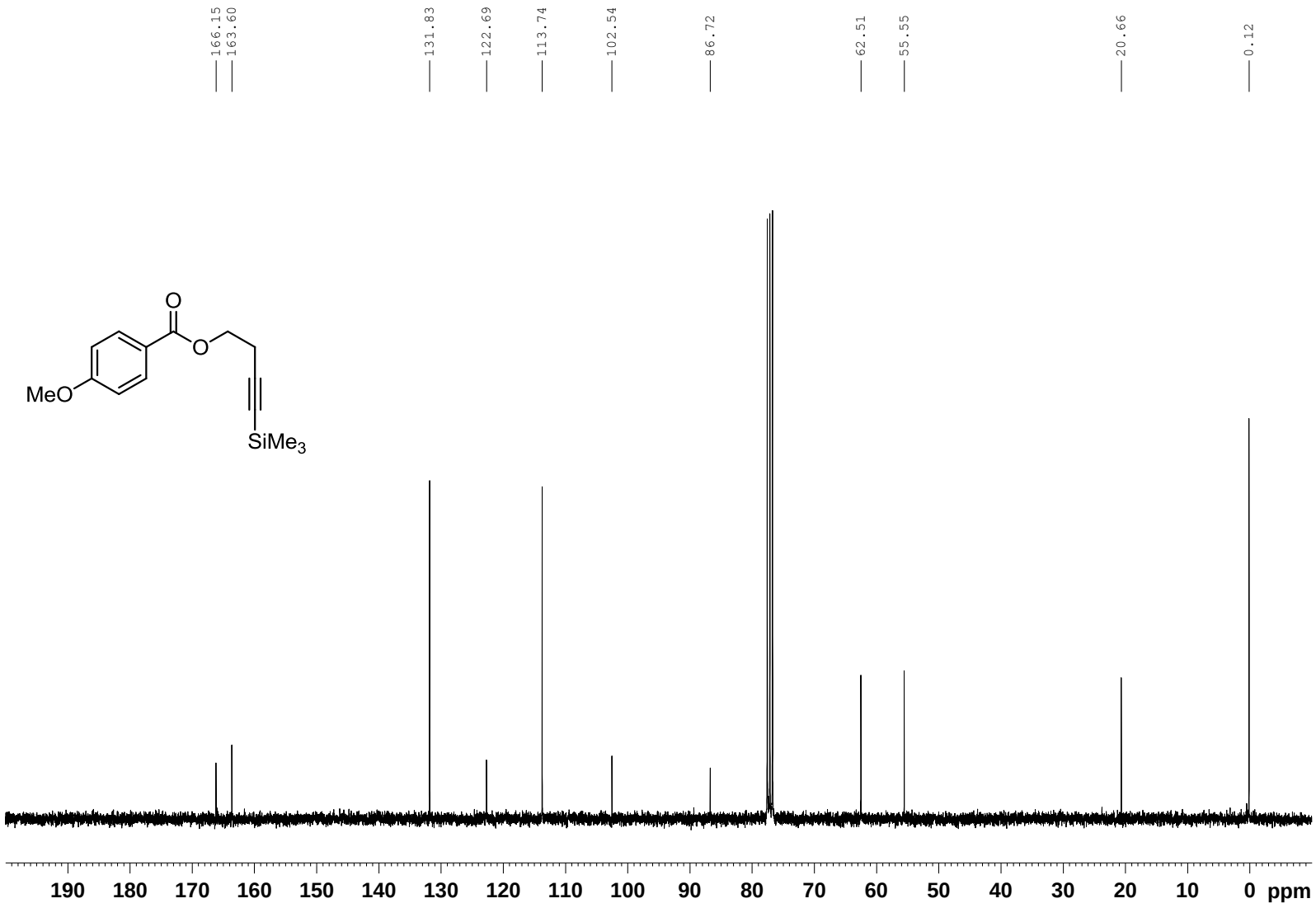


^{13}C NMR (100 MHz, $CDCl_3$)



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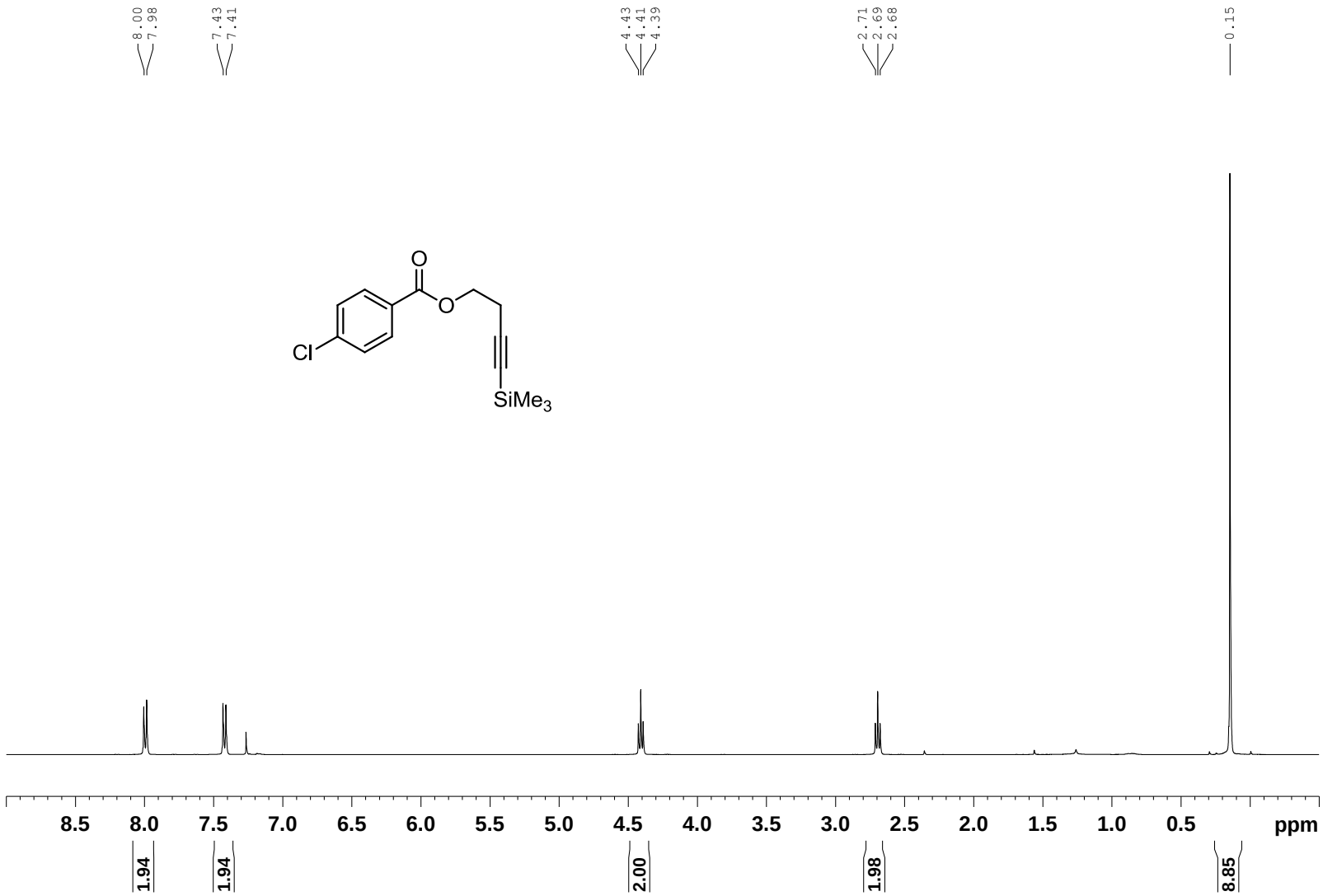
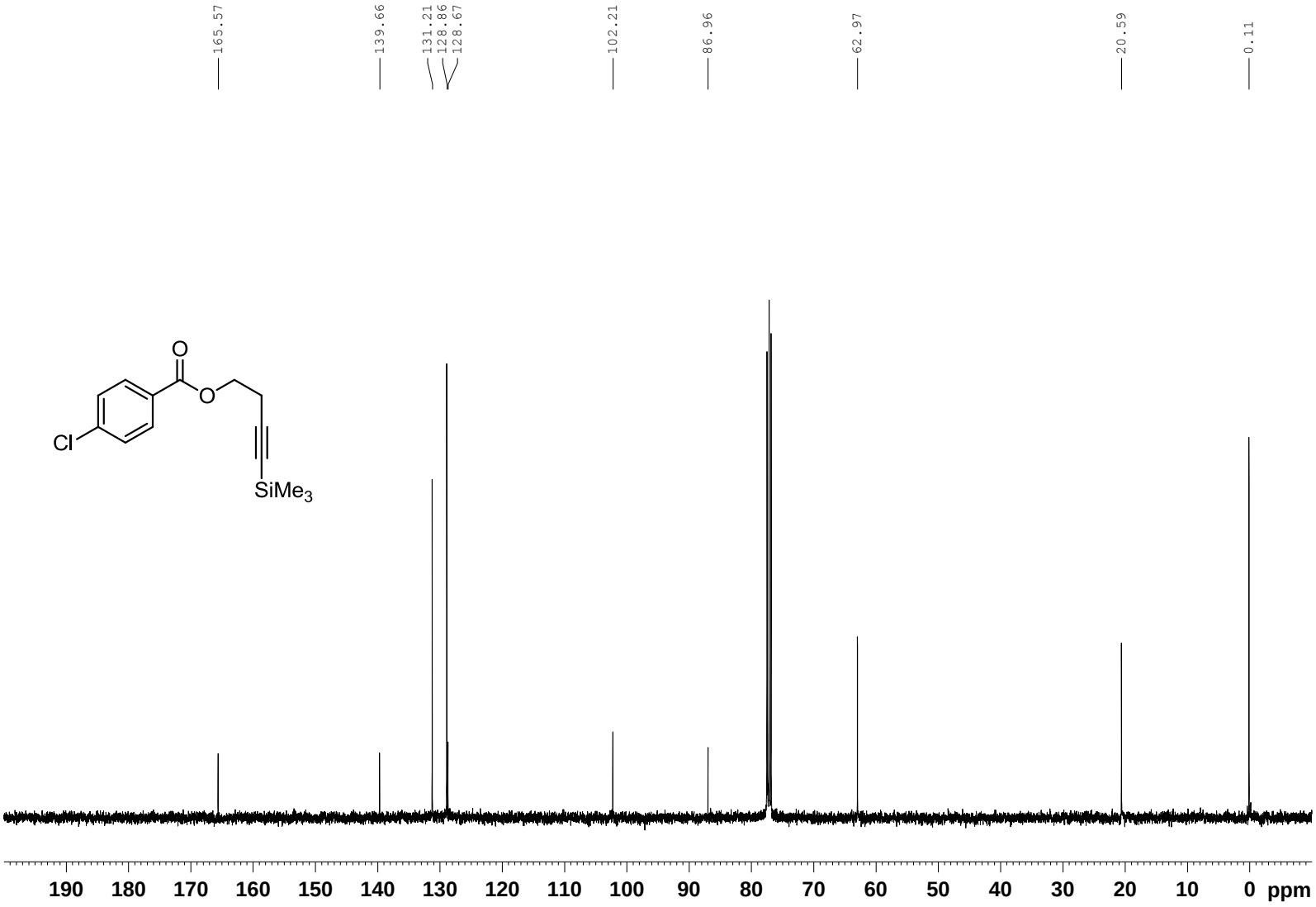
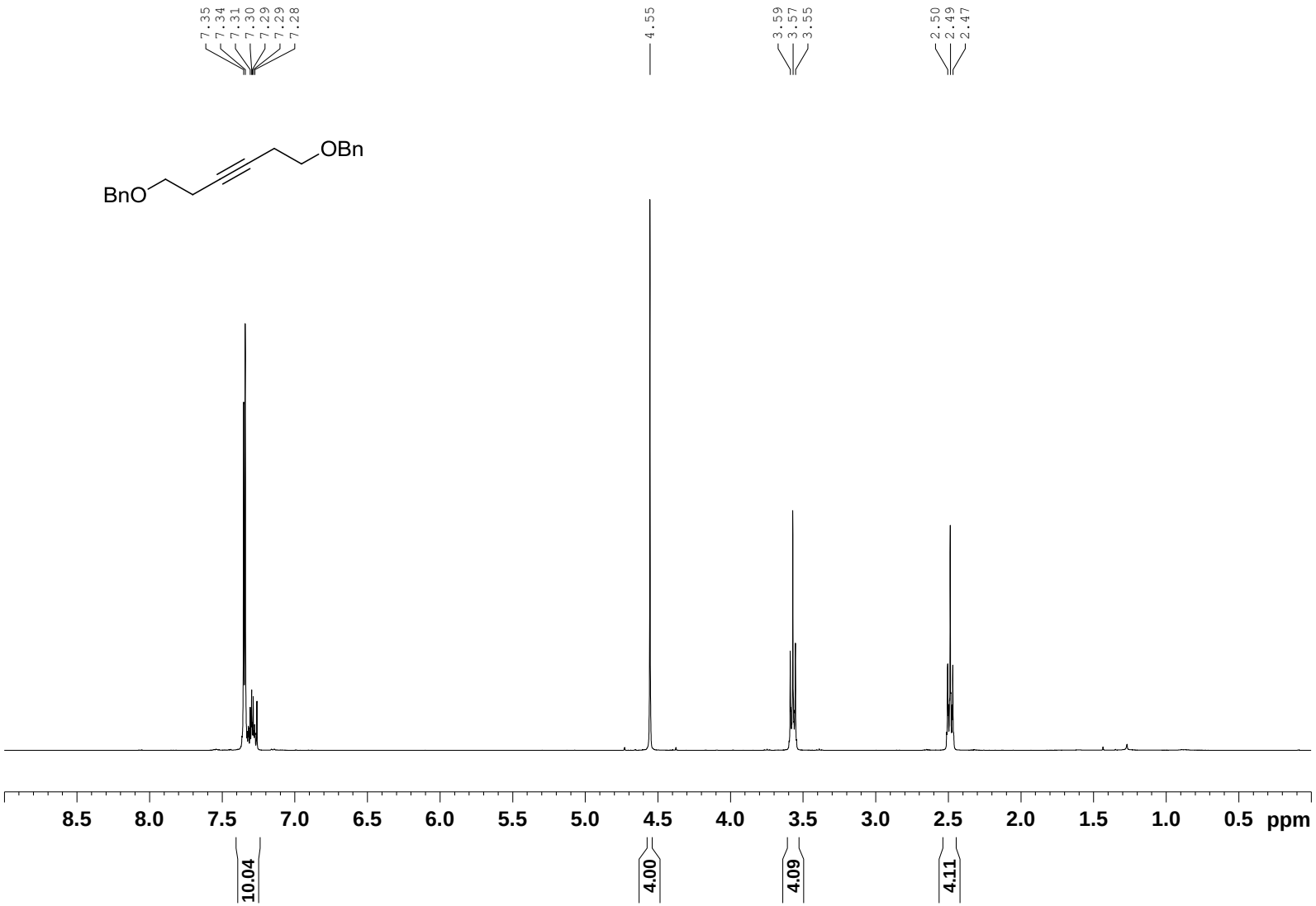


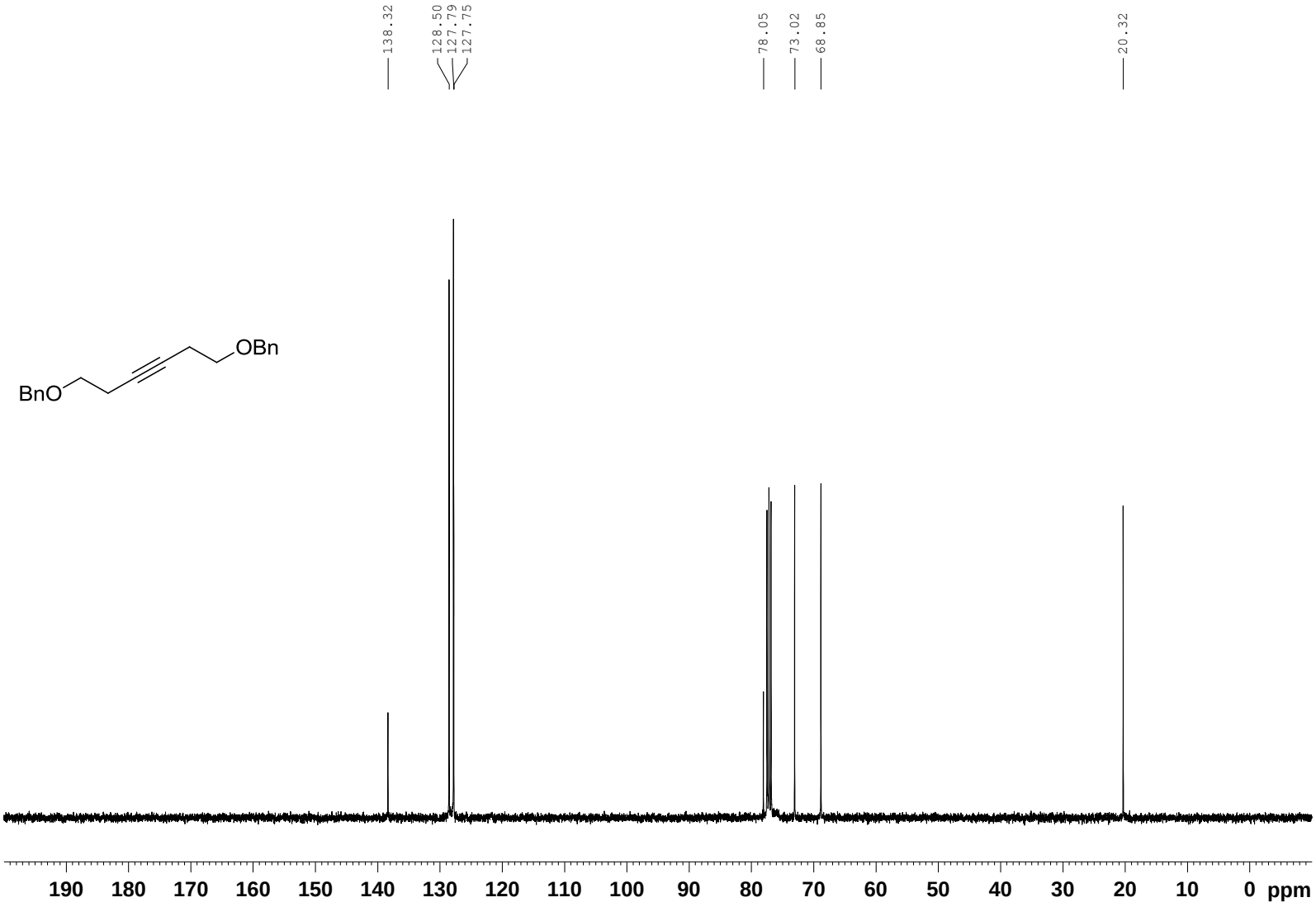
^{13}C NMR (75 MHz, $CDCl_3$)



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



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



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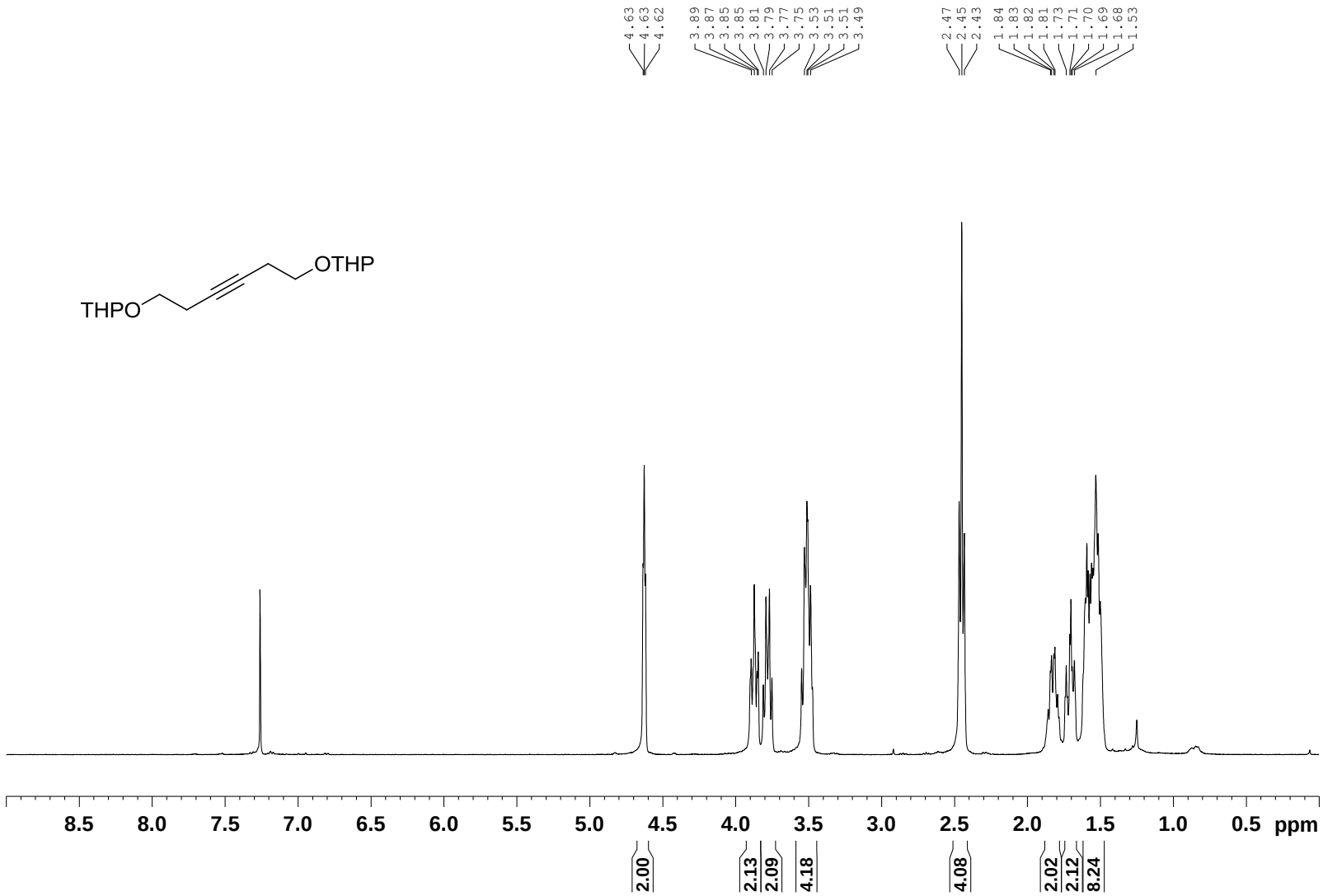

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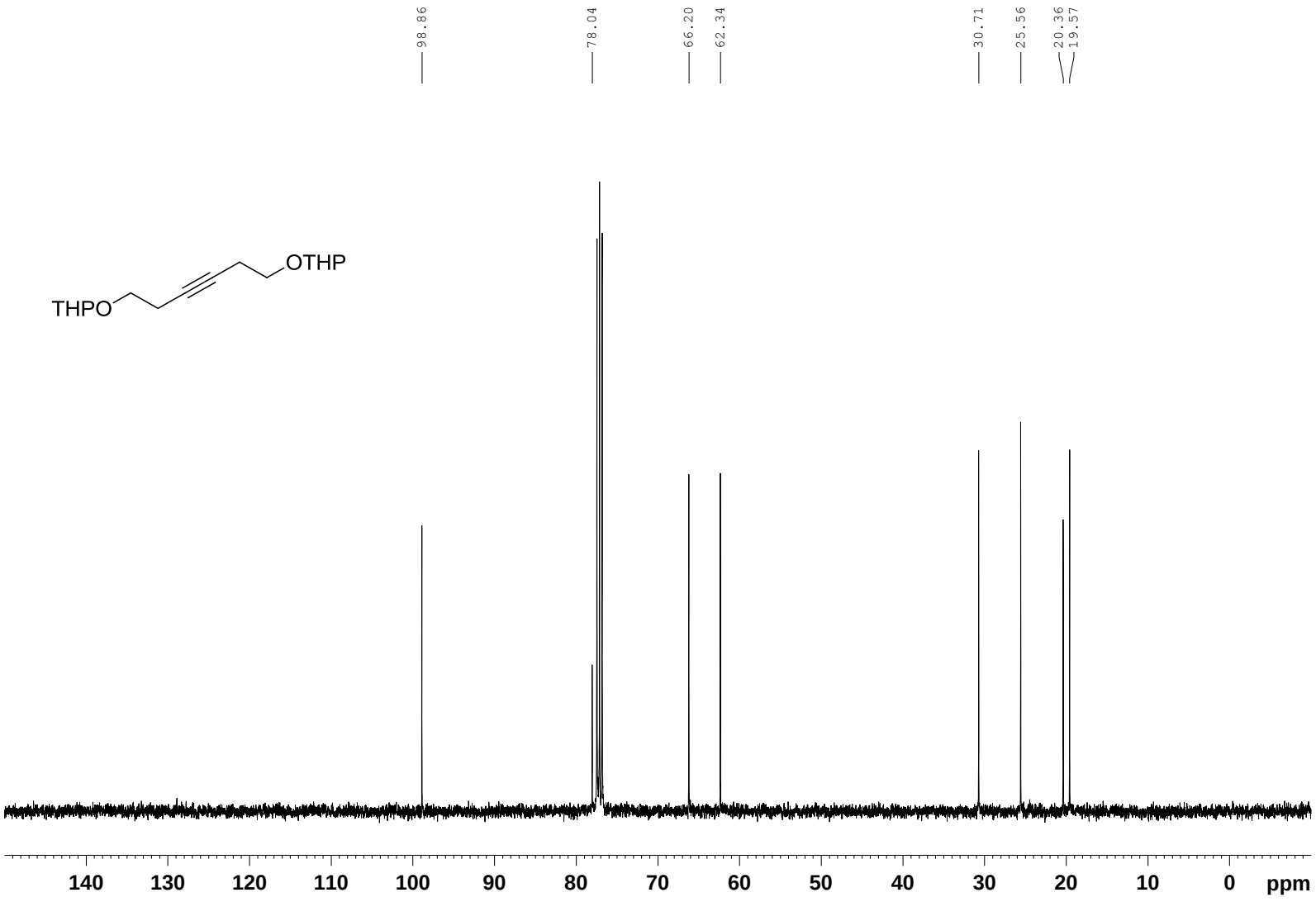

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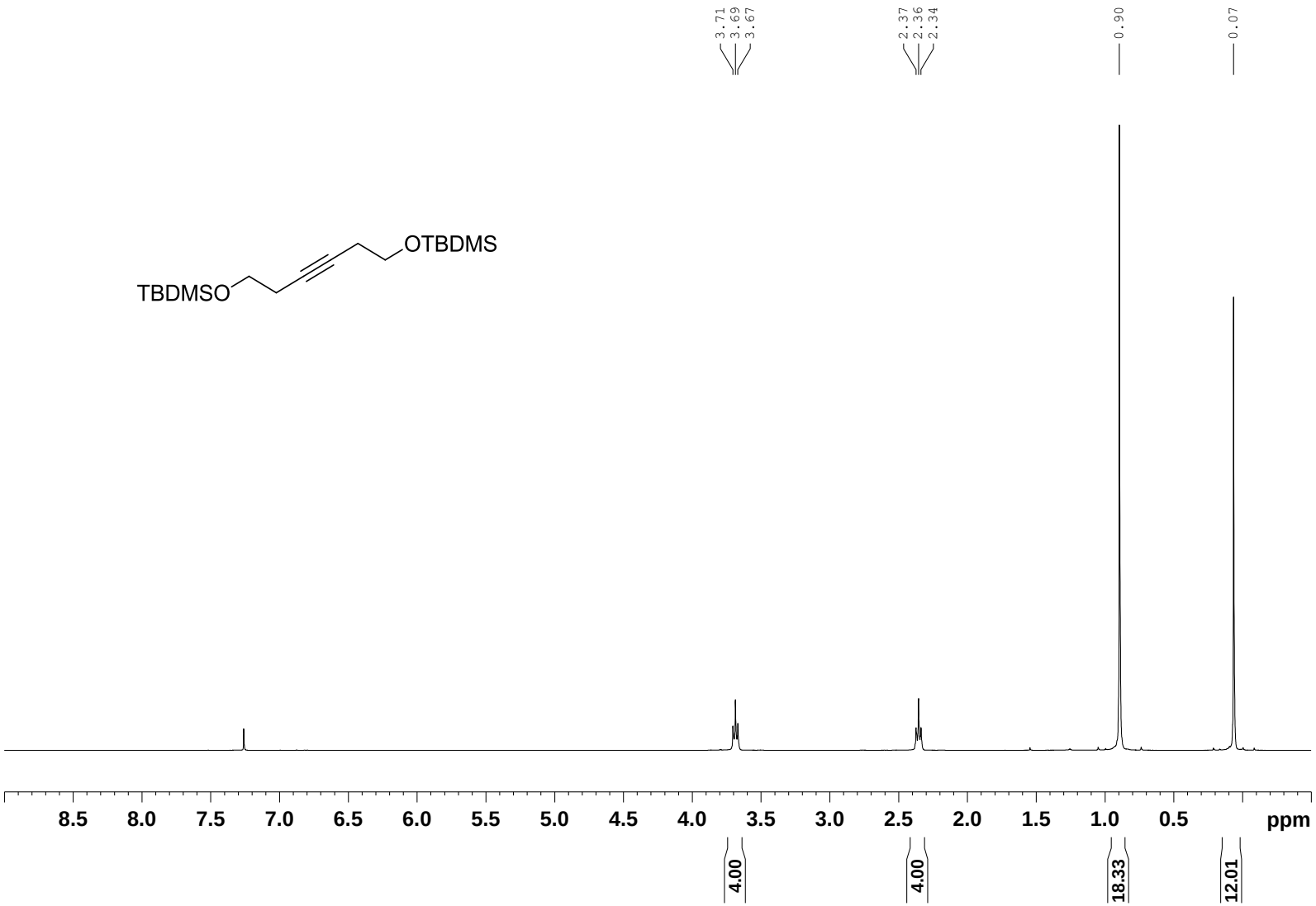

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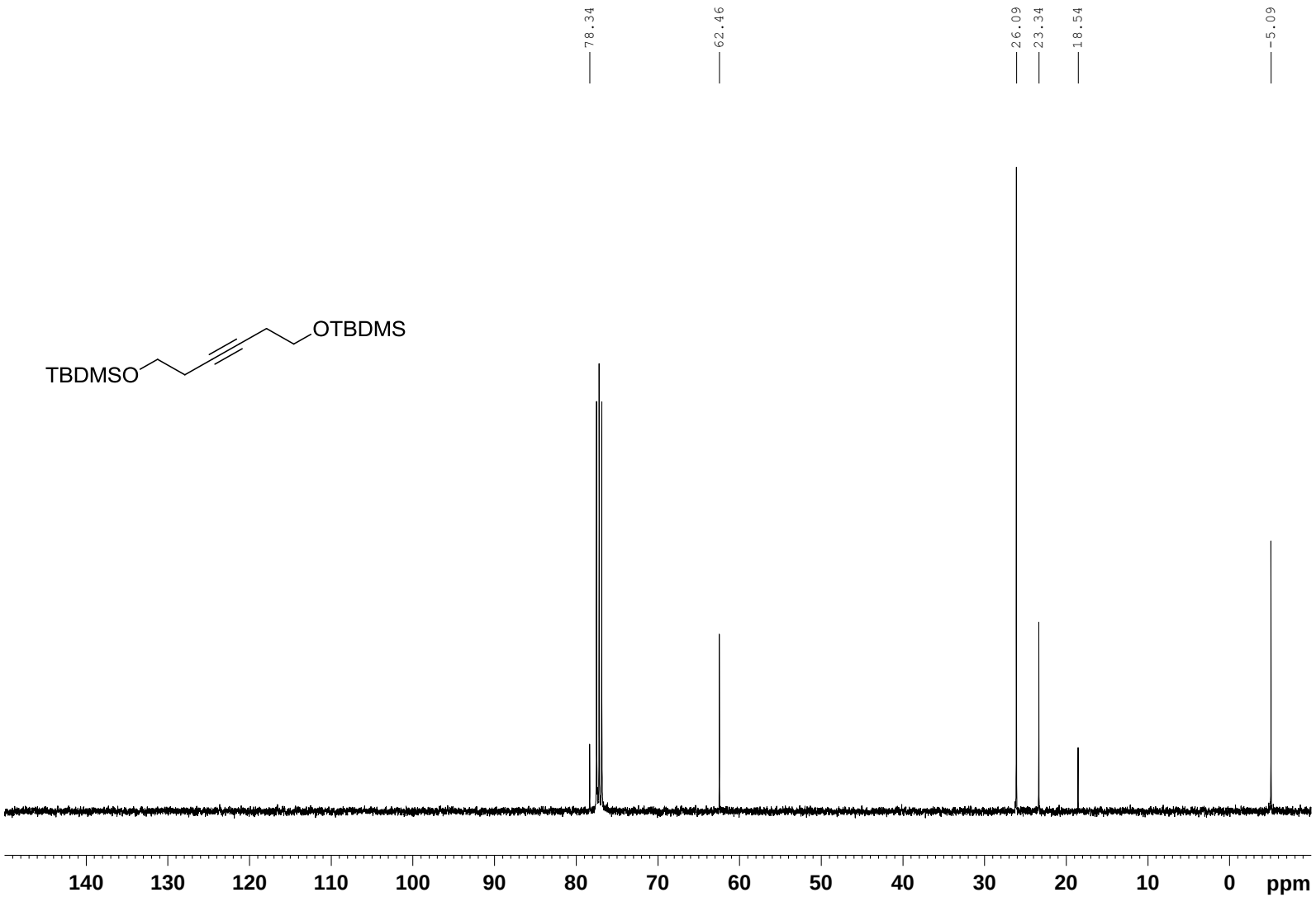

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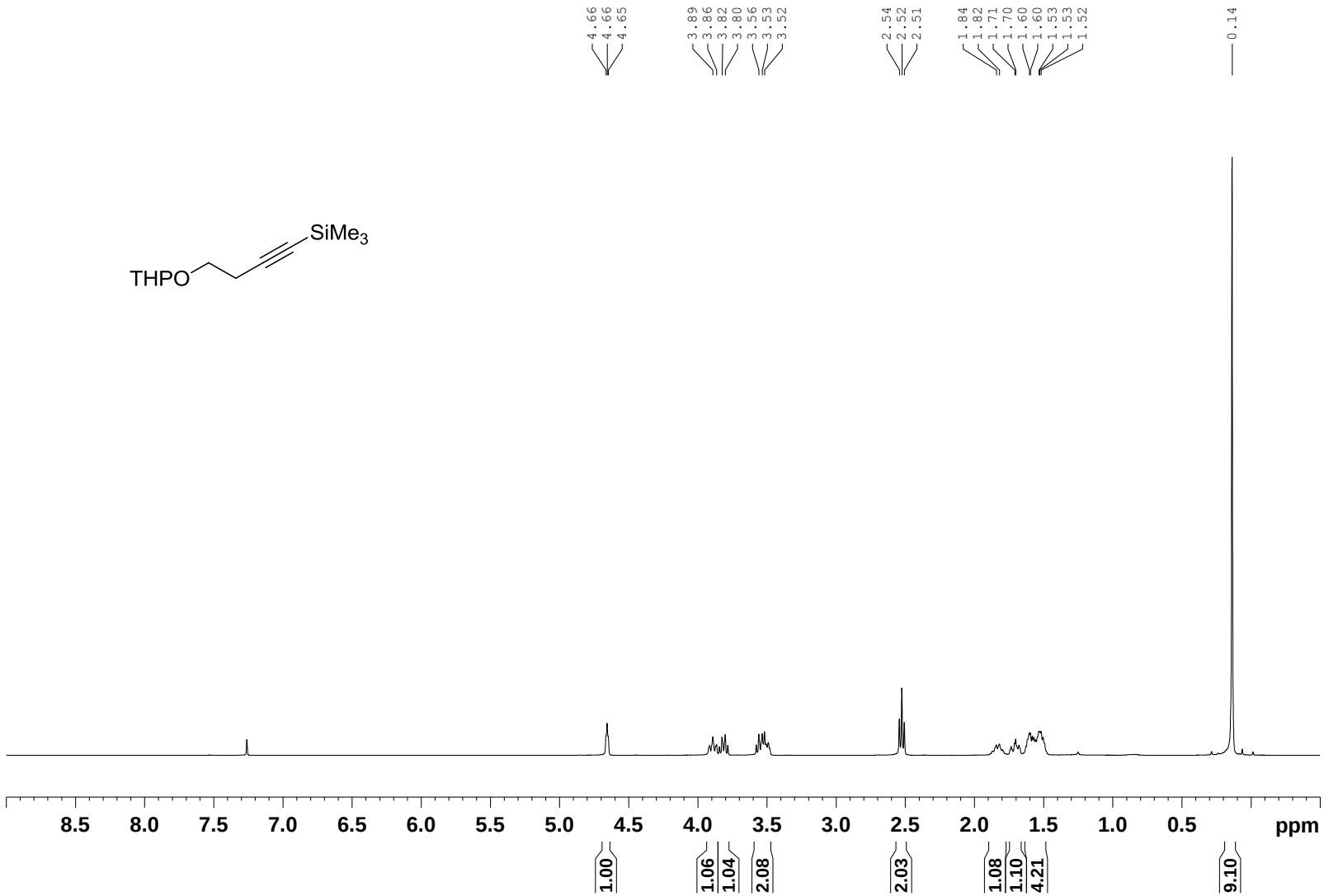

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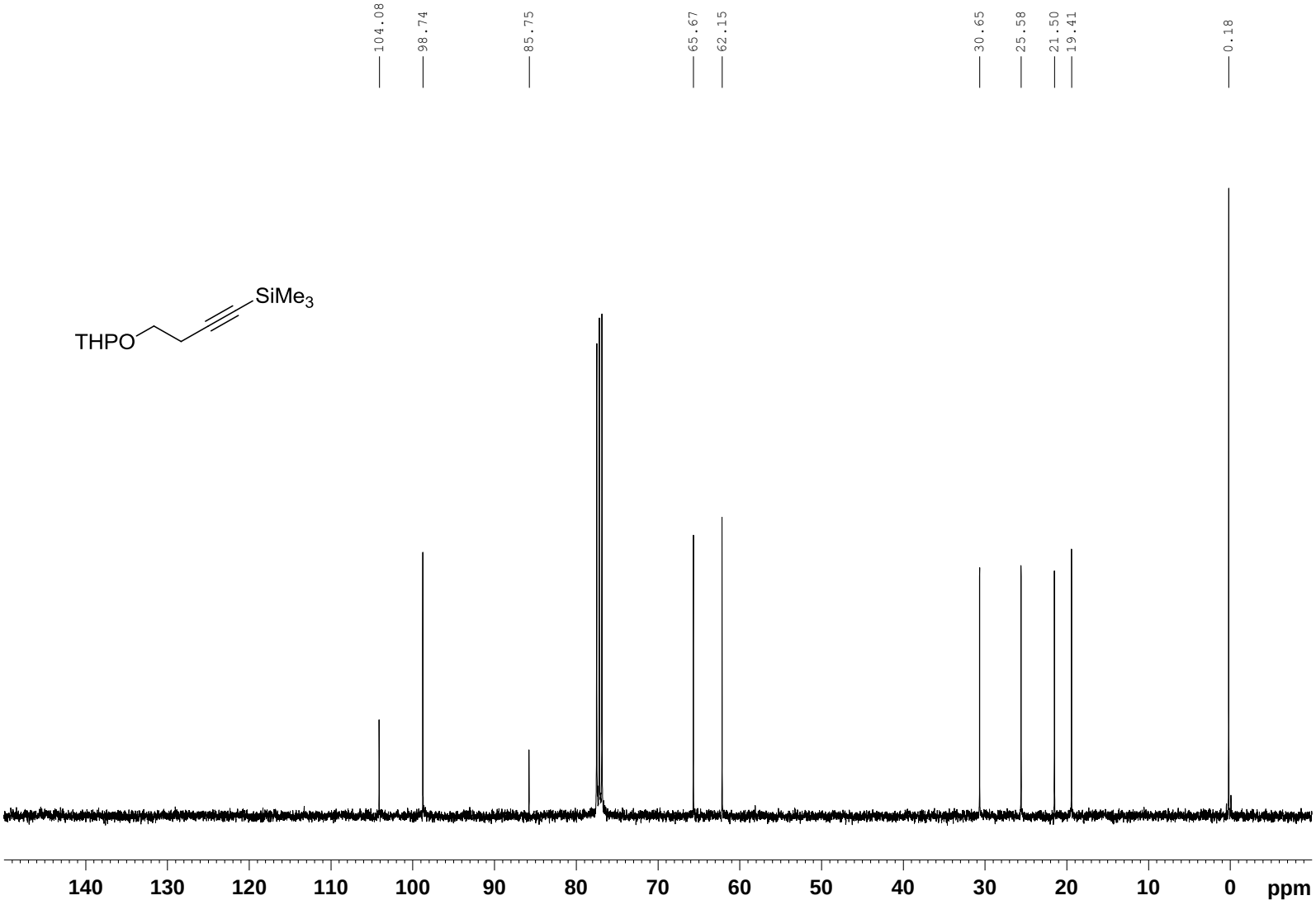

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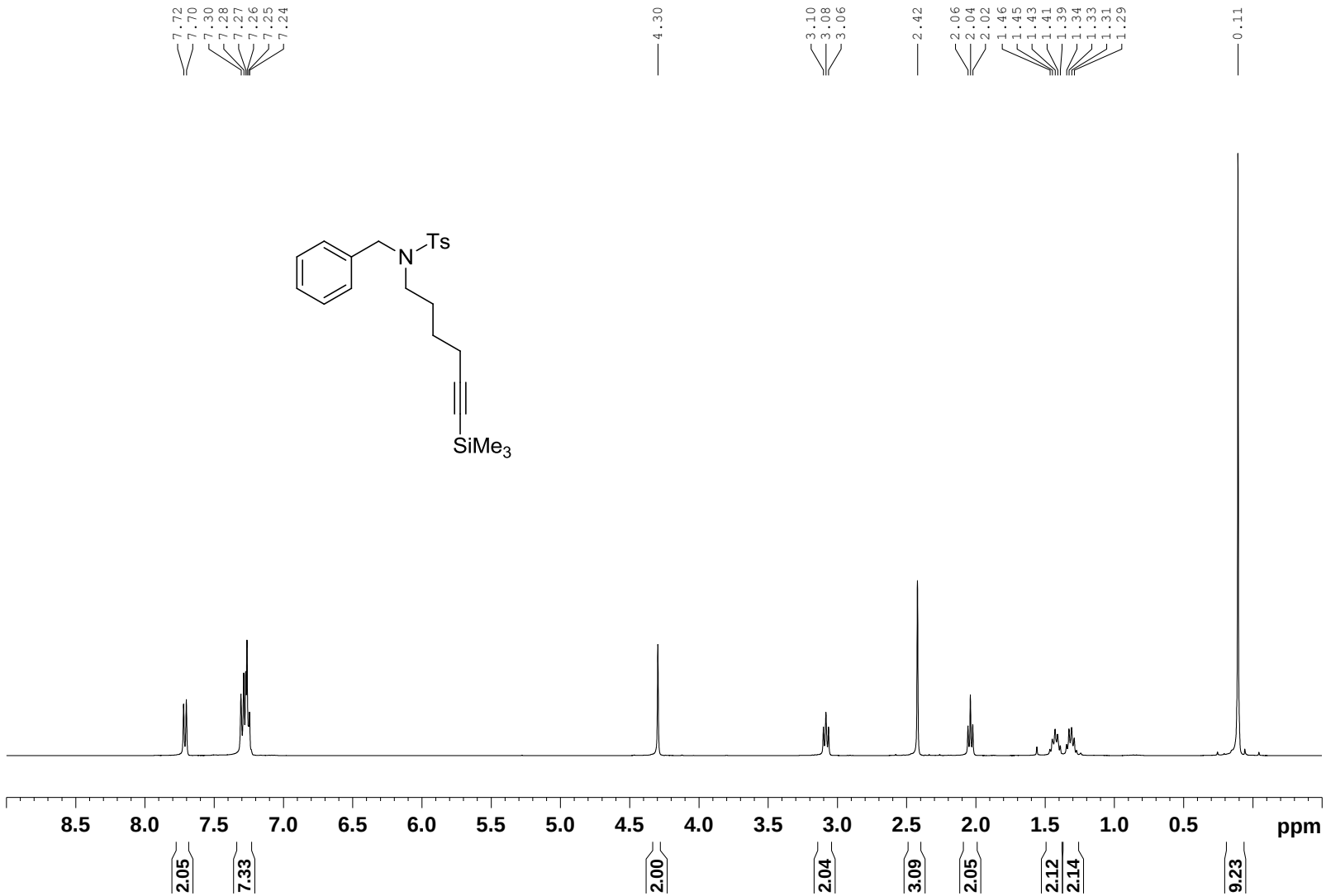

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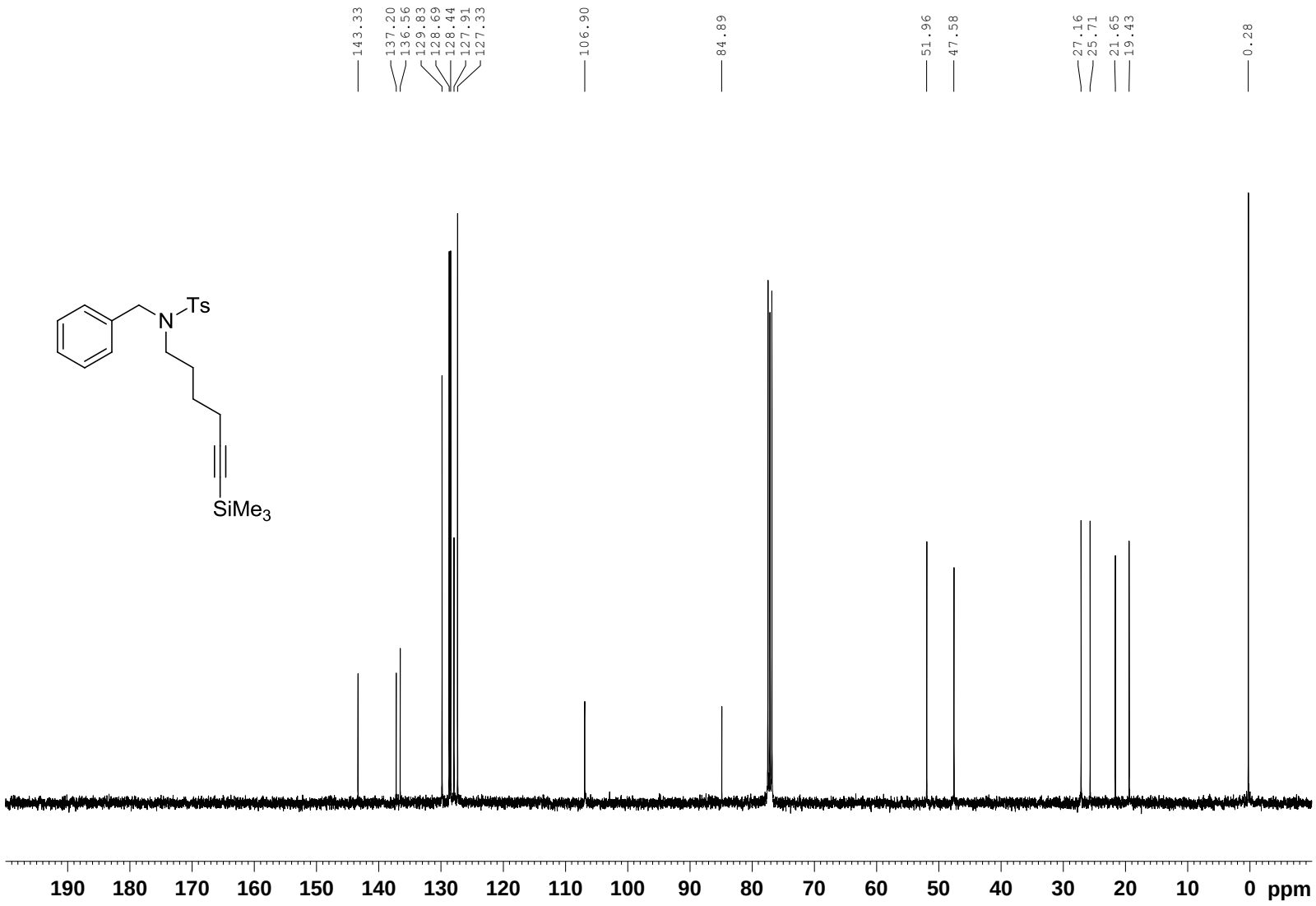

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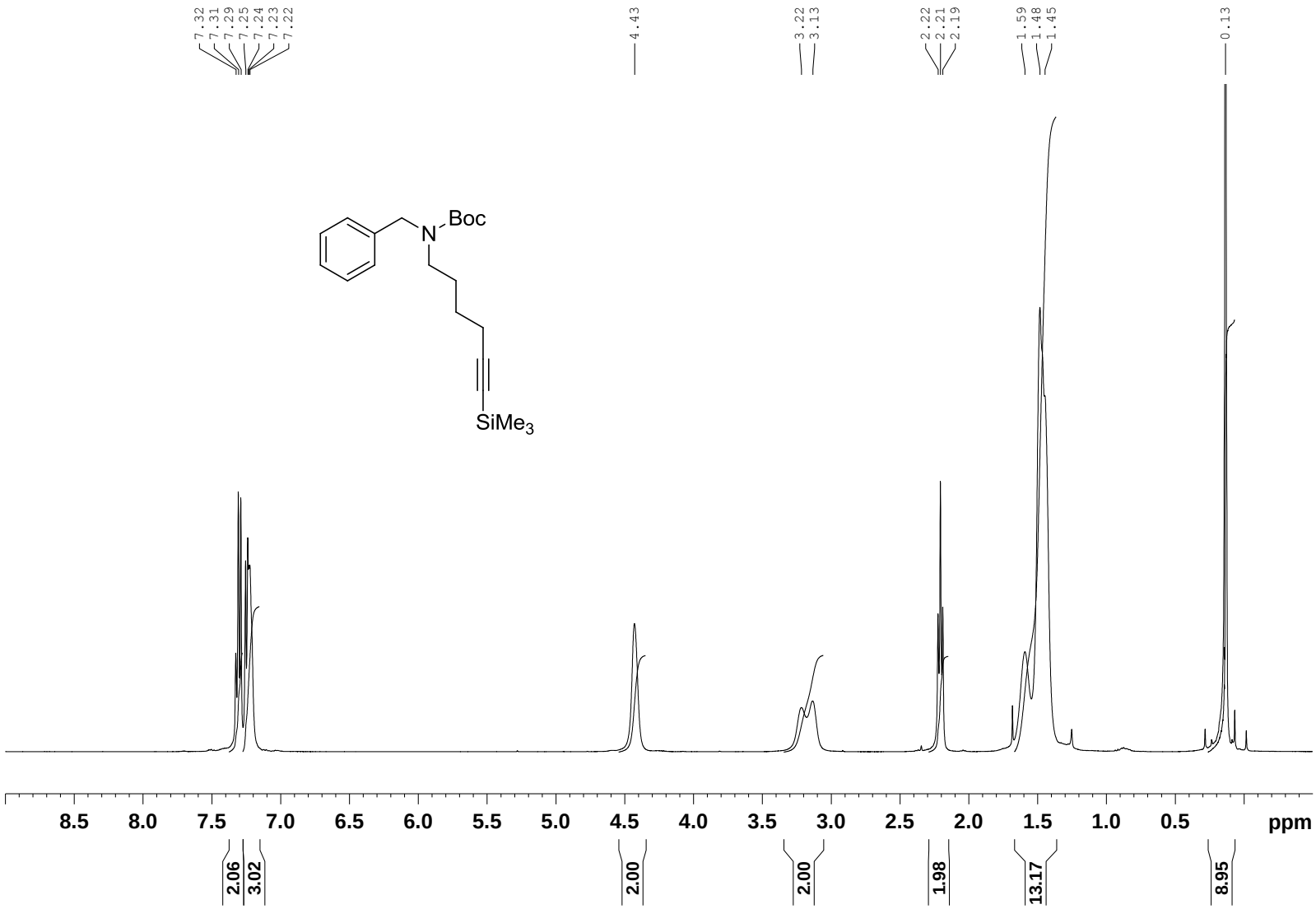

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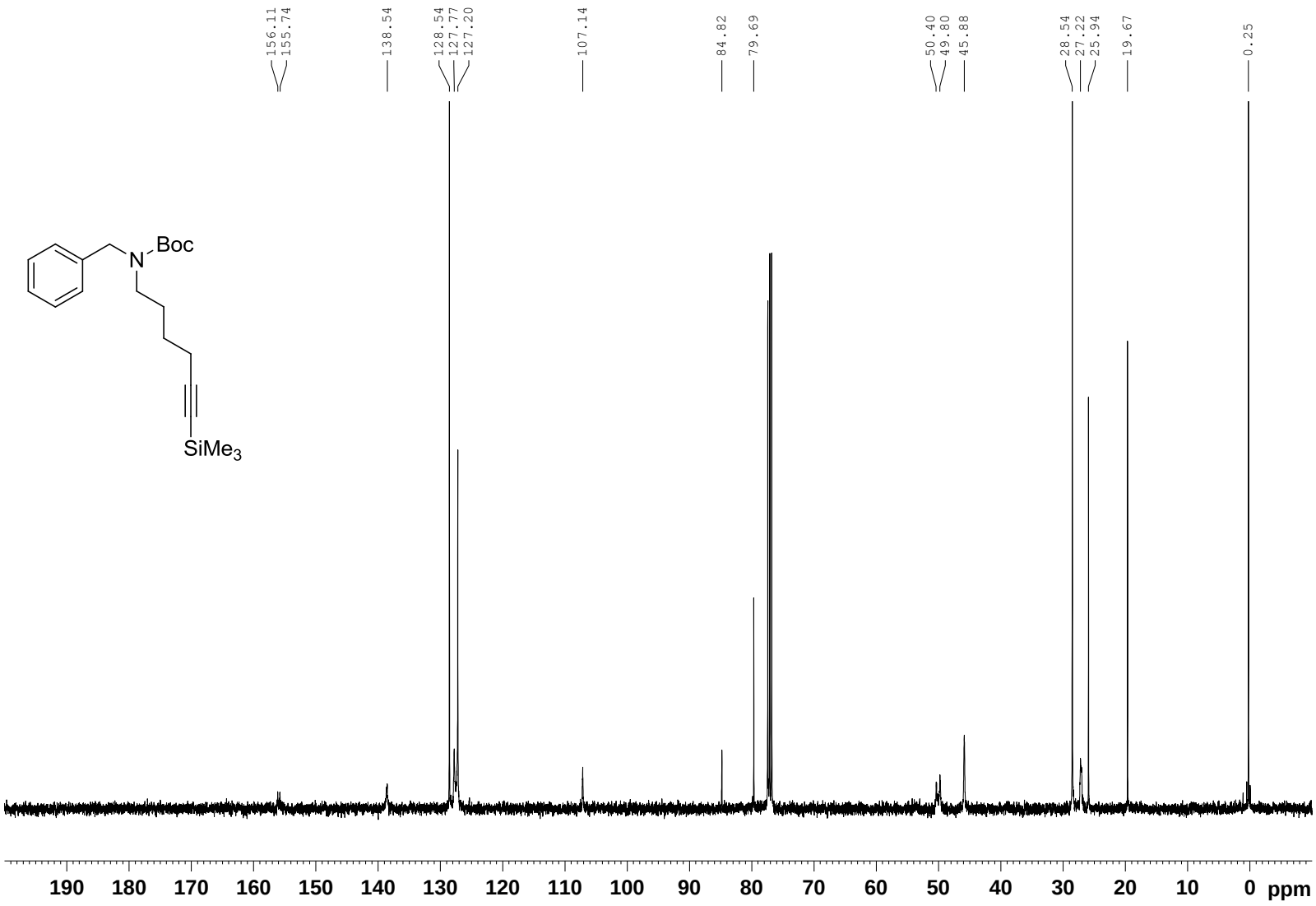

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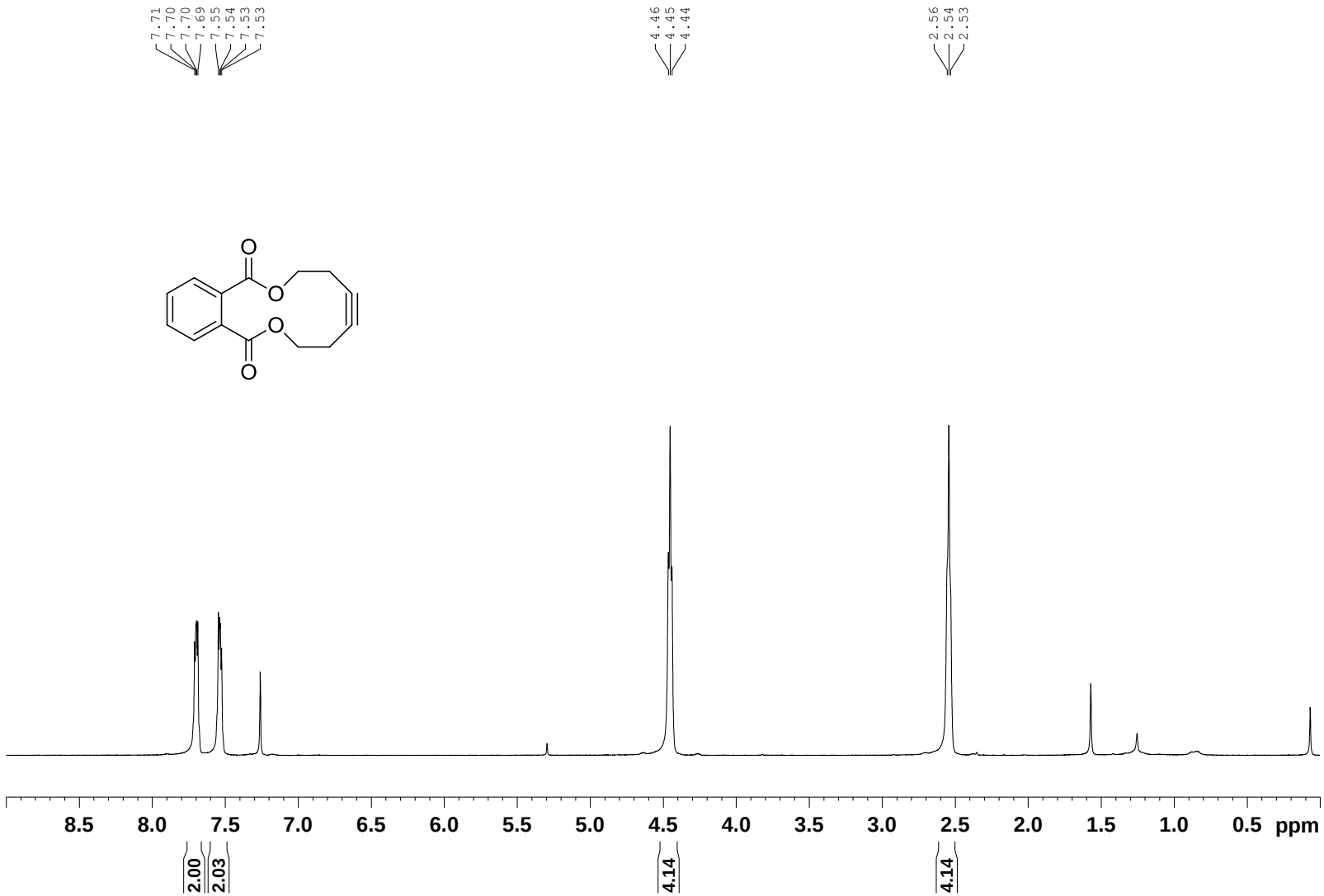

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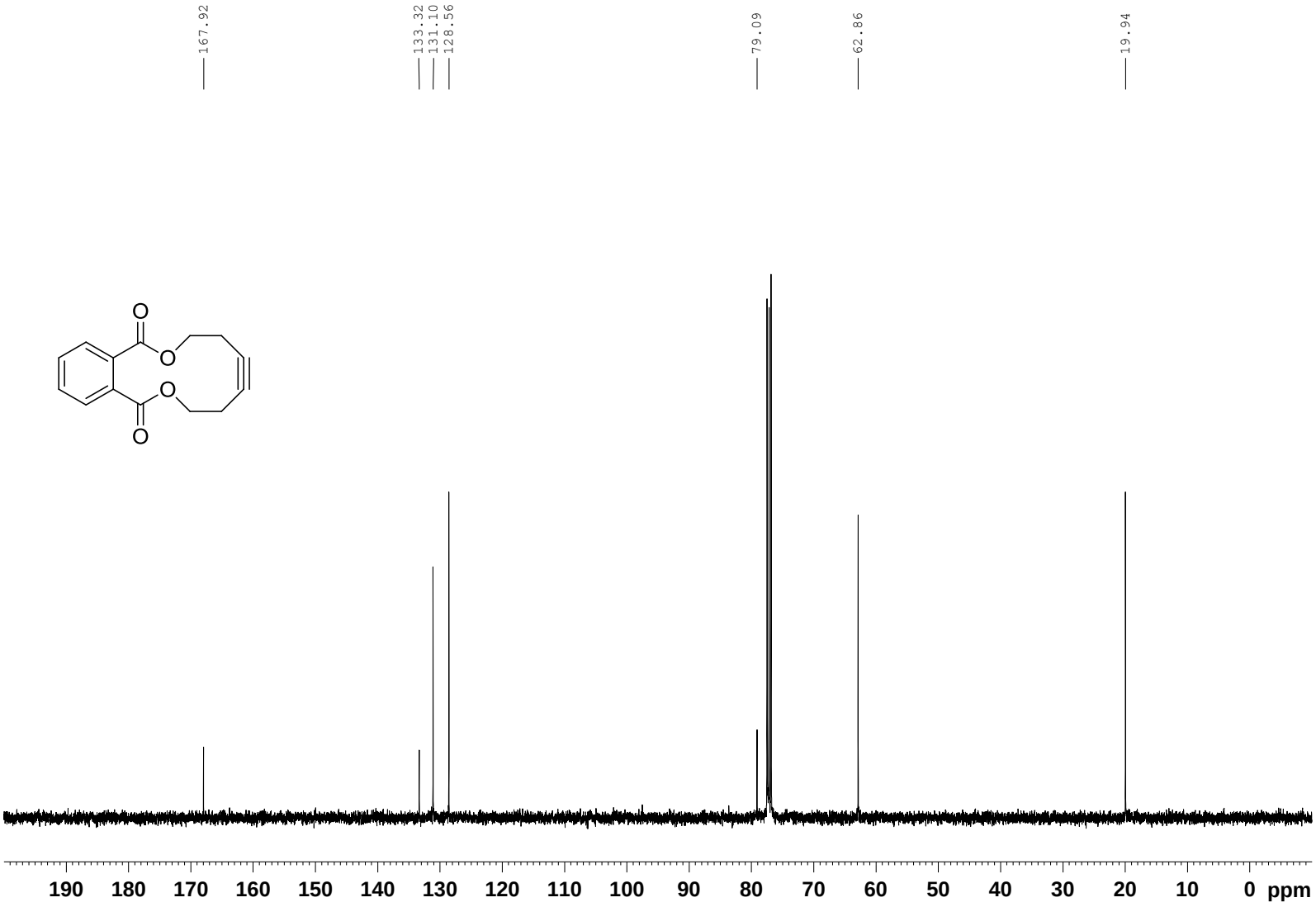

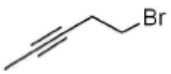
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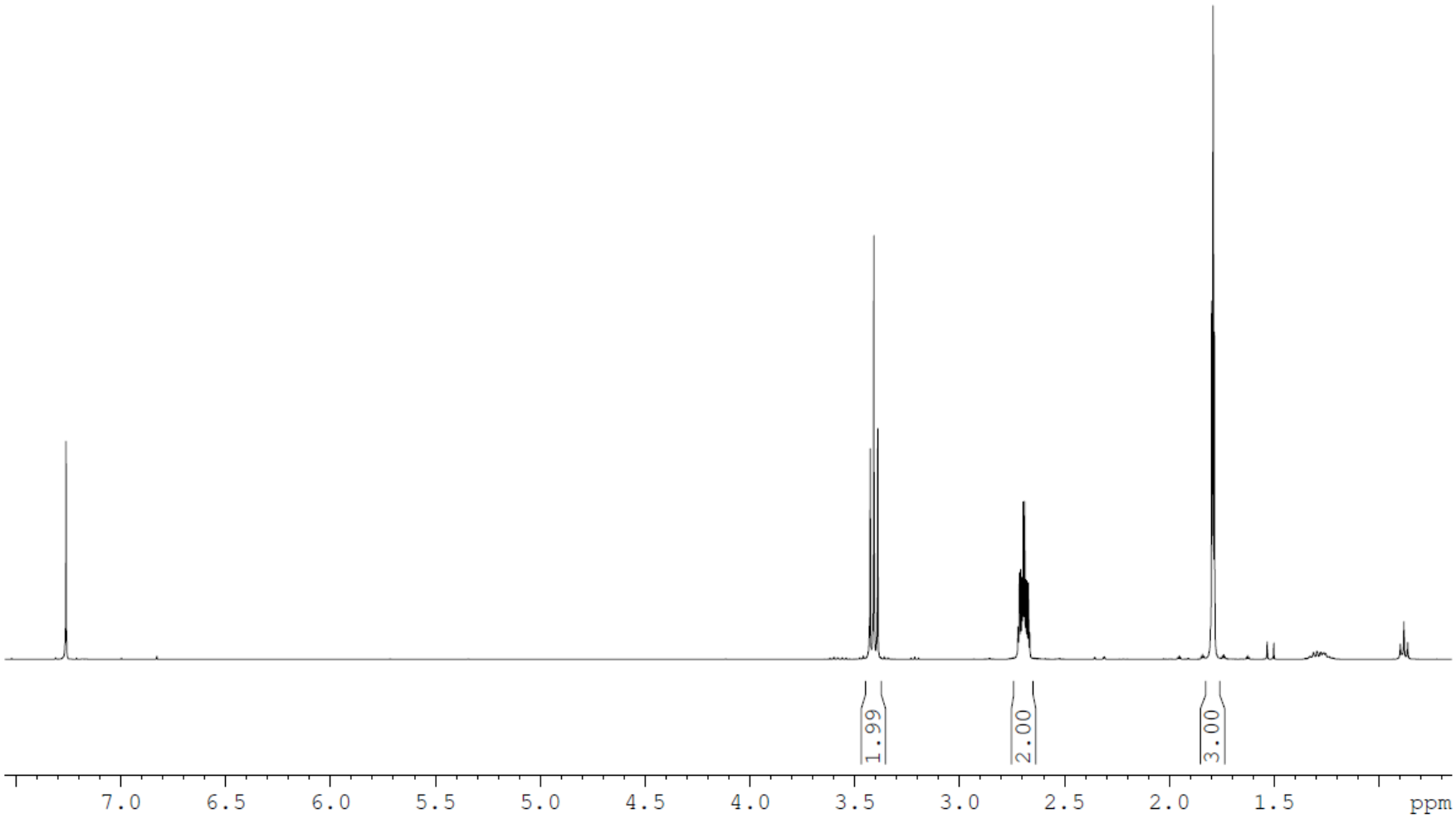
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5.5
5.0
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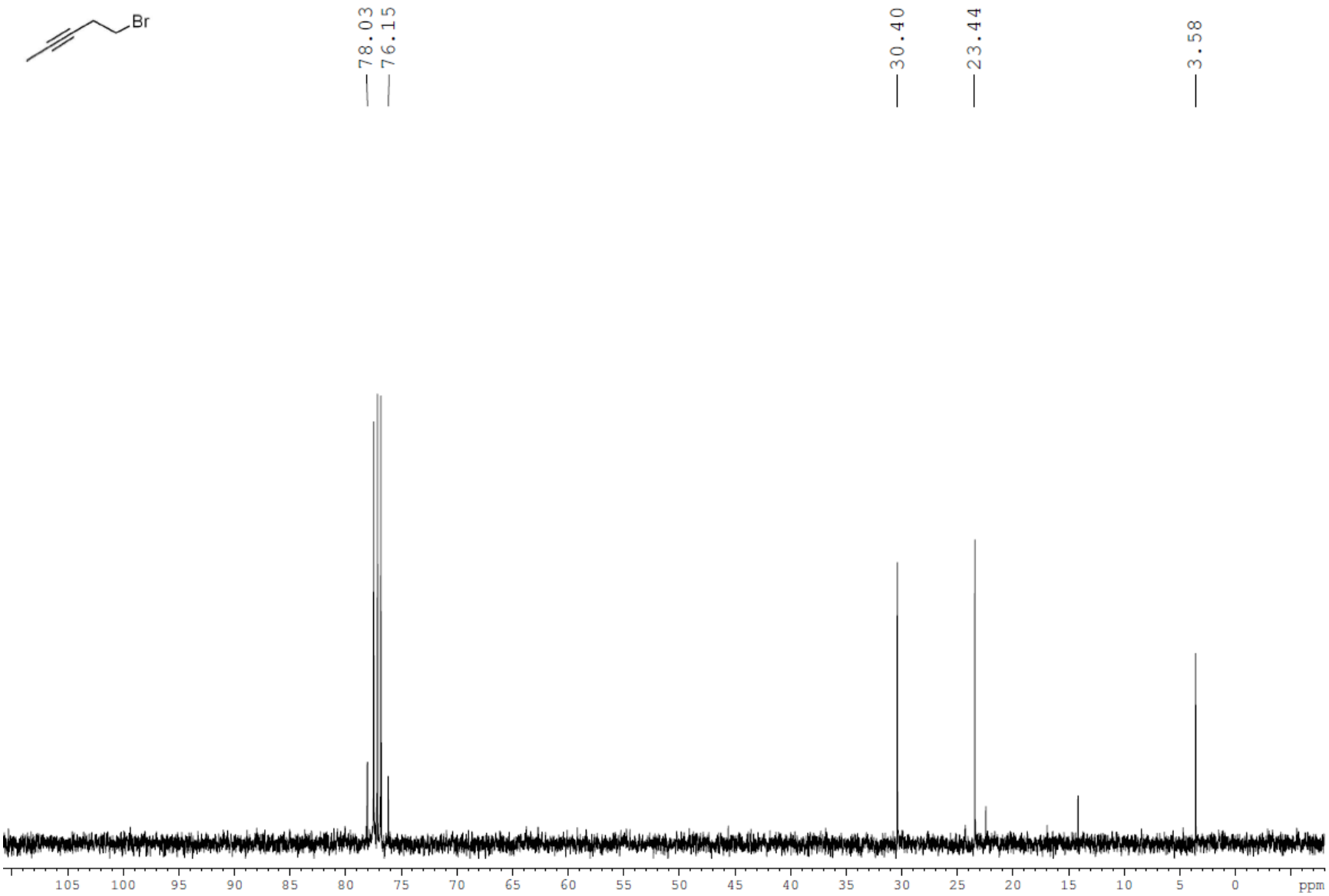
4.0
3.5
3.0
2.5
2.0
1.5
ppm


Br
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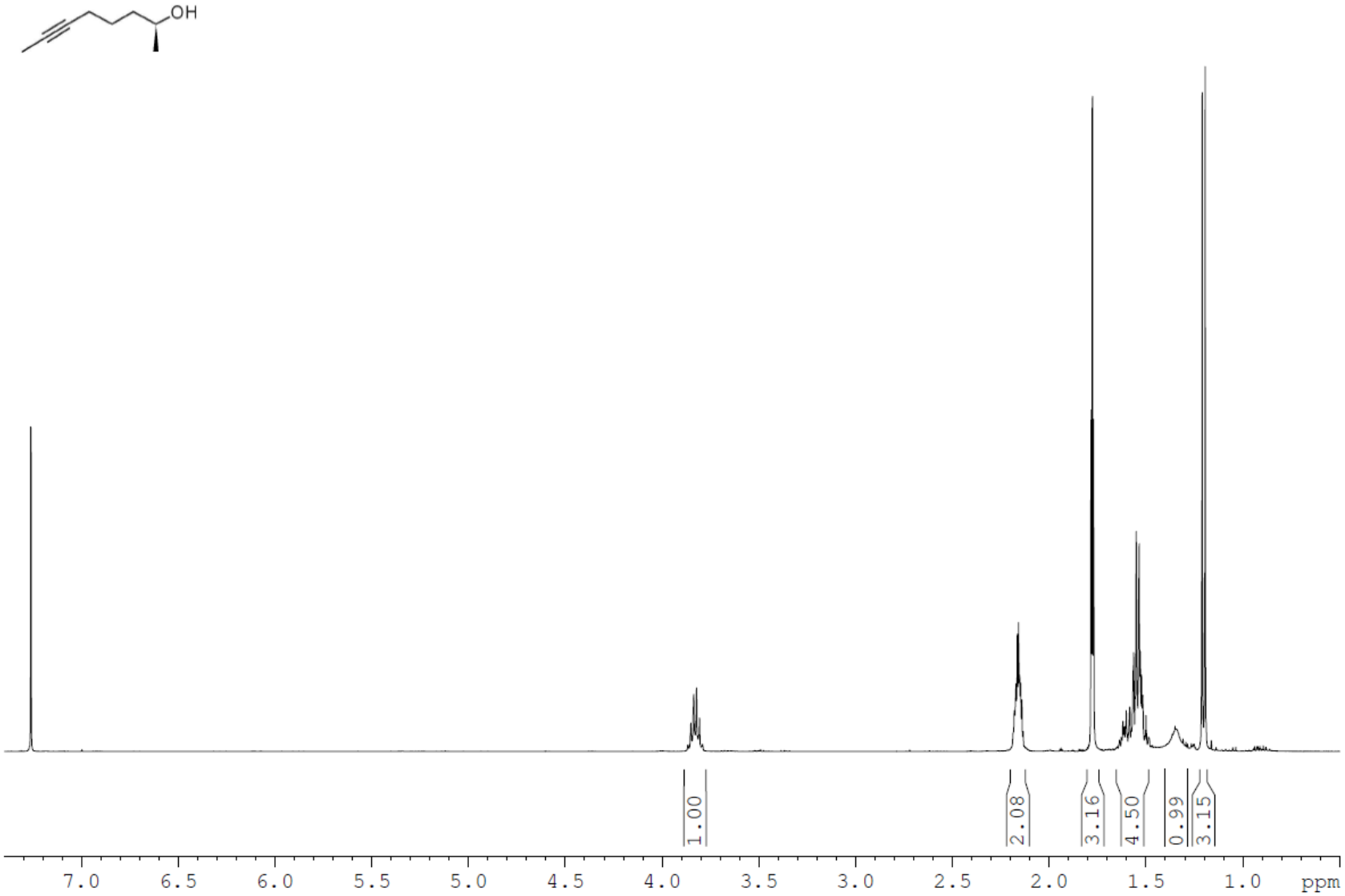
76.15
30.40
23.44
3.58
105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm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0.99
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7.0
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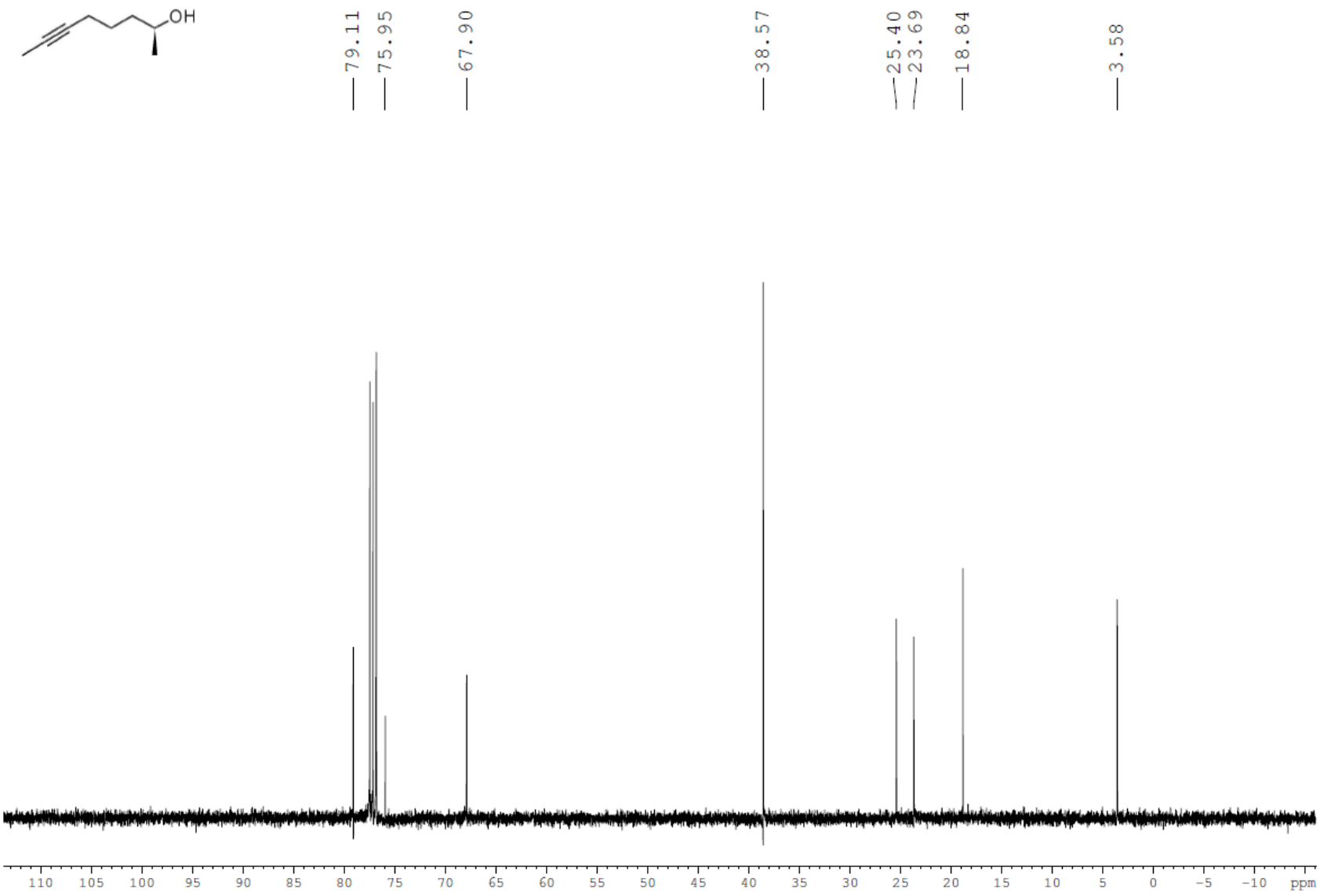
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


OH
79.11
75.95
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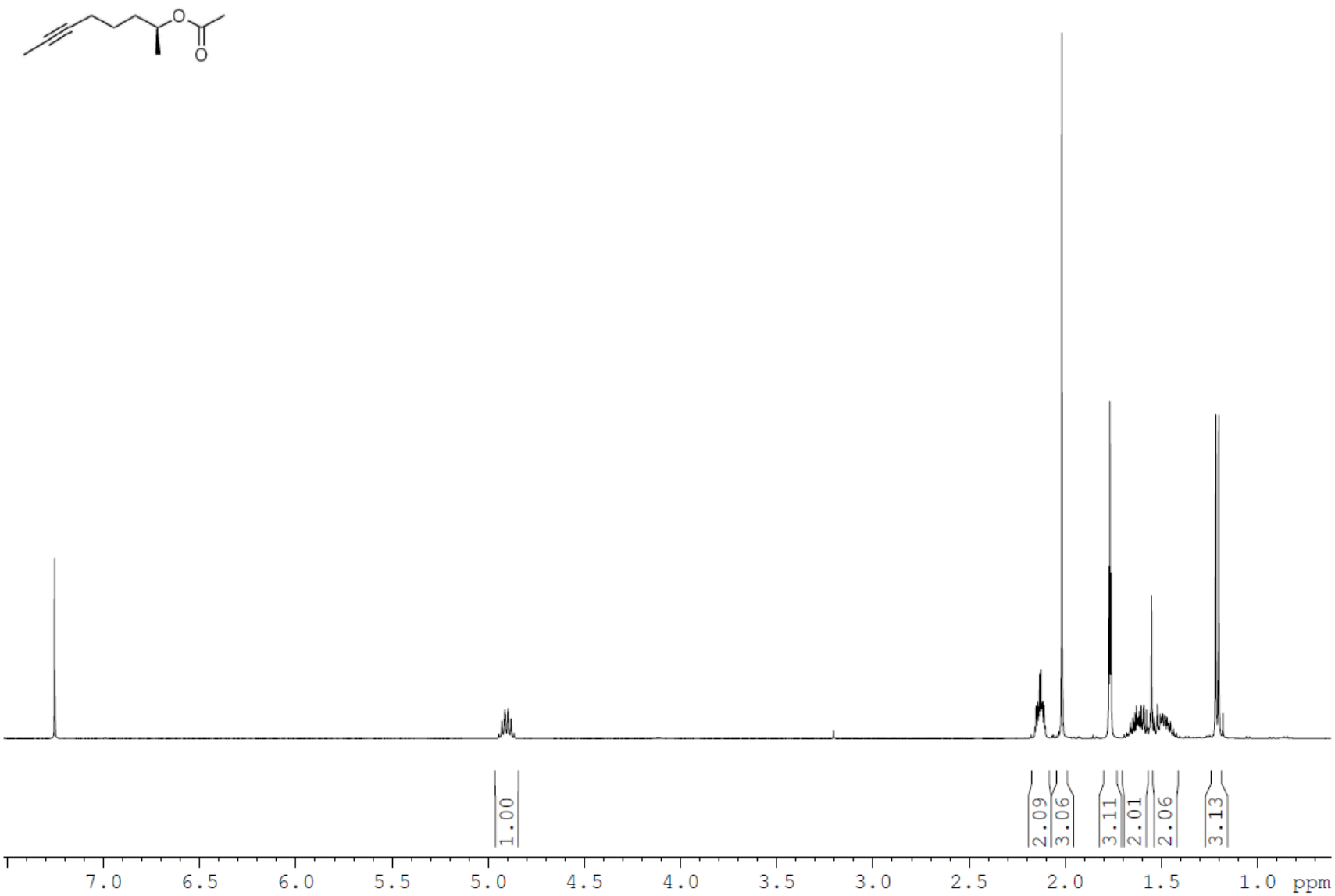
25.40
23.69
18.84
3.58
110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 ppm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2.5
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1.5
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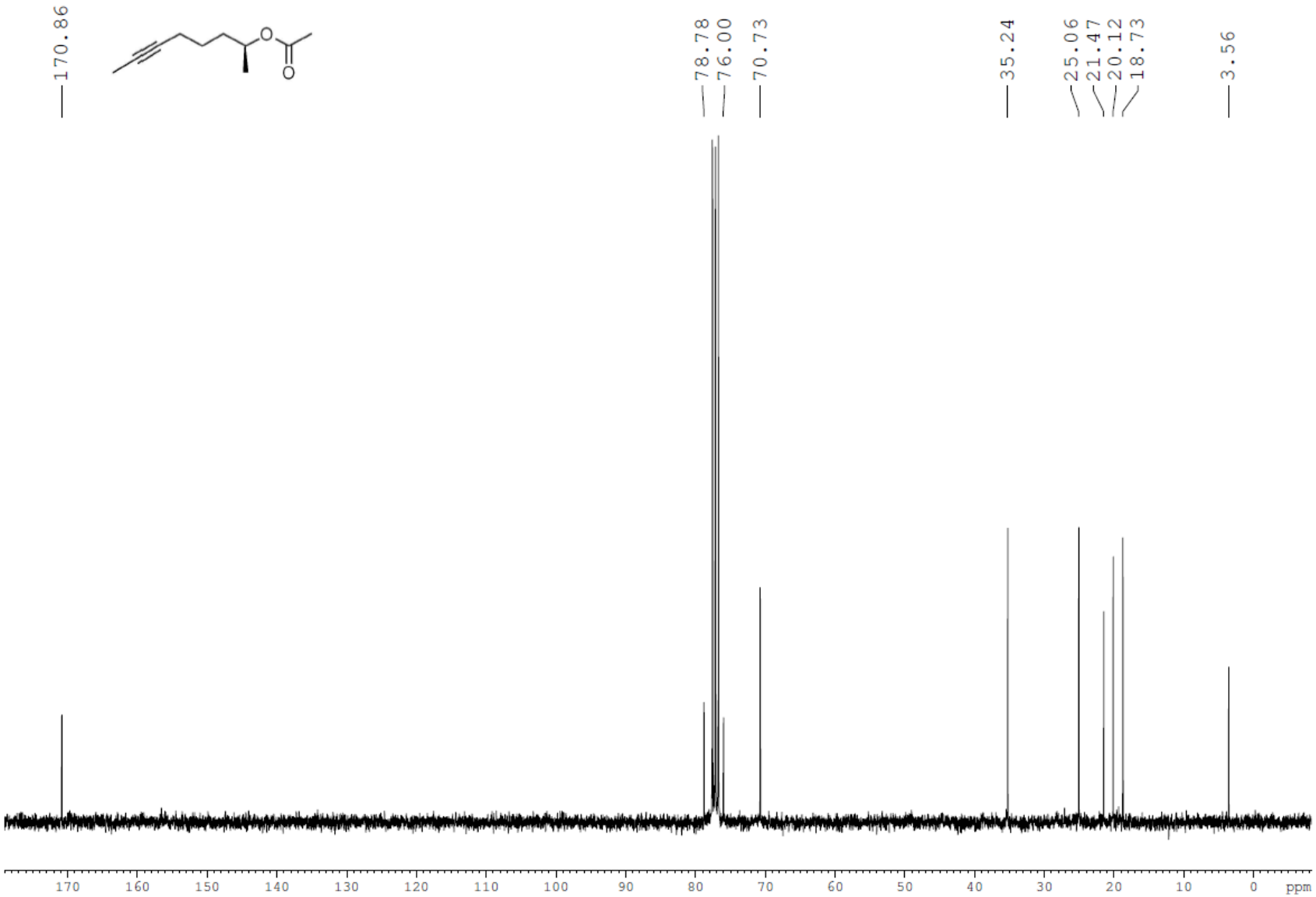
ppm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25.06
21.47
20.12
18.73
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100
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60
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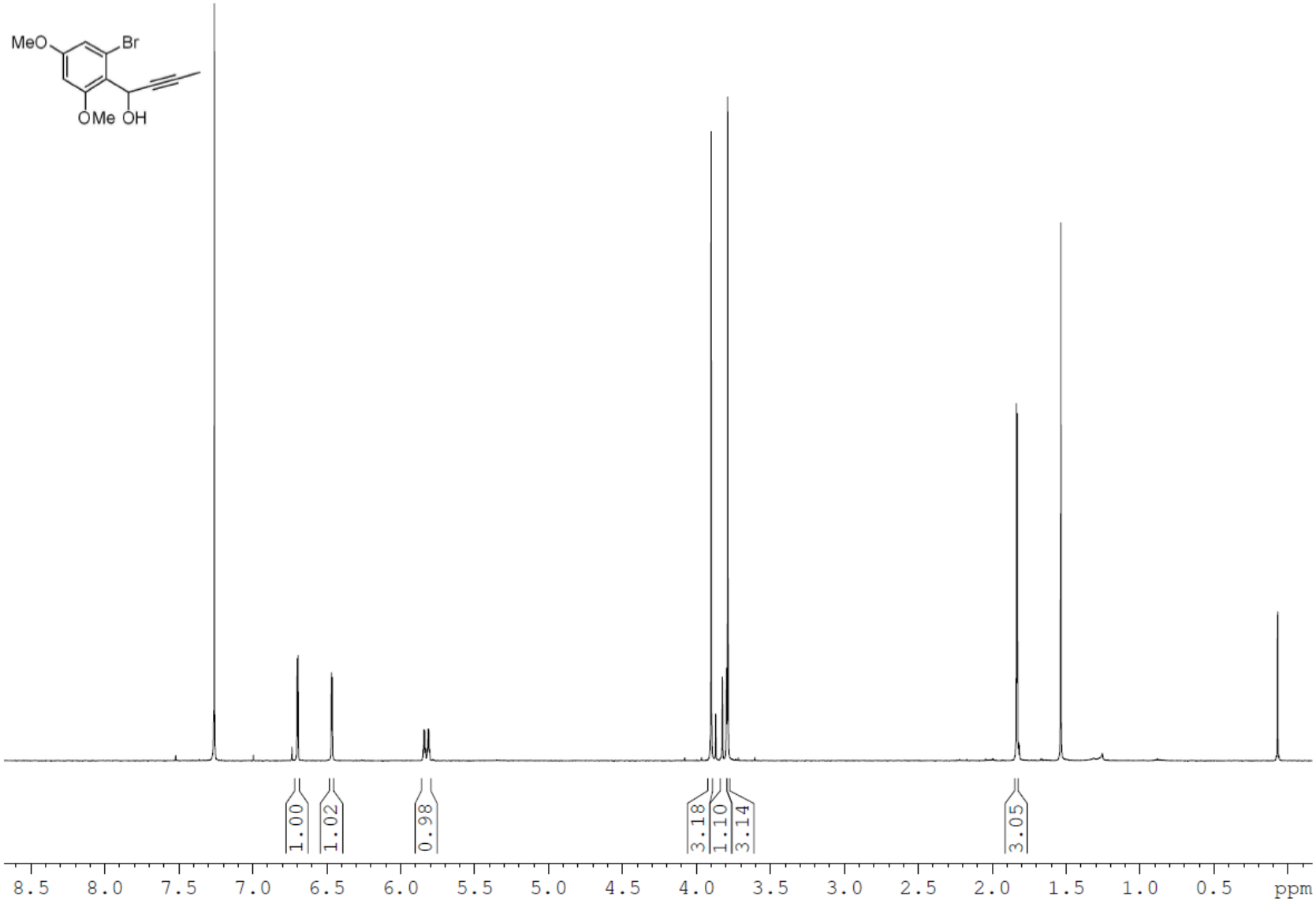
20
10
0
ppm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Br
OMe
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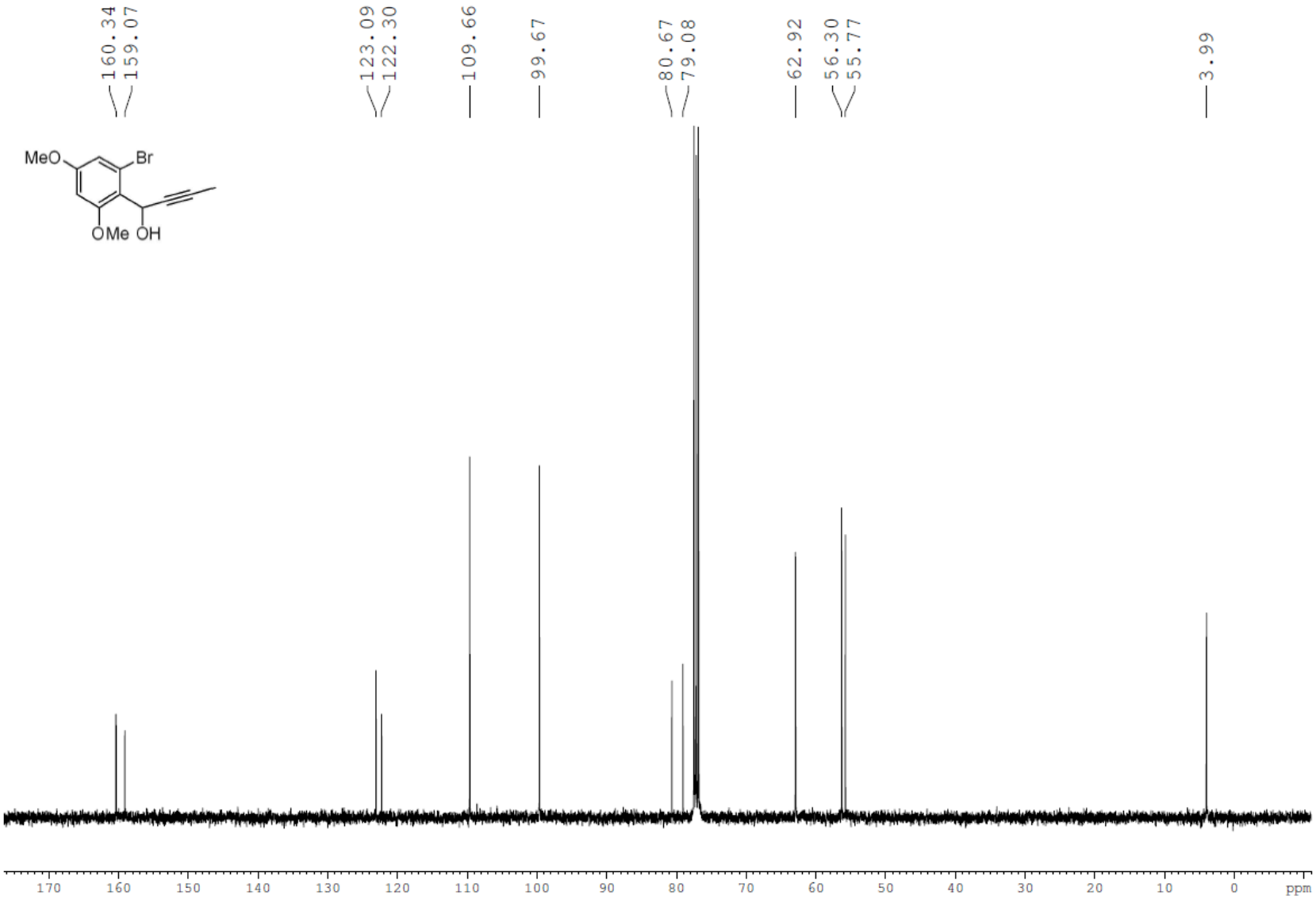
ppm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Br
OMe
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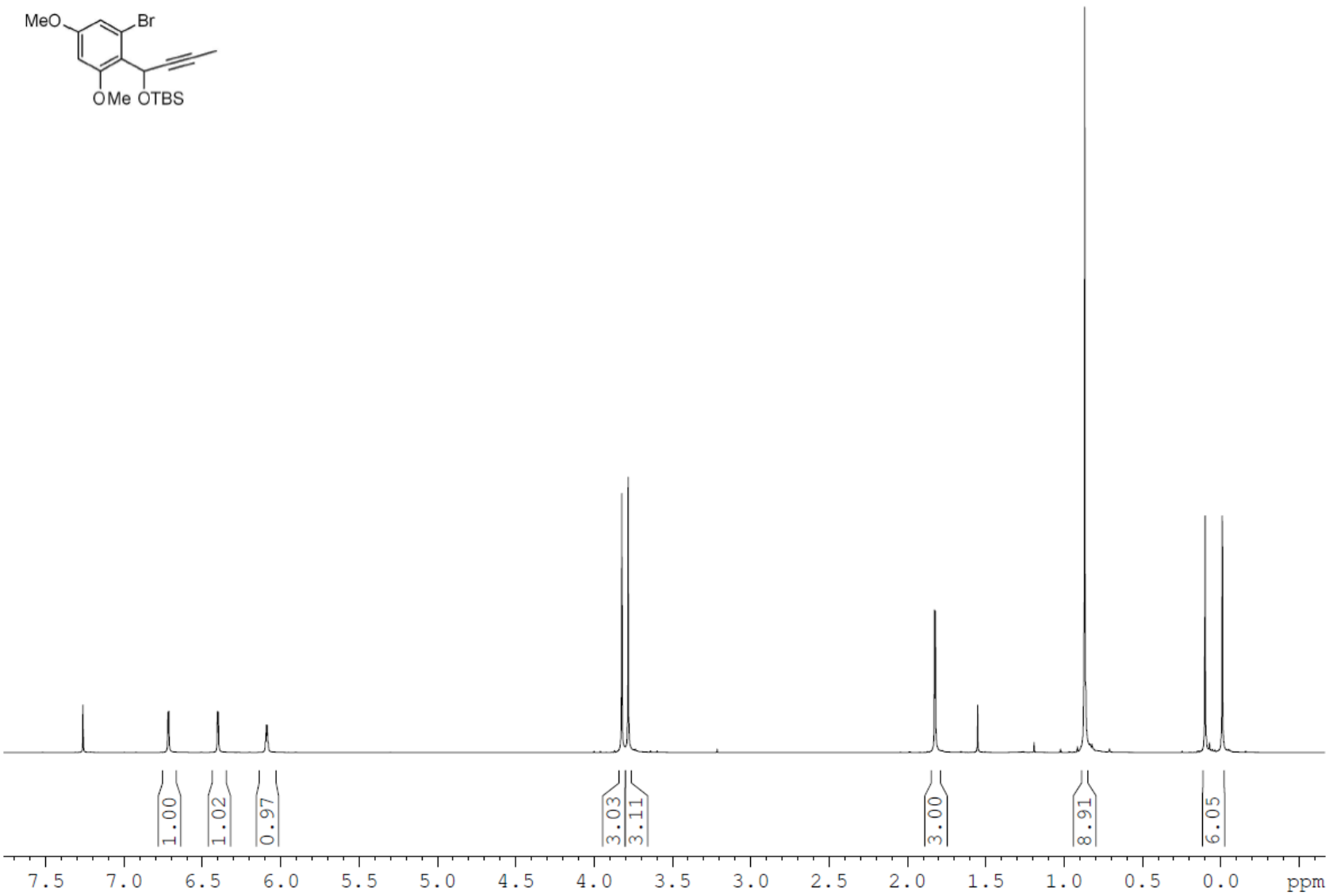
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7.0
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6.0
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5.0
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4.0
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3.0
2.5
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0.5
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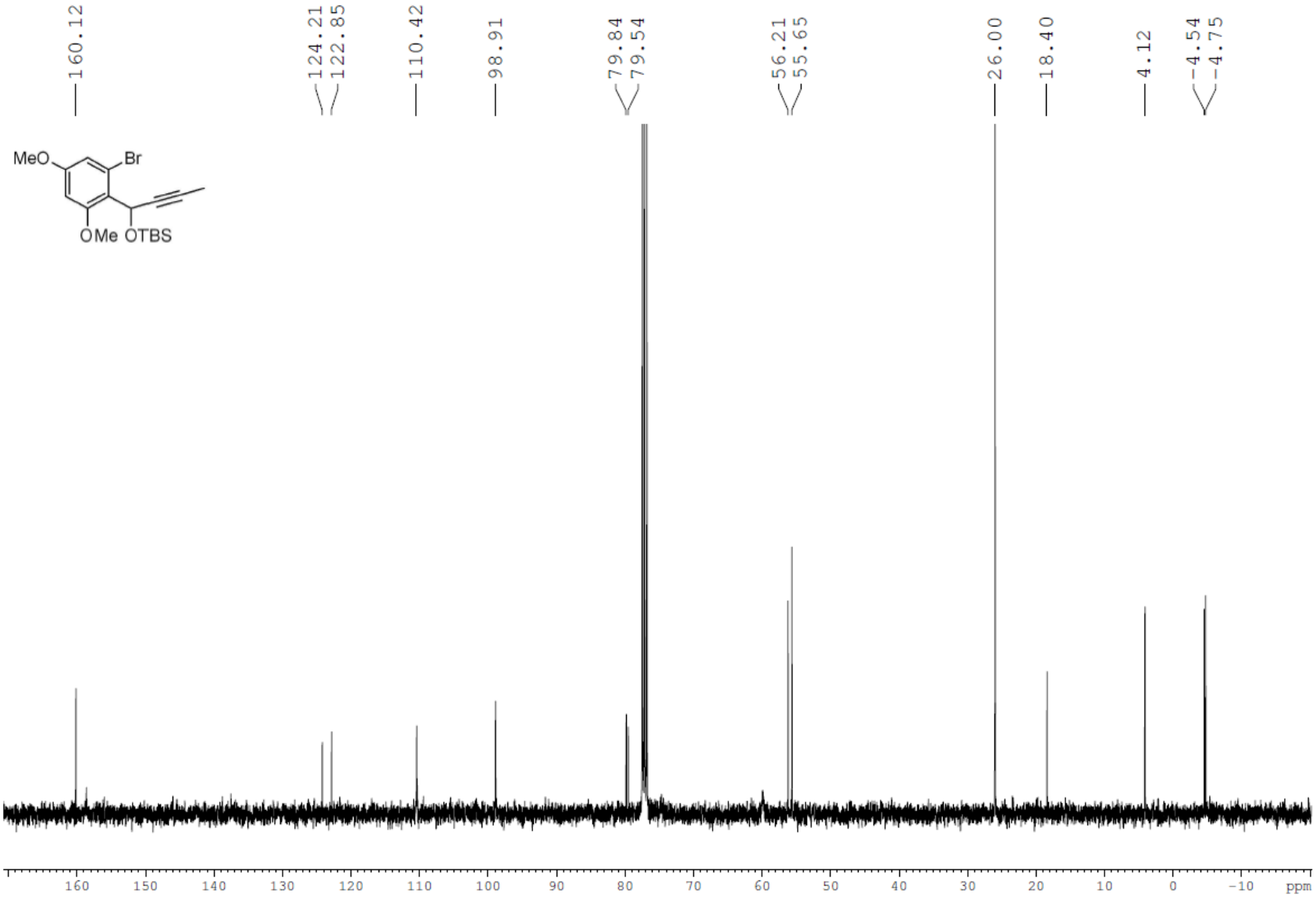
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-4.54
-4.75
MeO
Br
OMe
OTBS
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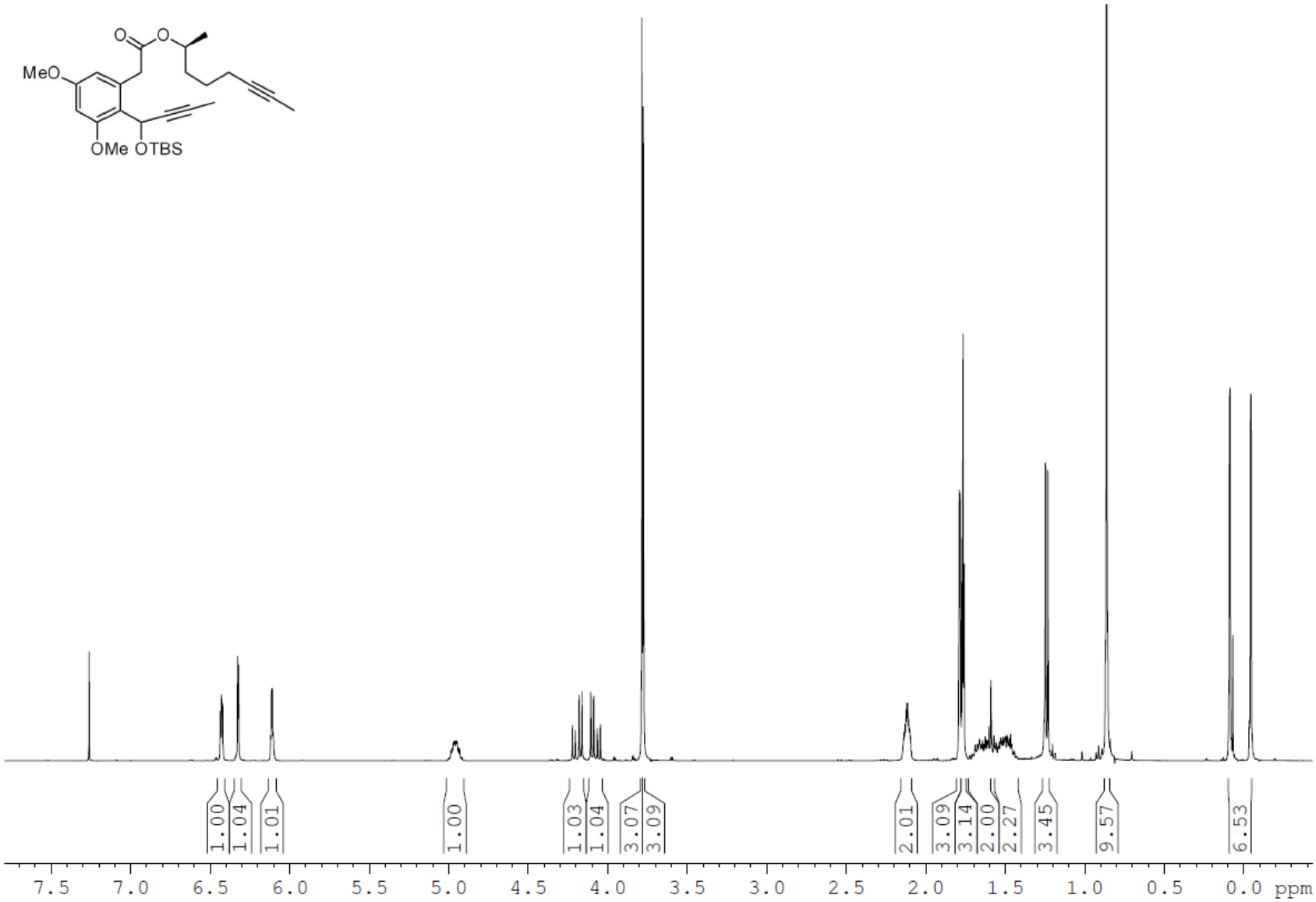
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3.45
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6.53
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6.5
6.0
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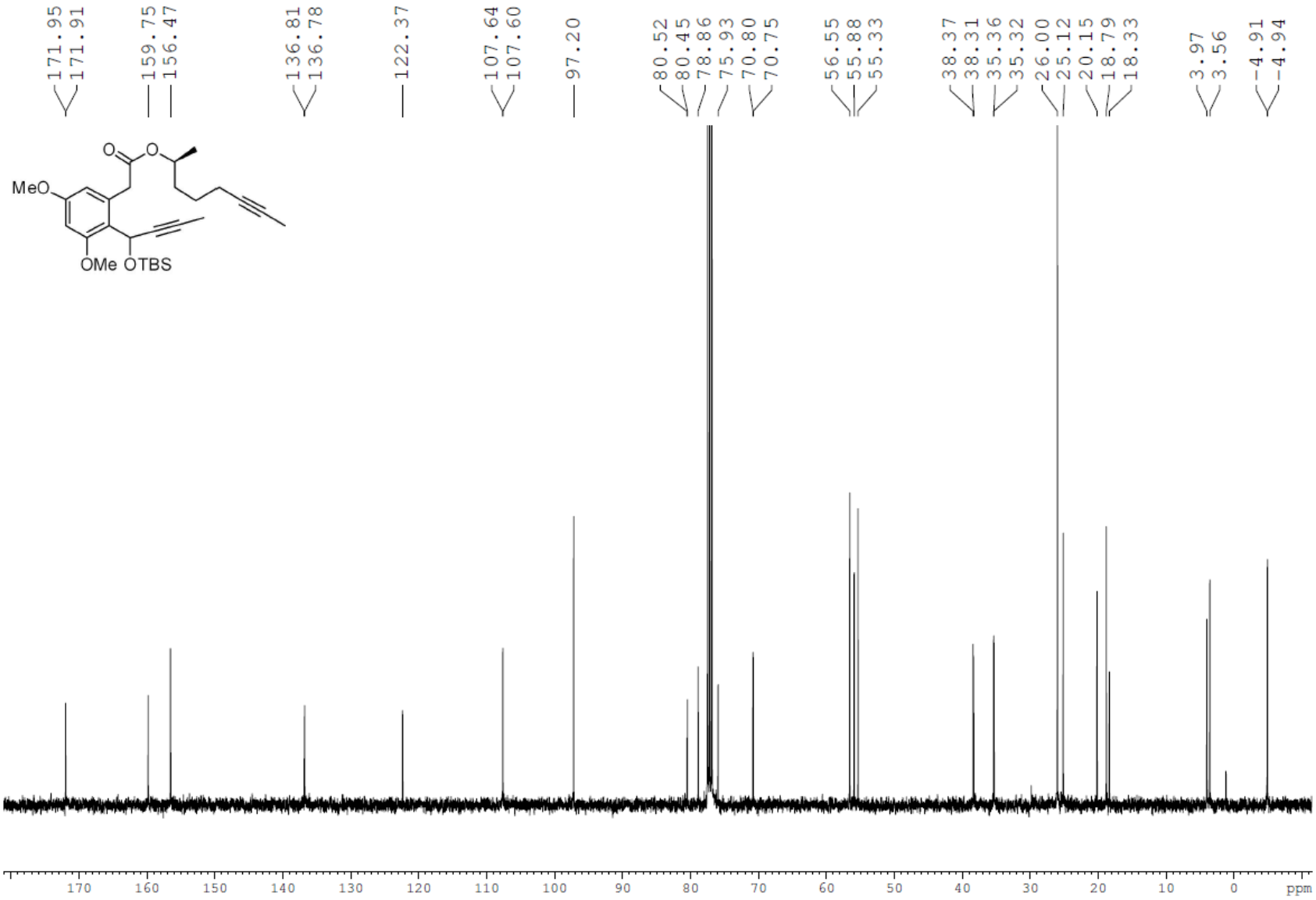
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75.93
70.80
70.75
56.55
55.88
55.33
38.37
38.31
35.36
35.32
26.00
25.12
20.15
18.79
18.33
3.97
3.56
-4.91
-4.94
MeO
OMe
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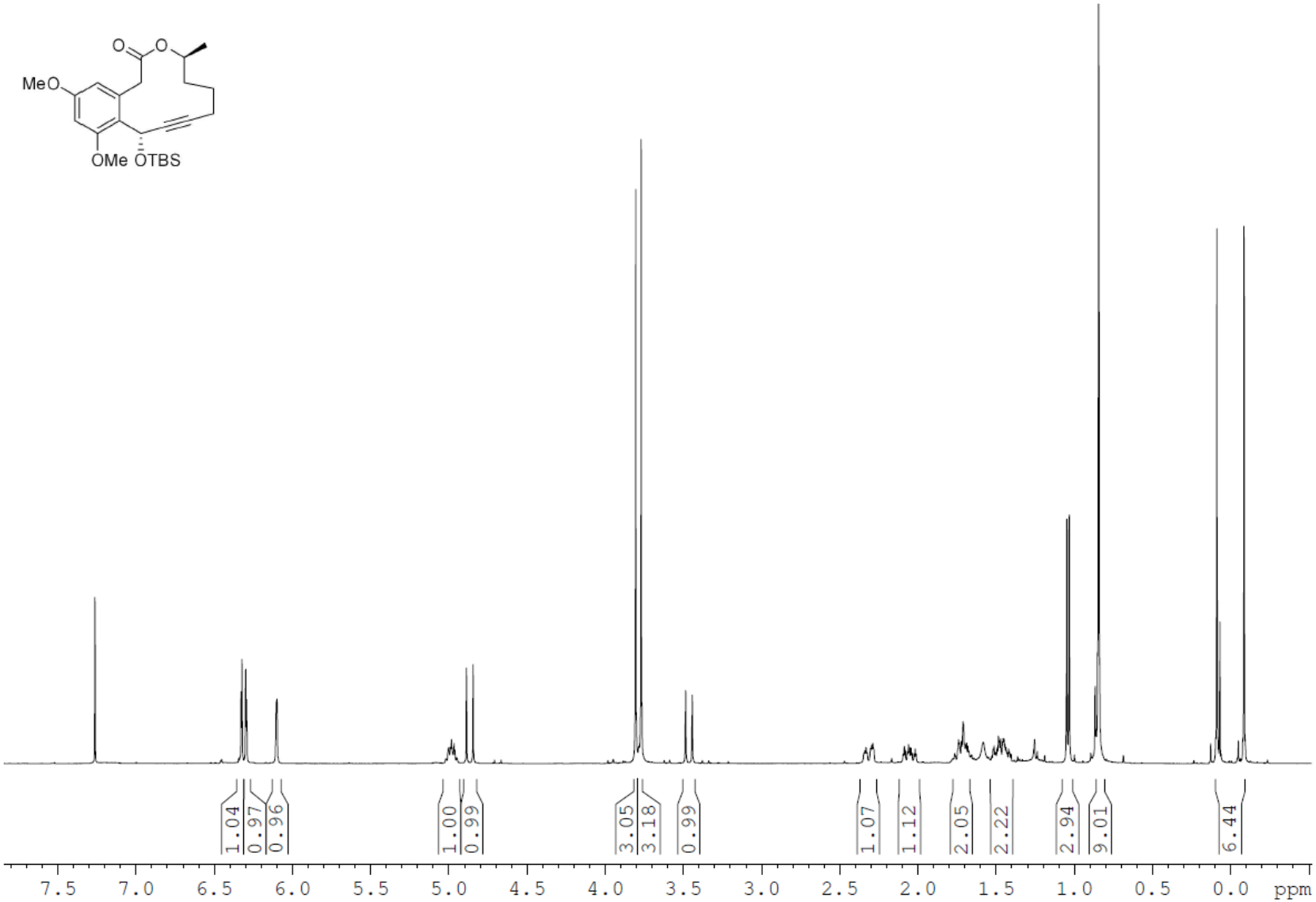
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2.22
2.94
9.01
6.44
7.5
7.0
6.5
6.0
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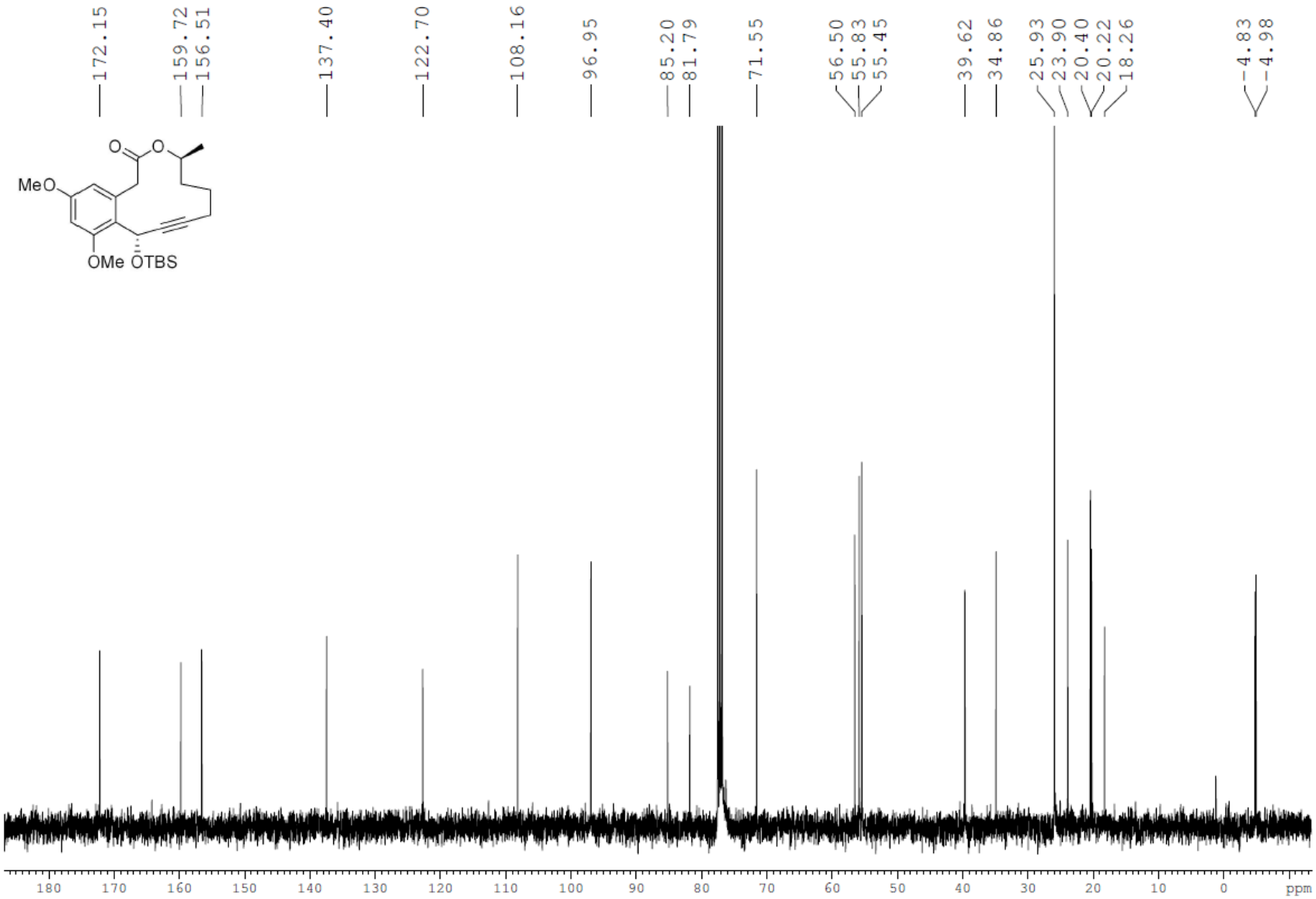
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39.62
34.86
25.93
23.90
20.40
20.22
18.26
-4.83
-4.98
MeO
OMe
OTBS
O
O
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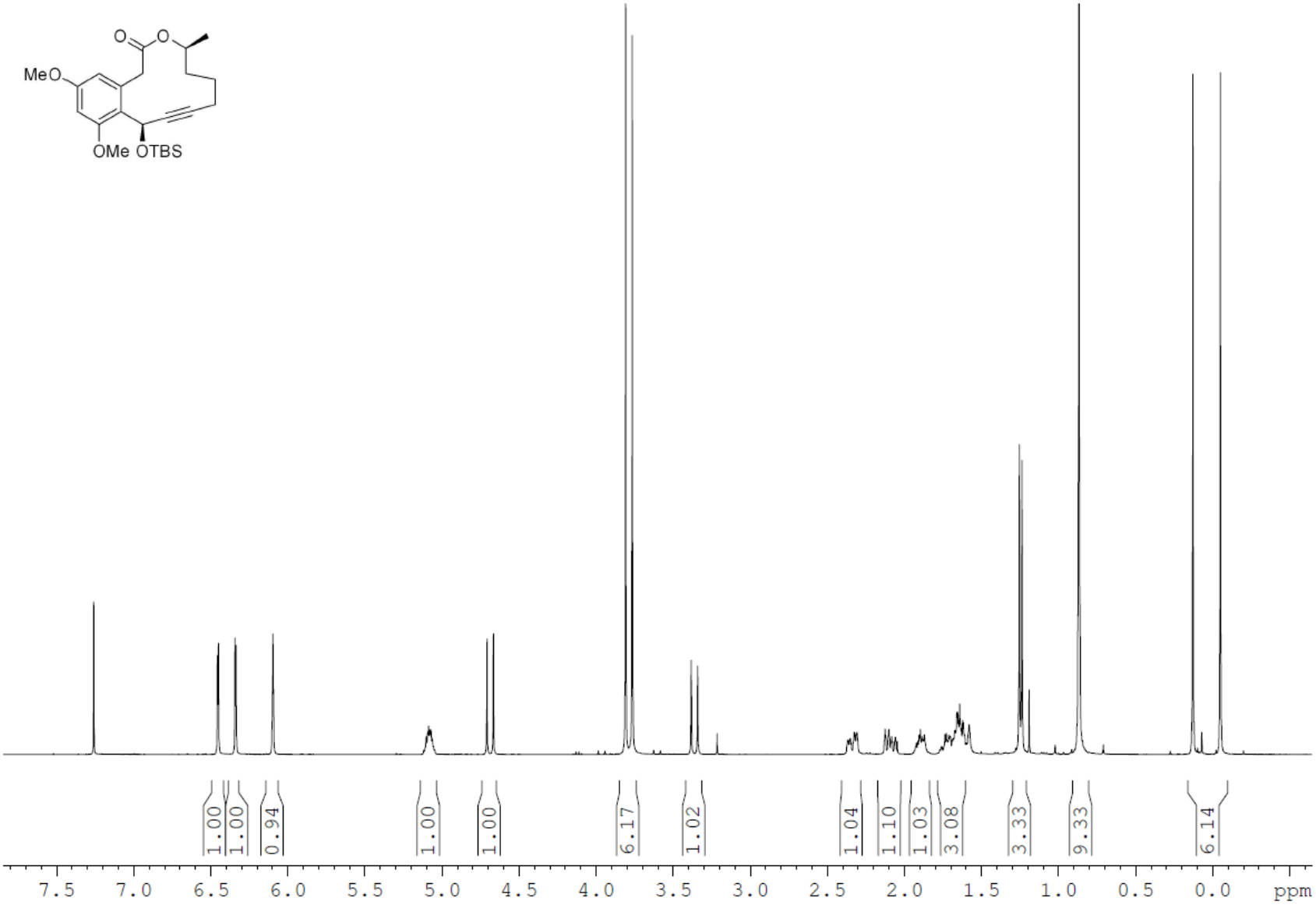
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OTBS
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1.10
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6.5
6.0
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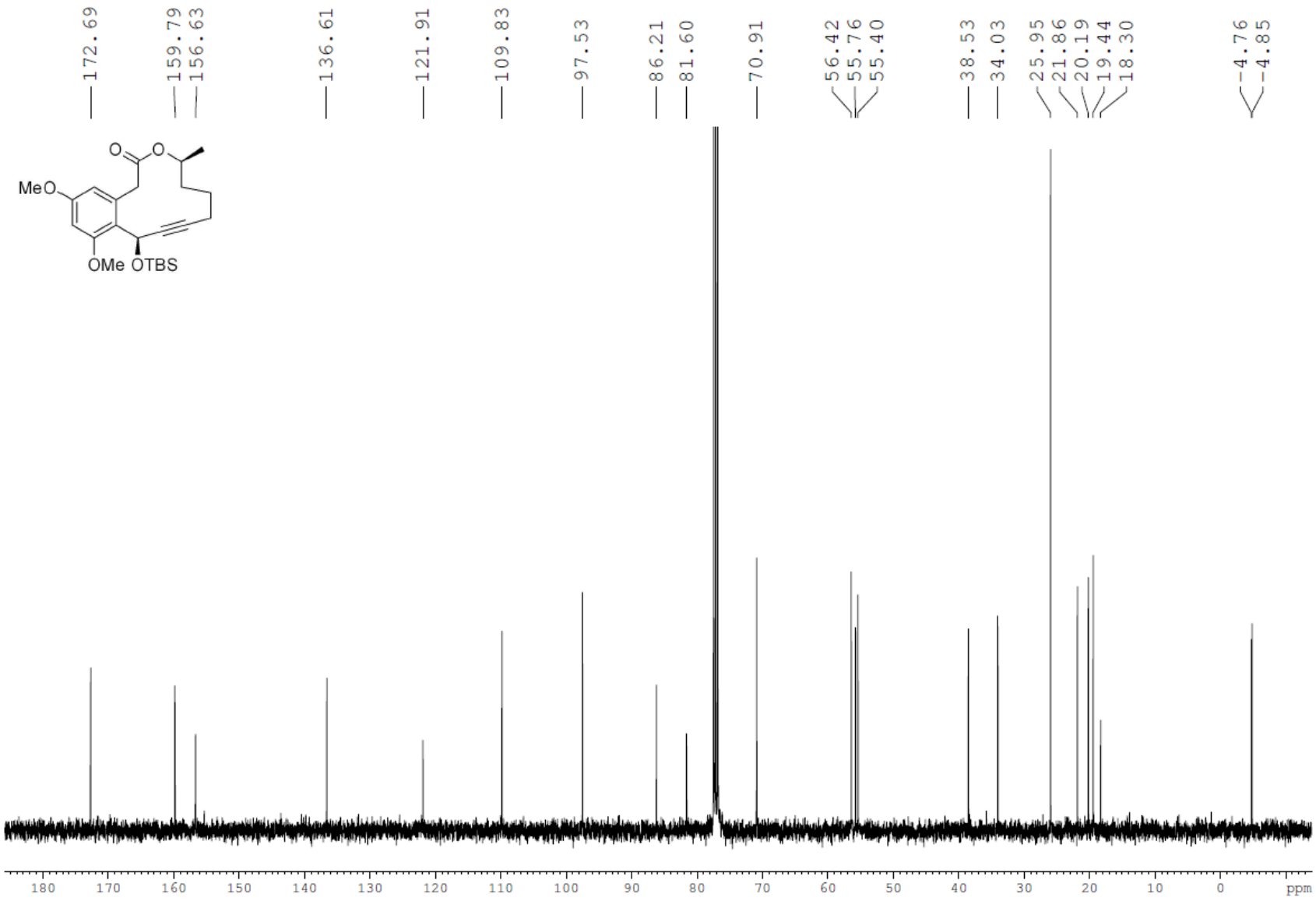
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38.53
34.03
25.95
21.86
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18.30
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-4.85
MeO
OMe OTBS
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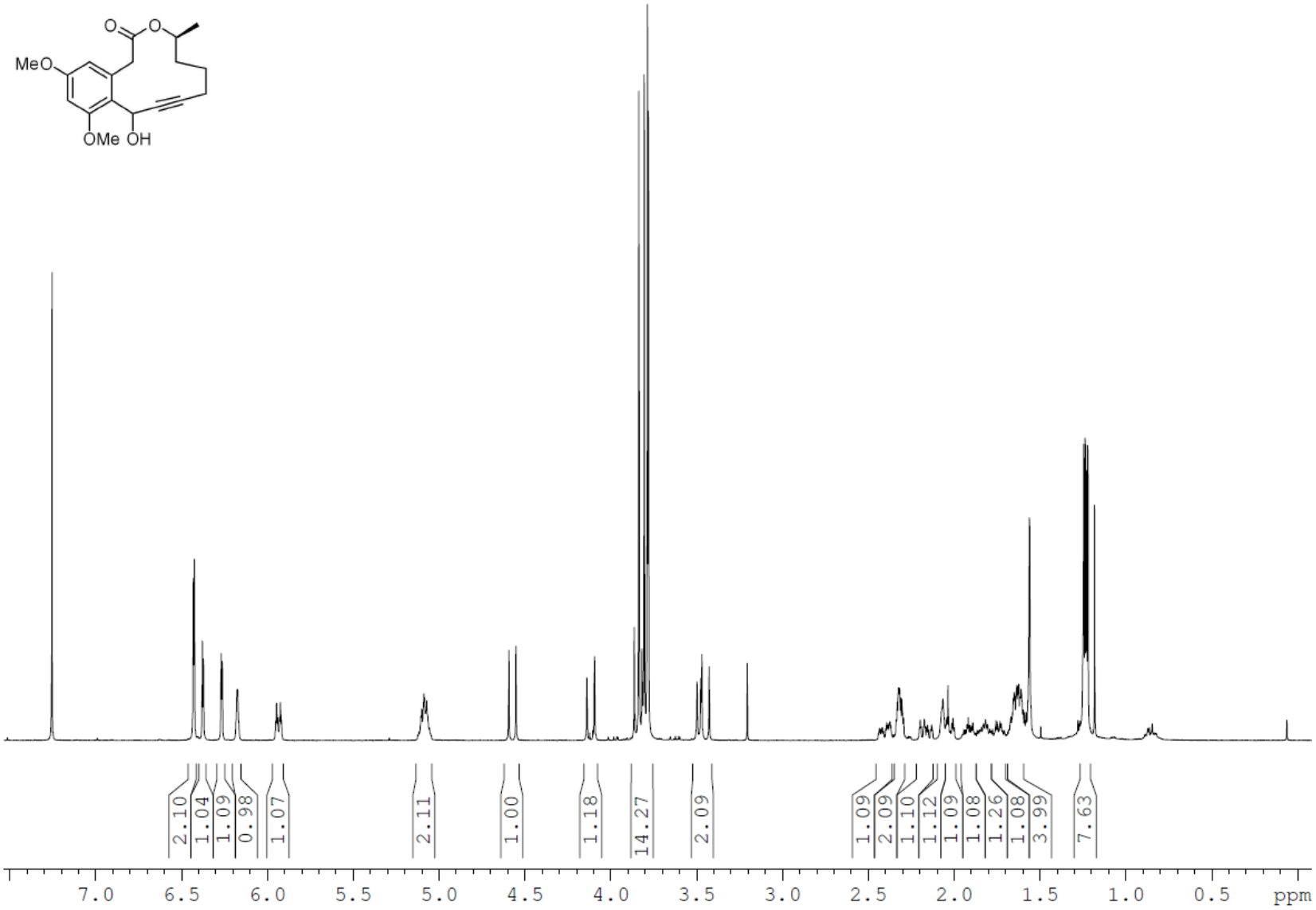
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2.09
1.10
1.12
1.09
1.08
1.26
1.08
3.99
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6.5
6.0
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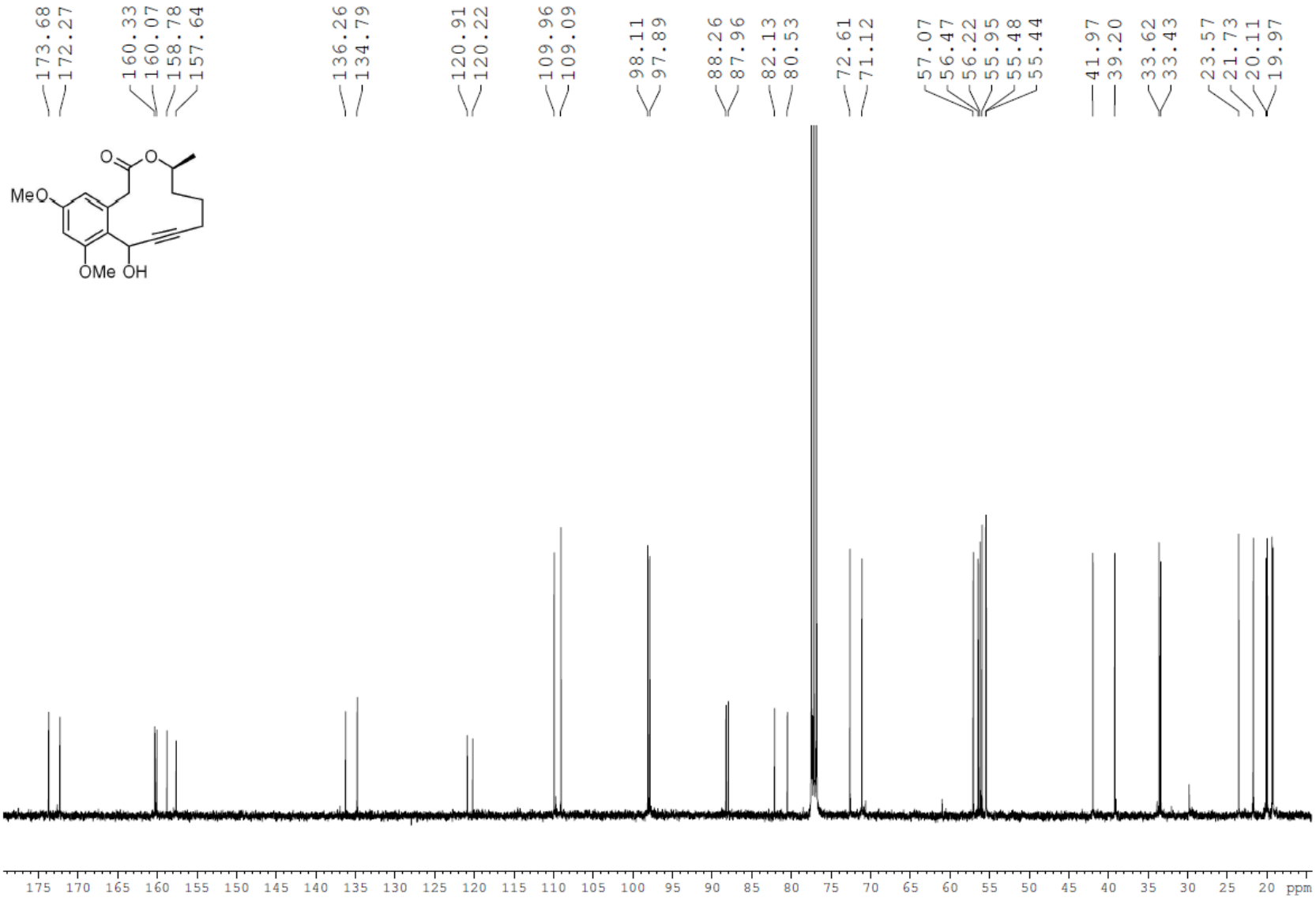
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134.79
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109.09
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97.89
88.26
87.96
82.13
80.53
72.61
71.12
57.07
56.47
56.22
55.95
55.48
55.44
41.97
39.20
33.62
33.43
23.57
21.73
20.11
19.97
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OMe
OH
O
O
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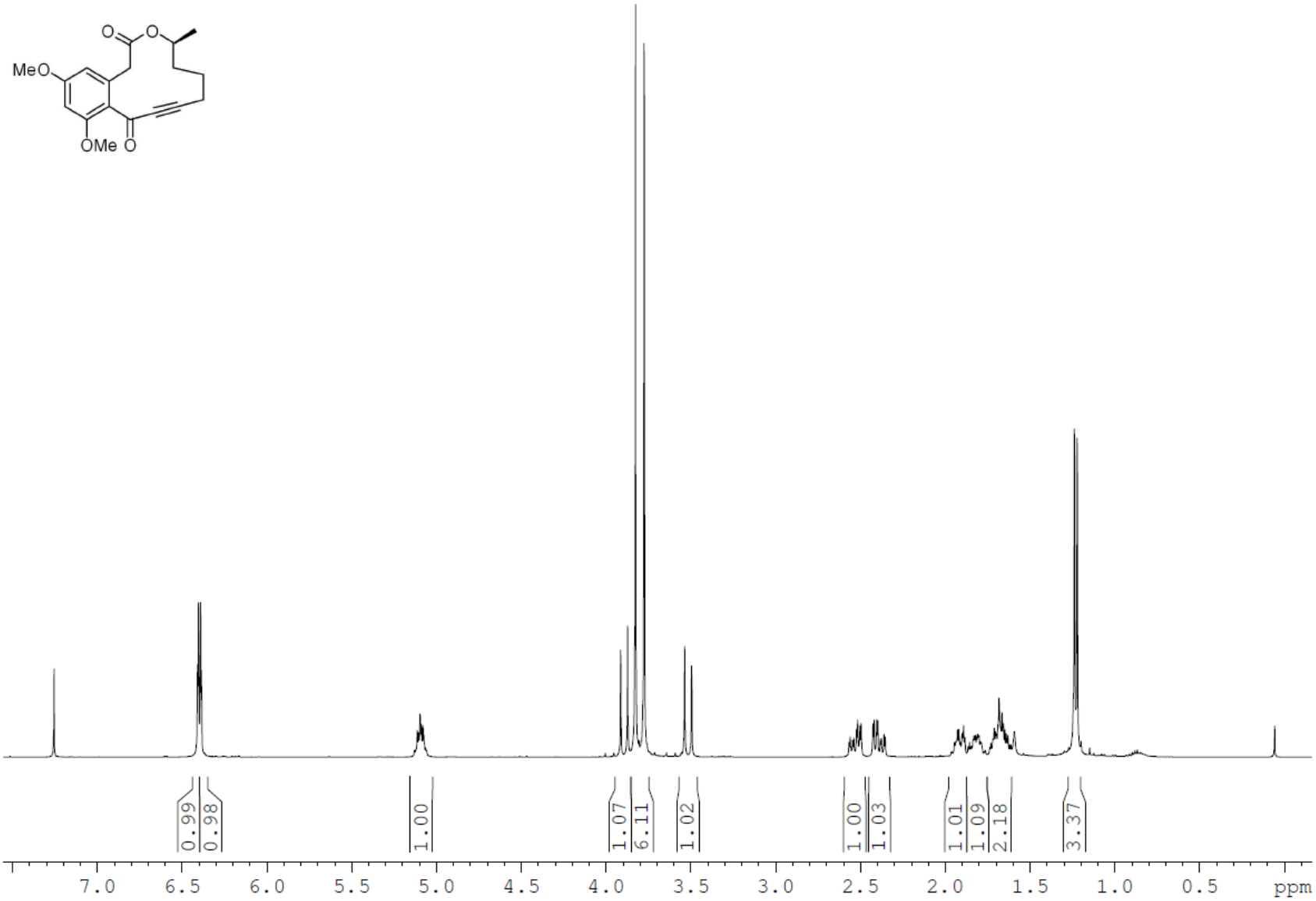
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OMe
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O
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O
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0.98
1.00
1.07
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1.00
1.03
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6.5
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4.0
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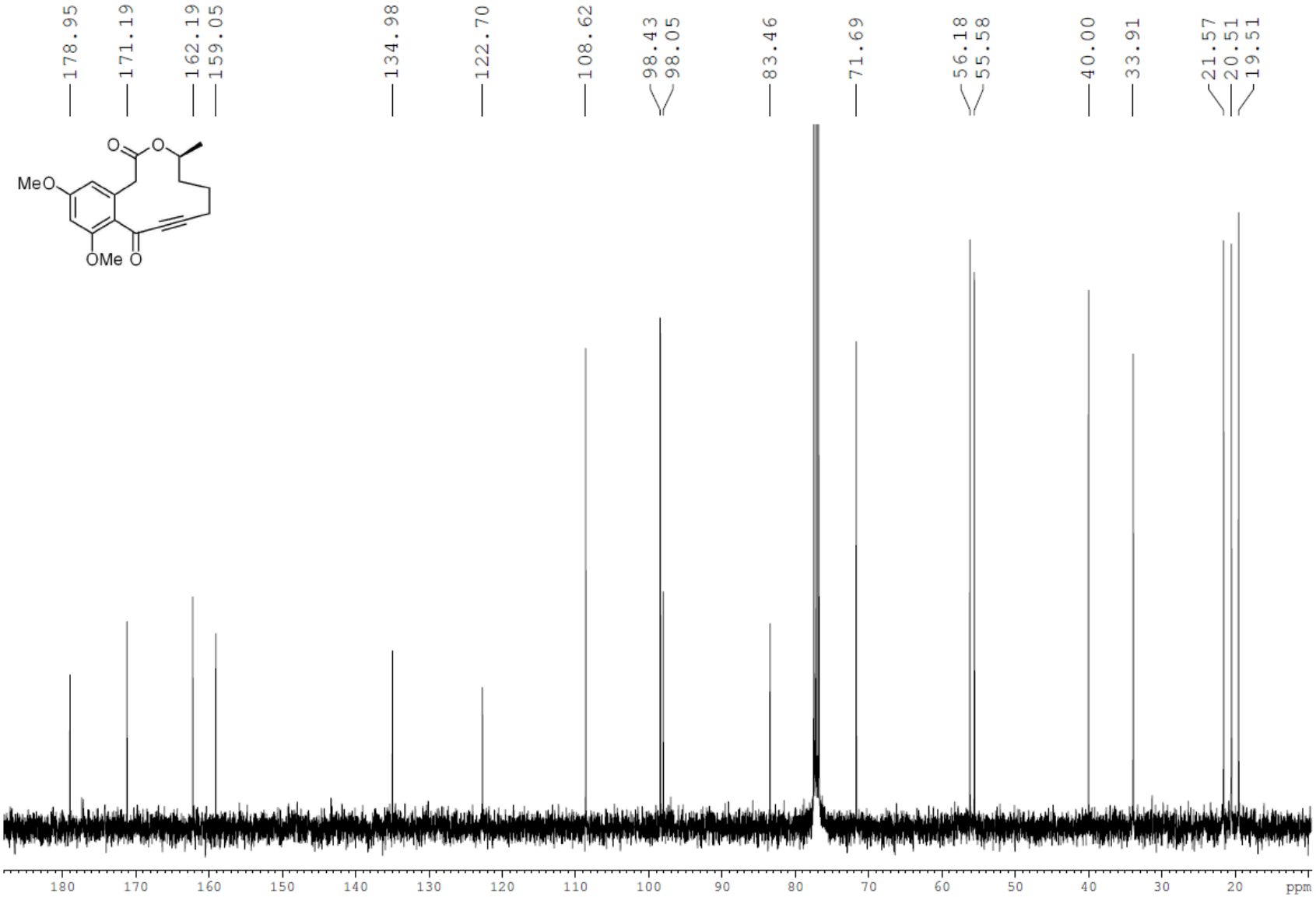
1.0
0.5
ppm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98.05
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71.69
56.18
55.58
40.00
33.91
21.57
20.51
19.51
MeO
OMe
O
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160
150
140
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120
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80
70
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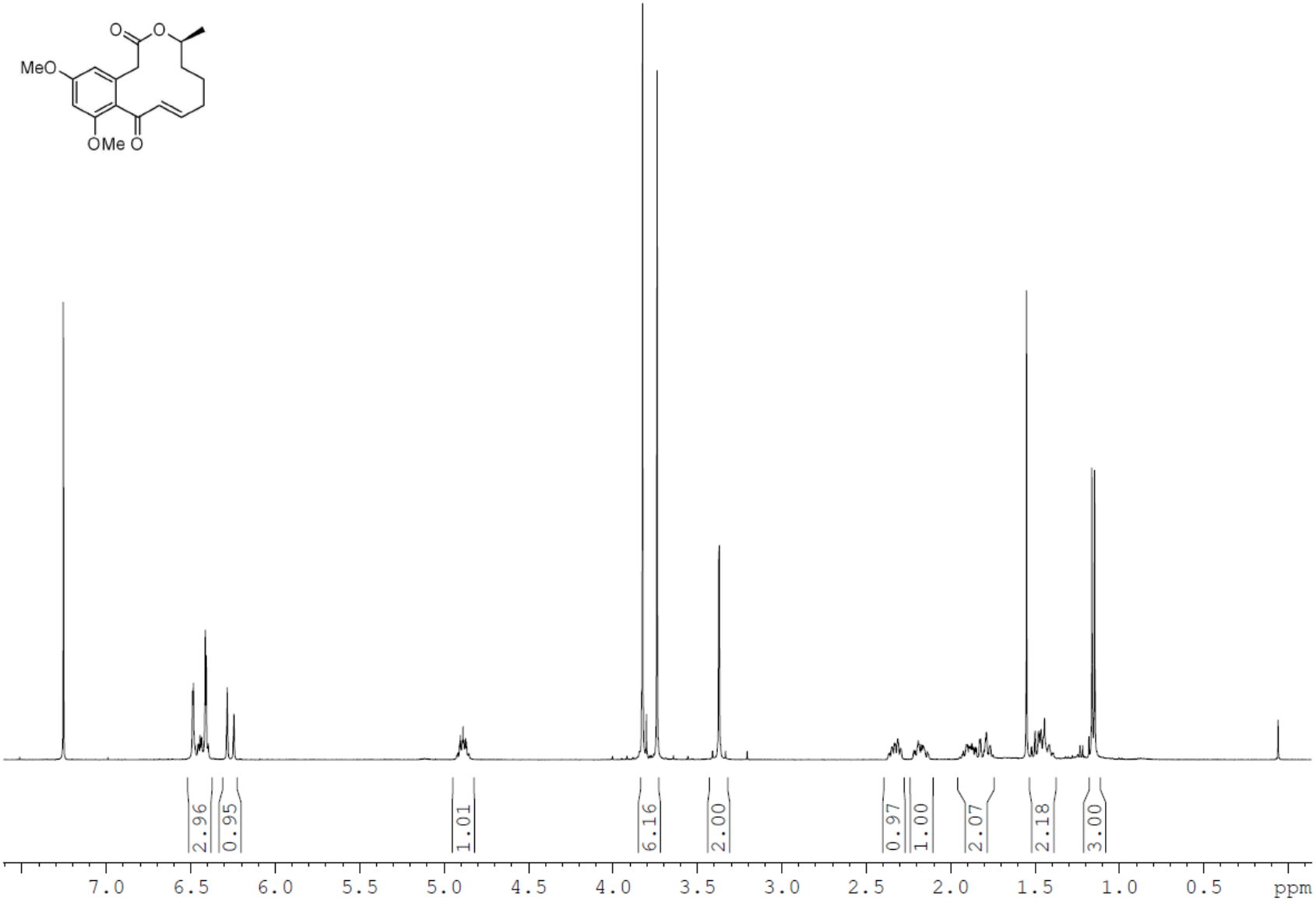
50
40
30
20
ppm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OMe
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3.00
7.0
6.5
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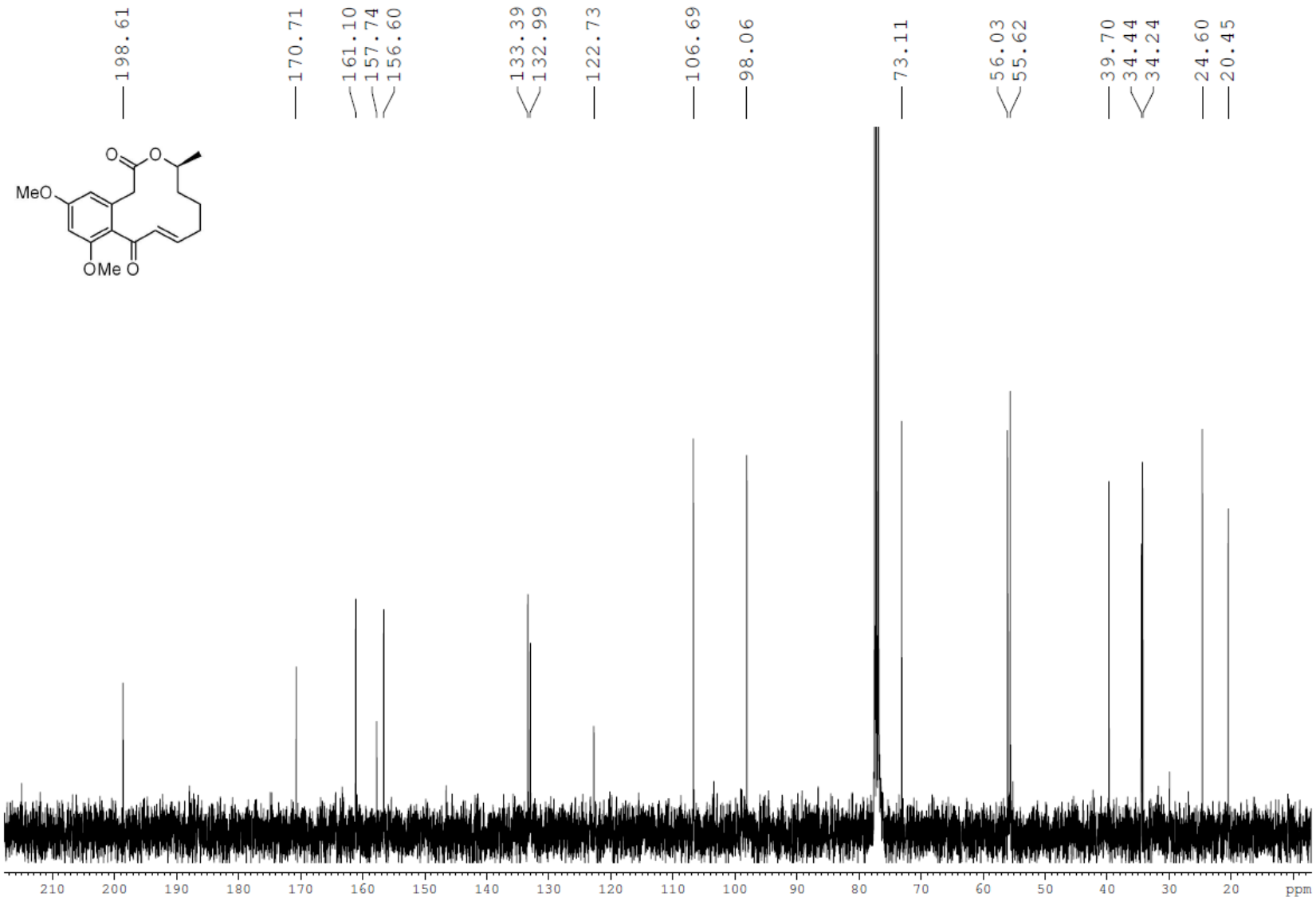
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73.11
56.03
55.62
39.70
34.44
34.24
24.60
20.45
MeO
OMe
O
O
O
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150
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120
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80
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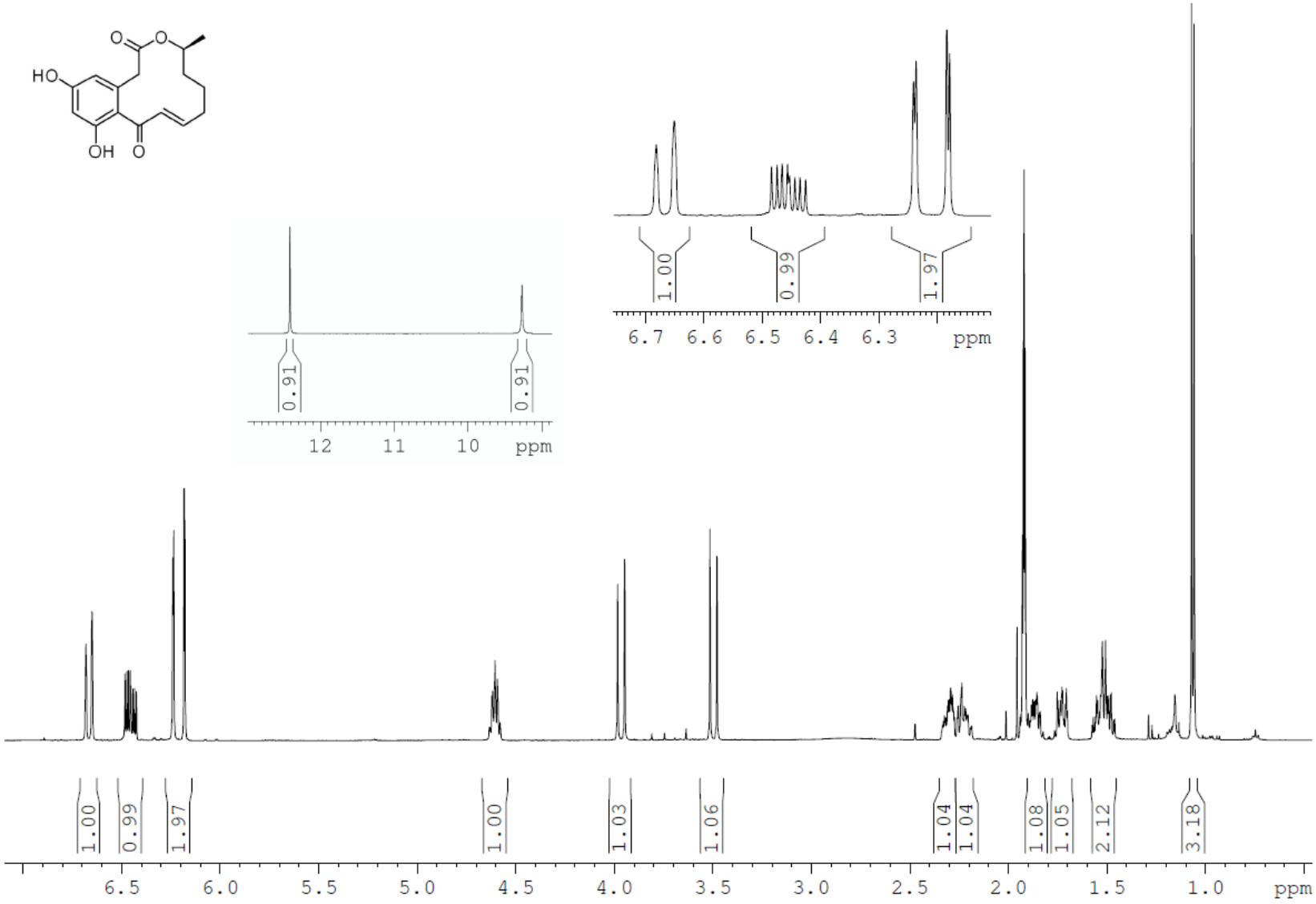
20
ppm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OH
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O
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0.91
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11
10
ppm
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6.6
6.5
6.4
6.3
ppm
1.00
0.99
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1.00
1.03
1.06
1.04
1.04
1.08
1.05
2.12
3.18
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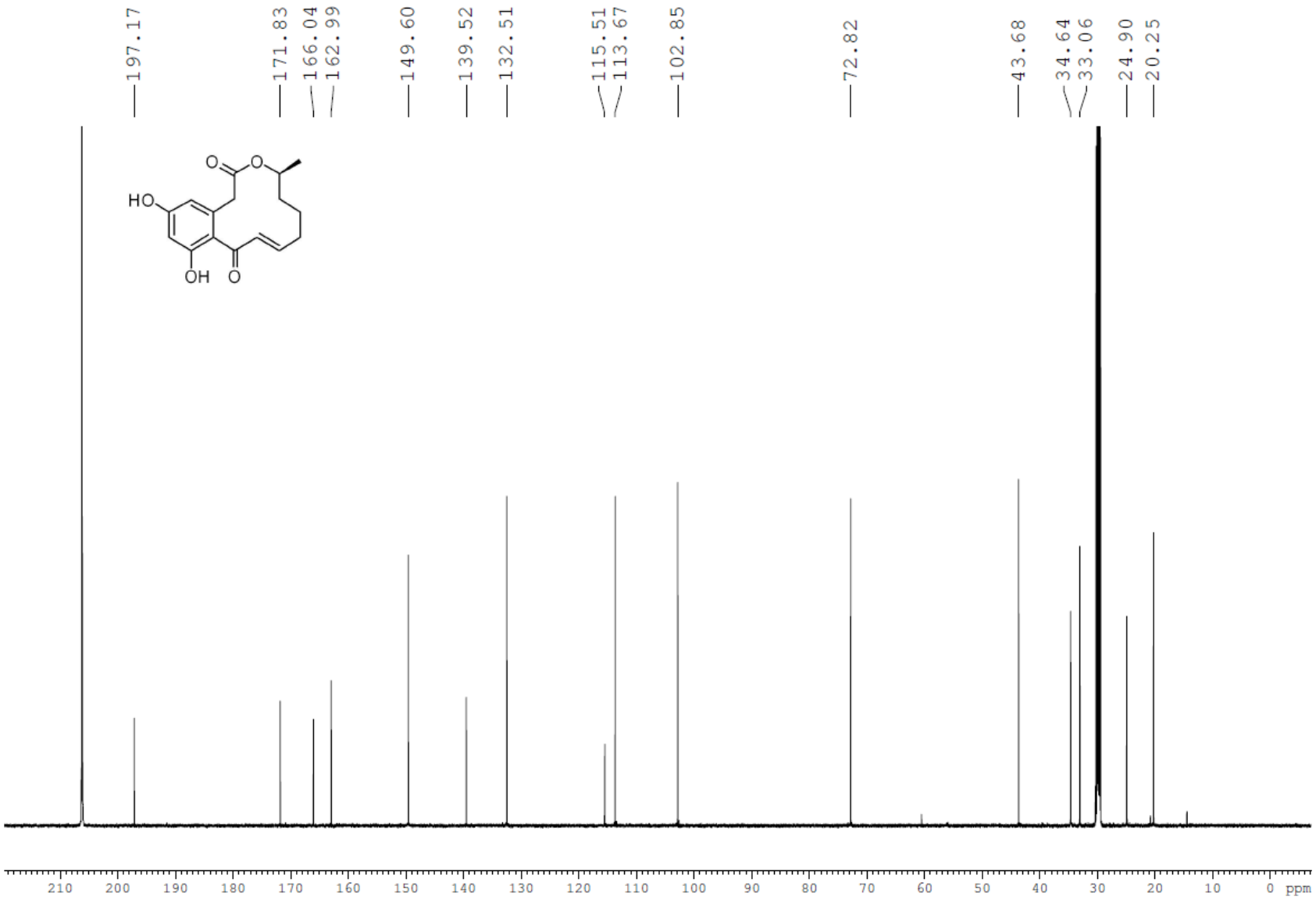
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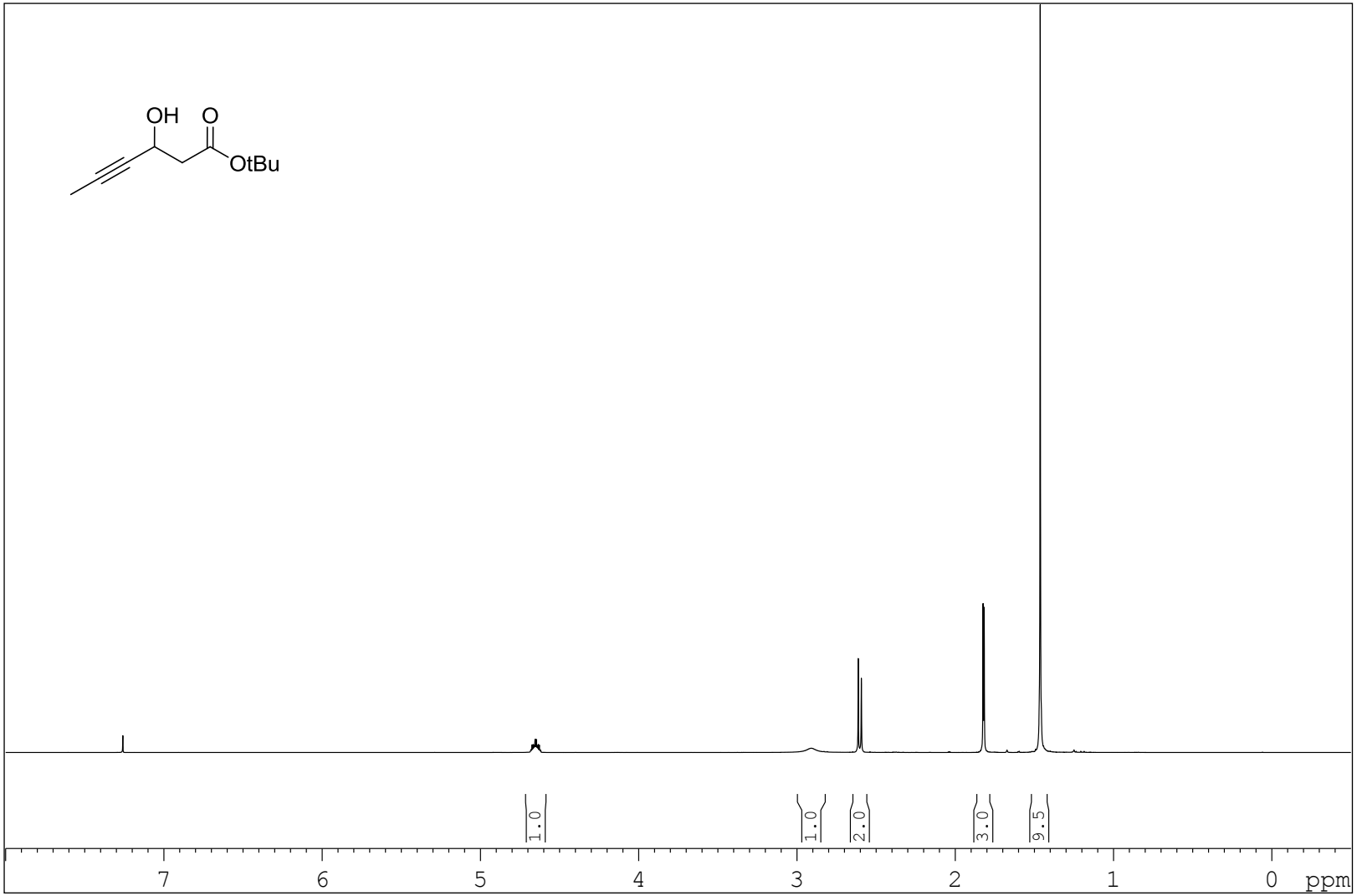
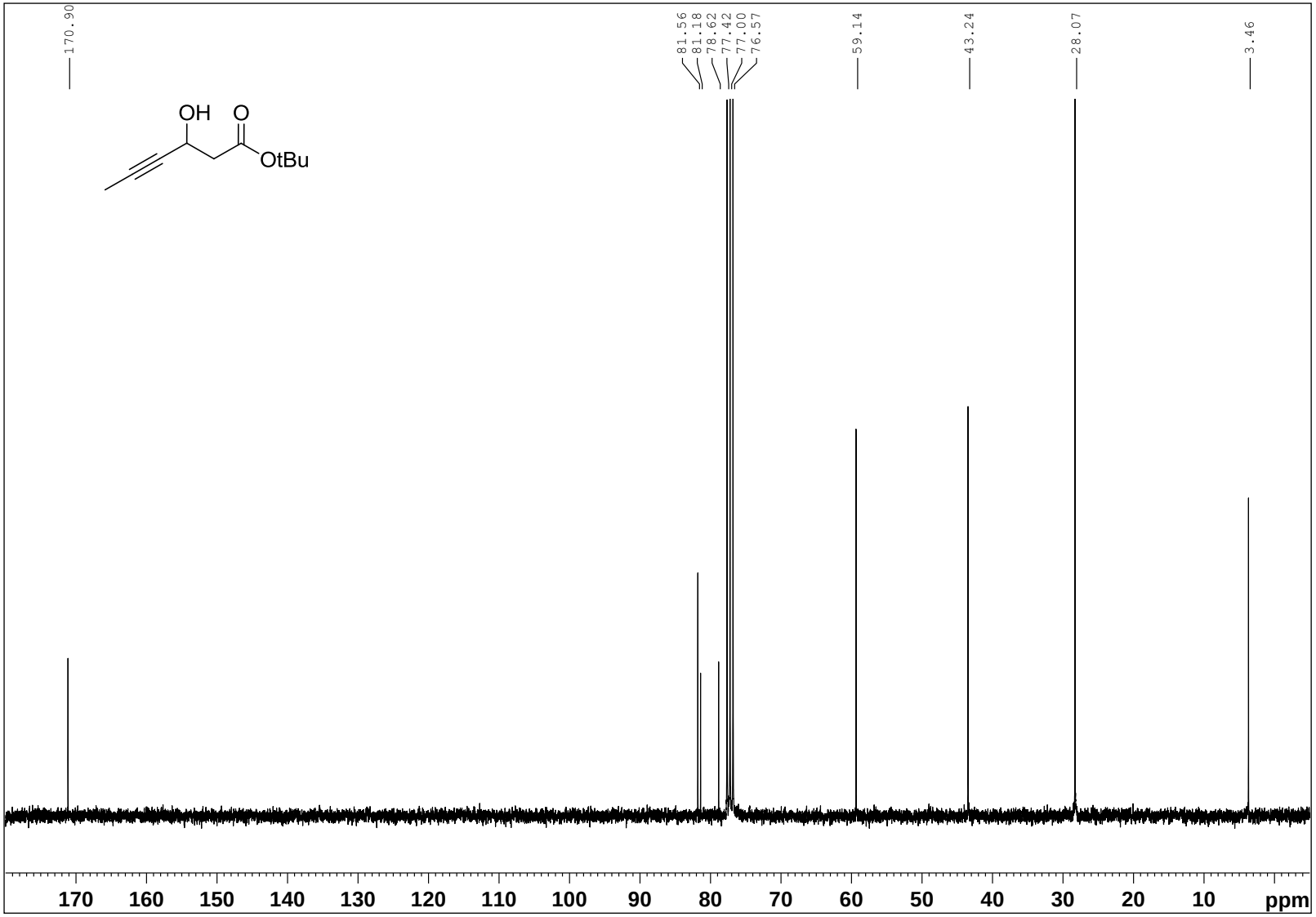
113.67
102.85
72.82
43.68
34.64
33.06
24.90
20.25
HO
OH
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

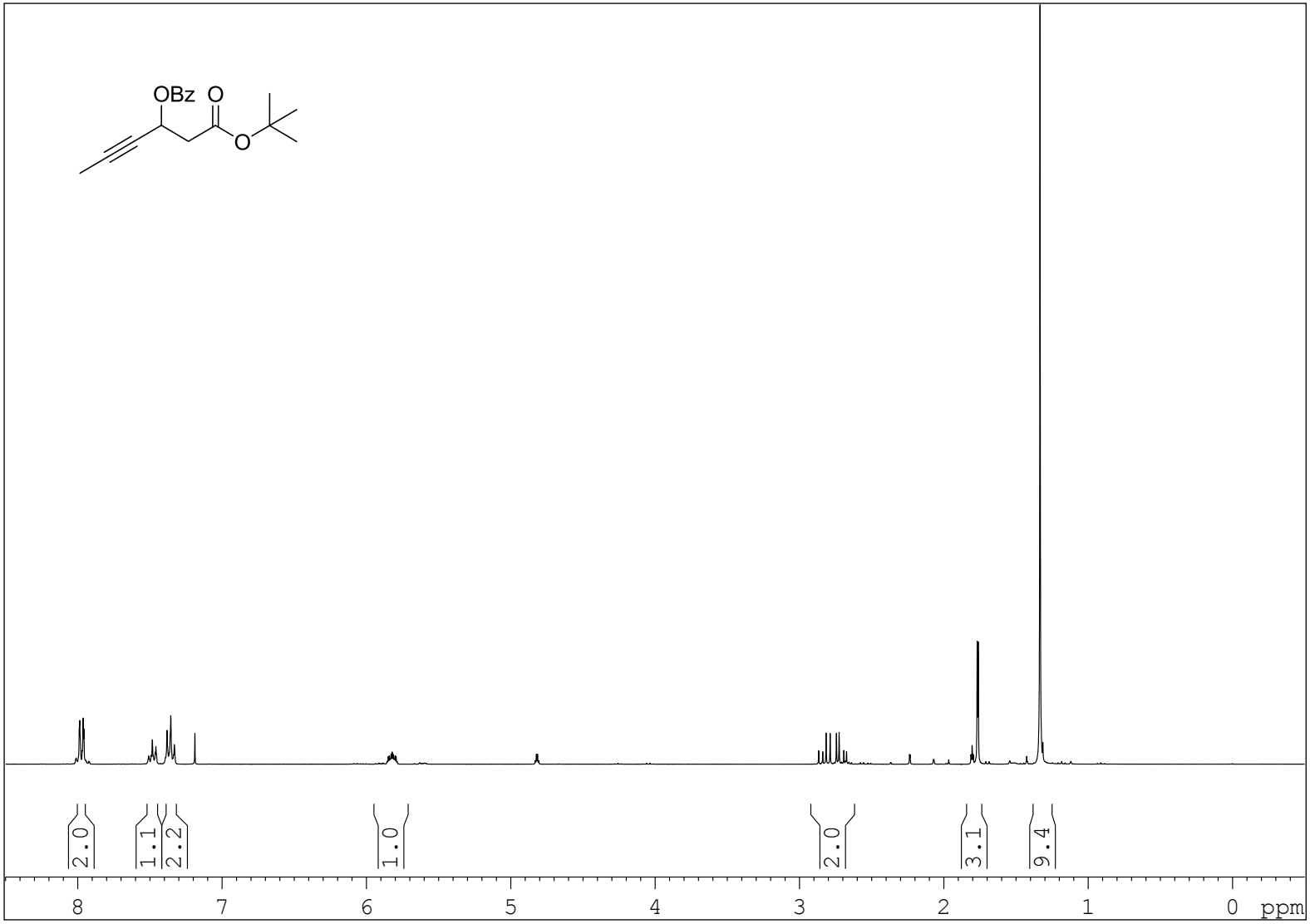
^{1}H NMR (400 MHz, $CDCl_3$) of *tert*-Butyl-3-hydroxyhex-4-ynoate



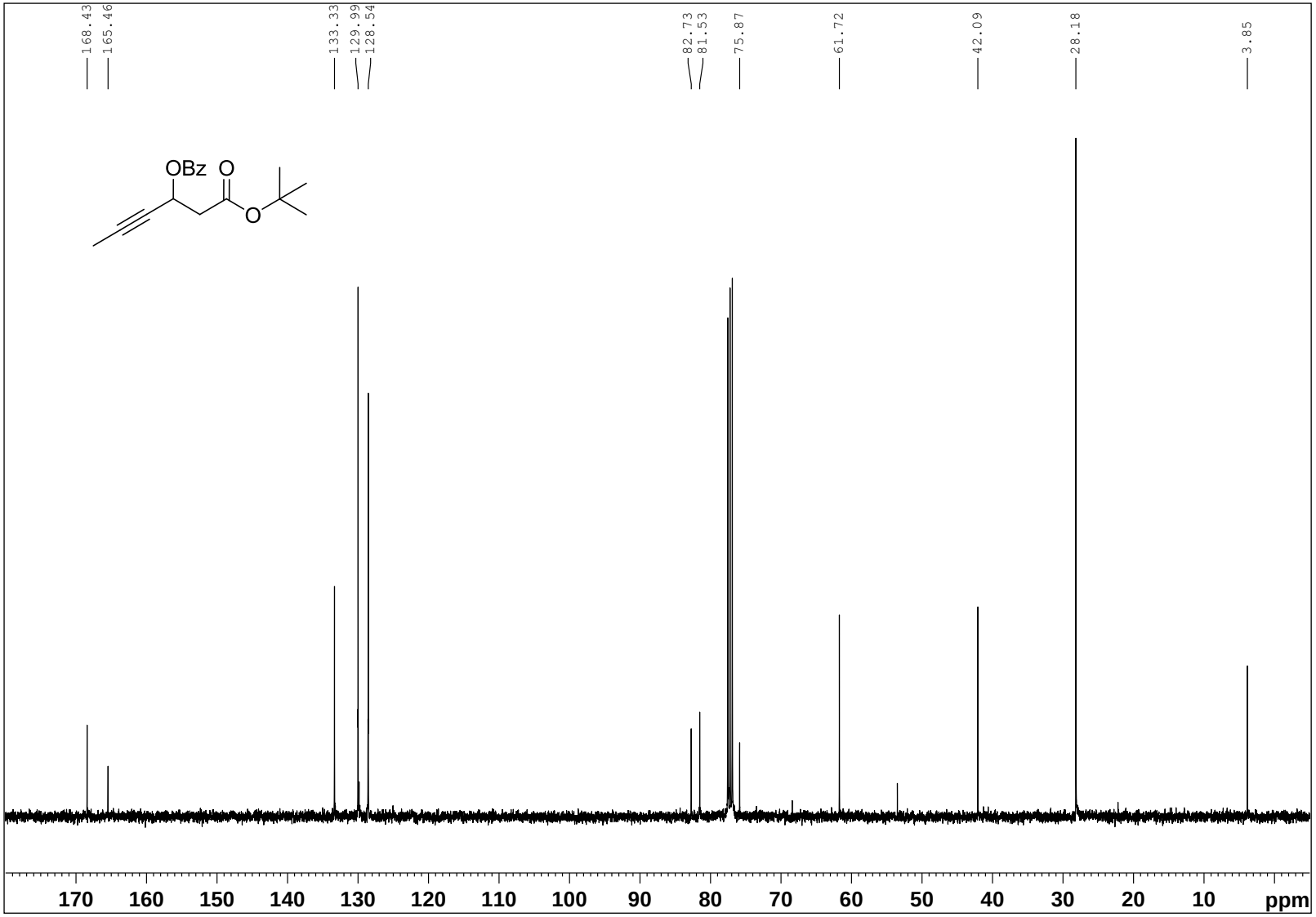
^{13}C NMR (100 MHz, $CDCl_3$) of *tert*-Butyl-3-hydroxyhex-4-ynoate



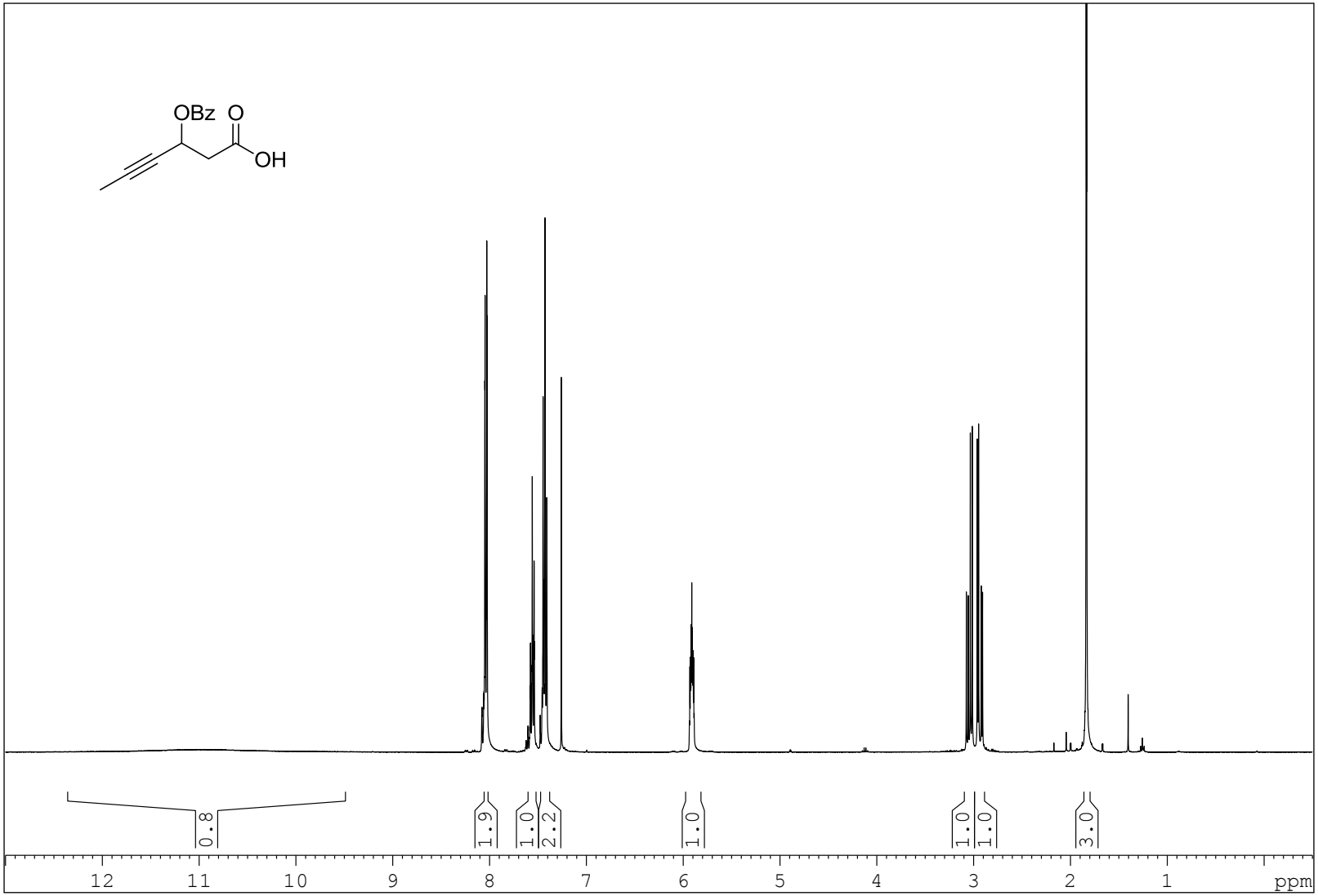
^{1}H NMR (400 MHz, $CDCl_3$) of *tert*-Butyl-3-(benzoyloxy)hex-4-ynoate



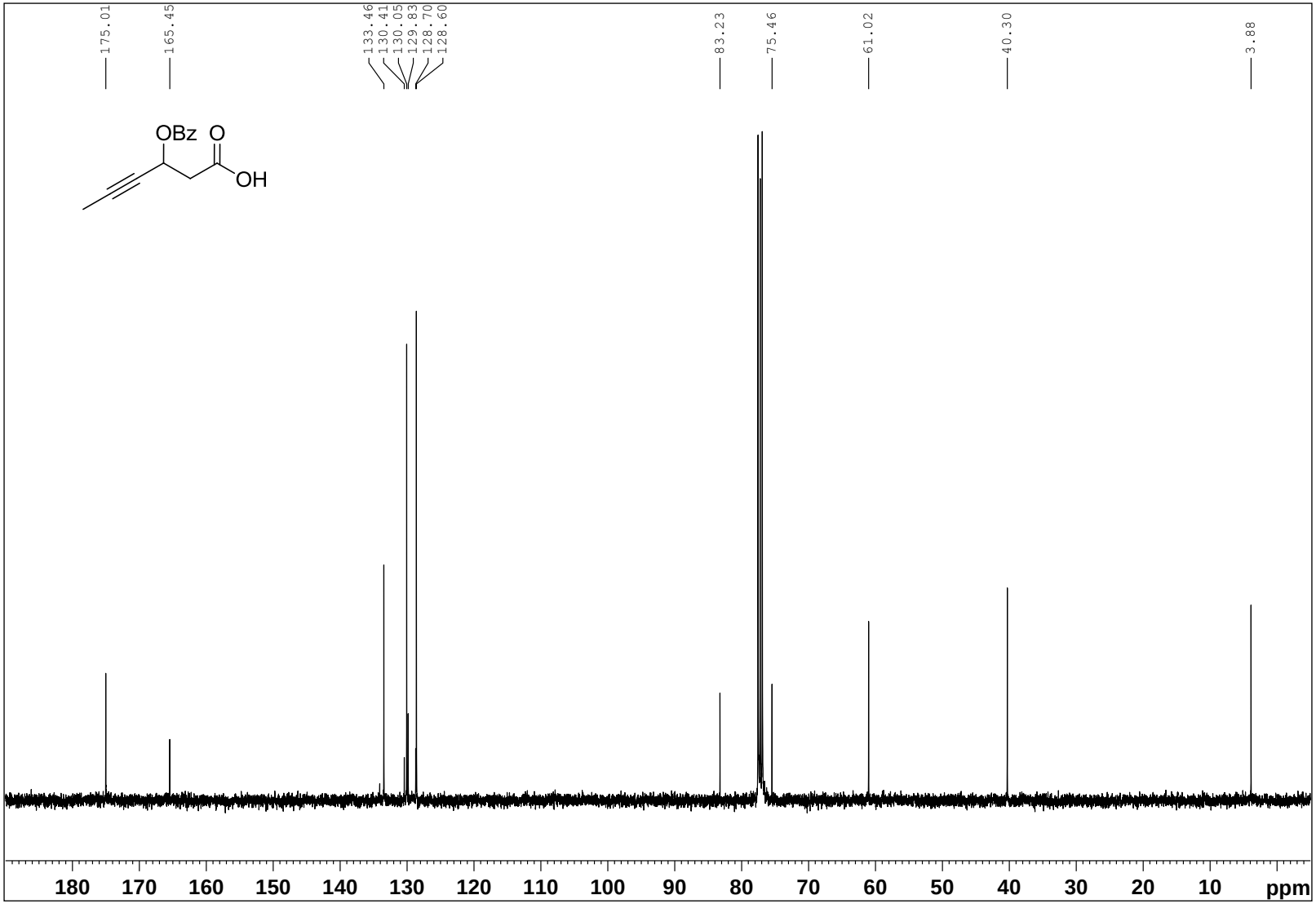
^{13}C NMR (100 MHz, $CDCl_3$) of *tert*-Butyl-3-(benzoyloxy)hex-4-ynoate (3)



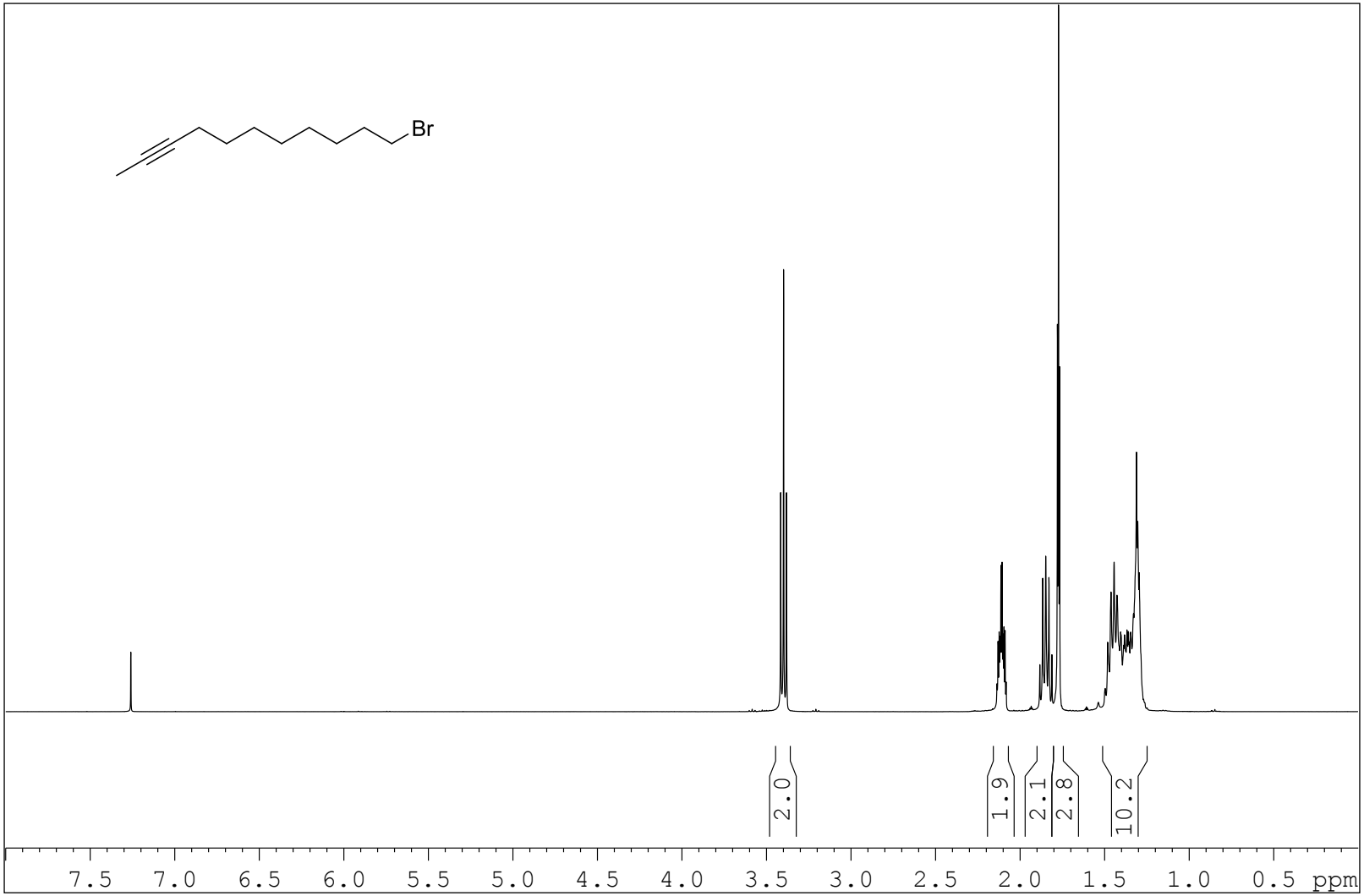
^{1}H NMR (400 MHz, $CDCl_3$) of 3-(Benzoyloxy)hex-4-ynoic acid



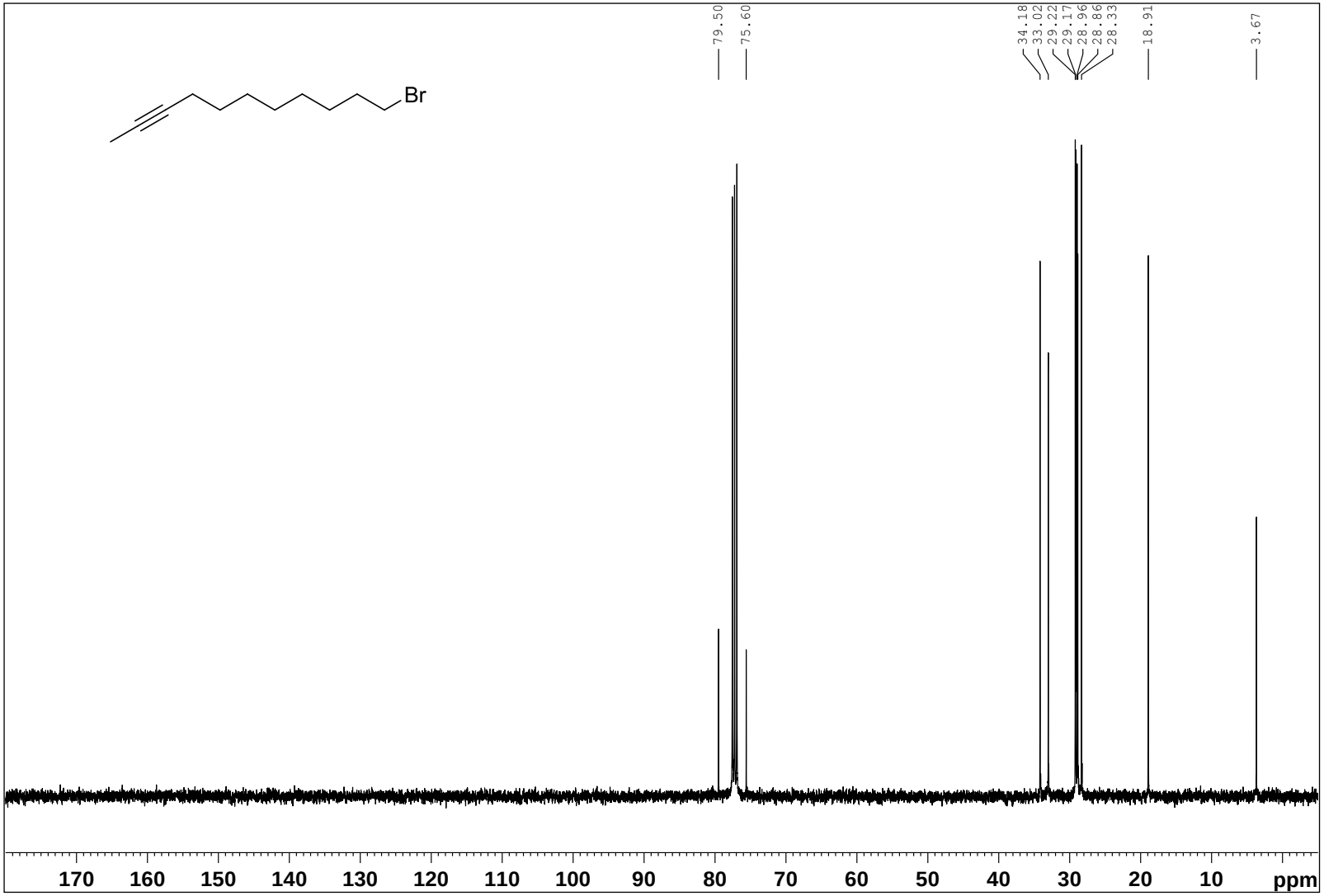
^{13}C NMR (100 MHz, $CDCl_3$) of 3-(Benzoyloxy)hex-4-ynoic acid



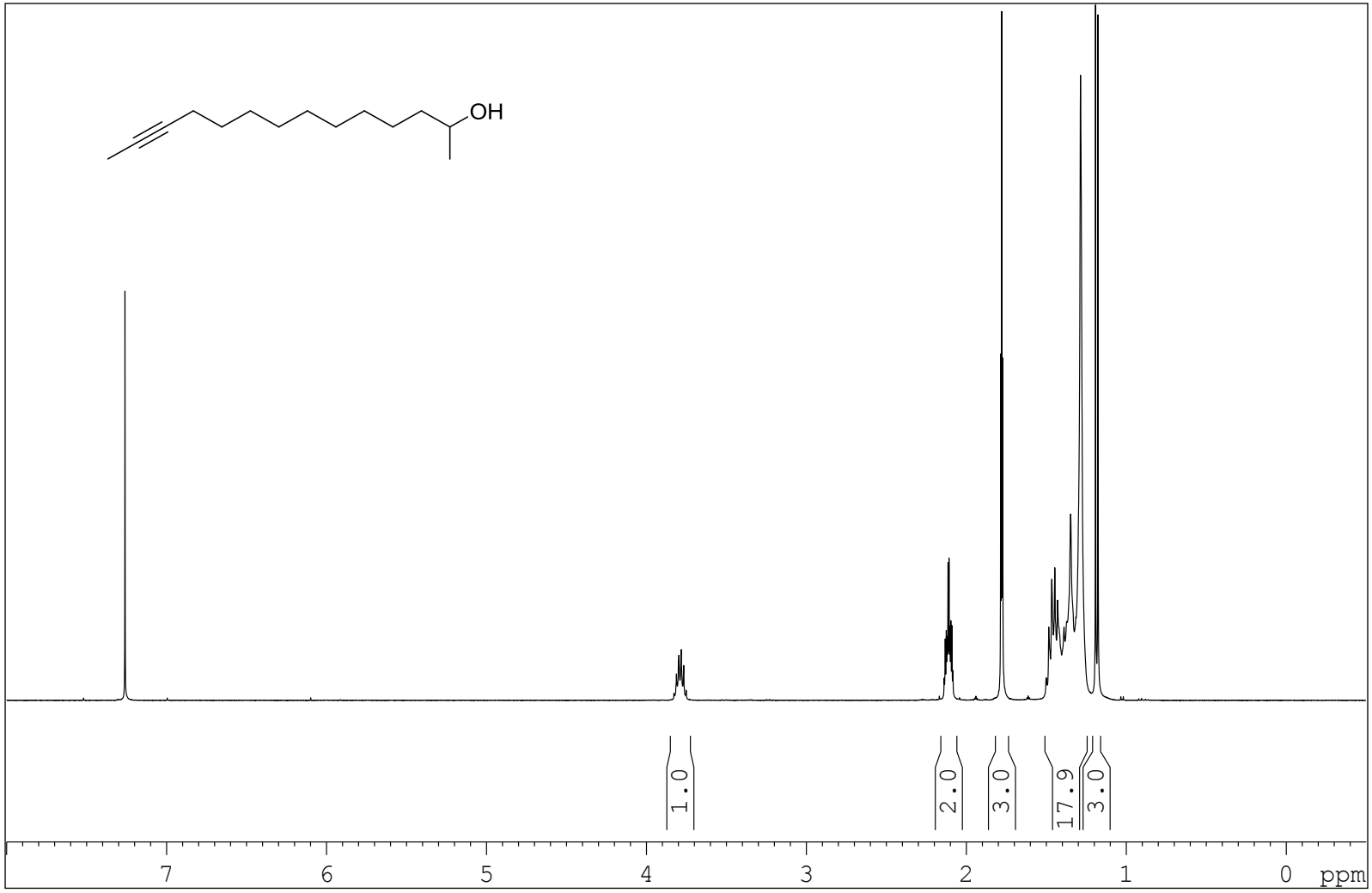
^{1}H NMR (400 MHz, $CDCl_3$) of 11-Bromo-2-undecyne



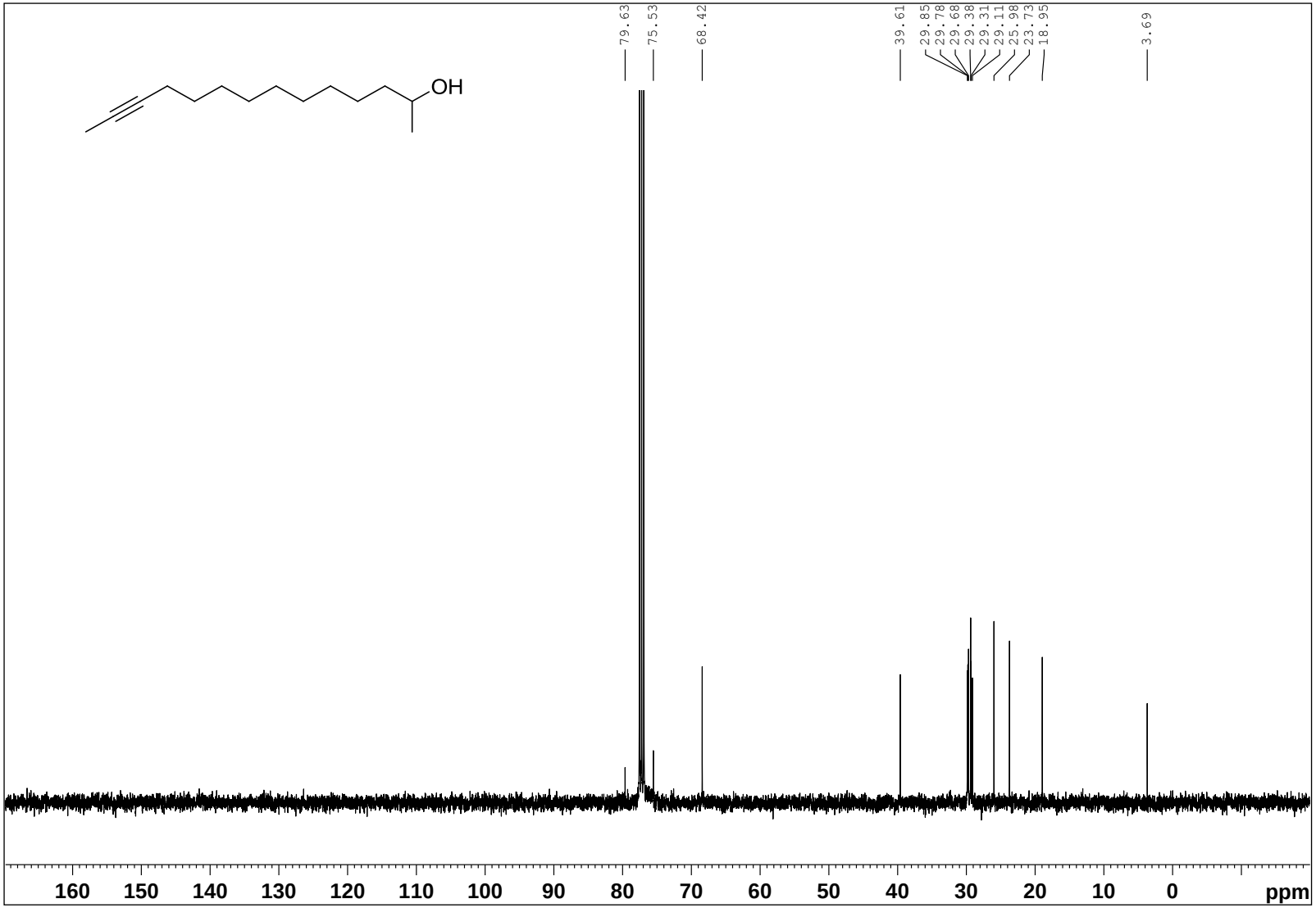
^{13}C NMR (100 MHz, $CDCl_3$) of 11-Bromo-2-undecyne



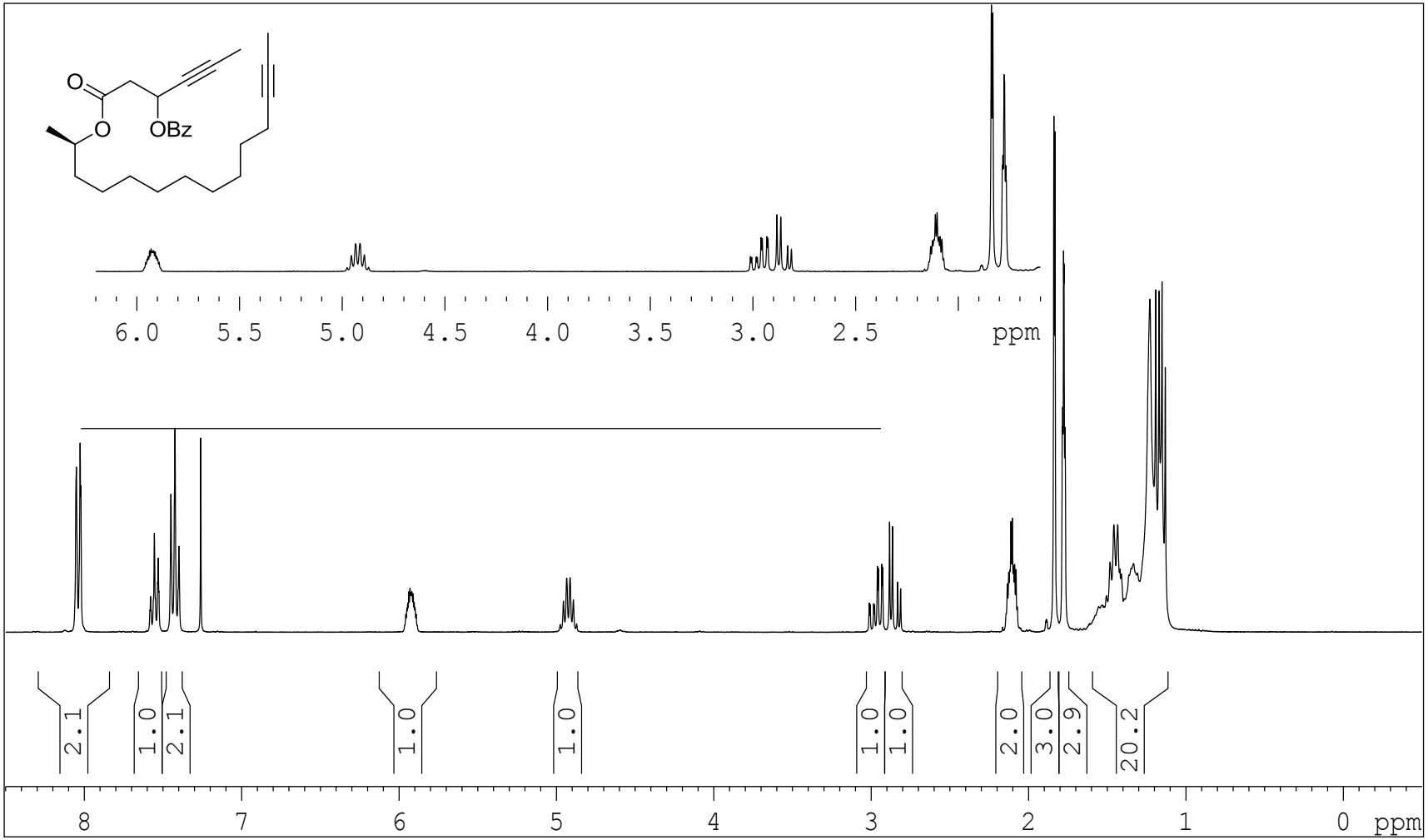
^{1}H NMR (400 MHz, $CDCl_3$) of 1-Methyl-11-tridecynol



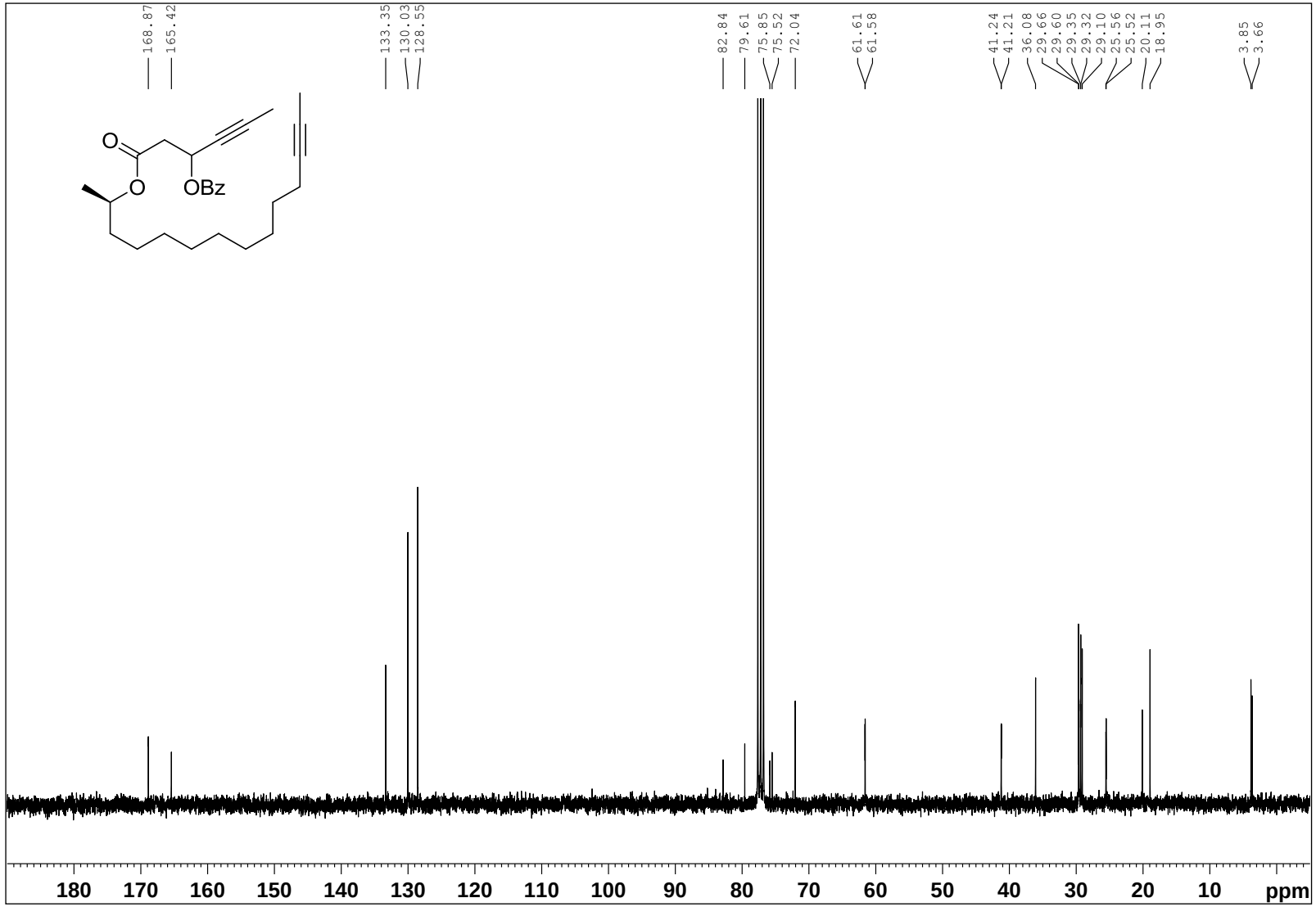
^{13}C NMR (100 MHz, $CDCl_3$) of 1-Methyl-11-tridecynol



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



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



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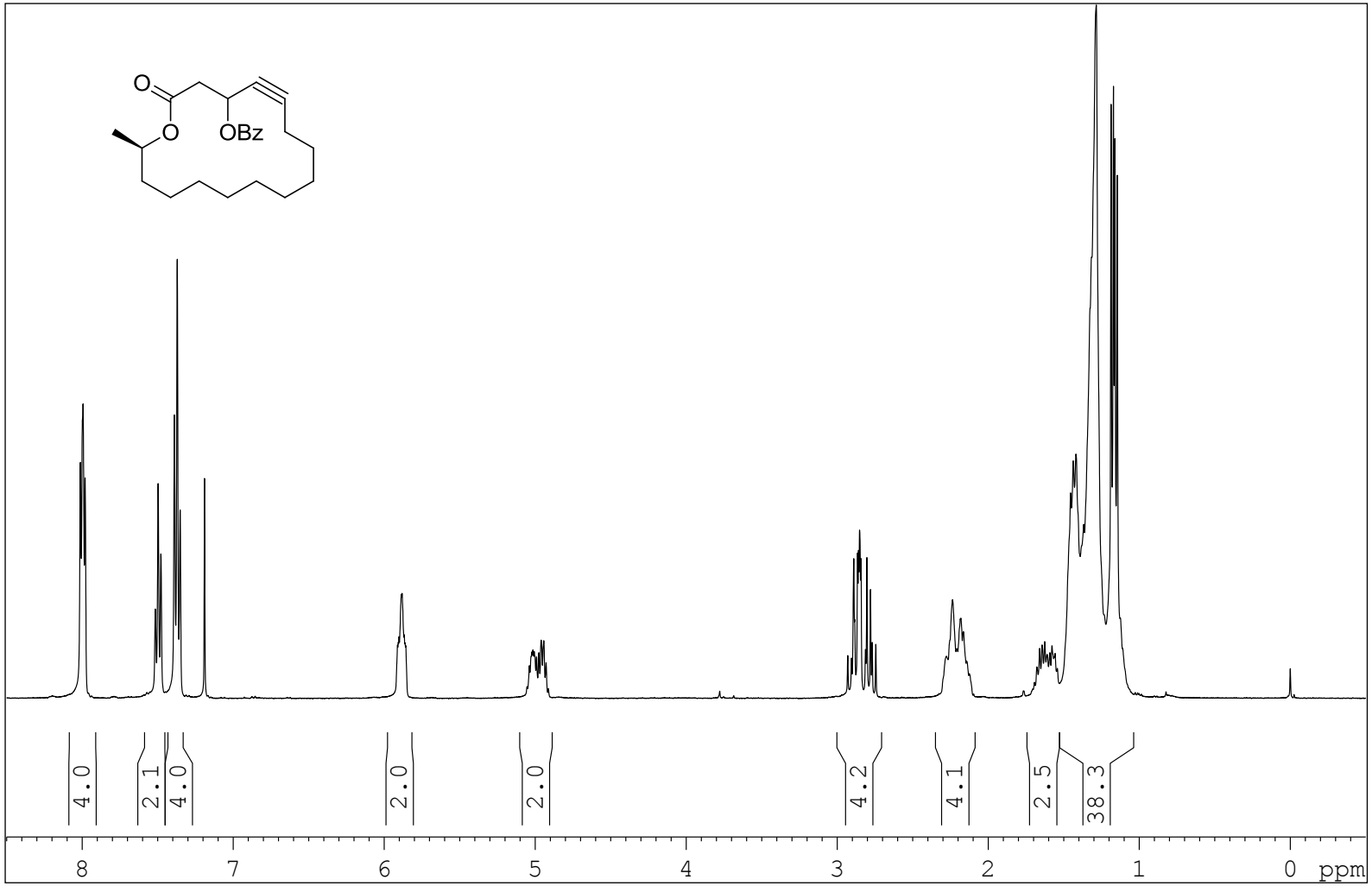
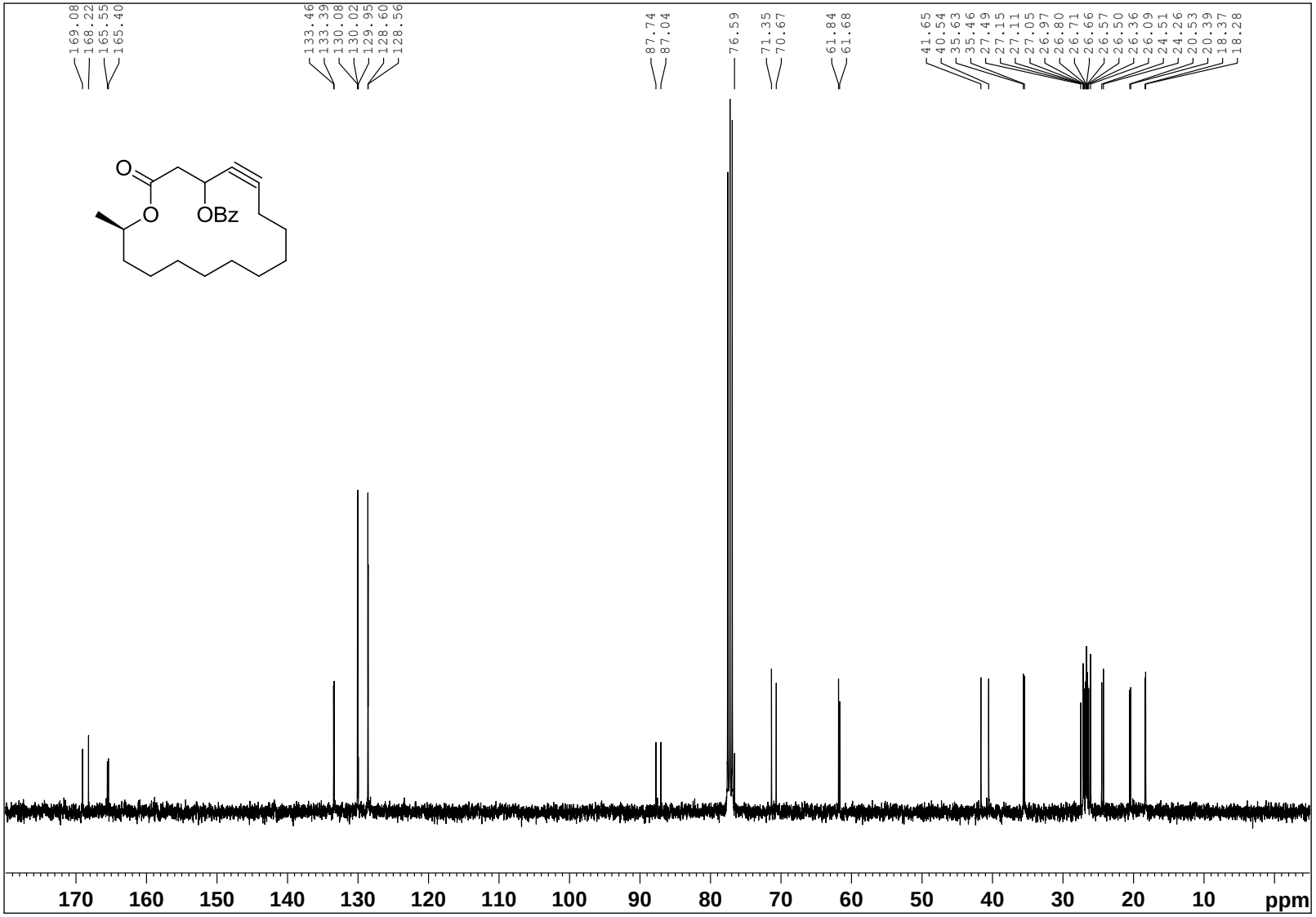
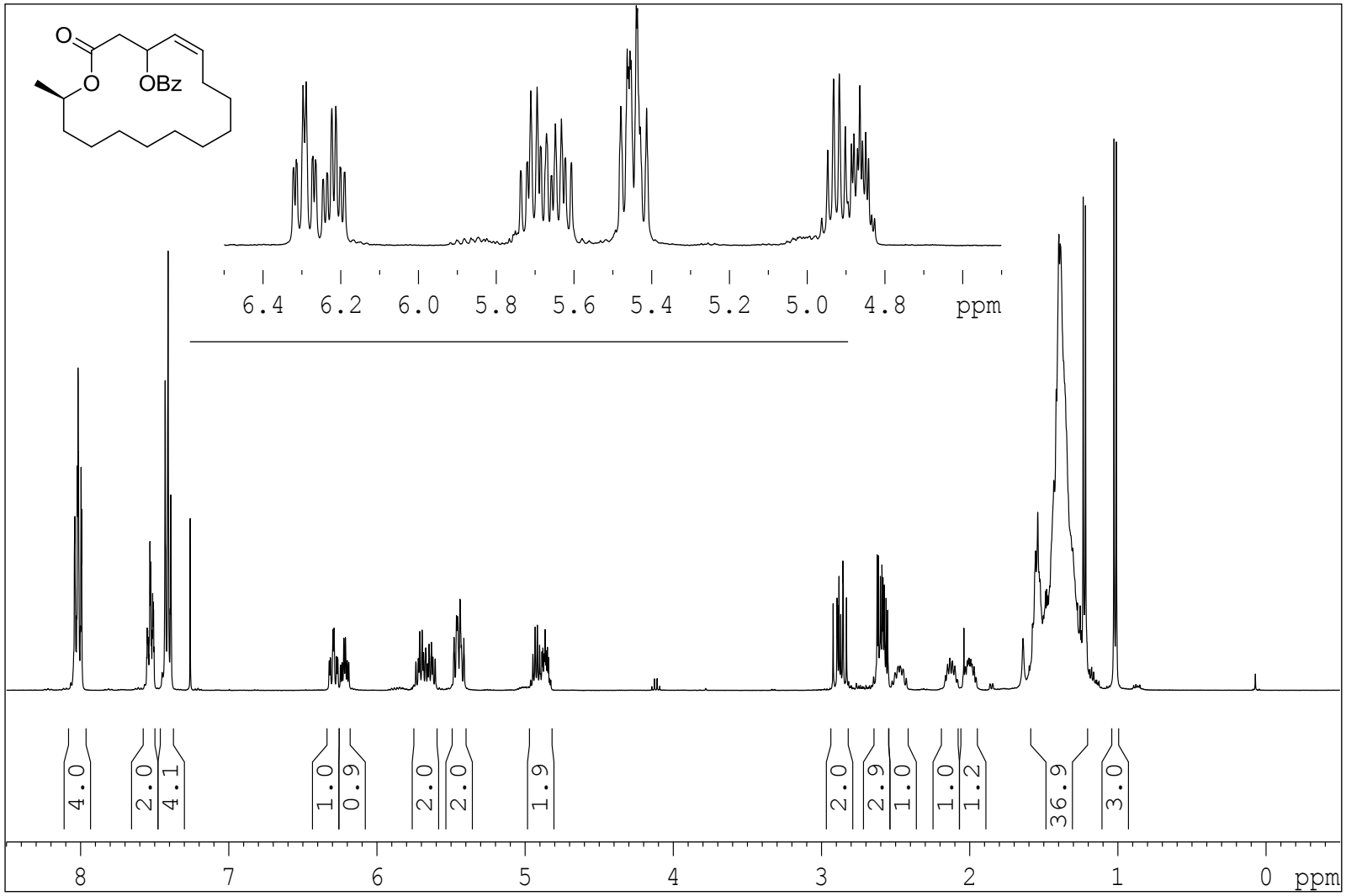


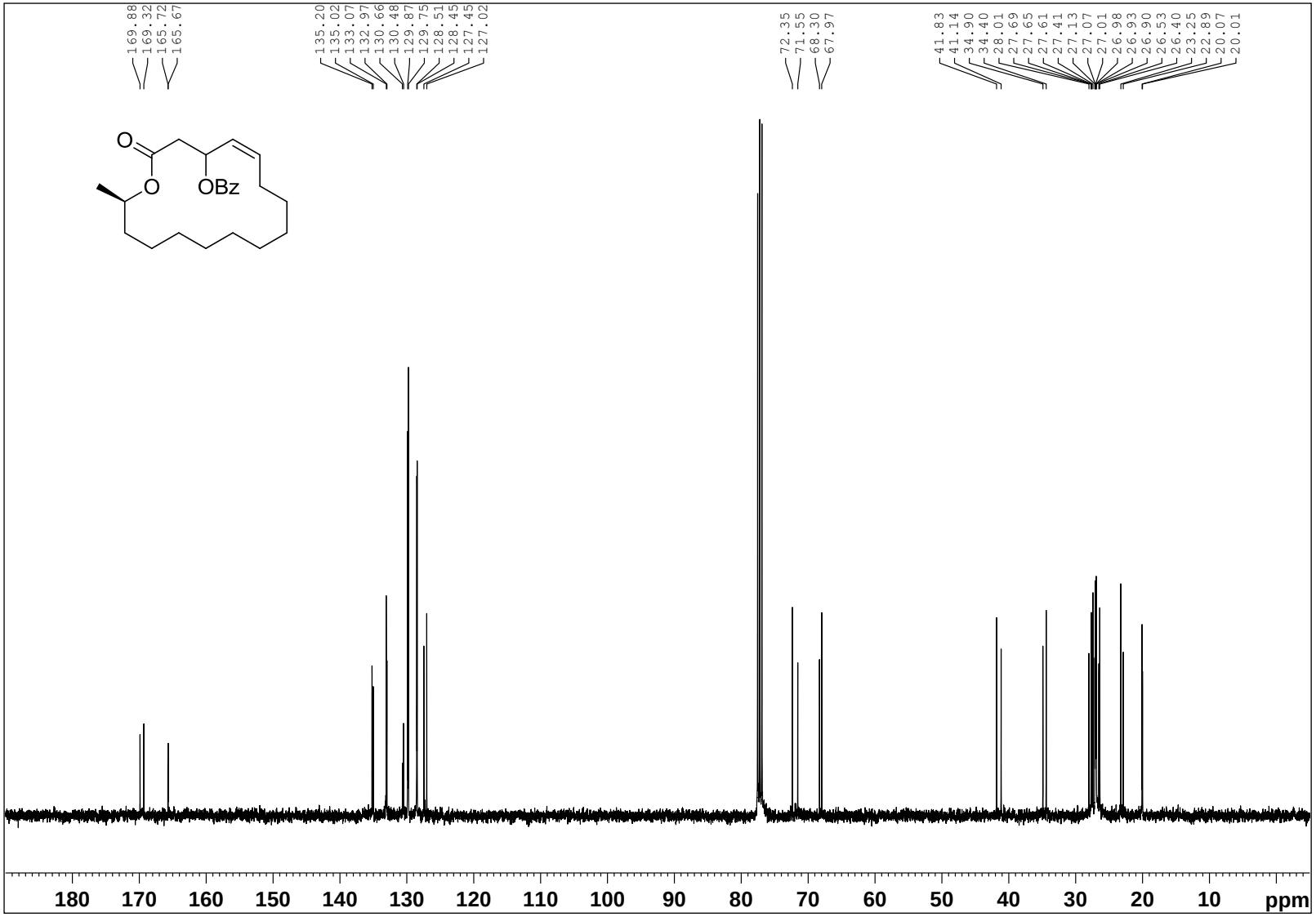
^{13}C NMR (100 MHz, $CDCl_3$)



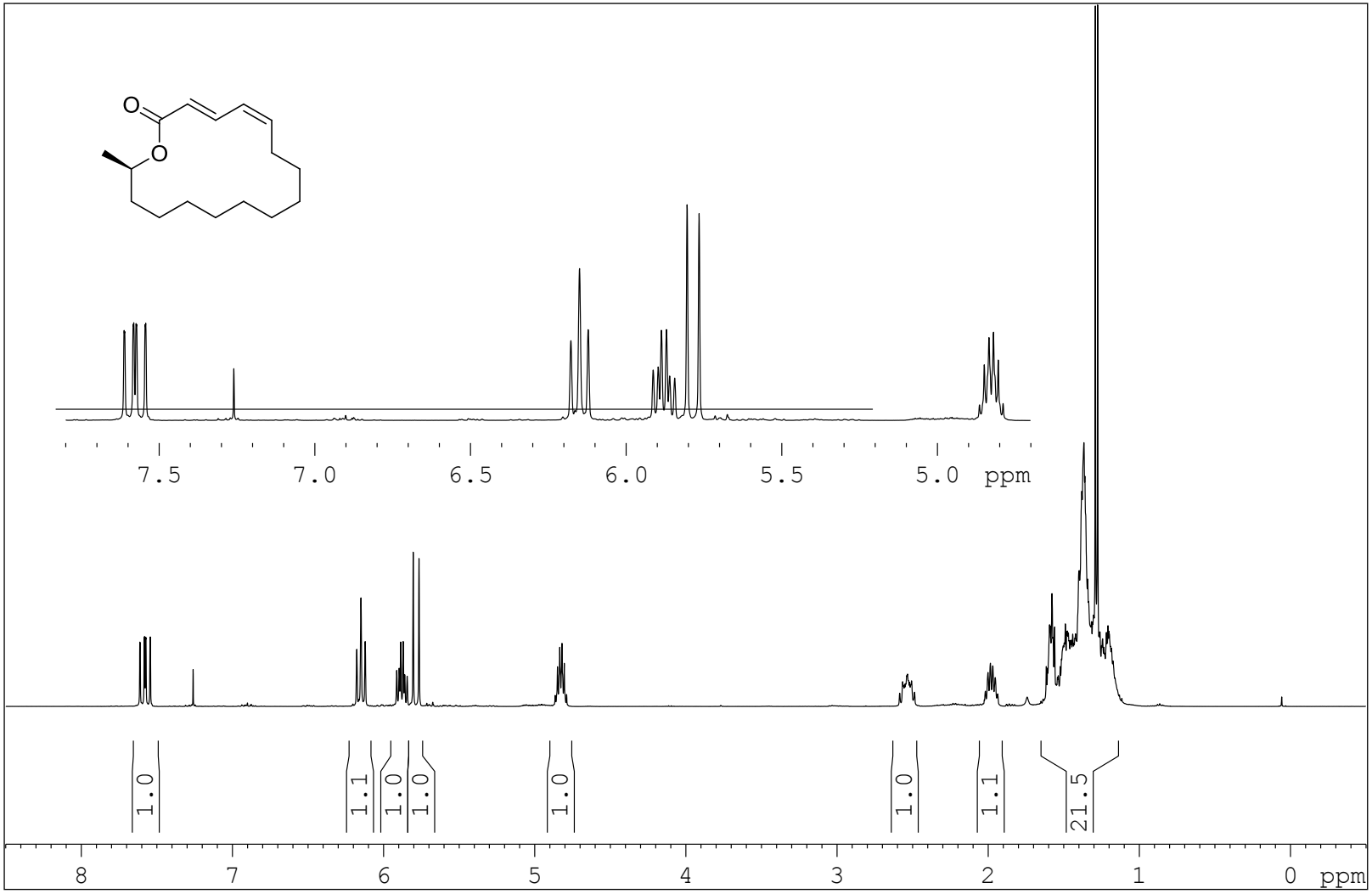
^{1}H NMR (400 MHz, $CDCl_3$)



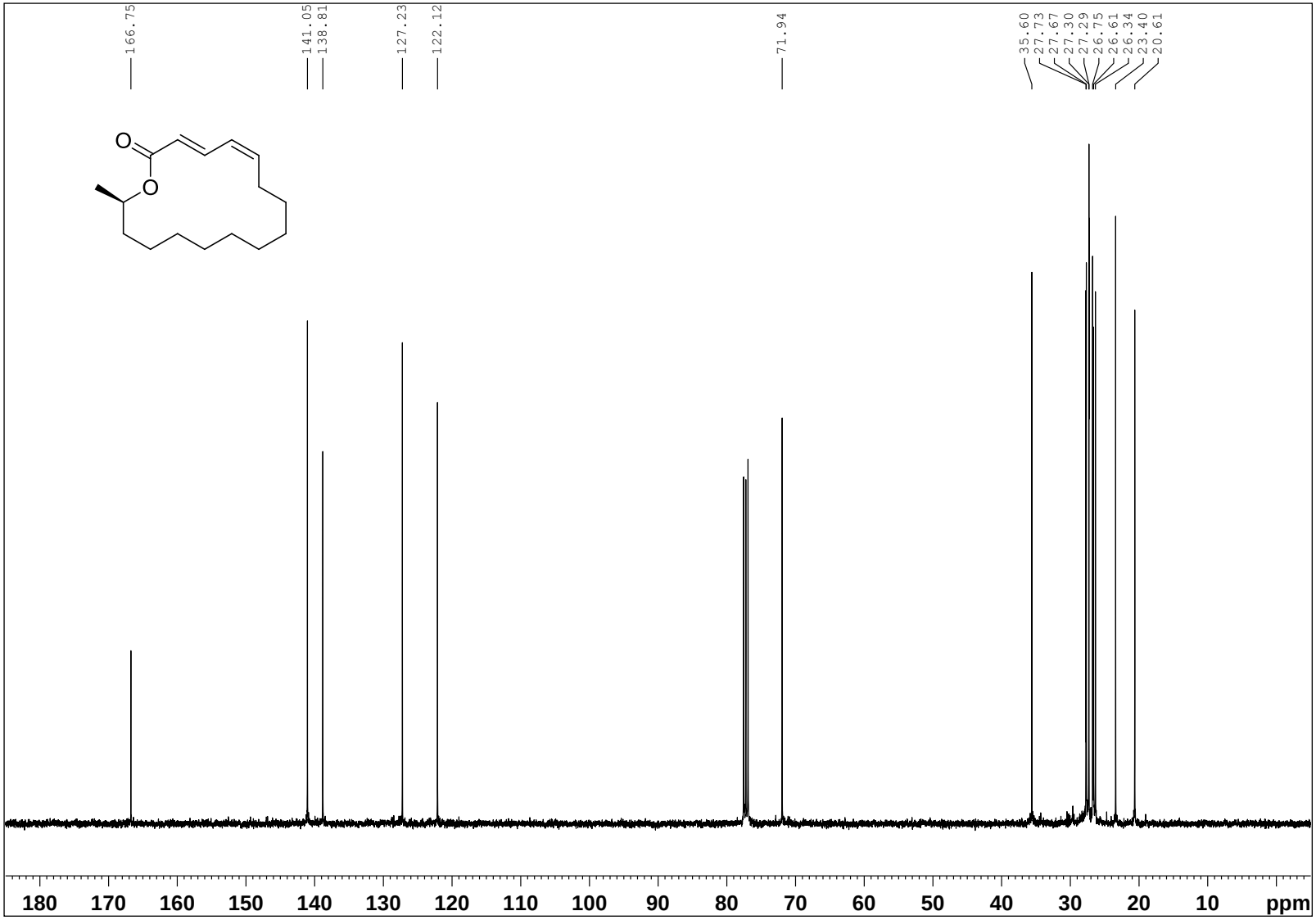
^{13}C NMR (100 MHz, $CDCl_3$)



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



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



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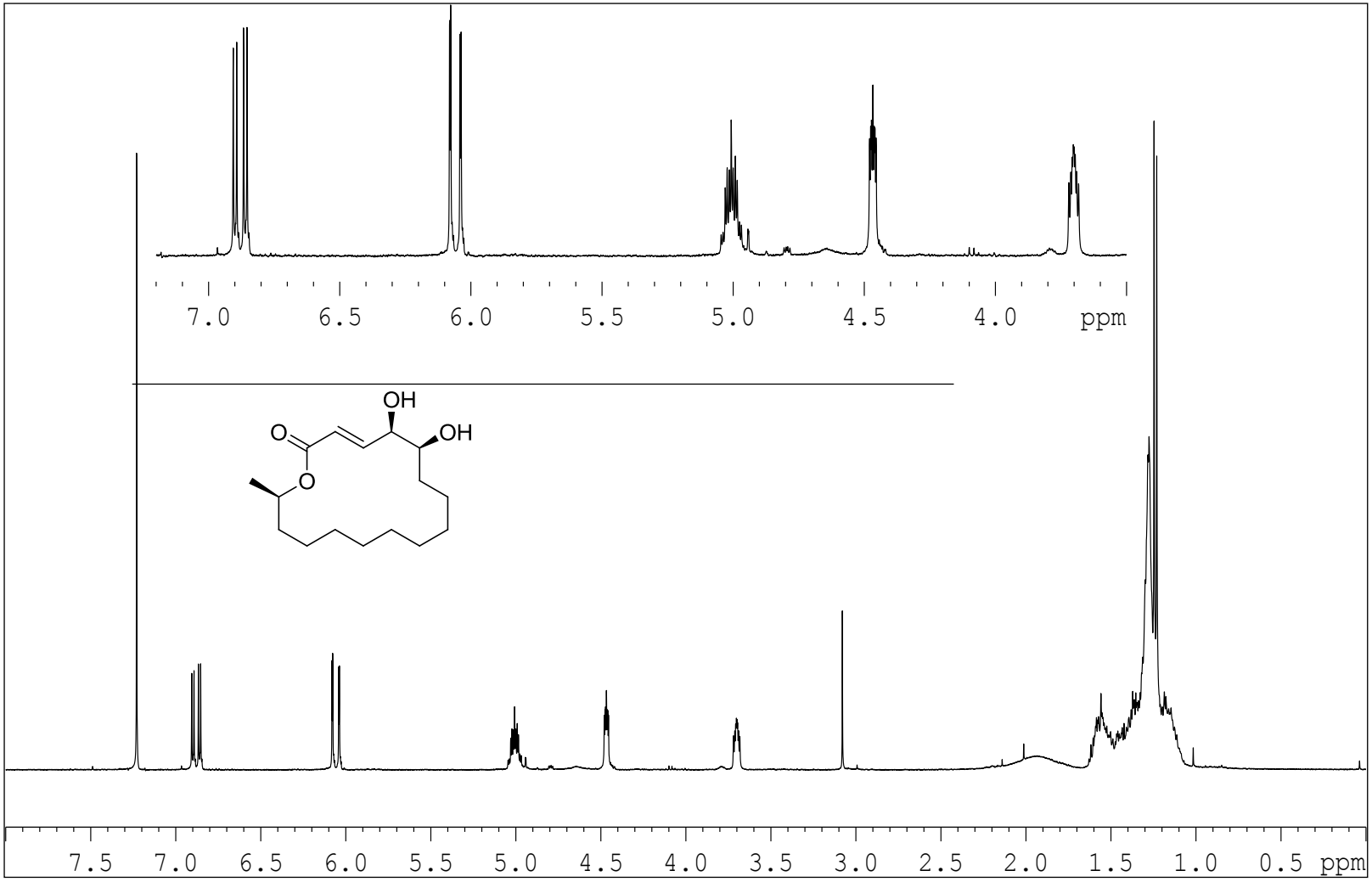

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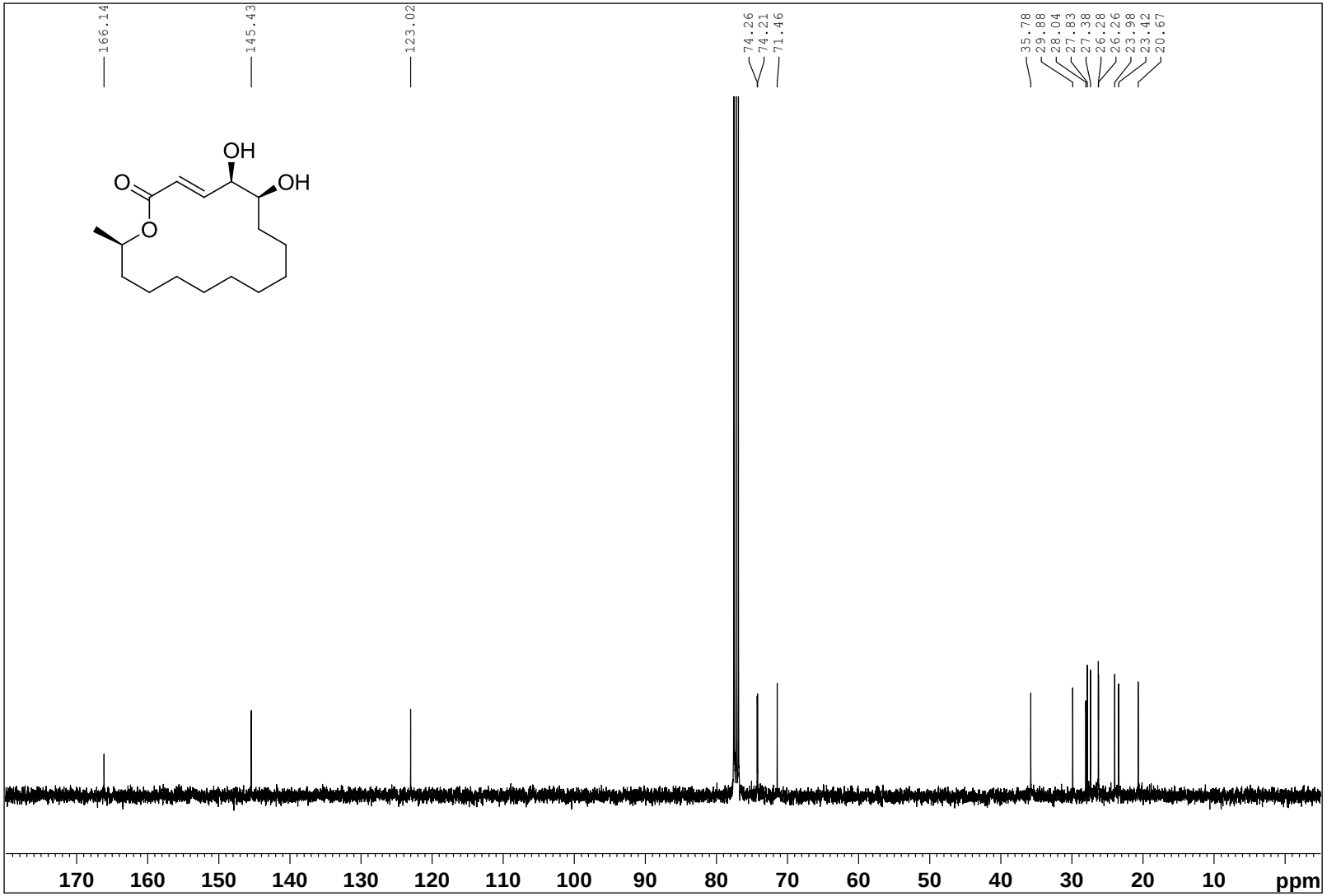

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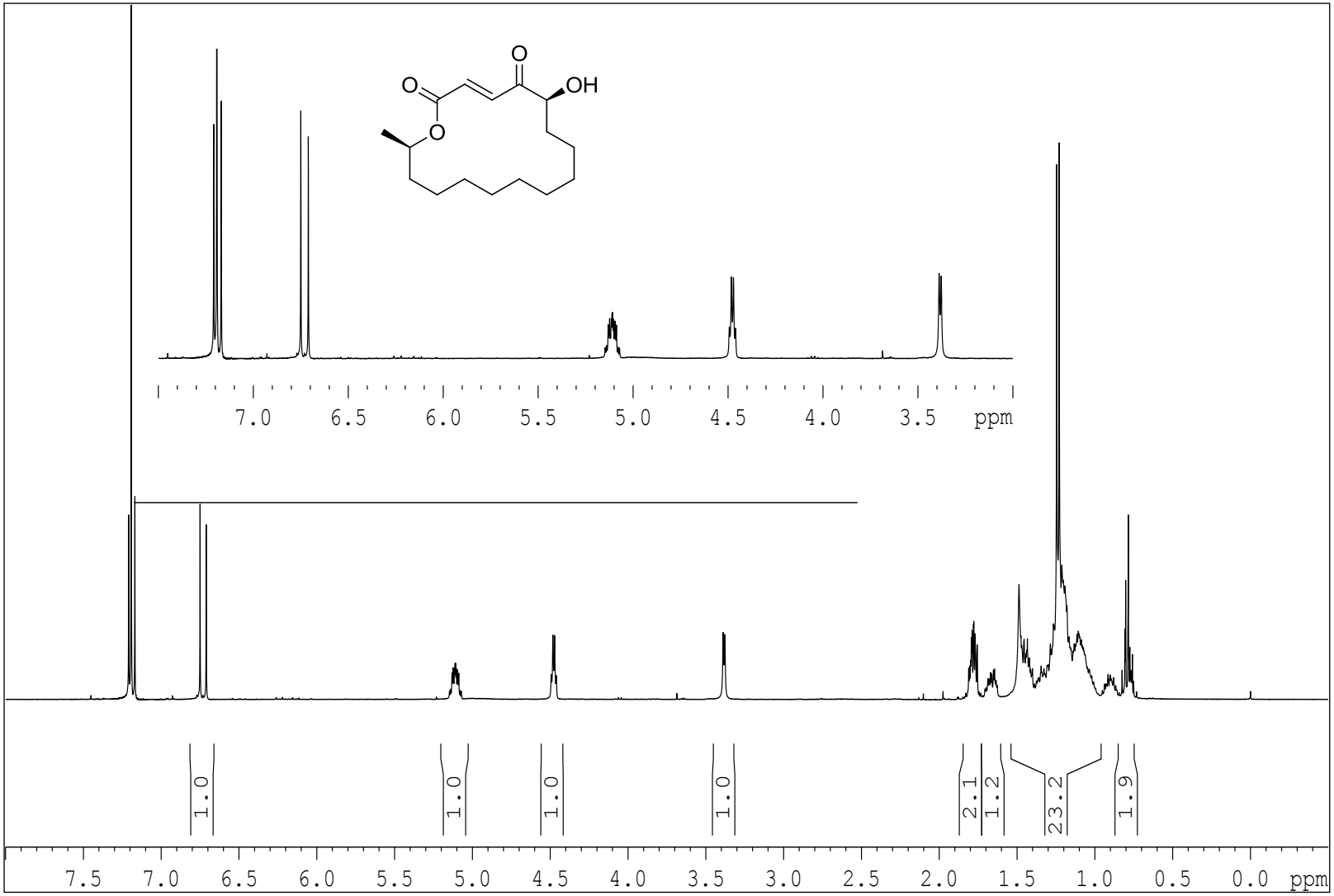
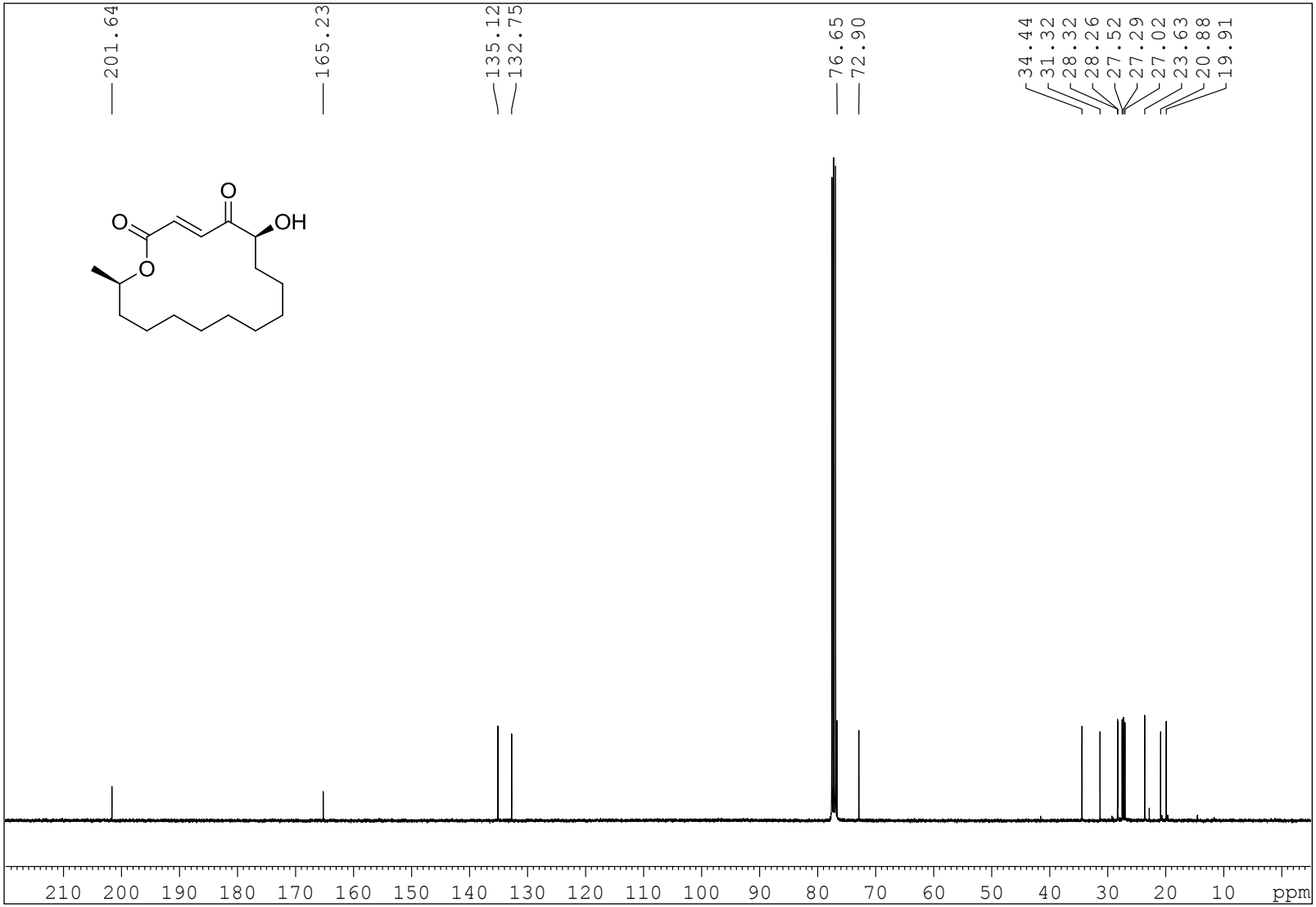


^{13}C NMR (100 MHz, $CDCl_3$)



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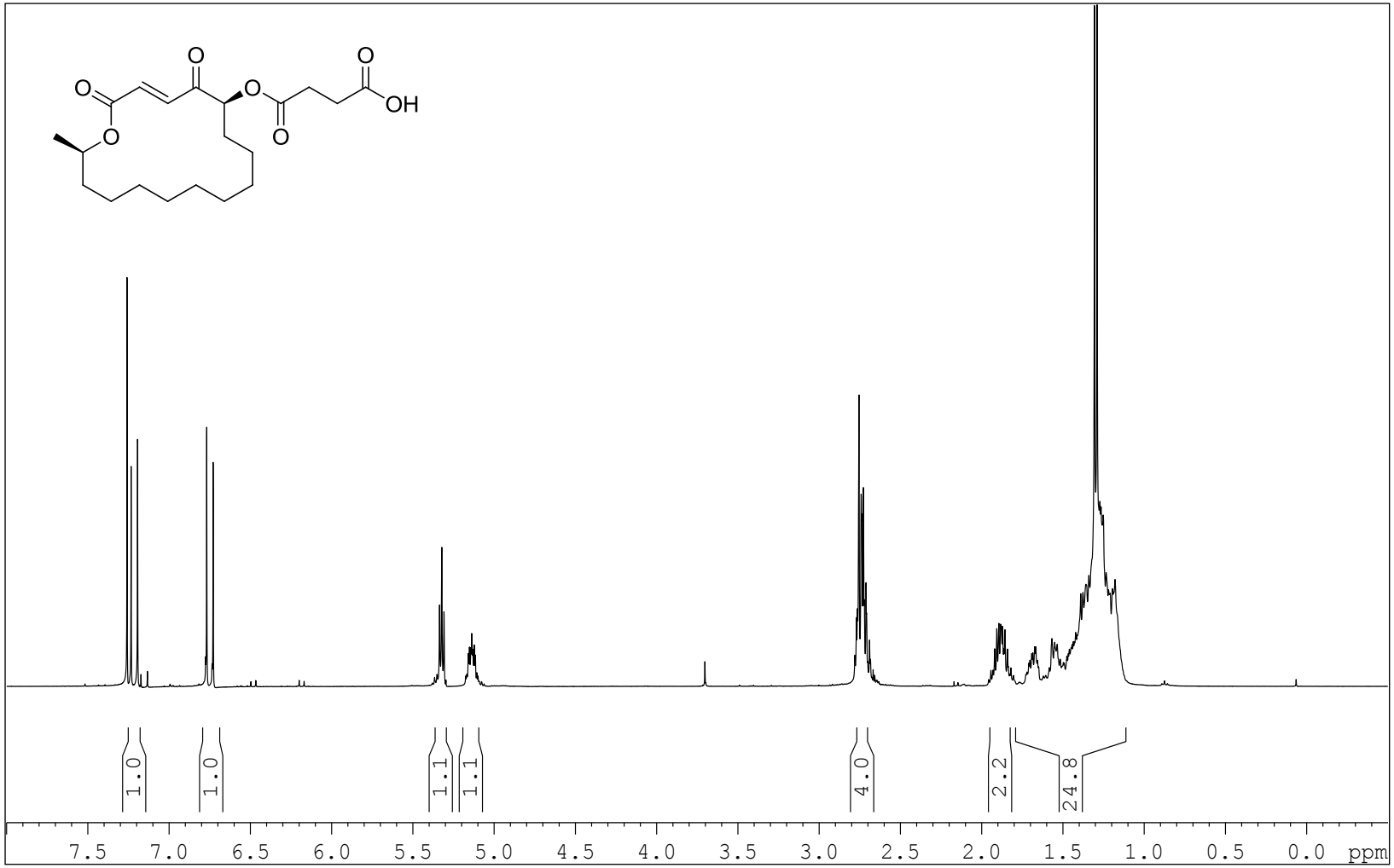
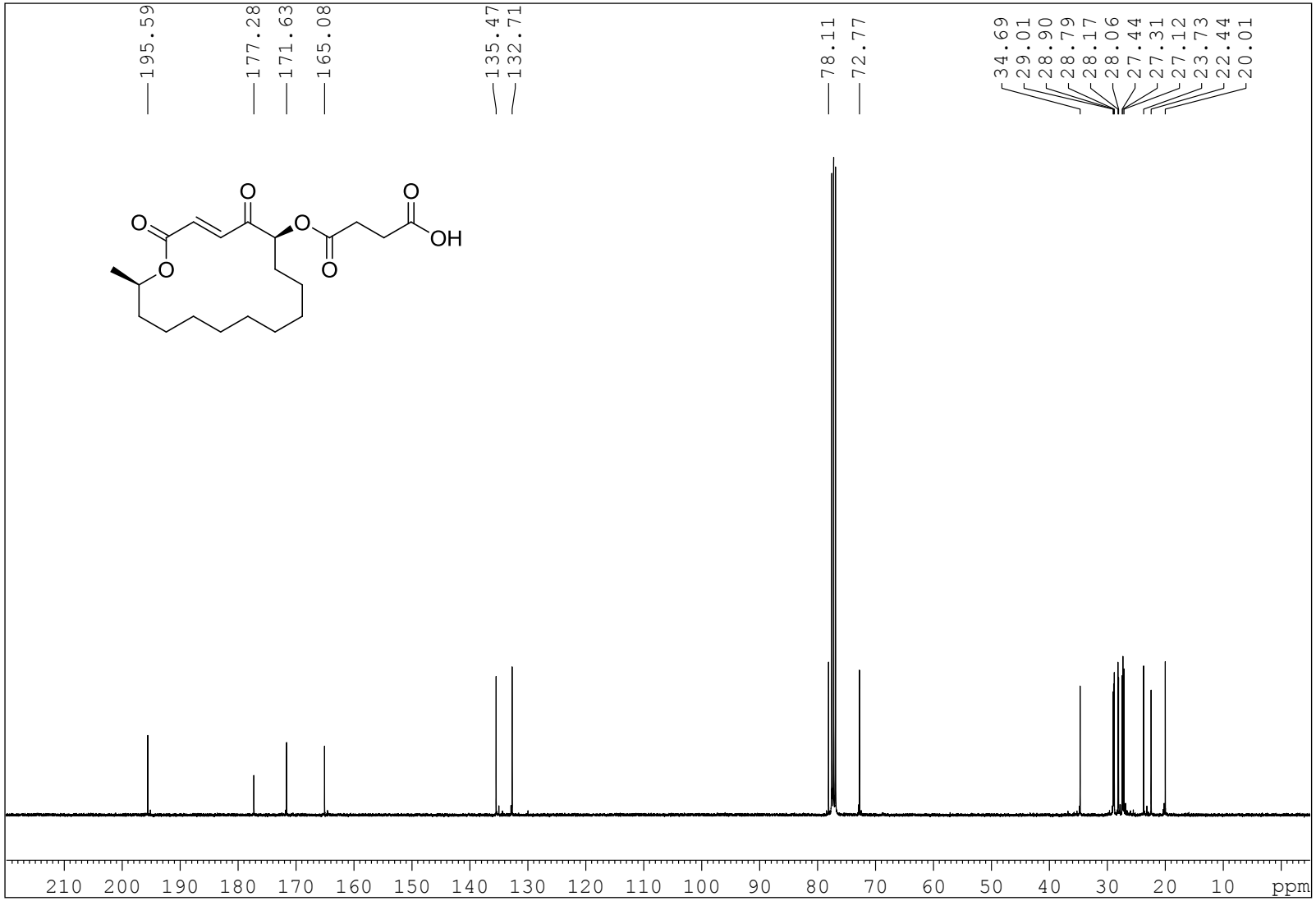
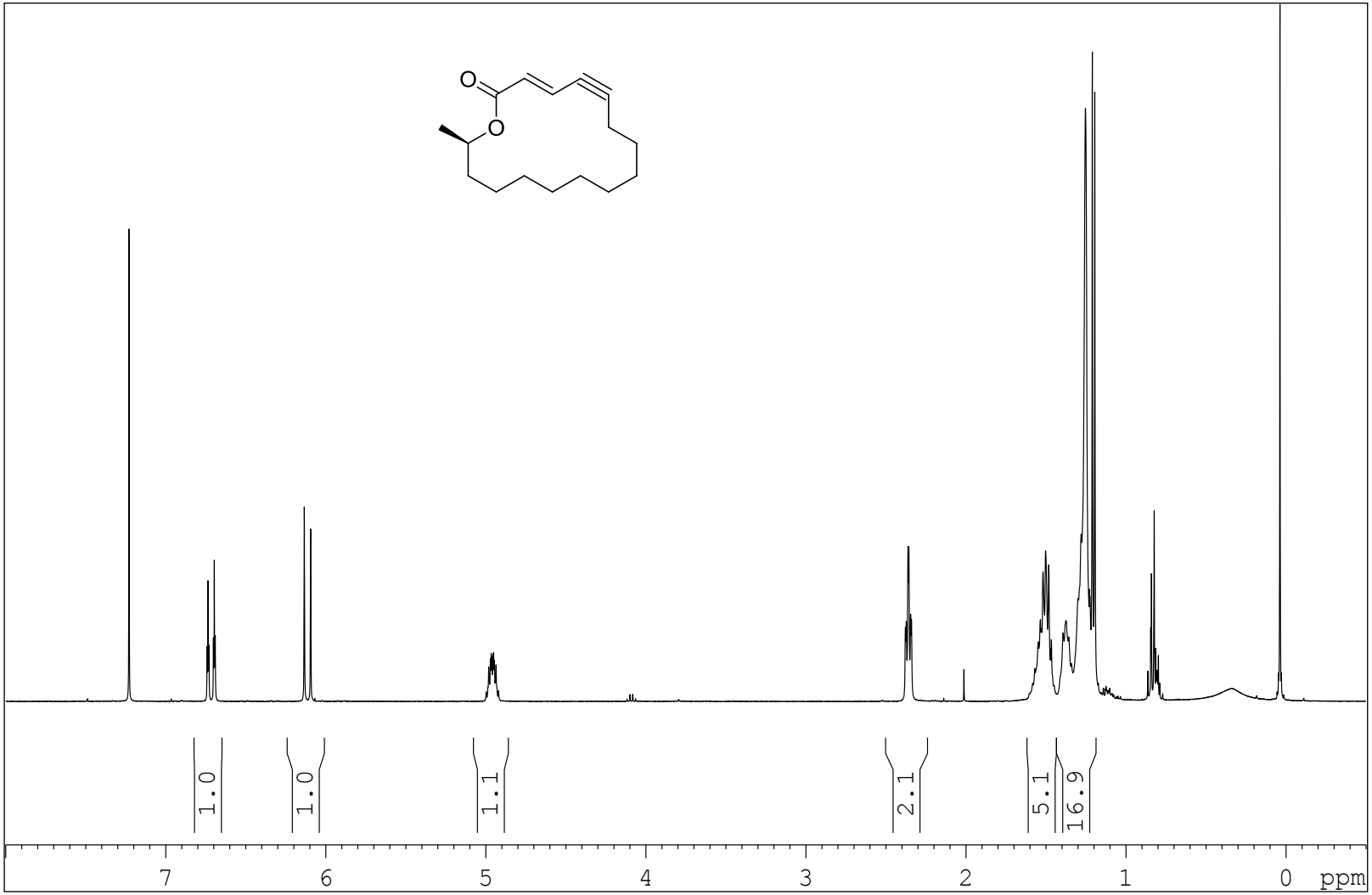


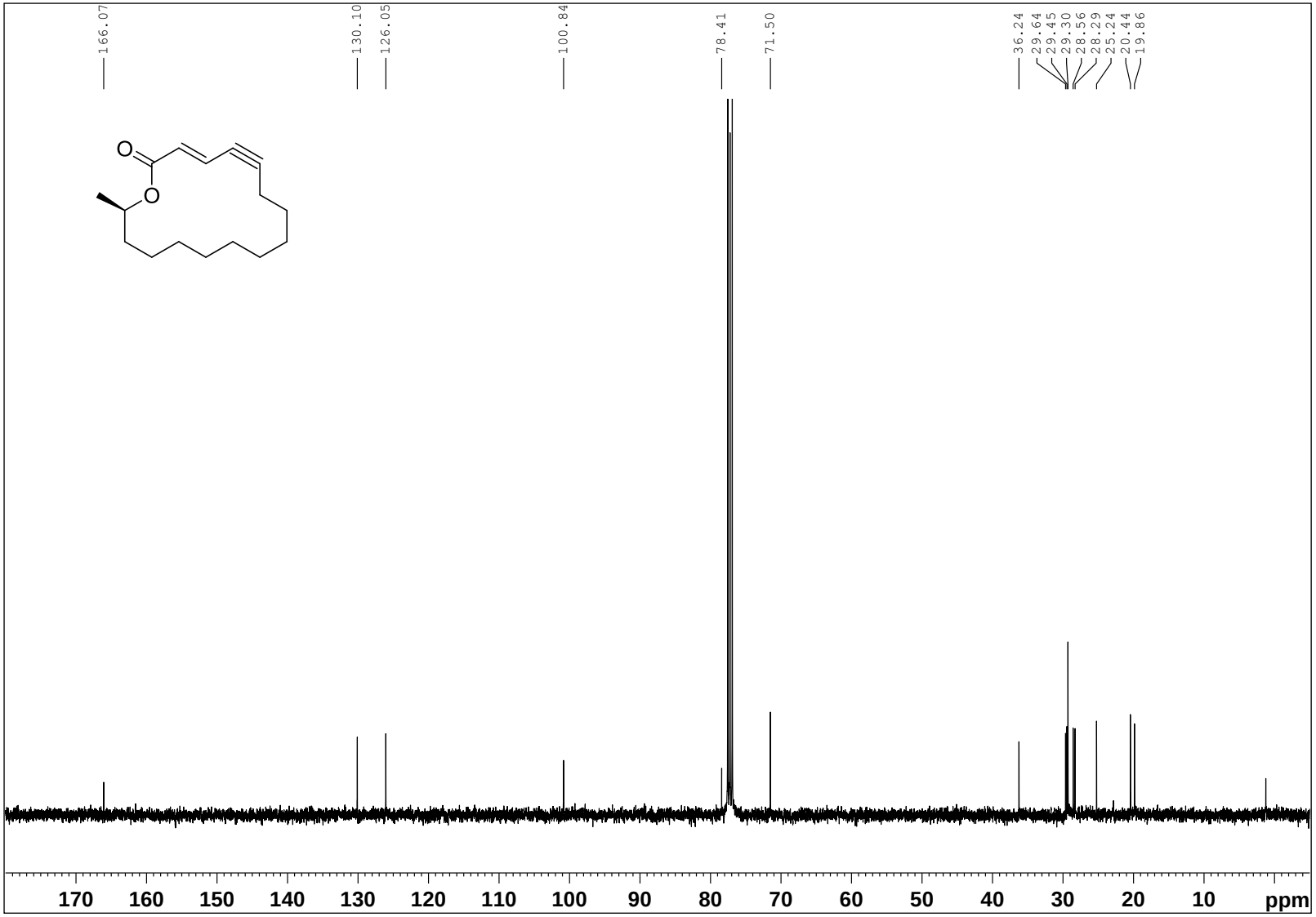
^{13}C NMR (100 MHz, $CDCl_3$)



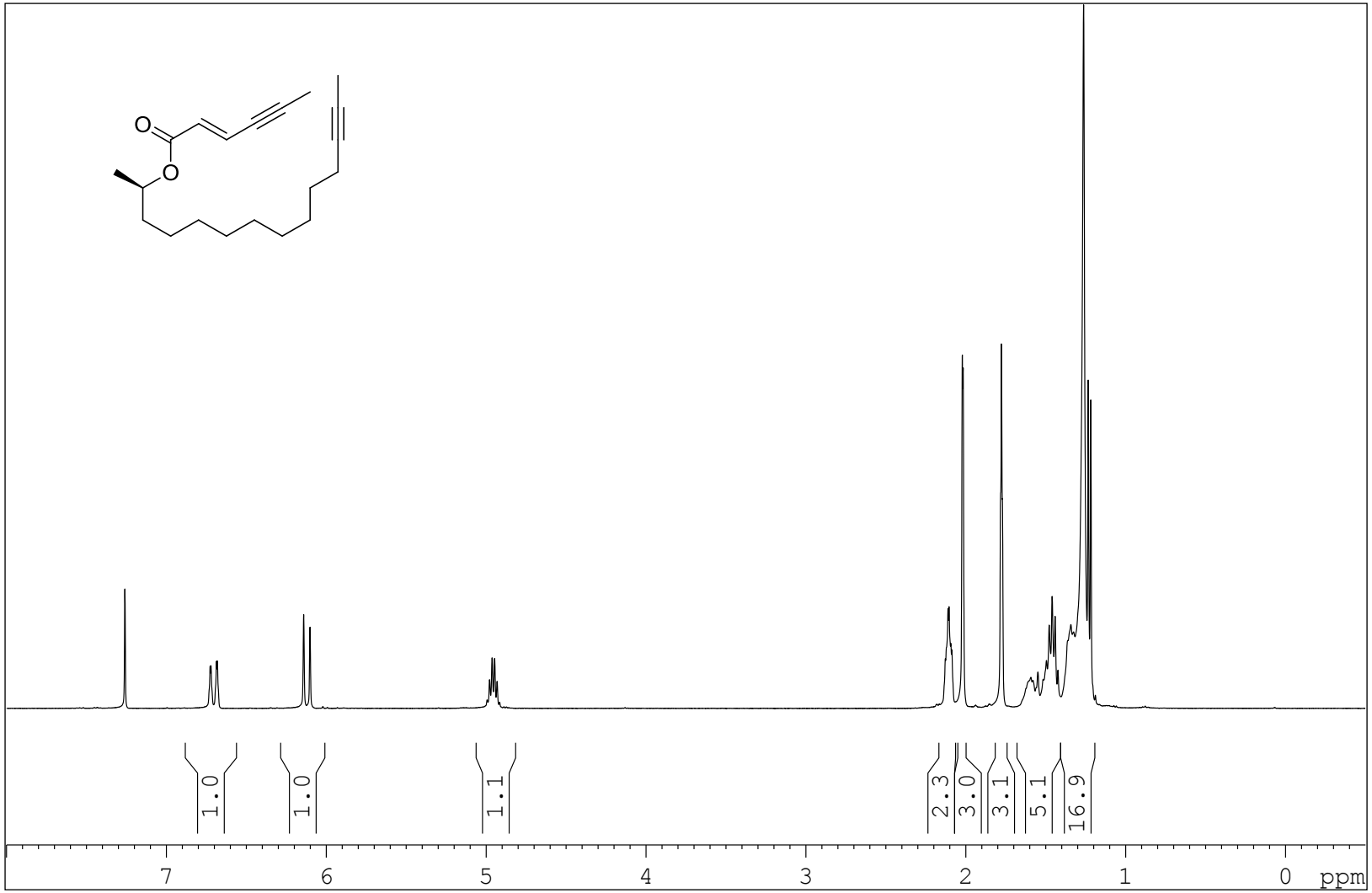
^{1}H NMR (400 MHz, $CDCl_3$)



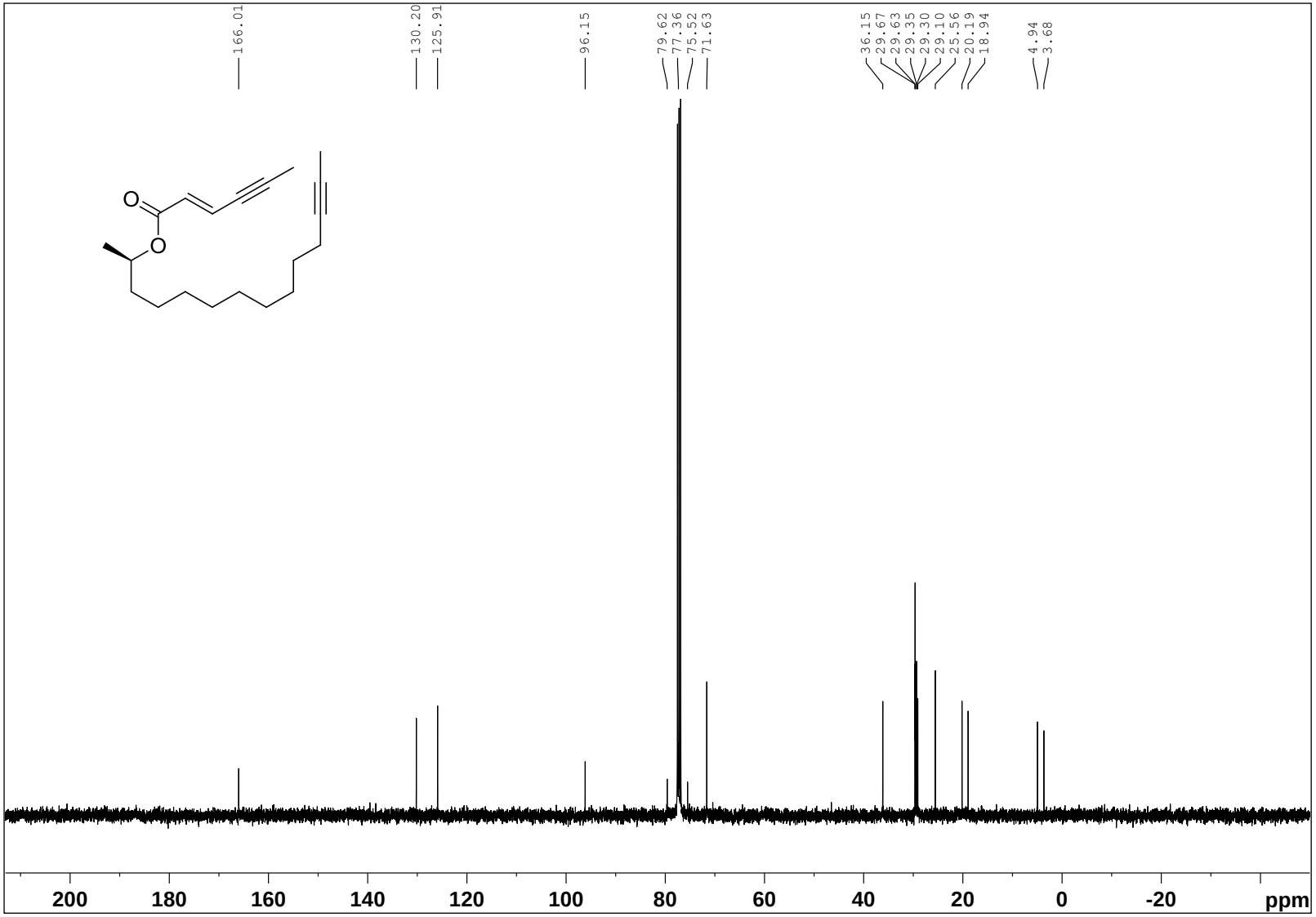
^{13}C NMR (100 MHz, $CDCl_3$)



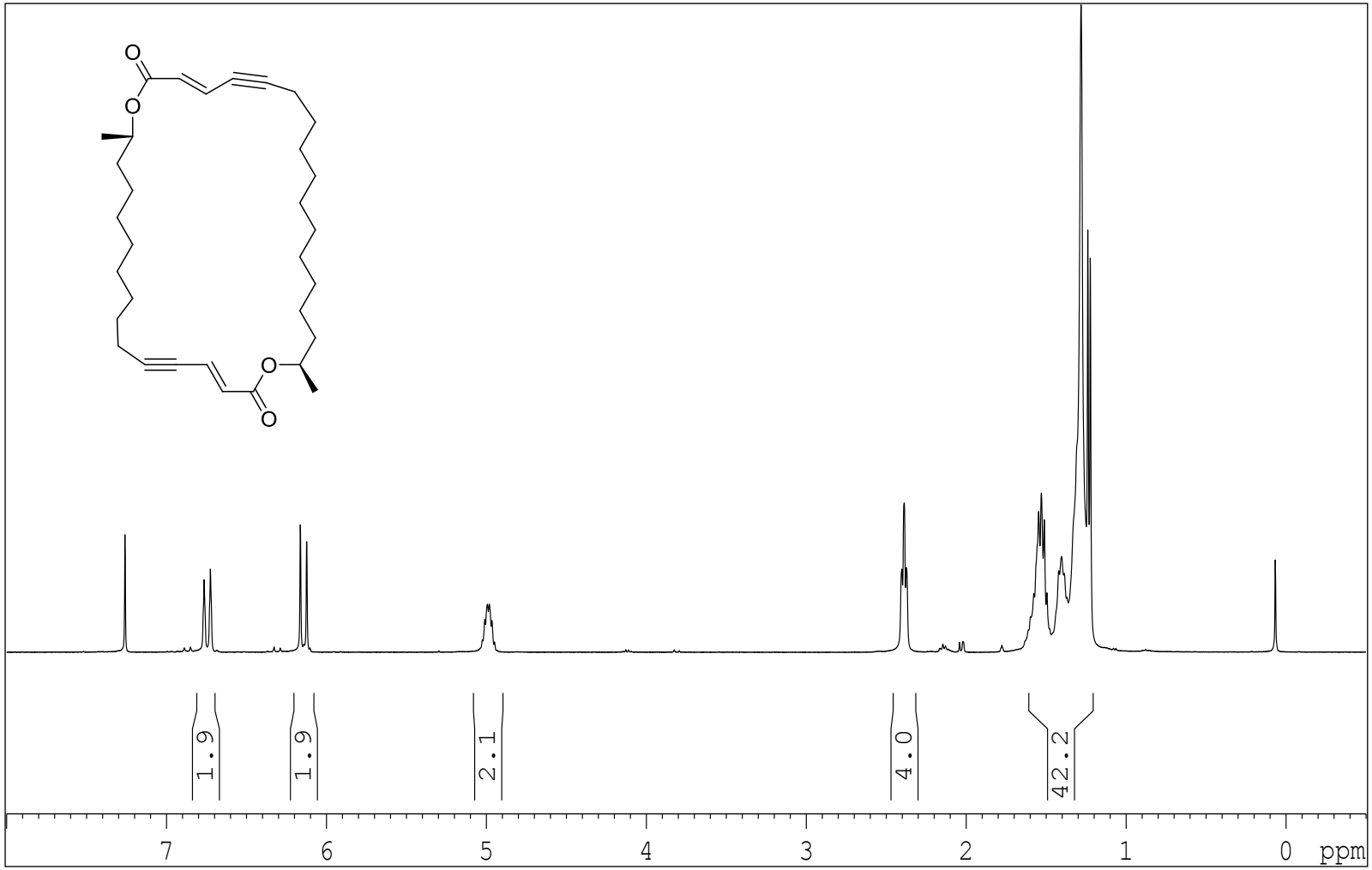
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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