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Supporting Information

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Total Synthesis of Tulearin C**

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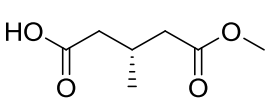
General. All reactions were carried out in flame-dried glassware under Argon. All solvents were purified by distillation over the drying agents indicated and were transferred under Argon: THF (Mg-anthracene), diethyl ether (Mg-anthracene), dichloromethane (CaH_2), acetonitrile (CaH_2), triethylamine (CaH_2), methanol (Mg), hexane (Na/K), toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200, MS (CI): Finnigan MAT 95, MS (ESI) ESQ 3000, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300, AV 400 and AV 600 spectrometer in the solvents indicated; ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references ($CDCl_3$ δ_H = 7.24 ppm, δ_C = 77.0 ppm; C_6D_6 δ_H = 7.15 ppm, δ_C = 128.00 ppm; $CD_3(CO)CD_3$ δ_H = 2.04 ppm, δ_C = 29.80 ppm) and the chemical shifts converted to the TMS scale. Unless stated otherwise, all commercially available compounds (ABCR, Acros, Aldrich, Fluka, Lancaster, Strem) were used as received.

Preparation of the Common Lactone Building Block

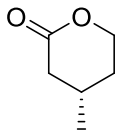
(*R*)-5-Methoxy-3-methyl-5-oxopentanoic acid (8). A 3 neck, 2 L cylindrical reactor with a cooling mantle connected to a cryostat was charged with KH_2PO_4/Na_2HPO_4 buffer (1.0 L, 0.1 M, pH 7), methanol (250 mL) and dimethyl 3-methylglutarate (45.0 g, 258 mmol). The mixture was cooled to –10 °C before pig liver esterase (1.81 g, 36290 U, E.C.3.1.1.1) was added. The necks of the reactor were closed with rubber septa; through one of them aq. NaOH (1.0 M, 260 mL, 260 mmol) was injected by syringe pump through a steel canula at such a rate as to maintain the pH as close to 7 as possible. After 63 h the NaOH feed was complete. The light brown emulsion was filtered, while still cold, through a pad of Celite (Ø = 10 cm, height = 5 cm), which was carefully rinsed with water (500 mL). The pH of the combined filtrates was adjusted to 3 with HCl (2 M) and the mixture separated in two equal parts, both of which were extracted with diethyl ether (6 × 100 mL each). The combined organic phases were dried over Na_2SO_4, filtered through a sintered glass filter, and evaporated to give the crude product, which was purified by flash chromatography (hexanes/ethyl acetate, 4:1) to give monoester **8** as a colorless oil (32.1 g, 78 %, 93 % *ee*). The corresponding diacid (1.1 g) and a small amount of the starting material (350 mg) were isolated as minor byproducts.



(–)-Cinchonidine (59.0 g, 200 mmol) was added to a solution of the enantioenriched monoester **8** in acetone (580 mL) and the resulting suspension heated to 40 °C. Water (about 60 mL) was added under vigorous stirring until a clear yellowish solution had formed. The solution was then allowed to rest overnight at 8 °C to give a cake of off-white amorphous material which was filtered off through a sintered glass filter, washed with ice-cold acetone (100 mL) and dried under reduced pressure. The dried material was dissolved in aq. HCl (2 M, 100 mL), the acidic layer was extracted with diethyl ether (5 × 40 mL) and the combined extracts were dried over Na_2SO_4, filtered and evaporated to give a clear colorless oil (19.3 g, 60 %, 98 % *ee*). From the mother liquor, additional crops of product can be obtained. $[\alpha]_D^{20}$ = –0.6 (*c* = 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 3H), 2.50-2.38 (m,

3H), 2.33-2.24 (m, 2H), 1.05 ppm (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.85, 172.73, 51.54, 40.49, 40.36, 27.18, 19.83 ppm; IR (film): $\tilde{\nu}$ = 2959, 1733, 1704, 1437, 1414, 1371, 1287, 1203, 1158, 1082, 1007, 876, 854, 697 cm^{-1}; MS (70 eV) *m*/*z* (%): 161 (1), 142 (30), 129 (92), 114 (84), 101 (83), 87 (19), 82 (25), 74 (72), 69 (77), 59 (100), 55 (39), 43 (59), 41 (36), 29 (17); HRMS (CI) *m*/*z*: calcd for $C_7H_{13}O_4$: 161.0815; found: 161.0814.

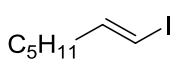
(*S*)-4-Methyltetrahydro-2H-pyran-2-one (10). Lithium hydroxide (0.2 M, 93.7 mL, 18.7 mmol) was slowly added to a solution of compound **8** (3.00 g, 18.7 mmol) and water (5 mL) at 0 °C and stirring was continued at ambient temperature for 1 h. The solvent was evaporated on a rotary evaporator (50 °C, 20 mbar) and the residue dried (90 °C, 3 × 10^{-3} mbar) for 4 h to give the corresponding lithium salt as a white solid.



THF (240 mL) and $LiBH_4$ (2.0 M in THF, 16 mL, 31 mmol) were added to this salt and the resulting mixture refluxed for 5 h under Ar with vigorous stirring. The suspension was cooled to room temperature, MeOH (48 mL) was added, and the resulting mixture stirred under reflux for 1 h. After reaching ambient temperature, the reaction was quenched with water (120 mL), and the organic solvents were evaporated. The aqueous solution was acidified with HCl (2.0 M) to pH 2, chloroform (100 mL) was added and the biphasic mixture stirred overnight. The layers were separated and the aqueous phase was extracted with chloroform (3 × 50 mL). The combined organic phases were dried over Na_2SO_4, filtered and evaporated, and the residue was purified by flash chromatography (pentanes/diethyl ether, 1:1), affording lactone **10** as a colorless liquid (1.96 g, 92 %). $[\alpha]_D^{20}$ = –22.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.41 (ddd, *J* = 11.4, 4.9, 4.0 Hz, 1H), 4.26 (ddd, *J* = 11.3, 10.6, 3.8 Hz, 1H), 2.71-2.63 (m, 1H), 2.14-2.03 (m, 2H), 1.93-1.88 (m, 1H), 1.56-1.47 (m, 1H), 1.06 ppm (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.15, 68.49, 38.15, 30.55, 26.48, 21.37 ppm; IR (film): $\tilde{\nu}$ = 2959, 2931, 2876, 1724, 1457, 1401, 1255, 1224, 1153, 1088, 1062, 994, 912, 823, 780, 690 cm^{-1}; MS (70 eV) *m*/*z* (%): 114 (49), 84 (4), 70 (26), 55 (91), 53 (4), 42 (100), 39 (20), 29 (17); HRMS (CI): *m*/*z* calcd for $C_6H_{10}O_2$: 114.0680, found 114.0681.

Synthesis of the Northern Fragment

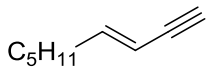
Alkenyl iodide 15. Dibal-H (1.0 M in dichloromethane, 60 mL, 60 mmol) was added dropwise to a solution of 1-heptyne (7.9 mL, 60 mmol) in hexane (30 mL) at –78 °C and the resulting mixture stirred at this temperature for 30 min and at ambient temperature for 16 h before the solvents were evaporated.



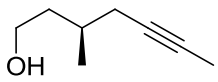
A solution of iodine (16.8 g, 66.0 mmol) in THF (60 mL) was added dropwise to a solution of the residue in THF (30 mL) at –78 °C and the resulting mixture was stirred at –78 °C for 30 min before it was slowly warmed to 0 °C. After 1 h at this temperature, the reaction was quenched with water (100 mL) and sat. aq. $Na_2S_2O_3$ (50 mL), the aqueous phase was extracted with diethyl ether (3 × 50 mL), the combined organic layers were dried over Na_2SO_4, filtered and evaporated, and the residue purified by flash chromatography (pentanes) to give vinyl iodide **15** as a colorless oil (11.93 g, 89 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.51 (dt, *J* = 14.3, 7.1 Hz, 1H), 5.97 (dt, *J* = 14.3, 1.4 Hz, 1H), 2.05 (tdd, *J* = 7.2, 7.2, 1.4 Hz, 2H), 1.43-1.34 (m, 2H), 1.34-1.22 (m, 4H), 0.89 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ = 146.81, 74.22, 36.00, 31.10, 28.03, 22.39, 13.96 ppm; IR (film): $\tilde{\nu}$ = 2956, 2925, 2856, 1606, 1464, 1378, 1277, 1235, 1208, 1192, 1173, 1101, 939, 844, 726, 659 cm^{-1}; MS (70 eV) *m/z* (%): 224 (39), 154 (19), 55 (100), 41 (54), 39 (28), 29 (28); HRMS (EI): *m/z* calcd for $C_7H_{13}I$: 224.0060, found: 224.0062.

Enyne 16. Ethynylmagnesium bromide (0.5 M in THF, 34 mL, 17 mmol) was added dropwise to the solution of alkenyl iodide **15** (2.50 g, 11.2 mmol) and $Pd(PPh_3)_4$ (390 mg, 0.33 mmol) in THF (50 mL). The yellow mixture was stirred for 16 h before the reaction was quenched with sat. aq. NH_4Cl (50 mL). The aqueous phase was extracted with pentane (2 × 50 mL), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the yellowish residue was purified by flash chromatography (pentanes) to give enyne **16** as a colorless oil (986 mg, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.25 (dt, *J* = 15.9, 7.1 Hz, 1H), 5.45 (dq, *J* = 15.9, 2.1 Hz, 1H), 2.77 (dd, *J* = 2.2, 0.5 Hz, 1H), 2.11 (tdd, *J* = 7.3, 7.3, 1.5 Hz, 2H), 1.44-1.34 (m, 2H), 1.34-1.22 (m, 4H), 0.88 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.00, 108.39, 82.61, 75.47, 32.98, 31.26, 28.20, 22.44, 13.97 ppm; IR (film): $\tilde{\nu}$ = 3314, 2958, 2927, 2858, 1630, 1466, 1379, 1194, 1050, 955, 726 cm^{-1}; MS (70 eV) *m/z* (%): 122 (32), 107 (24), 93 (51), 91 (39), 79 (100), 77 (42), 65 (36), 55 (50), 42 (40), 41 (83), 39 (61), 29 (54); HRMS(EI): *m/z* calcd for C_9H_{14}: 122.1094, found: 122.1096.



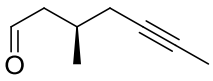
Alcohol 13. A mixture of CCl_4 (4.06 mL, 6.47 g, 42.1 mmol) and THF (5 mL) was added over 4 h to a refluxing solution of lactone **10** (200 mg, 1.75 mmol), PPh_3 (1.84 g, 7.01 mmol), and THF (40 mL). Once the addition was complete, reflux was continued for another 30 min until TLC showed complete conversion of the starting material. The mixture was cooled to room temperature and the reaction quenched with water (25 mL). The aqueous phase was extracted with diethyl ether (3 × 25 mL), the combined organic layers were washed with sat. aq. $NaHCO_3$ (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure to a volume of ca. 3-5 mL. Pentane (40 mL) was added, the precipitate was filtered off and the solution concentrated again. This cycle was repeated 3 times until no more precipitate was formed. The remaining solution was then passed through a silica gel plug (Ø 2 cm, height 2 cm), which was rinsed with pentanes/diethyl ether (9:1, 25 mL). The combined filtrates were evaporated and the crude dichloroolefin **11** was used in the next step without further purification.



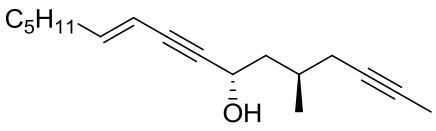
The crude dichloroolefin **11** was slowly added to a solution of MeLi (1.6 M in diethyl ether, 2.25 mL, 3.60 mmol) and THF (10 mL) at –78 °C. The resulting suspension was warmed to room temperature over the course of 30 min and then stirred for 1.5 h. For work up, the mixture was cooled to 0 °C and the reaction quenched with water (10 mL). Diethyl ether (20 mL) was added, the phases were separated, the aqueous layer was extracted with diethyl ether (3 × 10 mL), the combined extracts were dried over Na_2SO_4, and evaporated. Purification by flash chromatography (pentanes/diethyl ether, 1:1) afforded alcohol **13** as a colorless liquid (155 mg, 70 % over 2 steps). $[\alpha]_D^{20}$ = +3.2 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.71 (dt, *J* = 10.9, 6.5 Hz, 1H), 3.67 (dt, *J* = 10.9, 6.5 Hz, 1H), 2.12-2.07 (m, 2H), 1.84-1.65 (m, 3H), 1.78 (t, *J* = 2.6 Hz, 3H), 1.55-1.42 (m, 2H), 0.98 ppm (d,

J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 77.53, 77.20, 61.03, 38.79, 29.58, 26.13, 19.65, 3.44 ppm; IR (film): $\tilde{\nu}$ = 3339, 2970, 2956, 2920, 2875, 1738, 1455, 1434, 1375, 1366, 1229, 1217, 1206, 1092, 1053, 1006, 962, 888, 842cm^{-1}; MS (70 eV) *m*/*z* (%): 111 (31), 98 (65), 97 (13), 93 (33), 91 (22), 84 (24), 83 (11), 82 (100), 81 (14), 80 (20), 79 (38), 77 (31), 71 (19), 67 (46), 55 (85), 54 (36), 53 (44), 43 (58), 41 (43); HRMS (CI): *m*/*z* calcd for $C_8H_{15}O$: 127.1124, found 127.1123.

Aldehyde 14. A solution of alcohol **13** (450 mg, 3.6 mmol) in dichloromethane (5 mL) was added to a suspension of Dess-Martin periodinane (1.89 g, 4.46 mmol) in dichloromethane (15 mL) at 0 °C. The resulting mixture was stirred at ambient temperature until the starting material was consumed (ca 2 h) before it was poured into a sat. aq. $NaHCO_3$ (50 mL). The aqueous phase was extracted with dichloromethane (2 × 20 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure (22 °C, 350 mbar) to a small volume (about 5 mL). This solution was charged on top of a silica gel column and the product eluted with pentanes/diethyl ether (9:1). The fractions containing the volatile and unstable aldehyde **14** were combined and carefully concentrated under reduced pressure (22 °C, 500 mbar) to a small volume (about 5 mL). This solution was used in the next step as complete evaporation of the solvent leads to loss of material. Characteristic data of the aldehyde: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (t, *J* = 1.9 Hz, 1H), 2.60 (ddd, *J* = 16.2, 5.2, 1.7 Hz 1H), 2.34-2.05 (m, 4H), 1.77 (t, *J* = 2.5 Hz, 3H), 1.02 ppm (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.29, 77.62, 76.68, 49.81, 28.02, 26.04, 19.80, 3.41 ppm; IR (film): $\tilde{\nu}$ = 3339, 2970, 2956, 2920, 2875, 1738, 1455, 1434, 1375, 1366, 1229, 1217, 1206, 1092, 1053, 1006, 962, 888, 842 cm^{-1}; MS (70 eV) *m*/*z* (%):109 (25), 95 (13), 82 (38), 80 (100), 79 (75), 77 (17), 69 (17), 53 (43), 41 (53), 39 (48), 27 (41); HRMS (CI): *m*/*z* calcd for $C_8H_{12}O$: 124.0888, found 124.0888.



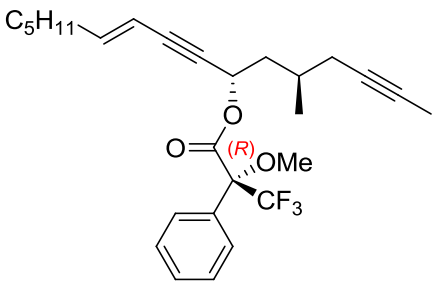
Propargylic alcohol 17. A Schlenk flask was charged with $Zn(OTf)_2$ (2.14 g, 5.88 mmol) (pre-dried at 120 °C, 1 × 10^{-3} mbar for 2 h), (–)-N-methylephedrine (1.17 g, 6.53 mmol), toluene (28 mL) and diisopropylethylamine (1.24 mL, 942 mg, 7.13 mmol). The resulting milky mixture was vigorously stirred for 2 h at room temperature before enyne **16** (654 mg, 5.35 mmol) was added and stirring of the resulting light yellow suspension continued for 30 min.



In parallel, the solution of aldehyde **14** (prepared as described above) was diluted with toluene (35 mL) and dried over MS 3Å pellets. This pre-dried solution was slowly added to the flask containing the zinc reagent and the enyne and the resulting mixture stirred for 2 h before the reaction was quenched with sat. aq. NH_4Cl (140 mL). Diethyl ether (30 mL) was added, the layers were separated, and the aqueous phase was extracted with diethyl ether (2 × 30 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated, and the crude material was purified by flash chromatography (pentanes/diethyl ether, 9:1) to afford the propargylic alcohol **17** as a pale yellow oil (501 mg, 57 % over 2 steps). $[\alpha]_D^{20}$ = –2.9 (*c* = 0.9, $CHCl_3$ for 96 % *de* sample); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.14 (dt, *J* = 15.8, 7.1 Hz, 1H), 5.48 (ddt, *J* = 15.8, 1.7, 1.7 Hz, 1H), 4.54 (dt,

J = 5.8, 1.6 Hz, 1H), 2.14-2.06 (m, 4H), 1.96-1.85 (m, 2H), 1.79 (t, *J* = 2.5 Hz, 3H), 1.67 (br s, 1H), 1.63-1.52 (m, 1H), 1.47-1.34 (m, 2H), 1.33-1.22 (m, 4H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.88 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.53, 108.77, 88.63, 83.66, 77.11, 76.92, 61.19, 44.04, 33.01, 31.25, 29.34, 28.32, 26.06, 22.44, 19.44, 13.97, 3.48 ppm; IR (film): $\tilde{\nu}$ = 3457, 3016, 2970, 2956, 2924, 2857, 1738, 1435, 1365, 1229, 1217, 1206, 1160, 1091, 1056, 1029, 953, 896, 848, 799, 668 cm^{-1}; MS (70 eV) *m*/*z* (%): 231 (11), 204 (31), 191 (43), 189 (54), 175 (61) 161 (41), 147 (52), 133 (41), 119 (41), 105 (64), 91 (68), 79 (67), 55 (80), 41 (100); HRMS (ESI+): *m*/*z* calcd for $C_{17}H_{26}ONa$: 269.1875, found 269.1876.

Mosher ester (*R*)-S1. (*S*)-α-Methoxy-α-trifluoromethyl phenylacetic acid chloride (13 mg, 53 µmol) was added to a solution of alcohol **17** (10 mg, 41 µmol), dichloromethane (1 mL), and 4-(dimethylamino)pyridine (7.4 mg, 61 µmol), and the mixture stirred for 16 h. Water (5 mL) was added, the aqueous phase was extracted with diethyl ether (3 × 5 mL), the combined organic layers were dried over Na_2SO_4, filtered, and evaporated, and the crude product was purified by flash chromatography (hexanes/ethyl acetate, 10:1) to give the corresponding Mosher ester as a colorless oil (18 mg, 96 %).



Mosher ester (*S*)-S1. Prepared analogously as a colorless oil (18 mg, 96 %) using (*R*)-α-methoxy-α-trifluoromethyl phenylacetic acid chloride as the reagent.

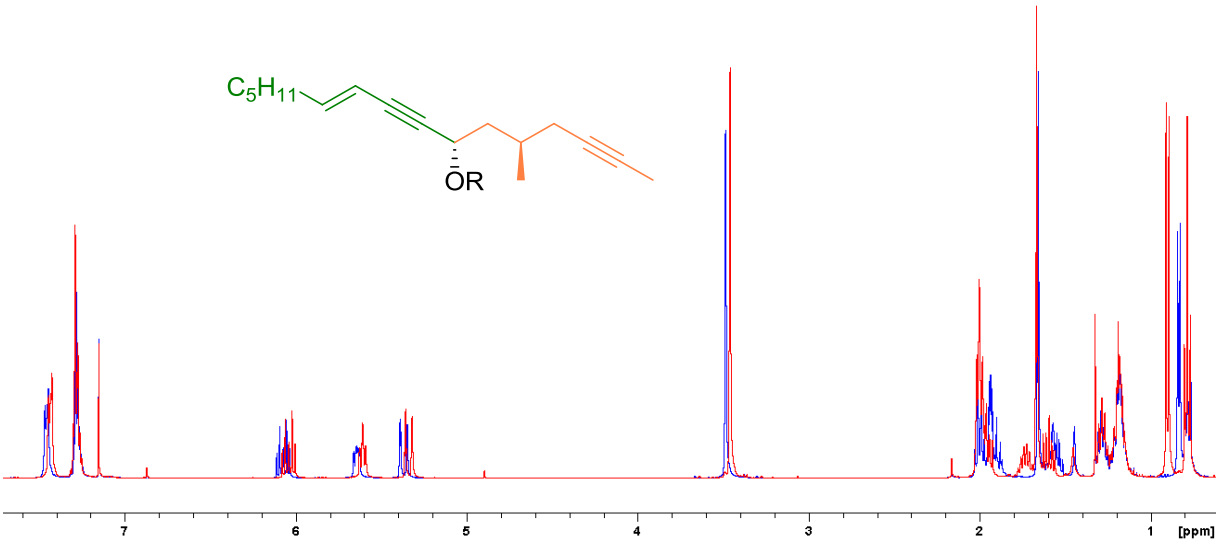
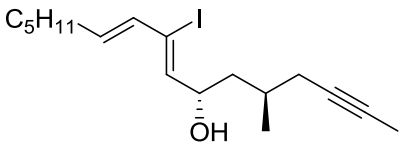
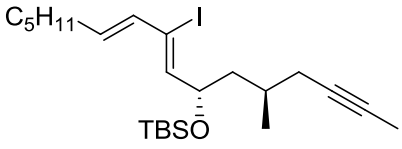


Figure S1. Superposition of the NMR spectra of the Mosher esters **(*R*)-S1** (shown in red) and **(*S*)-S1** (shown in blue). The protons from the left part of the molecule (in green) are more shielded in **(*R*)-S1**, whereas the protons from the right part (in orange) are more shielded in **(*S*)-S1**. This pattern confirms the (*S*) configuration of the secondary alcohol in **17**.

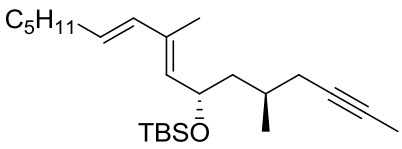
Vinyl iodide 18. A flask was charged with alcohol **17** (50 mg, 200 µmol), diethyl ether (3 mL) and some pellets of activated molecular sieves (MS 3Å). The mixture was stirred for 1 min and the solution transferred into another flask, rinsing the molecular sieves with additional diethyl ether (2 mL). The pre-dried solution was cooled to 0 °C and a solution of Red-Al (65 % *w*/*w* in toluene, 98 mL, 95 mg, 300 µmol) in diethyl ether (10 mL) was slowly added. The cooling bath was removed and the resulting solution stirred for 45 min before it was cooled to –20 °C and a solution of iodine (77 mg, 300 µmol) in diethyl ether (10 mL) was introduced. The resulting suspension was stirred for 45 min at –20 °C and the reaction subsequently quenched with sat. aq. $Na_2S_2O_3$ (30 mL). The aqueous phase was extracted with diethyl ether (3 × 15 mL), the combined organic layers were dried over Na_2SO_4 and evapoprated, and the crude product quickly passed through a short silica gel column, eluting with Et_2O, to give vinyl iodide **18** (77 mg, 99 %) as a pale yellow oil, which was used in the next step without delay. $[\alpha]_D^{20}$ = –42.4 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.03 (dt, *J* = 14.4, 7.1 Hz, 1H), 5.82 (d, *J* = 7.6 Hz, 1H), 5.69 (dd, *J* = 14.5, 1.0 Hz, 1H), 4.60 (ddd, *J* = 8.3, 8.3, 4.7 Hz, 1H), 2.21-2.10 (m, 4H), 1.90-1.72 (m, 2H), 1.79 (t, *J* = 2.5 Hz, 3H), 1.56 (br s, 1H), 1.48-1.36 (m, 3H), 1.36-1.20 (m, 4H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.89 ppm (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.60, 139.50, 131.18, 106.57, 77.37, 76.87, 74.33, 42.22, 31.93, 31.41, 29.18, 28.85, 26.71, 22.48, 19.33, 14.01, 3.52 ppm; IR (film): $\tilde{\nu}$ = 3345, 2956, 2922, 2856, 1642, 1600, 1456, 1433, 1378, 1348, 1297, 1234, 1189, 1140, 1115, 1040, 1010, 946, 893, 836, 798, 726 cm^{-1}; MS (70 eV) *m*/*z* (%): 274 (4), 319 (11), 247 (67), 229 (39), 159 (26) 152 (26), 123 (92), 105 (29), 95 (45), 82 (51), 81 (92), 67 (67), 55 (100), 43 (80); HRMS (EI): *m*/*z* calcd for $C_{17}H_{27}OI$: 374.1108; found 374.1107.



Compound 19. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (99 µL, 110 mg, 0.431 mmol) was slowly added at 0 °C to a solution of alkenyl iodide **18** (124 mg, 0.331 mmol) and 2,6-lutidine (116 µL, 106 mg, 0.994 mmol) in dichloromethane (3 mL) and the resulting mixture stirred at ambient temperature for 1 h once the addition was complete. The reaction was the quenched with methanol (50 µL), the mixture was evaporated and the residue purified by flash chromatography (hexanes/*tert*-butyl methyl ether, 98:2) to obtain product **19** as a colorless oil (152 mg, 94 %). $[\alpha]_D^{20}$ = –28.5 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.97 (dt, *J* = 14.4, 7.0 Hz, 1H), 5.75 (d, *J* = 7.6 Hz, 1H), 5.67 (dd, *J* = 14.5, 1.0 Hz, 1H), 4.54 (ddd, *J* = 8.8, 7.6, 4.1 Hz, 1H), 2.21-2.08 (m, 4H), 1.86-1.77 (m, 1H), 1.79 (t, *J* = 2.5 Hz, 3H), 1.66 (ddd, *J* = 13.6, 8.9, 4.6 Hz, 1H), 1.47-1.38 (m, 2H), 1.38-1.22 (m, 5H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H), 0.88 (s, 9H), 0.10 (s, 3H), 0.04 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.06, 139.48, 131.27, 103.75, 77.62, 77.20, 75.44, 43.29, 31.94, 31.46, 28.92, 28.74, 27.01, 25.87 (3C), 22.49, 19.05, 18.06, 14.01, 3.52, -3.98, -4.68 ppm; IR (film): $\tilde{\nu}$ = 2955, 2927, 2856, 1643, 1601, 1461, 1378, 1360, 1251, 1192, 1077, 990, 945, 912, 882, 834, 807, 774, 742, 667 cm^{-1}; MS (70 eV) *m*/*z* (%): 432 (16), 431 (61), 309 (100), 229 (49), 185 (27), 159 (20), 107 (72), 75 (64), 73 (84); HRMS (ESI+): *m*/*z* calcd for $C_{23}H_{41}OISiNa$: 511.1867; found 511.1864.

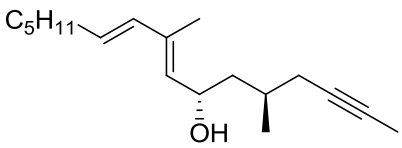


Diene S2. Note: The outcome of this reaction is strongly dependent on the quality of the Me_2Zn. Old or improperly handled solutions lead to higher reaction times and significant amounts of inseparable geometric olefin isomers.



$Pd(dppf)Cl_2 \bullet CH_2Cl_2$ (11 mg, 13 µmol) and dimethylzinc (1.0 M in heptane, 400 µL, 400 µmol) were successively added to a solution of compound **19** (131 mg, 268 µmol) in THF (20 mL) and triethylamine (110 µL, 81 mg, 800 µmol). The flask was placed into a pre-heated oil bath at 50 °C and the mixture stirred at this temperature for 1 h. For work up, the reaction was quenched with methanol (50 µL) and sat. aq. ammonium chloride (20 mL). The aqueous phase was extracted with diethyl ether (3 × 20 mL), the combined organic layers were dried over Na_2SO_4 and evaporated, and the residue purified by flash chromatography (hexanes/*tert*-butyl methyl ether, 100:0 → 98:2) to afford diene **S2** as a colorless oil (90 mg, 90 %). $[\alpha]_D^{20}$ = –9.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.01 (d, *J* = 15.6 Hz, 1H), 5.61 (dt, *J* = 15.5, 6.9 Hz, 1H), 5.29 (d, *J* = 8.6 Hz, 1H), 4.53 (dd, *J* = 8.5, 8.5, 5.0 Hz, 1H), 2.15-1.97 (m, 4H), 1.78 (t, *J* = 2.5 Hz, 3H), 1.75-1.63 (m, 2H), 1.73 (d, *J* = 1.1 Hz, 3H), 1.45-1.15 (m, 7H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.89 (t, *J* = 6.7 Hz, 3H), 0.87 (s, 9H), 0.07, (s, 3H), 0.03 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.34, 134.15, 132.07, 129.38, 77.67, 76.43, 67.59, 44.64, 32.86, 31.50, 29.28, 28.90, 26.67, 25.89 (3C), 22.55, 19.29, 18.16, 14.05, 12.89, 3.49, -4.09, -4.87 ppm; IR (film): $\tilde{\nu}$ = 2956, 2927, 2857, 1461, 1377, 1360, 1254, 1074, 989, 963, 915, 834, 808, 774, 666 cm^{-1}; MS (70 eV) *m*/*z* (%): 376 (12), 323 (27), 319 (42), 291 (24), 281 (84), 245 (37), 173 (30), 75 (100), 73 (98); HRMS (EI): *m*/*z* calcd for $C_{24}H_{44}OSi$: 376.3159, found 376.3161.

Alcohol 6. TBAF (1.0 M in THF, 1.3 mL, 1.3 mmol) was added to a solution of diene **S2** (100 mg, 266 µmol) in THF (3 mL) at 0 °C and the mixture stirred for 3.5 h at ambient temperature. The reaction was quenched with sat. aq. $NaHCO_3$ (30 mL), the aqueous phase was extracted with diethyl ether (3 × 20 mL), the combined extracts were dried over Na_2SO_4 and evaporated, and the residue purified by flash chromatography (hexanes/diethyl ether, 9:1) to give alcohol **6** (67 mg, 96 %) as a colorless oil. $[\alpha]_D^{20}$ = –10.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): δ = 6.10 (dd, *J* = 15.6, 0.6 Hz, 1H), 5.62 (dt, *J* = 15.4, 7.0 Hz, 1H), 5.36 (d, *J* = 8.5 Hz, 1H), 4.47 (ddd, *J* = 12.9, 8.7, 4.5 Hz, 1H), 2.18-2.03 (m, 4H), 2.05-1.88 (m, 1H), 1.87-1.73 (m, 1H), 1.67 (d, *J* = 1.2 Hz, 3H), 1.55 (t, *J* = 2.6 Hz, 3H), 1.41-1.21 (m, 7H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.80 ppm (d, *J* = 4.2 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6): δ = 135.01, 134.53, 134.06, 129.87, 78.00, 76.81, 66.44, 44.23, 33.25, 31.79, 29.71, 29.67, 27.04, 22.94, 19.60, 14.25, 12.96, 3.41 ppm; IR (film): $\tilde{\nu}$ = 3336, 2956, 2921, 2856, 1625, 1456, 1378, 1301, 1050, 1005, 962, 894, 846, 799, 726 cm^{-1}; MS (70 eV) *m*/*z* (%): 262 (6), 247 (13), 191 (30), 177 (33), 173 (50), 167 (54), 123 (100), 95 (48), 69 (42), 55 (53), 43 (57), 41 (58); HRMS (ESI+): *m*/*z* calcd for $C_{18}H_{30}ONa$: 285.2185; found 285.2189.



Synthesis of Southern Fragment

Alcohol S3. Prepared from commercial 3-butyn-1-ol according to a literature procedure;[1] colorless oil (1.13 g, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.55 (dt, J = 14.5, 7.3 Hz, 1H), 6.17 (dt, J = 14.4, 1.4 Hz, 1H), 3.69 (t, J = 6.2 Hz, 2H), 2.33 (dtd, J = 7.5, 6.3, 1.4 Hz, 2H), 1.53 ppm (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.60, 77.23, 60.99, 39.15 ppm; IR (film): $\tilde{\nu}$ = 3315, 2927, 2876, 1606, 1423, 1373, 1287, 1253, 1214, 1159, 1041, 940, 842, 792, 658 cm^{-1}; MS (EI, 70 eV) m/z (%): 198 (28), 168 (11), 167 (19), 127 (7), 71 (100), 53 (9), 43 (39), 41 (92), 39 (57), 31 (59); HRMS (EI): m/z calcd for C_4H_9OI: 197.9544; found 197.9542.

Alkenyl iodide 28. Trifluoromethanesulfonic acid anhydride (0.27 mL, 0.45 mg, 1.6 mmol) was added to a solution of pyridine (0.13 mL, 130 mg, 1.6 mmol) in dichloromethane (5 mL) at –20 °C and the resulting mixture stirred for 10 min before alcohol **S3** (300 mg, 1.50 mmol) was slowly introduced. The mixture was allowed to reach room temperature over 10 min before it was concentrated on a rotary evaporator (water bath temperature ≤ 20 °C). A solution of the resulting crude triflate **27** in THF (5 mL) was added to a solution of propynyllithium (348 mg, 7.55 mmol) in THF (10 mL) at –20 °C. Once the addition was complete, the mixture was stirred at 0 °C for 30 min before the reaction was quenched at 0 °C with water (20 mL) and diethyl ether (20 mL). The aqueous phase was extracted with diethyl ether (3 × 20 mL), the combined organic layers were dried over Na_2SO_4 and carefully evaporated, and the residue was purified by flash chromatography (pentanes) to obtain alkenyl iodide **28** (253 mg, 76 %, determined by ^{1}H NMR) as a concentrated solution in pentane (compete removal of the solvent leads to loss of material). Characteristic data: ^{1}H NMR (400 MHz, C_6D_6): δ = 6.33 (dt, J = 14.4, 7.0 Hz, 1H), 5.68 (dt, J = 14.4, 1.4 Hz, 1H), 1.87-1.82 (m, 2H), 1.77 (dt, J = 6.8, 1.2 Hz, 1H), 1.73 (dt, , J = 7.0, 1.2 Hz, 1H), 1.48 ppm (t, J = 2.5 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 144.84, 77.84, 76.71, 76.08, 35.45, 18.22, 3.25 ppm; IR (film): $\tilde{\nu}$ = 3047, 2916, 2846, 1717, 1606, 1433, 1375, 1337, 1282, 1240, 1210, 1151, 1004, 940, 827, 778, 450, 700, 660 cm^{-1}; MS (EI, 70 eV) m/z (%): 220 (2), 167 (55), 91 (100), 77 (85), 65 (17), 53 (55), 39 (82); HRMS (CI): m/z calcd for C_7H_9I: 219.9748; found 219.9749.

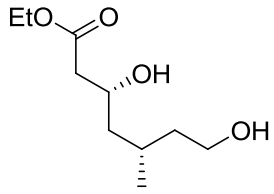
β-Ketoester 21. *n*-Butyllithium (1.6 M in hexane, 11.4 mL, 18.3 mmol) was slowly added to a solution of diisopropylamine (2.80 mL, 2.02 g, 20.0 mmol) in THF (15 mL) at –78 °C and the resulting mixture stirred for 10 min at this temperature and for 5 min at 0 °C.

Ethyl acetate (1.63 mL, 1.47 g, 16.7 mmol) was added dropwise to the solution of LDA thus formed at –78 °C and the mixture was stirred for 1 h at this temperture. A solution of lactone **10** (1.90 g, 16.6 mmol) in THF (10 mL) was then added and stirring continued for 3 h at –78 °C. The reaction was quenched with acidic acid (2 mL) while cold, the resulting suspension was warmed to ambient temperature, diluted with diethyl ether (30 mL) and

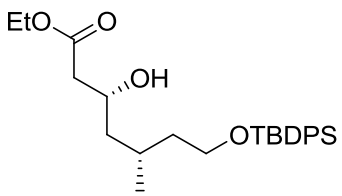
[1] Z. Huang, E. Negishi, *Org. Lett.* **2006**, *8*, 3675-3678.

absorbed on silica gel (about 10 g), which was added on top of a silica gel column. The product was eluted with hexanes/diethyl ether (3:1) to give β-ketoester **21** as a colorless oil (3.01 g, 90 %). $[\alpha]_D^{20}$ = +53 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of lactol and ketone): *δ* = 4.82 (br s, 1H), 4.20 (qd, *J* = 7.2, 1.4 Hz, 2H), 3.95 (ddd, *J* = 12.9, 11.3, 2.4 Hz, 1H), 3.64 (ddd, *J* = 11.2, 4.8, 1.4 Hz, 1H), 2.60 (d, *J* = 15.5 Hz, 1H), 2.53 (d, *J* = 15.5 Hz, 1H), 2.11-1.98 (m, 1H), 1.77 (ddd, *J* = 12.8, 3.8, 1.8 Hz, 1H), 1.53 (app d, *J* = 11.3 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.17 (ddd, *J* = 25.2, 13.0, 4.9 Hz, 1H), 1.04 (app t, *J* = 12.5 Hz, 1H), 0.90 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of hemiketal and ketone): *δ* = 172.36, 94.88, 61.16, 60.90, 45.08, 43.39, 33.72, 24.85, 22.10, 14.07 ppm; IR (film): $\tilde{\nu}$ = 3460, 2952, 2874, 1713, 1456, 1411, 1374, 1335, 1261, 1199, 1171, 1155, 1089, 1044, 1013, 971, 910, 884, 854, 846, 810, 775, 659 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 202 (2), 185 (3), 169 (1), 133 (100), 115 (59), 105 (8), 97 (10), 87 (27), 73 (19), 70 (47), 55 (55), 42 (55), 29 (44); HRMS (CI) *m/z* calcd for $C_{10}H_{18}O_4Na$: 225.1095; found: 225.1097.

β-Hydroxyester 22. An autoclave was charged with $RuCl_3$ (15 mg, 74 µmol) and (*R*)-SYNPHOS (47 mg, 74 µmol) and put under an inert atmosphere by three vacuum/Ar cycles. Ethanol (15 mL) and β-ketoester **21** (1.50 g, 7.42 mmol) were added under vigorous stirring, the autoclave was pressurized with hydrogen (10 bar) and the pressure was released. This purge cycle was repeated 3 times before the solution was stirred at 80 °C under hydrogen atmosphere (10 bar) for 24 h. For work up, the autoclave was vented at ambient temperature, the solvent was evaporated and the dark residue purified by flash chromatography (hexanes/ethyl acetate, 2:3) to afford β-hydroxyester **22** as a colorless oil (1.35 g, 89 %). $[\alpha]_D^{20}$ = –4.7 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 4.16 (q, *J* = 7.2 Hz, 2H), 4.14-4.08 (m, 1H), 3.74-3.62 (m, 2H), 2.86 (br s, 2H), 2.49-2.37 (m, 2H), 1.92-1.84 (m, 1H), 1.58 (ddd, *J* = 13.9, 10.0, 4.2 Hz, 1H), 1.50 (ddd, *J* = 12.8, 6.4, 2.0 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.14 (ddd, *J* = 13.9, 9.2, 3.2 Hz, 1H), 0.95 ppm (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 172.93, 66.02, 60.67, 60.39, 43.30, 42.13, 40.18, 25.85, 19.74, 14.14 ppm; IR (film): $\tilde{\nu}$ = 3354, 2930, 1716, 1462, 1373, 1299, 1279, 1248, 1163, 1094, 1021, 964, 858, 754, 666 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 205 (<1), 185 (<1), 156 (4), 141 (7), 130 (8), 117 (100), 99 (46), 95 (10), 89 (26), 81 (13), 71 (58), 60 (14), 55 (37), 43 (87), 29 (40); HRMS (CI): *m/z* calcd for $C_{10}H_{20}O_4Na$: 227.1253; found: 227.1254.



Compound 23. 4-(Dimethylamino)pyridine (38.0 mg, 0.31 mmol), triethylamine (990 µL, 7.10 mmol) and *tert*-butyl(chloro)diphenylsilane (1.76 mL, 6.79 mmol) were added to a solution of β-hydroxyester **22** (1.26 g, 6.17 mmol) in dichloromethane (13 mL) and the resulting mixture was stirred for 5 h before the reaction was quenched with water (15 mL). The aqueous phase was extracted with diethyl ether (3 × 15 mL), the combined organic layers were dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (hexanes/ethyl acetate 9:1) to give product **23** as a colorless oil (2.61 g, 95 %). $[\alpha]_D^{20}$ = –8.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): *δ* = 7.82-7.22 (m, 4H), 7.28-7.20 (m, 6H), 4.09-3.98 (m, 1H), 3.89 (q, *J* = 7.1 Hz, 2H), 3.77-3.66 (m, 2H), 2.77 (d, *J* = 4.2 Hz, 1H), 2.22 (dd, *J* = 16.3, 8.3 Hz, 2H), 2.15 (dd, *J* = 16.3, 4.0 Hz, 1H), 2.05-1.91 (m, 1H), 1.62-1.53 (m, 1H), 1.49-1.26 (m, 2H),



1.18 (s, 9H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.81 ppm (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 172.74, 136.05 (4C), 136.03 (4C), 134.46, 134.43, 129.90 (2C), 65.83, 62.35, 60.33, 44.16, 42.32, 40.62, 27.14 (3C), 26.21, 19.53, 19.45, 14.15 ppm; IR (film): $\tilde{\nu}$ = 3484, 2930, 2858, 1718, 1472, 1427, 1373, 1301, 1177, 1106, 1086, 1026, 939, 899, 822, 798, 737, 700, 687 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 397 (4), 385 (2), 367 (3), 355 (2), 339 (3), 321 (1), 307 (100), 297 (9), 265 (18), 237 (7), 199 (66), 183 (10), 139 (11), 95 (16), 81 (5), 43 (2); HRMS (CI): *m*/*z* calcd for $C_{26}H_{38}O_4SiNa$: 465.2430; found: 465.2432.

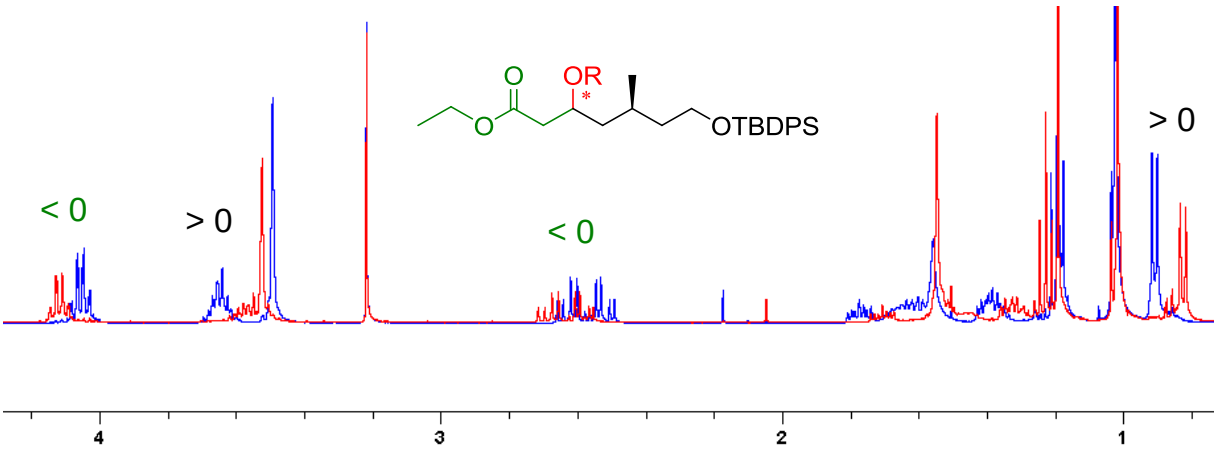
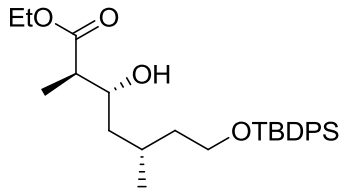


Figure S2. Superposition of the NMR spectra of the Mosher esters **(*S*)-S4** (shown in red) and **(*R*)-S4** (shown in blue) derived from **23**. The left part of the molecule (in green) is more shielded in **(*S*)-S4**, whereas the protons of the right part (in black) are more shielded in **(*R*)-S4**. This pattern confirms the (*R*) configuration of the secondary alcohol in compound **23**.[2, 3]

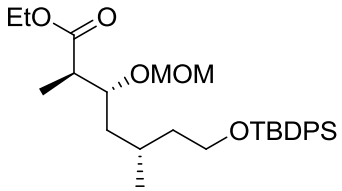
Compound S5. *n*-Butyllithium (1.6 M in hexane, 10.7 mL, 17.1 mmol) was added over 3 min to a solution of diisopropylamine (2.61 mL, 1.89 g, 18.7 mmol) in THF (18 mL) at –78 °C. The mixture was stirred for 15 min at –78 °C and for 20 min at 0 °C before it was cooled again to –78 °C. A solution of ester **23** (3.44 g, 7.77 mmol) in THF (10 mL) and DMPU (5 mL) was introduced via syringe pump over 45 min and stirring continued for 20 min at –78 °C and for 20 min at –40 °C. The solution was cooled to –78 °C before methyl iodide (0.61 mL, 9.7 mmol) was added, the mixture was stirred for 15 min at –78 °C and then slowly allowed to reach 0 °C. After 2.5 h, the reaction was quenched with sat. aq. NH_4Cl (30 mL), the aqueous phase was extracted with diethyl ether (3 × 30 mL), the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, and evaporated. Purification of the residue by flash chromatography (hexanes/ethyl acetate, 95:5) furnished compound **S5** (2.82 g, 79 %, 85:15 mixture of diastereomers) as a colorless oil. $[\alpha]_D^{20}$ = +2.9 (*c* = 1.0, $CHCl_3$, *dr* = 85:15); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.64 (m,



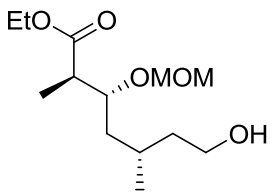
[2] J. A. Dale, D. L. Dull, H. S. Mosher, *J. Org. Chem.* **1969**, *34*, 2543-2549.
[3] T. R. Hoye, C. S. Jeffrey, F. Shao, *Nat. Protoc.* **2007**, *2*, 2451-2458.

4H), 7.42-7.36 (m, 6H), 4.16 (qd, *J* = 7.2, 2.2 Hz, 2H), 3.76-3.67 (m, 3H), 2.45 (dq, *J* = 7.0, 6.8 Hz, 1H), 1.92 (br s, 1H), 1.64-1.51 (m, 1H), 1.49-1.40 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 7.2 Hz, 3H), 1.22-1.15 (m, 1H) 1.04 (s, 9H), 0.87 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.01, 135.56 (4C), 134.00 (2C), 129.50 (2C), 127.57 (4C), 71.15, 62.02, 60.49, 45.80, 42.18, 40.36, 26.86 (3C), 26.07, 19.16, 14.27, 14.21 ppm; IR (film): $\tilde{\nu}$ = 3487, 2931, 2858, 1715, 1462, 1427, 1378, 1259, 1180, 1106, 939, 898, 822, 797, 737, 700, 687 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 411 (1), 381 (2), 353 (5), 321 (100), 297 (10), 265 (11), 231 (8), 199 (82), 183 (14), 139 (19), 109 (55), 99 (21), 81 (11), 67 (7), HRMS (CI): *m*/*z* calculated $C_{27}H_{40}O_4SiNa$: 479.2588; found: 479.2588.

Compound S6. Diisopropylethylamine (6.1 mL, 4.5 g, 35 mmol) and methoxymethyl chloride (1.3 mL, 1.2 mg, 18 mmol) were successively added to a solution of alcohol **S5** (1.60 g, 3.50 mmol) in dichloromethane (35 mL) at 0 °C. The resulting mixture was stirred at reflux temperature for 16 h before the reaction was quenched with sat. aq. NH_4Cl (30 mL). The aqueous phase was extracted with ethyl acetate (3 × 30 mL), the combined organic layers were dried over Na_2SO_4, filtered, and evaporated, and the residue was purified by flash chromatography (hexanes/ethyl acetate, 9:1) to give product **S6** as a colorless oil (1.71 g, 97 %, *dr* = 85:15). $[\alpha]_D^{20}$ = +11.2 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (dd, *J* = 7.9, 1.6 Hz, 4H), 7.43-7.35 (m, 6H), 4.67 (d, *J* = 7.0 Hz, 1H), 4.61 (d, *J* = 6.9 Hz, 1H), 4.21-4.06 (m, 2H), 3.96 (ddd, *J* = 9.4, 5.2, 2.2 Hz, 1H), 3.75-3.63 (m, 2H), 3.35 (s, 3H), 2.82 (dq, *J* = 7.0, 5.4 Hz, 1H), 1.92-1.74 (m, 1H), 1.65-1.53 (m, 3H), 1.46-1.37 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 7.1 Hz, 3H), 1.04 (s, 9H), 0.86 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.26, 135.56 (4C), 134.03 (2C), 129.49 (2C), 127.56 (4C), 96.27, 61.92, 60.33 (2C), 55.84, 43.56, 40.60, 38.60, 26.83 (3C), 25.79, 19.17, 19.03, 14.26, 10.80 ppm; IR (film): $\tilde{\nu}$ = 3071, 2931, 2892, 2857, 1733, 1589, 1472, 1463, 1428, 1380, 1299, 1246, 1187, 1141, 1105, 1092, 1034, 955, 917, 861, 822, 734, 700, 687 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 455 (3), 443 (26), 381 (84), 367 (10), 335 (12), 321 (75), 267 (19), 225 (19), 213 (69), 199 (100), 183 (53), 153 (13), 139 (33), 123 (12), 109 (70), 91 (28), 81 (13), 45 (60); HRMS (CI): *m*/*z* calcd for $C_{29}H_{44}O_5SiNa$: 523.2850; found: 523.2850.

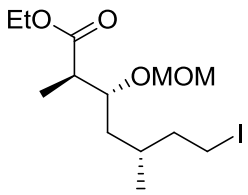


Compound 24. TBAF (1.0 M solution in THF, 0.60 mL, 0.60 mmol) was added to a solution of compound **S6** (250 mg, 0.50 mmol) in THF (5 mL) and the resulting mixture stirred for 13 h. The solvent was evaporated and the residue purified by flash chromatography (hexanes/ethyl acetate, 3:2) to give alcohol **24** in a diastereomerically pure form as a colorless oil (109 mg, 83 %). $[\alpha]_D^{20}$ = +32 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.69 (d, *J* = 7.0 Hz, 1H), 4.63 (d, *J* = 7.0 Hz, 1H), 4.19-4.09 (m, 2H), 3.99-3.94 (m, 1H), 3.73-3.64 (m, 2H), 3.38 (s, 3H), 2.83 (qd, *J* = 7.0, 5.4 Hz, 1H), 1.84-1.74 (m, 1H), 1.64-1.44 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 7.1 Hz, 3H), 1.10-1.04 (m, 1H), 0.93 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.20, 96.47, 77.25, 60.78, 60.39, 55.91, 43.62, 40.65, 38.27, 25.89, 19.42, 14.25, 10.72 ppm; IR (film): $\tilde{\nu}$ = 3448, 1731, 1462, 1378, 1299, 1247, 1184, 1141, 1095, 1030, 953, 917, 860, 795, 733, 678 cm^{-1}; MS (EI, 70 eV)



m/z (%): 261 (<1), 231 (1), 199 (3), 170 (2), 155 (10), 131 (9), 116 (5), 99 (67), 81 (5), 55 (9), 45 (100), 29 (12); HRMS (CI): *m/z* calcd for $C_{13}H_{26}O_5Na$: 285.1673; found: 285.1672.

Alkyl iodide 25. A solution of triphenylphosphine (400 mg, 1.52 mmol), iodine (390 mg, 1.52 mmol), imidazole (156 mg, 2.29 mmol), and alcohol **24** (200 mg, 0.76 mmol) in dichloromethane (10 mL) was stirred for 45 min before all volatile materials were evaporated. Purification of the residue by flash chromatography (hexanes/ethyl acetate, 95:5) afforded iodide **25** as a colorless oil (253 mg, 90 %). $[\alpha]_D^{20}$ = +8.4 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.69 (d, *J* = 7.0 Hz, 1H), 4.61 (d, *J* = 7.0 Hz, 1H), 4.18-4.08 (m, 2H), 3.96 (ddd, *J* = 9.7, 5.3, 2.2 Hz, 1H), 3.40 (s, 3H), 3.27-3.15 (m, 2H), 2.83 (qd, *J* = 7.0, 5.3 Hz, 1H), 1.89-1.65 (m, 3H), 1.55 (ddd, *J* = 14.2, 9.7, 3.1 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 7.1 Hz, 3H), 1.10-1.04 (m, 1H), 0,90 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.13, 96.36, 77.24, 60.41, 56.06, 43.50, 41.73, 37.82, 30.35, 18.13, 14.26, 10.68, 4.58 ppm; IR (film): $\tilde{\nu}$ = 2934, 1731, 1462, 1379, 1299, 1245, 1182, 1141, 1095, 1030, 957, 917, 862, 795, 763, 696 cm^{-1}; MS (EI, 70 eV) *m/z* (%): 327 (1), 310 (2), 297 (1), 271 (1), 237 (1), 225 (2), 197 (1), 185 (5), 169 (3), 155 (3), 146 (17), 131 (5), 99 (9), 81 (3), 55 (10), 45 (100); HRMS (CI): *m/z* calcd for $C_{13}H_{25}IO_4Na$: 395.0681; found: 395.0690.

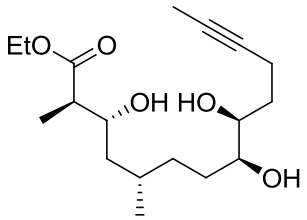


Diol 30. A flask was charged with Zn-Cu couple (24 mg, 370 µmol), toluene (1 mL), dimethylacetamide (67 µL, 63 mg, 720 µmol), and alkyl iodide **25** (92 mg, 250 µmol) and the resulting suspension was vigorously stirred at 70 °C for 4 h. The mixture was cooled to 60 °C before $Pd(PPh_3)_4$ (14 mg, 12 µmol) and vinyl iodide **28** (54 mg, 250 µmol) were added. After stirring for 1 h at this temperature, the reaction was quenched with sat. aq. NH_4Cl (6 mL) and the aqueous layer extracted with ethyl acetate (3 × 5 mL). The combined extracts were dried over Na_2SO_4, filtered, and evaporated, and the residue purified by flash chromatography (hexanes/diethyl ether 20:1) to give alkene **29** (61 mg, 72 %) as a pale yellow oil, which was directly used in the next step.

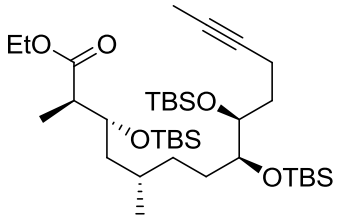
Methanesulfonamide (58 mg, 610 µmol) and AD-mix-α (878 mg, 608 µmol) were added to a solution of alkene **29** (147 mg, 435 µmol) in *tert*-butanol (8.5 mL), and water (8.5 mL) at 0 °C and the resulting mixture stirred at this temperature for 72 h. The reaction was quenched at 0 °C with NaS_2O_3 (500 mg), the mixture allowed to reach ambient temperature before it was diluted with water (15 mL). The mixture was extracted with ethyl acetate (3 × 30 mL), the combined organic phases were dried over Na_2SO_4, filtered and evaporated, and the resulting pale yellow oil was purified by flash chromatography (hexanes/ethyl acetate, 3:2) to give diol **30** as a viscous oil (135 mg, 83 %). $[\alpha]_D^{20}$ = +2.4 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): δ = 4.59 (d, *J* = 6.9 Hz, 1H), 4.52 (d, *J* = 6.9 Hz, 1H), 4.17-4.13 (m, 1H), 4.06-3.89 (m, 2H), 3.47 (br s, 1H), 3.22 (br s, 1H), 3.19 (s, 3H), 2.90 (dq, *J* = 7.0, 5.3 Hz, 1H), 2.74-2.42 (br s, 2H), 2.32 (m, 2H), 1.77-1.68 (m, 2H), 1.65-1.56 (m, 2H), 1.56 (t, *J* = 2.3 Hz 3H), 1.47-1.27 (m, 4H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.18-1.15 (m, 1H), 0.98 (t, *J* = 7.1 Hz, 3H), 0.94 ppm (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 173.93, 96.52, 79.37, 77.37, 76.06, 74.65, 73.61, 60.28, 55.63, 43.95, 38.89, 34.14, 33.41, 31.40, 29.51, 19.40, 15.72, 14.30, 10.99, 3.36 ppm; IR (film): $\tilde{\nu}$ = 3437, 2924, 1731, 1448, 1378, 1243, 1189, 1140, 1094, 1031, 955, 917, 862, 807, 754, 719, 690,

666 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 341 (1), 305 (9), 243 (35), 213 (13), 167 (22), 139 (11), 121 (14), 93 (17), 81 (21), 69 (15), 55 (23), 45 (100); HRMS (CI): *m*/*z* calcd for $C_{20}H_{36}O_6Na$: 395.2404; found: 395.2404.

Triol S7. Conc. HCl (1 drop) was added to a solution of compound **30** (25 mg, 67 µmol) in methanol (1 mL) at 0 °C and the resulting mixture stirred for 16 h at ambient temperature. The solvents were evaporated and the residue was dried under high vacuum (1 × 10^{-3} mbar) for 5 h to give triol **S7** (22 mg, 99 %) as a colorless syrup. The product was used in the next step without further purification. $[\alpha]_D^{20}$ = –6.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): δ = 4.10-3.94 (m, 2H), 3.94-3.80 (m, 1H), 3.70-3.30 (m, 5H), 2.51 (dq, *J* = 7.0, 7.0 Hz, 1H), 2.47-2.30 (m, 2H), 1.89 (br s, 1H), 1.76 (d, *J* = 6.8 Hz, 1H), 1.73 (d, *J* = 6.9 Hz, 1H), 1.60 (t, *J* = 2.2 Hz, 3H), 1.61-1.51 (m, 3H), 1.51-1.41 (m, 2H), 1.25-1.16 (m, 1H), 1.14 (d, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.94 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 175.76, 79.49, 75.98, 74.56, 73.77, 71.66, 60.47, 46.90, 42.08, 34.04, 33.49, 30.94, 29.26, 19.44, 15.81, 14.25, 13.89, 3.43 ppm; IR (film): $\tilde{\nu}$ = 3424, 2923, 1716, 1458, 1378, 1261, 1184, 1062 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 214 (34), 213 (100), 195 (19), 167 (66), 149 (34), 121 (34), 102 (56), 93 (31), 74 (29), 57 (33); 43 (30); HRMS (ESI+): *m*/*z* calcd for $C_{18}H_{32}O_5Na$: 351.2143; found: 351.2142.

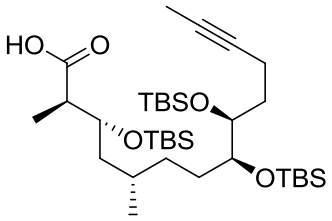


Compound S8. 2,6-Lutidine (250 µL, 230 mg, 2.2 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (250 µL, 290 mg, 1.1 mmol) were added to a solution of triol **S7** (71 mg, 0.22 mmol) in dichloromethane (3 mL) at 0 °C. The solution was stirred for 3 h at ambient temperature before the reaction was quenched with methanol (0.2 mL) at 0 °C. All volatile materials were evaporated under reduced pressure and the residue purified by flash chromatography (hexanes/methyl *tert*-butyl ether, 98:2) to give ester **S8** as a colorless oil (130 mg, 90 %). $[\alpha]_D^{20}$ = –26 (*c* = 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): δ = 4.32 (ddd, *J* = 8.7, 4.7, 2.4 Hz, 1H), 4.07-3.88 (m, 3H), 3.74 (ddd, *J* = 9.6, 4.1, 1.8 Hz, 1H), 2.76 (qd, *J* = 7.2, 5.0 Hz, 1H), 2.36-2.28 (m, 2H), 2.08-1.98 (m, 1H), 1.97-1.87 (m, 1H), 1.82-1.71 (m, 2H), 1.67-1.42 (m, 2H), 1.59 (t, *J* = 2.5 Hz, 3H), 1.39-1.12 (m, 2H), 1.25 (d, *J* = 7.1 Hz, 3H), 1.02 (s, 9H), 0.99 (s, 9H), 0.99 (s, 9H), 1.11-0.82 (m, 7H), 0.19 (s, 3H), 0.19 (s, 3H), 0.17 (s, 3H), 0.17 (s, 3H), 0.13 (s, 3H), 0.11 ppm (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 173.50, 79.39, 76.25, 76.16, 73.87, 71.62, 60.08, 46.44, 41.07, 36.14, 29.63, 29.58, 27.94 (2C), 26.10 (9C), 19.72, 18.32, 18.26, 15.96, 14.32, 10.69, 3.38, -3.93, -4.00, -4.22, -4.29, -4.34, -4.44 ppm; IR (film): $\tilde{\nu}$ = 2955, 2930, 2858, 1740, 1472, 1387, 1256, 1189, 1092, 1053, 1005, 911, 834, 810, 774 cm^{-1}; MS (ESI+, 70 eV) *m*/*z* (%): 698 (2), 697 (7), 696 (24), 694 (53), 693 (100), 679 (17); HRMS (ESI+): *m*/*z* calcd for $C_{36}H_{74}O_5Si_3Na$: 693.4736; found: 693.4743.



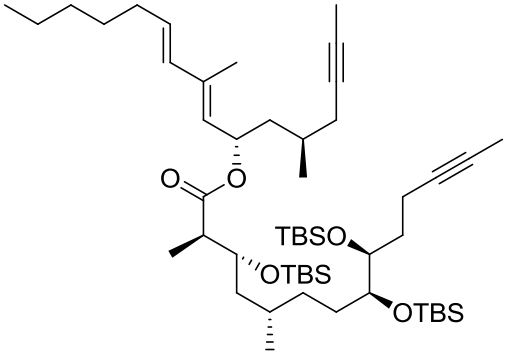
Acid 7. Lithium hydroxide (2.9 M in water, 206 µL, 596 µmol) was slowly added to a solution of ester **S8** (40 mg, 59.6 µmol) in THF (2 mL) and methanol (2 mL) at 0 °C. The ice bath was removed and the mixture stirred for 48 h at ambient temperature before the reaction was quenched with sat. aq.

NH_4Cl (5 mL) followed by addition of sodium acetate/acidic acid buffer (pH 4, 0.1 M, 40 mL). The aqueous layer was extracted with ethyl acetate (5 × 15 mL), the combined organic phases were dried over Na_2SO_4, filtered and evaporated, and the residue purified by flash chromatography (hexanes/ethyl acetate, 9:1) to give acid **7** as a colorless liquid (38 mg, 99 %). ^{1}H NMR (400 MHz, C_6D_6): δ = 4.25 (ddd, *J* = 8.1, 4.7, 3.0 Hz, 1H), 4.01 (ddd, *J* = 10.1, 4.3, 1.9 Hz, 1H), 3.72 (ddd, *J* = 9.5, 4.3, 1.7 Hz, 1H), 2.73 (qd, *J* = 7.1, 2.4 Hz , 1H), 2.36-2.25 (m, 2H), 2.08-1.96 (m, 1H), 1.94-1.83 (m, 1H), 1.78-1.67 (m, 2H), 1.64-1.36 (m, 3H), 1.59 (t, *J* = 2.5 Hz, 3H), 1.38-1.24 (m, 2H), 1.17 (d, *J* = 7.1 Hz, 3H), 1.08-0.76 (m, 3H), 1.02 (s, 9H), 0.99 (s, 9H), 0.98 (s, 9H), 0.19 (s, 3H), 0.19 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H), 0.10 (s, 3H), 0.09 ppm (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 180.52, 79.37, 76.26, 76.17, 73.85, 71.79, 46.41, 41.27, 35.91, 29.61, 29.51, 27.80, 26.11 (9C), 19.74, 18.32, 18.29, 18.26, 15.95, 11.01, 3.38, -3.92, -4.01, -4.22 (2C), -4.43, -4.45 ppm.



Completion of the Total Synthesis of Tulearin C

Ester 32. 4-(Dimethylamino)pyridine (7.6 mg, 62 µmol) and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC•HCl) (34 mg, 180 µmol) were successively added to a solution of acid **7** (38 mg, 59 µmol) and alcohol **6** (16 mg, 59 µmol) in dichloromethane (1.5 mL) at 0 °C. The ice bath was removed and the mixture stirred for 16 h at ambient temperature before it was poured into ice-cold water (50 mL) containing concentrated HCl (1 drop). The aqueous phase was extracted with hexanes/ethyl acetate (4:1, 3 × 15 mL), the combined extracts were dried over Na_2SO_4, filtered and evaporated, and the residue purified by flash chromatography (hexanes/ethyl acetate 20:1) to give ester **32** as a colorless viscous oil (52 mg, 98 %). $[\alpha]_D^{20}$ = –21 (*c* = 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, C_6D_6): δ = 6.10 (d, *J* = 16.3 Hz, 1H), 6.05 (ddd, *J* = 9.0, 9.0, 5.7 Hz, 1H), 5.64 (ddd, *J* = 15.5, 6.9, 6.9 Hz, 1H), 5.41 (d, *J* = 9.2 Hz, 1H), 4.39 (ddd, *J* = 9.3, 4.1, 2.5 Hz, 1H), 4.02 (ddd, *J* = 10.1, 4.3, 2.0 Hz, 1H), 3.75 (ddd, *J* = 9.6, 4.3, 1.9 Hz, 1H), 2.82 (qd, *J* = 7.0, 4.3 Hz, 1H), 2.36-2.28 (m, 2H), 2.16-1.79 (m, 10H), 1.93 (d, *J* = 1.1 Hz, 3H), 1.68-1.16 (m, 12H), 1.60 (t, *J* = 2.2 Hz, 3H), 1.59 (t, *J* = 2.2 Hz, 3H), 1.27 (d, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 7.7 Hz, 3H), 1.09 (d, *J* = 7.7 Hz, 3H), 1.02 (s, 9H), 1.00 (s, 9H), 0.99 (s, 9H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.20 (s, 3H), 0.19 (s, 3H), 0.17 (s, 6H), 0.16 (s, 3H), 0.13 ppm (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 172.83, 137.37, 134.49, 131.14, 128.73, 79.41, 77.49, 77.07, 76.20, 76.14, 73.90, 71.51, 69.49, 46.79, 41.72, 40.67, 36.15, 33.24, 31.78, 29.72, 29.67, 29.52, 29.47, 27.95, 26.88, 26.15, 26.12 (9C), 22.92, 19.69, 19.60, 18.33, 18.27, 15.97, 14.22, 13.36, 10.27, 3.44, 3.37, -3.93, -3.96, -4.19, -4.27, -4.37, -4.44 ppm; IR (film): $\tilde{\nu}$ = 2955, 2928, 2857, 1734, 1472, 1463, 1380, 1361, 1256, 1183, 1092, 1053, 1006, 963, 938, 910, 834, 810, 774, 720, 700 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 829 (<1), 453 (7), 246 (18), 245 (100), 244 (50), 211 (14), 161 (43), 119 (55), 73 (40); HRMS (ESI+): *m*/*z* calcd for $C_{52}H_{98}O_5Si_3Na$: 909.6614; found: 909.6616.



Cycloalkyne 33. A flask was charged with diyne **32** (52 mg, 59 µmol), toluene (26 mL), and powdered, activated molecular sieves 5Å (370 mg). The resulting suspension was stirred for 15 min at room temperature and then heated to 50 °C before a solution of the molybdenum complex **35** (4 mg, 2 µmol) in toluene (3.3 mL) was added dropwise. The reaction was stirred for 15 min at 50 °C, cooled to room temperature and filtered through a pad of silica gel, which was carefully rinsed with ethyl acetate (ca. 50 mL). The combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/ethyl acetate 20:1) to give cycloalkyne **33** as a colorless, viscous oil (47 mg, 96 %). $[\alpha]_D^{20}$ = 16 (*c* = 0.4, CH_2Cl_2); ^{1}H NMR (600 MHz, C_6D_6): δ = 6.10 (dm, *J* = 15.6 Hz, 1H), 5.95 (td, *J* = 9.2, 5.2 Hz, 1H), 5.64 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.38 (d, *J* = 9.1 Hz, 1H), 4.19 (dt, *J* = 9.5, 3.1 Hz, 1H), 4.10 (ddd, *J* = 7.8, 5.7, 2.2 Hz, 1H), 3.79 (ddd, *J* = 8.2, 4.5, 2.3 Hz, 1H), 2.63 (qd, *J* = 7.1, 3.3 Hz, 1H), 2.40 (m, 1H), 2.31 (m, 1H), 2.04 (m, 1H), 2.00 (m, 2H), 2.00 (m, 1H), 1.99 (m, 1H), 1.97 (m, 1H), 1.95 (m, 1H), 1.93 (d, *J* = 1.1 Hz, 3H), 1.90 (m, 1H), 1.88 (m, 1H), 1.87 (m, 1H), 1.86 (m, 1H), 1.74 (tt, *J* = 12.6, 4.3 Hz, 1H), 1.65 (tt, *J* = 12.6, 4.6 Hz, 1H), 1.43 (m, 1H), 1.38 (m, 1H), 1.30 (v.quin., 2H), 1.23 (m, 2H), 1.23 (d, *J* = 7.1 Hz, 3H), 1.20 (m, 2H), 1.16 (m, 1H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 3H), 1.03 (s, 9H), 1.01 (s, 9H), 1.00 (s, 9H), 0.85 (t, *J* = 7.1 Hz, 3H), 0.19 (s, 3H), 0.16 (s, 3H), 0.14 (s, 3H), 0.13 (s, 3H), 0.10 (s, 3H), 0.10 ppm (s, 3H); ^{13}C NMR (150 MHz, C_6D_6): δ = 172.45, 137.07, 134.45, 131.08, 128.93, 81.26, 79.38, 74.51, 72.76, 71.12, 69.36, 47.07, 42.04, 41.45, 33.79, 33.23, 32.71, 31.74, 30.86, 29.76, 29.48, 29.34, 26.92, 26.17 (3C), 26.17 (3C), 26.13 (3C), 22.90, 19.19, 18.75, 18.45, 18.41, 18.38, 15.41, 14.23, 13.32, 11.99, -3.75, -3.91, -3.91, -4.01, -4.04, -4.06 ppm; IR (film): $\tilde{\nu}$ = 2955, 2928, 2856, 1732, 1472, 1462, 1380, 1360, 1252, 1087, 1050, 1005, 963, 938, 906, 873, 833, 804, 771, 739, 705, 673 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%): 832 (5), 775 (15), 700 (5), 643 (17), 569 (15), 545 (3), 511 (17), 437 (10), 385 (7), 297 (13), 257 (31), 147 (51), 115 (21), 73 (100); HRMS (ESI+): *m*/*z* calcd for $C_{48}H_{92}O_5Si_3Na$: 855.6145; found: 855.6140.

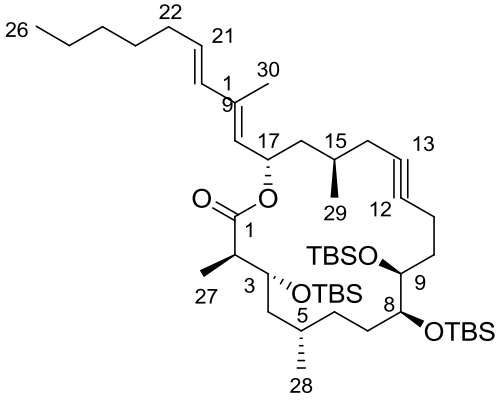
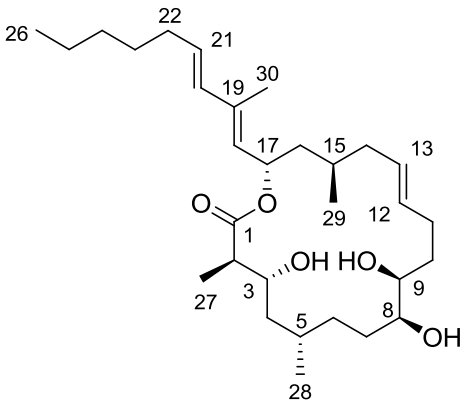


Table S1. NMR Spectra of Cycloalkyne **33** in C_6D_6 recorded with a Bruker AV 600 spectrometer. The assignments are unambiguous, except for the signals assigned to the individual OTBS groups, which may be interchanged.

Position	δ_C [ppm]	Multiplicity	δ_H [ppm]	Multiplicity	J [Hz]	Integration
1	172.45	s				
2	47.07	d	2.63	qd	7.1, 3.3	1H
3	71.12	d	4.19	dt	9.5, 3.1	1H
3-OTBS	26.17	q	1.01	s		9H
3-OTBS	18.45	s				
3-OTBS	-4.04	q	0.10	s		3H
3-OTBS	-4.06	q	0.13	s		3H
4	42.04	t	1.90	m		1H
4			1.43	m		1H
5	29.34	d	1.88	m		1H
6	33.79	t	1.65	tt	12.5, 9.2	1H
6			1.38	m		1H
7	30.86	t	1.95	m		1H
7			1.74	tt	12.6, 8.6	1H
8	74.51	d	3.79	ddd	8.2, 4.5, 2.3	1H
8-OTBS	26.13	q	1.00	s		9H
8-OTBS	18.41	s				
8-OTBS	-3.75	q	0.14	s		3H
8-OTBS	-4.01	q	0.10	s		3H
9	72.76	d	4.10	ddd	7.8, 5.7, 2.2	1H
9-OTBS	26.17	q	1.03	s		9H
9-OTBS	18.38	s				
9-OTBS	-3.91	q	0.19	s		3H
9-OTBS	-3.91	q	0.16	s		3H
10	32.71	t	1.99	m		1H
10			1.86	m		1H
11	15.41	t	2.40	m		1H
11			2.31	m		1H
12	81.26	s				
13	79.38	s				
14	26.92	t	2.04	m		1H
14			1.97	m		1H
15	29.76	d	1.87	m		1H
16	41.45	t	2.00	m		1H
16			1.16	m		1H
17	69.36	d	5.95	td	9.2, 5.2	1H
18	128.93	d	5.38	d	9.1	1H
19	137.07	s				
20	134.45	d	6.10	dm	15.6	1H
21	131.08	d	5.64	dt	15.5, 7.0	1H
22	33.23	t	2.00	m		2H
23	29.48	t	1.30	quin		2H
24	31.74	t	1.20	m		2H
25	22.90	t	1.23	m		2H
26	14.23	q	0.85	t	7.1	3H
27	11.99	q	1.23	d	7.1	3H
28	18.75	q	1.05	d	6.6	3H
29	19.19	q	1.09	d	6.6	3H
30	13.32	q	1.93	d	1.1	3H

Tulearin C 4. Triethoxysilane (16 µL, 14 mg, 86 µmol) and [Cp*Ru(CH_3CN)$_3$$PF_6$ (0.5 mg, 1 µmol) were added to a solution of compound **33** (9.0 mg, 11 µmol) in dichloromethane (1 mL) at 0 °C. The solvent was removed by passing a gentle stream of Ar over the mixture until a dark slurry remained, which was then stirred for 30 min. The mixture was dissolved in hexane (about 1 mL), the resulting solution filtered through a pad of silica, which was rinsed with methyl *tert*-butyl ether (5 mL). The combined filtrates were evaporated and the residue dried under high vacuum (1 × 10^{-3}mbar).



AgF (2.7 mg, 22 µmol) was added to a solution of the crude vinylsiloxane **34** thus formed in methanol (0.9 mL), water (0.1 mL), and THF (1 mL) and the resulting suspension stirred in the dark for 2.5 h. The mixture was filtered through a pad of silica, which was carefully rinsed with methyl *tert*-butyl ether (5 mL). The combined filtrates were evaporated, the residue azeotroped with toluene (10 mL) and dried under high vacuum (1 × 10^{-3}mbar).

The crude material was then dissolved in THF (1 mL) and a solution of TBAF (1.0 M in THF, 110 µL, 110 µmol) was added. After stirring for 12 h, the resulting mixture was evaporated and the residue purified by flash chromatography (hexanes/ethyl acetate, 1:1 → 0:1) to give tulearin C **4** as a white, amorphous solid (2.3 mg, 43 % over three steps). In other runs on a similar scale, up to 60 % of product were obtained. M.p. = 176-178 °C; $[\alpha]_D^{20}$ = –18 (*c* = 0.2, CH_2Cl_2); ^{1}H NMR (600 MHz, C_6D_6): δ = 6.14 (td, *J* = 9.4, 4.5 Hz, 1H), 6.11 (d, *J* = 15.5 Hz, 1H), 5.66 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.41 (d, *J* = 9.1 Hz, 1H), 5.34 (m, 1H), 5.31 (m, 1H), 3.58 (t, *J* = 10.3 Hz, 1H), 3.49 (br m, 1H), 3.32 (br m, 1H), 2.84 (d, *J* = 10.1 Hz, 1H), 2.29 (qd, *J* = 7.1, 2.5 Hz, 1H), 2.14 (m, 1H), 2.06 (m, 1H), 2.02 (q, *J* = 7.2 Hz, 2H), 1.92 (m, 1H), 1.92 (d, *J* = 1.0 Hz, 3H), 1.89 (dt, *J* = 12.8, 3.9 Hz, 1H), 1.81 (ddd, *J* = 13.9, 9.6, 4.4 Hz, 1H), 1.70 (dt, *J* = 13.0, 8.2 Hz, 1H), 1.66 (m, 1H), 1.63 (m, 1H), 1.59 (m, 1H), 1.57 (m, 1H), 1.54 (m, 1H), 1.47 (m, 1H), 1.44 (m, 1H), 1.38 (m, 1H), 1.31 (m, 1H), 1.31 (quin., *J* = 7.5 Hz, 2H), 1.24 (m, 2H), 1.22 (d, *J* = 7.1 Hz, 3H), 1.21 (m, 2H), 1.17 (m, 1H), 1.17 (m, 1H), 0.94 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, C_6D_6): δ = 176.28, 137.62, 134.25, 131.84, 131.58, 129.60, 128.43, 73.23, 71.78, 70.94, 69.36, 45.45, 44.26, 42.58, 40.71, 34.88, 33.24, 32.61, 31.76, 31.59, 29.94, 29.44, 29.26, 28.56, 22.90, 19.12, 18.52, 15.35, 14.23, 13.30 ppm; IR (film): $\tilde{\nu}$ = 3594, 2929, 2850, 1709, 1632, 1457, 1378, 1188, 1130, 1046, 970, 839 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 492 (32), 474 (7), 393 (9), 353 (6), 289 (11), 219 (21), 191 (70), 167 (42), 135 (23), 121 (34), 107 (48), 93 (100), 81 (75), 69 (34), 55 (49), 43 (39); HRMS (ESI+): *m/z* calcd for $C_{30}H_{52}O_5Na$: 515.3707, found: 515.3703.

Table S2. NMR Spectra of Synthetic Tulearin C (**7**) in C_6D_6 recorded with a Bruker AV 600 Spectrometer. The assignments are unambiguous, unless stated otherwise.

1	176.28	s				
2	45.45	d	2.29	qd	7.1, 2.5	1H
3	70.94	d	3.58	t	10.3	1H
3-OH			2.84	d	10.1	1H
4	44.26	t	1.59	m		1H
4			0.94	m		1H
5	29.26	d	1.92	m		1H
6	34.88	t	1.31	m		1H
6			1.17	m		1H
7	31.59	t	1.47	m		1H
7			1.38	m		1H
8	73.23	d	3.32	br m		1H
8-OH			1.57	m		1H
9	71.78	d	3.49	br m		1H
9-OH			1.66	m		1H
10	32.61	t	1.63	m		1H
10			1.44	m		1H
11	28.56	t	2.14	m		1H
11			2.06	m		1H
12	131.84	d	5.34	m		1H
13	129.60	d	5.31	m		1H
14	40.71	t	1.89	dt	12.8, 3.9	1H
14			1.70	dt	13.0, 8.2	1H
15	29.94	d	1.54	m		
16	42.58	t	1.81	ddd	13.9, 9.6, 4.4	1H
16			1.17	m		1H
17	69.36	d	6.14	td	9.4, 4.5	1H
18	128.43	d	5.41	d	9.1	1H
19	137.62	s				
20	134.25	d	6.11	d	15.5	1H
21	131.58	d	5.66	dt	15.5, 7.0	1H
22	33.24	t	2.02	q	7.2	2H
23	29.44	t	1.31	quin	7.5	2H
24	31.76	t	1.21	m		2H
25	22.90	t	1.24	m		2H
26	14.23	q	0.87	t	7.1	3H
27	15.35	q	1.22	d	7.1	3H
28	19.12	q	0.92	d	6.5	3H
29	18.52	q	0.93	d	6.5	3H
30	13.30	q	1.92	d	1.0	3H

Table S3. Comparison of the ^{13}C NMR ([D_6]-acetone) Data of Synthetic Tulearin C (150 MHz) with the Data of the Natural Product Reported in the Literature (125 MHz);[4] the assignments are unambiguous, unless stated otherwise.

	Isolated Product		**Synthetic Sample**		
Position	δ_C [ppm]	Multiplicity	δ_C [ppm]	Multiplicity	$\Delta\delta$ [ppm]
1	174.9	s	175.07	s	-0.2
2	46.4	d	46.42	d	0.0
3	70.8	d	70.90	d	-0.1
3-OH					
4	43.8	t	44.02	t	-0.2
5*	28.0	d	30.06	d	-2.1
6	34.9	t	34.91	t	0.0
7*	29.3	t	32.13	t	-2.8
8	72.3	d	73.02	d	-0.7
8-OH					
9	70.4	d	71.19	d	-0.8
9-OH					
10	32.1	t	32.88	t	-0.8
11	27.8	t	28.89	t	-1.1
12	131.9	d	132.16	d	-0.3
13	130.5	d	130.44	d	0.1
14	41.3	t	41.46	t	-0.2
15*	29.7	d	30.42	d	-0.7
16	42.8	t	42.92	t	-0.1
17	69.6	d	69.58	d	0.0
18	129.5	d	129.61	d	-0.1
19	136.6	s	136.74	s	-0.1
20	134.6	d	134.75	d	-0.2
21	131.2	d	131.40	d	-0.2
22	33.6	t	33.46	t	0.1
23*	29.4	t	29.85	t	-0.5
24	31.3	t	32.13	t	-0.8
25	23.0	t	23.14	t	-0.1
26	14.1	q	14.26	q	-0.2
27§	14.0	q	14.37	q	-0.4
28§	18.6	q	18.74	q	-0.1
29§	18.2	q	18.26	q	-0.1
30§	12.9	q	13.08	q	-0.2

* Signals hidden under the solvent peaks

§ The assignment made in the original publication was corrected.

[4] a) A. Bishara, , A. Rudi, I. Goldberg, M. Aknin, Y. Kashman, *Tetrahedron Lett*. **2009**, *50*, 3820-3822; b) A. Bishara, A. Rudi, M. Aknin, D. Neumann, , N. Ben-Califa, Y. Kashman, *Org. Lett*. **2008**, *10*, 153-156.

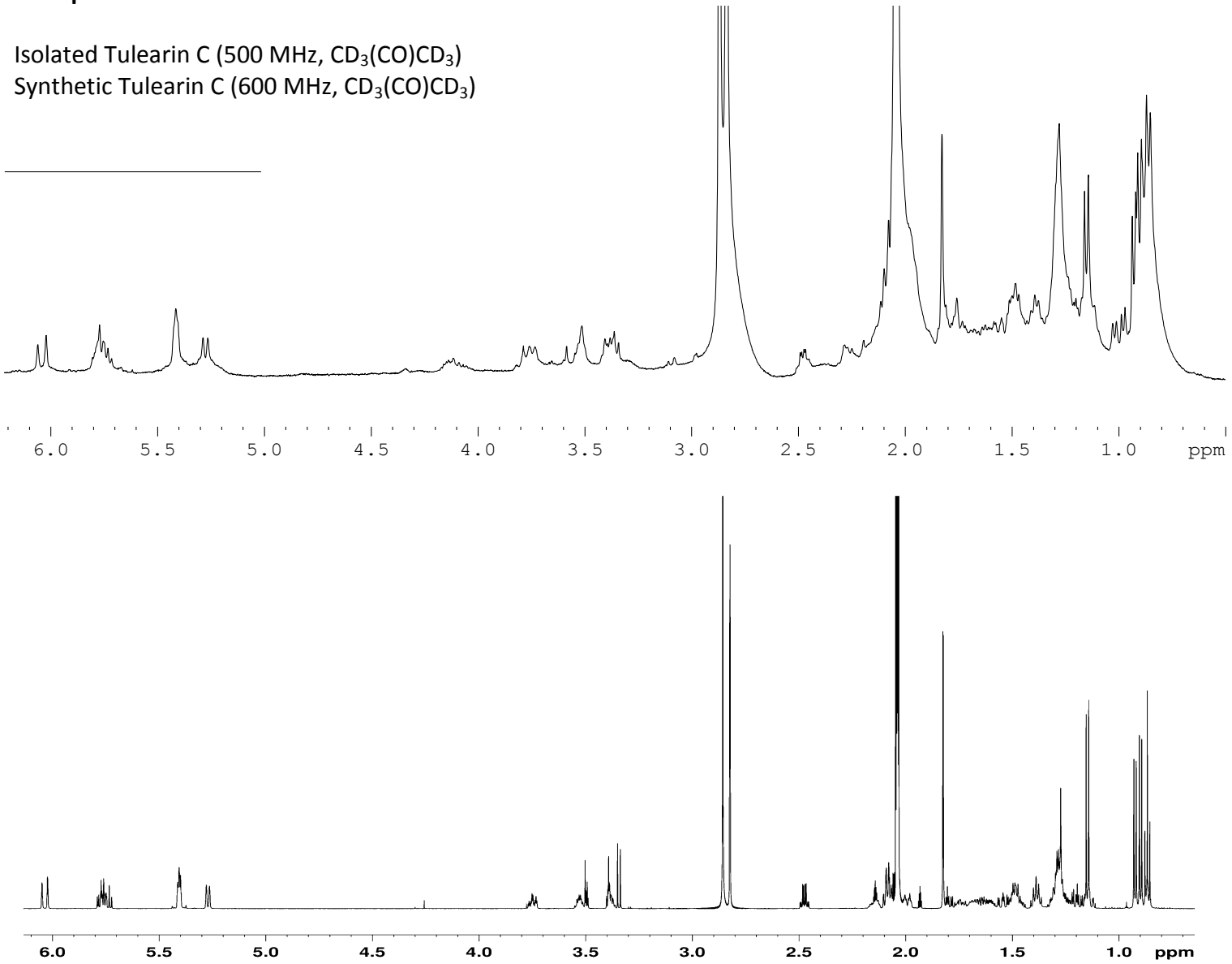
Table S4. Comparison of the ^{1}H NMR ([D_6]-acetone) Data of Synthetic Tulearin C (600 MHz) with the Data of the Natural Product Reported in the Literature (500 MHz).[4]

	Isolated Product				Synthetic Samples				
Positioin	δ_H [ppm]	Mult.	J [Hz]	Integration	δ_H [ppm]	Mult.	J [Hz]	Integration	$\Delta\delta$
1									
2	2.50	qd	7.6, 2.8	1H	2.48	qd	7.1, 3.0	1H	0.02
3	3.77	m		1H	3.75	dddd	11.4, 8.0, 3.0, 2.2	1H	0.02
3-OH	3.35	d	7.6	1H	3.34	d	8	1H	0.01
4	1.54	td	13.7, 4.4	1H	1.54	ddd	13.7, 11.5, 3.5	1H	0.00
4	1.17	br t	13.7	1H	1.14	m		1H	0.03
5	1.67	m		1H	1.69	m		1H	-0.02
6	1.32	m		1H	1.27	m		1H	0.05
6	1.22	m		1H	1.24	m		1H	-0.02
7	1.23	m		2H	1.49	m		2H	-0.26
8	3.30	td	5.5, 3.9	1H	3.38	m		1H	-0.08
8-OH	n/a				3.40	d	5.7	1H	n/a
9	3.46	m		1H	3.53	m		1H	-0.07
9-OH	3.38	d	7.2	1H	3.50	d	6.1	1H	-0.12
10	1.59	m		2H	1.65	m		1H	-0.06
10					1.47	m		1H	
11	2.13	q	6.0	2H	2.14	m		1H	-0.01
11					2.07	m		1H	
12	5.40	m		1H	5.41	m		1H	-0.01
13	5.44	m		1H	5.41	m		1H	0.03
14	1.99	m		1H	1.99	dt	13.6, 3.5	1H	0.00
14	1.78	m		1H	1.75	m		1H	0.03
15	1.62	m		1H	1.60	m		1H	0.02
16	1.83	td	13.1, 4.4	1H	1.81	ddd	14.1, 10.4, 3.9	1H	0.02
16	1.24	td	13.1, 4.4	1H	1.20	ddd	14.0, 10.6, 3.8	1H	0.04
17	5.80	td	9.1, 4.4	1H	5.77	ddd	10.4, 8.9, 3.8	1H	0.03
18	5.28	d	9.1	1H	5.27	d	8.9	1H	0.01
19									
20	6.04	d	15.5	1H	6.04	d	15.6	1H	0.00
21	5.75	dt	15.5, 6.9	1H	5.75	dt	15.5, 7.0	1H	0.00
22	2.08	q	7.0	2H	2.09	dt	7.4, 7.1	2H	-0.01
23	1.40	quin	7.0	1H	1.39	quin	7.4	2H	0.01
23	1.29	m		1H					
24	1.28	m		2H	1.28	m		2H	0.00
25	1.30	m		2H	1.29	m		2H	0.01
26	0.87	t	7.0	3H	0.87	t	7.1	3H	0.00
27*	1.15	d	6.5	3H	1.15	d	7.1	3H	0.00
28*	0.90	d	7.1	3H	0.90	d	6.6	3H	0.00
29*	0.94	d	6.7	3H	0.93	d	6.5	3H	0.01
30*	1.85	s		3H	1.83	d	1.2	3H	0.02

* The assignment made in the original publication was corrected.

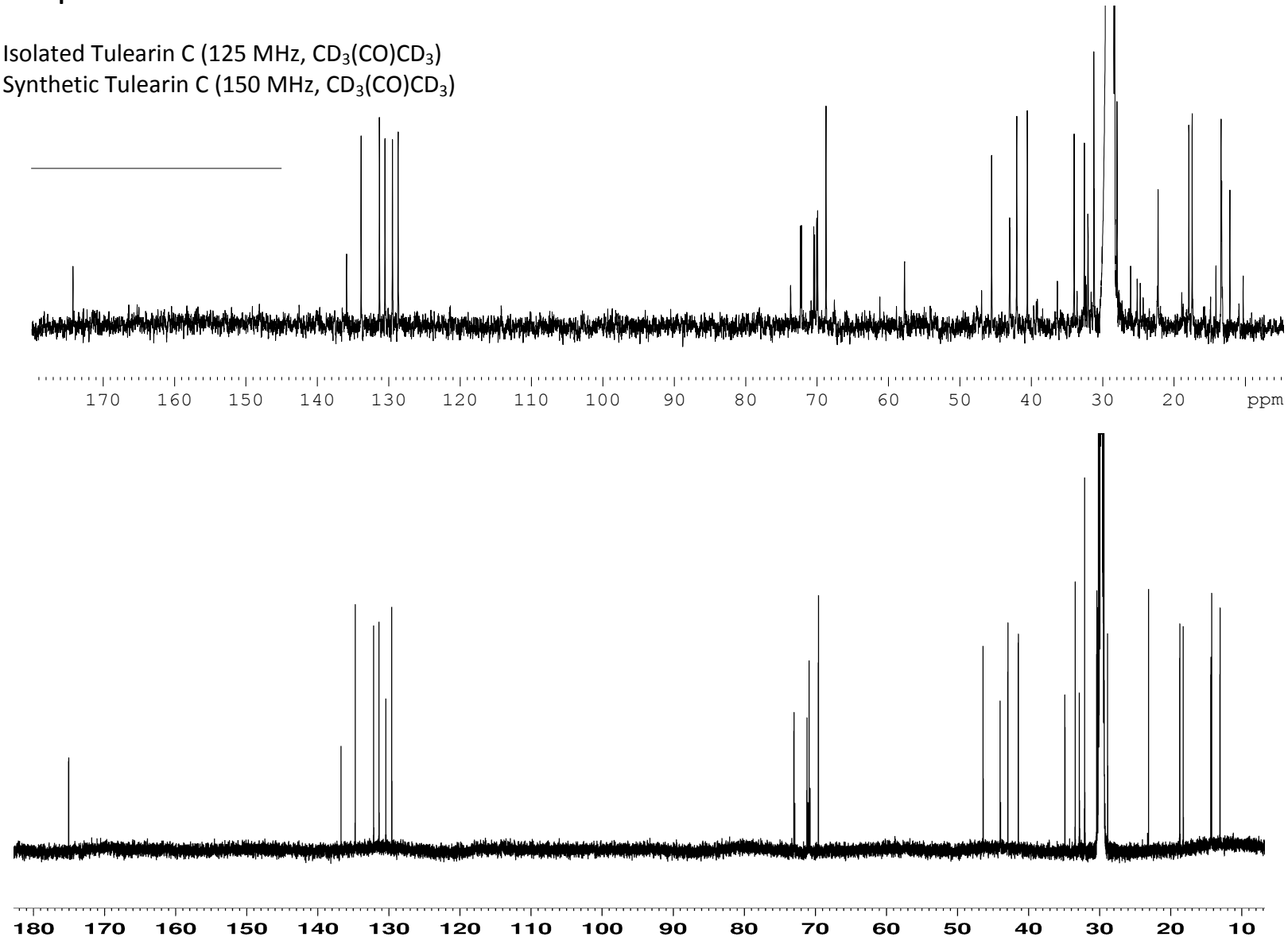
Comparison of spectra

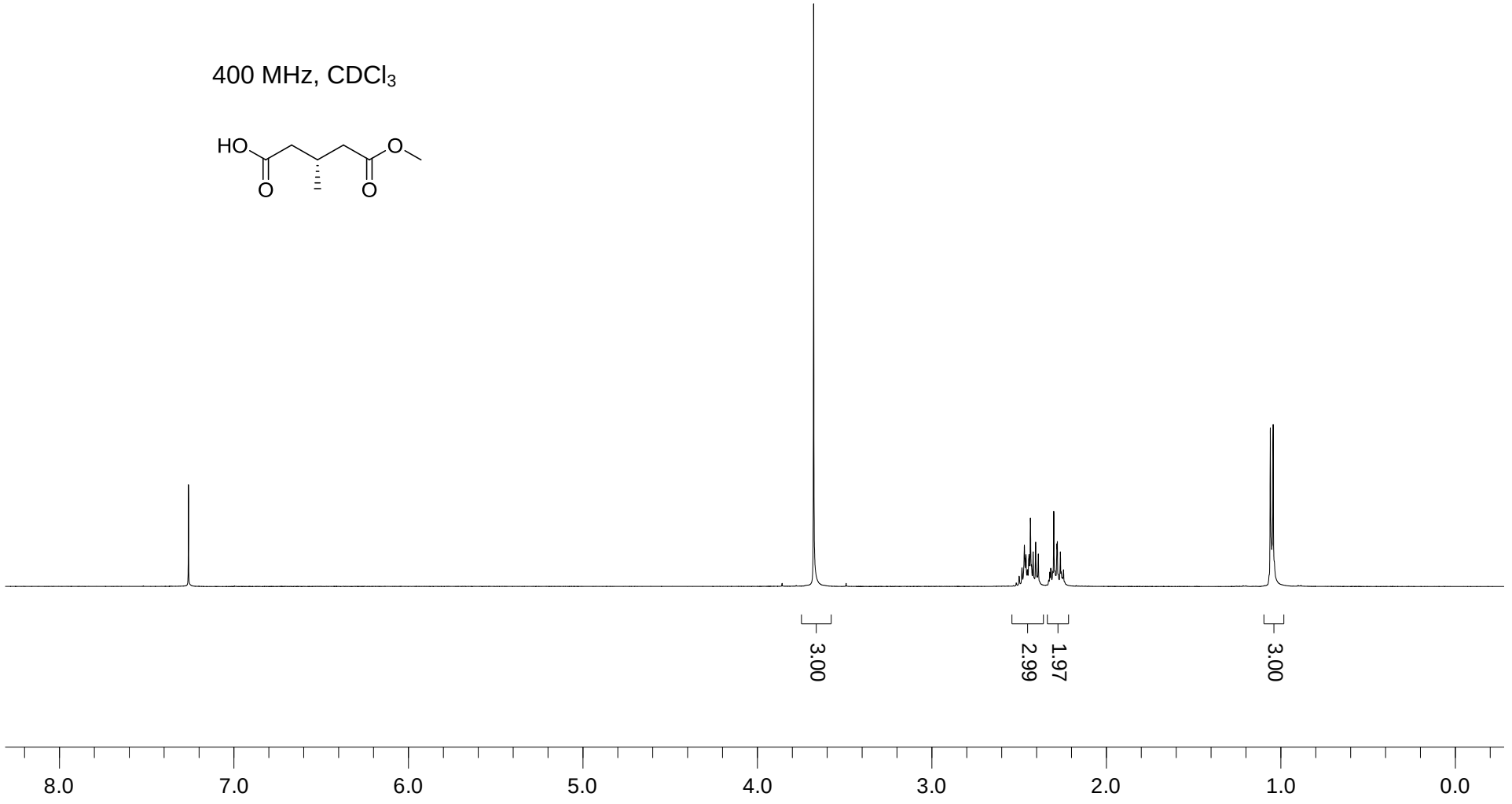
Top Isolated Tulearin C (500 MHz, $CD_3(CO)CD_3$)
Bottom Synthetic Tulearin C (600 MHz, $CD_3(CO)CD_3$)

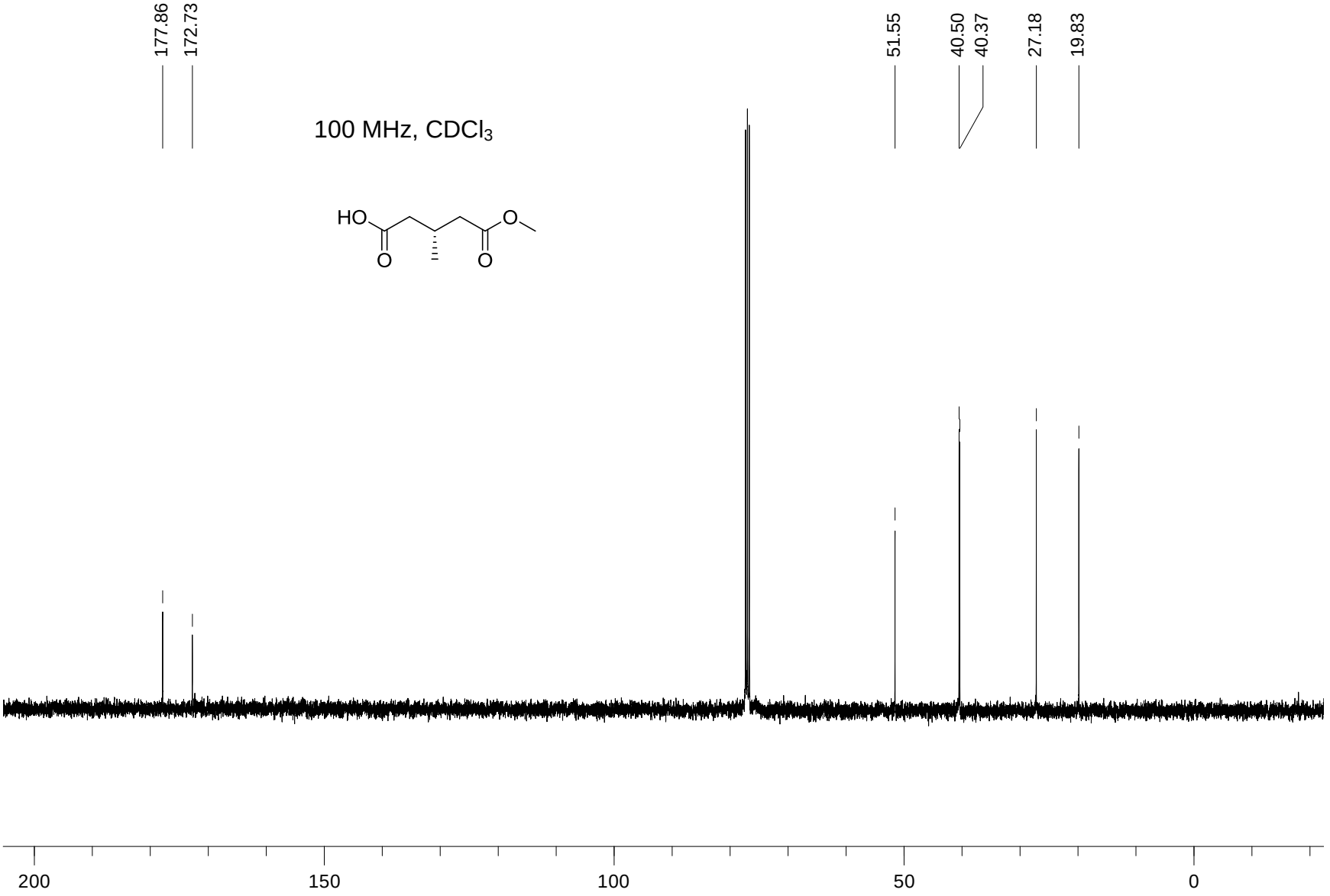


Comparison of spectra

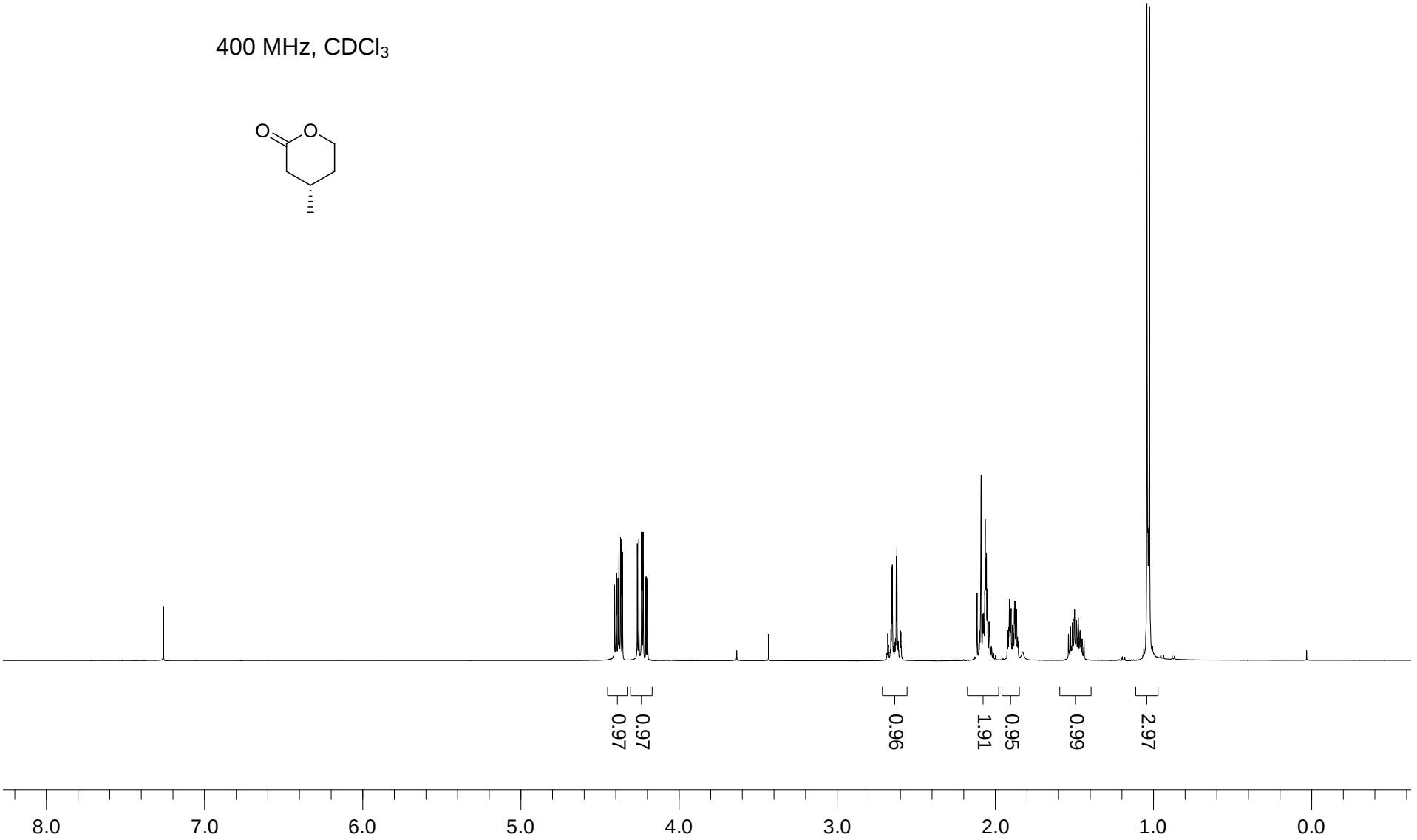
Top Isolated Tulearin C (125 MHz, $CD_3(CO)CD_3$)
Bottom Synthetic Tulearin C (150 MHz, $CD_3(CO)CD_3$)

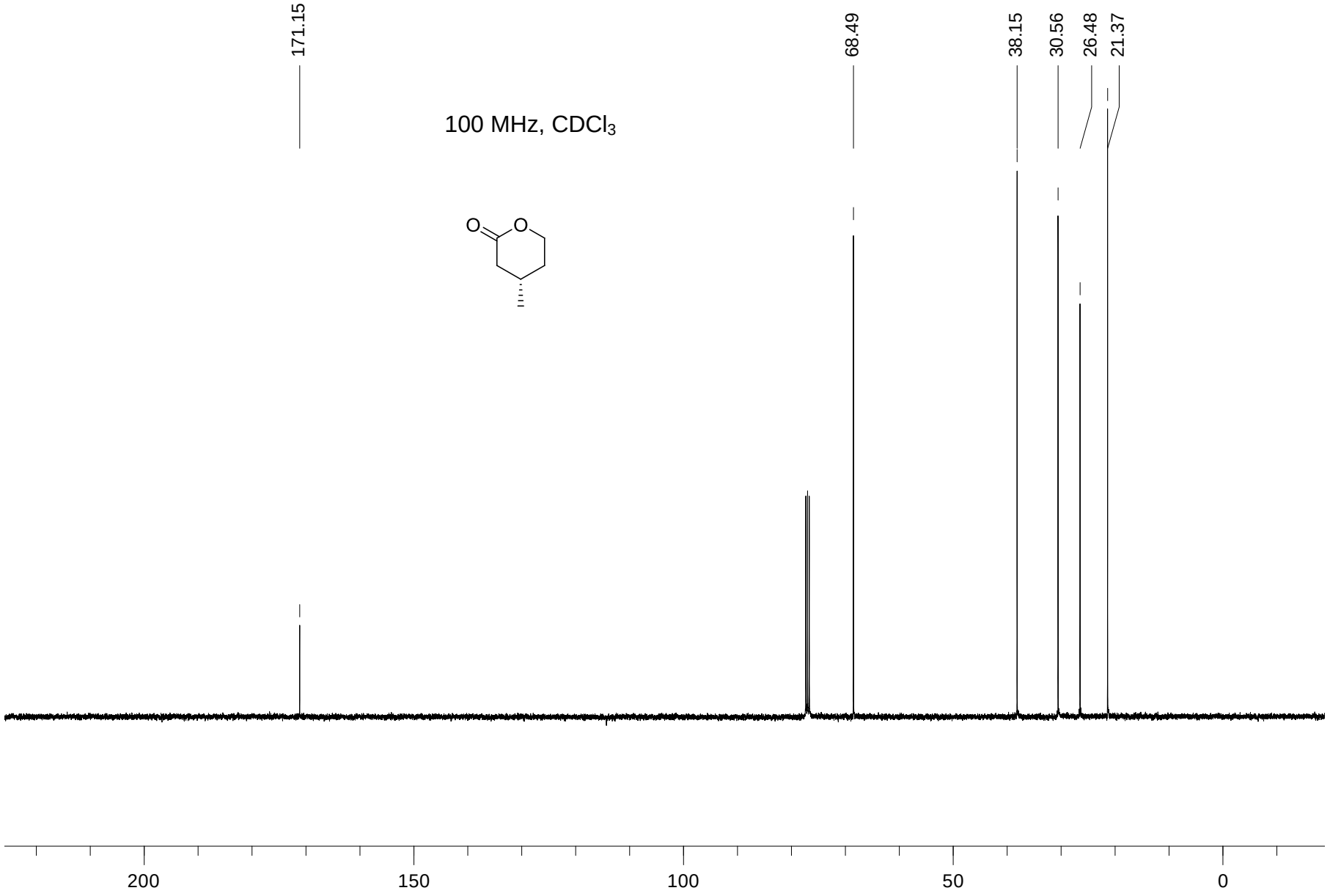



400 MHz, CDCl3
HO
O
O
O
3.00
2.99
1.97
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

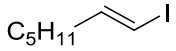

177.86
172.73
51.55
40.50
40.37
27.18
19.83
100 MHz, CDCl3
HO
O
O
O
200
150
100
50
0

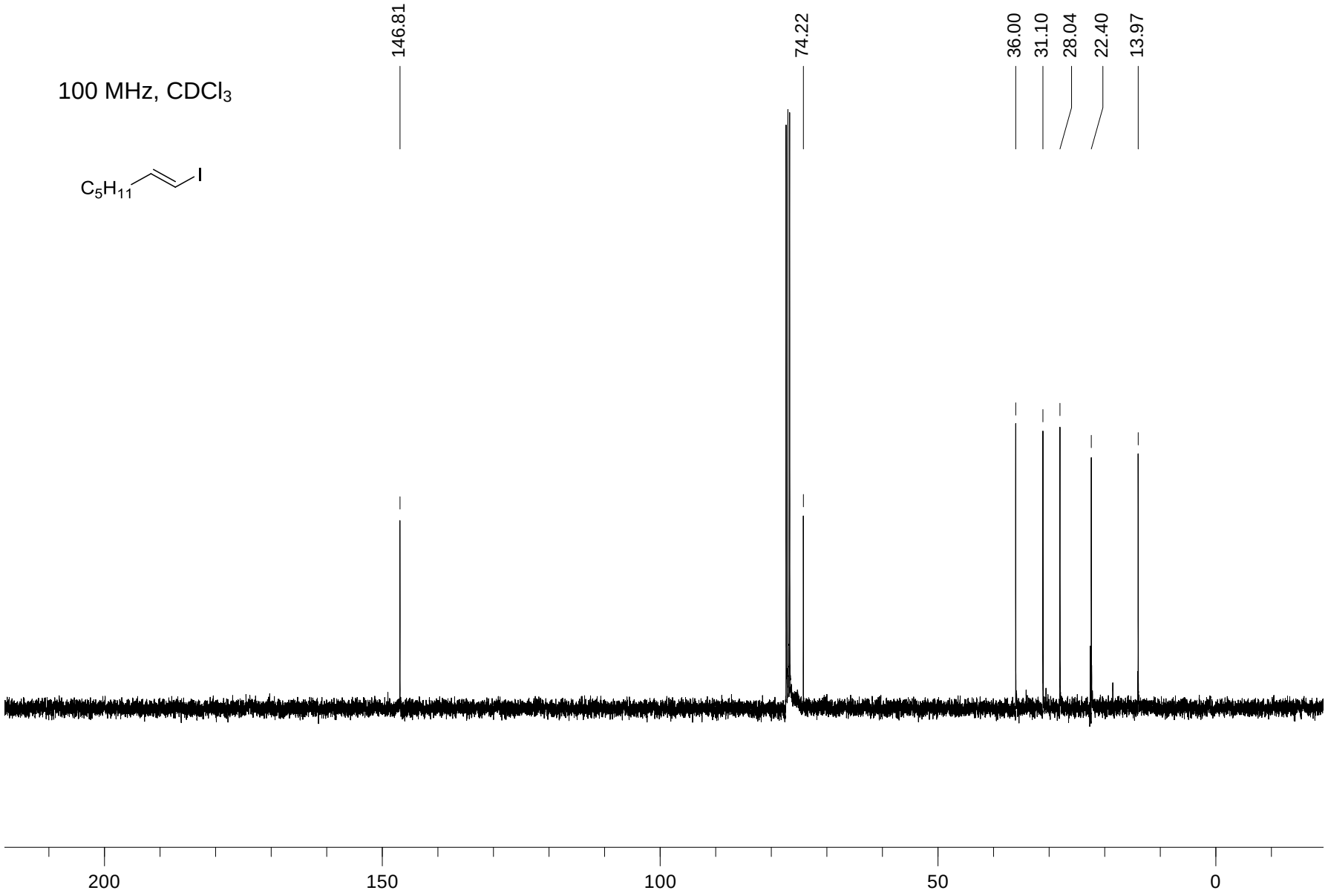
400 MHz, $CDCl_3$



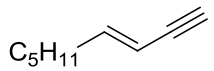

171.15
68.49
38.15
30.56
26.48
21.37
100 MHz, CDCl3
O
O
200
150
100
50
0

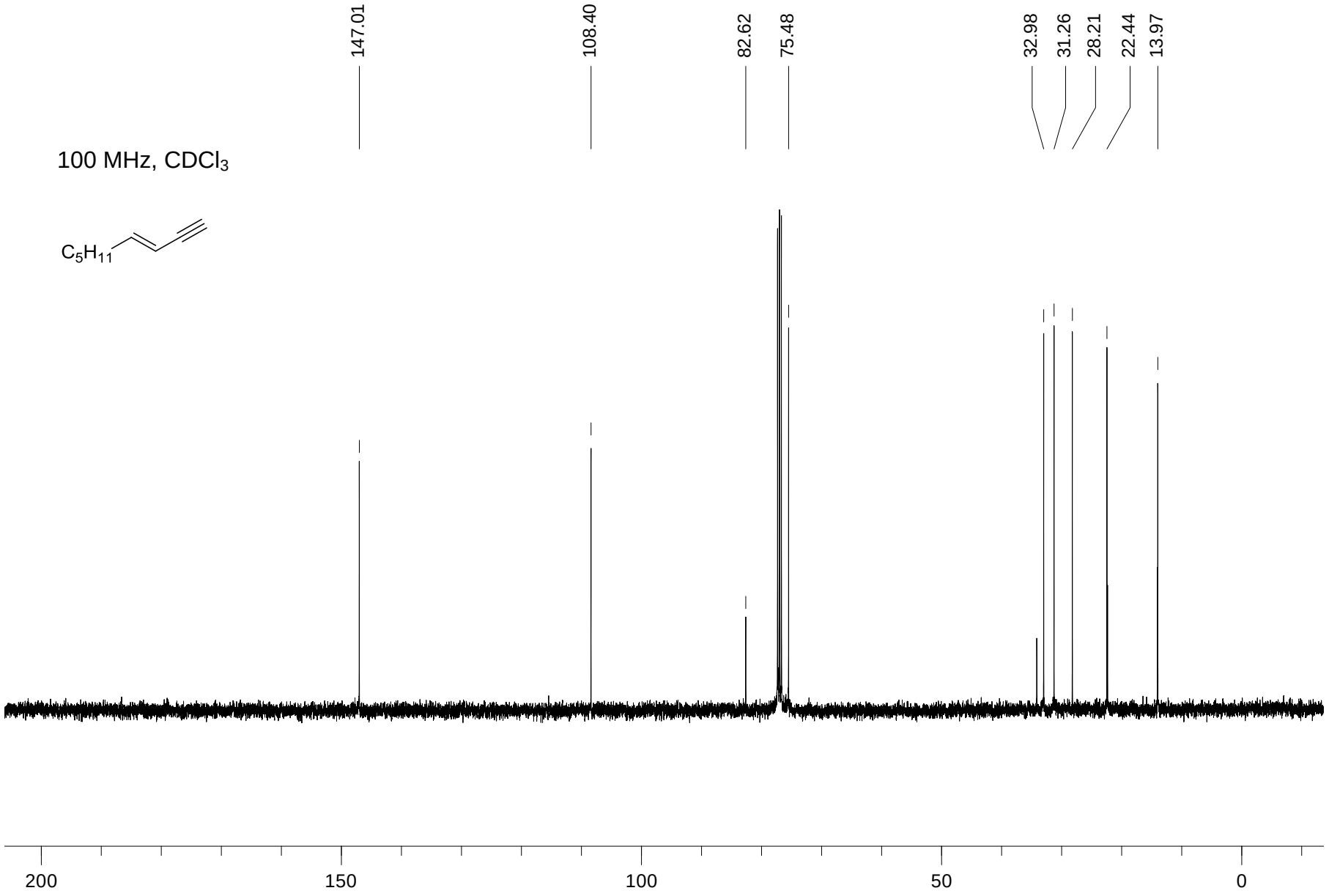
400 MHz, $CDCl_3$

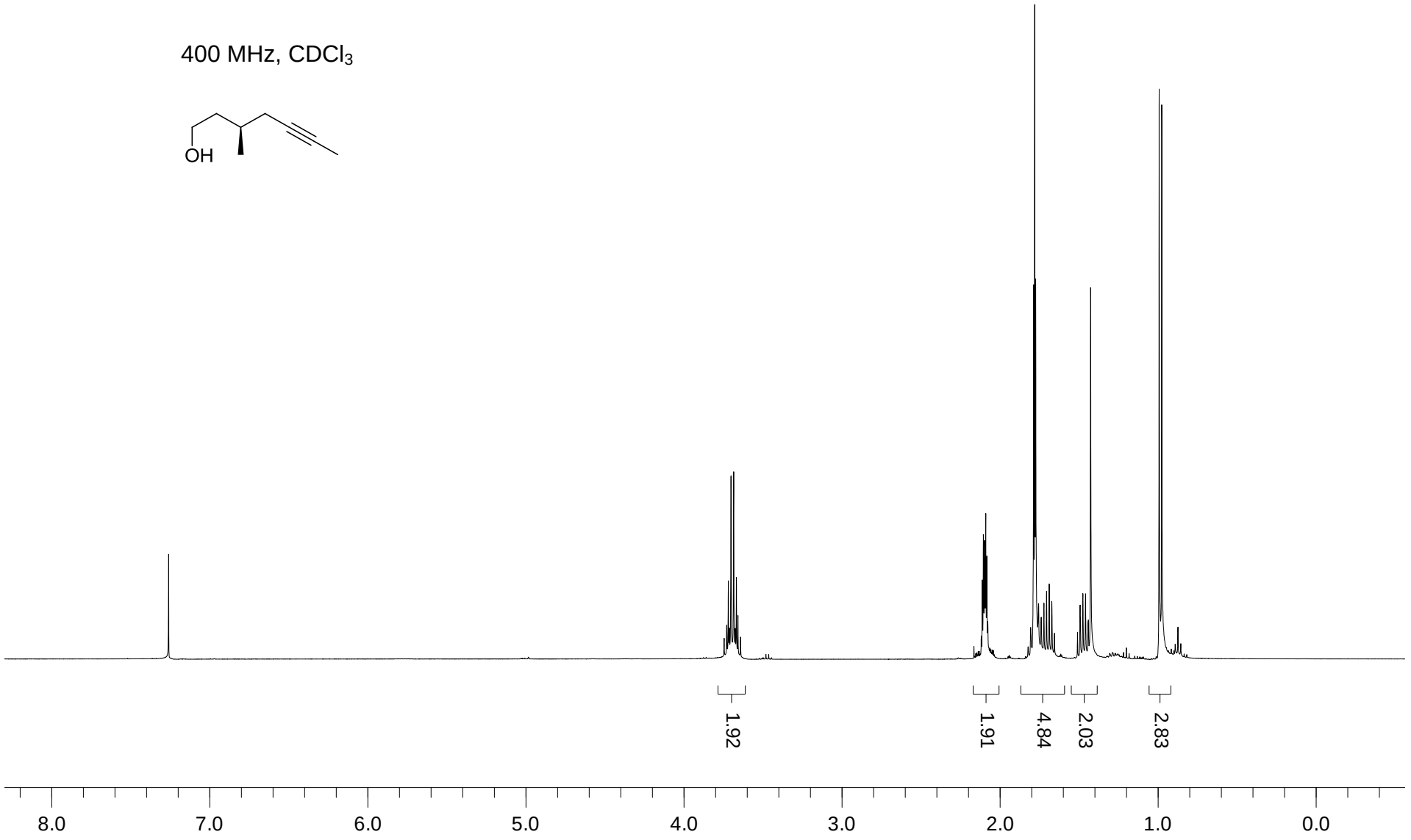


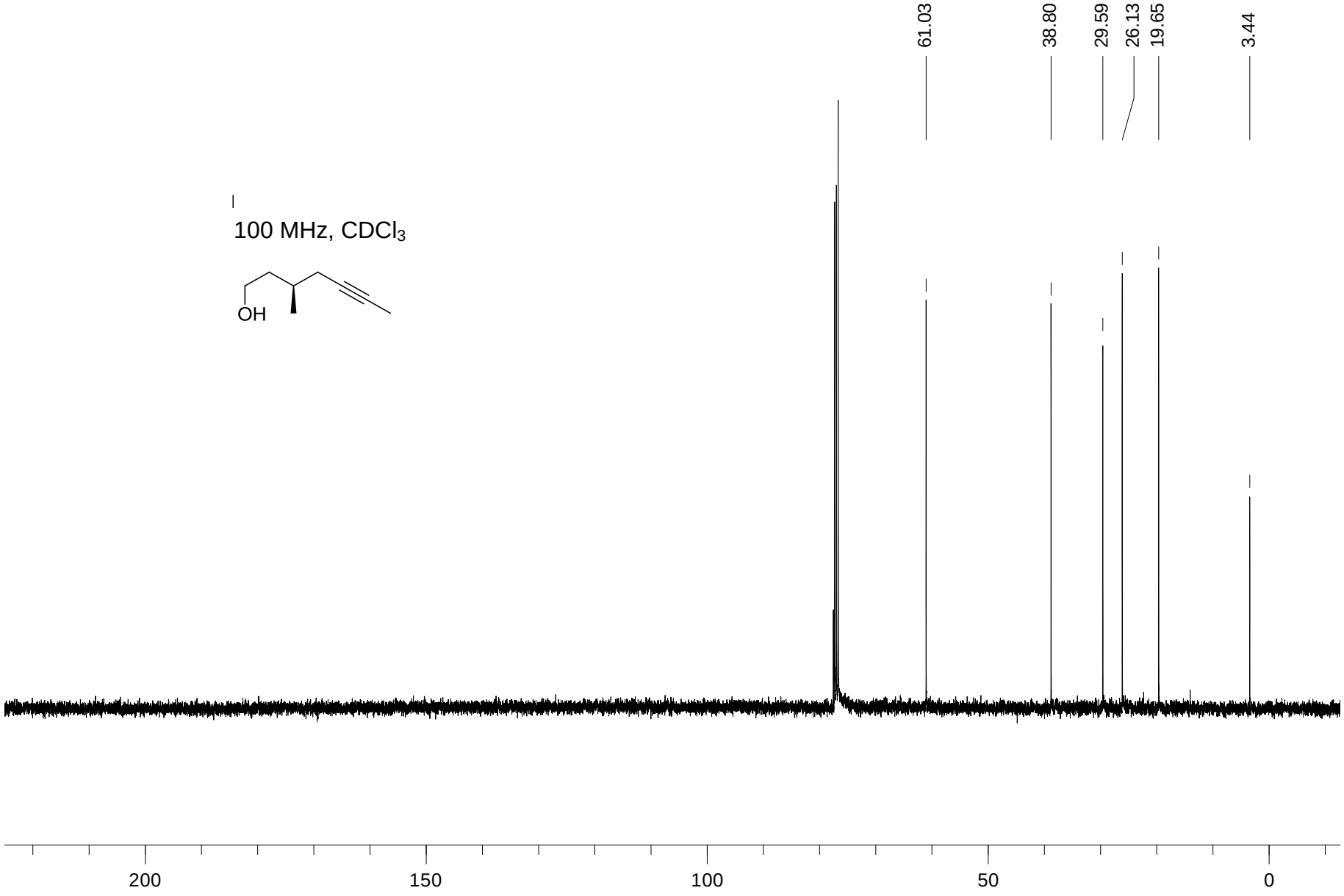

146.81
74.22
36.00
31.10
28.04
22.40
13.97
100 MHz, CDCl3
C5H11
I
200
150
100
50
0

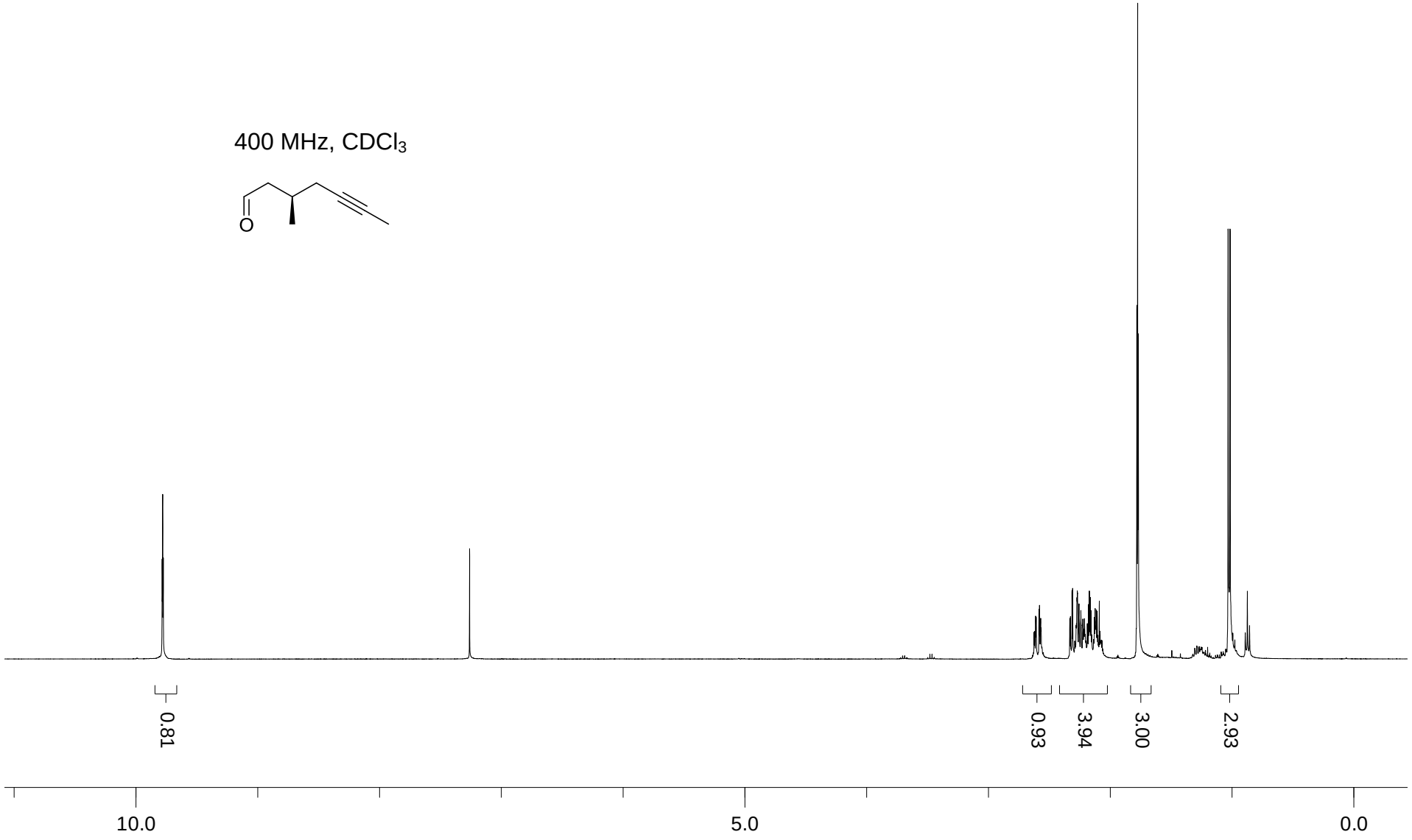
400 MHz, $CDCl_3$

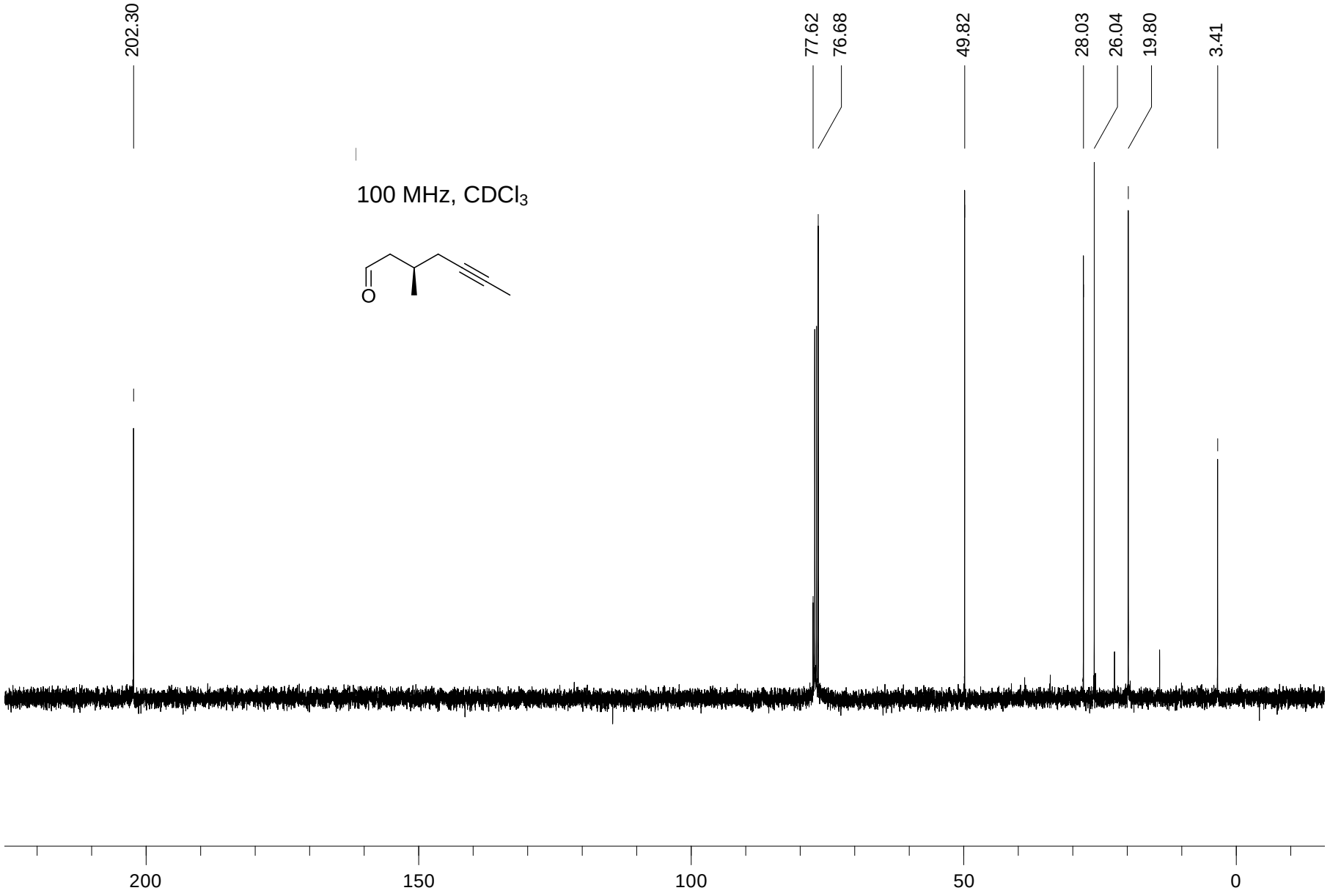



147.01
108.40
82.62
75.48
32.98
31.26
28.21
22.44
13.97
100 MHz, CDCl3
C5H11
200
150
100
50
0

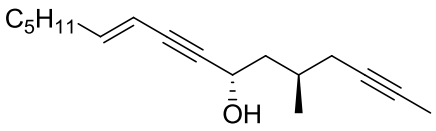

400 MHz, CDCl3
OH
1.92
1.91
4.84
2.03
2.83
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

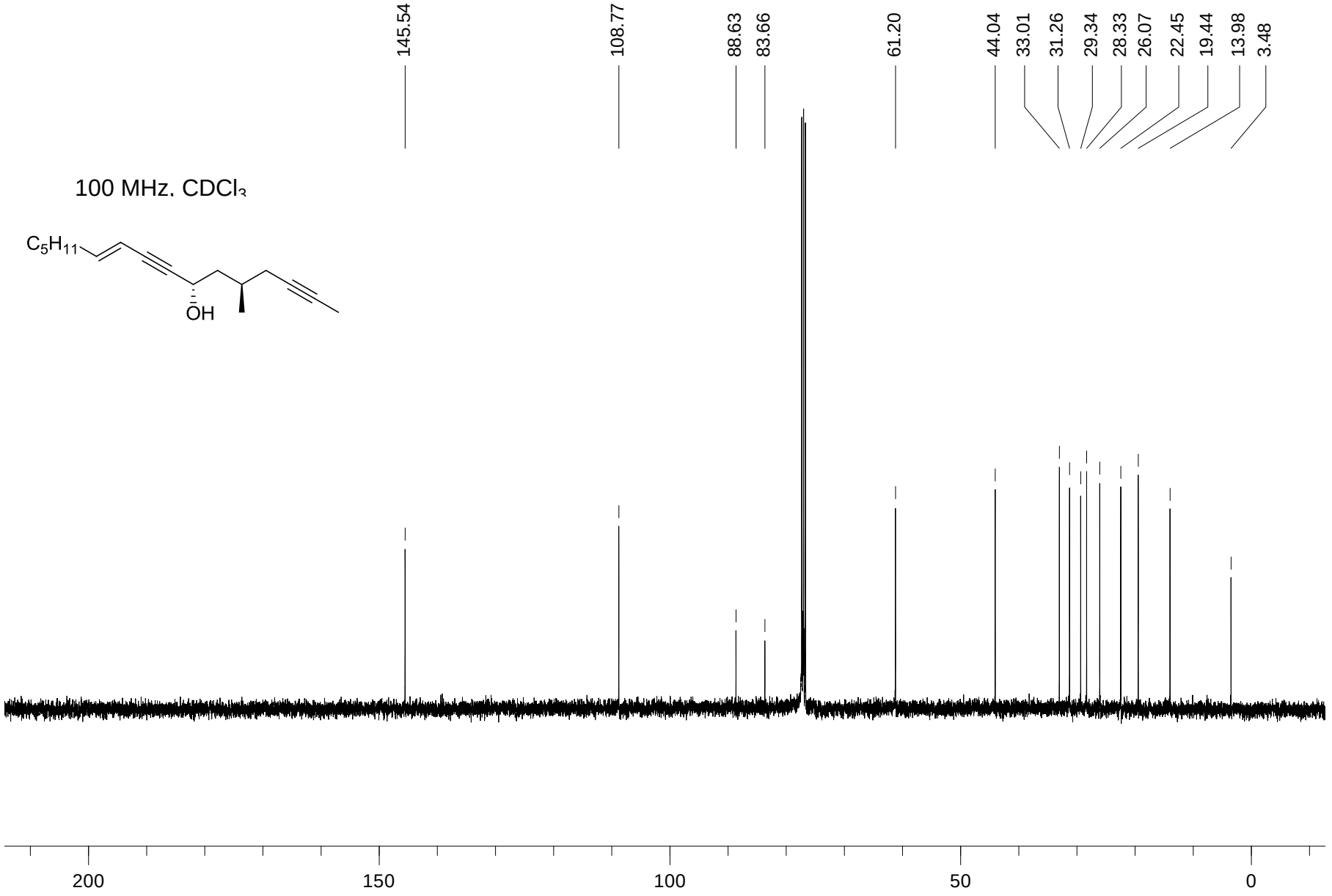

61.03
38.80
29.59
26.13
19.65
3.44
100 MHz, CDCl3
OH
200
150
100
50
0

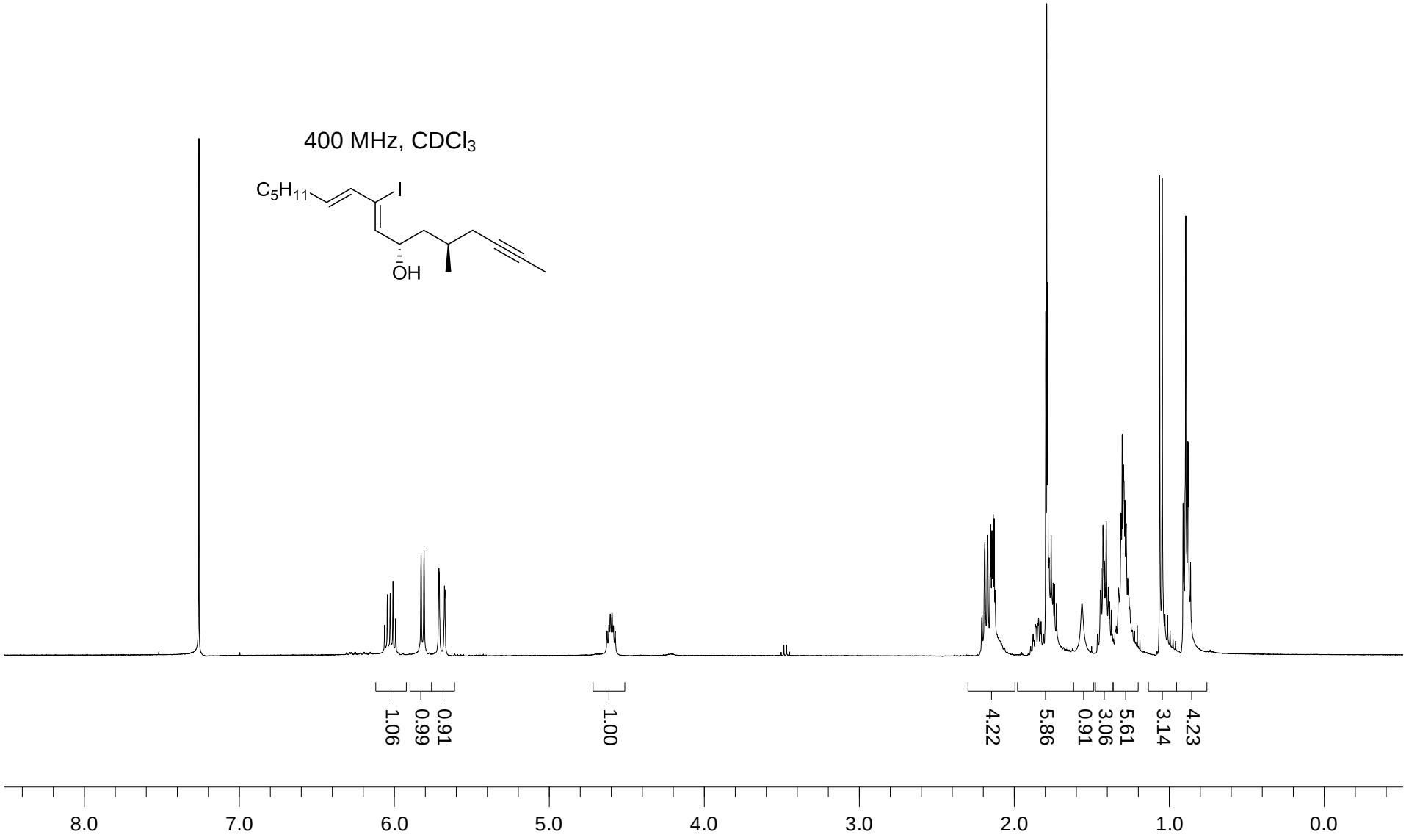

400 MHz, CDCl3
O
0.81
0.93
3.94
3.00
2.93
10.0
5.0
0.0

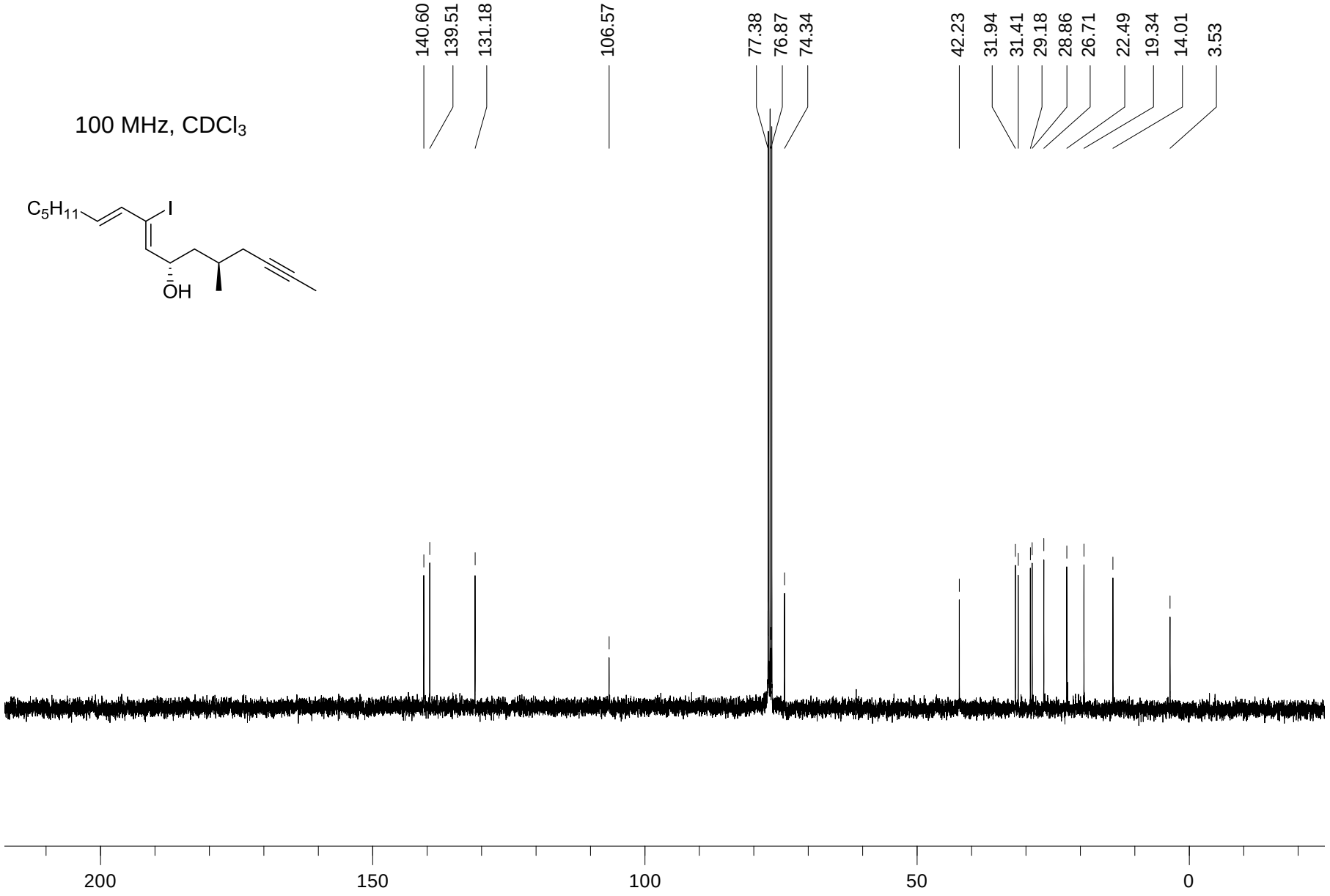

202.30
77.62
76.68
49.82
28.03
26.04
19.80
3.41
100 MHz, CDCl3
O
200
150
100
50
0

400 MHz, $CDCl_3$

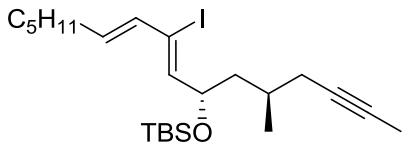


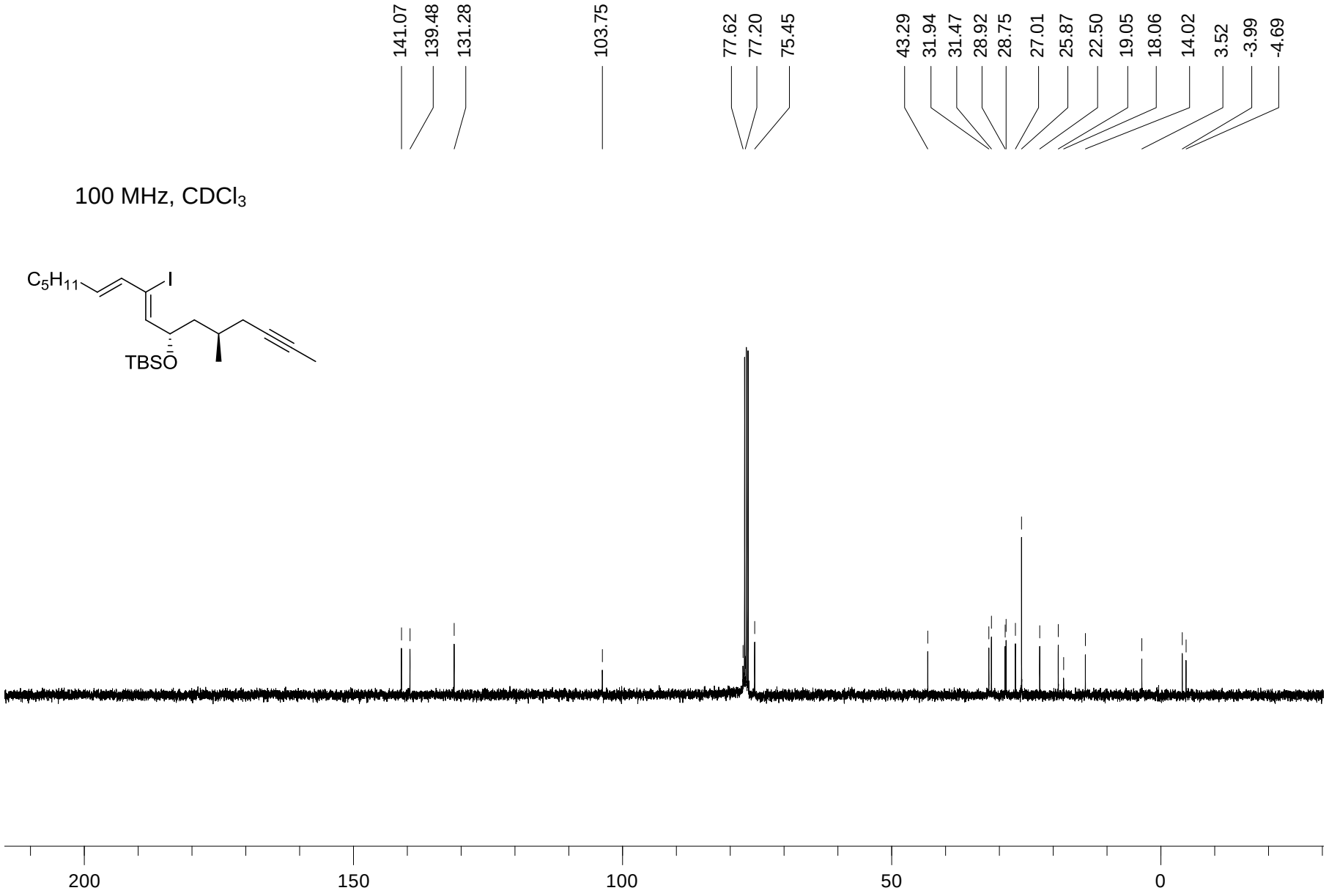

145.54
108.77
88.63
83.66
61.20
44.04
33.01
31.26
29.34
28.33
26.07
22.45
19.44
13.98
3.48
100 MHz, CDCl3
C5H11
OH
200
150
100
50
0

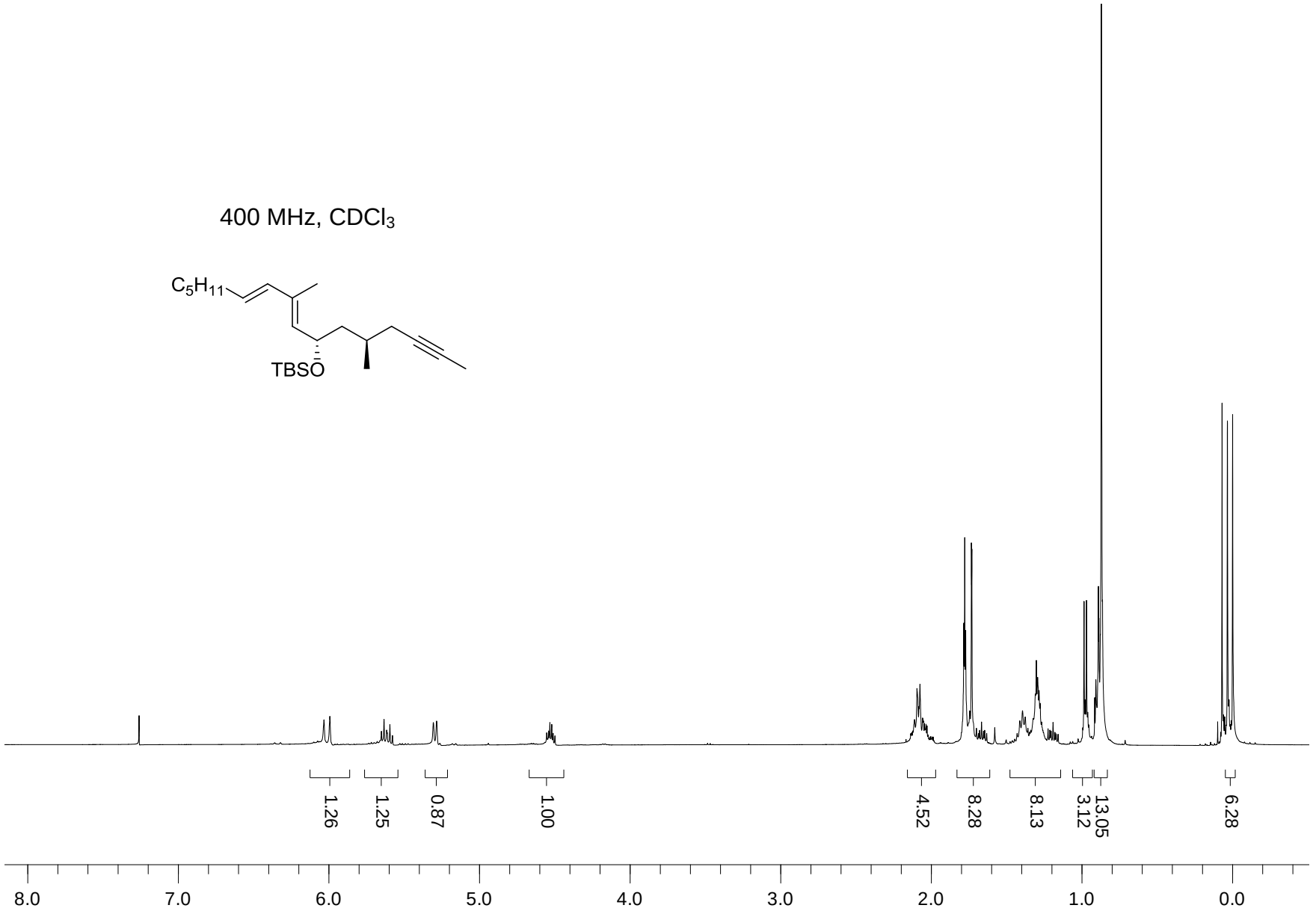

400 MHz, CDCl3
C5H11
I
OH
1.06
0.99
0.91
1.00
4.22
5.86
0.91
3.06
5.61
3.14
4.23
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

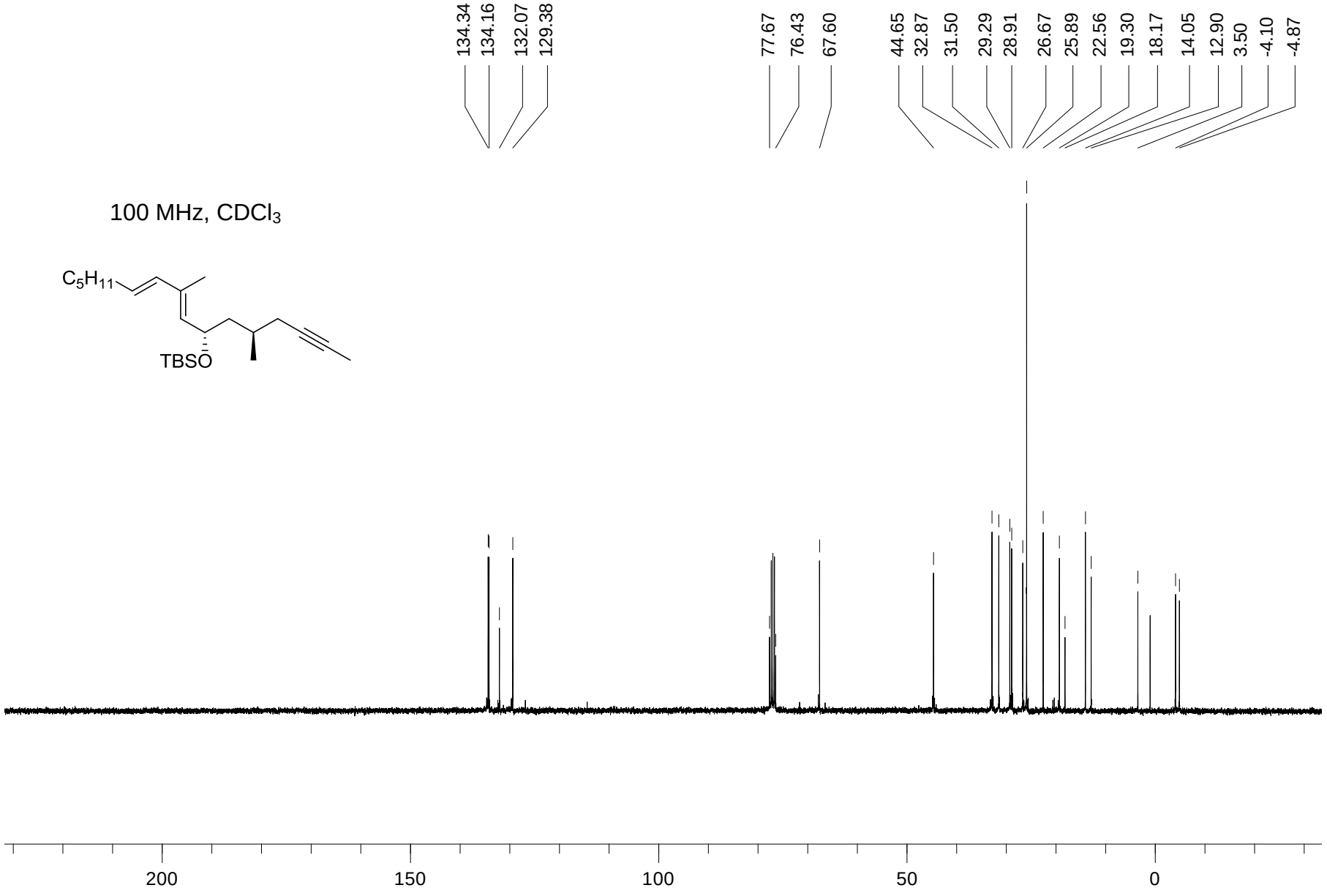

140.60
139.51
131.18
106.57
77.38
76.87
74.34
42.23
31.94
31.41
29.18
28.86
26.71
22.49
19.34
14.01
3.53
100 MHz, CDCl3
C5H11
I
OH
200
150
100
50
0

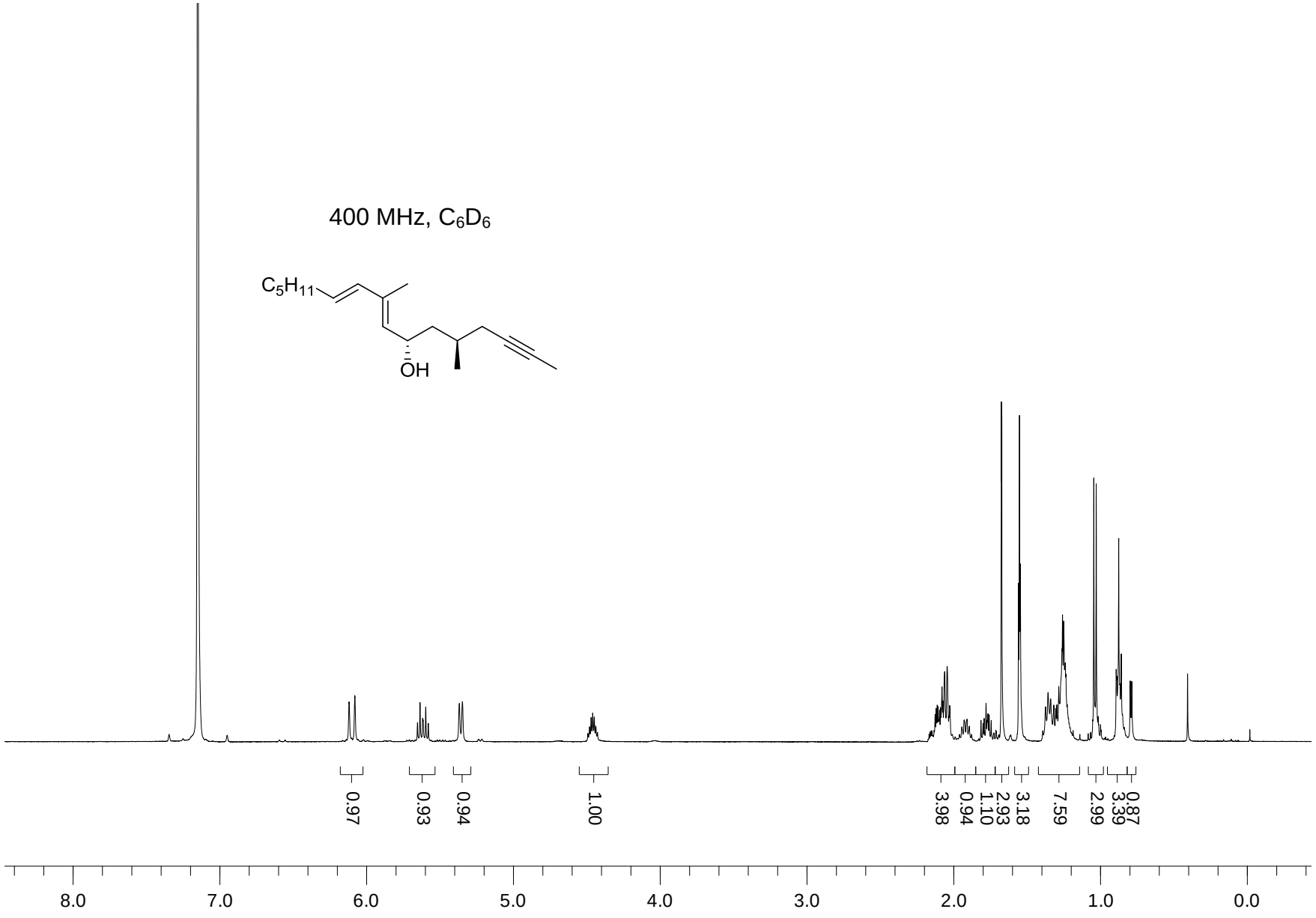
400 MHz, $CDCl_3$

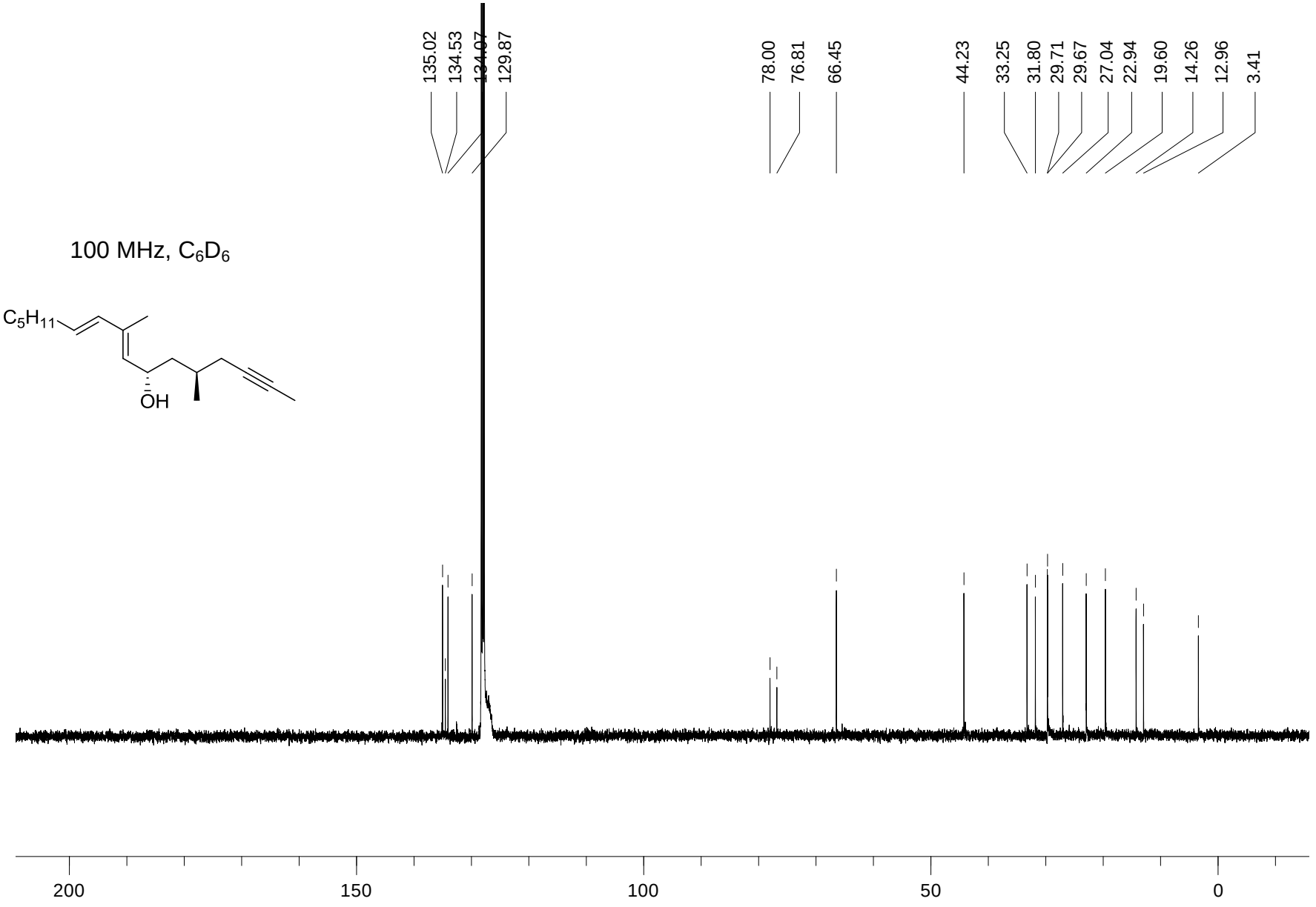


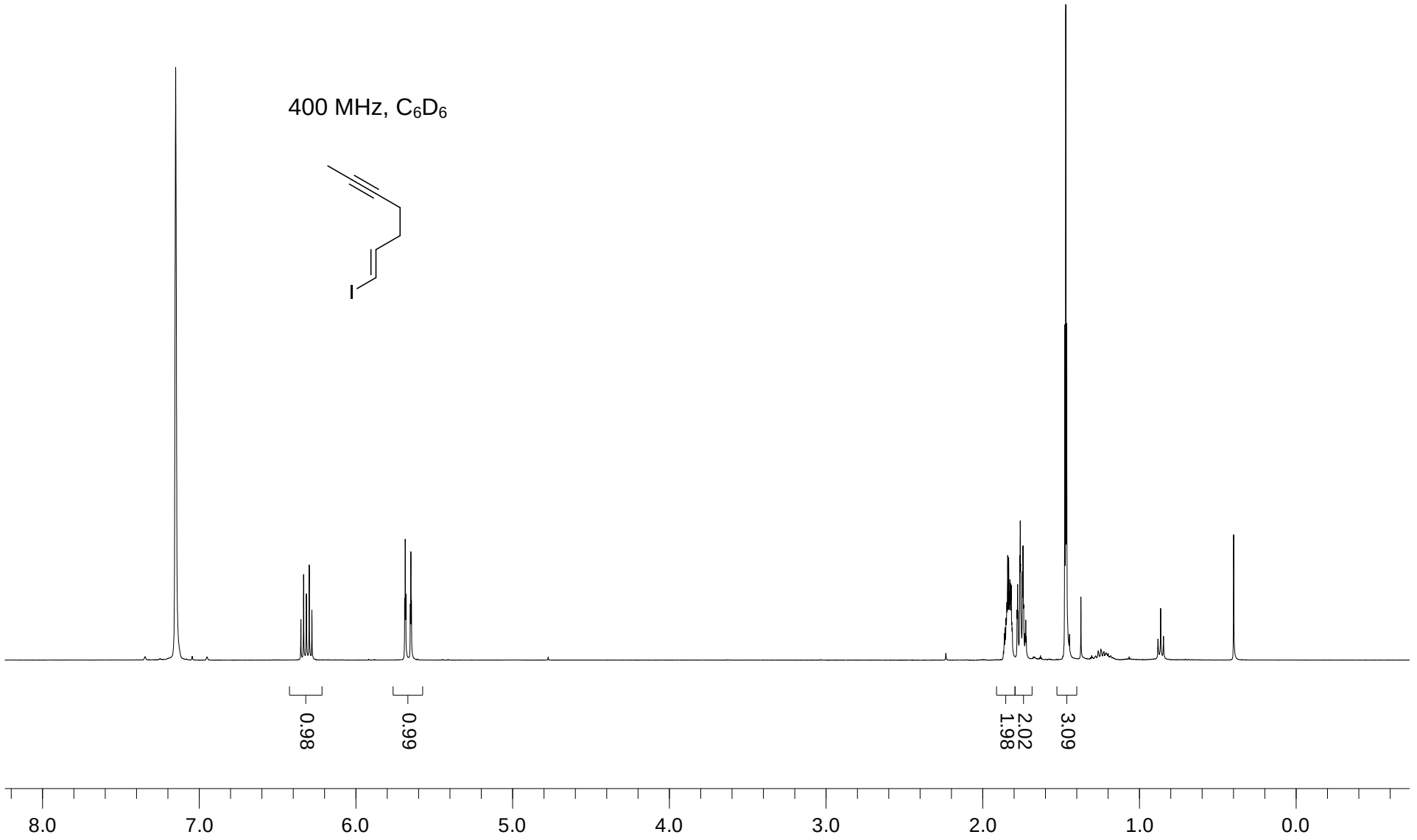

141.07
139.48
131.28
103.75
77.62
77.20
75.45
43.29
31.94
31.47
28.92
28.75
27.01
25.87
22.50
19.05
18.06
14.02
3.52
-3.99
-4.69
100 MHz, CDCl3
C5H11
I
TBSO
200
150
100
50
0

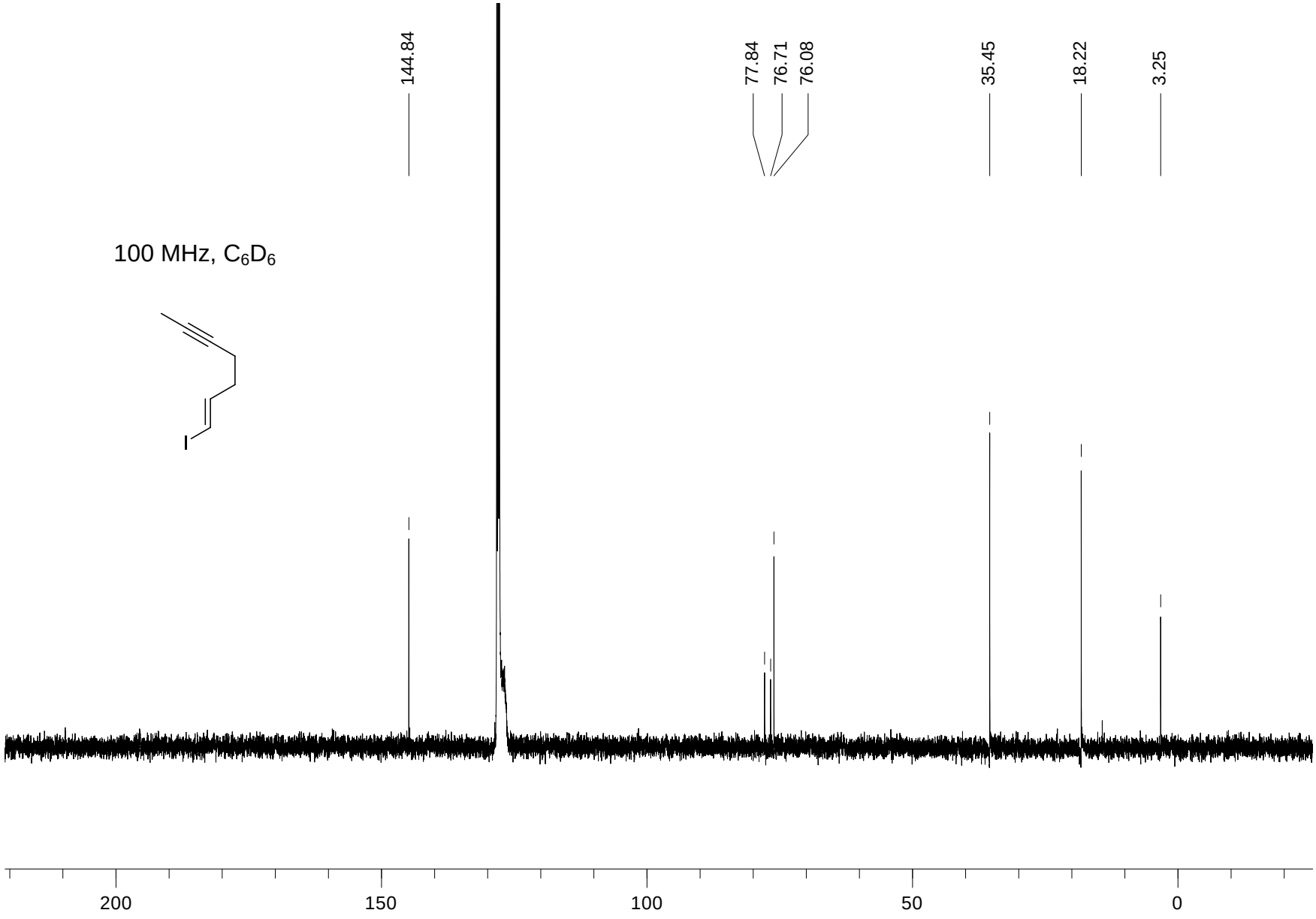

400 MHz, CDCl3
C5H11
TBSO
1.26
1.25
0.87
1.00
4.52
8.28
8.13
3.12
13.05
6.28
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


134.34
134.16
132.07
129.38
77.67
76.43
67.60
44.65
32.87
31.50
29.29
28.91
26.67
25.89
22.56
19.30
18.17
14.05
12.90
3.50
-4.10
-4.87
100 MHz, CDCl3
C5H11
TBSO
200
150
100
50
0

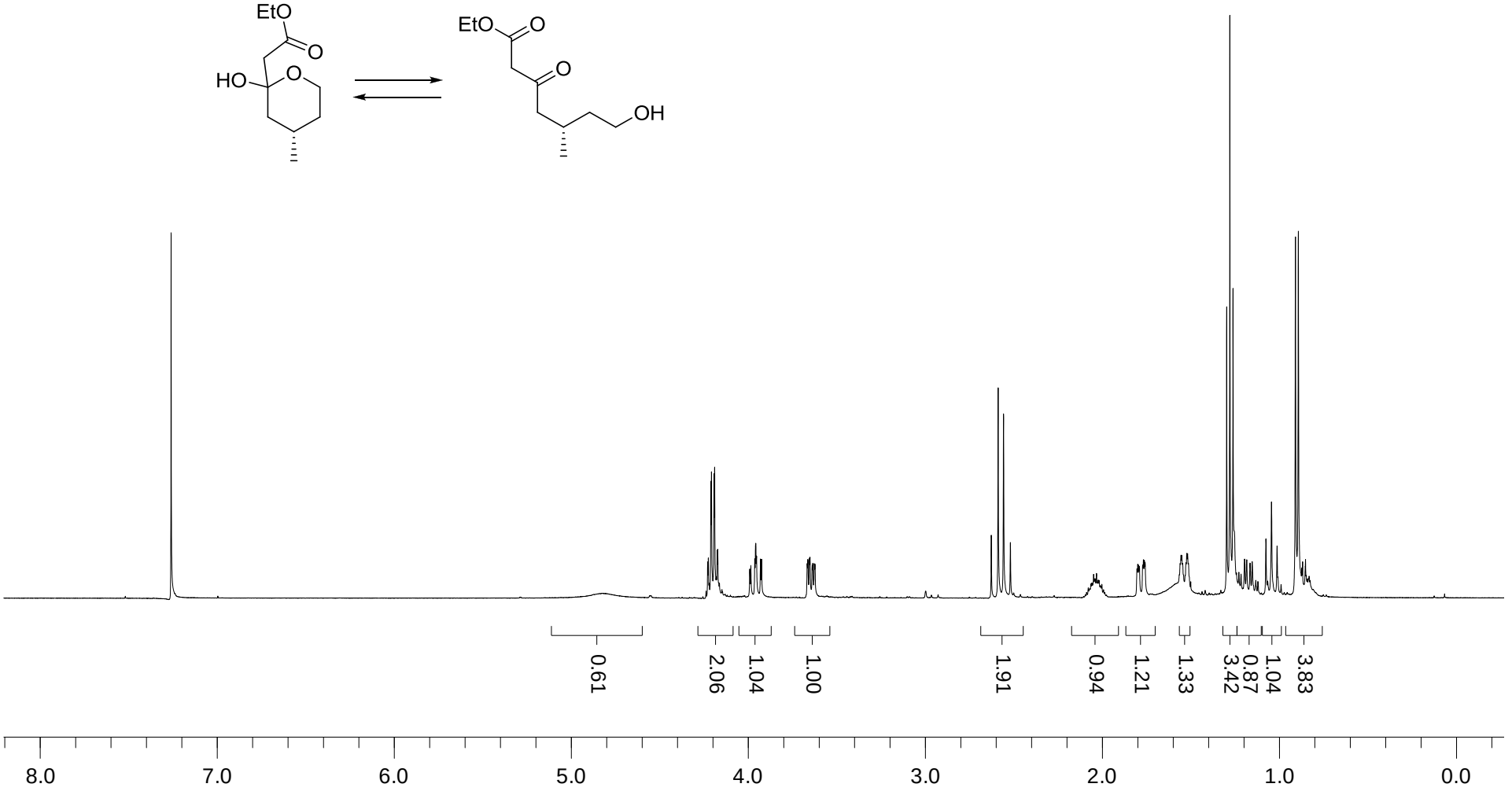

400 MHz, C6D6
C5H11
OH
0.97
0.93
0.94
1.00
3.98
0.94
1.10
2.93
3.18
7.59
2.99
3.39
0.87
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

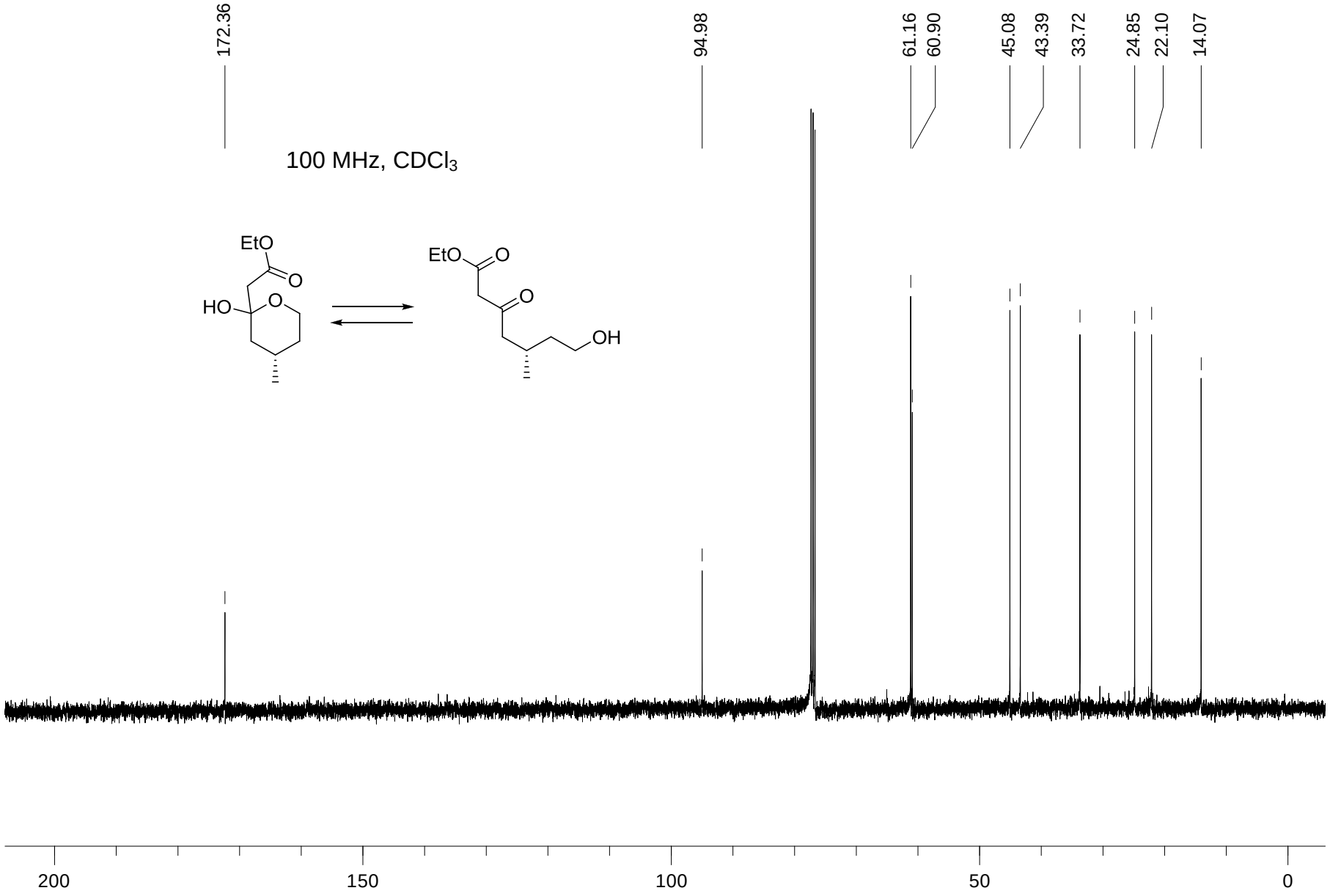

135.02
134.53
134.07
129.87
78.00
76.81
66.45
44.23
33.25
31.80
29.71
29.67
27.04
22.94
19.60
14.26
12.96
3.41
100 MHz, C6D6
C5H11
OH
200
150
100
50
0

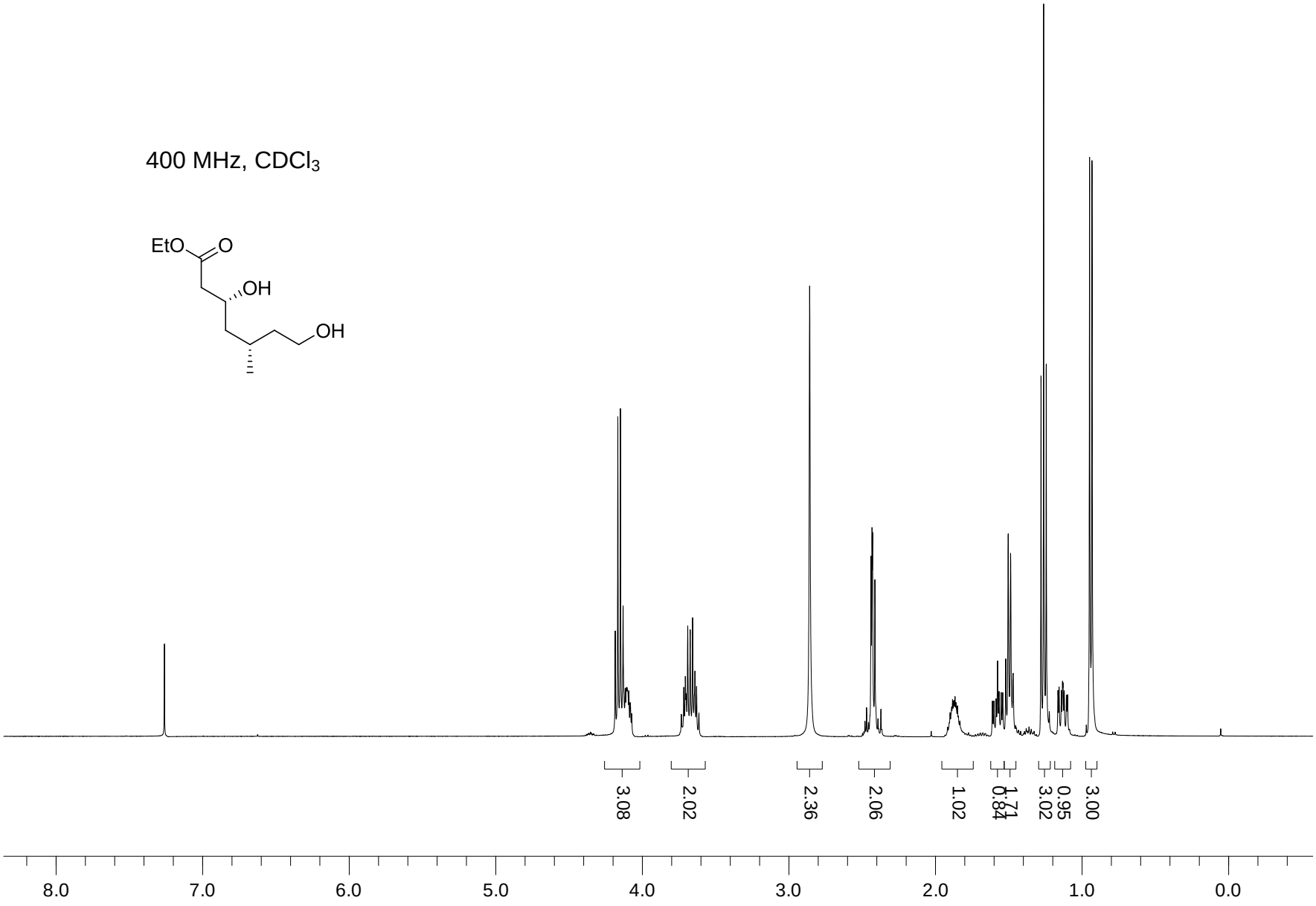

400 MHz, C6D6
I
0.98
0.99
1.98
2.02
3.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

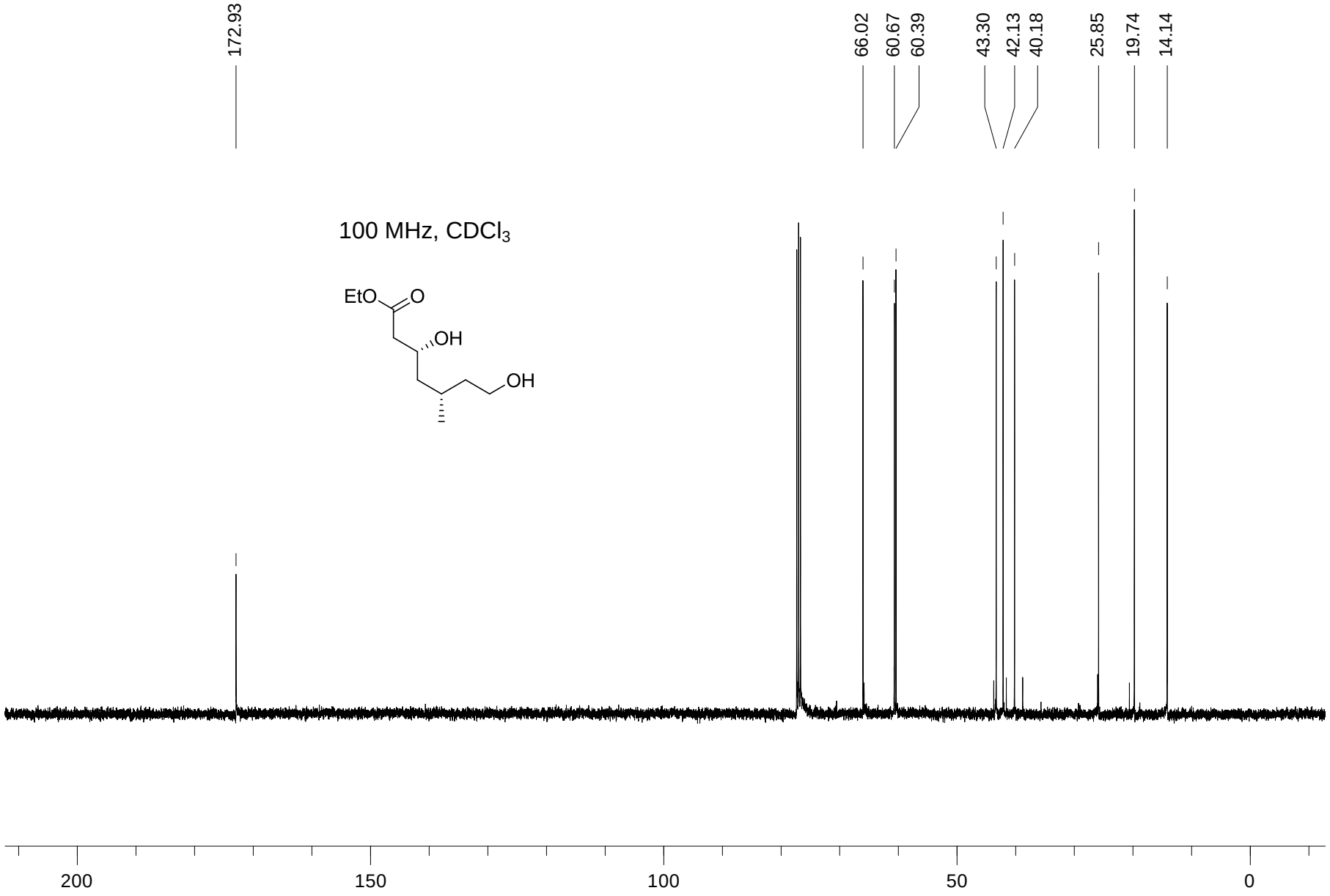

144.84
77.84
76.71
76.08
35.45
18.22
3.25
100 MHz, C6D6
I
200
150
100
50
0

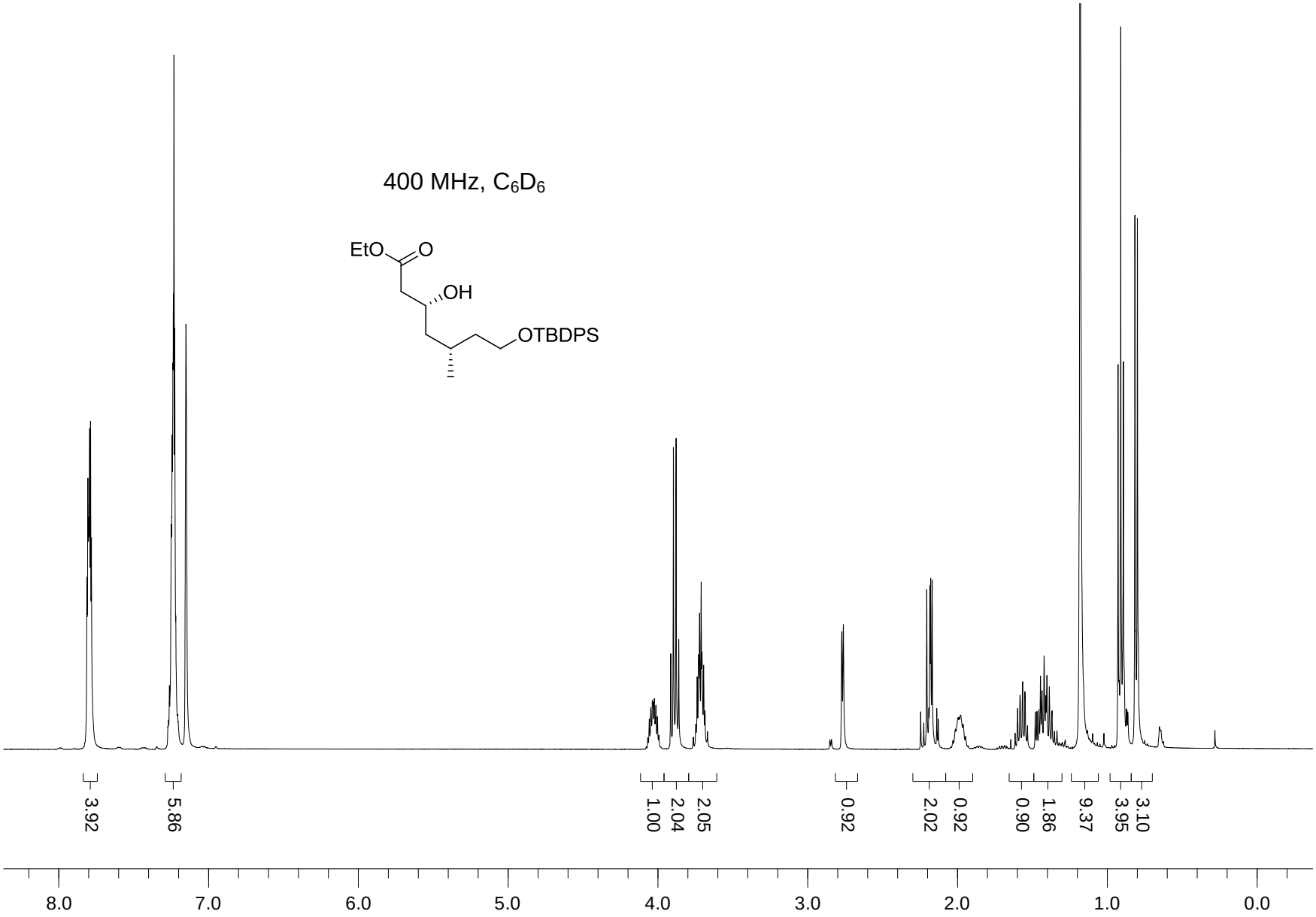
400 MHz, $CDCl_3$

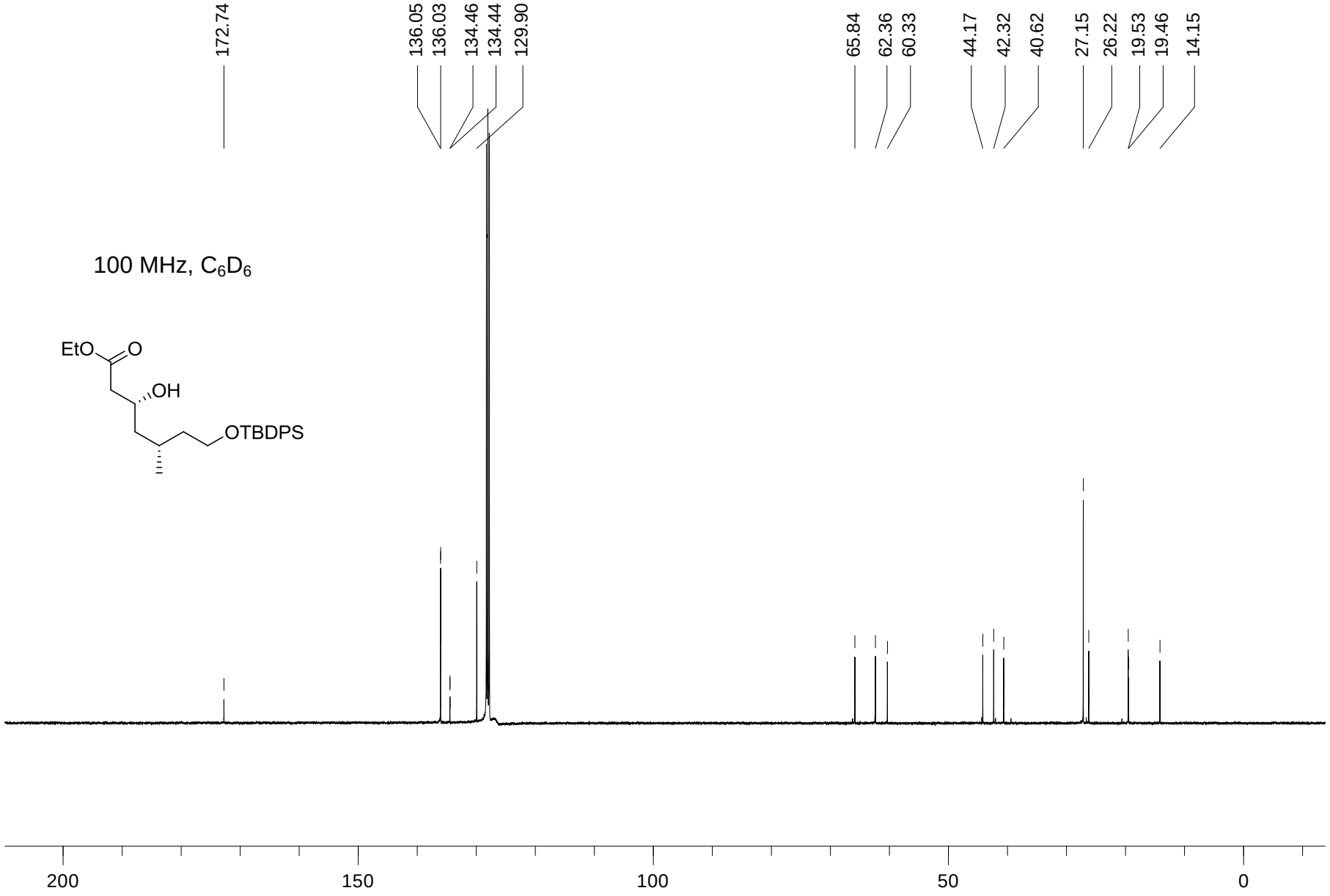


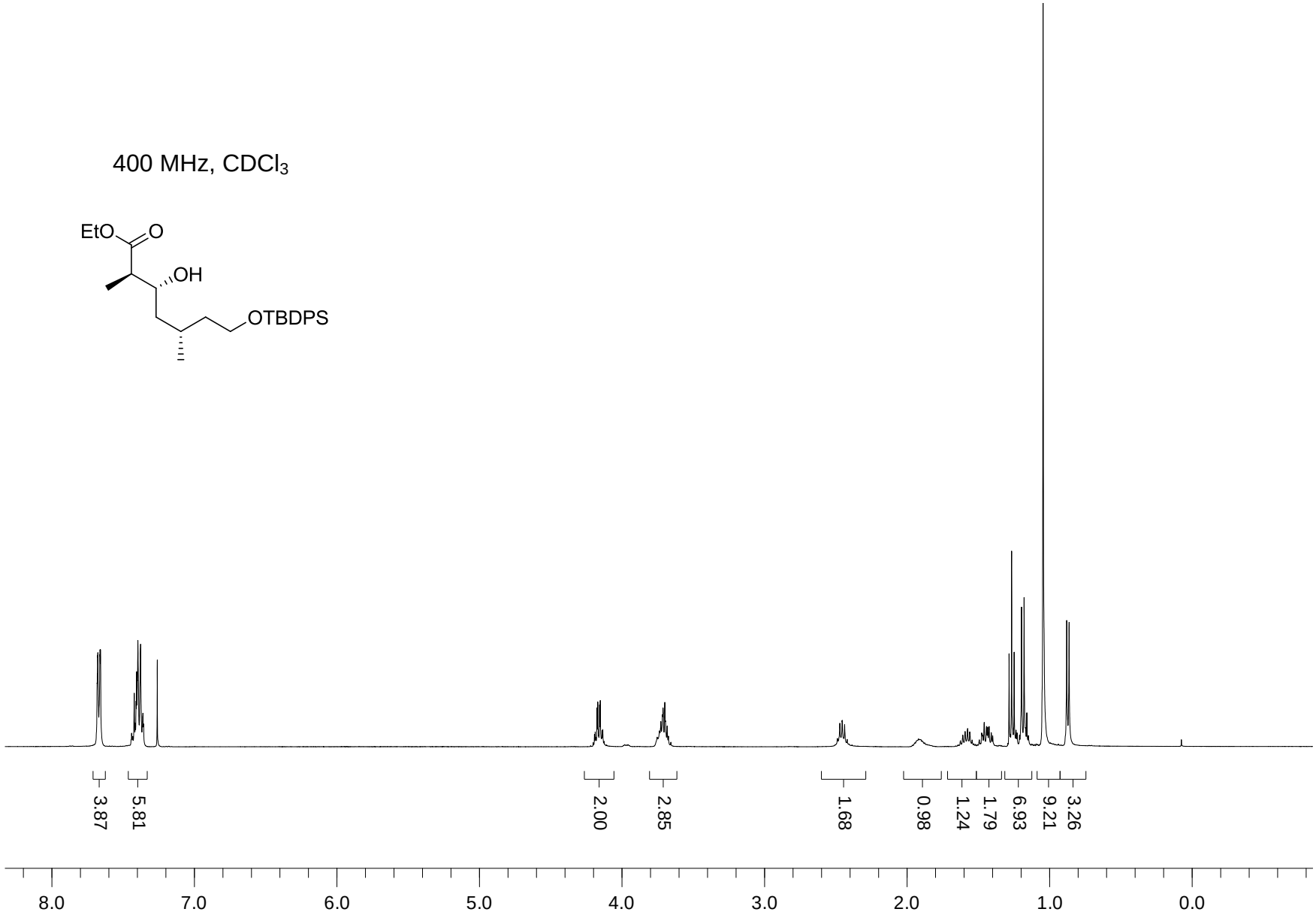

172.36
94.98
61.16
60.90
45.08
43.39
33.72
24.85
22.10
14.07
100 MHz, CDCl3
EtO
O
HO
O
EtO
O
O
OH
200
150
100
50
0

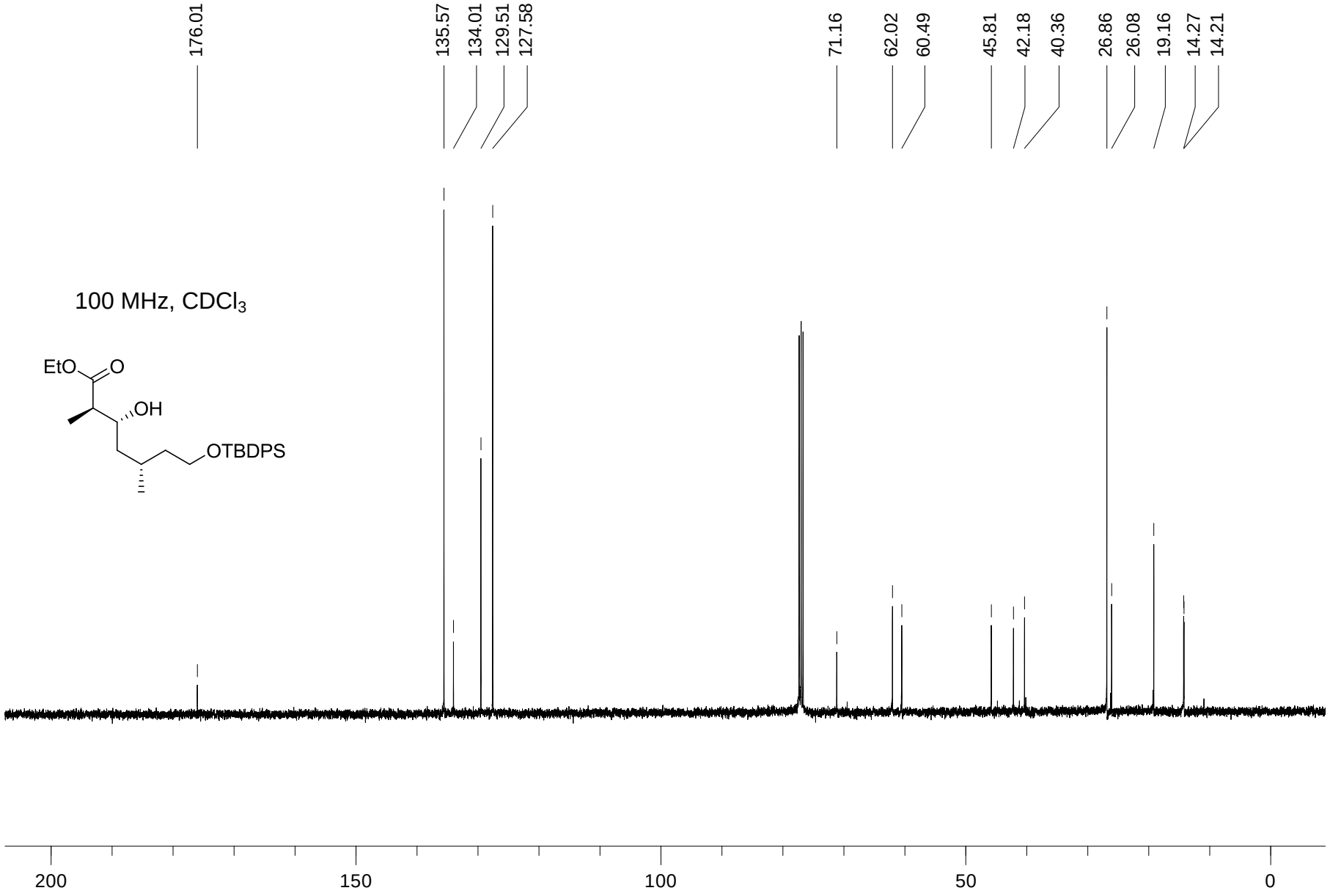

400 MHz, CDCl3
EtO
O
OH
OH
3.08
2.02
2.36
2.06
1.02
1.71
0.84
3.02
0.95
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

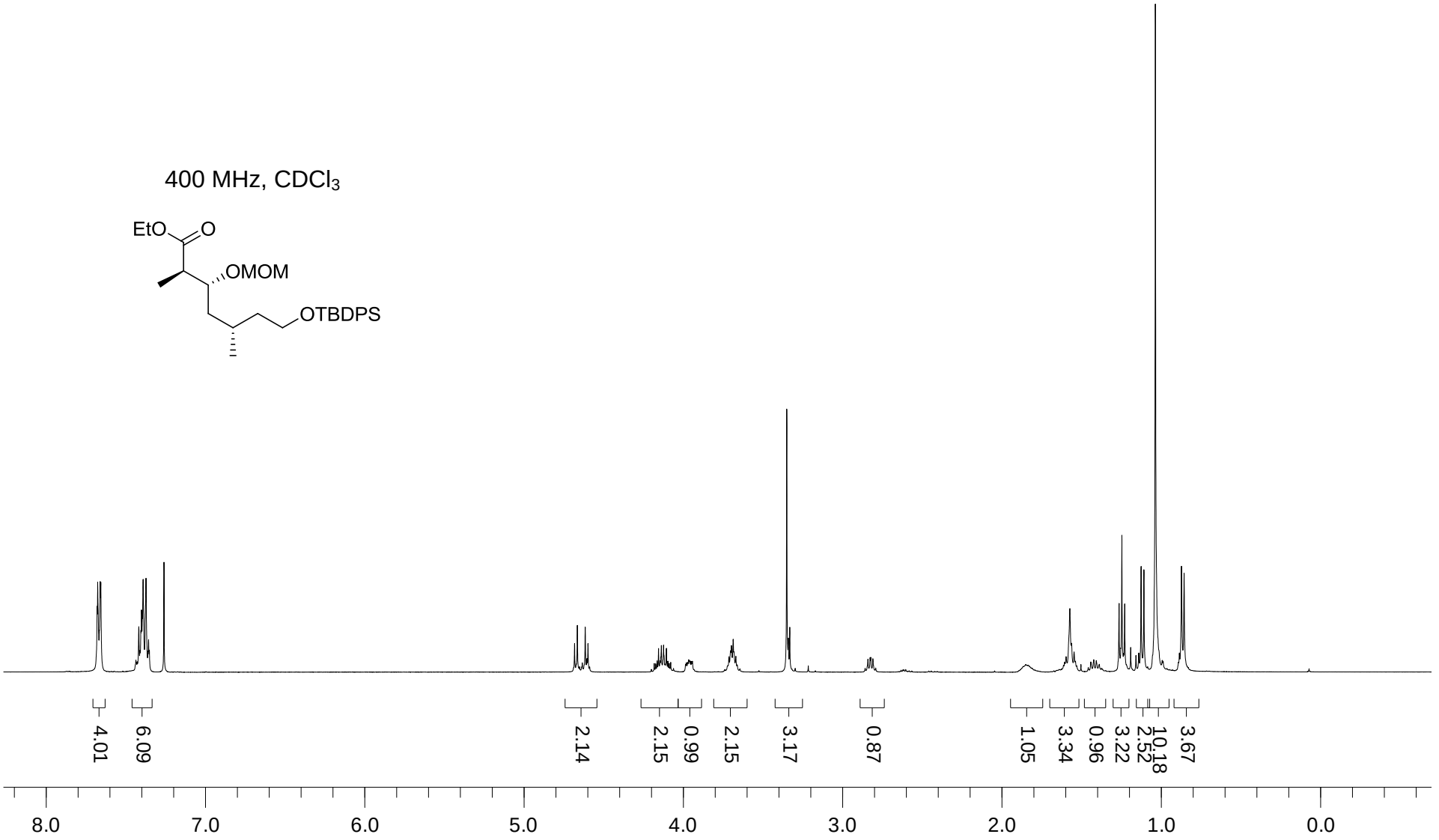

172.93
66.02
60.67
60.39
43.30
42.13
40.18
25.85
19.74
14.14
100 MHz, CDCl3
EtO
O
OH
OH
200
150
100
50
0

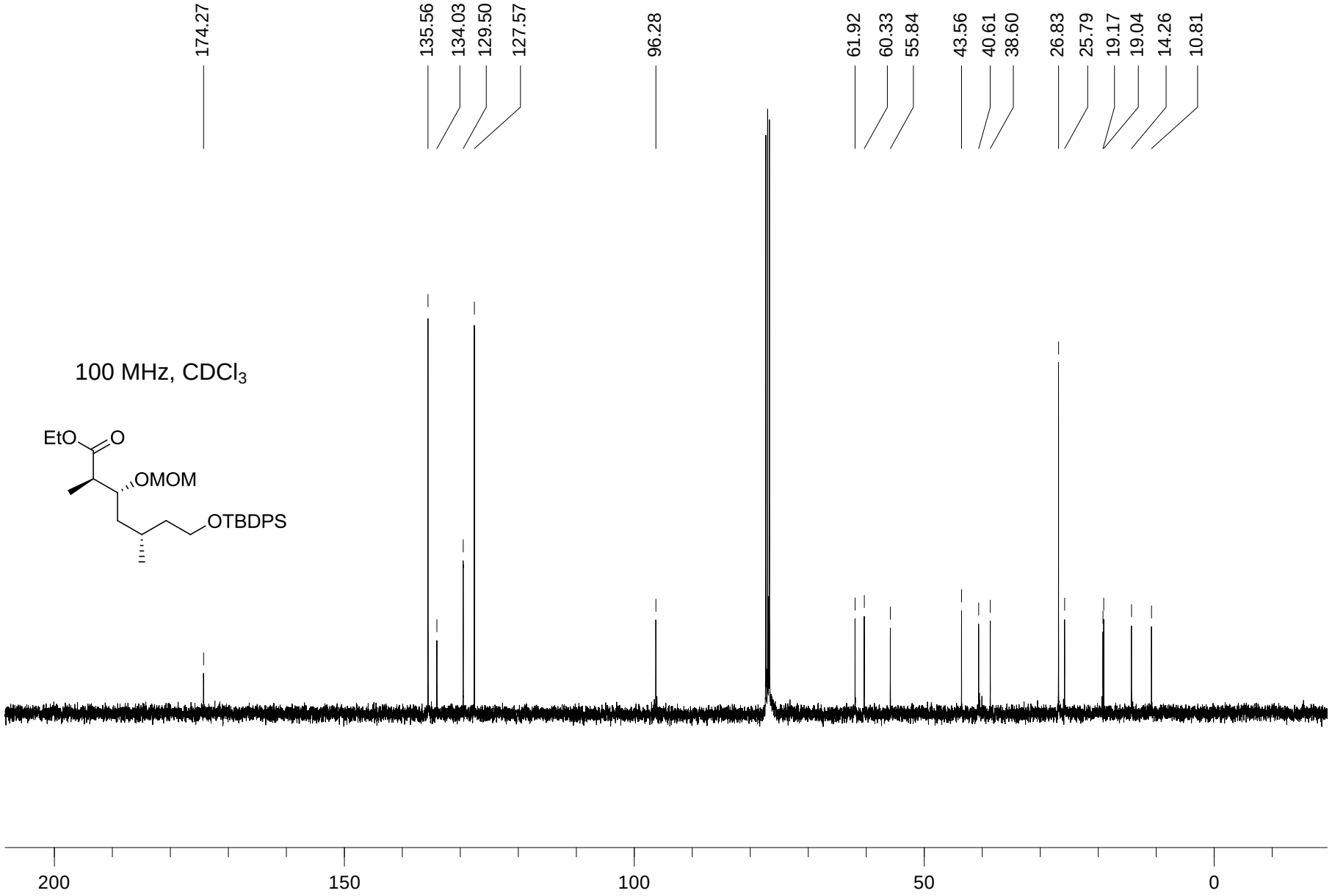

400 MHz, C6D6
EtO
O
OH
OTBDPS
3.92
5.86
1.00
2.04
2.05
0.92
2.02
0.92
0.90
1.86
9.37
3.95
3.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

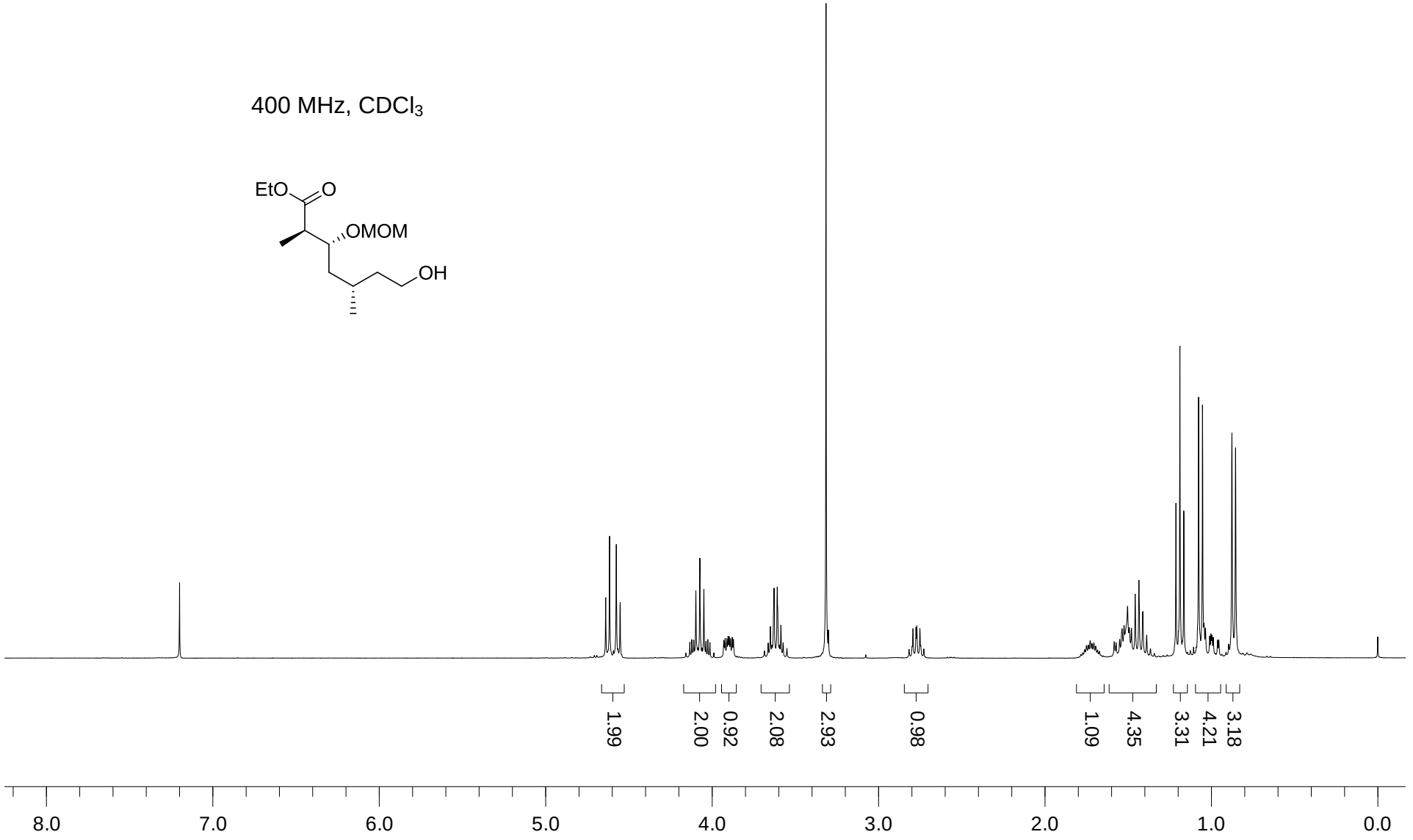

172.74
136.05
136.03
134.46
134.44
129.90
65.84
62.36
60.33
44.17
42.32
40.62
27.15
26.22
19.53
19.46
14.15
100 MHz, C6D6
EtO
O
OH
OTBDPS
200
150
100
50
0

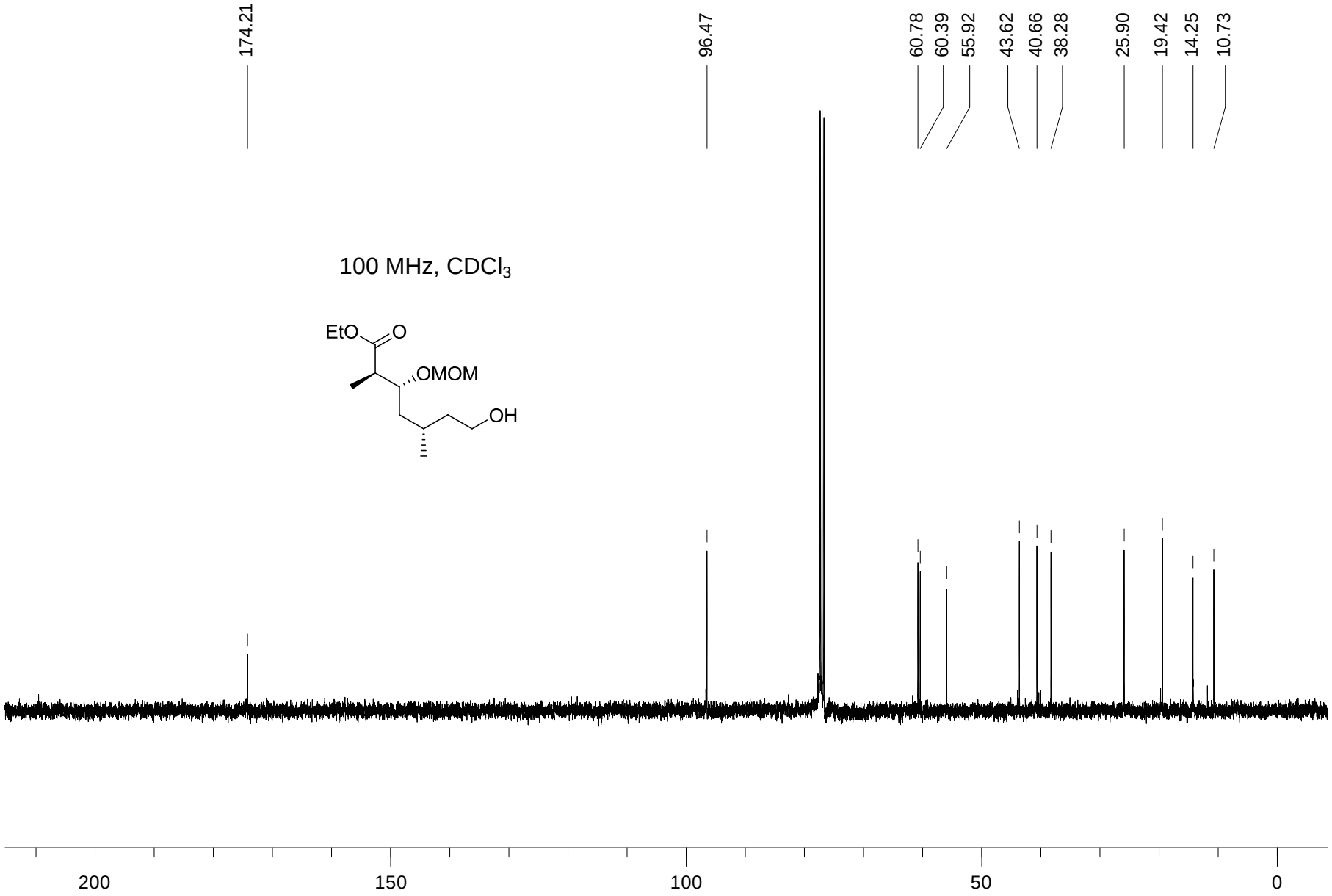

400 MHz, CDCl3
EtO
O
OH
OTBDPS
3.87
5.81
2.00
2.85
1.68
0.98
1.24
1.79
6.93
9.21
3.26
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

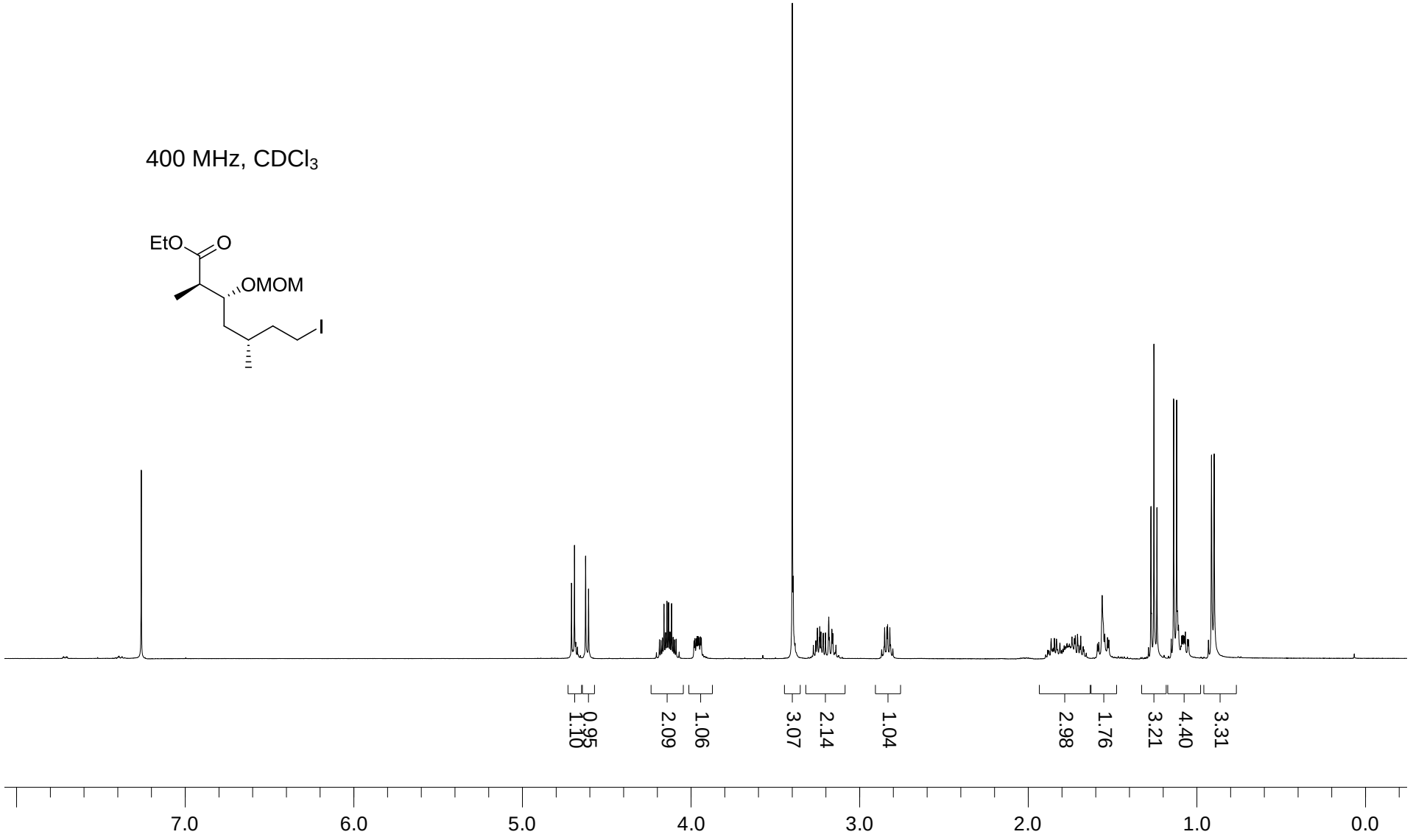

176.01
135.57
134.01
129.51
127.58
71.16
62.02
60.49
45.81
42.18
40.36
26.86
26.08
19.16
14.27
14.21
100 MHz, CDCl3
EtO
O
OH
OTBDPS
200
150
100
50
0

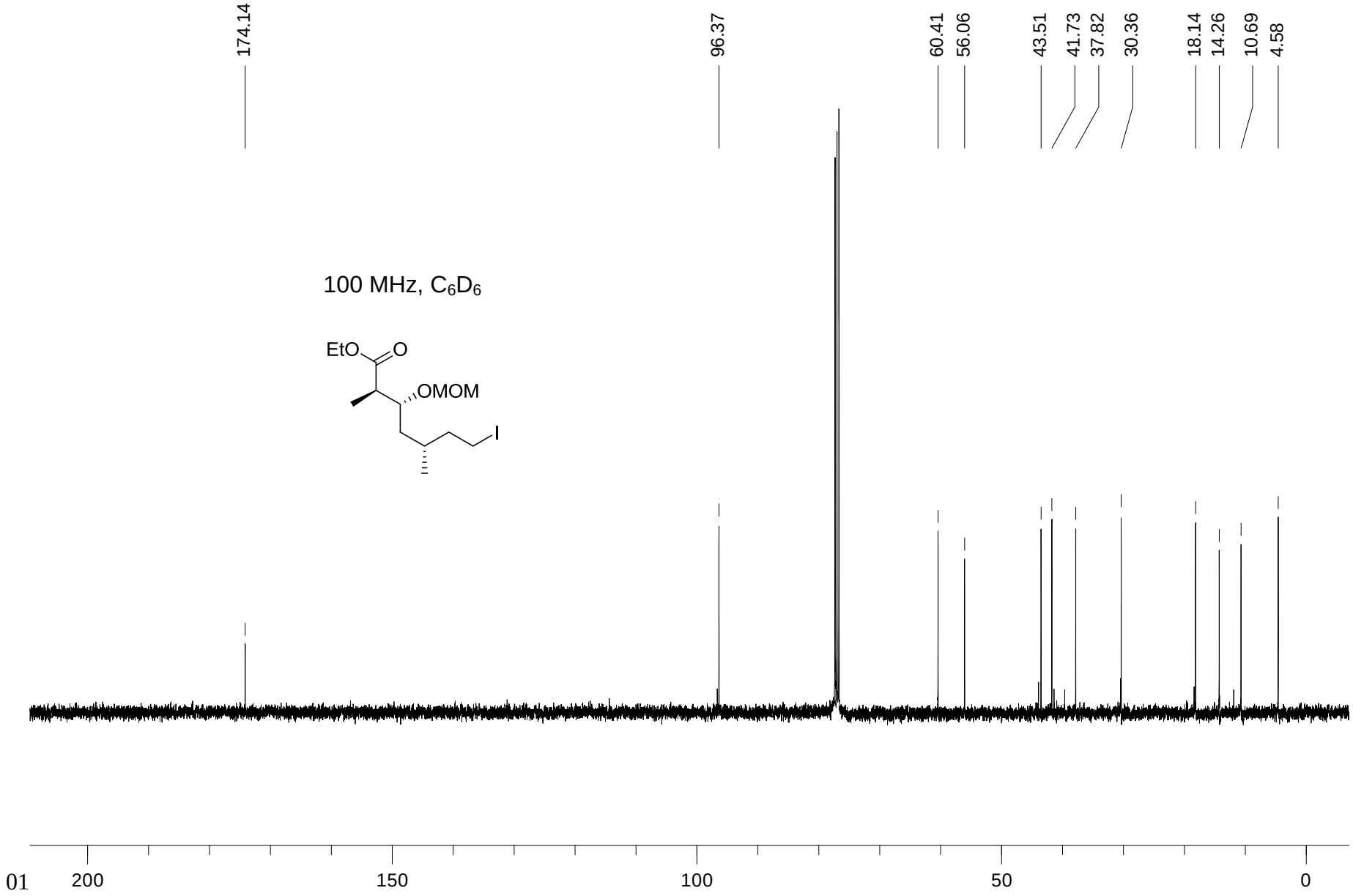

400 MHz, CDCl3
EtO
O
OMOM
OTBDPS
4.01
6.09
2.14
2.15
0.99
2.15
3.17
0.87
1.05
3.34
0.96
3.22
2.52
10.18
3.67
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

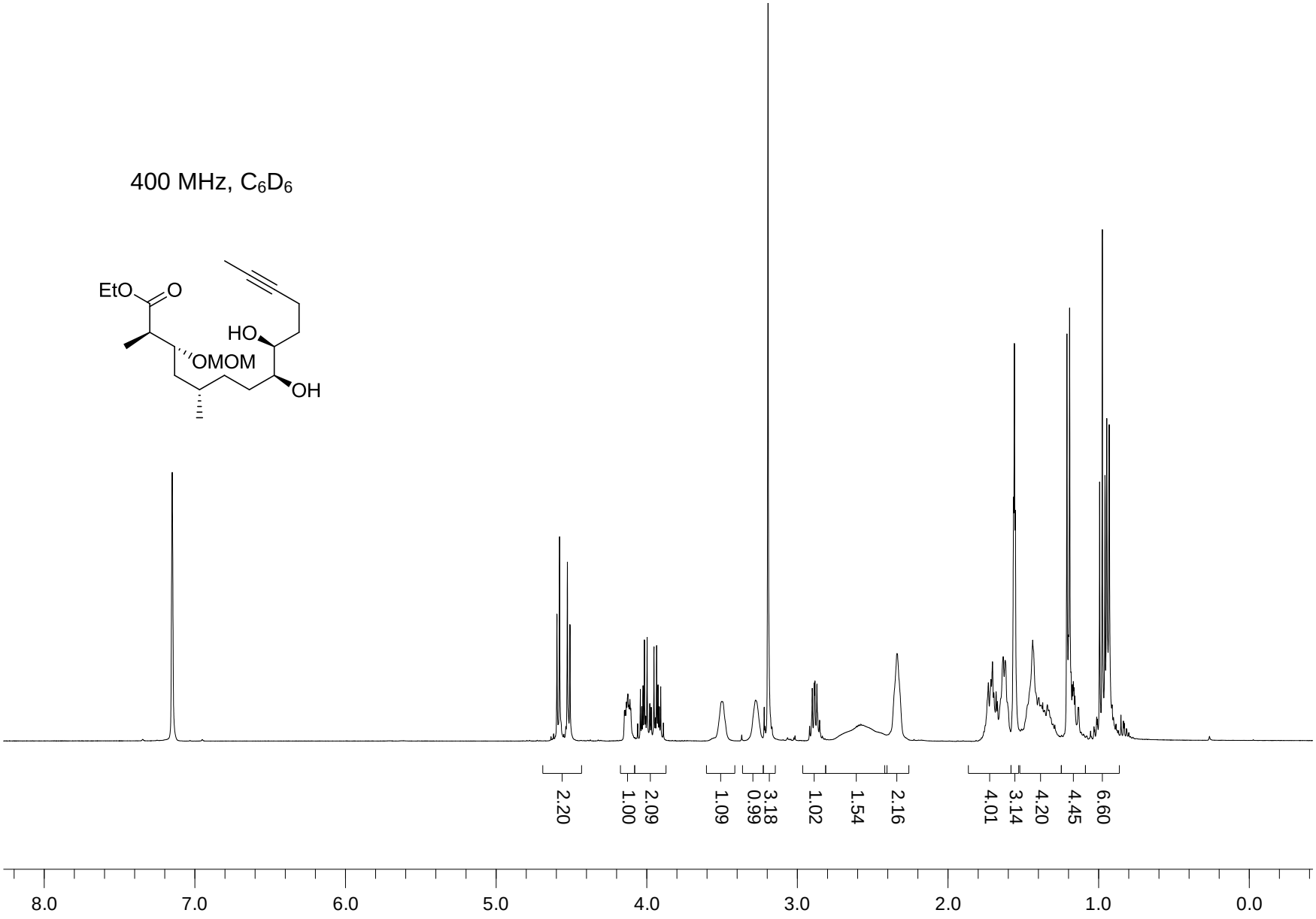

174.27
135.56
134.03
129.50
127.57
96.28
61.92
60.33
55.84
43.56
40.61
38.60
26.83
25.79
19.17
19.04
14.26
10.81
100 MHz, CDCl3
EtO
O
OMOM
OTBDPS
200
150
100
50
0

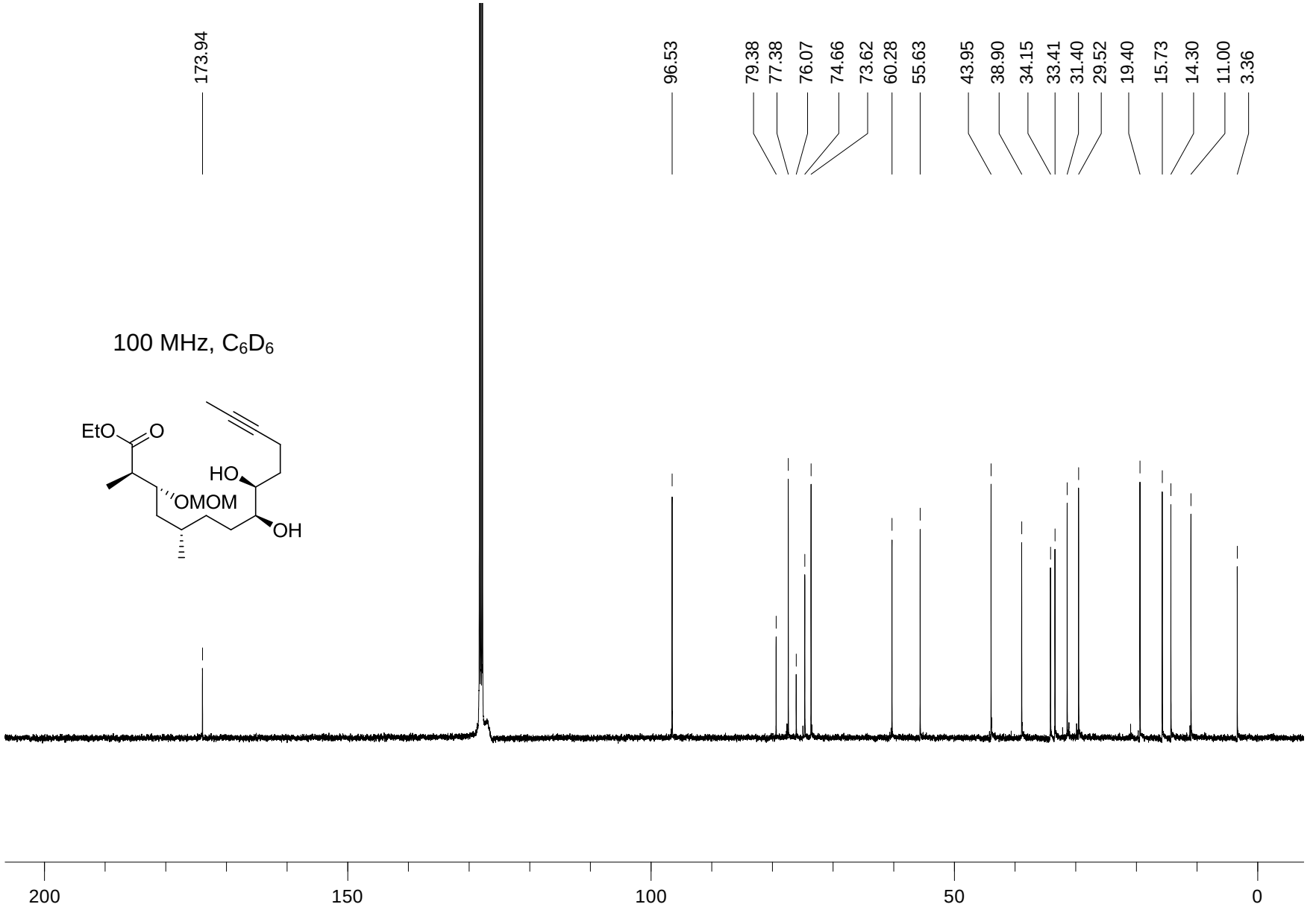

400 MHz, CDCl3
EtO
O
OMOM
OH
1.99
2.00
0.92
2.08
2.93
0.98
1.09
4.35
3.31
4.21
3.18
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

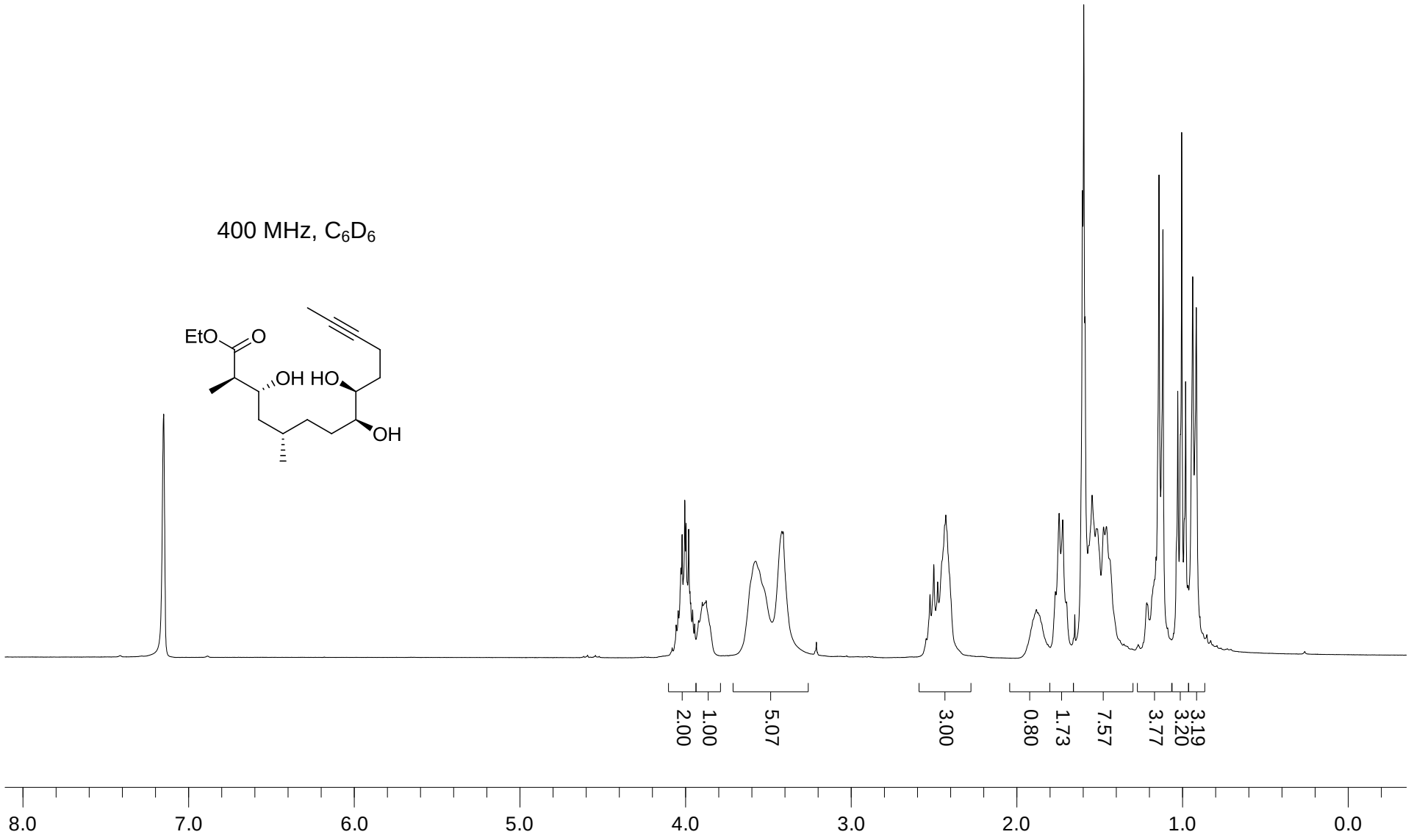

174.21
96.47
60.78
60.39
55.92
43.62
40.66
38.28
25.90
19.42
14.25
10.73
100 MHz, CDCl3
EtO
O
OMOM
OH
200
150
100
50
0

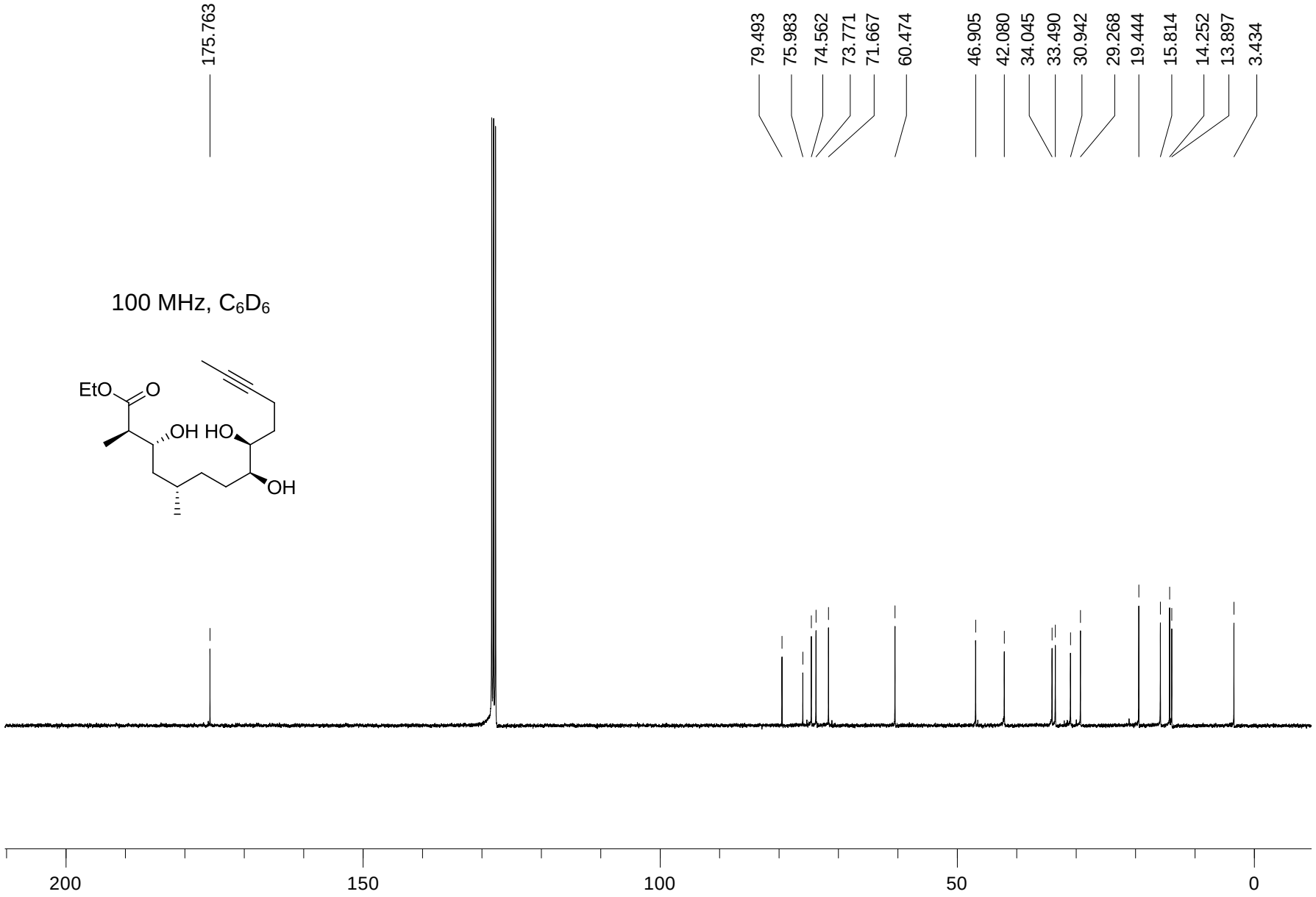

400 MHz, CDCl3
EtO
O
OMOM
I
1.10
0.95
2.09
1.06
3.07
2.14
1.04
2.98
1.76
3.21
4.40
3.31
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

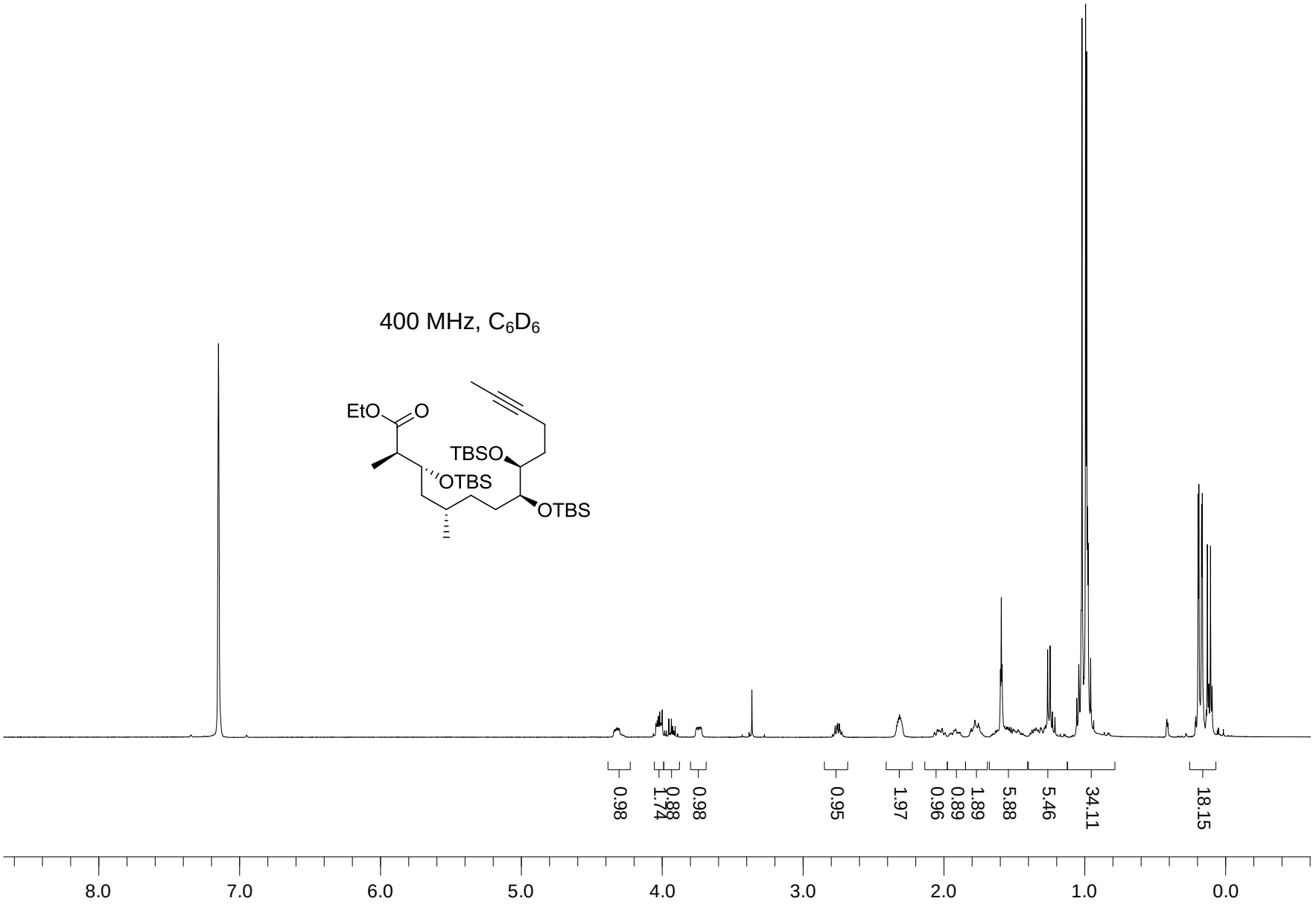

174.14
96.37
60.41
56.06
43.51
41.73
37.82
30.36
18.14
14.26
10.69
4.58
100 MHz, C6D6
EtO
O
OMOM
I
01
200
150
100
50
0

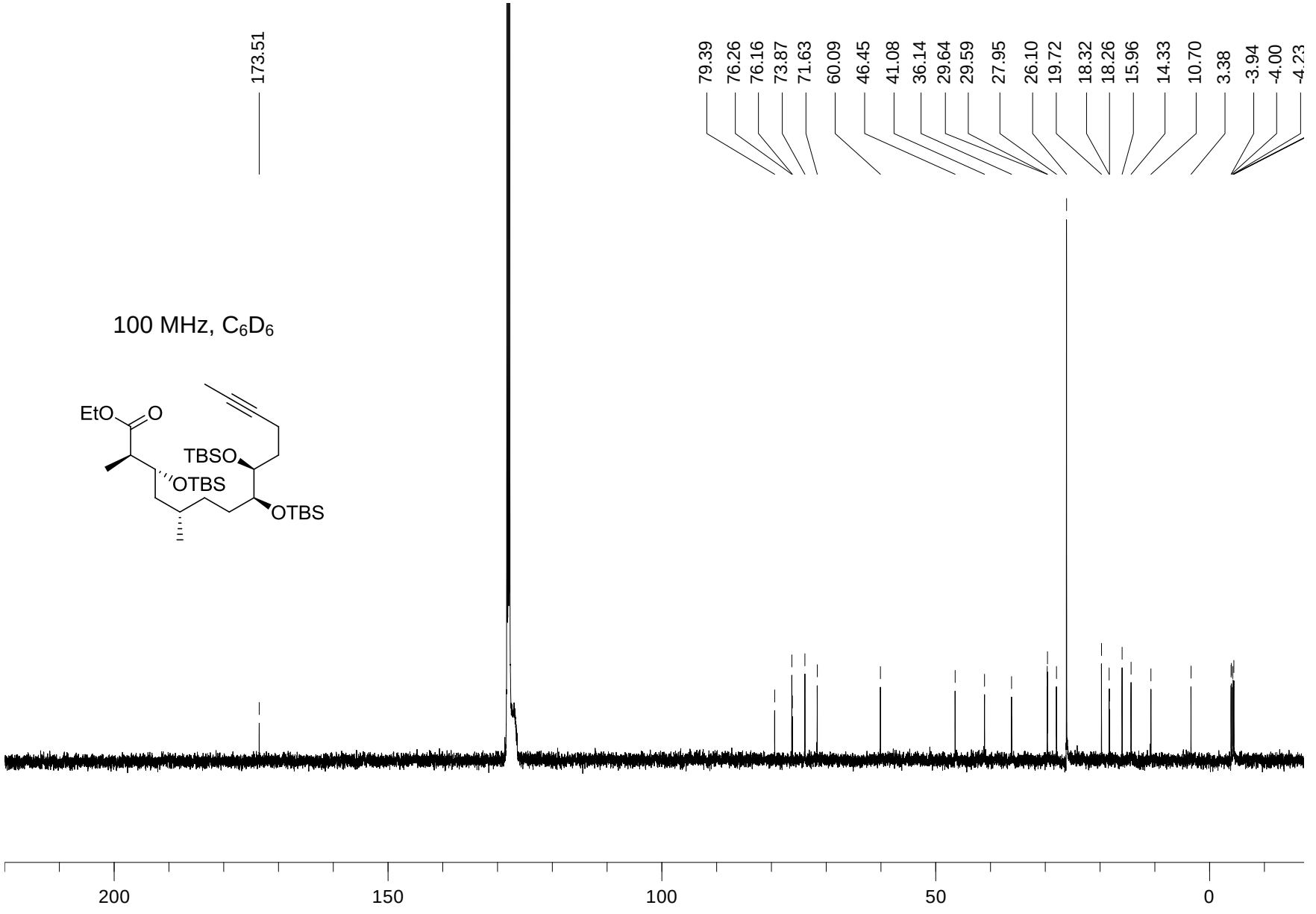

400 MHz, C6D6
EtO
O
HO
OMOM
OH
2.20
1.00
2.09
1.09
0.99
3.18
1.02
1.54
2.16
4.01
3.14
4.20
4.45
6.60
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

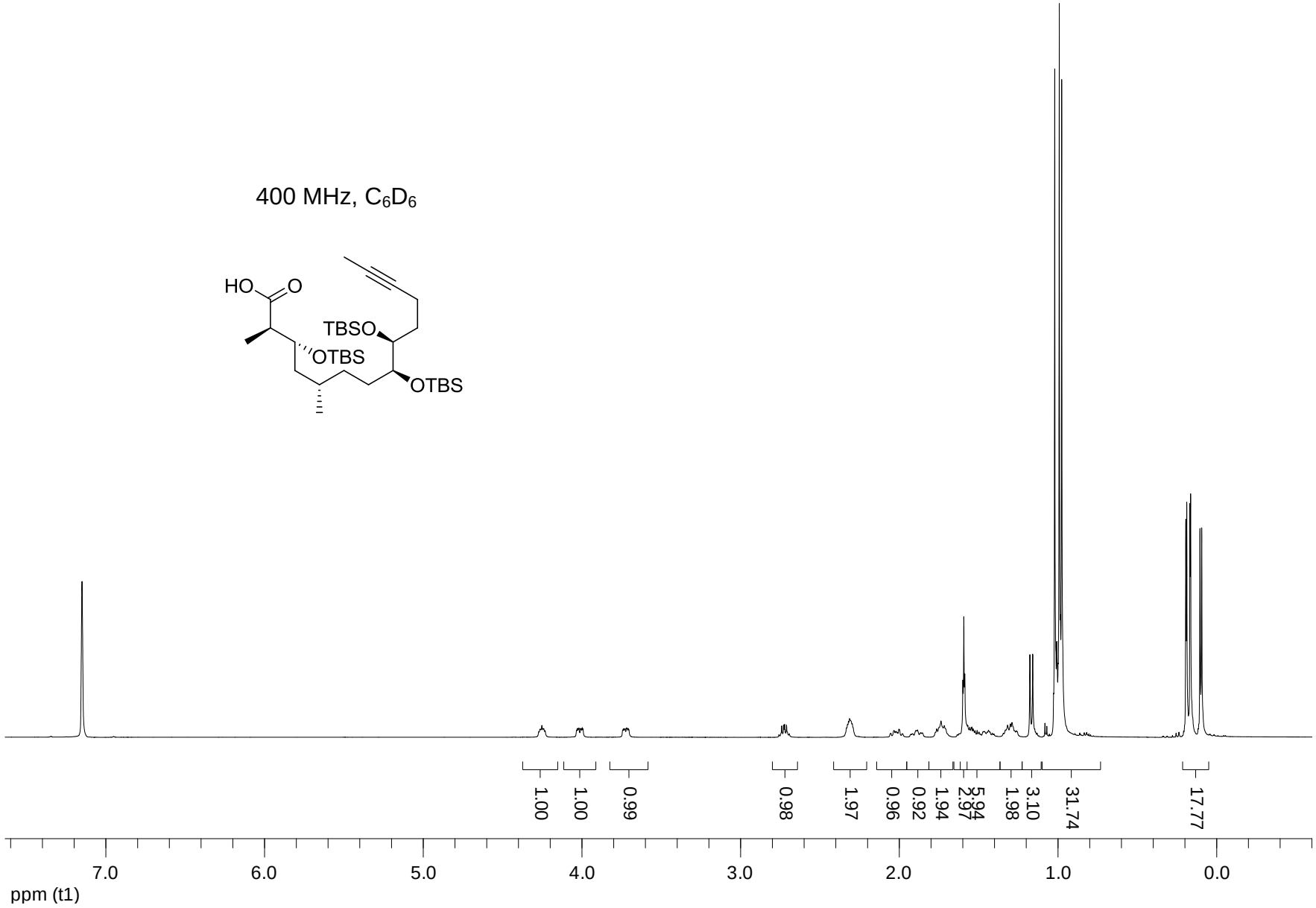

173.94
96.53
79.38
77.38
76.07
74.66
73.62
60.28
55.63
43.95
38.90
34.15
33.41
31.40
29.52
19.40
15.73
14.30
11.00
3.36
100 MHz, C6D6
EtO
O
HO
OMOM
OH
200
150
100
50
0

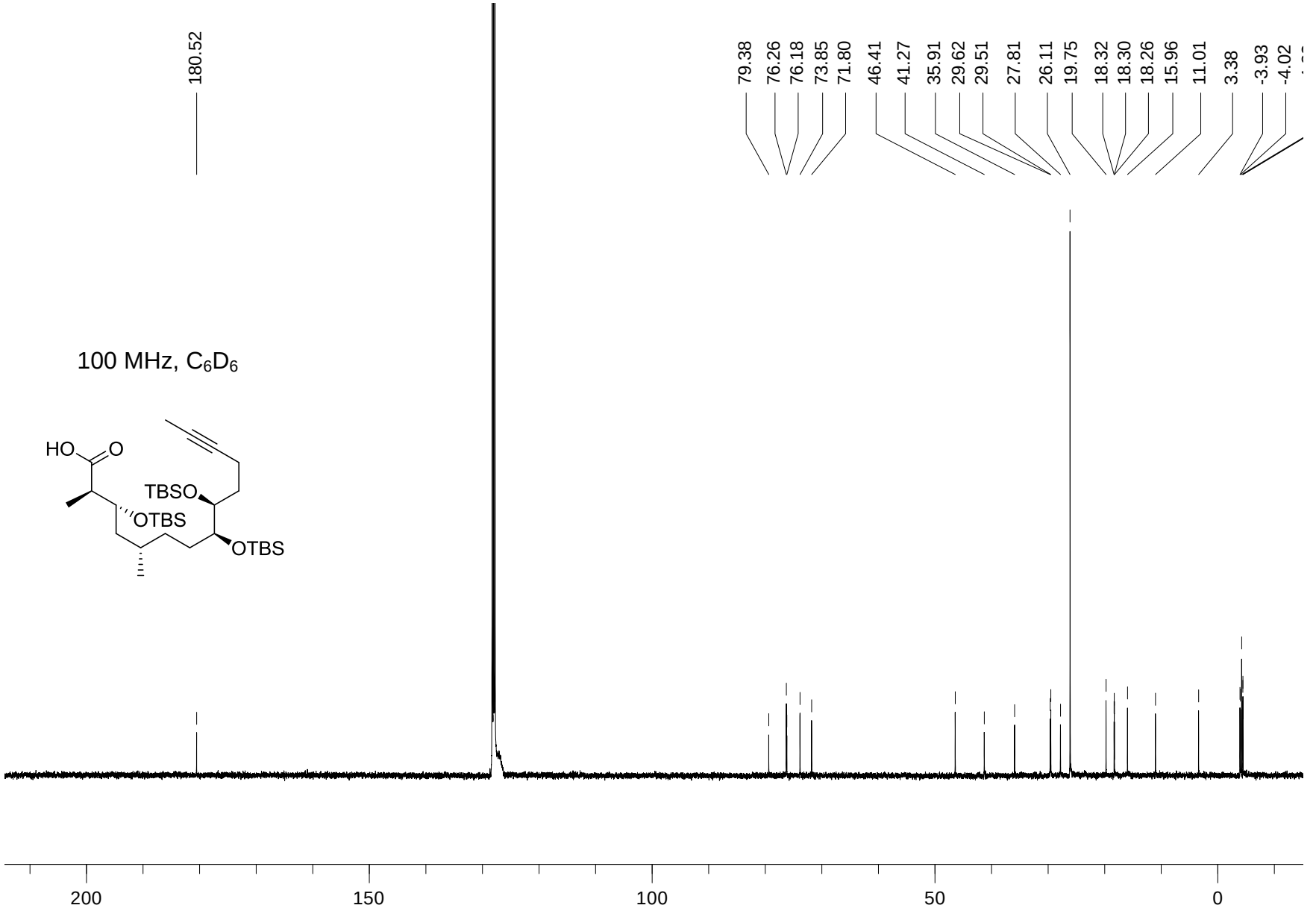

400 MHz, C6D6
EtO
O
OH
HO
OH
2.00
1.00
5.07
3.00
0.80
1.73
7.57
3.77
3.20
3.19
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

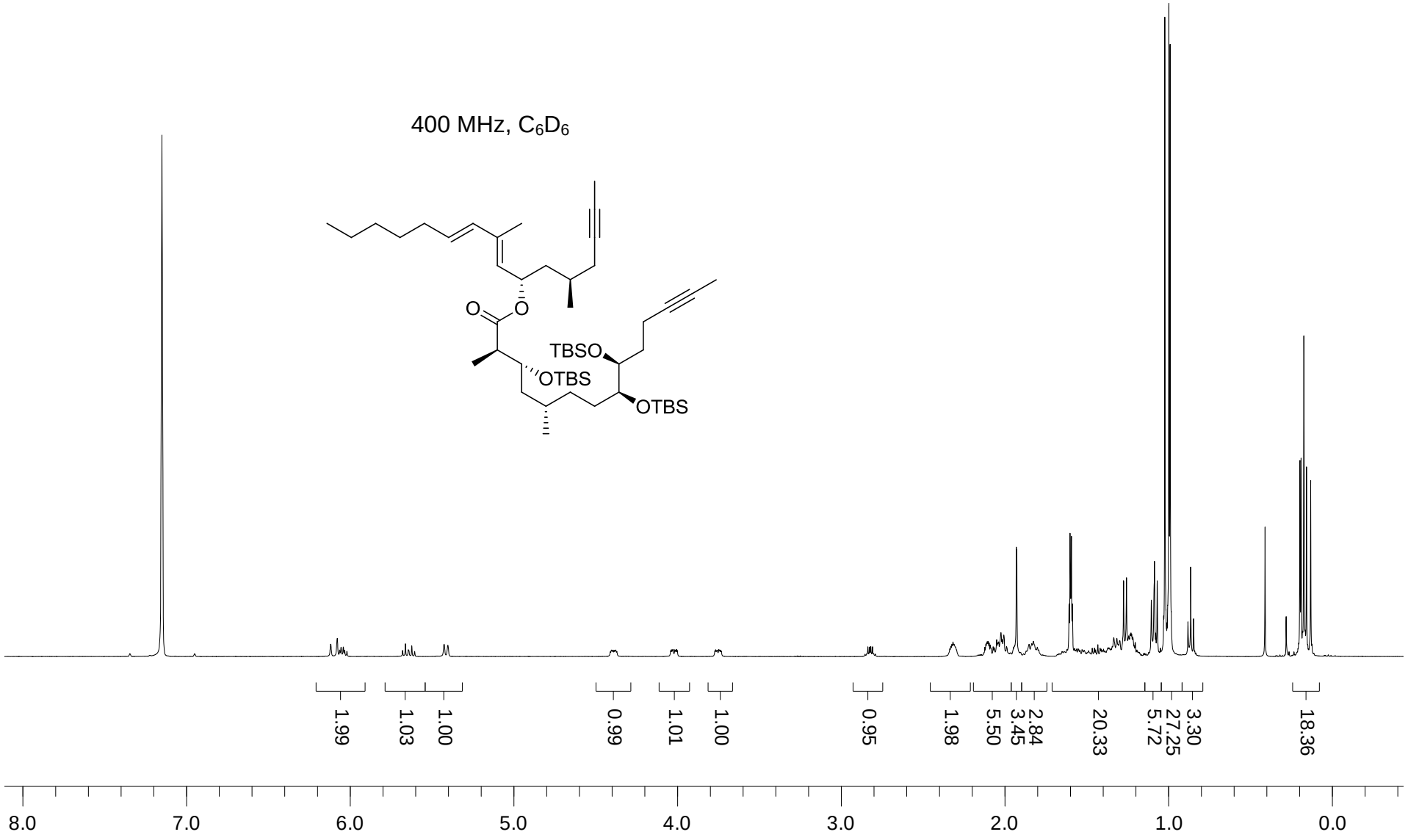

175.763
79.493
75.983
74.562
73.771
71.667
60.474
46.905
42.080
34.045
33.490
30.942
29.268
19.444
15.814
14.252
13.897
3.434
100 MHz, C6D6
EtO
O
OH
HO
OH
200
150
100
50
0

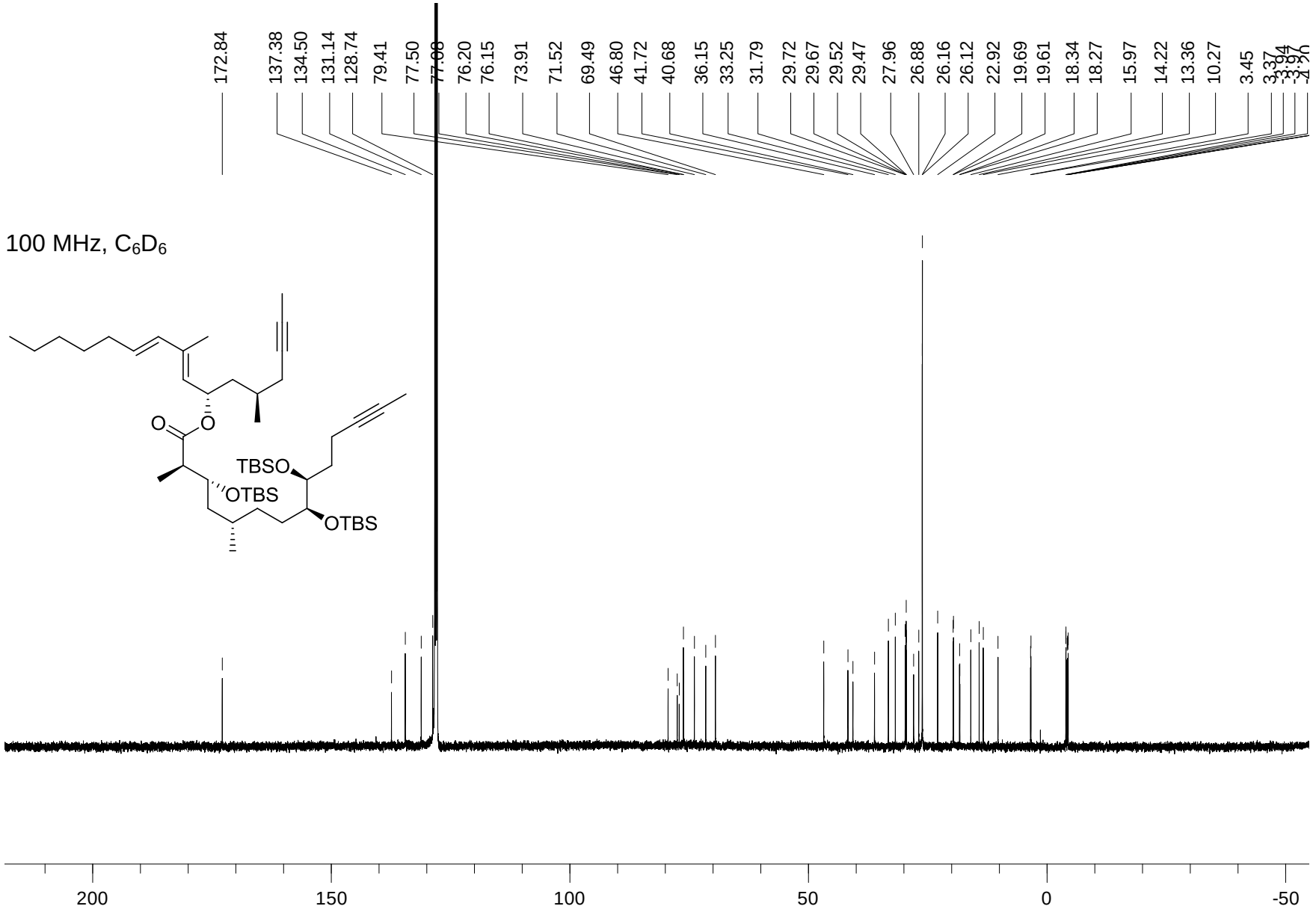

400 MHz, C6D6
EtO
O
TBSO
OTBS
OTBS
0.98
1.74
0.98
0.95
1.97
0.96
0.89
1.89
5.88
5.46
34.11
18.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

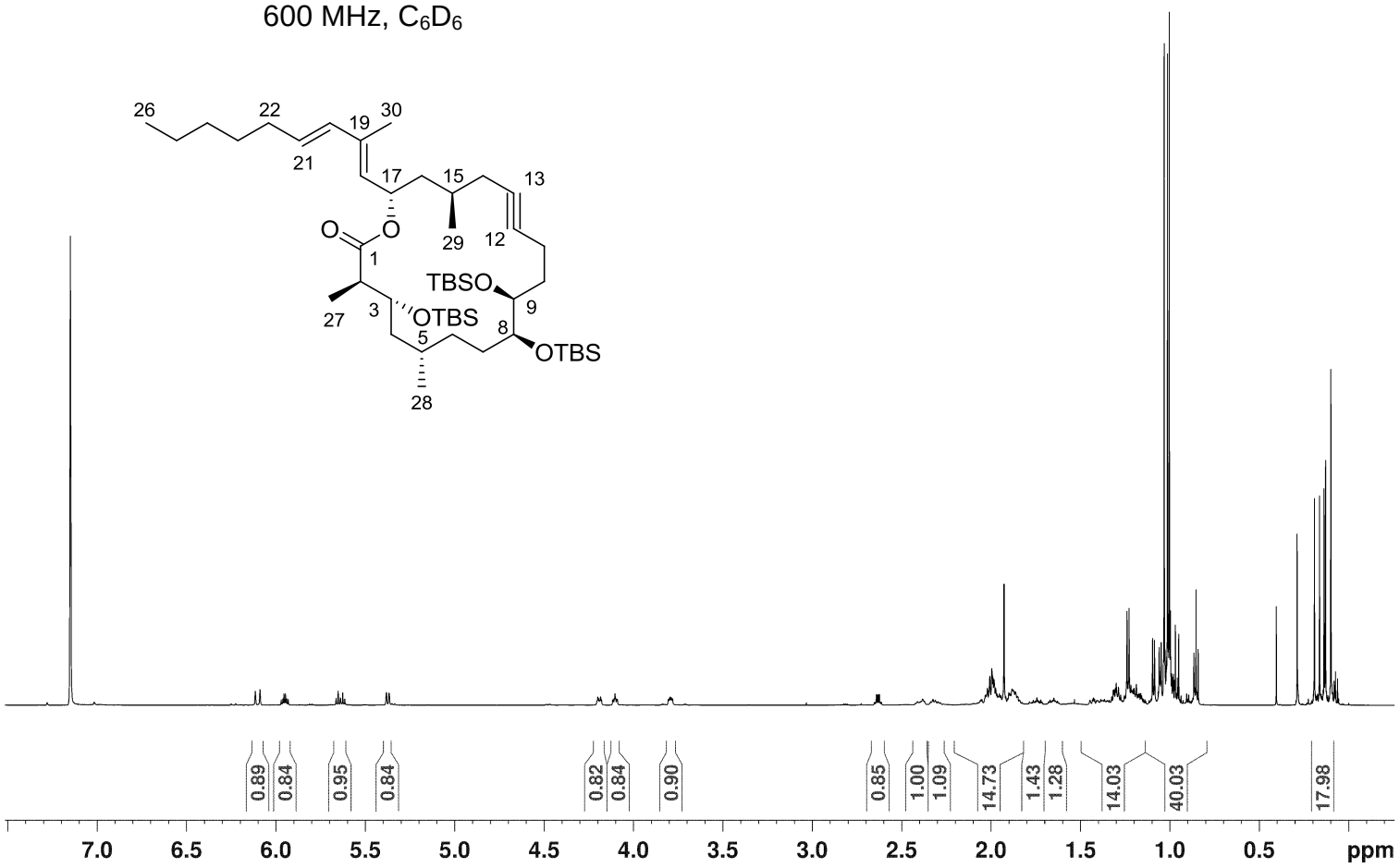

173.51
79.39
76.26
76.16
73.87
71.63
60.09
46.45
41.08
36.14
29.64
29.59
27.95
26.10
19.72
18.32
18.26
15.96
14.33
10.70
3.38
-3.94
-4.00
-4.23
100 MHz, C6D6
EtO
O
TBSO
OTBS
OTBS
200
150
100
50
0

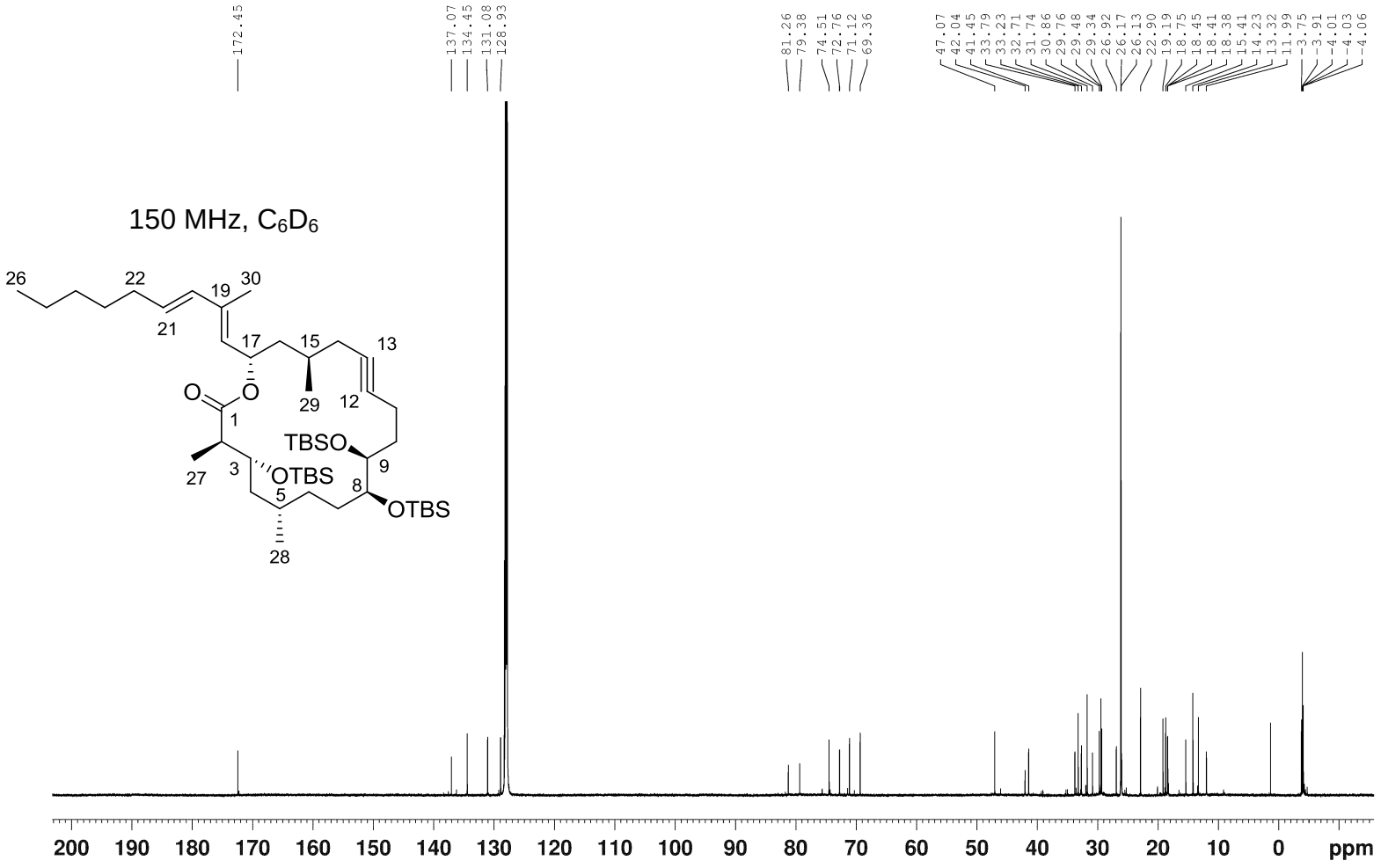

400 MHz, C6D6
HO
O
TBSO
OTBS
OTBS
1.00
1.00
0.99
0.98
1.97
0.96
0.92
1.94
2.97
5.94
1.98
3.10
31.74
17.77
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

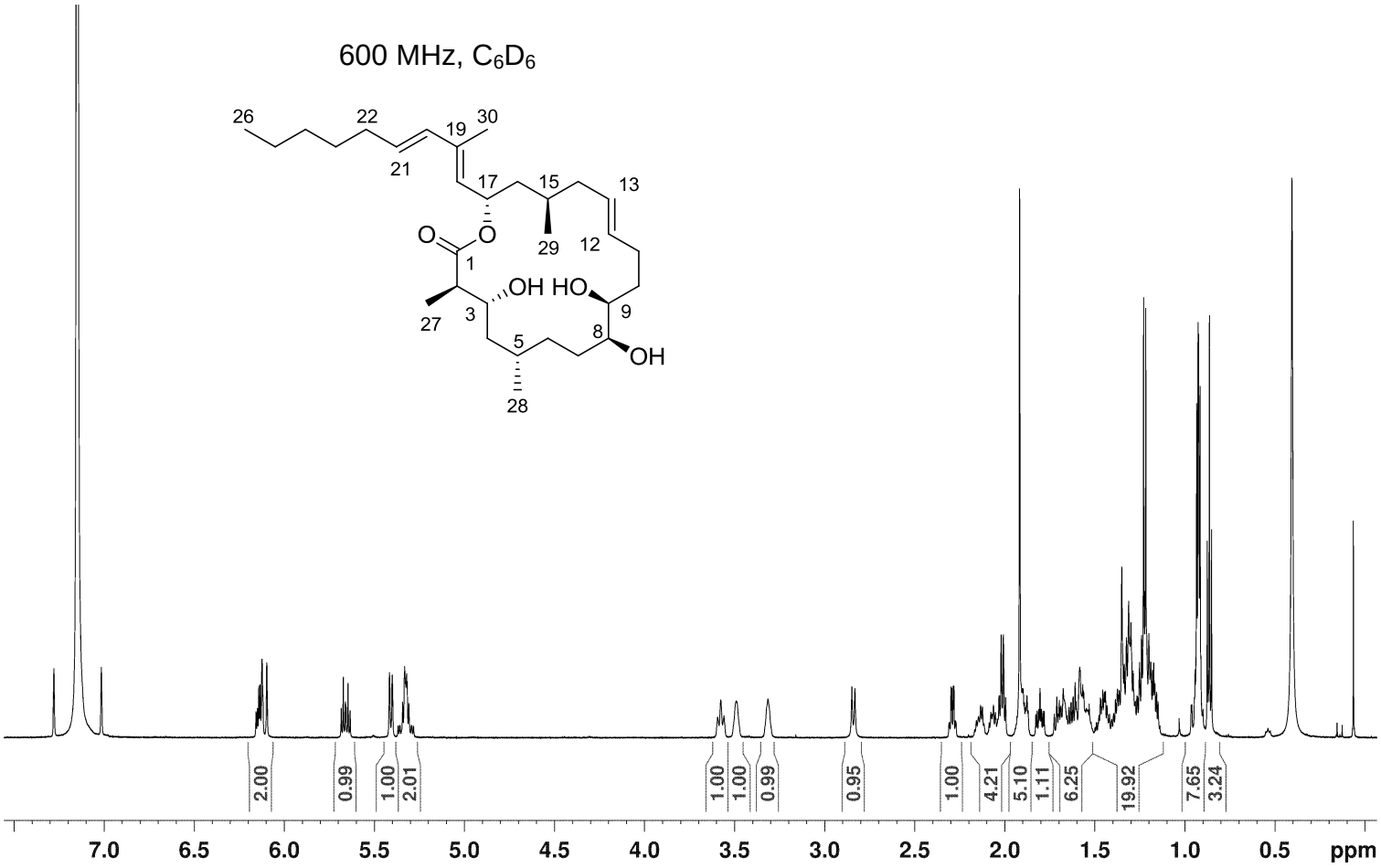

180.52
79.38
76.26
76.18
73.85
71.80
46.41
41.27
35.91
29.62
29.51
27.81
26.11
19.75
18.32
18.30
18.26
15.96
11.01
3.38
-3.93
-4.02
100 MHz, C6D6
HO
O
TBSO
OTBS
OTBS
200
150
100
50
0

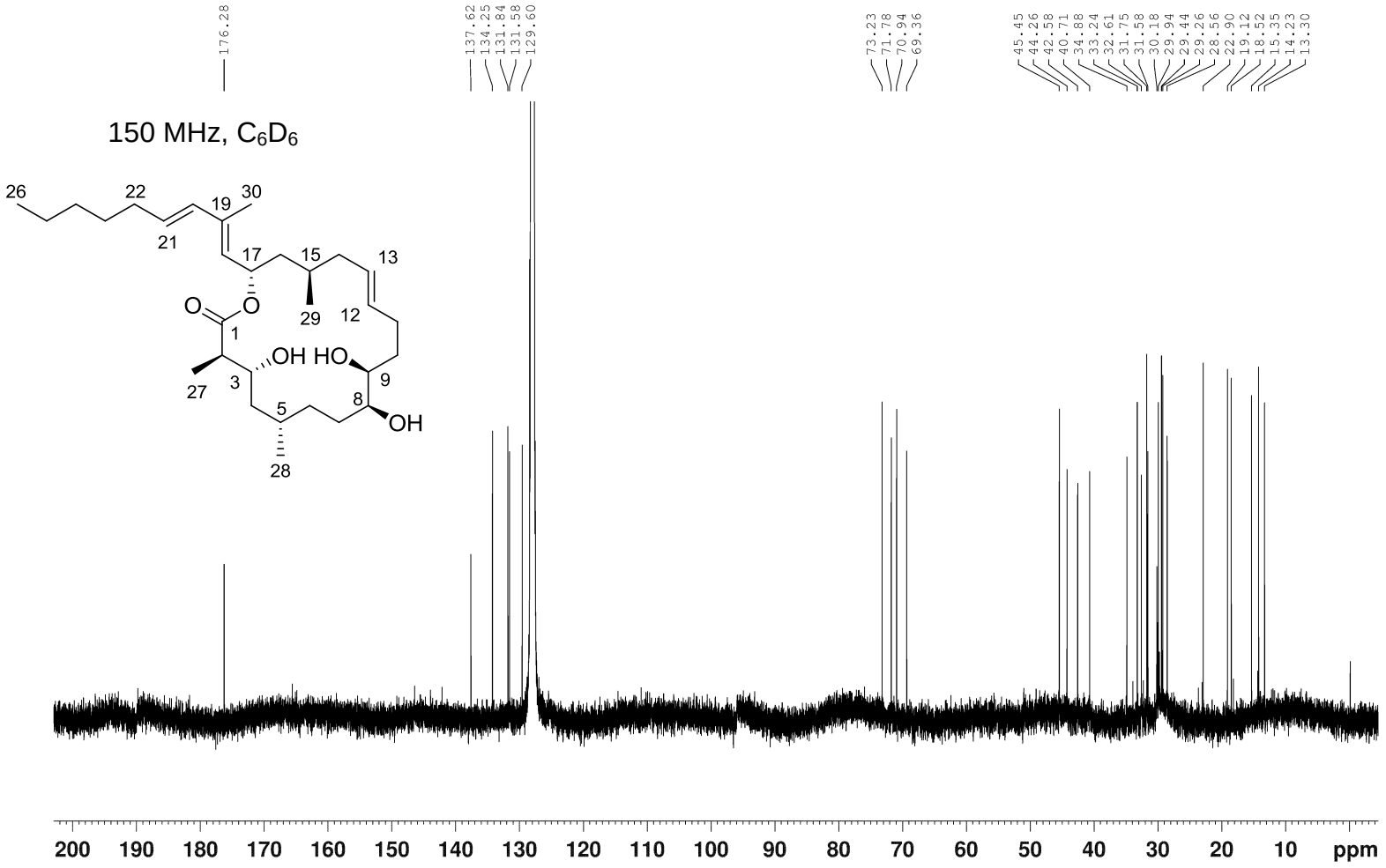

400 MHz, C6D6
O
O
TBSO
OTBS
OTBS
1.99
1.03
1.00
0.99
1.01
1.00
0.95
1.98
5.50
3.45
2.84
20.33
5.72
27.25
3.30
18.36
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

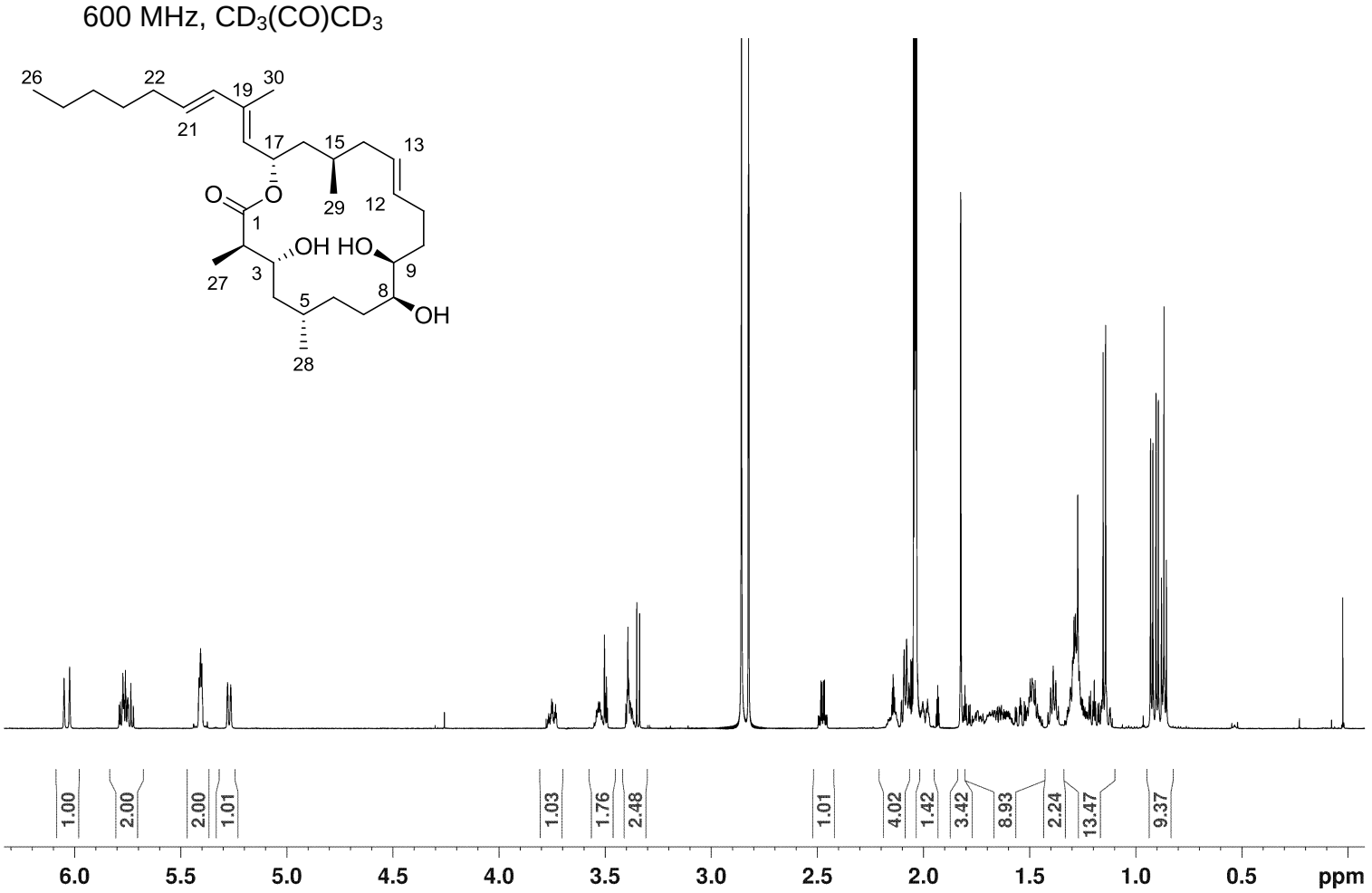

172.84
137.38
134.50
131.14
128.74
79.41
77.50
77.08
76.20
76.15
73.91
71.52
69.49
46.80
41.72
40.68
36.15
33.25
31.79
29.72
29.67
29.52
29.47
27.96
26.88
26.16
26.12
22.92
19.69
19.61
18.34
18.27
15.97
14.22
13.36
10.27
3.45
3.37
-3.84
-3.87
-4.30
100 MHz, C6D6
O
O
TBSO
OTBS
OTBS
200
150
100
50
0
-50

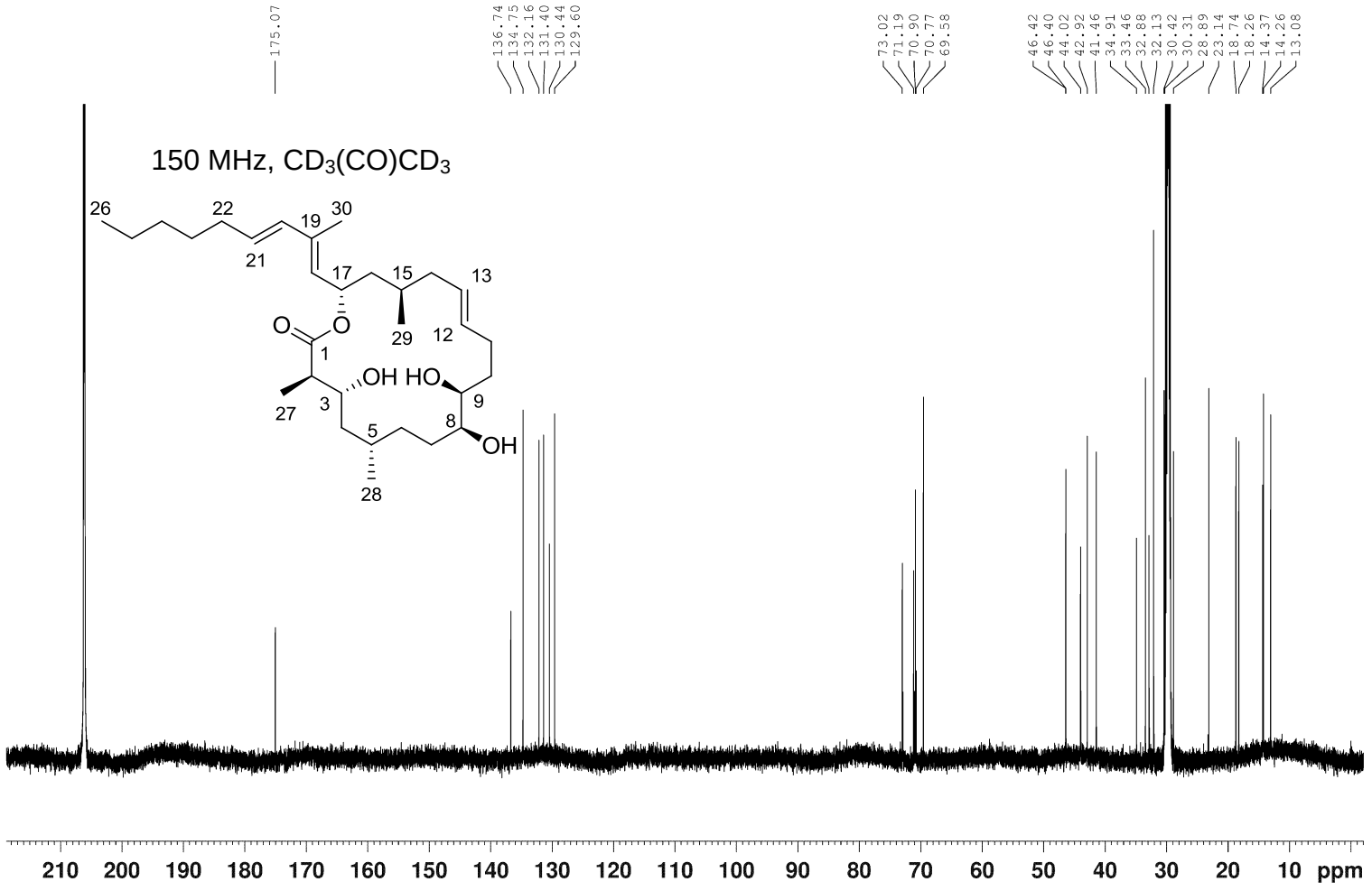

600 MHz, C6D6
26
22
19
30
21
17
15
13
O
O
29
12
1
TBSO
27
3
OTBS
9
5
8
OTBS
28
0.89
0.84
0.95
0.84
0.82
0.84
0.90
0.85
1.00
1.09
14.73
1.43
1.28
14.03
40.03
17.98
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


172.45
137.07
134.45
131.08
128.93
81.26
79.38
74.51
72.76
71.12
69.36
47.07
42.04
41.45
33.79
33.23
32.71
31.74
30.86
29.76
29.48
29.34
26.92
26.17
26.13
22.90
19.19
18.75
18.45
18.41
18.38
15.41
14.23
13.32
11.99
-3.75
-3.91
-4.01
-4.03
-4.06
150 MHz, C6D6
26
22
19
30
21
17
15
13
O
O
1
29
12
TBSO
9
27
3
OTBS
8
5
OTBS
28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


600 MHz, C6D6
26
22
19
30
21
17
15
13
O
O
29
12
1
OH HO
27
3
9
8
5
OH
28
2.00
0.99
1.00
2.01
1.00
1.00
0.99
0.95
1.00
4.21
5.10
1.11
6.25
19.92
7.65
3.24
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


176.28
137.62
134.25
131.84
131.58
129.60
73.23
71.78
70.94
69.36
45.45
44.26
42.58
40.71
34.88
33.24
32.61
31.75
31.58
30.18
29.94
29.44
29.26
28.56
22.90
19.12
18.52
15.35
14.23
13.30
150 MHz, C6D6
26
22
19
30
21
17
15
13
O
O
29
12
1
OH HO
27
3
9
8
5
OH
28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


600 MHz, CD3(CO)CD3
26
22
19
30
21
17
15
13
O
O
29
12
1
OH HO
27
3
9
8
5
OH
28
1.00
2.00
2.00
1.01
1.03
1.76
2.48
1.01
4.02
1.42
3.42
8.93
2.24
13.47
9.37
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


175.07
136.74
134.75
132.16
131.40
130.44
129.60
73.02
71.19
70.90
70.77
69.58
46.42
46.40
44.02
42.92
41.46
34.91
33.46
32.88
32.13
30.42
30.31
28.89
23.14
18.74
18.26
14.37
14.26
13.08
150 MHz, CD3(CO)CD3
26
22
19
30
21
17
15
13
O
O
29
12
1
OH HO
27
3
9
8
5
OH
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm