ELECTRONIC SUPPORTING INFORMATION (ESI)

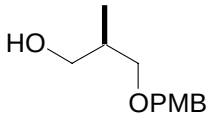
A Highly Stereoselective Synthesis of the C10-C23 fragment of Dictyostatin

Chiara Monti, Ofer Sharon and Cesare Gennari*

Dipartimento di Chimica Organica e Industriale, Centro di Eccellenza C.I.S.I., Università degli Studi di Milano, Via G. Venezian, 21, 20133 Milano, Italy. E-mail: cesare.gennari@unimi.it; Fax: +39 02 5031 4072; Tel: +39 02 5031 4091

General procedure:

All reactions were carried out in oven or flame-dried glassware under an argon atmosphere, unless otherwise noted. All commercially available reagents were used as received. The solvents were dried by distillation over the following drying agents and were transferred under nitrogen: CH_3CN (CaH_2), CH_2Cl_2 (CaH_2), $(CH_2Cl)_2$ (CaH_2), MeOH (CaH_2), Et_3N (CaH_2), *i*Pr_2EtN (CaH_2), $HN(TMS)_2$ (CaH_2), THF (Na), Et_2O (Na), benzene (Na), toluene (Na), *n*-hexane (Na). Organic extracts were dried over anhydrous Na_2SO_4. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using silica gel 60 F_{254} precoated glass plates (0.25 mm thickness) or basic alumina supported on aluminium foils. Flash chromatography was performed with silica gel 60Å (particle size 0.040- 0.062 mm) following the procedure by Still and co-workers.[1] Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Proton NMR spectra were recorded on 400 MHz spectrometers. Proton chemical shifts are reported in ppm (δ) with the solvent reference relative to tetramethylsilane (TMS) employed as the internal standard ($CDCl_3$, δ 7.26 ppm). The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, dd = doublet of doublet. Carbon NMR spectra were recorded on 400 (100 MHz) spectrometers with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.0). Infrared spectra were recorded on a standard Infrared Spectrophotometer; peaks are reported in cm^{-1}. Optical rotation values were measured on an automatic polarimeter at the sodium D line. High resolution mass spectra (HRMS) were performed on a hybrid quadrupole time of flight mass spectrometer equipped with an ESI ion source. A Reserpine solution 100 pg/µl (about 100 count/s), 0.1% HCOOH/CH_3CN 1:1, was used as reference compound (Lock Mass).

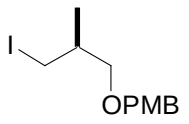


6

$C_{12}H_{18}O_3$
Exact Mass: 210,13
Mol. Wt.: 210,27

Alcohol **6** was prepared from methyl (*S*)-3-benzyloxy-2-methylpropionate following a procedure described by Smith III and co-workers.[2,3]

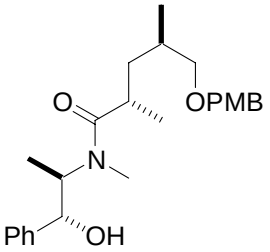
[1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.
[2] A. B. Smith III, T. J. Beauchamp, M. J. LaMarche, M. D. Kaufman, Y. Qiu, H. Arimoto, D. R. Jones, K. Kobayashi, *J. Am. Chem. Soc*. **2000**, *122*, 8654-8664.
[3] L. -S. Deng, X. -P. Huang, G. Zhao, *J. Org. Chem.* **2006**, *71*, 4625, and references therein.



$C_{12}H_{17}IO_2$
Exact Mass: 320,03
Mol. Wt.: 320,17

7

1-((*S*)-3-Iodo-2-methyl-propoxymethyl)-4-methoxy-benzene (**7**).
Imidazole and triphenylphosphine were crystallized from ethanol prior to use.
Imidazole (769 mg, 11.3 mmol, 2.5 equiv), triphenylphosphine (2.96 g, 11.3 mmol, 2.5 equiv) and iodine (2.29 g, 9.04 mmol, 2 equiv)[4] were added sequentially to a solution of the alcohol (950 mg, 4.52 mmol, 1 equiv) in a mixture of diethyl ether : acetonitrile 2:1 (90 mL). The reaction mixture was stirred for 1.5 h at room temperature and then quenched with a saturated aqueous solution of sodium thiosulfate. The organic phase was separated and the aqueous layer extracted with diethyl ether (2 x 30 mL). The combined organic phases were washed with brine and dried over Na_2SO_4, and concentrated. Purification of the crude product by flash chromatography (*n*-hexane/diethyl ether 98/2) afforded the iodide **7** (1.37 g, 4.29 mmol, 95%) as a colorless liquid.[5]
$[\alpha]_D^{27}$ = + 9.7 (c 0.53, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28 (2H, d, *J* = 8.6 Hz), 6.90 (2H, d, *J* = 8.6 Hz), 4.47 (2H, s), 3.83 (3H, s), 3.41-3.26 (4H, m), 1.82-1.74 (1H, m), 1.00 (3H, d, *J* = 6.7 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.9, 131.1, 130.0, 114.5, 74.5, 73.6, 56.0, 35.8, 18.4, 14.9; FT-IR (film): ν= 2855, 1608, 1505, 1243, 1088, 808 cm^{-1}; HRMS (FAB$^+$) calcd. for $C_{12}H_{17}O_2I$ (M^+) 320.0273. found 320.0272; HRMS (ESI): calcd for $C_{12}H_{17}O_2INa$: 343.01654 [*M*+Na]$^+$; found: 343.01625 (resolution 68400).



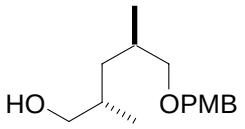
$C_{25}H_{35}NO_4$
Exact Mass: 413,26
Mol. Wt.: 413,55

8

(2*S*,4*R*)-5-(4-Methoxy-benzyloxy)-2,4-dimethyl-pentanoic acid ((1*R*,2*R*)-2-hydroxy-1-methyl-2-phenyl-ethyl)-methyl-amide (**8**).
Lithium chloride was flame dried under vacuum.[6]
A solution of *n*-butyllithium in hexanes (1.6 M, 7.5 mL, 12 mmol, 4.0 equiv) was slowly added to a suspension of lithium chloride (1.6 g, 38.1 mmol, 12.7 equiv) and diisopropylamine (1.8 mL, 12.9 mmol, 4.3 equiv) in dry THF (16 mL) at 0 °C. After 30 min at 0 °C, the suspension was cooled to –78 °C. An ice-cooled solution of the Myers amide (1.39 g, 6.3 mmol, 2.1 equiv) in THF (12 mL, followed by a 2-mL rinse) was added. The mixture was stirred at -78 °C for 1 h, at 0 °C for 15 min, and at 23 °C for 5 min. The mixture was cooled to 0 °C, and the iodide (0.96 g, 3 mmol, 1 equiv) was added neat to the reaction. After 5 minutes, the ice bath was removed and the suspension stirred for 18/20 h at room temperature. The reaction mixture was than treated with half-saturated aqueous ammonium chloride solution (20 mL), and the resulting mixture was extracted with ethyl acetate (4

[4] P. J. Garegg, B. Samuelson, *J. Chem. Soc. Perkin 1* **1980**, 2866; S. Kawahara, M. J. Gaunt, A. Scolaro, S. Yamanoi, S. V. Ley, *Synlett* **2005**, 2031.
[5] J. D. White, M. Kawasaki, *J. Org. Chem.* **1992**, *57*, 5292.
[6] A. G. Myers, B. H. Yang, H. Chen, L. McKinstry, D. J. Kopecky, J. L. Gleason, *J. Am. Chem. Soc.* **1997**, *119,* 6496; B. G. Vong, S. Abraham, A. X. Xiang, E. A. Theodorakis, *Org. Lett.* **2003**, *5*, 1617; X. -T. Zhou, L. Lu, D. P. Furkert, C. E. Wells, R. G. Carter, *Angew. Chem. Int. Ed.* **2006**, *45*, 7622-7626.

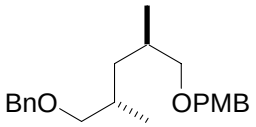
x 15 mL). The combined organic extracts were dried over sodium sulfate and concentrated. Purification of the residue by flash column chromatography (*n*-hexane/EtOAc, 65/35) afforded the amide **8** as a highly viscous, yellow oil containing mixture of rotamers (1.14 g, 2.74 mmol, 92%). (Minor resonances are denoted by an asterisk).
$[\alpha]_D^{20}$= –43.02 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-6.85 (9H, m), 4.62 (1H, t, J = 7.2 Hz), 4.50-4.47 (1H, m) 4.43 (3H, s), 3.83 (2.7H, s), 3.81* (0.3H, s), 3.36-3.21 (2H, m), 2.89* (0.3H, s), 2.84 (2.7H, s), 2.79-2.74 (0.7H, m), 2.69-2.63* (0.3H, m), 1.83-1.71 (2H, m), 1.13 (3H, d, J = 6.8 Hz), 1.10 (2.7H, d, J = 6.8 Hz), 0.99* (0.3H, d, J = 6.8 Hz), 0.95* (0.3H, d, J = 6.8 Hz), 0.89 (2.7H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$), δ 179.8, 159.7, 143.2, 141.8*, 131.4, 130.0*, 129.8, 129.4*, 129.0, 128.2, 127.7*, 127.0, 114.4, 77.2, 76.8*, 76.2, 75.9*, 73.3, 58.8*, 56.0, 39.7*, 38.8, 34.9*, 34.7, 32.6*, 31.8, 27.6, 19.7, 19.0, 18.4, 18.3, 16.2, 15.1; FT-IR (CCl_4): ν= 3413, 3299, 2934, 2847, 1742, 1628, 1612, 1513, 1464, 1248, 1084, 1041 cm^{-1}; HRMS (ESI): calcd for $C_{25}H_{35}NaNO_4$: 436.24583 [M+Na]$^+$; found: 436.24541 (resolution 53100).



9

$C_{15}H_{24}O_3$
Exact Mass: 252,17
Mol. Wt.: 252,35

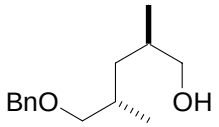
(2*S*,4*R*)-5-(4-Methoxy-benzyloxy)-2,4-dimethyl-pentan-1-ol (**9**).
A solution of *n*-butyllithium in hexanes (1.6 M, 6.6 mL, 10.6 mmol, 3.9 equiv) was added to a solution of diisopropylamine (1.6 mL, 11.4 mmol, 4.2 equiv) in dry tetrahydrofuran (11 mL) at 0 °C. After 30 min at 0°C, borane-ammonia complex (90%, 336 mg, 10.9 mmol, 4.0 equiv) was added in one portion, and the suspension was stirred at 0 °C for 15 min and then warmed up to 23 °C. After 15 min, the suspension was cooled to 0 °C and a solution of the amide (1.13 g, 2.72 mmol, 1 equiv) in tetrahydrofuran (5 mL, followed by a 2-mL rinse) was added over 5 min. The reaction mixture was warmed to 23 °C, kept at that temperature for 2 h, and then cooled to 0 °C where excess hydride was quenched by the careful addition of 3 N aqueous hydrochloric acid solution (25 mL). The mixture was stirred for 30 min at 0 °C and then extracted with four 60-mL portions of diethyl ether. The combined organic extracts were washed sequentially with 3N aqueous hydrochloric acid solution (30 mL), 2 N aqueous sodium hydroxide solution (20 mL), and brine (20 mL). The ether extracts were dried over sodium sulfate and concentrated. Purification of the residue by flash column chromatography (*n*-hexane/ethyl acetate, 60/40) afforded the alcohol **9** as a colorless oil (652 mg, 2.58 mmol, 95% yield).
$[\alpha]_D^{20}$= –5.43 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (2H, d, J = 8.5 Hz), 6.90 (2H, d, J = 8.5 Hz), 4.45 (2H, s), 3.82 (3H, s), 3.50-3.39 (2H, m), 3.32-3.21 (2H, m), 1.90 (1H, br. s), 1.89-1.82 (1H, m), 1.75-1.67 (1H, m), 1.52-1.45 (1H, m), 0.99-0.89 (1H, m), 0.96 (3H, d, J = 5.2 Hz), 0.95 (3H, d, J = 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 131.3, 129.8, 114.4, 76.3, 73.4, 68.5, 55.9, 38.3, 33.9, 31.7, 18.8, 18.3; FT-IR (CCl_4): ν= 3640, 3466, 2954, 2872, 1613, 1513, 1462, 1301, 1098, 1040 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{24}NaO_3$: 275.16177 [M+Na]$^+$; found: 275.16153 (resolution 84000).



$C_{22}H_{30}O_3$
Exact Mass: 342,22
Mol. Wt.: 342,47

10

1-((2*R*,4*S*)-5-Benzyloxy-2,4-dimethyl-pentyloxymethyl)-4-methoxy-benzene (**10**).
A solution of the alcohol (563 mg, 2.23 mmol) in dry THF (2 mL) was added to a suspension of NaH (178.4 mg of 60% in oil, 4.46 mmol, 2 equiv) in THF (12 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 1.5 h, and then recooled to 0 °C before the addition of BnBr (397 μL, 3.34 mmol, 1.5 equiv) and *n*-Bu_4NI (24.7 mg, 0.067 mmol, 0.03 equiv).[7] The reaction mixture was allowed to warm to 25 °C and stirred for 11 h. After the excess NaH was quenched by the addition of MeOH (1 mL), the reaction mixture was diluted with diethyl ether (20 mL), washed with a saturated aqueous ammonium chloride solution (2 x 20 mL), dried (Na_2SO_4), and concentrated. The residue was purified by flash column chromatography (*n*-hexane/EtOAc 10/1) to afford the benzyl ether (633.9 mg, 1.85 mmol, 83%).
$[\alpha]_D^{20}$= –0.49 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.26 (7H, m), 6.91 (2H, d, *J* = 8.6 Hz), 4.53 (2H, d, *J* = 2.2 Hz), 4.46 (2H, d, *J* = 2.2 Hz), 3.84 (3H, s), 3.41-3.34 (2H, m), 3.27-3.20 (2H, m), 1.91 (2H, septet, *J* = 6.6 Hz), 1.55-1.48 (1H, m), 1.01 (3H, d, *J* = 6.6 Hz), 0.99 (3H, d, *J* = 6.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 139.5, 131.6, 129.7, 129..0, 128.2, 128.1, 114.4, 76.6, 76.3, 73.7, 73.3, 56.0, 38.9, 31.7, 18.8; FT-IR (CCl_4): ν= 3066, 3032, 2853, 2790, 1613, 1513, 1455, 1245, 1095, 1041 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{30}NaO_3$: 365.20872 [*M*+Na]$^+$; found: 365.20817 (resolution 63000).

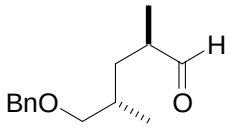


$C_{14}H_{22}O_2$
Exact Mass: 222,16
Mol. Wt.: 222,32

11

(2*R*,4*S*)-5-Benzyloxy-2,4-dimethyl-pentan-1-ol (**11**).
Ceric ammonium nitrate (2.66 g, 4.86 mmol, 3 equiv) was added at 0 °C, in four portions, to a solution of the PMB ether (555 mg, 1.62 mmol) in acetonitrile/water 4:1 (95 mL).[8] The temperature is maintained at 0°C for 15 min, than the reaction mixture was warmed to room temperature. After 2 h, the reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed with brine (100 mL) and water (100 mL). After drying (Na_2SO_4), filtration and concentration, flash chromatography (*n*-hexane/EtOAc 85/15) gave the product as a colourless oil (334.9 mg, 1.51 mmol, 93%).
$[\alpha]_D^{20}$= +6.85 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (5H, m), 4.52 (2H, d, *J*= 2 Hz), 3.54-3.42 (2H, m), 3.37-3.25 (2H, m), 1.93-1.83 (1H, m), 1.78-1.68 (1H, m), 1.54 (1H, br.s), 1.54-1.47 (2H, m), 0.99 (3H, d, *J*=6.8 Hz), 0.96 (3H, d, *J*= 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$), 139.3, 129.0, 128.2, 128.1, 76.5, 73.7, 68.7, 38.3, 34.0, 31.7, 18.3, 17.7; FT-IR (CCl_4): ν= 3640, 3488, 2957, 2926, 2872, 1496, 1455, 1362, 1097, 1028 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{22}NaO_2$: 245.15120 [*M*+Na]$^+$; found: 245.15070 (resolution 94400).

[7] K. C. Nicolaou, M. E. Bunnage, D. G. McGarry, S. Shi, P. K. Somers, P. A. Wallace, X. Chu, K. A. Agrios, J. L. Gunzner, Z. Yang, *Chem. Eur. J.* **1999**, *5,* 599.
[8] D. Enders, G. Geibel, S. Osborne, *Chem. Eur. J.* **2000**, *6,* 1302.

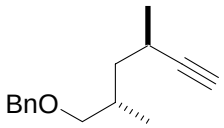


$C_{14}H_{20}O_2$
Exact Mass: 220,15
Mol. Wt.: 220,31

(2*R*,4*S*)-5-Benzyloxy-2,4-dimethyl-pentanal

Pyridine (270 µL, 3.34 mmol, 2.5 equiv) and DMP (681 mg, 1.6 mmol, 1.2 equiv)[9] were added to a 0 °C solution of the alcohol (298 mg, 1.34 mmol) in dichloromethane (7.5 mL). The reaction mixture was warmed to room temperature, and stirred for 1 h. The proceeding of the reaction was monitored by TLC, and on disappearance of the alcohol the reaction mixture was quenched by addition of $NaHCO_3$ and $Na_2S_2O_3$ (2.4 g, 9.76 mmol, 7.3 equiv). After stirring for 30 min, the phases were separated, and the aqueous phase was extracted with diethyl ether (3 x 30 mL). Combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The crude aldehyde was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (1H, d, *J*= 2.4 Hz), 7.38-7.28 (5H, m), 4.51 (2H, s), 3.32 (2H, d, *J*= 6.0 Hz), 2.51-2.44 (1H, m), 1.95-1.83 (2H, m), 1.25-1.16 (1H, m), 1.08 (3H, d, *J* = 6.9 Hz), 0.94 (3H, d, *J* = 6.6 Hz).



4

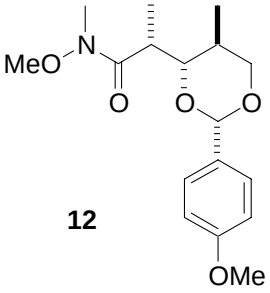
$C_{15}H_{20}O$
Exact Mass: 216,15
Mol. Wt.: 216,32

((2*S*,4*R*)-2,4-Dimethyl-hex-5-ynyloxymethyl)-benzene (**4**).

A solution of *n*-butyllithium in hexanes (1.6 M, 1.17 mL, 1.87 mmol, 1.4 equiv) was added to a solution of diisopropylamine (262 µL, 1.87 mmol, 1.4 equiv) in dry tetrahydrofuran (10 mL) at 0 °C. After 30 min at 0°C, the mixture was cooled to –78 °C, and trimethylsilyldiazomethane (2.0 M in diethyl ether, 935 µL, 1.87 mmol, 1.4 equiv) was added.[10] After 30 min, a solution of the aldehyde (1.34 mmol) in tetrahydrofuran (3.5 mL) was slowly added. After 1 h at –78 °C, the temperature was raised to 23 °C, and stirring was maintained overnight. The mixture was then poured into ice-cooled water, and extract with diethyl ether (3 x). Combined organic extracts were dried and concentrated. The residue was purified by flash column chromatography (*n*-hexane/EtOAc 100/1) to afford the product as a yellow oil (176.9 mg, 0.82 mmol, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (5H, m), 4.54 (2H, s), 3.39-3.30 (2H, m), 2.62-2.50 (1H, m), 2.20-2.08 (1H, m), 2.05 (1H, d, *J*= 2.4 Hz), 1.68-1.58 (1H, m), 1.23 (3H, d, *J* = 6.8 Hz), 1.22-1.17 (1H, m), 0.98 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 139.2, 128.7, 127.9, 127.8, 89.4, 76.5, 73.3, 68.8, 41.2, 32.0, 23.8, 22.0, 16.9; HRMS (ESI): calcd for $C_{15}H_{20}NaO$: 239.14064 [*M*+Na]$^+$; found: 239.14059 (resolution 97800).

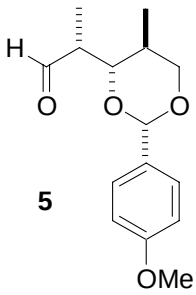
[9] D. B. Dess, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 7277-7287.
[10] K. Miwa, T. Aoyama, T. Shioiri, *Synlett* **1994**, 107-108.



12

$C_{17}H_{25}NO_5$
Exact Mass: 323,17
Mol. Wt.: 323,38

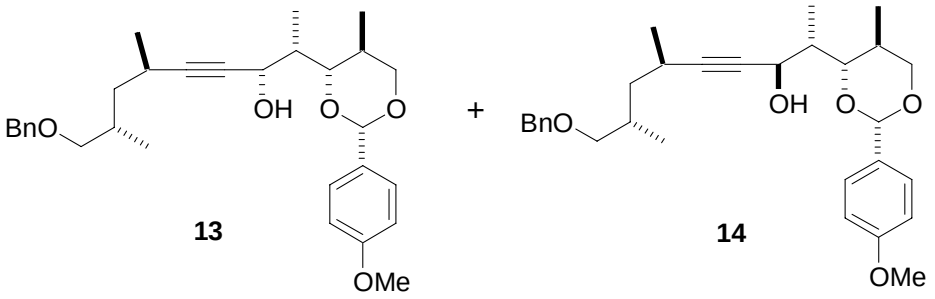
(*R*)-*N*-Methoxy-2-[(2*S*,4*S*,5*S*)-2-(4-methoxy-phenyl)-5-methyl-1,3-dioxinan-4-yl]-*N*-methyl-propionamide (**12**).[2]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, d, *J*= 8.8 Hz), 6.86 (2H, d, *J*= 8.8 Hz), 5.46 (1H, s), 4.03 (1H, dd, *J* = 11.3 Hz, 4.7 Hz), 3.82 (1H, dd, *J* = 9.8 Hz, 6.4 Hz), 3.78 (3H, s), 3.69 (3H, s), 3.51 (1H, t, *J* = 11.2 Hz), 3.21-3.14 (1H, m), 3.18 (3H, s), 2.00-1.89 (1H, m), 1.26 (3H, d, *J*= 7.0 Hz), 0.75 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 175.8, 159.7, 131.2, 127.2, 113.5, 100.7, 82.8, 72.8, 61.3, 55.2, 38.9, 33.7, 32.6, 13.0, 12.4.



5

$C_{15}H_{20}O_4$
Exact Mass: 264,14
Mol. Wt.: 264,32

Aldehyde **5** was prepared according to Smith III and co-workers.[2]
(*R*)-2-[(4*S*,5*S*)-2-(4-Methoxy-phenyl)-5-methyl-1,3-dioxinan-4-yl]-propionaldehyde (**5**).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (1H, s), 7.36 (2H, d, *J* = 8.6 Hz), 6.88 (2H, d, *J* = 8.6 Hz), 5.51 (1H, s), 4.17 (1H, dd, *J* = 11.2 Hz, *J* = 4.8 Hz), 4.09 (1H, dd, *J* = 10.0 Hz, *J* = 2.4 Hz), 3.81 (3H, s), 3.61 (1H, t, *J* = 11.2 Hz), 2.62-2.58 (1H, m), 2.14-2.10 (1H, m), 1.27 (3H, d, *J* = 7.2 Hz), 0.84 (3H, d, *J* = 6.8 Hz).

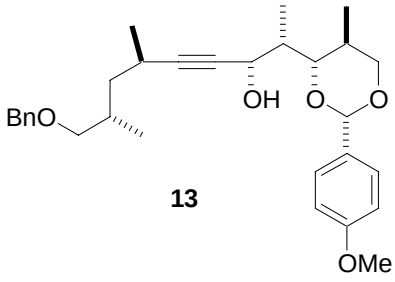


13 **14**

$C_{30}H_{40}O_5$
Exact Mass: 480,29
Mol. Wt.: 480,64

n-BuLi (1.6 M solution in hexane, 940 µL, 0.15 mmol, 1.5 equiv) was added slowly to a stirred solution of alkyne **4** (25.9 mg, 0.12 mmol, 1.2 equiv) in THF (2.0 mL) at –78 °C. The yellowish solution was stirred for 90 min at –78 °C. A solution of aldehyde **5** (26.4 mg, 0.10 mmol) in THF (0.35 mL) was added dropwise and the solution became colorless. The reaction was stirred overnight at –78 ON. A saturated NH_4Cl aqueous solution was then added, the layers were separated and the aqueous phase extracted with ether (3x4 mL). The combined organic extracts were dried over Na_2SO_4. Purification of the crude product by flash chromatography (*n*-

hexane/EtOAc 9/1) afforded a mixture of distereomeric propargylic alcohols **13** and **14** in a 7:3 ratio (29.3 mg, 0.061 mmol, 61%) as a colorless oil. The diastereomeric ratio was determined by NMR.



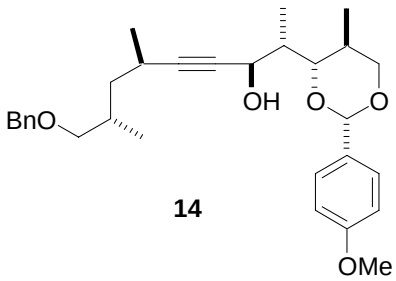
13

$C_{30}H_{40}O_5$
Exact Mass: 480,29
Mol. Wt.: 480,64

(2*S*,3*S*,6*R*,8*S*)-9-Benzyloxy-2-[(4*S*,5*S*)-2-(4-methoxy-phenyl)-5-methyl-1,3-dioxinan-4-yl]-6,8-dimethyl-non-4-yn-3-ol (**13**).[11,12]

Zinc triflate (474 mg, 1.3 mmol, 4.3 equiv) was flame-dried under vacuum; (-)-*N*-methylephedrine (179.3 mg, 1 mmol, 3.3 equiv) was added, and the flask was purged with nitrogen for 15 min. Toluene (6.6 ml) was added, followed by triethylamine (140 µl, 1 mmol, 3.3 equiv). After 2 hours, a solution of the alkyne (220 mg, 1 mmol, 3.3 equiv) in toluene (0.4 ml) was added. After 30 min, a solution of the aldehyde (79.3 mg, 0.3 mmol, 1 equiv) in toluene (1 ml) was slowly added through a syringe pomp over 6 hours.[13] The reaction mixture was left under stirring overnight. The reaction was monitored by TLC (benzene/diethyl ether 95/5). On disappearence of the aldehyde, the reaction mixture was quenched with a saturated aqueous solution of ammonium chloride (12 ml), and extracted with diethyl ether (3 x 15 ml). The combined organic extracts are dried and concentrated in vacuo. Purification of the crude product by flash chromatography (*n*-hexane/EtOAc 8/2) afforded afforded diastereoisomerically pure propargylic alcohol **13** (96.6 mg, 0.2 mmol, 67%) as a colorless oil.

$[\alpha]_D^{20}$= + 35.89 (*c* 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.68 (2H, d, *J* = 8.6 Hz), 7.43-7.18 (5H, m), 6.89 (2H, d, *J* = 8.6 Hz), 5.61 (1H, s), 4.75 (1H, d, *J* = 5.6 Hz), 4.46 (2H, s), 4.02 (1H, dd, *J* = 11.2 Hz, *J* = 4.8 Hz), 3.87 (1H, dd, *J* = 10.0 Hz, *J* = 2.0 Hz), 3.43-3.34 (1H, m), 3.34 (3H, s), 3.31-3.16 (2H, m), 2.69-2.62 (1H, m), 2.43-2.38 (1H, m), 2.25 (1H, br. s), 2.05-1.97 (2H, m), 1.84-1.77 (1H, m), 1.38 (3H, d, *J* = 6.8 Hz), 1.25 (3H, d, *J* = 6.8 Hz), 1.22-1.12 (1H, m), 1.07 (3H, d, *J* = 6.8 Hz), 0.45 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, C_6D_6) 161.2, 136.7, 132.4, 129.0, 114.3, 102.0, 89.7, 85.8, 82.7, 76.7, 73.6, 67.0, 55.2, 41.8, 41.7, 32.8, 31.2, 24.5, 22.6, 17.1, 12.1, 9.2; FT-IR ($CHCl_3$): ν = 3501, 3040, 3024, 2969, 2933, 2874, 2851, 1732, 1615, 1518, 1462 cm^{-1}; HRMS (ESI): calcd for $C_{30}H_{40}O_5Na$: 503.27680 $[M+Na]^+$; found: 503.27575 (resolution 45700).



14

$C_{30}H_{40}O_5$
Exact Mass: 480,29
Mol. Wt.: 480,64

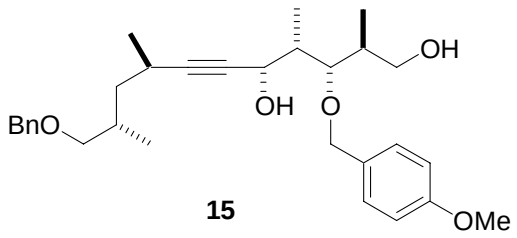
[11] D. E. Frantz, R. Fässler, E. M. Carreira, *J. Am. Chem. Soc.* **2000**, *122*, 1806 –1807; E. El-Sayed, N. K. Anand, E. M. Carreira, *Org. Lett.* **2001**, *3*, 3017-3020; D. Boyall, D. E. Frantz, E. M. Carreira, *Org. Lett.* **2002**, *4*, 2605-2606, and references therein.

[12] For high "reagent-control" in the Carreira alkynylation reaction between two chiral coupling partners, see: N. Kojima, N. Maezaki, H. Tominaga, M. Yanai, D. Urabe, T. Tanaka, *Chem. Eur. J.* **2004**, *10*, 672-680; H. Tominaga, N. Maezaki, M. Yanai, N. Kojima, D. Urabe, R. Ueki, T. Tanaka, *Eur. J. Org. Chem.* **2006**, 1422-1429.

[13] B. J. Albert, A. Sivaramakrishnan, T. Naka, N. L. Czaicki, K. Koide, *J. Am. Chem. Soc.* **2007**, *129*, 2648-2659.

(2*S*,3*R*,6*R*,8*S*)-9-Benzyloxy-2-[(4*S*,5*S*)-2-(4-methoxy-phenyl)-5-methyl-1,3-dioxinan-4-yl]-6,8-dimethyl-non-4-yn-3-ol (**14**).[11]

Zinc triflate (474 mg, 1.3 mmol, 4.3 equiv) was flame-dried under vacuum; (+)-*N*-methylephedrine (179.3 mg, 1 mmol, 3.3 equiv) was added, and the flask was purged with nitrogen for 15 min. Toluene (6.6 ml) was added, followed by triethylamine (140 µl, 1 mmol, 3.3 equiv). After 2 hours, a solution of the alkyne (220 mg, 1 mmol, 3.3 equiv) in toluene (0.4 ml) was added. After 30 min, a solution of the aldehyde (79.3 mg, 0.3 mmol, 1 equiv) in toluene (1 ml) was slowly added. The reaction mixture was left under stirring overnight. The reaction was monitored by TLC (benzene/diethyl ether 95/5). On disappearence of the aldehyde, the reaction mixture was quenched with a saturated aqueous solution of ammonium chloride (12 ml), and extracted with diethyl ether (3 x 15 ml). The combined organic extracts are dried and concentrated in vacuo. Purification of the crude product by flash chromatography (*n*-hexane/EtOAc 8/2) afforded a mixture of distereomeric propargylic alcohols **13** and **14** in a 7:93 ratio (7.2 mg, 0.015 mmol, 5%) as a colorless oil. The diastereomeric ratio was determined by NMR.



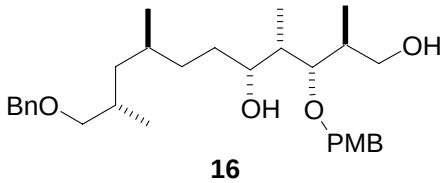
15

$C_{30}H_{42}O_5$
Exact Mass: 482,30
Mol. Wt.: 482,65

(2*S*,3*S*,4*S*,5*S*,8*R*,10*S*)-11-Benzyloxy-3-(4-methoxy-benzyloxy)-2,4,8,10-tetramethyl-undec-6-yne-1,5-diol (**15**).

A solution of PMP acetal (96.6 mg, 0.2 mmol) in dichloromethane (20 ml) is cooled to –20°C; DIBAL-H (1.0 M in hexane, 2.0 mL, 2 mmol, 10 equiv)[2] is added over 10 min. After 30 min, the temperature is raised to 0°C, and the reaction mixture is stirred for additional 2 hours. On completion of the reaction (TLC *n*-hexane/EtOAc 75/25) the mixture is quenched with saturated aqueous solution of Rochelle's salt (2.5 ml). After 1 hour under vigorous stirring, the reaction mixture is diluted with diethyl ether (190 ml) and washed with a saturated aqueous solution of Rochelle's salt and brine, dried and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/EtOAc 85/25) to afford the product as a pale yellow oil (72.4 mg, 0.15 mmol, 75%).

$[\alpha]_D^{28}$= + 12.55 (*c* 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.43-7.19 (7H, m), 6.90 (2H, d, *J* = 8.8 Hz), 4.74 (2H, AB system, ν_A= 4.77, ν_B= 4.71, J_{AB} = 10.8 Hz), 4.52 (1H, dd, *J* = 7.2 Hz, *J* = 2.0 Hz), 4.45 (2H, s), 4.03-3.97 (1H, m), 3.81 (1H, dd, *J* = 10.8 Hz, *J* = 4.0 Hz), 3.69 (1H, dd, *J* = 10.8 Hz, *J* = 5.6 Hz), 3.41 (3H, s), 3.31-3.22 (2H, m), 2.66-2.60 (1H, m), 2.42-2.34 (2H, m + bs), 2.10-2.04 (2H, m), 1.81-1.74 (1H, m), 1.34 (3H, d, *J* = 6.8 Hz), 1.24 (3H, d, *J* = 6.8 Hz), 1.18-1.10 (1H, m), 1.06 (3H, d, *J* = 6.8 Hz), 0.97 (3H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, C_6D_6) 160.1, 139.7, 131.9, 130.0, 129.0, 114.6, 90.6, 83.9, 82.9, 76.8, 75.0, 73.7, 66.6, 66.0, 55.2, 43.8, 41.8, 39.2, 32.8, 24.5, 22.5, 17.1, 15.1, 10.9; FT-IR ($CHCl_3$): ν = 3048, 3024, 2963, 2932, 2874, 1730, 1613, 1514, 1455, 1263 cm^{-1}; HRMS (ESI): calcd for $C_{30}H_{42}O_5Na$: 505.29245 $[M+Na]^+$; found: 505.29115 (resolution 45400).



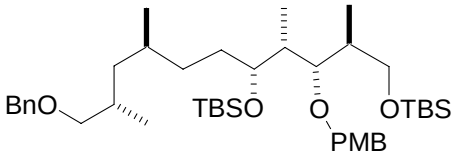
16

$C_{30}H_{46}O_5$
Exact Mass: 486,33
Mol. Wt.: 486,68

(2*S*,3*S*,4*S*,5*R*,8*S*,10*S*)-11-Benzyloxy-3-(4-methoxy-benzyloxy)-2,4,8,10-tetramethyl-undecane-1,5-diol (**16**).

Wilkinson's catalyst $Rh(PPh_3)_3Cl$ (13.9 mg, 0.015 mmol, 0.1 equiv)[14] was added to a degassed solution of diol **15** (72.4 mg, 0.15 mmol) in dry benzene (6 mL) in an autoclave. The reaction mixture was purged with hydrogen, and stirred overnight with 60 psi hydrogen pressure (approximately 4 bar H_2 pressure). Silica gel was added to the reaction mixture and the solvent was evaporated. Purification of the crude product by flash chromatography (*n*-hexane/EtOAc 7/3) afforded diol **16** (51.1 mg, 0.105 mmol, 70%) as a yellowish oil.

$[\alpha]_D^{28}$= + 14.50 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.44-7.19 (7H, m), 6.88 (2H, d, *J* = 8.6 Hz), 4.65 (2H, AB system, ν_A= 4.65, ν_B= 4.59, J_{AB} = 10.6 Hz), 4.47 (2H, d, *J* = 3.0 Hz), 3.82-3.78 (2H, m), 3.69-3.63 (2H, m), 3.40 (3H, s), 3.35 (1H, dd, *J* = 8.8 Hz, *J* = 5.6 Hz), 3.26 (1H, dd, *J* = 8.8 Hz, *J* = 6.4 Hz), 2.14-2.00 (2H, m), 1.86-1.56 (7H, m), 1.24-1.02 (1H, m), 1.16 (3H, d, *J* = 7.0 Hz), 1.12 (3H, d, *J* = 6.7 Hz), 1.04 (3H, d, *J* = 6.4 Hz), 1.01 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, C_6D_6). 160.3, 140.0, 131.4, 130.2, 129.0, 128.1, 128.0, 114.7, 86.2, 76.5, 75.5, 74.7, 73.6, 65.6, 55.2, 42.4, 40.4, 38.6, 34.1, 33.3, 31.9, 31.1, 21.1, 18.7, 15.2, 8.6; FT-IR (film): ν = 3442, 2955, 2928, 2871, 1738, 1613, 1514, 1455, 1374, 1301, 1247 cm^{-1}; HRMS (ESI): calcd for $C_{30}H_{46}O_5Na$: 509.32375 $[M+Na]^+$; found: 509.32290 (resolution 46200).



$C_{42}H_{74}O_5Si_2$
Exact Mass: 714,51
Mol. Wt.: 715,20

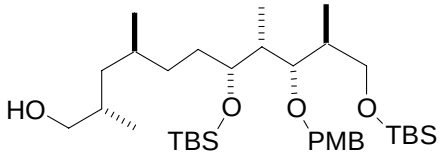
1-{(1*S*,2*R*,3*R*,6*S*,8*S*)-9-Benzyloxy-3-(*tert*-butyl-dimethyl-silanyloxy)-1-[(*S*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-methyl-ethyl]-2,6,8-trimethyl-nonyloxymethyl}-4-methoxy-benzene.

Freshly distilled 2,6-lutidine (93 µl, 0.8 mmol, 8 equiv) and TBSOTf (69 µl, 0.3 mmol, 3 equiv) were added to a stirred solution of diol **16** (48.6 mg, 0.1 mmol) in dichloromethane (2.5 mL) at -20 °C. The proceeding of the reaction was monitored by TLC *n*-hexane/EtOAc, 8/2. On completion of the reaction (approximately 1.5 hours), the mixture was quenched with a saturated NH_4Cl aqueous solution. The organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4 and evaporated. Purification of the crude product by flash chromatography (n-hexane/EtOAc 8/2) afforded the product (69.4 mg, 0.097 mmol, 97%) as a colorless oil.

$[\alpha]_D^{26}$= + 1.23 (*c* 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.48-7.19 (7H, m), 6.95 (2H, d, *J* = 8.4 Hz), 4.78 (2H, AB system, ν_A= 4.82, ν_B= 4.75, J_{AB} = 10.8 Hz), 4.48 (2H, d, *J* = 2.8 Hz), 3.99-3.93 (2H, m), 3.85-3.77 (2H, m), 3.42 (3H, s), 3.37 (1H, dd, *J* = 8.8 Hz, *J* = 5.6 Hz), 3.28 (1H, dd, *J* = 8.8 Hz, *J* = 6.4 Hz), 2.14-2.05 (3H, m), 1.90-1.59 (6H, m), 1.35-1.29 (1H, m), 1.34 (3H, d, *J* = 6.8 Hz), 1.21 (3H, d, *J* = 6.8 Hz), 1.18 (9H, s), 1.15 (3H, d, *J* = 6.8 Hz), 1.12 (9H, s), 1.07 (3H, d, *J* = 6.8 Hz), 0.40 (3H, s), 0.26 (6H, s), 0.19 (3H, s); ^{13}C NMR (100 MHz, C_6D_6). 160.0, 140.0, 132.6,

[14] D. J. Nelson, R. Li, C. Brammer, *J. Org. Chem.* **2005**, *70*, 761-767, and references therein; G. L. Nattrass, E. Diez, M. M. McLachlan, D. J. Dixon, S. V. Ley, *Angew. Chem. Int. Ed.* **2005**, *44*, 580-584.

129.4, 129.0, 114.5, 81.5, 76.5, 75.4, 74.7, 73.6, 65.5, 55.2, 42.3, 40.6, 39.8, 32.8, 32.2, 32.0, 31.3, 26.8, 26.7, 26.3, 21.2, 18.9, 18.7, 16.0, 11.0, 1.8, -3.4, -3.6, -4.7; FT-IR (film): ν = 2955, 2928, 2856, 1613, 1586, 1514, 1462, 1360, 1251 cm^{-1}; HRMS (ESI): calcd for $C_{42}H_{74}O_5Si_2Na$: 737.49670 $[M+Na]^+$; found: 737.49705 (resolution 31200).



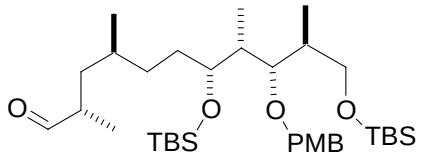
17

$C_{35}H_{68}O_5Si_2$
Exact Mass: 624,46
Mol. Wt.: 625,08

(2*S*,4*S*,7*R*,8*R*,9*S*,10*S*)-7,11-Bis-(*tert*-butyl-dimethyl-silanyloxy)-9-(4-methoxy-benzyloxy)-2,4,8,10-tetramethyl-undecan-1-ol (**17**).

Raney-Nickel[15] was washed with water until the washings were pH neutral and then rinsed five times with absolute EtOH. A solution of substrate (69.4 mg, 0.097 mmol) in absolute EtOH (6.5 mL) was added, the mixture was accurately degassed and then purged three times with hydrogen. After stirring for 24 h, the Raney-Nickel was removed by filtration and the filtrate purified by flash chromatography (*n*-hexane/EtOAc 9/1) to afford alcohol **17** (49.1 mg, 0.078 mmol, 81%) as a colorless oil.

$[\alpha]_D^{18}$= - 4.72 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.46 (2H, d, *J* = 8.4 Hz), 6.95 (2H, d, *J* = 8.4 Hz), 4.77 (2H, AB system, ν_A= 4.81, ν_B= 4.73, J_{AB} = 11.2 Hz), 4.00-3.91 (2H, m), 3.84-3.76 (2H, m), 3.44 (3H, s), 3.43-3.39 (1H, m), 3.32-3.27 (1H, m), 2.15-2.09 (2H, m), 1.90-1.42 (5H, m), 1.29 (3H, d, *J* = 7.2 Hz), 1.20 (3H, d, *J* = 7.2 Hz), 1.20-1.10 (2H, m), 1.17 (9H, s), 1.12 (9H, s), 1.04 (3H, d, *J* = 6.0 Hz), 1.01 (3H, d, *J* = 6.8 Hz), 1.04-0.93 (1H, m), 0.25 (6H, s), 0.19 (6H, s); ^{13}C NMR (100 MHz, C_6D_6) 160.0, 132.6, 129.5, 114.5, 81.4, 75.3, 74.7, 68.5, 65.5, 55.2, 41.8, 40.6, 39.8, 33.9, 32.7, 32.1, 31.3, 26.7, 21.2, 19.0, 18.9, 18.0, 16.0, 11.0, -3.4, -3.6, -4.7; FT-IR (film): ν = 3377, 2954, 2928, 2857, 1614, 1587, 1515, 1471, 1463, 1387, 1360, 1301, 1250 cm^{-1}; HRMS (ESI): calcd for $C_{35}H_{69}O_5Si_2$: 625.46780 $[M+H]^+$; found: 625.46921 (resolution 35500); calcd for $C_{35}H_{68}O_5Si_2Na$: 647.44975 $[M+Na]^+$; found: 647.44807 (resolution 35500).



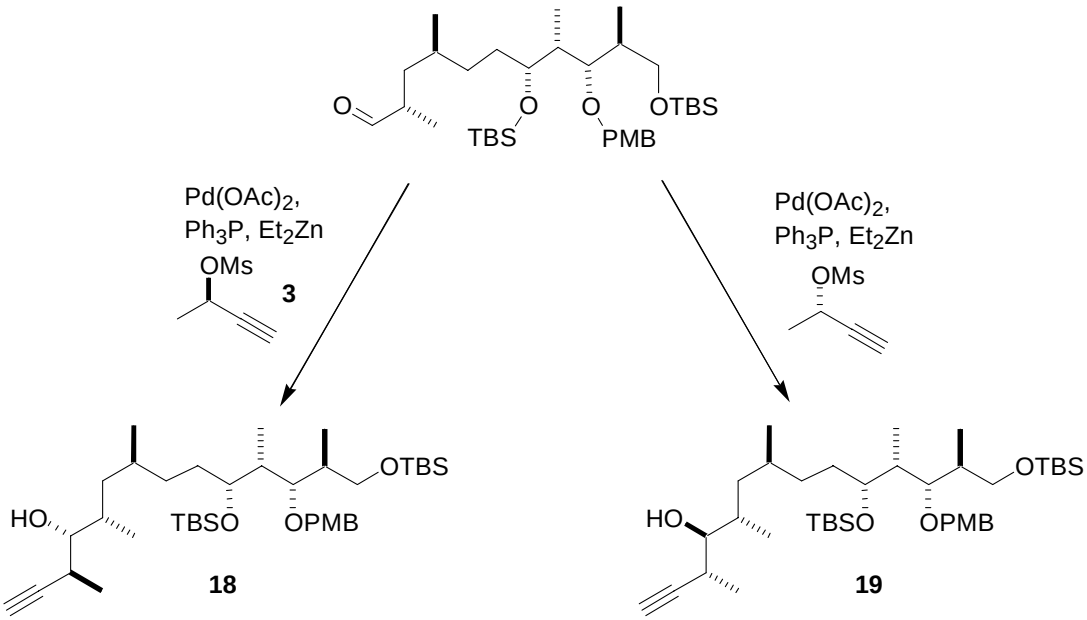
$C_{35}H_{66}O_5Si_2$
Exact Mass: 622,44
Mol. Wt.: 623,07

(2*S*,4*S*,7*R*,8*R*,9*S*,10*S*)-7,11-Bis-(*tert*-butyl-dimethyl-silanyloxy)-9-(4-methoxy-benzyloxy)-2,4,8,10-tetramethyl-undecanal.

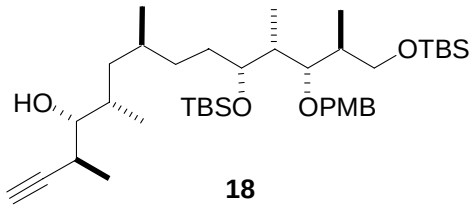
Solid TPAP (2.4 mg, 0.0068 mmol, 0.05 equiv) was added to a stirred solution of alcohol (84.4 mg, 0.135 mmol) and NMO (23.7 mg, 0.202 mmol, 1.5 equiv) in dichloromethane (270 μl), in presence of 4Å molecular sieves (500 mg/mmol), at room temperature, under nitrogen.[16] On completion of

[15] K. Horita, T. Yoshioka, T. Tanaka, Y. Oikawa, O. Yonemitsu, *Tetrahedron* **1986,** *42,* 3021; D. A. Evans, W. C. Trenkle, J. Zhang, J. D. Burch, *Org. Lett.* **2005**, *7*, 3335; D. R. Williams, K. Shamin, *Org. Lett.* **2005**, *7*, 4161.
[16] W. P. Griffith, S. V. Ley, G. P. Whitcombe, A. D. White, *J. Chem. Soc., Chem. Commun*. **1987**, 1625; S. V. Ley, J. Norman, W. P. Griffith, S. P. Marsden, *Synthesis* **1994**, 639-666.

the reaction, the mixture was filtered through a pad of celite, eluting EtOAc. The solvent was removed in vacuo, and the crude aldehyde was used without further purification (quantitative).
^{1}H NMR (400 MHz, C_6D_6) δ 9.44 (1H, d, J = 2.0 Hz), 7.44 (2H, d, J = 8.4 Hz), 6.95 (2H, d, J = 8.4 Hz), 4.76 (2H, AB system, ν_A= 4.81, ν_B= 4.72, J_{AB} = 11.2 Hz), 4.04-3.75 (4H, m), 3.46 (3H, s), 2.12-1.21 (7H, m), 1.24 (3H, d, J = 7.2 Hz), 1.20-1.10 (2H, m), 1.17 (3H, d, J = 7.2 Hz), 1.15 (9H, s), 1.11 (9H, s), 1.10 (3H, d, J = 6.4 Hz), 1.04-0.90 (1H, m), 0.98 (3H, d, J = 7.2 Hz), 0.38 (6H, s), 0.18 (6H, s).



In the Marshall-Tamaru reaction [$Pd(OAc)_2$, PPh_3, Et_2Zn, and either (*R*)-mesyl-butynol or (*S*)-mesyl-butynol] high diastereoselectivity is observed with *both* enantiomers of the mesyl-butynol, leading to the *anti, anti* and the *anti, syn* adducts. The preference for the *anti* transition state overrides Felkin-Anh consideration in these additions with a resulting absence of mismatching. Both the additions are therefore highly stereoselective.[17]

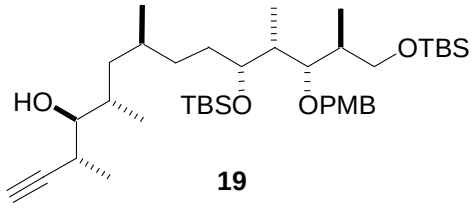


$C_{39}H_{72}O_5Si_2$
Exact Mass: 676,49
Mol. Wt.: 677,16

(3*S*,4*R*,5*S*,7*S*,10*R*,11*R*,12*S*,13*S*)-10,14-Bis-(*tert*-butyl-dimethyl-silanyloxy)-12-(4-methoxy-benzyloxy)-3,5,7,11,13-pentamethyl-tetradec-1-yn-4-ol (18).[17] [*Anti*, *syn* adduct][18]

[17] Y. Tamaru, S. Goto, A. Tanaka, M. Shimizu, M. Kimura, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 878-880; J. A. Marshall, N. D. Adams, *J. Org. Chem.* **1998**, *63*, 3812-3813; J. A. Marshall, N. D. Adams, *J. Org. Chem.* **1999**, *64*, 5201; J. A. Marshall, C. M. Grant, *J. Org. Chem.* **1999**, *64*, 8214; J. A. Marshall, *Chem. Rev.* **2000**, *100*, 3163; J. A. Marshall, G. M. Schaaf, *J. Org. Chem.* **2001**, *66*, 7825-7831; J. A. Marshall, H. R. Chobanian, M. M. Yanik, *Org. Lett*. **2001**, *3*, 3369; J. A. Marshall, N. D. Adams, *J. Org. Chem.* **2002**, *67*, 733; J. A. Marshall, K. Ellis, *Tetrahedron Lett*. **2004**, *45*, 1351; J. A. Marshall, G. Schaaf, A. Nolting, *Org. Lett*. **2005**, *7*, 5331; J. A. Marshall, P. Eidam, H. Schenck Eidam, *J. Org. Chem.* **2006**, *71*, 4840; A. Fürstner, C. Nevado, M. Tremblay, C. Chevrier, F. Teply, C. Aïssa, M. Waser, *Angew. Chem. Int. Ed.* **2006**, *45,* 5837-5942.
[18] J. A. Marshall, K. Maxson, *J. Org. Chem.* **2000**, *65*, 630-633.

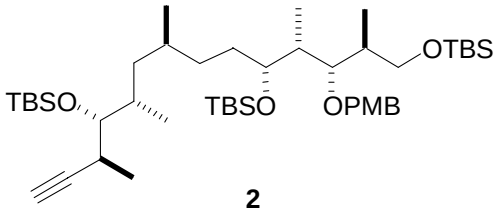
Triphenylphosphine (recrystallized from ethanol prior to use, 1.2 mg, 0.0045 mmol, 0.05 equiv), the crude aldehyde (56.0 mg, 0.09 mmol) and (*R*)-mesyl-butynol (20.0 mg, 0.135 mmol, 1.5 equiv) were subsequentially added to a cooled (-78°C) solution of $Pd(OAc)_2$ (1.0 mg, 0.0045 mmol, 0.05 equiv) in tetrahydrofurane (0.9 ml). Diethylzinc (1.0M in hexane, 270 µl, 0.27 mmol, 3 equiv) was added over 15 min. After 10 min., the temperature was raised to –20°C, and the reaction mixture was left overnight under stirring at –20°C. The mixture was than quenched with NH_4Cl/Et_2O 1/1. The Et_2O layer was washed with brine, dried and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/EtOAc 95/5) to afford the product as a yellow oil (50.2 mg, 0.074 mmol, 82% over two steps) with very high diastereoselectivity (>98:2).
$[\alpha]_D^{22}$= - 4.51 (*c* 0.605, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.49 (2H, d, J = 8.4 Hz), 6.97 (2H, d, J = 8.8 Hz), 4.80 (2H, AB system, ν_A= 4.83, ν_B= 4.77, J_{AB} = 10.8 Hz), 4.00-3.92 (2H, m), 3.87-3.80 (2H, m), 3.43 (3H, s), 3.28 (1H, dd, J = 10.8 Hz, J = 6.0 Hz), 2.67-2.62 (1H, m), 2.19-2.11 (2H, m), 1.95-1.62 (9H, m), 1.31 (3H, d, J = 6.9 Hz), 1.22 (3H, d, J = 6.9 Hz), 1.18 (9H, s), 1.17 (3H, d, J = 6.8 Hz), 1.13 (9H, s), 1.06 (3H, d, J = 6.8 Hz), 1.04 (3H, d, J = 6.8 Hz), 0.27 (6H, s), 0.20 (6H, s); ^{13}C NMR (100 MHz, C_6D_6) 160.0, 132.6, 129.5, 114.5, 86.6, 81.4, 77.5, 75.5, 74.6, 71.7, 65.5, 55.2, 42.1, 40.7, 39.9, 33.6, 32.7, 32.1, 31.7, 31.0, 26.8, 26.7, 21.2, 18.9, 18.0, 16.0, 14.5, 11.1, -3.4, -3.6, -4.7; FT-IR ($CHCl_3$): ν = 3306, 2956, 2930, 2882, 2857 cm^{-1}; HRMS (ESI): calcd for $C_{39}H_{72}O_5Si_2Na$: 699.48105 [M+Na]$^+$; found: 699.48154 (resolution 32600).



19

$C_{39}H_{72}O_5Si_2$
Exact Mass: 676,49
Mol. Wt.: 677,16

(3*R*,4*S*,5*S*,7*S*,10*R*,11*R*,12*S*,13*S*)-10,14-Bis-(*tert*-butyl-dimethyl-silanyloxy)-12-(4-methoxy-benzyloxy)-3,5,7,11,13-pentamethyl-tetradec-1-yn-4-ol (19).[17] [*Anti*, *anti* adduct]
Triphenylphosphine (recrystallized from ethanol prior to use, 0.6 mg, 0.00225 mmol, 0.05 equiv), the crude aldehyde (28.0 mg, 0.045 mmol) and (*S*)-mesyl-butynol (10.0 mg, 0.0675 mmol, 1.5 equiv) were subsequentially added to a cooled (-78°C) solution of $Pd(OAc)_2$ (0.5 mg, 0.00225 mmol, 0.05 equiv) in tetrahydrofurane (0.45 ml). Diethylzinc (1.0M in hexane, 135 µl, 0.135 mmol, 3 equiv) was added over 15 min. After 10 min., the temperature was raised to –20°C, and the reaction mixture was left overnight under stirring at –20°C. The mixture was than quenched with NH_4Cl/Et_2O 1/1. The Et_2O layer was washed with brine, dried and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/EtOAc 95/5) to afford the product as a yellow oil (25.6 mg, 0.0378 mmol, 84% over two steps), with high diastereoselectivity (95:5).
$[\alpha]_D^{23}$= - 4.61 (*c* 0.505, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.48 (2H, d, J = 8.4 Hz), 6.96 (2H, d, J = 8.4 Hz), 4.79 (2H, AB system, ν_A= 4.82, ν_B= 4.76, J_{AB} = 11.2 Hz), 4.00-3.79 (4H, m), 3.43 (3H, s), 3.15-2.94 (1H, m), 2.74-2.61 (1H, m), 2.20-2.06 (3H, m), 1.95-1.46 (11H, m), 1.30 (3H, d, J = 7.2 Hz), 1.26 (3H, d, J = 6.8 Hz), 1.22 (3H, d, J = 6.8 Hz), 1.18 (9H, s), 1.13 (9H, s), 1.15-1.03 (1H, m), 1.10 (3H, d, J = 6.8 Hz), 1.00 (3H, d, J = 6.4 Hz), 0.26 (6H, s), 0.20 (6H, s); ^{13}C NMR (100 MHz, C_6D_6) 160.0, 132.6, 129.5, 114.5, 81.4, 79.6, 75.6, 74.6, 71.8, 65.6, 55.2, 40.8, 40.6, 39.9, 35.7, 32.1, 32.0, 31.5, 31.0, 21.9, 18.9, 18.8, 17.3, 16.0, 11.1, -3.4, -3.6, -4.7; FT-IR (film): ν = 3309, 2960, 2933, 2850, 2663, 2655, 1727, 1613, 1514, 1470, 1462, 1386, 1360, 1301, 1255 cm^{-1}; HRMS (ESI): calcd for $C_{39}H_{72}O_5Si_2Na$: 699.48105 [M+Na]$^+$; found: 699.47937 (resolution 33400).



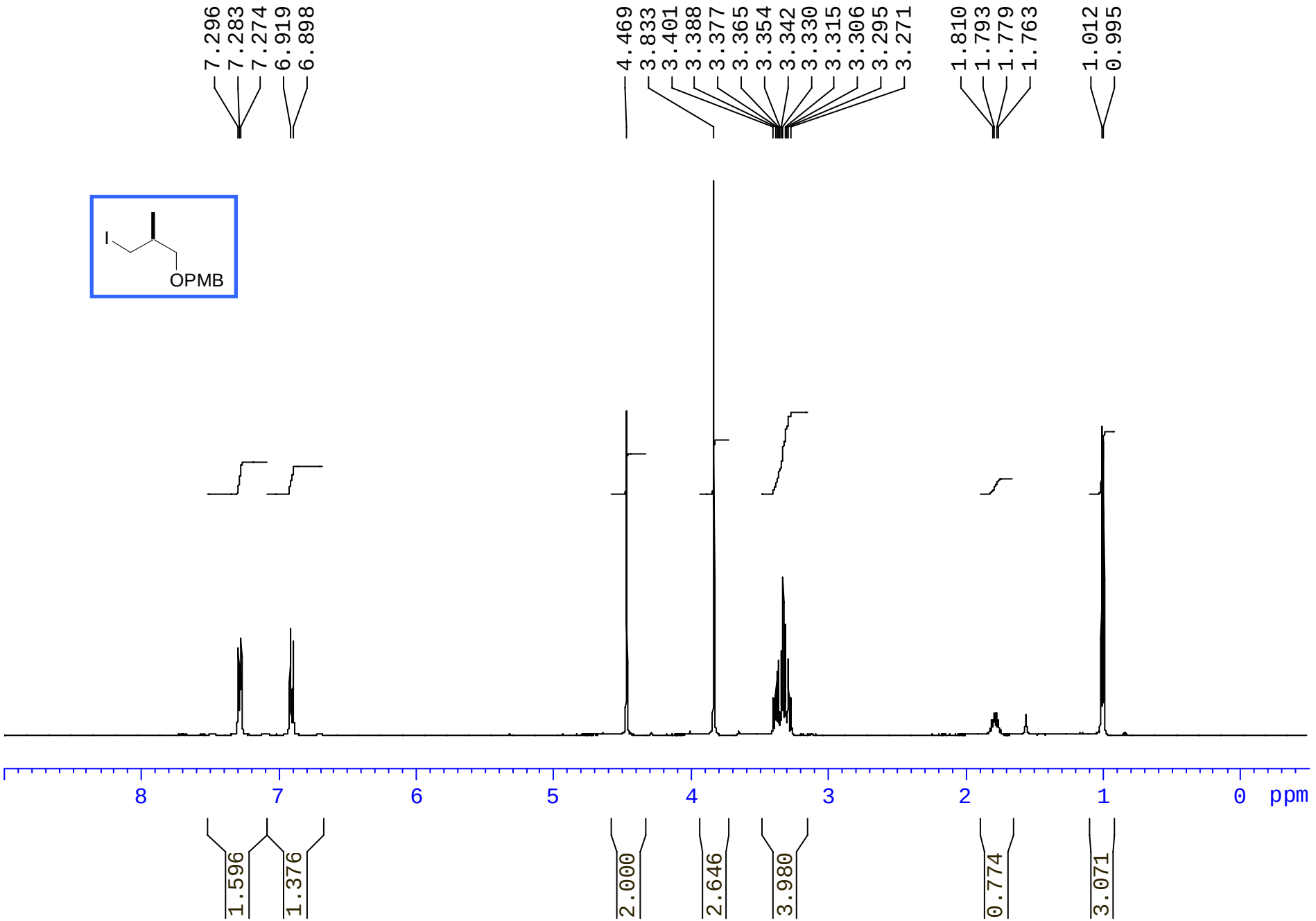
2

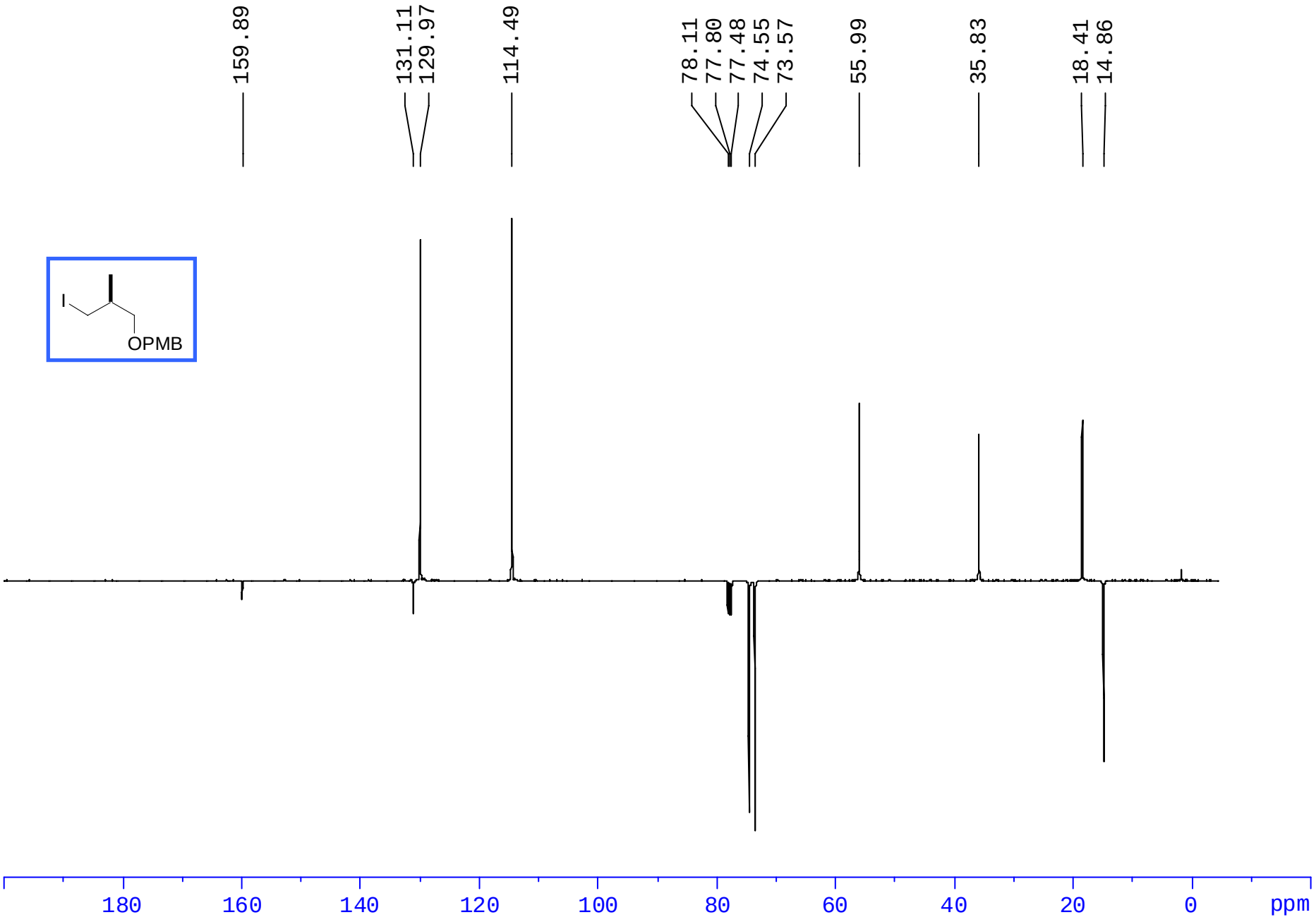
$C_{45}H_{86}O_5Si_3$
Exact Mass: 790,58
Mol. Wt.: 791,42

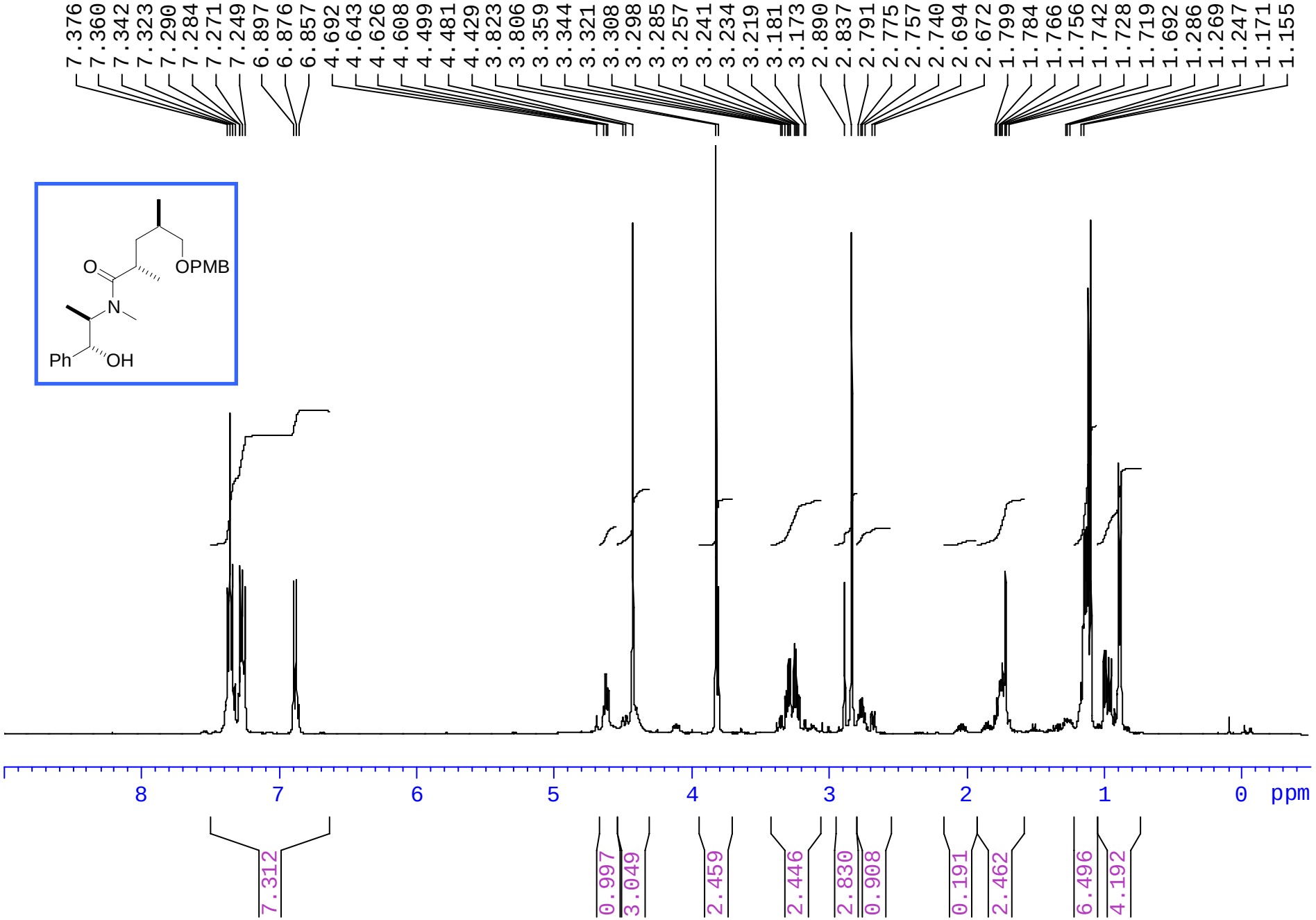
1-{(1*S*,2*R*,3*R*,6*S*,8*S*,9*R*,10*S*)-3,9-Bis-(*tert*-butyl-dimethyl-silanyloxy)-1-[(*S*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-methyl-ethyl]-2,6,8,10-tetramethyl-dodec-11-ynyloxymethyl}-4-methoxy-benzene (**2**).

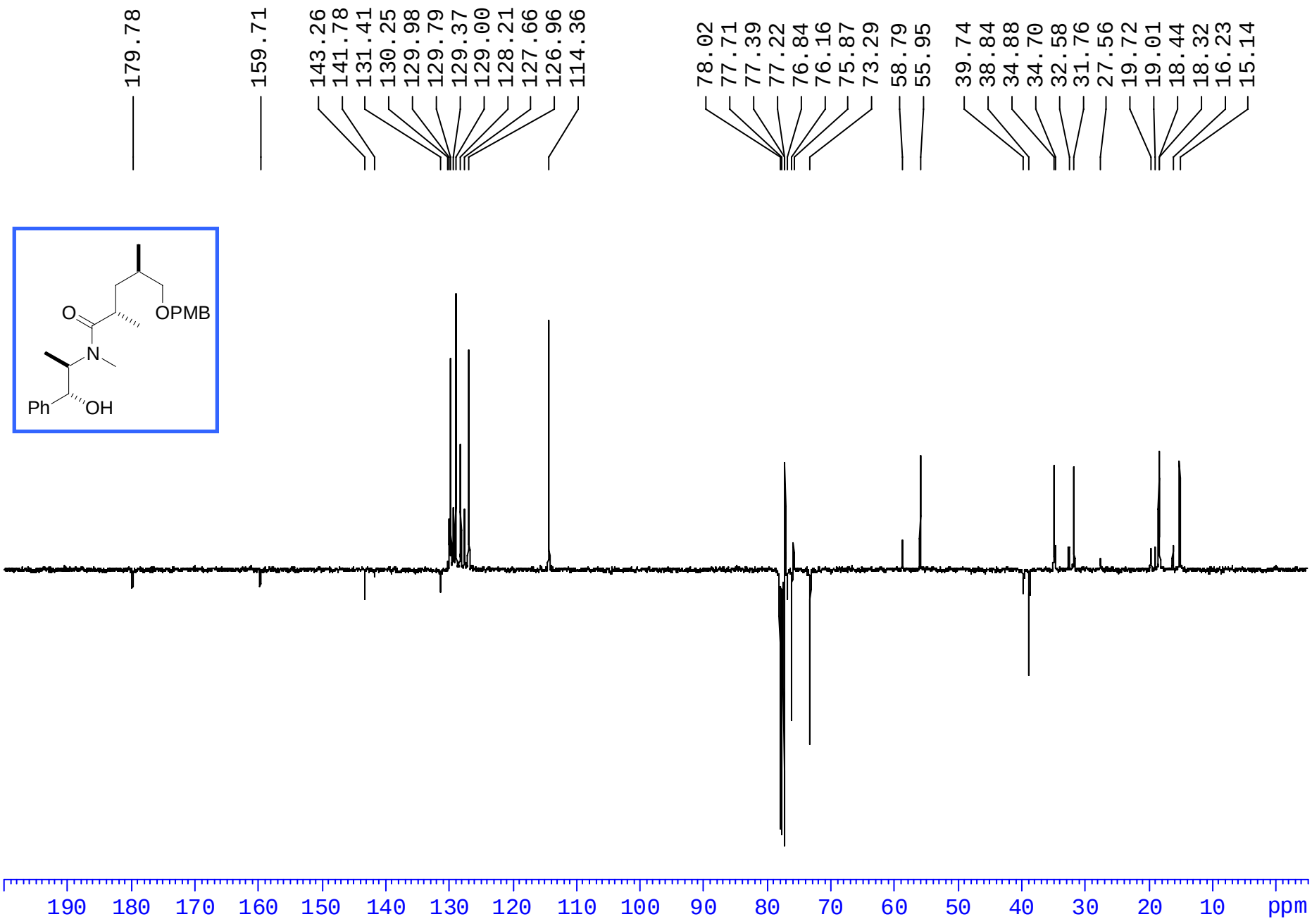
Freshly distilled 2,6-lutidine (9.3 µl, 0.08 mmol, 4 equiv) and TBSOTf (6.9 µl, 0.03 mmol, 1.5 equiv) were added to a stirred solution of compuond **18** (13.5 mg, 0.02 mmol) in dichloromethane (0.5 mL) at -20 °C. The proceeding of the reaction was monitored by TLC *n*-hexane/EtOAc, 8/2. On completion of the reaction (approximately 2 hours), the mixture was quenched with a saturated NH_4Cl aqueous solution. The organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4 and evaporated. Purification of the crude product by flash chromatography (*n*-hexane/EtOAc 7/3) afforded compound **2** (11.7 mg, 0.0148 mmol, 74%) as a colorless oil.

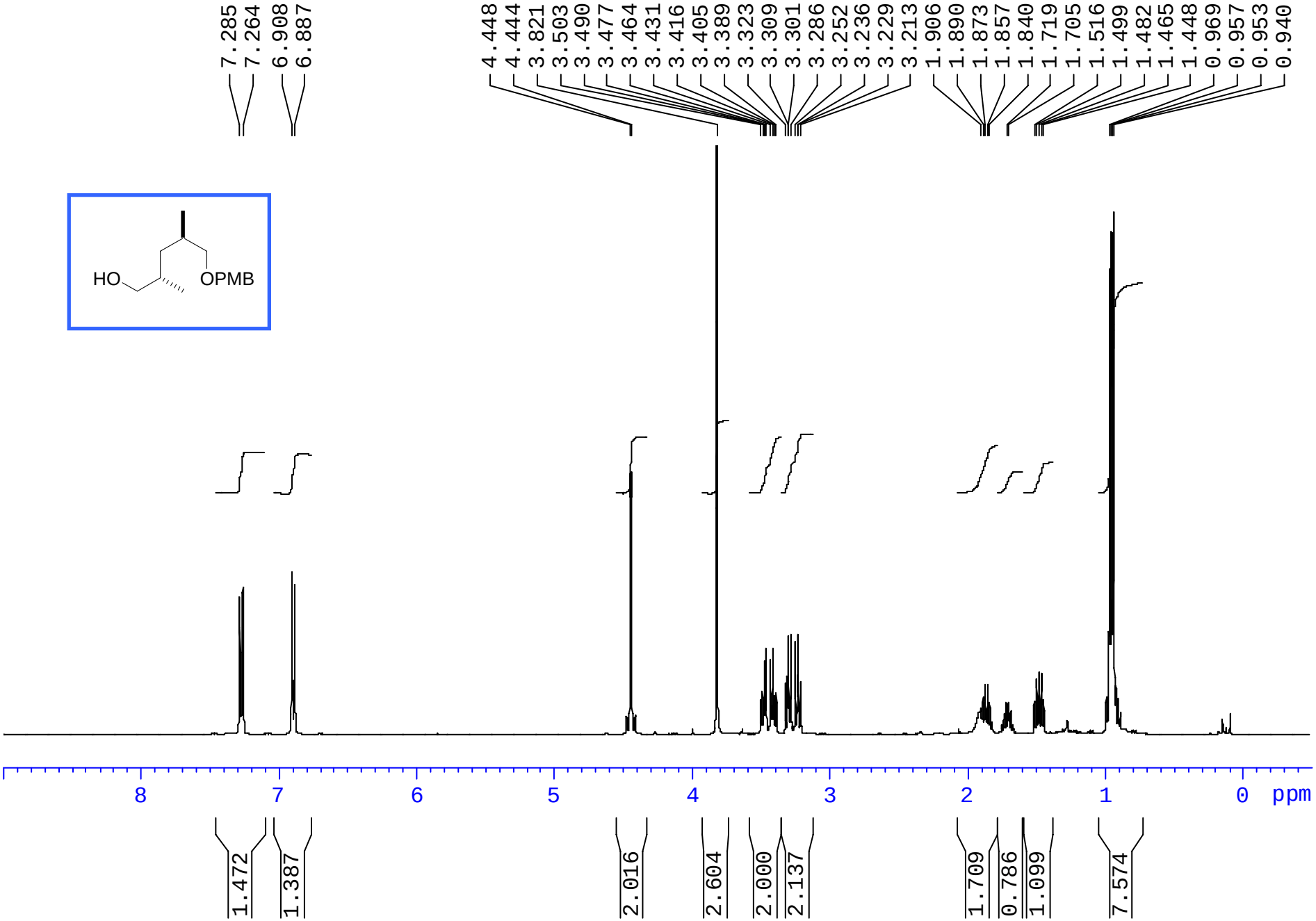
$[\alpha]_D^{22}$= - 3.10 (*c* 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.49 (2H, d, J = 8.4 Hz), 6.97 (2H, d, J = 8.4 Hz), 4.80 (2H, AB system, ν_A= 4.83, ν_B= 4.77, J_{AB} = 10.8 Hz), 4.01-3.69 (5H, m), 3.43 (3H, s), 2.79-2.71 (1H, m), 2.17-2.13 (3H, m), 2.02 (1H, d, J = 2.4 Hz), 2.01-1.96 (1H, m), 1.81-1.64 (4H, m), 1.32-1.13 (2H, m), 1.31 (3H, d, J = 6.4 Hz), 1.30 (3H, d, J = 6.8 Hz), 1.23 (3H, d, J = 7.2 Hz), 1.19 (9H, s), 1.16 (9H, s), 1.13 (9H, s), 1.12 (3H, d, J = 6.8 Hz), 1.10 (3H, d, J = 7.2 Hz), 0.28 (3H, s), 0.27 (3H, s), 0.26 (3H, s), 0.25 (3H, s), 0.21 (6H, s); ^{13}C NMR (100 MHz, C_6D_6) 160.0, 132.6, 129.5, 114.5, 87.9, 81.5, 78.5, 75.4, 74.7, 71.2, 65.6, 55.2, 43.7, 40.7, 39.9, 34.1, 32.9, 32.7, 32.4, 31.4, 26.8, 26.7, 26.6, 20.9, 18.0, 16.0, 15.9, 11.0, -3.1, -3.2, -3.3, -3.6, -4.7; FT-IR (film): ν = 3312, 2957, 2929, 2904, 2884, 2856, 1614, 1587, 1514, 1471, 1256 cm^{-1}; HRMS (ESI): calcd for $C_{45}H_{86}O_5Si_3Na$: 813.56753 [M+Na]$^+$; found: 813.56718 (resolution 28900).

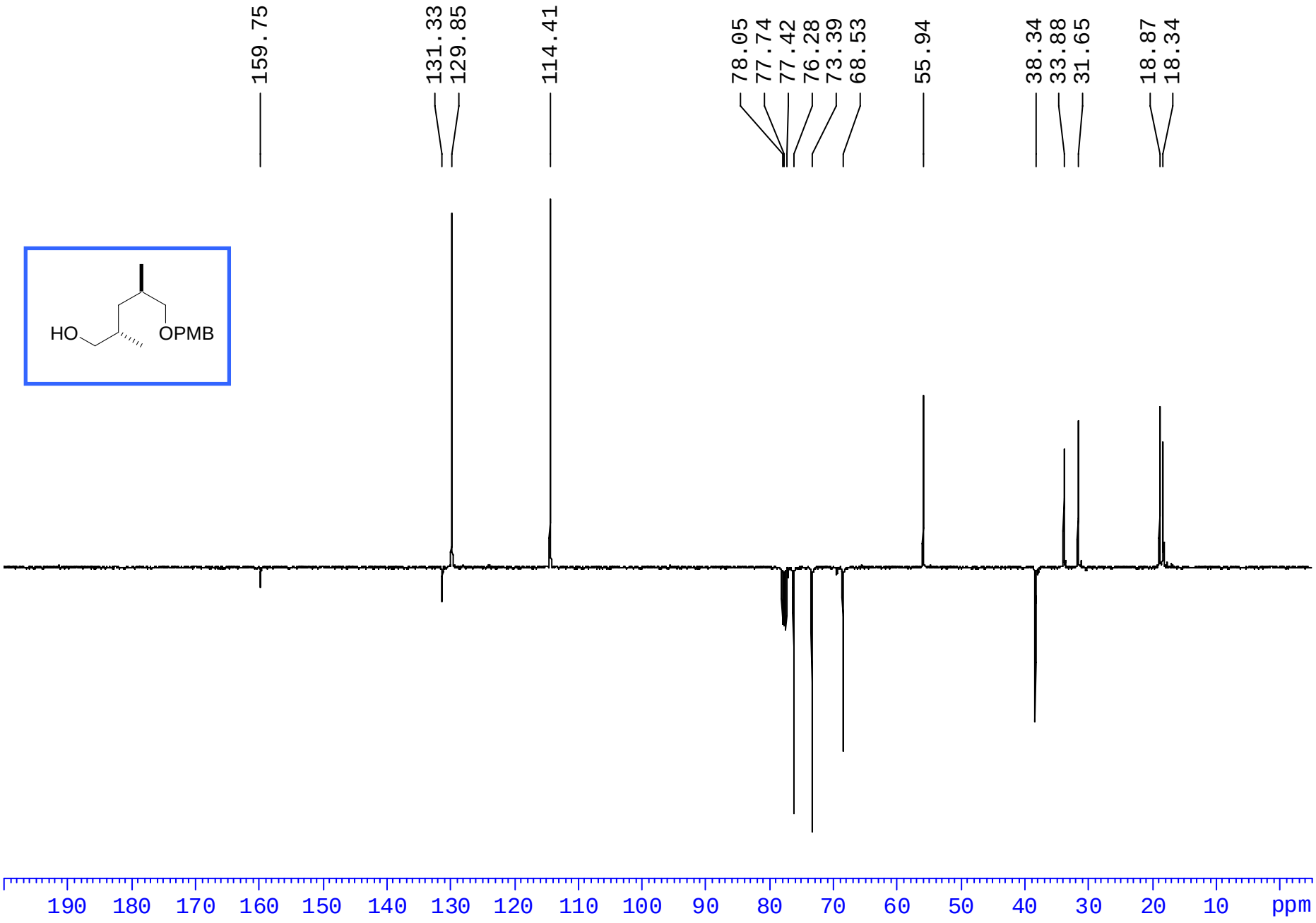

7.296
7.283
7.274
6.919
6.898
4.469
3.833
3.401
3.388
3.377
3.365
3.354
3.342
3.330
3.315
3.306
3.295
3.271
1.810
1.793
1.779
1.763
1.012
0.995
I
OPMB
8
7
6
5
4
3
2
1
0
ppm
1.596
1.376
2.000
2.646
3.980
0.774
3.071

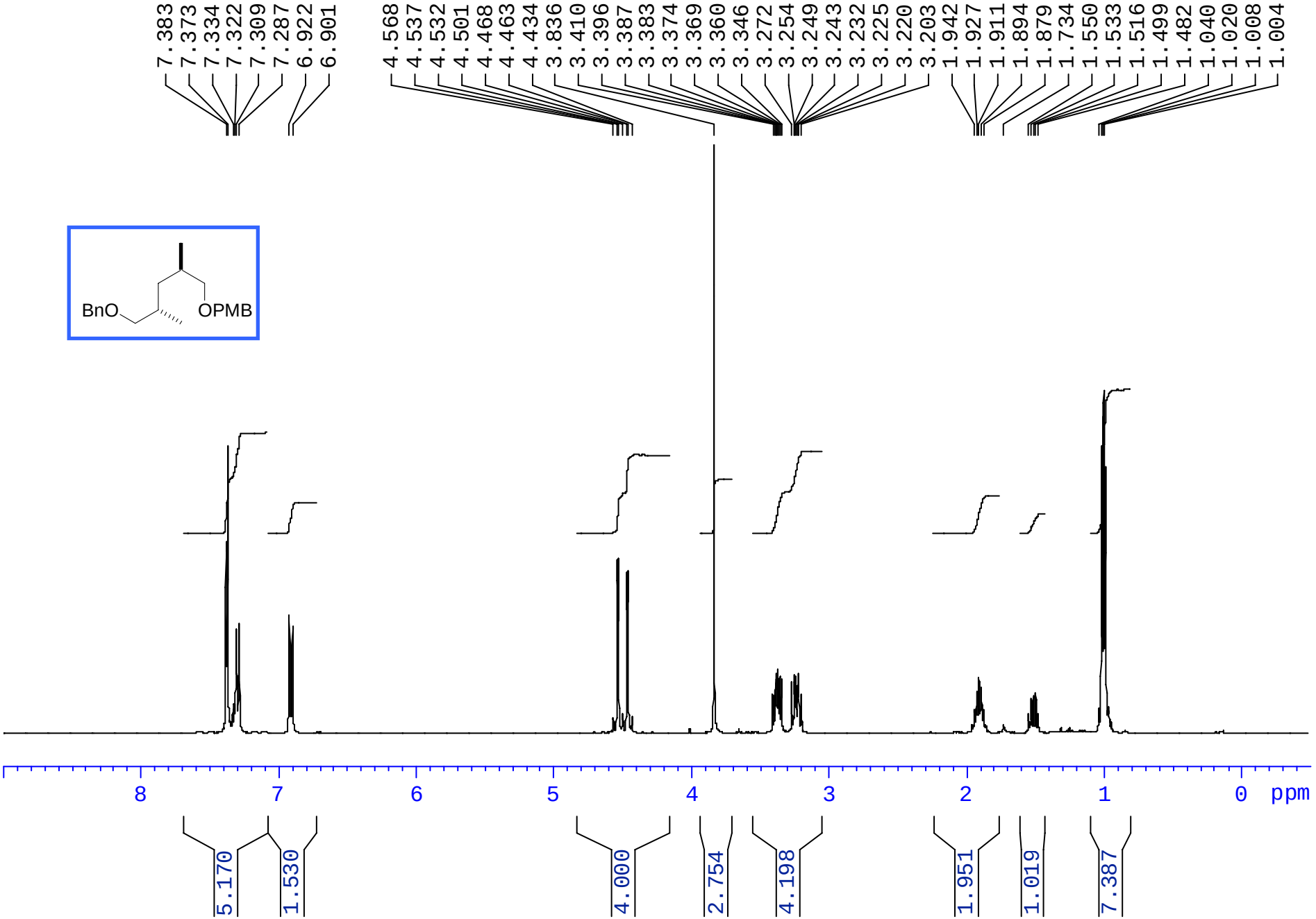

159.89
131.11
129.97
114.49
78.11
77.80
77.48
74.55
73.57
55.99
35.83
18.41
14.86
I
OPMB
180
160
140
120
100
80
60
40
20
0
ppm

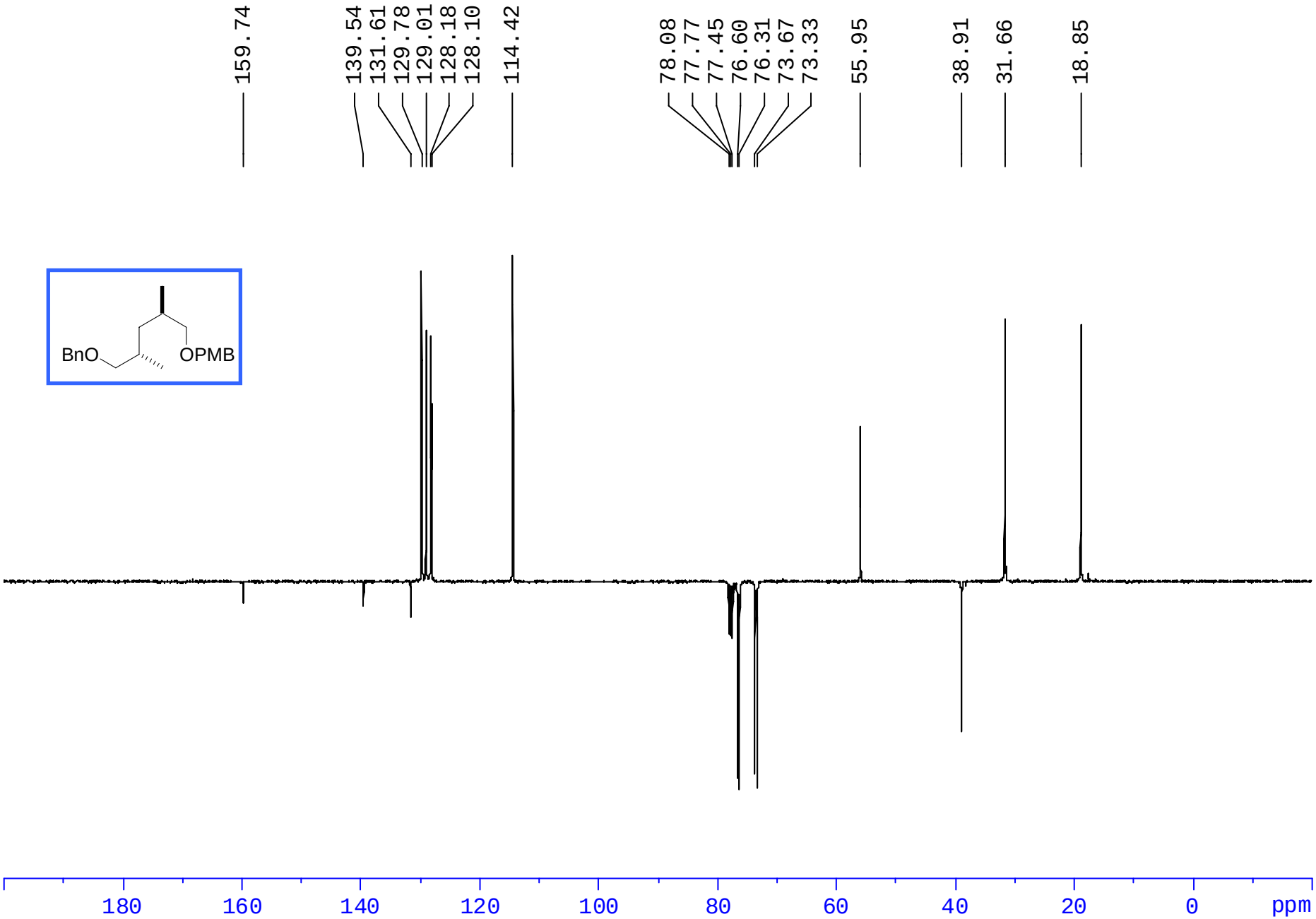

7.376
7.360
7.342
7.323
7.290
7.284
7.271
7.249
6.897
6.876
6.857
4.692
4.643
4.626
4.608
4.499
4.481
4.429
3.823
3.806
3.359
3.344
3.321
3.308
3.298
3.285
3.257
3.241
3.234
3.219
3.181
3.173
2.890
2.837
2.791
2.775
2.757
2.740
2.694
2.672
1.799
1.784
1.766
1.756
1.742
1.728
1.719
1.692
1.286
1.269
1.247
1.171
1.155
O
OPMB
N
Ph
OH
8
7
6
5
4
3
2
1
0
ppm
7.312
0.997
3.049
2.459
2.446
2.830
0.908
0.191
2.462
6.496
4.192

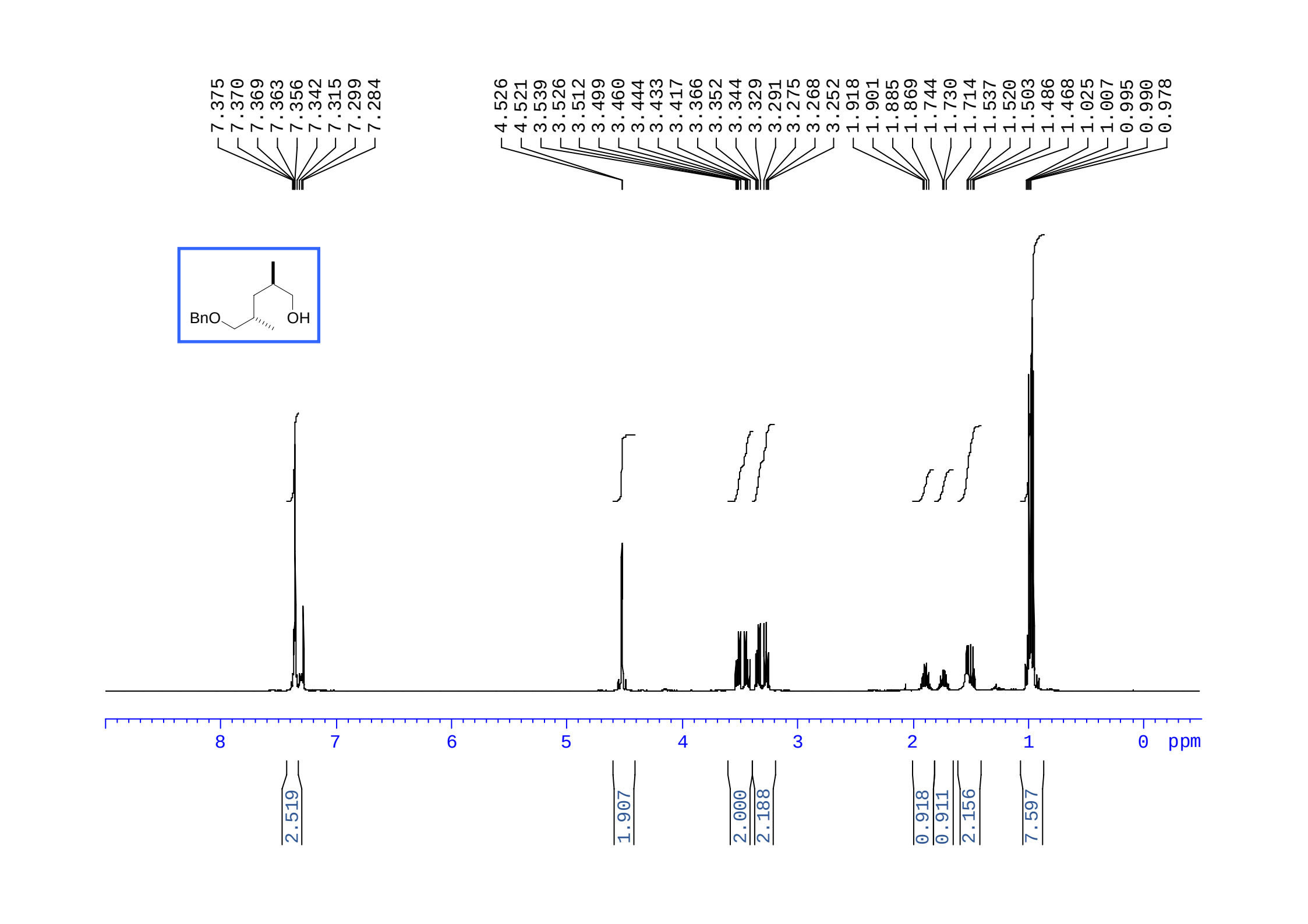

179.78
159.71
143.26
141.78
131.41
130.25
129.98
129.79
129.37
129.00
128.21
127.66
126.96
114.36
78.02
77.71
77.39
77.22
76.84
76.16
75.87
73.29
58.79
55.95
39.74
38.84
34.88
34.70
32.58
31.76
27.56
19.72
19.01
18.44
18.32
16.23
15.14
O
OPMB
N
Ph
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

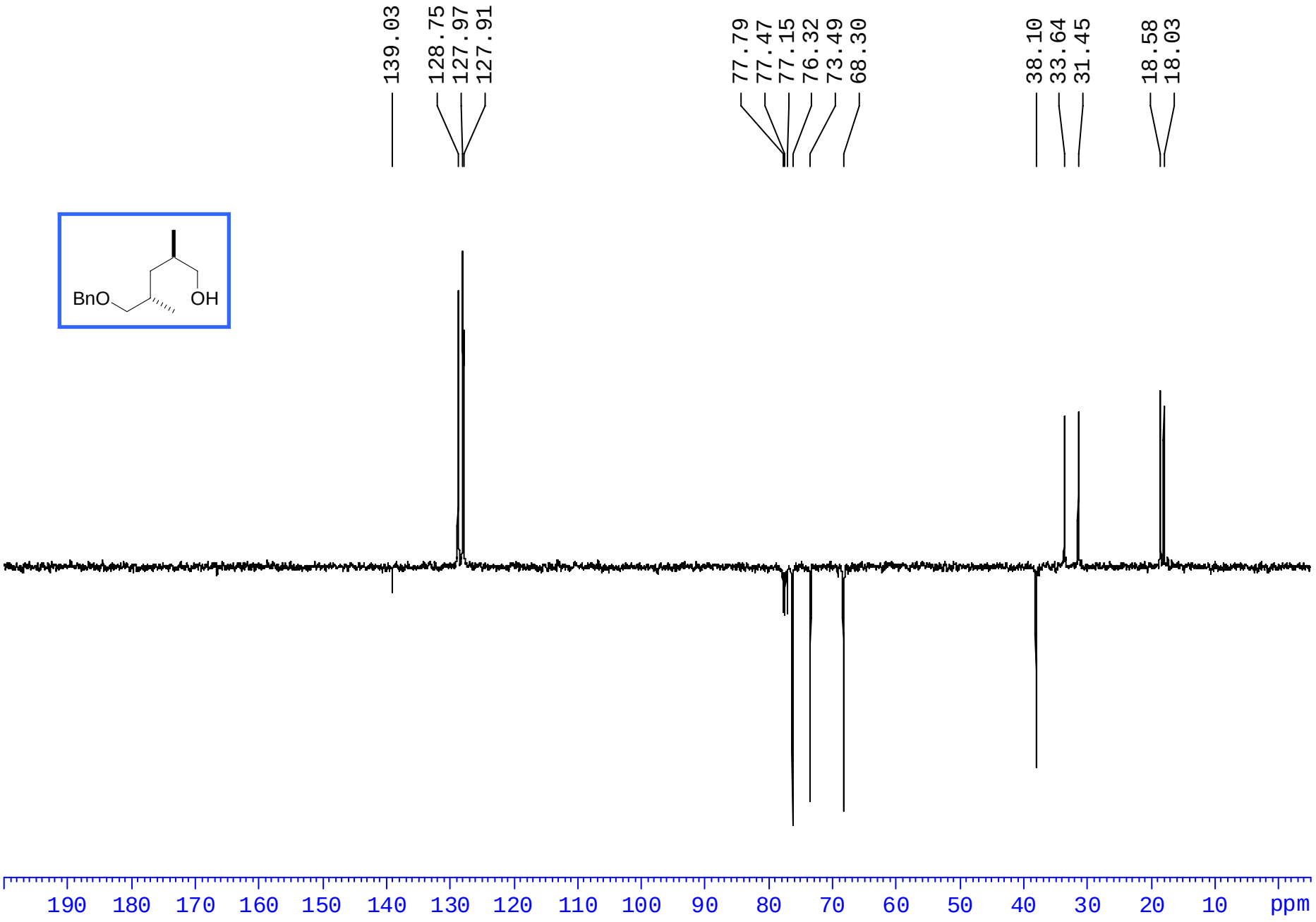

7.285
7.264
6.908
6.887
4.448
4.444
3.821
3.503
3.490
3.477
3.464
3.431
3.416
3.405
3.389
3.323
3.309
3.301
3.286
3.252
3.236
3.229
3.213
1.906
1.890
1.873
1.857
1.840
1.719
1.705
1.516
1.499
1.482
1.465
1.448
0.969
0.957
0.953
0.940
HO
OPMB
8
7
6
5
4
3
2
1
0
ppm
1.472
1.387
2.016
2.604
2.000
2.137
1.709
0.786
1.099
7.574

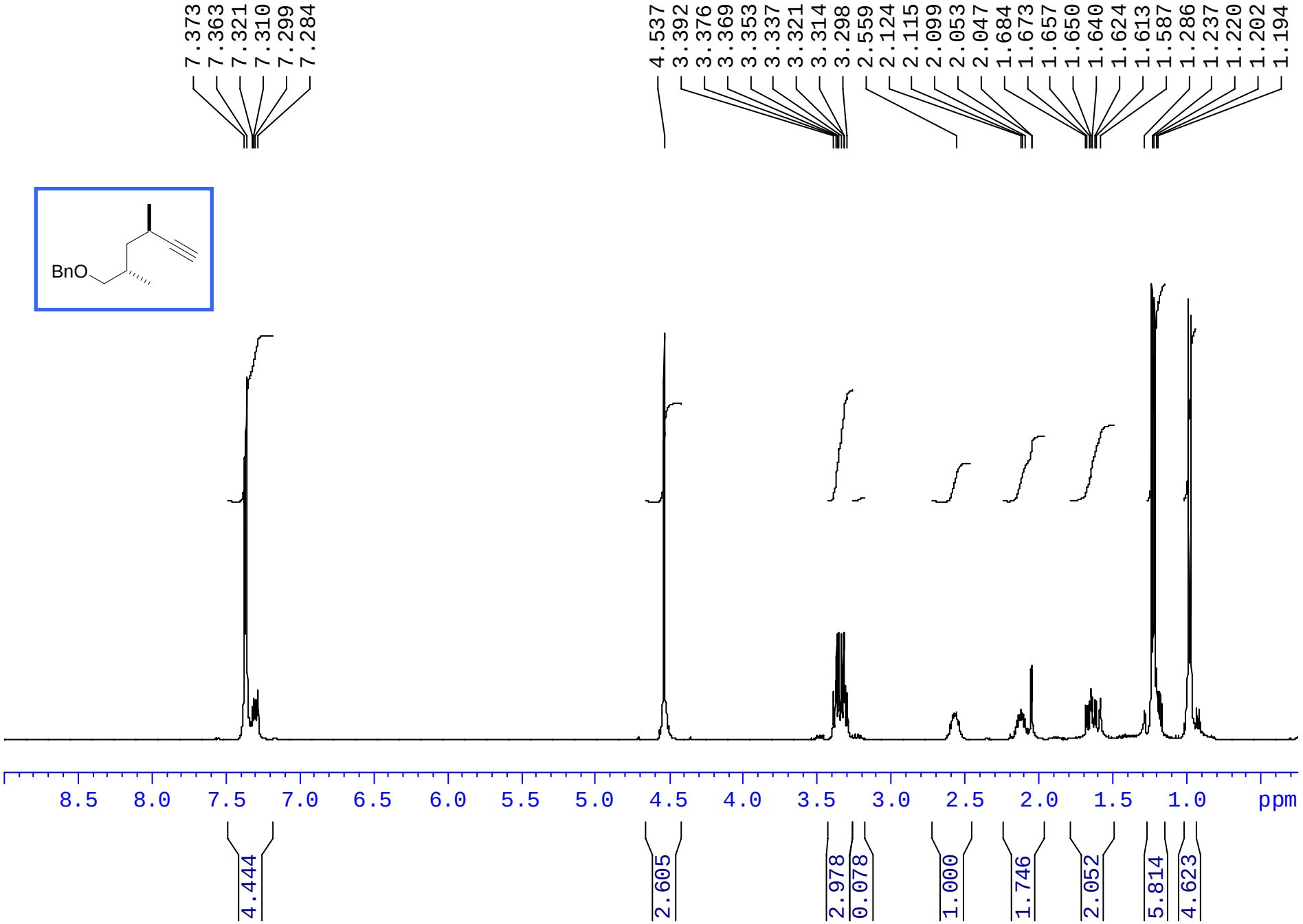

159.75
131.33
129.85
114.41
78.05
77.74
77.42
76.28
73.39
68.53
55.94
38.34
33.88
31.65
18.87
18.34
HO
OPMB
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

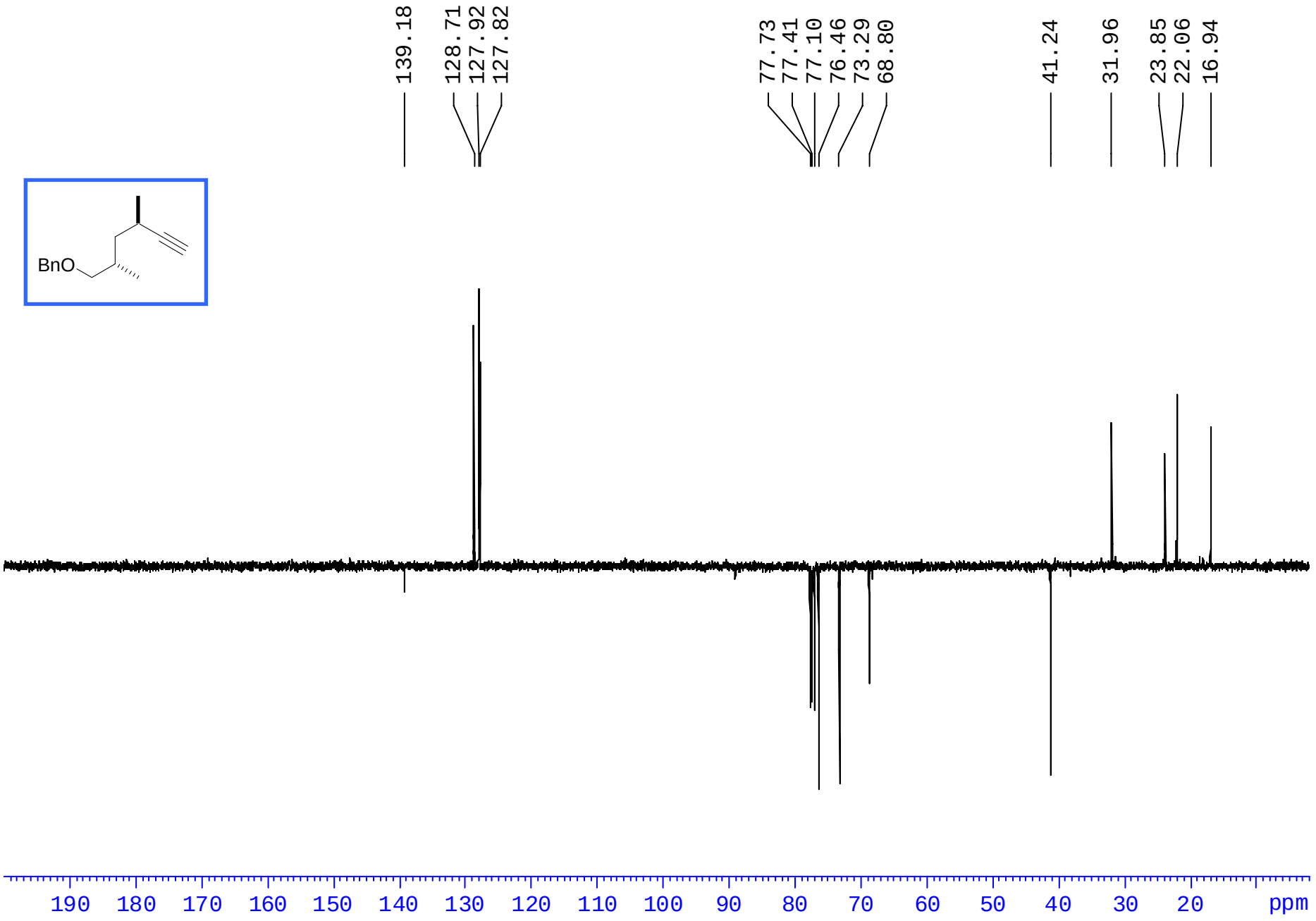

7.383
7.373
7.334
7.322
7.309
7.287
6.922
6.901
4.568
4.537
4.532
4.501
4.468
4.463
4.434
3.836
3.410
3.396
3.387
3.383
3.374
3.369
3.360
3.346
3.272
3.254
3.249
3.243
3.232
3.225
3.220
3.203
1.942
1.927
1.911
1.894
1.879
1.734
1.550
1.533
1.516
1.499
1.482
1.040
1.020
1.008
1.004
BnO
OPMB
8
7
6
5
4
3
2
1
0
ppm
5.170
1.530
4.000
2.754
4.198
1.951
1.019
7.387

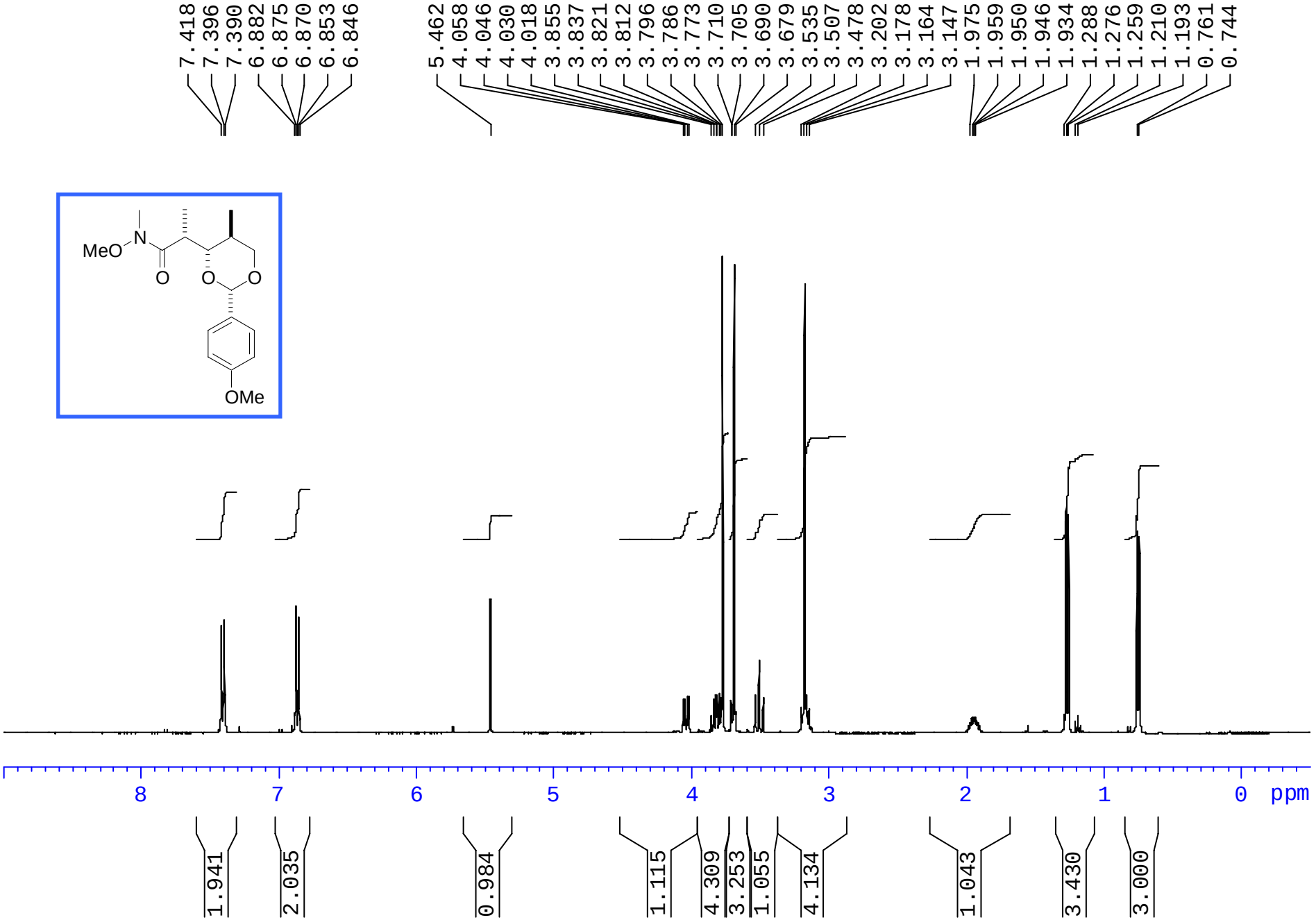

159.74
139.54
131.61
129.78
129.01
128.18
128.10
114.42
78.08
77.77
77.45
76.60
76.31
73.67
73.33
55.95
38.91
31.66
18.85
BnO
OPMB
180
160
140
120
100
80
60
40
20
0
ppm

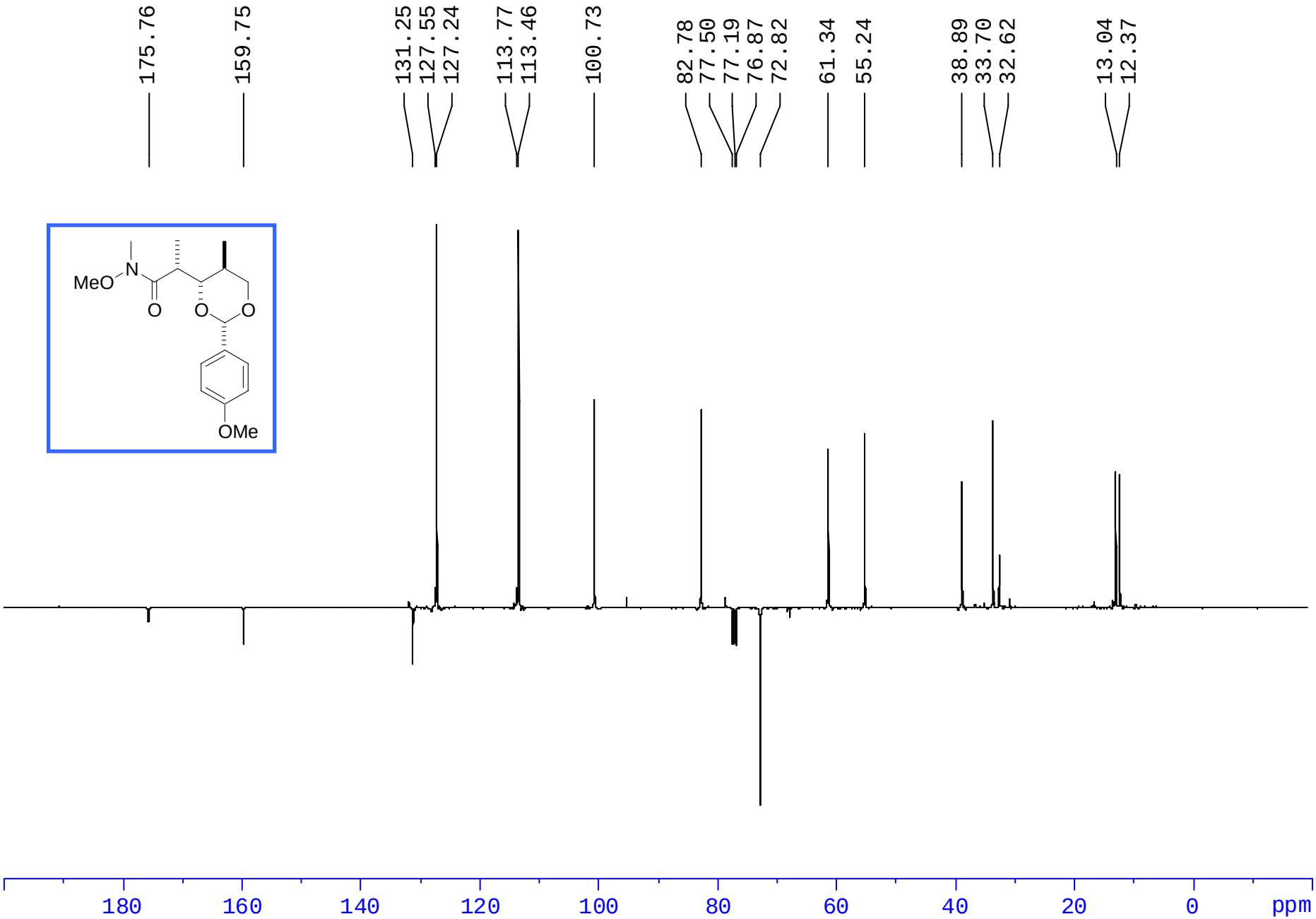

7.375
7.370
7.369
7.363
7.356
7.342
7.315
7.299
7.284
4.526
4.521
3.539
3.526
3.512
3.499
3.460
3.444
3.433
3.417
3.366
3.352
3.344
3.329
3.291
3.275
3.268
3.252
1.918
1.901
1.885
1.869
1.744
1.730
1.714
1.537
1.520
1.503
1.486
1.468
1.025
1.007
0.995
0.990
0.978
BnO
OH
8
7
6
5
4
3
2
1
0
ppm
2.519
1.907
2.000
2.188
0.918
0.911
2.156
7.597

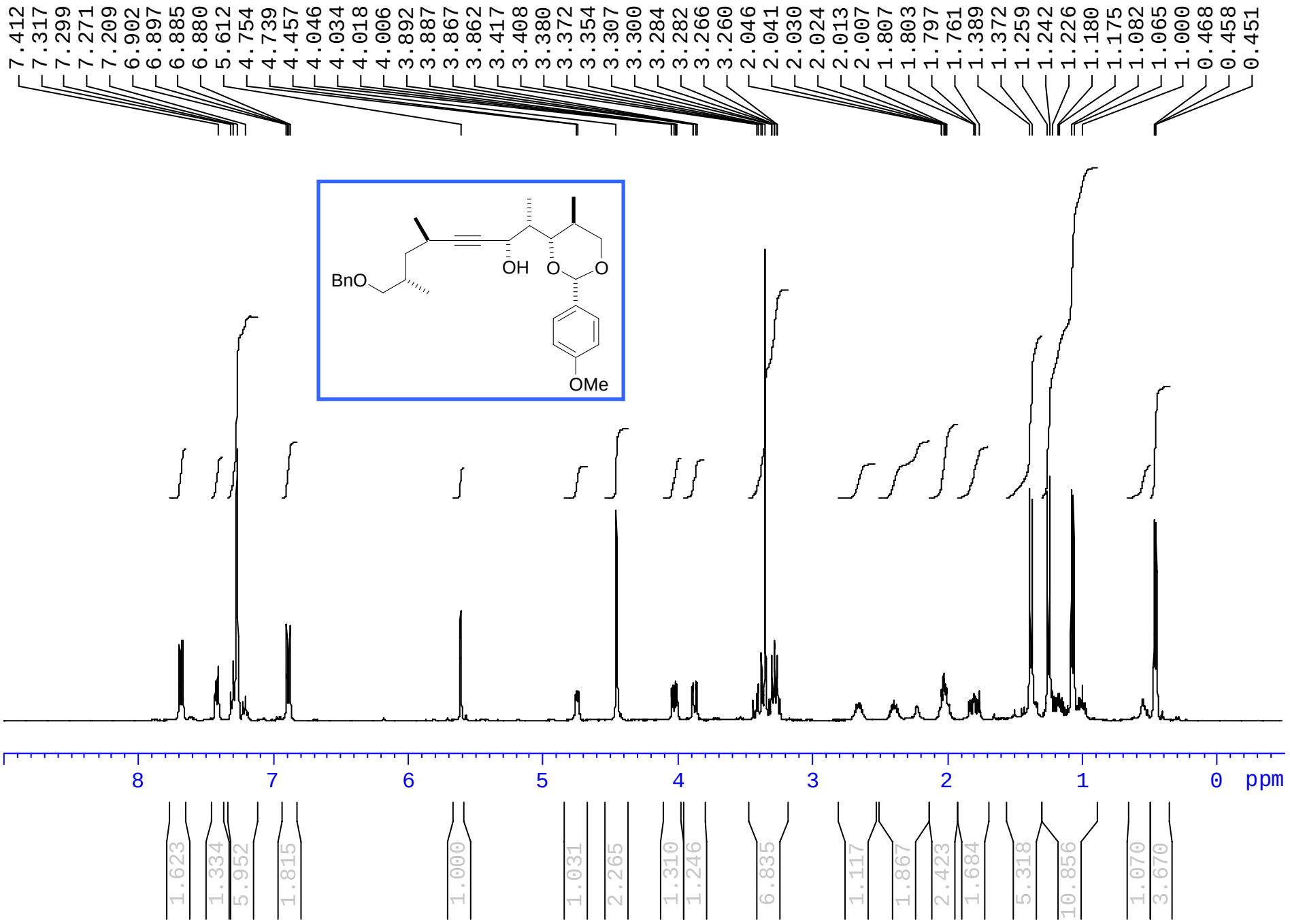

139.03
128.75
127.97
127.91
77.79
77.47
77.15
76.32
73.49
68.30
38.10
33.64
31.45
18.58
18.03
BnO
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

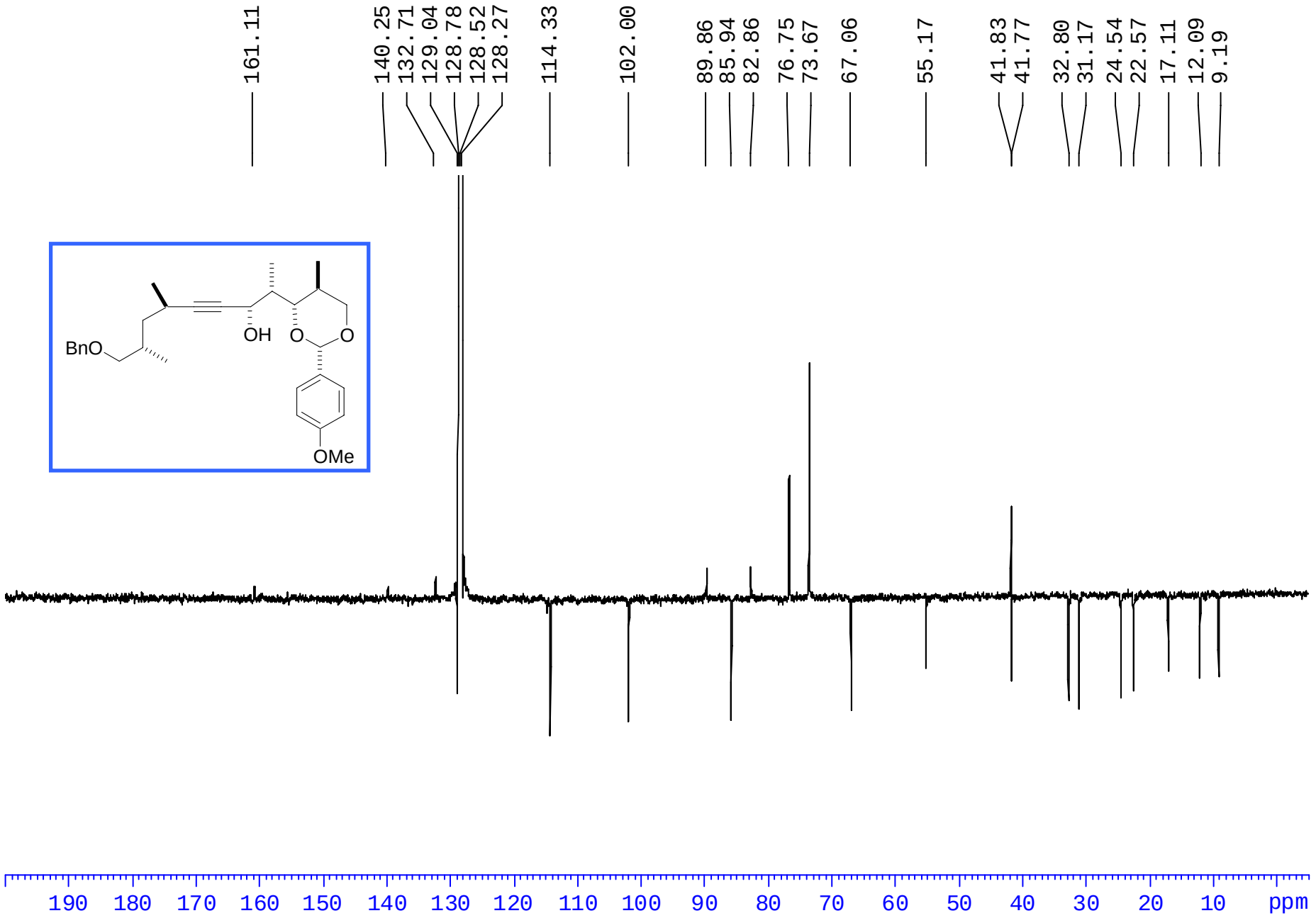

7.373
7.363
7.321
7.310
7.299
7.284
4.537
3.392
3.376
3.369
3.353
3.337
3.321
3.314
3.298
2.559
2.124
2.115
2.099
2.053
2.047
1.684
1.673
1.657
1.650
1.640
1.624
1.613
1.587
1.286
1.237
1.220
1.202
1.194
BnO
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.444
2.605
2.978
0.078
1.000
1.746
2.052
5.814
4.623

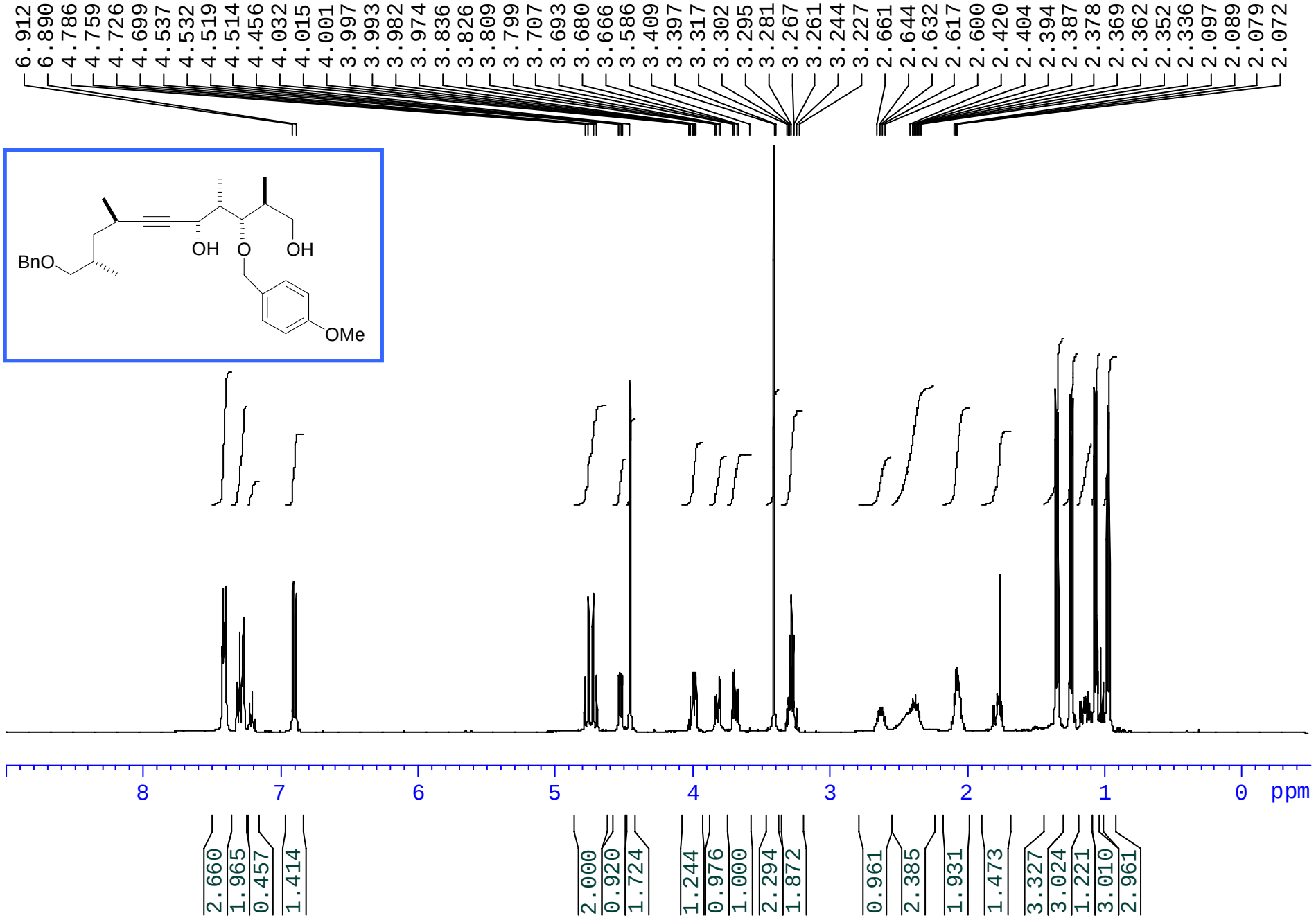

139.18
128.71
127.92
127.82
77.73
77.41
77.10
76.46
73.29
68.80
41.24
31.96
23.85
22.06
16.94
BnO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

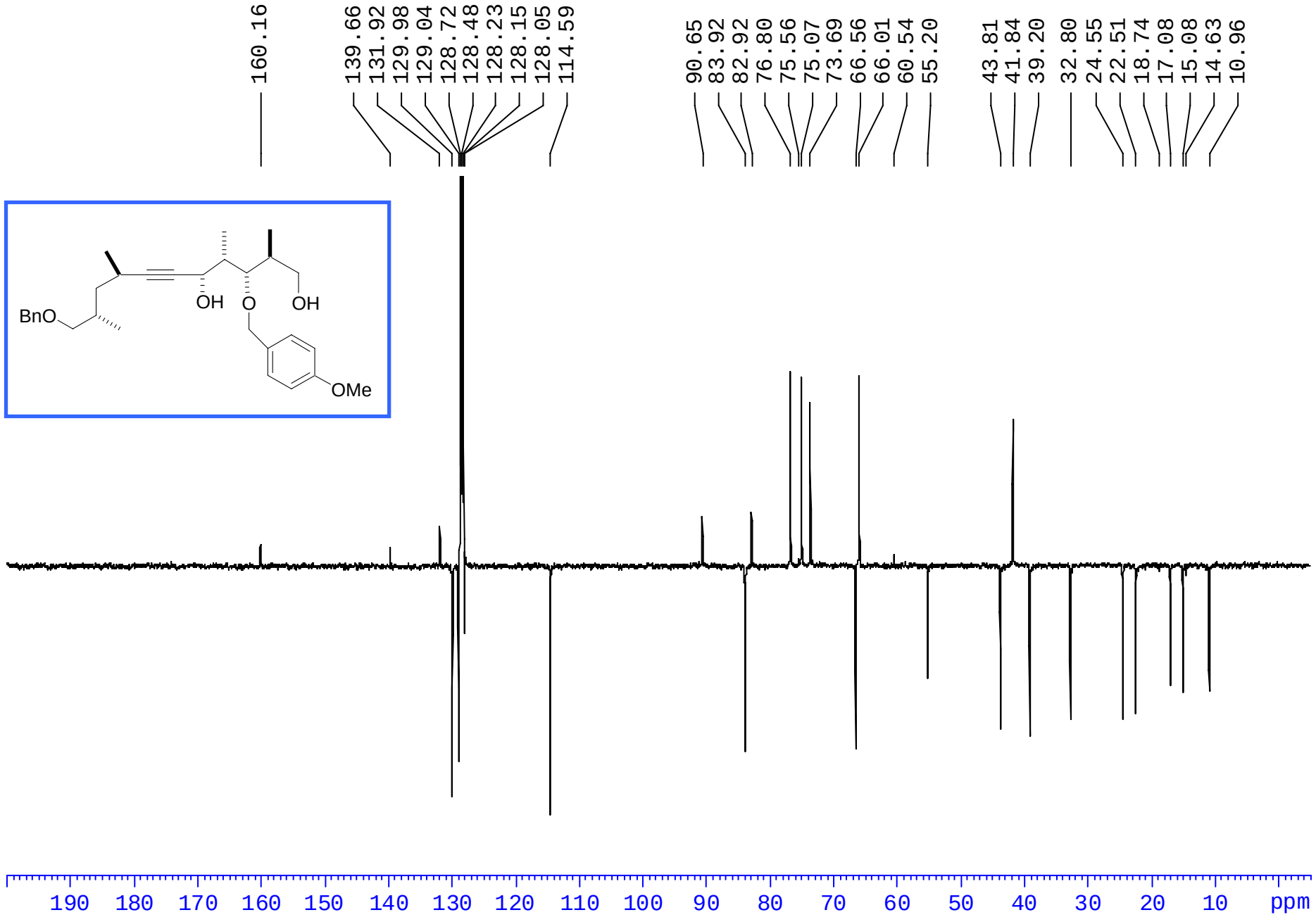

7.418
7.396
7.390
6.882
6.875
6.870
6.853
6.846
5.462
4.058
4.046
4.030
4.018
3.855
3.837
3.821
3.812
3.796
3.786
3.773
3.710
3.705
3.690
3.679
3.535
3.507
3.478
3.202
3.178
3.164
3.147
1.975
1.959
1.950
1.946
1.934
1.288
1.276
1.259
1.210
1.193
0.761
0.744
MeO
N
O
O
O
OMe
8
7
6
5
4
3
2
1
0
ppm
1.941
2.035
0.984
1.115
4.309
3.253
1.055
4.134
1.043
3.430
3.000

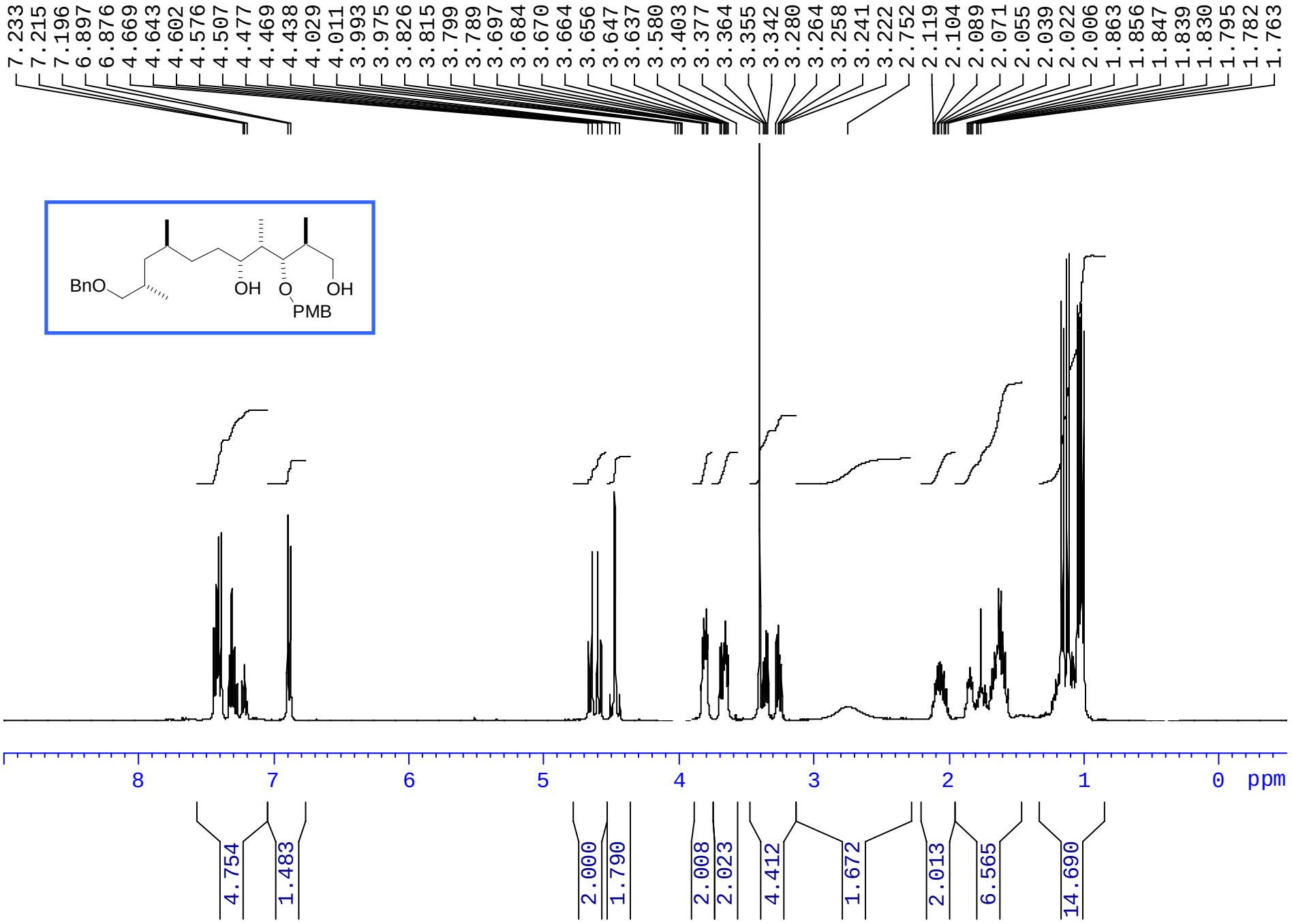

175.76
159.75
131.25
127.55
127.24
113.77
113.46
100.73
82.78
77.50
77.19
76.87
72.82
61.34
55.24
38.89
33.70
32.62
13.04
12.37
MeO
N
O
O
O
O
OMe
180
160
140
120
100
80
60
40
20
0
ppm

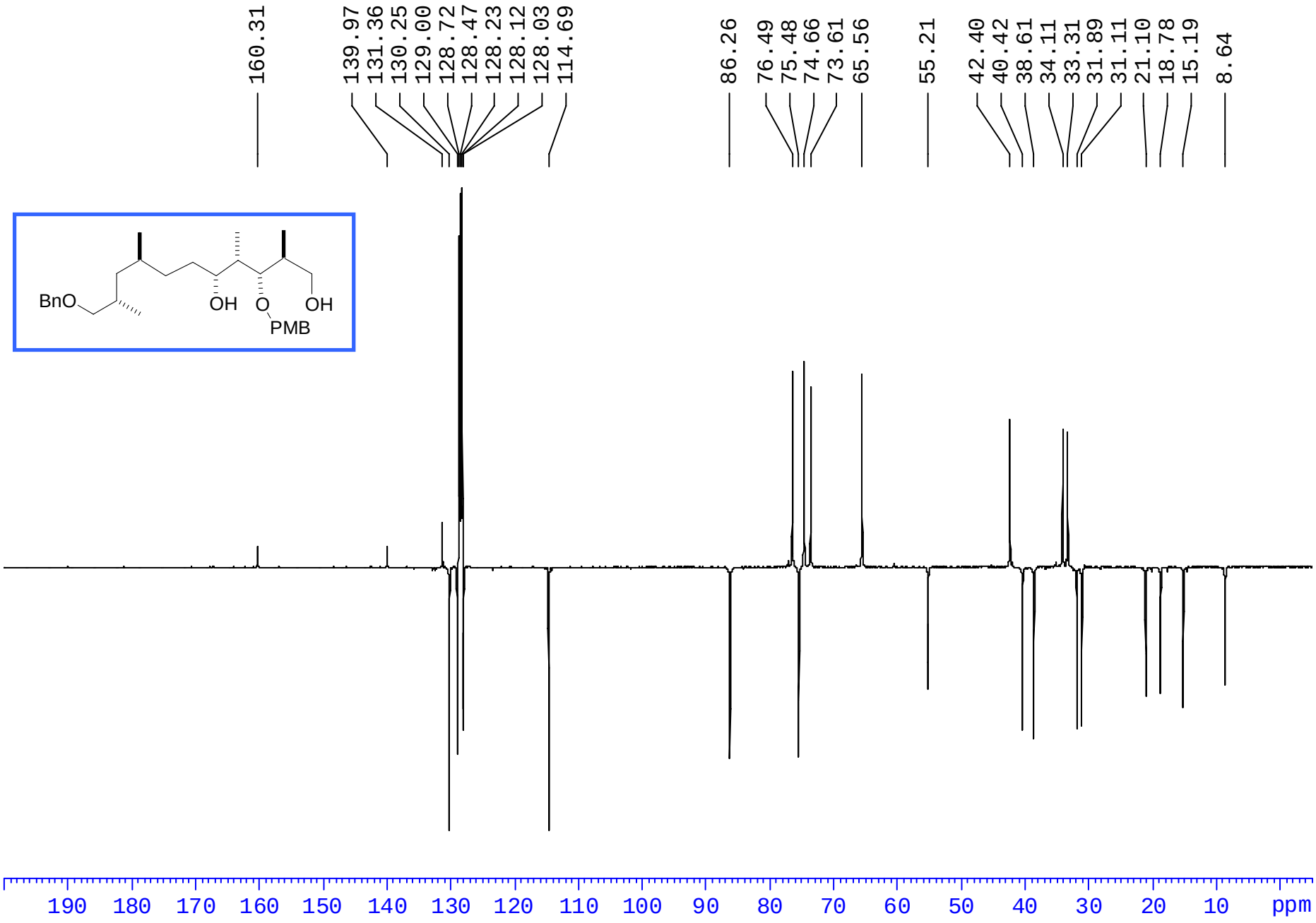

7.412
7.317
7.299
7.271
7.209
6.902
6.897
6.885
6.880
5.612
4.754
4.739
4.457
4.046
4.034
4.018
4.006
3.892
3.887
3.867
3.862
3.417
3.408
3.380
3.372
3.354
3.307
3.300
3.284
3.282
3.266
3.260
2.046
2.041
2.030
2.024
2.013
2.007
1.807
1.803
1.797
1.761
1.389
1.372
1.259
1.242
1.226
1.180
1.175
1.082
1.065
1.000
0.468
0.458
0.451
BnO
OH
O
O
OMe
8
7
6
5
4
3
2
1
0
ppm
1.623
1.334
5.952
1.815
1.000
1.031
2.265
1.310
1.246
6.835
1.117
1.867
2.423
1.684
5.318
10.856
1.070
3.670

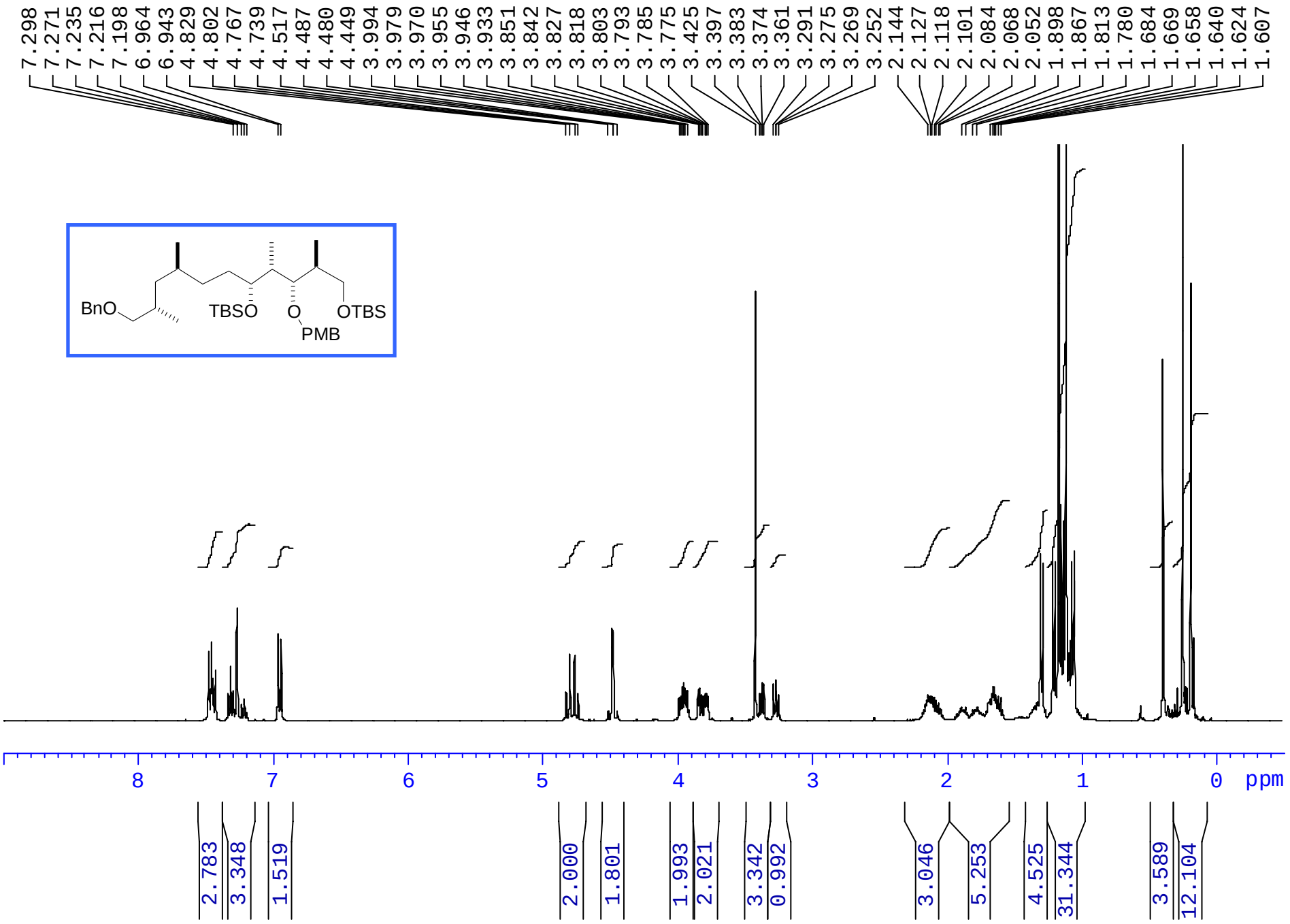

161.11
140.25
132.71
129.04
128.78
128.52
128.27
114.33
102.00
89.86
85.94
82.86
76.75
73.67
67.06
55.17
41.83
41.77
32.80
31.17
24.54
22.57
17.11
12.09
9.19
BnO
OH
O
O
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

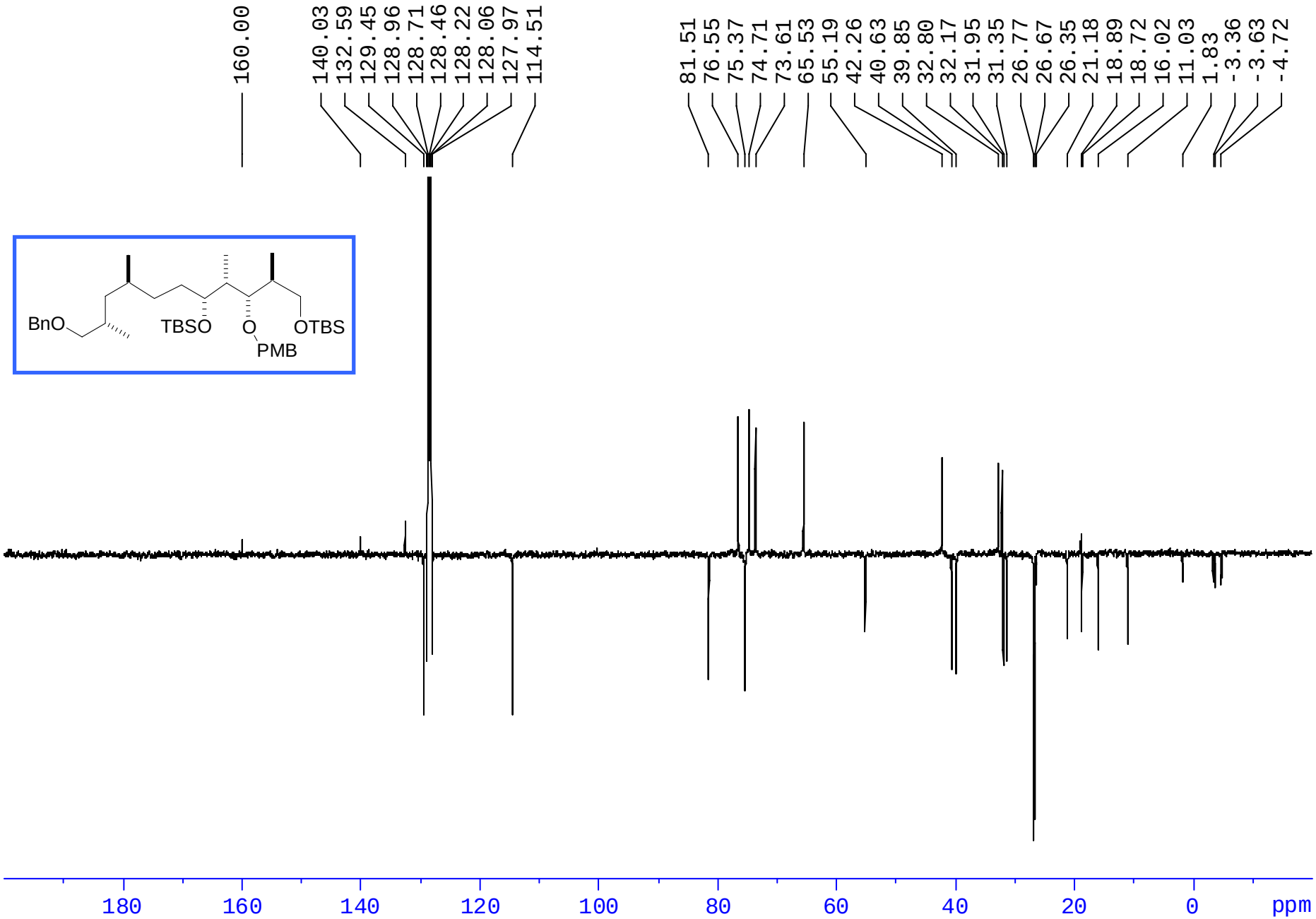

6.912
6.890
4.786
4.759
4.726
4.699
4.537
4.532
4.519
4.514
4.456
4.032
4.015
4.001
3.997
3.993
3.982
3.974
3.836
3.826
3.809
3.799
3.707
3.693
3.680
3.666
3.586
3.409
3.397
3.317
3.302
3.295
3.281
3.267
3.261
3.244
3.227
2.661
2.644
2.632
2.617
2.600
2.420
2.404
2.394
2.387
2.378
2.369
2.362
2.352
2.336
2.097
2.089
2.079
2.072
BnO
OH
O
OH
OMe
8
7
6
5
4
3
2
1
0
ppm
2.660
1.965
0.457
1.414
2.000
0.920
1.724
1.244
0.976
1.000
2.294
1.872
0.961
2.385
1.931
1.473
3.327
3.024
1.221
3.010
2.961

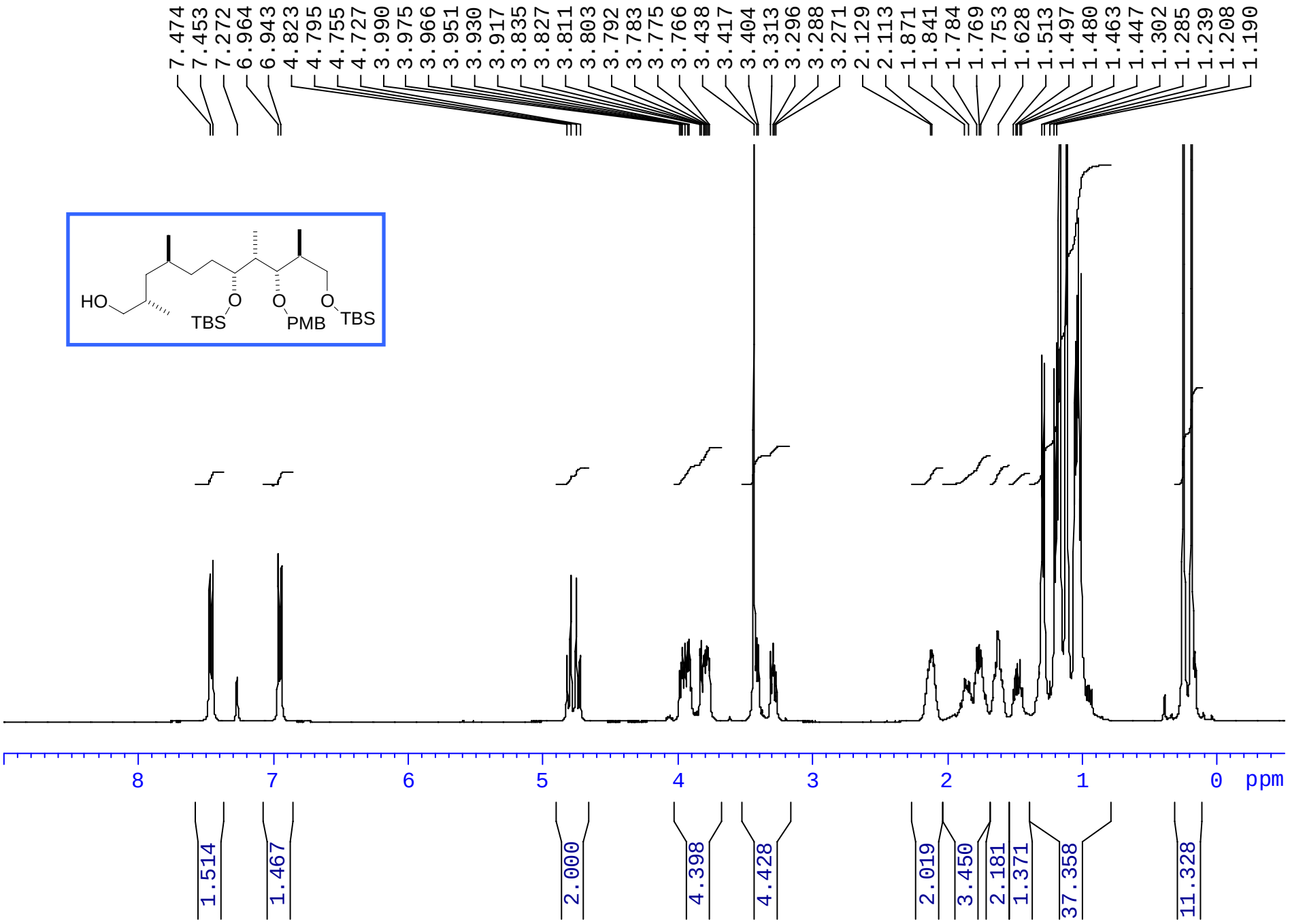

160.16
139.66
131.92
129.98
129.04
128.72
128.48
128.23
128.15
128.05
114.59
90.65
83.92
82.92
76.80
75.56
75.07
73.69
66.56
66.01
60.54
55.20
43.81
41.84
39.20
32.80
24.55
22.51
18.74
17.08
15.08
14.63
10.96
BnO
OH
O
OH
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

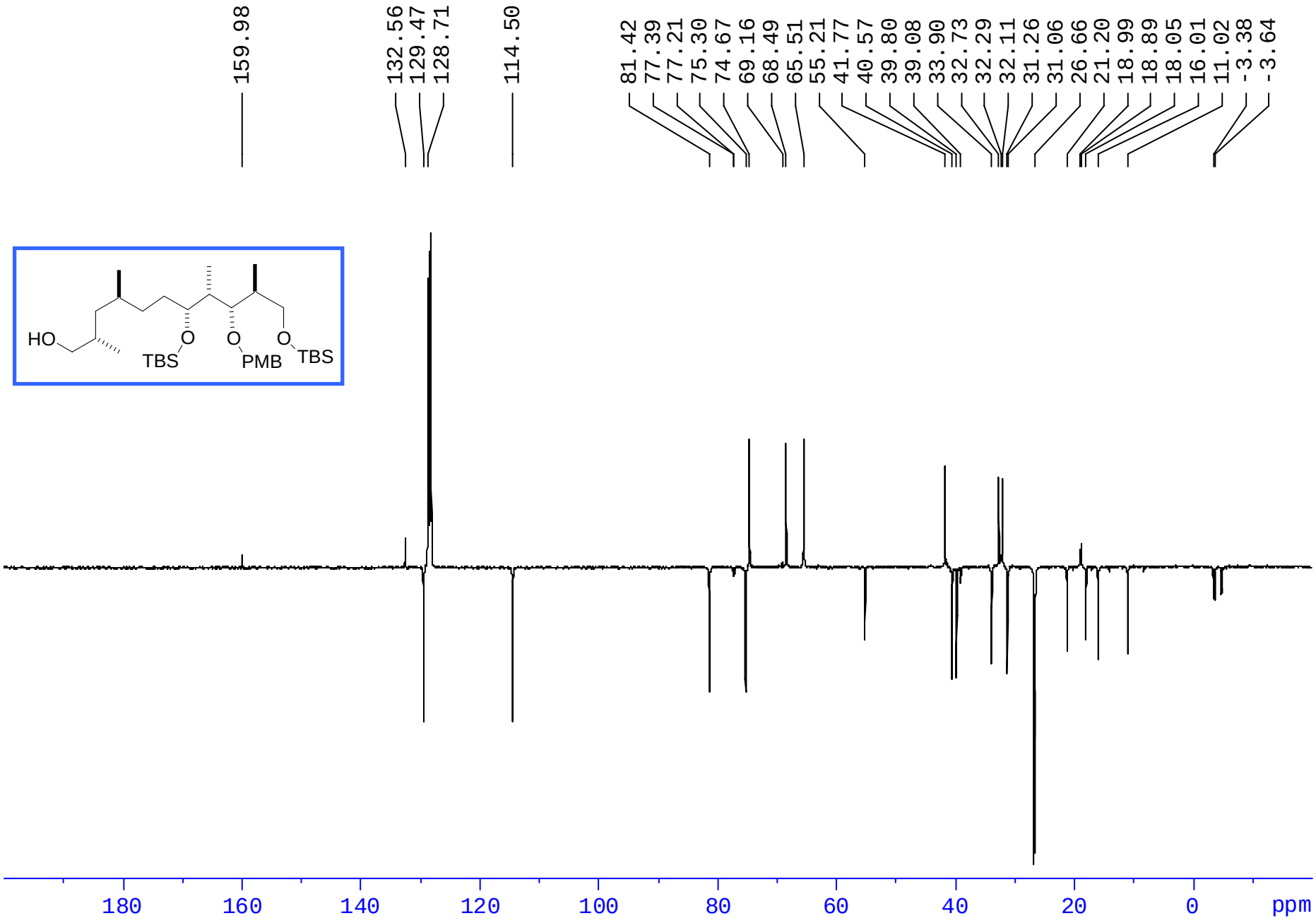

7.233
7.215
7.196
6.897
6.876
4.669
4.643
4.602
4.576
4.507
4.477
4.469
4.438
4.029
4.011
3.993
3.975
3.826
3.815
3.799
3.789
3.697
3.684
3.670
3.664
3.656
3.647
3.637
3.580
3.403
3.377
3.364
3.355
3.342
3.280
3.264
3.258
3.241
3.222
2.752
2.119
2.104
2.089
2.071
2.055
2.039
2.022
2.006
1.863
1.856
1.847
1.839
1.830
1.795
1.782
1.763
BnO
OH
O
OH
PMB
8
7
6
5
4
3
2
1
0
ppm
4.754
1.483
2.000
1.790
2.008
2.023
4.412
1.672
2.013
6.565
14.690

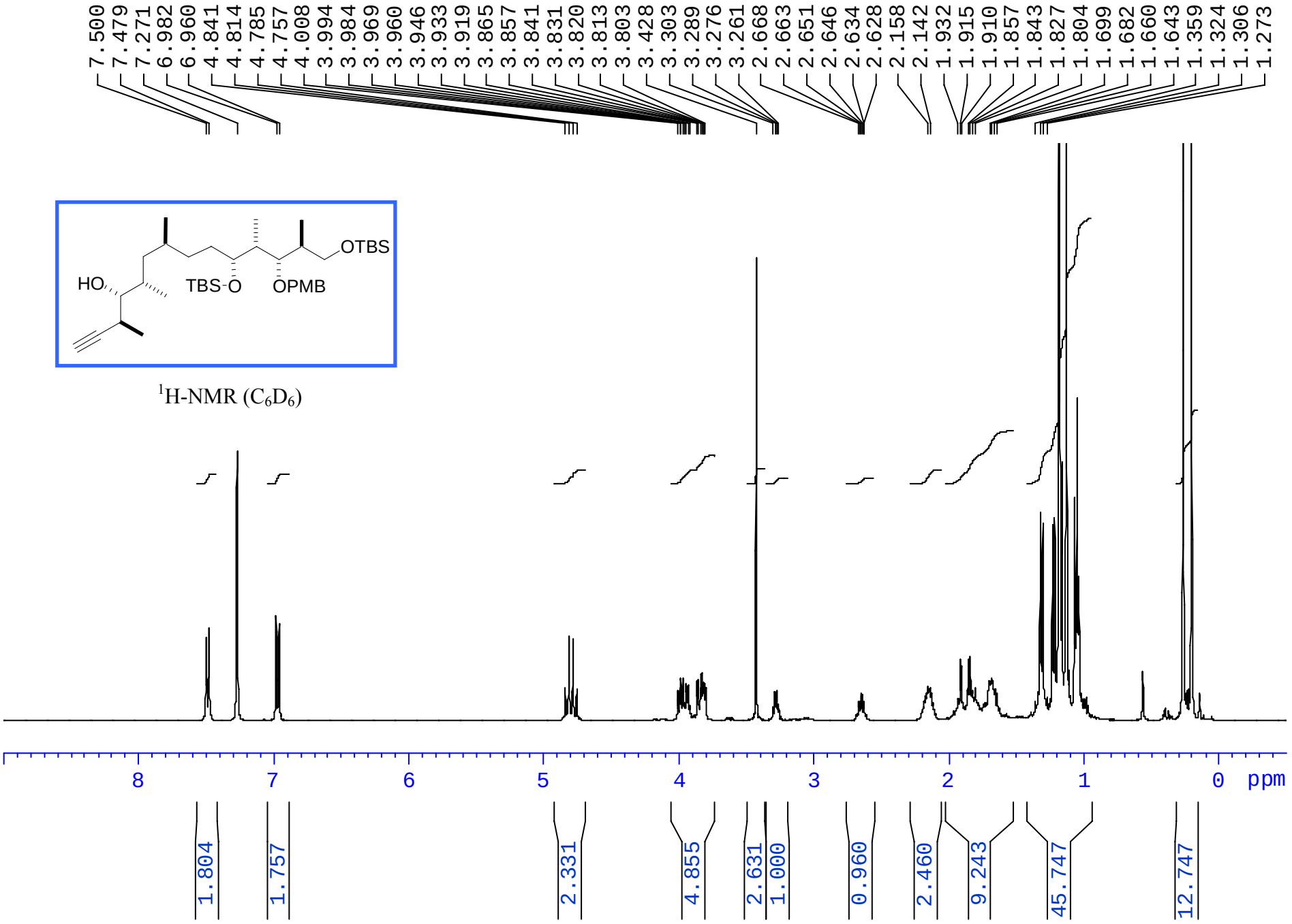

160.31
139.97
131.36
130.25
129.00
128.72
128.47
128.23
128.12
128.03
114.69
86.26
76.49
75.48
74.66
73.61
65.56
55.21
42.40
40.42
38.61
34.11
33.31
31.89
31.11
21.10
18.78
15.19
8.64
BnO
OH
O
OH
PMB
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.298
7.271
7.235
7.216
7.198
6.964
6.943
4.829
4.802
4.767
4.739
4.517
4.487
4.480
4.449
3.994
3.979
3.970
3.955
3.946
3.933
3.851
3.842
3.827
3.818
3.803
3.793
3.785
3.775
3.425
3.397
3.383
3.374
3.361
3.291
3.275
3.269
3.252
2.144
2.127
2.118
2.101
2.084
2.068
2.052
1.898
1.867
1.813
1.780
1.684
1.669
1.658
1.640
1.624
1.607
BnO
TBSO
O
PMB
OTBS
8
7
6
5
4
3
2
1
0
ppm
2.783
3.348
1.519
2.000
1.801
1.993
2.021
3.342
0.992
3.046
5.253
4.525
31.344
3.589
12.104

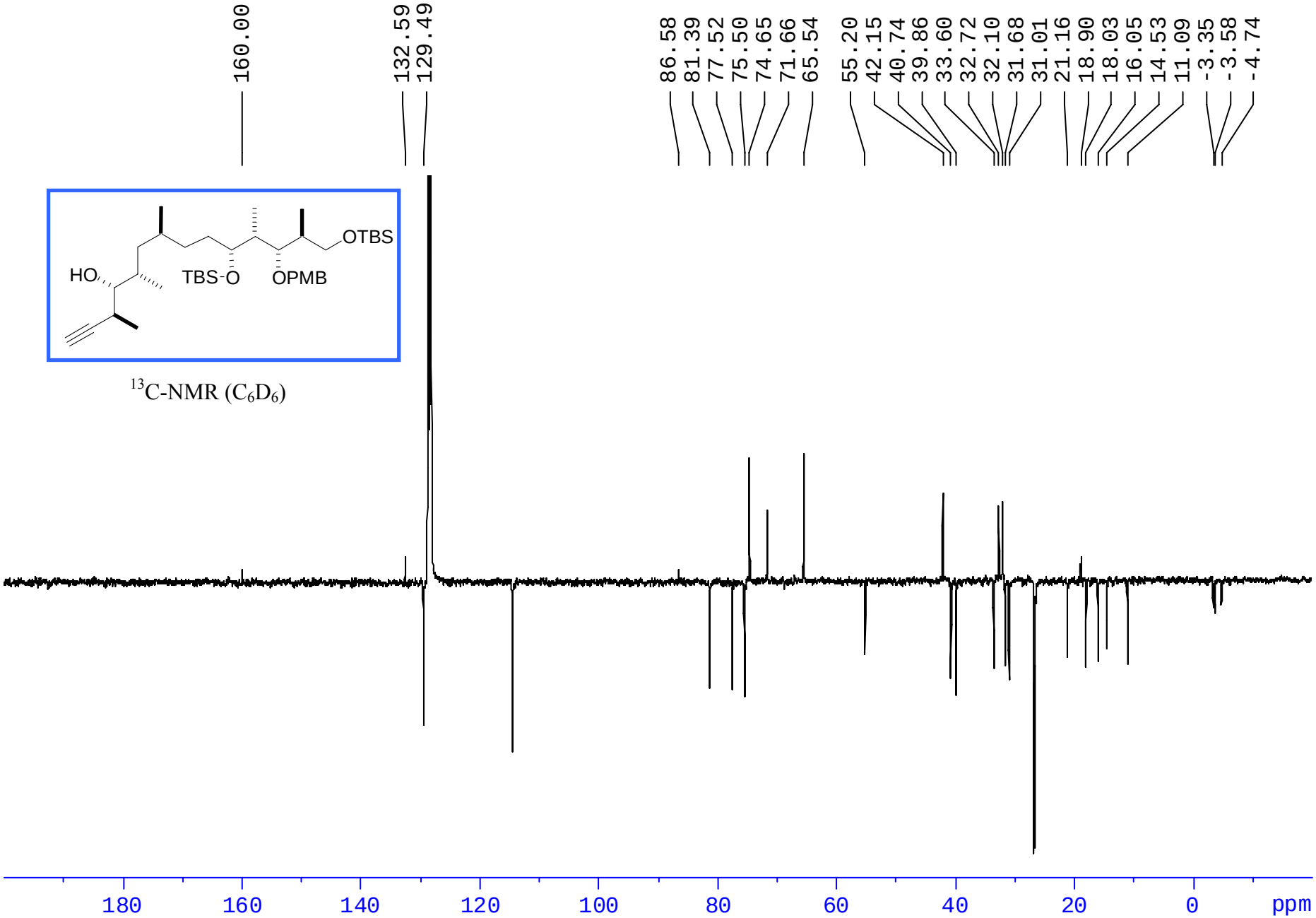

160.00
140.03
132.59
129.45
128.96
128.71
128.46
128.22
128.06
127.97
114.51
81.51
76.55
75.37
74.71
73.61
65.53
55.19
42.26
40.63
39.85
32.80
32.17
31.95
31.35
26.77
26.67
26.35
21.18
18.89
18.72
16.02
11.03
1.83
-3.36
-3.63
-4.72
BnO
TBSO
O
PMB
OTBS
180
160
140
120
100
80
60
40
20
0
ppm


7.474
7.453
7.272
6.964
6.943
4.823
4.795
4.755
4.727
3.990
3.975
3.966
3.951
3.930
3.917
3.835
3.827
3.811
3.803
3.792
3.783
3.775
3.766
3.438
3.417
3.404
3.313
3.296
3.288
3.271
2.129
2.113
1.871
1.841
1.784
1.769
1.753
1.628
1.513
1.497
1.480
1.463
1.447
1.302
1.285
1.239
1.208
1.190
HO
O
TBS
O
PMB
O
TBS
8
7
6
5
4
3
2
1
0
ppm
1.514
1.467
2.000
4.398
4.428
2.019
3.450
2.181
1.371
37.358
11.328

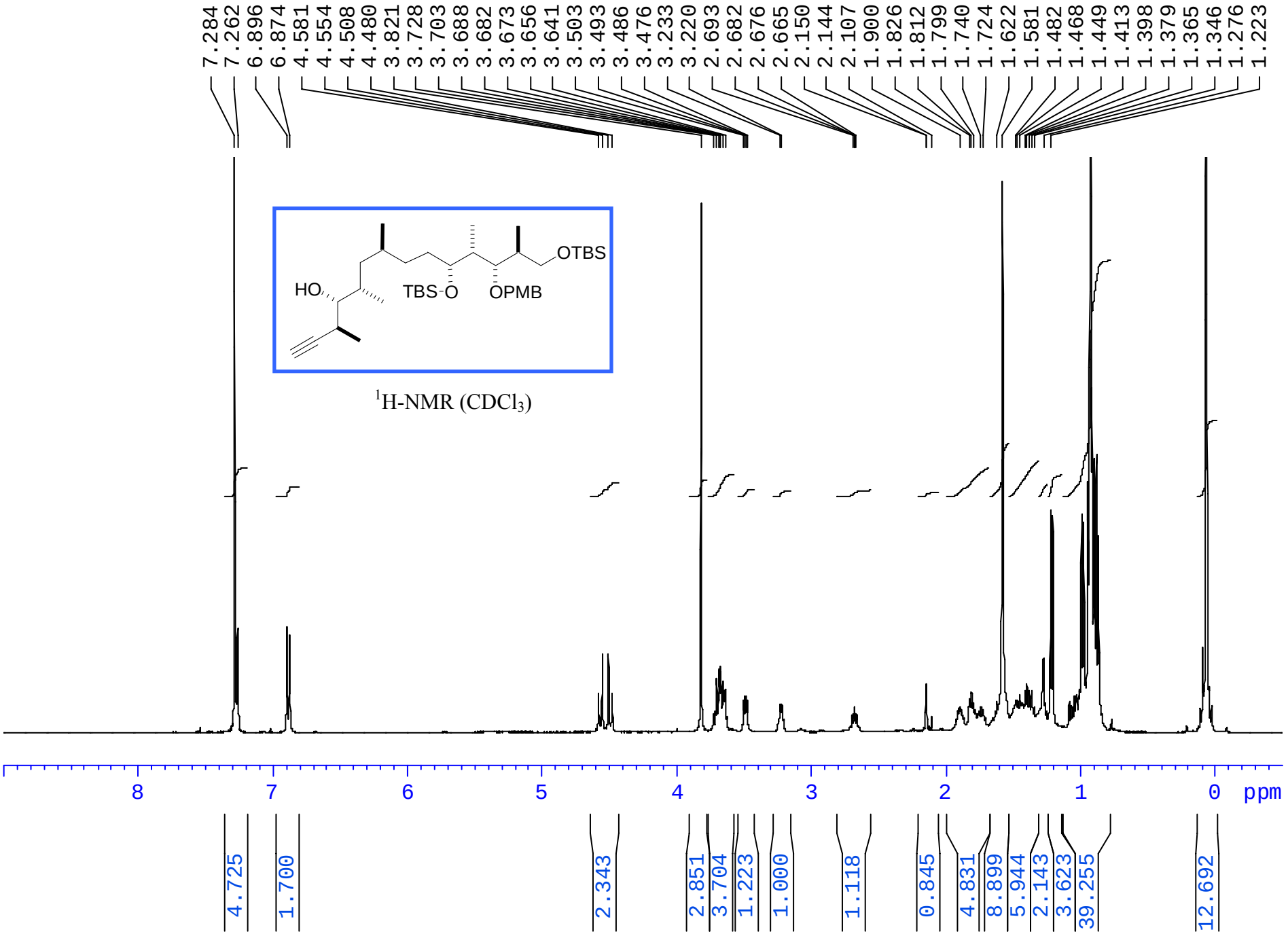

159.98
132.56
129.47
128.71
114.50
81.42
77.39
77.21
75.30
74.67
69.16
68.49
65.51
55.21
41.77
40.57
39.80
39.08
33.90
32.73
32.29
32.11
31.26
31.06
26.66
21.20
18.99
18.89
18.05
16.01
11.02
-3.38
-3.64
HO
O
TBS
O
PMB
O
TBS
180
160
140
120
100
80
60
40
20
0
ppm


7.500
7.479
7.271
6.982
6.960
4.841
4.814
4.785
4.757
4.008
3.994
3.984
3.969
3.960
3.946
3.933
3.919
3.865
3.857
3.841
3.831
3.820
3.813
3.803
3.428
3.303
3.289
3.276
3.261
2.668
2.663
2.651
2.646
2.634
2.628
2.158
2.142
1.932
1.915
1.910
1.857
1.843
1.827
1.804
1.699
1.682
1.660
1.643
1.359
1.324
1.306
1.273
HO
TBS-O
OPMB
OTBS
8
7
6
5
4
3
2
1
0
ppm
1.804
1.757
2.331
4.855
2.631
1.000
0.960
2.460
9.243
45.747
12.747

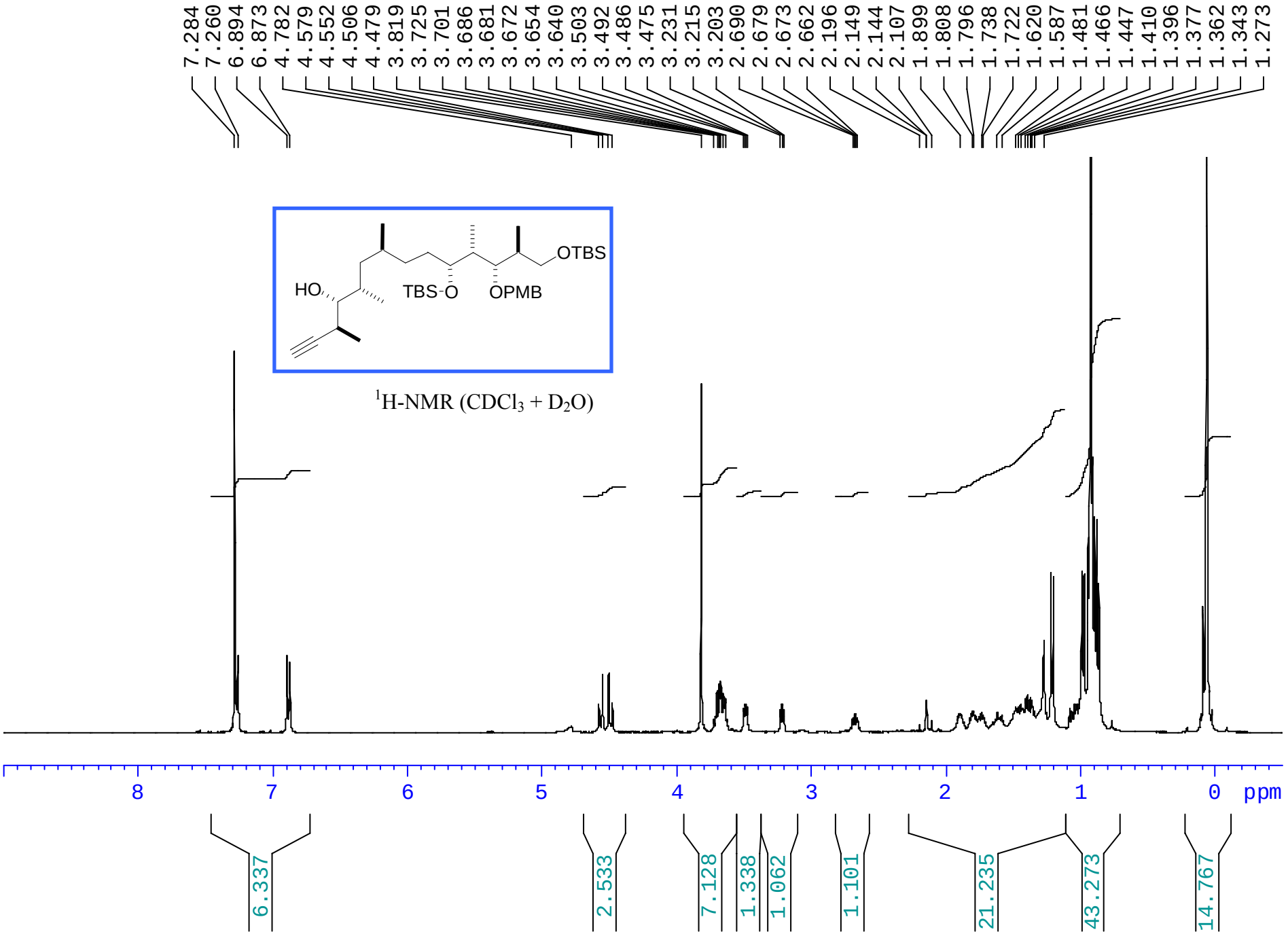
^{1}H-NMR (C_6D_6)

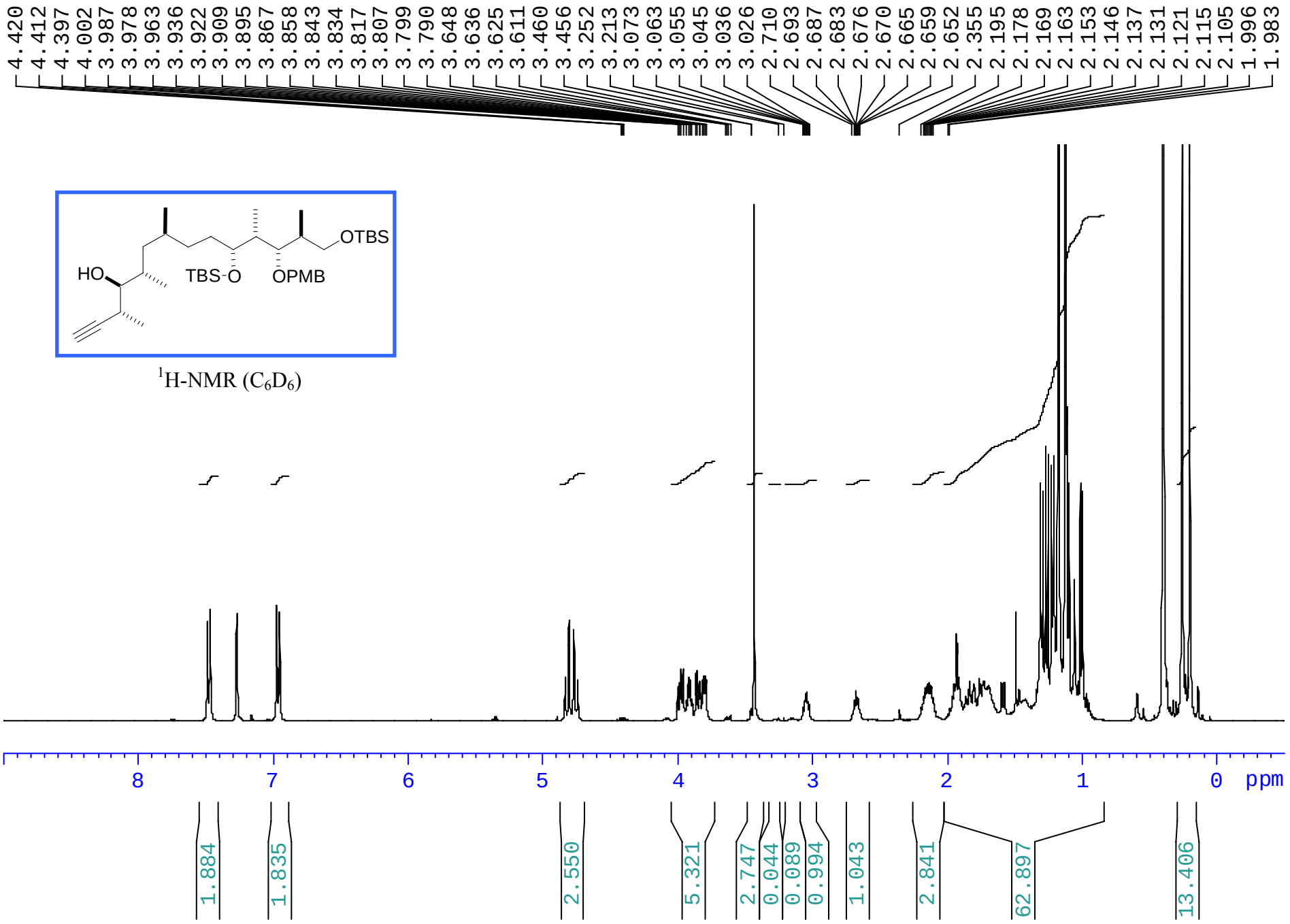

160.00
132.59
129.49
86.58
81.39
77.52
75.50
74.65
71.66
65.54
55.20
42.15
40.74
39.86
33.60
32.72
32.10
31.68
31.01
21.16
18.90
18.03
16.05
14.53
11.09
-3.35
-3.58
-4.74
HO
TBS-O
OPMB
OTBS
180
160
140
120
100
80
60
40
20
0
ppm

^{13}C-NMR (C_6D_6)

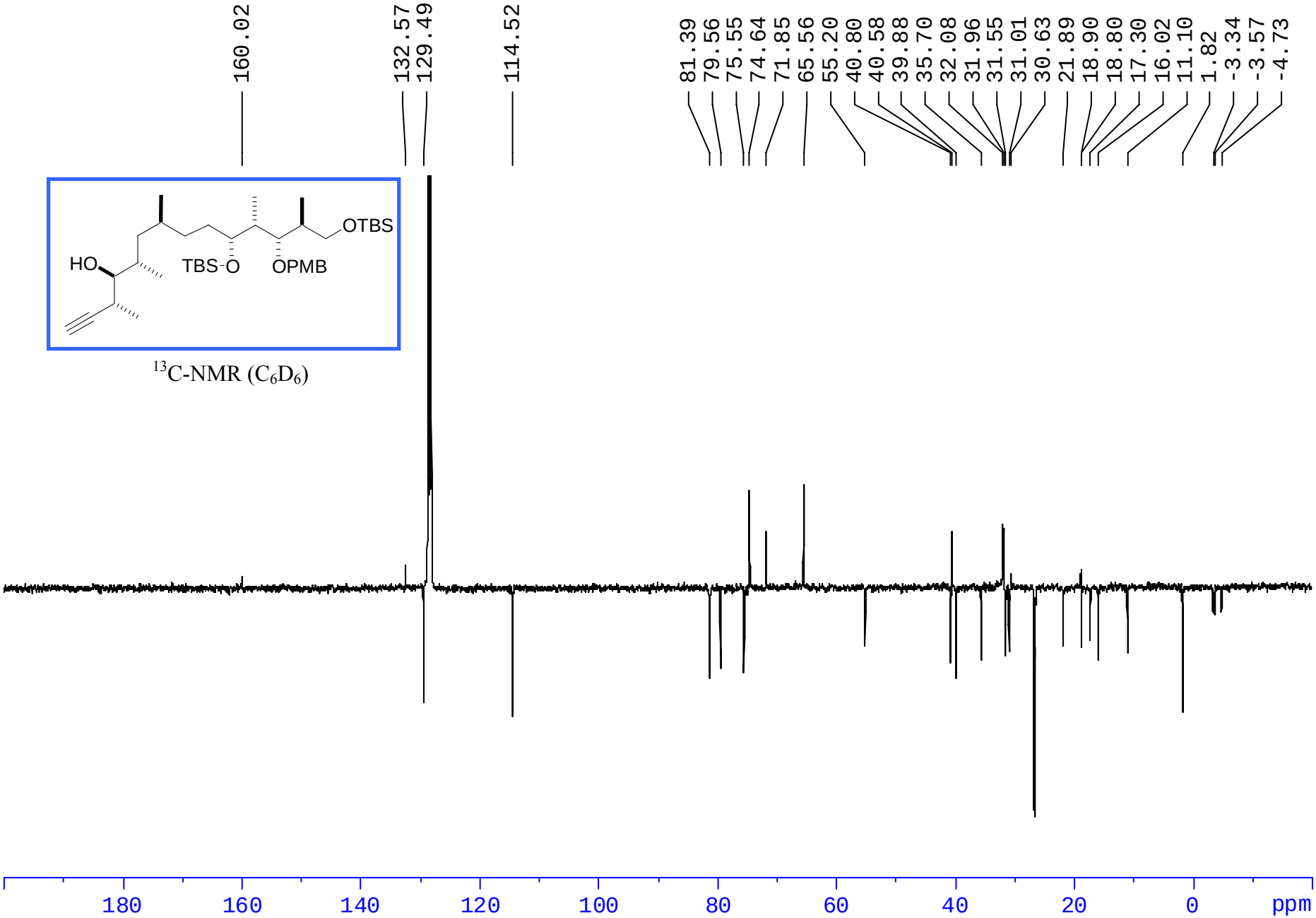

7.284
7.262
6.896
6.874
4.581
4.554
4.508
4.480
3.821
3.728
3.703
3.688
3.682
3.673
3.656
3.641
3.503
3.493
3.486
3.476
3.233
3.220
2.693
2.682
2.676
2.665
2.150
2.144
2.107
1.900
1.826
1.812
1.799
1.740
1.724
1.622
1.581
1.482
1.468
1.449
1.413
1.398
1.379
1.365
1.346
1.276
1.223
HO
TBS-O
OPMB
OTBS
8
7
6
5
4
3
2
1
0
ppm
4.725
1.700
2.343
2.851
3.704
1.223
1.000
1.118
0.845
4.831
8.899
5.944
2.143
3.623
39.255
12.692

^{1}H-NMR ($CDCl_3$)

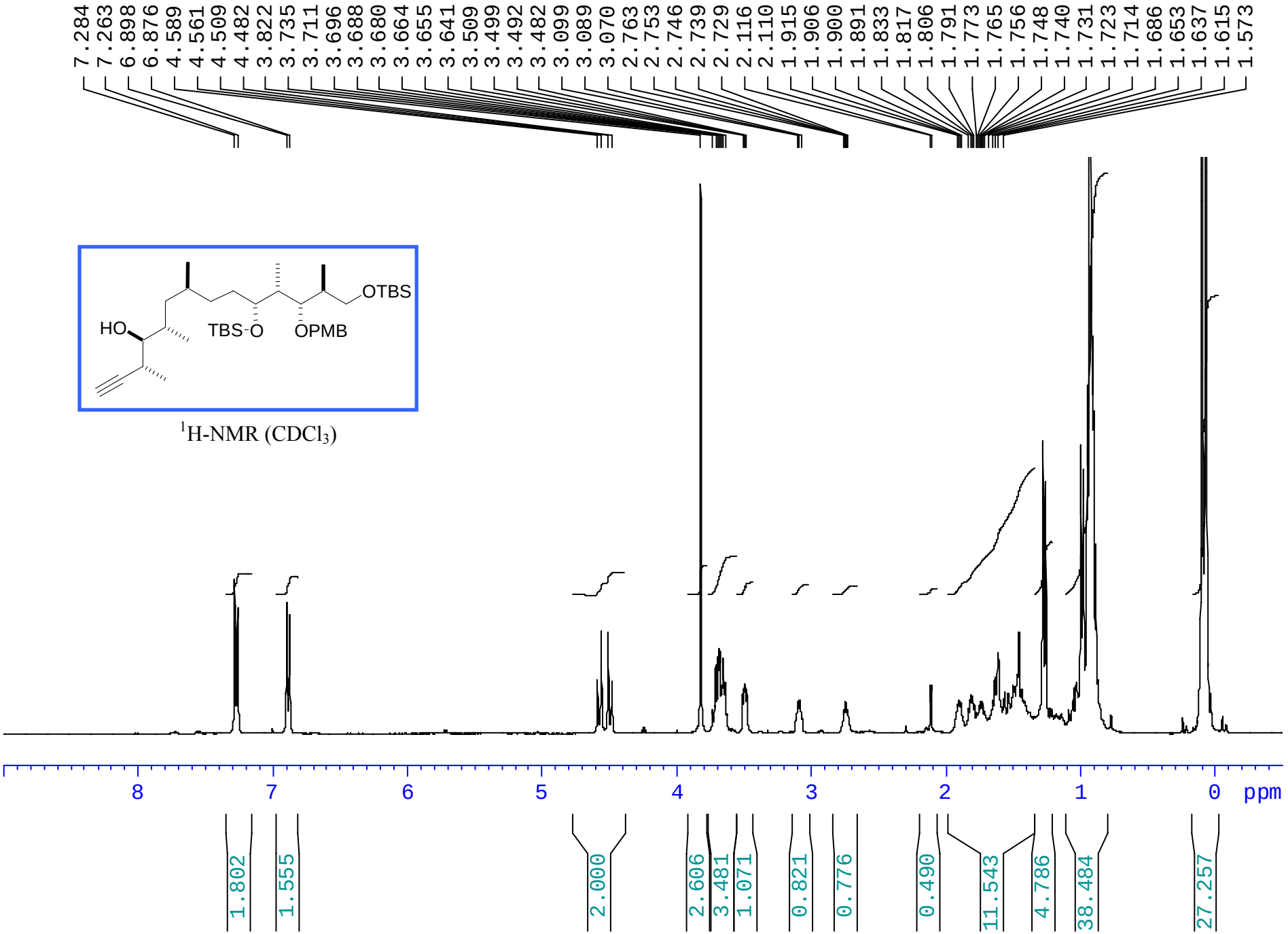

7.284
7.260
6.894
6.873
4.782
4.579
4.552
4.506
4.479
3.819
3.725
3.701
3.686
3.681
3.672
3.654
3.640
3.503
3.492
3.486
3.475
3.231
3.215
3.203
2.690
2.679
2.673
2.662
2.196
2.149
2.144
2.107
1.899
1.808
1.796
1.738
1.722
1.620
1.587
1.481
1.466
1.447
1.410
1.396
1.377
1.362
1.343
1.273
HO
TBS-O
OPMB
OTBS
1H-NMR (CDCl3 + D2O)
8
7
6
5
4
3
2
1
0
ppm
6.337
2.533
7.128
1.338
1.062
1.101
21.235
43.273
14.767


4.420
4.412
4.397
4.002
3.987
3.978
3.963
3.936
3.922
3.909
3.895
3.867
3.858
3.843
3.834
3.817
3.807
3.799
3.790
3.648
3.636
3.625
3.611
3.460
3.456
3.252
3.213
3.073
3.063
3.055
3.045
3.036
3.026
2.710
2.693
2.687
2.683
2.676
2.670
2.665
2.659
2.652
2.355
2.195
2.178
2.169
2.163
2.153
2.146
2.137
2.131
2.121
2.115
2.105
1.996
1.983
HO
TBS-O
OPMB
OTBS
8
7
6
5
4
3
2
1
0
ppm
1.884
1.835
2.550
5.321
2.747
0.044
0.089
0.994
1.043
2.841
62.897
13.406

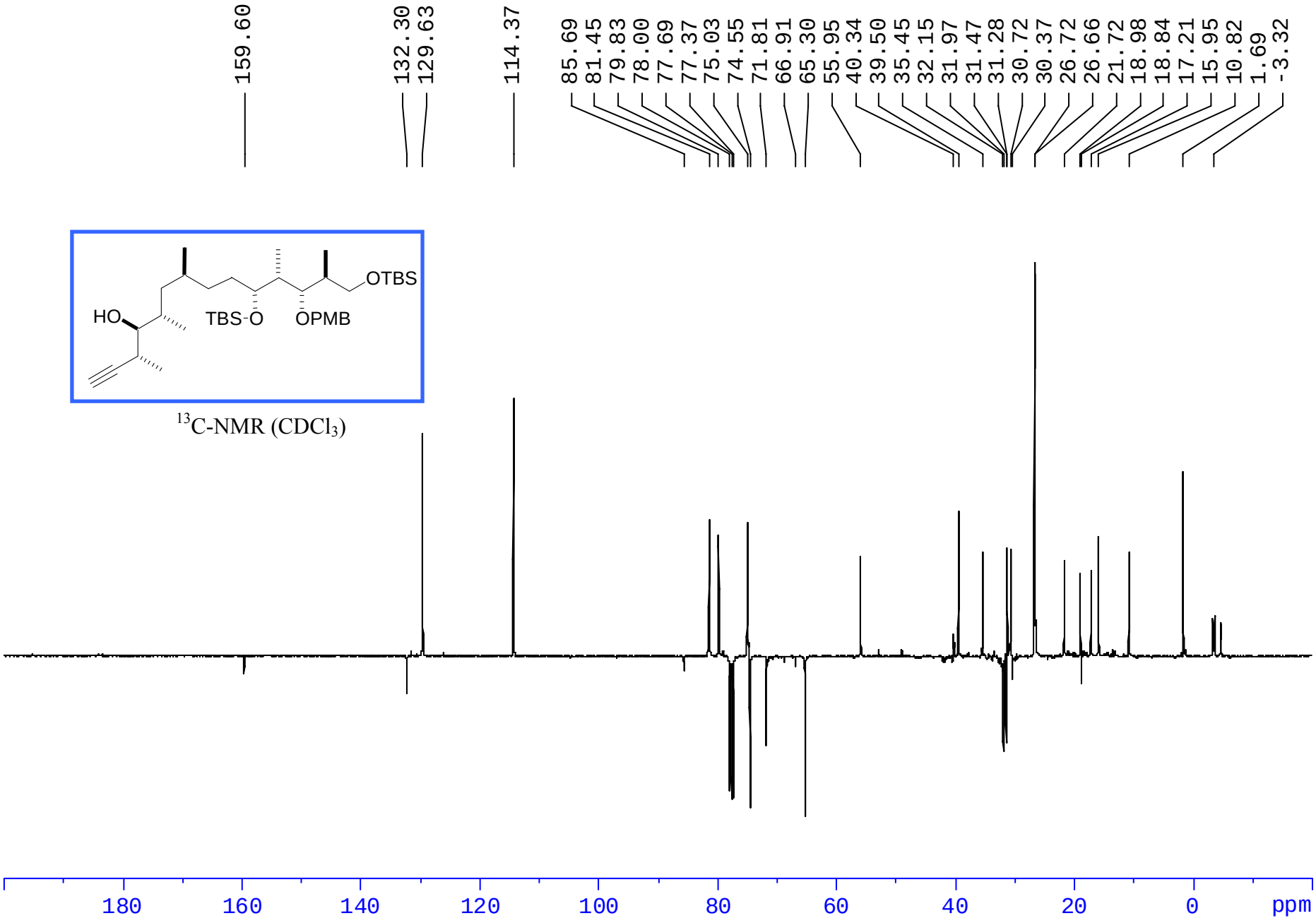
^{1}H-NMR (C_6D_6)


160.02
132.57
129.49
114.52
81.39
79.56
75.55
74.64
71.85
65.56
55.20
40.80
40.58
39.88
35.70
32.08
31.96
31.55
31.01
30.63
21.89
18.90
18.80
17.30
16.02
11.10
1.82
-3.34
-3.57
-4.73
HO
TBS-O
OPMB
OTBS
180
160
140
120
100
80
60
40
20
0
ppm

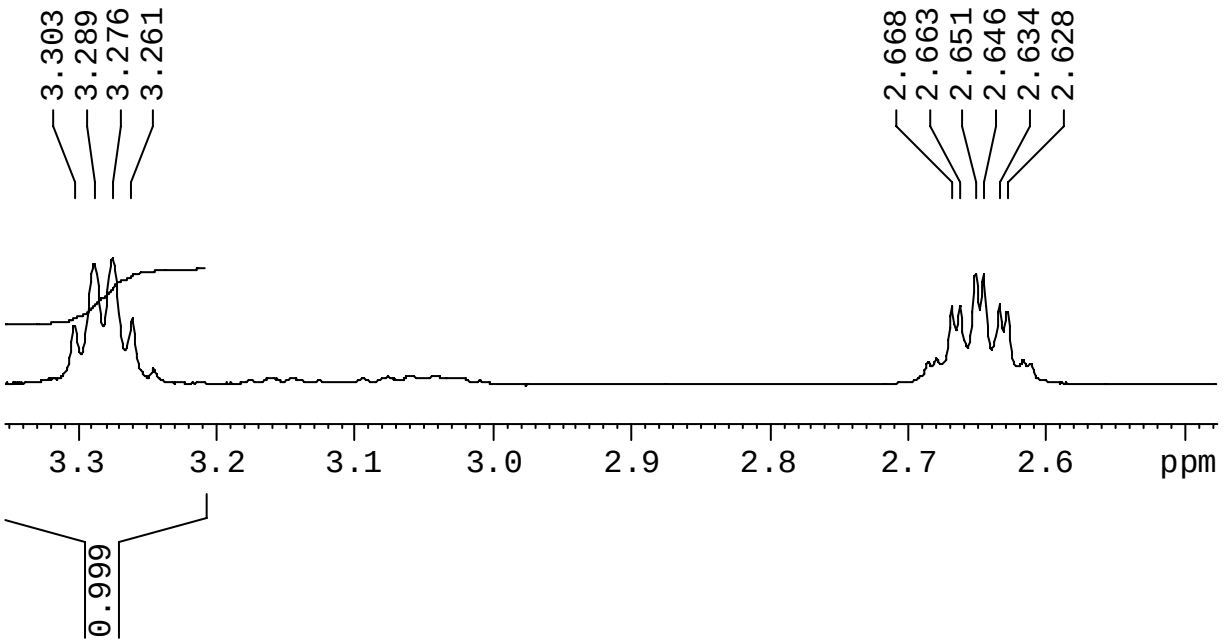
^{13}C-NMR (C_6D_6)

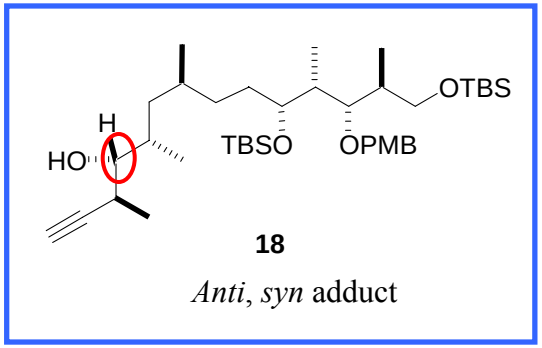

7.284
7.263
6.898
6.876
4.589
4.561
4.509
4.482
3.822
3.735
3.711
3.696
3.688
3.680
3.664
3.655
3.641
3.509
3.499
3.492
3.482
3.099
3.089
3.070
2.763
2.753
2.746
2.739
2.729
2.116
2.110
1.915
1.906
1.900
1.891
1.833
1.817
1.806
1.791
1.773
1.765
1.756
1.748
1.740
1.731
1.723
1.714
1.686
1.653
1.637
1.615
1.573
HO
TBS-O
OPMB
OTBS
8
7
6
5
4
3
2
1
0
ppm
1.802
1.555
2.000
2.606
3.481
1.071
0.821
0.776
0.490
11.543
4.786
38.484
27.257

^{1}H-NMR ($CDCl_3$)



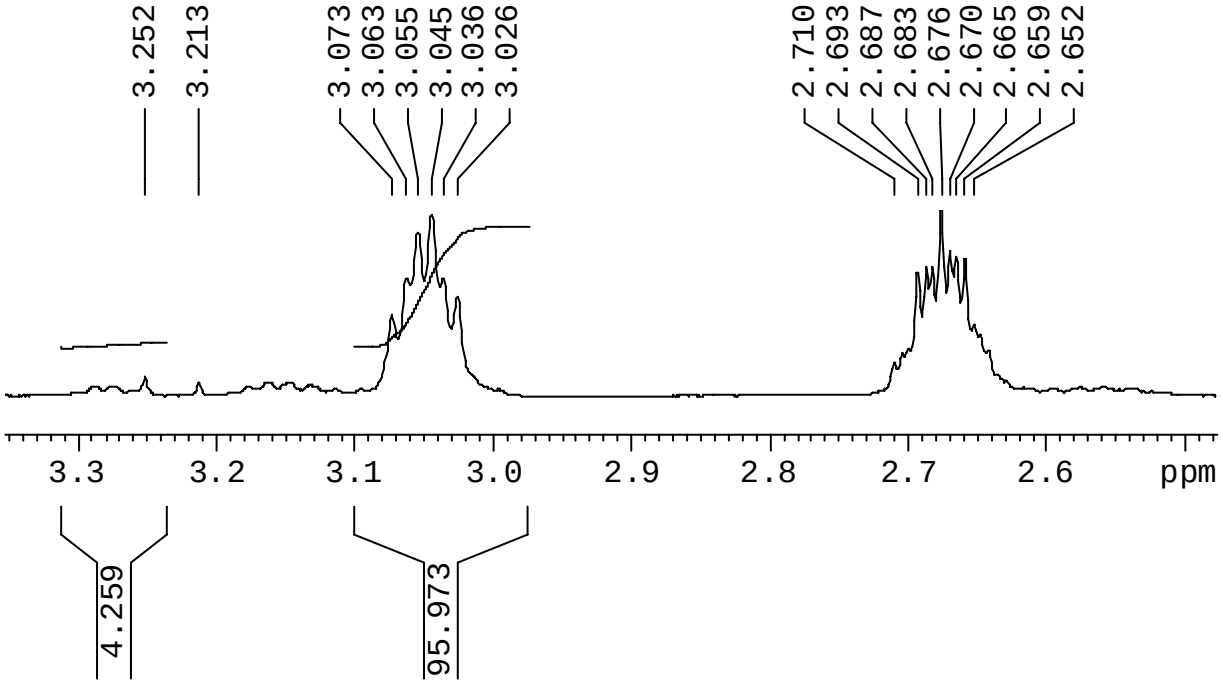
^{13}C-NMR ($CDCl_3$)

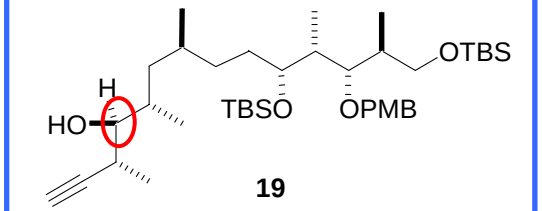




18

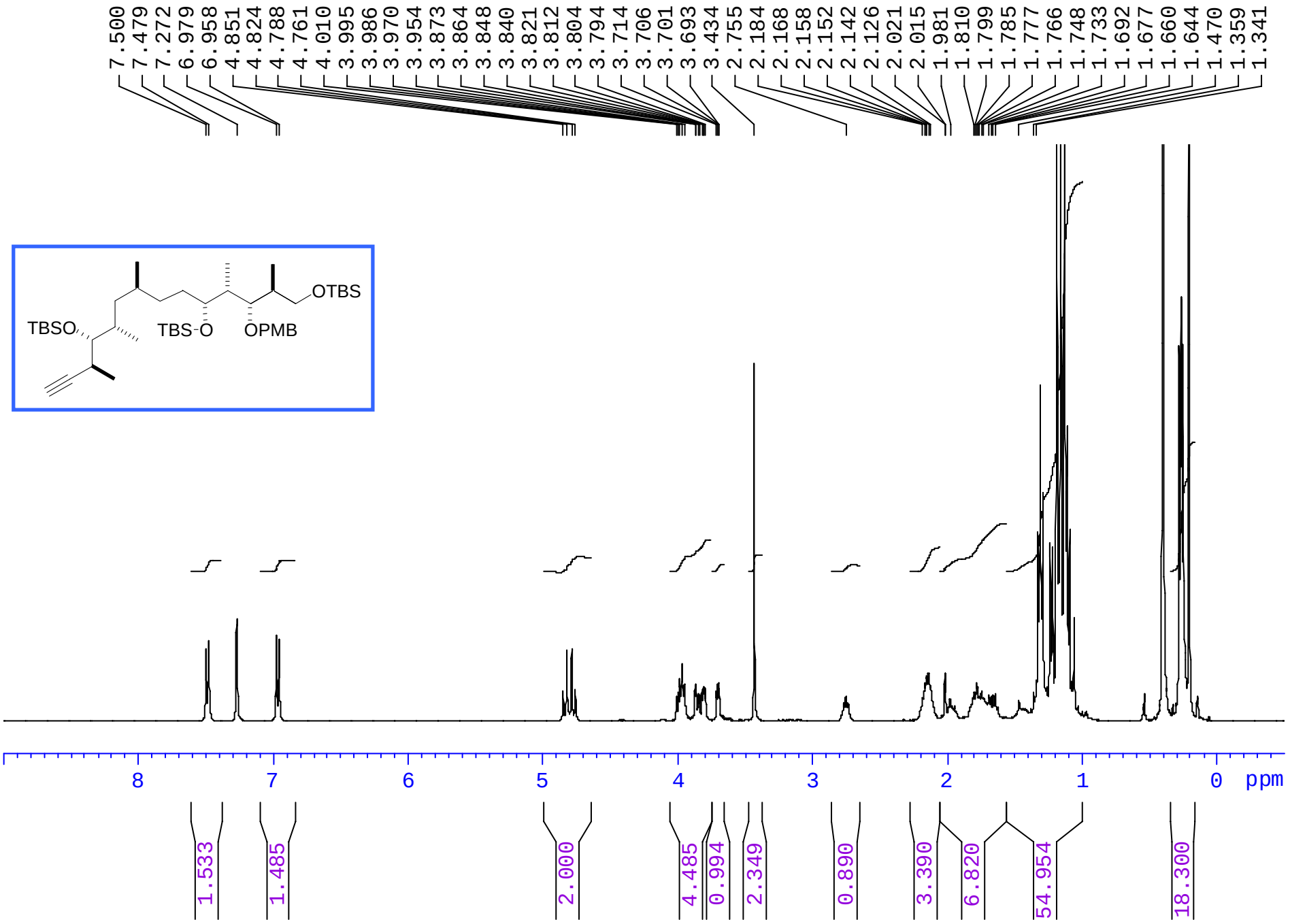
Anti, *syn* adduct

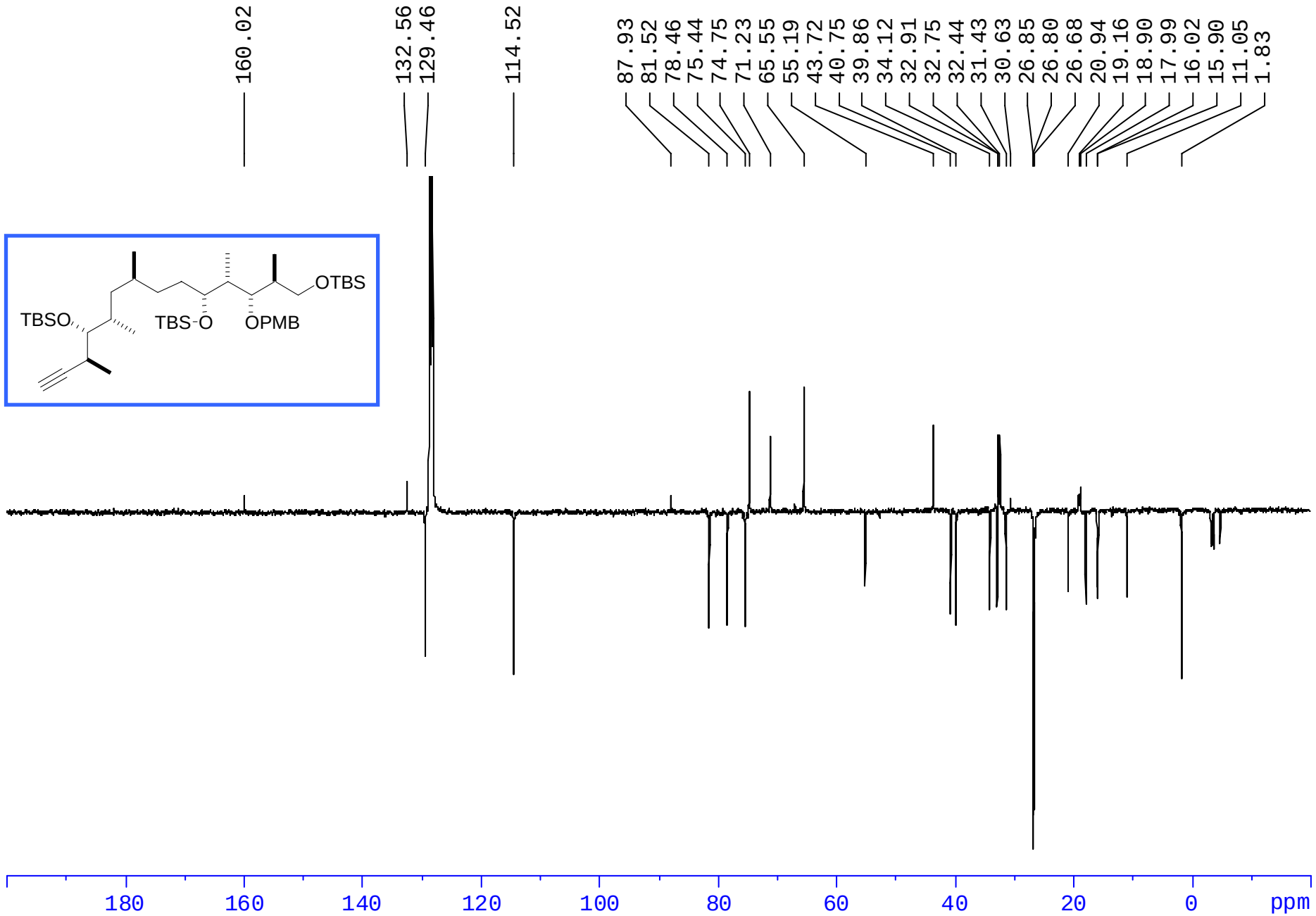




19

Anti, *anti* adduct


7.500
7.479
7.272
6.979
6.958
4.851
4.824
4.788
4.761
4.010
3.995
3.986
3.970
3.954
3.873
3.864
3.848
3.840
3.821
3.812
3.804
3.794
3.714
3.706
3.701
3.693
3.434
2.755
2.184
2.168
2.158
2.152
2.142
2.126
2.021
2.015
1.981
1.810
1.799
1.785
1.777
1.766
1.748
1.733
1.692
1.677
1.660
1.644
1.470
1.359
1.341
TBSO
TBS-O
OPMB
OTBS
8
7
6
5
4
3
2
1
0
ppm
1.533
1.485
2.000
4.485
0.994
2.349
0.890
3.390
6.820
54.954
18.300


160.02
132.56
129.46
114.52
87.93
81.52
78.46
75.44
74.75
71.23
65.55
55.19
43.72
40.75
39.86
34.12
32.91
32.75
32.44
31.43
30.63
26.85
26.80
26.68
20.94
19.16
18.90
17.99
16.02
15.90
11.05
1.83
TBSO
TBS-O
OPMB
OTBS
180
160
140
120
100
80
60
40
20
0
ppm