Supporting Information for

Synthesis of the C1-C21 Domain of Azaspiracid-3

Zhigao Zhang, Yue Ding, Jianyan Xu, Yong Chen, and Craig J. Forsyth*

Department of Chemistry & Biochemistry, The Ohio State University, Columbus, Ohio 43210

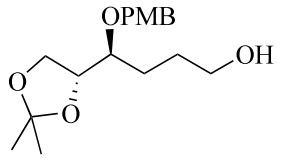
forsyth@chemistry.ohio-state.edu

Contents

General Methods:

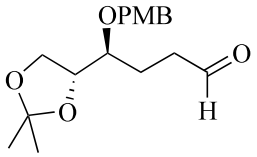
Unless otherwise noted, all reactions were carried out under an argon atmosphere in over-dried glassware using standard syringe, cannula, and septa techniques. Dichloromethane, tetrahydrofuran, diethyl ether, toluene, and dimethylformamide were purified with a Pure Solv MD-6 solvent purification system. Triethylamine, diisopropylethylamine, acetonitrile, methanol were distilled from calcium hydride under nitrogen. All other solvents were used as received.

Analytical thin layer chromatography (TLC) was performed using 0.25 mm Silicycle silica gel 60 F_{254} plates. Solvents for chromatography are listed as volume: volume ratios. Optical rotations were measured on a Perkin-Elmer polarimeter. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX 400 spectrometer, operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts are reported in ppm on the δ scale relative to residual $CHCl_3$ (δ = 7.28 for ^{1}H NMR and δ = 77.2 for ^{13}C NMR) as an internal reference. The coupling constant values (*J*) are in Hertz (Hz). The following abbreviations have been used for signal multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. ESI mass spectra were measured on a Bruker MicroOTOF instrument.



11

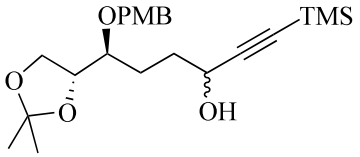
(*S*)-4-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-4-((4-methoxybenzyl)oxy)butan-1-ol (11). To a solution of **8**[1] (10.8 g, 37 mmol) in THF (200 mL) at 0 ^{o}C was added dropwise BH_3 (37.0 mL, 1.0 M in THF, 37 mmol). After 2 h at rt, the reaction mixture was cooled to 0 ^{o}C. Water (4.0 mL), 3 M aqueous NaOH (13.2 mL) and 30% aqueous H_2O_2 (8.7 mL) were added sequentially. The mixture was stirred for 2 h at rt then diluted with water (200 mL). The pH was adjusted to 6-7 with 10% aqueous HCl. The aqueous phase was extracted with diethyl ether (3 x 200 mL) and the combined organic phase was washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 3:1, v/v) to provide alcohol **11** (7.94 g, 26 mmol, 70%) as a colorless oil: R_f = 0.33 (hexanes-ethyl acetate, 1:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz), 4.59 (q_{AB}, Δν = 16 Hz, J_{AB} = 11 Hz, 2H), 4.12 (q, J = 6.2 Hz, 1H), 4.06 (dd, J = 6.4 Hz, 1.6 Hz, 1H), 3.88 (dd, J = 6.4 Hz, 1.5 Hz, 1H), 3.82 (s, 3H), 3.64 (m, 2H), 3.57 (td, J = 6.0 Hz, 3.2 Hz, 1H), 1.72 (m, 3H), 1.63 (m, 3H), 1.44 (s, 3H), 1.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.3, 130.3, 129.5, 113.8, 109.1, 78.58, 77.5, 72.3, 66.6, 62.9, 55.3, 28.1, 27.4, 26.6, 25.23; IR (neat): 3436, 2935, 1612, 1513, 1454, 1370, 1301, 1248, 1069 cm^{-1}; $[\alpha]_D^{25}$ + 17.1 (*c* 1.56, $CHCl_3$); HRMS-ESI(m/z) calculated for $[M+Na]^+$ 333.1673, found 333.1687.



12

(*S*)-4-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-4-((4-methoxybenzyl)oxy)butanal (12). To a solution of oxalyl chloride (2.3 mL, 26 mmol) in CH_2Cl_2 (100 mL) at -78 ^{o}C was added dropwise DMSO (3.6 mL, 52 mmol). After 20 min at -78 ^{o}C, a solution of **11** (4.0

g, 13 mmol) in CH_2Cl_2 (30 mL) was added, then the solution was warmed to -60 ^oC. After 1 h at -60 ^oC, *i*-Pr_2NEt (13.5 mL, 77.4 mmol) was added. The mixture was stirred for 10 min at – 60 ^oC and 10 min at 0 ^oC. Cold 1 M aqueous HCl solution (48 mL) was added. The organic phase was mixed with pH 7 aqueous buffer. The aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were washed with brine and dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 5:1, v/v) to provide aldehyde **12** (3.92 g, 12.7 mmol, 99%) as a colorless oil: R_f = 0.8 (hexanes-ethyl acetate, 1:1, v/v); ^1H NMR ($CDCl_3$, 400 MHz): δ 9.75 (t, *J* = 1.44 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.54 (q_{AB}, Δν = 19 Hz, J_{AB} = 11.1 Hz, 2H), 4.08 (m, 2H), 3.86 (m, 1H), 3.82 (s, 3H), 3.54 (m, 1H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.01 (m, 1H), 1.85 (m, 1H), 1.42 (s, 3H), 1.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): 202.1, 159.4, 130.1, 129.6, 113.9, 109.2, 77.7, 72.2, 66.6, 55.3, 39.3, 26.6, 25.2, 23.3; IR (neat): 2984.3, 2930.1, 2883.6, 1721.5, 1613.0, 1512.3, 1307.7, 1248.7, 1070.7, 1032.0, 846.0; $[\alpha]_D^{25}$ + 8.14 (*c* 1.5, $CHCl_3$); HRMS-ESI(m/z) calculated for $[M+Na]^+$: 331.1516, found 331.1521.

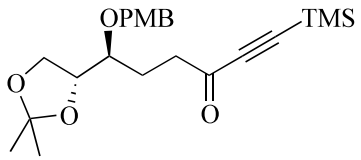


12a

(3R/S,6*S*)-6-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-6-((4-methoxybenzyl)oxy)-1-(trimethylsilyl)hex-1-yn-3-ol (12a).

To a solution of trimethylsilylacetylene (6.22 mL, 43.8 mmol) in THF (130 mL) at – 78 ^oC was added dropwise a solution of *n*-BuLi (15.7 mL, 2.5 M in THF, 40 mmol). After 30 min at -78 ^oC, a solution of **12** (4.5 g, 15 mmol) in THF (16 mL) was added slowly. The solution was allowed to stir for 1 h before saturated aqueous NH_4Cl was added. The aqueous phase was extracted with diethyl ether (3 x 80 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 4:1, v/v) to provide **12a** (5.0 g, 13 mmol, 87%) as a colorless oil:

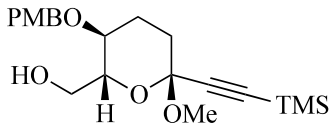
R_f = 0.43 (hexanes-ethyl acetate, 3:1 v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (m, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.57 (m, 2H), 4.40 (q, 1H), 4.08 (m, 2H), 3.88 (m, 1H), 3.82 (s, 3H), 3.57 (m, 1H), 1.90 (m, 5H), 1.43 (d, 3H), 1.36 (d, 3H), 0.19 (d, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.33, 159.27, 130.30, 130.06, 129.66, 129.51, 113.84, 113.82, 109.12, 109.09, 106.76, 106.61, 89.52, 89.42, 78.35, 78.32, 77.29, 71.99, 71.85, 66.86, 66.62, 62.70, 62.55, 55.23, 32.87, 32.44, 26.66, 26.60, 26.23, 25.66, 25.28, 25.26, -0.12, -0.15; IR (neat): 3441.4(broad), 2937.9, 1613.6, 1514.0, 1249.4, 1073.8, 843.5; HRMS-ESI(m/z) calculated for $[M+Na]^+$: 429.2068, found 429.2060.



13

(S*)*-6-((R*)*-2,2-Dimethyl-1,3-dioxolan-4-yl)-6-((4-methoxybenzyl)oxy)-1-(trimethylsilyl)hex-1-yn-3-one (13).

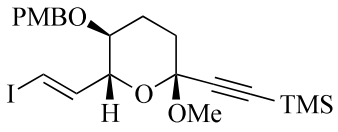
To a solution of **12a** (4.5 g, 11 mmol) in CH_2Cl_2 (100 mL) and DMSO (20 mL) at 0 ^{o}C were sequentially added Et_3N (9.2 mL, 67 mmol) and SO_3·Py (7.6g, 48 mmol). After 2 h at 0 ^{o}C, saturated aqueous NH_4Cl (100 mL) was added. The aqueous phase was extracted with diethyl ether (3 x 80 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 5:1, v/v) to provide ketone **13** (3.7 g, 9.2 mmol, 83%) as colorless oil: R_f = 0.57 (hexanes-ethyl acetate, 3:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.53 (s, 2H), 4.07 (m, 2H), 3.85 (m, 1H), 3.82 (s, 3H), 3.53 (m, 1H), 2.71 (m, 2H), 2.06 (m, 1H), 1.87 (m, 1H), 1.43 (s, 3H), 1.36 (s, 3H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 187.3, 159.3, 130.3, 129.5, 113.9, 109.2, 102.0, 97.8, 77.6, 72.2, 66.7, 55.3, 40.5, 26.6, 25.3, 24.8, -0.8; IR(neat): 2957.5, 2945.6, 2899.2, 1676.8, 1612.3, 1513.8, 1250.7, 1072.8, 847.1, 761.5; $[\alpha]_D^{25}$ + 9.56 (*c* 0.5, $CHCl_3$); HRMS (ESI+) calculated for $[M+Na]^+$: 427.1911, found 427.1903.



14

((2*R*,3*S*,6*R*)-6-Methoxy-3-((4-methoxybenzyl)oxy)-6-((trimethylsilyl)ethynyl)tetrahydro-2*H*-pyran-2-yl)methanol (14).

To a solution of **13** (3.58 g, 8.86 mmol) in methanol (30 mL) was added $TsOH \cdot H_2O$ (0.17 g, 0.89 mmol). After 2 h, diethyl ether and saturated aqueous $NaHCO_3$ were added. The aqueous phase was extracted with diethyl ether (3 x 50 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 8:1, v/v) to provide alcohol **14** (2.2 g, 5.8 mmol, 65%) as a colorless oil: R_f = 0.37 (hexanes-ethyl acetate, 3:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 4.43 (q_{AB}, Δν = 64 Hz, J_{AB} = 11.2 Hz, 2H), 3.82 (s, 3H), 3.75 (m, 2H), 3.57 (m, 1H), 3.44 (td, J = 10.0 Hz, 4.4 Hz, 1H), 3.38 (s, 3H), 3.10 (m, 3H), 1.91 (m, 2H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.3, 130.1, 129.3, 113.9, 101.9, 94.1, 89.0, 73.2, 72.5, 70.3, 62.7, 55.2, 50.4, 35.6, 24.3, -0.27; IR (neat): 3502(broad), 2957, 2899, 1612, 1513, 1250, 1152, 1089, 1040, 846, 760; $[\alpha]_D^{25}$ + 6.84 (*c* 2.1, $CHCl_3$); HRMS-ESI(m/z) calculated for $[M+Na]^+$: 401.1755, found 401.1763.

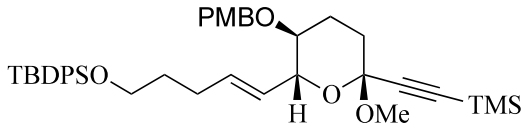


15

(((2*R*,5*S*,6*R*)-6-((*E*)-2-Iodovinyl)-2-methoxy-5-((4-methoxybenzyl)oxy)tetrahydro-2*H*-pyran-2-yl)ethynyl)trimethylsilane (15).

To a solution of **14** (1.0 g, 2.7 mmol) in CH_2Cl_2 (30mL) and DMSO (6 mL) at 0 ^oC were sequentially added *i*-Pr_2NEt (2.78 mL, 15.9 mmol) and $SO_3 \cdot Py$ (1.8 g, 11.4 mmol). After 5 min at 0 ^oC, cold 1 M aqueous HCl (10 mL) was added. The separated organic phase was neutralized with pH 7 aqueous buffer. The aqueous phase was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography

(hexanes-ethyl acetate, 4:1, v/v) to provide the aldehyde ((2*R*,3*S*,6*R*)-6-methoxy-3-((4-methoxybenzyl)oxy)-6-((trimethylsilyl)ethynyl)tetrahydro-2*H*-pyran-2-yl)methanal as a colorless oil (0.99 g, 2.6 mmol, 96%). A solution of the aldehyde (0.99 g, 2.6 mmol) and CHI_3 (1.56 g, 3.96 mmol) in 1,4-dioxane (4 mL) was added dropwise via cannula to a 0 ^oC stirred suspension of powdered anhydrous $CrCl_2$ (1.95 g, 15.9 mmol) in THF (24 mL). The mixture was allowed to warm to rt over 3 h. After stirring for an additional 9 h, saturated aqueous $NaHCO_3$ was added. The separated aqueous phase was extracted with diethyl ether (3 x 30 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 40:1, v/v) to provide vinyl iodide **15** (0.8 g, 2 mmol, 75%) as a colorless oil: R_f = 0.60 (hexanes-ethyl acetate, 5:1, v/v); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.65 (dd, *J* = 14.8 Hz, 6.4 Hz, 1H), 6.51 (dd, *J* = 14.8 Hz, 1.2 Hz, 1H), 4.53 (q_{AB}, Δν = 54 Hz, J_{AB} = 11.3 Hz, 2H), 3.91 (ddd, *J* = 6.2 Hz, 3.3 Hz, 1.1 Hz, 1H), 3.83 (s, 3H), 3.36 (s, 3H), 3.21 (td, *J* = 10 Hz, 4.4 Hz, 1H), 2.11 (m, 1H), 1.91 (m, 3H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.3, 143.2, 130.1, 129.4, 113.9, 101.7, 94.1, 89.1, 79.8, 75.2, 75.1, 70.8, 55.3, 50.5, 35.5, 24.8, -0.03; IR (neat): 2955, 1513, 1249, 1085, 1043, 944, 859, 844, 760; $[\alpha]_D^{25}$ + 6.57 (*c* 1.6, $CHCl_3$); HRMS-ESI(m/z) calculated for $[M+Na]^+$: 523.0772, found 523.0765.

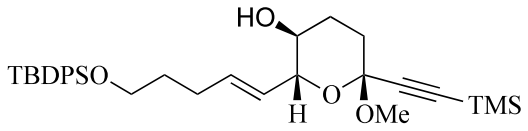


16

***tert*-Butyl(((*E*)-5-((2*R*,3*S*,6*R*)-6-methoxy-3-((4-methoxybenzyl)oxy)-6-((trimethylsilyl)ethynyl)tetrahydro-2*H*-pyran-2-yl)pent-4-en-1-yl)oxy)diphenylsilane (16).**

To a solution of 3-(*O*-*tert*-butyldimehtylsilyl)oxy-propene (720 mg, 2.4 mmol) in THF (13 mL) at 0 ^oC was slowly added a solution of 9-BBN (6.4 mL, 0.5 M in THF, 3.2 mmol). The solution was slowly warmed to rt then stirred at rt for 2 h. To this solution was added a solution of 3 M aqueous K_3PO_4 (1.06 mL, 1.2 mmol) in DMF (1.1 mL). After stirring for 30 min at rt, the mixture was added to a mixture of vinyl iodide (600 mg, 1.2 mmol) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (98 mg, 0.12 mmol) via cannula. After 5 min

diethyl ether (10 mL) and H_2O (10 mL) were added. The separated aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 40:1, v/v) to provide **16** (760 mg, 1.16 mmol, 95%) as a colorless oil: R_f = 0.62 (hexanes-ethyl acetate, 5:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (dd, *J* = 7.8 Hz, 1.6 Hz, 4H), 7.42 (m, 6H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.85 (dt, *J* = 15.4 Hz, 6.8 Hz, 1H), 5.52 (dd, *J* = 15.2 Hz, 7.6 Hz, 1H), 4.50 (q_{AB}, Δν = 25 Hz, J_{AB} = 11.3 Hz, 2H), 3.88 (t, *J* = 8.1 Hz, 1H), 3.79 (s, 3H), 3.71 (t, *J* = 6.3 Hz, 2H), 3.38 (s, 3H), 3.20 (td, *J* = 9.5 Hz, 4.5 Hz, 1H), 2.22 (q, *J* = 6.4 Hz, 2H), 2.10 (m, 1H), 1.97 (m, 2H), 1.87 (m, 1H), 1.71 (m, 2H), 1.08 (s, 9H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 135.6, 134.9, 134.0, 130.5, 129.5, 129.3, 127.9, 127.6, 113.7, 102.3, 94.0, 88.5, 75.7, 74.6, 70.9, 63.5, 55.2, 50.4, 35.9, 31.9, 28.9, 26.9, 25.1, 19.2, -0.2; IR (neat): 2933.1, 2856.8, 1612.0, 1513.0, 1249.5, 1109.9, 844.2, 702.5; $[\alpha]_D^{25}$ + 4.32 (*c* 1.6, $CHCl_3$); HRMS-ESI(m/z) calculated for $[M+Na]^+$: 693.3402, found 693.3434.

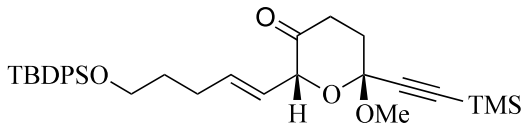


16a

(2*R*,3*S*,6*R*)-2-((*E*)-5-((*tert*-Butyldiphenylsilyl)oxy)pent-1-en-1-yl)-6-methoxy-6-((trimethylsilyl)ethynyl)tetrahydro-2*H*-pyran-3-ol (16a).

To a stirred, rt mixture of **16** (406 mg, 0.60 mmol) in CH_2Cl_2 (10 mL), pH 7 aqueous buffer (1 mL), and *tert*-butanol (0.5 mL) was added DDQ (412 mg, 1.8 mmol). After 10 min, diethyl ether (10 mL) and saturated aqueous $NaHCO_3$ (15 mL) were added. The separated aqueous phase was extracted with diethyl ether (3 x 15 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 20:1, v/v) to provide **16a** (299 mg, 0.54 mmol, 90%) as a colorless oil: R_f = 0.62 (hexanes-ethyl acetate, 3:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (dd, *J* = 7.7 Hz, 1.6 Hz, 4H), 7.42 (m, 6H), 5.87 (dt, *J* = 15.4 Hz, 6.6 Hz, 1H), 5.50 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.71 (m, 1H), 3.40 (m, 4H), 2.23 (q, *J* = 6.8 Hz 2H), 2.12 (m, 1H), 2.06 (td, *J* = 13

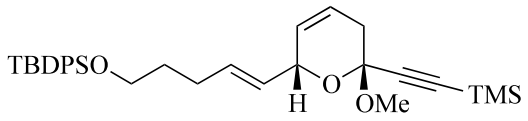
Hz, 4.3 Hz, 1H), 1.94 (m, 1H), 1.85 (m, 1H), 1.70 (m, 2H), 1.54 (d, J = 3.0 Hz, 1H), 1.07 (s, 9H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.2, 135.6, 134.0, 129.6, 127.6, 127.2, 102.1, 94.1, 88.8, 76.7, 68.6, 63.2, 50.5, 35.9, 31.7, 28.8, 26.9, 26.8, 19.2, -0.2; IR (neat): 3420.1 (broad), 3070.8, 2933.8, 2858.0, 1428.2, 1251.1, 1111.3, 1049.6, 944.6, 860.0, 702.1; $[\alpha]_D^{25}$ + 5.48 (*c* 1.07, $CHCl_3$); HRMS-ESI(m/z) calculated for $[M+Na]^+$: 573.2852, found 573.2827.



17

(2*R*,6*R*)-2-((*E*)-5-((*tert*-Butyldiphenylsilyl)oxy)pent-1-en-1-yl)-6-methoxy-6-((trimethylsilyl)ethynyl)dihydro-2*H*-pyran-3(4*H*)-one (17).

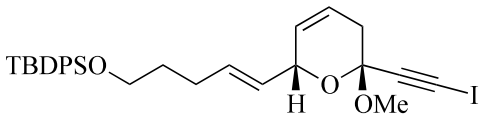
To a stirred solution of **16a** (410 mg, 0.75 mmol) in CH_2Cl_2 (6 mL) and DMSO (2 mL) at 0 ^oC were sequentially added *i*-Pr_2NEt (0.77 mL, 4.5 mmol) and SO_3·Py (510 mg, 3.2 mmol). After 10 min at 0 ^oC, an aqueous 1 M solution of HCl (3 mL) was added. The organic phase was separated and neutralized with pH 7 aqueous buffer. The separated aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 15:1, v/v) to provide **17** (400 mg, 0.72 mmol, 96%) as a colorless oil: R_f = 0.72 (hexanes-ethyl acetate, 5:1, v/v); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (dd, J = 7.7 Hz, 1.4 Hz, 4H), 7.42 (m, 6H), 5.78 (dt, J = 12.3 Hz, 5.3 Hz, 1H), 5.56 (dd, J = 12.4 Hz, 5.4 Hz, 1H), 4.44 (d, J = 6.9 Hz, 1H), 3.69 (t, J = 6.3 Hz, 2H), 3.49 (s, 3H), 2.59 (m, 3H), 2.31 (m, 1H), 2.23 (q, J = 5.6 Hz, 2H), 1.71 (m, 2H), 1.07 (s, 9H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 207.6, 136.7, 135.5, 134.0, 129.5, 127.6, 122.8, 101.0, 94.8, 90.0, 77.1, 63.2, 51.4, 35.6, 33.7, 31.6, 28.8, 26.8, 19.2, -0.3; IR (neat): 3048.1, 2957.1, 2856.7, 1733.7, 1471.8, 1427.7, 1250.9, 1110.8, 1048.2, 932.3, 844.4, 702.5; $[\alpha]_D^{25}$ + 10.8 (*c* 0.59, $CHCl_3$); HRMS-ESI(m/z) calculated for $[M+Na]^+$: 571.2666, found 571.2670.



18

***tert*-Butyl(((*E*)-5-((2*R*,6*R*)-6-methoxy-6-((trimethylsilyl)ethynyl)-5,6-dihydro-2*H*-pyran-2-yl)pent-4-en-1-yl)oxy)diphenylsilane (18).**

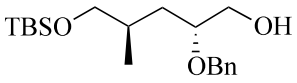
To a stirred solution of **17** (420 mg, 0.76 mmol) in THF (8 mL) at -78 ^{o}C was sequentially added Comins' reagent (450 mg, 1.14 mmol) and KHMDS (2.3 mL, 0.5 M in THF, 1.14 mmol). After 10 min at -78 ^{o}C, pH 7 aqueous buffer (8 mL) was added. The separated aqueous phase was extracted with diethyl ether (3 x 15 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes + 0.3% Et_3N, v/v) to provide the vinyl triflate (477 mg, 0.70 mmol, 92%) as a pale yellow oil. To a stirred rt solution of the vinyl triflate (477 mg, 0.70 mmol) in THF (7 mL) was added LiCl (294 mg, 7 mmol) and *n*Bu_3SnH (0.55 mL, 2.1 mmol). To the mixture was slowly added $Pd(PPh_3)_4$ (81 mg, 0.07 mmol). After stirring for 10 min at rt, saturated aqueous $NaHCO_3$ (8 mL) was added. The separated aqueous phase was extracted with diethyl ether (3 x 10 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 200:1, v/v) to provide **18** (289 mg, 0.54 mmol, 77%) as a colorless oil: R_f = 0.58 (hexanes-ethyl acetate, 10:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (dd, *J* = 7.7 Hz, 1.5 Hz, 4H), 7.42 (m, 6H), 5.73 (m, 2H), 5.62 (dt, *J* = 10.5 Hz, 1.3 Hz, 1H), 5.48 (dd, *J* = 15.3 Hz, 7.8 Hz, 1H), 4.50 (s-broad, 1H), 3.69 (t, *J* = 6.3 Hz, 2H), 3.52 (s, 3H), 2.72 (m, 1H), 2.34 (m, 1H), 2.18 (q, *J* = 7 Hz, 2H), 1.69 (m, 2H), 1.07 (s, 9H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.6, 134.0, 133.9, 129.5, 128.6, 127.6, 127.5, 120.1, 102.2, 94.0, 89.2, 71.0, 63.3, 51.3, 36.1, 31.7, 28.6, 26.9, 19.2, -0.2; IR (neat): 3042.9, 2956.4, 1659.9, 1471.7, 1250.3, 1182.5, 1110.8, 1016.6, 863.5, 701.9, 613.4; $[\alpha]_D^{25}$ + 3.5 (*c* 1.5, $CHCl_3$); HRMS-ESI(m/z) calculated for $[M+Na]^+$: 555.2727, found 555.2726.



6

***tert*-Butyl(((*E*)-5-((2*R*,6*R*)-6-(iodoethynyl)-6-methoxy-5,6-dihydro-2*H*-pyran-2-yl)pent-4-en-1-yl)oxy)diphenylsilane (6).**

To a stirred solution of **18** (87 mg, 0.16 mmol) in DMF (1.5 mL) at rt was added NIS (47 mg, 0.21 mmol) and AgOTf (36.1 mg, 0.16 mmol). Diethyl ether (3 mL) and saturated aqueous $Na_2S_2O_3$ (3 mL) were added. The aqueous phase was extracted with diethyl ether (3 x 5 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 40:1, v/v) to provide **6** (79 mg, 0.13 mmol, 82%) as a colorless oil: R_f = 0.42 (hexanes-ethyl acetate, 10:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (dd, *J* = 7.7 Hz, 1.5 Hz, 4H), 7.42 (m, 6H), 5.73 (m, 2H), 5.62 (dt, *J* = 10.4 Hz, 1.2 Hz, 1H), 5.48 (dd, *J* = 15 Hz, 7.8 Hz, 1H), 4.49 (s-broad, 1H), 3.69 (t, *J* = 6.3 Hz, 2H), 3.52 (s, 3H), 2.72 (m, 1H), 2.39 (m, 1H), 2.18 (q, *J* = 7.2 Hz, 2H), 1.70 (m, 2H), 1.07 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.6, 134.2, 134.0, 129.5, 128.3, 127.6, 127.5, 120.6, 95.0, 92.6, 71.1, 63.2, 51.6, 36.1, 31.7, 28.6, 26.9, 19.2, 3.8; IR (neat): 3069.7, 3042.9, 2930.9, 2855.5, 2180.9, 1660.0, 1588.9, 1470.6, 1427.2, 1232.0, 1182.4, 1110.2, 1016.2, 1036.6, 967.1, 822.9, 702.2, 505.5; $[\alpha]_D^{25}$ + 10.4 (*c* 0.85, $CHCl_3$); HRMS-ESI(m/z) calculated for $[M+Na]^+$: 609.1298, found 609.1294.

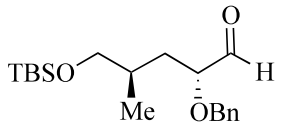


10a

(2R,4R)-2-(Benzyloxy)-5-((tert-butyldimethylsilyl)oxy)-4-methylpentan-1-ol (10a).

To a stirred solution of diol[2] **10** (92 mg, 0.37 mmol) in CH_2Cl_2 (2 mL) at rt was added benzaldehyde dimethoxy acetal (0.13 mL, 0.91 mmol) and PPTS (10 mg, 42 μmol). The solution was stirred at rt for 2 h before saturated aqueous $NaHCO_3$ (2 mL) was added. The organic phase was separated and the aqueous layer was extracted with diethyl ether (3 x 2 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-

ethyl acetate, 20:1 v/v) to give the benzylidene acetal (125 mg, 0.37 mmol, 99%) as a colorless oil. To a stirred solution of the benzylidene acetal (125 mg, 0.370 mmol) in CH_2Cl_2 (5 mL) at 0 ^oC was added a solution of DIBAL-H (0.75 mL of 1.0 M solution in PhMe, 0.75 mmol). The solution was warmed to rt over 1 h before a saturated aqueous solution of sodium potassium tartrate (10 mL) and diethyl ether (10 mL) were added. The separated aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 7:1, v/v) to give alcohol **10a** (88 mg, 0.26 mmol, 70%) as a colorless oil: R_f = 0.33 (hexanes-ethyl acetate, 4:1, v/v); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.38 (m, 5H), 4.63 (q_{AB}, $\Delta\nu$ = 11.4 Hz, J_{AB} = 11.3 Hz, 2H), 3.76 (ddd, *J* = 8.0 Hz, 6.8 Hz, 3.2 Hz, 1H), 3.68 (m, 1H), 3.56 (dt, *J* = 11.2 Hz, 5.6 Hz, 1H), 3.46 (d, *J* = 5.6 Hz, 2H), 1.97 (t, *J* = 6.0 Hz, 1H), 1.82 (m, 2H), 1.26 (ddd, *J* = 15.6 Hz, 10.0 Hz, 5.6 Hz, 1H), 0.91-0.93 (m, 13H), 0.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.5, 128.5, 127.8, 127.7, 77.9, 71.4, 68.4, 64.6, 34.9, 32.3, 25.9, 18.3, 17.2, -5.4; IR (neat): 3420, 2928, 2856, 1255, 1096 cm^{-1}; $[\alpha]_D^{25}$ - 6.2 (c 1.02, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+ Na^+]: 361.2175, found: 361.2169.

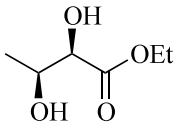


20

(2R,4R)-2-(Benzyloxy)-5-((tert-butyldimethylsilyl)oxy)-4-methylpentanal (20).

To a stirred solution of alcohol **10a** (75 mg, 0.22 mmol) in CH_2Cl_2 (3 mL) and DMSO (1 mL) at 0 ^oC were added *i*Pr_2NEt (233 μL, 1.34 mmol) and SO_3·Py (142 mg, 892 μmol). The solution was stirred at 0 ^oC for 5 min before a 0 ^oC 1 M aqueous solution of HCl (5 mL) was added. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic phase was washed with pH 7 buffer solution, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 12:1, v/v) to give aldehyde **20** (74 mg, 0.22 mmol, 99%) as a colorless oil.

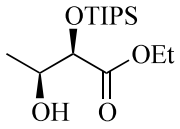
R_f = 0.43 (hexanes-ethyl acetate, 10:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.68 (d, *J* = 2.0 Hz, 1H), 7.32-7.38 (m, 5H), 4.72 (q_{AB}, Δν = 83 Hz, J_{AB} = 11.3 Hz, 2H), 3.89 (ddd, *J* = 9.2 Hz, 4.4 Hz, 2.0 Hz, 1H), 3.47 (d, *J* = 6.0 Hz, 2H), 1.92 (m, 1H), 1.83 (ddd, *J* = 14.0, 9.6, 4.8 Hz, 1H), 1.41 (ddd, *J* = 14.0, 8.8, 4.0 Hz, 1H), 0.91 (s, 9H), 0.87 (d, *J* = 6.8 Hz, 1H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.9, 137.4, 128.5, 128.1, 81.7, 72.6, 68.2, 33.4, 31.8, 25.9, 18.3, 16.2, -5.4; IR (neat): 2954, 2928, 1733, 1059 cm^{-1}; $[\alpha]_D^{25}$ -56.8 (c 1.05, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+MeOH+Na$^+$]: 391.2281, found: 391.2278.



21

(2R,3S)-Ethyl 2,3-dihydroxybutanoate (21).

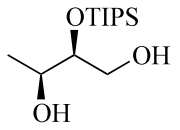
To a stirred suspension of AD-mix-α (24 g) in H_2O (80 mL) and *t*-BuOH (80 mL) at rt were added methyl sulfonamide (1.66 g, 17.5 mmol) and ethyl (2*E*)-butenoate (**9**, 2.00 g, 17.5 mmol). After stirring for 12 h, a saturated aqueous solution of Na_2SO_3 (50 mL) and diethyl ether (100 mL) were added. The separated aqueous phase was extracted with diethyl ether (3 x 50 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 2:1, v/v) to give diol **21** (1.86 g, 11.4 mmol, 65%) as a colorless oil: R_f = 0.79 (hexanes-ethyl acetate, 1:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.30 (q, *J* = 3.2 Hz, 2H), 4.10 (m, 1H), 4.03 (dd, *J* = 5.6 Hz, 2.8 Hz, 1H), 3.14 (d, *J* = 9.6 Hz, 1H), 2.17 (d, *J* = 8.4 Hz, 1H), 1.33-1.34 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.4, 74.3, 68.7, 62.1, 19.7, 14.1; IR (neat): 3417, 2980, 1735, 1144 cm^{-1}; $[\alpha]_D^{25}$ + 11 (c 1.8, $CHCl_3$);[3] HRMS-ESI (*m/z*) calculated for [M+Na$^+$]: 171.0633, found: 171.0630.



21a

(2R,3S)-Ethyl 3-hydroxy-2-((triisopropylsilyl)oxy)butanoate (21a).

To a stirred rt solution of **21** (1.86 g, 11.4 mmol) in DMF (20 mL) at rt was added imidazole (1.11 g, 16.3 mmol), TIPSCl (3.22 mL, 15.0 mmol) and DMAP (0.15 g, 1.3 mmol). After stirring for 12 h, diethyl ether (100 mL) and water were added. The separated aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 4:1, v/v) to give ester **21a** (1.7 g, 5.6 mmol, 44%) as a colorless oil: R_f = 0.61 (hexanes-ethyl acetate, 1:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.21-4.26 (m, 3H), 3.96 (m, 1H), 2.53 (d, *J* = 7.2 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 6.0 Hz, 3H), 1.08-1.17 (m, 21H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.2, 76.7, 69.9, 61.0, 18.9, 17.9, 14.2, 12.4; IR (neat): 3495, 2943, 2867, 1751, 1151 cm^{-1}; $[\alpha]_D^{25}$ + 22.2 (c 1.20, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na$^+$]: 327.1968, found: 327.1973.

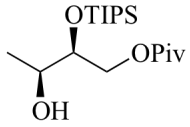


21b

(2S,3S)-2-((Triisopropylsilyl)oxy)butane-1,3-diol (21b).

To a stirred solution of **21a** (1.70 g, 5.59 mmol) in CH_2Cl_2 (40 mL) at 0 ^{o}C was added DIBAL (24.9 mL of 1.0 M solution in toluene, 24.9 mmol). The solution was warmed to rt over 30 min and saturated sodium potassium tartrate solution (30 mL) was added. The resulting mixture was diluted with diethyl ether (100 mL) and the separated aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 3:1, v/v) to give diol **21b** (1.28 g, 4.86 mmol, 87%) as a colorless oil: R_f = 0.46 (hexanes-ethyl acetate, 2:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.94 (dq, *J* = 10.8 Hz, 6.4 Hz, 1H), 3.75-3.81 (m, 2H), 3.71

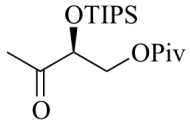
(m, 1H), 2.32 (d, J = 5.6 Hz, 1H), 2.10 (m, 1H), 1.26 (d, J = 6.4 Hz, 3H) 1.09-1.17 (m, 21H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 76.0, 68.8, 64.1, 19.1, 18.1, 12.6; IR (neat): 3368, 2942, 2866, 1462, 1086 cm^{-1}; $[\alpha]_D^{25}$ + 8.3 (c 1.30, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na$^+$]: 285.1862, found: 285.1861.



22

(2S,3S)-3-Hydroxy-2-((triisopropylsilyl)oxy)butyl pivalate (22).

To a stirred solution of **21b** (0.72 g, 2.8 mmol) in CH_2Cl_2 (20 mL) at rt was added pyridine (0.44 mL, 5.4 mmol), pivaloyl chloride (0.34 mL, 2.8 mmol) and DMAP (33 mg, 0.27 mmol). The solution was stirred at rt for 12 h then a saturated aqueous solution of $NaHCO_3$ (20 mL) was added. The resulting mixture was diluted with diethyl ether (100 mL) and the separated aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 20:1, v/v) to give alcohol **22** (1.28 g, 3.69 mmol, 77%) as a colorless oil: R_f = 0.60 (hexanes-ethyl acetate, 4:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.19 (dd, J = 10.6 Hz, 3.6 Hz, 1H), 4.12 (dd, J = 10.6 Hz, 6.0 Hz, 1H), 3.82-3.85 (m, 2H), 2.28 (d, J = 6.0 Hz, 1H), 1.24 (d, J = 6.4 Hz, 3H), 1.22 (s, 9H), 1.10-1.14 (m, 21H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.3, 74.5, 68.1, 65.0, 38.8, 27.2, 19.3, 18.1, 18.0, 12.6; IR (neat): 3486, 2944, 2867, 1731, 1161 cm^{-1}; $[\alpha]_D^{25}$ + 12.1 (c 1.35, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na$^+$]: 369.2437, found: 369.2431.

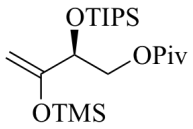


22a

(S)-3-Oxo-2-((triisopropylsilyl)oxy)butyl pivalate (22a).

To a stirred solution of **22** (1.05 g, 3.03 mmol) in CH_2Cl_2 (15 mL) and DMSO (8 mL) at 0 ^{o}C was added iPr$_2$NEt (3.16 mL, 18.2 mmol), and SO_3·Py (1.92 g, 12.6 mmol). The

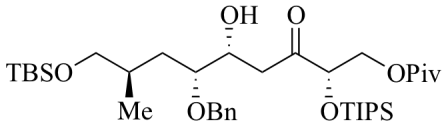
solution was stirred at 0 ^{o}C for 20 min before a cold 1 M HCl solution (30 mL) was added. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phase was washed with pH 7 aqueous buffer then brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 40:1, v/v) to give ketone **22a** (0.98 g, 2.9 mmol, 94%) as a colorless oil: R_f = 0.71 (hexanes-ethyl acetate, 4:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.30-4.33 (m, 2H), 4.22 (dd, *J* = 10.6 Hz, 6.0 Hz, 1H), 2.30 (s, 3H), 1.20 (s, 9H), 1.08-1.15 (m, 21H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 210.3, 178.0, 76.9, 68.3, 66.4, 38.7, 27.1, 26.1, 19.3, 18.0, 17.9, 12.2; IR (neat): 2944, 2867, 1735, 1143 cm^{-1}; $[\alpha]_D^{25}$ - 5.9 (c 1.01, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na^{+}]: 367.2281, found: 367.2282.



23

(S)-2-((Triisopropylsilyl)oxy)-3-((trimethylsilyl)oxy)but-3-en-1-yl pivalate (23).

To a stirred solution of **22a** (0.98 g, 2.85 mmol) in CH_2Cl_2 (20 mL) at rt was sequentially added Et_3N (1.2 mL, 8.61 mmol) and TMSOTf (1.04 mL, 5.75 mmol). The solution was stirred at rt for 30 min before saturated aqueous $NaHCO_3$ (10 mL) was added. The organic phase was separated and washed with saturated NH_4Cl solution (10 mL), pH 7 aqueous buffer (10 mL), and brine (10 mL), then dried over Na_2SO_4, filtered and concentrated. The residue was dissolved in benzene and concentrated to give enol ether **23** (1.17g, 2.85 mmol, 99%) as a yellow oil, which was used without further purification.

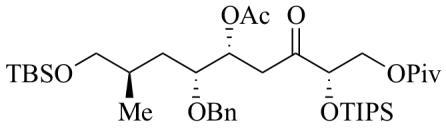


24

(2S,5R,6R,8R)-6-(Benzyloxy)-9-((tert-butyldimethylsilyl)oxy)-5-hydroxy-8-methyl-3-oxo-2-((triisopropylsilyl)oxy)nonyl pivalate (24).

To a stirred solution of aldehyde **20** (58 mg, 0.17 mmol) in CH_2Cl_2 (3 mL) at -78 ^{o}C was added $SnCl_4$ (0.1 mL, 0.9 mmol), the solution was stirred at -78 ^{o}C for 10 min before a

solution of enol ether **23** (218 mg, 524 μmol) in CH_2Cl_2 (2 mL) was added via cannula. The solution was stirred at -78 ^oC for 25 min before saturated aqueous $NaHCO_3$ (10 mL) was added. The mixture was diluted with diethyl ether and warmed to rt. The organic phase was separated and the aqueous layer was extracted with diethyl ether (2 x10 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 7: 1, v/v) to give ketone **24** (90 mg, 0.13 mmol, 76%) as a colorless oil: R_f = 0.25 (hexanes-ethyl acetate, 10:1, v/v); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.35 (m, 5H), 4.60 (s, 2H), 4.36 (dd, *J* = 4.8 Hz, 3.2 Hz, 1H), 4.28-4.32 (m, 2H), 4.24 (dd, d, *J* = 10.8 Hz, 3.2 Hz, 1H), 3.59 (dt, *J* = 8.8 Hz, 3.6 Hz, 1H), 3.48 (dd, *J* = 9.6 Hz, 5.6 Hz, 1H), 3.44 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 3.00 (dd, *J* = 18.4 Hz, 2.4 Hz, 1H), 2.90 (dd, *J* = 18.4 Hz, 9.2 Hz, 1H), 2.80 (d, *J* = 4.4 Hz, 1H), 1.86 (sextet, *J* = 6.8 Hz, 1H), 1.68 (ddd, *J* = 18.0 Hz, 8.4 Hz, 6.4 Hz, 1H), 1.39 (ddd, *J* = 18.0 Hz, 8.4 Hz, 4.8 Hz, 1H), 1.19 (s, 9H), 1.05-1.10 (m, 21H) 0.90-0.91 (m, 12H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.5, 178.2, 138.5, 128.3, 127.7, 127.6, 78.7, 72.1, 68.6, 67.8, 66.0, 41.2, 38.8, 33.4, 32.4, 27.1, 26.0, 18.4, 17.9, 16.8, 12.2, -5.3, -5.4; IR (neat): 3527, 2955, 1731, 1462, 1143 cm^{-1}; $[\alpha]_D^{25}$ + 13.2 (c 0.95, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na^+]: 703.4401, found: 703.4402.

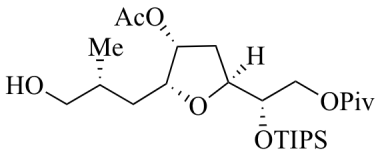


24a

(2S,5R,6R,8R)-5-Acetoxy-6-(benzyloxy)-9-((tert-butyldimethylsilyl)oxy)-8-methyl-3-oxo-2-((triisopropylsilyl)oxy)nonyl pivalate (24a).

To a stirred solution of ketone **24** (90 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) at rt was added sequentially pyridine (54 μL, 0.67 mmol), DMAP (3.2 mg, 26 μmol) and acetyl chloride (38 μL, 0.53 mmol). The solution was stirred at rt for 5 min before saturated aqueous $NaHCO_3$ (5 mL) was added. The resulting mixture was diluted with diethyl ether (10 mL) and the separated aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and

concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 20:1, v/v) to give ketone **24a** (90 mg, 0.13 mmol, 94%) as a colorless oil: R_f = 0.33 (hexanes-ethyl acetate, 10:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.34 (m, 5H), 5.64 (ddd, *J* = 9.2 Hz, 6.4 Hz, 4.8 Hz, 1H), 4.66 (q_{AB}, Δν = 37 Hz, J_{AB} = 11.2 Hz, 2H), 4.36 (dd, *J* = 4.8 Hz, 3.6 Hz, 1H), 4.29 (dd, *J* = 11.2 Hz, 4.8 Hz, 1H), 4.23 (dd, *J* = 11.2 Hz, 3.6 Hz, 1H), 3.75 (dt, *J* = 10.0 Hz, 3.6 Hz, 1H), 3.45 (dd, *J* = 10.0 Hz, 6.0 Hz, 1H), 3.41 (dd, *J* = 10.0 Hz, 6.0 Hz, 1H), 3.08 (m, 2H), 2.01 (s, 3H), 1.78 (m, 1H), 1.61 (ddd, *J* = 14.0 Hz, 10.0 Hz, 6.4 Hz, 1H), 1.20 (s, 9H), 1.05-1.11 (m, 21H) 0.91 (s, 9H), 0.78 (d, *J* = 6.4 Hz, 3H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 208.9, 178.0, 170.0, 138.3, 128.3, 127.8, 127.6, 76.8, 75.3, 71.9, 68.6, 68.4, 66.1, 38.8, 37.7, 33.2, 32.2, 27.1, 26.0, 21.0, 18.3, 17.9, 16.4, 12.2, -5.4; IR (neat): 2954, 1738, 1462, 1238, 1142 cm^{-1}; $[\alpha]_D^{25}$ + 10.1 (c 1.00, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na$^+$]: 745.4507, found: 745.4513.

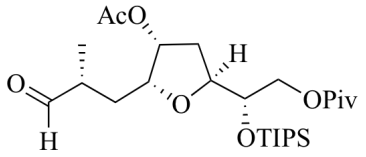


25a

(S)-2-((2S,4R,5R)-4-Acetoxy-5-((R)-3-hydroxy-2-methylpropyl)tetrahydrofuran-2-yl)-2-((triisopropylsilyl)oxy)ethyl pivalate (25a).

To a stirred solution of ketone **24a** (90 mg, 0.13 mmol) in ethyl acetate (5 mL) at rt was added $Pd(OH)_2$ on carbon (44 mg, 20%, 62 μmol). The resulting suspension was degassed and flushed with H_2 three times. The suspension was then stirred at rt for 15 min, filtered through celite and washed with ethyl acetate. The combined organic phase was concentrated and purified by flash chromatography (hexanes-ethyl acetate, 10:1, v/v) to give alcohol **25** (79 mg, 0.013 mmol, 99%) as a colorless oil. This was dissolved in CH_2Cl_2 (5 mL) and cooled to -78 ^{o}C. To the stirred solution were sequentially added Et_3SiH (0.15 mL, 1.2 mmol) and $SnCl_4$ (29 mL, 0.25 mmol). The solution was warmed to -30 ^{o}C over 1 h with stirring. Saturated aqueous $NaHCO_3$ (10 mL) was added. The resulting mixture was warmed to rt, diluted with diethyl ether (10 mL) and the separated aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic phase

was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 7:1, v/v) to give alcohol **25a** (38 mg, 77 μmol, 60%) as a colorless oil: R_f = 0.53 (hexanes-ethyl acetate, 2:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.35 (t, *J* = 4.0 Hz, 1H), 4.34 (ddd, *J* = 9.2 Hz, 6.8 Hz, 3.2 Hz, 1H), 4.23 (dd, *J* = 10.8 Hz, 6.0 Hz, 1H), 4.12-4.18 (m, 2H), 3.96 (m, 1H), 3.58 (m, 1H), 3.46 (m, 1H), 2.54 (m, 1H), 2.36 (ddd, *J* = 17.6 Hz, 9.2 Hz, 5.2 Hz, 1H), 2.12 (s, 3H), 2.03 (dd, *J* = 14.0 Hz, 6.8 Hz, 1H), 1.81 (octet, *J* = 6.4 Hz, 1H), 1.61 (ddd, *J* = 14.4 Hz, 10.0 Hz, 8.0 Hz, 1H), 1.43 (ddd, *J* = 14.4 Hz, 6.4 Hz, 2.0 Hz, 1H), 1.22 (s, 9H), 1.06-1.12 (m, 21H), 0.95 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.3, 170.6, 80.7, 77.8, 76.3, 72.2, 68.2, 65.4, 38.8, 34.5, 34.3, 34.0, 27.2, 21.1, 18.1, 17.8, 12.7; IR (neat): 3460, 2945, 2867, 1732, 1241, 1137 cm^{-1}; $[\alpha]_D^{25}$ + 10.0 (c 0.84, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na$^+$]: 525.3224, found: 525.3220.

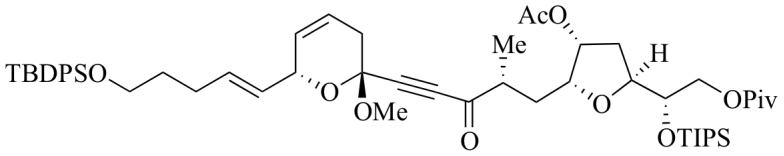


7

(S)-2-((2S,4R,5R)-4-Acetoxy-5-((R)-2-methyl-3-oxopropyl)tetrahydrofuran-2-yl)-2-((triisopropylsilyl)oxy)ethyl pivalate (7).

To a stirred solution of alcohol **25a** (38 mg, 77 μmol) in CH_2Cl_2 (2 mL) and DMSO (1 mL) at 0 ^{o}C was sequentially added *i*Pr_2NEt (0.10 mL, 0.58 mmol) and SO_3·Py (48 mg, 0.30 mmol). The solution was stirred at 0 ^{o}C for 5 min before a 0 ^{o}C aqueous solution of HCl (1 M, 3 mL) was added. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 3 mL). The combined organic phases were washed with pH = 7 aqueous buffer, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 10:1, v/v) to give aldehyde **7** (38 mg, 76 μmol, 99%) as a colorless oil: R_f = 0.43 (hexanes-ethyl acetate, 4:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.67 (d, 1.6 Hz, 1H), 5.34 (t, *J* = 4.0 Hz, 1H), 4.34 (ddd, *J* = 10.8 Hz, 6.8 Hz, 4.0 Hz, 1H), 4.17 (d, *J* = 5.2 Hz, 2H), 4.12 (dt, *J* = 10.0 Hz, 3.6 Hz, 1H), 3.94 (q, *J* = 4.8 Hz, 1H), 2.59 (sextet, *J* = 6.8 Hz, 1H), 2.33 (ddd, *J* = 14.0 Hz, 8.8 Hz, 4.2 Hz, 1H), 2.12 (s, 3H), 2.02-2.09 (m, 2H), 1.40 (ddd, *J* = 14.0 Hz, 8.0 Hz, 3.2 Hz, 1H), 1.22 (s,

9H), 0.95 (d, J = 6.8 Hz, 3H), 1.08-1.09 (m, 21H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 204.4, 178.3, 170.5, 78.8, 77.8, 75.7, 72.6, 65.5, 43.9, 38.8, 34.5, 30.2, 27.2, 21.0, 18.1, 13.2, 12.7; IR (neat): 2944, 2867, 2714, 1731, 1237, 1139 cm^{-1}; $[\alpha]_D^{25}$ + 4.0 (c 1.01, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na$^+$]: 523.3067, found: 523.3068.

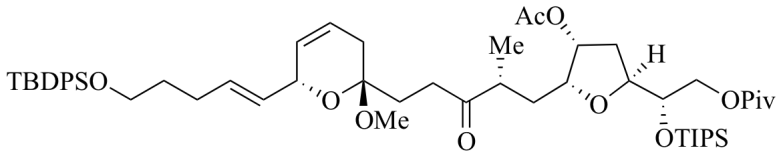


26a

(S)-2-((2S,4R,5R)-4-Acetoxy-5-((R)-5-((2R,6R)-6-((E)-5-((tert-butyldiphenylsilyl)oxy)pent-1-en-1-yl)-2-methoxy-3,6-dihydro-2H-pyran-2-yl)-2-methyl-3-oxopent-4-yn-1-yl)tetrahydrofuran-2-yl)-2-((triisopropylsilyl)oxy)ethyl pivalate (26a).

To a mixture of $CrCl_2$ (42 mg, 0.34 mmol) and $NiCl_2$ (0.2 mg, 1.5 μmol) at rt was added a solution of aldehyde **7** (38 mg, 76 μmol) and iodide **6** (35 mg, 60 μmol) in THF (3 mL) via cannula. The suspension was stirred at rt for 12 h before diethyl ether (10 mL) and an aqueous solution of 1 M serine saturated with $NaHCO_3$ (10 mL) were added. The resulting mixture was stirred at rt for 1 h. The organic phase was separated and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 5:1, v/v) to give alcohol **26** (45 mg, 47 μmol, 78%) as a colorless oil. This was dissolved in CH_2Cl_2 (2 mL) and DMSO (1 mL) at rt, and iPr$_2$NEt (0.10 mL, 0.58 mmol) and SO_3·Py (48 mg, 0.30 mmol) were added sequentially. The solution was stirred at rt for 5 min before a saturated aqueous solution of NH_4Cl (3 mL) was added. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 8:1, v/v) to give **26a** (35 mg, 36 μmol, 77%) as a colorless oil: R_f = 0.64 (hexanes-ethyl acetate, 4:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (dd, J = 8.0 Hz, 1.6 Hz, 4H), 7.38-7.46 (m, 6H), 5.70-5.80 (m, 2H), 5.63 (d, J = 10.4 Hz, 1H), 5.47 (dd, J = 15.2 Hz, 7.6 Hz, 1H), 5.34 (t, J = 3.6 Hz, 1H), 4.52 (m,

1H), 4.26 (ddd, J = 11.2 Hz, 7.2 Hz, 4.4 Hz, 1H), 4.17 (d, J = 5.2 Hz, 2H), 4.08 (dt, J = 6.4 Hz, 3.6 Hz, 1H), 3.95 (q, J = 4.8 Hz, 1H), 3.69 (t, J = 6.0 Hz, 2H), 3.54 (s, 3H), 2.83 (sextet, J = 6.8 Hz, 1H), 2.71 (dq, J = 14.0 Hz, 2.0 Hz, 1H), 2.43(dt, J = 14.0 Hz, 3.2 Hz, 1H), 2.32 (ddd, J = 12.8 Hz, 9.2 Hz, 4.2 Hz, 1H), 2.13-2.22 (m, 3H), 2.11 (s, 3H), 2.06 (dd, J = 13.2 Hz, 8.0 Hz, 1H), 1.69 (m, 2H), 1.47 (ddd, J = 14.0 Hz, 8.8, 4.4 Hz, 1H), 1.22-1.24 (m,12H), 1.09-1.12 (m, 21H), 1.07 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.4, 178.3, 170.4, 135.6, 134.2, 134.0, 129.5, 128.1, 127.6, 120.3, 94.3, 88.2, 80.9, 78.3, 77.8, 75.6, 72.6, 71.0, 65.5, 63.2, 51.8, 45.4, 38.8, 35.6, 34.5, 31.8, 31.3, 28.6, 27.2, 26.9, 21.0, 19.2, 18.1, 15.3, 12.7; IR (neat): 2939, 2865, 2218, 1738, 1681, 1236, 1137, 1112 cm^{-1}; $[\alpha]_D^{25}$ + 9.4 (c 0.67, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na$^+$]: 981.5344, found: 981.5338.

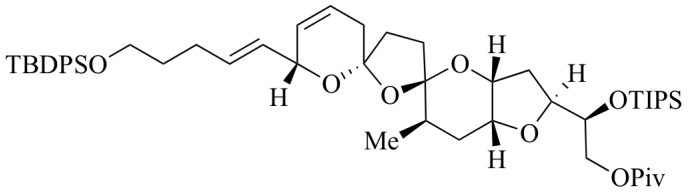


27

(S)-2-((2S,4R,5R)-4-Acetoxy-5-((R)-5-((2S,6R)-6-((E)-5-((tert-butyldiphenylsilyl)oxy)pent-1-en-1-yl)-2-methoxy-3,6-dihydro-2H-pyran-2-yl)-2-methyl-3-oxopentyl)tetrahydrofuran-2-yl)-2-((triisopropylsilyl)oxy)ethyl pivalate (27).

To $[CuH(PPh_3)]_6$ (139 mg, 82.2 μmol) at rt was added a solution of ketone **26a** (52.5 mg, 54.8 μmol) in degassed benzene (3 mL) via cannula. Degassed H_2O (15 mL) was then added. The suspension was stirred at rt for 12 h before a saturated aqueous $NaHCO_3$ (3 mL) was added. It was then diluted with diethyl ether (10 mL) and stirred under air at rt for 30 min. The organic phase was separated and the aqueous layer was extracted with diethyl ether (3 x 3 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 5:1, v/v) to give ketone **27** (40 mg, 42 μmol, 76%) as a colorless oil: R_f = 0.43 (hexanes-ethyl acetate, 4:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (dd, J = 7.6 Hz, 1.6 Hz, 4H), 7.37-7.46 (m, 6H), 5.69-5.78 (m, 2H), 5.64 (d, J = 10.4 Hz, 1H),

5.46 (dd, J = 15.2 Hz, 7.2 Hz, 1H), 5.31 (t, J = 3.6 Hz, 1H), 4.49 (m, 1H), 4.25 (ddd, J = 8.8 Hz, 7.8 Hz, 4.4 Hz, 1H), 4.17 (m, 2H), 4.07 (dt, J = 10.0 Hz, 3.4 Hz, 1H), 3.94 (q, J = 4.8 Hz, 1H), 3.69 (t, J = 6.4 Hz, 2H), 3.27 (s, 3H), 2.77 (sextet, J = 6.8 Hz, 1H), 2.61 (ddd, J = 17.6 Hz, 10.0 Hz, 6.0 Hz, 1H), 2.50 (ddd, 17.6, J = 17.6 Hz, 10.0 Hz, 5.2 Hz, 1H), 2.31 (ddd, J = 14.0 Hz, 8.8 Hz, 5.6 Hz, 1H), 2.16-2.23 (m, 3H), 2.10 (s, 3H), 2.01-2.09 (m, 3H), 1.91-1.99 (m, 2H), 1.69 (m, 2H), 1.41 (ddd, J = 14.0 Hz, 8.4 Hz, 3.2 Hz, 1H), 1.22 (s, 9H), 1.09-1.16 (m, 24H), 1.07 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.0, 178.3, 170.5, 135.6, 134.0, 133.0, 129.5, 129.2, 128.0, 127.6, 121.2, 98.7, 78.8, 77.7, 75.7, 72.6, 70.6, 65.5, 63.3, 48.3, 43.2, 38.8, 35.3, 34.4, 32.7, 31.9, 29.6, 28.6, 27.2, 26.7, 21.0, 19.2, 18.1, 16.1, 12.7; IR (neat): 2940, 2865, 1738, 1237, 1112 cm^{-1}; $[\alpha]_D^{25}$ - 3.9 (c 0.36, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na$^+$]: 985.5657, found: 985.5679.



4

(2S)-2-[(2R,3R,4aR,5'R,6S,6"R,7aR)-6"-[(1E)-5-[(tert-Butyldiphenylsilyl)oxy]pent-1-en-1-yl]-3-methyl-3,3",4,4a,6,6",7,7a-octahydrodispiro[furo[3,2-b]pyran-2,2'-oxolane-5',2"-pyran]-6-yl]-2-((triisopropylsilyl)oxy)ethyl pivalate (4).

To a stirred solution of ketone **27** (38 mg, 40 μmol) in methanol (2 mL) at rt was added K_2CO_3 (16 mg, 0.12 mmol). The mixture was stirred at rt for 30 min before diethyl ether (10 mL) and H_2O (3 mL) were added. The organic phase was separated and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes-ethyl acetate, 3:1, v/v) to give alcohol **5** (36 mg, 39 μmol, 93%) as a colorless oil. This was dissolved in CH_2Cl_2 (2 mL) at rt and PPTS (1.8 mg, 7.2 μmol) was added. The solution was stirred at rt for 30 min before a saturated aqueous solution of $NaHCO_3$ (0.5 mL) was added. The mixture was diluted with diethyl ether (5 mL), the organic phase was separated and the aqueous layer was extracted with diethyl ether (3 x 2 mL). The combined organic phases were washed with

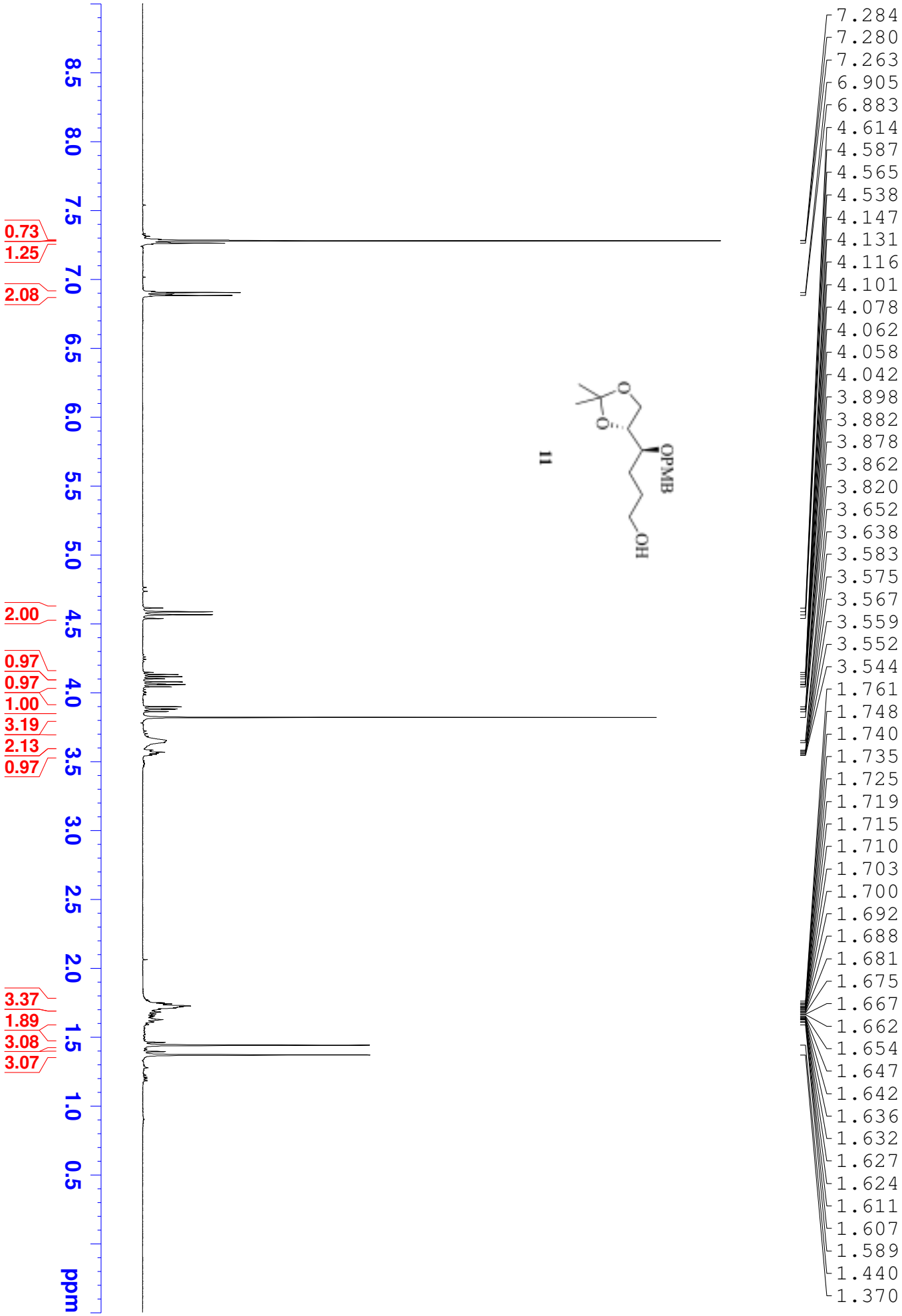
brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (hexanes–ethyl acetate, 20:1, v/v) to give spiroketal **4** (33 mg, 39 μmol, 99%) as a colorless oil: R_f = 0.42 (hexanes-ethyl acetate, 10:1, v/v); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, *J* = 6.8 Hz, 4H), 7.38-7.45 (m, 6H), 5.71-5.78 (m, 2H), 5.64 (d, *J* = 10.4 Hz, 1H), 5.47 (dd, *J* = 15.2 Hz, 7.6 Hz, 1H), 4.81 (m, 1H), 4.33 (m, 1H), 4.12-4.21 (m, 3H), 4.04 (q, *J* = 4.8 Hz, 1H), 3.89 (m, 1H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.53 (d, *J* = 17.6 Hz, 1H), 2.33(td, *J* = 12.0 Hz, 7.6 Hz, 1H), 2.12-2.18 (m, 4H), 2.00-2.05 (m, 3H), 1.93 (dd, *J* = 12.8 Hz, 6.4 Hz, 1H), 1.87 (d, *J* = 14.8 Hz, 1H), 1.78 (dd, *J* = 14.8 Hz, 4.0 Hz, 1H), 1.66-.172 (m, 3H), 1.22 (s, 9H), 1.09-1.12 (m, 21H), 1.07 (s, 9H), 0.94 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.5, 135.6, 134.0, 133.3, 129.5, 129.4, 128.5, 127.6, 122.5, 110.0, 105.6, 79.2, 76.7, 72.5, 72.0, 71.0, 66.0, 63.3, 38.8, 36.7, 35.2, 34.9, 32.2, 31.8, 31.4, 29.5, 28.7, 27.2, 26.9, 19.2, 18.2, 18.1, 16.2, 12.7; IR (neat): 2940, 2865, 2361, 1731, 1138 cm^{-1}; $[\alpha]_D^{25}$ -11.4 (c 0.79, $CHCl_3$); HRMS-ESI (*m/z*) calculated for [M+Na^+]: 911.5289, found: 911.5318.

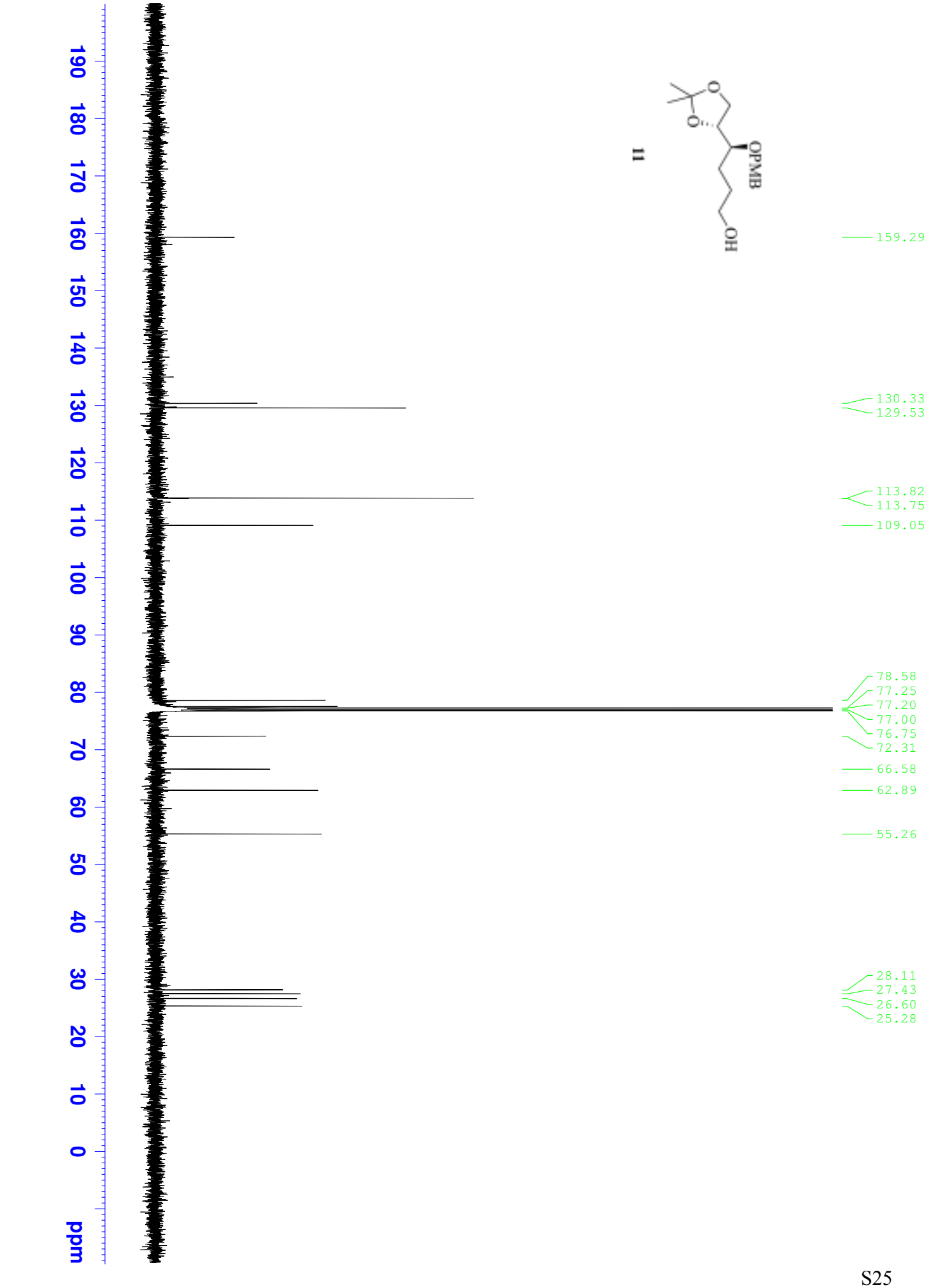
References:

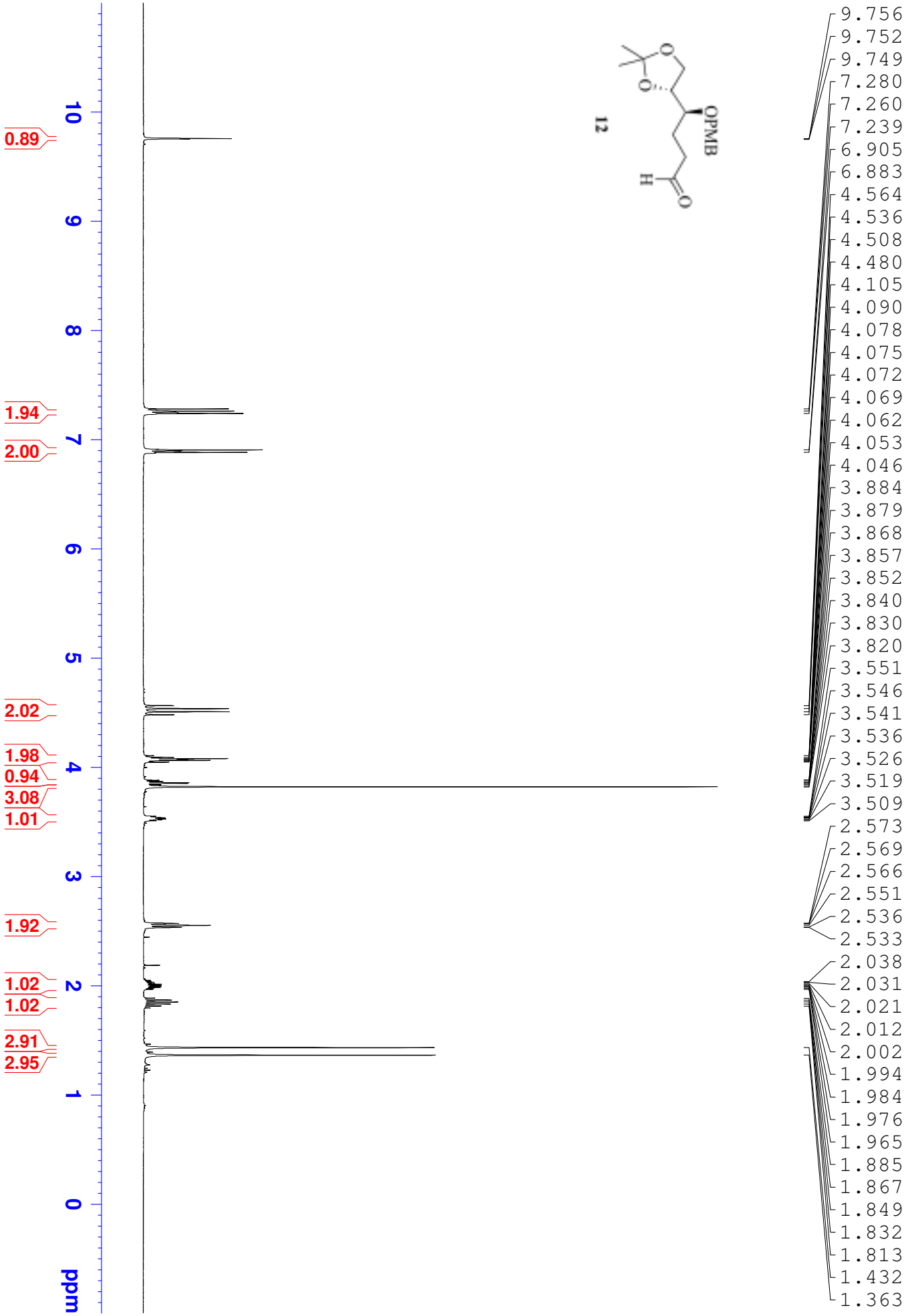
(1) Rao, K. S.; Chattapadhyay, A. K.; Ghosh, S. *Synlett.* **2010**, *20*, 3078.

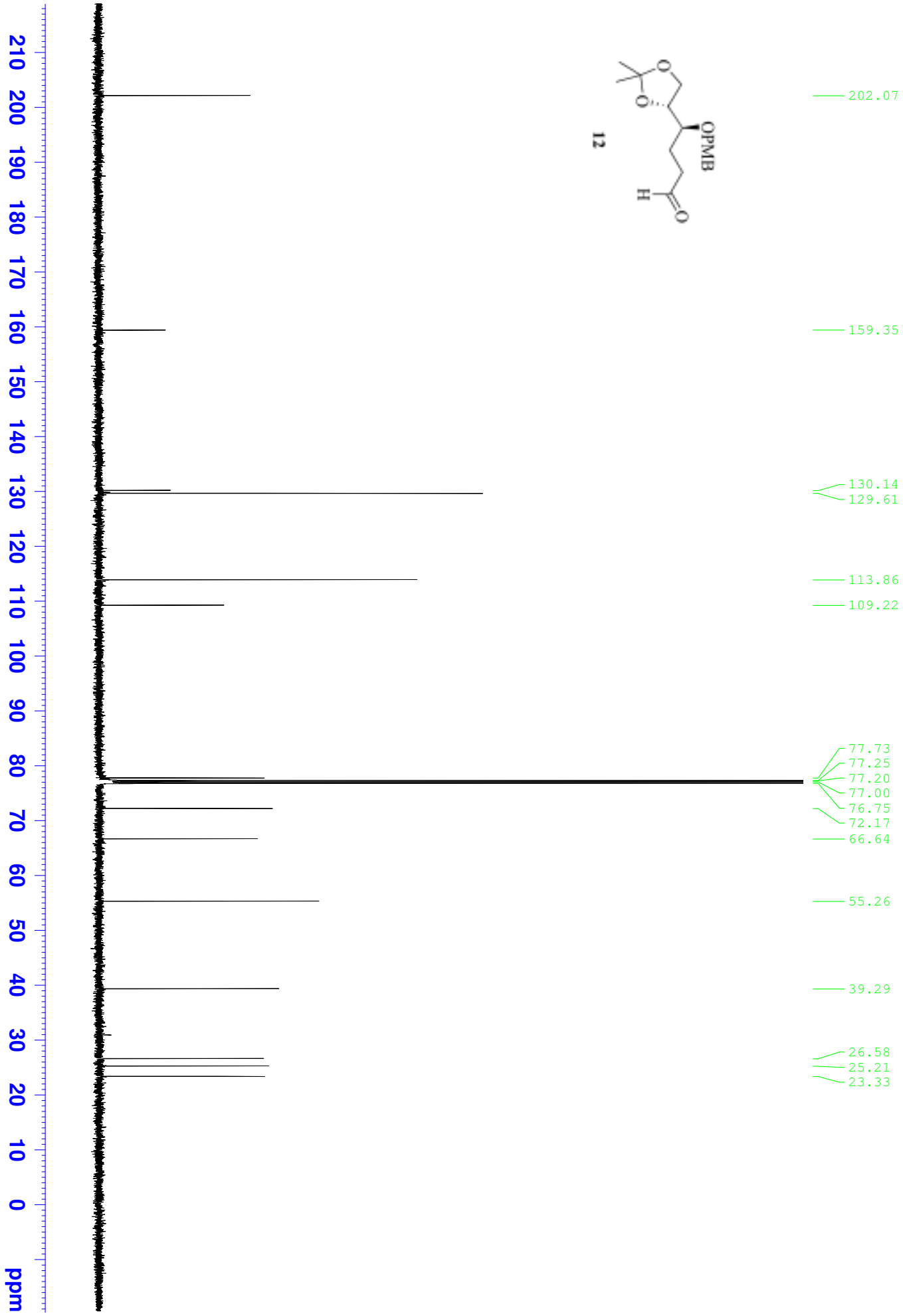
(2) Fürstner, A.; Bouchez, L. C.; Funel, J. A.; Liepins, V.; Porée, F. H.; Gilmour, R.; Beaufils, F.; Laurich, D.; Tamiya, M. *Angew. Chem. Int. Ed*. **2007**, *46*, 9265.

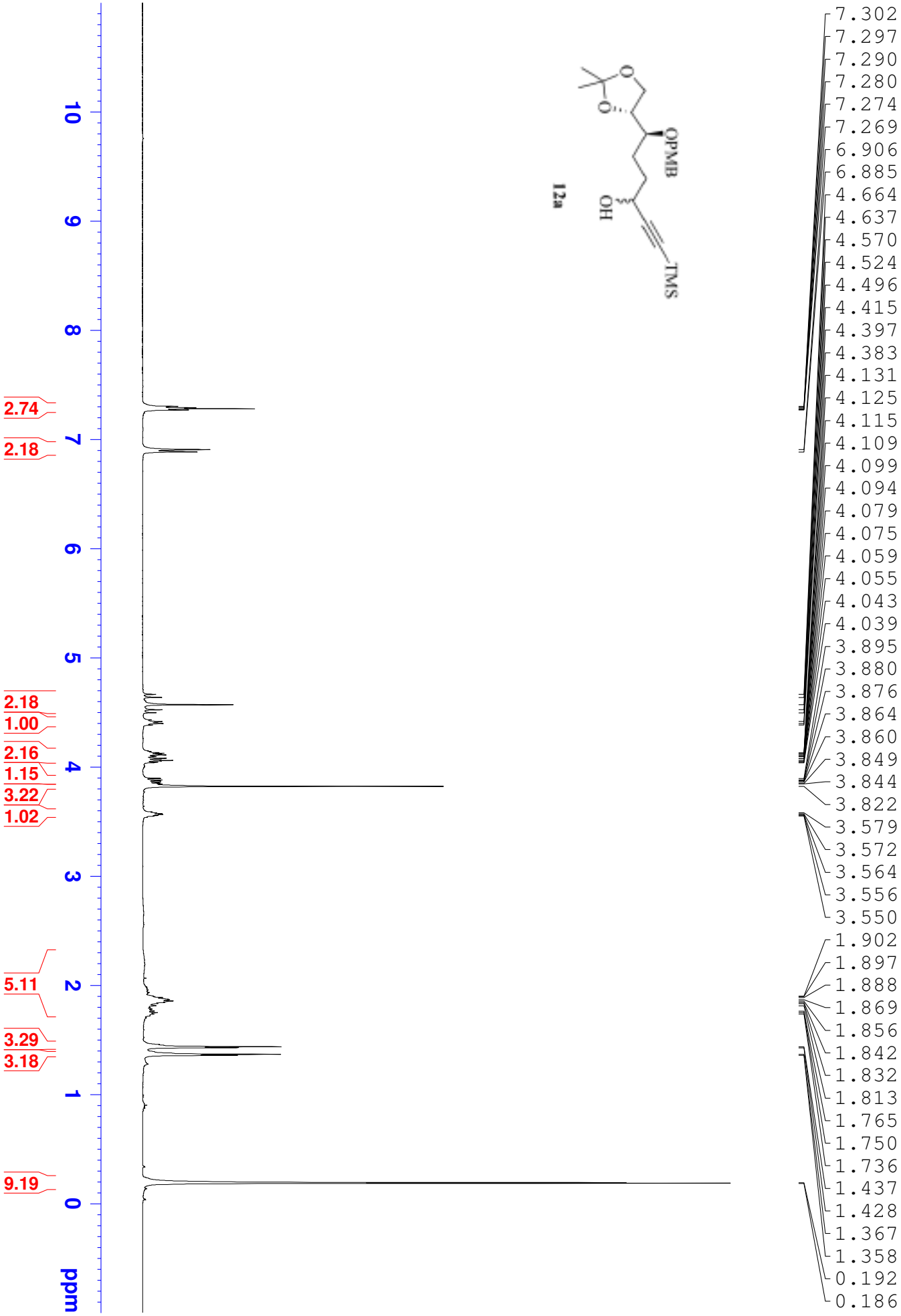
(3) Bull, J. A.; Balskus, E. P.; Horan, R. J.; Langer, M.; Ley, S. V. *Chem. Eur. J.* **2007**, *13*, 5515.

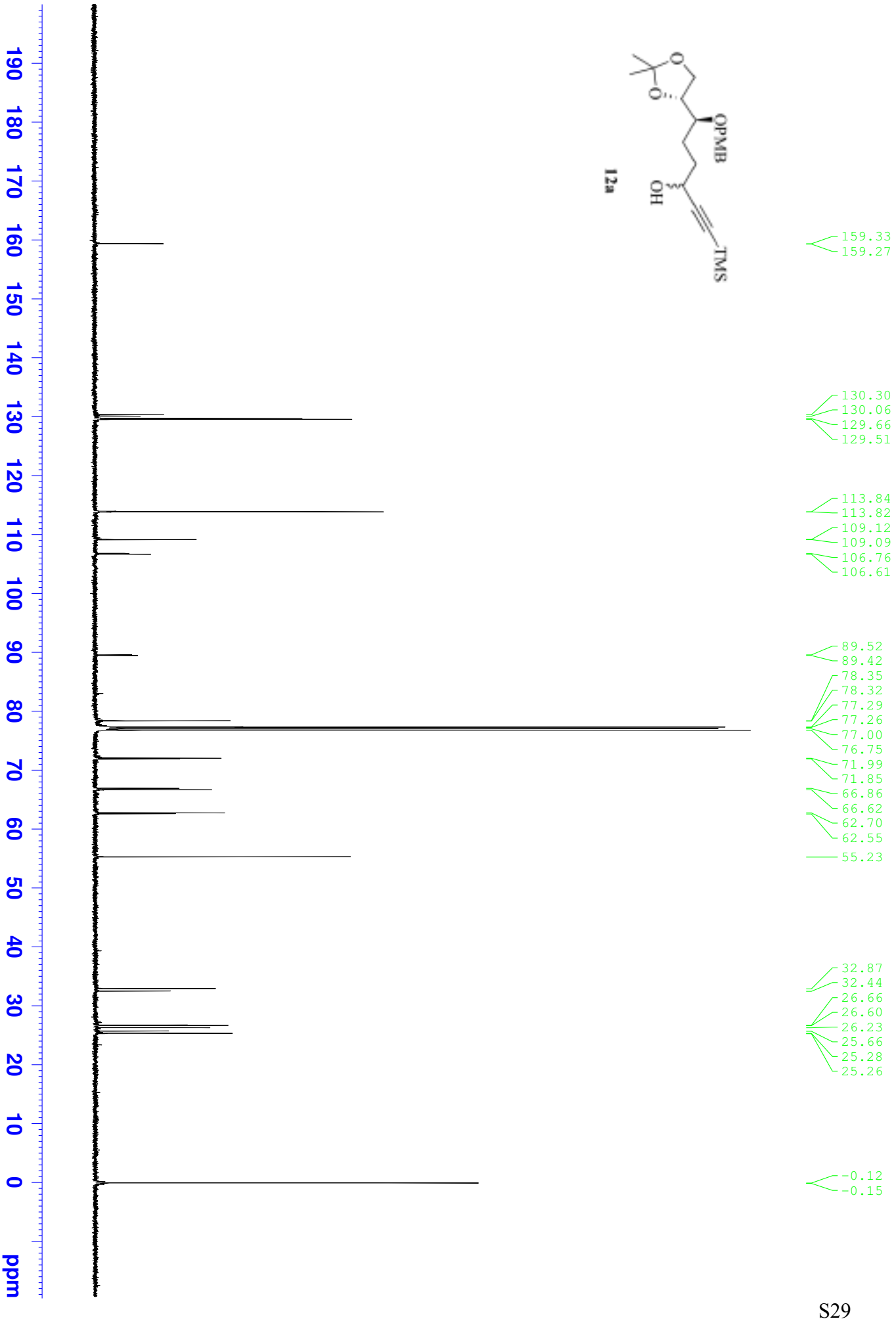

11
OPMB
HO
0.73
1.25
2.08
2.00
0.97
0.97
1.00
3.19
2.13
0.97
3.37
1.89
3.08
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
7.284
7.280
7.263
6.905
6.883
4.614
4.587
4.565
4.538
4.147
4.131
4.116
4.101
4.078
4.062
4.058
4.042
3.898
3.882
3.878
3.862
3.820
3.652
3.638
3.583
3.575
3.567
3.559
3.552
3.544
1.761
1.748
1.740
1.735
1.725
1.719
1.715
1.710
1.703
1.700
1.692
1.688
1.681
1.675
1.667
1.662
1.654
1.647
1.642
1.636
1.632
1.627
1.624
1.611
1.607
1.589
1.440
1.370

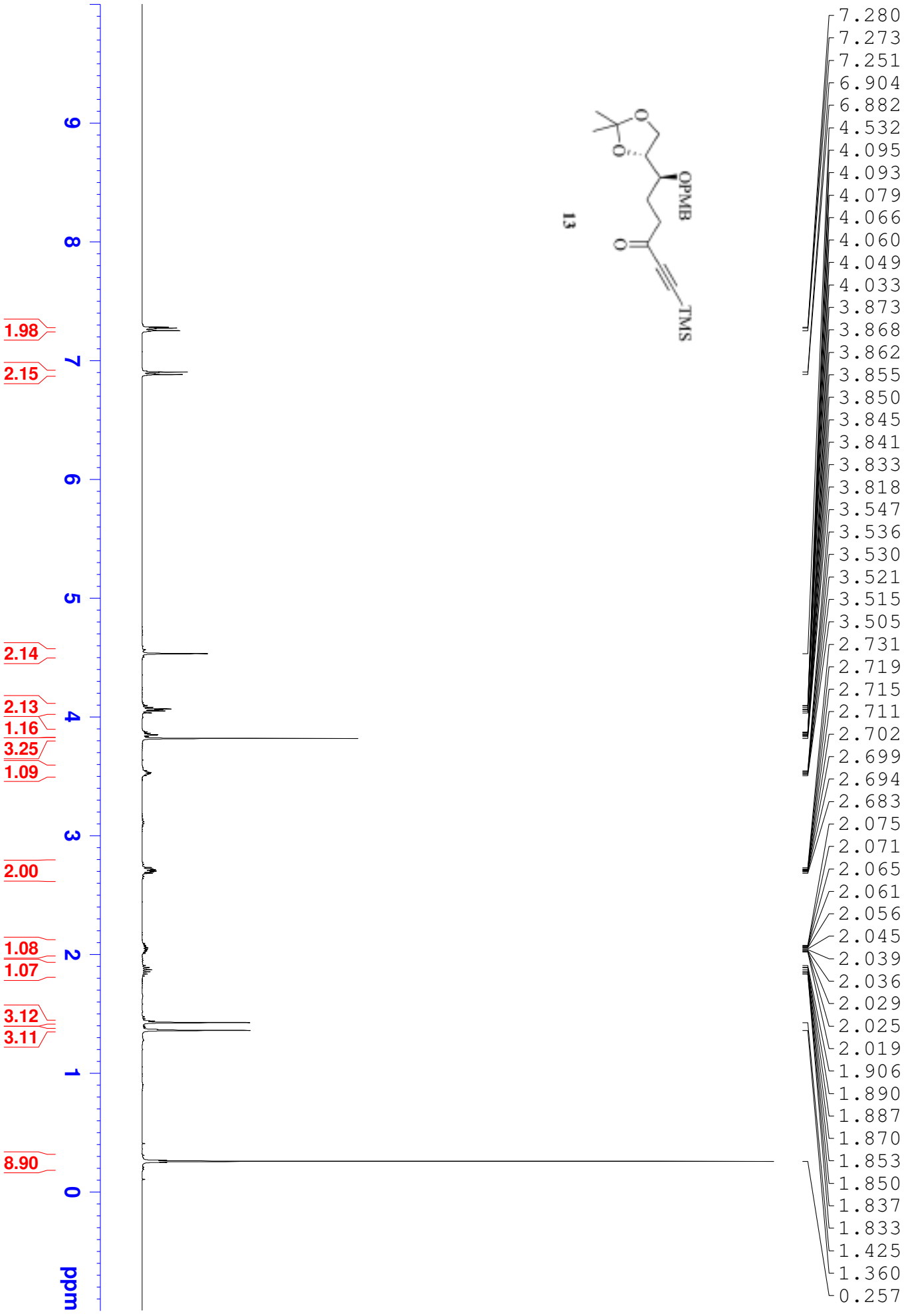

11
OPMB
OH
159.29
130.33
129.53
113.82
113.75
109.05
78.58
77.25
77.20
77.00
76.75
72.31
66.58
62.89
55.26
28.11
27.43
26.60
25.28
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

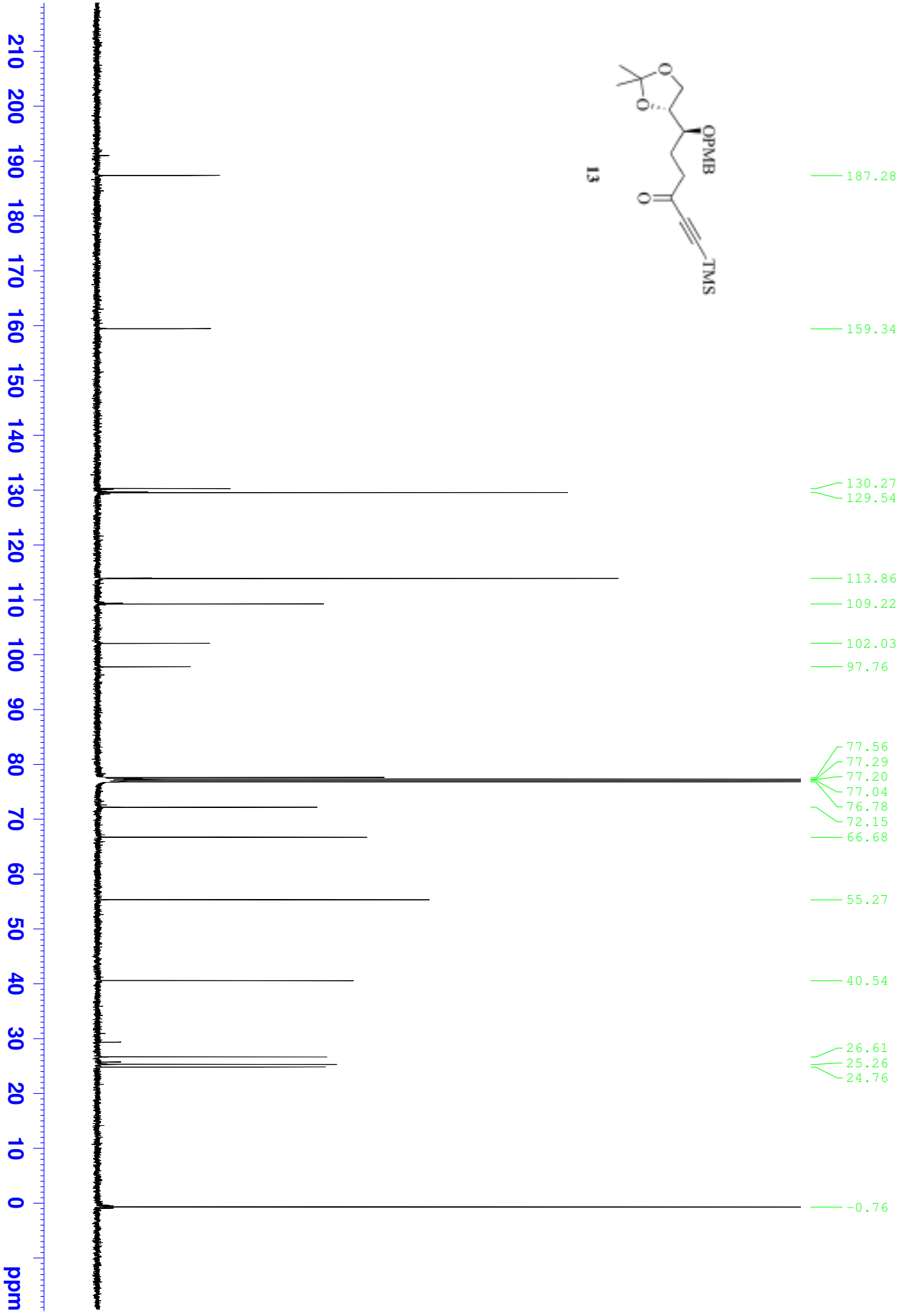

12
OPMB
O
O
H
O
9.756
9.752
9.749
7.280
7.260
7.239
6.905
6.883
4.564
4.536
4.508
4.480
4.105
4.090
4.078
4.075
4.072
4.069
4.062
4.053
4.046
3.884
3.879
3.868
3.857
3.852
3.840
3.830
3.820
3.551
3.546
3.541
3.536
3.526
3.519
3.509
2.573
2.569
2.566
2.551
2.536
2.533
2.038
2.031
2.021
2.012
2.002
1.994
1.984
1.976
1.965
1.885
1.867
1.849
1.832
1.813
1.432
1.363
0.89
1.94
2.00
2.02
1.98
0.94
3.08
1.01
1.92
1.02
1.02
2.91
2.95
10
9
8
7
6
5
4
3
2
1
0
ppm

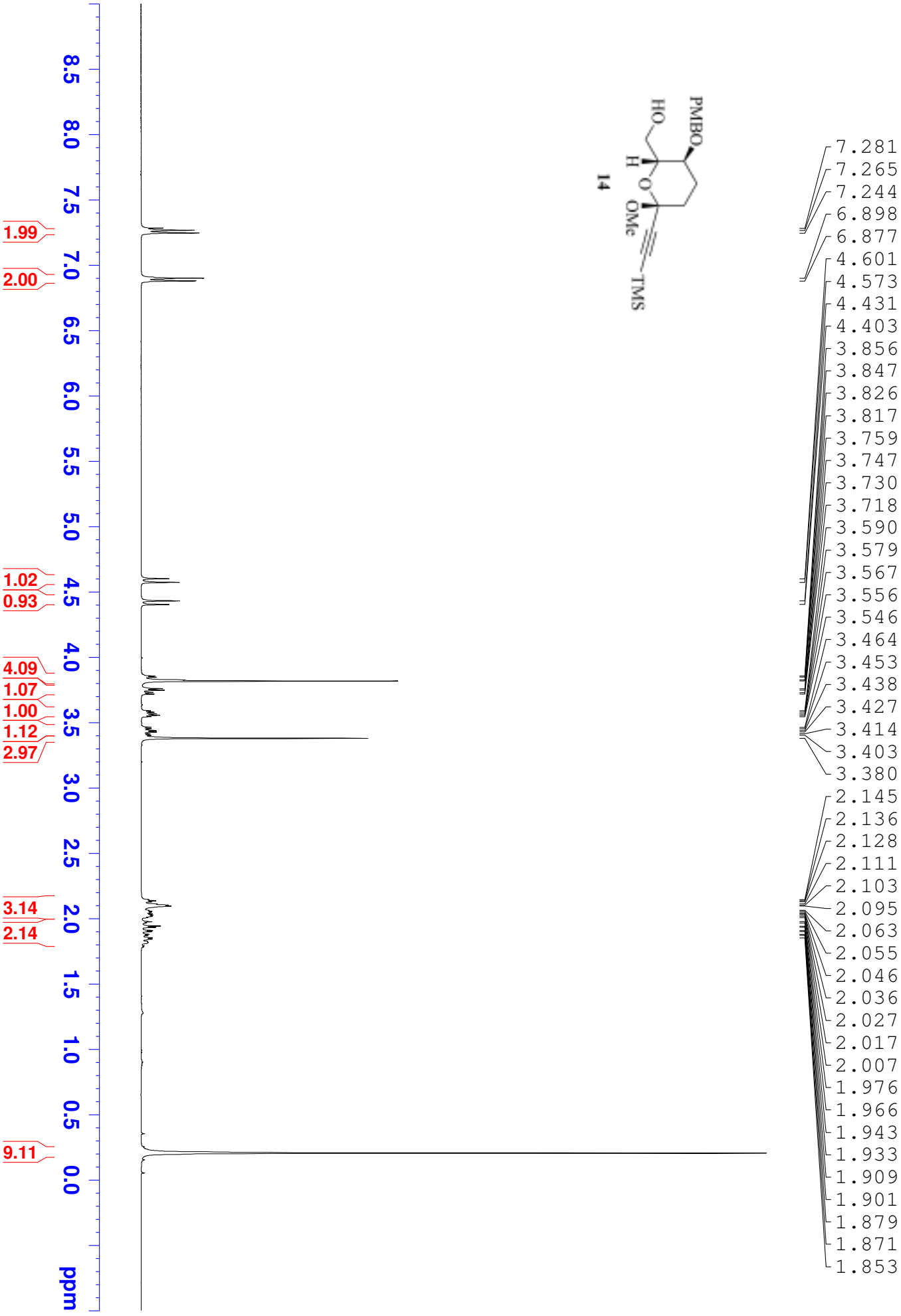

12
OPMB
O
O
H
O
202.07
159.35
130.14
129.61
113.86
109.22
77.73
77.25
77.20
77.00
76.75
72.17
66.64
55.26
39.29
26.58
25.21
23.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

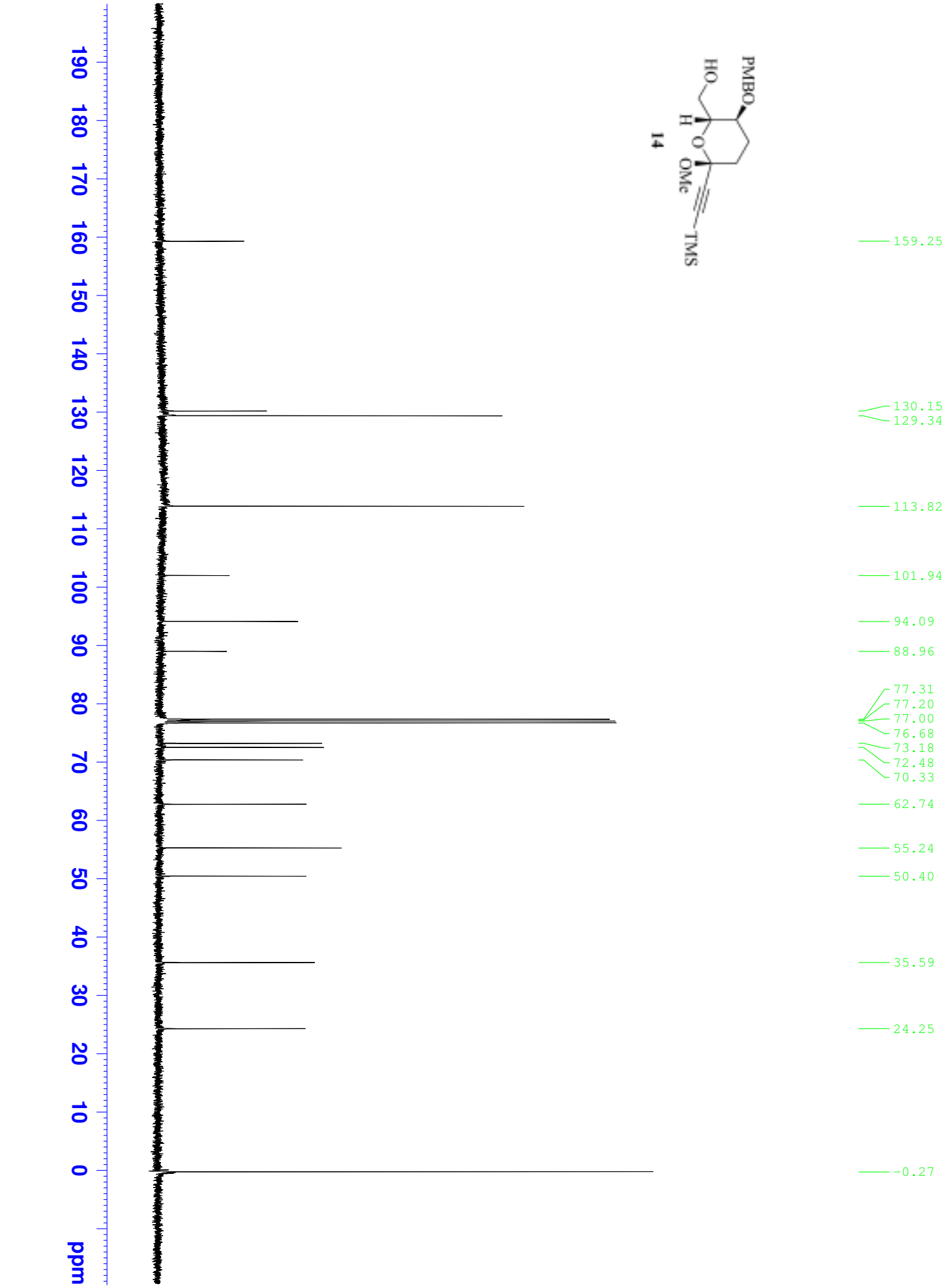

12a
OPMB
OH
TMS
7.302
7.297
7.290
7.280
7.274
7.269
6.906
6.885
4.664
4.637
4.570
4.524
4.496
4.415
4.397
4.383
4.131
4.125
4.115
4.109
4.099
4.094
4.079
4.075
4.059
4.055
4.043
4.039
3.895
3.880
3.876
3.864
3.860
3.849
3.844
3.822
3.579
3.572
3.564
3.556
3.550
1.902
1.897
1.888
1.869
1.856
1.842
1.832
1.813
1.765
1.750
1.736
1.437
1.428
1.367
1.358
0.192
0.186
2.74
2.18
2.18
1.00
2.16
1.15
3.22
1.02
5.11
3.29
3.18
9.19
10
9
8
7
6
5
4
3
2
1
0
ppm

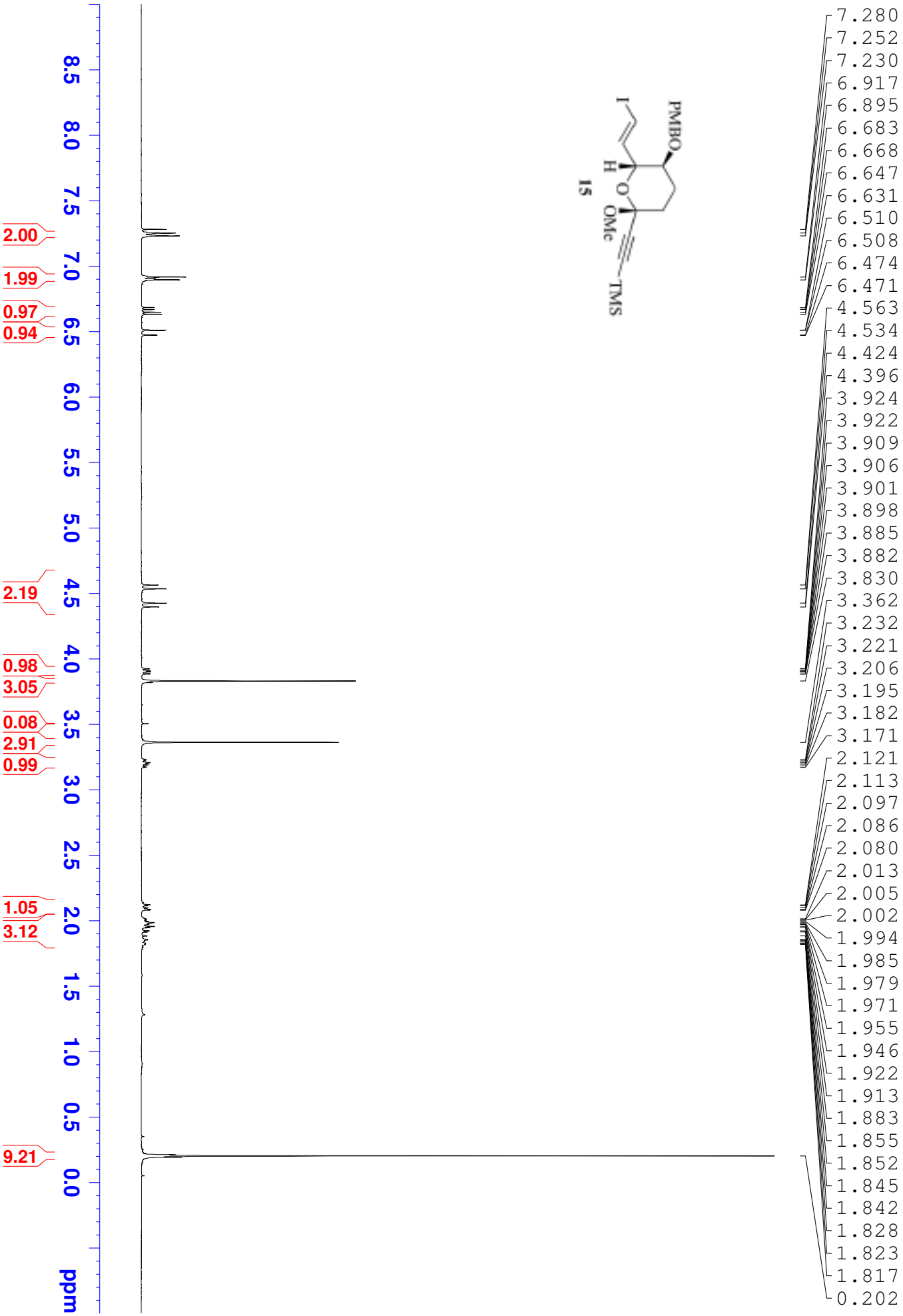

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
OPMB
OH
TMS
12a
159.33
159.27
130.30
130.06
129.66
129.51
113.84
113.82
109.12
109.09
106.76
106.61
89.52
89.42
78.35
78.32
77.29
77.26
77.00
76.75
71.99
71.85
66.86
66.62
62.70
62.55
55.23
32.87
32.44
26.66
26.60
26.23
25.66
25.28
25.26
-0.12
-0.15

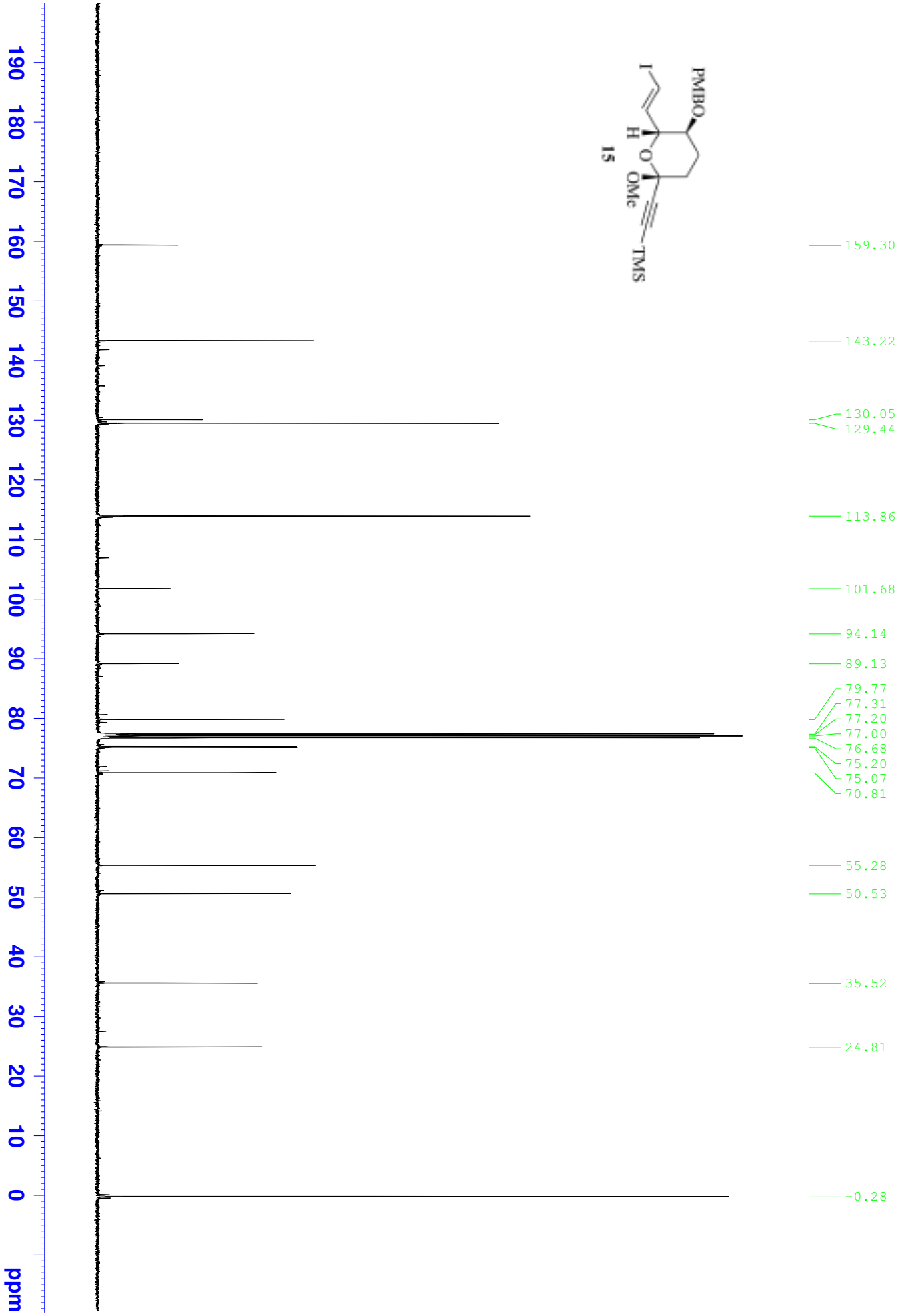

13
OPMB
TMS
7.280
7.273
7.251
6.904
6.882
4.532
4.095
4.093
4.079
4.066
4.060
4.049
4.033
3.873
3.868
3.862
3.855
3.850
3.845
3.841
3.833
3.818
3.547
3.536
3.530
3.521
3.515
3.505
2.731
2.719
2.715
2.711
2.702
2.699
2.694
2.683
2.075
2.071
2.065
2.061
2.056
2.045
2.039
2.036
2.029
2.025
2.019
1.906
1.890
1.887
1.870
1.853
1.850
1.837
1.833
1.425
1.360
0.257
1.98
2.15
2.14
2.13
1.16
3.25
1.09
2.00
1.08
1.07
3.12
3.11
8.90
ppm

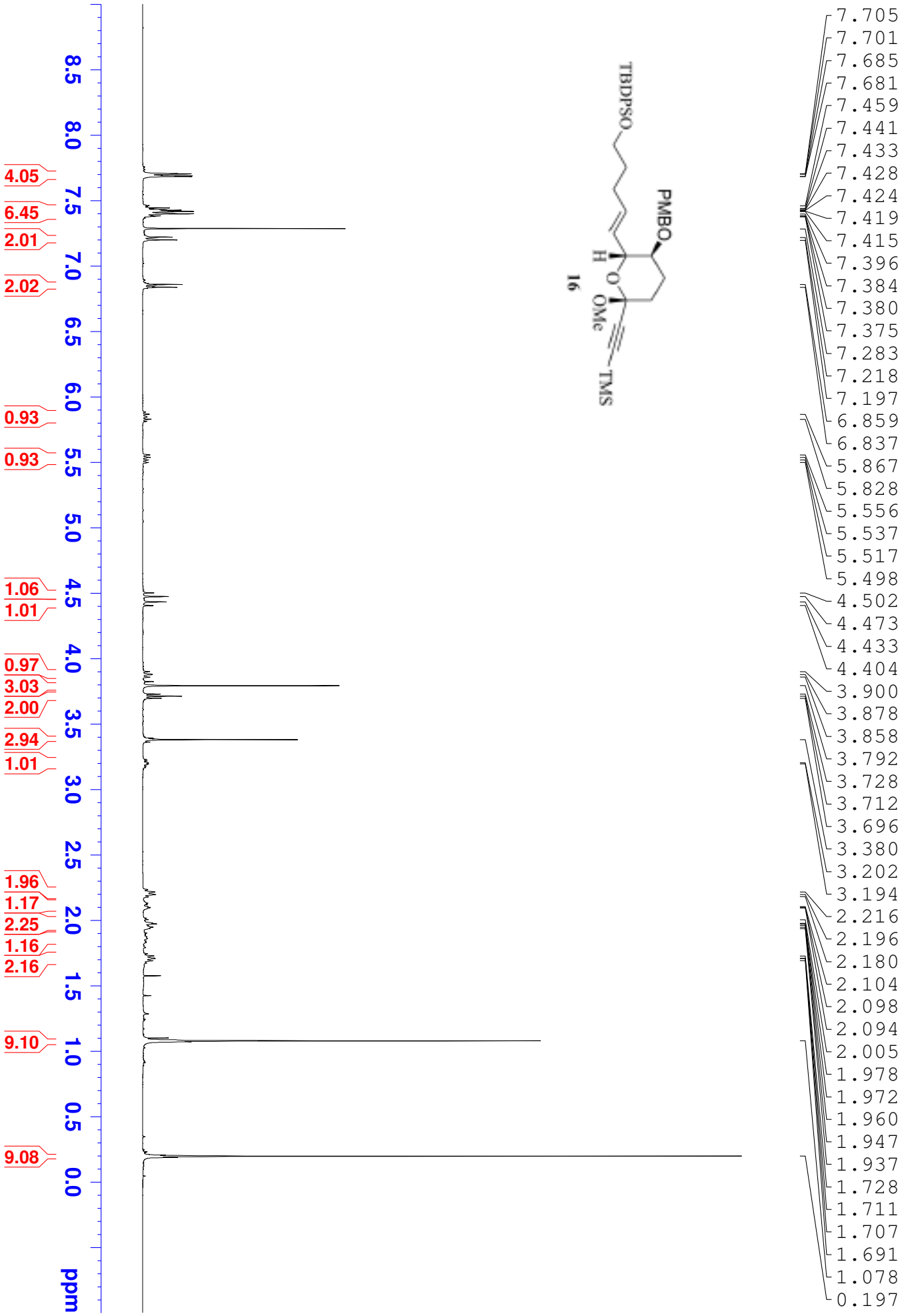

13
OPMB
TMS
O
O
O
187.28
159.34
130.27
129.54
113.86
109.22
102.03
97.76
77.56
77.29
77.20
77.04
76.78
72.15
66.68
55.27
40.54
26.61
25.26
24.76
-0.76
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

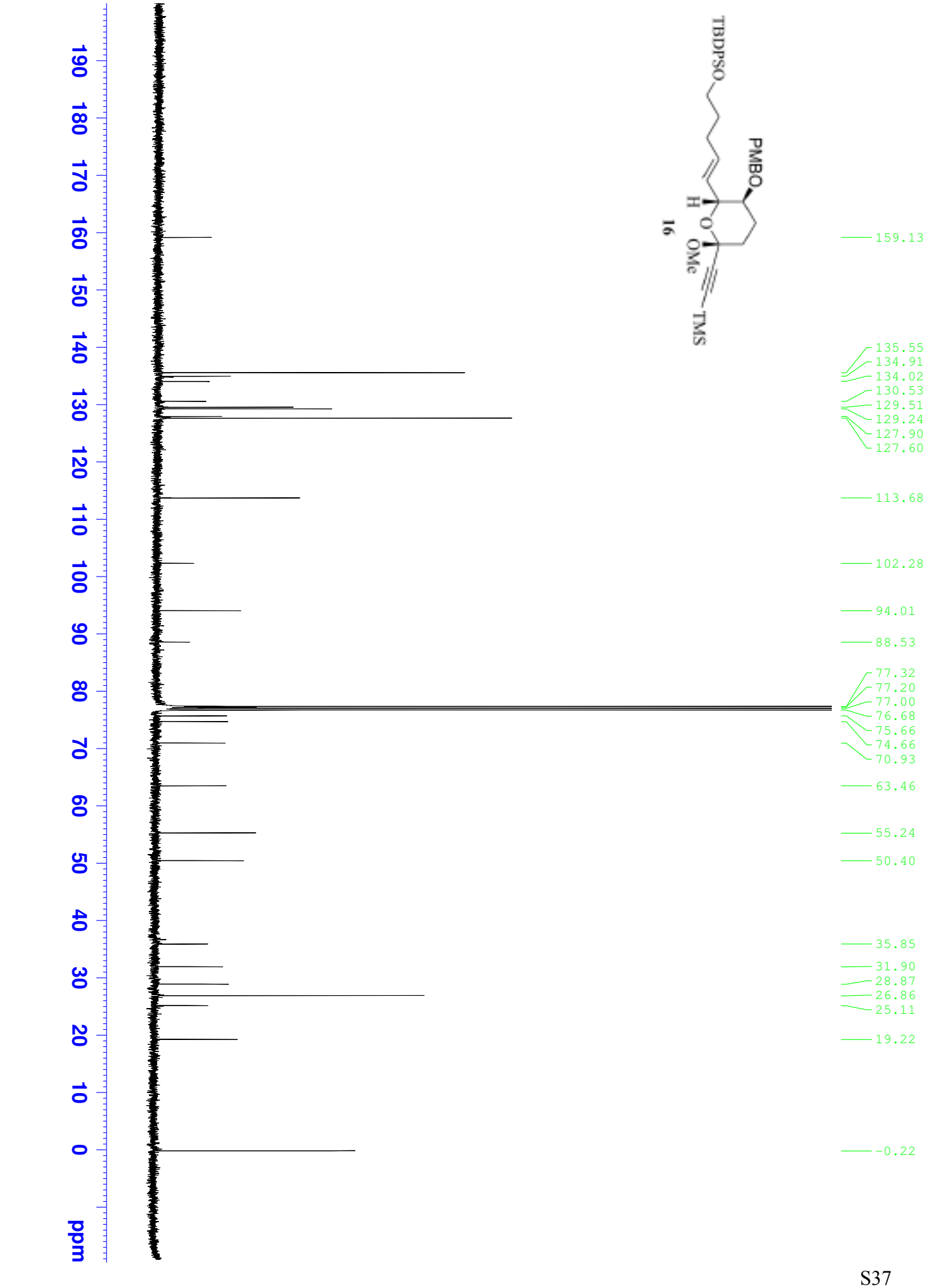

PMBO
HO
H
O
OMe
TMS
14
7.281
7.265
7.244
6.898
6.877
4.601
4.573
4.431
4.403
3.856
3.847
3.826
3.817
3.759
3.747
3.730
3.718
3.590
3.579
3.567
3.556
3.546
3.464
3.453
3.438
3.427
3.414
3.403
3.380
2.145
2.136
2.128
2.111
2.103
2.095
2.063
2.055
2.046
2.036
2.027
2.017
2.007
1.976
1.966
1.943
1.933
1.909
1.901
1.879
1.871
1.853
1.99
2.00
1.02
0.93
4.09
1.07
1.00
1.12
2.97
3.14
2.14
9.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

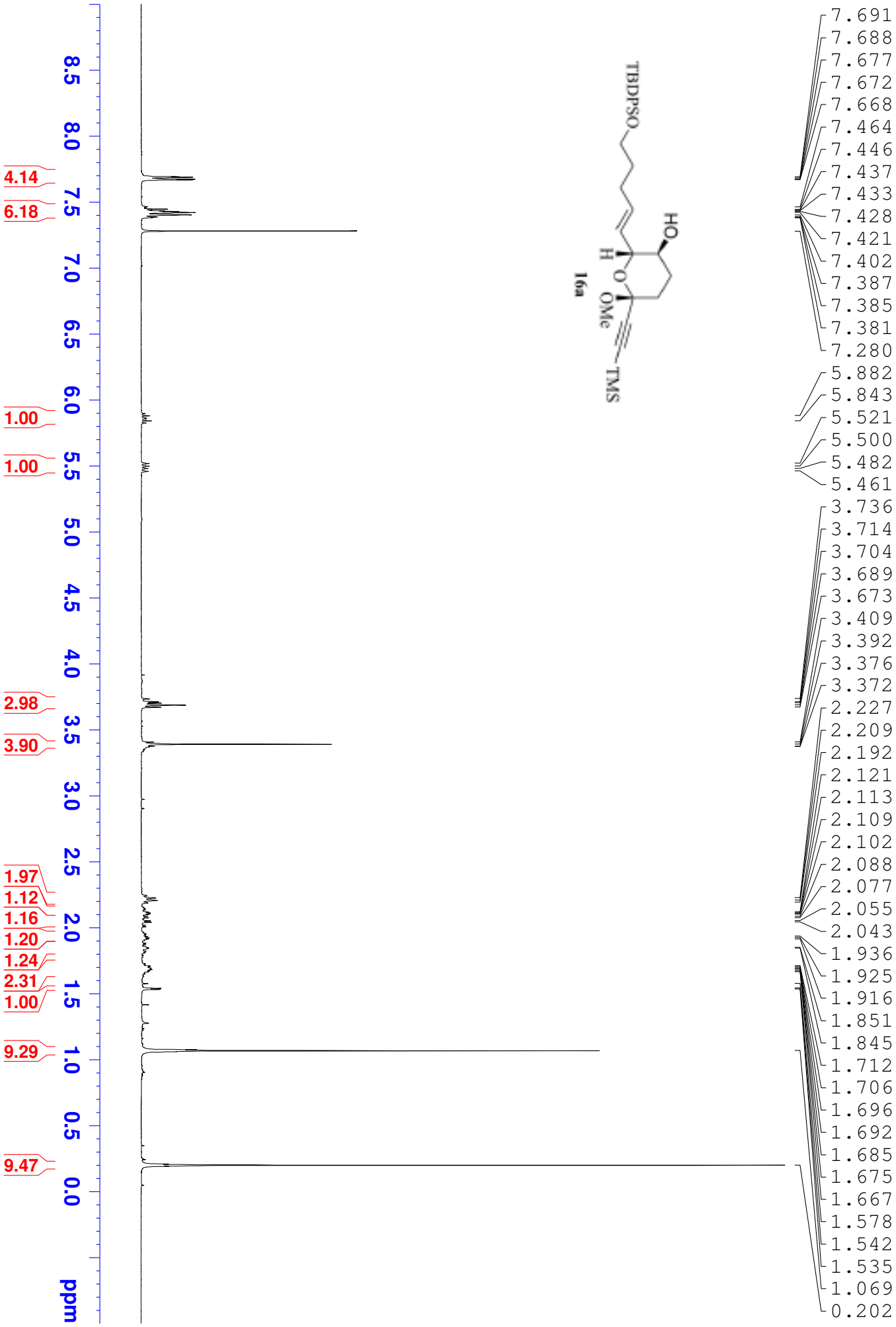

PMBO
HO
H
O
OMe
TMS
14
159.25
130.15
129.34
113.82
101.94
94.09
88.96
77.31
77.20
77.00
76.68
73.18
72.48
70.33
62.74
55.24
50.40
35.59
24.25
-0.27
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

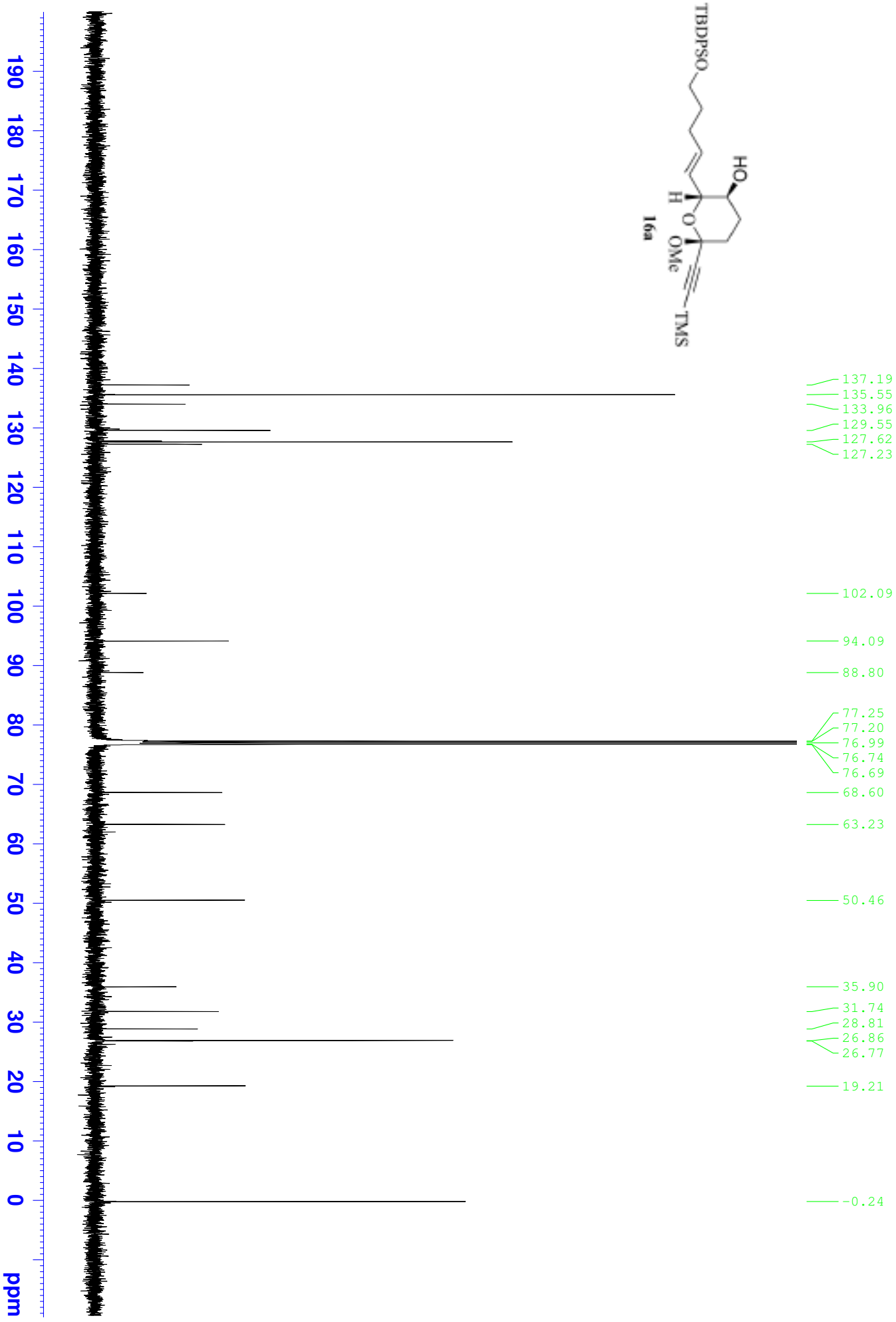

PMBO
H
O
OMe
TMS
I
15
7.280
7.252
7.230
6.917
6.895
6.683
6.668
6.647
6.631
6.510
6.508
6.474
6.471
4.563
4.534
4.424
4.396
3.924
3.922
3.909
3.906
3.901
3.898
3.885
3.882
3.830
3.362
3.232
3.221
3.206
3.195
3.182
3.171
2.121
2.113
2.097
2.086
2.080
2.013
2.005
2.002
1.994
1.985
1.979
1.971
1.955
1.946
1.922
1.913
1.883
1.855
1.852
1.845
1.842
1.828
1.823
1.817
0.202
2.00
1.99
0.97
0.94
2.19
0.98
3.05
0.08
2.91
0.99
1.05
3.12
9.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

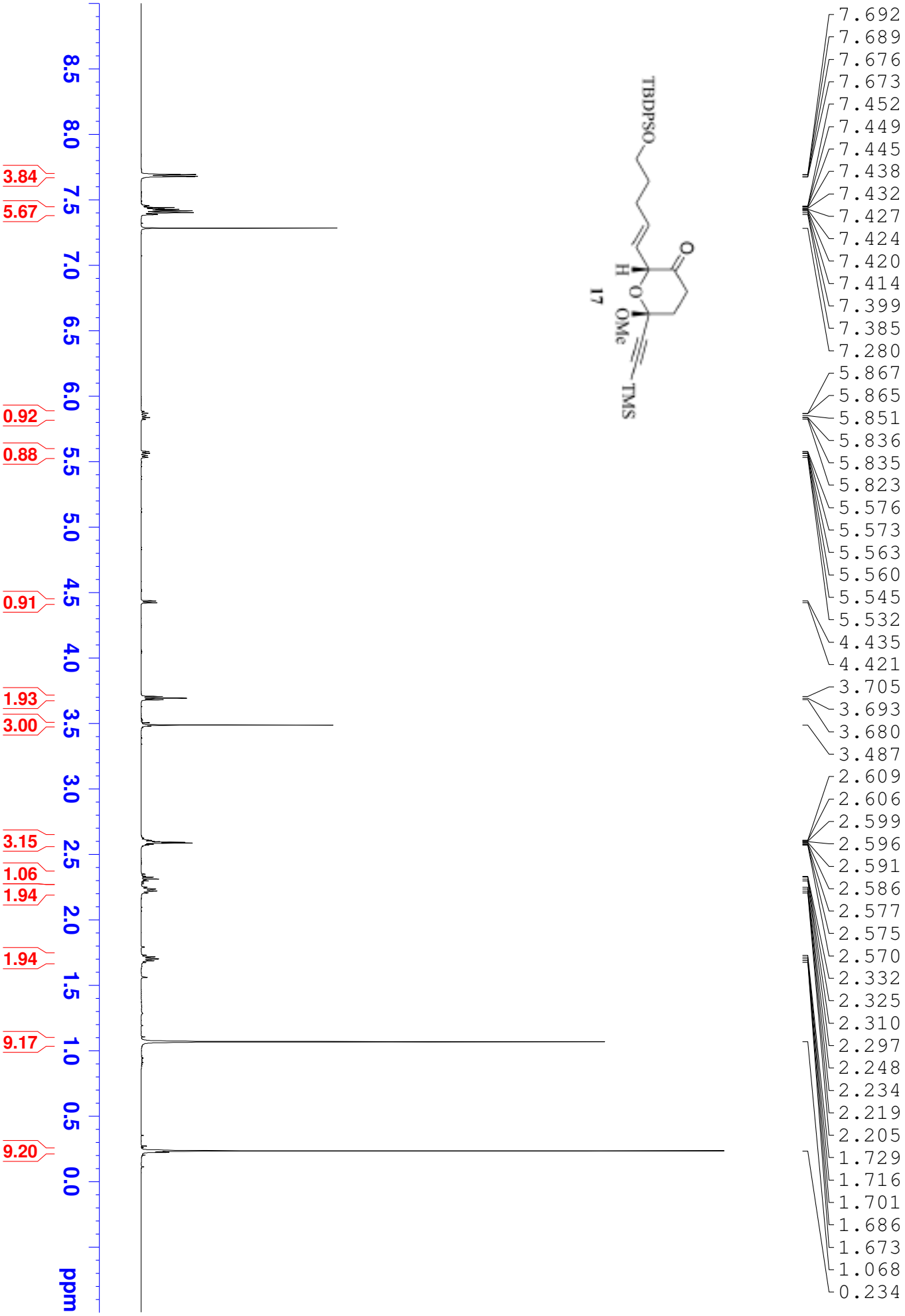

PMBO
I
H
O
OMe
TMS
15
159.30
143.22
130.05
129.44
113.86
101.68
94.14
89.13
79.77
77.31
77.20
77.00
76.68
75.20
75.07
70.81
55.28
50.53
35.52
24.81
-0.28
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

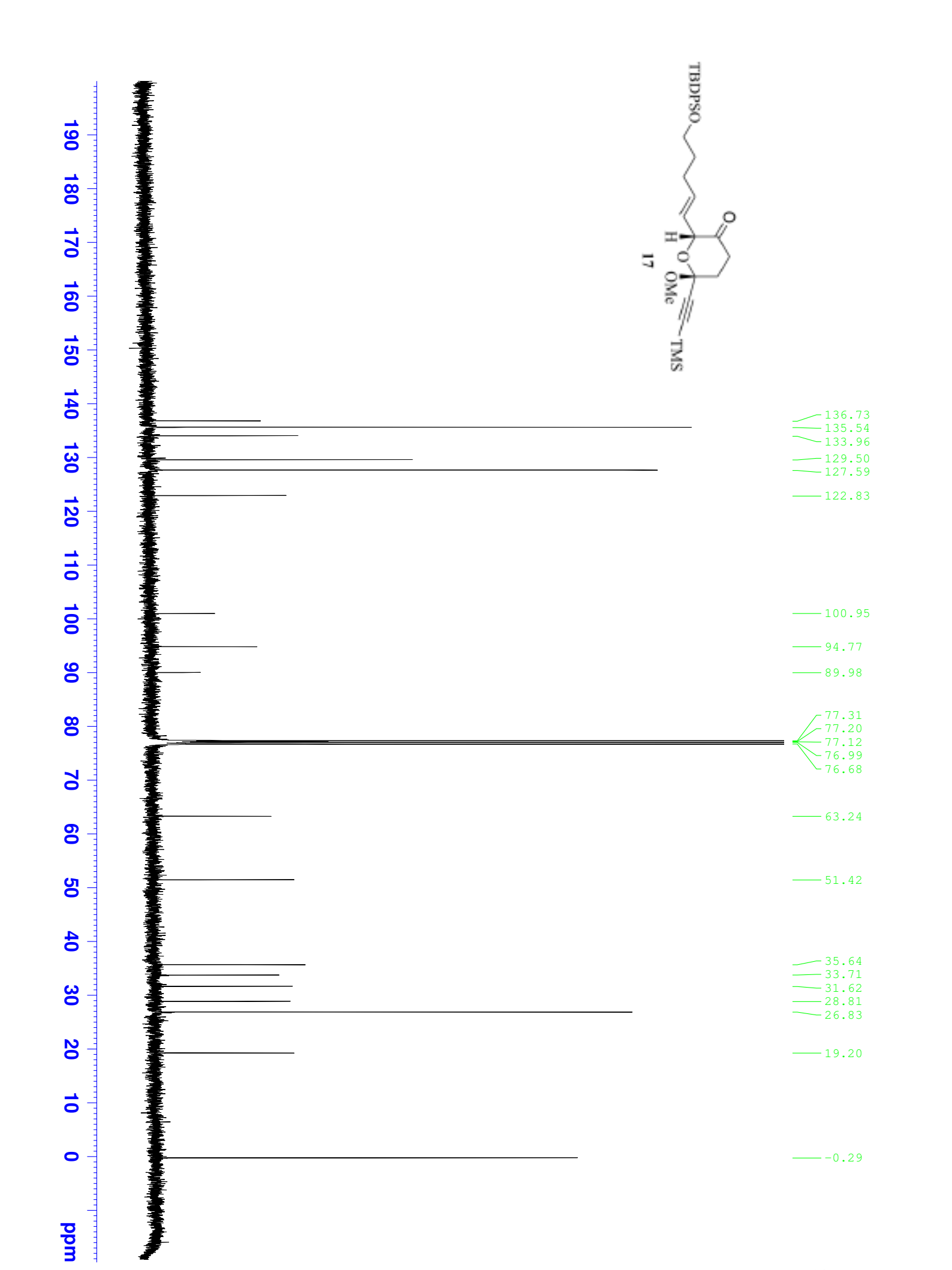

TBDPSO
PMBO
H
O
OMe
TMS
16
7.705
7.701
7.685
7.681
7.459
7.441
7.433
7.428
7.424
7.419
7.415
7.396
7.384
7.380
7.375
7.283
7.218
7.197
6.859
6.837
5.867
5.828
5.556
5.537
5.517
5.498
4.502
4.473
4.433
4.404
3.900
3.878
3.858
3.792
3.728
3.712
3.696
3.380
3.202
3.194
2.216
2.196
2.180
2.104
2.098
2.094
2.005
1.978
1.972
1.960
1.947
1.937
1.728
1.711
1.707
1.691
1.078
0.197
4.05
6.45
2.01
2.02
0.93
0.93
1.06
1.01
0.97
3.03
2.00
2.94
1.01
1.96
1.17
2.25
1.16
2.16
9.10
9.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

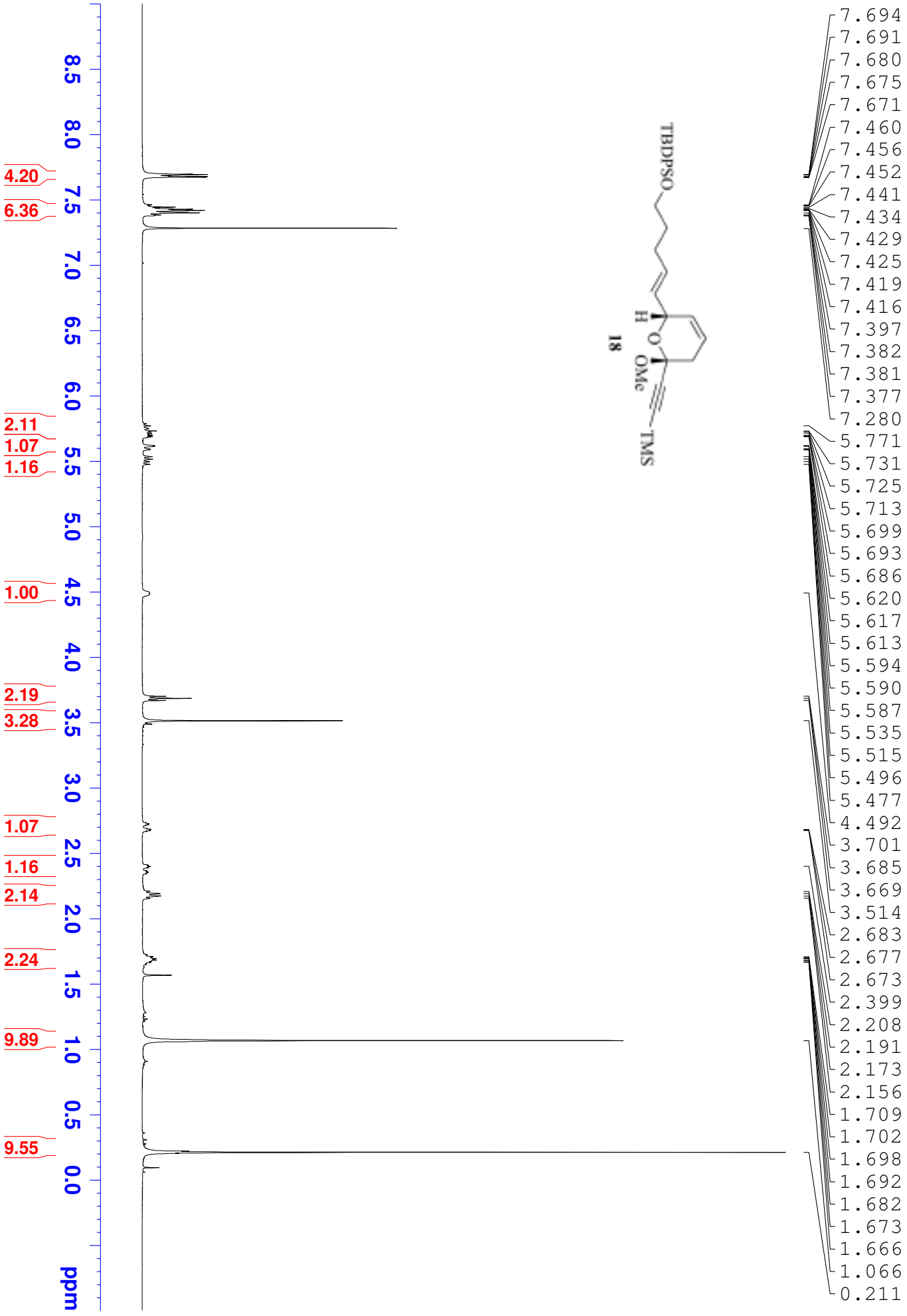

TBDPSO
PMBO
H
O
OMe
TMS
16
159.13
135.55
134.91
134.02
130.53
129.51
129.24
127.90
127.60
113.68
102.28
94.01
88.53
77.32
77.20
77.00
76.68
75.66
74.66
70.93
63.46
55.24
50.40
35.85
31.90
28.87
26.86
25.11
19.22
-0.22
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

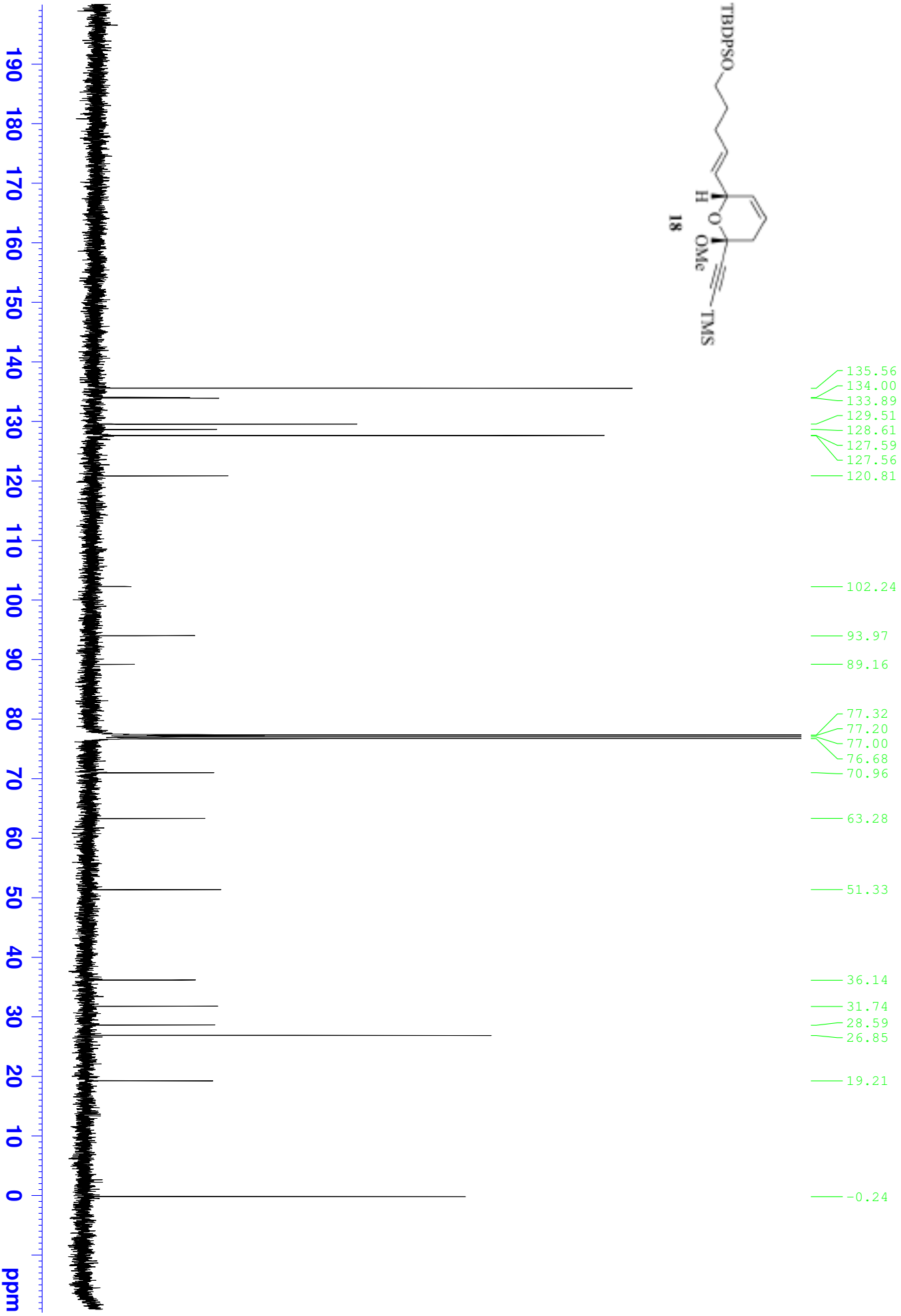

TBDPSO
H
O
OMe
TMS
HO
16a
7.691
7.688
7.677
7.672
7.668
7.464
7.446
7.437
7.433
7.428
7.421
7.402
7.387
7.385
7.381
7.280
5.882
5.843
5.521
5.500
5.482
5.461
3.736
3.714
3.704
3.689
3.673
3.409
3.392
3.376
3.372
2.227
2.209
2.192
2.121
2.113
2.109
2.102
2.088
2.077
2.055
2.043
1.936
1.925
1.916
1.851
1.845
1.712
1.706
1.696
1.692
1.685
1.675
1.667
1.578
1.542
1.535
1.069
0.202
4.14
6.18
1.00
1.00
2.98
3.90
1.97
1.12
1.16
1.20
1.24
2.31
1.00
9.29
9.47
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


TBDPSO
HO
H
O
OMe
TMS
16a
137.19
135.55
133.96
129.55
127.62
127.23
102.09
94.09
88.80
77.25
77.20
76.99
76.74
76.69
68.60
63.23
50.46
35.90
31.74
28.81
26.86
26.77
19.21
-0.24
ppm

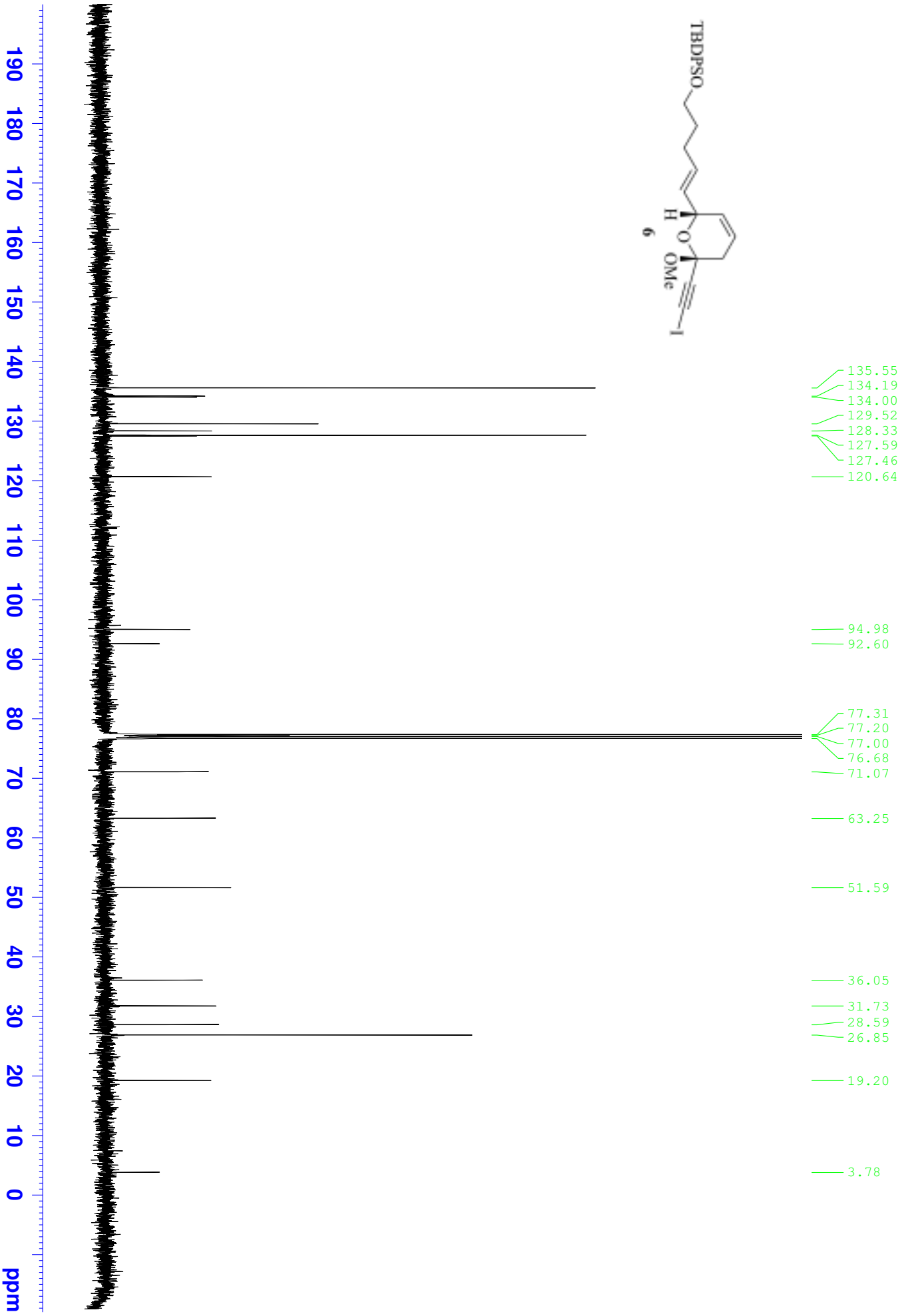

TBDPSO
H
O
OMe
TMS
O
17
7.692
7.689
7.676
7.673
7.452
7.449
7.445
7.438
7.432
7.427
7.424
7.420
7.414
7.399
7.385
7.280
5.867
5.865
5.851
5.836
5.835
5.823
5.576
5.573
5.563
5.560
5.545
5.532
4.435
4.421
3.705
3.693
3.680
3.487
2.609
2.606
2.599
2.596
2.591
2.586
2.577
2.575
2.570
2.332
2.325
2.310
2.297
2.248
2.234
2.219
2.205
1.729
1.716
1.701
1.686
1.673
1.068
0.234
3.84
5.67
0.92
0.88
0.91
1.93
3.00
3.15
1.06
1.94
1.94
9.17
9.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

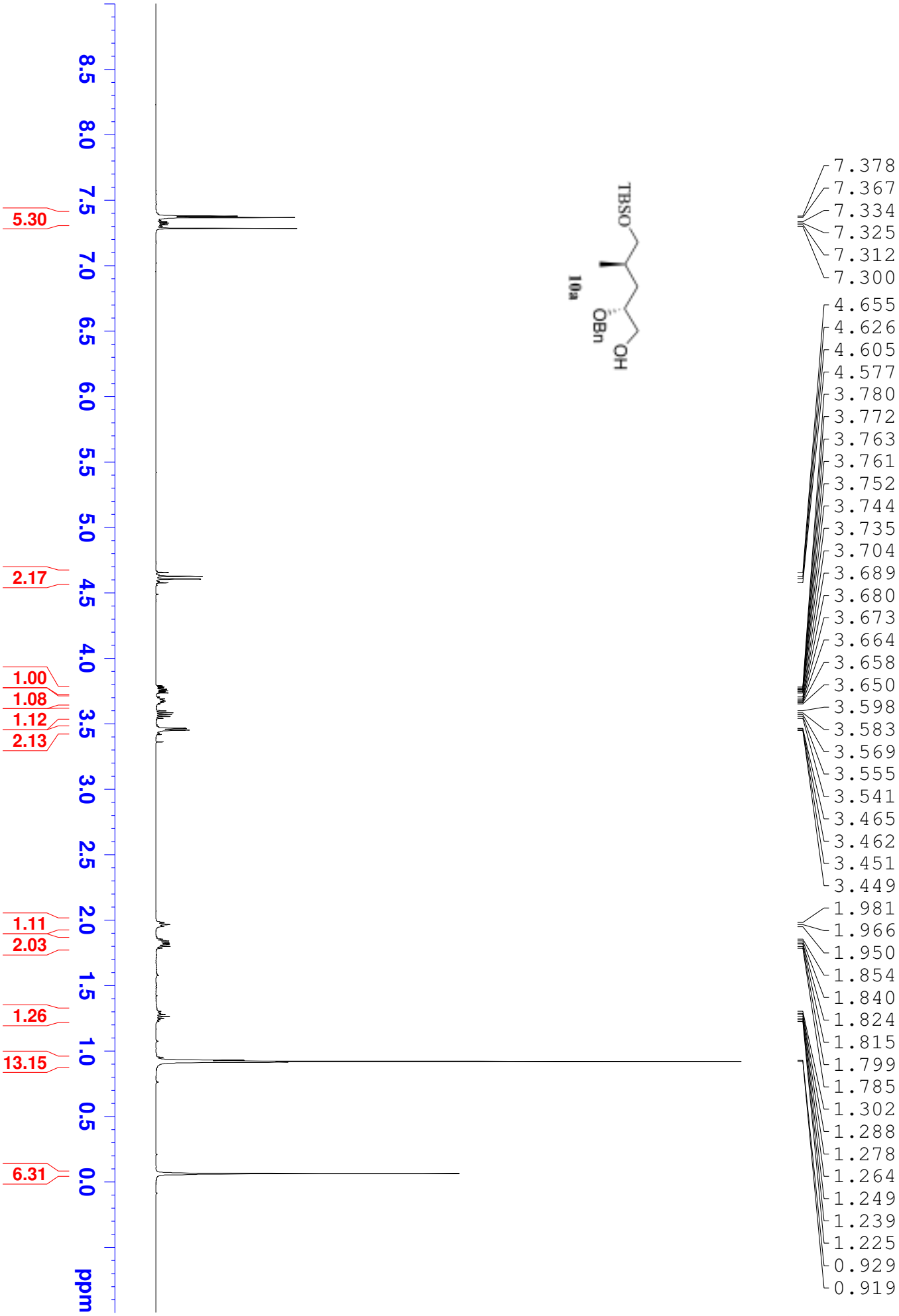

TBDPSO
H
O
O
OMe
TMS
17
136.73
135.54
133.96
129.50
127.59
122.83
100.95
94.77
89.98
77.31
77.20
77.12
76.99
76.68
63.24
51.42
35.64
33.71
31.62
28.81
26.83
19.20
-0.29
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

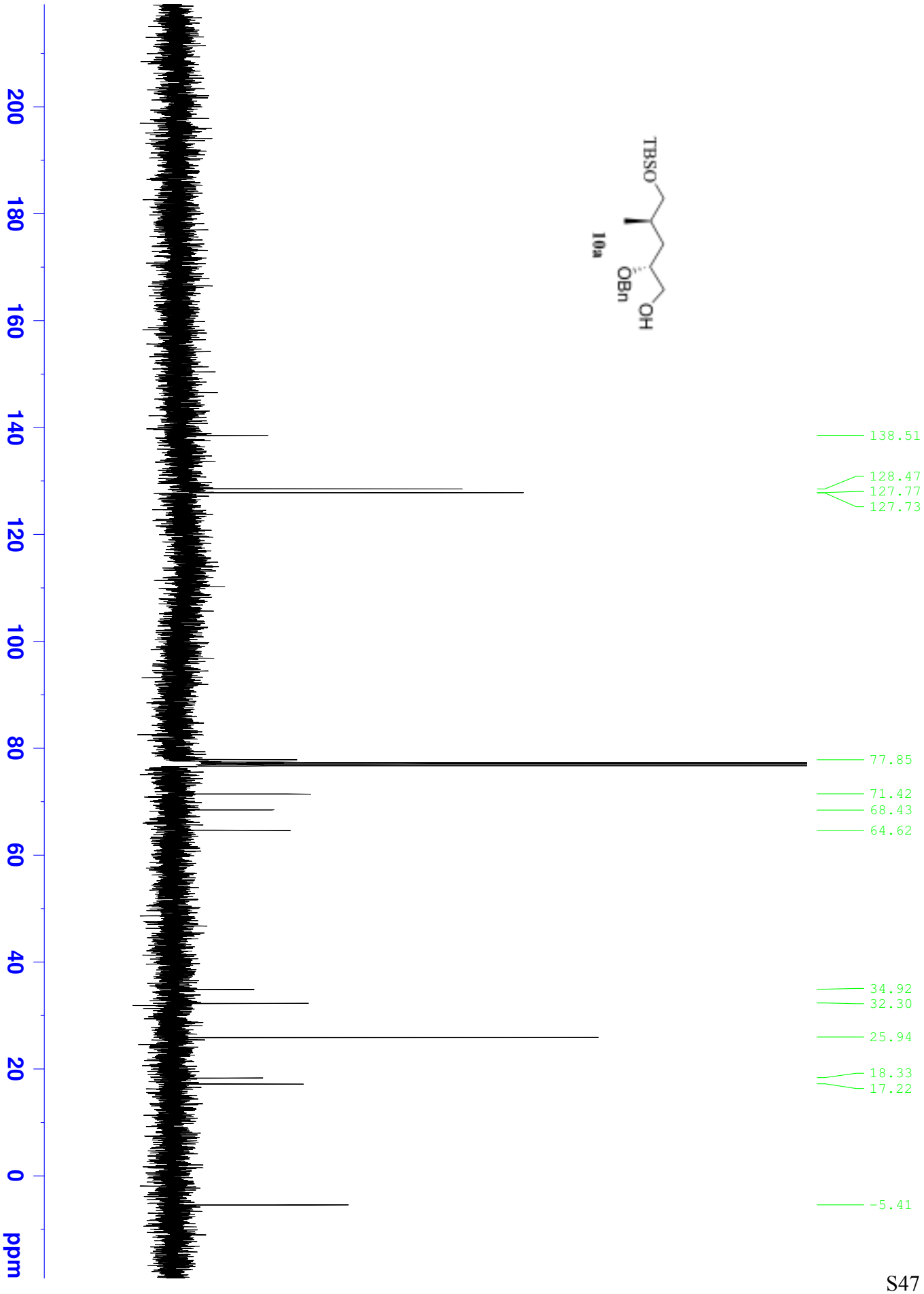

TBDPSO
H
O
OMe
TMS
18
7.694
7.691
7.680
7.675
7.671
7.460
7.456
7.452
7.441
7.434
7.429
7.425
7.419
7.416
7.397
7.382
7.381
7.377
7.280
5.771
5.731
5.725
5.713
5.699
5.693
5.686
5.620
5.617
5.613
5.594
5.590
5.587
5.535
5.515
5.496
5.477
4.492
3.701
3.685
3.669
3.514
2.683
2.677
2.673
2.399
2.208
2.191
2.173
2.156
1.709
1.702
1.698
1.692
1.682
1.673
1.666
1.066
0.211
4.20
6.36
2.11
1.07
1.16
1.00
2.19
3.28
1.07
1.16
2.14
2.24
9.89
9.55
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

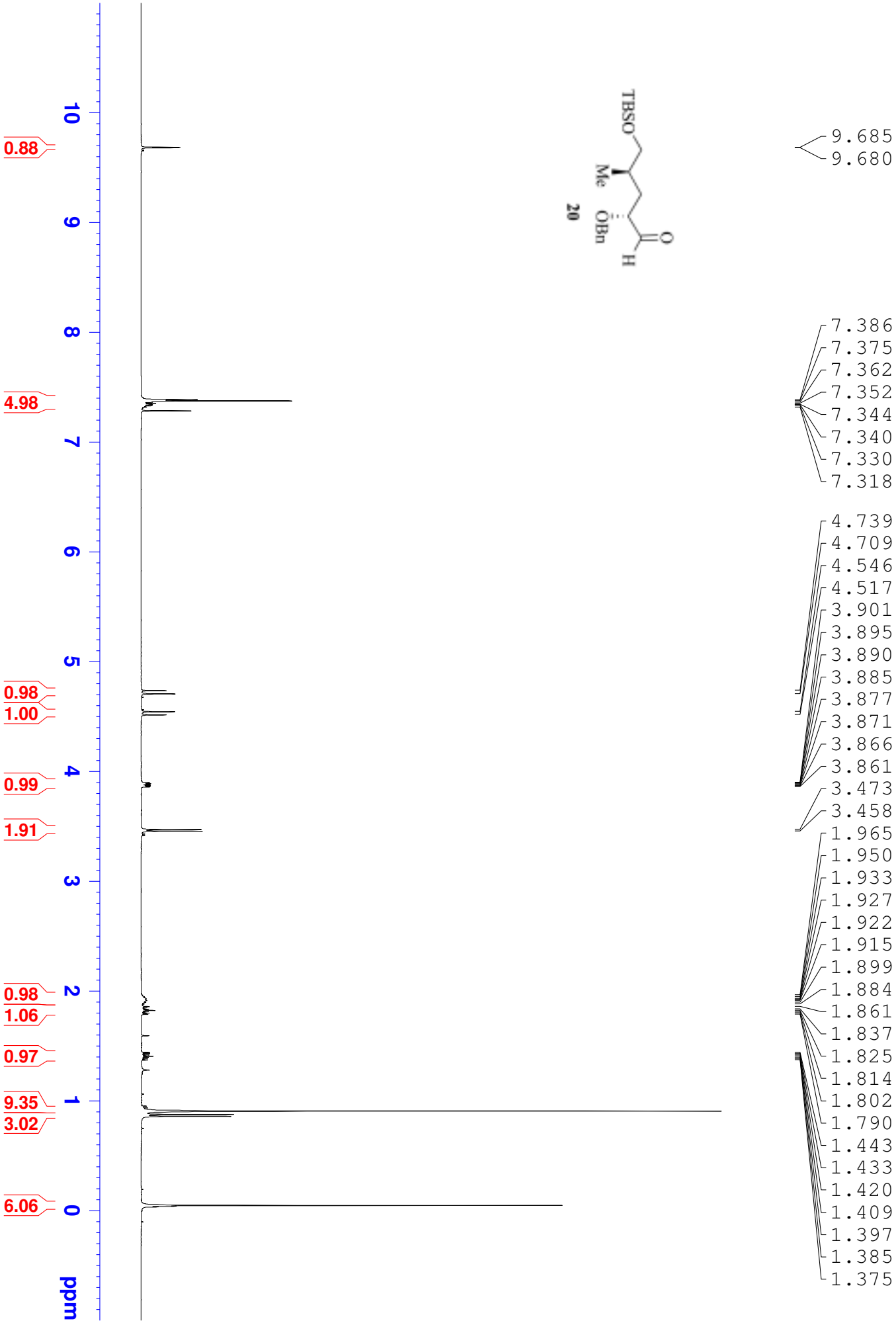

TBDPSO
H
O
OMe
TMS
18
135.56
134.00
133.89
129.51
128.61
127.59
127.56
120.81
102.24
93.97
89.16
77.32
77.20
77.00
76.68
70.96
63.28
51.33
36.14
31.74
28.59
26.85
19.21
-0.24
ppm

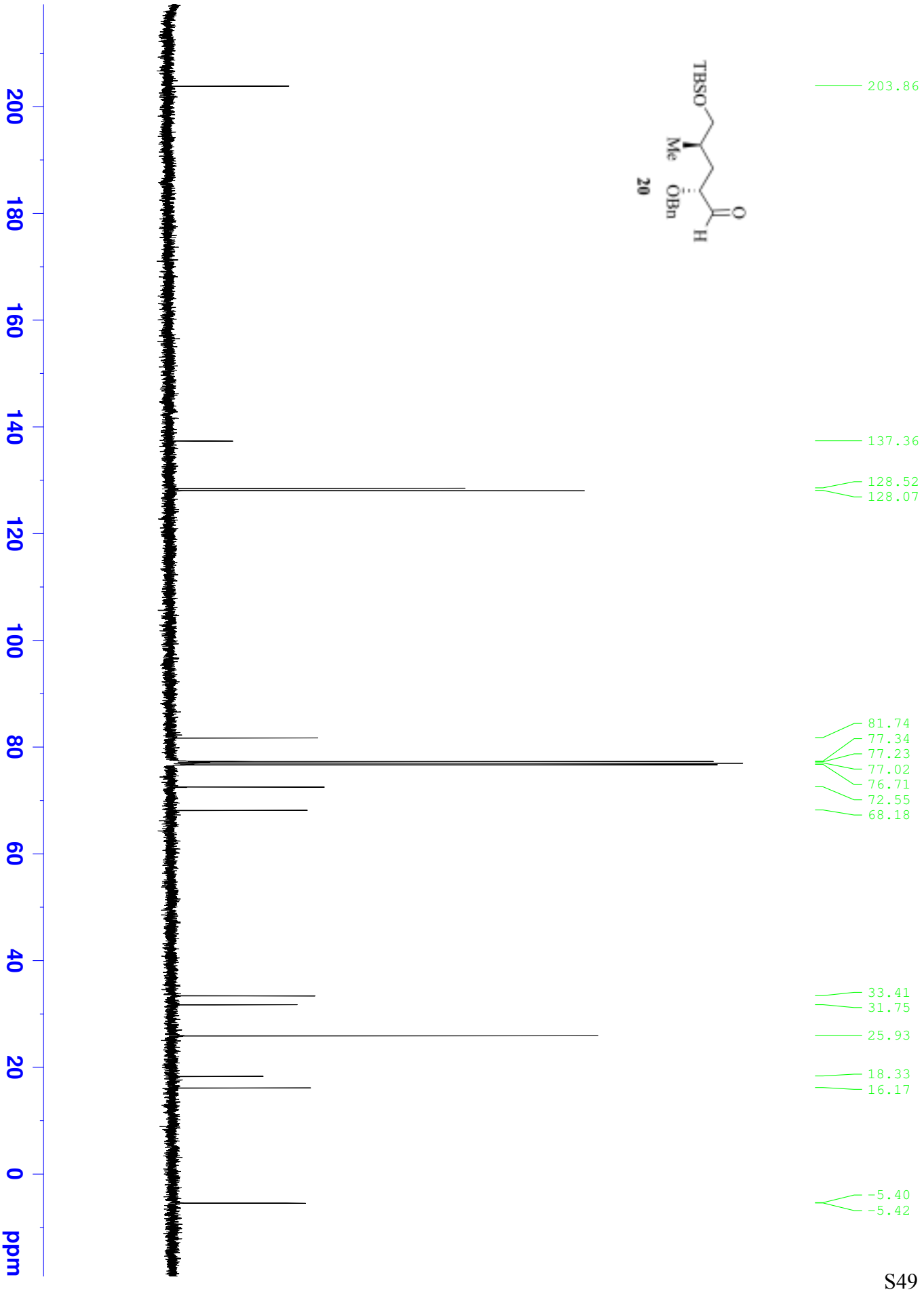
7.696
7.692
7.676
7.672
7.462
7.453
7.444
7.436
7.431
7.427
7.418
7.399
7.384
7.382
7.379
7.280
5.780
5.742
5.728
5.723
5.715
5.702
5.696
5.689
5.622
5.619
5.615
5.596
5.592
5.589
5.515
5.496
5.477
5.457
4.489
3.704
3.688
3.672
3.519
2.736
2.692
2.688
2.686
2.682
2.401
2.397
2.215
2.197
2.179
2.162
1.711
1.706
1.701
1.695
1.686
1.676
1.670
1.069
TBDPSO
H
O
OMe
I
6
4.00
6.53
2.00
0.99
0.99
0.97
2.09
2.93
1.04
1.06
2.04
2.20
9.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

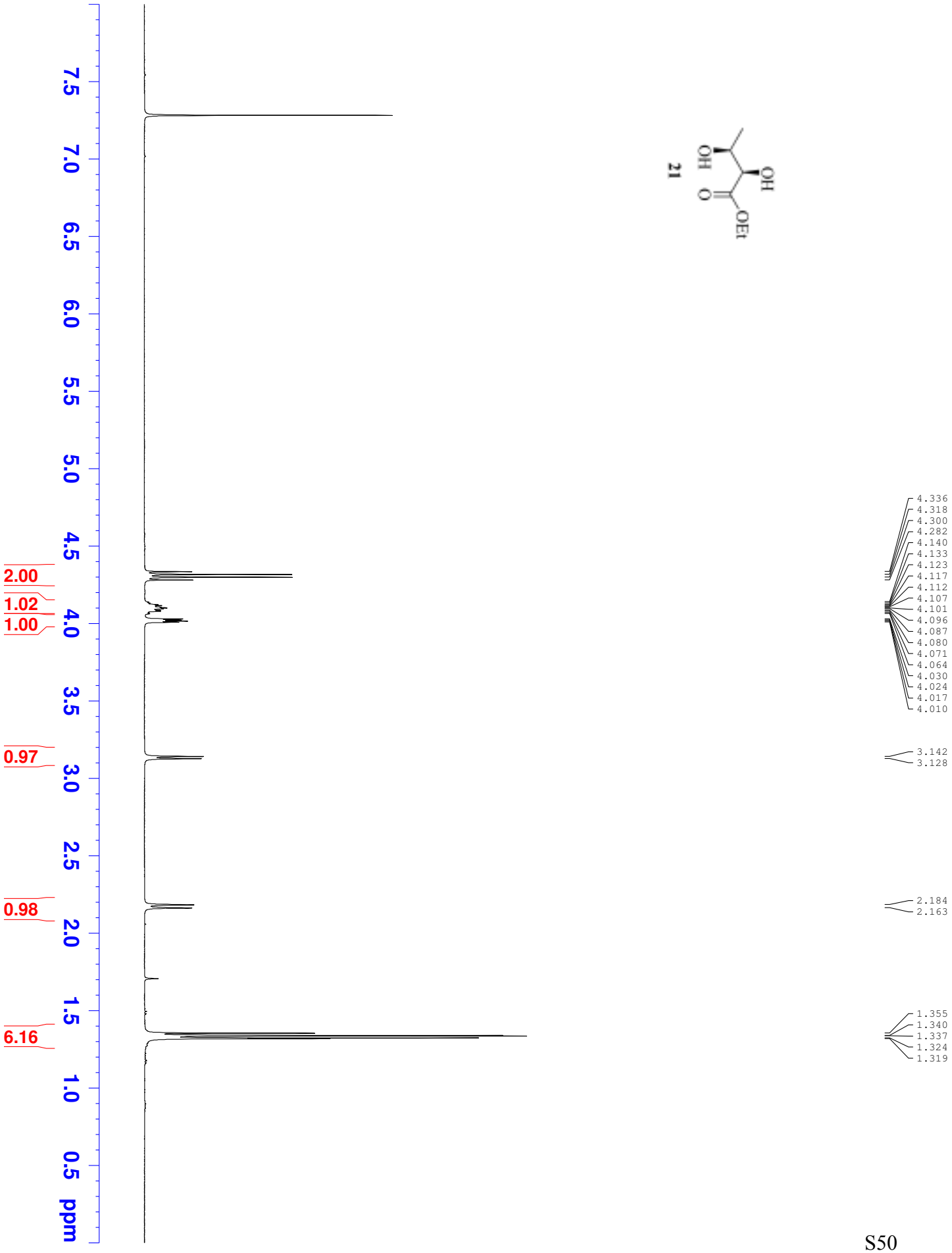

TBDPSO
H
O
OMe
I
9
135.55
134.19
134.00
129.52
128.33
127.59
127.46
120.64
94.98
92.60
77.31
77.20
77.00
76.68
71.07
63.25
51.59
36.05
31.73
28.59
26.85
19.20
3.78
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

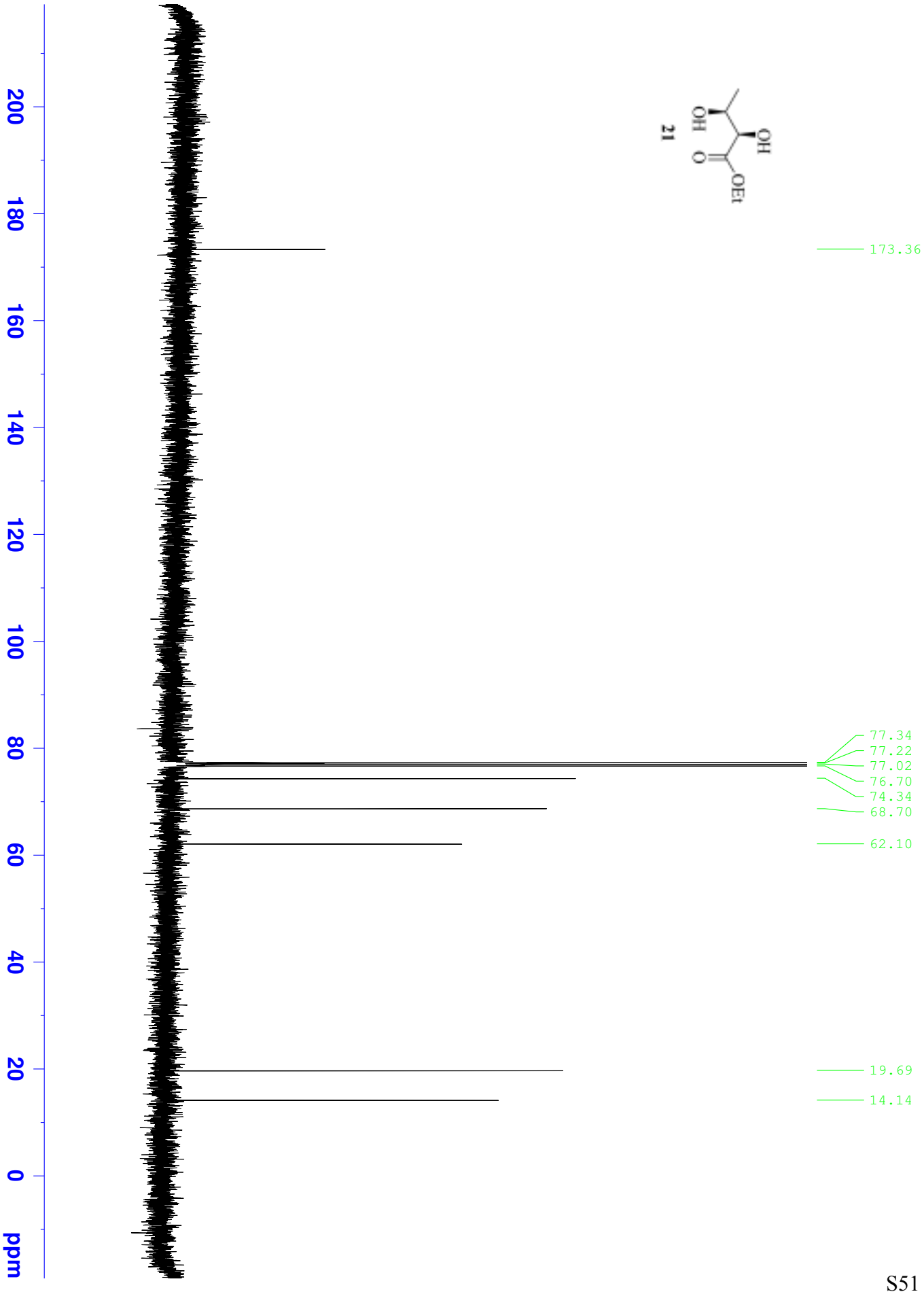

TBSO
OBn
OH
10a
7.378
7.367
7.334
7.325
7.312
7.300
4.655
4.626
4.605
4.577
3.780
3.772
3.763
3.761
3.752
3.744
3.735
3.704
3.689
3.680
3.673
3.664
3.658
3.650
3.598
3.583
3.569
3.555
3.541
3.465
3.462
3.451
3.449
1.981
1.966
1.950
1.854
1.840
1.824
1.815
1.799
1.785
1.302
1.288
1.278
1.264
1.249
1.239
1.225
0.929
0.919
5.30
2.17
1.00
1.08
1.12
2.13
1.11
2.03
1.26
13.15
6.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

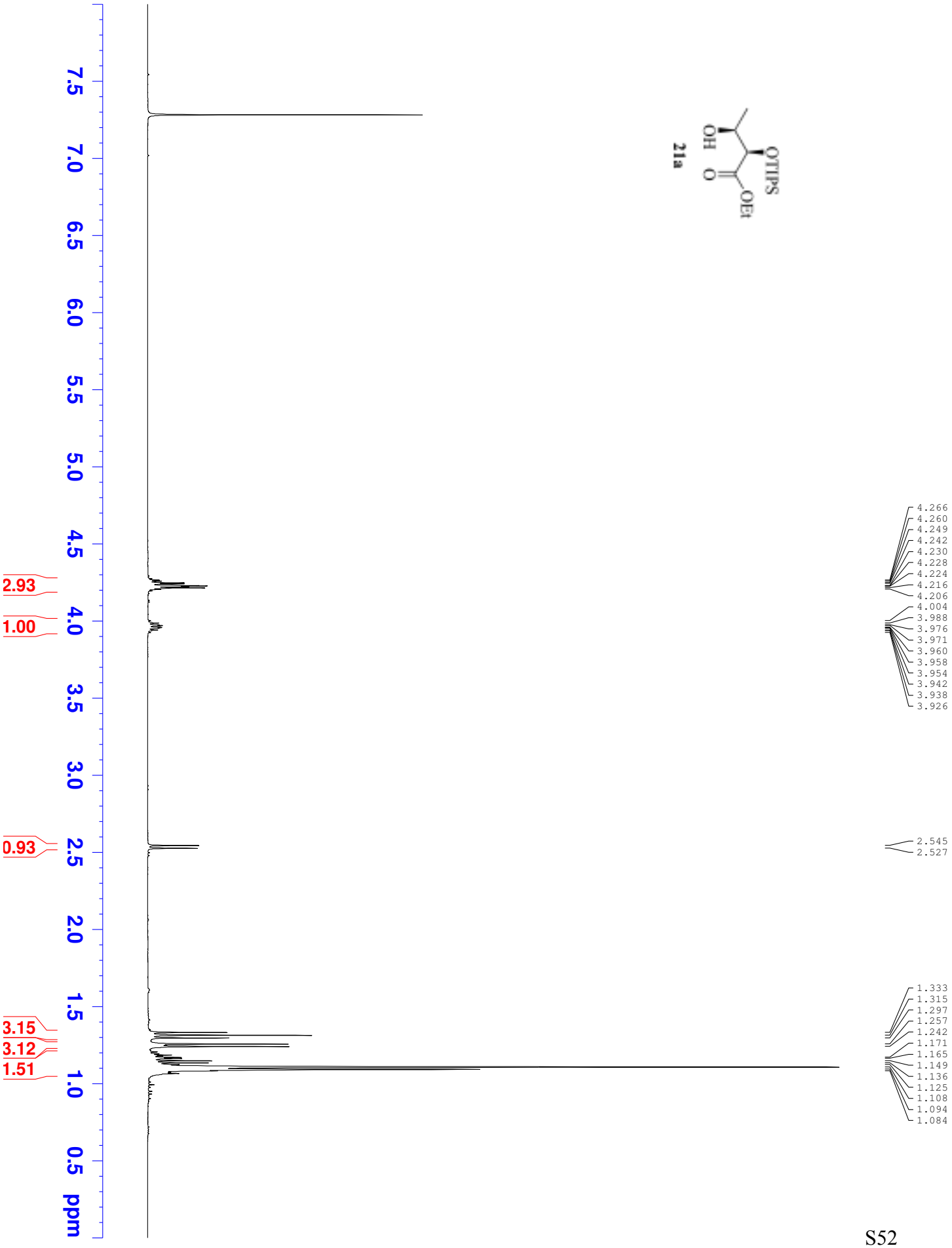

TBSO
OBn
OH
10a
138.51
128.47
127.77
127.73
77.85
71.42
68.43
64.62
34.92
32.30
25.94
18.33
17.22
-5.41
200
180
160
140
120
100
80
60
40
20
0
ppm

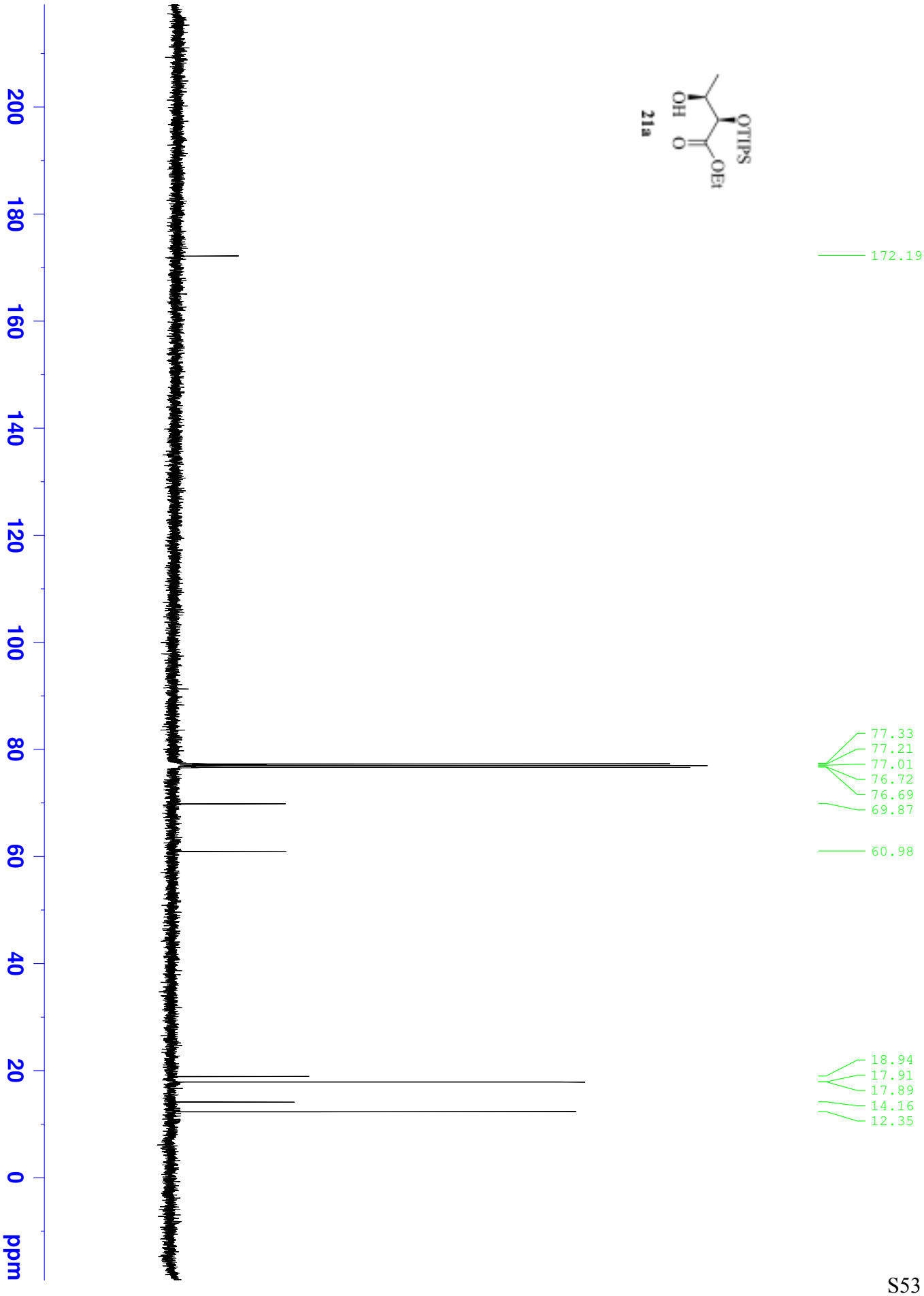

TBSO
Me
OBn
O
H
20
9.685
9.680
7.386
7.375
7.362
7.352
7.344
7.340
7.330
7.318
4.739
4.709
4.546
4.517
3.901
3.895
3.890
3.885
3.877
3.871
3.866
3.861
3.473
3.458
1.965
1.950
1.933
1.927
1.922
1.915
1.899
1.884
1.861
1.837
1.825
1.814
1.802
1.790
1.443
1.433
1.420
1.409
1.397
1.385
1.375
0.88
4.98
0.98
1.00
0.99
1.91
0.98
1.06
0.97
9.35
3.02
6.06
10
9
8
7
6
5
4
3
2
1
0
ppm

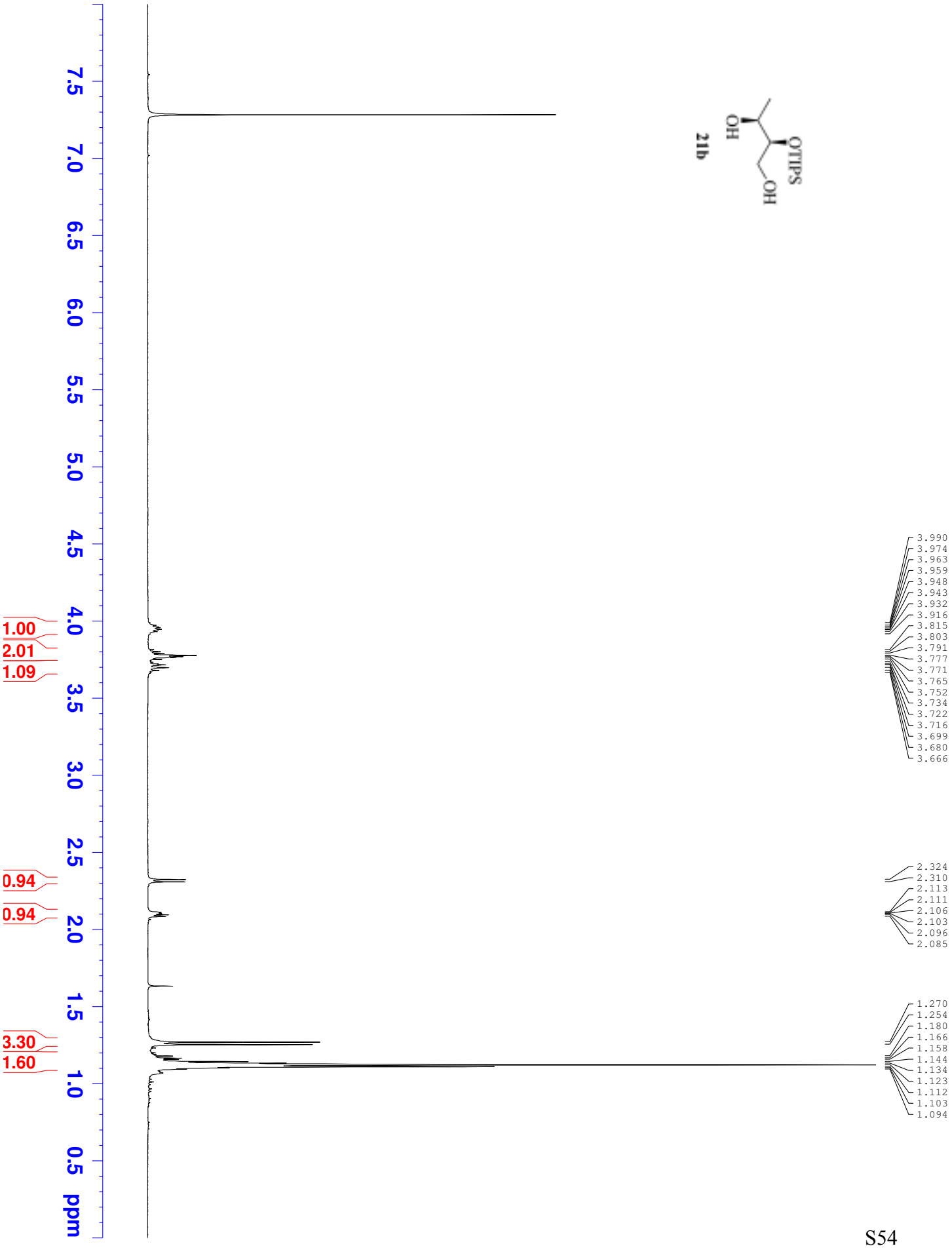

TBSO
Me
OBn
O
H
20
203.86
137.36
128.52
128.07
81.74
77.34
77.23
77.02
76.71
72.55
68.18
33.41
31.75
25.93
18.33
16.17
-5.40
-5.42
200
180
160
140
120
100
80
60
40
20
0
ppm


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.02
1.00
0.97
0.98
6.16
OH
OH
O
OEt
21
4.336
4.318
4.300
4.282
4.140
4.133
4.123
4.117
4.112
4.107
4.101
4.096
4.087
4.080
4.071
4.064
4.030
4.024
4.017
4.010
3.142
3.128
2.184
2.163
1.355
1.340
1.337
1.324
1.319

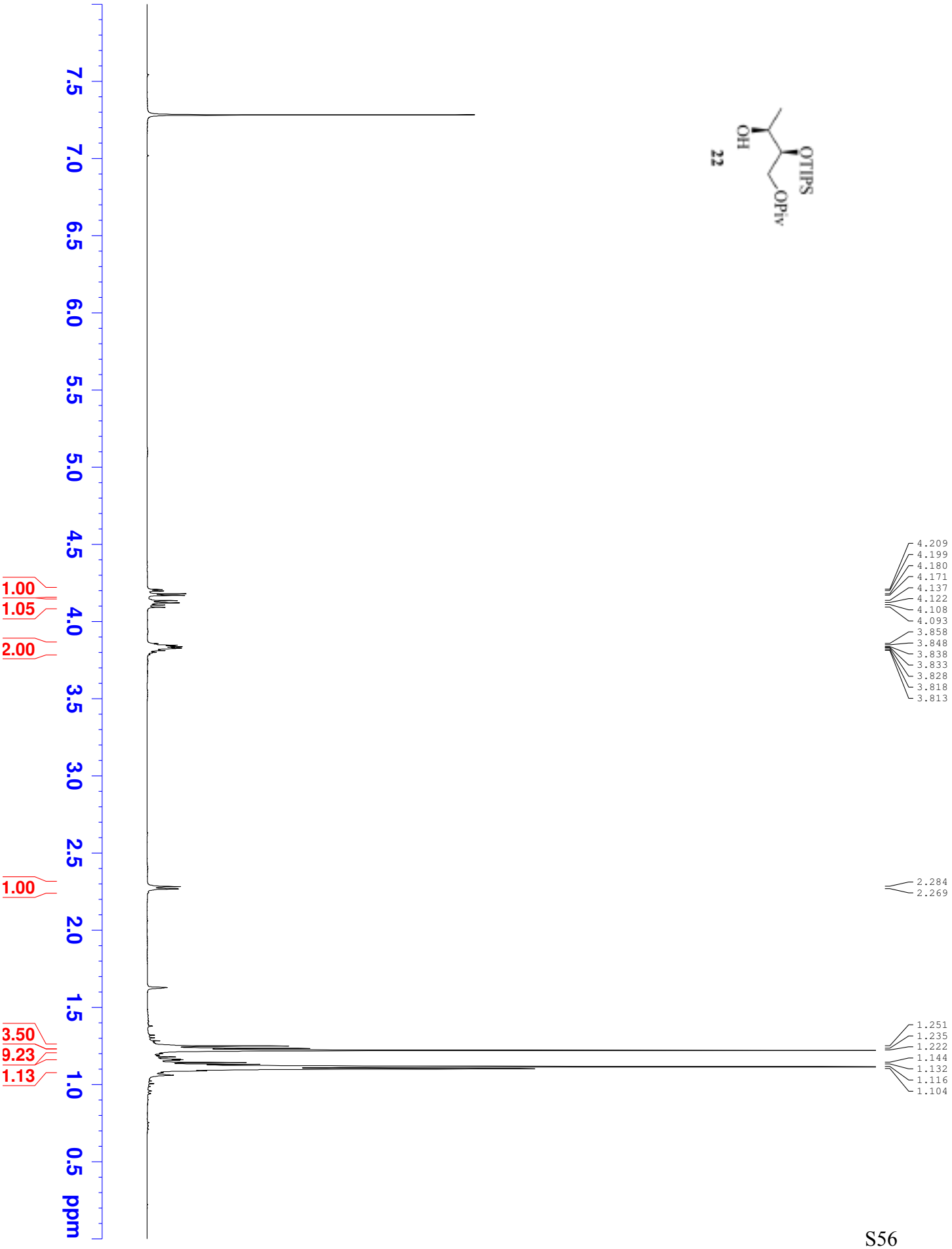

21
OH
OH
O
OEt
173.36
77.34
77.22
77.02
76.70
74.34
68.70
62.10
19.69
14.14
200
180
160
140
120
100
80
60
40
20
0
ppm

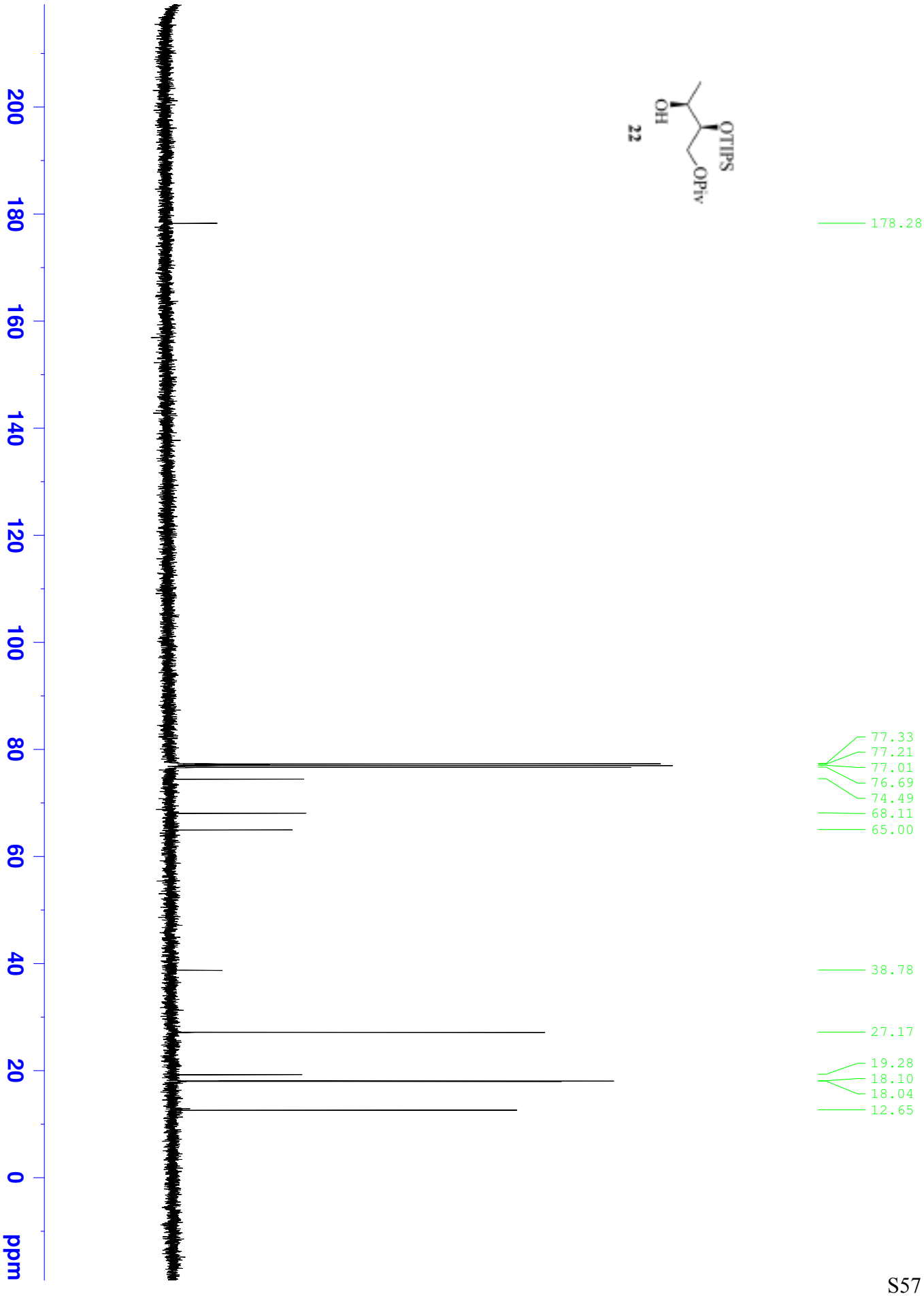

21a
OH
O
OTIPS
OEt
4.266
4.260
4.249
4.242
4.230
4.228
4.224
4.216
4.206
4.004
3.988
3.976
3.971
3.960
3.958
3.954
3.942
3.938
3.926
2.545
2.527
1.333
1.315
1.297
1.257
1.242
1.171
1.165
1.149
1.136
1.125
1.108
1.094
1.084
2.93
1.00
0.93
3.15
3.12
1.51
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

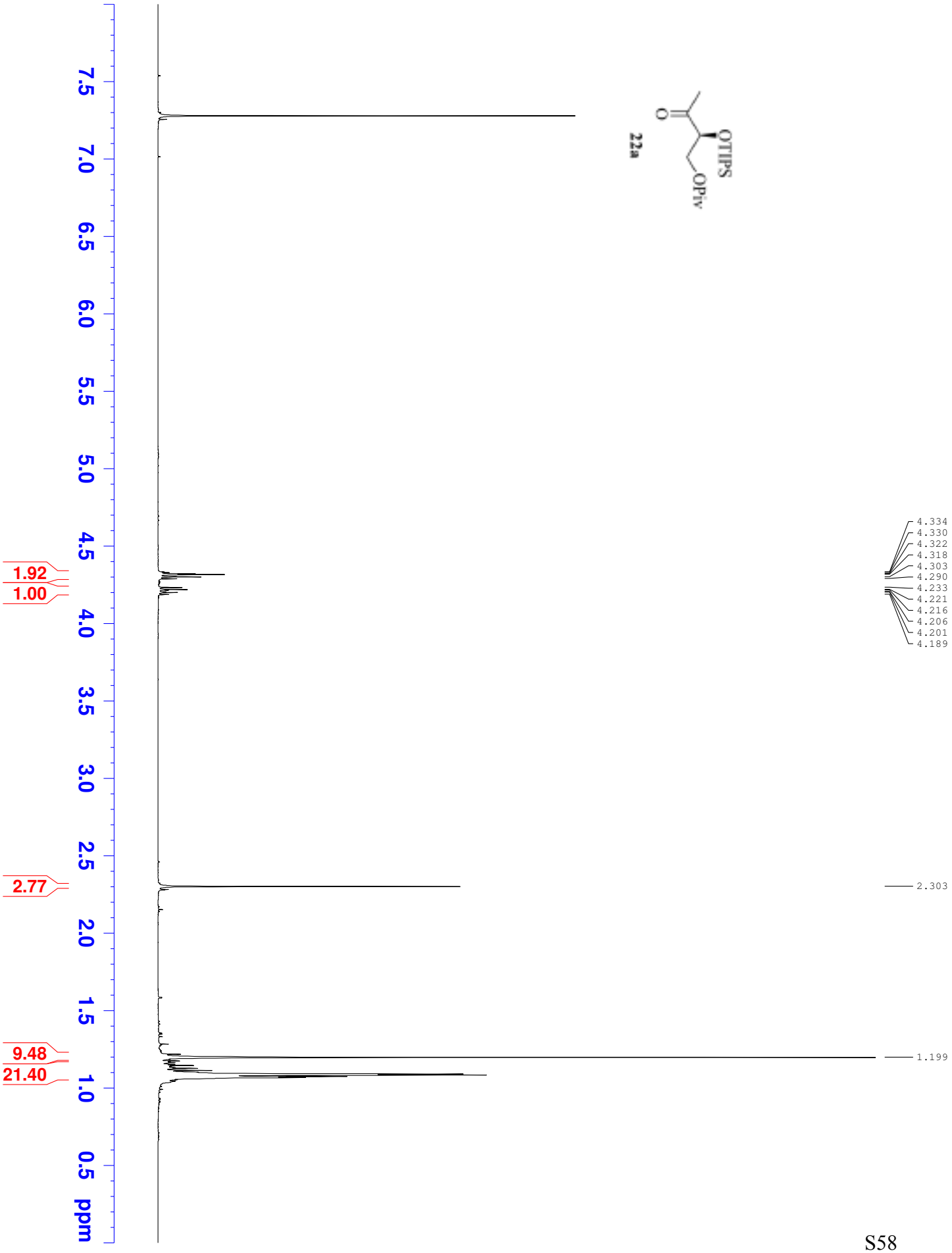

OTIPS
OH
O
OEt
21a
172.19
77.33
77.21
77.01
76.72
76.69
69.87
60.98
18.94
17.91
17.89
14.16
12.35
200
180
160
140
120
100
80
60
40
20
0
ppm

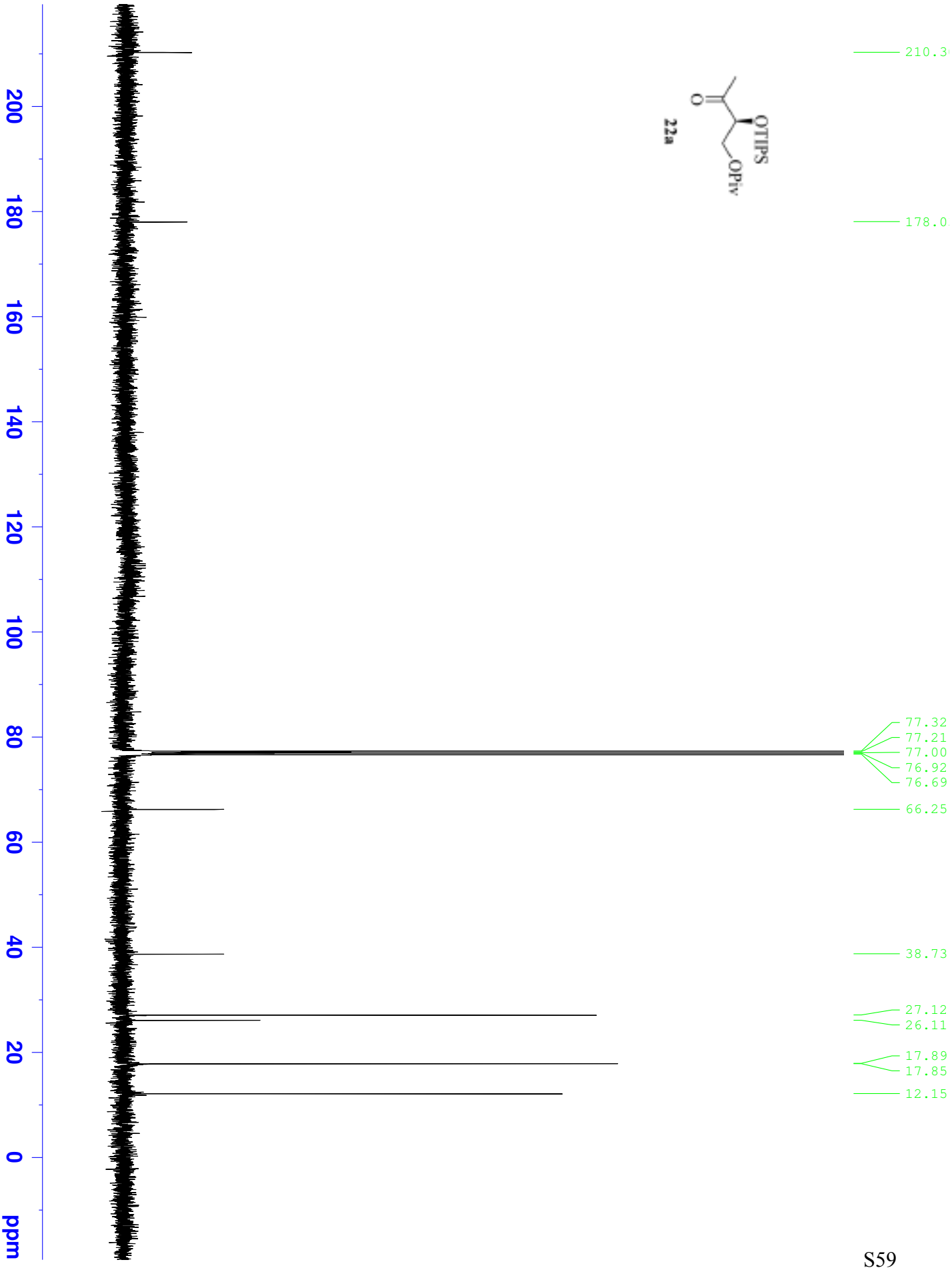

21b
OH
OTIPS
OH
3.990
3.974
3.963
3.959
3.948
3.943
3.932
3.916
3.815
3.803
3.791
3.777
3.771
3.765
3.752
3.734
3.722
3.716
3.699
3.680
3.666
2.324
2.310
2.113
2.111
2.106
2.103
2.096
2.085
1.270
1.254
1.180
1.166
1.158
1.144
1.134
1.123
1.112
1.103
1.094
1.00
2.01
1.09
0.94
0.94
3.30
1.60
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

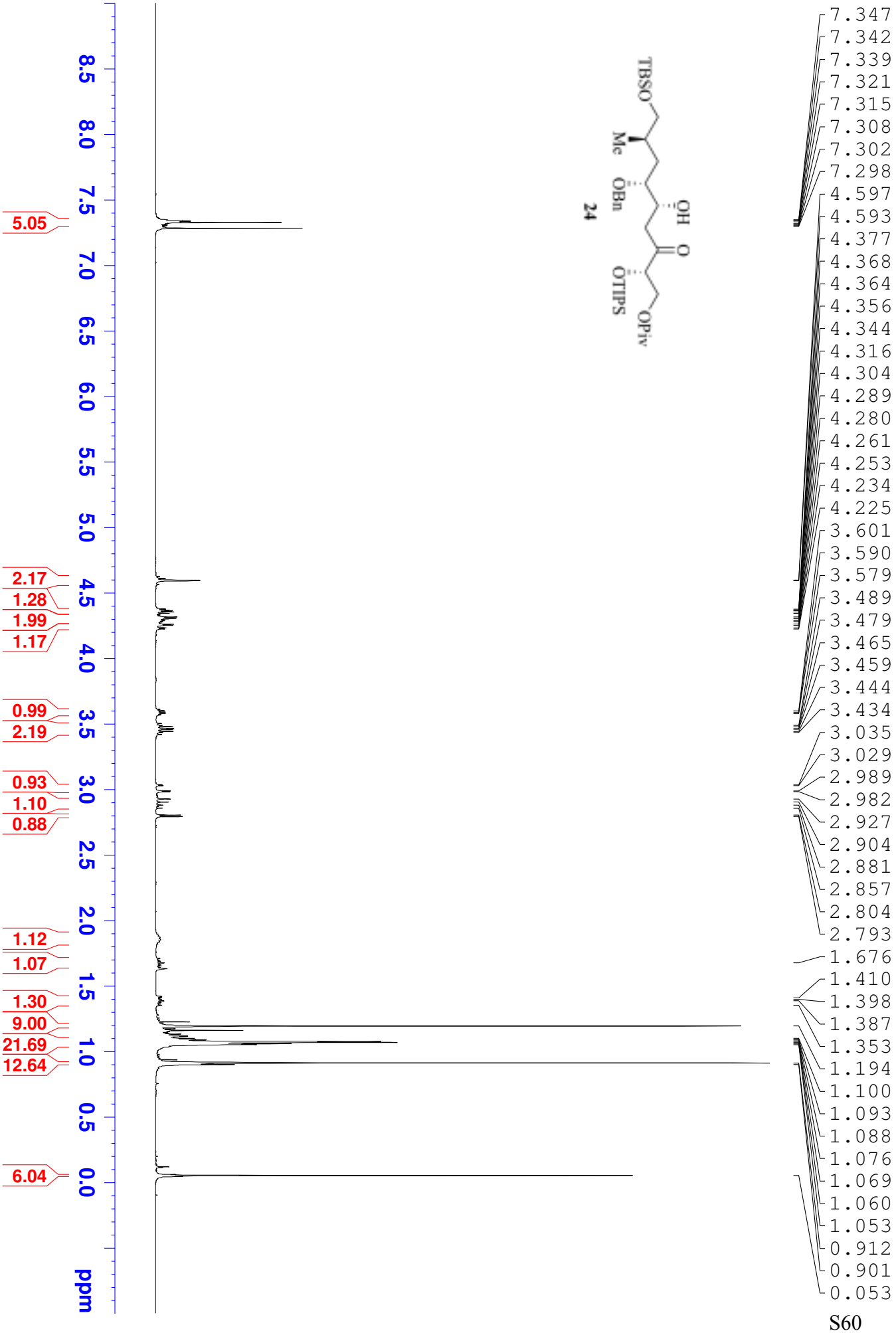
21q
OH
OTIPS
OH
77.33
77.21
77.01
76.69
75.99
68.80
64.13
19.08
18.12
18.08
12.64
200
180
160
140
120
100
80
60
40
20
0
ppm

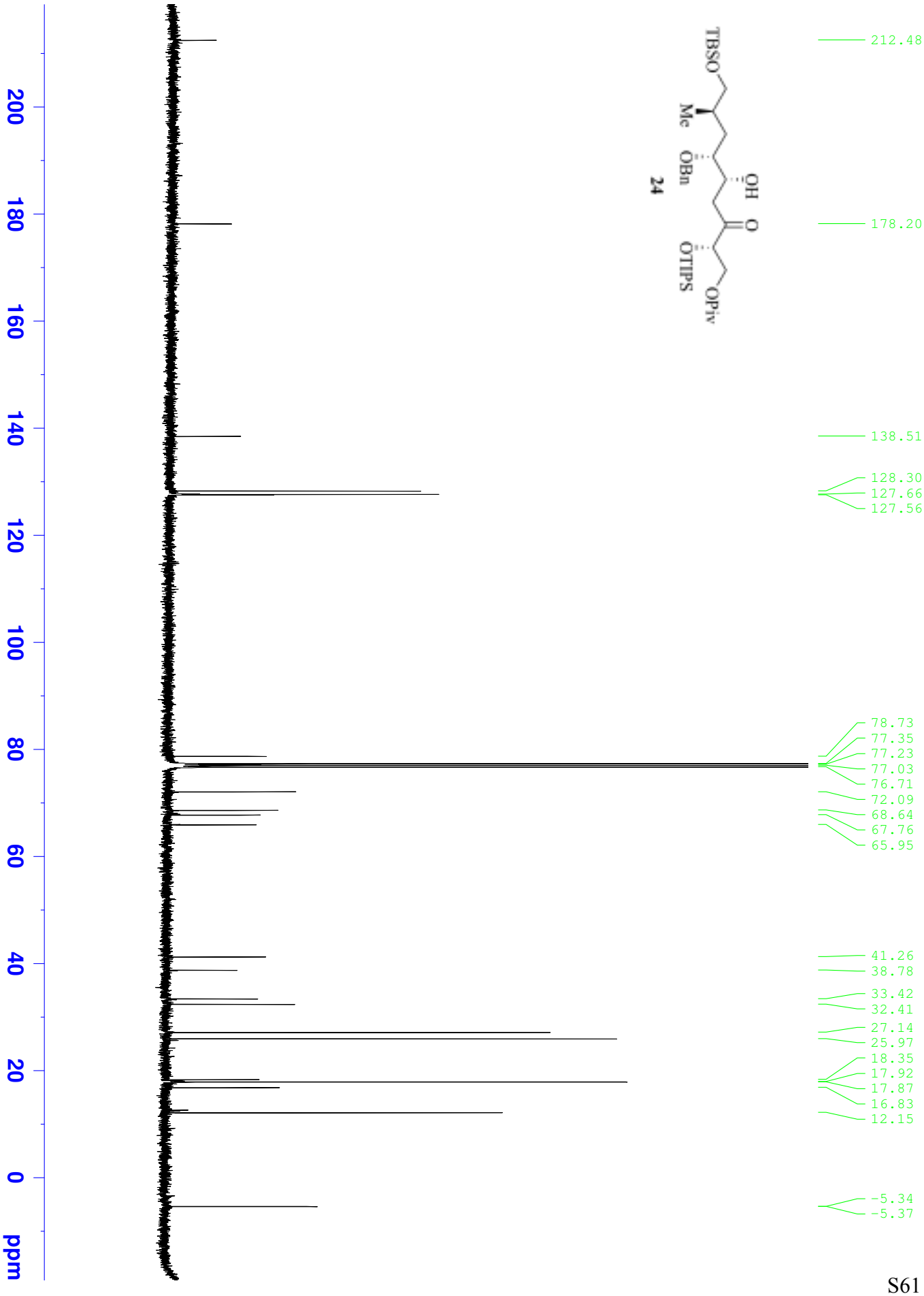

22
OH
OTIPS
OPiv
4.209
4.199
4.180
4.171
4.137
4.122
4.108
4.093
3.858
3.848
3.838
3.833
3.828
3.818
3.813
2.284
2.269
1.251
1.235
1.222
1.144
1.132
1.116
1.104
1.00
1.05
2.00
1.00
3.50
9.23
1.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


22
OH
OTIPS
OPiv
178.28
77.33
77.21
77.01
76.69
74.49
68.11
65.00
38.78
27.17
19.28
18.10
18.04
12.65
200
180
160
140
120
100
80
60
40
20
0
ppm

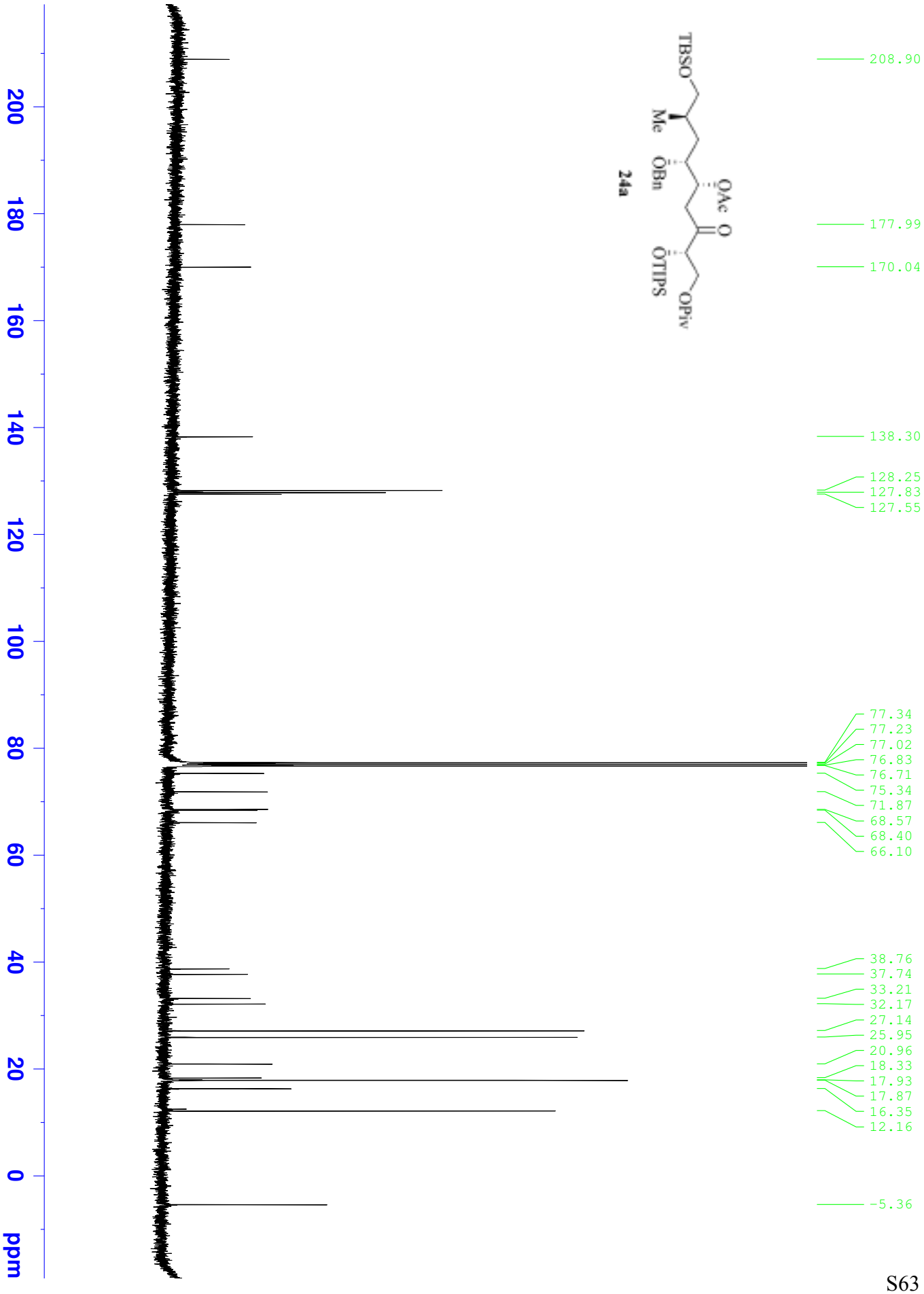

22a
OTIPS
OPiv
4.334
4.330
4.322
4.318
4.303
4.290
4.233
4.221
4.216
4.206
4.201
4.189
2.303
1.199
1.92
1.00
2.77
9.48
21.40
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

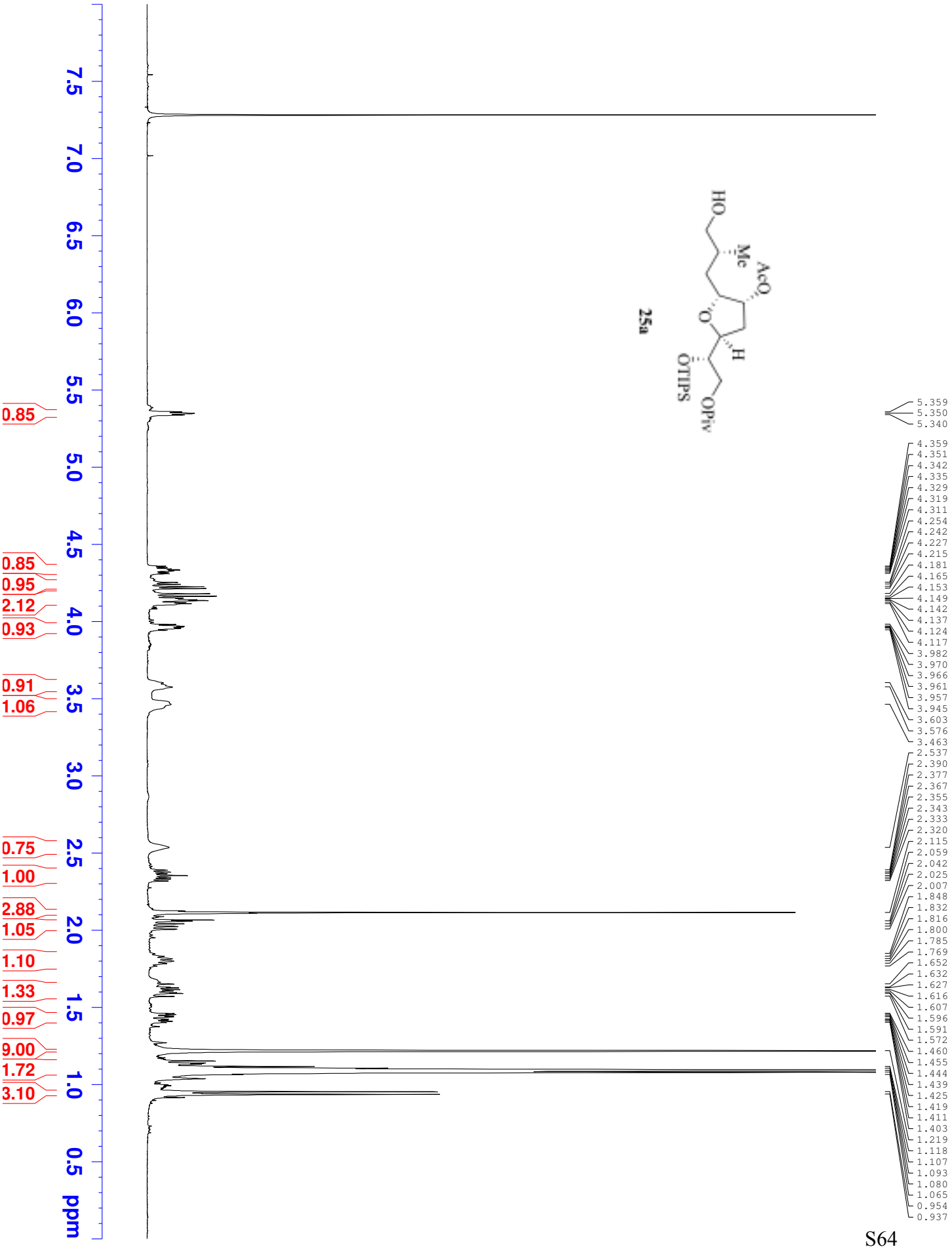

210.3
178.0
77.32
77.21
77.00
76.92
76.69
66.25
38.73
27.12
26.11
17.89
17.85
12.15
OTIPS
OPiv
O
22a
200
180
160
140
120
100
80
60
40
20
0
ppm

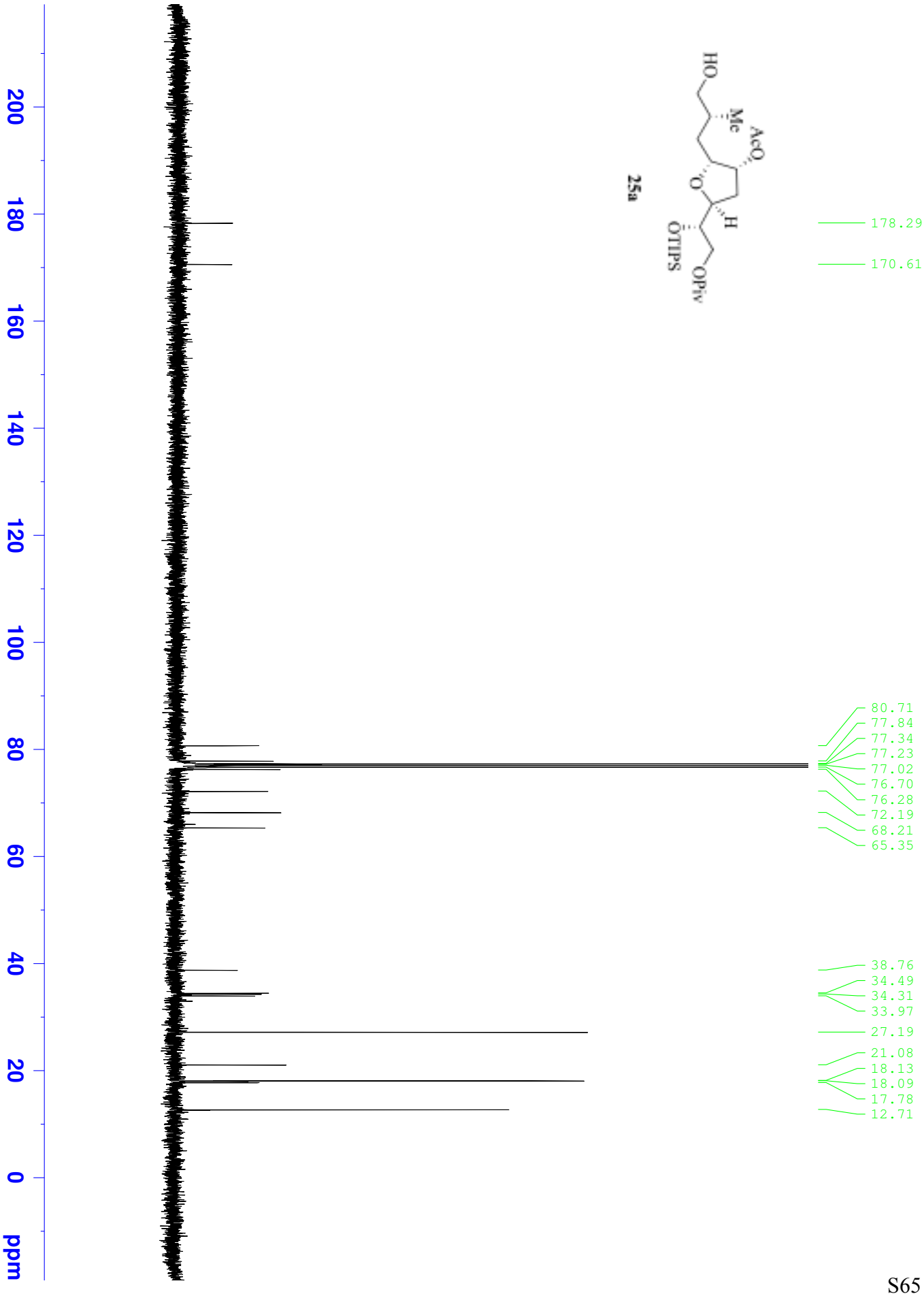

TBSO
Me
OBn
OH
O
OTIPS
OPiv
24
7.347
7.342
7.339
7.321
7.315
7.308
7.302
7.298
4.597
4.593
4.377
4.368
4.364
4.356
4.344
4.316
4.304
4.289
4.280
4.261
4.253
4.234
4.225
3.601
3.590
3.579
3.489
3.479
3.465
3.459
3.444
3.434
3.035
3.029
2.989
2.982
2.927
2.904
2.881
2.857
2.804
2.793
1.676
1.410
1.398
1.387
1.353
1.194
1.100
1.093
1.088
1.076
1.069
1.060
1.053
0.912
0.901
0.053
5.05
2.17
1.28
1.99
1.17
0.99
2.19
0.93
1.10
0.88
1.12
1.07
1.30
9.00
21.69
12.64
6.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


TBSO
Me
OBn
OH
O
OTIPS
OPiv
24
212.48
178.20
138.51
128.30
127.66
127.56
78.73
77.35
77.23
77.03
76.71
72.09
68.64
67.76
65.95
41.26
38.78
33.42
32.41
27.14
25.97
18.35
17.92
17.87
16.83
12.15
-5.34
-5.37
200
180
160
140
120
100
80
60
40
20
0
ppm

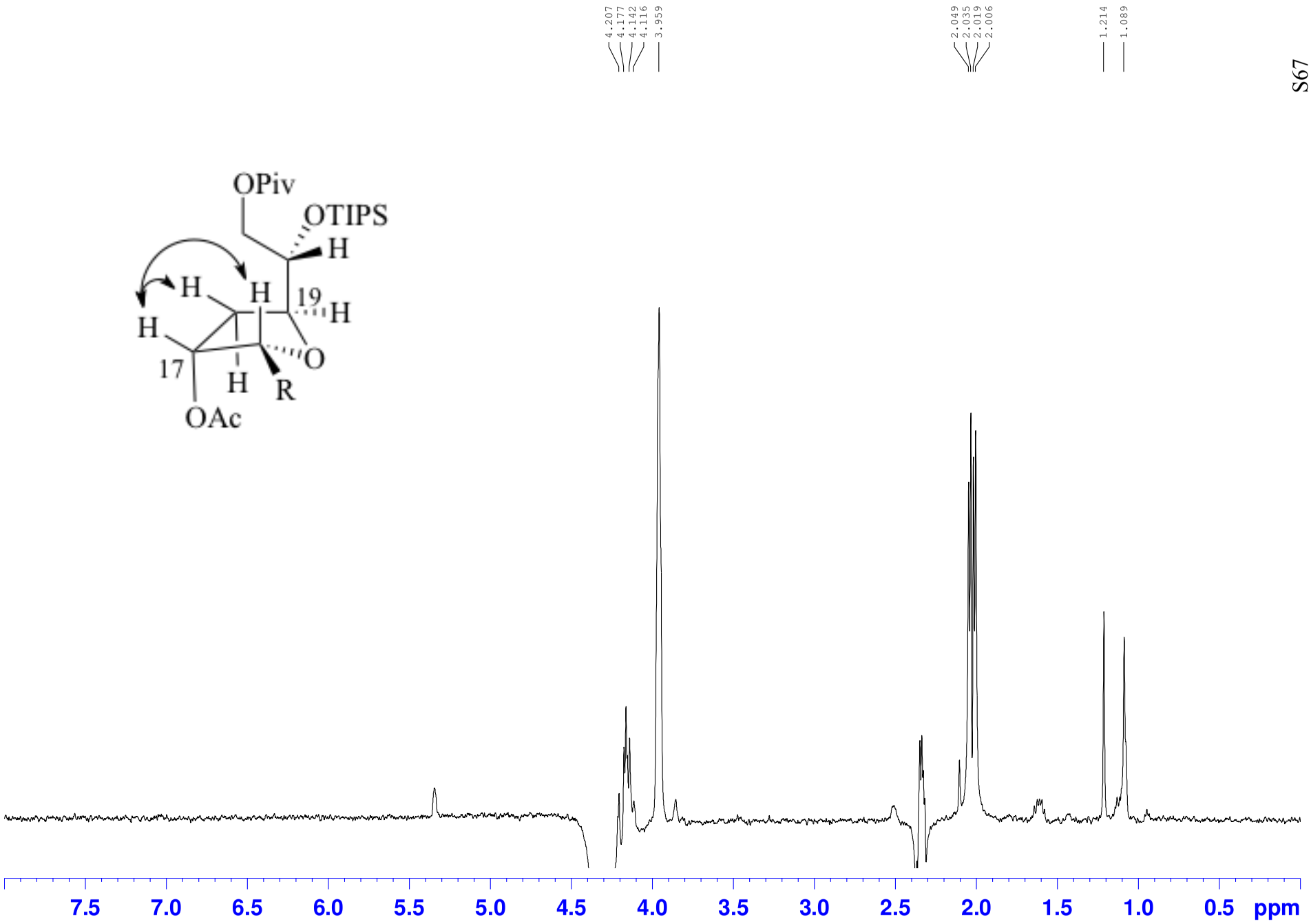
TBSO
Me
OBn
OAc
O
OTIPS
OPiv
24a
7.342
7.334
7.323
7.298
5.652
5.646
5.641
5.636
4.681
4.653
4.585
4.556
4.367
4.358
4.355
4.347
4.322
4.310
4.294
4.289
4.282
4.244
4.235
4.216
4.207
3.760
3.751
3.744
3.735
3.726
3.473
3.459
3.449
3.434
3.427
3.412
3.402
3.387
3.090
3.077
3.072
2.014
1.629
1.614
1.594
1.204
1.111
1.097
1.089
1.080
1.071
1.065
1.055
1.048
0.910
0.785
0.769
0.048
7.04
1.00
0.98
1.02
1.04
1.03
1.03
1.00
1.99
1.78
3.09
1.13
1.43
8.90
22.50
9.04
2.90
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

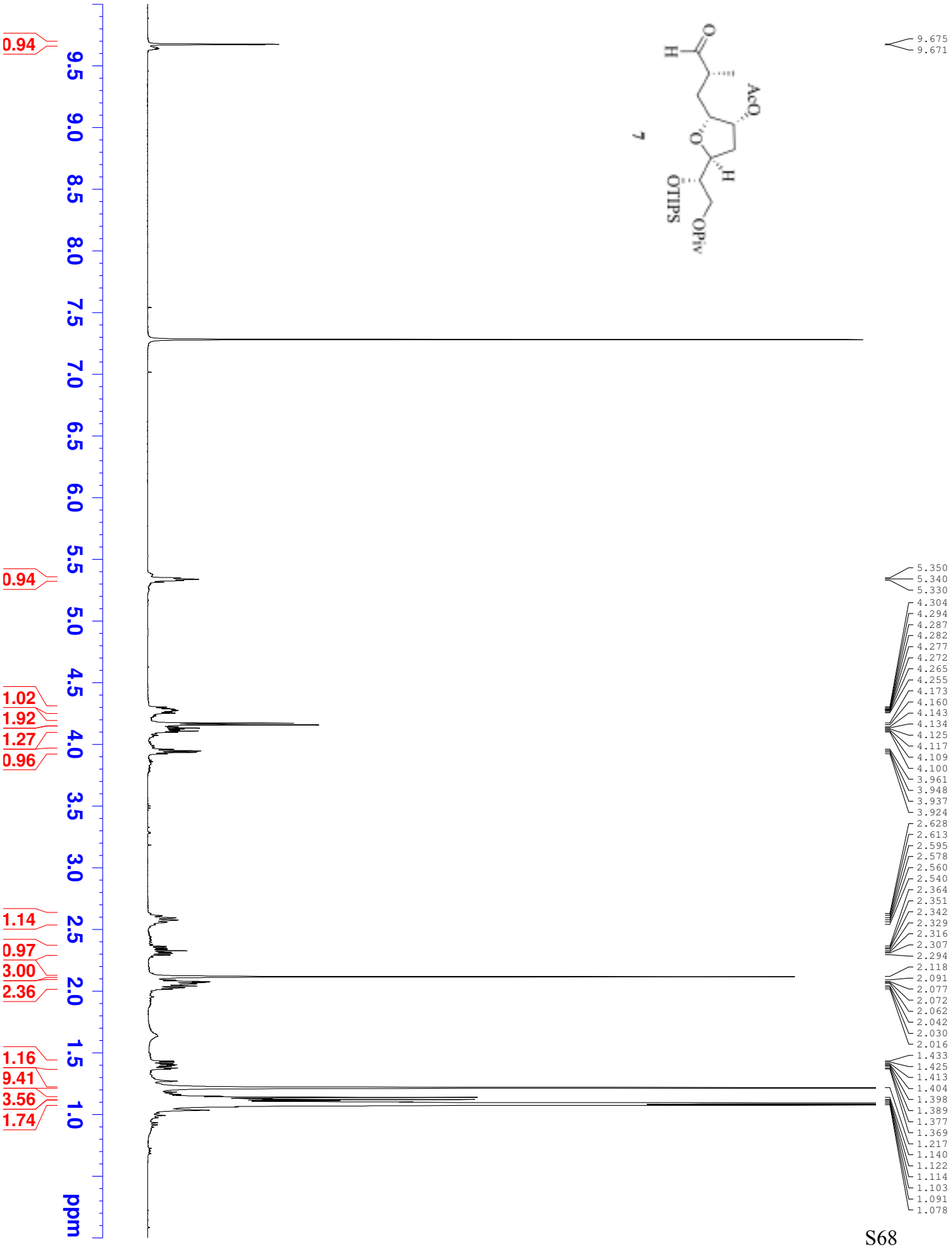

TBSO
Me
OBn
OAc
O
OTIPS
OPiv
24a
208.90
177.99
170.04
138.30
128.25
127.83
127.55
77.34
77.23
77.02
76.83
76.71
75.34
71.87
68.57
68.40
66.10
38.76
37.74
33.21
32.17
27.14
25.95
20.96
18.33
17.93
17.87
16.35
12.16
-5.36
200
180
160
140
120
100
80
60
40
20
0
ppm

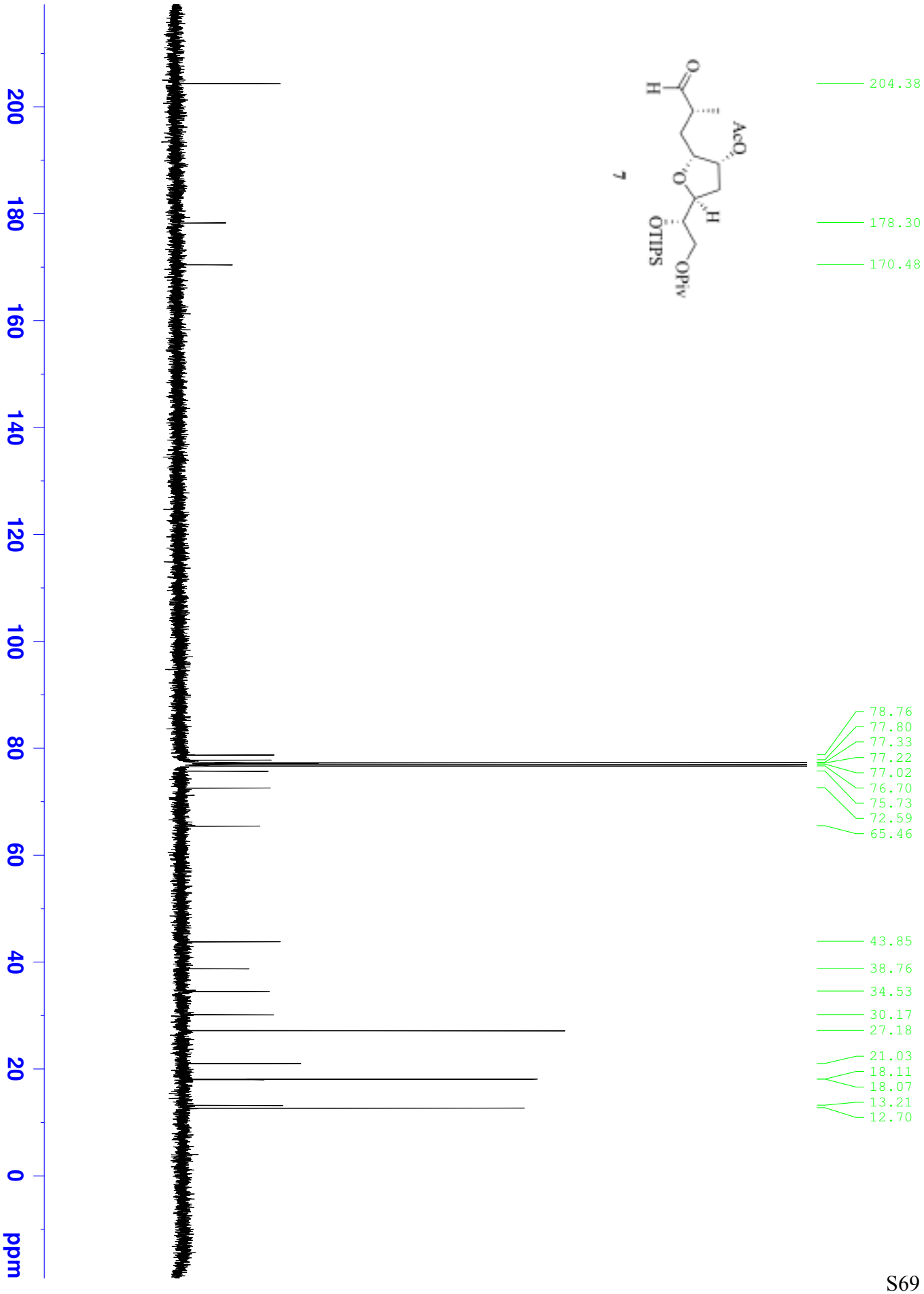

HO
Me
AcO
O
H
OTIPS
OPiv
25a
0.85
0.85
0.95
2.12
0.93
0.91
1.06
0.75
1.00
2.88
1.05
1.10
1.33
0.97
9.00
1.72
3.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.359
5.350
5.340
4.359
4.351
4.342
4.335
4.329
4.319
4.311
4.254
4.242
4.227
4.215
4.181
4.165
4.153
4.149
4.142
4.137
4.124
4.117
3.982
3.970
3.966
3.961
3.957
3.945
3.603
3.576
3.463
2.537
2.390
2.377
2.367
2.355
2.343
2.333
2.320
2.115
2.059
2.042
2.025
2.007
1.848
1.832
1.816
1.800
1.785
1.769
1.652
1.632
1.627
1.616
1.607
1.596
1.591
1.572
1.460
1.455
1.444
1.439
1.425
1.419
1.411
1.403
1.219
1.118
1.107
1.093
1.080
1.065
0.954
0.937

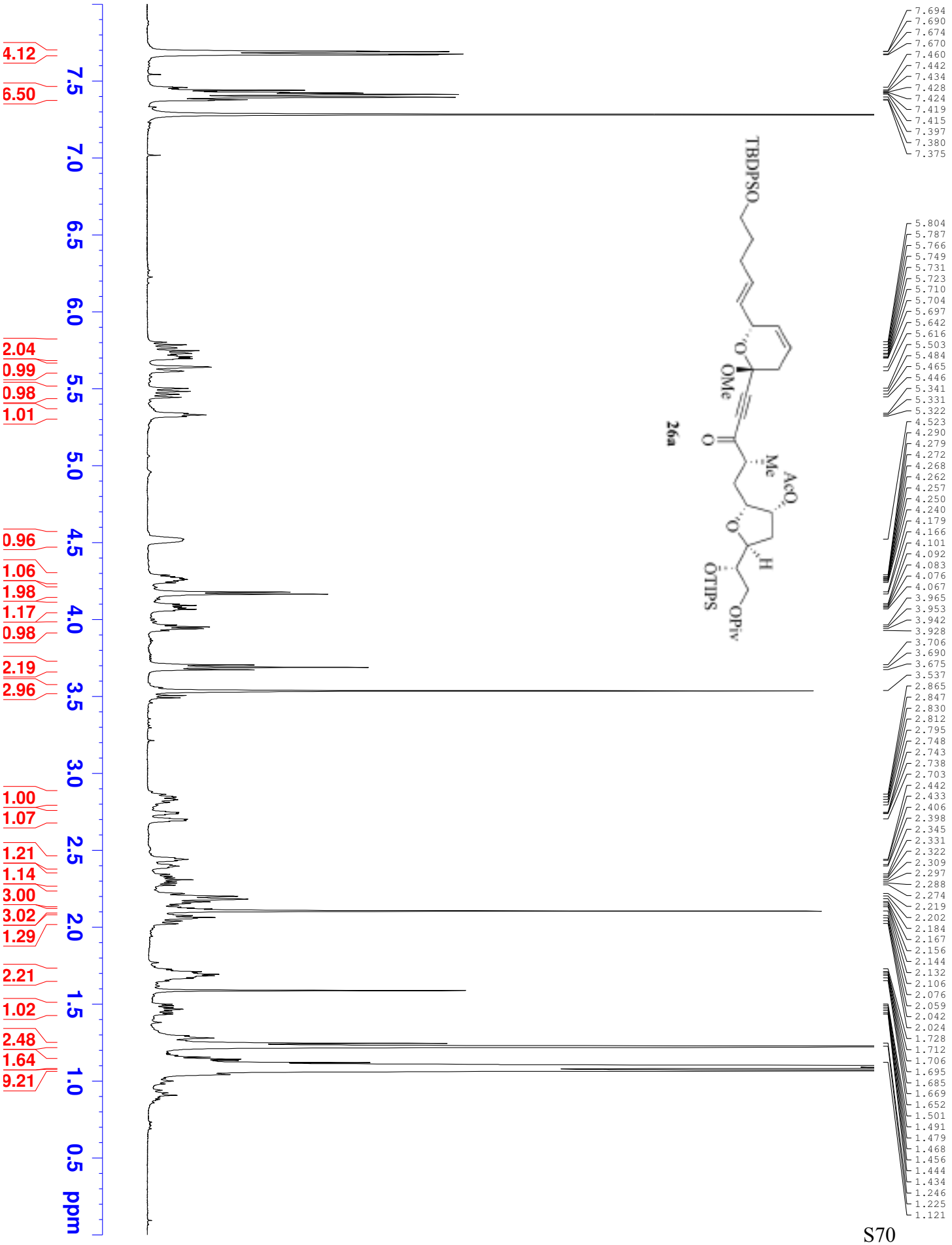

25a
HO
Me
AcO
O
H
OTIPS
OPiv
178.29
170.61
80.71
77.84
77.34
77.23
77.02
76.70
76.28
72.19
68.21
65.35
38.76
34.49
34.31
33.97
27.19
21.08
18.13
18.09
17.78
12.71
200
180
160
140
120
100
80
60
40
20
0
ppm

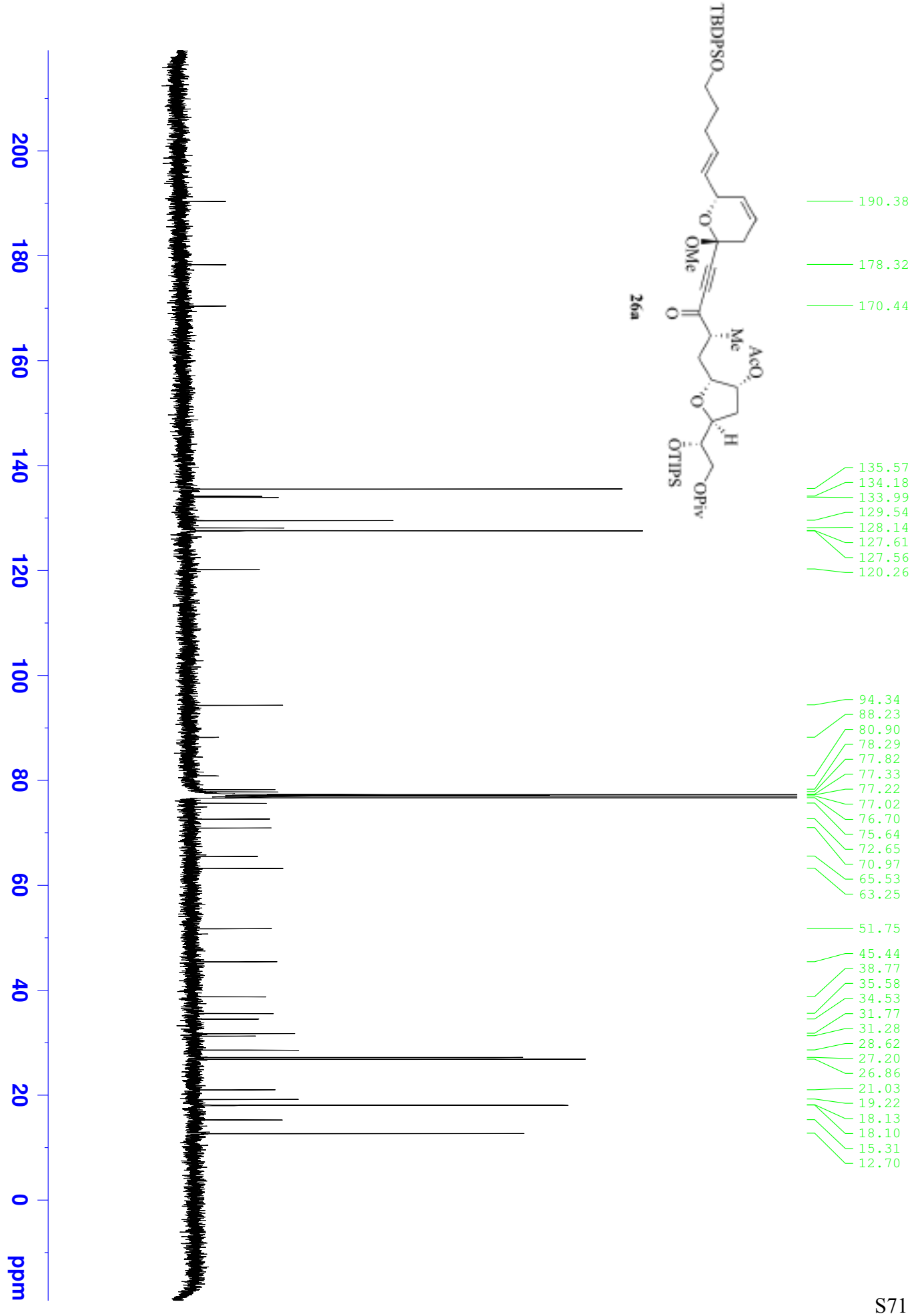
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.343
4.228
1.437
1.428
1.409
1.213
1.088
1.078
0.947
0.934
OAc
H
17
H
H
H
R
O
19
H
H
OTIPS
OPiv

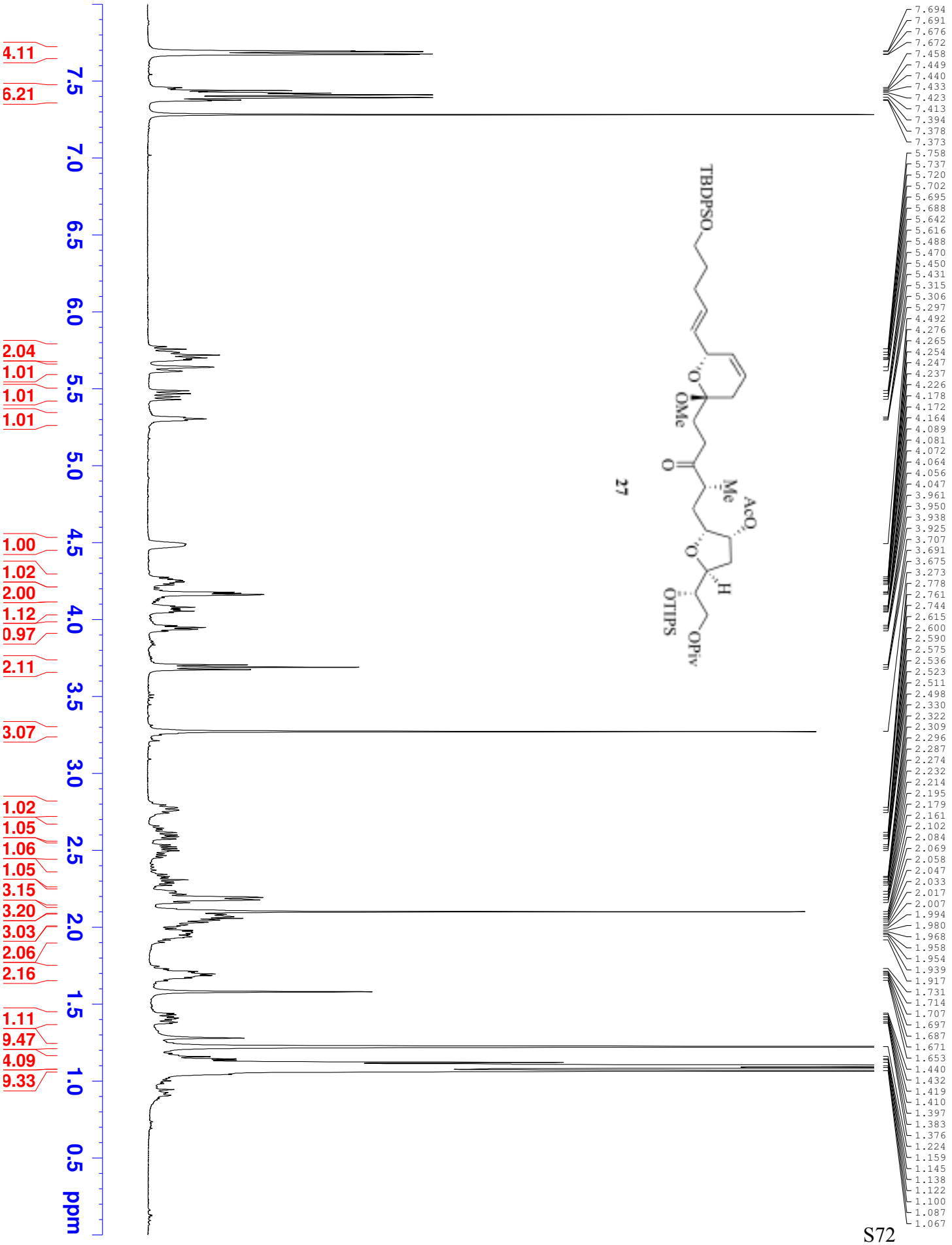

4.207
4.177
4.142
4.116
3.959
2.049
2.035
2.019
2.006
1.214
1.089
OPiv
OTIPS
H
H
H
19
H
H
17
H
O
R
OAc
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

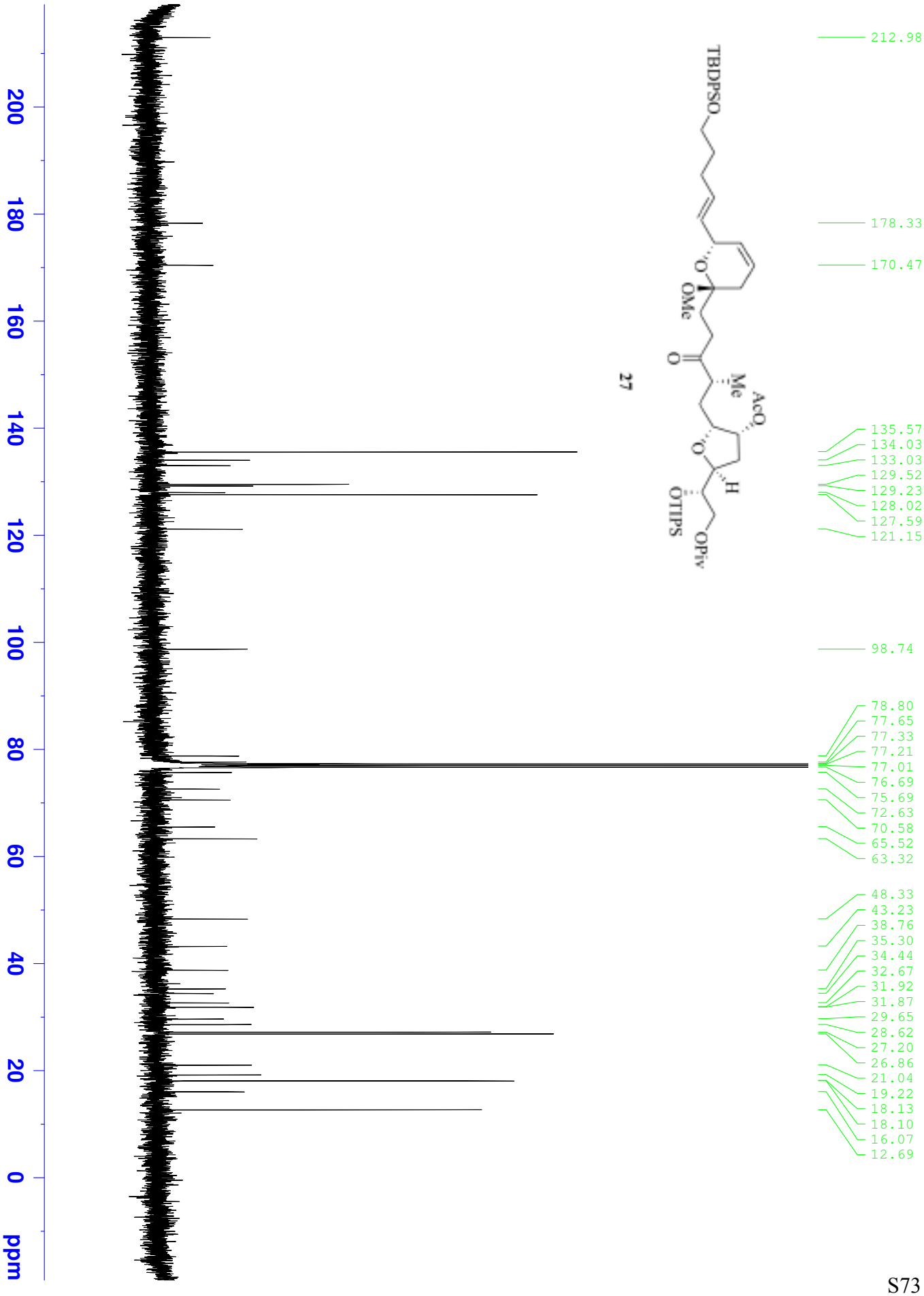

0.94
0.94
1.02
1.92
1.27
0.96
1.14
0.97
3.00
2.36
1.16
9.41
3.56
1.74
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
AcO
OTIPS
OPiv
7
9.675
9.671
5.350
5.340
5.330
4.304
4.294
4.287
4.282
4.277
4.272
4.265
4.255
4.173
4.160
4.143
4.134
4.125
4.117
4.109
4.100
3.961
3.948
3.937
3.924
2.628
2.613
2.595
2.578
2.560
2.540
2.364
2.351
2.342
2.329
2.316
2.307
2.294
2.118
2.091
2.077
2.072
2.062
2.042
2.030
2.016
1.433
1.425
1.413
1.404
1.398
1.389
1.377
1.369
1.217
1.140
1.122
1.114
1.103
1.091
1.078

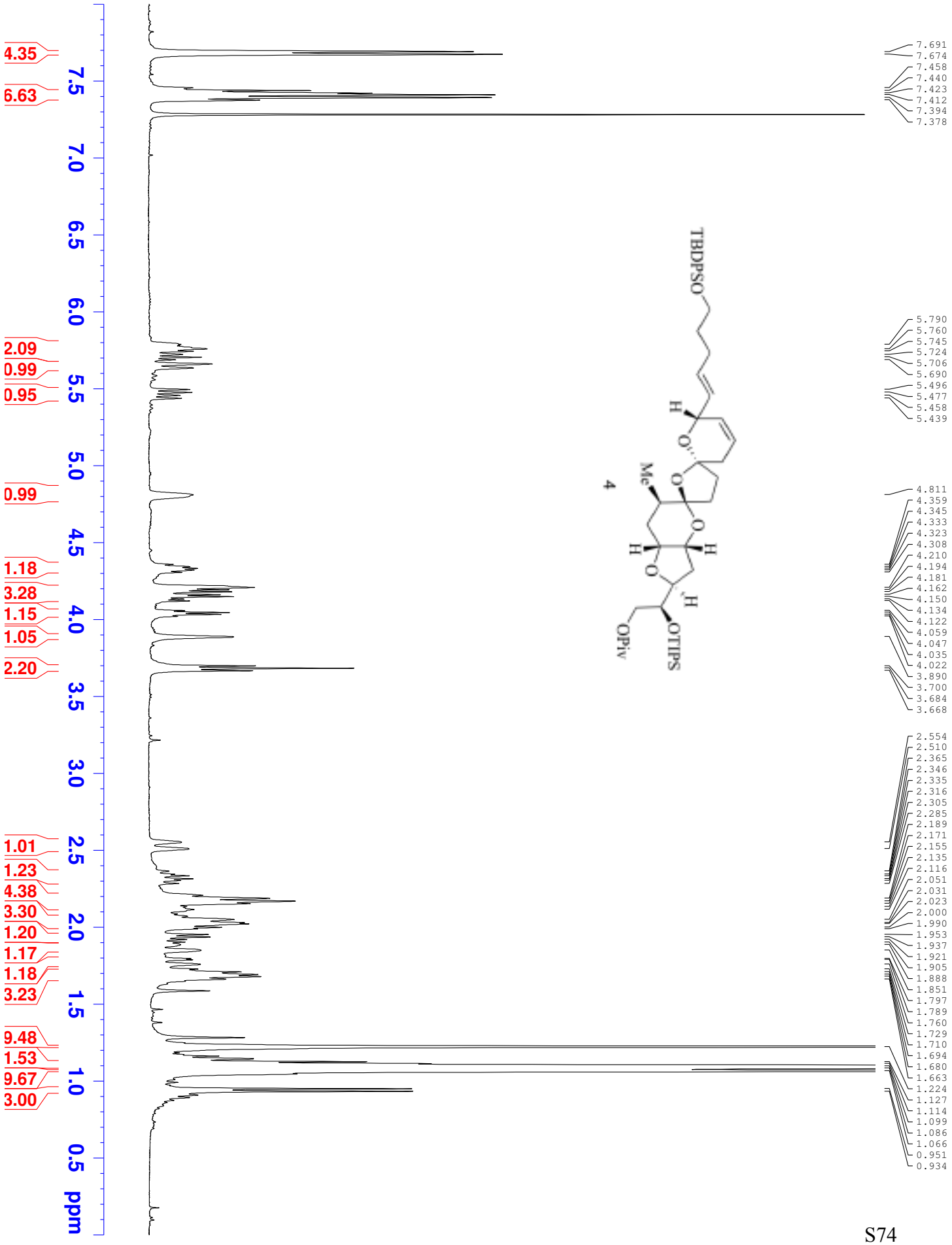

204.38
178.30
170.48
78.76
77.80
77.33
77.22
77.02
76.70
75.73
72.59
65.46
43.85
38.76
34.53
30.17
27.18
21.03
18.11
18.07
13.21
12.70
200
180
160
140
120
100
80
60
40
20
0
ppm

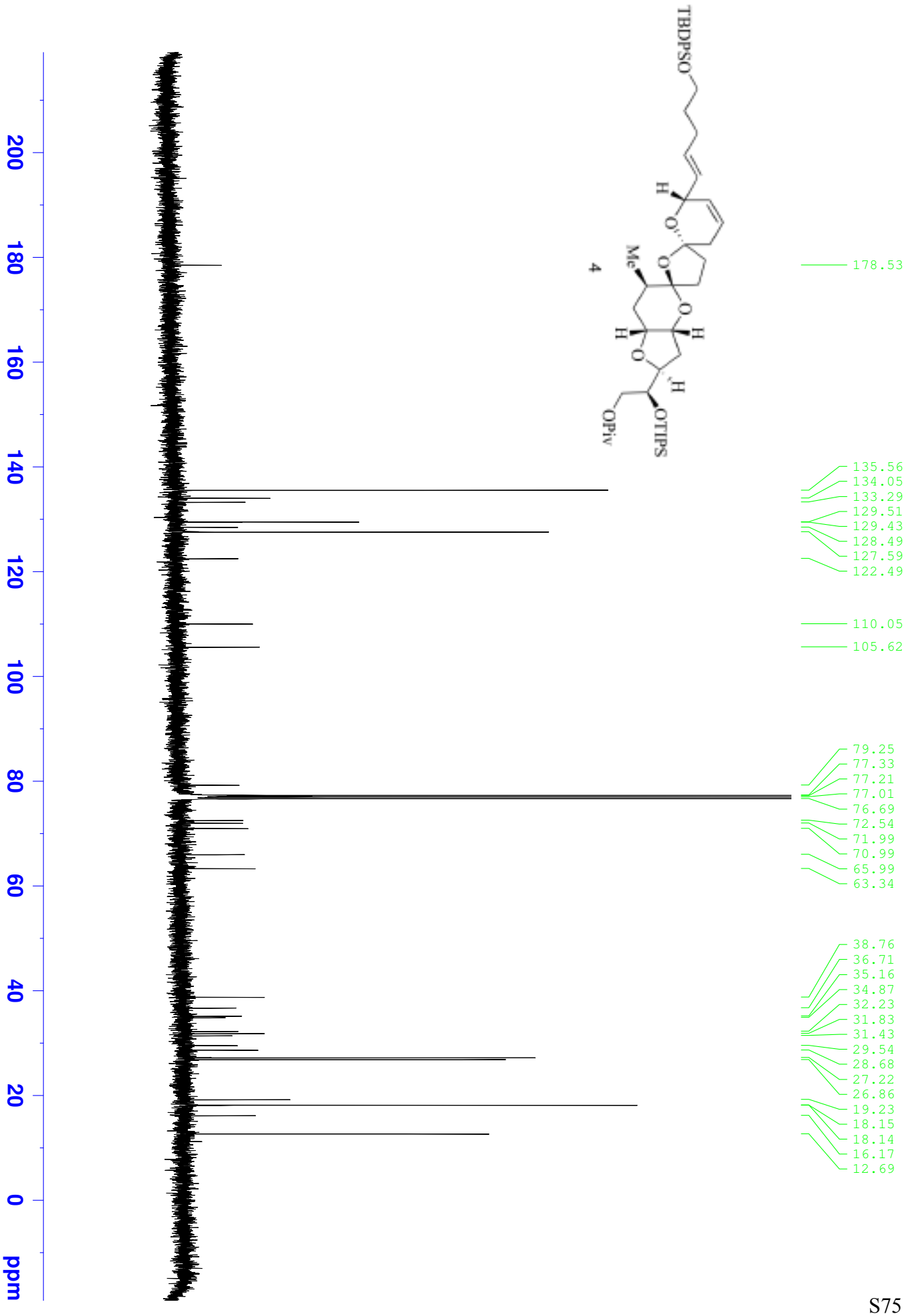

4.12
6.50
2.04
0.99
0.98
1.01
0.96
1.06
1.98
1.17
0.98
2.19
2.96
1.00
1.07
1.21
1.14
3.00
3.02
1.29
2.21
1.02
2.48
1.64
9.21
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
TBDPSO
OMe
O
AcO
Me
H
OTIPS
OPiv
26a
7.694
7.690
7.674
7.670
7.460
7.442
7.434
7.428
7.424
7.419
7.415
7.397
7.380
7.375
5.804
5.787
5.766
5.749
5.731
5.723
5.710
5.704
5.697
5.642
5.616
5.503
5.484
5.465
5.446
5.341
5.331
5.322
4.523
4.290
4.279
4.272
4.268
4.262
4.257
4.250
4.240
4.179
4.166
4.101
4.092
4.083
4.076
4.067
3.965
3.953
3.942
3.928
3.706
3.690
3.675
3.537
2.865
2.847
2.830
2.812
2.795
2.748
2.743
2.738
2.703
2.442
2.433
2.406
2.398
2.345
2.331
2.322
2.309
2.297
2.288
2.274
2.219
2.202
2.184
2.167
2.156
2.144
2.132
2.106
2.076
2.059
2.042
2.024
1.728
1.712
1.706
1.695
1.685
1.669
1.652
1.501
1.491
1.479
1.468
1.456
1.444
1.434
1.246
1.225
1.121


TBDPSO
OMe
O
O
26a
Me
AcO
O
H
OTIPS
OPiv
190.38
178.32
170.44
135.57
134.18
133.99
129.54
128.14
127.61
127.56
120.26
94.34
88.23
80.90
78.29
77.82
77.33
77.22
77.02
76.70
75.64
72.65
70.97
65.53
63.25
51.75
45.44
38.77
35.58
34.53
31.77
31.28
28.62
27.20
26.86
21.03
19.22
18.13
18.10
15.31
12.70
200
180
160
140
120
100
80
60
40
20
0
ppm


4.11
6.21
2.04
1.01
1.01
1.01
1.00
1.02
2.00
1.12
0.97
2.11
3.07
1.02
1.05
1.06
1.05
3.15
3.20
3.03
2.06
2.16
1.11
9.47
4.09
9.33
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
TBDPSO
OMe
O
Me
AcO
O
H
OTIPS
OPiv
27
7.694
7.691
7.676
7.672
7.458
7.449
7.440
7.433
7.423
7.413
7.394
7.378
7.373
5.758
5.737
5.720
5.702
5.695
5.688
5.642
5.616
5.488
5.470
5.450
5.431
5.315
5.306
5.297
4.492
4.276
4.265
4.254
4.247
4.237
4.226
4.178
4.172
4.164
4.089
4.081
4.072
4.064
4.056
4.047
3.961
3.950
3.938
3.925
3.707
3.691
3.675
3.273
2.778
2.761
2.744
2.615
2.600
2.590
2.575
2.536
2.523
2.511
2.498
2.330
2.322
2.309
2.296
2.287
2.274
2.232
2.214
2.195
2.179
2.161
2.102
2.084
2.069
2.058
2.047
2.033
2.017
2.007
1.994
1.980
1.968
1.958
1.954
1.939
1.917
1.731
1.714
1.707
1.697
1.687
1.671
1.653
1.440
1.432
1.419
1.410
1.397
1.383
1.376
1.224
1.159
1.145
1.138
1.122
1.100
1.087
1.067


212.98
178.33
170.47
135.57
134.03
133.03
129.52
129.23
128.02
127.59
121.15
98.74
78.80
77.65
77.33
77.21
77.01
76.69
75.69
72.63
70.58
65.52
63.32
48.33
43.23
38.76
35.30
34.44
32.67
31.92
31.87
29.65
28.62
27.20
26.86
21.04
19.22
18.13
18.10
16.07
12.69
200
180
160
140
120
100
80
60
40
20
0
ppm
TBDPSO
OMe
O
Me
AcO
O
H
OTIPS
OPiv
27


4.35
6.63
2.09
0.99
0.95
0.99
1.18
3.28
1.15
1.05
2.20
1.01
1.23
4.38
3.30
1.20
1.17
1.18
3.23
9.48
1.53
9.67
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
7.691
7.674
7.458
7.440
7.423
7.412
7.394
7.378
5.790
5.760
5.745
5.724
5.706
5.690
5.496
5.477
5.458
5.439
4.811
4.359
4.345
4.333
4.323
4.308
4.210
4.194
4.181
4.162
4.150
4.134
4.122
4.059
4.047
4.035
4.022
3.890
3.700
3.684
3.668
2.554
2.510
2.365
2.346
2.335
2.316
2.305
2.285
2.189
2.171
2.155
2.135
2.116
2.051
2.031
2.023
2.000
1.990
1.953
1.937
1.921
1.905
1.888
1.851
1.797
1.789
1.760
1.729
1.710
1.694
1.680
1.663
1.224
1.127
1.114
1.099
1.086
1.066
0.951
0.934
TBDPSO
Me
OTIPS
OPiv
4


TBDPSO
Me
OPiv
OTIPS
4
178.53
135.56
134.05
133.29
129.51
129.43
128.49
127.59
122.49
110.05
105.62
79.25
77.33
77.21
77.01
76.69
72.54
71.99
70.99
65.99
63.34
38.76
36.71
35.16
34.87
32.23
31.83
31.43
29.54
28.68
27.22
26.86
19.23
18.15
18.14
16.17
12.69
200
180
160
140
120
100
80
60
40
20
0
ppm