Supporting Information

Diastereo- and Enantioselective Synthesis of 1,3,5,7-Tetraol Structural Units Using a Prins Cyclisation/Reductive Cleavage Sequence

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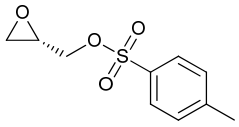
General Experimental Methods

All reactions were carried out under anhydrous conditions, using flame-dried glassware and under argon atmosphere. CH_2Cl_2, Et_3N and iPr_2NEt were distilled from CaH_2, Et_2O and THF were distilled from Na/benzophenone. Other reagents were obtained from commercial suppliers and used as received. TLC was performed on Merck 60F254 silica gel plates with UV and *p*-anisaldehyde stain visualization. Flash chromatography was performed on silica gel (230-400 mesh). Optical rotations were measured with a Perkin Elmer model 343 polarimeter with a 1 dm path length. Infrared (IR) spectra were recorded on a Bruker TENSORTM 27 (IRFT) on an ATR plate, wave numbers are indicated in cm-1. NMR was performed on a Bruker Avance-1 400 instrument. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ and data are reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, m = multiplet or overlap of non-equivalent resonances, br = broad), integration. ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ($CDCl_3$, 77.16 ppm), multiplicity, with respect to proton (deduced from DEPT experiment, s = quaternary, d = CH, t = CH_2, q = CH_3). Mass spectra were obtained with a Shimadzu GCMS-QP2010S gas chromatograph–mass spectrometer. High resolution mass spectra (HRMS) were performed by the Groupe de Spectrométrie de Masse de l'Université Pierre et Marie Curie (Paris-France).

Experimental and Spectral Data

Synthesis of homoallylic alcohols 2

(*S*)-Oxiran-2-ylmethyl 4-methylbenzenesulfonate

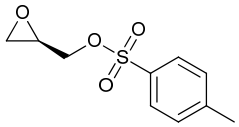


$C_{10}H_{12}O_4S$
M = 228.05 g/mol

To a solution of (*R*)-glycidol (2 mL, 30.1 mmol, 1 equiv) in dry CH_2Cl_2 (30 mL) were added Et_3N (8.4 mL, 60.4 mmol, 2 equiv) and DMAP (184 mg, 1.5 mmol, 0.05 equiv). The solution was cooled to 0 °C, and a solution of tosyl chloride (5.75 g, 30.1 mmol, 1 equiv) in CH_2Cl_2 (30 mL) was canulated. The mixture was progressively allowed to reach rt and stirred for 3 h. The reaction was then quenched by addition of an aqueous solution of HCl (10% in weight, 40 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/3) to afford the tosylated glycidol (6.75 g, 29.6 mmol, 98%) as a colorless oil. Spectral data match those reported in the literature.[1]

$[\alpha]_D^{20}$ = + 17.9 (*c* 1.02, $CHCl_3$).
IR: *ν* 2929, 1597, 1450, 1359, 1293, 1256, 1189, 1174, 1096, 1019, 960, 913, 812, 773, 664 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.78 (d, 2H, *J* = 8.3 Hz), 7.34 (d, 2H, *J* = 8.3 Hz), 4.25 (dd, 1H, *J* = 11.4 Hz, *J* = 3.4 Hz), 3.92 (dd, 1H, *J* = 11.4 Hz, *J* = 6.1 Hz), 3.17 (m, 1H), 2.79 (t_{app}, 1H, *J* = 4.4 Hz), 2.57 (dd, 1H, *J* = 4.8 Hz, J = 2.5 Hz), 2.44 (s, 3H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 145.2 (s), 132.7 (s), 130.0 (2d), 128.0 (2d), 70.5 (t), 48.9 (d), 44.6 (t), 21.7 (q).
MS (EI) *m/z*: 228 ($M^{+\cdot}$, 6), 212 (1), 197 (1), 185 (1), 172 (7), 155 (Ts^+, 39), 91 (100), 65 (24).

(*R*)-Oxiran-2-ylmethyl 4-methylbenzenesulfonate



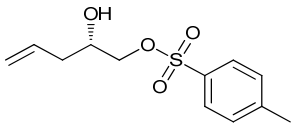
$C_{10}H_{12}O_4S$
M = 228.05 g/mol

To a solution of (*S*)-glycidol (2 mL, 30.1 mmol, 1 equiv) in dry CH_2Cl_2 (30 mL) were added Et_3N (8.4 mL, 60.4 mmol, 2 equiv) and DMAP (184 mg, 1.5 mmol, 0.05 equiv). The solution was cooled to 0 °C, and a solution of tosyl chloride (5.75 g, 30.1 mmol, 1 equiv) in CH_2Cl_2 (30 mL) was canulated. The mixture was progressively allowed to reach rt and stirred for 3 h. The reaction was then quenched by addition of an aqueous solution of HCl (10% in weight, 40 mL) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layers were dried over

$MgSO_4$, filtered and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 7/3) to afford the tosylated glycidol (6.53 g, 28.6 mmol, 95%) as a colorless oil. Spectral data match those reported in the literature.[1]

$[\alpha]_D^{20}$ = − 18.1 (*c* 1.2, $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, 2H, *J* = 8.3 Hz), 7.34 (d, 2H, *J* = 8.3 Hz), 4.25 (dd, 1H, *J* = 11.4 Hz, *J* = 3.4 Hz), 3.94 (dd, 1H, *J* = 11.4 Hz, *J* = 6.1 Hz), 3.17 (m, 1H), 2.79 (t_{app}, 1H, *J* = 4.4 Hz), 2.57 (dd, 1H, *J* = 4.8 Hz, *J* = 2.5 Hz), 2.44 (s, 3H).

(*S*)-2-Hydroxypent-4-en-1-yl 4-methylbenzenesulfonate (+)-2

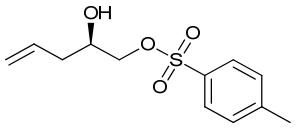


$C_{12}H_{16}O_4S$
M = 256.08 g/mol

To a solution of Li_2CuCl_4 (9.2 mL, 0.1 M in THF, 0.92 mmol, 0.06 equiv) cooled to −40 °C was added vinylmagnesium bromide (24.5 mL, 1M in THF, 24.5 mmol, 1.6 equiv). After stirring for 1 h at −40 °C, a solution of (*S*)-tosylated glycidol (3.49 g, 15.3 mmol, 1 equiv) in dry THF (40 mL) was added dropwise by dropping funnel over 1 h, and the resulting solution was stirred for 3 h. The reaction mixture was quenched by addition of a saturated aqueous solution of NH_4Cl (60 mL), allowed to reach rt, stirred for 1 h and diluted with EtOAc (40 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 8/2 to 7/3) to afford the homoallylic alcohol **(+)-2** (3.75 g, 14.6 mmol, 96%) as a yellow oil. Spectral data match those reported in the literature.[2]

$[\alpha]_D^{20}$ = + 10.5 (*c* 1.05, $CHCl_3$).
IR: *ν* 3531, 3076, 2980, 2924, 1643, 1598, 1444, 1355, 1293, 1189, 1173, 1096, 975, 915, 812, 665 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, 2H, *J* = 8.2 Hz), 7.35 (d, 2H, *J* = 8.2 Hz), 5.74 (m, 1H), 5.14-5.07 (m, 2H), 4.04 (m, 1H), 3.95-3.88 (m, 2H), 2.45 (s, 3H), 2.31-2.19 (m, 2H), 2.19 (br s, 1H, OH).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.1 (s), 132.9 (d), 132.6 (s), 130.0 (2d), 128.0 (2d), 118.9 (t), 73.1 (t), 68.6 (d), 37.4 (t), 21.7 (q).
MS (EI) *m/z*: 238 ($M^{+\bullet}$-H_2O, 1), 226 (2), 215 (M-allyl$^+$, 21), 155 (Ts^+, 57), 91 (100), 71 (12), 65 (27).

(*R*)-2-Hydroxypent-4-en-1-yl 4-methylbenzenesulfonate (−)-2



$C_{12}H_{16}O_4S$
M = 256.08 g/mol

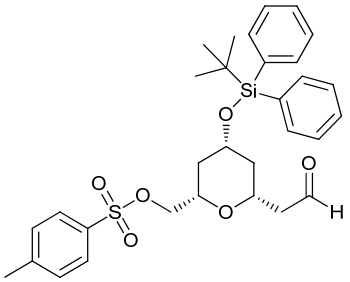
To a solution of Li_2CuCl_4 (9.2 mL, 0.1 M in THF, 0.92 mmol, 0.06 equiv) cooled to −40 °C was added vinylmagnesium bromide (24.5 mL, 1M in THF, 24.5 mmol, 1.6 equiv). After stirring for 1 h at −40 °C, a solution of (*R*)-tosylated glycidol (3.5 g, 15.3 mmol, 1 equiv) in dry THF (40 mL) was added dropwise by dropping funnel over 1 h, and the resulting solution was stirred for 4 h. The reaction mixture was quenched by addition of a saturated aqueous solution of NH_4Cl (60 mL), allowed to reach rt and stirred for 1 h. The mixture was diluted with EtOAc (40 mL), the layers were then separated and the aqueous layer was extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 8/2 to 7/3) to afford the homoallylic alcohol **(−)-2** (3.55 g, 13.9 mmol, 91%) as a yellow oil. Spectral data match those reported in the literature.[2]

$[\alpha]_D^{20}$ = − 9.6 (*c* 0.9, $CHCl_3$).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d_{app}, 2H, *J* = 8.2 Hz), 7.35 (d_{app}, 2H, *J* = 8.2 Hz), 5.74 (m, 1H), 5.14-5.08 (m, 2H), 4.04 (m, 1H), 3.96-3.89 (m, 2H), 2.45 (s, 3H), 2.31-2.18 (m, 2H), 2.16 (d_{app}, 1H, *J* = 4.1 Hz, OH).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.1 (s), 132.9 (d), 132.6 (s), 130.0 (2d), 128.0 (2d), 118.9 (t), 73.1 (t), 68.6 (d), 37.4 (t), 21.7 (q).

Synthesis of tetrahydropyrans 1a and 1b

Tetrahydropyrans **1a** and **1b** were synthesized according to the following sequence of reactions : a Prins cyclisation under the conditions reported by Yadav and co-workers[3] applied to benzyloxypropanal and homoallylic alcohol **(+)-2** afforded the corresponding tetrahydropyrans as a mixture of diastereomers precursors of **1a** and **1b**, which were separated by flash column chromatography (petroleum ether/ethyl acetate = 7/3 to 5/5) and then converted respectively to **1a** and **1b** by classical protection/deprotection/oxidation reactions.

{(2*R*,4*R*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-(2-oxoethyl)tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 1a

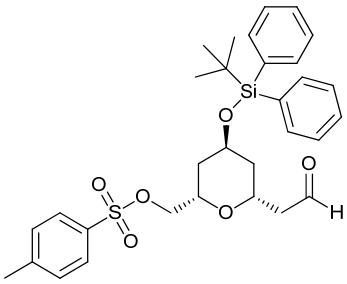


$C_{31}H_{38}O_6SSi$
M = 566.22 g/mol

$[\alpha]_D^{20}$ = + 4.4 (*c* 0.61, $CHCl_3$).
IR: *ν* 3071, 3050, 2956, 2931, 2888, 2858, 2734, 1726, 1598, 1472, 1428, 1362, 1190, 1177, 1111, 1075, 982, 913, 816, 791, 739, 704, 667 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.60 (dd, 1H, J = 2.4 Hz, J = 1.9 Hz), 7.74 (d_{app}, 2H, J = 8.3 Hz), 7.65-7.61 (m, 4H), 7.47-7.41 (m, 2H), 7.40-7.35 (m, 4H), 7.32 (d, 2H, J = 8.3 Hz), 3.90 (d, 2H, J = 5.0 Hz), 3.76 (m, 1H), 3.60 (m, 1H), 3.39 (m, 1H), 2.46 (ddd_{AB}, 1H, J = 16.5 Hz, J = 7.8 Hz, J = 2.6 Hz), 2.44 (s, 3H), 2.32 (ddd_{AB}, 1H, J = 16.5 Hz, J = 4.5 Hz, J = 1.8 Hz), 1.75-1.65 (m, 2H), 1.35-1.24 (m, 2H), 1.03 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.6 (d), 144.8 (s), 135.7 (4d), 133.85 (s), 133.81 (s), 132.9 (s), 129.86 (d), 129.84 (d), 129.79 (2d), 128.0 (2d), 127.72 (2d), 127.70 (2d), 73.0 (d), 71.7 (t), 70.8 (d), 68.4 (d), 49.0 (t), 40.6 (t), 36.6 (t), 26.8 (3q), 21.6 (q), 19.0 (s).
HRMS (ESI): Calculated for $C_{31}H_{38}O_6SSiNa$ $[M + Na]^+$: 589.2051, found: 589.2050.

{(2*S*,4*S*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-(2-oxoethyl)tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 1b



$C_{31}H_{38}O_6SSi$
M = 566.22 g/mol

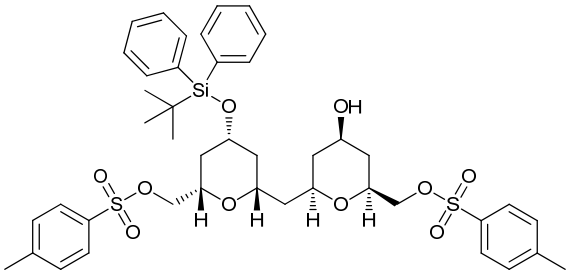
$[\alpha]_D^{20}$ = + 2.7 (c 0.52, $CHCl_3$).
IR: ν 3071, 2930, 2858, 1725, 1598, 1472, 1427, 1360, 1189, 1176, 1105, 1075, 1037, 981, 909, 820, 730, 702, 665 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.68 (t_{app}, 1H, J = 2.3 Hz), 7.76 (d_{app}, 2H, J = 8.4 Hz), 7.61 (m, 4H), 7.47-7.41 (m, 2H), 7.40-7.35 (m, 4H), 7.32 (d_{app}, 2H, J = 8.3 Hz), 4.42 (m, 1H), 4.25-4.17 (m, 2H), 3.98-3.89 (m, 2H), 2.44 (s, 3H), 2.41 (ddd, 1H, J = 16.4 Hz, J = 8.1 Hz, J = 2.7 Hz), 2.32 (ddd, 1H, J = 16.4 Hz, J = 4.9 Hz, J = 2.0 Hz), 1.56-1.43 (m, 2H), 1.31-1.21 (m, 2H), 1.07 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.2 (d), 144.8 (s), 135.68 (2d), 135.66 (2d), 133.6 (2s), 133.0 (s), 129.93 (d), 129.92 (d), 129.8 (2d), 128.0 (2d), 127.80 (2d), 127.77 (2d), 72.4 (t), 69.7 (d), 67.6 (d), 65.1 (d), 49.3 (t), 38.1 (t), 34.2 (t), 27.0 (3q), 21.7 (q), 19.3 (s).
HRMS (ESI): Calculated for $C_{31}H_{38}O_6SSiNa$ $[M + Na]^+$: 589.2051, found: 589.2049.

General procedure for the synthesis of the *bis*-tetrahydropyrans 3 and 3'

To a solution of homoallylic alcohol **(+)-2** or **(−)-2** (1.5 equiv) and aldehyde **1a** or **1b** (1.0 equiv) in dry CH_2Cl_2 (c = 0.11 M) was added dropwise trifluoroacetic acid (26 equiv). The mixture was stirred for 3 h at rt, and treated with a saturated aqueous solution of $NaHCO_3$. The pH was adjusted to a value > 7 by addition of Et_3N and the resulting mixture was stirred at rt for an additional 2 h and then diluted with EtOAc. The layers were separated and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 6/4 to 5/5) to afford the alcohols **3** and **3'** as mixtures of diastereomers and as gummy liquids, which then could be separated by column chromatography.

The previously described general procedure was applied to the aldehyde **1a** (185 mg, 0.326 mmol, 1.0 equiv) and the homoallylic alcohol **(+)-2** (126 mg, 0.49 mmol, 1.5 equiv) to afford compounds **3a** and **3a'** as a mixture of diastereomers (177 mg, **3a**/**3'a** = 70:30, 0.215 mmol, 66%). Purification of the mixture by column chromatography on silica gel (petroleum ether/EtOAc = 65/35 to 6/4) afforded pure **3a** and **3'a**.

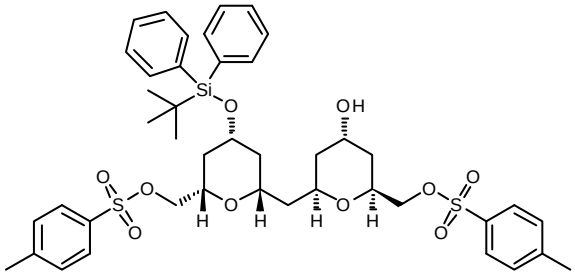
{(2*S*,4*R*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-[((2*R*,4*R*,6*S*)-4-hydroxy-6-(tosyloxymethyl)tetrahydro-2*H*-pyran-2-yl)methyl]tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 3a



$C_{43}H_{54}O_{10}S_2Si$
M = 822.29 g/mol

[α] $_D^{20}$ = − 8.8 (*c* 0.64, $CHCl_3$).
IR: *ν* 3546, 3070, 2951, 2858, 1598, 1428, 1359, 1189, 1175, 1111, 1097, 1076, 977, 910, 814, 731, 703, 667 cm^{-1}.
^{1}**H NMR** ($CDCl_3$, 400 MHz): *δ* 7.75 (d, 2H, *J* = 8.3 Hz), 7.74 (d, 2H, *J* = 8.3 Hz), 7.66-7.61 (m, 4H), 7.46-7.41 (m, 2H), 7.40-7.35 (m, 4H), 7.32 (d, 2H, *J* = 8.0 Hz), 7.27 (d, 2H, *J* = 8.0 Hz), 3.99-3.88 (m, 3H), 3.86 (dd_{systAB}, 1H, *J* = 10.2 Hz, *J* = 3.6 Hz), 3.80-3.68 (m, 2H), 3.46 (m, 1H), 3.40-3.19 (m, 3H), 2.43 (s, 3H), 2.39 (s, 3H), 2.03 (br s, 1H, OH), 1.90-1.80 (m, 2H), 1.69-1.58 (m, 2H), 1.49-1.37 (m, 2H), 1.29-1.18 (m, 2H), 1.14-1.00 (m, 2H), 1.03 (s, 9H).
^{13}**C NMR** ($CDCl_3$, 100 MHz): *δ* 144.84 (s), 144.80 (s), 135.7 (4d), 134.1 (s), 134.0 (s) 133.0 (s), 132.9 (s), 129.9 (2d), 129.8 (4d), 127.95 (2d), 127.92 (2d), 127.7 (4d), 72.7 (d), 72.6 (d), 72.4 (d), 72.2 (t), 71.9 (d), 71.9 (t), 68.9 (d), 67.4 (d), 42.0 (t), 41.4 (t), 41.2 (t), 36.8 (t), 36.6 (t), 26.9 (3q), 21.7 (q), 21.6 (q), 19.1 (s).
HRMS (ESI): Calculated for $C_{43}H_{54}O_{10}S_2SiNa$ $[M + Na]^+$: 845.2820, found: 845.2818.

{(2*S*,4*R*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-[((2*R*,4*S*,6*S*)-4-hydroxy-6-(tosyloxymethyl)tetrahydro-2*H*-pyran-2-yl)methyl]tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 3'a

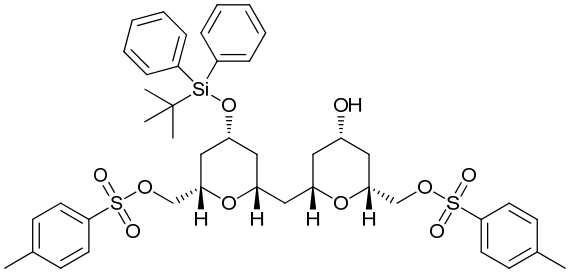


$C_{43}H_{54}O_{10}S_2Si$
M = 822.29 g/mol

$[\alpha]_D^{20}$ = − 8.7 (*c* 2.5, $CHCl_3$).
IR: *ν* 3552, 3071, 2950, 2858, 1598, 1428, 1358, 1189, 1175, 1111, 1076, 1020, 978, 924, 814, 733, 703, 666 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.75 (d, 2H, *J* = 8.3 Hz), 7.74 (d, 2H, *J* = 8.3 Hz), 7.66-7.62 (m, 4H), 7.46-7.41 (m, 2H), 7.40-7.35 (m, 4H), 7.32 (d_{app}, 2H, *J* = 8.3 Hz), 7.26 (d_{app}, 2H, *J* = 8.2 Hz), 4.19 (m, 1H), 3.96-3.90 (m, 4H), 3.88-3.80 (m, 2H), 3.76 (m, 1H), 3.32-3.20 (m, 2H), 2.42 (s, 3H), 2.39 (s, 3H), 1.85 (br s, 1H , OH), 1.70-1.51 (m, 4H), 1.46-1.18 (m, 6H), 1.03 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 144.8 (s), 144.7 (s), 135.7 (4d), 134.1 (s), 134.0 (s), 133.0 (s), 132.9 (s), 129.9 (2d), 129.8 (4d), 128.0 (2d), 127.9 (2d), 127.7 (4d), 72.6 (t), 72.6 (d), 72.3 (d), 72.2 (t), 69.2 (d), 68.89 (d), 68.86 (d), 63.9 (d), 42.3 (t), 41.5 (t), 38.9 (t), 36.8 (t), 34.0 (t), 26.9 (3q), 21.7 (q), 21.6 (q), 19.1 (s).
HRMS (ESI): Calculated for $C_{43}H_{54}O_{10}S_2SiNa$ $[M + Na]^+$: 845.2820, found: 845.2824.

The previously described general procedure was applied to the aldehyde **1a** (325 mg, 0.57 mmol, 1.0 equiv) and the homoallylic alcohol **(−)-2** (245 mg, 0.86 mmol, 1.5 equiv) to afford compounds **3b** and **3'b** as a mixture of diastereomers (240 mg, **3b**/**3'b** = 75:25, 0.29 mmol, 51%). Purification of the mixture by column chromatography on silica gel (petroleum ether/EtOAc = 65/35 to 6/4) afforded pure **3b** and **3'b**.

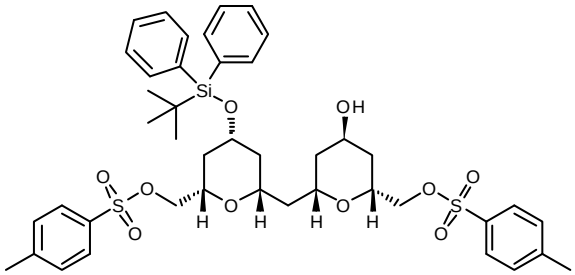
{(2*S*,4*R*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-[((2*S*,4*S*,6*R*)-4-hydroxy-6-(tosyloxymethyl)tetrahydro-2*H*-pyran-2-yl)methyl]tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 3b



$C_{43}H_{54}O_{10}S_2Si$
M = 822.29 g/mol

$[\alpha]_D^{20}$ = + 3.4 (*c* 2.3, $CHCl_3$).
IR: *ν* 3540, 2929, 2858, 1599, 1428, 1359, 1189, 1176, 1112, 1097, 978, 906, 814, 790, 727, 704, 667, 649 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.76 (d, 2H, *J* = 8.2 Hz), 7.74 (d, 2H, *J* = 8.2 Hz), 7.66-7.61 (m, 4H), 7.46-7.40 (m, 2H), 7.39-7.34 (m, 4H), 7.32 (d, 2H, *J* = 8.0 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 3.99-3.84 (m, 4H), 3.78-3.65 (m, 2H), 3.45 (m, 1H), 3.36-3.23 (m, 2H), 3.16 (m, 1H), 2.43 (s, 3H), 2.42 (s, 3H), 1.94 (br s, 1H, OH), 1.90-1.80 (m, 2H), 1.72-1.60 (m, 3H), 1.35 (m, 1H), 1.28-1.03 (m, 4H), 1.03 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 144.9 (s), 144.8 (s), 135.72 (2d), 135.68 (2d), 134.1 (s), 134.0 (s), 132.9 (2s), 129.9 (2d), 129.8 (4d), 128.0 (2d), 127.9 (2d), 127.7 (4d), 72.83 (d), 72.80 (d), 72.4 (d), 72.2 (t), 71.93 (t), 71.87 (d), 68.9 (d), 67.5 (d), 41.0 (t), 40.8 (t), 40.2 (t), 36.8 (2t), 26.9 (3q), 21.7 (2q), 19.1 (s).
HRMS (ESI): Calculated for $C_{43}H_{54}O_{10}S_2SiNa$ $[M + Na]^+$: 845.2820, found: 845.2831.

{(2*S*,4*R*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-[((2*S*,4*R*,6*R*)-4-hydroxy-6-(tosyloxymethyl)tetrahydro-2*H*-pyran-2-yl)methyl]tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 3'b

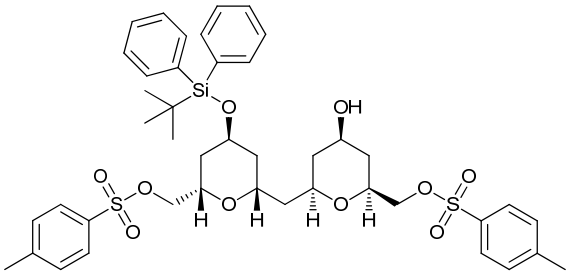


$C_{43}H_{54}O_{10}S_2Si$
M = 822.29 g/mol

[α] $_D^{20}$ = + 6.9 (*c* 1.7, $CHCl_3$).
IR: *ν* 3554, 3070, 2953, 2930, 2886, 2858, 1668, 1598, 1472, 1428, 1360, 1257, 1214, 1189, 1176, 1111, 1020, 980, 835, 757, 704, 667, 614 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.78-7.73 (m, 4H), 7.66-7.61 (m, 4H), 7.46-7.40 (m, 2H), 7.39-7.34 (m, 4H), 7.31 (d_{app}, 2H, *J* = 8.0 Hz), 7.30 (d_{app}, 2H, *J* = 8.0 Hz), 4.21 (m, 1H), 3.98-3.85 (m, 5H), 3.83-3.69 (m, 2H), 3.33 (m, 1H), 3.14 (m, 1H), 2.43 (s, 3H), 2.42 (s, 3H), 1.86 (br s, 1H, OH), 1.70-1.62 (m, 3H), 1.60-1.54 (m, 2H), 1.46-1.13 (m, 5H), 1.03 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 144.9 (s), 144.7 (s), 135.73 (2d), 135.68 (2d), 134.1 (2s), 133.0 (s), 132.9 (s), 129.9 (4d), 129.8 (2d), 128.0 (2d), 127.9 (2d), 127.7 (4d), 73.0 (d), 72.6 (t), 72.3 (t), 72.0 (d), 69.2 (d), 68.9 (d), 68.3 (d), 63.7 (d), 41.2 (t), 40.8 (t), 37.7 (t), 36.8 (t), 34.0 (t), 26.9 (3q), 21.67 (q), 21.65 (q), 19.1 (s).
HRMS (ESI): Calculated for $C_{43}H_{54}O_{10}S_2SiNa$ $[M + Na]^+$: 845.2820, found: 845.2825.

The previously described general procedure was applied to the aldehyde **1b** (102 mg, 0.18 mmol, 1.0 equiv) and the homoallylic alcohol **(+)-2** (70 mg, 0.27 mmol, 1.5 equiv) to afford compounds **3c** and **3'c** as a mixture of diastereomers (118 mg, **3c**/**3'c** = 65:35, 0.143 mmol, 80%). Purification of the mixture by column chromatography on silica gel (petroleum ether/EtOAc = 65/35 to 6/4) afforded pure **3c** and **3'c**.

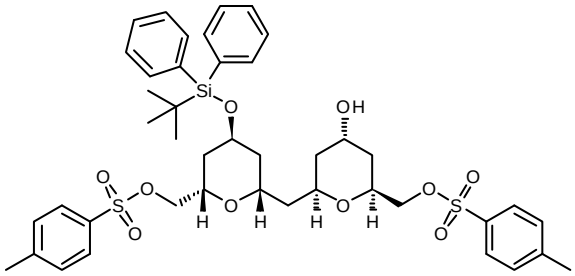
{(2*S*,4*S*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-[((2*R*,4*R*,6*S*)-4-hydroxy-6-(tosyloxymethyl)tetrahydro-2*H*-pyran-2-yl)methyl]tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 3c



$C_{43}H_{54}O_{10}S_2Si$
M = 822.29 g/mol

$[\alpha]_D^{20} = -12.3$ (*c* 1.06, $CHCl_3$).
IR: *ν* 3546, 3060, 2929, 2858, 1598, 1428, 1360, 1189, 1176, 1110, 1037, 979, 913, 816, 776, 733, 704, 666 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.78 (d, 2H, *J* = 8.3 Hz), 7.77 (d, 2H, *J* = 8.3 Hz), 7.62-7.57 (m, 4H), 7.45-7.40 (m, 2H), 7.38-7.29 (m, 8H), 4.20-4.11 (m, 2H), 4.07-4.00 (m, 2H), 3.98-3.93 (m, 2H), 3.88 (dd_{systAB}, 1H, *J* = 10.4 Hz, *J* = 3.6 Hz), 3.80 (m, 1H), 3.56 (m, 1H), 3.43 (m, 1H), 2.44 (s, 3H), 2.42 (s, 3H), 2.03 (m, 1H), 1.92 (m, 1H), 1.47-1.38 (m, 4H), 1.22-1.08 (m, 4H), 1.05 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 144.8 (s), 144.7 (s), 135.70 (2d), 135.66 (2d), 133.9 (s), 133.8 (s), 133.2 (s), 133.0 (s), 129.84 (2d), 129.81 (2d), 128.0 (4d), 127.9 (2d), 127.7 (4d), 73.3 (d), 72.8 (t), 72.7 (d), 71.9 (t), 69.5 (d), 69.0 (d), 67.6 (d), 65.5 (d), 42.2 (t), 41.5 (t), 38.9 (t), 36.8 (t), 34.4 (t), 27.0 (3q), 21.7 (2q), 19.2 (s).
HRMS (ESI): Calculated for $C_{43}H_{54}O_{10}S_2SiNa$ $[M + Na]^+$: 845.2820, found: 845.2828.

{(2*S*,4*S*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-[((2*R*,4*S*,6*S*)-4-hydroxy-6-(tosyloxymethyl)tetrahydro-2*H*-pyran-2-yl)methyl]tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 3'c

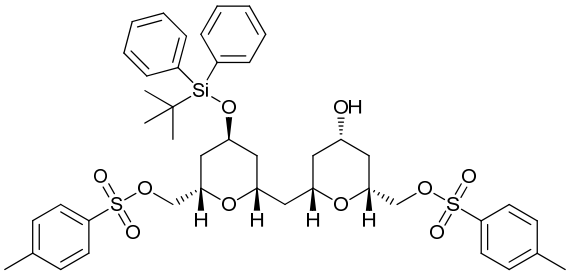


$C_{43}H_{54}O_{10}S_2Si$
M = 822.29 g/mol

$[\alpha]_D^{20} = -11.9$ (*c* 0.5, $CHCl_3$).
IR: *ν* 3551, 3080, 2928, 2858, 1599, 1428, 1359, 1189, 1176, 1106, 981, 816, 756, 704, 666 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.78 (d_{app}, 4H, *J* = 8.3 Hz), 7.63-7.58 (m, 4H), 7.45-7.40 (m, 2H), 7.39-7.28 (m, 8H), 4.23 (m, 1H), 4.20-4.11 (m, 2H), 4.08-3.87 (m, 7H), 2.43 (s, 3H), 2.41 (s, 3H), 1.85 (br s, 1H, OH), 1.77 (m, 1H), 1.61 (m, 1H), 1.52-1.33 (m, 6H), 1.28-1.12 (m, 2H), 1.05 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 144.8 (s), 144.7 (s), 135.72 (2d), 135.67 (2d), 133.9 (s), 133.8 (s), 133.1 (s), 133.0 (s), 129.9 (2d), 129.8 (4d), 128.0 (2d), 127.9 (2d), 127.7 (4d), 72.9 (t), 72.6 (t), 69.6 (d), 69.5 (d), 69.4 (d), 69.2 (d), 65.5 (d), 64.0 (d), 42.5 (t), 39.2 (t), 38.9 (t), 34.5 (t), 34.1 (t), 27.0 (3q), 21.7 (2q), 19.2 (s).
HRMS (ESI): Calculated for $C_{43}H_{54}O_{10}S_2SiNa$ $[M + Na]^+$: 845.2820, found: 845.2825.

The previously described general procedure was applied to the aldehyde **1b** (216 mg, 0.38 mmol, 1.0 equiv) and the homoallylic alcohol **(−)-2** (147 mg, 0.57 mmol, 1.5 equiv) to afford compounds **3d** and **3'd** as a mixture of diastereomers (172 mg, **3d**/**3'd** = 75:25, 0.21 mmol, 55%). Purification of the mixture by column chromatography on silica gel (petroleum ether/EtOAc = 65/35 to 6/4) afforded pure **3d** and **3'd**.

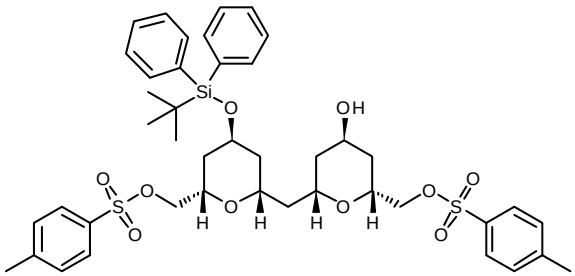
{(2*S*,4*S*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-[((2*S*,4*S*,6*R*)-4-hydroxy-6-(tosyloxymethyl)tetrahydro-2*H*-pyran-2-yl)methyl]tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 3d



$C_{43}H_{54}O_{10}S_2Si$
M = 822.29 g/mol

[α] $_D^{20}$ = + 1.2 (*c* 2.3, $CHCl_3$).
IR: *ν* 3537, 3020, 2928, 2857, 1599, 1428, 1360, 1215, 1189, 1176, 1098, 1038, 1020, 981, 815, 753, 704, 666, 612 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.78 (d, 2H, *J* = 8.3 Hz), 7.77 (d, 2H, *J* = 8.3 Hz), 7.62-7.56 (m, 4H), 7.46-7.39 (m, 2H), 7.39-7.28 (m, 8H), 4.19 (m, 1H), 4.13 (m, 1H), 4.03-3.89 (m, 5H), 3.77 (m, 1H), 3.53 (m, 1H), 3.38 (m, 1H), 2.43 (s, 3H), 2.41 (s, 3H), 1.99-1.91 (m, 3H), 1.67 (m, 1H), 1.48-1.40 (m, 2H), 1.35 (m, 1H), 1.28-1.11 (m, 4H), 1.03 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 144.9 (s), 144.8 (s), 135.7 (2d), 135.6 (2d), 133.84 (s), 133.78 (s), 133.1 (s), 132.9 (s), 129.87 (2d), 129.85 (4d), 128.0 (2d), 127.9 (2d), 127.8 (4d), 72.8 (d), 72.8 (t), 72.5 (d), 71.9 (t), 69.7 (d), 68.4 (d), 67.5 (d), 65.4 (d), 41.4 (t), 40.3 (t), 38.3 (t), 37.0 (t), 34.5 (t), 27.0 (3q), 21.7 (2q), 19.2 (s).
HRMS (ESI): Calculated for $C_{43}H_{54}O_{10}S_2SiNa$ $[M + Na]^+$: 845.2820, found: 845.2825.

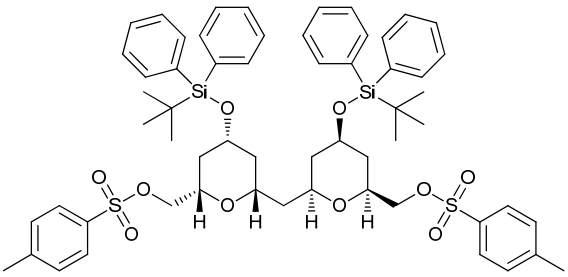
{(2*S*,4*S*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-6-[((2*S*,4*R*,6*R*)-4-hydroxy-6-(tosyloxymethyl)tetrahydro-2*H*-pyran-2-yl)methyl]tetrahydro-2*H*-pyran-2-yl}methyl 4-methylbenzenesulfonate 3'd



$C_{43}H_{54}O_{10}S_2Si$
M = 822.29 g/mol

[α] $_D^{20}$ = + 2.9 (*c* 1.8, $CHCl_3$).
IR: *ν* 3556, 3026, 2928, 2858, 1599, 1428, 1359, 1189, 1176, 1111, 980, 815, 755, 704, 666, 612 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.80-7.75 (m, 4H), 7.61-7.57 (m, 4H), 7.46-7.40 (m, 2H), 7.39-7.28 (m, 8H), 4.29 (m, 1H), 4.19 (m, 1H), 4.15 (m, 1H), 4.05-3.86 (m, 7H), 2.43 (s, 3H), 2.41 (s, 3H), 1.88 (br s, 1H, OH), 1.73-1.61 (m, 3H), 1.53-1.38 (m, 4H), 1.32-1.13 (m, 3H), 1.03 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 144.8 (s), 144.7 (s), 135.7 (2d), 135.6 (2d), 133.9 (s), 133.7 (s), 133.1 (s), 133.0 (s), 129.9 (4d), 129.8 (2d), 128.0 (2d), 127.9 (2d), 127.7 (4d), 72.9 (t), 72.5 (t), 69.9 (d), 69.2 (d), 68.4 (d), 68.3 (d), 65.4 (d), 63.8 (d), 41.5 (t), 38.3 (t), 37.8 (t), 34.5 (t), 34.2 (t), 27.0 (3q), 21.7 (2q), 19.2 (s).
HRMS (ESI): Calculated for $C_{43}H_{54}O_{10}S_2SiNa$ $[M + Na]^+$: 845.2820, found: 845.2824.

***bis*{(2*S*,4*R*,6*S*)-4-[(*tert*-Butyldiphenylsilyl)oxy]-2-(tosyloxymethyl)tetrahydro-2*H*-pyran-6-yl} methane 3e**



$C_{59}H_{72}O_{10}S_2Si_2$
M = 1060.41 g/mol

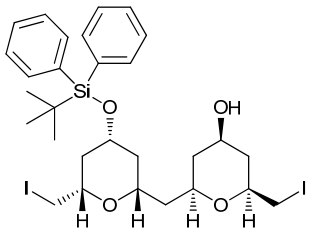
To a solution of alcohol **3a** (142 mg, 0.173 mmol, 1.0 equiv) in dry CH_2Cl_2 (2 mL) were added imidazole (47 mg, 0.69 mmol, 4.0 equiv) and TBDPSCl (0.13 mL, 0.51 mmol, 3.0 equiv) dropwise. The mixture was stirred at rt for 24 h, and water was then added. The layers were separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were then dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was purified by column chromatography on silica gel (petroleum ether/EtOAc = 9/1 to 8/2) to afford the silylated compound **3e** (169 mg, 0.159 mmol, 92%) as a colorless gummy liquid.

$[\alpha]_D^{20}$ = + 5.1 (*c* 0.59, $CHCl_3$).
IR: *ν* 3071, 2931, 2857, 1598, 1428, 1361, 1189, 1177, 1111, 1076, 979, 909, 823, 788, 732, 703, 667, 649 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.70 (d_{app}, 4H, *J* = 8.4 Hz), 7.64-7.61 (m, 8H), 7.46-7.33 (m, 12H), 7.23 (d, 4H, *J* = 8.4 Hz), 3.86 (dd_{systAB}, 2H, *J* = 10.2 Hz, *J* = 5.7 Hz), 3.82 (dd_{systAB}, 2H, *J* = 10.5 Hz, *J* = 4.2 Hz), 3.72 (m, 2H), 3.23-3.13 (m, 4H), 2.38 (s, 6H), 1.64-1.56 (m, 4H), 1.31 (m, 2H), 1.26-1.11 (m, 4H), 1.02 (s, 18H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 144.7 (2s), 135.7 (8d), 134.1 (4d), 133.0 (2s), 129.8 (4d), 129.7 (4d), 127.9, 127.7 (12d), 72.5 (2d), 71.9 (2t), 71.6 (2d), 68.8 (2d), 42.1 (t), 41.4 (2t), 37.0 (2t), 26.9 (6q), 21.6 (2q), 19.1 (2s).
HRMS (ESI): Calculated for $C_{59}H_{72}O_{10}Si_2Na$ $[M + Na]^+$: 1083.3998, found: 1083.3981.

General procedure for the synthesis of the iodinated *bis*-tetrahydropyrans I

To a solution of tosylated *bis*-tetrahydropyran (1.0 equiv) in pure acetone (*c* = 0.05 M) was added NaI (10 equiv). The mixture was heated at 120 °C under microwave irradiation, in a sealed vial, for 2 h. Water (20 mL per mmol) and EtOAc (20 mL per mmol) were then added. The layers were separated, the aqueous layer was extracted once with ethyl acetate and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 75/25) to afford the iodinated compound as a gummy liquid.

(2*R*,4*R*,6*S*)-2-{[(2*S*,4*R*,6*S*)-4-(*tert*-Butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2*H*-pyran-2-yl]methyl}-6-(iodomethyl)tetrahydro-2*H*-pyran-4-ol Ia

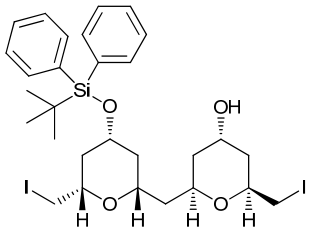


$C_{29}H_{40}I_2O_4Si$
M = 734.08 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **3a** (48 mg, 0.058 mmol, 1.0 equiv) to afford the *bis*-iodinated compound **Ia** (34 mg, 0.046 mmol, 79%).

$[\alpha]_D^{20}$ = + 13.9 (*c* 1.9, $CHCl_3$).
IR: *ν* 3373, 3071, 2944, 2857, 1589, 1428, 1372, 1269, 1184, 1149, 1112, 1077, 908, 831, 733, 703, 648 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.67-7.63 (m, 4H), 7.46-7.35 (m, 6H), 3.89-3.80 (m, 2H), 3.68 (m, 1H), 3.50 (m, 1H), 3.39 (m, 1H), 3.21 (m, 1H), 3.17-3.07 (m, 4H), 2.15 (m, 1H), 1.93-1.87 (m, 2H), 1.74 (m, 1H), 1.60-1.51 (m, 2H), 1.34-1.06 (m, 4H), 1.04 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 135.7 (4d), 134.2 (s), 134.1 (s), 129.7 (2d), 127.7 (4d), 75.0 (d), 74.9 (d), 72.0 (d), 71.8 (d), 69.1 (d), 67.9 (d), 41.9 (t), 41.3 (t), 41.1 (2t), 40.8 (t), 26.9 (3q), 19.1 (s), 9.3 (t), 8.9 (t).
HRMS (ESI): Calculated for $C_{29}H_{40}I_2O_4SiNa$ $[M + Na]^+$: 757.0677, found: 757.0683.

(2*R*,4*S*,6*S*)-2-{[(2*S*,4*R*,6*S*)-4-(*tert*-Butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2*H*-pyran-2-yl]methyl}-6-(iodomethyl)tetrahydro-2*H*-pyran-4-ol I'a



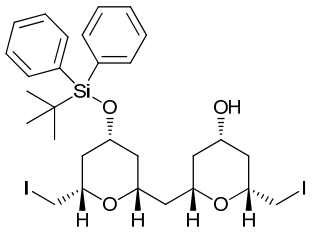
$C_{29}H_{40}I_2O_4Si$
M = 734.08 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **3'a** (59 mg, 0.07 mmol, 1.0 equiv) to afford the *bis*-iodinated compound **I'a** (45 mg, 0.06 mmol, 85%).

$[\alpha]_D^{20}$ = + 10.2 (*c* 1.3, $CHCl_3$).
IR: *ν* 3071, 2930, 2857, 1589, 1427, 1373, 1187, 1110, 1072, 907, 829, 730, 702 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.68-7.63 (m, 4H), 7.46-7.35 (m, 6H), 4.23 (m, 1H), 4.11 (m, 1H), 3.89-3.77 (m, 2H), 3.51 (m, 1H), 3.21 (m, 1H), 3.17-3.06 (m, 4H), 1.92 (m, 1H), 1.84 (m, 1H), 1.75 (m, 1H), 1.63 (m, 1H), 1.61 (br s, 1H, OH), 1.58-1.35 (m, 4H), 1.34-1.20 (m, 2H), 1.04 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.8 (2d), 135.7 (2d), 134.2 (s), 134.1 (s), 129.7 (2d), 127.7 (4d), 74.9 (d), 71.9 (d), 71.4 (d), 69.1 (d), 68.7 (d), 64.7 (d), 42.1 (t), 41.4 (t), 41.1 (t), 38.9 (t), 38.3 (t), 26.9 (3q), 19.1 (s), 10.1 (t), 9.4 (t).
HRMS (ESI): Calculated for $C_{29}H_{40}I_2O_4SiNa$ $[M + Na]^+$: 757.0677, found: 757.0682.

(2*S*,4*S*,6*R*)-2-{[(2*S*,4*R*,6*S*)-4-(*tert*-Butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2*H*-pyran-2-yl]methyl}-6-(iodomethyl)tetrahydro-2*H*-pyran-4-ol Ib

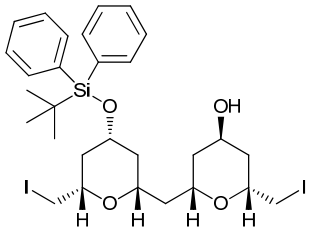


$C_{29}H_{40}I_2O_4Si$
M = 734.08 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **3b** (46 mg, 0.056 mmol, 1.0 equiv) to afford the *bis*-iodinated compound **Ib** (37 mg, 0.050 mmol, 90%).

$[\alpha]_D^{20}$ = + 3.8 (*c* 1.9, $CHCl_3$).
IR: *ν* 3386, 3070, 3000, 2944, 2857, 1589, 1427, 1374, 1328, 1268, 1216, 1189, 1112, 1073, 824, 756, 703 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69-7.64 (m, 4H), 7.46-7.35 (m, 6H), 3.87-3.76 (m, 2H), 3.47 (m, 1H), 3.39-3.25 (m, 2H), 3.21-3.08 (m, 5H), 2.15 (m, 1H), 1.98-1.87 (m, 3H), 1.80 (br s, 1H, OH), 1.74 (m, 1H), 1.50 (m, 1H), 1.34-1.23 (m, 2H), 1.17-1.05 (m, 2H), 1.06 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.8 (2d), 135.75 (2d), 134.2 (2s), 129.8 (2d), 127.7 (4d), 75.1 (d), 75.0 (d), 72.5 (d), 72.3 (d), 69.1 (d), 67.8 (d), 41.2 (t), 41.1 (t), 40.7 (t), 40.5 (t), 40.3 (t), 27.0 (3q), 19.1 (s), 9.4 (t), 8.9 (t).
HRMS (ESI): Calculated for $C_{29}H_{40}I_2O_4SiNa$ $[M + Na]^+$: 757.0677, found: 757.0682.

(2*S*,4R,6*R*)-2-{[(2*S*,4*R*,6*S*)-4-(*tert*-Butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2*H*-pyran-2-yl]methyl}-6-(iodomethyl)tetrahydro-2*H*-pyran-4-ol I'b



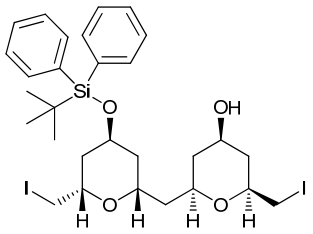
$C_{29}H_{40}I_2O_4Si$
M = 734.08 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **3'b** (66 mg, 0.080 mmol, 1.0 equiv) to afford the *bis*-iodinated compound **I'b** (46 mg, 0.063 mmol, 78%).

$[\alpha]_D^{20}$ = + 8.7 (*c* 2.3, $CHCl_3$).
IR: *ν* 3449, 3002, 2930, 2858, 1589, 1514, 1472, 1428, 1384, 1215, 1110, 1075, 755, 703 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69-7.64 (m, 4H), 7.46-7.36 (m, 6H), 4.24 (m, 1H), 3.92 (m, 1H), 3.83 (m, 1H), 3.72 (m, 1H), 3.39 (m, 1H), 3.22-3.05 (m, 5H), 1.95-1.78 (m, 4H), 1.51-1.62 (m, 2H), 1.50-1.36 (m, 3H), 1.34-1.23 (m, 2H), 1.05 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.8 (2d), 135.75 (2d), 134.2 (s), 134.1 (s), 129.8 (2d), 127.7 (4d), 75.1 (d), 72.4 (d), 71.3 (d), 69.1 (d), 68.7 (d), 64.6 (d), 41.3 (t), 41.1 (t), 40.4 (t), 38.2 (t), 38.1 (t), 27.0 (3q), 19.1 (s), 10.1 (t), 9.5 (t).
HRMS (ESI): Calculated for $C_{29}H_{40}I_2O_4SiNa$ $[M + Na]^+$: 757.0677, found: 757.0678.

(2*R*,4*R*,6*S*)-2-{[(2*S*,4*S*,6*S*)-4-(*tert*-Butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2*H*-pyran-2-yl]methyl}-6-(iodomethyl)tetrahydro-2*H*-pyran-4-ol Ic

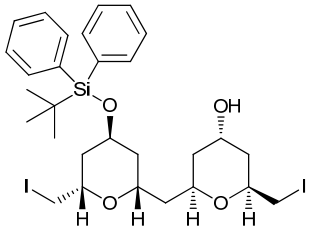


$C_{29}H_{40}I_2O_4Si$
M = 734.08 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **3c** (75 mg, 0.091 mmol, 1.0 equiv) to afford the *bis*-iodinated compound **Ic** (56 mg, 0.076 mmol, 84%).

$[\alpha]_D^{20}$ = − 4.1 (*c* 2.7, $CHCl_3$).
IR: *ν* 3365, 3000, 2946, 2857, 1589, 1427, 1216, 1111, 1081, 1037, 1007, 752, 702 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68-7.64 (m, 4H), 7.46-7.35 (m, 6H), 4.37 (m, 1H), 4.21 (m, 1H), 4.01 (m, 1H), 3.89 (m, 1H), 3.76 (m, 1H), 3.48 (m, 1H), 3.27-3.19 (m, 2H), 3.17-3.08 (m, 2H), 2.18 (m, 1H), 1.93 (m, 1H), 1.72 (m, 1H), 1.68 (br s, 1H, OH), 1.58-1.52 (m, 2H), 1.50 (m, 1H), 1.29-1.13 (m, 4H), 1.10 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.8 (4d), 134.1 (s), 134.0 (s), 129.7 (2d), 127.7 (4d), 74.9 (d), 72.0 (d), 71.7 (d), 68.9 (d), 68.0 (d), 66.2 (d), 42.2 (t), 41.2 (t), 40.9 (t), 39.0 (t), 38.8 (t), 27.2 (3q), 19.4 (s), 10.5 (t), 8.8 (t).
HRMS (ESI): Calculated for $C_{29}H_{40}I_2O_4SiNa$ $[M + Na]^+$: 757.0677, found: 757.0681.

(2*R*,4*S*,6*S*)-2-{[(2*S*,4*S*,6*S*)-4-(*tert*-Butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2*H*-pyran-2-yl]methyl}-6-(iodomethyl)tetrahydro-2*H*-pyran-4-ol I'c

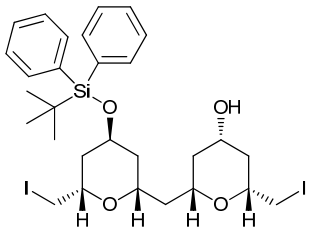


$C_{29}H_{40}I_2O_4Si$
M = 734.08 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **3'c** (76 mg, 0.092 mmol, 1.0 equiv) to afford the *bis*-iodinated compound **I'c** (57 mg, 0.078 mmol, 84%).

[α] $_D^{20}$ = − 9.4 (*c* 2.8, $CHCl_3$).
IR: *ν* 3425, 2999, 2929, 2857, 1589, 1471, 1427, 1346, 1217, 1190, 1110, 1081, 1039, 755, 702, 670, 612 cm^{-1}.
^{1}**H NMR** ($CDCl_3$, 400 MHz): *δ* 7.68-7.64 (m, 4H), 7.46-7.35 (m, 6H), 4.37 (m, 1H), 4.26 (m, 1H), 4.23-4.14 (m, 2H), 4.01 (m, 1H), 3.88 (m, 1H), 3.24-3.10 (m, 4H), 1.88 (d, 1H, *J* = 13.8 Hz), 1.75-1.65 (m, 2H), 1.58-1.41 (m, 5H), 1.29-1.15 (m, 2H), 1.10 (s, 9H).
^{13}**C NMR** ($CDCl_3$, 100 MHz): *δ* 135.8 (4d), 134.1 (s), 134.0 (s), 129.7 (2d), 127.7 (4d), 71.7 (d), 71.3 (d), 69.1 (d), 68.7 (d), 66.2 (d), 64.8 (d), 42.4 (t), 39.1 (2t), 38.8 (t), 38.4 (t), 27.2 (3q), 19.4 (s), 10.6 (t), 10.0 (t).
HRMS (ESI): Calculated for $C_{29}H_{40}I_2O_4SiNa$ $[M + Na]^+$: 757.0677, found: 757.0680.

(2*S*,4*S*,6*R*)-2-{[(2*S*,4*S*,6*S*)-4-(*tert*-Butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2*H*-pyran-2-yl]methyl}-6-(iodomethyl)tetrahydro-2*H*-pyran-4-ol Id

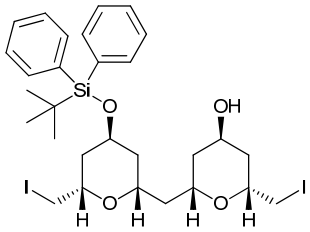


$C_{29}H_{40}I_2O_4Si$
M = 734.08 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **3d** (43 mg, 0.052 mmol, 1.0 equiv) to afford the *bis*-iodinated compound **Id** (34 mg, 0.046 mmol, 89%).

[α] $_D^{20}$ = − 9.7 (*c* 1.65, $CHCl_3$).
IR: *ν* 3385, 3070, 2927, 2856, 1589, 1471, 1427, 1362, 1185, 1106, 1080, 1036, 938, 756, 701, 677, 611 cm^{-1}.
^{1}**H NMR** ($CDCl_3$, 400 MHz): *δ* 7.66-7.61 (m, 4H), 7.46-7.35 (m, 6H), 4.22 (m, 1H), 4.14 (m, 1H), 3.96-3.84 (m, 2H), 3.62 (m, 1H), 3.36 (m, 1H), 3.21-3.09 (m, 4H), 2.22 (m, 1H), 2.06 (m, 1H), 1.91 (m, 1H), 1.76 (m, 1H), 1.66 (br s, 1H, OH), 1.55-1.47 (m, 2H), 1.34-1.15 (m, 4H), 1.09 (s, 9H).
^{13}**C NMR** ($CDCl_3$, 100 MHz): *δ* 135.7 (4d), 133.9 (2s), 129.8 (2d), 127.7 (4d), 75.0 (d), 72.7 (d), 71.8 (d), 69.1 (d), 67.9 (d), 66.0 (d), 41.5 (t), 40.8 (t), 40.1 (t), 38.7 (t), 38.5 (t), 27.1 (3q), 19.3 (s), 10.4 (t), 8.8 (t).
HRMS (ESI): Calculated for $C_{29}H_{40}I_2O_4SiNa$ $[M + Na]^+$: 757.0677, found: 757.0679.

(2*S*,4*R*,6*R*)-2-{[(2*S*,4*S*,6*S*)-4-(*tert*-Butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2*H*-pyran-2-yl]methyl}-6-(iodomethyl)tetrahydro-2*H*-pyran-4-ol I'd

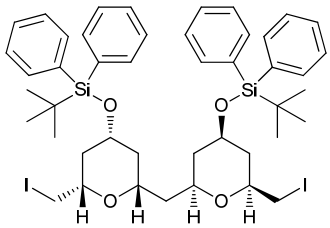


$C_{29}H_{40}I_2O_4Si$
M = 734.08 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **3'd** (218 mg, 0.26 mmol, 1.0 equiv) to afford the *bis*-iodinated compound **I'd** (181 mg, 0.25 mmol, 93%).

[α] $_D^{20}$ = − 7.8 (*c* 1.3, $CHCl_3$).
IR: *ν* 3439, 3070, 2927, 2856, 1589, 1471, 1427, 1389, 1347, 1312, 1254, 1192, 1157, 1106, 1079, 1060, 1038, 915, 822, 756, 701, 676, 611 cm^{-1}.
^{1}**H NMR** ($CDCl_3$, 400 MHz): *δ* 7.67-7.62 (m, 4H), 7.46-7.36 (m, 6H), 4.31 (m, 1H), 4.22 (m, 1H), 4.17 (m, 1H), 4.05 (m, 1H), 3.95 (m, 1H), 3.79 (m, 1H), 3.14 (d, 2H, *J* = 5.7 Hz), 3.13 (d, 2H, *J* = 6.0 Hz), 1.94-1.84 (m, 2H), 1.79-1.70 (m, 2H), 1.64 (br s, 1H, OH), 1.58-1.42 (m, 4H), 1.32-1.20 (m, 2H), 1.09 (s, 9H).
^{13}**C NMR** ($CDCl_3$, 100 MHz): *δ* 135.7 (4d), 134.0 (s), 133.9 (s), 129.8 (2d), 127.75 (2d), 127.73 (2d), 71.9 (d), 71.2 (d), 69.1 (d), 68.7 (d), 66.1 (d), 64.7 (d), 41.7 (t), 38.7 (t), 38.5 (t), 38.2 (t), 37.9 (t), 27.1 (3q), 19.4 (s), 10.6 (t), 10.1 (t).
HRMS (ESI): Calculated for $C_{29}H_{40}I_2O_4SiNa$ $[M + Na]^+$: 757.0677, found: 757.0679.

bis[(2_S_,4_R_,6_S_)-4-(_tert_-Butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2_H_-pyran-2-yl]methane Ie



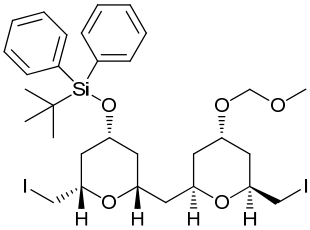
$C_{45}H_{58}I_2O_4Si_2$
M = 972.20 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **3e** (153 mg, 0.14 mmol, 1.0 equiv) and the *bis*-iodinated compound **Ie** (127 mg, 0.13 mmol, 91%) was isolated after purification by column chromatography (petroleum ether/EtOAc = 99/1 to 98/2).

[α] $_D^{20}$ = + 13.3 (*c* 0.42, $CHCl_3$).
IR: *ν* 3071, 2931, 2857, 1589, 1472, 1427, 1373, 1270, 1185, 1110, 1068, 907, 822, 731, 700, 611 cm^{-1}.
^{1}**H NMR** ($CDCl_3$, 400 MHz): *δ* 7.72-7.67 (m, 8H), 7.48-7.38 (m, 12H), 3.87 (m, 2H), 3.51 (m, 2H), 3.21 (m, 2H), 3.09 (d, 2H, *J* = 5.2 Hz), 3.08 (d, 2H, *J* = 6.9 Hz), 1.94 (m, 2H), 1.77 (m, 2H), 1.54 (dd, 2H, *J* = 7.0 Hz, *J* = 5.8 Hz), 1.36-1.21 (m, 4H), 1.09 (s, 18H).
^{13}**C NMR** ($CDCl_3$, 100 MHz): *δ* 135.8 (8d), 134.3 (2s), 134.1 (2s), 129.8 (4d), 127.7 (8d), 74.9 (2d), 71.8 (2d), 69.2 (2d), 42.0 (t), 41.4 (2t), 41.1 (2t), 27.0 (6q), 19.2 (2s), 9.3 (2t).

HRMS (ESI): Calculated for $C_{45}H_{58}I_2O_4Si_2Na$ $[M + Na]^+$: 995.1855, found: 995.1840.

tert-Butyl{(2_S_,4_R_,6_S_)-2-(iodomethyl)-6-[((2_S_,4_S_,6_S_)-6-(iodomethyl)-4-(methoxymethoxy)tetrahydro-2_H_-pyran-2-yl)methyl]tetrahydro-2_H_-pyran-4-yloxy}diphenylsilane If

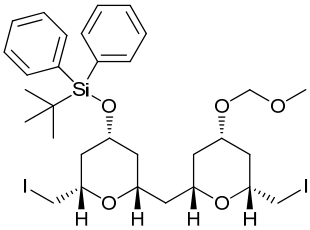


$C_{31}H_{44}I_2O_5Si$
M = 778.10 g/mol

To a solution of alcohol **I'a** (33 mg, 0.045 mmol, 1.0 equiv) in dry CH_2Cl_2 (1 mL) were added diisopropylethylamine (44 µL, 0.27 mmol, 6 equiv) and MOMCl (13 µL, 0.18 mmol, 4.0 equiv) dropwise. The mixture was stirred at rt for 16 h and then quenched by addition of water (2 mL). The layers were separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 95/5 to 90/10) to afford the fully protected *bis*-tetrahydropyran **If** (23 mg, 0.030 mmol, 66%).

$[\alpha]_D^{20}$ = + 14.7 (*c* 0.9, $CHCl_3$).
IR: *ν* 3071, 3000, 2947, 2886, 2858, 1589, 1472, 1428, 1373, 1216, 1186, 1148, 1111, 1078, 1039, 916, 828, 757, 703 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.67-7.64 (m, 4H), 7.45-7.35 (m, 6H), 4.67 (d_{systAB}, 1H, *J* = 6.9 Hz), 4.64 (d_{systAB}, 1H, *J* = 6.9 Hz), 4.06 (m, 1H), 4.00 (m, 1H), 3.85 (m, 1H), 3.76 (m, 1H), 3.51 (m, 1H), 3.36 (s, 3H), 3.20 (m, 1H), 3.15-3.05 (m, 4H), 1.97-1.88 (m, 2H), 1.78-1.69 (m, 2H), 1.53 (dd, 1H, *J* = 9.5 Hz, *J* = 3.2 Hz), 1.49 (dd, 1H, *J* = 9.5 Hz, *J* = 3.2 Hz), 1.36-1.19 (m, 4H), 1.04 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 135.7 (4d), 134.2 (s), 134.1 (s), 129.7 (2d), 127.6 (4d), 94.9 (t), 74.8 (d), 71.9 (d), 71.8 (d), 69.8 (d), 69.2 (d), 69.1 (d), 55.5 (q), 42.2 (t), 41.5 (t), 41.1 (t), 36.5 (t), 36.3 (t), 26.9 (3q), 19.1 (s), 10.1 (t), 9.3 (t).
HRMS (ESI): Calculated for $C_{31}H_{44}I_2O_5SiNa$ $[M + Na]^+$: 801.0940, found: 801.0943.

tert-Butyl{(2_S_,4_R_,6_S_)-2-(iodomethyl)-6-[((2_R_,4_S_,6_R_)-6-(iodomethyl)-4-(methoxymethoxy)tetrahydro-2_H_-pyran-2-yl]methyl)tetrahydro-2_H_-pyran-4-yloxy}diphenylsilane Ig

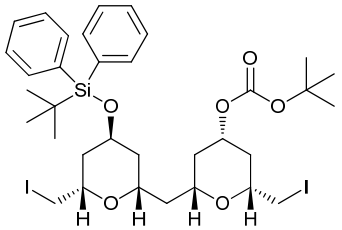


$C_{31}H_{44}I_2O_5Si$
M = 778.10 g/mol

To a solution of alcohol **Ib** (72 mg, 0.098 mmol, 1.0 equiv) in dry CH_2Cl_2 (2.2 mL) were added diisopropylethylamine (0.1 mL, 0.605 mmol, 6.2 equiv) and MOMCl (30 µL, 0.395 mmol, 4.0 equiv) dropwise. The mixture was stirred at rt for 18 h and then quenched by addition of water (4 mL). The layers were separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed with water, dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 90/10) to afford the fully protected *bis*-tetrahydropyran **Ig** (55 mg, 0.071 mmol, 72%).

$[\alpha]_D^{20}$ = + 5.9 (*c* 2.2, $CHCl_3$).
IR: *ν* 3071, 3011, 2949, 2885, 2857, 1589, 1472, 1428, 1375, 1216, 1187, 1142, 1112, 1039, 824, 756, 703 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.69-7.64 (m, 4H), 7.47-7.35 (m, 6H), 4.67 (s, 2H), 3.83-3.70 (m, 2H), 3.47 (m, 1H), 3.35 (s, 3H), 3.41-3.25 (m, 2H), 3.21-3.09 (m, 5H), 2.19 (m, 1H), 1.99-1.89 (m, 3H), 1.74 (m, 1H), 1.50 (m, 1H), 1.34-1.23 (m, 2H), 1.20 (dd_{systAB}, 1H, *J* = 11.5 Hz, *J* = 5.7 Hz), 1.14 (dd_{systAB}, 1H, *J* = 11.1 Hz, *J* = 6.1 Hz), 1.05 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 135.8 (4d), 134.2 (2s), 129.8 (2d), 127.7 (4d), 94.4 (t), 75.1 (2d), 72.6 (d), 72.5 (d), 72.3 (d), 69.1 (d), 55.4 (q), 41.2 (t), 41.1 (t), 40.5 (t), 38.2 (t), 37.6 (t), 27.0 (3q), 19.1 (s), 9.2 (t), 8.9 (t).
HRMS (ESI): Calculated for $C_{31}H_{44}I_2O_5SiNa$ $[M + Na]^+$: 801.0940, found: 801.0942.

tert-Butyl {(2*R*,4*S*,6*R*)-2-[(2*S*,4*S*,6*S*)-4-(*tert*-butyldiphenylsilyl)oxy-6-(iodomethyl)tetrahydro-2H-pyran-2-yl]methyl-6-(iodomethyl)tetrahydro-2*H*-pyran-4-yl} carbonate Ih



$C_{34}H_{48}I_2O_6Si$
M = 834.64 g/mol

To a solution of alcohol **Id** (65 mg, 0.088 mmol, 1.0 equiv) in dry CH_2Cl_2 (2.0 mL) cooled to 0 °C were added triethylamine (61 µL, 0.44 mmol, 5.0 equiv), DMAP (13 mg, 0.11 mmol, 1.2 equiv) and Boc_2O (0.1 mL, 0.47 mmol, 5.3 equiv) dropwise. The mixture was allowed to reach rt and stirred for 14 h. The reaction was quenched by addition of an aqueous solution of HCl (10 % in weight, 2 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 90/10) to afford the protected *bis*-tetrahydropyran **Ih** (59 mg, 0.071 mmol, 80%) as a yellow oil.

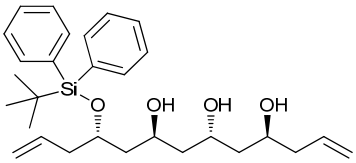
$[\alpha]_D^{20}$ = − 5.9 (*c* 1.2, $CHCl_3$).
IR: *ν* 3071, 2930, 2857, 1739, 1589, 1473, 1428, 1369, 1281, 1255, 1159, 1108, 1083, 1039, 756, 703 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.66-7.61 (m, 4H), 7.46-7.35 (m, 6H), 4.76 (m, 1H), 4.21 (m, 1H), 4.13 (m, 1H), 3.92 (m, 1H), 3.62 (m, 1H), 3.37 (m, 1H), 3.15 (d, 2H, *J* = 11.8 Hz), 3.14 (d, 2H, *J* = 12.1 Hz), 2.31 (m, 1H), 2.09 (m, 1H), 1.90 ($quint_{app}$, 1H, *J* = 7.2 Hz), 1.78 (br d, 1H, *J* = 13.0 Hz), 1.50 (s, 9H), 1.55-1.40 (m, 2H), 1.42-1.20 (m, 4H), 1.08 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.8 (s), 135.8 (2d), 135.7 (2d), 133.9 (2s), 129.8 (2d), 127.8 (2d), 127.7 (2d), 82.4 (s), 74.7 (d), 72.7 (d), 72.5 (d), 71.7 (d), 69.0 (d), 66.0 (d), 41.6 (t), 38.7 (t), 38.4 (t), 37.1 (t), 36.5 (t), 27.8 (3q), 27.1 (3q), 19.3 (s), 10.3 (t), 8.4 (t).
HRMS (ESI): Calculated for $C_{34}H_{48}I_2O_6SiNa$ $[M + Na]^+$: 857.1202, found: 857.1206.

General procedure for the opening of the *bis*-tetrahydropyrans

To a solution of iodinated *bis*-tetrahydropyran (1.0 equiv) in pure ethanol (c = 0.05 M) were added activated zinc (30 equiv) and NH_4Cl (10 equiv). The mixture was heated at 120 °C in a sealed vial until no more evolution could be visible by TLC analysis, then diluted with EtOAc, filtered through a pad of Celite® and concentrated under *vacuum*. The crude material was then purified by column chromatography on silica gel to afford the protected tetraol as a colorless oil.

(4*S*,6*R*,8*S*,10*S*)-10-[(*tert*-Butyldiphenylsilyl)oxy]trideca-1,12-diene-4,6,8-triol 4a

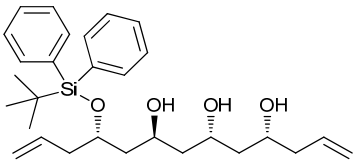


$C_{29}H_{42}O_4Si$
M = 482.29 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **Ia** (29 mg, 0.04 mmol, 1.0 equiv) and the monoprotected tetraol **4a** (12 mg, 0.025 mmol, 63%) was isolated after purification by column chromatography on silica gel (petroleum ether/EtOAc = 7/3 to 6/4).

$[\alpha]_D^{20}$ = + 10.6 (c 0.66, $CHCl_3$).
IR: ν 3344, 3073, 2932, 2858, 1641, 1472, 1428, 1363, 1109, 1076, 997, 910, 822, 735, 703 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73-7.67 (m, 4H), 7.49-7.37 (m, 6H), 5.83 (m, 1H), 5.50 (m, 1H), 5.13 (d_{app}, 1H, J = 17.8 Hz), 5.12 (d_{app}, 1H, J = 9.8 Hz), 4.92 (d_{app}, 1H, J = 10.2 Hz), 4.86 (d_{app}, 1H, J = 17.1 Hz), 4.30 (m, 1H), 4.24 (m, 1H), 4.06-3.94 (m, 2H), 3.57 (br s, 1H, OH), 3.43 (br s, 1H, OH), 2.77 (br s, 1H, OH), 2.38 (m, 1H), 2.27 (t, 2H, J = 6.7 Hz), 2.23 (m, 1H), 1.81 (ddd, 1H, J = 14.3 Hz, J = 10.5 Hz, J = 3.7 Hz), 1.72-1.60 (m, 2H), 1.58-1.46 (m, 3H), 1.07 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.0 (2d), 135.9 (2d), 135.0 (d), 134.0 (d), 133.4 (s), 133.1 (s), 130.03 (d), 130.0 (d), 127.8 (2d), 127.7 (2d), 117.8 (t), 117.6 (t), 72.0 (d), 68.3 (d), 66.5 (d), 66.2 (d), 42.7 (t), 42.1 (t), 42.0 (t), 40.5 (t), 40.4 (t), 27.0 (3q), 19.2 (s).
HRMS (ESI): Calculated for $C_{29}H_{42}O_4SiNa$ $[M + Na]^+$: 505.2745, found: 505.2742.

(4*R*,6*R*,8*S*,10*S*)-10-[(*tert*-Butyldiphenylsilyl)oxy]trideca-1,12-diene-4,6,8-triol 4'a

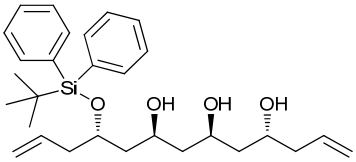


$C_{29}H_{42}O_4Si$
M = 482.29 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **I'a** (21 mg, 0.029 mmol, 1.0 equiv) and the monoprotected tetraol **4'a** (9.5 mg, 0.020 mmol, 69%) was isolated after purification by column chromatography on silica gel (petroleum ether/EtOAc = 7/3 to 6/4).

$[\alpha]_D^{20}$ = + 3.7 (*c* 0.47, $CHCl_3$).
IR: *ν* 3383, 3073, 2932, 2858, 1641, 1590, 1472, 1428, 1109, 1078, 998, 912, 822, 737, 703 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.72-7.67 (m, 4H), 7.49-7.37 (m, 6H), 5.83 (m, 1H), 5.52 (m, 1H), 5.12 (d_{app}, 1H, *J* = 17.0 Hz), 5.11 (d_{app}, 1H, *J* = 10.9 Hz), 4.92 (d_{app}, 1H, *J* = 10.3 Hz), 4.87 (d_{app}, 1H, *J* = 17.1 Hz), 4.29 (m, 1H), 4.12 (m, 1H), 4.02 (m, 1H), 3.97-3.88 (m, 2H), 3.60 (br s, 1H), 3.43 (br s, 1H), 2.38 (m, 1H), 2.27-2.18 (m, 3H), 1.77 (ddd, 1H, *J* = 14.2 Hz, *J* = 10.4 Hz, *J* = 3.6 Hz), 1.61-1.45 (m, 5H), 1.07 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 136.0 (2d), 135.9 (2d), 134.7 (d), 134.0 (d), 133.4 (s), 133.2 (s), 130.04 (d), 130.01 (d), 127.84 (2d), 127.75 (2d), 117.8 (t), 117.6 (t), 71.8 (2d), 70.5 (d), 66.0 (d), 43.1 (t), 42.4 (t), 42.2 (t), 40.7 (t), 40.6 (t), 27.0 (3q), 19.2 (s).
HRMS (ESI): Calculated for $C_{29}H_{42}O_4SiNa$ $[M + Na]^+$: 505.2745, found: 505.2743.

(4*R*,6*S*,8*S*,10*S*)-10-[(*tert*-Butyldiphenylsilyl)oxy]trideca-1,12-diene-4,6,8-triol 4b

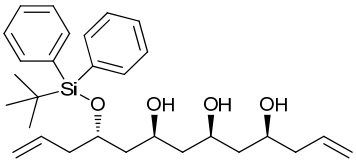


$C_{29}H_{42}O_4Si$
M = 482.29 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **Ib** (29 mg, 0.040 mmol, 1.0 equiv) and the monoprotected tetraol **4b** (12 mg, 0.025 mmol, 63%) was isolated after purification by column chromatography on silica gel (petroleum ether/EtOAc = 7/3 to 6/4).

$[\alpha]_D^{20}$ = + 7.7 (*c* 0.68, $CHCl_3$).
IR: *ν* 3383, 3073, 2932, 2858, 1641, 1428, 1363, 1106, 997, 910, 822, 735, 702, 611 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.72-7.67 (m, 4H), 7.49-7.36 (m, 6H), 5.84 (m, 1H), 5.48 (m, 1H), 5.15-5.08 (m, 2H), 4.91 (d_{app}, 1H, *J* = 10.2 Hz), 4.85 (d_{app}, 1H, *J* = 17.2 Hz), 4.25-4.16 (m, 3H), 4.02-3.95 (m, 2H), 3.69 (br s, 1H, OH), 3.20 (br s, 1H, OH), 2.36 (m, 1H), 2.30-2.16 (m, 3H), 1.75-1.50 (m, 5H), 1.36 (d_{app}, 1H, *J* = 14.4 Hz), 1.07 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 136.0 (2d), 135.9 (2d), 135.1 (d), 133.9 (d), 133.4 (s), 133.0 (s), 130.1 (d), 130.0 (d), 127.9 (2d), 127.7 (2d), 117.7 (t), 117.5 (t), 71.9 (d), 70.4 (d), 69.8 (d), 68.1 (d), 43.1 (t), 42.14 (t), 42.07 (t), 41.4 (t), 40.6 (t), 27.0 (3q), 19.2 (s).
HRMS (ESI): Calculated for $C_{29}H_{42}O_4SiNa$ $[M + Na]^+$: 505.2745, found: 505.2741.

(4*S*,6*S*,8*S*,10*S*)-10-[(*tert*-Butyldiphenylsilyl)oxy]trideca-1,12-diene-4,6,8-triol 4'b

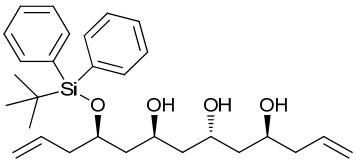


$C_{29}H_{42}O_4Si$
M = 482.29 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **I'b** (44 mg, 0.060 mmol, 1.0 equiv) to give the monoprotected tetraol **4'b** (23 mg, 0.048 mmol, 80%) after purification by column chromatography on silica gel (petroleum ether/EtOAc = 7/3 to 6/4).

[α] $_D^{20}$ = + 12.8 (*c* 0.8, $CHCl_3$).
IR: *ν* 3420, 3073, 3012, 2933, 2859, 1641, 1428, 1216, 1110, 998, 918, 756, 703 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.73-7.66 (m, 4H), 7.49-7.34 (m, 6H), 5.84 (m, 1H), 5.48 (m, 1H), 5.15-5.07 (m, 2H), 4.91 (d_{app}, 1H, *J* = 10.1 Hz), 4.85 (d_{app}, 1H, *J* = 17.1 Hz), 4.42 (br s, 1H, OH), 4.20 (m, 1H), 4.08 (m, 1H), 3.99 (m, 1H), 3.93 (m, 1H), 3.78 (br s, 1H, OH), 3.70 (br s, 1H, OH), 2.36 (m, 1H), 2.30-2.12 (m, 3H), 1.71 (m, 1H), 1.60-1.45 (m, 4H), 1.38 (m, 1H), 1.07 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 136.0 (2d), 135.9 (2d), 134.9 (d), 133.9 (d), 133.4 (s), 133.0 (s), 130.1 (d), 130.0 (d), 127.8 (2d), 127.7 (2d), 117.7 (t), 117.5 (t), 73.4 (d), 71.9 (d), 71.5 (d), 69.6 (d), 44.1 (t), 42.8 (t), 42.3 (t), 41.3 (t), 40.6 (t), 27.0 (3q), 19.2 (s).
HRMS (ESI): Calculated for $C_{29}H_{42}O_4SiNa$ $[M + Na]^+$: 505.2745, found: 505.2742.

(4*S*,6*R*,8*S*,10*R*)-10-[(*tert*-Butyldiphenylsilyl)oxy]trideca-1,12-diene-4,6,8-triol 4c

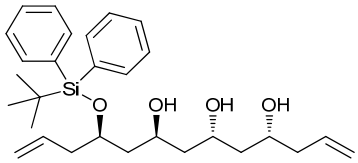


$C_{29}H_{42}O_4Si$
M = 482.29 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **Ic** (48 mg, 0.065 mmol, 1.0 equiv) and the monoprotected tetraol **4c** (21 mg, 0.044 mmol, 67%) was isolated after purification by column chromatography on silica gel (petroleum ether/EtOAc = 7/3 to 6/4).

[α] $_D^{20}$ = − 23.9 (*c* 1.0, $CHCl_3$).
IR: *ν* 3299, 3072, 2931, 2857, 1641, 1472, 1427, 1362, 1106, 1066, 998, 909, 822, 734, 701, 611 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.75-7.69 (m, 4H), 7.48-7.37 (m, 6H), 5.83 (m, 1H), 5.52 (m, 1H), 5.13 (d_{app}, 1H, *J* = 17.7 Hz), 5.12 (d_{app}, 1H, *J* = 9.9 Hz), 4.91 (d, 1H, *J* = 10.2 Hz), 4.78 (d, 1H, *J* = 17.1 Hz), 4.24 (m, 1H), 4.15 (m, 1H), 4.03-3.95 (m, 2H), 3.68 (br s, 1H, OH), 3.54 (br s, 1H, OH), 2.83 (br s, 1H, OH), 2.27 (t, 2H, *J* = 6.7 Hz), 2.13 (t, 2H, *J* = 6.5 Hz), 1.81-1.59 (m, 4H), 1.53 (ddd_{systAB}, 1H, *J* = 14.3 Hz, *J* = 8.5 Hz, *J* = 3.2 Hz), 1.45 (ddd_{systAB}, 1H, *J* = 14.4 Hz, *J* = 7.2 Hz, *J* = 2.5 Hz), 1.05 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 135.9 (4d), 134.9 (d), 133.9 (d), 133.2 (2s), 130.0 (d), 129.8 (d), 127.8 (2d), 127.6 (2d), 117.9 (t), 117.7 (t), 73.8 (d), 68.8 (d), 68.2 (d), 66.4 (d), 42.5 (t), 42.4 (t), 42.14 (t), 42.06 (t), 42.02 (t), 27.0 (3q), 19.3 (s).
HRMS (ESI): Calculated for $C_{29}H_{42}O_4SiNa$ $[M + Na]^+$: 505.2745, found: 505.2742.

(4*R*,6*R*,8*S*,10*R*)-10-[(*tert*-Butyldiphenylsilyl)oxy]trideca-1,12-diene-4,6,8-triol 4'c

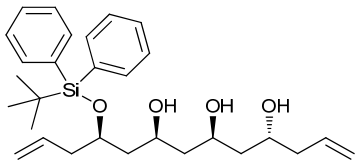


$C_{29}H_{42}O_4Si$
M = 482.29 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **I'c** (55 mg, 0.075 mmol, 1.0 equiv) and the monoprotected tetraol **4'c** (28 mg, 0.058 mmol, 77%) was isolated after purification by column chromatography on silica gel (petroleum ether/EtOAc = 65/35 to 6/4).

$[\alpha]_D^{20}$ = − 27.4 (*c* 1.3, $CHCl_3$).
IR: *ν* 3364, 3073, 2932, 2858, 1641, 1590, 1472, 1428, 1328, 1217, 1110, 1080, 998, 917, 822, 757, 703 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.74-7.69 (m, 4H), 7.48-7.37 (m, 6H), 5.82 (m, 1H), 5.54 (m, 1H), 5.15-5.08 (m, 2H), 4.91 (d_{app}, 1H, *J* = 10.2 Hz), 4.79 (d_{app}, 1H, *J* = 17.1 Hz), 4.19-4.10 (m, 2H), 4.07 (br s, 1H, OH), 4.00 (m, 1H), 3.92 (m, 1H), 3.63-3.58 (br s, 2H, OH), 2.24 (t_{app}, 2H, *J* = 6.4 Hz), 2.14 (t, 2H, *J* = 6.4 Hz), 1.75 (m, 1H), 1.64-1.47 (m, 5H), 1.06 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 135.9 (4d), 134.6 (d), 133.9 (d), 133.3 (2s), 130.0 (d), 129.8 (d), 127.8 (2d), 127.6 (2d), 117.9 (t), 117.6 (t), 73.6 (d), 71.8 (d), 70.4 (d), 68.4 (d), 43.0 (t), 42.6 (t), 42.4 (t), 42.2 (t), 42.0 (t), 27.0 (3q), 19.3 (s).
HRMS (ESI): Calculated for $C_{29}H_{42}O_4SiNa$ $[M + Na]^+$: 505.2745, found: 505.2743.

(4*R*,6*S*,8*S*,10*R*)-10-[(*tert*-Butyldiphenylsilyl)oxy]trideca-1,12-diene-4,6,8-triol 4d

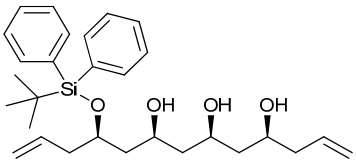


$C_{29}H_{42}O_4Si$
M = 482.29 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **Id** (32 mg, 0.044 mmol, 1.0 equiv) to give the monoprotected tetraol **4d** (16 mg, 0.033 mmol, 76%) after purification by column chromatography on silica gel (petroleum ether/EtOAc = 7/3 to 65/35).

$[\alpha]_D^{20}$ = − 25.2 (*c* 0.75, $CHCl_3$).
IR: *ν* 3358, 3072, 2932, 2857, 1641, 1428, 1362, 1110, 1090, 998, 915, 822, 739, 703, 612 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.73-7.68 (m, 4H), 7.48-7.36 (m, 6H), 5.83 (m, 1H), 5.54 (m, 1H), 5.16-5.08 (m, 2H), 4.92 (d_{app}, 1H, *J* = 10.2 Hz), 4.80 (d_{app}, 1H, *J* = 17.3 Hz), 4.15 (m, 1H), 4.06 (m, 1H), 4.00-3.93 (m, 2H), 2.32-2.21 (m, 2H), 2.13 (t_{app}, 2H, *J* = 6.6 Hz), 1.73-1.53 (m, 5H), 1.35 (m, 1H), 1.05 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 135.88 (2d), 135.86 (2d), 134.9 (d), 133.9 (d), 133.3 (2s), 130.0 (d), 129.8 (d), 127.8 (2d), 127.6 (2d), 117.74 (t), 117.67 (t), 73.1 (d), 71.8 (d), 70.4 (d), 68.1 (d), 43.5 (t), 42.9 (t), 42.12 (t), 42.08 (t), 42.07 (t), 27.0 (3q), 19.3 (s).
HRMS (ESI): Calculated for $C_{29}H_{42}O_4SiNa$ $[M + Na]^+$: 505.2745, found: 505.2742.

(4*S*,6*S*,8*S*,10*R*)-10-[(*tert*-Butyldiphenylsilyl)oxy]trideca-1,12-diene-4,6,8-triol 4'd

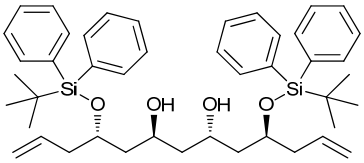


$C_{29}H_{42}O_4Si$
M = 482.29 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyrane **I'd** (52 mg, 0.071 mmol, 1.0 equiv) to give the monoprotected tetraol **4'd** (24 mg, 0.050 mmol, 70%) after purification by column chromatography on silica gel (petroleum ether/EtOAc = 7/3 to 65/35).

[α] $_D^{20}$ = − 19.8 (*c* 0.55, $CHCl_3$).
IR: *ν* 3385, 3072, 2932, 2857, 1641, 1592, 1428, 1379, 1325, 1189, 1175, 1109, 1085, 998, 916, 822, 740, 703, 654, 612 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.73-7.66 (m, 4H), 7.47-7.36 (m, 6H), 5.83 (m, 1H), 5.55 (m, 1H), 5.12 (d_{app}, 1H, *J* = 15.6 Hz), 5.12 (d_{app}, 1H, *J* = 11.6 Hz), 4.92 (d_{app}, 1H, *J* = 10.2 Hz), 4.81 (d_{app}, 1H, *J* = 16.8 Hz), 4.38 (br s, 1H, OH), 4.07-3.87 (m, 4H), 3.61 (br s, 1H, OH), 3.55 (br s, 1H, OH), 2.28-2.20 (m, 2H), 2.14 (t_{app}, 2H, *J* = 6.4 Hz), 1.72-1.55 (m, 2H), 1.54-1.43 (m, 3H), 1.34 (m, 1H), 1.05 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 135.89 (2d), 135.87 (2d), 134.7 (d), 133.9 (d), 133.3 (2s), 130.0 (d), 129.8 (d), 127.8 (2d), 127.6 (2d), 117.8 (t), 117.7 (t), 73.4 (d), 73.0 (d), 71.6 (d), 71.5 (d), 43.7 (t), 43.5 (t), 42.8 (t), 42.3 (t), 42.1 (t), 27.0 (3q), 19.3 (s).
HRMS (ESI): Calculated for $C_{29}H_{42}O_4SiNa$ $[M + Na]^+$: 505.2745, found: 505.2742.

(5*S*,7*S*,9*S*,11*S*)-5,11-Diallyl-2,2,14,14-tetramethyl-3,3,13,13-tetraphenyl-4,12-dioxa-3,13-disilapentadecane-7,9-diol 4e



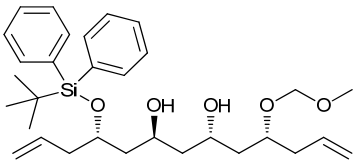
$C_{45}H_{60}O_4Si_2$
M = 720.40 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **Ie** (115 mg, 0.12 mmol, 1.0 equiv) and the protected tetraol **4e** (63 mg, 0.087 mmol, 74%) was isolated after purification by column chromatography on silica gel (petroleum ether/EtOAc = 9/1).

[α] $_D^{20}$ = + 13.6 (*c* 0.53, $CHCl_3$).
IR: *ν* 3074, 3072, 2931, 2857, 1640, 1590, 1472, 1428, 1363, 1189, 1110, 1080, 998, 913, 822, 739, 702, 611 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.76-7.70 (m, 8H), 7.48-7.38 (m, 12H), 5.58 (m, 2H), 4.94 (dd, 2H, *J* = 10.2 Hz, *J* = 1.9 Hz), 4.87 (dd, 2H, *J* = 17.1 Hz, *J* = 1.9 Hz), 4.20 (m, 2H), 4.05 (m, 2H), 3.22 (d, 2H, *J* = 2.3 Hz, OH), 2.35 (m, 2H), 2.20 (m, 2H), 1.71 (ddd, 2H, *J* = 14.3 Hz, *J* = 10.2 Hz, *J* = 4.0 Hz), 1.51 (ddd, 2H, *J* = 14.3 Hz, *J* = 5.9 Hz, *J* = 2.1 Hz), 1.44 (t, 2H, *J* = 6.0 Hz), 1.09 (s, 18H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.01 (4d), 135.99 (4d), 134.3 (2d), 133.9 (2s), 133.5 (2s), 129.9 (2d), 129.8 (2d), 127.7 (4d), 127.6 (4d), 117.4 (2t), 71.7 (2d), 65.6 (2d), 44.0 (t), 41.8 (2t), 41.0 (2t), 27.1 (6q), 19.3 (2s).
HRMS (ESI): Calculated for $C_{45}H_{60}O_4Si_2Na$ $[M + Na]^+$: 743.3922, found: 743.3923.

(5*R*,7*S*,9*S*,11*S*)-5,11-Diallyl-14,14-dimethyl-13,13-diphenyl-2,4,12-trioxa-13-silapentadecane-7,9-diol 4f

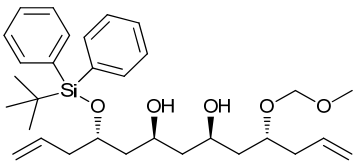


$C_{31}H_{46}O_5Si$
M = 526.31 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **If** (10 mg, 0.013 mmol, 1.0 equiv) and the protected tetraol **4f** (5.5 mg, 0.010 mmol, 81%) was isolated after purification by column chromatography on silica gel (petroleum ether/EtOAc = 9/1 to 8/2).

$[\alpha]_D^{20}$ = − 12.9 (*c* 0.34, $CHCl_3$).
IR: *ν* 3485, 3074, 2933, 2859, 1641, 1472, 1428, 1364, 1106, 1038, 910, 733, 704 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73-7.67 (m, 4H), 7.47-7.36 (m, 6H), 5.78 (m, 1H), 5.52 (m, 1H), 5.09 (d_{app}, 1H, J = 16.3 Hz), 5.08 (d_{app}, 1H, J = 10.9 Hz), 4.90 (d_{app}, 1H, J = 10.3 Hz), 4.84 (d_{app}, 1H, J = 17.4 Hz), 4.74 (d_{systAB}, 1H, J = 6.9 Hz), 4.66 (d_{systAB}, 1H, J = 6.9 Hz), 4.25 (m, 1H), 4.08-4.00 (m, 2H), 3.85 (m, 1H), 3.52 (br s, 1H, OH), 3.47 (br s, 1H, OH), 3.39 (s, 3H), 2.40-2.32 (m, 3H), 2.18 (m, 1H), 1.78-1.67 (m, 2H), 1.60-1.43 (m, 4H), 1.07 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.0 (4d), 134.2 (d), 134.0 (d), 133.7 (s), 133.4 (s), 129.88 (d), 129.85 (d), 127.7 (2d), 127.6 (2d), 117.7 (t), 117.4 (t), 95.3 (t), 76.7 (d), 71.9 (d), 68.0 (d), 65.4 (d), 55.9 (q), 43.8 (t), 41.4 (t), 41.3 (t), 40.7 (t), 38.9 (t), 27.0 (3q), 19.2 (s).
HRMS (ESI): Calculated for $C_{31}H_{46}O_5SiNa$ $[M + Na]^+$: 549.3007, found: 549.3000.

(5*R*,7*R*,9*S*,11*S*)-5,11-Diallyl-14,14-dimethyl-13,13-diphenyl-2,4,12-trioxa-13-silapentadecane-7,9-diol 4g



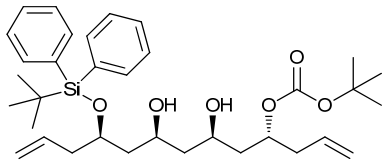
$C_{31}H_{46}O_5Si$
M = 526.31 g/mol

The previously described general procedure was applied to the *bis*-tetrahydropyran **Ig** (42 mg, 0.054 mmol, 1.0 equiv) to give the protected tetraol **4g** (24 mg, 0.046 mmol, 84%) after purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 9/1 to 8/2).

$[\alpha]_D^{20}$ = − 8.2 (*c* 0.9, $CHCl_3$).

IR: ν 3473, 3073, 3012, 2933, 2858, 1641, 1472, 1428, 1364, 1216, 1147, 1106, 1039, 917, 756, 704 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73-7.67 (m, 4H), 7.47-7.36 (m, 6H), 5.80 (m, 1H), 5.54 (m, 1H), 5.13-5.05 (m, 2H), 4.92 (d_{app}, 1H, J = 10.1 Hz), 4.86 (d_{app}, 1H, J = 17.1 Hz), 4.72 (d_{systAB}, 1H, J = 6.7 Hz), 4.69 (d_{systAB}, 1H, J = 6.7 Hz), 4.13 (m, 1H), 4.05-3.97 (m, 2H), 3.93-3.85 (m, 2H), 3.70 (br s, 1H, OH), 3.41 (s, 3H), 2.37-2.26 (m, 3H), 2.19 (m, 1H), 1.72-1.63 (m, 2H), 1.59-1.47 (m, 3H), 1.35 (m, 1H), 1.06 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.0 (2d), 135.9 (2d), 134.4 (d), 134.2 (d), 133.8 (s), 133.4 (s), 129.9 (d), 129.8 (d), 127.7 (2d), 127.6 (2d), 117.5 (t), 117.4 (t), 96.5 (t), 74.6 (d), 71.5 (d), 69.1 (d), 68.4 (d), 55.8 (q), 44.0 (t), 42.3 (t), 42.1 (t), 41.0 (t), 39.7 (t), 27.0 (3q), 19.3 (s).
HRMS (ESI): Calculated for $C_{31}H_{46}O_5SiNa$ $[M + Na]^+$: 549.3007, found: 549.3001.

tert-Butyl [(4_R_,6_R_,8_S_,10_R_)-10-(_tert_-butyldiphenylsilyl)oxy-6,8-dihydroxytrideca-1,12-dien-4-yl] carbonate 4h



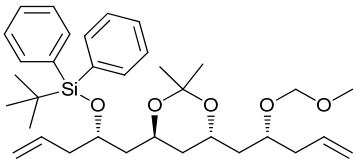
$C_{34}H_{50}O_6Si$
M = 582.84 g/mol

To a solution of iodinated *bis*-tetrahydropyran **Ih** (58 mg, 0.069 mmol, 1.0 equiv) in THF (2 mL) and H_2O (0.4 mL) was added activated zinc (136 mg, 2.08 mmol, 30 equiv). The mixture was heated at 70 °C in a sealed vial for 1 h, and was then filtered through a pad of Celite®. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under *vacuum*. The crude material was purified by column chromatography on silica gel (petroleum ether/EtOAc = 80/20) to afford the protected tetraol **4h** (35 mg, 0.060 mmol, 87%) as a colorless oil.

$[\alpha]_D^{20}$ = − 18.1 (c 1.0, $CHCl_3$).
IR: ν 3470, 3073, 2933, 2858, 1739, 1715, 1642, 1590, 1473, 1428, 1393, 1368, 1282, 1255, 1163, 1110, 998, 917, 823, 742, 704 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.65 (m, 4H), 7.46-7.34 (m, 6H), 5.78 (ddt, 1H, J = 17.1 Hz, J = 10.2 Hz, J = 7.0 Hz), 5.63 (ddt, 1H, J = 17.1 Hz, J = 10.0 Hz, J = 7.1 Hz), 5.14-5.06 (m, 2H), 4.96-4.81 (m, 3H), 4.01-3.88 (m, 2H), 3.89 (br s, 1H, OH), 3.78 (br s, 1H, OH), 3.73 (m, 1H), 2.44-2.29 (m, 2H), 2.24-2.12 (m, 2H), 1.69 (m, 1H), 1.60-1.43 (m, 3H), 1.50 (s, 9H), 1.39 (m, 1H), 1.27 (br d, 1H, J = 15.3 Hz), 1.05 (s, 9H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.4 (s), 135.91 (2d), 135.87 (2d), 134.3 (d), 134.2 (s), 133.6 (s), 133.3 (d), 129.8 (d), 129.7 (d), 127.7 (2d), 127.6 (2d), 118.1 (t), 117.4 (t), 82.5 (s), 73.3 (d), 71.9 (d), 70.4 (d), 68.3 (d), 43.5 (t), 42.9 (t), 42.6 (t), 41.8 (t), 39.3 (t), 27.8 (3q), 27.0 (3q), 19.3 (s).
HRMS (ESI): Calculated for $C_{34}H_{50}O_6SiNa$ $[M + Na]^+$: 605.3269, found: 605.3268.

Synthesis of acetonides 5

tert-Butyl{(*S*)-1-[(4*S*,6*R*)-6-((*R*)-2-(methoxymethoxy)pent-4-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl]pent-4-en-2-yloxy}diphenylsilane 5f

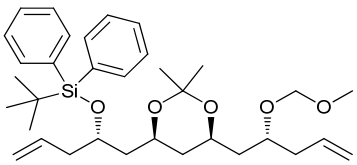


$C_{34}H_{50}O_5Si$
M = 566.34 g/mol

To a solution of diol **4f** (9 mg, 0.017 mmol, 1.0 equiv) in a solution of acetone (0.25 mL) and 2,2-dimethoxypropane (0.13 mL) was added PPTS (1 mg, 0.004 mmol, 0.24 equiv). The reaction mixture was stirred at rt for 4 h, and then quenched by addition of one drop of Et_3N. Evaporation of the solvents and purification of the crude material by column chromatography (petroleum ether/EtOAc = 96/4) gave the acetonide **5f** (8 mg, 0.014 mmol, 83%) as a colorless oil.

[α] $_D^{20}$ = − 9.7 (*c* 0.35, $CHCl_3$).
IR: *ν* 3073, 2931, 2857, 1640, 1428, 1378, 1224, 1105, 1041, 998, 915, 822, 739, 703, 611 cm^{-1}.
^{1}**H NMR** ($CDCl_3$, 400 MHz): *δ* 7.71-7.66 (m, 4H), 7.44-7.34 (m, 6H), 5.87-5.70 (m, 2H), 5.08 (d_{app}, 1H, *J* = 14.7 Hz), 5.07 (d_{app}, 1H, *J* = 12.0 Hz), 4.98 (d_{app}, 1H, *J* = 10.2 Hz), 4.93 (d_{app}, 1H, *J* = 17.3 Hz), 4.64 (d_{systAB}, 1H, *J* = 7.0 Hz), 4.61 (d_{systAB}, 1H, *J* = 7.0 Hz), 3.89 (m, 1H), 3.85-3.75 (m, 2H), 3.67 (m, 1H), 3.36 (s, 3H), 2.38-2.12 (m, 4H), 1.79-1.67 (m, 2H), 1.55-1.47 (m, 2H), 1.43-1.32 (m, 2H), 1.24 (s, 3H), 1.13 (s, 3H), 1.04 (s, 9H).
^{13}**C NMR** ($CDCl_3$, 100 MHz): *δ* 136.0 (2d), 135.9 (2d), 134.7 (d), 134.5 (d), 134.4 (s), 134.3 (s), 129.6 (2d), 127.52 (2d), 127.47 (2d), 117.5 (t), 117.1 (t), 100.0 (s), 95.5 (t), 73.8 (d), 70.4 (d), 63.7 (d), 63.4 (d), 55.6 (q), 43.3 (t), 42.0 (t), 40.3 (t), 38.9 (t), 38.8 (t), 27.0 (3q), 25.0 (q), 24.9 (q), 19.4 (s).
HRMS (ESI): Calculated for $C_{34}H_{50}O_5SiNa$ $[M + Na]^+$: 589.3320, found: 589.3316.

tert-Butyl{(*S*)-1-[(4*S*,6*S*)-6-((*R*)-2-(methoxymethoxy)pent-4-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl]pent-4-en-2-yloxy}diphenylsilane 5g



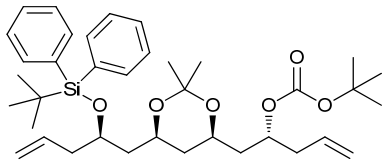
$C_{34}H_{50}O_5Si$
M = 566.34 g/mol

To a solution of diol **4g** (18 mg, 0.034 mmol, 1.0 equiv) in a solution of acetone (0.5 mL) and 2,2-dimethoxypropane (0.25 mL) was added PPTS (1 mg, 0.004 mmol, 0.12 equiv). The reaction mixture was stirred at rt for 15 h, and then quenched by addition of one drop of Et_3N. Evaporation of the solvents and purification of the crude material by column chromatography (petroleum ether/EtOAc = 96/4) gave the acetonide **5g** (17 mg, 0.030 mmol, 88%) as a colorless oil.

[α] $_D^{20}$ = + 5.1 (*c* 0.8, $CHCl_3$).

IR: ν 3073, 2994, 2933, 2858, 1641, 1590, 1473, 1428, 1379, 1198, 1151, 1106, 1042, 916, 756, 704 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.66 (m, 4H), 7.44-7.33 (m, 6H), 5.87-5.66 (m, 2H), 5.08 (d_{app}, 1H, J = 17.2 Hz), 5.07 (d_{app}, 1H, J = 10.2 Hz), 4.96 (d_{app}, 1H, J = 10.2 Hz), 4.90 (d_{app}, 1H, J = 17.2 Hz), 4.67 (d_{systAB}, 1H, J = 6.8 Hz), 4.64 (d_{systAB}, 1H, J = 6.8 Hz), 4.03 (m, 1H), 3.95-3.79 (m, 3H), 3.38 (s, 3H), 2.36-2.23 (m, 2H), 2.22-2.10 (m, 2H), 1.60 (m, 1H), 1.53-1.46 (m, 3H), 1.27 (s, 3H), 1.25 (m, 1H), 1.17 (s, 3H), 1.05 (s, 9H), 1.02 (m, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.0 (2d), 135.9 (2d), 134.6 (d), 134.5 (s), 134.44 (d), 134.41 (s), 129.6 (d), 129.5 (d), 127.5 (4d), 117.3 (t), 117.1 (t), 98.4 (s), 96.3 (t), 73.6 (d), 69.6 (d), 65.7 (d), 65.1 (d), 55.6 (q), 43.8 (t), 42.2 (t), 41.9 (t), 39.9 (t), 38.0 (t), 30.3 (q), 27.1 (3q), 19.8 (q), 19.4 (s).
HRMS (ESI): Calculated for $C_{34}H_{50}O_5SiNa$ $[M + Na]^+$: 589.3320, found: 589.3317.

tert-Butyl {(_R_)-1-[(4_R_,6_S_)-6-((_R_)-2-(_tert_-butyldiphenylsilyloxy)pent-4-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl]pent-4-en-2-yl} carbonate 5h



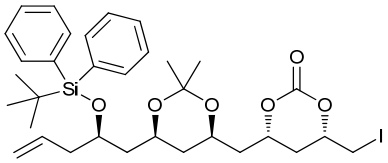
$C_{37}H_{54}O_6Si$
M = 622.91 g/mol

To a solution of diol **4h** (34 mg, 0.058 mmol, 1.0 equiv) in a mixture of acetone (1 mL) and 2,2-dimethoxypropane (0.5 mL) was added PPTS (1.5 mg, 0.006 mmol, 0.1 equiv). The mixture was stirred at rt for 3 h, and then quenched by addition of a drop of Et_3N. Evaporation of the solvents and purification of the crude material by column chromatography (petroleum ether/EtOAc = 96/4) gave the acetonide **5h** (32 mg, 0.051 mmol, 88%) as a colorless oil.

$[\alpha]_D^{20}$ = − 27.3 (c 0.8, $CHCl_3$).
IR: ν 3073, 2979, 2933, 2858, 1741, 1642, 1590, 1473, 1429, 1368, 1277, 1254, 1167, 1106, 998, 980, 916, 822, 741, 704 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.64 (m, 4H), 7.46-7.36 (m, 6H), 5.82-5.70 (m, 2H), 5.12-4.90 (m, 5H), 3.89-3.80 (m, 2H), 3.57 (m, 1H), 2.37-2.27 (m, 3H), 2.23 (m, 1H), 1.73 (ddd, 1H, J = 13.6 Hz, J = 7.4 Hz, J = 5.6 Hz), 1.49 (s, 9H), 1.50-1.40 (m, 3H), 1.28 (s, 3H), 1.20 (s, 3H), 1.06 (s, 9H), 0.82-0.74 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.2 (s), 136.0 (2d), 135.9 (2d), 134.6 (d), 134.1 (2s), 133.5 (d), 129.7 (2d), 127.7 (2d), 127.6 (2d), 117.8 (t), 117.3 (t), 98.4 (q), 81.5 (s), 72.5 (d), 69.2 (d), 65.9 (d), 64.9 (d), 42.9 (t), 41.9 (t), 40.5 (t), 39.5 (t), 36.7 (t), 30.1 (q), 27.8 (3q), 27.0 (3q), 19.4 (q), 19.4 (s).
HRMS (ESI): Calculated for $C_{37}H_{54}O_6SiNa$ $[M + Na]^+$: 645.3582, found: 645.3587.

<u>Differentiation of the terminal olefins</u>

(4_S_,6_S_)-4-{[(4_R_,6_S_)-6-((_R_)-2-(_tert_-Butyldiphenylsilyloxy)pent-4-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl]methyl}-6-(iodomethyl)-1,3-dioxan-2-one 6

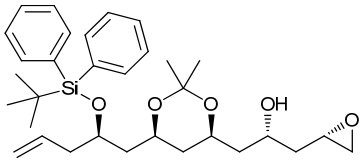


$C_{33}H_{45}IO_6Si$
M = 692.70 g/mol

To a solution of diene **5h** (15 mg, 0.024 mmol, 1.0 equiv) in dry CH_3CN (1.7 mL) cooled to −40 °C was added NIS (54 mg, 0.24 mmol, 10 equiv). The mixture was warmed to 0 °C and then progressively allowed to reach rt. After 4.5 h, the reaction was quenched by addition of a saturated aqueous solution of $Na_2S_2O_3$. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under *vacuum*. Purification of the crude material by column chromatography on silica gel (petroleum ether/EtOAc = 80/20) afforded the iodocarbonate **6** as a mixture of diastereomers [*cis*/*trans* (C2/C4) = 9:1, 12 mg, 0.017 mmol, 72%] and as a yellow oil.

IR (mixture of diastereomers *cis*/*trans* (C2/C4)): *ν* 3071, 2993, 2932, 2858, 1747, 1640, 1589, 1428, 1379, 1246, 1170, 1110, 756, 704 cm^{-1}.
^{1}H NMR ($CDCl_3$, 400 MHz, *cis* major diastereomer): *δ* 7.72-7.64 (m, 4H), 7. 47-7.36 (m, 6H), 5.78 (ddt, 1H, *J* = 17.2 Hz, *J* = 10.3 Hz, *J* = 7.0 Hz), 5.04-4.94 (m, 2H), 4.63 (m, 1H), 4.44 (m, 1H), 3.92-3.78 (m, 3H), 3.40 (dd_{systAB}, 1H, *J* = 10.5 Hz, *J* = 4.2 Hz), 3.26 (dd_{systAB}, 1H, *J* = 10.6 Hz, *J* = 7.5 Hz), 2.40-2.32 (m, 2H), 2.25 (m, 1H), 1.75 (m, 1H), 1.63 (m, 1H), 1.54-1.48 (m, 2H), 1.44 (ddd, 1H, *J* = 13.8 Hz, *J* = 7.6 Hz, *J* = 4.1 Hz), 1.28 (s, 3H), 1.25 (s, 3H), 1.06 (s, 9H), 0.78-0.72 (m, 2H).
^{13}C NMR ($CDCl_3$, 100 MHz, *cis* major diastereomer): *δ* 148.4 (s), 136.0 (2d), 135.9 (2d), 134.5 (d), 134.1 (s), 134.0 (s), 129.8 (d), 129.7 (d), 127.8 (2d), 127.6 (2d), 117.4 (t), 98.6 (q), 77.2 (d), 74.6 (d), 69.1 (d), 65.7 (d), 64.0 (d), 42.9 (t), 42.1 (t), 42.0 (t), 36.6 (t), 33.9 (t), 30.1 (q), 27.0 (3q), 19.9 (q), 19.4 (s), 5.3 (t).
HRMS (ESI): Calculated for $C_{33}H_{45}IO_6SiNa$ $[M + Na]^+$: 715.1922, found: 715.1927.

(*R*)-1-{(4*S*,6*S*)-6-[(*R*)-2-(*tert*-Butyldiphenylsilyl)oxypent-4-en-1-yl]-2,2-dimethyl-1,3-dioxan-4-yl}-3-[(*S*)-oxiran-2-yl]propan-2-ol 7



$C_{32}H_{46}O_5Si$
M = 538.79 g/mol

To a solution of iodocarbonate **6** (11 mg, 0.016 mmol, 1.0 equiv) in dry CH_3OH (1.3 mL) was added K_2CO_3 (8 mg, 0.058 mmol, 3.6 equiv). The mixture was stirred at rt for 4 h and then heated at 40 °C for 4 h. The reaction mixture was then cooled to rt, a saturated aqueous solution of $NaHCO_3$ (1.5 mL) was added and the mixture was diluted with Et_2O (5 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under *vacuum*. Purification of the crude material by column chromatography on silica gel (petroleum ether/EtOAc = 70/30) afforded the epoxide **7** as a mixture of diastereomers [*syn*/*anti* (C2/C4) = 87:13, 6.5 mg, 0.012 mmol, 76%].

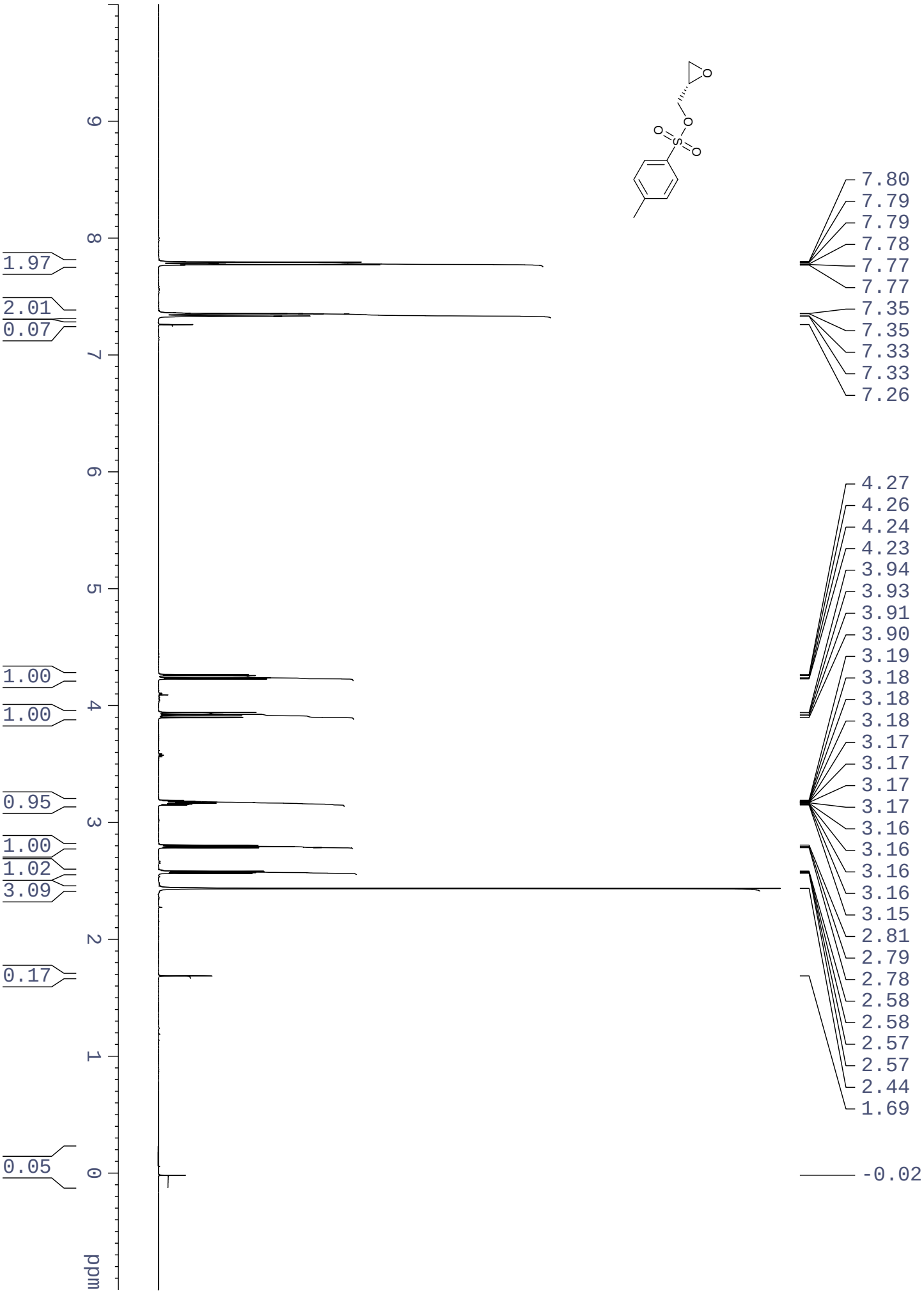
IR (mixture of diastereomers *syn*/*anti* (C2/C4)): *ν* 3485, 3072, 2993, 2931, 2857, 1640, 1473, 1428, 1380, 1266, 1199, 1165, 1110, 999, 943, 917, 822, 741, 704 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz, *syn* major diastereomer): *δ* 7.71-7.64 (m, 4H), 7.45-7.34 (m, 6H), 5.77 (ddt, 1H, *J* = 17.2 Hz, *J* = 10.0 Hz, *J* = 7.2 Hz), 5.00 (d_{app}, 1H, *J* = 10.5 Hz), 4.96 (dd_{app}, 1H, *J* = 17.3 Hz, *J* = 1.9 Hz), 4.04 (m, 1H), 3.95-3.81 (m, 3H), 3.13-3.05 (m, 2H), 2.78 (dd, 1H, *J* = 5.0 Hz, *J* = 4.1 Hz), 2.52 (dd, 1H, *J* = 5.0 Hz, *J* = 2.7 Hz), 2.34 (m, 1H), 2.24 (m, 1H), 1.76 (ddd, 1H, *J* = 13.7 Hz, *J* = 7.4 Hz, *J* = 5.7 Hz), 1.69-1.62 (m, 2H), 1.56-1.41 (m, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.06 (s, 9H), 1.01 (m, 1H), 0.80 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz, *syn* major diastereomer): *δ* 136.0 (2d), 135.9 (2d), 134.5 (d), 134.2 (s), 134.1 (s), 129.7 (2d), 127.7 (2d), 127.6 (2d), 117.4 (t), 98.5 (q), 69.2 (d), 66.9 (d), 66.6 (d), 65.9 (d), 50.2 (d), 46.7 (t), 42.8 (t), 41.9 (t), 41.8 (t), 39.9 (t), 35.8 (t), 30.2 (q), 27.0 (3q), 19.6 (q), 19.4 (s).

HRMS (ESI): Calculated for $C_{32}H_{46}O_5SiNa$ $[M + Na]^+$: 561.3007, found: 561.3007.

1. H. Weinstabl, T. Gaich, and J. Mulzer, *Org. Lett.*, 2012, **14**, 2834–2837.
2. S. Lee, S.-M. Paek, H. Yun, N.-J. Kim, and Y.-G. Suh, *Org. Lett.*, 2011, **13**, 3344–3347.
3. G. Sabitha, N. M. Reddy, M. N. Prasad, and J. S. Yadav, *Helv. Chim. Acta*, 2009, **92**, 967–976.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2.78
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2.58
2.57
2.57
2.44
1.69
-0.02
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1.00
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1.00
1.02
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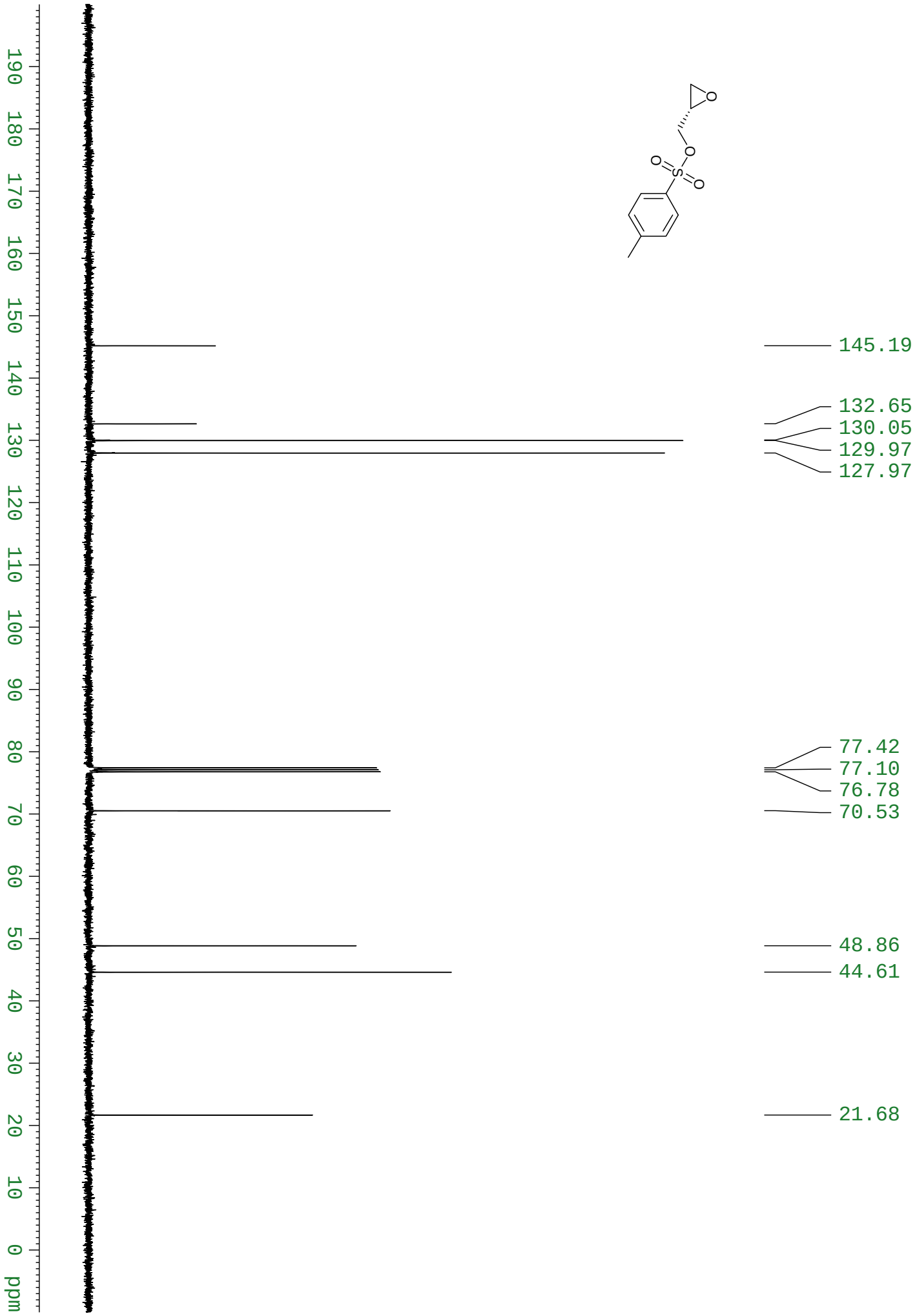
0.05
ppm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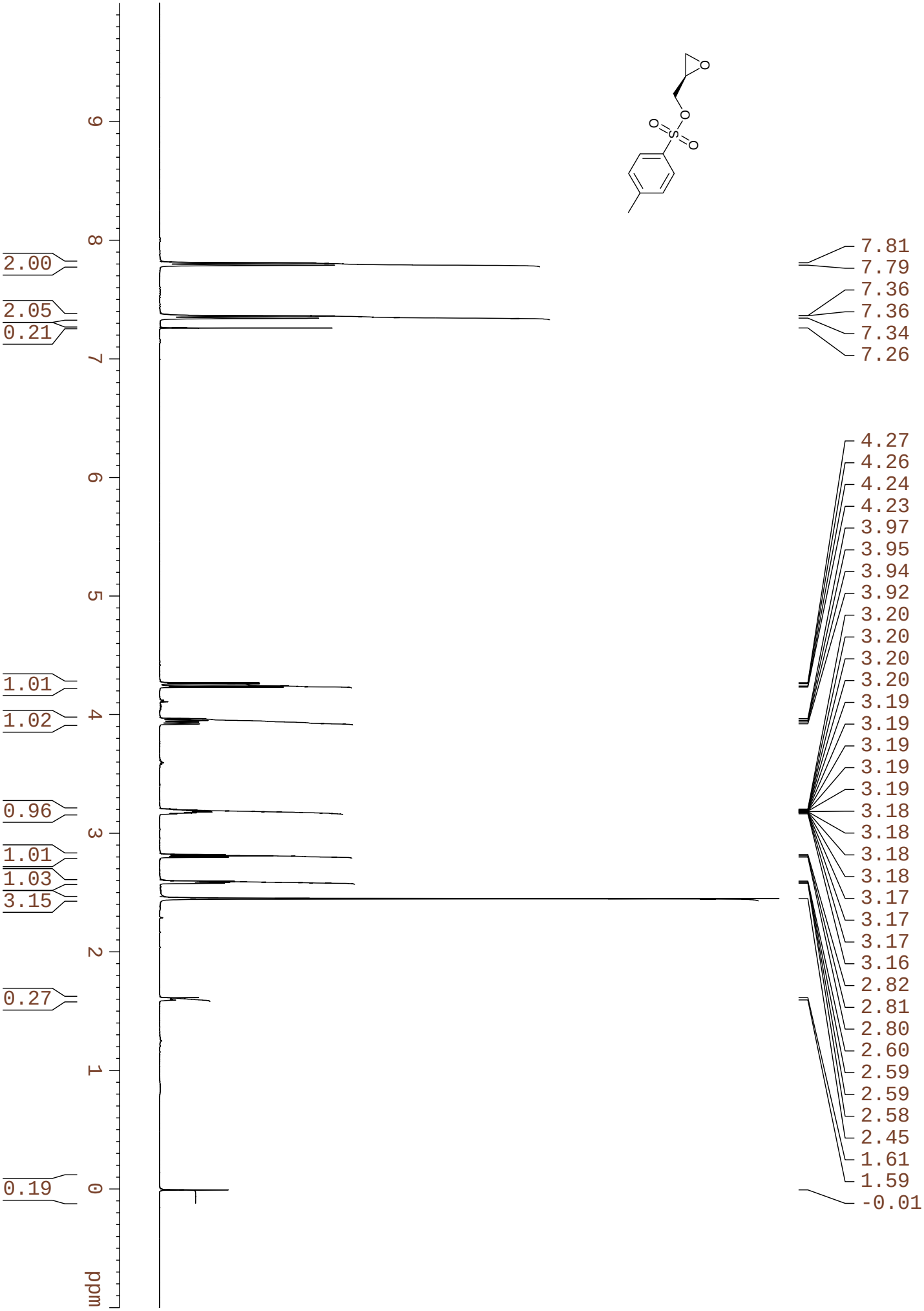
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1.03
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7.36
7.34
7.26
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4.26
4.24
4.23
3.97
3.95
3.94
3.92
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3.20
3.20
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3.19
3.19
3.19
3.19
3.19
3.18
3.18
3.18
3.18
3.17
3.17
3.17
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2.45
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1.59
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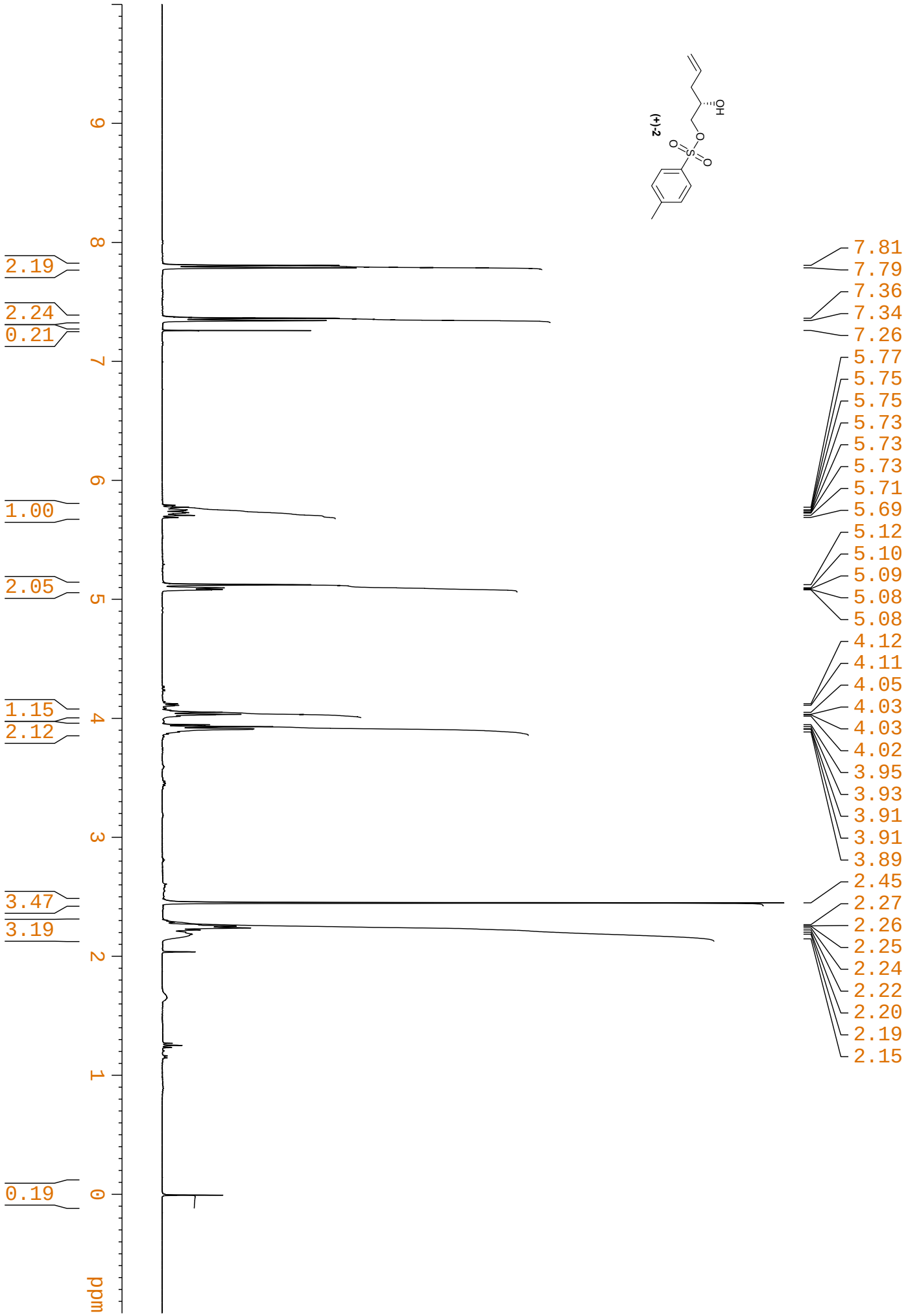
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O
S
O
O
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7.36
7.34
7.26
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5.75
5.75
5.73
5.73
5.73
5.71
5.69
5.12
5.10
5.09
5.08
5.08
4.12
4.11
4.05
4.03
4.03
4.02
3.95
3.93
3.91
3.91
3.89
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2.27
2.26
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2.24
2.22
2.20
2.19
2.15
2.19
2.24
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1.00
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6
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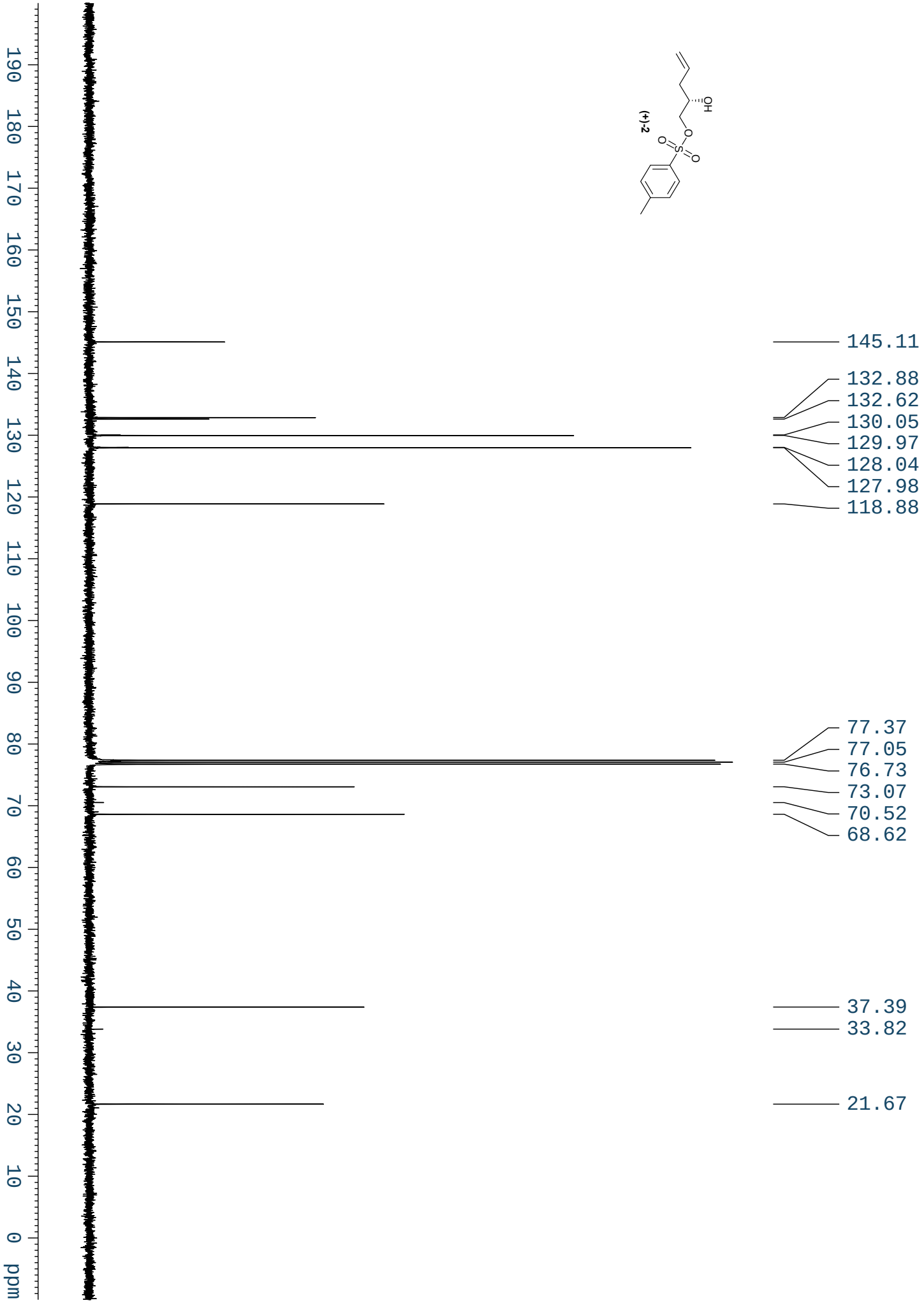
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S
O
O
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50
40
30
20
10
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ppm
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130.05
129.97
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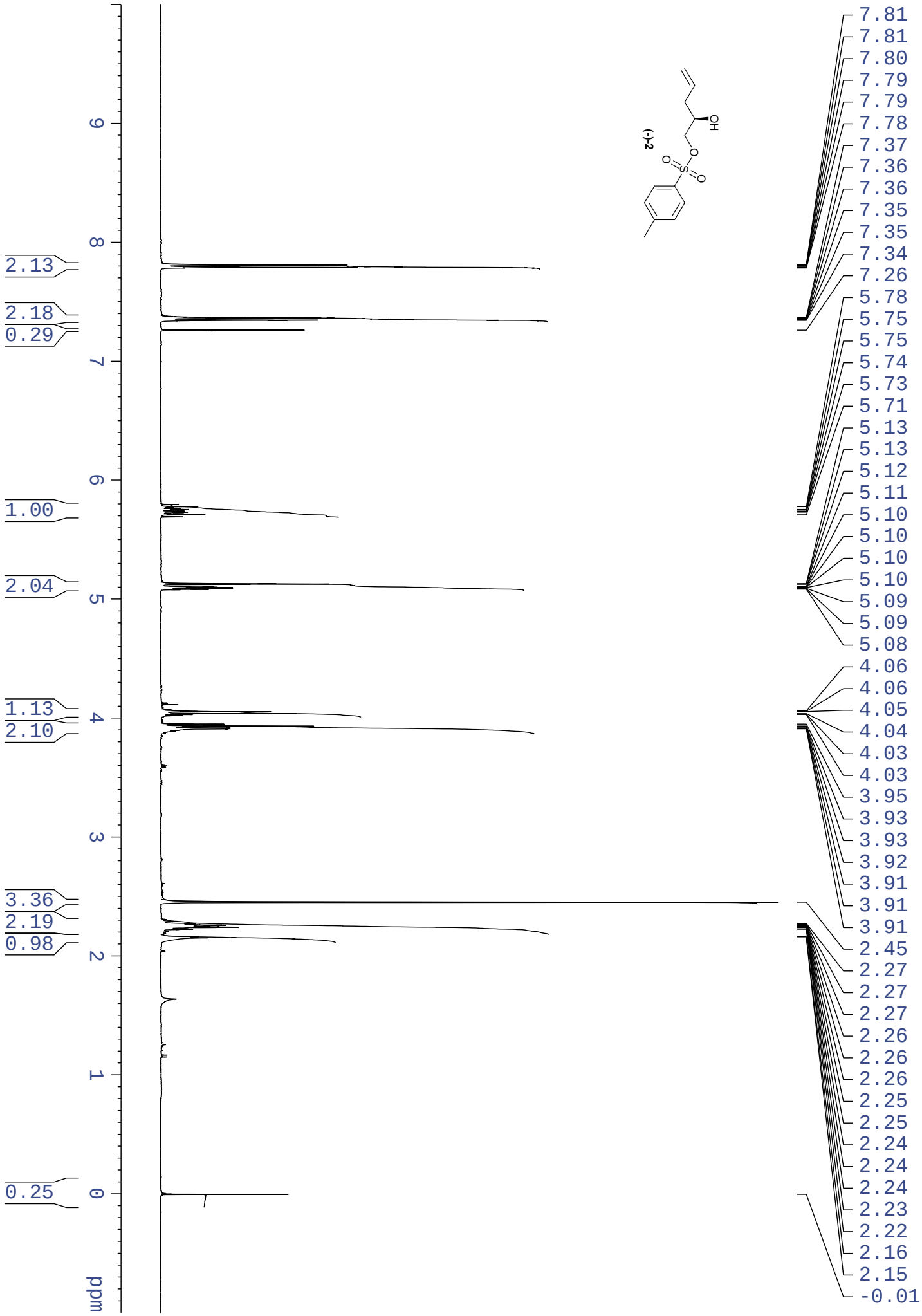
77.05
76.73
73.07
70.52
68.62
37.39
33.82
21.67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7.37
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7.36
7.35
7.35
7.34
7.26
5.78
5.75
5.75
5.74
5.73
5.71
5.13
5.13
5.12
5.11
5.10
5.10
5.10
5.10
5.09
5.09
5.08
4.06
4.06
4.05
4.04
4.03
4.03
3.95
3.93
3.93
3.92
3.91
3.91
3.91
2.45
2.27
2.27
2.27
2.26
2.26
2.26
2.25
2.25
2.24
2.24
2.24
2.23
2.22
2.16
2.15
-0.01
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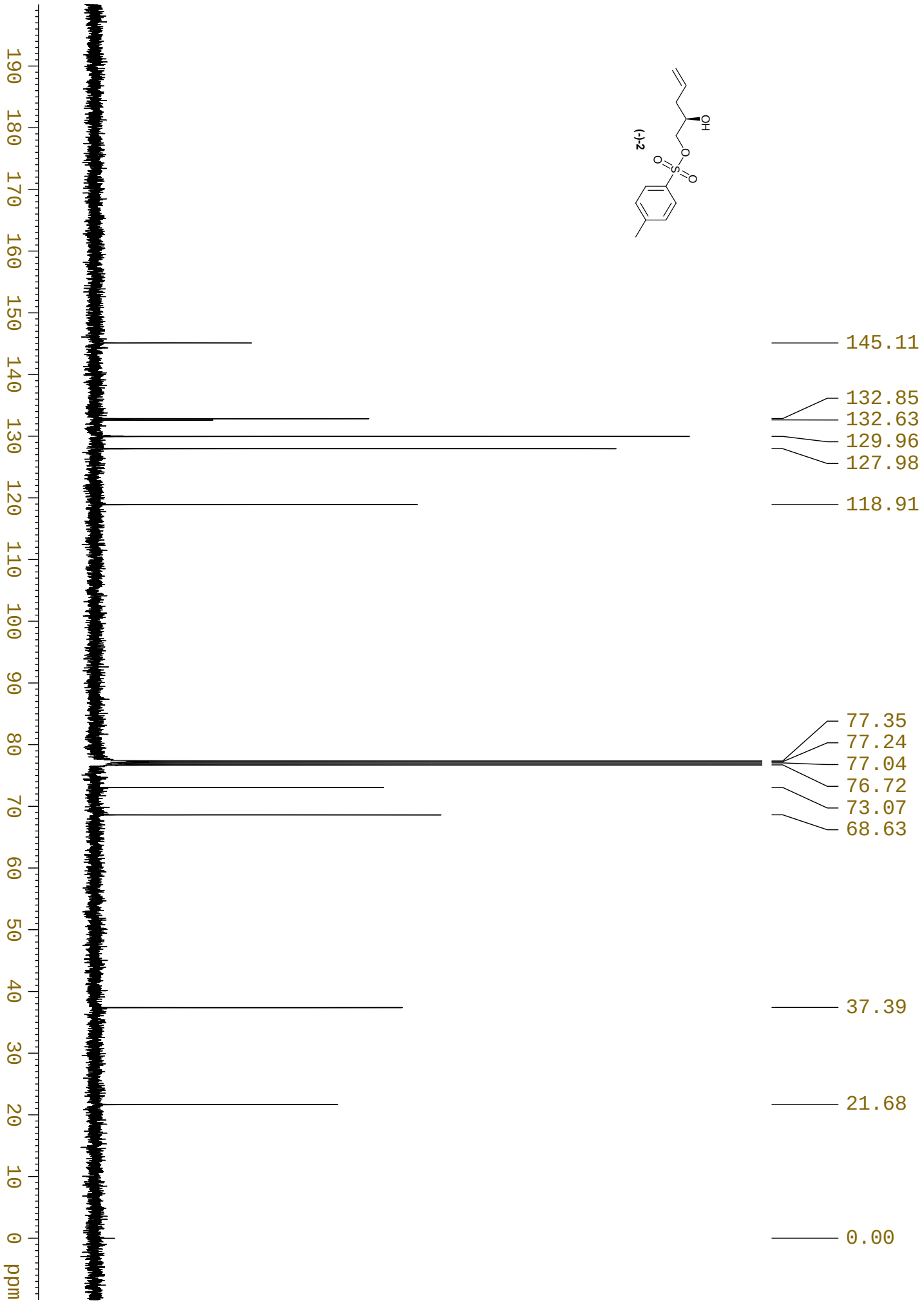
0.25
ppm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77.04
76.72
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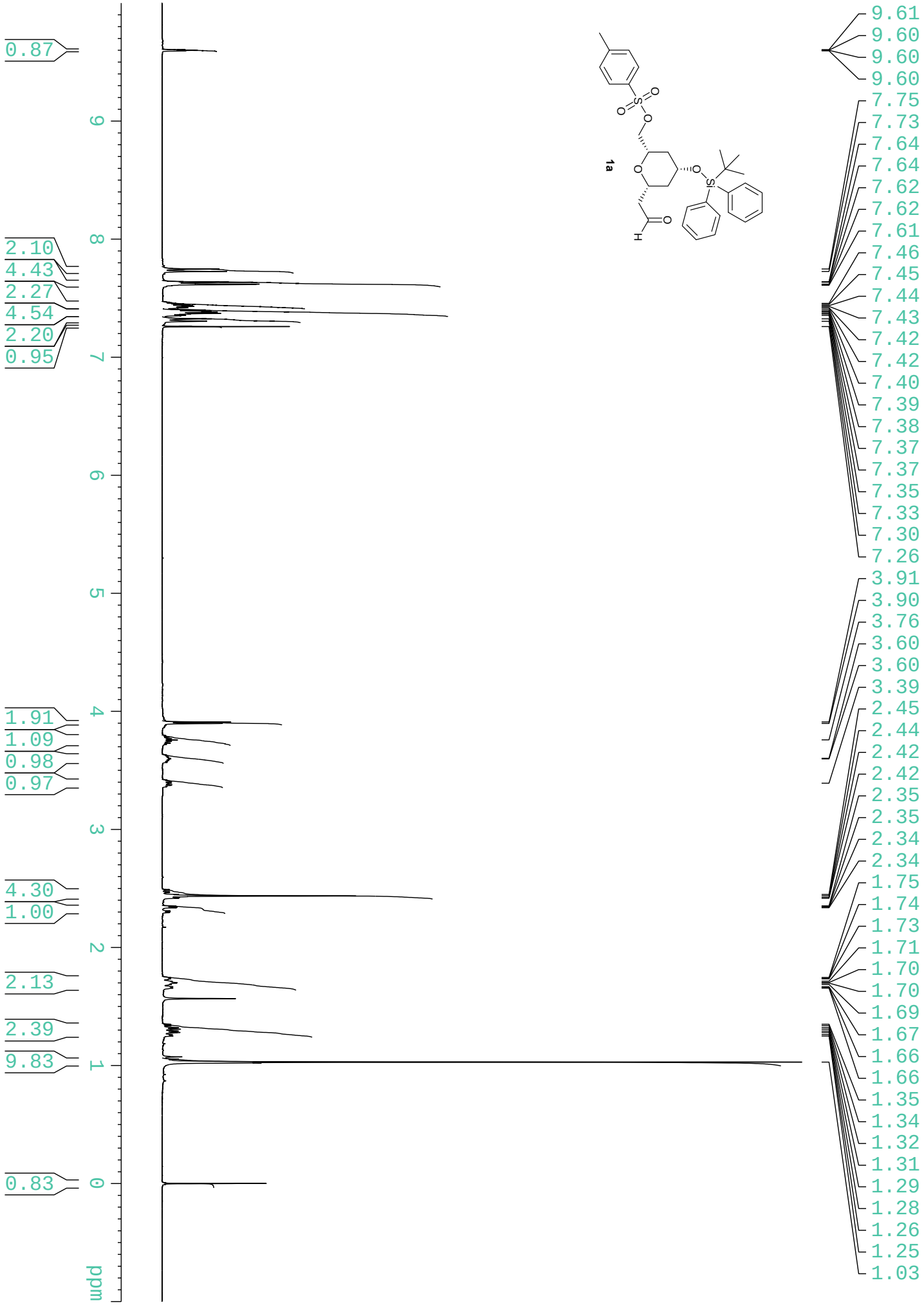
68.63
37.39
21.68
0.00
ppm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0.97
4.30
1.00
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2.39
9.83
0.83
9
8
7
6
5
4
3
2
1
0
ppm
1a
9.61
9.60
9.60
9.60
7.75
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7.64
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7.62
7.62
7.61
7.46
7.45
7.44
7.43
7.42
7.42
7.40
7.39
7.38
7.37
7.37
7.35
7.33
7.30
7.26
3.91
3.90
3.76
3.60
3.60
3.39
2.45
2.44
2.42
2.42
2.35
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1.70
1.69
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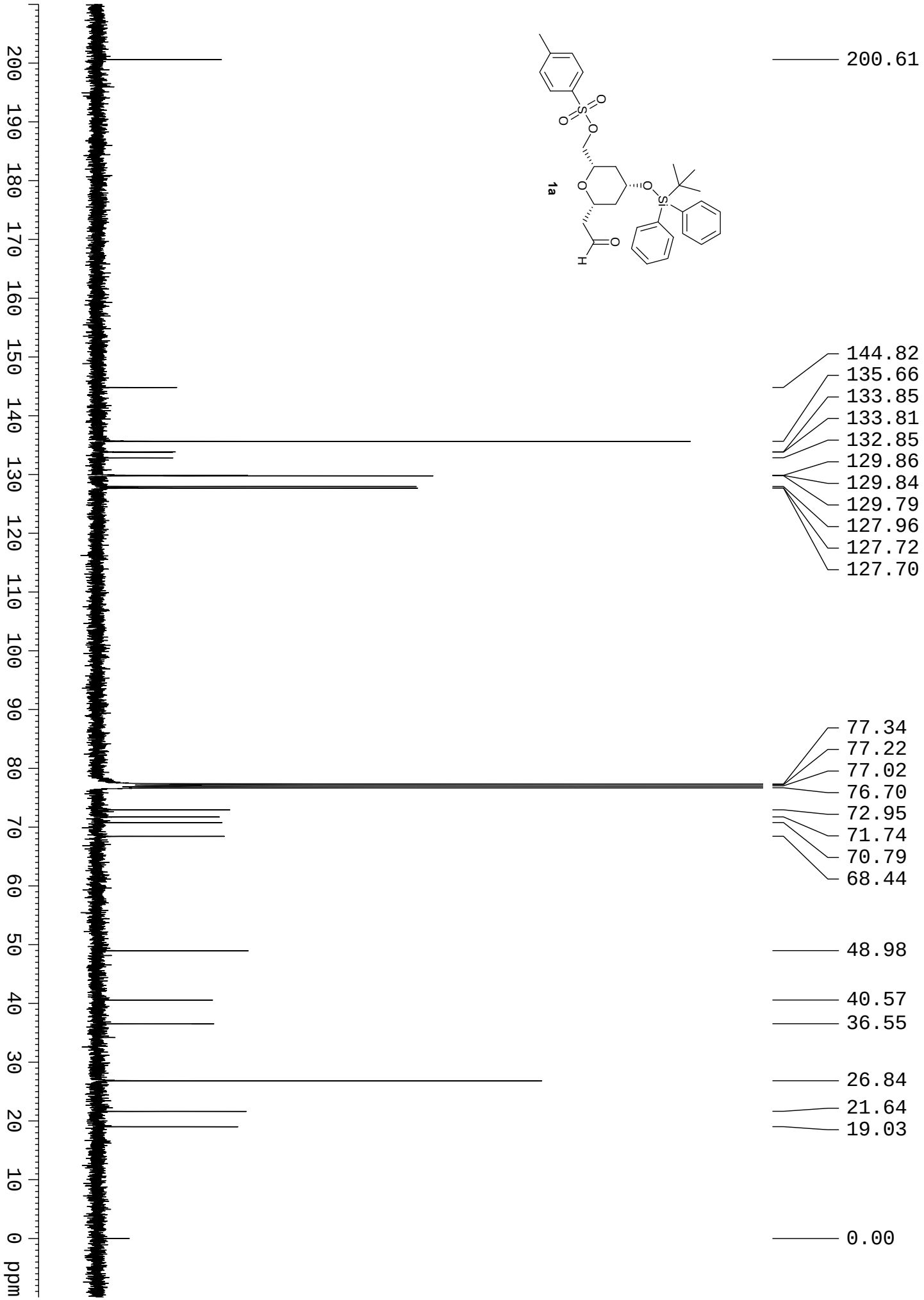
1.26
1.25
1.03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127.96
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127.70
77.34
77.22
77.02
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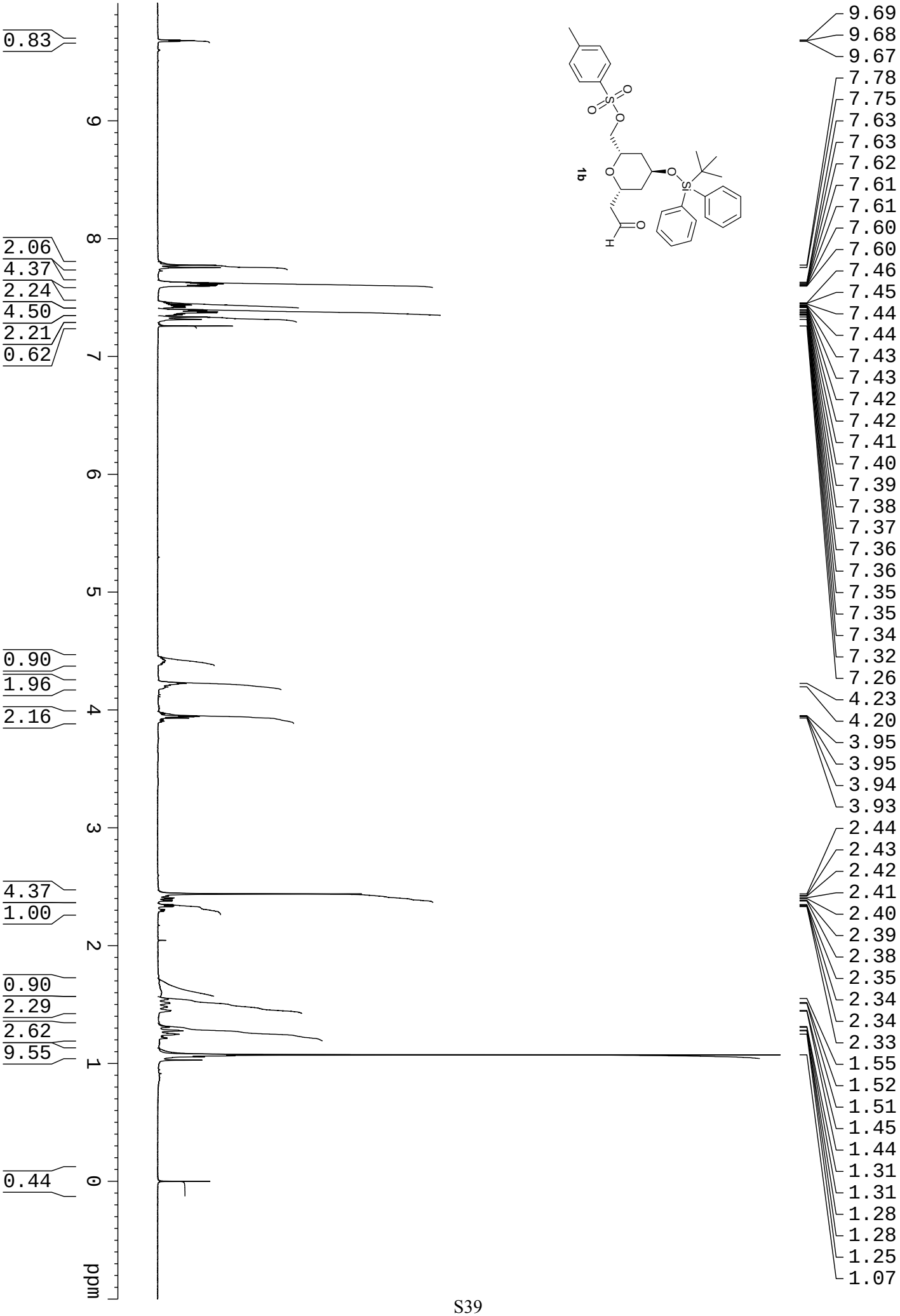
26.84
21.64
19.03
0.00
ppm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1.00
0.90
2.29
2.62
9.55
0.44
ppm
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5
4
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7.78
7.75
7.63
7.63
7.62
7.61
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7.60
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.42
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7.40
7.39
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.32
7.26
4.23
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3.95
3.94
3.93
2.44
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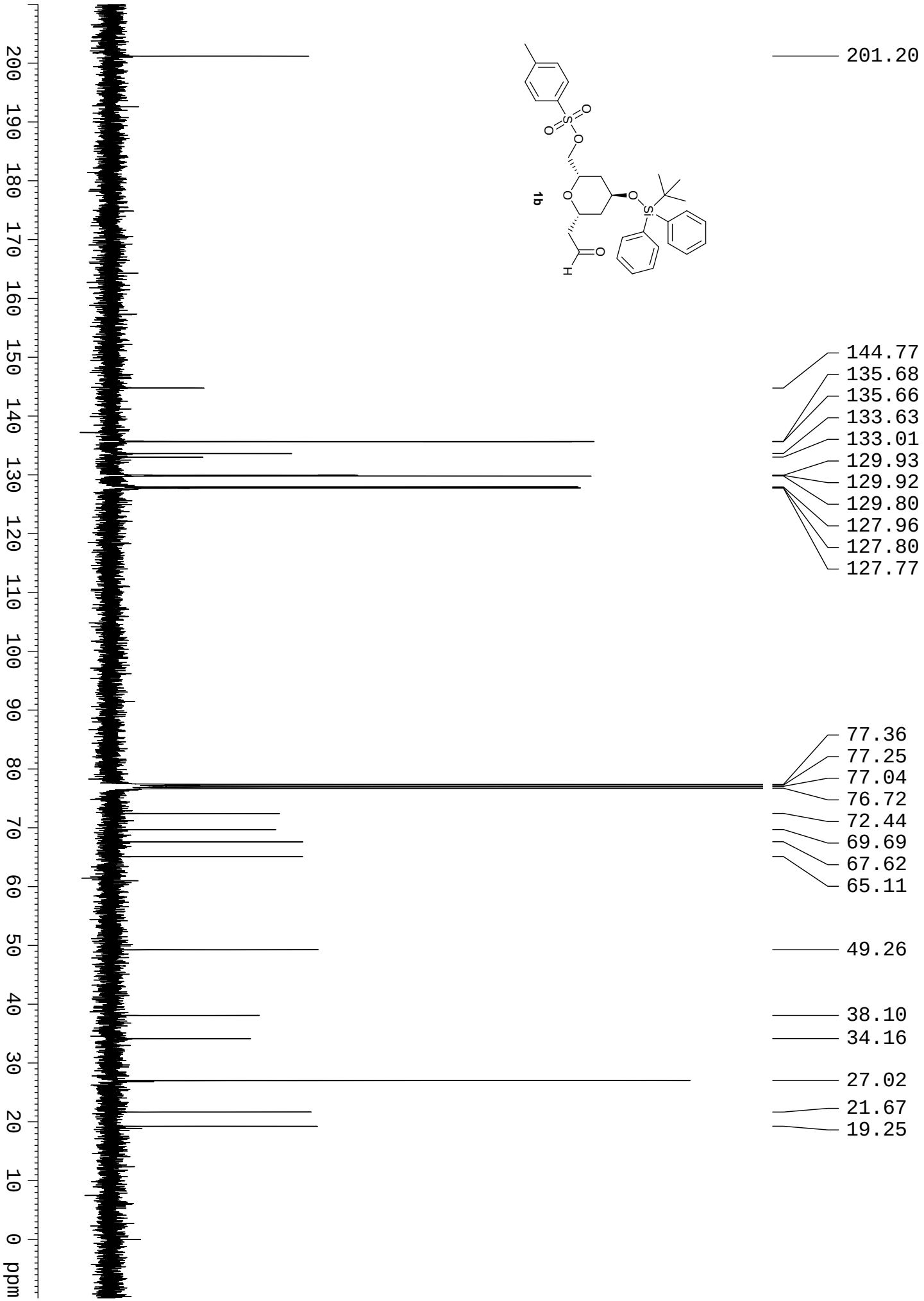
1.28
1.25
1.07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77.25
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69.69
67.62
65.11
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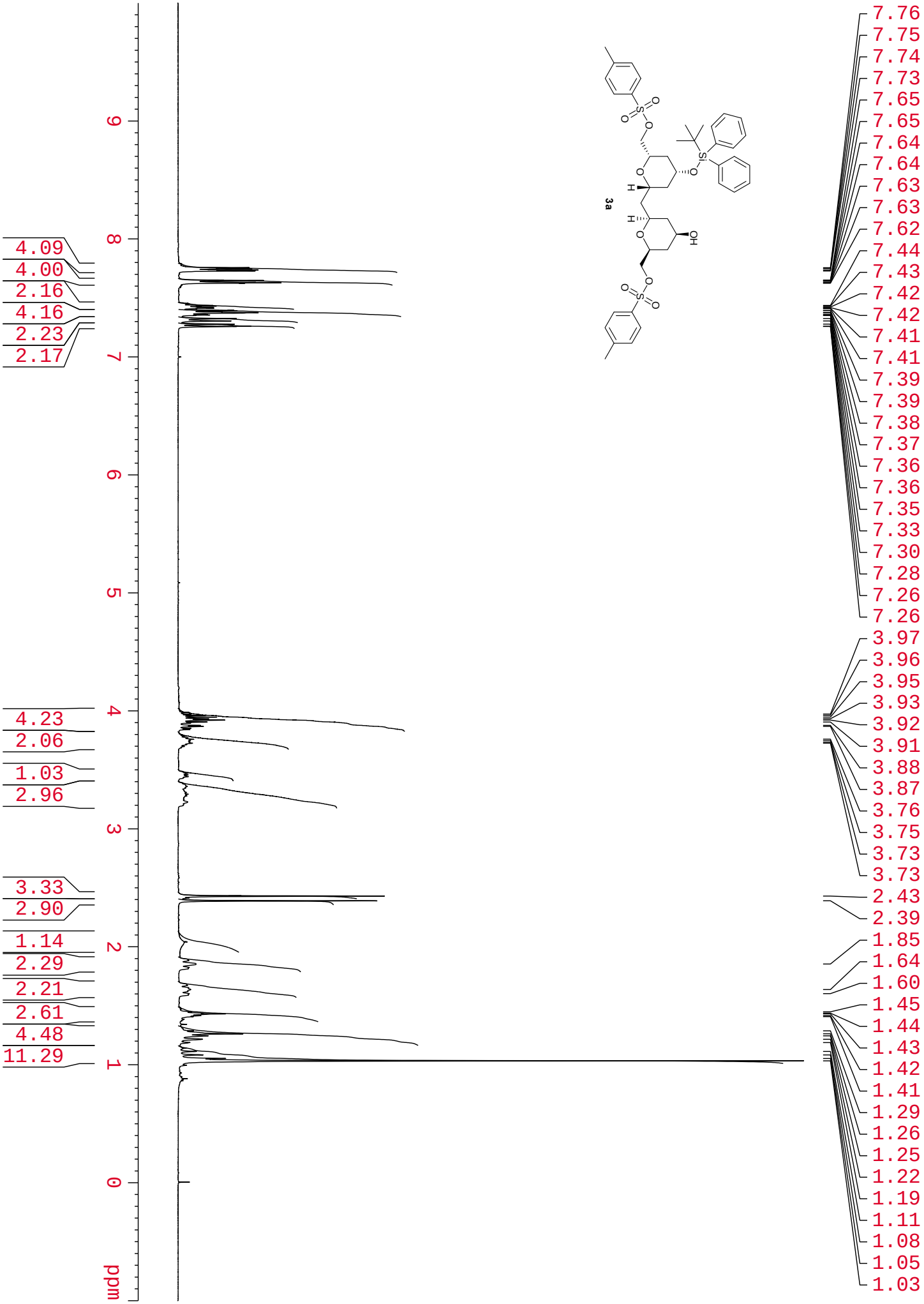
34.16
27.02
21.67
19.25
ppm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3.75
3.73
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1.44
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1.25
1.22
1.19
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1.05
1.03
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4.23
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3.33
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11.29
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6
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4
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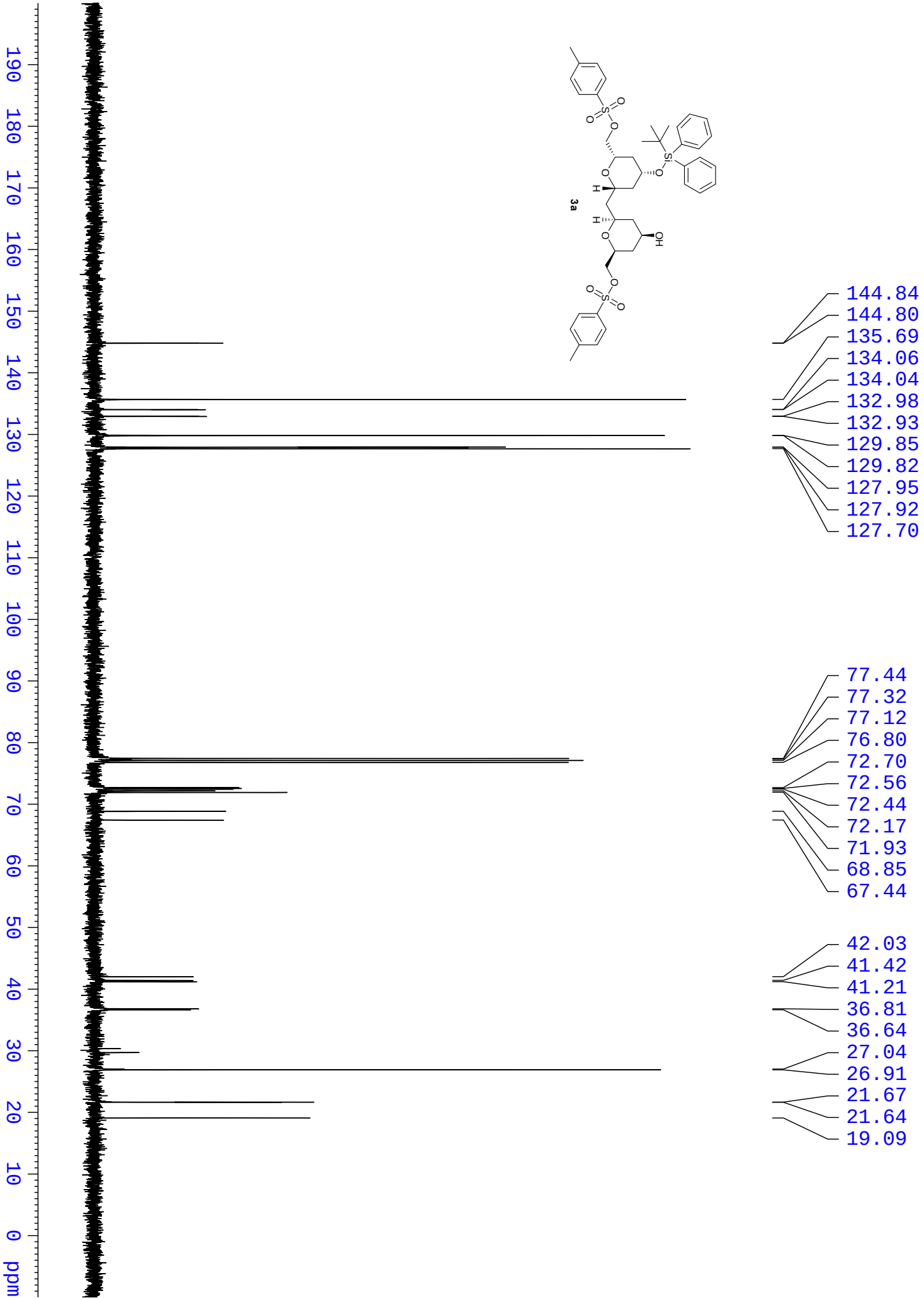
2
1
0
ppm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127.92
127.70
77.44
77.32
77.12
76.80
72.70
72.56
72.44
72.17
71.93
68.85
67.44
42.03
41.42
41.21
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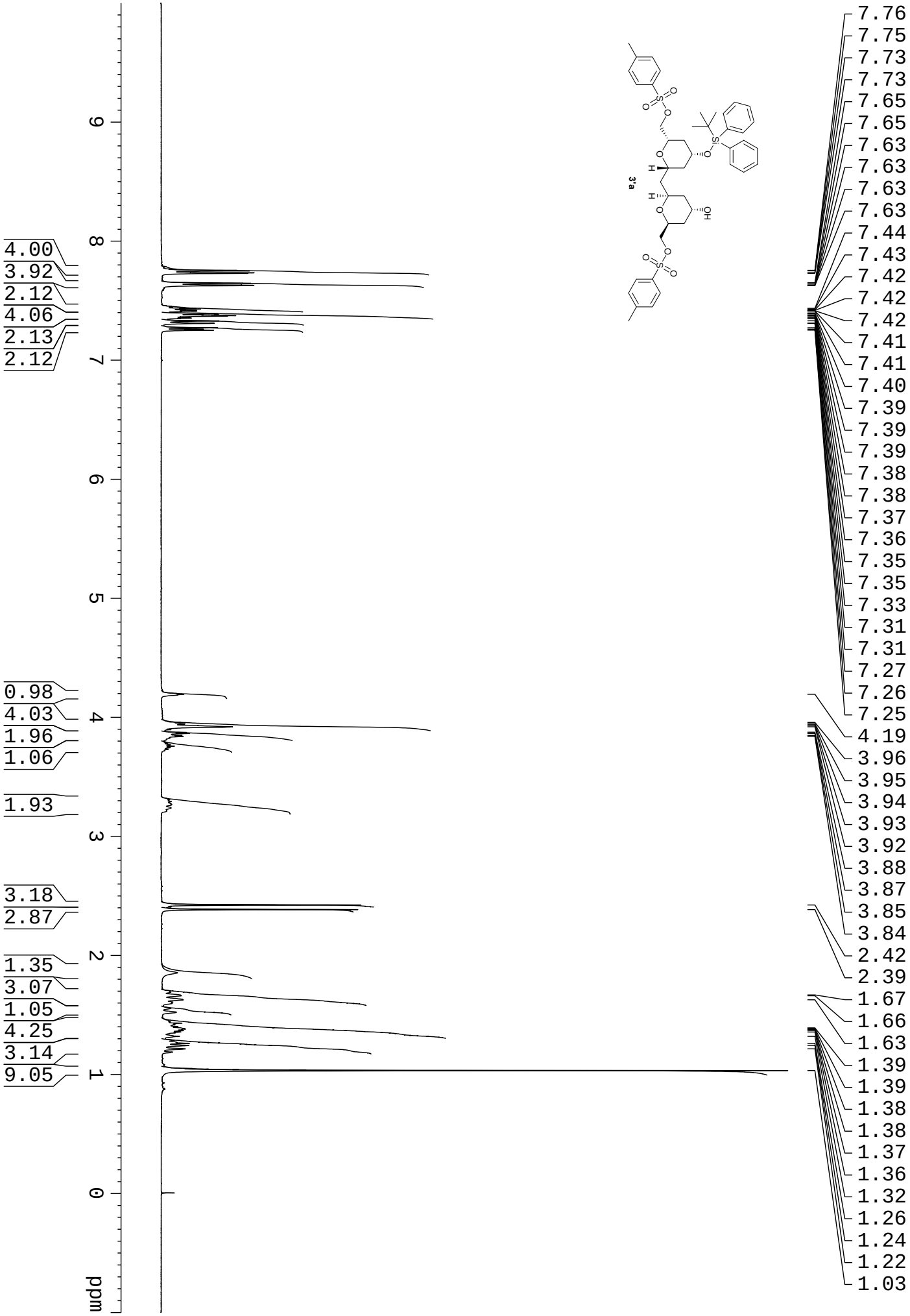
27.04
26.91
21.67
21.64
19.09
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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1.37
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1.26
1.24
1.22
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4.00
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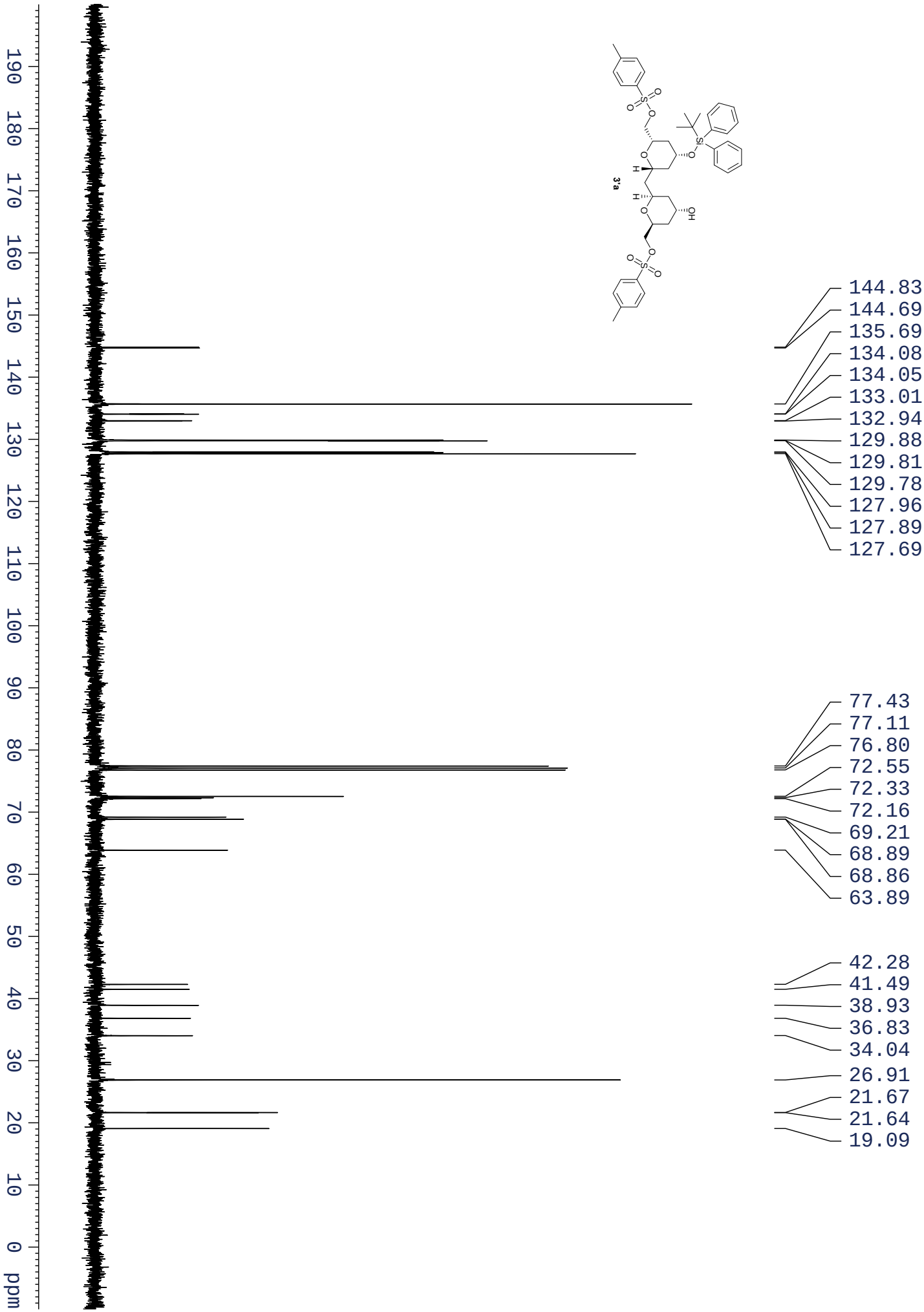
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127.96
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127.69
77.43
77.11
76.80
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72.33
72.16
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38.93
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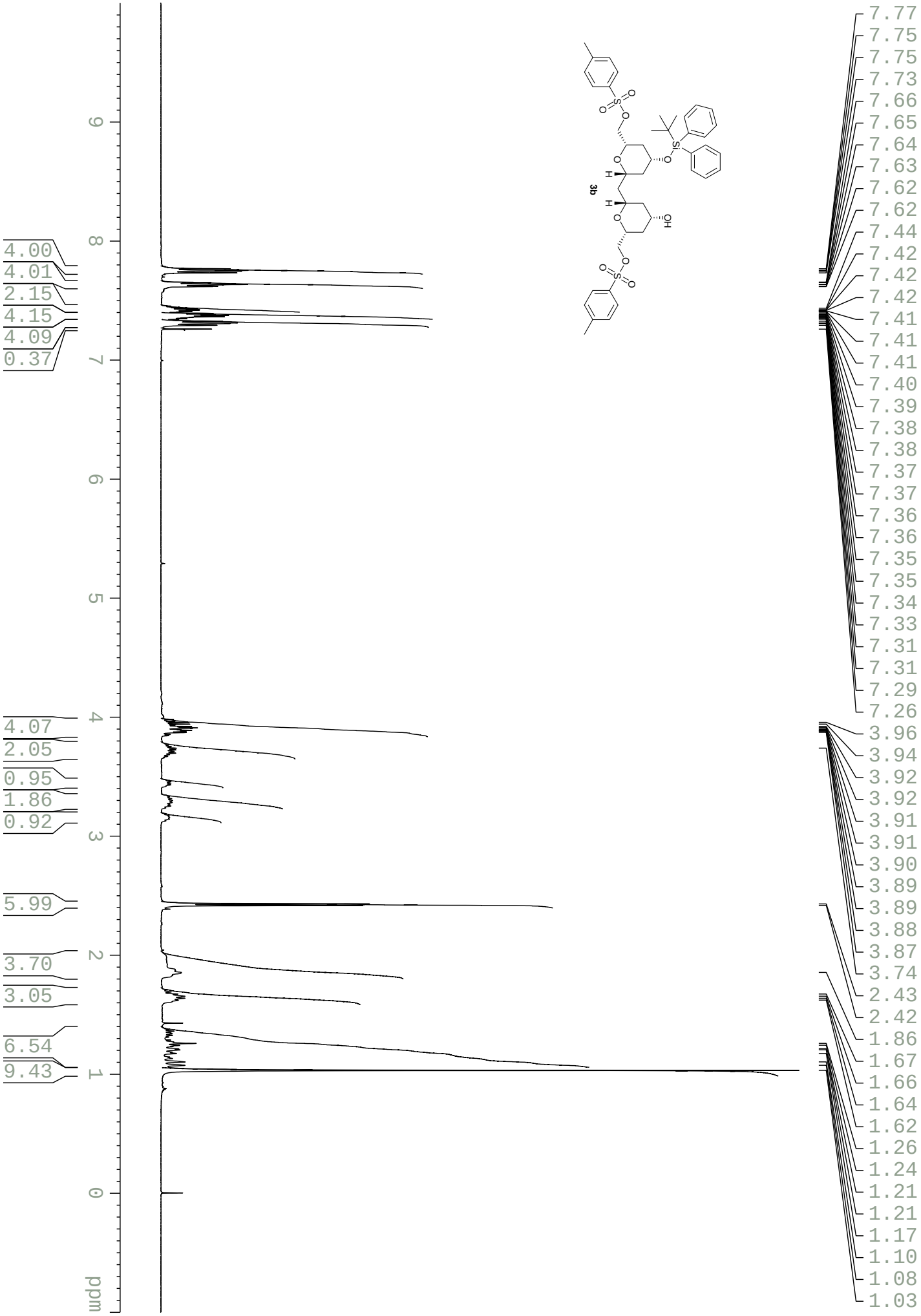
26.91
21.67
21.64
19.09
ppm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3.05
6.54
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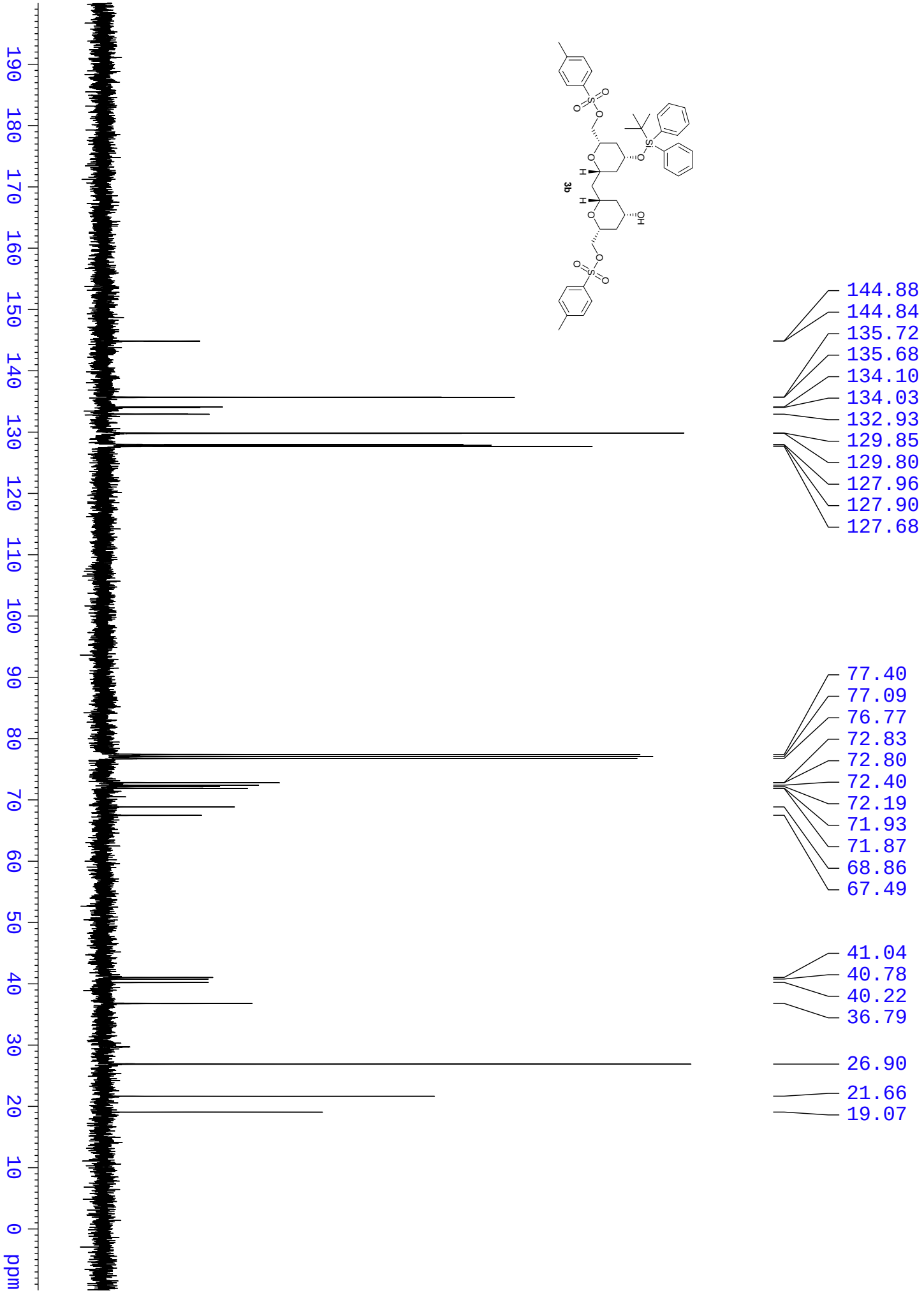
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127.90
127.68
77.40
77.09
76.77
72.83
72.80
72.40
72.19
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67.49
41.04
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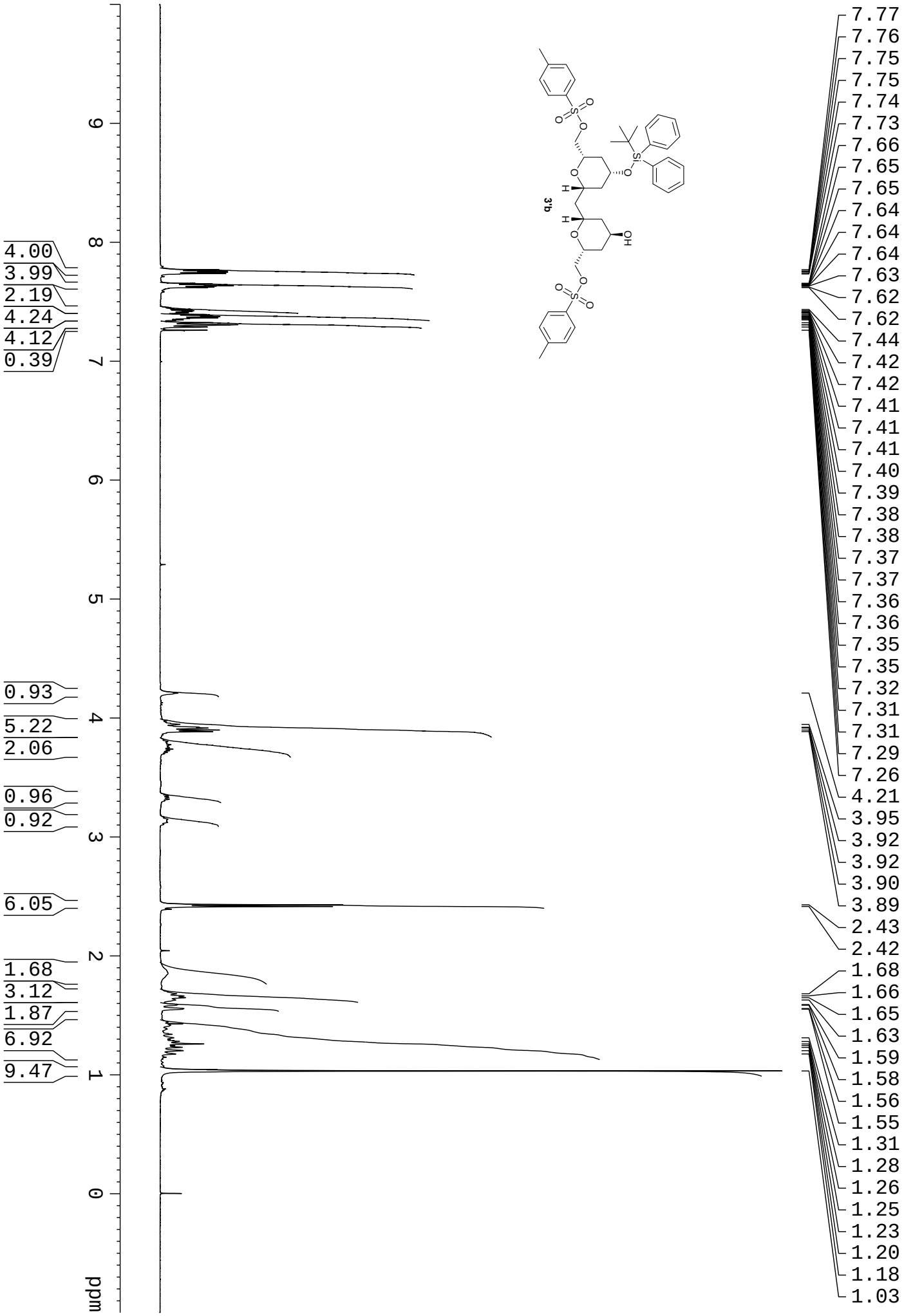
21.66
19.07
ppm


3'b
ppm
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0.93
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2.06
0.96
0.92
6.05
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3.89
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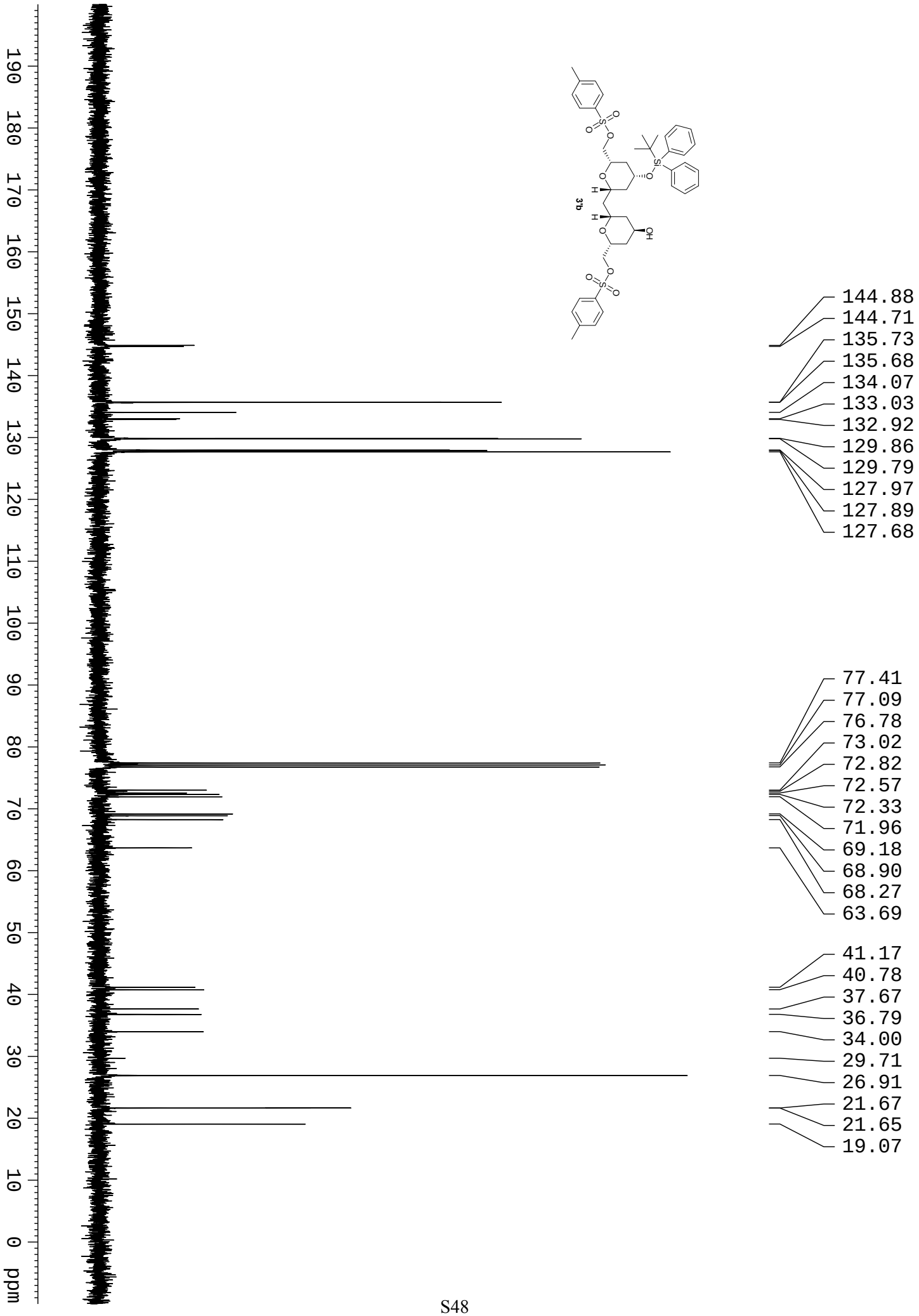
1.03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129.79
127.97
127.89
127.68
77.41
77.09
76.78
73.02
72.82
72.57
72.33
71.96
69.18
68.90
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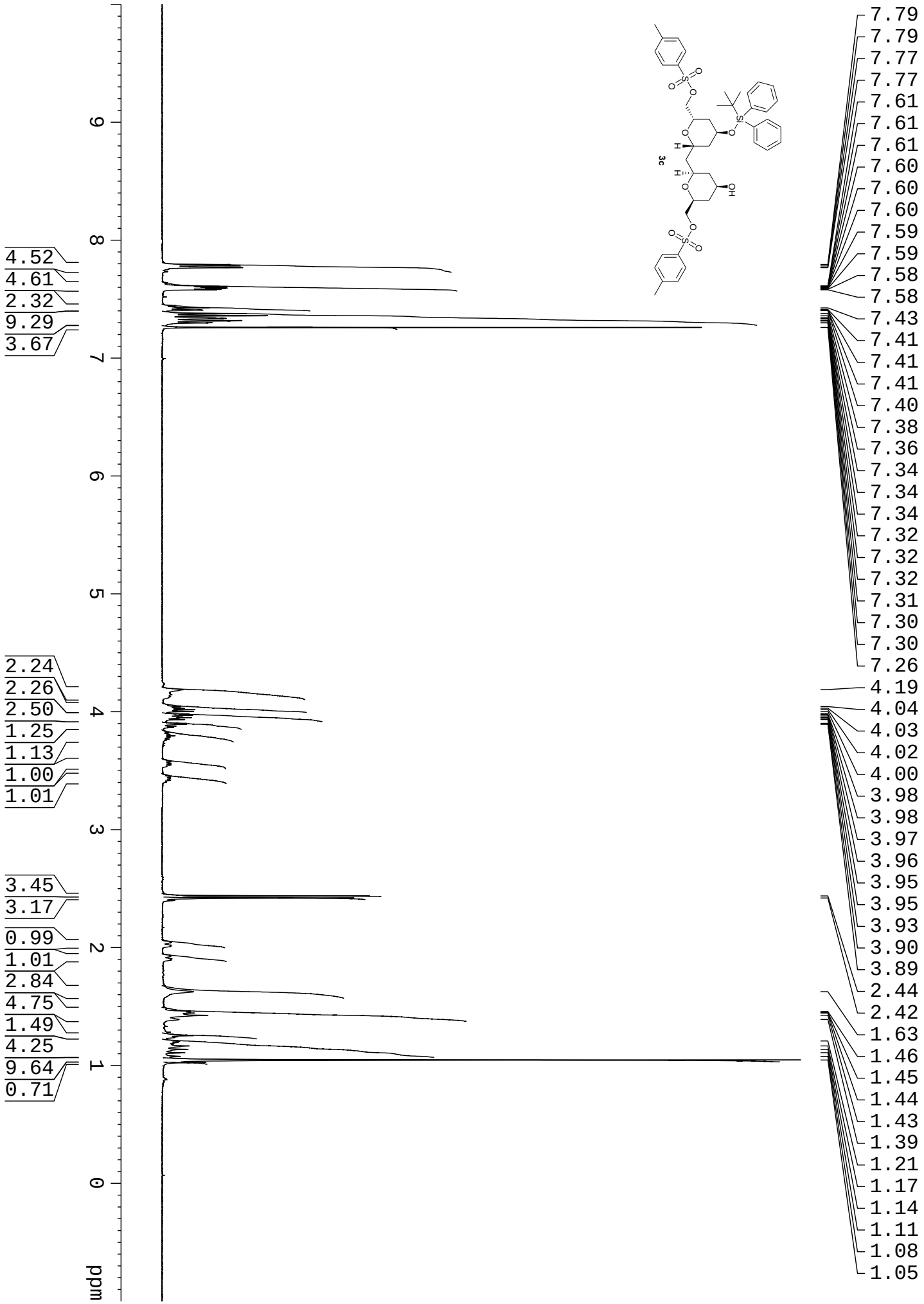
40.78
37.67
36.79
34.00
29.71
26.91
21.67
21.65
19.07
ppm


3c
ppm
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2.24
2.26
2.50
1.25
1.13
1.00
1.01
3.45
3.17
0.99
1.01
2.84
4.75
1.49
4.25
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7.79
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7.77
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7.61
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7.60
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7.59
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7.58
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3.96
3.95
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3.90
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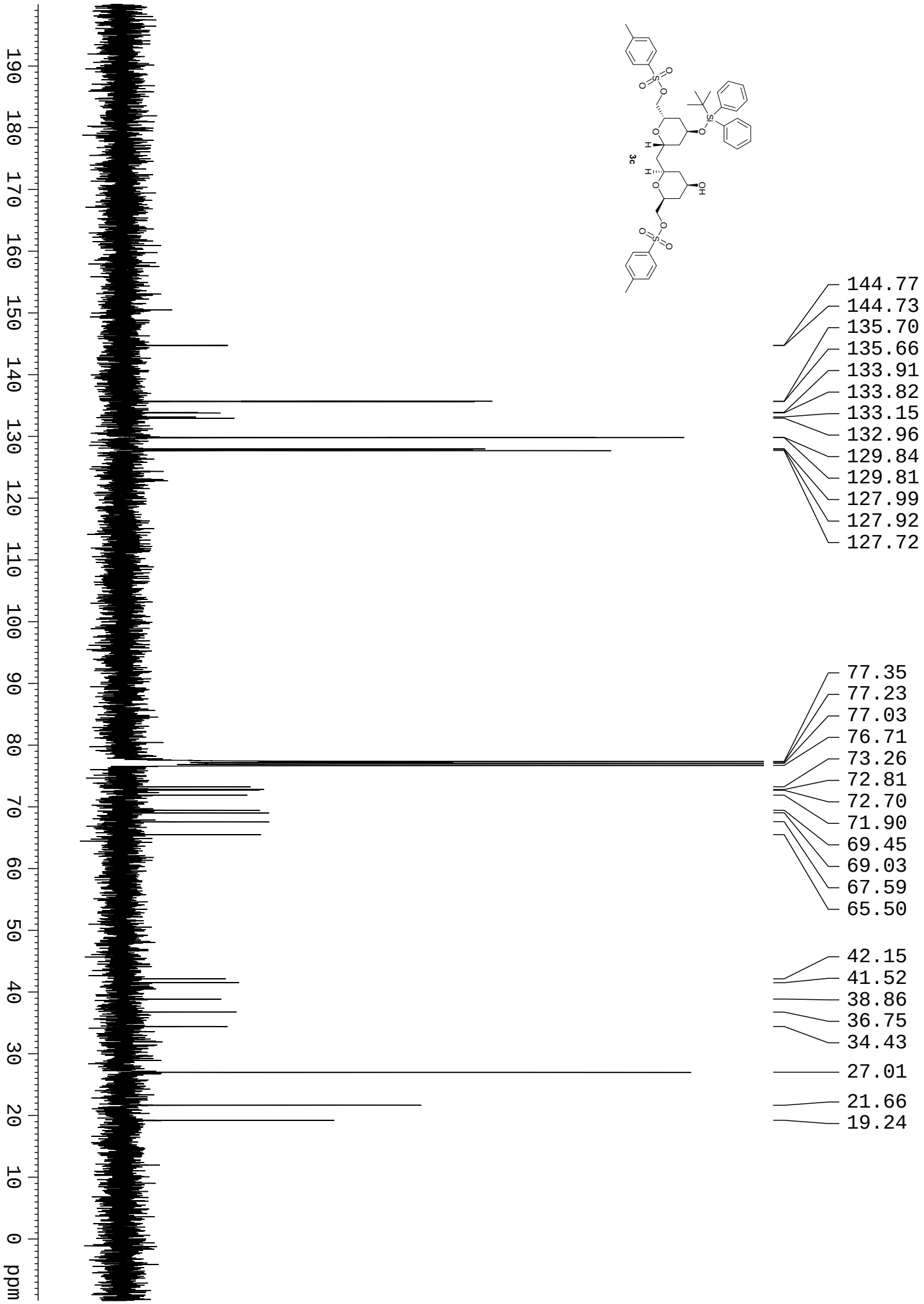
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127.99
127.92
127.72
77.35
77.23
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76.71
73.26
72.81
72.70
71.90
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69.03
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65.50
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41.52
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34.43
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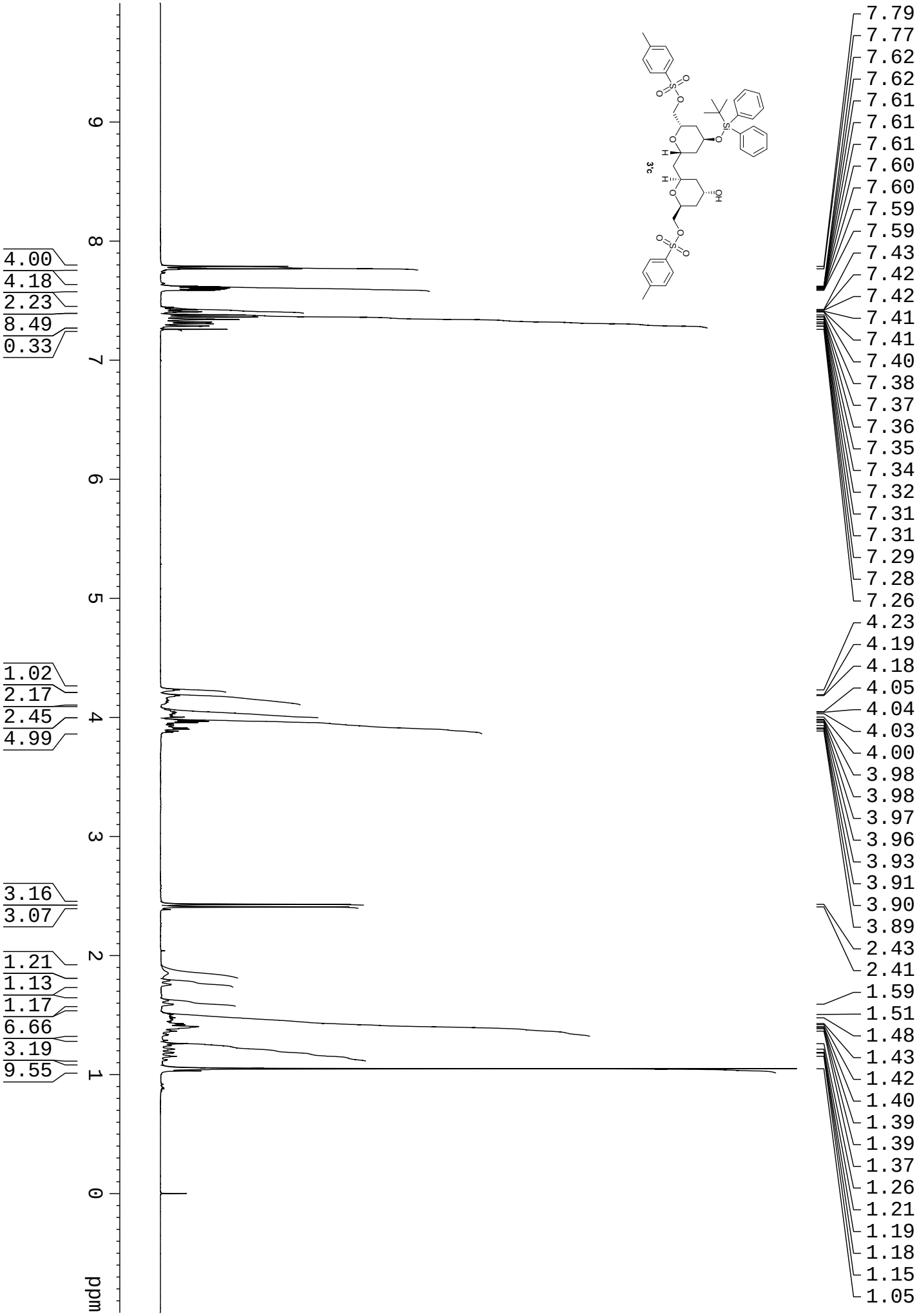
ppm


3c
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7.60
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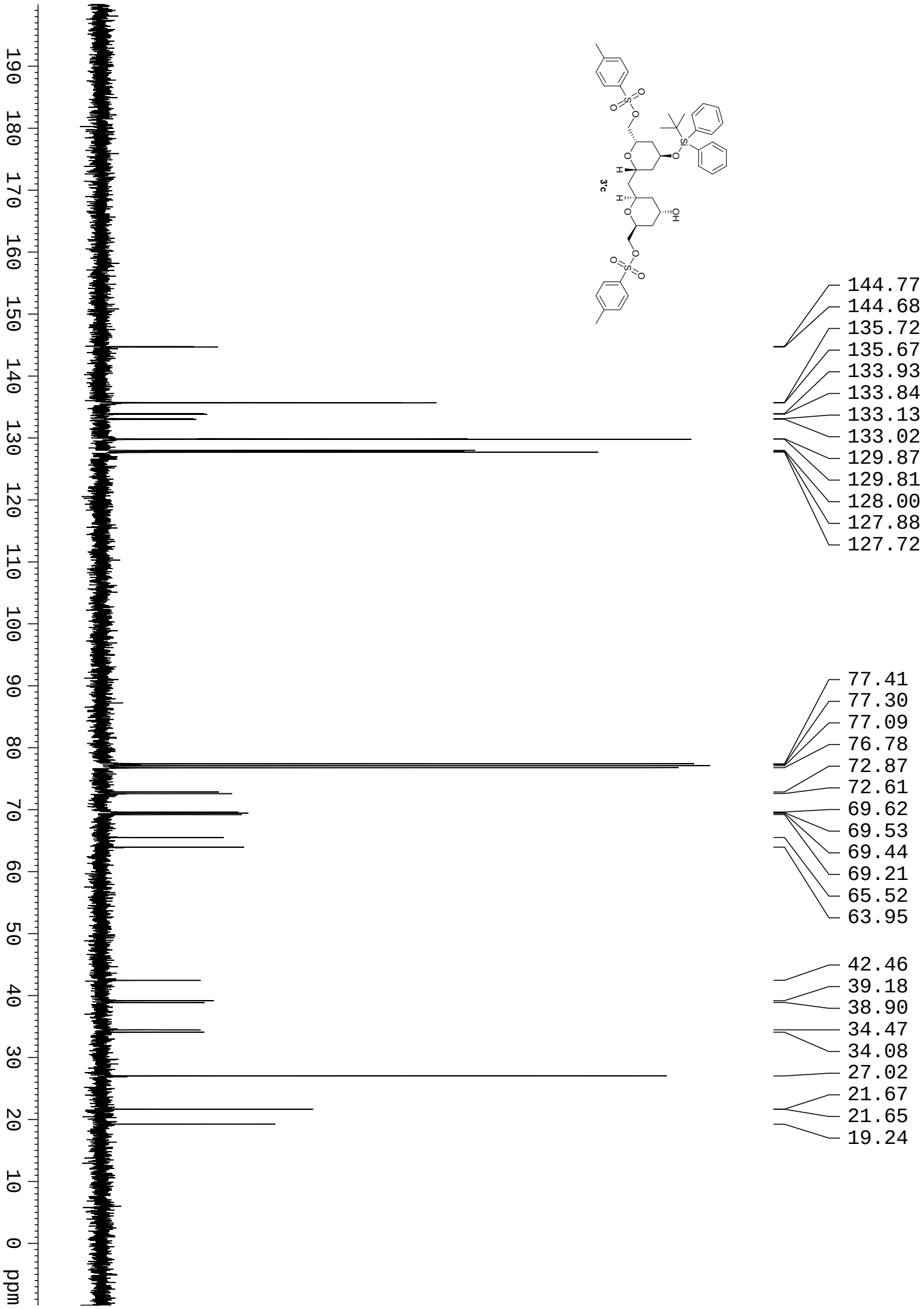
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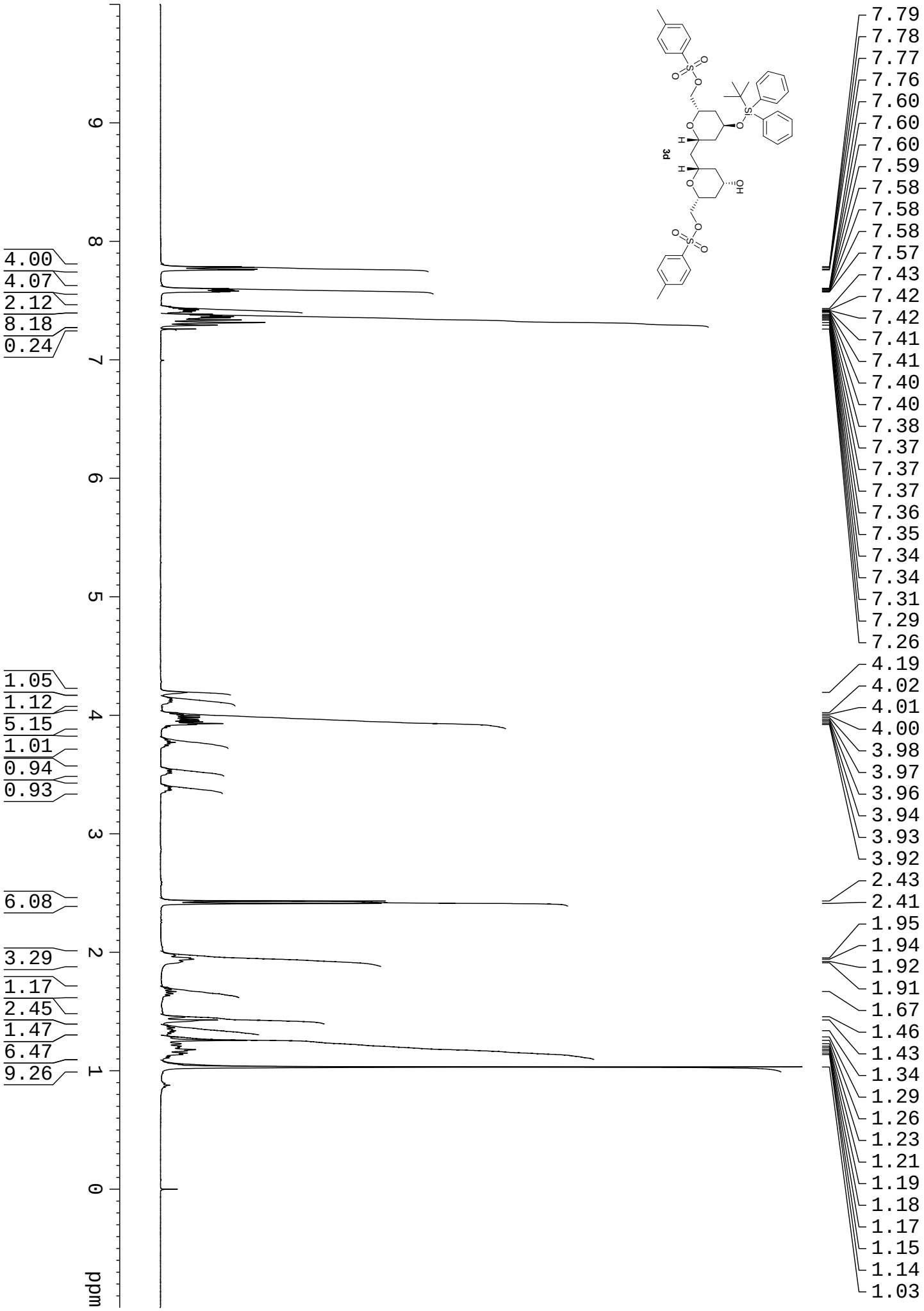
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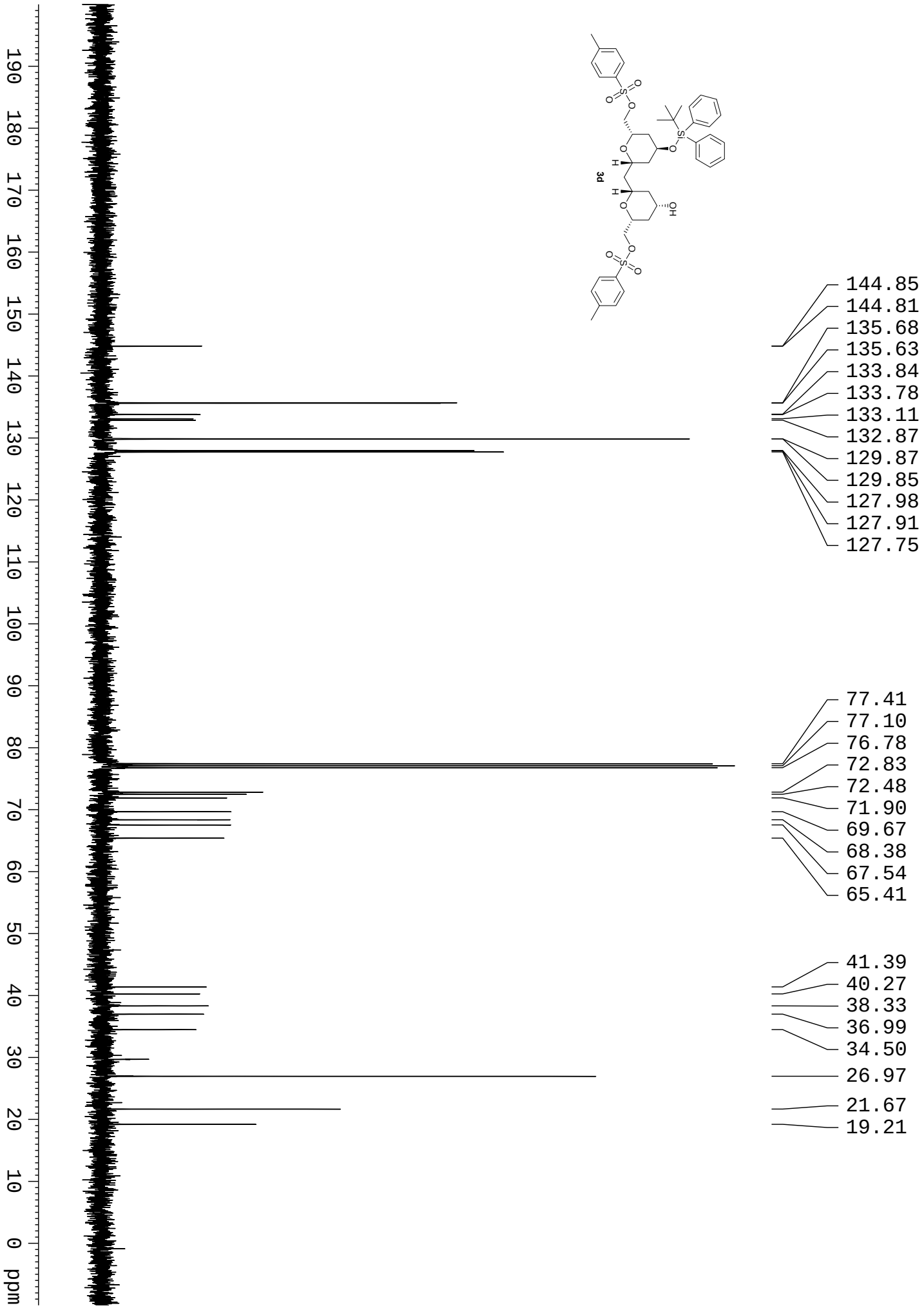
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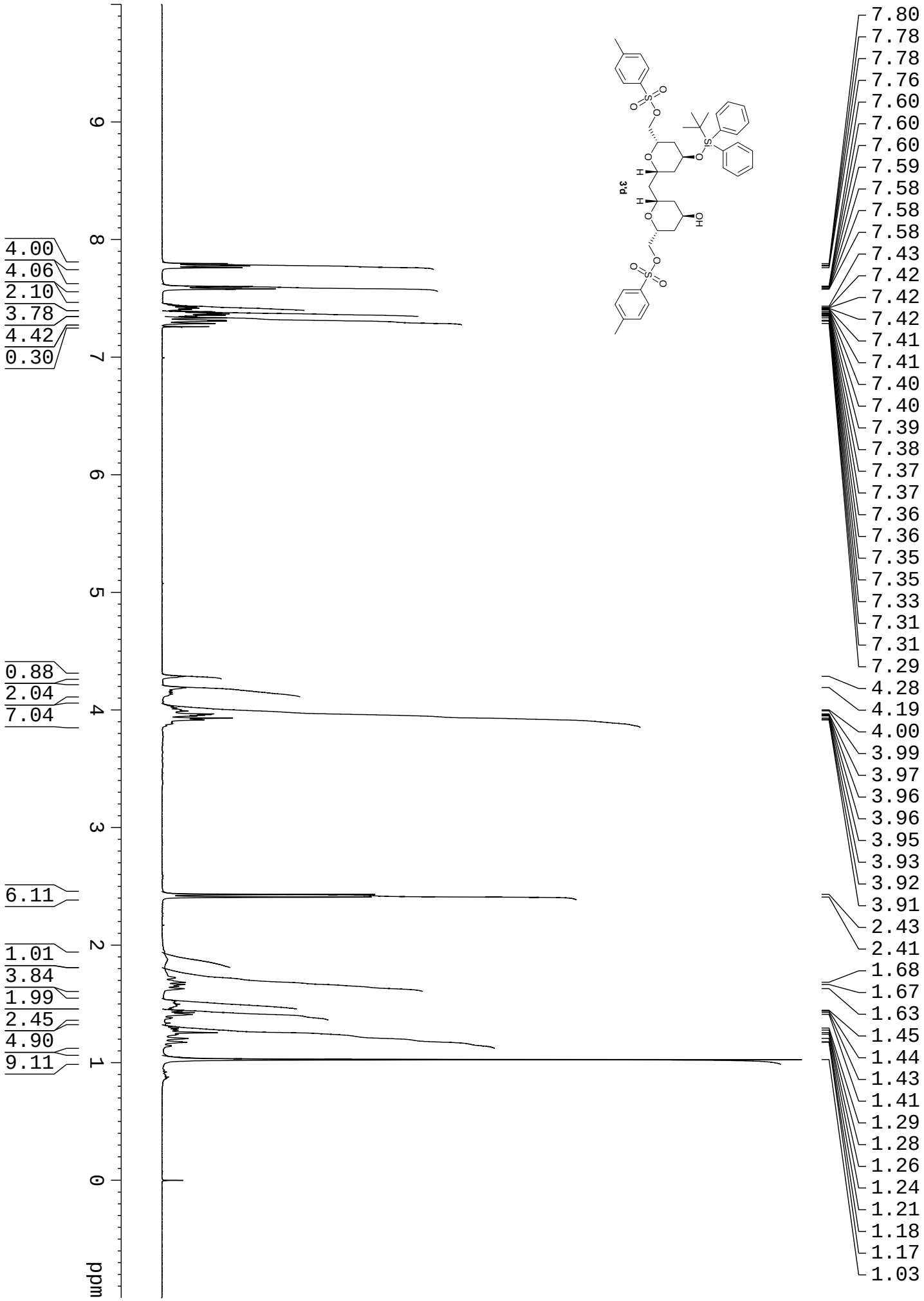
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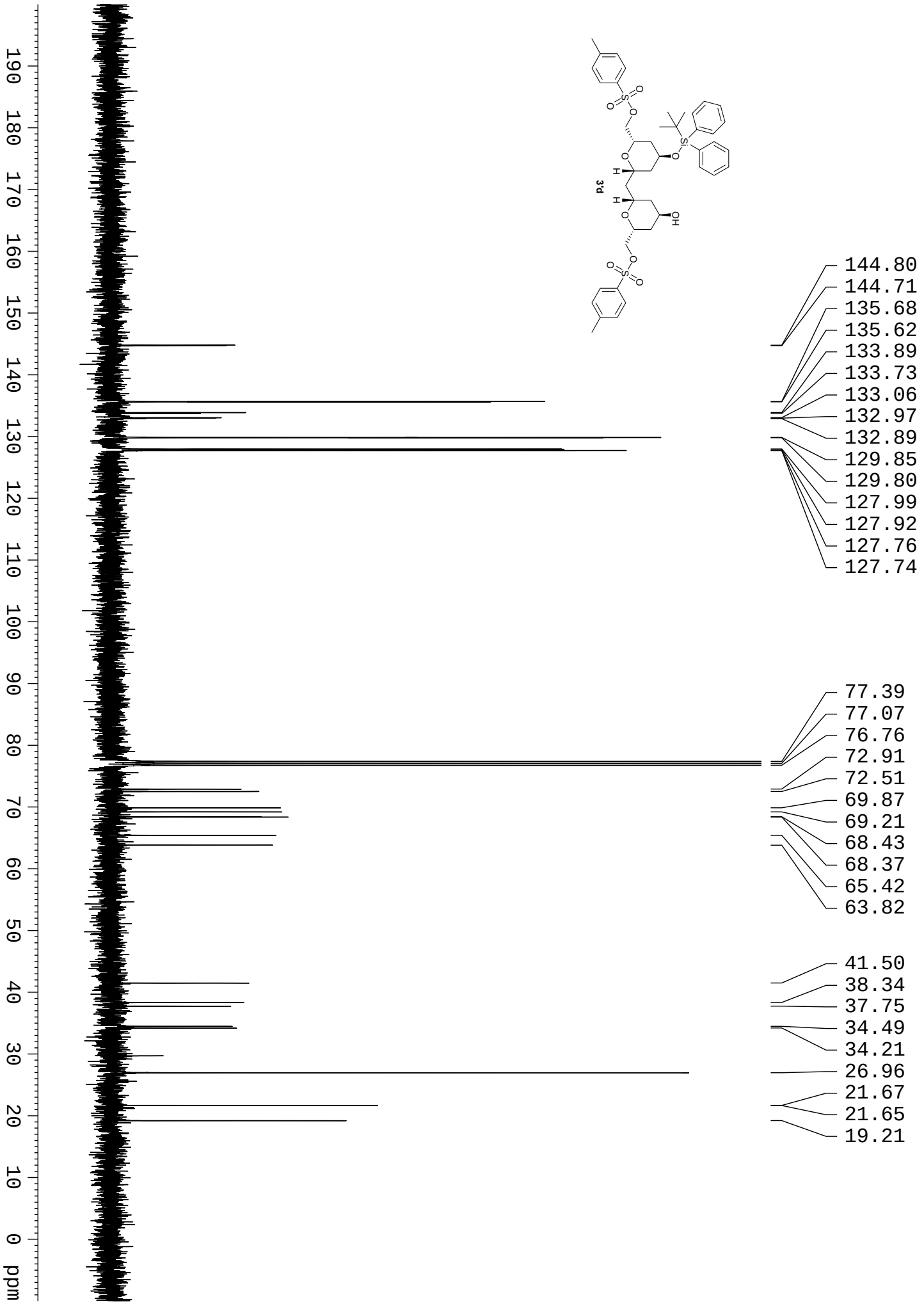
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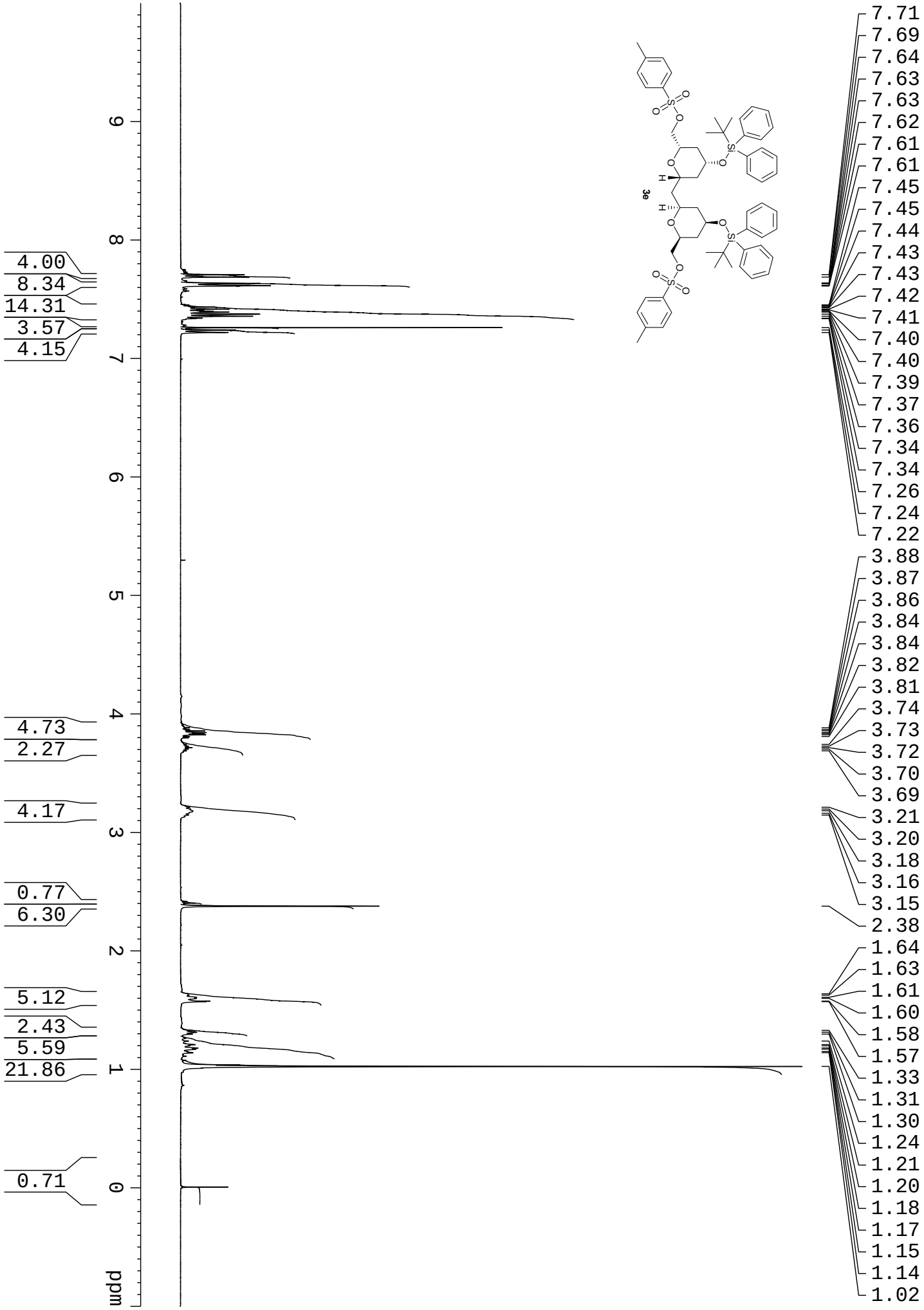
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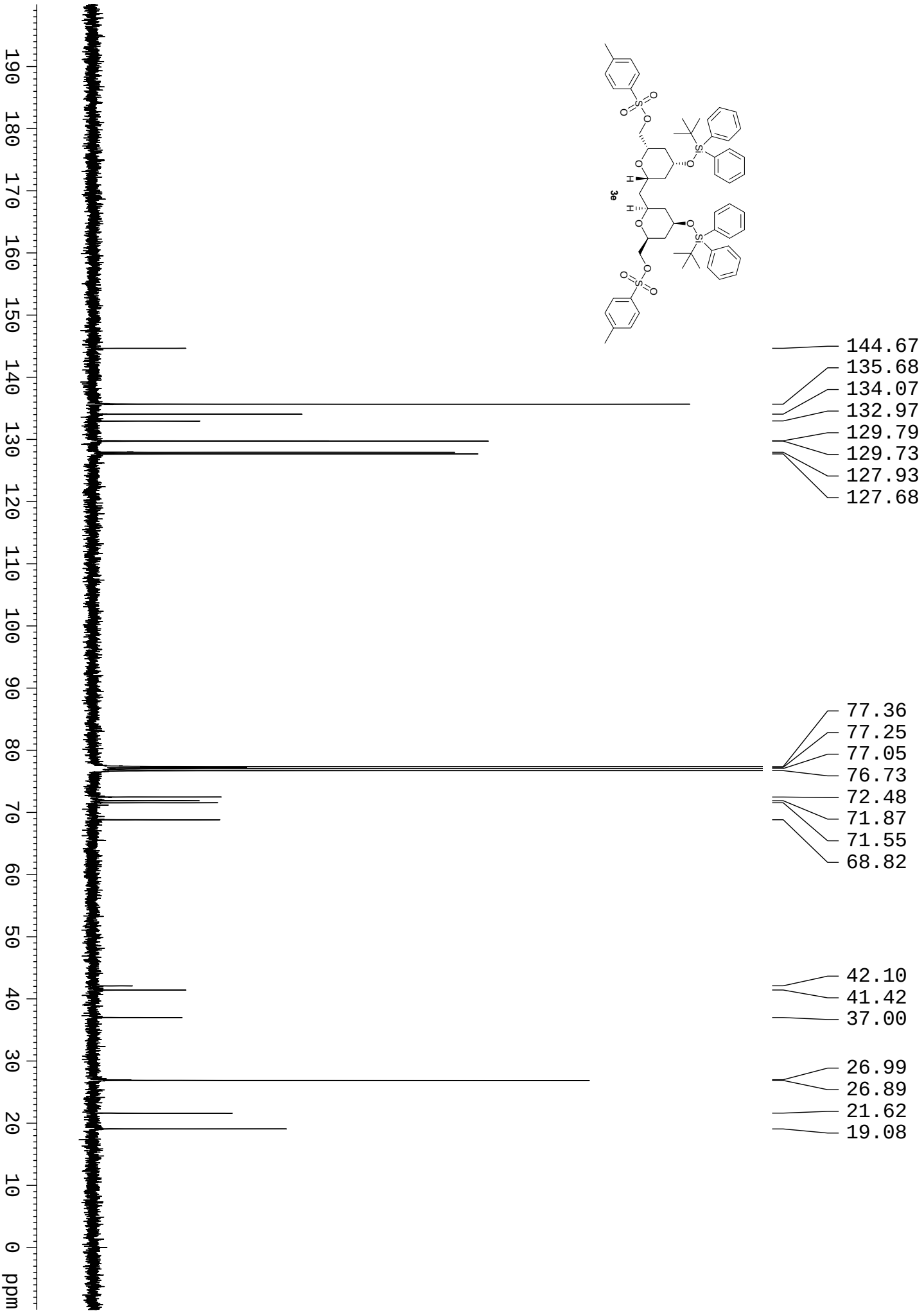
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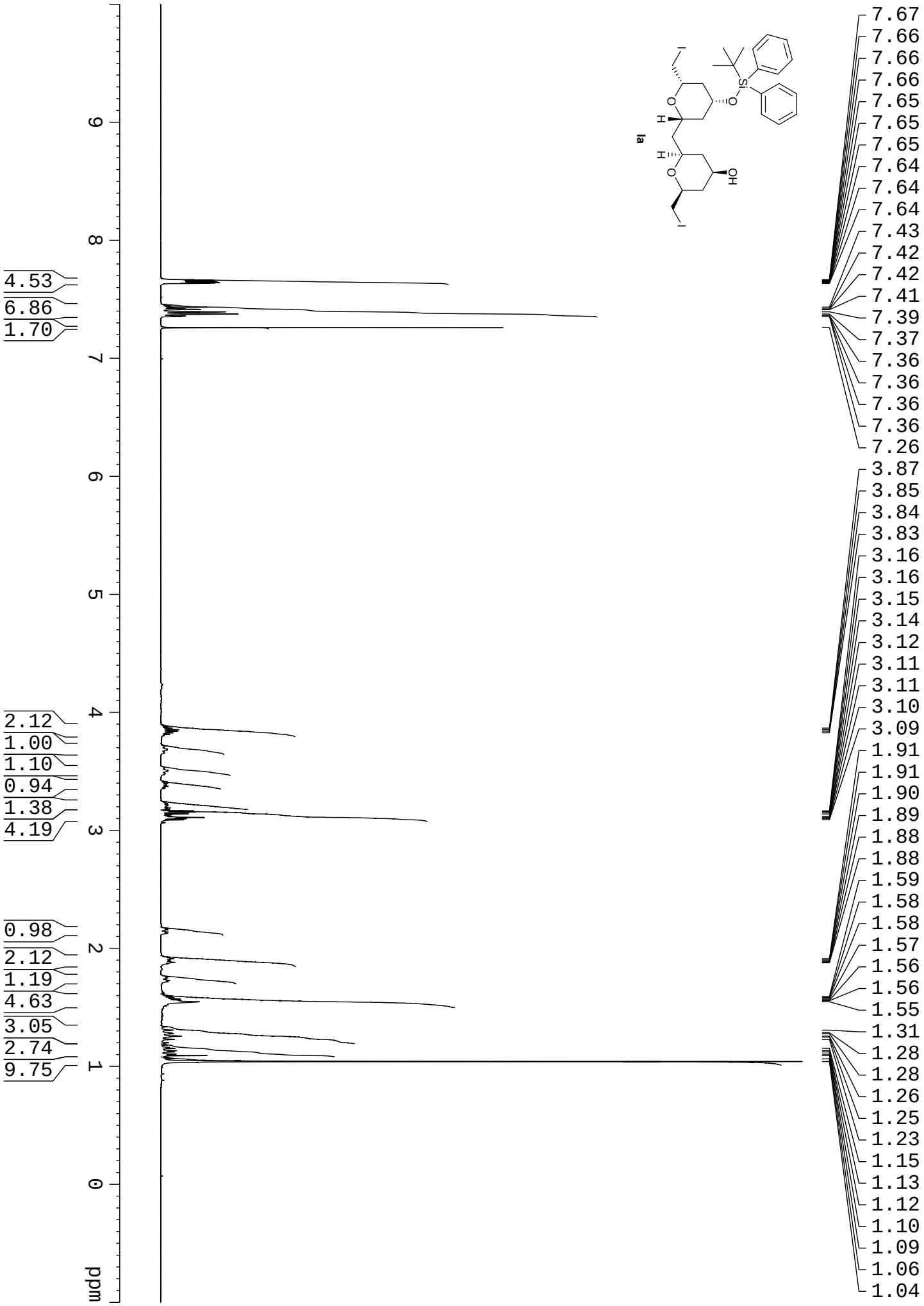
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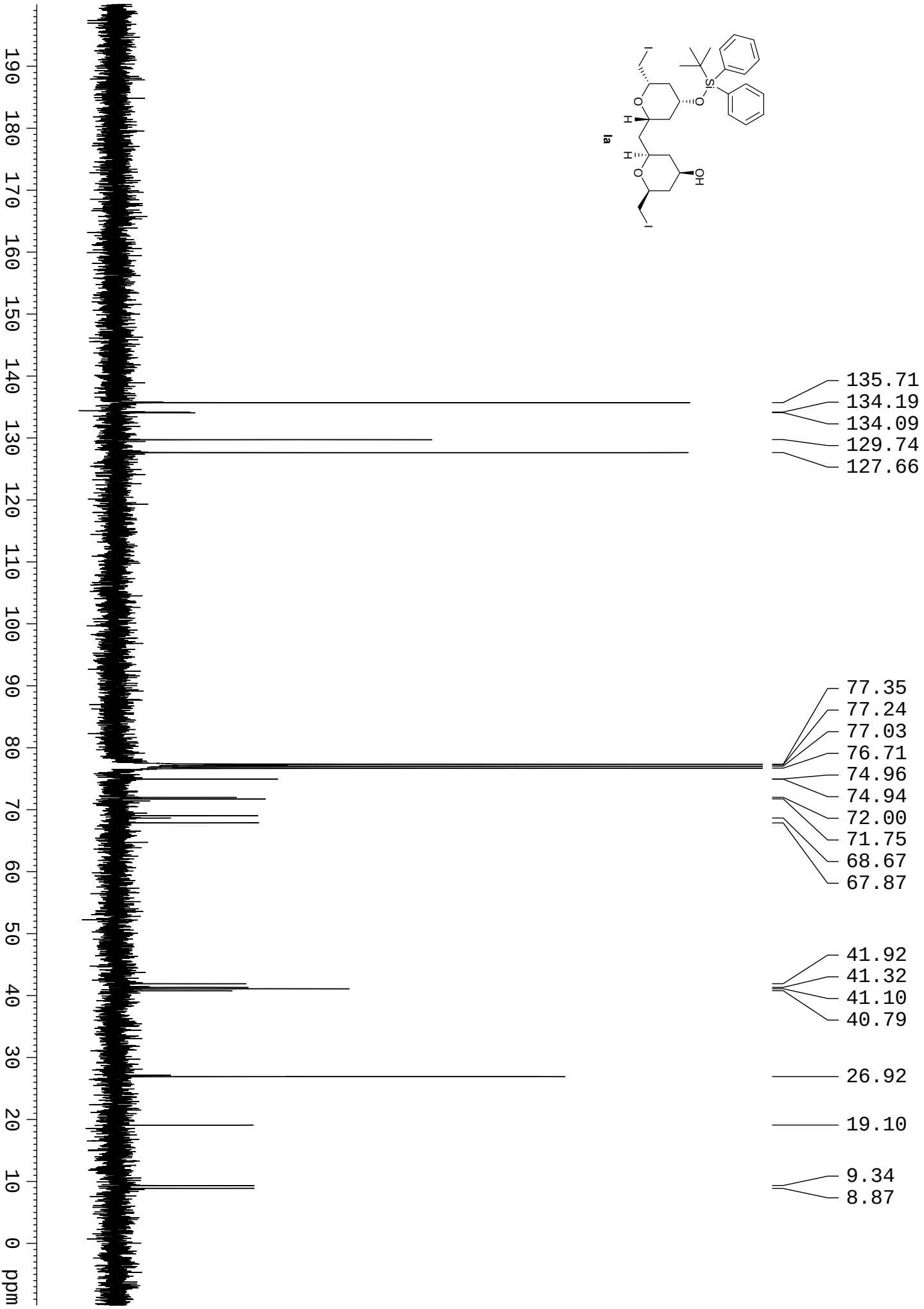
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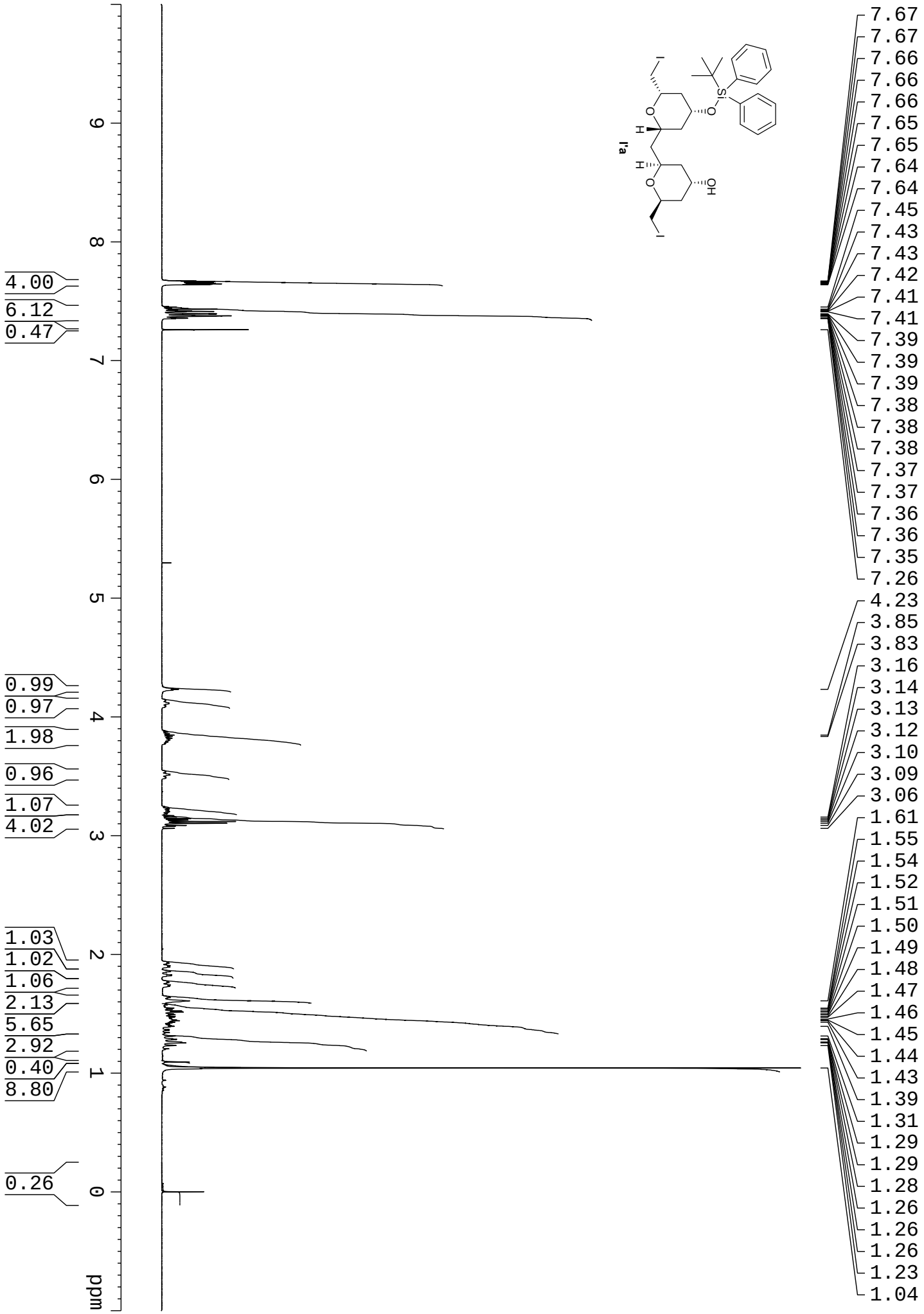
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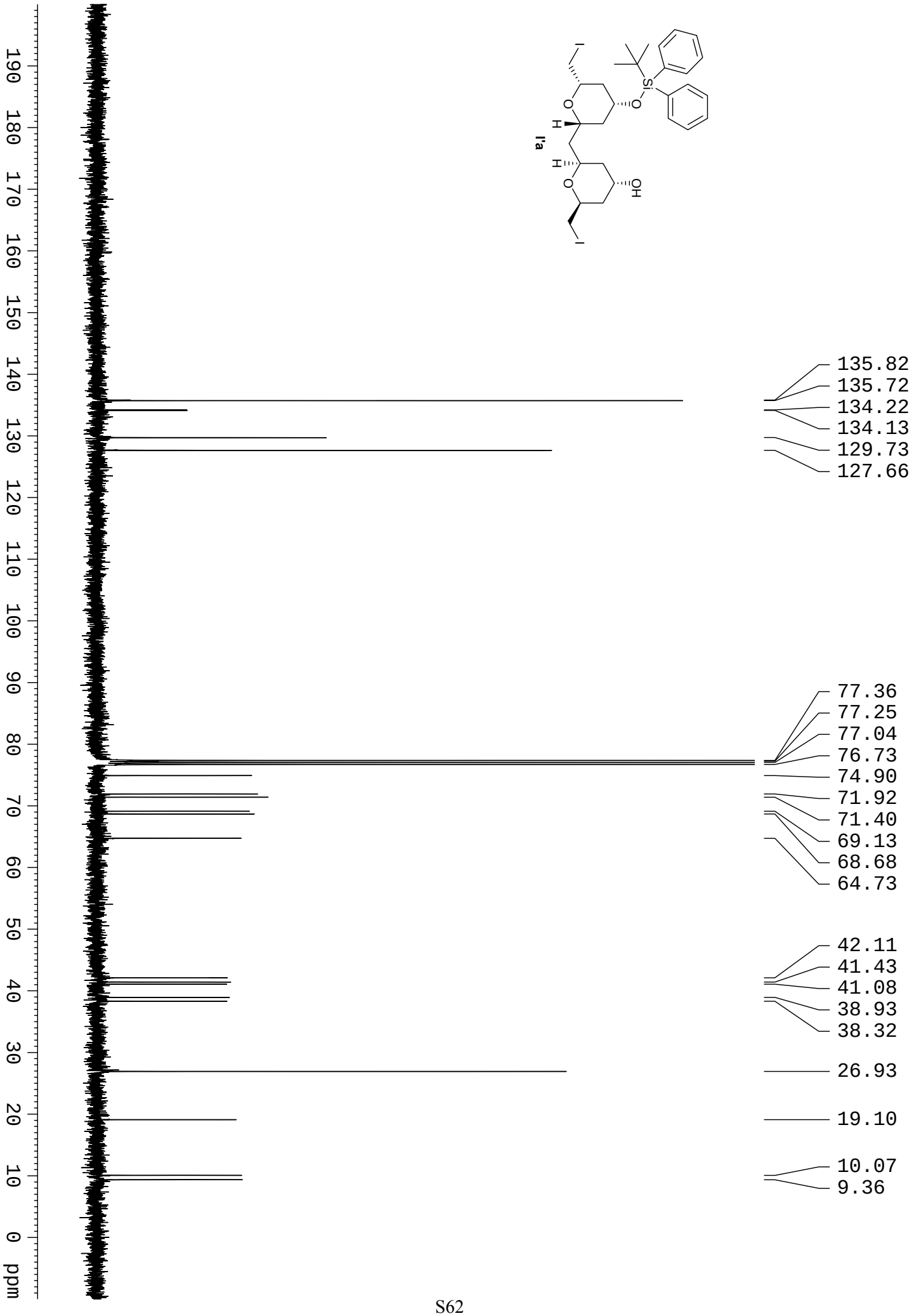
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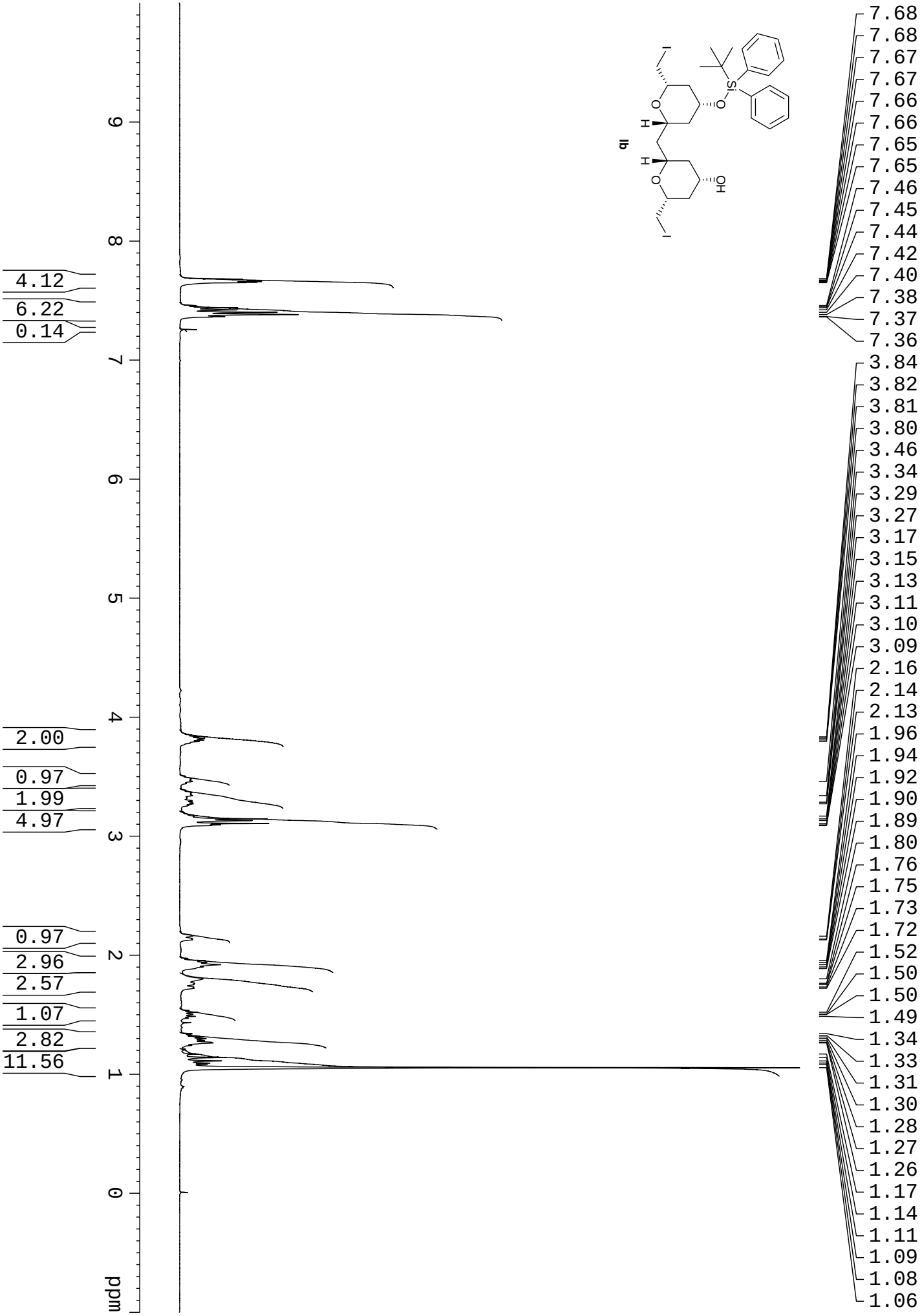
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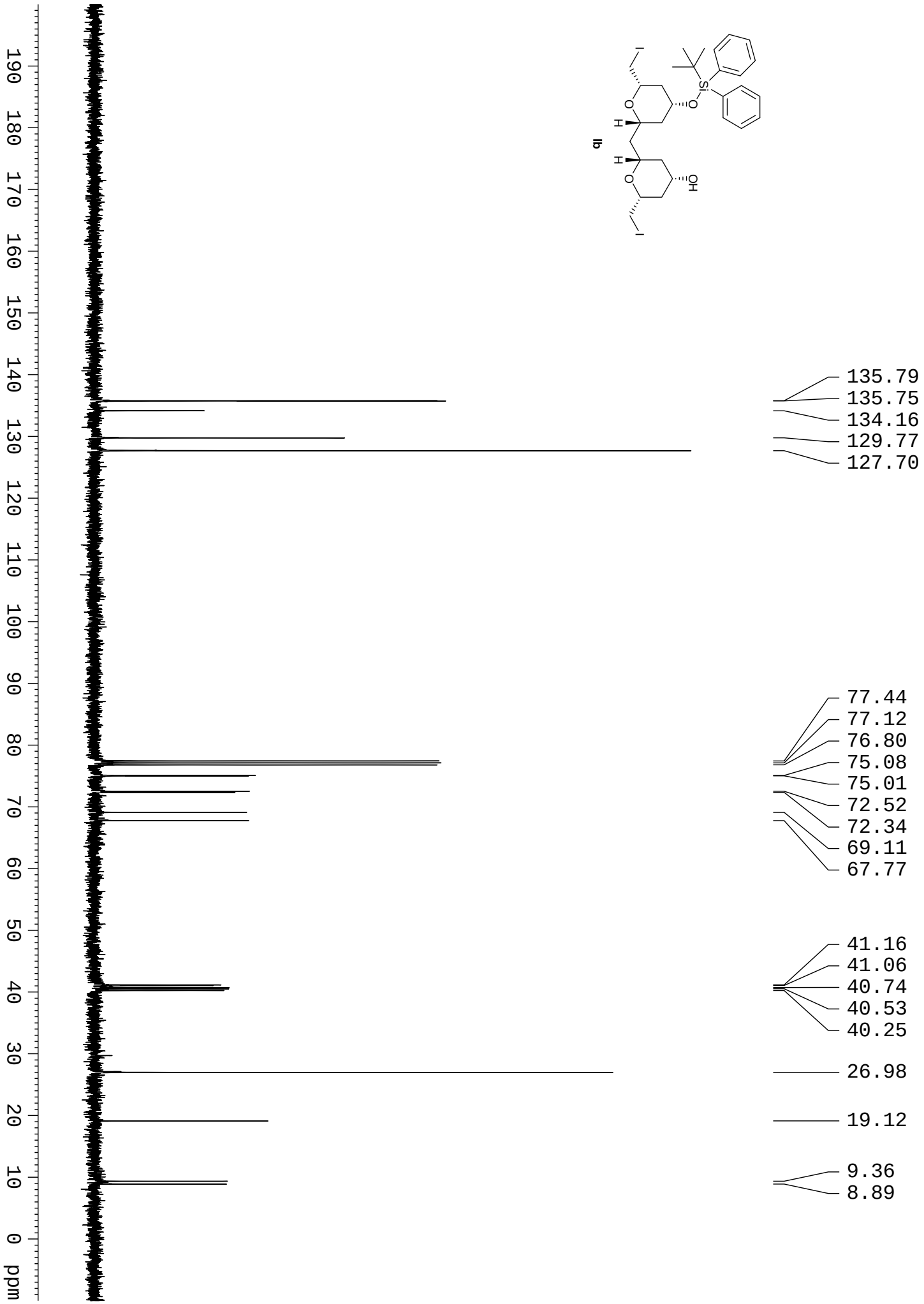
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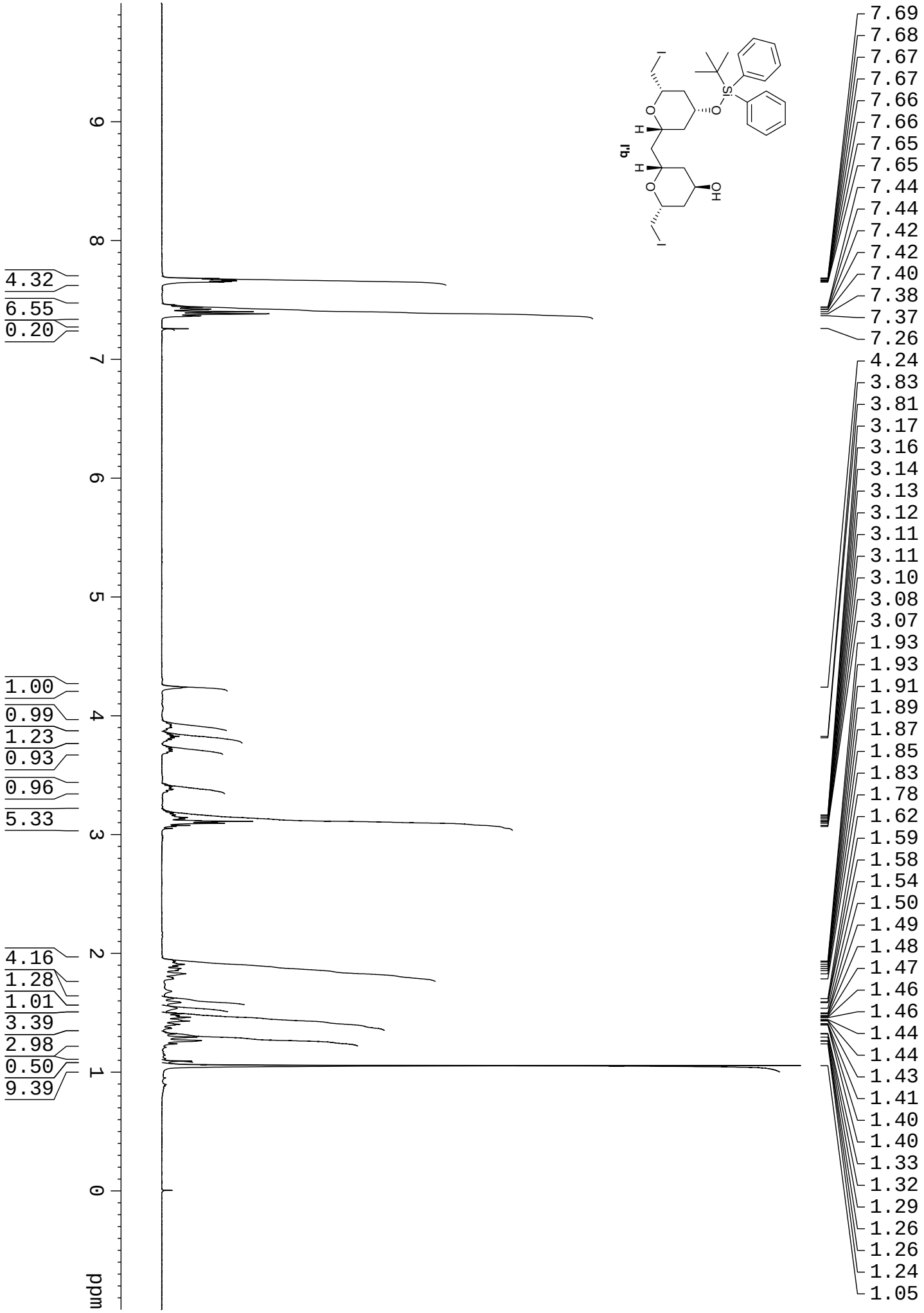
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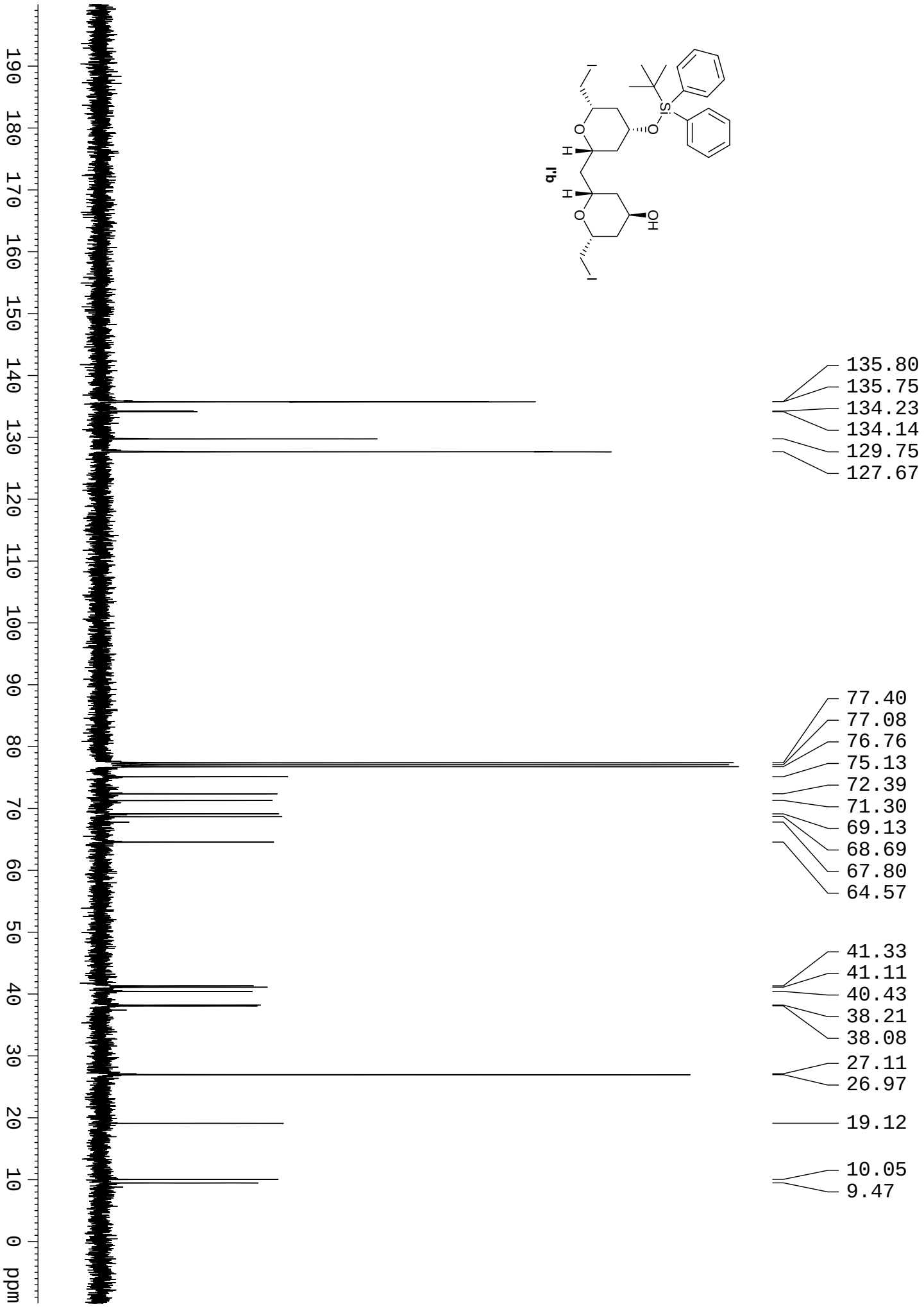
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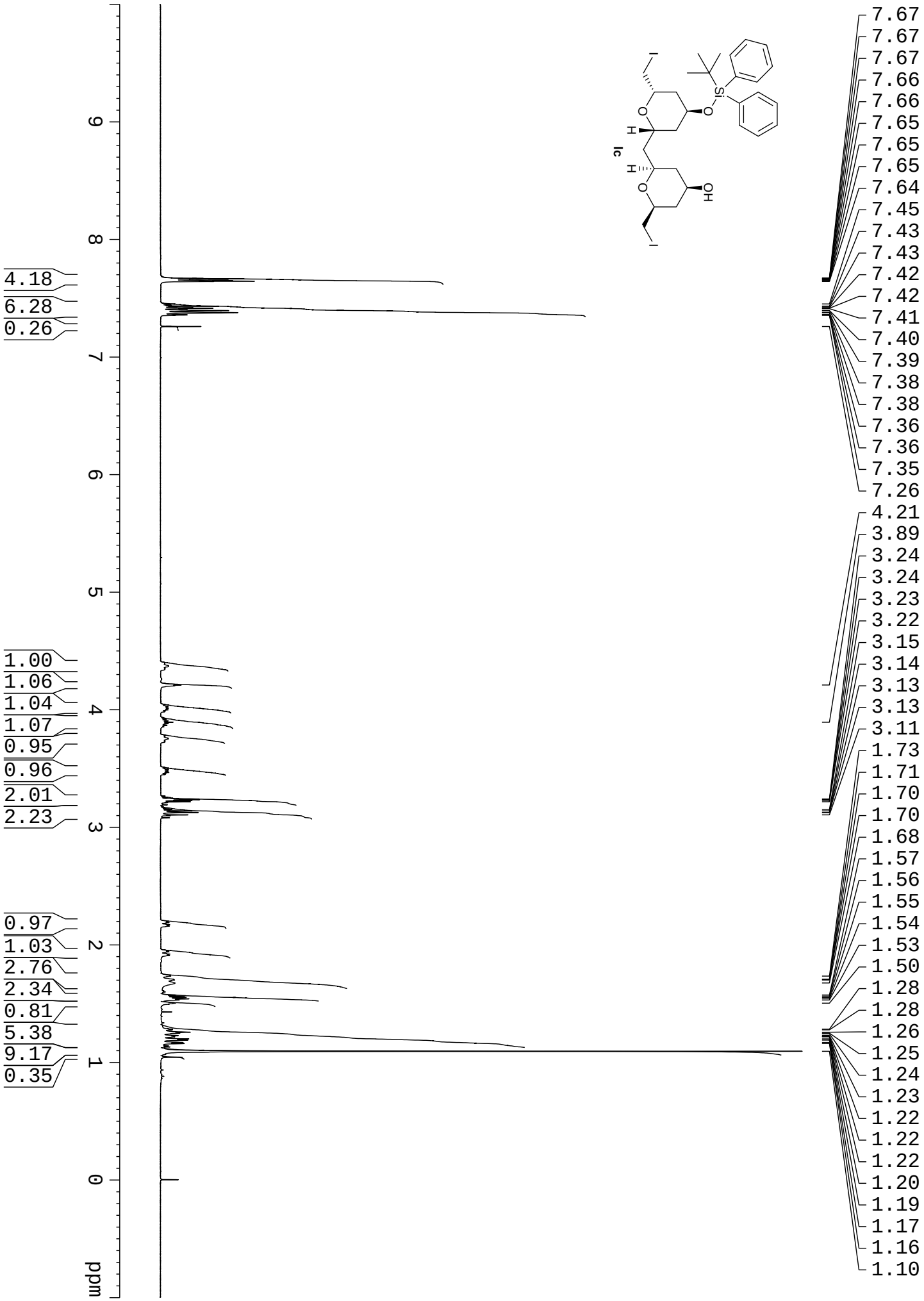
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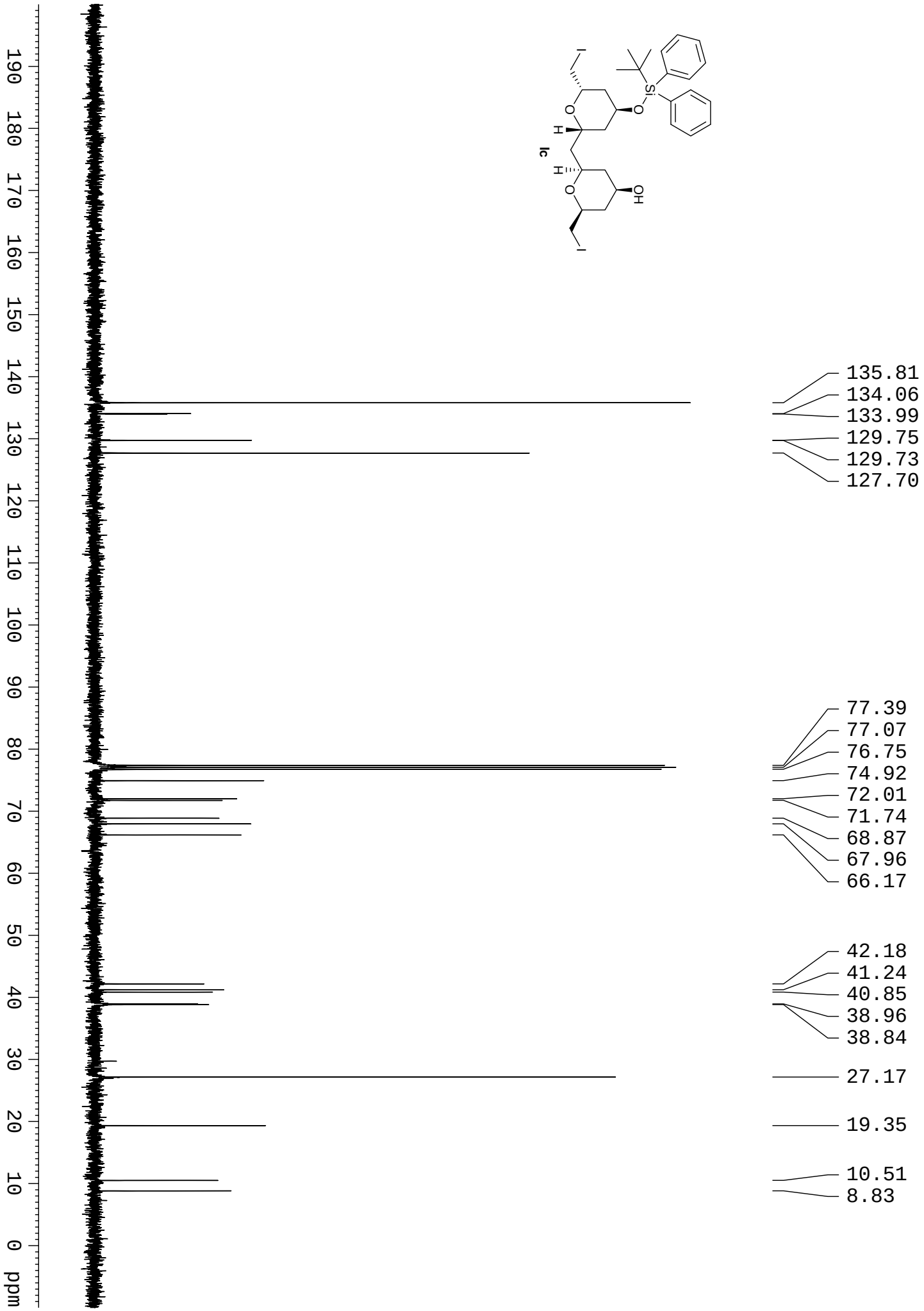
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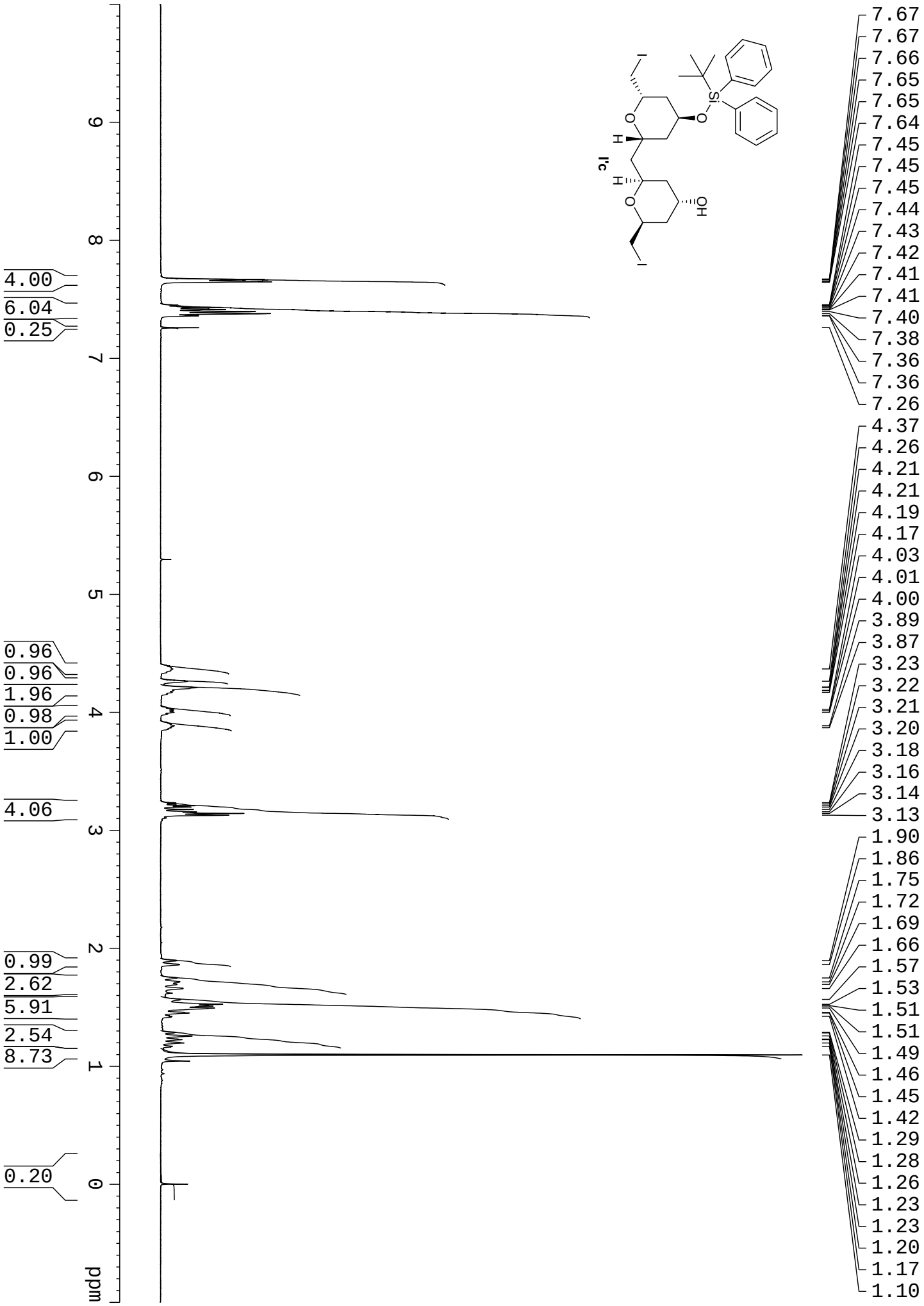
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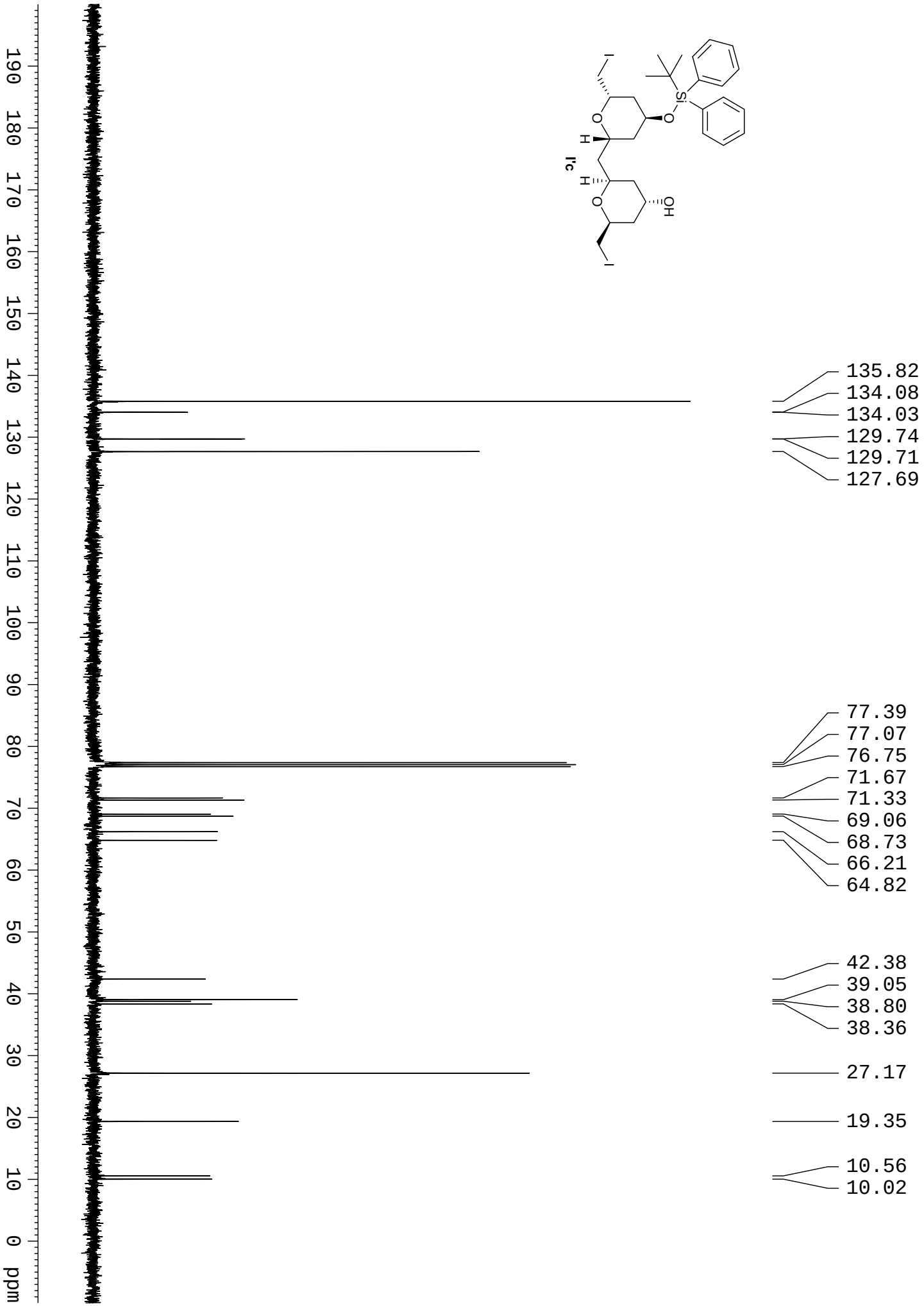
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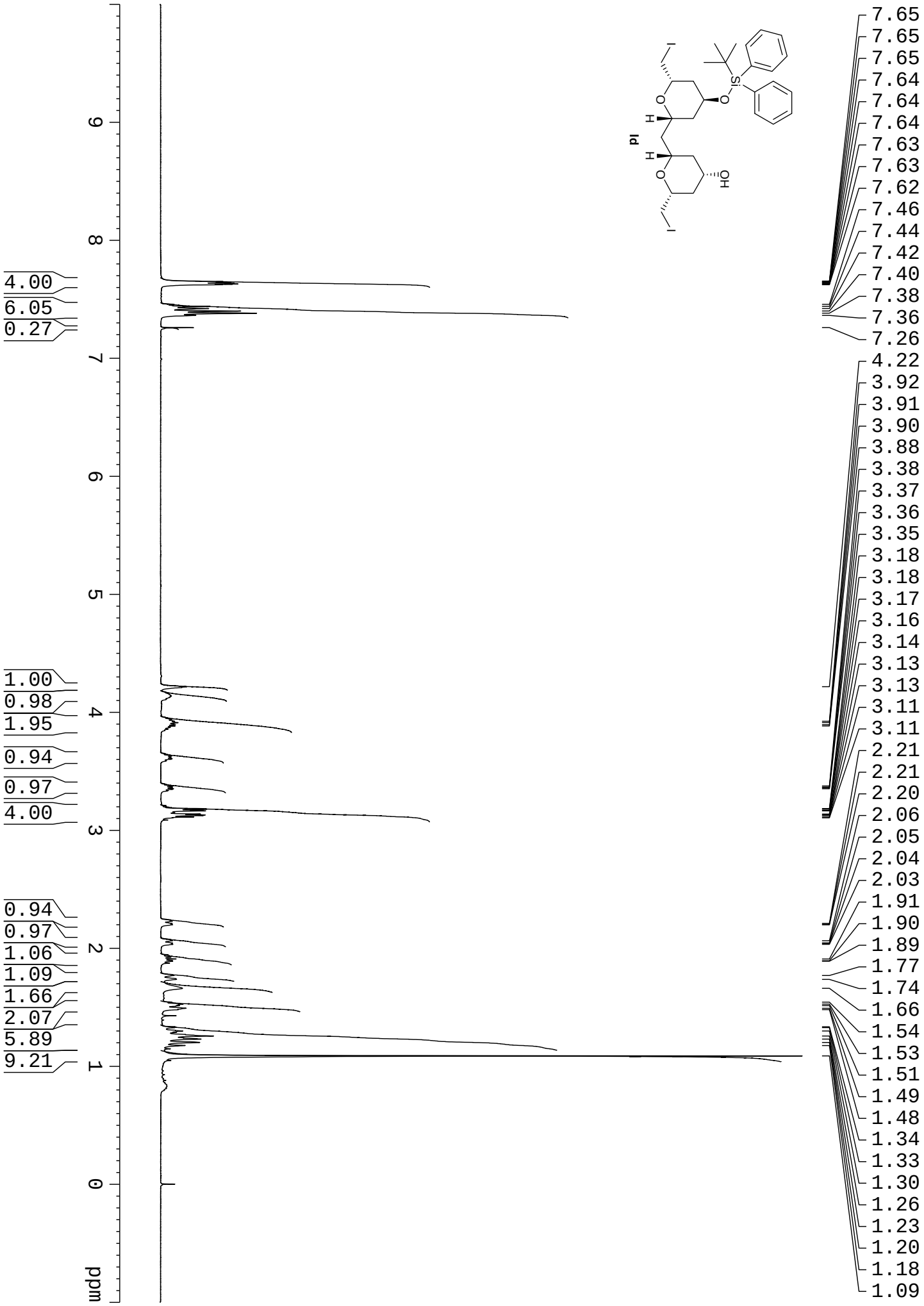
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7.38
7.36
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2.05
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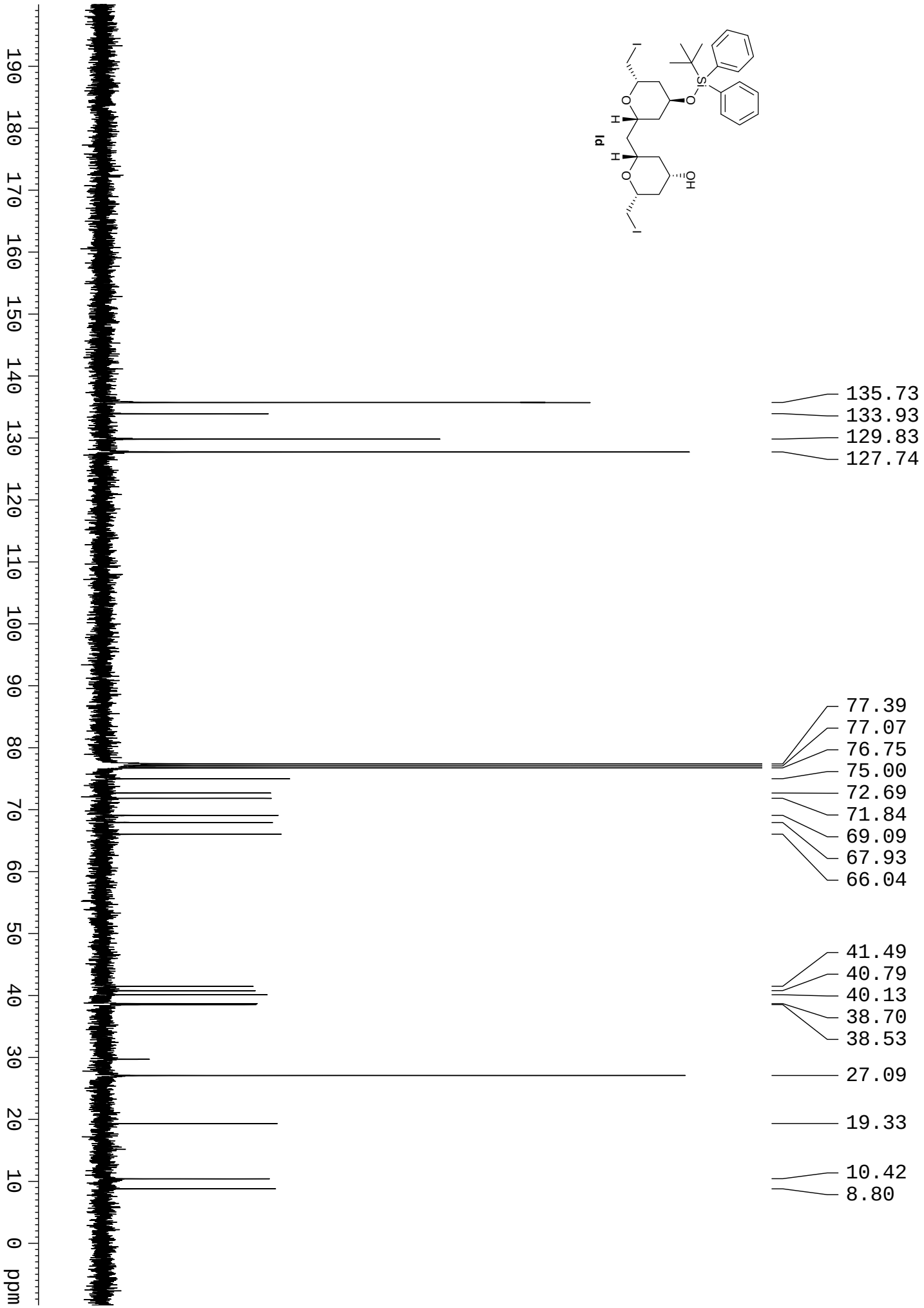
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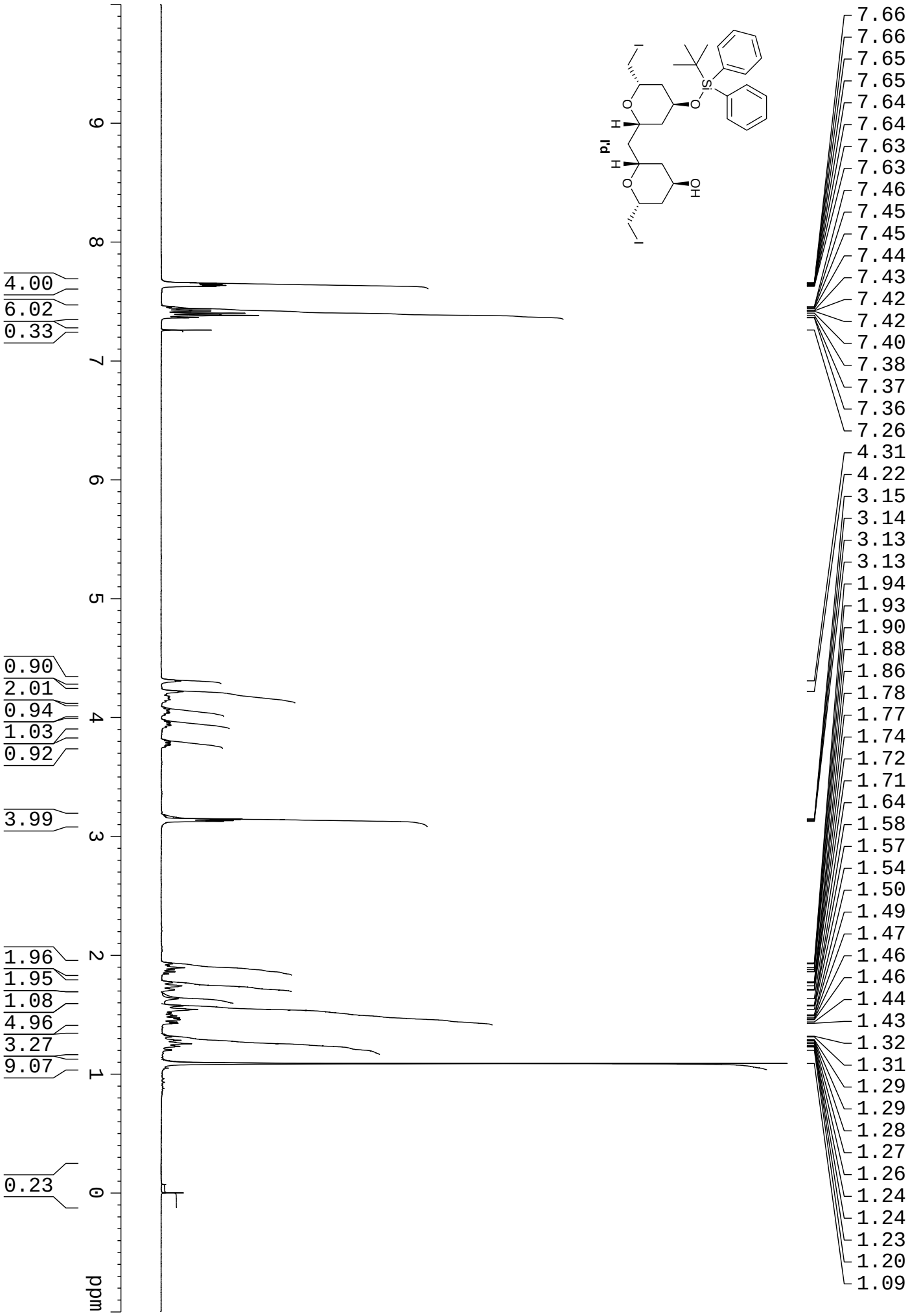
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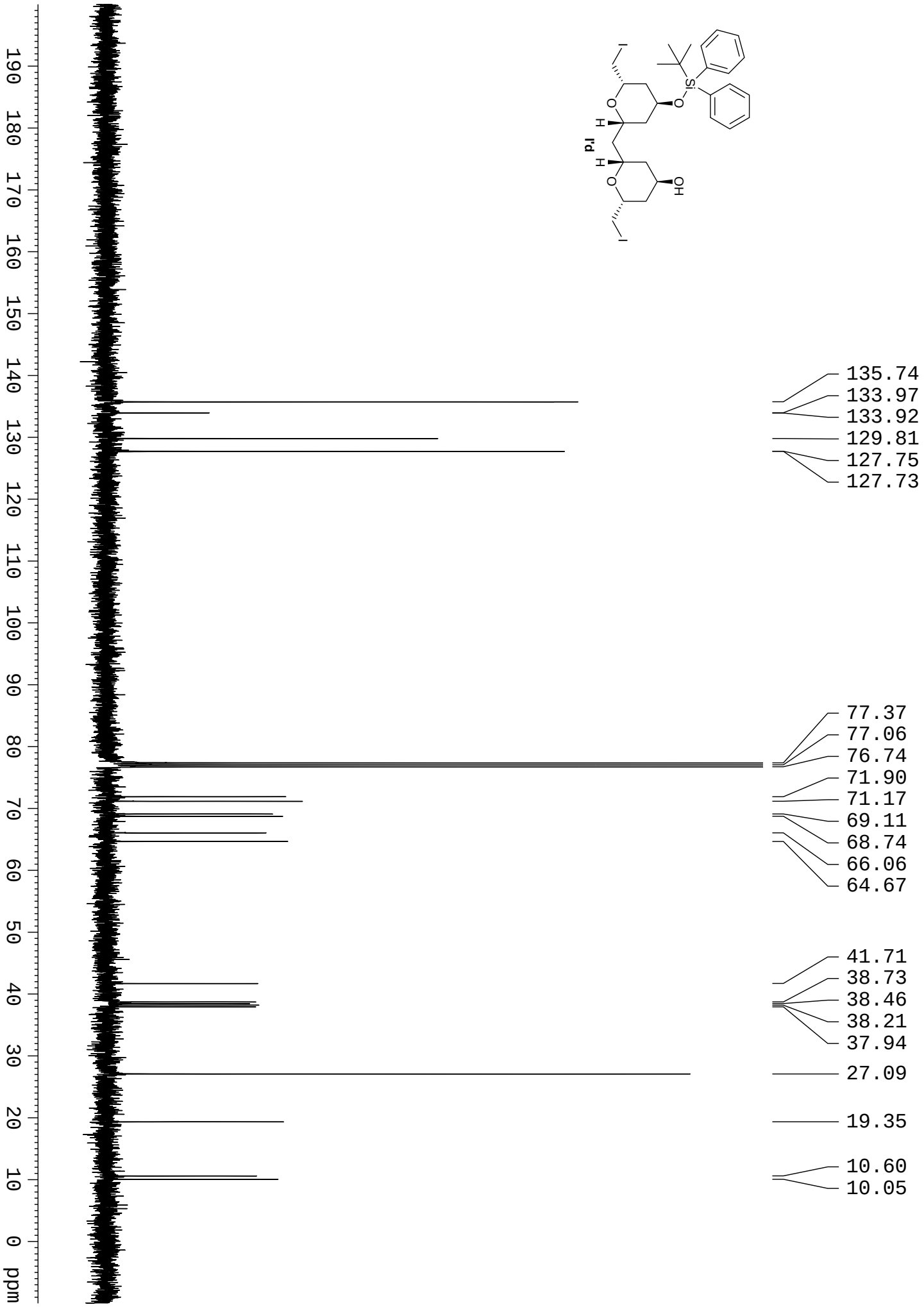
H
H
O
OH
O
Si
I
I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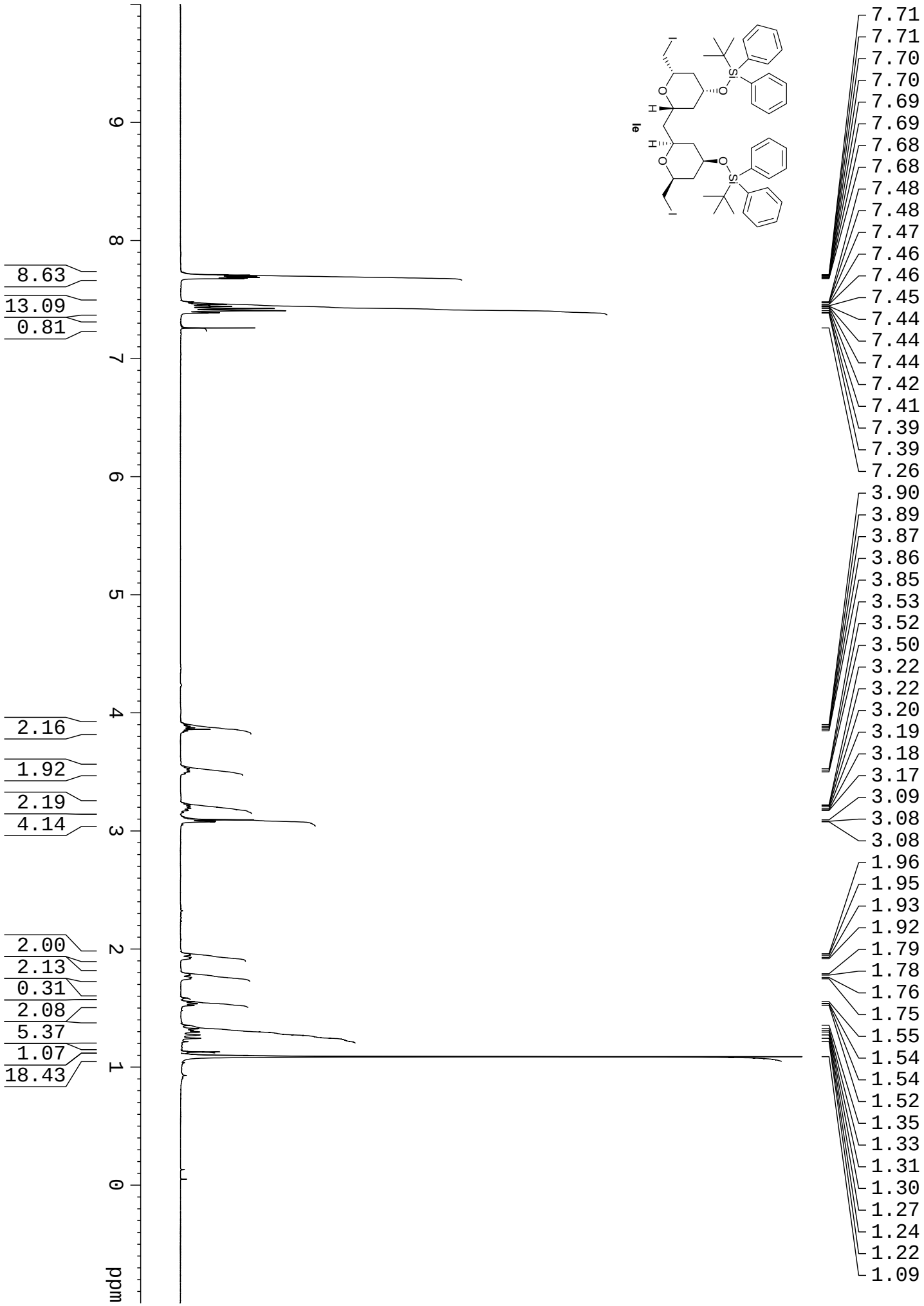
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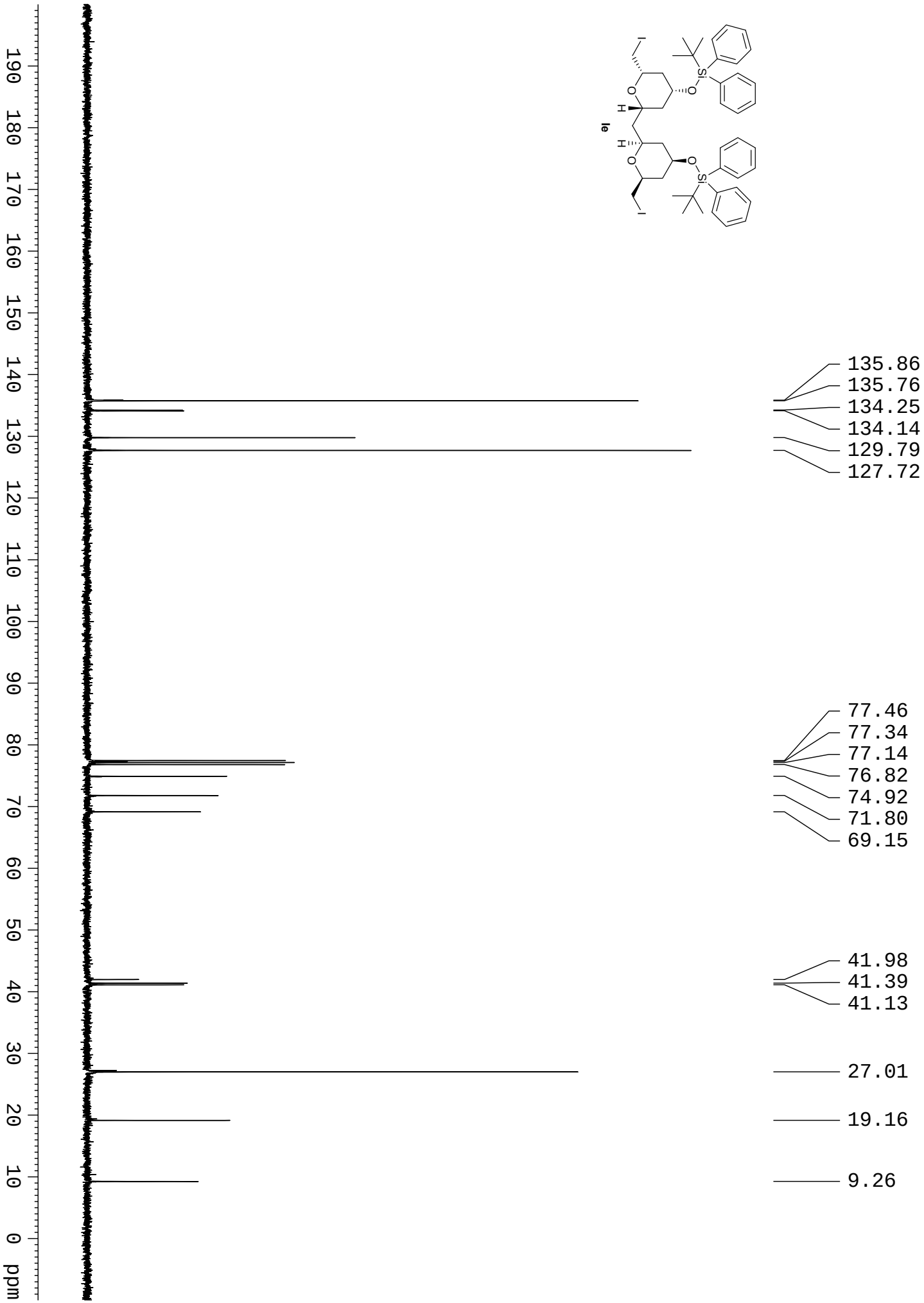
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190
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134.14
129.79
127.72
77.46
77.34
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69.15
41.98
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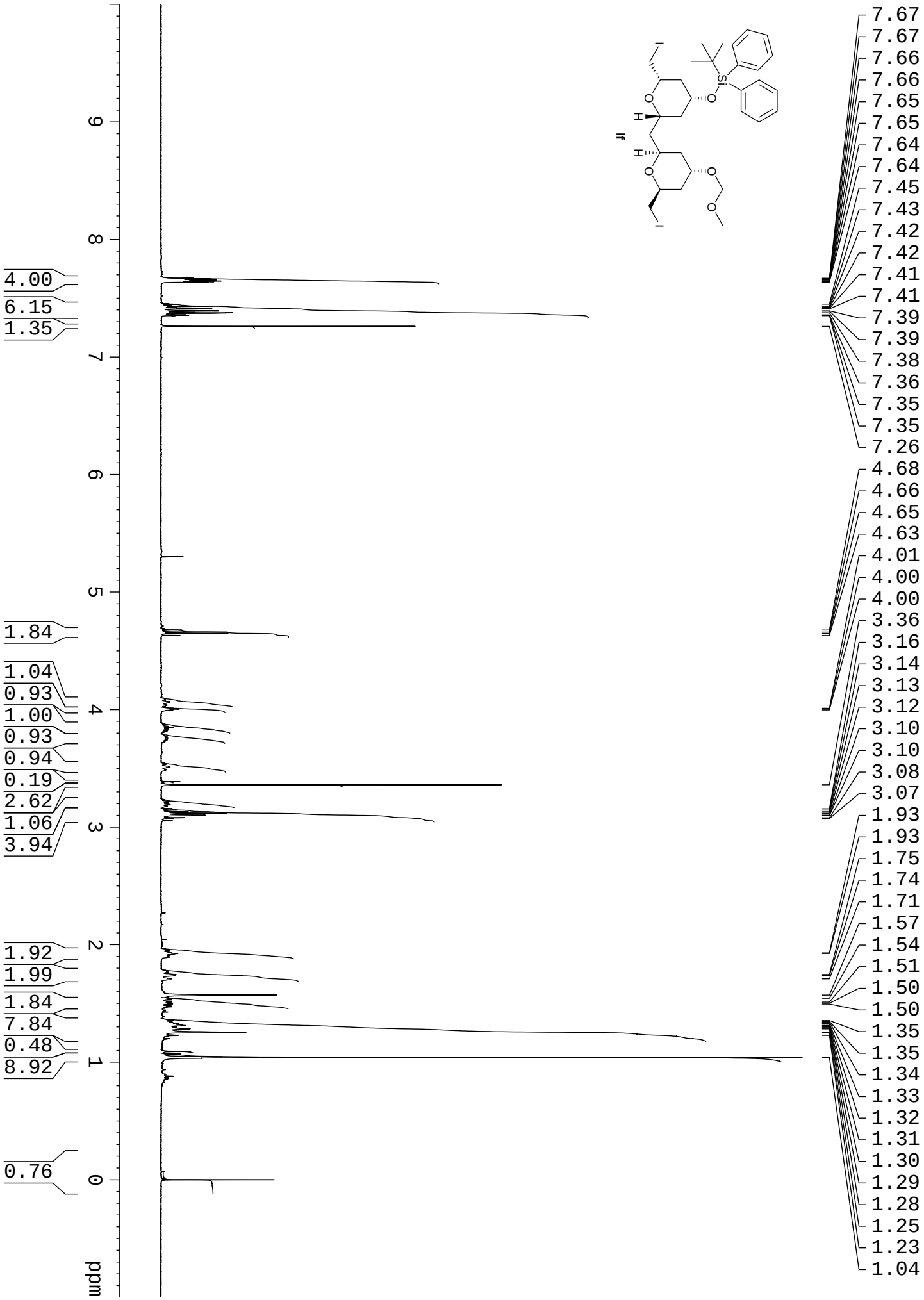
Ie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7.41
7.39
7.39
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7.36
7.35
7.35
7.26
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4.65
4.63
4.01
4.00
4.00
3.36
3.16
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3.13
3.12
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3.10
3.08
3.07
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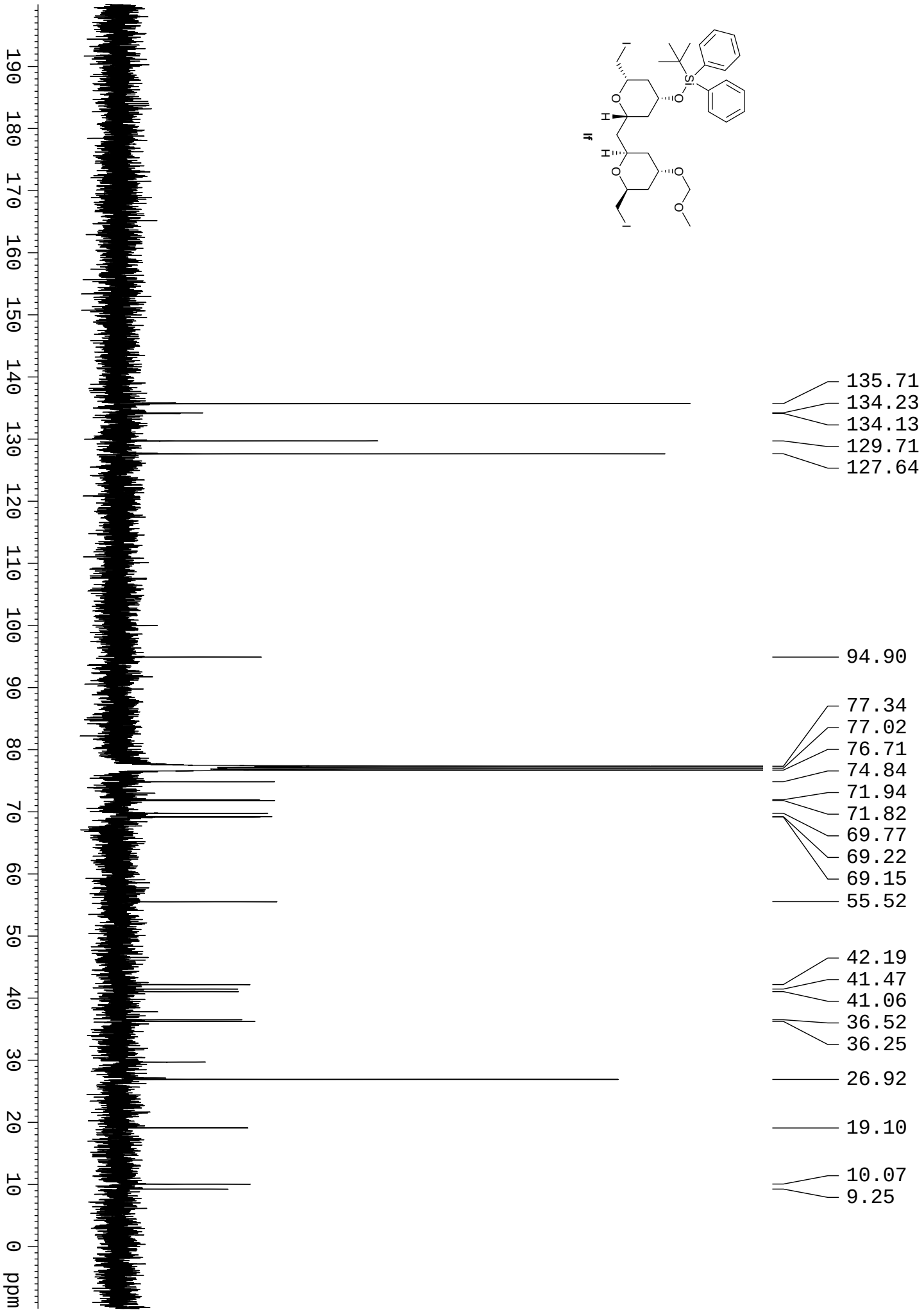
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71.94
71.82
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26.92
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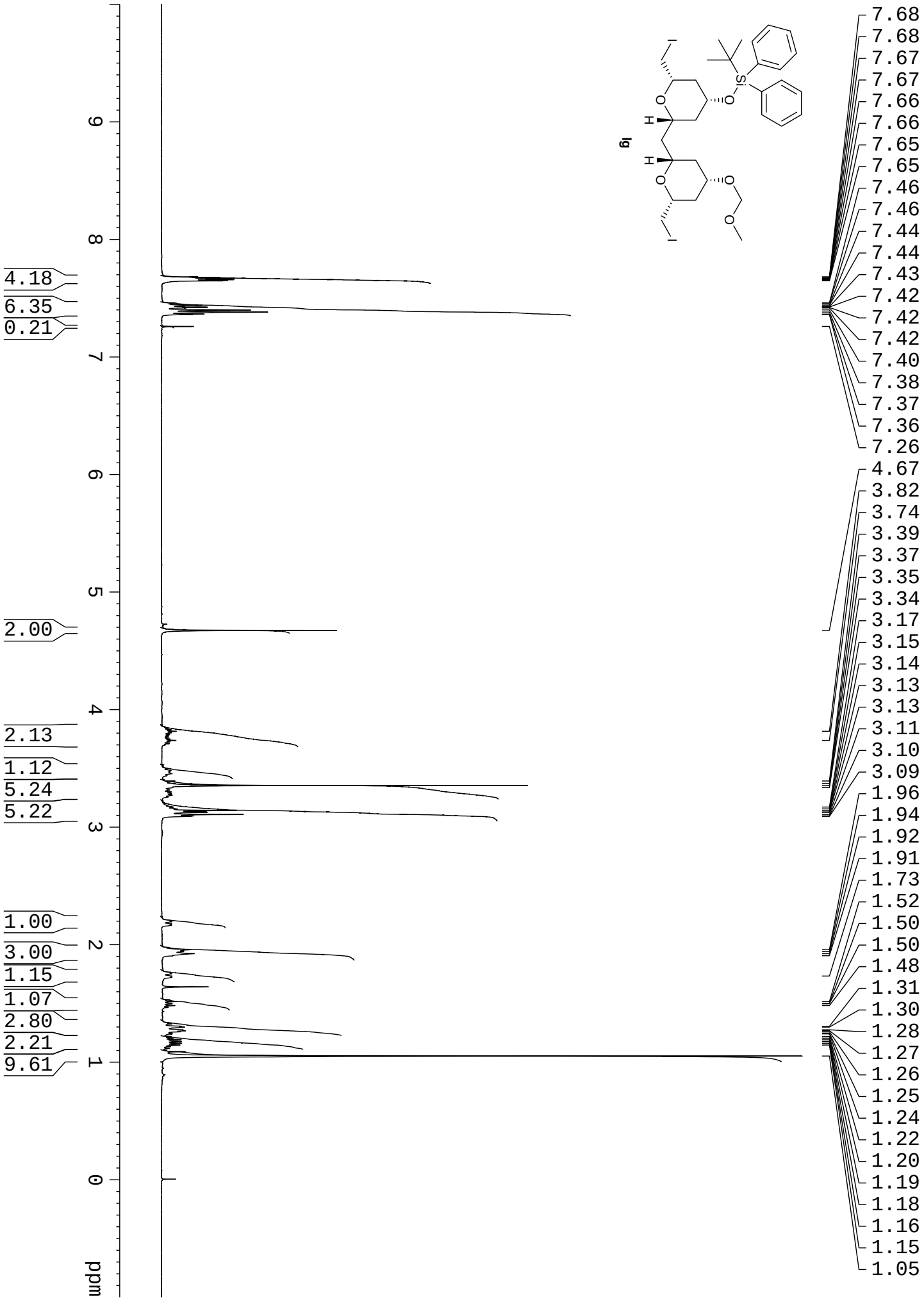
10.07
9.25
ppm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3.35
3.34
3.17
3.15
3.14
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3.13
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1.50
1.50
1.48
1.31
1.30
1.28
1.27
1.26
1.25
1.24
1.22
1.20
1.19
1.18
1.16
1.15
1.05
4.18
6.35
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2.13
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5.24
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1.00
3.00
1.15
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2.80
2.21
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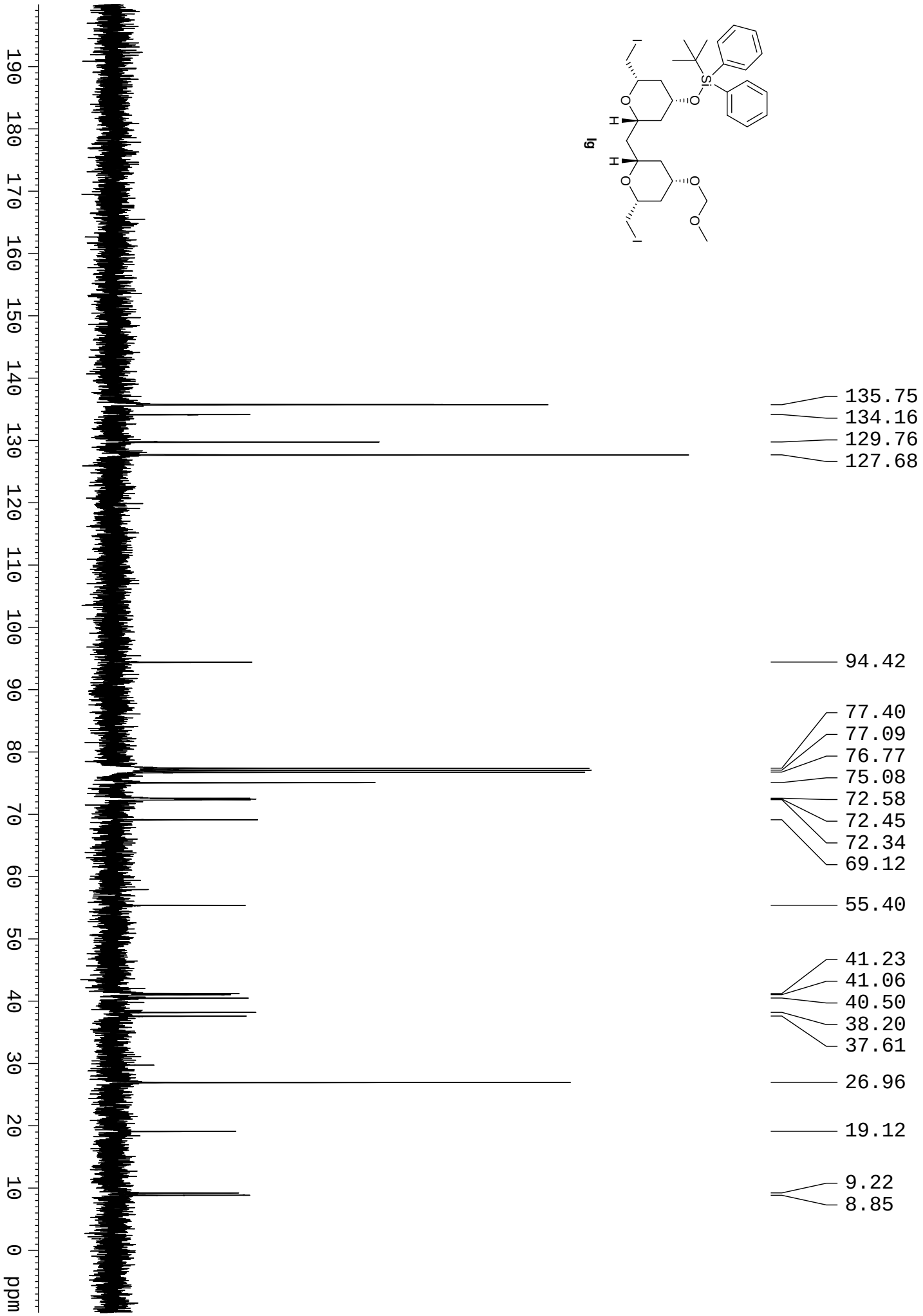
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30
20
10
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ppm
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134.16
129.76
127.68
94.42
77.40
77.09
76.77
75.08
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72.45
72.34
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41.23
41.06
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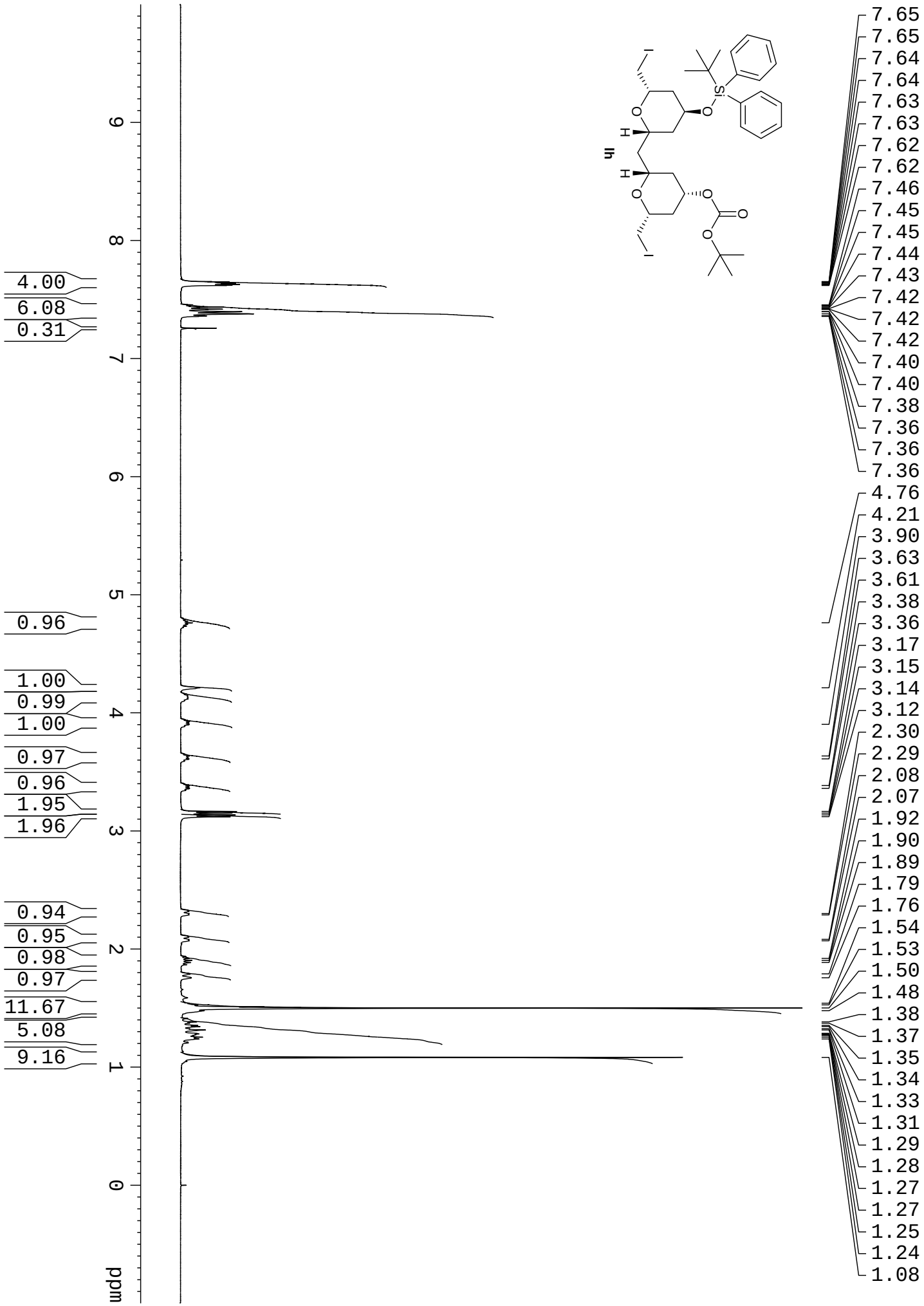
37.61
26.96
19.12
9.22
8.85
Ig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1.00
0.97
0.96
1.95
1.96
0.94
0.95
0.98
0.97
11.67
5.08
9.16
ppm
9
8
7
6
5
4
3
2
1
0
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7.65
7.64
7.64
7.63
7.63
7.62
7.62
7.46
7.45
7.45
7.44
7.43
7.42
7.42
7.42
7.40
7.40
7.38
7.36
7.36
7.36
4.76
4.21
3.90
3.63
3.61
3.38
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3.17
3.15
3.14
3.12
2.30
2.29
2.08
2.07
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1.90
1.89
1.79
1.76
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1.53
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1.28
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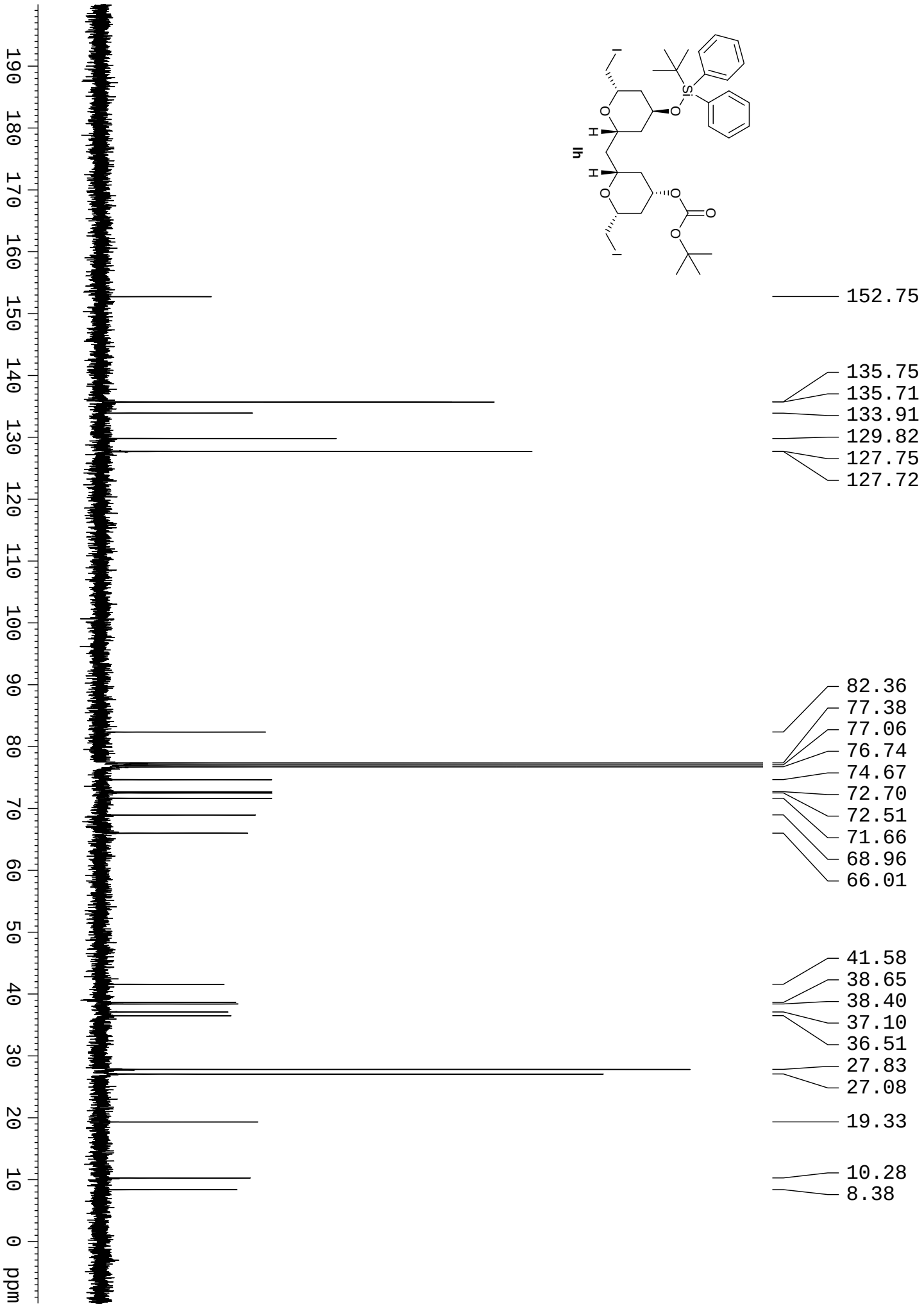
1.27
1.25
1.24
1.08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74.67
72.70
72.51
71.66
68.96
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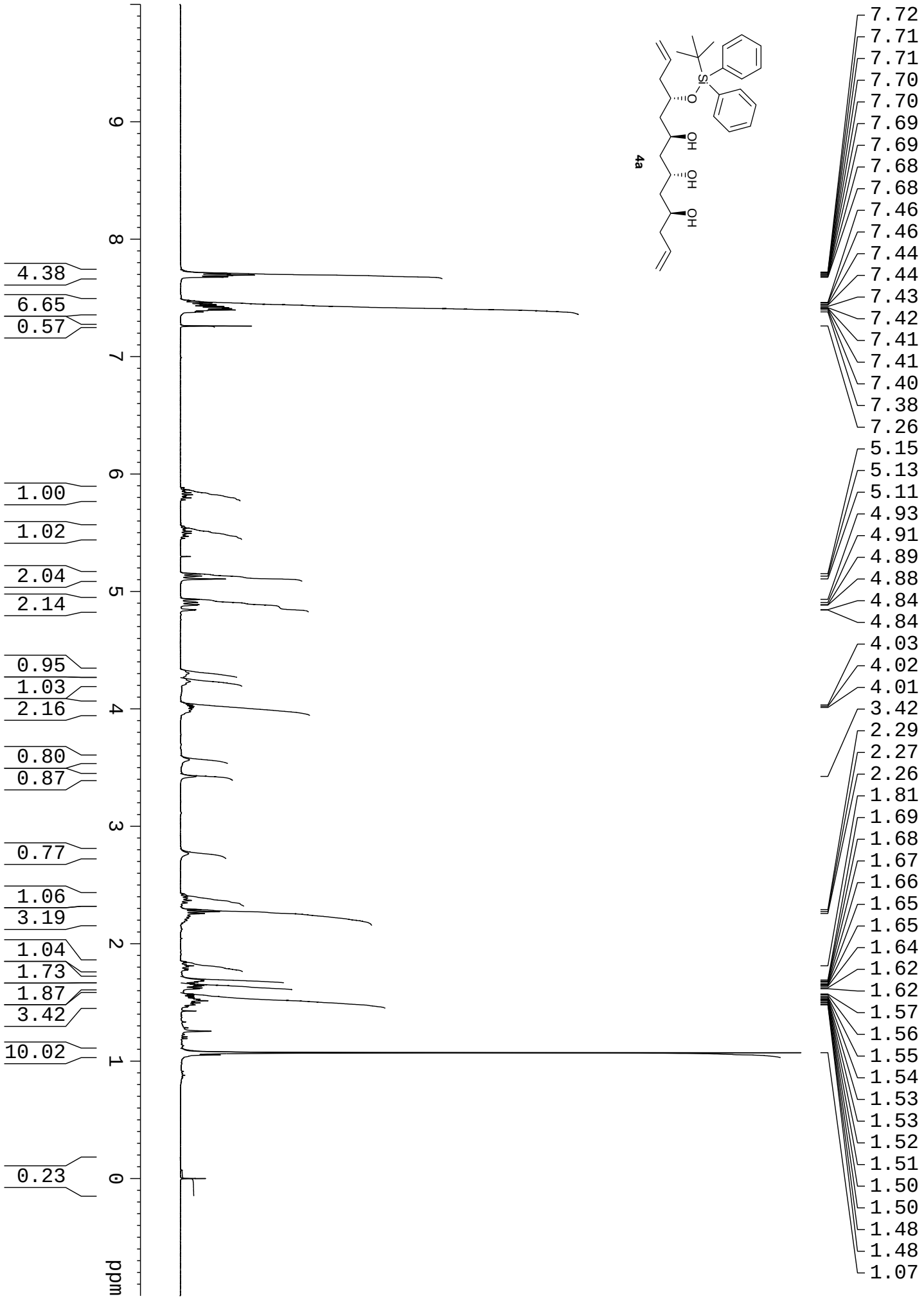
38.65
38.40
37.10
36.51
27.83
27.08
19.33
10.28
8.38
ppm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OH
OH
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7.46
7.44
7.44
7.43
7.42
7.41
7.41
7.40
7.38
7.26
5.15
5.13
5.11
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4.91
4.89
4.88
4.84
4.84
4.03
4.02
4.01
3.42
2.29
2.27
2.26
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1.69
1.68
1.67
1.66
1.65
1.65
1.64
1.62
1.62
1.57
1.56
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1.54
1.53
1.53
1.52
1.51
1.50
1.50
1.48
1.48
1.07
4.38
6.65
0.57
1.00
1.02
2.04
2.14
0.95
1.03
2.16
0.80
0.87
0.77
1.06
3.19
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3.42
10.02
0.23
9
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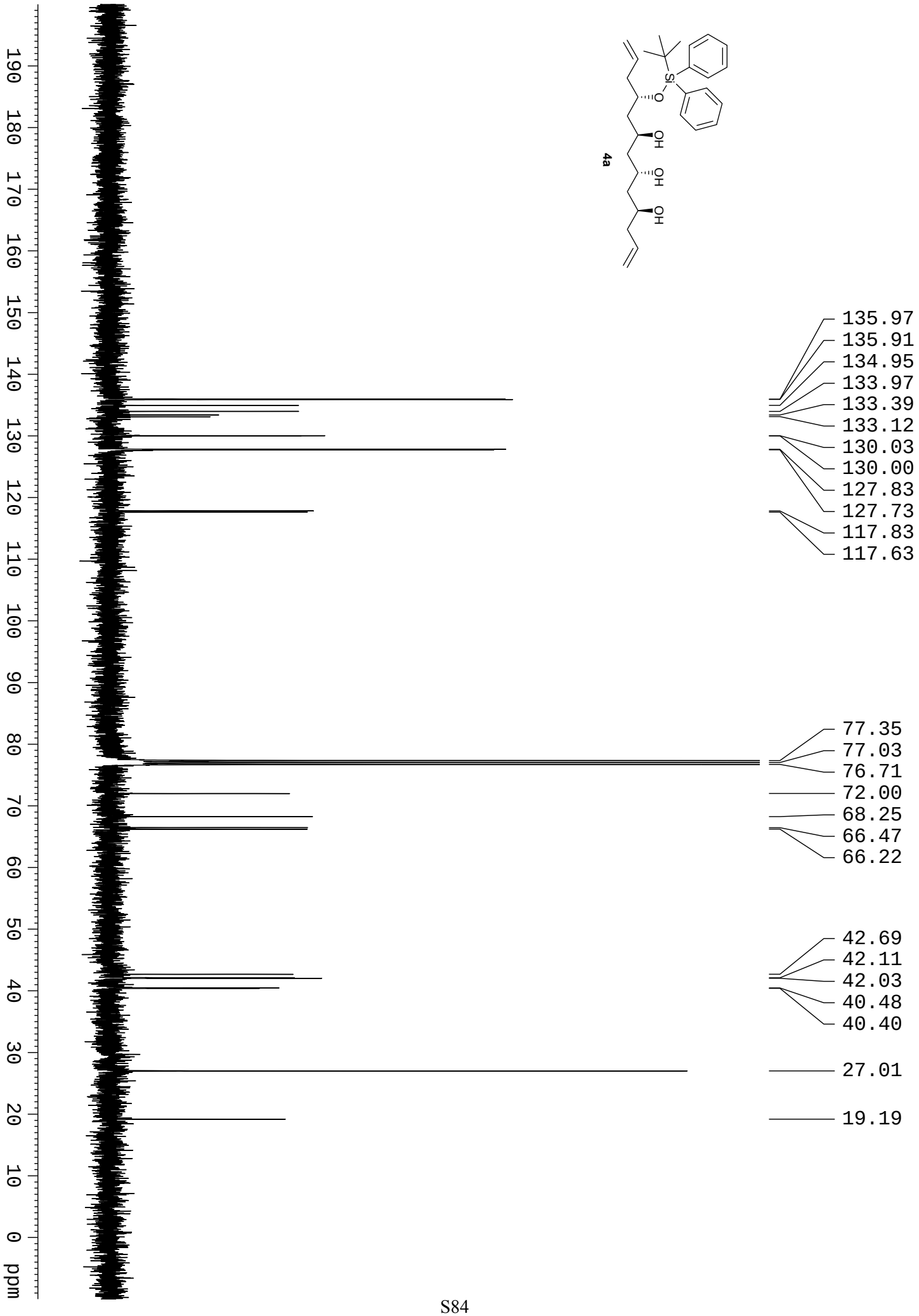
6
5
4
3
2
1
0
ppm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117.63
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77.03
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66.22
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42.11
42.03
40.48
40.40
27.01
19.19
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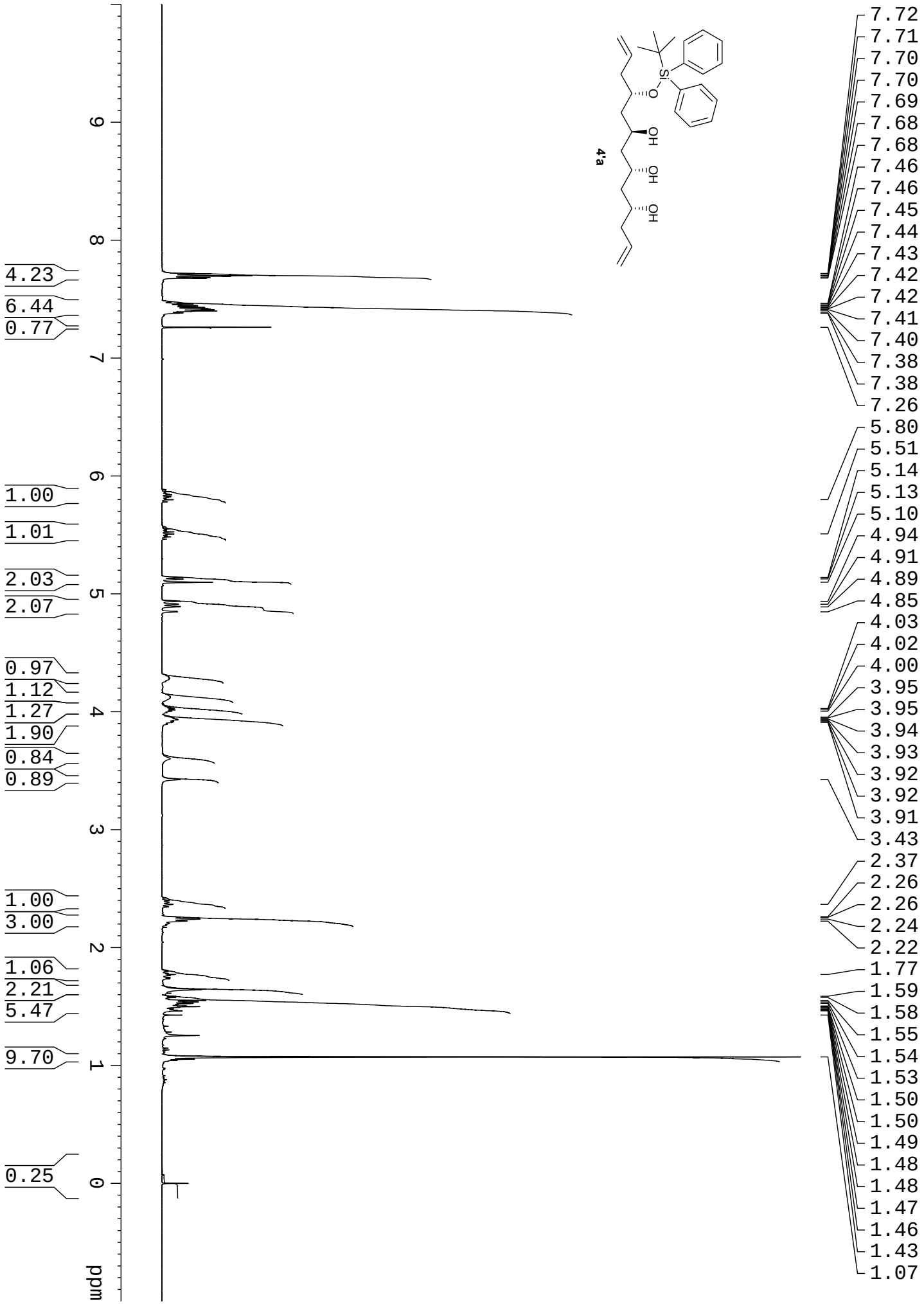
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Si
O
OH
OH
OH
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8
7
6
5
4
3
2
1
0
ppm
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1.01
2.03
2.07
0.97
1.12
1.27
1.90
0.84
0.89
1.00
3.00
1.06
2.21
5.47
9.70
0.25
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7.71
7.70
7.70
7.69
7.68
7.68
7.46
7.46
7.45
7.44
7.43
7.42
7.42
7.41
7.40
7.38
7.38
7.26
5.80
5.51
5.14
5.13
5.10
4.94
4.91
4.89
4.85
4.03
4.02
4.00
3.95
3.95
3.94
3.93
3.92
3.92
3.91
3.43
2.37
2.26
2.26
2.24
2.22
1.77
1.59
1.58
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1.50
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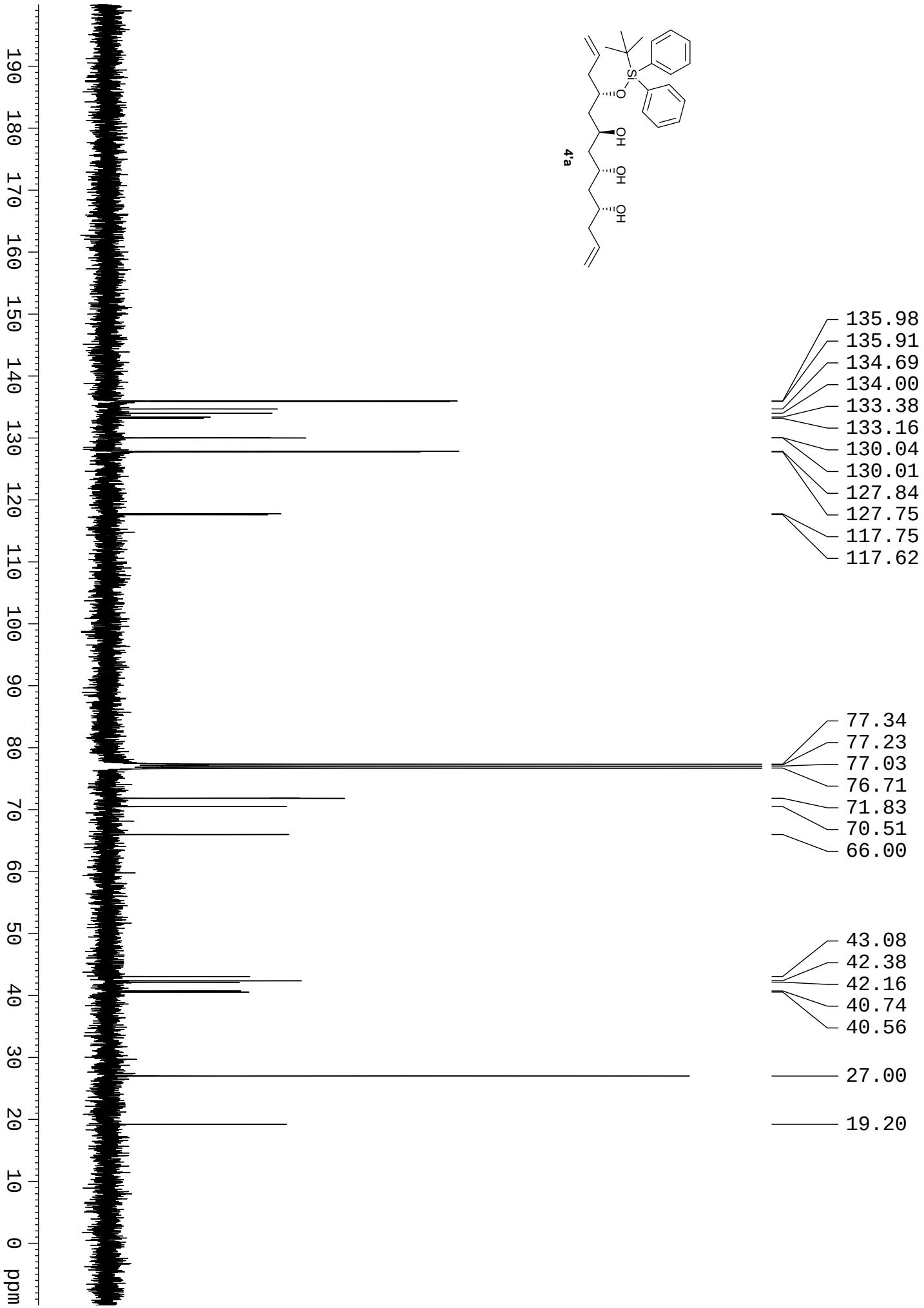
1.49
1.48
1.48
1.47
1.46
1.43
1.07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133.16
130.04
130.01
127.84
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117.75
117.62
77.34
77.23
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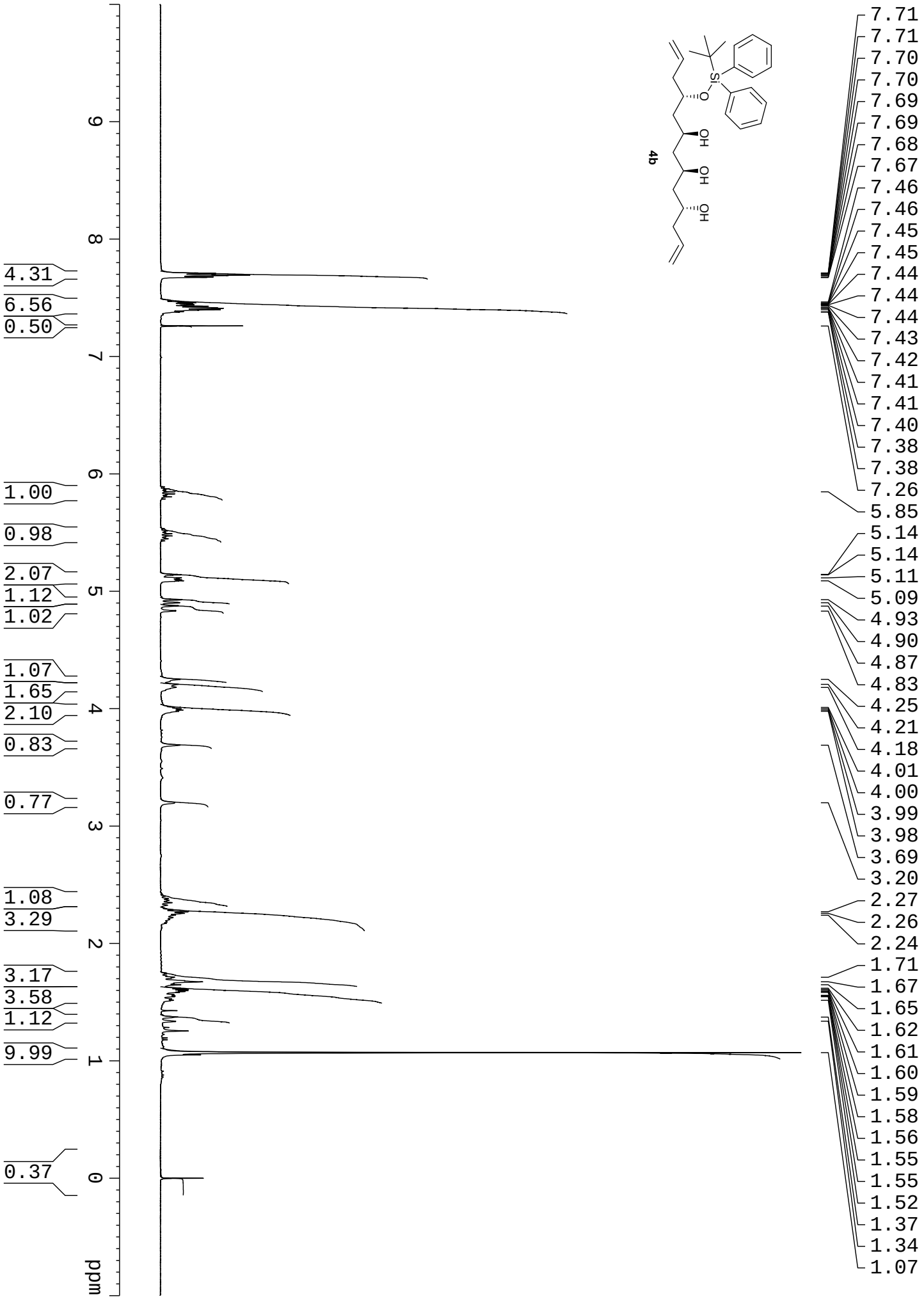
70.51
66.00
43.08
42.38
42.16
40.74
40.56
27.00
19.20
ppm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OH
OH
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7
6
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4
3
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1
0
ppm
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1.00
0.98
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1.12
1.02
1.07
1.65
2.10
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0.77
1.08
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1.12
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7.70
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7.46
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7.45
7.45
7.44
7.44
7.44
7.43
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7.41
7.40
7.38
7.38
7.26
5.85
5.14
5.14
5.11
5.09
4.93
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4.25
4.21
4.18
4.01
4.00
3.99
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2.26
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1.55
1.55
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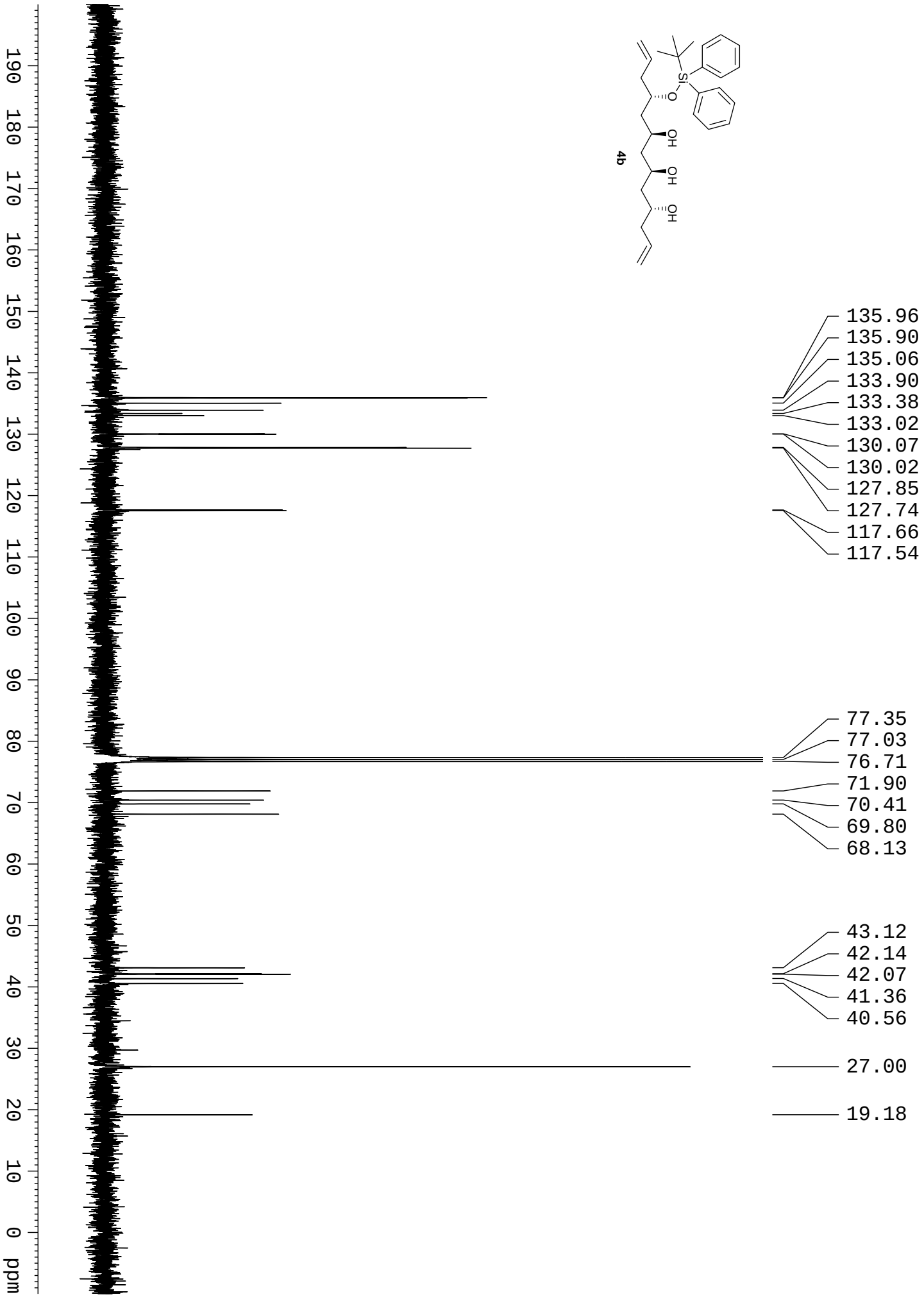
1.07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OH
OH
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135.90
135.06
133.90
133.38
133.02
130.07
130.02
127.85
127.74
117.66
117.54
77.35
77.03
76.71
71.90
70.41
69.80
68.13
43.12
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42.07
41.36
40.56
27.00
19.18
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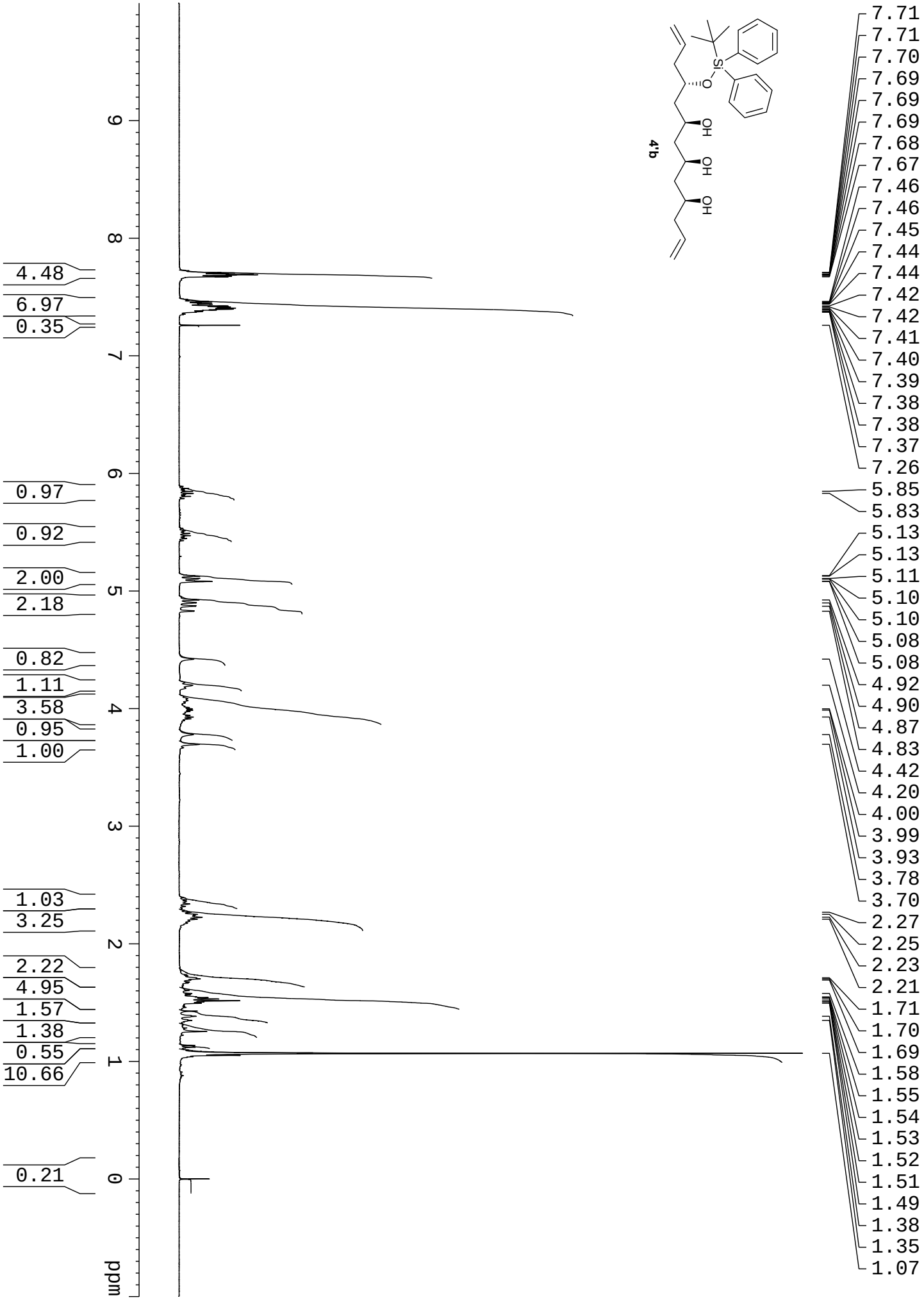
4b
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OH
OH
O
Si
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7.71
7.70
7.69
7.69
7.69
7.68
7.67
7.46
7.46
7.45
7.44
7.44
7.42
7.42
7.41
7.40
7.39
7.38
7.38
7.37
7.26
5.85
5.83
5.13
5.13
5.11
5.10
5.10
5.08
5.08
4.92
4.90
4.87
4.83
4.42
4.20
4.00
3.99
3.93
3.78
3.70
2.27
2.25
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2.21
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1.69
1.58
1.55
1.54
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1.52
1.51
1.49
1.38
1.35
1.07
4.48
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0.97
0.92
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1.11
3.58
0.95
1.00
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2.22
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7
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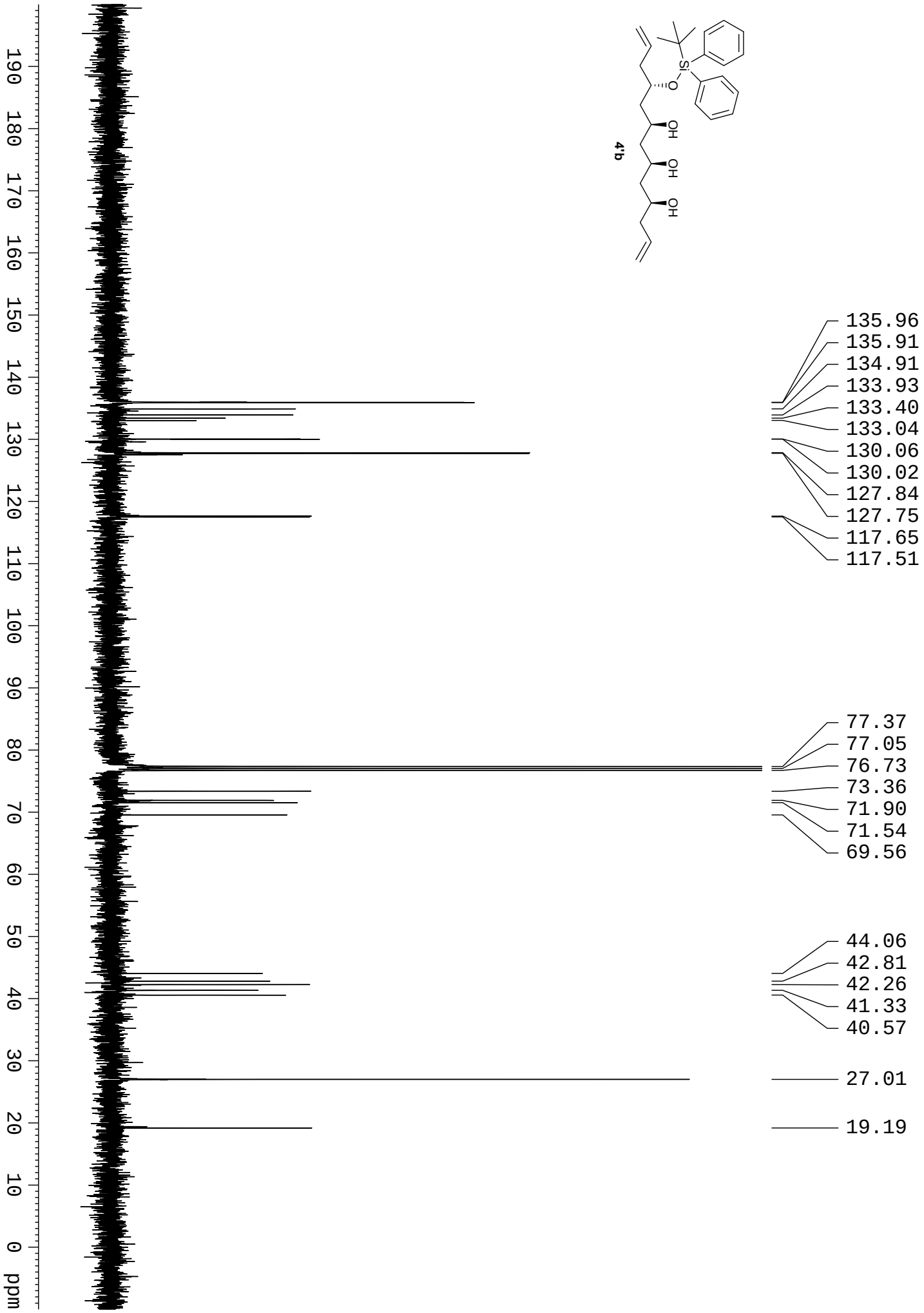
4b
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134.91
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130.06
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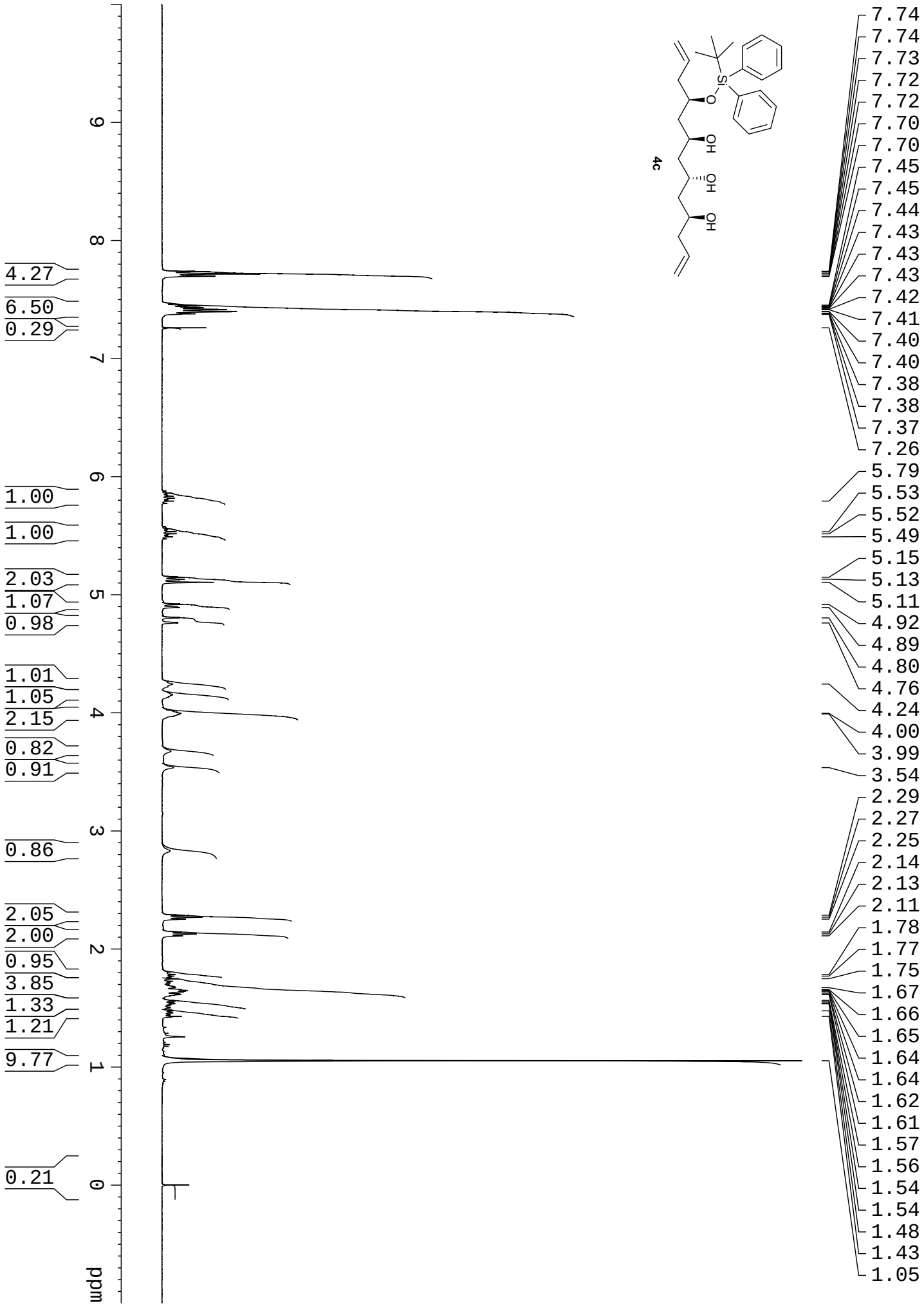
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2.05
2.00
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1.77
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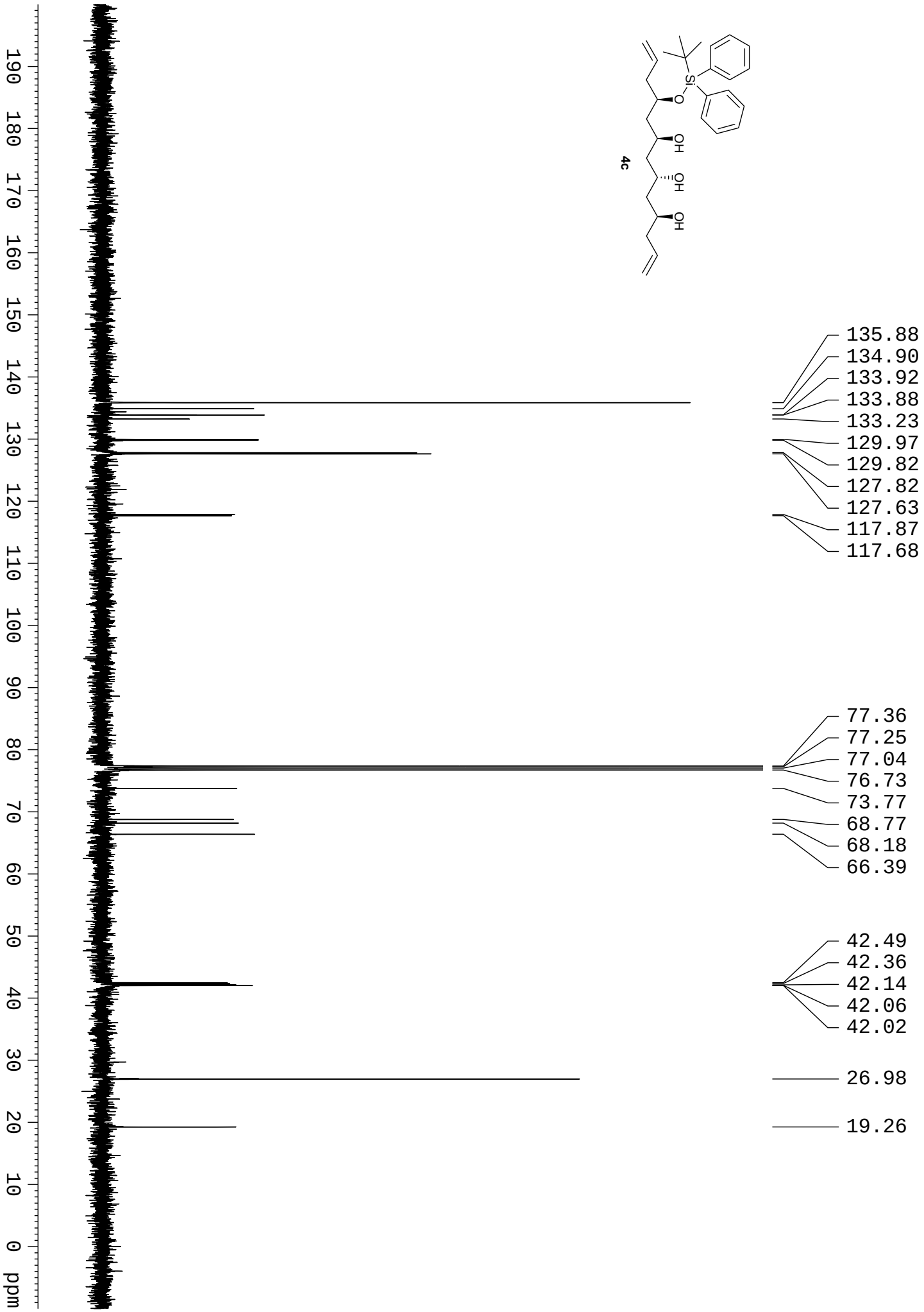
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77.25
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73.77
68.77
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66.39
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42.36
42.14
42.06
42.02
26.98
19.26
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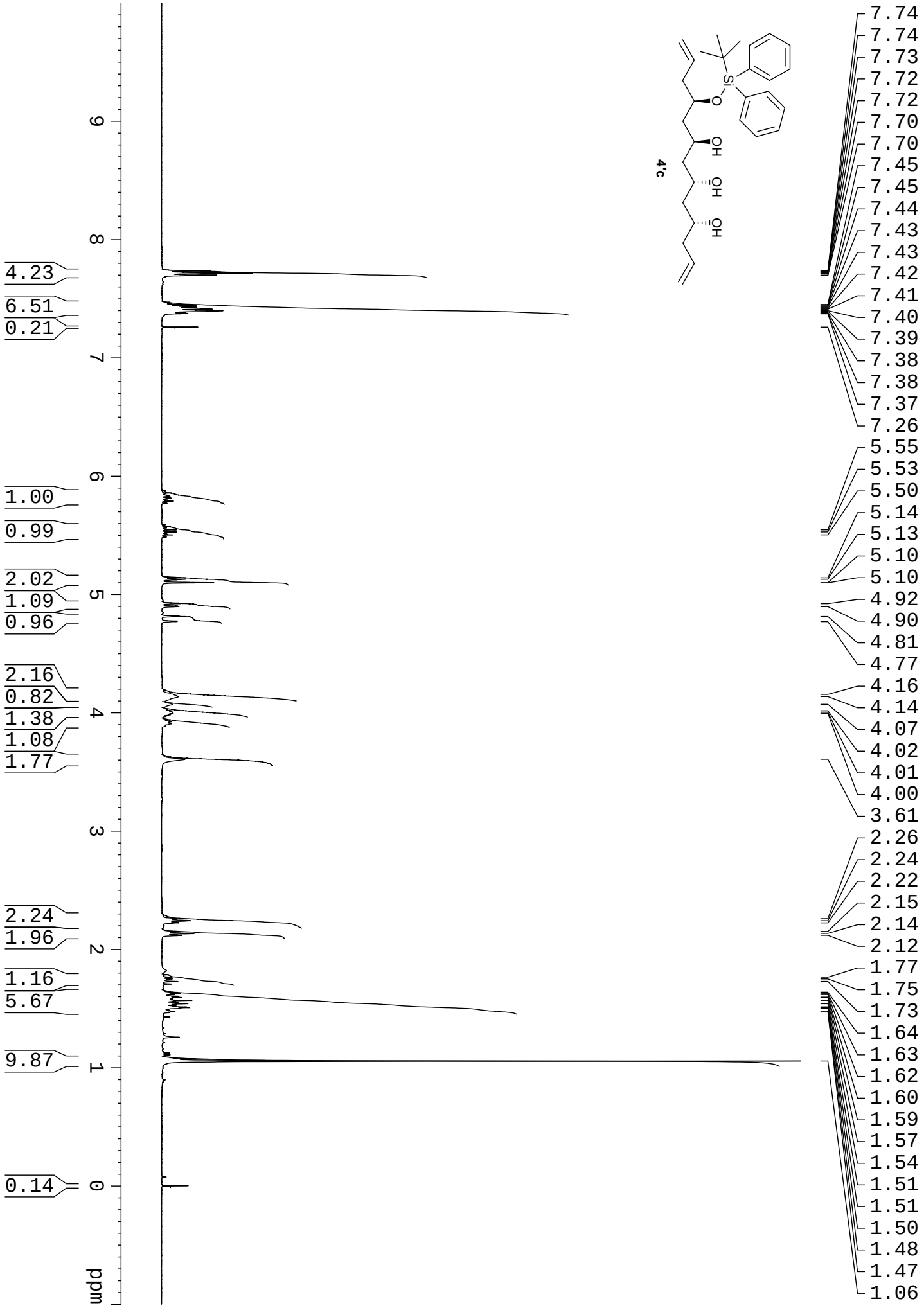
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ppm
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1.08
1.77
2.24
1.96
1.16
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7.74
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7.72
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7.43
7.42
7.41
7.40
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7.38
7.37
7.26
5.55
5.53
5.50
5.14
5.13
5.10
5.10
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4.90
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4.16
4.14
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4.02
4.01
4.00
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2.24
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2.15
2.14
2.12
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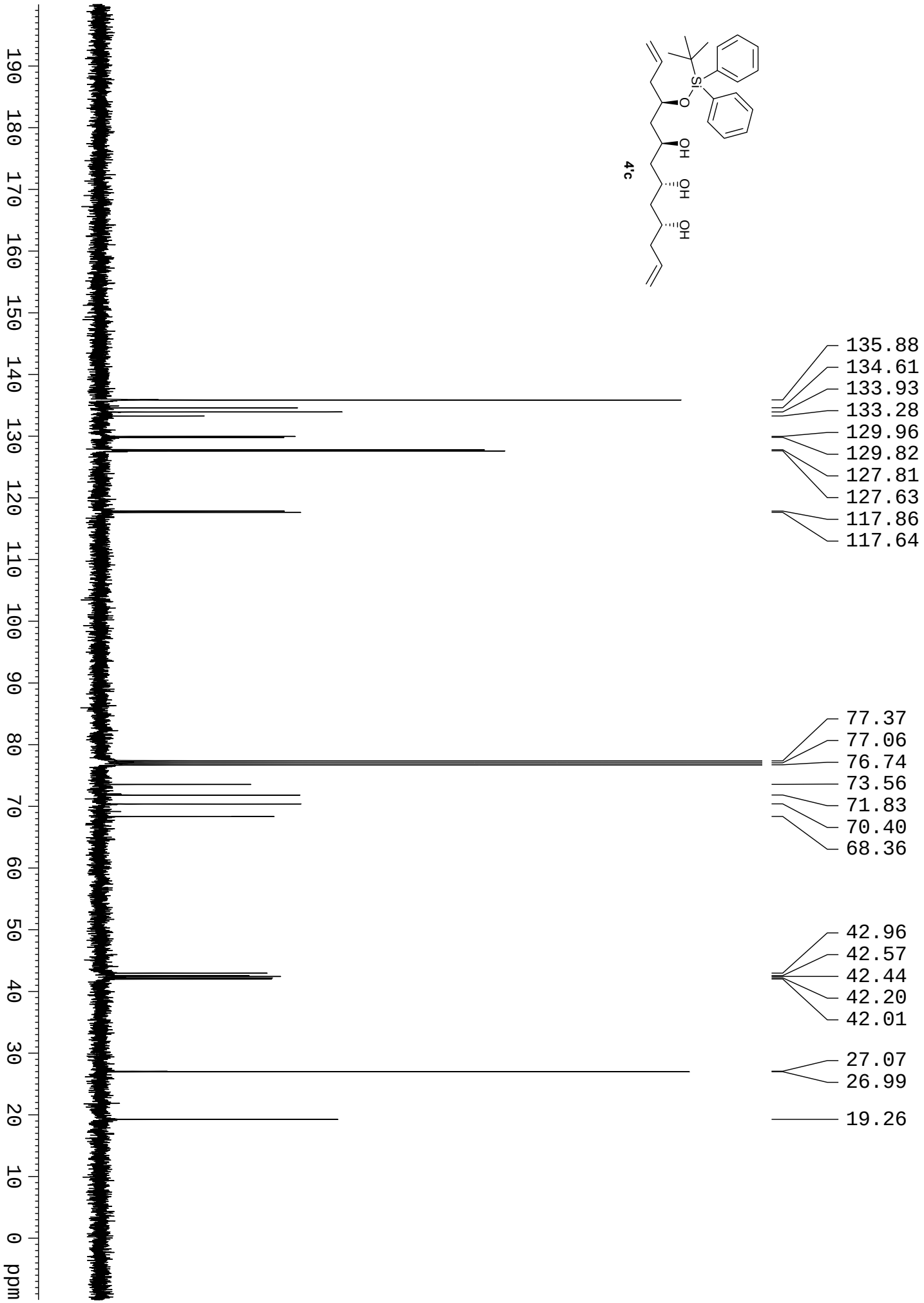
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127.63
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117.64
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71.83
70.40
68.36
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42.57
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42.20
42.01
27.07
26.99
19.26
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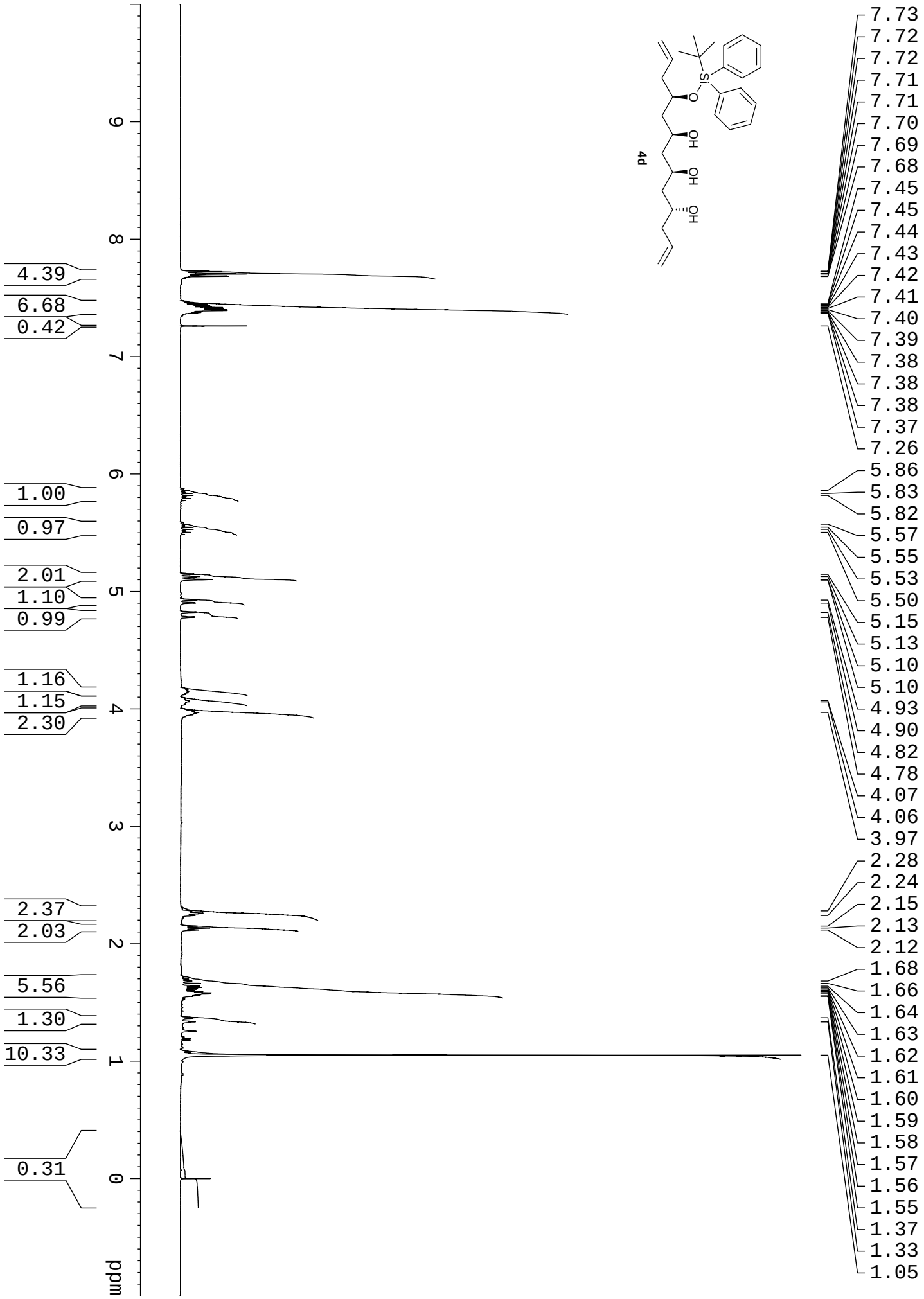
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7.45
7.45
7.44
7.43
7.42
7.41
7.40
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7.37
7.26
5.86
5.83
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5.57
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4.90
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2.12
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1.55
1.37
1.33
1.05
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1.00
0.97
2.01
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0.99
1.16
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6
5
4
3
2
1
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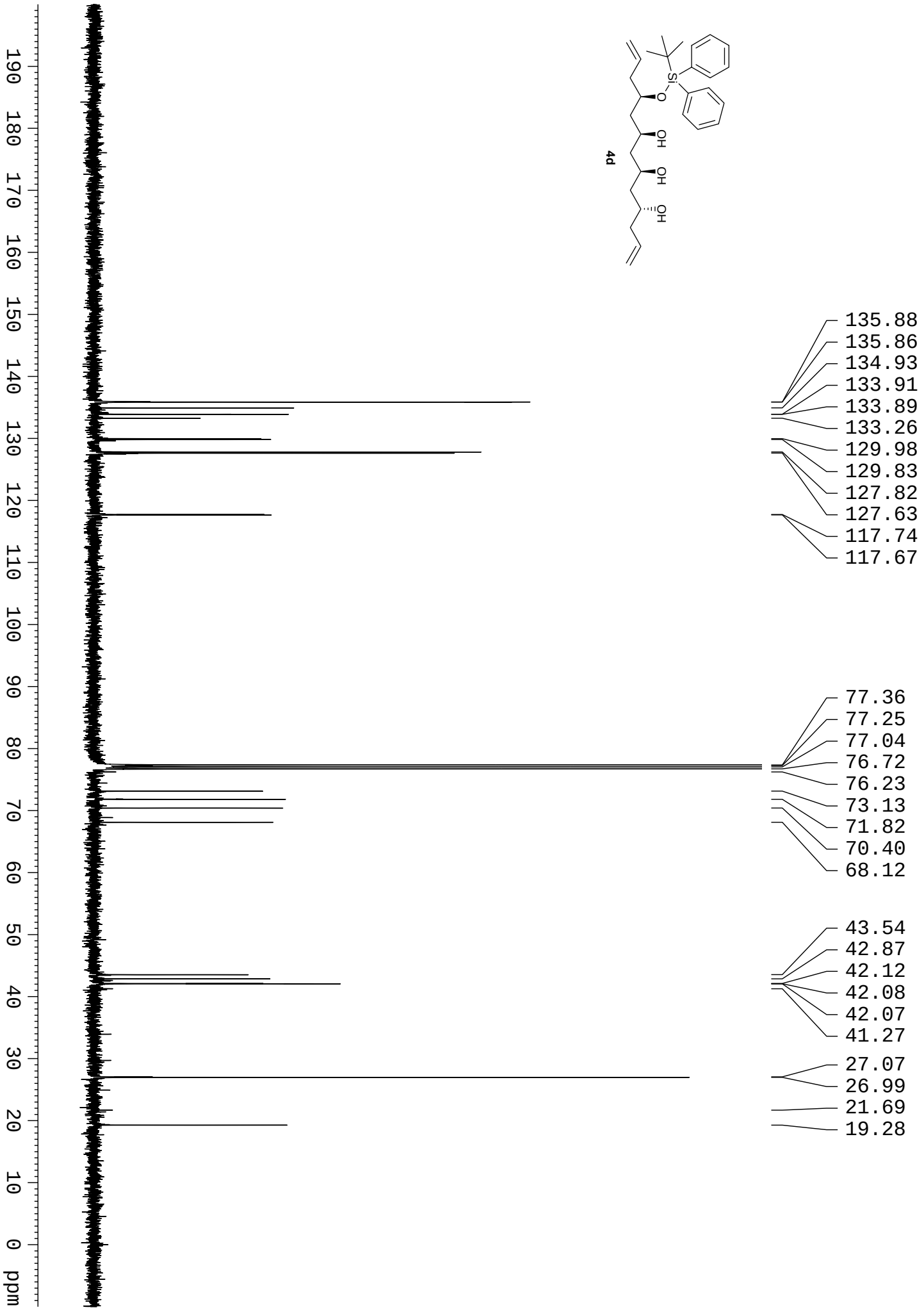
ppm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O
OH
OH
OH
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135.86
134.93
133.91
133.89
133.26
129.98
129.83
127.82
127.63
117.74
117.67
77.36
77.25
77.04
76.72
76.23
73.13
71.82
70.40
68.12
43.54
42.87
42.12
42.08
42.07
41.27
27.07
26.99
21.69
19.28
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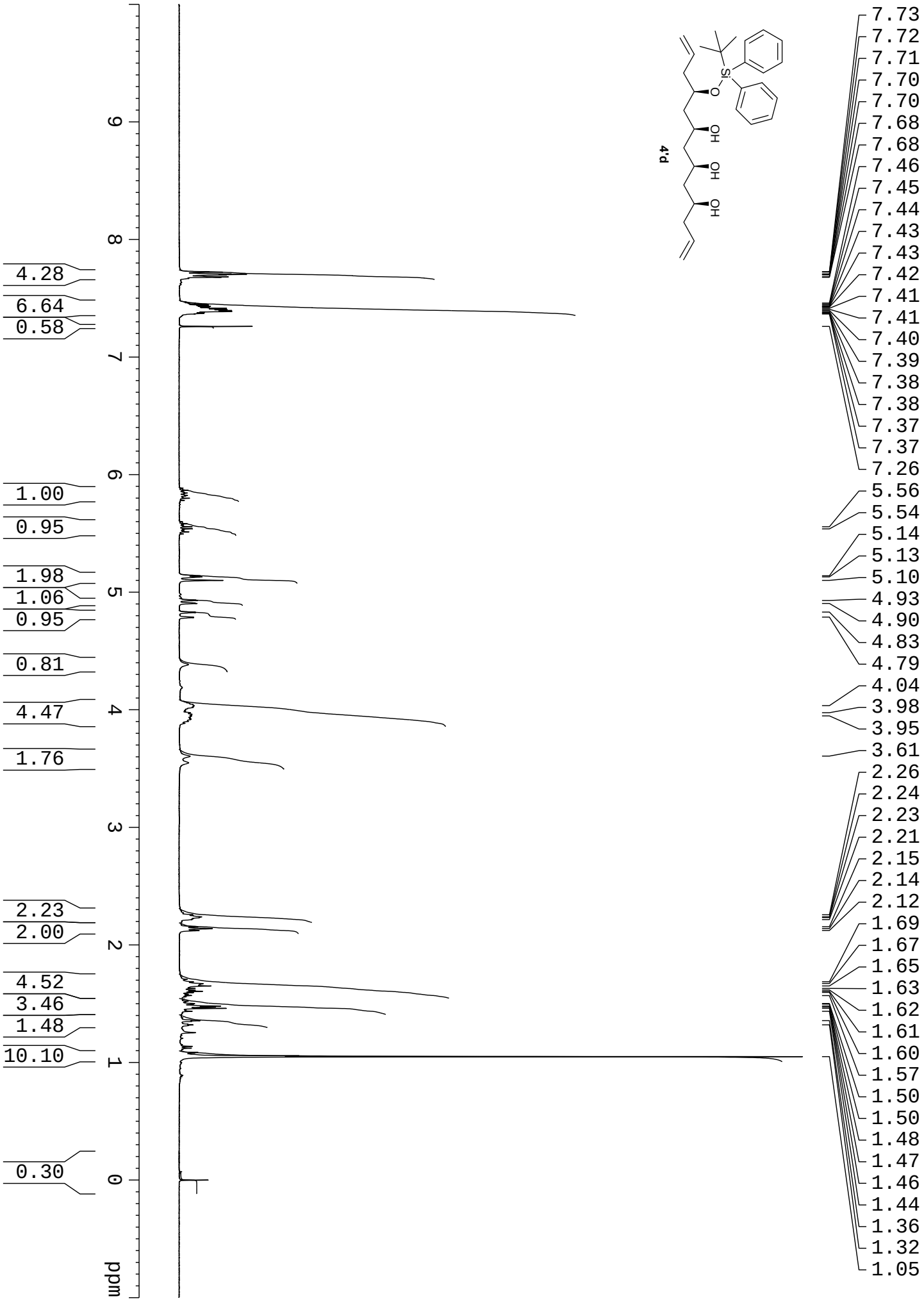
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2.00
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3.46
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10.10
0.30
ppm
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8
7
6
5
4
3
2
1
0
4'd
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7.70
7.70
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7.41
7.41
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7.26
5.56
5.54
5.14
5.13
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4.90
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4.04
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3.95
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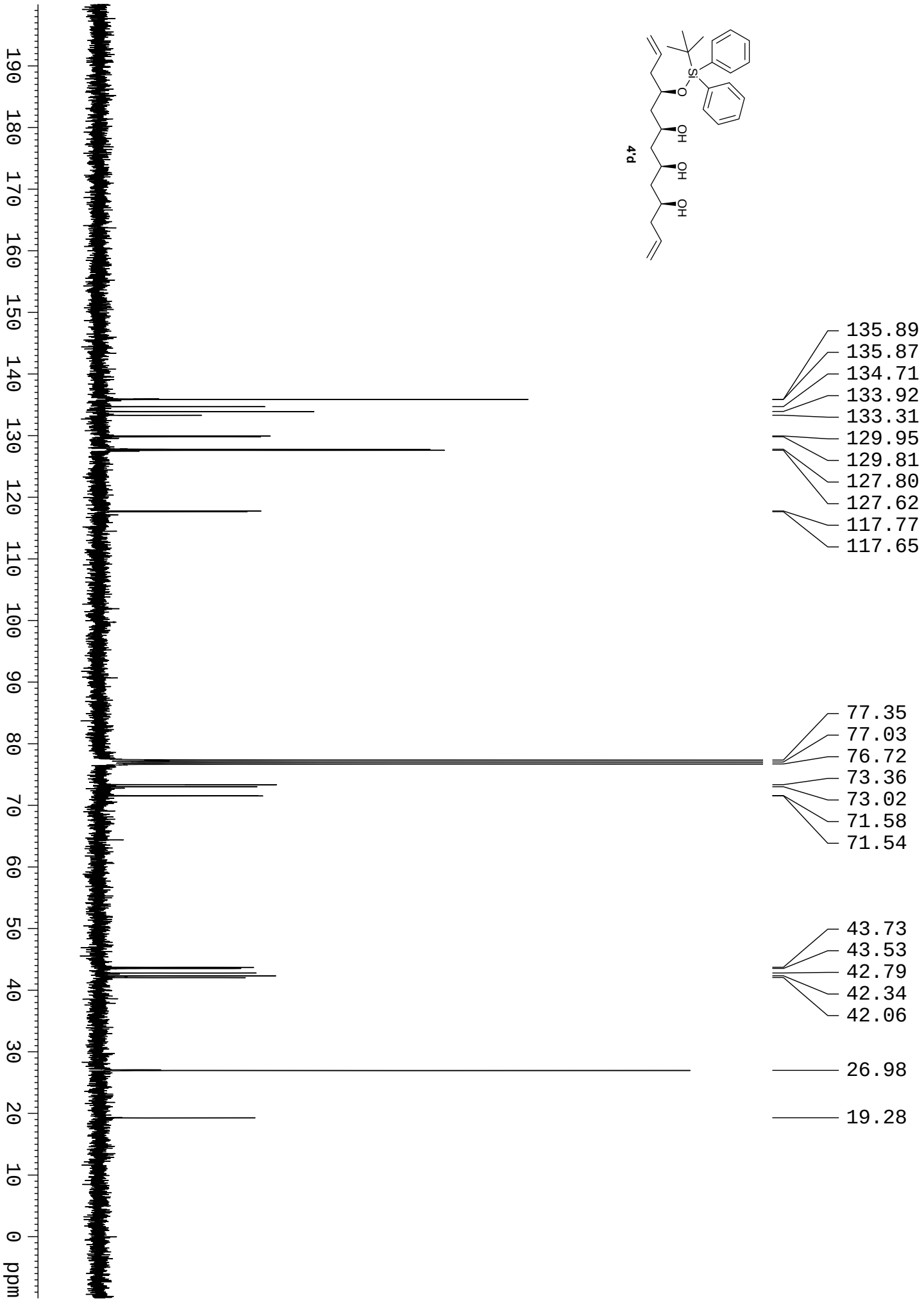
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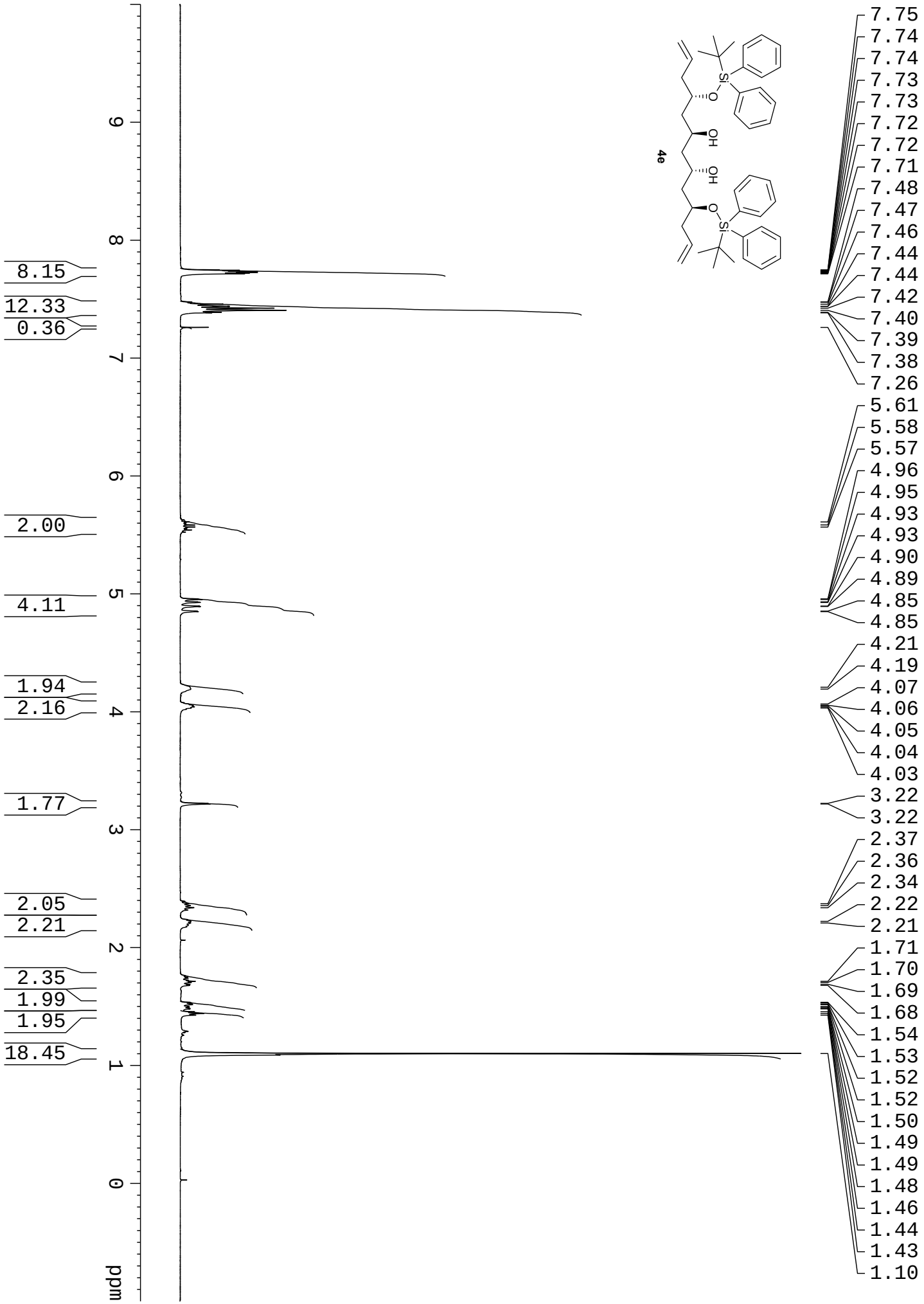
42.06
26.98
19.28
ppm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OH
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Si
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7.71
7.48
7.47
7.46
7.44
7.44
7.42
7.40
7.39
7.38
7.26
5.61
5.58
5.57
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4.93
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4.06
4.05
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4.03
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1.77
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1.99
1.95
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8
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6
5
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2
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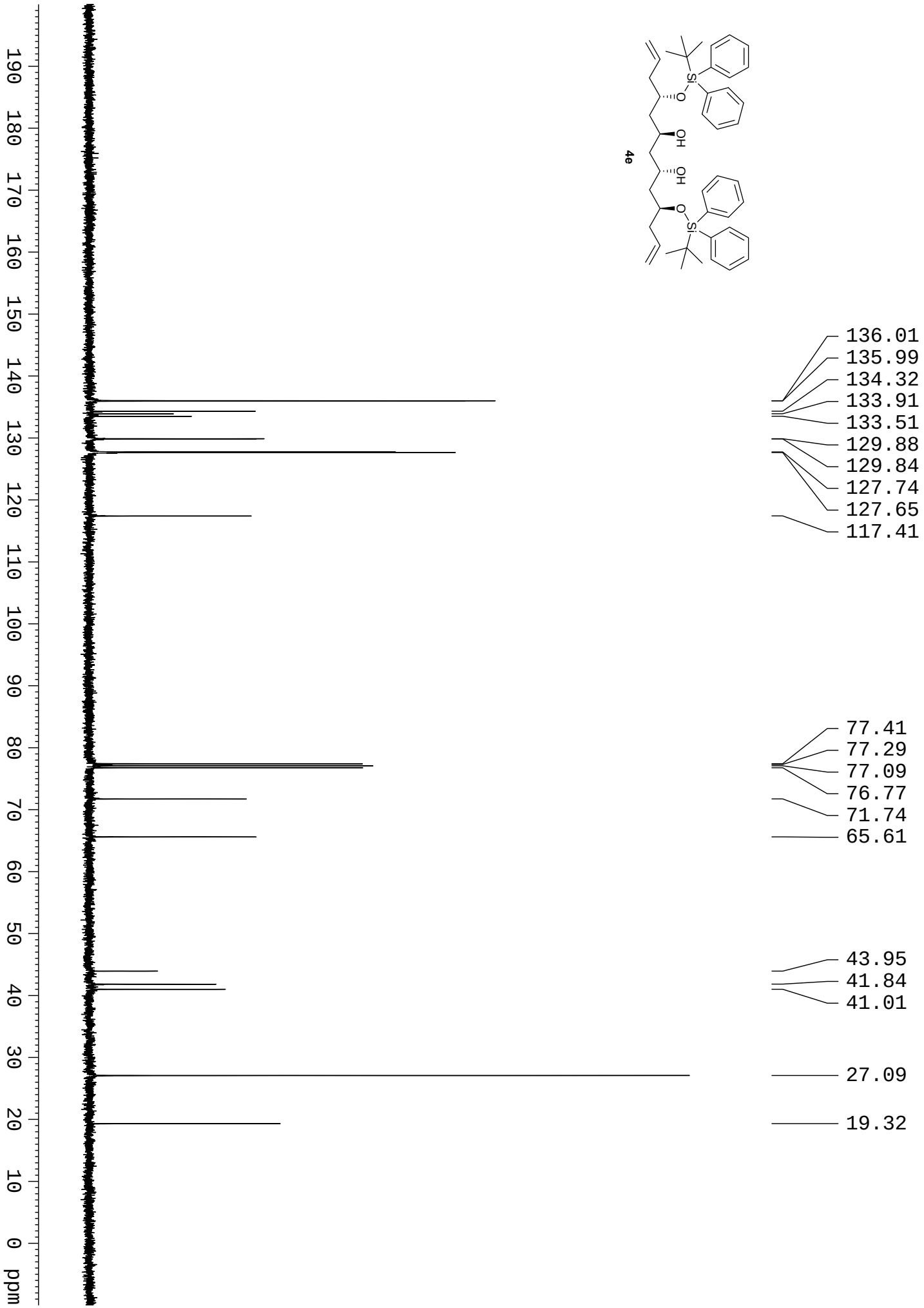
0
ppm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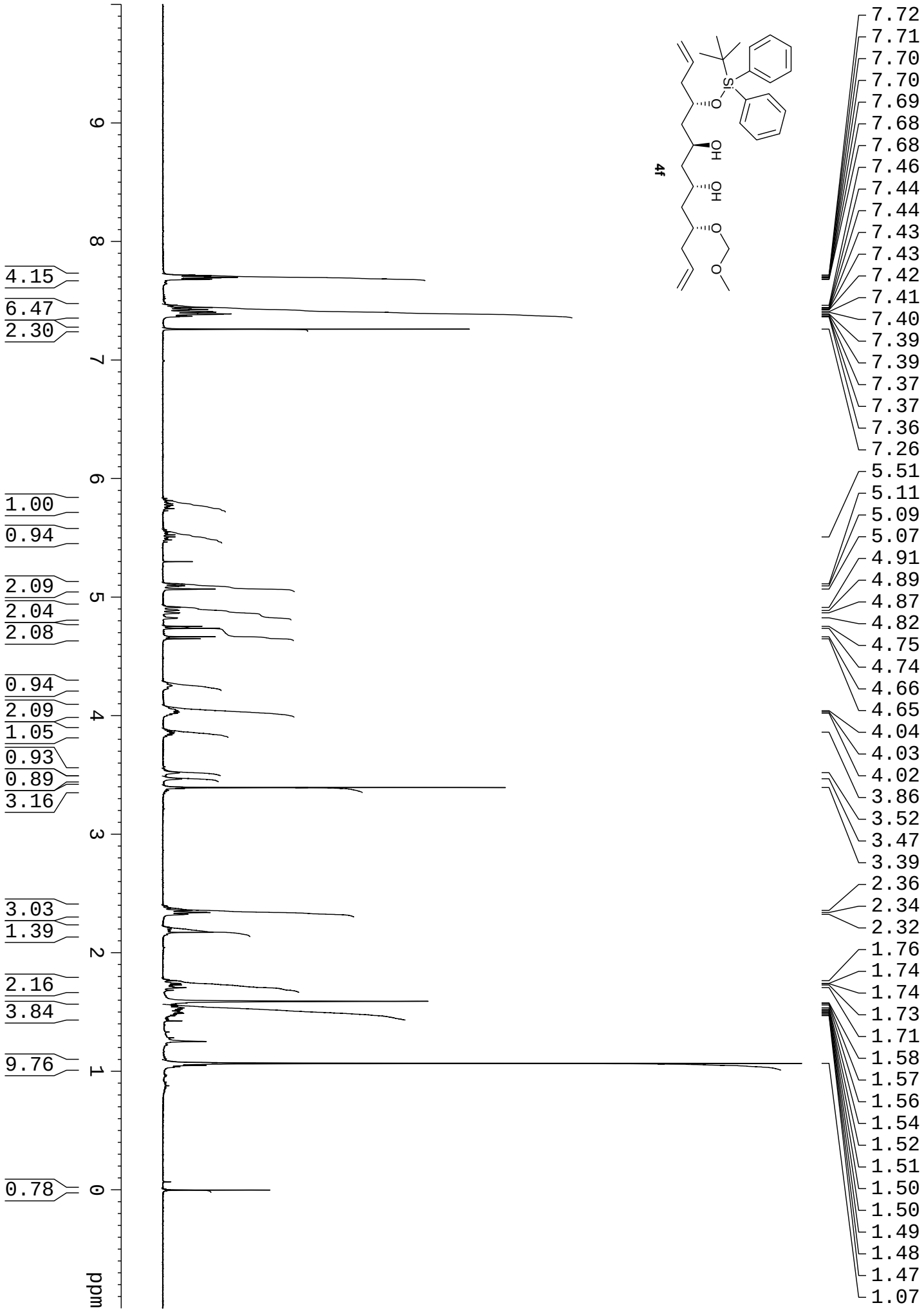
76.77
71.74
65.61
43.95
41.84
41.01
27.09
19.32
ppm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OH
OH
O
O
ppm
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6
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2
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1.00
0.94
2.09
2.04
2.08
0.94
2.09
1.05
0.93
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3.03
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7.42
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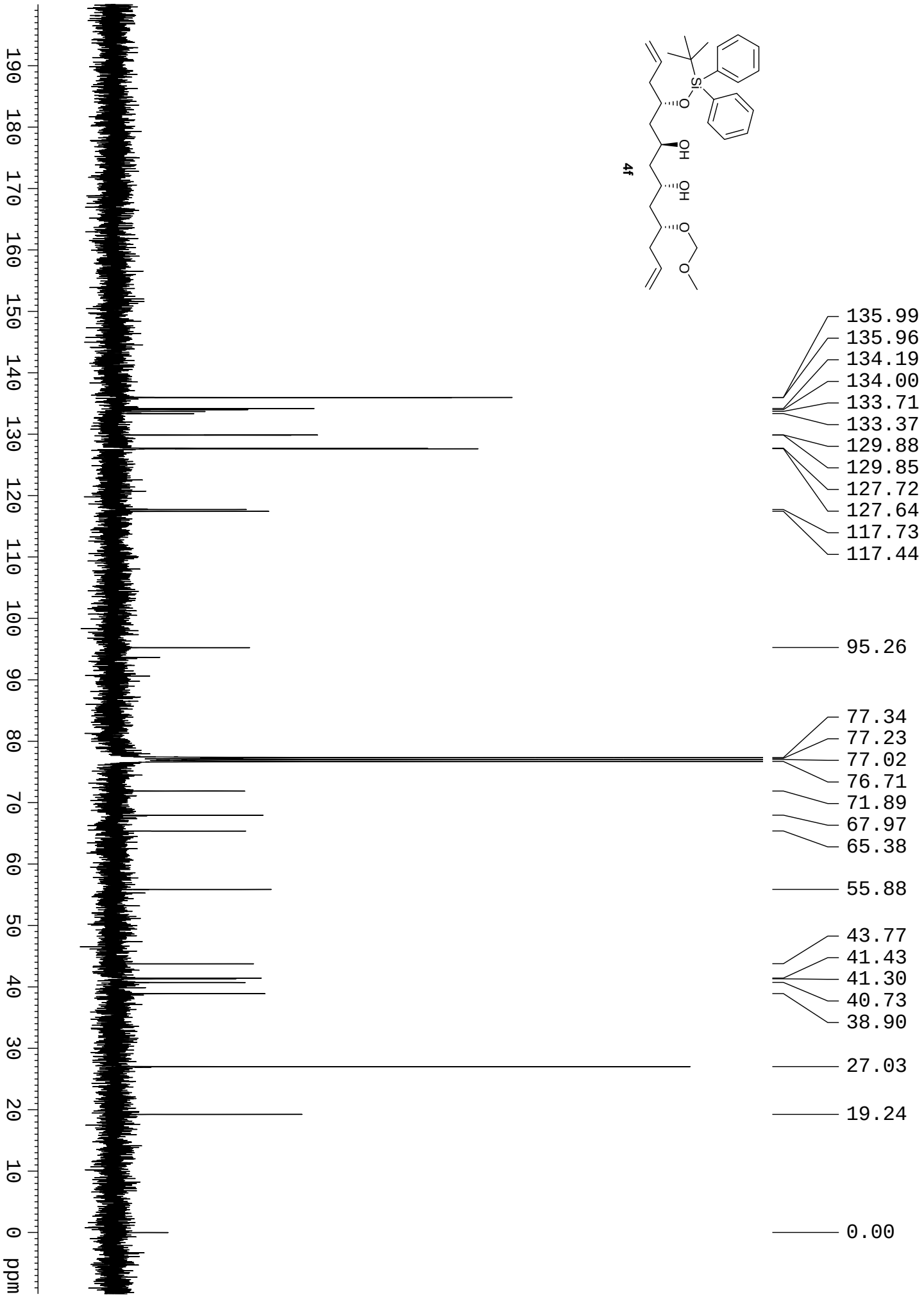
1.48
1.47
1.07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120
110
100
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60
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40
30
20
10
0
ppm
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135.96
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134.00
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129.85
127.72
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117.44
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19.24
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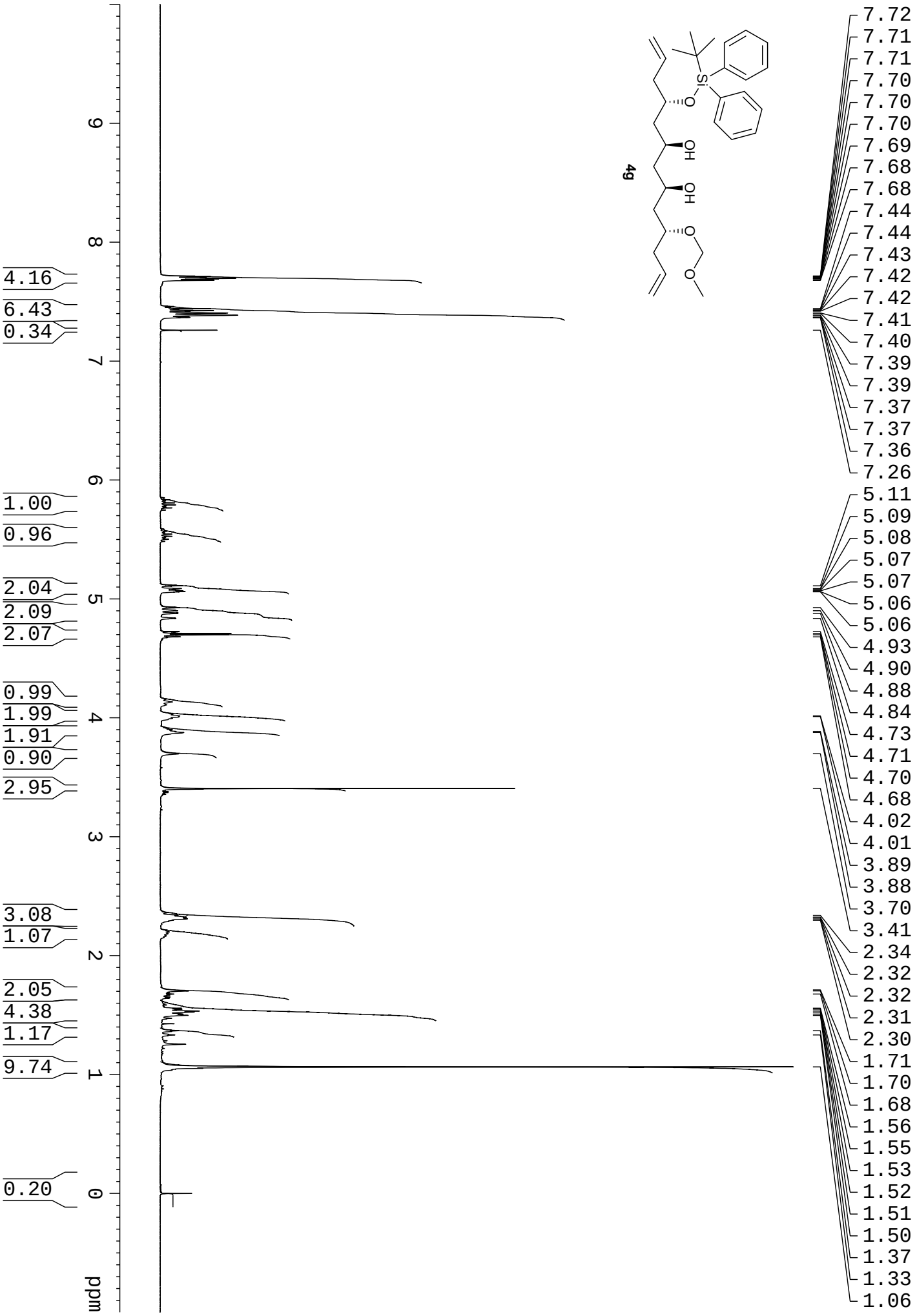
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7.42
7.41
7.40
7.39
7.39
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7.37
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5.08
5.07
5.07
5.06
5.06
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4.70
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1.50
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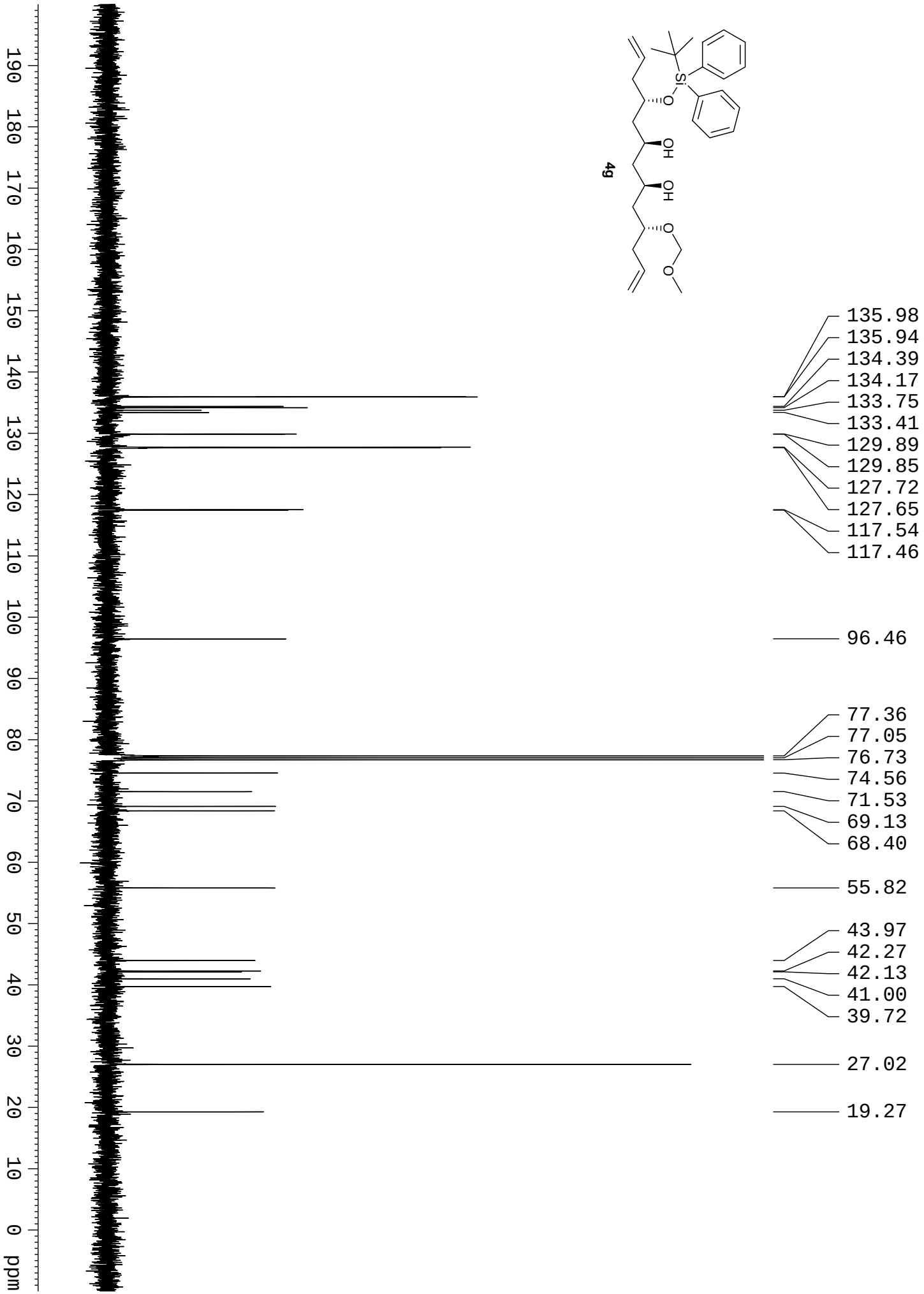
49
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133.41
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127.72
127.65
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117.46
96.46
77.36
77.05
76.73
74.56
71.53
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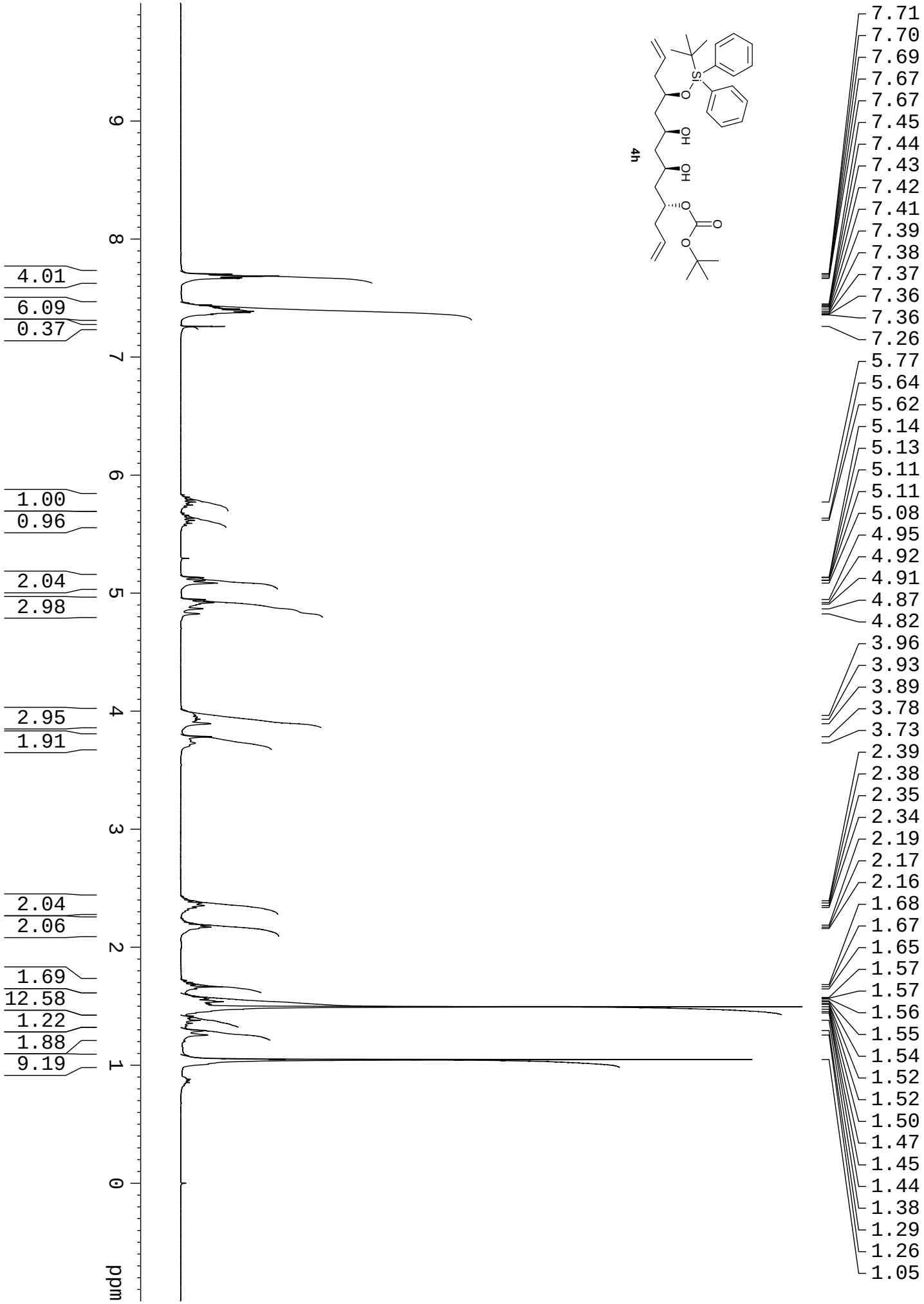
68.40
55.82
43.97
42.27
42.13
41.00
39.72
27.02
19.27
ppm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5.13
5.11
5.11
5.08
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3.93
3.89
3.78
3.73
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1.26
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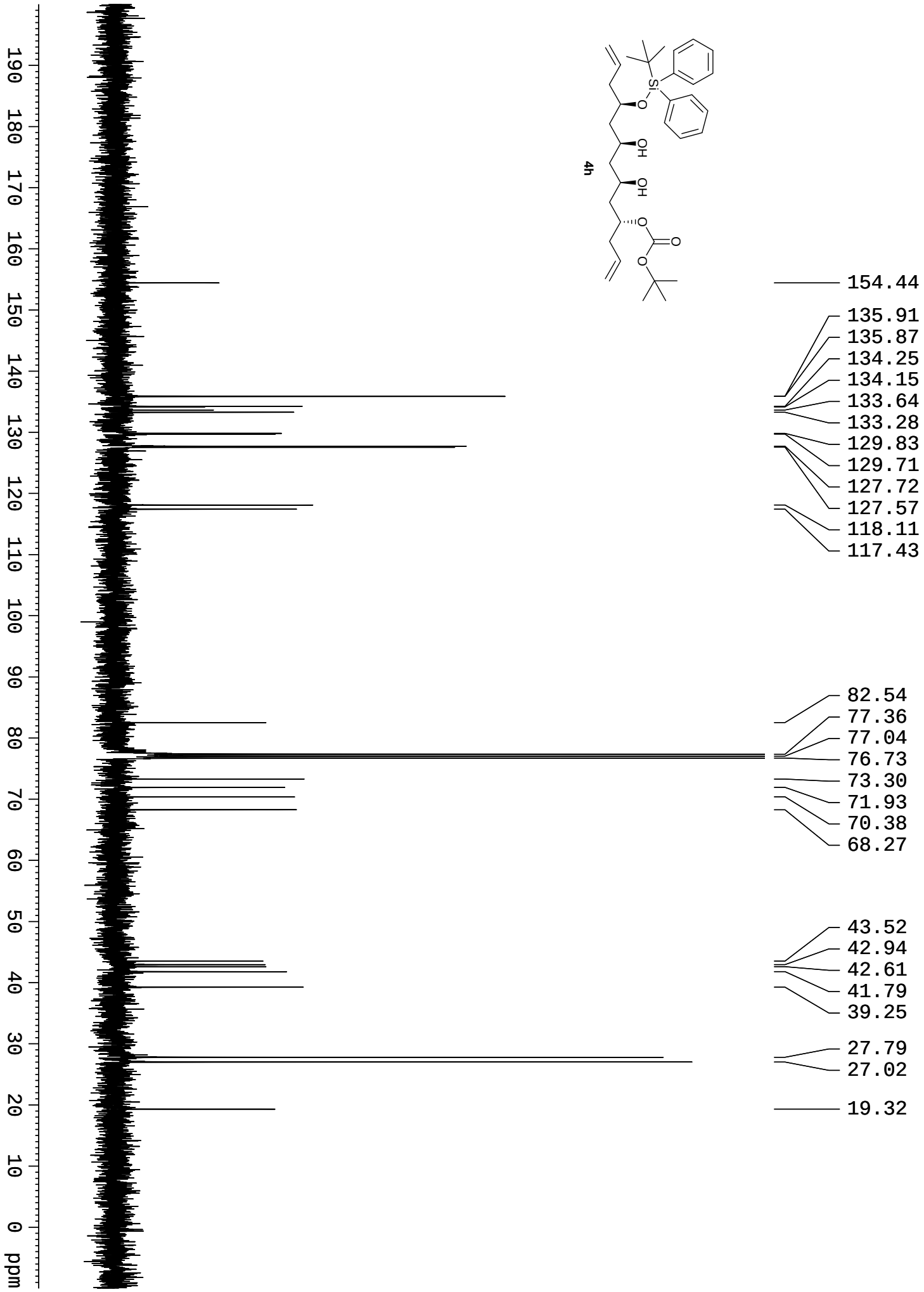
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OH
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129.71
127.72
127.57
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117.43
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77.36
77.04
76.73
73.30
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70.38
68.27
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42.94
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41.79
39.25
27.79
27.02
19.32
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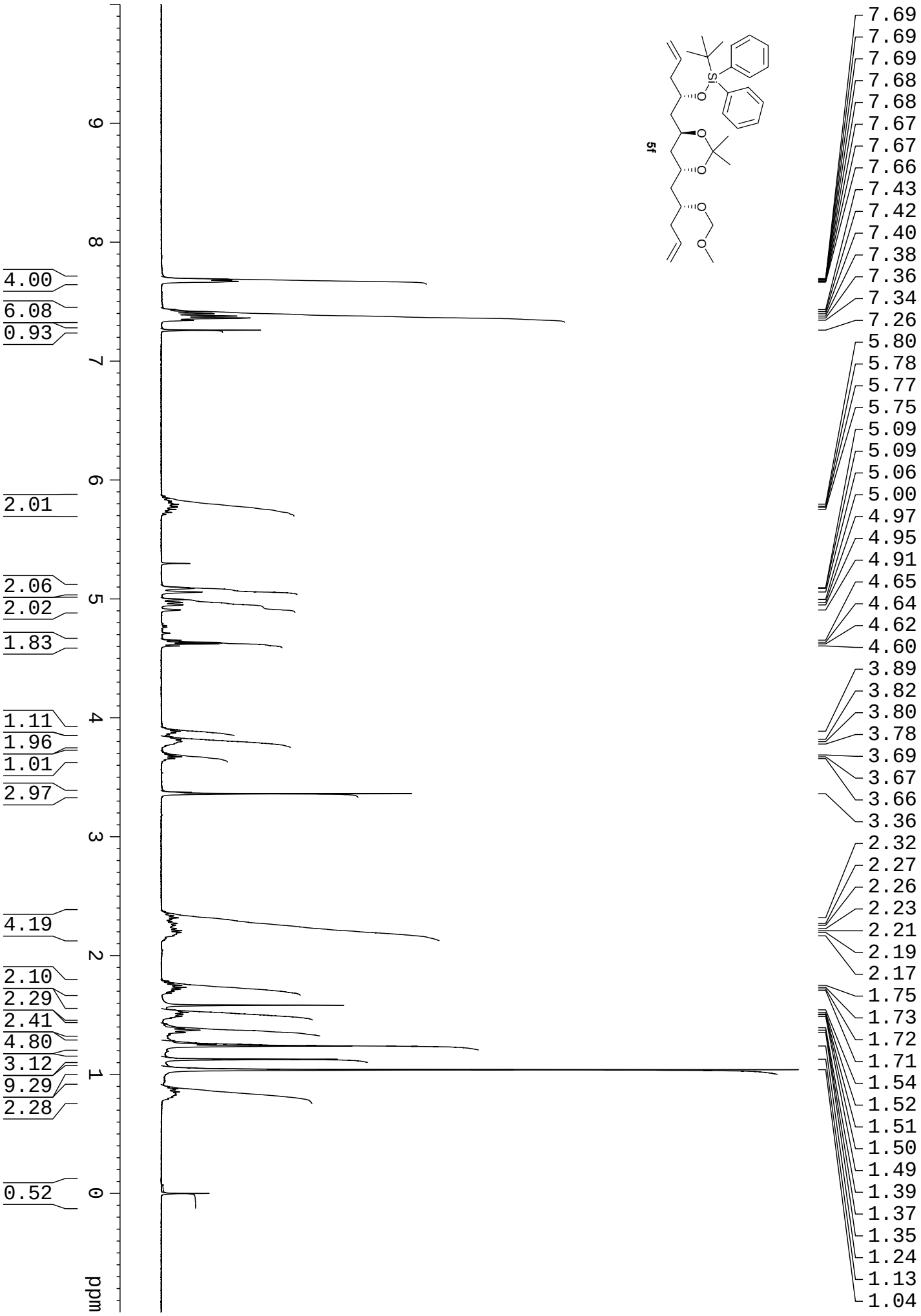
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Si
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O
O
O
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8
7
6
5
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3
2
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4.00
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2.01
2.06
2.02
1.83
1.11
1.96
1.01
2.97
4.19
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2.29
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4.80
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9.29
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7.69
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7.68
7.67
7.67
7.66
7.43
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7.34
7.26
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5.09
5.09
5.06
5.00
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4.95
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4.65
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4.60
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3.67
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3.36
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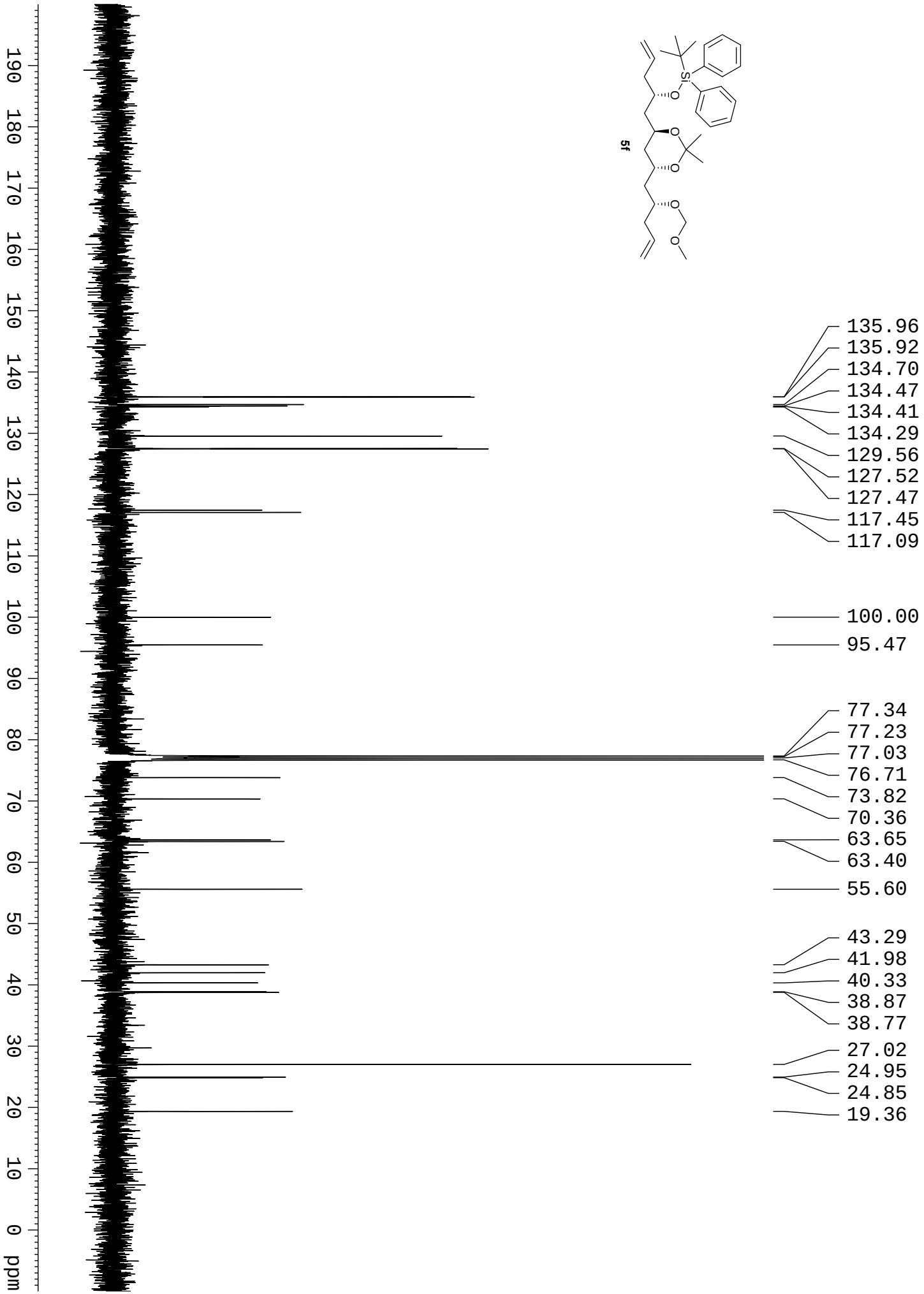
1.13
1.04


5f
Si
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O
O
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
135.96
135.92
134.70
134.47
134.41
134.29
129.56
127.52
127.47
117.45
117.09
100.00
95.47
77.34
77.23
77.03
76.71
73.82
70.36
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41.98
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38.87
38.77
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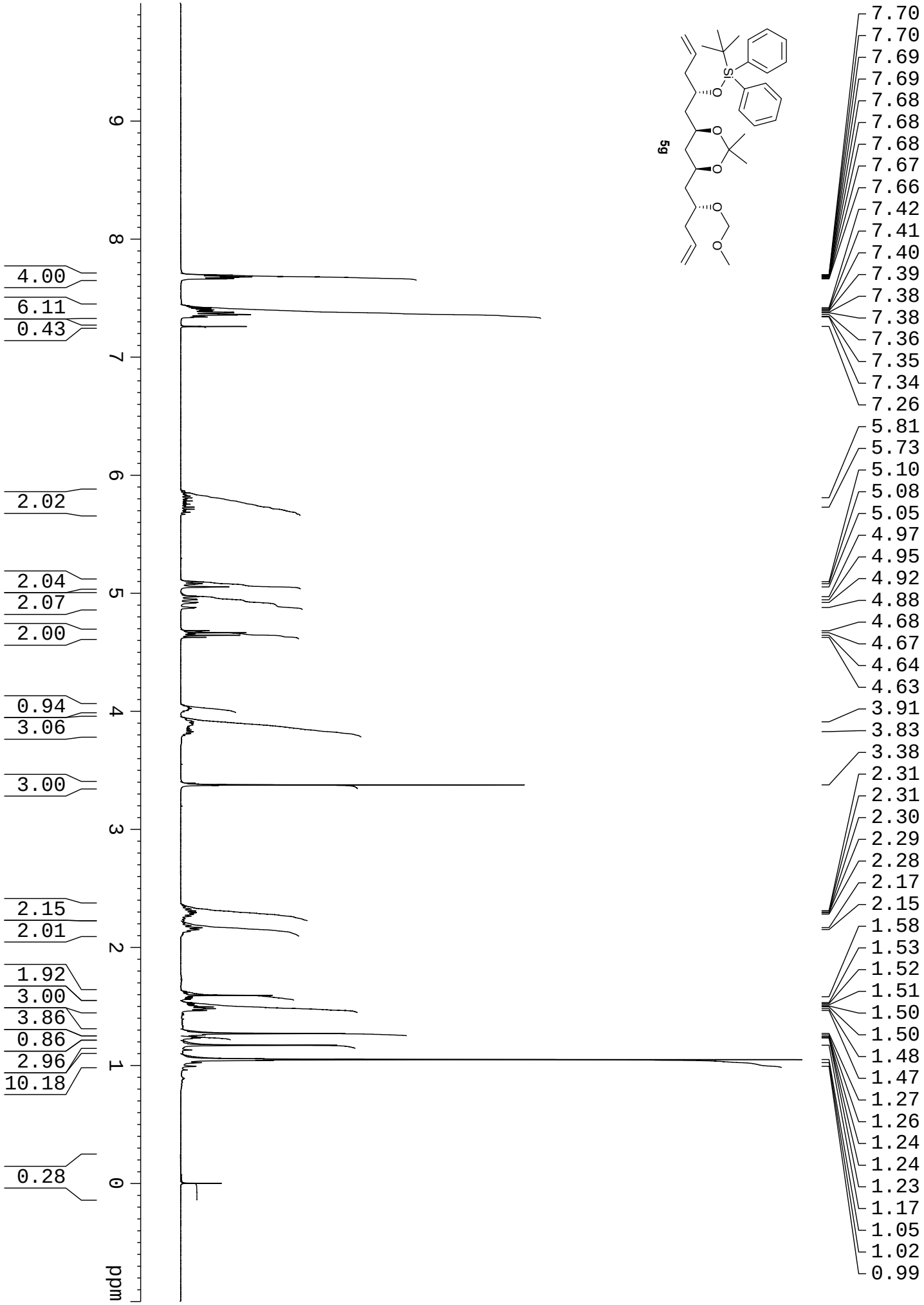
19.36


5g
Si
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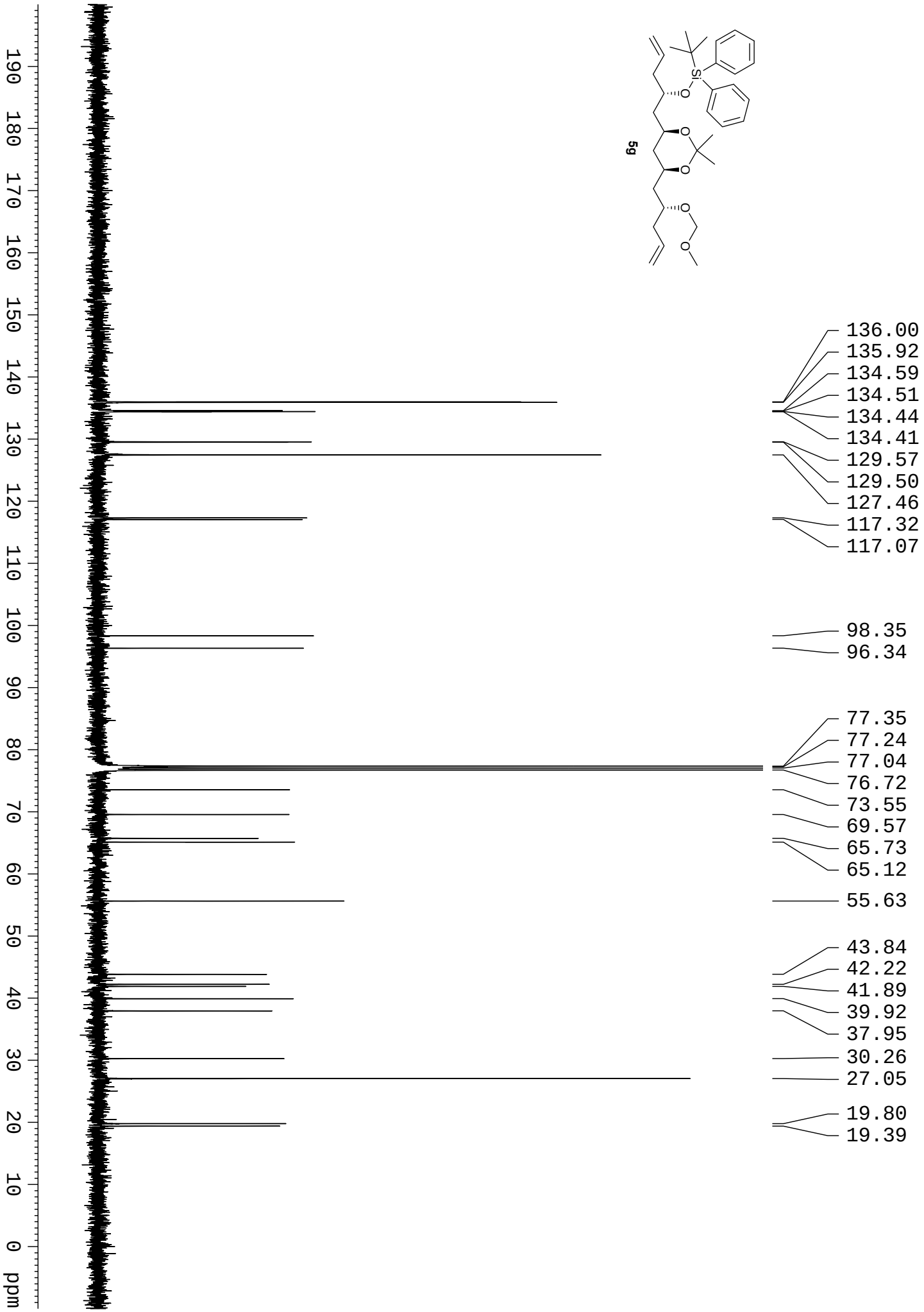
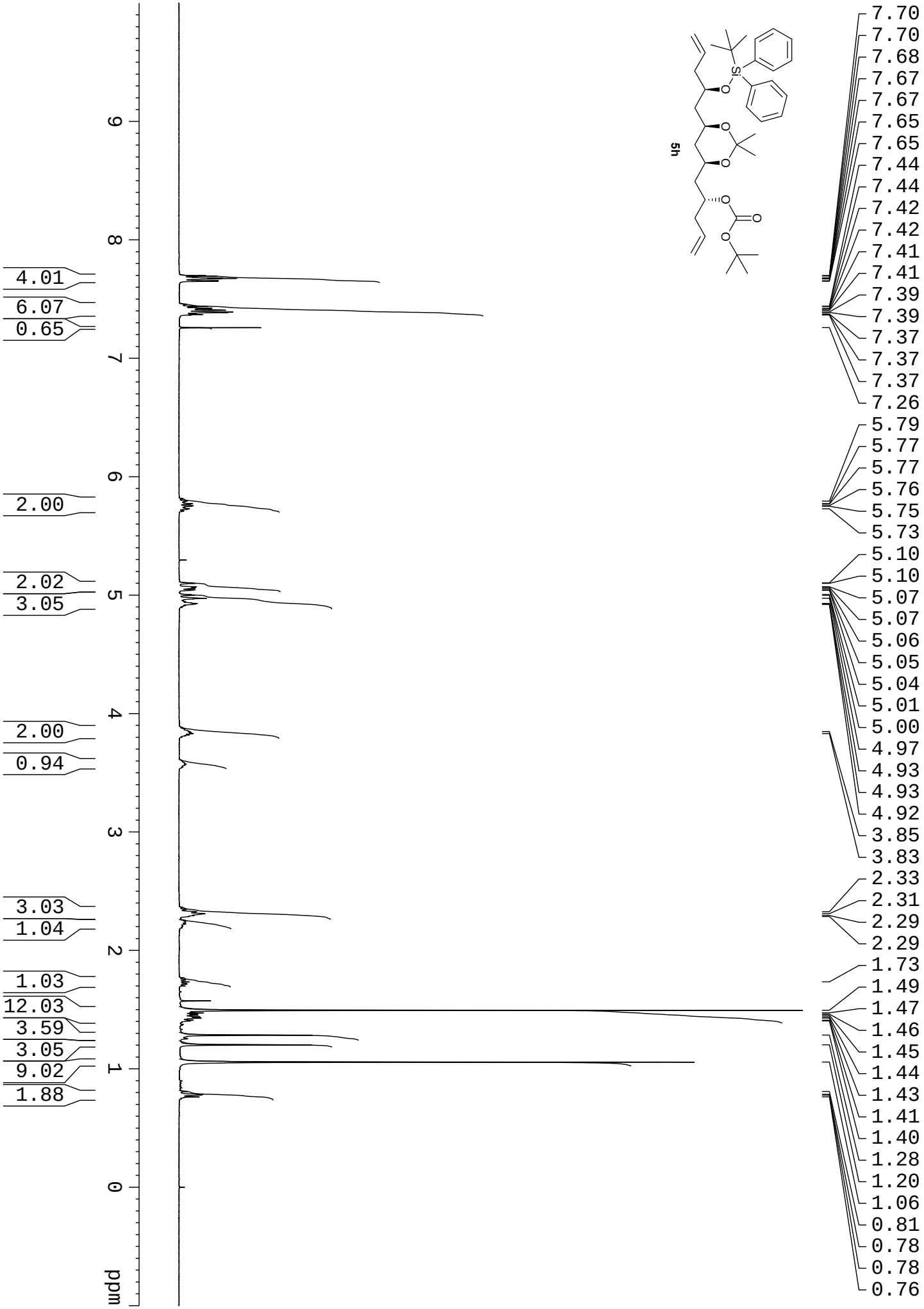
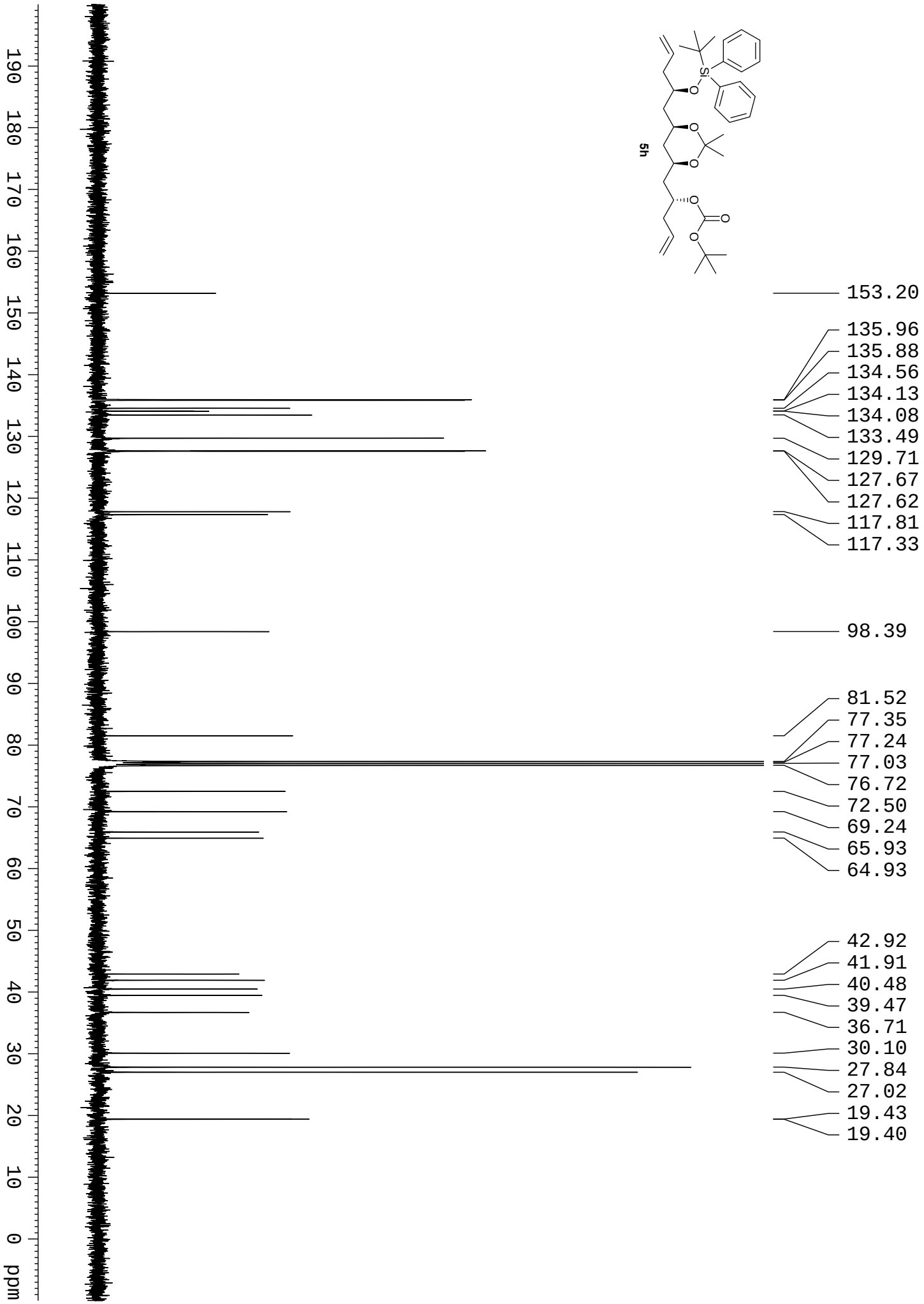
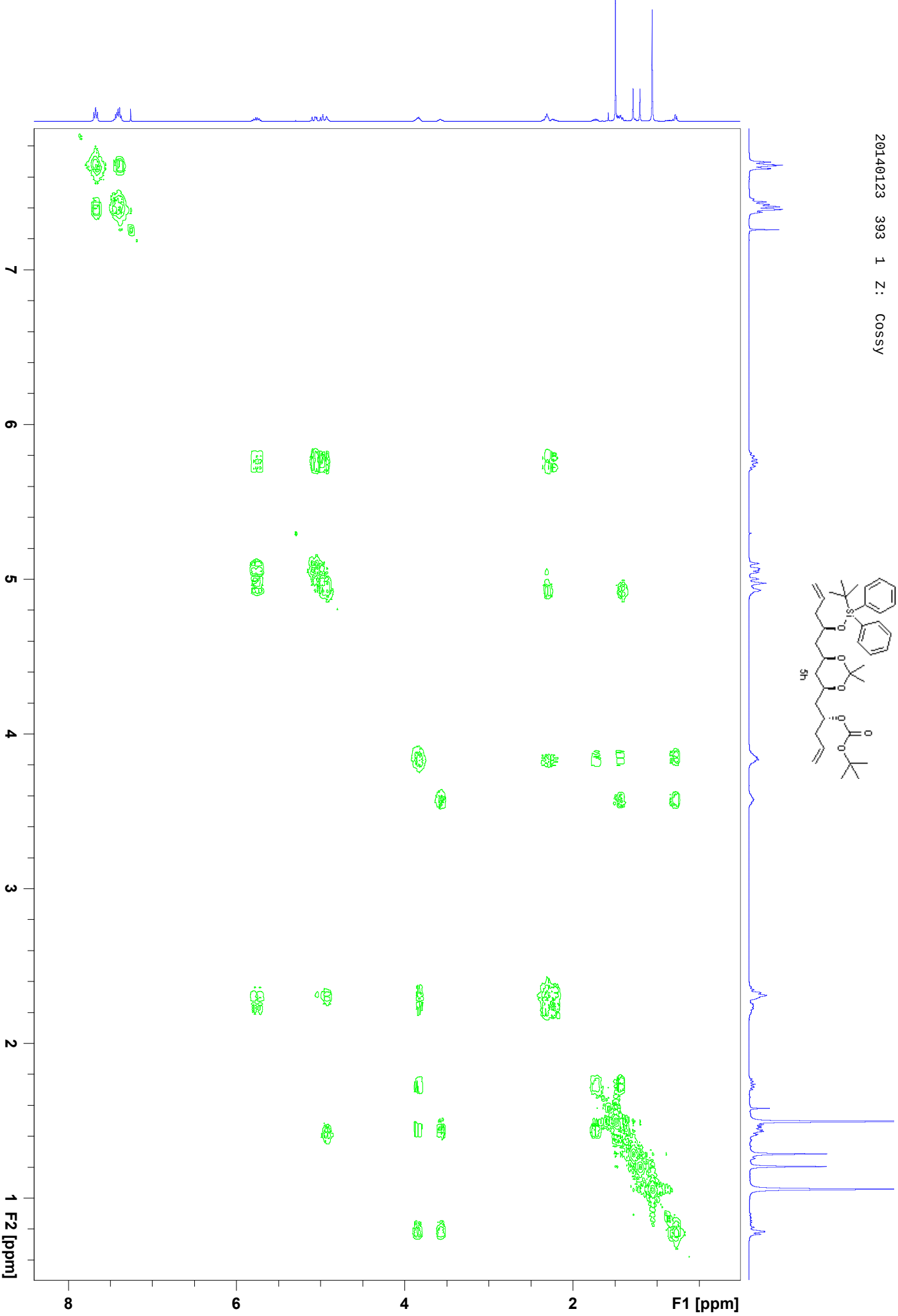
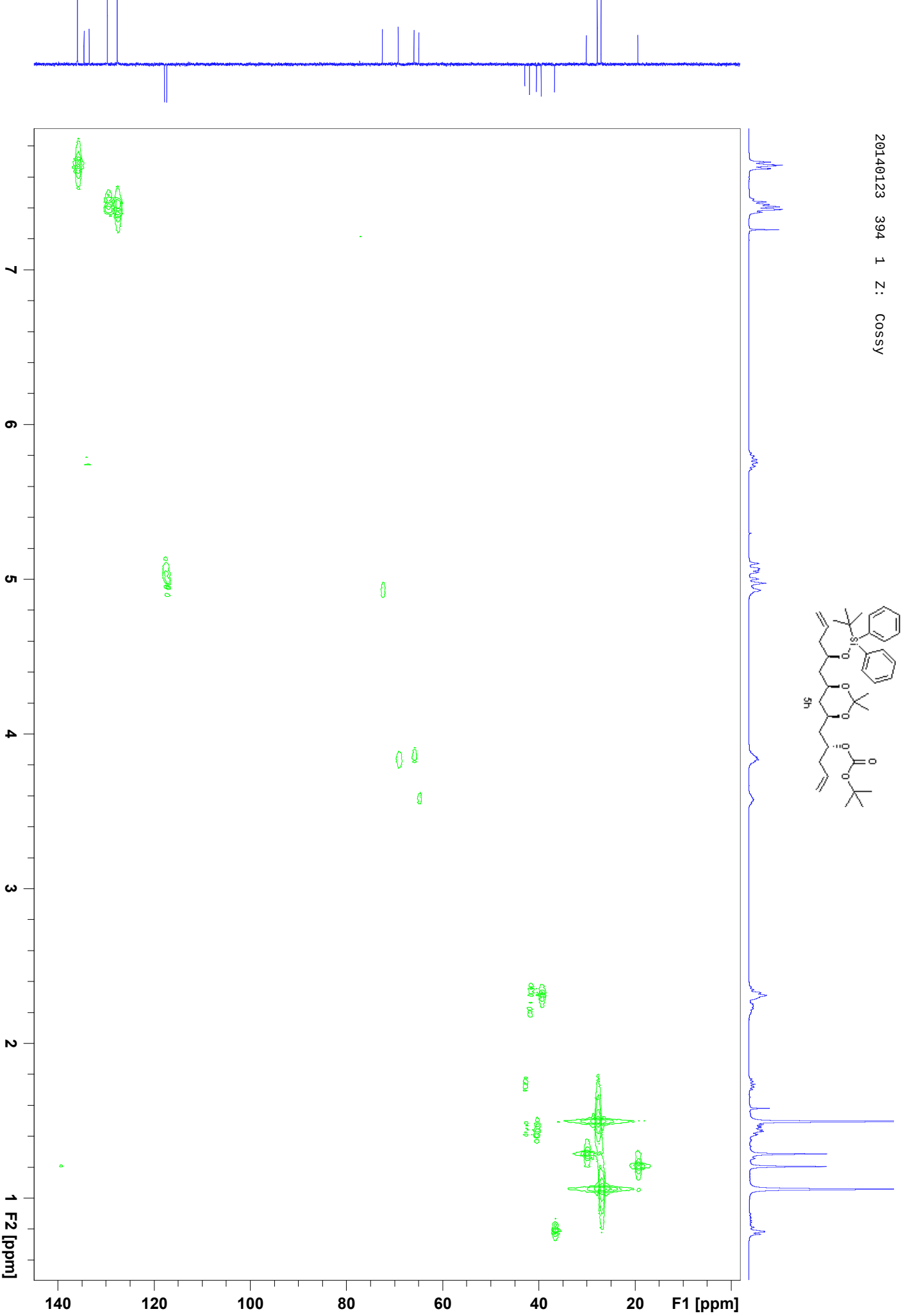
O
O
O
O
O
ppm
9
8
7
6
5
4
3
2
1
0
4.00
6.11
0.43
2.02
2.04
2.07
2.00
0.94
3.06
3.00
2.15
2.01
1.92
3.00
3.86
0.86
2.96
10.18
0.28
7.70
7.70
7.69
7.69
7.68
7.68
7.68
7.67
7.66
7.42
7.41
7.40
7.39
7.38
7.38
7.36
7.35
7.34
7.26
5.81
5.73
5.10
5.08
5.05
4.97
4.95
4.92
4.88
4.68
4.67
4.64
4.63
3.91
3.83
3.38
2.31
2.31
2.30
2.29
2.28
2.17
2.15
1.58
1.53
1.52
1.51
1.50
1.50
1.48
1.47
1.27
1.26
1.24
1.24
1.23
1.17
1.05
1.02
0.99

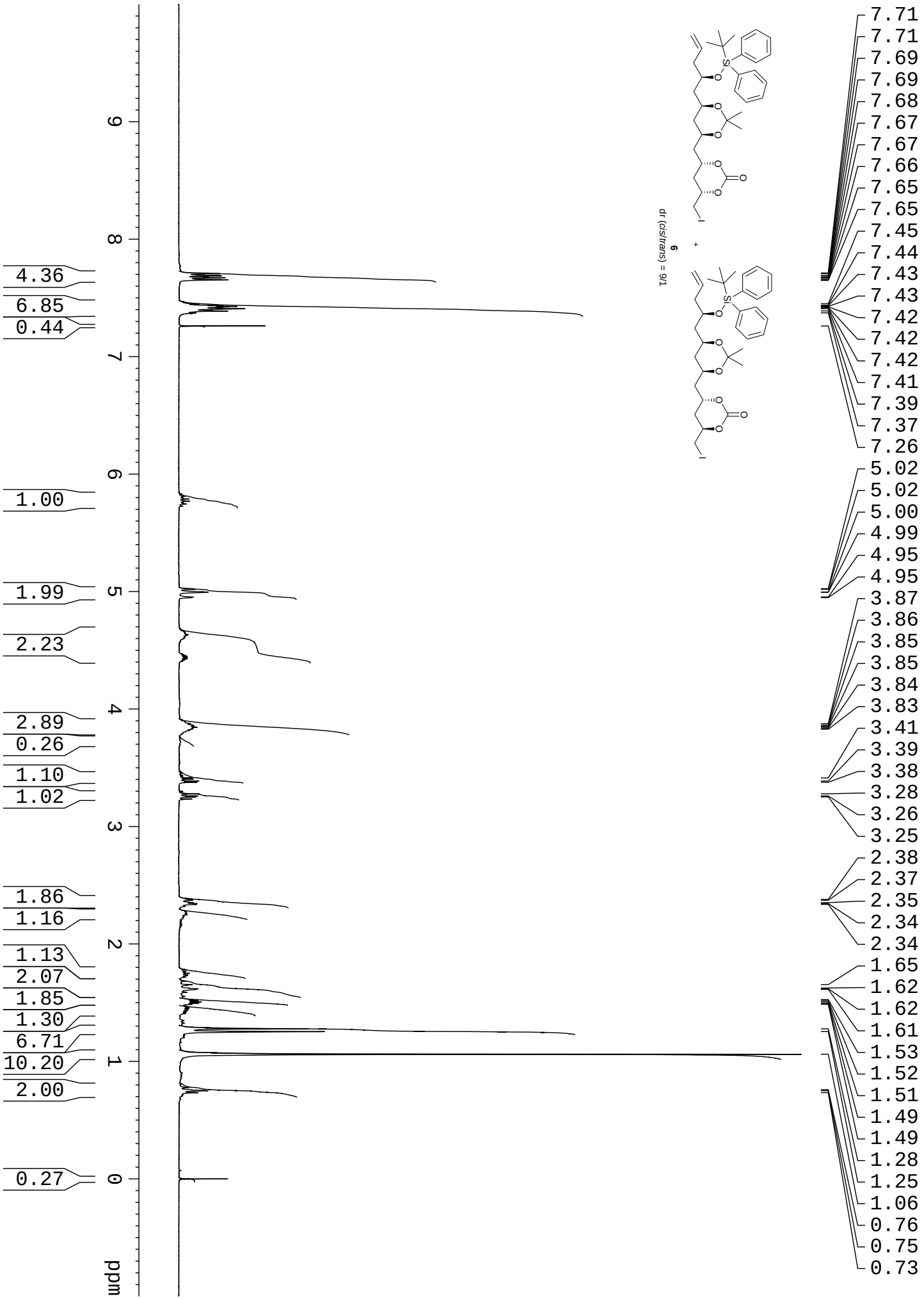

5g
Si
O
O
O
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
136.00
135.92
134.59
134.51
134.44
134.41
129.57
129.50
127.46
117.32
117.07
98.35
96.34
77.35
77.24
77.04
76.72
73.55
69.57
65.73
65.12
55.63
43.84
42.22
41.89
39.92
37.95
30.26
27.05
19.80
19.39

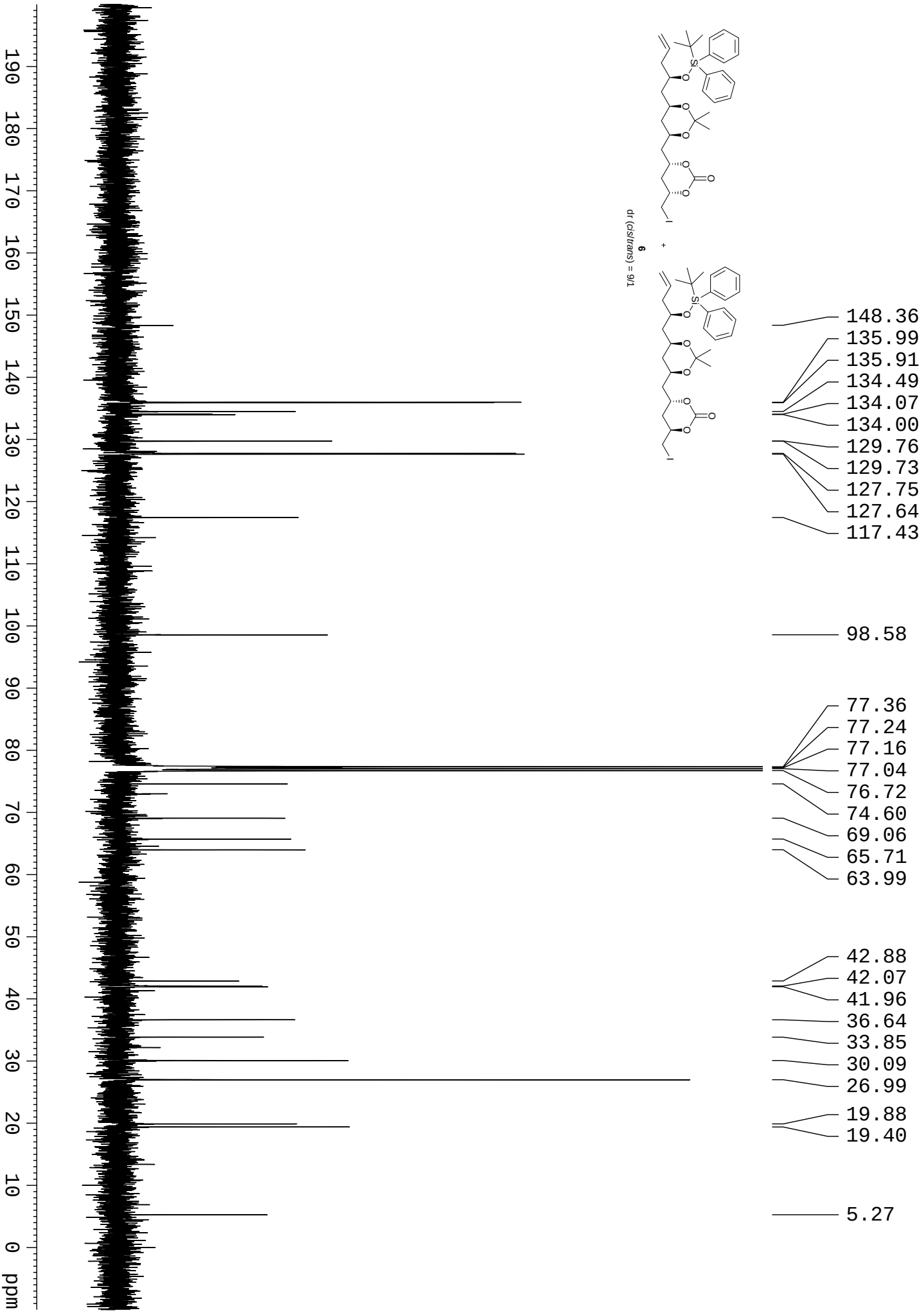

5h
7.70
7.70
7.68
7.67
7.67
7.65
7.65
7.44
7.44
7.42
7.42
7.41
7.41
7.39
7.39
7.37
7.37
7.37
7.26
5.79
5.77
5.77
5.76
5.75
5.73
5.10
5.10
5.07
5.07
5.06
5.05
5.04
5.01
5.00
4.97
4.93
4.93
4.92
3.85
3.83
2.33
2.31
2.29
2.29
1.73
1.49
1.47
1.46
1.45
1.44
1.43
1.41
1.40
1.28
1.20
1.06
0.81
0.78
0.78
0.76
4.01
6.07
0.65
2.00
2.02
3.05
2.00
0.94
3.03
1.04
1.03
12.03
3.59
3.05
9.02
1.88
9
8
7
6
5
4
3
2
1
0
ppm

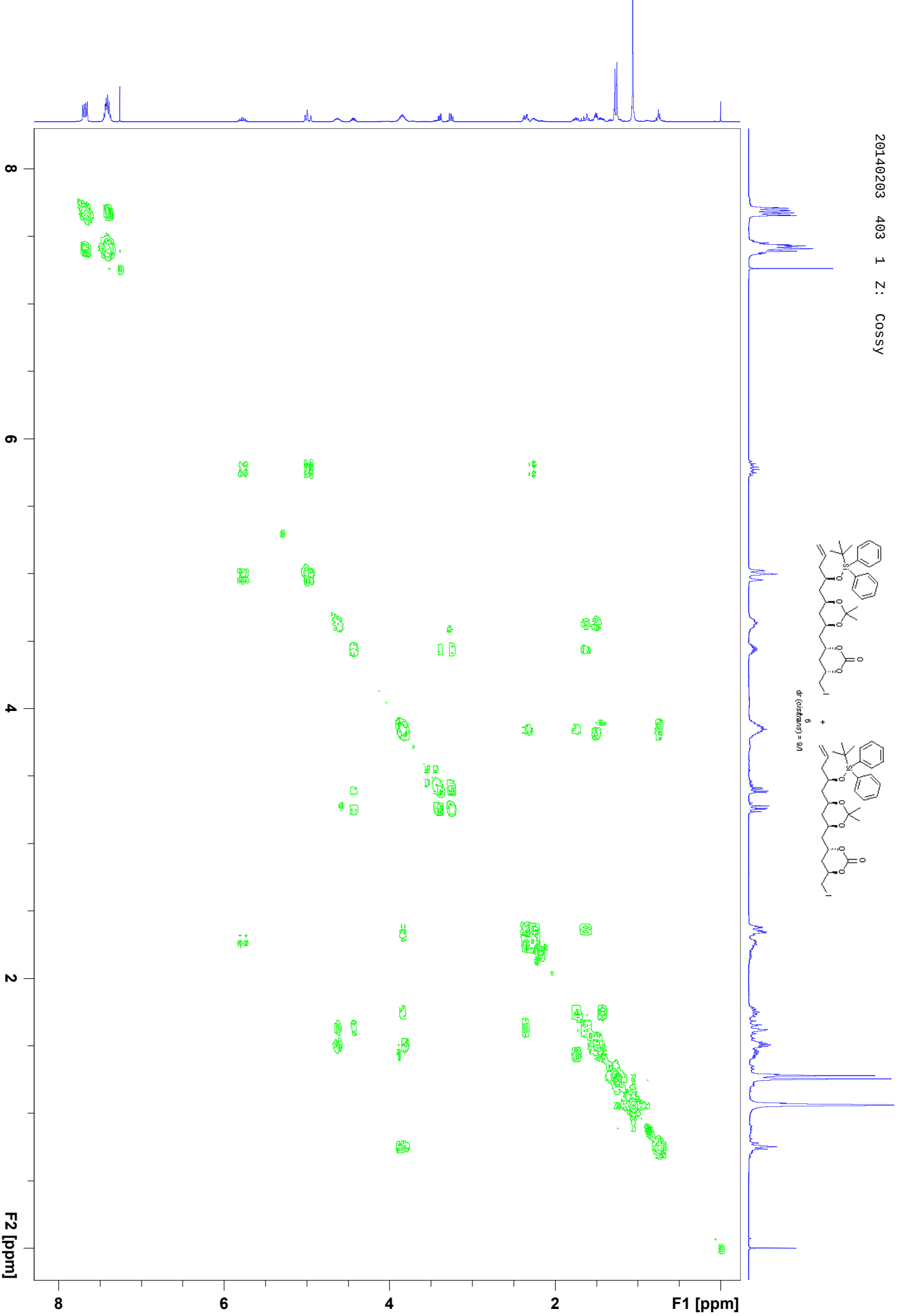

5h
153.20
135.96
135.88
134.56
134.13
134.08
133.49
129.71
127.67
127.62
117.81
117.33
98.39
81.52
77.35
77.24
77.03
76.72
72.50
69.24
65.93
64.93
42.92
41.91
40.48
39.47
36.71
30.10
27.84
27.02
19.43
19.40
ppm

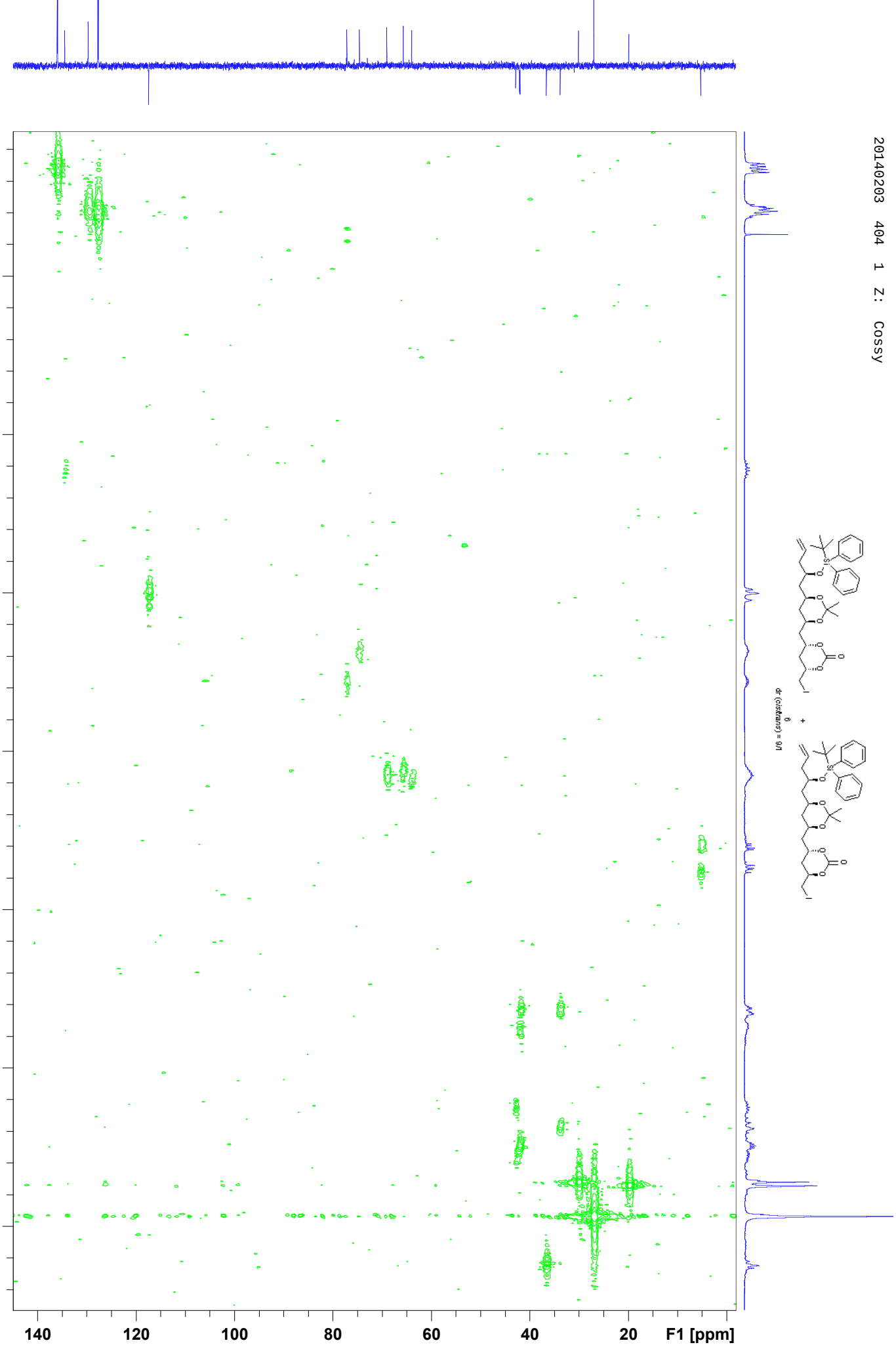

20140123 393 1 Z: Cossy
5h
F1 [ppm]
F2 [ppm]

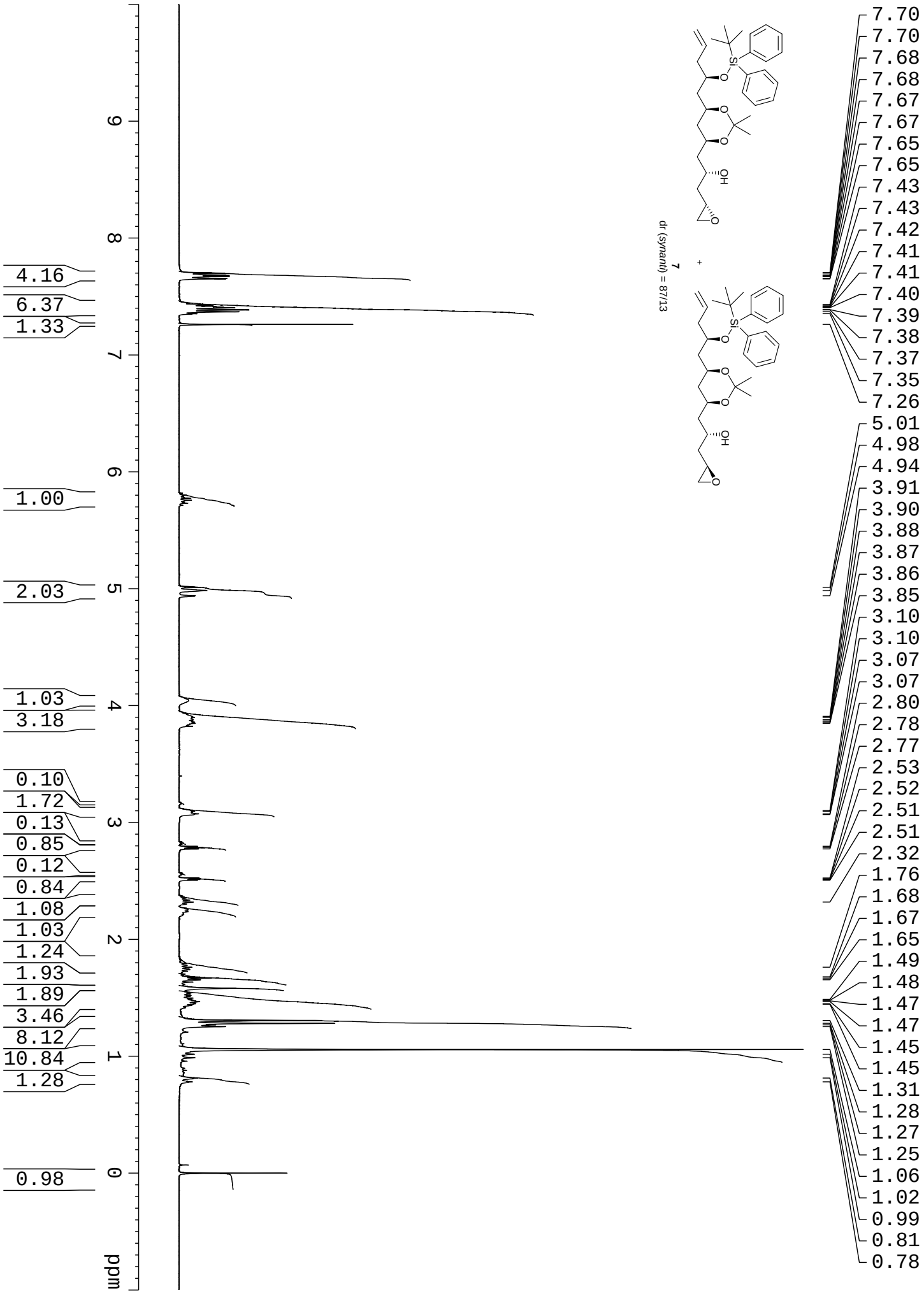

20140123 394 1 Z: Cossy
5h
F1 [ppm]
F2 [ppm]
140
120
100
80
60
40
20
1
2
3
4
5
6
7

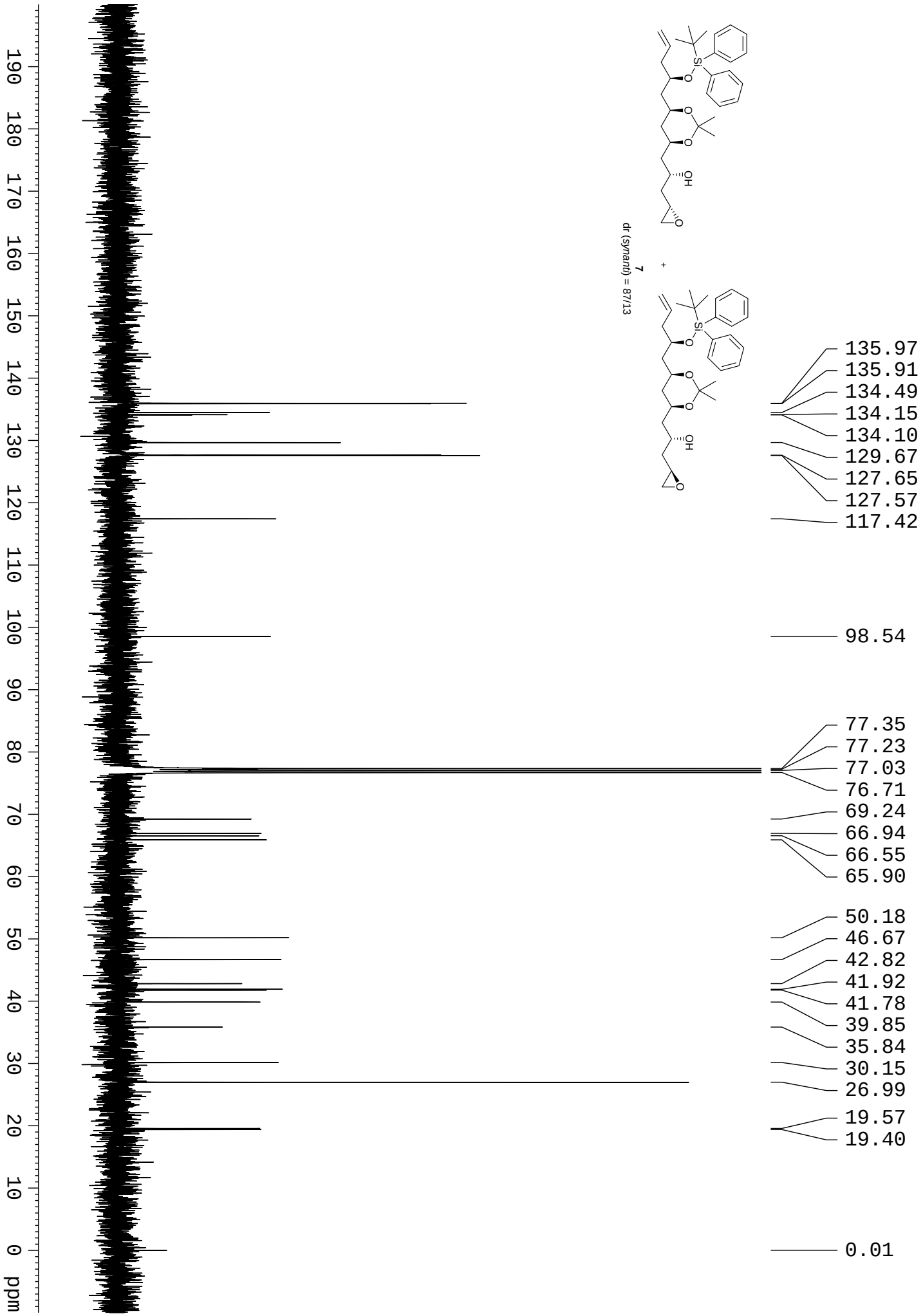

7.71
7.71
7.69
7.69
7.68
7.67
7.67
7.66
7.65
7.65
7.45
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.39
7.37
7.26
5.02
5.02
5.00
4.99
4.95
4.95
3.87
3.86
3.85
3.85
3.84
3.83
3.41
3.39
3.38
3.28
3.26
3.25
2.38
2.37
2.35
2.34
2.34
1.65
1.62
1.62
1.61
1.53
1.52
1.51
1.49
1.49
1.28
1.25
1.06
0.76
0.75
0.73
4.36
6.85
0.44
1.00
1.99
2.23
2.89
0.26
1.10
1.02
1.86
1.16
1.13
2.07
1.85
1.30
6.71
10.20
2.00
0.27
ppm
6
dr (cis/trans) = 9/1

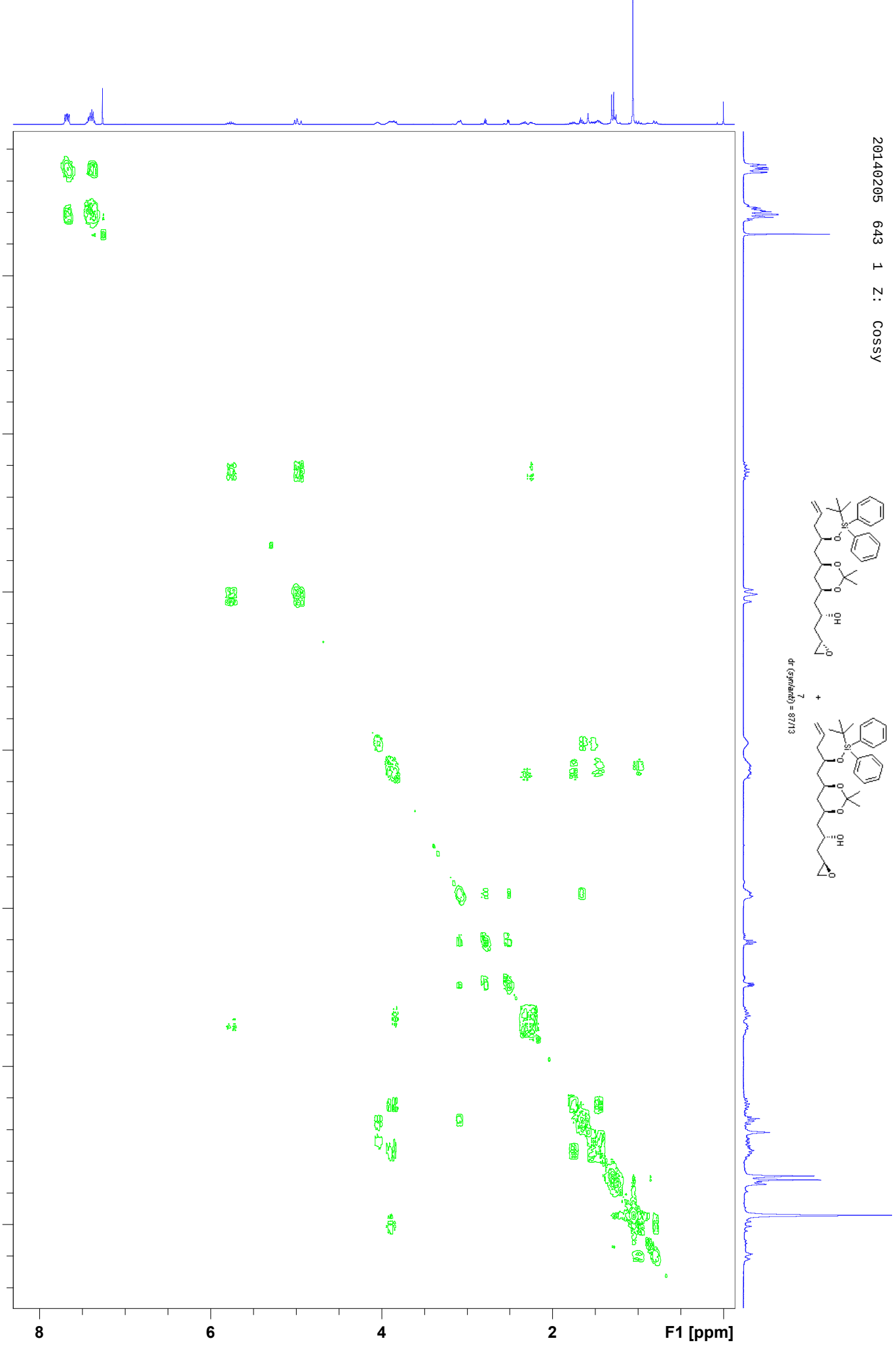

148.36
135.99
135.91
134.49
134.07
134.00
129.76
129.73
127.75
127.64
117.43
98.58
77.36
77.24
77.16
77.04
76.72
74.60
69.06
65.71
63.99
42.88
42.07
41.96
36.64
33.85
30.09
26.99
19.88
19.40
5.27
6
dr (cis/trans) = 9/1
ppm

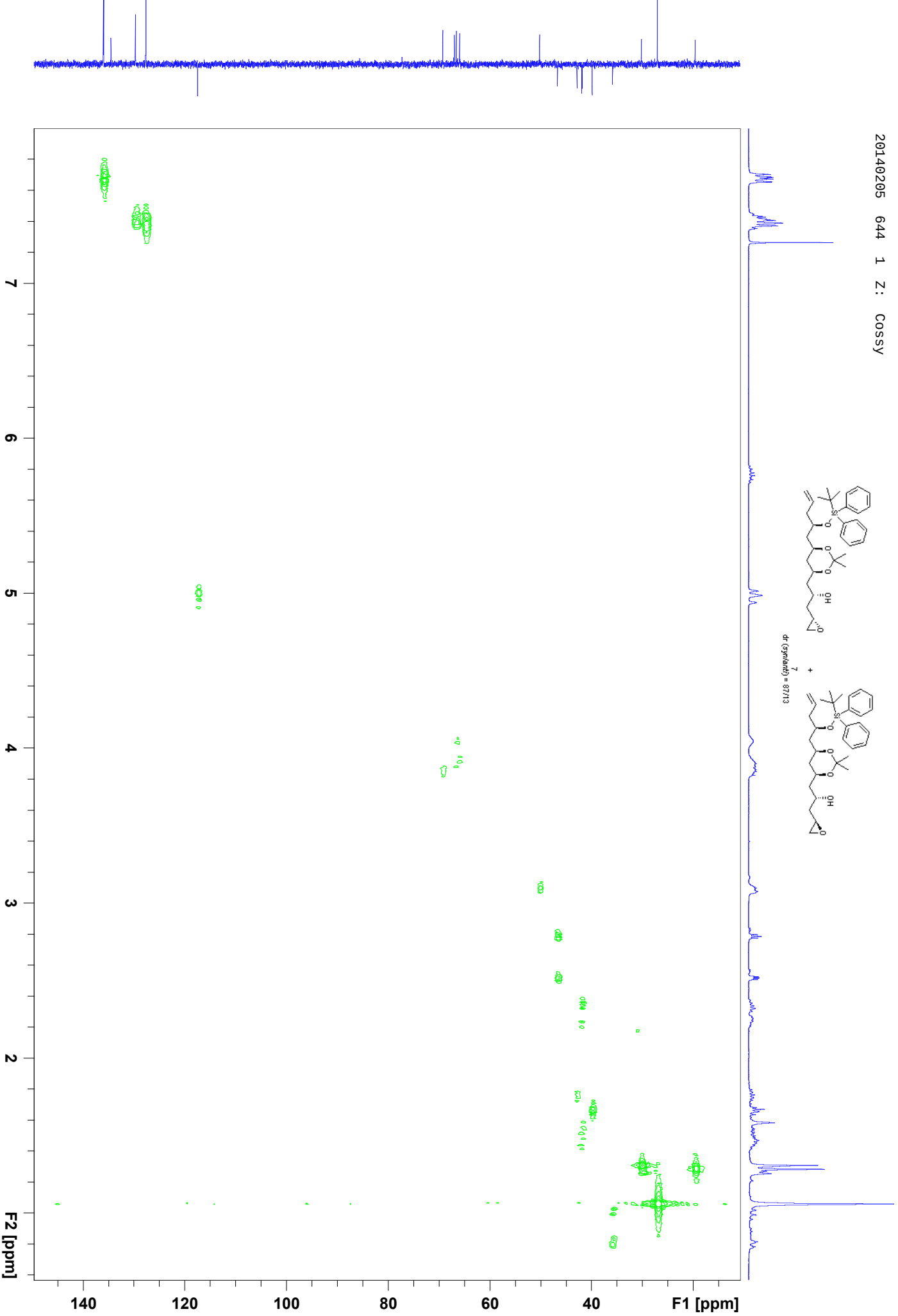

20140203 403 1 Z: Cossy
6
dr (cis&trans) = 9/1
+
F1 [ppm]
F2 [ppm]
8
6
4
2


20140203 404 1 Z: Cossy
dr (cis:trans) = 9:1
F1 [ppm]
F2 [ppm]
140
120
100
80
60
40
20
1
2
3
4
5
6
7


7.70
7.70
7.68
7.68
7.67
7.67
7.65
7.65
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.38
7.37
7.35
7.26
5.01
4.98
4.94
3.91
3.90
3.88
3.87
3.86
3.85
3.10
3.10
3.07
3.07
2.80
2.78
2.77
2.53
2.52
2.51
2.51
2.32
1.76
1.68
1.67
1.65
1.49
1.48
1.47
1.47
1.45
1.45
1.31
1.28
1.27
1.25
1.06
1.02
0.99
0.81
0.78
4.16
6.37
1.33
1.00
2.03
1.03
3.18
0.10
1.72
0.13
0.85
0.12
0.84
1.08
1.03
1.24
1.93
1.89
3.46
8.12
10.84
1.28
0.98
9
8
7
6
5
4
3
2
1
0
ppm
7
dr (syn/anti) = 87/13


7
dr (synanti) = 87/13
135.97
135.91
134.49
134.15
134.10
129.67
127.65
127.57
117.42
98.54
77.35
77.23
77.03
76.71
69.24
66.94
66.55
65.90
50.18
46.67
42.82
41.92
41.78
39.85
35.84
30.15
26.99
19.57
19.40
0.01
ppm


20140205 643 1 Z: Cossy
7
dr (syn/anti) = 87/13
F1 [ppm]
F2 [ppm]


20140205 644 1 Z: Cossy
7
dr (syn/anti) = 87/13
+
F2 [ppm]
F1 [ppm]
140
120
100
80
60
40
2
3
4
5
6
7