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Supporting Information

Polyunsaturated C-Glycosidic 4-Hydroxy-2-pyrone Derivatives: Total Synthesis Shows that Putative Orevactaene Is Likely Identical with Epipyrone A

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General. All reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2 (CaH_2), 1,4-dioxane (Na/K alloy), MeOH (Mg). DMF, pyridine and NEt_3 were dried by an absorption solvent purification system based on molecular sieves. *i*Pr_2NH was purified by distillation over CaH_2 and transferred under Ar. CH_3NO_2 was used in technical grade quality. Flash chromatography: Merck silica gel 60 (40–63 μm). NMR: Spectra were recorded on Bruker AV 400, Bruker AV 500 or Bruker AV 600 spectrometers in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: residual $CHCl_3$ in $CDCl_3$: $\delta_C \equiv 77.16$ ppm; $\delta_H \equiv 7.26$ ppm; [D_6]-DMSO: residual [D_5]-DMSO in [D_6]-DMSO $\delta_C \equiv 39.52$ ppm; $\delta_H \equiv 2.50$ ppm) IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers $\tilde{\nu}$ in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). Unless stated otherwise, all commercially available compounds (ABCR, Acros, Aldrich, Strem) were used as received.

D-*glycero*-D-*galacto*-Heptono-1,4-lactone[1], (2*E*,4*E*,6*E*)-7-(tributylstannyl)hepta-2,4,6-trien-1-ol[2], *(S)*-1-iodo-2-methylbutane[3], N-((1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl)-N-methylpropionamide[4], N-((1*R*,2*R*)-1-hydroxy-1-phenylpropan-2-yl)-N-methyl-propionamide[5], (*R*)-4-benzyl-3-butyryloxazolidin-2-one[6], 1-iodo-1-propyne[7], thexylborane[8], $PhMe_2SiLi$[9], $SPhosAuNTf_2$[10] and $[Ph_2PO_2][NBu_4]$[11] were prepared according to literature procedures.

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[7] L. Brandsma, J. W. Zwikker, *Science of Synthesis* **2006**, *8a*, 285–303.
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[9] I. Fleming, F. Roessler, *J. Chem. Soc., Chem. Commun.* **1980**, *6*, 276–277.
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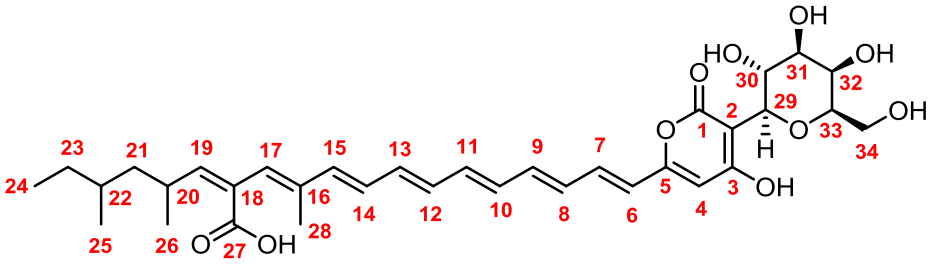
Table S-1. Comparison of the ^{13}C NMR Spectra (ppm) recorded in [D_4]-MeOH of **Epipyrone A** (**NP**)[a] with synthetic (20*S*,22*R*)-**2**, (22*S*,20*S*)-**2**, (22*R*,20*R*)-**2** and (20*R*,22*S*)-**2**; arbitrary numbering scheme as shown; signals marked * and ** have been mutually interchanged;[b] $\Delta\delta$ = shift (synth. sample – NP)

Color code: **orange: 0.5 ppm ≤ $|\Delta\delta|$ < 1 ppm**; **red: $|\Delta\delta| \geq$ 1 ppm**;



Nr	NP[a]	R S 22 20 OH	Δδ	S S 22 20 OH	Δδ	R R 22 20 OH	Δδ	S R 22 20 OH	Δδ
1	166,2*	166,2	0,0	166,3	0,1	166.2	0,0	166.2	0,0
2	101,5	101,9	0,4	101,9	0,4	101.9	0,4	101.9	0,4
3	171,1*	170,6	-0,5	170,5	-0,6	170.4	-0,7	170.4	-0,7
4	102,4	102,5	0,1	102,4	0,0	102.3	-0,1	102.3	-0,1
5	160,0	160,7	0,7	160,7	0,7	160.8	0,8	160.8	0,8
6	122,5	122,6	0,1	122,6	0,1	122.6	0,1	122.6	0,1
7	137,5	137,6	0,1	137,6	0,1	137.6	0,1	137.6	0,1
8	132,0	132,3	0,3	132,3	0,3	132.3	0,3	132.3	0,3
9	140,5	140,6	0,1	140,6	0,1	140.6	0,1	140.6	0,1
10	132,4**	133,7	1.3	133,7	1,3	133.6	1,2	133.7	1,3
11	138,2	138,1	-0,1	138,1	-0,1	138.1	-0,1	138.2	0,0
12	134,0	134,1	0,1	134,1	0,1	134.1	0,1	134.1	0,1
13	137,0	137,1	0,1	137,1	0,1	137.1	0,1	137.1	0,1
14	130,2**	130,1	-0,1	130,2	0,0	130.2	0,0	130.2	0,0
15	140,5	140,4	-0,1	140,4	-0,1	140.4	-0,1	140.4	-0,1
16	137,5	136,7	-0,8	136,7	-0,8	136.7	-0,8	136.7	-0,8
17	131,5	131,5	0,0	131,4	-0,1	131.4	-0,1	131.5	0,0
18	132,0	132,1	0,1	132,4	0,4	132.4	0,4	132.0	0,0
19	149,0	149,2	0,2	149,1	0,1	149.1	0,1	149.3	0,3

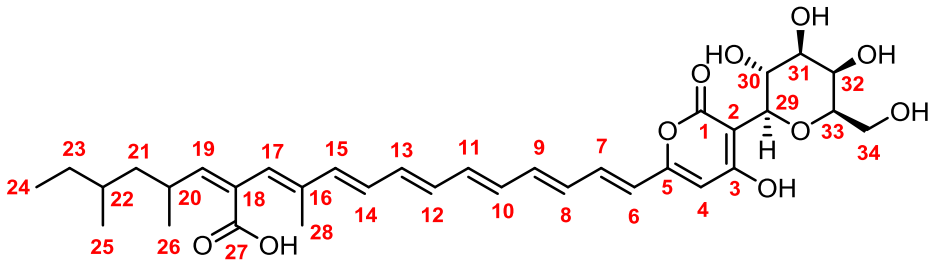
20	33,3	33,1	-0,2	33,2	-0,1	33.2	-0,1	33.1	-0,2
21	46,1	45,8	-0,3	45,9	-0,2	45.9	-0,2	45.8	-0,3
22	34,0	33,5	-0,5	33,9	-0,1	33.9	-0,1	33.5	-0,5
23	31,4	30,3	-1,1	31,3	-0,1	31.3	-0,1	30.3	-1,1
24	11,8	11,6	-0,2	11,8	0,0	11.7	-0,1	11.6	-0,2
25	19,5	20,0	0,5	19,6	0,1	19.6	0,1	20.0	0,5
26	22,0	21,1	-0,9	21,8	-0,2	21.8	-0,2	21.1	-0,9
27	172,3	172,2	-0,1	172,2	-0,1	172.1	-0,2	172.1	-0,2
28	14,0	13,8	-0,2	13,8	-0,2	13.8	-0,2	13.8	-0,2
29	76,7	76,5	-0,2	76,5	-0,2	76.5	-0,2	76.5	-0,2
30	70,5	70,5	0,0	70,4	-0,1	70.4	-0,1	70.5	0,0
31	76,8	76,7	-0,1	76,6	-0,2	76.6	-0,2	76.6	-0,2
32	71,3	71,1	-0,2	71,2	-0,1	71.2	-0,1	71.1	-0,2
33	81,0	81,1	0,1	81,0	0,0	81.1	0,1	81.1	0,1
34	62,9	62,8	-0,1	62,9	0,0	62.9	0,0	62.8	-0,1
[α][c]	**+27.8**	**+147.1**		**+14.2**		**–44.0**		**–118.4**	

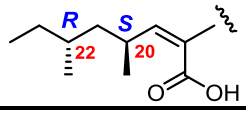
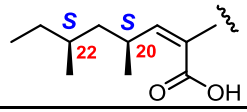
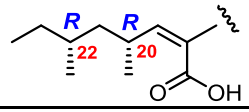
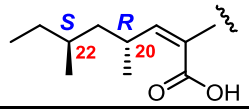
[a] C. Calder, S. Ford, A. I. Selwood, R. v. Ginkel, A. L. Wilkins, WO 2012/023865 A1;

[b] As the signal assignment for the synthetic samples is unambiguous, we assume that the signals of C1/C3 and C10/14 are mutually interchanged in the literature

[c] $[\alpha]_{\mathrm{D}}^{20}$ (c = 0.05, MeOH)

Table S-2. Comparison of the ^{13}C NMR Spectra (ppm) recorded in [D_6]-DMSO of **putative Orevactaene** (**NP**)[a] with synthetic (20*S*,22*R*)-**2**, (22*S*,20*S*)-**2**, (22*R*,20*R*)-**2** and (20*R*,22*S*)-**2**; arbitrary numbering scheme as shown; signals marked * and ** have been mutually interchanged;[b] Δδ = shift (synth. sample – NP)



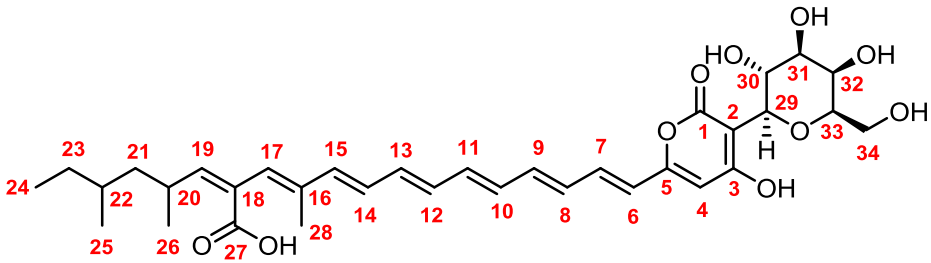
Nr	NP[a]		Δδ		Δδ		Δδ		Δδ
1	162.2*	162,3	0,1	162,2	0,0	162.2	0,0	162.3	0,1
2	101.4	101,4	0,0	101,4	0,0	101.4	0,0	101.4	0,0
3	167.6*	167,2	-0,4	167,0	-0,6	167.1	-0,5	167.1	-0.5
4	101.6	101,4	0,2	101,3	-0,3	101.3	-0,3	101.3	-0,3
5	157.8	157,7	0,1	157,8	0,0	157.7	-0,1	157.7	-0,1
6	122.5	122,3	0,2	122,3	-0,2	122.3	-0,2	122.3	-0,2
7	134.7	134,6	0,1	134,7	0,0	134.7	0,0	134.7	0,0
8	131.8	131,4	0,4	131,9	0,1	131.4	-0,4	131.4	-0,4
9	138.7	138,5	0,2	138,6	-0,1	138.5	-0,2	138.5	-0,2
10	132.8**	132,6	-0,2			132.6	-0,2	132.6	-0,2
11	136.4	136,2	0,2			136.2	-0,2	136.2	-0,2
12	133.1	132,9	0,2			132.9	-0,2	132.9	-0,2
13	135.5	135,4	0,1			135.4	-0,1	135.4	-0,1
14	129.0**	128,8	-0,2			128.8	-0,2	128.8	-0,2
15	139.1	138,9	0,2	138,9	-0,2	138.9	-0,2	138.9	-0,2
16	134.7	134,6	0,1	134,5	-0,2	134.5	-0,2	134.6	-0,1
17	130.6	130,4	0,2	130,4	-0,2	130.4	-0,2	130.4	-0,2
18	131.4	130,8	0,6	131,2	-0,2	131.4	0,0	130.8	-0,6
19	146.7	146,7	0,0	146,5	-0,2	146.5	-0,2	146.7	0,0
20	31.5	31,3	0,2	31,3	-0,2	31.3	-0,2	31.3	-0,2

21	44.1	43,0	1,1	43,9	-0,2	43.9	-0,2	43.8	-0,3
22	32.2	31,6	0,6	32,0	-0,2	32,0	-0,2	31.6	-0,6
23	29.7	28,4	1,3	29,6	-0,1	29.6	-0,1	28.5	-1,2
24	11.3	10,9	0,4	11.1	-0,2	11.1	-0,2	11.0	-0,3
25	18.9	19,3	-0,4	18,8	-0,1	18.8	-0,1	19.4	0,5
26	21.4	20,5	0,9	21,3	-0,1	21.3	-0,1	20.5	-0,9
27	169.6	169,4	0,2	169,4	-0,2	169.4	-0,2	169.4	-0,2
28	13.3	13,1	0,2	13,1	-0,2	13.1	-0,2	13.1	-0,2
29	74.5	74,4	0,1	74,3	-0,2	74.4	-0,1	74.4	-0,1
30	67.9	67,9	0,0	67,9	0,0	67.9	0,0	67.9	0,0
31	75.3	75,0	0,3	75,0	-0,3	75.0	-0,3	75.0	-0,3
32	69.1	68,9	0,2	68,9	-0,2	68.9	-0,2	68.9	-0,2
33	79.3	79,1	0,2	79,1	-0,2	79.1	-0,2	79.1	-0,2
34	60.9	60,7	0,2	60,7	-0,2	60.7	-0,2	60.7	-0,2

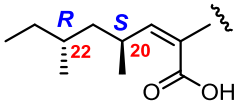
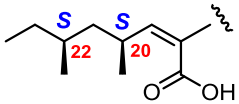
[a] Y.-Z. Shu, Q. Ye, H. Li, K. F. Kadow, R. A. Hussain, S. Huang, D. R. Gustavson, S. E. Lowe, L.-P. Chang, D. M. Pirnik, K. Kodukula, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2295-2298.

[b] As the signal assignment for the synthetic samples is unambiguous, we assume that the signals of C1/C3 and C10/14 are mutually interchanged in the literature

Table S-3. Comparison of the ^{1}H NMR Spectra (ppm) recorded in [D_4]-MeOH of **epipyrone A** (**NP**)[b] with synthetic (20*S*,22*R*)-**2**, (22*S*,20*S*)-**2** (part I) as well as with (22*R*,20*R*)-**2** and (20*R*,22*S*)-**2** (part II); arbitrary numbering scheme as shown

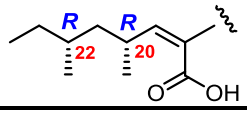
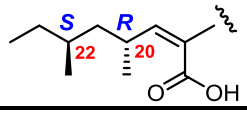


Part I

Nr	NP[b]		
4	6.08 (s, 1H)	6.08 (s, 1H)	6.08 (s, 1H)
6	6.18 (d, *J* = 14.8, 1H)	6.20 (d, *J* = 15.0 Hz, 1H)	6.19 (d, *J* = 15.1 Hz, 1H)
7	7.12 (m, 1H)[a]	7.14 (dd, *J* = 15.3, 11.3 Hz, 1H)	7.10 - 7.18 (m, 1H)
8	6.43 (m, 1H)[a]	6.42 (dd, *J* = 14.7 11.3 Hz, 1H)[a]	6.42 (m, 1H)[a]
9	6.62 (m, 1H)[a]	6.64 (dd, *J* = 14.7, 11.2, 1H)	6.64 (dd, *J* = 14.7, 11.2 Hz, 1H)
10	6.32 (m, 1H)[a]	6.39 (dd, *J* = 14.6, 11.2 Hz, 1H)[a]	6.39 (m, 1H)[a]
11	6.41 (m, 1H)[a]	6.50 (dd, *J* = 14.6, 10.3 Hz, 1H)	6.51 (dd, *J* = 14.7, 10.3 Hz, 1H)
12	6.47 (m, 1H)[a]	6.40 (d, *J* = 10.3 Hz, 1H)[a]	6.40 (m, 1H)[a]
13	6.39 (m, 1H)[a]	6.43 (m, 1H)[a]	6.46 (m, 1H)[a]
14	6.34 (1H)[a]	6.41 (m, 1H)[a]	6.41 (m, 1H)[a]
15	6.44 (m, 1H)[a]	6.41 (m, 1H)[a]	6.41 (m, 1H)[a]
17	6.13 (s, 1H)	6.13 -6.11 (m, 1H)	6.13 (s, 1H)
19	5.61 (d, *J* = 10.5 Hz, 1H)	5.64 (dd, *J* =10.4, 1.2, 1H)	5.60 (dd, *J* = 10.4, 1.2 Hz, 1H)
20	3.03 (m, 1H)	3.06 - 2.95 (m, 1H)	3.02 (m, 1H)
21	1.12 (m, 1H); 1.35 (m, 1H)	1.17 (m, 1H); 1.29 (m, 1H)	1.11 (m, 1H); 1.35 (m, 1H)
22	1.32 (m, 1H)	1.39 (m, 1H)	1.31 (m, 1H)
23	1.16 (m, 1H); 1.33 (m, 1H)	1.09 (dt, *J* = 12.8, 7.4, 1H); 1.39 (m, 1H)	1.16 (m, 1H); 1.31 (m, 1H)
24	0.87 (t, *J* = 7.6 Hz, 3H)	0.86 (t, *J* = 7.4, 3H)	0.87 (t, *J* = 7.3 Hz, 3H)
25	0.85 (d, *J* = 6.0 Hz, 3H)	0.86 (d, *J* = 6.5, 3H)	0.85 (d, *J* = 6.3 Hz, 3H)
26	1.02 (d, *J* = 6.6 Hz, 3H)	1.00 (d, *J* = 6.6, 3H)	1.02 (d, *J* = 6.6 Hz, 3H)
28	1.87 (s, 3H)	1.87 (d, *J* = 1.2, 3H)	1.87 (d, *J* = 1.2 Hz, 1H)

29	4.55 (d, *J* = 9.3 Hz, 1H)	4.53 (d, *J* = 9.7, 1H)	4.54 (d, *J* = 9.7 Hz, 1H)
30	4.21 (t, *J* = 9.9, 1H)	4.19 (t, *J* = 9.5, 1H)	4.19 (t, *J* = 9.5 Hz, 1H)
31	3.53 (dd, *J* = 2.7, 9.3 Hz, 1H)	3.51 (dd, *J* = 3.2, 9.4, 1H)	3.52 (dd, *J* = 9.4, 3.2 Hz, 1H)
32	3.93 (d, *J* = 2.7, 1H)	3.91 (d, *J* = 3.1, 1H)	3.92 (d, *J* = 3.1 Hz, 1H)
33	3.62 (m, 1H)	3.62-3.59 (m, 1H)	3.61 (m, 1H)
34	3.72-3.76 (m, 2H)	3.69 (dd, *J* = 11.6, 5.1, 1H); 3.73 (dd, *J* = 11.40, 6.9, 1H)	3.72 (m, 2H)

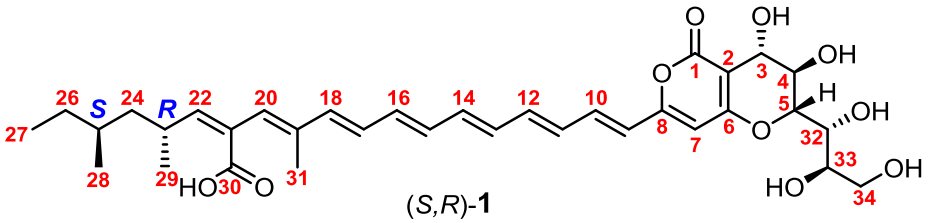
Part II

Nr	**NP[a]**		
4	6.08 (s, 1H)	6.08 (s, 1H)	6.08 (s, 1H)
6	6.18 (d, *J* = 14.8, 1H)	6.19 (d, *J* = 15.1 Hz, 1H)	6.20 (d, *J* = 15.1 Hz, 1H)
7	7.12 (m, 1H)[a]	7.14 (dd, *J* = 15.3, 11.5 Hz, 1H)	7.14 (dd, J = 15.2, 11.2 Hz, 1H)
8	6.43 (m, 1H)[a]	6.42 (dd, *J* = 14.4, 11.5 Hz, 1H)[a]	6.43 (dd, J = 14.5, 11.2 Hz, 1H)[a]
9	6.62 (m, 1H)[a]	6.64 (dd, *J* = 14.4, 11.1 Hz, 1H)	6.64 (dd, J = 14.5, 11.1 Hz, 1H)
10	6.32 (m, 1H)[a]	6.38 (dd, *J* = 14.8, 11.1 Hz, 1H)[a]	6.39 (dd, J = 14.7, 11.1 Hz, 1H)[a]
11	6.41 (m, 1H)[a]	6.50 (dd, *J* = 14.8, 10.1 Hz, 1H)	6.51 (dd, J = 14.7, 10.3 Hz, 1H)
12	6.47 (m, 1H)[a]	6.41 (d, *J* = 14.1 Hz, 1H)[a]	6.40 (d, J = 10.3 Hz, 1H)[a]
13	6.39 (m, 1H)[a]	6.42 (m, 1H)[a]	6.43 (m, 1H)[a]
14	6.34 (1H)[a]	6.40 (m, 1H)[a]	6.42 (m, 1H)[a]
15	6.44 (m, 1H)[a]	6.40 (m, 1H)[a]	6.41 (m, 1H)[a]
17	6.13 (s, 1H)	6.12 (s, 1H)	6.12 (m, 1H)
19	5.61 (d, *J* = 10.5 Hz, 1H)	5.60 (d, *J* = 10.3 Hz, 1H)	5.65 (dd, J = 10.3, 1.2 Hz, 1H)
20	3.03 (m, 1H)	3.01 (m, 1H)	3.00 (m, 1H)
21	1.12 (m, 1H); 1.35 (m, 1H)	1.11 (m, 1H); 1.35 (m, 1H)	1.17 (tdd, J = 13.2, 6.6, 5.6 Hz, 1H); 1.29 (dt, J = 13.4, 6.6 Hz, 1H)
22	1.32 (m, 1H)	1.30 (m, 1H)	1.37 (m, 1H)
23	1.16 (m, 1H); 1.33 (m, 1H)	1.16 (m, 1H); 1.30 (m, 1H)	1.09 (m); 1.41 (m)

24	0.87 (t, *J* = 7.6 Hz, 3H)	0.86 (m, 3H)	0.86 (m, 3H)
25	0.85 (d, *J* = 6.0 Hz, 3H)	0.85 (m, 3H)	0.86 (d, J = 6.6 Hz, 3H)
26	1.02 (d, *J* = 6.6 Hz, 3H)	1.01 (d, *J* = 6.5 Hz, 3H)	1.00 (d, J = 6.6 Hz, 3H)
28	1.87 (s, 3H)	1.87 (s, 3H)	1.87 (d, J = 1.2 Hz, 3H)
29	4.55 (d, *J* = 9.3 Hz, 1H)	4.53 (d, *J* = 9.7 Hz, 1H)	4.53 (d, J = 9.7 Hz, 1H)
30	4.21 (t, *J* = 9.9, 1H)	4.19 (t, *J* = 9.7 Hz, 1H)	4.19 (t, J = 9.5 Hz, 1H)
31	3.53 (dd, *J* = 2.7, 9.3 Hz, 1H)	3.52 (m, 1H)	3.51 (dd, J = 9.4, 3.2 Hz, 1H)
32	3.93 (d, *J* = 2.7, 1H)	3.91 (m, 1H)	3.91 (dd, J = 3.3, 0.9 Hz, 1H)
33	3.62 (m, 1H)	3.61 (m, 1H)	3.60 (m, 1H)
34	3.72-3.76 (m, 2H)	3.73 (m, 1H)	3.69 (dd, J = 11.5, 5.2 Hz, 1H); 3.74 (dd, J = 11.5, 6.8 Hz, 1H)

[a] overlapping signals; [b] data reported in *Bioorg. Med. Chem Lett.* **2012**, *22,* 3188 are used for the comparison; the data contained in the patent on epipyrone A (WO 2012/023865) are slightly different

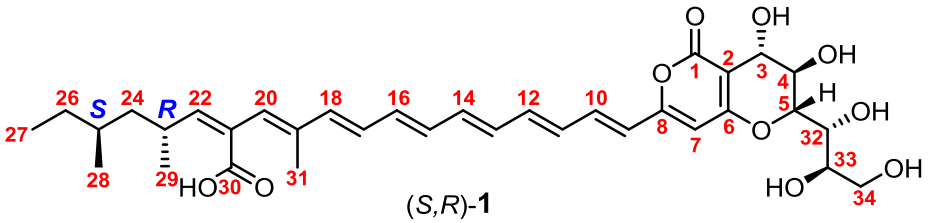
Table S-4. Comparison of the ^{13}C NMR data ([D_6]-DMSO) of **putative Orevactaene** (**NP**) and (*S,R*)-**1**, showing a severe mismatch in the head group; arbitrary numbering scheme as shown; signals marked * and ** have been mutually interchanged (see above); $\Delta\delta$ = ppm ((*S,R*)-**1** – **NP**)



Nr	Literature[a]	(*S,R*)-1	Δδ
1	162.2*	162.3	+0.1
2	101.4	99.8	–0.6
3	74.5	62.5	–12.0
4	67.9	68.9	+1.0
5	75.3	78.4	+3.1
6	167.6*	165.0	–2.6
7	101.6	100.9	–0.7
8	157.8	157.7	–0.1
9	122.5	122.1	–0.4
10	134.7	134.8	+0.1
11	131.8	131.4	–0.4
12	138.7	138.7	0.0
13	132.8**	132.6	–0.2
14	136.4	136.3	–0.1
15	133.1	132.9	–0.2
16	135.5	135.5	0.0
17	129.0**	128.8	–0.2
18	139.1	139.0	–0.1
19	134.7	134.5	–0.2
20	130.6	130.5	–0.1
21	131.4	131.3	–0.1
22	146.7	146.4	–0.3
23	31.5	31.3	–0.2
24	44.1	43.9	–0.2
25	32.2	32.0	–0.2
26	29.7	29.6	–0.1
27	11.3	11.1	–0.2
28	18.9	18.8	–0.1
29	21.4	21.3	–0.1
30	169.6	169.5	–0.1
31	13.3	13.2	–0.1
32	69.1	70.6	+1.5
33	79.3	70.1	–9.2
34	60.9	63.2	+2.3

[a] Y.-Z. Shu, Q. Ye, H. Li, K. F. Kadow, R. A. Hussain, S. Huang, D. R. Gustavson, S. E. Lowe, L.-P. Chang, D. M. Pirnik, K. Kodukula, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2295-2298.

Table S-5. Comparison of the ^{1}H NMR data ([D_6]-DMSO) of **putative Orevactaene** (**NP**) and (*S,R*)-**1**; arbitrary numbering scheme as shown

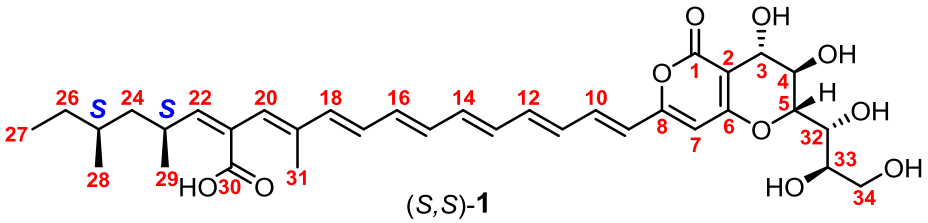


(*S,R*)-**1**

Nr	Literature[a]	(*S,R*)-**1**
3	4.25 (d, *J* = 9.5 Hz, 1H)	4.33 (ddd, *J* = 5.2, 3.8, 1.2 Hz, 1H)
4	4.11 (dd, *J* = 9.5, 9.3 Hz, 1H)	3.84 (ddd, *J* = 4.2, 3.8, 3.5 Hz, 1H)
5	3.27 (dd, *J* = 9.3, 2.8 Hz, 1H)	4.59 (dt, *J* = 3.5, 1.2 Hz, 1H)
7	6.18 (s, 1H)	6.21 (s, 1H)
9	6.30 d, *J* = 15.2 Hz, 1H)	6.33 (d, *J* = 15.2 Hz, 1H);
10	7.00 (dd, *J* = 15.2, 11.4 Hz, 1H)	7.04 (dd, *J* = 15.2, 11.3 Hz, 1H)
11	6.45 (dd, overlapping)	6.47 (m, 1H)
12	6.70 (dd, *J* = 14.8, 11.3 Hz, 1H)	6.73 (dd, *J* = 14.6, 11.3 Hz, 1H)
13	6.42 (dd, overlapping, 1H)	6.44 (m, 1H)
14	6.51 (dd, overlapping, 1H)	6.53 (dd, *J* = 14.4, 10.4 Hz, 1H)
15	6.41 (dd, overlapping, 1H)	6.45 (m, 1H)
16	6.47 (dd, overlapping, 1H)	6.49 (m, 1H)
17	6.40 (dd, overlapping, 1H)	6.42 (m, 1H)
18	6.40 (dd, overlapping, 1H)	6.43 (m, 1H)
20	6.11 (s, 1H)	6.13 (s, 1H)
22	5.56 (d, *J* = 10.3 Hz, 1H)	5.58 (d, *J* = 10.1 Hz, 1H)
23	2.90 (m, 1H)	2.92 (m, 1H)
24	1.24 (m, 1H)	1.31 (ddd, *J* = 13.0, 9.8, 4.0 Hz, 1H)
	1.08 (m, 1H)	1.08 (ddd, *J* = 13.0, 9.0, 4.6 Hz, 1H)
25	1.20 (m, 1H)	1.26 (m, 1H)
26	1.20 (m, 1H)	1.25 (m, 1H)
	1.10 (m, 1H)	1.11 (m, 1H)
27	0.80 (t, *J* = 7.6 Hz, 3H)	0.82 (t, *J* = 7.3 Hz, 3H)
28	0.78 (d, *J* = 7,1 Hz, 3H)	0.80 (d, *J* = 6.5 Hz, 3H)
29	0.96 (d, *J* = 7.1 Hz, 3H)	0.97 (d, *J* = 6.6 Hz, 3H)
30 CO_2H	8.00 (bs, 1H)	12.75 (bs, 1H)
31	1.79 (s, 3H)	1.81 (s, 3H)
32	3.70 (dd, *J* = 6.2, 2.8 Hz, 1H)	3.63 (ddd, *J* = 9.2, 4.1, 1.2 Hz, 1H)
33	3.37 (m, overlapping, 1H)	3.51 (dddd, *J* = 9.2, 6.0, 5.2, 3.0 Hz, 1H)
34	3.42 (m, 1H)	3.62 (m, 1H)
	3.39 (m, 1H)	3.40 (ddd, *J* = 11.2, 5.4, 5.2 Hz, 1H)
3-OH		6.17 (d, *J* = 5.2 Hz, 1H)
4-OH		5.45 (d, *J* = 4.2 Hz, 1H)
32-OH		5.13 (d, *J* = 4.1 Hz, 1H)
33-OH		4.81 (d, *J* = 6.0 Hz, 1H)
34-OH		4.37 (t, *J* = 5.4 Hz, 1H)

[a] Y.-Z. Shu, Q. Ye, H. Li, K. F. Kadow, R. A. Hussain, S. Huang, D. R. Gustavson, S. E. Lowe, L.-P. Chang, D. M. Pirnik, K. Kodukula, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2295-2298.

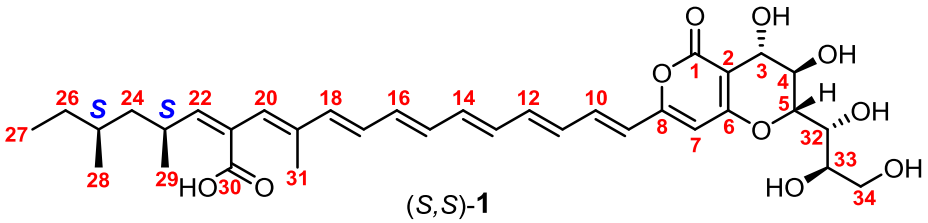
Table S-6. Comparison of the ^{13}C NMR data ([D_6]-DMSO) of **putative Orevactaene** (**NP**) and (*S,S*)-**1**, showing a severe mismatch in the head group; arbitrary numbering scheme as shown; signals marked * and ** have been mutually interchanged (see above); $\Delta\delta$ = ppm ((*S,S*)-**1** – **NP**); n.r. = not resolved



Nr	Literature[a]	(*S,S*)-1	Δδ
1	162.2*	162.3	+0.1
2	101.4	99.8	–1,6
3	74.5	62.5	–12.0
4	67.9	68.9	+1.0
5	75.3	78.4	+3.1
6	167.6*	165.0	–2.6
7	101.6	100.9	–0.7
8	157.8	157.7	–0.1
9	122.5	122.1	–0.4
10	134.7	134.8	+0.1
11	131.8	131.3	–0.5
12	138.7	138.7	0.0
13	132.8**	132.4	–0.4
14	136.4	136.4	0.0
15	133.1	132.7	–0.4
16	135.5	135.5	0.0
17	129.0**	128.5	–0.5
18	139.1	139.2	+0.1
19	134.7	n.r.	
20	130.6	n.r.	
21	131.4	n.r.	
22	146.7	n.r.	
23	31.5	31.2	–0.3
24	44.1	43.9	–0.2
25	32.2	31.6	–0.6
26	29.7	28.5	–1.2
27	11.3	11.0	–0.3
28	18.9	19.4	+0.5
29	21.4	20.6	–0.8
30	169.6	n.r.	
31	13.3	13.1	–0.2
32	69.1	70.6	+1.5
33	79.3	70.1	–9.2
34	60.9	63.2	+2.3

[a] Y.-Z. Shu, Q. Ye, H. Li, K. F. Kadow, R. A. Hussain, S. Huang, D. R. Gustavson, S. E. Lowe, L.-P. Chang, D. M. Pirnik, K. Kodukula, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2295-2298.

Table S-7. Comparison of the ^{1}H NMR data ([D_6]-DMSO) of **putative Orevactaene** (**NP**) and (*S,S*)-**1**; arbitrary numbering scheme as shown



(*S,S*)-**1**

Nr	Literature[a]	(*S,S*)-**1**
3	4.25 (d, *J* = 9.5 Hz, 1H)	4.33 (dd, *J* = 5.2, 3.8 Hz, 1H)
4	4.11 (dd, *J* = 9.5, 9.3 Hz, 1H)	3.84 (q, *J* = 3.8 Hz, 1H)
5	3.27 (dd, *J* = 9.3, 2.8 Hz, 1H)	4.58 (d, *J* = 3.8 Hz, 1H)
7	6.18 (s, 1H)	6.21 (s, 1H)
9	6.30 d, *J* = 15.2 Hz, 1H)	6.33 (d, *J* = 15.2 Hz, 1H)
10	7.00 (dd, *J* = 15.2, 11.4 Hz, 1H)	7.04 (dd, *J* = 15.2, 11.4 Hz, 1H)
11	6.45 (dd, overlapping)	6.47 (dd, *J* = 14.5, 11.4 Hz, 1H)
12	6.70 (dd, *J* = 14.8, 11.3 Hz, 1H)	6.73 (dd, *J* = 14.5, 11.3 Hz, 1H)
13	6.42 (dd, overlapping, 1H)	6.44 (dd, *J* = 14.4, 11.3 Hz, 1H)
14	6.51 (dd, overlapping, 1H)	6.53 (dd, *J* = 14.4, 10.5 Hz, 1H)
15	6.41 (dd, overlapping, 1H)	6.44 (m, 1H)
16	6.47 (dd, overlapping, 1H)	6.49 (m, 1H)
17	6.40 (dd, overlapping, 1H)	6.40 (m, 1H)
18	6.40 (dd, overlapping, 1H)	6.43 (m, 1H)
20	6.11 (s, 1H)	6.12 (s, 1H)
22	5.56 (d, *J* = 10.3 Hz, 1H)	5.55 (bs, 1H)
23	2.90 (m, 1H)	2.89 (m, 1H)
24	1.24 (m, 1H)	1.24 (m, 1H)
	1.08 (m, 1H)	1.12 (m, 1H)
25	1.20 (m, 1H)	1.32 (m, 1H)
26	1.20 (m, 1H)	1.34 (m, 1H)
	1.10 (m, 1H)	1.06 (m, 1H)
27	0.80 (t, *J* = 7.6 Hz, 3H)	0.81 (t, *J* = 7.4 Hz, 3H)
28	0.78 (d, *J* = 7,1 Hz, 3H)	0.81 (d, *J* = 6.8 Hz, 3H)
29	0.96 (d, *J* = 7.1 Hz, 3H)	0.94 (d, *J* = 6.4 Hz, 3H)
30 CO_2H	8.00 (bs, 1H)	12.76 (bs, 1H)
31	1.79 (s, 3H)	1.81 (s, 3H)
32	3.70 (dd, *J* = 6.2, 2.8 Hz, 1H)	3.64 (dd, J = 9.2, 4.0 Hz, 1H)
33	3.37 (m, overlapping, 1H)	3.51 (m, 1H)
34	3.42 (m, 1H)	3.62 (m, 1H)
	3.39 (m, 1H)	3.40 (m, 1H)
3-OH		6.17 (d, *J* = 5.2 Hz, 1H)
4-OH		5.45 (d, *J* = 4.0 Hz, 1H)
32-OH		5.14 (d, *J* = 4.0 Hz, 1H)
33-OH		4.82 (d, *J* = 5.9 Hz, 1H)
34-OH		4.38 (m, 1H)

[a] Y.-Z. Shu, Q. Ye, H. Li, K. F. Kadow, R. A. Hussain, S. Huang, D. R. Gustavson, S. E. Lowe, L.-P. Chang, D. M. Pirnik, K. Kodukula, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2295-2298.

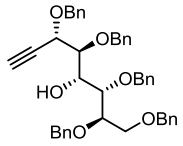
THE PUTATIVE OREVACTAENE SERIES

2,3,5,6,7 Penta-*O*-benzyl-D-*glycero*-D-*galacto*-heptono-1,4-lactone (6). TfOH (1.70 mL, 19.2 mmol) was added to a suspension of D-*glycero*-D-*galacto*-heptono-1,4-lactone (**5**)[1] (20.0 g, 96.1 mmol) and benzyl trichloroacetimidate (194.1 g, 768.6 mmol) in dioxane (890 mL) and the mixture was stirred for 18 h at room temperature. The reaction was quenched with sat. aq. $NaHCO_3$ and the aqueous layer extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The residue was boiled with aq. NaOH (1 M, 144 mL) for 30 min. After reaching ambient temperature, the mixture was acidified with aq. HCl and the aqueous layer extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (SiO_2, hexane:EtOAc, 20:1 to 5:1) afforded the title compound as a yellow oil (46.9 g, 74%). $[a]_D^{20}$: –19.3 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 – 7.24 (m, 21H), 7.23 – 7.20 (m, 2H), 7.16 -7.13 (m, 2H), 5.06 (d, *J* = 11.6 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.60 – 4.45 (m, 6H), 4.38 (d, *J* = 7.3 Hz, 1H), 4.30 (d, *J* = 11.4 Hz, 1H), 4.23 (t, *J* = 7.6 Hz, 1H), 4.17 (d, *J* = 11.6 Hz, 1H), 3.83 (dd, *J* = 8.3, 2.0 Hz, 1H), 3.80 – 3.70 (m, 2H), 3.63 (dd, *J* = 10.7, 3.2 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.8, 138.1, 138.0, 137.6, 137.1, 137.0, 128.7, 128.6, 128.53, 128.48, 128.3, 128.2, 128.1, 127.93, 127.87, 79.8, 78.9, 78.0 ,77.5, 75.0, 74.2, 73.5, 72.5, 72.4, 72.2, 67.7 ppm; IR (film): $\tilde{\nu}$ = 3063, 3030, 2867, 1787, 1655, 1603, 1586, 1496, 1454, 1209, 1095, 1028 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{42}H_{42}O_7Na^+$: 681.28225; found: 681.28228.

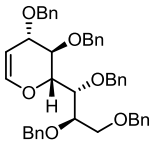
2,3,5,6,7 Penta-*O*-benzyl-D-*glycero*-D-*galacto*-heptofuranose (S1). DIBAL-H (27.6 mL, 27.6 mmol, 1 M in CH_2Cl_2) was added dropwise to a solution of **6** (14.0 g, 21.25 mmol) in CH_2Cl_2 (210 mL) at –78 °C. After stirring at –78 °C for 1 h, the mixture was warmed to –45 °C over 2 h and the reaction was quenched with methanol and sat. aq. Na/K tartrate. After warming to room temperature the mixture was extracted with *t*BuOMe (3 x). The combined organic layers were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 5:1) afforded the title compound as a yellow oil (11.94 g, 85%). $[a]_D^{20}$: –5.0 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 – 7.14 (m, 25H), 5.40 (d, *J* = 5.1 Hz, 0.5 H), 5.29 (dd, *J* = 11.6, 4.3 H, 0.5H), 4.72 – 4.25 (m, 11 H), 4.10 – 3.93 (m, 3H), 3.83 – 3.74 (m, 2H), 3.74 – 3.66 (m, 1H), 2.62 (d, *J* = 4.5 Hz, 0.5 H), 2.62 (bs, 0.5 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 139.2, 139.1, 139.0, 138.9, 138.8, 138.4 (2 C), 138.2, 138.1, 137.5, 129.2, 128.91, 128.85, 128.73, 128.66, 128.64, 128.56, 128.47, 128.41, 128.36, 128.31, 128.26, 128.21, 128.17, 128.14, 128.01, 127.98, 127.88, 127.85, 101.2, 96.5, 88.5, 85.4, 83.4, 82.5, 82.3, 81.6, 79.5, 79.3, 78.8, 77.98, 77.95,

75.2, 74.7, 73.7, 73.6, 72.8, 72.7, 72.4, 72.19, 72.15, 72.0, 70.0, 68.9 ppm; IR (film): $\tilde{\nu}$ = 3426, 3062, 3029, 2867, 1495, 1495, 1453, 1208, 1091, 1028 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{42}H_{44}O_7Na^+$: 683.29758; found: 283.29792.

1-Deoxy-3,4,6,7,8-penta-*O*-benzyl-D-*glycero*-D-*galacto*-oct-1-ynitol (7). *n*BuLi (1.6 M in hexane, 30.0 mL, 48.0 mmol) was added dropwise to a solution of *i*Pr_2NH (8.8 mL, 62.8 mmol) in THF (44 mL) at 0 °C. The resulting mixture was stirred for 15 min at 0 °C and then cooled to –78 °C. Diazomethyl)trimethylsilane (15.3 mL, 30.6 mmol, 2 M in hexane) was added dropwise and stirring was continued for 1 h at –78 °C. Next, a solution of **S1** (6.0 g, 9.1 mmol) in THF (44 mL) was added dropwise and the resulting mixture was warmed to room temperature over 18 h. The reaction was quenched with sat. aq. NH_4Cl and the aqueous phase extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 10:1) to give the title compound as a yellow oil (3.9 g, 65%). $[a]_D^{20}$: +1.5 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.14 (m, 25H), 4.90 (d, *J* = 11.4 Hz, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 14.6 Hz, 1H), 4.54 – 4.45 (m, 5H), 4.41 (d, *J* = 11.4 Hz, 1H), 4.31 (d, *J* = 11.6 Hz, 1H), 4.11 (dd, *J* = 8.1, 5.8 Hz, 1H), 3.92 – 3.86 (m, 2H), 3.77 – 3.68 (m, 2H), 3.66 – 3.61 (m, 1H), 3.14 (d, *J* = 5.6 Hz, 1H), 2.47 (d, *J* = 2.0 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.43 (2 C), 138.37, 138.2, 137.7, 128.5, 128.42, 128.38, 128.36, 128.2, 128.1, 127.9, 127.8, 127.70, 127.65, 81.4, 80.8, 79.3, 76.3, 76.0, 73.8, 73.5, 73.1, 72.8, 71.3, 69.87, 67.84, 68.2 ppm; IR (film): $\tilde{\nu}$ = 3500, 3287, 3087, 3062, 3030, 1496, 1453, 1208, 1088, 1068, 1027 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{43}H_{44}O_6Na^+$: 679.30262; found: 679.30301.



(2*R*,3*R*,4*S*)-3,4-Bis(benzyloxy)-2-((1*R*,2*R*)-1,2,3-tris(benzyloxy)propyl)-3,4-dihydro-2*H*-pyran (9). $W(CO)_6$ (42 mg, 0.12 mmol) was added to a degassed (pump and freeze) solution of **7** (500 mg, 0.76 mmol) and DABCO (dried by sublimation) in THF (4 mL) at room temperature and the resulting mixture was irradiated without cooling using UV-A lamps, causing gentle reflux. After 4 h the mixture was concentrated and the residue was purified by flash chromatography (SiO_2, hexanes:EtOAc, 10:1) to afford the title compound (342 mg, 68%). $[a]_D^{20}$: –13.4 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.17 (m, 25H), 6.37 (dd, *J* = 6.1, 1.3 Hz, 1H), 5.03 (d, *J* = 12.6, Hz, 1H), 4.88 (dd, *J* = 6.0, 2.3 Hz, 1H), 4.66 (t, *J* = 11.1 Hz, 2H), 4.61 – 4.49 (m, 7H), 4.39 (dt, *J* = 6.6, 1.8 Hz, 1H), 4.28 – 4.19 (m, 2H), 4.00 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.91 – 3.85 (m, 1H), 3.81 (dd, *J* = 10.7, 2.6 Hz, 1H), 3.66 (dd, *J* = 10.6, 4.3 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.3, 138.8, 138.6, 138.5, 138.4, 138.2, 128.6, 128.5, 128.4, 128.2, 128.1, 127.90, 127.88, 127.7, 127.5, 127.4, 99.9, 78.2, 77.3, 76.6, 75.5, 74.5, 74.0, 73.4, 72.7 (2 C), 70.3, 69.3 ppm; IR (film): $\tilde{\nu}$ =

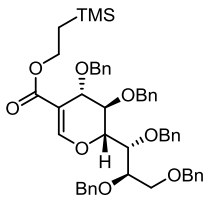


3062, 3029, 2963, 1648, 1496, 1553, 1361, 1330, 1208, 1090, 1027 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{43}H_{44}O_6Na^+$: 679.30260; found: 679.30301.

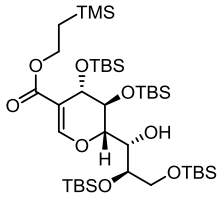
(2*R*,3*R*,4*S*)-3,4-Bis(benzyloxy)-2-((1*R*,2*R*)-1,2,3-tris(benzyloxy)propyl)-3,4-dihydro-2*H*-pyran-5-carbaldehyde (10). $POCl_3$ (4.00 mL, 42.91 mmol) was added dropwise over 1.5 h to a solution of **9** (1.40 g, 2.13 mmol) in DMF (4.5 mL) at 0 °C. The mixture was stirred for 24 h while warming slowly to room temperature. For work up, the reaction was quenched with sat. aq. $NaHCO_3$ and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 5:1) afforded the title compound as a yellow oil (950 mg, 65%). $[a]_D^{20}$: –24.7 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (s, 1H), 7.34 – 7.20 (m, 20H), 7.17 (s, 1H), 7.15 – 7.07 (m, 5H), 4.79 – 4.72 (m, 2H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.61 (d, *J* = 11.1 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.39 (dd, *J* = 2.9, 1.7 Hz, 1H), 4.32 – 4.19 (m, 5H), 3.97 (t, *J* = 2.6 Hz, 1H), 3.89 – 3.81 (m, 2H), 3.67 – 3.58 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.6, 165.0, 138.6, 138.5, 138.1, 137.9, 137.7, 128.5, 128.4, 128.3, 128.1, 128.02, 127.96 127.7, 127.7, 127.6, 127.5, 127.3, 118.1, 80.4, 78.4, 76.5, 75.2, 73.7, 73.2, 71.9, 71.8, 71.5, 68.8, 67.0 ppm; IR (film): $\tilde{\nu}$ 3063, 3030, 2866, 1672, 1624, 1454, 1206, 1090, 1072, 1028 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{44}H_{44}O_7Na^+$: 707.29789; found: 707.29792.

(2*R*,3*R*,4*S*)-3,4-Bis(benzyloxy)-2-((1*R*,2*R*)-1,2,3-tris(benzyloxy)propyl)-3,4-dihydro-2*H*-pyran-5-carboxylic acid (S2). NaH_2PO_4 (631 mg, 5.26 mmol) followed by H_2O_2 (0.9 mL, 9.26 mmol, 35% in water) were added to a solution of **10** (900 mg, 1.31 mmol) in *t*BuOH/CH_3CN/H_2O (2:2:1, 6.75 mL) at 0 °C. The mixture was stirred for 5 min before $NaClO_2$ (1.22 g, 10.79 mmol, 80%) was added and stirring was continued for 16 h at room temperature. The mixture was diluted with water and the aqueous phase was extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 3:1) afforded the title compound as a colorless oil (710 mg, 77%). $[a]_D^{20}$: –15.8 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (s, 1H), 7.40 – 7.01 (m, 25H), 4.80 – 4.66 (m, 3H), 4.66 – 4.56 (m, 2H), 4.52 – 4.42 (m, 2H), 4.39 – 4.14 (m, 6H), 3.99 – 3.94 (m, 1H), 3.90 – 3.79 (m, 2H), 3.63 (dd, *J* = 8.7, 3.7 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 158.1, 138.8, 138.7, 138.2, 138.1, 137.9, 128.64, 128.56, 128.55, 128.51, 128.48, 128.4, 128.3, 128.2, 128.12, 128.11, 128.0, 127.94, 127.85, 127.7, 127.4, 127.3, 105.0, 79.0, 78.6, 76.7, 75.5, 73.7, 72.9, 71.9, 71.8, 71.3, 69.1 (2 C) ppm; IR (film): $\tilde{\nu}$ = 3063, 3030, 2970, 1676, 1625, 1454, 1287, 1197, 1090, 1072, 1028 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{44}H_{44}O_8Na^+$: 723.29304; found: 723.29284.

2-(Trimethylsilyl)ethyl (2*R*,3*R*,4*S*)-3,4-bis(benzyloxy)-2-((1*R*,2*R*)-1,2,3-tris(benzyloxy)propyl)-3,4-dihydro-2*H*-pyran-5-carboxylate (11). DEAD (0.55 mL, 3.02 mmol) was added dropwise over 1 h to a solution of **S2** (700 mg, 1.00 mmol), 2-TMS-ethanol (0.43 mL, 3.00 mmol) and PPh_3 (945 mg, 3.60 mmol) in THF (5.00 mL) at 0 °C. The resulting mixture was stirred for 16 h while warming to room temperature, before the reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 20:1 to 10:1) afforded the title compound as a colorless oil (639 mg, 80%). $[a]_D^{20}$: −2.1 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 1H), 7.41 – 7.21 (m, 21H), 7.20 – 7.10 (m, 4H), 4.79 – 4.59 (m, 5H), 4.53 – 4.44 (m, 2H), 4.41 – 4.37 (m, 1H), 4.34 – 4.22 (m, 7H), 3.97 (t, *J* = 2.6 Hz, 1H), 3.91 – 3.86 (m, 1H), 3.86 – 3.79 (m, 1H), 3.65 (dd, *J* = 9.1, 4.3 Hz, 1H), 1.10 – 1.01 (m, 2H), 0.09 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.6, 155.7, 138.9, 138.7, 138.3, 138.1, 138.0, 128.6, 128.53, 128.47, 128.4, 128.31, 128.25, 128.10, 128.06, 127.93, 127.89, 127.8, 127.66, 127.57, 127.4, 127.2, 106.2, 78.6, 76.8, 75.5, 73.7, 73.0, 72.1, 71.7, 71.3, 69.5, 69.1, 62.4 (2 C), 17.6, −1.3 ppm; IR (film): $\tilde{\nu}$ = 3063, 3030, 2951, 1700, 1631, 1496, 1454, 1280, 1250, 1196, 1071 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{49}H_{56}O_8SiNa^+$: 823.36437; found: 823.36369.



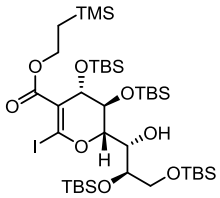
2-(Trimethylsilyl)ethyl (2*S*,3*S*,4*S*)-2-((1*S*,2*R*)-2,3-bis((tert-butyldimethylsilyl)oxy)-1-hydroxypropyl)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-3,4-dihydro-2*H*-pyran-5-carboxylate (12). $Pd(OH)_2$/C (62 mg, 20% loading) was added to a solution of **11** (620 mg, 0.77 mmol) in CH_3OH (3.7 mL) at room temperature. The suspension was purged with hydrogen and stirred for 5 h under hydrogen atmosphere (1 atm). The suspension was filtered through a plug of Celite®, which was rinsed with CH_3OH. The combined filtrates were concentrated and the residue was dried under high vacuum.



Pyridine (1.9 mL, 22.9 mmol) and TBSOTf (2.8 mL, 11.95 mmol) were added at 0 °C to a solution of the crude product in CH_2Cl_2 (1.9 mL). After stirring for 16 h at room temperature, the reaction was quenched with water and the mixture extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 1:0 to 100:1) afforded the title compound as a colorless oil (593 mg, 95%). $[a]_D^{20}$: −13.8 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1H), 4.70 (d, *J* = 1.0 Hz, 1H), 4.60 (t, *J* = 1.2 Hz, 1H), 4.42 (t, *J* = 2.1 Hz, 1H), ppm. 4.27 – 4.11 (m, 2H), 3.87 (dd, *J* = 2.4, 1.4 Hz, 1H), 3.80 (dd, *J* = 10.4, 3.0 Hz, 1H), 3.78 – 3.68 (m, 2H), 1.02 – 0.96 (m, 2H), 0.90 (s, 9H), 0.89 (s, 9H), 0.87 (s, 9H), 0.84 (s, 9H), 0.27 (s, 3H), 0.17 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H), 0.10 – 0.08 (m, 6H), 0.06 – 0.03 m, 12H), 0.03 (s, 3H) ppm; ^{13}C NMR

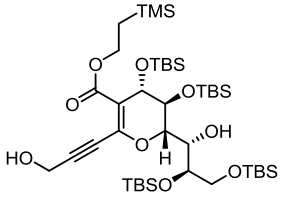
(101 MHz, $CDCl_3$): δ = 167.6, 158.2, 104.7, 77.6, 72.7, 71.8, 71.1, 64.3, 62.0, 26.2, 26.1, 25.9, 25.7, 18.6, 18.3, 18.2, 18.0, 17.6, -1.3, -4.0, -4.4, -4.6, -4.78, -4.78, -4.83 ppm; IR (film): $\tilde{\nu}$ = 3397, 2953, 2929, 2894, 2858, 1701, 1635, 1472, 1405, 1362, 1251, 1199, 1071 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{38}H_{82}O_8Si_5Na^+$: 829.47537; found: 829.47483.

2-(Trimethylsilyl)ethyl (2*S*,3S,4*S*)-2-((1*S*,2*R*)-2,3-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxypropyl)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-6-iodo-3,4-dihydro-2*H*-pyran-5-carboxylate (13). *n*BuLi (1.6 M



in hexanes, 4.1 mL, 6.56 mmol) was added dropwise to a solution of *i*Pr_2NH (1.4 mL, 9.99 mmol) in THF (6.3 mL) at 0 °C and the resulting mixture was stirred for 15 min. The solution was cooled to –78 °C and a solution of **12** (450 mg, 0.56 mmol) in THF (6.3 mL) was added dropwise. The mixture was stirred for 1.5 h at –78 °C before a solution of iodine (1.85 g, 7.29 mmol) in THF (6.3 mL) was added dropwise. Stirring was continued for 30 min at –78 °C before the reaction was quenched with sat. aq. $Na_2S_2O_3$. The mixture was extracted with *t*BuOMe, the combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 60:1) afforded the title compound as a colorless oil (370 mg, 71%). $[a]_D^{20}$: –19.1 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.67 – 4.64 (m, 1H), 4.64 – 4.61 (m, 1H), 4.60 (t, *J* = 2.2 Hz, 1H), 4.39 – 4.30 (m, 1H), 4.15 – 4.06 (m, 1H), 3.93 (dd, *J* = 2.3, 1.2 Hz, 1H), 3.84 (dd, *J* = 10.5, 2.7 Hz, 1H), 3.74 – 3.69 (m, 2H), 1.10 – 1.03 (m, 2H), 0.89 (s, 9H), 0.88 (s, 9H), 0.86 (s, 9H), 0.85 (s, 9H), 0.22 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H), 0.04 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.3, 123.8, 110.2, 83.0, 72.9, 71.1, 70.7, 66.5, 64.2, 63.0, 26.2, 26.1, 25.8, 25.7, 18.6, 18.3, 18.1, 18.0, 17.7, -1.4, -4.1, -4.4, -4.7 (3 C), -4.8, -5.2, -5.3 ppm; IR (film): $\tilde{\nu}$ = 3395, 2954, 2929, 2857, 1693, 1579, 1471, 1252, 1123, 1067 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{38}H_{81}O_8Si_5INa^+$: 955.37258; found: 955.37148.

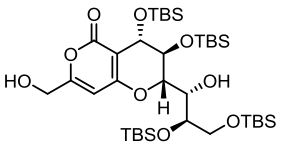
2-(Trimethylsilyl)ethyl (2*S*,3*S*,4*S*)-2-((1*S*,2*R*)-2,3-bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxypropyl)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-6-(3-hydroxyprop-1-yn-1-yl)-3,4-dihydro-2*H*-pyran-5-carboxylate (14). $Pd(PPh_3)_2Cl_2$ (34 mg, 0.05 mmol) and CuI (17 mg, 0.09 mmol) followed by



propargyl alcohol (150 µL, 2.6 mmol) were added to a degassed (pump and freeze, 3 cycles) solution of **13** (404 mg, 0.43 mmol) in NEt_3 (4.1 mL). The mixture was stirred for 18 h before the reaction was quenched with water. The aqueous phase was extracted with *t*BuOMe, and the combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the residue by flash chromatography (SiO_2, hexanes:EtOAc, 10:1) afforded the title compound as a colorless oil (318 mg, 85%). $[a]_D^{20}$: –34.6 (c = 1, $CHCl_3$);

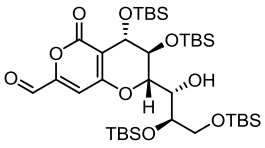
^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.62 – 4.56 (m, 2H), 4.51 (s, 1H), 4.46 (d, *J* = 6.1 Hz, 2H), 4.38 – 4.28 (m, 1H), 4.17 – 4.07 (m, 1H), 3.87 (t, *J* = 2.0 Hz, 1H), 3.82 (dd, *J* = 10.9, 2.3 Hz, 1H), 3.77 – 3.69 (m, 3H), 1.78 (bt, *J* = 6.1 Hz, 1H), 1.08 – 1.00 (m, 2H), 0.90 (s, 9H), 0.89 (s, 9H), 0.86 (s, 9H), 0.85 (s, 9H), 0.24 (s, 3H), 0.14 (s, 3H), 0.124 (s, 3H), 0.119 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H), 0.04 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 147.3, 108.8, 93.1, 80.9, 78.0, 72.8, 71.2, 71.1, 65.8, 64.2, 62.7, 51.8, 26.21, 26.15, 25.8, 25.7, 18.6, 18.3, 18.2, 18.0, 17.7, -1.4, -4.0, -4.4, -4.6, -4.65, -4.67, -4.72, -5.25, -5.32 ppm; IR (film): $\tilde{\nu}$ = 3414, 2954, 2930, 2894, 2858, 1689, 1600, 1472, 1390, 1253, 1113, 1072 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{41}H_{84}O_9Si_5Na^+$: 883.48639; found: 883.48540.

(2*S*,3*S*,4*S*)-2-((1*S*,2*R*)-2,3-Bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxypropyl)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-7-(hydroxymethyl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one (15).



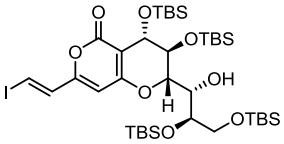
SPhosAuNTf$_2$[10] (2.3 mg, 0.003 mmol) was added to a solution of **14** (220 mg, 0.26 mmol) in CH_3NO_2 (2.6 mL) and the resulting mixture was stirred for 18 h at room temperature. The reaction was quenched with sat. aq. NH_4Cl and the mixture was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexane:EtOAc, 5:1) afforded the title compound as a white foam (160 mg, 82%). $[\alpha]_D^{20}$: –45.4 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.12 (s, 1H), 4.84 (s, 1H), 4.75 (t, *J* = 1.3 Hz, 1H), 4.50 (t, *J* = 1.9 Hz, 1H), 4.38 (t, *J* = 3.8 Hz, 1H), 3.95 (dd, *J* = 2.5, 1.5 Hz, 1H), 3.84 (dd, *J* = 8.7, 1.4 Hz, 1H), 3.79 (dd, *J* = 10.5, 3.2 Hz, 1H), 3.75 – 3.67 (m, 2H), 2.45 (bs, 1H), 0.91 (s, 9H), 0.88 (s, 9H), 0.88 (s, 9H), 0.82 (s, 9H), 0.31 (s, 3H), 0.24 (s, 3H), 0.13 (s, 6H), 0.10 (s, 3H), 0.09 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.4, 164.0, 163.4, 99.0, 97.9, 78.4, 72.6, 71.7, 70.8, 64.1, 64.0, 61.2, 26.2, 26.1, 25.9, 25.7, 18.6, 18.3, 18.2, 18.0, -4.0, -4.4, -4.7, -4.8 (2 C), -5.0, -5.3, -5.4 ppm; IR (film): $\tilde{\nu}$ = 3400, 2954, 2929, 2888, 2857, 1721, 1696, 1586, 1472, 1434, 1253, 1111, 1094 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{36}H_{72}O_9Si_4Na^+$: 783.41499; found: 783.41457.

(2*S*,3*S*,4*S*)-2-((1*S*,2*R*)-2,3-Bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxypropyl)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-5-oxo-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-7-carbaldehyde (S3). Dess-Martin periodinane (7 mg, 0.017 mmol) was added in one portion to a solution of **15** (10 mg, 0.013 mmol) in THF (0.1 mL) and the resulting mixture was stirred for 1 h. The reaction was quenched with sat. aq. $Na_2S_2O_3$ and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 10:1) afforded the title compound



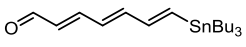
(9 mg, 90%) as a white foam. $[\alpha]_D^{20}$: –75.6 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.53 (s, 1H), 6.72 (s, 1H), 4.82 (t, *J* = 1.5 Hz, 1H), 4.63 (d, *J* = 1.8 Hz, 1H), 4.52 (t, *J* = 1.9 Hz, 1H), 3.98 (dd, *J* = 2.3, 1.5 Hz, 1H), 3.86 (dd, *J* = 8.7, 1.7 Hz, 1H), 3.79 (dd, *J* = 10.6, 3.3 Hz, 1H), 3.75 – 3.67 (m, 2H), 0.92 (s, 9H), 0.89 (s, 18H), 0.82 (s, 9H), 0.33 (s, 3H), 0.25 (s, 3H), 0.14 (s, 6H), 0.11 (s, 3H), 0.10 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.5, 164.3, 161.8, 153.5, 108.4, 104.8, 79.0, 72.6, 71.5, 70.7, 64.0, 63.9, 26.2, 26.1, 25.9, 25.6, 18.6, 18.3, 18.2, 17.9, -3.9, -4.4, -4.7 (2 C), -4.8, -4.9, -5.3, -5.4 ppm; IR (film): $\tilde{\nu}$ = 3404, 2955, 2930, 2858, 1715, 1643, 1583, 1434, 1389, 1362, 1255, 1111, 1067 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{36}H_{70}O_9Si_4Na^+$: 781.39864; found: 781.39892.

(2*S*,3*S*,4*S*)-2-((1*S*,2*R*)-2,3-Bis((*tert*-butyldimethylsilyl)oxy)-1-hydroxypropyl)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-7-((*E*)-2-iodovinyl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one (16). A solution



of CHI_3 (52 mg, 0.13 mmol) in dioxane (0.7 mL) was added dropwise to a suspension of $CrCl_2$ (50 mg, 0.41 mmol) and aldehyde **S3** (50 mg, 0.066 mmol) in THF (0.7 mL) at 0 °C. The resulting mixture was stirred for 1.5 h at 0 °C, the reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 50:1), affording the title compound as a colorless oil (33 mg, 57%). $[\alpha]_D^{20}$: –82.6 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 14.7 Hz, 1H), 6.94 (d, *J* = 14.7 Hz, 1H), 5.84 (s, 1H), 4.77 – 4.72 (m, 2H), 4.48 (t, *J* = 2.0 Hz, 1H), 3.93 (dd, *J* = 2.3, 1.5 Hz, 1H), 3.82 (dd, *J* = 8.9, 1.8 Hz, 1H), 3.81 – 3.67 (m, 3H), 0.91 (s, 9H), 0.88 (s, 9H), 0.88 (s, 9H), 0.82 (s, 9H), 0.31 (s, 3H), 0.24 (s, 3H), 0.13 (s, 6H), 0.10 (s, 3H), 0.09 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.7, 163.1, 157.1, 136.0, 101.2, 99.5, 78.3, 78.6, 72.7, 71.7, 70.8, 64.1, 64.0, 26.2, 26.1, 25.9, 25.7, 18.6, 18.3, 18.2, 18.0, -3.9, -4.4, -4.6, -4.8 (2C), -5.0, -5.3, -5.4 ppm; IR (film): $\tilde{\nu}$ = 3398, 2954, 2929, 2895, 2858, 1726, 1642, 1597, 1471, 1426, 1254, 1145, 1112 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{37}H_{71}O_8Si_4INa^+$: 905.31739; found: 905.31630.

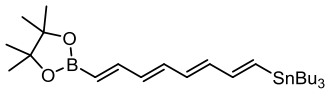
(2*E*,4*E*,6*E*)-7-(Tributylstannyl)hepta-2,4,6-trienal (S4). *This reaction was performed in the dark*. A



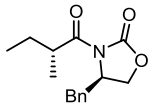
solution of SO_3/pyridine (556 mg, 3.49 mmol) in DMSO (2.60 mL) was added dropwise to a solution of (2*E*,4*E*,6*E*)-7-(tributylstannyl)hepta-2,4,6-trien-1-ol (**24**)[2] (465 mg, 1.16 mmol) and NEt_3 (0.82 mL, 5.88 mmol) in CH_2Cl_2 (6.5 mL) at 0 °C. The mixture was stirred for 3 h before it was concentrated and the residue was purified by flash chromatography (SiO_2, hexanes:*t*BuOMe, 25:1 + 2.5% NEt_3) to give the title compound as an orange-red oil (356 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.57 (d, *J* = 8.1 Hz, 1H), 7.14 (dd, *J* = 15.4, 11.1 Hz, 1H), 6.80 – 6.54 (m, 3H), 6.39 (dd, *J* = 14.1, 11.1 Hz, 1H), 6.18 (dd, *J* = 15.2, 8.1 Hz, 1H), 1.56 – 1.45 (m, 6H), 1.36 – 1.26 (m, 6H), 0.97 – 0.86 (m, 15H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.8, 152.6, 145.6, 145.3,

144.9, 131.8, 128.6, 29.2, 27.4, 13.9, 9.8 ppm; IR (film): $\tilde{\nu}$ = 2956, 2925, 1682, 1617, 1463, 1376, 1290, 1173, 1122, 1012 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{19}H_{34}OSnNa^+$: 421.15228; found: 421.15231.

Tributyl((1*E*,3*E*,5*E*,7*E*)-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,3,5,7-tetraen-1-yl)-stannane (35). *This reaction was carried out in the dark*. *n*BuLi (1.6 M in hexane, 2.31 mL, 3.70 mmol) was added dropwise to a solution of 2,2-6,6-tetramethylpiperidine (0.63 mL, 3.73 mmol) in THF (1.3 mL) at 0 °C and the resulting mixture was stirred for 30 min. A solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (**38**) (991 mg, 3.70 mmol) in THF (2.6 mL) was added dropwise and the resulting mixture was stirred for 10 min at 0 °C before it was cooled to −78 °C. A solution of **S4** (367 mg, 0.924 mmol) in THF (1.3 mL) was added dropwise. The suspension was stirred for 6 h at −78 °C, the reaction was quenched with sat. aq. NH_4Cl and the mixture was extracted with Et_2O. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes + 2.5% NEt_3) afforded the title compound as an orange oil (405 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (dd, *J* = 17.6, 10.0 Hz, 1H), 6.59 (dd, *J* = 18.5, 9.5 Hz, 1H), 6.44 – 6.16 (m, 5H), 5.55 (d, *J* = 17.7 Hz, 1H), 1.55 – 1.43 (m, 6H), 1.35 – 1.26 (m, 6H), 1.27 (s, 12H), 0.93 – 0.86 (m, 15H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.8, 146.8, 138.0, 137.5, 136.8, 134.9, 131.4, 120.7, 83.3, 29.2, 27.4, 24.9, 13.9, 9.7 ppm; IR (film): $\tilde{\nu}$ = 2956, 2925, 2852, 1614, 1582, 1541, 1387, 1358, 1322, 1269, 1144, 1010 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{26}H_{47}O_2BSn^+$: 522.26922; found: 522.26904.



(*R*)-4-Benzyl-3-((*R*)-2-methylbutanoyl)oxazolidin-2-one (S5). NaHMDS (42.8 mL, 42.8 mmol, 1 M in THF) was added dropwise to a solution of (*R*)-4-benzyl-3-butyryloxazolidin-2-one[6] (6.22 g, 25.15 mmol) in THF (36.7 mL) at −78 °C. The mixture was stirred for 30 min before CH_3I (4.7 mL, 75.46 mmol) was added dropwise. Stirring was continued for 4 h at −78 °C before the reaction was quenched with brine and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4, the drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexanes:EtOAc, 10:1), affording the title compound as a colorless oil (5.43 g, 83%). $[\alpha]_D^{20}$: −77.5 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.26 (m, 3H), 7.24 – 7.19 (m, 2H), 4.73 – 4.64 (m, 1H), 4.24 – 4.14 (m, 2H), 3.64 (q, *J* = 6.8 Hz, 1H), 3.27 (dd, *J* = 13.3, 3.2 Hz, 1H), 2.77 (dd, *J* = 13.4, 9.6 Hz, 1H), 1.84 – 1.70 (m, 1H), 1.54 – 1.41 (m, 1H), 1.22 (d, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.3, 153.2, 135.5, 129.6, 129.1, 127.5, 66.1, 55.5, 39.3, 38.0, 26.5, 17.0, 11.8 ppm; IR (film): $\tilde{\nu}$ = 2967, 2877, 1774, 1693, 1455, 1383, 1234, 1205, 1097, 1015 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{15}H_{19}O_3NNa^+$: 284.12571; found: 284.12551.



(*R*)-2-Methylbutan-1-ol (S6). $LiBH_4$ (11.41 g, 31.27 mmol) was added to a solution of **S5** (5.97 g, 22.85 mmol) in Et_2O (38.4 mL) and CH_3OH (3.2 mL) at –20 °C. The mixture was stirred for 2 h at 0 °C and for another 2 h at room temperature before the reaction was quenched with NaOH (1 M). The mixture was extracted with Et_2O, the combined extracts were dried over Na_2SO_4, the drying agent was filtered off and the solution was concentrated. The crude product was purified by flash chromatography (SiO_2, pentane:Et_2O 3:1), affording the title compound as a colorless oil (1.93 g, 96%, ee = 89%). $[\alpha]_D^{20}$: +5.7 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.51 (dd, *J* = 10.4, 5.8 Hz, 1H), 3.42 (dd, *J* = 10.5, 6.4 Hz, 1H), 1.59 – 1.49 (m, 1H), 1.49 – 1.40 (m, 1H), 1.39 – 12.7 (bs, 1H), 1.20 – 1.07 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 68.2, 37.5, 25.9, 16.3, 11.5 ppm; IR (film): $\tilde{\nu}$ = 3330, 2960, 2920, 2876, 1462, 1380, 1043, 1015 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_5H_{12}ONa^+$: 88.08882; found: 88.08885.

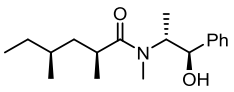
(*R*)-1-Iodo-2-methylbutane (*ent*-21). Iodine (10.54 g, 41.5 mmol) was added to a solution of imidazole (2.83 g, 41.5 mmol) and PPh_3 (10.89 g, 41.52 mmol) in CH_2Cl_2 (66 mL) at 0 °C and the resulting mixture was stirred for 10 min. A solution of **S6** (3.05 g, 34.6 mmol) in CH_2Cl_2 (33 mL) was added dropwise and stirring was continued for 3 h. The mixture was diluted with pentane (100 mL), the suspension was vigorously stirred for 5 min and filtered through a plug of silica. The filtrate was concentrated cautiously. The residue was again diluted with pentane and filtered through a plug of silica, affording the title compound as a colorless oil (5.07 g, 74%). $[\alpha]_D^{20}$: –9.4 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.23 (dd, *J* = 9.6, 4.6 Hz, 1H), 3.17 (dd, *J* = 9.6, 5.8 Hz, 1H), 1.47 – 1.34 (m, 2H), 1.32 – 1.22 (m, 1H), 0.98 (d, *J* = 6.3 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 36.5, 29.3, 20.3, 17.7, 11.5 ppm. IR (film): $\tilde{\nu}$ 2960, 29263, 2874, 1455, 1378, 1191 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_5H_{11}I$: 197.99055; found: 197.99039.

(2*R*,4*S*)-N-((1*S*,2*S*)-1-Hydroxy-1-phenylpropan-2-yl)-N,2,4-trimethylhexanamide (S7). *n*BuLi (1.6 M in hexane, 27.2 mL, 43.6 mmol) was added dropwise to a solution of *i*Pr_2NH (6.4 mL, 45.9 mmol) and LiCl (5.83 g, 42.4 mmol) in THF (15.5 mL) at –78 °C. The mixture was warmed to 0 °C, stirred for 15 min, and then re-cooled to –78 °C. A precooled (0 °C) solution of N-((1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl)-N-methylpropionamide[4] (5.1 g, 22.93 mmol) in THF (77.5 mL) was added dropwise and stirring was continued for 1 h at –78 °C, before the mixture was warmed to 0 °C. (*S*)-1-iodo-2-methylbutane[3] (2.2 g, 11.0 mmol) was added dropwise and stirring continued for 18 h at room temperature. The reaction was quenched with sat. aq. NH_4Cl, the aqueous phase was extracted with EtOAc, and the combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 3:2), affording the title compound as a colorless oil (2.35 g, 74%). $[\alpha]_D^{20}$: +76.3 (c = 1.04, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$, signals of the major conformer): δ = 7.41 – 7.22 (m, 5H), 4.62 (d, *J* = 7.6 Hz, 1H), 4.36 (bs, 1H), 2.84 (s, 3H), 2.72 – 2.60 (m, 1H), 1.49 – 1.19 (m, 5H), 1.18 – 1.09 (m, 1H), 1.15 (d, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.84 (t, *J* = 7.1 Hz, 3H), 0.82 (d, *J* = 6.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) of the major conformer: δ = 179.7, 142.8, 128.4, 127.6, 126.4, 76.7, 59.6, 40.8, 34.3, 33.3, 32.1, 29.8, 19.1, 17.1, 14.6, 11.4 ppm; IR (film): $\tilde{\nu}$ = 3370, 2961, 2931, 2874, 1615, 1453, 1408, 1376, 1112, 1084, 1049 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{29}O_2NNa^+$: 314.20905; found: 314.20922.

The analytical data of **(2*S*,4*R*)-N-((1*R*,2*R*)-1-hydroxy-1-phenylpropan-2-yl)-N,2,4-trimethylhexanamide (*ent*-S7)** are identical; $[a]_D^{20}$: –75.6 (c = 1, $CHCl_3$).

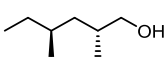
(2*S*,4*S*)-N-((1*R*,2*R*)-1-Hydroxy-1-phenylpropan-2-yl)-N,2,4-trimethylhexanamide (S8). Prepared



analogously using N-((1*R*,2*R*)-1-hydroxy-1-phenylpropan-2-yl)-N-methyl-propionamide[5] (1.5 g, 6.78 mmol), (*S*)-1-iodo-2-methylbutane[3] (644 mg, 3.25 mmol), *n*BuLi (1.6 M in hexane, 8.05 mL, 12.88 mmol), LiCl (1.72 g, 40.67 mmol), *i*Pr_2NH (1.95 mL, 13.90 mmol) in THF (28 mL). Yield: 750 mg, 79%. $[a]_D^{20}$: –60.7 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, signals of the major conformer): δ = 7.41 – 7.27 (m, 5H), 4.61 (d, *J* = 7.6 Hz, 1H), 4.38 (bs, 1H), 2.85 (s, 3H), 2.76 – 2.61 (m, 1H), 1.70 (ddd, J = 5.2, 8.5, 13.5 Hz, 1H), 1.46 – 1.19 (m, 3H), 1.14 (d, J = 7.1 Hz, 3H), 1.08 – 1.00 (m, 2H), 1.06 (d, J = 6.8 Hz, 3H), 0.86 (t, J = 7.5 Hz, 3H), 0.77 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) of the major conformer: δ = 179.4, 142.8, 128.4, 127.6, 126.4, 76.6, 59.5, 41.3, 34.3, 33.5, 32.1, 29.8, 19.3, 18.1, 14.6, 11.3 ppm; IR (film): $\tilde{\nu}$ = 3372, 2961, 2930, 2874, 1616, 1453, 1408, 1376, 1303, 1111, 1083, 1050 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{29}O_2NNa^+$: 314.20905; found: 314.20919.

The analytical data of **(2*R*,4*R*)-N-((1*S*,2*S*)-1-hydroxy-1-phenylpropan-2-yl)-N,2,4-trimethyl-hexanamide (*ent*-S8)** are identical; $[a]_D^{20}$: +63.2 (c = 1, $CHCl_3$).

(2*R*,4*S*)-2,4-Dimethylhexan-1-ol (2*R*,4*S*-22). *n*BuLi (1.6 M in hexane, 4.00 mL, 6.33 mmol) was added

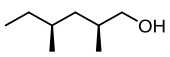


dropwise to a solution of *i*Pr_2NH (0.96 mL, 6.82 mmol) in THF (8 mL) at 0 °C. The mixture was stirred for 10 min before $BH_3{\cdot}NH_3$ (200 mg, 6.49 mmol) was added in one portion. Stirring was continued for 15 min at 0 °C and 15 min at ambient temperature. After re-cooling to 0 °C, a solution of **S7** (473 mg, 1.62 mmol) in THF (5 mL) was added dropwise and the mixture was stirred at room temperature for 3 h. The reaction was quenched cautiously at 0 °C with HCl (3 M) and extracted with Et_2O. The combined extracts were washed with HCl (3 M), NaOH (2 M) and brine, and then dried over Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. The crude product was purified by flash chromatography (SiO_2, hexane:EtOAc, 4:1), affording the title compound as a colorless oil (210 mg, 99%). $[a]_D^{20}$: +32.2 (c = 1, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 3.52 – 3.45 (m, 1H), 3.45 – 3.37 (m, 1H), 1.78 – 1.64 (m, 1H), 1.48 – 1.37 (m, 1H), 1.34 – 1.25 (m, 2H), 1.21 – 1.03 (m, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 69.3, 40.3, 33.3, 31.6, 30.6, 19.0, 16.4, 11.6 ppm; IR (film): $\tilde{\nu}$ = 3322, 2959, 2914, 2874, 1462, 1378, 1079, 1032 988 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_8H_{19}ONa^+$: 131.14359; found: 131.14347.

The analytical data of **(2*S*,4*R*)-2,4-dimethylhexan-1-ol (2*S*,4*R*-*22*)** are identical; $[a]_D^{20}$: +28.9 (c = 1.06, $CHCl_3$).

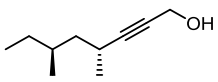
(2*S*,4*S*)-2,4-Dimethylhexan-1-ol (2*S*,4*S*-22). Prepared analogously using **S8** (200 mg, 0.69 mmol)



$BH_3{\cdot}NH_3$ (85 mg, 2.75 mmol) *n*BuLi (1.6 M in hexane, 1.7 mL, 2.68 mmol), *i*Pr_2NH (0.40 mL, 2.88 mmol) and THF (5 mL). Yield: 67 mg, 75%. $[a]_D^{20}$: –2.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 – 3.49 (m, 1H), 3.42 – 3.33 (m, 1H), 1.77 – 1.66 (m, 1H), 1.47 – 1.25 (m, 4H), 1.12 – 1.01 (m, 1H), 0.97 – 0.89 (m, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 68.5, 40.7, 33.2, 31.6, 29.1, 19.9, 17.4, 11.3 ppm; IR (film): $\tilde{\nu}$ = 3322, 2957, 2914, 2874, 1461, 1378, 1029 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_8H_{19}ONa^+$: 131.14359; found: 131.14367.

The analytical data of **(2*R*,4*R*)-2,4-dimethylhexan-1-ol ((2*R*,4*R*-22)** are identical; $[a]_D^{20}$: +3.6 (c = 1.16, $CHCl_3$).

(4*R*,6*S*)-4,6-Dimethyloct-2-yn-1-ol (4*R*,6*S*-23). DMSO (2.73 mL, 38.39 mmol) was added dropwise to



a solution of $(COCl)_2$ (1.85 mL, 21.50 mmol) in CH_2Cl_2 (30 mL) at –78 °C and the resulting mixture was stirred for 15 min. A solution of **4*R*,6*S*-22** (2.00 g, 15.35 mmol) in CH_2Cl_2 (35 mL) was added dropwise and stirring was continued for 30 min. NEt_3 (10.70 mL, 76.78 mmol) was added dropwise at –78 °C, the mixture was warmed to 0 °C and stirring was continued for 45 min. The reaction was quenched with sat. aq. NH_4Cl and the aqueous phase extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4, the drying agent was filtered off and the solvent was evaporated (bath temperature below 10 °C). The crude aldehyde was used without further purification.

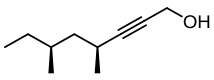
A solution of CBr_4 (9.32 g, 28.10 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of PPh_3 (14.54 g, 55.44 mmol) in CH_2Cl_2 (20 mL) at 0 °C and the resulting mixture was stirred for 15 min. A solution of the crude aldehyde in CH_2Cl_2 (20 mL) was added dropwise and stirring was continued for 15 min at 0 °C and for 2.5 h at ambient temperature. For work up, the mixture was poured onto Et_2O/hexanes (4:1, 100 mL), the biphasic mixture was stirred for 10 min and filtered through a pad of Florisil®. The filtrate was evaporated, the residue was dispersed in hexanes and the suspension

filtered through Florisil®. The filtrate was concentrated to give the crude dibromoolefin that was used without further purification.

*n*BuLi (1.6 M in hexane, 19.01 mL, 64.06 mmol) was added dropwise to a solution of the crude dibromoolefin in THF (29.4 mL) at –78 °C. The mixture was warmed to room temperature, stirred for 30 min and then re-cooled to –78 °C. *para*-Formaldehyde (2.17 g, 72.43 mmol) was added in one portion and stirring was continued for 18 h while warming to room temperature. The reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with CH_2Cl_2. The combined extracts were washed with brine and dried over Na_2SO_4. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, pentane:*t*BuOMe, 10:1) afforded the title compound as a colorless oil (1.27 g, 54%). $[a]_D^{20}$: –20.6 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.26 (dd, *J* = 6.1, 2.0 Hz, 2H), 2.48 (ht, *J* = 6.8, 1.9 Hz, 1H), 1.59 – 1.50 (m, 1H), 1.50 – 1.44 (m, 1H), 1.44 – 1.36 (m, 1H), 1.36 – 1.30 (m, 2H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.14 – 1.04 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 91.5, 78.2, 51.6, 44.1, 32.1, 28.8, 23.7, 21.1, 19.4, 11.2 ppm; IR (film): $\tilde{\nu}$ = 3317, 2962, 2917, 2874, 1455, 1377, 1333, 1172, 1075 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{10}H_{18}ONa^+$: 177.12498; found: 177.12499.

The analytical data of **(4*S*,6*R*)-4,6-dimethyloct-2-yn-1-ol (4*S*,6*R*-23)** are identical; $[a]_D^{20}$**:** +18.0 (c = 1.28, $CHCl_3$).

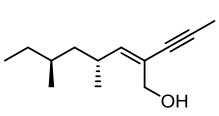
(4*S*,6*S*)-4,6-Dimethyloct-2-yn-1-ol (4*S*,6*S*-23). Prepared analogously (3.81 g, 51%). $[a]_D^{20}$: +38.0 (c =



1.24, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.25 (dd, *J* = 5.3, 1.8 Hz, 2H), 2.60 – 2.46 (m, 1H), 1.67 – 1.52 (m, 2H), 1.51 – 1.42 (m, 1H), 1.37 – 1.25 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.21 – 1.05 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 91.0, 78.5, 51.6, 44.1, 32.5, 30.1, 23.9, 21.8, 18.8, 11.4 ppm; IR (film): $\tilde{\nu}$ = 3325, 2962, 2925, 2874, 1460, 1378, 1328, 1226, 1171, 1076 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{10}H_{18}ONa^+$: 177.12498; found: 177.12516.

The analytical data of **(4*R*,6*R*)-4,6-dimethyloct-2-yn-1-ol (4*R*,6*R*-23)** are identical; $[a]_D^{20}$: **–**32.0 (c = 1.1, $CHCl_3$).

(4*R*,6*S*,*Z*)-4,6-Dimethyl-2-(prop-1-yn-1-yl)oct-2-en-1-ol (4*R*,6*S*-26). Ethyl-3,3,3-trifluoropyruvate

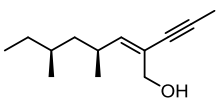


(0.93 mL, 7.02 mmol) was added dropwise to a solution of **4*R*,6*S*-23** (900 mg, 5.83 mmol) in THF (6.4 mL) and the resulting mixture was stirred for 30 min at room temperature before it was cooled to **–**78 °C. Thexylborane (7.50 mL, 7.00 mmol, 0.93 M in THF)[8] was added dropwise. The mixture was stirred for 10 min at **–**78 °C before

it was warmed to room temperature. Trimethylamine *N*-oxide (681 mg, 6.13 mmol) was added in one portion and stirring was continued for 30 min. Next, aq. KOH (14.6 mL, 43.8 mmol, 3 M in water) was added, followed by 1-iodo-1-propyne[7] (4.85 g, 29.22 mmol) and Pd(dppf)Cl_2 (477 mg, 0.58 mmol). The resulting mixture was heated to 70 °C for 1.5 h before it was allowed to cool to room temperature. The aqueous phase was extracted with *t*BuOMe and the combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 20:1) afforded the title compound as pale orange oil (645 mg, 57%). $[\alpha]_D^{20}$: –36.0 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.67 (d, *J* = 10.1 Hz, 1H), 4.23 – 4.06 (m, 2H), 2.63 – 2.44 (m, 1H), 1.97 (s, 3H), 1.71 t, *J* = 6.2 Hz, 1H), 1.39 – 1.18 (m, 3H), 1.12 – 1.00 (m, 2H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.87 – 0.79 (m, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.3, 121.2, 85.3, 79.1, 60.4, 44.4, 32.0, 30.4, 29.2, 20.9, 19.6, 11.3, 4.4 ppm; IR (film): $\tilde{\nu}$ = 3395, 2956, 2916, 2873, 1456, 1377, 1258, 1046, 992, 971 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{13}H_{22}ONa^+$: 217. 15628; found: 217.15627.

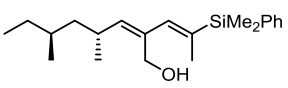
The analytical data of **(4*S*,6*R*,*Z*)-4,6-dimethyl-2-(prop-1-yn-1-yl)oct-2-en-1-ol (4*S*,6*R*-26)** are identical; $[\alpha]_D^{20}$**:** +45.5 (c = 1, $CHCl_3$).

(4*S*,6*S*,*Z*)-4,6-Dimethyl-2-(prop-1-yn-1-yl)oct-2-en-1-ol (4*S*,6*S*-26). Prepared analogously (597 mg, 57%). $[\alpha]_D^{20}$: +44.7 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.23 (d, *J* = 10.1 Hz, 1H), 4.16 (d, *J* = 5.6 Hz, 1H), 2.62 – 2.50 (m, 1H), 1.97 (s, 3H), 1.70 t, *J* = 5.9 Hz, 1H), 1.31 – 1.22 (m, 3H), 1.15 – 1.05 (m, 2H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H), 0.81 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.0, 121.7, 85.3, 79.2, 60.5, 44.6, 32.3, 30.6, 30.2, 21.8, 19.0, 11.4, 4.4 ppm; IR (film): $\tilde{\nu}$ = 3390, 2917, 2873, 1458, 1377, 1264, 1002 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{13}H_{22}ONa^+$: 217.15628; found: 217.15638.



The analytical data of **(4*R*,6*R*,*Z*)-4,6-dimethyl-2-(prop-1-yn-1-yl)oct-2-en-1-ol (4*R*,6*R*-26)** are identical; $[\alpha]_D^{20}$: –46.3 (c = 1, $CHCl_3$).

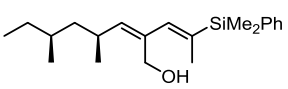
(4*R*,6*S*,*Z*)-2-((*E*)-2-(Dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-en-1-ol (4*R*,6*S*-27). $PhMe_2SiLi$ (3.30 mL, 3.30 mmol, 1 M in THF)[9] was added dropwise to a suspension of CuCN (127 mg, 1.42 mmol) in THF (1.10 mL) at –50 °C. The mixture was warmed to –10 °C, stirred for 45 min and then re-cooled to –50 °C. H_2O (72 µL, 4.00 mmol) was added, the solution was warmed to –10 °C, stirred for 30 min and re-cooled to –50 °C. A solution of **4*R*,6*S*-26** (110 mg, 0.57 mmol) in THF (1.10 mL) was added dropwise and the mixture stirred at –10 °C for 2 h before the reaction was quenched with sat. aq. NH_4Cl. The aqueous phase was extracted with *t*BuOMe, the combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude



product by flash chromatography (SiO_2, hexanes:EtOAc, 1:0 to 30:1) afforded the title compound as a colorless oil (165 mg, 88%). $[\alpha]_D^{20}$: –48.7 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.49 (m, 2H), 7.39 – 7.33 (m, 3H), 6.26 (t, *J* = 1.5 Hz, 1H), 5.28 (d, *J* = 9.8 Hz, 1H), 4.26 – 4.28 (m, 2H), 2.64 (dq, *J* = 9.8, 6.9 Hz, 1H), 1.86, (d, *J* = 1.8 Hz, 3H), 1.58 (bs, 1H), 1.42 – 1.33 (m, 2H), 1.31 – 1.25 (m, 1H), 1.13 – 1.06 (m, 2H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H), 0.38 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.9, 139.4, 138.4, 138.1, 134.3, 134.1, 129.1, 127.89, 127.88, 61.0, 45.0, 32.1, 30.2, 29.3, 21.5, 19.7, 16.7, 11.3, -3.3 ppm; IR (film): $\tilde{\nu}$ = 3344, 2957, 2925, 1597, 1460, 1427, 1376, 1247, 1111, 1016, cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{21}H_{34}OSiNa^+$: 353.22711; found: 353.22706

The analytical data of **(4*S*,6*R*,*Z*)-2-((*E*)-2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-en-1-ol (4*S*,6*R*-27)** are identical; $[\alpha]_D^{20}$: +38.7 (c = 1, $CHCl_3$).

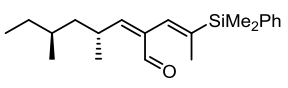
(4*S*,6*S*,*Z*)-2-((*E*)-2-(Dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-en-1-ol (4*S*,6*S*-27).



Prepared analoguously (107 mg, 90%). $[\alpha]_D^{20}$: +76.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.49 (m, 2H), 7.38 – 7.33 (m, 3H), 6.26 (t, *J* = 1.3 Hz, 1H), 5.22 (d, *J* = 10.1 Hz, 1H), 4.22 (s, 2H), 2.71 – 2.58 (m, 1H), 1.85 (d, *J* = 1.9 Hz, 3H), 1.58 – 1.53 (m, 1H), 1.32 – 1.24 (m, 2H), 1.14 – 1.09 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.95 – 0.88 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.84 (d, *J* = 6.0 Hz, 3H), 0.37 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.6, 139.4, 138.4, 138.1, 134.7, 134.2, 129.1, 127.9, 61.0, 44.9, 32.5, 30.4, 30.3, 22.5, 19.2, 16.8, 11.5, -3.3 ppm; IR (film): $\tilde{\nu}$ = 3355, 2957, 2925, 1459, 1427, 1377, 1247, 1111, 1015 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{21}H_{34}OSiNa^+$: 353.22711; found: 353.22713.

The analytical data of **(4*R*,6*R*,*Z*)-2-((*E*)-2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-en-1-ol (4*R*,6*R*-27)** are identical; $[\alpha]_D^{20}$: –43.9 (c = 1, $CHCl_3$).

(4*R*,6*S*,*Z*)-2-((*E*)-2-(Dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-enal (4*R*,6*S*-S9). Dess-

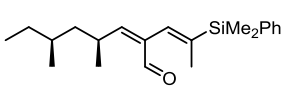


Martin periodinane (308 mg, 0.73 mmol) was added in one portion to a solution of **4*R*,6*S*-27** (160 mg, 0.48 mmol) in CH_2Cl_2 (4.8 mL) and the resulting mixture was stirred for 1.5 h before the reaction was quenched with sat. aq. $Na_2S_2O_3$. The aqueous phase was extracted with *t*BuOMe, the combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 50:1) afforded the title compound (155 mg, 98%). $[\alpha]_D^{20}$: –34.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.13 (s, 1H), 7.56 – 7.51 (m, 2H), 7.38 – 7.34 (m, 3H), 6.44 (t, *J* = 1.4 Hz, 1H), 6.32 (dd, *J* = 11.0, 0.9 Hz, 1H), 3.44 – 3.31 (m, 1H), 1.75 (d, J = 1.8 Hz, 3H), 1.46 – 1.32 (m, 3H), 1.27 – 1.08 (m, 2H), 1.09 (d, *J* = 6.3 Hz, 3H), 0.88 (d, *J* = 6.1 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H), 0.40 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.0, 158.2, 140.4,

138.0, 135.3, 134.2, 133.6, 129.1, 127.9, 44.6, 32.1, 29.4, 29.1, 21.4, 19.6, 16.9, 11.2, -3.4 ppm; IR (film): $\tilde{\nu}$ = 2960, 2928, 2874, 1682, 1603, 1457, 1376, 1428, 1248, 1111 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{21}H_{32}OSiNa^+$: 351. 21146; found: 351.21161.

The analytical data of **(4*S*,6*R*,*Z*)-2-((*E*)-2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-enal (4*S*,6*R*-S9)** are identical; $[\alpha]_D^{20}$**:** +32.2 (c = 0.97, $CHCl_3$).

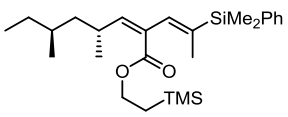
(4*S*,6*S*,*Z*)-2-((*E*)-2-(Dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-enal (4*S*,6*S*-S9).



Prepared analogously (55 mg, 92%). $[\alpha]_D^{20}$: +45.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.13 (s, 1H), 7.57 – 7.51 (m, 2H), 7.40 – 7.33 (m, 3H), 6.45 (dd, *J* = 1.6, 1.4 Hz, 1H), 6.27 (dd, *J* = 11.1, 1.0 Hz, 1H), 3.46 – 3.30 (m, 1H), 1.75 (d, *J* = 1.8 Hz, 3H), 1.43 – 1.14 (m, 5H), 1.12 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.40 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.0, 158.0, 140.4, 138.0, 135.8, 134.2, 133.6, 129.1, 127.9, 44.6, 32.6, 30.2, 29.5, 22.3, 19.1, 16.9, 11.4, -3.43, -3.45 ppm; IR (film): $\tilde{\nu}$ 2959, 2926, 2873, 1681, 1459, 1428, 1377, 1248, 1191, 1111 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{21}H_{32}OSiNa^+$: 351. 21146; found: 351.21153.

The analytical data of **(4*R*,6*R*,*Z*)-2-((*E*)-2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-enal (4*R*,6*R*-S9)** are identical; $[\alpha]_D^{20}$**:** –48.4 (c = 1, $CHCl_3$).

2-(Trimethylsilyl)ethyl (4*R*,6*S*,*Z*)-2-((*E*)-2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-enoate (4*R*,6*S*-28). NaH_2PO_4 (170 mg, 1.42 mmol) and H_2O_2 (0.26 mL, 2.68 mmol, 35% in water) were



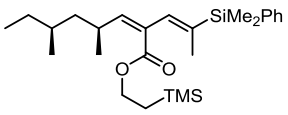
added to a solution of **4*R*,6*S*-S9** (155 mg, 0.47 mmol) in *t*BuOH/H_2O 1:1 (1.6 mL) at 0 °C and the resulting mixture was stirred for 5 min before $NaClO_2$ (256 mg, 2.26 mmol) was added. Stirring was continued for 16 h before the reaction was quenched with water and the aqueous phase was extracted with pentane. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off, the solution was concentrated and the residue used without further purification.

DEAD (0.31 mL, 1.65 mmol) was added dropwise to a solution of the crude acid, PPh_3 (495 mg, 1.89 mmol) and 2-(TMS)-ethanol (0.25 mL, 1.66 mmol) in THF (2.4 mL) at 0 °C within 15 min and the resulting mixture was stirred for 2 h at 0 °C. The reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes to hexanes:EtOAc, 200:1) afforded the title compound as a colorless oil (132 mg, 63%). $[\alpha]_D^{20}$: –18.4 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 – 7.46 (m, 2H), 7.39 – 7.20 (m, 3H), 6.33 (dd, *J* = 1.8, 1.3 Hz, 1H), 5.62 (dd, *J* = 10.2, 0.9 Hz,

1H), 4.29 – 4.20 (m, 2H), 3.06 – 2.89 (m, 1H), 1.72 (d, *J* = 1.8 Hz, 3H), 1.41 – 1.30 (m, 2H), 1.30 – 1.22 (m, 1H), 1.20 – 1.01 (m, 4H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.3 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.37 (s, 6H), 0.05 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.8, 149.1, 138.2, 137.5, 136.5, 134.2, 129.6, 129.1, 127.9, 44.5, 32.1, 31.5, 29.3, 20.7, 19.6, 17.5, 16.3, 11.3, -1.4, -3.4 ppm; IR (film): $\tilde{\nu}$ = 2956, 1717, 1428, 1249, 1203, 1167, 1111 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{26}H_{44}O_2Si_2Na^+$: 467.27721; found: 467.27751.

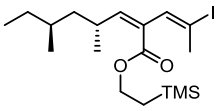
The analytical data of **2-(trimethylsilyl)ethyl (4*S*,6*R*,*Z*)-2-((*E*)-2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-enoate (4*S*,6*R*-28)** are identical; $[a]_D^{20}$: +19.5 (c = 1, $CHCl_3$).

2-(Trimethylsilyl)ethyl (4*S*,6*S*,*Z*)-2-((*E*)-2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-enoate (4*S*,6*S*-28). Prepared analogously (42 mg, 62%). $[a]_D^{20}$: +26.4 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.48 (m, 2H), 7.38 – 7.32 (m, 3H), 6.33 (d, *J* = 1.0 Hz, 1H), 5.57 (d, *J* = 10.4 Hz, 1H), 4.28 – 4.20 (m, 2H), 3.08 – 2.95 (m, 1H), 1.72 (d, *J* = 1.5 Hz, 3H), 1.35 – 1.24 (m, 4H), 1.20 – 1.05 (m, 3H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H), 0.83 (d, *J* = 7.3 Hz, 3H), 0.37 (s, 6H), 0.04 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.8, 148.8, 138.2, 137.5, 136.4, 134.2, 130.1, 129.1, 127.9, 62.9, 44.8, 32.6, 31.6, 30.2, 21.6, 19.2, 17.5, 16.3, 11.4, -1.4, -3.4 ppm; IR (film): $\tilde{\nu}$ = 2956, 2902, 1717, 1460, 1428, 1378, 1249, 1204, 1167, 1111 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{26}H_{44}O_2Si_2Na^+$: 467.27721; found: 467.27751.



The analytical data of **2-(trimethylsilyl)ethyl (4*R*,6*R*,*Z*)-2-((*E*)-2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)-4,6-dimethyloct-2-enoate (4*R*,6*R*-28)** are identical; $[a]_D^{20}$**:** –33.5 (c = 1, $CHCl_3$).

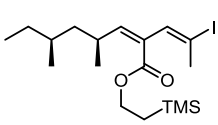
2-(Trimethylsilyl)ethyl (4*R*,6*S*,*Z*)-2-((*E*)-2-iodoprop-1-en-1-yl)-4,6-dimethyloct-2-enoate (4*R*,6*S*-29). NIS (83 mg, 0.37 mmol) was added in one portion to a solution of **4*R*,6*S*-28** (110 mg, 0.25 mmol) and 2,6-lutidine (43 µL, 0.37 mmol) in hexafluoroisopropanol (0.8 mL) at 0 °C and the resulting mixture was stirred for 2 min. The reaction was quenched with sat. aq. $Na_2S_2O_3$ and the aqueous phase extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes to hexanes:EtOAc, 200:1) afforded the title compound as a colorless oil (96 mg, 89%). $[a]_D^{20}$: –14.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (t, *J* = 1.5 Hz, 1H), 5.68 (dd, *J* = 10.1, 1.3 Hz, 1H), 4.27 – 4.20 (m, 2H), 3.23 – 3.12 (m, 1H), 2.45 (d, *J* = 1.8 Hz, 3H), 1.38 – 1.21 (m, 3H), 1.17 – 1.07 (m, 2H), 1.07 – 1.01 (m, 2H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 7.6 Hz, 3H), 0.83 (t, *J* = 8.3 Hz, 3H), 0.05 (s, 9H) ppm, ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 151.7, 138.5, 128.3, 98.1, 63.1, 44.3, 32.2, 31.4, 29.3, 29.0, 20.4, 19.5, 17.5, 11.3, -1.4 ppm; IR (film): $\tilde{\nu}$ = 2955, 2923,



2874, 1718, 1456, 1378, 1250, 1205, 1166, 1068 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{33}O_2SiINa^+$: 459.11868; found: 459.11850.

The analytical data of **2-(trimethylsilyl)ethyl (4*S*,6*R*,*Z*)-2-((*E*)-2-iodoprop-1-en-1-yl)-4,6-dimethyloct-2-enoate (4*S*,6*R*-29)** are identical; $[a]_D^{20}$**:** +16.8 (c = 1, $CHCl_3$).

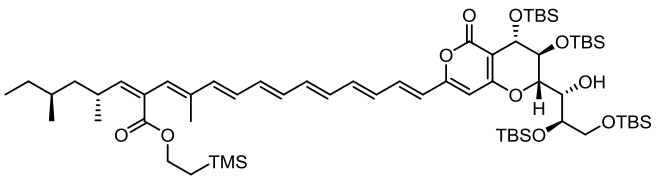
2-(Trimethylsilyl)ethyl (4*S*,6*S*,Z)-2-((E)-2-iodoprop-1-en-1-yl)-4,6-dimethyloct-2-enoate (4*S*,6*S*-29).



Prepared analoguously (96 mg, 89%). $[a]_D^{20}$: +24.4 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (t, *J* = 1.5 Hz, 1H), 5.63 (dd, *J* = 10.5, 1.2 Hz, 1H), 4.27 – 4.21 (m, 2H), 3.27 – 3.13 (m, 1H), 2.45 (d, *J* = 1.5 Hz, 3H), 1.34 – 1.22 (m, 3H), 1.16 – 1.08 (m, 2H), 1.06 – 1.01 (m, 2H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.82 (d, *J* = 6.3 Hz, 3H), 0.05 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 151.4, 138.5, 128.8, 98.1, 63.1, 44.6, 32.7, 31.5, 30.2, 29.0, 21.2, 19.2, 17.5, 11.5, -1.4 ppm; IR (film): $\tilde{\nu}$ = 2956, 2923, 2874, 1718, 1459, 1378, 1250, 1205, 1166, 1068 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{18}H_{33}O_2SiINa^+$: 459.11868; found: 459.11908.

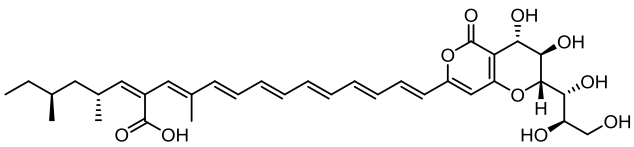
The analytical data of **2-(trimethylsilyl)ethyl (4*R*,6*R*,*Z*)-2-((*E*)-2-iodoprop-1-en-1-yl)-4,6-dimethyloct-2-enoate (4*R*,6*R*-29)** are identical; $[a]_D^{20}$**:** –22.3 (c = 1, $CHCl_3$).

Compound (*S,R*)-37. *This reaction was performed in the dark.* $Pd(CH_3CN)_2Cl_2$ (0.2 mg, 0.0007 mmol) was added to a degassed (pump and freeze, 3 cycles) solution of Ph_3As (0.45 mg, 0.0015 mmol) and flame dried $[Ph_2O_2P][NBu_4]$ (14 mg, 0.0305 mmol)[11] in DMF (0.1 mL). The resulting mixture was stirred for 5 min before it was transferred to a Schlenk tube containing alkenyl iodide **4*S*,6*R*-29** (6 mg, 0.0137 mmol) and tetraene **35** (7 mg, 0.0134 mmol). The mixture was stirred for 20 h at room temperature. aq. K_3PO_4 (3 M, 3.5 µL, 0.0105 mmol) was added in one portion and the mixture was stirred for 5 min before a degassed (pump and freeze, 3 cycles) solution of alkenyl iodide **16** (6 mg, 0.0068 mmol) in THF (0.1 mL) was added, followed by $Pd(dppf)Cl_2$ (0.6 mg, 0.0007 mmol). The suspension was stirred for 18 h before the reaction was quenched with water. The aqueous phase was extracted with Et_2O, the combined extracts were washed with brine and dried over $MgSO_4$, the drying agent was filtered off and the solvent was evaporated (below 25 °C). Purification of the crude product by flash chromatography (SiO_2, pentane + 2.5% NEt_3) afforded the title compound (4.4 mg, 55%) as a red oil. $[a]_D^{20}$: –142 (c = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (dd, *J* = 15.1, 11.2 Hz, 1H), 6.52, (dd, *J* = 14.0, 11.5 Hz, 1H), 6.46 – 6.27 (m, 7H), 6.13 (s, 1H), 6.01 (d, *J* = 15.2 Hz, 1H), 5.85 (s, 1H), 5.66 (d, *J* = 10.1 Hz, 1H), 4.82 (s, 1H), 4.73 (s, 1H), 4.53 (s, 1H), 4.30 – 4.22 (m, 2H), 3.94 (t, *J* = 1.0 Hz, 1H), 3.85 – 3.77 (m, 2H), 3.76 – 3.68 (m, 2H),

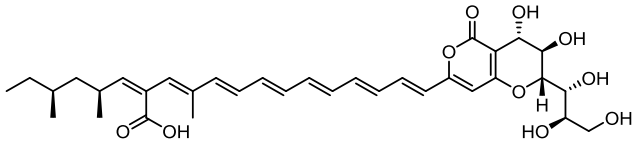


3.09 – 2.94 (m, 1H), 1.83 (s, 3H), 1.40 – 1.31 (m, 2H), 1.23 – 1.09 (m, 3H), 1.08 – 1.02 (m, 2H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.92 (s, 9H), 0.90 – 0.87 (m, 18H), 0.87 – 0.80 (m, 15H), 0.33 (s, 3H), 0.25 (s, 3H), 0.15 – 0.12 (m, 6H), 0.10 (s, 3H), 0.09 (s, 3H), 0.07 – 0.02 (m, 15H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.4, 166.2, 163.8, 158.7, 149.8, 139.4, 138.8, 136.6, 136.1, 135.7, 135.5, 132.7, 132.3, 131.2, 130.5, 129.6, 128.8 121.8, 100.9, 98.3, 78.4, 72.8, 71.9, 70.9, 64.2, 64.1, 63.1, 32.2, 31.8, 29.3, 26.2, 26.1, 25.9, 25.7, 20.7, 19.6, 18.6, 18.4, 18.3, 18.0, 17.6, 13.7, 11.3, -1.4, -3.9, -4.4, -4.6, -4.75, -4.78, -4.9, -5.27, −5.34 ppm; IR (film): $\tilde{\nu} =$ 2955, 2925, 2869, 2854, 1721, 1460, 1377, 1251, 1188, 1082 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{63}H_{112}O_{10}Si_5Na^+$: 1191.69941; found: 1191.70067.

Compound (*S,R*)-1. *This reaction was performed in the dark*. A solution of TASF (8 mg, 0.029 mmol) in DMF (40 µL) was added to a solution of **(*S,R*)-37** (3 mg, 0.0026 mmol) in DMF (40 µL) at 0 °C and the resulting mixture was stirred for 16 h at room temperature. The reaction was quenched with aq. HCl (pH = 3) and the aqueous phase was extracted with EtOAc. The combined extracts were dried over Na_2SO_4, the drying agent was filtered off and the solution was concentrated. The crude product was purified by HPLC (column: 150 mm YMC Actus, Ø = 20 mm; stationary phase: YMC ODS-A 5 µm, 20150 00456; mobile phase: methanol/TFA in water pH 3.5 =80:20) to give the title compound as an orange solid (1 mg, 64%). $[\alpha]_D^{20}$: −124 (c = 0.05, DMSO); ^{1}H NMR (600 MHz, [D_6]-DMSO): see Table **S-5**; ^{13}C NMR (150 MHz, [D_6]-DMSO): see Table **S-4**; IR (film): $\tilde{\nu} =$ 3375, 2940, 2915, 2824, 1657, 1436, 1407, 1313, 1018, 952 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{34}H_{43}O_{10}^-$: 611.28618; found: 611.28573.



Compound (*S,S*)-1. Prepared analogously as an orange-red solid after purification by HPLC (Column: 150 mm YMC Actus, Ø = 20 mm; stationary phase: YMC ODS-A 5 µm, 20150 00456; mobile phase: MeOH:TFA in water pH 3.5 = 80:20). $[\alpha]_D^{20}$: −82 (c = 0.05, $CHCl_3$). ^{1}H NMR (600 MHz, [D_6]-DMSO): see Table **S-7**; ^{13}C NMR (150 MHz, [D_6]-DMSO): see Table **S-6**; IR (film): $\tilde{\nu} =$ 3449, 2250, 2125, 1662, 1053, 1024, 1005 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{34}H_{43}O_{10}^-$: 611.28618; found: 611.28683.



THE EPIPYRONE A SERIES

6-Methyl-4-(2-(trimethylsilyl)ethoxy)-3-((2*S*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy) methyl)tetrahydro-2*H*-pyran-2-yl)-2*H*-pyran-2-one (S10). DIAD (5.3 mL, 26.91 mmol) was added dropwise to a solution of **43** (3.49 g, 5.38 mmol),[12] PPh_3 (8.47 g, 32.29 mmol) and 2-TMS-ethanol (3.86 mL, 26.91 mmol) in THF (17.5 mL) at 0 °C. The resulting mixture was stirred for 16 h before the reaction was quenched with sat. aq. NH_4Cl and the aqueous layer was extracted with *t*BuOMe. The combined org. extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 5:1 to 2:1) afforded the title compound as a colorless oil (3.34 g, 83%). $[\alpha]_D^{20}$**:** –18.1 (c = 0.84, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ = 7.50 – 7.04 (m, 20H), 5.94 – 5.57 (m, 1H), 5.13 – 4.33 (m, 10 H), 4.16 – 3.52 (m, 7H), 2.25 – 2.14 (m, 3H), 0.97 – 0.78 (m, 2H), 0.09 – –0.16 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers, some signals are overlapping): δ = 168.6, 168.4, 165.6, 164.0, 162.9, 162.6, 139.8, 139.6, 139.5, 139.4, 139.0, 138.8, 138.2, 138.1, 128.5, 128.22, 128.16, 128.1, 128.0, 127.83, 127.78, 127.7, 127.5, 127.4, 127.3, 127.1, 101.5, 101.0, 96.3, 95.2, 85.5, 77.6, 77.4, 75.7, 75.6, 75.1, 74.9, 74.7, 74.6, 74.3, 74.1, 73.8, 73.5, 72.7, 72.6, 72.4, 69.1, 68.6, 67.6, 20.7, 20.5, 17.9, 17.5, -1.3, -1.5 ppm; IR (film): $\tilde{\nu}$ = 3030, 2869, 1700, 1646, 1556, 1452, 1354, 1322, 1248, 1087 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{45}H_{52}O_8SiNa^+$: 771.33237; found: 771.33216.

6-Methyl-4-(2-(trimethylsilyl)ethoxy)-3-((2S,3S,4R,5S,6R)-3,4,5-tris((tert-butyldimethylsilyl)oxy)-6-(((tert-butyldimethylsilyl)oxy)methyl)tetrahydro-2H-pyran-2-yl)-2H-pyran-2-one (44). $Pd(OH)_2$/C (30 mg, 20% loading) was added to a solution of **S10** (300 mg, 0.40 mmol) in CH_3OH (4.3 mL), the suspension was purged with H_2 and stirred under hydrogen atmosphere for 16 h. The suspension was filtered through a plug of Celite®, the filtrate was concentrated and the residue dried under vacuum.

The crude product was dissolved in CH_2Cl_2 (2.1 mL), the solution was cooled to 0 °C and pyridine (2.1 mL) was added. After 5 min, TBSOTf (0.92 mL, 4.01 mmol) was added dropwise and stirring was continued for 16 h at room temperature. The reaction was quenched with sat. aq. NH_4Cl and the aqueous layer was extracted with *t*BuOMe. The combined organic phases were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 10:1) afforded the title compound as a colorless oil (280 mg, 83%). $[\alpha]_D^{20}$: –37.0 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$,

[12] A. Kanai, T. Kamino, K. Kuramochi, S. Kobayashi, *Org. Lett.* **2003**, *5*, 2837-2839.

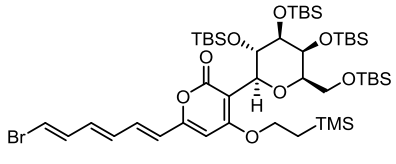
mixture of rotamers): δ = 5.90 – 5.81 (m, 1H), 4.77 – 4.38 (m, 2H), 4.17 – 3.99 (m, 3H), 3.75 – 3.51 (m, 3H), 3.44 – 3.28 (m, 1H), 2.25 – 2.14 (m, 3H), 1.18 – 1.07 (m, 2H), 1.01 – 0.91 (m, 18H), 0.88 – 0.83 (m, 9H), 0.76 – 0.70 (m, 9H), 0.19 – 0.17 (m, 3H), 0.16 – 0.00 (m, 27H), -0.20 – -0.25 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers, some signals are overlapping): δ = 168.3, 167.8, 165.7, 163.5, 162.7, 161.9, 102.4, 102.0, 96.0, 94.8, 79.6, 79.40, 79.36, 79.2, 74.3, 72.7, 71.7, 69.8, 68.5, 67.4, 67.3, 60.9, 27.3, 27.2, 26.6, 26.4, 26.24, 26.19, 25.9, 20.6, 19.5, 19.4, 19.0, 18.8, 18.7, 18.2, 18.13, 18.05, 18.0, 17.8, -1.1, -1.4, -1.9, -2.3, --3.2, -3.4, -3.5, -3.6, -3.7, -3.8, -3.9, -4.3, -4.58, −4.64, -5.0, -5.17, -5.21, -5.23 ppm; IR (film): $\tilde{\nu}$ = 2954, 2929, 2887, 2856, 1716, 1648, 1561, 1472, 1249, 1098, 1082 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{41}H_{84}O_8Si_5Na^+$: 867.49048; found: 867.49030.

6-((3*E*,5*E*)-6-Bromo-2-hydroxyhexa-3,5-dien-1-yl)-4-(2-(trimethylsilyl)ethoxy)-3-((2*S*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris((*tert*-butyldimethylsilyl)oxy)-6-(((*tert*-butyldimethylsilyl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl)-2*H*-pyran-2-one (S11). A solution of LiHMDS (806 mg, 4.82 mmol) in THF (4.8 mL) was added dropwise to a solution of **44** (815 mg, 0.964 mmol) in THF (5 mL) at –78 °C. The resulting mixture was stirred for 30 min at this temperature before a solution of (2*E*,4*E*)-5-bromopenta-2,4-dienal **45** (775.9 mg, 4.82 mmol)[13] in THF (19 mL) was added dropwise, followed by $Sc(OTf)_3$ (949 mg, 1.93 mmol). The mixture was stirred for 2.5 h before the reaction was quenched with sat. aq. NH_4Cl and the aqueous layer was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 5:1) afforded the title compound as a yellow oil (611 mg, 63%). $[\alpha]_D^{20}$**:** –23.5 (c = 1,05, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers and diastereomers): δ = 6.74 – 6.63 (m, 1H), 6.41 – 6.31 (m, 1H), 6.29 – 6.17 (m, 1H), 6.00 – 5.92 (m, 1H), 5.79 – 6.68 (m, 1H), 4.76 – 4.39 (m, 3H), 4.20 – 3.99 (m, 3H), 3.77 -3.51 (m, 3H), 3.46 – 3.31 (m, 1H), 2.75 – 2.52 (m, 2H), 1.86 – 1.73 (m, 1H), 1.16 – 1.07 (m, 2H), 1.02 – 0.92 (m, 18H), 0.88 – 0.84 (m, 9H), 0.77 – 0.71 (m, 9H), 0.21 – 0.18 (m, 3H), 0.17 – 0.13 (m, 6H), 0.12 – 0.09 (m, 9H), 0.08 – 0.06 (m, 3H), 0.06 – 0.04 (m, 3H), 0.03 – 0.00 (m, 6H), -0.19 – -0.25 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers and diastereomers, some signals are overlapping): δ = 168.05, 167.96, 167.5, 167.4, 165.6, 165.5, 162.8, 162.7, 162.1, 161.9, 161.8, 161.7, 136.6, 136.5, 136.43, 136.36, 135.8, 135.5, 128.5, 128.4, 128.2, 128.1, 110.2, 110.0, 109.8, 103.2, 103.1, 102.8, 102.7, 98.0, 97.9, 96.6, 96.5, 79.7, 79.6, 79.41, 79.36, 79.3, 77.4, 77.3, 74.4, 74.3, 72.9, 72.7, 72.0, 71.8, 70.61, 70.57, 70.1, 68.9, 68.8, 68.51, 68.47, 67.4, 61.5, 61.3, 61.0, 43.5, 43.4, 43.24, 43.21, 29.8, 27.31, 27.27, 26.6, 26.4, 26.31, 26.26, 26.0, 19.6, 19.5, 19.43, 19.41, 19.0, 18.8, 18.7, 18.3, 18.2, 18.1, 17.8, 0.6, 0.4, 0.3, -1.1, -1.4, -1.97, -2.00, -2.3, -2.4, -3.15,

[13] I. Paterson, G. J. Florence, A. C. Heimann, A. C. Mackay, *Angew. Chem. Int. Ed.* **2005**, *44*, 1130.

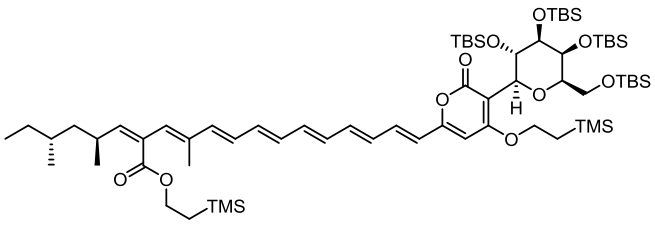
−3.19, -3.38, -3.44, -3.58, -3.60, -3.65, -3.66, -3.73, -3.76, -3.85, -3.87, -4.27, -4.32, -4.4, -4.5, -4.6, −4.94, -5.0, -5.07, -5.14, -5.2 ppm. IR (film): $\tilde{\nu}$ = 2929, 2856, 1704, 1643, 1557, 1472, 1410, 1360, 1249, 1097 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{46}H_{89}O_9Si_5BrNa^+$: 1027.44287; found: 1027.44276.

6-((1*E*,3*E*,5*E*)-6-Bromohexa-1,3,5-trien-1-yl)-4-(2-(trimethylsilyl)ethoxy)-3-((2*S*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris((*tert*-butyldimethylsilyl)oxy)-6-(((*tert*-butyldimethylsilyl)oxy)methyl)tetrahydro-2*H*-pyran-2-yl)-2*H*-pyran-2-one (46). Ac_2O (92 µL, 0.97 mmol) was added to a solution of **S11** (195 mg, 0.19 mmol), NEt_3 (0.16 mL, 1.16 mmol) and DMAP (2.4 mg, 0.02 mmol) in CH_2Cl_2 (2 mL) and the resulting mixture was stirred for 16 h at room temperature. The reaction was quenched with sat. aq. NH_4Cl and the aqueous layer was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated (bath temperature 25 °C). The residue was dried in vacuo and used without further purification.



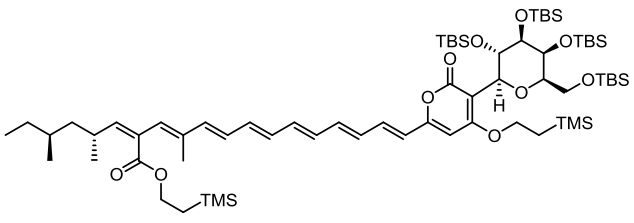
The crude product was dissolved in CH_2Cl_2 (2 mL), the solution was cooled to 0 °C and DBU (0.22 mL, 1.45 mmol) was added dropwise. The mixture was stirred for 3 h at 0 °C before the reaction was quenched with sat. aq. NH_4Cl and the aqueous layer was extracted with *t*BuOMe. The combined organic phases were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated (bath temperature 25 °C). Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 20:1) afforded the title compound as a yellow oil (168 mg, 88%). $[\alpha]_D^{20}$**:** −67.7 (c = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ = 7.23 – 7.09 (m, 1H), 6.85 – 6.75 (m, 1H), 6.56 – 6.48 (m, 1H), 6.44 – 6.24 (m, 2H), 6.14 – 6.04 (m, 1H), 5.97 – 5.89 (m, 1H), 4.78 – 4.40 (m, 2H), 4.20 – 4.02 (m, 3H), 3.77 – 3.52 (m, 3H), 3.47 – 3.30 (m, 1H), 1.76 – 1.09 (m, 2H), 1.03 – 0.93 (m, 18H), 0.88 – 0.84 (m, 9H), 0.75 – 0.71 (m, 9H), 0.21 – 0.18 (m, 3H), 0.16 – 0.13 (m, 6H), 0.12 – 0.10 (m, 9H), 0.09 – 0.07 (m, 3H), 0.06 – 0.04 (m, 3H), 0.03 – 0.00 (m, 3H), -0.17 – -0.24 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers, some signals are overlapping): δ = 167.9, 167.5, 164.6, 160.9, 159.4, 158.6, 137.24, 137.21, 135.69, 135.65, 135.3, 135.1, 131.7, 131.6, 123.7, 123.5, 112.7, 112.5, 104.5, 104.1, 97.4, 96.3, 79.6, 79.5, 79.4, 79.3, 77.4, 74.5, 72.7, 71.8, 69.9, 68.6, 67.4, 60.9, 27.31, 27.26, 26.6, 26.4, 26.3, 26.2, 26.0, 19.6, 19.4, 19.0, 18.8, 18.7, 18.23, 18.16, 18.09, 18.05, 17.8, -1.1, -1.4, -1.9, -2.3, -3.2, -3.4, -3.5, -3.6, -3.7, -3.8, -3.9, -4.3, -4.5, -4.6, -5.0, -5.1, -5.19, -5.20 ppm; IR (film): $\tilde{\nu}$ = 2929, 2886, 2856, 1719, 1630, 1598, 1537, 1472, 1249, 1098 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{46}H_{87}O_8Si_5BrNa^+$: 1009.43231; found: 1009.43200.

Compound (*R,S*)-48. *This reaction was performed in the dark.* $Pd(CH_3CN)_2Cl_2$ (1.7 mg, 0.0059 mmol)



was added to a degassed (pump and freeze, 3 cycles) solution of Ph_3As (3.6 mg, 0.0118 mmol) and flame dried $[Ph_2O_2P][NBu_4]$[11] (163.2 mg, 0.3551 mmol) in DMF (0.5 mL). The resulting mixture was stirred for 5 min before it was transferred to a Schlenk tube containing alkenyl iodide **(*R,S*)-29** (50 mg, 0.1184 mmol) and diene **47** (56 mg, 0.1194 mmol). The resulting mixture was stirred for 20 h at room temperature. Aq. K_3PO_4 (3 M, 44 µL, 0.1326 mmol) was added in one portion followed after 5 min by a degassed (pump and freeze, 3 cycles) solution of bromide **46** (105 mg, 0.1062 mmol) in THF (0.42 mL) and $Pd(dppf)Cl_2$ (8.7 mg, 0.0119 mmol). The mixture was stirred for 18 h, the reaction was quenched with water and the aqueous layer was extracted with Et_2O. The combined organic phases were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated (below 25 °C). Purification of the crude product by flash chromatography (SiO_2, pentane + 2.5% NEt_3) afforded the title compound (75 mg, 58%) as a red oil. $[a]_D^{20}$**:** –74 (c = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ = 7.32 – 7.18 (m, 1H), 6.62 – 6.24 (m, 8H), 6.17 – 6.10 (m, 1H), 6.05 – 5.96 (m, 1H), 5.93 – 5.85 (m, 1H), 5.72 – 5.58 (m, 1H), 4.82 – 4.39 (m, 2H), 4.32 – 4.30 (m, 2H), 4.20 – 4.00 (m, 3H), 3.80 – 3.52 (m, 3H), 3.49 – 3.28 (m, 1H), 3.09 – 2.96 (m, 1H), 1.83 (s, 3H), 1.23 – 1.05 (m, 7H), 1.03 – 1.00 (m, 9H), 0.98 – 0.92 (m, 12H), 0.88 – 0.82 (m, 15H), 0.76 – 0.70 (m, 9H), 0.22 – -0.02 (m, 39H), -0.16 – -0.25 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers, some signals are overlapping): δ = 168.4, 168.0, 167.6, 164.8, 163.4, 161.0, 159.9, 159.2, 149.8, 149.7, 139.6, 138.4, 139.2, 137.0, 136.8, 136.7, 136.0, 135.8, 135.5, 132.7, 132.6, 132.3, 132.2, 131.0, 130.9, 130.63, 130.56, 129.6, 128.71, 128.68, 121.8, 121.6, 103.9, 103.5, 96.7, 95.6, 79.52, 79.48, 79.4, 79.3, 77.40, 77.35, 74.5, 72.7, 71.8, 69.9, 68.6, 67.3, 63.0, 60.9, 45.2, 44.5, 32.2, 31.8, 29.8, 29.3, 27.30, 27.25, 26.6, 26.4, 26.3, 26.2, 25.9, 20.7, 19.6, 19.4, 19.0, 18.8, 18.7, 18.2, 18.14, 18.08, 18.0, 17.8, 17.6, 14.3, 13.7, 11.3, 9.1, -1.1, -1.4, -1.9, -2.3, -3.2, -3.4, -3.5, -3.6, -3.7, -3.8, -3.9, -4.3, -4.5, -4.6, -5.0, -5.16, -5.22 ppm; IR (film): $\tilde{\nu}$ = 2956, 2928, 2855, 1721, 1628, 1528, 1471, 1407, 1251, 1101, 1005 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{68}H_{124}O_{10}Si_6Na^+$: 1291.77024; found: 1291.76933.

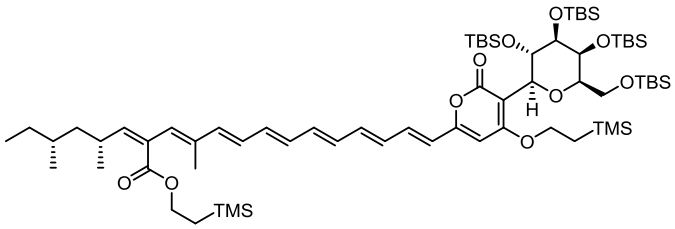
Compound (*S,R*)-48. Prepared analogously as a red oil (46.3 mg, 57%). $[a]_D^{20}$**:** –81.0 (c = 0.1, $CHCl_3$);



^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ = 7.29 -7.17 (m, 1H), 6.60 – 6.25 (m, 8H), 6.16 – 6.10 (m, 1H), 6.06 – 5.96 (m, 1H), 5.94 – 5.87 (m, 1H), 5.73 – 5.61 (m, 1H), 4.79 – 4.40 (m, 2H), 4.31 – 4.21 (m, 2H), 4.19

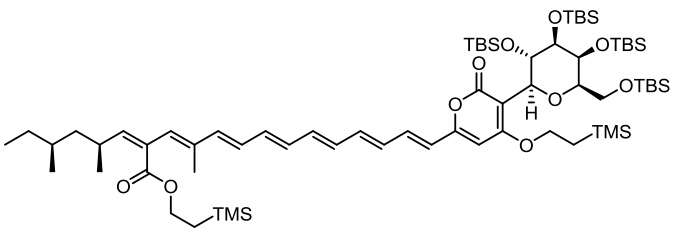
– 4.03 (m, 3H), 3.77 – 3.53 (m, 3H), 3.47 – 3.31 (m, 1H), 3.08 – 2.93 (m, 1H), 1.91 – 1.77 (m, 3H), 1.23 – 1.07 (m, 7H), 1.04 – 1.00 (m, 9H), 0.98 – 0.94 (m, 12 H), 0.88 – 0.84 (m, 15H), 0.75 – 0.71 (m, 9H), 0.21 – 0.00 (m, 39H), -0.16 - -0.24 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers, some signals are overlapping): δ = 168.39, 168.01, 167.62, 161.03, 159.92, 159.16, 149.75, 139.56, 139.46, 139.22, 136.98, 136.81, 136.74, 135.97, 135.83, 135.47, 132.66, 132.26, 131.02, 130.88, 130.64, 130.57, 129.61, 128.72, 121.81, 121.59, 103.52, 96.67, 95.58, 79.54, 79.48, 79.40, 79.36, 77.40, 77.35, 74.51, 72.69, 71.82, 69.90, 68.63 67.31, 63.03, 60.93, 46.09, 44.52, 32.22, 31.81, 29.84, 29.31, 27.31, 27.26, 26.57, 26.40, 26.30, 26.22, 25.95, 20.70, 19.56, 19.42, 18.96, 18.84, 18.69, 18.22, 18.15, 18.09, 18.06, 17.82, 17.57, 13.70, 11.31, 1.15, -1.06, -1.39, -1.93, -2.29, -3.18, -3.40, -3.46, -3.60, −3.69, -3.76, -3.87, -4.30, -4.44, -4.60, -5.01, -5.15, -5.21 ppm; IR (film): $\tilde{\nu}$ = 2955, 2929, 2856, 1722, 1628, 1528, 1462, 1408, 1251, 1100, 1006 cm^{-1} ; HRMS (ESI): *m/z* calcd. for $C_{68}H_{124}O_{10}Si_6Na^+$: 1291.77024; found: 1291.76961.

Compound (*R,R*)-48. Prepared analogously as a red oil (32.7 mg, 49%). $[\alpha]_D^{20}$**:** –62.0 (c = 0.1, $CHCl_3$);



^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ = 7.29 – 7.18 (m, 1H), 6.61 – 6.25 (m, 8H), 6.17 – 6.12 (m, 1H), 6.05 – 5.97 (m, 1H), 5.91 – 5.88 (m, 1H), 5.68 – 5.59 (m, 1H), 4.79 – 4.40 (m, 2H), 4.30 – 4.21 (m, 1H), 4.18 – 4.04 (m, 3H), 3.77 – 3.53 (m, 3H), 3.46 – 3.32 (m, 1H), 3.13 – 2.97 (m, 1H), 1.94 – 1.78 (m, 3H), 1.26 – 1.06 (m, 7H), 1.04 – 0.99 (m, 12H), 0.98 – 0.94 (m, 12H), 0.88 – 0.82 (m, 15H), 0.75 – 0.71 (m, 9H), 0.20 – 0.01 (m, 39H), -0.17 - -0.23 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers, some signals are overlapping): δ = 168.4, 168.0, 167.3, 164.8, 161.0, 159.9, 159.2, 149.5, 139.6, 139.5, 139.2, 137.0, 136.8, 136.8, 136.0, 135.8, 135.5, 132.7, 132.6, 132.3, 132.2, 131.0, 130.9, 130.6, 130.6, 130.1, 128.8, 125.7, 121.8, 121.6, 103.9, 103.5, 96.7, 95.6, 79.6, 79.5, 79.41, 79.4, 77.4, 77.3, 74.5, 72.7, 71.8, 69.9, 68.6, 67.3, 63.1, 60.9, 44.8, 32.7, 31.9, 30.5, 30.2, 27.3, 27.27, 26.6, 26.4, 26.3, 26.2, 25.9, 21.5, 19.6, 19.4, 19.2, 19.0, 18.8, 18.7, 18.2, 18.16, 18.1, 18.06, 17.8, 17.6, 13.7, 11.5, -1.1, -1.4, -1.9, -2.3, -3.2, -3.4, -3.44, -3.6, -3.7, -3.8, -3.9, -4.3, -4.4, -4.6, -5.0, −5.1, -5.2 ppm; IR (film): $\tilde{\nu}$ = 2955, 2929, 2857, 1722, 1629, 1529, 1471, 1407, 1251, 1167, 1101, 1006 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{68}H_{124}O_{10}Si_6Na^+$: 1291.77024; found: 1291.76927.

Compound (*S,S*)-48. Prepared analogously as a red oil (28.8 mg, 57%). $[\alpha]_D^{20}$**:** –33.0 (c = 0.1, $CHCl_3$);



^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ = 7.24 – 7.17 (m, 1H), 6.61 – 6.27 (m, 8H), 6.16 – 6.11 (m, 1H), 6.06 – 5.97 (m, 1H), 5.92 – 5.86 (m, 1H), 5.66 –

5.59 (m, 1H), 4.78 – 4.41 (m, 2H), 4.32 – 4.21 (m, 2H), 4.17 – 4.04 (m, 4H), 3.75 – 3.54 (m, 4H), 3.49 – 3.30 (m, 1H), 3.11 – 2.88 (m, 1H), 1.89 – 1.79 (m, 3H), 1.23 – 1.09 (m, 7H), 1.07 – 1.03 (m, 9H), 1.03 – 0.99 (m, 12 H), 0.98 – 0.94 (m, 15H), 0.88 – 0.84 (m, 15H), 0.75 – 0.71 (m, 9H), 0.21 – 0.02 (m, 39H), -0.16 - -0 24 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers, some signals are overlapping): δ = 168.42, 167.61, 161.01, 159.92, 159.16, 149.51, 139.55, 139.45, 139.21, 136.81, 136.74, 135.83, 135.46, 132.67, 132.27, 132.21, 131.03, 130.58, 130.10, 128.74, 121.82, 103.92, 103.53, 96.67, 95.58, 79.54, 79.49, 79.38, 79.34, 77.36, 74.51, 72.69, 71.82, 69.90, 68.63, 67.31, 63.05, 60.93, 46.34, 44.78, 32.67, 31.89, 30.22, 29.84, 27.31, 27.26, 26.57, 26.40, 26.30, 26.22, 25.94, 21.53, 19.55, 19.42, 19.20, 18.96, 18.84, 18.70, 18.22, 18.16, 18.09, 18.06, 17.82, 17.64, 17.56, 13.72, 11.65, 11.45, 1.15, -1.07, -1.39, -1.93, -2.29, -3.18, -3.40, -3.45, -3.59, -3.69, -3.76, -3.87, -4.29, -4.44, -4.59, -5.01, -5.15, -5.21 ppm; IR (film): $\tilde{\nu}$ = 2955, 2928, 2856, 1720, 1628, 1529, 1462, 1361, 1251, 1099, 1048, 1007 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{68}H_{124}O_{10}Si_6Na^+$: 1291.77024; found: 1291.76960.

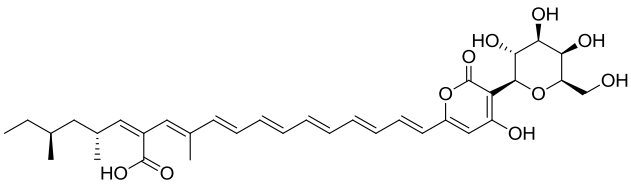
Compound (*R,S*)-2. *This reaction was performed in the dark.* TASF (65 mg, 0.236 mmol) was added to a solution of product **(*R,S*)-48** (25 mg, 0.0197 mmol) in DMF (0.5 mL) and the mixture was stirred for 16 h at room temperature. Another portion of TASF (65 mg, 0.236 mmol) was added and stirring continued for additional 16 h. This procedure was repeated two more times. For work up, aq. HCl was added, the aqueous layer (pH = 3) was extracted with EtOAc (5 x 5 mL) and the combined organic extracts were dried over Na_2SO_4. The drying agent was filtered off, the solvent was evaporated and the residue was purified by HPLC (Column: 150 mm YMC, Ø = 10 mm; stationary phase: YMC Triart C18 5 µm, 10150 00550; mobile phase: MeOH: 0.1% TFA in water, 85:15) to give the title compound as an orange-red solid (2.4 mg, 19%). $[a]_D^{20}$: 147.1 (c = 0.05, MeOH). ^{1}H NMR (600 MHz, [D$_4$]-MeOH): δ = 7.14 (dd, *J* = 15.3, 11.3 Hz, 1H), 6.64 (dd, *J* = 14.7, 11.2 Hz, 1H), 6.50 (dd, *J* = 14.6, 10.3 Hz, 1H), 6.47 – 6.33 (m, 6H), 6.20 (d, *J* =15.0 Hz, 1H), 6.13 – 6.11 (m, 1H), 6.08 (s, 1H), 5.64 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.53 (d, *J* = 9.7 Hz, 1H), 4.19 (t, *J* =9.5 Hz, 1H), 3.91 (d, *J* = 3.1 Hz, 1H), 3.73 (dd, *J* = 11.4, 6.9 Hz, 1H), 3.69 (dd, *J* =11.6, 5.1 Hz, 1H), 3.62 – 3.59 (m, 1H), 3.51 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.06 – 2.95 (m, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.45 – 1.32 (m, 2H), 1.33 – 1.25 (m, 2H), 1.21 – 1.13 (m, 1H), 1.09 (dt, *J* = 12.8, 7.4 Hz, 1H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (151 MHz, [D$_4$]-MeOH): see Table **S-1**;

^{1}H NMR (600 MHz, [D$_6$]-DMSO): δ = 12.71 (brs, 1H), 7.00 (dd, *J* = 15.1, 11.4 Hz, 1H), 6.72 (dd, *J* = 14.6, 11.2 Hz, 1H), 6.51 (dd, 14.4, 10.6 Hz, 1H), 6.48 – 6.39 (m, 6H), 6.32 (d, *J* = 15.2 Hz, 1H), 6.12 (s, 2H), 5.62 (d, *J* = 10.1 Hz, 1H), 4.66 (d, *J* = 5.6 Hz, 1H), 4.57 (t, *J* = 9.3 Hz, 1H), 4.25 (d, *J* = 9.5 Hz, 1H), 4.08 (t, *J* = 9.3 Hz, 1H), 3.70 – 3.68 (m, 1H), 3.48 – 3.39 (m, 2H), 2.91 – 2.83 (m, 1H), 1.80 (d, *J* =1.2 Hz, 3H),

1.36 – 1.28 (m, 2H), 1.28 – 1.21 (m, 1H), 1.12 (ddd, *J* = 13.6, 7.9, 6.3 Hz, 1H), 1.08 – 1.01 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H),0.80 (d, *J* = 6.8 Hz, 3H), 0.80 (t, *J* = 7.0, 3H) ppm; ^{13}C NMR (151 MHz, [D_6]-DMSO): see Tabel **S-2**;

IR (film): $\tilde{\nu} =$ 3410, 2924, 2169, 2149, 2039, 2003, 1958, 1637, 1543, 1454, 1003 cm-1; HRMS (ESI): *m/z* calcd. for $C_{34}H_{43}O_{10}$: 611.28618; found: 611.28667.

Compound (*S,R*)-2. Prepared analogously as an orange-red oil (3.6 mg, 16% after HPLC) (column: 150

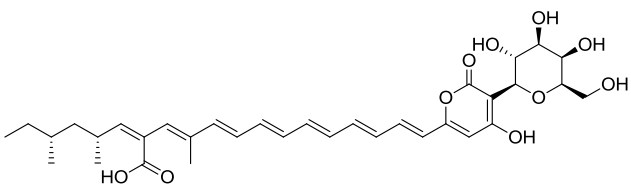


mm YMC, Ø = 10 mm; stationary phase: YMC Triart C18 5 µm, 10150 00550; mobile phase: MeOH: 0.1% TFA in water, 85:15). $[a]_D^{20}$: −118.4 (c = 0.05, MeOH). ^{1}H NMR (600 MHz, [D_4]-MeOH): δ = 7.14 (dd, *J* = 15.2, 11.2 Hz, 1H), 6.64 (dd, *J* = 14.5, 11.1 Hz, 1H), 6.51 (dd, *J* = 14.7, 10.3 Hz, 1H), 6.51 – 6.35 (m, 6H), 6.20 (d, *J* = 15.1 Hz, 1H), 6.14 – 6.10 (m, 1H), 6.08 (s, 1H), 5.65 (dd, *J* = 10.3, 1.2 Hz, 1H), 4.53 (d, *J* = 9.7 Hz, 1H), 4.19 (t, *J* = 9.5 Hz, 1H), 3.91 (dd, *J* = 3.3, 0.9 Hz, 1H), 3.74 (dd, *J* = 11.5, 6.8 Hz, 1H), 3.69 (dd, *J* = 11.5, 5.2, 1H), 3.62 – 3.59 (m, 1H), 3.51 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.05 – 2.95 (m, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.45 – 1.33 (m, 2H), 1.29 (dt, *J* = 13.4, 6.6 Hz, 1H), 1.17 (tdd, *J* = 13.2, 6.6, 5.6 Hz, 1H), 1.14 – 1.04 (m, 1H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (151 MHz, [D_4]-MeOH): see Table **S-1**;

^{1}H NMR (600 MHz, [D_6]-DMSO): δ = 12.75 (brs, 1H), 7.01 (dd, *J* =15.1, 11.3 Hz, 1H), 6.72 (dd, *J* = 14.7, 11.3 Hz, 1H), 6.55 – 6.40 (m, 7H), 6.33 (d, *J* = 15.1 Hz, 1H), 6.15 – 6.07 (m, 2H), 5.63 (d, *J* = 10.2 Hz, 1H), 4.66 (d, *J* = 5.6 Hz, 1H), 4.57 (t, *J* = 5.7 Hz, 1H), 4.25 (d, *J* = 9.5 Hz, 1H), 4.08 (t, *J* = 9.3 Hz, 1H), 3.69 (d, *J* = 3.0 Hz, 1H), 3.49 – 3.38 (m, 2H), 2.93 – 2.82 (m, 1H), 1.79 (d, *J* = 1.2 Hz, 3H), 1.36 – 1.28 (m, 2H), 1.24 (dt, *J* = 13.0, 6.4 Hz, 1H), 1.12 (tq, *J* = 14.5, 13.8, 8.0, 6.7, 6.4 Hz, 1H), 1.08 – 1.00 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.80 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (151 MHz, [D_6]-DMSO): see Table **S-2**;

IR (film): $\tilde{\nu} =$ 3296, 3018, 2959, 2923, 1637, 1550, 1493, 1211, 1139, 1003 cm-1; HRMS (ESI): *m/z* calcd. for $C_{34}H_{43}O_{10}$: 611.28618; found: 611.28681.

Compound (*R,R*)-2. Prepared analogously as an orange-red oil (3.5 mg, 22% after HPLC) (column: 150



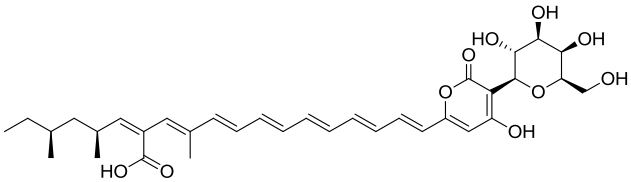
mm YMC, Ø = 10 mm; stationary phase: YMC Triart C18 5 µm, 10150 00550; mobile phase: MeOH: 0.1% TFA in water, 85:15). $[a]_D^{20}$: −44.0 (c = 0.05, MeOH). 1H NMR (600 MHz, [D_4]-MeOH): δ = 7.14 (dd, *J* = 15.3, 11.5 Hz, 1H), 6.64 (dd, *J* = 14.4, 11.1 Hz, 1H), 6.50 (dd, *J* = 14.8,

10.1 Hz, 1H), 6.46 – 6.35 (m, 6H), 6.19 (d, *J* = 15.1 Hz, 1H), 6.12 (s, 1H), 6.08 (s, 1H), 5.60 (d, *J* = 10.3 Hz, 1H), 4.53 (d, *J* = 9.7 Hz, 1H), 4.19 (t, *J* = 9.7 Hz, 1H), 3.94 – 3.89 (m, 1H), 3.77 – 3.67 (m, 2H), 3.63 – 3.59 (m, 1H), 3.56 – 3.47 (m, 1H), 3.06 – 2.97 (m, 1H), 1.87 (s, 3H), 1.38 – 1.25 (m, 3H), 1.19 – 1.07 (m, 2H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.87 – 0.83 (m, 6H) ppm; ^{13}C NMR (151 MHz, [D_4]-MeOH): see Table **S-1**;

^{1}H NMR (600 MHz, [D_6]-DMSO): δ = 12.75 (brs, 1H), 7.01 (dd, *J* = 15.1, 11.3 Hz, 1H), 6.72 (dd, *J* = 14.7, 11.2 Hz, 1H), 6.56 – 6.39 (m, 7H), 6.33 (d, *J* =15.1 Hz, 1H), 6.13 (s, 1H), 6.12 (s, 1H), 5.58 (d, *J* = 10.3 Hz, 1H), 4.66 (d, *J* = 5.6 Hz, 1H), 4.57 (t, *J* = 4.9 Hz, 1H), 4.25 (d, *J* = 9.5 Hz, 1H), 4.08 (t, *J* = 9.3 Hz, 1H), 3.69 (d, *J* = 3.0 Hz, 1H), 3.49 – 3.38 (m, 2H), 2.95 – 2.86 (m, 2H), 1.80 (s, 3H), 1.30 (ddd, *J* = 13.3, 9.5, 3.9 Hz, 1H), 1.27 – 1.19 (m, 2H), 1.14 – 1.06 (m, 2H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.79 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (151 MHz, [D_6]-DMSO): see Table **S-2**;

IR (film): $\tilde{\nu} =$ 3338, 3018, 2958, 2923, 1676, 1638, 1540, 1497, 1439, 1317,1207, 1139, 1003 cm-1; HRMS (ESI): *m/z* calcd. for $C_{34}H_{43}O_{10}$: 611.28618; found: 611.28648.

Compound (*S,S*)-2. Prepared analogously as an orange-red oil (2.2 mg, 17% after HPLC) (column: 150 mm YMC, Ø = 10 mm; stationary phase: YMC Triart C18 5 µm, 10150 00550; mobile phase: MeOH: 0.1% TFA in water 85:15). $[\alpha]_D^{20}$: 14.2 (c = 0.05, MeOH). ^{1}H NMR (600 MHz, [D_4]-MeOH): δ = 7.18 – 7.10 (m, 1H), 6.64 (dd, *J* = 14.7, 11.2 Hz, 1H), 6.51 (dd, *J* = 14.7, 10.3 Hz, 1H), 6.50 – 6.35 (m, 6H), 6.19 (d, *J* = 15.1 Hz, 1H), 6.13 (s, 1H), 6.06 – 6.09 (m, 1H), 5.60 (d, *J* = 10.4, 1.2 Hz, 1H), 4.54 (d, *J* = 9.7 Hz, 1H), 4.19 (t, *J* = 9.5 Hz, 1H), 3.92 (d, *J* = 3.1 Hz, 1H), 3.77 – 3.65 (m, 2H), 3.64 – 3.56 (m, 1H), 3.52 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.06 – 2.97 (m, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.39 – 1.25 (m, 3H), 1.20 – 1.07 (m, 2H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.85 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (151 MHz, [D_4]-MeOH): see Table **S-1**;

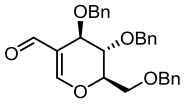


^{1}H NMR (600 MHz, [D_6]-DMSO): δ = 12.76 (brs, 1H), 10.80 (brs, 1H), 7.01 (dd, *J* = 15.2, 11.4 Hz, 1H), 6.73 (dd, *J* = 14.5, 11.3 Hz, 1H), 6.55 – 6.39 (m, 7H), 6.33 (d, *J* = 15.2 Hz, 1H), 6.13 (s, 1H), 6.12 (s, 1H), 5.58 (d, *J* = 10.3 Hz, 1H), 4.66 (d, *J* = 4.2 Hz, 1H), 4.61 (d, *J* = 5.4 Hz, 1H), 4.57 (t, *J* = 5.6 Hz, 1H), 4.25 (d, *J* = 9.5 Hz, 1H), 4.22 (s, 1H), 4.08 (t, *J* = 9.7 Hz, 1H), 3.69 (s, 1H), 3.47 – 3.39 (m, 2H), 3.35 (t, *J* = 6.2 Hz, 1H), 2.94 – 2.87 (m, 1H), 1.80 (s, 3H), 1.36 – 1.96 (m, 2H), 1.14 – 1.05 (m, 3H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.81 (t, *J* = 7.2 Hz, 3H), 0.79 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (151 MHz, [D_6]-DMSO): see Table **S-2**;

IR (film): $\tilde{\nu} =$ 3370, 2963, 2919, 1675, 1567, 1540, 1423, 1379, 1251, 1208, 1139, 1093, 1054, 1003 cm-1; HRMS (ESI): *m/z* calcd. for $C_{34}H_{43}O_{10}$: 611.28618; found: 611.28684.

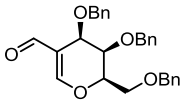
MODEL COMPOUNDS FOR COMPARISON (see Figure 1)

(2*R*,3*S*,4*R*)-3,4-Bis(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-carbaldehyde (S12).[14]



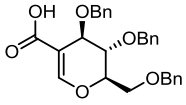
$POCl_3$ (2.45 mL, 26.16 mmol) was added dropwise over 1 h to a solution of tri-*O*-benzyl-D-glucal (1.00 g, 2.4 mmol) in DMF (4 mL) at 0 °C. The mixture was stirred for 24 h while warming to room temperature before the reaction was quenched with sat. aq. $NaHCO_3$. The aqueous phase was extracted with *t*BuOMe, and the combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 5:1) afforded the title compound as a colorless oil (807 mg, 76%). $[\alpha]_D^{20}$: +2.1 (c = 1, $CHCl_3$), Lit.:[14] $[\alpha]_D^{25}$: +6.8, c = 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (s, 1H), 7.42 – 7.20 (m, 15H), 4.77 – 4.71 (m, 1H), 4.71 – 4.44 (m, 7H), 4.42 (t, *J* = 2.3 Hz, 1H), 3.84 (t, *J* = 2.3 Hz, 1H), 3.80 (dd, *J* = 10.9, 7.8 Hz, 1H), 3.63 (dd, 10.7, 4.7 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.5, 164.4, 138.3, 137.8, 137.3, 128.7, 128.6, 128.5, 128.2, 128.0, 127.93, 127.87, 127.8, 117.9, 79.5, 73.5, 72.6, 71.8, 71.5, 68.5, 65.4 ppm; IR (film): $\tilde{\nu}$ = 3064, 3031, 2866, 1673, 1626, 1454, 1294, 1199, 1089, 1072 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{28}H_{28}O_5Na^+$: 467.18289; found: 467.18306.

(2*R*,3*R*,4*R*)-3,4-Bis(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-carbaldehyde (S13).



Prepared analogously from tri-*O*-benzyl-D-galactal as a colorless oil (5.12 g, 65%). $[\alpha]_D^{20}$: −6.1 (c = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.37 (s, 1H), 7.42 – 7.28 (m, 15H), 7.27 (s, 1H), 4.79 – 4.77 (m, 2H), 4.75 – 4.69 (m, 2H), 4.64 (dd, *J* = 3.5, 1.3 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 13.1 Hz, 1H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.02 (d, *J* = 5.3 Hz, 2H), 3.85 (dd, *J* = 5.3, 3.6 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.5, 164.5, 138.8, 137.9, 137.4, 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 127.7, 127.5, 119.2, 78.8, 73.7, 73.5, 73.1, 71.5, 68.5, 64.7 ppm; IR (film): $\tilde{\nu}$ = 3030, 2866, 1672, 1618, 1496, 1454, 1269, 1198, 1091, 1060, 1027 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{28}H_{28}O_5Na^+$: 467.18289; found: 467.18351.

(2*R*,3*S*,4*R*)-3,4-Bis(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-carboxylic acid (S14).

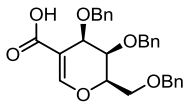


NaH_2PO_4 (5.60 g, 46.68 mmol) and H_2O_2 (35% in H_2O, 7.5 mL, 77.17 mmol) were added to a solution of **S12** (6.45 g, 15.49 mmol) in CH_3CN/*t*BuOH/H_2O (2:2:1, 70 mL) at 0 °C. The mixture was stirred for 5 min before $NaClO_2$ (8.4 g, 92.88 mmol) was added and stirring was continued for 16 h at room temperature. The mixture was diluted with water and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 5:1)

[14] N. G. Ramesh, K. K. Balasubramanian, *Tetrahedron Lett.* **1991**, *32*, 3875-3878.

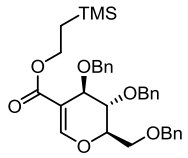
afforded the title compound (5.60 g, 79%). $[\alpha]_D^{20}$: –4.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (s, 1H), 7.39 – 7.21 (m, 15H), 4.72 – 4.63 (m, 2H), 4.59 – 4.49 (m, 4H), 4.44 (d, *J* = 12.1 Hz, 1H), 4.34 (t, *J* = 2.3 Hz, 1H), 3.82 (t, *J* = 2.2 Hz, 1H), 3.78 (dd, *J* = 10.7, 7.7 Hz, 1H), 3.62 (dd, *J* = 10.7, 4.9 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.9, 157.6, 138.3, 137.8, 137.5, 128.7, 128.6, 128.5, 128.15, 128.11 127.91, 127.88, 127.85, 127.1, 104.7, 77.5, 73.5, 72.4, 71.6, 71.4, 68.4, 67.8 ppm; IR (film): $\tilde{\nu}$ = 3063, 3030, 2863, 1647, 1453, 1362, 1238, 1097, 1069, 1047, 1027 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{28}H_{28}O_6Na^+$: 483.17781; found: 483.17805.

(2*R*,3*R*,4*R*)-3,4-Bis(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-carboxylic acid (S15).



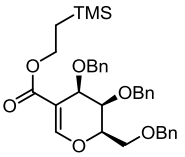
Prepared analogously (4.22 g, 80%). $[\alpha]_D^{20}$: –27.7 (c = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (s, 1H), 7.40 – 7.27 (m, 15H), 4.83 (d, *J* = 11.1 Hz, 1H), 4.76 (d, *J* = 11.1 Hz, 1H), 4.72 (d, *J* = 12.1 Hz, 1H), 4.69 – 4.63 (m, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H), 4.56 (dd, *J* = 3.5, 1.3 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 4.02 (d, *J* = 2.6 Hz, 1H), 4.00 – 3.98 (m, 1H), 3.91 (dd, J = 5.4, 3.6 Hz, 1H) ppm; ^{13}C NMR (76 MHz, $CDCl_3$): δ = 172.5, 157.6, 138.9, 138.1, 137.6, 128.7, 128.5, 128.3, 128.1, 128.0, 127.8, 127.8, 127.7, 127.5, 106.2, 77.3, 74.2, 73.9, 73.6, 71.8, 68.4, 67.4 ppm; IR (film): $\tilde{\nu}$ = 3030, 2866, 1674, 1619, 1496, 1453, 1433, 1369, 1305, 1190, 1075, 1027 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{28}H_{28}O_6Na^+$: 483.17781; found: 483.17772.

2-(Trimethylsilyl)ethyl (2*R*,3*S*,4*R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-carboxylate (S16). DEAD (6.70 mL, 36.77 mmol) was added dropwise over 60 min to a solution of



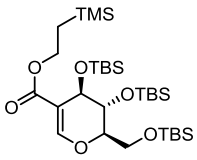
S14 (5.60 g, 12.15 mmol), 2-(TMS)-ethanol (4.5 mL, 31.39 mmol) and PPh_3 (11.50 g, 43.84 mmol) in THF (60 mL) at 0 °C. The resulting mixture was stirred for 16 h while warming to room temperature. The reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 10:1) afforded the title compound (5.25 g, 77%). $[\alpha]_D^{20}$: –15.8 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1H), 7.39 – 7.20 (m, 15H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.64 – 4.59 (m, 1H), 4.58 – 4.47 (m, 4H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.35 (t, *J* = 2.1 Hz, 1H), 4.29 – 4.21 (m, 2H), 3.80 (t, *J* = 2.3 Hz, 1H), 3.76 (dd, *J* = 10.6, 7.6 Hz, 1H), 3.61 (dd, *J* = 10.7, 4.9 Hz, 1H), 1.06 – 0.98 (m, 2H), 0.06 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.5, 155.3, 138.4, 137.9, 137.6, 128.7, 128.6, 128.5, 128.12, 128.10, 127.92, 127.86, 127.8, 105.7, 77.1, 73.5, 72.5, 71.61, 71.56, 68.4, 68.1, 62.5, 17.6, -1.3 ppm; IR (film): $\tilde{\nu}$ 3031, 2952, 2897, 1701, 1633, 1454, 1293, 1275, 1250, 1195, 1071, 1028 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{33}H_{40}O_6SiNa^+$: 583.24864; found: 583.24854.

2-(Trimethylsilyl)ethyl (2*R*,3*R*,4*R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2*H*-pyran-5-carboxylate (S17). Prepared analogously (4.00 g, 78%). $[\alpha]_D^{20}$: −39.3 (c = 1, $CHCl_3$); ^{1}H NMR



(300 MHz, $CDCl_3$): δ = 7.52 (s, 1H), 7.42 – 7.27 (m, 15H), 4.83 (d, *J* = 11.1 Hz, 1H), 4.76 (d, *J* = 11.2 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.67 – 4.55 (m, 4H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.30 – 4.20 (m, 2H), 4.01 (d, *J* = 3.1 Hz, 1H), 4.00 – 3.97 (m, 1H), 3.89 (dd, *J* = 5.5, 3.5 Hz, 1H), 1.09 – 0.96 (m, 2H), 0.07 (s, 9H) ppm; ^{13}C NMR (76 MHz, $CDCl_3$): δ = 167.0, 155.2, 139.2, 138.3, 137.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.7, 127.7, 127.4, 107.3, 76.9, 74.2, 74.2, 73.5, 71.7, 68.4, 67.7, 62.6, 17.6, -1.4 ppm; IR (film): $\tilde{\nu}$ = 3030, 2952, 1699, 1626, 1496, 1454, 1369, 1304, 1277, 1249, 1064, 1028 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{33}H_{40}O_6SiNa^+$: 583.24864; found: 583.24927.

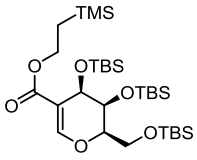
2-(Trimethylsilyl)ethyl (2*R*,3*R*,4*R*)-3,4-bis((tert-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-oxy)methyl)-3,4-dihydro-2*H*-pyran-5-carboxylate (S18). Pd(OH)$_2$/C (375 mg, 10%*w/w*) was added to



a solution of **S16** (3.75 g, 6.69 mmol) in CH_3OH (66 mL). The solution was purged with H_2 and stirred for 15 h at room temperature under H_2 atmosphere (1 atm). For work up, the suspension was filtered through a plug of Celite® and the filtrate was concentrated.

TBSOTf (6.20 mL, 26.99 mmol) was added to a solution of the crude triol and pyridine (6.50 mL, 80.36 mmol) in CH_2Cl_2 (16.5 mL) at 0 °C. The mixture was stirred for 16 h while warming to room temperature before the reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 60:1) afforded the title compound (3.72 g, 88%). $[\alpha]_D^{20}$: +4.3 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 1H), 4.36 – 4.20 (m, 3H), 4.20 – 4.08 (m, 1H), 3.93 (dd, *J* = 11.6, 8.1 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.73 (dd, *J* = 11.7, 3.9 Hz, 1H), 1.07 – 0.97 (m, 2H), 0.89 (s, 9H), 0.84 (s, 18H), 0.15 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H), 0.04 (s, 12H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.7, 154.4, 106.7, 82.3, 68.3, 63.8, 62.3, 62.1, 26.1, 25.84, 25.78, 18.5, 18.13, 18.10, 17.5, -1.3, -4.6, -4.67 (2 C), -4.71, -5.05, -5.14 ppm; IR (film): $\tilde{\nu}$ = 2954, 2930, 2896, 2858, 1706, 1635, 1472, 1252, 1197, 1076 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{30}H_{64}O_6Si_4Na^+$: 655.36722; found: 655.36777.

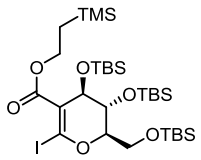
2-(Trimethylsilyl)ethyl (2*R*,3*S*,4*R*)-3,4-bis((tert-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-



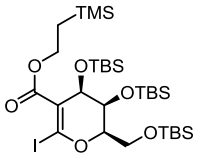
oxy)methyl)-3,4-dihydro-2*H*-pyran-5-carboxylate (S19). Prepared analogously (1.15 g, 33%). $[\alpha]_D^{20}$: +35.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (s, 1H), 4.49 (dd, *J* = 3.3, 1.5 Hz, 1H), 4.33 – 4.20 (m, 2H), 4.18 – 4.05 (m, 2H), 4.00 –

3.91 (m, 2H), 1.04 – 0.97 (m, 2H), 0.92 (s, 9H), 0.89 (s, 9H), 0.85 (s, 9H), 0.17 – 0.12 (m, 6H), 0.11 (s, 3H), 0.08 (s, 3H), 0.05 – 0.03 (m, 15H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.0, 154.5, 109.0, 81.5, 69.4, 63.8, 62.4, 61.9, 26.2, 26.14, 26.07, 18.6, 18.5 (2C), 17.5, -1.3, -4.3, –4.7, -4.8, -4.94, -4.96, -5.1 ppm; IR (film): $\tilde{\nu}$ = 2953, 2929, 2857, 1703, 1628, 1472, 1389, 1361, 1307, 1274, 1064 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{30}H_{64}O_6Si_4Na^+$: 655.36722; found: 655.36741.

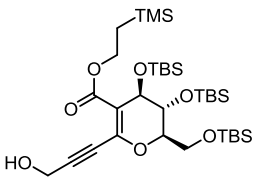
2-(Trimethylsilyl)ethyl (2*R*,3*R*,4*R*)-3,4-bis((tert-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-oxy)methyl)-6-iodo-3,4-dihydro-2*H*-pyran-5-carboxylate (S20). *n*BuLi (1.6 M in hexanes, 1.60 mL, 2.56 mmol) was added dropwise to a solution of *i*Pr_2NH (0.50 mL, 3.57 mmol) in THF (5.70 mL) at 0 °C and the resulting mixture was stirred for 15 min before it was cooled to –78 °C. A solution of **S18** (540 mg, 0.85 mmol) in THF (5.70 mL) was added dropwise and stirring was continued for 1.5 h. A solution of iodine (1.08 g, 4.26 mmol) in THF (5.70 mL) was then added dropwise and stirring was continued for 30 min before the reaction was quenched with sat. aq. $Na_2S_2O_3$ and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 20:1) afforded the title compound (598 mg, 92%). $[\alpha]_D^{20}$: +4.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.45 (t, *J* = 2.4 Hz, 1H), 4.41 – 4.32 (m, 1H), 4.32 – 4.26 (m, 1H), 4.15 – 4.06 (m, 1H), 4.02 – 3.94 (m, 2H), 3.79 (dd, *J* = 11.5, 4.9 Hz, 1H), 1.06 (dd, *J* = 9.6, 8.1 Hz, 2H), 0.89 (s, 9H), 0.85 (s, 9H), 0.83 (s, 9H), 0.11 (s, 3H), 0.08 (s, 9H), 0.06 – 0.02 (m, 15H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 119.6, 112.7, 87.1, 67.9, 66.5, 63.0, 61.7, 26.1, 25.78, 25.76, 18.5, 18.10, 18.07, 17.6, -1.4, -4.4, -4.5, -4.6, -4.8, -5.0, -5.2 ppm; IR (film): $\tilde{\nu}$ = 2953, 2929, 2894, 2857, 1698, 1584, 1471, 1521, 1113, 1064 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{30}H_{63}O_6Si_4INa^+$: 781.26387; found: 781.26417.



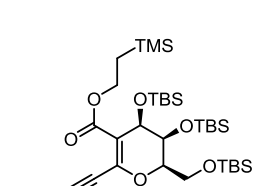
2-(trimethylsilyl)ethyl (2*R*,3*S*,4*R*)-3,4-bis((tert-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-oxy)methyl)-6-iodo-3,4-dihydro-2*H*-pyran-5-carboxylate (S21). Prepared analogously (791 mg, 88%). $[\alpha]_D^{20}$: +19.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.59 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.38 – 4.28 (m, 2H), 4.20 – 4.10 (m, 2H), 4.04 (dd, *J* = 5.7, 3.4 Hz, 1H), 3.91 (dd, *J* = 12.6, 1.1 Hz, 1H), 1.13 – 1.02 (m, 2H), 0.92 (s, 9H), 0.90 (s, 9H), 0.83 (s, 9H), 0.18 – 0.12 (m, 6H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 – 0.03 (m, 15H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.0, 115.0, 114.8, 85.9, 68.8, 66.2, 63.4, 61.4, 26.2, 26.1, 25.9, 18.6 , 18.5, 18.4, 17.4, -1.4, -4.2, -4.4, -4.8, -4.9, -5.2, -5.3 ppm; IR (film): $\tilde{\nu}$ = 2953, 2929, 2887, 2857, 1699, 1575, 1472, 1309, 1251, 1061 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{30}H_{63}O_6Si_4INa^+$: 781.26387; found: 781.26326.



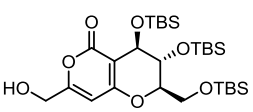
2-(Trimethylsilyl)ethyl (2*R*,3*R*,4*R*)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-oxy)methyl)-6-(3-hydroxyprop-1-yn-1-yl)-3,4-dihydro-2*H*-pyran-5-carboxylate (S22). $Pd(PPh_3)_2Cl_2$ (13 mg, 0.02 mmol) and CuI (7 mg, 0.04 mmol) were added to a degassed (pump and freeze, 3 cycles) solution of **S20** (147 mg, 0.19 mmol) in NEt_3 (1.3 mL). The mixture was stirred for 5 min before propargyl alcohol (36 µL, 0.62 mmol) was added. After stirring for 16 h, the reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 10:1) afforded the title compound (116 mg, 87%). $[\alpha]_D^{20}$: +6.9 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.50 – 4.45 (m, 2H), 4.45 (t, *J* = 2.4 Hz, 1H), 4.40 – 4.31 (m, 1H), 4.29 – 4.22 (m, 1H), 4.16 – 4.07 (m, 1H), 3.95 (dd, *J* = 2.6, 1.4 Hz, 1H), 3.88 (dd, *J* = 11.2, 7.4 Hz, 1H), 3.80 (dd, *J* = 11.4, 5.5 Hz, 1H), 2.26 (bs, 1H), 1.04 (dd, *J* = 9.5, 7.9 Hz, 1H), 0.88 (s, 9H), 0.85 (s, 9H), 0.83 (s, 9H), 0.13 (s, 3H), 0.08 (s, 6H), 0.06 (s, 6H), 0.04 (s, 12H), ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.9, 143.6, 111.1, 93.1, 82.6, 80.6, 67.5, 65.3, 62.8, 61.8, 51.6, 26.1, 25.81, 25.75, 18.5, 18.1, 17.5, 1.2, -1.4, -4.4, -4.58, -4.63, -4.8, -5.1, -5.2 ppm; IR (film): $\tilde{\nu}$ = 3429, 2953, 2930, 2896, 2857, 1692, 1601, 1472, 1389, 1251, 1220, 1070 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{33}H_{66}O_7Si_4Na^+$: 709.37782; found: 709.37779.



2-(Trimethylsilyl)ethyl (2*R*,3*S*,4*R*)-3,4-bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)-oxy)methyl)-6-(3-hydroxyprop-1-yn-1-yl)-3,4-dihydro-2*H*-pyran-5-carboxylate (S23). Prepared analogously (530 mg, 75%). $[\alpha]_D^{20}$: +19.4 (c = 0.53, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.62 (dd, *J* =3.3, 1.5 Hz, 1H), 4.46 (d, *J* = 6.3 Hz, 2H), 4.36 – 4.24 (m, 2H), 4.13 (dt, *J* = 6.3, 10.9 Hz, 1H), 4.08 (dd, *J* = 12.4, 8.7 Hz, 1H), 3.99 (dd, *J* = 5.8, 3.4 Hz, 1H), 3.92 (dd, *J* = 12.4, 0.8 Hz, 1H), 1.83 (t, *J* = 6.3 Hz, 1H), 1.11 – 0.99 (m, 2H), 0.92 (s, 9H), 0.89 (s, 9H), 0.83 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.063 (s, 3H), 0.055 (s, 3H), 0.05 (s, 9H), 0.04 (s, 3H), ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 143.4, 113.0, 93.6, 82.0, 80.3, 68.9, 65.0, 63.1, 61.7, 51.6, 26.2 (6 CH_3), 26.0, 18.6, 18.53, 18.47, 17.4, -1.4, -4.3, -4.4, −4.8, -4.9, -5.17, -5.21 ppm; IR (film): $\tilde{\nu}$ = 3465, 2953, 2929, 2895, 2857, 1677, 1597, 1472, 1388, 1344, 1285, 1250, 1218, 1177, 1077, 1043 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{33}H_{66}O_7Si_4Na^+$: 709.37779; found: 709.37757.

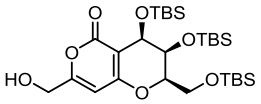


(2*R*,3*R*,4*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-7-(hydroxymethyl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one (S24). $SPhosAuNTf_2$ (2 mg, 0.002 mmol, 1 mol%) was added to a solution of **S22** (131 mg, 0.19 mmol) in CH_3NO_2 (1.3 mL) and the resulting mixture was stirred for 16 h. The reaction



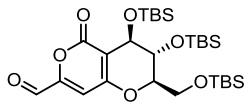
was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 2:1) afforded the title compound (100 mg, 89%). $[\alpha]_D^{20}$: +41.1 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.11 (s, 1H), 4.44 – 4.32 (m, 4H), 4.00 – 3.97 (m, 1H), 3.95 (dd, *J* = 10.7, 7.2 Hz, 1H), 3.81 (dd, *J* = 11.6, 4.3 Hz, 1H), 3.13 (bs, 1H), 0.88 (s, 9H), 0.85 (s, 9H), 0.81 (s, 9H), 0.19 (s, 3H), 0.14 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H), ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.3, 163.5, 163.2, 99.5, 99.2, 83.5, 68.1, 63.4, 62.4, 61.1, 26.0, 25.8, 25.7, 18.4, 18.2, 18.0, -4.6, −4.7, -4.8, -5.0, -5.1, -5.2 ppm; IR (film): $\tilde{\nu}$ = 3413, 2953, 2926, 2857, 1724, 1697, 1587, 1472, 1432, 1254, 1077 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{28}H_{54}O_7Si_3Na^+$: 609.30704; found: 609.30696.

(2*R*,3*S*,4*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-7-(hydroxymethyl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-one (S25). Prepared analogously



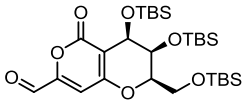
(198 mg, 89%). $[\alpha]_D^{20}$: +77.1 (c = 0.78, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.09 (s, 1H), 4.60 (dd, *J* = 3.2, 1.3 Hz, 1H), 4.41 (dd, *J* = 6.7, 0.7 Hz, 2H), 4.41 – 4.35 (m, 1H), 4.14 – 4.05 (m, 2H), 4.03 (dd, *J* = 5.8, 3.2 Hz, 1H), 2.06 (t, *J* = 6.7 Hz, 1H), 0.93 (s, 9H), 0.89 (s, 9H), 0.87 (s, 9H), 0.18 (s, 3H), 0.144 (s, 3H), 0.136 (s, 3H), 0.13 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.6, 163.4, 101.3, 99.1, 82.4, 69.1, 63.3, 62.2, 61.3, 26.1 (9 CH_3), 18.54, 18.52, 18.48, -4.3, -4.8 (4 CH_3), -4.9, -5.0, -5.1 ppm; IR (film): $\tilde{\nu}$ = 3413, 2929, 2857, 1719, 1654, 1580, 1471, 1423, 1361, 1286, 1252, 1178, 109, 1048, 1022, 1005 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{28}H_{54}O_7Si_3Na^+$: 609.30696; found: 609.30658.

(2*R*,3*R*,4*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-oxo-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-7-carbaldehyde (S26). Dess-Martin periodinane (564 mg, 1.33 mmol) was added in one portion to a solution of **S24** (600 mg, 1.02 mmol) in CH_2Cl_2 (5.1 mL) and the resulting mixture was stirred for 1.5 h. The reaction was quenched with sat aq. $Na_2S_2O_3$ and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 10:1) afforded the title compound (507 mg, 87%). $[\alpha]_D^{20}$: +68.5 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.52 (s, 1H), 6.71 (s, 1H), 4.47 – 4.41 (m, 1H), 4.40 (t, *J* = 2.5 Hz, 1H), 4.02 (dd, *J* = 2.8, 1.5 Hz, 1H), 3.96 (dd, *J* = 11.8, 8.2 Hz, 1H), 3.82 (dd, J = 11.9, 4.3 Hz, 1H), 0.89 (s, 9H), 0.86 (s, 9H), 0.82 (s, 9H), 0.22 (s, 3H), 0.17 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.5, 161.8, 161.3, 153.4, 108.7, 106.6, 84.0, 67.9 63.5, 62.2, 26.0, 25.8, 25.7, 18.5, 18.2, 18.0, -4.6, -4.7, -4.8, -4.9, -5.09, -5.12 ppm; IR (film):



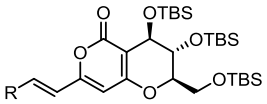
$\tilde{\nu}$ = 2953, 2929, 2857, 1734, 1714, 1642, 1584, 1432, 1254, 1081 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{28}H_{53}O_7Si_3Na^+$: 607.29131; found: 607.29207.

(2*R*,3*S*,4*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-oxo-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-7-carbaldehyde (S27). Prepared analogously (156 mg, 99%).



$[\alpha]_D^{20}$: +171.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): 9.50 (s, 1H), 6.69 (s, 1H), 4.62 (dd, *J* = 3.0, 1.3 Hz, 1H), 4.48 – 4.40 (m, 1H), 4.12 – 4.01 (m, 3H), 0.92 (s, 9H), 0.87 (s, 9H), 0.84 (s, 9H), 0.17 (s, 3H), 0.13 (m, 6H), 0.12 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.1, 161.6, 161.0, 153.7, 108.6, 107.8, 82.8, 68.8, 63.3, 61.9, 26.04 (6 CH_3), 26.03, 18.48, 18.47, 18.43, -4.3, -4.8, -4.89, -4.93, -5.0, -5.2 ppm; IR (film): $\tilde{\nu}$ = 2954, 2930, 2886, 2857, 1731, 1641, 1578, 1425, 1254, 1095 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{28}H_{53}O_7Si_3Na^+$: 607.30937; found: 607.30917.

(2*R*,3*R*,4*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-7-((*E*)-2-iodovinyl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-on (S28) and (2*R*,3*R*,4*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-7-vinyl-3,4-dihydro-2*H*,5*H*-pyrano-[4,3-*b*]pyran-5-on (S29). A solution of **S26** (540 mg, 0.92 mmol) and CHI_3 (727 mg, 1.85 mmol) in 1,4-dioxane (8.7 mL) was added dropwise to a suspension of $CrCl_2$·1.7 THF (1.36 g, 5.54 mmol) in THF (8.7 mL) at 0 °C. The mixture was stirred for 2 h before the reaction was quenched with sat. aq. NH_4Cl. The aqueous phase was extracted with *t*BuOMe, the combined organic extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solution was concentrated. The residue was purified by flash chromatography (SiO_2, hexane:EtOAc, 100:1) affording **S28** (365 mg, 56%) and **S29** (58 mg, 11%) as a yellow solid each.



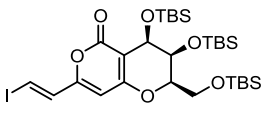
R = I **S28**
R = H **S29**

Analytical and spectral data of **S28:** $[\alpha]_D^{20}$: +53.1 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 14.4 Hz, 1H), 6.95 (d, *J* = 14.7 Hz, 1H), 5.82 (s, 1H), 4.41 – 4.31 (m, 2H), 4.00 – 3.91 (m, 2H), 3.79 (dd, *J* = 11.9, 4.0 Hz, 1H), 0.88 (s, 9H), 0.85 (s, 9H), 0.81 (s, 9H), 0.20 (s, 3H), 0.15 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.1, 162.7, 136.0, 101.3, 101.1, 87.2, 83.6, 68.2, 63.5, 62.4, 26.0, 25.9, 25.7, 18.5, 18.2, 18.1, -4.6, -4.7, -4.8, -4.9, -5.08, -5.13 ppm; IR (film): $\tilde{\nu}$ = 2953, 2929, 2857, 1726, 1642, 1579, 1471, 1422, 1255, 1077 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{53}O_6Si_3INa^+$: 731.20869; found: 731.20902.

Analytical and spectral data of **S29:**$[\alpha]_D^{20}$: +32.2 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (s, 1H), 7.01 (s, 2H), 6.57 (s, 1H), 4.44 – 4.38 (m, 1H), 4.37 (t, *J* = 2.3 Hz, 1H), 4.03 – 3.95 (m, 2H), 3.81 (dd, *J* = 11.9, 4.0 Hz, 1H), 0.89 (s, 9H), 0.86 (s, 9H), 0.83 (s, 9H), 0.22 (s, 3H), 0.18 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H) ppm, ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.1, 162.4, 130.6, 103.3,

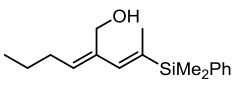
101.5, 84.9, 83.5, 68.2, 63.5, 62.4, 26.0, 25.9, 25.8, 18.5, 18.2, 18.1, -4.5, -4.6, -4.8, -4.96, -5.02, -5.1 ppm, IR (film): $\tilde{\nu}$ = 2954, 2929, 2857, 1722, 1639, 1579, 1423, 1255, 1076 cm^{-1}, HRMS (ESI): *m/z* calcd. for $C_{29}H_{54}O_6Si_3Na^+$: 582.32282, found: 582.32315.

(2*R*,3*S*,4*R*)-3,4-Bis((*tert*-butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-7-((*E*)-2-iodovinyl)-3,4-dihydro-2*H*,5*H*-pyrano[4,3-*b*]pyran-5-on (S30) Prepared analogously (105 mg, 55%).



$[\alpha]_D^{20}$: +41.6 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 14.6 Hz, 1H), 6.94 (d, J = 14.7 Hz, 1H), 5.82 (s, 1H), 4.59 (dd, J = 3.1, 1.1 Hz, 1H), 4.42 – 4.34 (m, 1H), 4.11 – 3.99 (m, 3H), 0.93 (s, 9H), 0.89 (s, 9H), 0.86 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.031 (s, 3H), 0.025 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.0, 162.4, 157.3, 135.8, 102.6, 101.2, 87.9, 82.4, 69.0, 63.3, 62.1, 26.11 (6 CH_3), 26.10, 18.6, 18.52, 18.48, -4.3, -4.8 (2 CH_3), -4.9, -5.0, -5.1 ppm; IR (film): $\tilde{\nu}$ = 2954, 2929, 2857, 1723, 1639, 1573, 1471, 1412, 1361, 1285, 1254, 1094, 1050 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{29}H_{53}O_6Si_3INa^+$: 731.20869; found: 731.20915.

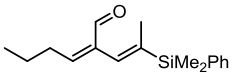
***(Z)*-2-(Prop-1-yn-1-yl)hex-2-en-1-ol (S31).** Ethyl-3,3,3-trifluoropyruvate (0.70 mL, 5.28 mmol) was added dropwise to a solution of 2-hexyn-1-ol (0.50 mL, 4.55 mmol) at room temperature and the resulting mixture was stirred for 30 min before it was cooled to –78 °C. Thexylborane (0.9 M in THF, 5.80 mL, 5.22 mmol)[8] was added dropwise, the mixture was stirred for 5 min at –78 °C before it was warmed to room temperature and stirred for 10 min. TMAO (531 mg, 4.78 mmol) was added in one portion and stirring was continued for 15 min at room temperature before a degassed solution of KOH (11.40 mL, 34.20 mmol, 3 M in H_2O) was introduced. After stirring for an additional 10 min, 1-iodo-1-propyne (3.78 g, 22.75 mmol)[7] and Pd(dppf)Cl_2 (371 mg, 0.46 mmol) were added and the mixture was stirred at 70 °C (bath temperature) for 1.5 h. The reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 10:1) afforded the title compound (420 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88 (t, *J* = 7.7 Hz, 1H), 4.15 (d, *J* = 6.0 Hz, 1H), 2.09 (q, *J* = 7.5 Hz, 2H), 1.97 (s, 3H), 1.71 (t, *J* = 6.2 Hz, 1H), 1.40 (hex, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.5, 123.2, 85.3, 79.2, 60.3, 30.2, 22.6, 13.9, 4.4 ppm; IR (film): $\tilde{\nu}$ = 3380, 2959, 2931, 2918, 2872, 1461, 1378, 1336, 1033, 998 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_9H_{14}ONa^+$: 161.09376, found: 161.09368.



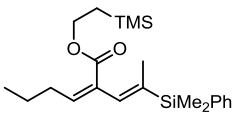
(*Z*)-2-((*E*)-2-(Dimethyl(phenyl)silyl)prop-1-en-1-yl)hex-2-en-1-ol (S32). $PhMe_2SiLi$ (1 M in THF, 45 mL, 45 mmol) was added dropwise to a suspension of CuCN (1.65 g, 18.42 mmol) in THF (15 mL) at –50 °C. The mixture was warmed to –10 °C and

stirred for 45 min. After cooling to –50 °C, water (0.95 mL, 52.73 mmol) was added, the mixture was warmed to –10 °C and stirring was continued for 45 min. After cooling to –50 °C, a solution of **S31** (1.07 g, 7.74 mmol) in THF (15 mL) was added dropwise, the mixture was warmed to –10 °C and stirred at this temperature for 2 h. The reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 20:1 to 10:1) afforded the title compound (1.76 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.49 (m, 2H), 7.37 – 7.33 (m, 3H), 6.27 (s, 1H), 5.53 (t, *J* = 7.6 Hz, 1H), 4.23 (s, 2H), 2.18 (q, *J* = 7.4 Hz, 2H), 1.86 (d, J = 1.8 Hz, 3H), 1.44 (hex, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.38 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 139.4, 138.4, 137.9, 136.4, 134.2, 134.1, 129.0, 127.9, 60.7, 30.1, 23.1, 16.8, 14.0, -3.3 ppm. IR (film): $\tilde{\nu}$ = 3355, 2957, 2872, 1591, 1427, 1377, 1247, 1110, 998, 949 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{17}H_{26}OSiNa^+$: 297.16429, found: 297.16451.

(*Z*)-2-((*E*)-2-(Dimethyl(phenyl)silyl)prop-1-en-1-yl)hex-2-enal (S33). Dess-Martin-periodinane (636 mg, 1.5 mmol) was added in one portion to a solution of **S32** (275 mg, 1.00 mmol) in CH_2Cl_2 (10 mL) at room temperature. The resulting mixture was stirred for 1.5 h before the reaction was quenched with sat. aq. $Na_2S_2O_3$ and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 20:1) afforded the title compound (226 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.13 (s, 1H), 7.55 – 7.51 (m, 2H), 7.37 – 7.33 (m, 3H), 6.54 (dt, *J* = 4.2, 1.0 Hz, 1H), 6.48 – 6.44 (m, 1H), 2.69 – 2.60 (m, 2H), 1.75 (d, *J* = 1.8 Hz, 3H), 1.62 – 1.52 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H), 0.40 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.0, 151.7, 140.4, 138.0, 137.1, 134.2, 133.6, 129.1, 127.9, 29.2, 23.0, 17.1, 13.9, -3.4 ppm; IR (film): $\tilde{\nu}$ = 2959, 2872, 1744, 1678, 1603, 1427, 1373, 1248, 1192, 1111 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{17}H_{24}OSiNa^+$: 272.15937, found: 272.15964.



2-(Trimethylsilyl)ethyl (*Z*)-2-((*E*)-2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)hex-2-enoate (S34). NaH_2PO_4 (745 mg, 6.21 mmol) and H_2O_2 (35% in water, 1.10 mL, 11.32 mmol) were added to a solution of **S33** (561 mg, 2.06 mmol) in *t*BuOH/water (1:1) (6.50 mL) at 0 °C. The mixture was stirred for 10 min, $NaClO_2$ (895 mg, 9.90 mmol) was added, and stirring was continued for 18 h at room temperature. The reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with hexane. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the



solvent was evaporated. The crude acid was dried in vacuum and used in the next step without further purification.

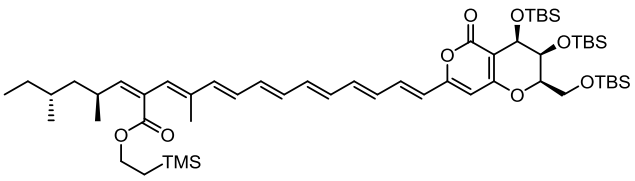
DEAD (1.14 mL, 6.26 mmol) was added over 30 min to a solution of the crude acid, PPh_3 (1.95 g, 7.43 mmol) and 2-TMS-ethanol (0.81 mL, 5.65 mmol) in THF (10.30 mL) at 0 °C. After stirring for 2 h, the reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 100:1) afforded the title compound (514 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 – 7.47 (m, 2H), 7.39 – 7.30 (m, 3H), 6.35 (dd, *J* = 1.5, 1.0 Hz, 1H), 5.88 (td, *J* = 3.8, 0.8 Hz, 1H), 4.30 – 4.19 (m, 2H), 2.38 (q, *J* = 7.4 Hz, 2H), 1.73 (d, *J* = 1.8 Hz, 3H), 1.53 – 1.41 (m, 2H), 1.07 – 1.00 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.37 (s, 6H), 0.05 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.7, 143.2, 138.2, 137.6, 136.3, 134.2, 131.3, 129.1, 127.9, 62.9, 31.6, 22.7, 17.4, 16.4, 14.1, -1.4, -3.4 ppm; IR (film): $\tilde{\nu}$ = 2956, 2899, 1456, 1428, 1380, 1328, 1249, 1211, 1157, 1111 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{22}H_{36}O_2Si_2Na^+$: 411.21468, found: 411.21461.

2-(Trimethylsilyl)ethyl (*Z*)-2-((*E*)-2-iodoprop-1-en-1-yl)hex-2-enoate (S35). NIS (165 mg, 0.73 mmol) was added in one portion to a solution of **S34** (190 mg, 0.49 mmol) and 2,6-lutidine (86 µL, 0.74 mmol) in hexafluoroisopropanol (1.50 mL) at 0 °C. The mixture was stirred for 2 min before the reaction was quenched with sat. aq. $Na_2S_2O_3$ and the aqueous phase was extracted with *t*BuOMe. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated. Purification of the crude product by flash chromatography (SiO_2, hexanes:EtOAc, 100:1) afforded the title compound (156 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85 – 6.78 (m, 1H), 5.94 (td, *J* = 3.8, 1.3 Hz, 1H), 4.28 – 4.20 (m, 2H), 2.49 – 2.40 (m, 2H), 2.46 (d, *J* = 1.5 Hz, 3H), 1.53 – 1.41 (m, 2H), 1.07 – 1.00 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H), 0.05 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6, 146.1, 138.4, 130.0, 89.3, 63.1, 31.6, 29.1, 22.5, 17.4, 14.0, -1.3 ppm; IR (film): $\tilde{\nu}$ = 2956, 1714, 1631, 1456, 1428, 1379, 1248, 1218, 1157, 1069 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{14}H_{25}O_2SiINa^+$: 403.05626, found: 403.05608.

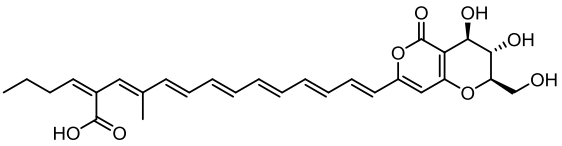
Compound S36. *This reaction was performed in the dark.* $Pd(CH_3CN)_2Cl_2$ (1.5 mg, 0.005 mmol) was added to a degassed (pump and freeze, 3 cycles) solution of Ph_3As (3.2 mg, 0.01 mmol) in DMF (0.05 mL) and the mixture was stirred for 5 min. The resulting mixture was transferred to a degassed (pump and freeze, 3 cycles) solution of **S34** (40 mg, 0.105 mmol), tetraene **35** (55 mg, 0.105 mmol) and $[Ph_2PO_2][NBu_4]$ (146 mg, 0.32 mmol)[11] in DMF (0.5 mL) and stirring was continued for 20 h at room temperature. Degassed K_3PO_4 (3 M in

water, 0.05 mL, 0.15 mmol) was then added, followed by a solution of pyrone **S28** (68 mg, 0.095 mmol) in THF (0.5 mL) and Pd(dppf)Cl_2 (7.7 mg, 0.01 mmol). The resulting mixture was stirred for 16 h, the reaction was quenched with water and the aqueous phase was extracted with Et_2O. The combined extracts were washed with brine and dried over $MgSO_4$. The drying agent was filtered off and the solvent was evaporated (below 20°C). Purification of the crude product by flash chromatography (SiO_2, hexanes + 2.5% NEt_3) afforded the title compound (48 mg, 54%). $[\alpha]_D^{20}$: +47.0 (c = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.52 (dd, *J* = 14.9, 10.6 Hz, 1H), 6.47 – 6.27 (m, 7H), 6.15 (s, 1H), 6.03 (d, *J* = 15.9 Hz, 1H), 5.92 (t, *J* = 7.6 Hz, 1H), 5.82 s, 1H), 4.42 – 4.33 (m, 2H), 4.29 – 4.22 (m, 2H), 4.01 – 3.92 (m, 2H), 3.81 (dd, *J* = 11.7, 4.2 Hz, 1H), 2.41 (q, *J* = 7.5 Hz, 2H), 1.83 (s, 3H), 1.48 (q, *J* = 7.4 Hz, 2H), 1.09 – 1.00 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.89 (s, 9H), 0.86 (s, 9H), 0.82 (s, 9H), 0.22 (s, 3H), 0.17 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.06 – 0.03 (m, 12H), 0.02 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.3, 163.7, 163.2, 158.4, 143.8, 139.3, 138.7, 136.5, 135.9, 135.64, 135.55, 132.7, 132.3, 131.3, 131.2, 130.4, 128.8, 121.8, 101.0, 100.0, 83.4, 68.4, 63.6, 63.0, 62.5, 31.9, 26.0, 25.9, 25.8, 22.7, 18.5, 18.2, 18.1, 17.5, 14.0, 13.8, -1.4, -4.55, -4.63, -4.8, -4.9, -5.07, -5.14 ppm; IR (film): $\tilde{\nu}$ = 2954, 2929, 2857, 1715, 1635, 1568, 1543, 1426, 1252, 1217, 1075, 1005 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{51}H_{86}O_8Si_4Na^+$: 731.20869, found: 731.20902.

Compound S37. Prepared analogously as a red oil (18 mg, 56%). $[\alpha]_D^{20}$: +88 (c = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (dd, *J* = 15.0, 11.4 Hz, 1H), 6.54 (dd, *J* = 14.5, 10.7 Hz, 1H), 6.50 – 6.27 (m, 7H); 6.13 (s, 1H), 6.02 (d, *J* = 15.1 Hz, 1H), 5.83 (s, 1H), 5.66 (dd, *J* = 10.3, 0.8 Hz, 1H); 4.62 (dd, *J* = 3.1, 1.2 Hz, 1H), 4.39 – 4.33 (m, 1H), 4.29 – 4.22 (m, 2H), 4.14 – 4.05 (m, 2H), 4.03 (dd, *J* = 5.6, 3.2 Hz, 1H), 3.08 – 2.95 (m, 1H), 1.83 (d, *J* = 0.9 Hz, 3H), 1.39 – 1.25 (m, 3H), 1.13 – 1.03 (m, 4H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.93 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.85 (d, *J* = 6.2 Hz, 3H), 0.84 (t, *J* = 6.6 Hz, 3H), 0.19 (s, 3H), 0.16 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.05 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.4, 163.5, 163.1, 158.9, 149.8, 139.5, 139.1, 136.8, 136.3, 135.9, 135.5, 132.7, 132.3, 131.0 ,130.6, 129.6, 128.7, 121.5, 101.5, 100.8, 82.2, 69.1, 63.4, 63.1, 62.3, 44.5, 32.2, 31.8, 29.3, 26.2, 26.1 (6 CH_3), 20.7, 19.6, 18.57, 18.55, 18.5, 17.6, 13.7, 11.3, -1.4, -4.2, -4.7, -4.8, -4.9, -5.0, -5.1 ppm; IR (film): $\tilde{\nu}$ = 2956, 2928, 2857, 1721, 1633, 1543, 1462, 1416, 1379, 1361, 1251, 1205, 1166, 1123, 1070, 1050, 1005 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{55}H_{94}O_8Si_4Na^+$: 1017.59180, found: 1017.59249.

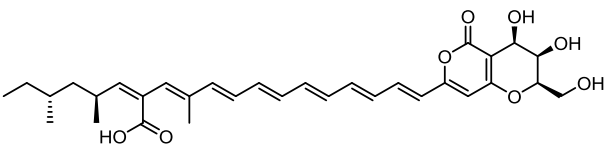


Compound 39. *This reaction was performed in the dark.* A solution of TASF (62 mg, 0.225 mmol) in

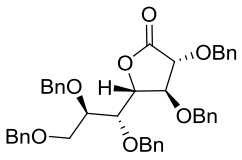


DMF (0.3 mL) was added to a solution of **S37** (30 mg, 0.031 mmol) in DMF (0.3 mL) at 0 °C. The resulting mixture was stirred for 30 min at 0 °C and for 18 h at room temperature before the reaction was quenched with aq. HCl. The aqueous phase (pH = 3) was extracted with EtOAc, the combined extracts were dried over $MgSO_4$, the drying agent was filtered off and the solvent was evaporated (below 20 °C). Purification of the crude product by HPLC (column: 150 mm YMC Actus, Ø = 20 mm; stationary phase: YMC ODS-A, 5 µm, 20150 00456; eluent: methanol / TFA in water pH 3.5 = 75:25) afforded the title compound (8.6 mg, 54%). $[\alpha]_D^{20}$: +10.2 (c = 0.5, DMSO); ^{1}H NMR (600 MHz, [D_6]-DMSO): δ = 12.72 (bs, 1H), 7.04 (dd, *J* = 15.2, 11.4 Hz, 1H), 6.72 (dd, *J* = 14.6, 11.2 Hz, 1H), 6.57 – 6.38 (m, 7H), 6.33 (d, *J* = 15.2 Hz, 1H), 6.21 (s, 1H), 6.15 (s, 1H), 5.88 (t, *J* = 7.8 Hz, 1H), 5.41 (d, *J* = 4.8 Hz, 1H), 5.32 (d, *J* = 3.8 Hz, 1H), 4.95 (t, *J* = 5.5 Hz, 1H), 4.29 (m, 1H), 4.23 (m, 1H), 3.88 – 3.80 (m, 1H), 3.75 – 3.68 (m, 1H), 3.66 – 3.58 (m, 1H), 2.30 (dt, *J* = 7.8, 7.3 Hz, 2H), 1.81 (s, 3H), 1.42 (h, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (151 MHz, [D_6]-DMSO): δ = 169.3, 163.2, 162.5, 157.6, 140.7, 138.9, 138.6, 136.3, 135.4, 134.62, 134.56, 132.9, 132.6, 132.5, 131.4, 130.4, 128.8, 122.1, 101.0, 100.2, 82.4, 67.0, 61.9, 60.2, 31.2, 22.1, 13.7, 13.2 ppm; IR (film): $\tilde{\nu}$ = 3450, 2995, 2912, 1662, 1436, 1407, 1310, 1042, 1026, 952 cm^{-1}; HRMS (EI): *m/z* calcd. for $C_{28}H_{31}O_8^-$: 495.20245, found: 495.20314.

Compound 40. Prepared analogously from (*R,S*)-**29** and **S30** as a red solid (5 mg, 50%). $[\alpha]_D^{20}$: –32 (c =



0.05, DMSO); ^{1}H NMR (600 MHz, [D_6]-DMSO): δ = 12.76 (bs, 1H), 7.04 (dd, *J* = 15.2, 11.4 Hz, 1H), 6.73 (dd, *J* = 14.5, 11.4 Hz, 1H), 6.53 (dd, *J* = 14.3, 10.5 Hz, 1H), 6.50 – 6.40 (m, 6H), 6.32 (d, *J* = 15.2 Hz, 1H), 6.20 (s, 1H), 6.13 (s, 1H), 5.64 (d, *J* = 10.3 Hz, 1H), 5.20 (bs, 1H), 5.10 (bd, *J* = 4.7 Hz, 1H), 4.96 (m, 1H), 4.50 (m, 1H), 4.22 (dt, *J* = 6.4, 3.8 Hz, 1H), 3.93 (dd, *J* = 5.8, 3.0 Hz, 1H), 3.78 – 3.67 (m, 2H), 2.88 (ddqd, *J* = 10.3, 7.7, 6.6, 6.4 Hz1H), 1.81 (s, 1H), 1.36 – 1.28 (m, 2H), 1.25 (dt, *J* = 13.3, 6.4 Hz, 1H), 1.13 (ddd, *J* = 13.3, 7.7, 6.1 Hz, 1H), 1.09 – 1.02 (m, 1H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.811 (d, *J* = 6.7 Hz, 3H), 0.806 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (151 MHz, [D_6]-DMSO): δ = 169.4, 164.2, 162.1, 157.7, 146.7, 139.0, 138.7, 136.4, 135.5, 134.8, 134.6, 132.9, 132.6, 131.3, 130.8, 130.4, 128.8, 122.0, 101.0, 100.7, 80.1, 64.7, 61.6, 59.3, 43.8, 31.6, 31.3, 28.5, 20.6, 19.4, 13.2, 11.0 ppm; IR (film): $\tilde{\nu}$ = 3396, 2940, 2913, 2822, 2253, 2126, 1662, 1446, 1411, 1050, 1023, 1003 cm^{-1}; HRMS (ESI): *m/z* calcd. for $C_{32}H_{39}O_8^-$:, 551.26505 found: 551.26579.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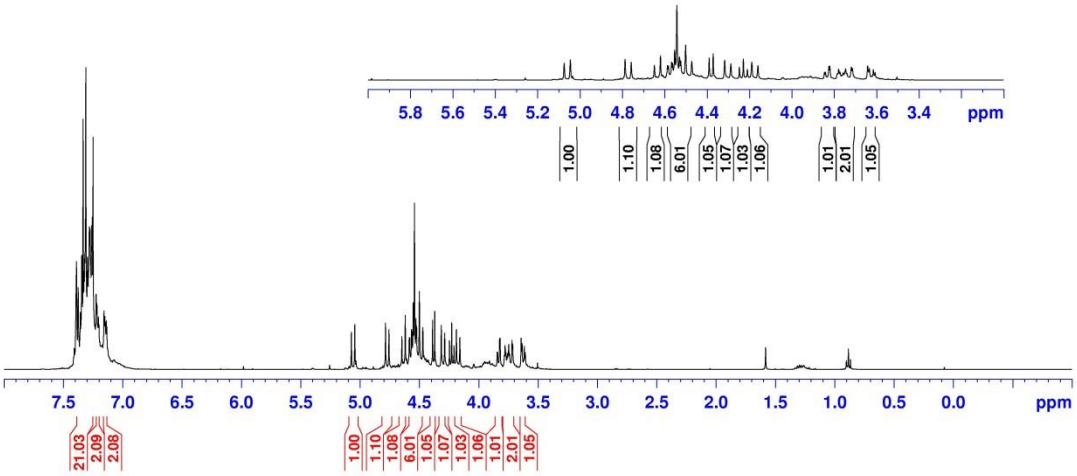
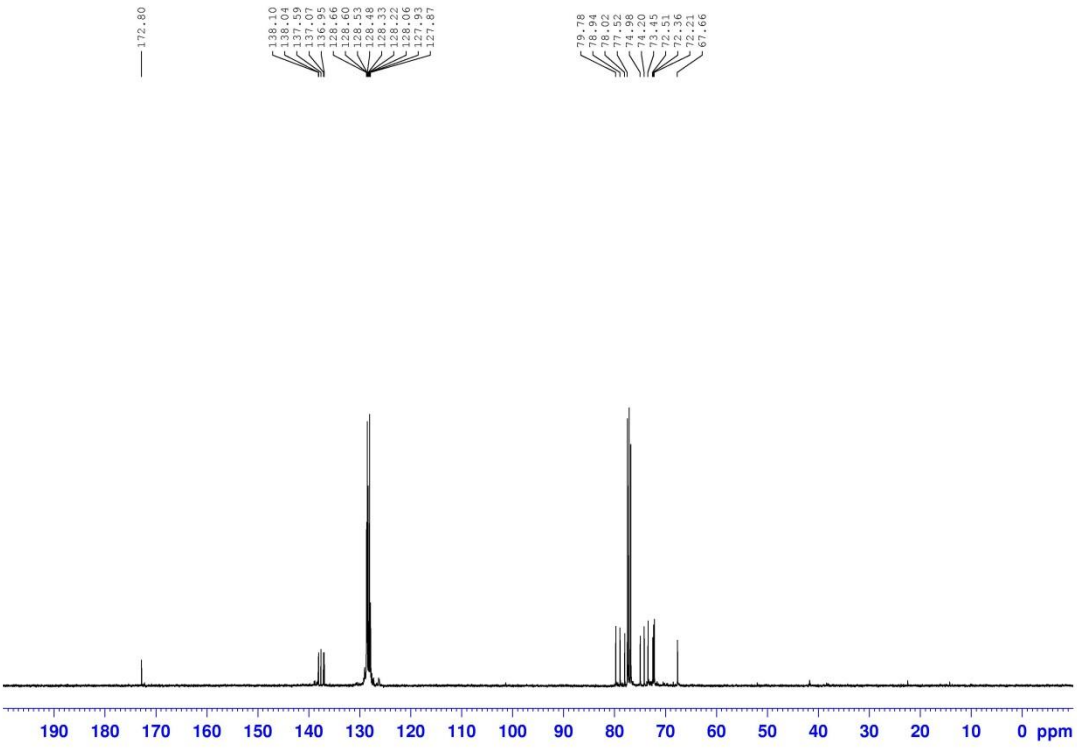
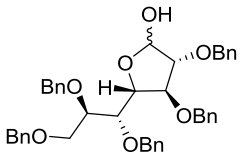
O
OBn
BnO
H
OBn
BnO
OBn


5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm
1.00 1.10 1.08 6.01 1.05 1.07 1.03 1.06 1.01 2.01 1.05
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
21.03 2.09 2.08
1.00 1.10 1.08 6.01 1.05 1.07 1.03 1.06 1.01 2.01 1.05


172.80
138.10
138.04
137.59
137.07
136.95
128.66
128.60
128.53
128.48
128.33
128.22
128.06
127.93
127.87
79.78
78.94
78.02
77.52
74.98
74.00
73.45
72.51
72.36
72.21
67.66
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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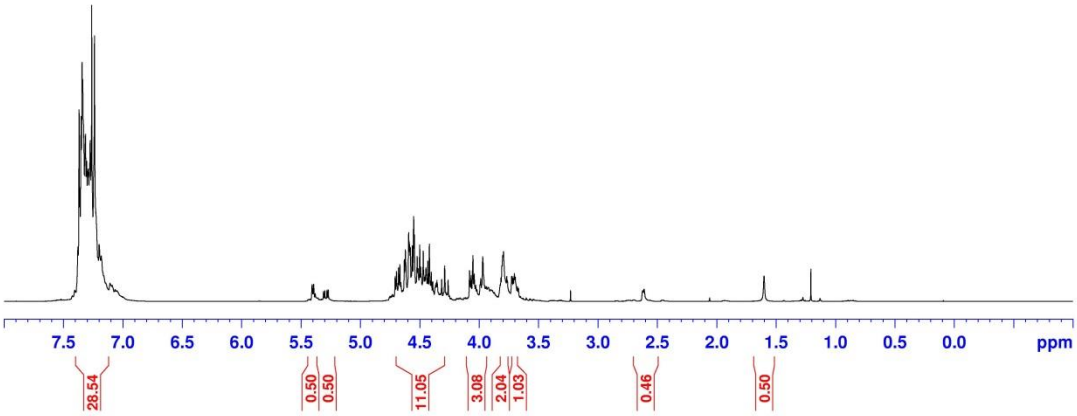
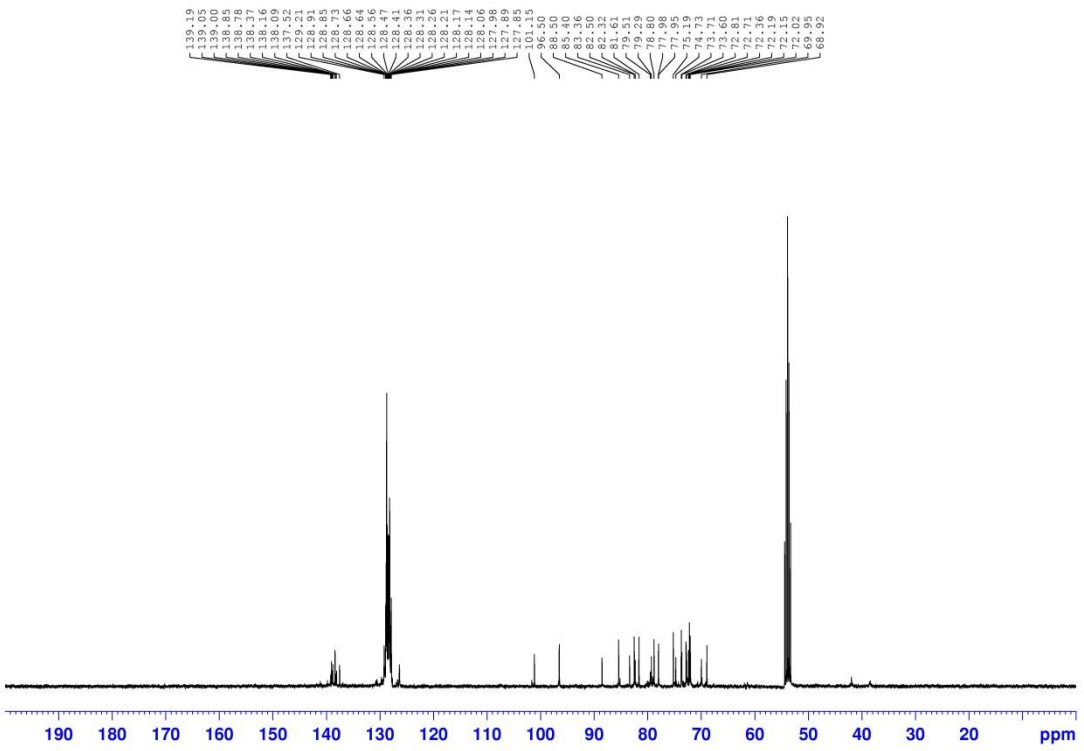
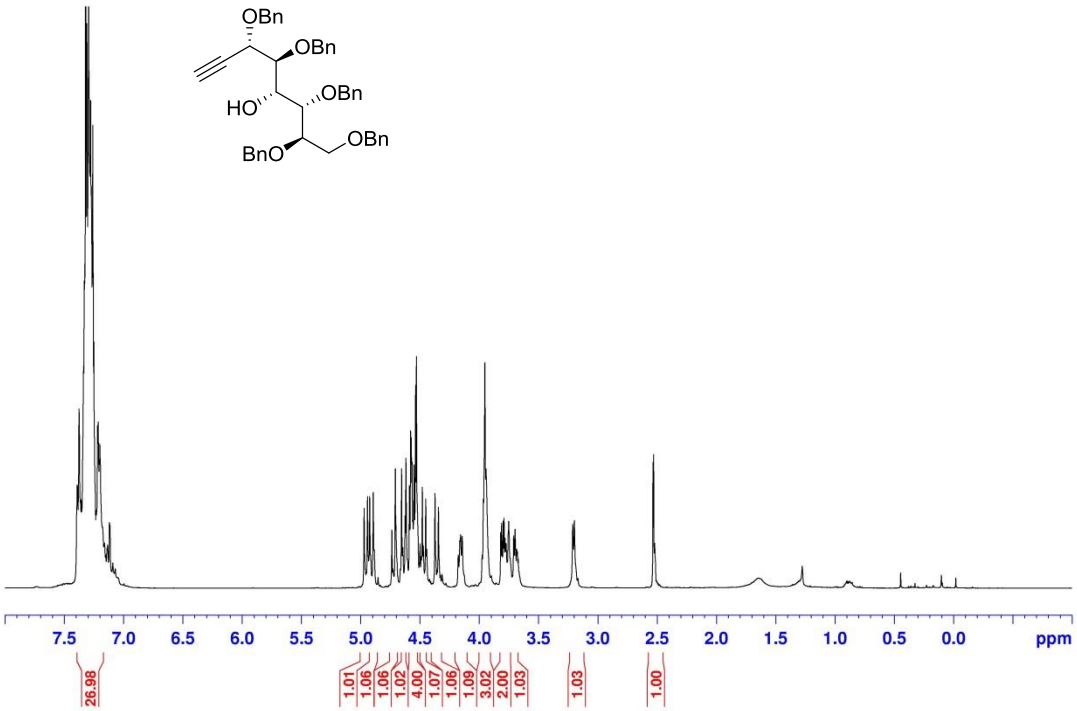
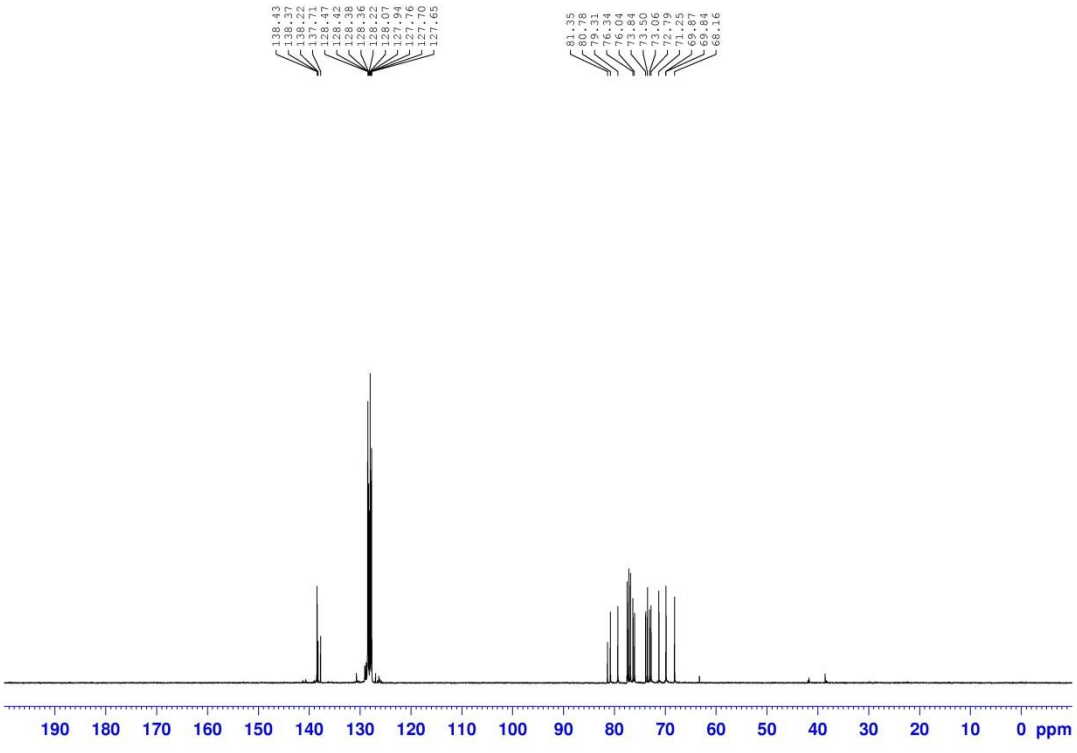
O
OBn
BnO
H
OBn
BnO
OBn


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
28.54
0.50
0.50
11.05
3.08
2.04
1.03
0.46
0.50


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


OBn
OBn
HO
OBn
BnO
OBn
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
26.98
1.01
1.06
1.06
1.02
4.00
1.07
1.06
1.09
3.02
2.00
1.03
1.03
1.00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137.71
128.47
128.42
128.38
128.36
128.22
128.07
127.94
127.76
127.70
127.65
81.35
80.78
79.31
76.34
76.04
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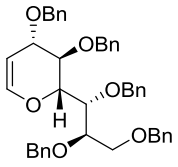
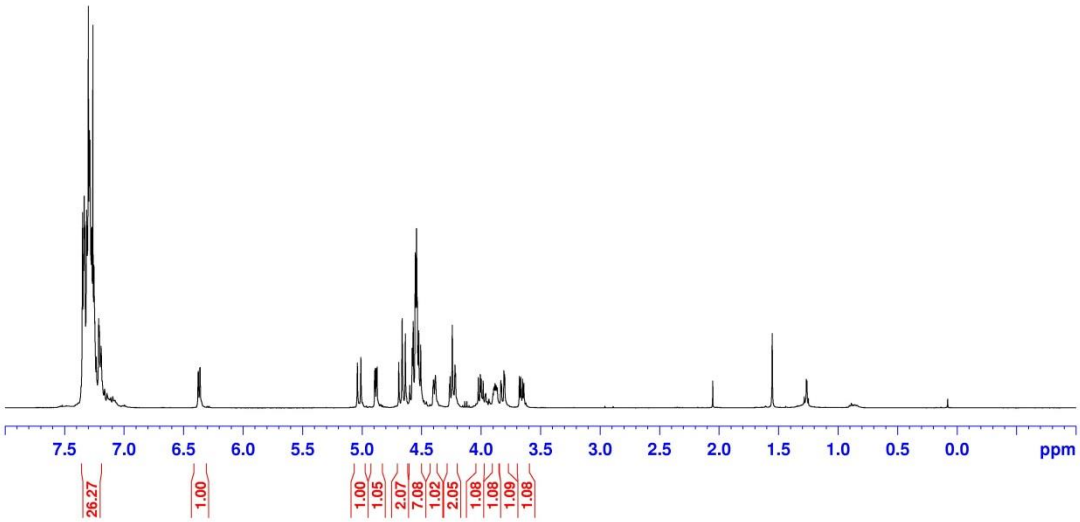
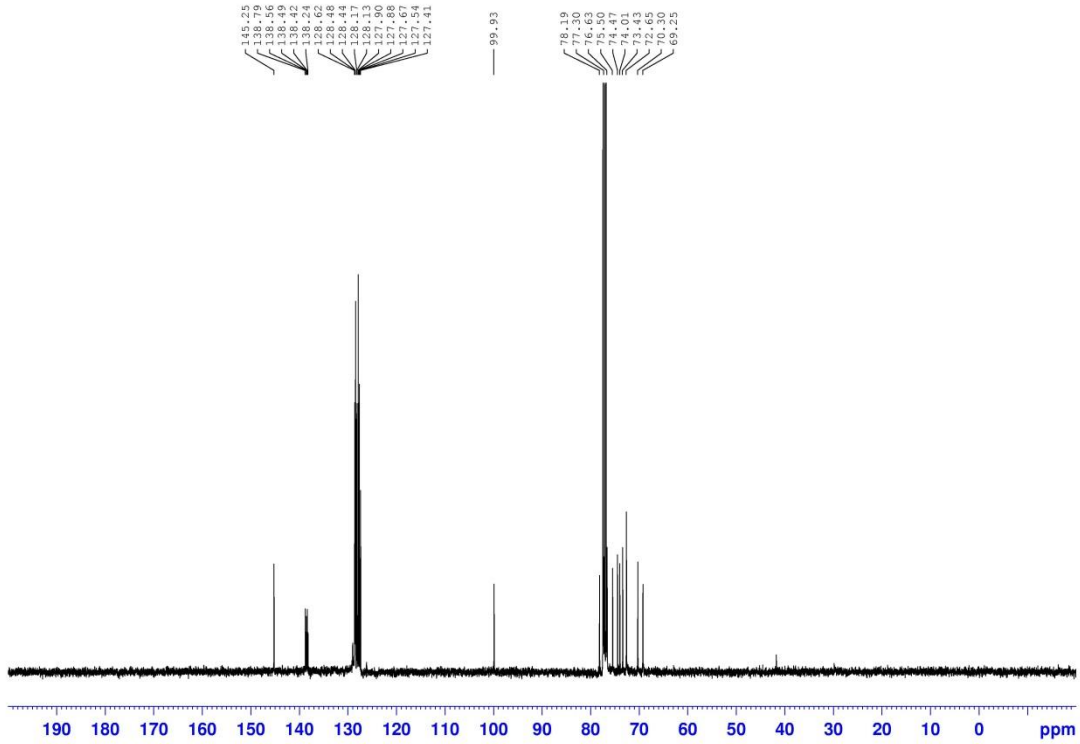
68.16
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OBn
OBn
OBn
O
H
BnO
OBn


7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
26.27
1.00
1.00
1.05
2.07
7.08
1.02
2.05
1.08
1.08
1.09
1.08


145.25
138.79
138.56
138.49
138.42
138.24
128.62
128.48
128.44
128.17
128.13
127.90
127.88
127.67
127.54
127.41
99.93
78.19
77.30
76.63
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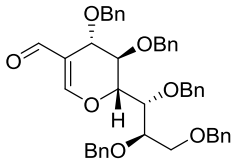
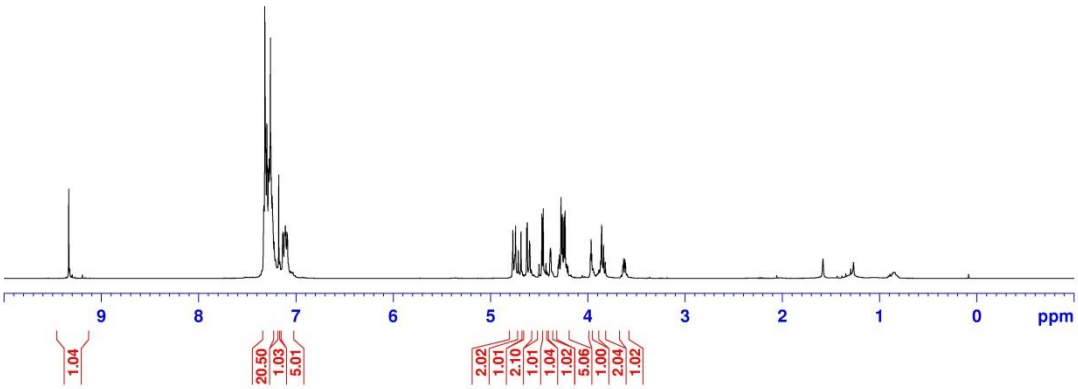
69.25
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OBn
OBn
OBn
O
O
H
BnO
OBn


9
8
7
6
5
4
3
2
1
0
ppm
1.04
20.50
1.03
5.01
2.02
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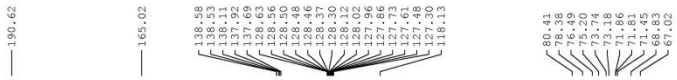
1.04
1.02
5.06
1.00
2.04
1.02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137.92
137.69
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128.56
128.50
128.48
128.46
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128.30
128.12
128.02
127.96
127.86
127.73
127.61
127.48
127.30
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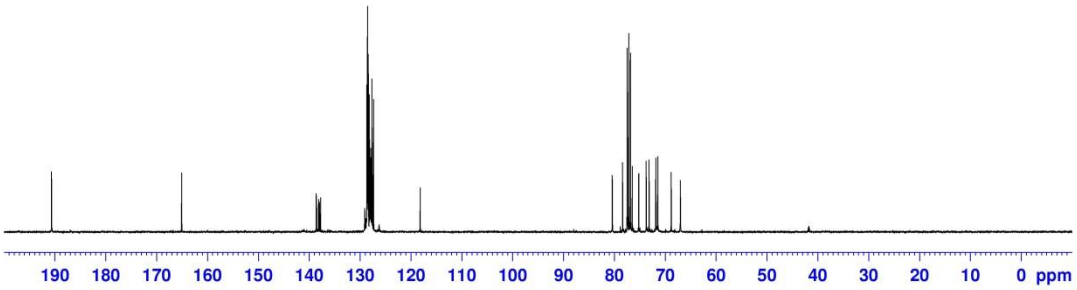
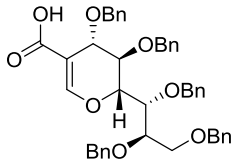
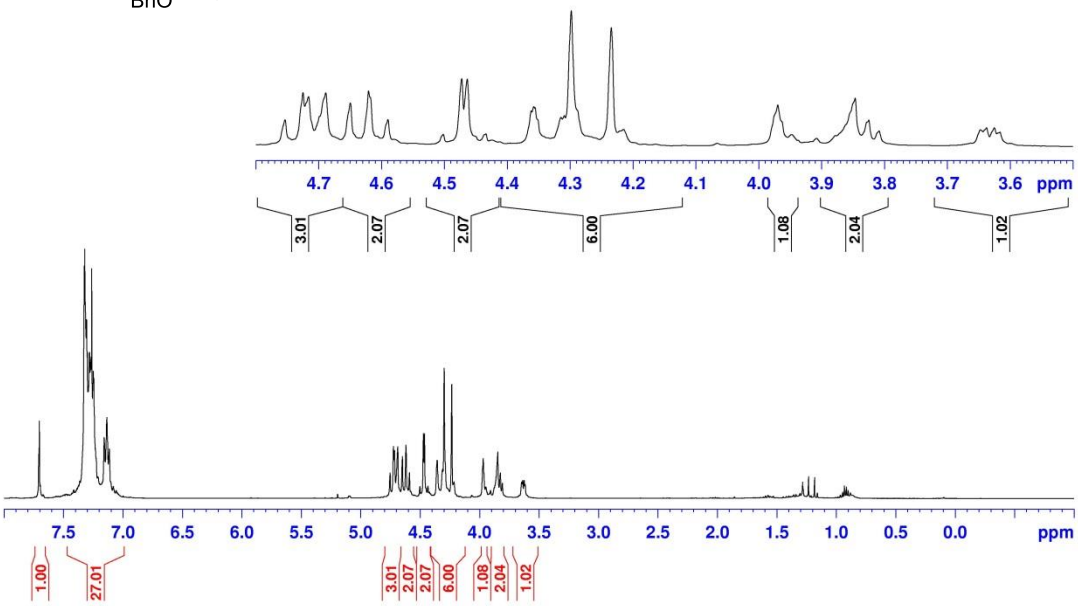
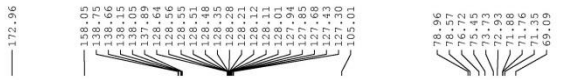
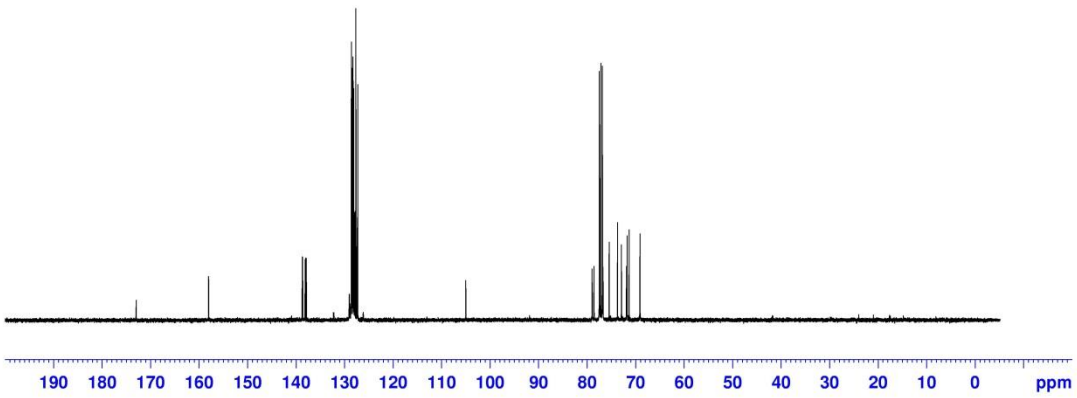
73.18
71.86
71.61
71.45
69.83
67.02

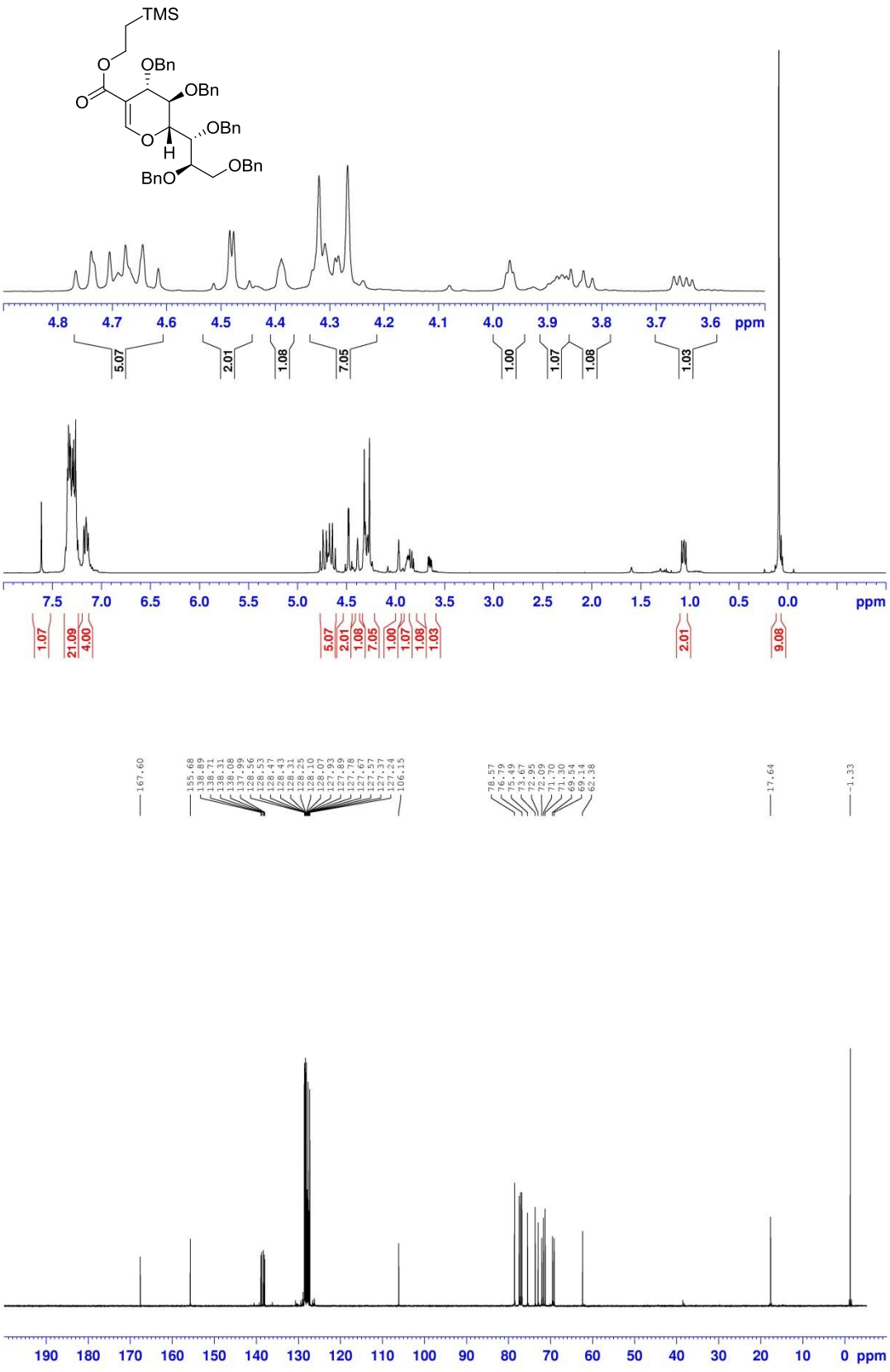

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

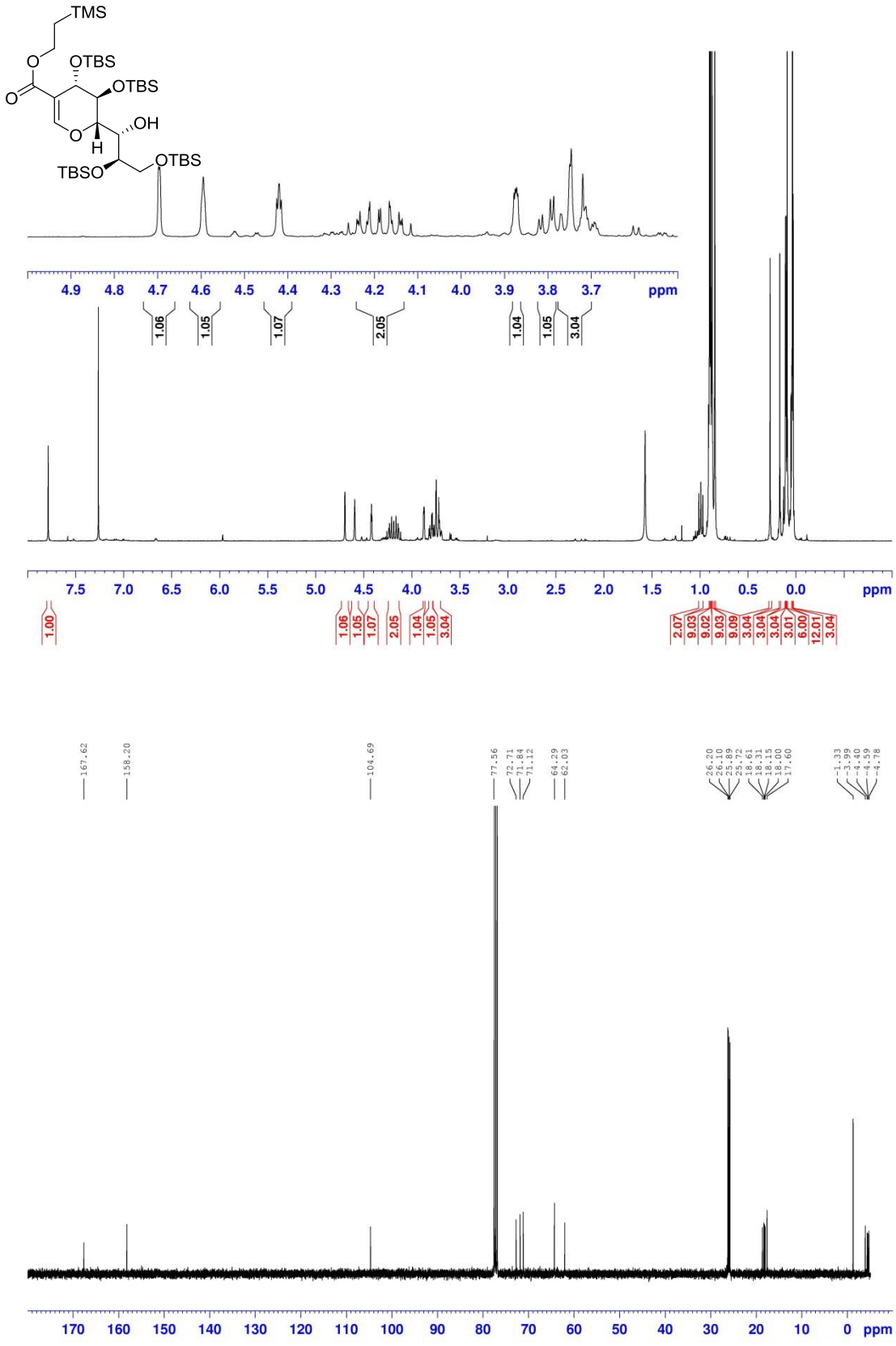

OH
OBn
OBn
OBn
OBn
O
O
H
BnO

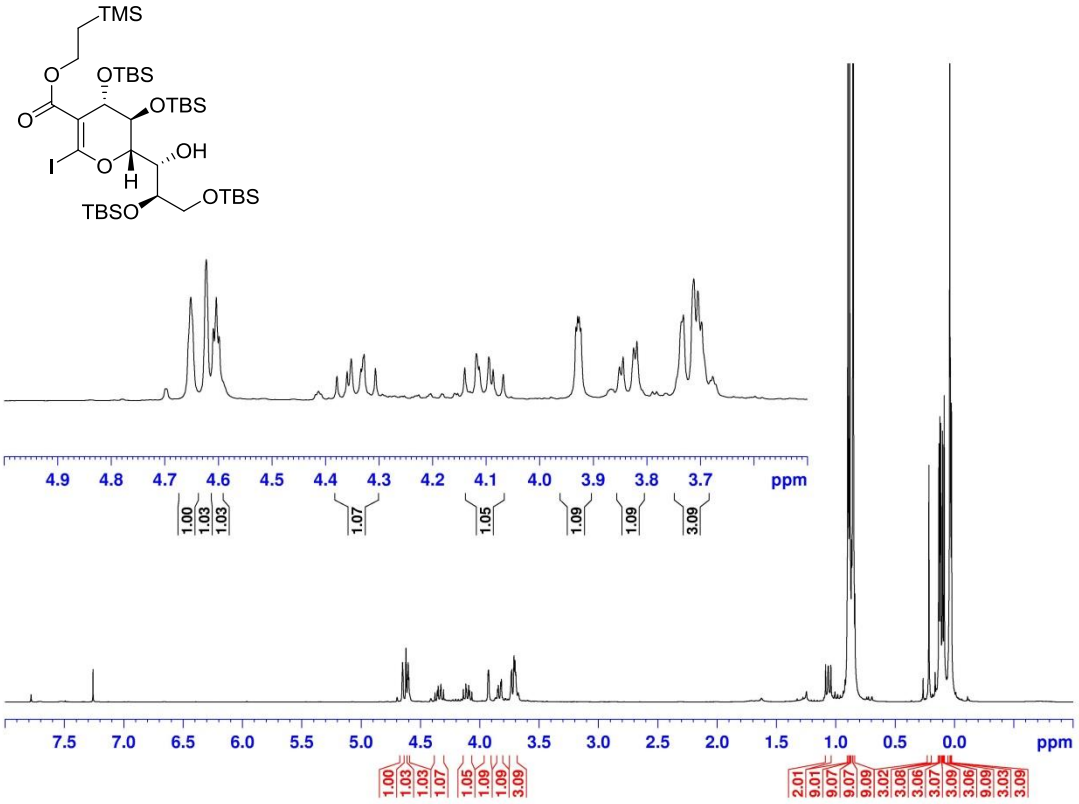

4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 ppm
3.01 2.07 2.07 6.00 1.08 2.04 1.02
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 27.01 3.01 2.07 2.07 6.00 1.08 2.04 1.02

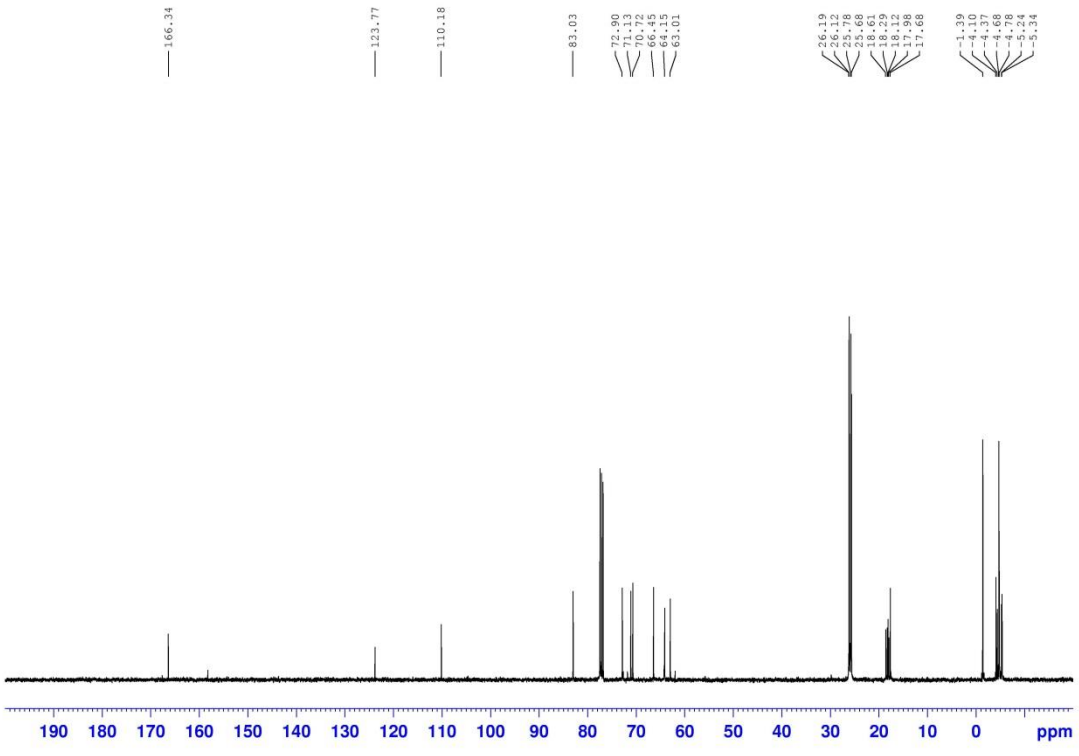

172.96
158.05
138.75
138.66
138.15
138.05
137.89
128.64
128.56
128.55
128.51
128.48
128.35
128.28
128.21
128.12
128.11
128.01
127.94
127.85
127.68
127.43
127.30
105.01
78.96
78.57
76.72
76.45
73.73
72.93
71.88
71.76
71.35
69.09

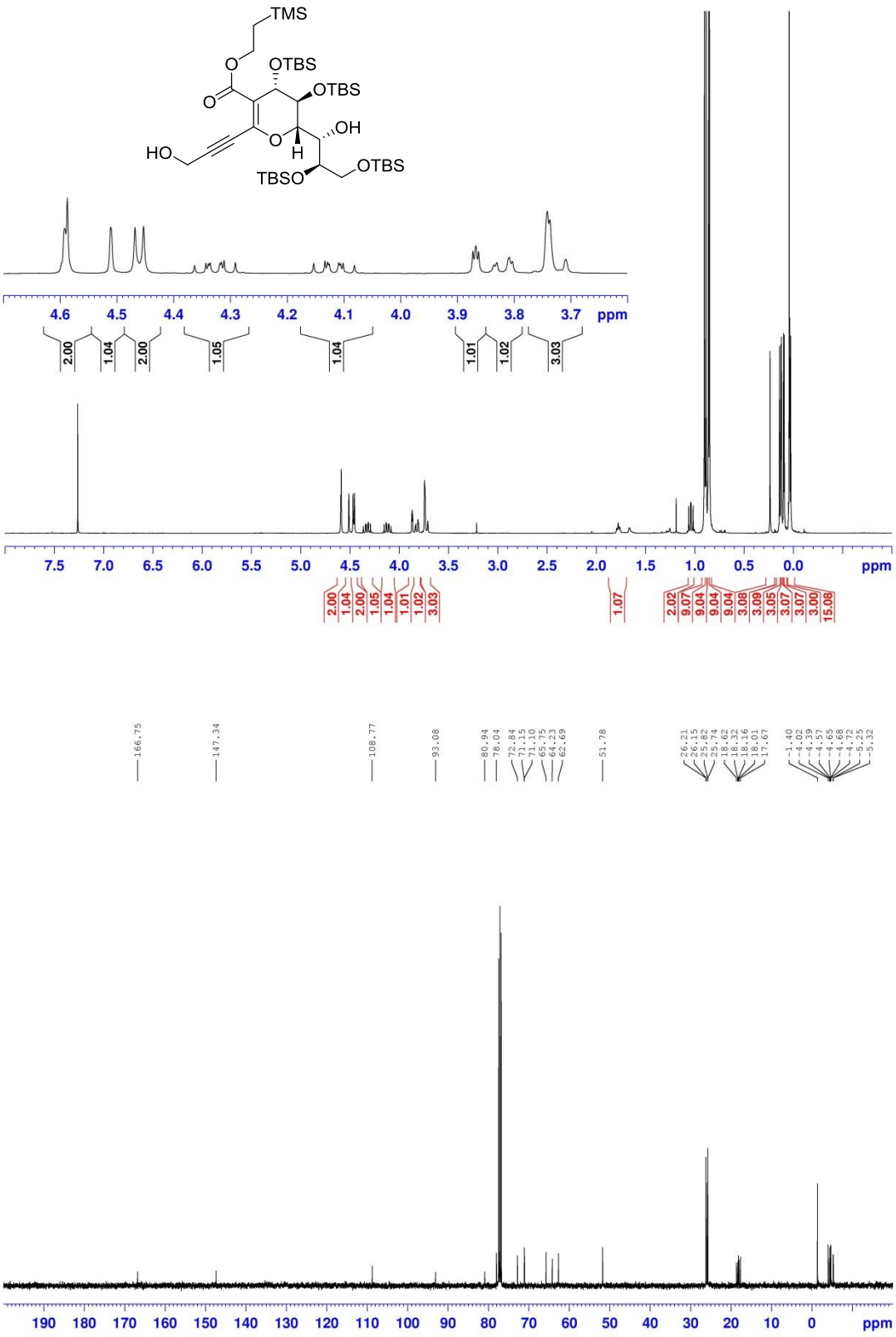

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OBn
OBn
OBn
O
H
O
BnO
OBn
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 ppm
5.07 2.01 1.08 7.05 1.00 1.07 1.08 1.03
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.07 21.09 4.00 5.07 2.01 1.08 7.05 1.00 1.07 1.08 1.03 2.01 9.08
167.60
155.68 138.89 138.71 138.31 138.08 137.99 128.56 128.53 128.47 128.43 128.31 128.25 128.10 128.07 127.93 127.89 127.78 127.67 127.57 127.37 127.24 106.15
78.57 76.79 75.49 73.67 72.95 72.09 71.70 71.30 69.54 69.14 62.38
17.64
-1.33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OTBS
O
OTBS
OH
O
H
TBSO
OTBS
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 ppm
1.06 1.05 1.07 2.05 1.04 1.05 3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.06 1.05 1.07 2.05 1.04 1.05 3.04 2.07 9.03 9.02 9.03 9.09 3.04 3.04 3.04 3.01 6.00 12.01 3.04
167.62
158.20
104.69
77.56
72.71
71.84
71.12
64.29
62.03
26.20
26.10
25.89
25.72
18.61
18.31
18.15
18.00
17.60
-1.33
-3.99
-4.40
-4.59
-4.78
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OTBS
O
OTBS
I
O
H
OH
TBSO
OTBS
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 ppm
1.00 1.03 1.03 1.07 1.05 1.09 1.09 3.09
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.03 1.03 1.07 1.05 1.09 1.09 3.09
2.01 9.01 9.07 9.07 9.09 3.02 3.06 3.06 3.07 3.09 3.06 9.09 3.03 3.09


166.34
123.77
110.18
83.03
72.90
71.73
70.72
66.45
64.15
63.01
26.19
26.12
25.78
25.68
18.61
18.29
18.12
17.98
17.68
-1.39
-4.10
-4.37
-4.68
-4.78
-5.24
-5.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OTBS
O
OTBS
OH
O
H
HO
TBSO
OTBS
4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 ppm
2.00 1.04 2.00 1.05 1.04 1.01 1.02 3.03
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00 1.04 2.00 1.05 1.04 1.01 1.02 3.03 1.07 2.02 9.07 9.04 9.04 3.08 3.09 3.05 3.07 3.07 3.00 15.08
166.75
147.34
108.77
93.08
80.94
78.04
72.84
71.15
71.10
65.75
64.23
62.69
51.78
26.21
26.15
25.82
25.74
18.62
18.32
18.16
18.01
17.67
-1.40
-1.02
-4.39
-4.57
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-4.68
-4.72
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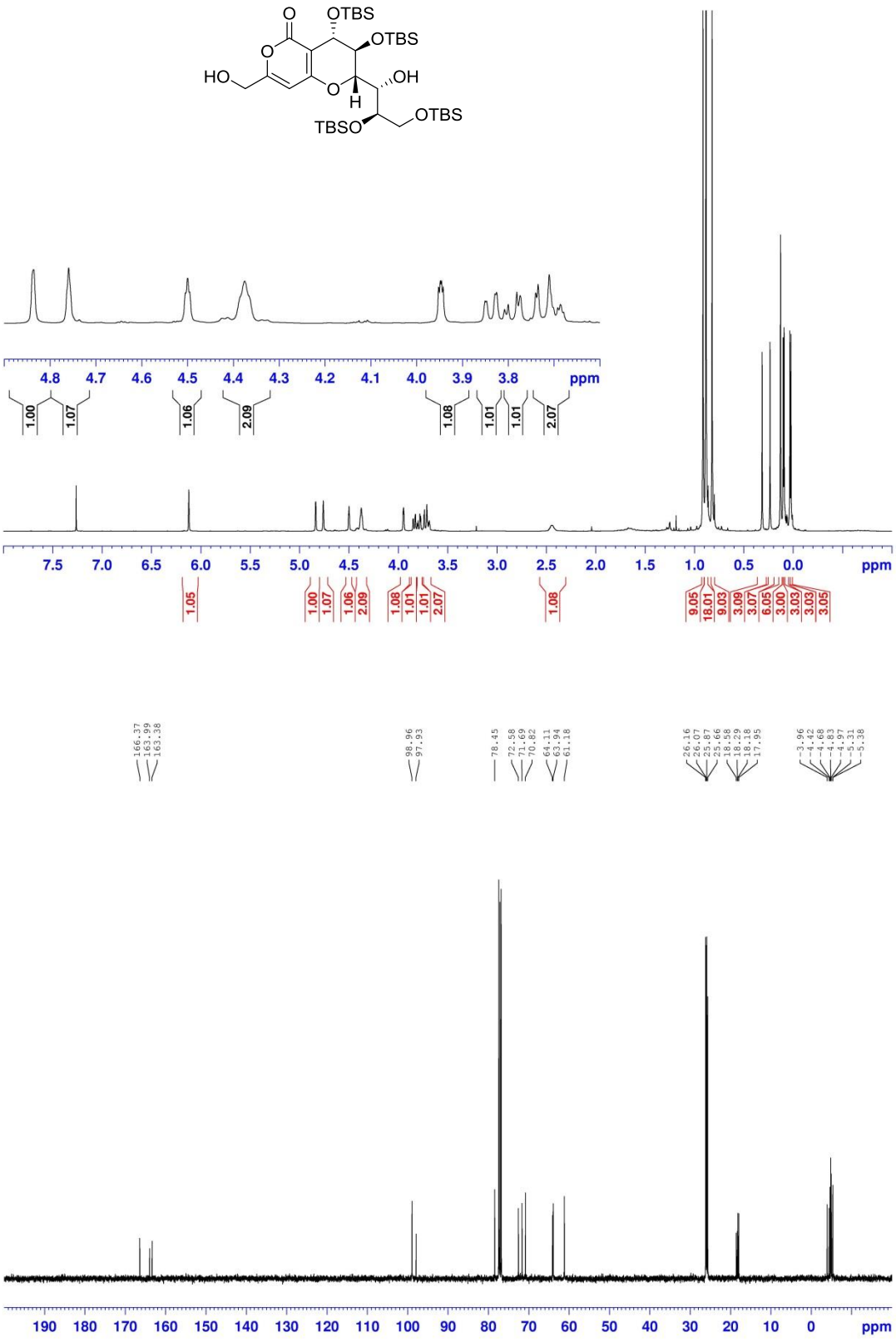
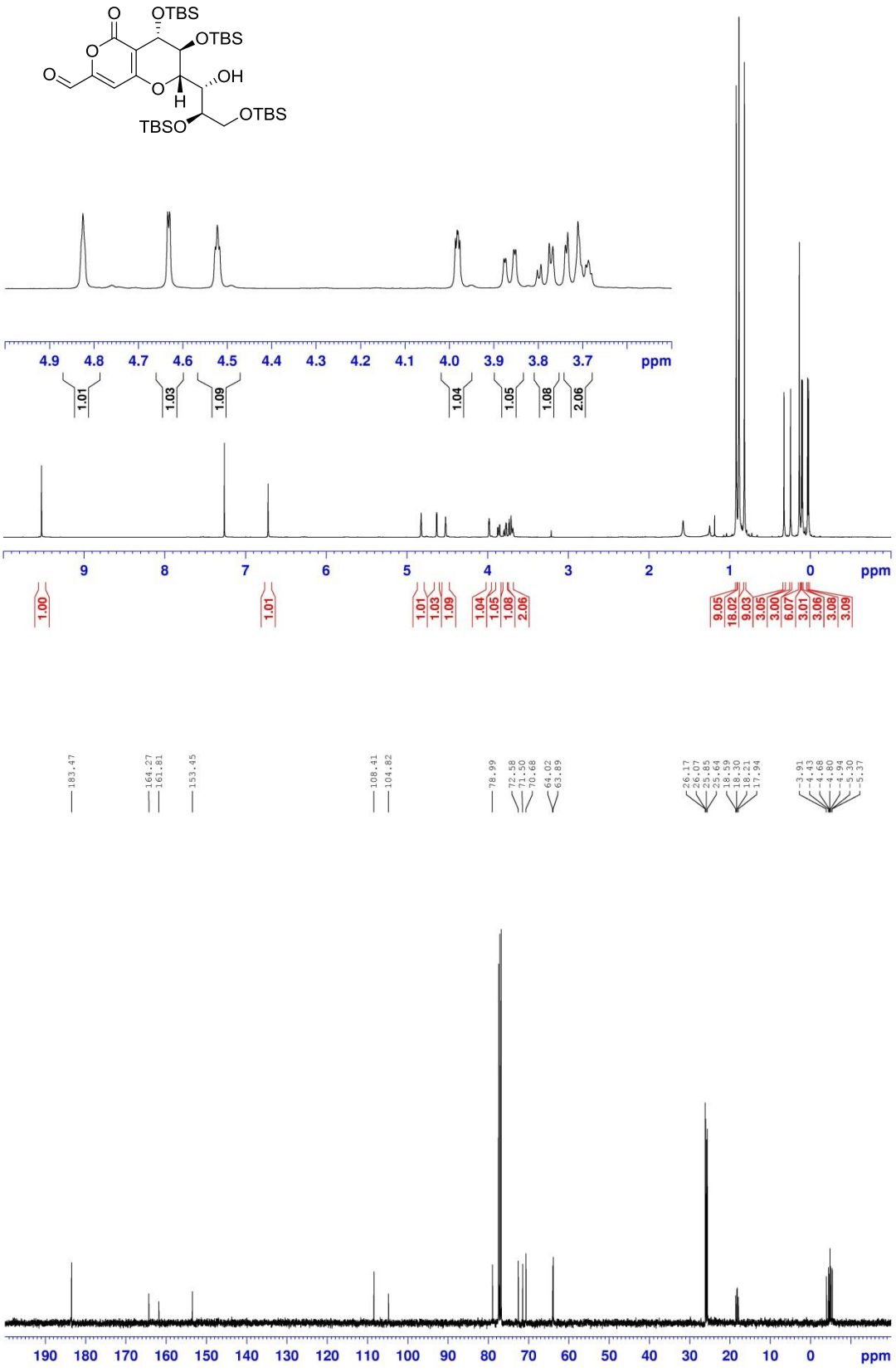
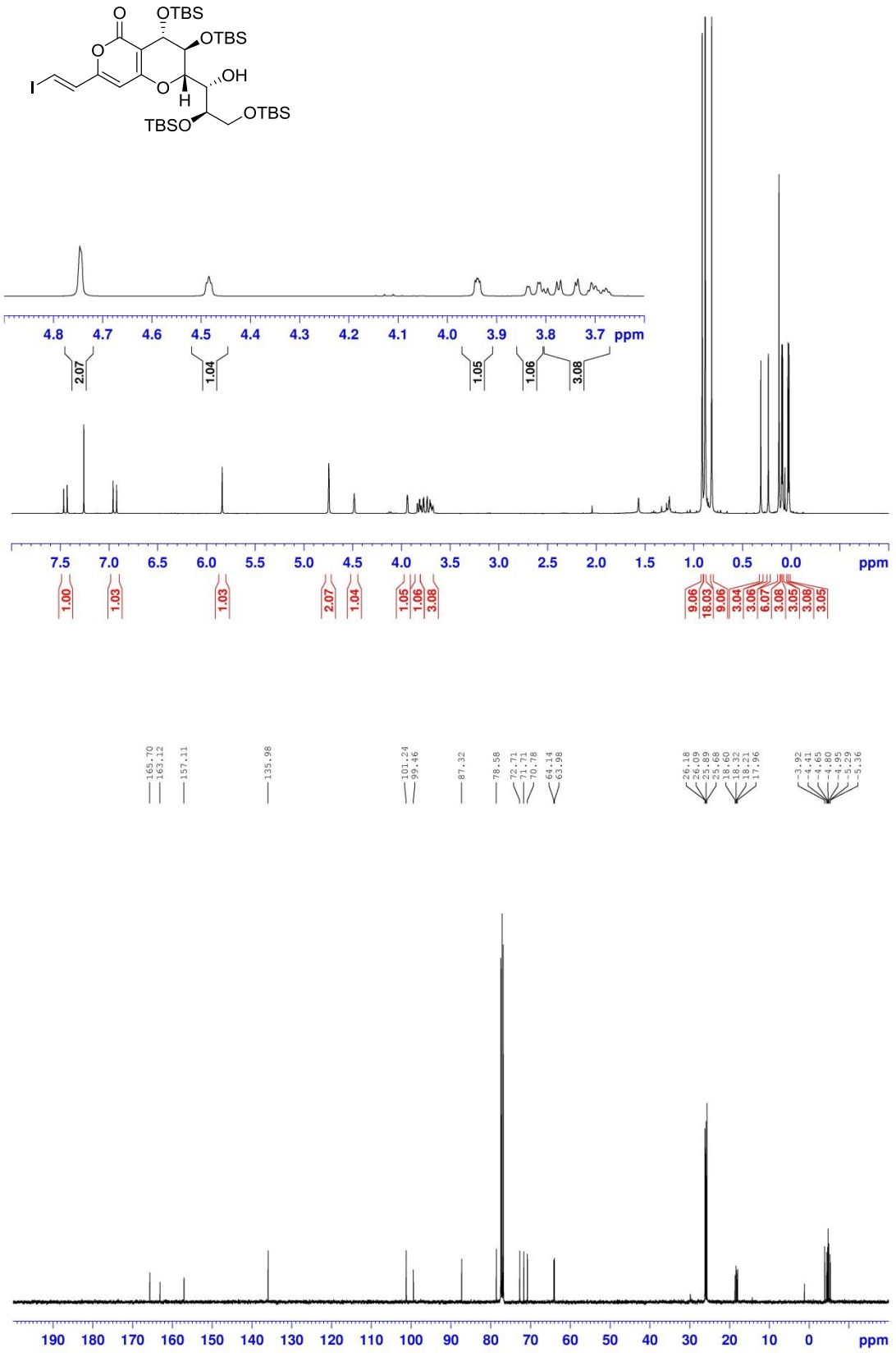
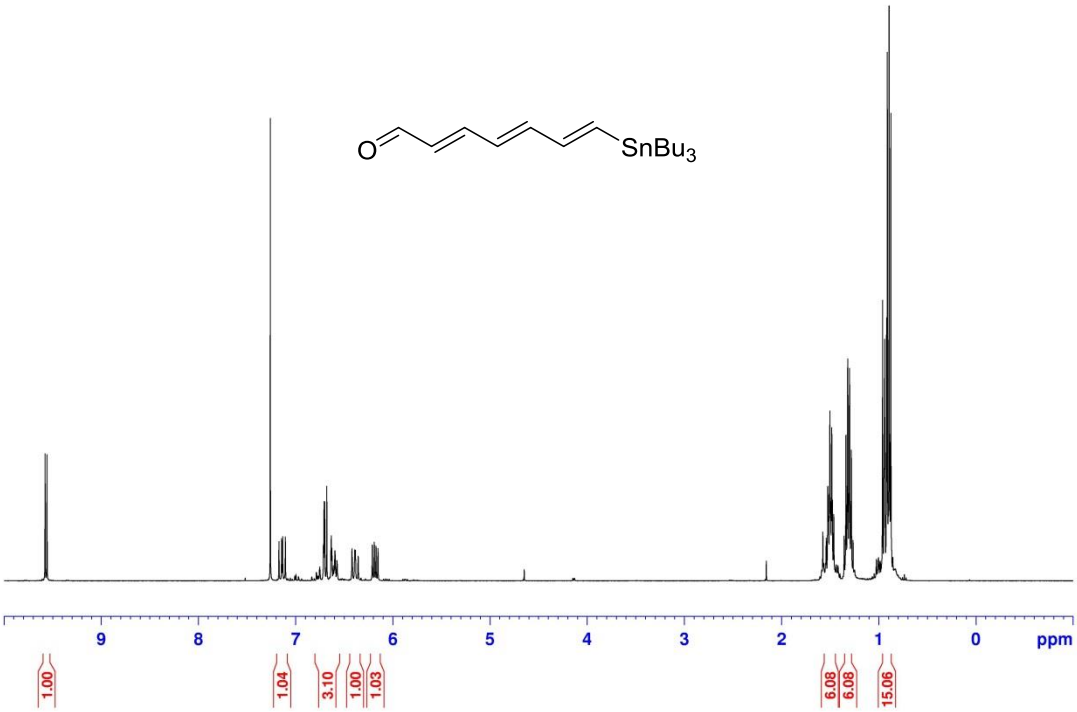
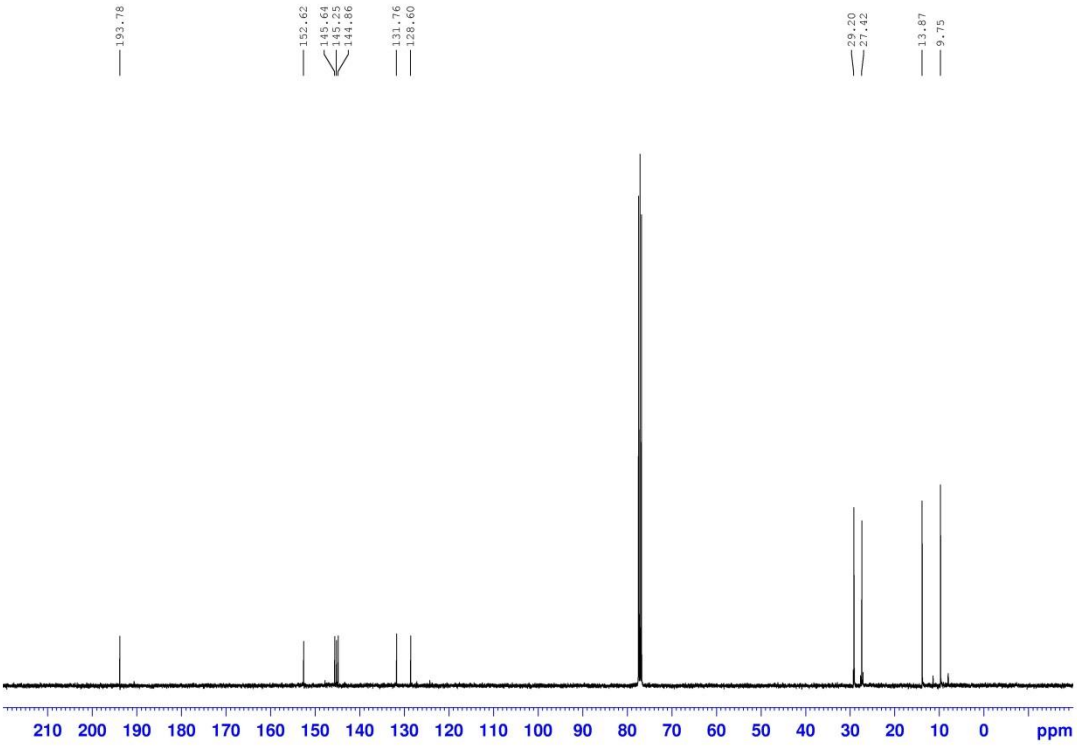
-5.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

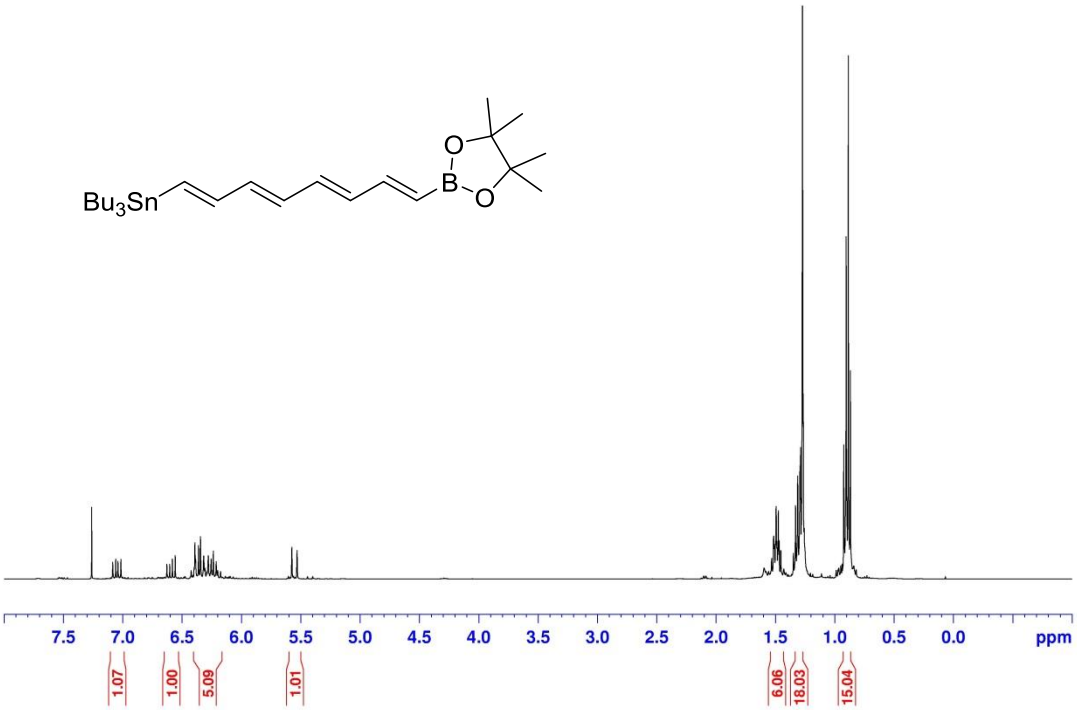

O
OTBS
OTBS
HO
O
O
H
OH
TBSO
OTBS
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 ppm
1.00 1.07 1.06 2.09 1.08 1.01 1.01 2.07
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.05 1.00 1.07 1.06 2.09 1.08 1.01 1.01 2.07 1.08 9.05 18.01 9.03 3.09 3.07 6.05 3.00 3.03 3.03 3.05
166.37
163.99
163.38
98.96
97.93
78.45
72.58
71.69
70.22
64.11
63.84
61.18
26.16
26.07
25.77
25.66
18.58
18.29
18.18
17.95
-3.96
-4.42
-4.68
-4.83
-4.97
-5.31
-5.38
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

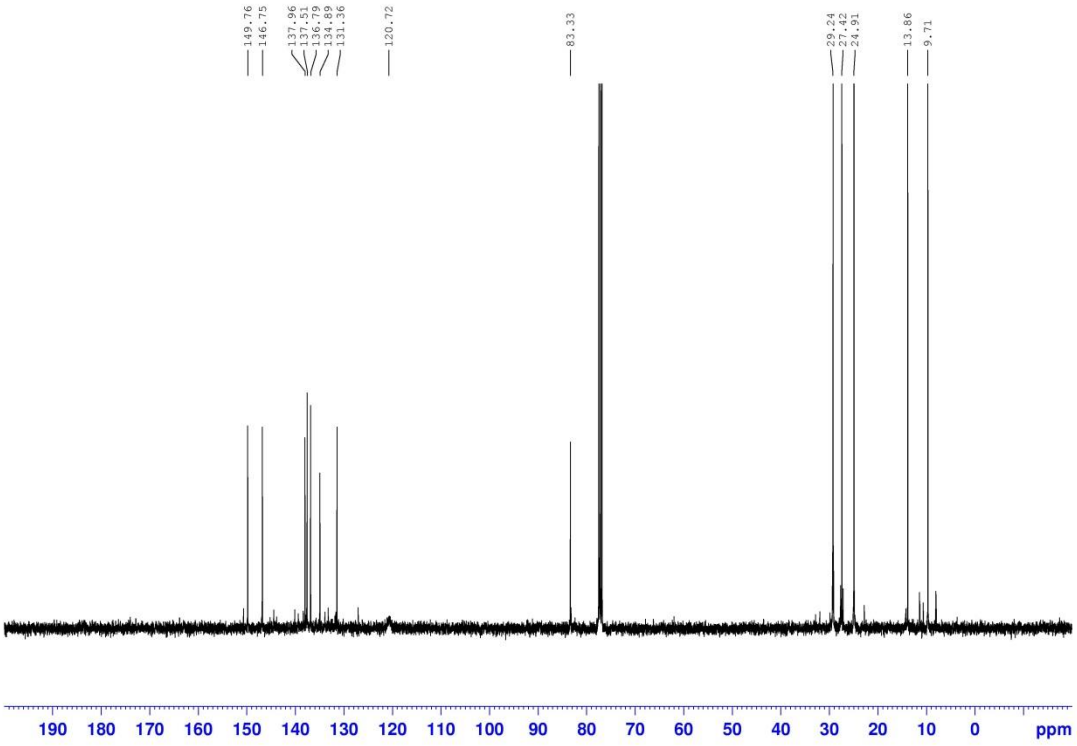

OTBS
OTBS
OH
OTBS
TBSO
ppm
183.47
164.27
161.81
153.45
108.41
104.82
78.99
72.58
71.50
70.68
64.02
63.89
26.17
26.07
25.85
25.64
18.59
18.30
18.21
17.94
-3.91
-4.43
-4.63
-4.68
-4.80
-4.94
-5.30
-5.37

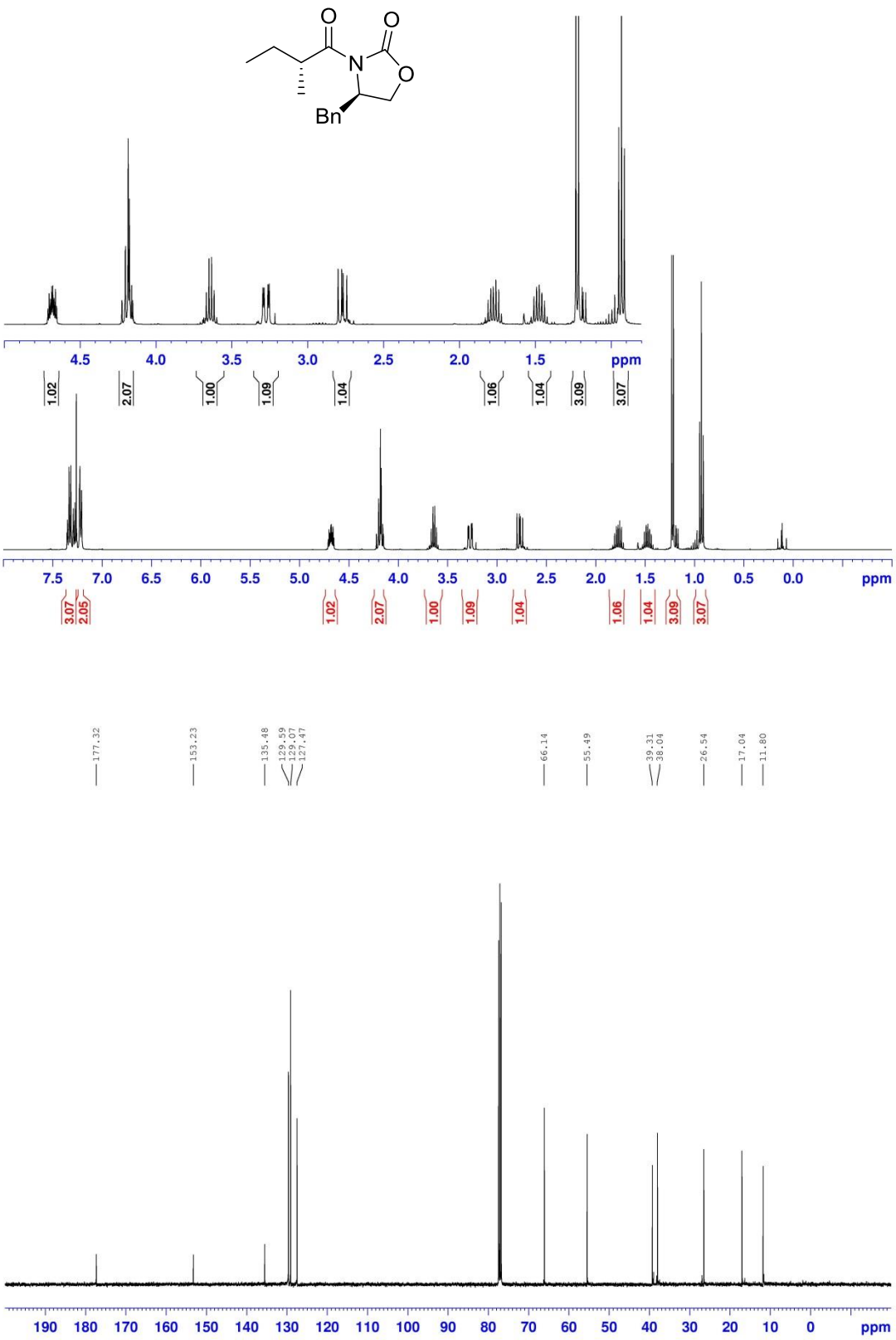

OTBS
OTBS
OH
OTBS
TBSO
I
O
O
O
H
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 ppm
2.07 1.04 1.05 1.06 3.08
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.03 1.03 2.07 1.04 1.05 1.06 3.08 9.06 18.03 9.06 3.04 3.06 6.07 3.08 3.05 3.08 3.05
165.70
163.12
157.11
135.98
101.24
99.46
87.32
78.58
72.71
71.71
70.78
64.14
63.98
26.18
26.09
25.88
25.68
18.60
18.32
18.21
17.96
-3.92
-4.41
-4.65
-4.80
-4.95
-5.29
-5.36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

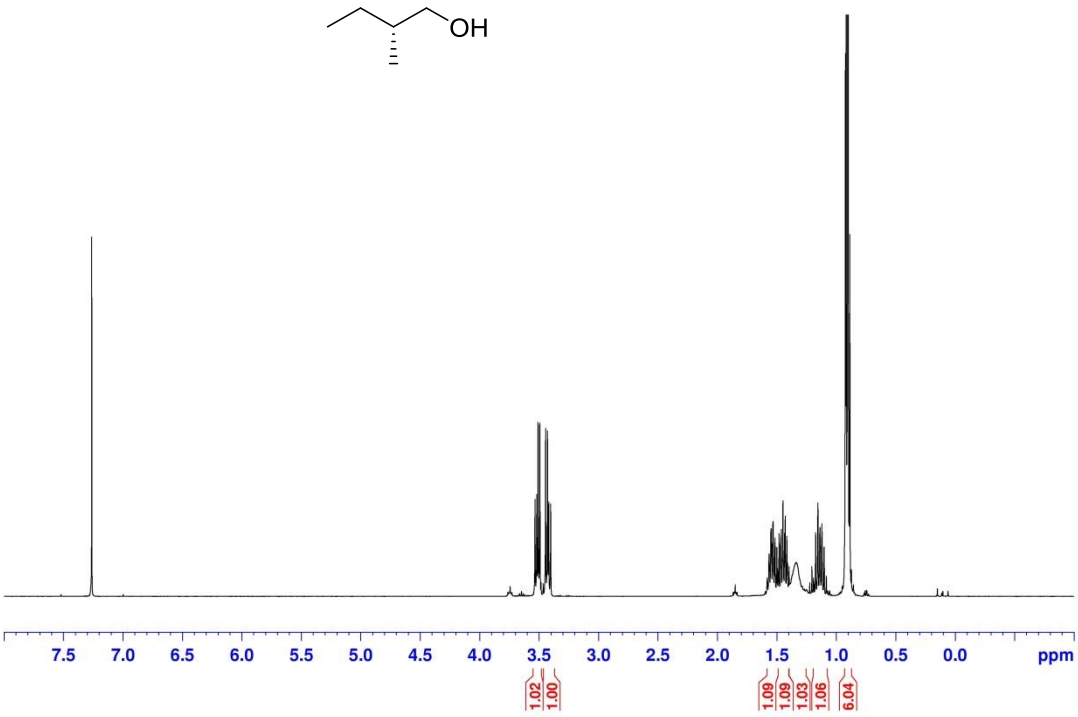

O
SnBu3
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
3.10
1.00
1.03
6.08
6.08
15.06

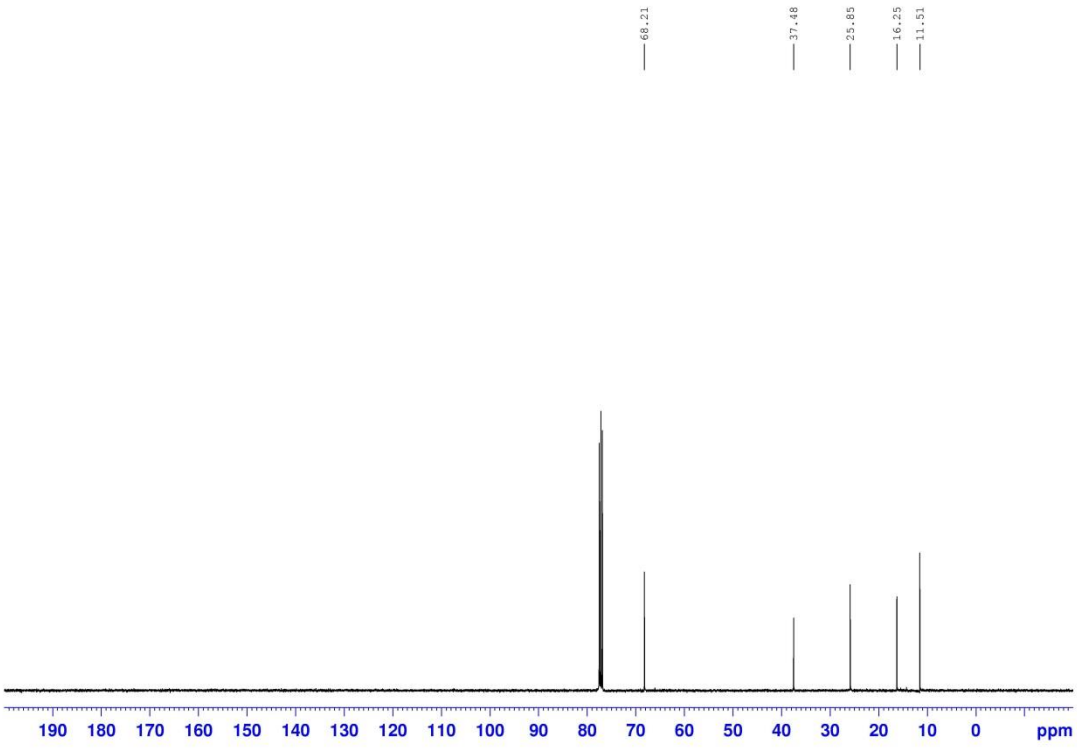

193.78
152.62
145.64
145.25
144.86
131.76
128.60
29.20
27.42
13.87
9.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

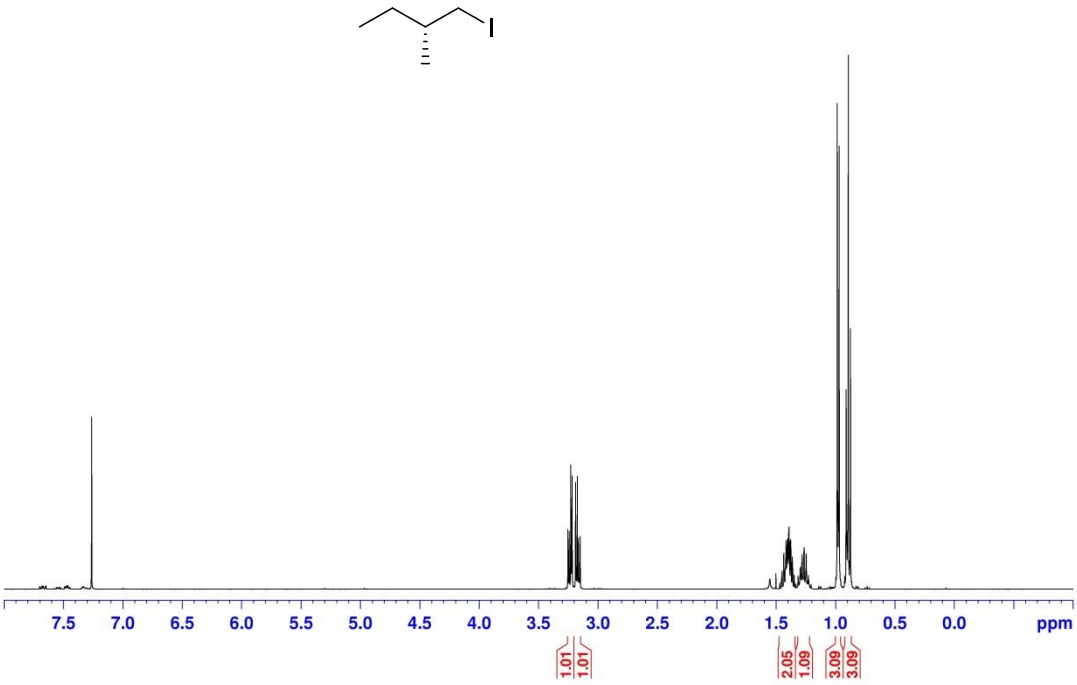

Bu3Sn
O
B
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.07
1.00
5.09
1.01
6.06
18.03
15.04

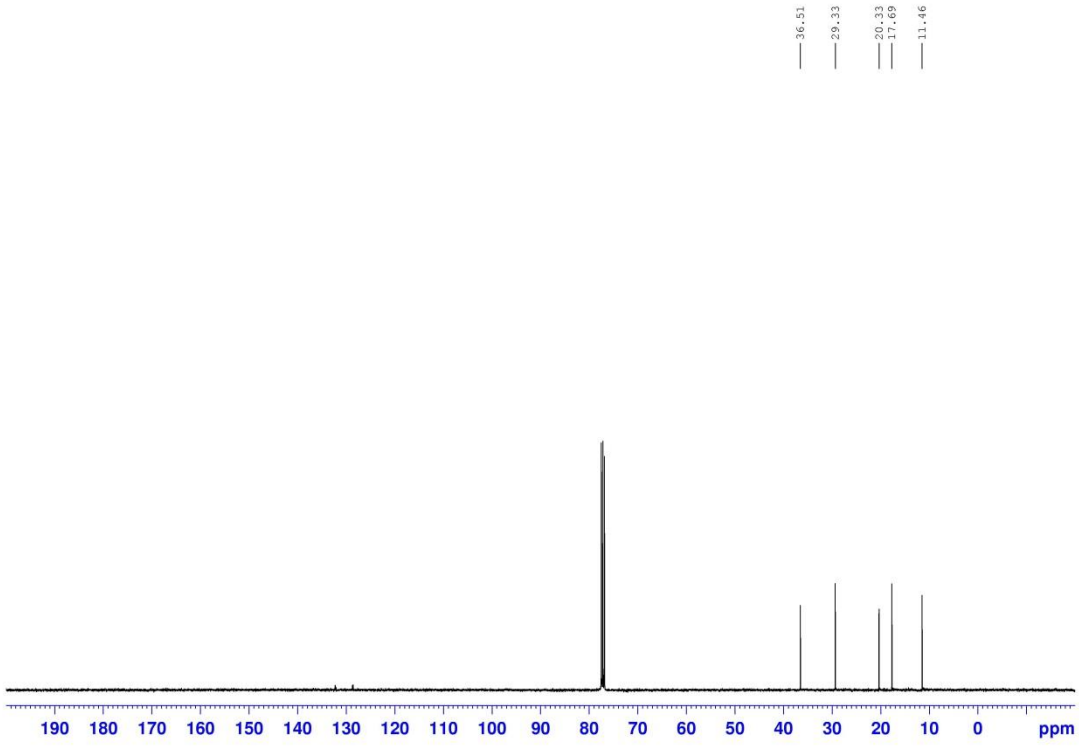

149.76
146.75
137.96
137.51
136.79
134.89
131.36
120.72
83.33
29.24
27.42
24.91
13.86
9.71
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

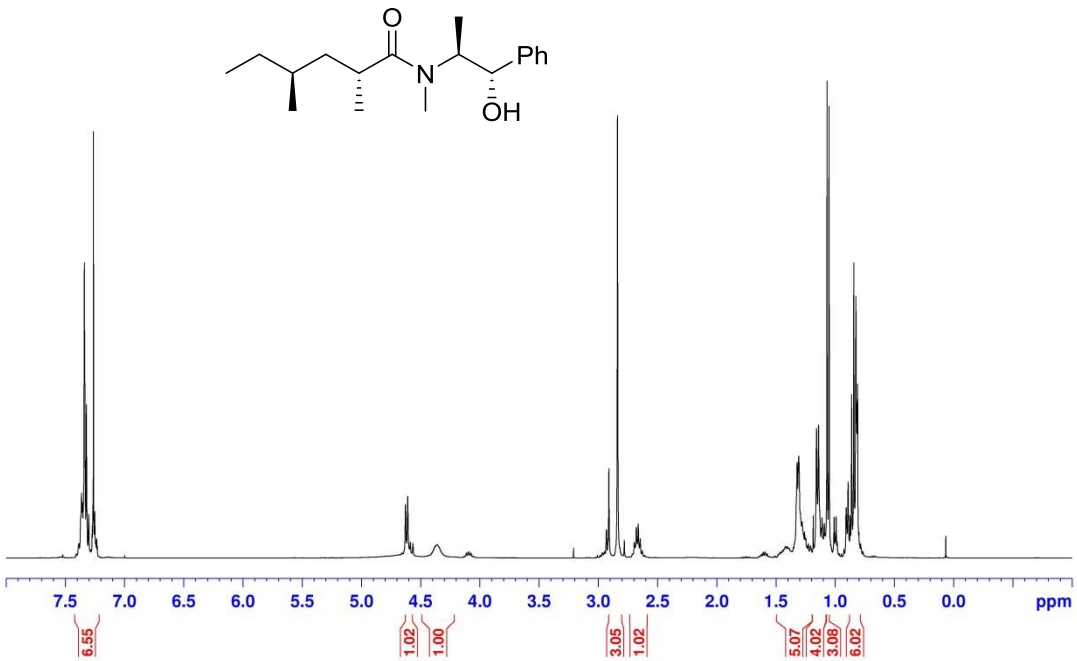

O
O
N
O
Bn
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.02
2.07
1.00
1.09
1.04
1.06
1.04
3.09
3.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.07
2.05
1.02
2.07
1.00
1.09
1.04
1.06
1.04
3.09
3.07
177.32
153.23
135.48
129.59
129.07
127.47
66.14
55.49
39.31
38.04
26.54
17.04
11.80
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

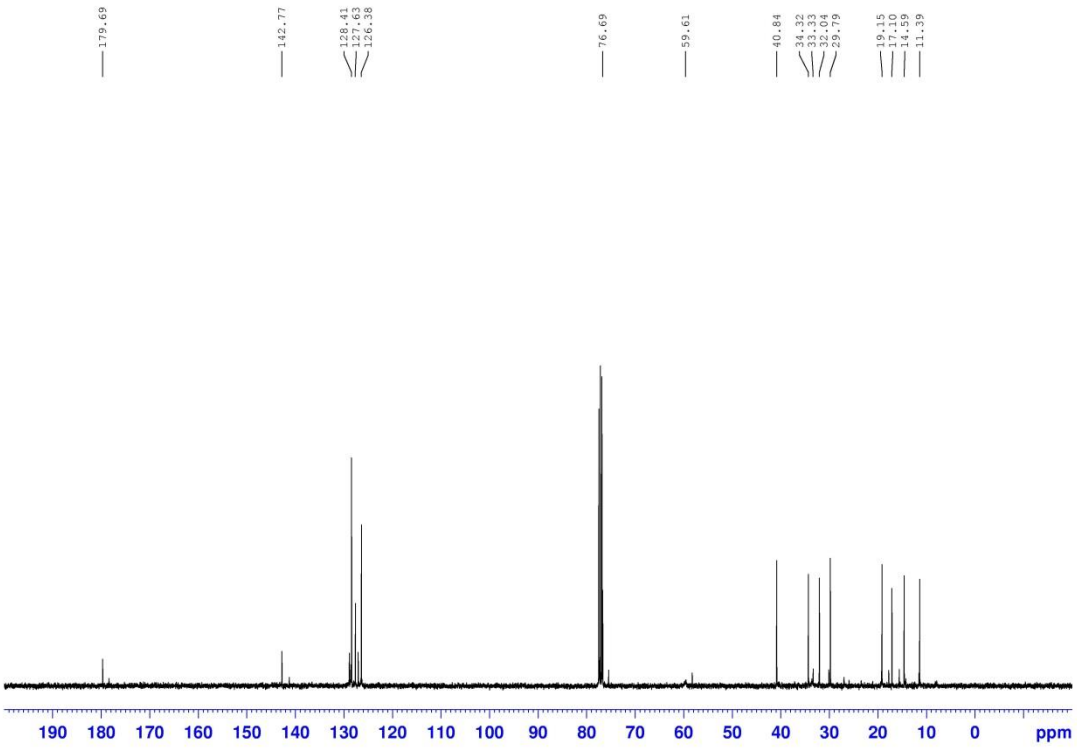

OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.02
1.00
1.09
1.09
1.03
1.06
6.04

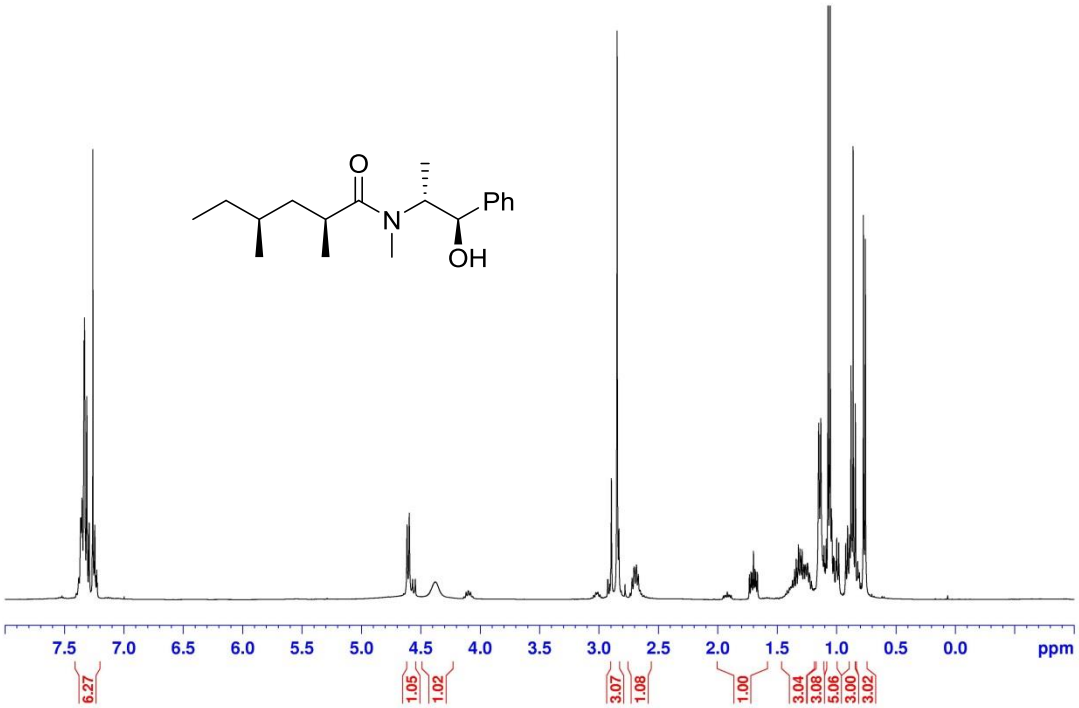

68.21
37.48
25.85
16.25
11.51
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
1.01
2.05
1.09
3.09
3.09

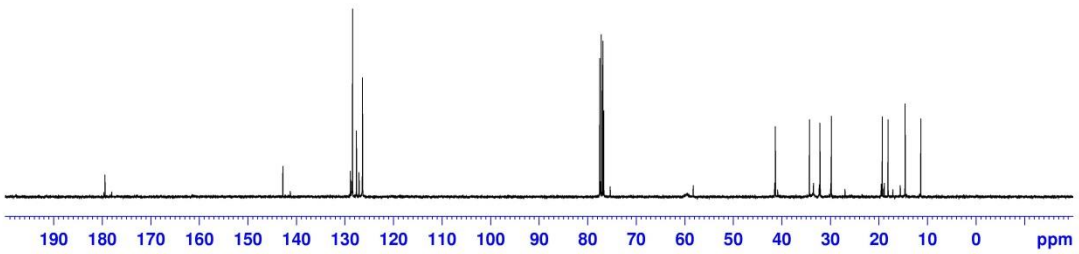

36.51
29.33
20.33
17.69
11.46
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

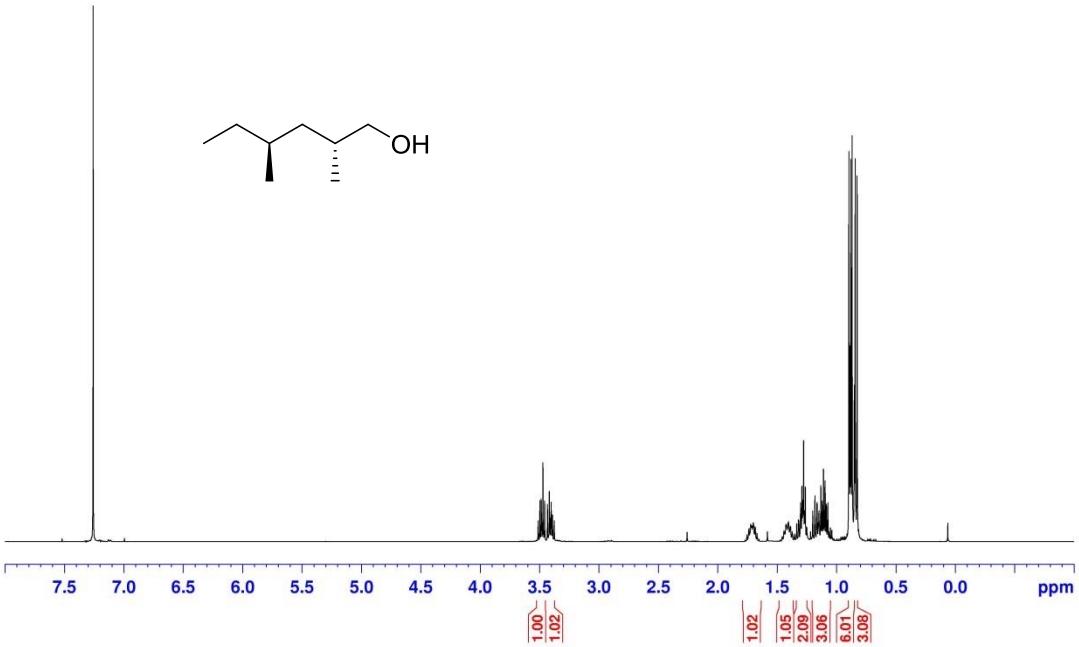

O
N
Ph
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
6.55
1.02
1.00
3.05
1.02
5.07
4.02
3.08
6.02

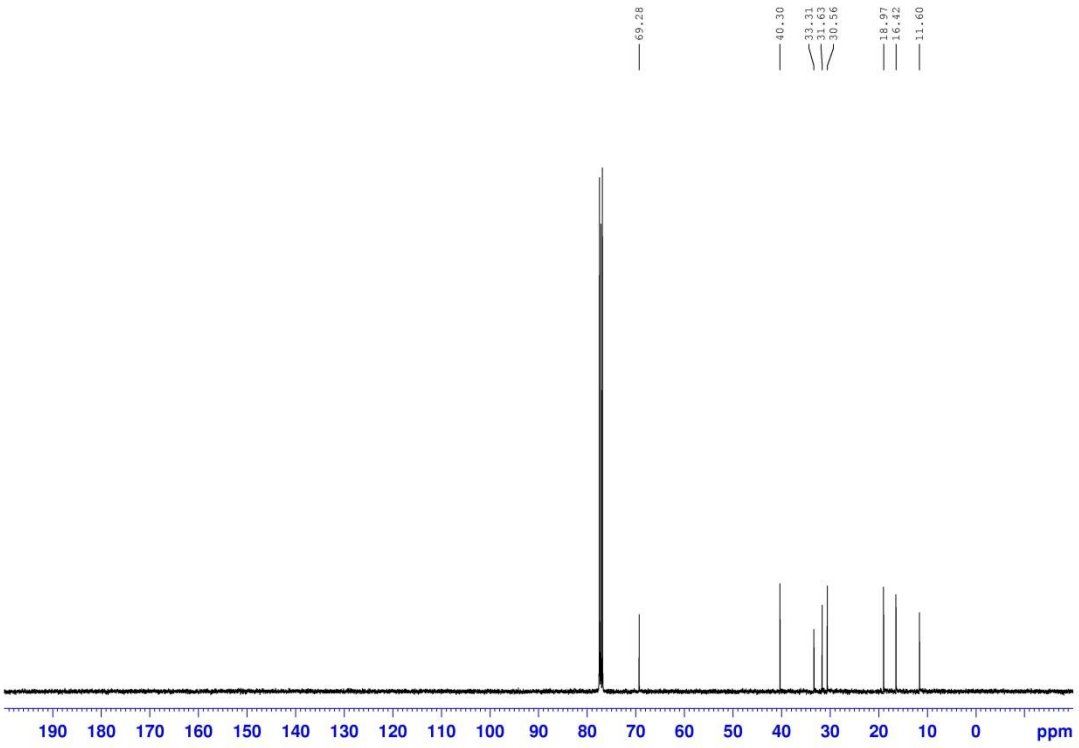

179.69
142.77
128.41
127.63
126.38
76.69
59.61
40.84
34.32
33.33
30.04
29.79
19.15
17.10
14.59
11.39
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

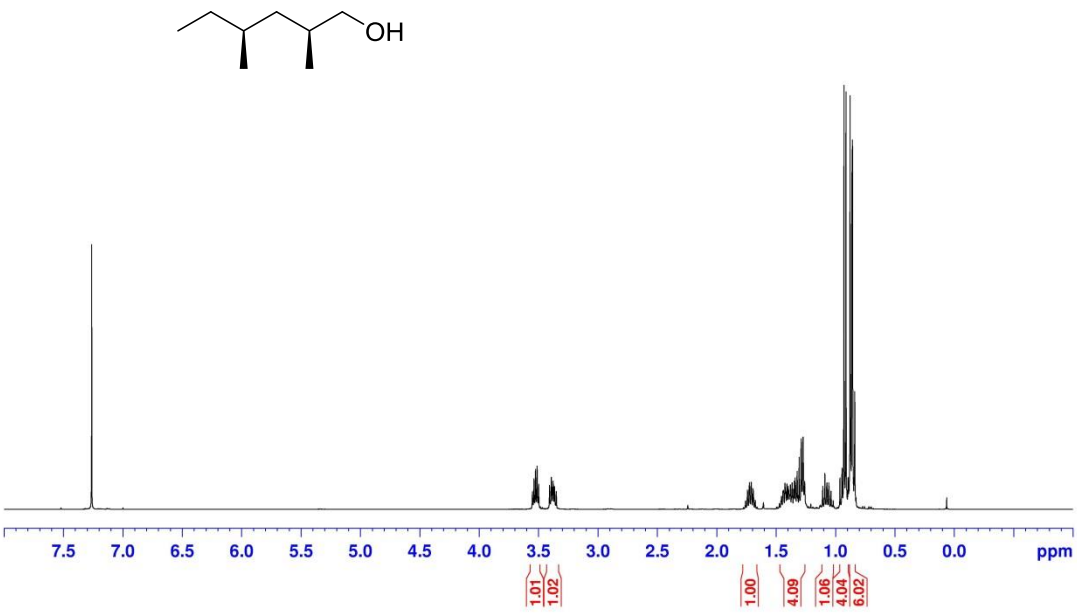

O
N
Ph
OH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
6.27
1.05
1.02
3.07
1.08
1.00
3.04
3.08
5.06
3.00
3.02

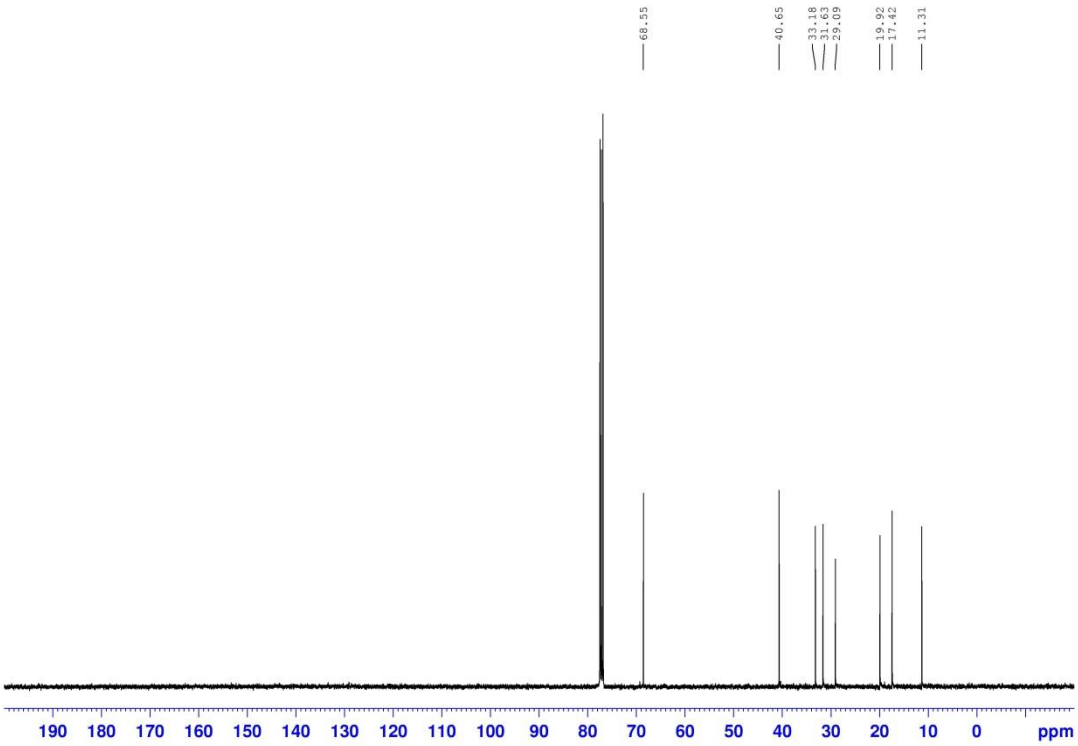

179.40
142.75
128.40
127.59
126.36
76.64
59.47
41.30
34.27
33.45
32.12
29.76
19.27
18.68
14.57
11.33

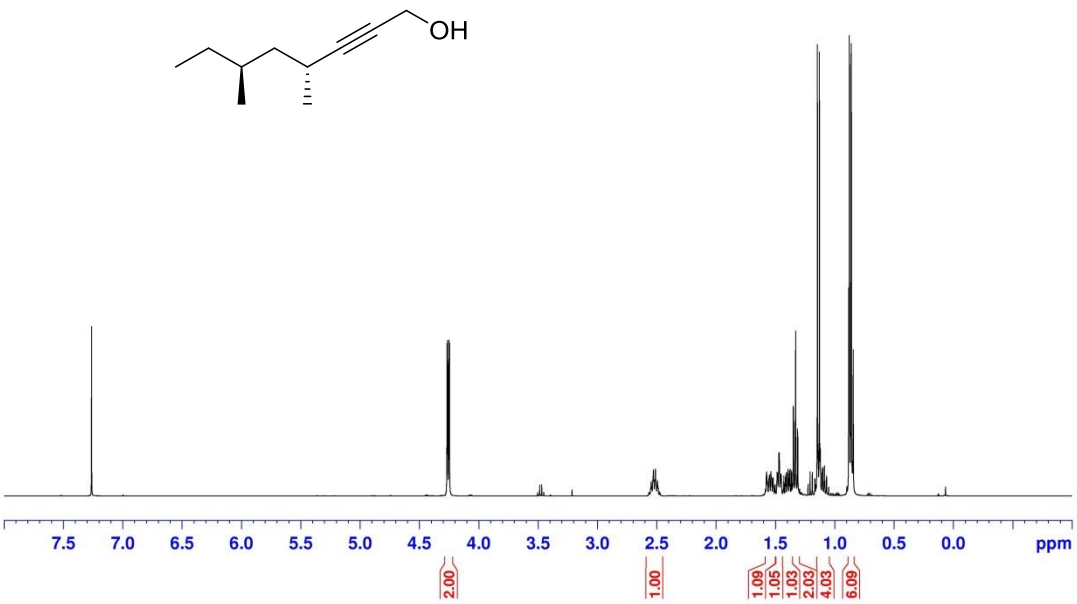

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

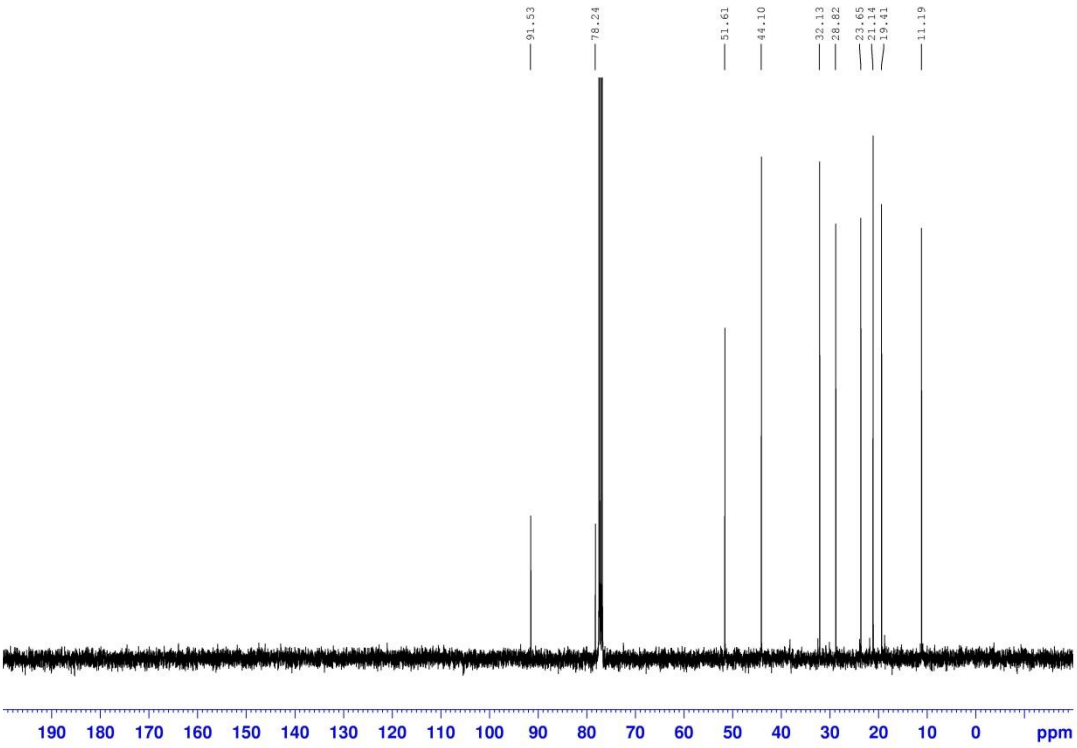

OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.02
1.02
1.05
2.09
3.06
6.01
3.08

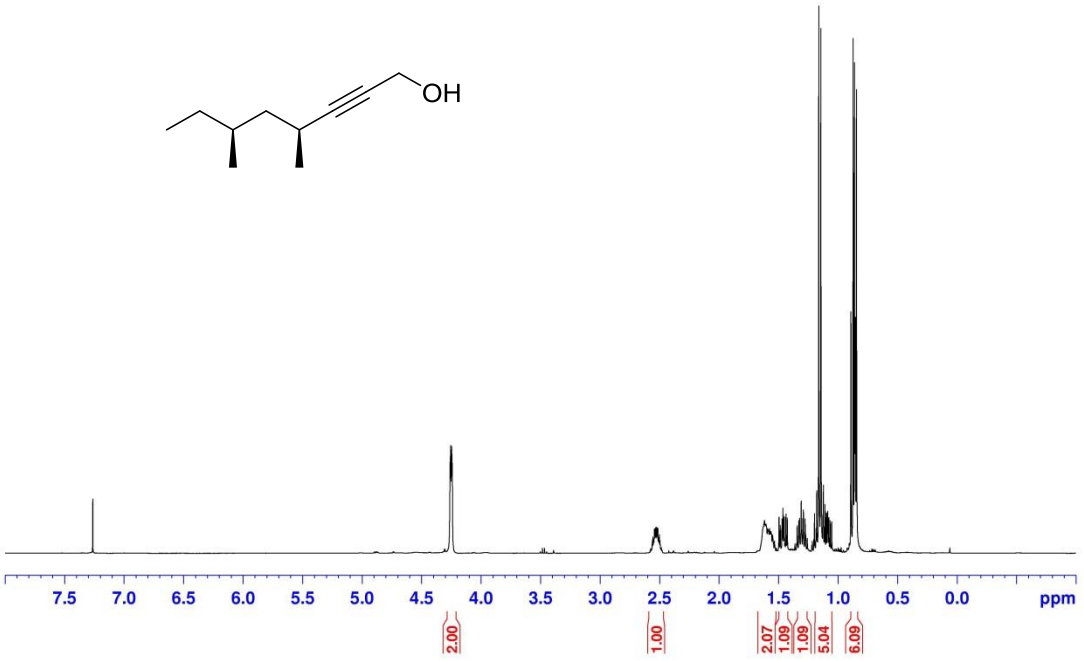

69.28
40.30
33.31
31.63
30.56
18.97
16.42
11.60
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
1.02
1.00
4.09
1.06
4.04
6.02


68.55
40.65
33.18
31.63
29.09
19.92
17.42
11.31
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
1.00
1.09
1.05
1.03
2.03
4.03
6.09


91.53
78.24
51.61
44.10
32.13
28.82
23.65
21.14
19.41
11.19
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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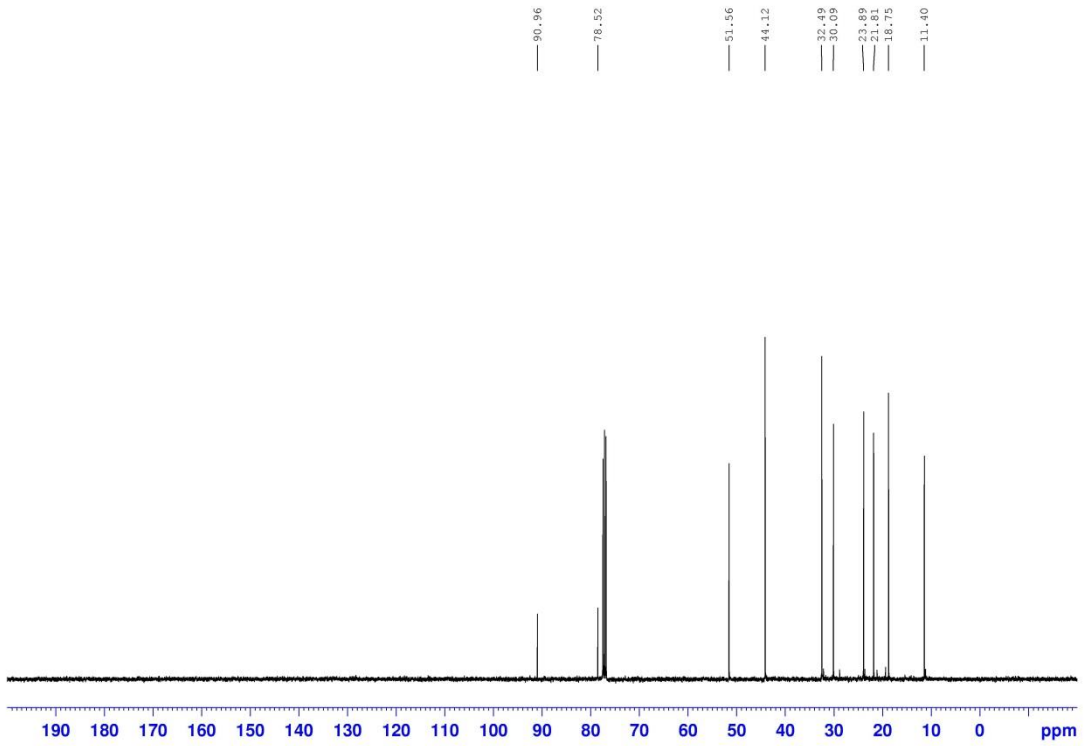
1.00
2.07
1.09
1.09
5.04
6.09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78.52
51.56
44.12
32.49
30.09
23.89
21.81
18.75
11.40
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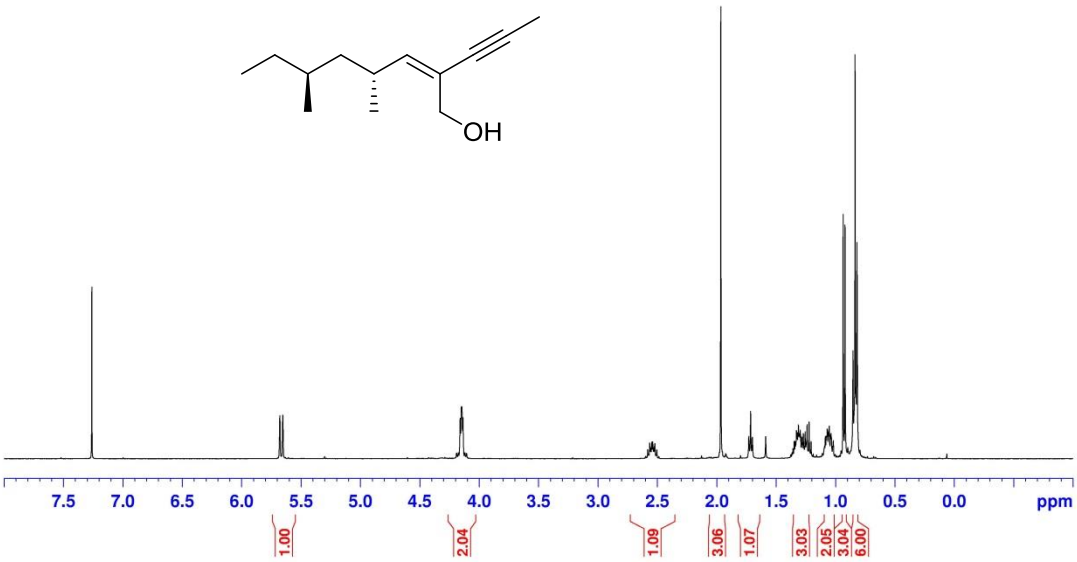
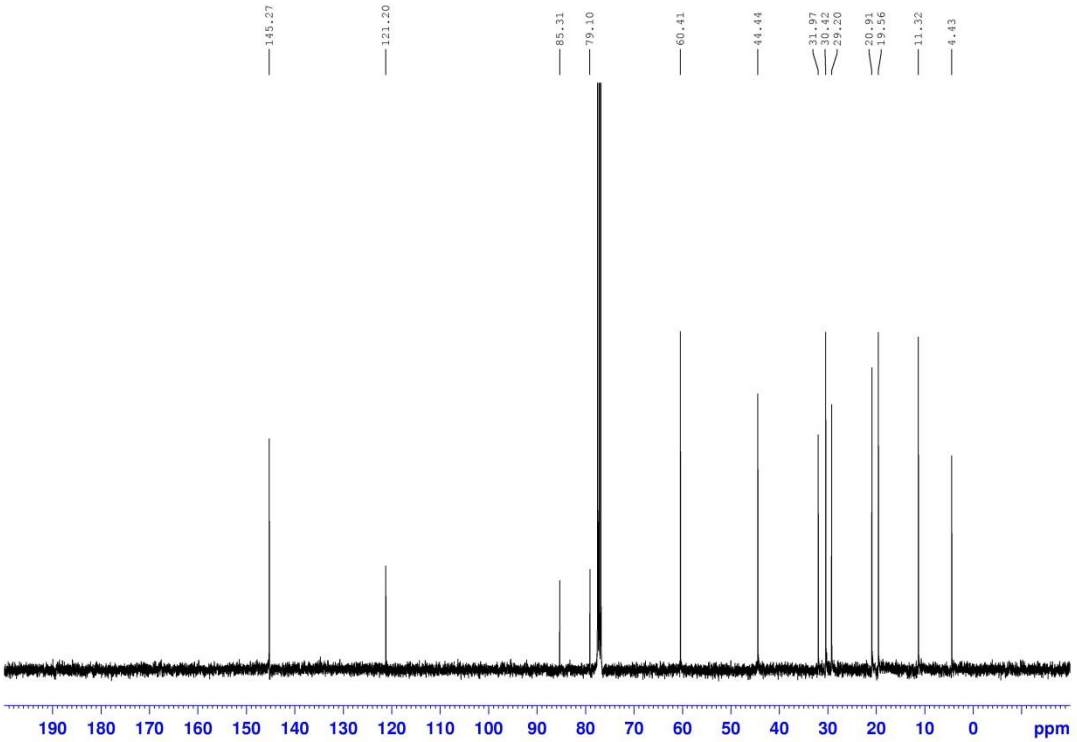
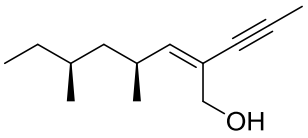
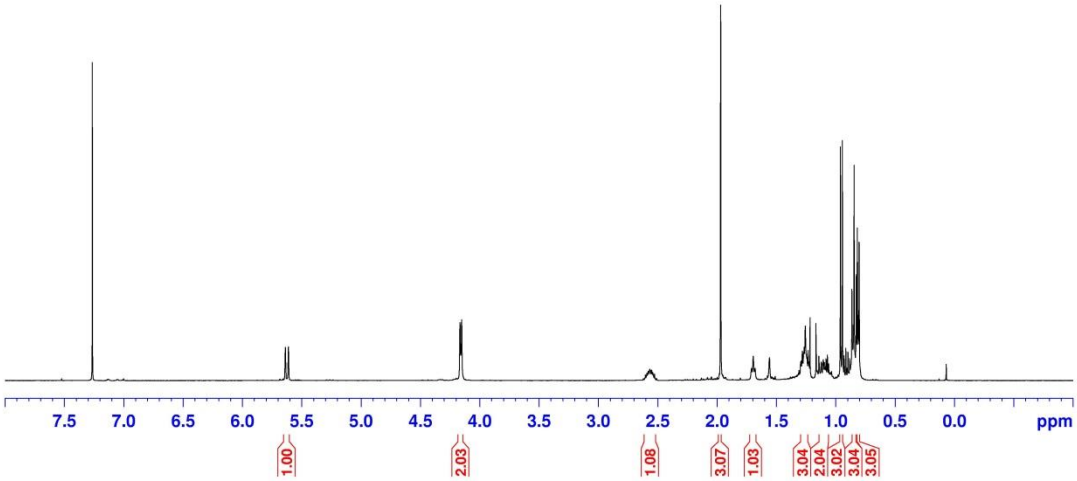
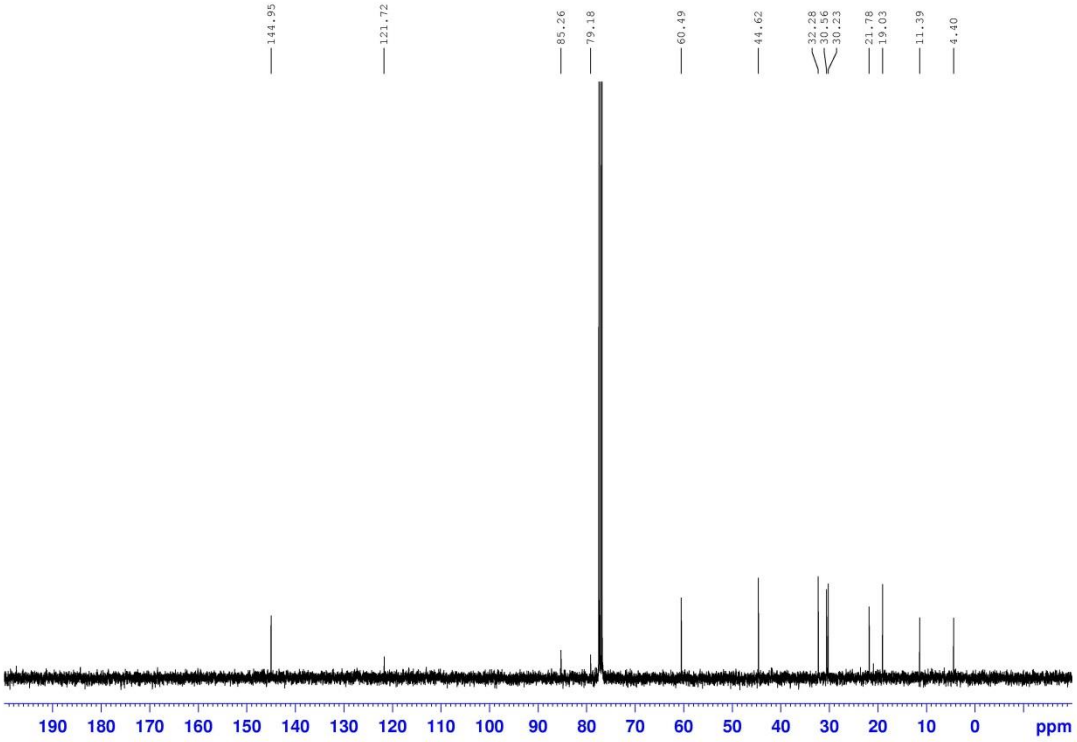
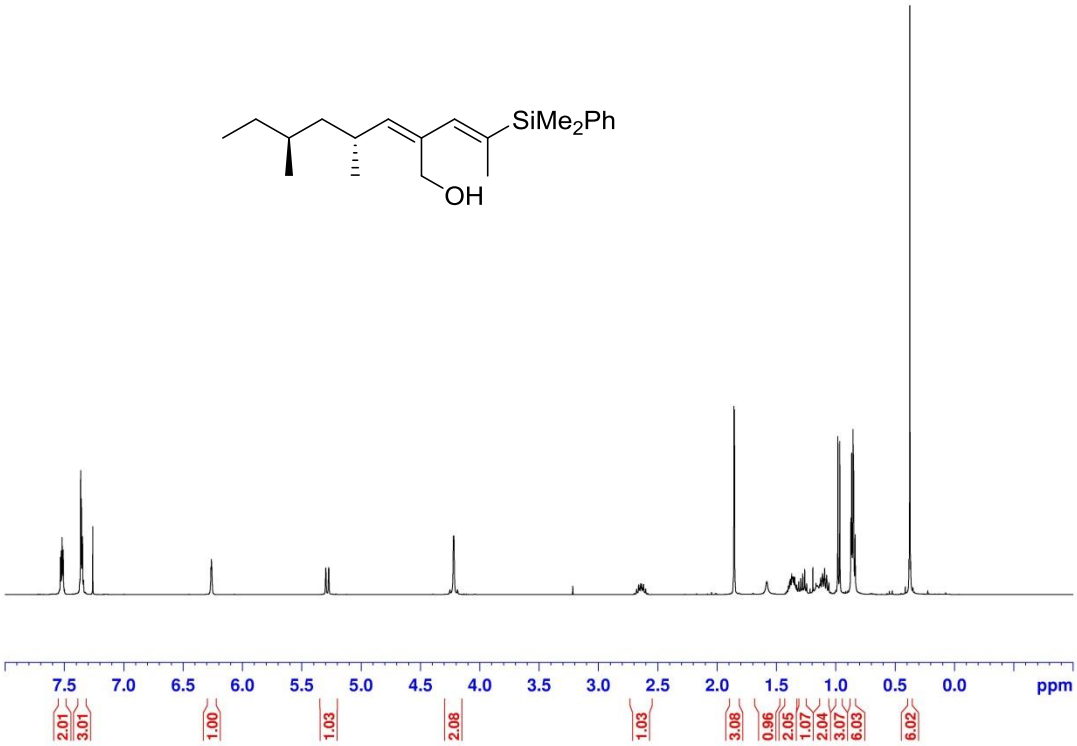

OH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 2.04 1.09 3.06 1.07 3.03 2.05 3.04 6.00

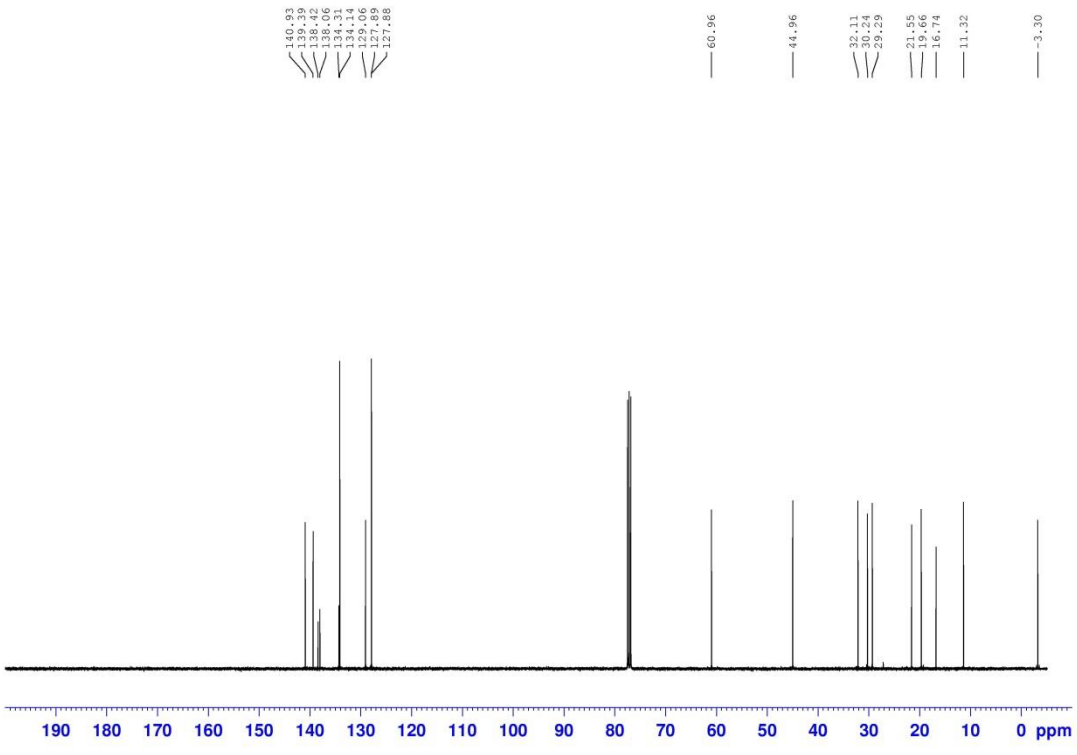

145.27
121.20
85.31
79.10
60.41
44.44
31.97
30.42
29.20
20.91
19.56
11.32
4.43
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

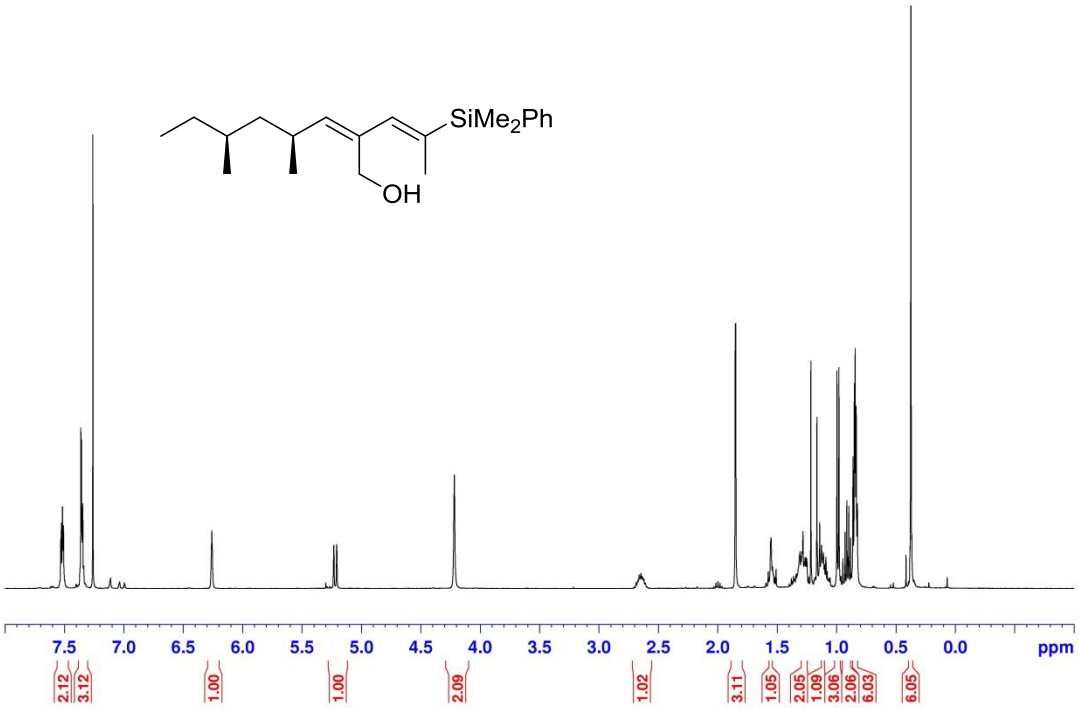

OH

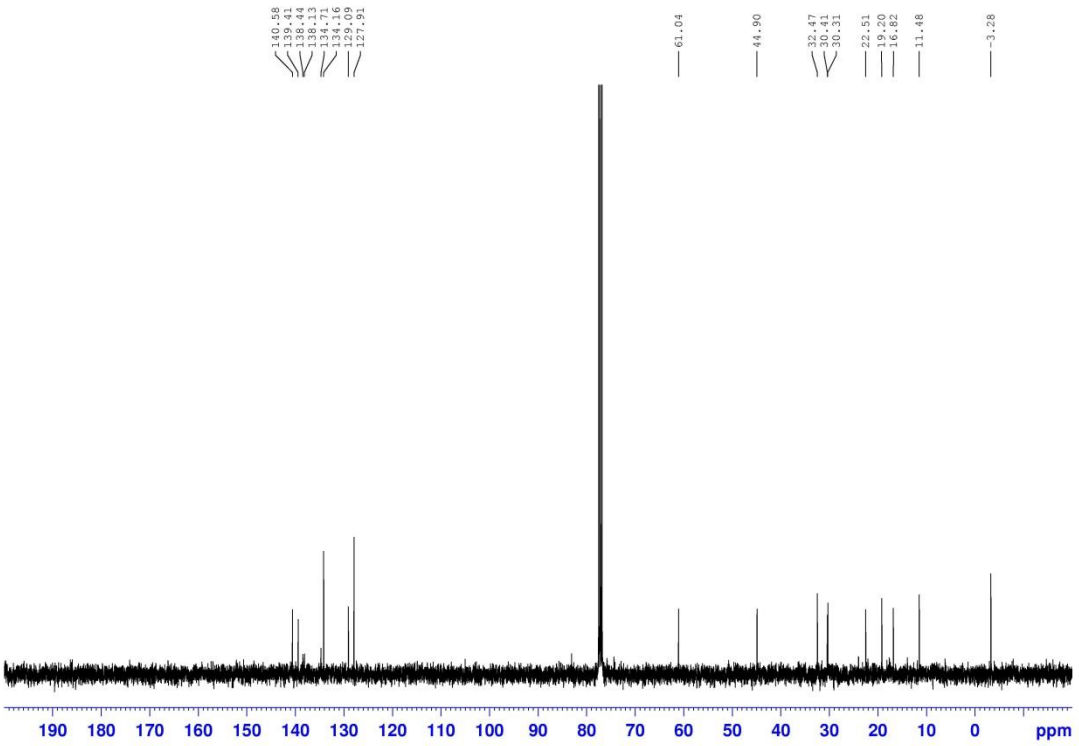

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.03
1.08
3.07
1.03
3.04
2.04
3.02
3.04
3.05

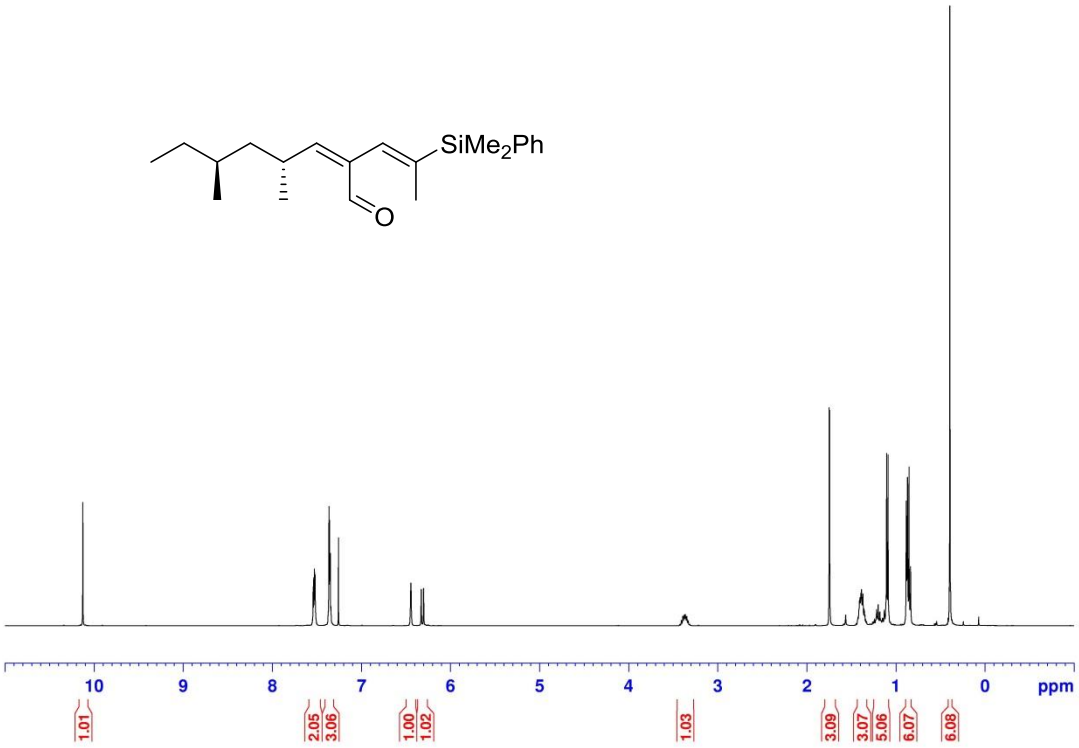

144.95
121.72
85.26
79.18
60.49
44.62
32.28
30.56
30.23
21.78
19.03
11.39
4.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

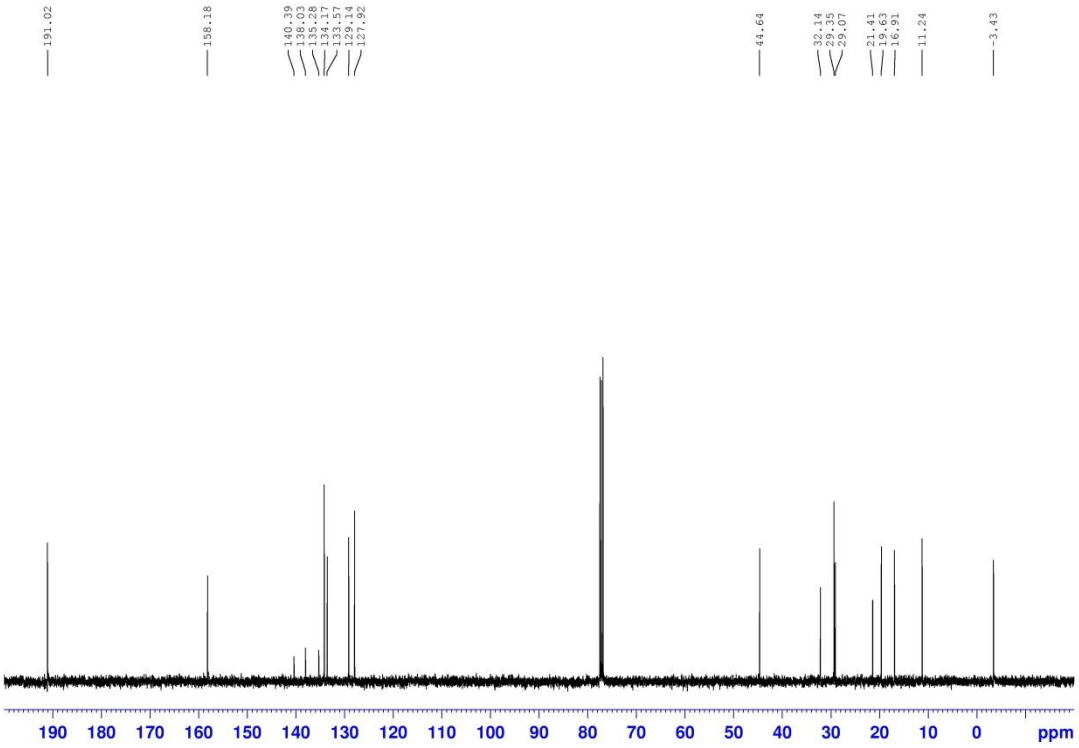

SiMe2Ph
OH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01 3.01 1.00 1.03 2.08 1.03 3.08 0.96 2.05 1.07 2.04 3.07 6.03 6.02

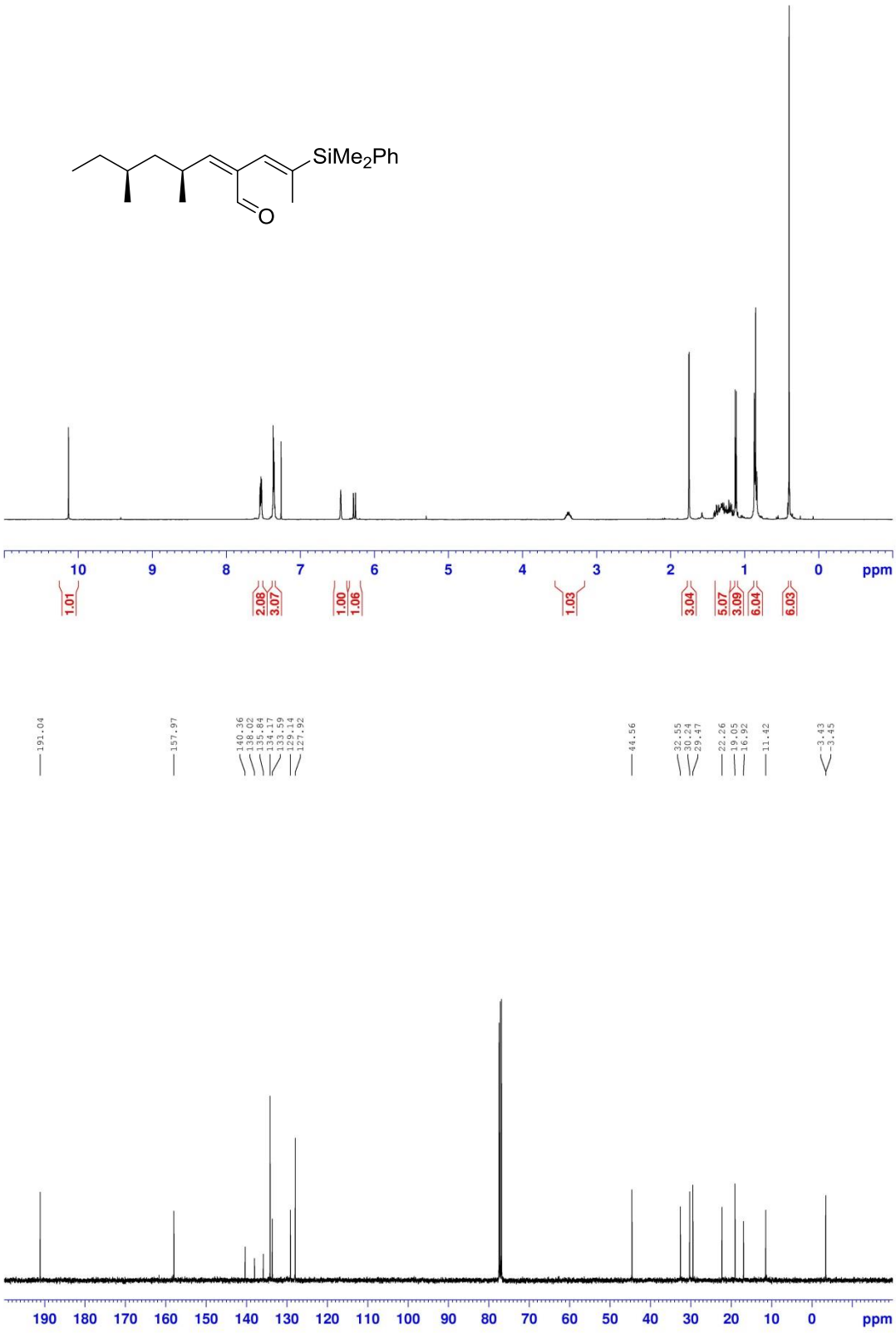

140.93
139.39
138.42
138.06
134.31
134.14
129.06
127.89
127.88
60.96
44.96
32.11
30.24
29.29
21.55
19.66
16.74
11.32
-3.30
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

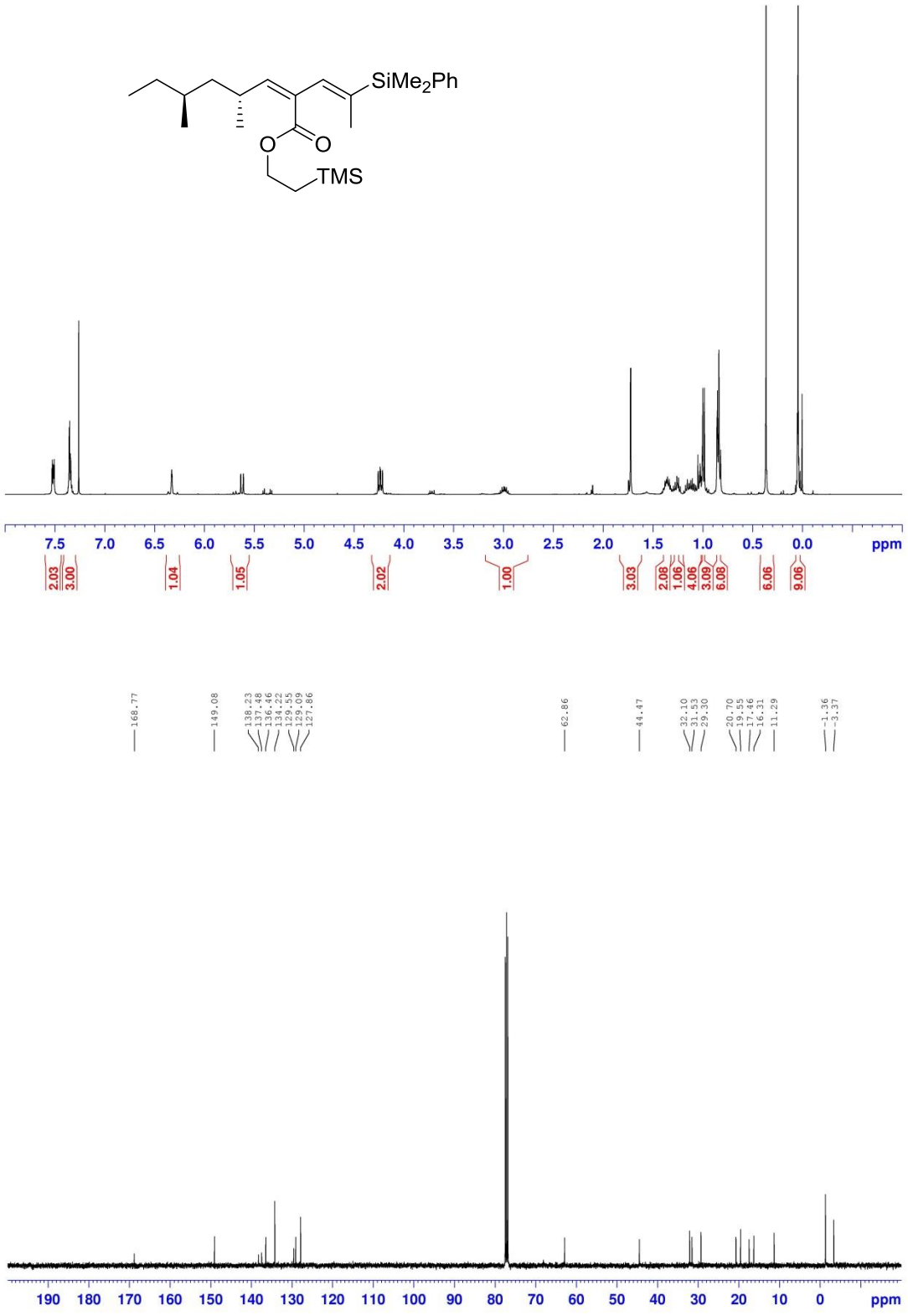

SiMe2Ph
OH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.12 3.12 1.00 1.00 2.09 1.02 3.11 1.05 2.05 1.09 3.06 2.06 6.03 6.05

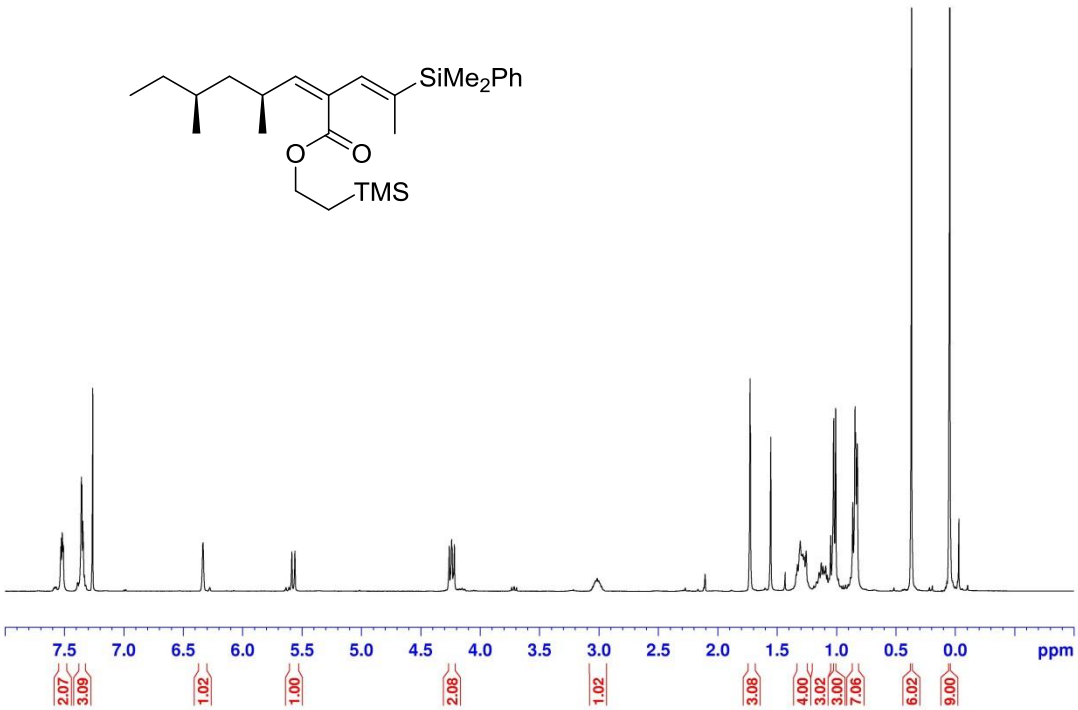

140.58
139.41
138.44
138.13
134.71
134.16
129.09
127.91
61.04
44.90
32.47
30.41
30.31
22.51
19.20
16.82
11.48
-3.28
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

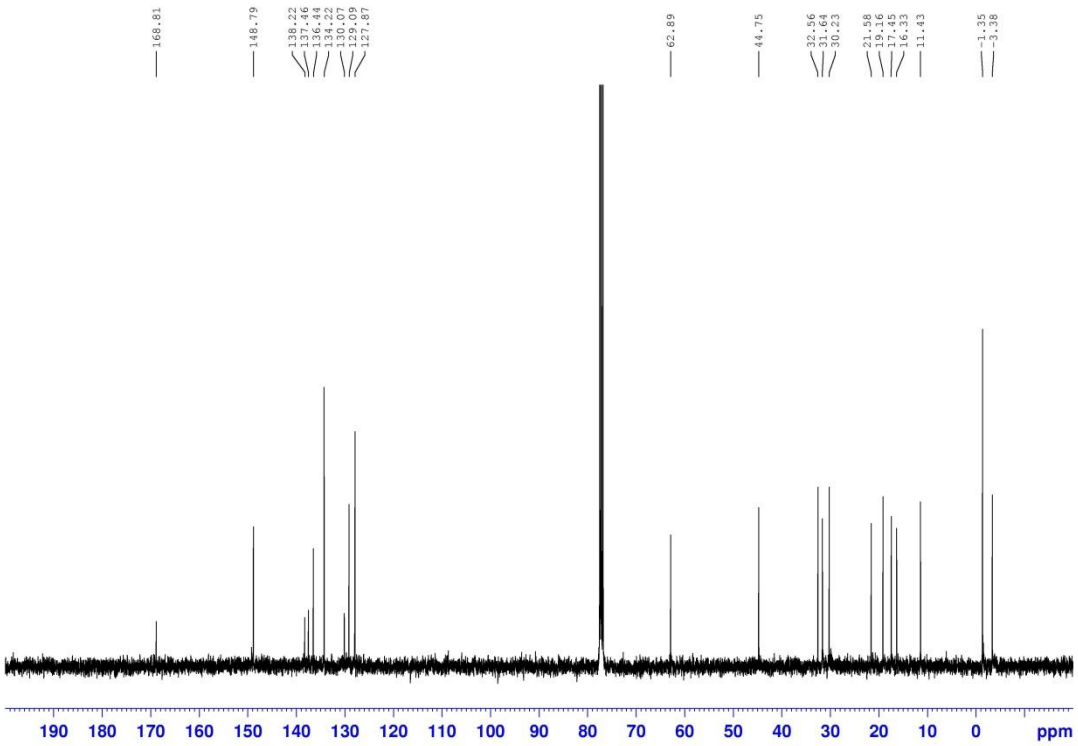

SiMe2Ph
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
2.05
3.06
1.00
1.02
1.03
3.09
3.07
5.06
6.07
6.08


191.02
158.18
140.39
138.03
135.28
134.17
133.57
129.14
127.92
44.64
32.14
29.35
29.07
21.41
19.63
16.91
11.24
-3.43
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SiMe2Ph
O
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
2.08
3.07
1.00
1.06
1.03
3.04
5.07
3.09
6.04
6.03
191.04
157.97
140.36
138.02
135.84
134.17
133.59
129.14
127.92
44.56
32.55
30.24
29.47
22.26
19.05
16.92
11.42
-3.43
-3.45
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


SiMe2Ph
O
O
TMS
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.03 3.00 1.04 1.05 2.02 1.00 3.03 2.08 1.06 4.06 3.09 6.08 6.06 9.06
168.77 149.08 138.23 137.48 136.46 134.22 129.55 129.09 127.86 62.86 44.47 32.10 31.53 29.30 20.70 19.55 17.66 16.31 11.29 -1.36 -3.37
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


SiMe2Ph
O
O
TMS
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.07
3.09
1.02
1.00
2.08
1.02
3.08
4.00
3.02
3.00
7.06
6.02
9.00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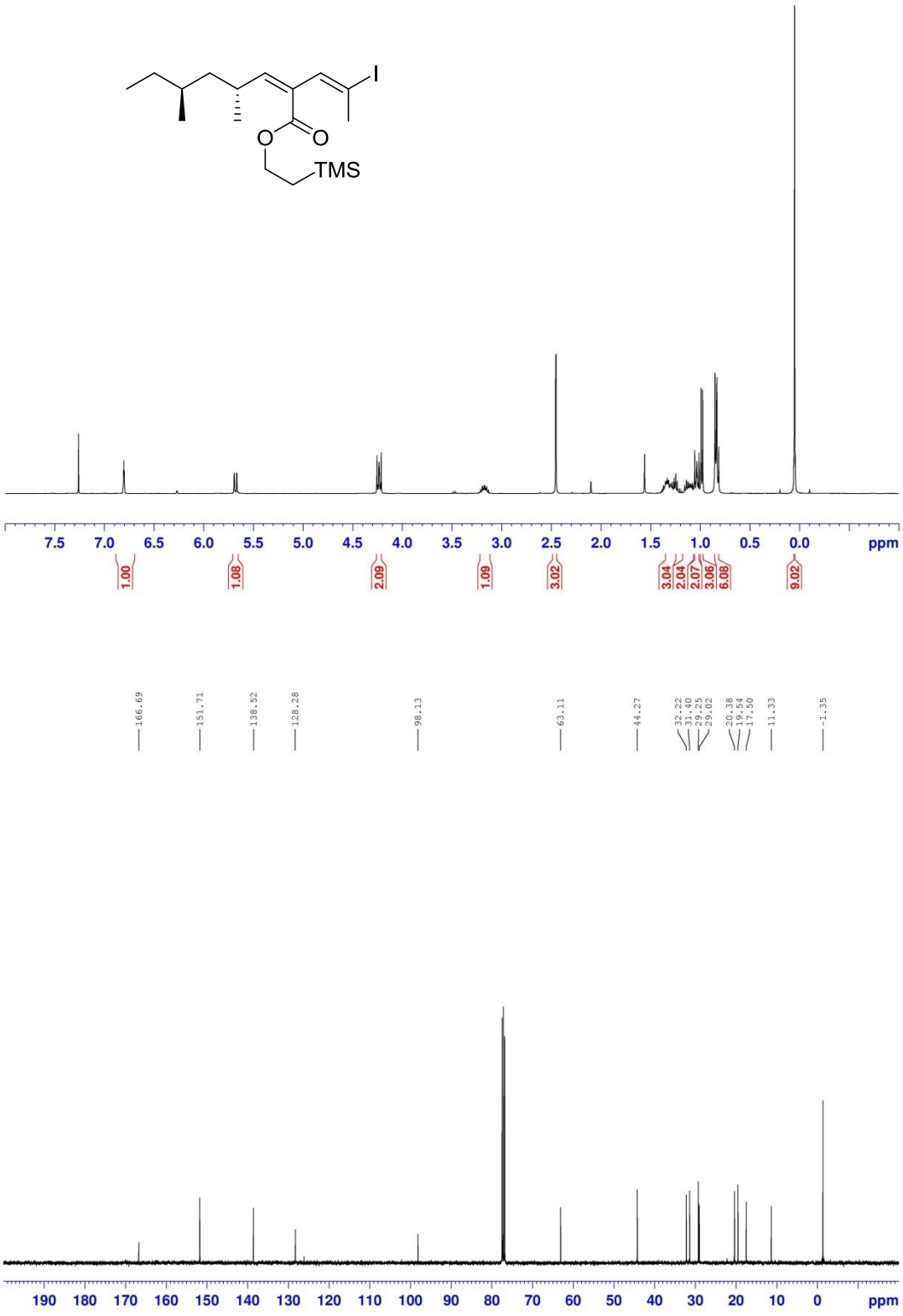
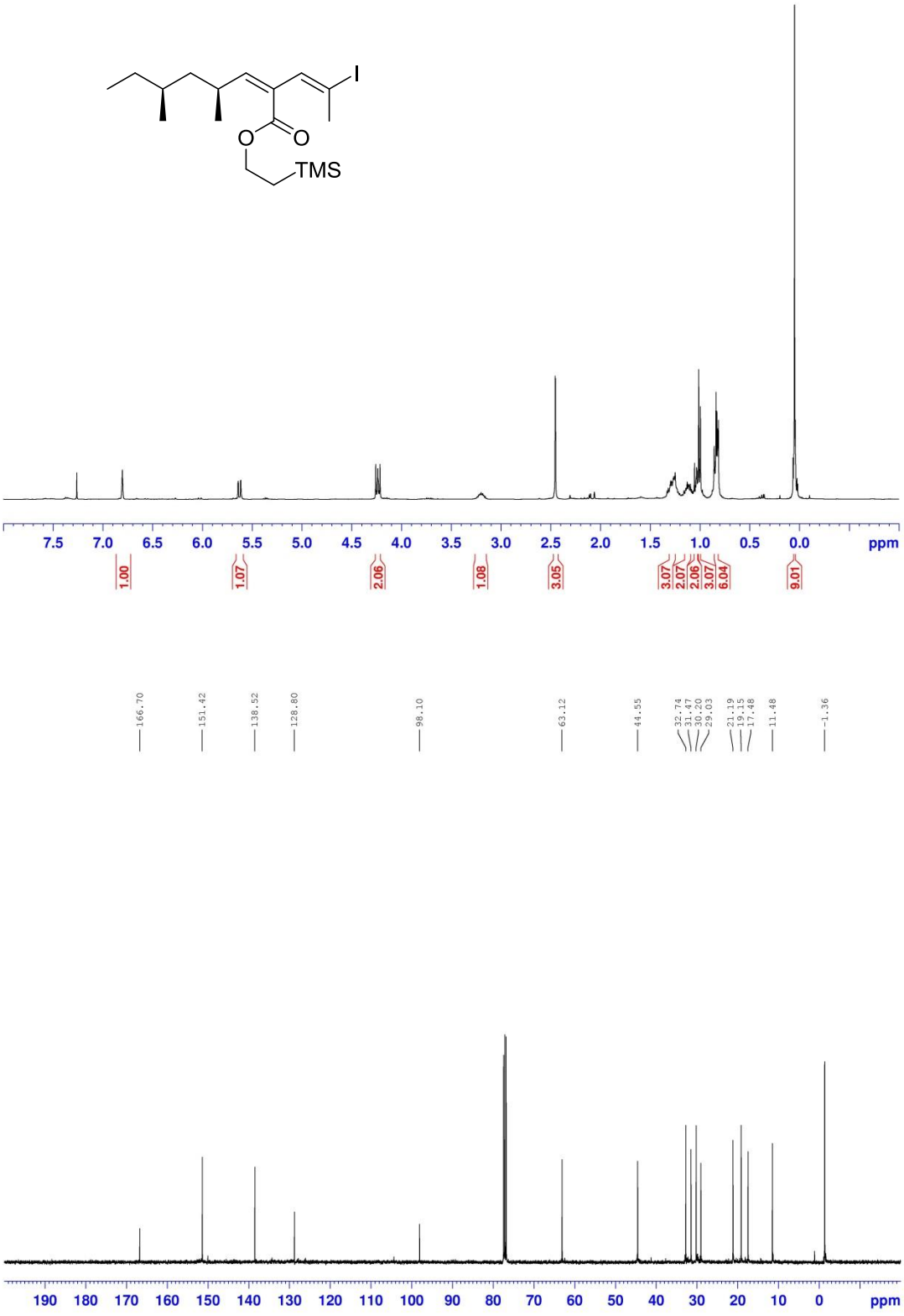
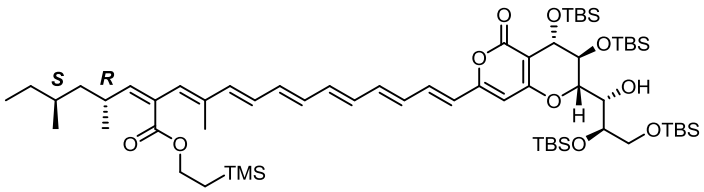
148.79
138.22
137.46
136.44
134.22
130.07
129.09
127.87
62.89
44.75
32.56
31.64
30.23
21.58
19.16
17.45
16.33
11.43
-1.35
-3.38
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


I
O
O
TMS
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.08 2.09 1.09 3.02 3.04 2.04 2.07 3.06 6.08 9.02
166.69 151.71 138.52 128.28 98.13 63.11 44.27 32.22 31.40 29.25 29.02 20.38 19.54 17.50 11.33 -1.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


I
O
O
TMS
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.07 2.06 1.08 3.05 3.07 2.07 2.06 3.07 6.04 9.01
166.70 151.42 138.52 128.80 98.10 63.12 44.55 32.74 31.47 30.20 29.03 21.19 19.15 17.48 11.48 -1.36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


S
R
O
OTBS
OTBS
O
O
OH
H
TBSO
OTBS
O
O
TMS

7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
1.03
1.03
7.08
1.05
1.04
1.05
1.03
1.05
1.05
1.04
2.09
1.05
2.09
2.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.03
1.03
7.08
1.05
1.04
1.05
1.03
1.05
1.05
1.04
2.09
1.05
2.09
2.09
1.00
3.02
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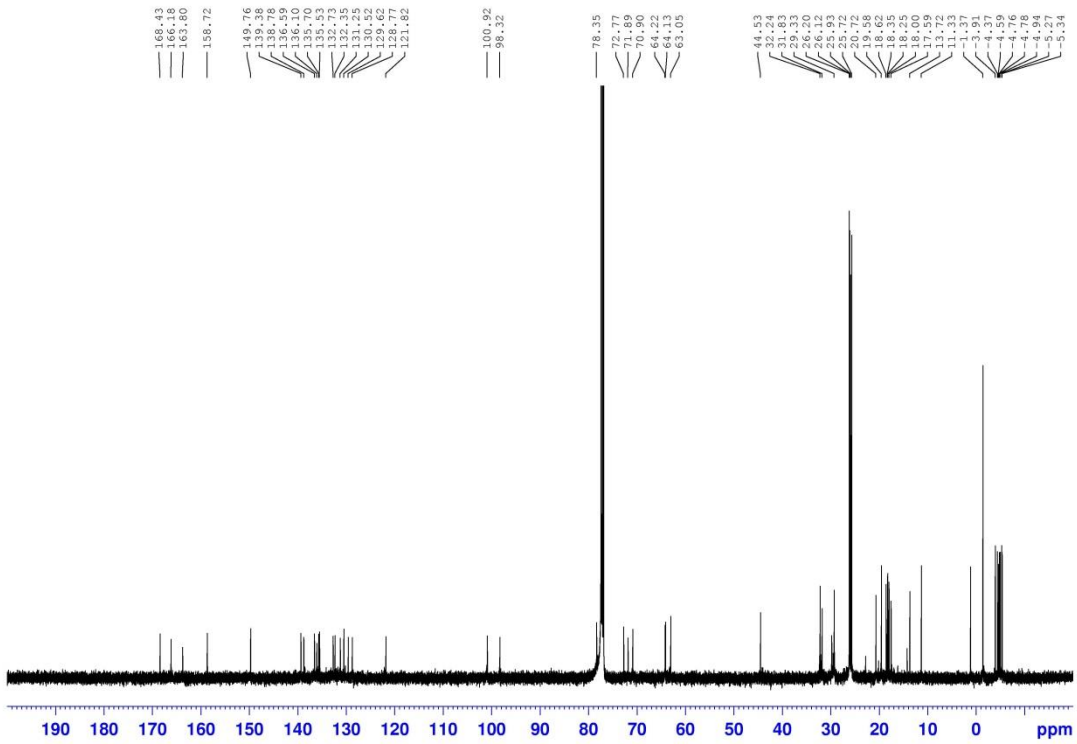
15.00
3.09
3.07
6.09
6.07
15.09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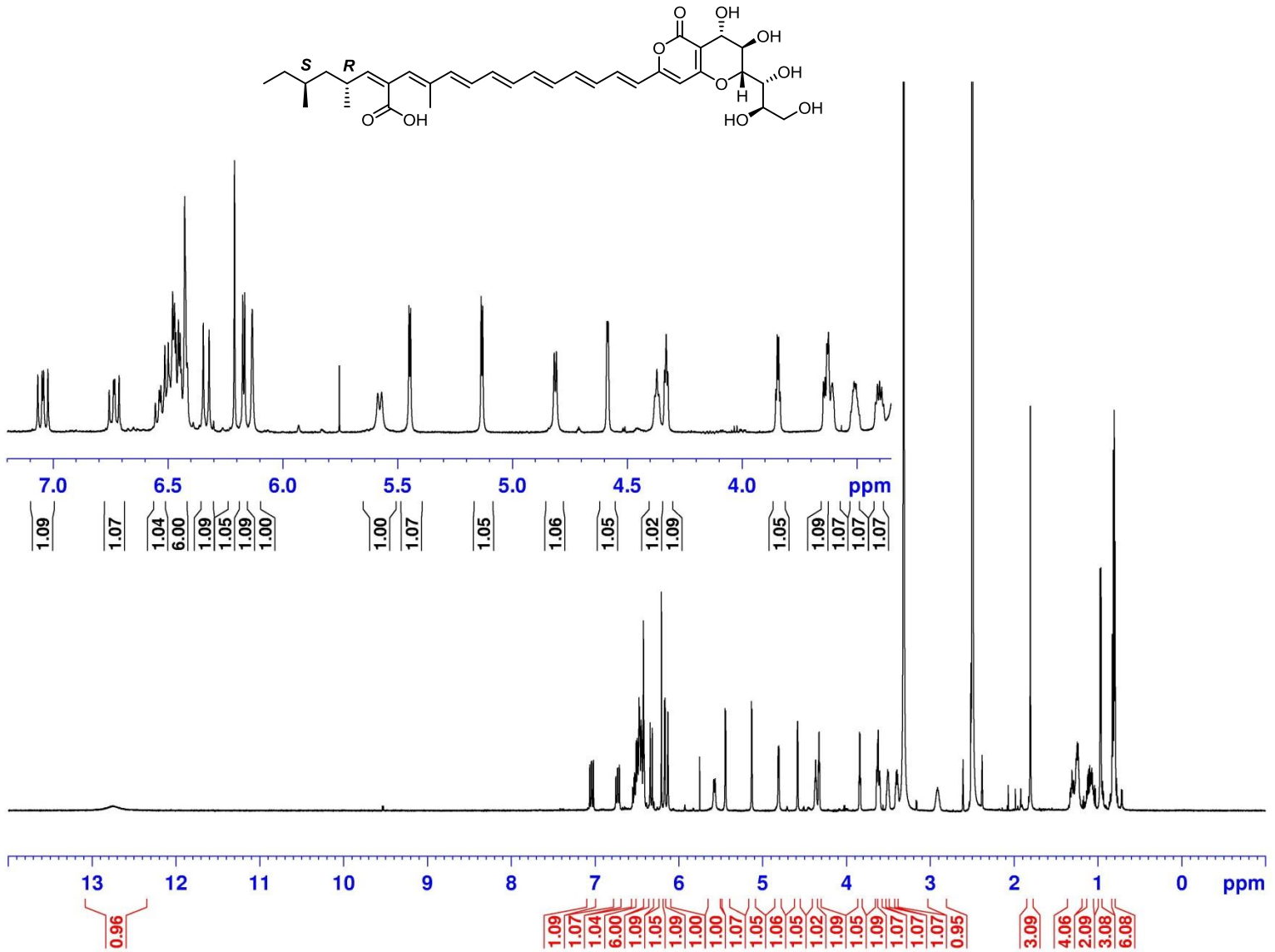
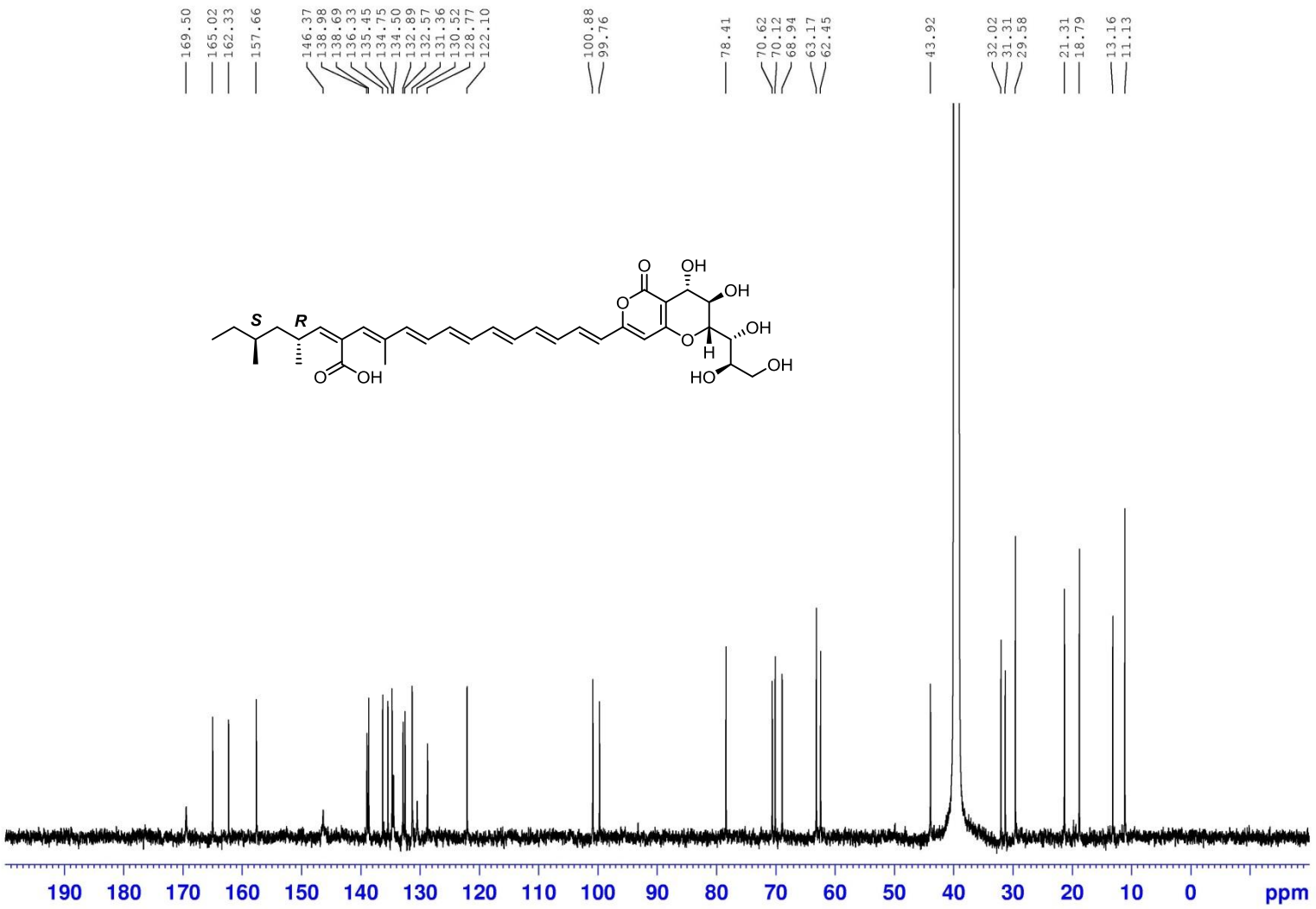
139.38
138.78
136.59
136.10
135.70
135.53
132.73
132.35
131.25
130.52
129.62
128.77
121.82
100.92
98.32
78.35
72.77
71.89
70.90
64.22
64.13
63.05
44.53
32.24
31.83
31.33
26.20
26.12
25.93
25.72
20.72
19.88
19.62
18.55
18.25
18.00
17.59
13.72
11.33
-1.37
-3.91
-4.37
-4.59
-4.76
-4.78
-4.78
-4.94
-5.27
-5.34
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


S
R
O
OH
OH
OH
OH
O
O
H
HO
OH
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
1.09
1.07
1.04
6.00
1.09
1.05
1.09
1.00
1.00
1.07
1.05
1.06
1.05
1.02
1.09
1.05
1.09
1.07
1.07
1.07
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
1.09
1.07
1.04
6.00
1.09
1.05
1.09
1.00
1.00
1.07
1.05
1.06
1.05
1.02
1.09
1.05
1.09
1.07
1.07
1.07
0.95
3.09
4.06
2.09
3.08
6.08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136.33
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134.75
134.50
132.89
132.57
131.36
130.52
128.77
122.10
100.88
99.76
78.41
70.62
70.12
68.94
63.17
62.45
43.92
32.02
31.31
29.58
21.31
18.79
13.16
11.13
S
R
O
OH
OH
OH
OH
H
HO
190
180
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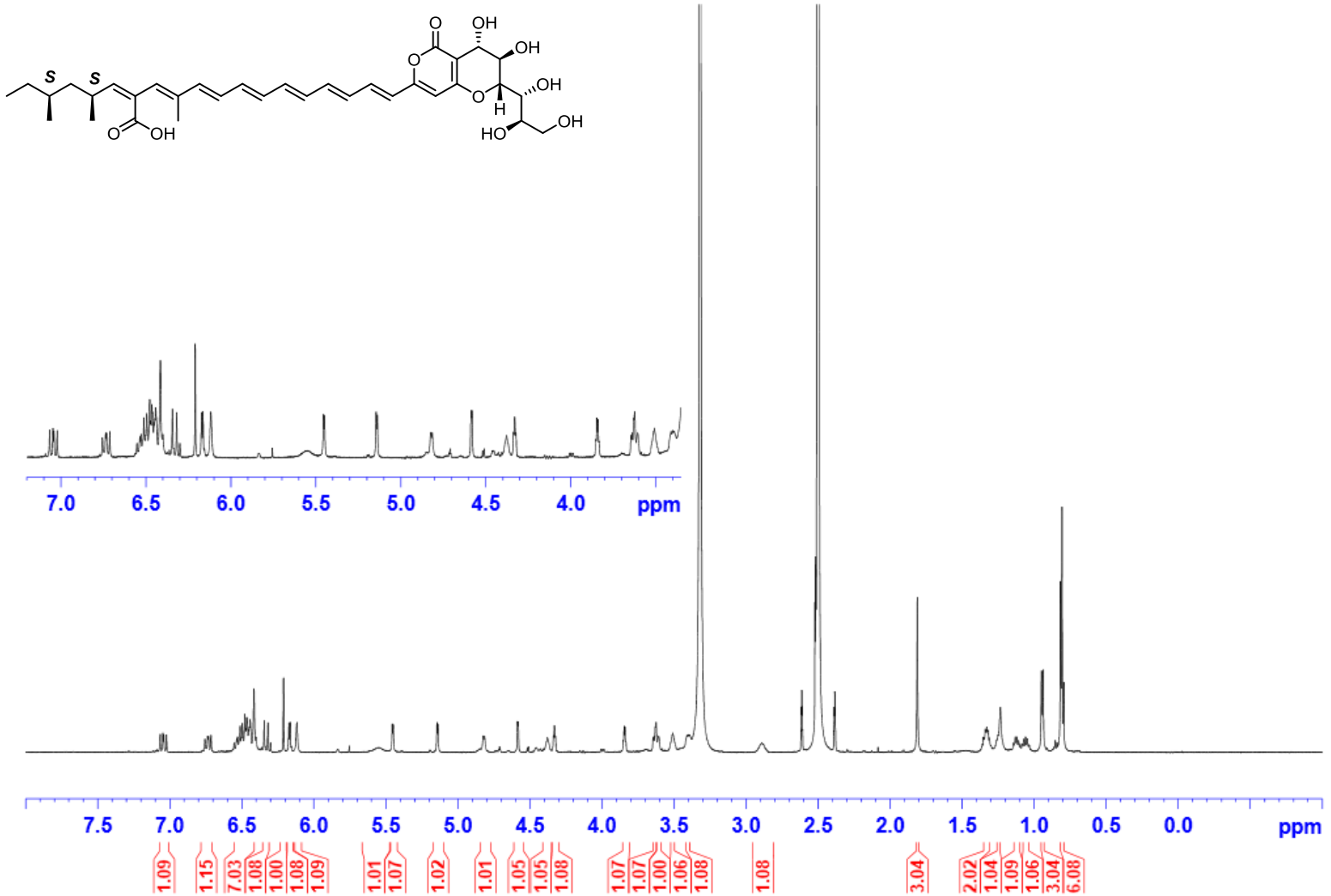
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


S
S
O
OH
O
OH
OH
OH
H
HO
OH
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.09
1.15
7.03
1.08
1.00
1.08
1.09
1.01
1.07
1.02
1.01
1.05
1.05
1.08
1.07
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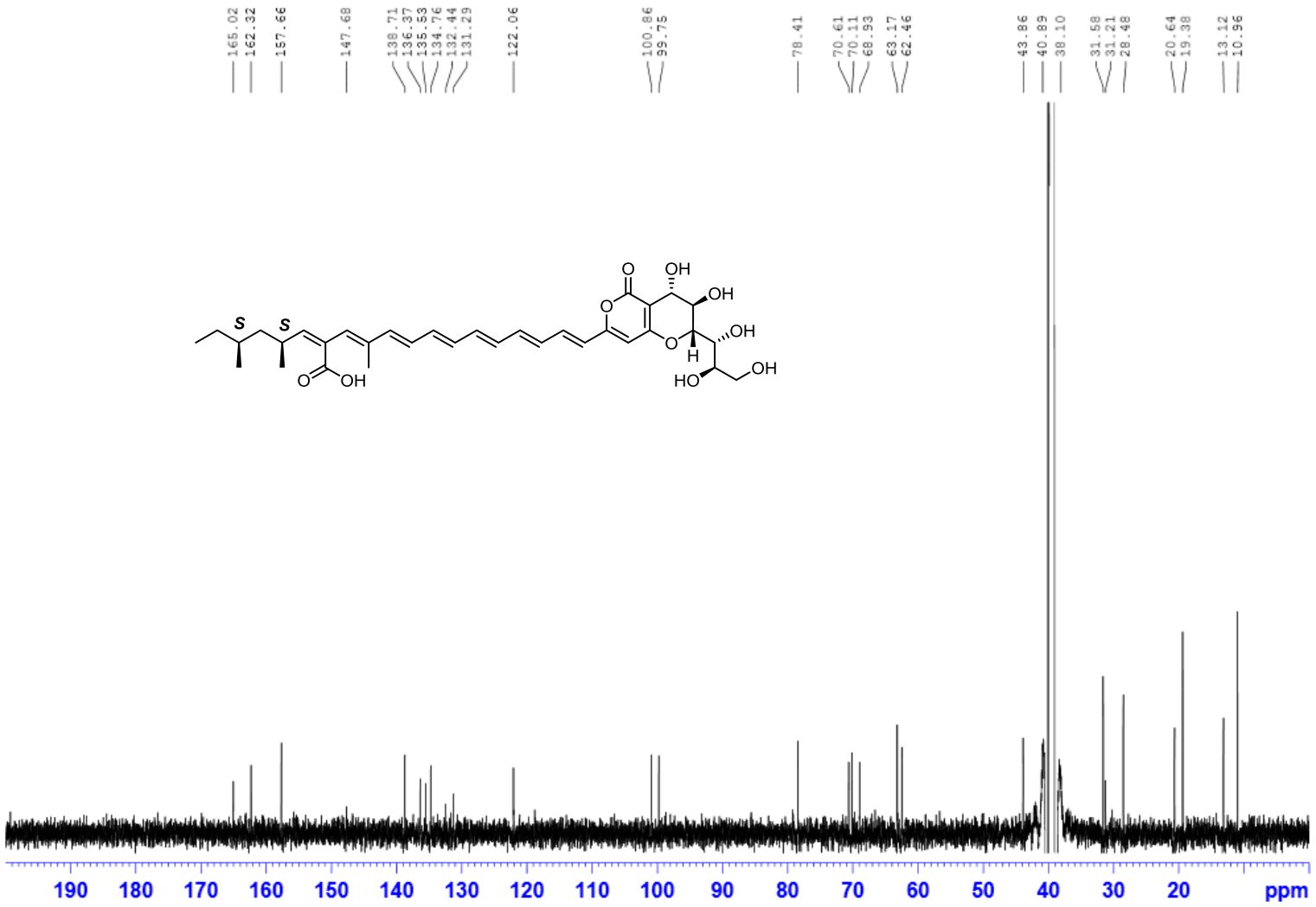
2.02
1.04
1.09
1.06
3.04
6.08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147.68
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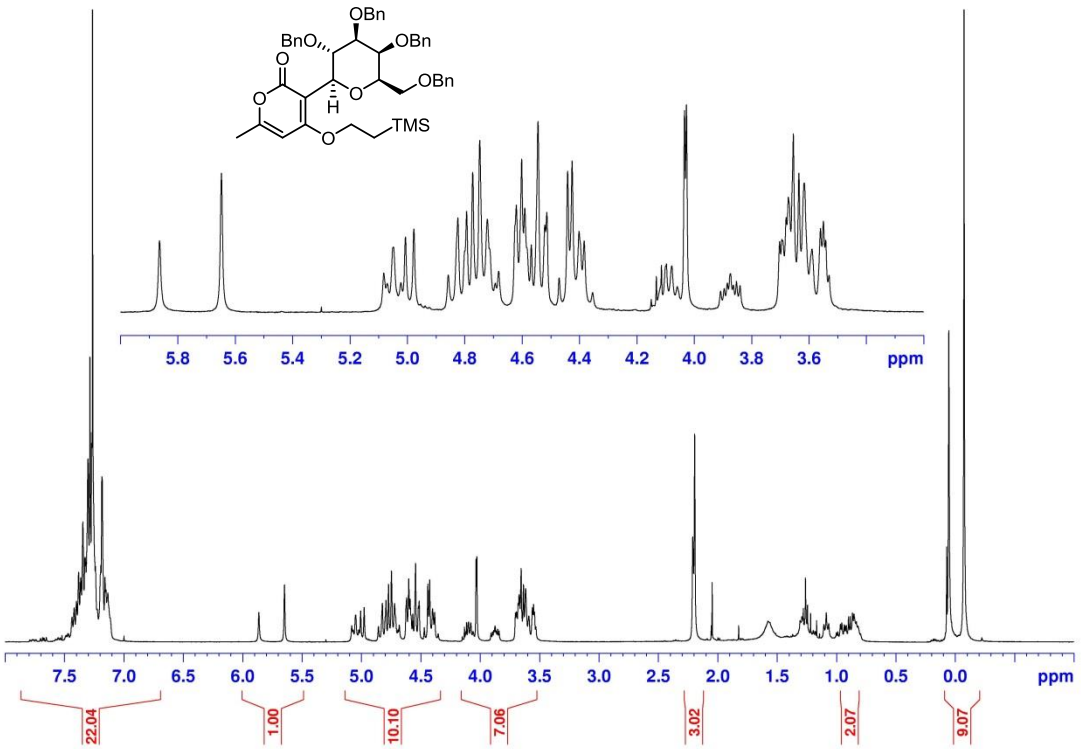
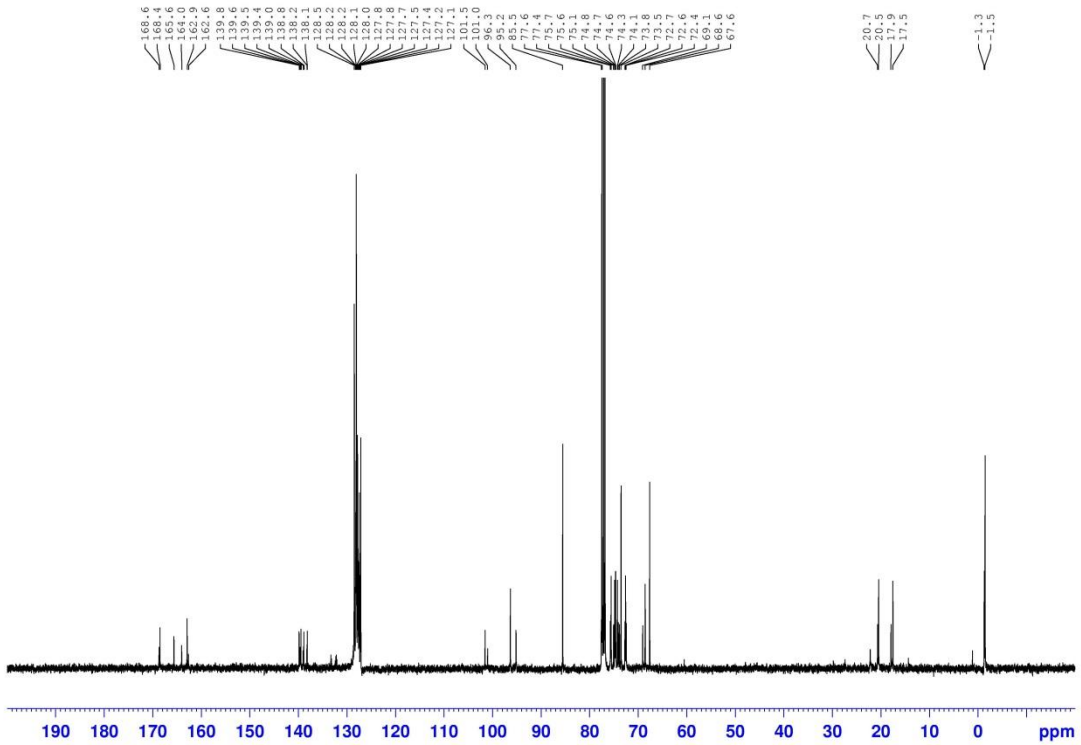
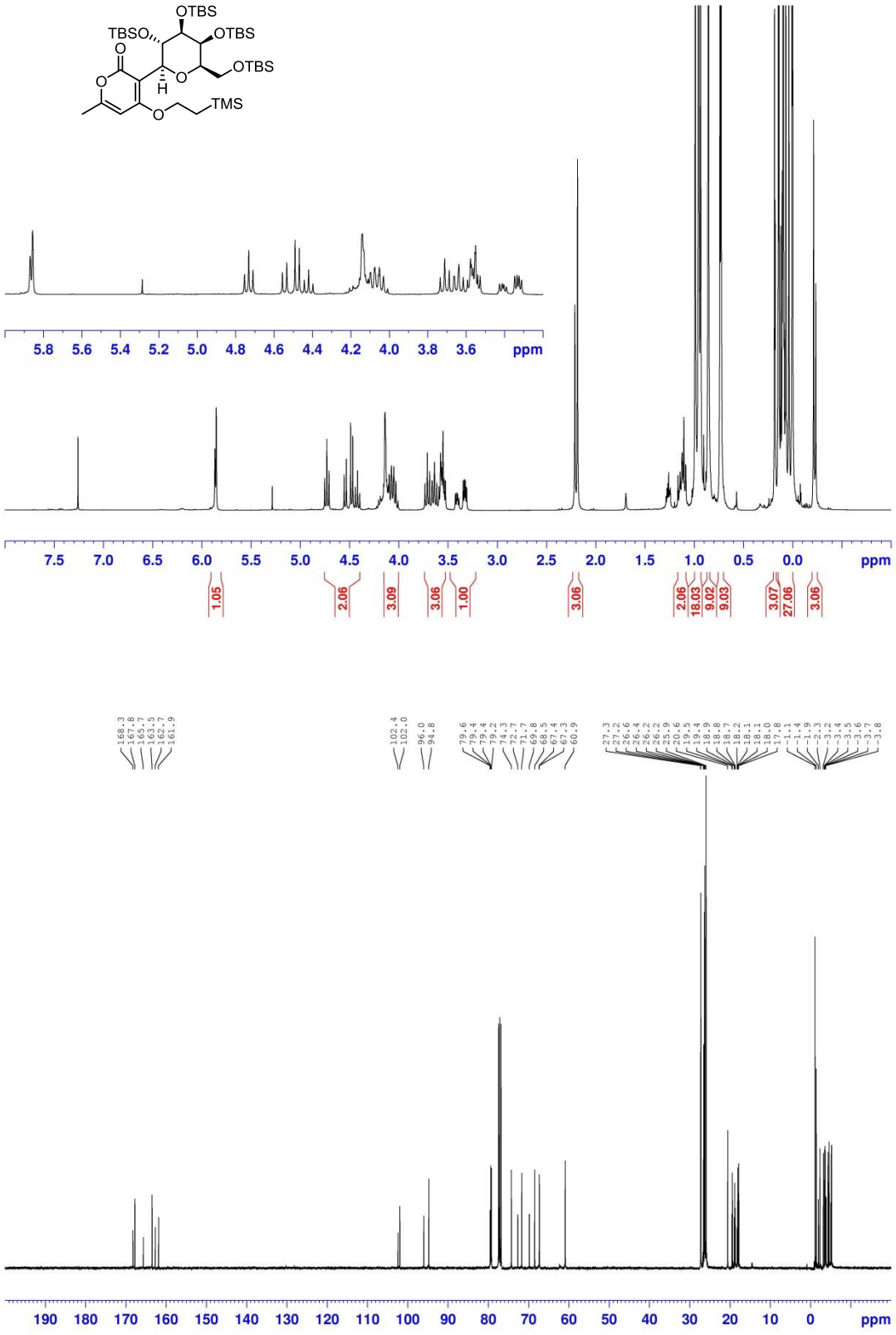
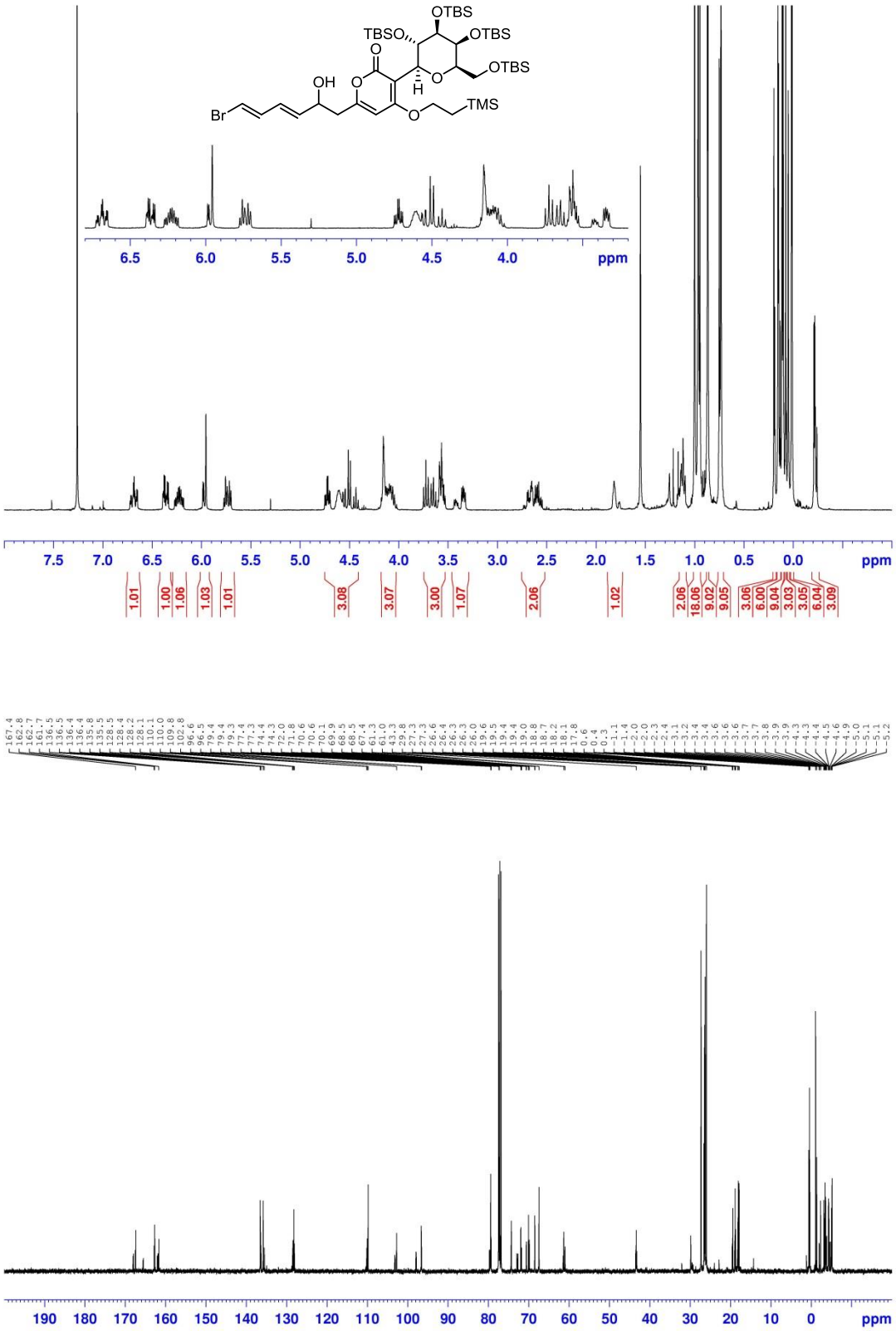
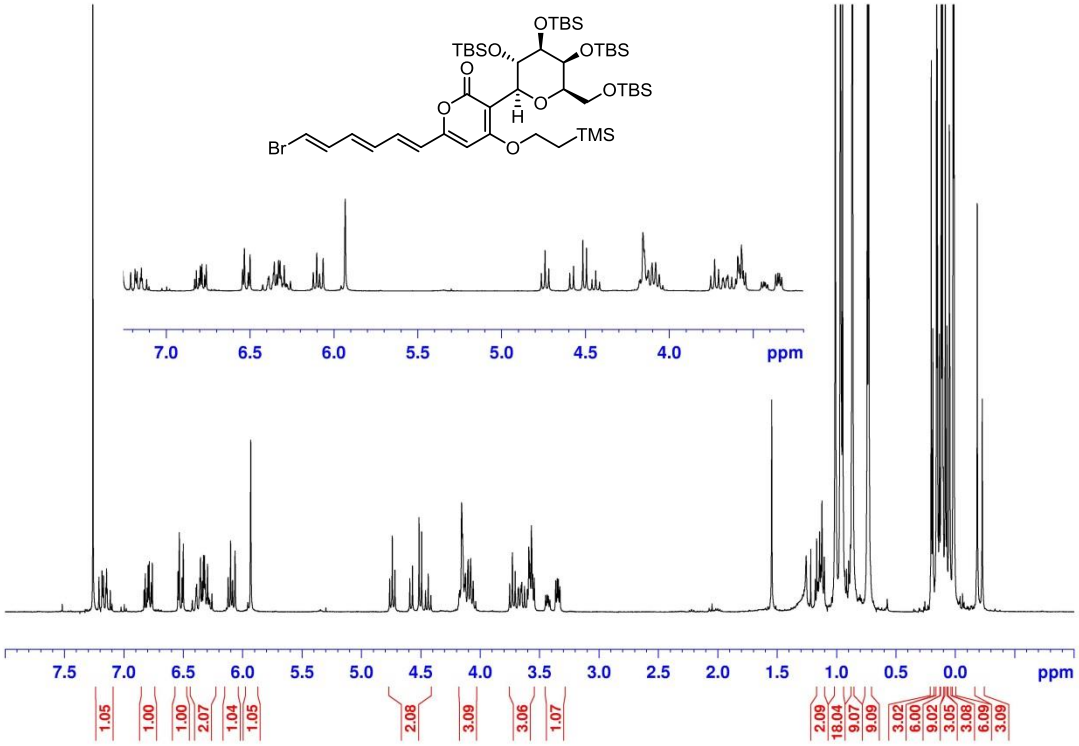
134.76
132.44
131.29
122.06
100.86
99.75
78.41
70.61
70.11
68.93
63.17
62.46
43.86
40.89
38.10
31.58
31.21
28.48
20.64
19.38
13.12
10.96
S
S
O
OH
O
OH
OH
OH
H
HO
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

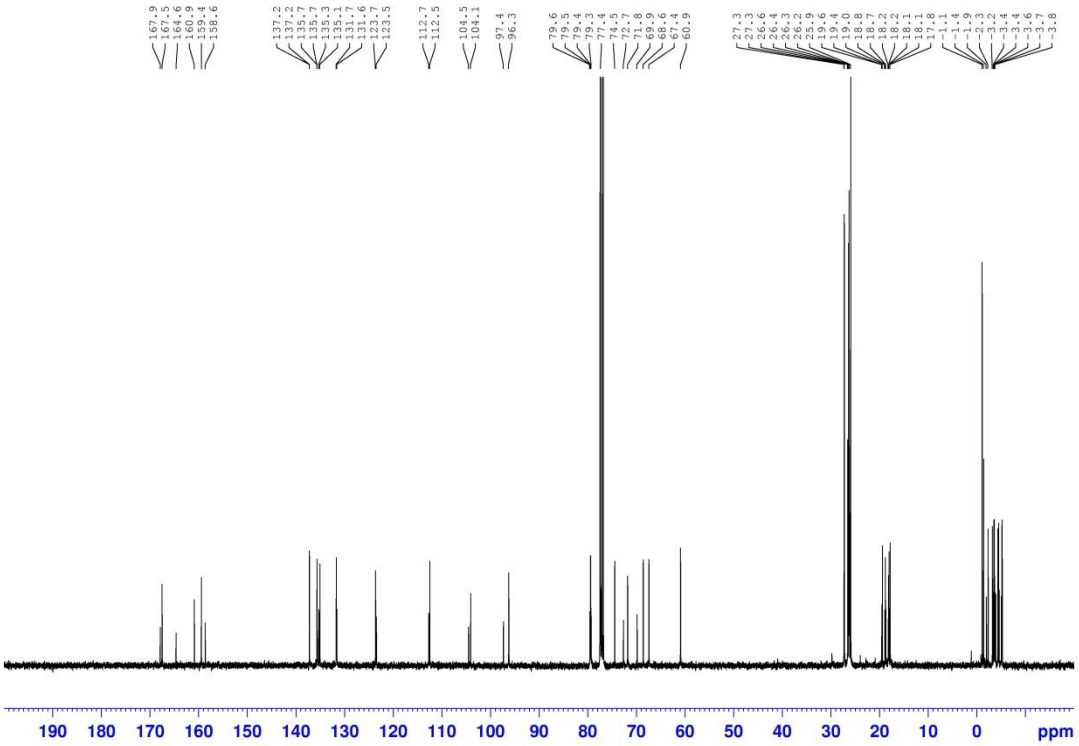

OBn
BnO
OBn
OBn
O
O
O
H
TMS
O
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
22.04
1.00
10.10
7.06
3.02
2.07
9.07

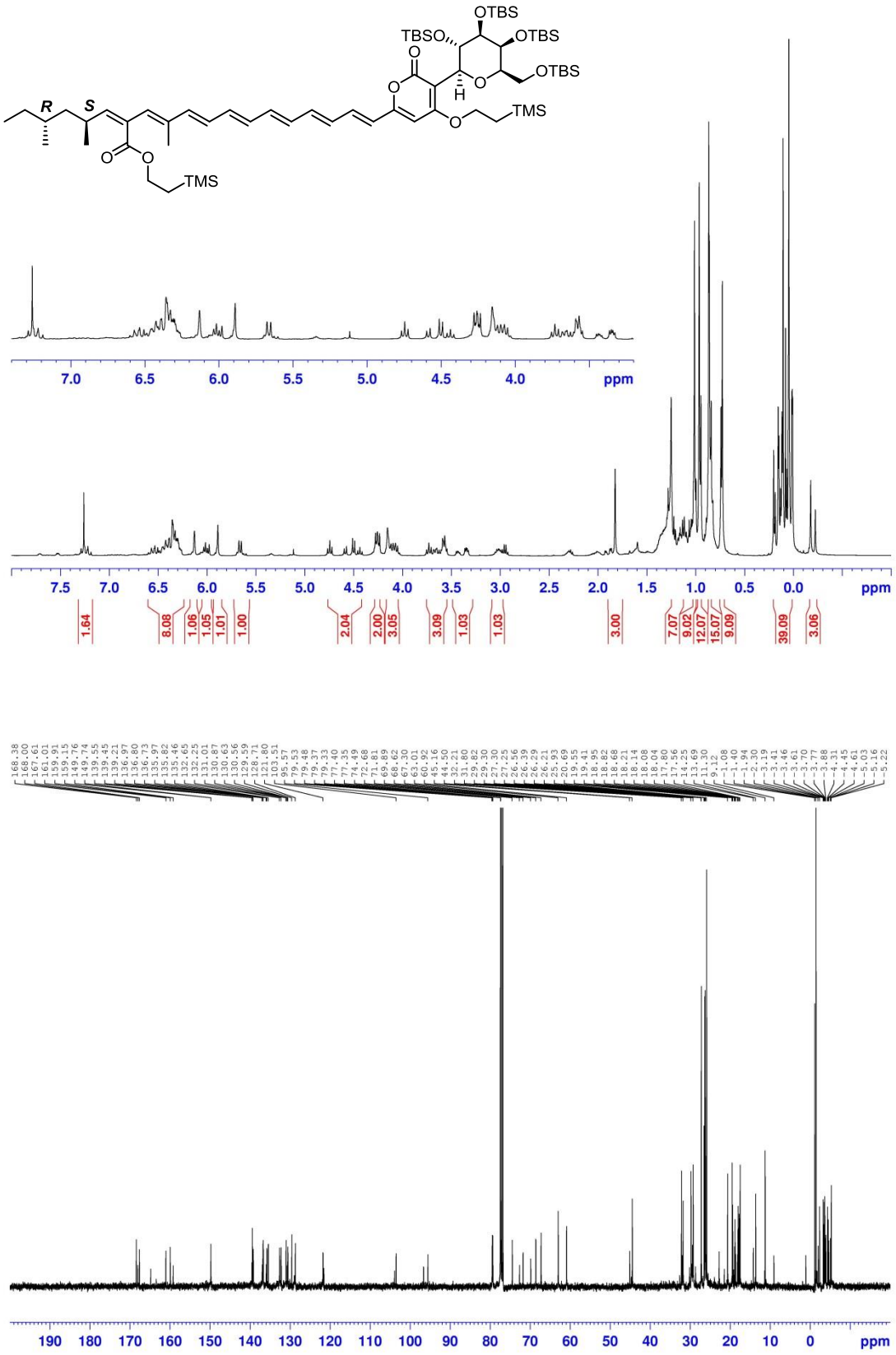

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

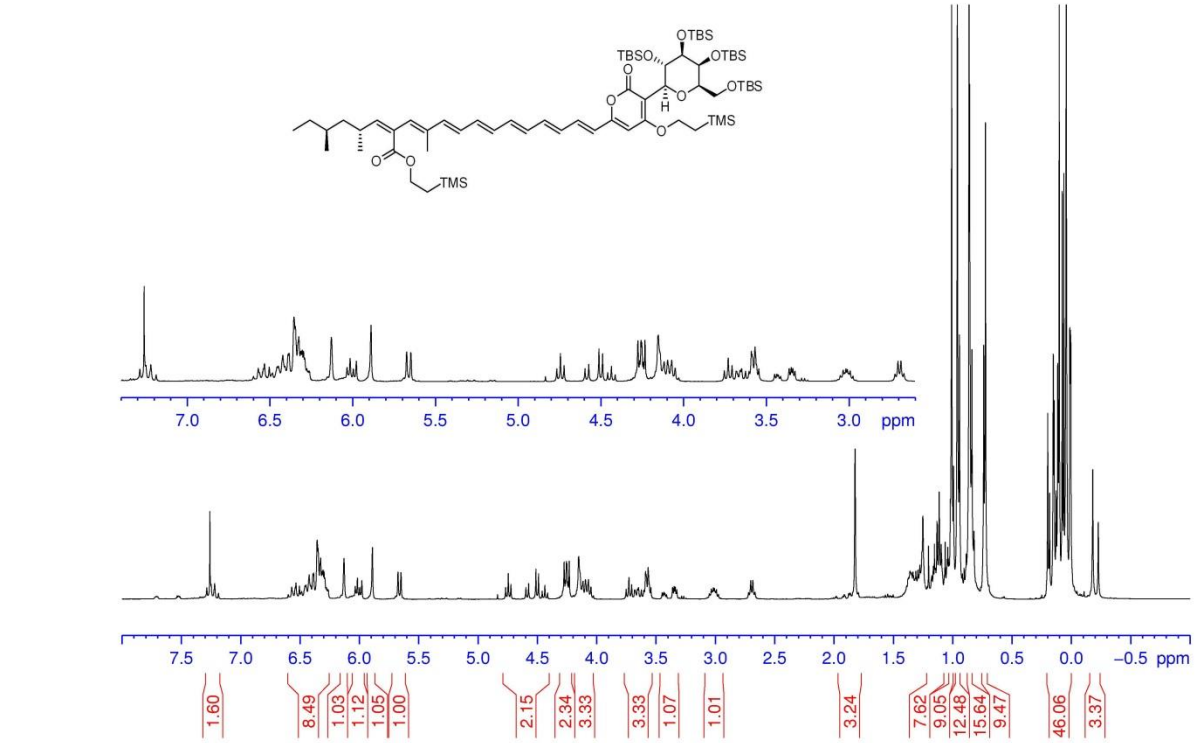

OTBS
TBSO
OTBS
OTBS
O
O
O
H
TMS
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.05 2.06 3.09 3.06 1.00 3.06 2.06 18.03 9.02 9.03 3.07 27.06 3.06
168.3 167.8 165.7 163.5 162.7 161.9
102.4 102.0 96.0 94.8
79.6 79.4 79.4 79.2 74.3 72.7 71.7 69.8 69.5 67.4 67.3 60.9
27.3 27.2 26.6 26.4 26.2 26.2 25.9 20.6 19.5 19.4 18.9 18.8 18.7 18.2 18.1 18.1 18.0 17.8 -1.1 -1.4 -1.9 -2.3 -3.2 -3.4 -3.5 -3.6 -3.7 -3.8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

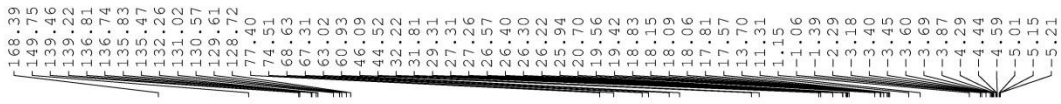

OTBS
TBSO
OTBS
OTBS
O
O
O
H
OH
Br
TMS
6.5
6.0
5.5
5.0
4.5
4.0
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
1.00
1.06
1.03
1.01
3.08
3.07
3.00
1.07
2.06
1.02
2.06
18.06
9.02
9.05
3.06
6.00
9.04
3.03
3.05
6.04
3.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

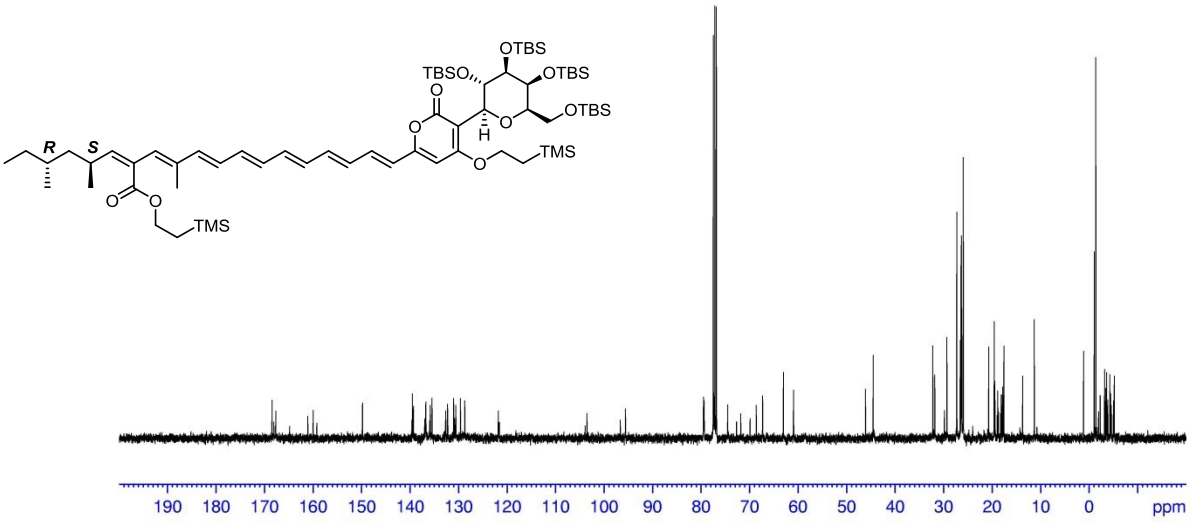

OTBS
TBSO
OTBS
OTBS
O
O
O
H
Br
O
TMS
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.05
1.00
1.00
2.07
1.04
1.05
2.08
3.09
3.06
1.07
2.09
18.04
9.07
9.09
3.02
6.00
9.02
3.05
3.08
6.09
3.09

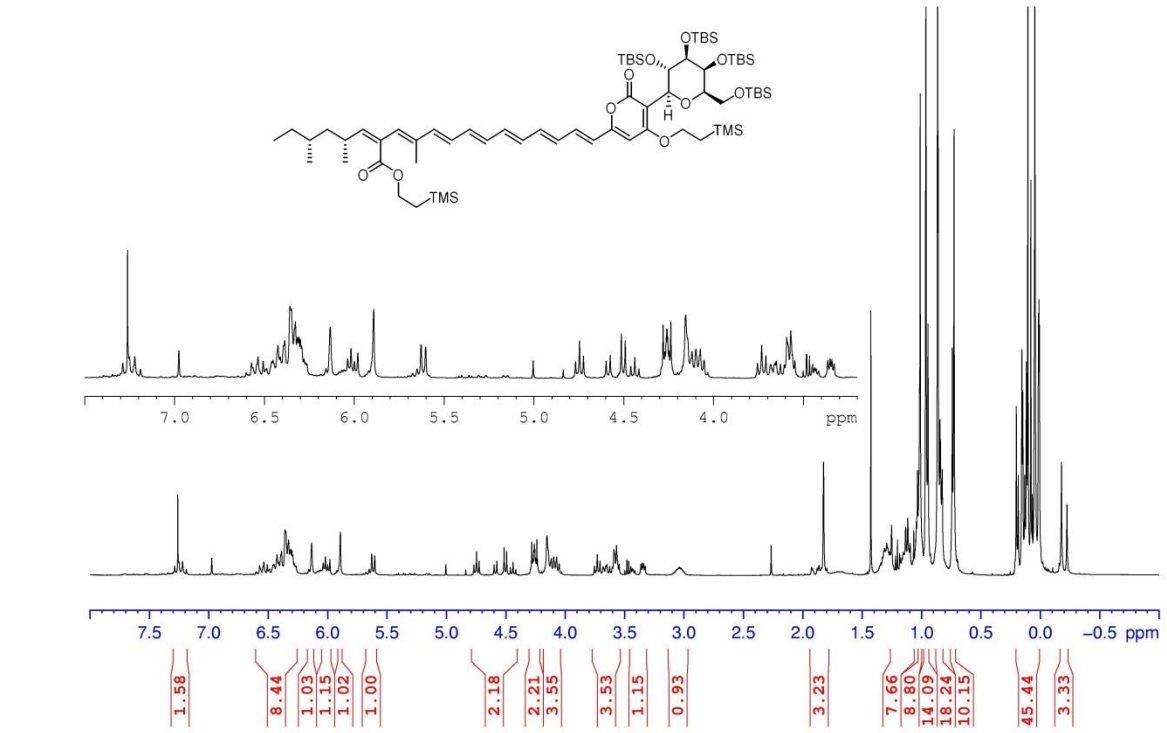

167.9
167.5
164.6
160.9
159.4
158.6
137.2
137.2
135.7
135.7
135.3
135.1
131.7
131.6
123.7
123.5
112.7
112.5
104.5
104.1
97.4
96.3
79.6
79.5
79.4
79.3
77.4
74.5
72.7
71.8
69.9
68.6
67.4
60.9
27.3
27.3
26.6
26.4
26.3
26.2
25.9
25.6
19.4
19.0
18.8
18.7
18.2
18.2
18.1
18.1
17.8
-1.1
-1.4
-1.9
-2.3
-3.2
-3.4
-3.4
-3.6
-3.7
-3.8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

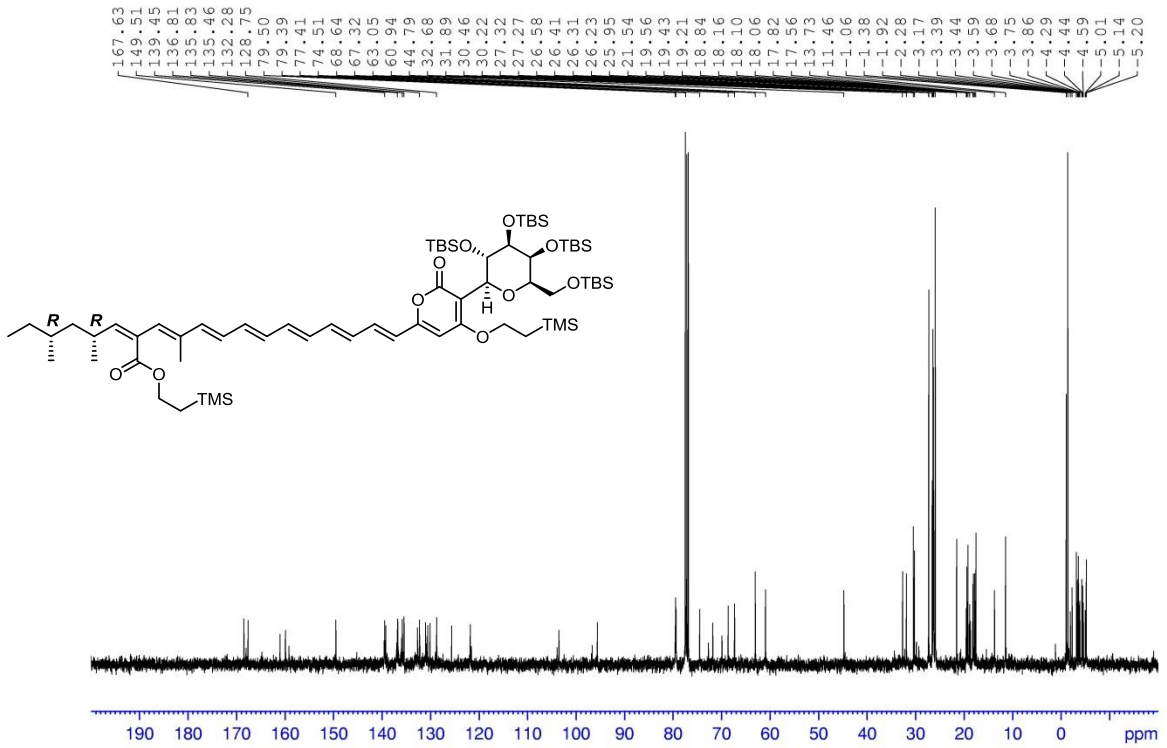

OTBS
TBSO
OTBS
OTBS
O
O
O
H
R
S
TMS
O
O
O
TMS
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.64
8.08
1.06
1.05
1.01
1.00
2.04
2.00
3.05
3.09
1.03
1.03
3.00
7.07
9.02
12.07
15.07
9.09
39.09
3.06
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

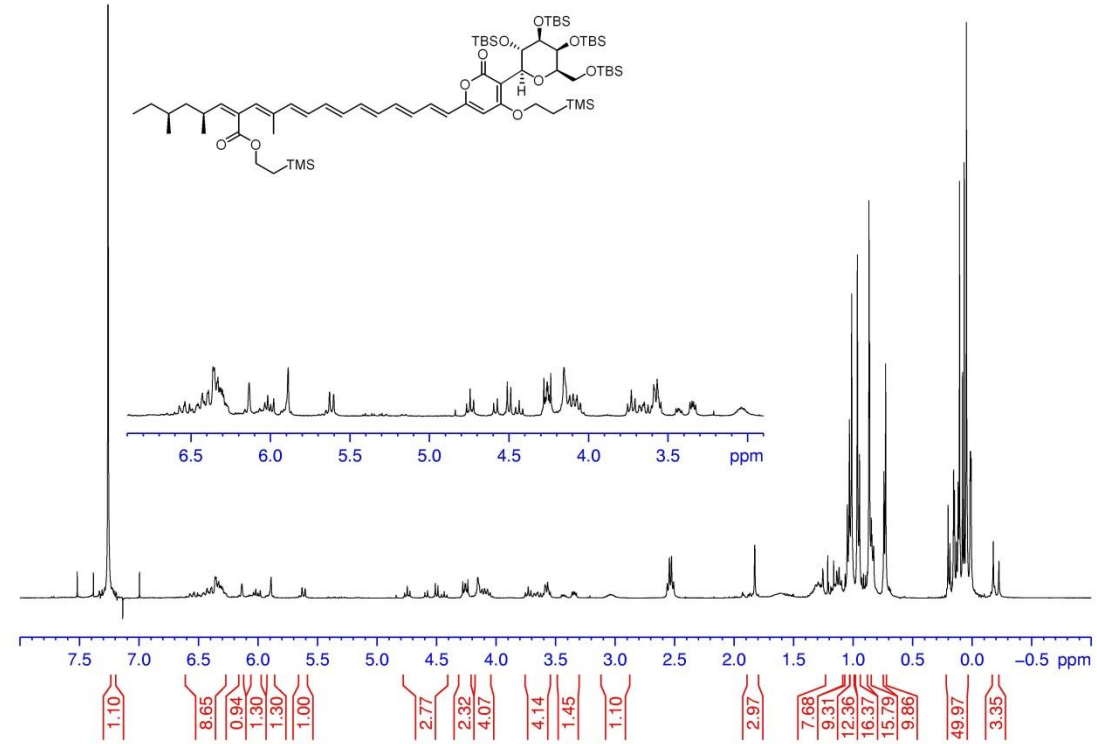

OTBS
TBSO
OTBS
OTBS
TMS
TMS
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
1.60 8.49 1.03 1.12 1.05 1.00 2.15 2.34 3.33 3.33 1.07 1.01 3.24 7.62 9.05 12.48 15.64 9.47 46.06 3.37

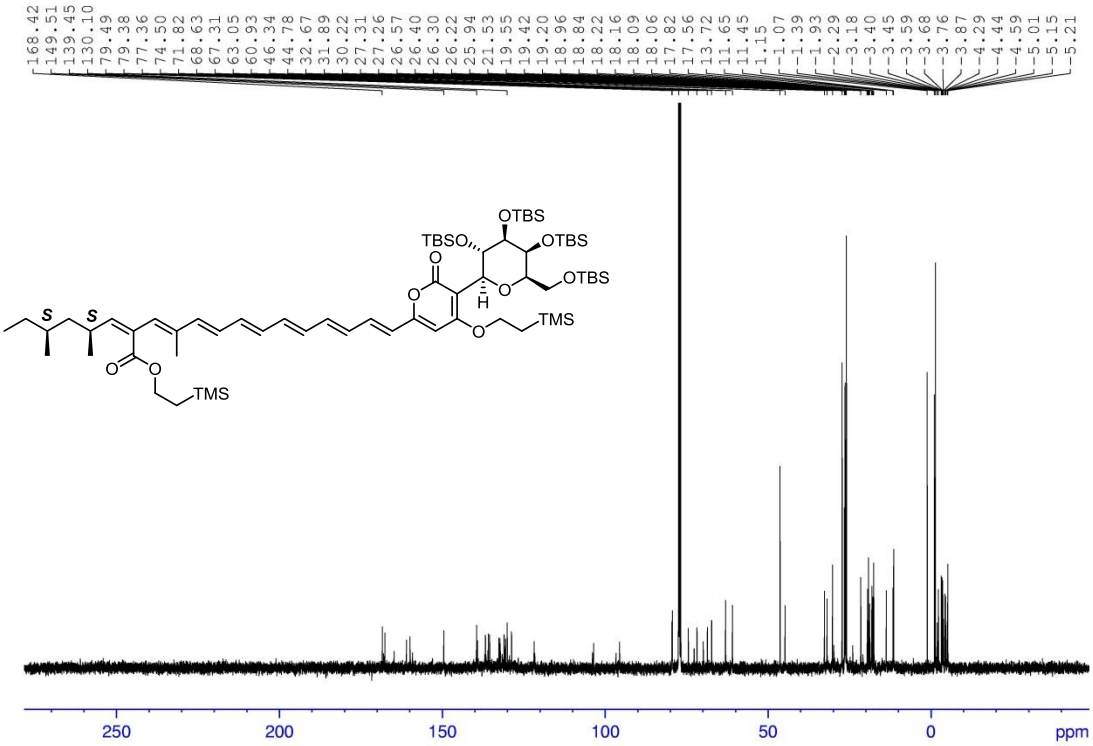

168.39
149.75
139.46
139.22
136.81
136.74
135.83
135.47
132.26
131.02
130.57
129.61
128.72
77.40
74.51
68.63
67.31
63.02
60.93
46.09
44.52
32.22
31.81
29.31
27.31
27.26
26.57
26.40
26.30
26.22
25.94
20.70
19.56
19.42
18.83
18.15
18.09
18.06
17.81
17.57
13.70
11.31
1.15
-1.06
-1.39
-2.29
-3.18
-3.40
-3.45
-3.60
-3.69
-3.87
-4.29
-4.44
-4.59
-5.01
-5.15
-5.21

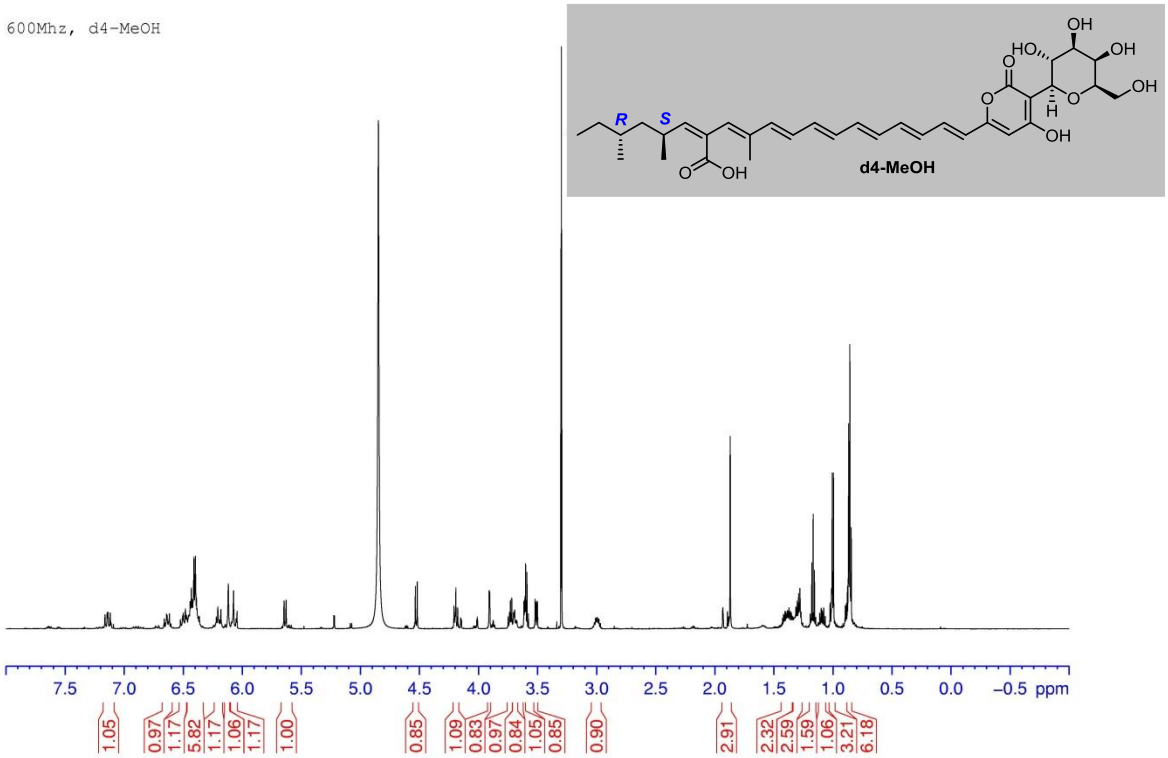

OTBS
TBSO
OTBS
OTBS
R
S
TMS
TMS
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

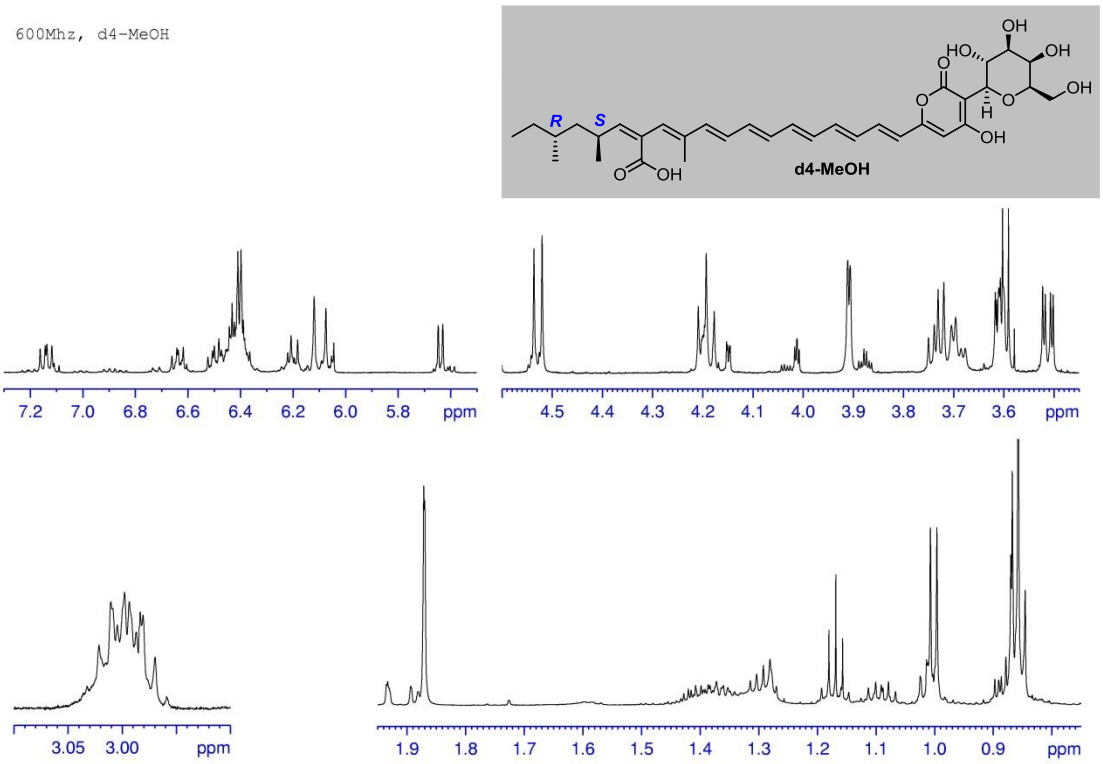

OTBS
TBSO
OTBS
OTBS
TMS
TMS
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
1.58
8.44
1.03
1.15
1.02
1.00
2.18
2.21
3.55
3.53
1.15
0.93
3.23
7.66
8.80
14.09
18.24
10.15
45.44
3.33

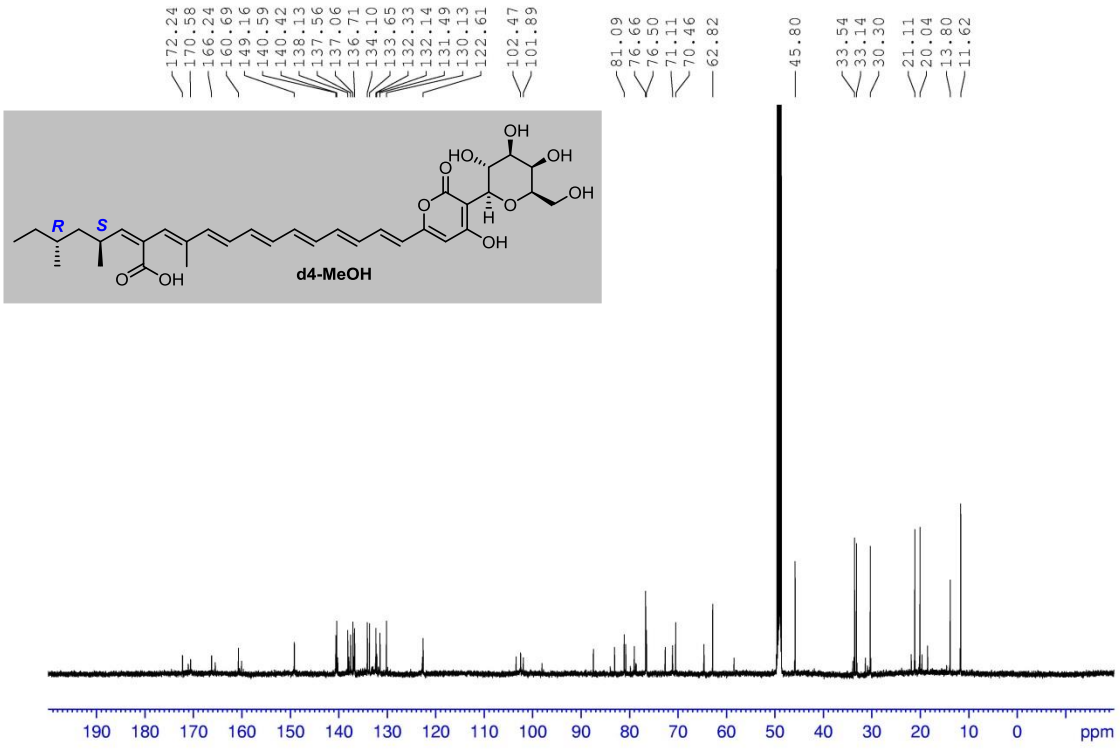

167.63
149.51
139.45
136.81
135.83
135.46
132.28
128.75
79.50
79.39
77.41
74.51
68.64
67.32
63.05
60.94
44.79
32.68
31.89
30.46
30.22
27.32
27.27
26.58
26.41
26.31
26.23
25.95
21.54
19.56
19.43
19.21
18.84
18.16
18.10
18.06
17.82
17.56
13.73
11.46
1.06
1.38
1.92
2.28
3.17
3.39
3.44
3.59
3.68
3.75
3.86
4.29
4.44
4.59
5.01
5.14
5.20
OTBS
TBSO
OTBS
OTBS
R
R
TMS
TMS
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

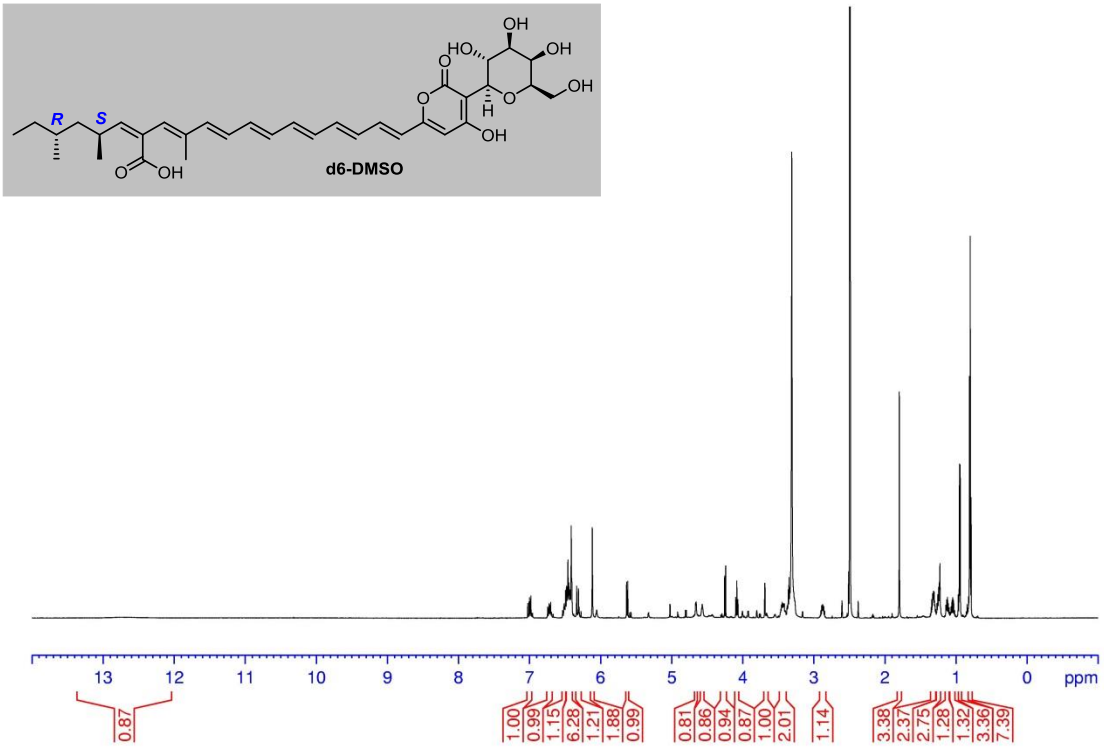

OTBS
TBSO
OTBS
OTBS
TMS
TMS
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5 ppm
1.10
8.65
0.94
1.30
1.30
1.00
2.77
2.32
4.07
4.14
1.45
1.10
2.97
7.68
9.31
12.36
16.37
15.79
9.86
49.97
3.35

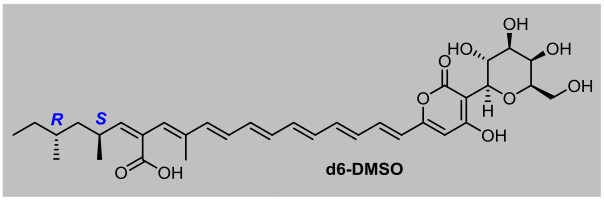

168.42
149.51
139.45
130.10
79.49
79.38
77.36
74.50
71.82
68.63
67.31
63.05
60.93
46.34
44.78
32.67
31.89
30.22
27.31
27.26
26.57
26.40
26.30
26.22
25.94
21.53
19.55
19.42
19.20
18.96
18.84
18.22
18.16
18.09
18.06
17.82
17.56
13.72
11.65
11.45
1.15
1.07
1.39
1.93
2.29
3.18
3.40
3.45
3.59
3.68
3.76
3.87
4.29
4.44
4.59
5.01
5.15
5.21
OTBS
TBSO
OTBS
OTBS
TMS
TMS
250
200
150
100
50
0
ppm

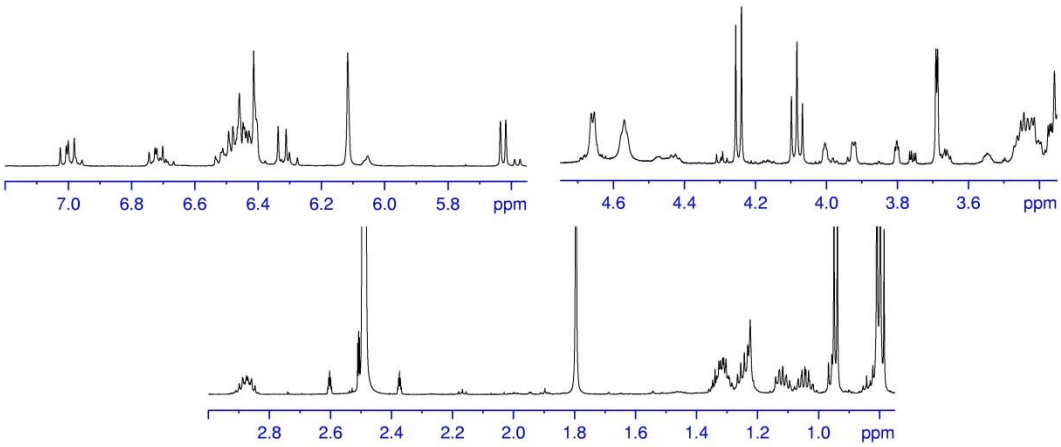

600Mhz, d4-MeOH
d4-MeOH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
1.05 0.97 1.17 5.82 1.17 1.06 1.17 1.00 0.85 1.09 0.83 0.97 0.84 1.05 0.85 0.90 2.91 2.32 2.59 1.59 1.06 3.21 6.18

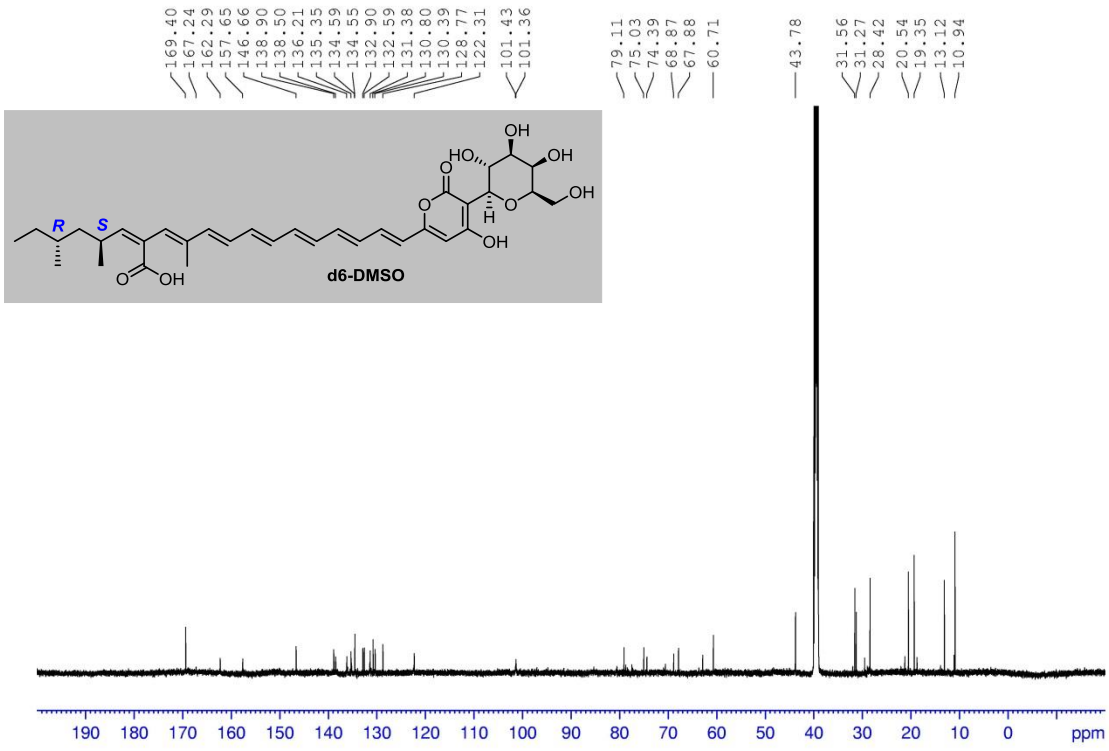

600Mhz, d4-MeOH
d4-MeOH
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 ppm
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 ppm
3.05 3.00 ppm
1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 ppm

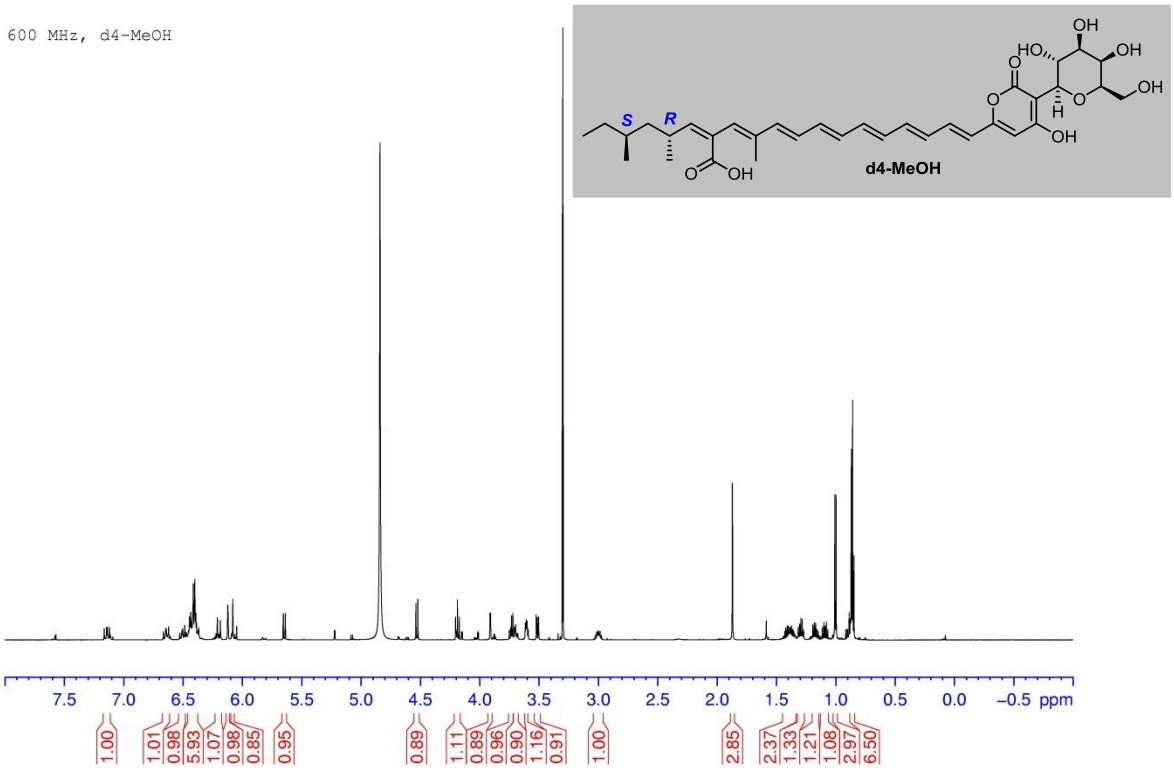

172.24
170.58
166.24
160.69
149.16
140.59
140.42
138.13
137.56
137.06
136.71
134.10
133.65
132.33
132.14
131.49
130.13
122.61
102.47
101.89
81.09
76.66
76.50
71.11
70.46
62.82
45.80
33.54
33.14
30.30
21.11
20.04
13.80
11.62
d4-MeOH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

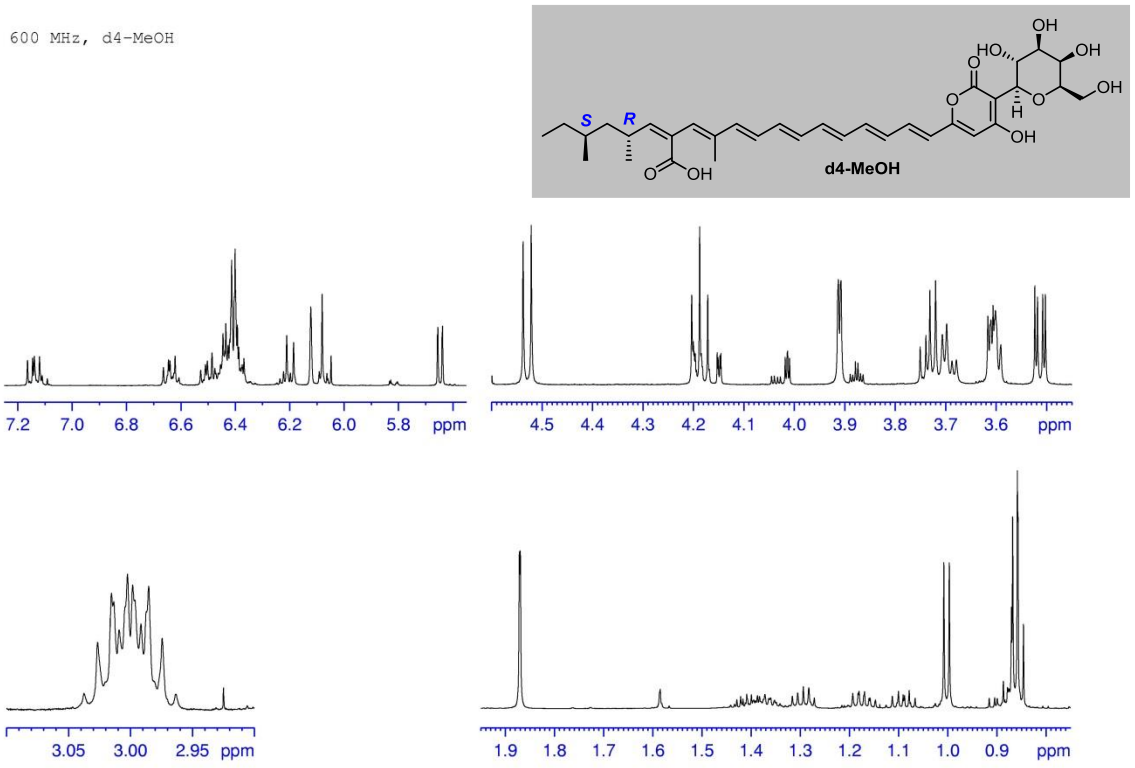

d6-DMSO
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.87
1.00
0.99
1.15
6.28
1.21
1.88
0.99
0.81
0.86
0.94
0.87
1.00
2.01
1.14
3.38
2.37
2.75
1.28
1.32
3.36
7.39

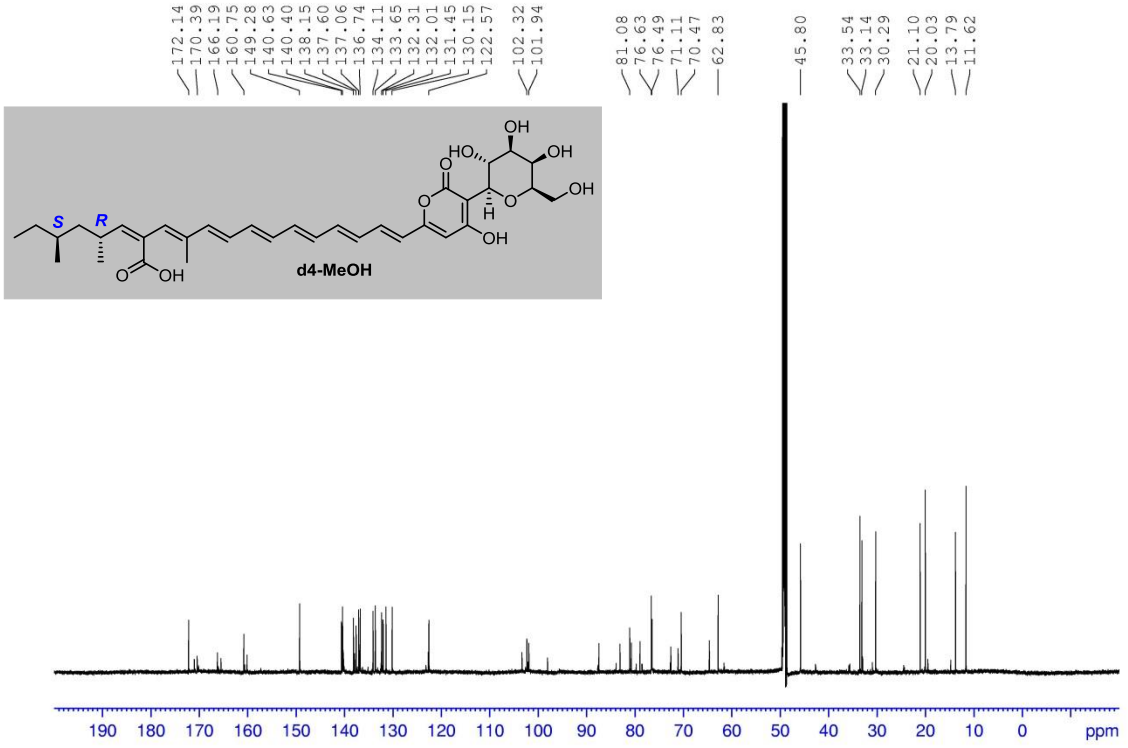

OH
HO
OH
O
OH
O
O
H
R
S
OH
O
OH
d6-DMSO

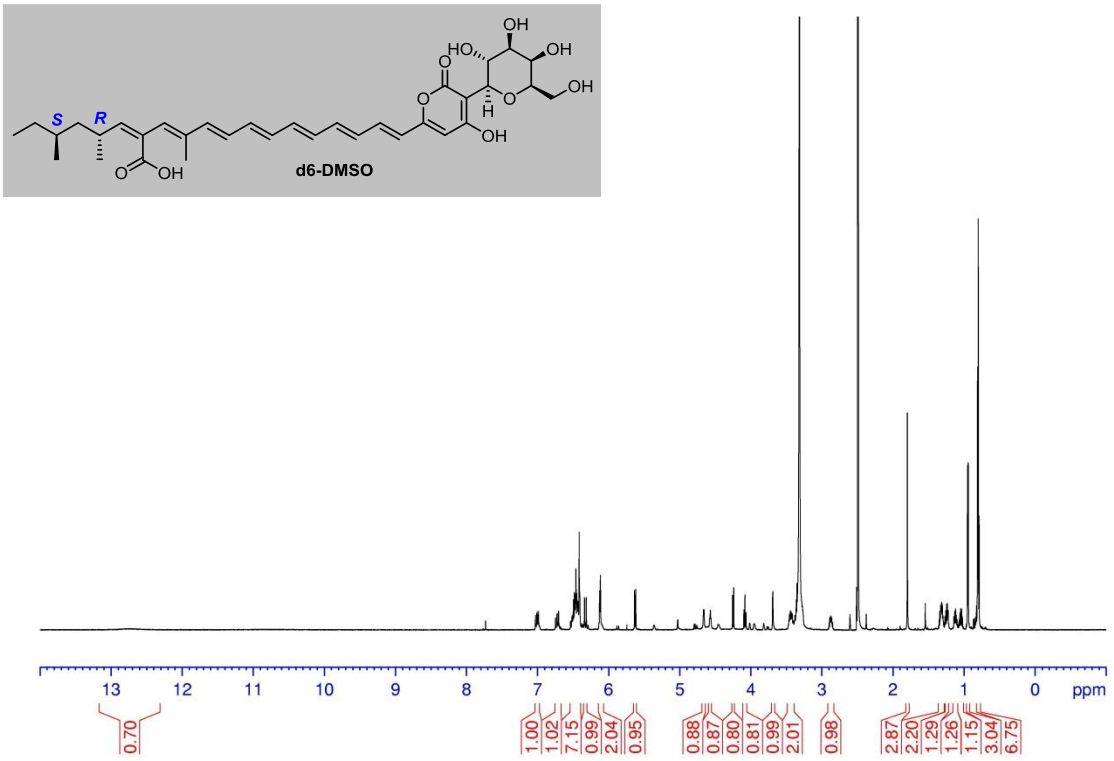

7.0
6.8
6.6
6.4
6.2
6.0
5.8
ppm
4.6
4.4
4.2
4.0
3.8
3.6
ppm
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
ppm

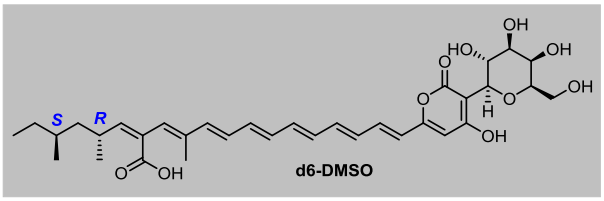

169.40
167.24
162.29
157.65
146.66
138.90
138.50
136.21
135.35
134.59
134.55
132.90
132.59
131.38
130.80
130.39
128.77
122.31
101.43
101.36
79.11
75.03
74.39
68.87
67.88
60.71
43.78
31.56
31.27
28.42
20.54
19.35
13.12
10.94
OH
HO
OH
O
OH
O
O
H
R
S
OH
O
OH
d6-DMSO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

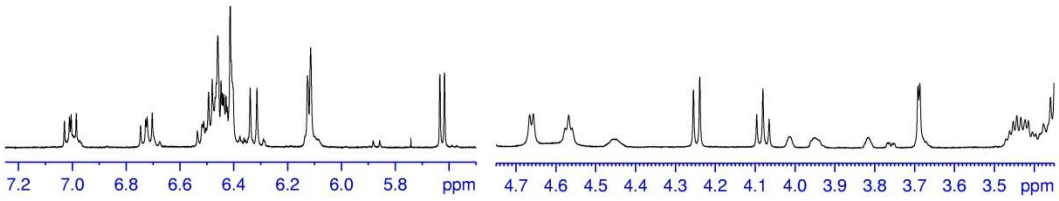

600 MHz, d4-MeOH
d4-MeOH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
1.00 1.01 0.98 5.93 1.07 0.98 0.85 0.95 0.89 1.11 0.89 0.96 0.90 1.16 0.91 1.00 2.85 2.37 1.33 1.21 1.08 2.97 6.50

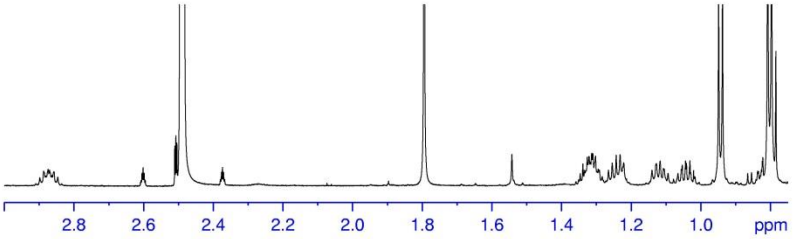

600 MHz, d4-MeOH
d4-MeOH
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 ppm
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 ppm
3.05 3.00 2.95 ppm
1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 ppm

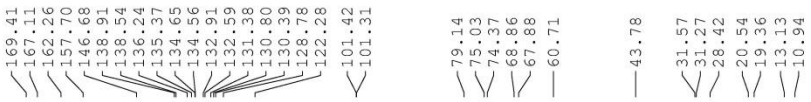

172.14
170.39
166.19
160.75
149.28
140.63
140.40
138.15
137.60
137.06
136.74
134.11
133.65
132.31
132.01
131.45
130.15
122.57
102.32
101.94
81.08
76.63
76.49
71.11
70.47
62.83
45.80
33.54
33.14
30.29
21.10
20.03
13.79
11.62
d4-MeOH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

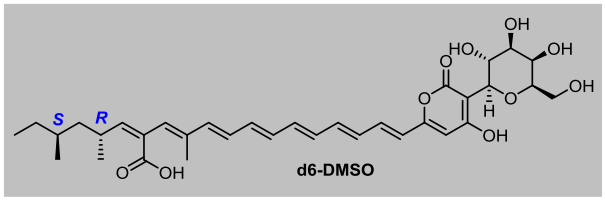

d6-DMSO
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.70
1.00
1.02
7.15
0.99
2.04
0.95
0.88
0.87
0.80
0.81
0.99
2.01
0.98
2.87
2.20
1.29
1.26
1.15
3.04
6.75


OH
HO
OH
O
OH
O
H
S
R
OH
O
OH
d6-DMSO

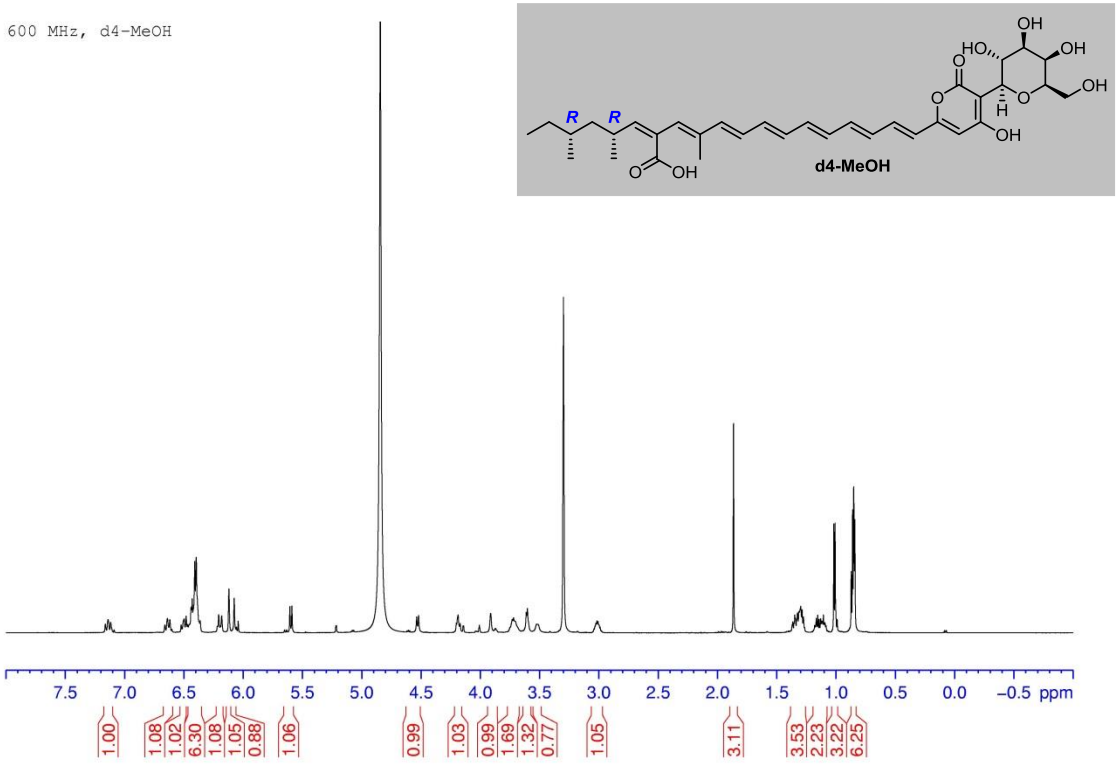

7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 ppm
4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 ppm

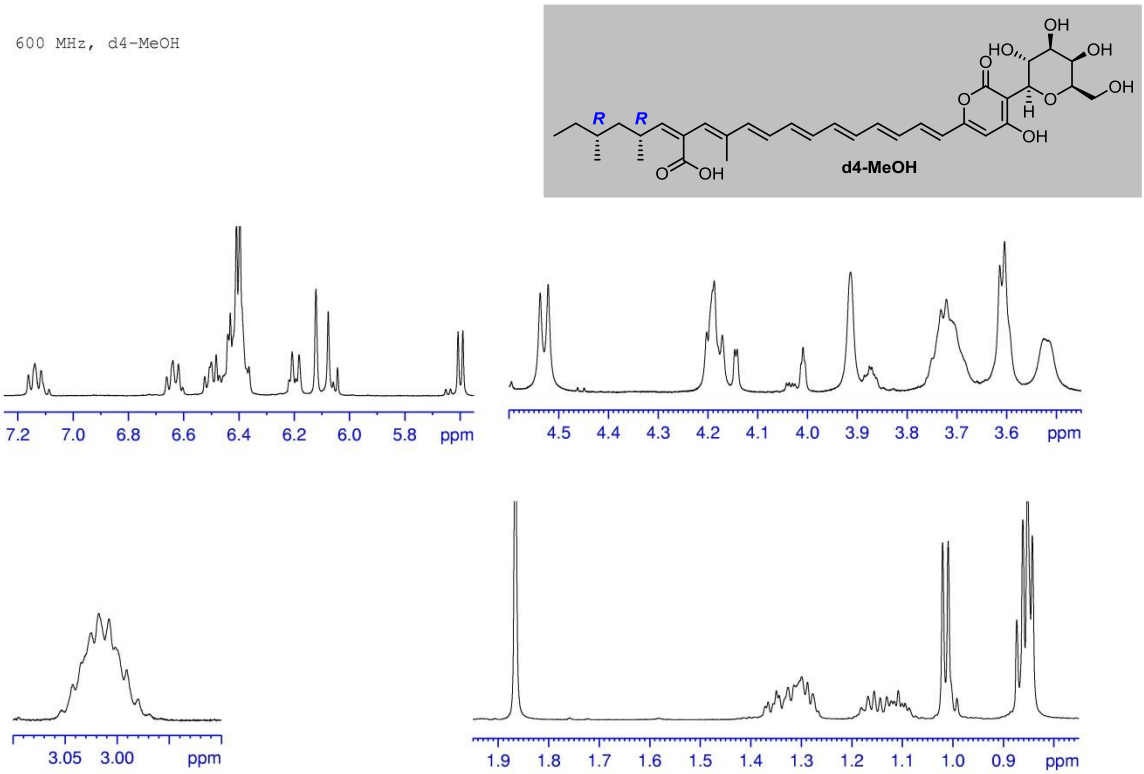

2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 ppm

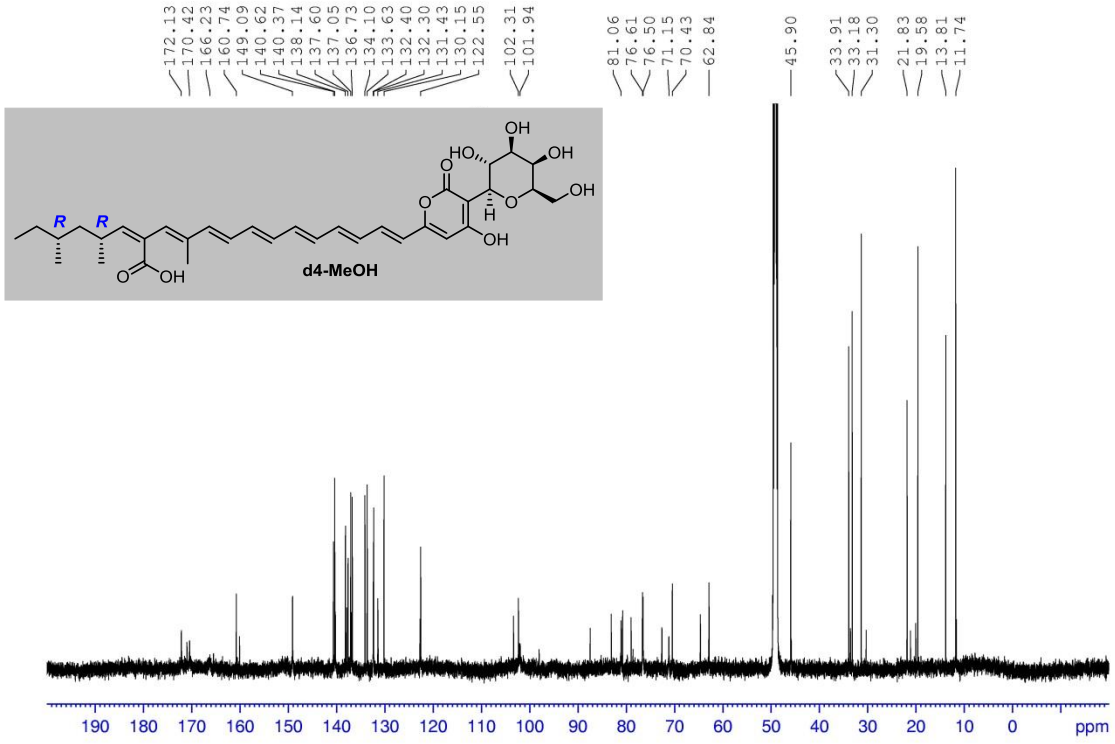

169.41
167.11
162.26
157.70
146.68
138.91
138.54
136.24
135.37
134.65
134.56
132.91
132.59
131.38
130.80
130.39
128.78
122.28
101.42
101.31
79.14
75.03
74.37
68.86
67.88
60.71
43.78
31.57
31.27
28.42
20.54
19.36
13.13
10.94

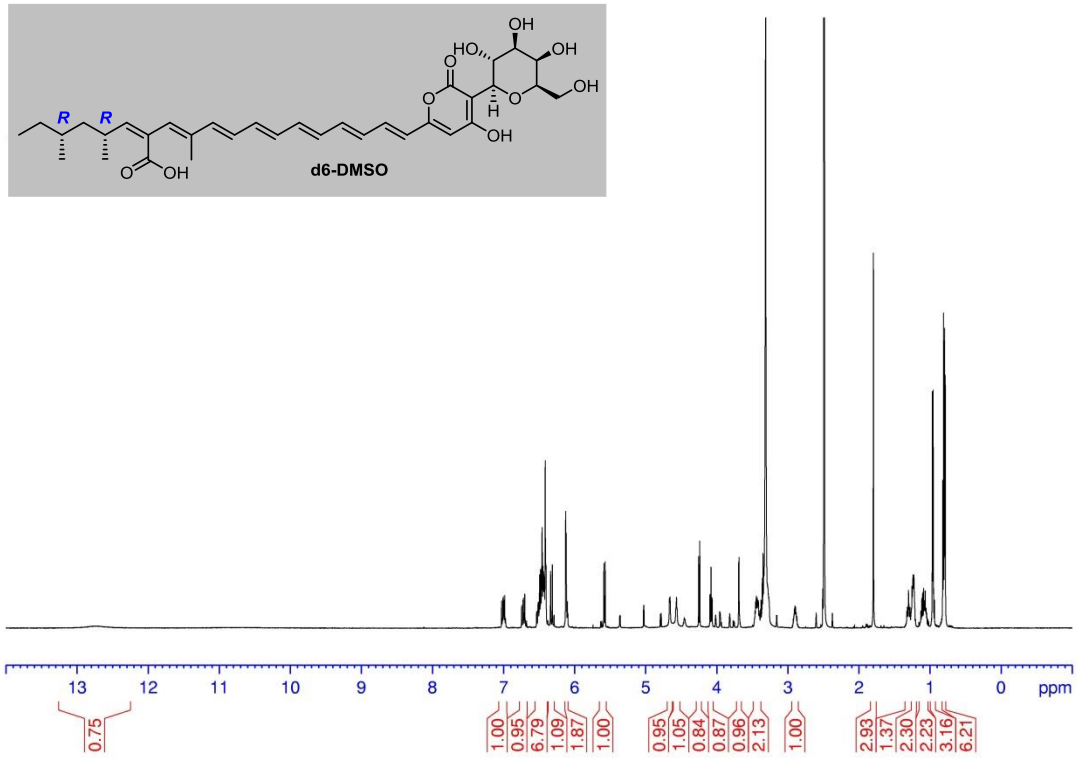

OH
HO
OH
O
OH
O
H
S
R
OH
O
OH
d6-DMSO

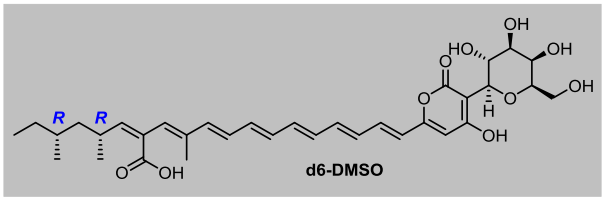
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

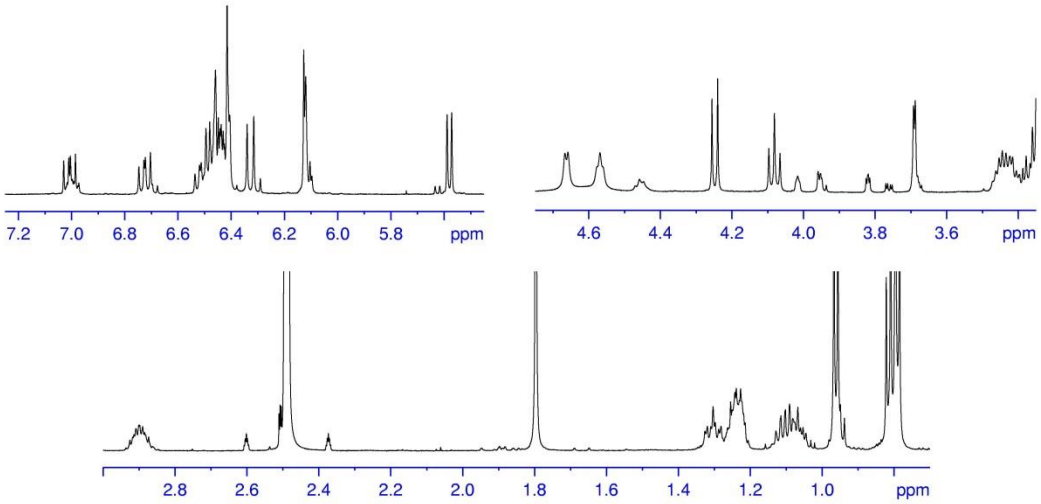

600 MHz, d4-MeOH
d4-MeOH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
1.00 1.08 1.02 6.30 1.08 1.05 0.88 1.06 0.99 1.03 0.99 1.69 1.32 0.77 1.05 3.11 3.53 2.23 3.22 6.25

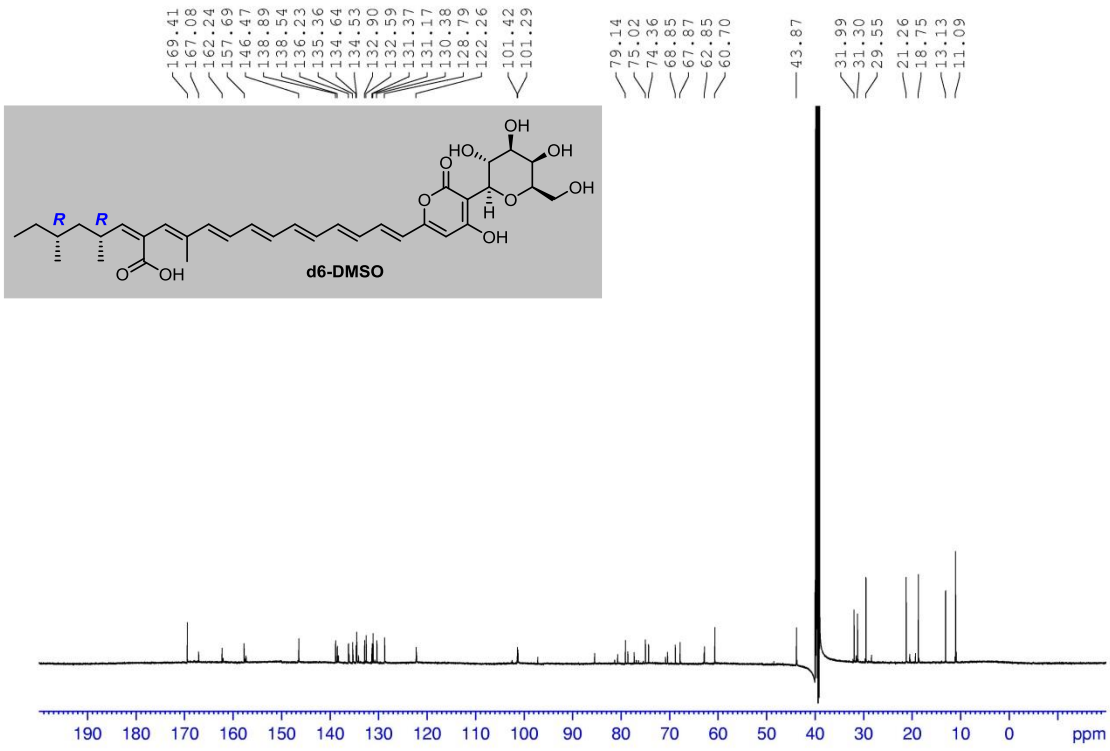

600 MHz, d4-MeOH
d4-MeOH
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 ppm
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 ppm
3.05 3.00 ppm
1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 ppm

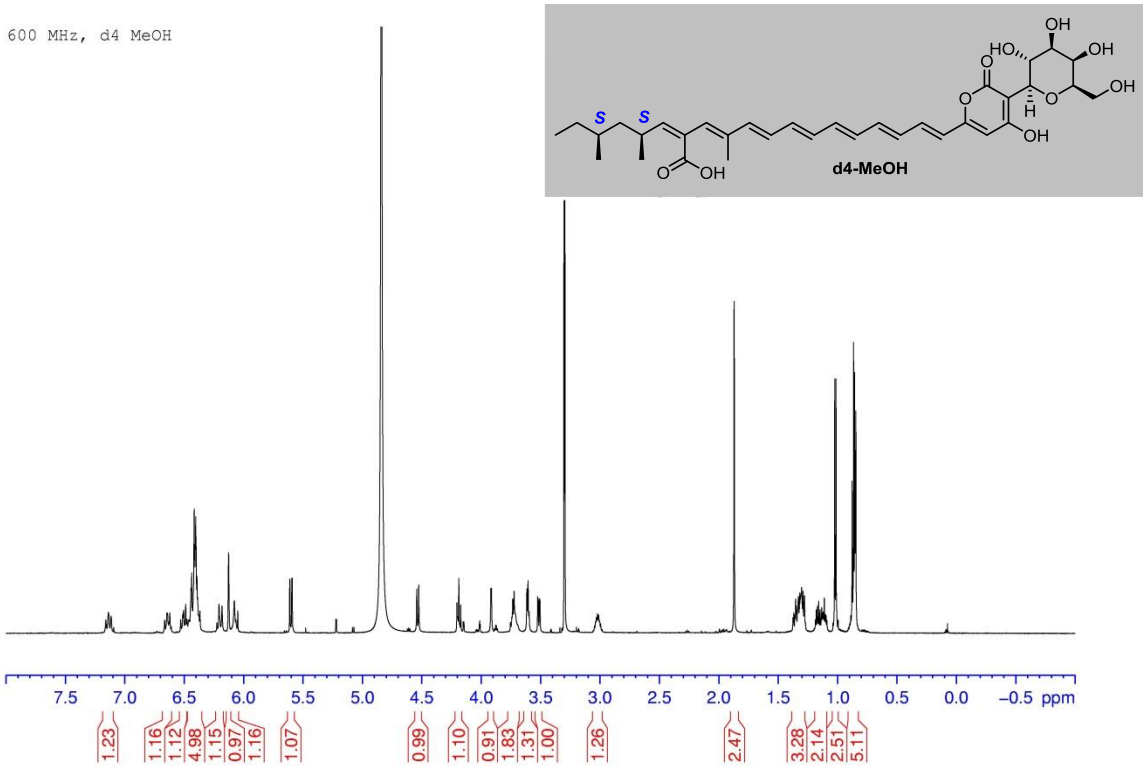

172.13
170.42
166.23
160.74
149.09
140.62
140.37
138.14
137.60
137.05
136.73
134.10
133.63
132.40
132.30
131.43
130.15
122.55
102.31
101.94
81.06
76.61
76.50
71.15
70.43
62.84
45.90
33.91
33.18
31.30
21.83
19.58
13.81
11.74
d4-MeOH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

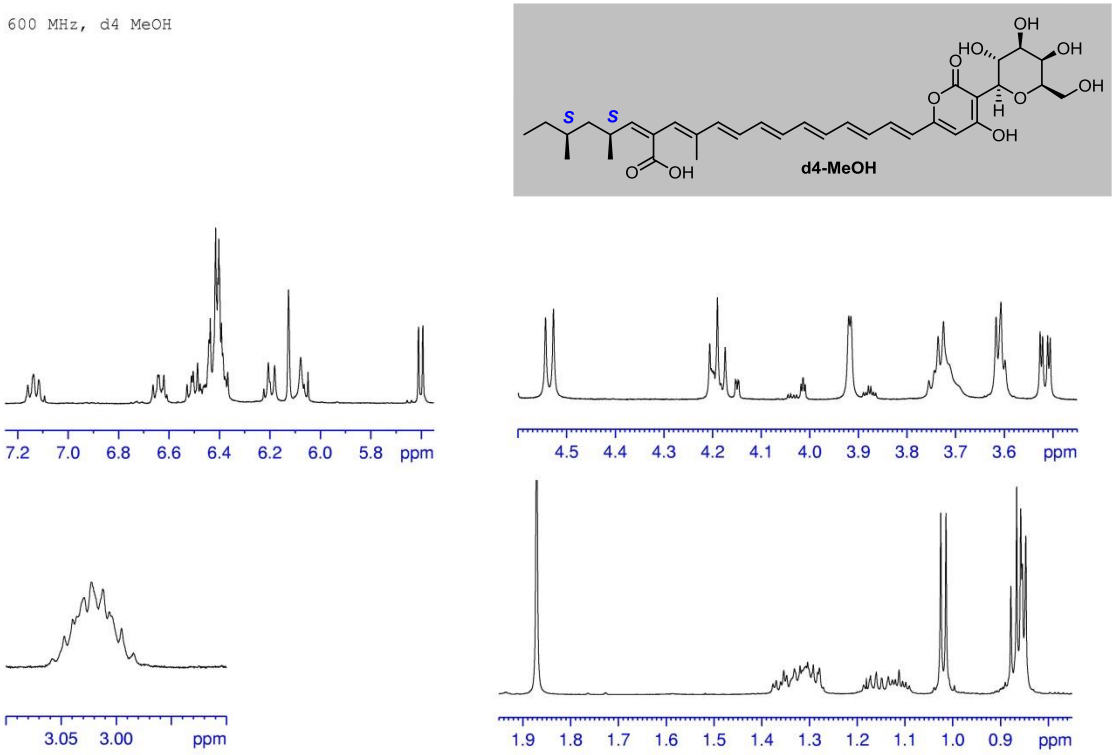

d6-DMSO
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.75
1.00
0.95
6.79
1.09
1.87
1.00
0.95
1.05
0.84
0.87
0.96
2.13
1.00
2.93
1.37
2.30
2.23
3.16
6.21

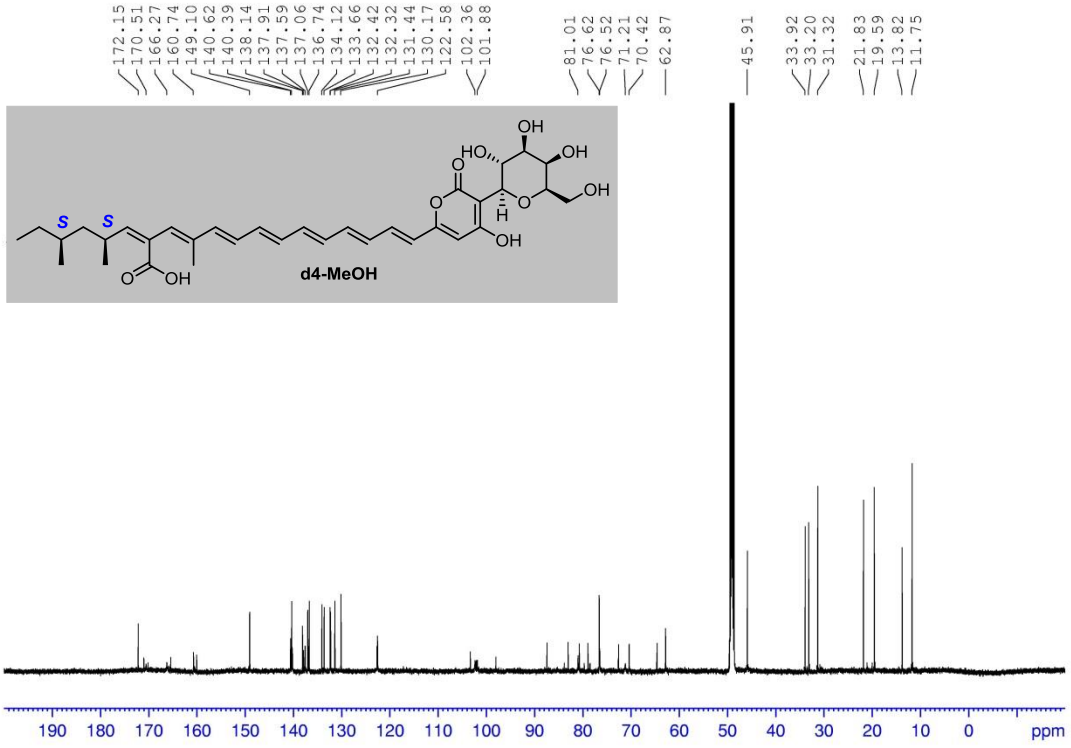

OH
HO
OH
O
OH
O
H
O
R
R
OH
O
OH
d6-DMSO

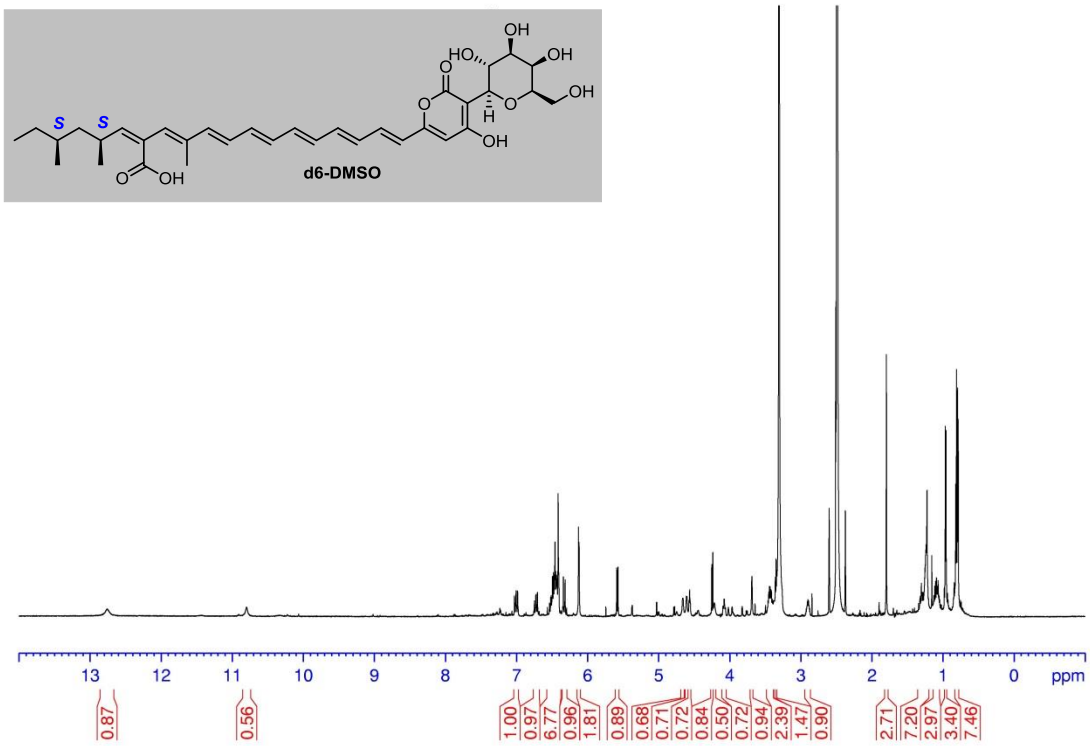

7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 ppm
4.6 4.4 4.2 4.0 3.8 3.6 ppm
2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 ppm

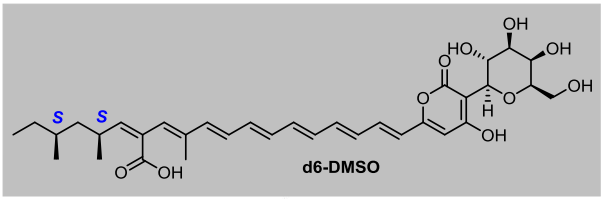

169.41
167.08
162.24
157.69
146.47
138.89
138.54
136.23
135.36
134.64
134.53
132.90
132.59
131.37
131.17
130.38
128.79
122.26
101.42
101.29
79.14
75.02
74.36
68.85
67.87
62.85
60.70
43.87
31.99
31.30
29.55
21.26
18.75
13.13
11.09
OH
HO
OH
O
OH
O
H
O
R
R
OH
O
OH
d6-DMSO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

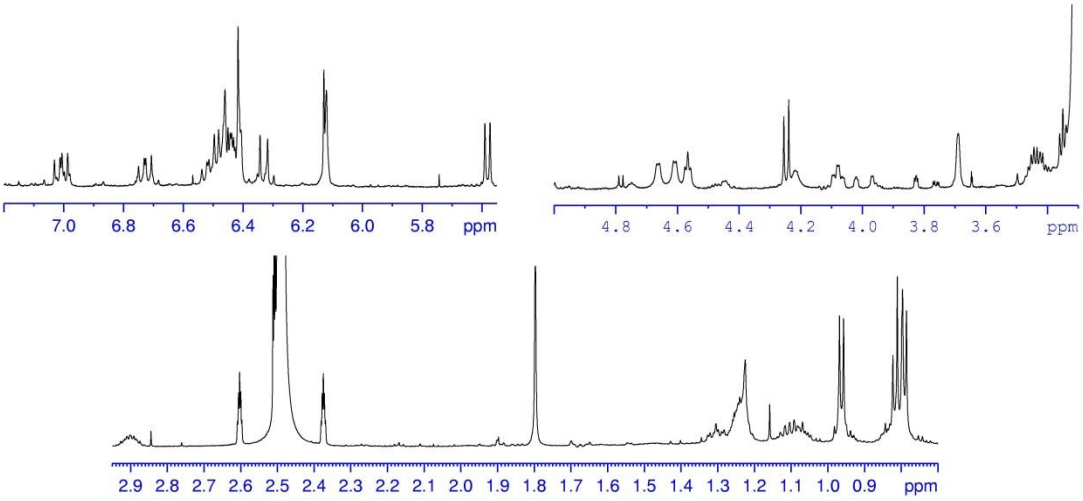

600 MHz, d4 MeOH
d4-MeOH
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 –0.5 ppm
1.23 1.16 1.12 4.98 1.15 0.97 1.16 1.07 0.99 1.10 0.91 1.83 1.31 1.00 1.26 2.47 3.28 2.14 2.51 5.11

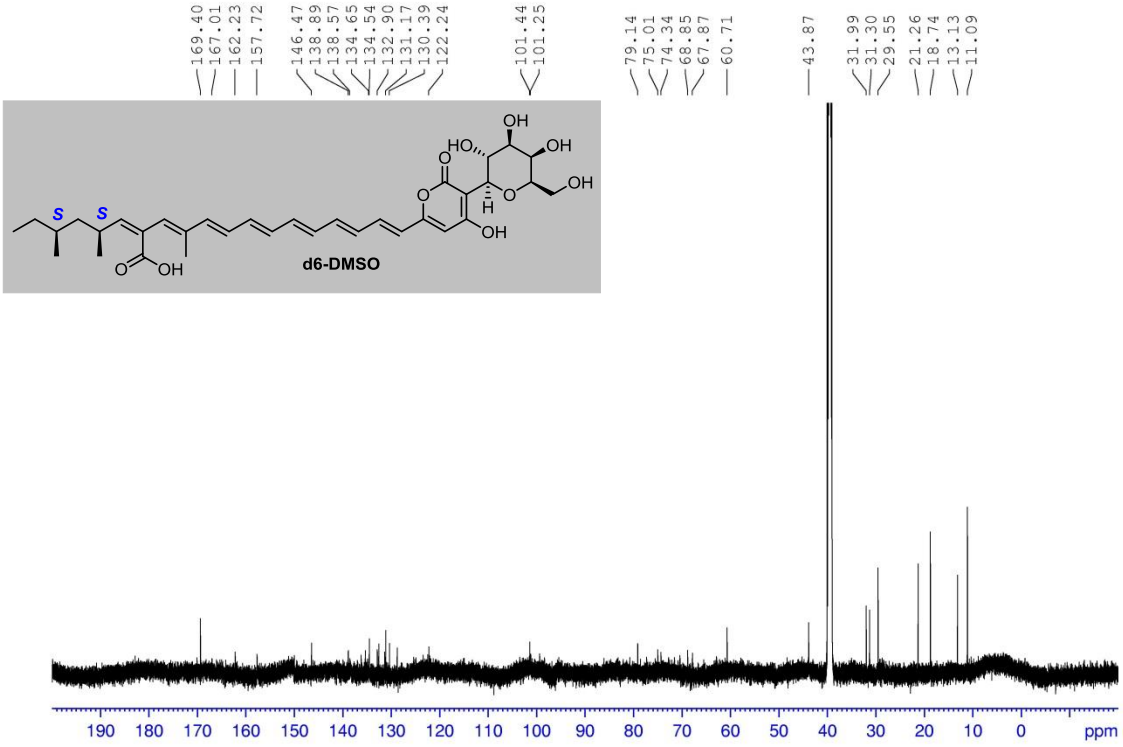

600 MHz, d4 MeOH
d4-MeOH
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 ppm
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 ppm
3.05 3.00 ppm
1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 ppm


172.15
170.51
166.27
160.74
149.10
140.62
140.39
138.14
137.91
137.59
137.06
136.74
134.12
133.66
132.42
132.32
131.44
130.17
122.58
102.36
101.88
81.01
76.62
76.52
71.21
70.42
62.87
45.91
33.92
33.20
31.32
21.83
19.59
13.82
11.75
d4-MeOH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

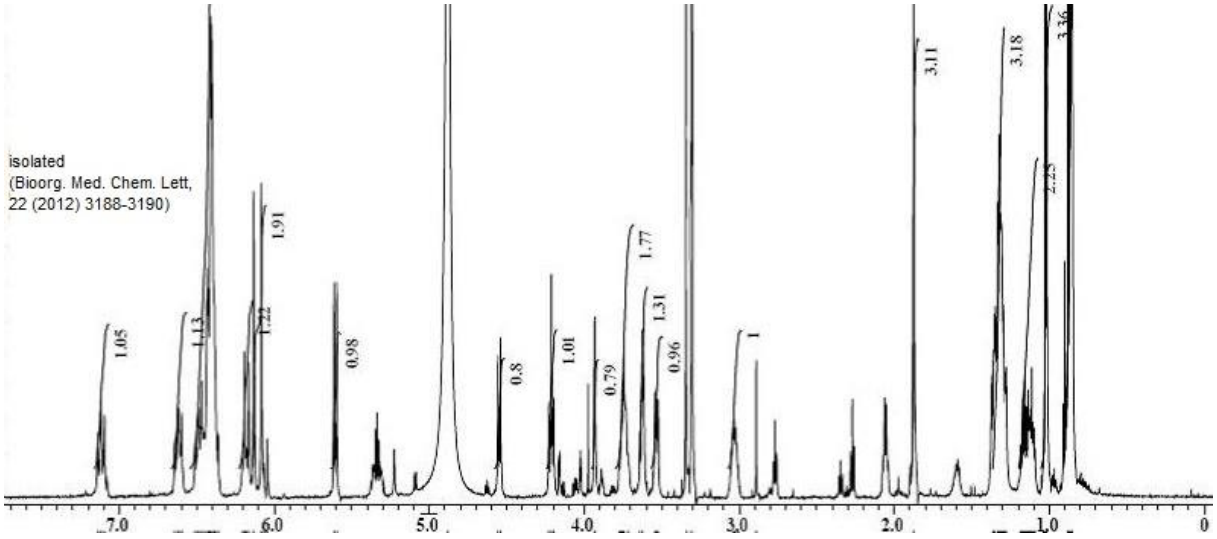

d6-DMSO
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.87
0.56
1.00
0.97
6.77
0.96
1.81
0.89
0.68
0.71
0.72
0.84
0.50
0.72
0.94
2.39
1.47
0.90
2.71
7.20
2.97
3.40
7.46

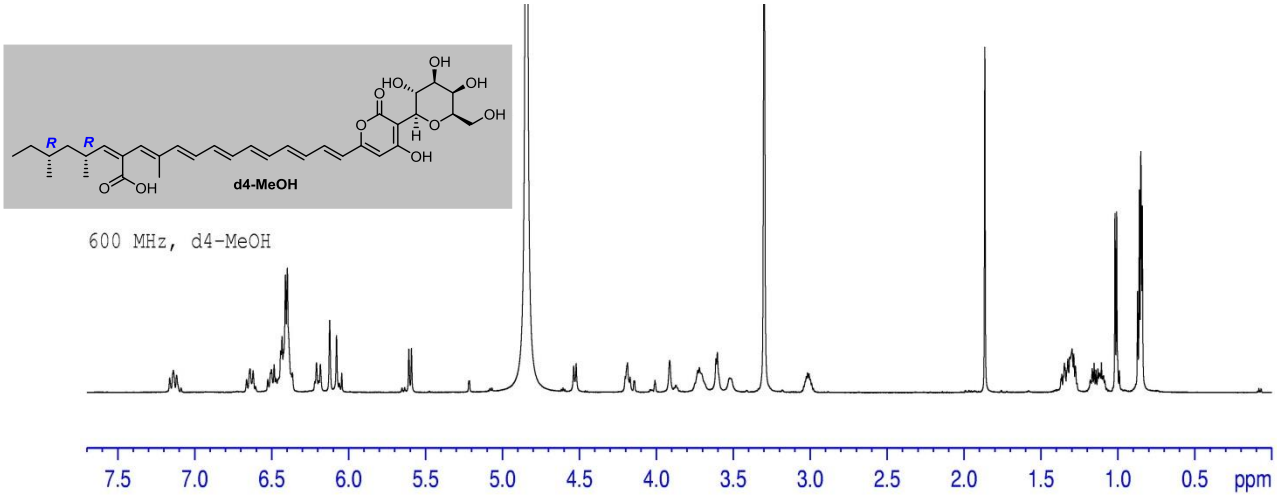

d6-DMSO

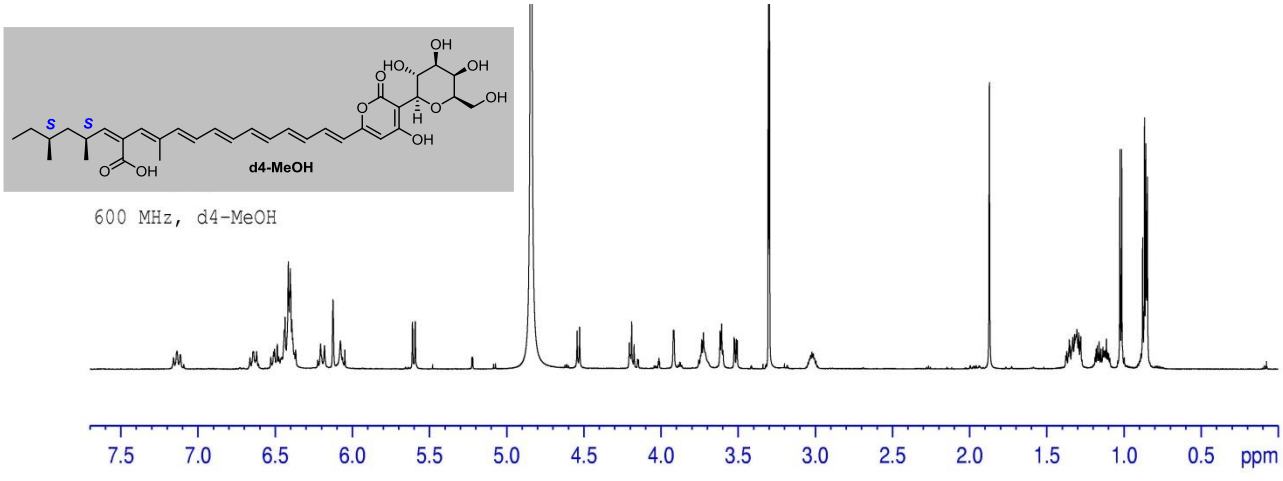

7.0 6.8 6.6 6.4 6.2 6.0 5.8 ppm
4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 ppm

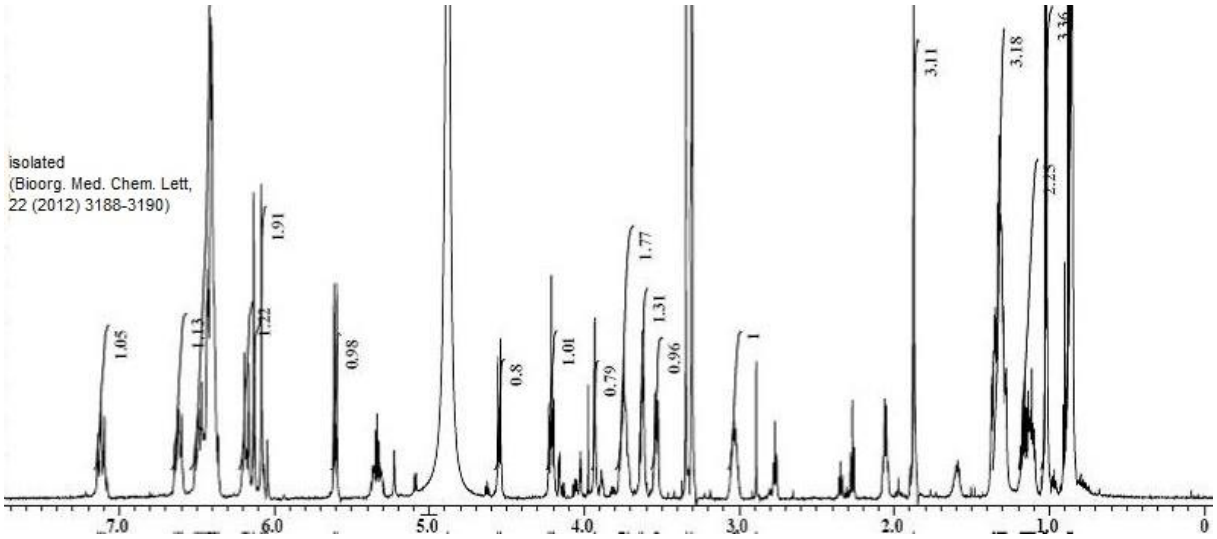

169.40
167.01
162.23
157.72
146.47
138.89
138.57
134.65
134.54
132.90
131.17
130.39
122.24
101.44
101.25
79.14
75.01
74.34
68.85
67.87
60.71
43.87
31.99
31.30
29.55
21.26
18.74
13.13
11.09
d6-DMSO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

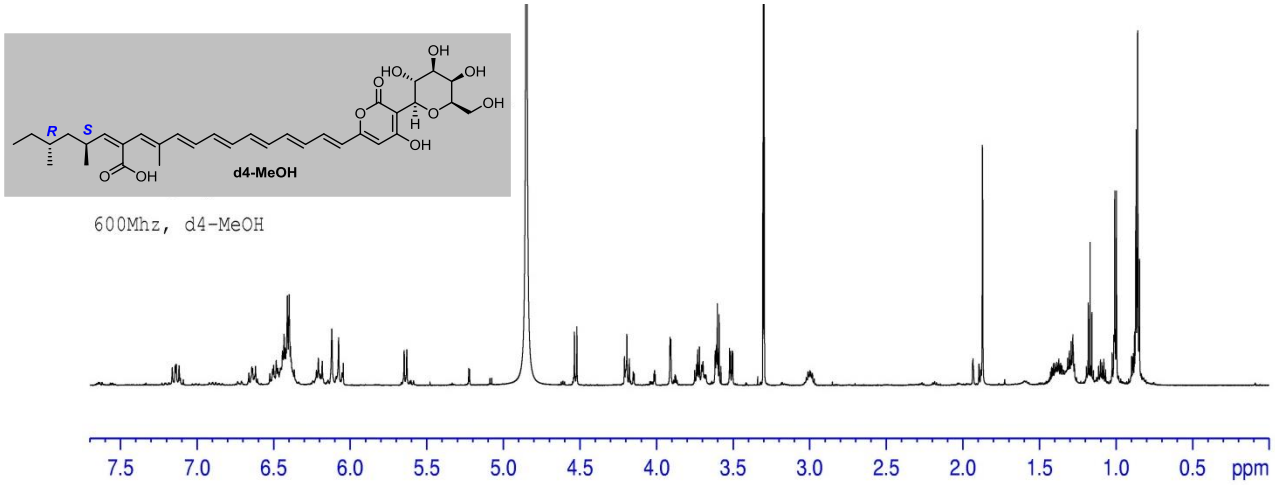
Spectra comparison of isolated and synthetic compounds

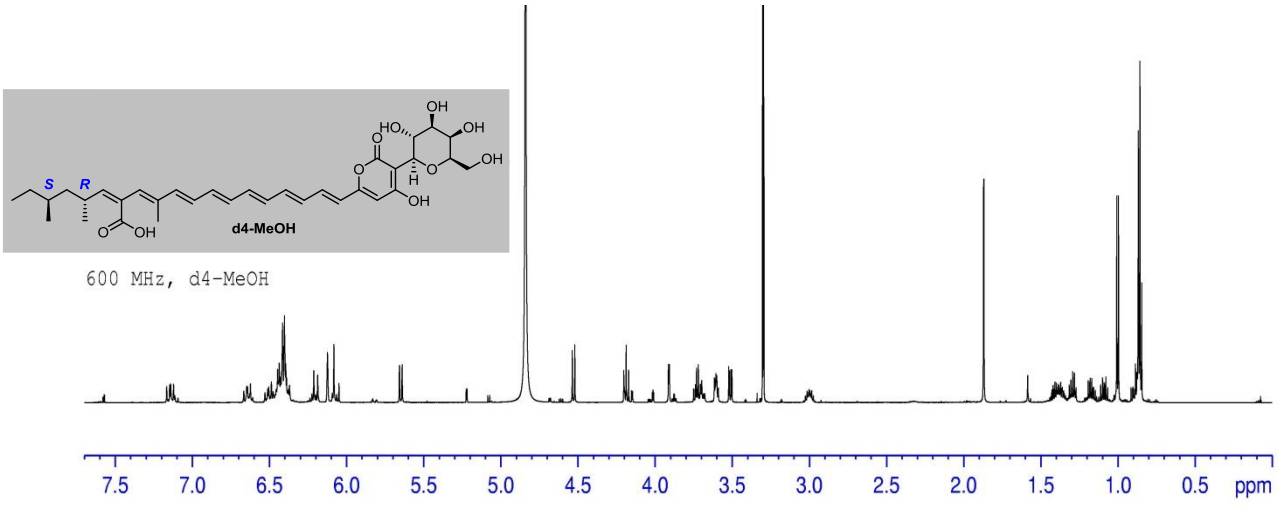


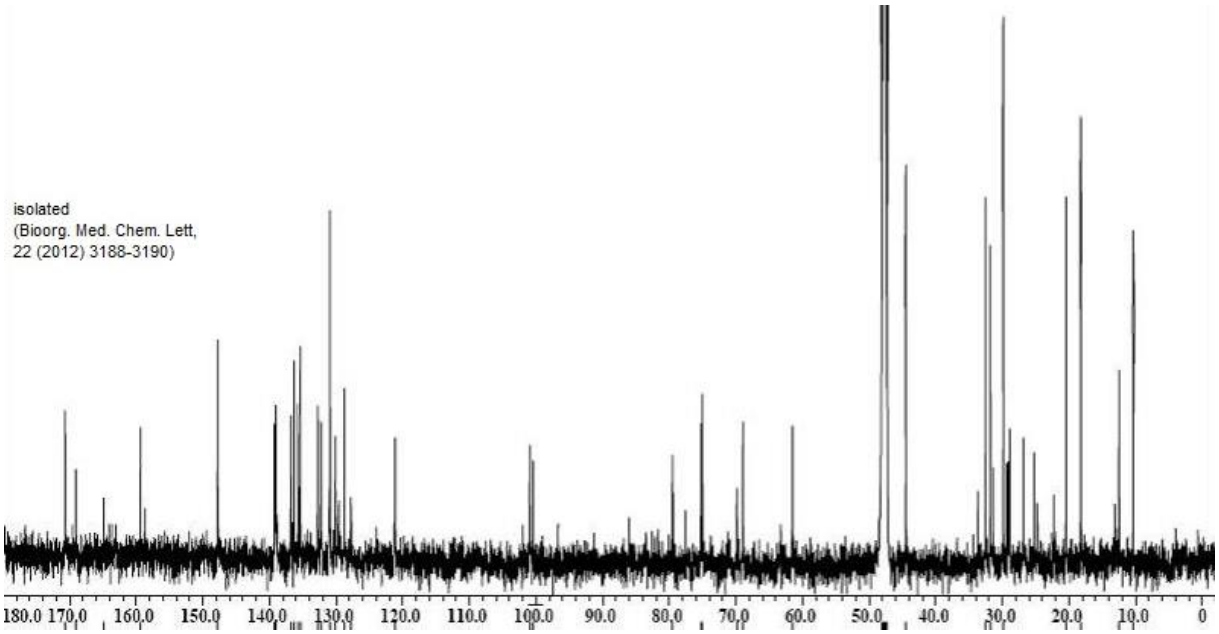


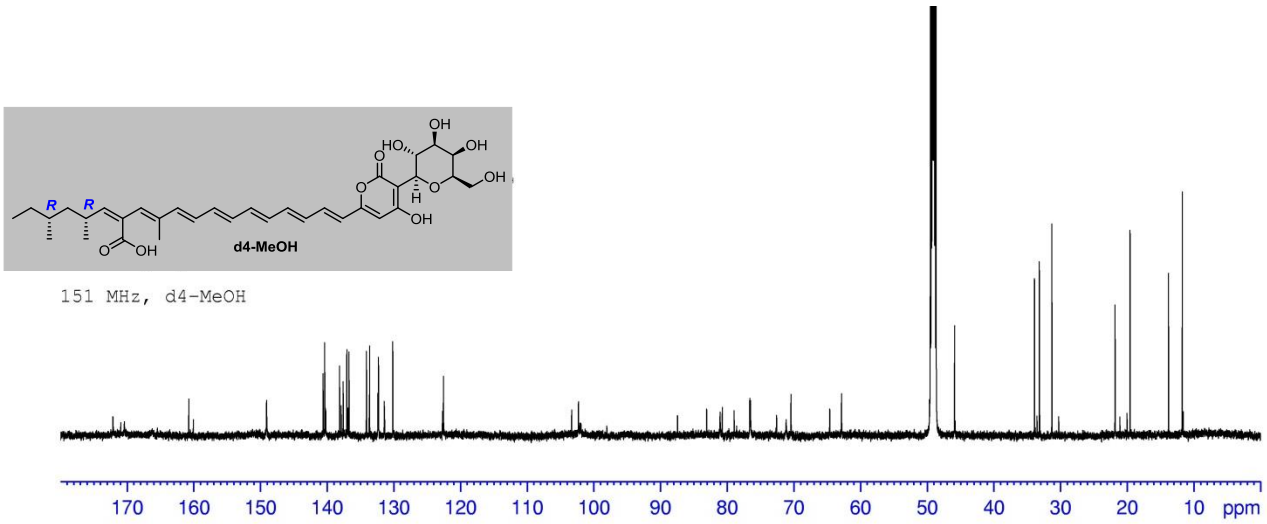


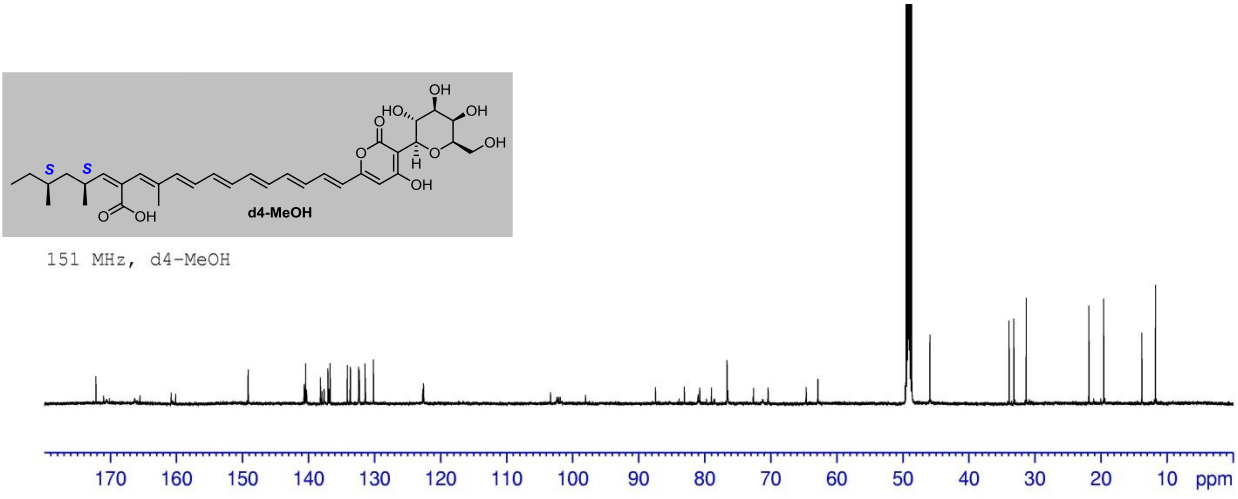

isolated
(Bioorg. Med. Chem. Lett,
22 (2012) 3188-3190)
1.05
1.13
1.22
1.91
0.98
0.8
1.01
0.79
1.77
1.31
0.96
1
3.11
3.18
3.36
2.25
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

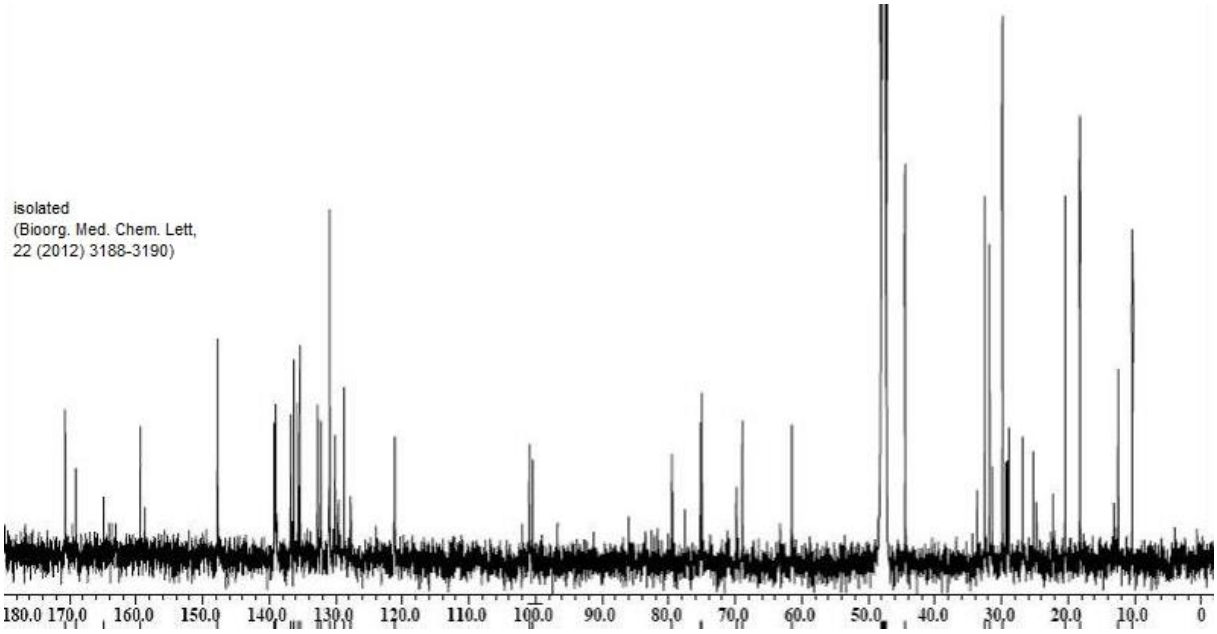

R
S
OH
HO
O
H
d4-MeOH
600Mhz, d4-MeOH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

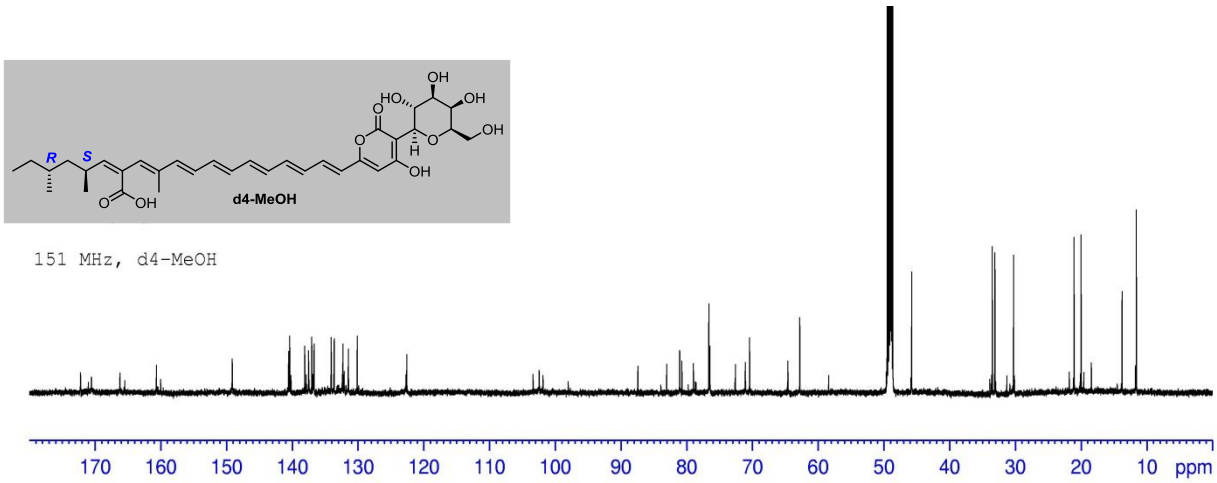

S
R
OH
HO
O
H
d4-MeOH
600 MHz, d4-MeOH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

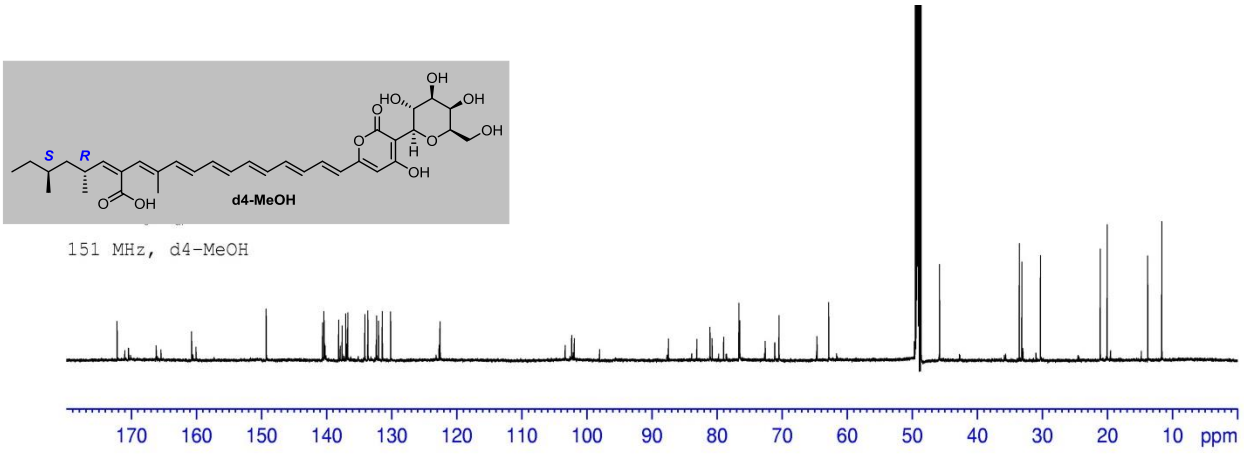

isolated
(Bioorg. Med. Chem. Lett,
22 (2012) 3188-3190)
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

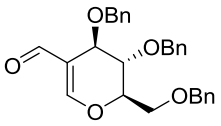

R
R
OH
HO
O
H
d4-MeOH
151 MHz, d4-MeOH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

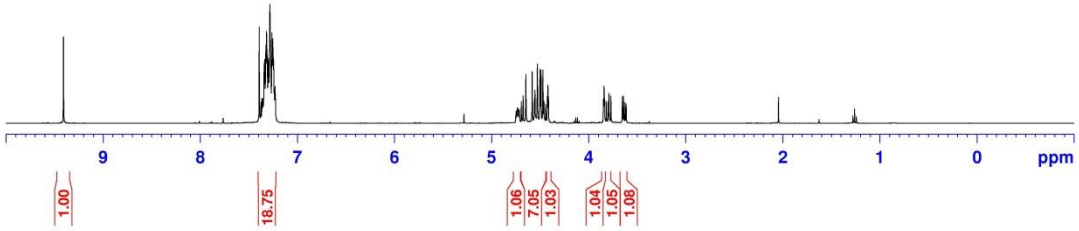

S
S
OH
HO
O
H
d4-MeOH
151 MHz, d4-MeOH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


isolated
(Bioorg. Med. Chem. Lett,
22 (2012) 3188-3190)
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

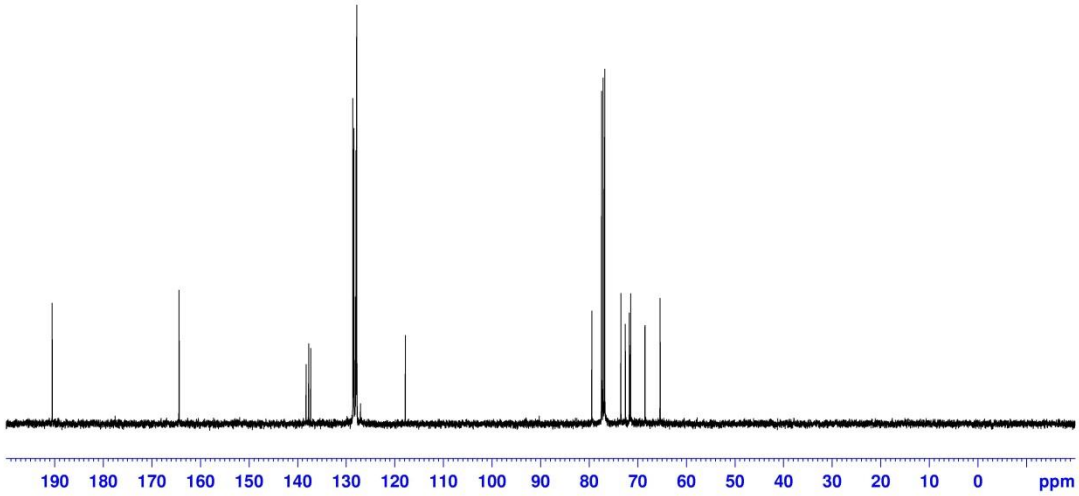

d4-MeOH
151 MHz, d4-MeOH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

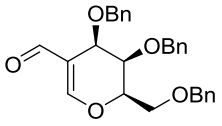

d4-MeOH
151 MHz, d4-MeOH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

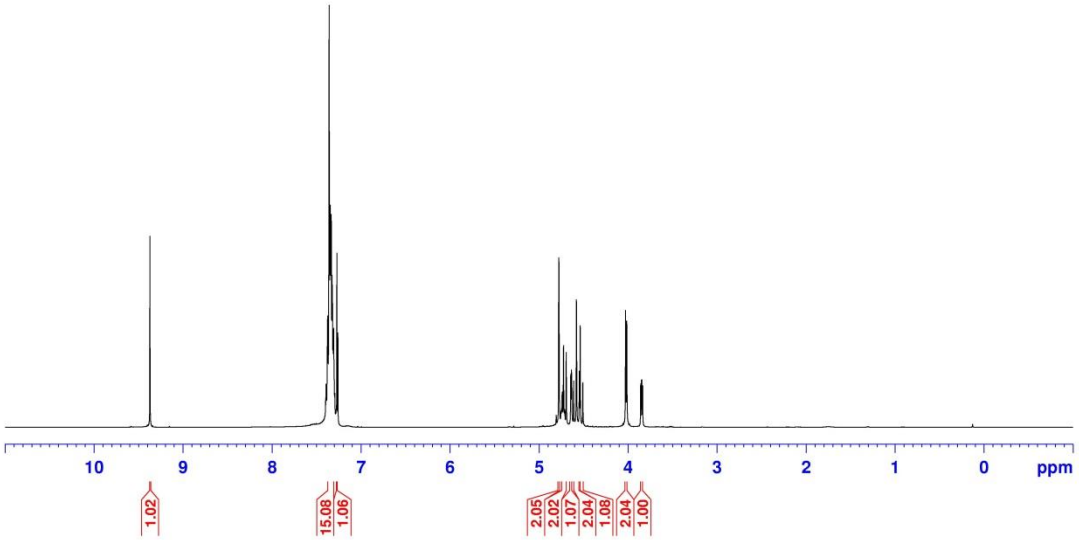

OBn
OBn
OBn
O
O


9
8
7
6
5
4
3
2
1
0
ppm
1.00
18.75
1.06
7.05
1.03
1.04
1.05
1.08


190.48
164.43
138.27
137.75
137.34
128.66
128.55
128.46
128.15
128.02
127.93
127.87
127.81
117.86
79.47
73.48
72.57
71.75
71.49
68.53
65.41


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OBn
OBn
OBn
O
O


10
9
8
7
6
5
4
3
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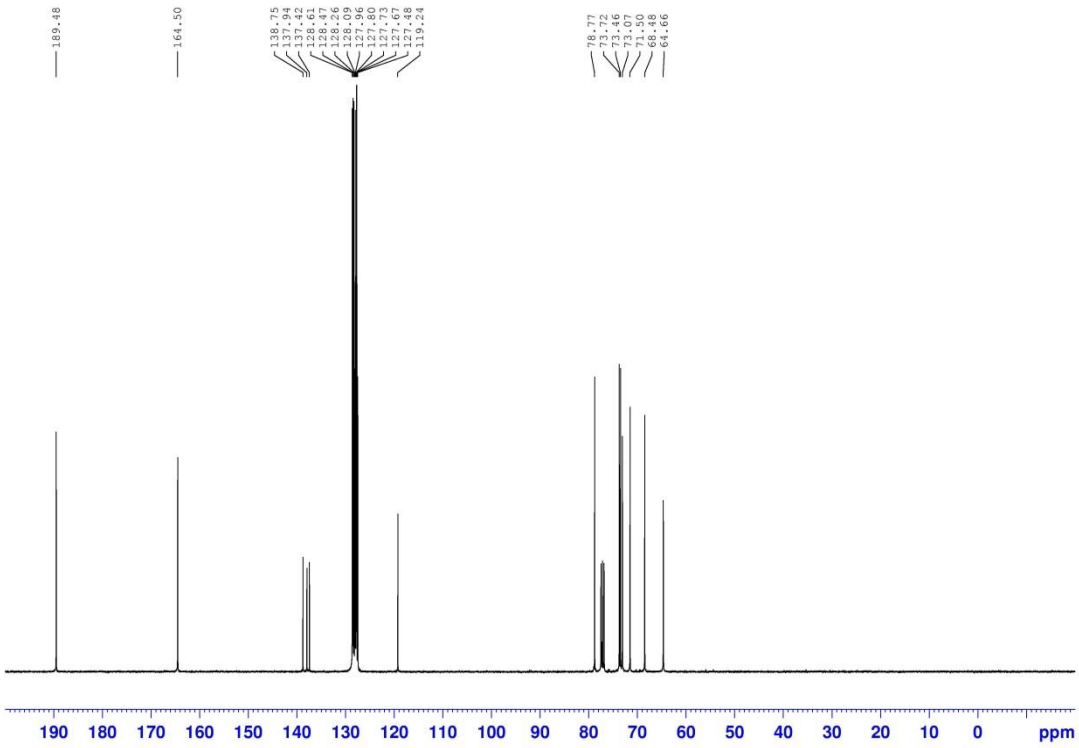
1.02
15.08
1.06
2.05
2.02
1.07
2.04
1.08
2.04
1.00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164.50
138.75
137.94
137.42
128.61
128.47
128.26
128.09
127.96
127.80
127.73
127.67
127.48
119.24
78.77
73.72
73.46
73.07
71.50
68.48
64.66
190
180
170
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150
140
130
120
110
100
90
80
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60
50
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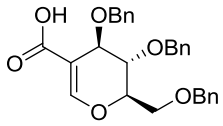
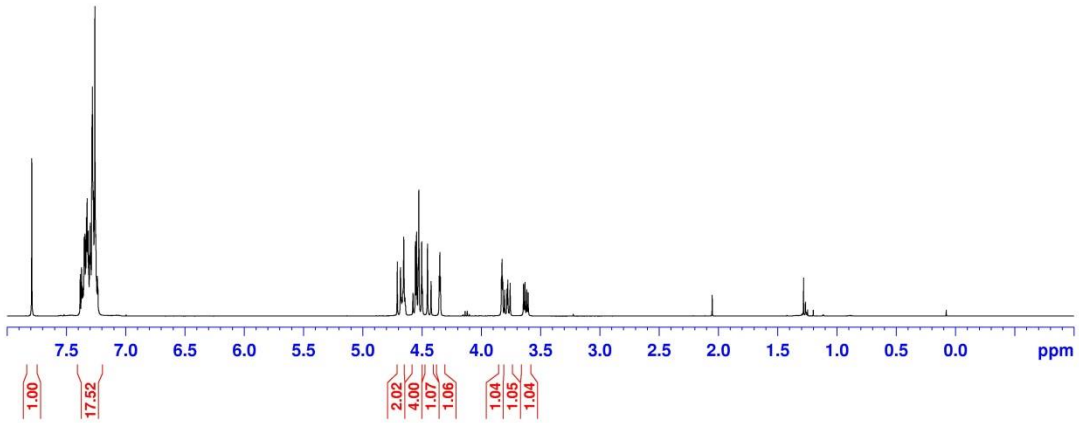
30
20
10
0
ppm


OH
OBn
OBn
OBn
O
O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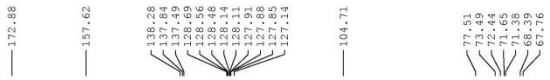
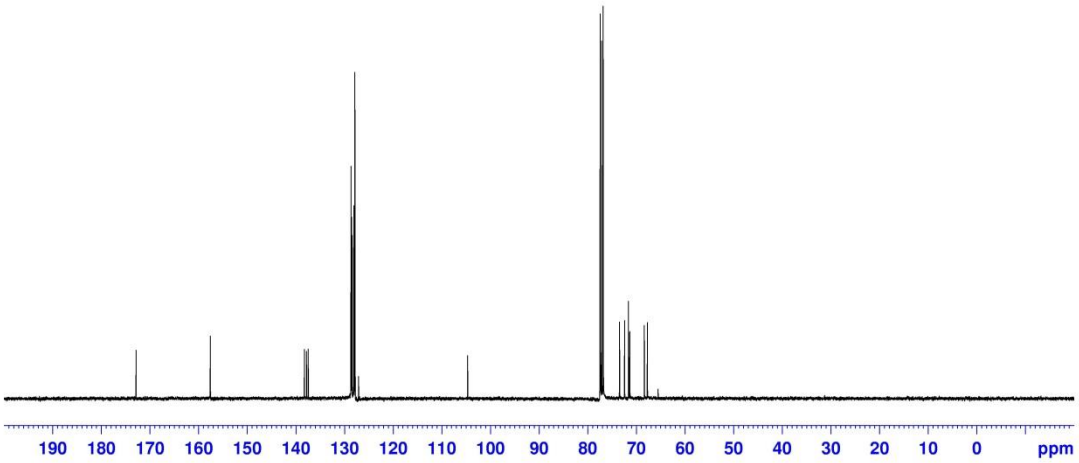
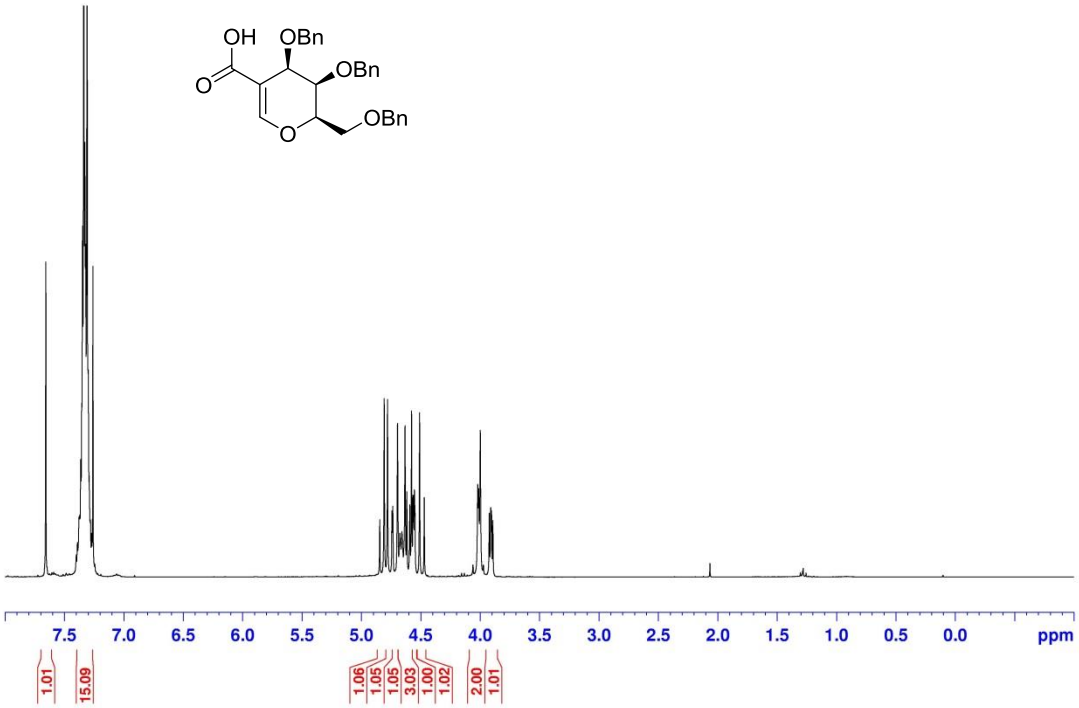
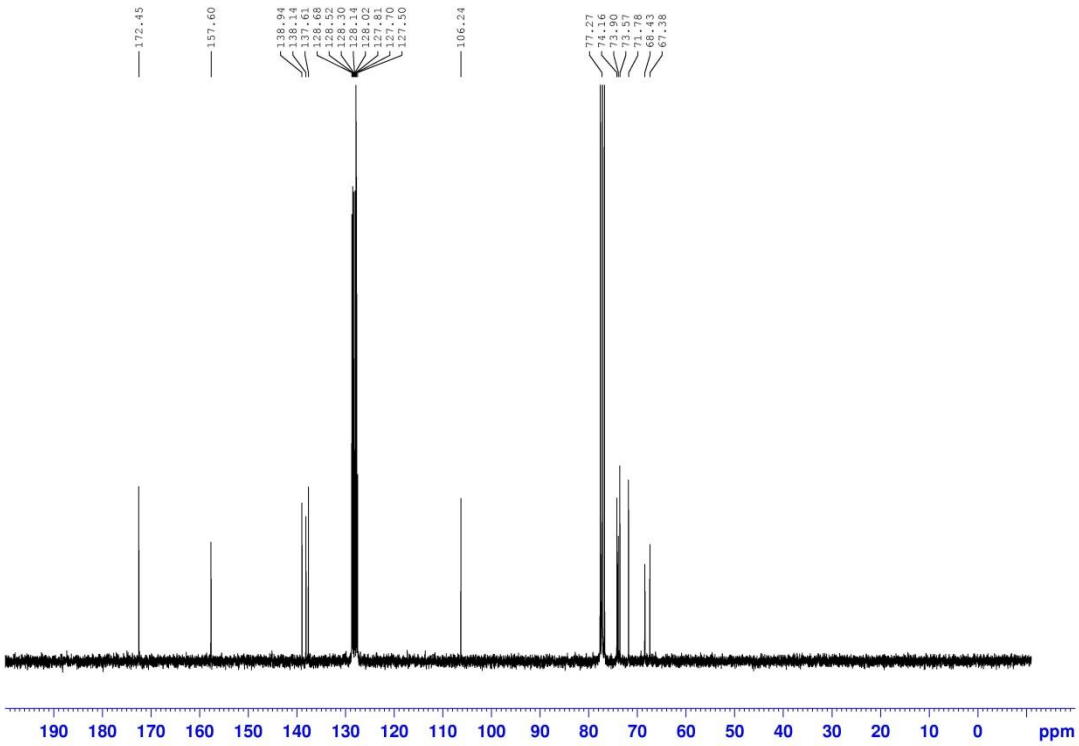
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
17.52
2.02
4.00
1.07
1.06
1.04
1.05
1.04


172.88
157.62
138.28
137.84
137.49
128.69
128.56
128.48
128.14
128.11
127.91
127.88
127.85
127.14
104.71
77.51
73.49
72.44
71.65
71.38
68.39
67.76


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OH
OBn
OBn
OBn
O
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.01
15.09
1.06
1.05
1.05
3.03
1.00
1.02
2.00
1.01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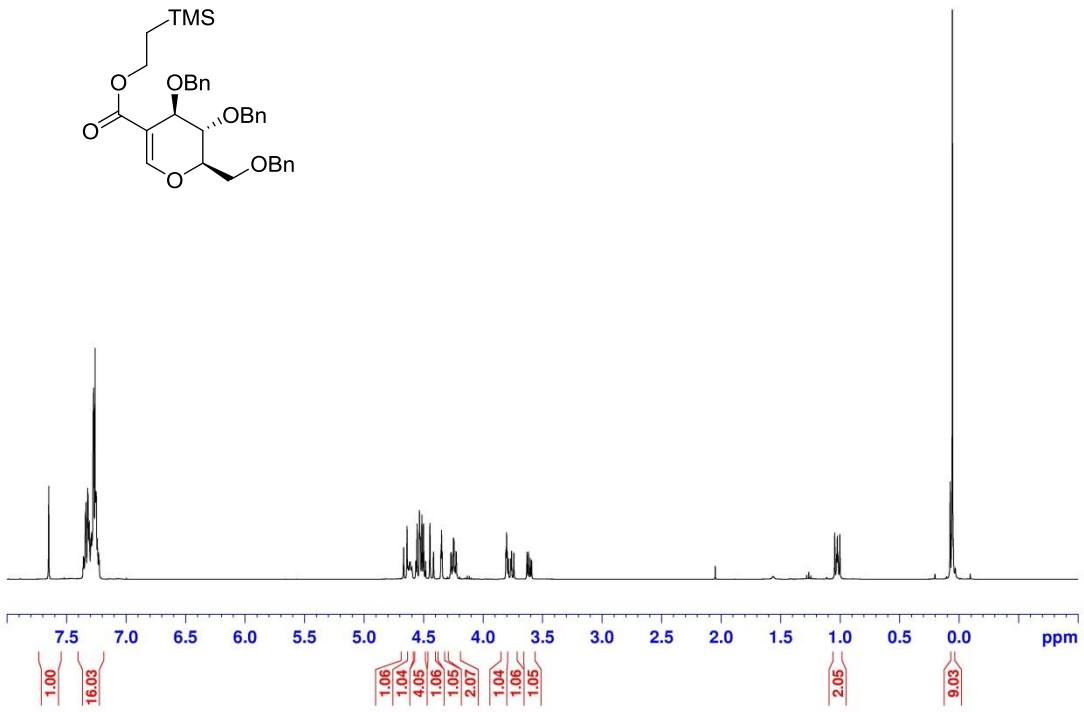
157.60
138.94
138.14
137.61
128.68
128.52
128.30
128.14
128.02
127.81
127.70
127.50
106.24
77.27
74.16
73.90
73.37
71.78
68.43
67.38
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OBn
OBn
O
OBn
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
16.03
1.06
1.04
4.05
1.06
1.05
2.07
1.04
1.06
1.05
2.05
9.03


167.53
155.33
138.41
137.93
137.66
128.66
128.55
128.47
128.12
128.10
127.92
127.86
127.83
105.72
77.07
73.48
72.48
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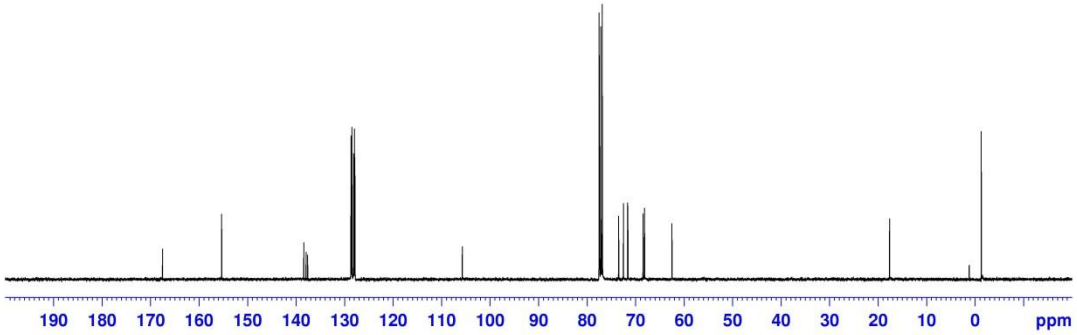
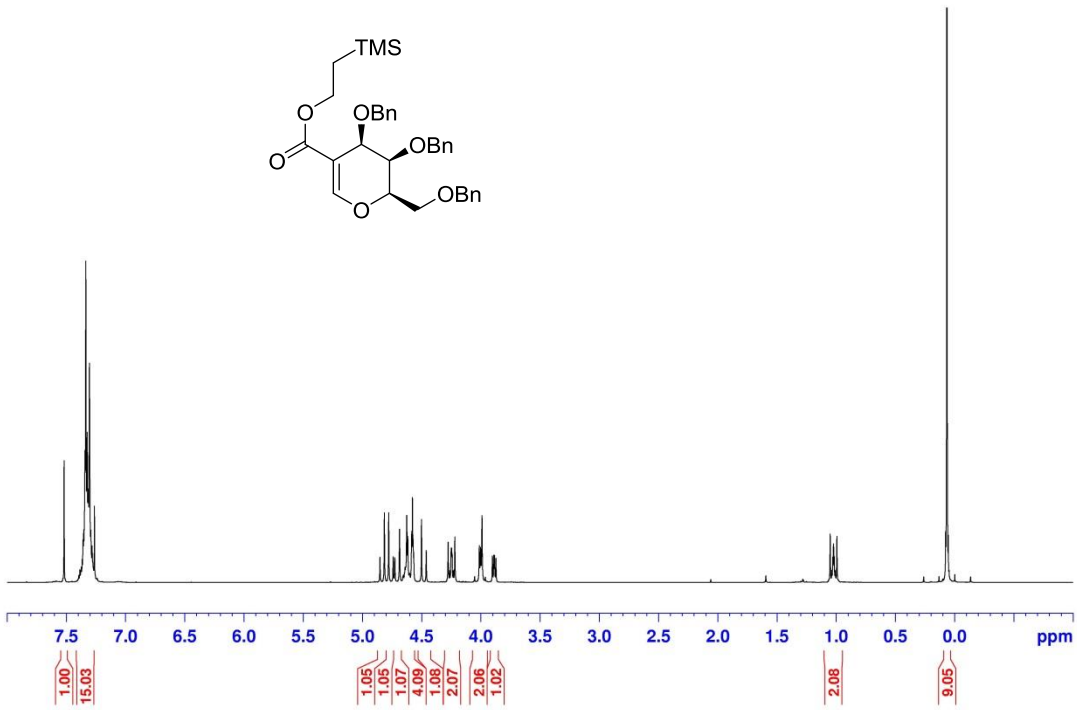
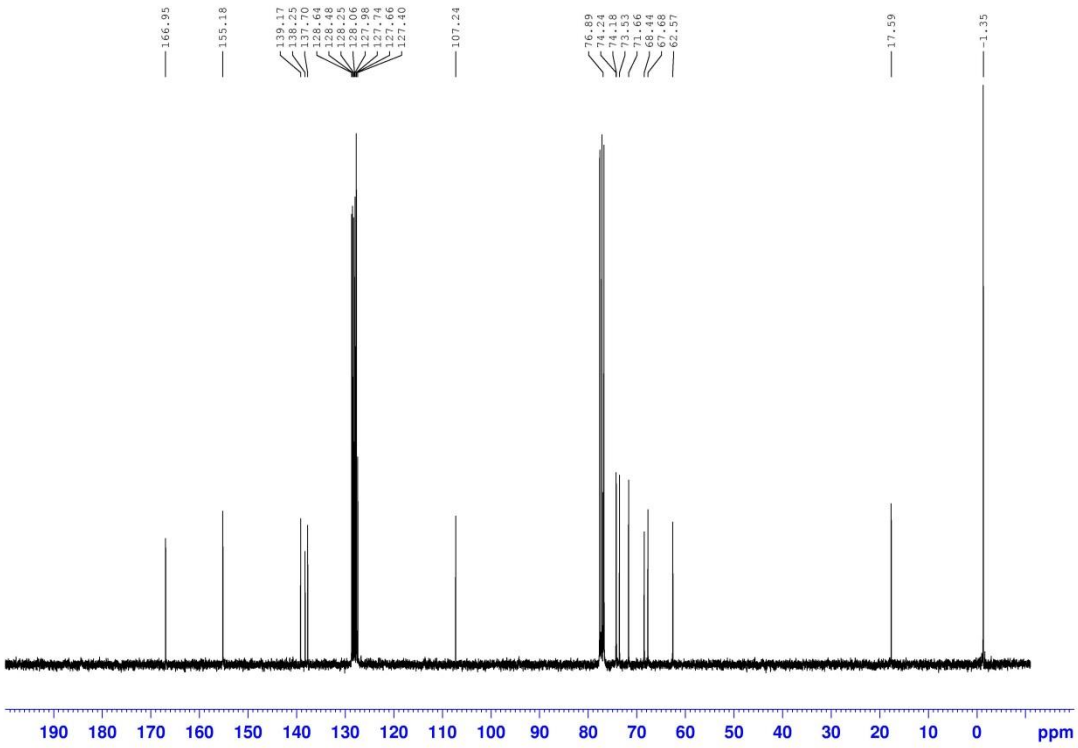
68.43
68.13
62.48
17.61
-1.31


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OBn
OBn
O
OBn
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 15.03 1.05 1.05 1.07 4.09 1.08 2.07 2.06 1.02 2.08 9.05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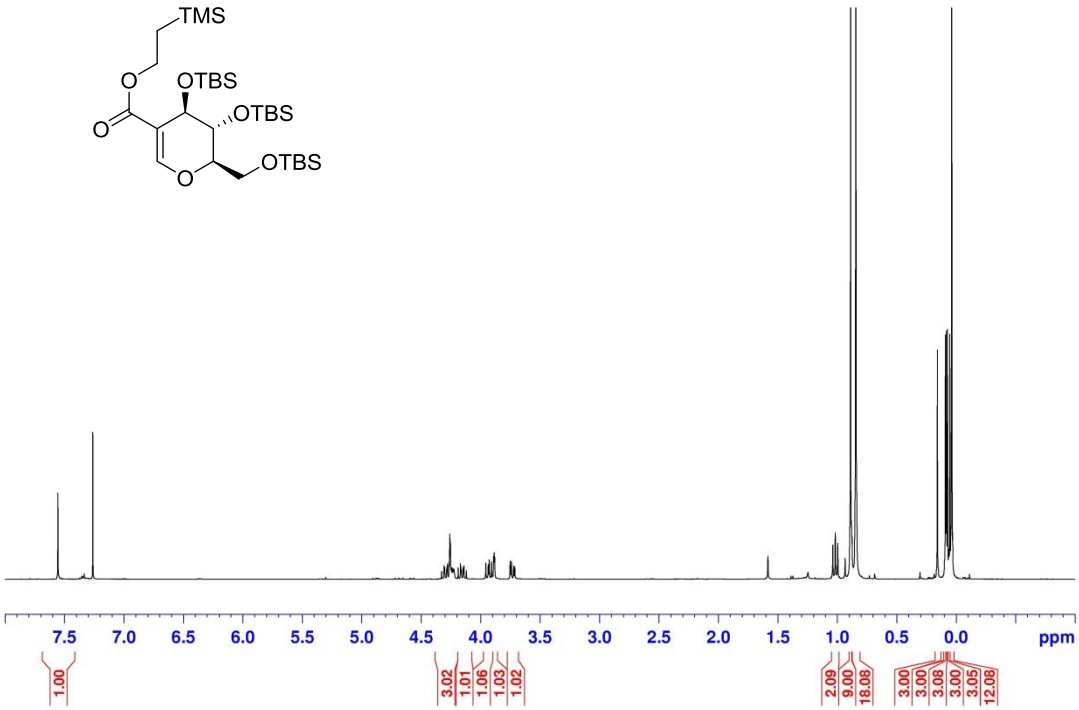
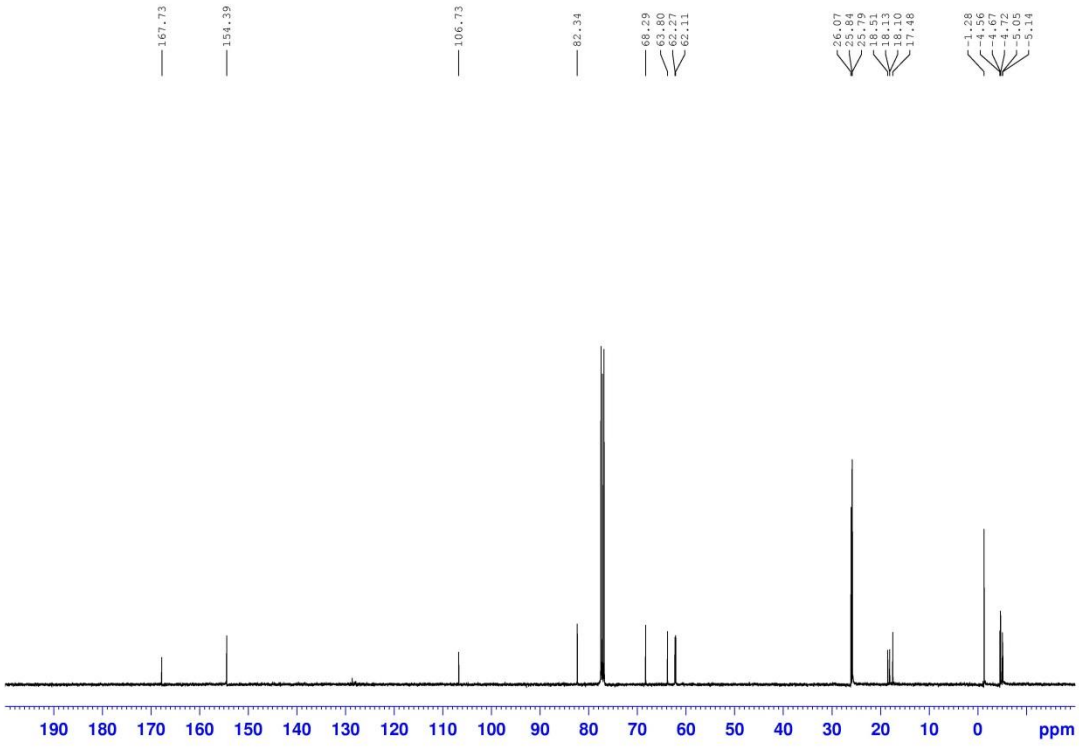
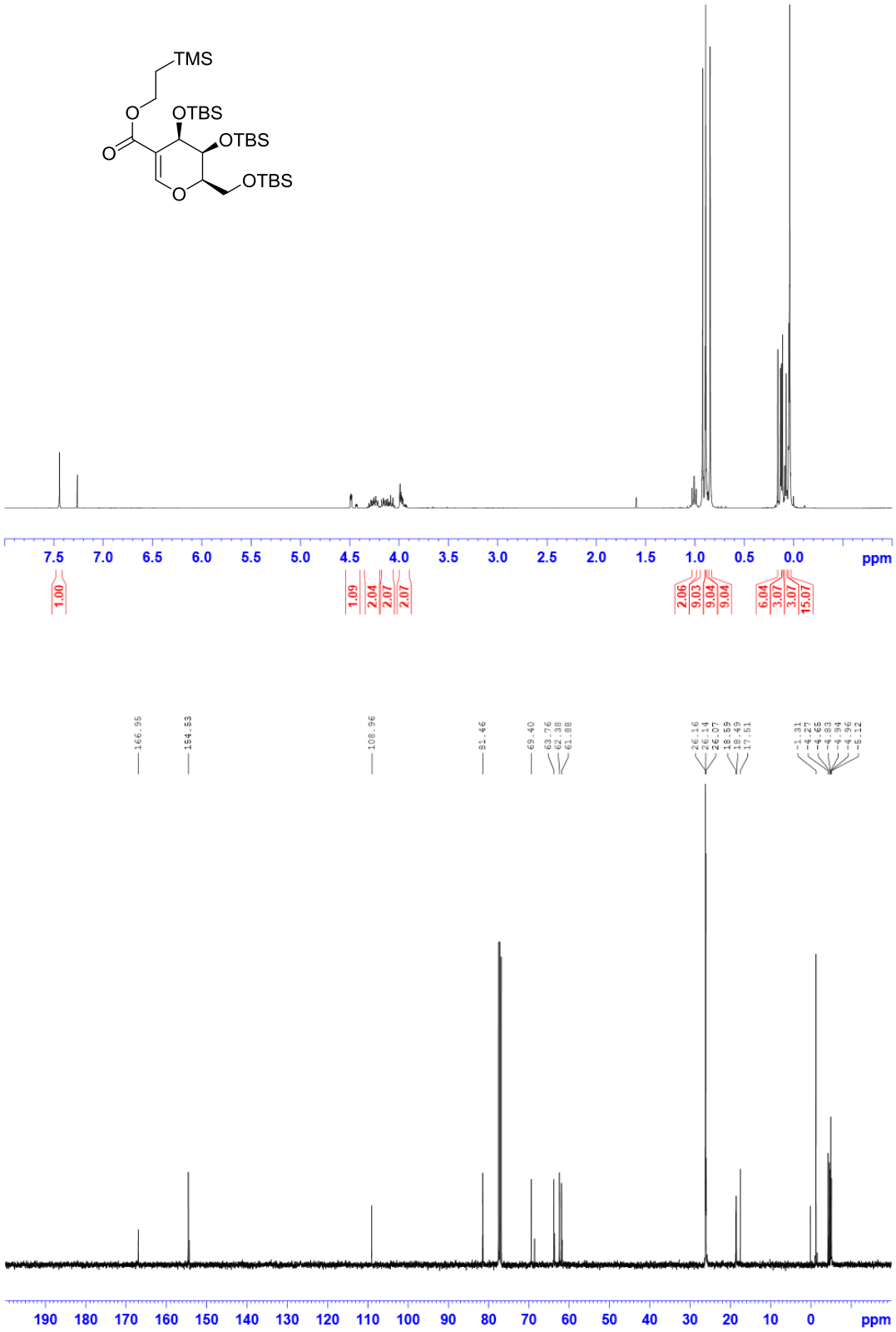
155.18
139.17
138.25
137.70
128.64
128.48
128.25
128.06
127.98
127.74
127.66
127.40
107.24
76.89
74.24
74.18
73.53
71.66
68.44
67.68
62.57
17.59
-1.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OTBS
O
OTBS
OTBS
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
3.02
1.01
1.06
1.03
1.02
2.09
9.00
18.08
3.00
3.00
3.08
3.00
3.05
12.08


167.73
154.39
106.73
82.34
68.29
63.80
62.27
62.11
26.07
25.84
25.79
18.51
18.13
18.10
17.48
-1.28
-4.56
-4.67
-4.72
-5.05
-5.14
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
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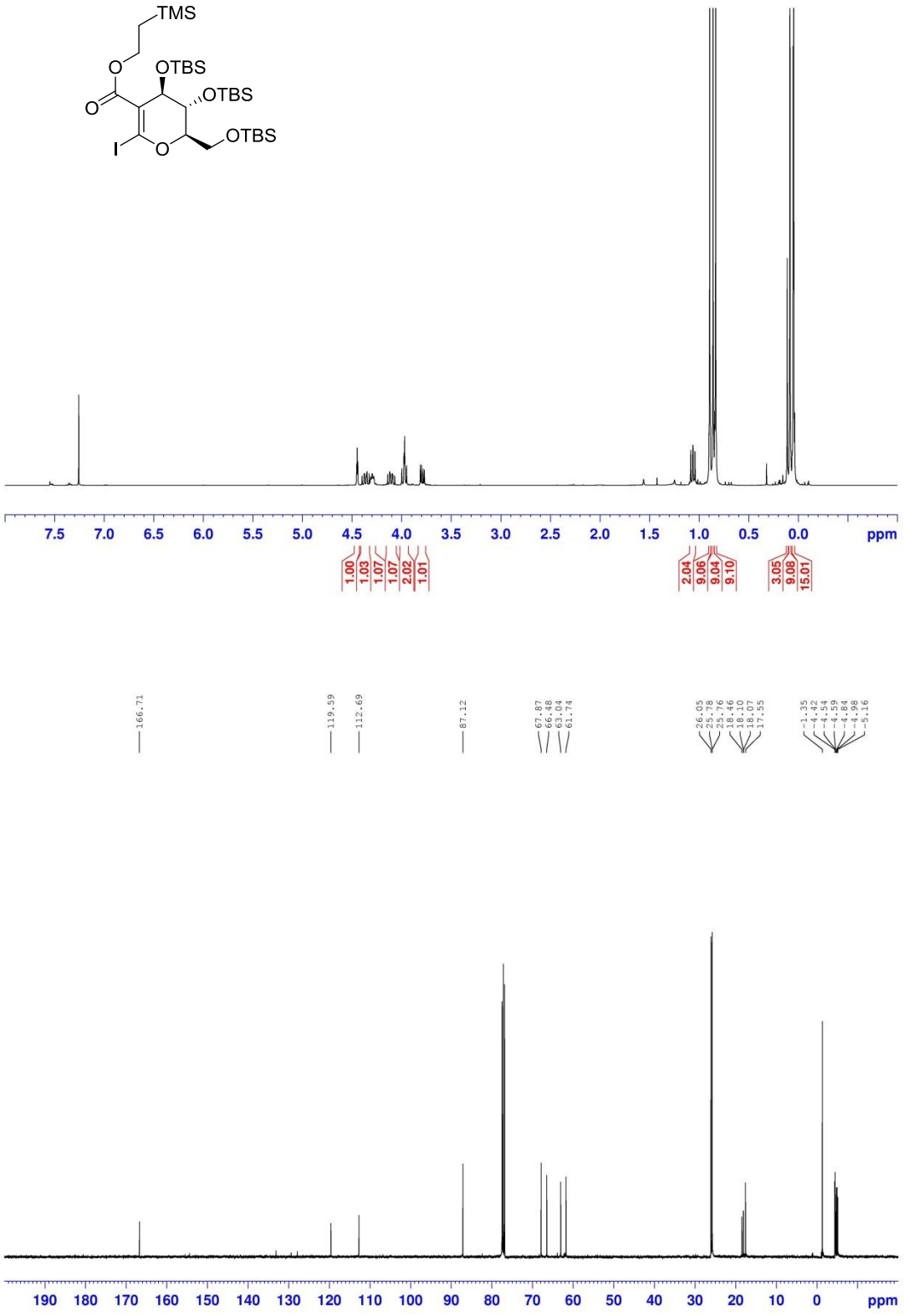
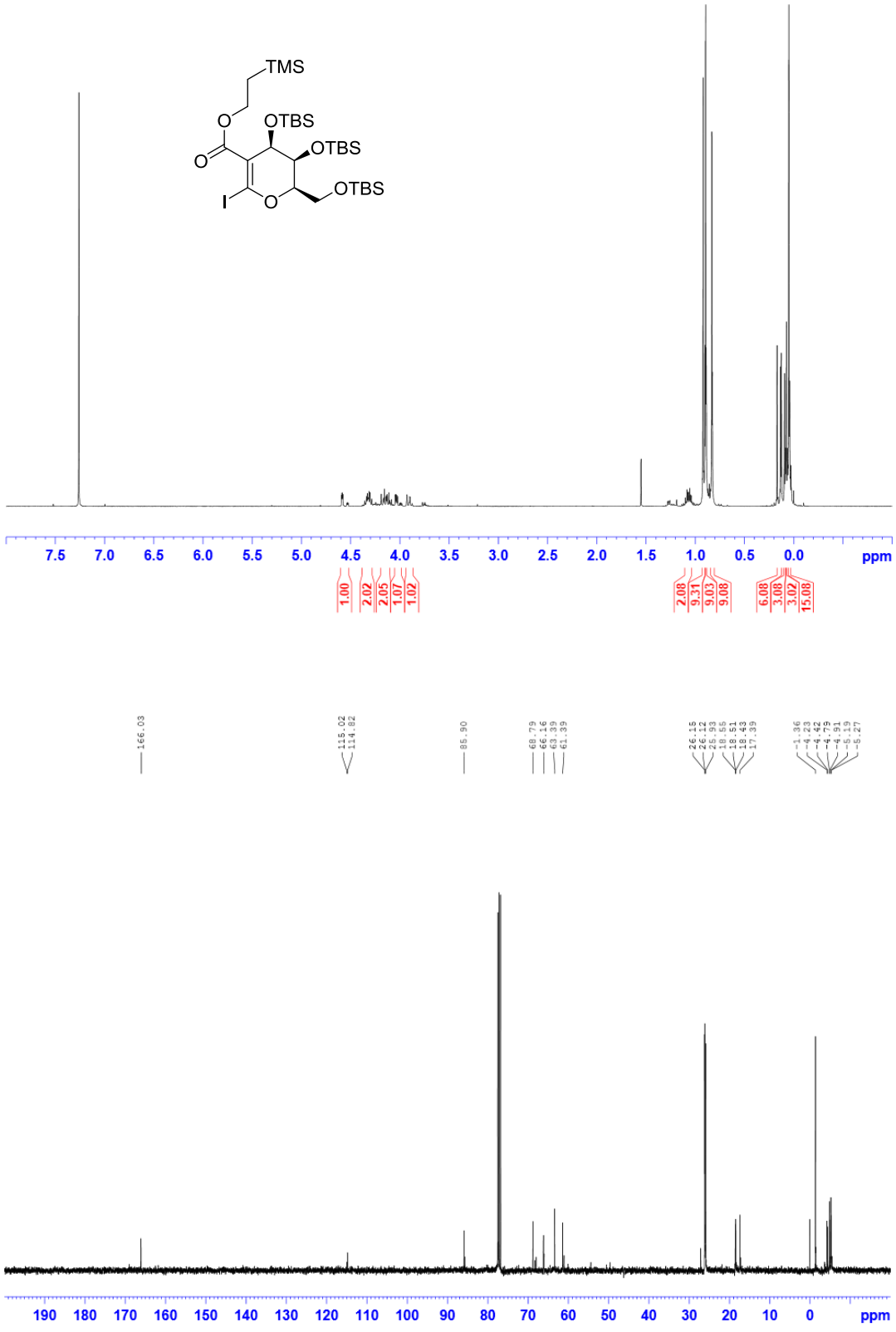
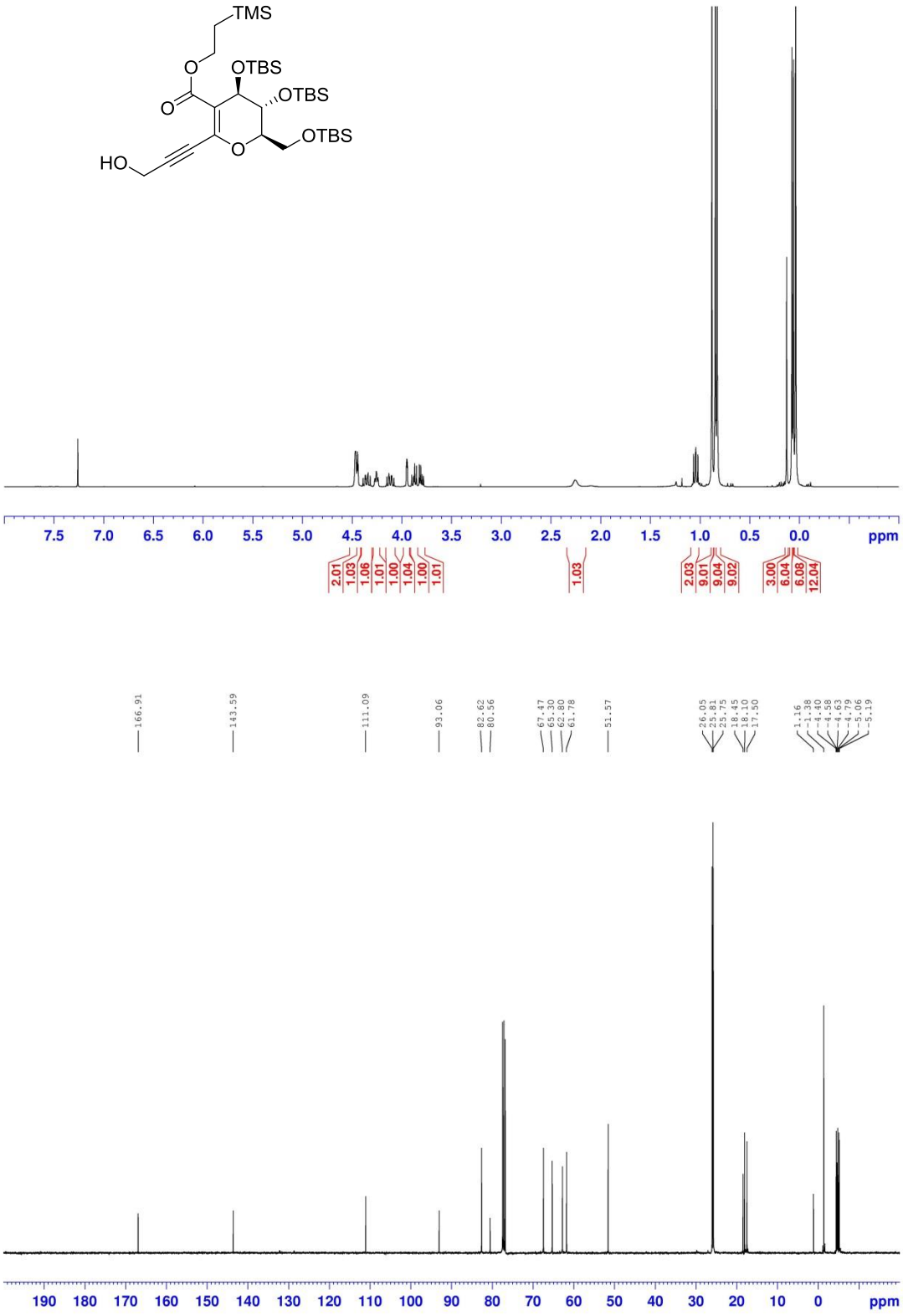
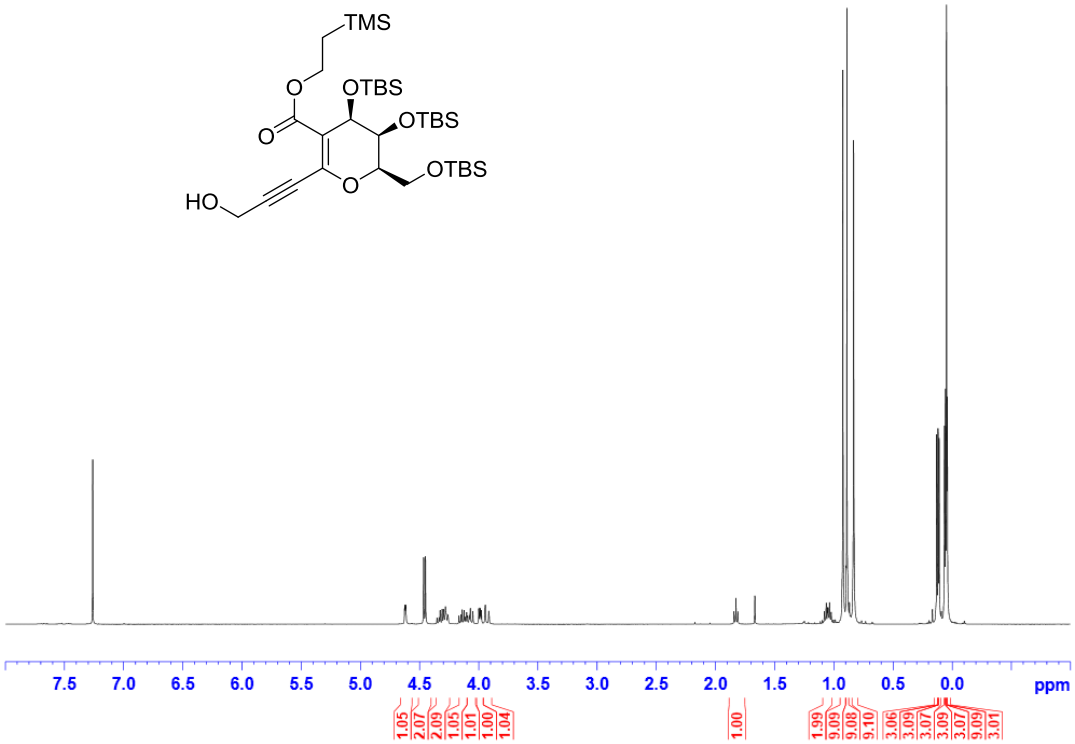
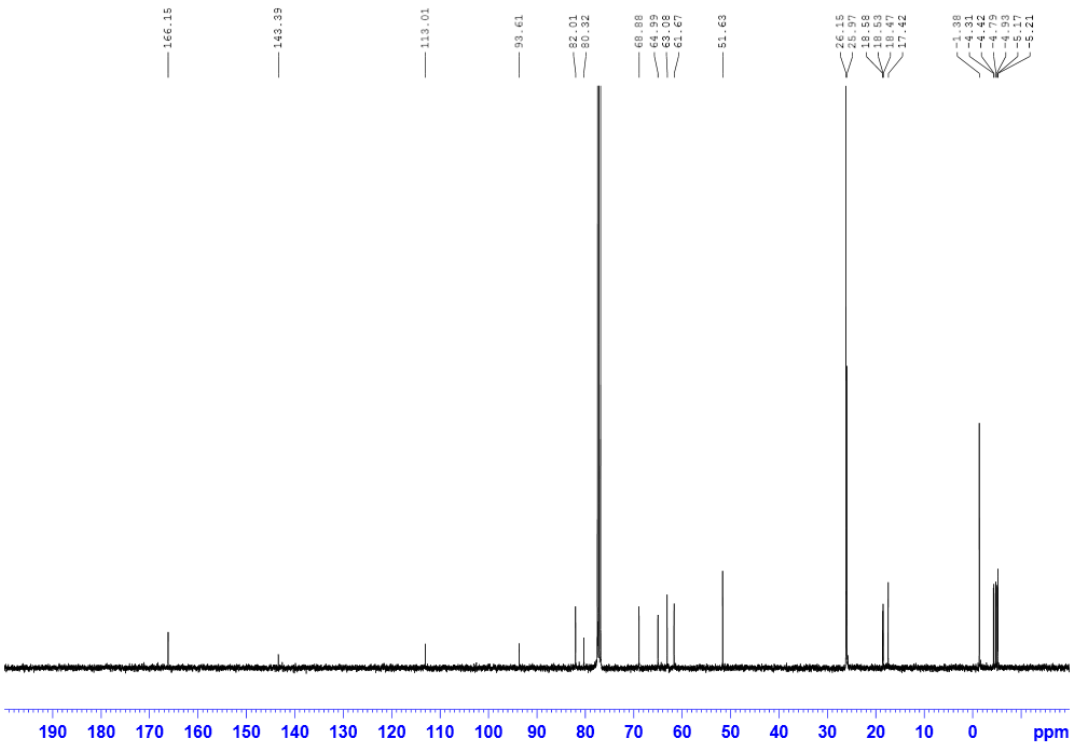
OTBS
O
OTBS
OTBS
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.09
2.04
2.07
2.07
2.06
9.03
9.04
9.04
6.04
3.01
3.07
15.07
166.95
154.53
108.96
81.46
69.40
63.76
62.38
61.88
26.16
26.14
26.07
18.59
18.49
17.51
-1.31
-4.27
-4.65
-4.83
-4.94
-4.96
-5.12
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OTBS
O
OTBS
OTBS
I
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.03 1.07 1.07 2.02 1.01
2.04 9.06 9.04 9.10
3.05 9.08 15.01
166.71
119.59
112.69
87.12
67.87
66.48
65.04
61.74
26.05
25.78
25.76
18.46
18.10
18.07
17.55
-1.35
-4.42
-4.54
-4.59
-4.84
-4.98
-5.16
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OTBS
O
OTBS
OTBS
I
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 2.02 2.05 1.07 1.02
2.08 9.31 9.03 9.08
6.08 3.08 3.02 15.08
166.03
115.02
114.82
85.90
69.79
66.16
63.39
61.39
26.15
26.12
25.93
18.55
18.51
18.43
17.89
-1.36
-4.23
-4.42
-4.79
-4.91
-5.19
-5.27
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OTBS
O
OTBS
OTBS
O
HO
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01 1.03 1.06 1.01 1.00 1.04 1.00 1.01 1.03 2.03 9.01 9.04 9.02 3.00 6.04 6.08 12.04
166.91 143.59 111.09 93.06 82.62 80.56 67.47 65.30 62.80 61.78 51.57 26.05 25.81 25.55 18.45 18.10 17.50 1.16 -1.38 -4.00 -4.58 -4.63 -4.74 -4.79 -5.06 -5.19
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
OTBS
O
OTBS
OTBS
O
HO
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.05 2.07 2.09 1.05 1.01 1.00 1.04 1.00 1.99 9.09 9.08 9.10 3.06 3.09 3.07 3.09 3.07 9.09 3.01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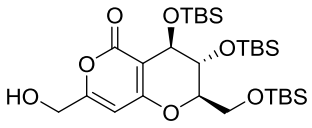
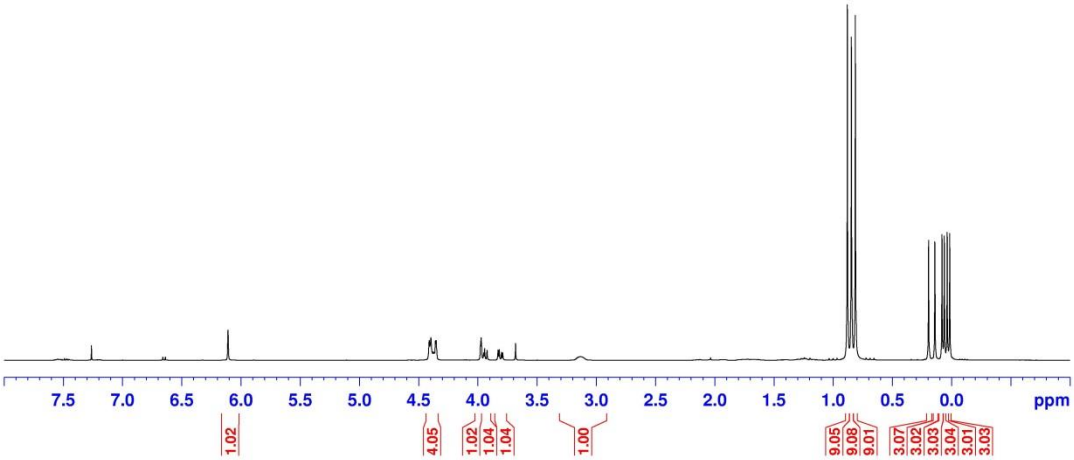
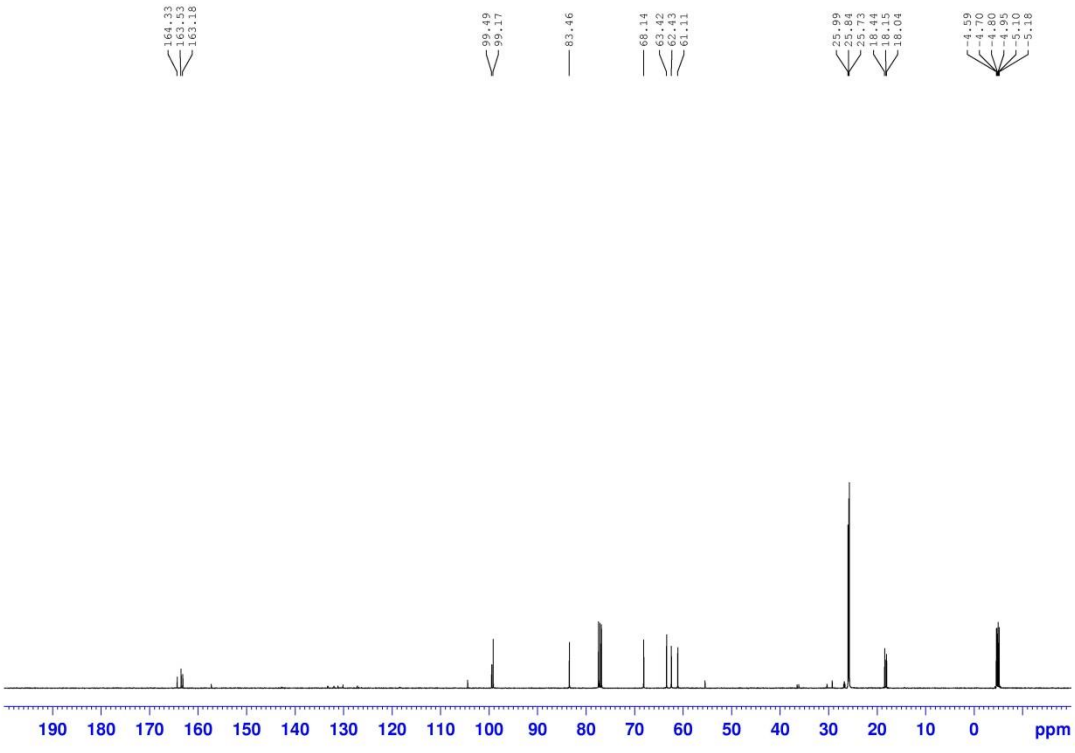
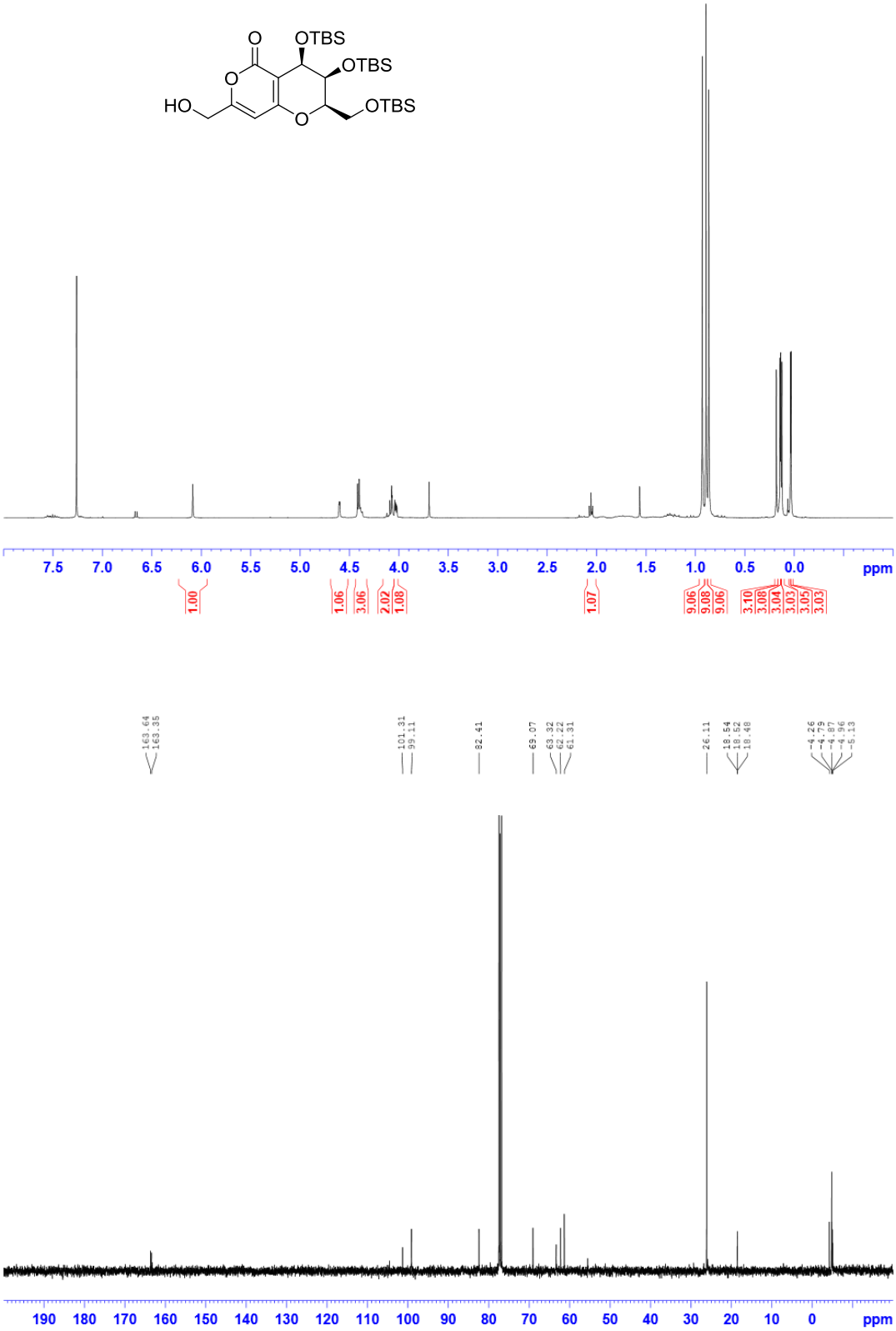
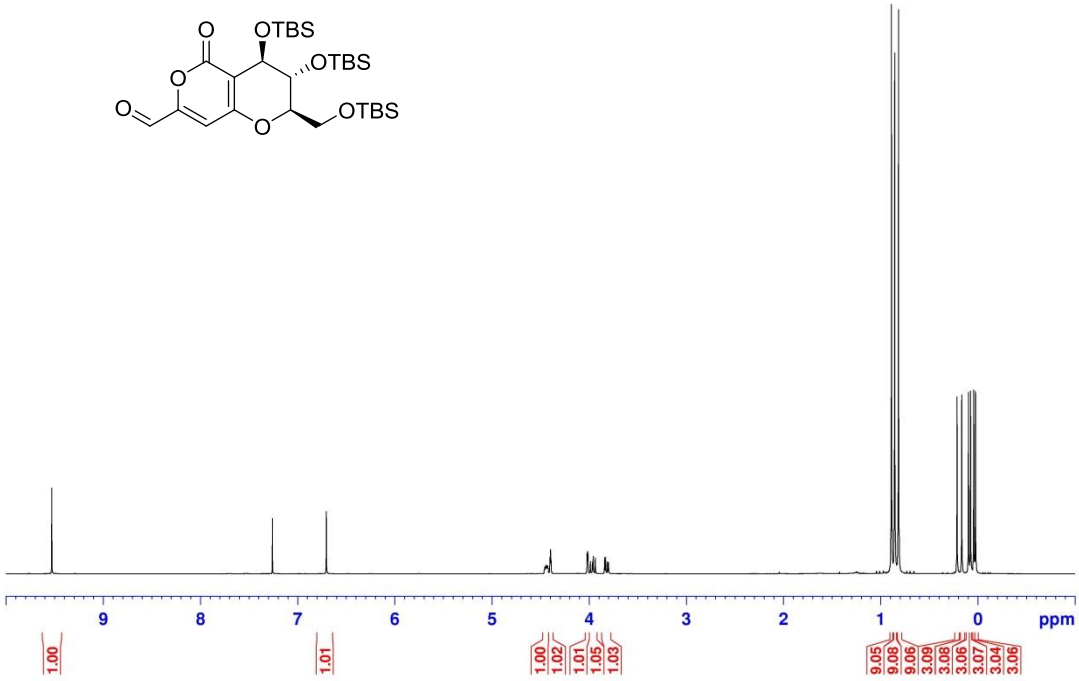
113.01
93.61
82.01
80.32
60.88
64.39
63.88
61.67
51.63
26.15
25.97
18.58
18.53
18.47
17.42
-1.38
-4.31
-4.42
-4.79
-4.93
-5.17
-5.21
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

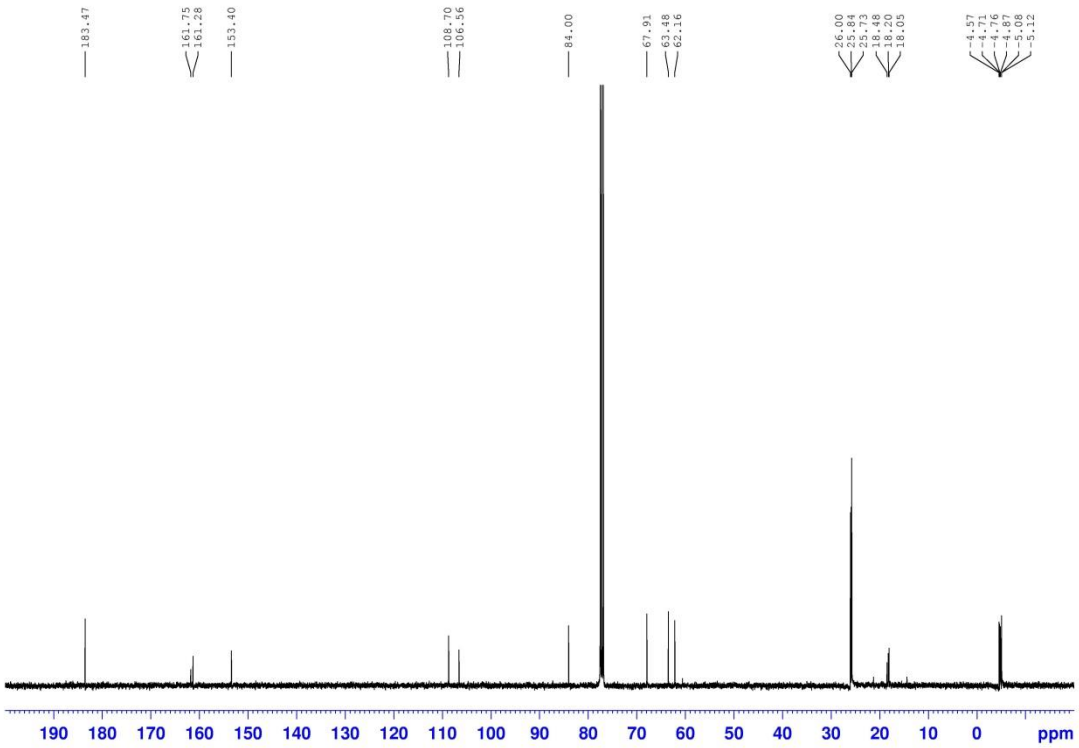

O
OTBS
OTBS
O
HO
O
OTBS

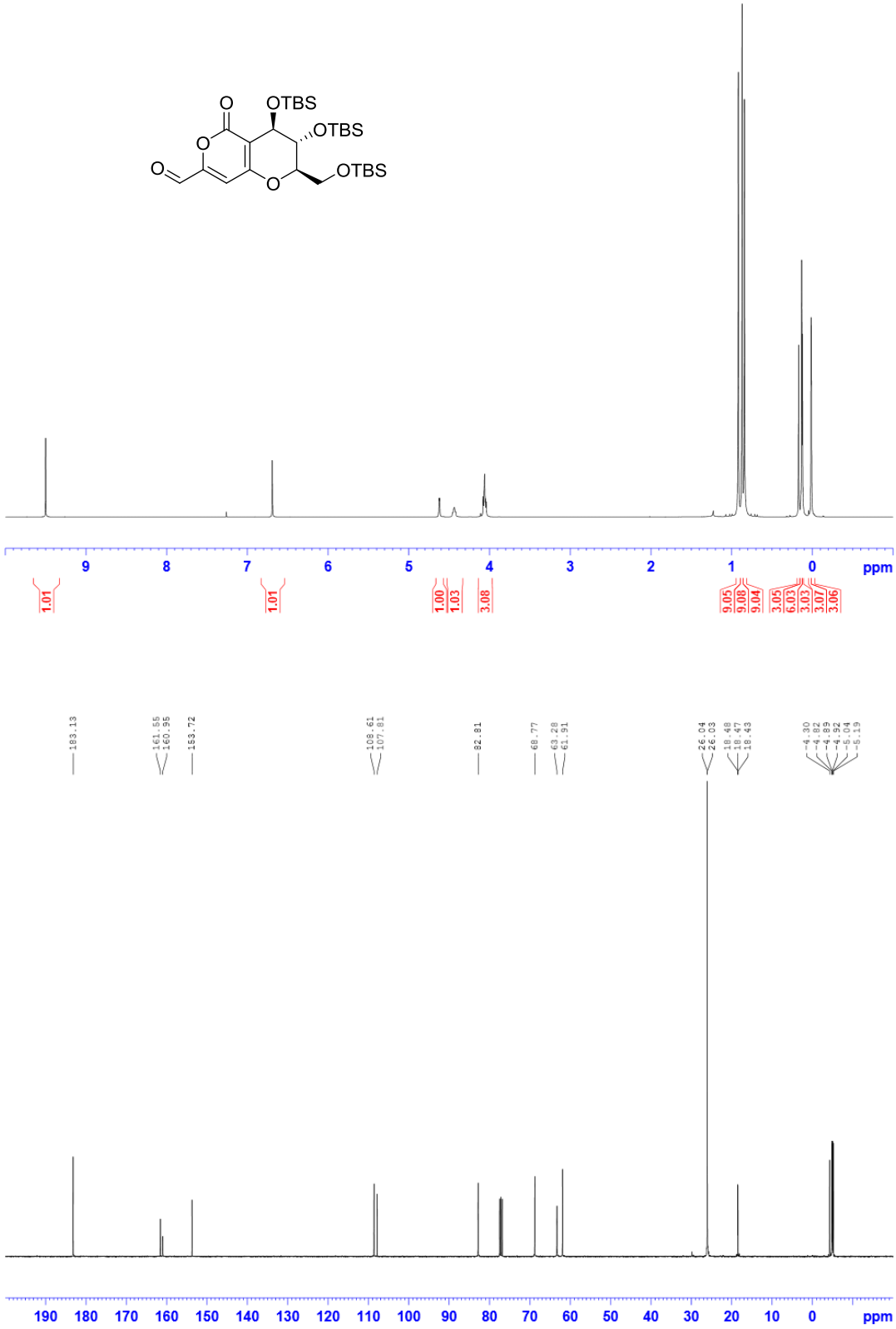

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.02
4.05
1.02
1.04
1.04
1.00
9.05
9.08
9.01
3.07
3.02
3.03
3.04
3.01
3.03

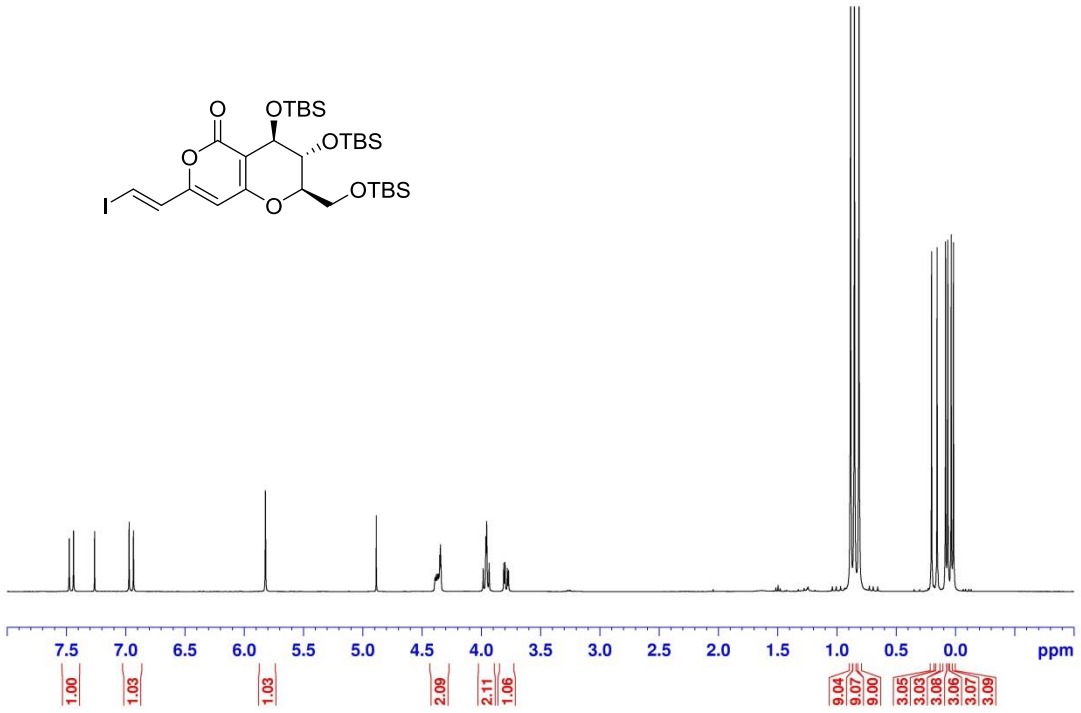

164.33
163.53
163.18
99.49
99.17
83.46
68.14
63.42
62.43
61.11
25.99
25.84
25.73
18.44
18.15
18.04
-4.59
-4.70
-4.80
-4.95
-5.10
-5.18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

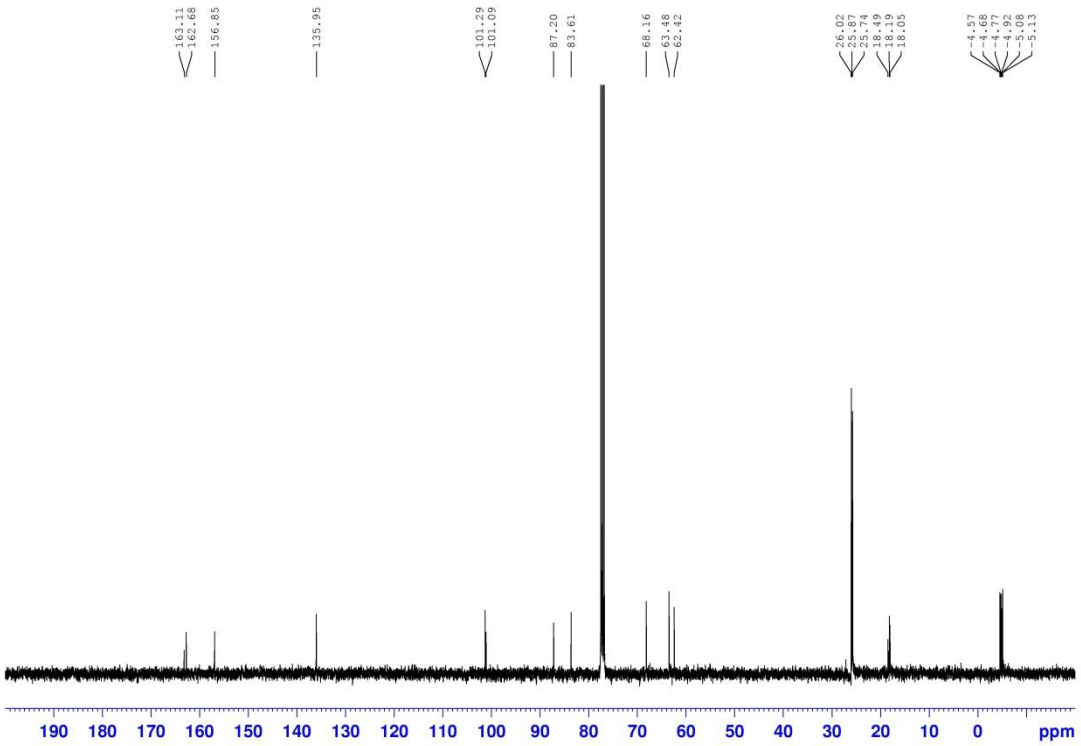

O
OTBS
OTBS
HO
O
O
OTBS
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00 1.06 3.06 2.02 1.08 1.07 9.06 9.08 9.06 3.10 3.08 3.04 3.03 3.05 3.03
163.64 163.35 101.31 99.11 82.41 69.07 63.32 62.22 61.31 26.11 18.54 18.52 18.48 -4.26 -4.79 -4.87 -4.96 -5.13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


OTBS
OTBS
OTBS
O
O
O
O
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.00
1.02
1.01
1.05
1.03
9.05
9.08
9.06
3.09
3.08
3.06
3.07
3.04
3.06


183.47
161.75
161.28
153.40
108.70
106.56
84.00
67.91
63.48
62.16
26.00
25.84
25.53
18.48
18.20
18.05
-4.57
-4.71
-4.76
-4.87
-5.08
-5.12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
OTBS
OTBS
O
O
OTBS
O
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.01
1.00
1.03
3.08
9.05
9.08
9.04
3.05
6.03
3.03
3.07
3.06
183.13
161.55
160.95
153.72
108.61
107.81
82.81
68.77
63.28
61.91
26.04
26.03
18.48
18.47
18.43
-4.30
-4.82
-4.89
-4.92
-5.04
-5.19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
OTBS
OTBS
OTBS
O
O
I
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.03
1.03
2.09
2.11
1.06
9.04
9.07
9.00
3.05
3.03
3.08
3.06
3.07
3.09


163.11
162.68
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135.95
101.29
101.09
87.20
83.61
68.16
63.48
62.42
26.02
25.97
25.94
18.49
18.19
18.05
-4.57
-4.68
-4.77
-4.92
-5.08
-5.13
190
180
170
160
150
140
130
120
110
100
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80
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60
50
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20
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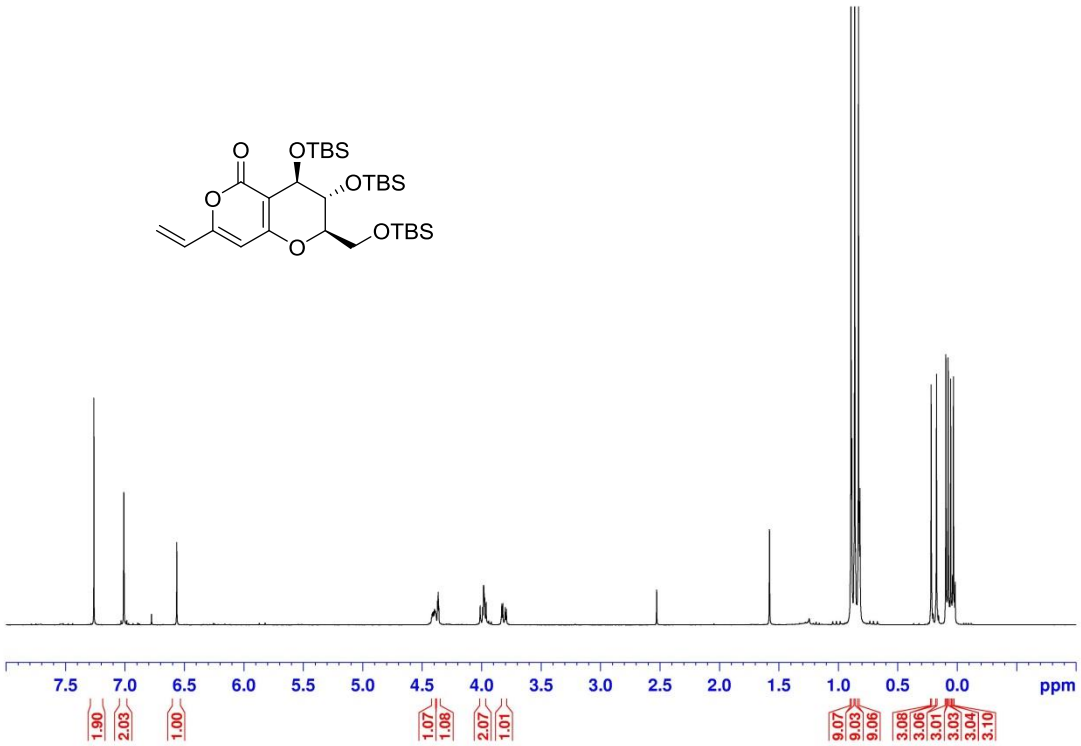
0
ppm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OTBS
OTBS
OTBS
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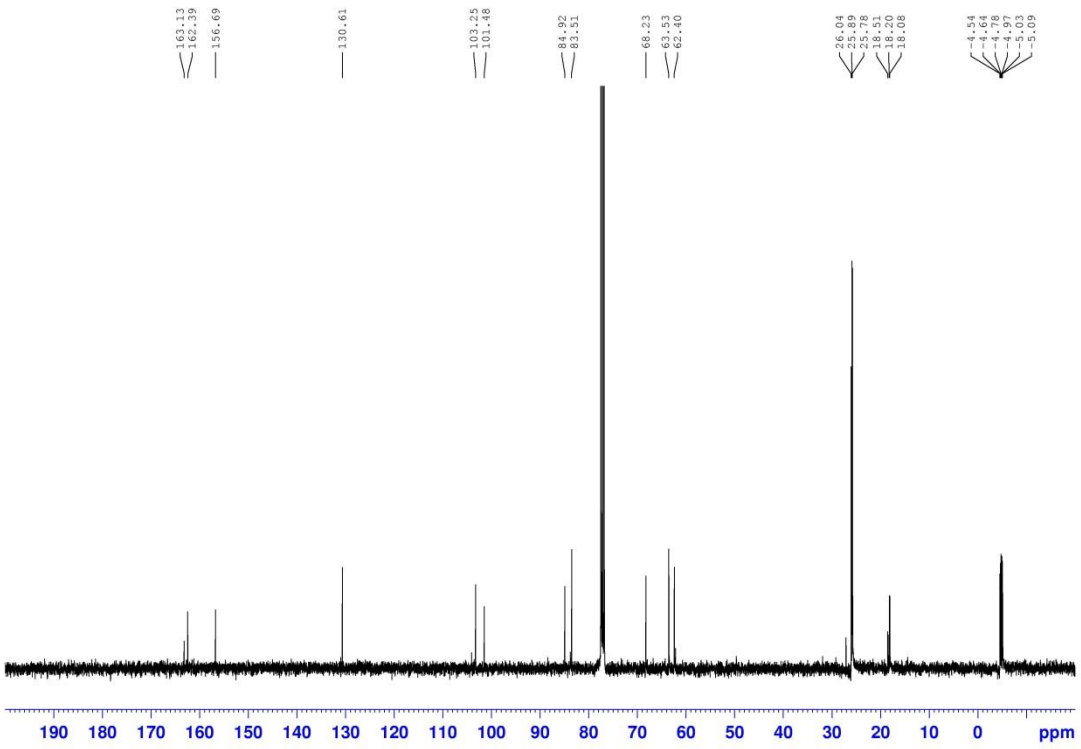
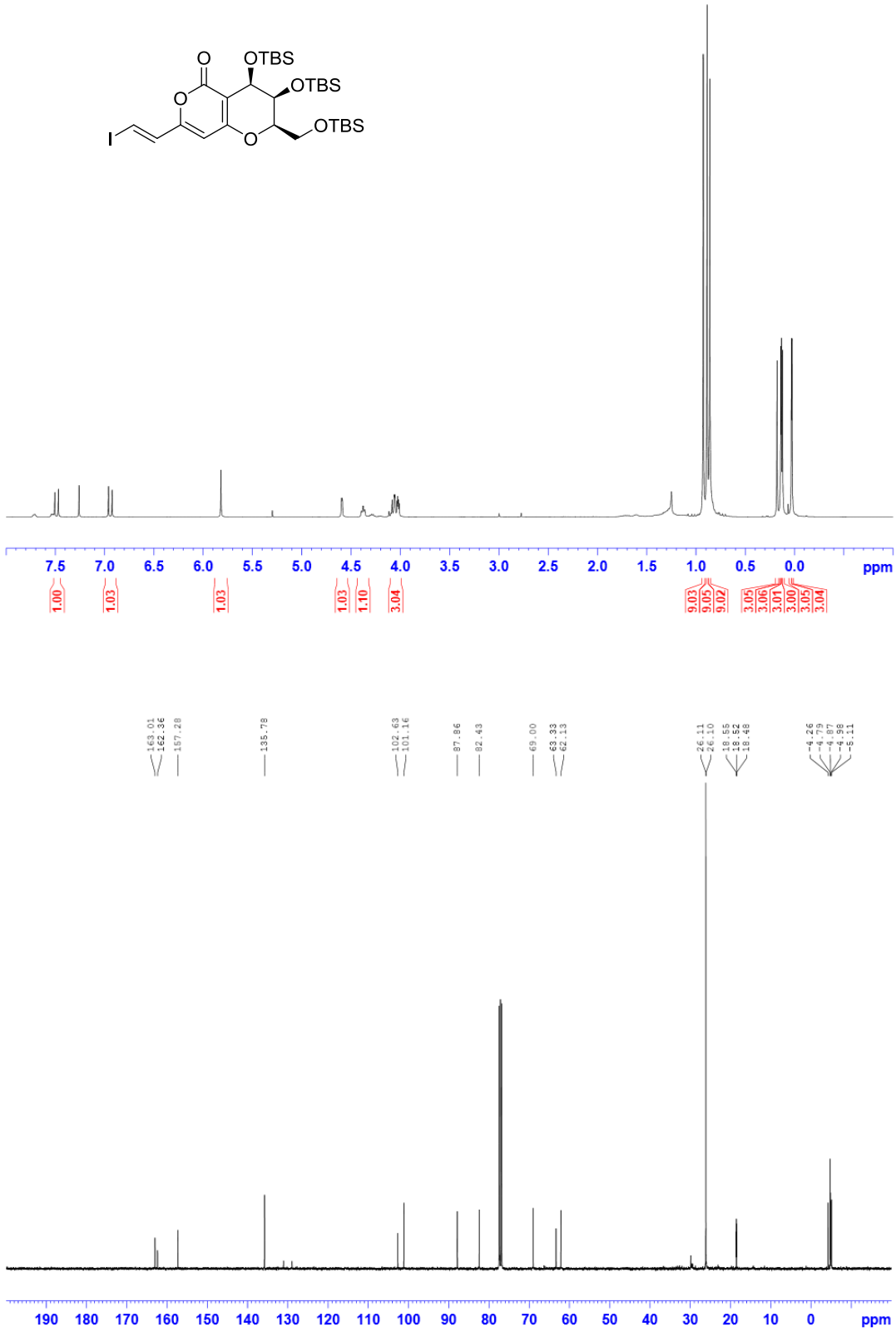
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.90 2.03 1.00 1.07 1.08 2.07 1.01 9.07 9.03 9.06 3.08 3.06 3.01 3.03 3.04 3.10


163.13
162.39
156.69
130.61
103.25
101.48
84.92
83.51
68.23
63.53
62.40
26.04
25.89
25.78
18.51
18.20
18.08
-4.54
-4.64
-4.78
-4.97
-5.03
-5.09
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
OTBS
OTBS
O
O
OTBS
I
7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.03
1.03
1.03
1.10
3.04
9.03
9.05
9.02
3.05
3.06
3.01
3.00
3.05
3.04
163.01
162.36
157.28
135.78
102.63
101.16
87.86
82.43
69.00
63.33
62.13
26.11
26.10
18.55
18.52
18.48
-4.26
-4.79
-4.87
-4.98
-5.11
190
180
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150
140
130
120
110
100
90
80
70
60
50
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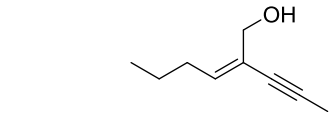
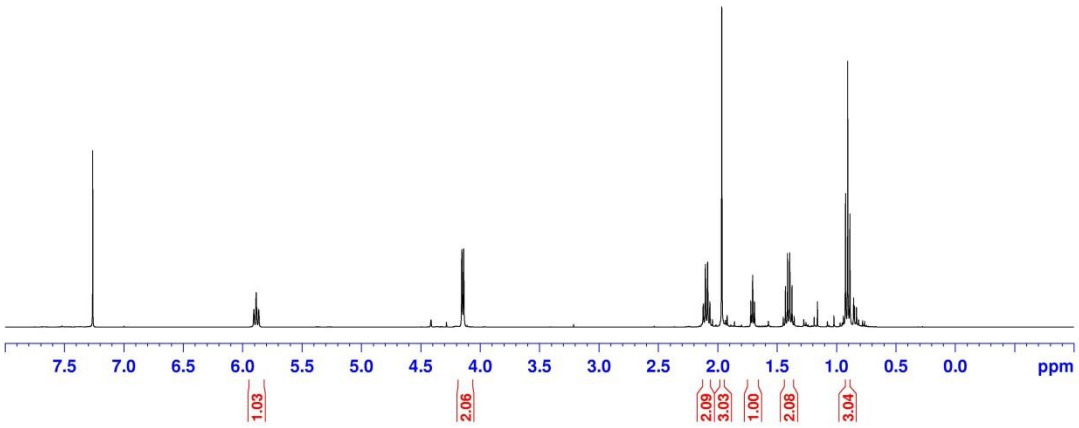
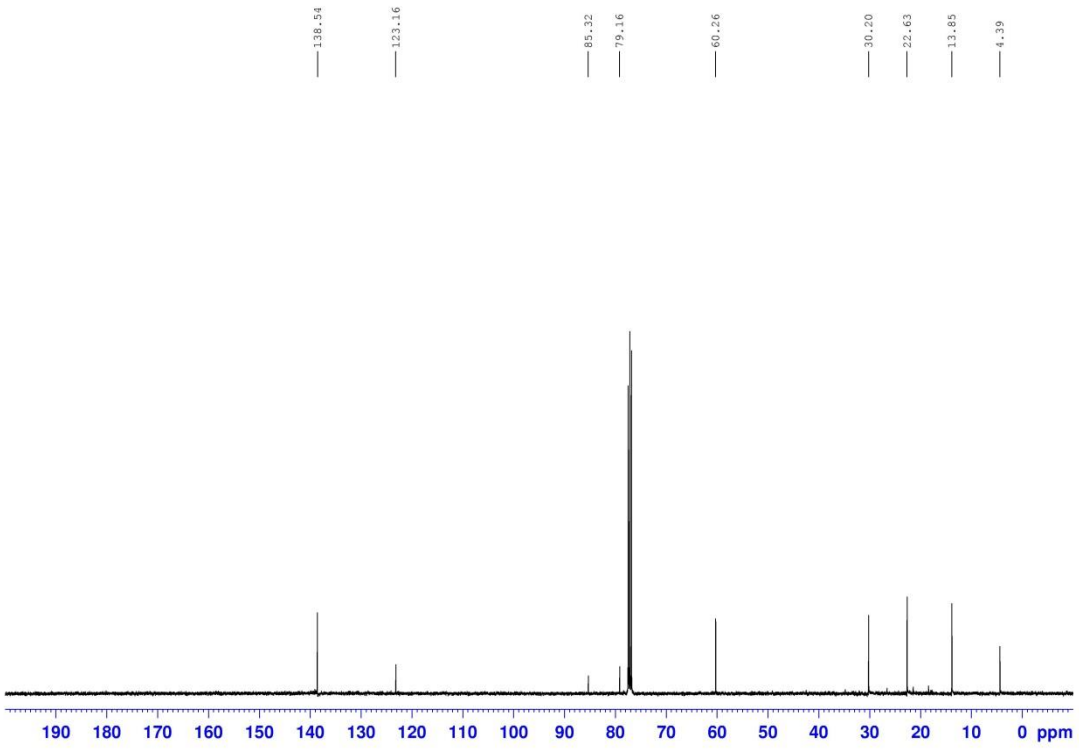
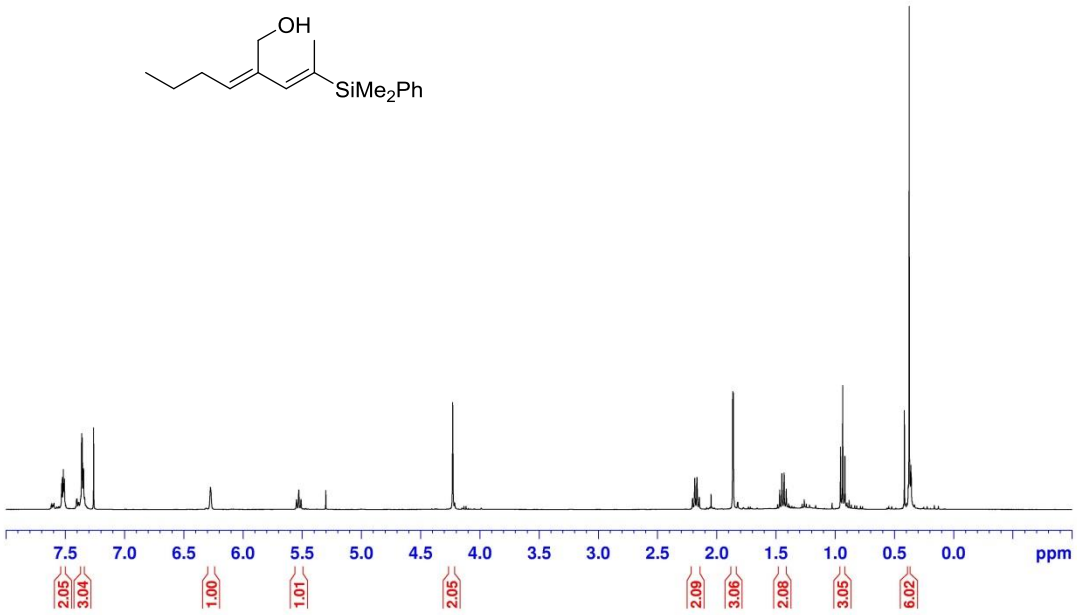
30
20
10
0
ppm

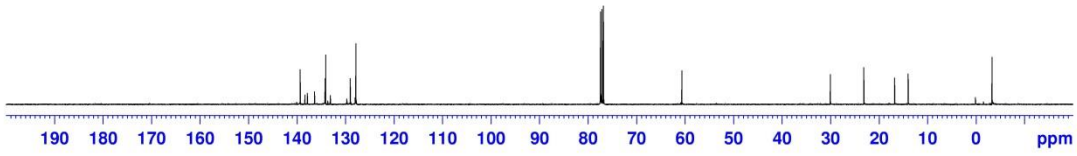

OH

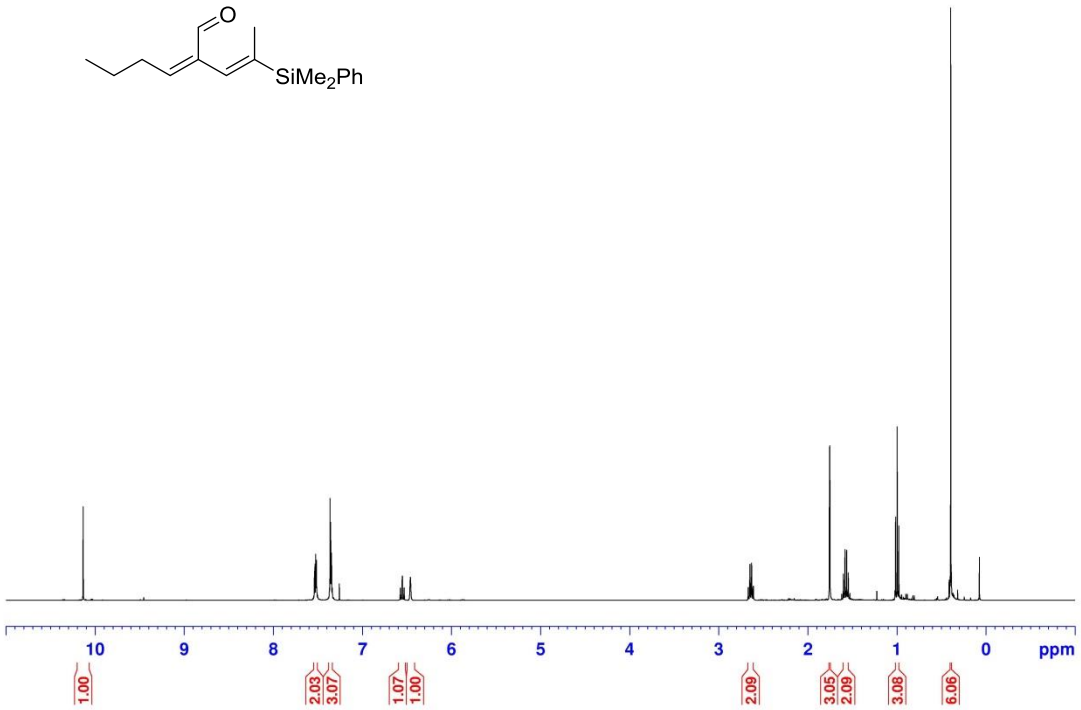

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.03
2.06
2.09
3.03
1.00
2.08
3.04

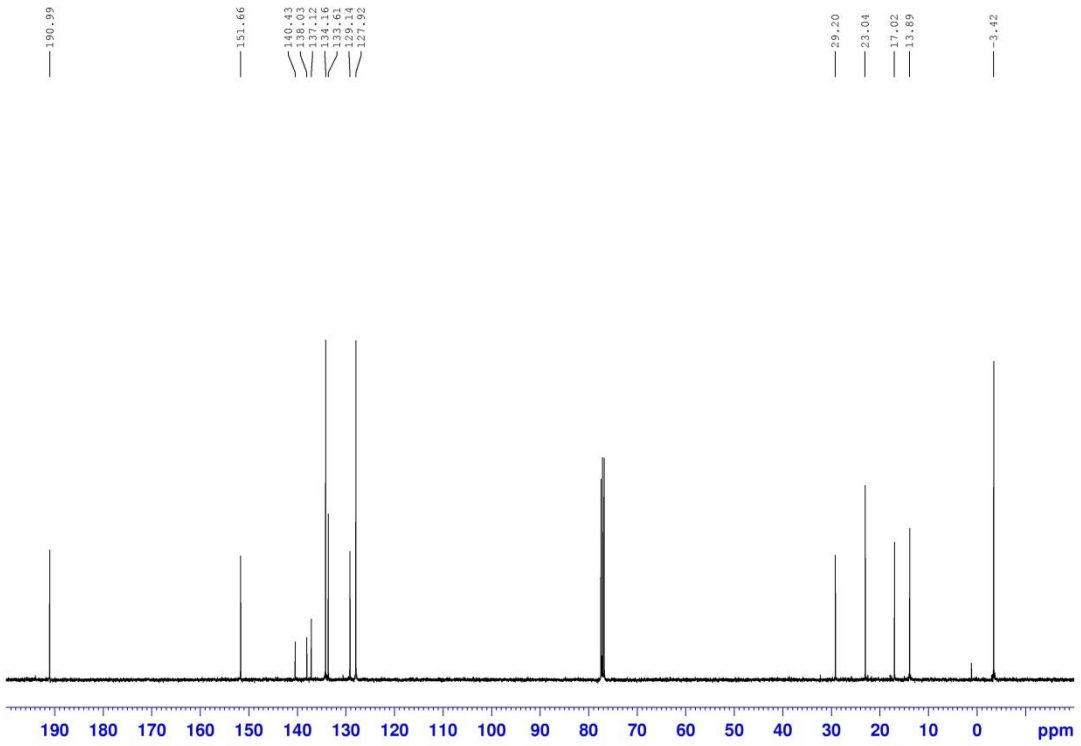

138.54
123.16
85.32
79.16
60.26
30.20
22.63
13.85
4.39
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


OH
SiMe2Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.05 3.04 1.00 1.01 2.05 2.09 3.06 2.08 3.05 6.02


139.38
138.40
137.89
136.41
134.23
134.12
129.05
127.88
60.67
30.05
23.14
16.79
13.99
-3.30


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O
SiMe2Ph
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.03
3.07
1.07
1.00
2.09
3.05
2.09
3.08
6.06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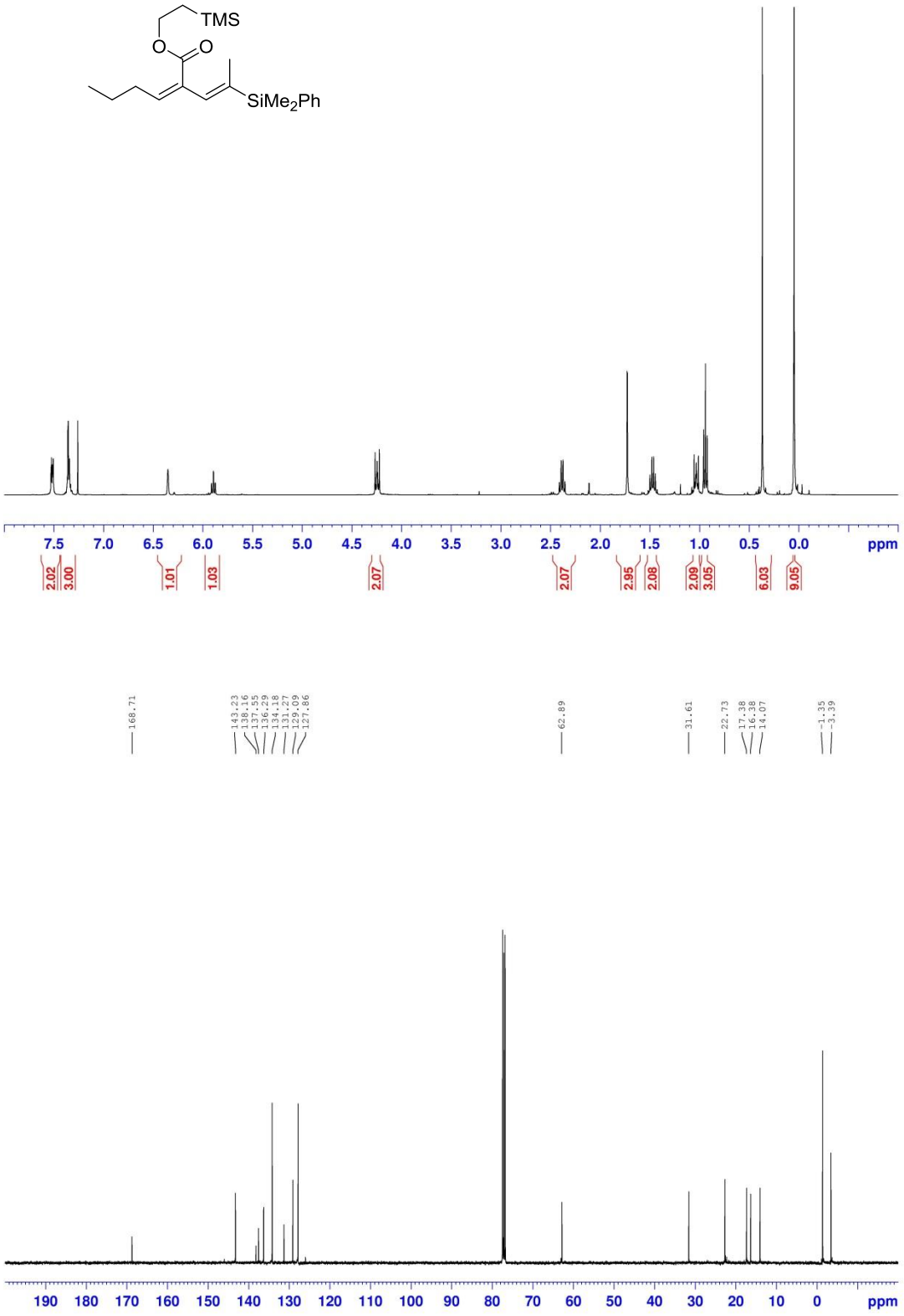
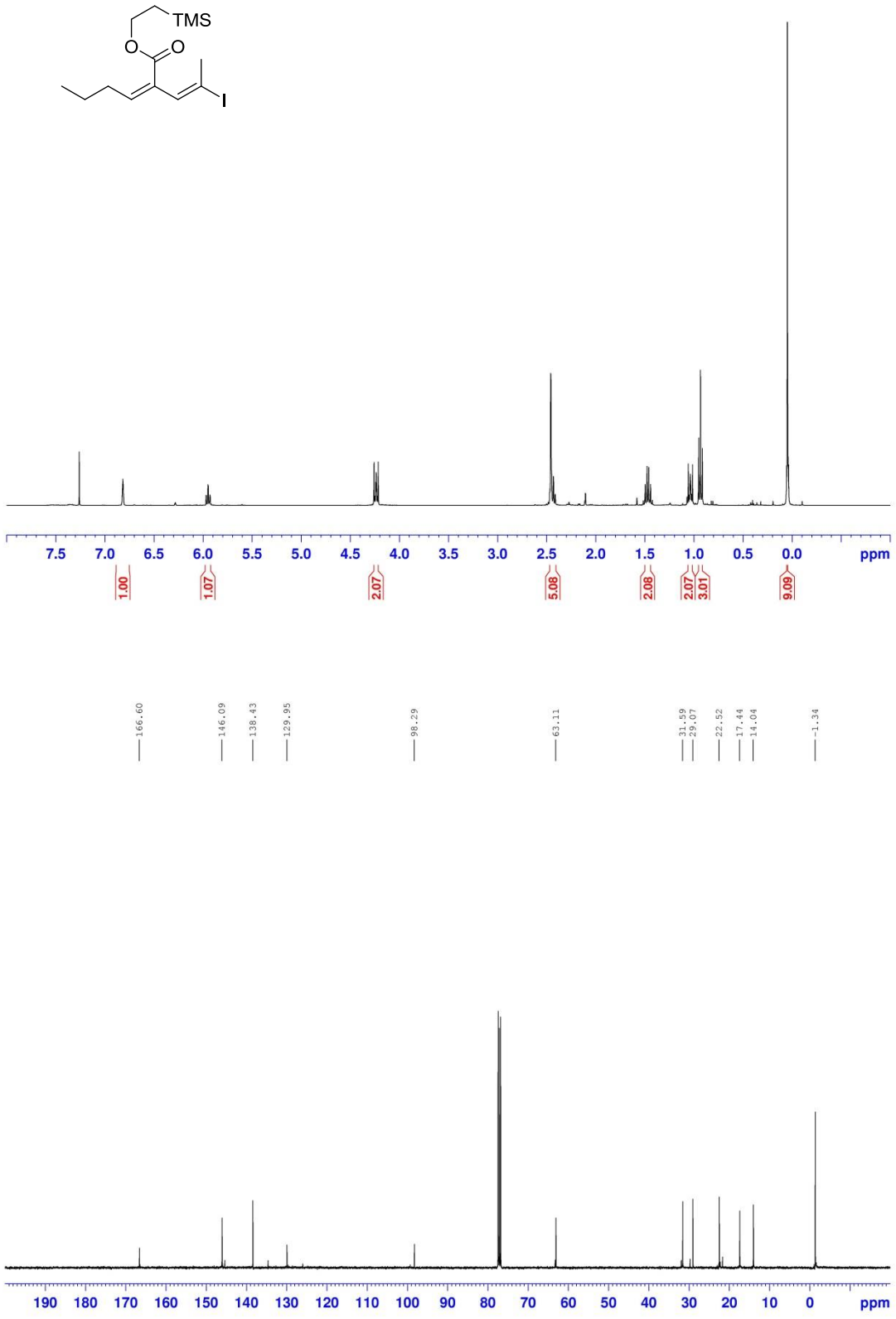
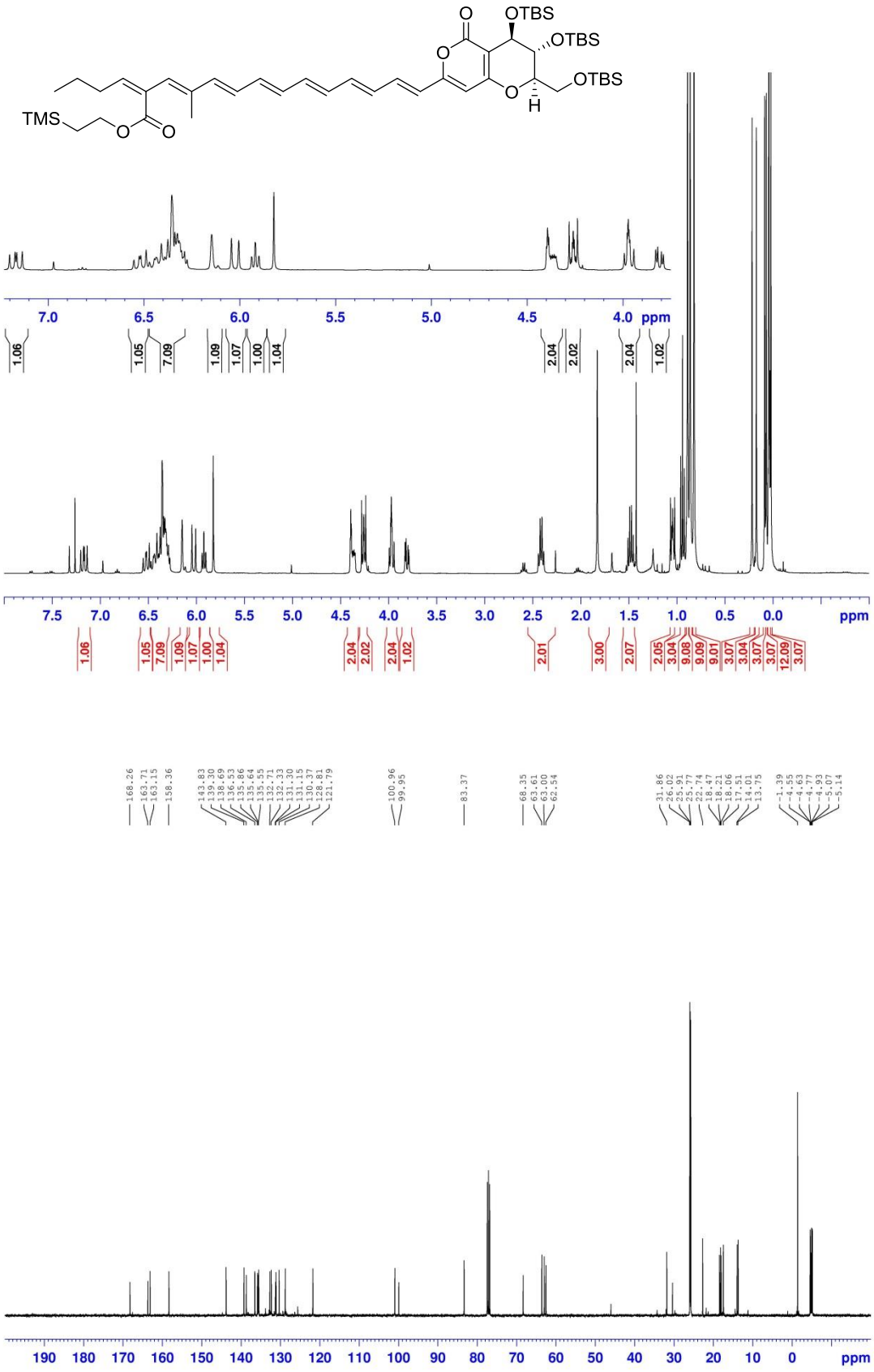
140.43
138.03
137.12
134.16
133.61
129.14
127.92
29.20
23.04
17.02
13.89
-3.42
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


TMS
O
O
SiMe2Ph
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02 3.00 1.01 1.03 2.07 2.07 2.95 2.08 2.09 3.05 6.03 9.05
168.71
143.23
138.16
137.55
136.29
134.18
131.27
129.09
127.86
62.89
31.61
22.73
17.38
16.38
14.07
-1.35
-3.39
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TMS
O
O
I
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.07
2.07
5.08
2.08
2.07
3.01
9.09
166.60
146.09
138.43
129.95
98.29
63.11
31.59
29.07
22.52
17.44
14.04
-1.34
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
OTBS
OTBS
OTBS
O
O
H
TMS
O
O
7.0
6.5
6.0
5.5
5.0
4.5
4.0 ppm
1.06
1.05
7.09
1.09
1.07
1.00
1.04
2.04
2.02
2.04
1.02
7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.06
1.05
7.09
1.09
1.07
1.00
1.04
2.04
2.02
2.04
1.02
2.01
3.00
2.07
2.05
3.04
9.08
9.09
9.01
3.07
3.04
3.07
12.09
3.07
168.26
163.71
163.15
158.36
143.83
139.30
138.69
136.53
135.86
135.64
135.55
132.71
132.33
131.30
131.15
130.37
128.81
121.79
100.96
99.95
83.37
68.35
63.61
63.00
62.54
31.86
26.02
25.91
25.77
22.74
18.47
18.21
18.06
17.51
14.01
13.75
-1.39
-4.55
-4.63
-4.77
-4.93
-5.07
-5.14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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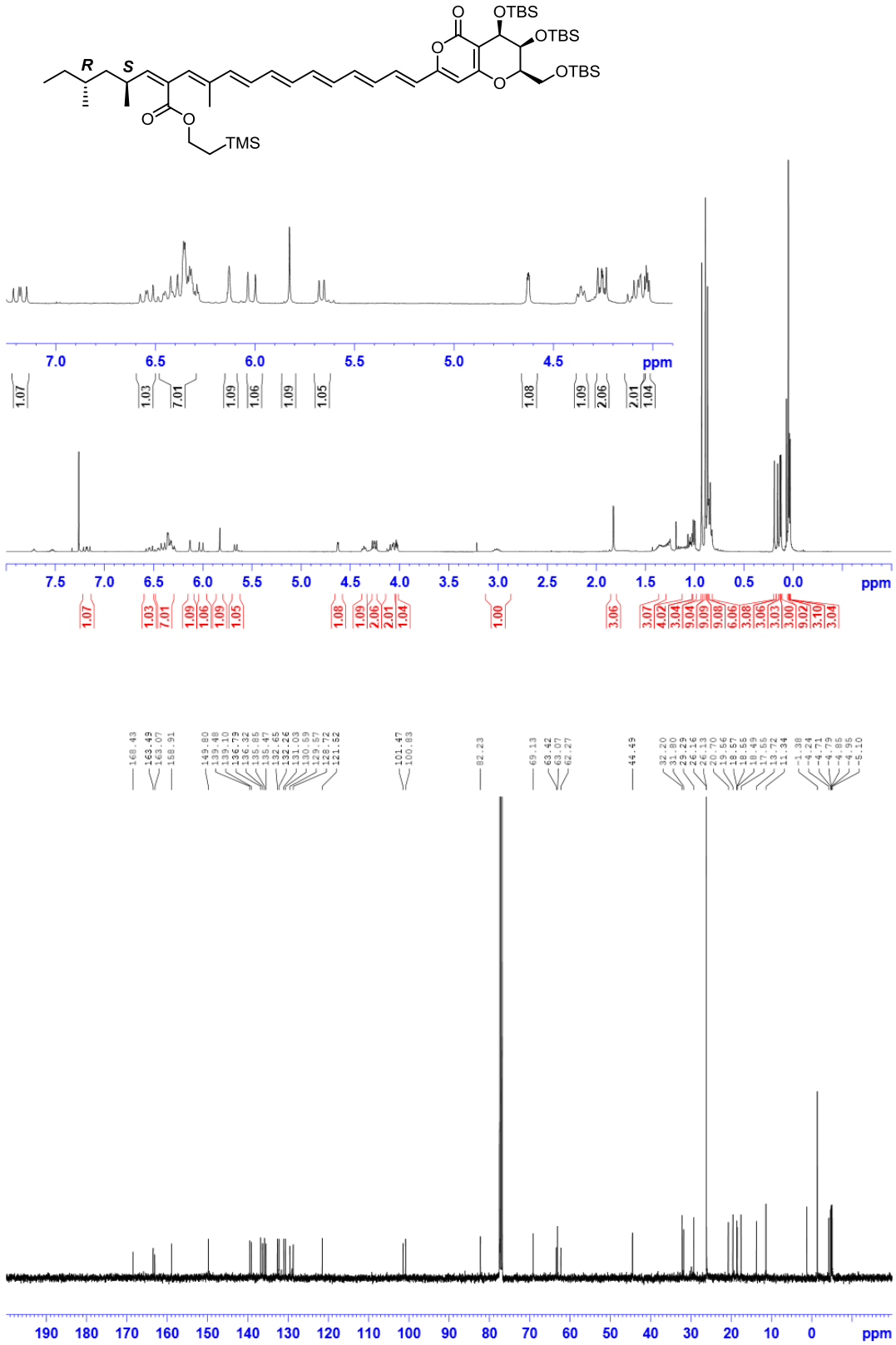
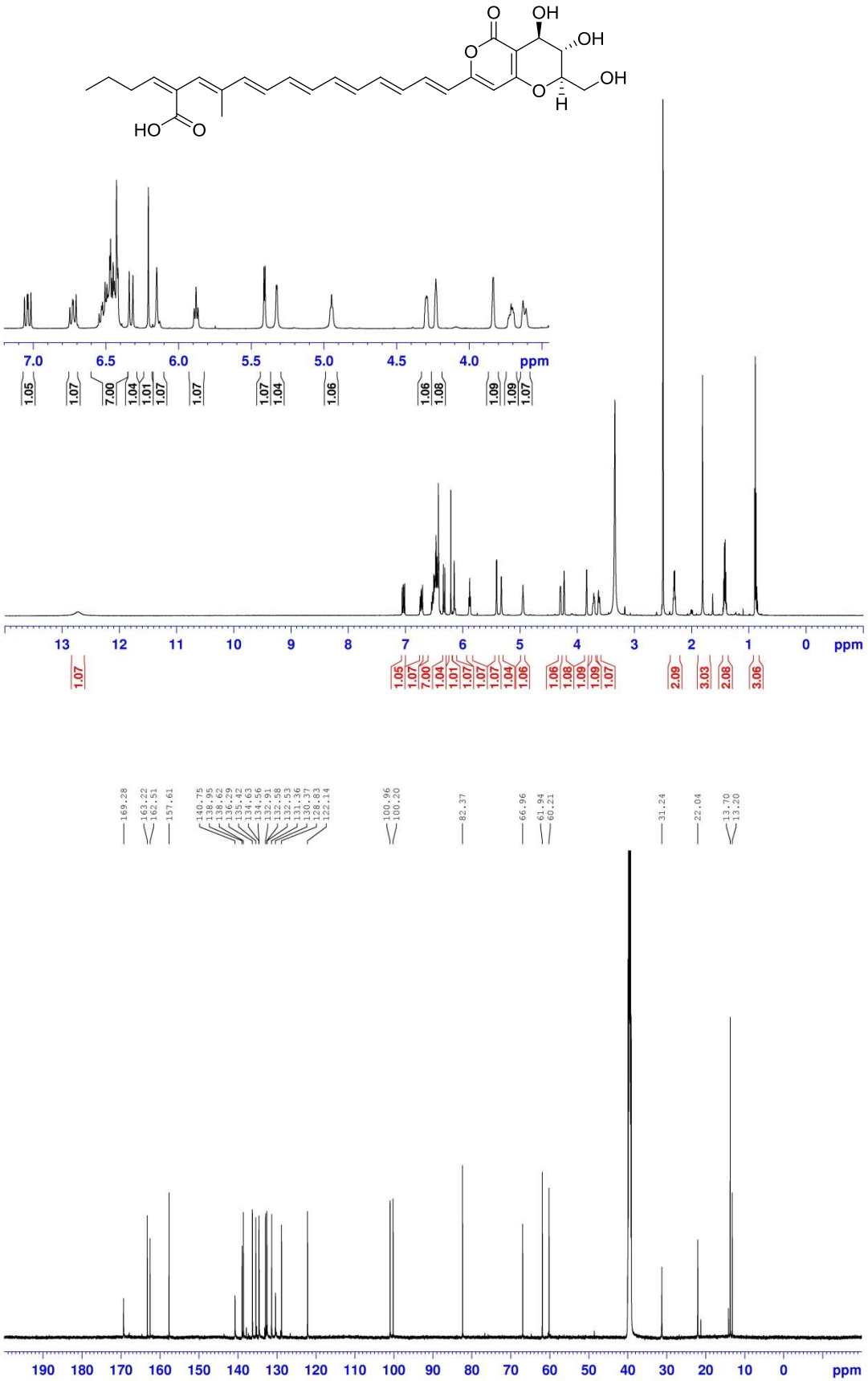
20
10
0
ppm


OTBS
OTBS
OTBS
R
S
TMS
ppm


O
OH
OH
OH
O
O
H
HO
O
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
1.05
1.07
7.00
1.04
1.01
1.07
1.07
1.07
1.04
1.06
1.06
1.08
1.09
1.09
1.07
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.07
1.05
1.07
7.00
1.04
1.01
1.07
1.07
1.07
1.04
1.06
1.06
1.08
1.09
1.09
1.07
2.09
3.03
2.08
3.06
169.28
163.22
162.51
157.61
140.75
138.95
138.62
136.29
135.42
134.63
134.56
132.91
132.58
132.53
131.36
130.37
128.83
122.14
100.96
100.20
82.37
66.96
61.94
60.21
31.24
22.04
13.70
13.20
190
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140
130
120
110
100
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80
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50
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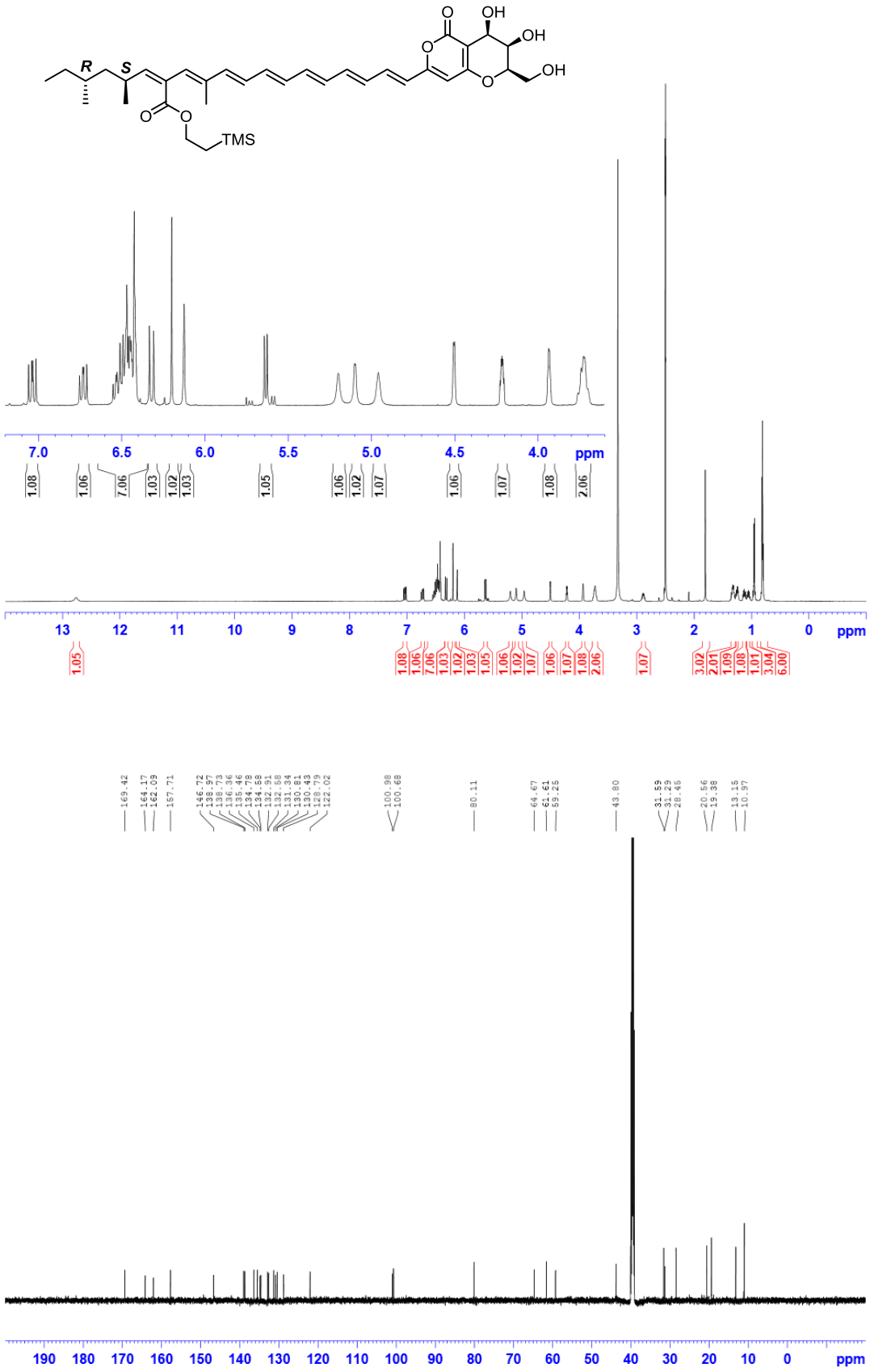
20
10
0
ppm


R
S
O
OH
OH
OH
O
O
O
O
TMS
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm