Supplementary Information

A general stereodivergent enantioselective total synthetic approach toward macrosphelides A-G, and M

Christine Häcker and Bernd Plietker*

Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany.
bernd.plietker@oc.uni-stuttgart.de

Table of contents

Comparison of NMR data for natural and synthetic macrosphelides

Supplementary Table 1. Comparison of NMR data for natural and synthetic macrosphelide D (in $CDCl_3$)

^{1}H: macrosphelide D (isolated)[1]	^{1}H: macrosphelide D (synthetic)	^{13}C: macrosphelide D (isolated)[1]	^{13}C: macrosphelide D (synthetic)
6.64 (dd, 1H) *J* = 15.8, 7.9 Hz	6.65 (dd, 1H) *J* = 15.8, 7.9 Hz	169.7	169.7
6.59 (dd, 1H) *J* = 15.8, 8.6 Hz	6.58 (dd, 1H) *J* = 16.0, 8.4 Hz	164.4	164.3
5.96 (d, 2H) *J* = 15.8 Hz	5.95 (*app*. d, 2H) *J* = 15.9 Hz	164.1	164.1
5.35 (m, 1H)	5.31-5.38 (m, 1H)	145.8	145.6
5.05 (dd, 1H) *J* = 8.6, 4.0 Hz	5.05 (*app.* dd, 1H) *J* = 8.5, 3.9 Hz	140.8	140.8
4.76 (dq, 1H) *J* = 7.9, 6.3 Hz	4.76 (dq, 1H) *J* = 8.2, 6.4 Hz	126.9	126.9
4.16 (dd, 1H) *J* = 8.6, 4.0 Hz	4.16 (*app*. t, 1H) *J* = 8.2 Hz	124.3	124.4
4.06 (dq, 1H) *J* = 6.6, 4.0 Hz	4.06 (dq, 1H) *J* = 6.1, 5.1 Hz	77.7	77.7
2.65 (dd, 1H) *J* = 13.5, 11.5 Hz	2.64 (dd, 1H) *J* = 13.7, 11.7 Hz	75.9	76.0
2.52 (dd, 1H) *J* = 13.5, 3.3 Hz	2.52 (dd, 1H) *J* = 13.8, 3.0 Hz	72.5	72.5
1.47 (d, 3H) *J* = 6.3 Hz	1.47 (d, 3H) *J* = 6.3 Hz	69.2	69.2
1.35 (d, 3H) *J* = 6.3 Hz	1.35 (d, 3H) *J* = 6.3 Hz	68.1	68.2
1.22 (d, 3H) *J* = 6.6 Hz	1.21 (d, 3H) *J* = 6.5 Hz	41.5	41.5
		20.2	20.2
		18.3	18.4
		17.8	17.8

Supplementary Table 2. Comparison of NMR data for natural and synthetic macrosphelide M (in d_6-acetone)

^{1}H: macrosphelide M (isolated)[2]	^{1}H: macrosphelide M (synthetic)	^{13}C: macrosphelide M (isolated)[2]	^{13}C: macrosphelide M (synthetic)
7.04 (dd, 1H) *J* = 15.8, 4.5 Hz	7.04 (dd, 1H) *J* = 15.6, 3.8 Hz	169.1	169.1
6.47 (dd, 1H) *J* = 15.2, 8.8 Hz	6.46 (dd, 1H) *J* = 15.8, 8.7 Hz	166.2	166.2
6.08 (dd, 1H) *J* = 15.8, 2.2	6.08 (dd, 1H) *J* = 15.6, 1.5 Hz	164.7	164.7
5.89 (dd, 1H) *J* = 15.2, 1.1 Hz	5.89 (*app.* d, 1H) *J* = 16.0 Hz	147.3	147.3
5.28 (ddq, 1H) *J* = 10.6, 6.0, 4.1 Hz	5.24-5.31 (m, 1H)	144.4	144.4
5.18 (ddd, 1H) *J* = 8.8, 5.5, 1.1 Hz	5.17 (*app*. dd, 1H) *J* = 8.5, 4.9 Hz	126.2	126.2
5.12 (dq, 1H) *J* = 6.2, 3.0 Hz	5.12 (dq, 1H) *J* = 6.8, 2.6 Hz	122.9	122.9
4.56 (d, 1H, OH) *J* = 4.9 Hz	4.57 (d, 1H, OH) *J* = 4.8 Hz	78.2	78.2
4.47 (bs, 1H)	4.45-4.48 (m, 1H)	75.2	75.2
4.17 (d, 1H, OH) *J* = 4.9 Hz	4.17 (d, 1H, OH) *J* = 5.3 Hz	75.1	75.1
3.90 (ddq, 1H) *J* = 6.0, 5.5, 4.9 Hz	3.90 (ddq, 1H) *J* = 5.9, 5.9, 5.8 Hz	69.0	69.0
2.89 (dd, 1H) *J* = 15.2, 4.1 Hz	2.89 (dd, 1H) *J* = 14.9, 3.9 Hz	68.5	68.5
2.51 (dd, 1H) *J* = 15.2, 10.6 Hz	2.50 (dd, 1H) *J* = 15.0, 10.2 Hz	42.1	42.1
1.39 (d, 3H) *J* = 6.2 Hz	1.38 (d, 3H) *J* = 6.8 Hz	20.1	20.1
1.36 (d, 3H) *J* = 6.0 Hz	1.35 (d, 3H) *J* = 6.3 Hz	19.1	19.1
1.14 (d, 3H) *J* = 6.0 Hz	1.13 (d, 3H) *J* = 6.4 Hz	18.0	17.9

Supplementary Table 3. Comparison of NMR data for natural and synthetic macrosphelide A (in $CDCl_3$)

^{1}H: macrosphelide A (isolated)[3]	^{1}H: macrosphelide A (synthetic)	^{13}C: macrosphelide A (isolated)[3]	^{13}C: macrosphelide A (synthetic)
6.88 (dd, 1H) *J* = 15.5, 3.3 Hz	6.87 (dd, 1H) *J* = 15.7, 4.6 Hz	170.2	170.2
6.87 (dd, 1H) *J* = 15.5, 3.3 Hz	6.87 (dd, 1H) *J* = 15.7, 4.8 Hz	165.8	165.8
6.04 (dd, 1H) *J* = 15.5, 1.5 Hz	6.05 (dd, 1H) *J* = 15.8, 1.1 Hz	164.7	164.6
6.03 (dd, 1H) *J* = 15.5, 1.8 Hz	6.04 (dd, 1H) *J* = 15.7, 1.4 Hz	146.2	146.0
5.38 (m, 1H)	5.36-5.42 (m, 1H)	145.2	145.0
4.97 (q, 1H) *J* = 6.6 Hz	4.96 (dq, 1H) *J* = 6.4, 4.8 Hz	122.7	122.7
4.86 (q, 1H) *J* = 6.6 Hz	4.86 (dq, 1H) *J* = 6.5, 6.5 Hz	122.2	122.3
4.25 (bs, 1H)	4.22-4.24 (m, 1H)	74.8	75.0
4.13 (bs, 1H)	4.13-4.15 (m, 1H)	74.7	74.8
3.15 (bs, 1H, OH)	2.92 (bs, 1H, OH)	73.9	74.1
2.60 (dd, 2H) *J* = 8.3, 4.3 Hz	2.62 (dd, 1H) *J* = 15.6, 9.1 Hz	73.0	73.1
	2.57 (dd, 1H) *J* = 15.5, 3.3 Hz	67.7	67.7
2.85 (bs, 1H, OH)	1.64 (bs, 1H, OH)	40.9	41.0
1.45 (d, 3H) *J* = 6.6 Hz	1.45 (d, 3H) *J* = 6.6 Hz	19.6	19.7
1.37 (d, 3H) *J* = 6.6 Hz	1.37 (d, 3H) *J* = 6.4 Hz	17.9	18.0
1.33 (d, 3H) *J* = 6.3 Hz	1.33 (d, 3H) *J* = 6.4 Hz	17.8	17.8

Supplementary Table 4. Comparison of NMR data for natural and synthetic macrosphelide C (in $CDCl_3$)

^{1}H: macrosphelide C (isolated)[1]	^{1}H: macrosphelide C (synthetic)	^{13}C: macrosphelide C (isolated)[1]	^{13}C: macrosphelide C (synthetic)
6.89 (dd, 1H) *J* = 15.5, 4.8 Hz	6.89 (dd, 1H) *J* = 15.7, 4.9 Hz	170.0	170.0
6.85 (ddd, 1H) *J* = 15.5, 9.5, 6.5 Hz	6.86 (ddd, 1H) *J* = 15.6, 9.2, 6.3 Hz	165.0	165.0
6.06 (dd, 1H) *J* = 15.5, 2.0 Hz	6.06 (dd, 1H) *J* = 15.7, 1.6 Hz	164.8	164.8
5.80 (ddd, 1H) *J* = 15.5, 1.5, 1.5 Hz	5.80 (*app*. d, 1H) *J* = 15.7 Hz	144.9	144.9
5.30 (m, 1H)	5.27-5.33 (m, 1H)	143.8	143.8
5.10 (m, 1H)	5.07-5.13 (m, 1H)	124.7	124.7
4.92 (dq, 1H) *J* = 6.5, 4.8 Hz	4.92 (dq, 1H) *J* = 6.4, 6.4 Hz	123.0	123.0
4.16 (dd, 1H) *J* = 4.8, 4.8 Hz	4.16 (*app*. dd, 1H) *J* = 5.1, 5.1 Hz	73.7	73.7
2.63 (dd, 1H) *J* = 14.5, 3.0 Hz	2.63 (dd, 1H) *J* = 14.7, 2.9 Hz	72.9	72.9
2.55 (m, 1H)	2.52-2.57 (m, 1H)	69.0	69.0
2.51 (dd, 1H) *J* = 14.5, 8.5 Hz	2.51 (dd, 1H) *J* = 14.7, 8.4 Hz	67.4	67.4
2.36 (dddd, 1H) *J* = 13.9, 10.1, 9.5, 1.5 Hz	2.33-2.40 (m, 1H)	40.9	40.9
	2.06 (bs, 1H, OH)	38.8	38.8
1.38 (d, 3H) *J* = 5.5 Hz	1.37 (d, 3H) *J* = 6.7 Hz	20.5	20.5
1.36 (d, 3H) *J* = 6.3 Hz	1.36 (d, 3H) *J* = 6.6 Hz	19.5	19.5
1.33 (d, 3H) *J* = 5.5 Hz	1.33 (d, 3H) *J* = 6.5 Hz	17.5	17.5

Supplementary Table 5. Comparison of NMR data for natural and synthetic macrosphelide E (in $CDCl_3$)

^{1}H: macrosphelide E (isolated)[4]	^{1}H: macrosphelide E (synthetic)	^{13}C: macrosphelide E (isolated)[4]	^{13}C: macrosphelide E (synthetic)
7.03 (dd, 1H) *J* = 15.7, 4.2 Hz	7.02 (dd, 1H) *J* = 15.6, 4.2 Hz	170.8	170.9
6.81 (dd, 1H) *J* = 15.6, 5.3 Hz	6.80 (dd, 1H) *J* = 15.7, 5.1 Hz	166.5	166.8
6.12 (dd, 1H) *J* = 15.7, 1.5 Hz	6.11 (dd, 1H) *J* = 15.7, 1.3 Hz	165.4	165.3
6.04 (dd, 1H) *J* = 15.6, 1.5 Hz	6.07 (dd, 1H) *J* = 15.7, 1.2 Hz	145.5	145.4
5.31 (ddq, 1H) *J* = 7.0, 6.5, 3.3 Hz	5.29-5.35 (m, 1H)	145.2	145.0
5.11 (dq, 1H) *J* = 6.8, 2.0 Hz	5.12 (dq, 1H) *J* = 6.8, 1.7 Hz	123.0	123.0
4.97 (dq, 1H) *J* = 6.5, 5.3 Hz	4.98 (dq, 1H) *J* = 6.5, 4.4 Hz	122.4	122.3
4.37 (bs, 1H)	4.36-4.38 (m, 1H)	75.7	76.1
4.16 (bdt) *J* = 7.1, 5.3 Hz	4.18-4.19 (m, 1H)	75.0	75.4
3.59 (d, 1H, OH) *J* = 7.3 Hz	3.37 (d, 1H, OH) *J* = 6.7 Hz	74.9	75.2
3.36 (d, 1H, OH) *J* = 7.1 Hz	3.09 (d, 1H, OH) *J* = 5.4 Hz	73.6	73.8
2.75 (dd, 1H) *J* = 15.8, 3.3 Hz	2.72 (dd, 1H) *J* = 16.0, 3.0 Hz	66.8	66.6
2.58 (dd, 1H) *J* = 15.8, 7.0 Hz	2.60 (dd, 1H) *J* = 16.0, 7.5 Hz	40.4	40.5
1.41 (d, 3H) *J* = 6.8 Hz	1.43 (d, 3H) *J* = 6.8 Hz	19.5	19.6
1.40 (d, 3H) *J* = 6.5 Hz	1.39 (d, 3H) *J* = 6.5 Hz	17.6	17.8
1.30 (d, 3H) *J* = 6.5 Hz	1.32 (d, 3H) *J* = 6.6 Hz	17.3	17.3

Supplementary Table 6. Comparison of NMR data for natural and synthetic macrosphelide F (in $CDCl_3$)

^{1}H: macrosphelide F (isolated)[4]	^{1}H: macrosphelide F (synthetic)	^{13}C: macrosphelide F (isolated)[4]	^{13}C: macrosphelide F (synthetic)
6.88 (dt, 1H) *J* = 15.7, 7.5 Hz	6.88 (dt, 1H) *J* = 14.9, 7.4 Hz	170.8	171.0
6.85 (dd, 1H) *J* = 15.6, 4.2 Hz	6.84 (dd, 1H) *J* = 15.6, 4.3 Hz	165.1	165.1
6.09 (dd, 1H) *J* = 15.6, 1.9 Hz	6.09 (dd, 1H) *J* = 15.5, 1.7 Hz	164.9	165.0
5.79 (dd, 1H) *J* = 15.7, 1.8 Hz	5.80 (*app*. d, 1H) *J* = 15.8 Hz	144.1	144.2
5.30 (ddq, 1H) *J* = 7.5, 6.5, 3.3 Hz	5.27-5.33 (m, 1H)	143.4	143.6
5.14 (ddq, 1H) *J* = 7.5, 6.4, 5.0 Hz	5.12-5.18 (m, 1H)	124.6	124.7
4.96 (dq, 1H) *J* = 6.6, 3.7 Hz	4.94 (dq, 1H) *J* = 6.5, 3.9 Hz	123.0	123.1
4.21 (dddd, 1H) *J* = 7.7, 4.2, 3.7, 1.9 Hz	4.19-4.23 (m, 1H)	76.0	76.0
2.91 (d, 1H, OH) *J* = 7.7 Hz	2.98 (d, 1H, OH) *J* = 7.6 Hz	73.6	73.6
2.70 (dddd, 1H) *J* = 14.6, 7.5, 5.0, 1.8 Hz	2.69-2.74 (m, 1H)	68.9	68.9
2.66 (dd, 1H) *J* = 15.8, 3.3 Hz	2.67 (dd, 1H) *J* = 15.9, 2.9 Hz	66.5	66.5
2.58 (dd, 1H) *J* = 15.8, 7.5 Hz	2.59 (dd, 1H) *J* = 15.8, 7.8 Hz	40.7	40.7
2.41 (dt, 1H) *J* = 14.6, 7.5 Hz	2.39 (ddd, 1H) *J* = 14.5, 7.2, 7.2 Hz	37.7	37.7
1.39 (d, 3H) *J* = 6.4 Hz	1.39 (d, 3H) *J* = 6.4 Hz	19.9	19.8
1.35 (d, 3H) *J* = 6.5 Hz	1.36 (d, 3H) *J* = 6.5 Hz	19.8	19.7
1.31 (d, 3H) *J* = 6.6 Hz	1.31 (d, 3H) *J* = 6.5 Hz	17.5	17.4

Supplementary Table 7. Comparison of ^{1}H-NMR data for natural and synthetic macrosphelide G (in $CDCl_3$)

^{1}H: macrosphelide G (isolated)[4]	^{1}H: macrosphelide G (isolated)[5]	^{1}H: macrosphelide G (synthetic)[6]	^{1}H: macrosphelide G (synthetic)
7.00 (dd, 1H) *J* = 15.7, 3.9 Hz	7.05 (dd, 1H) *J* = 15.7, 3.9 Hz	7.05 (dd, 1H) *J* = 15.3, 3.7 Hz	7.05 (dd, 1H) *J* = 15.6, 3.7 Hz
6.78 (dt, 1H) *J* = 15.6, 7.6 Hz	6.80 (ddd, 1H) *J* =15.6, 9.3, 6.2 Hz	6.80 (ddd, 1H) J = 15.3, 8.5, 6.1 Hz	6.80 (ddd, 1H) *J* = 15.3, 8.7, 6.3 Hz
6.11 (dd, 1H) *J* = 15.7, 1.6 Hz	6.11 (dd, 1H) *J* =15.7, 1.6 Hz	6.11 (dd, 1H) *J* = 15.9, 1.8 Hz	6.11 (dd, 1H) *J* = 15.5, 1.6 Hz
5.80 (d, 1H) *J* = 15.6 Hz	5.80 (dt, 1H) *J* = 15.6, 1.5 Hz	5.80 (dt, 1H) *J* = 15.8, 1.2 Hz	5.80 (dt, 1H) *J* = 15.6, 1.3 Hz
5.21 (ddq, 1H) *J* = 6.6, 6.1, 3.9 Hz	5.20 (d quint) *J* = 6.6, 3.9 Hz	5.24 (d quint, 1H) *J* = 6.7, 4.3 Hz	5.21-5.27 (m, 1H)
5.05 (m, 1H)	5.09 (m, 1H)	5.09 (m, 1H)	5.05-5.11 (m, 2H)
5.03 (m, 1H)	5.08 (m, 1H)	5.08 (m, 1H)	
4.33 (bs, 1H)	4.36 (bs, 1H)	4.35 (bs, 1H)	4.34-4.37 (m, 1H)
3.38 (bs, 1H, OH)	3.41 (bs, 1H, OH)	3.32 (bs, 1H, OH)	3.37 (d, 1H, OH) *J* = 8.2 Hz
2.70 (dd, 1H) *J* = 15.7, 3.9 Hz	2.76 (dd, 1H) *J* = 15.7, 3.9 Hz	2.76 (dd, 1H) *J* = 15.3, 3.7 Hz	2.76 (dd, 1H) *J* = 15.7, 3.9 Hz
2.51 (dd, 1H) *J* = 15.7, 6.1 Hz	2.51 (dd, 1H) *J* = 15.7, 6.6 Hz	2.50 (dd, 1H) *J* = 15.3, 6.1 Hz	2.35-2.53 (m, 3H)
2.47 (m, 1H)	2.50 (m, 1H)	2.28–2.42 (m, 2H)	
2.38 (m, 1H)	2.39 (ddt, 1H) *J* = 15.2, 9.3, 1.5 Hz		
1.42 (d, 3H) *J* = 6.6 Hz	1.41 (d, 3H) *J* = 6.8 Hz	1.44 (d, 3H) *J* = 6.4 Hz	1.45 (d, 3H) *J* = 6.5 Hz
1.37 (d, 3H) *J* = 6.8 Hz	1.26 (d, 3H) *J* = 6.4 Hz	1.40 (d, 3H) *J* = 6.7 Hz	1.41 (d, 3H) *J* = 6.9 Hz
1.22 (d, 3H) *J* = 6.4 Hz	1.16 (d, 3H) *J* = 6.6 Hz	1.26 (d, 3H) *J* = 6.8 Hz	1.26 (d, 3H) *J* = 6.3 Hz

Supplementary Table 8. Comparison of ^{13}C-NMR data for natural and synthetic macrosphelide G (in $CDCl_3$)

^{13}C: macrosphelide G (isolated)[4]	^{13}C: macrosphelide G (isolated)[5]	^{13}C: macrosphelide G (synthetic)[6]	^{13}C: macrosphelide G (synthetic)
169.2	169	169	169.4
166.9	167	167	167.1
165.3	165	165	165.5
145.3	145	145	145.5
145.3	145		145.5
123.3	123	123	123.4
121.8	122	122	121.9
76.4	76.4	76.4	76.4
75.3	75.3	75.3	75.3
70.0	70	70	70.0
67.2	67.2	67.2	67.2
40.0	40	40.0	39.9
38.3	38.3	38.3	38.3
20.3	20.3	20.3	20.2
19.3	19.3	19.3	19.2
17.9	17.9	17.9	17.8

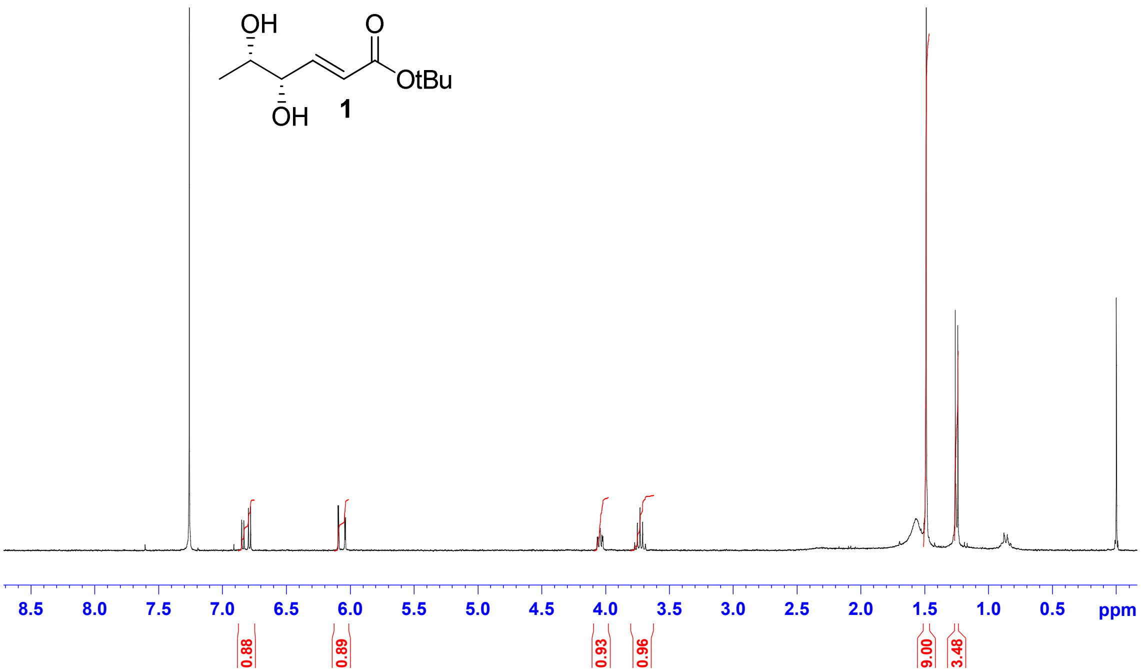
For isolated macrosphelide G different ^{1}H-data was found in literature.[4,5] Both are included in supplementary table 1. Both isolated ^{1}H-data show differences to the synthetical macrosphelide G reported from Sharma[6], which matches with the data reported in this work. Nevertheless, ^{13}C data of both, synthetical and isolated macrosphelide G, are in good accordance.

Supplementary Table 9. Comparison of NMR data for natural and synthetic macrosphelide B (in $CDCl_3$)

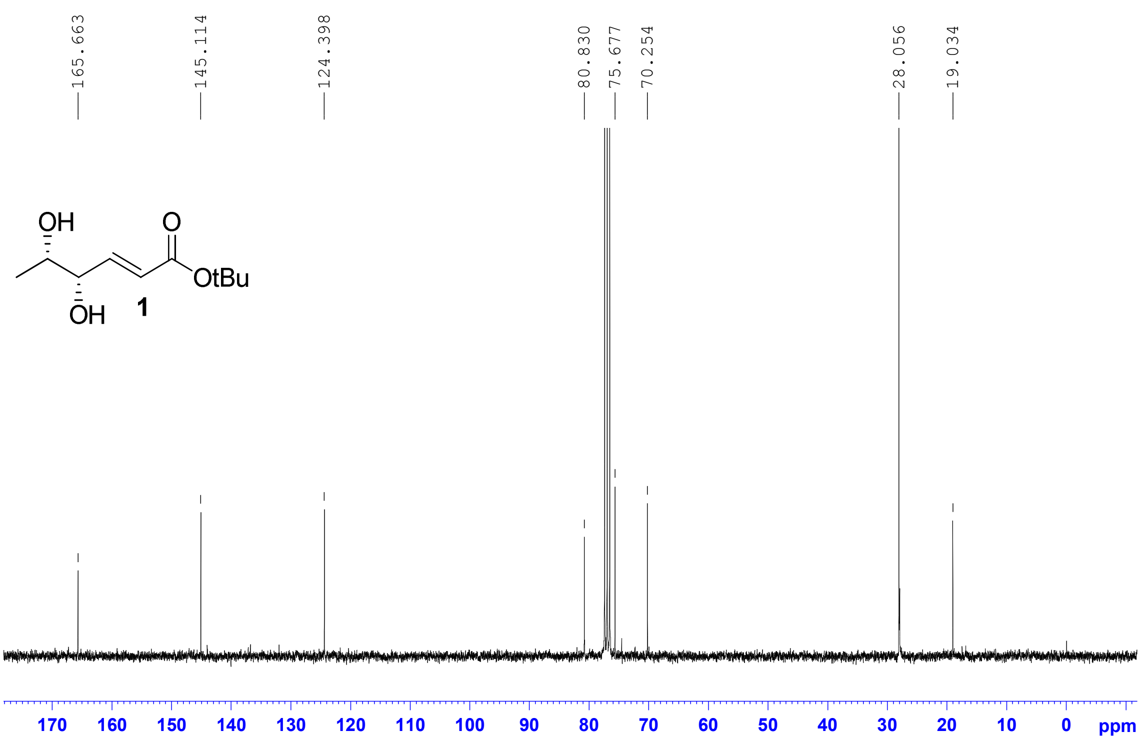
^{1}H: macrosphelide B (isolated)[3]	^{1}H: macrosphelide B (synthetic)	^{13}C: macrosphelide B (isolated)[3]	^{13}C: macrosphelide B (synthetic)
7.03 (d, 1H) *J* = 15.8 Hz	7.03 (d, 1H) *J* = 15.8 Hz	196.2	196.2
6.94 (dd, 1H) *J* = 15.8, 3.6 Hz	6.92 (dd, 1H) *J* = 15.7, 3.5 Hz	170.4	170.3
6.73 (d, 1H) *J* = 15.8 Hz	6.74 (d, 1H) *J* = 15.8 Hz	165.2	165.4
6.08 (dd, 1H) *J* = 15.8, 3.0 Hz	6.09 (dd, 1H) *J* = 15.7, 2.0 Hz	164.3	164.1
5.45 (m, 1H)	5.44-5.50 (m, 1H)	144.5	144.2
5.08 (m, 1H)	5.05-5.10 (m, 1H)	132.6	132.5
5.08 (m, 1H)	5.06 (q, 1H) *J* = 7.1 Hz	132.1	132.1
4.32 (bs, 1H)	4.31-4.34 (m, 1H)	122.4	122.6
3.44 (bs, 1H, OH)	2.86 (d, 1H, OH) *J* = 8.3 Hz	76.5	76.9
2.83 (dd, 1H) *J* = 16.2, 10.9 Hz	2.83 (dd, 1H) *J* = 16.2, 11.1 Hz	75.7	75.8
2.64 (dd, 1H) *J* = 16.2, 3.0 Hz	2.62 (dd, 1H) *J* = 16.2, 2.1 Hz	74.6	74.9
1.49 (d, 3H) *J* = 6.6 Hz	1.50 (d, 3H) *J* = 6.8 Hz	67.7	67.7
1.43 (d, 3H) *J* = 6.9 Hz	1.44 (d, 3H) *J* = 7.0 Hz	40.6	40.6
1.36 (d, 3H) *J* = 6.6 Hz	1.36 (d, 3H) *J* = 6.4 Hz	19.7	19.8
		17.8	17.9
		16.0	16.1

NMR-Spectra of compounds 1-24

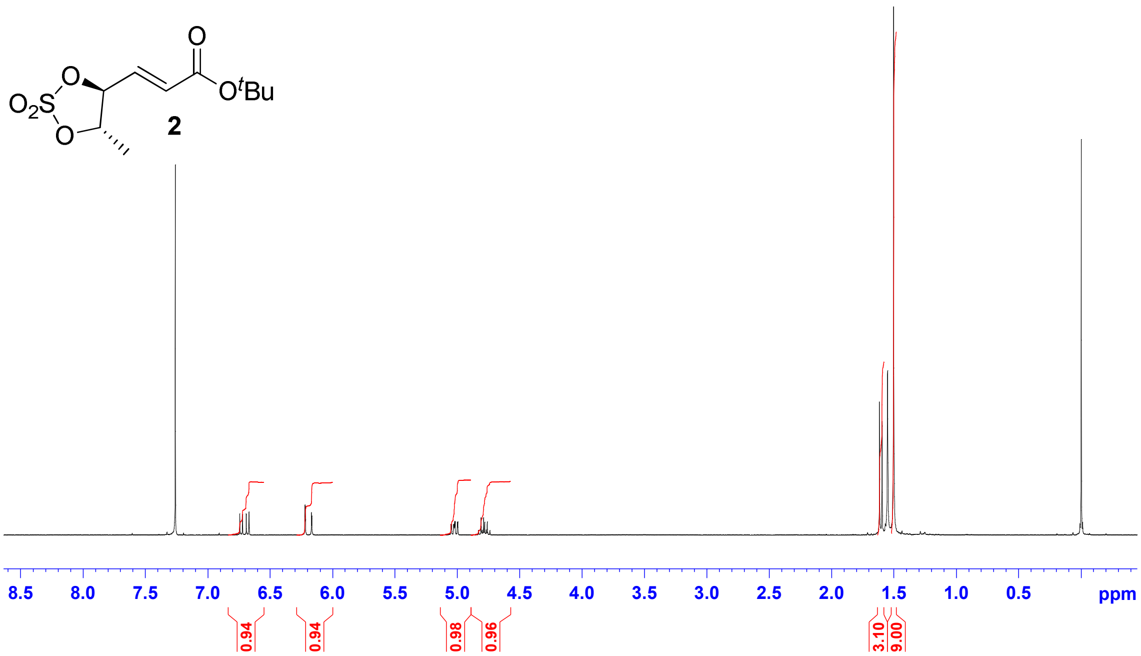
Supplementary Figure 1. ^{1}H NMR spectrum of compound **1**



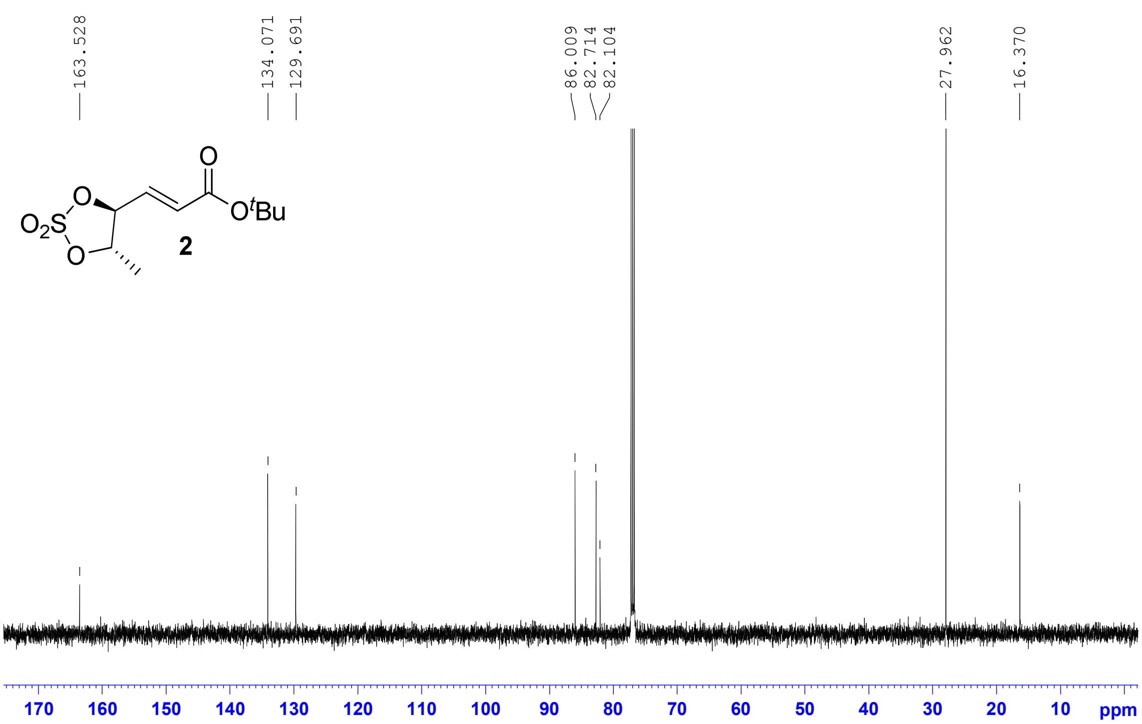
Supplementary Figure 2. ^{13}C NMR spectrum of compound **1**



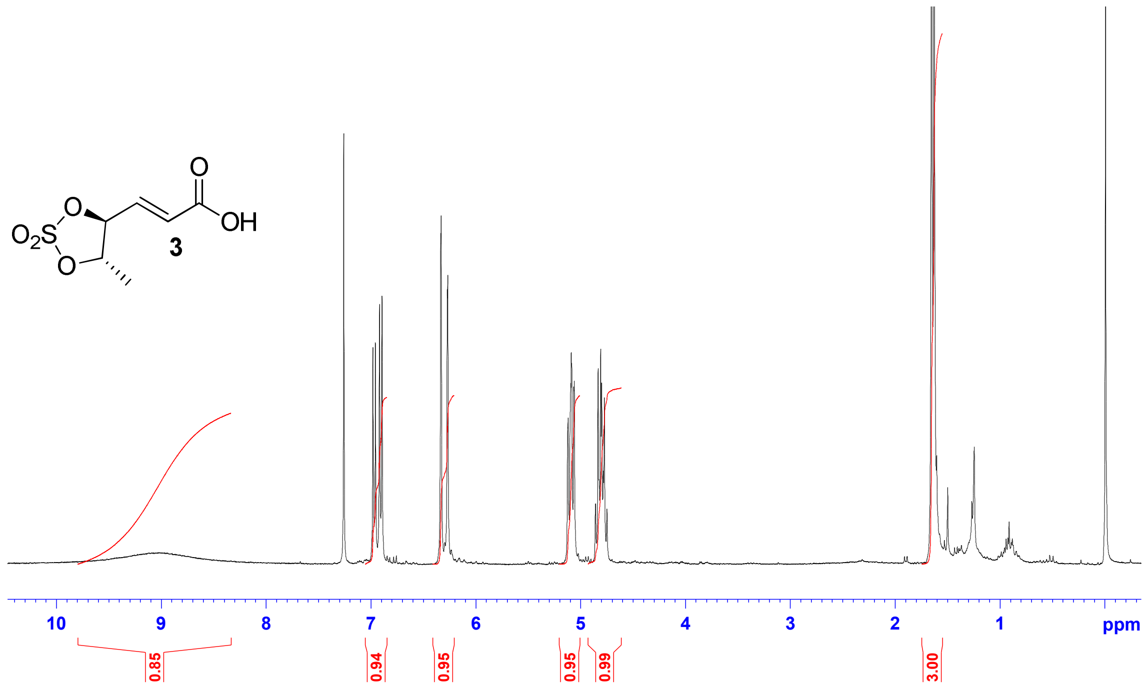
Supplementary Figure 3. ^{1}H NMR spectrum of compound **2**



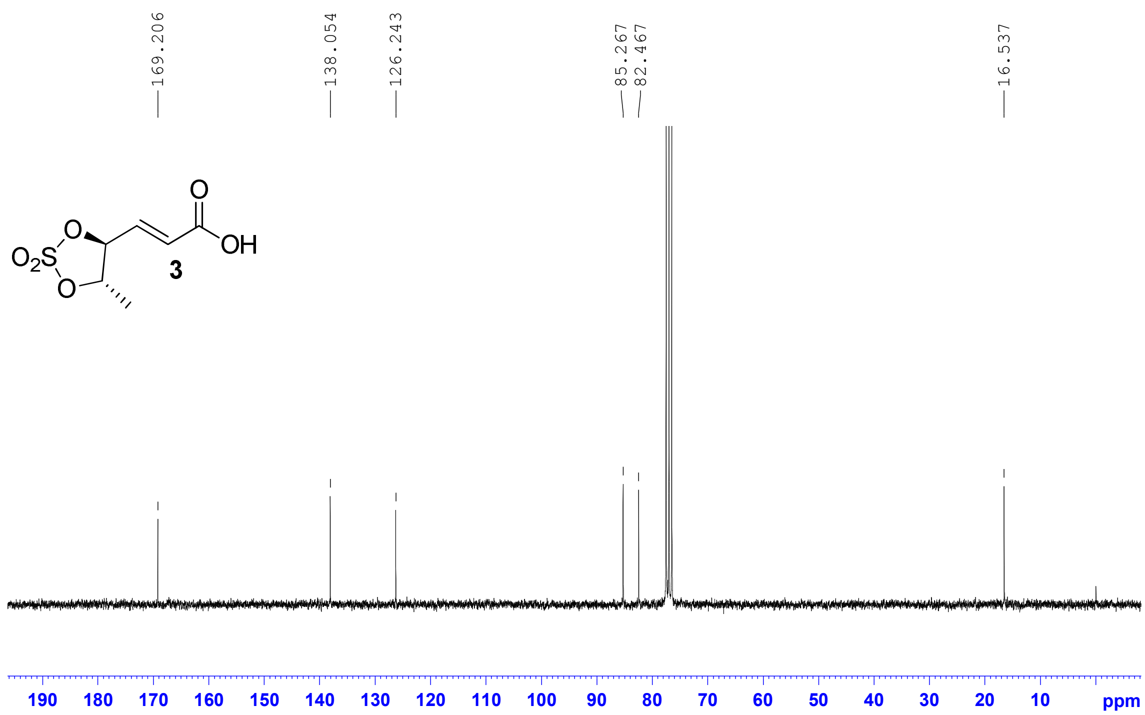
Supplementary Figure 4. ^{13}C NMR spectrum of compound **2**



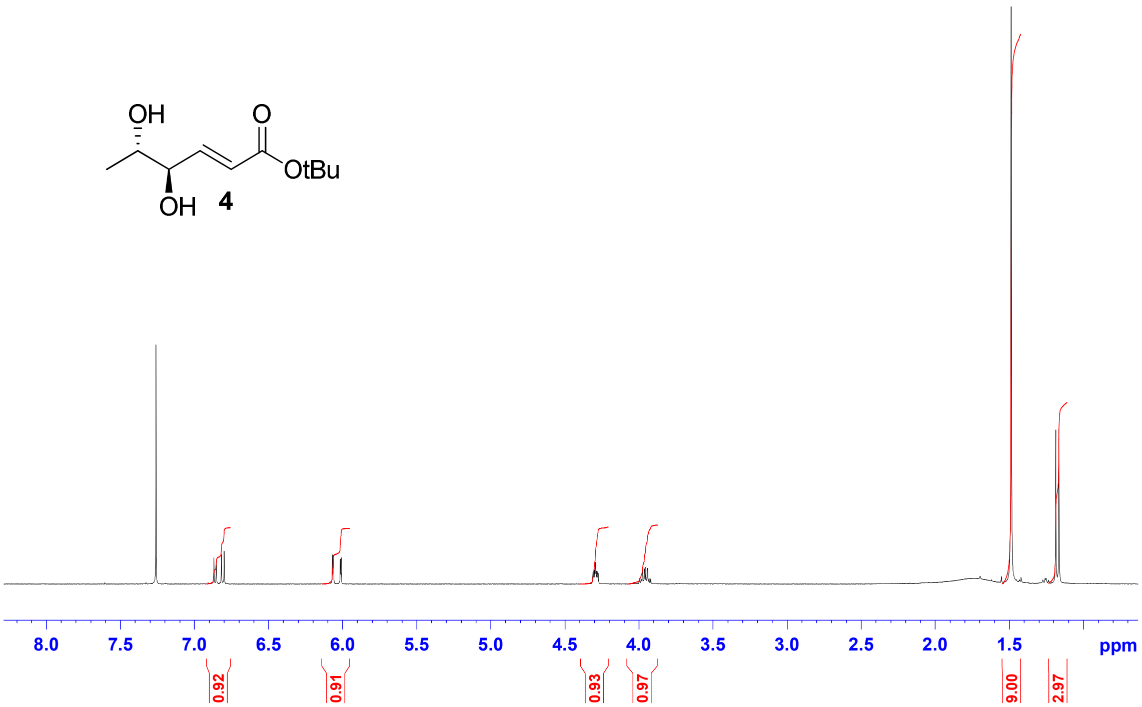
Supplementary Figure 5. ^{1}H NMR spectrum of compound **3**



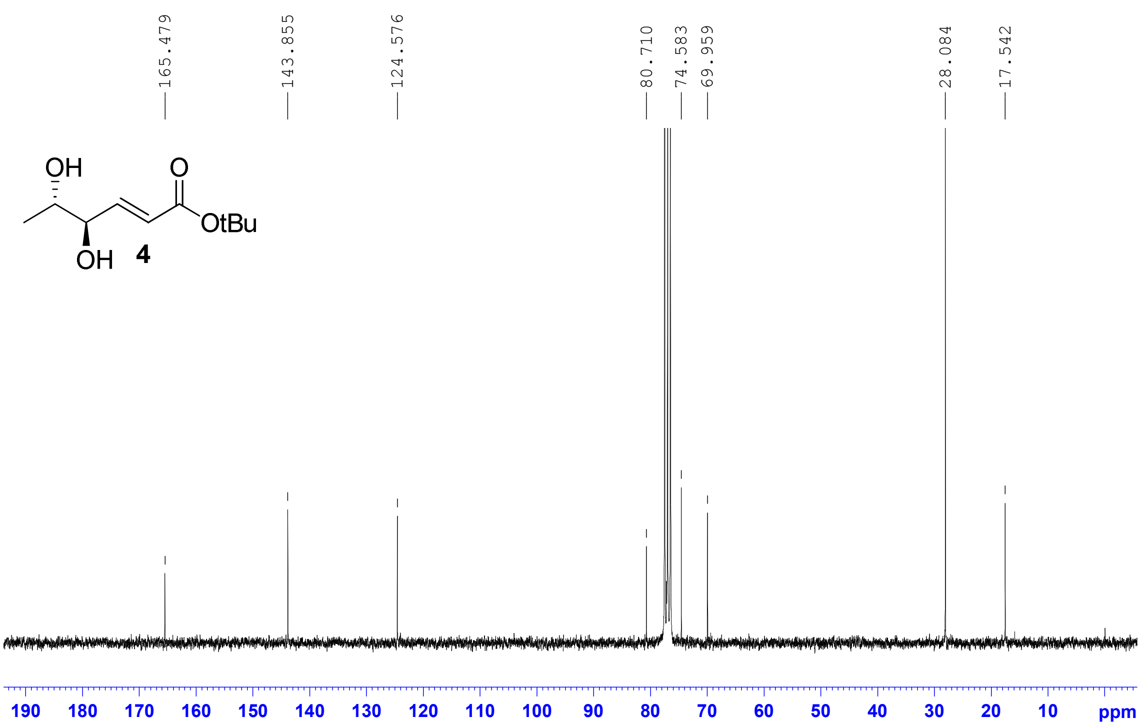
Supplementary Figure 6. ^{13}C NMR spectrum of compound **3**



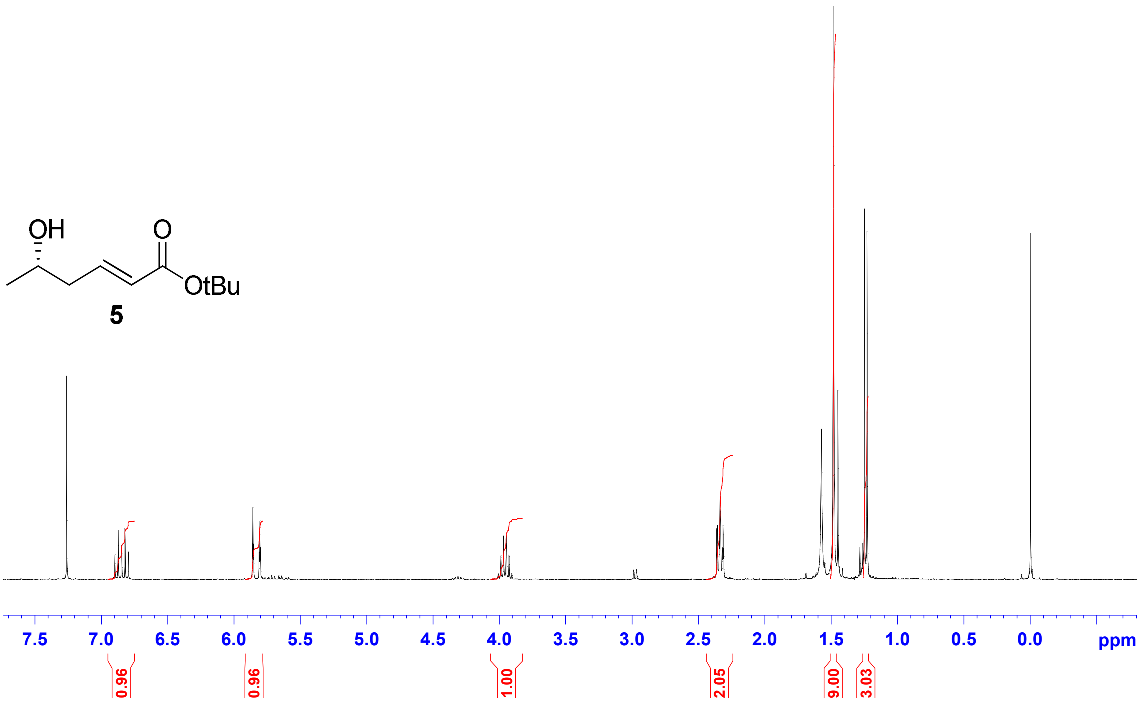
Supplementary Figure 7. ^{1}H NMR spectrum of compound **4**



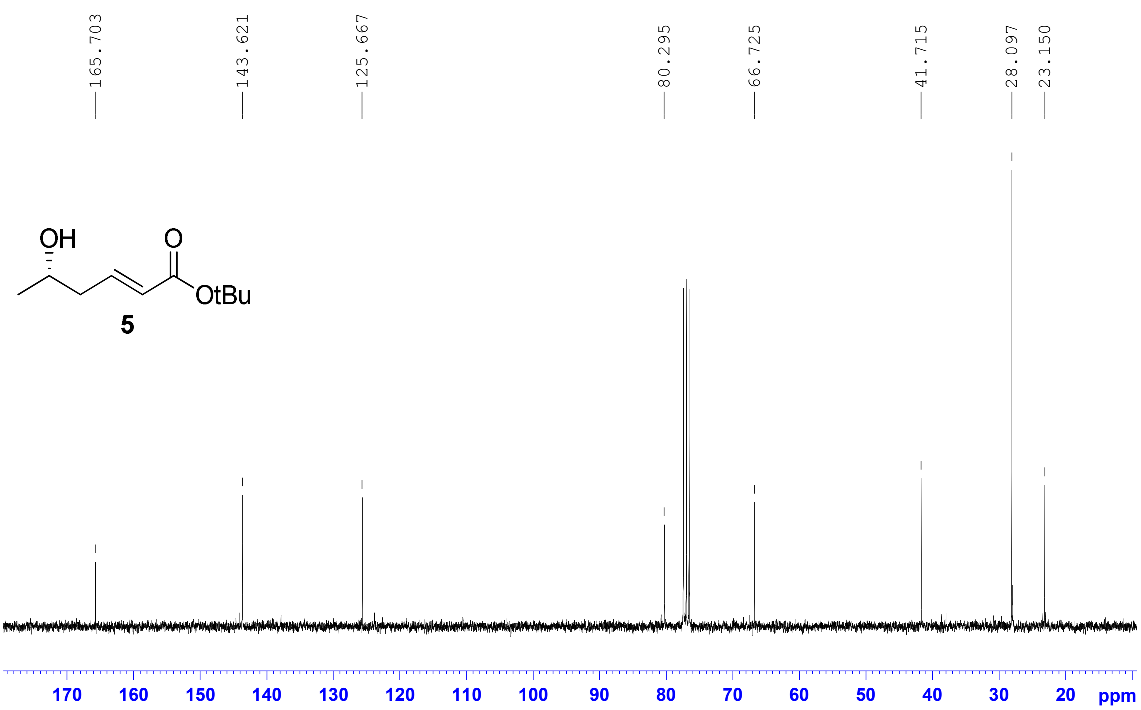
Supplementary Figure 8. ^{13}C NMR spectrum of compound **4**



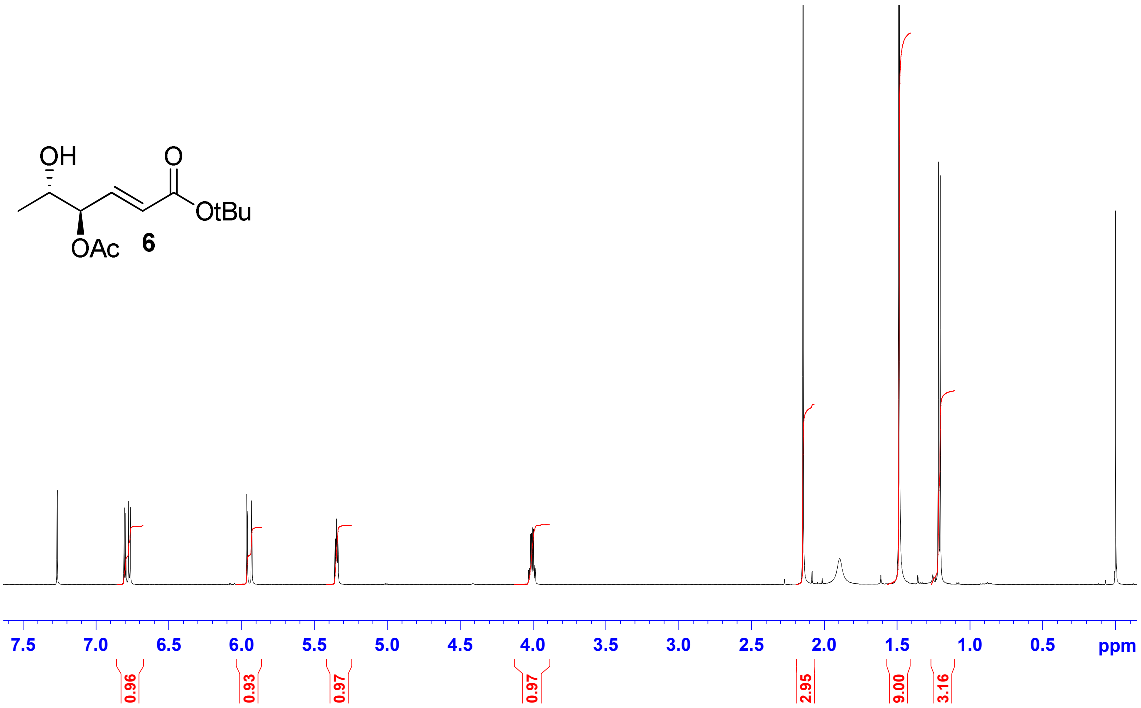
Supplementary Figure 9. ^{1}H NMR spectrum of compound **5**



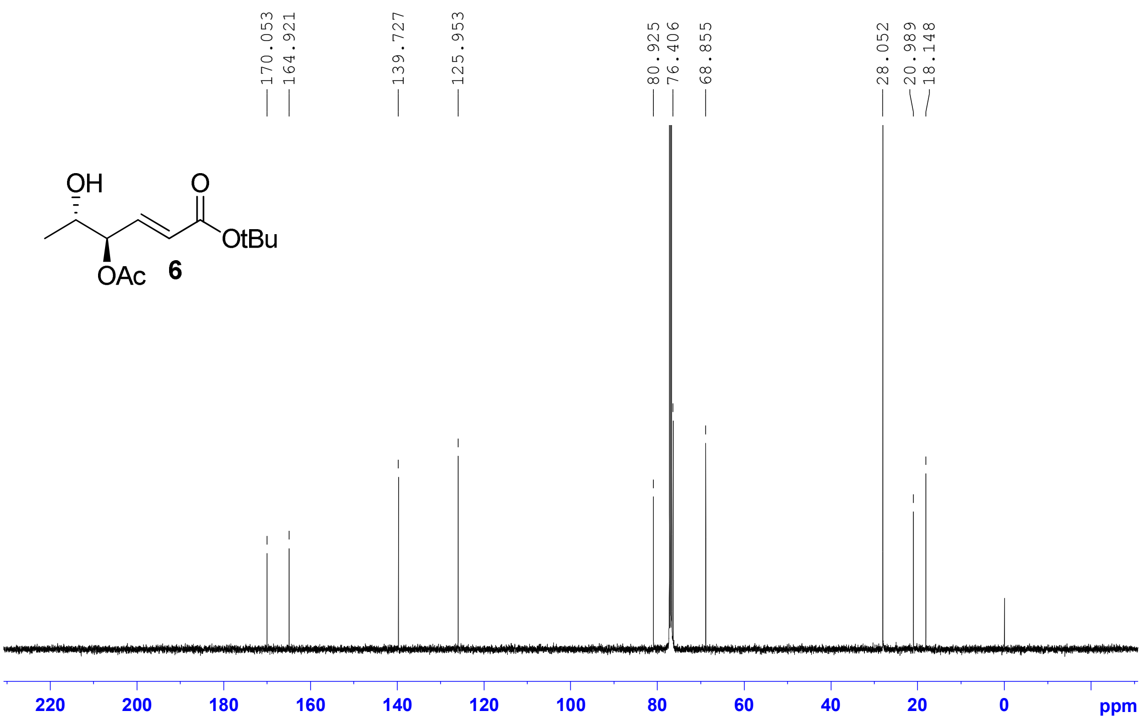
Supplementary Figure 10. ^{13}C NMR spectrum of compound **5**



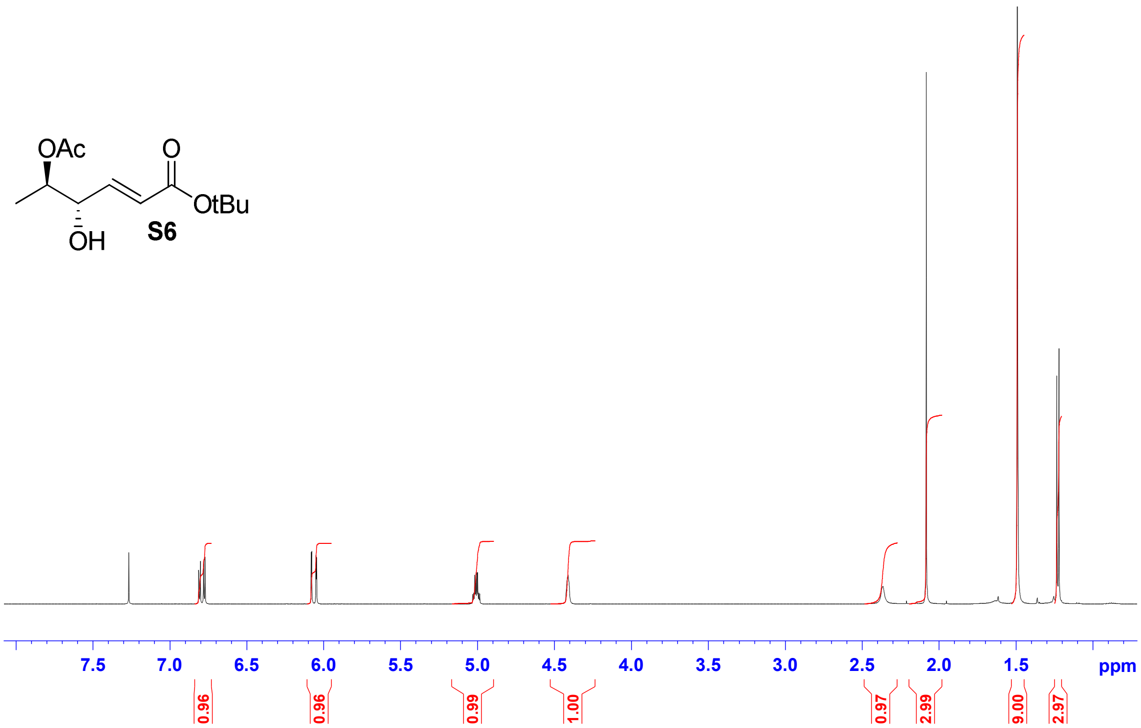
Supplementary Figure 11. ^{1}H NMR spectrum of compound **6**



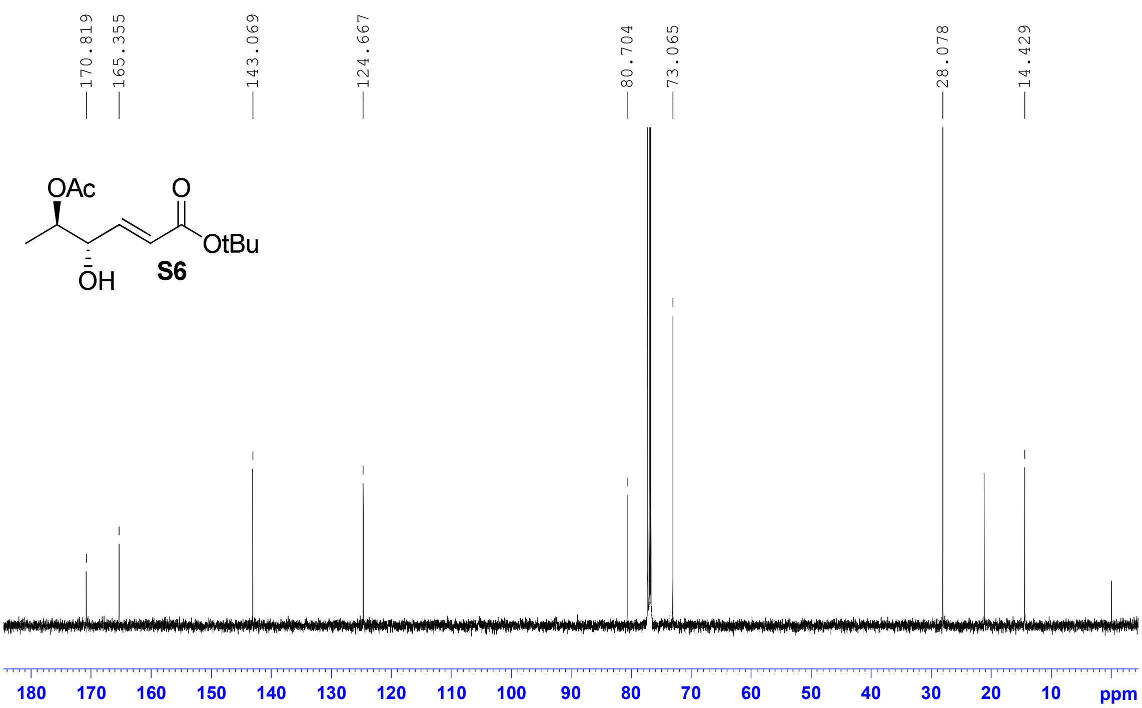
Supplementary Figure 12. ^{13}C NMR spectrum of compound **6**



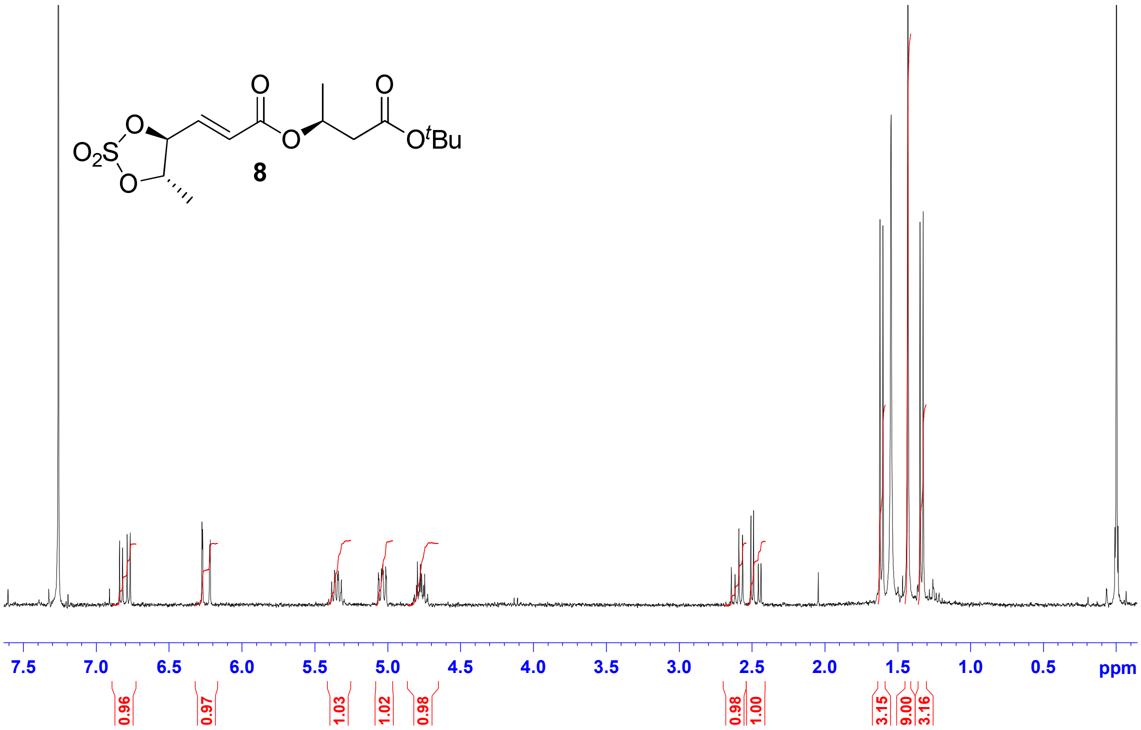
Supplementary Figure 13. ^{1}H NMR spectrum of compound **S6**



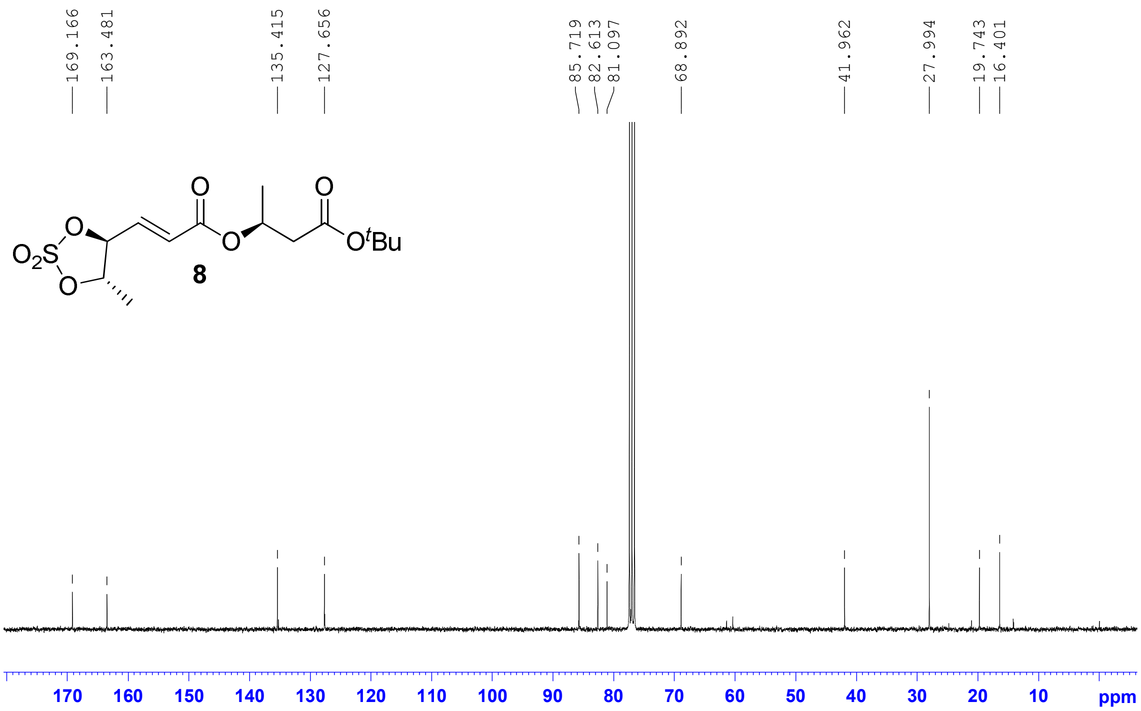
Supplementary Figure 14. ^{13}C NMR spectrum of compound **S6**



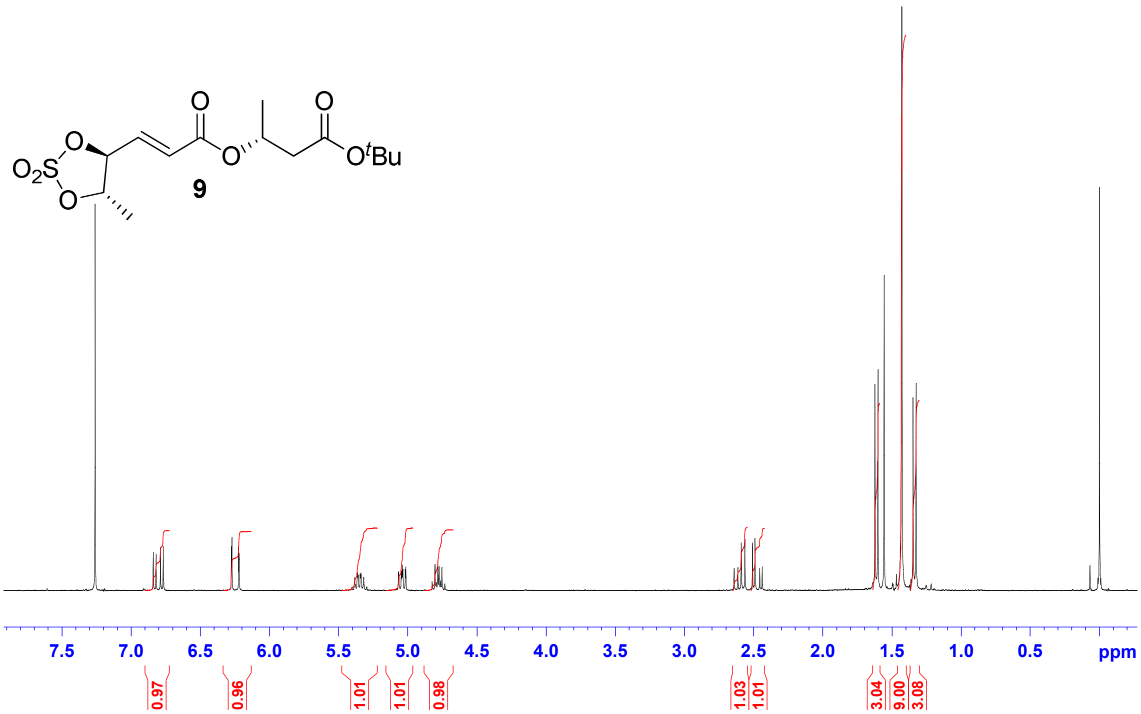
Supplementary Figure 15. ^{1}H NMR spectrum of compound **8**



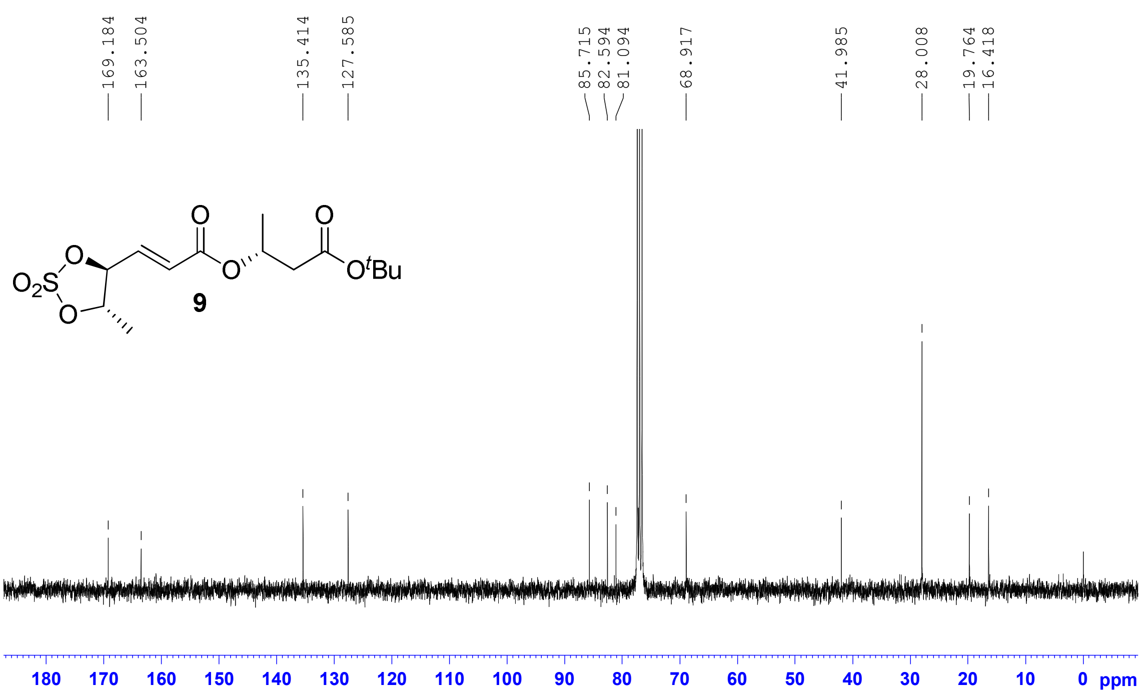
Supplementary Figure 16. ^{13}C NMR spectrum of compound **8**



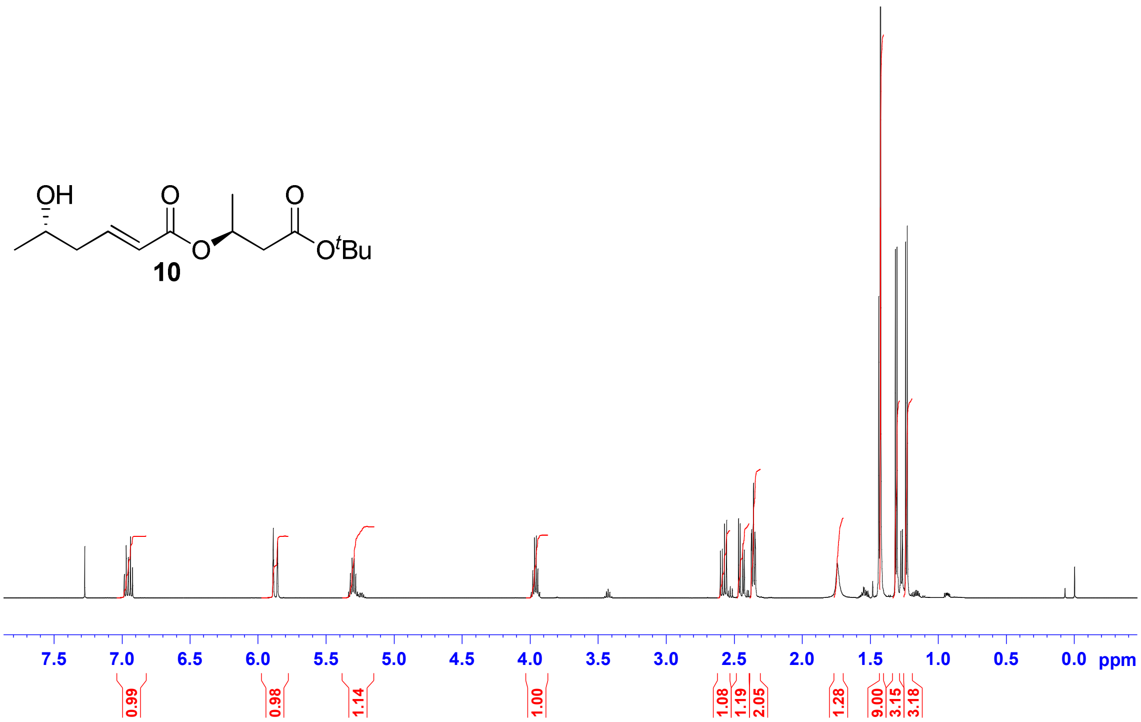
Supplementary Figure 17. ^{1}H NMR spectrum of compound **9**



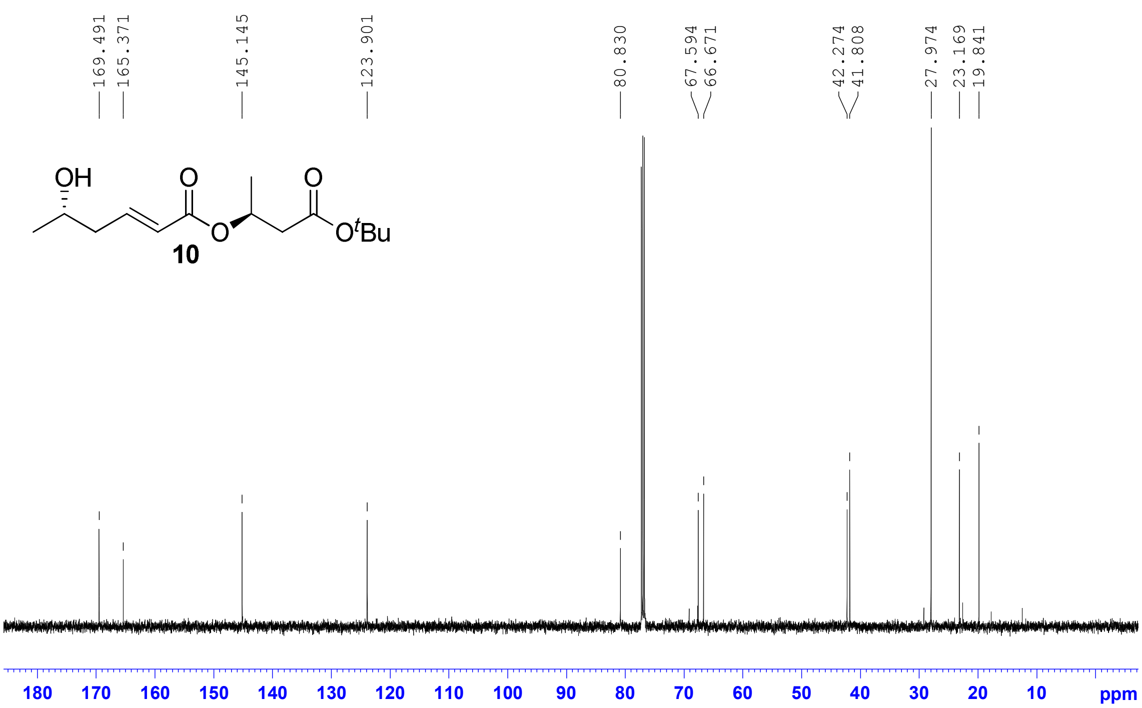
Supplementary Figure 18. ^{13}C NMR spectrum of compound **9**



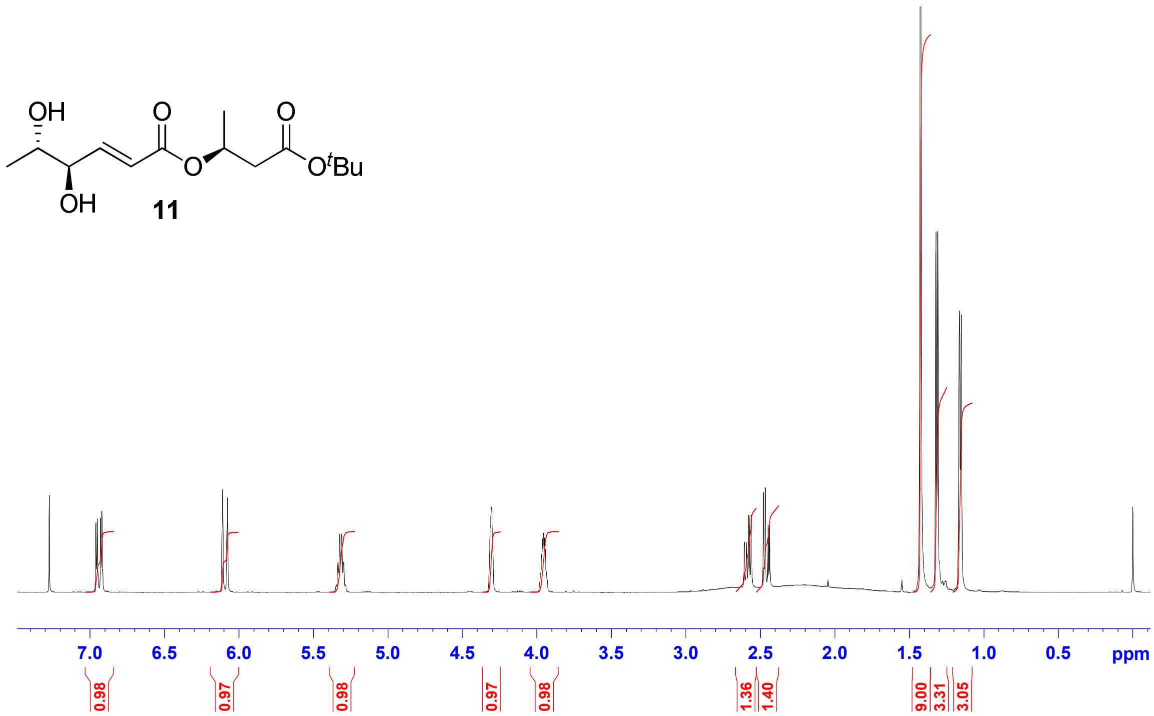
Supplementary Figure 19. ^{1}H NMR spectrum of compound **10**



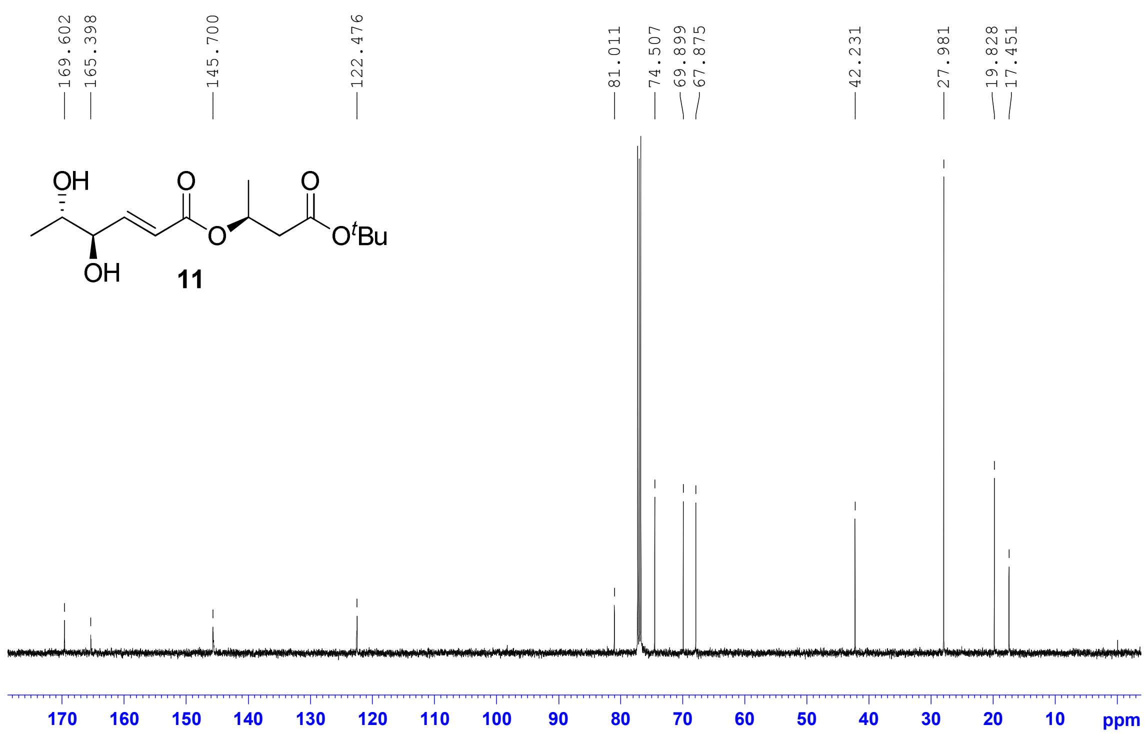
Supplementary Figure 20. ^{13}C NMR spectrum of compound **10**



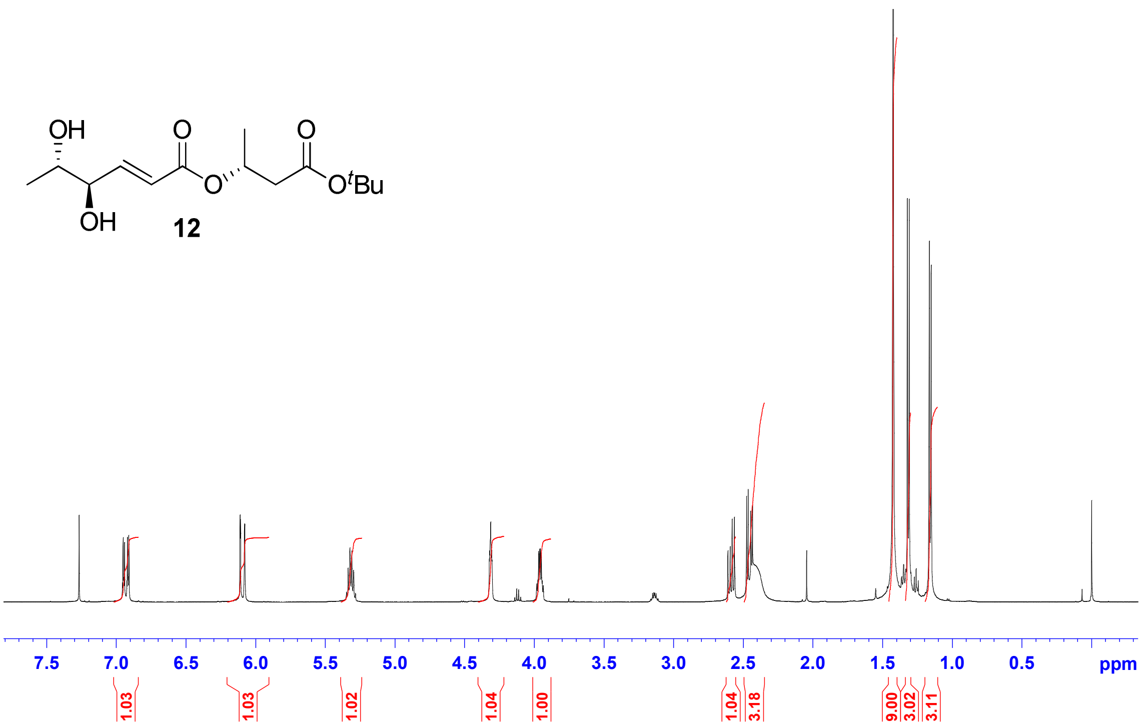
Supplementary Figure 21. ^{1}H NMR spectrum of compound **11**



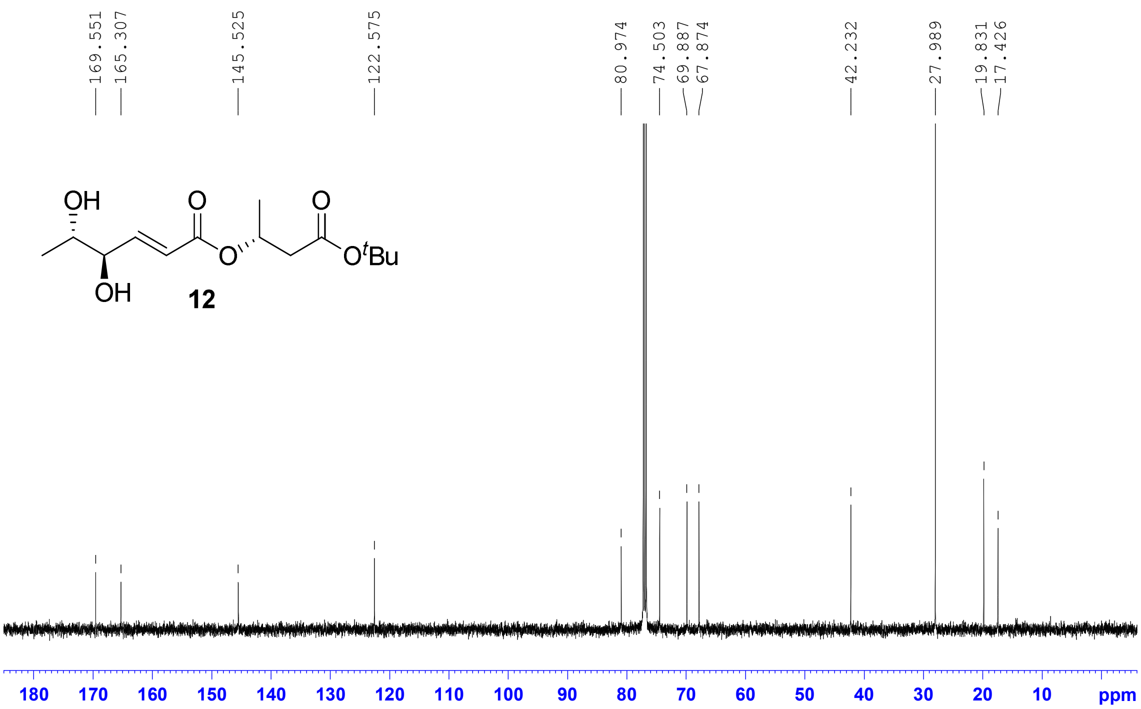
Supplementary Figure 22. ^{13}C NMR spectrum of compound **11**



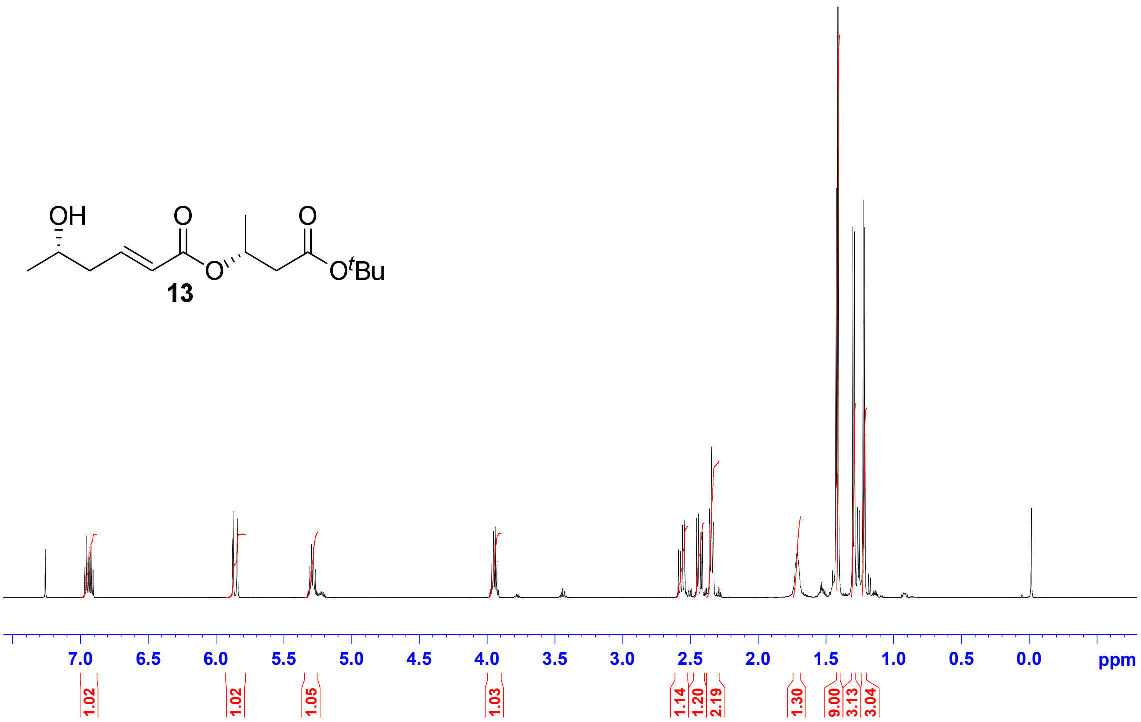
Supplementary Figure 23. ^{1}H NMR spectrum of compound **12**



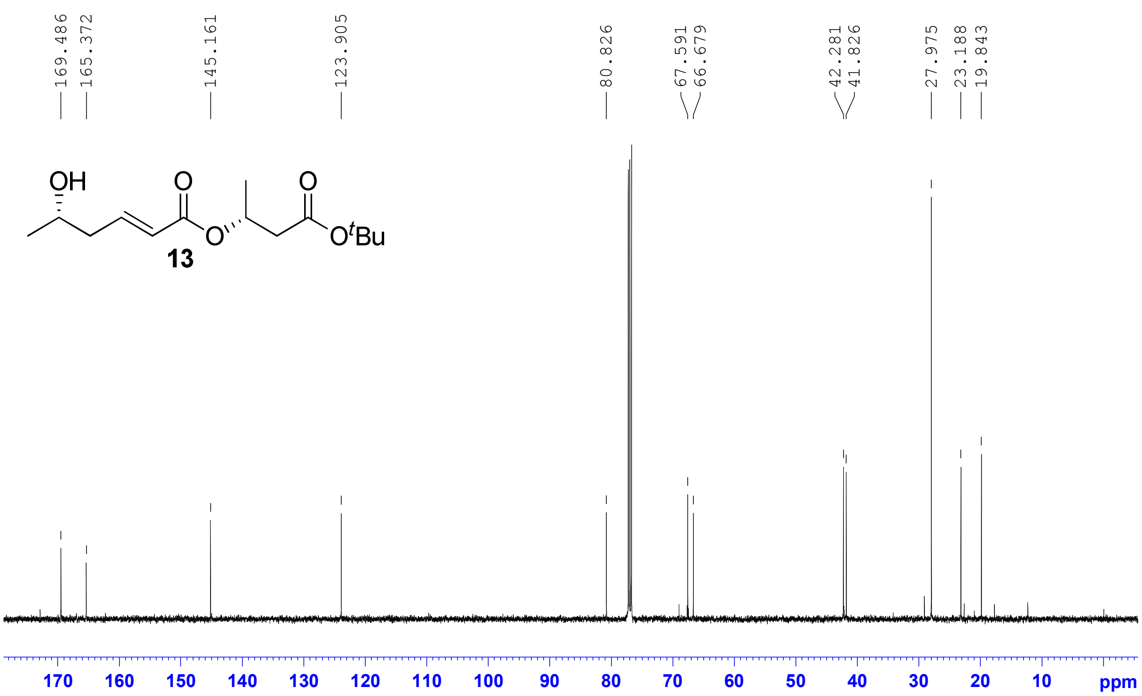
Supplementary Figure 24. ^{13}C NMR spectrum of compound **12**



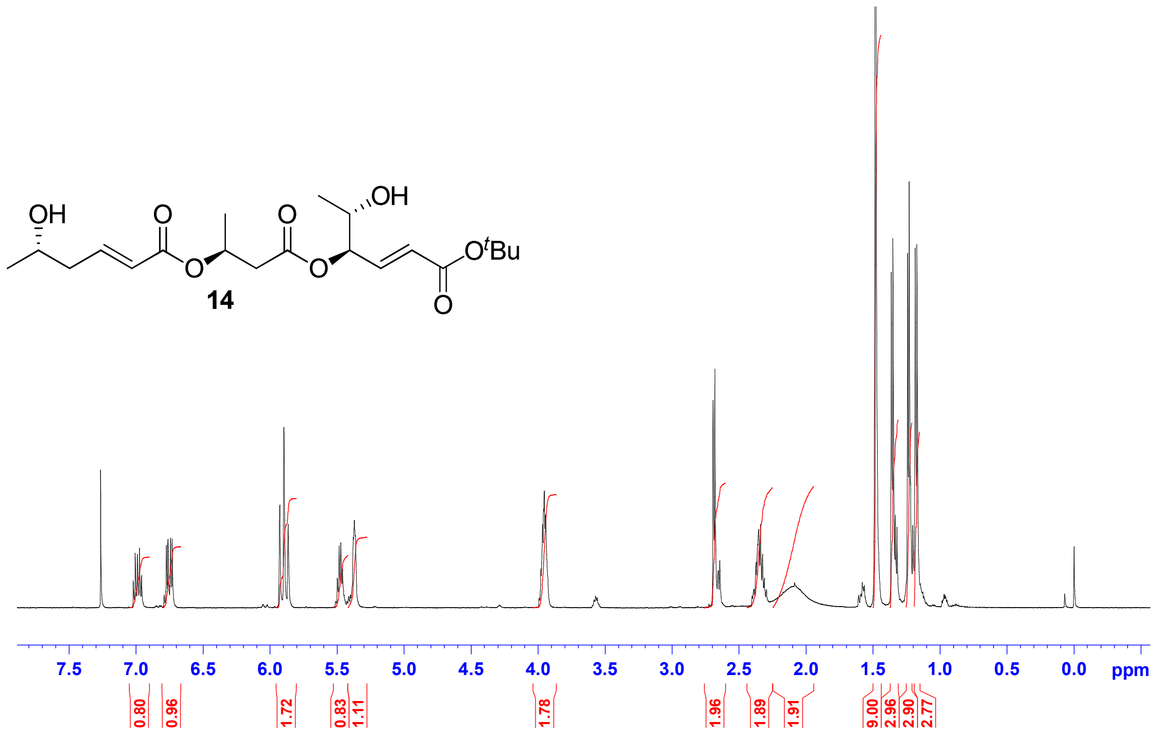
Supplementary Figure 25. ^{1}H NMR spectrum of compound **13**



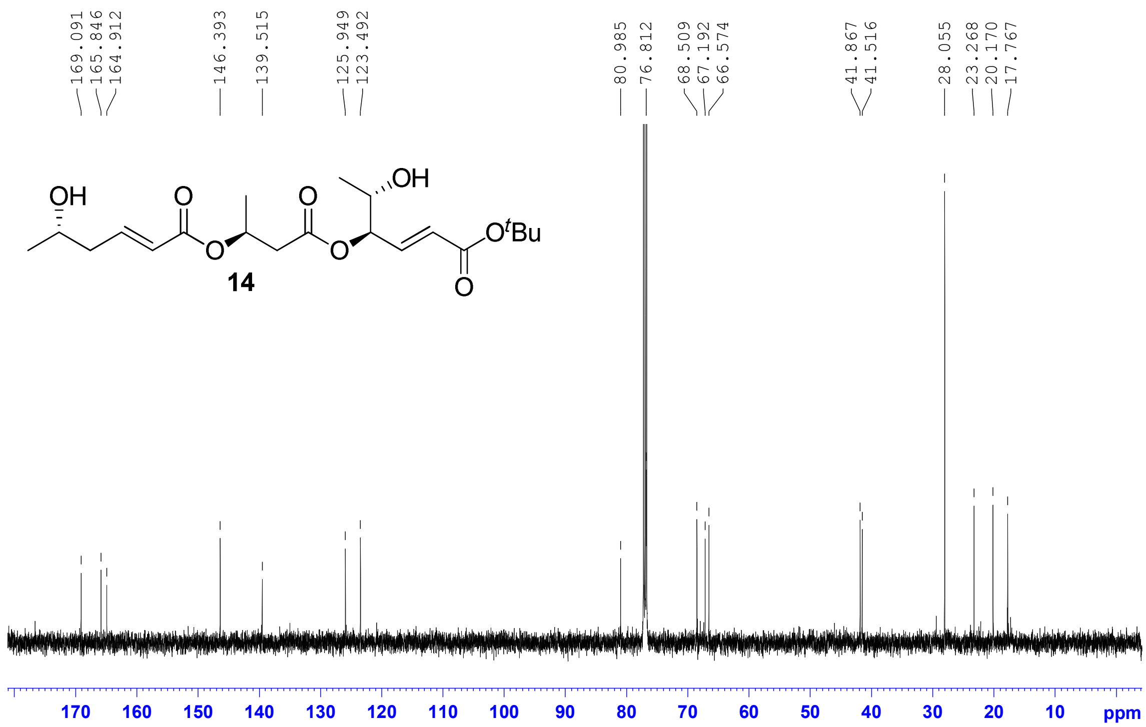
Supplementary Figure 26. ^{13}C NMR spectrum of compound **13**



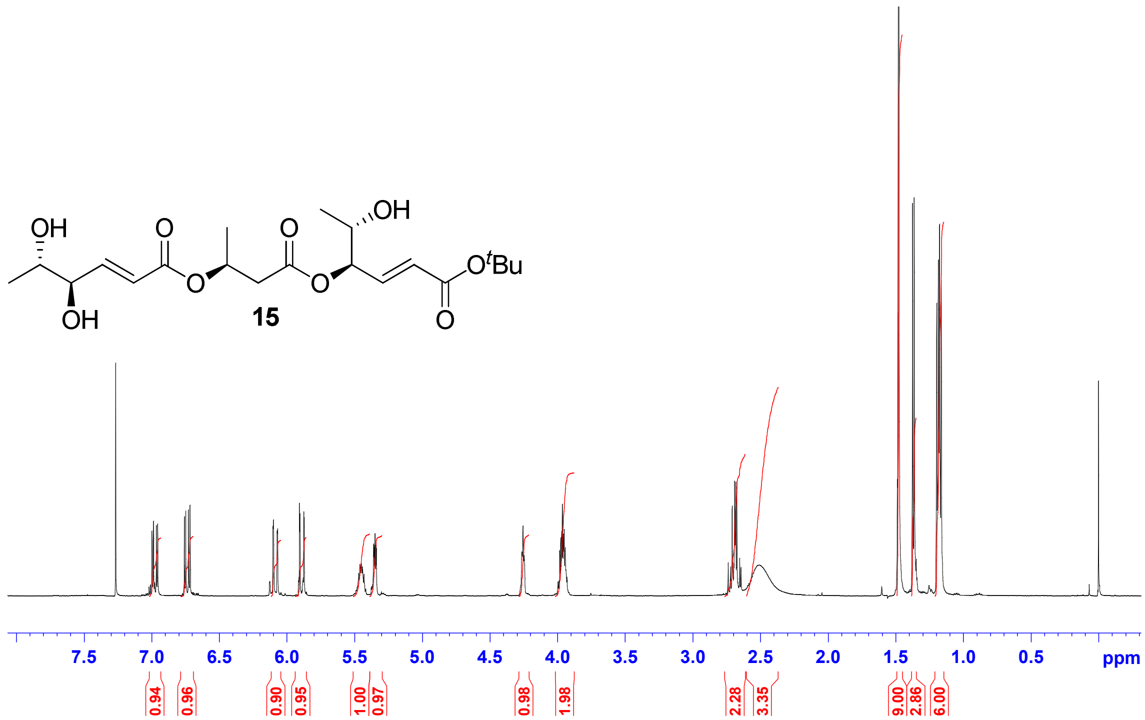
Supplementary Figure 27. ^{1}H NMR spectrum of compound **14**



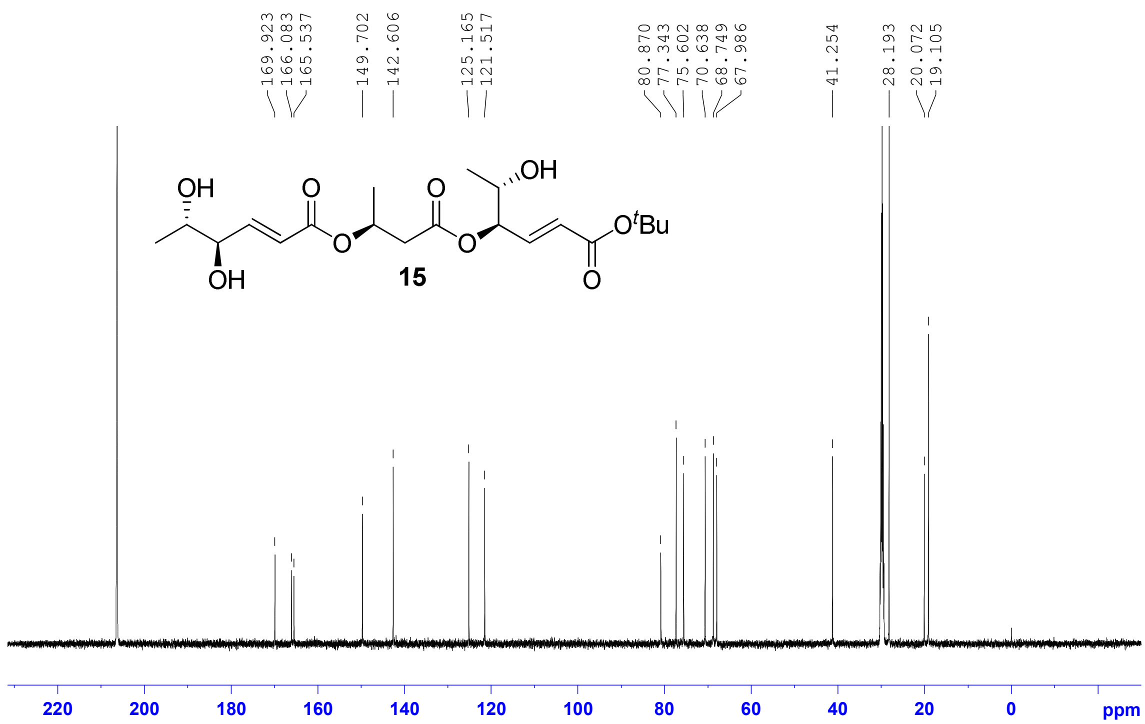
Supplementary Figure 28. ^{13}C NMR spectrum of compound **14**



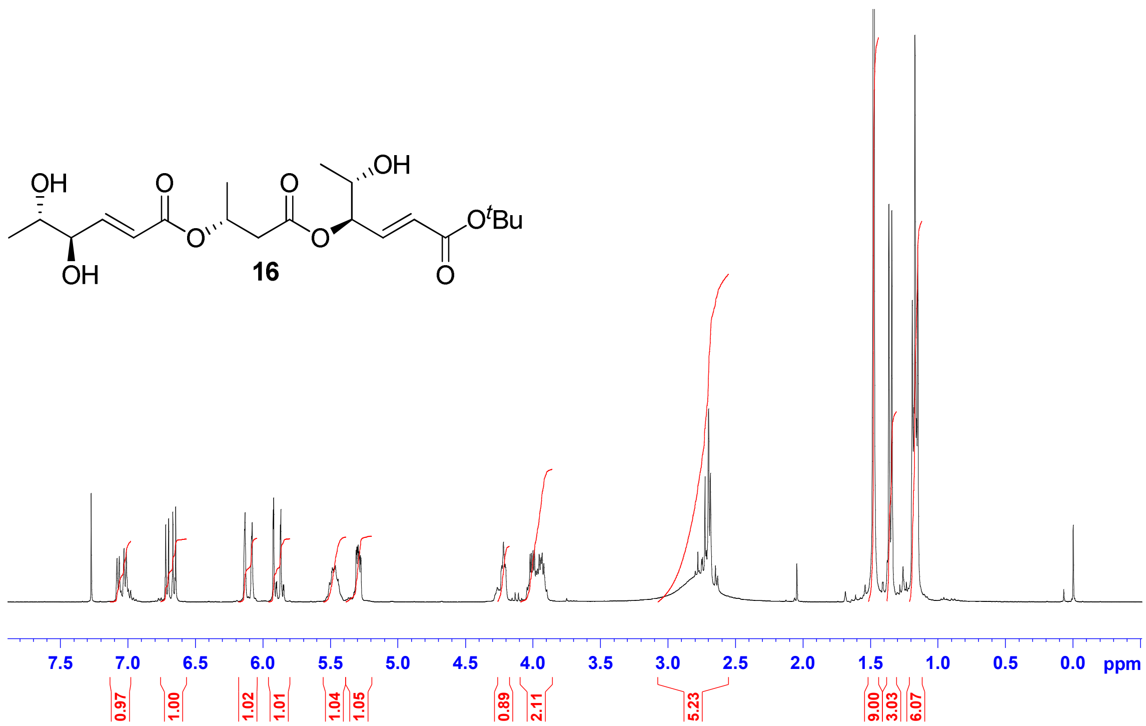
Supplementary Figure 29. ^{1}H NMR spectrum of compound **15**



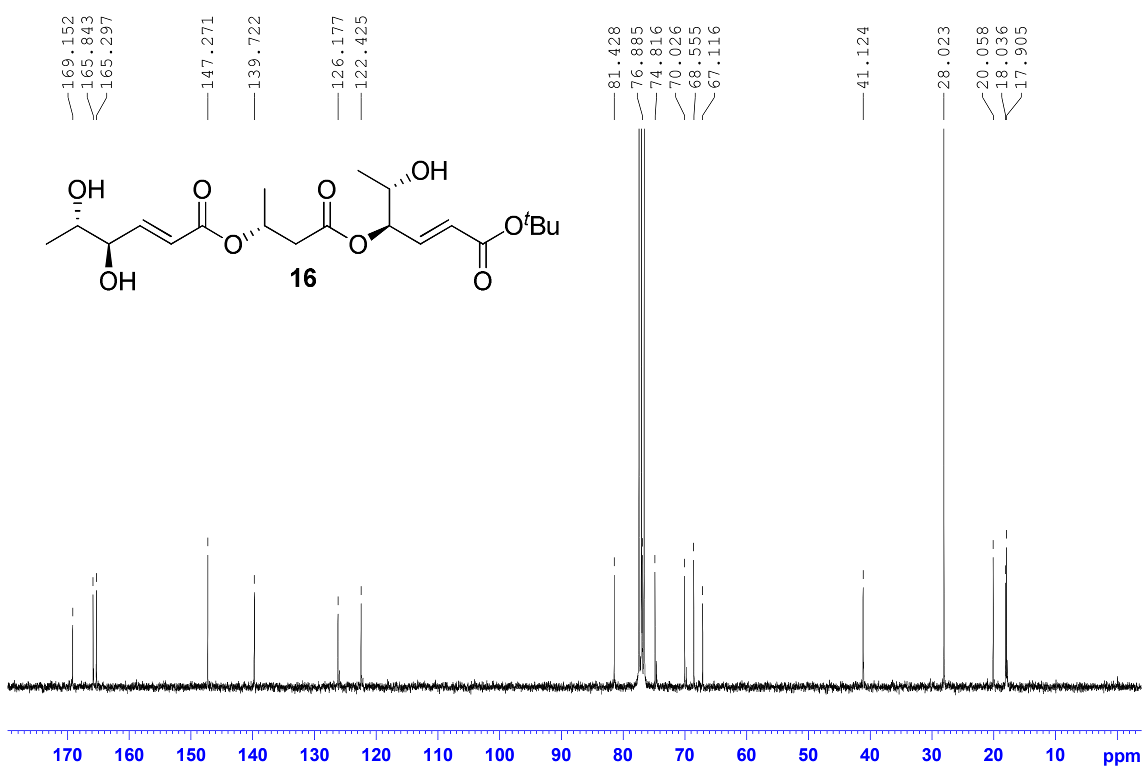
Supplementary Figure 30. ^{13}C NMR spectrum of compound **15**



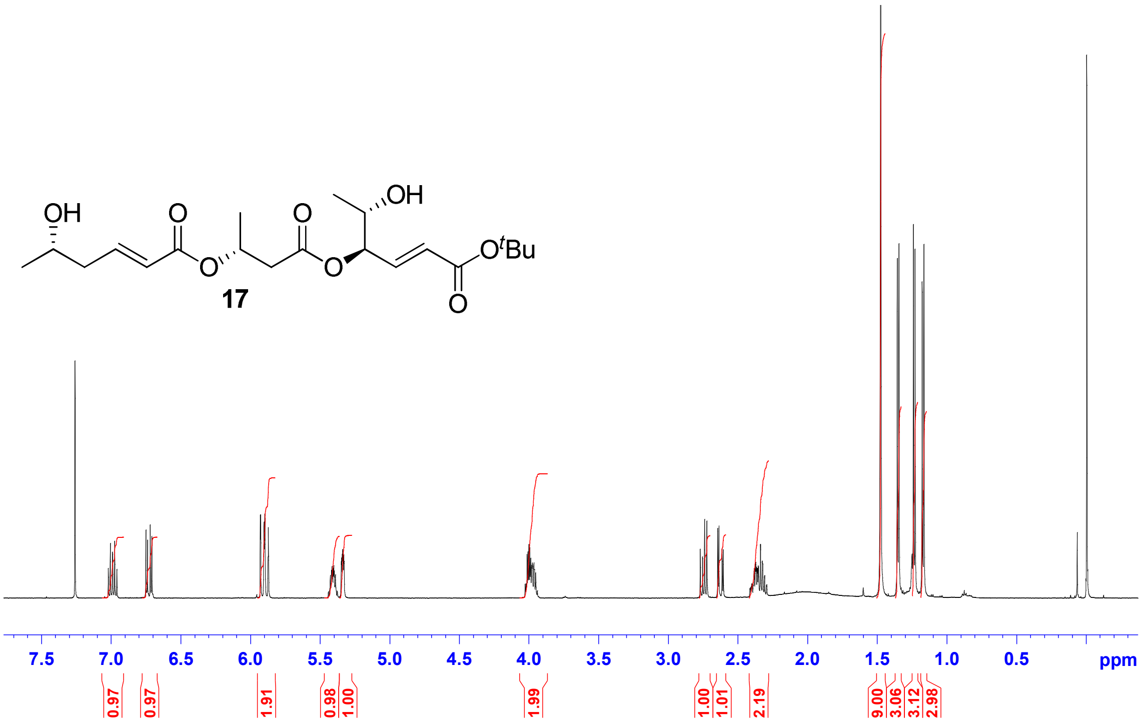
Supplementary Figure 31. ^{1}H NMR spectrum of compound **16**



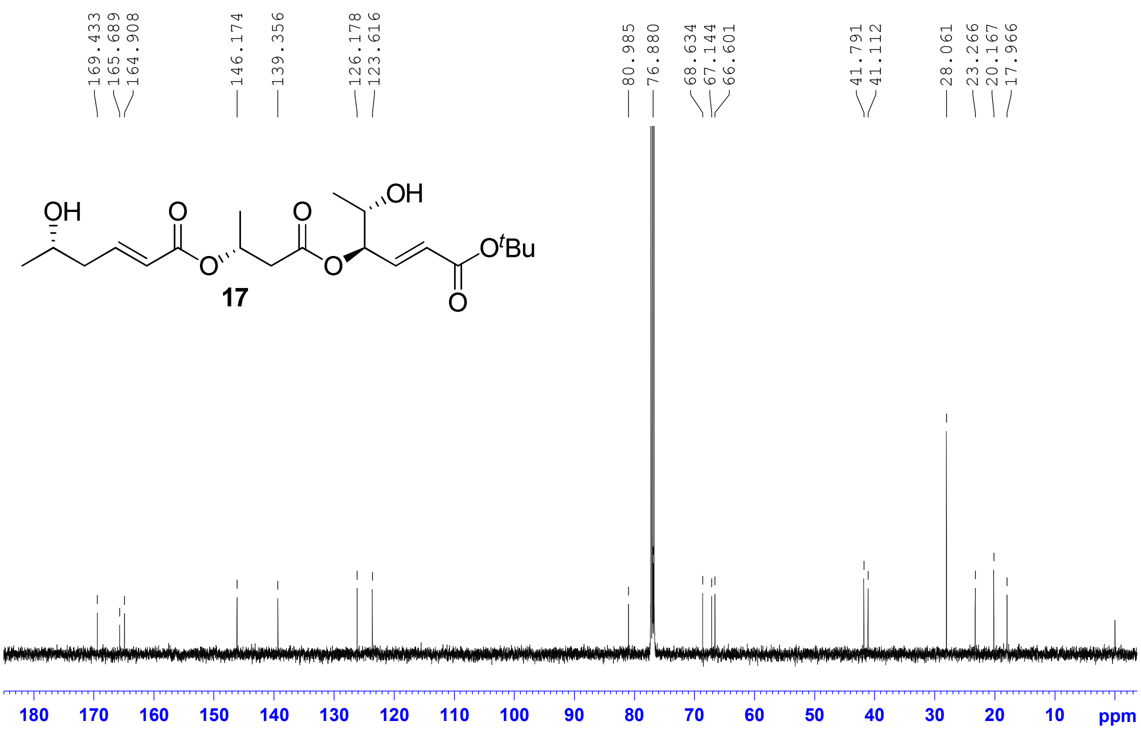
Supplementary Figure 32. ^{13}C NMR spectrum of compound **16**



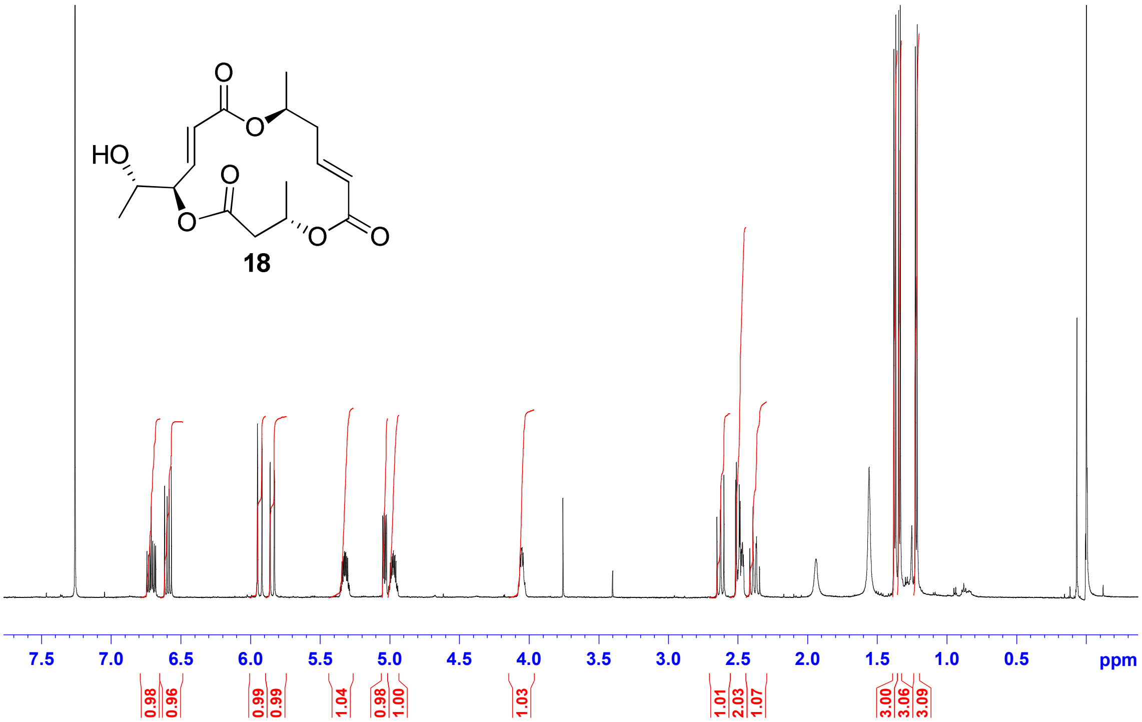
Supplementary Figure 33. ^{1}H NMR spectrum of compound **17**



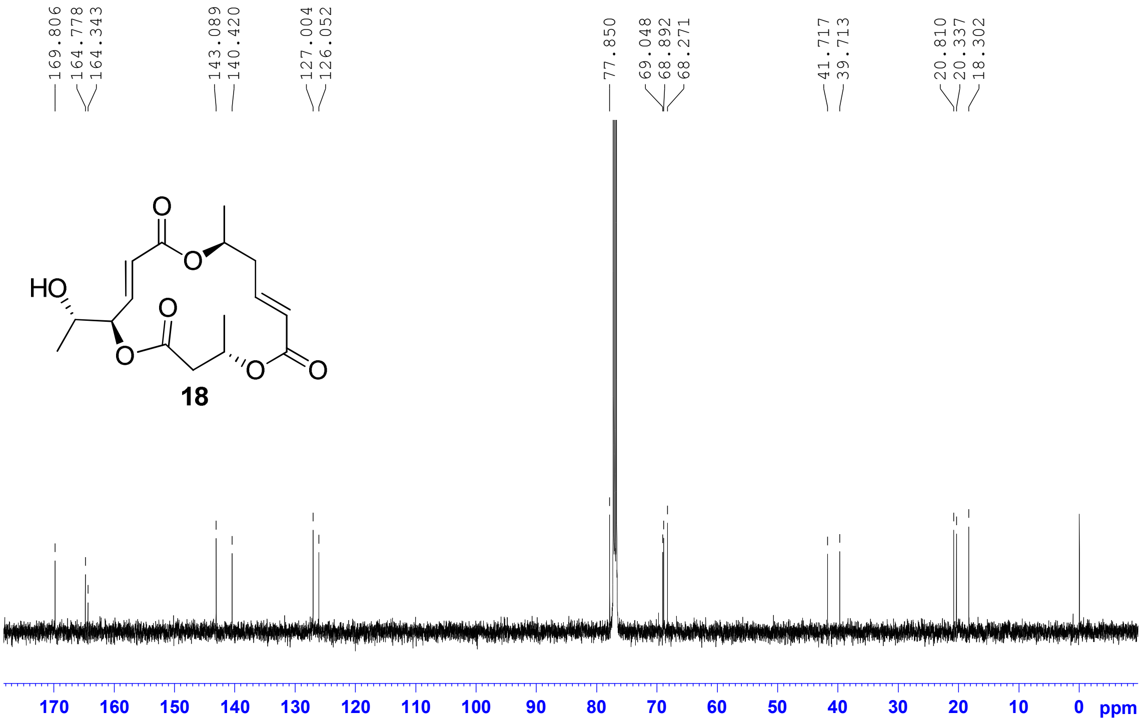
Supplementary Figure 34. ^{13}C NMR spectrum of compound **17**



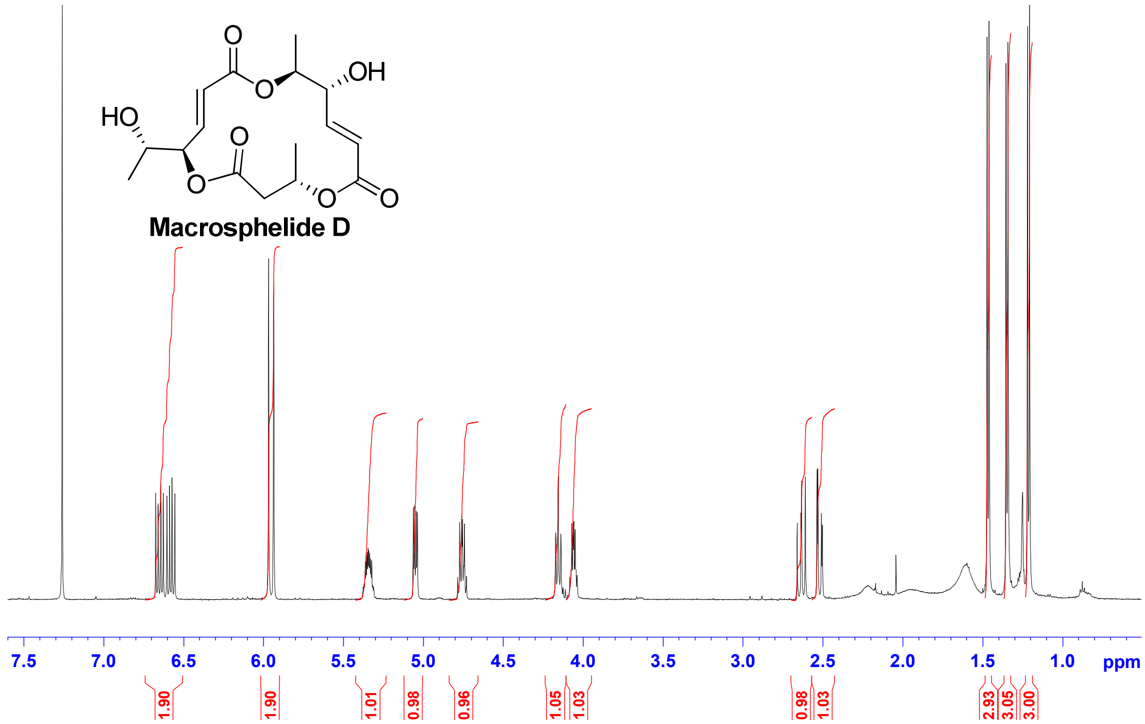
Supplementary Figure 35. ^{1}H NMR spectrum of compound **18**



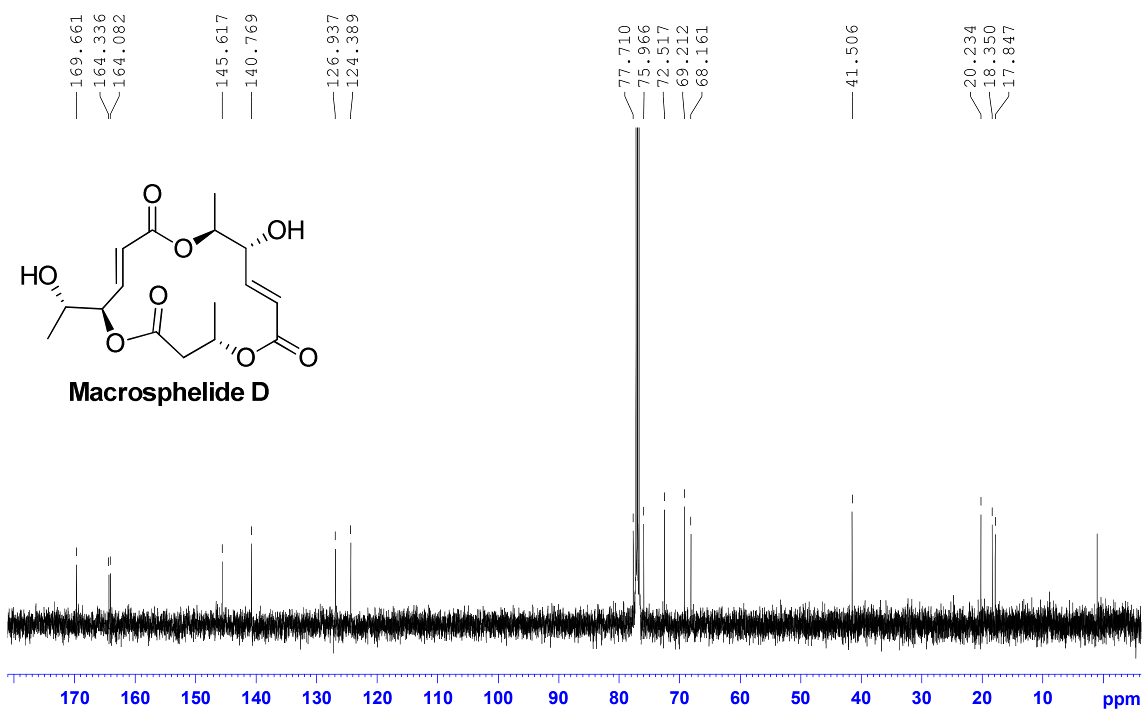
Supplementary Figure 36. ^{13}C NMR spectrum of compound **18**



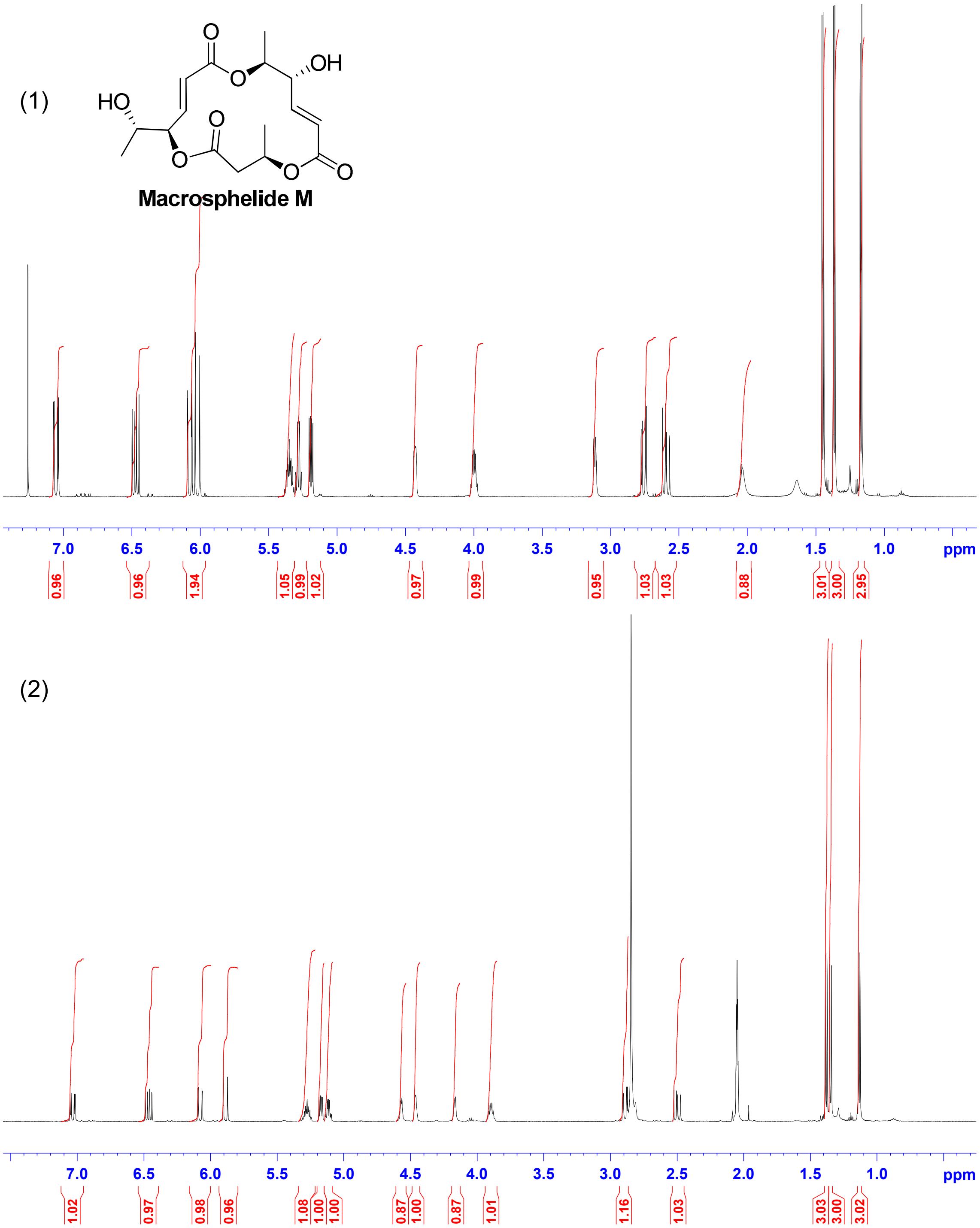
Supplementary Figure 37. ^{1}H NMR spectrum of macrosphelide D



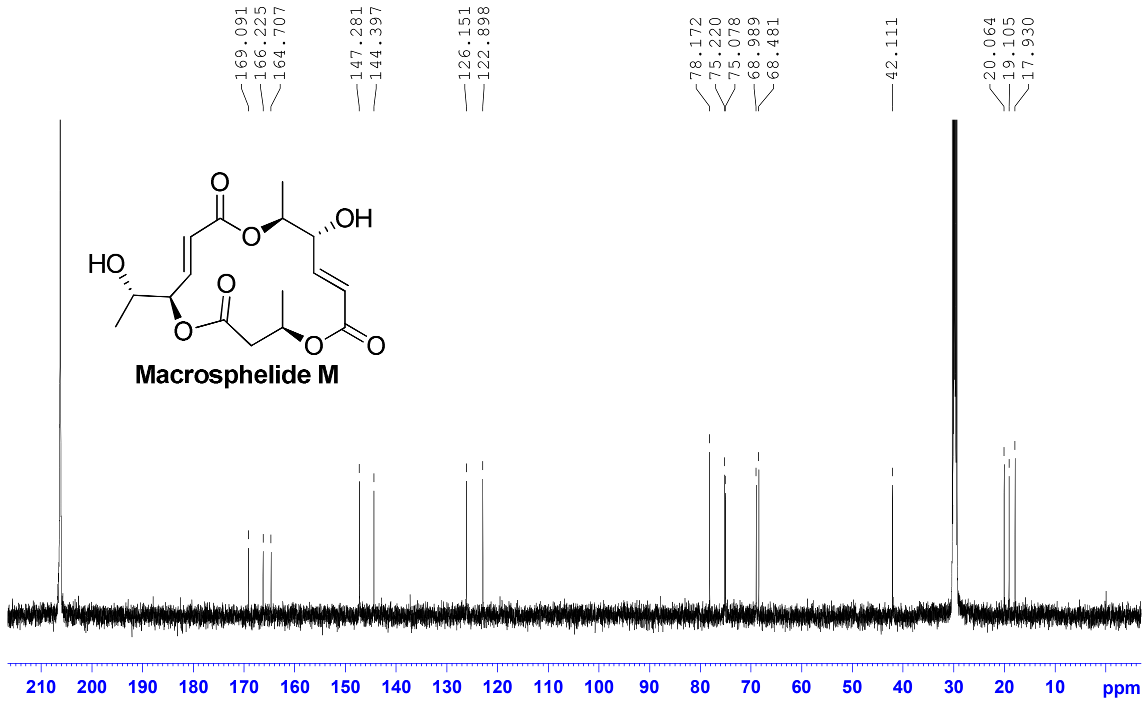
Supplementary Figure 38. ^{13}C NMR spectrum of macrosphelide D



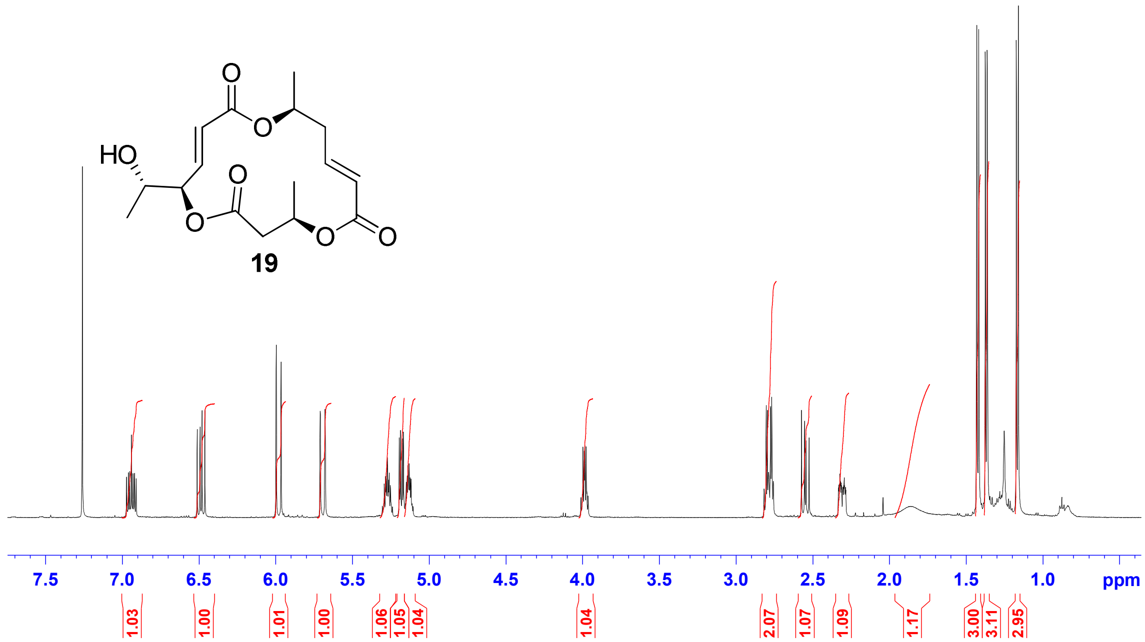
Supplementary Figure 39. ^{1}H NMR spectrum of macrosphelide M (in $CDCl_3$ (1) and d_6-acetone (2))



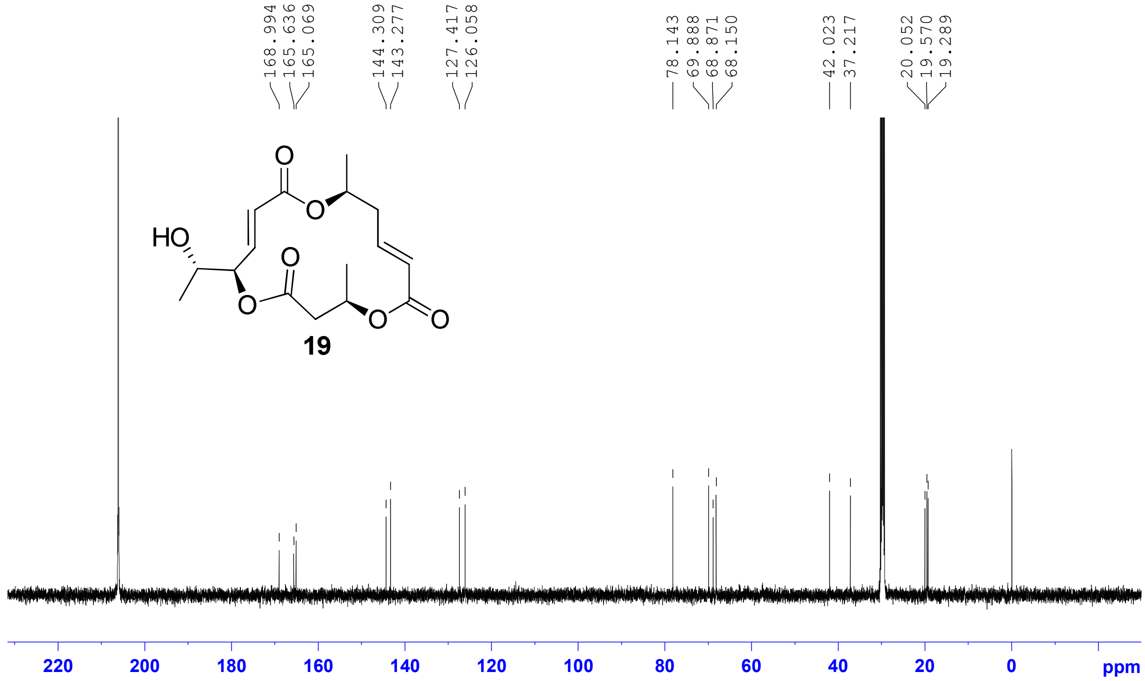
Supplementary Figure 40. ^{13}C NMR spectrum of macrosphelide M



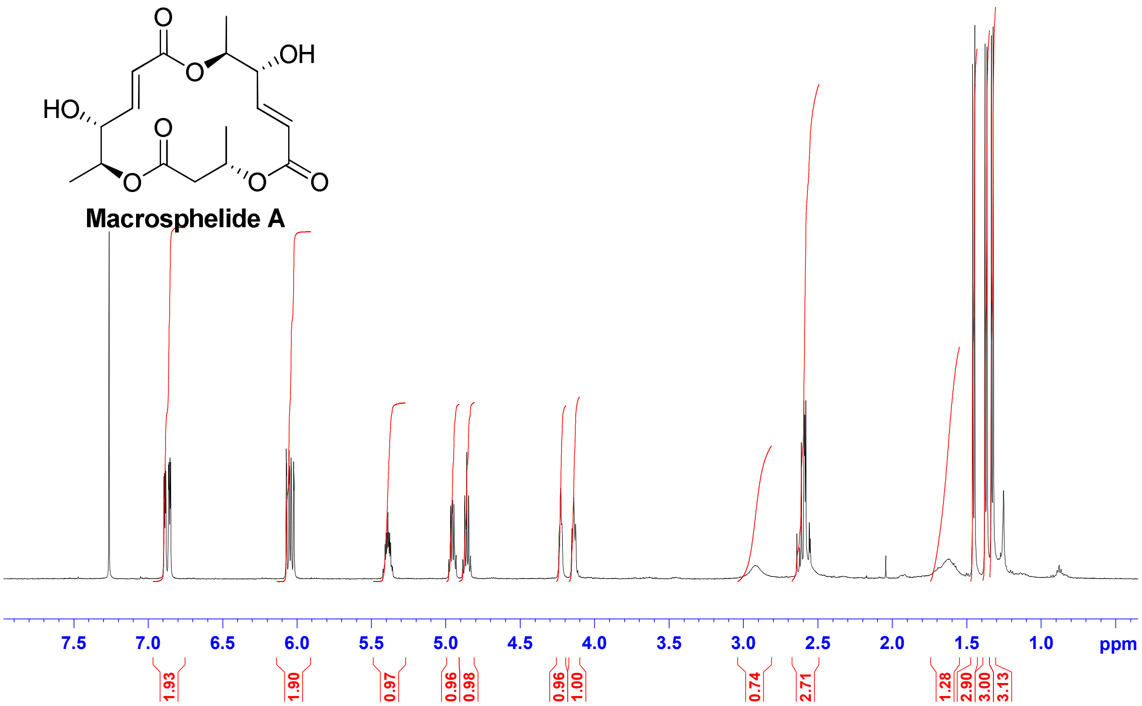
Supplementary Figure 41. ^{1}H NMR spectrum of compound **19**



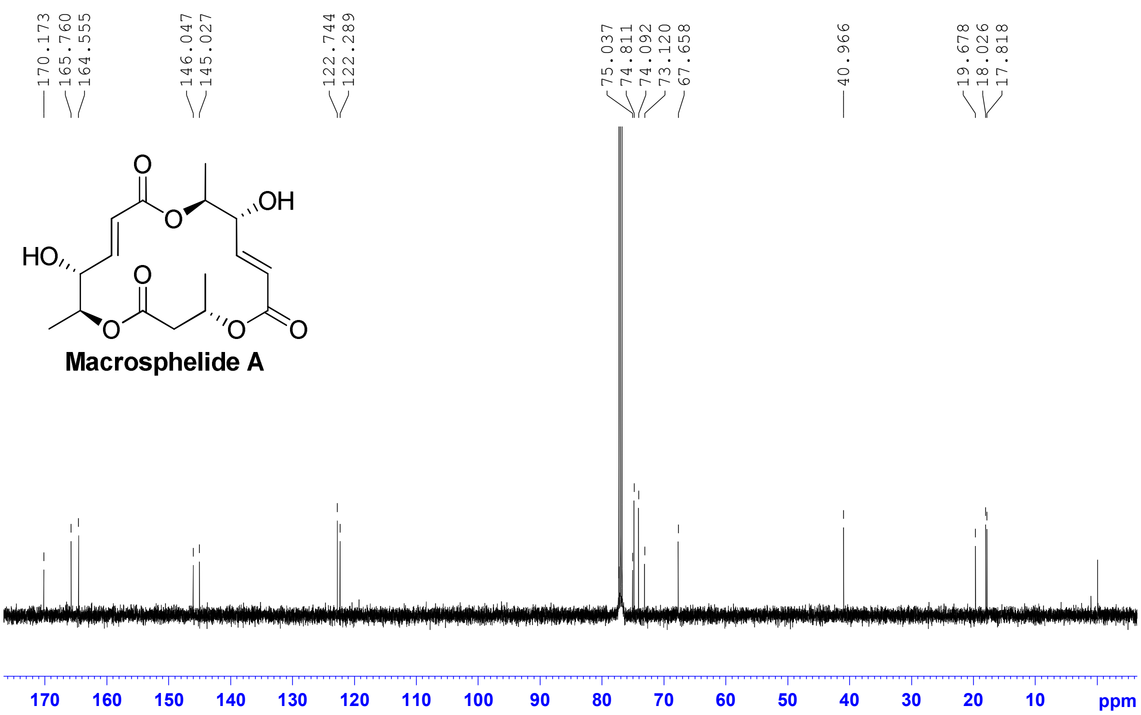
Supplementary Figure 42. ^{13}C NMR spectrum of compound **19**



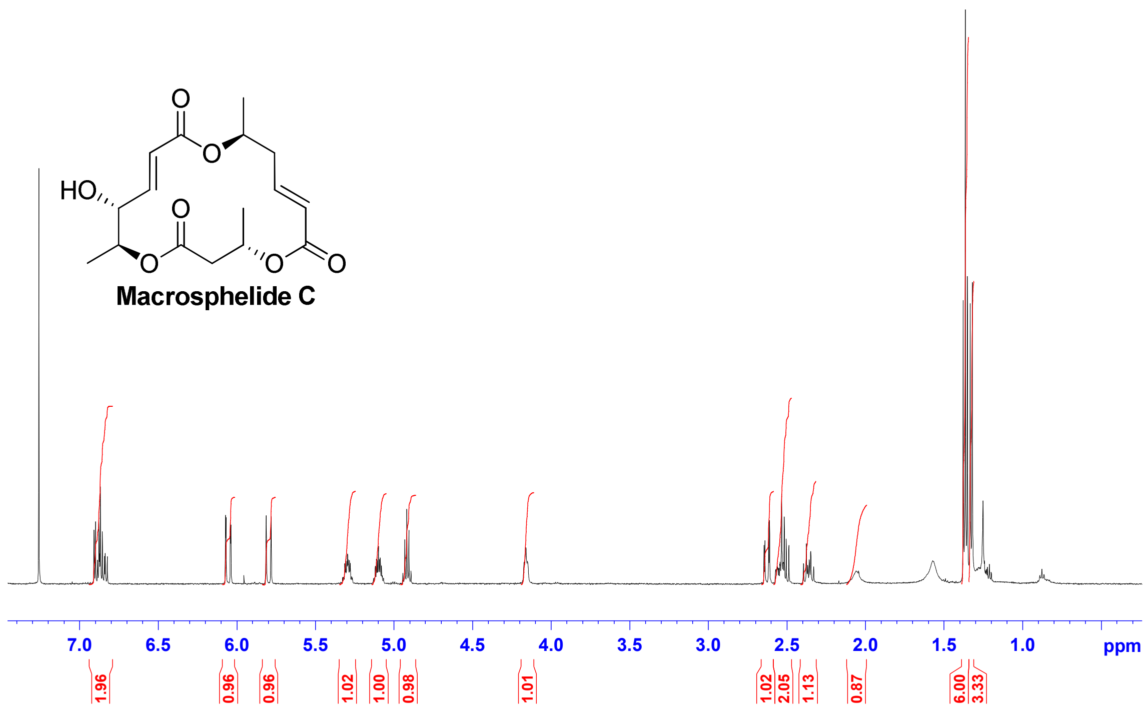
Supplementary Figure 43. ^{1}H NMR spectrum of macrosphelide A



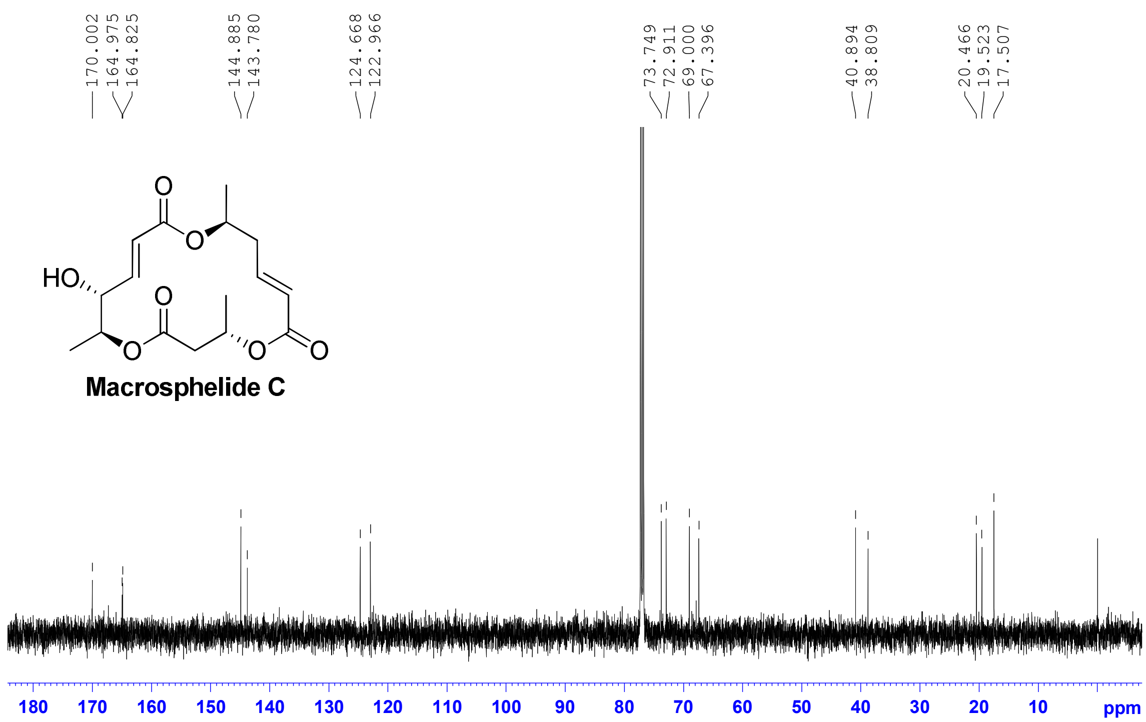
Supplementary Figure 44. ^{13}C NMR spectrum of macrosphelide A



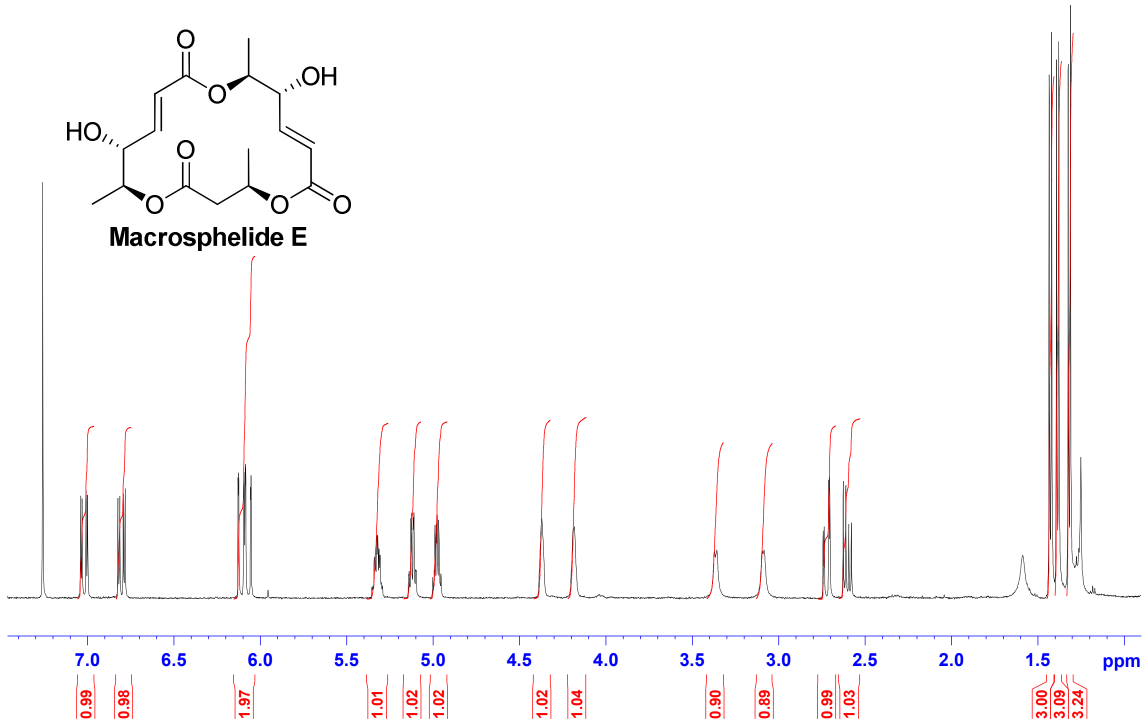
Supplementary Figure 45. ^{1}H NMR spectrum of macrosphelide C



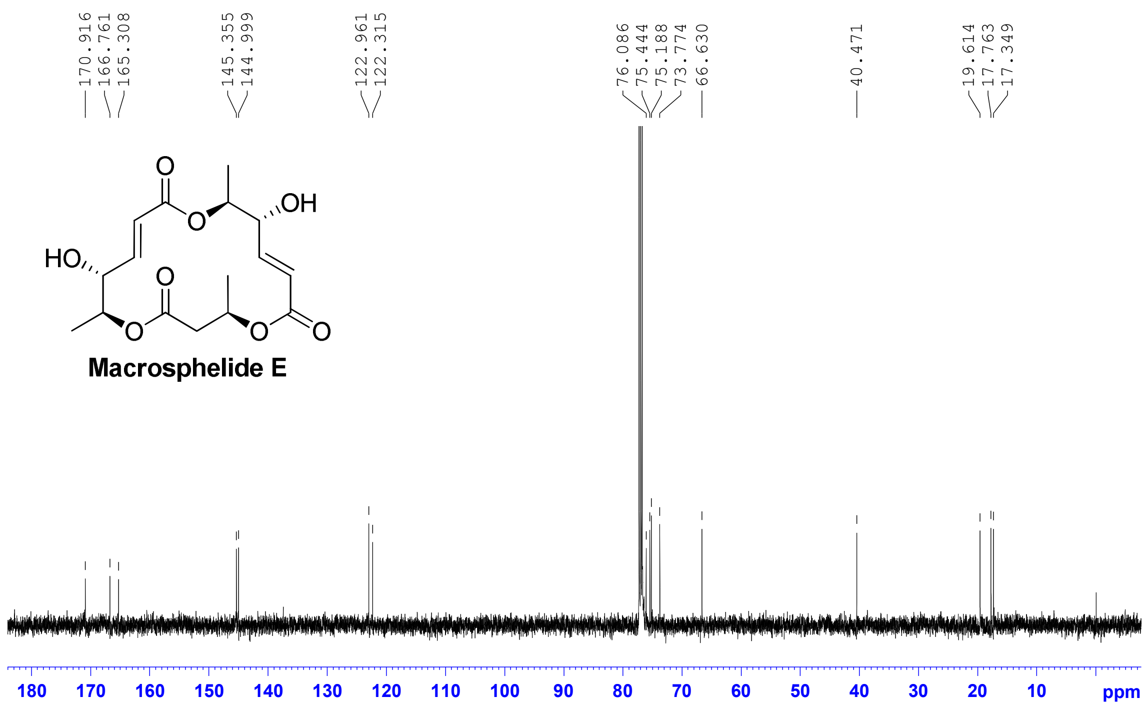
Supplementary Figure 46. ^{13}C NMR spectrum of macrosphelide C



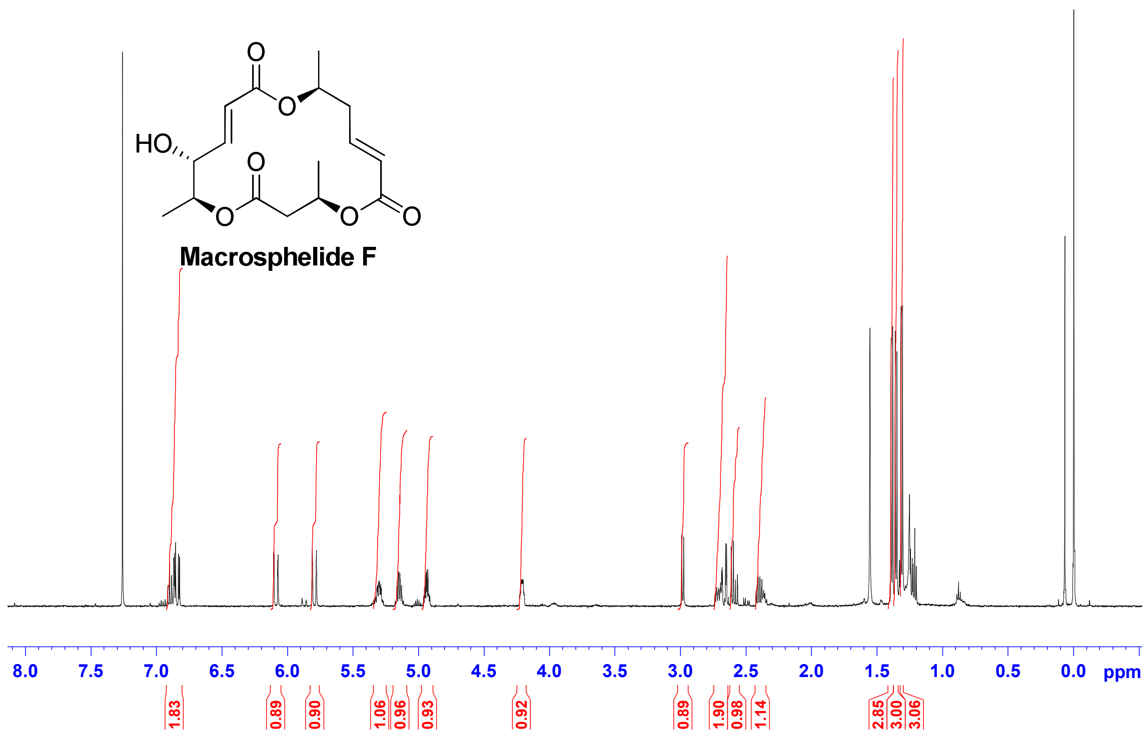
Supplementary Figure 47. ^{1}H NMR spectrum of macrosphelide E



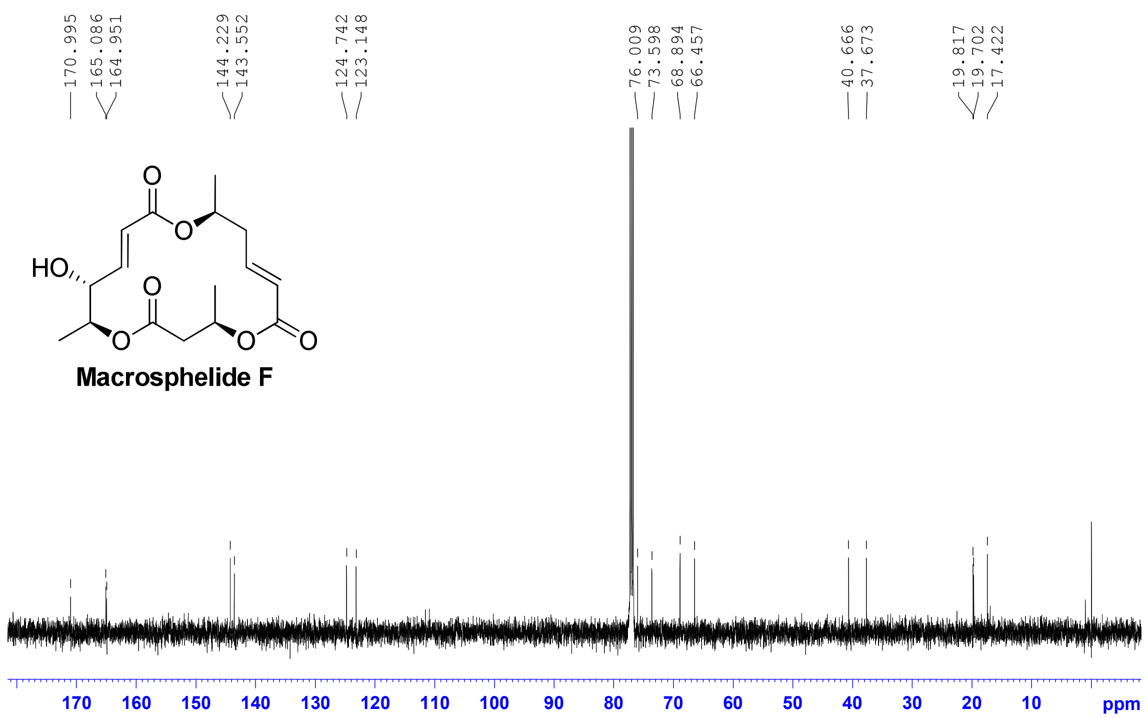
Supplementary Figure 48. ^{13}C NMR spectrum of macrosphelide E



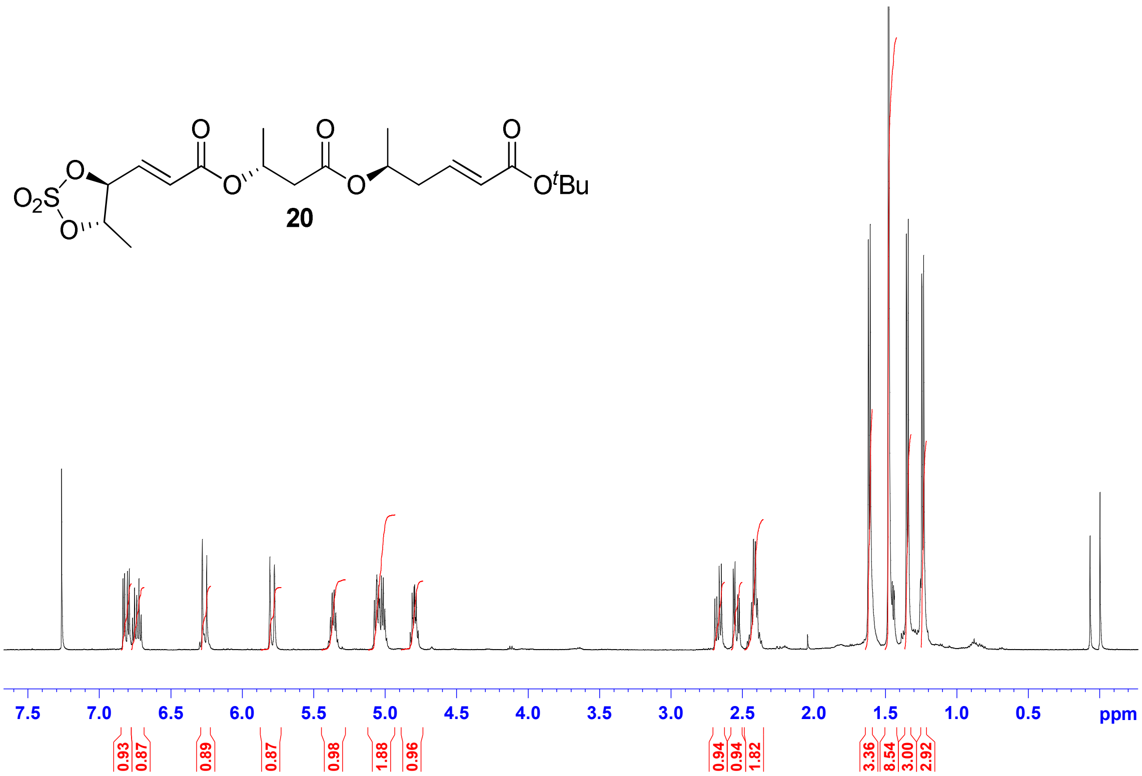
Supplementary Figure 49. ^{1}H NMR spectrum of macrosphelide F



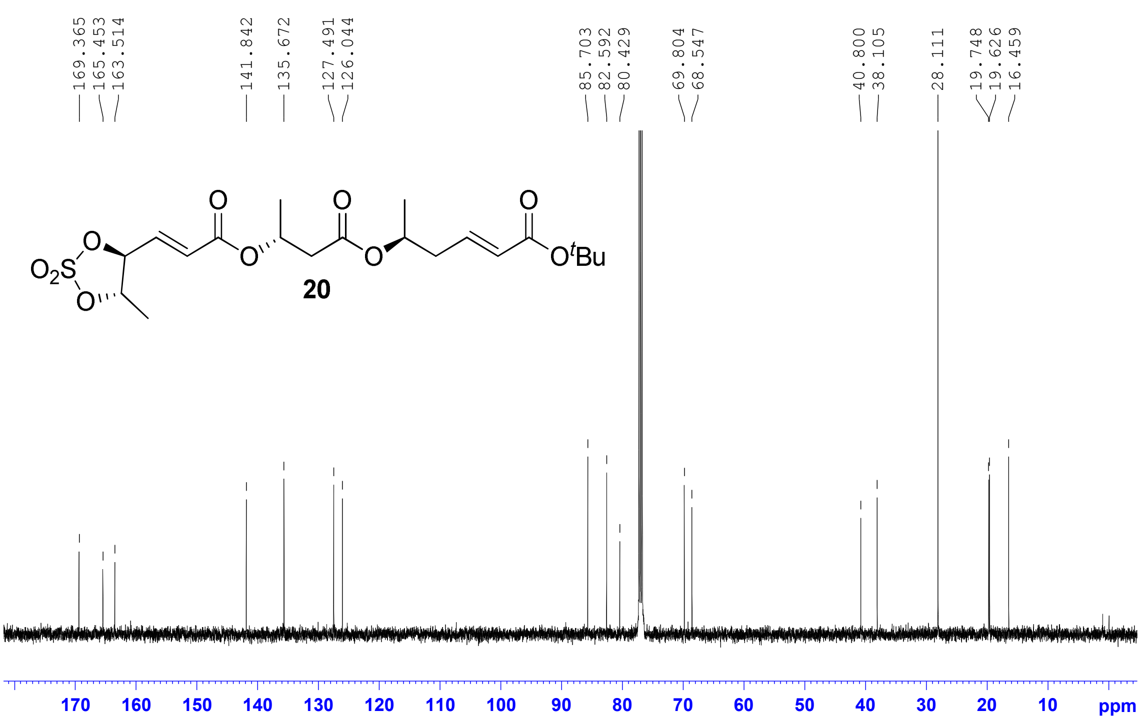
Supplementary Figure 50. ^{13}C NMR spectrum of macrosphelide F



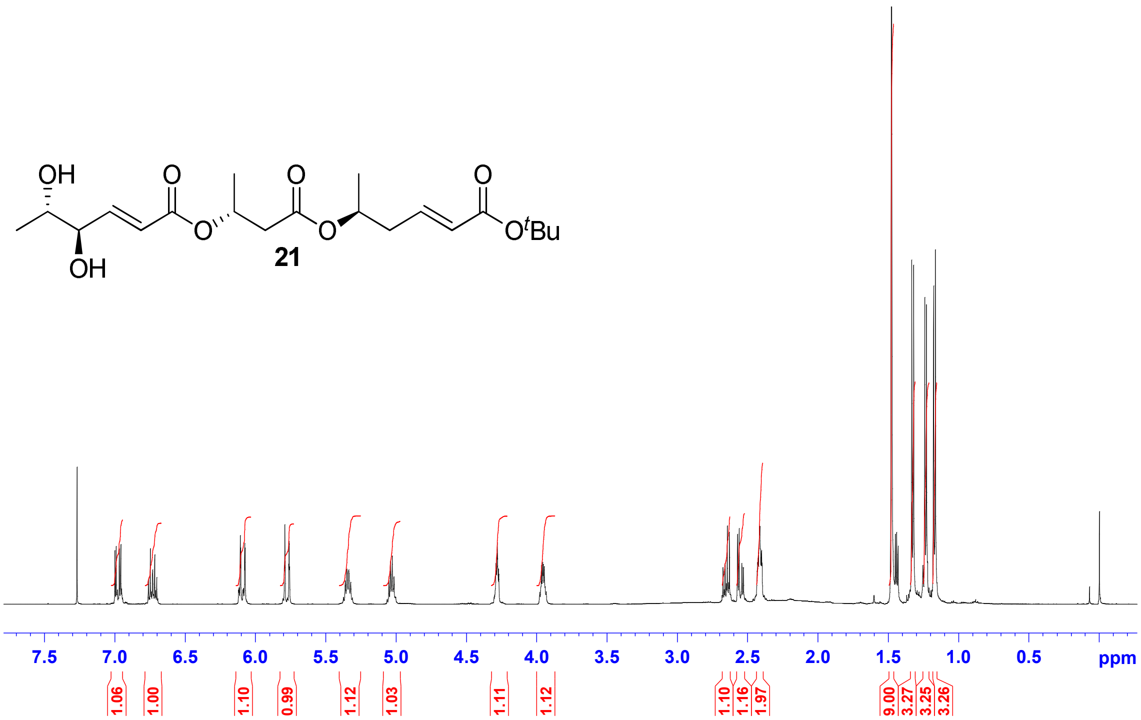
Supplementary Figure 51. ^{1}H NMR spectrum of compound **20**



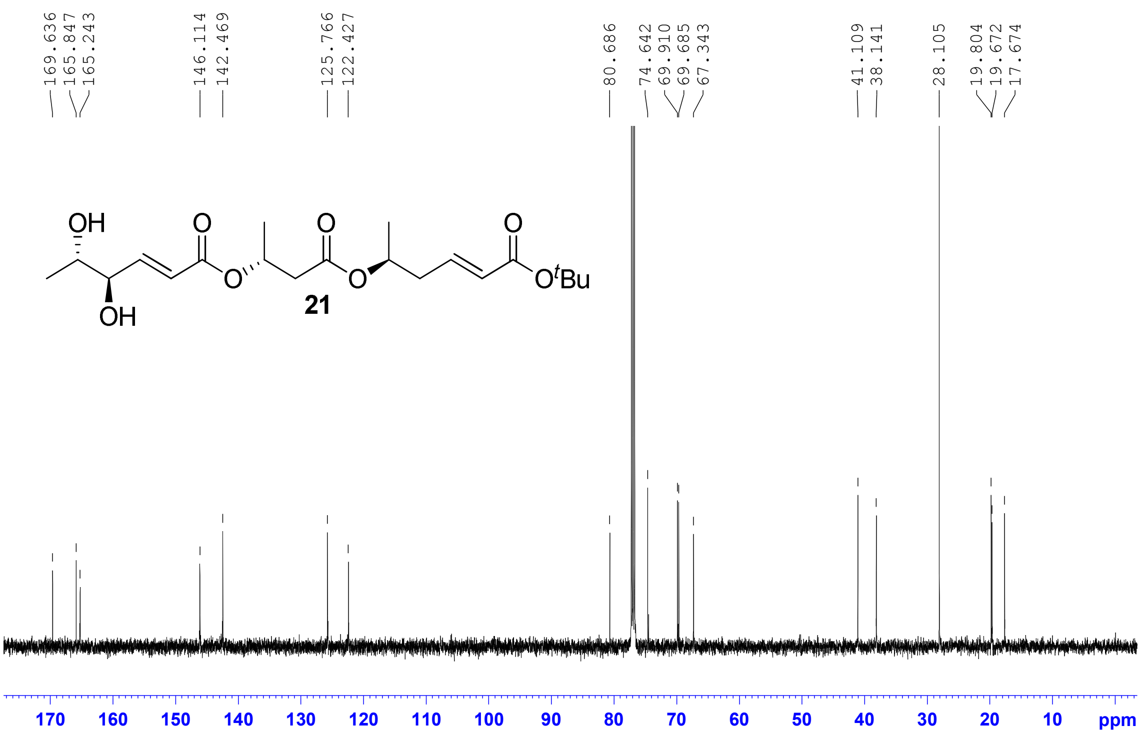
Supplementary Figure 52. ^{13}C NMR spectrum of compound **20**



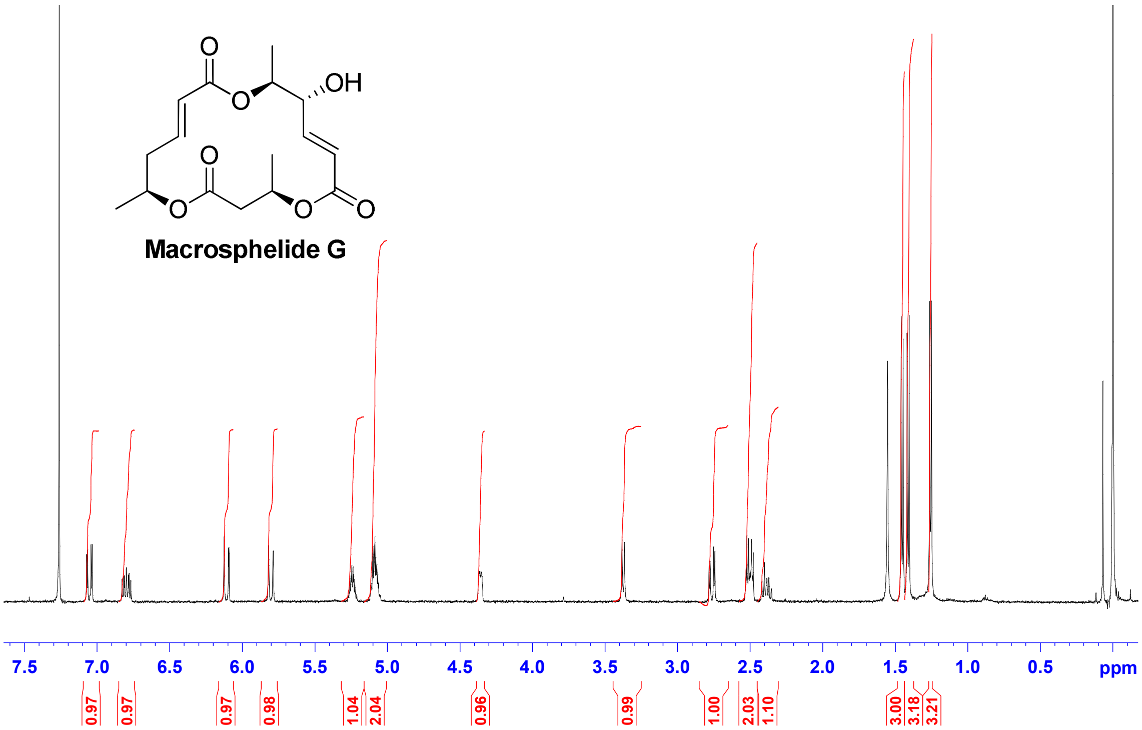
Supplementary Figure 53. ^{1}H NMR spectrum of compound **21**



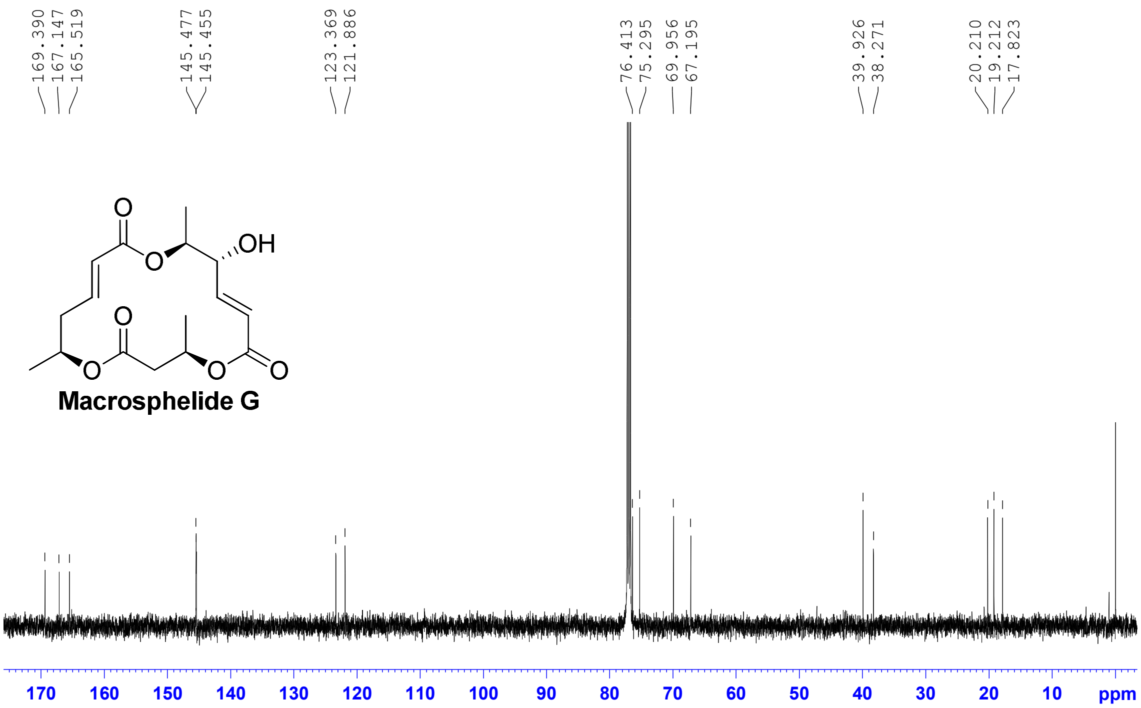
Supplementary Figure 54. ^{13}C NMR spectrum of compound **21**



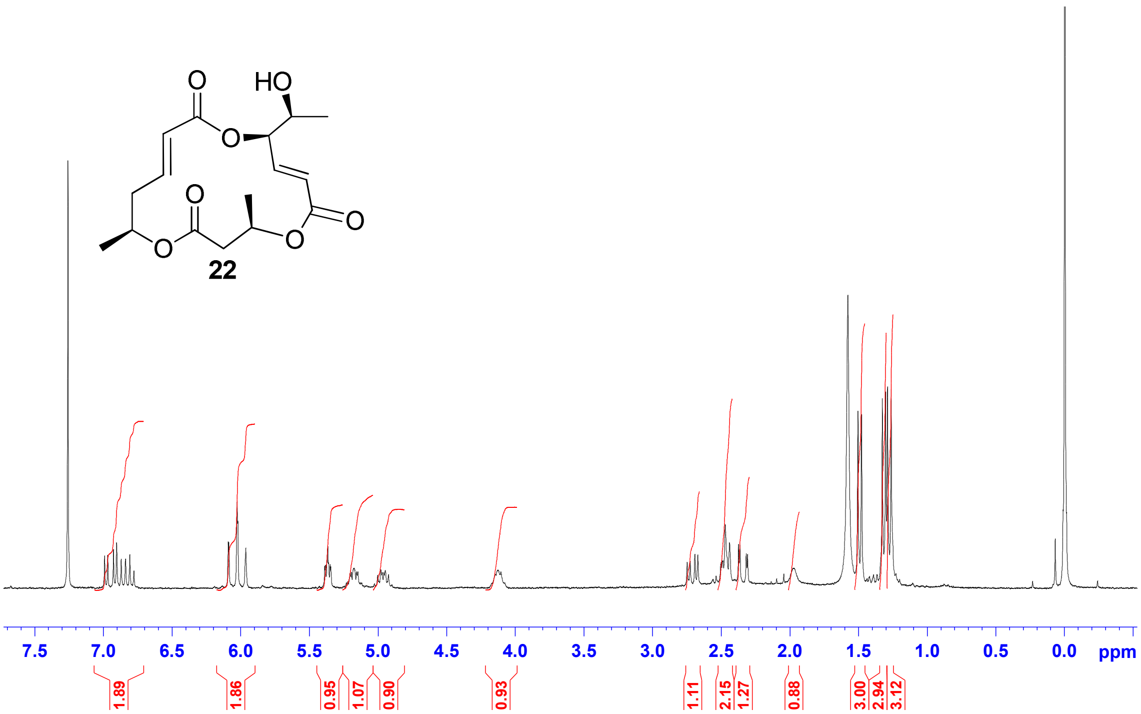
Supplementary Figure 55. ^{1}H NMR spectrum of macrosphelide G



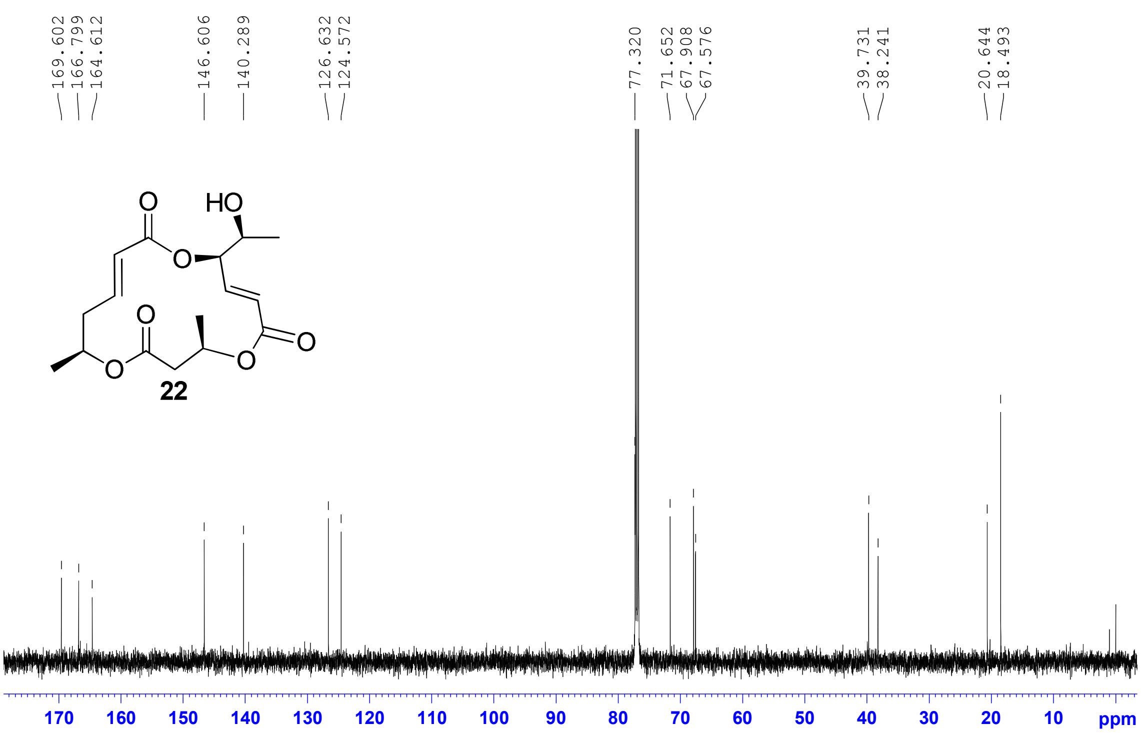
Supplementary Figure 56. ^{13}C NMR spectrum of macrosphelide G



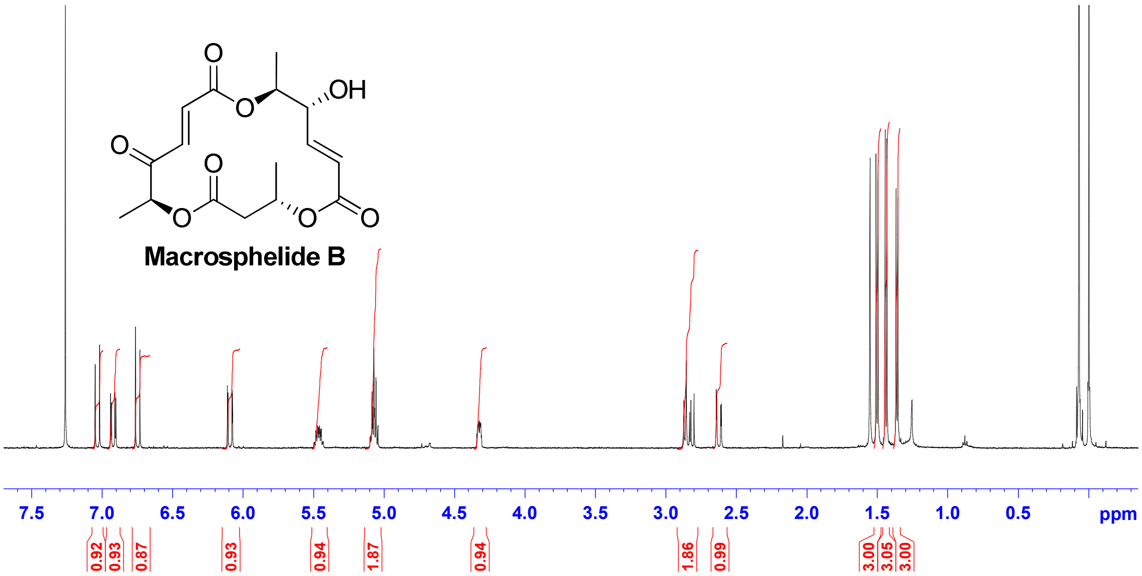
Supplementary Figure 57. ^{1}H NMR spectrum of compound **22**



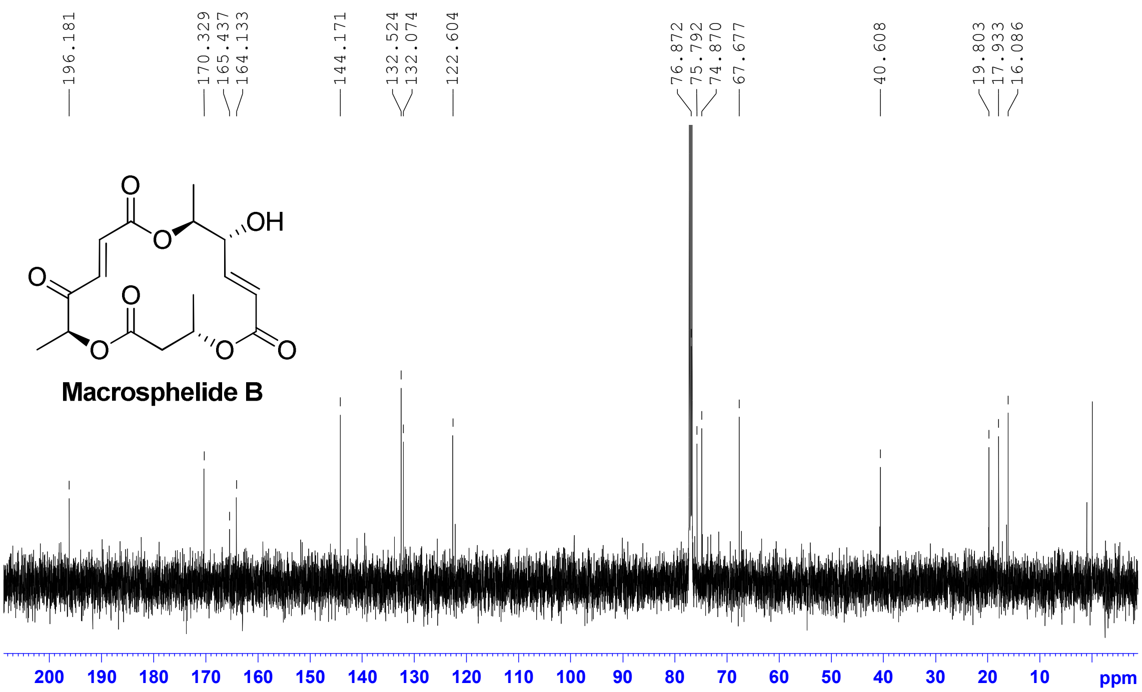
Supplementary Figure 58. ^{13}C NMR spectrum of compound **22**



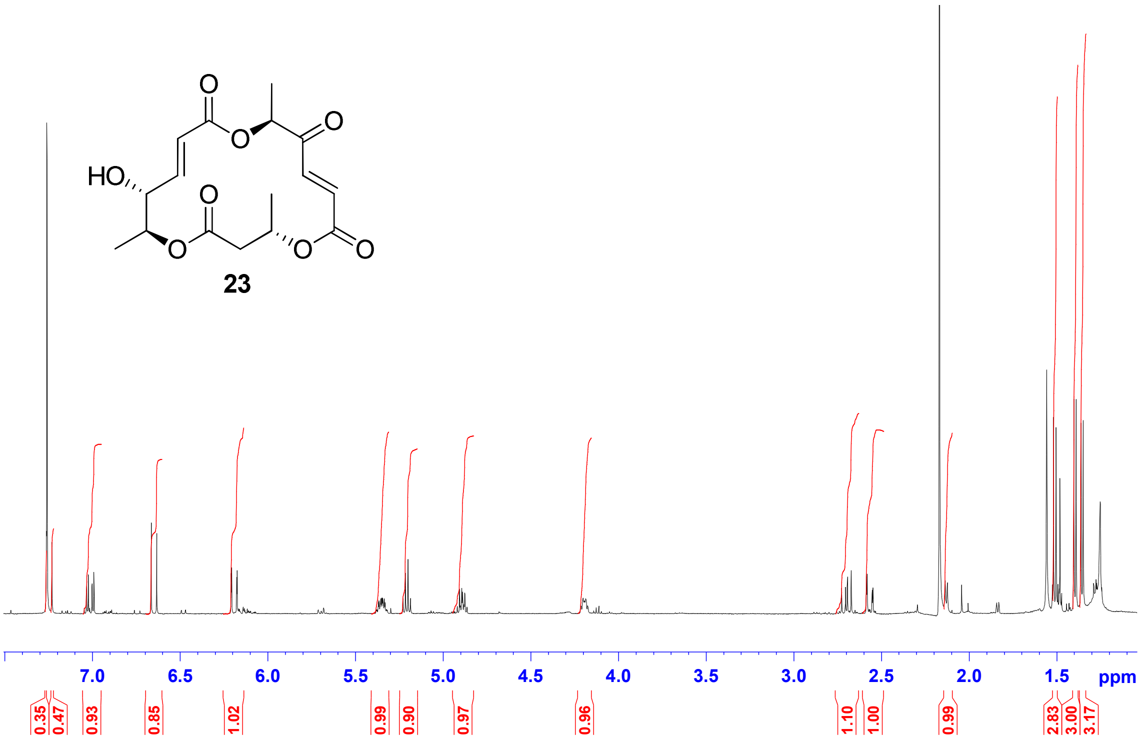
Supplementary Figure 59. ^{1}H NMR spectrum of macrosphelide B



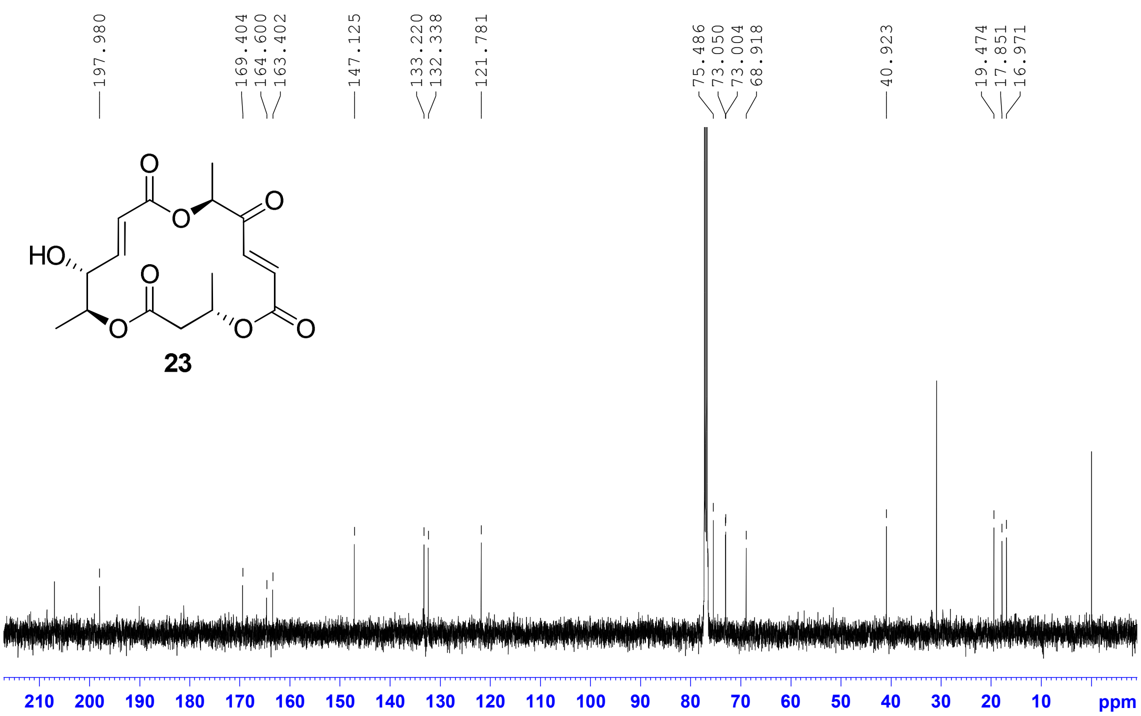
Supplementary Figure 60. ^{13}C NMR spectrum of macrosphelide B



Supplementary Figure 61. ^{1}H NMR spectrum of compound **23**[1]

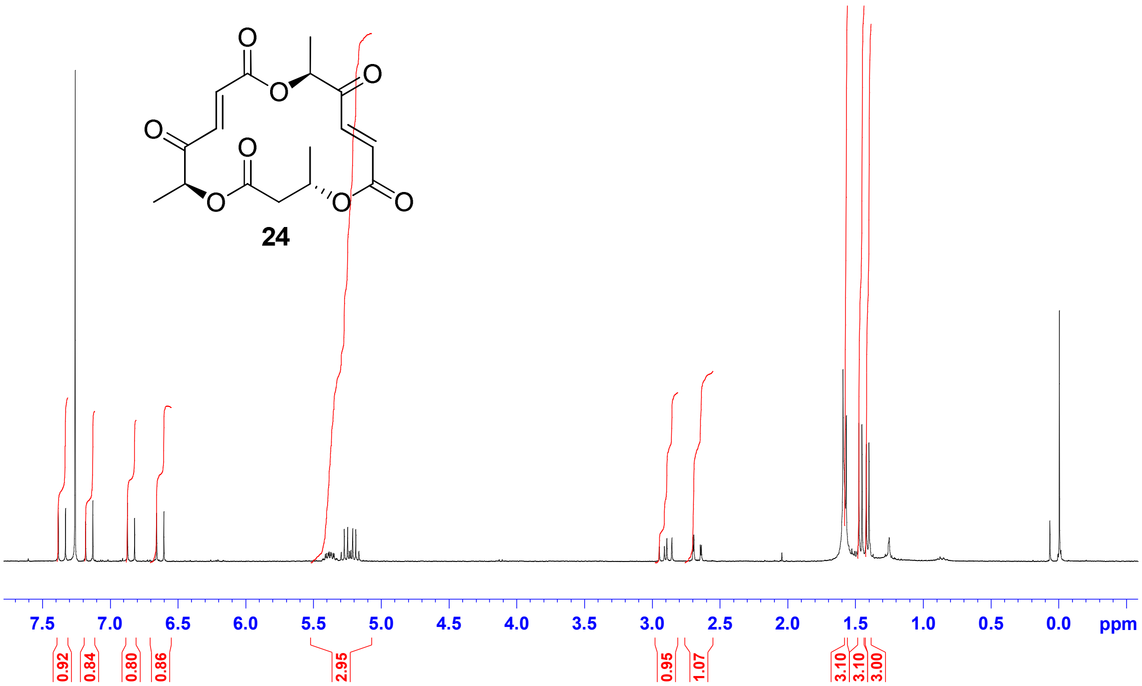


Supplementary Figure 62. ^{13}C NMR spectrum of epi-macrosphelide B **23**[1]

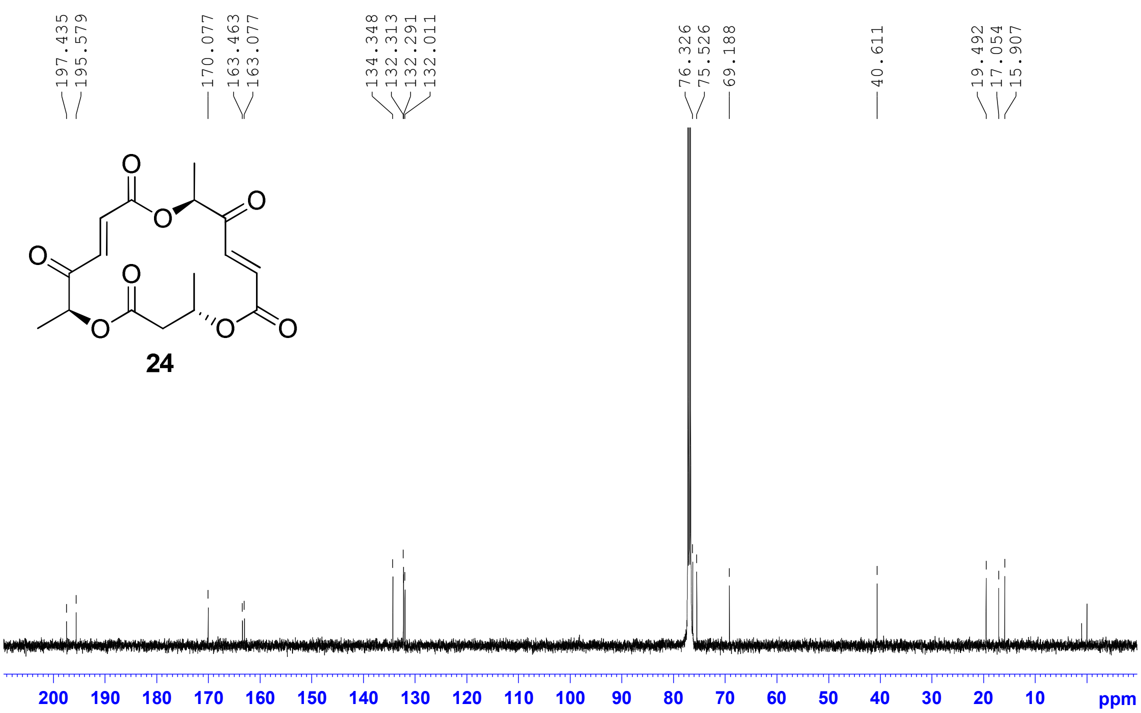


[1]both spectra containing acetone

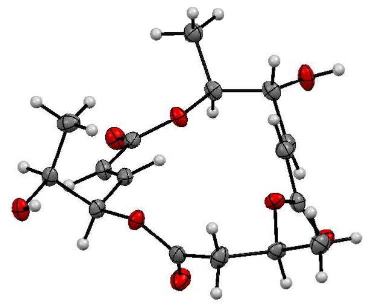
Supplementary Figure 63. ^{1}H NMR spectrum of compound **24**



Supplementary Figure 64. ^{13}C NMR spectrum of compound **24**



Crystal structure of macrosphelide D



Supplementary Figure 65. X-ray structure of macrosphelide D (ellipsoids are shown at a 50% probability level). Primary atom site location: structure-invariant direct methods; Secondary atom site location: difference Fourier map; Hydrogen site location: inferred from neighbouring sites; H-atom parameters constrained using typical riding models. Data collection: APEX2[7]; cell refinement: SAINT[7]; program(s) used to solve structure: SHELXS97[8]; program(s) used to refine: SHELXTL-Plus[8]. Remark: Absolute configuration determined by anomalous dispersion (CuK$_{\alpha}$-radiation).

Supplementary Table 10. Crystal data and structure refinement

Empirical formula	$C_{16}H_{22}O_8$
Formula weight	342.34
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system, space group	monoclinic, P 21
Unit cell dimensions	a = 5.5897(4) Å, alpha = 90 deg.
	b = 16.6860(11) Å, beta = 97.632(3)
	c = 9.1104(6) Å, gamma = 90 deg.
Volume	842.20(10) Å^3
Z; Calculated density	2; 1.350 mg/m^3
Absorption coefficient	0.923 mm^{-1}
F(000)	364
Crystal size	0.16 x 0.11 x 0.04 mm
Theta range for data collection	4.90 to 65.87 deg.
Limiting indices	-6<=h<=6, -19<=k<=19, -7<=l<=10
Reflections collected / unique	12539 / 2848 [R(int) = 0.0329]
Completeness to theta = 65.87	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. und min. transmission	0.7528 and 0.6675

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2848 / 1 / 229
Goodness-of-fit on F^2	1.047
Final R indices [I>2σ(I)]	R1 = 0.0224, wR2 = 0.0559
R indices (all data)	R1 = 0.0237, wR2 = 0.0565
Absolute structure parameter	0.03(11)
Extinction coefficient	0.0026(4)
Largest diff. peak and hole	0.140 and -0.145 e.A^{-3}

Supplementary Table 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for macrosphelide D. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U (eq)
O(1)	7410(2)	10319(1)	8782(1)	18(1)
C(1)	7011(2)	9384(1)	6719(1)	15(1)
O(2)	8683(2)	9634(1)	1632(1)	20(1)
C(2)	8086(2)	9121(1)	5366(1)	15(1)
O(3)	10147(2)	8581(1)	3020(1)	17(1)
C(3)	7986(2)	9553(1)	4142(1)	16(1)
O(4)	11490(2)	6932(1)	744(1)	23(1)
C(4)	8975(2)	9277(1)	2807(1)	15(1)
O(5)	5457(2)	6237(1)	4416(1)	23(1)
C(5)	11014(2)	8205 (1)	1753(1)	16(1)
O(6)	7633(2)	6789(1)	6437(1)	17(1)
C(6)	13439(3)	8555(1)	1539(2)	21(1)
O(7)	3929(2)	8168(1)	6096(1)	24(1)
C(7)	11230(2)	7310(1)	2120(2)	17(1)
O(8)	6890(2)	8706(1)	7707(1)	16(1)
C(8)	9124(3)	6980(1)	2797(2)	18(1)
C(9)	9255(2)	6880(1)	4244(2)	19(1)
C(10)	7223(2)	6589(1)	4987(2)	17(1)
C(11)	5708(2)	6645(1)	7343(2)	17(1)
C(12)	6372(3)	5919(1)	8301(2)	22(1)
C(13)	5561(3)	7406(1)	8234(2)	20(1)
C(14)	5311(2)	8122(1)	7223(1)	17(1)
C(15)	8574(2)	10019(1)	7588(1)	16(1)
C(16)	11109(2)	9725(1)	8123(2)	23(1)

Supplementary Table 12. Bond lengths [Å]

O(1)-C(15)	1.4298(16)	C(6)-H(6C)	0.9800
O(1)-H(1A)	0.80(2)	O(7)-C(14)	1.2026(17)
C(1)-O(8)	1.4537(16)	C(7)-C(8)	1.504(2)
C(1)-C(2)	1.5065(19)	C(7)-H(7)	1.0000
C(1)-C(15)	1.5261(18)	O(8)-C(14)	1.3480(17)
C(1)-H(1)	1.0000	C(8)-C(9)	1.321(2)
O(2)-C(4)	1.2171(17)	C(8)-H(8)	0.9500
C(2)-C(3)	1.323(2)	C(9)-C(10)	1.479(2)
C(2)-H(2)	0.9500	C(9)-H(9)	0.9500
O(3)-C(4)	1.3338(17)	C(11)-C(12)	1.509(2)
O(3)-C(5)	1.4524(16)	C(11)-C(13)	1.515(2)
C(3)-C(4)	1.4754(19)	C(11)-H(11)	1.0000
C(3)-H(3)	0.9500	C(12)-H(12A)	0.9800
O(4)-C(7)	1.4274(17)	C(12)-H(12B)	0.9800
O(4)-H(4A)	0.88(2)	C(12)-H(12C)	0.9800
O(5)-C(10)	1.2062(18)	C(13)-C(14)	1.505(2)
C(5)-C(6)	1.512(2)	C(13)-H(13A)	0.9900
C(5)-C(7)	1.532(2)	C(13)-H(13B)	0.9900
C(5)-H(5)	1.0000	C(15)-C(16)	1.518(2)
O(6)-C(10)	1.3519(17)	C(15)-H(15)	1.0000
O(6)-C(11)	1.4606(16)	C(16)-H(16A)	0.9800
C(6)-H(6A)	0.9800	C(16)-H(16B)	0.9800
C(6)-H(6B)	0.9800	C(16)-H(16C)	0.9800

Supplementary Table 13. Bond angles [deg]

C(15)-O(1)-H(1A)	108.0(15)	C(7)-C(8)-H(8)	119.6
O(8)-C(1)-C(2)	109.62(11)	C(8)-C(9)-C(10)	123.64(13)
O(8)-C(1)-C(15)	106.87(10)	C(8)-C(9)-H(9)	118.2
C(2)-C(1)-C(15)	111.33(11)	C(10)-C(9)-H(9)	118.2
O(8)-C(1)-H(1)	109.7	O(5)-C(10)-O(6)	124.36(12)
C(2)-C(1)-H(1)	109.7	O(5)-C(10)-C(9)	126.65(13)
C(15)-C(1)-H(1)	109.7	O(6)-C(10)-C(9)	108.98(12)
C(3)-C(2)-C(1)	123.62(13)	O(6)-C(11)-C(12)	108.43(11)
C(3)-C(2)-H(2)	118.2	O(6)-C(11)-C(13)	105.16(11)
C(1)-C(2)-H(2)	118.2	C(12)-C(11)-C(13)	112.89(11)

C(4)-O(3)-C(5)	118.02(10)	O(6)-C(11)-H(11)	110.1
C(2)-C(3)-C(4)	123.07(13)	C(12)-C(11)-H(11)	110.1
C(2)-C(3)-H(3)	118.5	C(13)-C(11)-H(11)	110.1
C(4)-C(3)-H(3)	118.5	C(11)-C(12)-H(12A)	109.5
C(7)-O(4)-H(4A)	105.5(12)	C(11)-C(12)-H(12B)	109.5
O(2)-C(4)-O(3)	124.00(12)	H(12A)-C(12)-H(12B)	109.5
O(2)-C(4)-C(3)	123.44(13)	C(11)-C(12)-H(12C)	109.5
O(3)-C(4)-C(3)	112.52(11)	H(12A)-C(12)-H(12C)	109.5
O(3)-C(5)-C(6)	109.54(11)	H(12B)-C(12)-H(12C)	109.5
O(3)-C(5)-C(7)	105.85(10)	C(14)-C(13)-C(11)	110.18(11)
C(6)-C(5)-C(7)	111.03(11)	C(14)-C(13)-H(13A)	109.6
O(3)-C(5)-H(5)	110.1	C(11)-C(13)-H(13A)	109.6
C(6)-C(5)-H(5)	110.1	C(14)-C(13)-H(13B)	109.6
C(7)-C(5)-H(5)	110.1	C(11)-C(13)-H(13B)	109.6
C(10)-O(6)-C(11)	118.02(10)	H(13A)-C(13)-H(13B)	108.1
C(5)-C(6)- H(6A)	109.5	O(7)-C(14)-O(8)	123.44(13)
C(5)-C(6)-H(6B)	109.5	O(7)-C(14)-C(13)	124.79(13)
H(6A)-C(6)-H(6B)	109.5	O(8)-C(14)-C(13)	111.74(11)
C(5)-C(6)-H(6C)	109.5	O(1)-C(15)-C(16)	111.64(11)
H(6A)-C(6)-H(6C)	109.5	O(1)-C(15)-C(1)	110.51(11)
H(6B)-C(6)-H(6C)	109.5	C(16)-C(15)-C(1)	112.79(12)
O(4)-C(7)-C(8)	112.04(11)	O(1)-C(15)-H(15)	107.2
O(4)-C(7)-C(5)	104.65(11)	C(16)-C(15)-H(15)	107.2
C(8)-C(7)-C(5)	113.78(11)	C(1)-C(15)-H(15)	107.2
O(4)-C(7)-H(7)	108.7	C(15)-C(16)-H(16A)	109.5
C(8)-C(7)-H(7)	108.7	C(15)-C(16)-H(16B)	109.5
C(5)-C(7)-H(7)	108.7	H(16A)-C(16)-H(16B)	109.5
C(14)-O(8)-C(1)	116.27(10)	C(15)-C(16)-H(16C)	109.5
C(9)-C(8)-C(7)	120.85(13)	H(16A)-C(16)-H(16C)	109.5
C(9)-C(8)-H(8)	119.6	H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms

Supplementary Table 14. Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	**U22**	**U33**	**U23**	**U13**	**U12**
O(1)	27(1)	16(1)	12(1)	-1(1)	6(1)	2(1)

C(1)	18(1)	13(1)	14(1)	4(1)	5(1)	0(1)
O(2)	26(1)	21(1)	16(1)	3(1)	5(1)	4(1)
C(2)	14(1)	14(1)	17(1)	-3(1)	2(1)	0(1)
O(3)	22(1)	17(1)	12(1)	0(1)	4(1)	5(1)
C(3)	19(1)	13(1)	17(1)	-1(1)	3(1)	2(1)
O(4)	38(1)	15(1)	18(1)	0(1)	12(1)	4(1)
C(4)	15(1)	14(1)	16(1)	-1(1)	1(1)	-1(1)
O(5)	24(1)	26(1)	18(1)	-5(1)	3(1)	-7(1)
C(5)	19(1)	18(1)	10(1)	-3(1)	4(1)	1(1)
O(6)	17(1)	20(1)	14(1)	-1(1)	4(1)	-3(1)
C(6)	22(1)	20(1)	22(1)	-3(1)	6(1)	-1(1)
O(7)	24(1)	20(1)	26(1)	1(1)	-4(1)	-2(1)
C(7)	20(1)	19(1)	13(1)	-1(1)	3(1)	3(1)
O(8)	20(1)	14(1)	14(1)	1(1)	4(1)	-3(1)
C(8)	21(1)	14(1)	18(1)	0(1)	4(1)	2(1)
C(9)	20(1)	17(1)	19(1)	-1(1)	4(1)	2(1)
C(10)	21(1)	13(1)	16(1)	2(1)	3(1)	2(1)
C(11)	17(1)	18(1)	17(1)	2(1)	6(1)	-3(1)
C(12)	25(1)	19(1)	24(1)	4(1)	5(1)	-2(1)
C(13)	26(1)	17(1)	17(1)	-1(1)	6(1)	-5(1)
C(14)	18(1)	15(1)	19(1)	-3(1)	8(1)	0(1)
C(15)	20(1)	14(1)	14(1)	-2(1)	8(1)	-2(1)
C(16)	19(1)	29(1)	21(1)	-5(1)	4(1)	-3(1)

Supplementary Table 15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3)

	x	y	z	U (eq)
H(1A)	7800(30)	10043(13)	9490(20)	31(5)
H(1)	5352	9602	6416	18
H(2)	8880	8617	5393	18
H(3)	7242	10066	4122	20
H(4A)	11970(30)	6439(13)	970(20)	33(5)
H(5)	9830	8290	842	19
H(6A)	13251	9126	1298	32
H(6B)	14074	8275	728	32
H(6C)	14563	8492	2453	32
H(7)	12738	7220	2823	21

H(8)	7682	6841	2176	21
H(9)	10735	7003	4840	22
H(11)	4145	6550	6695	20
H(12A)	6528	5452	7669	34
H(12B)	5110	5819	8928	34
H(12C)	7911	6016	8926	34
H(13A)	4155	7376	8789	23
H(13B)	7036	7461	8960	23
H(15)	8726	10477	6899	19
H(16A)	12093	10172	8561	35
H(16B)	11831	9507	7284	35
H(16C)	11041	9305	8868	35

Supplementary Table 16. Torsion angles [deg]

O(8)-C(1)-C(2)-C(3)	165.80(12)	C(7)-C(8)-C(9)-C(10)	177.53(13)
C(15)-C(1)-C(2)-C(3)	-76.17(17)	C(11)-O(6)-C(10)-O(5)	-6.59(19)
C(1)-C(2)-C(3)-C(4)	-177.90(12)	C(11)-O(6)-C(10)-C(9)	172.67(11)
C(5)-O(3)-C(4)-O(2)	-3.47(19)	C(8)-C(9)-C(10)-O(5)	18.5(2)
C(5)-O(3)-C(4)-C(3)	174.32(11)	C(8)-C(9)-C(10)-O(6)	-160.76(13)
C(2)-C(3)-C(4)-O(2)	172.47(13)	C(10)-O(6)-C(11)-C(12)	104.83(13)
C(2)-C(3)-C(4)-O(3)	-5.34(19)	C(10)-O(6)-C(11)-C(13)	-134.17(12)
C(4)-O(3)-C(5)-C(6)	84.44(14)	O(6)-C(11)-C(13)-C(14)	52.44(14)
C(4)-O(3)-C(5)-C(7)	-155.79(11)	C(12)-C(11)-C(13)-C(14)	170.47(12)
O(3)-C(5)-C(7)-O(4)	166.02(10)	C(1)-O(8)-C(14)-O(7)	-5.40(18)
C(6)-C(5)-C(7)-O(4)	-75.19(13)	C(1)-O(8)-C(14)-C(13)	172.65(10)
O(3)-C(5)-C(7)-C(8)	43.40(14)	C(11)-C (13)-C(14)-O(7)	46.98(18)
C(6)-C(5)-C(7)-C(8)	162.19(11)	C(11)-C(13)-C(14)-O(8)	-131.04(12)
C(2)-C(1)-O (8)-C(14)	-68.37(14)	O(8)-C(1)-C(15)-O(1)	-66.07(13)
C(15)-C(1)-O(8)-C(14)	170.86(10)	C(2)-C(1)-C(15)-O(1)	174.25(11)
O(4)-C(7)-C(8)-C(9)	142.33(14)	O(8)-C(1)-C(15)-C(16)	59.68(13)
C(5)-C(7)-C(8)-C(9)	-99.20(15)	C(2)-C(1)-C(15)-C(16)	-59.99(14)

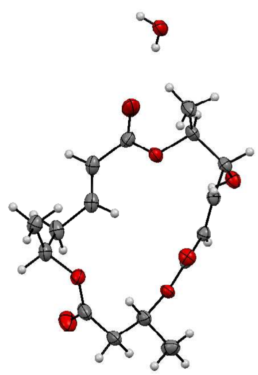
Symmetry transformations used to generate equivalent atoms.

Supplementary Table 17. Hydrogen bonds [Å und deg.]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...O(2)#1	0.80(2)	2.06(2)	2.840(1)	164(2)
O(4)-H(4A)...O(1)#2	0.88(2)	1.91(2)	2.783(2)	170(2)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z+1; #2 -x+2,y-1/2,-z+1

Crystal structure of macrosphelide G



Supplementary Figure 66. X-ray structure of macrosphelide G (ellipsoids are shown at a 50% probability level). Primary atom site location: structure-invariant direct methods; Secondary atom site location: difference Fourier map; Hydrogen site location: inferred from neighbouring sites; H-atom parameters constrained using typical riding models. Data collection: APEX2[7]; cell refinement: SAINT[7]; program(s) used to solve structure: SHELXS97[8]; program(s) used to refine: SHELXTL-Plus[8]. Remark: Absolute configuration determined by anomalous dispersion (CuK$_\alpha$-radiation).

Supplementary Table 18. Crystal data and structure refinement

Empirical formula	C16 H22.25 O7.13
Formula weight	328.59
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system, space group	orthorhombic, P 21 21 21
Unit cell dimensions	a = 5.8884(7) Å, alpha = 90 deg.
	b = 14.8186(16) Å, beta = 90 deg.
	c = 19.816(2) Å, gamma = 90 deg.
Volume	1729.1(3) Å^3

Z; Calculated density	4; 1.262 mg/m^3
Absorption coefficient	0.837 mm^{-1}
F(000)	701
Crystal size	0.10 x 0.08 x 0.03 mm
Theta range for data collection	3.72 to 66.07 deg.
Limiting indices	-6<=h<=6, -9<=k<=17, -21<=l<=23
Reflections collected / unique	11338 / 2918 [R(int) = 0.0529]
Completeness to theta = 66.07	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. und min. transmission	0.7528 and 0.6669
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2918 / 10 / 230
Goodness-of-fit on F^2	1.019
Final R indices [I>2σ(I)]	R1 = 0.0307, wR2 = 0.0644
R indices (all data)	R1 = 0.0414, wR2 = 0.0675
Absolute structure parameter	0.01(17)
Largest diff. peak and hole	0.147 and -0.151 e.A^{-3}

Supplementary Table 19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for macrosphelide G. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	**y**	**z**	**U (eq)**
O(1)	4928(2)	3847(1)	3576(1)	23(1)
C(1)	6620(3)	4385(1)	3362(1)	25(1)
O(2)	7984(2)	4727(1)	3738(1)	41(1)
C(2)	6579(3)	4513(1)	2626(1)	26(1)
O(3)	1612(2)	3390(1)	1281(1)	25(1)
C(3)	5348(3)	4023(1)	2203(1)	26(1)
O(4)	3674(3)	2571(1)	541(1)	41(1)
C(4)	5349(3)	4117(1)	1451(1)	29(1)
O(5)	679(2)	1792(1)	2217(1)	21(1)
C(5)	2992(3)	4189(1)	1137(1)	25(1)
O(6)	-1840(2)	2339(1)	2969(1)	26(1)
C(6)	1659(3)	4978(1)	1402(1)	28(1)
O(7)	5828(2)	2081(1)	4173(1)	26(1)
C(7)	2078(4)	2637(1)	923(1)	30(1)
C(8)	346(4)	1904(1)	1025(1)	30(1)

C(9)	-1000(3)	1910(1)	1677(1)	25(1)
C(10)	-2749(3)	1165(1)	1705(1)	31(1)
C(11)	60(3)	2069(1)	2833(1)	20(1)
C(12)	1998(3)	2046(1)	3304(1)	20(1)
C(13)	1972(3)	2512(1)	3869(1)	22(1)
C(14)	3983(3)	2664(1)	4324(1)	21(1)
C(15)	4726(3)	3654(1)	4294(1)	25(1)
C(16)	3080(4)	4314(1)	4611(1)	33(1)
O(1X)	6732(19)	5749(7)	5107(5)	29(2)

Supplementary Table 20. Bond lengths [Å].

O(1)-C(1)	1.344(2)	C(7)-C(8)	1.505(3)
O(1)-C(15)	1.456(2)	C(8)-C(9)	1.516(3)
C(1)-O(2)	1.208(2)	C(8)-H(8A)	0.9900
C(1)-C(2)	1.470(3)	C(8)-H(8B)	0.9900
C(2)-C(3)	1.325(3)	C(9)-C(10)	1.510(3)
C(2)-H(2)	0.9500	C(9)-H(9)	1.0000
O(3)-C(7)	1.350(2)	C(10)-H(10A)	0.9800
O(3)-C(5)	1.465(2)	C(10)-H(10B)	0.9800
C(3)-C(4)	1.498(2)	C(10)-H(10C)	0.9800
C(3)-H(3)	0.9500	C(11)-C(12)	1.474(2)
O(4)-C(7)	1.210(2)	C(12)-C(13)	1.316(2)
C(4)-C(5)	1.525(3)	C(12)-H(12)	0.9500
C(4)-H(4A)	0.9900	C(13)-C(14)	1.506(2)
C(4)-H(4B)	0.9900	C(13)-H(13)	0.9500
O(5)-C(11)	1.338(2)	C(14)-C(15)	1.532(3)
O(5)-C(9)	1.468(2)	C(14)-H(14)	1.0000
C(5)-C(6)	1.503(2)	C(15)-C(16)	1.514(2)
C(5)-H(5)	1.0000	C(15)-H(15)	1.0000
O(6)-C(11)	1.218(2)	C(16)-H(16A)	0.9800
C(6)-H(6A)	0.9800	C(16)-H(16B)	0.9800
C(6)-H(6B)	0.9800	C(16)-H(16C)	0.9800
C(6)-H(6C)	0.9800	O(1X)-H(1X)	0.778(11)
O(7)-C(14)	1.421(2)	O(1X)-H(2X)	0.777(10)
O(7)-H(7)	0.83(2)		

Supplementary Table 21. Bond angles [deg]

C(1)-O(1)-C(15)	119.04(14)	O(5)-C(9)-C(10)	110.24(14)
O(2)-C(1)-O(1)	123.18(18)	O(5)-C(9)-C(8)	105.59(15)
O(2)-C(1)-C(2)	124.64(18)	C(10)-C(9)-C(8)	112.53(15)
O(1)-C(1)-C(2)	112.18(16)	O(5)-C(9)-H(9)	109.5
C(3)-C(2)-C(1)	124.45(17)	C(10)-C(9)-H(9)	109.5
C(3)-C(2)-H(2)	117.8	C(8)-C(9)-H(9)	109.5
C(1)-C(2)-H(2)	117.8	C(9)-C(10)-H(10A)	109.5
C(7)-O(3)-C(5)	116.86(14)	C(9)-C(10)-H(10B)	109.5
C(2)-C(3)-C(4)	125.40(18)	H(10A)-C(10)-H(10B)	109.5
C(2)-C(3)-H(3)	117.3	C(9)-C(10)-H(10C)	109.5
C(4)-C(3)-H(3)	117.3	H(10A)-C(10)-H(10C)	109.5
C(3)-C(4)-C(5)	114.39(15)	H(10B)-C(10)-H(10C)	109.5
C(3)-C(4)-H(4A)	108.7	O(6)-C(11)-O(5)	123.45(16)
C(5)-C(4)-H(4A)	108.7	O(6)-C(11)-C(12)	125.42(16)
C(3)-C(4)-H(4B)	108.7	O(5)-C(11)-C(12)	111.06(15)
C(5)-C(4)-H(4B)	108.7	C(13)-C(12)-C(11)	121.15(17)
H(4A)-C(4)-H(4B)	107.6	C(13)-C(12)-H(12)	119.4
C(11)-O(5)-C(9)	116.47(14)	C(11)-C(12)-H(12)	119.4
O(3)-C(5)-C(6)	105.71(14)	C(12)-C(13)-C(14)	125.41(17)
O(3)-C(5)-C(4)	111.59(14)	C(12)-C(13)-H(13)	117.3
C(6)-C(5)-C(4)	112.76(16)	C(14)-C(13)-H(13)	117.3
O(3)-C(5)-H(5)	108.9	O(7)-C(14)-C(13)	112.58(14)
C(6)-C(5)-H(5)	108.9	O(7)-C(14)-C(15)	110.85(16)
C(4)-C(5)-H(5)	108.9	C(13)-C(14)-C(15)	110.15(14)
C(5)-C(6)-H(6A)	109.5	O(7)-C(14)-H(14)	107.7
C(5)-C(6)-H(6B)	109.5	C(13)-C(14)-H(14)	107.7
H(6A)-C(6)-H(6B)	109.5	C(15)-C(14)-H(14)	107.7
C(5)-C(6)-H(6C)	109.5	O(1)-C(15)-C(16)	109.37(14)
H(6A)-C(6)-H(6C)	109.5	O(1)-C(15)-C(14)	104.47(14)
H(6B)-C(6)-H(6C)	109.5	C(16)-C(15)-C(14)	114.77(16)
C(14)-O(7)-H(7)	110.3(16)	O(1)-C(15)-H(15)	109.4
O(4)-C(7)-O(3)	123.65(18)	C(16)-C(15)-H(15)	109.4
O(4)-C(7)-C(8)	123.48(17)	C(14)-C(15)-H(15)	109.4
O(3)-C(7)-C(8)	112.83(17)	C(15)-C(16)-H(16A)	109.5
C(7)-C(8)-C(9)	117.70(15)	C(15)-C(16)-H(16B)	109.5

C(7)-C(8)-H(8A)	107.9	H(16A)-C(16)-H(16B)	109.5
C(9)-C(8)-H(8A)	107.9	C(15)-C(16)-H(16C)	109.5
C(7)-C(8)-H(8B)	107.9	H(16A)-C(16)-H(16C)	109.5
C(9)-C(8)-H(8B)	107.9	H(16B)-C(16)-H(16C)	109.5
H(8A)-C(8)-H(8B)	107.2	H(1X)-O(1X)-H(2X)	108(3)

Symmetry transformations used to generate equivalent atoms.

Supplementary Table 22. Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a^{*2} U11 + ... + 2 h k a* b* U12].

	U11	**U22**	**U33**	**U23**	**U13**	**U12**
O(1)	24(1)	29(1)	17(1)	1(1)	0(1)	-5(1)
C(1)	25(1)	19(1)	31(1)	3(1)	-3(1)	-2(1)
O(2)	44(1)	40(1)	39(1)	8(1)	-13(1)	-20(1)
C(2)	22(1)	26(1)	29(1)	8(1)	2(1)	-1(1)
O(3)	31(1)	20(1)	25(1)	2(1)	3(1)	1(1)
C(3)	23(1)	26(1)	28(1)	8(1)	4(1)	3(1)
O (4)	59(1)	38(1)	27(1)	0(1)	15(1)	7(1)
C(4)	26(1)	34(1)	26(1)	7(1)	4(1)	4(1)
O(5)	24(1)	23(1)	16(1)	-1(1)	-4(1)	1(1)
C(5)	27(1)	26(1)	22(1)	7(1)	3(1)	0(1)
O(6)	22(1)	29(1)	26(1)	-1(1)	1(1)	3(1)
C(6)	26(1)	26(1)	33(1)	4(1)	1(1)	-2(1)
O(7)	26(1)	28(1)	22(1)	2(1)	1(1)	6(1)
C(7)	43(1)	28(1)	17(1)	3(1)	-1(1)	5(1)
C(8)	48(1)	24(1)	19(1)	0(1)	-8(1)	2(1)
C(9)	31(1)	23(1)	22(1)	2(1)	-9(1)	2(1)
C(10)	31(1)	28(1)	33(1)	-4(1)	-10(1)	0(1)
C(11)	28(1)	14(1)	19(1)	1(1)	-1(1)	-1(1)
C(12)	20(1)	20(1)	22(1)	2(1)	-1(1)	1(1)
C(13)	20(1)	25(1)	21(1)	3(1)	4(1)	0(1)
C(14)	23(1)	25(1)	16(1)	0(1)	2(1)	1(1)
C(15)	31(1)	28(1)	15(1)	2(1)	-4(1)	0(1)
C(16)	52(1)	26(1)	21(1)	0(1)	4(1)	6(1)
O(1X)	35(4)	33(4)	19(4)	0(3)	2(4)	-10(4)

Supplementary Table 23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3)

	x	y	z	U (eq)
H(2)	7498	4978	2442	31
H(3)	4384	3576	2393	31
H(4A)	6135	3588	1254	34
H(4B)	6231	4661	1328	34
H(5)	3156	4253	636	30
H(6A)	185	5006	1173	42
H(6B)	2501	5537	1317	42
H(6C)	1421	4906	1888	42
H(7)	6410(40)	2221(16)	3804(12)	51(8)
H(8A)	1139	1316	993	37
H(8B)	-747	1932	646	37
H(9)	-1771	2507	1731	30
H(10A)	-1991	579	1661	46
H(10B)	-3835	1242	1334	46
H(10C)	-3556	1192	2137	46
H(12)	3289	1689	3197	24
H(13)	568	2774	4000	26
H(14)	3488	2535	4797	25
H(15)	6248	3719	4512	29
H(16A)	3748	4920	4610	49
H(16B)	2764	4130	5077	49
H(16C)	1662	4320	4352	49
H(1X)	6900(300)	6250(20)	5000(60)	43
H(2X)	7140(50)	5450(70)	4810(40)	43

Supplementary Table 24. Torsion angles [deg]

C(15)-O(1)-C(1)-O(2)	-0.7(3)	C(7)-C(8)-C(9)-O(5)	-62.22(19)
C(15)-O(1)-C(1)-C(2)	-179.84(15)	C(7)-C(8)-C(9)-C(10)	177.47(16)
O(2)-C(1)-C(2)-C(3)	167.86(19)	C(9)-O(5)-C(11)-O(6)	5.8(2)
O(1)-C(1)-C(2)-C(3)	-13.0(3)	C(9)-O(5)-C(11)-C(12)	-171.16(13)
C(1)-C(2)-C(3)-C(4)	-177.42(17)	O(6)-C(11)-C(12)-C(13)	-16.0(3)
C(2)-C(3)-C(4)-C(5)	-130.2(2)	O(5)-C(11)-C(12)-C(13)	160.88(16)
C(7)-O(3)-C(5)-C(6)	160.61(15)	C(11)-C(12)-C(13)-C(14)	-169.04(15)
C(7)-O(3)-C(5)-C(4)	-76.46(19)	C(12)-C(13)-C(14)-O(7)	-14.0(2)

C(3)-C(4)-C(5)-O(3)	-60.1(2)	C(12)-C(13)-C(14)-C(15)	110.32(19)
C(3)-C(4)-C(5)-C(6)	58.7(2)	C(1)-O(1)-C(15)-C(16)	94.30(19)
C(5)-O(3)-C(7)-O(4)	6.8(3)	C(1)-O(1)-C(15)-C(14)	-142.37(15)
C(5)-O(3)-C(7)-C(8)	-170.77(14)	O(7)-C(14)-C(15)-O(1)	74.77(18)
O(4)-C(7)-C(8)-C(9)	157.54(18)	C(13)-C(14)-C(15)-O(1)	-50.51(19)
O(3)-C(7)-C(8)-C(9)	-24.9(2)	O(7)-C(14)-C(15)-C(16)	-165.47(15)
C(11)-O(5)-C(9)-C(10)	-79.76(18)	C(13)-C(14)-C(15)-C(16)	69.2(2)
C(11)-O(5)-C(9)-C(8)	158.44(14)		

Symmetry transformations used to generate equivalent atoms.

Supplementary Literature

[1] Takamatsu, S.; Hiraoka, H.; Kim, Y.-P.; Hayashi, M.; Natori, M.; Komiyama, K.; Ōmura, S. *J. Antibiot.***1997**, *50*, 878-880.

[2] Yamada, T. ; Minoura, K.; Tanaka, R.; Numata, A. *J. Antibiot.***2007**, *60*, 370-375.

[3] Takamatsu, S.; Kim, Y.-P.; Hayashi, M.; Hiraoka, H.; Natori, M.; Komiyama, K.; Ōmura, S. *J. Antibiot.* **1996**, *49*, 95-98.

[4] Numata, A.; Iritani, M.; Ymada, T.; Minoura, K.; Matsumura, E.; Yamori, T.; Tsuruo, T. *Tetrahedron Lett.* **1997**, *38*, 8215-8218.

[5] Yamada, T.; Iritani, M.; Doi, M.; Minoura, K.; Ito, T.; Numata, A. *J. Chem. Soc., Perkin Trans. 1* **2001**, *3046*-3053.

[6] G. V. M. Sharma, K. V. Babu *Tetrahedron: Asymmetry* **2007**, *18*, 2175–2184.

[7] Bruker *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

[8] Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.