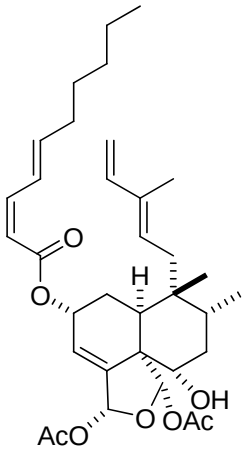
Clerodane diterpenes from *Casearia arguta* that act as synergistic TRAIL sensitizers

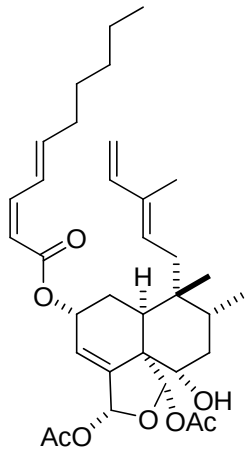
Emily L. Whitson, Cheryl L. Thomas, Curtis J. Henrich, Thomas J. Sayers, James B. McMahon, and Tawnya C. McKee

Supporting Info

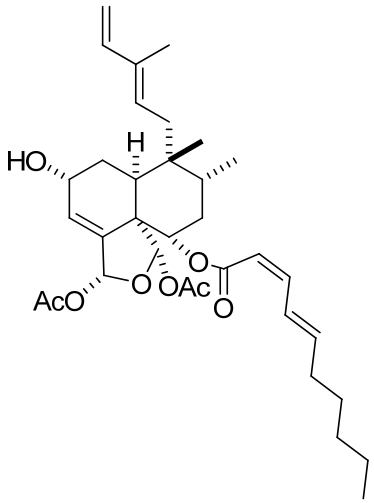
^{1}H NMR Spectrum of Argutin A (**1**) in $CDCl_3$



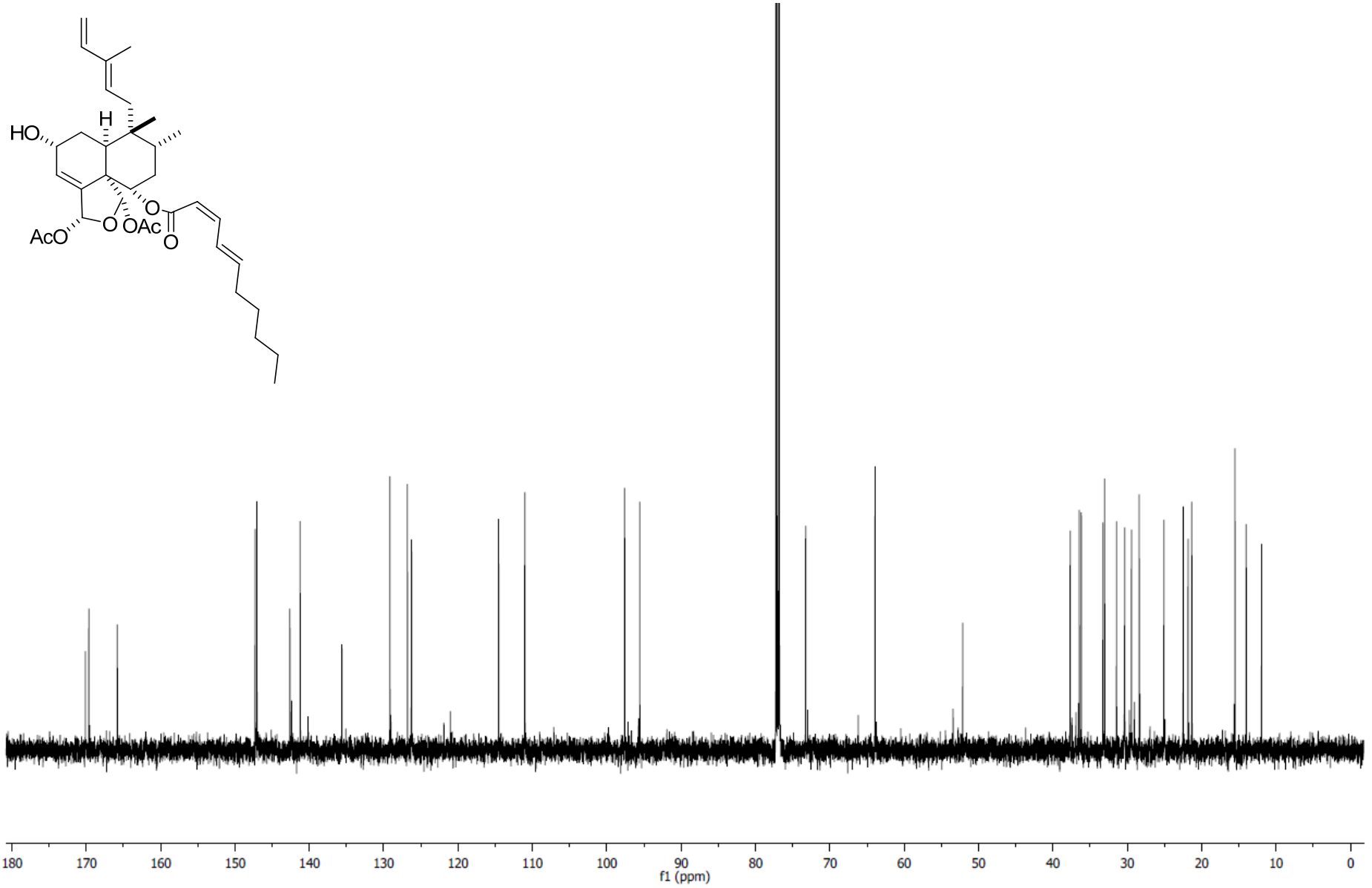
^{13}C NMR Spectrum of Argutin A (**1**) in $CDCl_3$



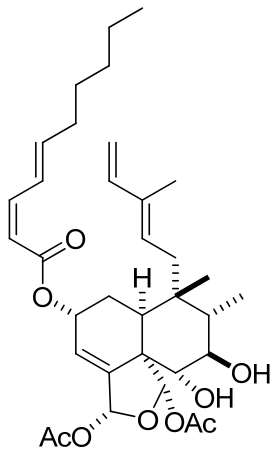
^{1}H NMR Spectrum of Argutin B (**2**) in $CDCl_3$



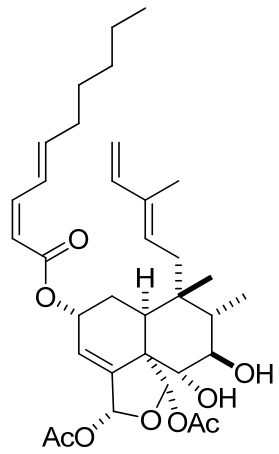
^{13}C NMR Spectrum of Argutin B (**2**) in $CDCl_3$

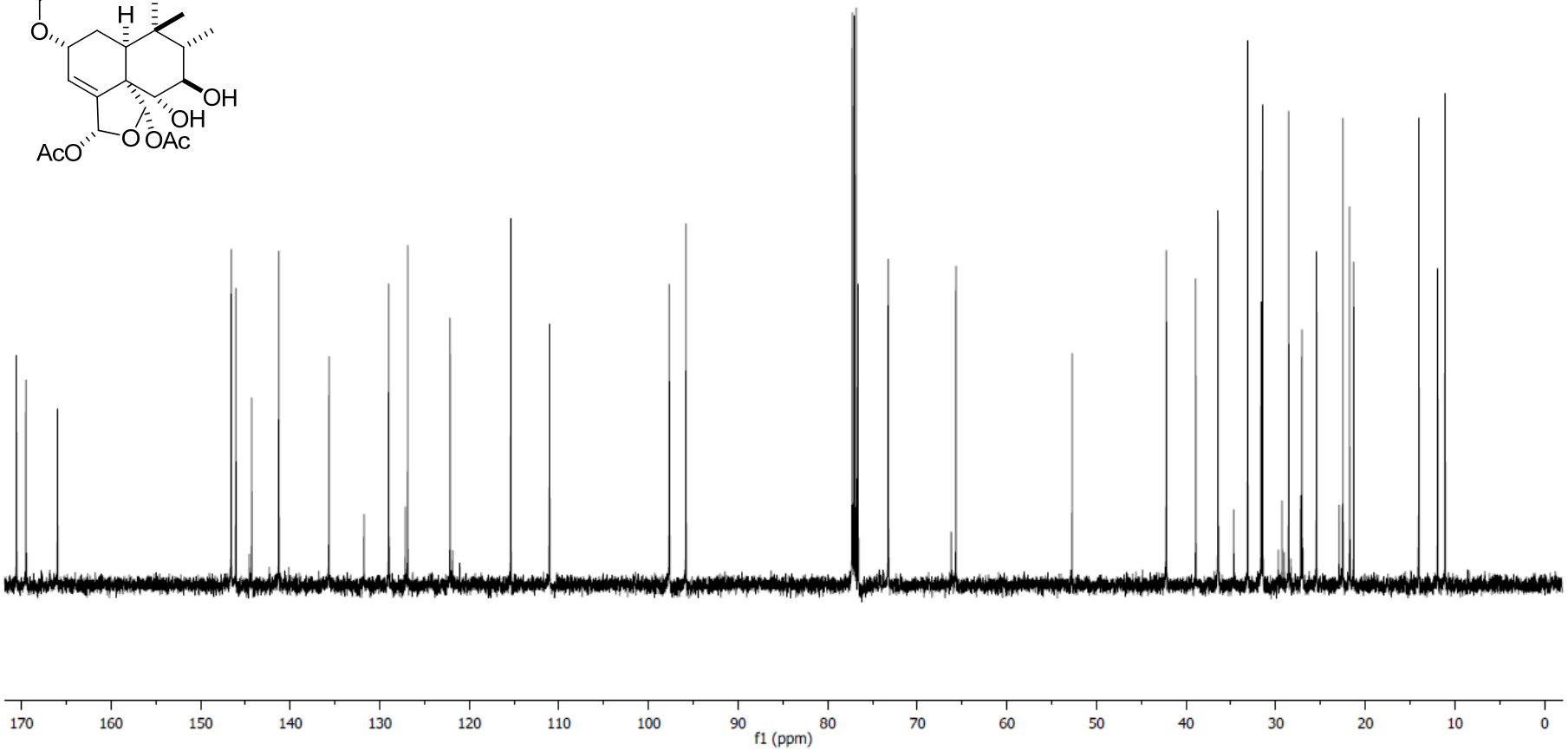


^{1}H NMR Spectrum of Argutin C (**3**) in $CDCl_3$

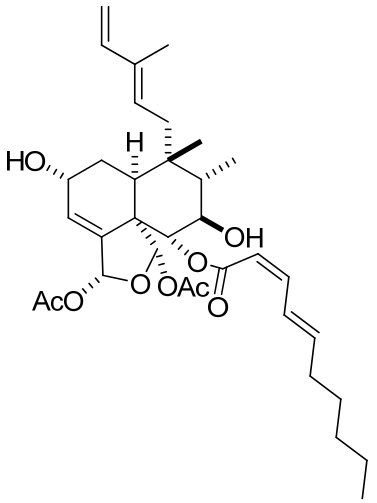


^{13}C NMR Spectrum of Argutin C (**3**) in $CDCl_3$

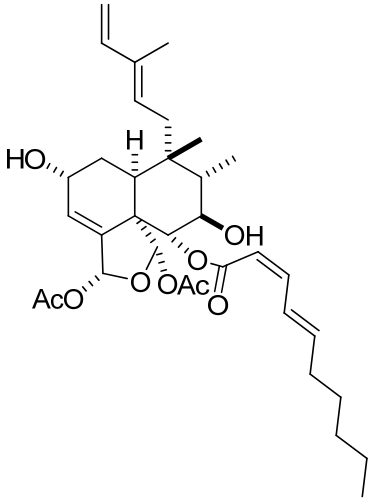




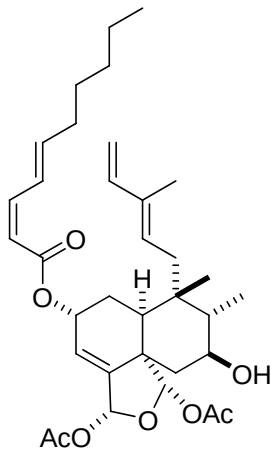
^{1}H NMR Spectrum of Argutin D (**4**) in $CDCl_3$



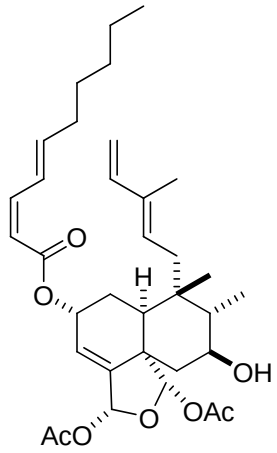
^{13}C NMR Spectrum of Argutin D (**4**) in $CDCl_3$



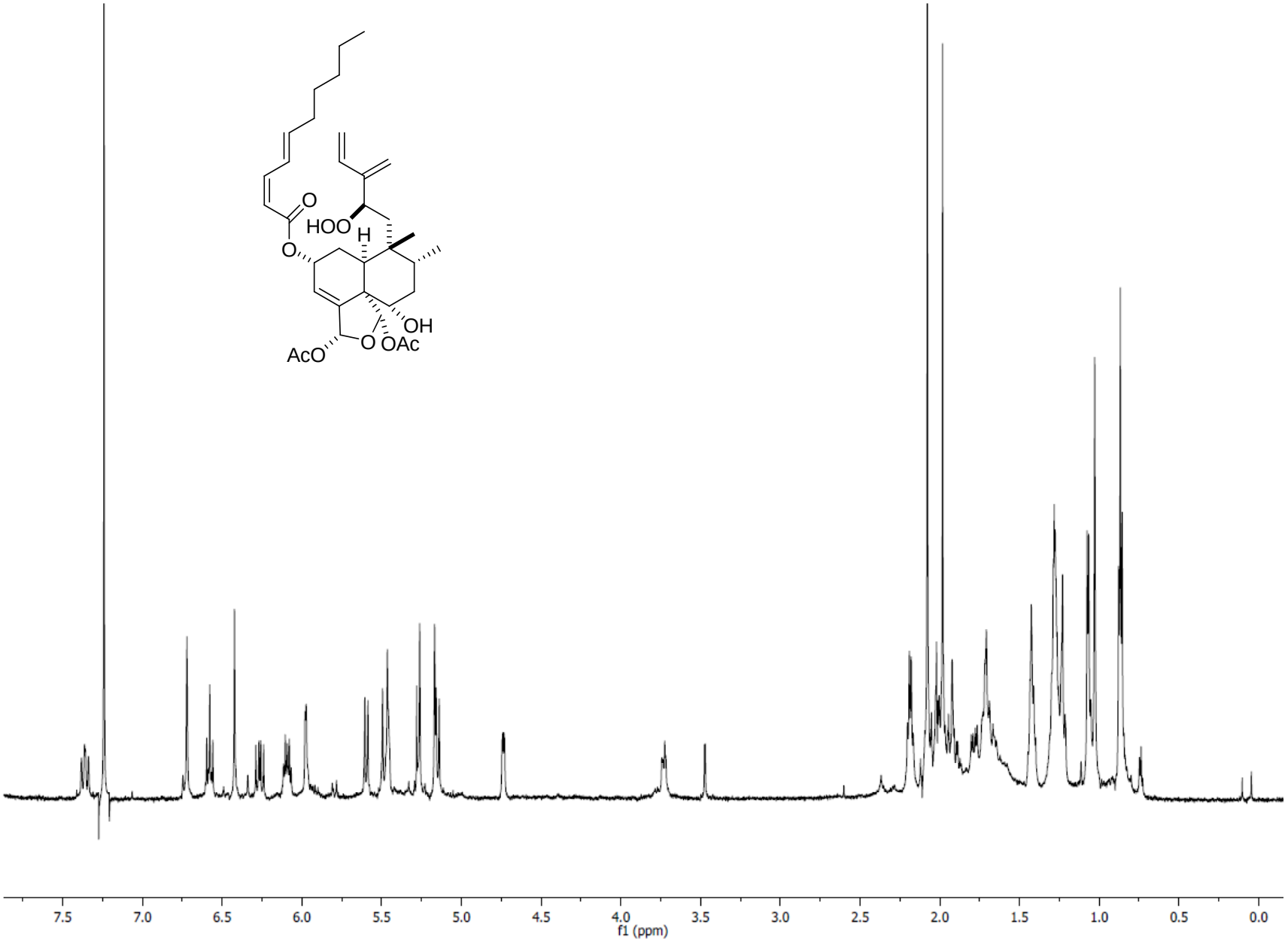
^{1}H NMR Spectrum of Argutin E (**5**) in $CDCl_3$



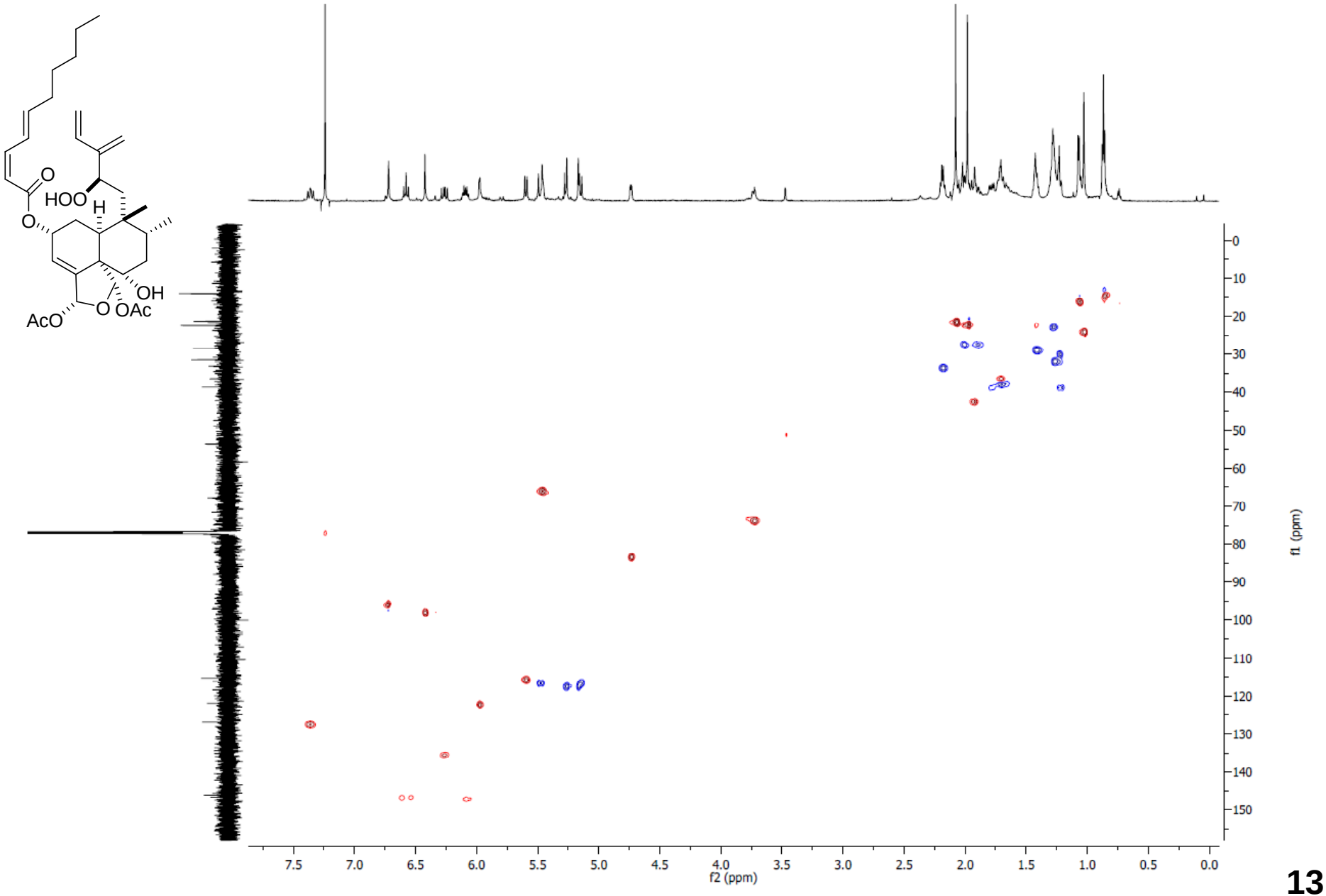
^{13}C NMR Spectrum of Argutin E (**5**) in $CDCl_3$



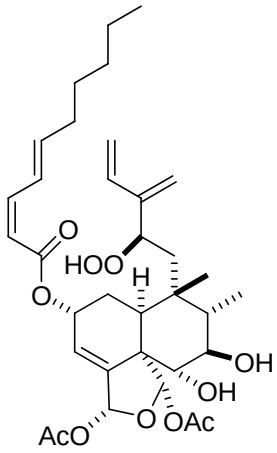
^{1}H NMR Spectrum of Argutin F (**6**) in $CDCl_3$



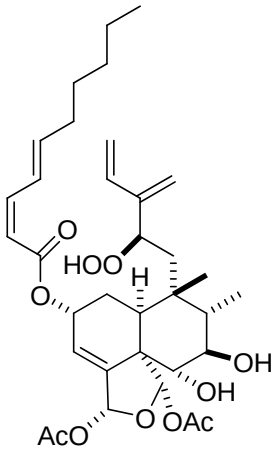
HSQC Spectrum of Argutin F (**6**) in $CDCl_3$



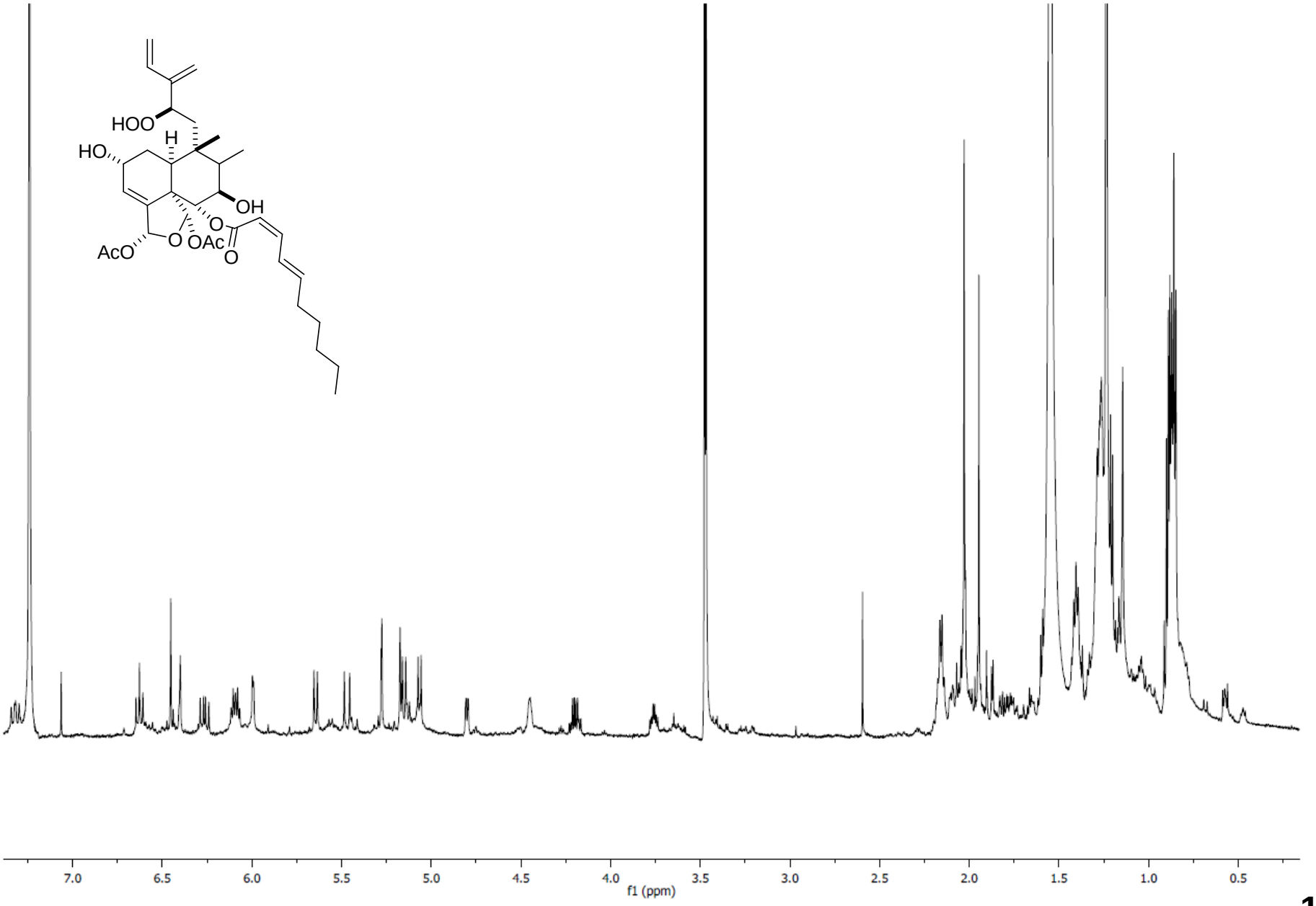
^{1}H NMR Spectrum of Argutin G (**7**) in $CDCl_3$



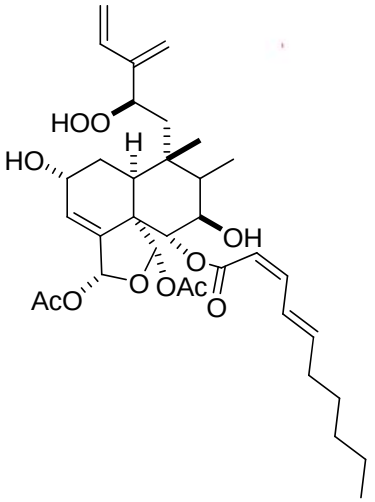
HSQC Spectrum of Argutin G (**7**) in $CDCl_3$



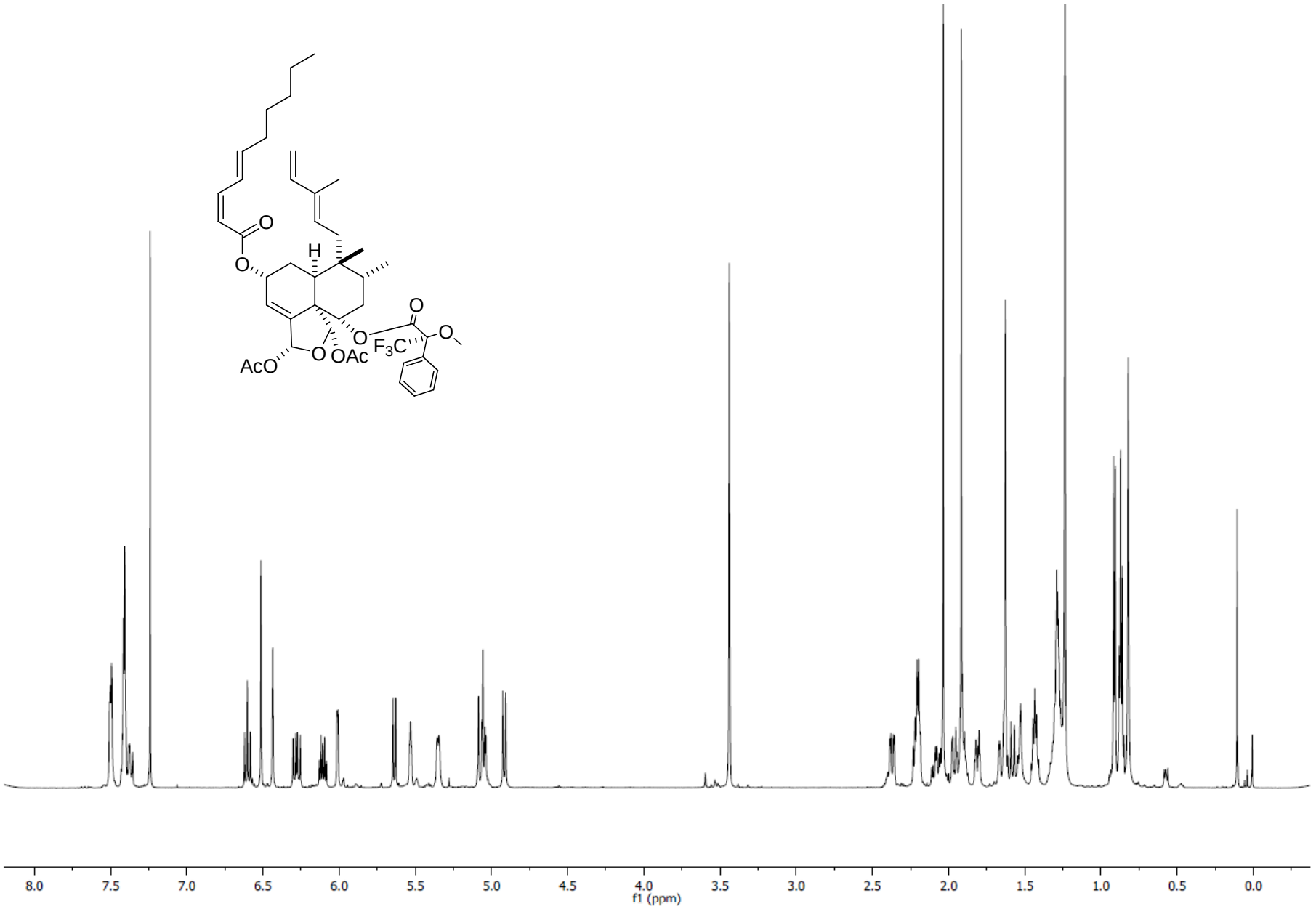
^{1}H NMR Spectrum of Argutin H (**8**) in $CDCl_3$



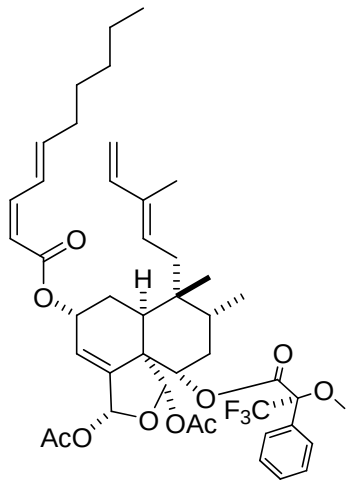
HSQC Spectrum of Argutin H (**8**) in $CDCl_3$



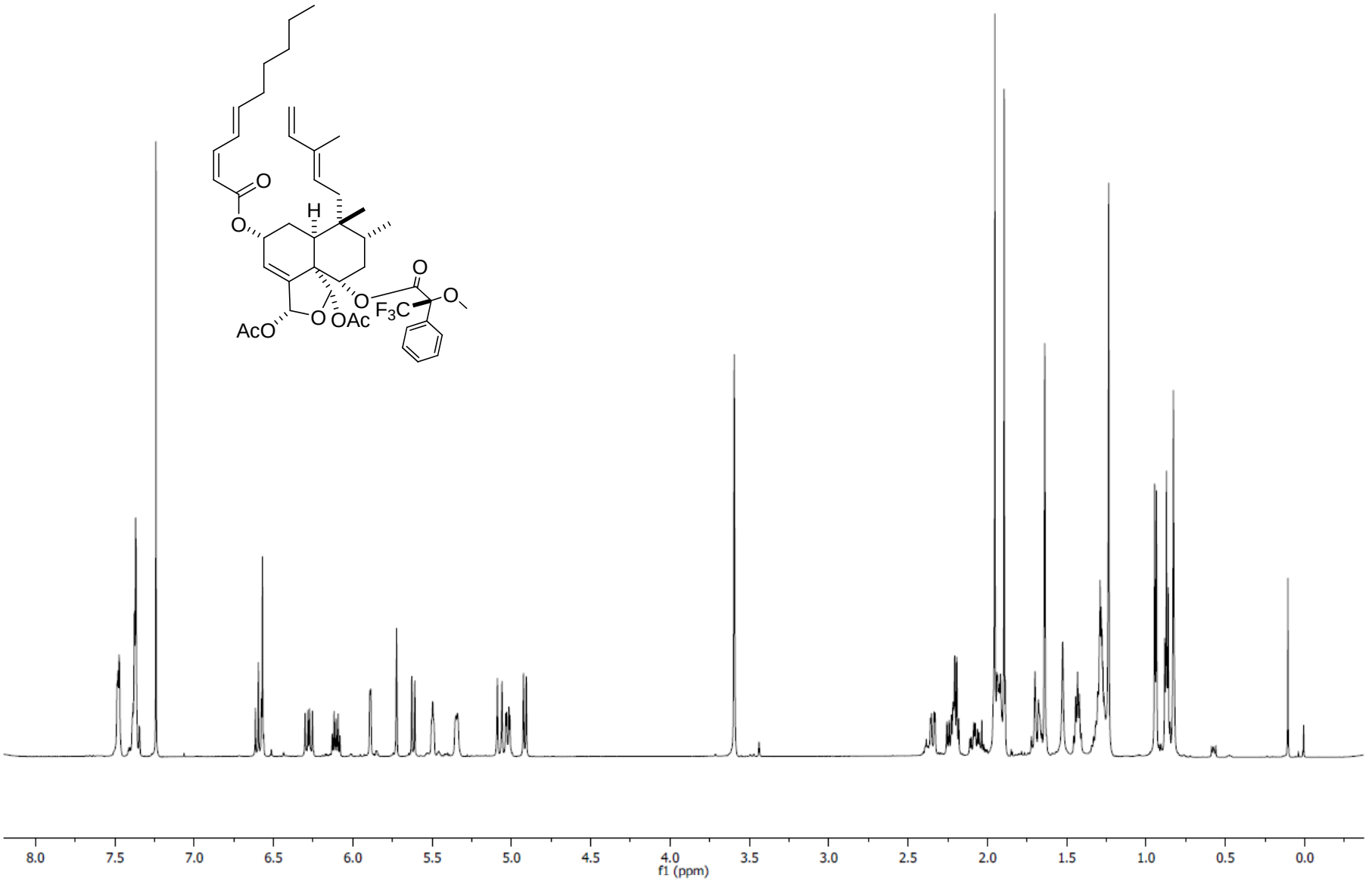
^{1}H NMR Spectrum of Argutin A (*S*)-MTPA Ester (**1S**) in $CDCl_3$



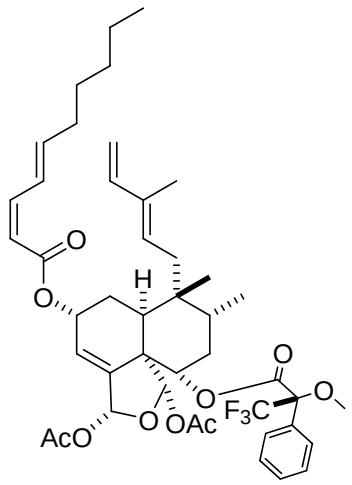
^{13}C NMR Spectrum of Argutin A (*S*)-MTPA Ester (**1S**) in $CDCl_3$



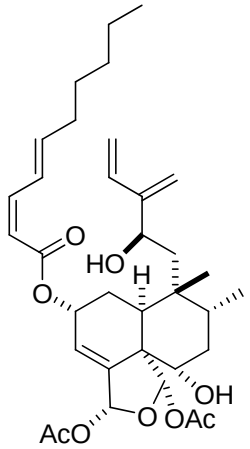
^{1}H NMR Spectrum of Argutin A (*R*)-MTPA Ester (**1R**) in $CDCl_3$



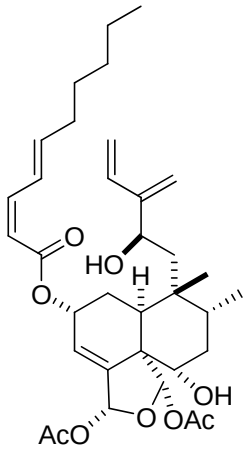
^{13}C NMR Spectrum of Argutin A (*R*)-MTPA Ester (**1R**) in $CDCl_3$



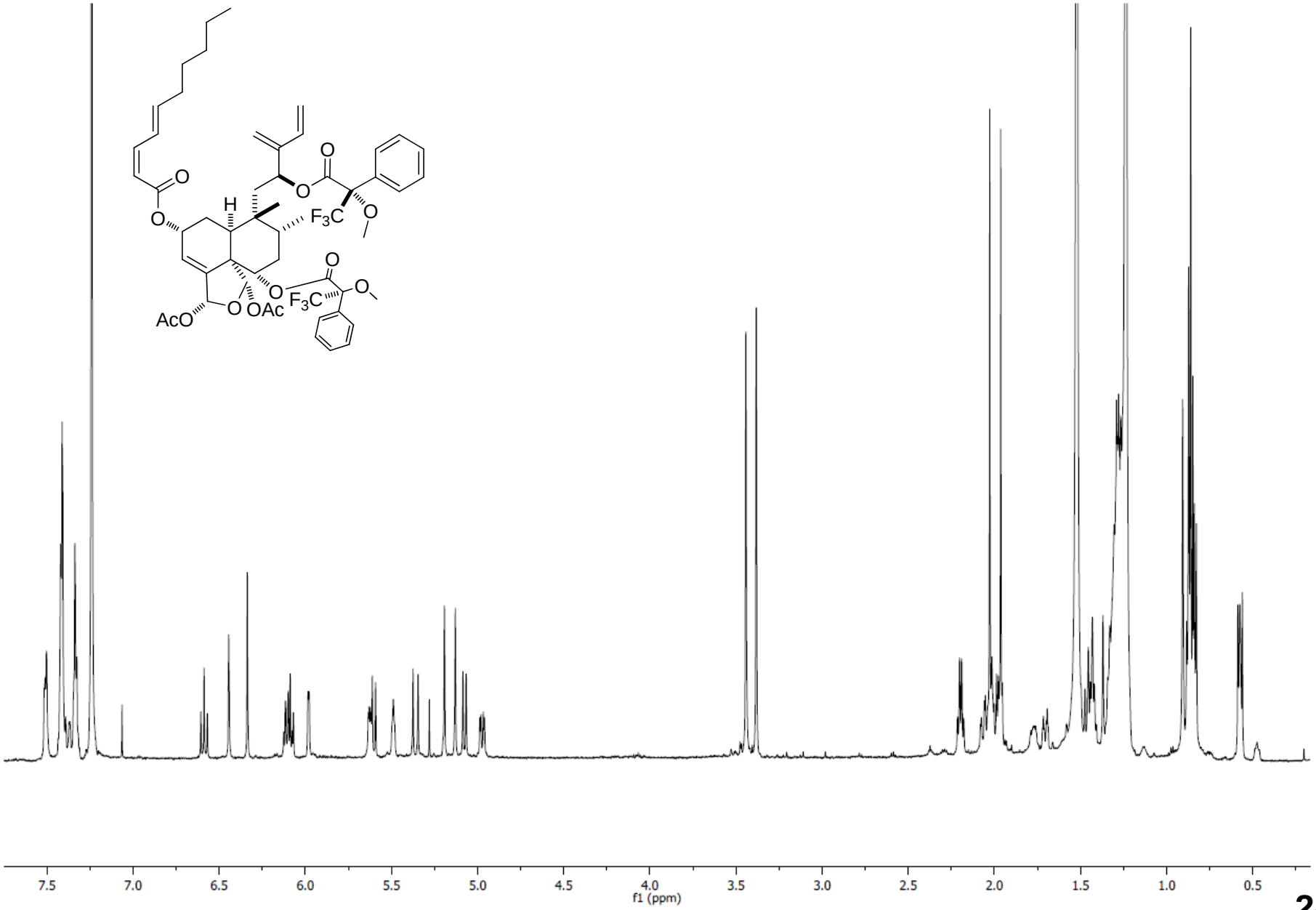
^{1}H NMR Spectrum of Deoxoargutin F (**9**) in $CDCl_3$



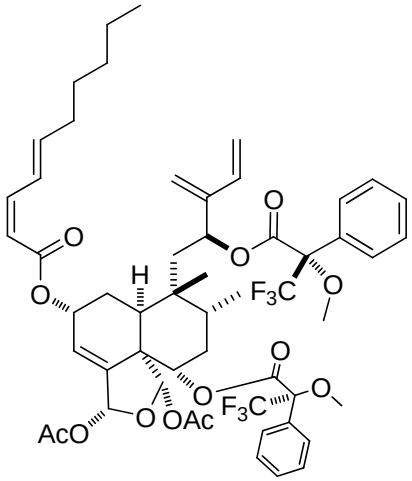
^{13}C NMR Spectrum of Deoxoargutin F (**9**) in $CDCl_3$



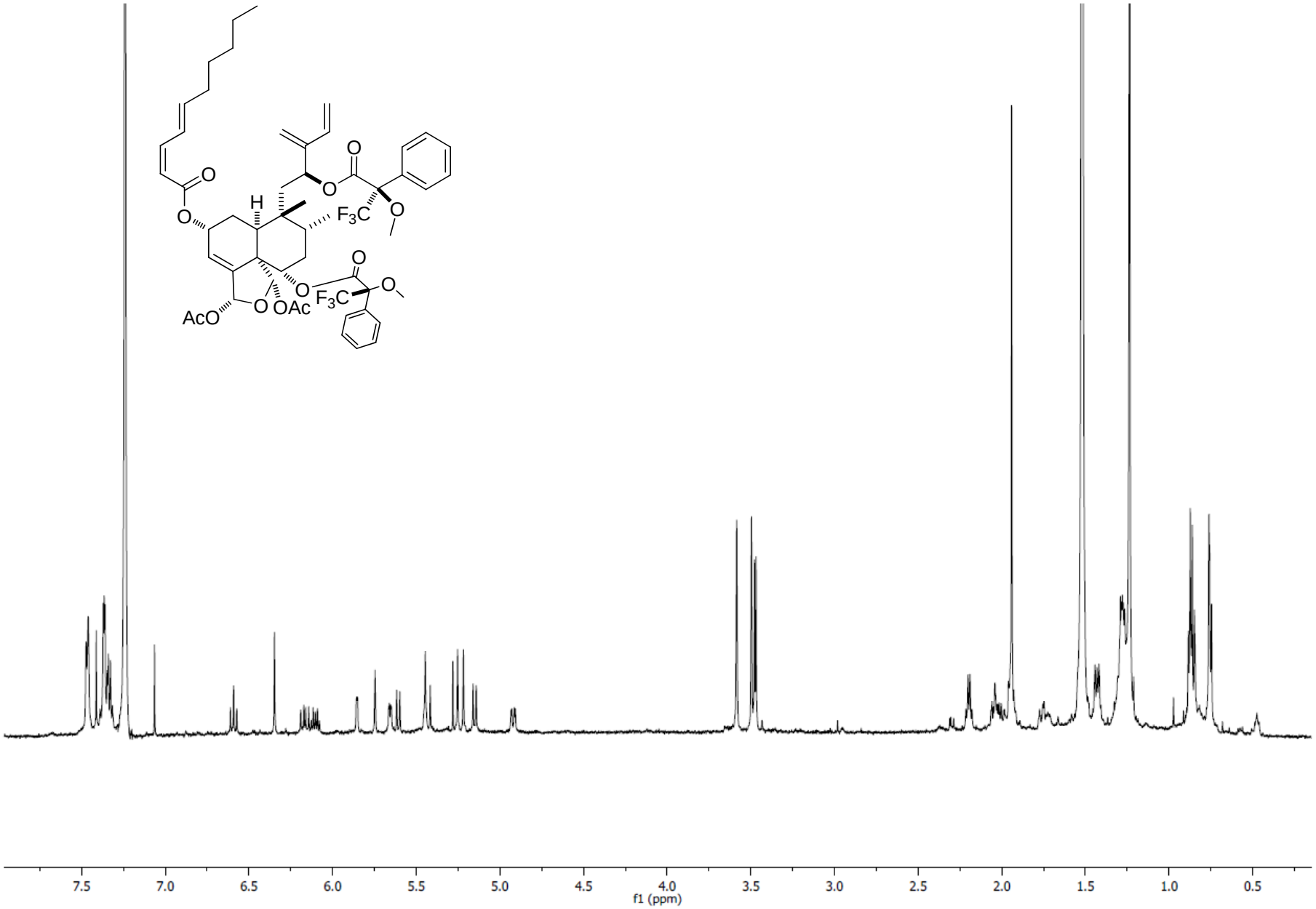
^{1}H NMR Spectrum of Deoxoargutin F (*S*)-MTPA Ester (**9S**) in $CDCl_3$



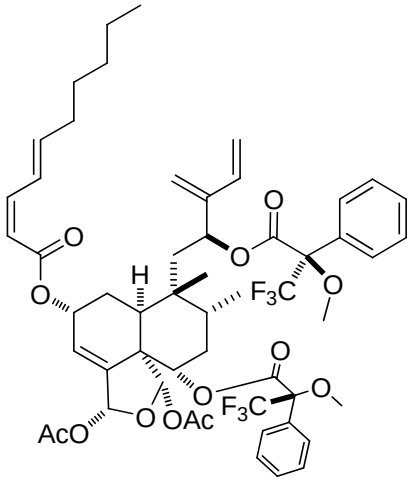
HSQC Spectrum of Deoxoargutin F (*S*)-MTPA Ester (**9S**) in $CDCl_3$



^{1}H NMR Spectrum of Deoxoargutin F (*R*)-MTPA Ester (**9R**) in $CDCl_3$



HSQC Spectrum of Deoxoargutin F (*R*)-MTPA Ester (**9R**) in $CDCl_3$



Supplemental Table 1. NMR Data for the MTPA esters of argutin A (**1S, 1R**) (600 MHz, $CDCl_3$)

	1S		**1R**		$\Delta\delta^{SR}$
position	δ_C	δ_H mult (*J*, Hz)	δ_C	δ_H mult (*J*, Hz)	$\delta^S - \delta^R$
1a	27.1	2.08, ddd (13.8, 5.7, 5.3)	27.1	2.07, ddd (13.9, 5.8, 5.5)	+0.01
1b		1.95, m		1.93,[b] m	+0.02
2	65.7	5.53, br t (4.0)	65.6	5.50, br t (4.1)	+0.03
3	124.1	6.01, br d (4.0)	124.1	5.89, br d (4.1)	+0.12
4	144.1	—	144.1	—	—
5	51.9	—	51.8	—	—
6	77.8	5.05, dd (12.1, 4.0)	77.7	5.02, dd (12.1, 3.9)	+0.03
7a	32.7	1.80, ddd (13.0, 6.8, 4.0)	33.1	1.92,[b] m	-0.12
7b		1.56, ddd (13.0, 13.0, 12.1)		1.67,[b] m	-0.11
8	36.3	1.90,[a] m (6.8)	36.4	1.93,[b] m (6.7)	-0.03
9	37.9	—	37.9	—	—
10	37.9	2.37, dd (13.8, 3.5)	37.9	2.34, dd (13.9, 3.6)	+0.03
11a	30.5	2.21,[b] m	30.6	2.22,[b] m	-0.01
11b		1.64,[a] m		1.67,[b] m	-0.03
12	129.0	5.35, br d (7.6)	129.0	5.35, br d (7.8)	0.00
13	136.0	—	136.1	—	—
14	141.4	6.28, dd (17.3, 10.7)	141.4	6.28, dd (17.3, 10.8)	0.00
15a	111.4	5.06, d (17.3)	111.4	5.07, d (17.3)	-0.01
15b		4.91, d (10.7)		4.92, d (10.7)	-0.01
16	12.2	1.63, s	12.2	1.64, s	-0.01
17	15.8	0.91, d (6.8)	15.7	0.94, d (6.7)	-0.03
18	95.7	6.44, t (1.6)	95.5	5.72, t (1.6)	+0.72
19	97.3	6.51, s	97.3	6.57, s	-0.06
20	25.2	0.82, s	25.2	0.83, s	-0.01
1′	166.0	—	166.0	—	—
2′	115.4	5.64, d (11.3)	115.4	5.62, d (11.3)	+0.02
3′	146.5	6.60, t (11.3)	146.6	6.59, t (11.3)	+0.01
4′	127.1	7.38,[b] m	127.1	7.37,[b] m	+0.01
5′	147.0	6.11, ddd (15.1, 7.5, 7.1)	147.1	6.11, ddd (15.2, 7.7, 7.1)	0.00
6′	33.4	2.20,[b] m	33.4	2.20,[b] m	0.00
7′	28.7	1.43, ddd (14.5, 7.4, 7.1)	28.8	1.43, ddd (14.6, 7.4, 7.1)	0.00
8′	31.7	1.28,[b] m	31.7	1.28,[b] m	0.00
9′	22.7	1.29,[b] m	22.7	1.29,[b] m	0.00
10′	14.3	0.87, t (6.7)	14.2	0.87, t (6.7)	0.00
18-OAc	170.1	—	169.7[d]	—	—
	21.5	2.03, s	21.4	1.95, s	+0.08
19-OAc	169.7	—	169.6[d]	—	
	22.1	1.92, s	22.0	1.89, s	+0.03
OMTPA[c]	—	—	—	—	—
C=O	167.1	—	166.9	—	—
OMe	55.6	3.44, s	56.1	3.60, s	—
	128.9	7.41,[b] m	128.8	7.38,[b] m	—
	129.0	7.40,[b] m	130.0	7.37,[b] m	—
	127.9	7.50, m	127.2	7.48,[b] m	—

[a]Signal obscured by overlapping methyl signal. [b]Signals overlapped. [c]Not all MTPA carbons were assigned. [d]Assignment may be reversed.

Supplemental Table 2. NMR data for deoxoargutin F (**9**) (600 MHz, $CDCl_3$)

	deoxoargutin F (**9**)	
position	δ_C	δ_H mult (*J*, Hz)
1a	27.1	2.03, m
1b		1.93,[a] m
2	65.7	5.47, br t (4.1)
3	122.1	5.98, br d (4.1)
4	145.1	—
5	54.0	—
6	73.4	3.74, dd (11.5, 4.1)
7a	37.8	1.69,[b] m
7b		1.65,[b] m
8	37.3	1.70,[b] m (6.6)
9	38.7	—
10	40.7	2.09, m
11a	39.9	1.71,[b] m
11b		1.36, m
12	67.7	4.46, br d (7.8)
13	150.1	—
14	136.6	6.28, dd (17.8, 11.2)
15a	115.4	5.44, d (17.8)
15b		5.15, d (11.2)
16a	115.1	5.13, s
16b		5.12, s
17	16.0	1.04, d (6.6)
18	95.3	6.72, br t (1.5)
19	97.7	6.39, s
20	24.5	1.06, s
1′	166.1	—
2′	115.4	5.61, d (11.3)
3′	146.3	6.58, t (11.3)
4′	127.0	7.37, dd (15.3, 11.3)
5′	147.0	6.10, ddd (15.3, 7.7, 7.0)
6′	33.2	2.19, ddd (14.6, 7.4, 7.0)
7′	29.0	1.43, ddd (14.4, 7.4, 7.1)
8′	31.8	1.27,[b] m
9′	22.8	1.28,[b] m
10′	14.3	0.86,t (6.8)
18-OAc	170.3	—
	21.3	2.06, s
19-OAc	170.0	—
	21.9	1.93, s

[a]Signal obscured by overlapping methyl signal. [b]Signals overlapped.

Supplemental Table 3. NMR Data for the MTPA esters of **9** (**9S, 9R**) (600 MHz, $CDCl_3$)

	9S[a]		**9R**[a]		$\Delta\delta^{SR}$
position	δ_C	δ_H mult (*J*, Hz)	δ_C	δ_H mult (*J*, Hz)	
1a	27.1	2.02,[b] m	26.9	1.99,[c] m	+0.03
1b		1.94,[b] m		1.94,[b] m	0.00
2	65.3	5.49, br t (4.0)	65.1	5.44,[c] br t (4.1)	+0.05
3	124.0	5.98, br d (4.0)	124.0	5.85, br d (4.1)	+0.13
6	77.5	4.97, dd (12.1, 3.9)	77.5	4.92, dd (12.3, 4.0)	+0.05
7a	32.4	1.70, ddd (13.2, 6.8, 3.9)	32.7	1.76, ddd (13.2, 6.7, 3.9)	-0.06
7b		1.45,[c] m		1.50, m	-0.05
8	36.2	1.77, m (6.9)	36.4	1.72, m (7.0)	+0.05
10	42.4	2.06, dd (13.7, 3.6)	41.9	2.05, dd (13.8, 3.5)	+0.01
11a	38.9	1.99,[b] m	38.1	2.02,[c] m	-0.03
11b		1.44,[c] m		1.43,[c] m	+0.01
12	75.4	5.63, dd (7.0, 3.3)	75.3	5.66, dd (7.1, 2.8)	-0.03
14	133.9	6.07,[c] dd (17.7, 11.2)	134.0	6.17, dd (17.6, 11.1)	-0.10
15a	117.0	5.36, d (17.7)	117.2	5.43,[c] d (17.6)	-0.07
15b		5.07, d (11.2)		5.15, d (11.1)	-0.08
16a	117.4	5.19, s	118.1	5.25, s	-0.06
16b		5.13, s		5.21, s	-0.08
17	15.9	0.83, d (6.9)	15.7	0.75, d (7.0)	+0.08
18	95.4	6.44, br t (1.6)	94.9	5.75, br t (1.6)	+0.69
19	97.7	6.34, s	97.5	6.35, s	-0.01
20	23.2	0.91, s	23.1	0.76, s	+0.15
2′	115.1	5.60, d (11.3)	115.1	5.61, d (11.3)	-0.01
3′	146.6	6.59. t (11.3)	146.8	6.59, t (11.3)	0.00
4′	127.2	7.36,[c] m	127.1	7.37,[c] m	0.00
5′	147.2	6.09,[c] m	147.2	6.10, ddd (15.3, 7.8, 7.4)	0.00
6′	33.3	2.20, ddd (14.7, 7.4, 7.2)	33.2	2.20, ddd (14.7, 7.7, 7.4)	0.00
7′	28.7	1.43,[c] m	28.7	1.43,[c] m	0.00
8′	31.9	1.28,[c] m	31.8	1.28,[c] m	0.00
9′	22.8	1.28,[c] m	22.8	1.28,[c] m	0.00
10′	14.2	0.86, t (6.9)	14.1	0.86, t (7.0)	0.00
18-OAc	21.3	2.03, s	21.7	1.94,[c] s	+0.09
19-OAc	22.1	1.96, s	21.7	1.94,[c] s	+0.02
OMTPA	—	—	—	—	—
OMe	55.4	3.44, s	55.7	3.58, s	—
OMe	55.3	3.38, s	55.6	3.49, s	—
	128.2	7.41,[c] m	128.0	7.36,[c] m	—
	129.6	7.41,[c] m	129.2	7.36,[c] m	—
	128.8	7.34,[c] m	127.5	7.33,[c] m	—
	129.4	7.34,[c] m	128.7	7.33,[c] m	—
	127.9	7.50, m	127.3	7.46, m	—

[a]Quaternary carbons were not assigned. [b]Signal obscured by overlapping methyl signal. [c]Signals overlapped.