Electronic Supplementary Information (ESI)

Unified total synthesis of (+)-chinensiolide and (+)-epigrosheimin

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Comparison ^{1}H NMR data of the Hall's intermediate:

Sl No	Hall's Intermediate	Compound 14
1	6.20 (d, *J* =3.5, 1H),	6.18 (d, *J*=3.4, 1H),
2	5.47 (d, *J* =3.2, 1H)	5.46 (d, J = 3.1 Hz, 1H)
3	5.44 (br s, 1H)	5.45 – 5.39 (m, 1H)
4	4.11 (br t, 1H, *J* =4.4)	4.12 – 4.05 (m, 1H),
5	3.92 (dd, *J* =11.3, 8.9, 1H),	3.91 (dd, *J* =11.2, 8.8, 1H),
6	3.19-3.07 (m, 1H),	3.14-3.06 (m,1H),
7	2.74-2.67 (m,1H),	2.74 – 2.64 (m, 1H),
8	2.64-2.56 (m, 1H),	2.64 – 2.54 (m, 1H),
9	2.29-2.17 (m, 1H),	2.21 (ddd, J = 12.2, 7.0, 5.3 Hz, 1H),
10	2.08-2.03 (m, 1H),	2.05 – 2.01 (m, 1H),
11	2.03-1.95 (m, 1H)	1.98-1.90 (m,1H),
12	1.91(ddd, 1H, *J* = 11.2,8.6,5.4),	1.91 – 1.85 (m, 1H),
13	1.78 (s, 3H),	1.78 – 1.74 (m, 3H),
14	1.54 (ddd, *J* = 12.5,12.5,3.9, 1H),	1.51 (td, *J* =12.7, 4.0, 1H),
15	1.10 (d, *J* =7.0, 3H),	1.08 (d, *J* =7.0, 3H),
16	0.90 (s, 9H),	0.88 (s, 9H),
17	0.07 (s, 3H), 0.06 (s, 3H)	0.05 (s, 3H), 0.04 (s, 3H).

Comparison ^{13}C NMR data of the Hall's intermediate:

Sl No	Hall's Intermediate	Compound 14
1	170.4	170.4
2	140.3	140.2
3	137.0	137.0
4	120.1	120.0
5	119.9	119.9
6	87.3	87.3
7	73.6	73.6
8	52.3	52.1
9	45.3	45.2
10	44.7	44.6
11	42.7	42.6
12	42.3	42.2
13	30.7	30.6
14	28.5	28.4
15	25.9	25.8

16	18.2	18.1
17	15.8	15.8
18	-4.7,-4.9	-4.7, -4.9

Comparison of optical rotation of the Hall's intermediate:

Sl No	**Hall's Intermediate**	**Compound 14**
1	-42.8 (*c* 0.50, $CHCl_3$)	- 63.78 (*c* 0.50, $CHCl_3$)

Comparison of ^{1}H NMR data (+)-chinensiolide B 17:

Sl No	**(+)-chinensiolide B synthesized by Hall Group**	**Synthesized (+)-chinensiolide B 17**
1	6.24 (d, *J* = 3.5, 1H),	6.24 (d, *J* = 3.6, 1H),
2	5.52 (d, *J* = 3.1, 1H)	5.53 (d, *J* = 3.3, 1H),
4	4.11 (dd, *J* = 9.9,9.9,1H)	4.11 (t, J = 9.9 1H),
5	3.12-3.02 (m, 1H),	3.09-3.03 (m, 1H),
6	2.66-2.57 (m, 2H),	2.65-2.58 (m, 2H),
7	2.51-2.34 (m,3H),	2.55-2.31 (m, 3H),
8	2.32-2.22 (m, 1H),	2.30-2.23 (m, 1H),
9	1.99 (d,*J* = 14.5,6.1,6.1, 1H),	2.01-1.95 (m, 1H),
11	1.78(ddd, *J* = 14.3,8.3,5.8,1H),	1.80-1.73 (m, 1H),
12	1.57-1.47 (m, 1H),	1.54-1.44 (m, 1H),
13	1.25 (d, *J* = 7.2, 3H),	1.24 (d, *J* = 7.2, 3H),
14	1.22 (s, 3H),	1.22 (s, 3H),

Comparison of ^{13}C NMR data of Hall's synthesis and our synthetic (+)-chinensiolide B 17

Sl No	**(+)-chinensiolide B synthesized by Hall Group**	**Synthesized (+)-chinensiolide B 17**
1	219.0	219.2
2	169.7	169.8
3	139.8	139.7
4	120.5	120.5
5	85.0	85.0
6	74.2	74.1
7	50.5	50.4
8	48.0	47.9
9	46.0	45.9
10	44.3	44.2
11	39.8	39.8
12	39.8	39.8

13	28.0	30.8
14	25.3	25.3
15	15.9	15.8

Comparison of optical rotation:

Sl No	(+)-chinensiolide B synthesized by Hall Group	Synthesized (+)-chinensiolide B 17
1	+4.8 (*c* 0.11, $CHCl_3$)	+4.9 (*c* 0.12, $CHCl_3$)

Comparison ^{1}H NMR data of (+)-8-epigrosheimin 20:

Sl No	(-)-epigrosheimin synthesized by Xu Group	Synthesized (+)-epigrosheimin 20
1	6.45(d, J = 3.3, 1H)	6.45(d, J = 3.2, 1H)
2	5.68 (d, J = 3.0, 1H)	5.67 (d, J = 3.2, 1H)
4	5.08 (s.1H)	5.08 (s.1H),
5	5.08 (s.1H)	---
6	4.83 (s.1H)	4.84 (s.1H)
7	4.55 (t, J = 9.1, 1H)	4.55 (t, J = 8.8, 1H)
8	4.46 (s.1H)	4.46 (s.1H)
9	3.13-3.16 (m, 1H)	3.15-3.13 (m, 1H)
11	3.06 (dt, J = 3.4,8.0, 1H)	3.05 (dt, J = 3.2,7.6, 1H)
12	2.69 (dd, j = 3.0, 13.9, 1H)	2.69 (m, 1H)
13	2.55-2.59 (m, 2H)	2.58-2.52 (m, 2H)
14	2.50 (dd, J = 4.0,13.8, 1H)	2.50 (m, 1H)
15	2.25-2.39 (m, 2H)	2.27-2.33 (m, 2H)
16	1.28 (d, J = 6.8. 3H)	1.25 (d, J = 6.6. 3H)

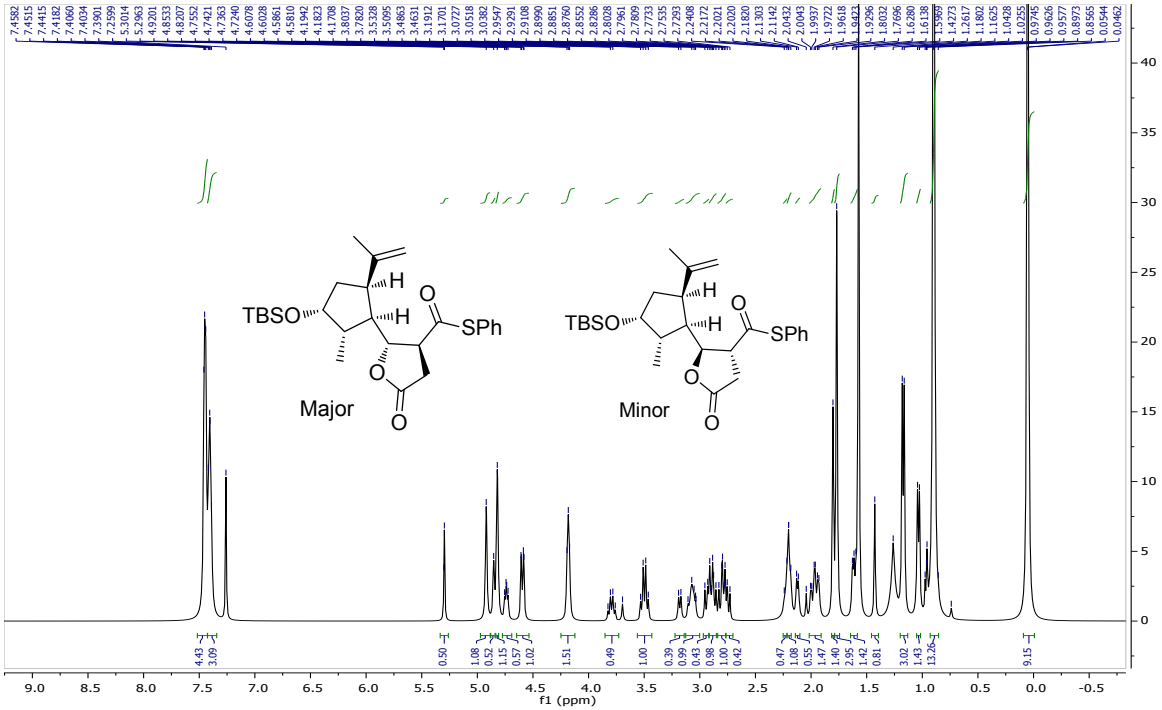
Comparison ^{13}C NMR data of 8-epigrosheimin 21:

Sl No	(-)-8-epigrosheimin synthesized by Xu Group	Synthesized (+)-8-epigrosheimin 20
1	14.1	14.4
2	39.8	40.17
3	43.7	44.07
4	46.7	46.9
5	47.0	47.3
6	48.3	48.7
7	50.2	50.5
8	65.8	66.3
9	81.2	81.3

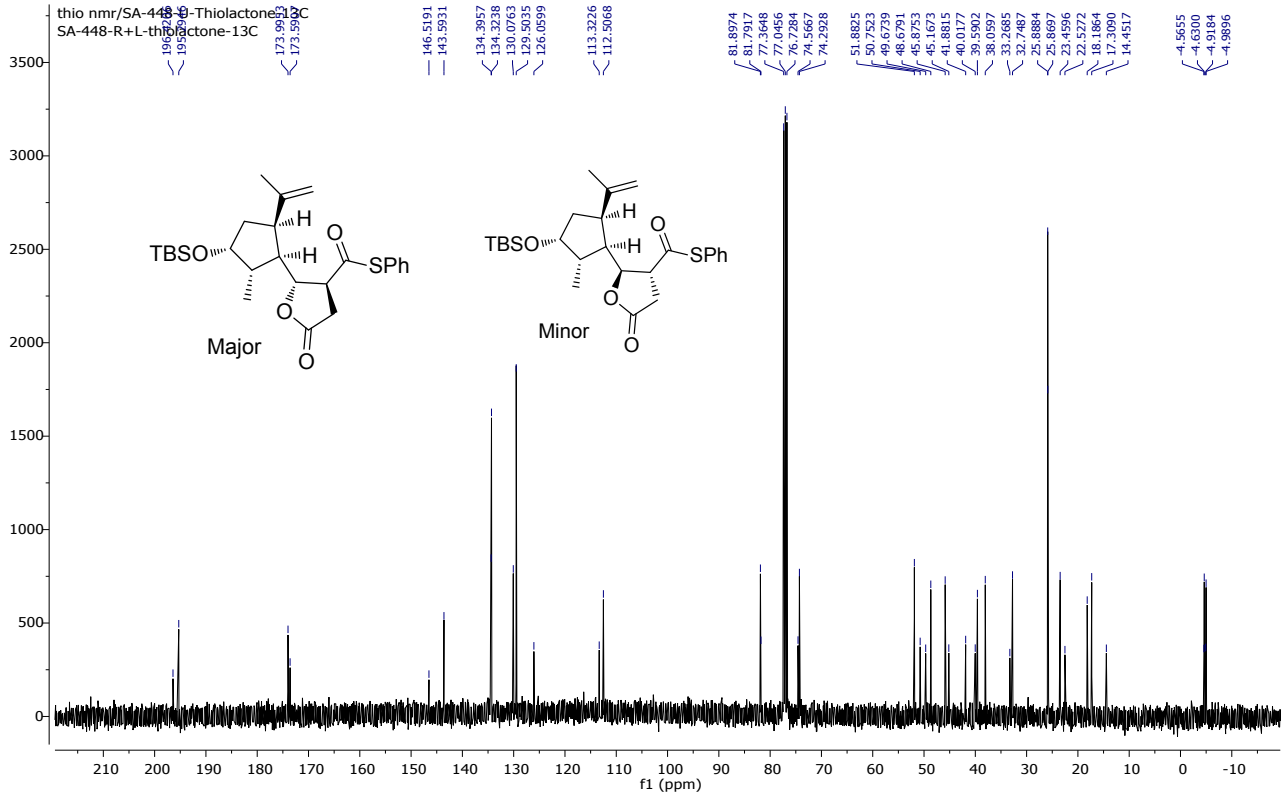
10	115.7	116.3
11	122.1	122.3
12	135.9	136.2
13	143.7	143.9
14	169.7	169.6
15	219.5	219.3

Comparison of optical rotation:

Sl No	**(-)-8-Epigrosheimin synthesized by Xu Group**	**Synthesized (+)-8-epigrosheimin 20**
1	-34.4 (*c* 1.18, $CHCl_3$)	+ 34.8 (*c* 1.1, $CHCl_3$)



400 MHz 1H spectra of compound 8



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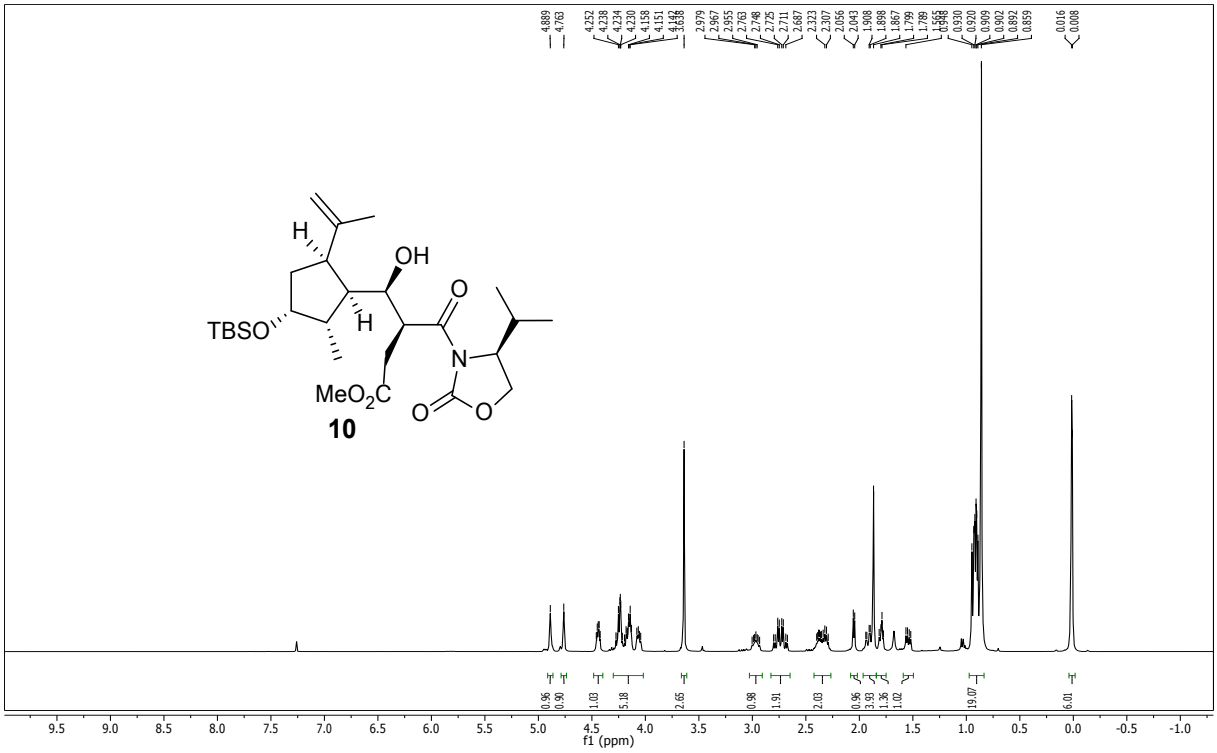

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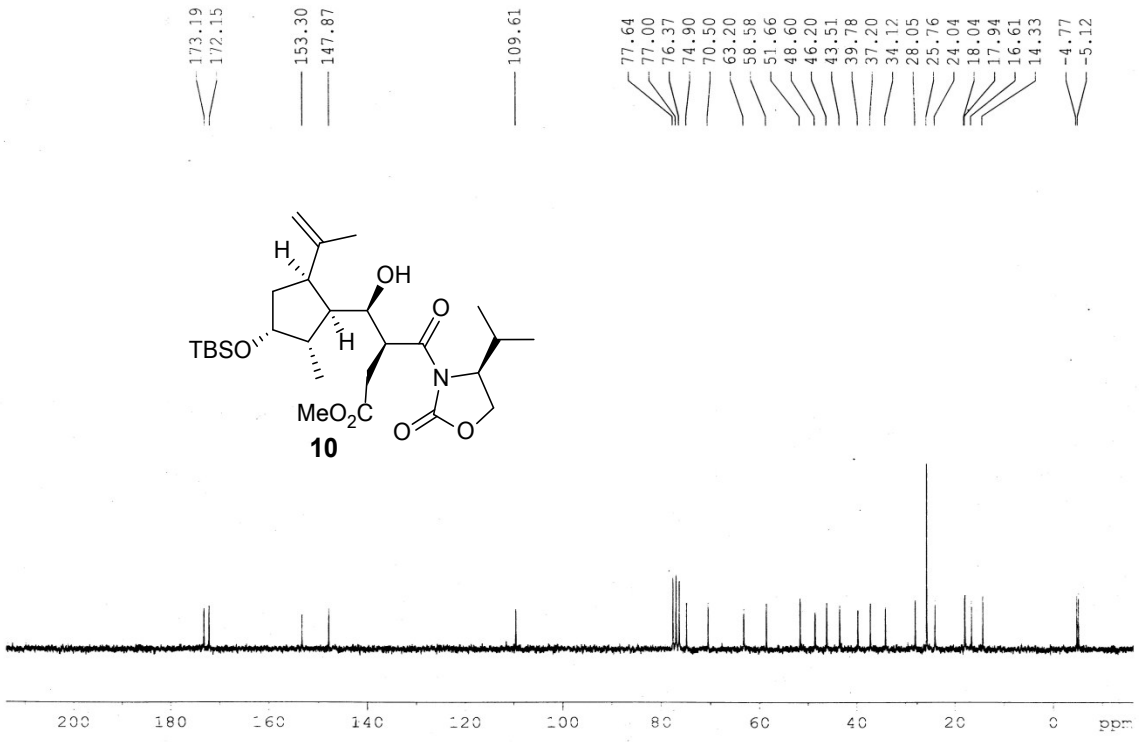
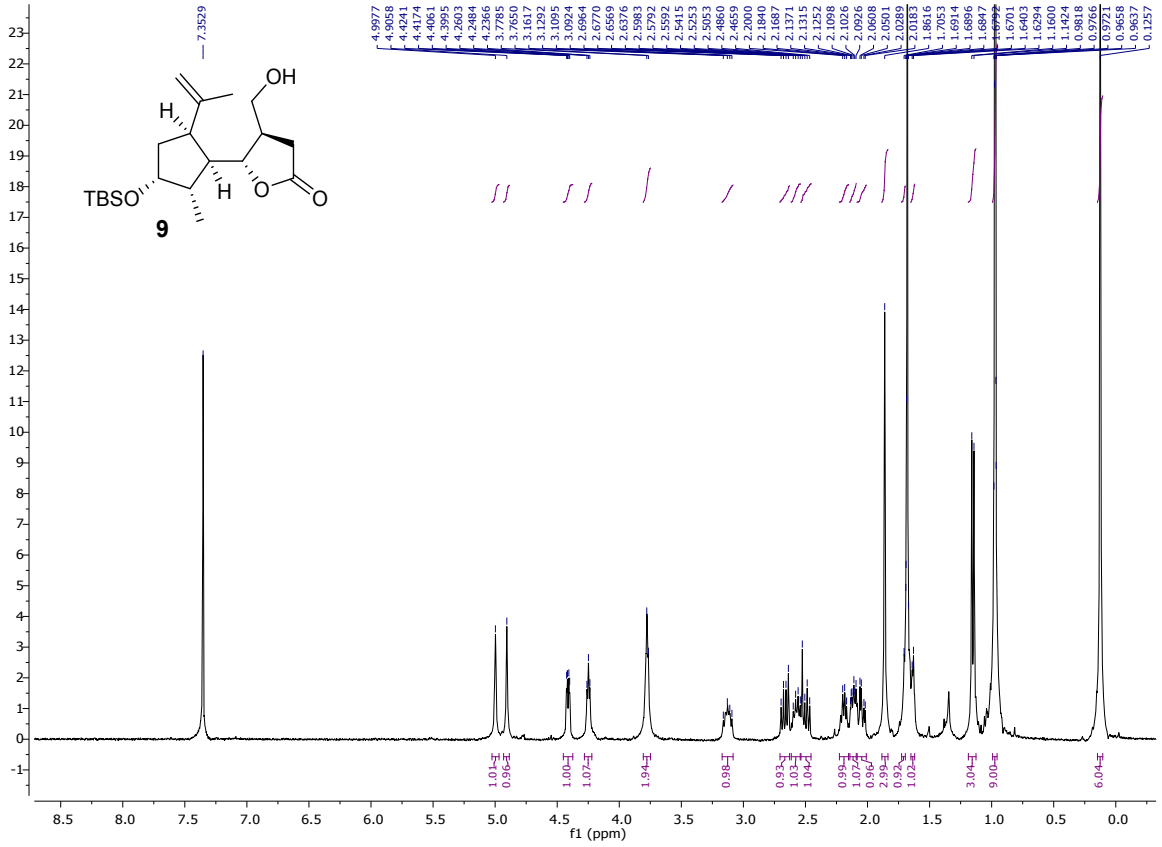
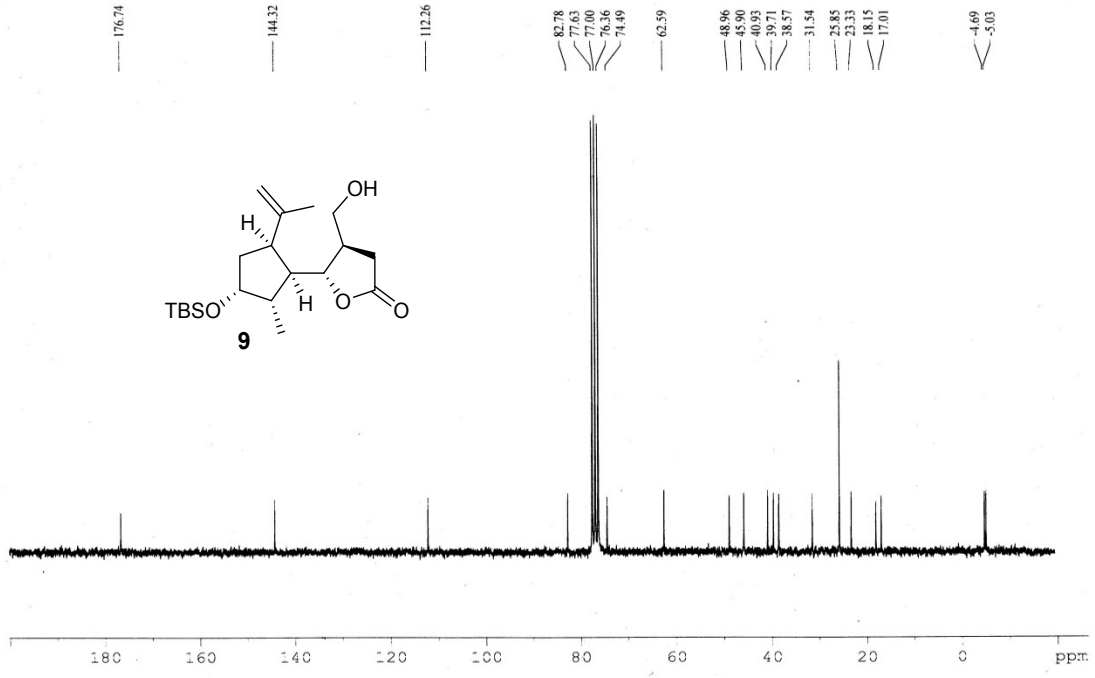


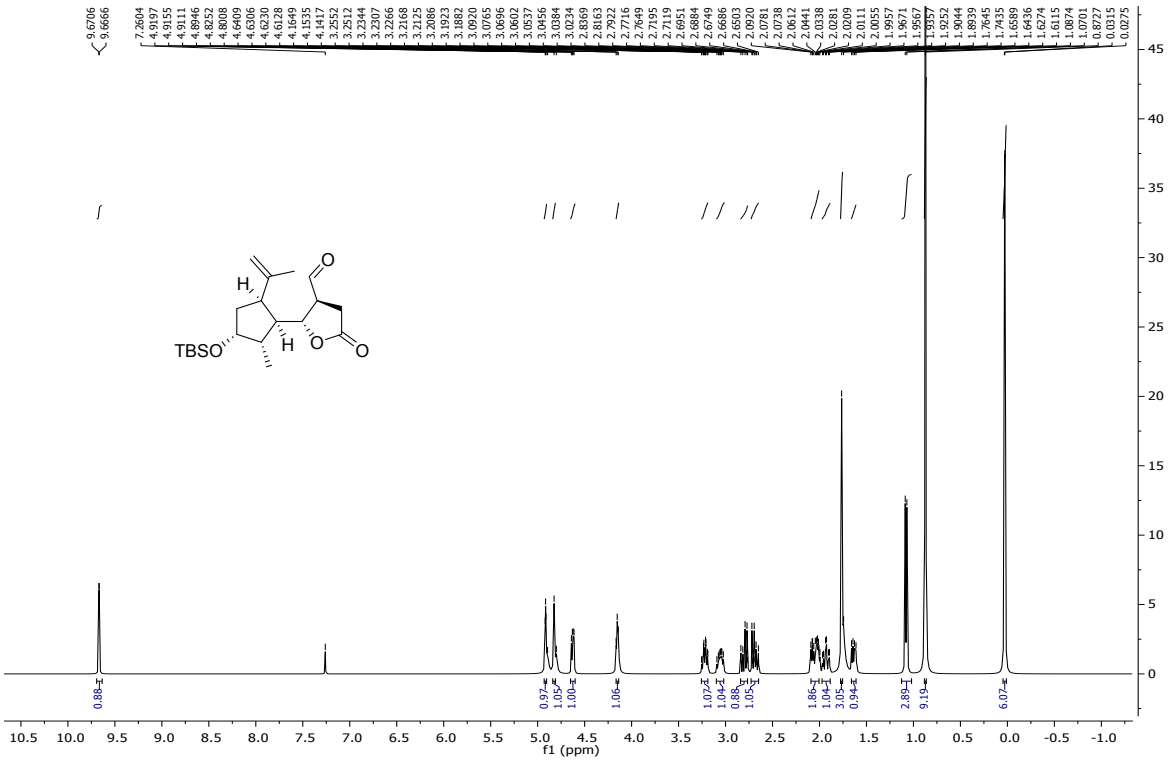
100 MHz ^{13}C spectra of compound 10



400 MHz 1H spectra of compound 9



100 MHz ^{13}C spectra of compound 9



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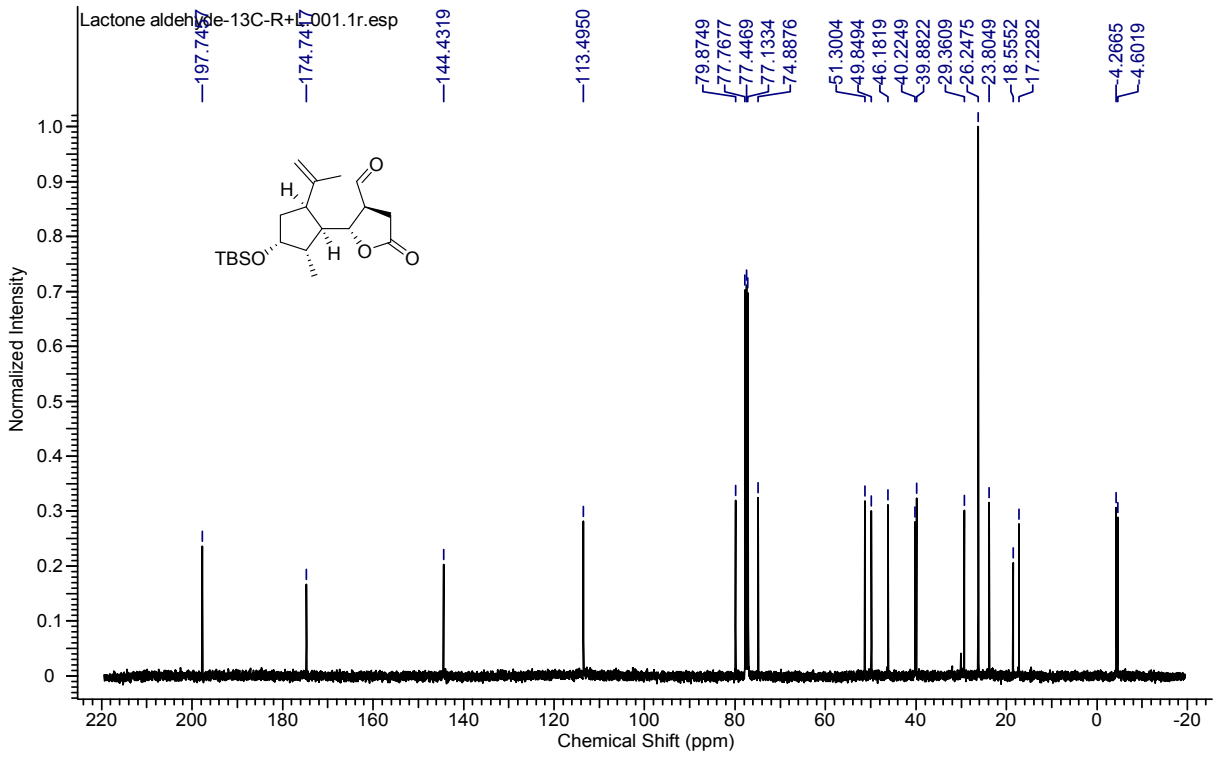
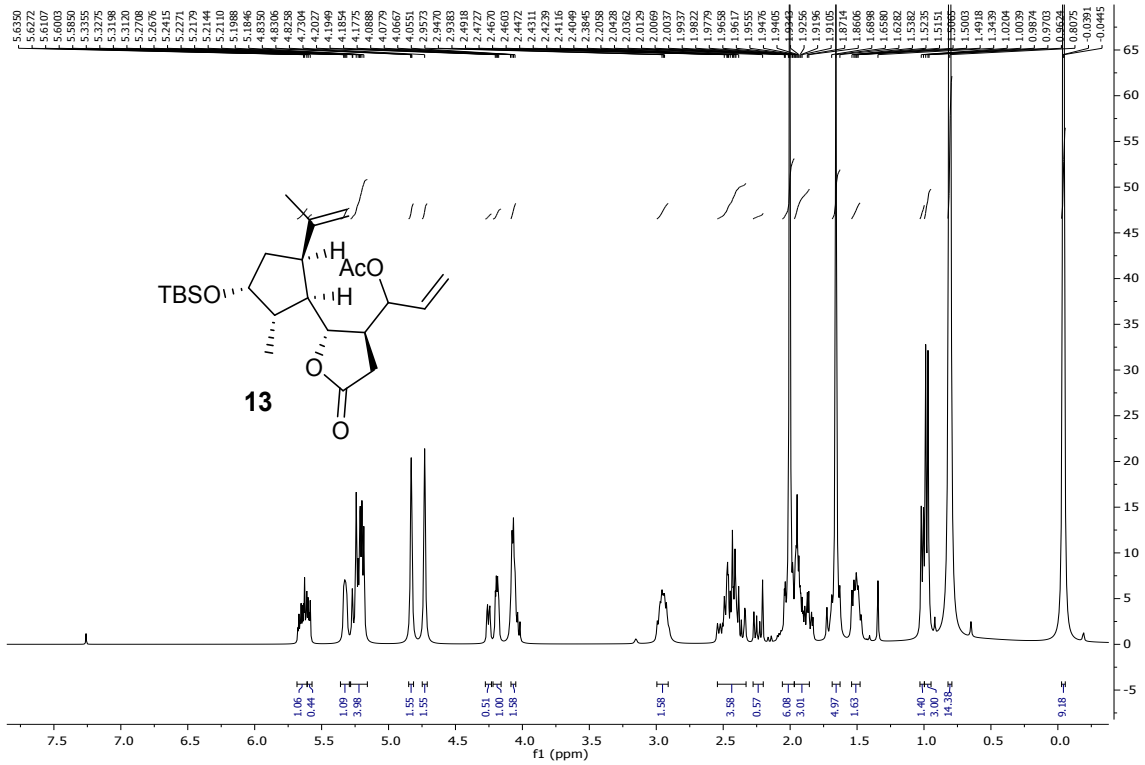
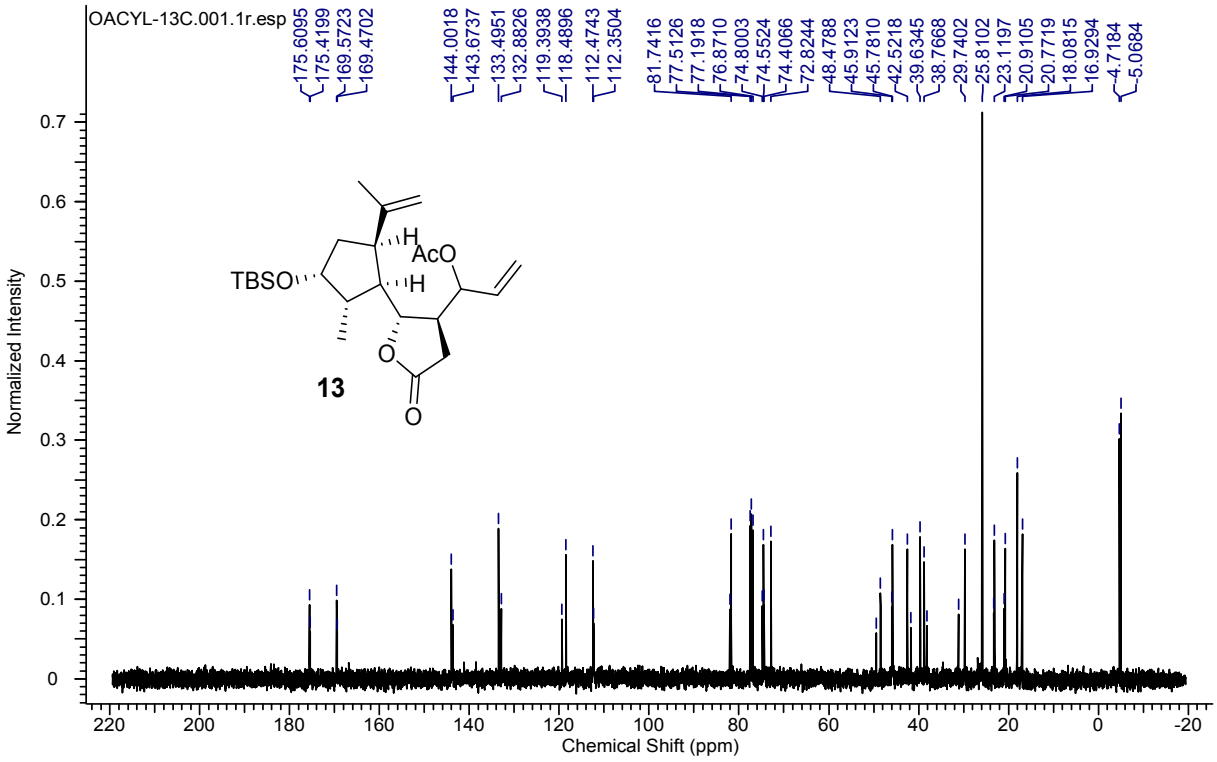


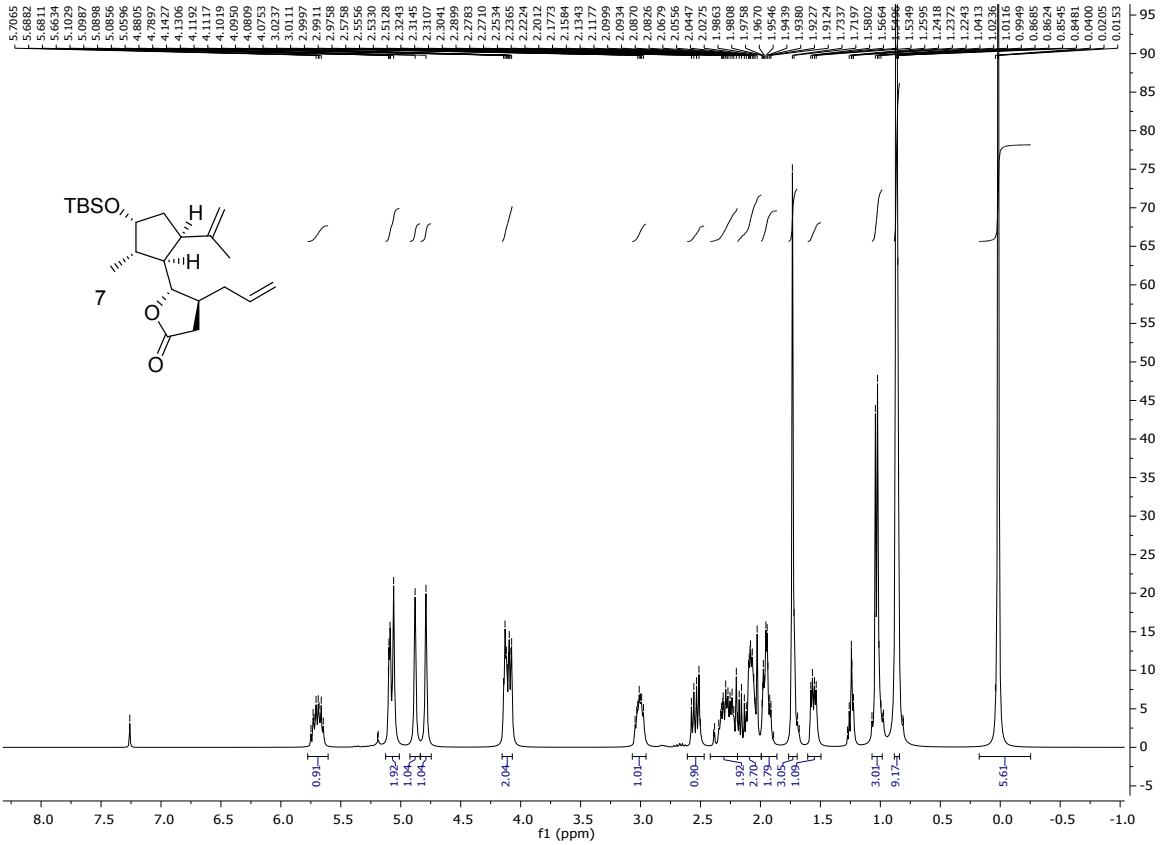
100 MHz ^{13}C spectra of compound 6



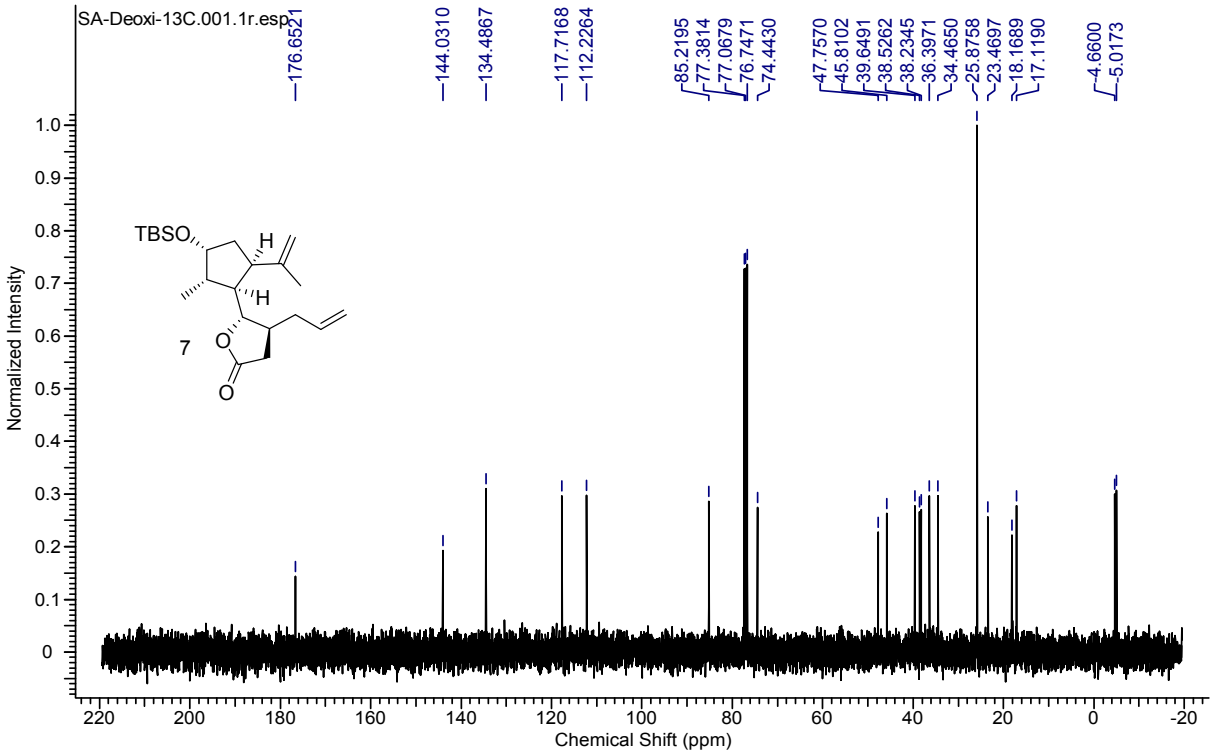
400 MHz 1H spectra of compound 13



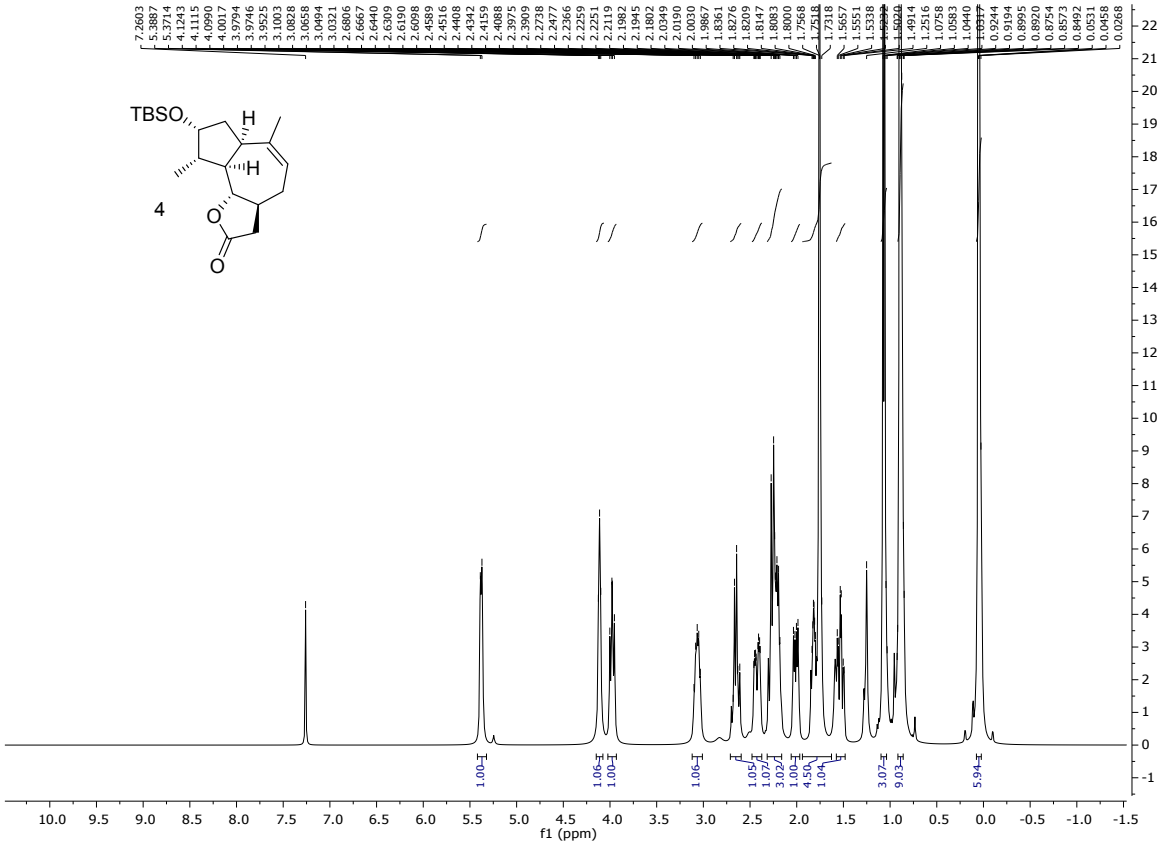
100 MHz ^{13}C spectra of compound 13



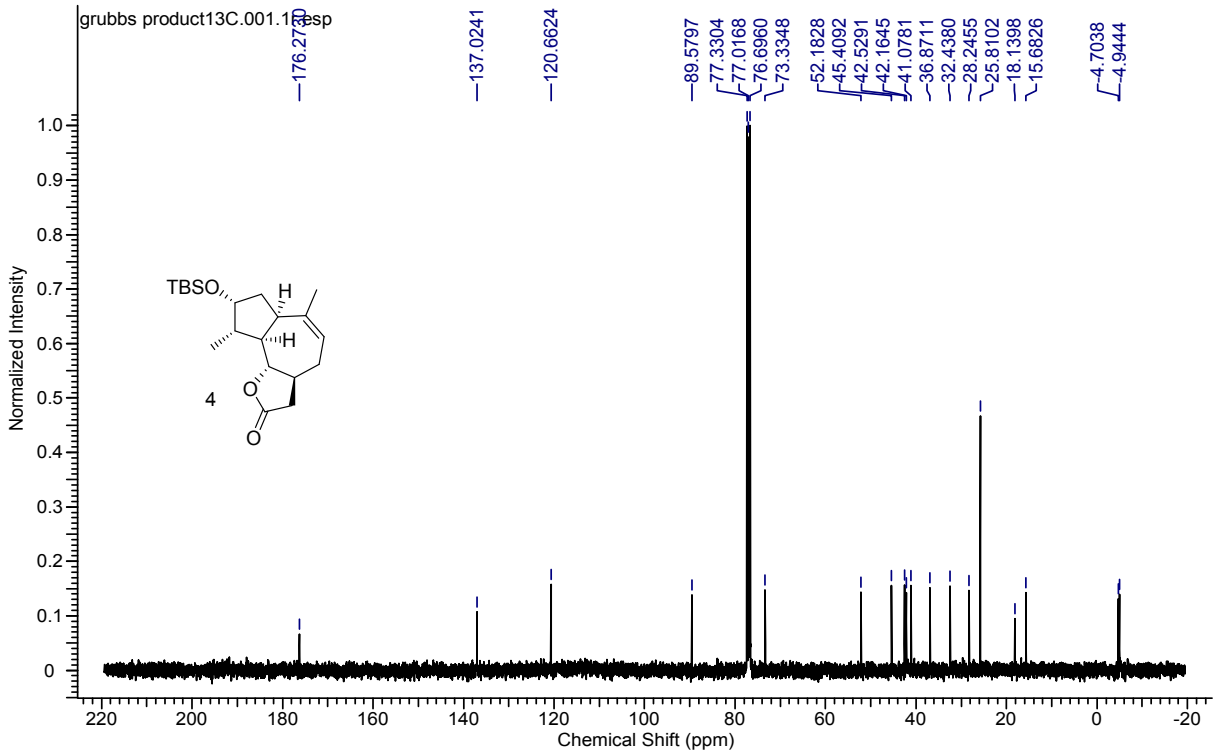
400 MHz 1H spectra of compound 7



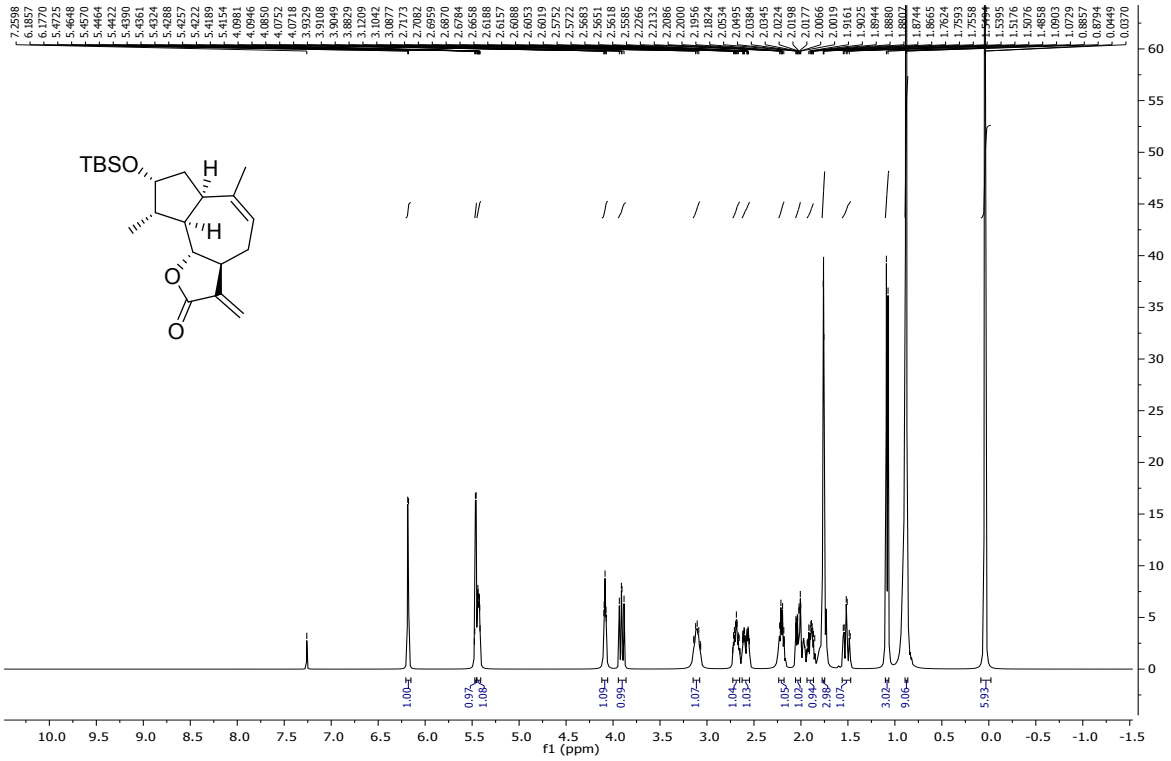
100 MHz ^{13}C spectra of compound 7



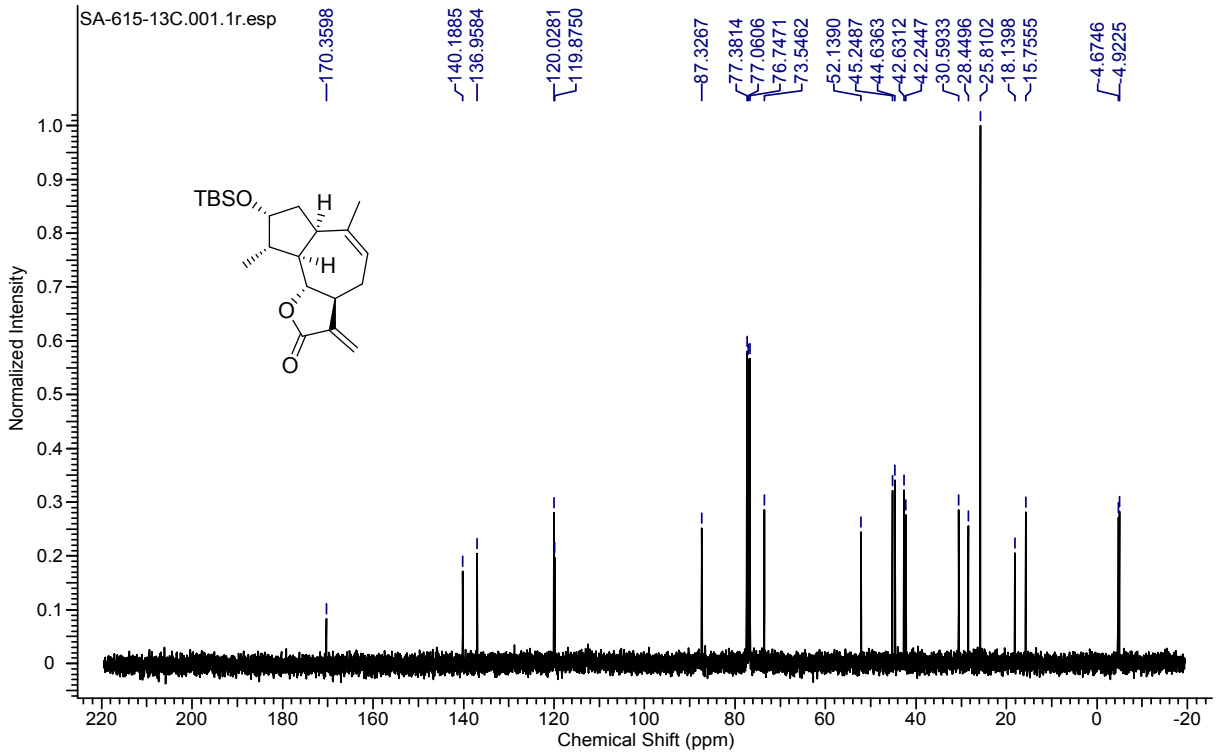
400 MHz 1H spectra of compound 4



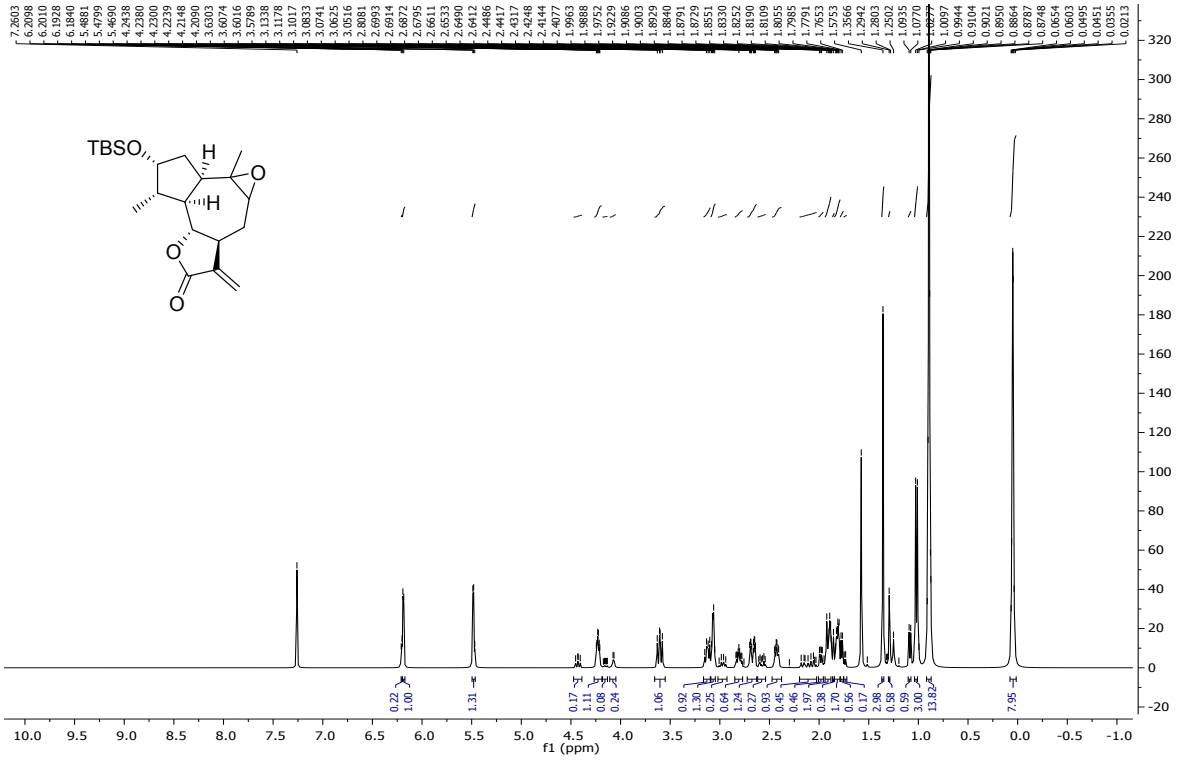
100 MHz ^{13}C spectra of compound 4



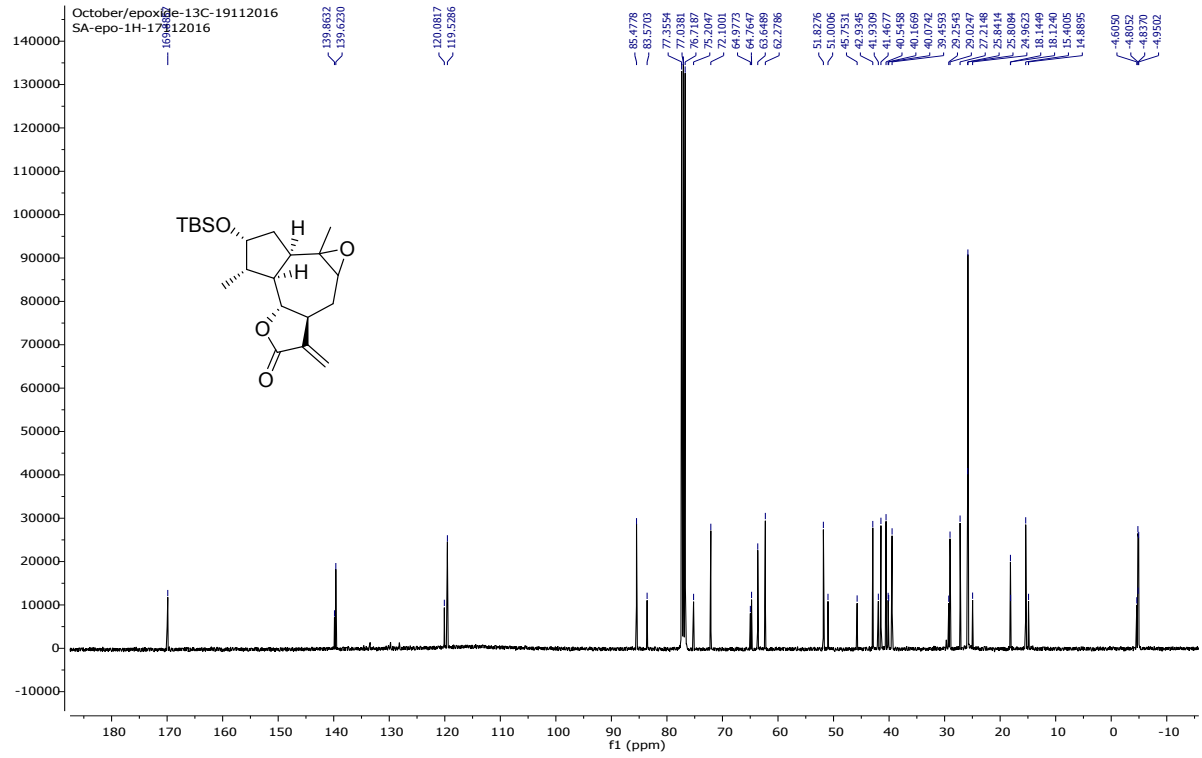
400 MHz 1H spectra of compound 14



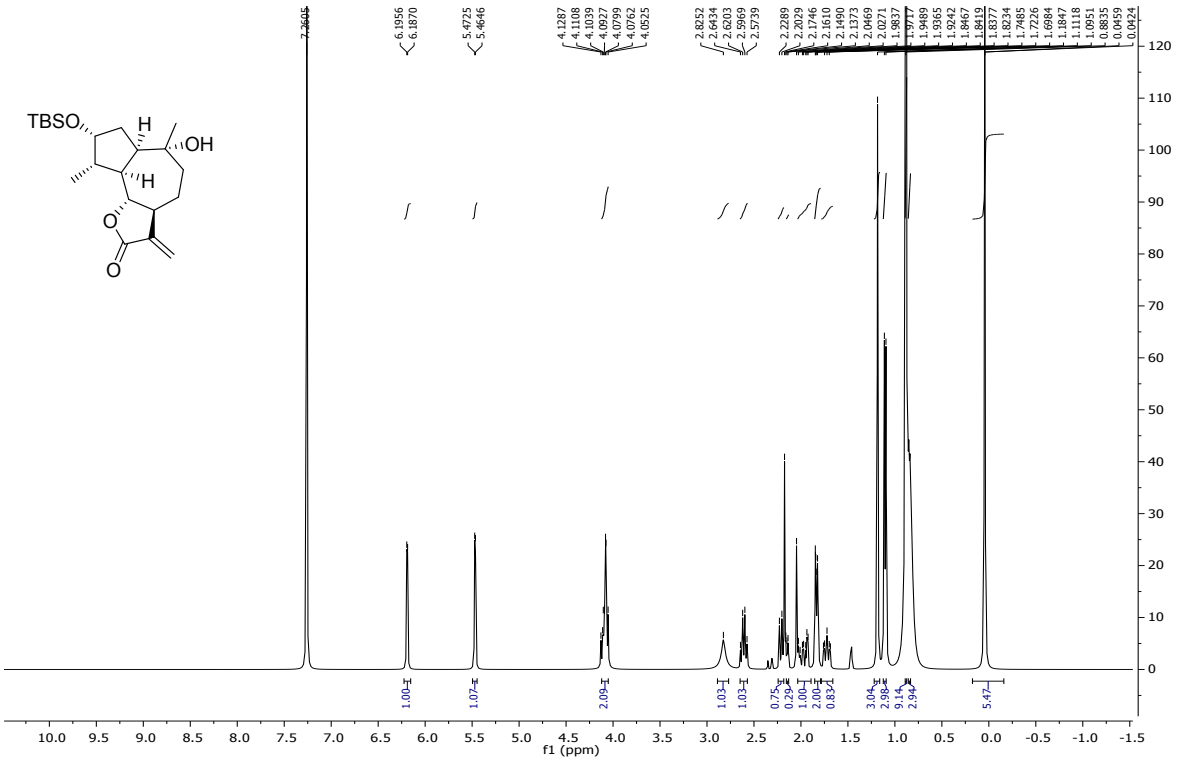
100 MHz ^{13}C spectra of compound 14



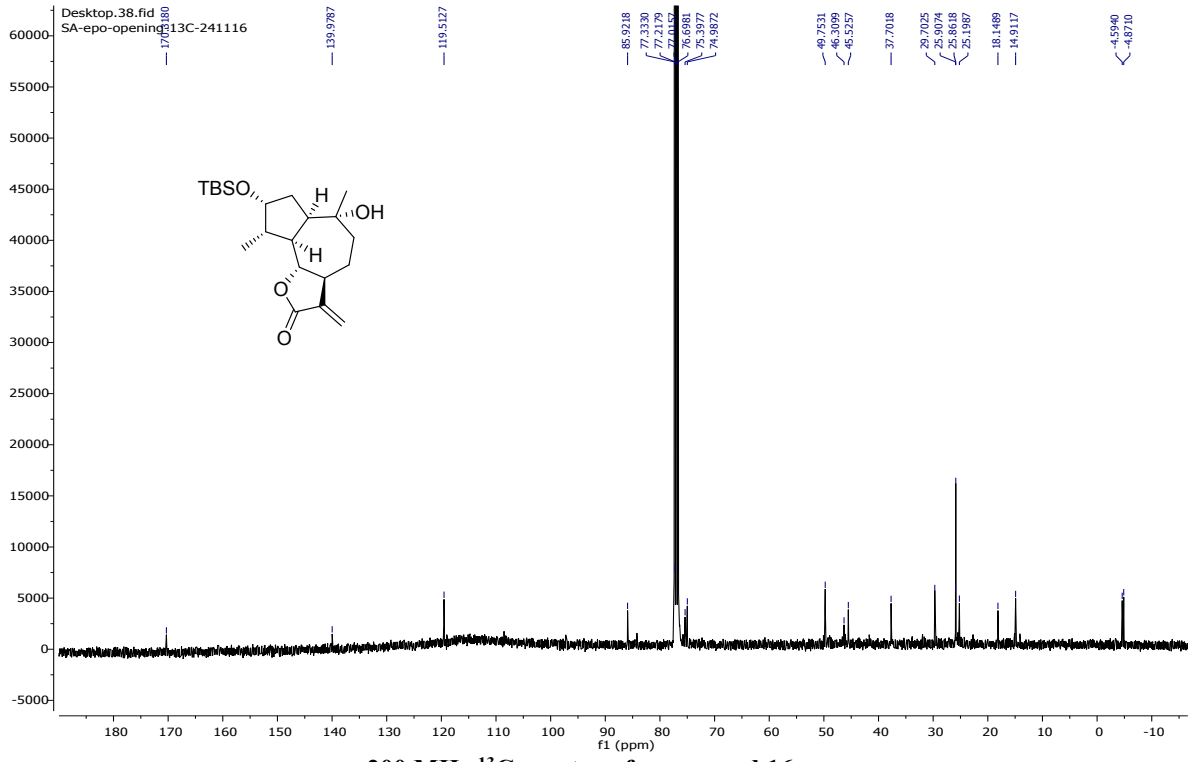
400 MHz 1H spectra of compound 15



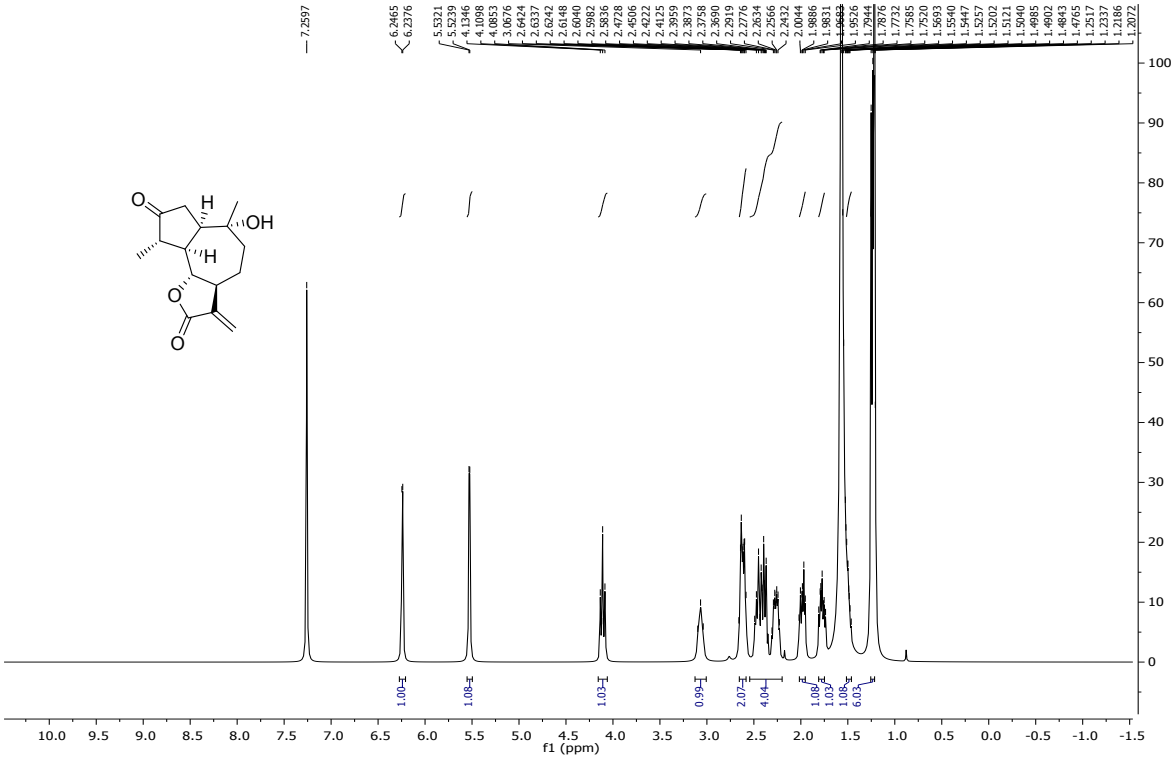
100 MHz ^{13}C spectra of compound 15



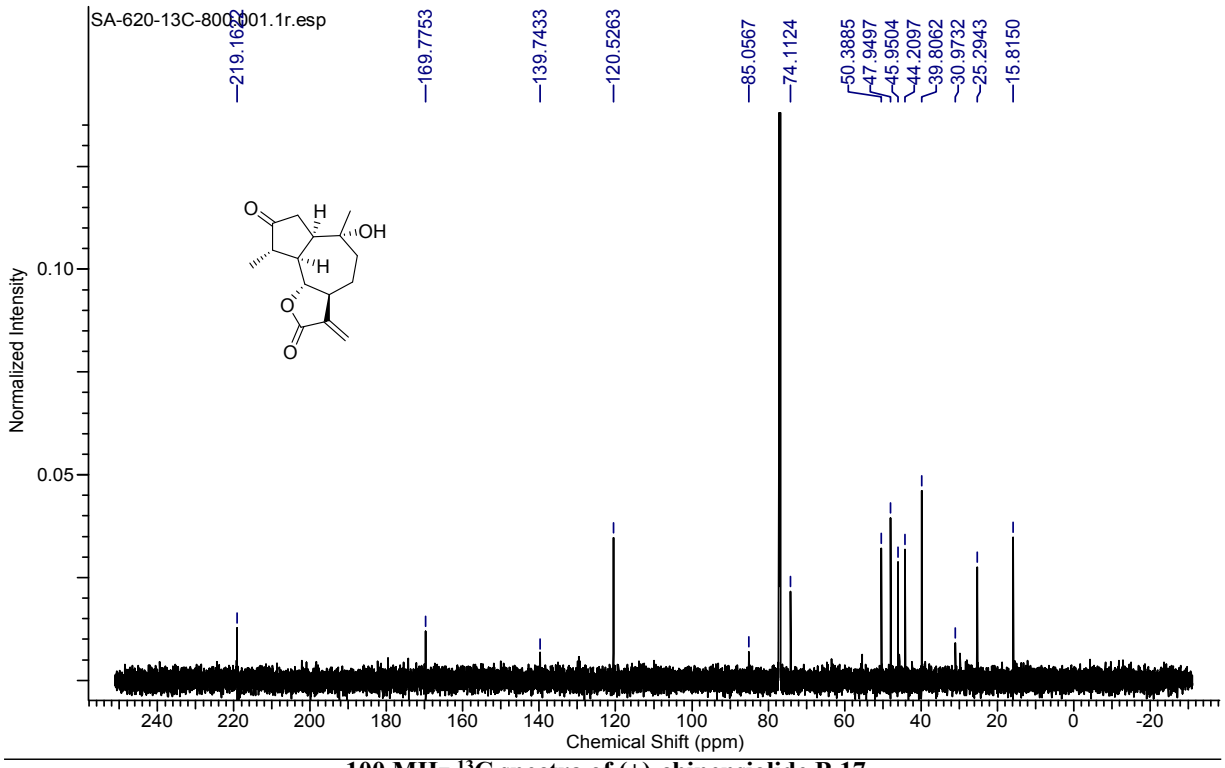
400 MHz 1H spectra of compound 16



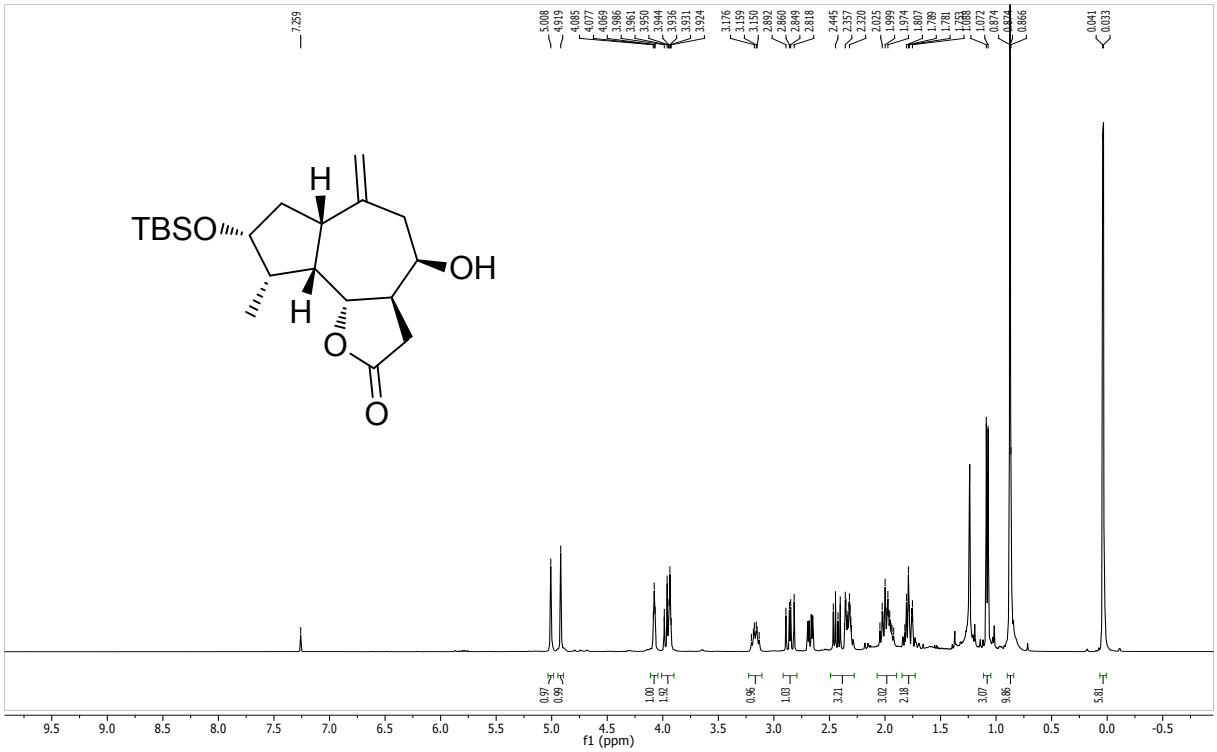
200 MHz ^{13}C spectra of compound 16



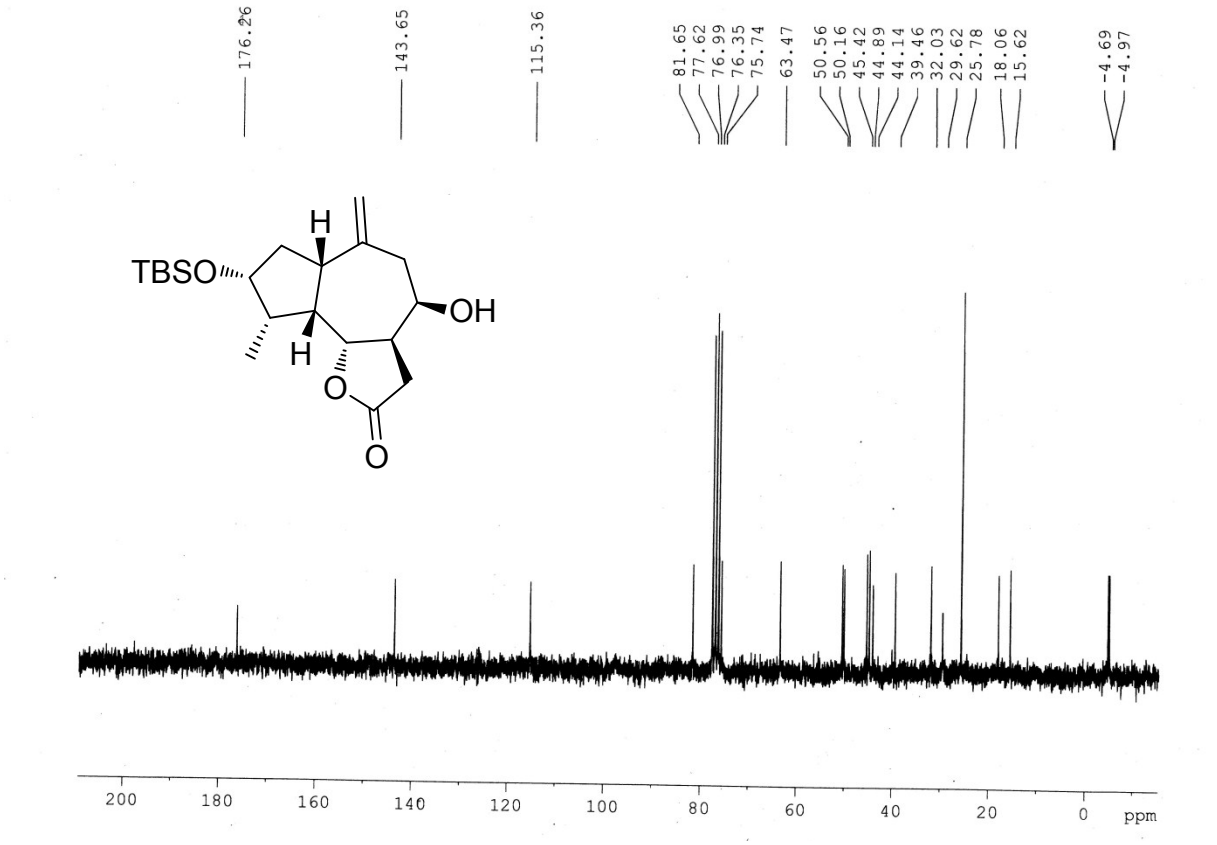
400 MHz 1H spectra of (+)-chinensiolide B 17



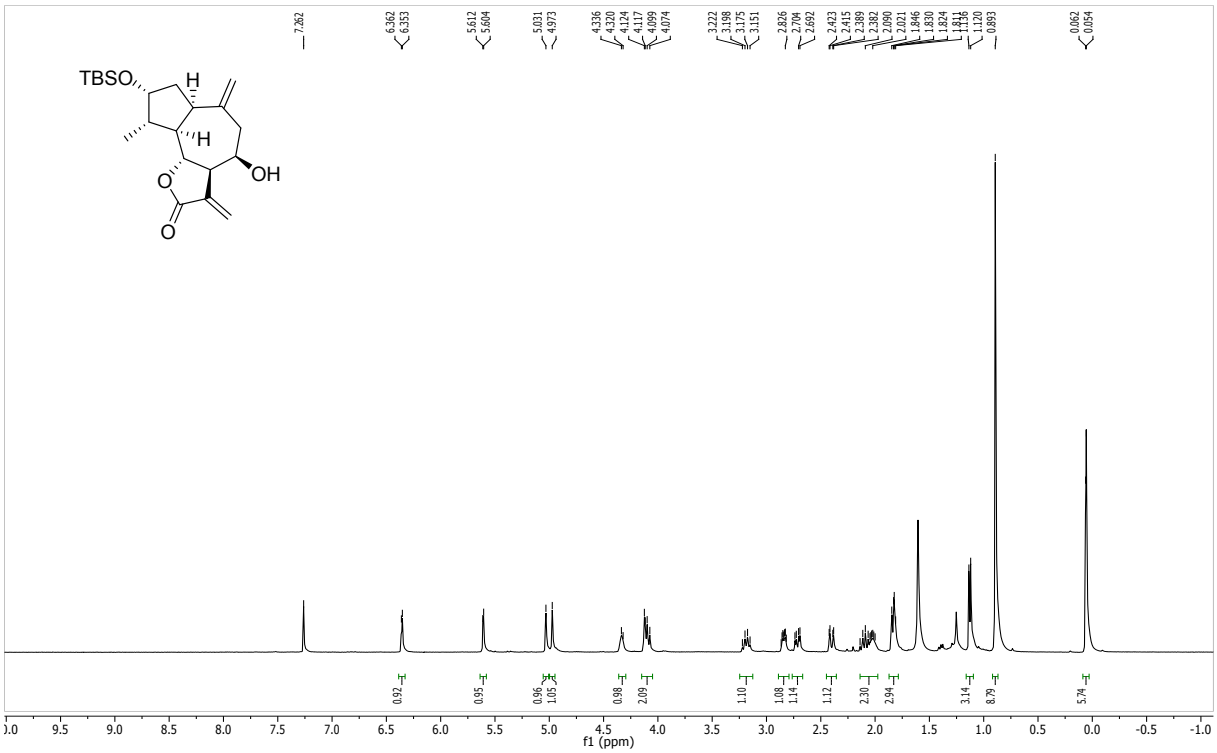
100 MHz ^{13}C spectra of (+)-chinensiolide B 17



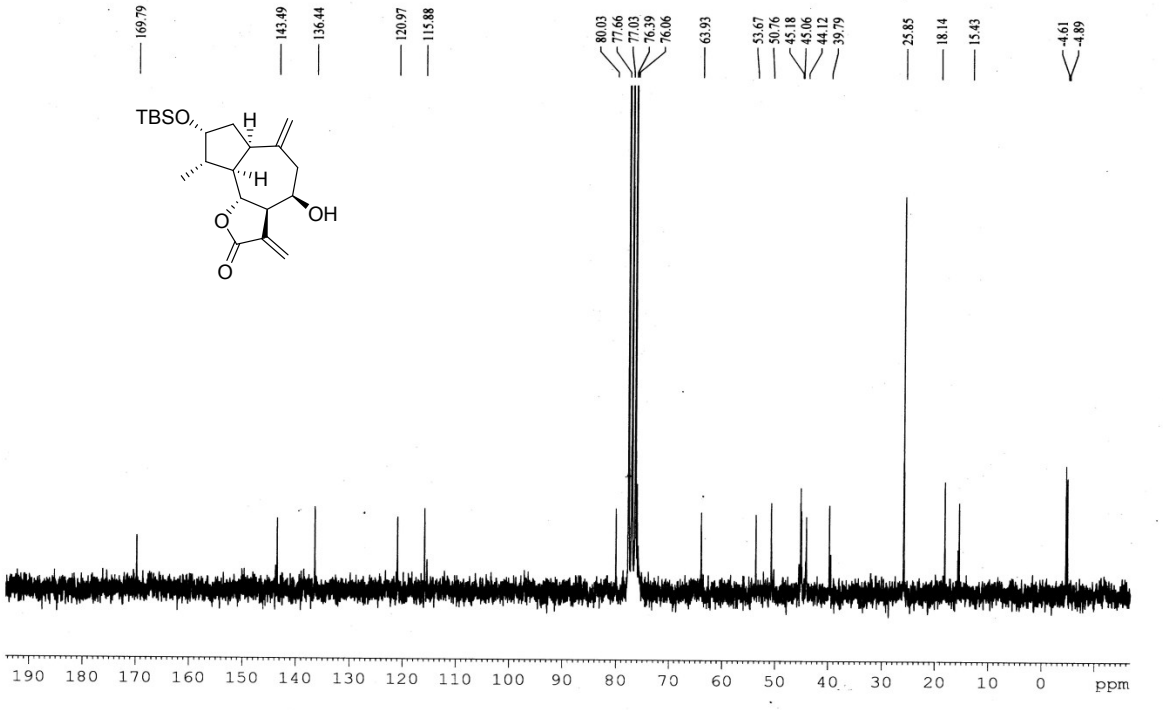
400 MHz 1H spectra of compound 5



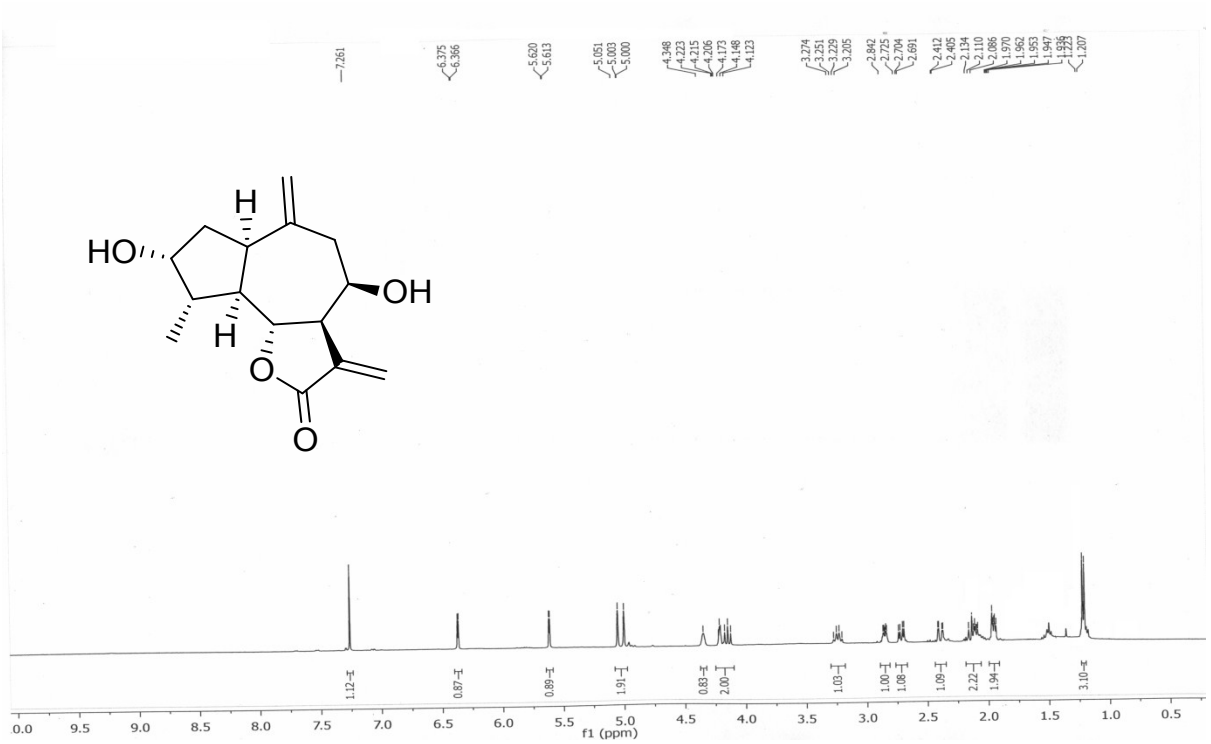
100 MHz ^{13}C spectra of compound 5



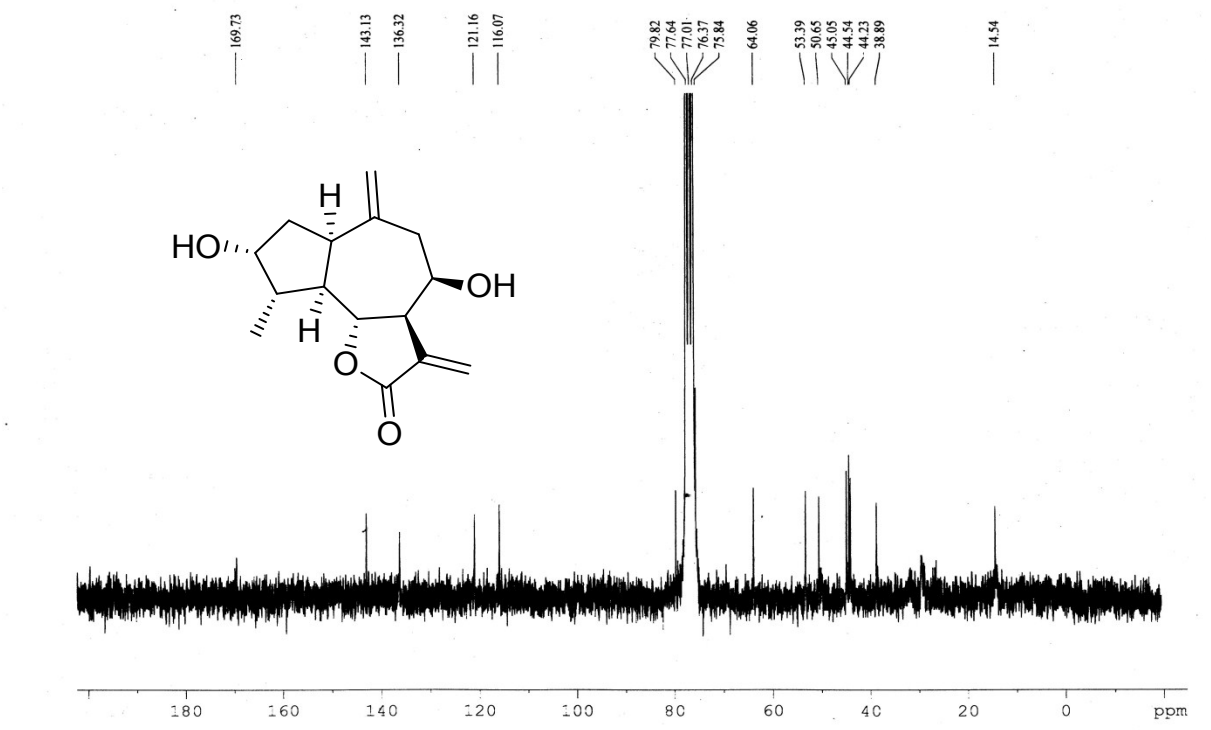
400 MHz 1H spectra of compound 18



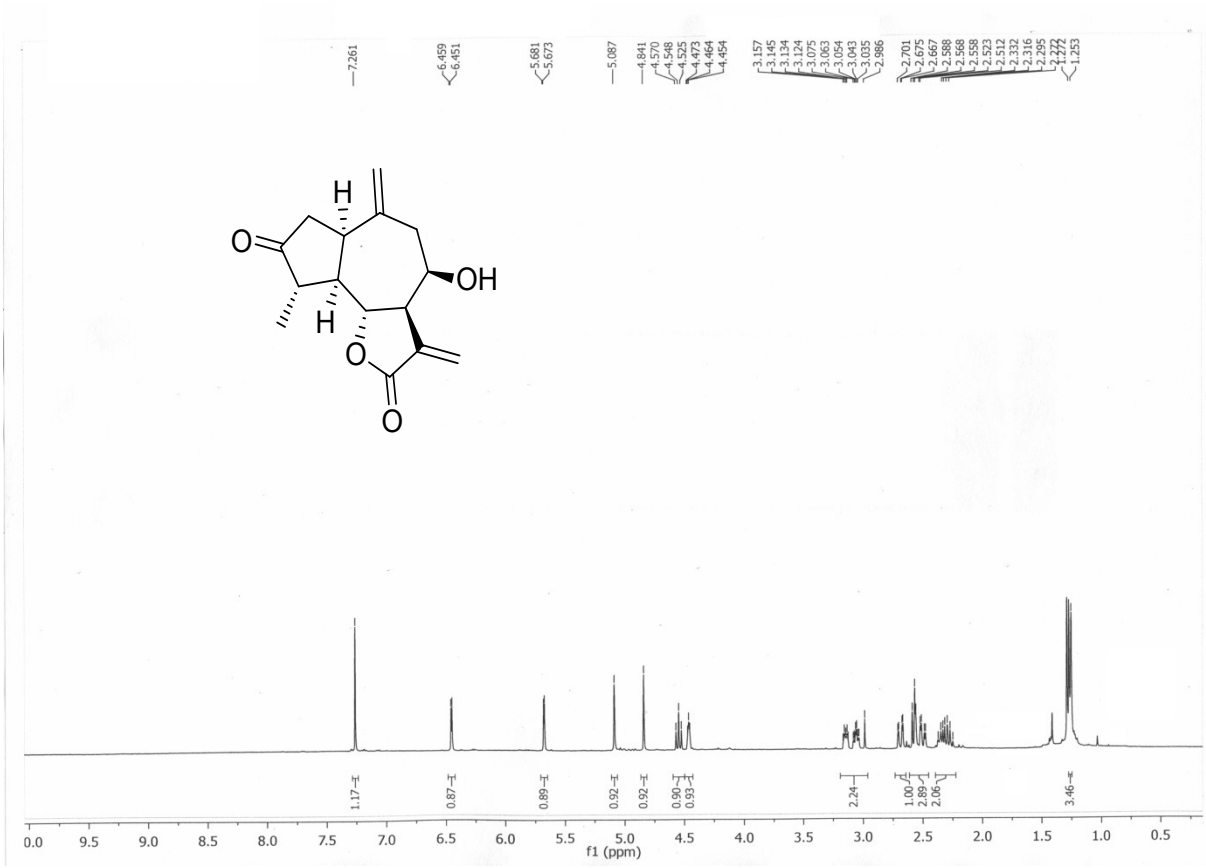
100 MHz ^{13}C spectra of compound 18



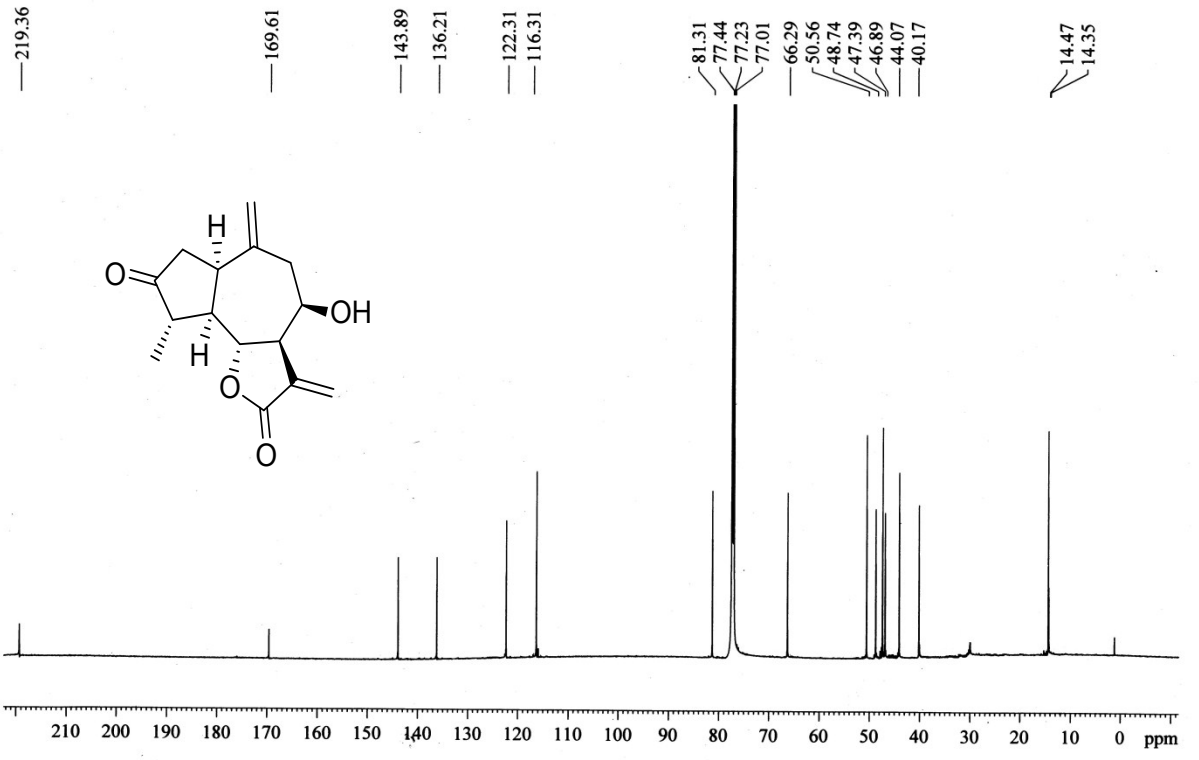
400 MHz 1H spectra of compound 19



100 MHz ^{13}C spectra of compound 19



400 MHz 1H spectra of compound 20



100 MHz ^{13}C spectra of compound 20