Supporting Information

Asymmetric Synthesis of the C15–C32 Fragment of Alotamide and Determination of the Relative Stereochemistry

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[a]Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 501 Haike Road, Shanghai 201203, China.

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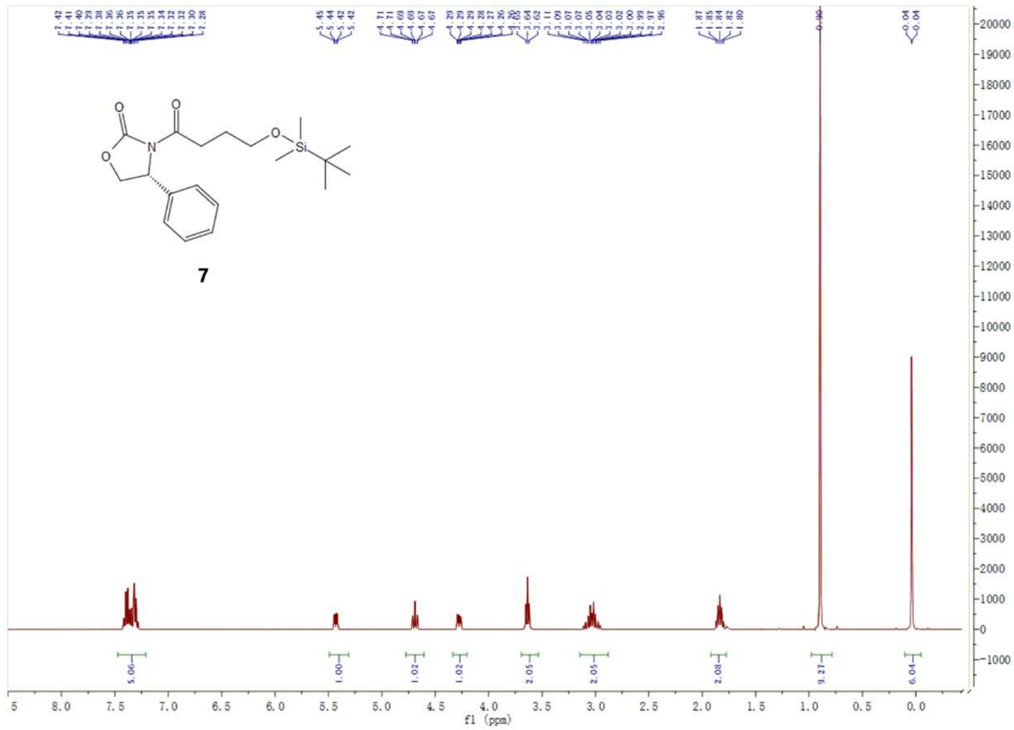
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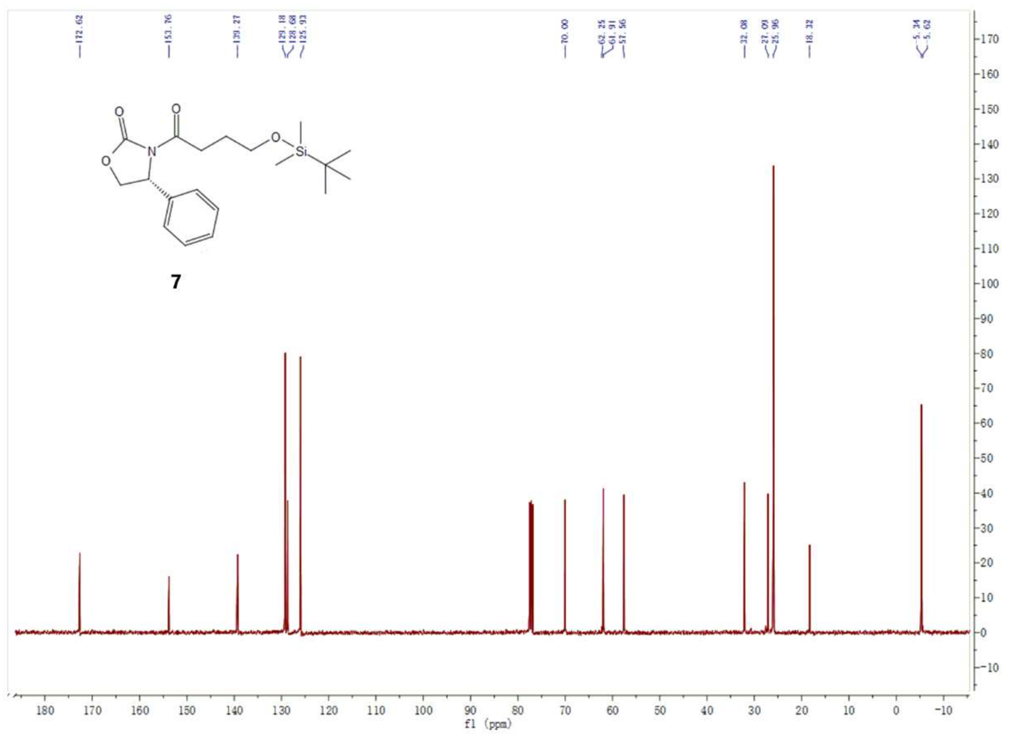
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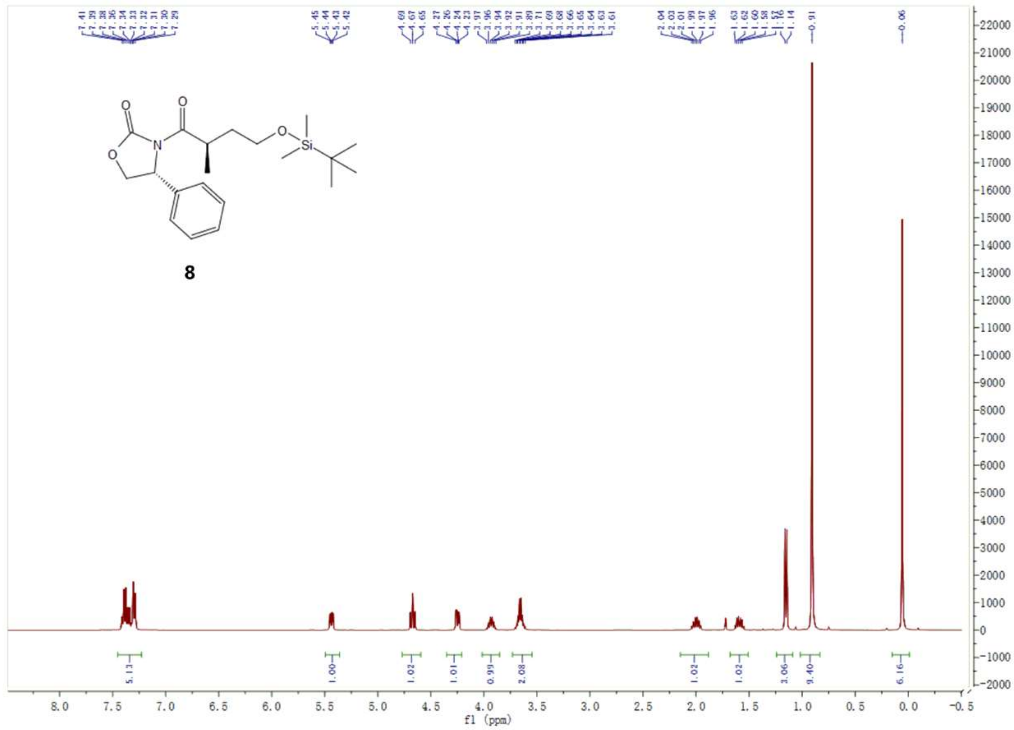

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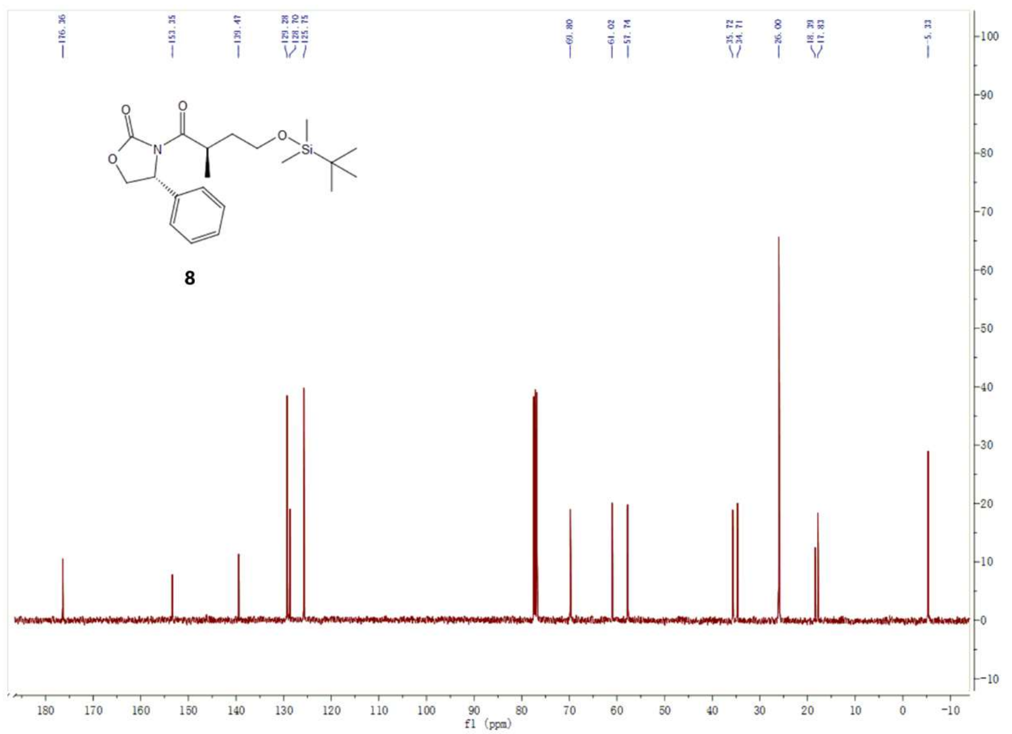

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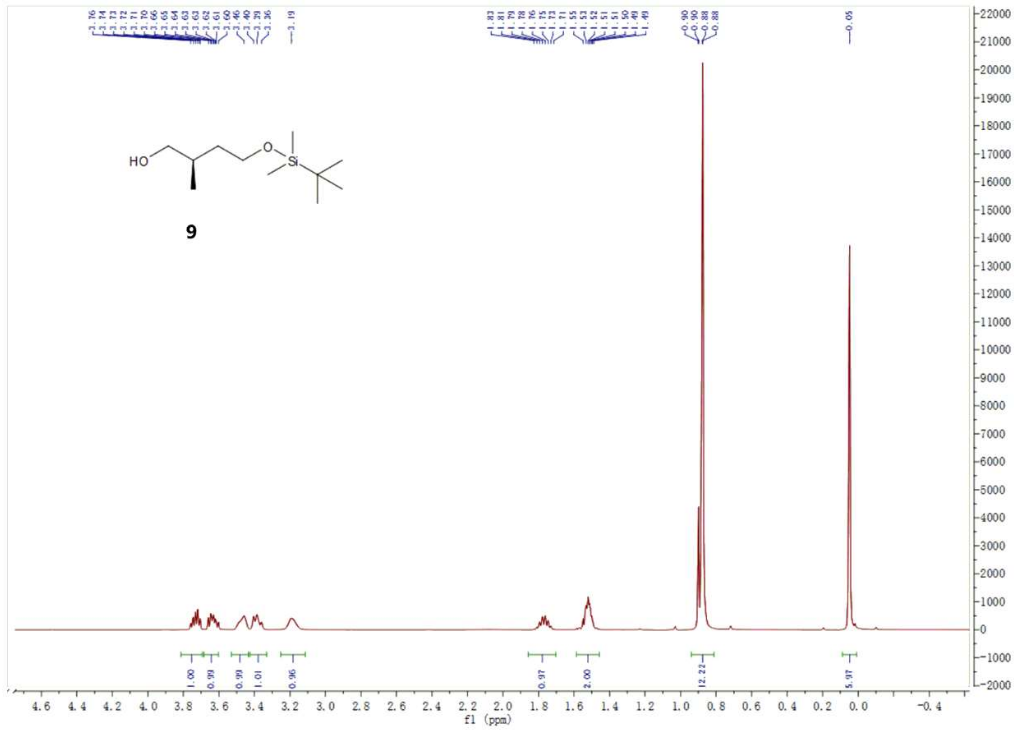

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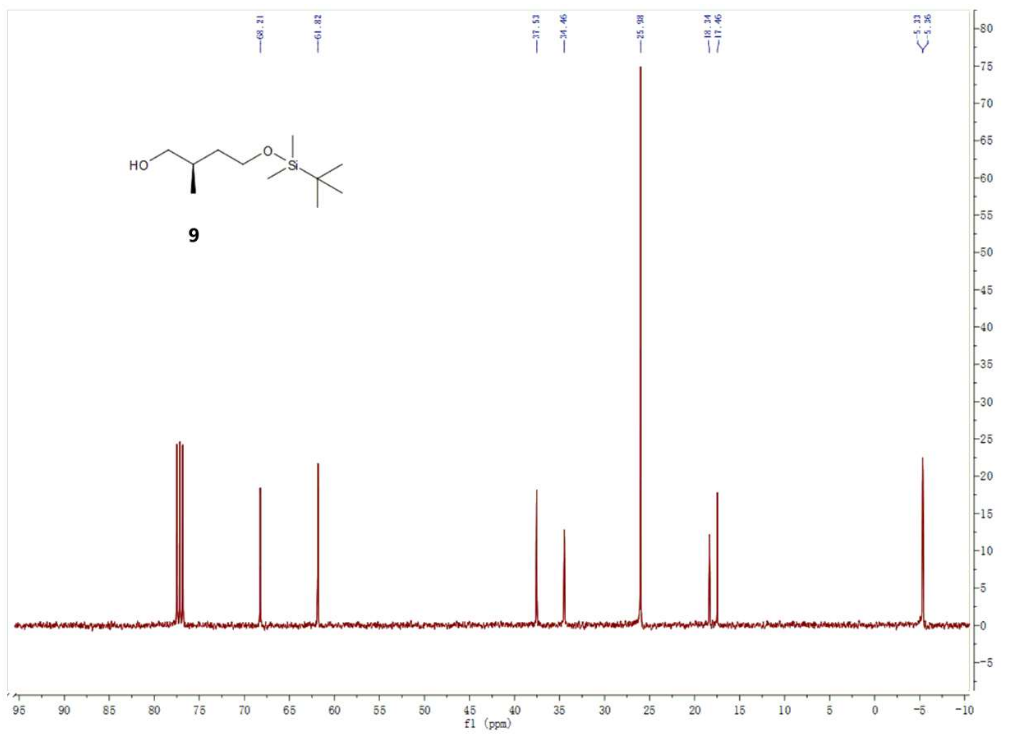

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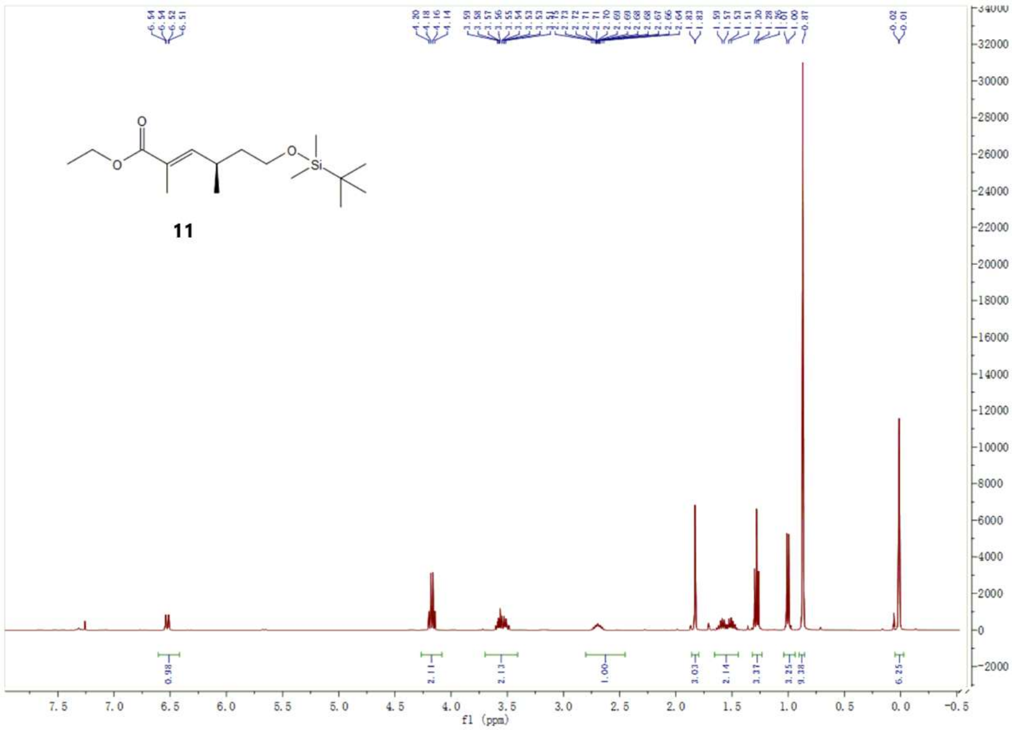

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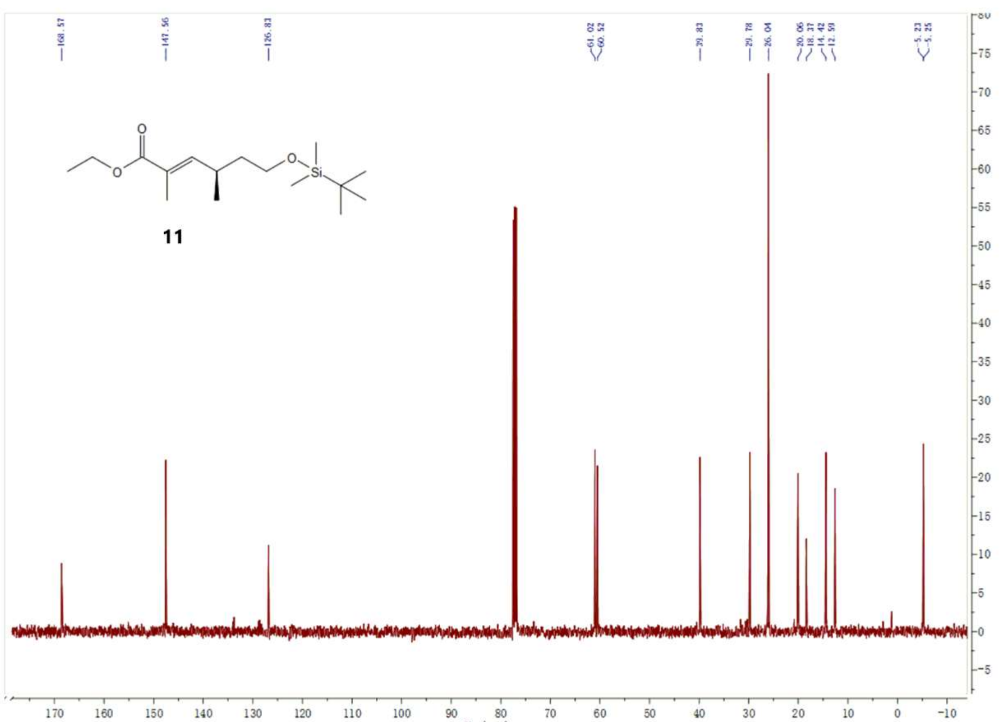

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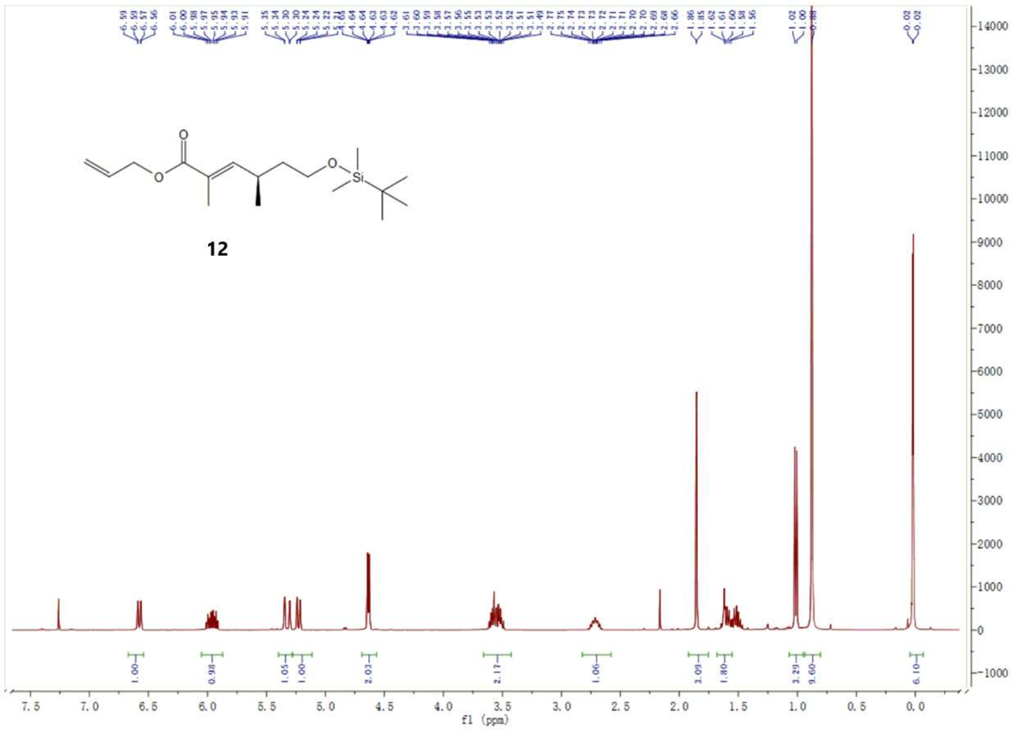
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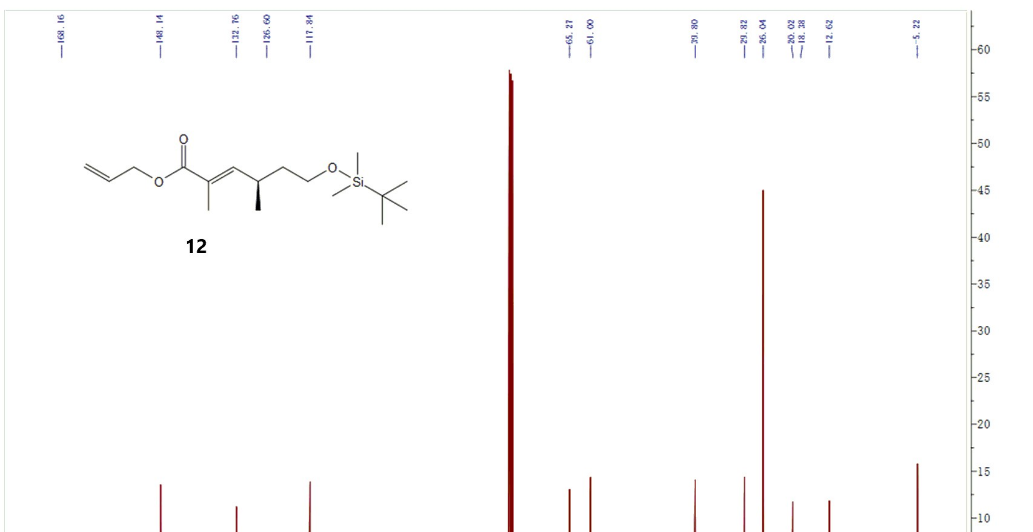
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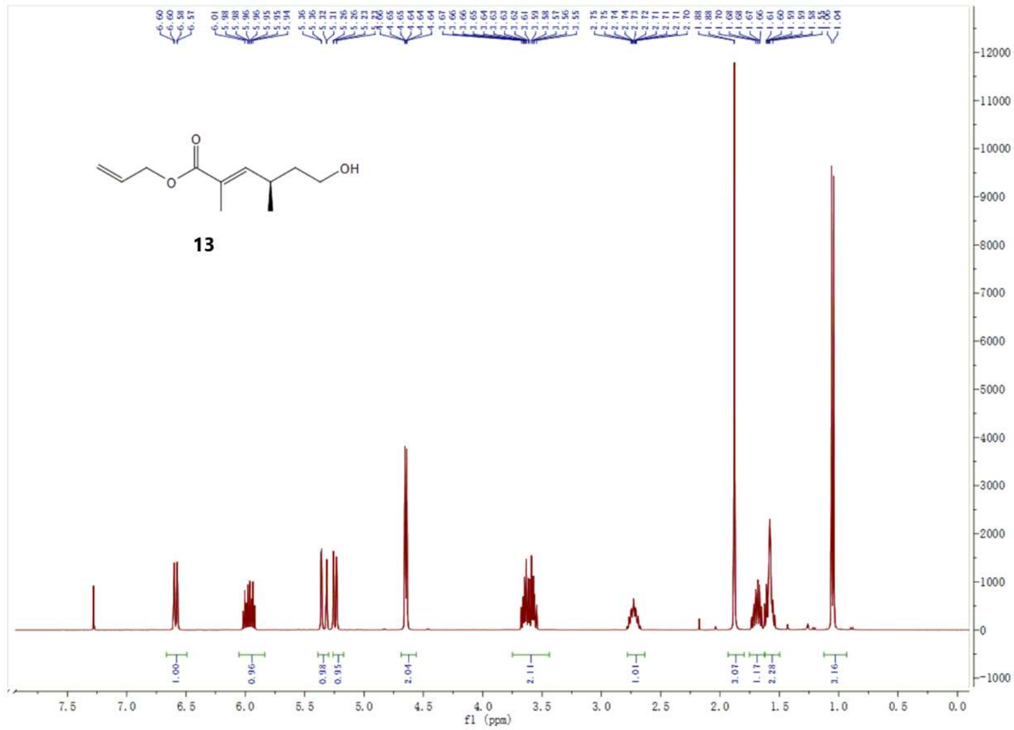

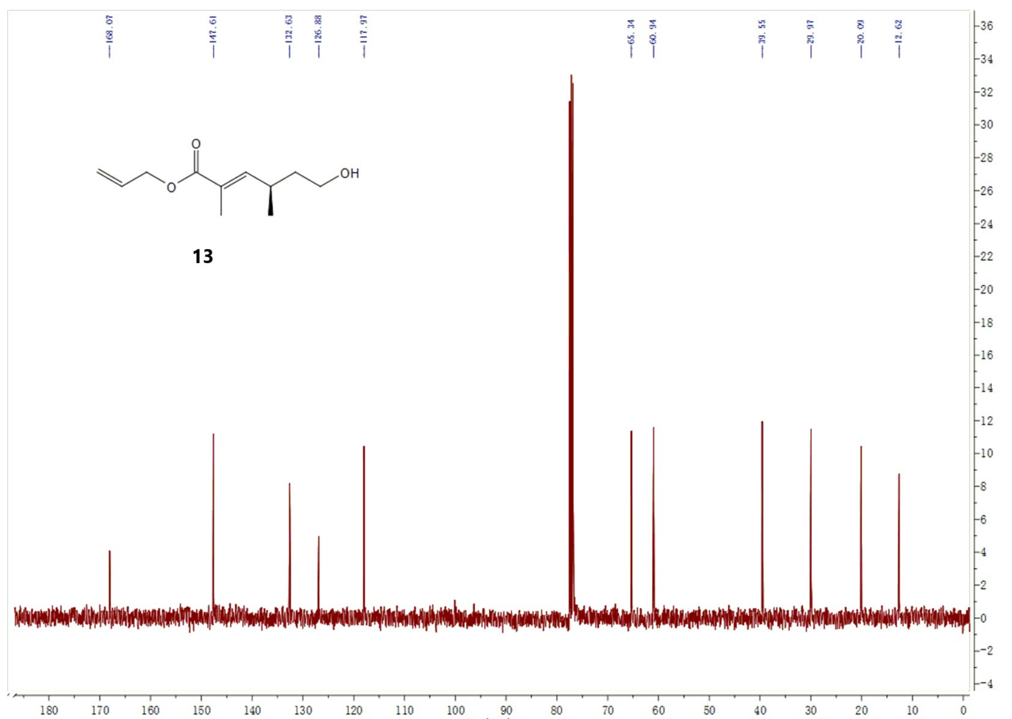

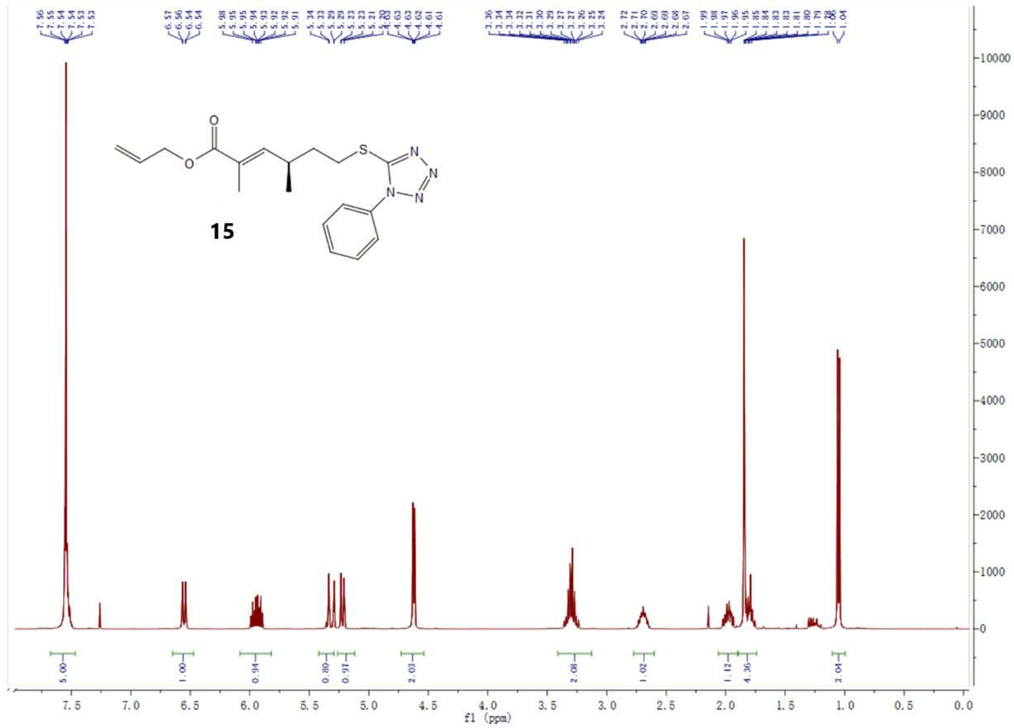

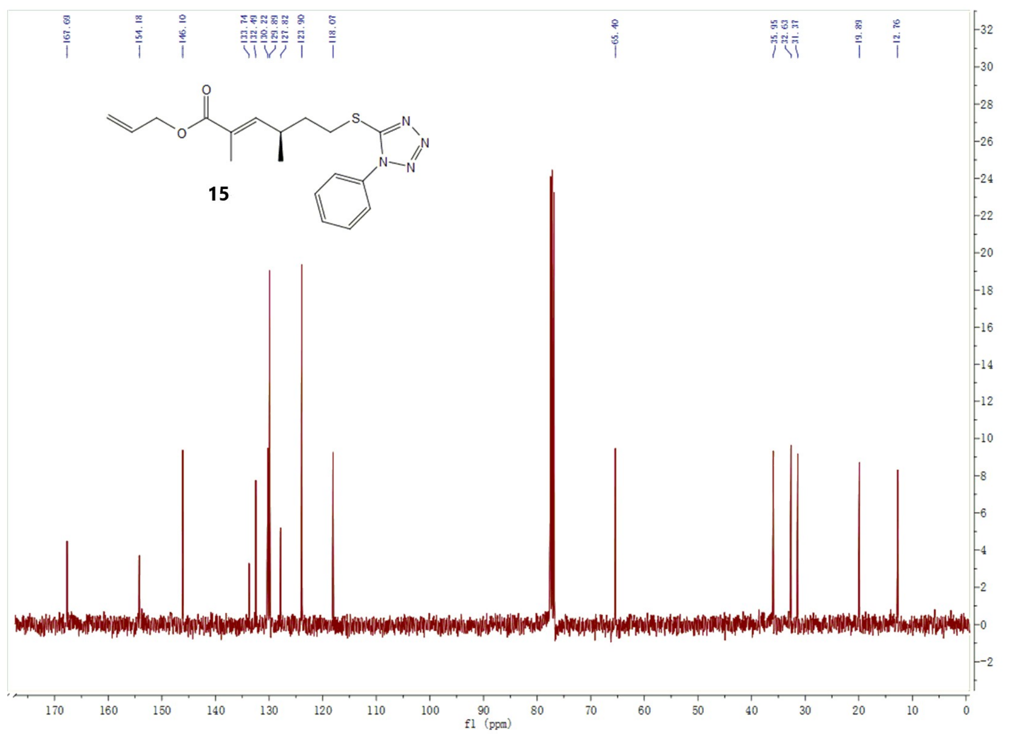

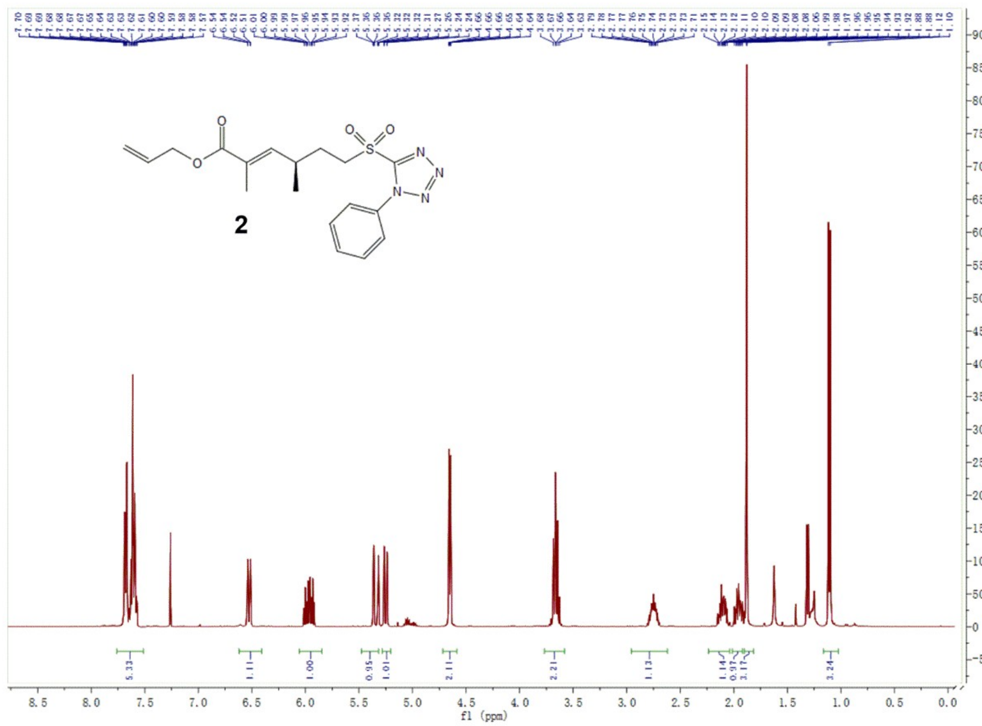
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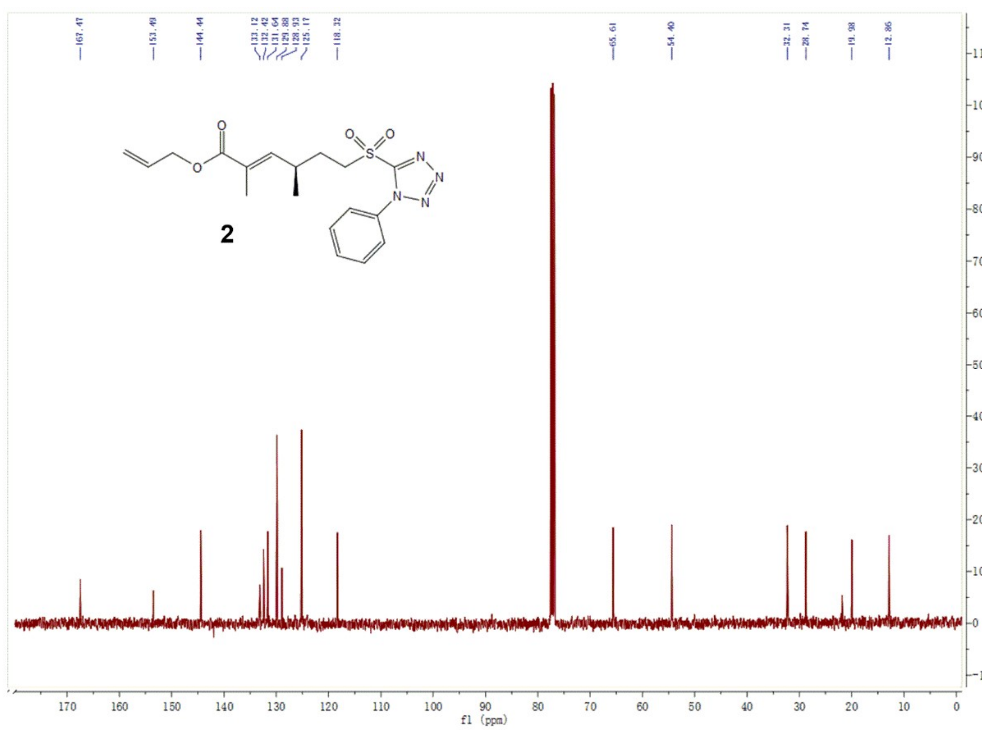
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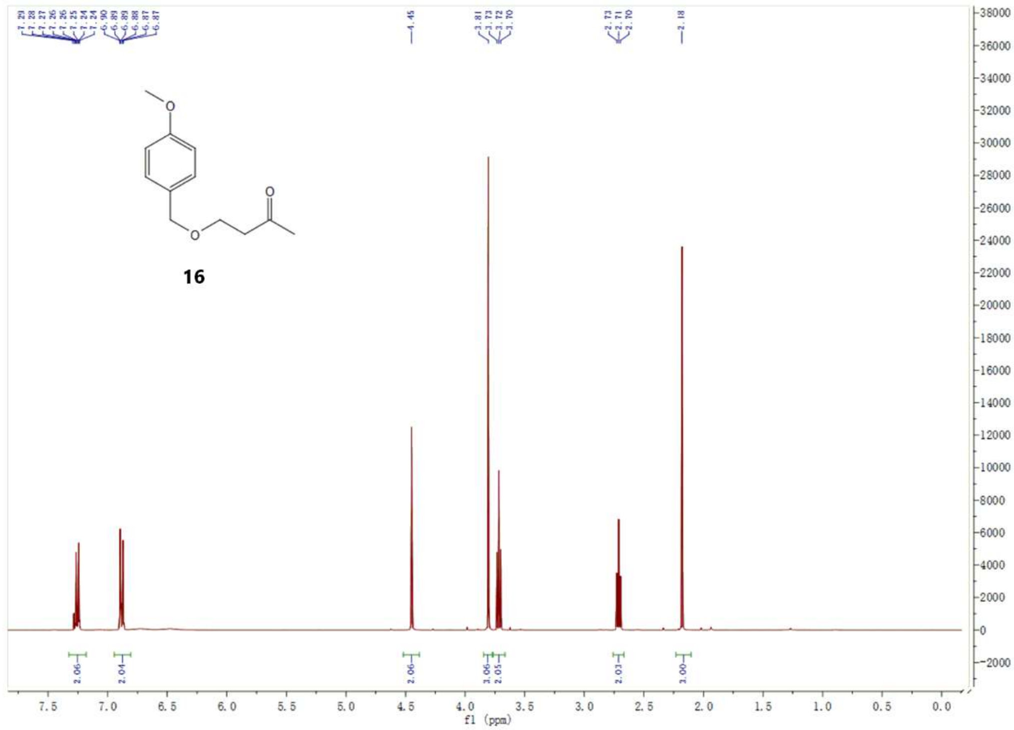
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4.45
3.81 3.73 3.72 3.70
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2.18
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O
O
16
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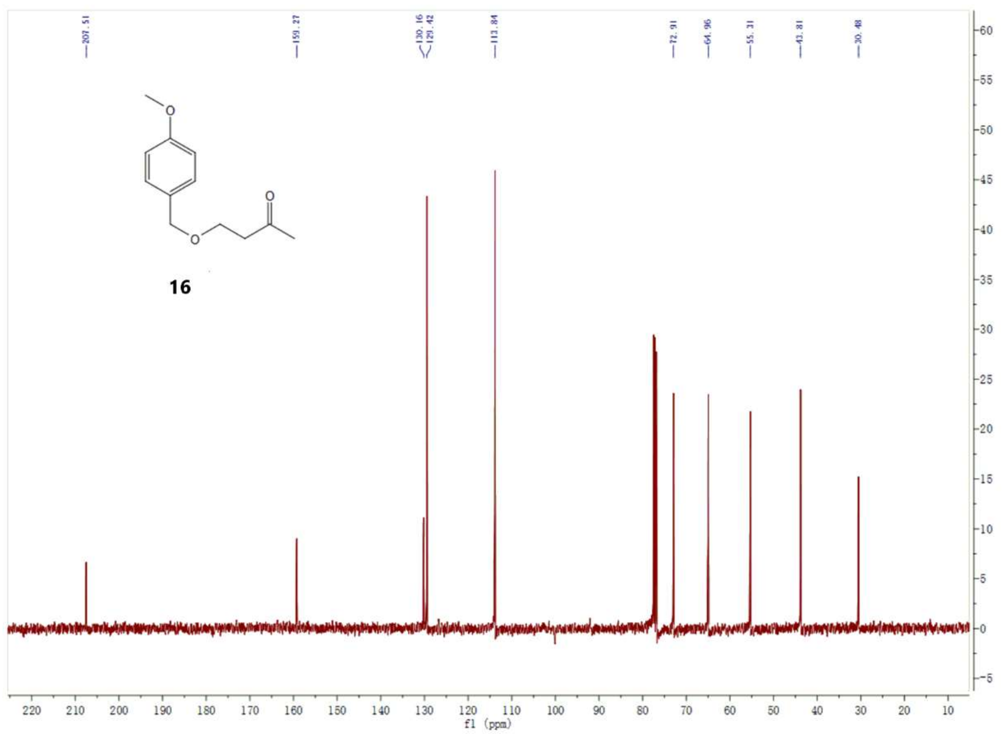
f1 (ppm)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O
O
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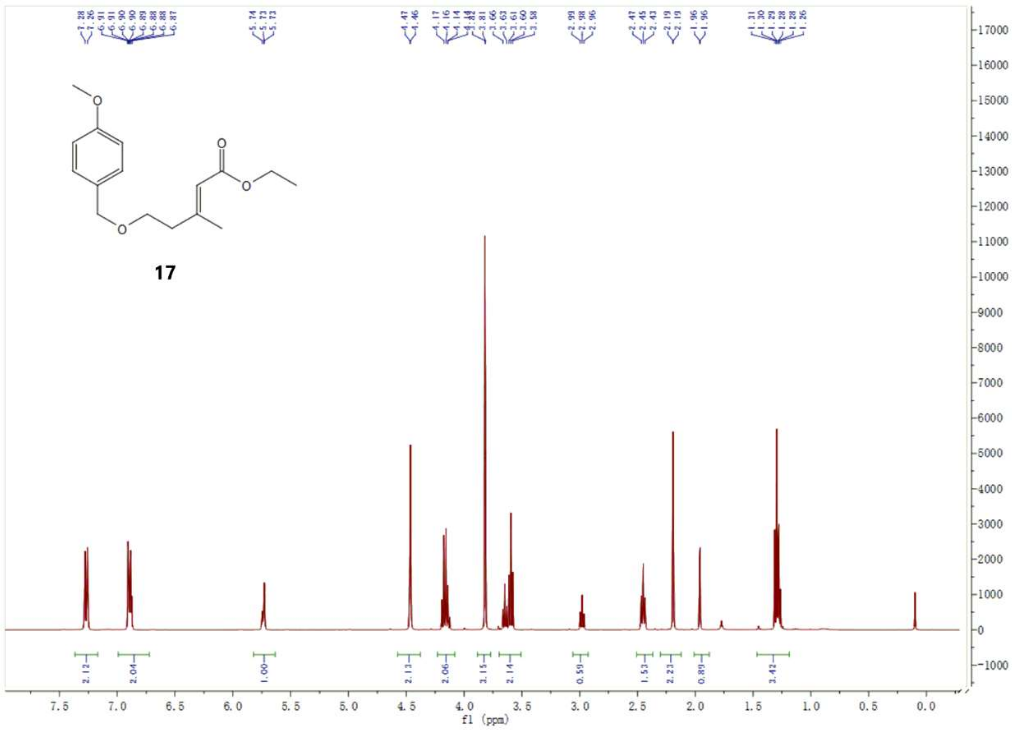
f1 (ppm)



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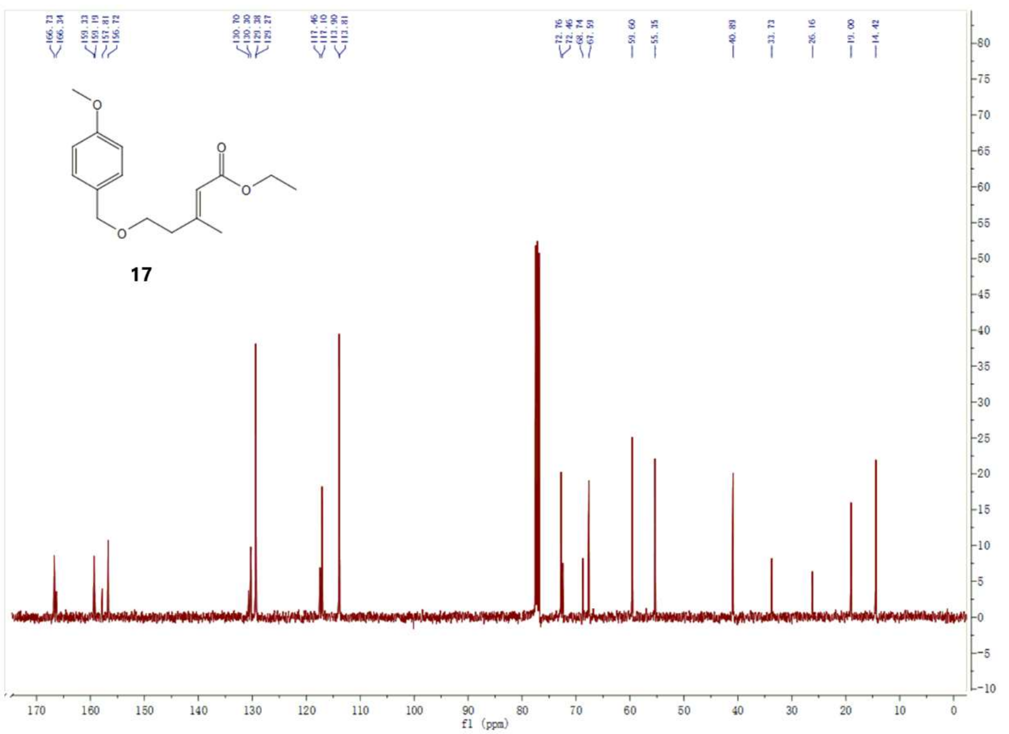

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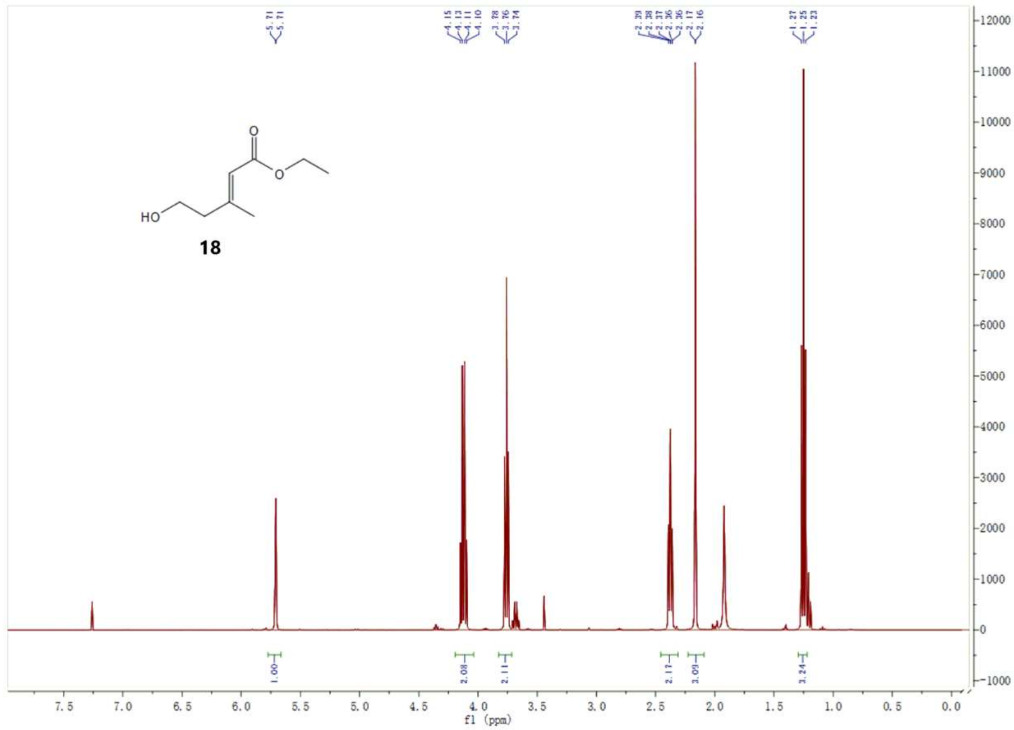

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5.71
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4.10
3.78
3.76
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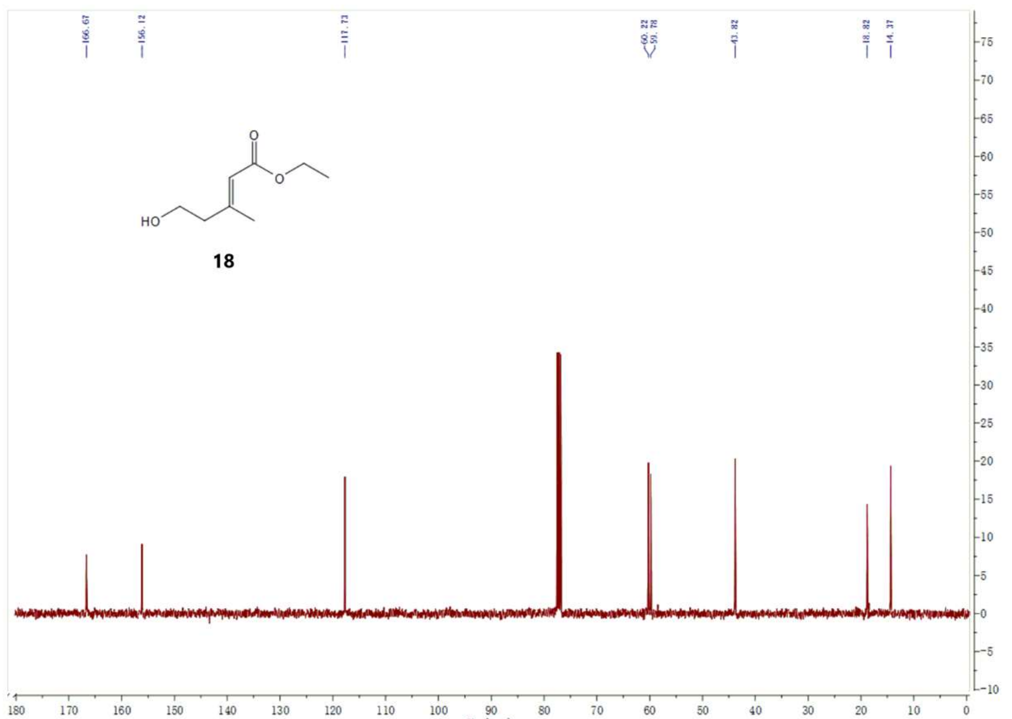
2.39
2.38
2.37
2.36
2.36
2.17
2.16
1.27
1.25
1.23
O
O
HO
18
1.00
2.08
2.11
2.17
3.09
3.24
f1 (ppm)



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O
O
HO
18
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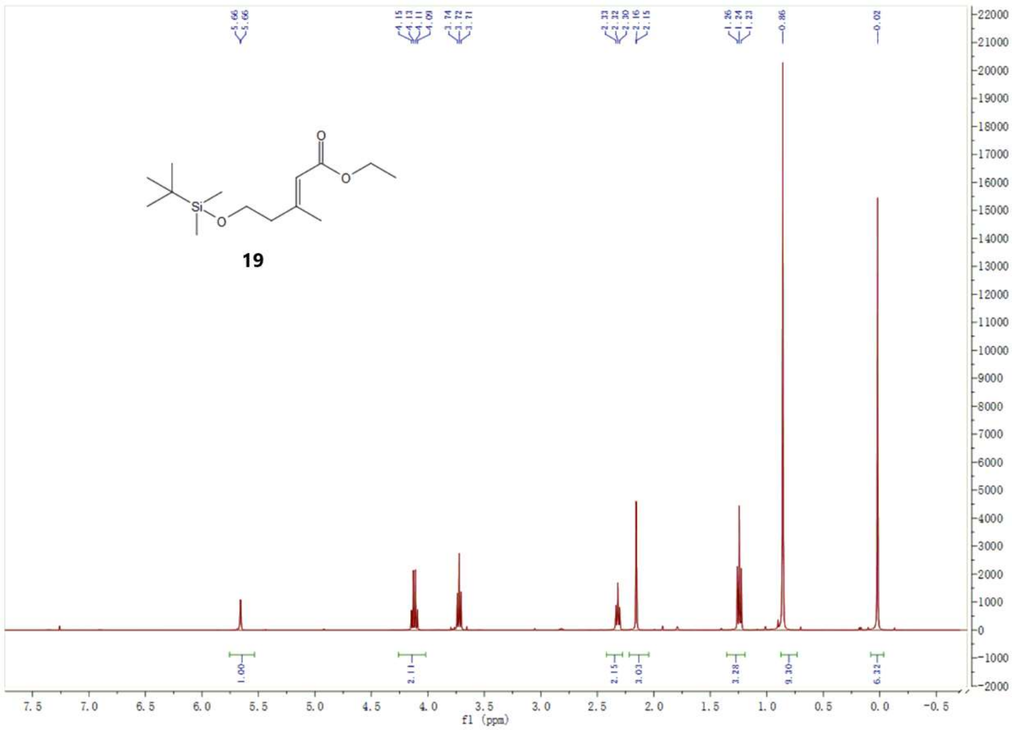

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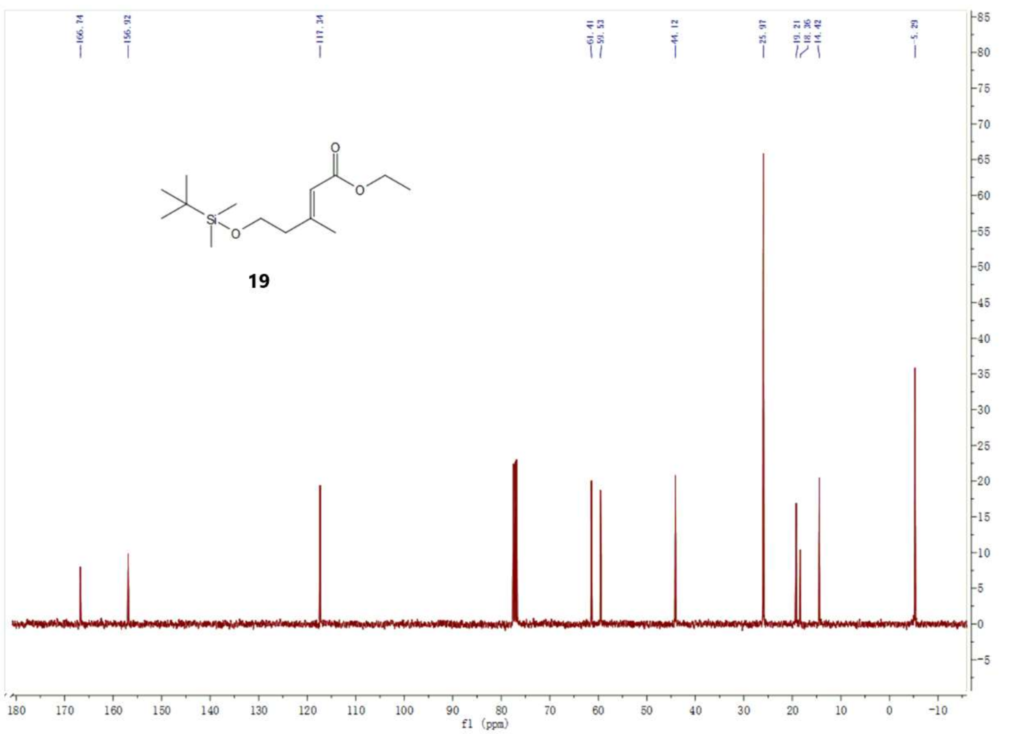

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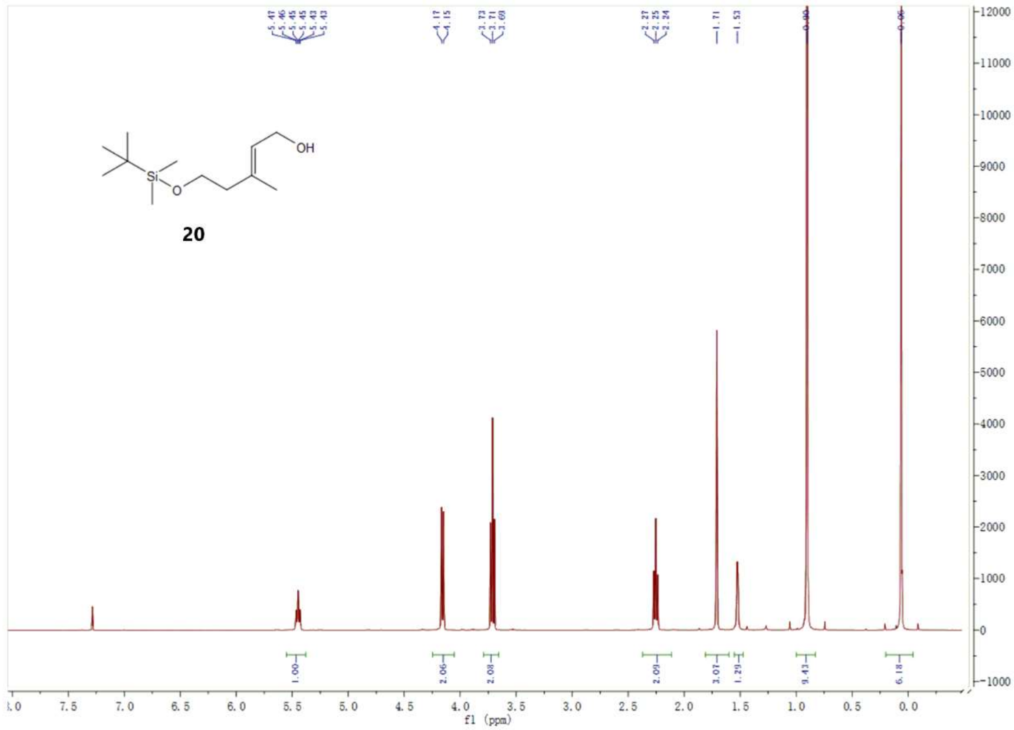

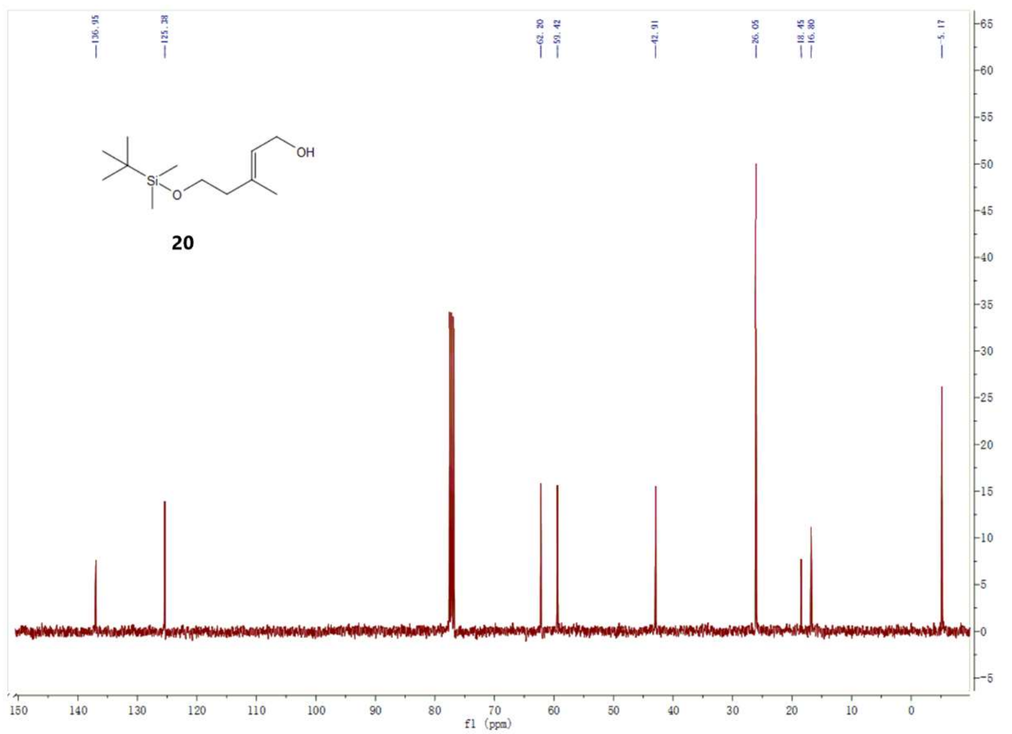

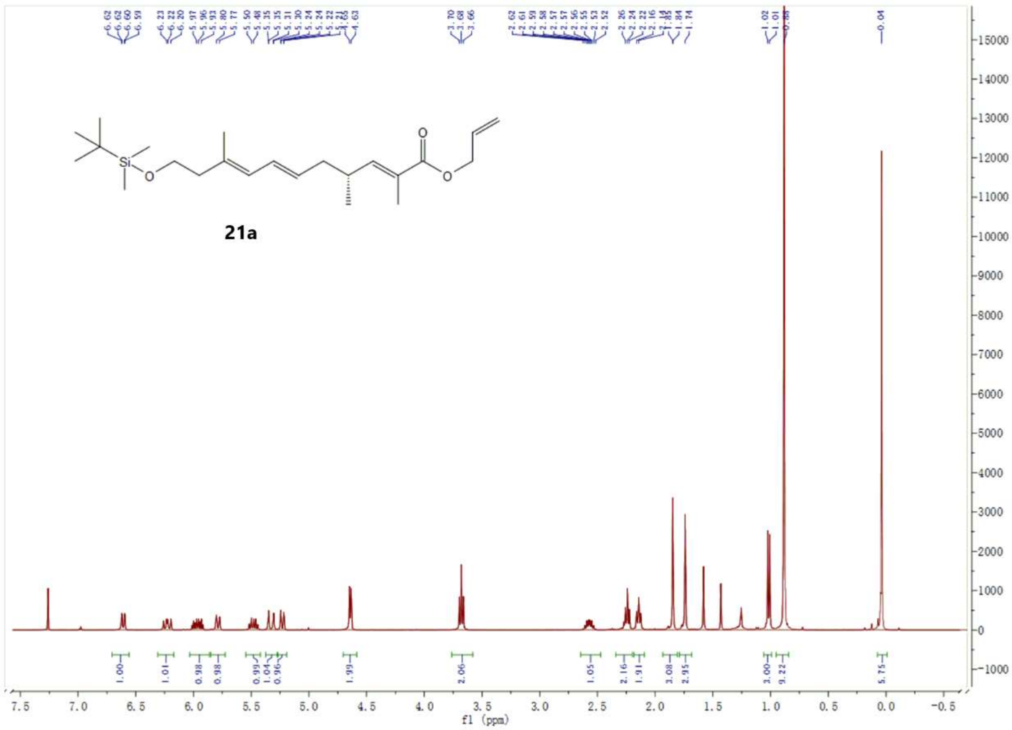

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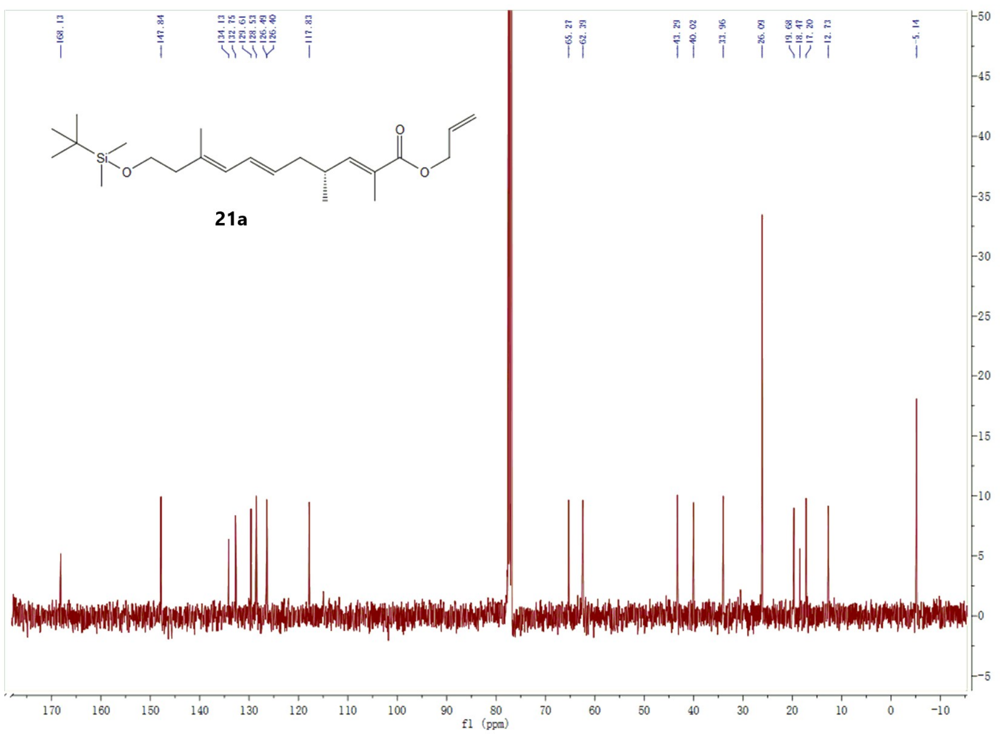

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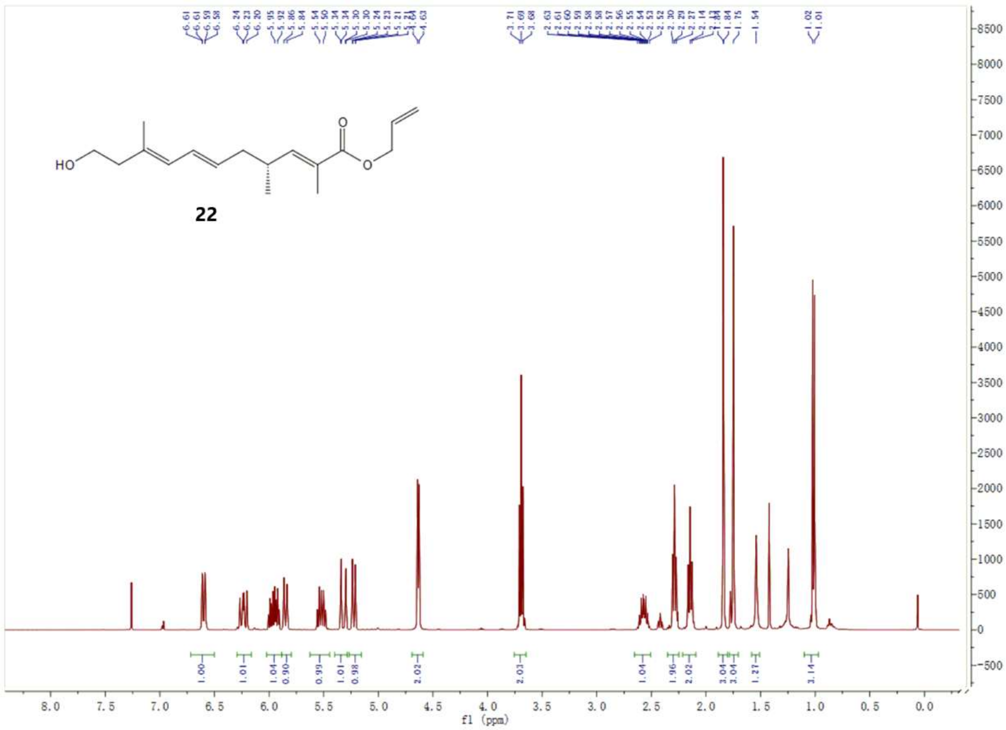
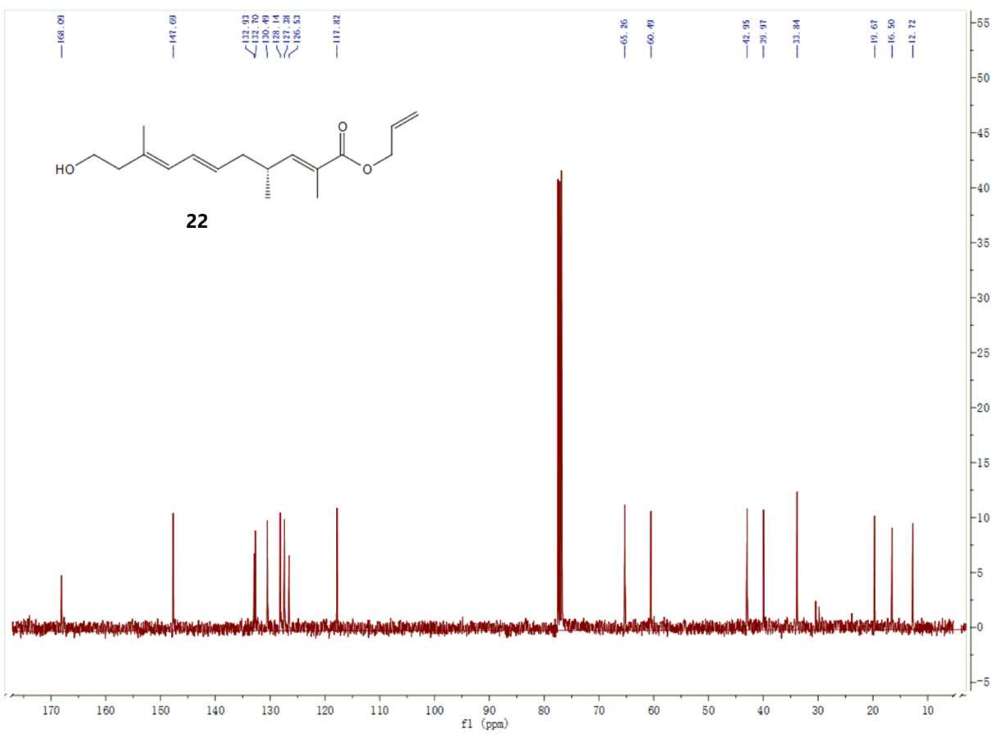


HO
O
O
22
f1 (ppm)



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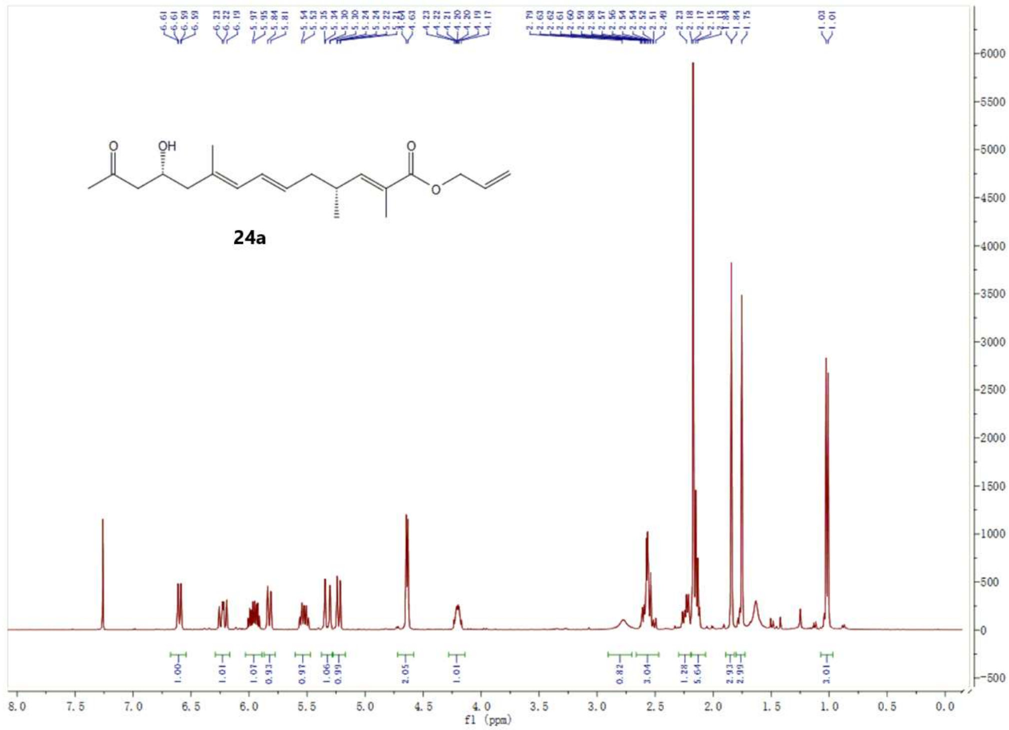
19.67
16.50
12.72
HO
O
O
22
f1 (ppm)



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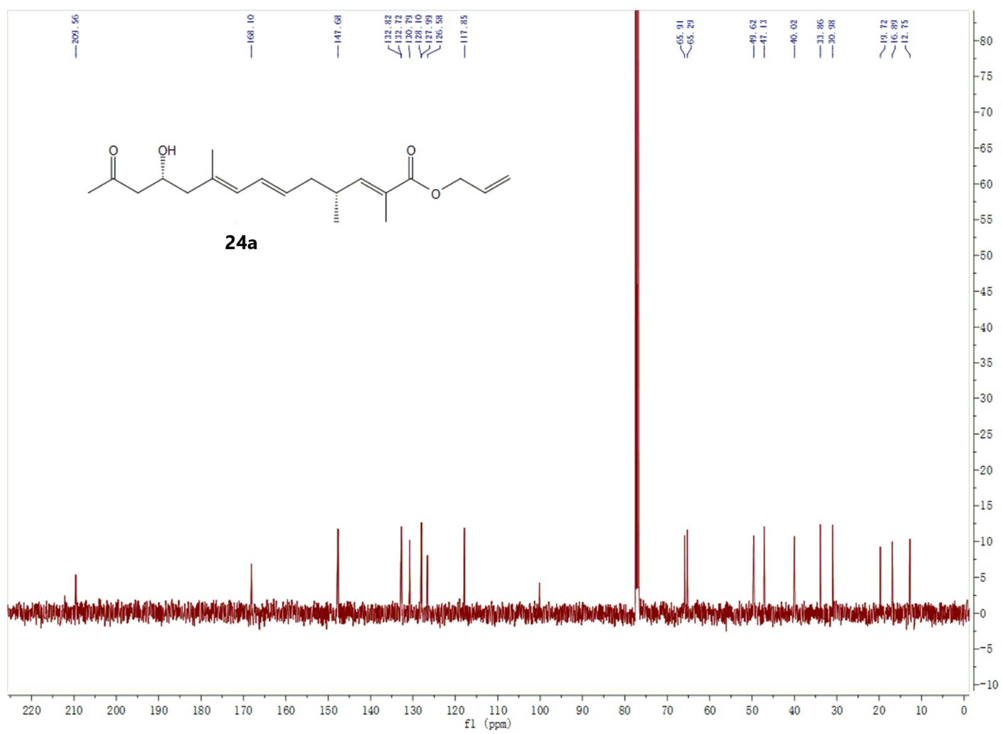

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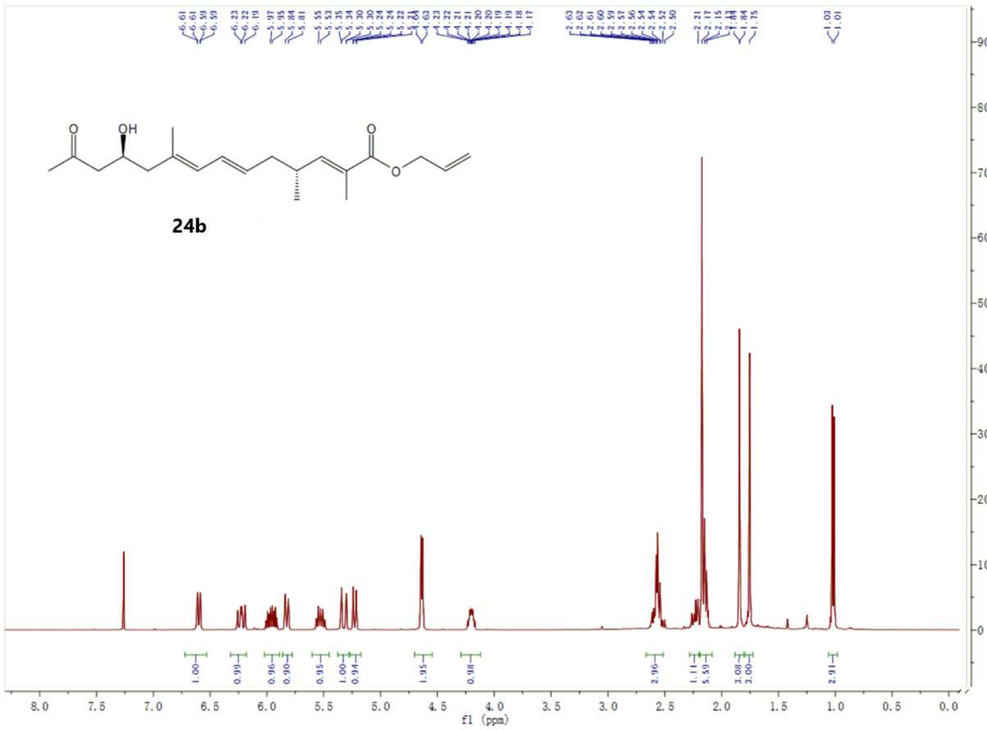

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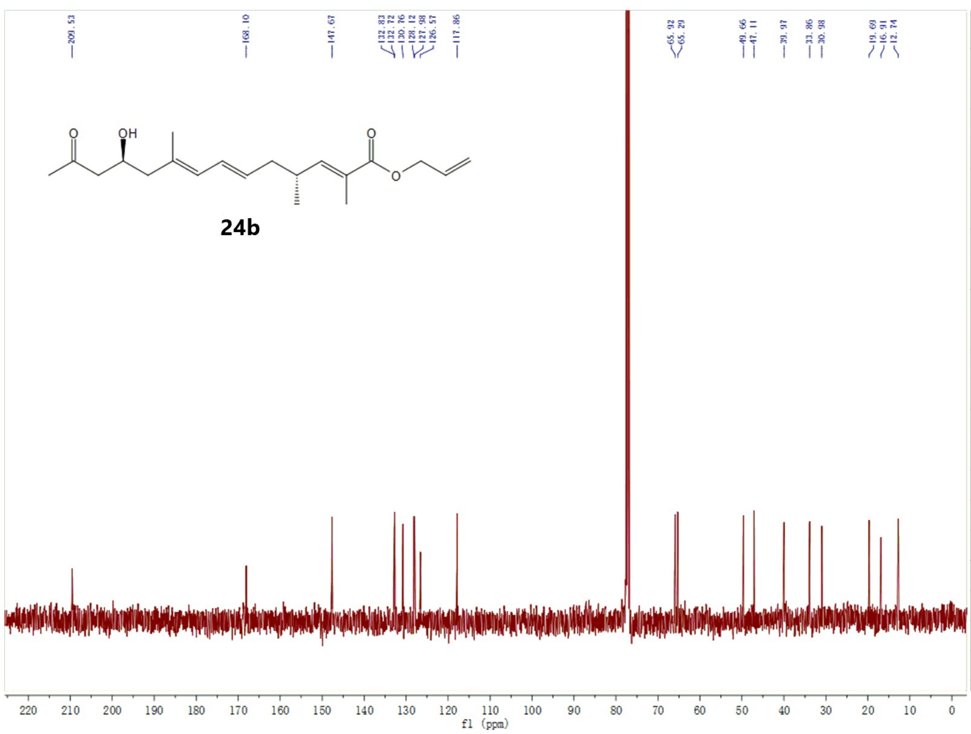

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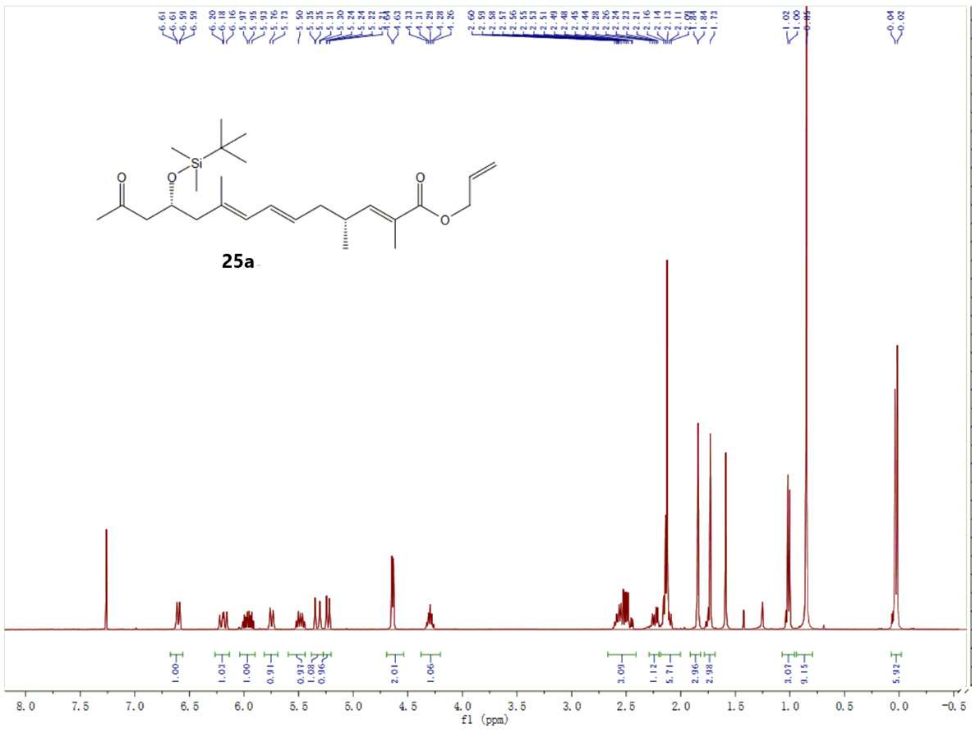
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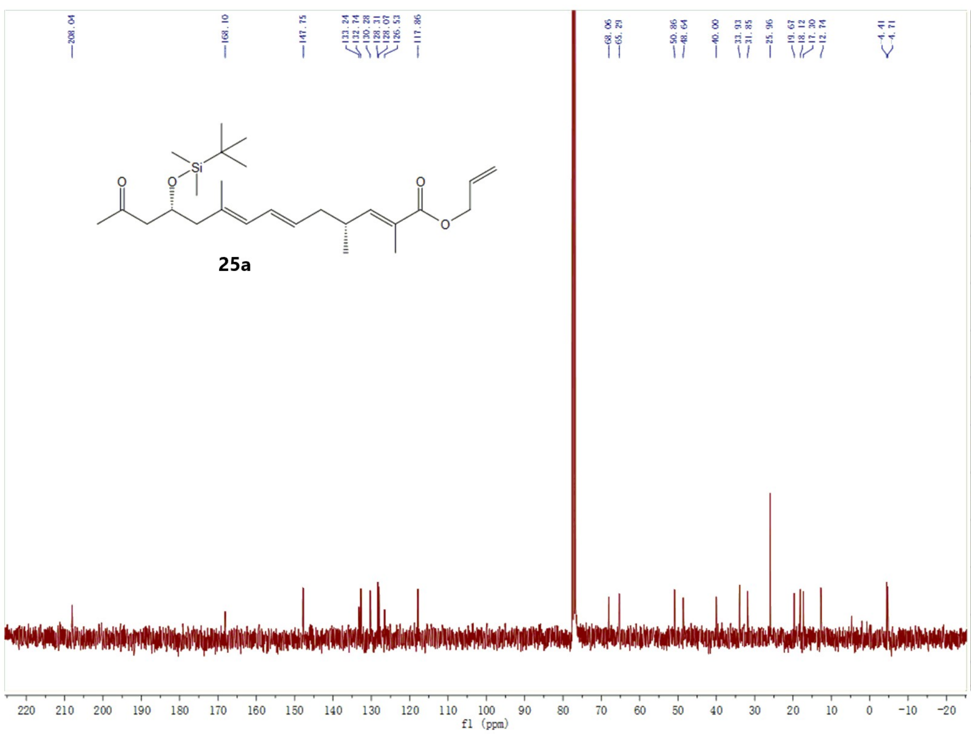
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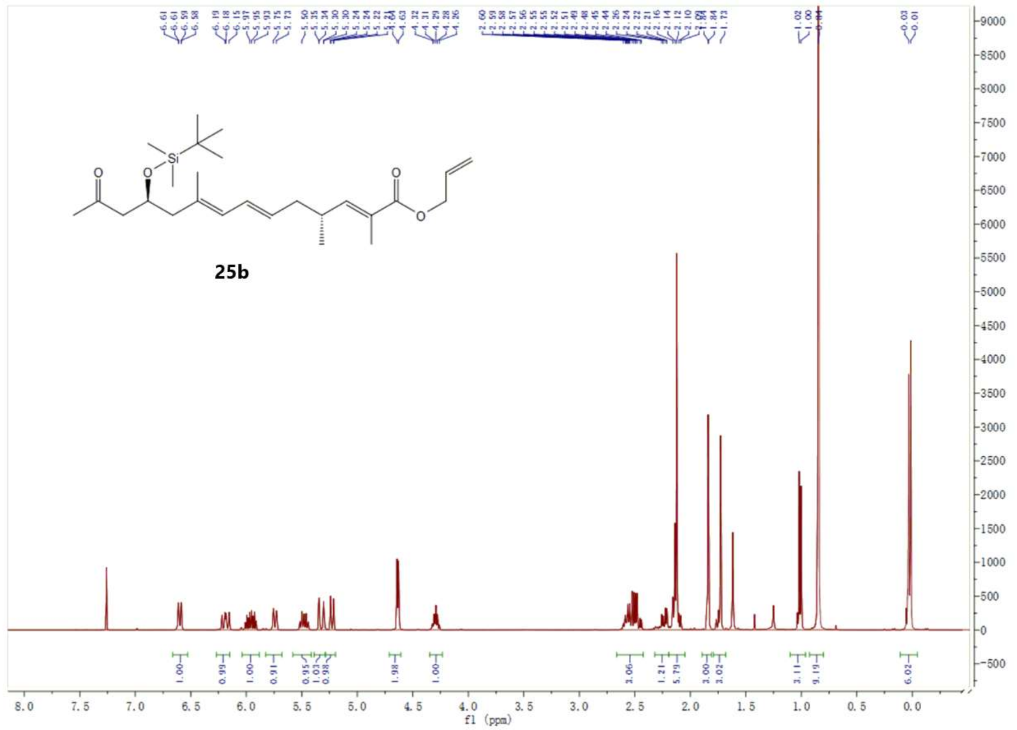
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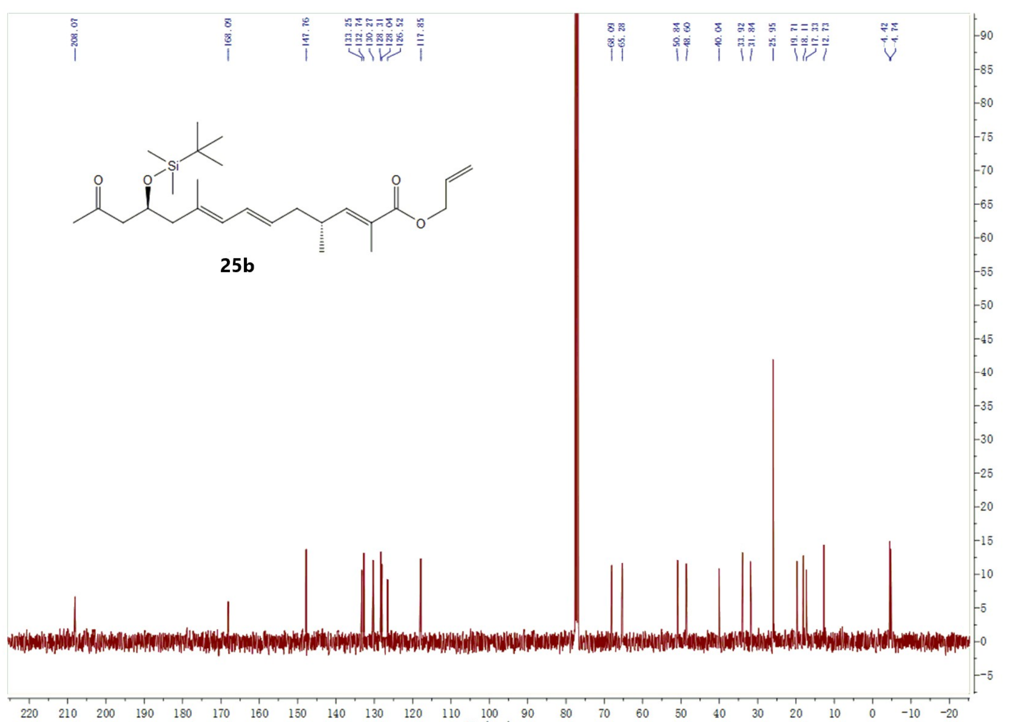
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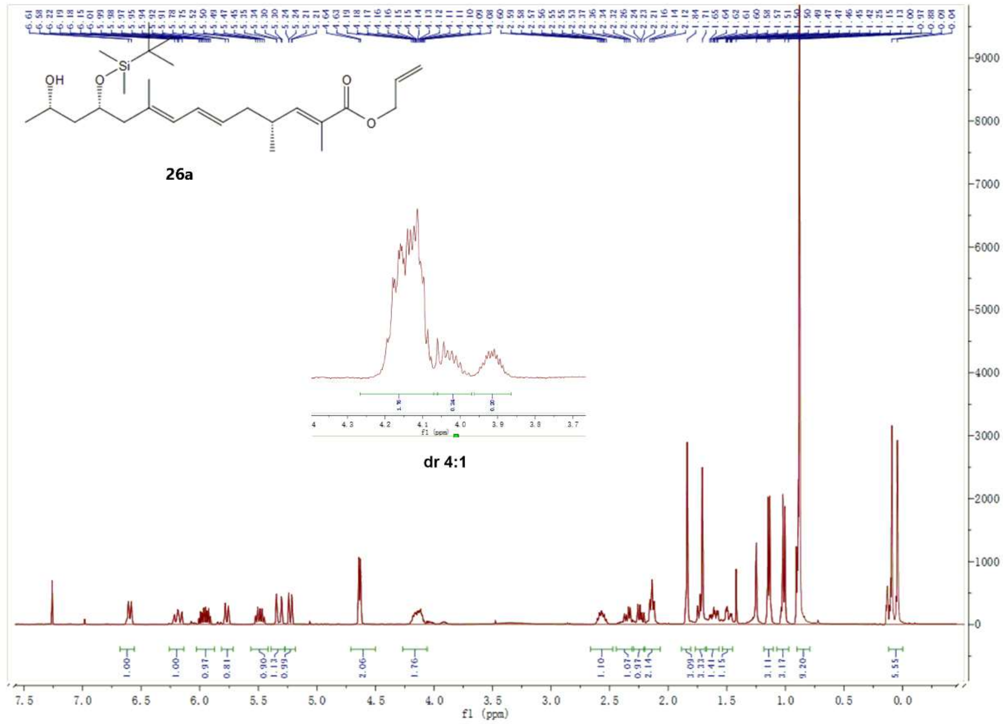

26a
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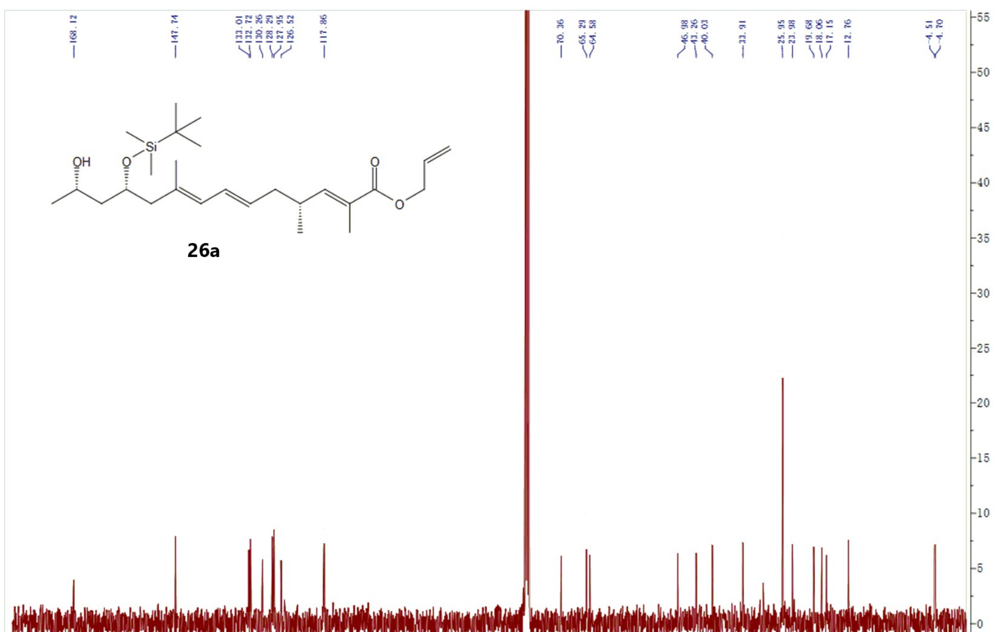

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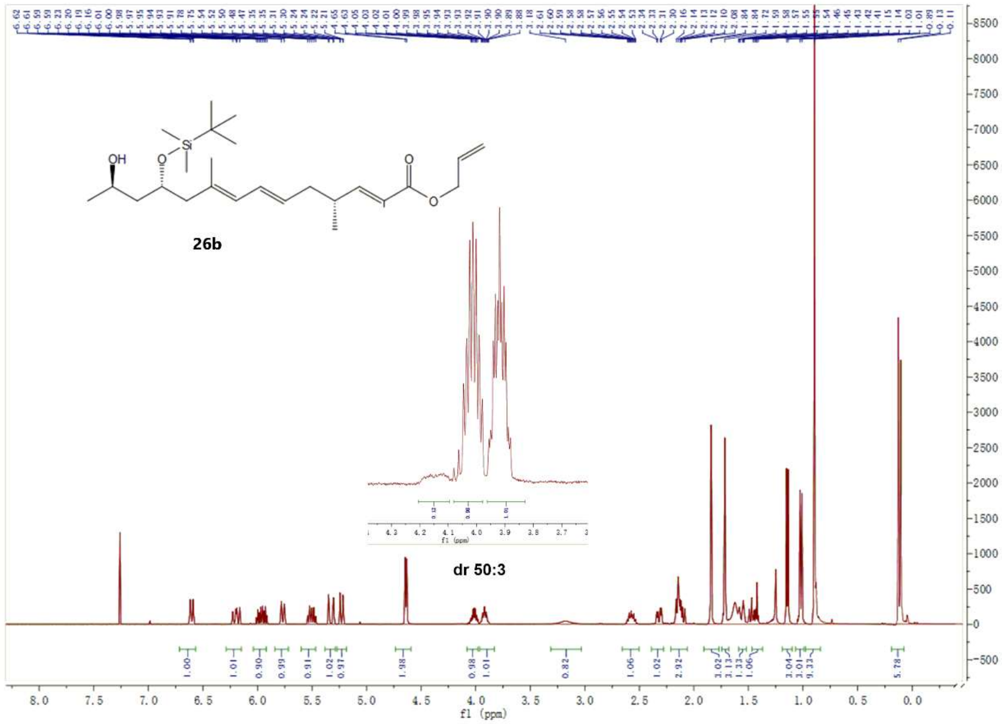
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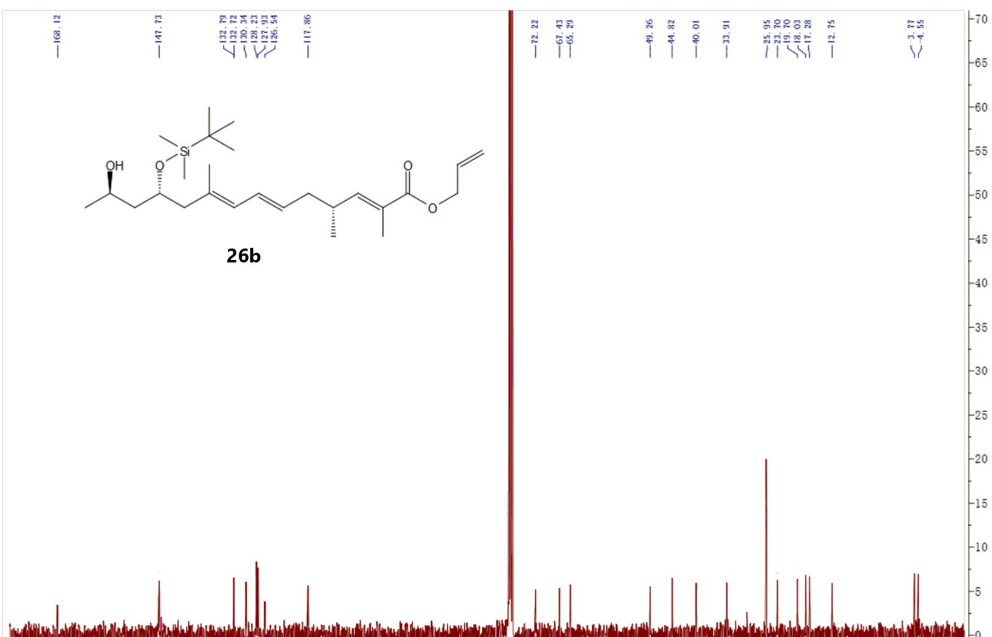
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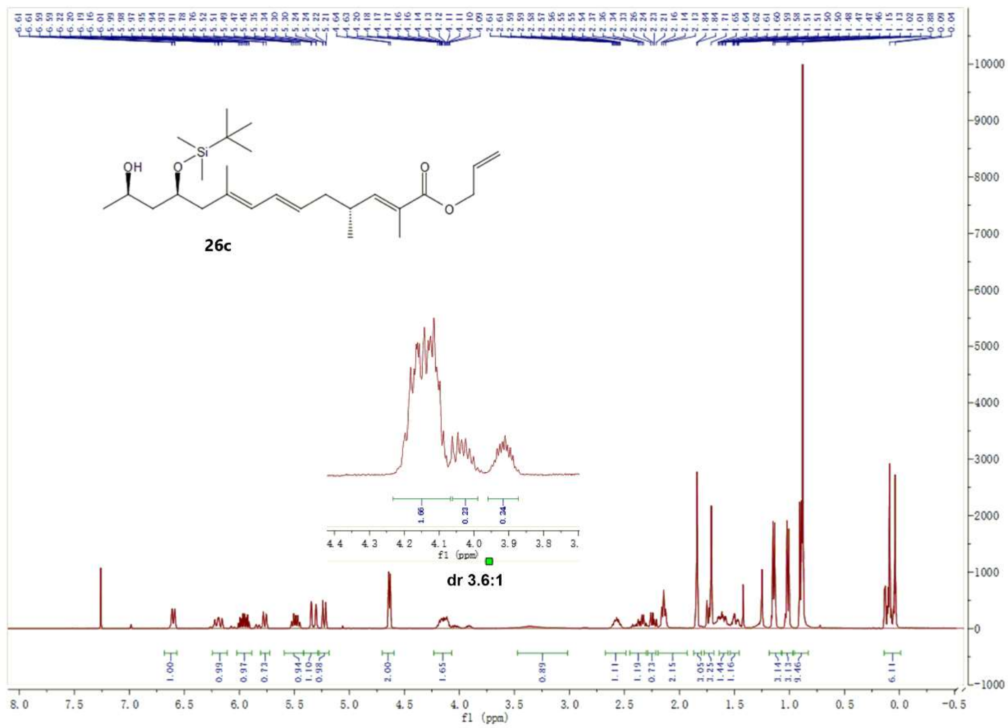
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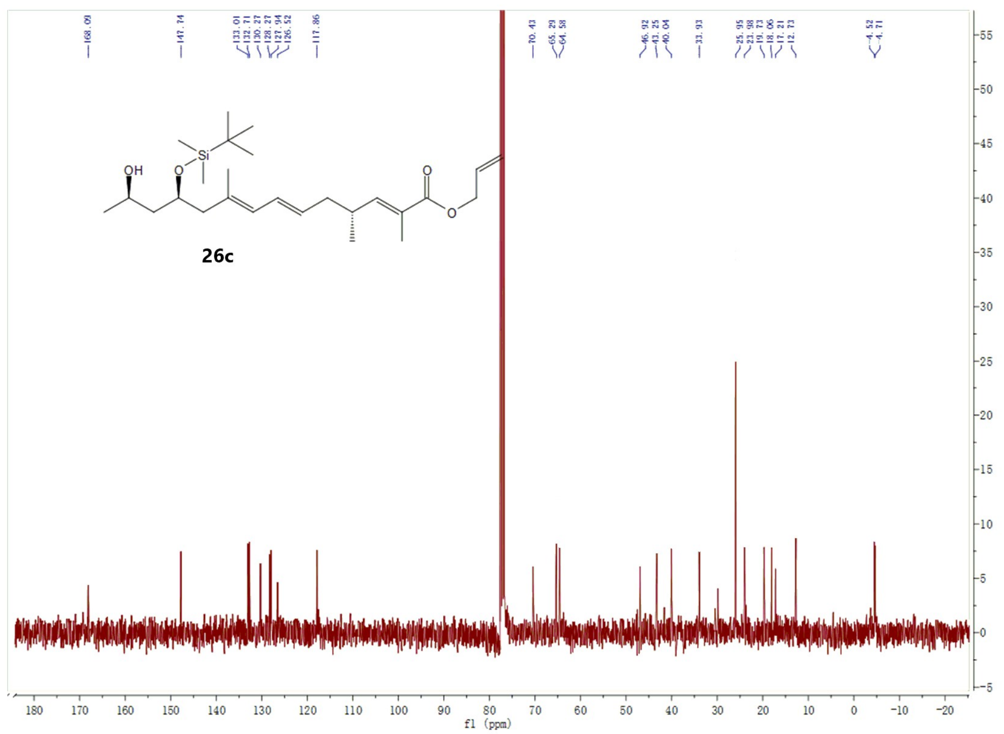
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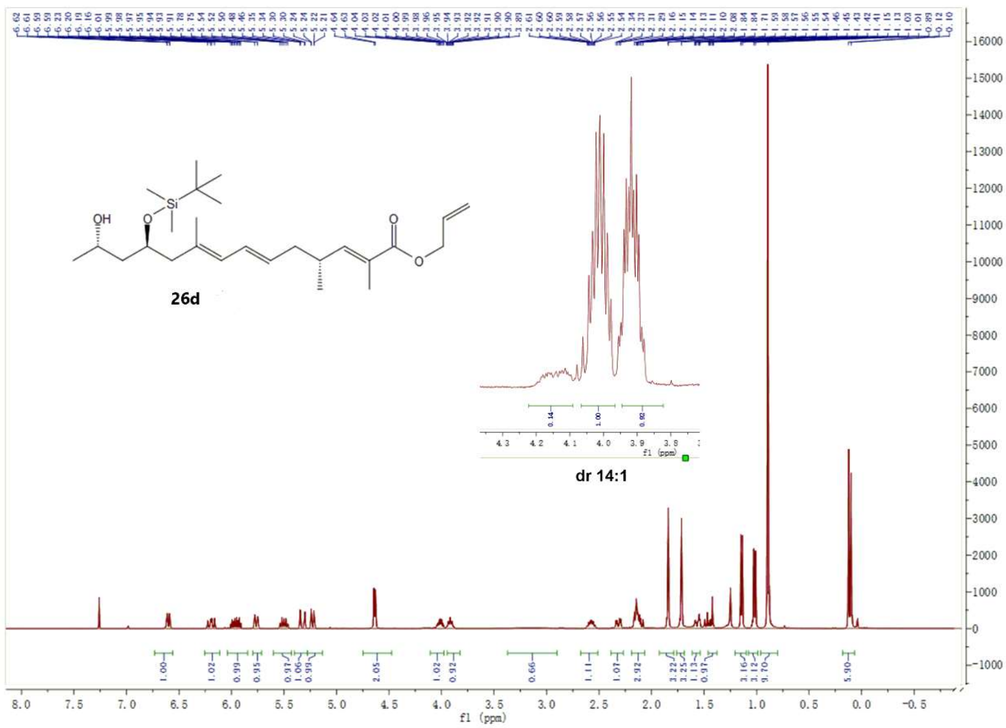

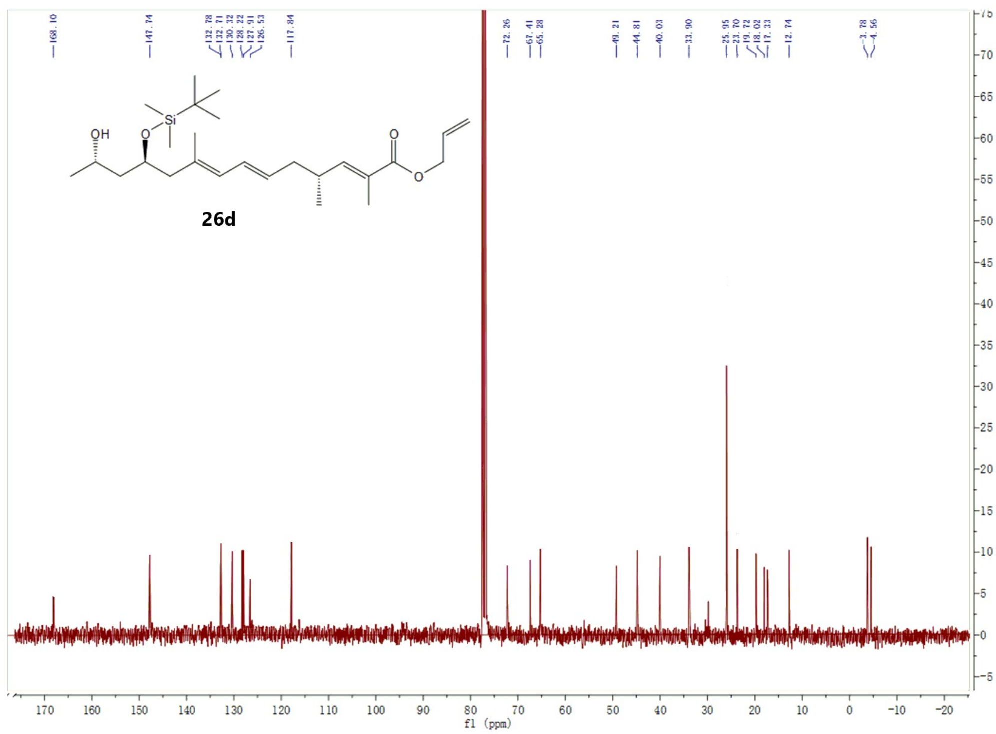

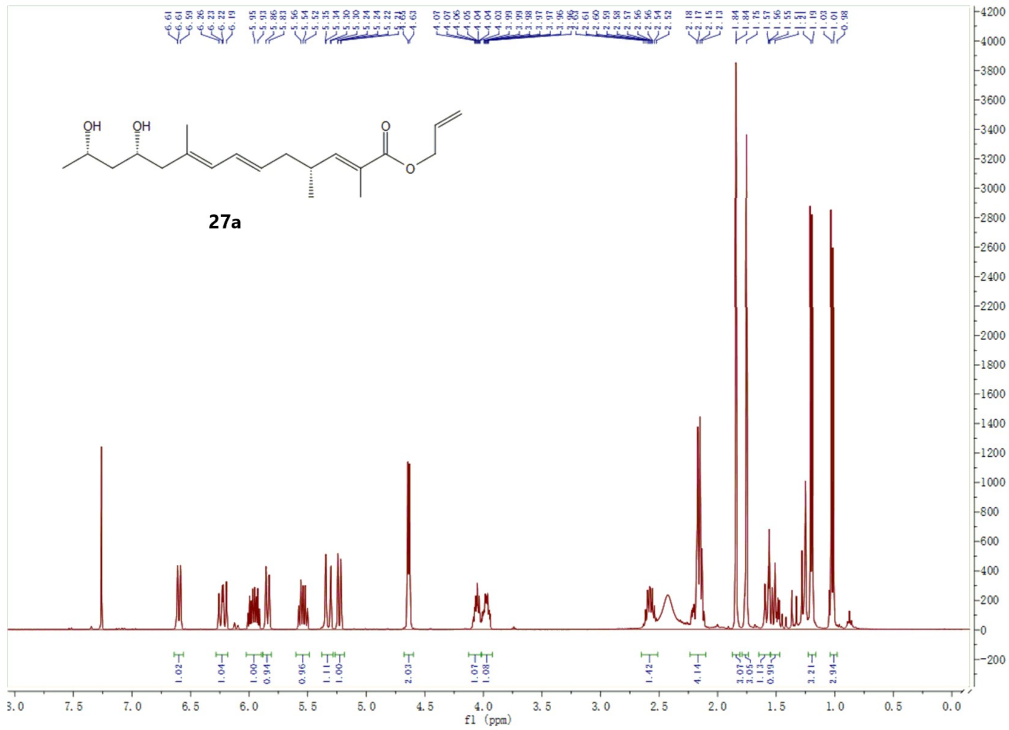

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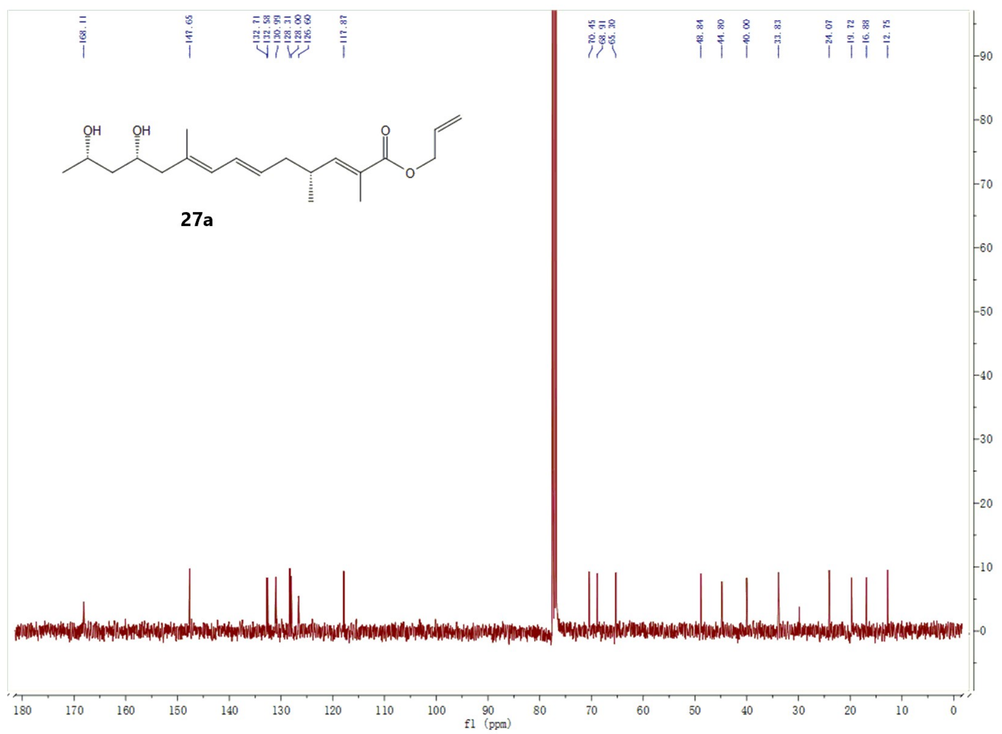

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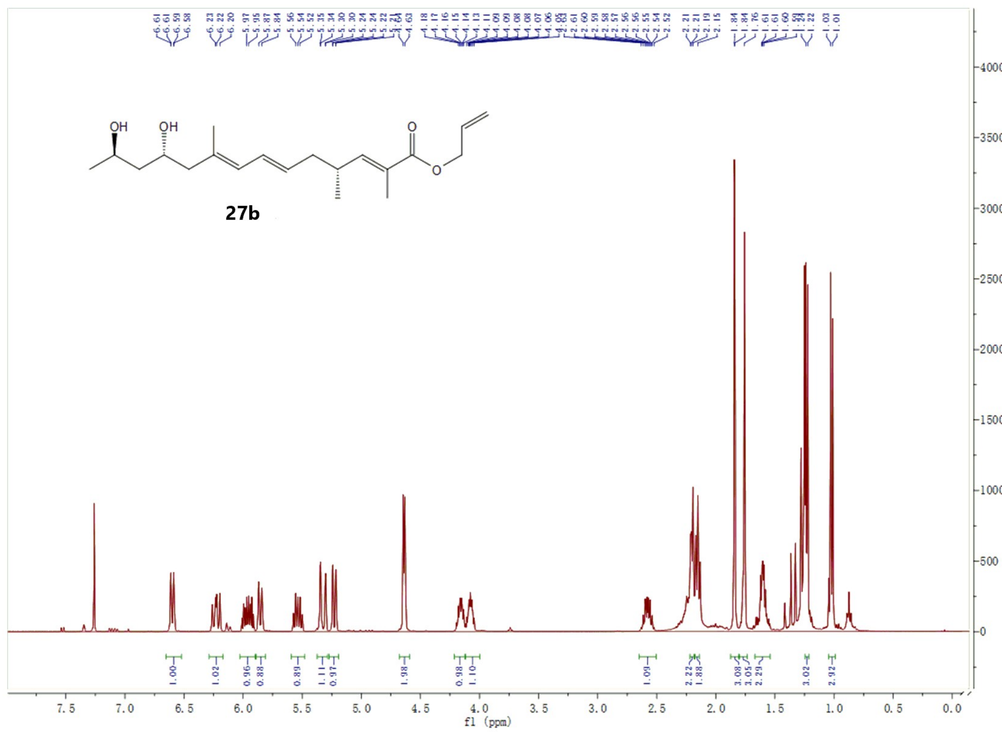
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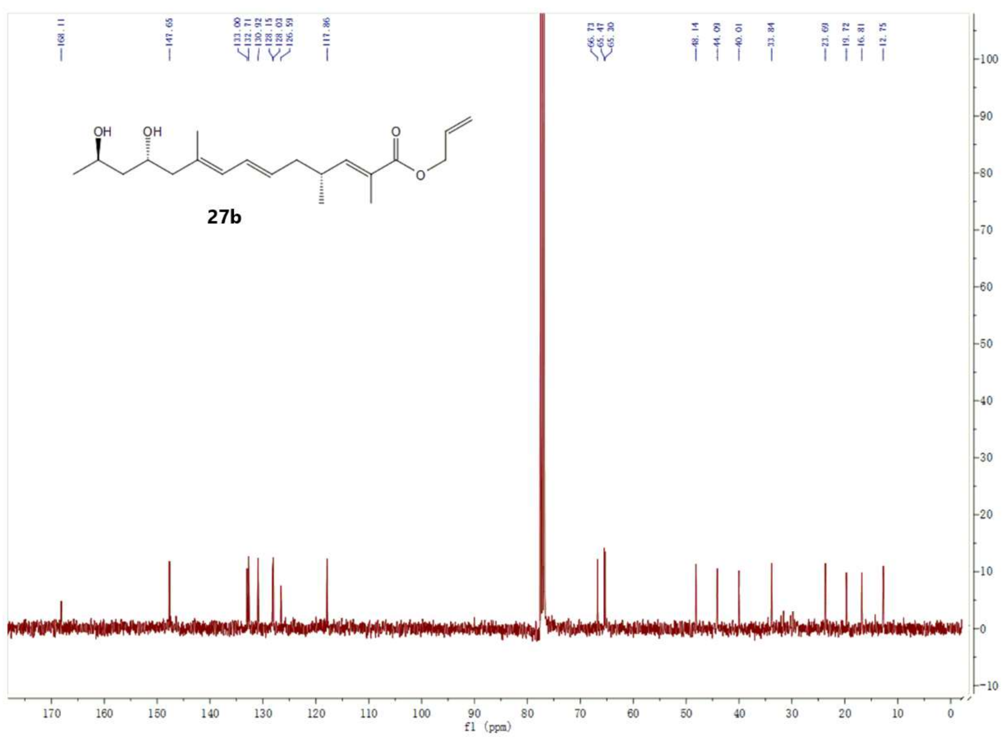
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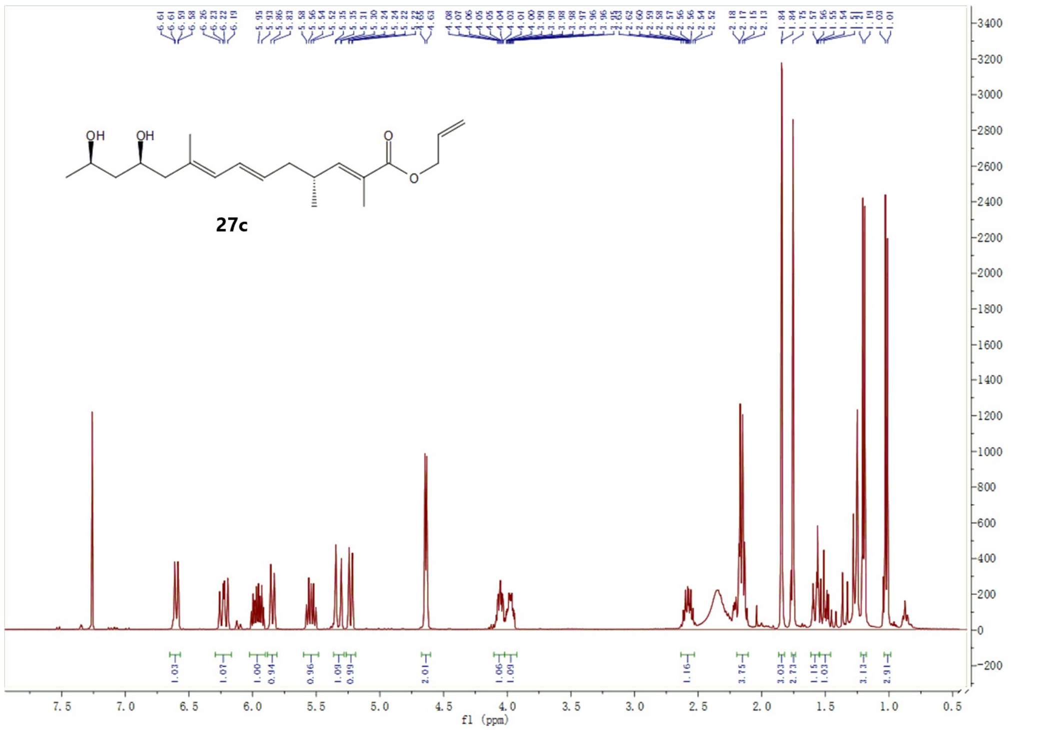
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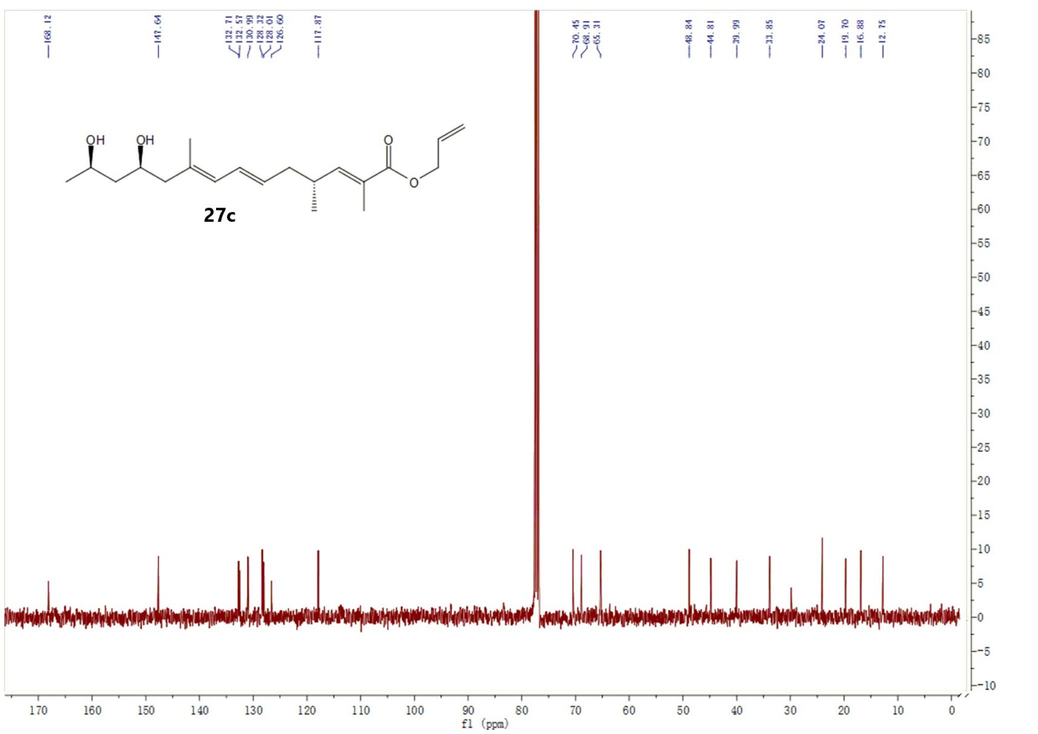
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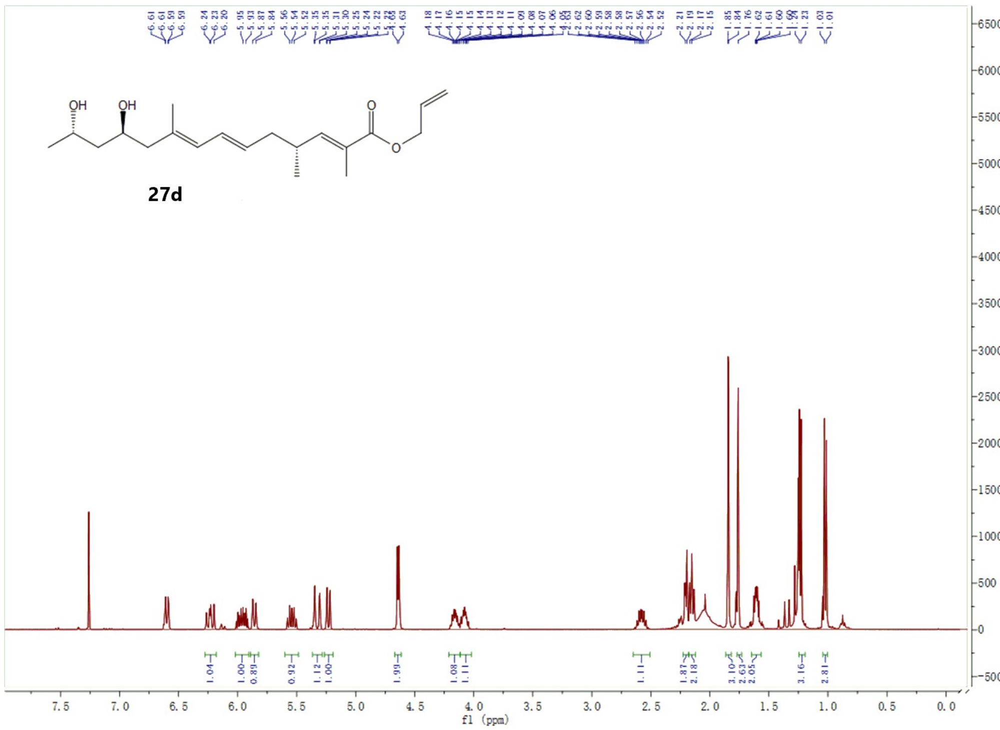

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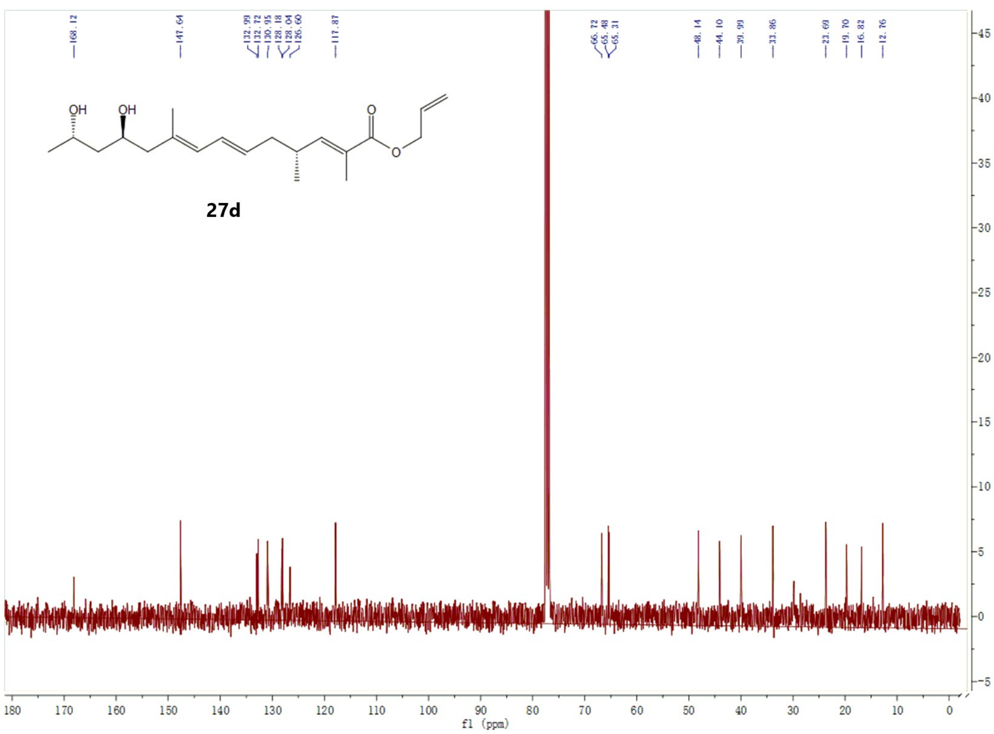

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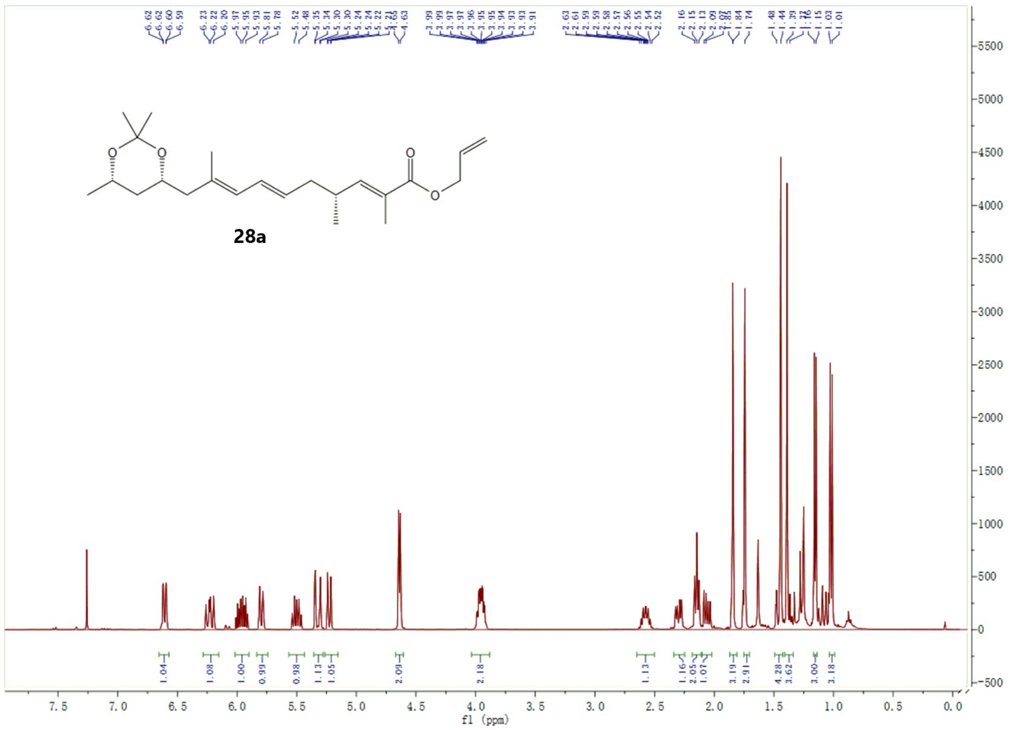

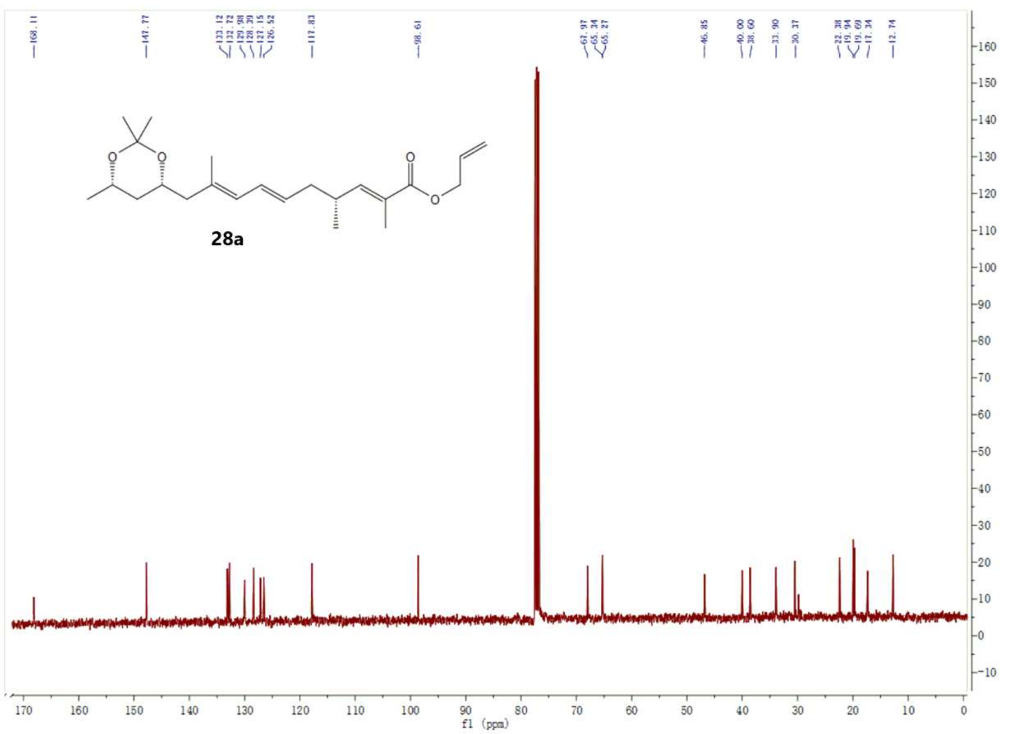

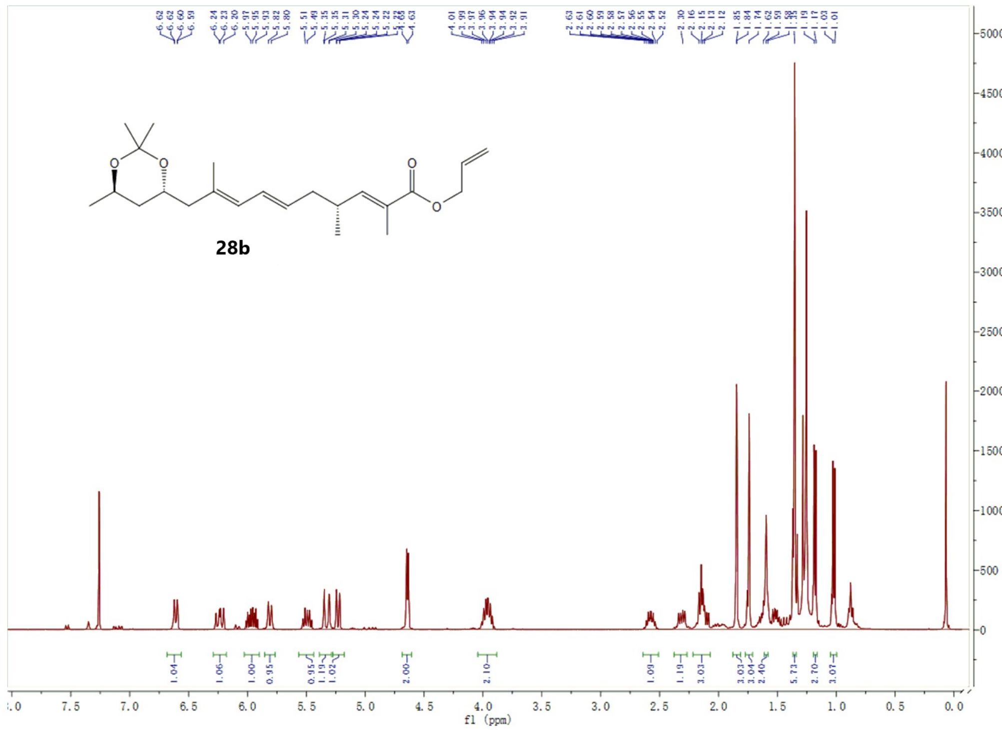

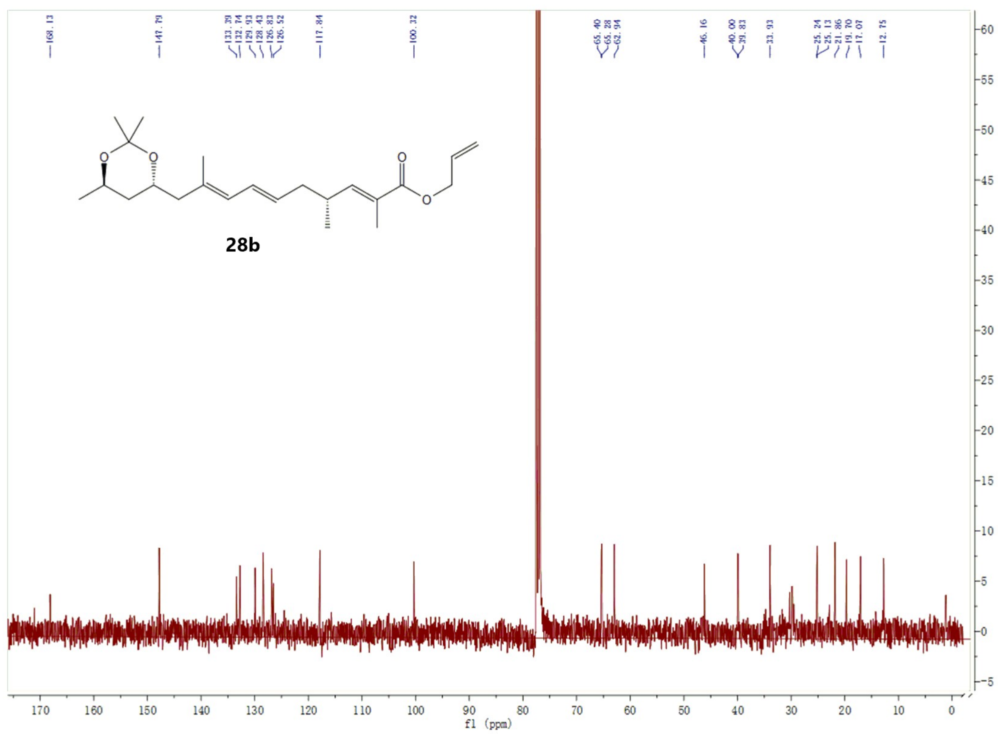

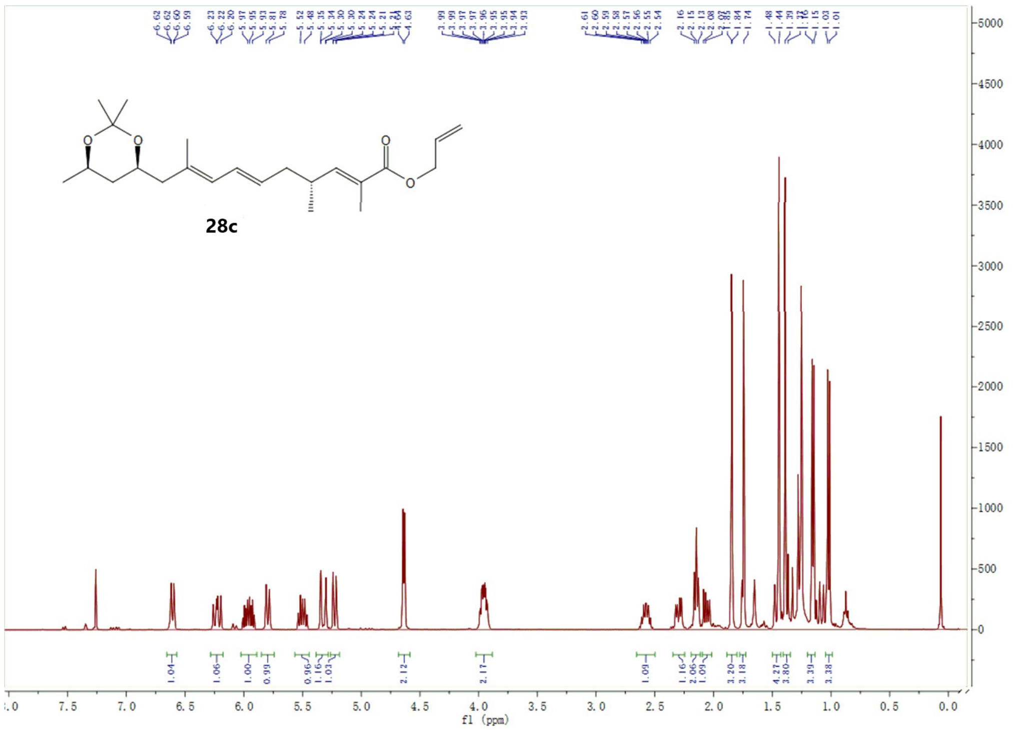

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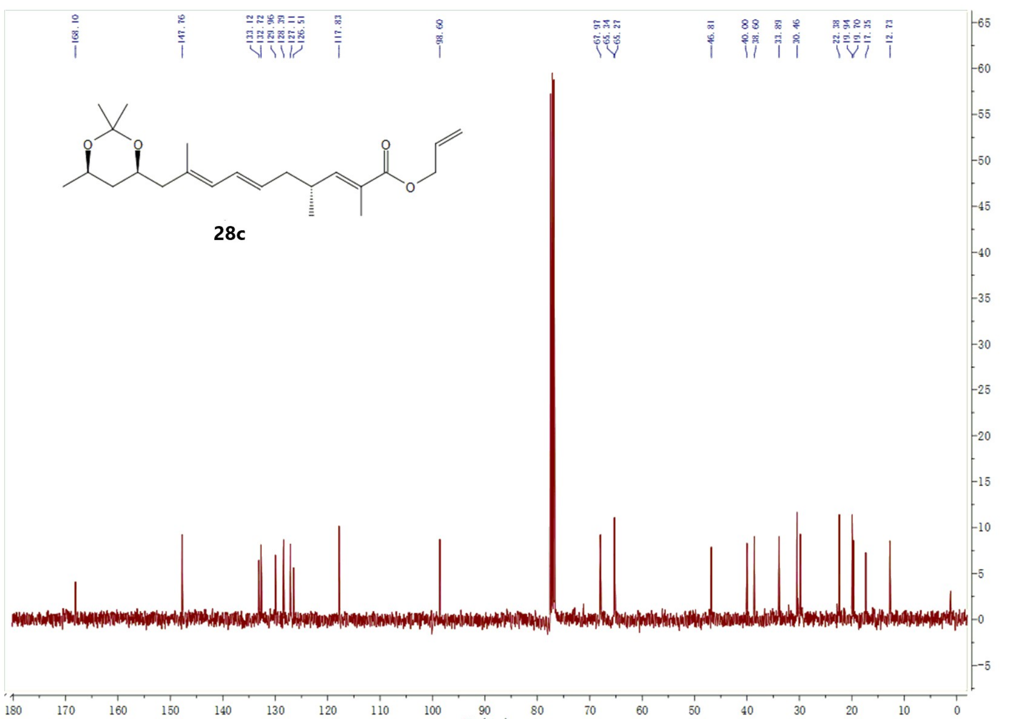

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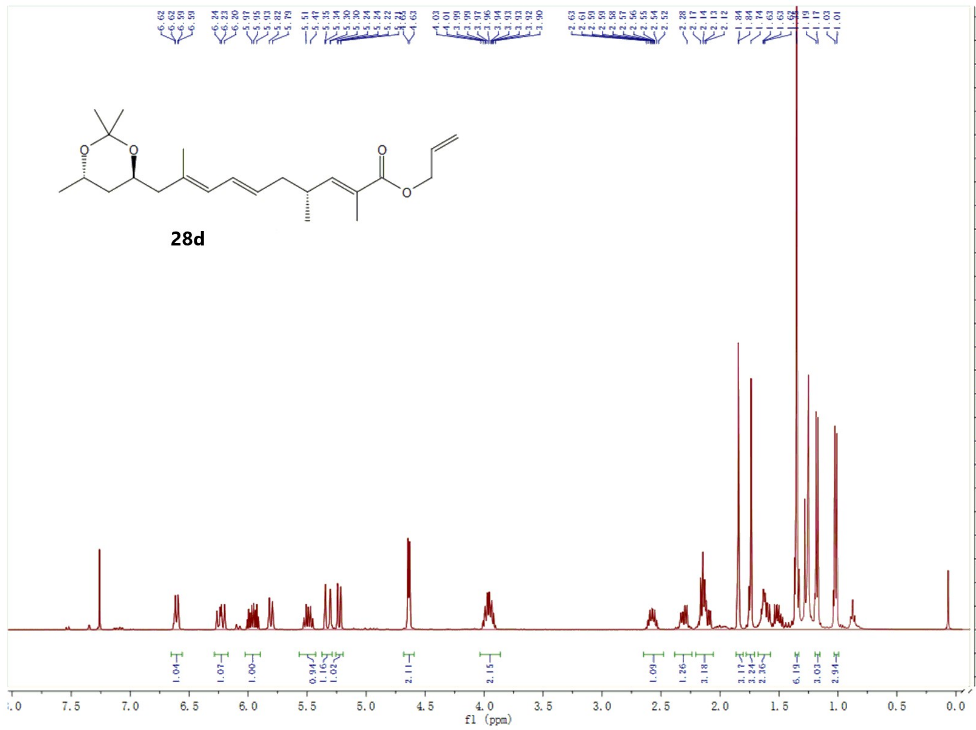
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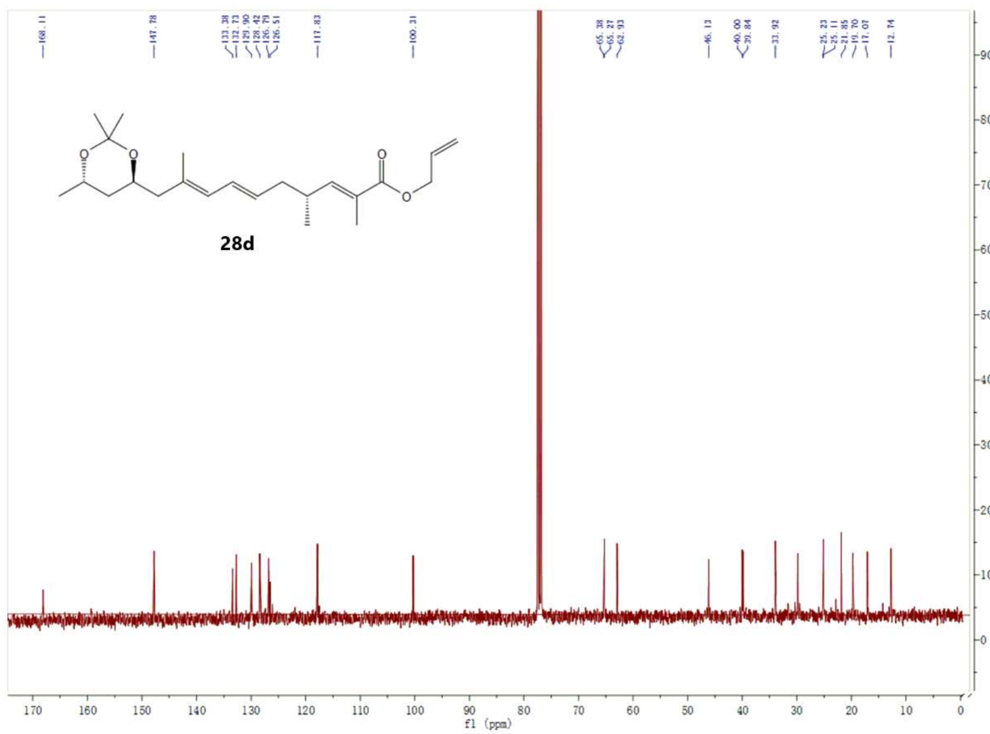
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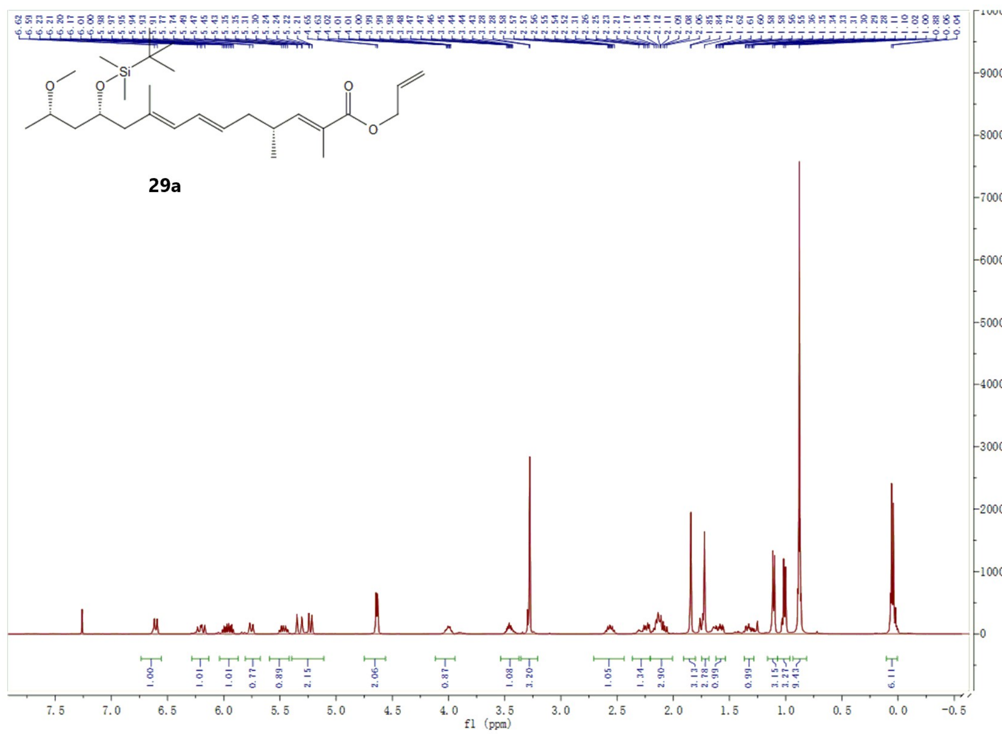

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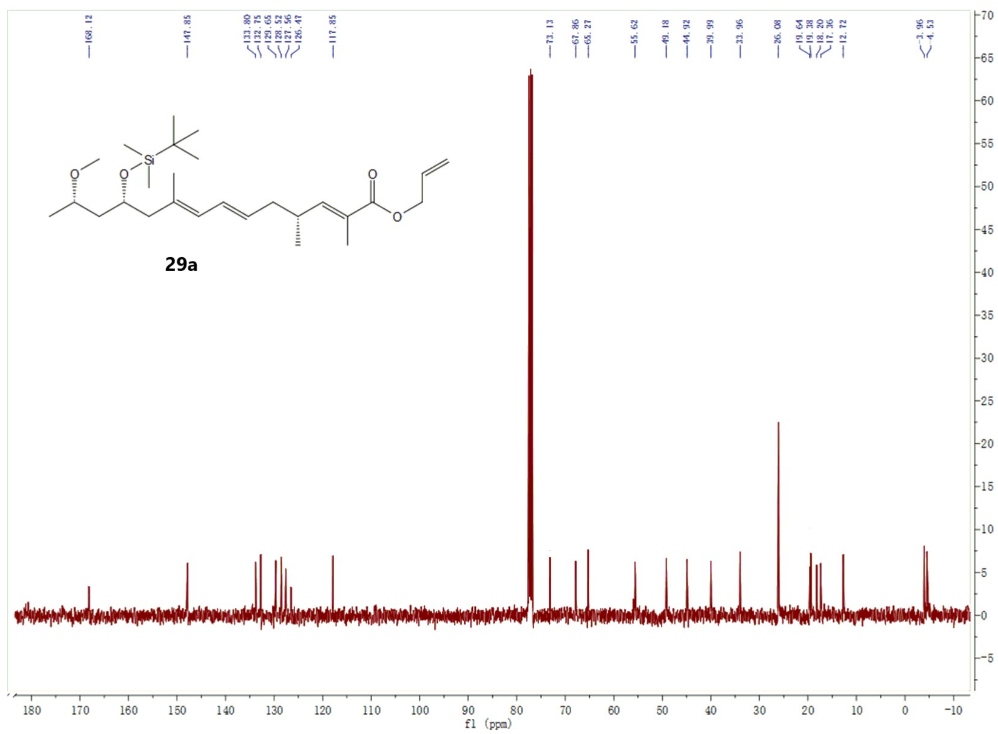

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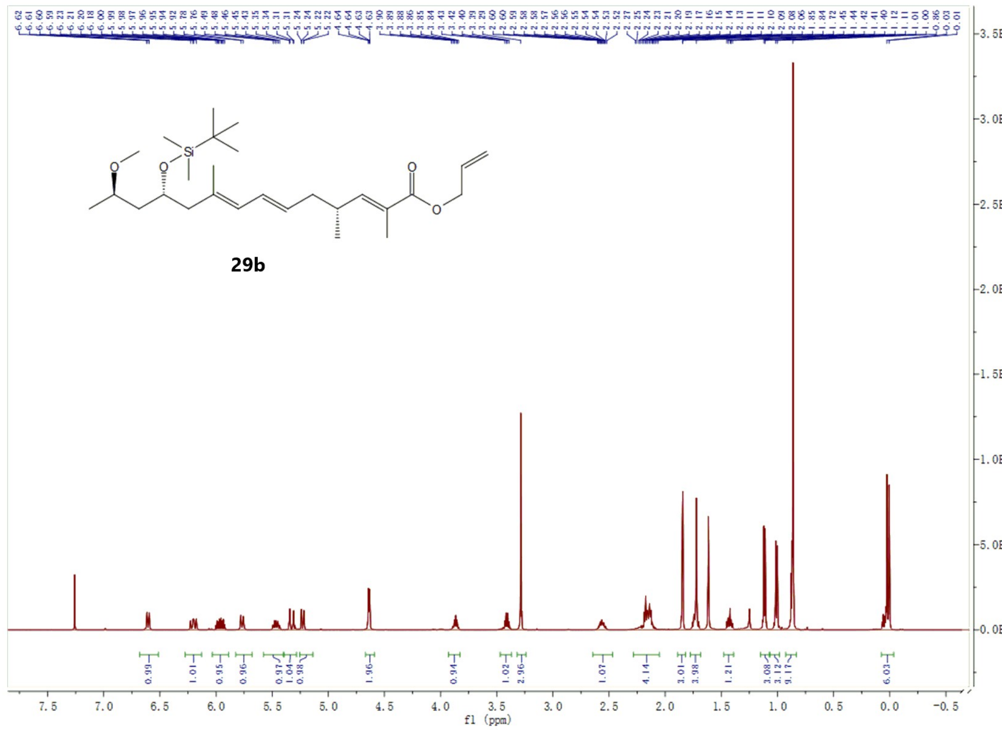
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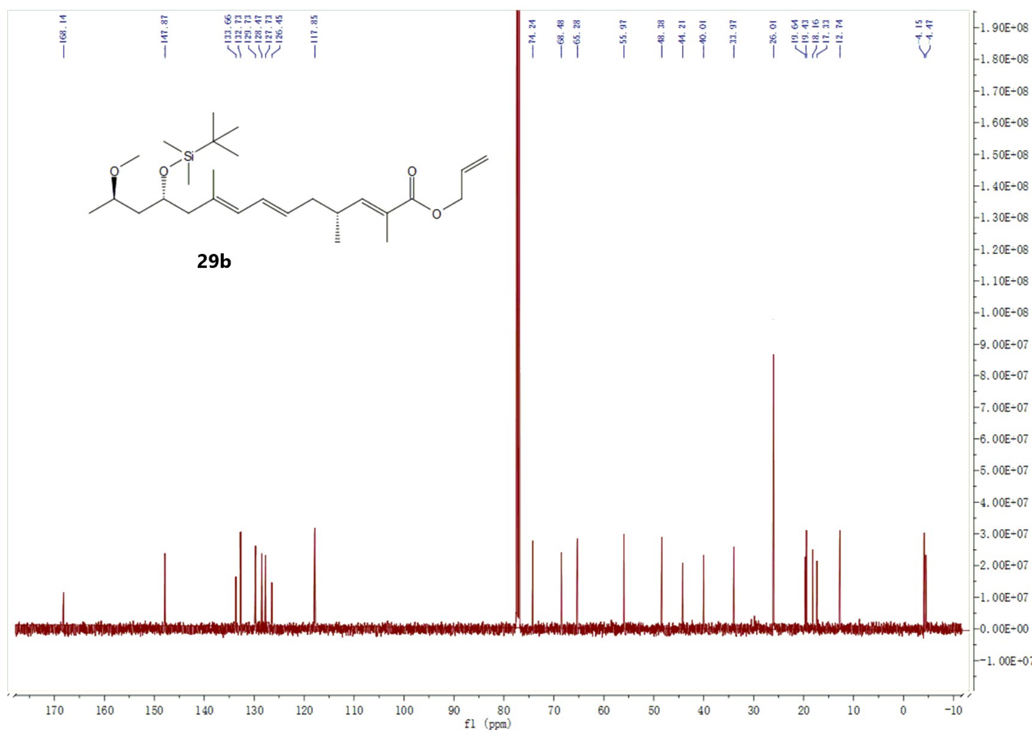
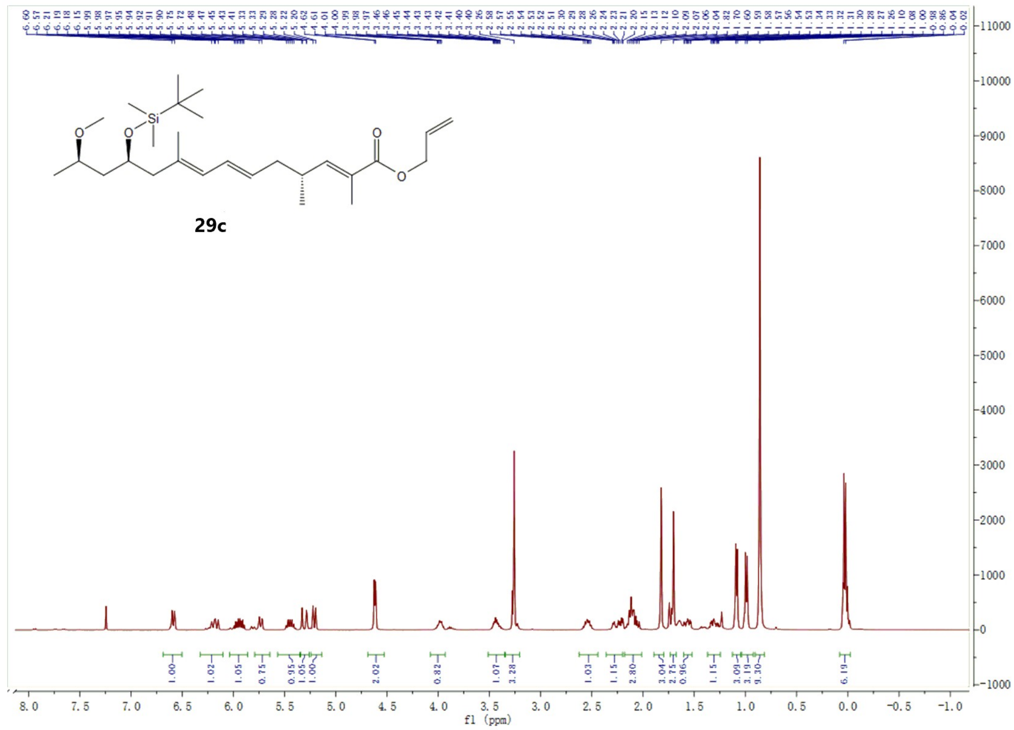
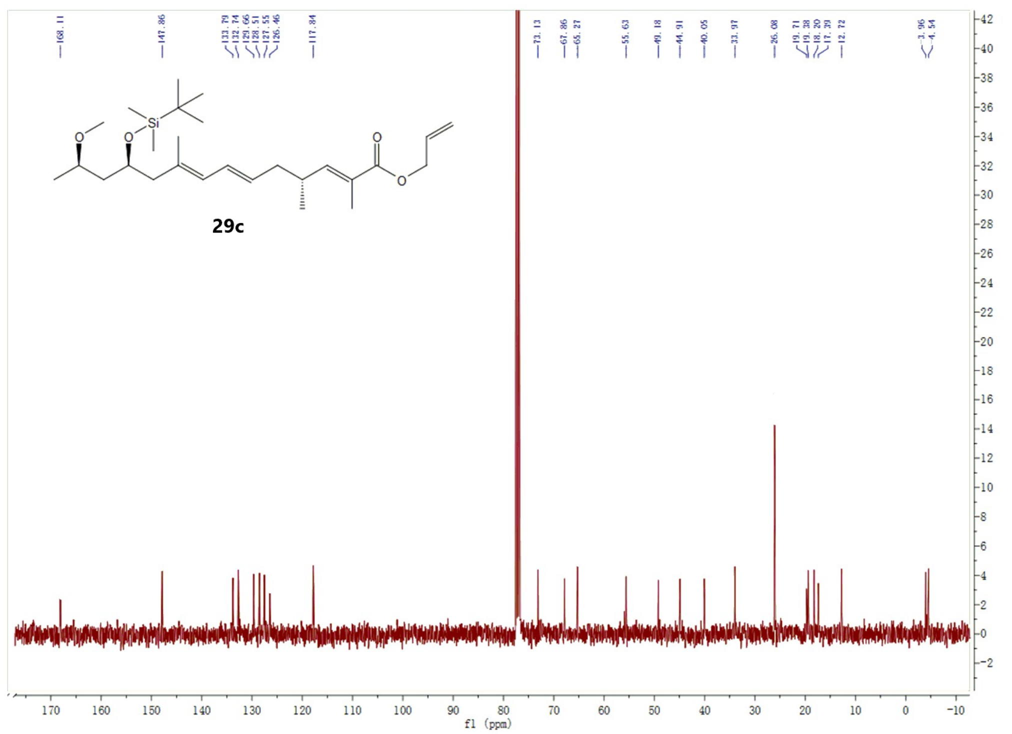
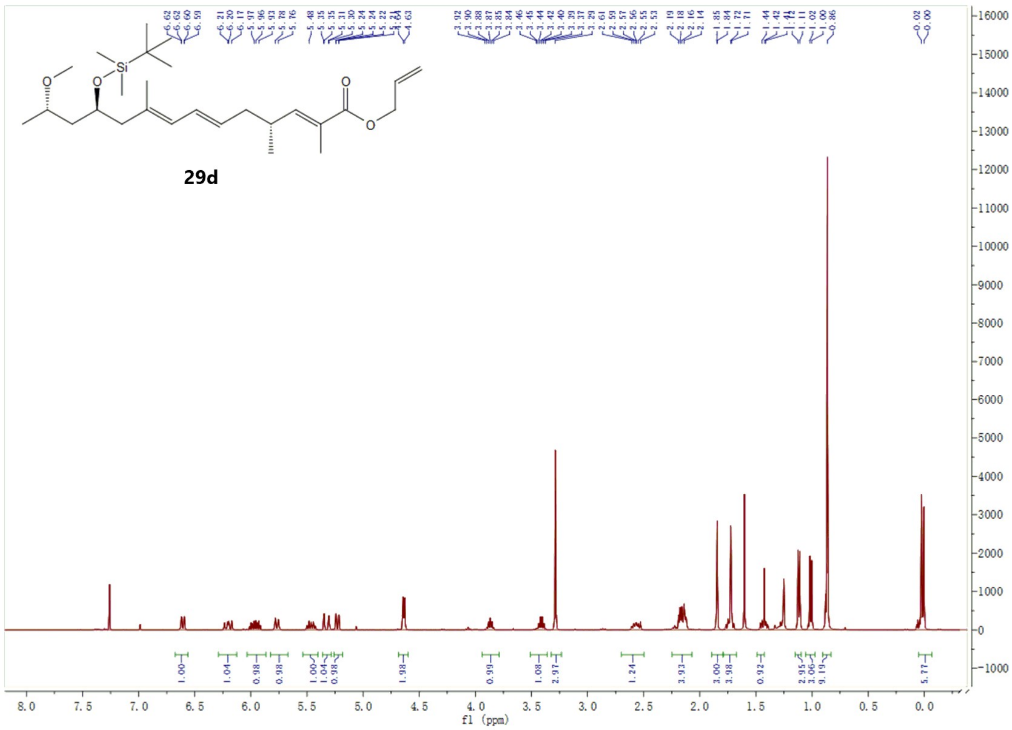
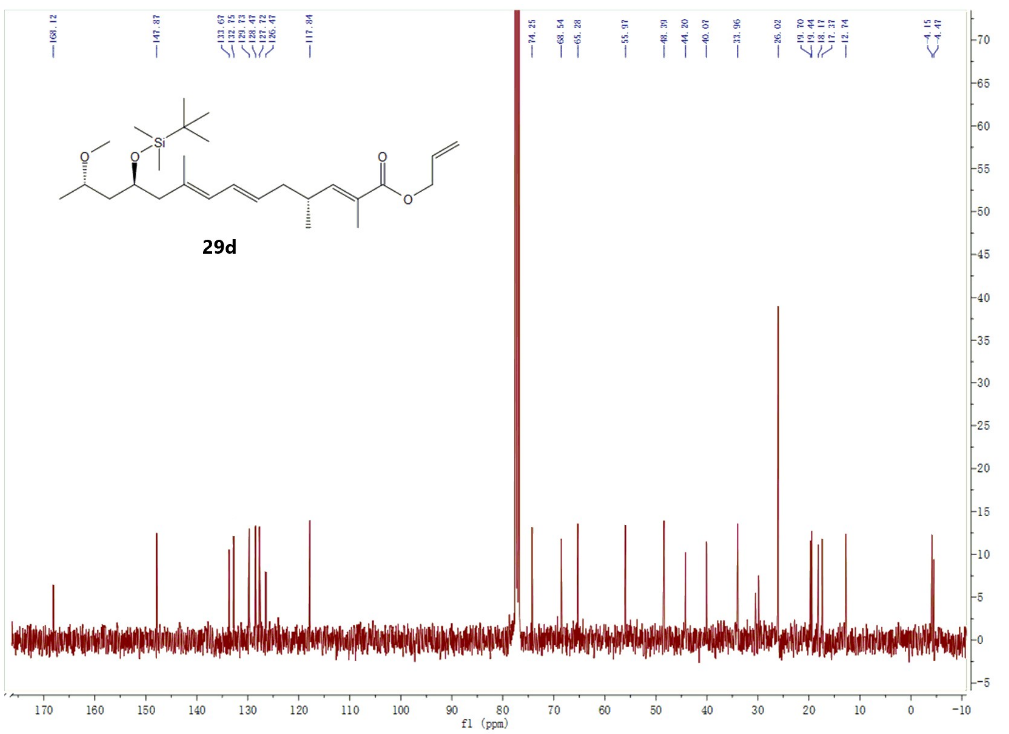
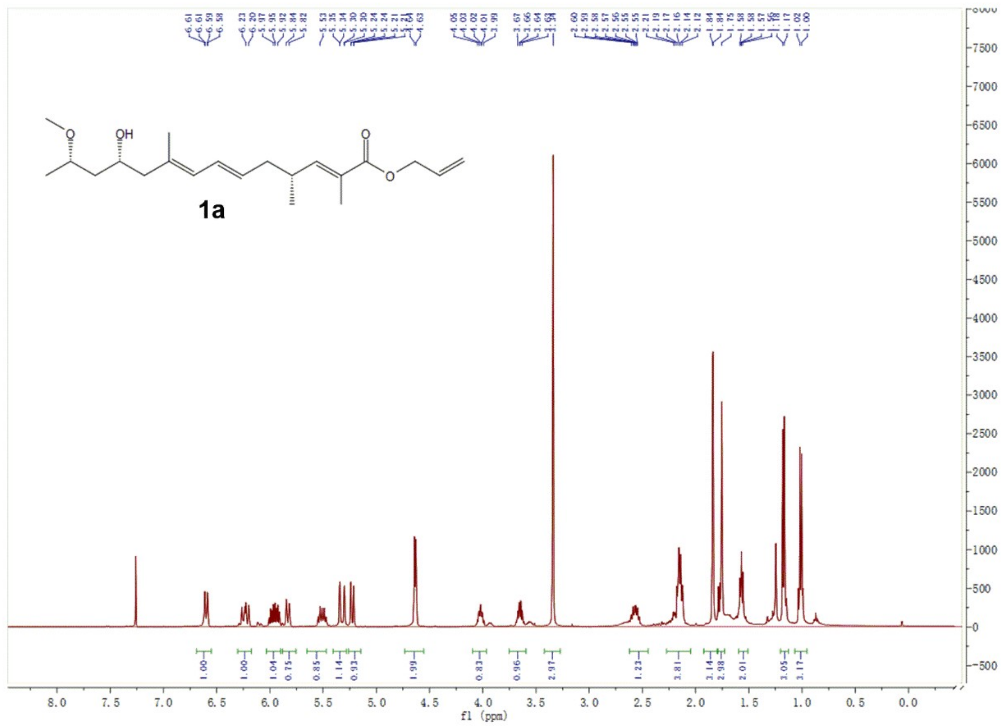

29b
f1 (ppm)



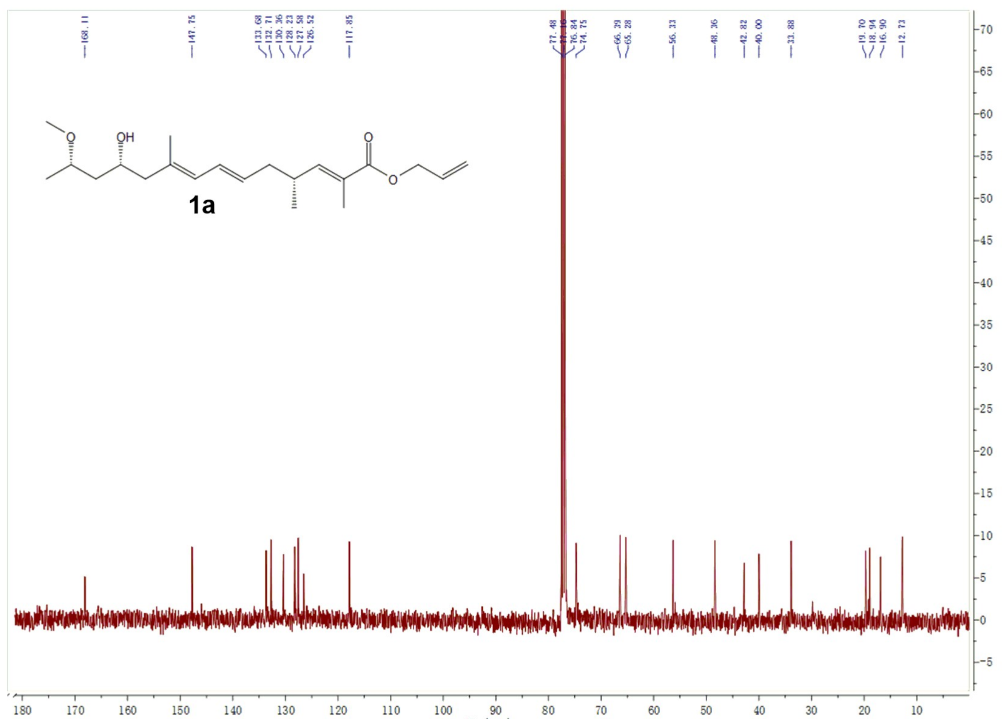




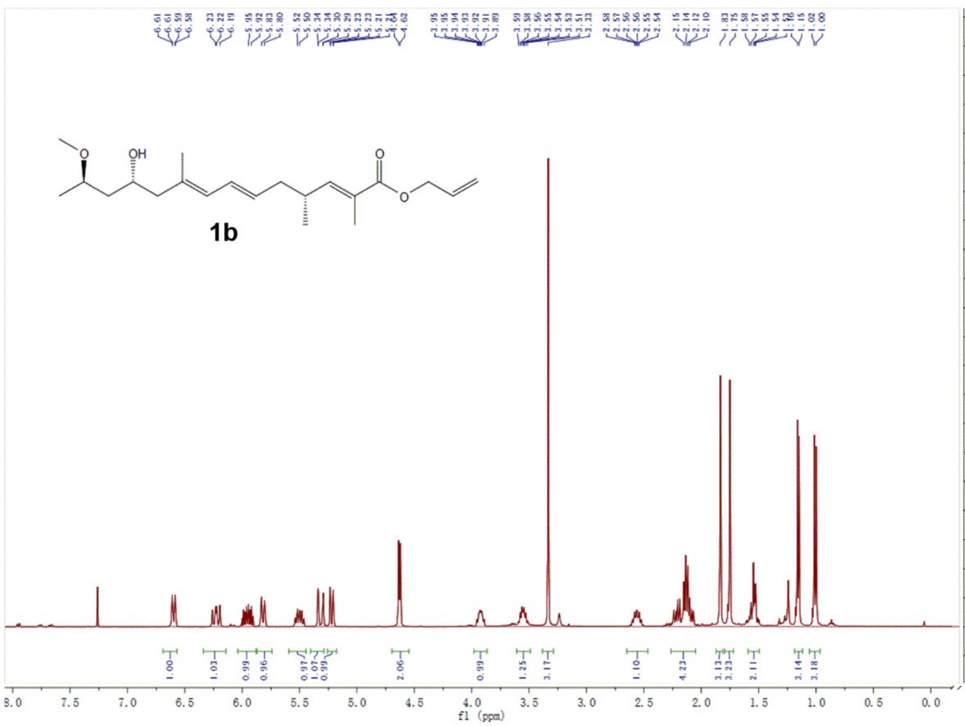


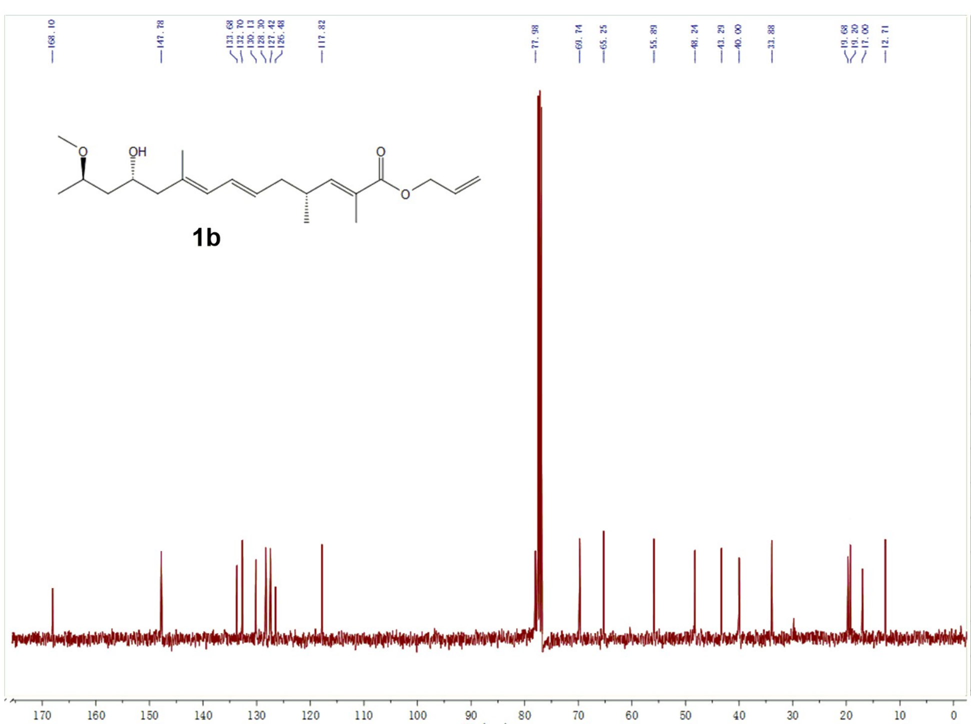


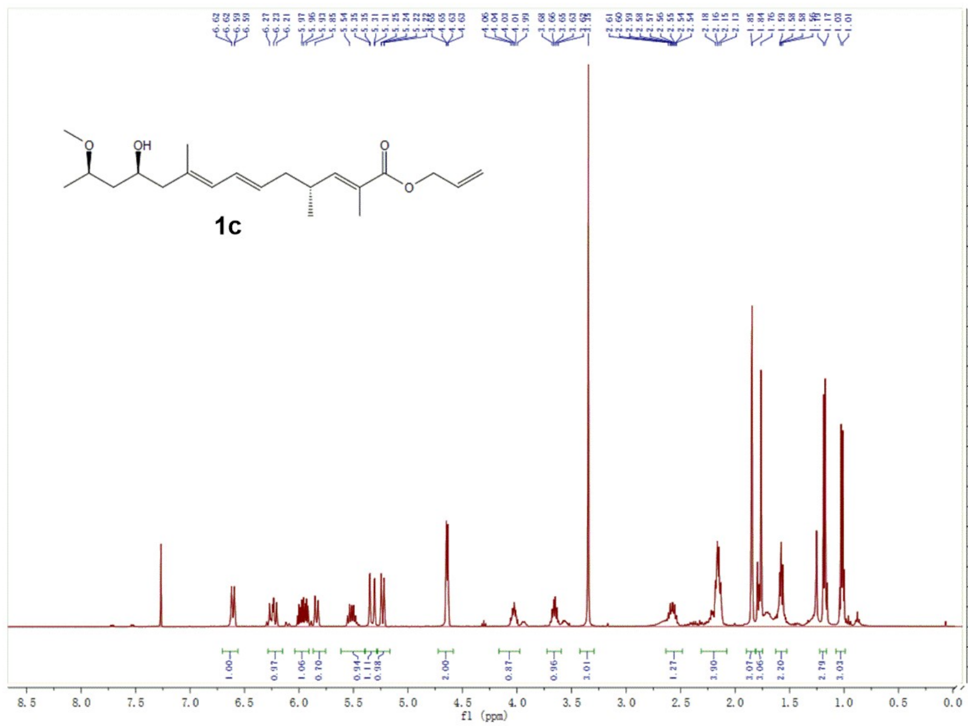
1a



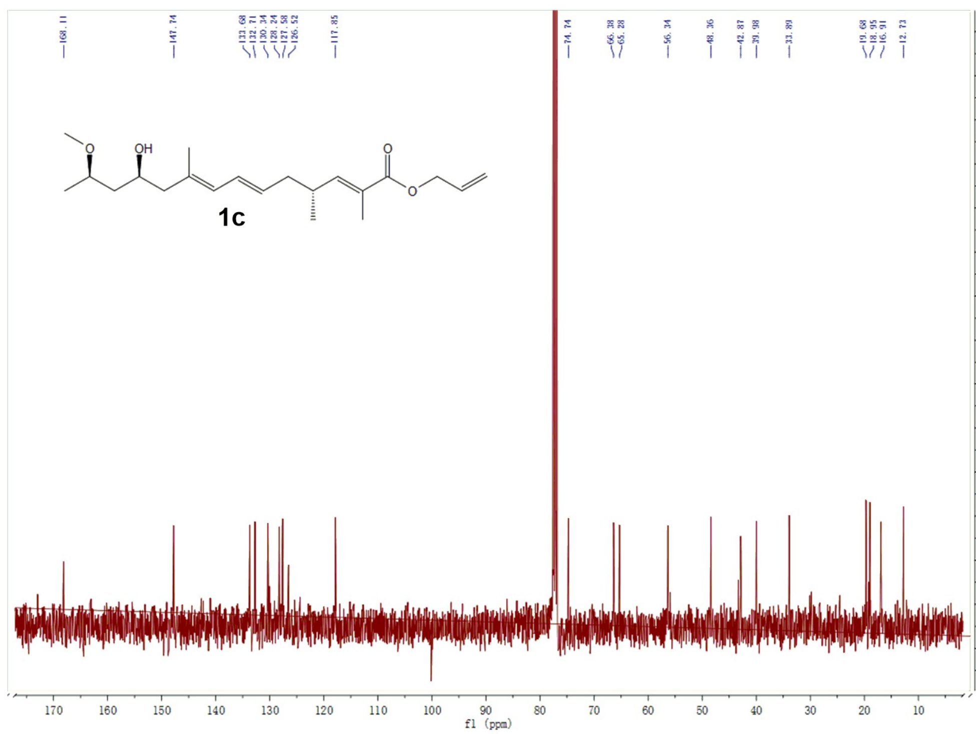
1a



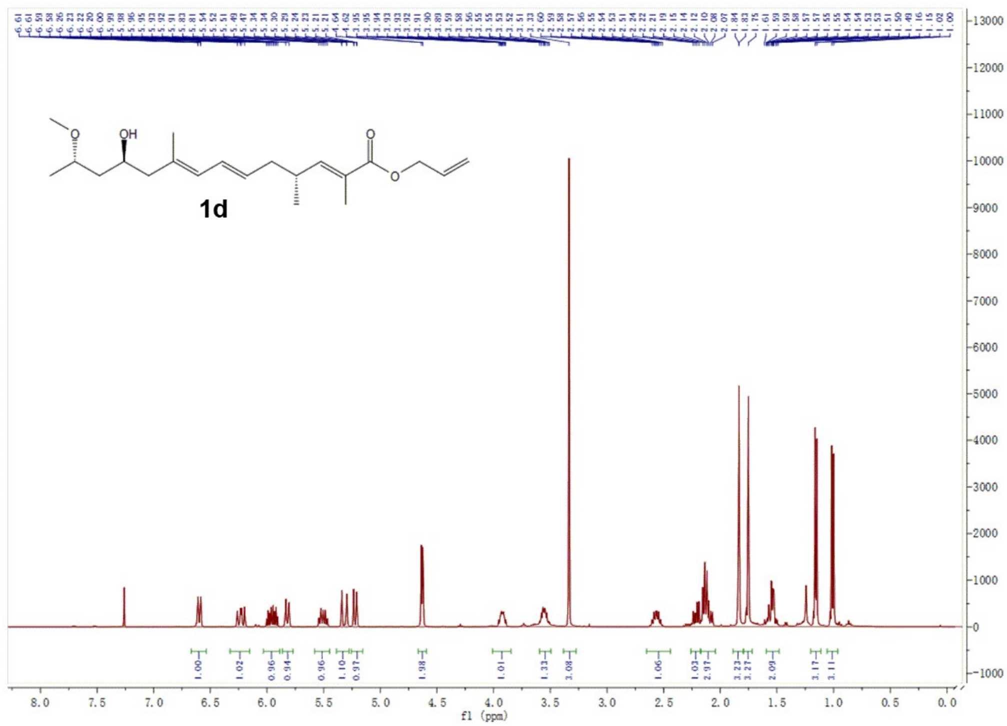


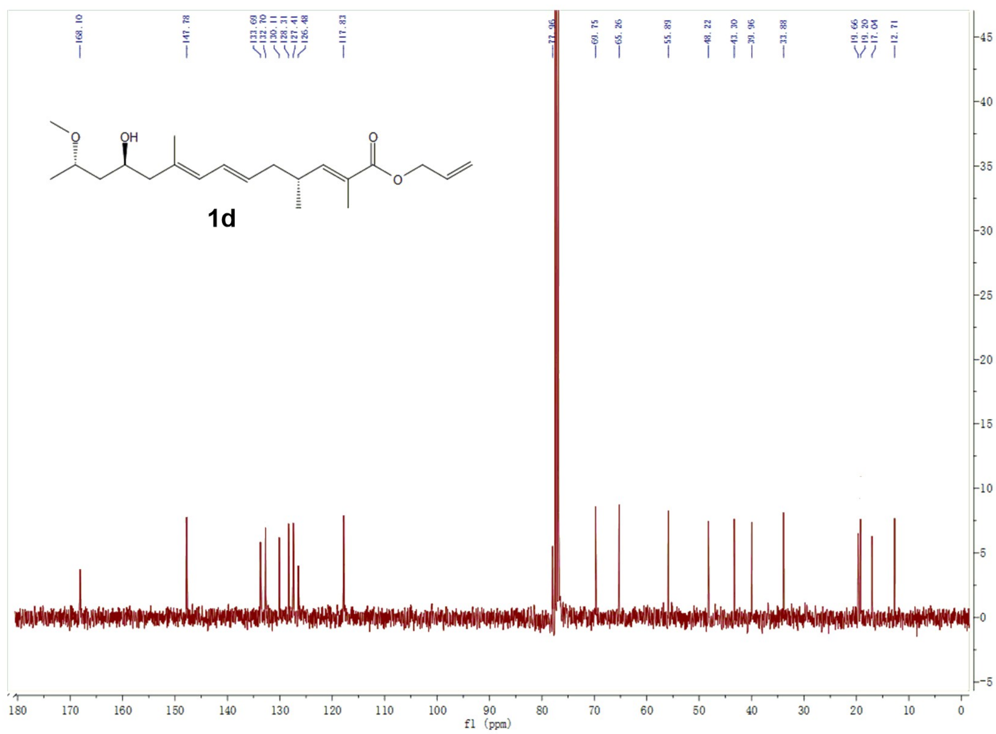


OH
O
1c
f1 (ppm)



OH
O
1c
f1 (ppm)


OH
O
1d
f1 (ppm)


OH
O
1d
f1 (ppm)

NMR data for **1a-1d**

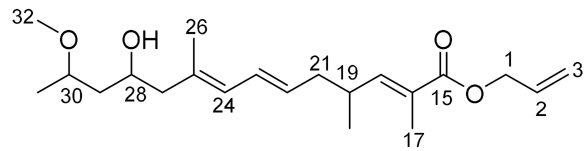


Table 1. NMR data for 1a

Carbon	δC	δH, m, ³J[Hz]
15	168.11	
16	126.52	
17	12.73	1.84 (d, *J* = 1.3 Hz, 3H)
18	147.75	6.60 (dd, *J* = 9.9, 1.3 Hz, 1H)
19	33.89	2.57 (m, 1H)
20	19.70	1.01 (d, *J* = 6.6 Hz, 3H)
21	40.00	2.17 (m, 2H)
22	130.36	5.59 – 5.42 (m, 1H)
23	128.23	6.23 (dd, *J* = 15.0, 10.8 Hz, 1H)
24	127.58	5.83 (d, *J* = 10.8 Hz, 1H)
25	133.68	
26	16.91	1.75 (s, 3H)
27	48.36	2.17 (m, 2H)
28	66.38	4.10 – 3.98 (m, 1H)
29	42.82	1.57 (m, 2H)
30	74.75	3.69-3.61 (m, 1H)
31	18.94	1.17 (d, *J* = 6.2 Hz, 3H)
32	56.34	3.34 (s, 3H)
1	65.28	4.63 (d, *J* = 5.5 Hz, 2H)
2	132.71	5.96 (ddt, *J* = 17.1, 10.5, 5.6 Hz, 1H)
3	117.85	5.32 (dd, *J* = 17.2, 1.5 Hz, 1H) 5.22 (dd, *J* = 10.4, 1.2 Hz, 1H)

Table 2. NMR data for 1b

Carbon	δC	δH, m, ³J[Hz]
15	168.10	
16	126.48	
17	12.71	1.83 (d, *J* = 1.3 Hz, 3H)
18	147.78	6.60 (dd, *J* = 9.9, 1.1 Hz, 1H)
19	33.88	2.56 (m, 1H)
20	19.68	1.01 (d, *J* = 6.7 Hz, 3H)
21	40.00	2.14 (m, 2H)
22	130.13	5.50 (dt, *J* = 14.8, 7.3 Hz, 1H)
23	128.30	6.23 (dd, *J* = 15.0, 10.8 Hz, 1H)
24	127.42	5.82 (d, *J* = 10.8 Hz, 1H)
25	133.68	
26	17.00	1.75 (s, 3H)
27	48.24	2.21 (m, 1H), 2.10 (m, 1H)
28	69.74	3.93 (m, 1H)

29	43.29	1.54 (m, 2H)
30	77.98	3.55 (m, 1H)
31	19.20	1.17 (d, *J* = 6.0 Hz, 3H)
32	55.89	3.33 (s, 3H)
1	65.25	4.63 (d, *J* = 5.5 Hz, 2H)
2	132.70	5.95 (ddt, *J* = 17.1, 10.5, 5.6 Hz, 1H)
3	117.82	5.32 (dd, *J* = 17.2, 1.5 Hz, 1H) 5.22 (dd, *J* = 10.4, 1.2 Hz, 1H)

Table 3. NMR data for 1c

Carbon	δ_C	δ_H, m, ^3J[Hz]
15	168.11	
16	126.52	
17	12.73	1.84 (d, *J* = 1.3 Hz, 3H)
18	147.74	6.60 (dd, *J* = 9.9, 1.3 Hz, 1H)
19	33.89	2.57 (m, 1H)
20	19.68	1.01 (d, *J* = 6.6 Hz, 3H)
21	39.98	2.17 (m, 2H)
22	130.34	5.59 – 5.42 (m, 1H)
23	128.24	6.23 (dd, *J* = 15.0, 10.8 Hz, 1H)
24	127.58	5.83 (d, *J* = 10.8 Hz, 1H)
25	133.68	
26	16.91	1.75 (s, 3H)
27	48.36	2.17 (m, 2H)
28	66.38	4.10 – 3.98 (m, 1H)
29	42.87	1.57 (m, 2H)
30	74.74	3.69-3.61 (m, 1H)
31	18.96	1.17 (d, *J* = 6.2 Hz, 3H)
32	56.34	3.34 (s, 3H)
1	65.28	4.63 (d, *J* = 5.5 Hz, 2H)
2	132.71	5.96 (ddt, *J* = 17.1, 10.5, 5.6 Hz, 1H)
3	117.85	5.32 (dd, *J* = 17.2, 1.5 Hz, 1H) 5.22 (dd, *J* = 10.4, 1.2 Hz, 1H)

Table 4. NMR data for 1d

Carbon	δ_C	δ_H, m, ^3J[Hz]
15	168.10	
16	126.48	
17	12.71	1.83 (d, *J* = 1.3 Hz, 3H)
18	147.78	6.60 (dd, *J* = 9.9, 1.1 Hz, 1H)
19	33.88	2.56 (m, 1H)
20	19.66	1.01 (d, *J* = 6.7 Hz, 3H)
21	39.96	2.14 (m, 2H)
22	130.11	5.50 (dt, *J* = 14.8, 7.3 Hz, 1H)
23	128.31	6.23 (dd, *J* = 15.0, 10.8 Hz, 1H)
24	127.41	5.82 (d, *J* = 10.8 Hz, 1H)
25	133.69	
26	17.04	1.75 (s, 3H)
27	48.22	2.21 (m, 1H), 2.10 (m, 1H)

28	69.75	3.93 (m, 1H)
29	43.30	1.54 (m, 2H)
30	77.96	3.55 (m, 1H)
31	19.20	1.17 (d, J = 6.0 Hz, 3H)
32	55.89	3.33 (s, 3H)
1	65.26	4.63 (d, J = 5.5 Hz, 2H)
2	132.70	5.95 (ddt, J = 17.1, 10.5, 5.6 Hz, 1H)
3	117.83	5.32 (dd, J = 17.2, 1.5 Hz, 1H) 5.22 (dd, J = 10.4, 1.2 Hz, 1H)