

Supporting Information

Asymmetric Synthesis and Absolute Stereochemistry of A Labdane-type Diterpenoid

Isolated from the Rhizomes of *Isodan yuennanensis*

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Table of Contents

Tables S1 and S2 (NMR comparison between synthetic and natural samples).....	S3
NMR Spectra for New Compounds.....	S4

Table S1. Comparison of ^1H NMR data for natural 2 with those of synthetic 2¹

Position	Natural (400 MHz, CDCl ₃)	Synthetic (400 MHz, CDCl ₃)	$\Delta\delta(\text{ppm})$
1a	1.95 (overlap)	1.95 (m)	0.00
1b	1.21 (dd, 13.4, 4.2 Hz)	1.21 (dd, 13.5, 4.3 Hz)	0.00
2a	2.10 (qt, 13.7, 3.3 Hz)	2.10 (m)	0.00
2b	1.51	1.50 (m)	-0.01
3a	1.47	1.46 (m)	-0.01
3b	1.13 (dd, 12.9, 3.3 Hz)	1.13 (dd, 13.1, 3.1 Hz)	0.00
4	--	--	--
5	1.38 (dd, 12.7, 4.6 Hz)	1.38 (m)	0.00
6	1.62 (overlap)	1.63 (m)	0.01
7	1.92 (overlap)	1.90 (m)	-0.02
8	--	--	--
9	1.77 (dd, 7.5, 4.9 Hz)	1.76 (dd, 7.6, 4.9 Hz)	-0.01
10	--	--	--
11	2.27 (m)	2.27 (m)	0.00
12	5.41 (t, 6.8 Hz)	5.41 (t, 6.7 Hz)	0.00
13	--	--	--
14	6.33 (dd, 17.3, 10.7 Hz)	6.33 (dd, 17.4, 10.7 Hz)	0.00
15a	5.09 (d, 17.3 Hz)	5.09 (d, 17.4 Hz)	0.00
15b	4.94 (d, 10.7 Hz)	4.94 (d, 10.7 Hz)	0.00
16	1.72 (s)	1.71 (s)	-0.01
17	--	--	--
18	0.9 (s)	0.9 (s)	0.00
19	0.9 (s)	0.9 (s)	0.00

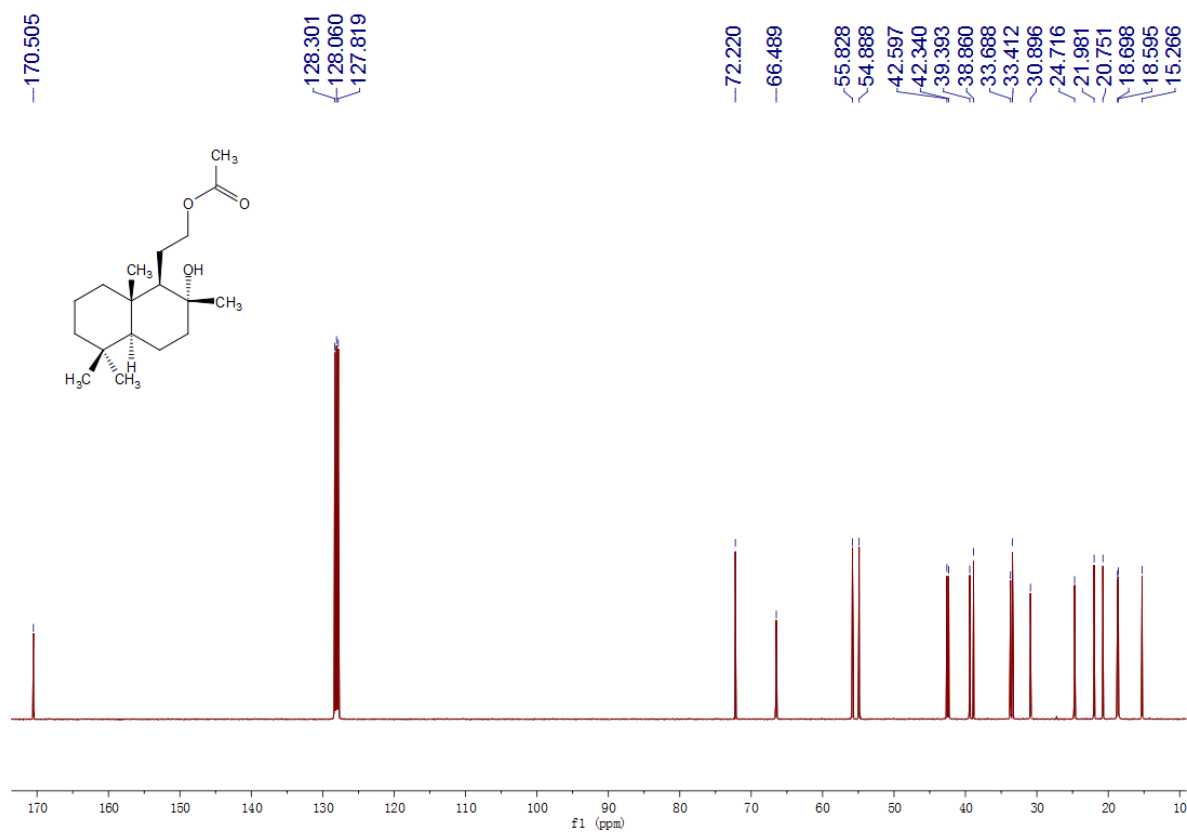
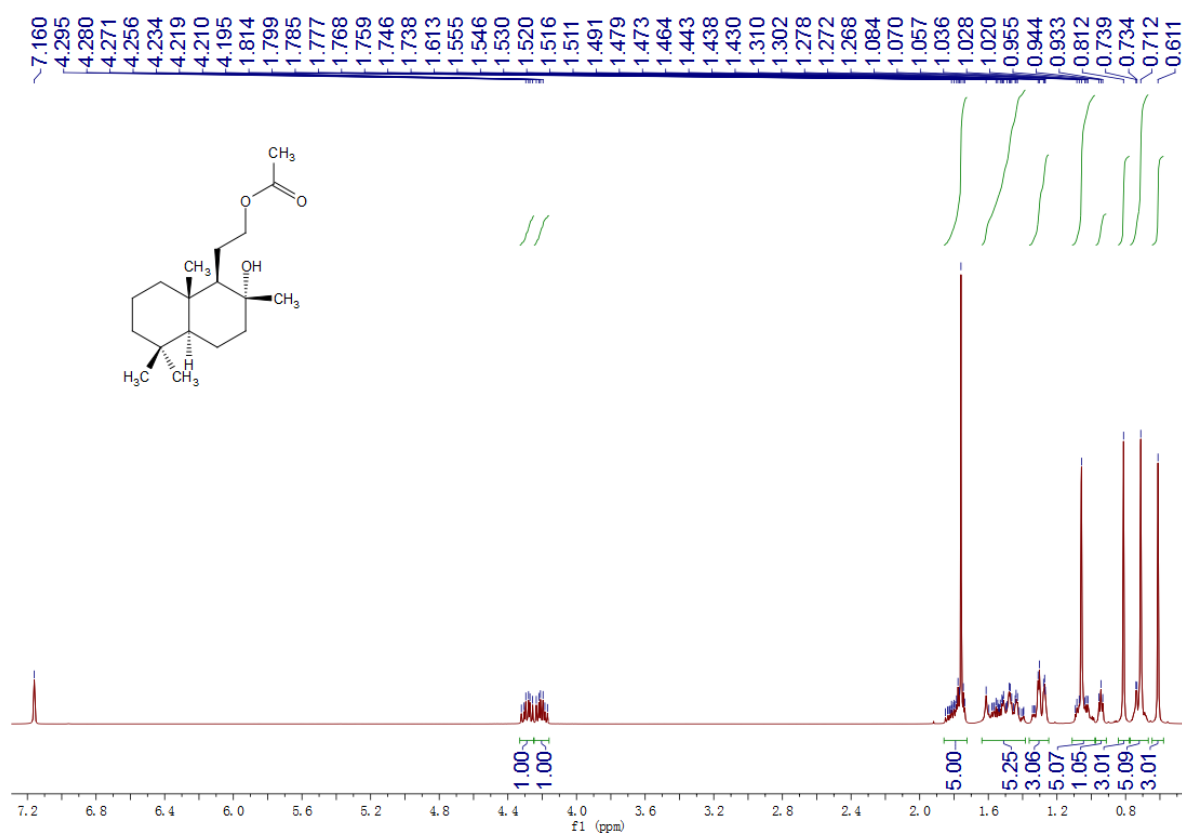
Table S2. Comparison of ^{13}C NMR data of natural **2 with those of synthetic **2**¹**

Position	Natural (100 MHz, CDCl ₃)	Synthetic (100 MHz, CDCl ₃)	$\Delta\delta(\text{ppm})$
1	29.5	29.6	0.1
2	18.6	18.6	0.0
3	41.5	41.6	0.1
4	34.1	34.1	0.0
5	50.8	50.9	0.1
6	21.4	21.4	0.0
7	37.0	37.1	0.1
8	84.0	84.0	0.0
9	59.5	59.5	0.0
10	50.1	50.2	0.1
11	24.4	24.5	0.1
12	131.3	131.3	0.0
13	134.6	134.6	0.0
14	141.0	141.1	0.1
15	111.1	111.1	0.0
16	11.9	12.0	0.1
17	22.6	22.7	0.1
18	32.2	32.2	0.0
19	20.2	20.2	0.0
20	179.9	179.9	0.0

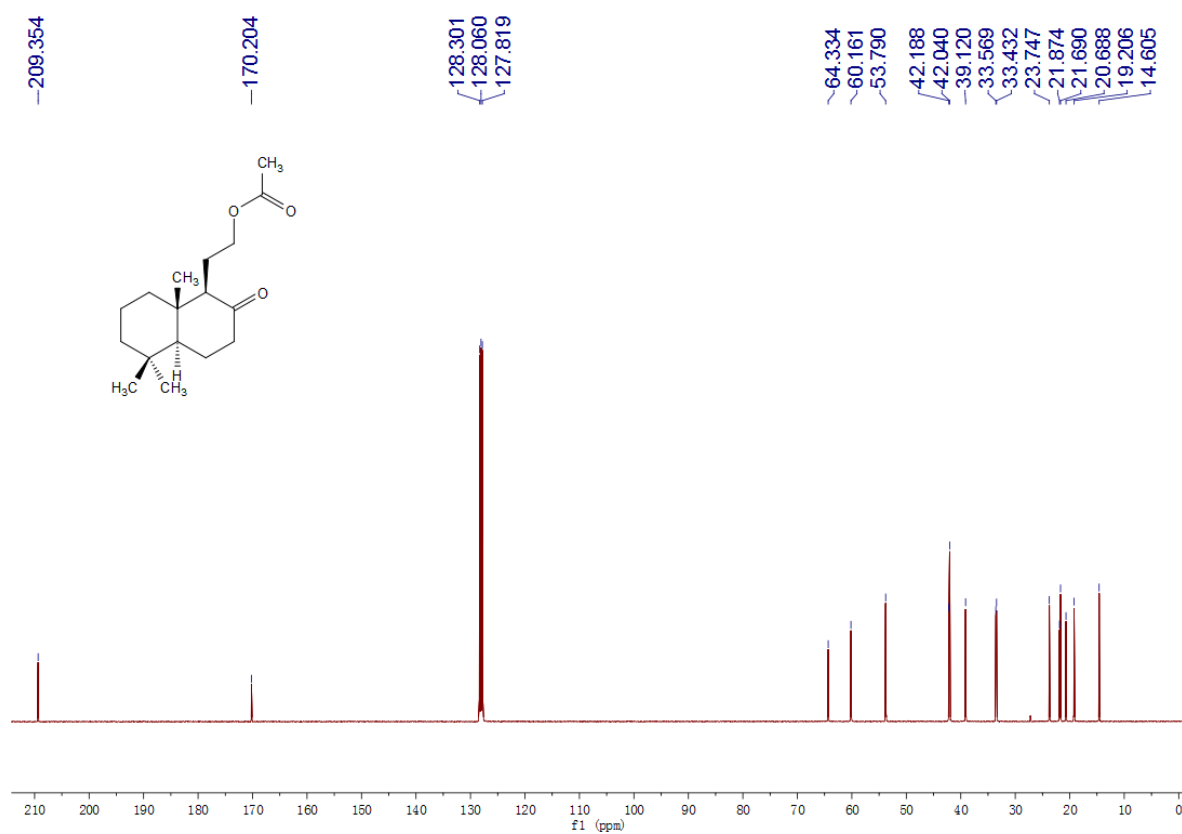
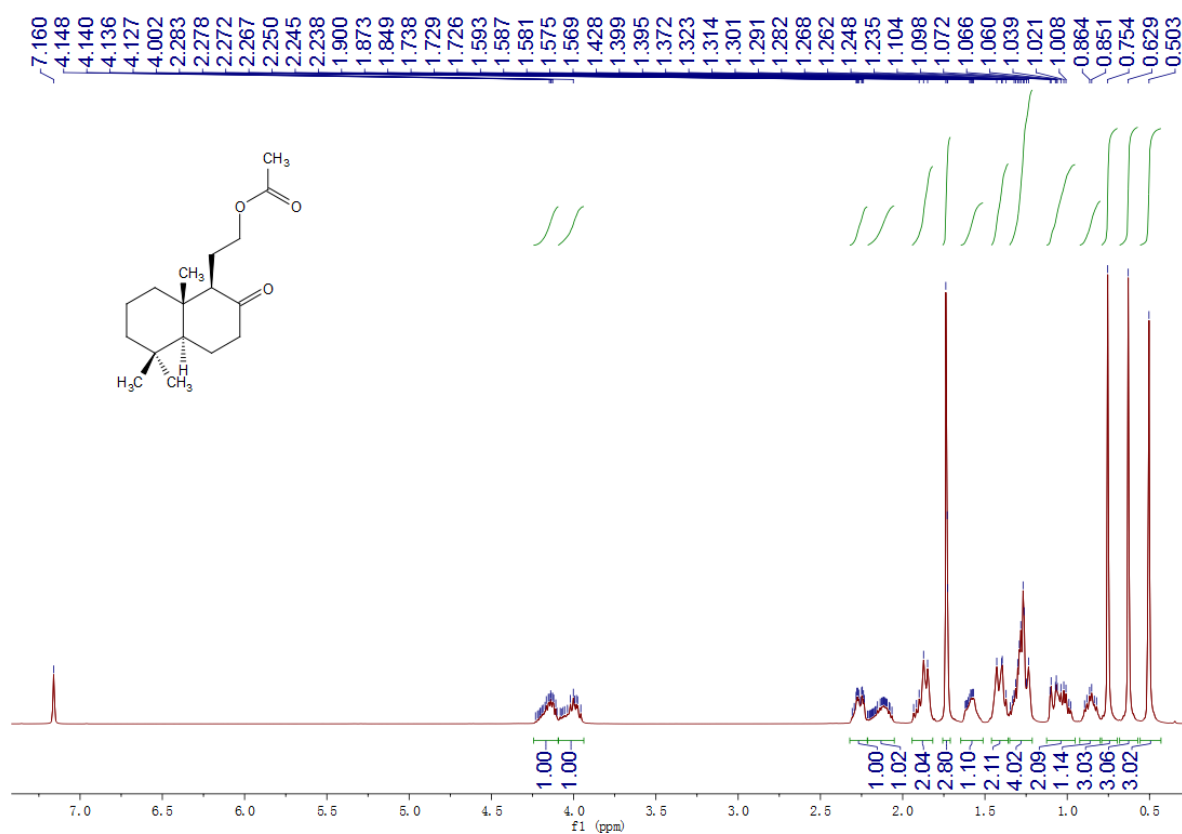
References:

1. Zhen-Yuan Huang, Bo Huang, Chao-Jiang Xiao, Xiang Dong & Bei Jiang. *Natural Product Research*, 2015, Vol. 29, No. 7, 628–63.,

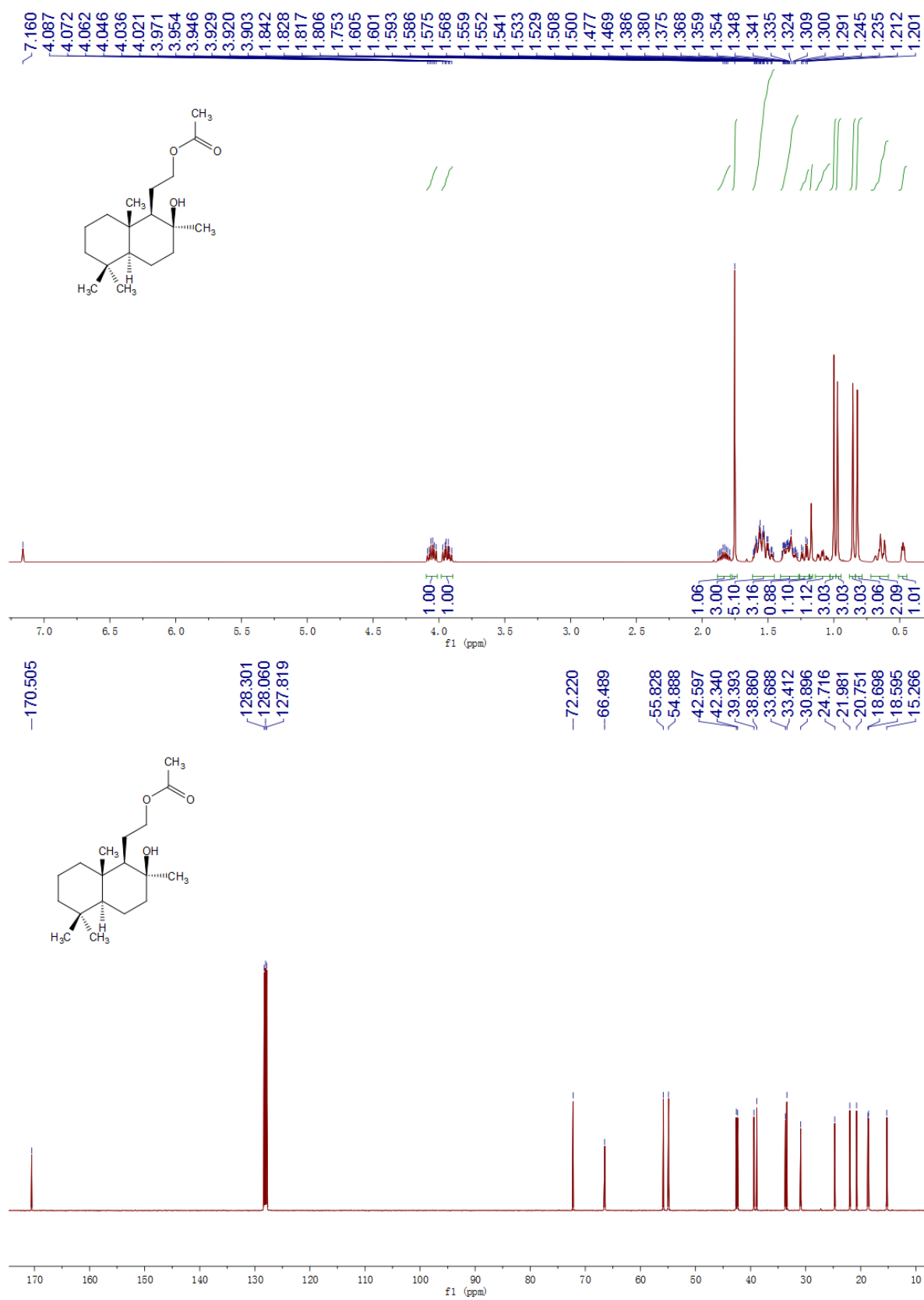
^1H and ^{13}C NMR spectra of compound 4



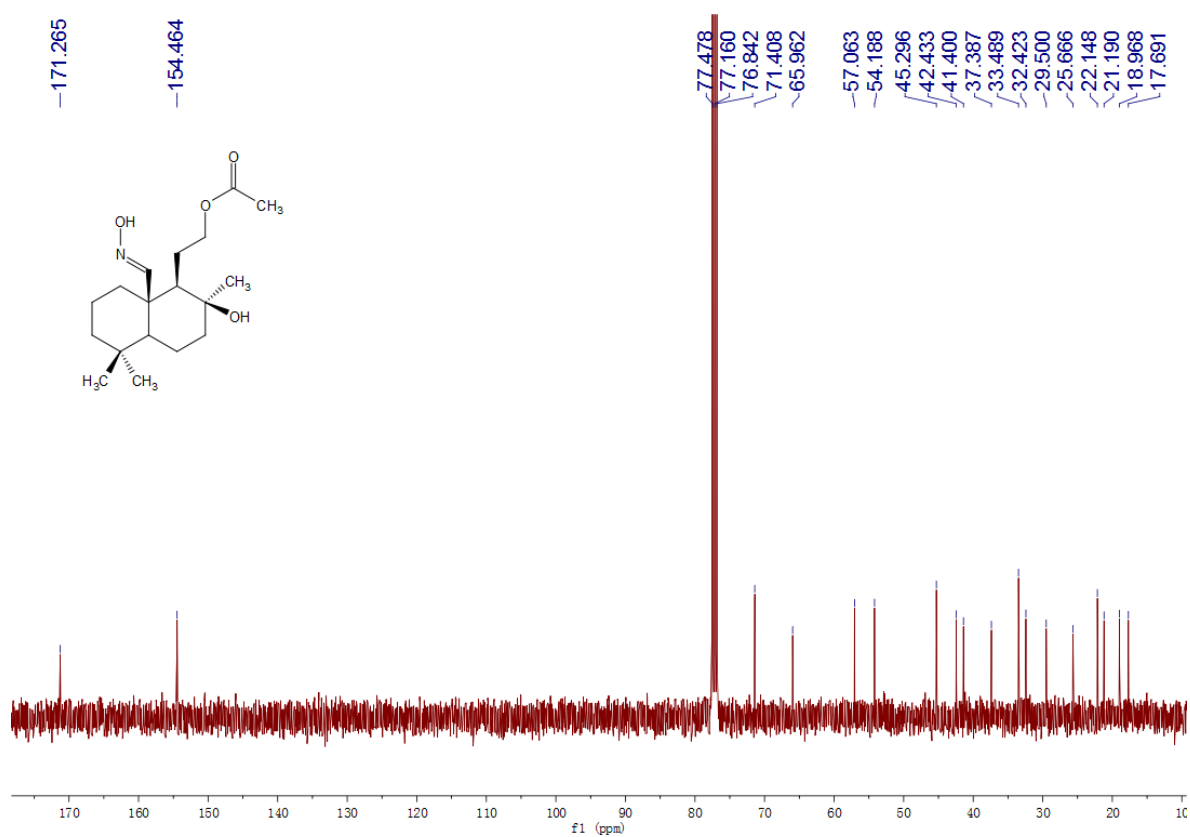
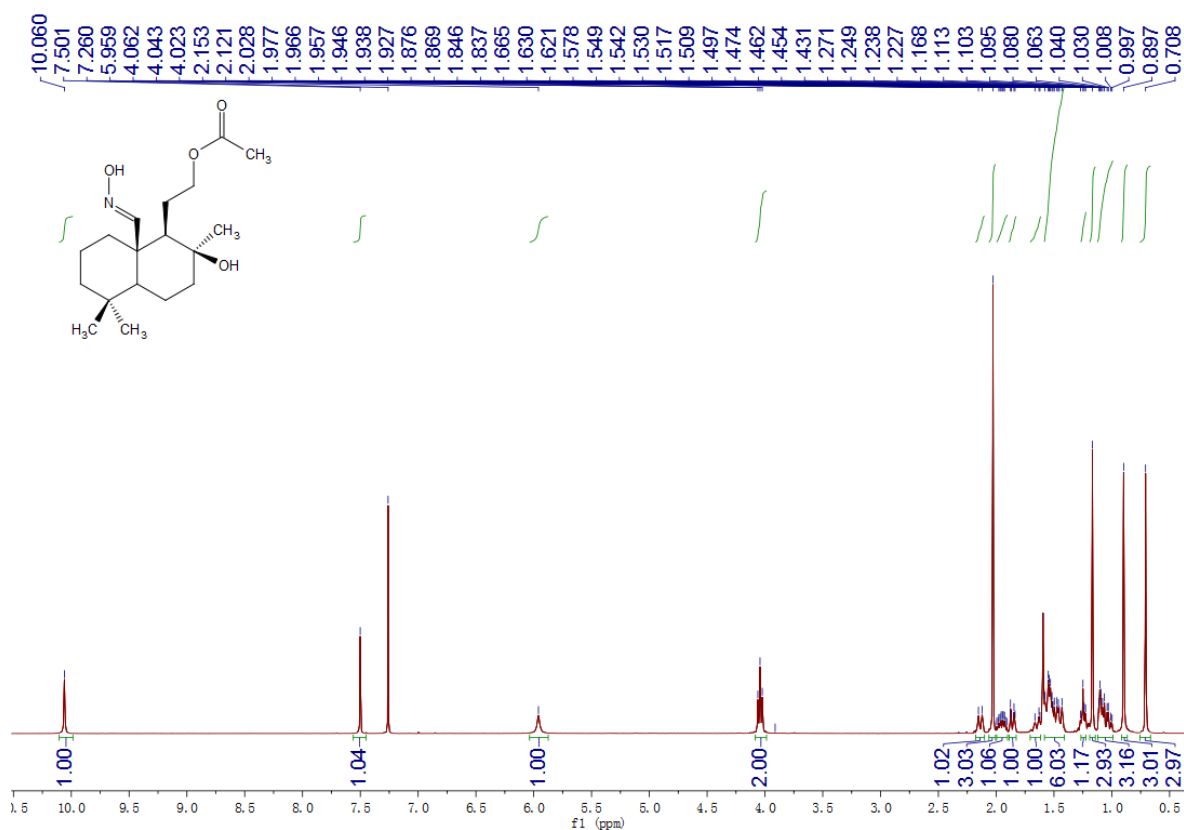
^1H and ^{13}C NMR spectra of compound 6



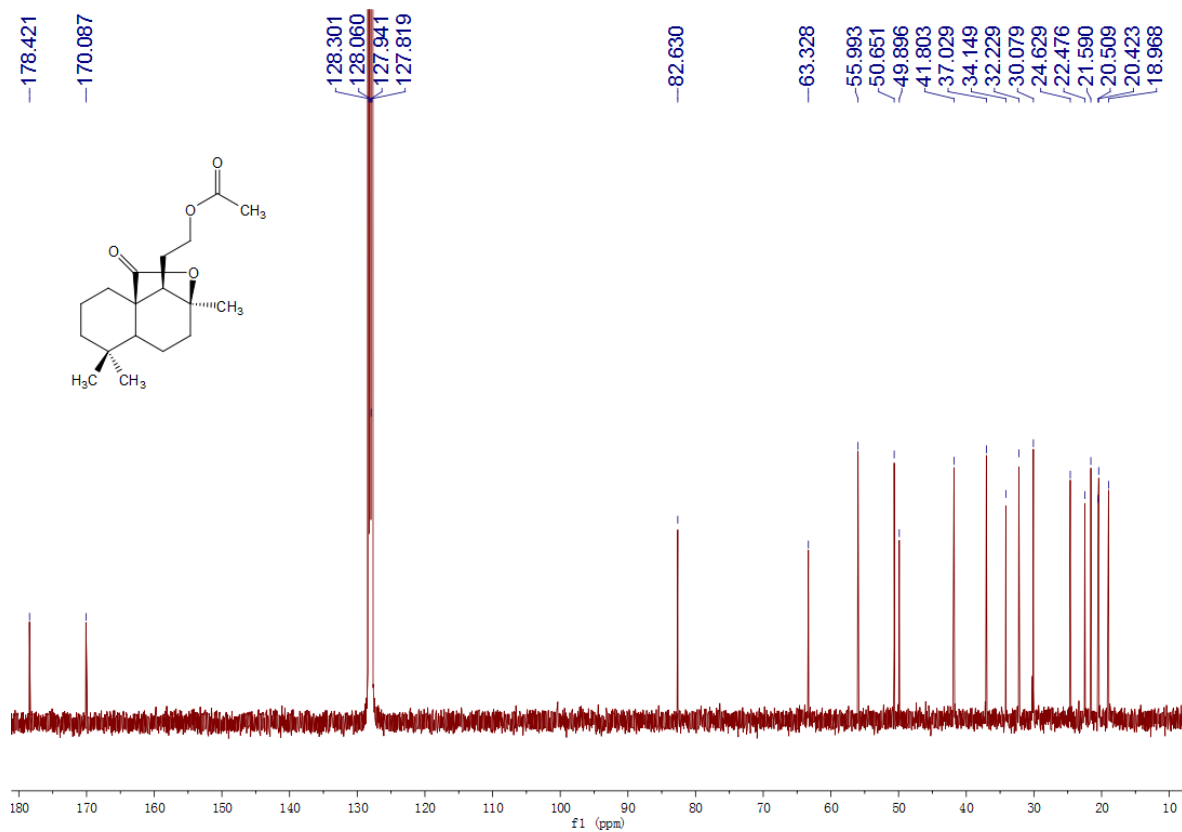
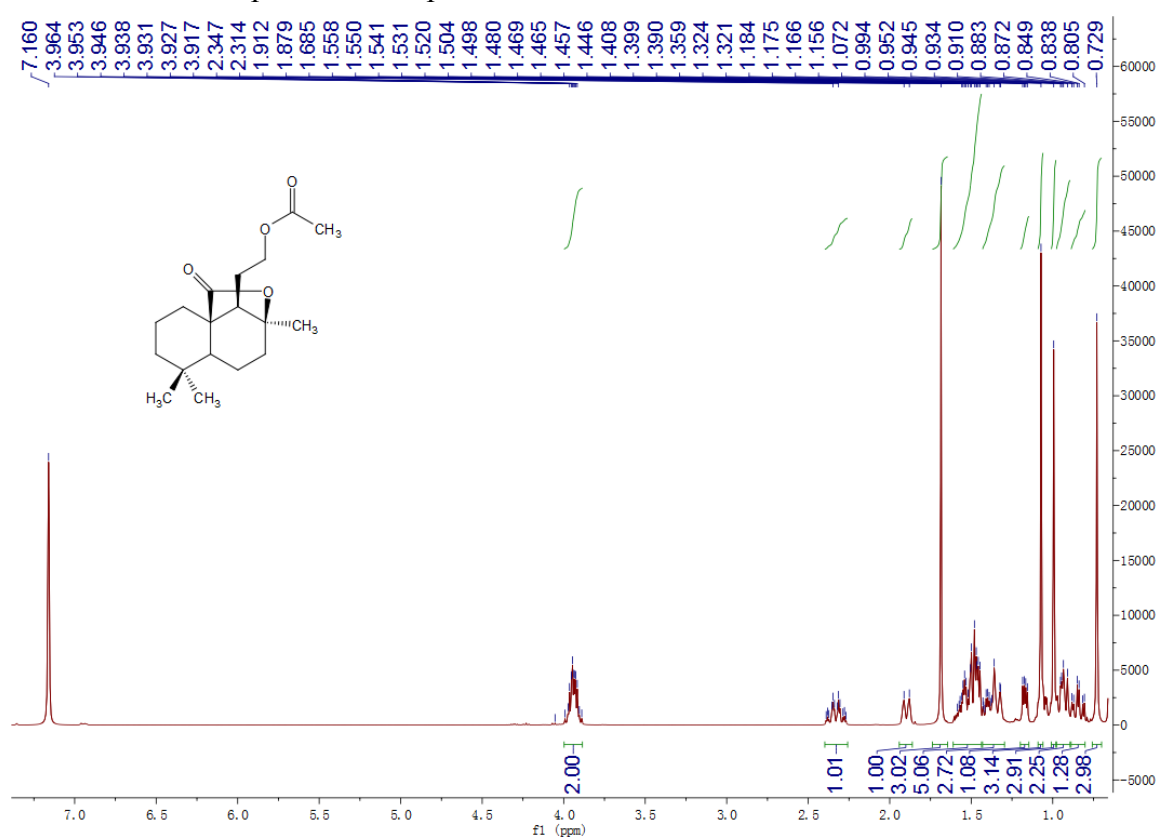
^1H and ^{13}C NMR spectra of compound 7



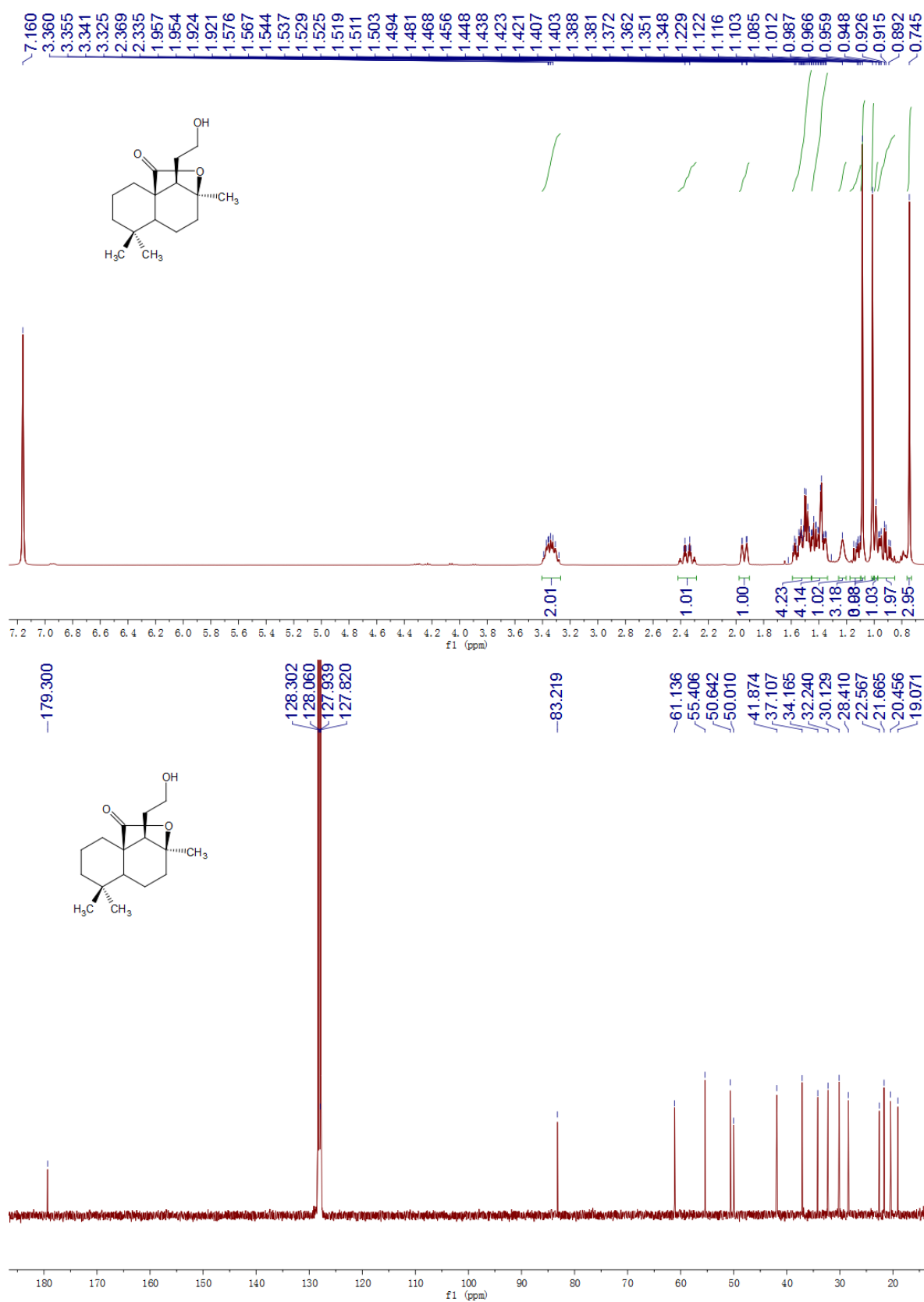
^1H and ^{13}C NMR spectra of compound **9**



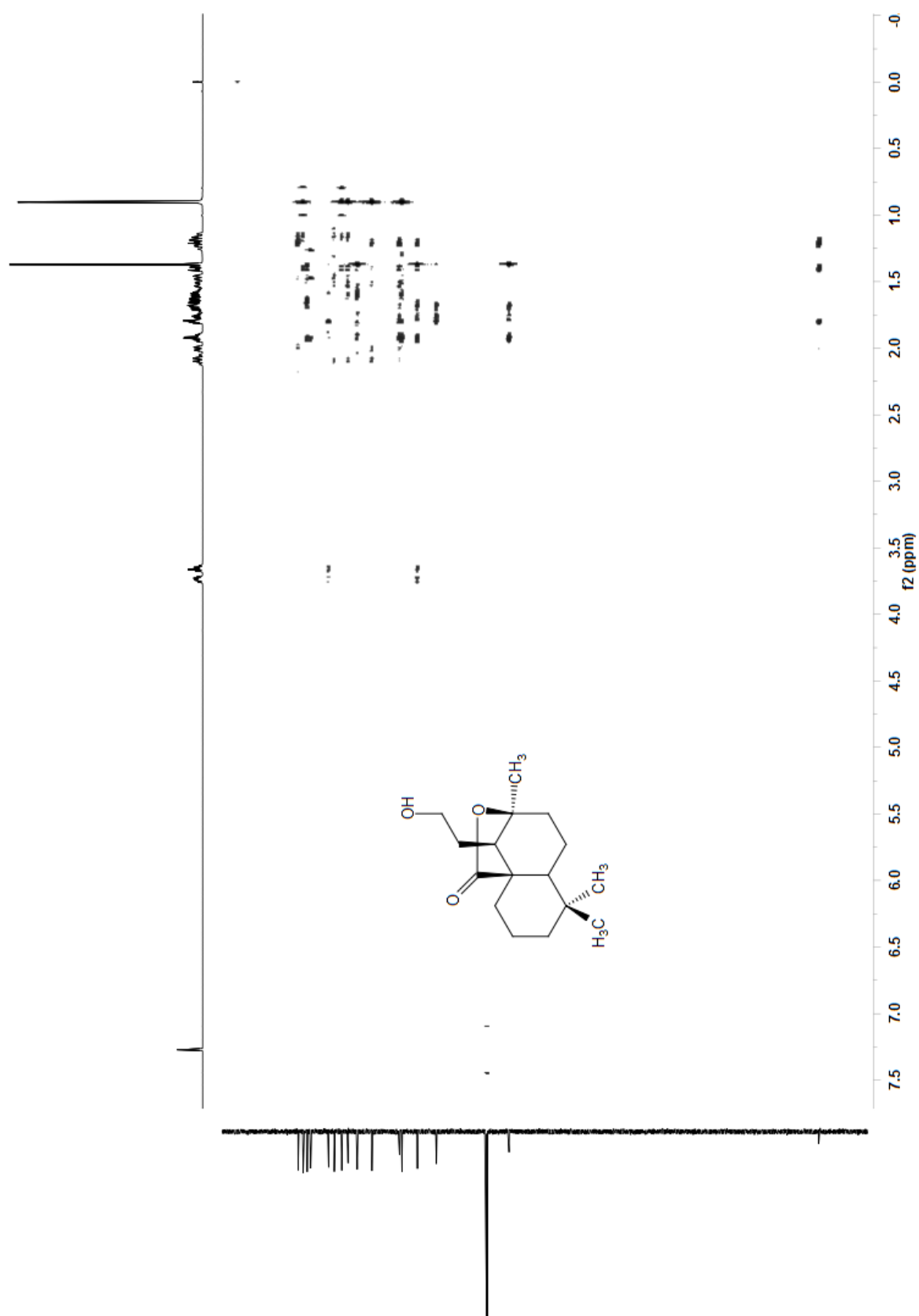
^1H and ^{13}C NMR spectra of compound **10**



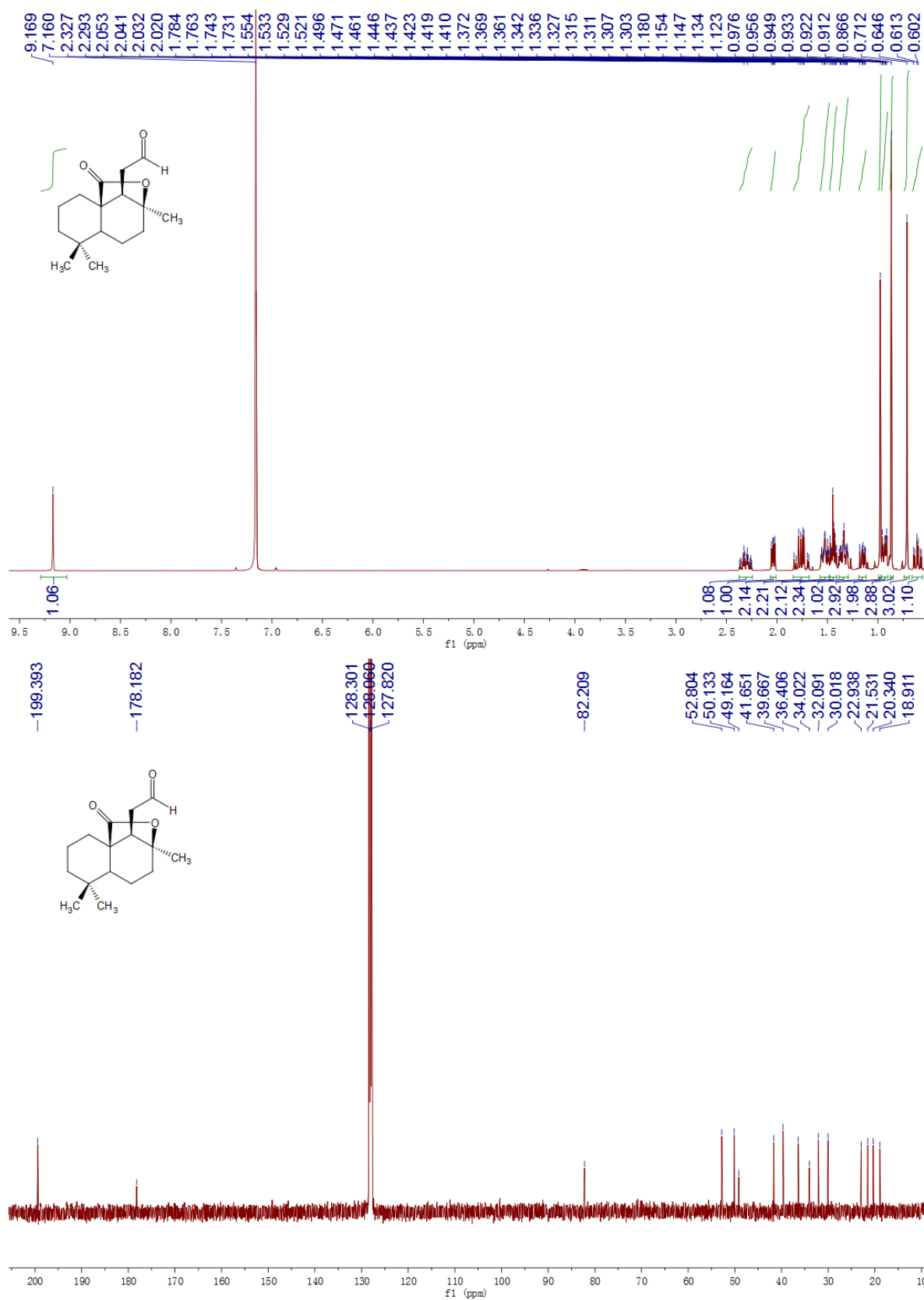
^1H and ^{13}C NMR spectra of compound 11



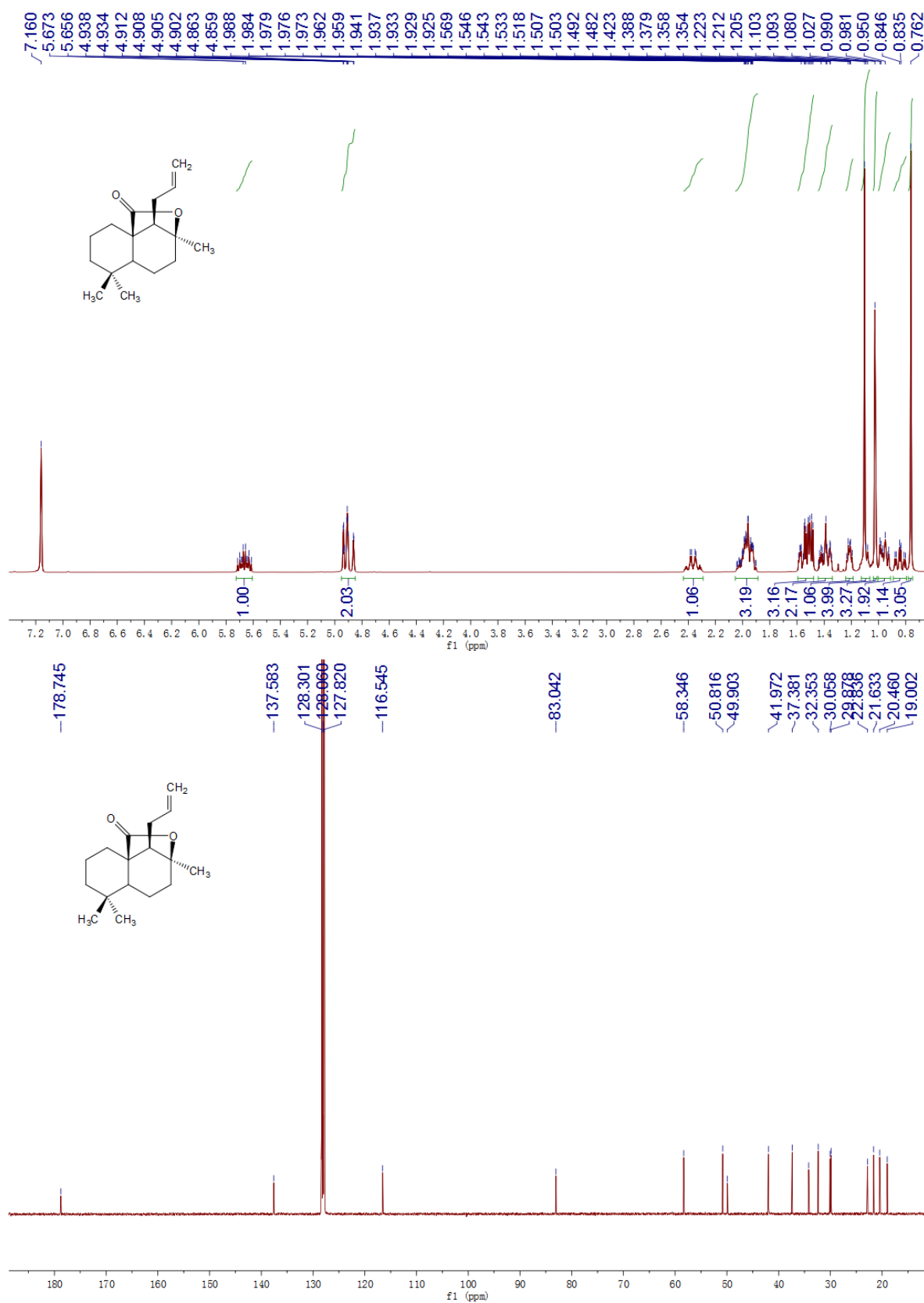
HMBC for compound **11** in CDCl₃



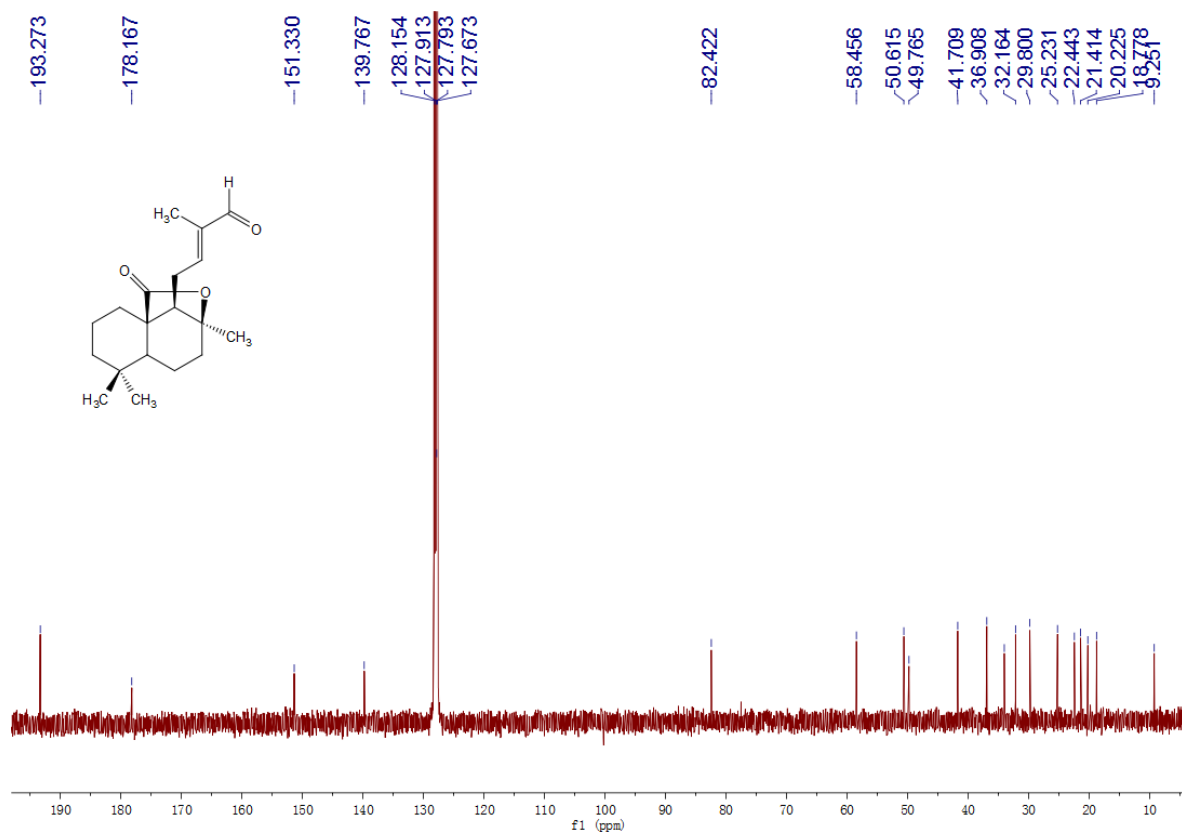
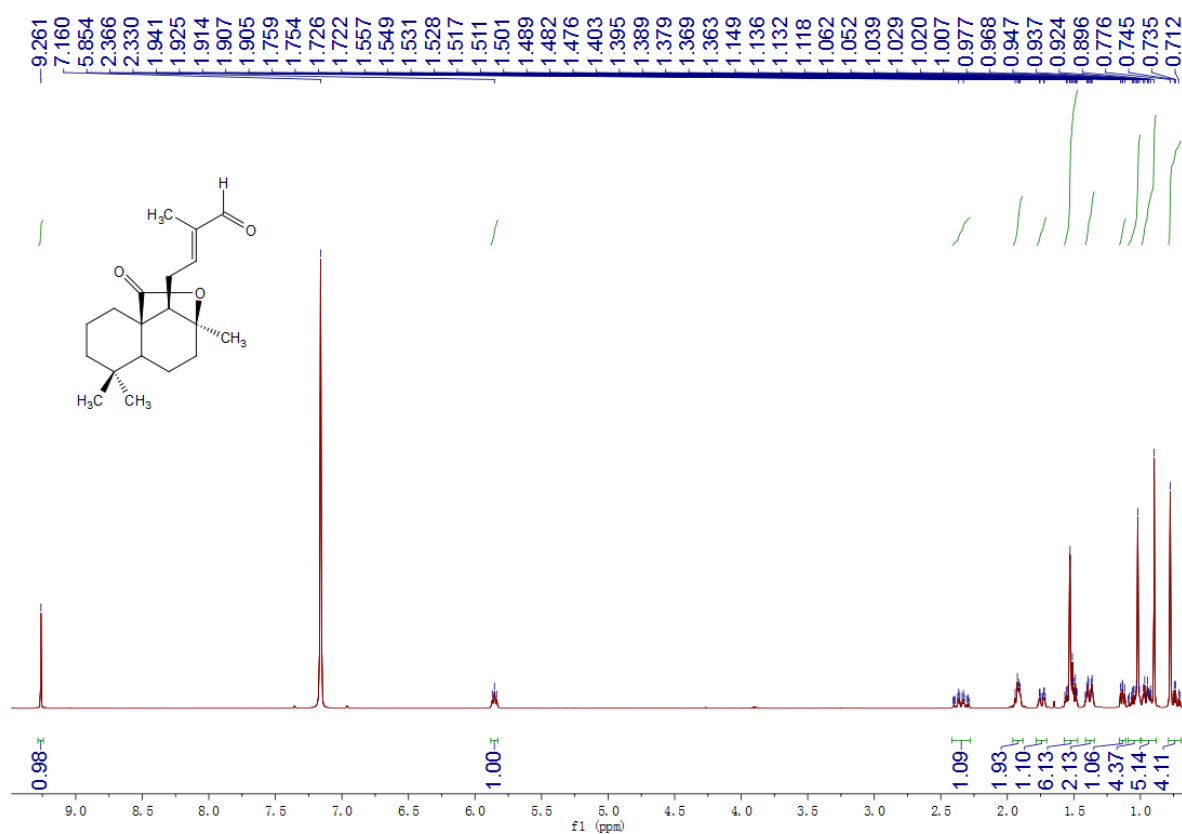
^1H and ^{13}C NMR spectra of compound 12



^1H and ^{13}C NMR spectra of compound **13**



^1H and ^{13}C NMR spectra of compound **14**



^1H and ^{13}C NMR spectra of compound 2

