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Supporting Information

Total Syntheses of Five Natural Eremophilane-type Sesquiterpenoids

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Table S1 Comparison of ^{1}H NMR data between natural A with those of synthetic A

Position	Natural (400 MHz, $CDCl_3$)	Synthetic (400 MHz, $CDCl_3$)	Δδ(ppm)
1a	2.02, m	2.41, m	--
1b	1.82, m	--	--
2a	1.63, m	1.99, m	--
2b	1.46, m	--	--
3a	1.33, m	1.41, m	--
3b	1.02, m	--	--
4	1.53, m	1.54, m	+0.01
5	--	--	--
6	6.33, s	6.32, s	-0.01
7	--	--	--
8	--	--	--
9	6.19, s	6.17, s	-0.02
10	--	--	--
11	1.15, s	1.13, s	-0.02
12	1.08, d (5.2)	1.06, d (6.2)	-0.02
OH	7.27, s	6.36, s	--

Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

From table S1, we can see inconsistency among three pairs of chemical shifts for hydrogens at C1, C2 and C3. Almost all of these chemical shifts are shifted to the downfield. In fact, the chemical shifts of hydrogens at C1, C2 and C3 in our synthetic compound A are δ2.41(2H, m), δ1.99(1H, m) and δ1.41(3H, m) respectively.

According to the single-crystal structure of compound **A**, intermolecular hydrogen

bonds were formed between the two isomers. Guessing it was the reason that resulted in the great difference between natural **A** and the synthetic one.

Table S2 Comparison of ^{13}C NMR data between natural A with those of synthetic A

Position	Natural (100 MHz, $CDCl_3$)	Synthetic (100 MHz, $CDCl_3$)	Δδ(ppm)
1	33.4	33.3	-0.1
2	28.5	28.4	-0.1
3	30.2	30.1	-0.1
4	44.6	44.5	-0.1
5	43.1	43.1	0.0
6	124.6	124.5	-0.1
7	146.4	146.3	-0.1
8	182.1	182.0	-0.1
9	121.5	121.4	-0.1
10	173.2	173.1	-0.1
11	18.3	18.2	-0.1
12	16.7	16.6	-0.1

Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

Table S3 Comparison of ^{1}H NMR data between natural B with those of synthetic B

Position	Natural (400 MHz, $CDCl_3$)	Synthetic (400 MHz, $CDCl_3$)	Δδ(ppm)
1	2.38, m	2.38, m	0.00
2a	1.99, m	1.99, m	0.00
2b	1.39, m	1.39, m	0.00
3	1.56, m	1.56, m	0.00
4	1.52, m	1.52, m	0.00
5	--	--	--
6	7.02, s	7.02, s	0.00
7	--	--	--
8	--	--	--
9	6.09, s	6.08, s	-0.01
10	--	--	--
11	--	--	--
12	4.19, s	4.16, s	-0.03
13a	5.22, d (1.7)	5.21, d (1.6)	-0.01
13b	5.28, d (1.7)	5.28, s	0.00
14	1.15, s	1.14, s	-0.01
15	1.07, d (6.1)	1.06, d (5.9)	-0.01

Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

Table S4 Comparison of ^{13}C NMR data between natural B with those of synthetic B

Position	Natural (100 MHz, $CDCl_3$)	Synthetic (100 MHz, $CDCl_3$)	Δδ(ppm)
1	33.0	32.8	-0.2
2	28.0	28.1	+0.1
3	30.2	30.2	0.0
4	41.8	41.8	0.0
5	44.1	44.2	+0.1
6	154.2	154.4	+0.2
7	146.9	146.8	-0.1
8	186.8	186.9	+0.1
9	124.1	124.2	+0.1
10	169.5	169.7	+0.2
11	138.6	138.5	-0.1
12	65.3	65.1	-0.2
13	117.8	117.7	-0.1
14	17.2	17.2	0.0
15	16.3	16.3	0.0

Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

Table S5 Comparison of ^{1}H NMR data between natural C with those of synthetic C

Position	Natural (400 MHz, $CDCl_3$)	Synthetic (400 MHz, $CDCl_3$)	Δδ(ppm)
1	4.59, br s	4.57, br s	-0.02
2a	2.05-2.32, m	2.07-2.12, m	0.00
2b	1.60-1.70, m	1.57-1.69, m	0.00
3a	1.80-1.90, m	1.85-1.96, m	0.00
3b	1.40-1.50, m	1.43-1.53, m	0.00
5	--	--	--
6	6.33, s	6.34, s	+0.01
7	--	--	--
8	--	--	--
9	6.28, s	6.26, s	-0.02
10	--	--	--
14	1.38, s	1.37, s	-0.01
15	1.10, d (6.3)	1.11, d (6.6)	+0.01
OH	6.20, s	--	--

Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

Table S6 Comparison of ^{13}C NMR data between natural C with those of synthetic C

Position	Natural (100 MHz, $CDCl_3$)	Synthetic (100 MHz, $CDCl_3$)	Δδ(ppm)
1	74.2	74.0	-0.2
2	35.0	34.9	-0.1
3	25.0	24.9	-0.1
4	43.0	42.9	-0.1
5	44.7	44.7	0.0
6	126.7	126.8	+0.1
7	146.0	146.0	0.0
8	182.4	182.4	0.0
9	123.7	123.6	-0.1
10	169.4	169.5	+0.1
14	19.6	19.5	-0.1
15	16.7	16.5	-0.2

Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

Table S7 Comparison of ^{1}H NMR data between natural D with those of synthetic D

Position	Natural (400 MHz, $CDCl_3$)	Synthetic (400 MHz, $CDCl_3$)	Δδ(ppm)
1	5.50, t (3.0)	5.48, t (2.5)	-0.02
2a	2.13, m	2.09, m	-0.04
2b	1.86, dddd (14.0,4.0,4.0,3.0)	1.85, m	-0.01
3a	1.49, m	--	--
3b	1.62, m	1.54-1.70, m, 3H	--
4	1.71, m	--	--
5	--	--	--
6	7.67, s	7.65, s	-0.02
7	--	--	--
8	--	--	--
9	6.31, s	6.34, s	+0.03
10	--	--	--
11	--	--	--
12	--	--	--
13	2.56, s	2.54, s	-0.02
14	1.29, s	1.28, s	-0.01
15	1.15, d (6.6)	1.14, d (6.6)	-0.01
OAc	2.06, s	2.04, s	-0.02

Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

Table S8 Comparison of ^{13}C NMR data between natural D with those of synthetic D

Position	Natural (100 MHz, $CDCl_3$)	Synthetic (100 MHz, $CDCl_3$)	Δδ(ppm)
1	74.3	74.4	+0.1
2	32.1	32.0	-0.1
3	21.5	25.5	+4.0
4	41.1	40.7	-0.4
5	43.8	43.9	+0.1
6	160.7	161.0	+0.3
7	135.8	136.2	+0.4
8	185.3	184.0	-1.3
9	128.8	129.4	+0.6
10	159.4	159.6	+0.2
11	198.5	198.7	+0.2
12	--	--	--
13	30.9	31.1	+0.2
14	18.1	17.9	-0.2
15	16.1	16.1	0.0
OAc	169.7	169.9	+0.2
	21.2	21.3	+0.1

Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

Table S9 Comparison of ^{1}H NMR data between natural E with those of synthetic E

Position	Natural (400 MHz, $CDCl_3$)	Synthetic (400 MHz, $CDCl_3$)	Δδ(ppm)
1	4.56, t (2.8)	4.54, m	-0.02
2a	2.09, dddd (13.5,4.0,4.0,3.2)	--	--
2b	2.02, dddd (14.0,13.5,13.5,3.2)	2.01, m, 2H	-0.01
3a	1.52, m	--	--
3b	1.61, m	1.49-1.68, m, 3H	--
4	1.68, m	--	--
5	--	--	--
6	7.68, s	7.67, s	-0.01
7	--	--	--
8	--	--	--
9	6.18, s	6.18, s	0.00
10	--	--	--
11	--	--	--
12	--	--	--
13	2.56, s	2.55, s	-0.01
14	1.38, s	1.39, s	+0.01
15	1.15, d (6.6)	1.14, d (6.6)	-0.01

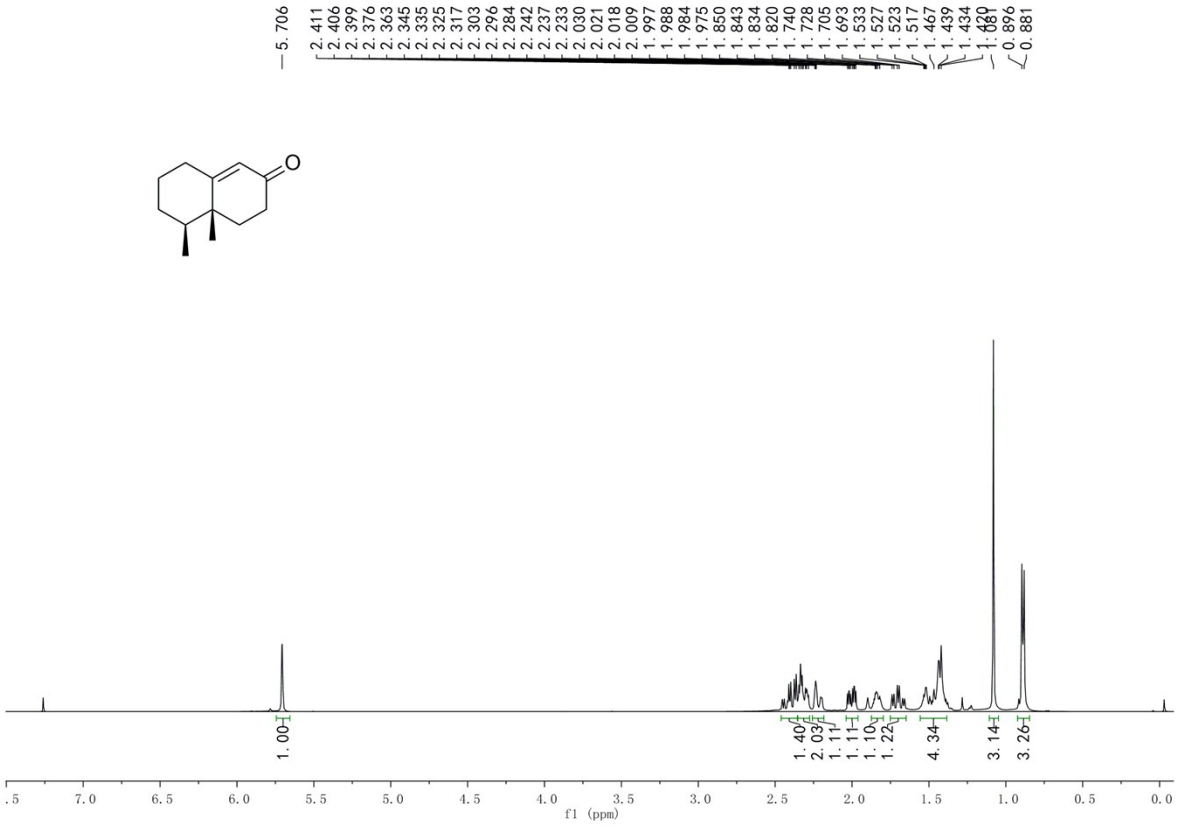
Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

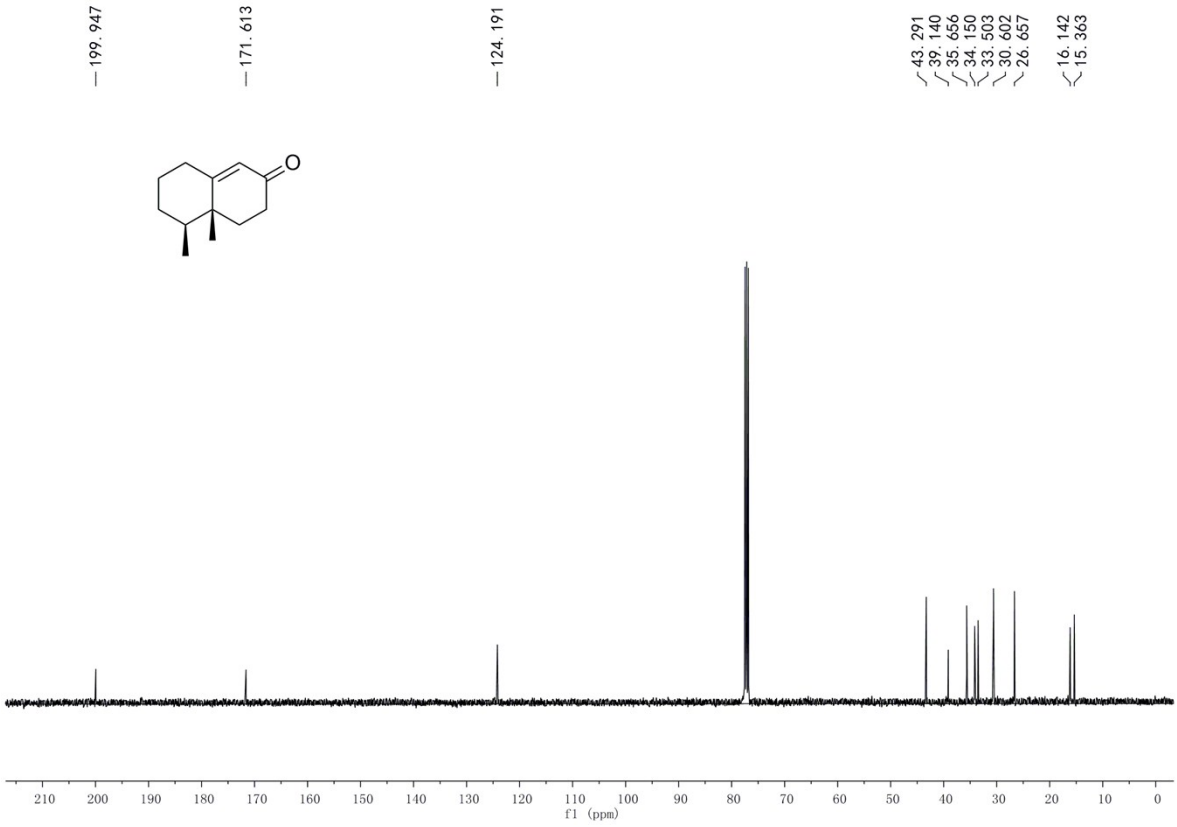
Table S10 Comparison of ^{13}C NMR data between natural E with those of synthetic E

Position	Natural (100 MHz, $CDCl_3$)	Synthetic (100 MHz, $CDCl_3$)	Δδ(ppm)
1	73.2	73.5	+0.3
2	34.3	34.5	+0.2
3	24.8	25.0	+0.2
4	40.8	41.0	+0.2
5	44.1	44.2	+0.1
6	161.7	161.8	+0.1
7	135.8	136.1	+0.3
8	184.3	184.5	+0.2
9	126.8	127.0	+0.2
10	165.2	165.0	-0.2
11	198.6	198.8	+0.2
12	--	--	--
13	30.9	31.1	+0.2
14	18.6	18.8	+0.2
15	16.0	16.1	+0.1

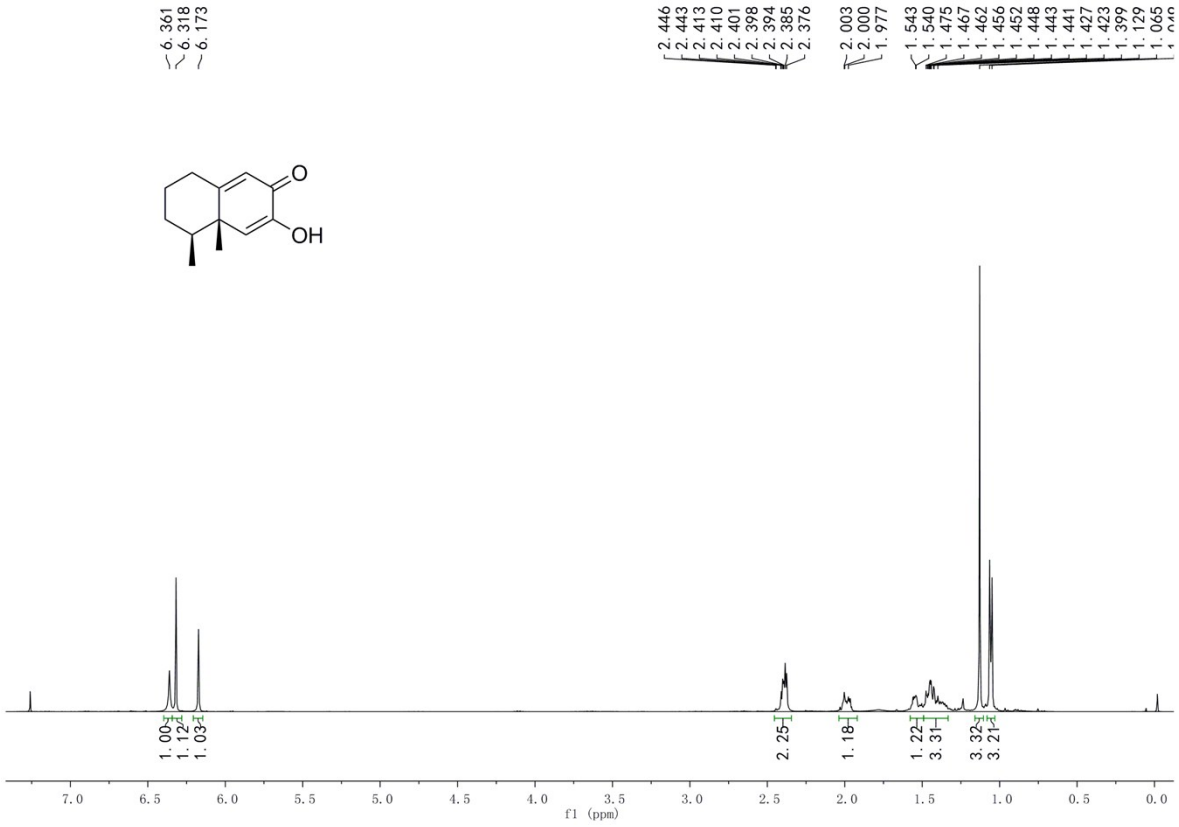
Δδ= the chemical shift of synthetic sample minus the chemical shift of natural sample.

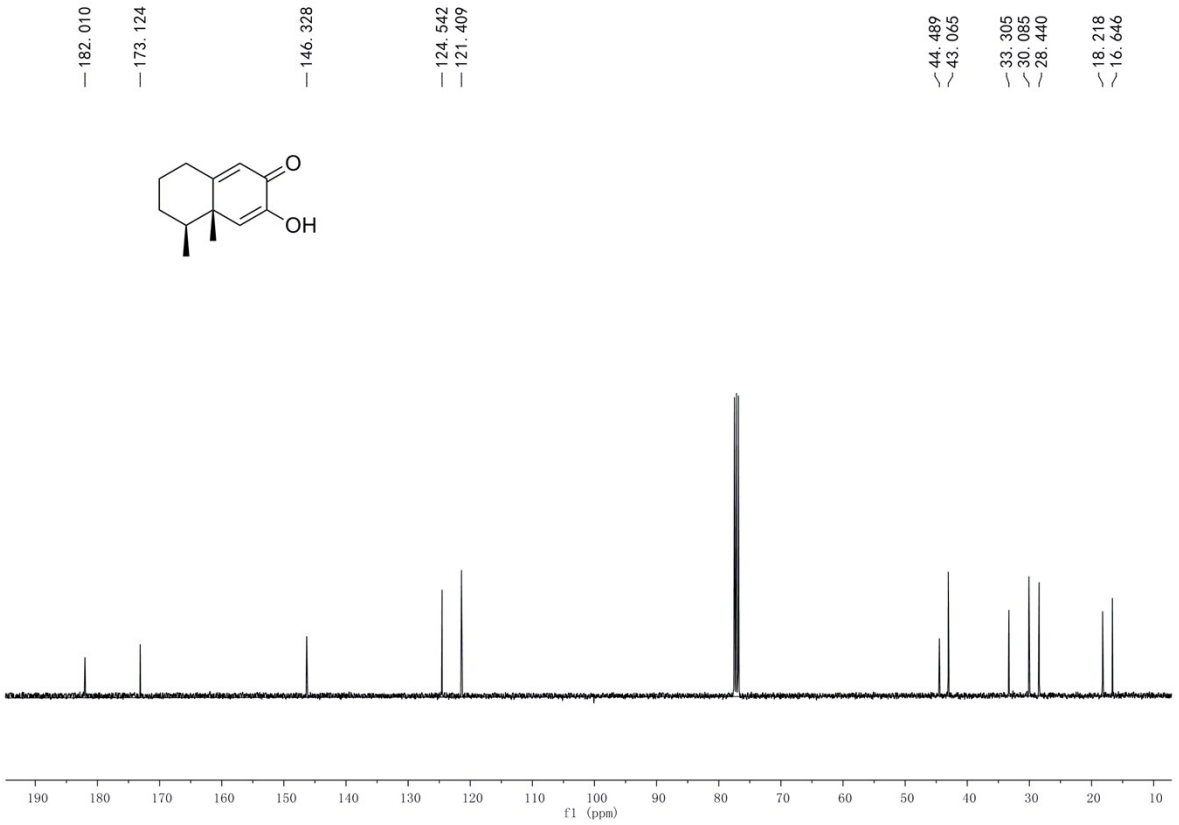
^{1}H and ^{13}C NMR spectra of compound **3**



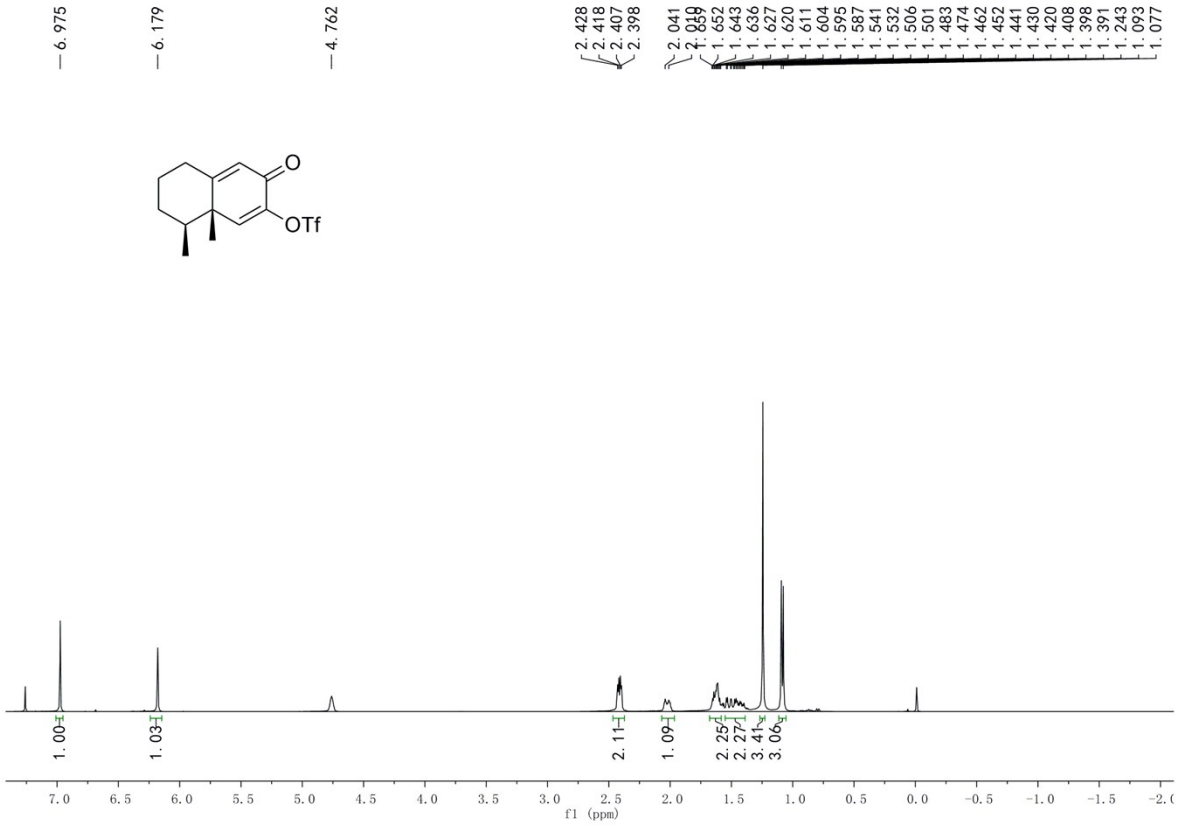


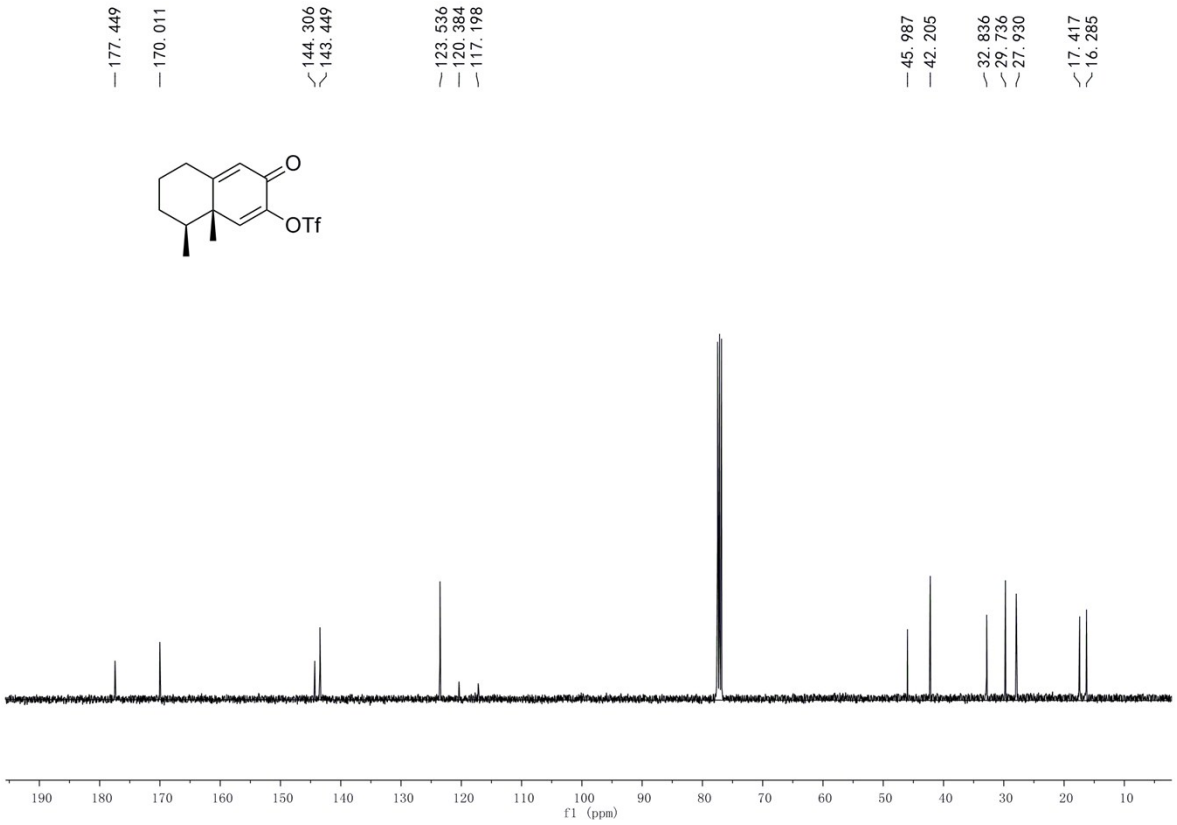
^{1}H and ^{13}C NMR spectra of compound **A**



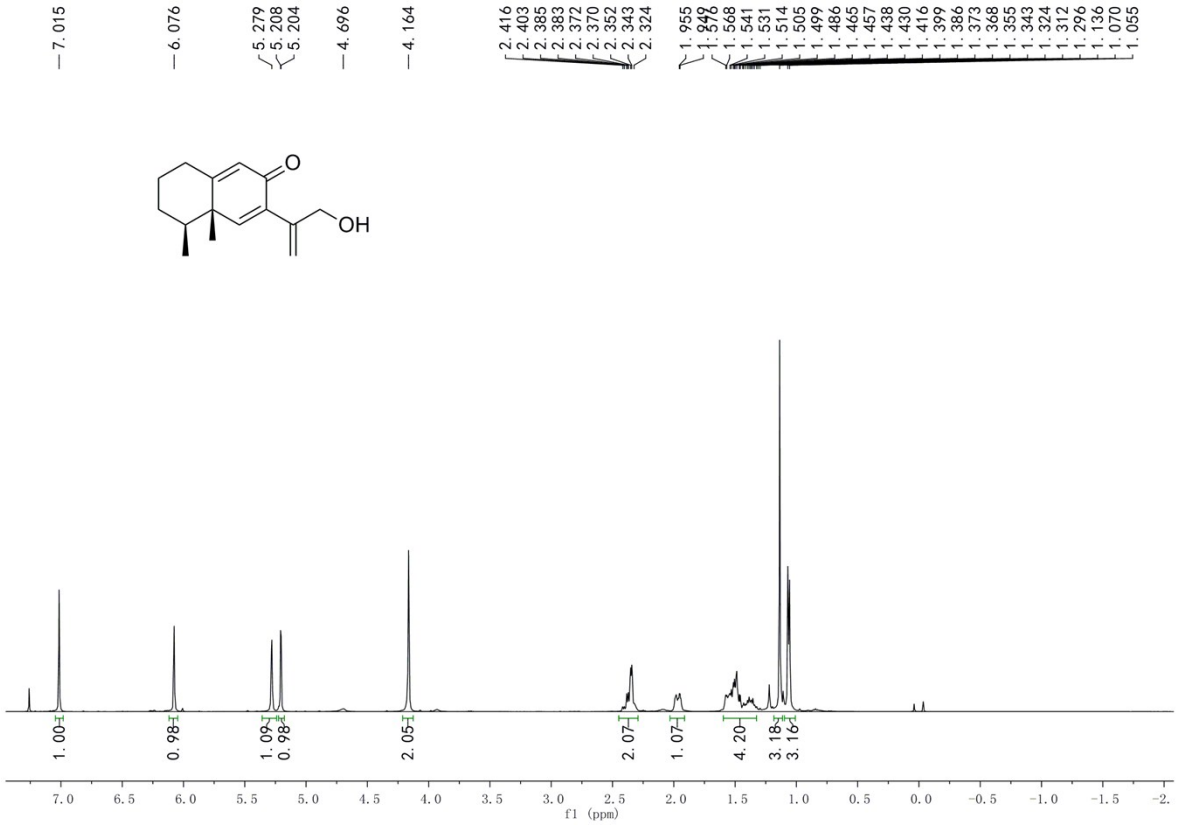


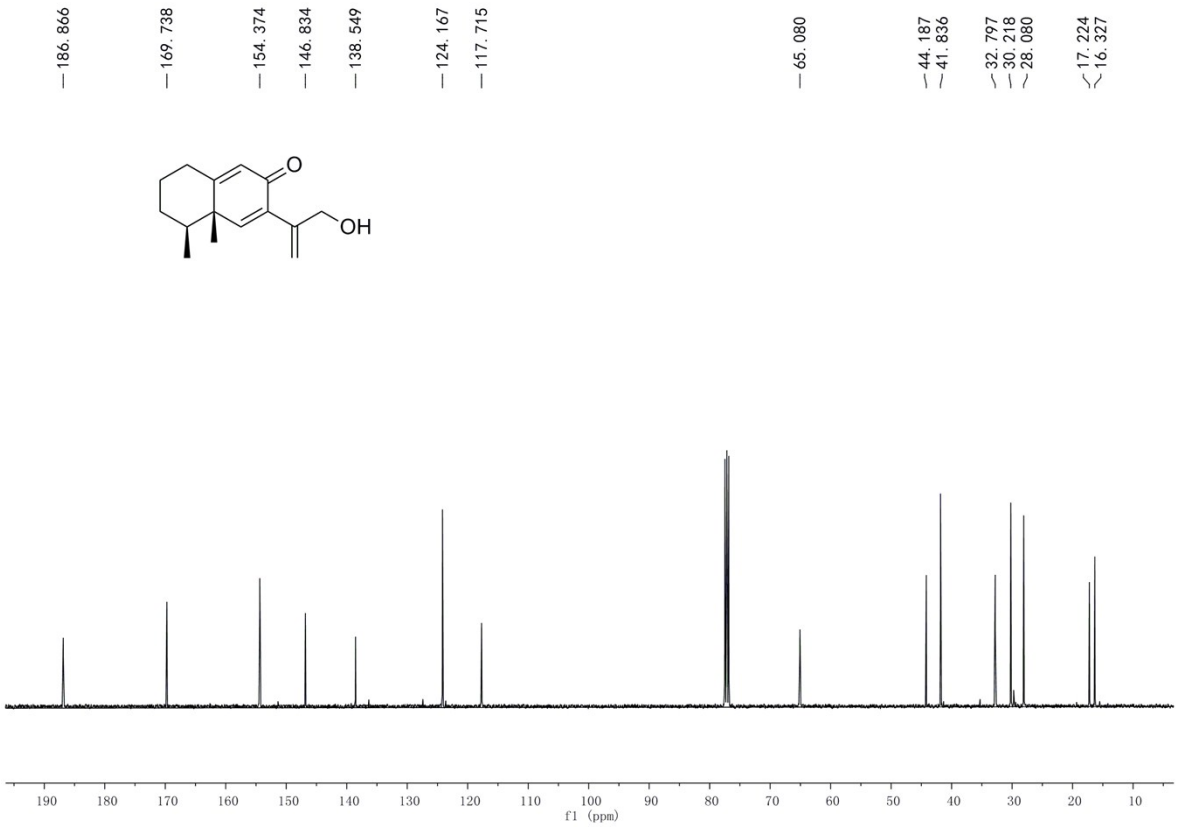
^{1}H and ^{13}C NMR spectra of compound **1**



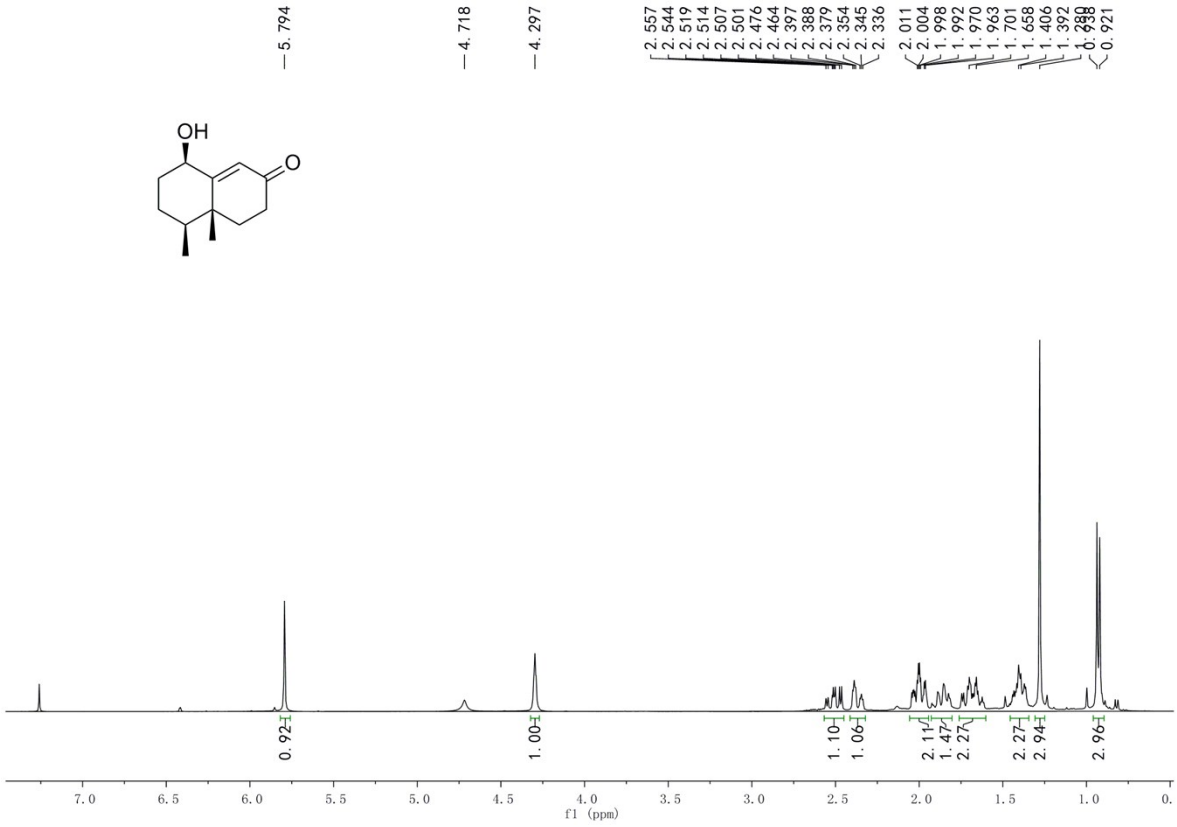


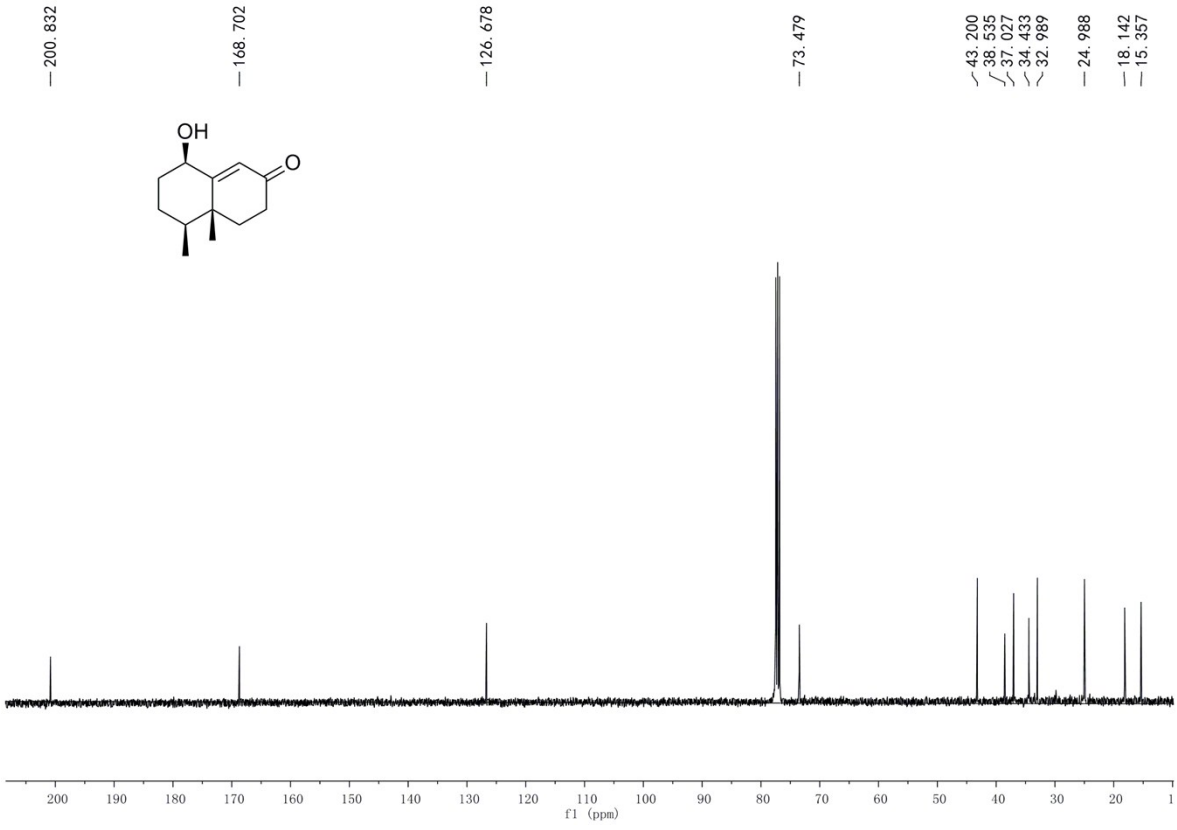
^{1}H and ^{13}C NMR spectra of compound **B**



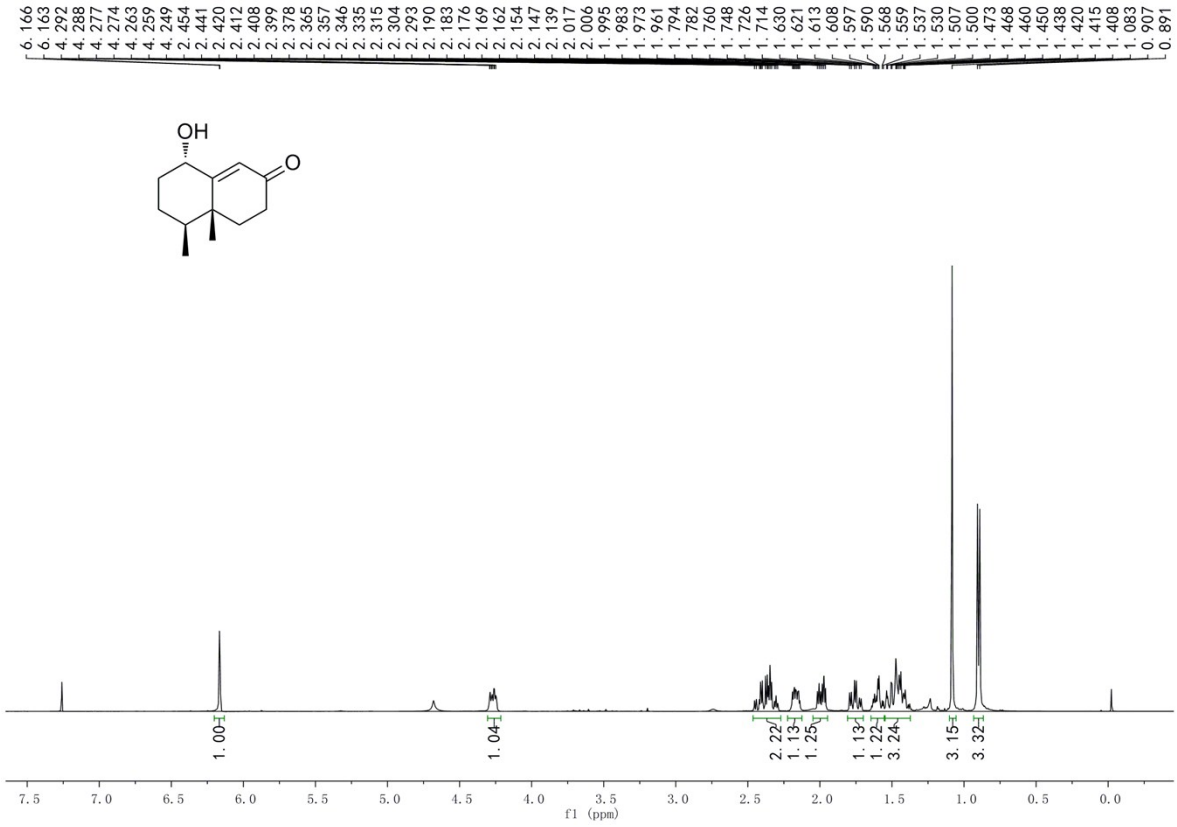


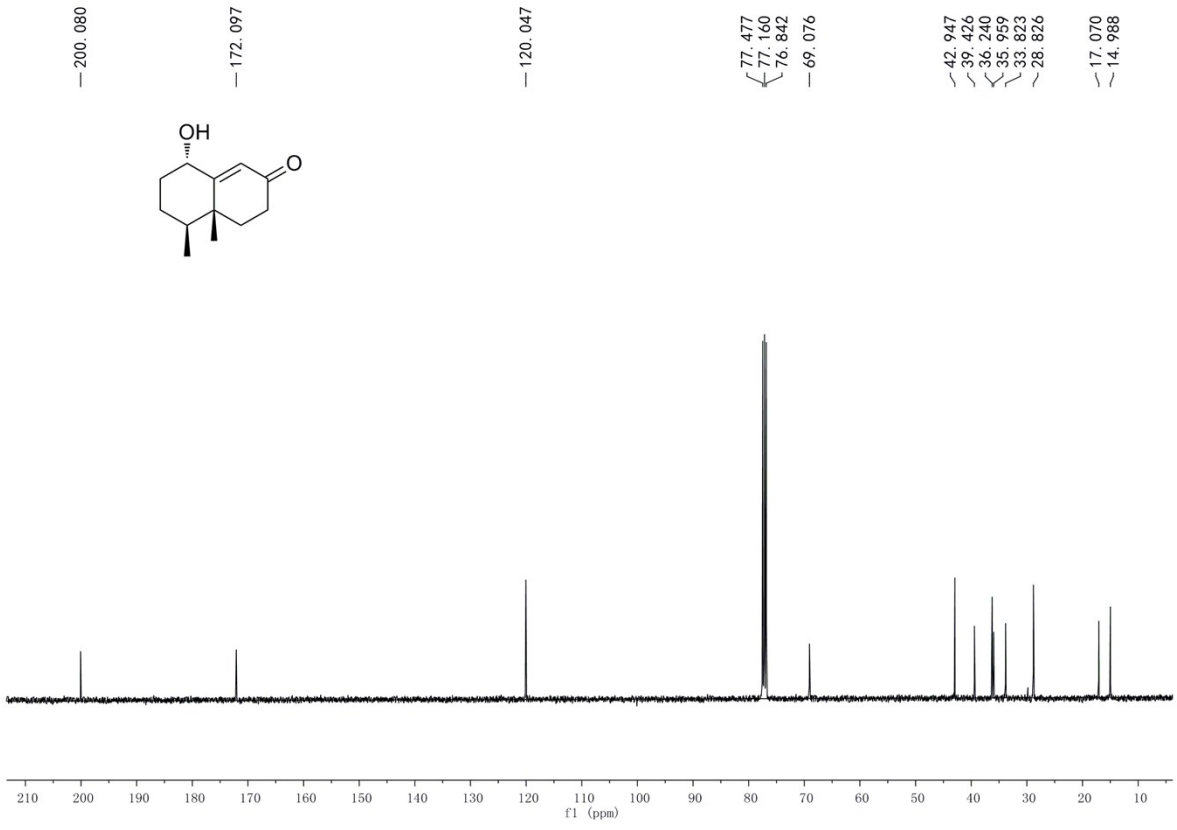
^{1}H and ^{13}C NMR spectra of compound **11**



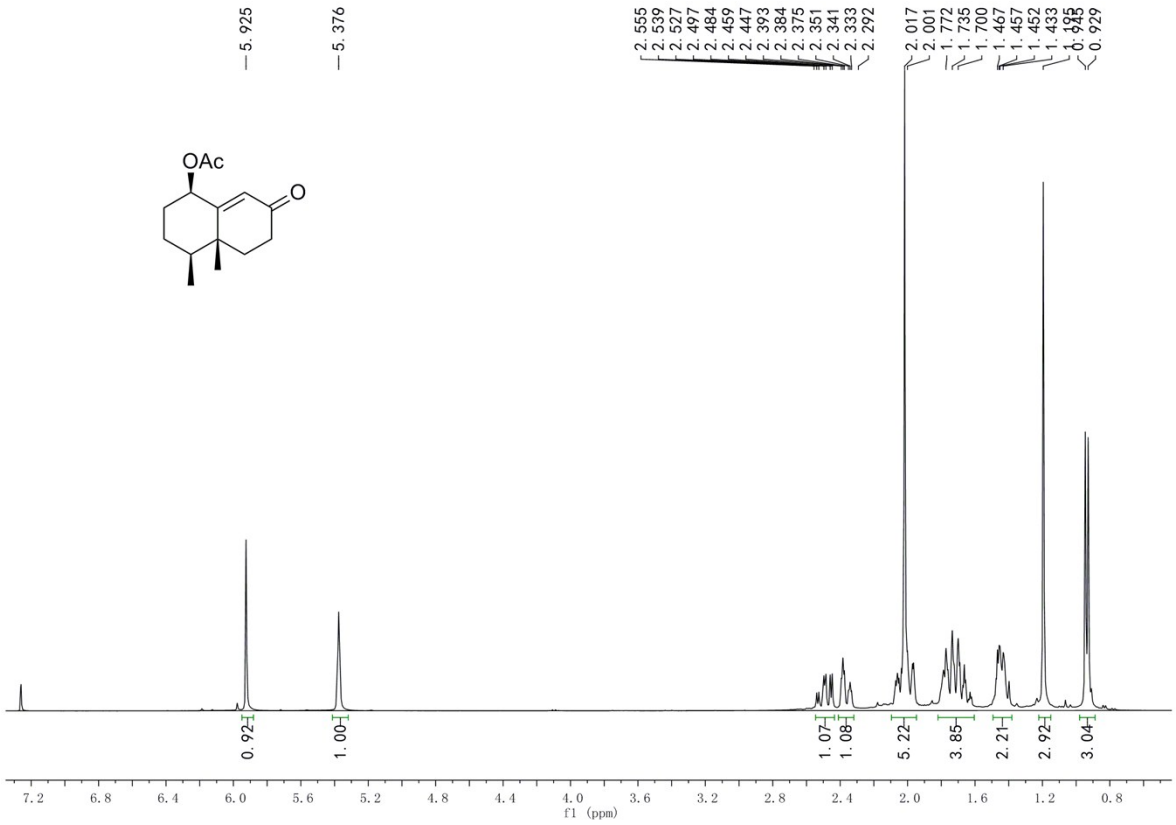


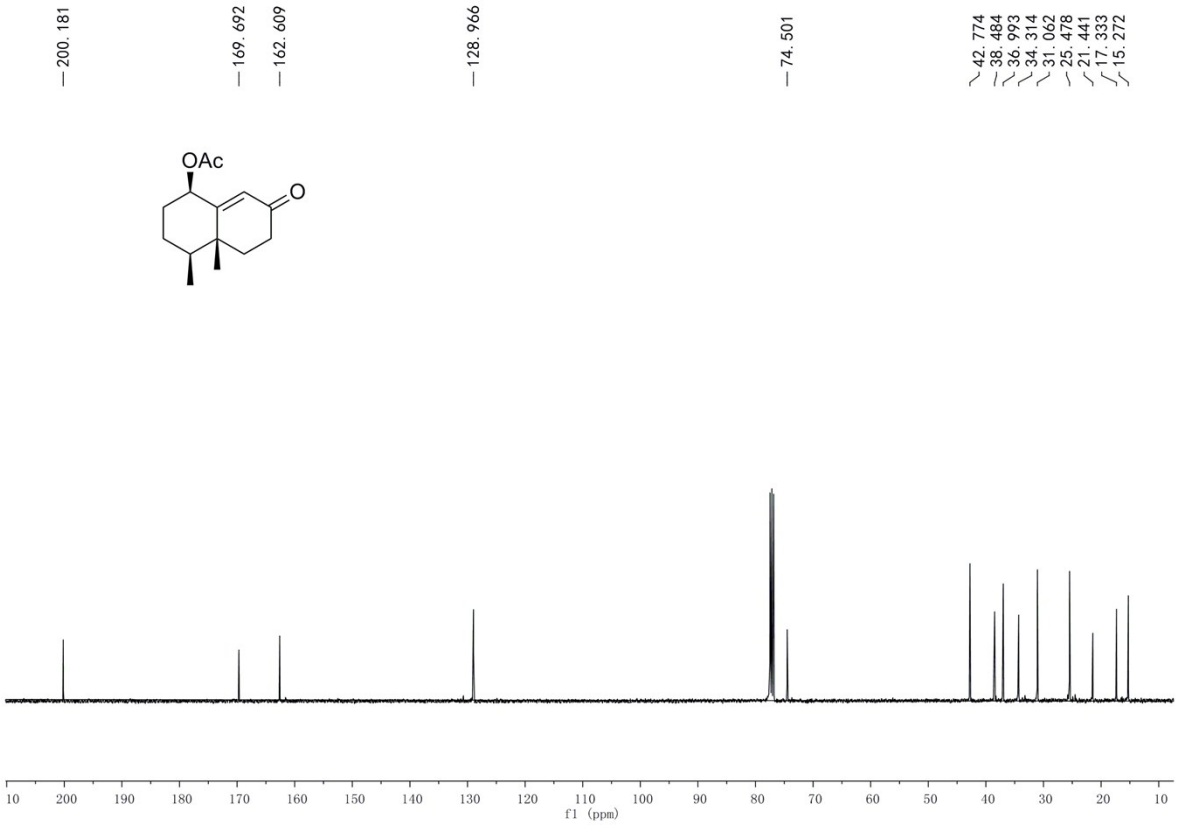
^{1}H and ^{13}C NMR spectra of compound **12**



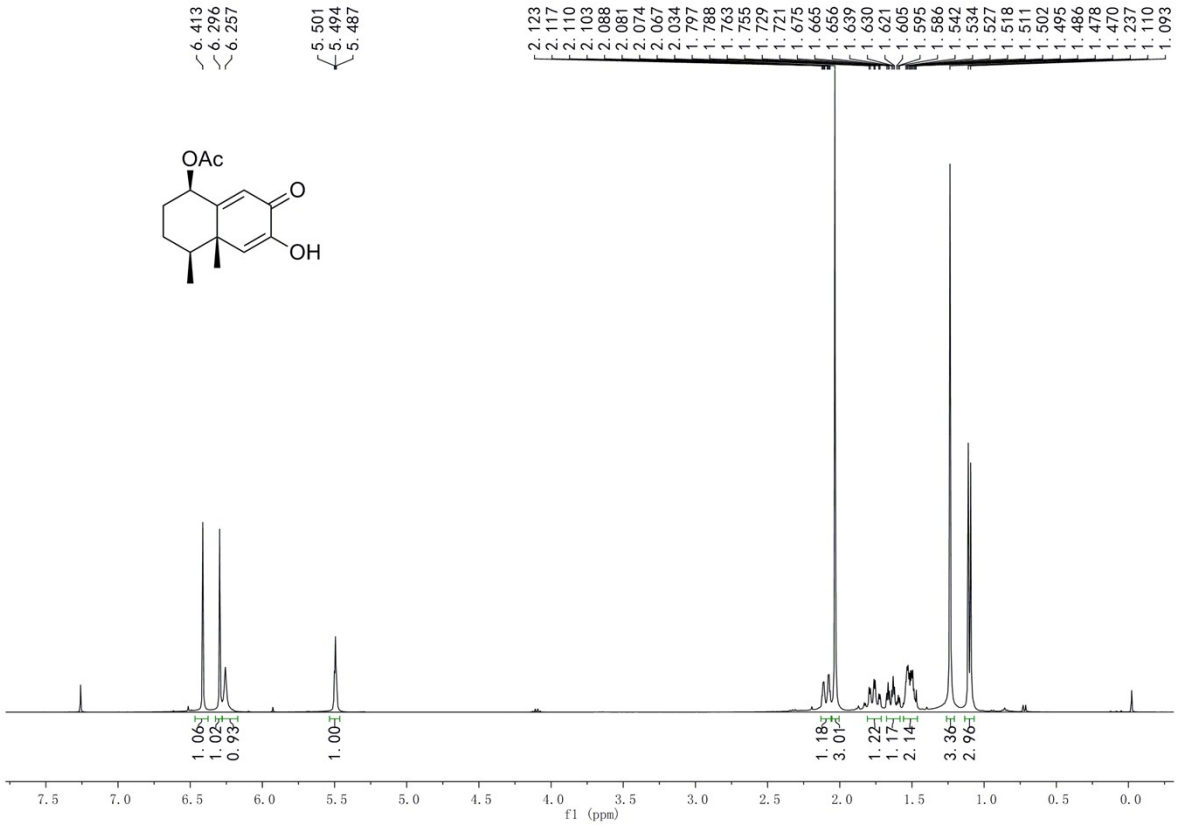


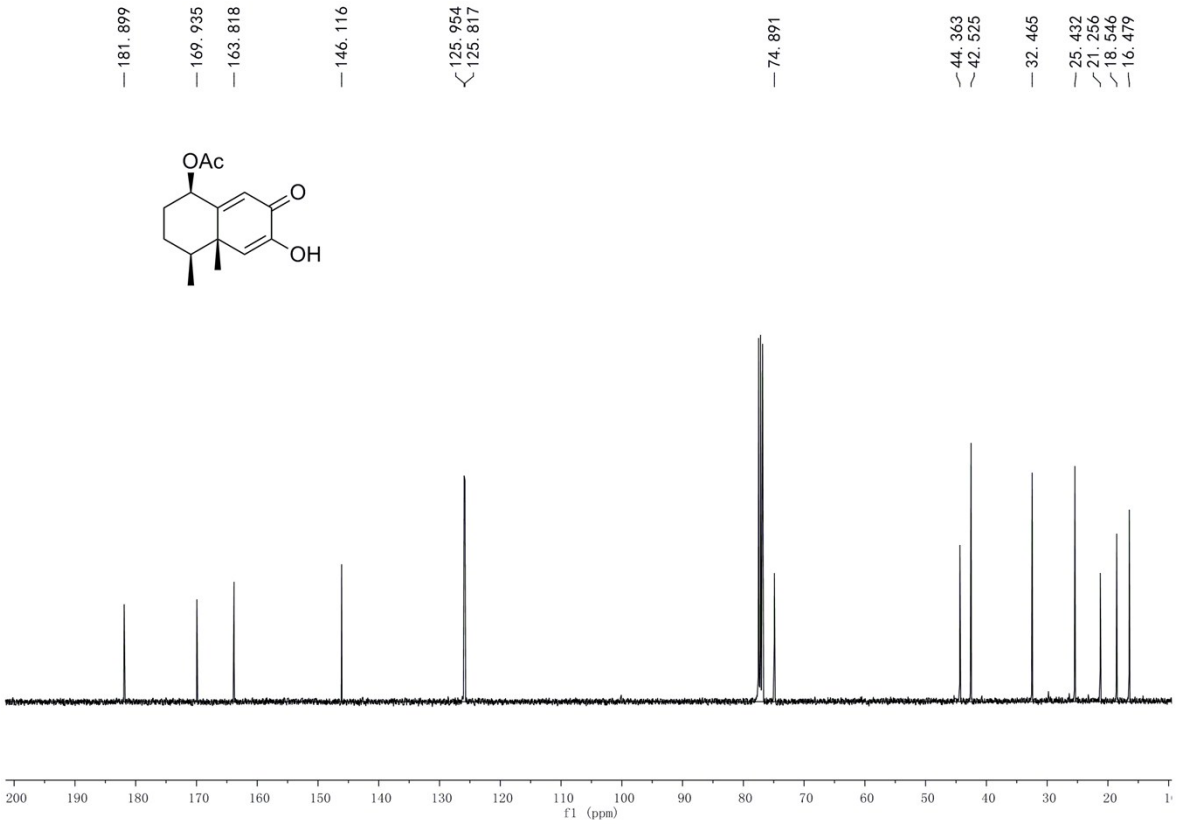
^{1}H and ^{13}C NMR spectra of compound **10**



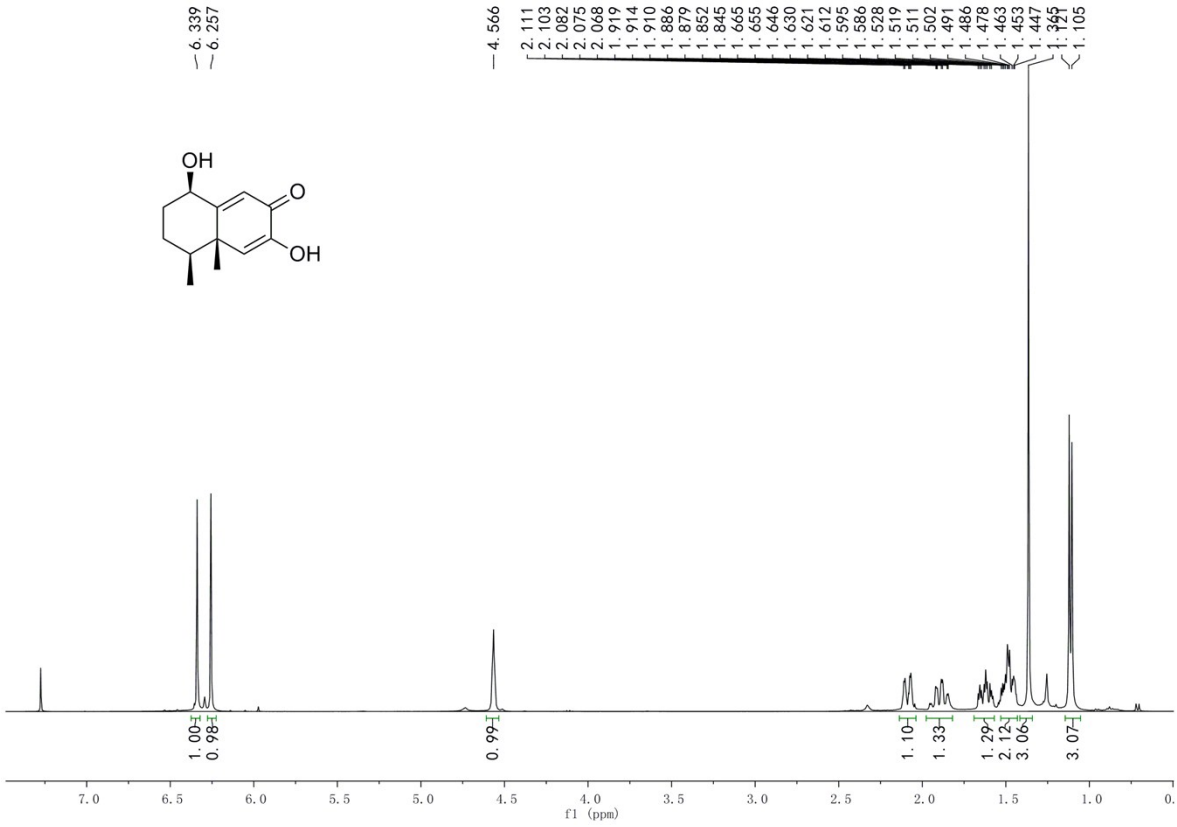


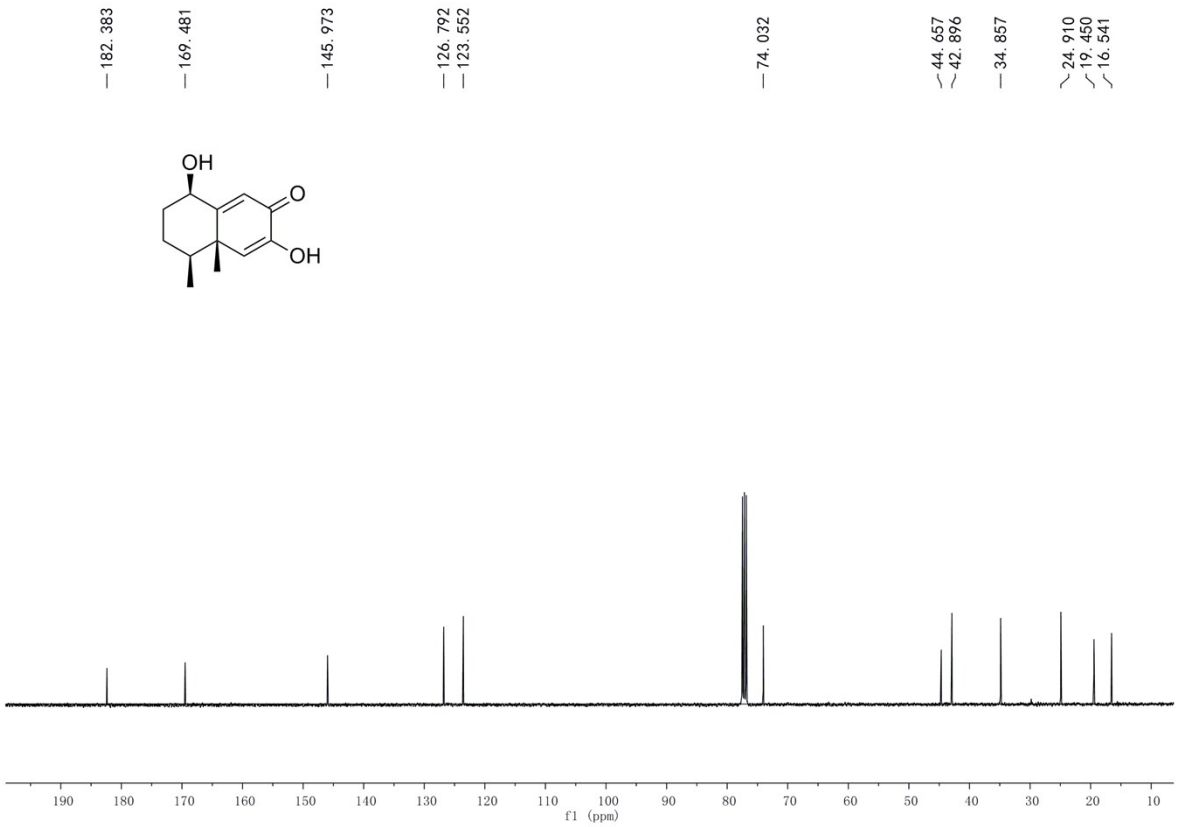
^{1}H and ^{13}C NMR spectra of compound **9**



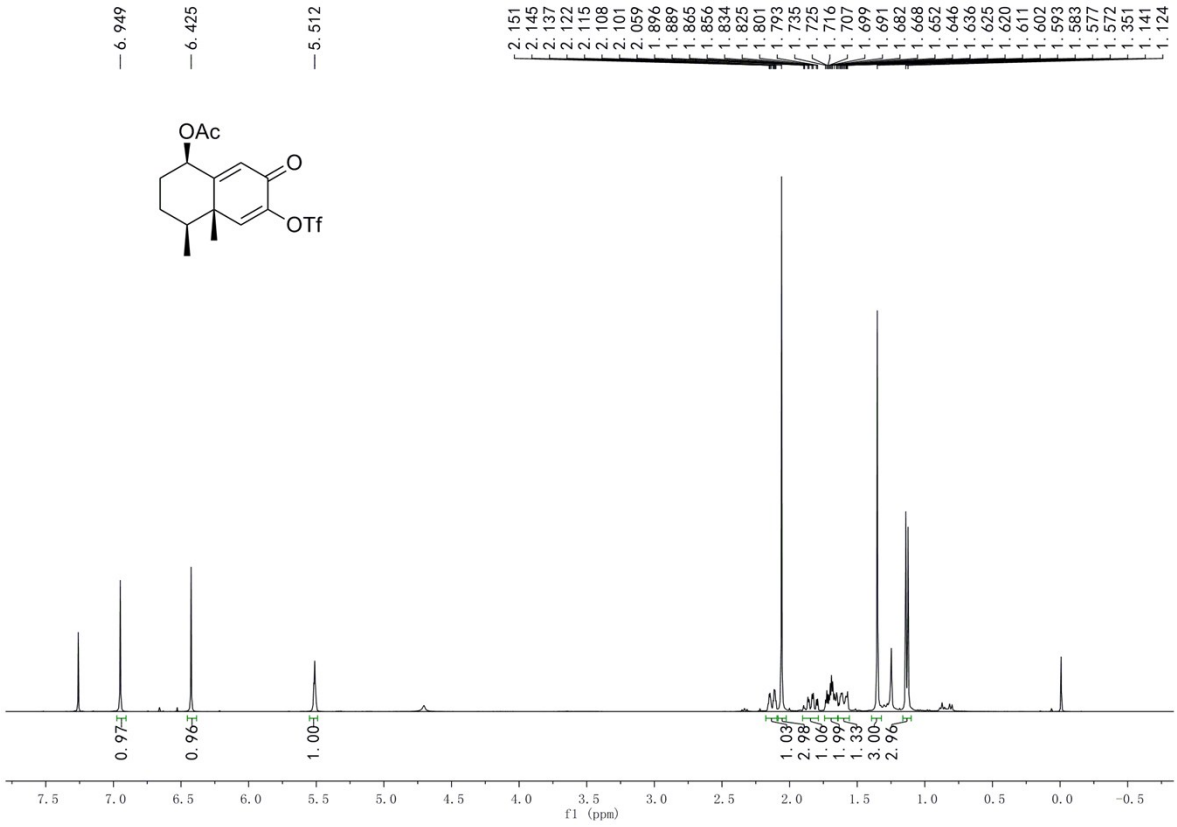


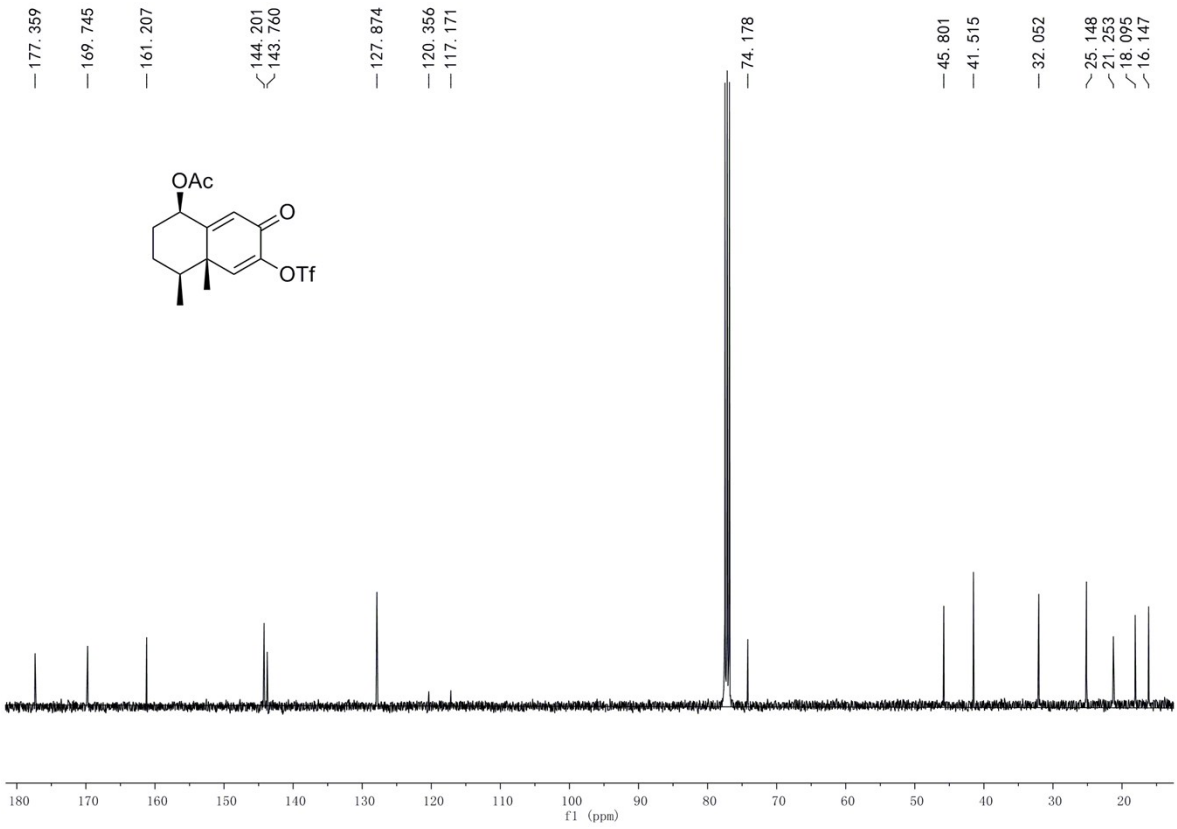
^{1}H and ^{13}C NMR spectra of compound **C**



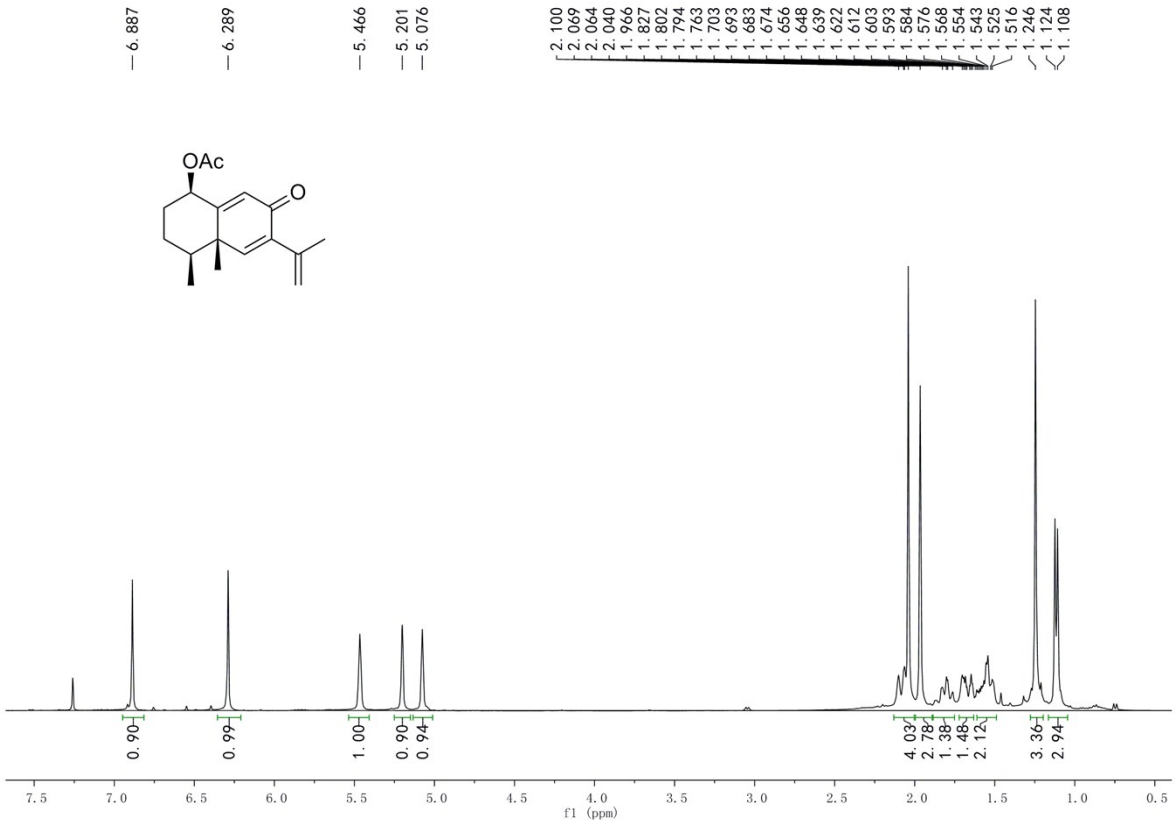


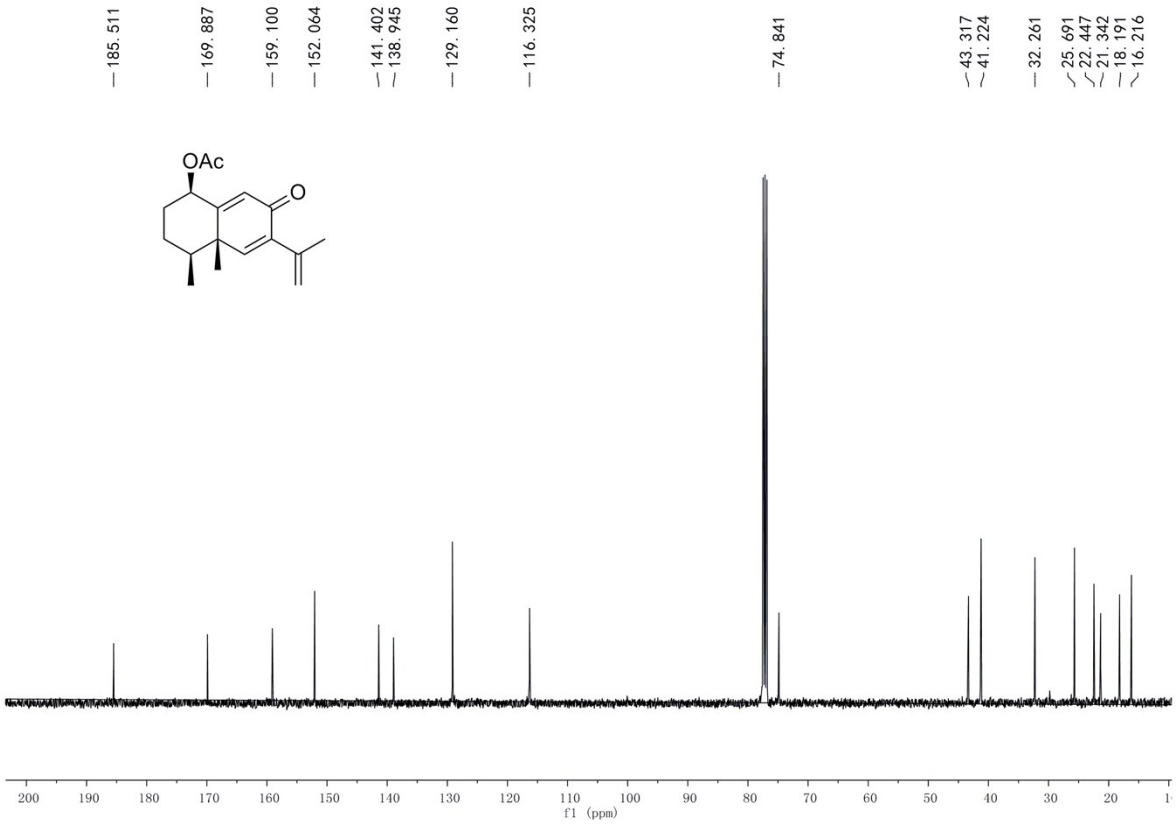
^{1}H and ^{13}C NMR spectra of compound **8**



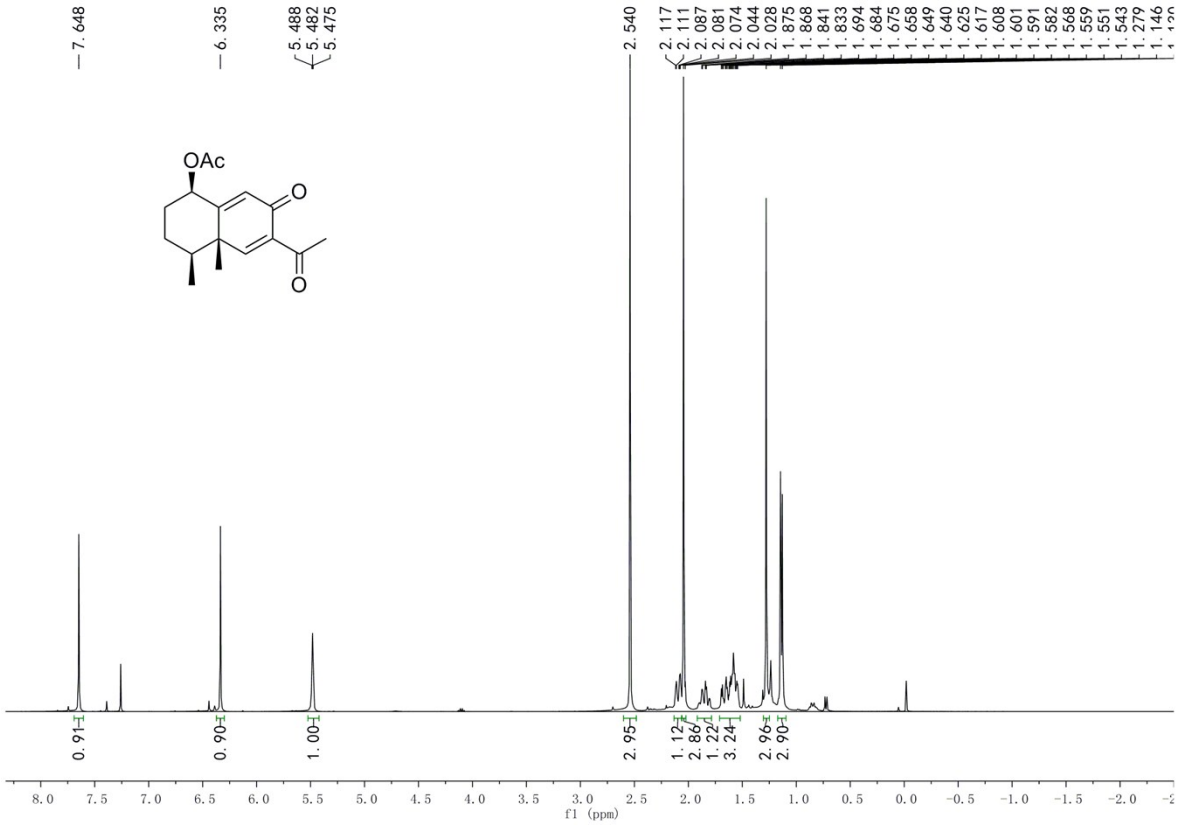


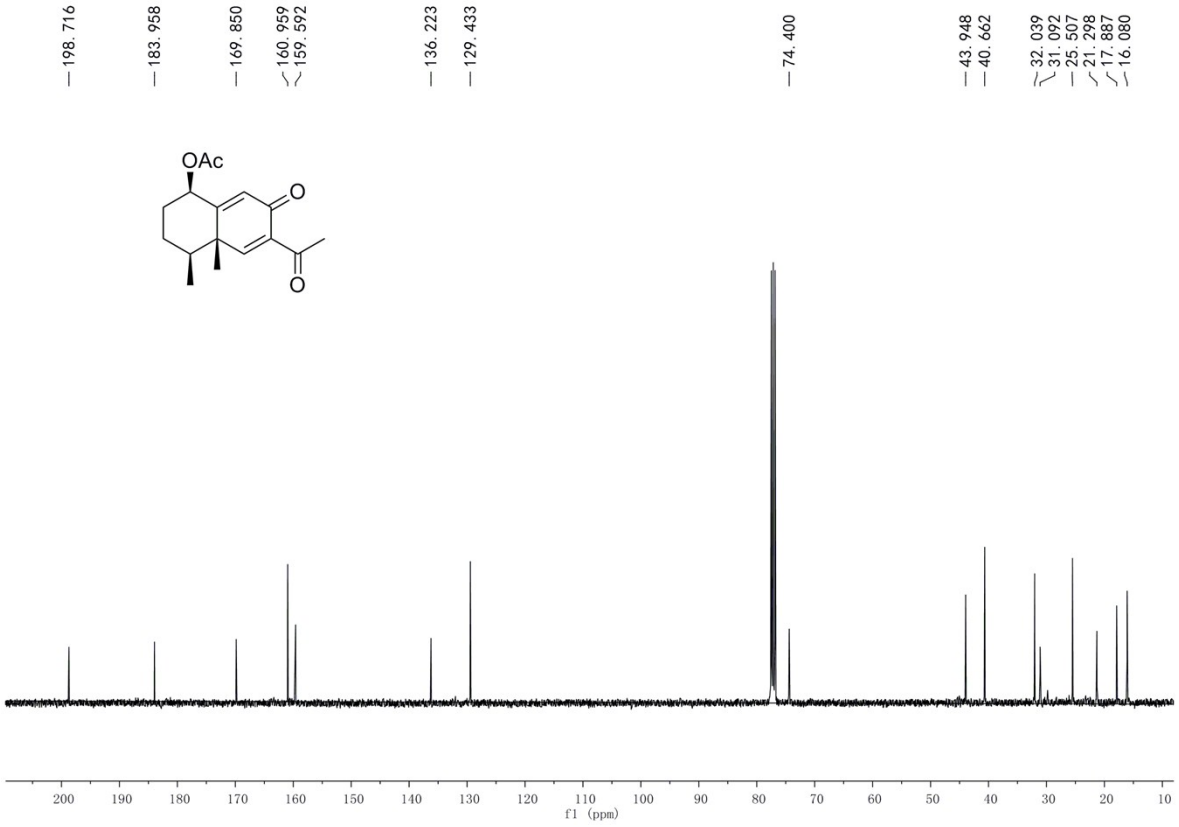
^{1}H and ^{13}C NMR spectra of compound **7**



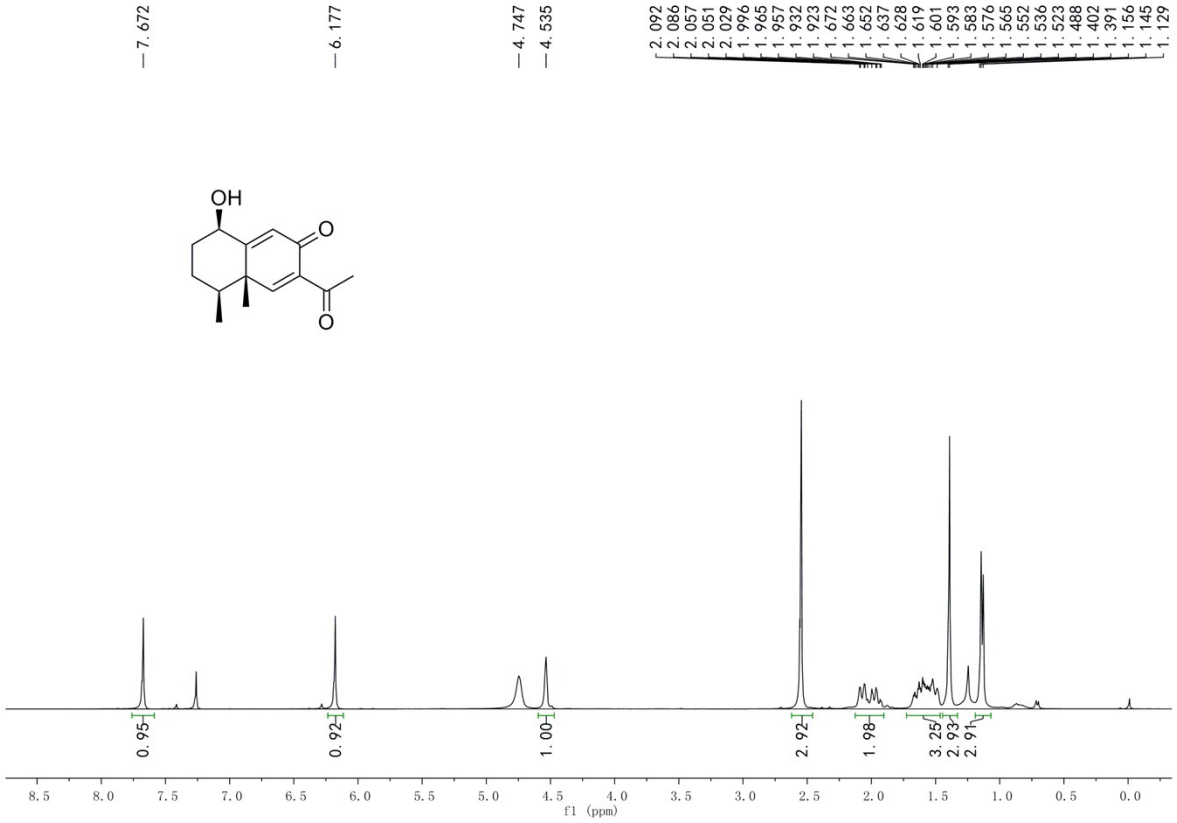


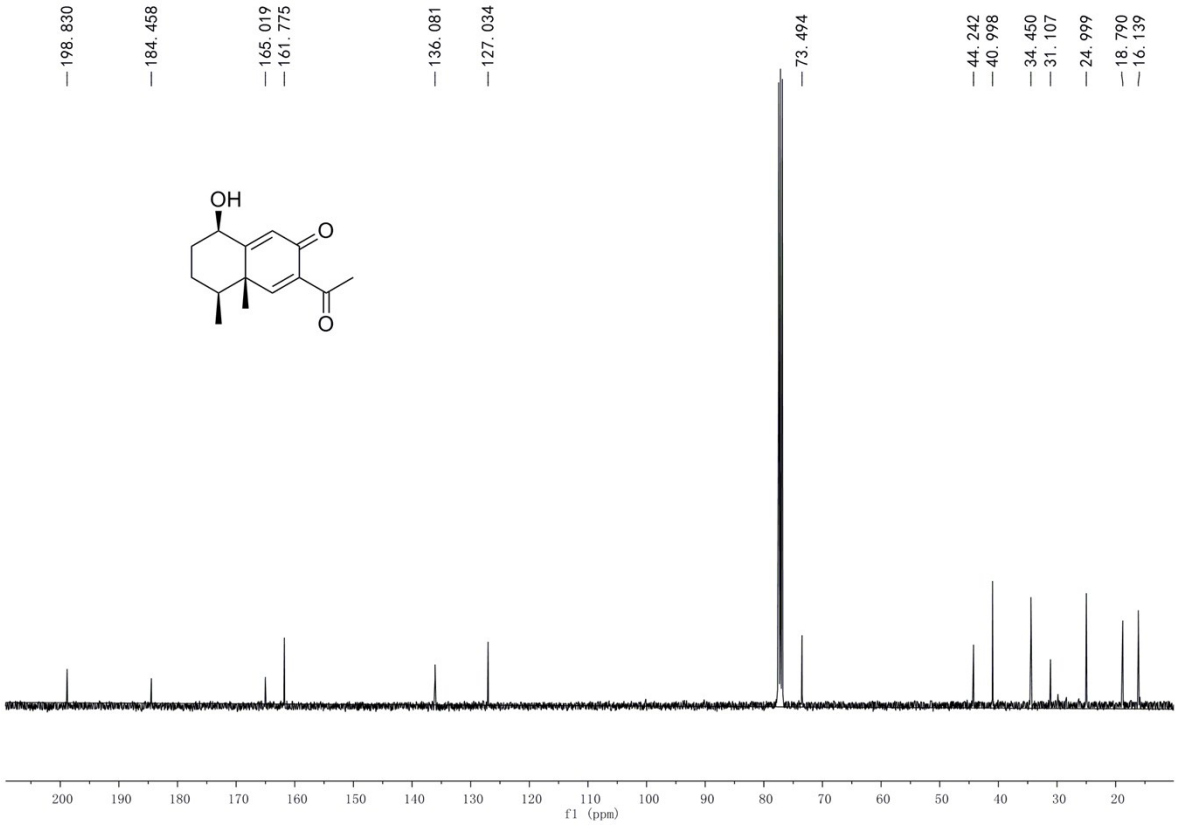
^{1}H and ^{13}C NMR spectra of compound **D**



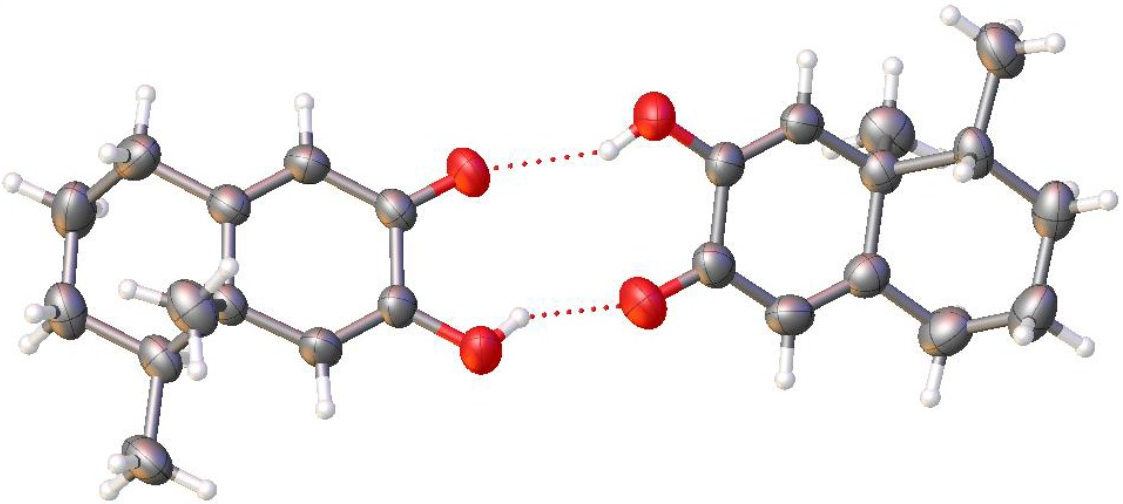


^{1}H and ^{13}C NMR spectra of compound **E**





X-Ray Crystallographic Data for compound **A**



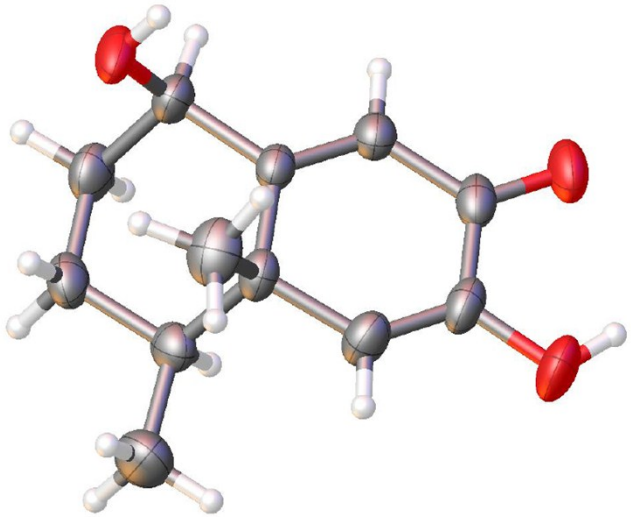
Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1578461).

Crystal data and structure refinement for CCDC 1578461

Empirical formula	$C_{12}H_{16}O_2$
Formula weight	192.25
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.4159(7)
b/Å	16.6808(9)
c/Å	17.3970(6)
α/°	90
β/°	106.212(4)
γ/°	90
Volume/Å^3	4295.8(3)
Z	16
ρ_{calc}g/cm^3	1.189
μ/mm^{-1}	0.079
F(000)	1664.0
Crystal size/mm^3	0.3 × 0.25 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.892 to 52.744
Index ranges	$-16 \leq h \leq 19$, $-12 \leq k \leq 20$, $-21 \leq l \leq 16$
Reflections collected	20240
Independent reflections	8766 [R_{int} = 0.0215, R_{sigma} = 0.0398]
Data/restraints/parameters	8766/0/517

Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	$R_1 = 0.0493$, $wR_2 = 0.1170$
Final R indexes [all data]	$R_1 = 0.0909$, $wR_2 = 0.1397$
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.16

X-Ray Crystallographic Data for compound **C**



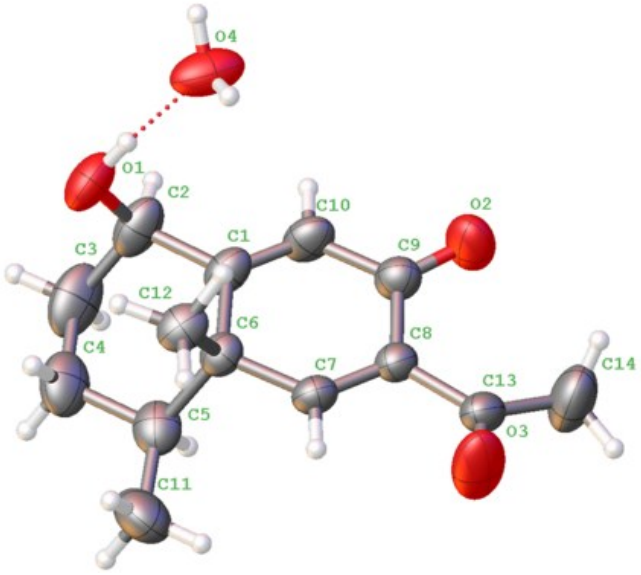
Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1578462).

Crystal data and structure refinement for CCDC 1578462

Empirical formula	$C_{12}H_{16}O_3$
Formula weight	208.25
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
a/Å	7.3633(6)
b/Å	8.6583(8)
c/Å	9.2145(9)
α/°	95.128(8)
β/°	98.931(8)
γ/°	111.272(8)
Volume/Å^3	533.98(9)
Z	2
ρ_{calc}g/cm^3	1.295
μ/mm^{-1}	0.092
F(000)	224.0
Crystal size/mm^3	0.35 × 0.3 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.062 to 52.74
Index ranges	$-9 \leq h \leq 8$, $-10 \leq k \leq 10$, $-11 \leq l \leq 11$
Reflections collected	4508
Independent reflections	2184 [R_{int} = 0.0157, R_{sigma} = 0.0290]
Data/restraints/parameters	2184/0/143

Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.1011
Final R indexes [all data]	R_1 = 0.0637, wR_2 = 0.1131
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.16

X-Ray Crystallographic Data for compound **E**



Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1585496).

Crystal data and structure refinement for CCDC 1585496

Empirical formula	$C_{14}H_{20}O_4$
Formula weight	252.30
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.0329(6)
b/Å	7.9949(3)
c/Å	11.4441(6)
α/°	90
β/°	97.344(4)
γ/°	90
Volume/Å^3	1364.15(11)
Z	4
ρ_{calc}g/cm^3	1.228
μ/mm^{-1}	0.089
F(000)	544.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.234 to 52.744
Index ranges	$-18 \leqslant h \leqslant 17$, $-9 \leqslant k \leqslant 9$, $-14 \leqslant l \leqslant 8$

Reflections collected	5658
Independent reflections	2778 [R_{int} = 0.0159, R_{sigma} = 0.0297]
Data/restraints/parameters	2778/0/189
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ(I)]	R_1 = 0.0487, wR_2 = 0.1132
Final R indexes [all data]	R_1 = 0.0746, wR_2 = 0.1303
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.16