Supporting Information

Efficient construction of bioactive trans-$5_A5_B6_C$ spirolactones via bicyclo[4.3.0] α-hydroxyketones

Y. J. Zhu,[a] J. Q. Huo,[b] Z. J. Fan,[a,c *] Q. F. Wu,[a] X. Li,[a] S. Zhou,[a] L. X. Xiong,[a] T. Kalinina[d] and T. Glukhareva[d*]

[a.] *State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, P. R. China. E-mail: fanzj@nankai.edu.cn*

[b.] *College of Plant Protection, Agricultural University of Hebei, Baoding 071001, P. R. China.*

[c.] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, P. R. China.*

[d.] *The Ural Federal University Named after the First President of Russia B. N. Yeltsin, 19 Mira Str., Ekaterinburg 620002, Russia.E-mail: taniagluhareva@yandex.ru*

Table of Contents for the Supporting Information

1. Biological activity data

Table 2 Fungicidal activity of $5_A5_B6_C$ tricyclic spirolactones and their intermediates at 50 μg/ml (%)

Compound	PI	CA	AS	BC	GZ	PP	SS	RC	PS
7	27	89	73	36	80	88	81	93	100
8a+8b	15	78	73	34	73	98	69	96	57
9a+9b	12	51	0	73	30	12	57	0	36
3+3a	14	0	20	20	18	33	16	16	14
11+11a	16	24	14	57	0	40	71	43	23
2a	40	24	3	64	0	26	36	0	25
2b	15	95	78	30	73	98	38	79	41
2c	31	51	14	39	47	73	10	40	0
2d	11	46	12	48	0	11	78	61	19
2e	25	62	35	36	27	38	17	0	18
12a	29	84	68	77	53	98	64	82	57
12b	11	51	35	55	43	99	76	32	11
12c	2	23	7	45	36	5	76	40	4
12d	31	68	14	34	60	81	43	50	0
12e	19	30	14	50	20	15	52	0	45
12f	0	26	34	13	46	0	9	59	24
1a	24	92	70	25	67	100	69	96	68
1b	7	27	39	25	84	8	0	71	20
1c	23	24	0	55	13	69	0	29	23
1d	4	46	7	49	21	11	66	41	6
1e	0	33	39	25	14	8	11	61	5
Ryanodine	30	10	25	25	20	24	25	50	32

ND: not detected

Table 4 Insecticidal activity of $5_A5_B6_C$ tricyclic spirolactones and their intermediates at 100 μg/ml (%)

Compound	Nematode	Armyworm	Bollworm	Corn borer
7	47	10	0	0
8a+8b	10	30	10	5
9a+9b	5	40	20	15
3+3a	8	0	0	0
11+11a	8	25	5	5
2a	7	25	5	5
2b	20	20	10	10
2c	40	100	50	40
2d	60	0	0	0
2e	5	0	0	0
12a	-	40	10	10
12b	5	0	0	0
12c	7	0	0	0
12d	8	10	0	0
12e	22	20	5	0
12f	25	ND	ND	ND
1a	60	40	15	10
1b	30	ND	ND	ND
1c	8	0	0	0
1d	15	0	0	0
1e	15	ND	ND	ND
Ryanodine	5	100	100	100
Nemadectin	85	ND	ND	ND

ND: not detected

Table 5 Inactivation activityof $5_A5_B6_C$ tricyclic spirolactones and their intermediates against tobacco mosaic virus at 100 μg/ml (%)

Compound	Inactivation activity	Compound	Inactivation activity
7	50	**12e**	5
8a+8b	10	**12f**	86
9a+9b	48	**1a**	23
3+3a	41	**1b**	-
11+11a	40	**12c**	63
2a	54	**12d**	58
2b	37	**1c**	40
2c	24	**1d**	63
2d	38	**1e**	39
2e	54	**1c**	40
12a	82	**Ryanodine**	6
12b	58	**Ribavirin**	37

Method for screening the test compounds against *Caenorhabditis elegans*

Nematode ***Caenorhabditis elegans*** was cultured using NGM medium, 75 μL M9 buffer + 20 μL nematode (about 20 nematode 20 μL + 5 μL test compound for screening. Methanol was used as a blank, nimoxidine was used as Positive control group. Mortality was calculated according to the same method as for insecticide screening.

Method for toxicity determination against Italian honeybee

Five to eight concentration level of the test compounds were set between 20.0 μg a.i./honeybee to 0.01 μg a.i./honeybee by diluting the mother solution in acetone with 50% of sucrose water, dimethoate and ryanodine were used as positive control，sucrose water were used as CK. Each concentration was repeated for at least twice each with 10 honeybees in a special honeybee cage. All the honeybees were raised in the culture room at 23 ^{o}C~27 ^{o}C in 50%~70% of humidity without sunlight and feed by 200 μl of test compound solutions for the first 3~6 h, afterwards, clear sucrose water were used as foods, 24 h and 48 h of death rate were checked according to the poison situation, the whole body cannot move was treated as death. The oral toxicity results were shown in **Table 6**. If the compound had toxicity against honeybee, LD_{50} will be calculated by SPSS 19.0, only two positive controls can get the results because of their toxicity against honeybee **(Table 7)**. The toxicity level of the pesticide was judged according to the official standard of Department of Agriculture, China as described in **Table 8** (GB/T31270.10-2014).

Table 6 Oral toxicity determination of the test compounds against Italian honeybee

Treatment	Dosage (μga.i./Honeybee)	Honeybee Number	Died Number (24 h)	Died Number (48 h)	Death rate(%)
CK	0	10	0	0	0
		10	0	0	
3+3a	19.3	10	0	0	0
		10	0	0	
3+3a	7.63	10	0	0	0
		10	0	0	
1a	15.5	10	0	0	0
		10	0	0	
1a	9.54	10	0	0	0
		10	0	0	
12a	19.9	10	0	0	0
		10	0	0	
12a	9.36	10	0	0	0
		10	0	0	
2d	9.46	10	0	0	0
		10	0	0	
2d	8.17	10	0	0	0
		10	0	0	
2e	19.7	10	0	1	10.0
		10	0	1	
2e	9.93	10	0	0	0
		10	0	0	
2a	12.6	10	0	1	15.0
		10	0	2	
2a	9.69	10	0	0	10.0
		10	0	2	
12e	10.6	10	1	1	5.0
		10	0	0	
12e	4.97	10	0	1	5.0
		10	0	0	
12b	15.2	10	0	1	10.0
		10	0	1	
12b	9.87	10	0	0	0
		10	0	0	
9a+9b	9.05	10	0	0	0
		10	0	0	
9a+9b	7.87	10	0	0	5.0
		10	0	1	
1c	16.4	10	0	0	0
		10	0	0	
1c	9.77	10	0	0	0
		10	0	0	
12d	10.6	10	0	1	10.0
		10	0	1	
12d	6.08	10	0	0	0
		10	0	0	
12c	7.70	10	0	0	0
		10	0	0	
12c	5.40	10	0	0	0
		10	0	0	
Dimethoate	0.109	10	2	ND	16.7
		10	1	ND	
		10	2	ND	
Dimethoate	0.166	10	5	ND	40.0
		10	4	ND	
		10	3	ND	
Dimethoate	0.294	10	6	ND	53.3
		10	6	ND	
		10	4	ND	
Dimethoate	0.476	10	5	ND	70.0
		10	7	ND	

		10	9	ND	
Dimethoate	0.830	10	9	ND	76.7
		10	8	ND	
		10	6	ND	
Ryanodine	3.65	10	1	10	100
		10	5	10	
Ryanodine	1.54	10	4	10	100
		10	5	10	
Ryanodine	1.19	10	2	8	90.0
		10	1	10	
Ryanodine	0.395	10	4	10	100
		10	8	10	
Ryanodine	0.275	10	2	7	85.0
		10	1	10	
Ryanodine	0.102	10	1	6	65.0
		10	0	7	
Ryanodine	8.80×10^{-3}	10	6	4	30.0
		10	4	2	
Ryanodine	7.08×10^{-3}	10	0	0	0
		10	0	0	

ND: not detected

Table 7 Precision oral toxicity of positive controls against Italian honeybee

Compound Time(h)	Regression equation	r	LD_{50} (μga.i./Honeybee	95% Confidence Limit (μg a.i./ honeybee)
Dimethoate 24	y=1.676+2.997x	0.939	0.276	0.204~0.369
Ryanodine 48	y=1.854+1.385x	0.969	0.046	0.0138~0.109

Table 8 Toxicity level of the pesticide issued by Chinese government

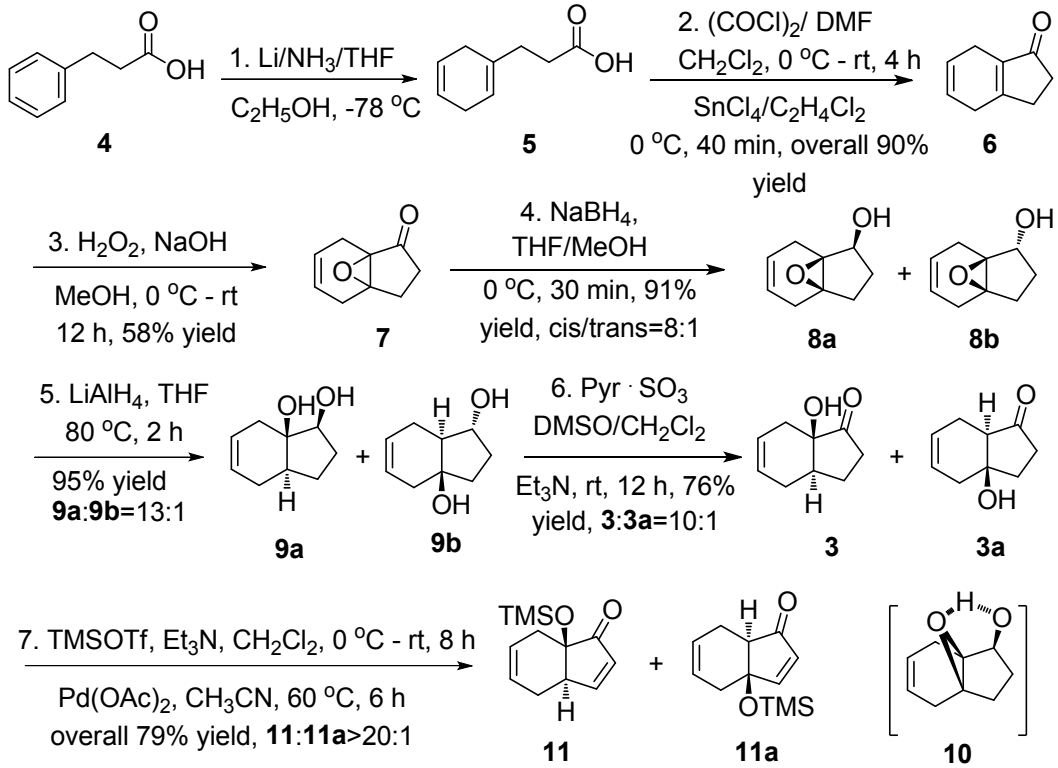
Toxicity Level	LD_{50} (48 h)/(μg a.i./honeybee)
Rank poison	$LD_{50}\leqslant0.001$
High toxicity	$0.001<LD_{50}\leqslant2.0$
Moderate toxicity	$2.0<LD_{50}\leqslant11.0$
Low toxicity	$LD_{50}>11.0$

2. Experimental procedures for the synthesis of the target compounds

2.1 General method

NMR (^{1}H, ^{13}C, NOESY) spectra were recorded on Bruker model Avance 400 (^{1}H at 400 MHz; ^{13}C at 101 MHz). Optical rotations were determined using a Jasco P1010 polarimeter. Mass spectra were obtained using a Micromass Quattro II (triple quad with non-electrospray ionization. Thin-layer chromatography (TLC) was conducted on silica gel F_{254}TLC plates. All reagents and starting materials were purchased from commercial sources and used as supplied, unless otherwise indicated. Anhydrous tetrahydrofuran (THF) was obtained through distillation over sodium / benzophenone under argon, diethyl ether (Et_2O) and dichloromethane (CH_2Cl_2) were obtained through distillation over calcium hydride (CaH_2) under argon, and toluene (PhMe) was dried over 4 Å molecular sieves and degased under argon. Dimethyl sulfoxide (DMSO) was distilled from CaH_2 under reduced pressure and stored over 4Å molecular sieves. All compounds purified by chromatography were sufficiently pure for use in further experiments, unless indicated otherwise.

2.2 General synthetic procedure for *α, β* -unsaturated enone 11

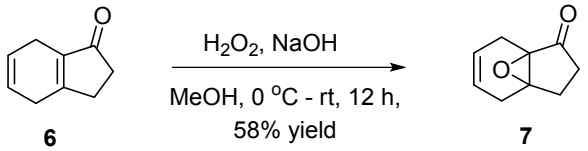


2.2.1 Procedure for compound 6

Compound **5** (2.20 g, 14.46 mmol) was mixed with 30 ml CH_2Cl_2, successively treated with oxalyl chloride (3.67 g, 28.91 mmol) and DMF (0.1 ml) at 0 °C stirred for an additional 1 h, the mixture was allowed to room temperature and stirred for 4 h, then concentrated in vacuo to afford a mixture of acid chlorides, which was dissolved in 50 ml of 1,2-dichloroethane and cooled to 0

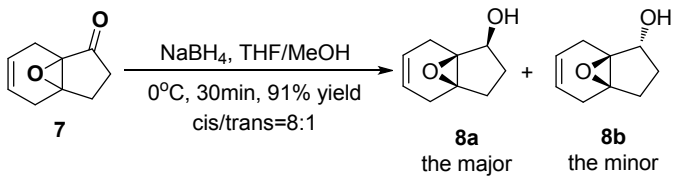
°C under argon, to the stirred solution was slowly added 3.38 ml of $SnC1_4$ (7.53 g, 28.92 mmol), after 40 min at 0 °C, the resultant mixture was diluted with saturated solution of sodium bicarbonate and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated. The crude material was purified by flash chromatography (eluent: petroleum ether / ethyl acetate =10 / 1) gave 1.70 g the target compound **6** (yield 90%) as colorless crystalline. The product was identical in all respects with the reported compound.

2.2.2 Procedure for compound 7



To a stirred solution of **6** (0.60 g, 44.72 mmol) in methanol (30 ml) was successively added 30% H_2O_2 aq. (10.14 g, 89.44 mmol) and 1 mol/l NaOH aq. (22.36 ml, 22.36 mmol) at 0 °C and stirred for an additional 30 mine, the mixture was allowed to room temperature and stirred for 12 h. The mixture was diluted with water and extracted with ethyl acetate. The extract was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (eluent: petroleum ether / ethyl acetate =6 / 1) gave 3.90 g (yield 58%) of the pure desired epoxide **7** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60–5.46 (m, 2H), 2.87–2.77 (m, 1H), 2.72-2.65 (m, 1H), 2.59–2.51 (m, 2H), 2.48–2.39 (m, 2H), 2.16-2.08 (m, 1H), 2.01-1.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.25, 121.14, 121.02, 66.67, 62.59, 31.75, 28.48, 26.91, 20.82.

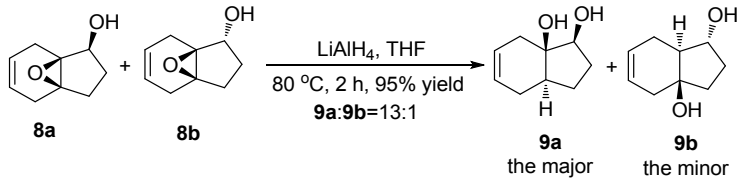
2.2.3 Procedure for compound 8 (8a+8b)



To a stirring solution of **7** (2.50 g, 16.65 mmol) in THF (30 ml) and water (1 ml) was added sodium borohydride (0.63 g, 16.65 mmol) at 0 °C stirring for 30 mine. Saturated solution of sodium bicarbonate was then added, the organic layer was separated and the aqueous layer was further extracted with EtOAc for three times. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (eluent:

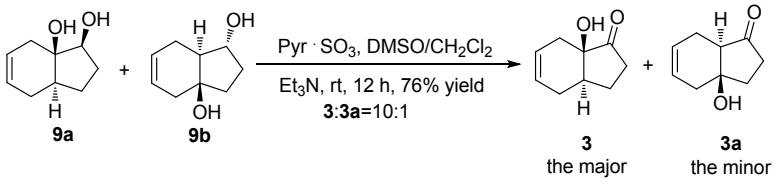
petroleum ether / ethyl acetate =3 / 1) gave 2.30 g mixture of the *cis*-bicyclic epoxy alcohol **8a** as the major component with minor isomer **8b** (yield 91%, d.r. = 8:1) as a white solid, m.p. 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (d, *J* = 10.4 Hz, 1H), 5.49 (d, *J* = 11.0 Hz, 1H), 4.15 (q, *J* = 7.8 Hz, 1H), 2.80-2.70 (m, 1H), 2.66-2.55 (m, 1H), 2.50-2.41 (m, 1H), 2.39-2.30 (m, 1H), 2.23–2.07 (m, 2H), 2.02–1.97 (m, 1H), 1.62–1.54 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 121.85, 121.73, 76.58, 66.20, 64.81, 29.16, 28.70, 28.16, 25.49. HRMS (ESI-TOF) m/z calcd for $C_9H_{13}O_2$ [M+H$^+$] 153.0916, found 153.0910.

2.2.4 Procedure for the synthesis of compound 9 (9a+9b)



To a stirred suspension of $LiAlH_4$ (1 g, 26.28 mmol) in dry THF at 0 °C was added the mix alcohol **8** (2 g, 13.14 mmol) dropwise. The mixture was heated to reflux for 2 h, and then quenched by the addition of H_2O, the organic layer was separated and the aqueous layer was further extracted with EtOAc for three times. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (eluent: petroleum ether / ethyl acetate =4 / 1) gave 2 g mixture of diol **9a**, **9b** (yield 95%, r.r. = 13:1) as colorless oil. The major isomer **9a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69–5.54 (m, 2H), 3.99 (d, *J* = 6.6 Hz, 1H), 3.62 (br, 1H), 2.48–2.18 (m, 4H), 2.0-1.96 (m, 1H), 1.90–1.72 (m, 3H), 1.60–1.48 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 124.64, 124.31, 79.95, 78.77, 49.83, 36.29, 35.20, 31.91, 26.80. HRMS (ESI-TOF) m/z calcd for $C_9H_{14}NaO_2$ [M+Na$^+$] 177.0891, found 177.0884. Selected NMR signals of the minor isomer **9b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (d, *J* = 6.7 Hz, 0.08H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 79.38, 54.72, 34.95, 34.10, 32.31, 27.22.

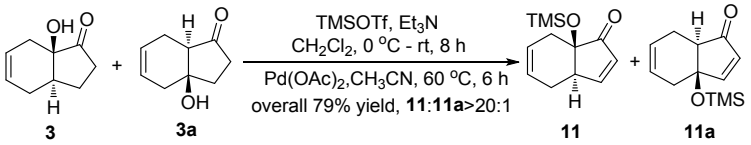
2.2.5 Procedure for the synthesis of compound 3 (3+3a)



To a stirred solution of diol **9** (2 g, 12.97 mmol) in DMSO (15 ml) and CH_2Cl_2 (15 ml) was

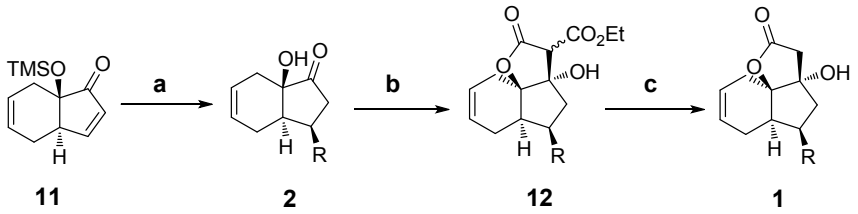
added triethylamine (3.94 g, 38.91 mmol), pyridine-sulfurtrioxide complex (3.10 g, 19.46 mmol) at room temperature stirring for 12 h. Saturated ammonium chloride aqueous was added to the reaction, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 for another three times. The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (eluent: petroleum ether / ethyl acetate =10 / 1) gave 1.50 g mixture of the α-hydroxy ketone **3**, **3a** (yield 76%, **3**:**3a** = 10:1) as pale yellow oil. The major isomer **3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82–5.76 (m, 1H), 5.70–5.61 (m, 1H), 2.68 (br, 1H), 2.61–2.45 (m, 1H), 2.29–2.19 (m, 3H), 2.18–2.06 (m, 1H), 2.03–1.74 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.87, 127.00, 123.34, 73.82, 41.32, 35.20, 32.28, 26.65, 24.29. Selected NMR signals of the minor isomer **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81–2.77 (m, 0.09H), 2.43–2.39 (m, 0.12H), 1.72–1.70 (m, 0.07H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 124.47, 122.27, 74.87, 45.80, 35.02, 30.24, 25.69, 24.81, 24.11.

2.2.6 Procedure for the synthesis of compound 11

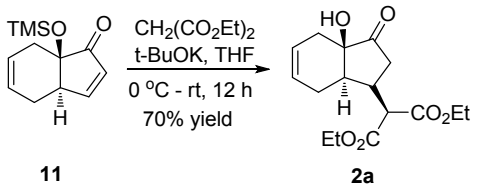


NEt_3 (6.65 g, 65.71 mmol) and TMSOTf (7.30 g, 32.85 mmol) were sequentially added to the solution of **3** (2 g, 13.14 mmol) in CH_2Cl_2 at 0°C. The reaction mixture was stirred at 0 °C for 0.5 h followed by stirring at room temperature for an additional 8 h. The reaction mixture was then quenched by saturated $NaHCO_3$ solution and extracted with EtOAc, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to give the crude residue, which was further dissolved in CH_3CN and treated with $Pd(OAc)_2$ (2.95 g, 13.14 mmol). The reaction mixture was stirred at 60 °C for 6 h and then filtered through celite. The filtrate was concentrated in vacuo to give the crude product, which was purified by flash chromatography (eluent: petroleum ether / ethyl acetate =100 / 1) to give 2.30 g the title compounds **11**, **11a** (yield 79%, **11**:**11a** > 20:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 5.4 Hz, 1H), 6.05 (dd, J = 6.0, 2.9 Hz, 1H), 5.73-5.70 (m, 1H), 5.61-5.59 (m, 1H), 2.62-2.59 (m, 1H), 2.42–2.12 (m, 4H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.25, 159.59, 130.29, 126.23, 123.52, 76.12, 46.72, 30.13, 23.46, 0.00. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{19}O_2Si$ [M+H$^+$] 223.1154, found 223.1147.

2.3 General synthetic procedure for tricyclic spirolactones 1

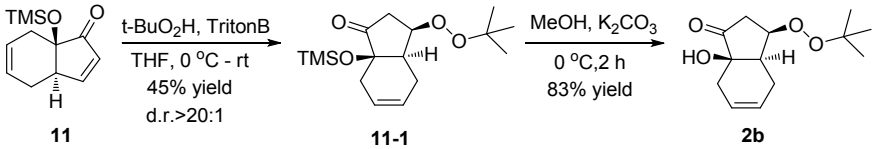


2.3.1 Synthetic procedure for compound 2a



To a stirred solution of potassium tert-butoxide (0.11 g, 0.90 mmol) in dry THF was added diethylmalonate (0.14 g, 0.90 mmol) at 0 °C stirring for 10 mine, and then was added a solution of compound **11** (0.10 g, 0.45 mmol) in THF followed by stirring at room temperature for an additional 12 h. The reaction mixture was then quenched by saturated $NaHCO_3$ solution and extracted with EtOAc, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: petroleum ether / ethyl acetate =6 / 1) to give 0.10 g the target compound **2a** (yield 70%, d.r. > 20:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75-5.65 (m, 1H), 5.61-5.53 (m, 1H), 4.27-4.09 (m, 4H), 3.41 (d, *J* = 6.7 Hz, 1H), 2.96-2.73 (m, 2H), 2.26-2.12 (m, 6H), 1.29-1.17 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.56, 168.54, 168.06, 126.53, 123.15, 74.80, 61.69, 61.58, 53.55, 44.59, 39.35, 37.21, 32.49, 26.29, 14.09, 14.05. HRMS (ESI-TOF) m/z calcd for $C_{16}H_{23}O_6$ [M+H$^+$] 311.1495, found 311.1488.

2.3.2 Synthetic procedure for compound 2b

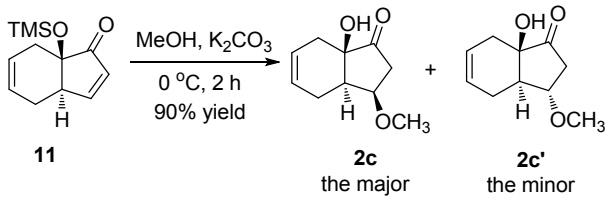


TBHP (0.12 g, 0.90 mmol) and Triton B (0.10 g, 0.22 mmol) were added to a solution of **11** (0.10 g, 0.45 mmol) in THF at 0 °C, and the mixture was stirred for 1 h at the same temperature. EtOAc and saturated aqueous $Na_2S_2O_3$ were added, and the separated EtOAc layer was washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and

concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: petroleum ether / ethyl acetate =100 / 1) to give 0.06 g the epoxide **11-1** (yield 45%, d.r. > 20:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61 (br, 1H), 5.46 (br, 1H), 4.52-4.46 (m, 1H), 3.98-3.93 (m, 1H), 2.87-2.81 (m, 1H), 2.36-2.08 (m, 4H), 1.60-1.54 (m, 1H), 1.12 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, CDCl3) δ 211.11, 126.95, 123.04, 82.58, 80.29, 78.90, 47.29, 41.41, 31.34, 26.49, 25.59, 14.67, 0.00.

To a stirred solution of **11-1** (0.10 g, 0.32 mmol) in methanol was added potassium carbonate (0.09 g, 0.64 mmol) at 0 °C, the reaction mixture was stirred for another 2 h at room temperature. Saturated aqueous brine was added to the reaction, extracted with EtOAc, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (eluent: petroleum ether / ethyl acetate =6 / 1) yielded 0.12 g the target compound **2b** (yield 93%, d.r. > 20:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80-5.77 (m, 1H), 5.64–5.58 (m, 1H), 4.72-4.66 (m, 1H), 3.04-2.95 (m, 1H), 2.61–2.51 (m, 1H), 2.43–2.13 (m, 4H), 1.88–1.80 (m, 1H), 1.22 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.33, 125.94, 121.81, 81.39, 79.46, 75.52, 44.62, 40.38, 31.41, 25.34, 24.42. HRMS (ESI-TOF) m/z calcd for $C_{13}H_{24}NO_4$ [M+NH_4^+] 258.1705, found 258.1699.

2.3.3 Synthetic procedure for compound 2c

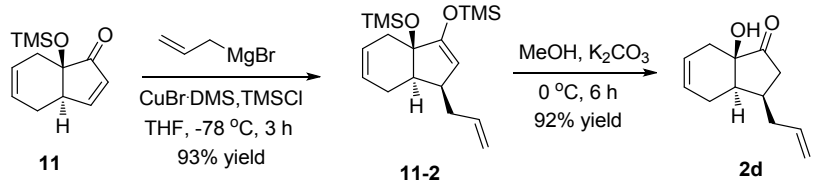


11 **2c** the major **2c'** the minor

To a stirred solution of **11** (0.30 g, 1.85 mmol) in methanol was added potassium carbonate (0.37 g, 2.70 mmol) at 0 °C, after stirring for another 2 h, saturated aqueous brine was added, the reaction mixture was extracted with EtOAc, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (eluent: petroleum ether / ethyl acetate =5 / 1) yielded 0.22 g the target compound **2c** (yield 90%, d.r.=8:1) as pale yellow oil. The major isomer **2c**: ^{1}H NMR (400 MHz, CDCl3) δ 5.83–5.75 (m, 1H), 5.67–5.59 (m, 1H), 4.08–3.96 (m, 1H), 3.38 (s, 3H), 3.00-2.90 (m, 1H), 2.56–2.46 (m, 1H), 2.35–2.25 (m, 2H), 2.20–2.03 (m, 2H), 1.84–1.74 (m, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 211.63, 126.86, 122.91, 80.25, 76.31, 58.05, 47.29, 42.15, 32.49, 24.94. HRMS (ESI-TOF) m/z calcd for $C_{10}H_{15}O_3$ [M+H^+] 183.1021, found 183.1015. Selected NMR signals of the minor isomer **2c'**: ^{1}H NMR (400 MHz,

CDCl3) δ 5.75–5.70 (m, 0.11H), 1.90-1.83 (m, 0.11H). ^{13}C NMR (101 MHz, CDCl3) δ 125.91, 123.83, 78.99, 57.47, 45.10, 41.41, 31.14, 21.74.

2.3.4 Synthetic procedure for compound 2d

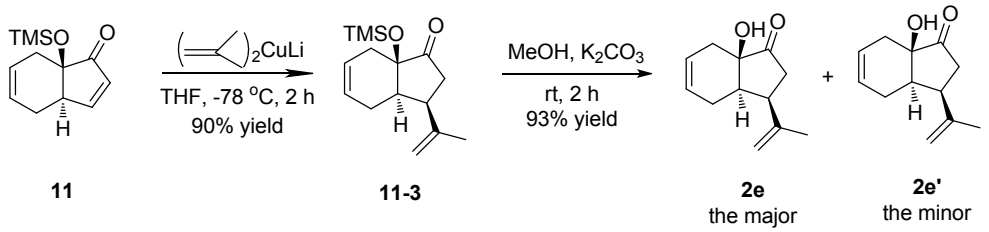


$CuBr{\cdot}SMe_2$ (2 g, 9.81 mmol) and dry LiCl (0.42 g, 0.81 mmol) were added in a two-neck 250 ml round-bottom flask equipped with a stir bar and sealed with two septa. The flask was evacuated with a vacuum pump and then purged with argon while drying with a heat gun, this process being repeated three times. THF (20 ml) was injected and the mixture was stirred for 10 min to yield a yellow, homogeneous solution which was then cooled to -78 °C. Concurrently, the Grignard solution was transferred via syringe (8.92 mmol) dropwise to the copper complex, TMSCl (1.07 g, 9.81 mmol) was added followed immediately by the addition of **11** (1 g, 4.46 mmol) in THF. The reaction was allowed to proceed for 3 h before being quenched at -78 °C with saturated aqueous NH_4Cl. Then the reaction mixture was extracted with EtOAc, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (eluent: petroleum) yielded 1.40 g the target compound **11-2** (yield 93%, d.r. > 20:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80–5.66 (m, 2H), 5.52–5.43 (m, 1H), 4.95–4.85 (m, 2H), 4.77 (d, J = 3.0 Hz, 1H), 2.38–1.97 (m, 6H), 1.88-1.76 (m, 2H), 0.17 (s, 9H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.54, 138.93, 128.59, 124.32, 114.76, 108.74, 79.95, 46.92, 42.55, 36.35, 36.13, 24.34, 1.98, 0.00.

To a stirred solution of **11-2** (2.30 g, 6.84 mmol) in methanol was added potassium carbonate (1.89 g, 13.67 mmol) at 0 °C stirring for 6 h. Then saturated aqueous brine was added to the reaction mixture, extracted with EtOAc, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the residue by flash chromatography (eluent: petroleum ether / ethyl acetate =15 / 1) gave 1.20 g the target compound **2d** (yield 92%, d.r. > 20:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84–5.78 (m, 1H), 5.77-5.68 (m, 1H), 5.64–5.58 (m, 1H), 5.05-4.99 (m, 2H), 2.55–2.24 (m, 6H), 2.20–2.01 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.62, 137.85, 127.48, 123.19, 116.07, 74.26, 43.57, 41.05, 35.48, 35.03, 33.95, 23.52. HRMS (ESI-TOF) m/z

calcd for $C_{12}H_{16}NaO_2$ [M+Na$^+$] 215.1048, found 215.1039.

2.3.5 Synthetic procedure for compound 2e

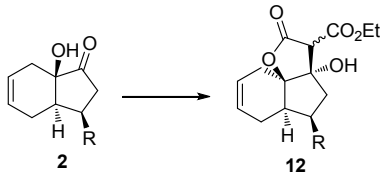


11 **11-3** **2e** the major **2e'** the minor

To a stirring solution of 2-allyl bromide (0.12 g, 0.99 mmol) in dry THF was added n-BuLi (1.26 ml, 2.03 mmol) at -78 °C, and the mixture stirred for 30 min followed by the addition of CuCN (0.05 g, 0.51 mmol), and then warmed up to 0 °C for 30 min of stirring until CuCN completely dissolved, and then kept the temperature to -78 °C, a solution of **11** (0.10 g, 0.45 mmol) in THF was added to the mixture and stirred for 2 h. And then, the reaction was quenched by saturated NH_4Cl solution and extracted with EtOAc, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the residue by flash chromatography (eluent: petroleum ether / ethyl acetate =100 / 1) gave 0.11 g the target compound **11-3** (yield 90%) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66-5.63 (m, 1H), 5.57–5.44 (m, 1H), 4.74 (s, 2H), 2.80–2.68 (m, 1H), 2.59-2.51 (m, 1H), 2.34–2.24 (m, 1H), 2.14–2.02 (m, 3H), 1.97–1.85 (m, 1H), 1.61 (s, 3H), 1.56-1.49(m, 1H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.12, 143.09, 125.68, 121.79, 110.10, 76.04, 44.95, 43.30, 39.39, 30.49, 23.74, 18.34, 0.00.

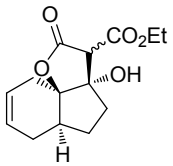
To a stirred solution of **11-3** (0.10 g, 0.38 mmol) in methanol was added potassium carbonate (0.11 g, 0.76 mmol) at room temperature, after stirring for 2 h, saturated aqueous brine was added to the reaction mixture, extracted with EtOAc, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (eluent: petroleum ether / ethyl acetate =5 / 1) gave 0.07 g the target compound **2e** (yield 93%, d.r. = 11:1) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85–5.78 (m, 1H), 5.72–5.64 (m, 1H), 4.87 (s, 2H), 2.98–2.88 (m, 1H), 2.76-2.68 (m, 1H), 2.35–2.24 (m, 3H), 2.21–2.05 (m, 2H), 1.83-1.75 (m, 1H), 1.73 (d, *J* = 3.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.74, 144.04, 127.15, 123.16, 111.76, 75.20, 44.89, 44.59, 41.19, 32.94, 25.03, 19.66.

2.3.6 General Procedure for the Synthesis of compounds 12



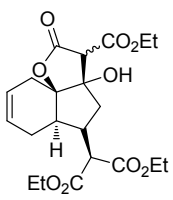
To a stirred suspension of potassium tert-butoxide (12.48 mmol) in dry THF was add diethyl malonate (12.48 mmol) at 0 °C，then compound **2** (6.24 mmol) in dry THF was added, and the mixture was heated to reflux for 12 h. Saturated sodium bicarbonate solution was added for washing, the aqueous phase was further extracted with EtOAC. The organic phase was combined, dried over Na_2SO_4, and concentrated under reduced pressure. The mixture was purification by flash column chromatography (eluent: petroleum ether / ethyl acetate =3 / 1) giving the title compound **12**.

(3aS, 5aS, 9aR)-Ethyl 3a-hydroxy-2-oxo-2, 3, 3a, 4, 5, 5a, 6, 9-octahydroindeno[7a, 1-b]furan-3-carboxylate (12a).



Isolated yield 0.30 g (yield 95%). White solid, m.p. 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80–5.72 (m, 1H), 5.70–5.62 (m, 1H), 4.35–4.24 (m, 2H), 3.89 (d, J = 0.7 Hz, 1H), 2.70–2.56 (m, 1H), 2.51–2.37 (m, 1H), 2.33-2.24 (m, 1H), 2.18–1.88 (m, 6H), 1.33 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.16, 167.28, 126.36, 123.02, 95.36, 82.84, 62.78, 58.37, 41.44, 30.91, 27.60, 13.99. HRMS (ESI-TOF) m/z calcd for $C_{14}H_{19}O_5$ [M+H$^+$] 267.1232, found 267.1231.

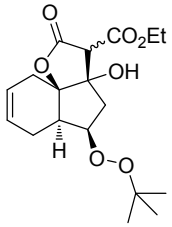
Diethyl 2-((3aS, 5S, 5aR, 9aR)-3-(ethoxycarbonyl)-3a-hydroxy-2-oxo-2, 3, 3a, 4, 5, 5a, 6, 9-octahydroindeno[7a, 1-b]furan-5-yl)malonate (12b).



Isolated yield 0.27 g (91%). White solid, m.p. 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72–5.62 (m, 1H), 5.60-5.55 (m, 1H), 4.26–4.07 (m, 6H), 3.84-3.65 (m, 1H), 3.45-3.34 (m, 1H), 2.80–2.51 (m, 1H), 2.41–2.27 (m, 2H), 2.18–1.96 (m, 4H), 1.91–1.83 (m, 1H), 1.28–1.16 (m, 9H).

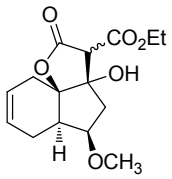
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.76, 168.68, 168.56, 168.22, 167.94, 167.00, 166.46, 126.15, 125.69, 123.07, 122.86, 94.95, 93.63, 83.50, 81.44, 62.73, 61.95, 61.78, 61.76, 61.66, 61.64, 58.23, 55.48, 53.64, 53.02, 46.34, 44.23, 42.76, 40.05, 39.60, 39.08, 31.05, 30.27, 26.68, 26.48, 14.15, 14.10, 14.05, 14.00, 13.95. HRMS (ESI-TOF) m/z calcd for $C_{21}H_{32}NO_9$ [M+NH_4^+] 442.2077, found 442.2080.

(3aS, 5R, 5aR, 9aR)-Ethyl 5-(tert-butylperoxy)-3a-hydroxy-2-oxo-2, 3, 3a, 4, 5, 5a, 6, 9-octahydroindeno[7a, 1-b]furan-3-carboxylate (12c).



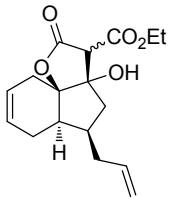
Isolated yield 0.08 g (yield 80%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76-5.66 (m, 1H), 5.61–5.55 (m, 1H), 4.29–4.13 (m, 3H), 3.61 (s, 1H), 2.71-2.56 (m, 1H), 2.51-2.40 (m, 2H), 2.27–1.87 (m, 4H), 1.27 (dt, *J* = 13.5, 6.8 Hz, 3H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.04, 167.13, 126.17, 122.64, 94.14, 84.44, 80.74, 80.58, 63.00, 57.61, 47.06, 44.50, 31.06, 26.78, 26.31, 13.98. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{25}O_7$ [M–H^-] 353.1606, found 353.1602.

(3aS, 5R, 5aR, 9aR)-Ethyl 3a-hydroxy-5-methoxy-2-oxo-2, 3, 3a, 4, 5, 5a, 6, 9-octahydroindeno[7a, 1-b]furan-3-carboxylate (12d).



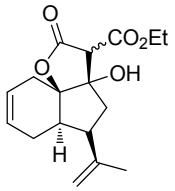
Isolated yield 0.28 g (yield 93%). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78–5.68 (m, 1H), 5.62–5.55 (m, 1H), 4.27–4.06 (m, 3H), 3.57–3.44 (m, 1H), 3.29 (s, 3H), 2.69–2.54 (m, 1H), 2.51–2.35 (m, 2H), 2.31–1.95 (m, 4H), 1.27 (q, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.46, 166.91, 125.92, 122.90, 94.03, 82.19, 80.51, 62.84, 58.10, 55.93, 48.06, 45.84, 30.96, 26.36, 13.95. HRMS (ESI-TOF) m/z calcd for $C_{15}H_{21}O_6$ [M+H^+] 297.1338, found 297.1327.

(3aS, 5R, 5aR, 9aR)-Ethyl 5-allyl-3a-hydroxy-2-oxo-2, 3, 3a, 4, 5, 5a, 6, 9-octahydroindeno[7a, 1-b]furan-3-carboxylate (12e).



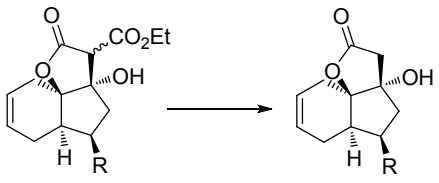
Isolated yield 0.35 g (yield 90%). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80-5.75 (m, 1H), 5.67–5.51 (m, 2H), 5.09–4.86 (m, 2H), 4.33–4.19 (m, 2H), 3.81-3.61 (m, 1H), 2.69-2.57 (m, 1H), 2.43–1.90 (m, 8H), 1.88–1.65 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.77, 167.98, 167.24, 166.63, 137.28, 137.26, 126.94, 126.59, 122.92, 122.56, 116.49, 116.38, 96.44, 94.40, 84.42, 83.24, 62.81, 61.99, 58.33, 56.51, 47.22, 43.57, 42.46, 42.19, 37.53, 37.38, 35.95, 35.45, 32.06, 30.93, 24.65, 24.34, 14.16, 13.98. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{23}O_5$ [M+H$^+$] 307.1545, found 307.1540.

(3aS, 5S, 5aR, 9aR)-Ethyl 3a-hydroxy-2-oxo-5-(prop-1-en-2-yl)-2, 3, 3a, 4, 5, 5a, 6, 9-octahydroindeno[7a, 1-b]furan-3-carboxylate (12f).



Isolated yield 0.22 g (yield 91%). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.75 (m, 1H), 5.71–5.65 (m, 1H), 4.83 (d, *J* = 8.0 Hz, 2H), 4.36–4.27 (m, 2H), 4.07-3.72 (s, 1H), 2.88–2.53 (m, 2H), 2.46–2.28 (m, 2H), 2.25–2.15 (m, 2H), 2.09–1.93 (m, 2H), 1.71 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.37, 143.09, 126.32, 122.92, 112.35, 95.35, 81.83, 62.92, 58.07, 47.90, 44.12, 31.21, 26.41, 19.22, 13.98. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{23}O_5$ [M+H$^+$] 307.1545, found 307.1537.

2.3.7 General Procedure for the Synthesis of Compounds 1

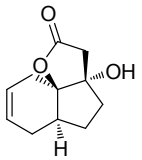


12 **1**

To a stirring solution of **12** (5.22 mmol) in DMSO (10 ml) and water (1 ml) was added lithium chloride (5.22 mmol), the reaction mixture was heated to 135 °C for 12 h. Water was

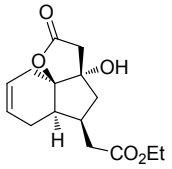
added and the mixture was extracted with EtOAc, The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the residue by flash column chromatography (eluent: petroleum ether / ethyl acetate =3 / 1) gave the target compound **1**.

(3aS, 5aS, 9aR)-3a-hydroxy-3, 3a, 4, 5, 5a, 6-hexahydroindeno[7a, 1-b]furan-2(9H)-one (1a).



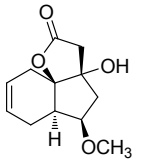
Isolated yield 0.13 g (yield 91%, d.r. > 20:1). White solid, m.p. 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78–5.69 (m, 1H), 5.68–5.64 (m, 1H), 3.28 (s, 1H), 2.98-2.90 (m, 1H), 2.76-2.71 (m, 1H), 2.62-2.52 (m, 1H), 2.32–2.03 (m, 4H), 2.00–1.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.76, 126.60, 123.02, 95.17, 81.79, 43.50, 41.82, 41.20, 30.65, 27.91, 27.60. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{15}O_3$ [M+H$^+$] 195.1021, found 195.1013.

ethyl 2-((3aS, 5S, 5aR, 9aR)-3a-hydroxy-2-oxo-2, 3, 3a, 4, 5, 5a, 6, 9-octahydroindeno[7a, 1-b]furan-5-yl)acetate (1b).



Isolated yield 0.25 g (yield 90%, d.r. > 20:1). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80–5.71 (m, 1H), 5.70–5.62 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.95-2.90 (m, 1H), 2.80-2.74 (m, 1H), 2.64-2.49 (m, 2H), 2.45-2.36 (m, 1H), 2.27-2.17 (m, 3H), 2.15–2.00 (m, 2H), 1.77–1.67 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.08, 172.67, 126.18, 123.27, 94.87, 80.98, 60.74, 48.17, 45.64, 43.25, 37.26, 30.79, 26.24, 14.20. HRMS (ESI-TOF) m/z calcd for $C_{15}H_{24}NO_5$ [M+NH_4^+] 298.1654, found 298.1649.

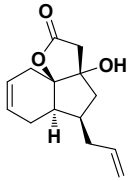
(3aS, 5R, 5aR, 9aR)-3a-hydroxy-5-methoxy-3, 3a, 4, 5, 5a, 6-hexahydroindeno[7a, 1-b]furan-2(9H)-one (1c).



Isolated yield 0.32 g (yield 93%, d.r. > 20:1). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ

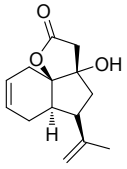
5.81–5.76 (m, 1H), 5.69-5.65 (m, 1H), 3.60-3.54 (m, 1H), 3.36 (s, 3H), 2.93-2.87 (m, 1H), 2.77-2.72 (m, 1H), 2.68–2.56 (m, 2H), 2.49-2.42 (m, 1H), 2.29–2.00 (m, 3H), 1.93-1.87 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.41, 126.33, 122.80, 93.52, 82.97, 79.62, 58.16, 47.60, 45.76, 43.33, 30.47, 26.45. HRMS (ESI-TOF) m/z calcd for $C_{12}H_{17}O_4$ [M+H $^+$] 225.1127, found 225.1119.

(3aS, 5R, 5aR, 9aR)-5-allyl-3a-hydroxy-3, 3a, 4, 5, 5a, 6-hexahydroindeno[7a, 1-b]furan-2(9H)-one (1d).



Isolated yield 0.62 g (yield 93%, d.r. > 20:1). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86–5.77 (m, 1H), 5.72–5.59 (m, 2H), 5.01-4.96 (m, 2H), 2.92-2.85 (m, 1H), 2.79-2.71 (m, 1H), 2.65-2.59 (m, 1H), 2.39–2.11 (m, 6H), 2.10–1.95 (m, 2H), 1.87–1.70 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.34, 137.45, 126.91, 122.97, 116.26, 96.23, 82.17, 46.66, 44.01, 43.31, 37.81, 35.49, 31.63, 24.65. HRMS (ESI-TOF) m/z calcd for $C_{14}H_{19}O_3$ [M+H$^+$] 235.1334, found 235.1331.

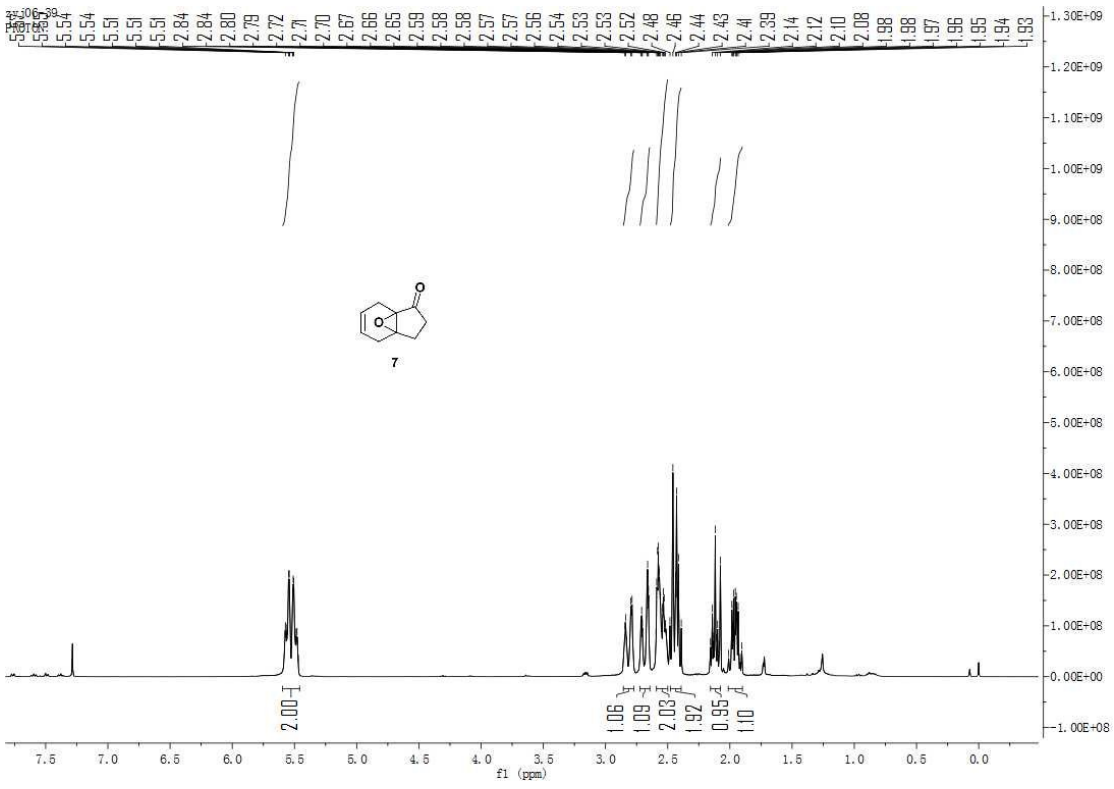
(3aS, 5S, 5aR, 9aR)-3a-hydroxy-5-(prop-1-en-2-yl)-3, 3a, 4, 5, 5a, 6-hexahydroindeno[7a, 1-b]furan-2(9H)-one(1e).



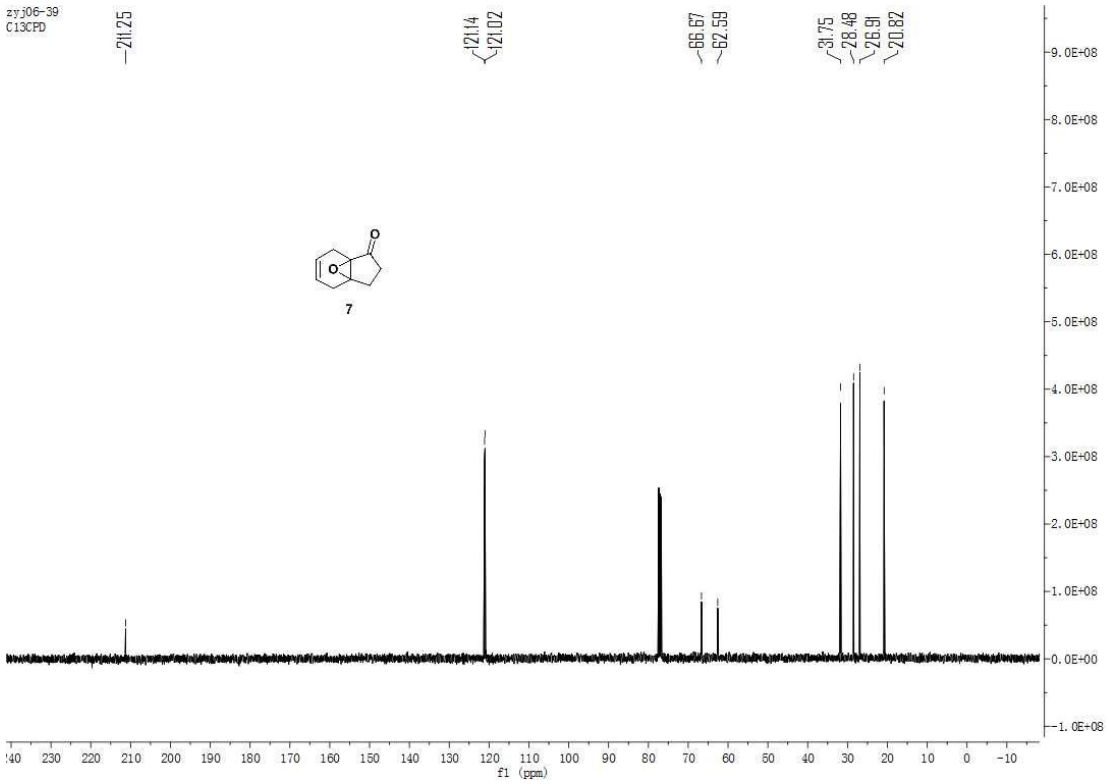
Isolated yield 0.27 g (yield 90%, d.r. > 20:1). Pale yellow oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75-5.72 (m, 1H), 5.66–5.63(m, 1H), 4.79–4.73 (m, 2H), 3.00-2.94 (m, 1H), 2.83-2.77 (m, 1H), 2.69-2.58 (m, 1H), 2.32–2.13 (m, 3H), 2.04–1.82 (m, 4H), 1.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.71, 143.57, 126.61, 123.07, 111.85, 95.40, 80.73, 48.27, 43.91, 43.58, 31.00, 26.41, 19.39, 14.13. HRMS (ESI-TOF) m/z calcd for $C_{14}H_{22}NO_3$ [M+H $^+$] 252.1600, found 252.1597.

3. NMR-Spectra

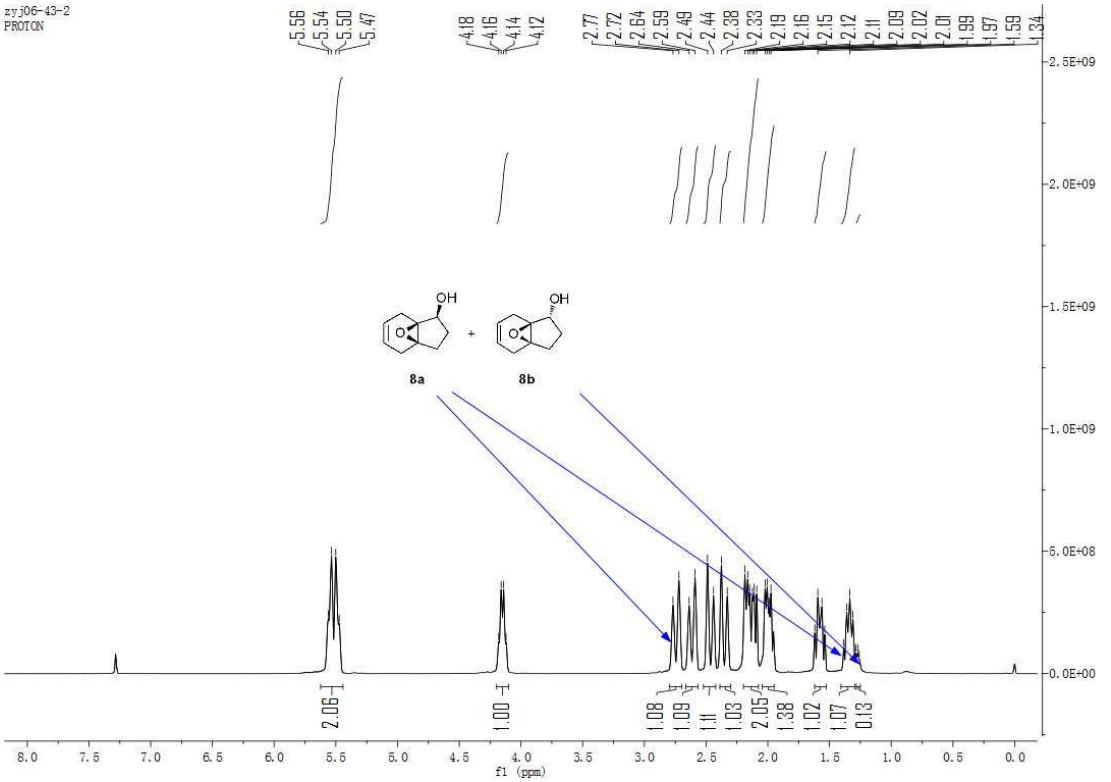
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**



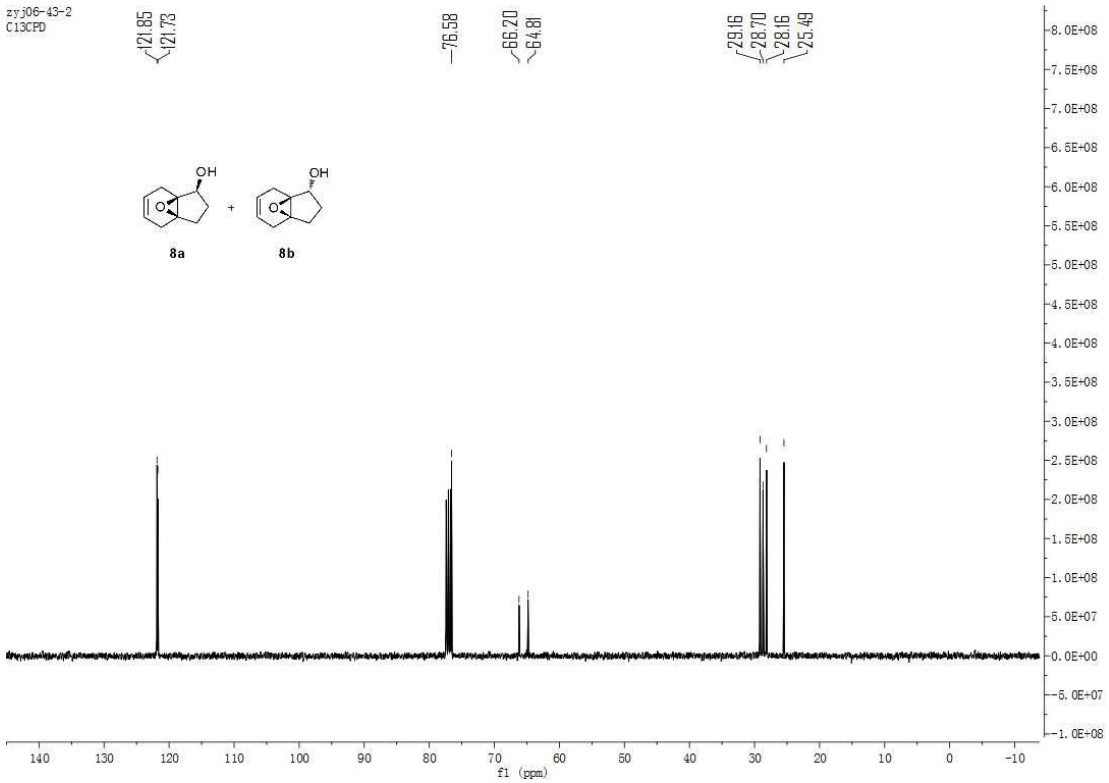
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7**



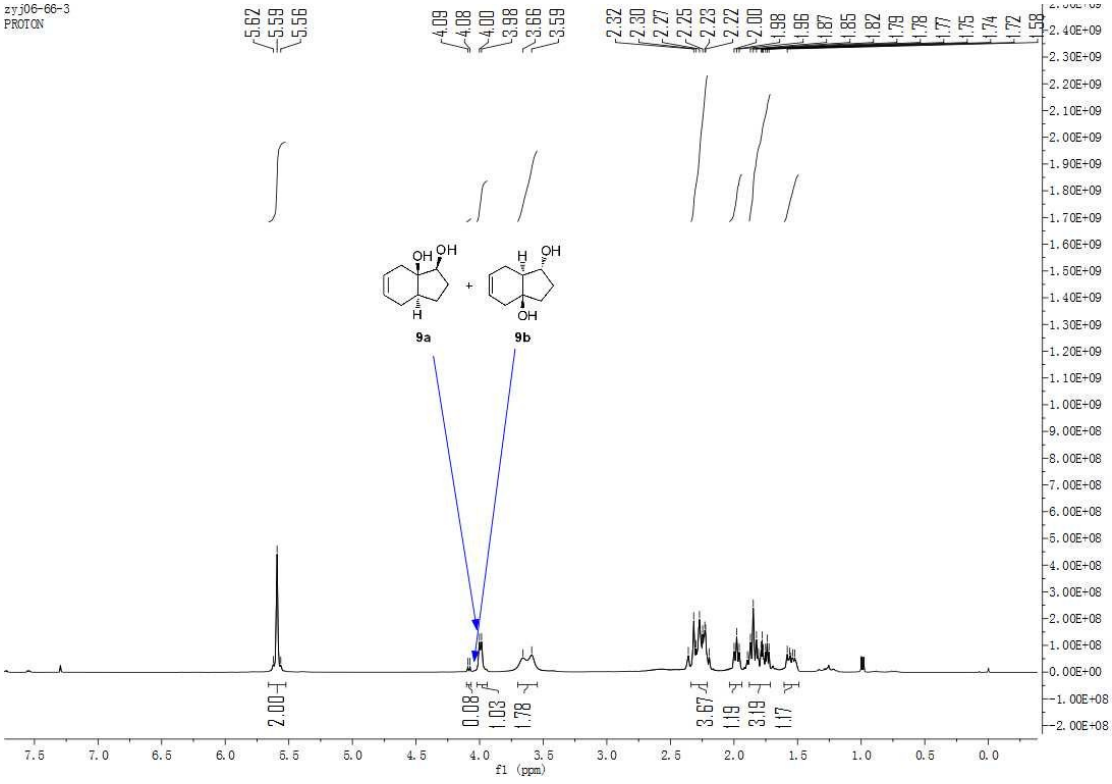
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8a+8b**



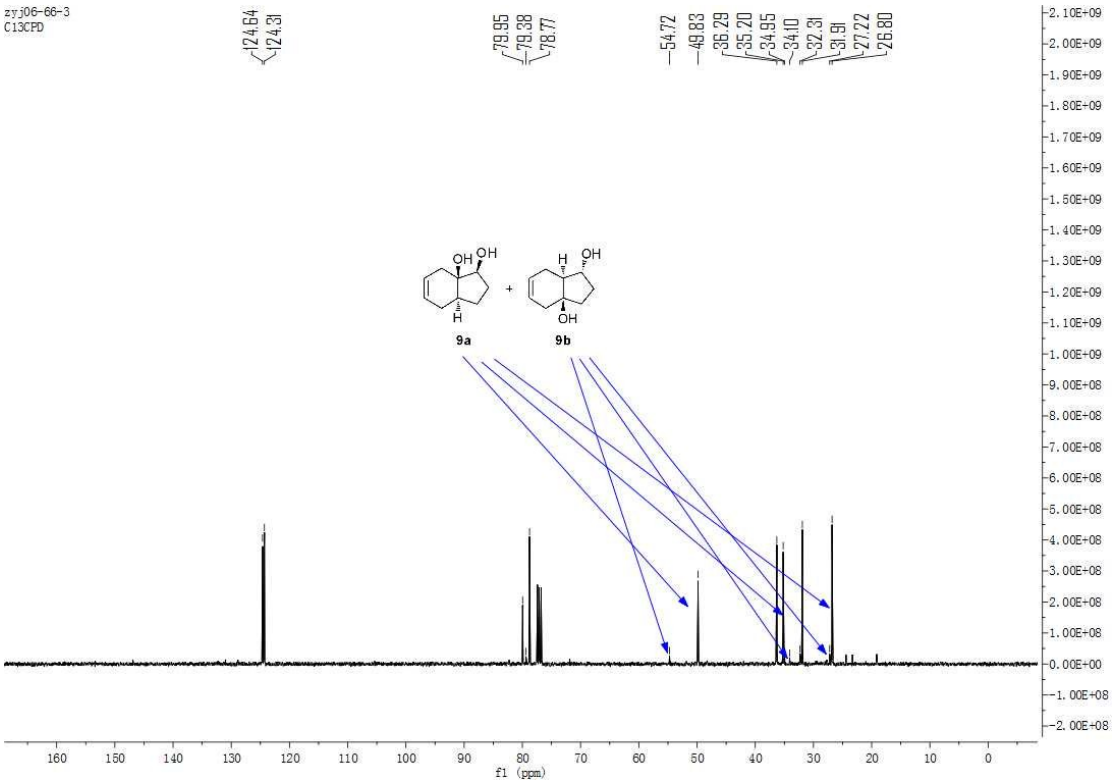
^{13}C NMR (100 MHz, $CDCl_3$) of compound **8a+8b**



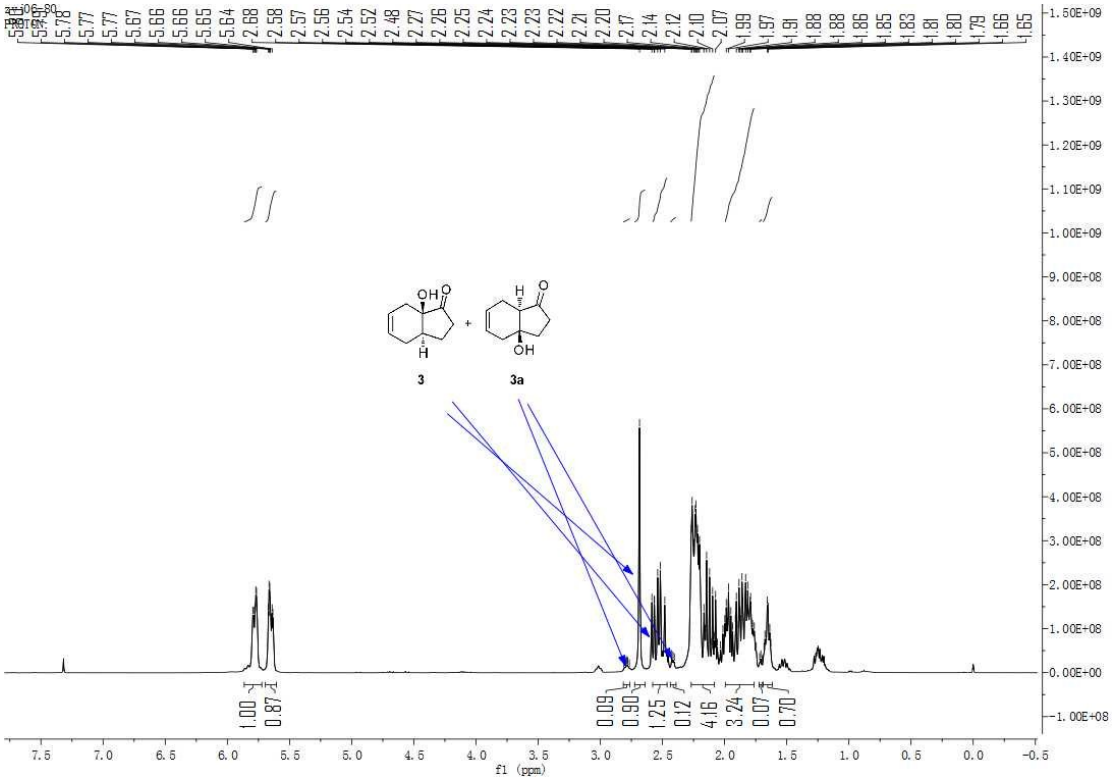
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9a+9b**



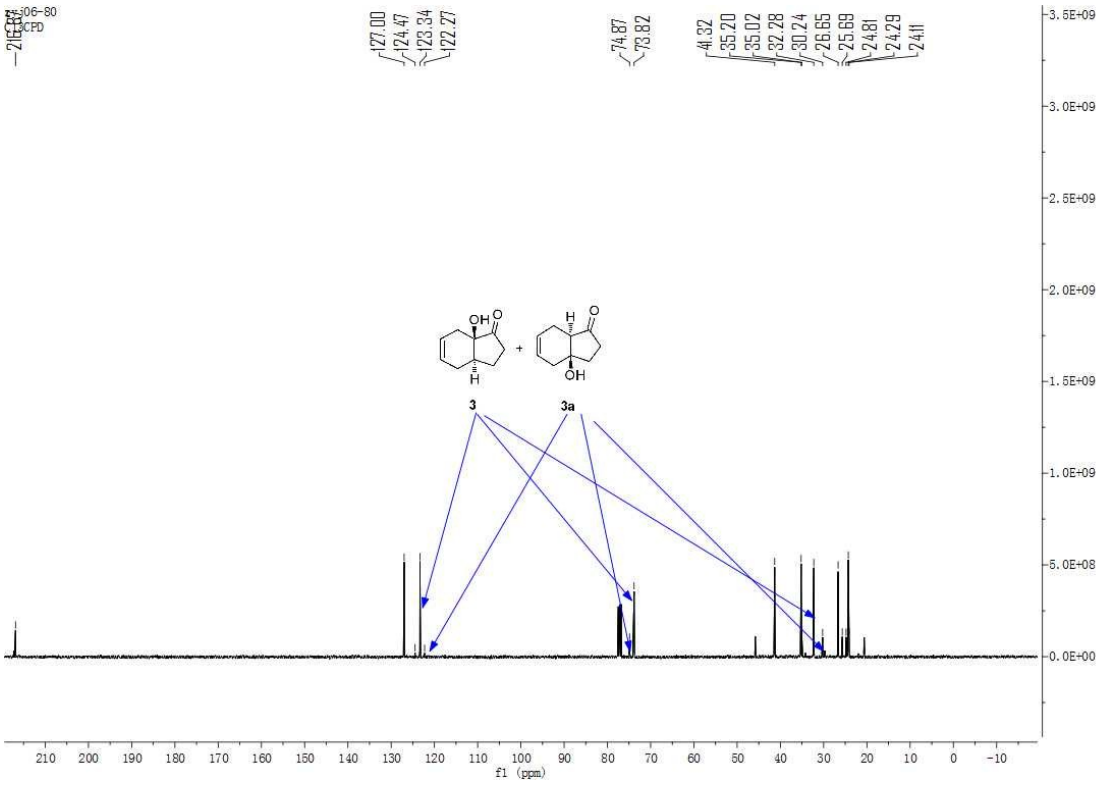
^{13}C NMR (100 MHz, $CDCl_3$) of compound **9a+9b**



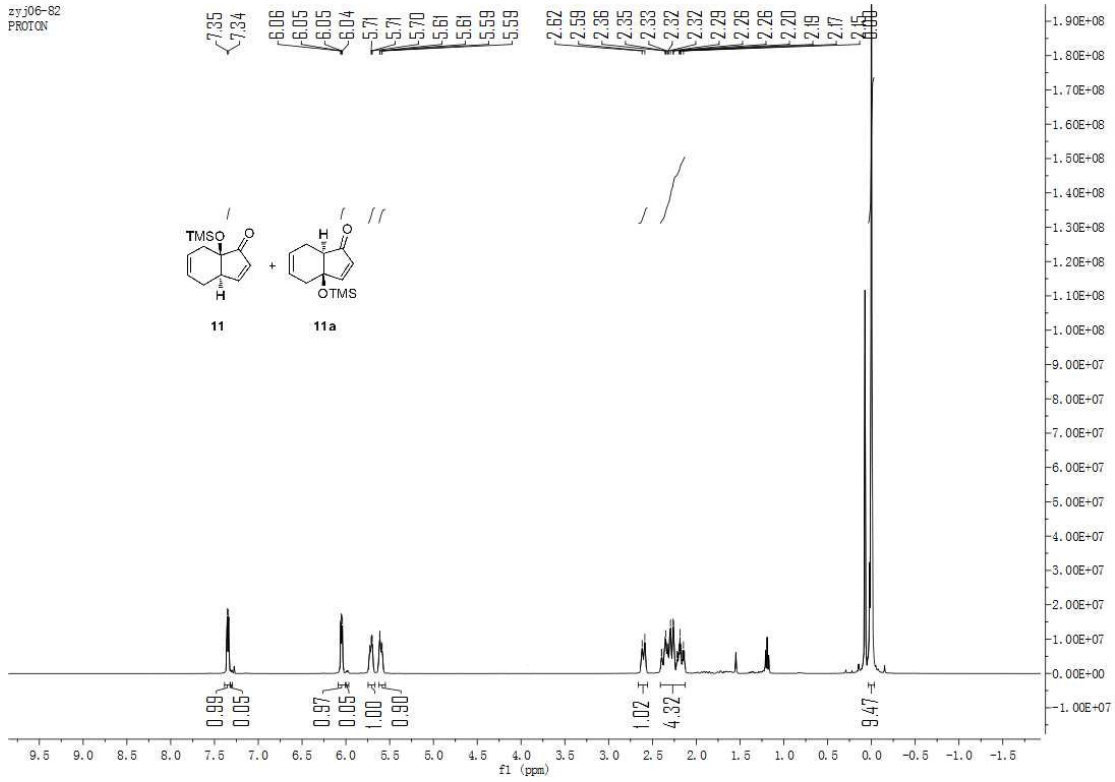
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3+3a**



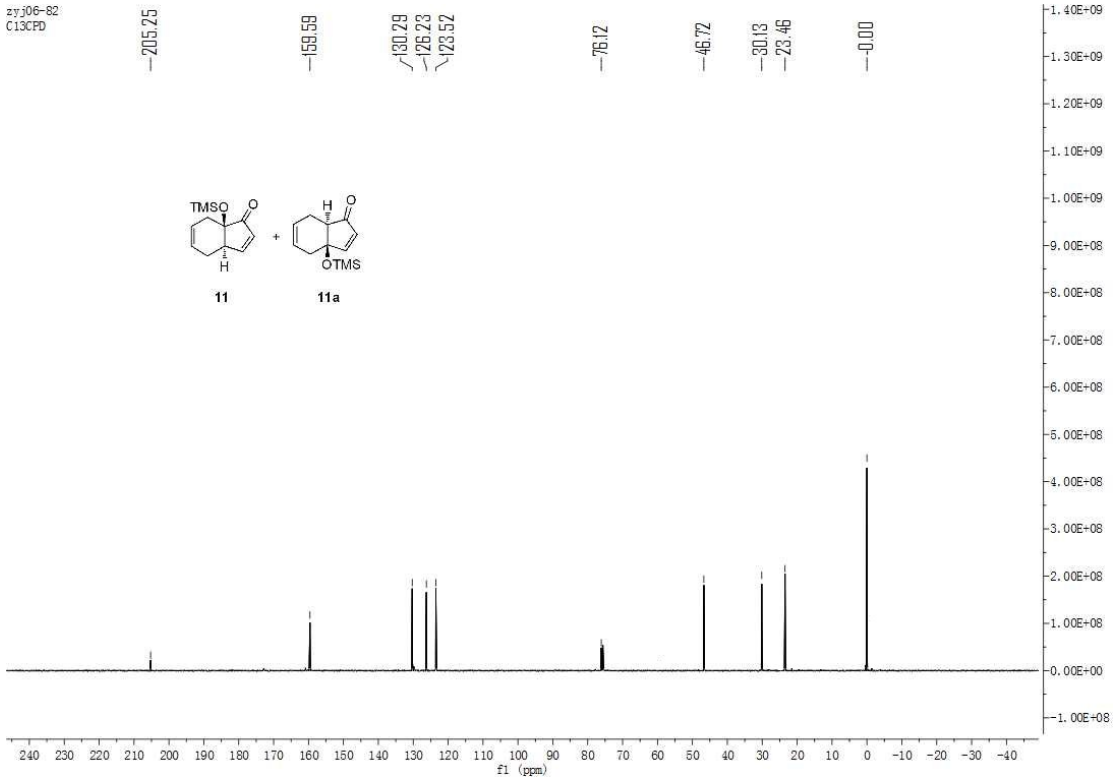
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3+3a**



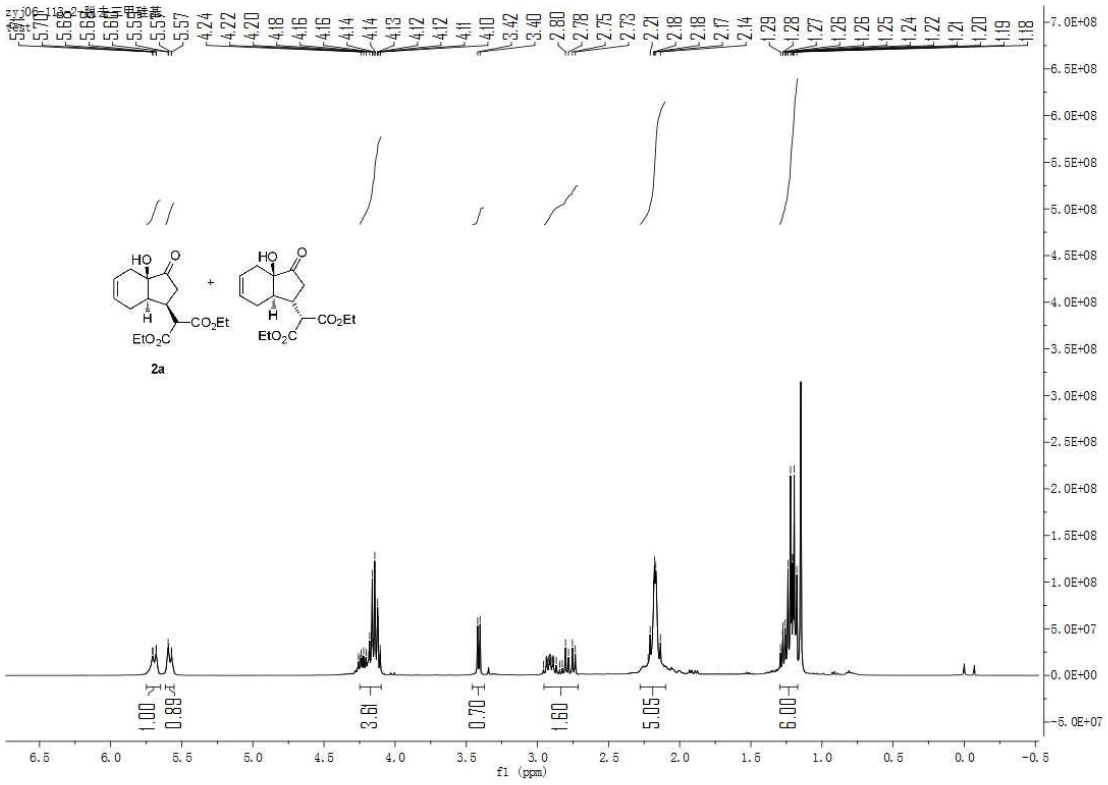
^{1}H NMR (400 MHz, $CDCl_3$) of compound **11+11a**



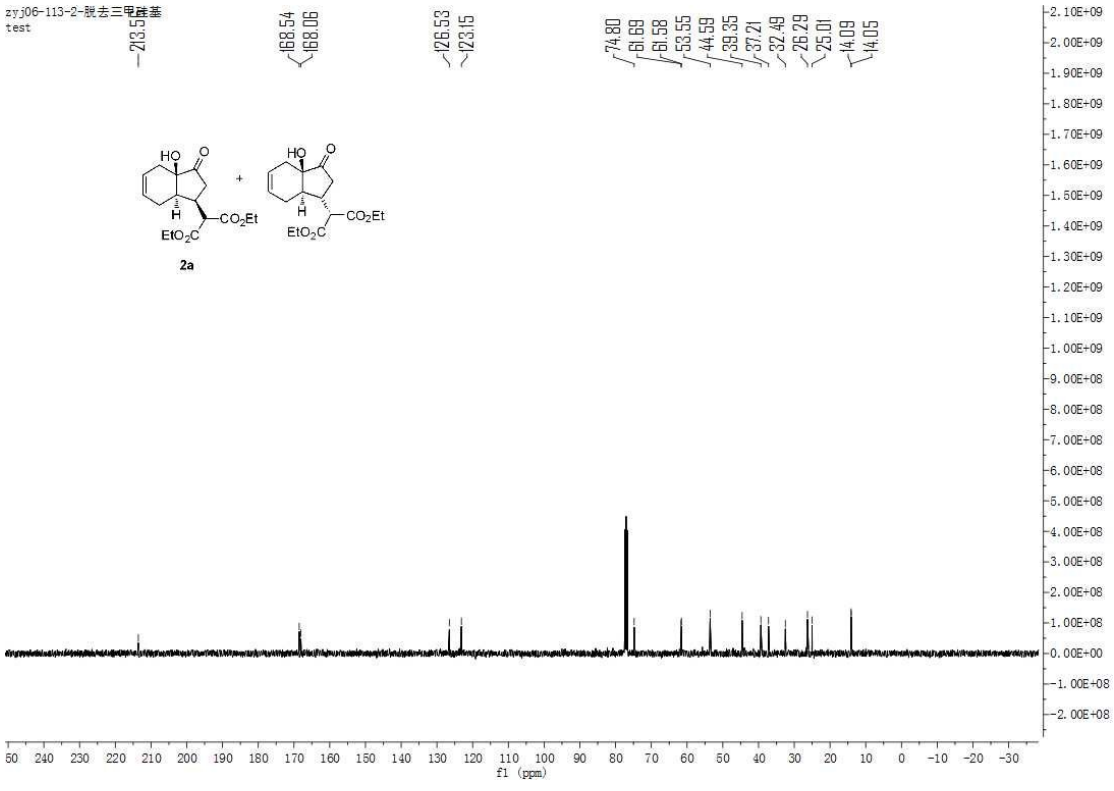
^{13}C NMR (100 MHz, $CDCl_3$) of compound **11+11a**



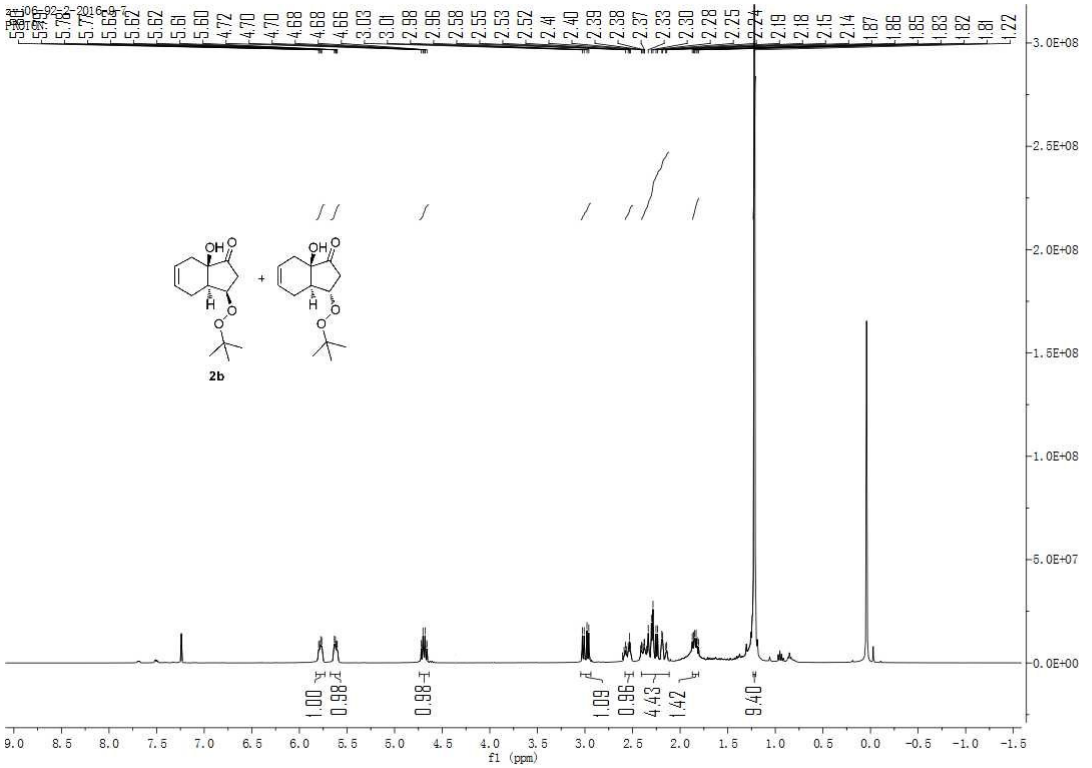
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**



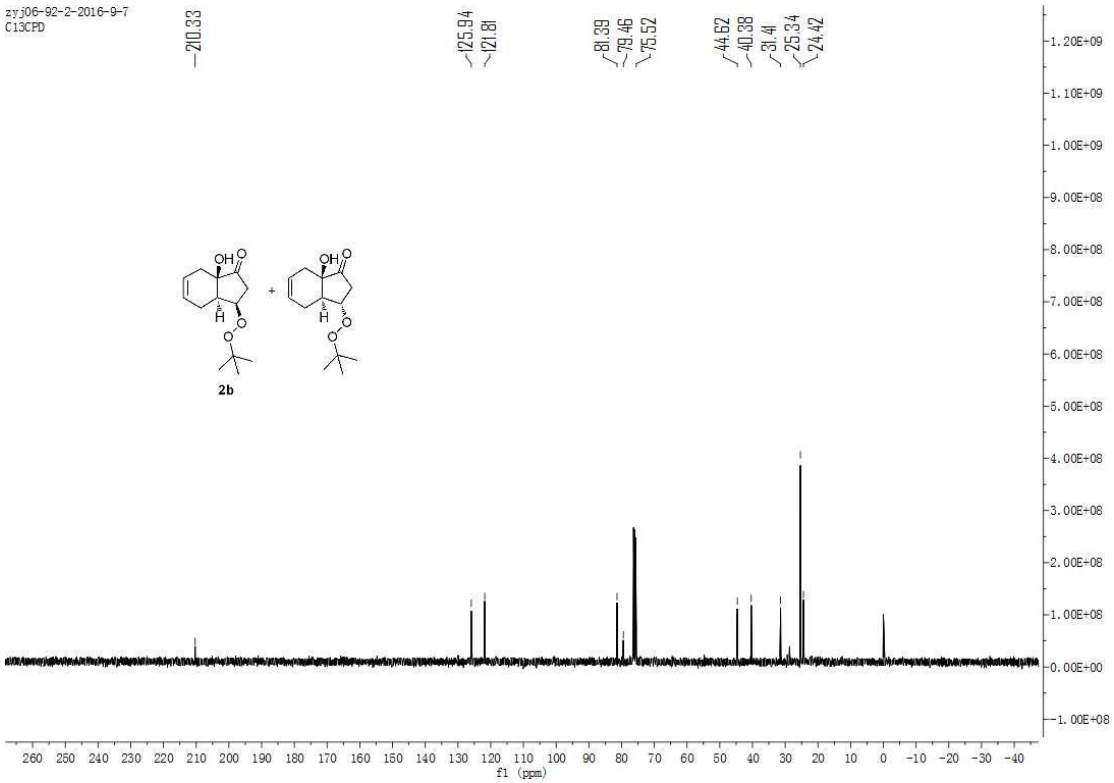
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**



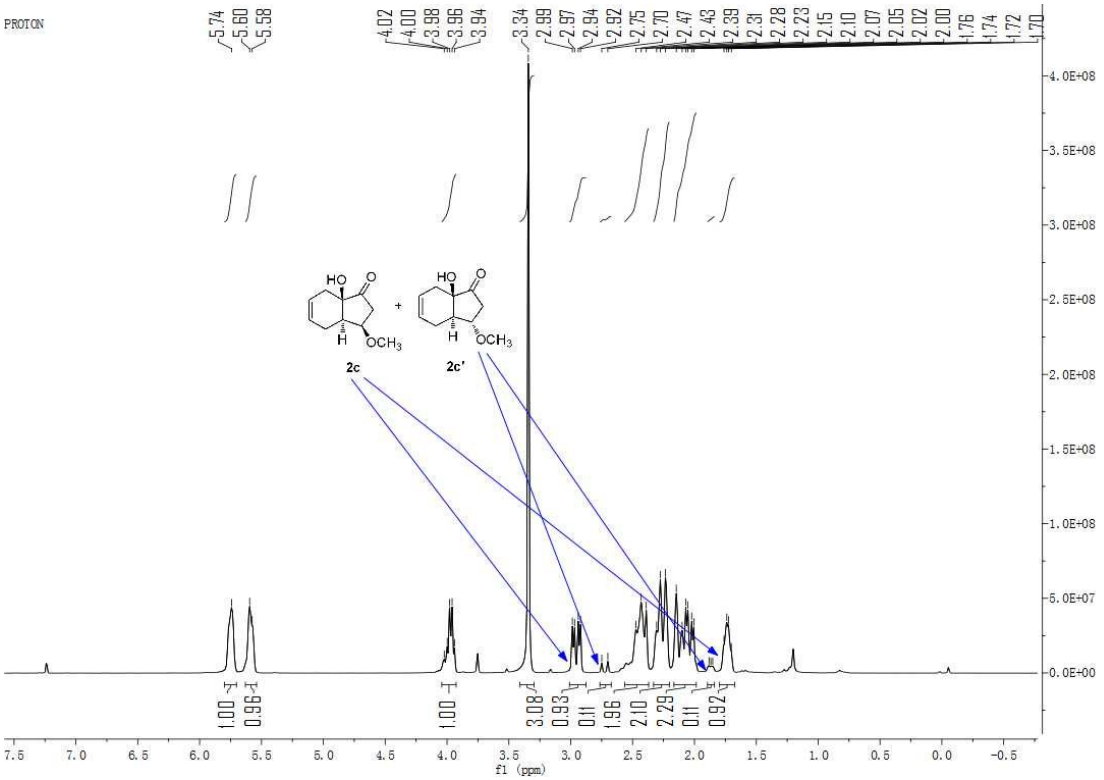
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**



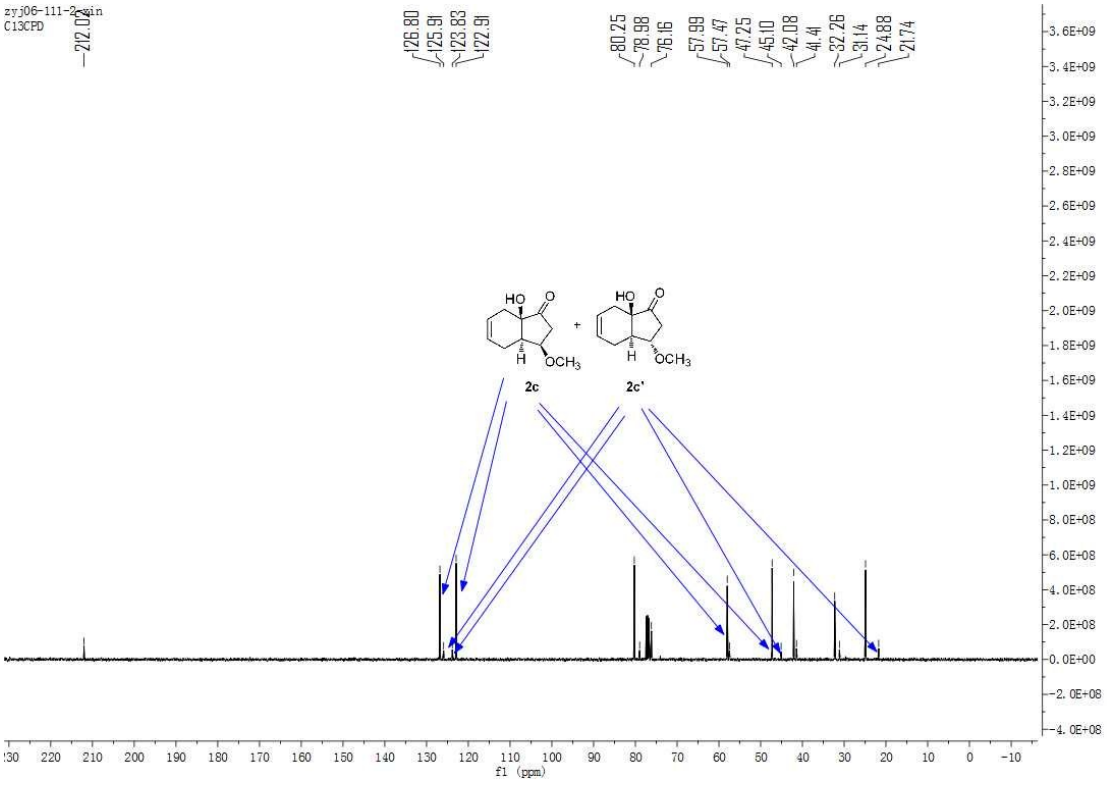
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b**



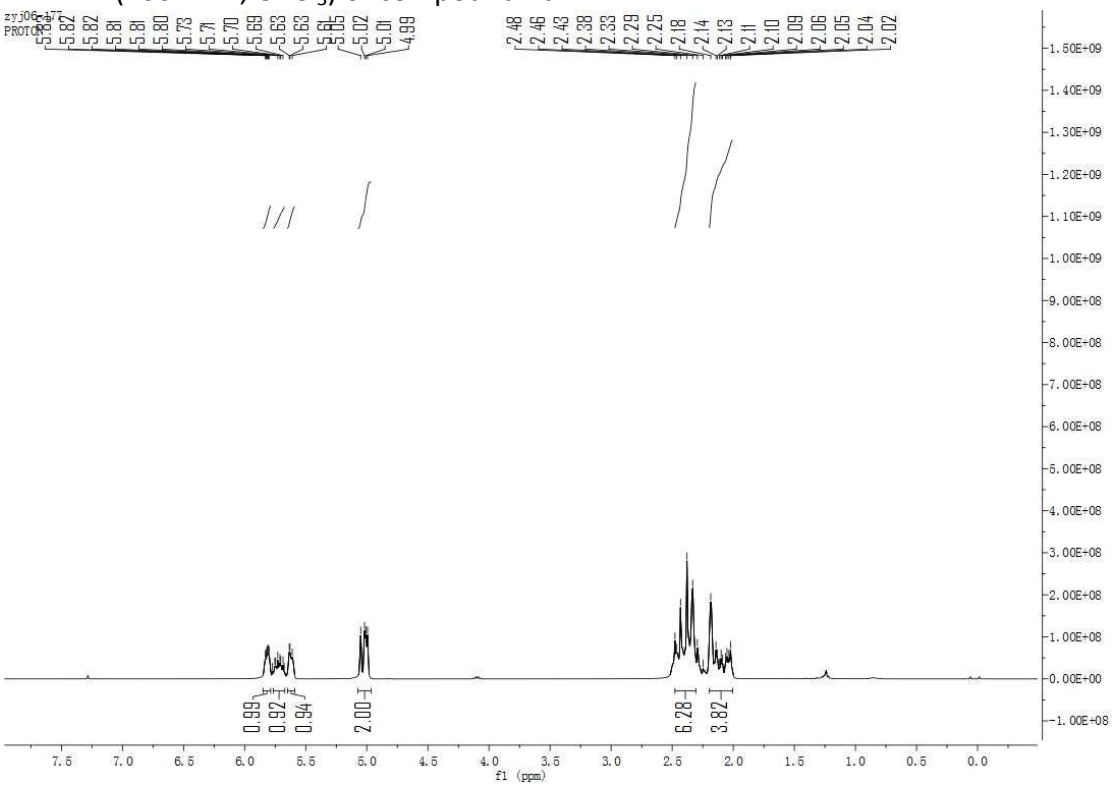
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2c**



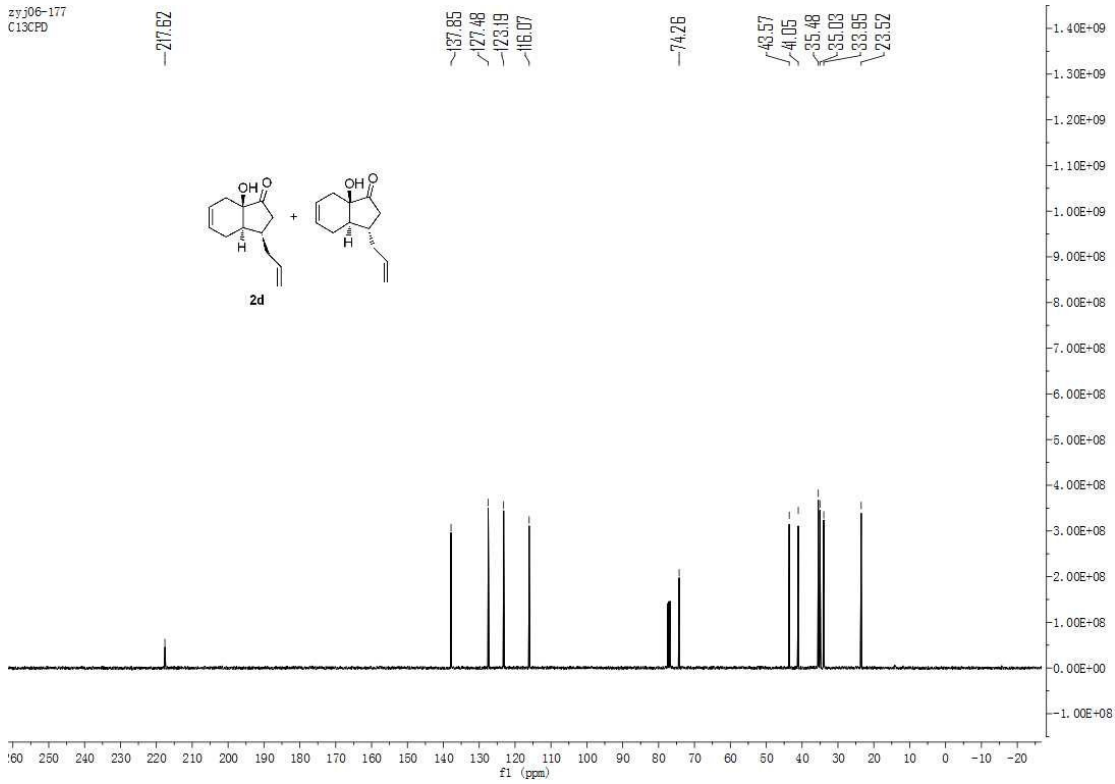
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2c**



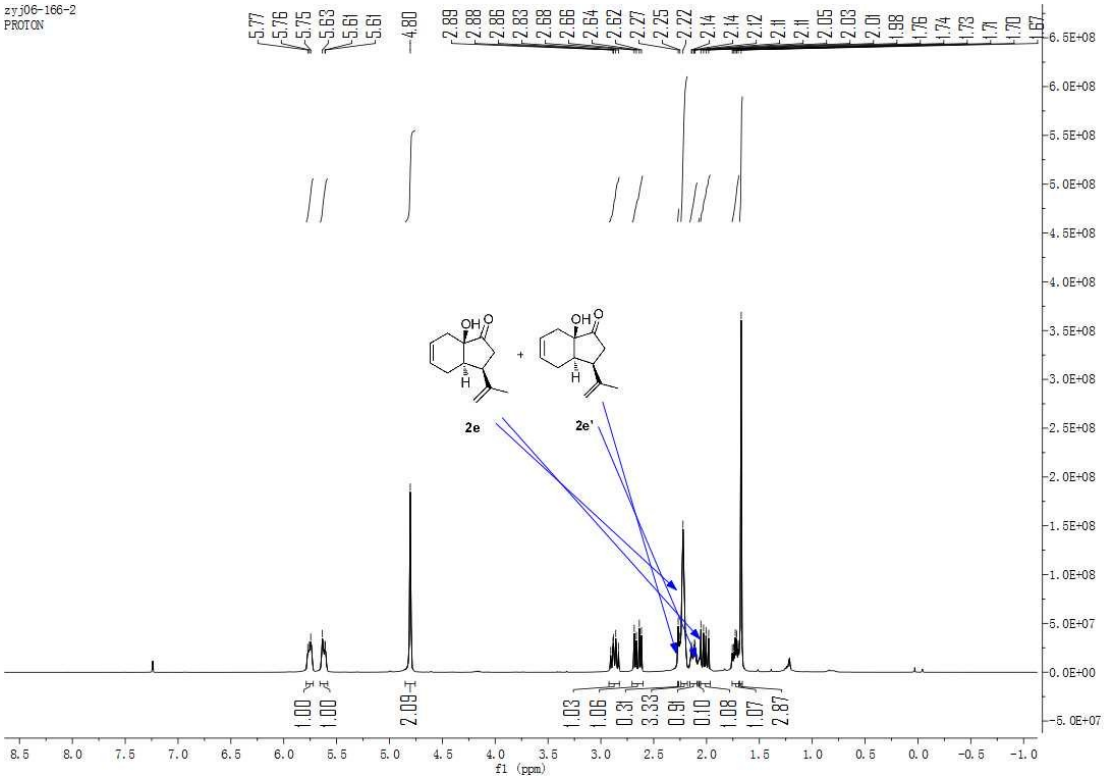
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2d**



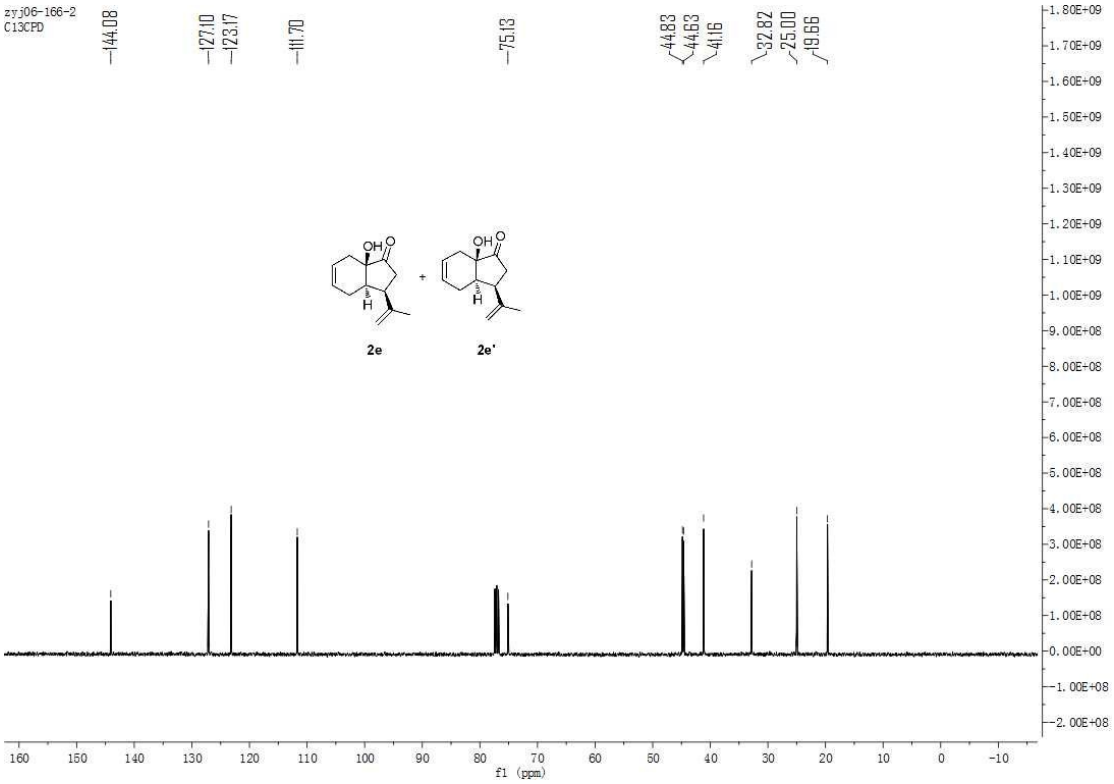
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2d**



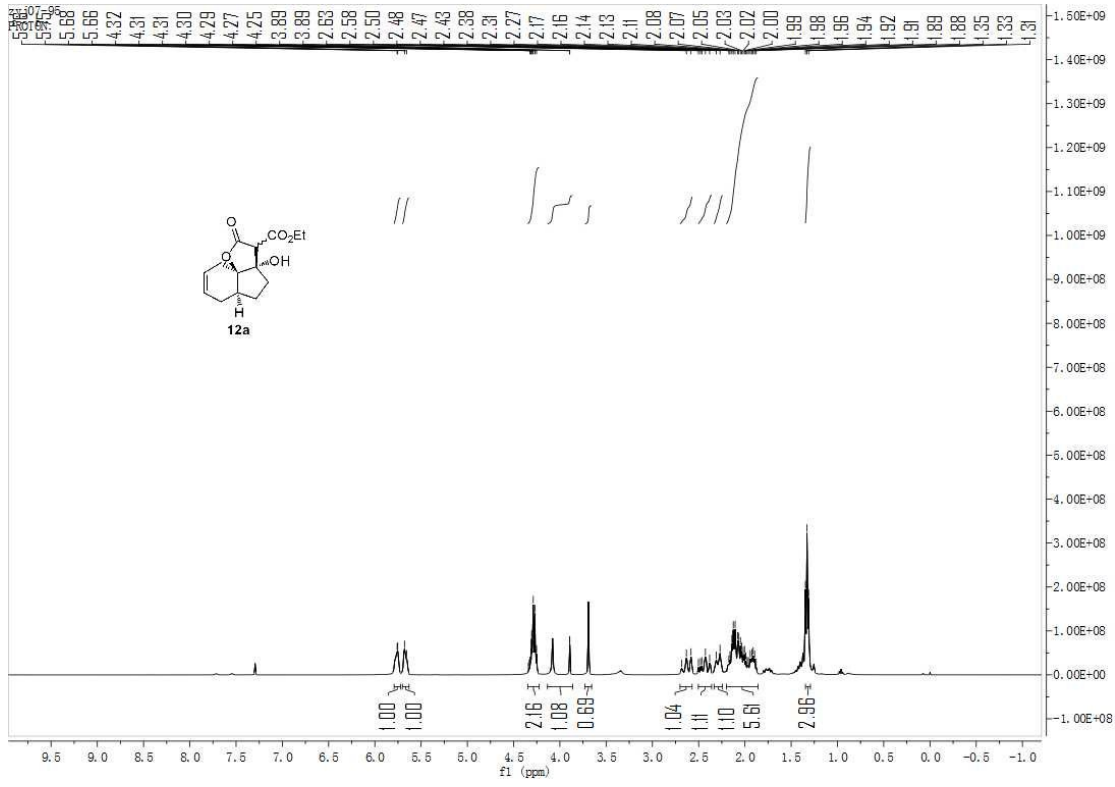
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2e**



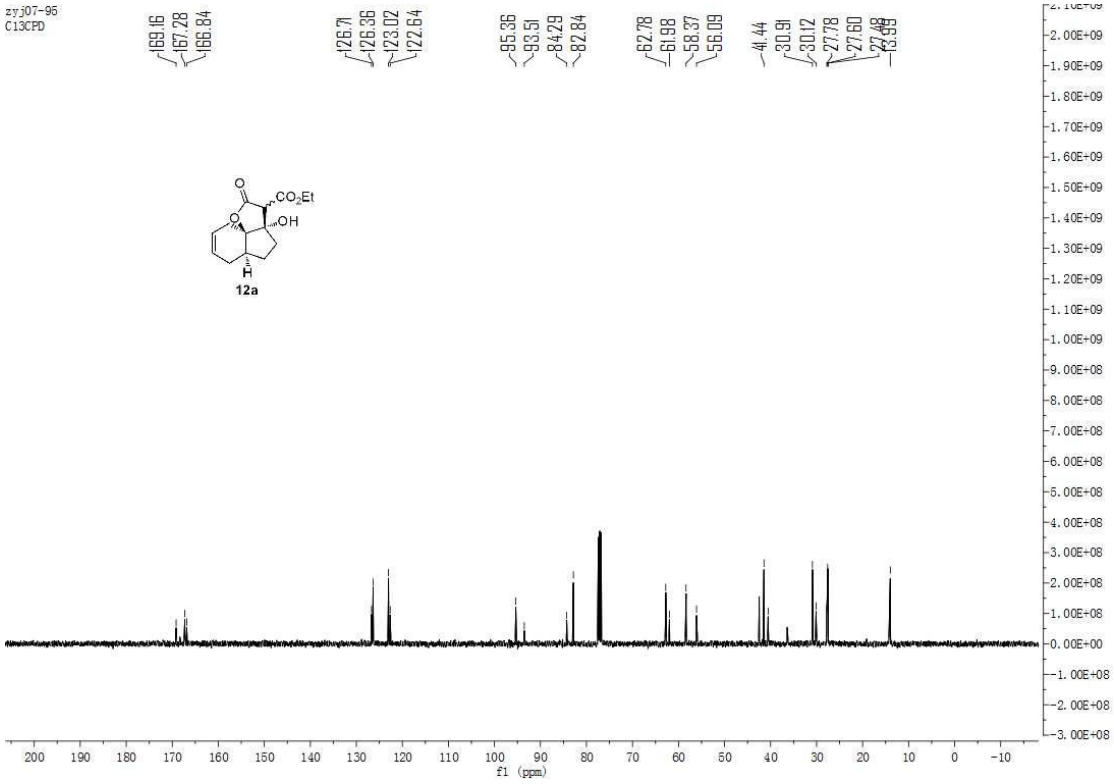
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2e**



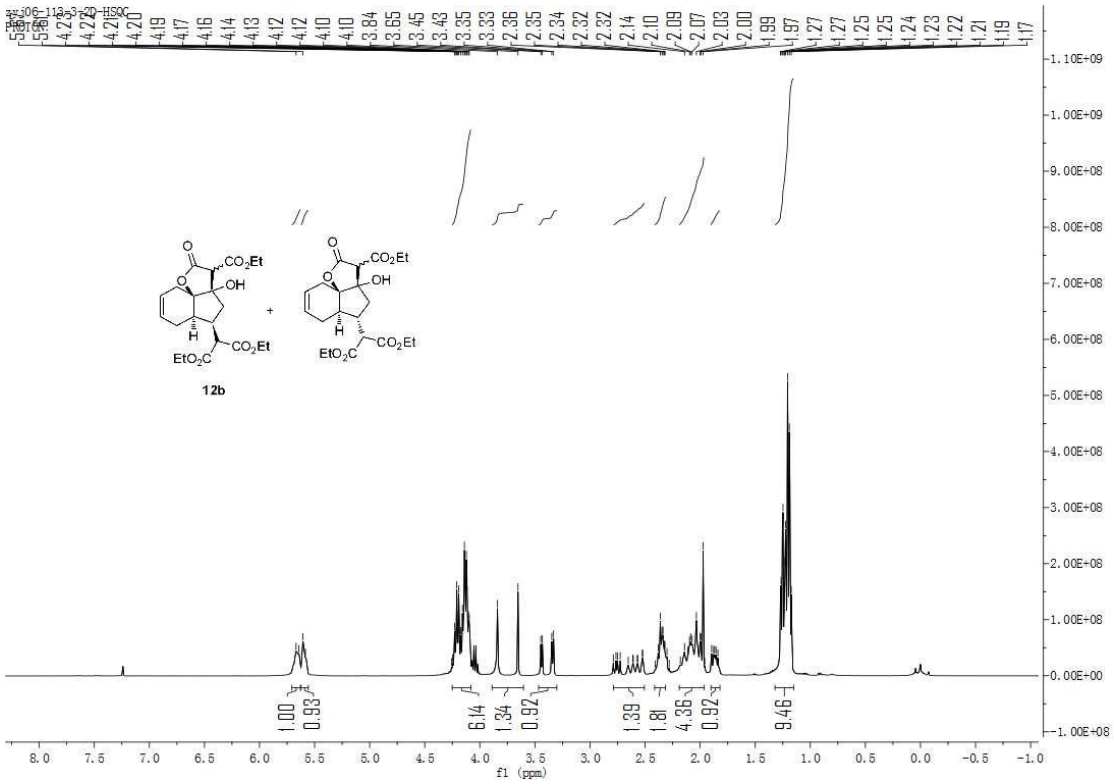
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12a**



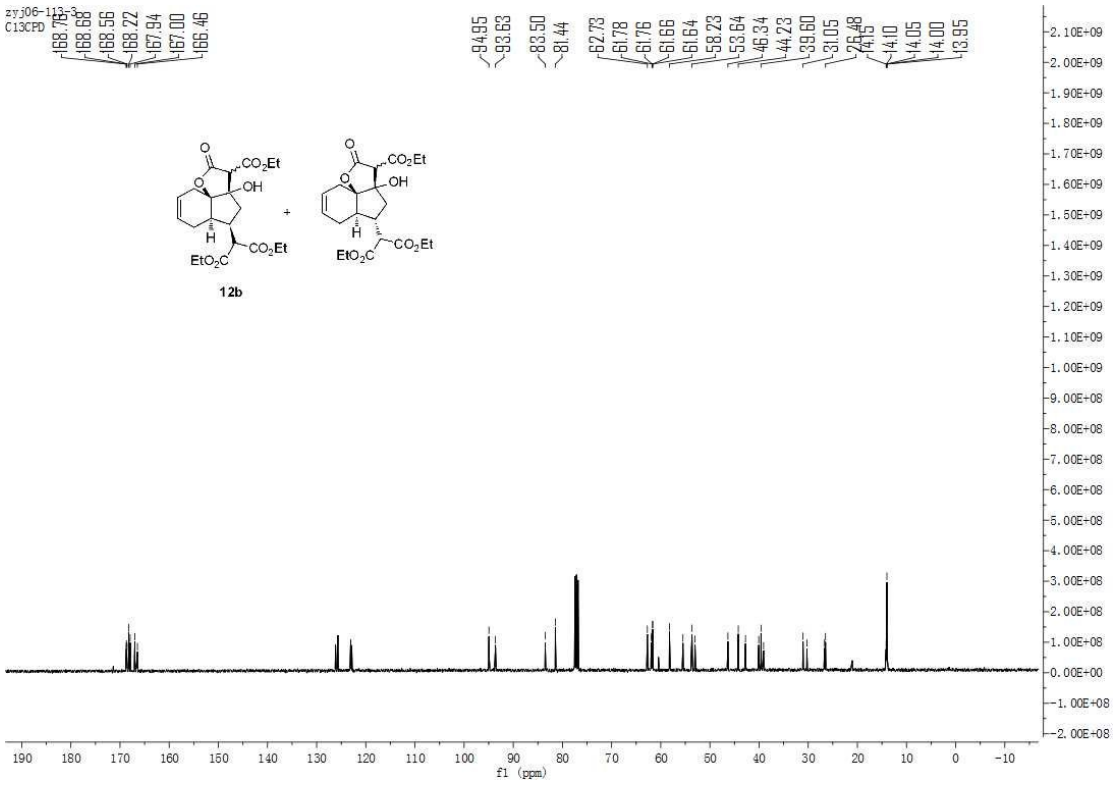
^{13}C NMR (100 MHz, $CDCl_3$) of compound **12a**



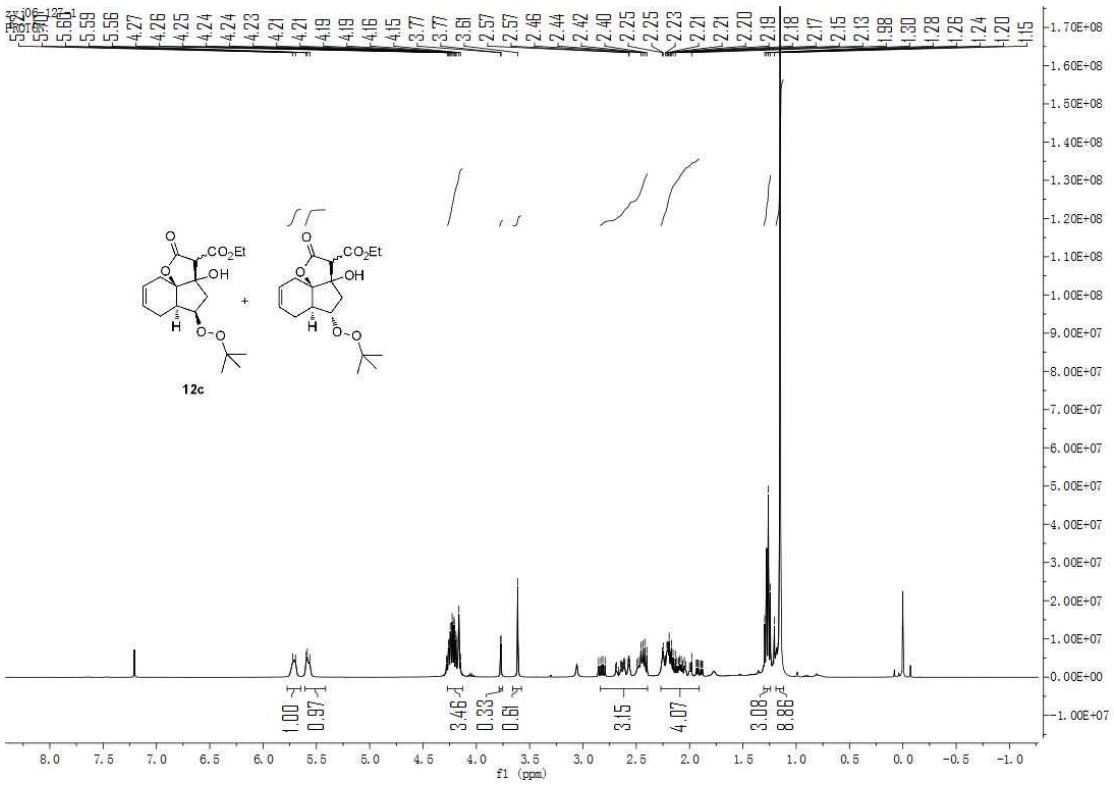
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12b**



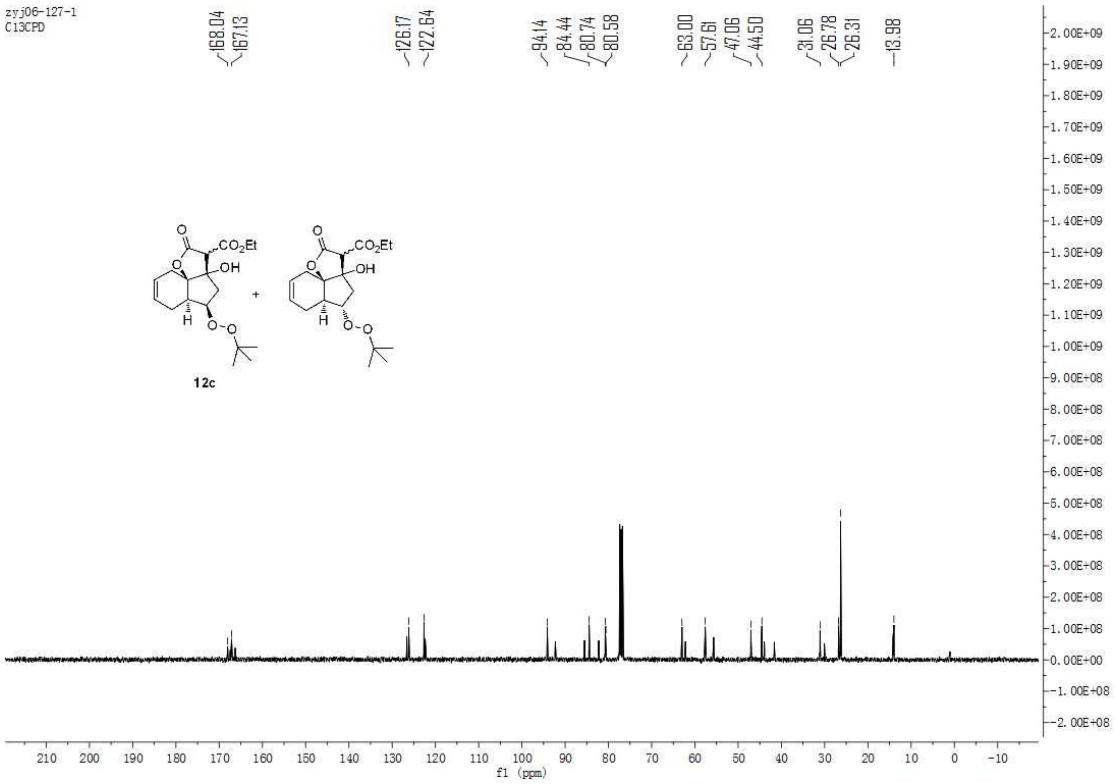
^{13}C NMR (100 MHz, $CDCl_3$) of compound **12b**



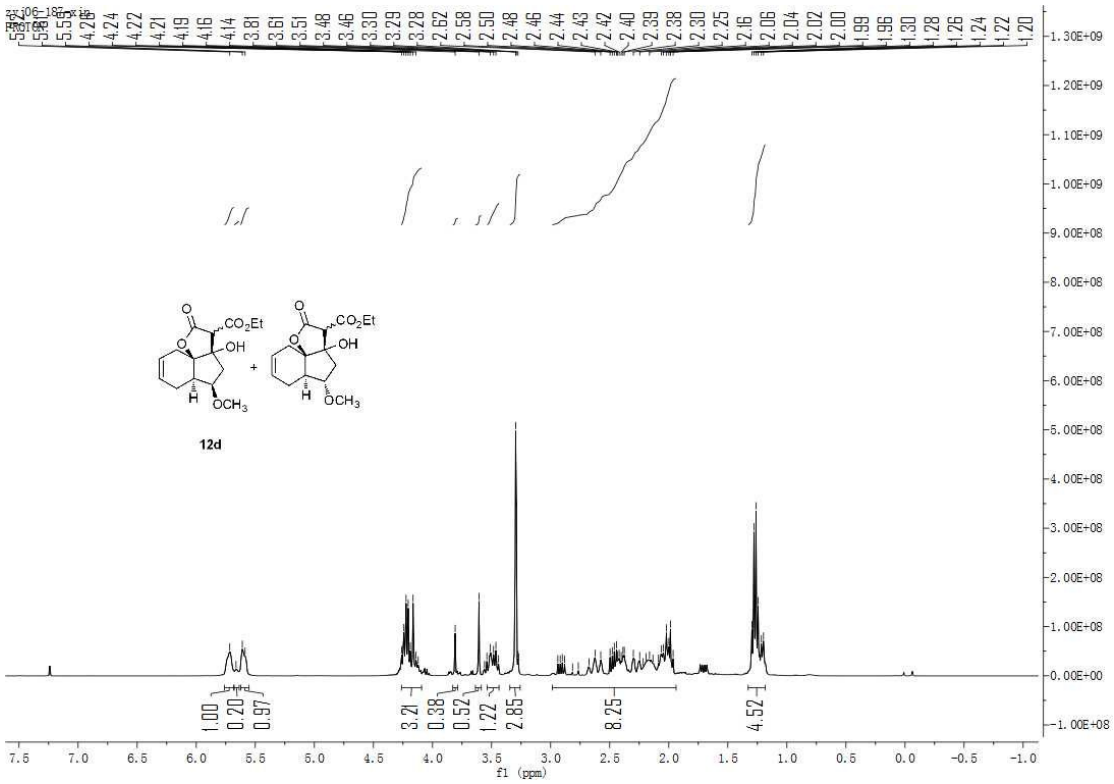
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12c**



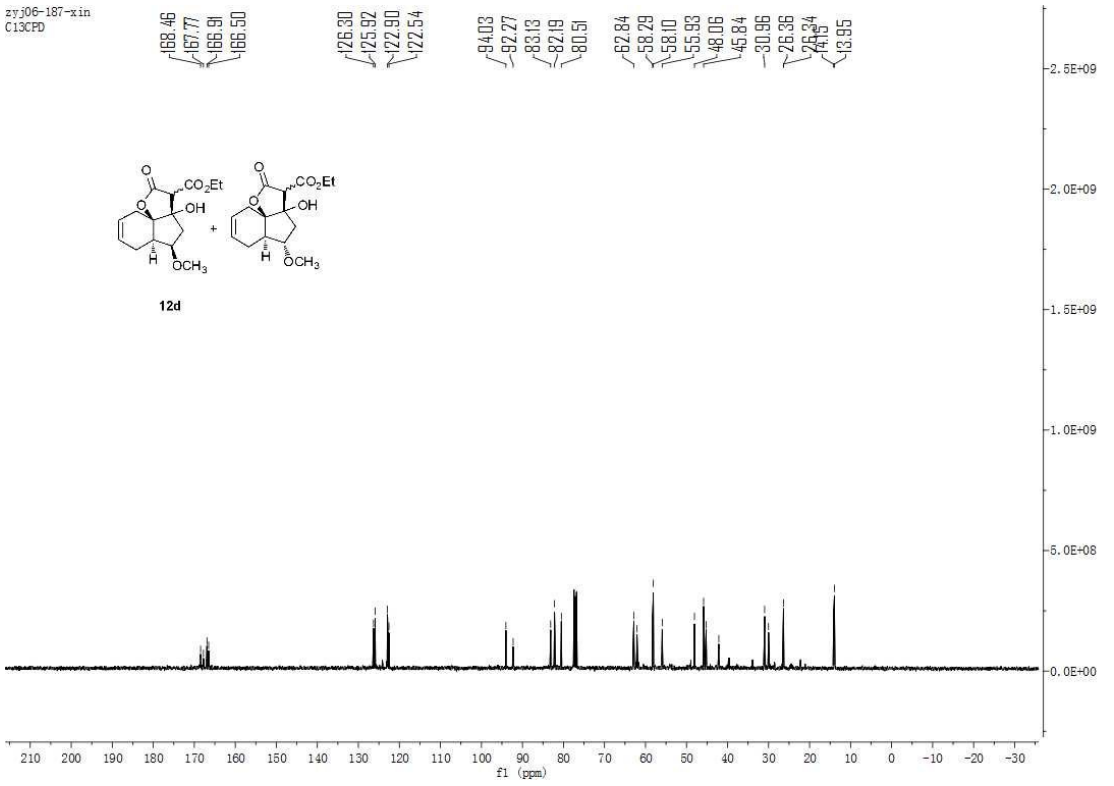
^{13}C NMR (100 MHz, $CDCl_3$) of compound **12c**



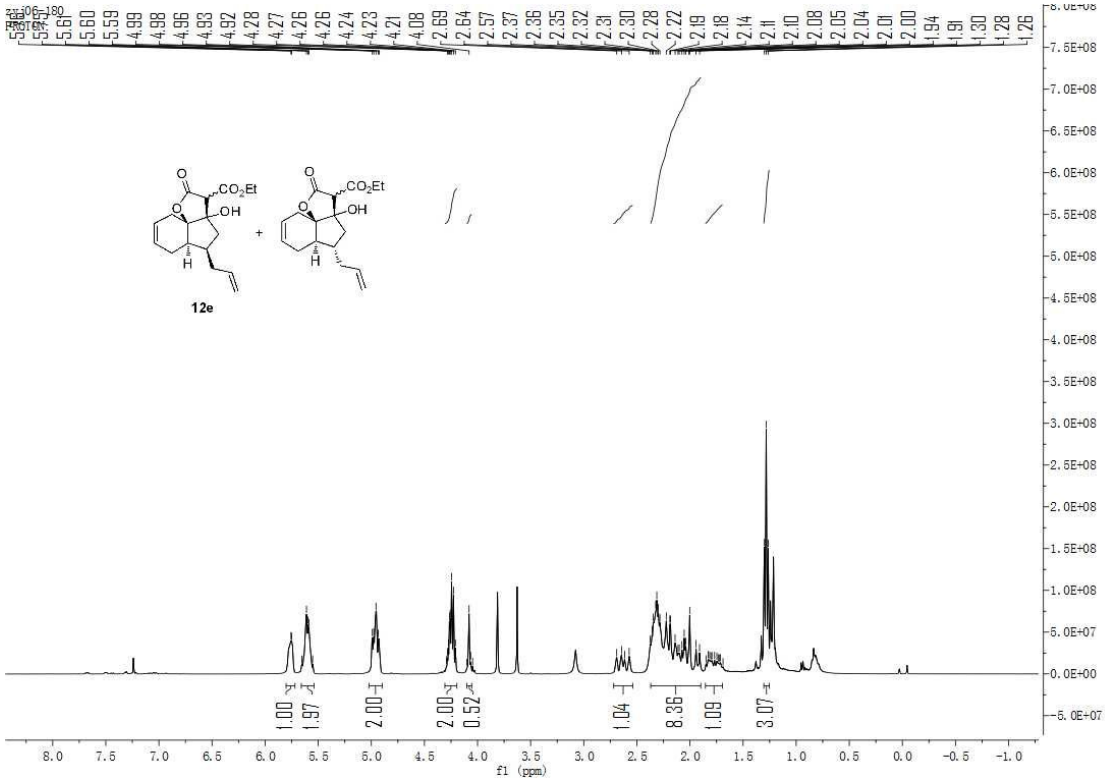
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12d**



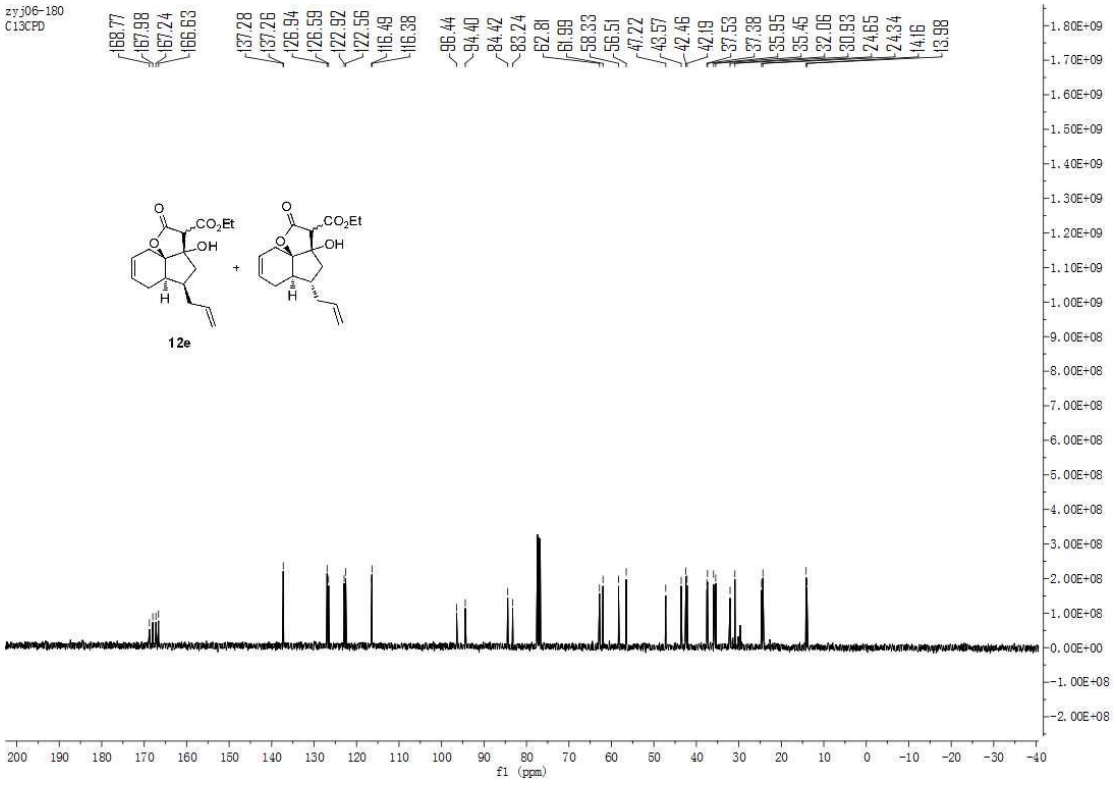
^{13}C NMR (100 MHz, $CDCl_3$) of compound **12d**



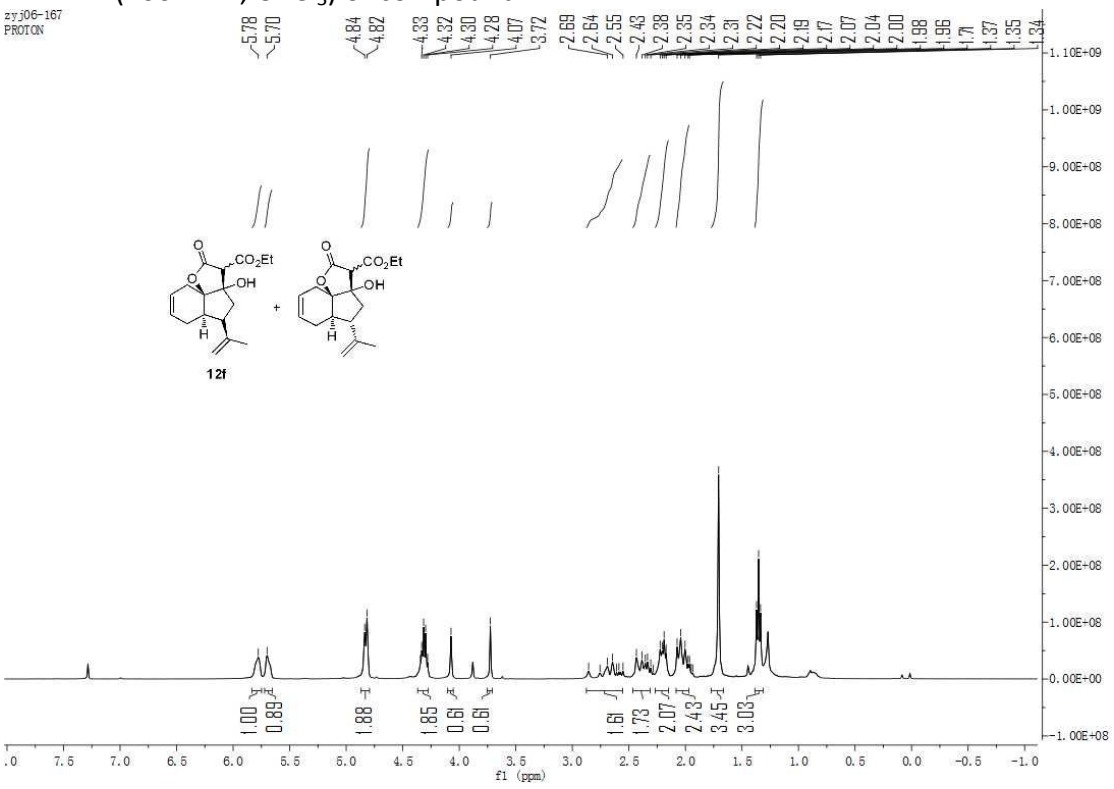
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12e**



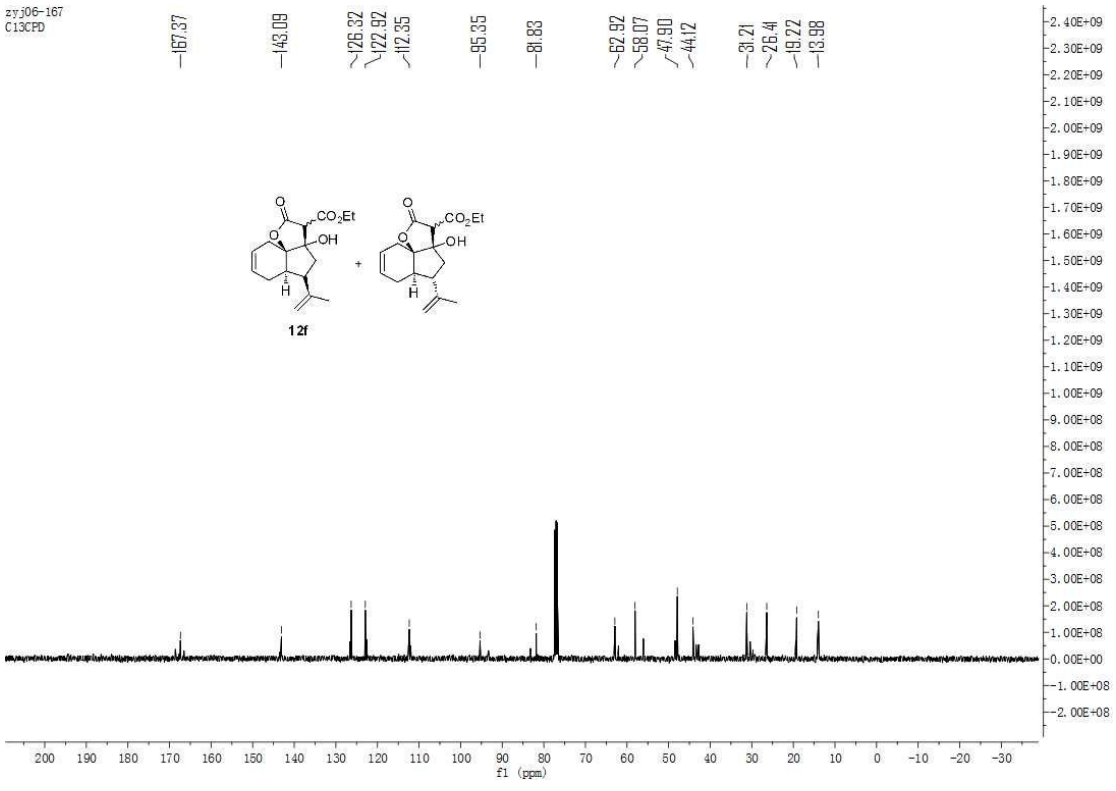
^{13}C NMR (100 MHz, $CDCl_3$) of compound **12e**



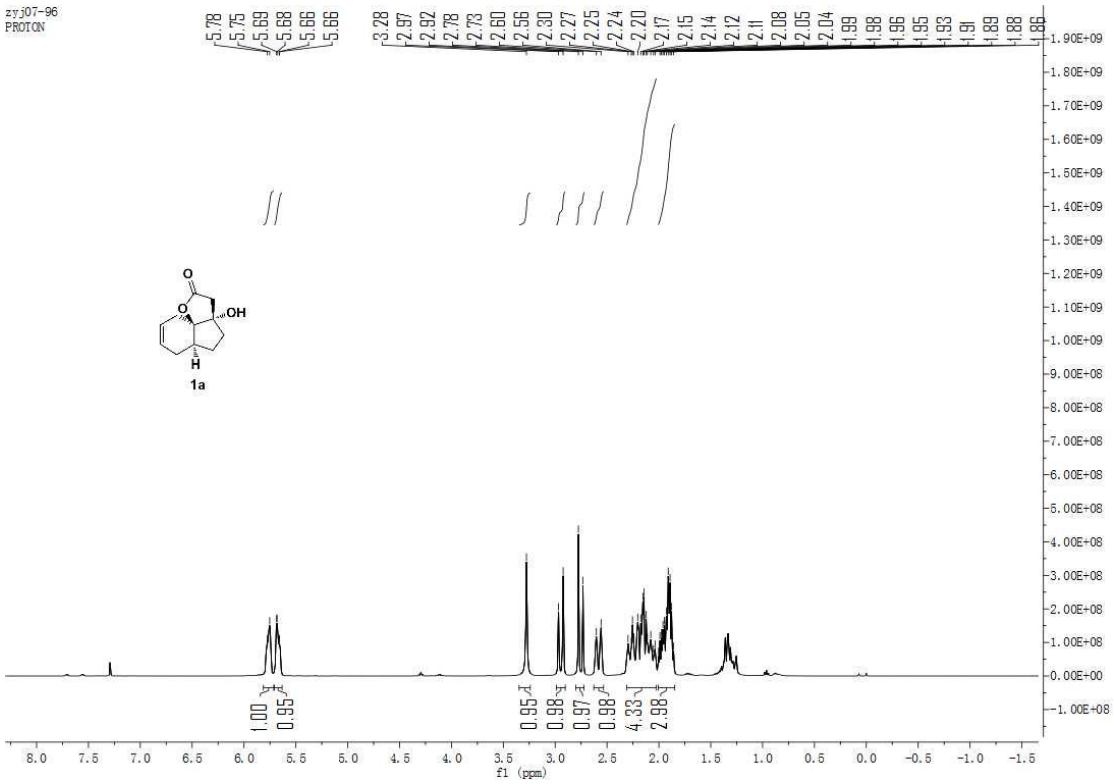
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12f**



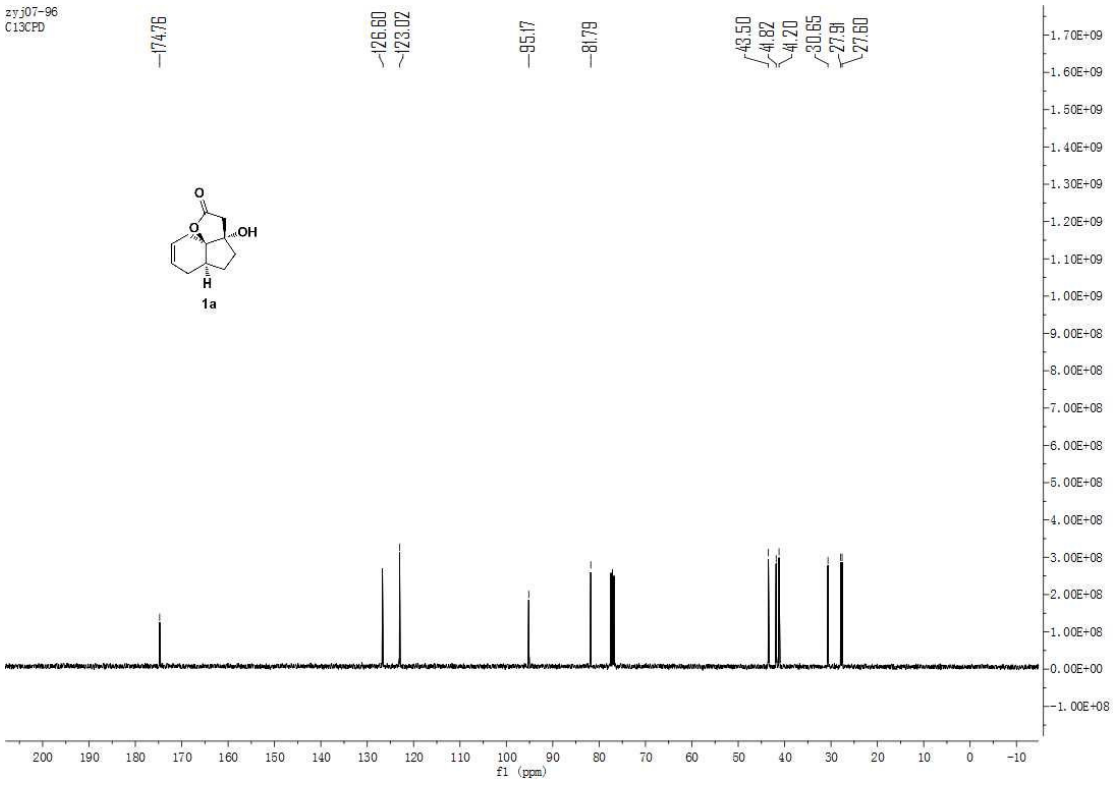
^{13}C NMR (100 MHz, $CDCl_3$) of compound **12f**



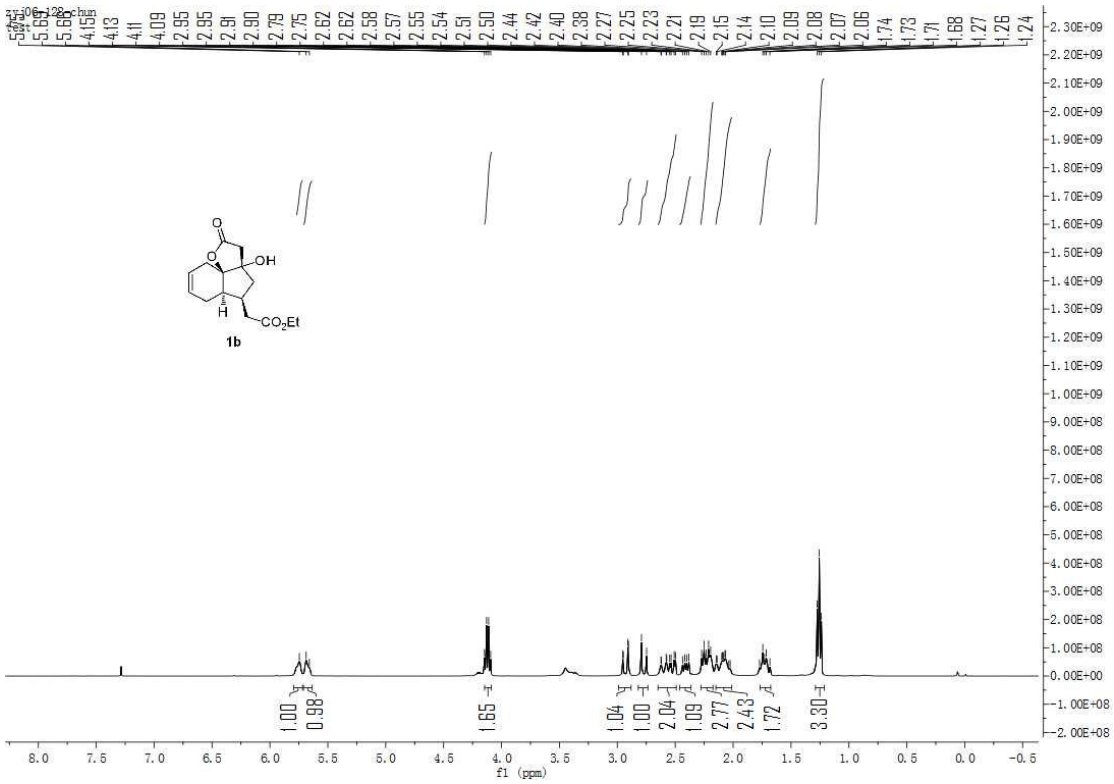
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1a**



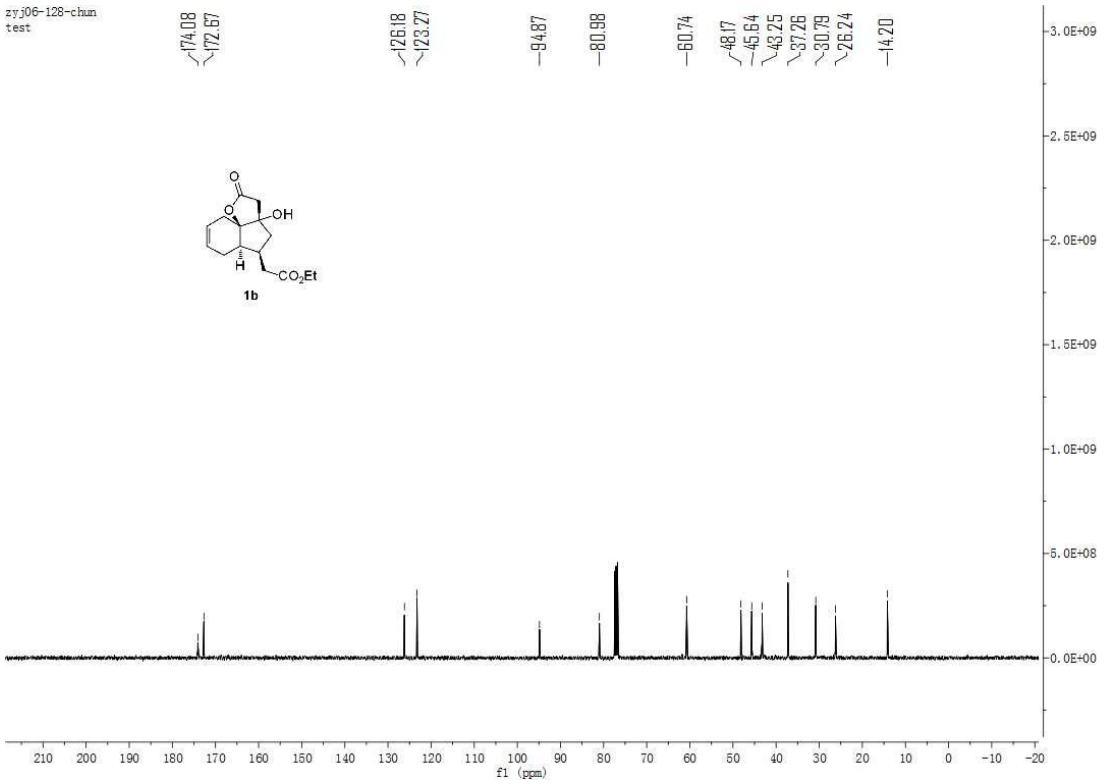
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1a**



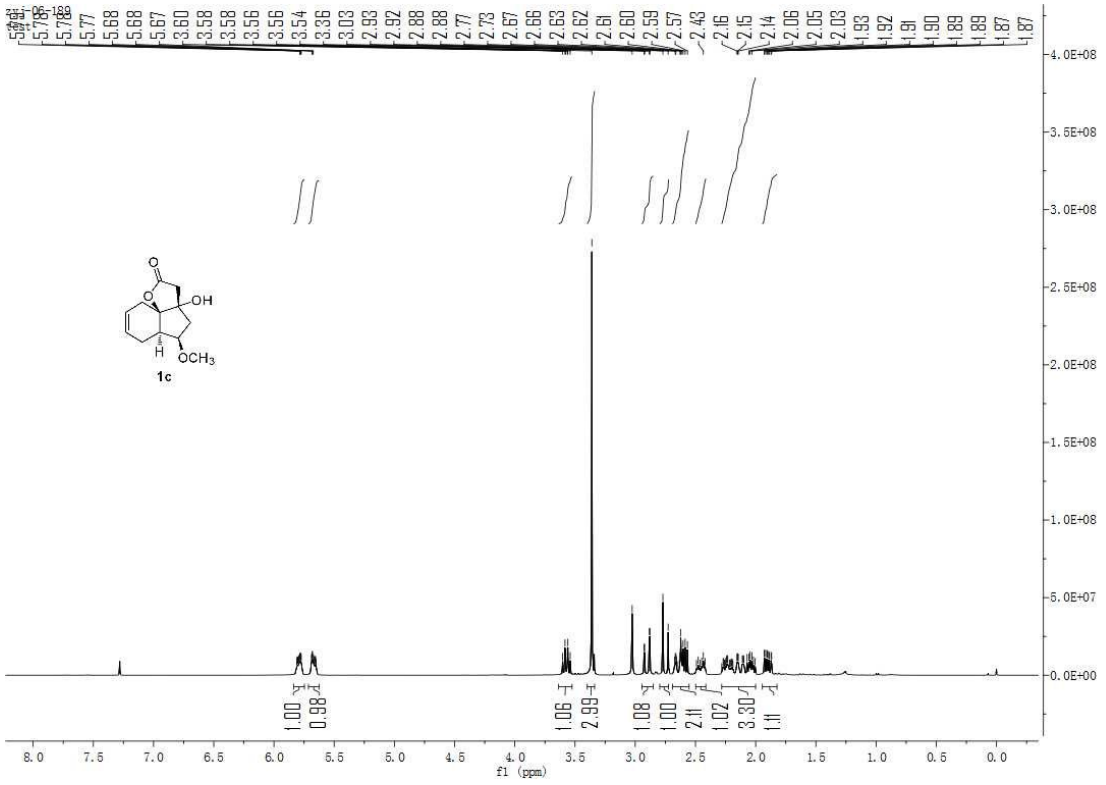
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1b**



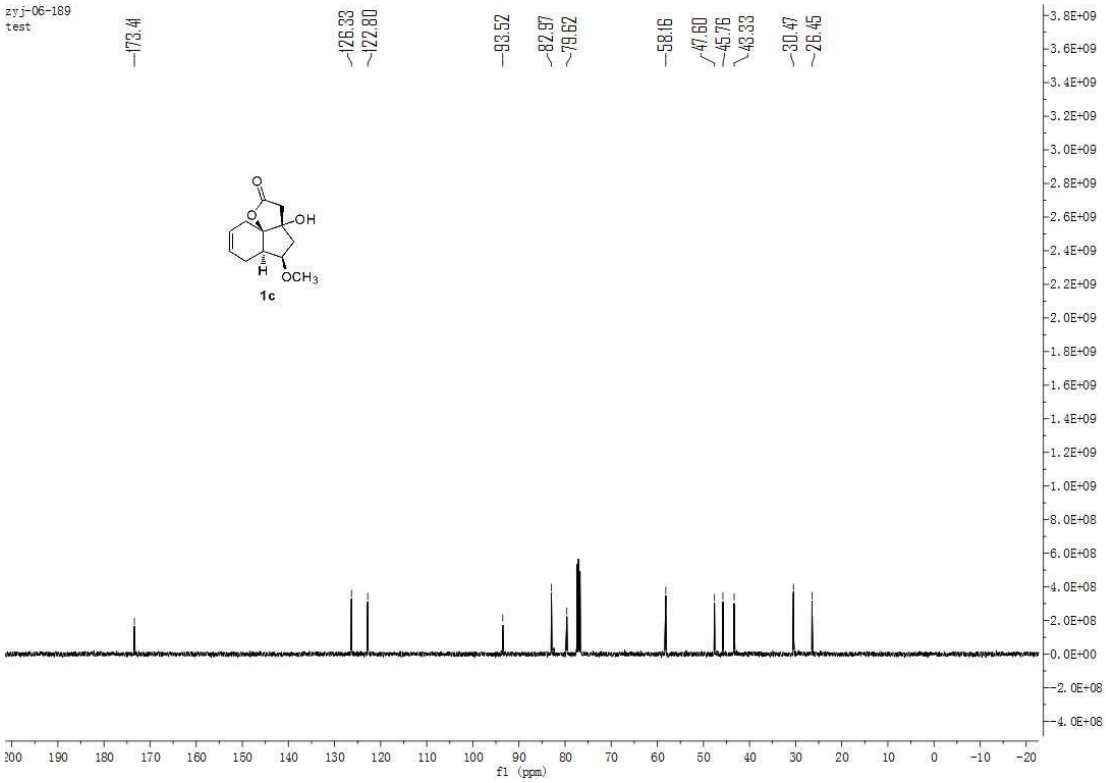
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1b**



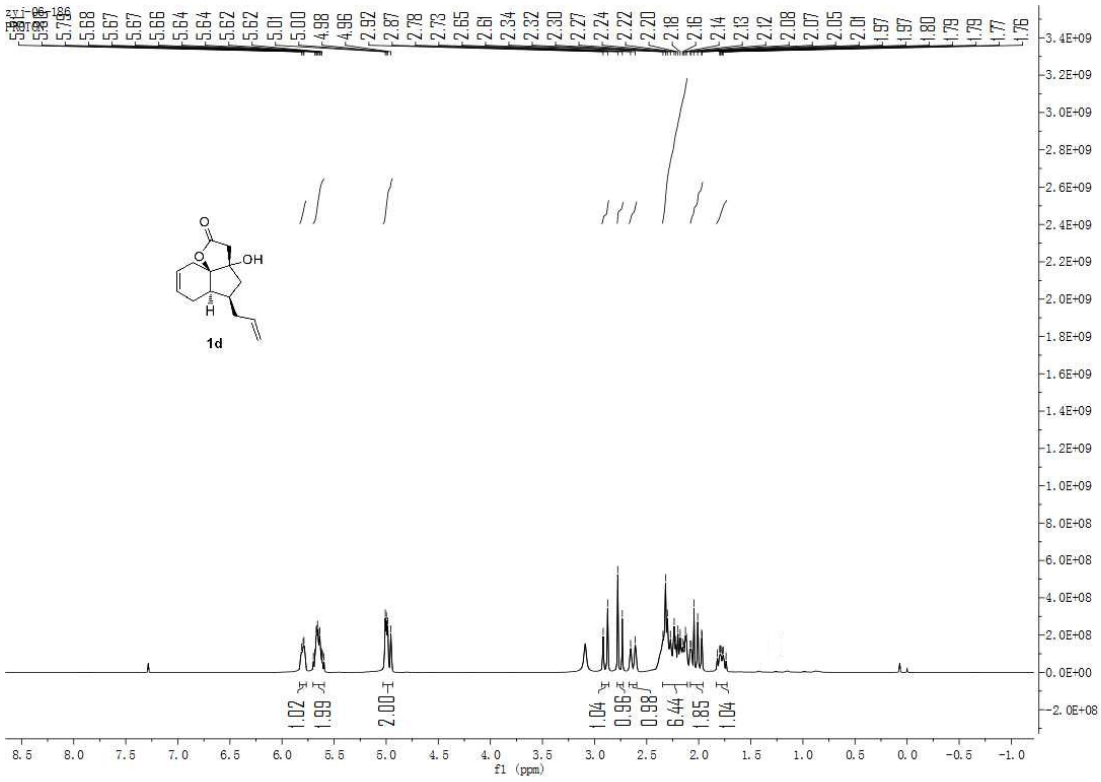
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1c**



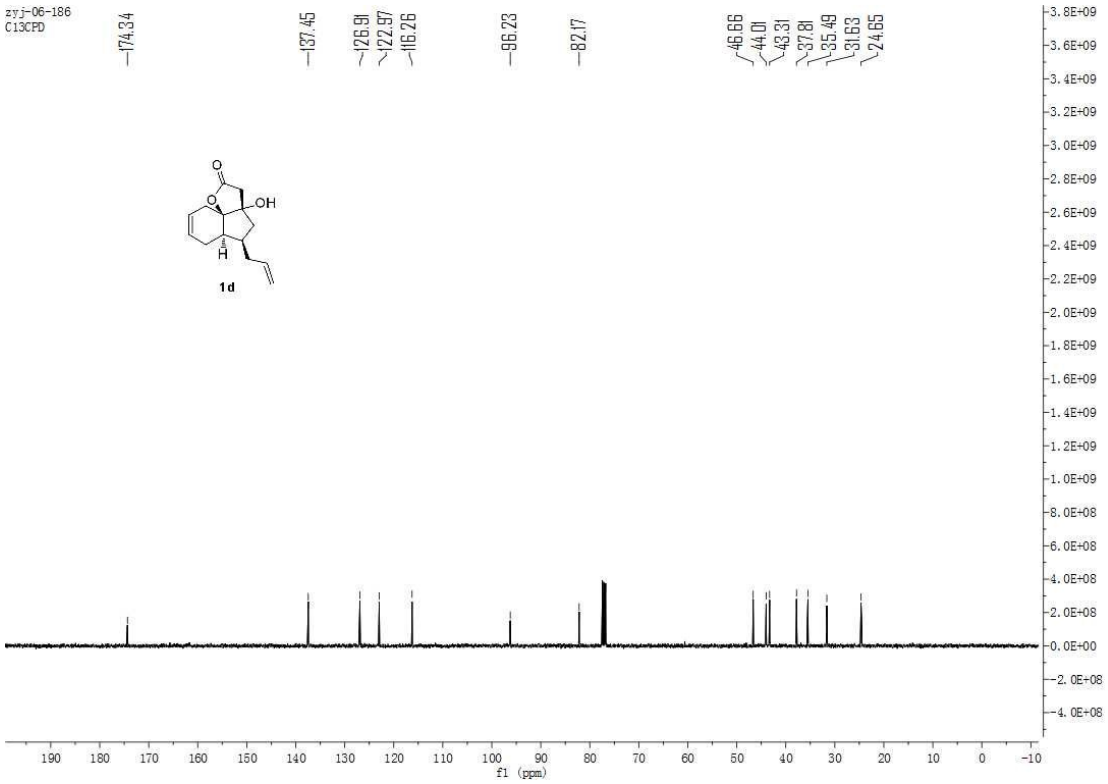
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1c**



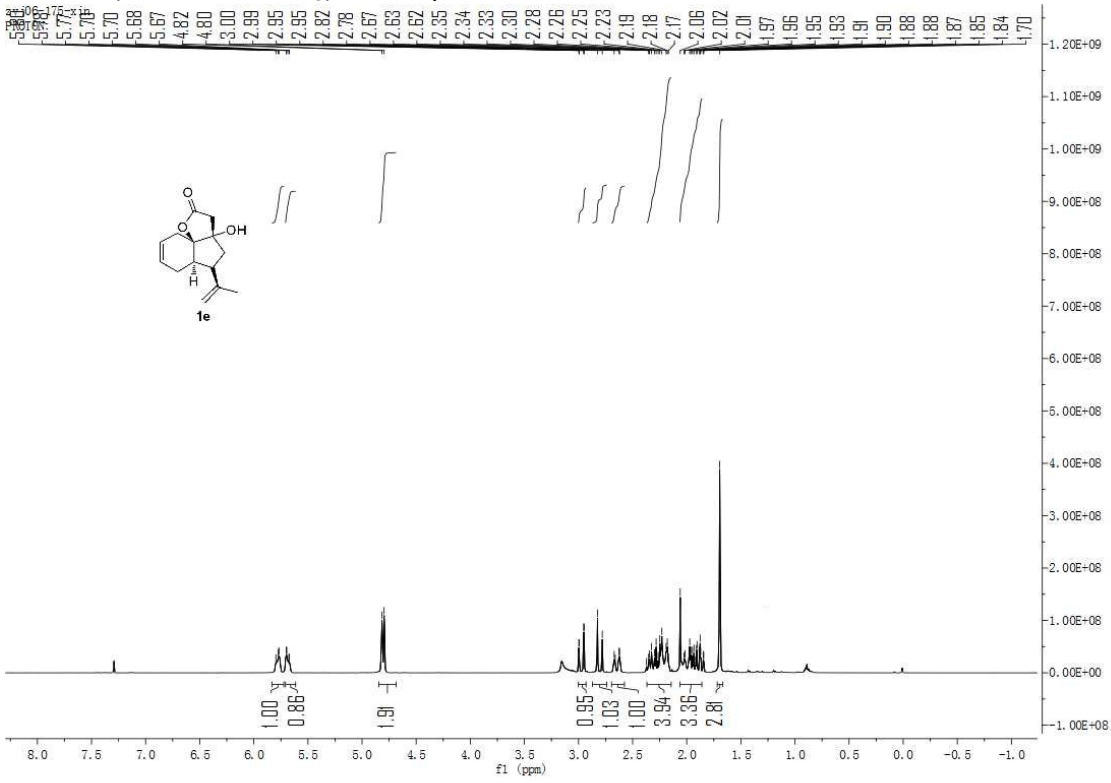
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1d**



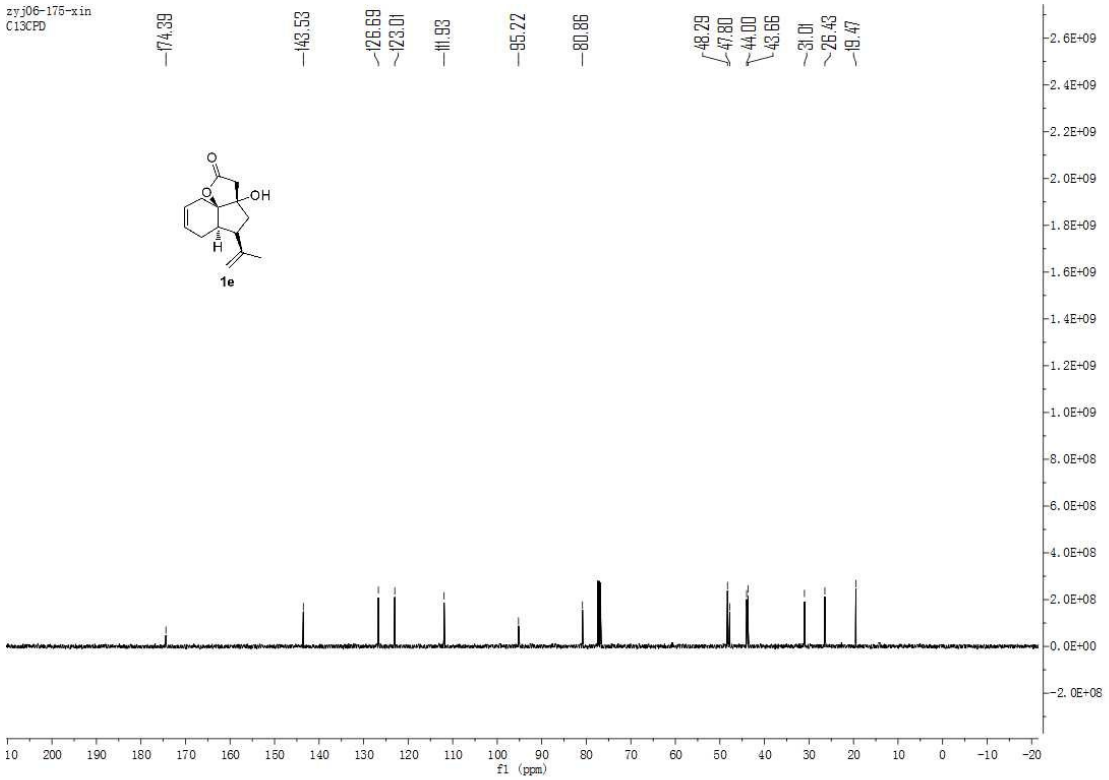
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1d**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **1e**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **1e**



4. Single Crystal Structure of Compound **8a**

The single crystals of compound **8a** were obtained by slowly evaporating the solvent from the solution in mixed solvent of dichloromethane/ether.

Datablock m20170616a1 - ellipsoid plot