Supporting Information for

6,7-seco-*ent*-Kauranoids Derived from Oridonin as Potential Anticancer Agents

Shengtao Xu,[†,#] Hong Yao,[†,#] Mei Hu,[†] Dahong Li,[†,‡] Zheying Zhu,[§] Weijia Xie,[†] Hequan Yao,[†] Liang Wu,[†] Zhe-Sheng Chen,[⊥] and Jinyi Xu*[†]*

[†]State Key Laboratory of Natural Medicines, and Jiangsu Key Laboratory of Drug Screening, China Pharmaceutical University, Nanjing 210009, People's Republic of China

[§]Division of Molecular Therapeutics & Formulation, School of Pharmacy, The University of Nottingham, University Park Campus, Nottingham NG7 2RD, U.K.

[⊥]College of Pharmacy and Health Sciences, St. John's University, Queens, New York, NY 11439, United States

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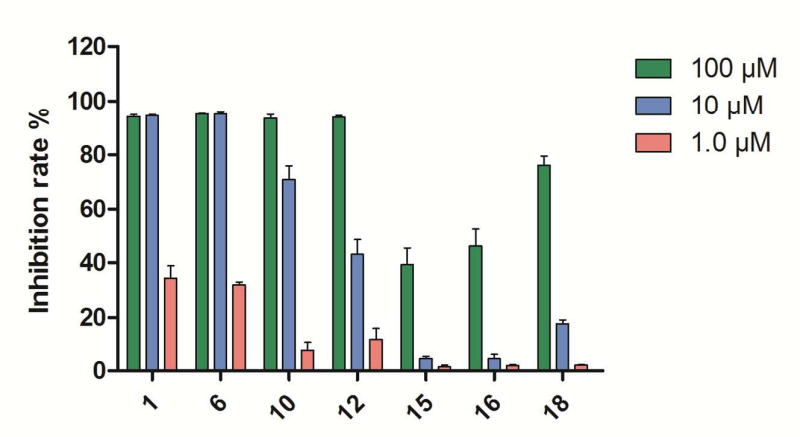


Figure S1. Growth inhibitory effects of compounds **1**, **6**, **10**, **15**, **16** and **18** on human hepatocellular carcinoma Bel-7402 cells. Bel-7402 cells were treated with varying concentrations of indicated compounds for 72 h. Values are the mean ± SD of three independent experiments.

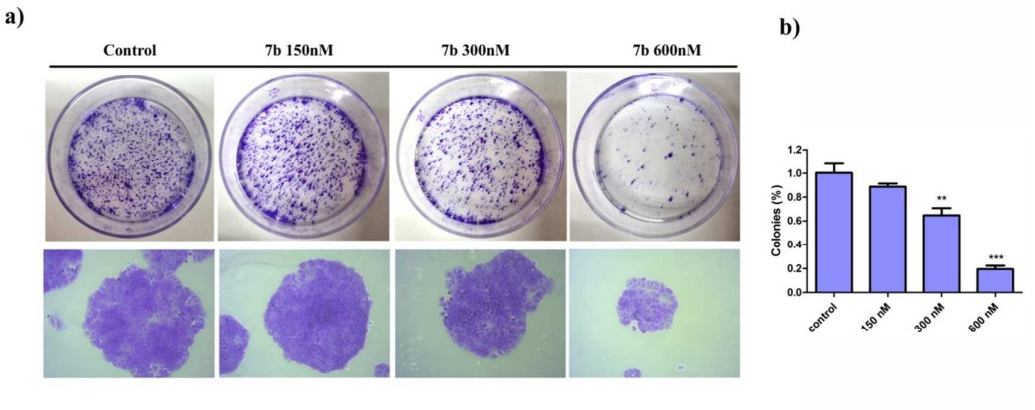


Figure S2. The colony forming ability of MCF-7 cells was inhibited by **7b** treatment. MCF-7 cells were treated with varying concentrations of **7b** (0, 150, 300, and 600 nM) for 10 days and fixed with crystal violet. (a) The photomicrographic differences of colonies were taken of stained single colonies observed under a microscope; (b) Bar chart showing the decreased proportion of the cloned ratio after treatment with **7b**. One colony was defined to be an aggregate of >50 cells.

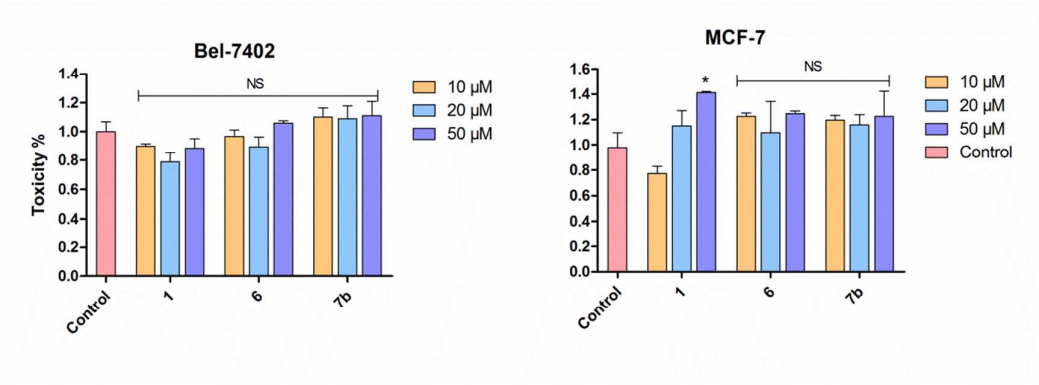


Figure S3. LDH assay of compounds **1**, **6**, and **7b** on Bel-7402 and MCF-7 cells. Cytotoxicity was assayed by LDH assay from culture media of indicated cells which were pretreated with different concentrations (10, 20, and 50 μM) of compounds for 24 h. The data are expressed as percentage of unstimulated cells

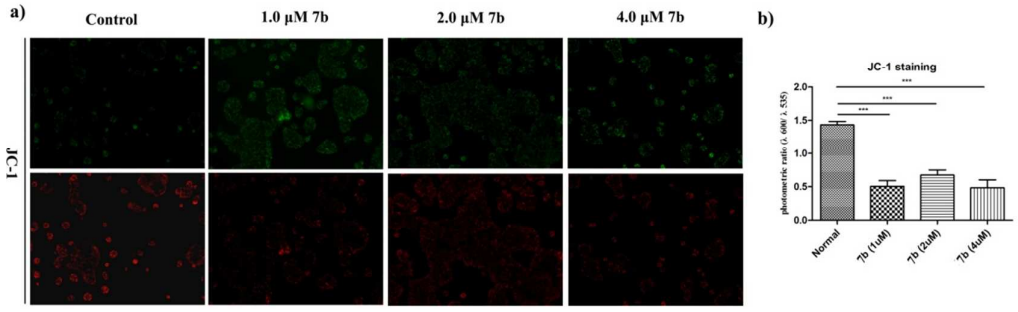


Figure S4. Fluorescence photomicrograph of changes in the MMP after treatment with **7b** for 36 h in MCF-7, **7b** (1.0, 2.0, and 4.0 μM) significantly changed the fluorescence intensity from red to green in treated cells.

Table S1. NMR Spectroscopic Data for Compound **6**[a,b]

Carbon no.	δ_C ppm, type	δ_H ppm (J in Hz)	HMBC[c]
1	122.7 CH	5.47 d (J = 10.53 Hz)	3, 9, 20
2	130.7 CH	6.03 m	3, 19
3	40.8 CH_2	1.91 m	1, 2, 18, 19
4	32.1 C		3, 5, 18, 19
5	58.7 CH	2.33 d (J = 4.59 Hz)	1, 3, 6, 18, 19
6	203.7 CH	9.85 d (J = 4.65 Hz)	5
7	172.8 C		20
8	60.9 C		9, 11, 13, 14
9	47.3 CH	2.25 m	11, 12, 20
10	43.4 C		1, 9, 20
11	18.3 CH_2	1.57 m, 1.47 m	9, 12, 13, 20
12	29.2 CH_2	2.39 m, 1.71 m	11, 14, 17
13	42.6 CH	3.09 d (J = 8.85 Hz)	12, 14(OH), 17
14	72.2 CH	4.60 s	9, 12, 13, 14(OH)
15	198.3 C		9, 13, 14, 17,
16	148.5 C		12, 13, 14, 17
17	122.0 CH_2	6.22 s, 5.62 s	13
18	23.1 CH_3	1.30 s	3, 5, 19
19	30.3 CH_3	1.03 s	3, 5, 18
20	70.5 CH_2	4.74, 4.35, dd (J_A = J_B = 10.89 Hz)	5, 18
OH (14)		5.35 s	

[a] ^{1}H spectra were recorded in $CDCl_3$ at 300 MHz. Assignments were made based on analysis of HMBC and HMQC data. [b]HMBC correlations are from the proton(s) stated to the indicated carbons.

Table S2. NMR Spectroscopic Data for Compound **15**[a,b]

Carbon no.	δ_C ppm, type	δ_H ppm (J in Hz)	HMBC[c]
1	76.3 CH	4.40 m	20, 9, 2, 3,
2	30.7 CH_2	1.53 m, 1.27 m	3, 18
3	22.6 CH_2	1.95 m, 1.78 m	1, 2
4	30.6 C		6, 3, 5, 18, 19
5	53.6 CH	1.90 s	6, 20, 3, 18
6	101.1 CH	5.32 s	20, 5
7	173.0 C		9
8	99.6 C		9, 17, 15(OH)
9	40.7 CH	2.84 m	1, 20, 12, 11
10	46.4 C		6, 20, 9, 5
11	36.8 CH_2	2.26 m, 1.80 m	12, 9
12	22.2 CH_2	2.97 m, 1.70 m	14, 11
13	140.6 C		14, 12, 17, 15(OH)
14	189.5 CH	10.24 s	12

15	175.0	C		9, 11
16	147.0	C		12, 17, 15(OH)
17	12.2	CH_3	2.34 s	
18	32.3	CH_3	1.05 s	3, 19
19	22.9	CH_3	0.96 s	3
20	73.7	CH_2	4.02, 3.75, dd (J_A =J_B = 9.0Hz)	6, 1, 9, 5
OH (15)			13.99 s	

[a] ^{1}H spectra were recorded in $CDCl_3$ at 300 MHz. Assignments were made based on analysis of HMBC and HMQC data. [b]HMBC correlations are from the proton(s) stated to the indicated carbons.

Table S3. IC_{50}[a] Values (μM) of Representative Compounds in the Drug-resistant and Drug-sensitive Cancer Cells[b].

Compounds	IC_{50} (μM)					
	KB-3-1	KB /CP4	NCI-H460	NCI-H460 /MX20	Bel-7404	Bel-7404 /CP20
1	13.2	10.8	20.5	25.9	17.9	17.2
6	16.9	9.6	12.7	18.1	16.3	16.8
7b	26.8	6.6	9.2	8.5	8.9	23.8
Cisplatin	2.6	9.4	/	/	2.9	22.8

[a]MTT method, cells were incubated with indicated compounds for 48 h, the values are the means of three independent experiments. [b]MTT cytotoxicity assay was assessed in pairs of drug-sensitive and drug-resistant cancer cell lines: KB-3-1, human cervix carcinoma; KB/CP4, cisplatin resistant; NCI-H460, human lung carcinoma; NCI-H460/MX20, mitoxantrone resistant; Bel-7404, human hepatocellular carcinoma; Bel-7404/CP20, cisplatin resistant.

General procedure for the synthesis of compounds 2-18

*ent-1α,6β-Dihydroxy-7,14-isopropylideneketal-15-oxo-7,20-epoxy-16-kaurene (**2**).* Compound **1** (2 g, 5.49 mmol) was dissolved in anhydrous acetone (30 mL), and a catalytic amount of TsOH and 3 mL 2,2-dimethoxypropane were added to this solution. The mixture was stirred at 56 °C for 30 min, then diluted with water and extracted with dichloromethane. The extract was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to afford compound **2** (2.10 g, 95%) as a white powder: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.15 (1H, s), 5.78 (1H, d, J = 8.1 Hz), 5.56 (1H, s), 4.80 (1H, d, J = 1.2 Hz), 4.24, 4.04 (each 1H , dd, J_A = J_B = 10.2 Hz), 3.90 (1H, m), 3.47 (1H, m), 3.06 (1H, d, J = 9.0 Hz), 2.50 (1H, m), 2.08 (1H, m), 1.91 (2H, m), 1.73 (3H, m), 1.68 (2H, m), 1.67 (3H, s), 1.44 (1H, m), 1.37 (3H, s), 1.28 (3H, s), 1.14 (3H, s); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 206.3, 151.5, 119.7, 100.1, 94.6, 72.7, 72.4, 70.0, 62.8, 58.8, 56.3, 50.5, 40.5, 38.7, 33.4, 30.4, 29.2, 25.8, 22.4, 19.6; ESIMS *m/z* 405.2 $[M+H]^+$, 439.4 $[M+Cl]^-$.

*ent-(1α-O-methylsulfonyl)-6β-hydroxy-7,14-isopropylideneketal-15-oxo-7,20-epoxy-16-kaurene (**3**).* To a solution of compound **2** (2.10 g, 5.19 mmol) in 20 mL of anhydrous CH_2Cl_2 was added 3 mL triethylamine at 0 °C. Methylsulfonyl chloride (2 mL) was added dropwisely into the solution within 1 hour, then the mixture was allowed to stir for another 1 h. The mixture was quenched with water and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to yield a crude product, which was purified by column chromatography (MeOH/CH_2Cl_2 1:100, v/v) to obtain pure compound **3** (2.01 g, 80%) as a white solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.17(1H, s), 5.79 (1H, d, J = 12.0 Hz), 5.58 (1H, s), 4.75 (1H, d, J = 1.2 Hz), 4.60 (1H, m), 4.14 (s, 2H), 3.93 (1H, m), 3.07 (1H, d, J = 9.3 Hz), 2.99 (3H, s), 2.51 (1H, m), 2.07 (1H, m), 1.89 (2H, m), 1.76 (3H, m), 1.59 (3H, s), 1.50 (1H, m), 1.42 (2H, m), 1.33 (3H, s), 1.19 (3H, s), 1.18 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 204.7, 149.9, 120.0, 100.6, 84.2, 72.5, 69.4, 61.9, 59.0, 52.3, 49.5, 40.2, 39.7, 37.8, 32.7, 32.4, 29.7, 29.6, 25.9, 24.9, 21.9, 18.3; ESIMS *m/z* 483.2$[M+H]^+$; HRESIMS *m/z* 505.1873 $[M+Na]^+$ (calcd for $C_{24}H_{34}NaO_8S$ 505.1867).

*ent-6β-Hydroxy-7,14-isopropylideneketal-15-oxo-7,20-epoxy-1-alkene-16-kaurene (**4**).* To a solution of compound **3** (2.01 g, 4.17 mmol) in 20 mL anhydrous dimethyl formamide (DMF) was added lithium carbonate (3.08 g, 41.65 mmol) and lithium bromide (3.62 g, 41.65 mmol). The mixture was stirred violently at 110 °C for 1 h and then cooled to room temperature. After the inorganic precipitate was filtered off, the reaction mixture was diluted with 150 mL CH_2Cl_2 and then washed with water (20 mL × 3) and brine (20 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to yield a crude product, which was purified by column chromatography using CH_2Cl_2 to obtain pure compound **4** (1.21 g, 75 %) as a white solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.09 (1H, s), 5.68 (1H, m), 5.49 (1H, s), 5.31 (1H, d, J = 12.0 Hz), 5.11 (1H, dd, J=10.2, 2.5 Hz), 4.75 (1H, s), 3.91, 3.73 (each 1H, dd, $J_A = J_B$ = 9.9 Hz), 3.81 (1H, m), 3.00 (1H, d, J = 6.0 Hz), 2.46 (1H, m), 1.85 (1H, m), 1.67 (4H, m), 1.58 (3H, s), 1.52 (2H, m), 1.28 (3H, s), 1.11 (3H, s), 0.98 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.8, 150.3, 129.8, 123.7, 119.8, 86.1, 71.5, 69.6, 64.3, 57.5, 48.6, 40.7, 39.8, 37.7, 31.7, 30.6, 29.8, 29.7, 25.0, 21.6, 16.8; ESIMS *m/z* 387.2 $[M+H]^+$; HRESIMS *m/z* 409.1989 $[M+Na]^+$ (calcd for $C_{23}H_{30}NaO_5$ 409.1985).

*ent-6β,7β,14β-Trihydroxy-15-oxo-7,20-epoxy-1-alkene-16-kaurene (**5**).* Compound **4** (1.21 g, 3.13 mmol) was added to 20 ml of 10% HCl/THF (1:1) and the solution was stirred at room temperature for 1h. Then the mixture was diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give compound **5** (0.98 g, 90%) as a white powder: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.14 (1H, s), 6.03 (1H, s), 5.96 (1H, S), 5.74 (1H, m), 5.63 (1H, S), 5.52 (1H, d, J = 10.8 Hz), 5.22 (1H, dd, J = 10.5, 2.4 Hz), 4.78 (1H, s), 3.83, 3.72 (each 1H, dd, $J_A = J_B$ = 9.9 Hz), 3.58 (1H, m), 2.91 (1H, d, J = 9.3 Hz), 2.42 (1H, m), 1.88 (2H, m), 1.80 (1H, m), 1.62 (1H, m), 1.52 (1H, m), 1.47 (1H, m), 1.38 (1H, m), 1.05 (3H, s), 0.96 (3H, s); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 207.0, 151.5, 129.4, 124.9, 120.4, 97.4, 72.3, 72.1, 64.2, 61.4, 58.3, 51.6, 42.6, 40.6,

37.8, 31.9, 30.7, 29.6, 21.6, 17.0; ESIMS *m/z* 347.2 $[M+H]^+$; HRESIMS *m/z* 369.1679 $[M+Na]^+$ (calcd for $C_{20}H_{26}NaO_5$ 369.1672).

*ent-6,7,15-Trioxo-7,20-epoxy-14β-hydroxy-1-alkene-6,7-seco-16-kaurene (**6**).* To a solution of compound **5** (200 mg, 0.58 mmol) in 20 mL of THF was added lead tetraacetate (0.51 g, 1.15 mmol) and potassium carbonate (40 g, 2.89 mmol). The mixture was stirred at room temperature for 5 min, after the inorganic precipitate was filtered off, the reaction mixture was diluted with 50 mL CH_2Cl_2 and then washed with water (20 mL × 3) and brine (10 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to yield a crude product, which was purified by column chromatography ($MeOH/CH_2Cl_2$ 1:150, v/v) to obtain pure compound **2** (165 mg, 83%) as a white solid: ^1H NMR ($CDCl_3$, 300 MHz) δ 9.85 (1H, d, J = 4.65 Hz), 6.22 (1H, s), 6.03 (1H, m), 5.62 (1H, s), 5.47 (1H, d, J = 10.53 Hz), 5.35 (1H, s), 4.60 (1H, s), 4.74, 4.35 (each 1H, dd, $J_A = J_B$ = 10.89 Hz), 3.09 (1H, d, J = 8.85 Hz), 2.39 (1H, m), 2.33 (1H, d, J = 4.59 Hz), 2.25 (1H, m), 1.91 (2H, m), 1.71 (1H, m), 1.57 (1H, m), 1.47 (1H, m), 1.30 (3H, s), 1.03 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.7, 198.3, 172.8, 148.5, 130.7, 122.7, 122.0, 72.2, 70.5, 60.9, 58.7, 47.3, 43.4, 42.6, 40.8, 32.1, 30.3, 29.2, 23.1, 18.3; ESIMS *m/z* 345.2 $[M+H]^+$; HRESIMS *m/z* 367.1520 $[M+Na]^+$ (calcd for $C_{20}H_{24}NaO_5$ 367.1516).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-propionyl)-1-alkene-6,7-seco-16-kaurene (**7a**).* Compound **6** (72 mg, 0.2 mmol) was dissolved in dichloromethane, then EDCI, DMAP and propionic acid (15 mg, 0.24 mmol) were added. The reaction mixture was stirred at room temperature for about 2 h. Then the mixture was washed with 10% HCl. The organic layer was washed with brine, dried over anhydrous Na_2SO_4. After flash chromatography ($MeOH/CH_2Cl_2$ 1: 300, v/v), compound **7a** was obtained as a white solid (48 mg, 66%): ^1H NMR ($CDCl_3$, 300 MHz) δ 9.90 (1H, d, J = 4.8 Hz), 6.16 (1H, s), 5.99 (1H, m), 5.67 (1H, s), 5.48 (1H, d, J = 5.4 Hz), 5.40 (1H, br), 4.81, 4.62 (each1H, dd, $J_A = J_B$ = 10.8 Hz), 3.17 (1H, d, J = 8.7 Hz), 2.36 (3H, m), 2.01 (2H, m), 1.91 (2H, m), 1.44 (3H, m), 1.59 (3H, m), 1.30 (3H, s), 1.03 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.7, 198.3, 172.8, 148.5, 130.7, 122.7, 122.0, 72.2, 70.5, 60.9, 58.7, 47.3, 43.4, 42.6, 40.8, 32.1, 30.3, 29.2, 23.1, 18.3; ESIMS *m/z* 401.2 $[M+H]^+$; HRESIMS *m/z* 423.1785 $[M+Na]^+$ (calcd for $C_{23}H_{28}NaO_6$ 423.1778).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-p-florobenzoyl)-1-alkene-6,7-seco-16-kauren e (7**b**).* Following the procedure described for preparation of compound **7a**, compound **7b** was obtained as a white solid (yield 69%): ^1H NMR ($CDCl_3$, 300 MHz) δ 9.91 (1H, d, J = 5.7 Hz), 7.85 (2H, m), 6.98 (2H, t, J = 8.4 Hz), 6.21 (1H, s), 5.99 (1H, m), 5.67 (2H, m), 5.47 (1H, s), 4.85, 4.60 (each 1H, dd, $J_A = J_B$ = 10.8 Hz), 3.32 (1H, s), 2.27 (1H, m), 2.21 (1H, m), 1.97 (1H, d, J = 5.7 Hz), 1.88 (3H, m), 1.59 (3H, m), 1.18 (3H, s), 0.91 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.6, 197.4, 167.8, 144.5, 132.9, 132.8, 132.6, 132.5, 131.7, 126.6, 119.6, 115.6, 75.7, 67.4, 62.9, 61.1, 45.5, 43.5, 43.2, 40.1, 32.5, 31.2, 30.1, 22.5, 17.8; ESIMS *m/z* 467.2 $[M+H]^+$; HRESIMS (ESI) *m/z* 489.1682 $[M+Na]^+$ (calcd for $C_{27}H_{27}NaFO_6$ 489.1684).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-m-nitrylphenylvinoyl)-1-alkene-6,7-seco-16-k aurene (7**c**)*. Following the procedure described for preparation of compound **7a**, compound **7c** was obtained as a white solid (yield 76%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.91 (1H, d, J = 5.4 Hz), 8.24 (1H, s), 8.15 (1H, d, J = 8.1 Hz), 7.71 (1H, d, J = 8.1 Hz), 7.56, 6.41 (each 1H, dd, $J_A = J_B$ = 15.6 Hz), 7.52 (1H, t, J = 8.1 Hz), 6.20 (1H, s), 5.99 (1H, m), 5.69 (1H, d, J = 8.1 Hz), 5.68 (1H, s), 5.49 (1H, s), 4.85, 4.63 (each 1H, dd, $J_A = J_B$ = 10.8 Hz), 3.28 (1H, s), 2.27 (1H, m), 2.21 (1H, m), 1.97 (1H, d, J = 5.7 Hz), 1.87 (3H, m), 1.47 (2H, m), 1.21 (3H, s), 0.96 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.7, 197.4, 165.9, 143.7, 135.7, 133.8, 131.6, 130.0, 126.6, 124.9, 122.7, 119.8, 119.7, 75.7, 67.4, 62.9, 61.1, 45.5, 43.5, 43.0, 40.1, 32.5, 31.3, 30.1, 22.5, 17.8; ESIMS *m/z* 520.2 $[M+H]^+$; HRESIMS *m/z* 542.1786 $[M+Na]^+$ (calcd for $C_{29}H_{29}NNaO_8$ 542.1785).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-m-methylbenzoyl)-1-alkene-6,7-seco-16-kaurene (7**d**)*. Following the procedure described for preparation of compound **7a**, compound **7d** was obtained as a white solid (yield 72%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.91 (1H, d, J = 5.7 Hz), 7.63 (2H, m), 7.26 (1H, m), 7.17 (1H, m), 6.20 (1H, s), 6.00 (1H, m), 5.67 (2H, m), 5.47 (1H, s), 4.85, 4.64 (each 1H, dd, $J_A = J_B$ = 10.8 Hz), 3.32 (1H, s), 2.27 (4H, m), 2.21 (1H, m), 1.96 (1H, d, J = 5.7 Hz), 1.88 (3H, m), 1.59 (2H, m), 1.18 (3H, s), 0.91 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.7, 197.6, 167.7, 144.6, 138.2, 134.4, 131.5, 130.3, 128.3, 127.1, 126.7, 119.4, 75.6, 67.3, 63.0, 61.2, 45.6, 43.5, 43.2, 40.1, 32.5, 31.3, 30.1, 22.4, 21.2, 17.8; ESIMS *m/z* 463.2 $[M+H]^+$; HRESIMS *m/z* 485.1936 $[M+Na]^+$ (calcd for $C_{28}H_{30}NaO_6$ 485.1935).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-p-nitrylbenzoyl)-1-alkene-6,7-seco-16-k aurene (7**e**)*. Following the procedure described for preparation of compound **7a**, compound **7e** was obtained as a white solid (yield 67%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.91 (1H, d, J = 5.7 Hz), 8.18 (2H, d, J = 8.7 Hz), 8.00 (2H, d, J = 8.7 Hz), 6.24 (1H, s), 6.02 (1H, m), 5.77 (1H, s), 5.71 (1H, d, J = 11.5 Hz), 5.52 (1H, s), 4.85, 4.64 (each 1H dd, $J_A = J_B$ = 10.8 Hz), 3.35 (1H, s), 2.27 (1H, m), 2.16 (1H, m), 1.96 (1H, d, J = 5.7 Hz), 1.86 (3H, m), 1.53 (2H, m), 1.18 (3H, s), 0.93 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.5, 197.0, 164.6, 144.3, 134.2, 131.8, 131.1, 126.3, 123.6, 120.0, 76.5, 67.6, 62.7, 61.0, 45.6, 43.4, 43.0, 40.1, 32.5, 31.2, 30.1, 22.4, 17.8; ESIMS *m/z* 494.2 $[M+H]^+$; HRESIMS *m/z* 516.1627 $[M+Na]^+$ (calcd for $C_{27}H_{27}NNaO_8$ 516.1629).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-acetyl)-1-alkene-6,7-seco-16-kaurene (7**f**)*. Following the procedure described for preparation of compound **7a**, compound 7**f** was obtained as a withe solid (yield 78%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.90 (1H, d, J = 4.8 Hz), 6.16 (1H, s), 5.99 (1H, m), 5.64 (1H, d, J = 5.4 Hz), 5.47 (1H, s),5.44 (1H, s), 4.83, 4.59 (each 1H, dd, $J_A = J_B$ = 10.8 Hz), 3.17 (1H, d, J = 8.7 Hz), 2.16 (3H, m), 1.99 (2H, m), 1.91 (4H, m), 1.44 (3H, m), 1.59 (2H, m), 1.21 (3H, s), 0.91 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202.7, 196.4, 170.3, 166.7, 143.3, 130.4, 125.6, 118.4, 74.1, 66.2, 61.9, 60.1, 44.2, 42.3, 41.8, 39.0, 31.4, 30.2, 29.1, 28.6, 21.3, 19.8, 16.6; ESIMS

m/z 387.2 $[M+H]^+$; HRESIMS *m/z* 387.1811 $[M+H]^+$ (calcd for $C_{22}H_{27}O_6$ 387.1802).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-valeryl)-1-alkene-6,7-seco-16-kaurene (**7g**).* Following the procedure described for preparation of compound **7a**, compound **7g** was obtained as a white solid (yield 82%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.94 (1H, d, J = 4.8 Hz), 6.19 (1H, s), 6.01 (1H, m), 5.69 (J = 5.4 Hz, 1H, d), 5.53 (1H, s), 5.48 (1H, s), 4.86, 4.66 (each 1H, dd, $J_A = J_B$ = 10.8 Hz), 3.21 (1H, d, J = 8.7 Hz), 2.21 (3H, m), 2.12 (1H, m), 1.97 (1H, m), 1.79 (3H, m), 1.47 (4H, m), 1.29 (7H, m), 0.95 (3H, s), 0.82 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.2, 197.0, 173.7, 167.0, 144.0, 130.9, 126.2, 118.8, 74.5, 66.7, 62.5, 60.7, 44.8, 42.9, 42.4, 39.6, 32.0, 29.6, 25.9, 21.6, 17.2, 13.1; ESIMS *m/z* 429.2 $[M+H]^+$; HRESIMS *m/z* 429.2282 $[M+H]^+$ (calcd for $C_{25}H_{33}O_6$ 429.2272).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-2-pyrazineyl)-1-alkene-6,7-seco-16-kaur ene (**7h**).* Following the procedure described for preparation of compound **7a**, compound **7h** was obtained as a white solid (yield 56%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.90 (1H, d, J = 5.7 Hz), 9.06 (1H, d, J = 1.2 Hz), 8.65 (2H, dd, J = 9.0, 1.2 Hz), 6.24 (1H, s), 6.03 (1H, m), 5.83 (1H, s), 5.72 (1H, d, J = 11.5 Hz), 5.54 (1H, s), 4.87, 4.66 (each 1H dd, $J_A = J_B$ = 10.8 Hz), 3.41 (1H, s), 2.27 (1H, m), 2.15 (1H, m), 1.98 (1H, d, J = 5.7 Hz), 1.86 (3H, m), 1.53 (2H, m), 1.18 (3H, s), 0.93 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202.7, 197.0, 164.6, 146.9, 145.4, 143.6, 130.7, 125.3, 125.3, 119.2, 76.5, 66.4, 61.6, 44.5, 42.3, 41.8, 39.0, 31.4, 30.1, 29.1, 27.7, 24.6, 21.4, 16.7; ESIMS *m/z*: 451.2 $[M+H]^+$; HRESIMS *m/z* 451.1874 $[M+H]^+$ (calcd for $C_{25}H_{27}N_2O_6$ 451.1864).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-phenylvinoyl)-1-alkene-6,7-seco-16-kaurene (**7i**).* Following the procedure described for preparation of compound **7a**, compound **7i** was obtained as a white solid (yield 73%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.99 (1H, d, J = 5.7 Hz), 7.63 (1H, d, J = 15.3 Hz), 7.49 (2H, m), 7.32 (3H, m), 6.36 (1H, d, J = 15.3 Hz), 6.26 (1H, s), 6.05 (1H, m), 5.80 (1H, d, J = 11.2 Hz), 5.69 (1H, s), 5.53 (1H, s), 4.92, 4.74 (each 1H, dd, $J_A = J_B$ = 10.8 Hz), 3.33 (1H, s), 2.04 (1H, m), 2.01 (1H, m), 1.91 (1H, d, J = 5.7 Hz), 1.86 (3H, m), 1.53 (2H, m), 1.26 (3H, s), 0.99 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.2, 197.0, 166.8, 166.3, 146.2, 144.1, 130.9, 128.4, 127.9, 126.3, 118.9, 116.0, 74.8, 66.8, 62.3, 60.7, 45.0, 43.0, 42.6, 39.6, 30.8, 29.2, 21.9, 17.3; ESIMS *m/z* 475.2 $[M+H]^+$; HRESIMS *m/z*: 475.2123 $[M+H]^+$ (calcd for $C_{29}H_{31}O_6$ 475.2115).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-2-furanyl)-1-alkene-6,7-seco-16-kaurene (**7j**).* Following the procedure described for preparation of compound **7a**, compound **7j** was obtained as a white solid (yield 81%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.96 (1H, d, J = 5.7 Hz), 7.55 (1H, d, J = 2.7 Hz), 7.13 (2H, d, J = 2.7 Hz), 6.45 (1H, m), 6.26 (1H, s), 6.04 (1H, m), 5.77 (2H, m), 5.49 (1H, s), 4.89, 4.66 (each1H, dd, $J_A = J_B$ = 10.8 Hz), 3.37 (1H, s), 2.30 (1H, m), 2.16 (1H, m), 1.96 (1H, d, J = 5.7 Hz), 1.87 (3H, m), 1.53 (2H, m), 1.22 (3H, s), 0.98 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.7, 197.8, 166.9, 158.3, 147.2, 144.3, 131.5, 131.4, 126.3,119.8, 119.7, 112.1, 75.6, 67.3, 62.6, 61.1,

45.6, 43.5, 43.0, 40.1, 32.5, 31.3, 30.1, 22.4, 17.7; ESIMS *m/z* 439.2 $[M+H]^+$; HRESIMS *m/z* 439.1755 $[M+H]^+$ (calcd for $C_{25}H_{27}O_7$ 439.1751).

*ent-6,7,15-Trioxo-7,20-epoxy-(14β-O-methylsulfonyl)-1-alkene-6,7-seco-16-kauren e (**7k**).* Following the procedure described for preparation of compound **7a**, compound **7k** was obtained as a white solid (yield 84%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.90 (1H, d, J = 5.7 Hz), 6.20 (1H, s), 6.01 (1H, m), 5.61 (1H, d, J = 11.5 Hz), 5.51 (2H, s), 4.39, 4.35 (each 1H, dd, $J_A = J_B$ = 10.8 Hz), 3.38 (1H, s), 2.97 (3H, s), 2.27 (1H, m), 2.12 (1H, m), 1.96 (1H, d, J = 5.7 Hz), 1.86 (3H, m), 1.43 (2H, m), 1.18 (3H, s), 0.98 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.1, 195.9, 166.4, 142.8, 131.4, 125.6, 120.2, 78.7, 66.8, 62.2, 60.8, 43.8, 42.8, 39.5, 38.7, 31.1, 30.5, 29.6, 21.9, 17.0; ESIMS *m/z* 423.2 $[M+H]^+$; HRESIMS *m/z* 423.1484 $[M+H]^+$ (calcd for $C_{21}H_{27}O_7S$ 423.1472).

*ent-1β,2β-Epoxy-6β-hydroxy-7,14-isopropylideneketal-15-oxo-7,20-epoxy-16-kaure ne (**8**).* Metachloroperbenzoic acid (*m*-CPBA, 134 mg, 0.78 mmol) was added to a solution of **4** (200 mg, 0.52 mmol) in 30 mL dichloromethane. The mixture was stirred at room temperature for 72 h and then the mixture was diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give a crude product, which was purified by column chromatography ($MeOH/CH_2Cl_2$ 1:200, v/v) to obtain compound **8** (148 mg, 71 %) as a white powder: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.18 (1H, s), 5.58 (1H, s), 5.49 (1H, d, J = 11.7 Hz), 4.83 (1H, s), 4.11, 3.99 (each 1H, dd, $J_A = J_B$ = 9.6 Hz), 3.79 (1H, m), 3.24 (1H, m), 3.07 (1H, d, J = 6.0 Hz), 2.58 (1H, d, J = 3.9 Hz), 2.51 (1H, m), 2.04 (1H, m), 1.85 (2H, m), 1.67 (4H, m), 1.61 (3H, s), 1.29 (3H, s), 1.19 (3H, s), 1.17 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.9, 149.8, 120.2, 100.9, 94.8, 71.4, 69.5, 64.4, 53.9, 52.7, 51.9, 45.1, 39.9, 39.7, 35.5, 33.2, 29.8, 29.6, 29.5, 25.0, 23.0, 16.1; ESIMS *m/z* 403.2 $[M+H]^+$; HRESIMS *m/z* 425.1938 $[M+Na]^+$ (calcd for $C_{23}H_{30}NaO_6$ 425.1935).

*ent-1β,2β-Epoxy-6β,7β,14β-trihydroxy-15-oxo-7,20-epoxy-16-kaurene (**9**).* Compound **8** (100 mg, 0.25 mmol) was added to 10 mL of 10 % H_2SO_4/THF (1:1) and the solution was stirred at room temperature for 0.5 h. Then the mixture was diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give compound **9** (58 mg, 65%) as a white powder: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.18 (2H, m), 5.62 (1H, s), 5.53 (1H, s), 4.83 (1H, s), 4.56 (1H, s), 4.07, 3.98 (each1H, dd, $J_A = J_B$ = 9.6 Hz), 3.63 (1H, m), 3.18 (1H, m), 2.98 (1H, d, J = 9.0 Hz), 2.51 (1H, d, J = 3.6 Hz), 2.46 (1H, m), 2.02 (1H, m), 1.81 (1H, m), 1.77 (1H, m), 1.67 (3H, m), 1.47 (1H, s), 0.97 (3H, s), 0.95 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 205.9, 150.4, 121.2, 97.1, 73.0, 71.7, 65.0, 61.2, 53.4, 52.8, 52.1, 48.4, 42.3, 39.5, 36.0, 31.9, 29.5, 29.1, 22.8, 16.3; ESIMS *m/z* 363.2 $[M+H]^+$; HRESIMS (ESI) *m/z* 385.1628 $[M+Na]^+$ (calcd for $C_{20}H_{26}NaO_6$ 385.1622).

*ent-1β,2β-Epoxy-6,7,15-trioxo-7,20-epoxy-14β-hydroxy-6,7-seco-16-kaurene (**10**).*

To a solution of compound **9** (200 mg, 0.55 mmol) in 20 ml of THF was added lead tetraacetate (0.51 g, 1.15 mmol) and potassium carbonate (0.4 g, 2.89 mmol). The mixture was stirred at room temperature for 5 min, after the inorganic precipitate was filtered off, the reaction mixture was diluted with 50 mL CH_2Cl_2 and then washed with water (20 mL× 3) and brine (10 mL× 3). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to yield a crude product, which was purified by column chromatography (MeOH/CH_2Cl_2 1:150, v/v) to obtain pure compound **10** (170 mg, 85%) as a white solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.90 (1H, d, J = 4.65 Hz), 6.16 (1H, s), 5.49 (1H, s), 4.76 (1H, s), 4.93, 4.73 (each 1H, dd, $J_A = J_B$ = 10.89 Hz), 3.14 (4H, m), 2.64 (2H, m), 2.41 (1H, m), 2.25 (1H, m), 1.98 (1H, m), 1.71 (3H, m), 1.24 (3H, m), 1.04 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 211.9, 203.7, 145.5, 119.4, 93.6, 70.8, 68.3, 62.0, 56.8, 53.2, 49.7, 41.5, 40.2, 39.5, 38.3, 32.1, 30.9, 26.3, 24.1, 19.9; ESIMS *m/z* 361.2 $[M+H]^+$; HRESIMS *m/z* 383.1455 $[M+Na]^+$ (calcd for $C_{20}H_{25}NaO_6$ 383.1465).

*ent-(1α-O-methylsulfonyl)-6β,7β,14β-trihydroxy-15-oxo-7,20-epoxy-16-kaurene (**11**).* Compound **3** (1.21 g, 2.51 mmol) was added to 20 ml of 10% HCl/THF (1:1) and the solution was stirred at room temperature for 0.5 h. Then the mixture was diluted with water and extracted with dichloromethane. The extract was washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to give compound **11** (0.98 g, 88%) as a white powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.42, (1H, d, J = 12.0 Hz), 6.20 (1H, s), 5.59 (1H, s), 5.27 (1H, s), 4.88 (1H, s), 4.59 (1H, s), 4.44 (1H, m), 4.14 (2H, s), 3.81 (1H, m), 3.09 (1H, d, J = 9.3 Hz), 3.00 (3H, s), 2.51 (1H, m), 2.12 (1H, m), 1.89 (2H, m), 1.50 (1H, m), 1.41 (2H, m), 1.16 (3H, s), 1.15 (3H, s); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 208.4, 151.6, 119.6, 96.7, 83.1, 72.4, 72.8, 62.0, 61.0, 59.2, 50.8, 42.6, 39.7, 39.2, 37.1, 33.1, 32.8, 29.8, 26.2, 21.4, 18.1; ESIMS *m/z* 443.2$[M+H]^+$; HRESIMS (ESI) *m/z* 465.1558 $[M+Na]^+$ (calcd for $C_{21}H_{30}NaO_8S$ 465.1554).

*ent-(1α-O-methylsulfonyl)-6,7,15-trioxo-7,20-epoxy-14β-hydroxy-6,7-seco-16-kaurene (**12**).* Following the procedure described for preparation of compound **6**, compound **12** was obtained as a white solid (yield 79%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.72 (1H, d, J = 4.5 Hz), 6.23 (1H, s), 5.64 (1H, s), 5.29 (1H, s), 5.18 (1H, d, J = 10.53 Hz), 4.82 (1H, s), 4.79, 4.57 (each 1H, dd, $J_A = J_B$ = 10.89 Hz), 3.07 (3H, m), 2.44 (2H, m), 2.40 (1H, d, J = 4.59 Hz), 2.22 (1H, m), 2.16 (1H, m), 1.98 (2H, m), 1.62 (2H, m), 1.51 (2H, m), 1.03 (3H, s), 0.87 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 200.7, 197.8, 148.2, 122.1, 80.8, 76.1, 71.1, 66.8, 60.4, 44.5, 43.6, 41.8, 39.6, 39.3, 32.2, 31.3, 28.9, 24.2, 23.5, 16.2; ESIMS *m/z* 441.2 $[M+H]^+$; HRESIMS *m/z* 441.1583 $[M+H]^+$ (calcd for $C_{21}H_{29}O_8S$ 441.1578).

*ent-(1α-O-methylsulfonyl)-6,7,15-trioxo-7,20-epoxy-(14β-O-p-florobenzoy)-6,7-seco-16-kaurene (**13a**).* Following the procedure described for preparation of compound **7a**, compound **13a** was obtained as a white solid (yield 70%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.76 (1H, d, J = 4.5 Hz), 7.89 (2H, m), 7.04 (2H, d, J = 9.0 Hz), 6.33 (1H, s),

6.24 (1H, s), 5.68 (1H, s), 5.16, 4.65 (each 1H, dd, $J_A = J_B = 10.89$ Hz), 4.64 (1H, m), 4.13 (1H, m), 3.25 (1H, m), 3.13 (3H, s), 2.52 (2H, m), 2.30 (4H, m), 2.04 (1H, s), 2.16 (1H, m), 1.98 (2H, m), 1.62 (2H, m), 1.65 (2H, m), 1.19 (3H, s), 1.03 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.0, 196.4, 147.0, 132.1, 132.0, 121.9, 115.1, 114.8, 79.6, 72.1, 65.8, 61.3, 59.6, 45.6, 43.9, 41.7, 39.0, 33.3, 32.2, 29.2, 29.1, 24.5, 23.6, 16.4; ESIMS *m/z* 463.2 $[M+H]^+$; HRESIMS (ESI) *m/z* 463.1751 $[M+H]^+$ (calcd for $C_{28}H_{32}O_9FS$ 563.1746).

*ent-(1α-O-methylsulfonyl)-6,7,15-trioxo-7,20-epoxy-(14β-O-valeryl)-6,7-seco-16-kaurene (**13b**).* Following the procedure described for preparation of compound **7a**, compound **13b** was obtained as a white solid (yield 72%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.73 (1H, d, J = 4.5 Hz), 6.24 (1H, s), 6.03 (1H, s), 5.62 (1H, s), 5.29, 4.62 (each 1H, dd, $J_A = J_B = 10.89$ Hz), 4.57 (1H, m), 3.13 (3H, s), 3.06 (1H, s), 2.49 (2H, m), 2.25 (9H, m), 1.62 (7H, m), 1.35 (6H, m), 1.29 (3H, s), 1.00 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.0, 196.4, 172.6, 166.2, 147.0, 121.5, 79.4, 71.0, 65.7, 61.4, 59.4, 45.5, 44.0, 41.6, 39.0, 33.6, 33.3, 32.4, 29.2, 29.0, 26.2, 24.5, 23.6, 21.7, 16.4, 13.2; ESIMS *m/z* 525.2 $[M+H]^+$; HRESIMS *m/z* 525.2161 $[M+H]^+$ (calcd for $C_{26}H_{37}O_9S$ 525.2153).

*ent-(1α-O-methylsulfonyl)-6,7,15-trioxo-7,20-epoxy-(14β-O-2-furanyl)-6,7-seco-16-kaurene (**13c**).* Following the procedure described for preparation of compound **7a**, compound **13c** was obtained as a white solid (yield 68%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.75 (1H, d, J = 4.5 Hz), 7.54 (1H, s), 7.01 (1H, d, J = 2.7 Hz), 6.44 (1H, d, J = 2.7 Hz), 6.38 (1H, s), 6.21 (1H, s), 5.68 (1H, s), 5.14, 4.74 (each 1H, dd, $J_A = J_B = 10.89$ Hz), 4.62 (1H, m), 3.16 (3H, s), 3.12 (1H, m), 2.50 (2H, m), 2.24 (4H, m), 1.66 (2H, m), 1.21 (1H, m), 1.19 (3H, s), 1.02 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.0, 196.1, 166.3, 157.1, 147.0, 146.2, 127.6, 118.2, 111.4, 79.5, 71.8, 65.8, 61.3, 59.5, 45.7, 43.9, 41.7, 39.0, 33.1, 32.2, 29.2, 24.2, 23.6, 16.4; ESIMS *m/z* 463.3 $[M+H]^+$; HRESIMS *m/z* 535.1633 $[M+H]^+$ (calcd for $C_{26}H_{31}O_{10}S$ 535.1632).

*ent-(1α-O-methylsulfonyl)-6,7,15-trioxo-7,20-epoxy-(14β-O-methylsulfonyl)-6,7-seco-16-kaurene (**13d**).* Following the procedure described for preparation of compound **7a**, compound **13d** was obtained as a white solid (yield 57%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.73 (1H, d, J = 4.5 Hz), 6.31 (1H, s), 6.24 (1H, s), 5.715. (1H, s), 5.65 (1H, s), 5.09, 4.74 (each 1H, dd, $J_A = J_B = 10.89$ Hz), 4.53 (1H, m), 3.36 (1H, d, J = 8.7 Hz), 3.15 (3H, s), 3.12 (3H, s), 2.52 (1H, m), 2.30 (3H, m), 2.02 (1H, m), 1.63 (4H, m), 1.42 (2H, m), 1.19 (3H, s), 1.04 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.0, 145.9, 123.2, 80.7, 79.0, 65.6, 59.5, 46.0, 43.1, 42.3, 39.9, 39.0, 38.0, 33.3, 32.3, 29.6, 29.2, 23.8, 23.6, 16.6; ESIMS *m/z* 519.2 $[M+H]^+$; HRESIMS *m/z* 541.1180 $[M+Na]^+$ (calcd for $C_{22}H_{30}O_{10}NaS_2$ 541.1173).

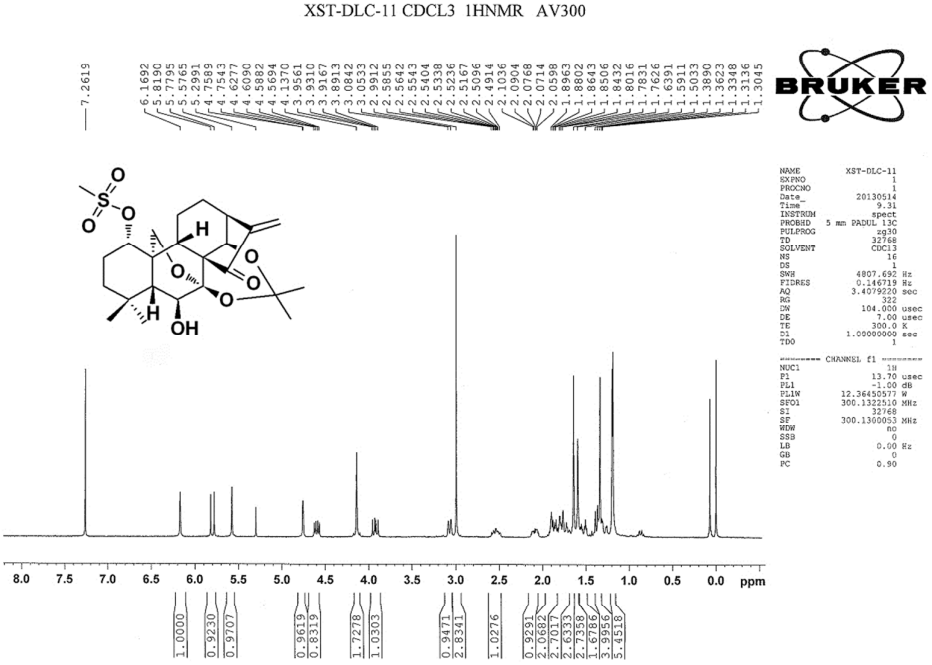
*Compound **15*** To a solution of compound **14** (100 mg, 0.27 mmol) in 15 mL of DCM was added 10% HCl, and the mixture was stirred at room temperature for 72 h. The reaction mixture was diluted with 50 mL CH_2Cl_2 and then washed with water (20

mL× 3) and brine (10 mL× 3). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to yield a crude product, which was purified by column chromatography (MeOH/CH_2Cl_2 1:300, v/v) to obtain compound **15** (71 mg, 71%) as a white solid: ^{1}H NMR($CDCl_3$, 300 MHz) δ 13.99 (1H, s), 10.24 (1H, s), 5.32 (1H, d, J = 2.4Hz), 4.40 (1H, m), 4.02, 3.75 (each 1H, dd, $J_A = J_B$ = 9.0Hz), 2.97 (1H, m), 2.84 (1H, m), 2.34 (3H, s), 2.26 (1H, m), 1.95 (1H, m), 1.90 (1H, s), 1.80 (1H, m), 1.78 (1H, m), 1.70 (1H, m), 1.53 (1H, m), 1.27 (1H, m), 1.05 (3H, s), 0.96 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 189.5, 175.0, 173.0, 147.0, 140.6, 101.1, 99.6, 76.3, 73.7, 53.6, 46.4, 40.7, 37.0, 36.8, 32.3, 30.6, 22.9, 22.6, 22.2, 12.2; ESIMS *m/z* 363.3 $[M+H]^+$; HRESIMS *m/z* 363.1806 $[M+H]^+$ (calcd for $C_{20}H_{27}O_6$ 363.1802).

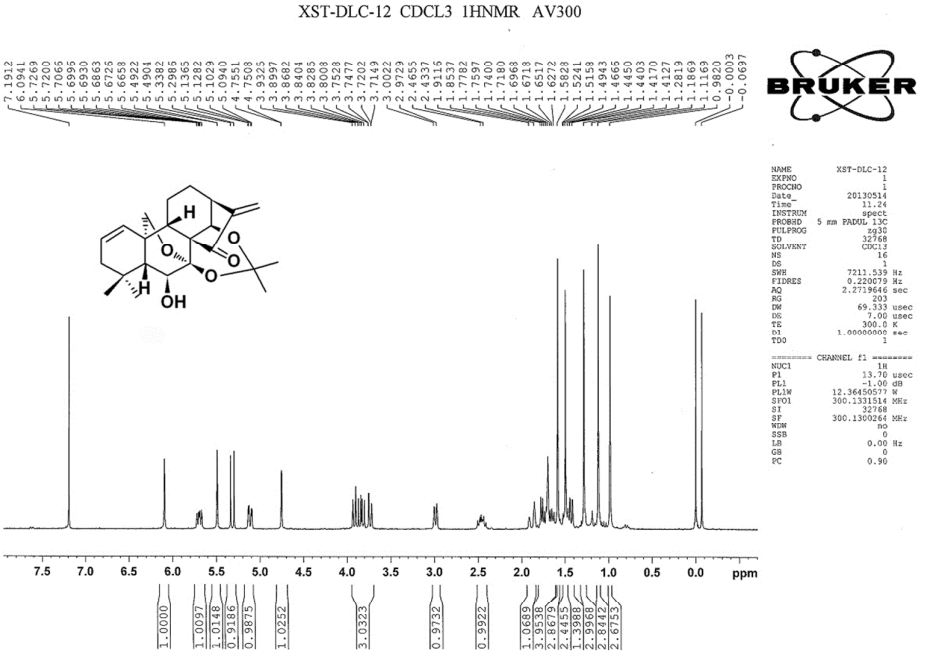
*Compound **18*** Following the procedure described for preparation of compound **15**, compound **18** was obtained as a white solid (yield 68%): ^{1}H NMR($CDCl_3$, 300 MHz) δ 13.96 (1H, s), 10.24 (1H, s), 4.43 (1H, m), 4.34, 3.88 (each 1H, dd, $J_A = J_B$ = 9.0Hz), 2.98 (1H, m), 2.36 (3H, s), 2.28 (2H, m), 1.93 (2H, m), 1.82 (1H, m), 1.78 (1H, m), 1.70 (1H, m), 1.53 (1H, m), 1.27 (1H, m), 1.06 (3H, s), 0.98 (3H, s); ^{13}C NMR($CDCl_3$, 75 MHz) δ 189.0, 175.2, 175.0, 172.2, 146.5, 140.3, 97.7, 74.8, 70.9, 50.4, 44.5, 38.9, 36.5, 35.7, 32.5, 31.7, 23.1, 22.4, 21.6, 12.1; ESIMS *m/z* 361.3 $[M+H]^+$; HRESIMS *m/z* 361.1644 $[M+H]^+$ (calcd for $C_{20}H_{25}O_6$ 361.1646).

^{1}H NMR and ^{13}C NMR spectra of compounds

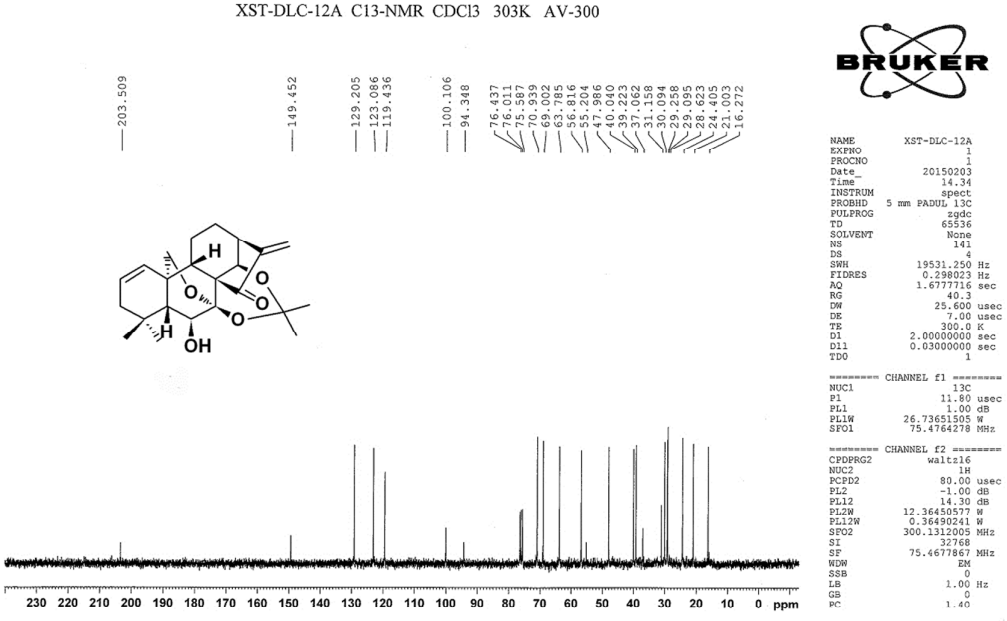
^{1}H NMR of compound **3**



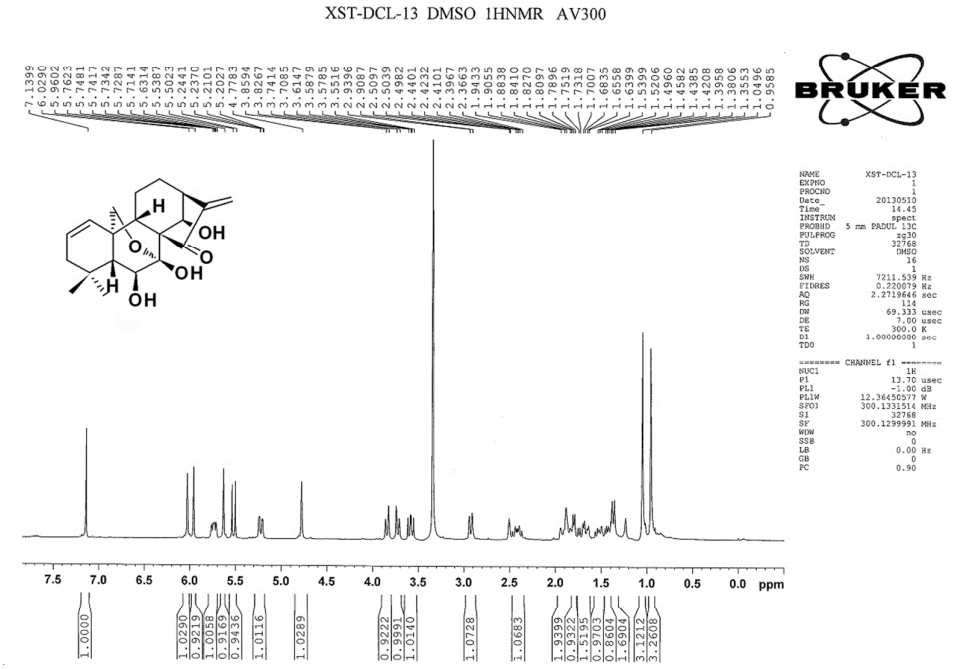
^{1}H NMR of compound **4**



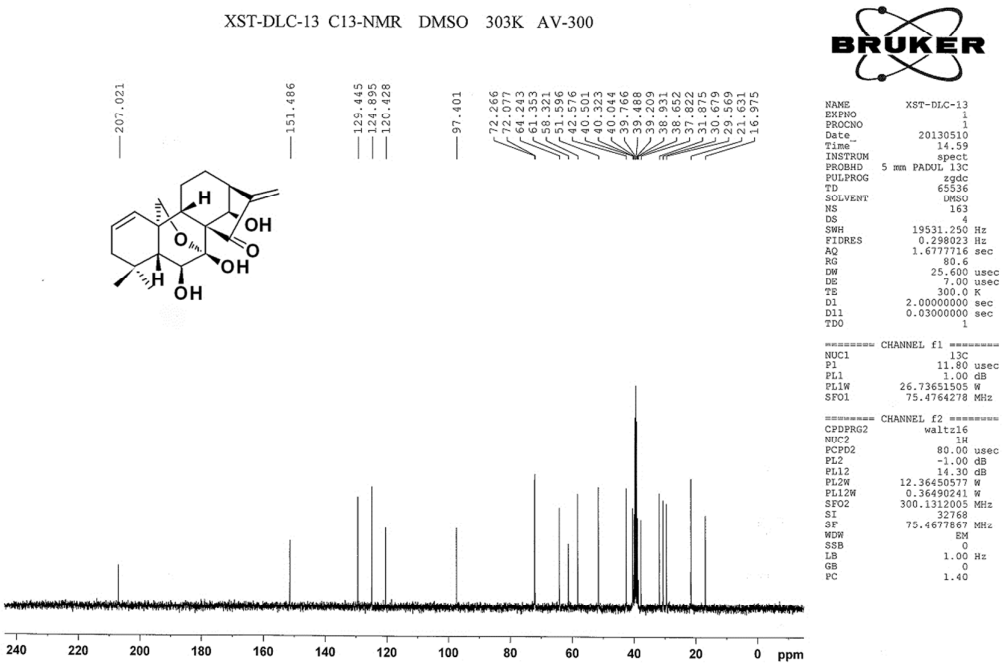
^{13}C NMR of compound **4**



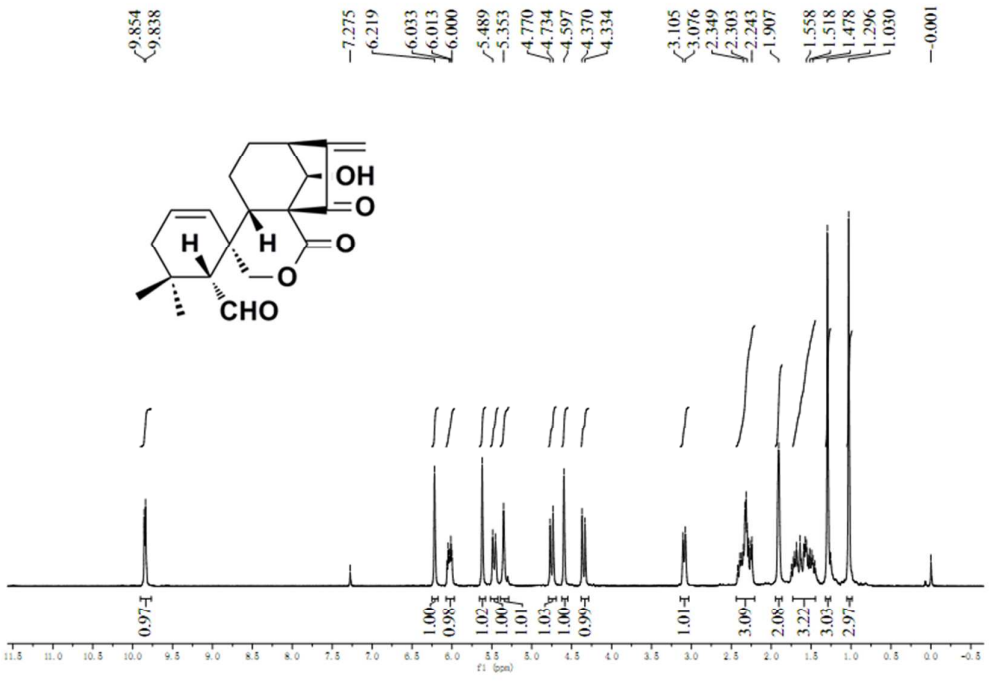
^{1}H NMR of compound **5**



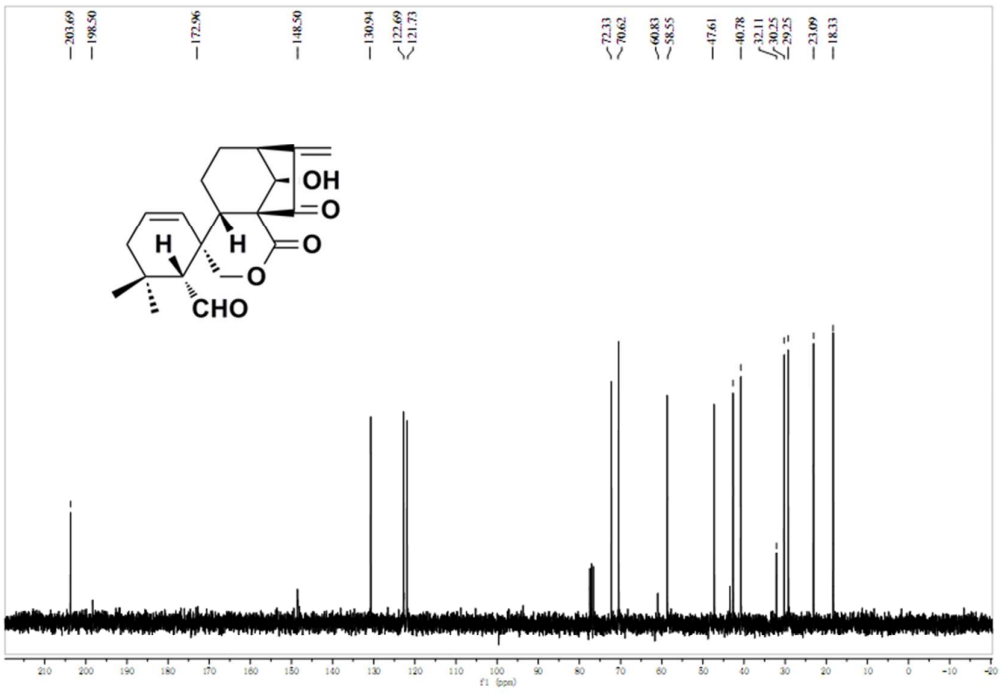
^{13}C NMR of compound **5**



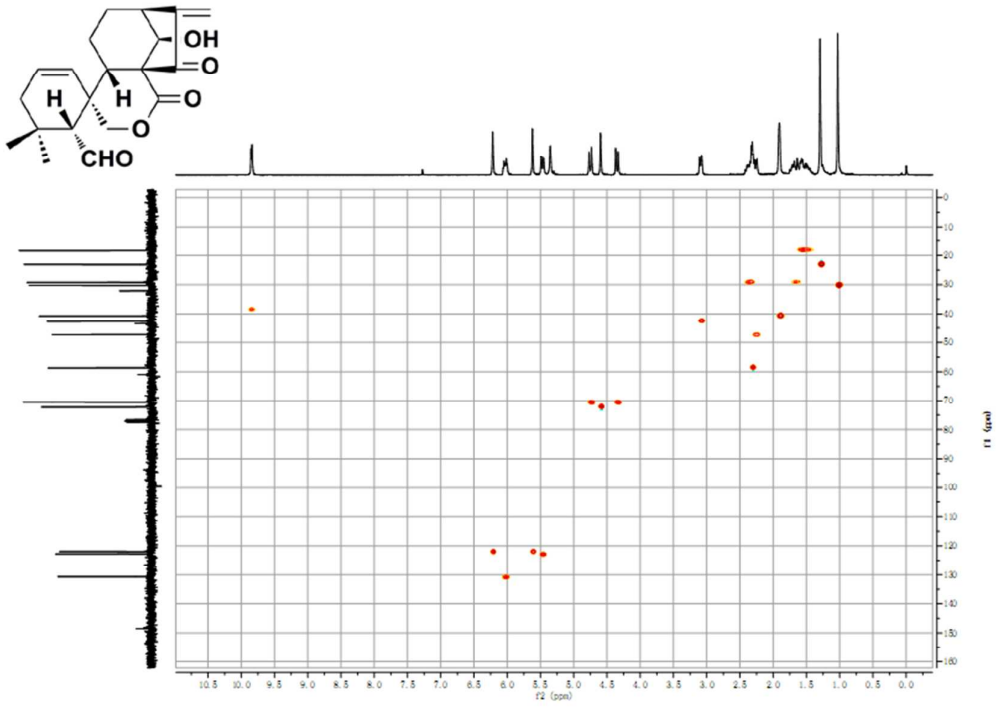
^{1}H NMR of compound **6**



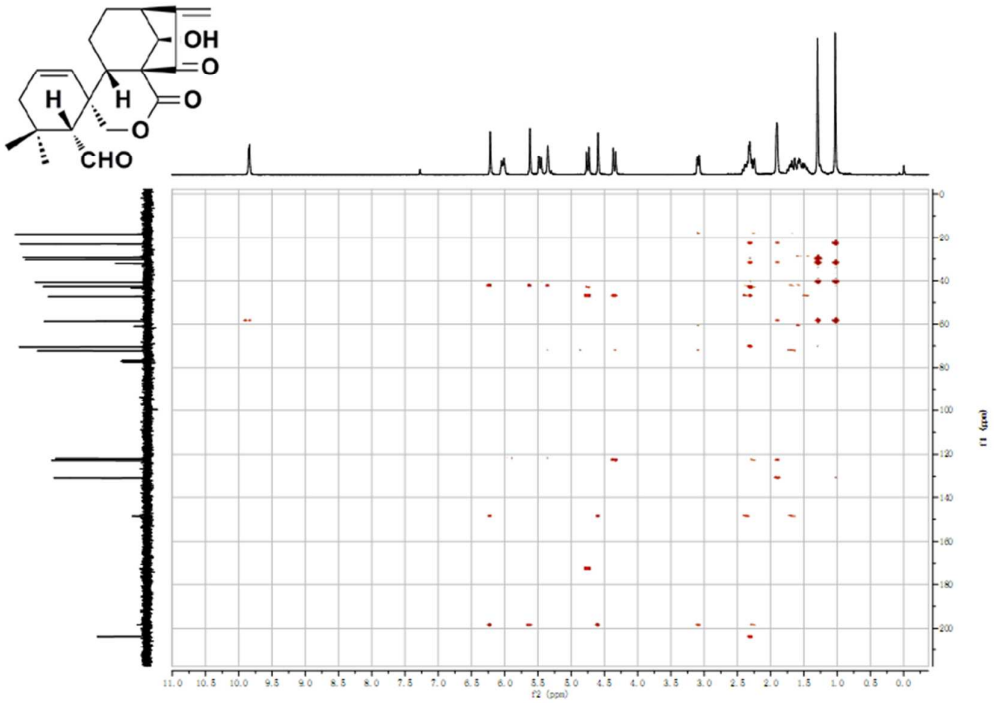
^{13}C NMR of compound **6**



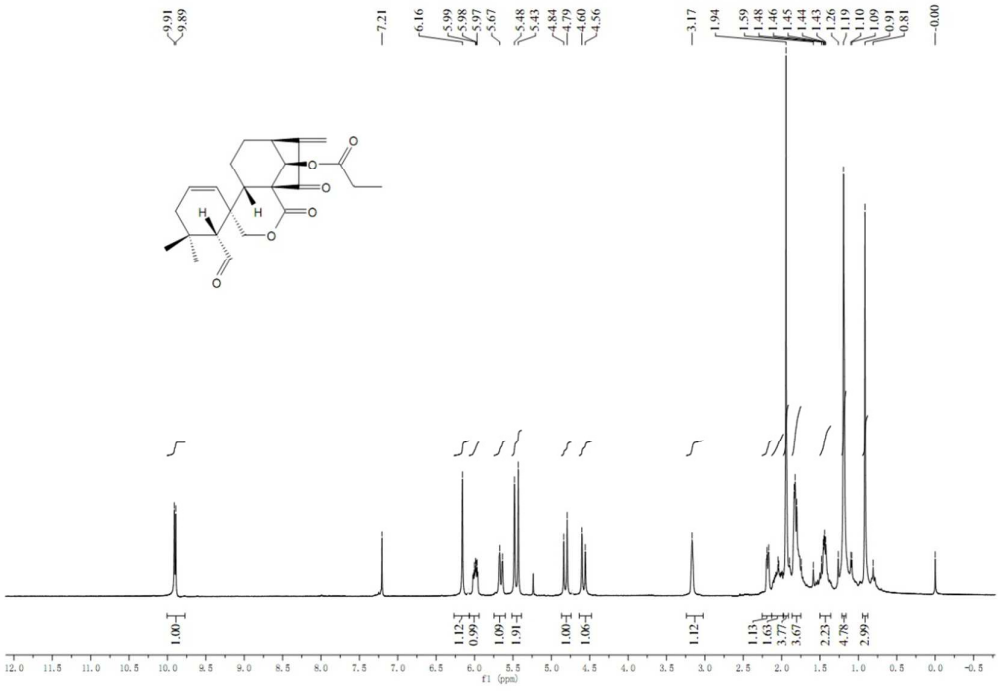
HMQC of compound **6**



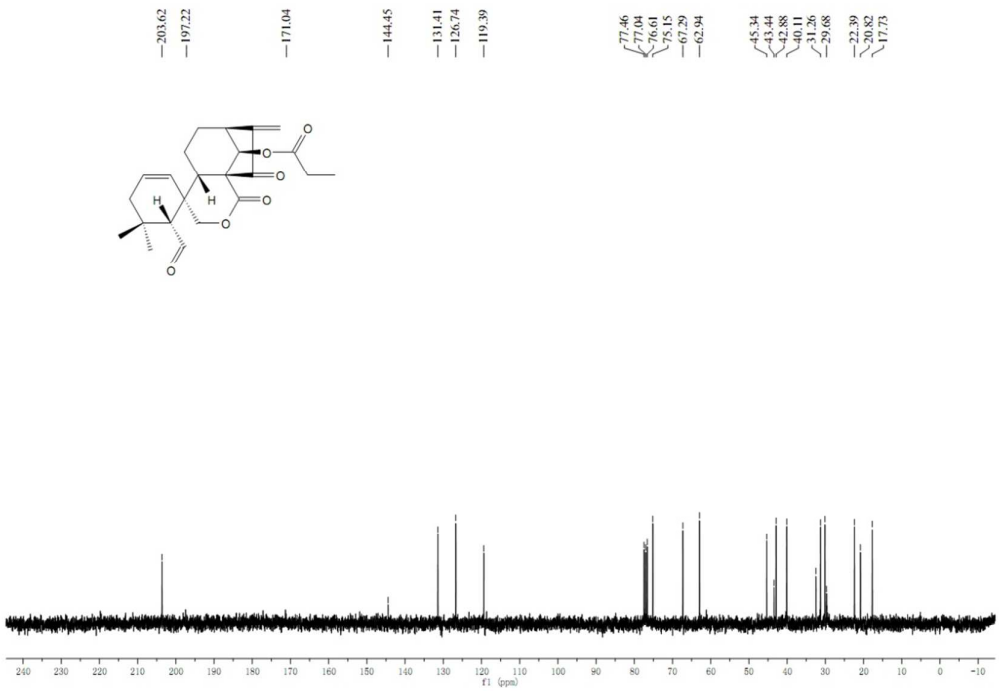
HMBC of compound **6**



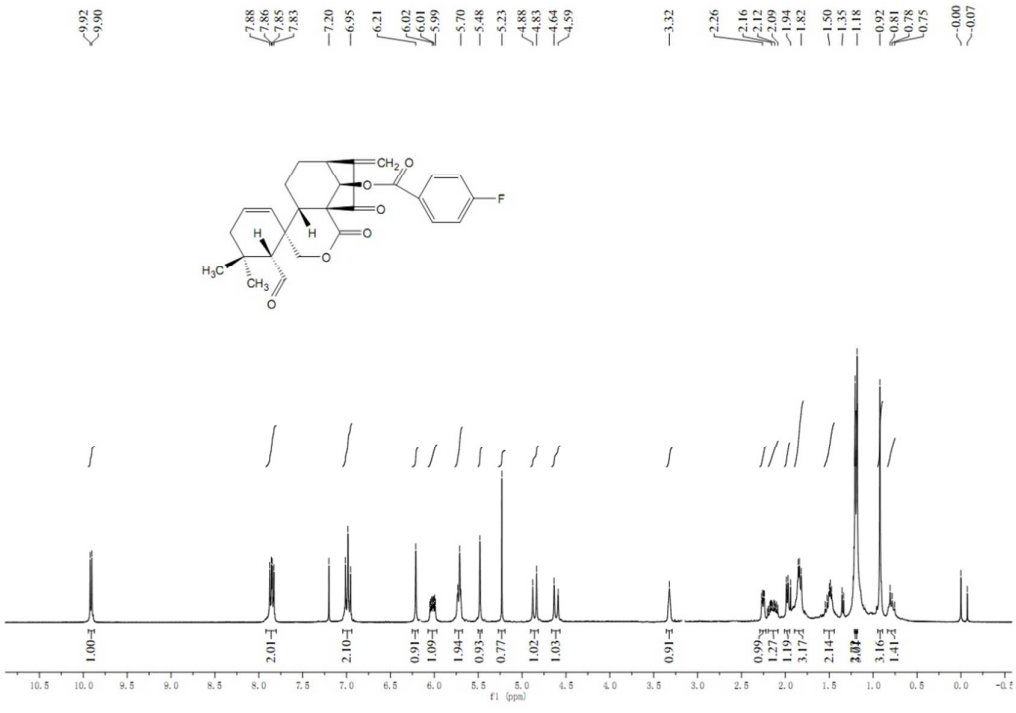
^{1}H NMR of compound **7a**



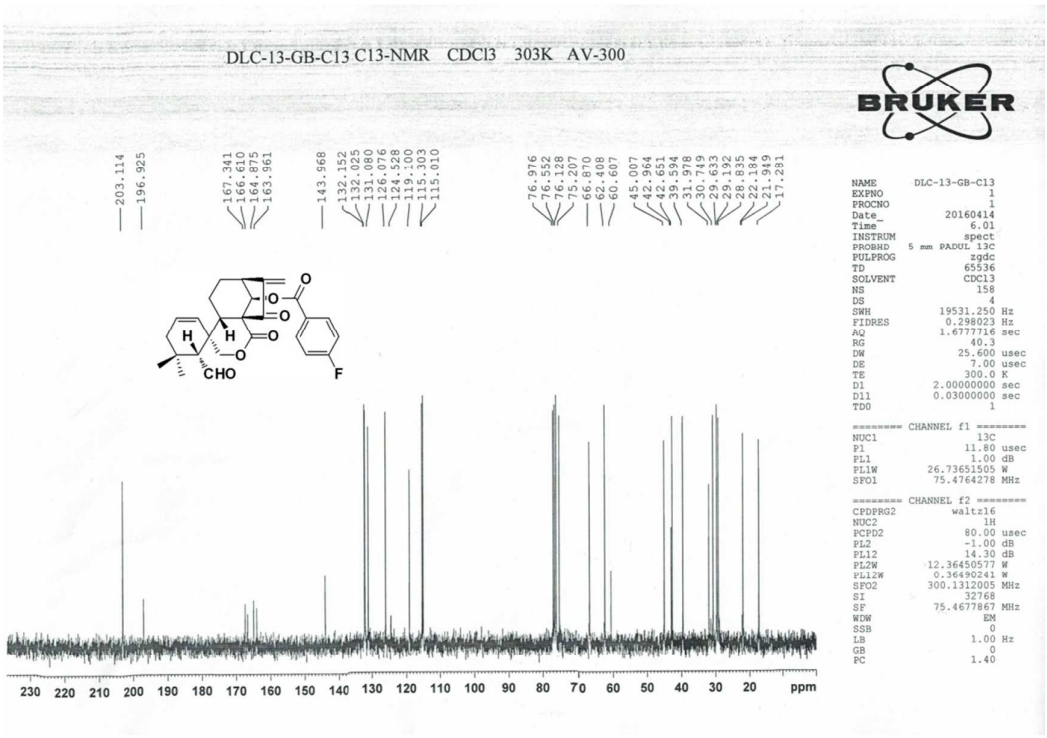
^{13}C NMR of compound **7a**



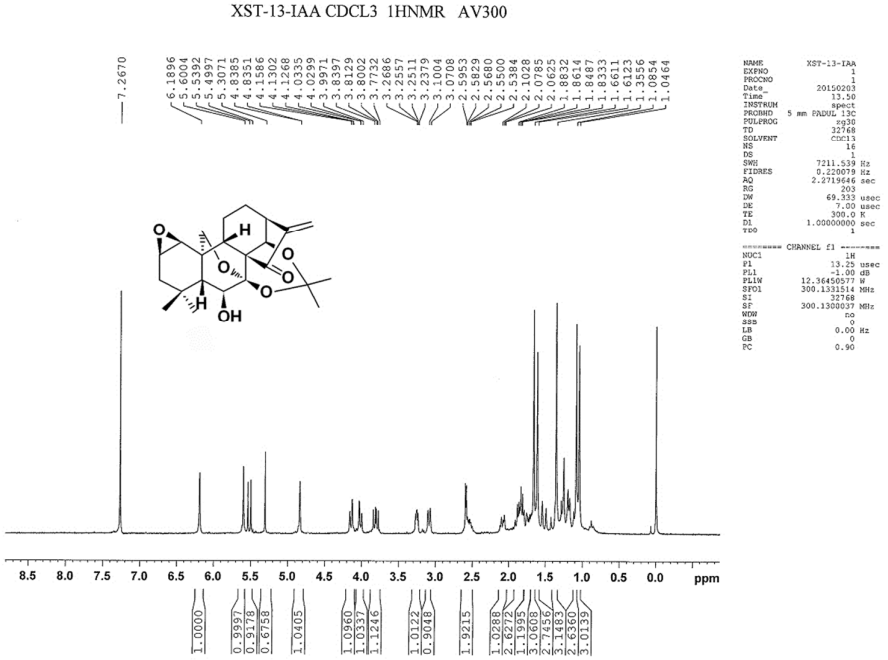
^{1}H NMR of compound **7b**



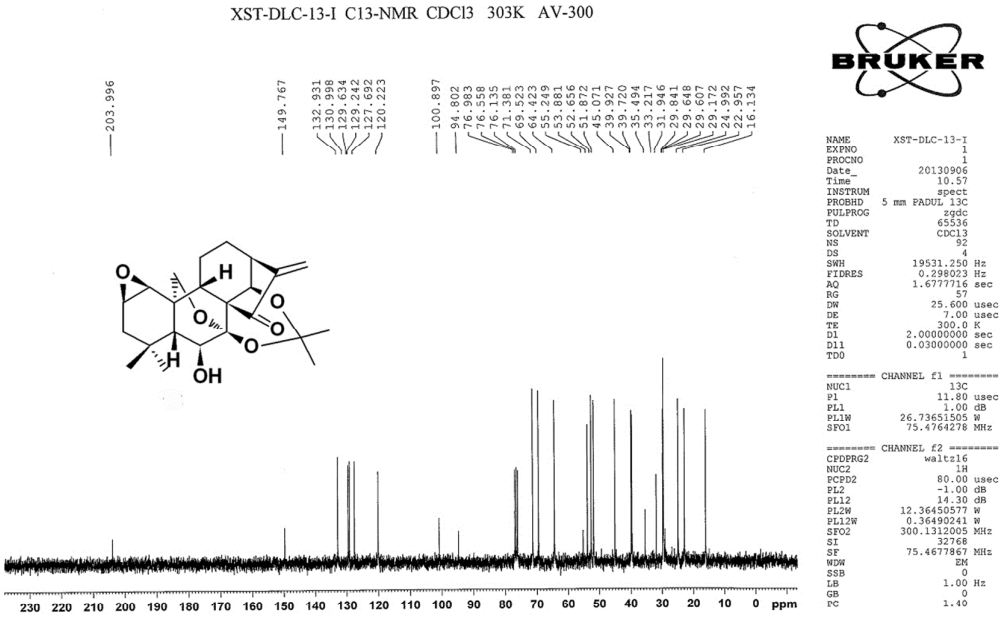
^{13}C NMR of compound **7b**



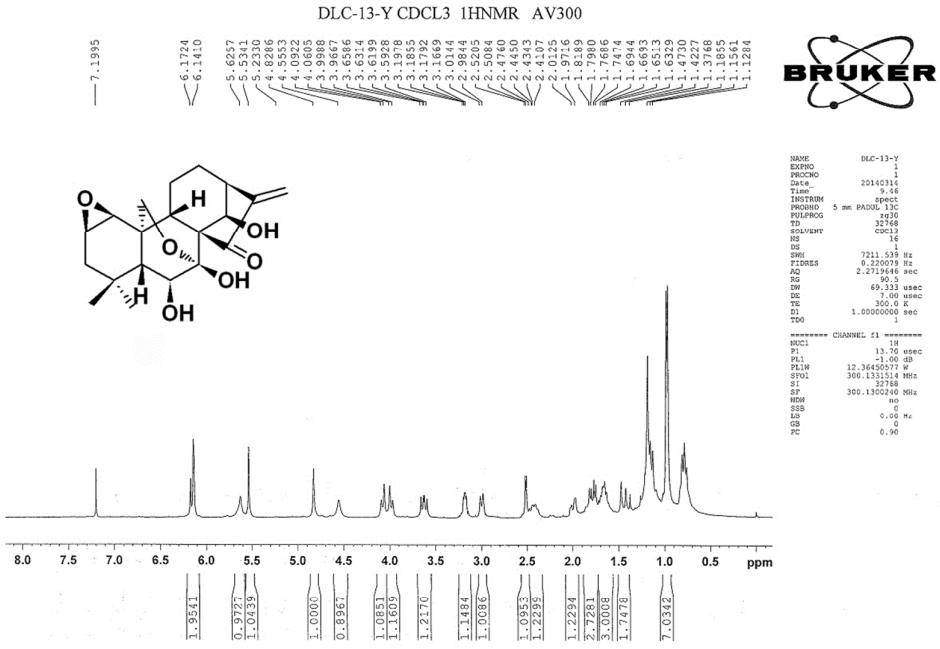
^{1}H NMR of compound **8**



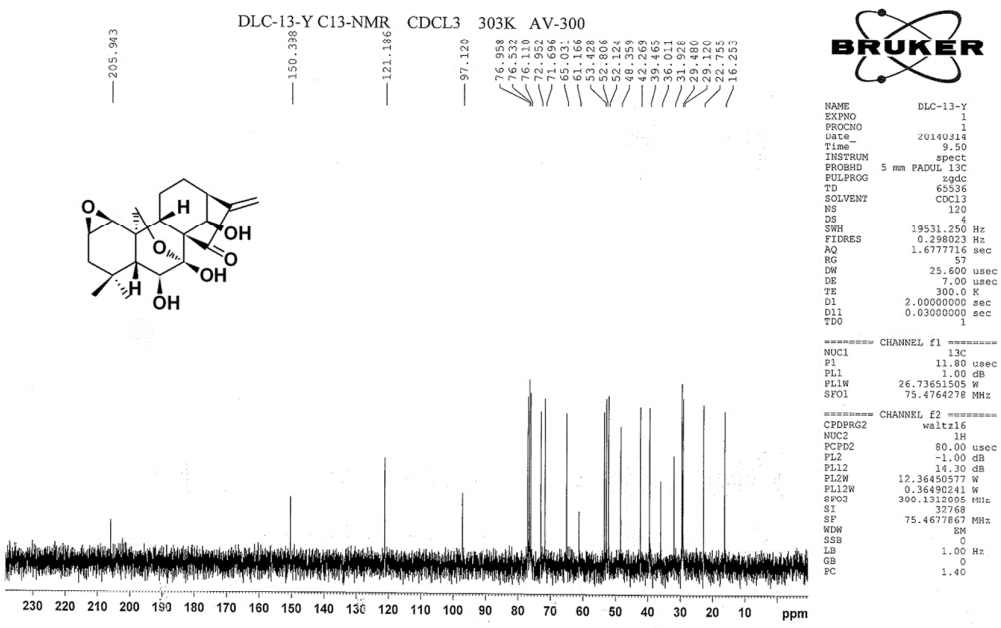
^{13}C NMR of compound **8**



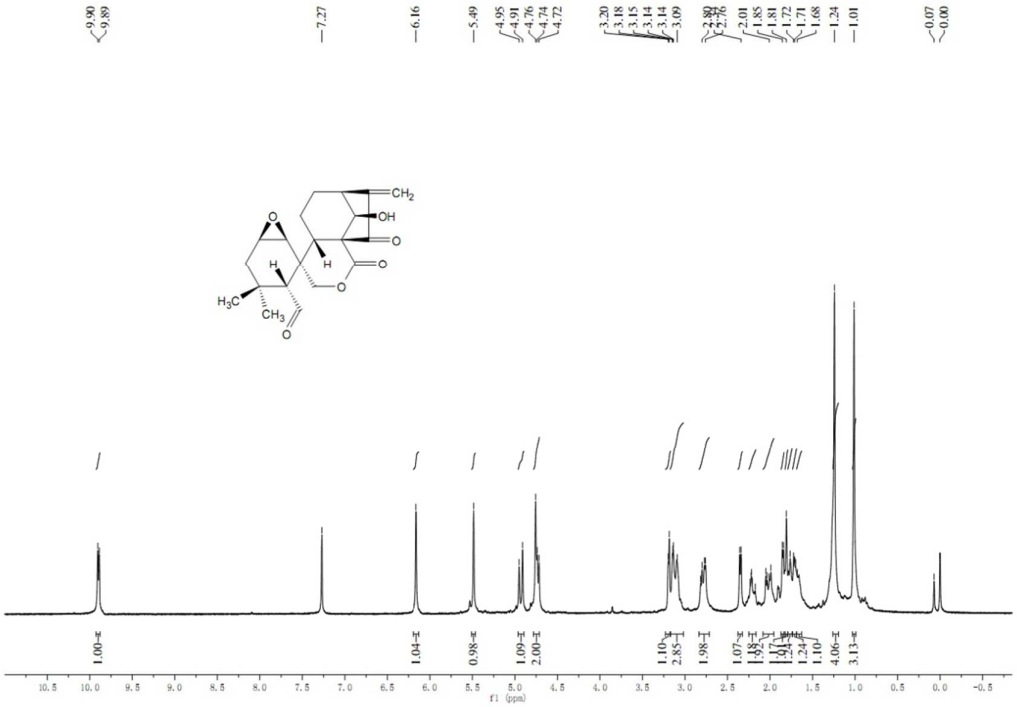
^{1}H NMR of compound **9**



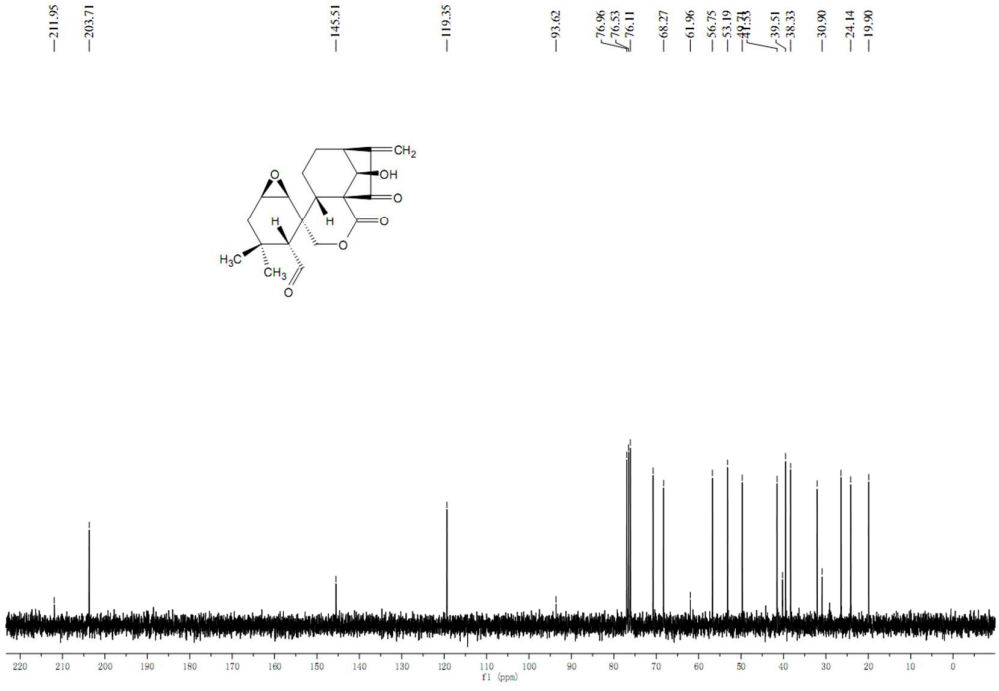
^{13}C NMR of compound **9**



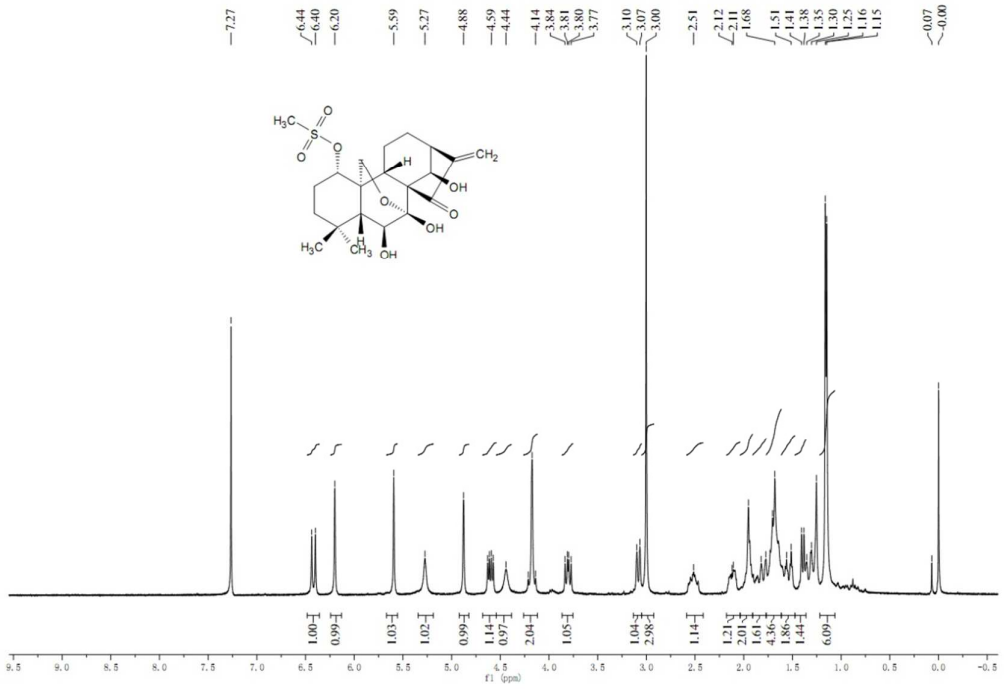
^{1}H NMR of compound **10**



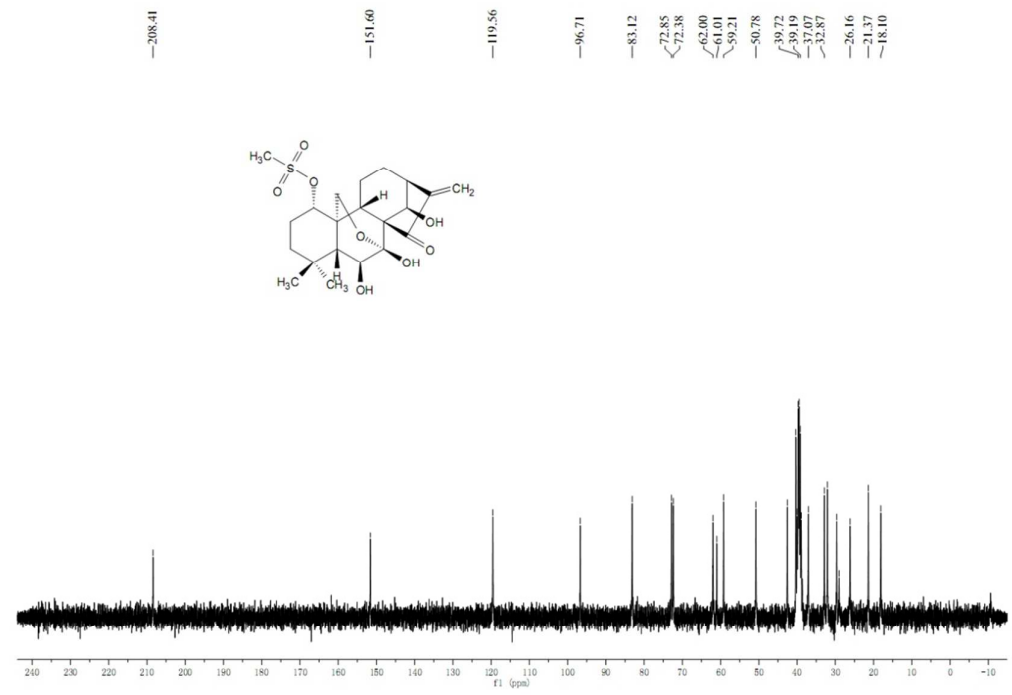
^{13}C NMR of compound **10**



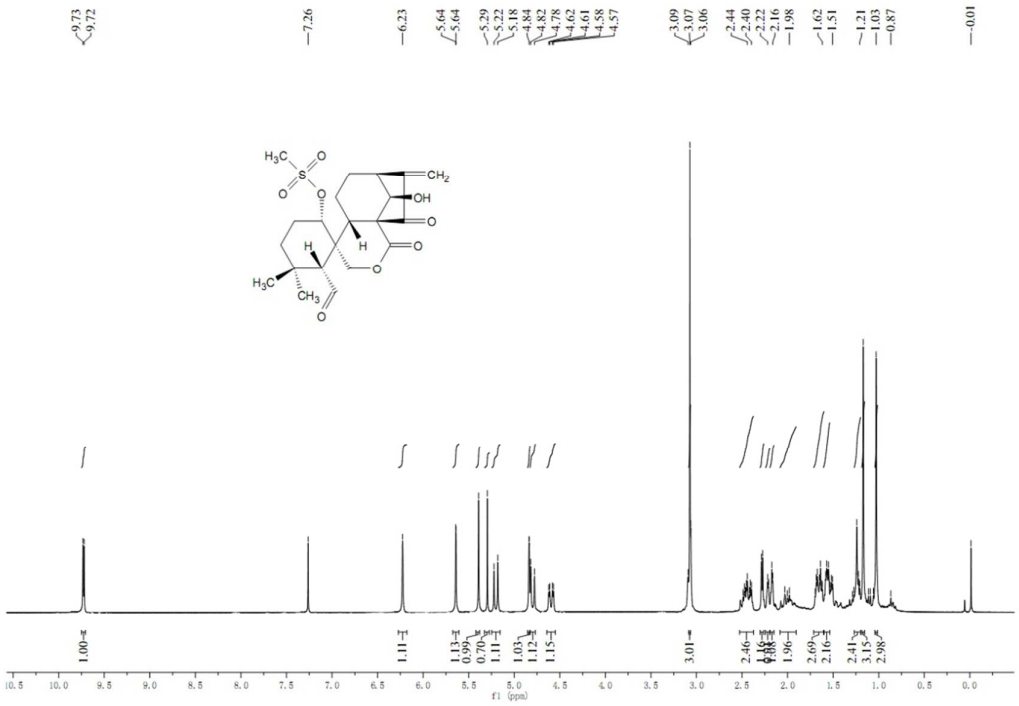
^{1}H NMR of compound **11**



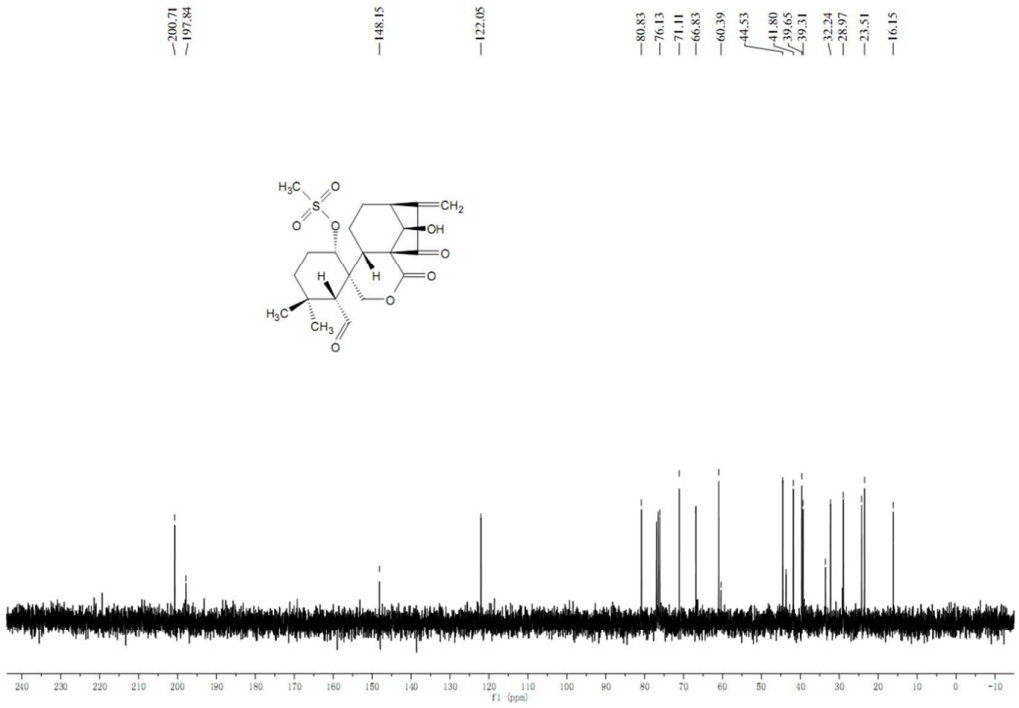
^{13}C NMR of compound **11**



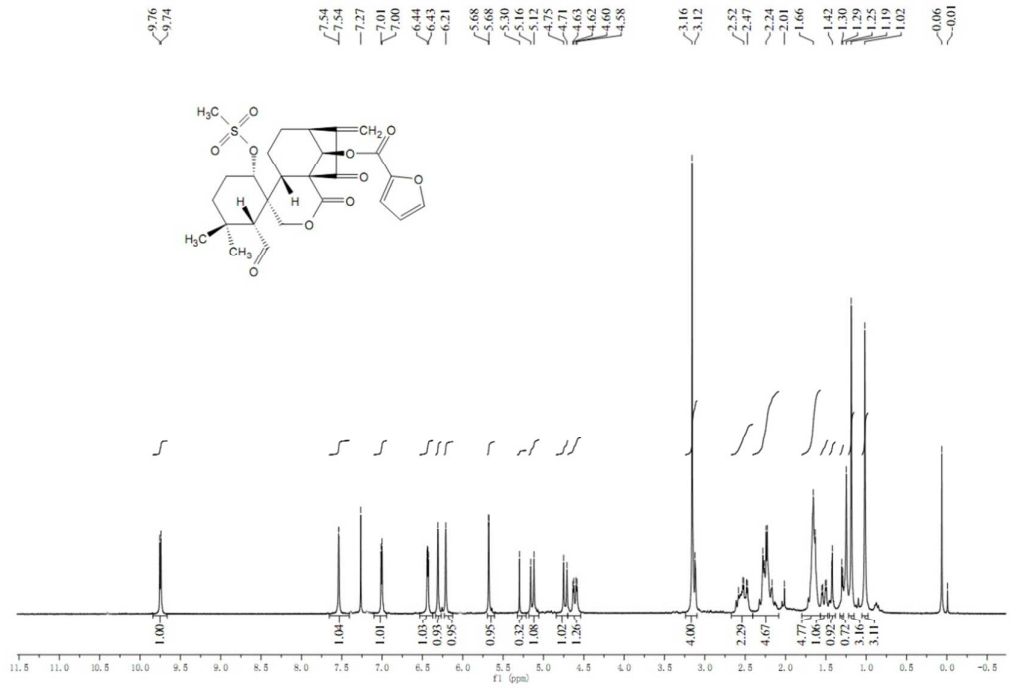
^{1}H NMR of compound **12**



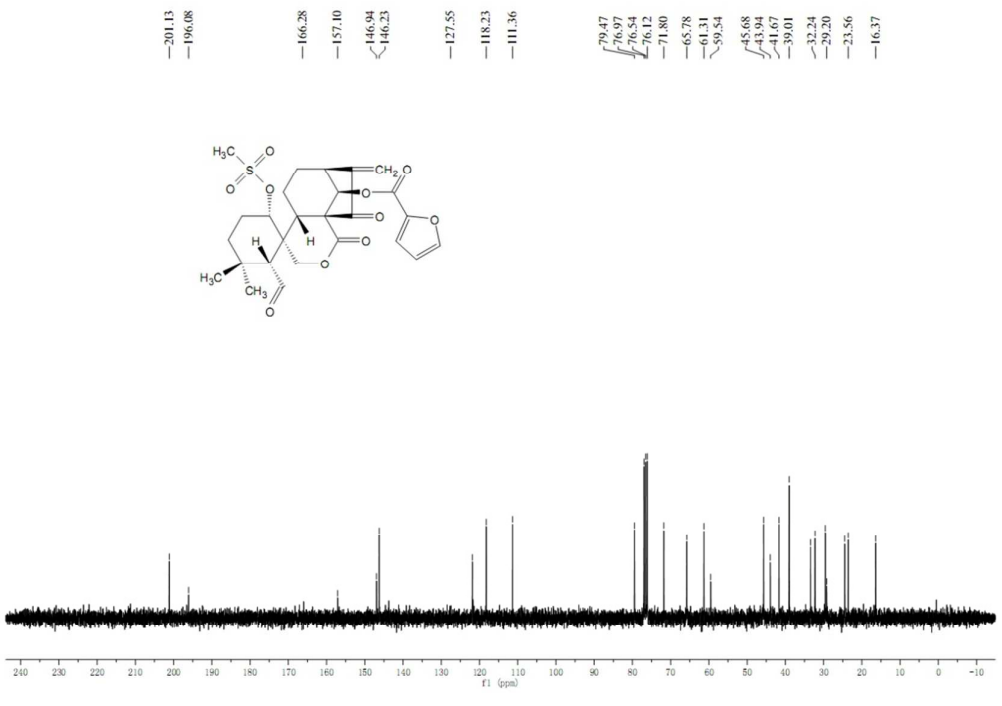
^{13}C NMR of compound **12**



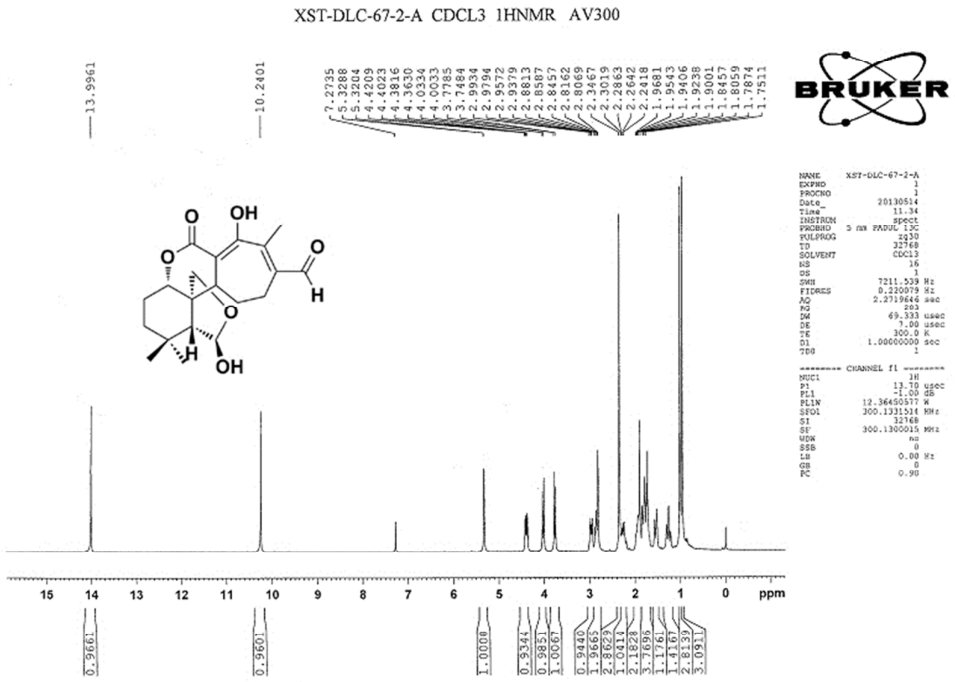
^{1}H NMR of compound **13c**



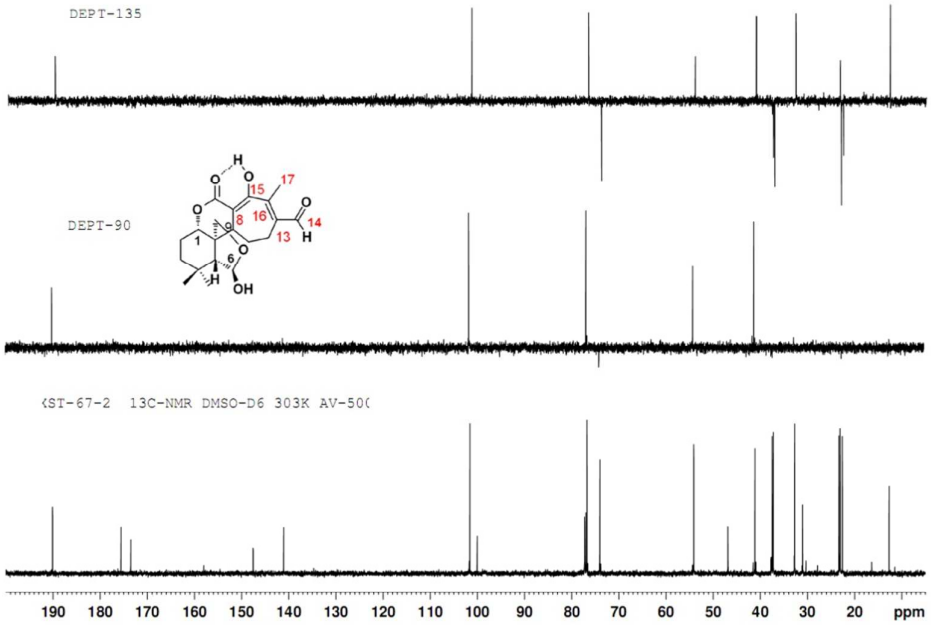
^{13}C NMR of compound **13c**



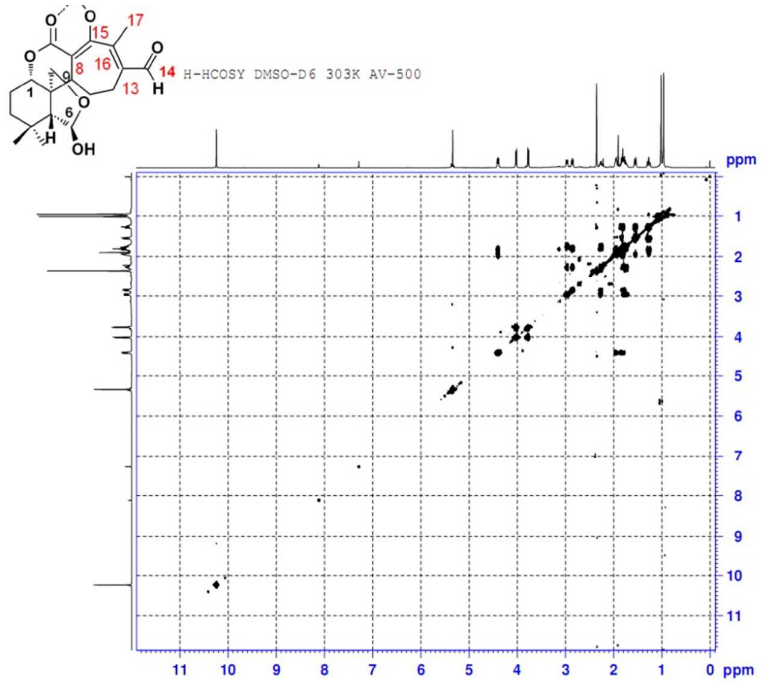
^{1}H NMR of compound **15**



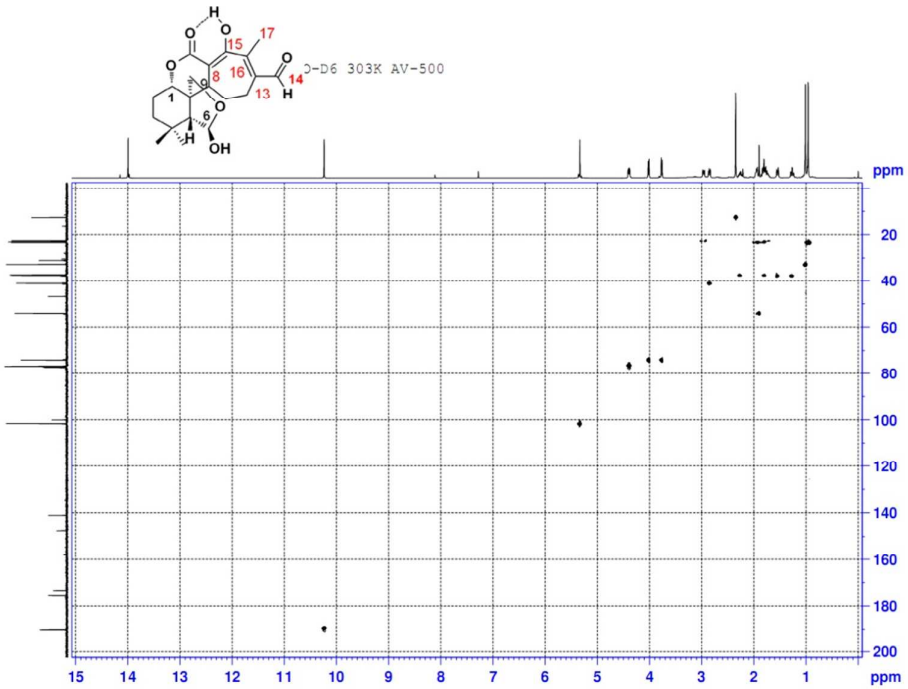
DEPT of compound **15**



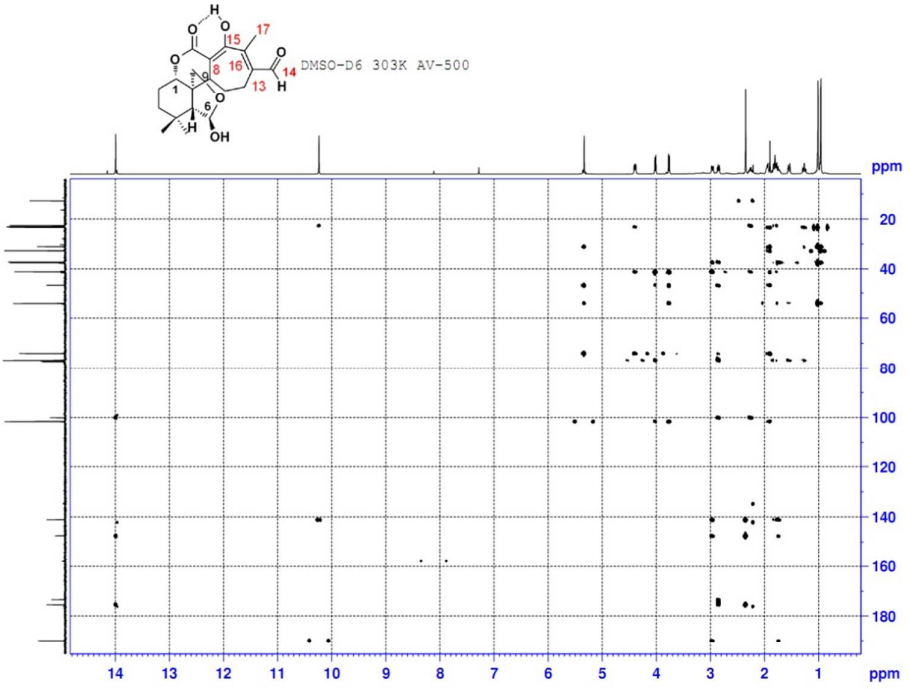
H-H COSY of compound **15**



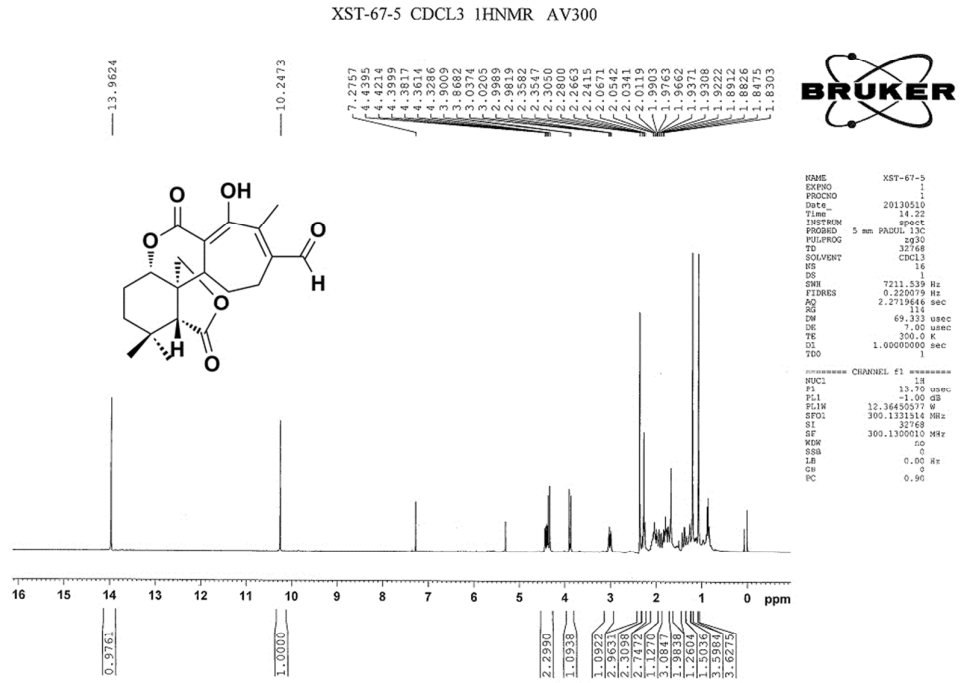
HMQC of compound **15**



HMBC of compound **15**



^{1}H NMR of compound **18**



^{13}C NMR of compound **18**