Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

## Isolation, structural elucidation, and synthetic studies of salviyunnanone A, an abietane derived diterpenoid with 7/5/6/3 ring system from *Salvia yunnanensis*

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## **S-1**. Physical data of salviyunnanone A (**1**)

Salviyunnanone A (1): yellow powder; $[\alpha]^{17}_{D}$ + 37.9 (*c* 0.13, MeOH); UV (MeOH) λmax (log ε): 294.0 (3.62) nm, 203.0 (3.86) nm; IR (KBr) νmax 2960, 2922, 2867, 2851, 1691, 1662, 1639, 1465, 1385, 1122, 1093, 1058, 1041, 922, 840, 804, 677 cm–1; $^{1}$H and $^{13}$C NMR data, see Table 1; ESIMS *m*/*z* 337 $[M+Na]^{+}$ ; HRESIMS *m*/*z* 337.1786 $[M+Na]^{+}$ (calcd for $C_{20}H_{26}O_3Na$, 337.1780).

## **S-2.** Computational Methods for configuration determination of salviyunnanone A (**1**)

The CONFLEX searches based on molecular mechanics with MMFF94S force fields were performed for **1** which gave 9 stable conformers.[1,2] Selected conformers (3) with distributions higher than 1% were further optimized by the density functional theory method at the B3LYP/6-31G** level in Gaussian 03 program package,[3] leading to one minimum geometry, which was further checked by frequency calculation and resulted in no imaginary frequencies. ECD calculation were performed on the Gaussian 03 program using TD-DFT-B3LYP/6-31G (d, p) level of theory on B3LYP/6-31G (d) optimized geometry through the IEFPCM model (in MeOH). The calculated ECD curve was generated using SpecDis with σ=0.28 ev, and UV shift -20 nm. The magnetic shieldings were computed at the B3LYP/6-311+G(2d,p) level of theory by using the B3LYP/6-31G(d) optimized geometries.

Standard orientation of **1** at B3LYP/6-31G(d,p) level:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | 3.262033 | 1.895249 | 0.257913 |
| 2 | 6 | 0 | 4.041562 | 0.759334 | -0.432430 |
| 3 | 6 | 0 | 3.900587 | -0.650661 | 0.184645 |
| 4 | 6 | 0 | 2.438613 | -1.153127 | 0.188661 |
| 5 | 6 | 0 | 1.455973 | -0.566162 | -0.847523 |
| 6 | 6 | 0 | 0.963848 | 0.904543 | -0.488540 |
| 7 | 6 | 0 | 1.798325 | 1.578561 | 0.618366 |
| 8 | 6 | 0 | 0.189705 | -1.379958 | -0.933145 |

| | | | | | |
|---|---|---|---|---|---|
| 9 | 6 | 0 | -0.885720 | -0.711446 | -0.482663 |
| 10 | 6 | 0 | -0.479333 | 0.636254 | -0.006727 |
| 11 | 6 | 0 | -2.275817 | -1.108523 | -0.411025 |
| 12 | 6 | 0 | -3.280165 | -0.234693 | -0.142282 |
| 13 | 6 | 0 | -2.975058 | 1.219459 | 0.016499 |
| 14 | 6 | 0 | -1.542453 | 1.628483 | 0.258366 |
| 15 | 6 | 0 | 4.460825 | -0.698767 | 1.618154 |
| 16 | 6 | 0 | 4.681764 | -1.659987 | -0.695810 |
| 17 | 8 | 0 | 2.082624 | -2.030913 | 0.951773 |
| 18 | 1 | 0 | 1.977847 | -0.548934 | -1.814290 |
| 19 | 6 | 0 | 0.908960 | 1.756975 | -1.771683 |
| 20 | 1 | 0 | -1.361812 | 2.700888 | 0.199041 |
| 21 | 8 | 0 | -0.874003 | 0.947653 | 1.338771 |
| 22 | 8 | 0 | -3.841351 | 2.081466 | -0.072976 |
| 23 | 6 | 0 | -4.748193 | -0.610798 | -0.065571 |
| 24 | 6 | 0 | -5.243307 | -0.534554 | 1.395717 |
| 25 | 6 | 0 | -5.079954 | -1.974160 | -0.683530 |
| 26 | 1 | 0 | 3.302958 | 2.776878 | -0.394187 |
| 27 | 1 | 0 | 3.776090 | 2.188086 | 1.181640 |
| 28 | 1 | 0 | 5.108614 | 1.018904 | -0.436533 |
| 29 | 1 | 0 | 3.753661 | 0.711960 | -1.490480 |
| 30 | 1 | 0 | 1.299946 | 2.509502 | 0.915376 |
| 31 | 1 | 0 | 1.762539 | 0.940805 | 1.509229 |
| 32 | 1 | 0 | 0.183502 | -2.400824 | -1.302739 |
| 33 | 1 | 0 | -2.504515 | -2.153074 | -0.607447 |
| 34 | 1 | 0 | 4.341344 | -1.698233 | 2.042654 |
| 35 | 1 | 0 | 5.526570 | -0.441943 | 1.613429 |
| 36 | 1 | 0 | 3.945554 | 0.004792 | 2.280442 |
| 37 | 1 | 0 | 4.607175 | -2.671475 | -0.284144 |
| 38 | 1 | 0 | 4.305831 | -1.679840 | -1.726254 |
| 39 | 1 | 0 | 5.741013 | -1.379690 | -0.734454 |
| 40 | 1 | 0 | 0.519078 | 2.758633 | -1.558936 |
| 41 | 1 | 0 | 0.255453 | 1.293618 | -2.519588 |
| 42 | 1 | 0 | 1.900482 | 1.873852 | -2.221047 |
| 43 | 1 | 0 | -5.287511 | 0.164785 | -0.624253 |
| 44 | 1 | 0 | -6.319385 | -0.738395 | 1.443097 |
| 45 | 1 | 0 | -4.727933 | -1.273281 | 2.020976 |
| 46 | 1 | 0 | -5.069181 | 0.458226 | 1.820518 |
| 47 | 1 | 0 | -6.163547 | -2.134424 | -0.673195 |
| 48 | 1 | 0 | -4.739896 | -2.043764 | -1.723212 |
| 49 | 1 | 0 | -4.625199 | -2.798838 | -0.120539 |

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1. Goto, H.; Osawa, E.; *J. Am. Chem. Soc.* **1989**, *111*, 8950–8951.

2. Goto, H.; Osawa, E.; *J. Chem. Soc., Perkin Trans. 2*, **1993**, 187–198.

3. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb,M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2005.

## **S-3.** Detailed experimental procedures

The roots of *S. yunnanensis* were collected in Kunming, Yunnan Province, P. R. China, in October 2010. The plant was identified by Dr. En-De Liu, Kunming Institute of Botany, Kunming, P. R. China. A voucher specimen was deposited at the Kunming Institute of Botany with identification number 201010S01.

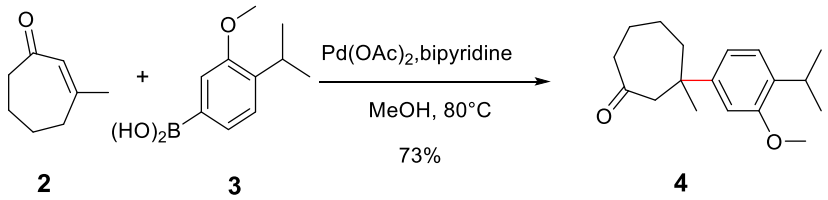
The air-dried powdered material (20 kg) was extracted with acetone (3 × 50 L × 24 h) at room temperature and the solution was evaporated in vacuum to give a crude extract (1.2 kg). The extract was subjected to column chromatography over silica gel, eluting with Chloroform-EtOAC to afford six fractions (I-VI). Fraction II (311 g) was further chromatographed on silica gel (eluting with a gradient of EtOAc in petroleum ether) to yield seven subfractions (A-G). Fraction C (36.0 g) was separated over a silica column and obtained four fractions (Fr. C1–C8). Fr. C5 (4.3 g) was subjected to a RP-18 silica column (MeOH–$H_2O$ from 60:40 to 100:0), and five fractions (Fr.

C5a–C5e) was obtained. Fr. C5d (300 mg) was purified by preparative TLC and semipreparative HPLC to afford salviyunnanenone A (**1) (**1.7 mg).

All reactions were performed with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF) were distilled over sodium. Dichloromethane were distilled over calcium hydride. Reagents were used as received without further purification, unless otherwise stated. Silica gel (200–300 mesh, Qingdao Marine Chemical Ltd., China), light petroleum ether (bp 60–90 ℃) and ethyl acetate were used for product purification by flash column chromatography. Melting Point (MP) was determined with a X-4 Taike micro melting point apparatus and was uncorrected. Proton nuclear magnetic resonance ($^{1}$H NMR) spectra were recorded on Bruker Avance 400 and 800 spectrometer at 400 MHz and 800 MHz. Carbon-13 nuclear magnetic resonance ($^{13}$C NMR) was recorded on Bruker Avance 400 and 800 spectrometer at 100 and 200 MHz. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Mass spectra were recorded on a VG-Auto-Spec-3000 spectrometer. High-resolution mass spectral analysis (HRMS) data were recorded via electron impact mass spectrometry using a time of flight analyzer.

## S-4. Experimental details and characterization data for synthesized compounds

**(1)**

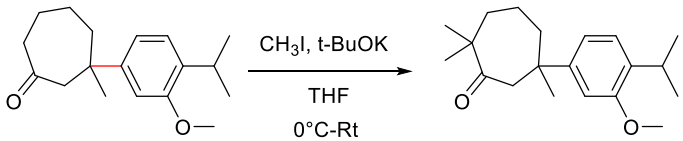



**2** **3** **4**

(R)-3-(4-isopropyl-3-methoxyphenyl)-3-methylcycloheptan-1-one (**4**): to a solution of $Pd(OAc)_2$ (2.25mg, 0.01mmol), Bipyridine (2.45mg, 0.015mmol) and **3** (39mg, 0.2mmol) in MeOH (0.5ml) in sealed tubes was added **2** (12.4mg, 0.1mmol). The reaction mixture was stirred at 80℃ for 12h and filtered with Kieselguhr and concentration afforded the crude product. The crude product was purified by flash chromatography (PE/EtOAc = 25 : 1) to afford **4** (20mg, 73%) as yellow oil. IR (neat) ν 2959, 2932, 2866, 1695, 1610, 1571, 1504, 883, 820; $^{1}$H NMR (400 MHz, $CDCl_3$):

δ 7.12 (d, *J* = 8.0 Hz, 1H), 6.85 (br d, *J* = 8.0 Hz, 1H), 6.78 (br s, 1H), 3.81 (s, 3H), 3.26 (m, 1H), 3.17 (d, *J* =14.4 Hz, 1H), 2.72 (d, 14.4 Hz, 1H), 2.44 – 2.18 (m, 3H), 1.81 – 1.75 (m, 5H), 1.27 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.18 (d, J = 6.9 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 241.2, 156.8, 146.3, 134.5, 125.9, 117.6, 108.2, 55.9, 55.4, 44.2, 43.5, 39.9, 32.1, 26.4, 25.8, 23.9, 22.6, 22.6; HRMS (EI) calcd for $C_{18}H_{26}O_2$ $[M]^+$: 274.1935, found 274,1933.

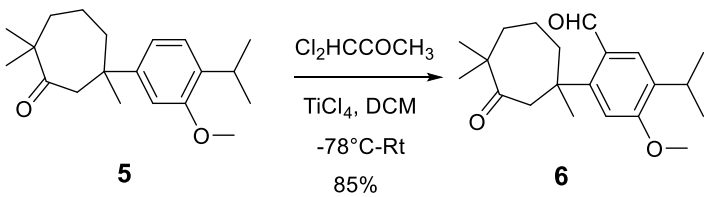
**(2)**




**4** **5**

(R)-6-(4-isopropyl-3-methoxyphenyl)-2,2,6-trimethylcycloheptan-1-one (**5**): to a solution of t-BuOK (34mg, 0.3mmol) in dry THF(0.5ml) was added **4** (27mg, 0.1mmol) and $CH_3I$ (38μl, 0.6mmol) at 0℃,after being stirred 30 min the mixture was stirred at room temperature for 1h and filtered and concentration afforded the crude product. The crude product was purified by flash chromatography (PE/EtOAc = 30 : 1) to afford **5** (22.7mg, 75%) as yellow oil. IR (neat) ν 2960, 2932, 2866, 1698, 1610, 1571, 1504, 873, 817; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.0 Hz, 1H), 6.92 (br d, *J* = 8.0 Hz, 1H), 6.78 (br s, 1H), 3.85 (s, 3H), 3.26 (m, 1H), 3.26 (d, *J* =11.2 Hz, 1H), 2.52 (d, *J* =11.2 Hz, 1H), 2.12–1.52 (m, 6H), 1.25 (s, 3H), 1.19 (d, *J* = 7.2 Hz, 6H), 1.13 (s, 3H), 1.03 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 216.9, 156.6, 148.2, 134.6, 125.6, 117.2, 108.1, 55.4, 51.7, 47.5, 43.4, 39.7, 39.5, 27.8, 27.4, 26.4, 24.4, 22.7, 22.7, 21.0; HRMS (EI) calcd for $C_{20}H_{30}O_2$ $[M]^+$: 302.2246, found 302.2249.

**(3)**

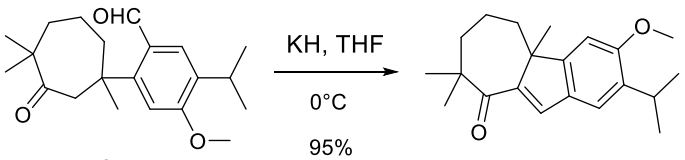



**5** **6**

(R)-5-isopropyl-4-methoxy-2-(1,4,4-trimethyl-3-oxocycloheptyl)benzaldehyde (**6**): to

a solution of **5** (182mg, 0.602mmol) in dry DCM (5ml) was added $Cl_2CHOCH_3$ (96.3μl, 0.963mmol) and $TiCl_4$ (80μl, 0.722mmol) at -78℃. After rising to room temperature the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with DCM (3×10 mL). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to give the crude product. The crude product was purified by flash chromatography (PE/EtOAc = 50:1) to afford **6** (169mg, 85%) as white solid. Mp 110–112 ºC; IR (neat) ν 2958, 2923, 2866, 1762, 1684, 1603, 1547, 1504, 864; $^1$H NMR (400 MHz, $CDCl_3$): δ10.48 (s, 1H), 7.80 (s, 1H), 6.96 (s, 1H), 3.92 (s, 3H), 3.82 (d, *J* = 11.2 Hz, 1H), 3.25 (m, 1H), 2.47 (d, *J* = 11.2 Hz, 1H), 2.00 (m, 1H), 1.99 (m, 1H), 1.77–1.62 (m, 4H), 1.43 (s, 3H), 1.21 (d, *J* = 6.5 Hz, 6H ), 1.14 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 216.5, 191.8, 160.6, 151.0, 134.8, 133.1, 127.8, 108.8, 55.4, 51.0, 47.7, 42.1, 41.1, 38.4, 28.2, 27.8, 26.4, 24.2, 22.3, 22.2, 21.4; HRMS (EI) calcd for $C_{21}H_{30}O_3$ $[M]^+$: 330.2195, found 330.2194.

**(4)**

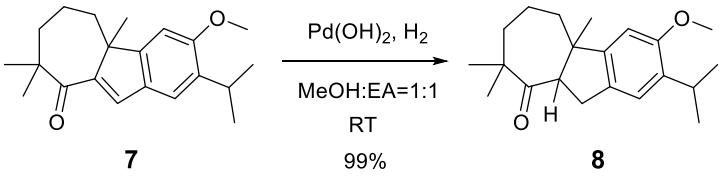



**6** **7**

(R)-2-isopropyl-3-methoxy-4b,8,8-trimethyl-5,6,7,8-tetrahydrobenzo[a]azulen-9(4bH)-one (**7**) : to a solution of **6** (151mg, 0.457mmol) under argon atmosphere in dry THF (5ml) was added KH (18mg, 0.457mmol) at 0℃, then the mixture was stirred at the same temperature for 1 h. The reaction was quenched with ice water, extracted with EA (3×5 mL), The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to give the crude product. The crude product was purified by flash chromatography (PE/EtOAc = 100: 1) to afford **7** (135mg, 95%) as yellow solid. Mp 127–129 ºC; IR (neat) ν 3065, 2963, 2940, 2869, 1643, 1613, 1543, 1504, 882; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 1H), 7.19 (s, 1H), 6.76 (s, 1H), 3.87 (s, 3H), 3.31 (m, 1H), 2.27 (m, 1H), 2.00 (m, 1H), 1.86 (m,

1H), 1.74 (m, 1H), 1.55 (m, 1H), 1.33 (s, 3H), 1.26 (s, 3H), 1.21 (d, *J* = 7.8 Hz, 3H), 1.19 (s, 3H), 0.98 (d, *J* = 7.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 209.2, 157.1, 155.2, 154.7, 136.1, 136.0, 131.7, 120.6, 103.9, 55.6, 52.9, 45.9, 40.7, 40.1, 29.9, 26.8, 24.2, 22.8, 22.8, 22.1, 20.0; HRMS (EI) calcd for $C_{21}H_{28}O_2$ $[M]^+$: 312.2089, found 312.2093.

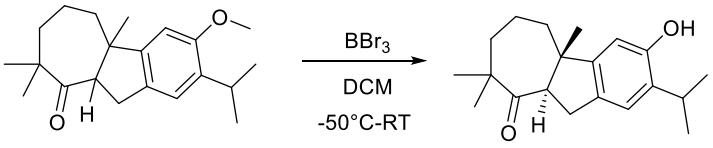
**(5)**




**7** **8**

(4bS)-2-isopropyl-3-methoxy-4b,8,8-trimethyl-5,6,7,8,9a,10-hexahydrobenzo[a]azulen-9(4bH)-one (**8**): to a solution of **7** (127mg, 0.407mmol) under hydrogen atmosphere in EA:MeOH(1:1 4ml) was added catalytic amount of $Pd(OH)_2$ at room temperature, then the mixture was stirred at the same temperature for 5 h and filtered with Kieselguhr and concentration afforded the crude product. The crude product was purified by flash chromatography (PE/EtOAc = 100: 1) to afford **8** (126mg, 99%) as white solid: mp 99–101 ℃.

**(6)**

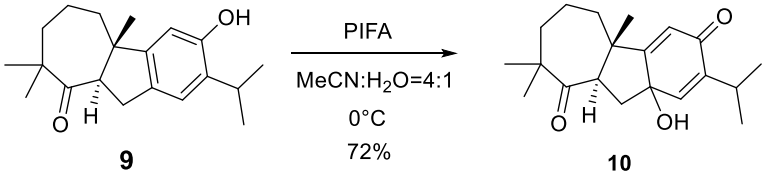



**8** **9**

(4bS)-3-hydroxy-2-isopropyl-4b,8,8-trimethyl-5,6,7,8,9a,10-hexahydrobenzo[a]azulen-9(4bH)-one(**9**): to a solution of **8** (119mg, 0.378mmol) in dry DCM (3ml) was added $BBr_3$ (75.7μl/1M in DCM, 0.076mmol) at -50℃,after naturally rising to room temperature the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with DCM (3×3 mL). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to give the crude product. The crude product was purified by flash chromatography (PE/EtOAc=20: 1)

to afford **9** (53 mg, 46%) as white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.03 (s, 1H), 6.47 (s, 1H), 4.69 (s, 1H), 3.67 (m, 1H), 3.44 (m, 1H), 3.15 (step, *J* = 6.9 Hz, 1H), 2.58 (m, 1H), 2.18 (m, 1H), 1.84 (m, 2H), 1.80 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.19 (s, 3H), 1.05 (s, 3H), 0.83 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 216.0, 151.8, 149.9, 132.7, 132.5, 122.2, 108.6, 58.9, 48.5, 47.1, 40.7, 39.3, 30.8, 29.9, 27.0, 23.0, 22.8, 22.6, 22.1, 20.7.

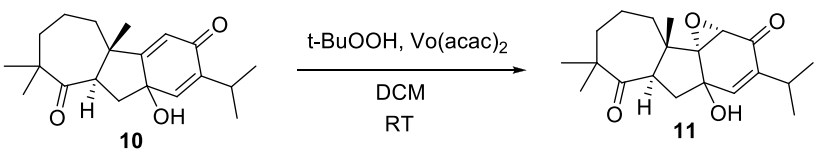
**(7)**




**9** **10**

(4bS,9aR)-10a-hydroxy-2-isopropyl-4b,8,8-trimethyl-4b,5,6,7,8,9a,10,10a-octahydrobenzo[a]azulene-3,9-dione(**10**): to a solution of **9** (10mg, 0.033mmol) in MeOH-$H_2O$ (1ml) was added PIFA (17mg, 0.04mmol) at 0℃. After being stirred 30 min the mixture was stirred at room temperature for 2h and concentration afforded the crude product. The crude product was purified by flash chromatography (PE/EtOAc = 8: 1) to afford **10** (7.5mg, 72%) as yellow solid. IR (neat) ν 3394, 2963, 2933, 2869, 1701, 1672, 1639, 1457, 1384; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 6.72 (s, 1H), 5.92 (s, 1H), 4.02 (m, 1H), 2.92 (m, 1H), 2.09–1.60 (m, 6H), 1.50–1.25 (m, 2H), 1.18 (s, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.07 (s, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.84 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 215.8, 186.7, 174.4, 145.1, 138.8, 122.1, 73.5, 54.1, 46.8, 45.9, 40.9, 38.8, 35.5, 30.2, 26.2, 23.8, 22.8, 21.7, 21.6, 20.7; HRMS (EI) calcd for $C_{20}H_{28}O_3$ $[M]^+$: 316.2038, found 316.2035.

**(8)**

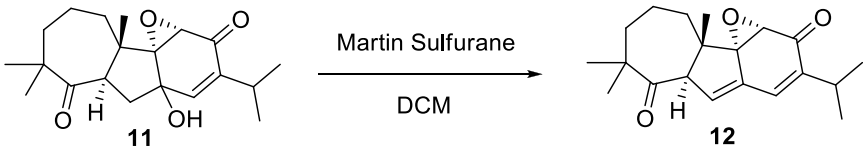



**10** **11**

(1aS,5aR,10aS,10bR)-4a-hydroxy-3-isopropyl-7,7,10a-trimethyl-4a,5,5a,7,8,9,10,10a-octahydro-6H-cyclohepta[2,3]indeno[3a,4-b]oxirene-2,6(1aH)-dione(**11**): to a solution

of **10** (12mg, 0.038mmol) in DCM (0.5ml) was added $Vo(acac)_2$ (2mg, 0.0076mmol) at room temperature, then the mixture was stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ and extracted with DCM (3×3 mL). The combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to give the crude product without further purification.

**(9)**




**11** **12**

(1aS,5aR,10aS,10bS)-3-isopropyl-7,7,10a-trimethyl-5a,7,8,9,10,10a-hexahydro-6H-cyclohepta[2,3]indeno[3a,4-b]oxirene-2,6(1aH)-dione(**12**): to a solution of **11** (10mg, 0.03mmol) in DCM (0.5ml) was added Martin Sulfurane (40mg, 0.06mmol) at 0℃, then the mixture was stirred at the room temperature for 2 h and concentration afforded the crude product. The crude product was purified by flash chromatography (PE/EtOAc = 6:1) to afford **12** (7.5mg, 60%) as yellow solid.

Compound **12**:

$^1$H NMR (800 MHz, acetone-$d_6$): δ 7.05 (s, 1H), 6.51 (d, *J* = 2.1 Hz, 1H), 3.71 (s, 1H), 2.90 (step, *J* = 6.8 Hz, 1H), 1.98 (m, 1H), 1.82 (m, 1H), 1.76–1.67 (m, 3H), 1.50 (m, 1H), 1.16 (s, 3H), 1.10 (s, 3H), 1.09 (d, *J* = 6.8 Hz，3H), 1.00 (d, *J* = 6.8 Hz，3H), 1.00 (s, 3H), 0.86 (s, 3H); $^{13}$C NMR (200 MHz, acetone-$d_6$): δ 214.5, 194.3, 144.3, 138.8, 136.3, 130.5, 77.1, 62.9, 57.8, 47.3, 46.8, 39.5, 34.3, 30.4, 27.6, 23.1, 22.2, 21.4, 21.0, 20.3; HRESIMS *m/z* 313.1808 $[M-H]^-$ (calcd for $C_{20}H_{26}O_3$, 313.1809).

$^1$H NMR (800 MHz, $CDCl_3$): δ 6.78 (s, 1H), 6.44 (d, *J* = 2.0 Hz，1H), 4.38 (d, *J* = 2.0Hz，1H), 3.62 (s, 1H), 2.94 (step, *J* = 6.9 Hz，1H), 1.84 (m, 2H), 1.80 (m, 1H), 1.78 (m, 1H), 1.71 (q, *J* = 7.5 Hz, 1H), 1.64 (m, 1H), 1.42 (m, 1H), 1.18 (s, 3H), 1.14 (d, *J* = 6.9 Hz，3H), 1.12 (d, *J* = 6.9 Hz，3H), 1.09 (s, 3H), 1.02 (s, 3H) ; $^{13}$C NMR (200 MHz, $CDCl_3$): δ 214.6, 193.9, 144.3, 137.0, 135.7, 129.6, 76.4, 62.2, 57.6, 46.8, 46.2, 39.3, 33.9, 30.3, 26.9, 22.8, 21.9, 21.2, 20.9, 19.6.

**Table 1**. NMR Data of compounds **1**and **12** in $CDCl_3$.

| no | $\delta_C$, type | | $\Delta\delta C$ | $\delta_H$ ($J$ in Hz) | |
|---|---|---|---|---|---|
| | Compound **1**[a] | Compound **12**[b] | | Compound **1**[a] | Compound **12**[b] |
| 1 | 27.3, $CH_2$ | 33.9, $CH_2$ | 6.6 | 1.15, m | 1.42. m |
| | | | | 1.36, m | 1.64, m |
| 2 | 18.8, $CH_2$ | 19.6, $CH_2$ | 0.8 | 1.76, m | 1.80, m |
| | | | | | 1.78, m |
| 3 | 34.6, $CH_2$ | 39.3, $CH_2$ | 4.7 | 1.58, m | 1.71, q (7.5) |
| | | | | 2.04, m | 1.84, m |
| 4 | 46.2, C | 46.2, C | 0 | | |
| 5 | 215.2, C | 214.6, C | -0.6 | | |
| 6 | 63.1, CH | 62.6, CH | -0.5 | 3.93, d (2.9) | 4.38, d (2.0) |
| 7 | 136.0, CH | 137.0, CH | 1.0 | 6.24, d (2.9) | 6.44, d (2.0) |
| 8 | 135.9, C | 135.7, C | -0.2 | | |
| 9 | 75.8, C | 76.4, C | 1.4 | | |
| 10 | 43.7, C | 46.8, C | 3.1 | | |
| 11 | 57.5, CH | 57.6, CH | 0.1 | 3.60, s | 3.62, s |
| 12 | 194.8, C | 193.9, C | -0.9 | | |
| 13 | 144.1, C | 144.3, C | 0.2 | | |
| 14 | 129.3, CH | 129.6, CH | 0.3 | 6.90, s | 6.78, s |
| 15 | 27.0, CH | 26.9, CH | -0.1 | 2.92, sept (6.8) | 2.94, sept (6.9) |
| 16 | 21.8, $CH_3$ | 21.9, $CH_3$ | 0.1 | 1.01, d (6.8) | 1.14, d (6.9) |
| 17 | 21.1, $CH_3$ | 21.2, $CH_3$ | 0.1 | 1.09, d (6.8) | 1.12, d (6.9) |
| 18 | 28.8, $CH_3$ | 30.3, $CH_3$ | 1.5 | 1.12, s | 1.09, s |
| 19 | 21.3, $CH_3$ | 22.8, $CH_3$ | 1.5 | 1.12, s | 1.02, s |
| 20 | 24.6, $CH_3$ | 20.9, $CH_3$ | -3.7 | 1.28, s | 1.18, s |

[a]Recorded on 400MHz, [b]Recorded on 800MHz.

## **S-5.** Spectra of compounds **1** to **12**

Figure **1**. $^{1}$H NMR spectrum of salviyunnanone A (**1**) (400MHz, $CDCl_3$)

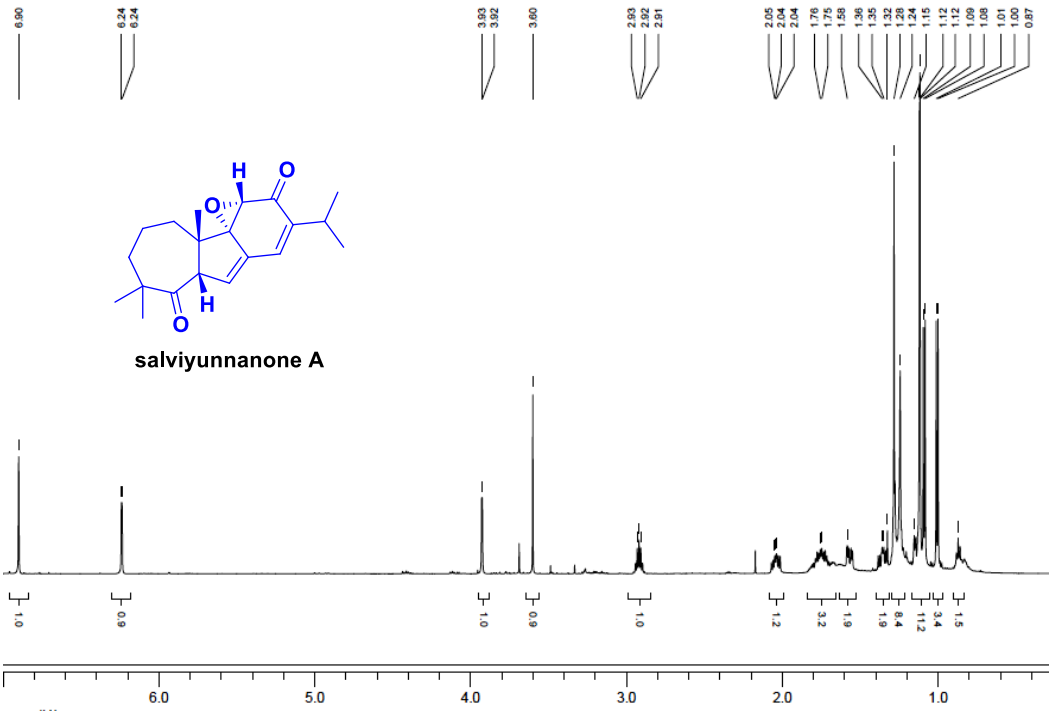



Figure **2**. $^{13}$C NMR spectrum of salviyunnanone A (**1**) (100MHz, $CDCl_3$)

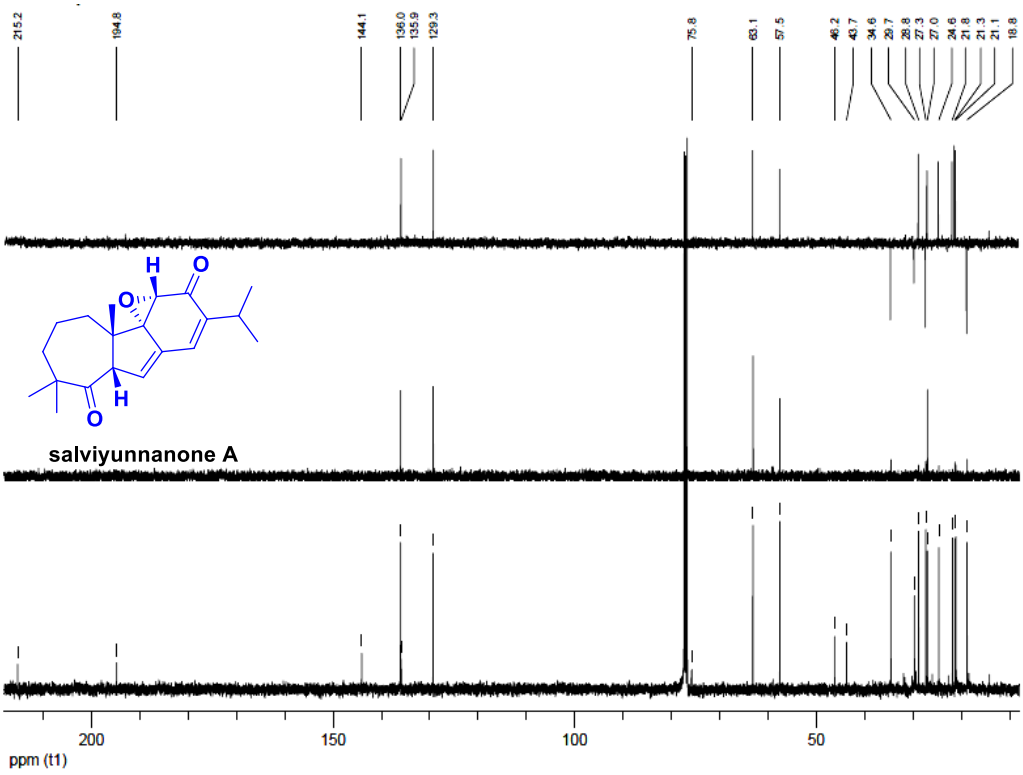


Figure **3**. HSQC spectrum of salviyunnanone A (**1**)

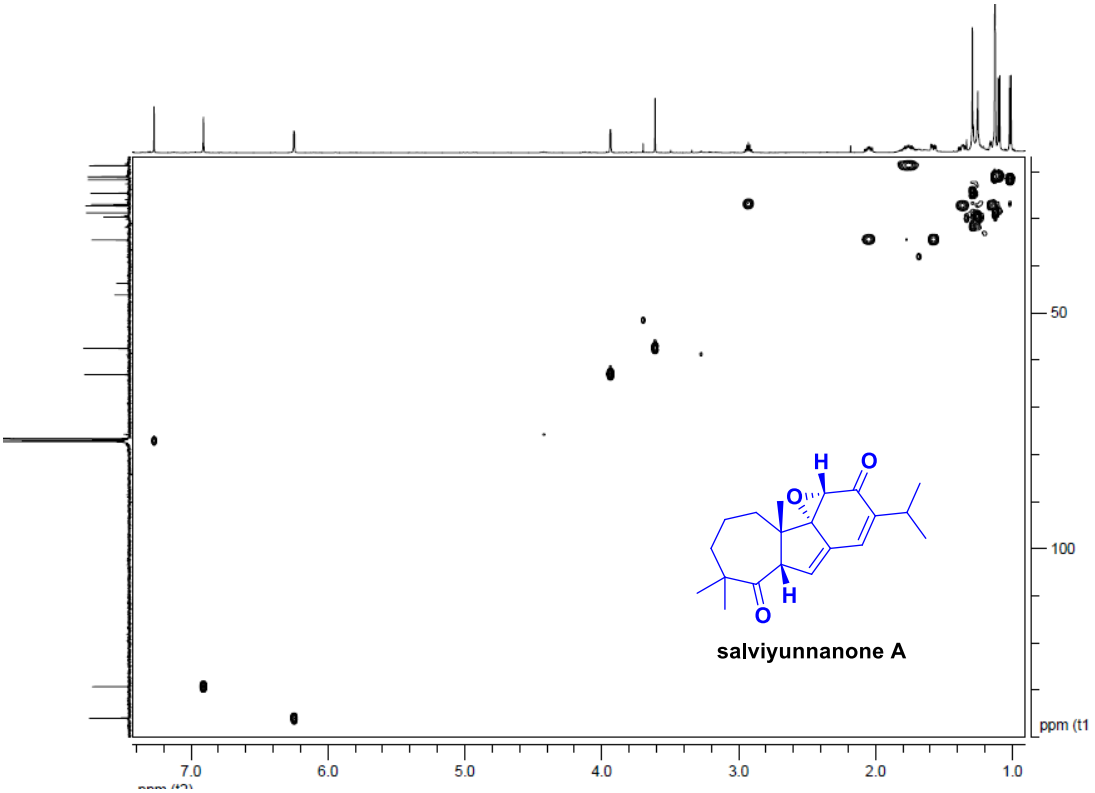



Figure **4**. $^{1}$H-$^{1}$H COSY spectrum of salviyunnanone A (**1**)

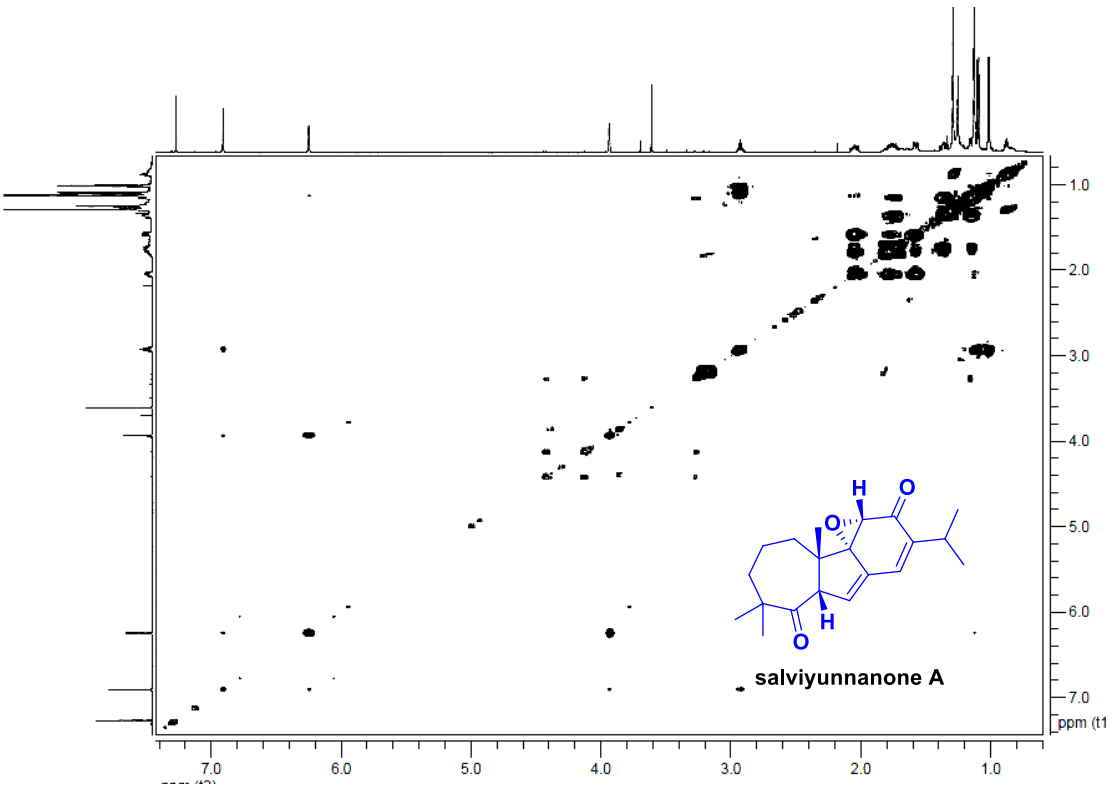


Figure **5**. HMBC spectrum of salviyunnanone A (**1**)

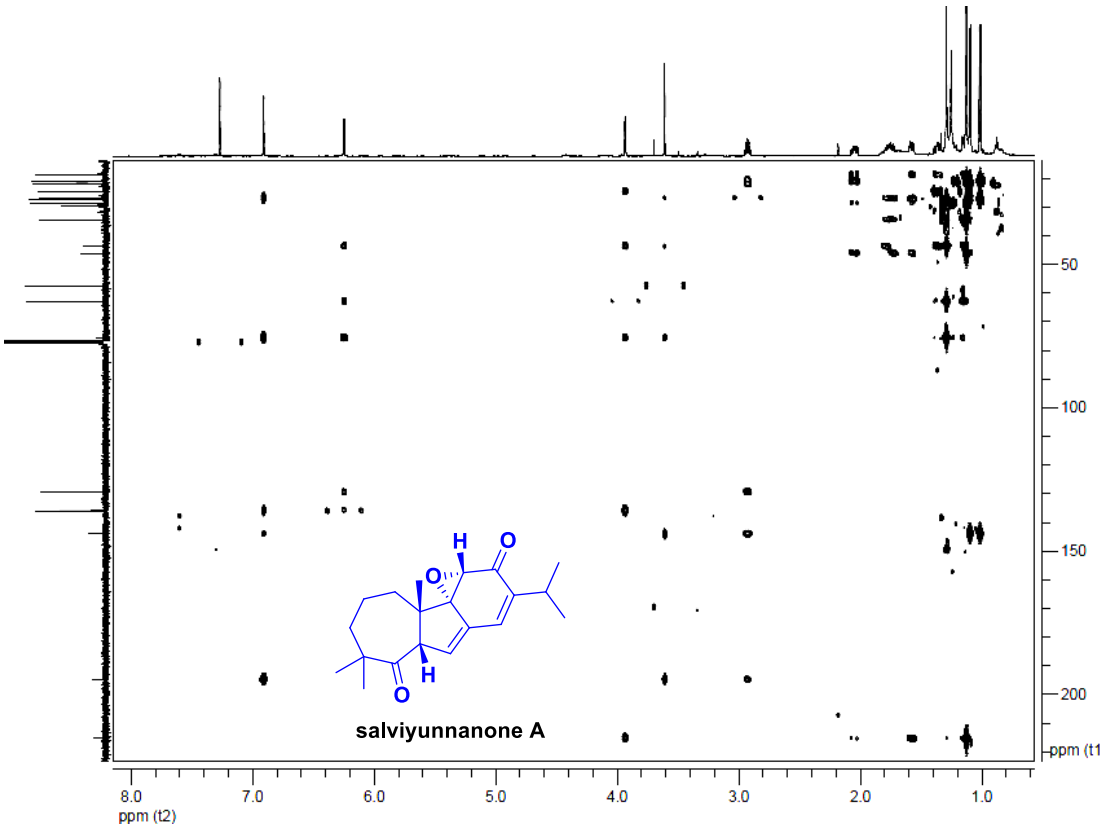



Figure **6**. ROESY spectrum of salviyunnanone A (**1**)

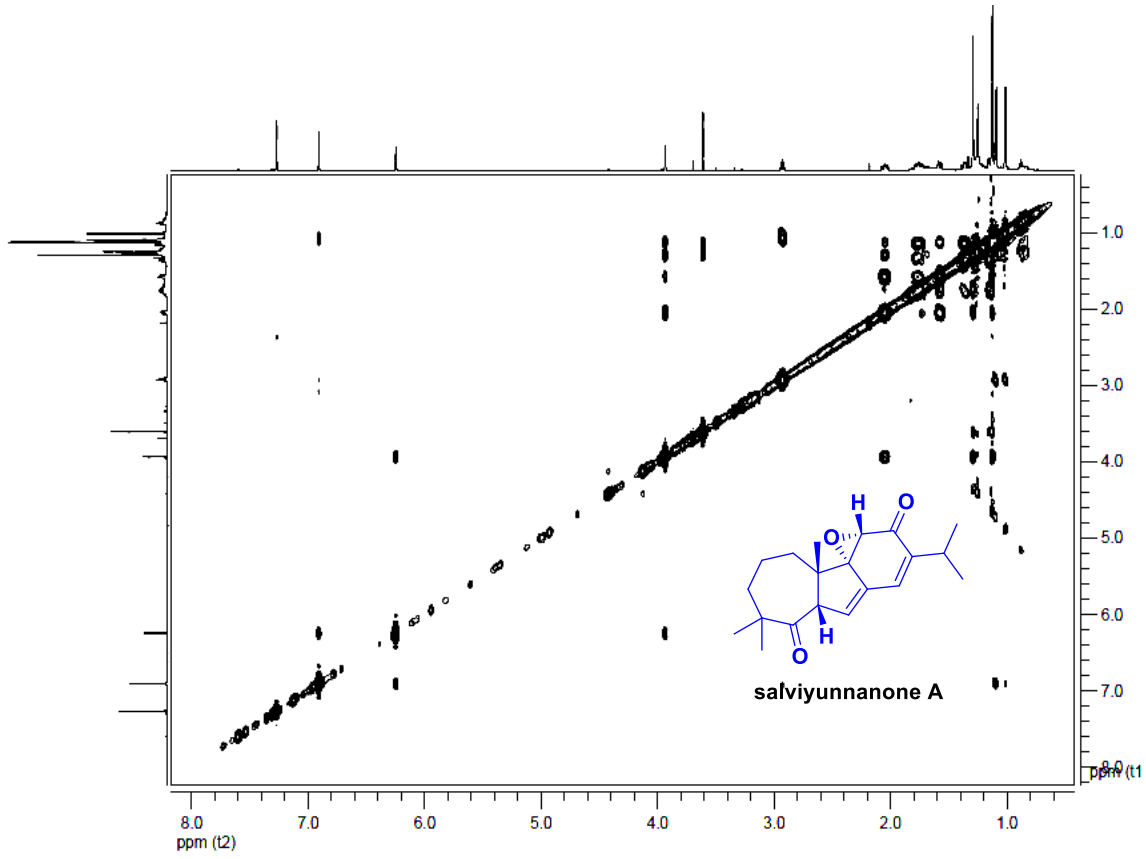


Figure **7**. ESIMS spectrum of salviyunnanone A (**1**)

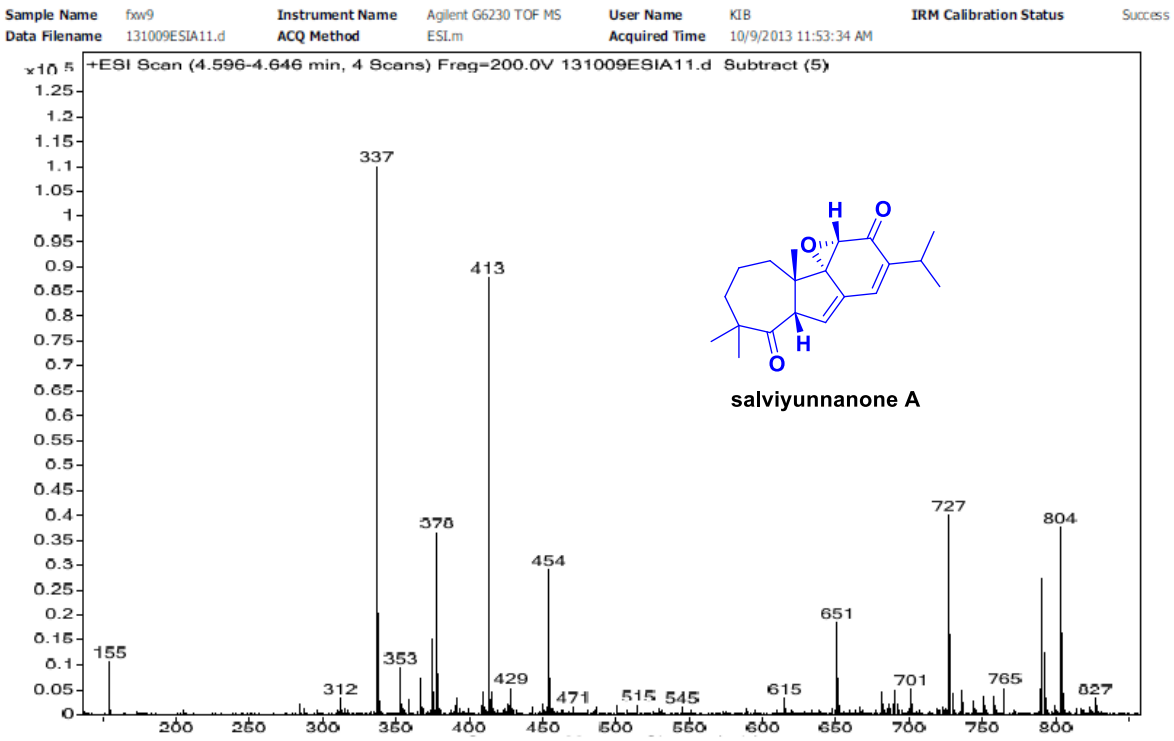
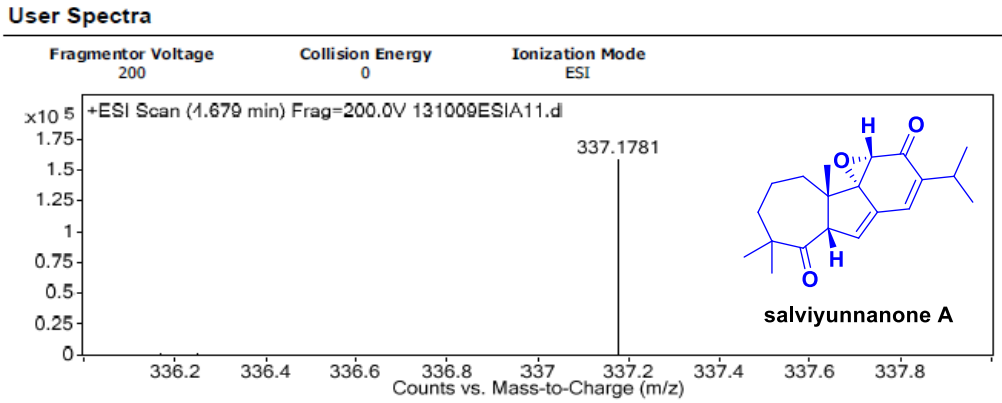



Figure **8**. HRESIMS spectrum of salviyunnanone A (1)




**Formula Calculator Element Limits**

| Element | Min | Max |
|---|---|---|
| C | 0 | 200 |
| H | 0 | 400 |
| O | 2 | 4 |
| Na | 1 | 1 |

**Formula Calculator Results**

| Formula | Calculated Mass | Measured Mass | Diff. (mDa) | Diff. (ppm) | DBE |
|---|---|---|---|---|---|
| C20 H26 Na O3 | 337.1780 | 337.1786 | -0.7 | -2.0 | 7.5 |

--- End Of Report ---

Figure **9**.[1]H NMR (400 MHz, $CDCl_3$) of compound **4**

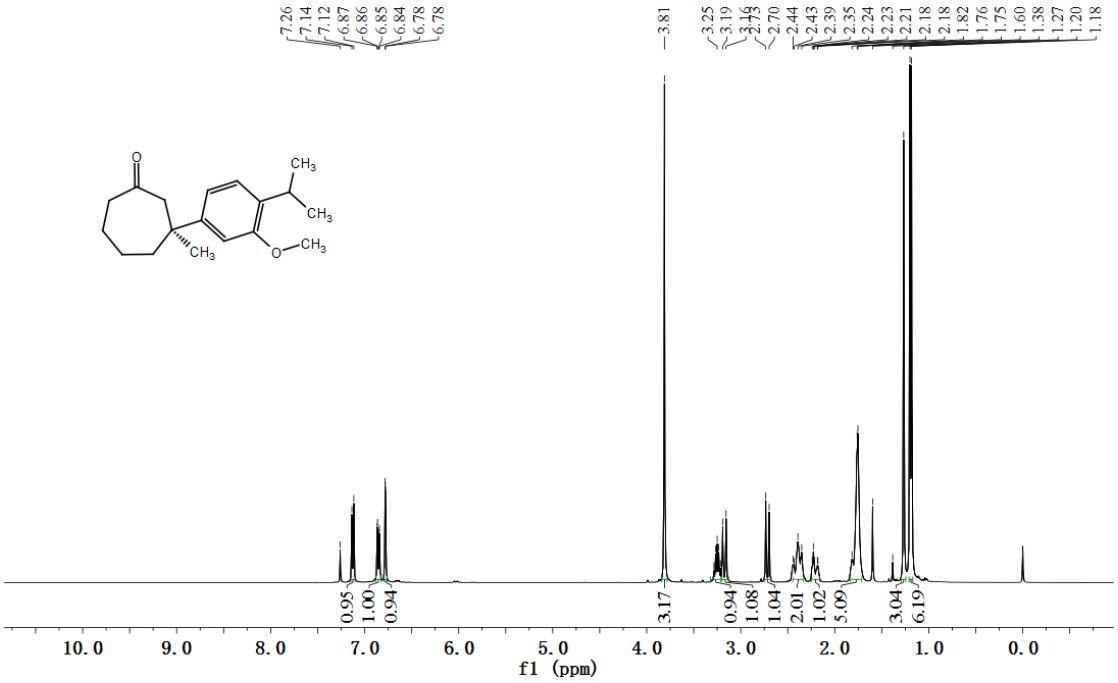



Figure **10**.[13]C NMR (100 MHz, $CDCl_3$) of compound **4**

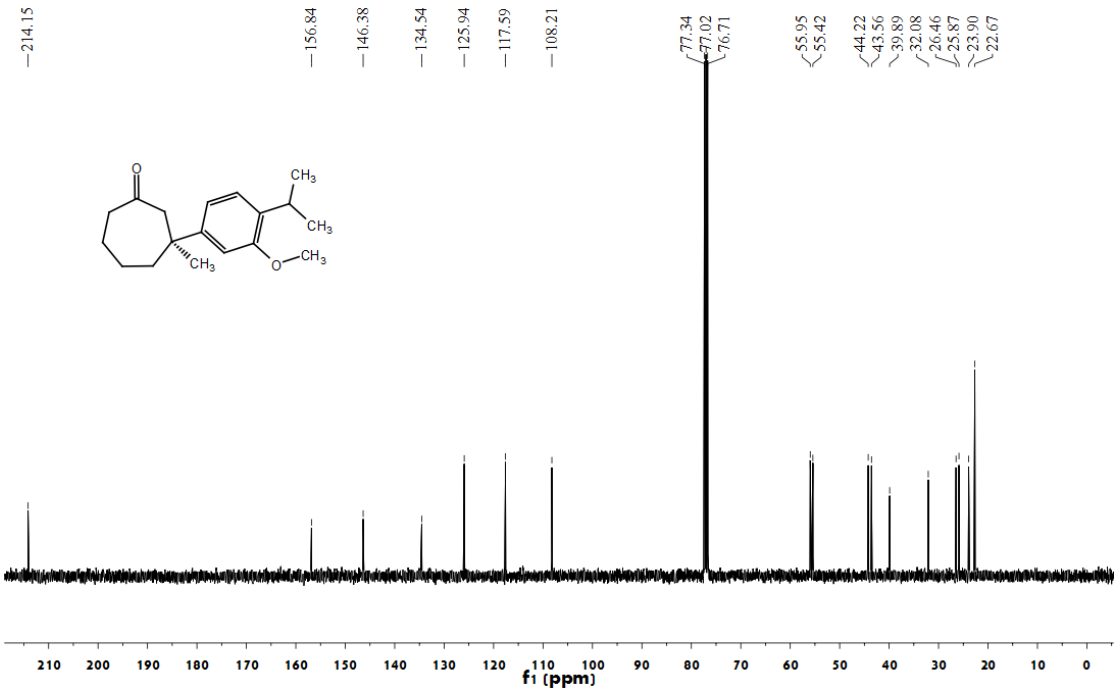


Figure **11**.[1]H NMR (400 MHz, $CDCl_3$) of compound **5**

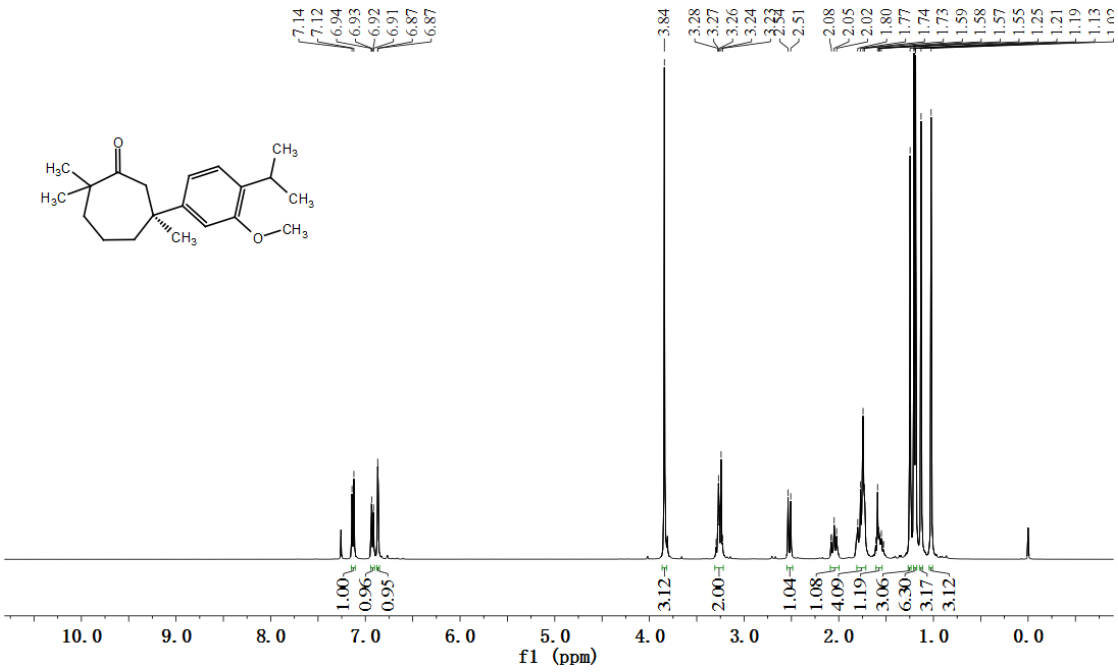



Figure **12**.[13]C NMR (100 MHz, $CDCl_3$) of compound **5**

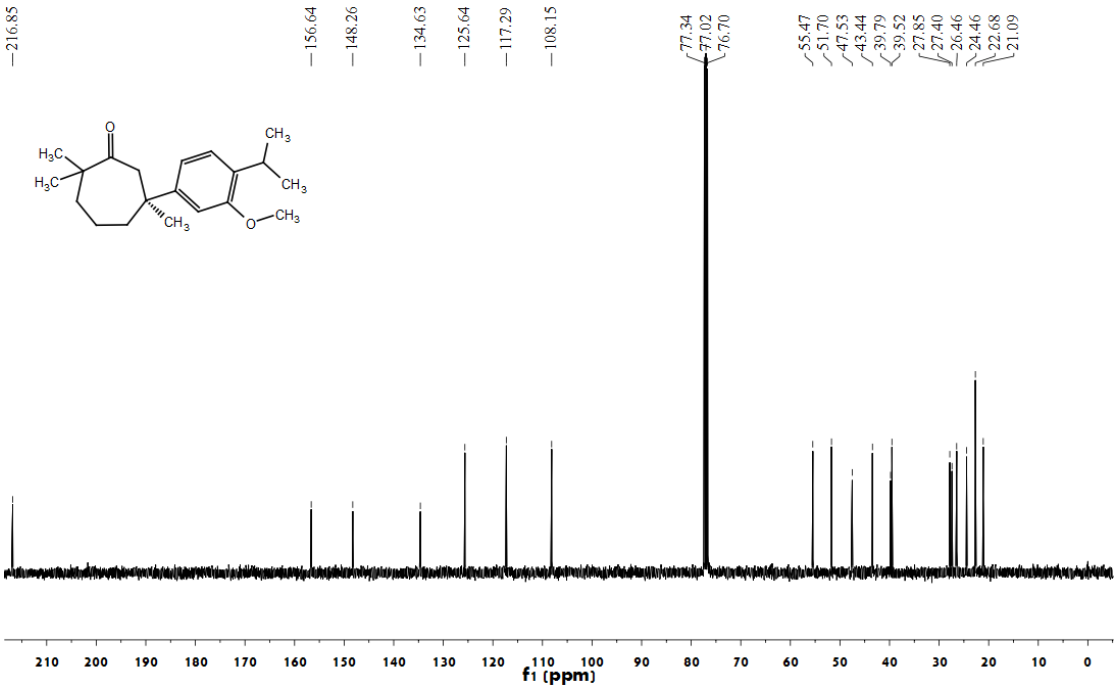


Figure **13**.[1]H NMR (400 MHz, $CDCl_3$) of compound **6**

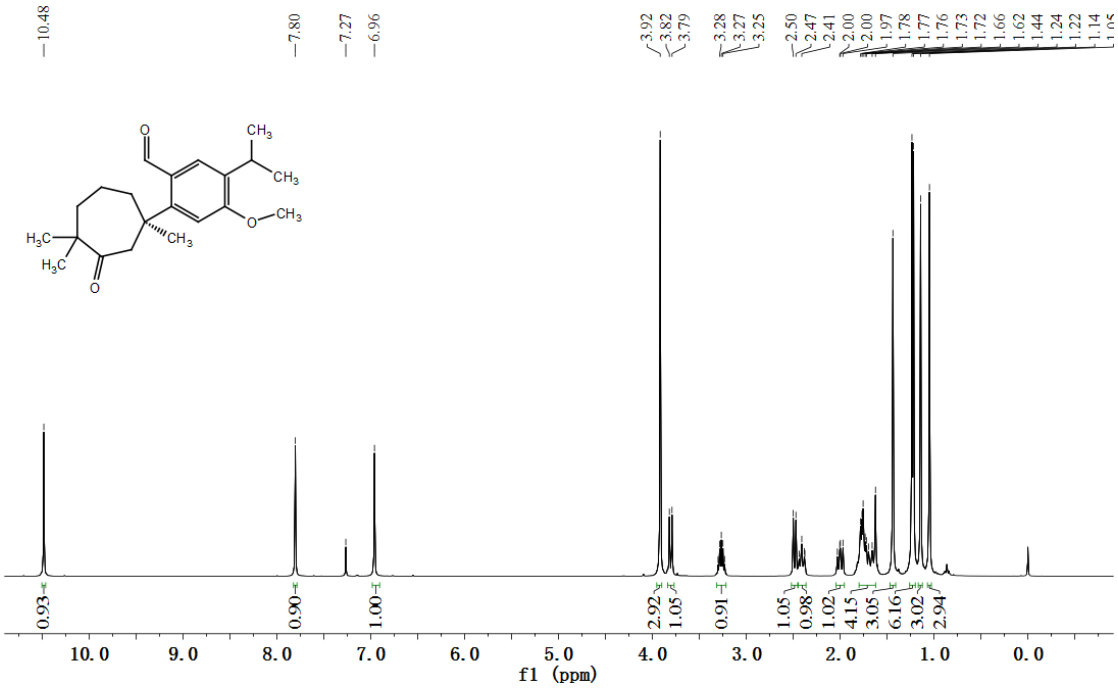



Figure **14**.[13]C NMR (100 MHz, $CDCl_3$) of compound **6**

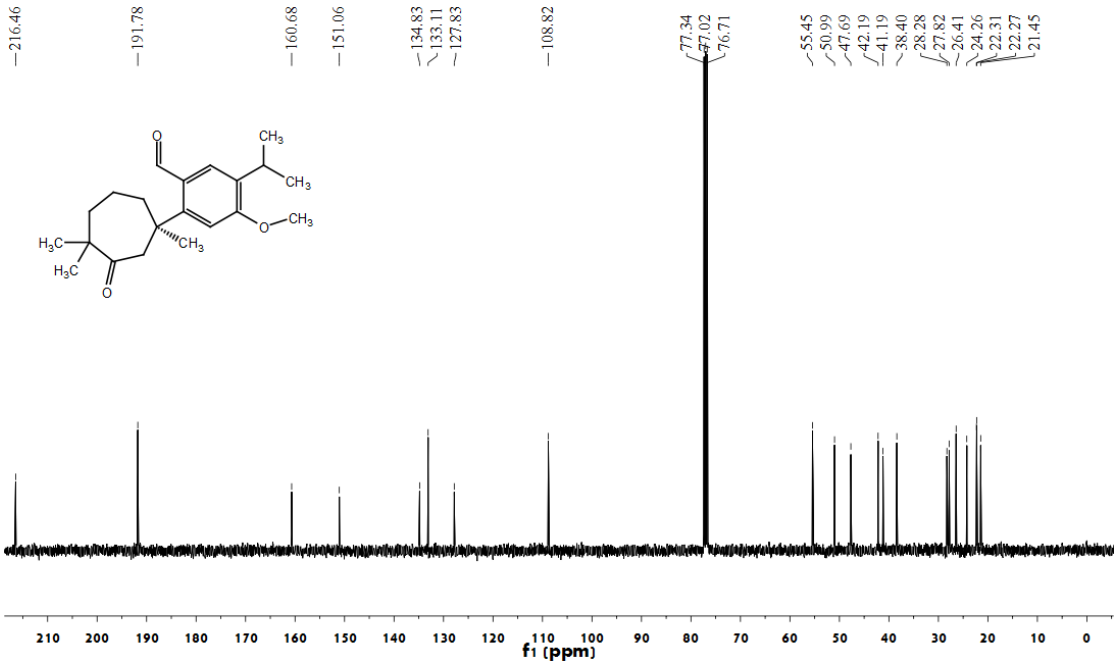


Figure **15**.[1]H NMR (400 MHz, $CDCl_3$) of compound **7**

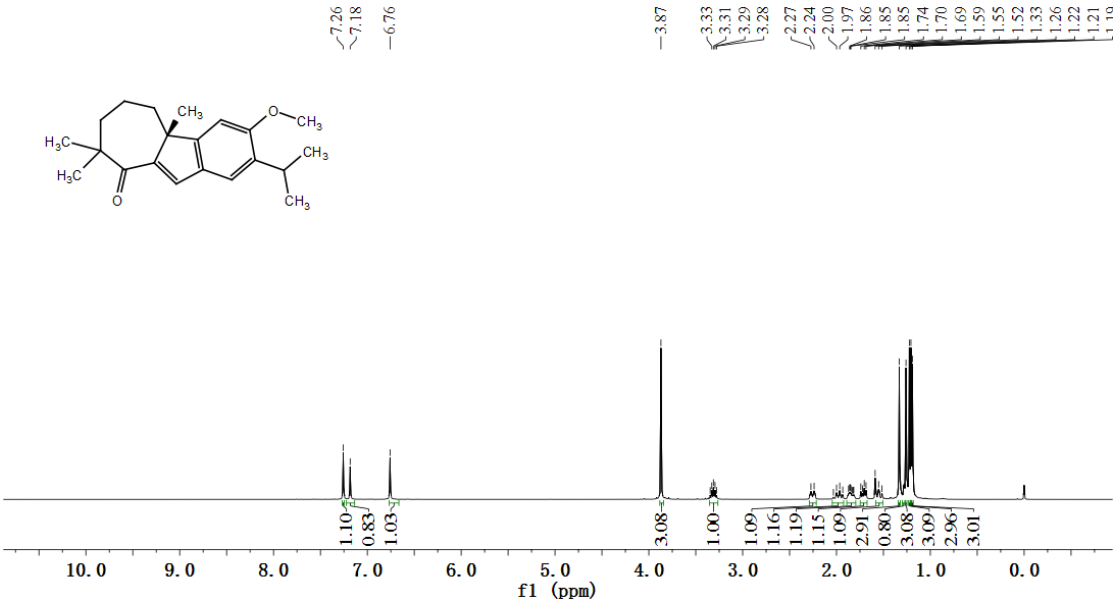



Figure **16**.[13]C NMR (100 MHz, $CDCl_3$) of compound **7**

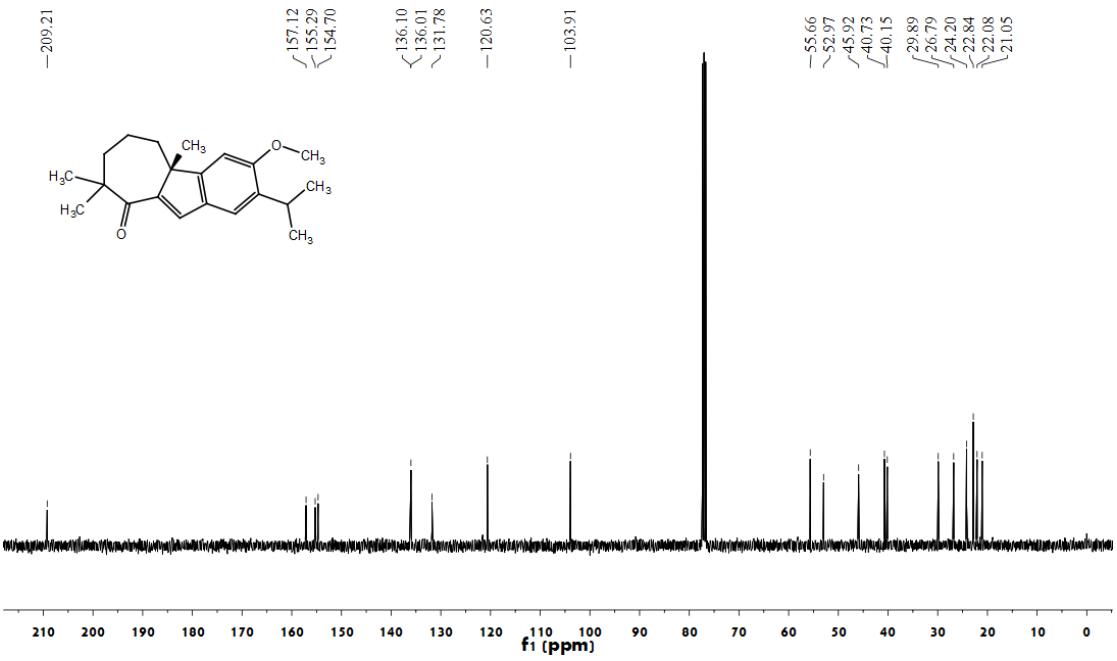


Figure **17**.[1]H NMR (400 MHz, $CDCl_3$) of compound **8 (isomers)**

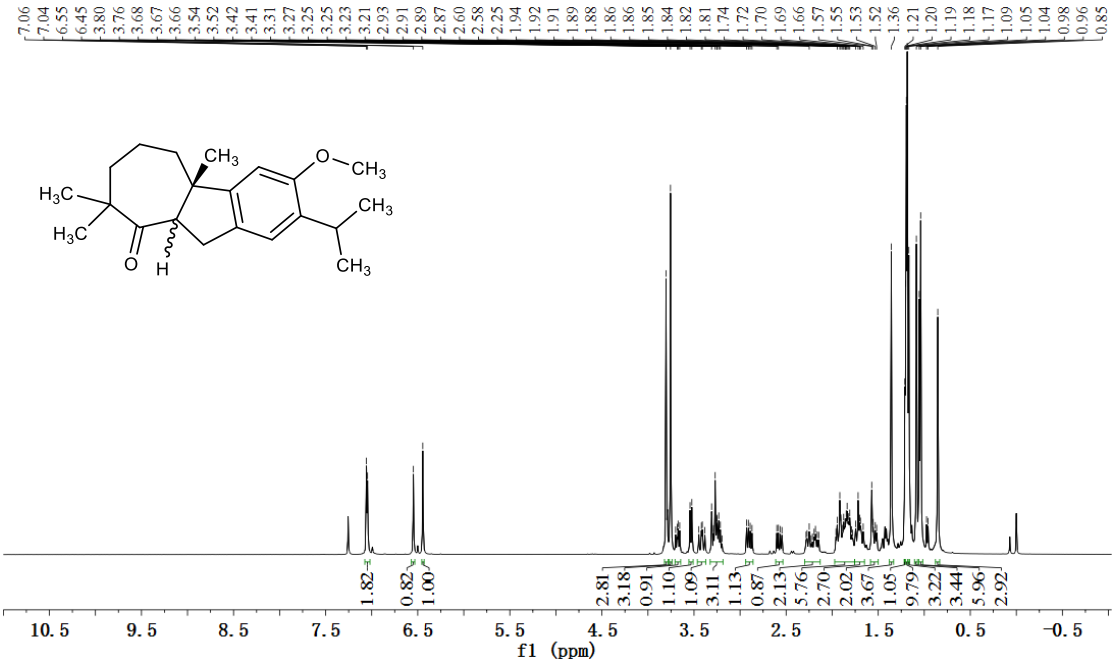



Figure **18**.[13]C NMR (100 MHz, $CDCl_3$) of compound **8 (isomers)**

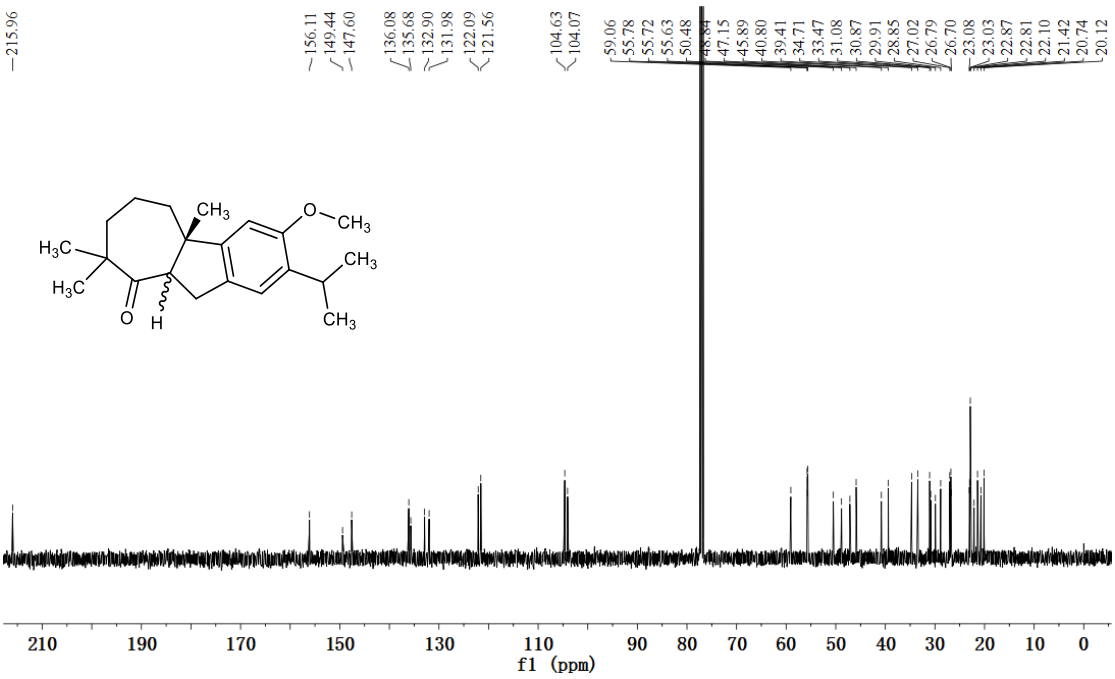


Figure **19**.[1]H NMR (400 MHz, $CDCl_3$) of compound **9**

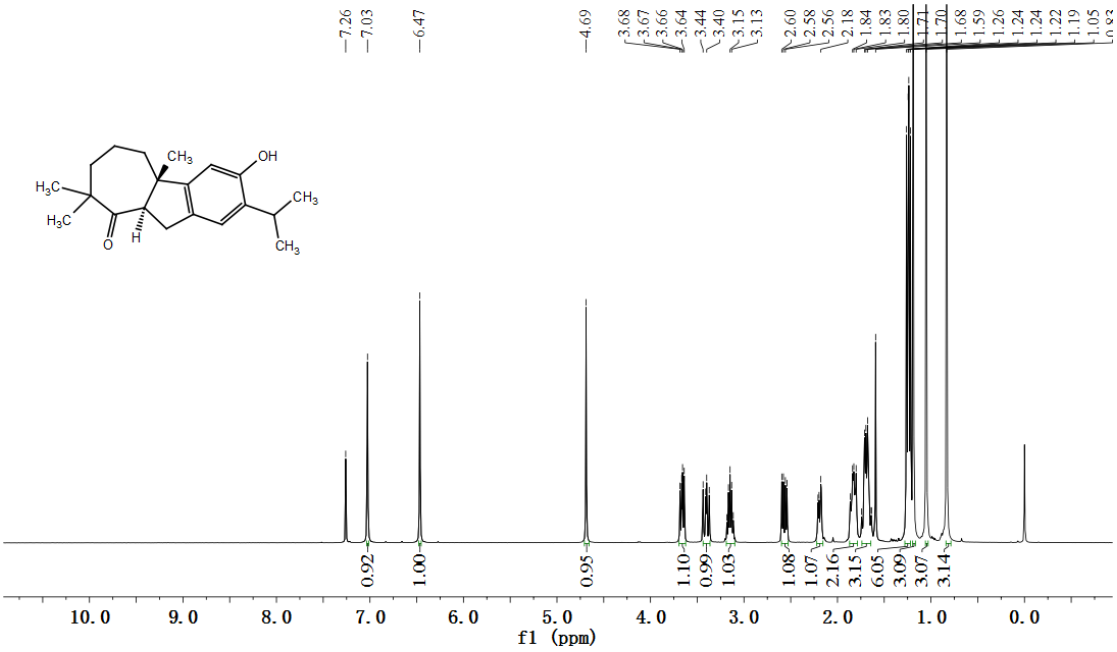



Figure **20**.[13]C NMR (100 MHz, $CDCl_3$) of compound **9**

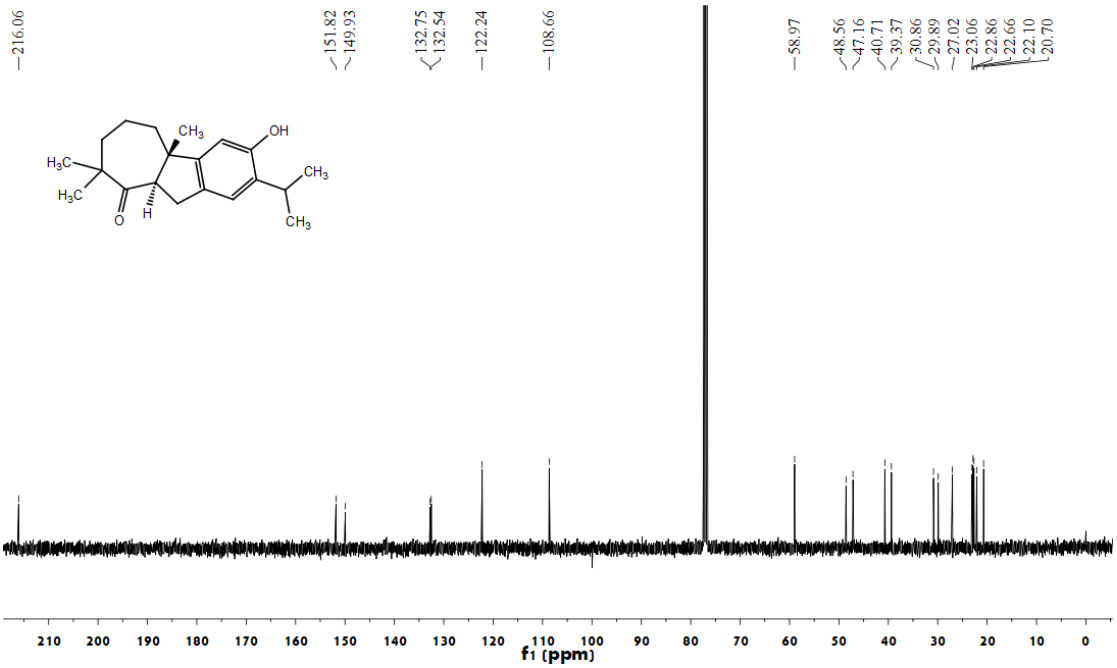


Figure **21**.[1]H NMR (400 MHz, $CDCl_3$) of compound **10**

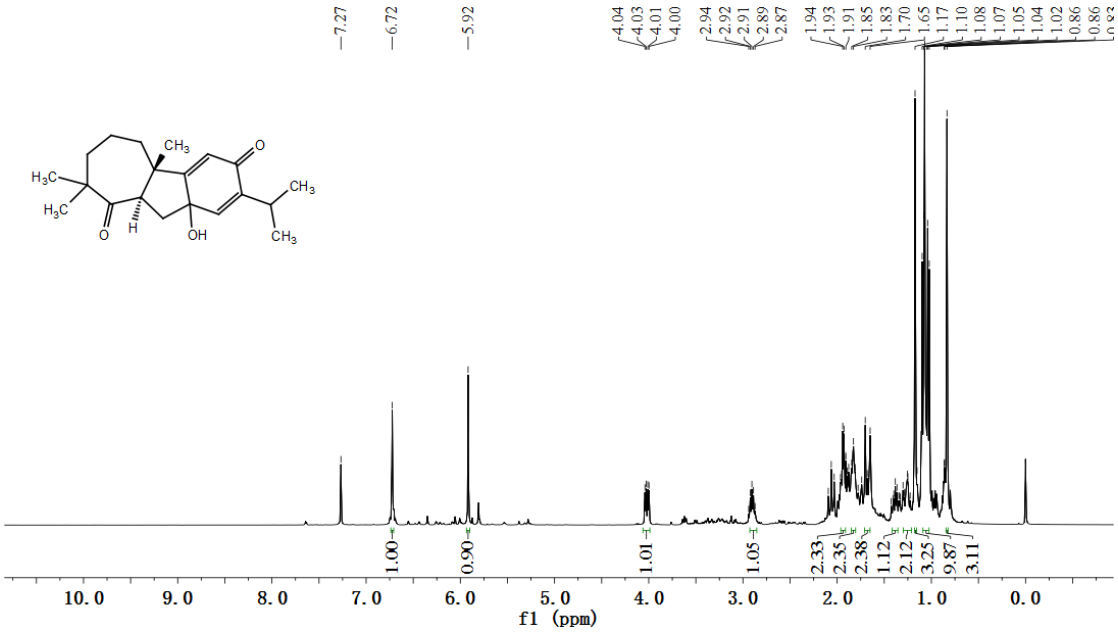



Figure **22**.[13]C NMR (100 MHz, $CDCl_3$) of compound **10**

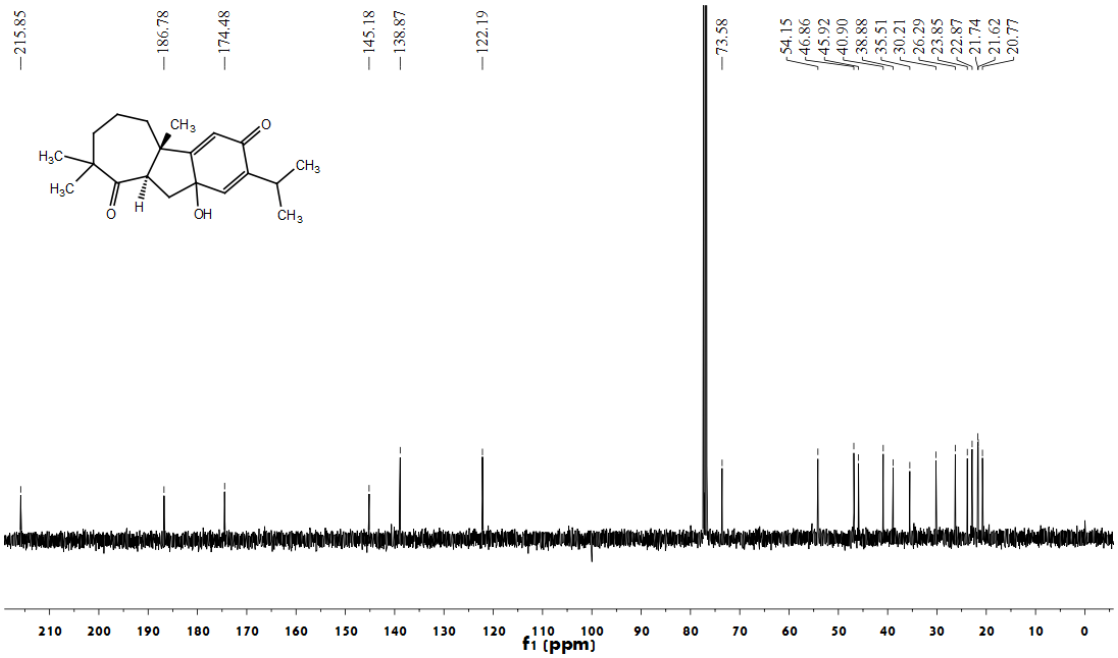


Figure **23**.[1]H NMR (800 MHz, Acetone-$d_6$) of (±)-6-*epi*-salviyunnanone A (**12**)

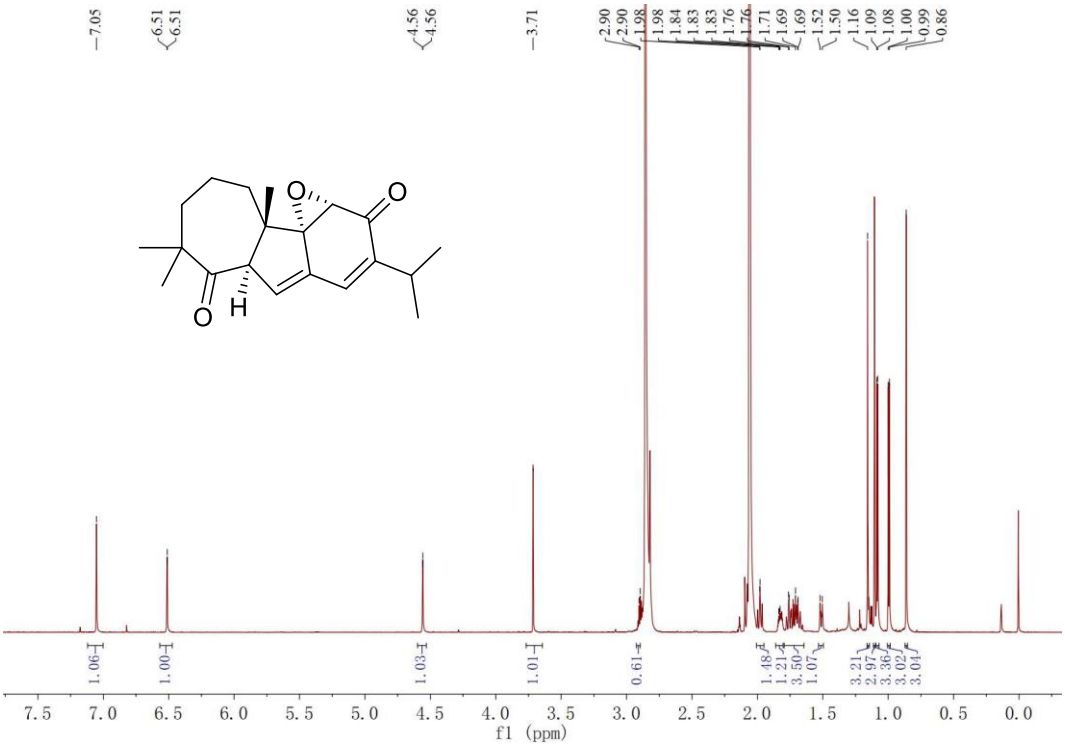



Figure **24**.[13]C NMR (200 MHz, Acetone-$d_6$) of (±)-6-*epi*-salviyunnanone A (**12**)

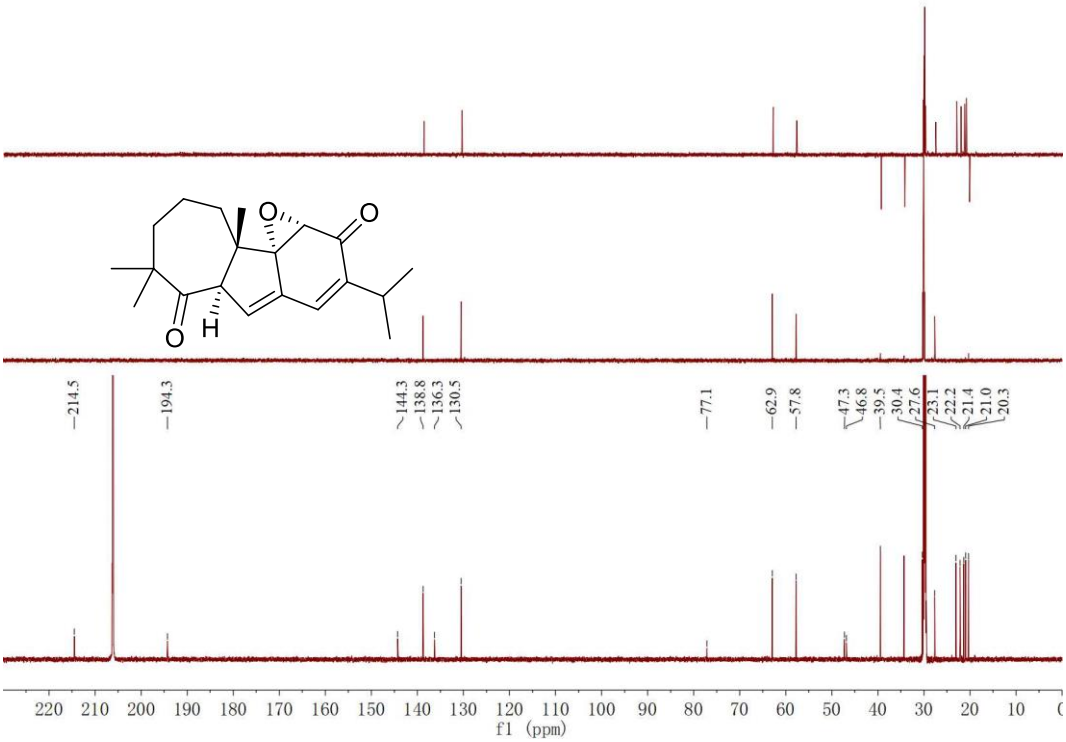


Figure **25**.[1]H NMR (800 MHz,$CDCl_3$) of (±)-6-*epi*-salviyunnanone A (**12**)

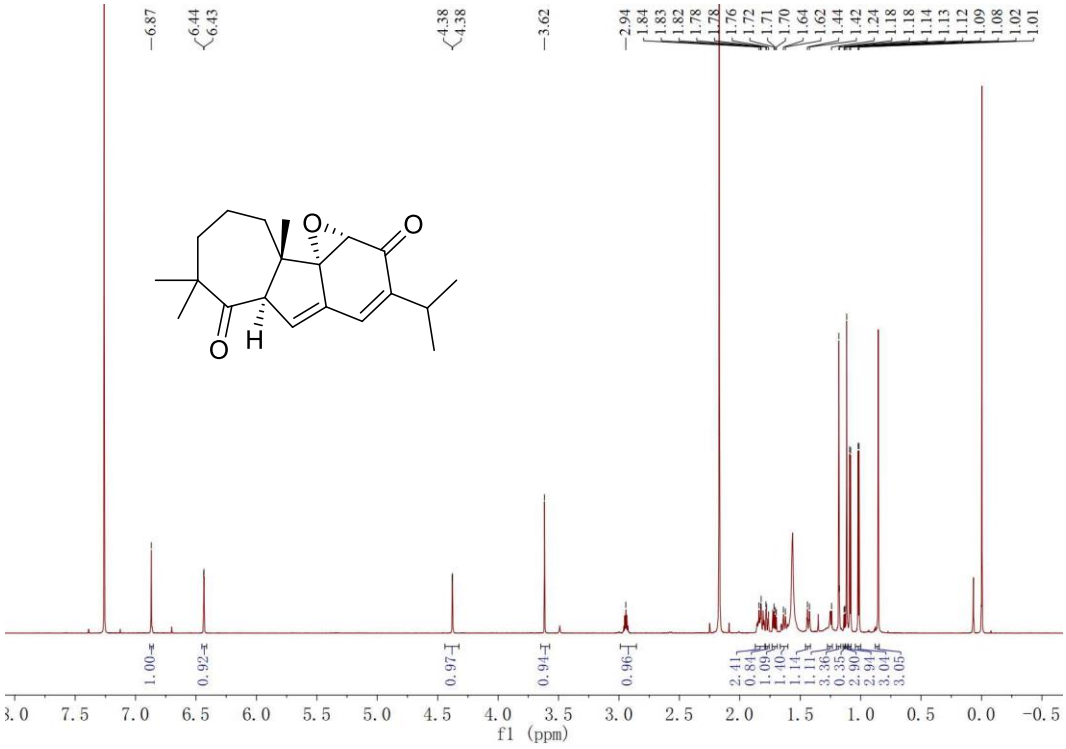



Figure **26**.[13]C NMR (200 MHz, $CDCl_3$) of (±)-6-*epi*-salviyunnanone A (**12**)

Figure **27**. HSQC spectrum of (±)-6-*epi*-salviyunnanone A (**12**)

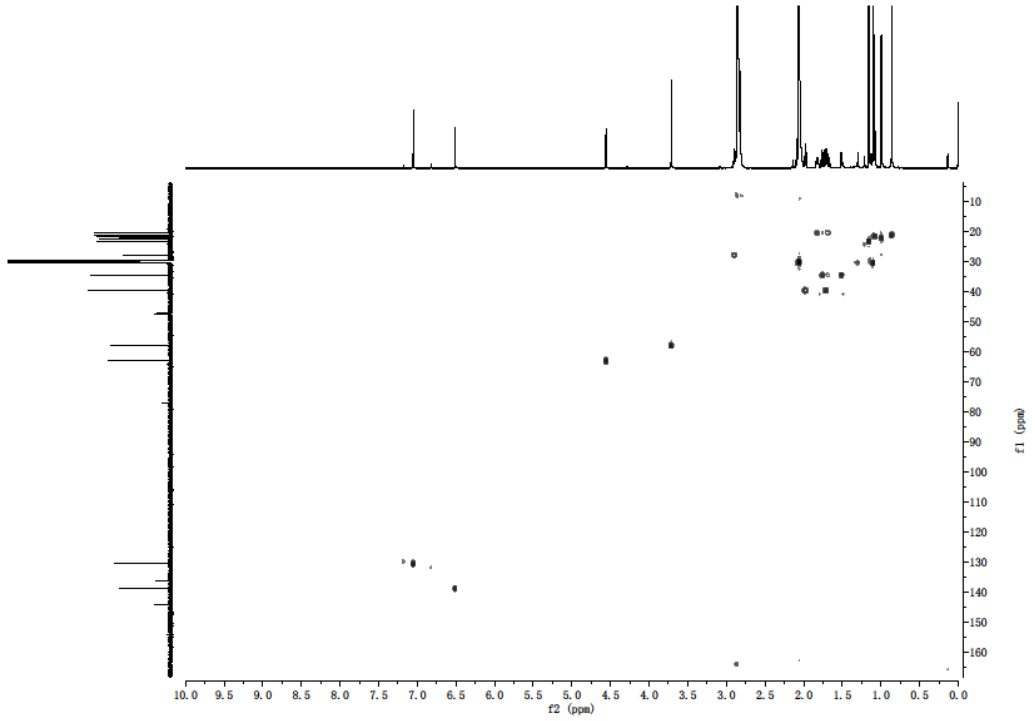



Figure **28**. $^{1}$H-$^{1}$H COSY spectrum of (±)-6-*epi*-salviyunnanone A (**12**)

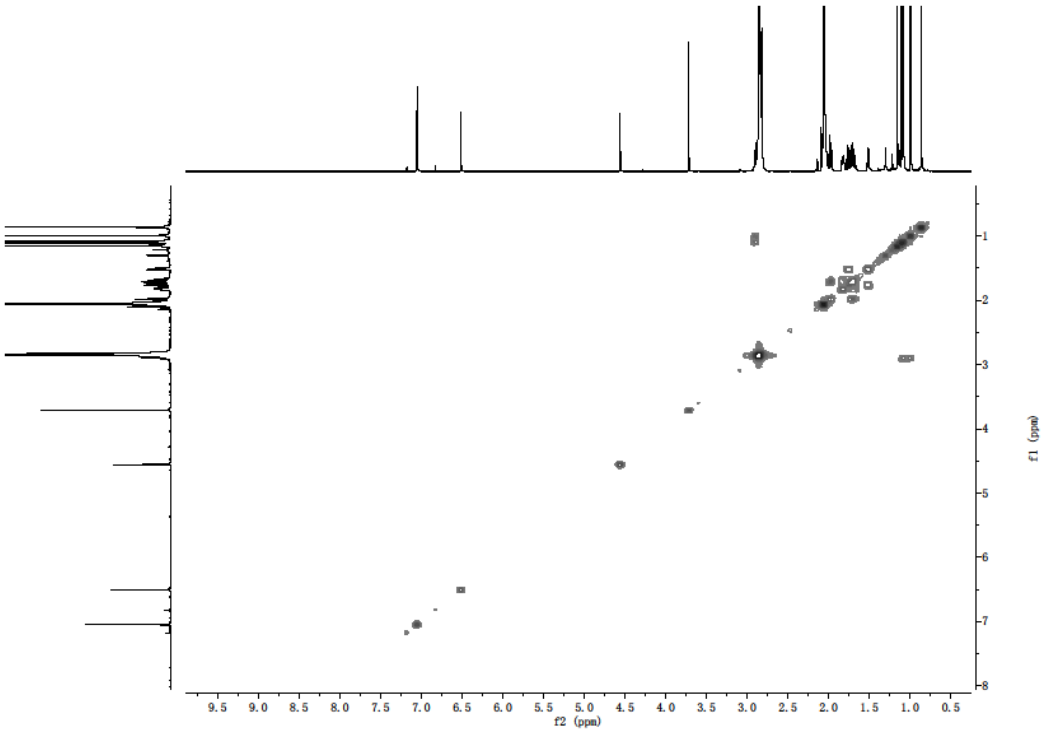


Figure **29**. HMBC spectrum of (±)-6-*epi*-salviyunnanone A (**12**)

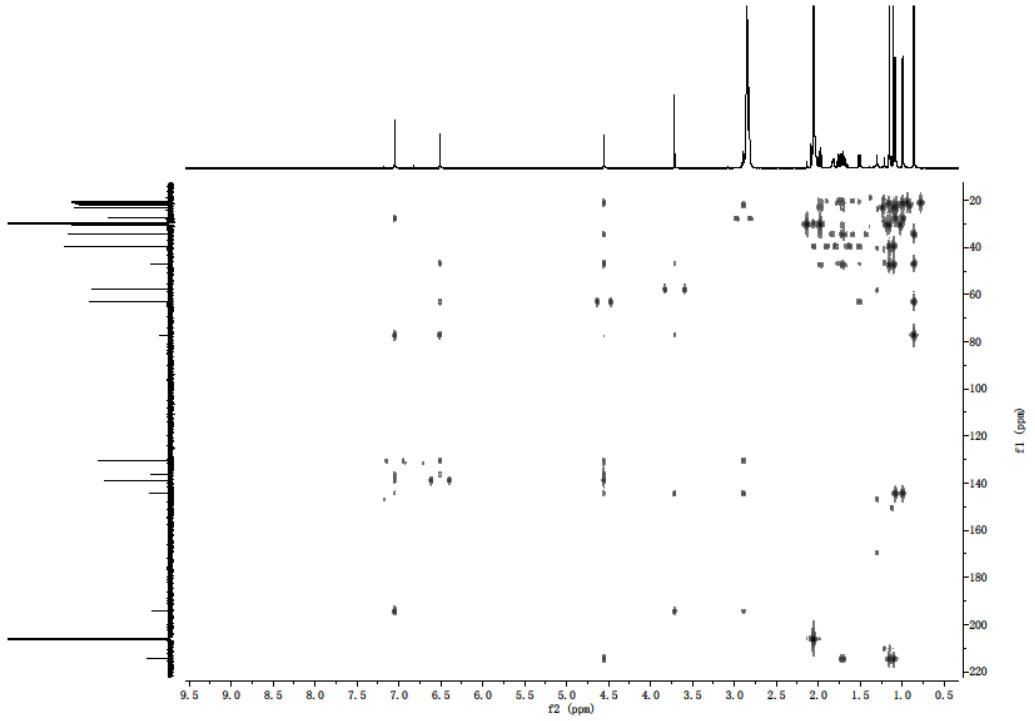



Figure **30**. ROESY spectrum of (±)-6-*epi*-salviyunnanone A (**12**)

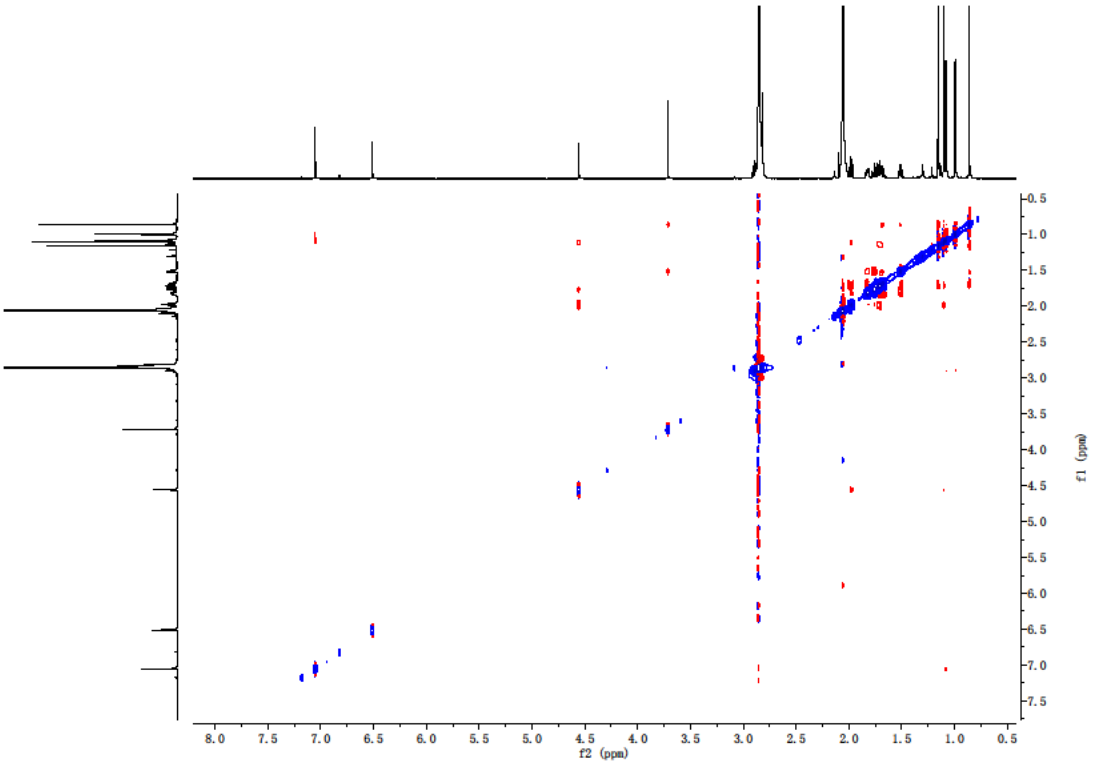


Figure **31**. HRESIMS spectrum of (±)-6-*epi*-salviyunnanone A (**12**)