Total synthesis and structural reassignment of garcinielliptone FC, a polycyclic polyprenylated acylphloroglucinol with diverse bioactivity

Yang Luo,[a] Robert B. Grossman,[b] Xiao-Bin Nie,[a] and Xing-Wei Yang[a,*]

[a] School of Pharmaceutical Sciences (Shenzhen), Sun Yat-sen University, Shenzhen 518107, People's Republic of China

[b] Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055, United States

Electronic Supplementary Information

Table of contents

SI-1 Table for NMR Data of GFC and Xanthochymol

Table S1. The ^{1}H NMR Data of GFC and Xanthochymol in Different Solvent

no.	GFC[a,b]	xanthochymol[b] (synthetic)	xanthochymol[c] (synthetic)	xanthochymol[c] (natural)[d]
6	2.37, brd (13.9)	2.37, brd (13.9)	2.25, d (14.0)	2.26, m
	2.07, brd (13.9)	2.06, dd (13.9, 6.8)	2.04, m	2.05, m
7	1.45, m	1.43, m	1.50, m	1.51, m
10	2.74, brd (13.6)	2.73, dd (13.5, 9.8)	2.71, dd (13.5, 9.4)	2.77, m
	2.58, brd (13.6)	2.58, brd (13.5)	2.54, m	2.51, m
11	5.09, t (7.2)	5.08, t (7.5)	5.03, m	5.07, m
13	1.80, s	1.80, s	1.73, s	1.74, s
14	1.73, s	1.74, s	1.68, s	1.69, s
17	7.03, d (1.7)	6.99, s	7.18, d (2.1)	7.21, d (2.1)
20	6.67, d (8.2)	6.66, d (8.5)	6.70, d (8.3)	6.72, d (8.0)
21	7.01, dd (8.2, 1.7)	7.00, d (8.5)	6.98, dd (8.3, 2.1)	7.00, dd (8.0, 2.1)
22		2.17, m	2.01, m	2.02, m
	1.88, m, 2H[e]	1.88, m	1.92, dd, (14.0, 5.7)	1.93, m
23	2.64 brd (13.6)	2.64, m	2.54, m	2.51, m
25	4.43, 2H, s	4.42, 4.41, s	4.50, brs, 2H	4.53, brs, 2H
26	1.56, s	1.55, s	1.60, s	1.59, s
27	2.12, m[e]	1.47, m, 2H	1.46, m	1.46, m, 2H
	1.95, m[e]		1.40, m	
28	1.88, m, 2H	1.86, m, 2H	1.87, 1.83, m	1.85, m, 2H
30	4.66, 4.64, s	4.66, 4.63, s	4.64, 4.62, s	4.65, brs, 2H
31	1.69, s	1.70, s	1.68, s	1.69, s
32	2.16, dd (14.5, 8.0)	2.13, m	2.09, m	2.03, m, 2H
	1.99, dd (14.5, 7.2)	1.95, m	1.98, m	
33	4.91, t (7.2)	4.92, t (7.5)	4.87, overlap	4.88, m
35	1.70, s	1.70, s	1.65, s	1.67, s
36	1.53, s	1.53, s	1.49, s	1.50, s
37	1.15, s	1.15, s	1.15, s	1.17, s
38	1.00, s	1.00, s	0.99, s	1.01, s

[a] Data from *J. Nat. Prod.* **2008**, 246-250. [b] Recorded in $CDCl_3$. [c] Recorded in methanol-d_4 +0.1% TFA. [d] Data from *J. Nat. Prod.* **2000**, 1070-1076. [e] Signals were most probably assigned incorrectly.

Table S2. The ^{13}C NMR Data of GFC and Xanthochymol in Different Solvent

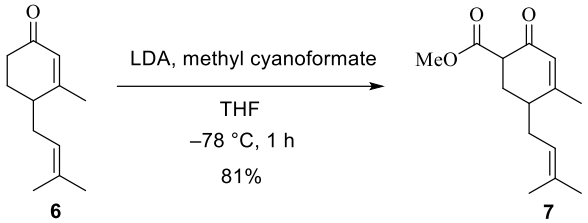
no.	GFC[a,b]	xanthochymol[b] (synthetic)	xanthochymol[c] (synthetic)	xanthochymol[c] (natural)[d]	Difference in CD_3OD
1	69.1	69.7	69.7	69.8	-0.1
2	194.0	194.4	194.1	194.4	-0.3
3	116.0	115.9	117.9	117.9	0
4	198.1	198.4	195.6	195.7	-0.1
5	57.8	57.9	59.8	59.9	-0.1
6	42.6	42.5	43.7	43.9	-0.2
7	46.8	46.8	47.9	48.1	-0.2
8	49.6	49.6	50.2	50.4	-0.1
9	209.2	209.3	210.6	209.8	+0.8
10	26.4	26.3	27.0	27.2	-0.2
11	120.2	120.2	121.3	121.4	-0.1
12	135.1	135.2	135.9	136.0	-0.1
13	26.1	25.8	26.4	26.6	-0.2
14	17.9	18.2	18.3	18.5	-0.2
15	195.8	193.9	195.7	196.4	-0.7
16	128.3	128.1	129.5	129.5	0
17	116.5	116.5	117.3	117.5	-0.2
18	143.3	143.4	147.0	147.0	0
19	149.4	149.5	152.5	152.5	0
20	114.4	114.3	115.1	115.2	-0.1
21	124.3	124.2	125.2	125.3	-0.1
22	36.5[e]	36.6	37.7	37.8	-0.1
23	43.6	43.3	44.7	44.8	-0.1
24	148.1	147.4	148.9	149.0	-0.1
25	113.2	113.2	113.5	113.7	-0.2
26	17.1	17.2	17.7	17.9	-0.2
27	31.9	31.8	32.7	32.9	-0.2
28	35.5	35.5	36.8	36.9	-0.1
29	146.0	146.0	146.3	146.5	-0.2
30	109.6	109.6	110.4	110.6	-0.2
31	22.5[e]	22.7	22.8	23.0	-0.2
32	29.1[f]	28.9	30.3	30.4	-0.1
33	123.9	123.8	125.6	125.7	-0.1
34	132.9	132.9	133.7	133.7	0
35	25.8[e]	26.1	26.0	26.1	-0.1
36	17.7	17.9	18.2	18.4	-0.2
37	22.7	22.6	23.2	23.3	-0.1
38	27.0	27.0	27.3	27.5	-0.2

[a] Data from *J. Nat. Prod.* **2008**, 246-250. [b] Recorded in $CDCl_3$. [c] Recorded in methanol-d_4 +0.1% TFA. [d] Data from *J. Nat. Prod.* **2000**, 1070-1076. [e] Exchanged signals. [f] Revised data based on the data of its keto-enol tautomeric isomer (*J. Nat. Prod.* **2008**, 246-250).

SI-2 Experimental Procedures

General Experimental Procedures. NMR spectra were recorded on a Bruker DRX-500 or DRX-600 spectrometer with TMS as the internal standard in $CDCl_3$ or CD_3OD. Chemical shifts (δ) are expressed in ppm with reference to the solvent signals. ESIMS and HREIMS data were acquired on an Agilent Q-TOF mass spectrometer. X-ray data were generated using a Bruker Apex Duo instrument. Preparative HPLC was performed on an Agilent 1260 HPLC with a Waters SunFire C18 OBD 5 μm column (19 × 250 mm). Silica gel (200–300 mesh, Qingdao Marine Chemical Co., Ltd.) were used for column chromatography. Fractions were monitored by TLC (GF 254, Qingdao Marine Chemical Co., Ltd.), and spots were visualized by heating silica gel plates immersed in H_2SO_4 in ethanol.

Synthesis of α-ketoester 7



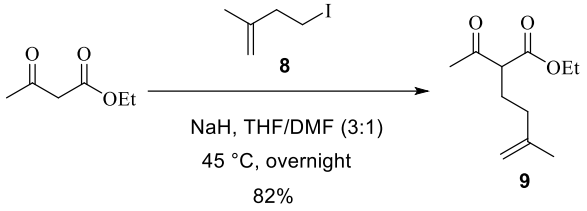
To a solution of cyclohexanone **6** (5.348 g, 30 mmol, 1.0 equiv) in THF (125 mL) was added dropwise a solution of LDA (33 mmol, 1.1 equiv) at –78 °C. After stirring the reaction mixture at that temperature for 1 h, methyl cyanoformate (5.103 g, 60 mmol, 2.0 equiv) was added. The stirring was continued for an additional period of 1 hour, after which the reaction mixture was quenched with saturated aq. NH_4Cl, allowed to warm to 25 °C, and extracted two times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 filtered and concentrated in vacuo. Purification of the residue by column chromatograph (silica gel, petroleum ether/EtOAc, 9:1) to afford α-ketoester **7** (5.734g, 81% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (s, 0.5H, b), 5.87 (s, 1H, a), 5.09 (t, J = 7.3 Hz, 1.1H, a), 5.02 (t, J = 7.0 Hz, 0.6H, b), 3.75 (s, 1.5H, b), 3.74 (s, 3.3H, a), 3.46 (dd, J = 11.3, 5.1 Hz, 1H, a), 3.36 (dd, J = 13.7, 4.7 Hz, 0.5H, b), 2.48 – 2.29 (m, 4.6H, a + b), 2.21 – 2.10 (m, 2.4H, a + b), 2.08 – 2.03 (m, 1.7H, a + b), 1.98 (s, 3H, a), 1.97 (s, 1.7H, b), 1.71 (s, 2.9H, a), 1.70 (s, 1.9H, b), 1.62 (s,

2.9H, a), 5.93 (s, 1.7H, b); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 194.0 (b), 193.7 (a), 171.3 (b), 171.2 (a), 166.3 (a), 165.4 (b), 134.8 (b), 134.7 (a), 127.2 (b), 126.0 (a), 121.4 (a), 120.3 (b), 53.6 (b), 52.4 (a), 52.3 (b), 49.7 (a), 39.6 (b), 39.0 (a), 30.9 (b), 30.5 (b), 29.9 (a), 29.6 (a), 26.0 (b), 26.0 (a), 23.2 (a), 22.4 (b), 18.1 (b), 18.0 (a).

MS positive ESIMS *m/z* 259 $[M + Na]^+$, 495 $[2M + Na]^+$.

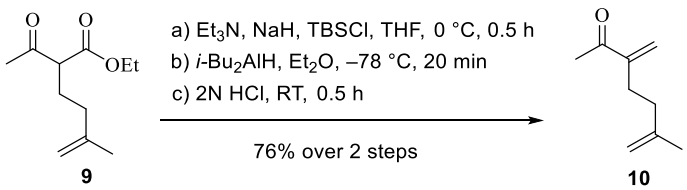
Synthesis of ester 9



To a solution of ethyl acetoacetate (10.2 mL, 80 mmol, 1.0 equiv) in anhydrous THF (150 mL) was added portion-wise NaH (60 % in mineral oil, 3.68 g, 92 mmol, 1.15 equiv) under argon at 0 °C. After stirring for 1 h the iodide **8** (10 mL, 80mmol, 1.0 equiv) in DMF (50 mL) was added to the mixture. The reaction mixture was now allowed to warm to 45 °C and stirred overnight in the dark. The mixture was quenched with saturated aq. NH_4Cl and diluted with EtOAc, extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by column chromatography (silica gel, petroleum ether/EtOAc, 10:1) to afford ester **9** (12.988 g, 82% yield).

The spectral data of ester **9** matched with those in the literature.[1]

Synthesis of enone 10



To a solution of corresponding ester **9** (9.9 g, 50 mmol, 1.0 equiv) in anhydrous THF (120 mL) was successively added Et_3N (6.9 mL, 50 mmol, 1.0 equiv) and NaH (60 % in mineral oil, 2.256 g, 56.4 mmol, 1.15 equiv) under argon at 0 °C, After stirring for 10 min at this temperature TBSCl (11.304 g, 75 mmol, 1.5 equiv) was added and the mixture was stirred for 30 min at 0 °C. The

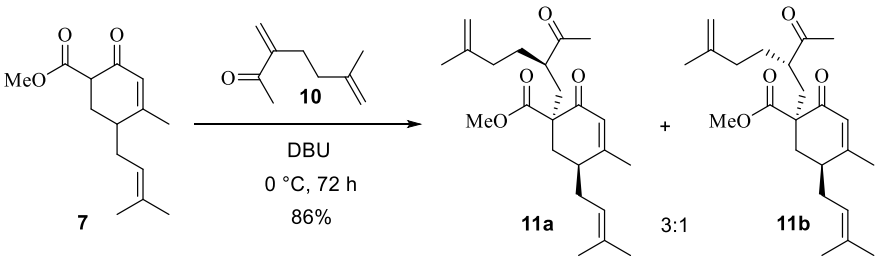
solution was quenched with saturated aq. $NaHCO_3$ and diluted with EtOAc, extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was used without further purification.

To a solution of the crude product in anhydrous Et_2O (10 mL) was added dropwise *i*-Bu_2AlH (150 mL, 3M in hexanes, 3.0 equiv) under argon at –78 °C. The resulting solution was allowed to stir at the same temperature for 20 min. The reaction was quenched with saturated aq. potassium sodium tartrate at –78 °C and gradually warm to room temperature. The resulting suspension was diluted with EtOAc, extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was used without further purification.

The crude product was added aq. 2N HCl (10 mL) at room temperature. After stirring at that temperature for 30 min, the resulting mixture was extracted three times with *n*-pentane. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by column chromatography (silica gel, *n*-pentane/acetone, 50:1) to afford enone **10** (5.244 g, 76% overall yield).

The spectral data of enone **10** matched with those in the literature.[2]

Synthesis of compound 11



α-Ketoester **7** (2.36 g, 10 mmol, 1.0 equiv) was charged to a flame dried flask and enone **10** (2.76 g, 20 mmol, 2.0 equiv) was added under argon. The resulting mixture was cooled to 0 °C and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (299 μL, 2 mmol, 0.2 equiv) was added to obtain a yellow solution. After stirring the solution for 72 hours at 0 °C, the reaction was quenched with aq. 2N HCl, and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by column chromatography to

(silica gel, petroleum ether/EtOAc, 6:1) afford a pair of diastereoisomers **11a** and **11b** (2.412 g for **11a** and 0.801 g for **11b**, 3:1, 86% yield).

11a: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.86 (s, 1H), 5.01 (t, J = 7.1 Hz, 1H), 4.70 (s, 1H), 4.64 (s, 1H), 3.72 (s, 3H), 2.72 – 2.68 (m, 1H), 2.42 (brs, 2H), 2.28 – 2.22 (m, 2H), 2.20 (s, 3H), 2.07 – 2.02 (m, 1H), 1.98 (s, 3H), 1.96 – 1.89 (m, 2H), 1.80 – 1.72 (m, 2H), 1.71 (s, 3H), 1.69 – 1.65 (m, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.51 – 1.45 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 210.9, 195.6, 172.1, 164.0, 144.1, 133.6, 124.9, 119.7, 109.4, 56. 9, 51.5, 47.5, 35.6, 33.75, 33.71, 32.1, 30.9, 29.6, 29.2, 25.0, 21.6, 21.4, 17.1.

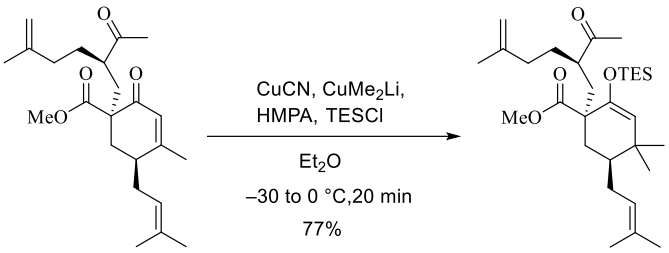
MS positive ESIMS *m*/*z* 375 $[M + H]^+$, 413 $[M + K]^+$, 771 $[2M + Na]^+$. **HRESIMS** *m*/*z* 397.2358 $[M + Na]^+$ (calcd for $C_{23}H_{34}O_4Na$, 397.2349).

11b: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77 (s, 1H), 5.04 (t, J = 7.0 Hz, 1H), 4.71 (s, 1H), 4.67 (s, 1H), 3.70 (s, 3H), 2.89 – 2.85 (m, 1H), 2.58 (brs, 1H), 2.47 – 2.39 (m, 2H), 2.20 (dd, J = 13.8, 10.3 Hz, 1H), 2.09 (s, 3H), 2.04 – 2.00 (m, 2H), 1.98 (s, 3H), 1.95 (dd, J = 13.7, 4.9 Hz, 1H), 1.72 – 1.67 (m, 3H), 1.71 (s, 3H), 1.61 (s, 3H), 1.50 – 1.42 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 210.4, 196.1, 172.9, 162.9, 144.3, 133.7, 126.0, 119.6, 109.3, 55.9, 51.4, 47.0, 36.5, 35.7, 33.8, 31.9, 30.7, 29.5, 28.7, 25.0, 21.7, 21.4, 17.1.

MS positive ESIMS *m*/*z* 375 $[M + H]^+$, 397 $[M + Na]^+$,413 $[M + K]^+$, 771 $[2M + Na]^+$. **HRESIMS** *m*/*z* 397.2357 $[M + Na]^+$ (calcd for $C_{23}H_{34}O_4Na$, 397.2349).

Crystal data for 11b: $C_{23}H_{34}O_4$, M = 374.50, a = 9.1816(5) Å, b = 23.6417(12) Å, c = 10.0047(5) Å, α = 90°, β = 102.444(2)°, γ = 90°, V = 2120.69(19) Å^3, T = 100.(2) K, space group $P121/n1$, Z = 4, μ(Cu Kα) = 0.624 mm^{-1}, 21766 reflections measured, 4182 independent reflections (R_{int} = 0.1293). The final R_1 values were 0.0786 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2113 ($I > 2\sigma(I)$). The final R_1 values were 0.1086 (all data). The final $wR(F^2)$ values were 0.2536 (all data). The goodness of fit on F^2 was 1.114.

Synthesis of silyl-ether 12



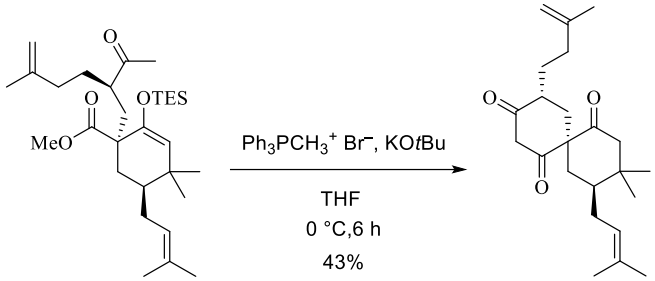
11a **12**

CuCN (107.5 mg, 1.2 mmol, 0.3 equiv) was charged to a flame dried flask and $CuMe_2Li$ (22.4 mL, 0.5 M in Et_2O, 11.2 mmol, 2.8 equiv) was added dropwise under argon at –30 °C. After stirring 2 min, compound **11a** (1.5 g, 4 mmol, 1.0 equiv) in anhydrous Et_2O (20 mL) was added dropwise. The resulting bright yellow suspension was continued to stir at the same temperature for 20 min. HMPA (2.78 mL, 16 mmol, 4.0 equiv) and TESCl (1.68 mL, 10 mmol, 2.5 equiv) were successively added and the reaction mixture was gradually warmed to 0 °C and additionally stirred for 5 min at 0 °C. The reaction mixture was quenched by saturated aq. $NaHCO_3$ and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by column chromatography (silica gel, petroleum ether/EtOAc, 30:1) to afford silyl-ether **12** (1.552 g, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.02 (t, J = 7.2 Hz, 1H), 4.68 (s, 1H), 4.65 (s, 1H), 4.52 (s, 1H), 3.63 (s, 3H), 2.85 – 2.80 (m, 1H), 2.20 (dd, J = 14.3, 6.3 Hz, 1H), 2.16 (s, 1H), 2.11 – 2.06 (brs, 1H), 1.93 (t, J = 8.1 Hz, 2H), 1.84 (dd, J = 14.6, 3.3 Hz, 1H), 1.79 – 1.72 (m, 2H), 1.69 (s, 6H), 1.67 – 1.59 (m, 2H), 1.57 (s, 3H), 1.41 – 1.35 (m, 2H), 1.01 (s, 3H), 0.95 (t, J = 8.0 Hz, 9H), 0.87 (s, 3H), 0.67 – 0.62 (m, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 212.4, 176.2, 149.0, 145.7, 132.5, 123.8, 115.4, 110.0, 52.2, 51.9, 48.9, 39.6, 35.9, 35.2, 34.9, 33.5, 31.9, 29.8, 29.7, 29.6, 28.7, 26.2, 23.5, 22.7, 18.0, 14.3, 6.9, 5.2.

MS positive ESIMS *m/z* 505 $[M + H]^+$, 527 $[M + Na]^+$, 1032 $[2M + Na]^+$. **HRESIMS** *m/z* 527.3523 $[M + Na]^+$ (calcd for $C_{25}H_{40}O_3Na$, 527.3527).

Synthesis of compound 13



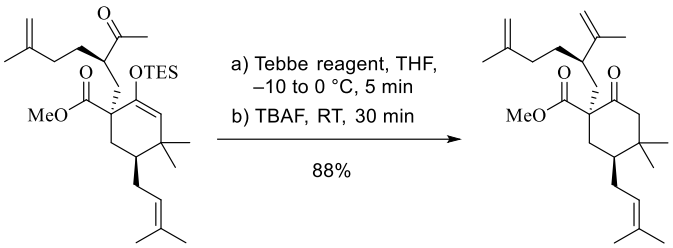
12 **13**

To a solution of $Ph_3PCH_3^+ Br^-$ (1.072 g, 3 mmol, 3 equiv) in THF (10 mL) was added one portion KO*t*Bu (393 mg, 3.5 mmol, 3.5 equiv) under argon at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 1 h, the yellow suspension was cooled to 0 °C again followed by dropwise addition of silyl-ether **12** (504 mg, 1 mmol, 1.0 equiv, dissolved in 5 mL THF). Subsequently, the mixture was further stirred at room temperature for 6 hours. The reaction mixture was quenched with saturated aq. NH_4Cl and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 filtered and concentrated in vacuo. Purification of the residue by column chromatograph (silica gel, petroleum ether/EtOAc 2:1) to afford compound **13** (154 mg, 43% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.08 (brs, 1H), 4.75 (s, 1H), 4.69 (s, 1H), 3.92 (d, J = 17.2, 1H), 3.42 (d, J = 17.2, 1H), 2.68 (dd, J = 14.6, 4.9 Hz, 1H), 2.62 (d, J = 13.6, 1H), 2.31 – 2.24 (m, 3H), 2.14 – 2.04 (m, 4H), 1.79 – 1.74 (m, 2H), 1.72 (s, 3H), 1.70 (s, 3H), 1.65 – 1.60 (m, 2H), 1.62 (s, 3H), 1.45 – 1.38 (m, 2H), 1.12 (s, 3H), 0.83 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 211.8, 203.7, 203.0, 144.9, 133.5, 122.9, 111.2, 63.1, 59.0, 53.1, 45.3, 42.3, 39.9, 35.5, 35.0, 34.9, 29.9, 28.2, 26.1, 26.0, 22.2, 19.9, 18.1.

MS positive ESIMS *m*/*z* 359 $[M + H]^+$, 381 $[M + Na]^+$, 397 $[M + K]^+$, 739 $[2M + Na]^+$. **HRESIMS** *m*/*z* 381.2404 $[M + Na]^+$ (calcd for $C_{25}H_{40}O_3Na$, 381.2400).

Synthesis of cyclohexanone 14



12 **14**

Preparation of Tebbe reagent: To a solution of titanocene dichloride (3.734 g, 15 mmol, 1.0 equiv) in anhydrous toluene (13.5 mL) was added dropwise $AlCl_3$ (31.5 mL, 1M in hexanes, 2.1 equiv) under argon at 0 °C. The resulting suspension was allowed to warm to 45 °C and stirred for 48 hours. The crude product was used for Tebbe olefination without purification.

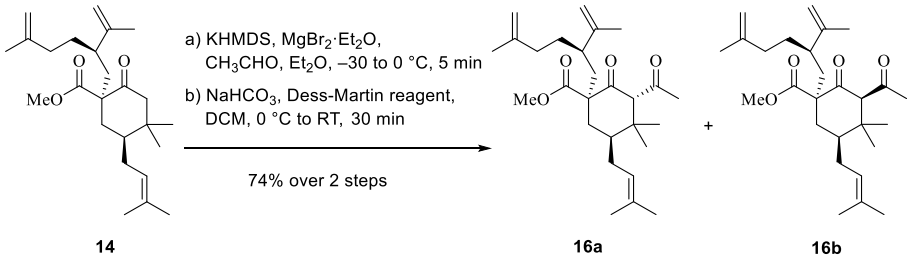
To a solution of silyl-ether **12** (1.008 g, 2.0 mmol, 1.0 equiv) in anhydrous THF (6 mL) was added dropwise Tebbe reagent (30 mL, 10 mmol, 5 equiv) under argon at –10 °C. After stirring for 5 min, the resulting suspension was gradually warm to 0 °C and then quenched with saturated aq. potassium sodium tartrate, extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was used without further purification.

The crude product was dissolved in THF (3 mL) and tetrabutylammonium fluoride (3 mL) was added at room temperature. After stirring for 30 min, the resulting mixture was quenched with aq. 2N HCl and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by column chromatography (silica gel, petroleum ether/EtOAc, 50:1) to afford cyclohexanone **14** (683 mg, 88% overall yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.11 (t, J = 7.4 Hz, 1H), 4.75 (s, H), 4.71 (s, H), 4.66 (s, H), 4.60 (s, H), 3.73 (s, 3H), 2.50 (d, J = 13.6 Hz, 1H), 2.23 – 2.19 (brs, 1H), 2.15 – 1.75 (m, 8H), 1.73 – 1.52 (m, 2H), 1.70 (s, 3H), 1.66 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H), 1.41 – 1.35 (m, 2H), 1.04 (s, 3H), 0.82 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 209.2, 172.9, 147.3, 145.8, 132.7, 123.2, 112.9, 109.8, 62.3, 53.0, 52.1, 43.9, 42.4, 39.1, 35.8, 35.4, 32.9, 31.9, 29.8, 28.2, 26.1, 22.7, 20.5, 18.7, 17.9.

HRESIMS *m/z* 411.2875 $[M + Na]^+$ (calcd for $C_{25}H_{40}O_3Na$, 411.2870).

Synthesis of compound 16



To a solution of cyclohexanone **14** (544 mg, 1.4 mmol, 1.0 equiv) in anhydrous Et_2O (3 mL) was added dropwise potassium bis(trimethylsilyl)amide (2.8 mL, 1 M in THF, 2.8 mmol, 2.0 equiv) under argon at –30 °C. After stirring the reaction mixture at that temperature for 1 h, a freshly prepared mixture of $MgBr_2 \cdot Et_2O$ (1.085 g, 4.2 mmol, 3.0 equiv) in Et_2O (9 mL) was added. After stirring for 10 min at –30 °C, acetaldehyde (0.26 mL, 4.2 mmol, 3.0 equiv) was added at –30 °C and then gradually warm to 0 °C and additionally stirred for 5 min at 0 °C. The reaction mixture was quenched with saturated aq. NH_4Cl solution, extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was used without further purification.

To a solution of crude product in DCM (7.5 mL) was successively added $NaHCO_3$ (118 mg, 1.4 mmol, 1.0 equiv) and Dess-Martin reagent (1.188 g, 2.8 mmol, 2.0 equiv) under argon at 0 °C. Subsequently, the reaction mixture was allowed to warm to room temperature. After stirring for 30 min at room temperature, the reaction mixture was quenched with saturated aq. $NaHCO_3$ and extracted three times with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by column chromatography (silica gel, petroleum ether/EtOAc, 15:1) to afford a pair of enantiomers diketones **16a** and **16b** (294 mg for **16a** and 151 mg for **16b**, 1.95:1, 74% overall yield).

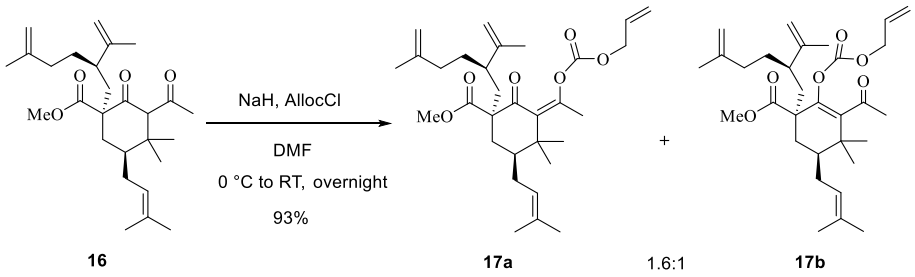
16a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (t, J = 6.5 Hz, 1H), 4.78 (s, 1H), 4.73 (s, 1H), 4.68 (s, 1H), 4.62 (s, 1H), 3.75 (s, 3H), 3.66 (s, 1H), 2.25 – 2.20 (brs, 1H), 2.18 – 1.95 (m, 5H), 2.13 (s, 3H), 1.90 – 1.79 (m, 2H), 1.79 – 1.56 (m, 6H), 1.71 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.44 – 1.39 (m, 2H), 1.10 (s, 3H), 1.04 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 206.5, 204.7, 172.1, 147.0, 145.6, 133.2,

122.8, 113.3, 109.9, 69.7, 62.7, 52.4, 44.3, 44.1, 43.2, 36.2, 35.3, 32.8, 32.7, 32.2, 27.5, 26.8, 26.1, 22.7, 18.8, 17.9, 16.0.

16b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (t, J = 6.8 Hz, 1H), 4.73 (s, 1H), 4.66 (s, 1H), 4.63 (s, 2H), 3.82 (s, 1H), 3.66 (s, 3H), 2.34 – 2.22 (m, 3H), 2.18 (s, 3H), 1.93 – 1.82 (m, 3H), 1.78 – 1.66 (m, 3H), 1.72 (s, 3H), 1.69 (s, 3H), 1.63 – 1.33 (m, 5H), 1.60 (s, 3H), 1.59 (s, 3H), 1.09 (s, 3H), 1.02 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 205.6, 204.4, 173.2, 146.5, 146.1, 133.0, 123.1, 113.1, 109.7, 69.6, 59.9, 51.9, 43.7, 43.5, 42.1, 37.9, 35.4, 35.0, 33.0, 32.2, 26.9, 26.0, 24.6, 22.8, 18.0, 17.7.

MS positive ESIMS m/z 431 $[M + H]^+$, 453 $[M + Na]^+$, 469 $[M + K]^+$. **HRESIMS** m/z 453.2981 $[M + Na]^+$.

Synthesis of compound 17



16 **17a** 1.6:1 **17b**

To a solution of diketone **16** (280 mg, 0.65 mmol, 1.0 equiv) in DMF was added portion-wise NaH (60% in mineral oil, 30 mg, 0.75 mmol, 1.15 equiv) under argon at 0 °C. The mixture was stirred for 1 h at this temperature and then allylchloroformiate (172 μL, 1.625 mmol, 2.5 equiv) was added dropwise. The mixture was allowed to warm to room temperature and was further stirred overnight. The reaction mixture was quenched with saturated aq. NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by column chromatography (silica gel, petroleum ether/EtOAc, 12:1) to afford two regioisomeric allyl vinyl carbonates **17a** and **17b** (192 mg for **17a** and 119 mg for **17b**, 1.6:1, 93% overall yield).

17a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98 – 5.90 (m, 1H), 5.38 (d, J = 17.2 Hz, 1H), 5.30 (d, J = 10.5 Hz, 1H), 4.99 (t, J = 7.4 Hz, 1H), 4.71 (s, 1H), 4.68 – 4.65 (m, 4H), 4.61 (s, 1H), 3.69 (s, 3H), 2.42 (t, J = 13.9 Hz, 1H), 2.11 – 2.02 (m, 3H), 1.93 (s, 3H), 1.89 (dd, J = 14.6, 3.4 Hz, 1H), 1.85 –

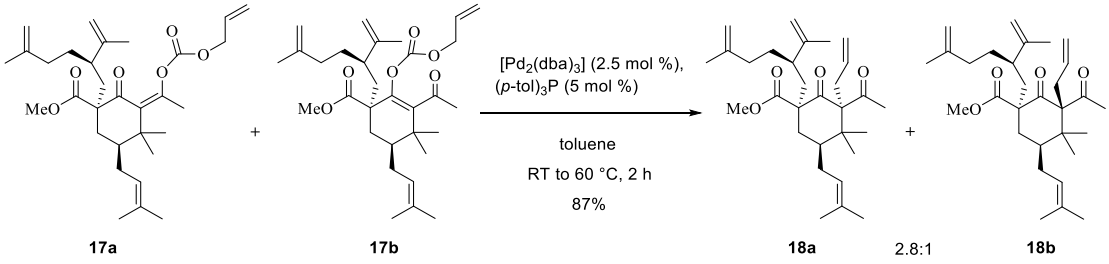
1.80 (m, 2H), 1.74 (q, J = 7.0 Hz, 1H), 1.70 – 1.65 (m, 1H), 1.67 (s, 3H), 1.65 – 1.55 (m, 1H), 1.61 (s, 3H), 1.58 (s, 3H), 1.45 – 1.30 (m, 2H), 1.18 (s, 3H), 1.11 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 203.2, 171.9, 151.9, 149.2, 147.5, 145.9, 135.6, 133.4, 131.2, 123.0, 119.7, 112.7, 109.7, 69.2, 60.5, 52.5, 43.9, 42.9, 41.9, 37.6, 35.4, 32.8, 32.3, 27.5, 26.5, 26.0, 22.7, 18.9, 18.2, 18.1, 18.0.

MS positive ESIMS m/z 515 $[M + H]^+$, 537 $[M + Na]^+$, 553 $[M + K]^+$. **HRESIMS** m/z 537.3188 $[M + Na]^+$ (calcd for $C_{31}H_{46}O_6Na$, 537.3187).

17b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 – 5.85 (m, 1H), 5.35 (d, J = 17.2 Hz, 1H), 5.27 (d, J = 10.5 Hz, 1H), 4.74 (s, 1H), 4.70 (s, 1H), 4.66 (s, 1H), 4.61 (s, 1H), 4.58 (d, J = 5.8 Hz, 2H), 3.61 (s, 3H), 2.26 (s, 3H), 2.22 – 2.05 (m, 4H), 1.96 (dd, J = 14.5, 2.7 Hz, 1H), 1.88 – 1.58 (m, 5H), 1.71 (s, 3H), 1.67 (s, 3H), 1.63 (s, 3H), 1.61 (s, 3H), 1.43 – 1.34 (m, 3H), 1.15 (s, 3H), 1.04 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 204.2, 173.2, 152.6, 147.4, 145.9, 144.5, 140.2, 133.1, 131.2, 123.1, 119.6, 112.8, 109.7, 69.4, 52.6, 50.1, 43.8, 40.7, 38.7, 37.9, 35.4, 32.3, 31.6, 29.5, 28.0, 26.1, 25.1, 22.8, 21.1, 18.4, 17.9.

HRESIMS m/z 537.3197 $[M + Na]^+$ (calcd for $C_{31}H_{46}O_6Na$, 537.3187).

Synthesis of compound 18



Tris(dibenzylideneacetone)dipalladium(0) (8.3 mg, 0.009 mmol, 0.025 equiv) and tri(p-tolyl)phosphine (6.6 mg, 0.0216 mmol, 0.06 equiv) were dissolved in toluene (5 mL) and stirred for 30 min at room temperature. Then, a solution of the pair of regioisomers **17** (185 mg, 0.36 mmol, 1.0 equiv) in toluene (2 mL) was added slowly. The resulting mixture was stirred at 60 °C for 2 h, and then filtered through a plug of silica gel using petroleum ether/ethyl acetate (7:1) to afford C-allylated diketone **18a** and **18b**. The desired product **18a** was purified by HPLC ($MeOH/H_2O$, 93:7). (108 mg for **18a** and 38 mg for **18b**, 2.8:1, 87% overall yield).

18a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.36 – 5.28 (m, 1H), 5.10 (t, J = 6.0 Hz, 1H), 4.93 (d, J = 10.2

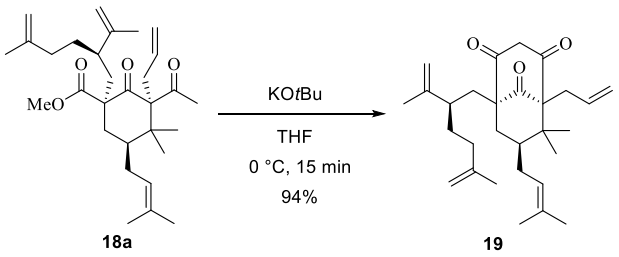
Hz, 1H), 4.88 (d, *J* = 16.9 Hz, 1H), 4.80 (s, 1H), 4.76 (s, 1H), 4.67 (s, 1H), 4.63 (s, 1H), 3.74 (s, 3H), 3.17 (dd, *J* = 14.3, 5.0 Hz, 1H), 2.26 – 2.17 (m, 3H), 2.10 (s, 3H), 1.89 – 1.75 (m, 6H), 1.74 – 1.58 (m, 2H), 1.79 (s, 3H), 1.69 (s, 3H), 1.65 (s, 3H), 1.61 (s, 3H), 1.51 – 1.38 (m, 2H), 1.03 (s, 3H), 0.96 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 208.0, 205.6, 172.3, 146.2, 145.1, 133.2, 132.0, 122.0, 116.4, 112.0, 108.7, 72.9, 59.6, 51.5, 42.6, 39.5, 36.9, 36.5, 36.0, 34.4, 32.0, 31.4, 30.1, 27.0, 25.2, 21.8, 21.3, 20.8, 18.1, 17.0.

HRESIMS *m*/*z* 493.3293 $[M + Na]^+$ (calcd for $C_{30}H_{46}O_4Na$, 493.3288).

18b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 – 5.61 (m, 1H), 5.10 – 5.02 (m, 2H), 5.01 (d, *J* = 10.1 Hz, 1H), 4.77 (s, 1H), 4.68 (s, 1H), 4.66 (s, 1H), 4.61 (s, 1H), 3.74 (s, 3H), 3.04 (dd, *J* = 16.5, 5.7 Hz, 1H), 2.62 (q, *J* = 8.2 Hz,1H), 2.32 – 2.22 (brs, 2H), 2.08 – 2.01 (m, 3H), 2.05 (s, 3H), 1.87 – 1.84 (m, 3H), 1.79 – 1.66 (m, 2H), 1.70 (s, 3H), 1.67 (s, 3H), 1.64 – 1.57 (m, 2H), 1.61 (s, 3H), 1.60 (s, 3H), 1.49 – 1.36 (m, 3H), 0.82 (s, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 207.9, 204.8, 172.7, 146.9, 145.9, 135.5, 132.5, 123.4, 117.4, 113.3, 109.8, 75.0, 64.0, 52.4, 44.5, 42.9, 37.9, 36.3, 35.4, 35.2, 32.8, 31.3, 29.9, 29.8, 28.4, 26.2, 24.1, 22.8, 20.0, 18.9, 18.0.

HRESIMS *m*/*z* 493.3295 $[M + Na]^+$ (calcd for $C_{30}H_{46}O_4Na$, 493.3288).

Synthesis of compound 19



18a **19**

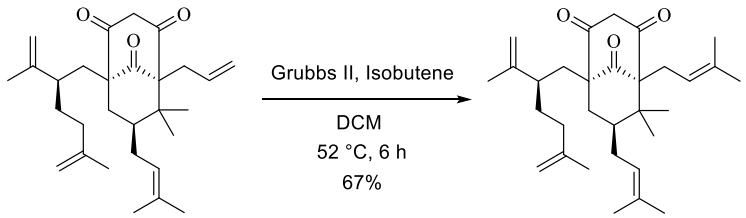
To a solution of diketone **18a** (80 mg, 0.17 mmol, 1.0 equiv) in anhydrous THF (4.5 mL) was added one portion KO*t*Bu (58 mg, 0.51 mmol, 3 equiv) under argon at 0 °C. After stirring for 15 min at this temperature, the reaction was quenched with saturated aq. NH_4Cl and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by column chromatography (silica gel, petroleum ether/EtOAc, 15:1) to afford compound **19** (70 mg, 94% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 – 5.60 (m, 1H), 5.08 (d, *J* = 17.1, 1H), 5.04 (d, *J* = 10.2, 1H),

4.83 (t, *J* = 6.7 Hz, 1H), 4.68 (d, *J* = 15.7 Hz, 2H), 4.54 (d, *J* = 11.8 Hz, 2H), 3.56 (d, *J* = 17.1 Hz, 2H), 3.40 (d, *J* = 17.2 Hz, 2H), 2.81 – 2.74 (m, 1H), 2.47 (dd, *J* = 12.5, 8.7 Hz, 1H), 2.31 (d, *J* = 13.9 Hz, 1H), 2.16 (brs, 1H), 2.08 (dd, *J* = 14.0, 11.3 Hz, 1H), 1.97 (dd, *J* = 13.8, 6.3 Hz, 1H), 1.86 (t, *J* = 8.1 Hz, 2H), 1.72 (s, 3H), 1.71 – 1.68 (m, 1H), 1.66 (s, 3H), 1.51 (s, 3H), 1.41 (s, 3H), 1.45 – 1.36 (m, 3H), 1.33 – 1.28 (m, 2H), 1.22 (s, 3H), 0.97 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 210.8, 202.7, 202.5, 148.6, 146.1, 133.9, 132.5, 122.6, 120.5, 114.6, 109.8, 71.5, 64.0, 63.1, 52.5, 46.8, 44.7, 43.4, 38.4, 35.4, 32.3, 32.2, 29.1, 26.5, 25.9, 23.4, 22.7, 18.1, 16.5.

HRESIMS *m*/*z* 437.3062 $[M - H]^-$ (calcd for $C_{29}H_{41}O_3$, 437.3061).

Synthesis of compound 20



19 **20**

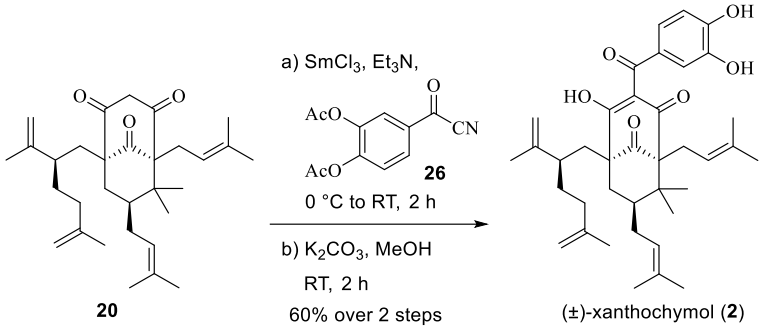
Grubbs 2nd generation catalyst (10.2 mg, 0.012 mmol, 0.1 equiv) was added to a dried 15 mL glass pressure tube. The tube was then cooled to –78 °C, compound **19** (53 mg, 0.12 mmol, 1.0 equiv) dissolved in DCM (2 mL) was added quickly under argon. Subsequently, isobutylene (6.8 mL) was condensed along the bottom of the tube at –78 °C. The tube was sealed and slowly warmed to 52 °C. After stirring for 6 h at that temperature, the tube was re-cooled to –78 °C for 5 min before opened to the air. Then, the reaction mixture was allowed to warm to room temperature for evaporation of isobutylene. The resulting solution was concentrated and filtered through a plug of silica gel using petroleum ether/EtOAc (3:1). The product was purified by HPLC (MeOH/H_2O, 93:7) to afford **20** (37.5 mg, 67% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.91 (t, *J* = 7.3 Hz, 1H), 4.83 (t, *J* = 6.7 Hz, 1H), 4.69 (s, 1H), 4.65 (s, 1H), 4.57 (s, 1H), 4.55 (s, 1H), 3.54 (d, *J* = 17.2 Hz, 1H), 3.46 (d, *J* = 17.3 Hz, 1H), 2.85 – 2.80 (m, 1H), 2.57 (s, 1H), 2.56 (s, 1H), 2.29 (d, *J* = 13.8 Hz, 1H), 2.18 – 2.12 (brs, 1H), 2.09 (dd, *J* = 13.8, 11.3 Hz, 1H), 1.96 (dd, *J* = 13.9, 6.3 Hz, 1H), 1.90 – 1.82 (m, 2H), 1.73 – 1.69 (m, 1H), 1.72 (s, 3H), 1.66 (s, 3H), 1.64 (s, 3H), 1.62 (s, 3H), 1.50 (s, 3H), 1.47 (s, 3H), 1.46 – 1.36 (m, 3H), 1.31

– 1.27 (m, 1H), 1.24 (s, 3H), 0.97 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 211.2, 203.2, 202.9, 148.7, 146.2, 136.4, 133.8, 122.7, 118.0, 114.5, 109.8, 71.1, 63.8, 63.0, 52.4, 46.8, 44.9, 43.3, 38.4, 35.5, 32.2, 29.1, 27.0, 26.6, 26.2, 25.9, 23.5, 22.7, 18.1, 18.0, 16.6.

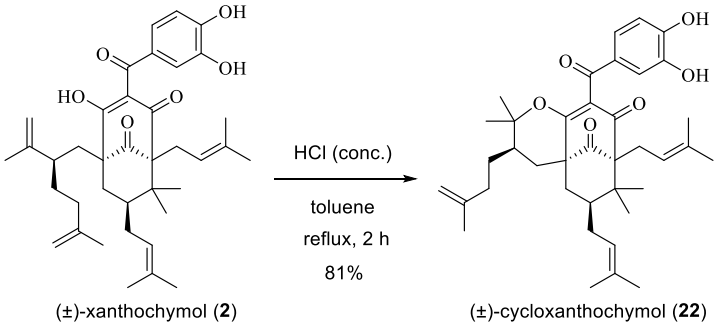
MS positive ESIMS *m/z* 467 $[M + H]^+$, 489 $[M + Na]^+$. **HRESIMS** *m/z* 489.3342 $[M + Na]^+$ (calcd for $C_{29}H_{41}O_3$, 489.3339).

Synthesis of (±)-xanthochymol



To a solution of compound **20** (23 mg, 0.05 mmol, 1.0 equiv), samarium (III) chloride (4 mg, 0.005 mmol, 0.1 equiv), triethylamine (9 μL, 0.06 mmol, 1.2 equiv) in 3 mL of toluene under argon was stirred at 0 °C for 10 min. After 4-(cyanocarbonyl)-1,2-phenylene diacetate (24.7 mg, 0.1 mmol, 2.0 equiv) was added, the mixture was warmed to room temperature and stirred for 2 hours. Then toluene was evaporated and potassium carbonate (5.6 mg, 0.04 mmol) and methanol (2 mL) were added into the resulting solution and stirred for 2 hours. The reaction was quenched with aq. 2N HCl. and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by HPLC (MeOH/H_2O with 0.1% HCOOH, 95:5) to afford (±)-xanthochymol (18.1 mg, 60% overall yield).

Synthesis of (±)-cycloxanthochymol



To a solution of (±)-xanthochymol (12 mg, 0.02 mmol, 1.0 equiv) in toluene (5 mL), HCl (37% solution, 5 μL) was added under argon. The mixture was refluxed for 2 h and then diluted with water, extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. Purification of the residue by HPLC (MeOH/H_2O with 0.1% HCOOH, 95:5) to afford (±)-cycloxanthochymol (9.8 mg, 81% yield).

^{1}H NMR (600 MHz, CD_3OD) δ 7.28 (d, J = 2.0 Hz, 1H), 6.96 (dd, J = 8.2, 2.0 Hz, 1H), 6.70 (d, J = 8.2 Hz, 1H), 4.79 (s, 2H), 4.60 (s, 2H), 3.09 (dd, J = 14.2, 3.4 Hz, 1H), 2.74 – 2.56 (m, 2H), 2.46 (dd, J = 13.5, 5.9 Hz, 1H), 2.29 – 2.24 (m, 2H), 2.19 – 2.09 (m, 2H), 2.04 (q, J = 7.3 Hz, 1H), 1.73 (s, 3H), 1.69 (s, 3H), 1.67 (s, 3H), 1.63 – 1.56 (m, 2H), 1.59 (s, 6H), 1.54 – 1.47 (m, 2H), 1.35 – 1.29 (m, 3H), 1.24 (s, 3H), 1.20 – 1.13 (m, 1H), 1.15 (s, 3H), 1.08 – 0.99 (m, 3H), 1.00 (s, 2H), 0.84 (s, 3H); **^{13}C NMR (150 MHz, CD_3OD)** δ 207.9, 196.4, 194.2, 173.8, 152.6, 146.7, 146.0, 135.5, 134.0, 131.2, 126.8, 126.3, 124.6, 121.2, 115.9, 115.5, 111.8, 88.5, 69.5, 52.9, 47.5, 47.1, 43.0, 39.8, 36.2, 30.6, 29.4, 28.8, 28.8, 27.0, 26.6, 26.6, 26.1, 22.9, 22.3, 21.5, 18.6, 18.3.

References

(1) S. Wolff, W. C. Agosta, *J. Am. Chem. Soc.*, 2002, **105**, 1299-1304.

(2) K. Żukowska, Ł. Pączek, K. Grela, *Chem. Cat. Chem.*, 2016, **8**, 2817-2823.

SI-3. The Original NMR and MS Spectra of New Compounds

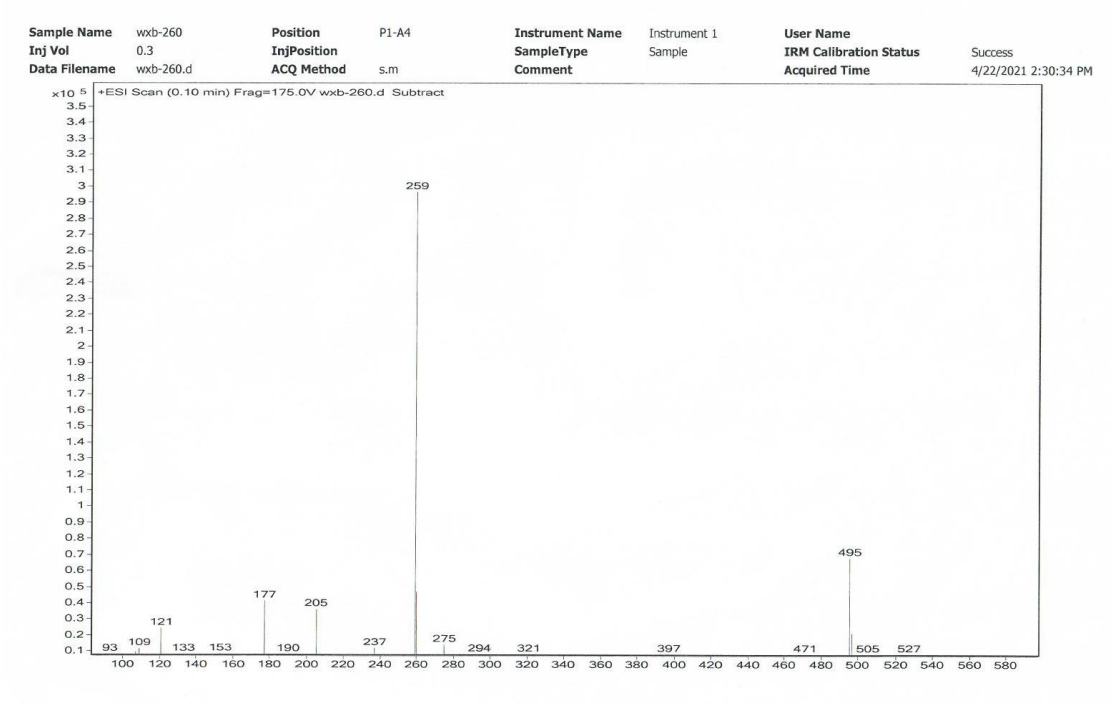


Figure S1. ESIMS of **7**.

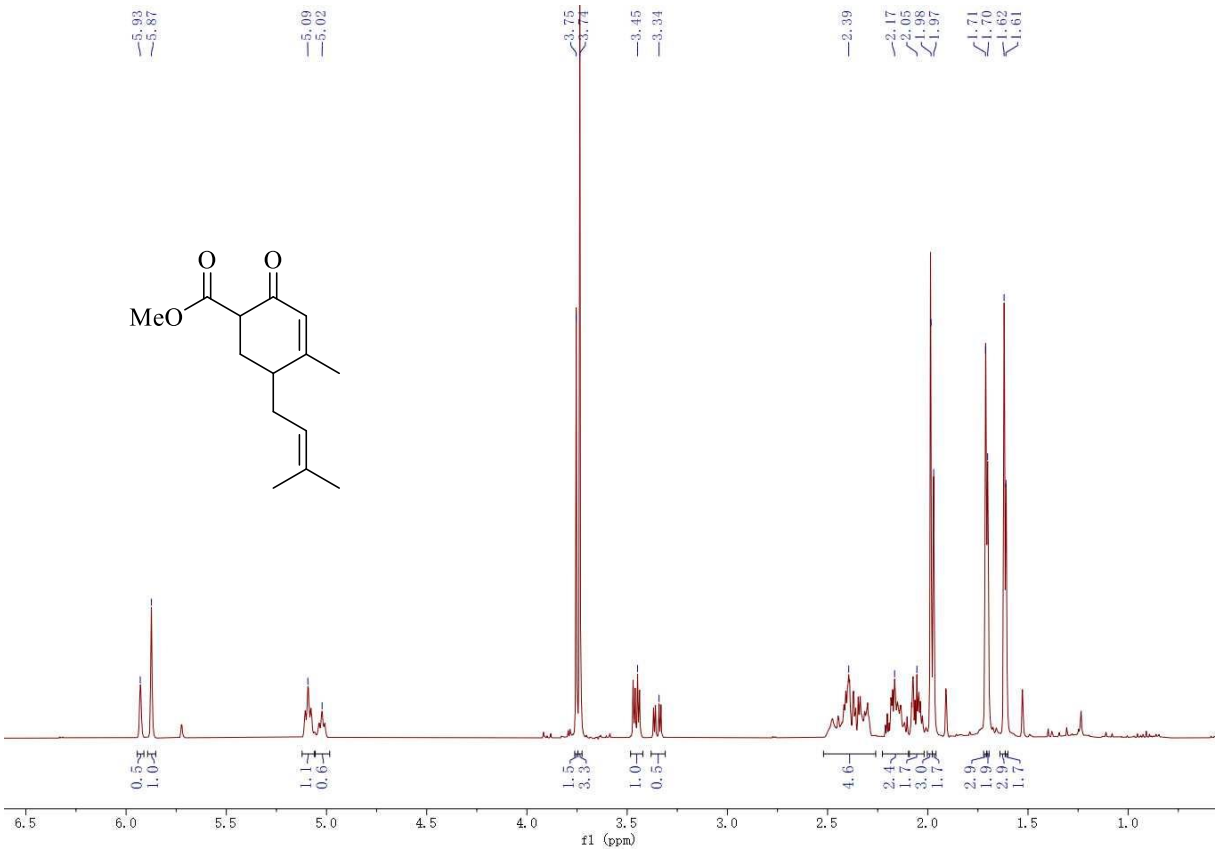


Figure S2. ^{1}H NMR spectrum of **7** in $CDCl_3$.

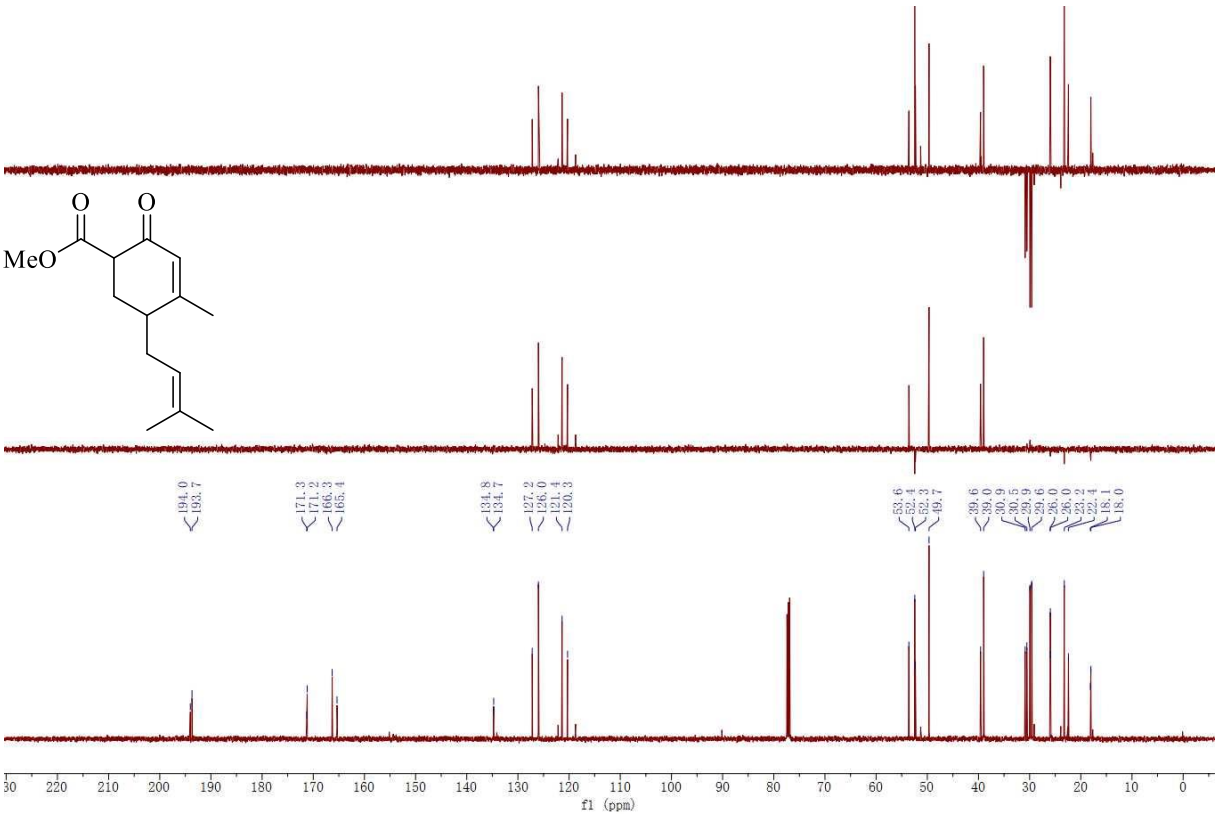


Figure S3. ^{13}C NMR spectrum of **7** in $CDCl_3$.

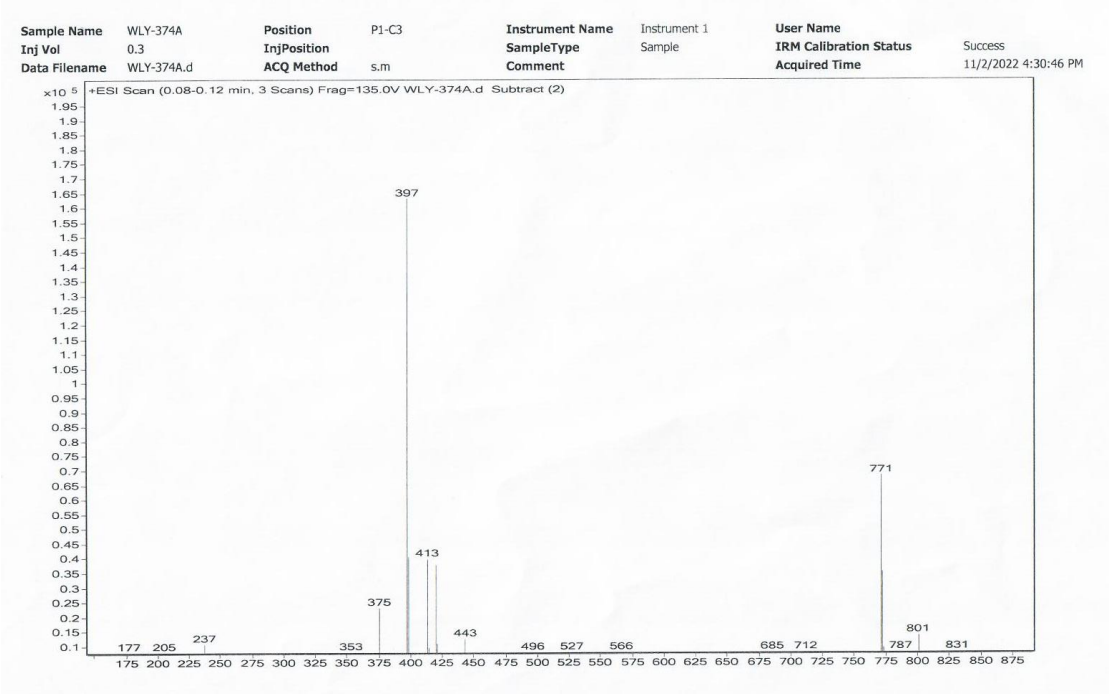


Figure S4. ESIMS of **11a**.

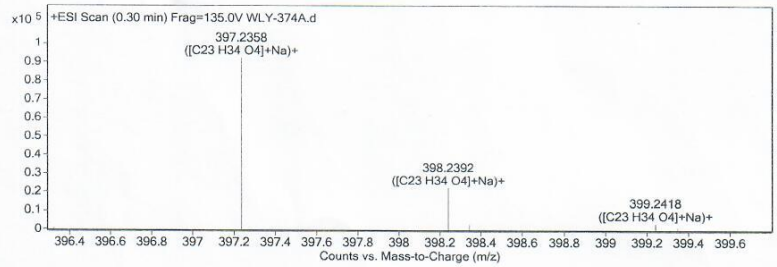
Qualitative Analysis Report

Data Filename	WLY-374A.d	**Sample Name**	WLY-374A
Sample Type	Sample	**Position**	P1-C3
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	11/2/2022 4:30:46 PM
IRM Calibration Status	Success	**DA Method**	PCDL.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
121.0509	1	32419.39		
123.0917	1	22828.04		
397.2358	1	91934.23	C23 H34 O4	(M+Na)+
413.2098	1	27891.68		
420.3115	1	26868.9		
426.3012	1	89908.26		
427.3049	1	27286.9		
576.3546	1	169242.75		
577.3575	1	55982.57		
922.0098	1	101889.73		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C23 H34 O4	374.2457	397.2349	397.2358	-0.90	-2.27	7.0000

--- End Of Report ---

Figure S5. HRESIMS of **11a**.

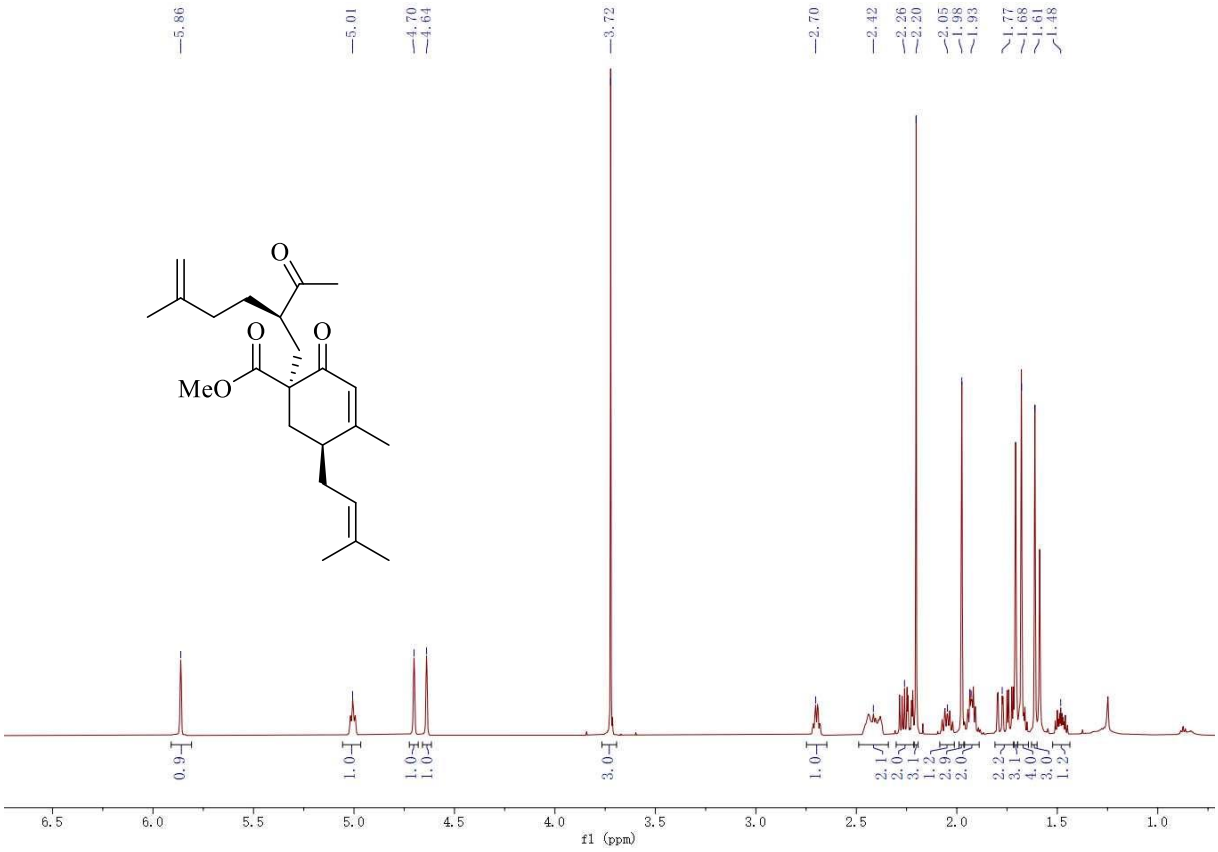


Figure S6. ^{1}H NMR spectrum of **11a** in $CDCl_3$.

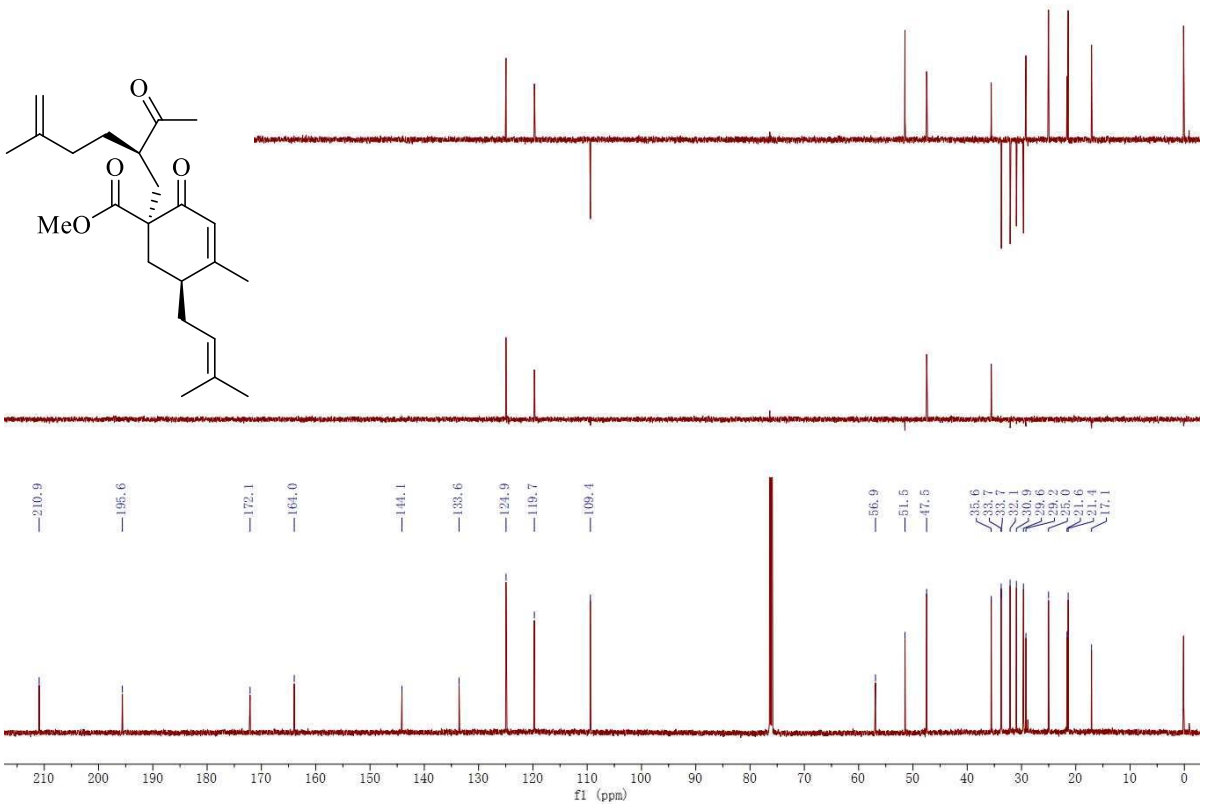


Figure S7. ^{13}C NMR spectrum of **11a** in $CDCl_3$.

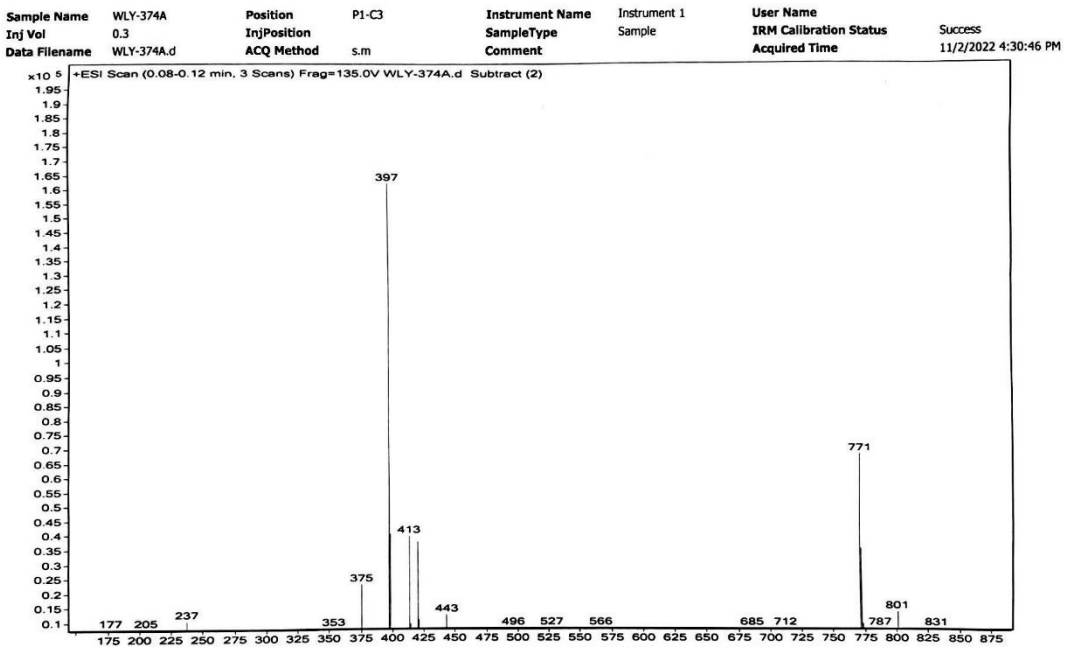


Figure S8. ESIMS of **11b**.

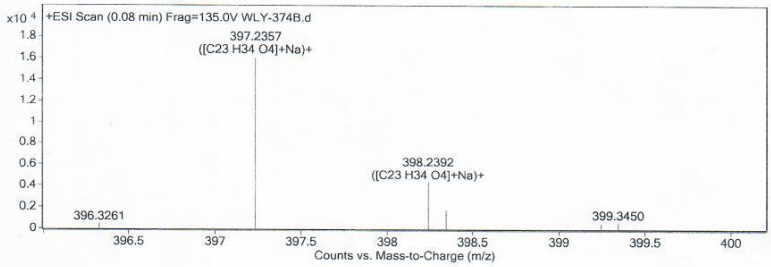
Qualitative Analysis Report

Data Filename	WLY-374B.d	**Sample Name**	WLY-374B
Sample Type	Sample	**Position**	P1-C4
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	11/2/2022 4:31:57 PM
IRM Calibration Status	Success	**DA Method**	PCDL.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
121.0509	1	28877.82		
123.0917	1	21653.16		
397.2357	1	16017.15	C23 H34 O4	(M+Na)+
413.2094	1	9873.28		
426.301	1	35116.43		
427.305	1	9832.37		
576.3541	1	65032.89		
577.3576	1	25578.9		
922.0098	1	89186.45		
923.012	1	18342.83		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C23 H34 O4	374.2457	397.2349	397.2357	-0.80	-2.01	7.0000

--- End Of Report ---

Figure S9. HRESIMS of **11b**.

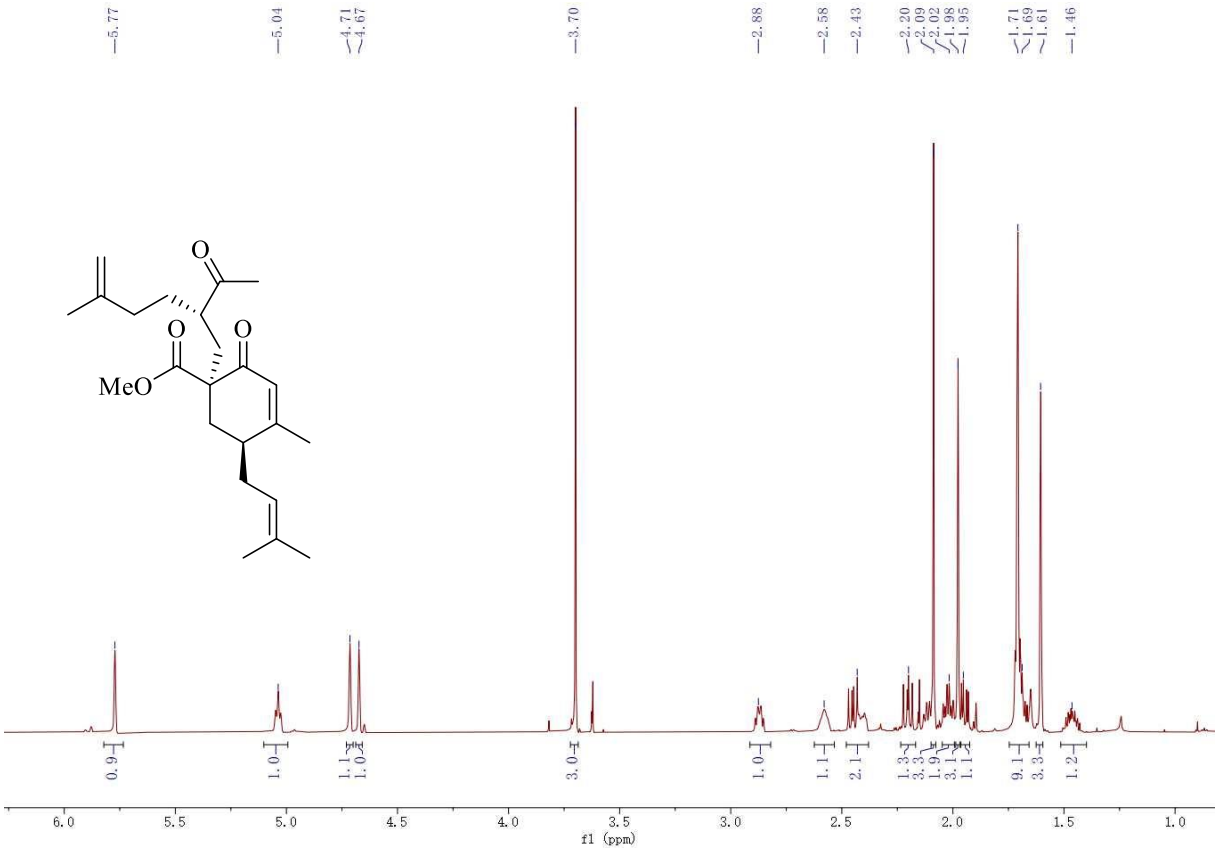


Figure S10. ^{1}H NMR spectrum of **11b** in $CDCl_3$.

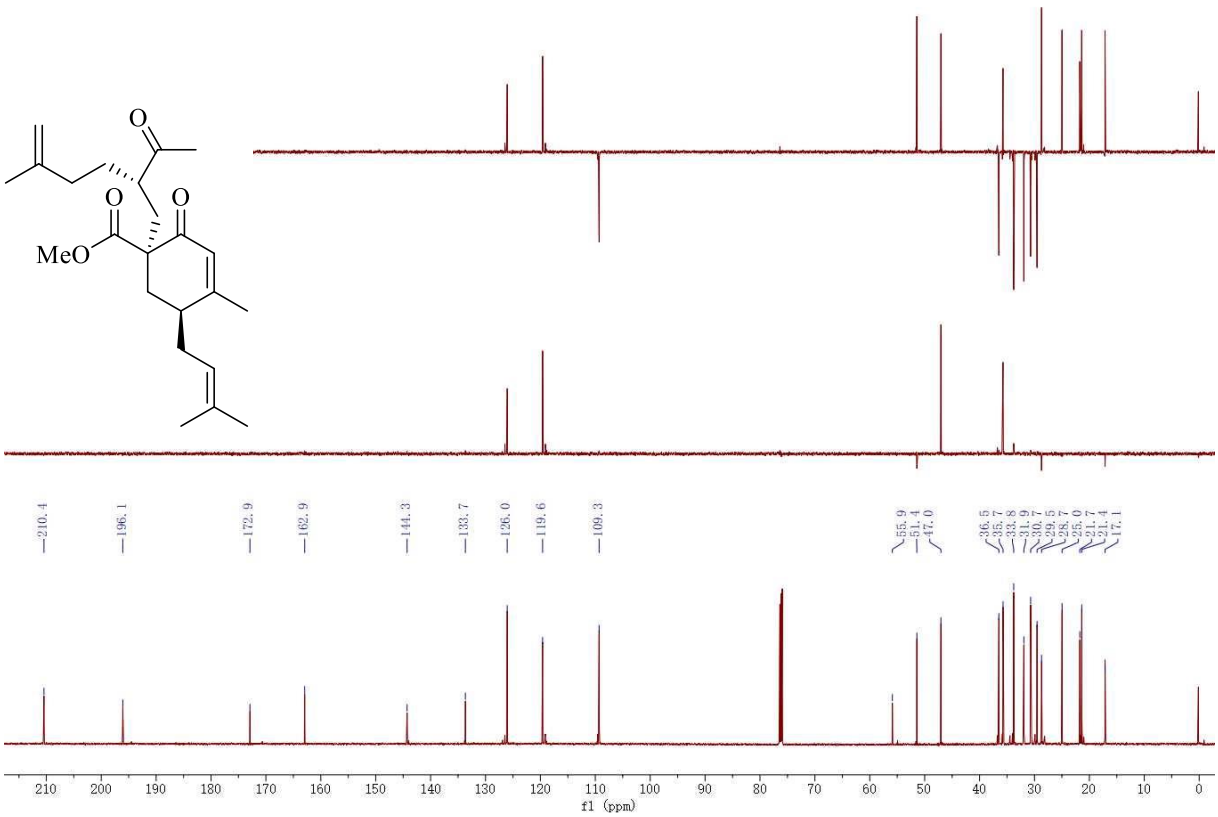


Figure S11. ^{13}C NMR spectrum of **11b** in $CDCl_3$.

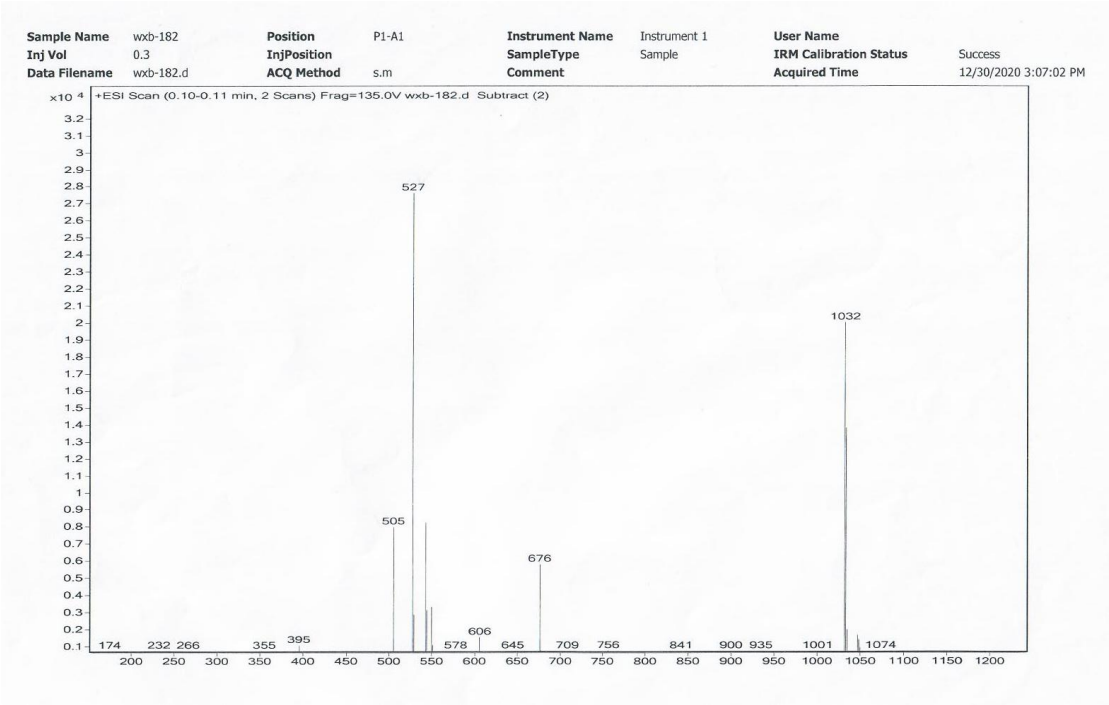


Figure S12. ESIMS of **12**.

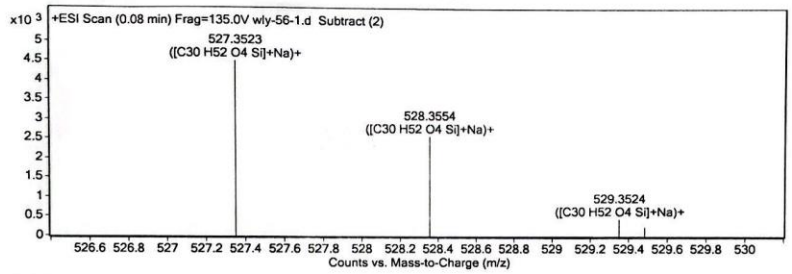
Qualitative Analysis Report

Data Filename	wly-56-1.d	**Sample Name**	wly-56-1
Sample Type	Sample	**Position**	P1-A3
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	2/13/2023 4:06:12 PM
IRM Calibration Status	Success	**DA Method**	PCDL.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	**Collision Energy**	**Ionization Mode**
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
94.0402	1	536.24		
197.078	1	536.58		
205.0859	1	721.41		
373.2724	1	943.29		
414.221	1	547.32		
505.3707	1	4309.92		
506.3741	1	1487.59		
527.3523	1	4514.11	C30 H52 O4 Si	(M+Na)+
528.3554	1	2592.71	C30 H52 O4 Si	(M+Na)+
543.3266	1	919.06		

Formula Calculator Element Limits

Element	Min	Max
C	3	100
H	0	200
O	0	20
Si	0	1

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C30 H52 O4 Si	504.3635	527.3527	527.3523	0.40	0.76	6.0000

--- End Of Report ---

Figure S13. HRESIMS of **12**.

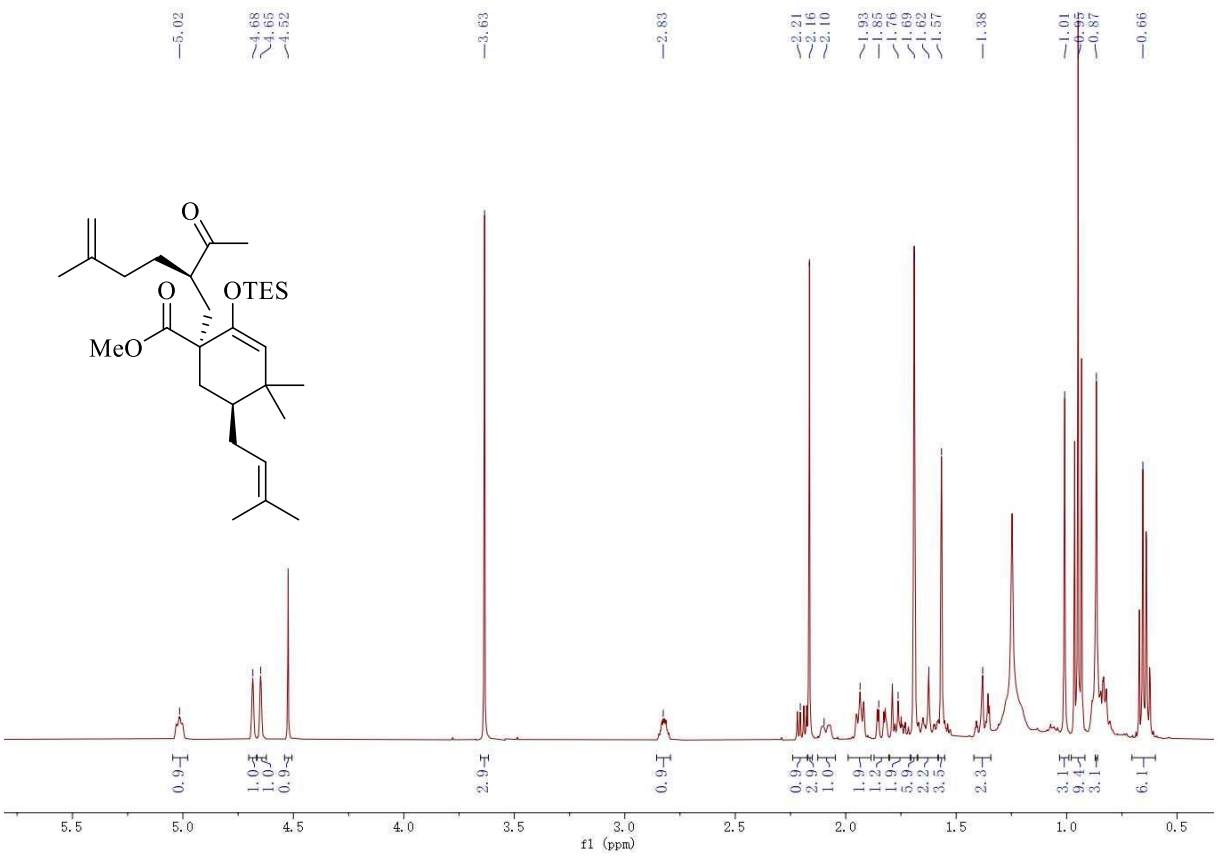


Figure S14. ^{1}H NMR spectrum of **12** in $CDCl_3$.

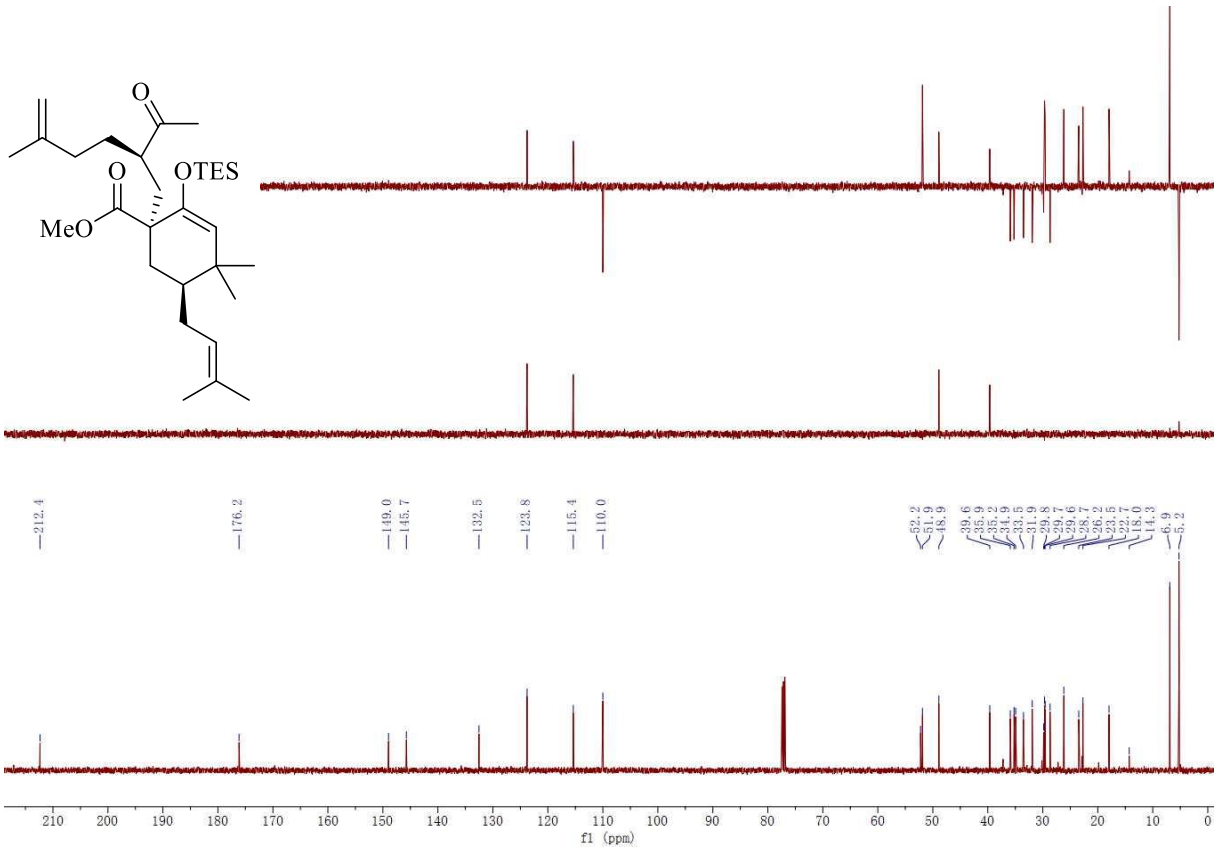


Figure S15. ^{13}C NMR spectrum of **12** in $CDCl_3$.

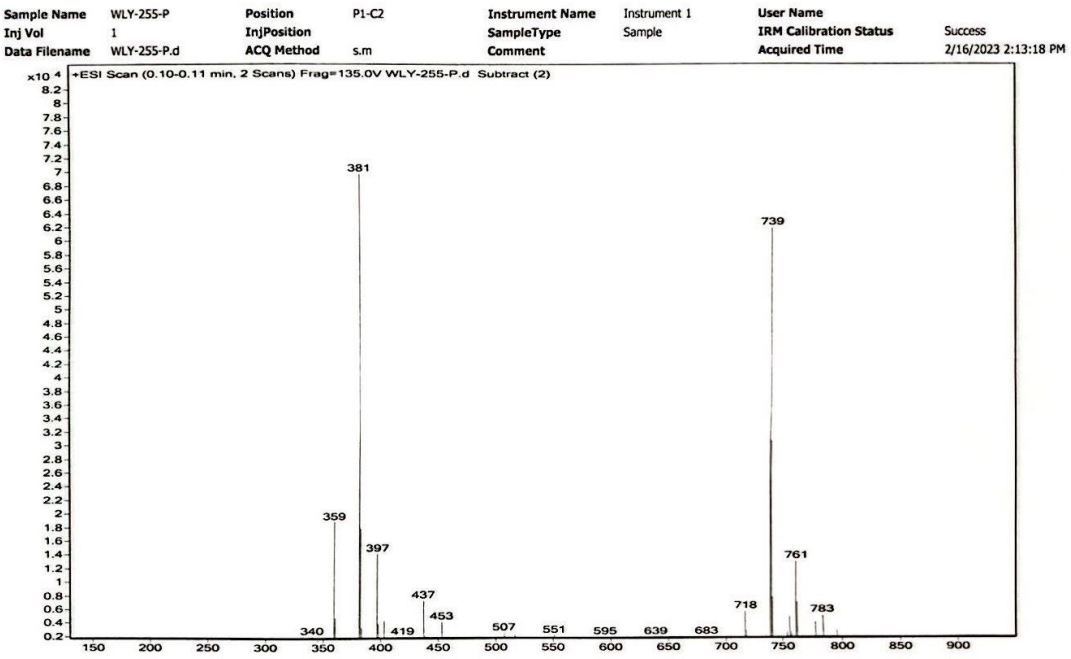


Figure S16. ESIMS of **13**.

Qualitative Analysis Report

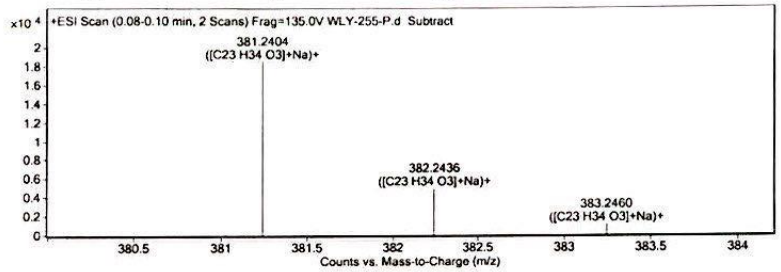
Data Filename	WLY-255-P.d	**Sample Name**	WLY-255-P
Sample Type	Sample	**Position**	P1-C2
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	2/16/2023 2:13:18 PM
IRM Calibration Status	Success	**DA Method**	PCDL.m
Comment			

Sample Group **Info.**

Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
359.2589	1	6923.14		
381.2404	1	18536.19	C23 H34 O3	(M+Na)+
382.2436	1	4913.63	C23 H34 O3	(M+Na)+
397.218	1	2812.57		
437.1941	1	2134.92		
717.5096	1	1912.54		
739.4929	1	12362.87		
740.4954	1	7010.28		
761.4733	1	2116.29		
922.0098	1	10543.73		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	200
O	0	20

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C23 H34 O3	358.2508	381.2400	381.2404	-0.40	-1.05	7.0000

--- End Of Report ---

Figure S17. HRESIMS of **13**.

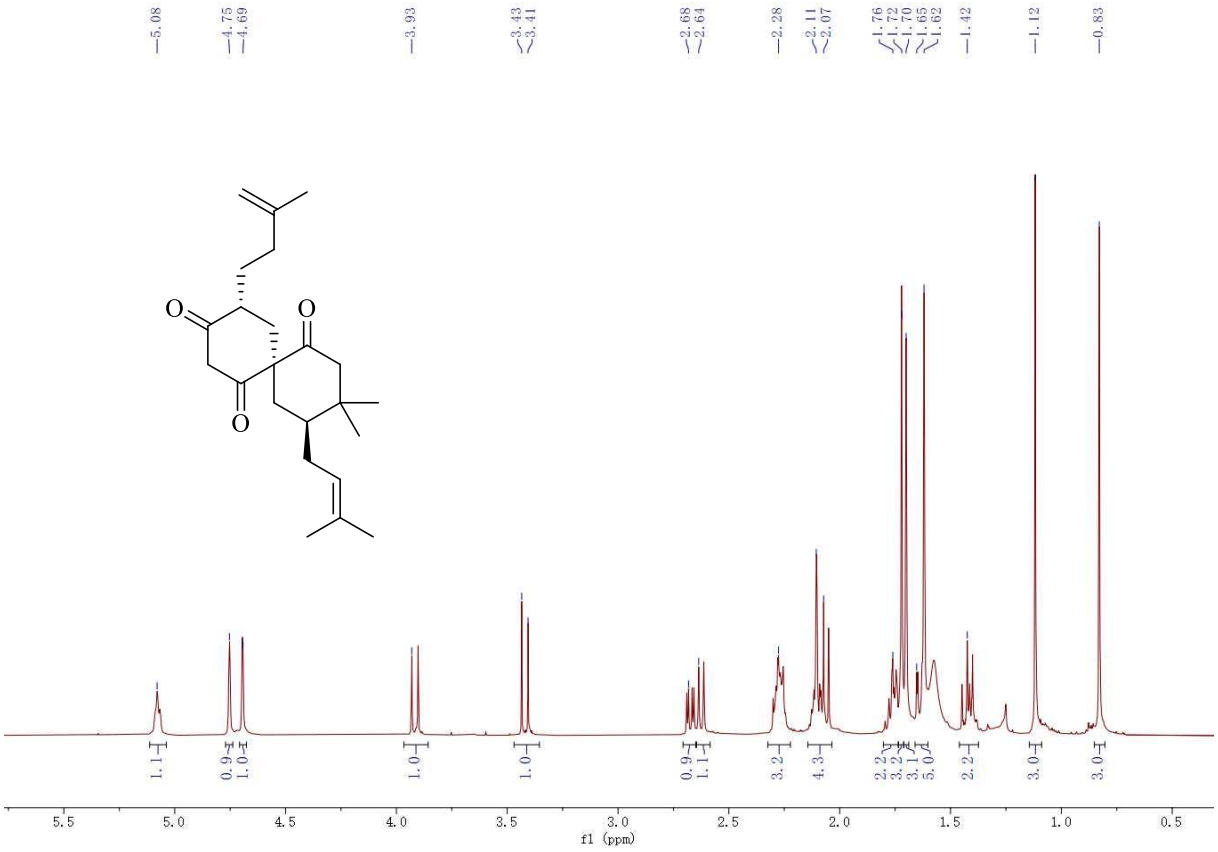


Figure S18. ^{1}H NMR spectrum of **13** in $CDCl_3$.

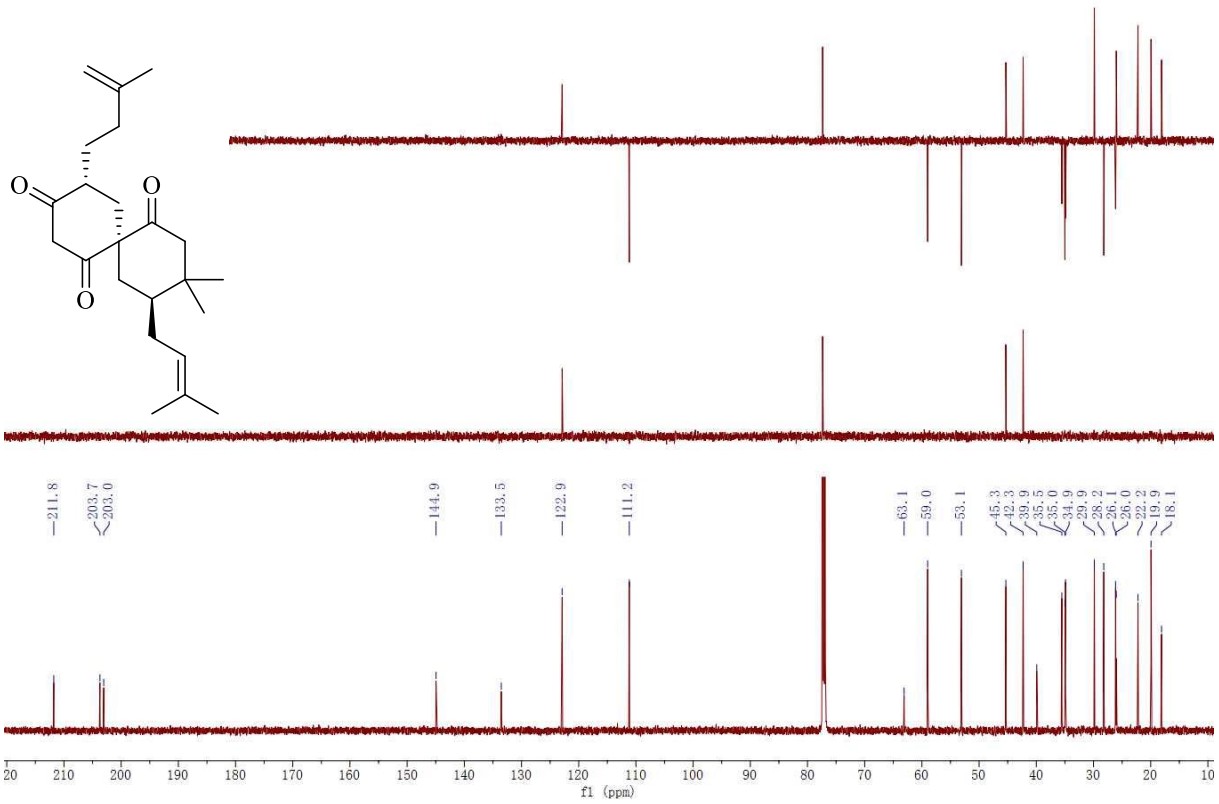


Figure S19. ^{13}C NMR spectrum of **13** in $CDCl_3$.

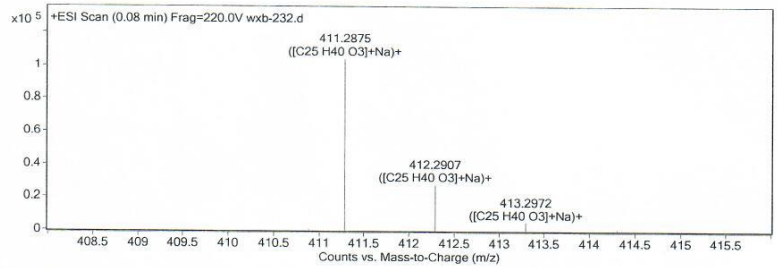
Qualitative Analysis Report

Data Filename	wxb-232.d	**Sample Name**	wxb-232
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	3/18/2021 9:33:53 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
220	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
128.9533		20770.53		
411.2875	1	103920.65	C25 H40 O3	(M+Na)+
412.2907	1	27546.24	C25 H40 O3	(M+Na)+
427.3181	1	17732.37		
799.5851	1	26121.45		
800.5885	1	11877.6		
801.5912	1	5134.71		
815.6172	1	9831.85		
816.619	1	5399.65		
959.9647	1	13225.54		

Formula Calculator Element Limits

Element	Min	Max
C	3	120
H	0	240
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C25 H40 O3	388.2978	411.2870	411.2875	-0.50	-1.22	6.0000

--- End Of Report ---

Figure S20. HRESIMS of **14**.

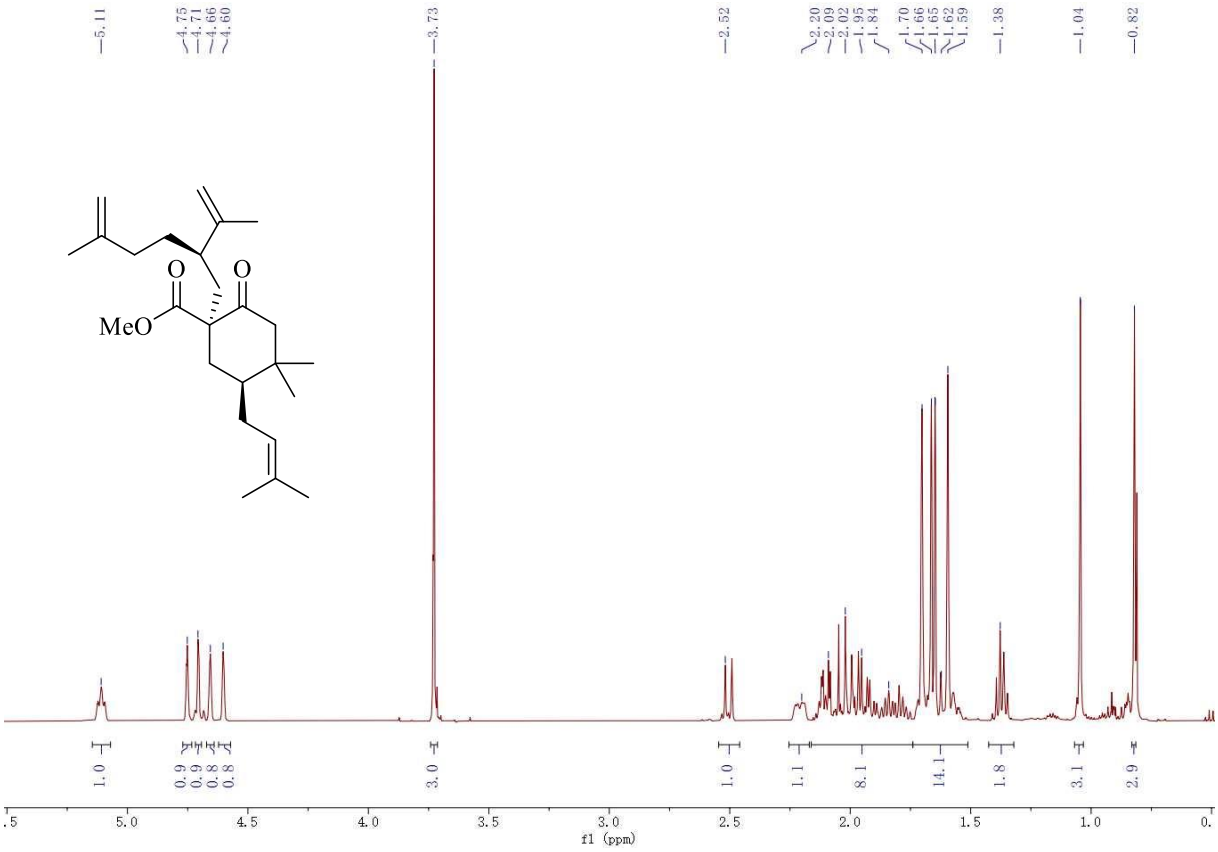


Figure S21. ^{1}H NMR spectrum of **14** in $CDCl_3$.

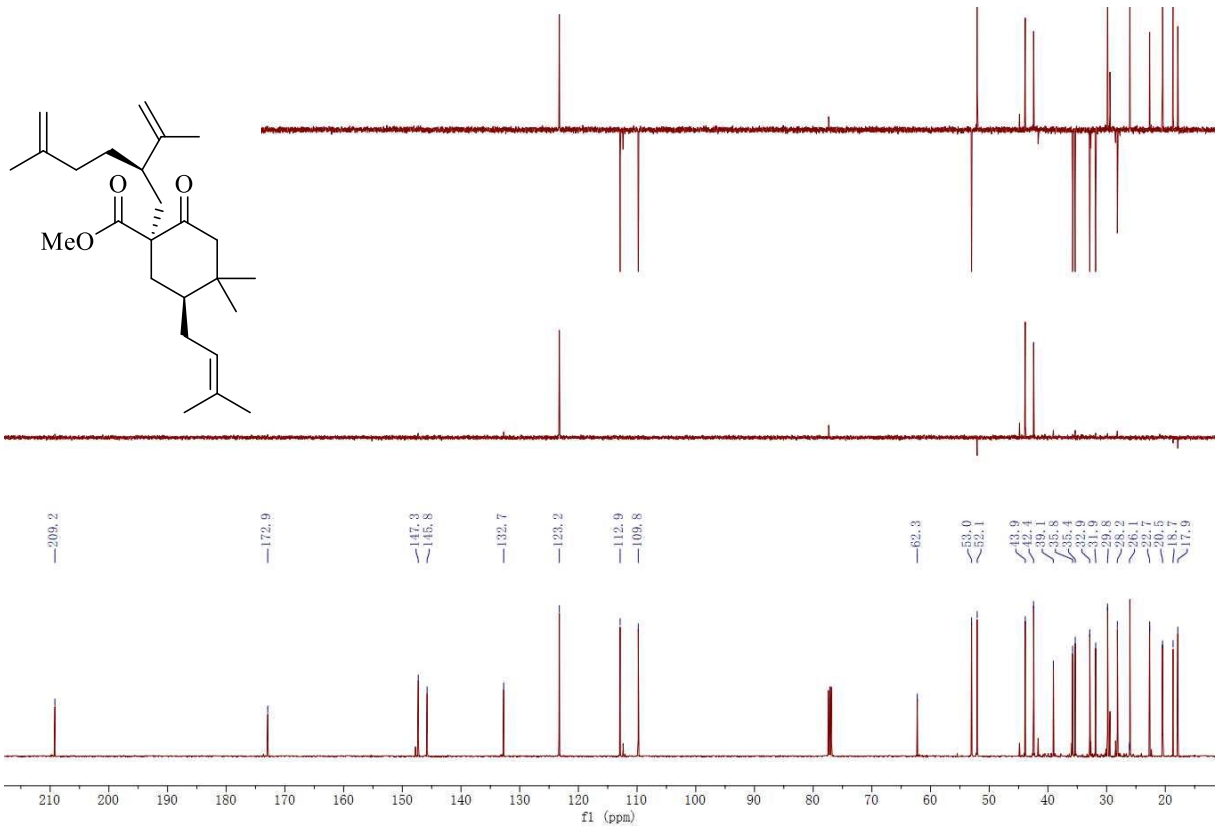


Figure S22. ^{13}C NMR spectrum of **14** in $CDCl_3$.

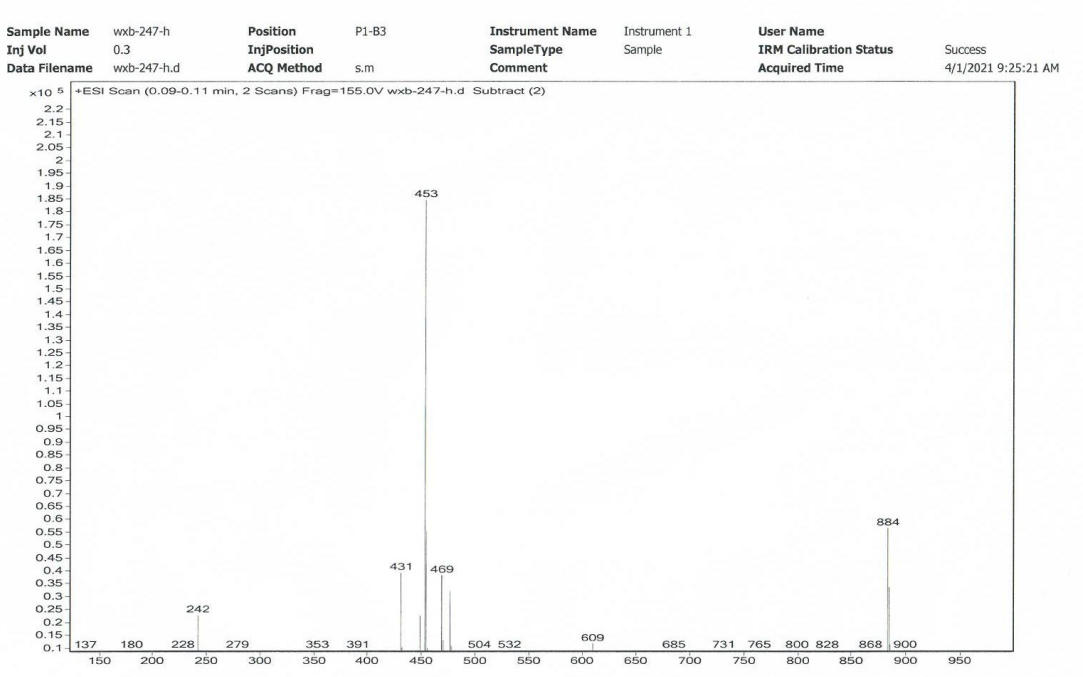


Figure S23. ESIMS of **16**.

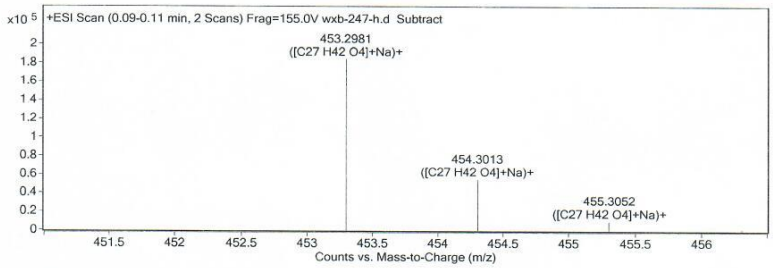
Qualitative Analysis Report

Data Filename	wxb-247-h.d	**Sample Name**	wxb-247-h
Sample Type	Sample	**Position**	P1-B3
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	4/1/2021 9:25:21 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
155	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
242.2847	1	22669.49		
431.316	1	39134.65		
448.3424	1	22609.05		
453.2981	1	184522.42	C27 H42 O4	(M+Na)+
454.3013	1	55140.71	C27 H42 O4	(M+Na)+
469.2752	1	38066.14		
470.2777	1	12853.61		
476.3738	1	32110.84		
883.6067	1	56496.33		
884.6098	1	33506.25		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C27 H42 O4	430.3083	453.2975	453.2981	-0.60	-1.32	7.0000

--- End Of Report ---

Figure S24. HRESIMS of **16**.

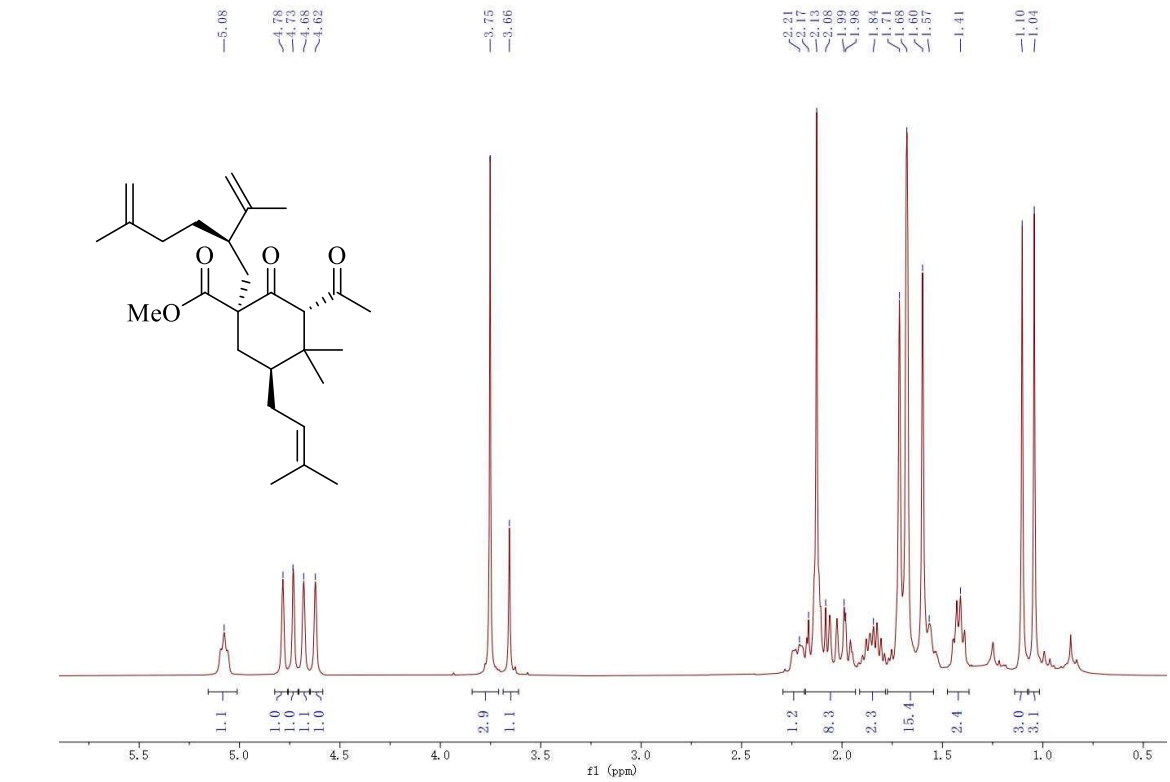


Figure S25. ^{1}H NMR spectrum of **16a** in $CDCl_3$.

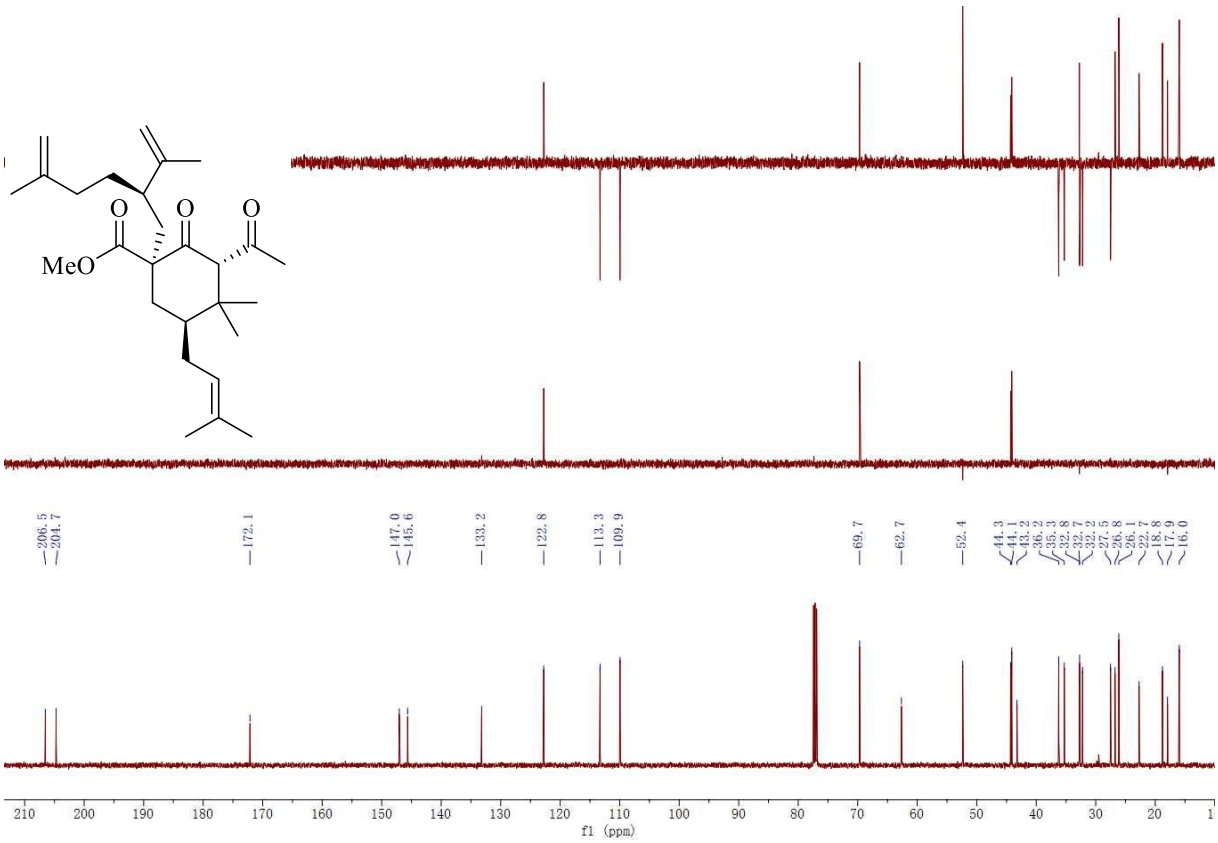


Figure S26. ^{13}C NMR spectrum of **16a** in $CDCl_3$.

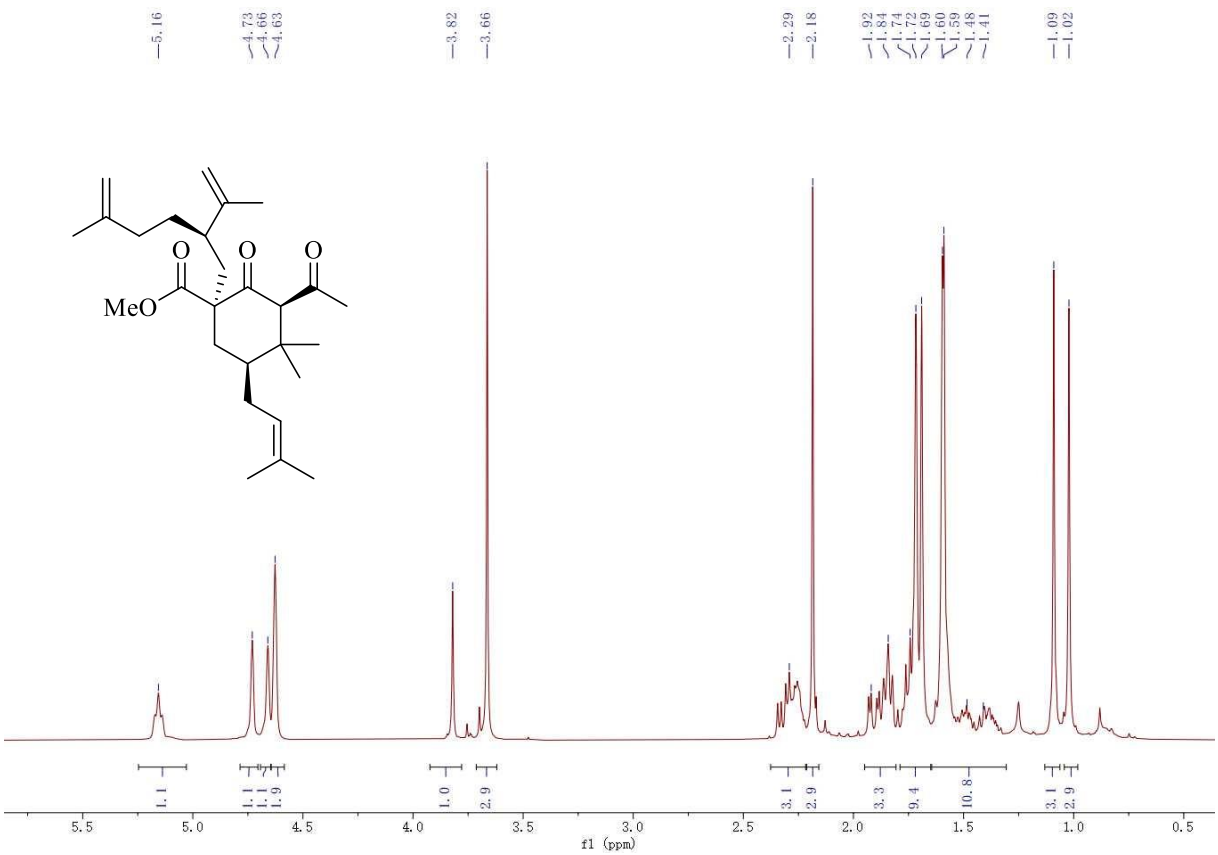


Figure S27. ^{1}H NMR spectrum of **16b** in $CDCl_3$.

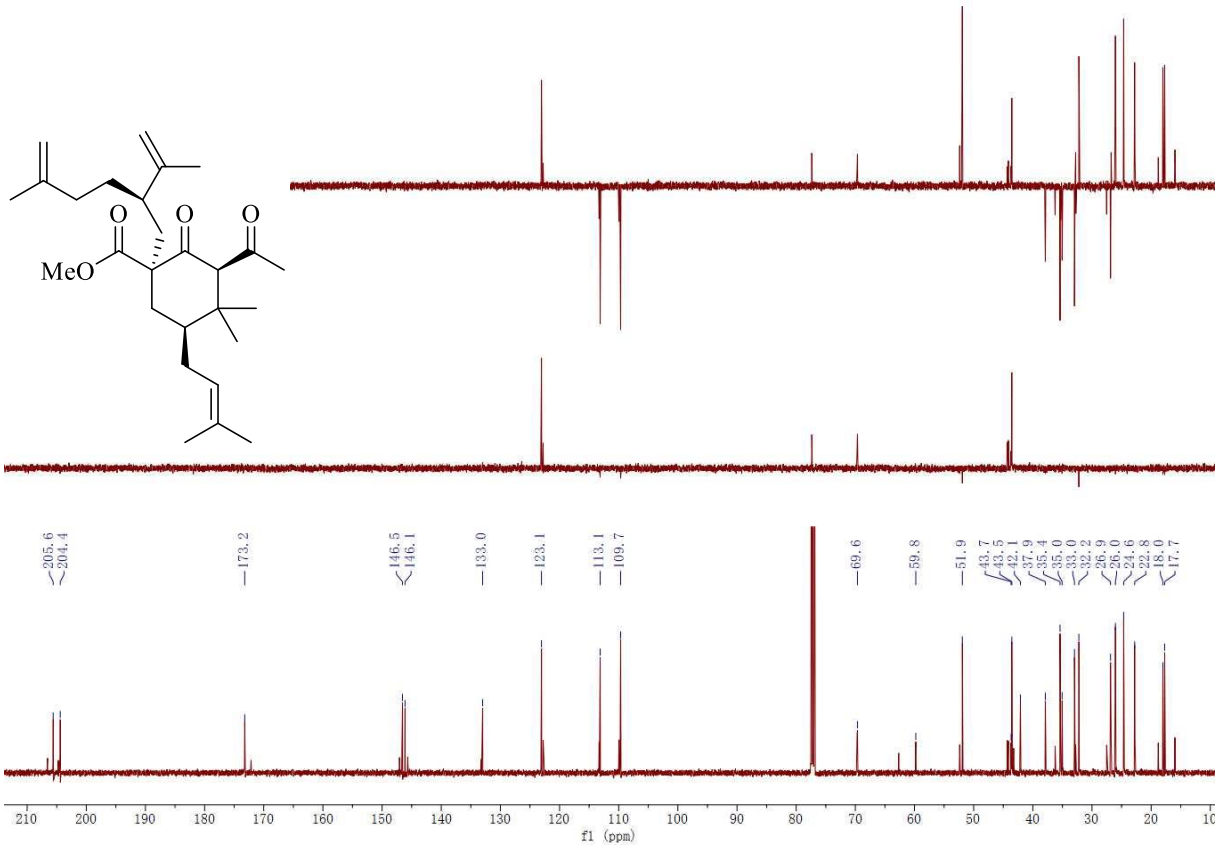


Figure S28. ^{13}C NMR spectrum of **16b** in $CDCl_3$.

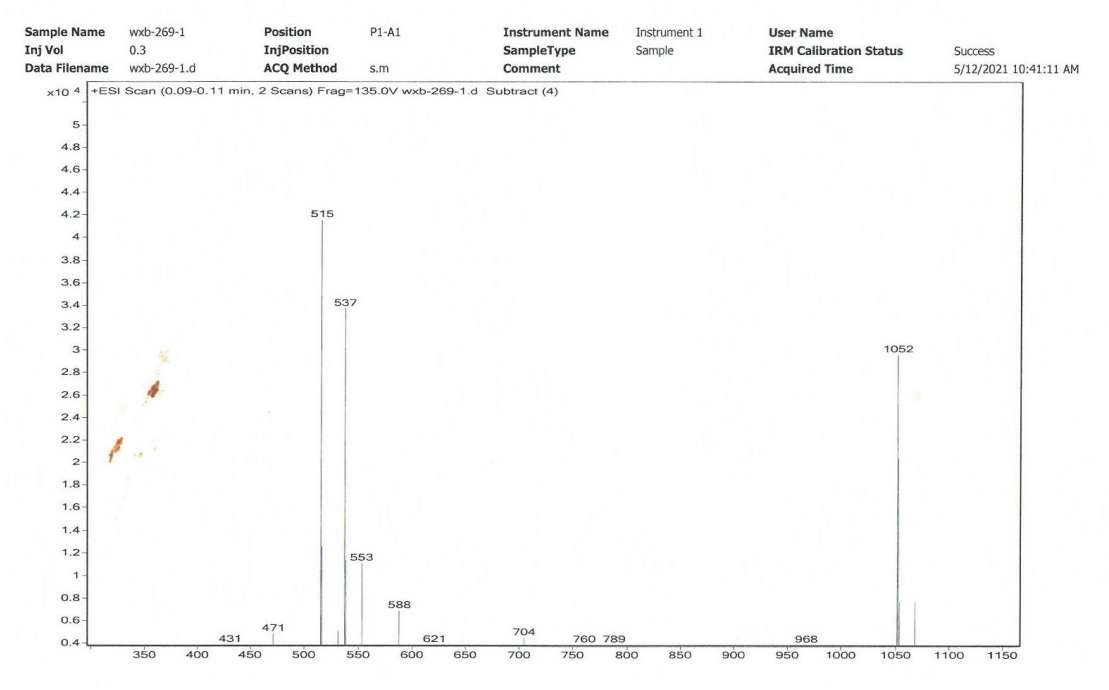


Figure S29. ESIMS of **17a**.

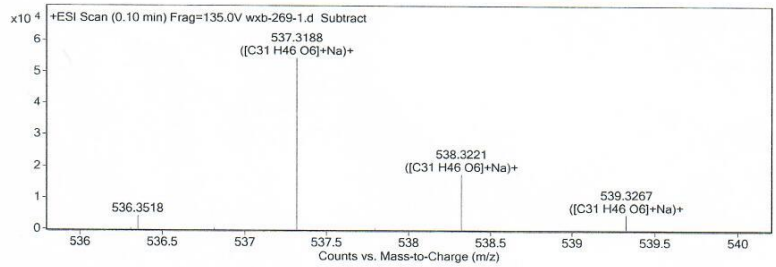
Qualitative Analysis Report

Data Filename	wxb-269-1.d	**Sample Name**	wxb-269-1
Sample Type	Sample	**Position**	P1-A1
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	5/12/2021 10:48:39 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
102.1288	1	79509.98		
130.1598	1	74187.02		
153.1389	1	24169.68		
242.2849	1	40659.8		
264.2327	1	27779.49		
515.3366	1	53373.25		
537.3188	1	54265.02	C31 H46 O6	(M+Na)+
704.4148	1	44123.65		
1051.6445	1	39641.26		
1052.6478	1	25778.69		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C31 H46 O6	514.3294	537.3187	537.3188	-0.10	-0.19	9.0000

--- End Of Report ---

Figure S30. HRESIMS of **17a**.

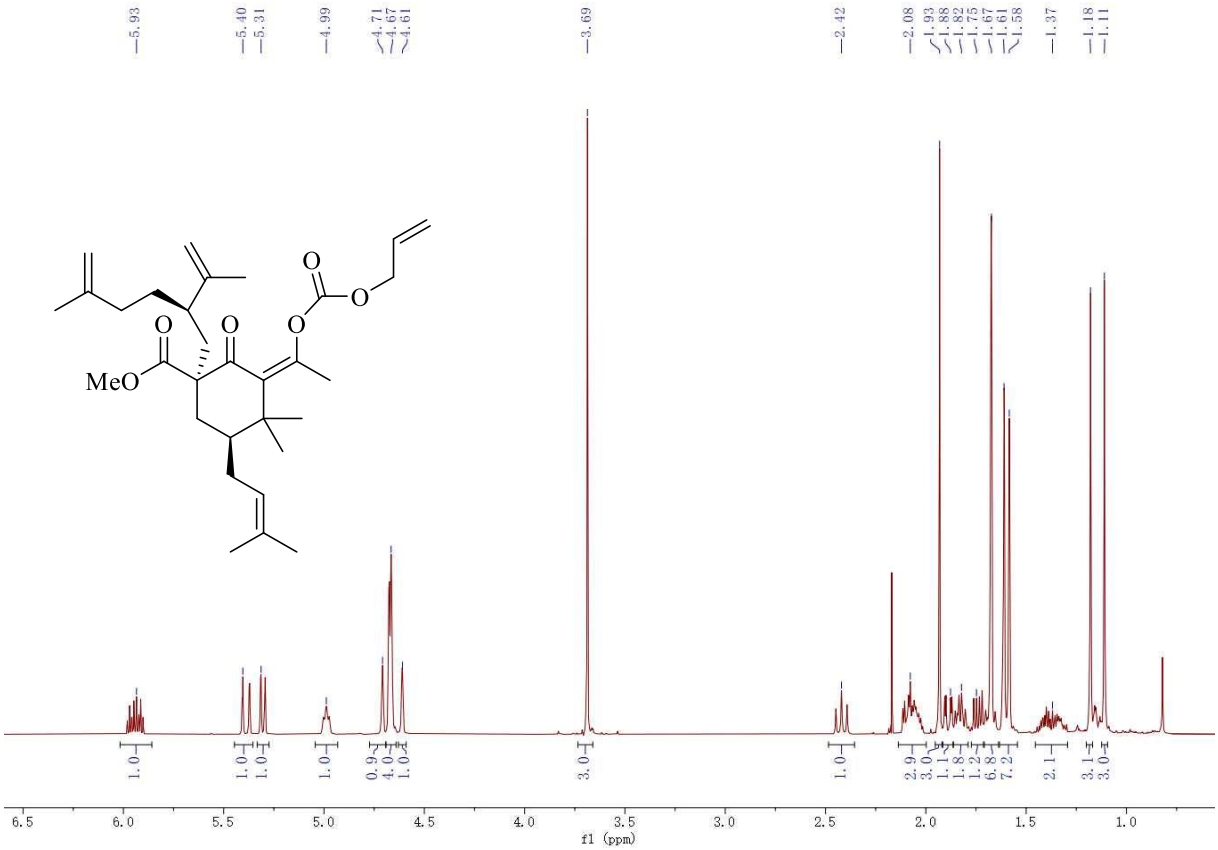


Figure S31. ^{1}H NMR spectrum of **17a** in $CDCl_3$.

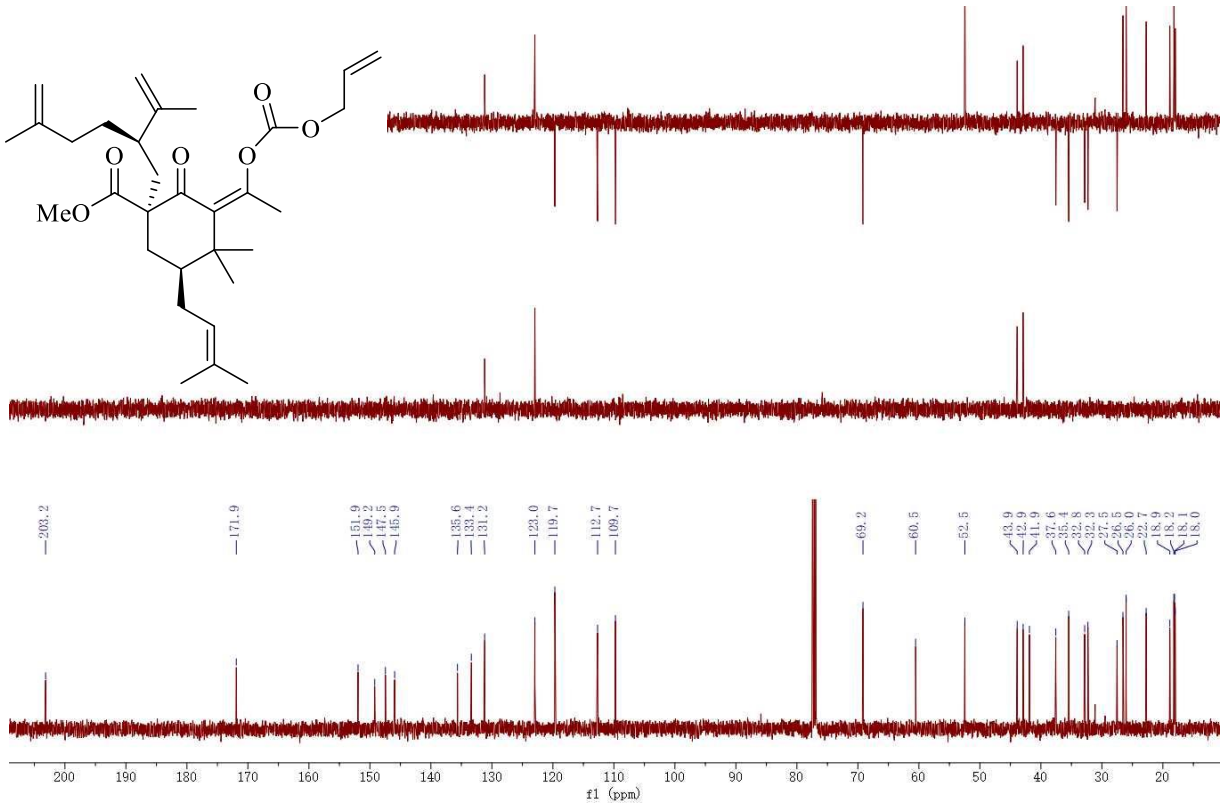


Figure S32. ^{13}C NMR spectrum of **17a** in $CDCl_3$.

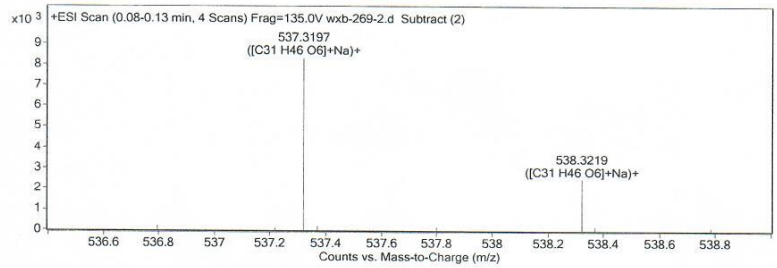
Qualitative Analysis Report

Data Filename	wxb-269-2.d	**Sample Name**	wxb-269-2
Sample Type	Sample	**Position**	P1-A2
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	5/12/2021 10:49:54 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund
153.1394	1	4235841
154.1423	1	459318.63
169.1337	1	53855.1
291.2433	1	27371.02
321.2653	1	29003.7
341.2468	1	36301.64
375.2534	1	27515.32
397.2353	1	34005.95
559.3816	1	26847.85
771.4825		28539.75

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C31 H46 O6	514.3294	537.3187	537.3197	-1.00	-1.86	9.0000

--- End Of Report ---

Figure S33. HRESIMS of **17b**.

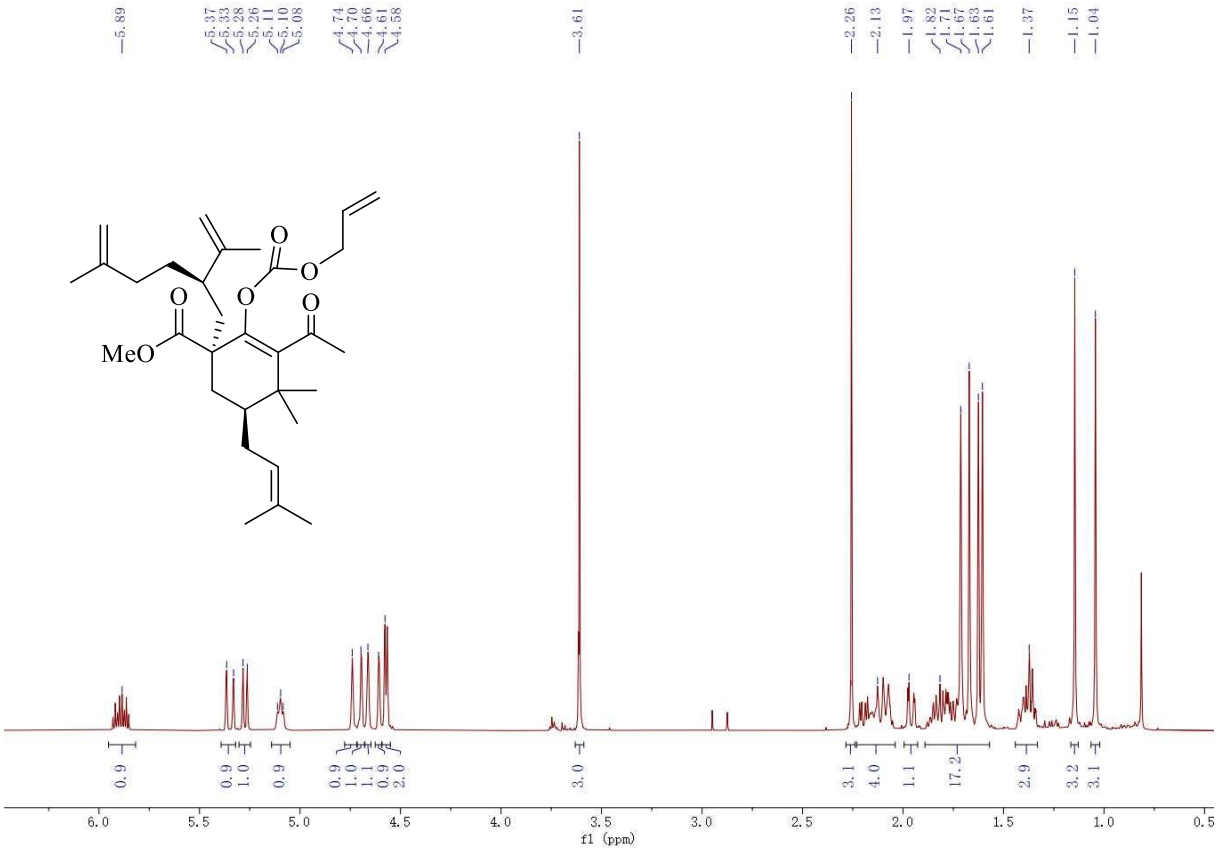


Figure S34.[1]H NMR spectrum of **17b** in $CDCl_3$.

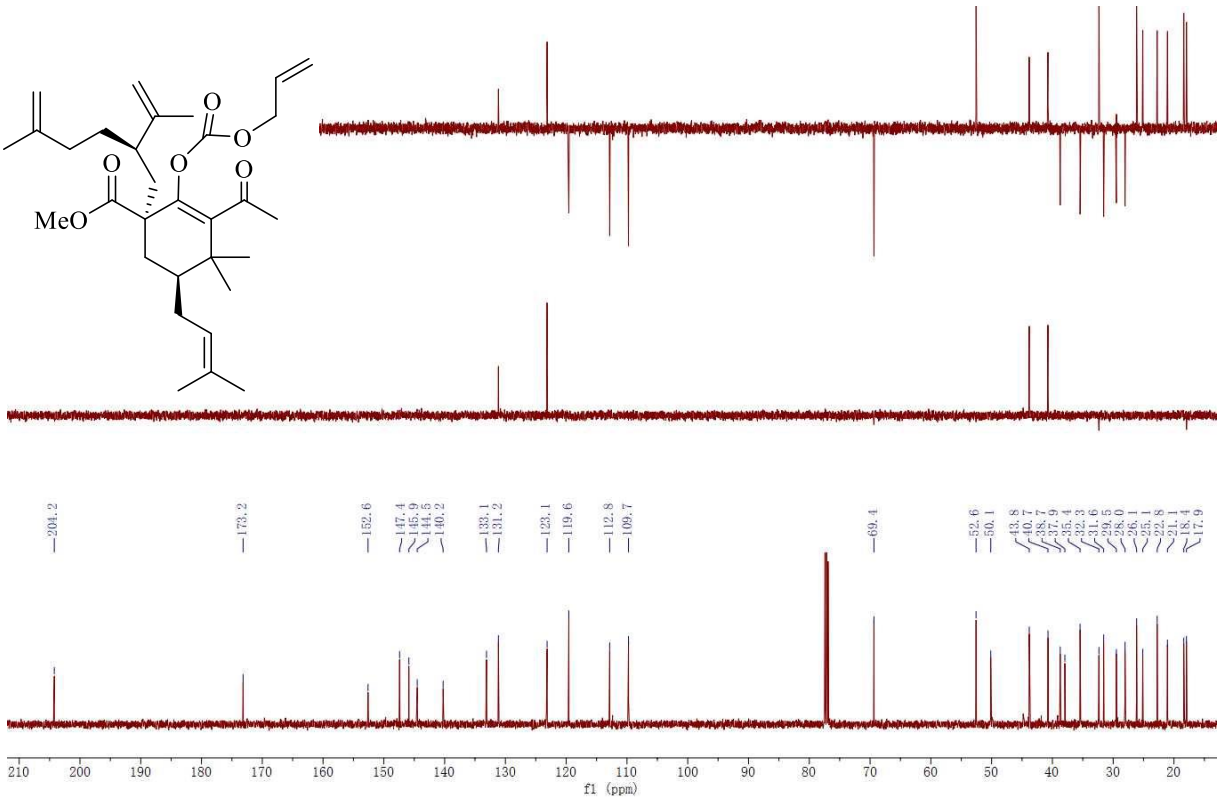


Figure S35. [13]C NMR spectrum of **17b** in $CDCl_3$.

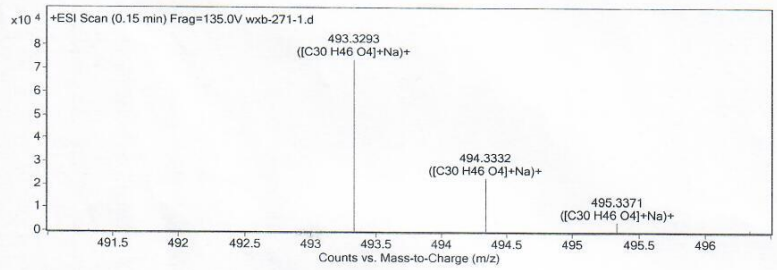
Qualitative Analysis Report

Data Filename	wxb-271-1.d	**Sample Name**	wxb-271-1
Sample Type	Sample	**Position**	P1-C1
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	5/17/2021 2:04:47 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
102.1273	1	460297.94		
103.1304	1	35493.7		
180.1254	1	17220.6		
202.1071	1	15149.2		
242.2838	1	18103.5		
471.3475	1	22198.11		
493.3293	1	73924.98	C30 H46 O4	(M+Na)+
494.3332	1	22871.47	C30 H46 O4	(M+Na)+
509.3038	1	39573.56		
963.672	1	23217.61		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C30 H46 O4	470.3396	493.3288	493.3293	-0.50	-1.01	8.0000

--- End Of Report ---

Figure S36. ESIMS of **18a**.

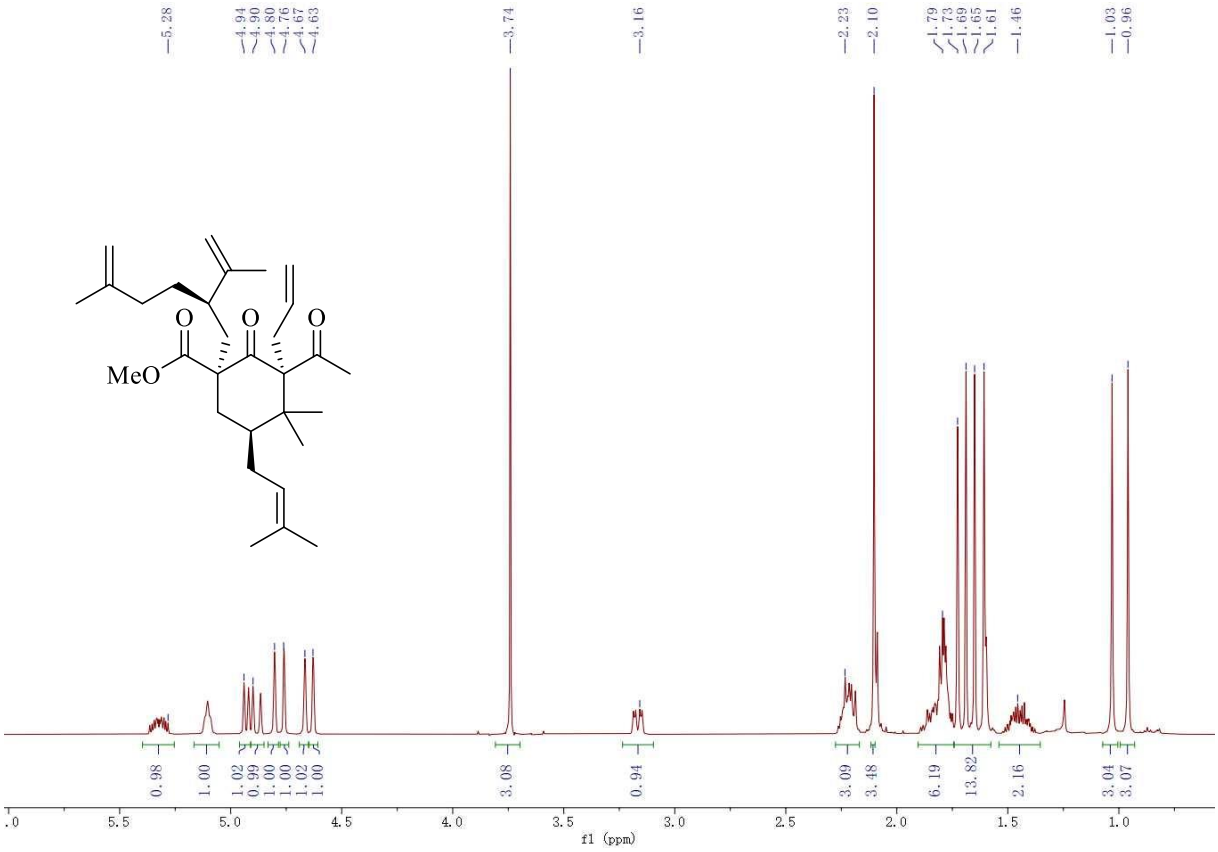


Figure S37.[1]H NMR spectrum of **18a** in $CDCl_3$.

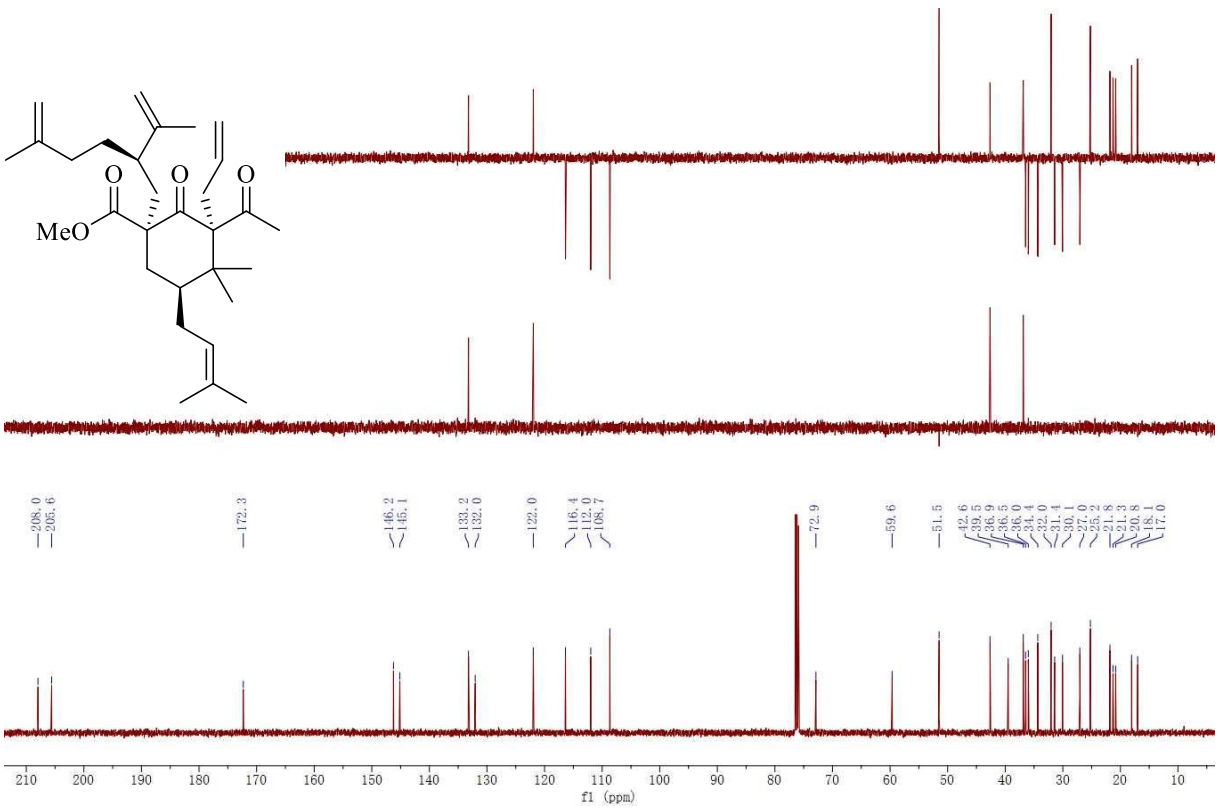


Figure S38. [13]C NMR spectrum of **18a** in $CDCl_3$.

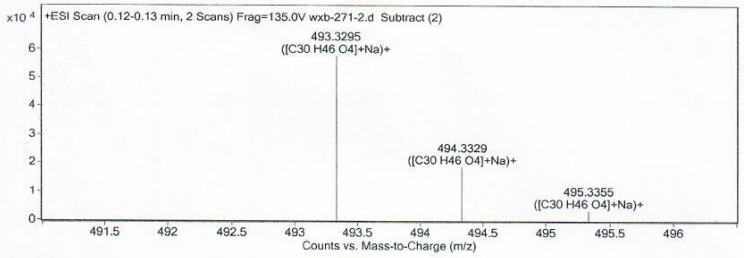
Qualitative Analysis Report

Data Filename	wxb-271-2.d	**Sample Name**	wxb-271-2
Sample Type	Sample	**Position**	P1-C1
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	5/21/2021 9:16:39 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

Sample Group	**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
102.1282		4925.16		
130.1593	1	36687.91		
275.6641	2	6173.03		
488.3741	1	16235.37		
489.3774	1	5355.07		
493.3295	1	57530.7	C30 H46 O4	(M+Na)+
494.3329	1	18451.21	C30 H46 O4	(M+Na)+
509.3032	1	23351.3		
510.3063	1	7946.87		
680.4812	1	4599.17		
963.67	1	7578.02		
964.6738	1	4630.06		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C30 H46 O4	470.3396	493.3288	493.3295	-0.70	-1.42	8.0000

--- End Of Report ---

Figure S39. ESIMS of **18b**.

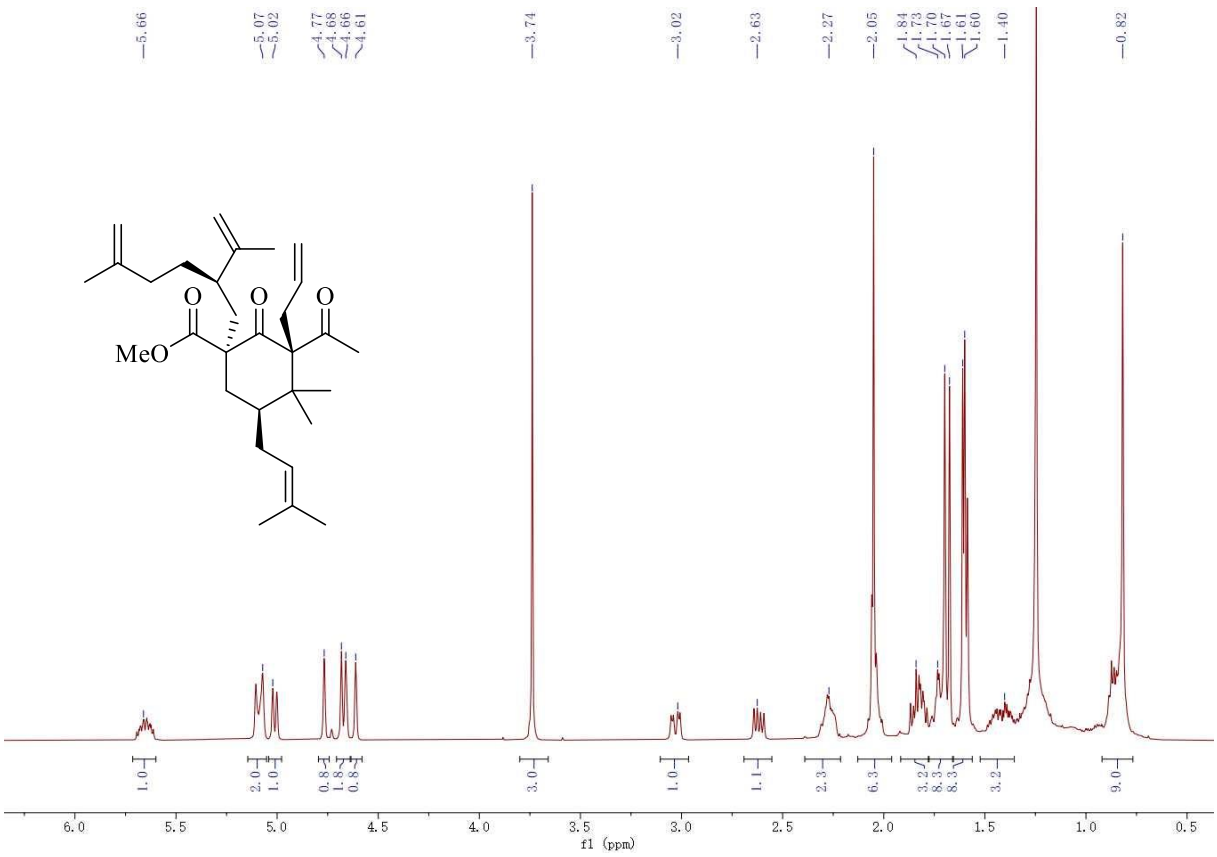


Figure S40.[1]H NMR spectrum of **18b** in $CDCl_3$.

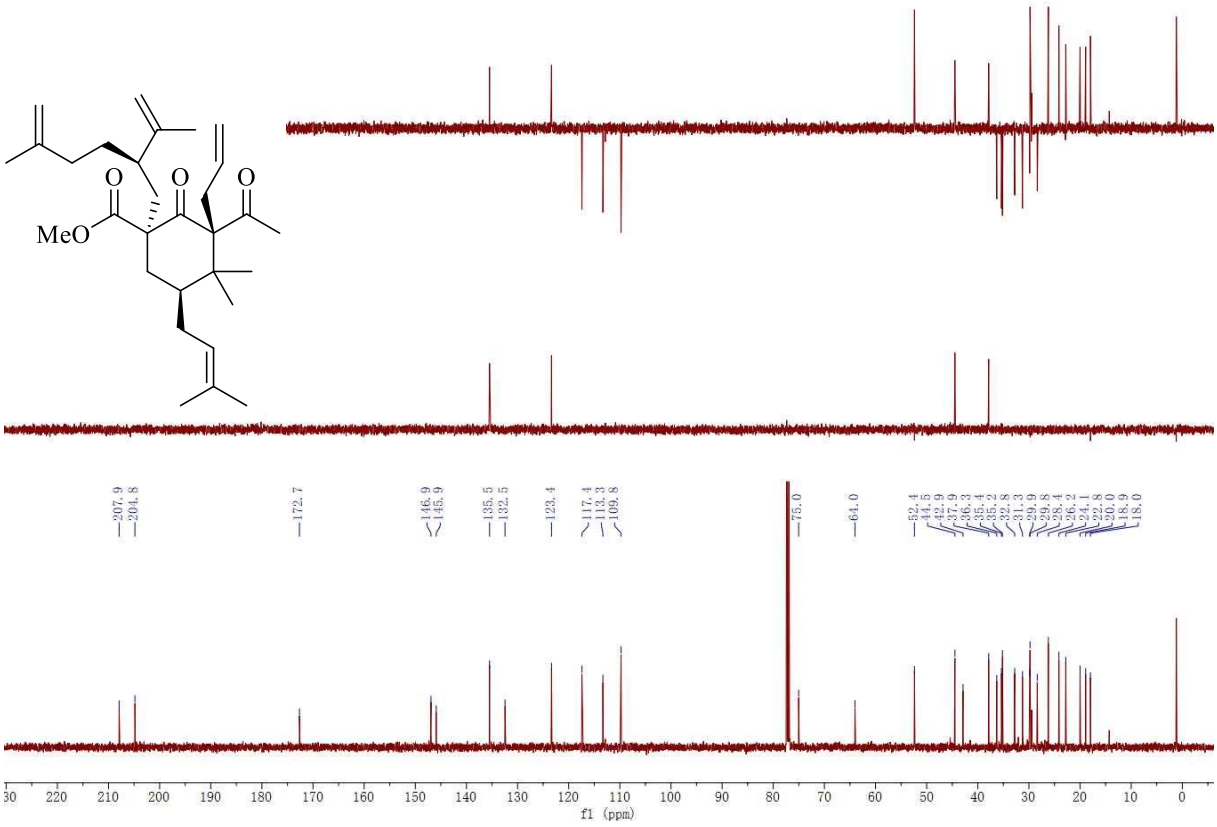


Figure S41. [13]C NMR spectrum of **18b** in $CDCl_3$.

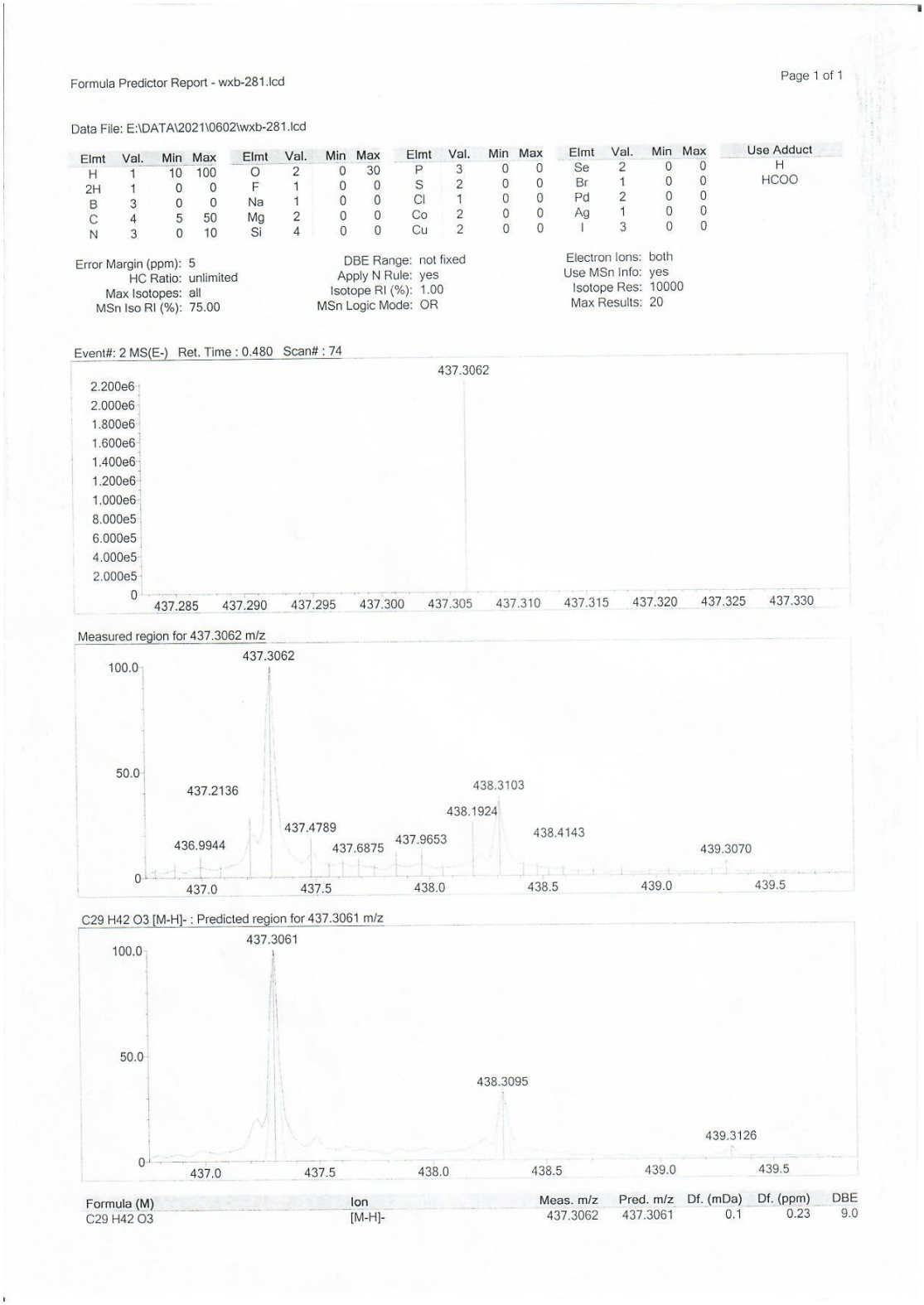


Figure S42. HRESIMS of **19**.

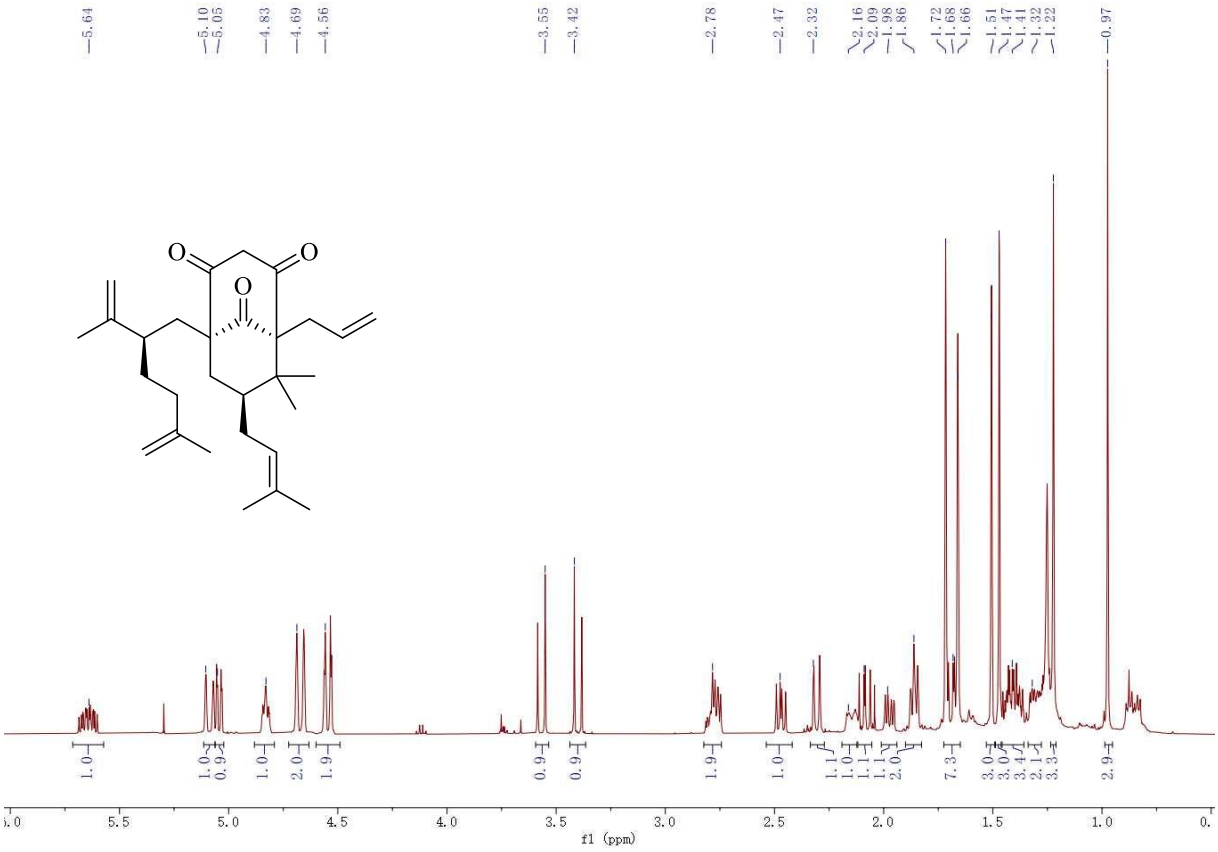


Figure S43. ^{1}H NMR spectrum of **19** in $CDCl_3$.

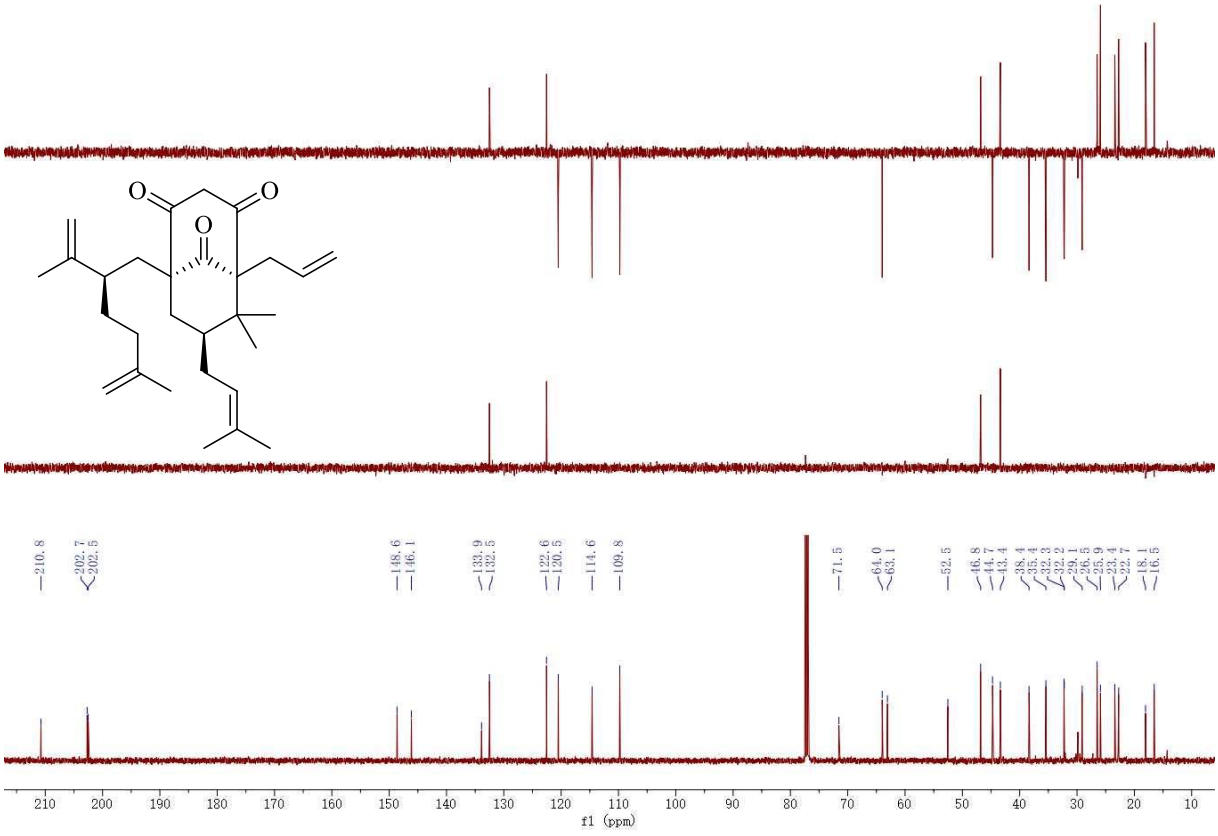


Figure S44. ^{13}C NMR spectrum of **19** in $CDCl_3$.

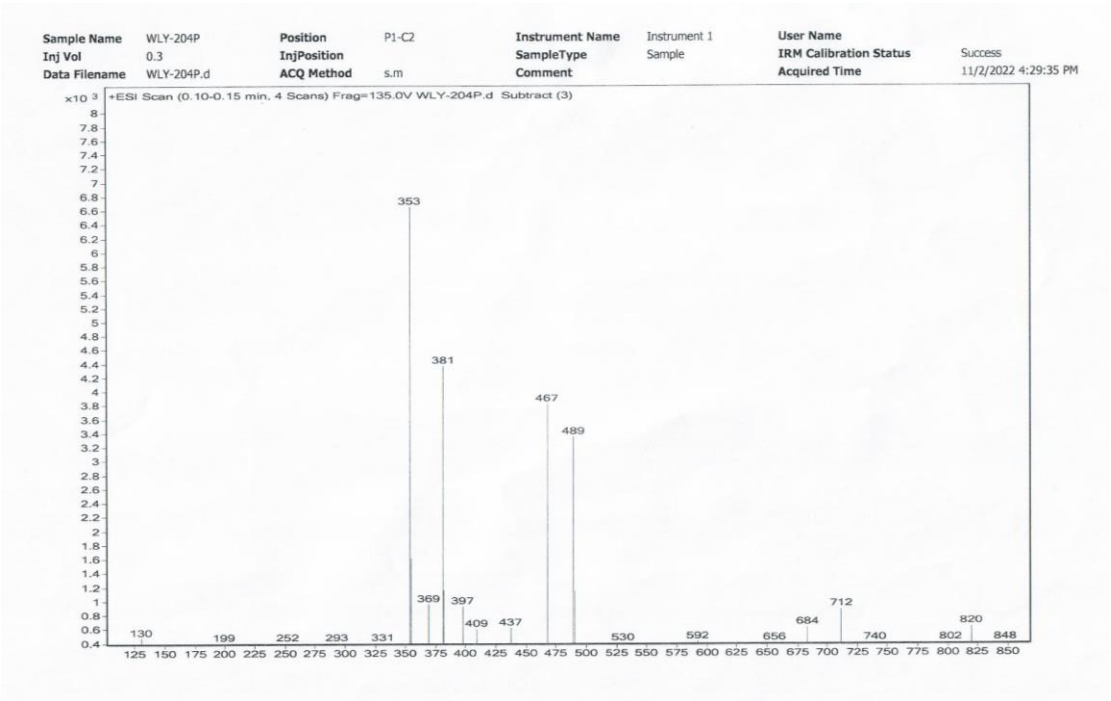


Figure S45. ESIMS of **20**.

Qualitative Analysis Report

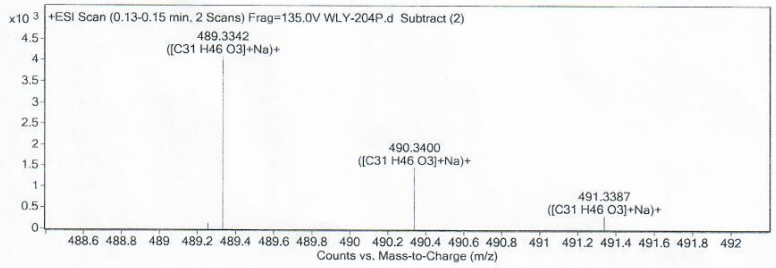
Data Filename	WLY-204P.d	**Sample Name**	WLY-204P
Sample Type	Sample	**Position**	P1-C2
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	11/2/2022 4:29:35 PM
IRM Calibration Status	Success	**DA Method**	PCDL.m
Comment			

Sample Group **Info.**

Acquisition SW Version 6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
353.2672	1	8412.51		
354.2699	1	2029.73		
381.2984	1	5447.96		
467.3522	1	5047.95		
489.3342	1	4072.97	C31 H46 O3	(M+Na)+
1012.5393	1	1965.36		
1065.6858	1	2150.98		
1173.6836	1	13457.11		
1174.687	1	7883.38		
1175.69	1	4353.58		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C31 H46 O3	466.3447	489.3339	489.3342	-0.30	-0.61	9.0000

--- End Of Report ---

Figure S46. HRESIMS of **20**.

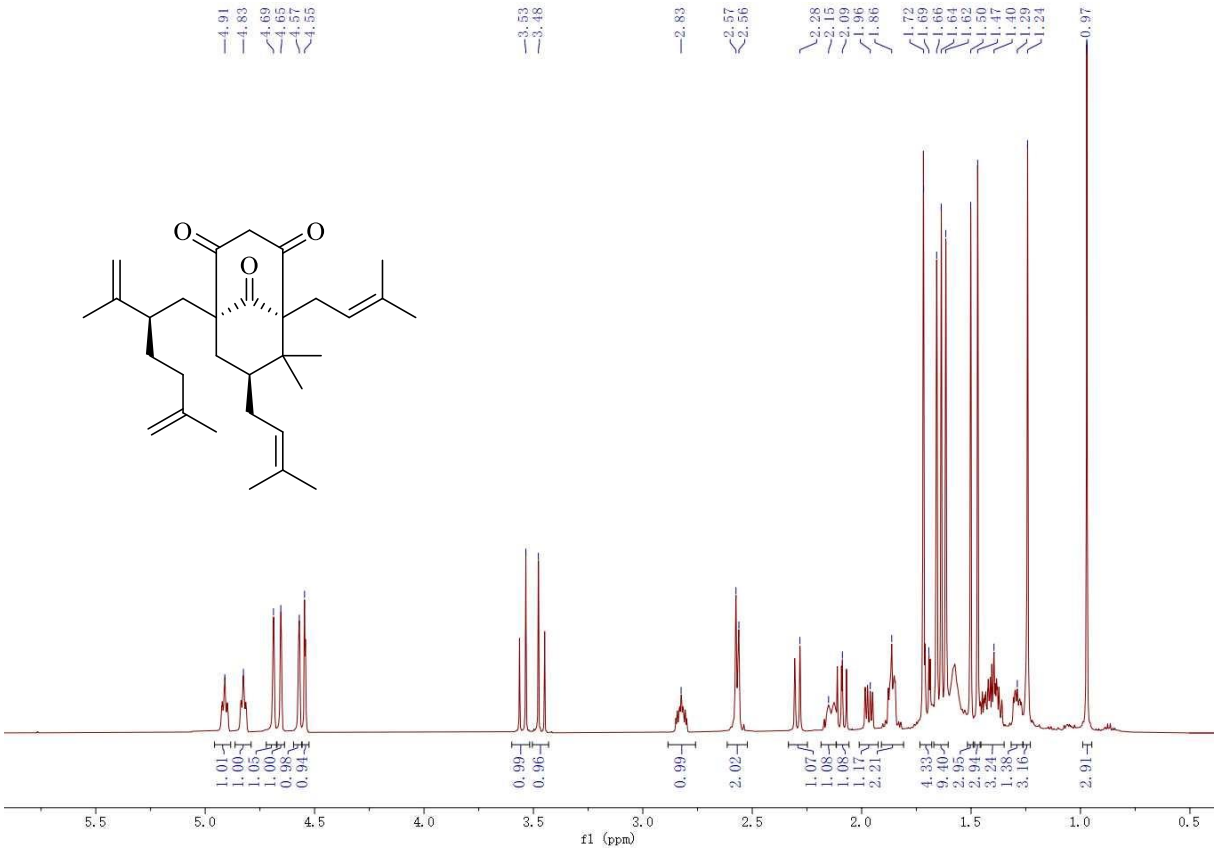


Figure S47. ^{1}H NMR spectrum of **20** in $CDCl_3$.

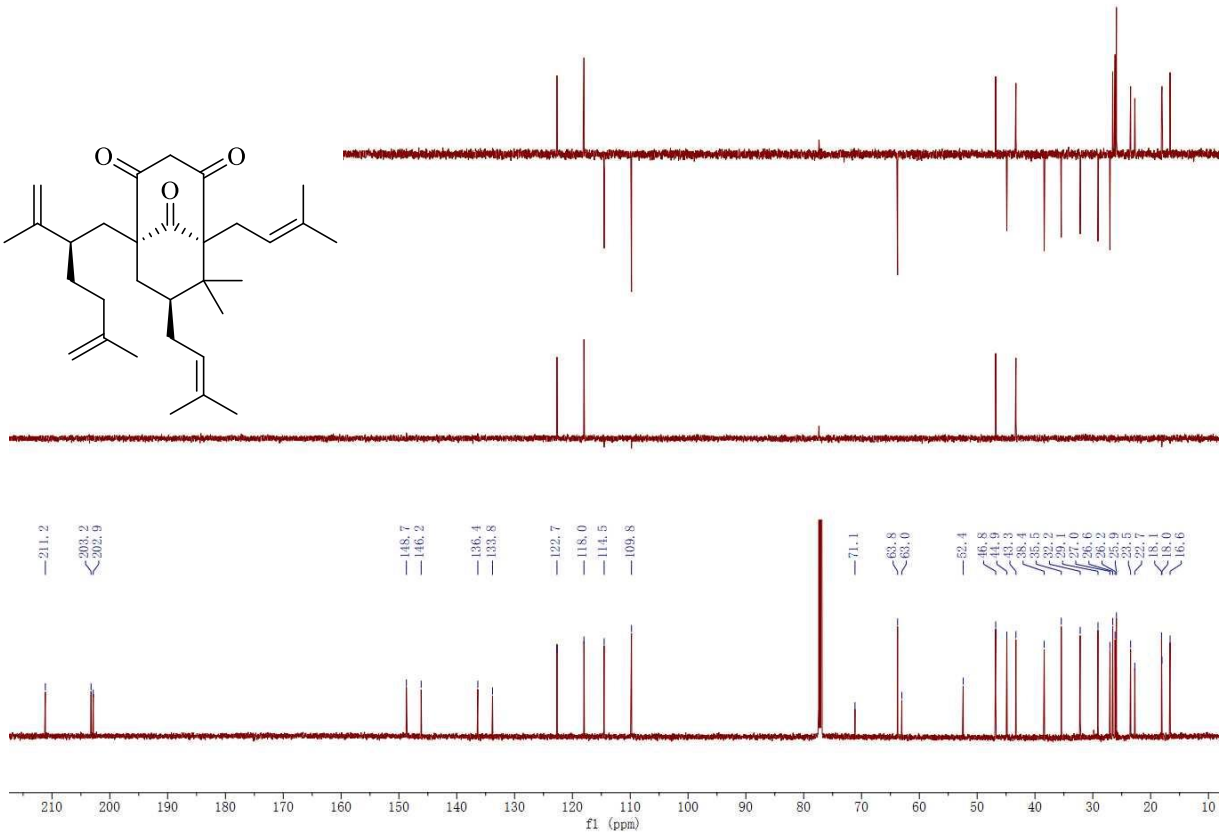


Figure S48. ^{13}C NMR spectrum of **20** in $CDCl_3$.

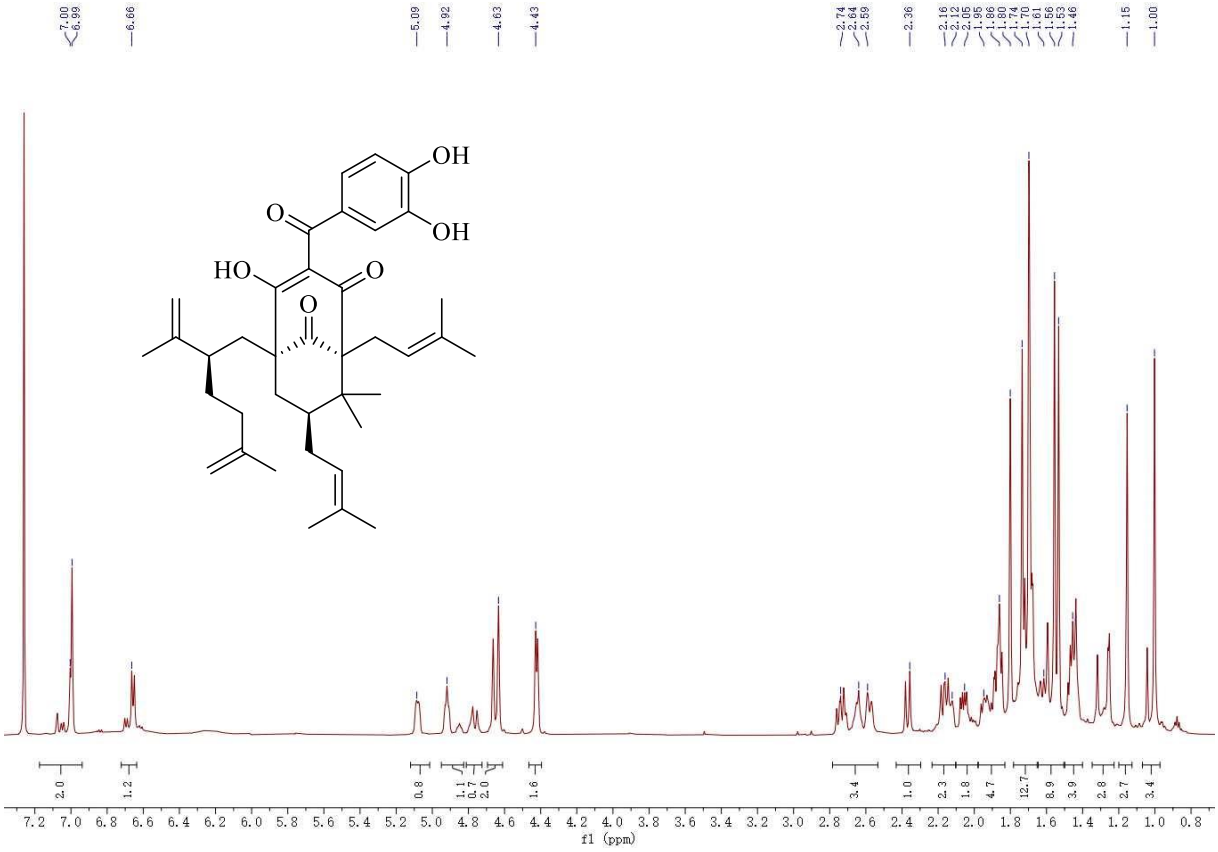


Figure S49. ^{1}H NMR spectrum of **(±)-xanthochymol** in $CDCl_3$.

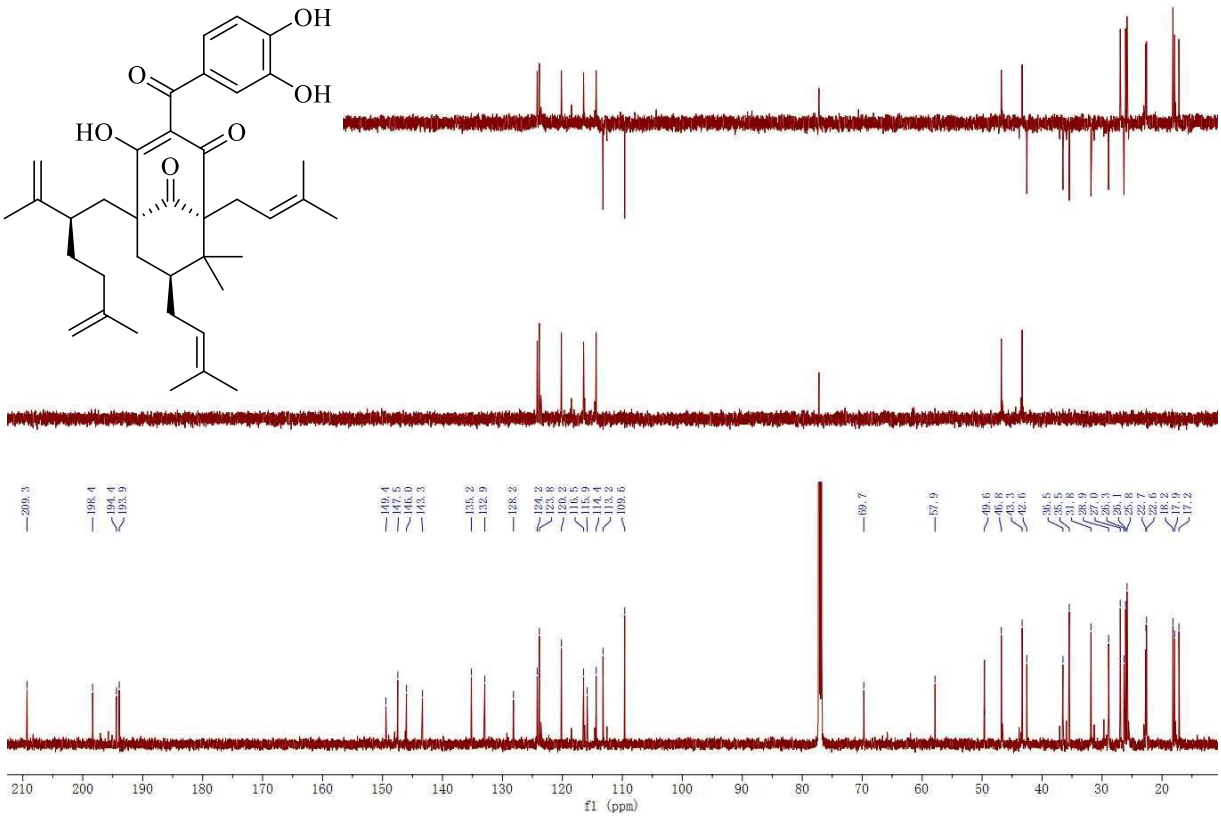


Figure S50. ^{13}C NMR spectrum of **(±)-xanthochymol** in $CDCl_3$.

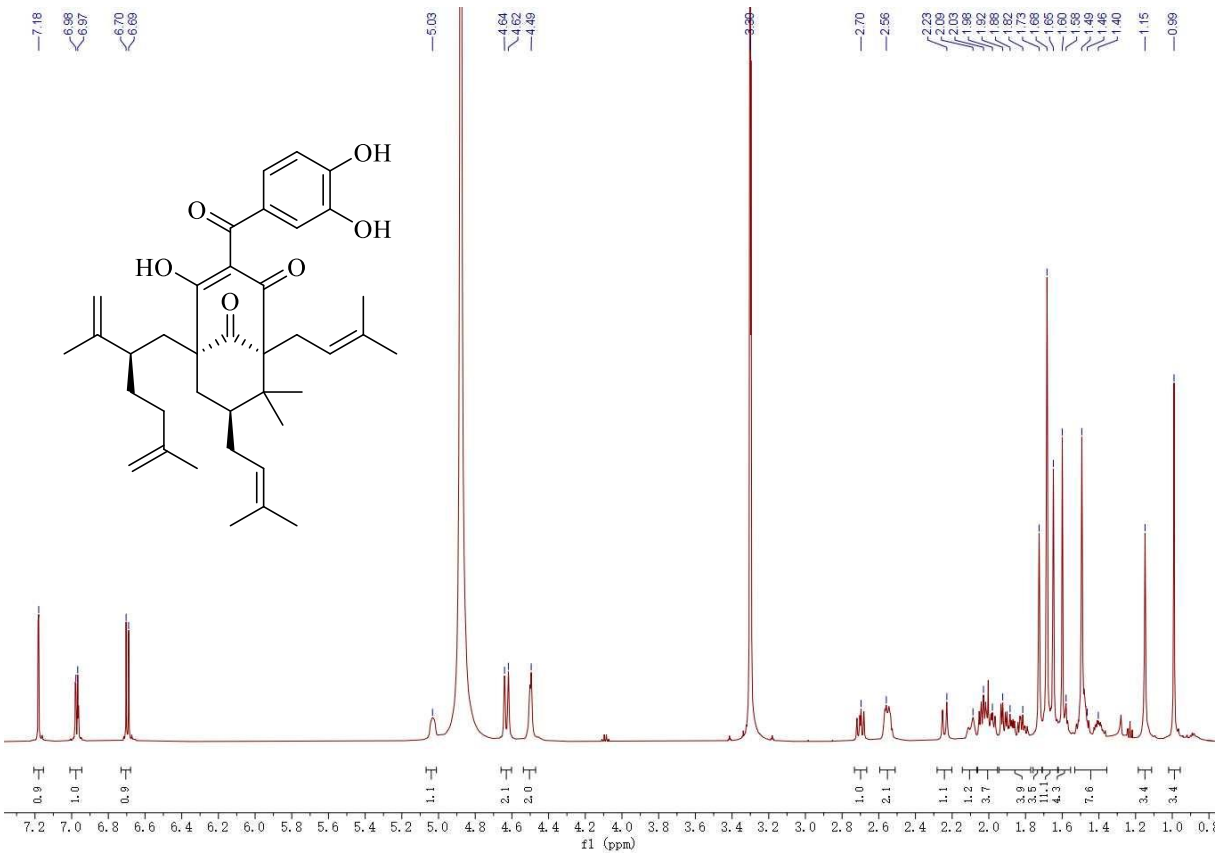


Figure S51. ^{1}H NMR spectrum of **(±)-xanthochymol** in CD_3OD.

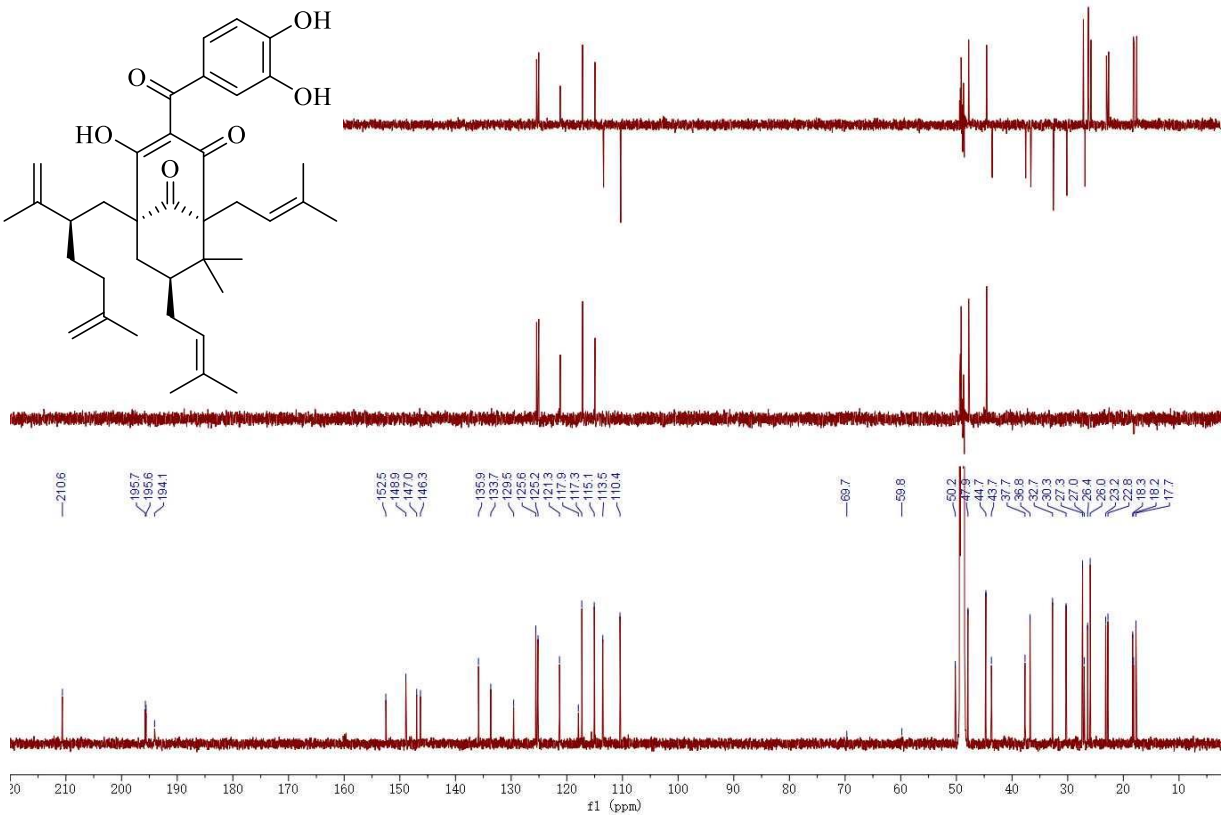


Figure S52. ^{13}C NMR spectrum of **(±)-xanthochymol** in CD_3OD.

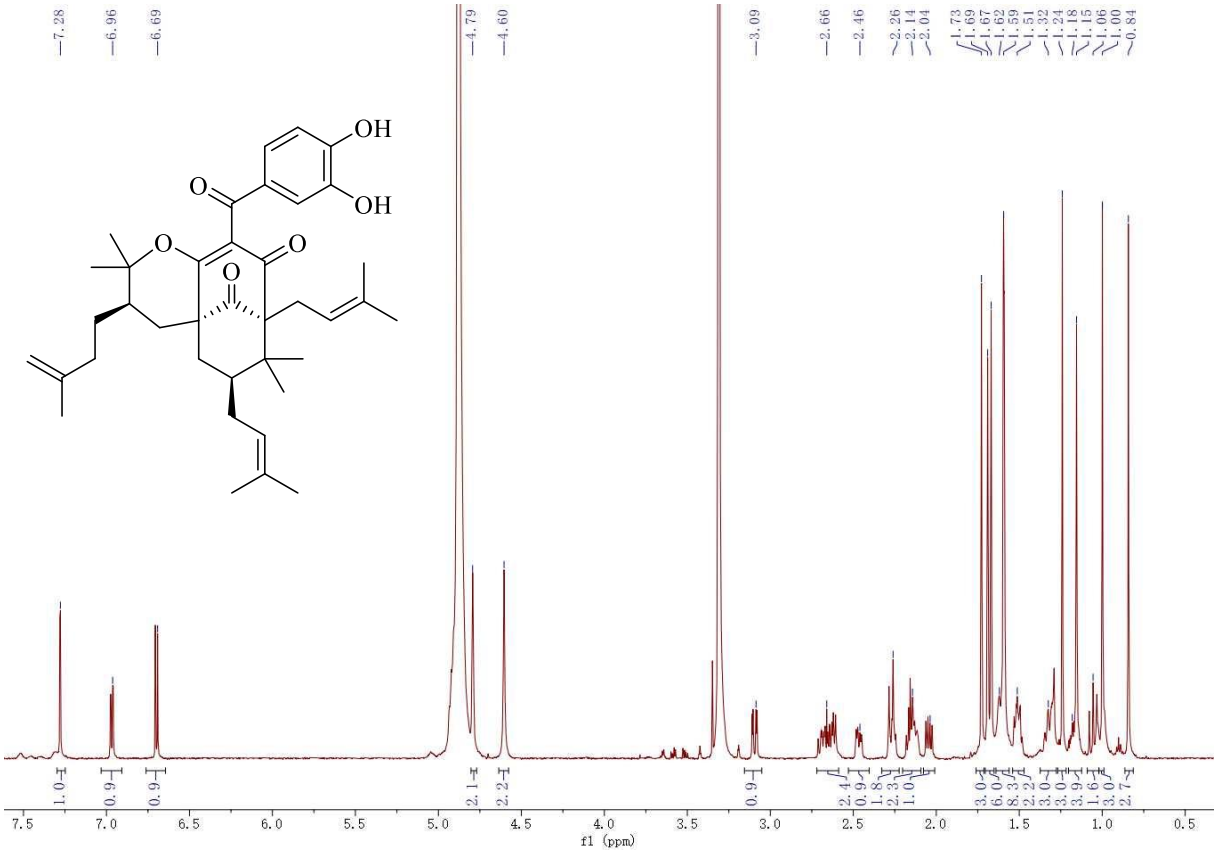


Figure S53. ^{1}H NMR spectrum of **(±)-cycloxanthochymol** in CD_3OD.

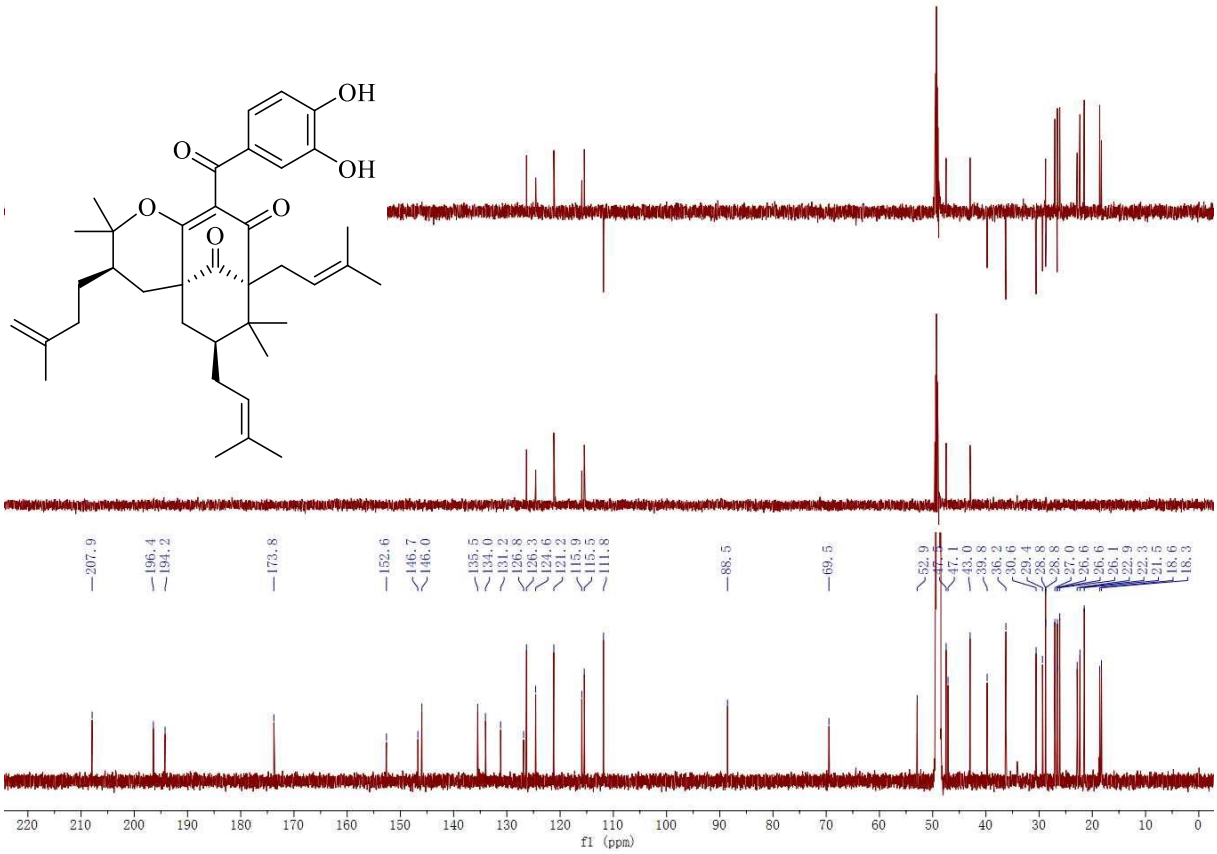


Figure S54. ^{13}C NMR spectrum of **(±)-cycloxanthochymol** in CD_3OD.