Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cytotoxic triterpenoids from *Antrodia camphorata* as sensitizers of paclitaxel

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Contents

Table S1. X-ray crystallographic data for **1**

Identification code	exp_5337	
Empirical formula	$C_{29}H_{48}O_3$	
Formula weight	444.67	
Temperature	106.1 K	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.57494(8) Å	= 90 °C
	b = 18.2337(2) Å	= 90 °C
	c = 19.1563(2) Å	= 90 °C
Volume	2645.85(5) $Å^3$	
Z	4	
Density (calculated)	1.116 mg/mm^3	
Absorption coefficient	0.537 mm^{-1}	
F(000)	984.0	
Crystal size	0.3 × 0.25 × 0.14 mm^3	
Theta range for data collection	9.7 to 142.22°	
Index ranges	$-9 \leq h \leq 4$, $-22 \leq k \leq 20$, $-23 \leq l \leq 15$	
Reflections collected	9215	
Independent reflections	4994[R(int) = 0.0286]	
Data/restraints/parameters	4994/0/298	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R_1 = 0.0416, wR_2 = 0.1055	
R indices (all data)	R_1 = 0.0447, wR_2 = 0.1090	
Largest diff. peak and hole	0.25 and -0.26 e.$Å^{-3}$	
Flack parameter	-0.1(2)	

Spectroscopic data for known compounds

Antcin A (25*R*, *S*; 19, 20): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 2.41, 2.55 (2H, m, H-2), 2.35 (1H, m, H-4), 1.30 (1H, m, H-5), 1.30, 1.64 (2H, m, H-6), 1.26, 1.89 (2H, m, H-7), 2.37 (1H, d, *J* = 14.2 Hz, H-12a), 2.91 (1H, d, *J* = 14.3 Hz, H-12b), 2.50 (1H, m, H-14), 1.38 (1H, m, H-17), 0.71 (3H, s, H-18), 1.44 (3H, s, H-19), 0.88 (3H, d, *J* = 4.4 Hz, H-21), 1.36, 1.70 (2H, m, H-22), 3.48 (1H, m, H-25), 1.54 (3H, d, *J* = 7.0 Hz, H-27), 5.10 (1H, s, H-28a), 5.26 (1H, s, H-28b), 1.13 (3H, d, *J* = 6.5 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 36.4 (C-1), 38.5 (C-2), 212.2 (C-3), 44.8 (C-4), 51.1 (C-5), 21.5 (C-6), 30.6 (C-7), 157.4 (C-8), 139.1 (C-9), 37.3 (C-10), 199.8 (C-11), 58.4 (C-12), 47.7 (C-13), 53.4(C-14), 24.2 (C-15), 28.1 (C-16), 55.6 (C-17), 12.4 (C-18), 18.0 (C-19), 35.8 (C-20), 18.8 (C-21), 34.7 (C-22), 32.2 (C-23), 150.7 (C-24), 46.9 (C-25), 177.2 (C-26), 17.4 (C-27), 110.9 (C-28), 12.5 (C-29)[1].

Antcin B (25*R*, *S*; 21, 22):^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.40, 3.19 (2H, m, H-1), 2.41, 2.57 (2H, m, H-2), 2.44 (1H, m, H-4), 2.50 (1H, m, H-12a), 3.01 (1H, m, H-12b), 0.70 (3H, s, H-18), 1.61 (3H, s, H-19), 0.90 (3H, d, *J* = 5.1 Hz, H-21), 1.53 (3H, d, *J* = 7.0 Hz, H-27), 5.09 (1H, s, H-28a), 5.26 (1H, s, H-28b), 1.04 (3H, d, *J* = 6.6 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 35.4 (C-1), 38.2 (C-2), 210.3 (C-3), 44.4 (C-4), 49.3 (C-5), 39.6 (C-6), 201.2 (C-7), 145.9 (C-8), 152.4 (C-9), 39.0 (C-10), 203.1 (C-11), 57.9 (C-12), 47.7 (C-13), 49.9 (C-14), 25.7 (C-15), 28.4 (C-16), 54.4 (C-17), 12.5 (C-18), 16.7 (C-19), 36.3 (C-20), 19.0 (C-21), 34.8 (C-22), 32.0 (C-23), 150.8 (C-24), 47.2 (C-25), 177.3 (C-26), 17.6 (C-27), 110.9 (C-28), 12.0

(C-29)[1].

Antcin D (25*R*, *S*; 23, 24): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.62, 3.06 (2H, m, H-1), 2.64 (1H, m, H-12a), 2.81 (1H, d, J =14.3 Hz, H-12b), 1.26 (3H, s, H-18), 1.52 (3H, s, H-19), 0.98 (3H, d, J = 5.6 Hz, H-21), 3.48 (1H, q, J =7.0 Hz, H-25), 1.50 (3H, d, J = 3.1 Hz, H-27), 5.09 (1H, s, H-28a), 5.24 (1H, s, H-28b), 1.04 (3H, d, J = 6.6 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 35.7 (C-1), 38.0 (C-2), 209.9 (C-3), 44.1 (C-4), 47.9 (C-5), 40.0 (C-6), 203.0 (C-7), 145.8 (C-8), 153.4 (C-9), 38.5 (C-10), 202.3 (C-11), 53.8 (C-12), 50.8 (C-13), 81.9 (C-14), 37.7 (C-15), 27.3 (C-16), 53.3 (C-17), 16.9 (C-18),16.1 (C-19), 35.1 (C-20), 20.5 (C-21), 33.5 (C-22), 33.1 (C-23), 150.8 (C-24), 47.1 (C-25), 177.1 (C-26), 17.5 (C-27), 110.8 (C-28), 11.7 (C-29)[2].

Antcin E (25*R*, *S*; 25, 26): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.35, 3.10 (2H, m, H-1), 2.56 (1H, m, H-12a), 2.81 (1H, d, J = 13.2 Hz, H-12b), 0.97 (3H, s, H-18), 1.53 (3H, s, H-19), 0.89 (3H, d, J = 6.4 Hz, H-21), 3.50 (1H, q, J = 7.0 Hz, H-25), 1.54 (3H, d, J = 7.0 Hz, H-27), 5.11 (1H, s, H-28a), 5.27 (1H, s, H-28b), 1.13 (3H, d, J = 6.5 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 35.7 (C-1), 38.4 (C-2), 211.8 (C-3), 44.7 (C-4), 50.8 (C-5),21.3 (C-6), 28.3 (C-7), 139.3 (C-8), 143.5 (C-9), 37.5 (C-10), 200.5 (C-11), 56.6 (C-12), 48.9 (C-13), 149.0 (C-14), 126.7 (C-15),36.6 (C-16), 57.1 (C-17), 18.0 (C-18),18.6 (C-19), 34.1 (C-20), 18.9 (C-21), 34.5 (C-22), 32.0 (C-23), 150.7 (C-24), 46.9 (C-25), 176.8 (C-26), 17.4 (C-27), 111.0 (C-28), 12.4 (C-29)[2].

Antcin F (27) :^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.37, 2.99 (2H, m, H-1), 2.65 (1H, d, J = 13.2 Hz, H-12a), 2.85 (1H, d, J = 13.2 Hz, H-12b), 1.02 (3H, s, H-18), 1.63 (3H, s, H-19), 0.91 (3H, d, J = 6.4 Hz, H-21), 3.48 (1H, q, J = 7.1 Hz, H-25), 1.52 (3H, d, J = 7.0 Hz, H-27), 5.09 (1H, s, H-28a), 5.25 (1H, s, H-28b), 1.16 (3H, d, J = 6.5 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 36.1 (C-1), 38.4 (C-2), 211.4 (C-3), 44.3 (C-4), 48.2 (C-5), 33.1 (C-6), 67.4 (C-7), 146.8 (C-8), 140.0 (C-9), 37.9 (C-10), 201.8 (C-11), 56.9 (C-12), 49.7 (C-13), 145.3 (C-14), 130.0 (C-15), 37.2 (C-16), 56.7 (C-17), 17.8 (C-18),18.9 (C-19), 34.1 (C-20), 18.5 (C-21), 34.5 (C-22), 31.9 (C-23), 150.3 (C-24), 46.9 (C-25), 177.2 (C-26), 17.4 (C-27), 111.0 (C-28), 12.3 (C-29)[2].

Antcin G (25*R*, *S*; 28, 29):^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.36, 3.28 (2H, m, H-1), 2.46 (1H, m, H-12a), 2.96 (1H, d, J = 14.4 Hz, H-12b), 0.71 (3H, s, H-18), 1.43 (3H, s, H-19), 0.88 (3H, d, J = 4.9 Hz, H-21), 3.50 (1H, q, J = 7.1 Hz, H-25), 1.53 (3H, d, J = 7.0 Hz, H-27), 5.08 (1H, s, H-28a), 5.24 (1H, s, H-28b), 1.08 (3H, d, J = 6.5 Hz, H-29), 2.21 (3H, s, H-31). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 35.4 (C-1), 38.2 (C-2), 211.6 (C-3), 44.1 (C-4), 46.1 (C-5), 28.6 (C-6), 69.1 (C-7), 150.7 (C-8), 143.3 (C-9), 37.8 (C-10), 200.6 (C-11), 58.2 (C-12), 48.0 (C-13), 51.5 (C-14), 23.5 (C-15),28.0 (C-16), 55.4 (C-17), 12.4 (C-18), 16.8 (C-19), 36.3 (C-20), 18.8 (C-21), 34.6 (C-22), 32.1 (C-23), 150.5 (C-24), 46.1 (C-25), 177.2 (C-26), 17.4 (C-27), 111.0 (C-28), 12.3 (C-29), 170.5 (C-30), 21.5 (C-31)[2].

Camphoratin A (25*R*, *S*; 30, 31): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 3.92 (1H, s, H-3), 1.67 (1H, m, H-4), 2.16 (1H, m, H-5), 4.54 (1H, t, J = 8.4 Hz, H-7), 4.47 (1H, s, H-12), 3.58 (1H, m, H-14),1.01 (3H, s, H-18), 1.59 (3H, s, H-19), 1.12 (3H, d, J = 6.3 Hz,H-21), 3.47 (1H, q, J = 7.1 Hz, H-25), 1.50 (3H, d, J = 7.1 Hz,H-27),5.25 (1H, s, H-28a), 5.08 (1H, s, H-28b),1.18 (3H, d, J = 6.7 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 29.9 (C-1), 30.9 (C-2), 70.6 (C-3), 35.7 (C-4), 40.6 (C-5), 33.2 (C-6), 70.4 (C-7), 154.6 (C-8), 141.5 (C-9), 38.0 (C-10), 203.1 (C-11), 81.9 (C-12), 51.0 (C-13), 47.6 (C-14), 25.7 (C-15), 28.0 (C-16), 46.2 (C-17), 12.7 (C-18), 18.5 (C-19), 36.7 (C-20), 18.5 (C-21), 35.2 (C-22), 32.4 (C-23), 150.4 (C-24), 47.1 (C-25),177.2 (C-26), 17.6 (C-27), 110.8 (C-28), 17.4 (C-29)[3].

Antcamphin C (32): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 2.43 (1H, m, H-12a),2.94 (1H, d, J = 14.2 Hz, 12b), 0.73 (3H, s, H-18), 1.46 (3H, s, H-19), 0.88 (3H, d, J = 6.0 Hz,H-21), 10.30 (1H, s, H-26), 1.86 (3H, s, H-27), 2.07 (1H, s, H-28), 1.13 (3H, d, J = 6.6 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 35.8 (C-1), 38.4 (C-2), 212.2 (C-3), 44.8 (C-4), 51.0 (C-5), 21.4 (C-6), 30.5 (C-7), 157.3 (C-8), 139.1 (C-9), 37.3 (C-10), 199.7 (C-11), 58.3 (C-12), 47.4 (C-13), 53.4 (C-14), 24.2 (C-15), 28.0 (C-16), 55.1 (C-17), 12.4 (C-18), 18.0 (C-19), 36.8 (C-20), 18.8 (C-21), 33.5 (C-22), 35.8 (C-23), 159.7 (C-24), 131.9 (C-25), 191.7 (C-26), 11.0 (C-27), 17.6 (C-28), 12.5 (C-29)[4].

Antcamphin E/F (33, 34): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.61, 3.32 (2H, m,

H-1), 2.52, 3.08 (2H, m, H-2), 4.69 (1H, t, *J* = 8.5 Hz, H-7), 2.51 (1H, m, H-12a), 3.02 (1H, d, *J* = 14.1 Hz, 12b), 0.90 (3H, s, H-18), 1.92 (3H, s, H-19), 0.92 (3H, d, *J* = 5.2 Hz,H-21), 3.49 (1H, q, *J* = 7.0 Hz, H-25), 1.53 (3H, d, *J* = 7.1 Hz, H-27), 5.10 (1H, s, H-28a), 5.27 (1H, s, H-28b), 1.56 (3H, s, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 37.1 (C-1), 34.8 (C-2),214.6 (C-3), 76.7 (C-4), 51.0 (C-5), 30.9 (C-6), 70.7 (C-7), 155.8 (C-8), 142.2 (C-9), 38.1 (C-10), 201.5 (C-11), 58.9 (C-12), 48.1 (C-13), 54.0 (C-14), 26.0 (C-15), 28.7 (C-16), 55.2 (C-17), 12.9 (C-18), 21.1 (C-19), 36.6 (C-20), 19.1 (C-21), 34.9 (C-22), 32.1 (C-23), 150.9 (C-24), 47.2 (C-25),177.3 (C-26), 17.6 (C-27), 110.9 (C-28), 24.8 (C-29)[4].

Antcamphin I (35): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 4.50 (3H, s, H-12), 0.80 (3H, s, H-18), 1.66 (3H, s, H-19), 1.08 (3H, d, *J* = 6.4 Hz, H-21), 1.51 (3H, d, *J* = 7.1 Hz, H-27), 5.08 (1H, s, H-28a), 5.24 (1H, s, H-28b), 1.01 (3H, d, *J* = 6.6 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 34.7 (C-1), 37.9 (C-2), 210.2 (C-3), 44.1 (C-4), 48.9 (C-5), 39.5 (C-6), 200.7 (C-7), 145.1 (C-8), 151.4 (C-9), 38.5 (C-10), 203.8 (C-11), 80.8 (C-12), 50.3 (C-13), 42.9 (C-14), 24.7 (C-15), 27.5 (C-16), 46.2 (C-17), 11.9 (C-18), 16.7 (C-19), 36.0 (C-20), 18.3 (C-21), 34.7 (C-22), 32.2 (C-23), 150.5 (C-24), 46.7 (C-25), 177.1 (C-26), 17.2 (C-27), 110.7 (C-28), 11.7 (C-29)[4].

Camphoratin C (36): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 0.75 (3H, s, H-18), 1.46 (3H, s, H-19), 0.89 (3H, d, *J* = 5.6 Hz, H-21), 1.52 (3H, m, H-27), 5.09 (1H, s, H-28a), 5.25 (1H, s, H-28b), 1.64 (3H, s, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 29.0

(C-1), 26.9 (C-2), 74.5 (C-3), 74.2 (C-4), 44.9 (C-5), 37.2 (C-6), 203.8 (C-7), 155.2 (C-8), 144.5 (C-9), 40.7 (C-10), 203.2 (C-11), 58.2 (C-12), 47.9 (C-13), 50.1 (C-14), 25.9 (C-15), 28.4 (C-16), 54.5 (C-17), 12.5 (C-18), 19.9 (C-19), 36.4 (C-20), 18.9 (C-21), 34.8 (C-22), 32.1 (C-23), 150.8 (C-24), 46.9 (C-25), 177.2 (C-26), 17.6 (C-27), 110.0 (C-28), 27.7 (C-29)[3].

Camphoratin D (37): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.50 (2H, m, H-1),2.42 (1H, m, H-4), 1.53 (1H, m, H-5), 4.99 (1H, m, H-7), 1.24 (1H, s, H-18), 1.47 (3H, s, H-19), 1.57 (1H, m, H-20), 1.03 (3H, d, J = 6.4 Hz, H-21), 3.47 (1H, m, H-25),1.49 (3H, m, H-27), 5.09 (1H, s, H-28a), 5.23 (1H, s, H-28b), 1.13 (3H, d, J = 6.6 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 36.6 (C-1), 38.4 (C-2), 211.4 (C-3), 44.2 (C-4), 48.1 (C-5), 35.4 (C-6), 70.9 (C-7), 154.7 (C-8), 141.6 (C-9), 38.9 (C-10), 199.9 (C-11), 49.9 (C-12), 47.9 (C-13), 83.6 (C-14), 32.5 (C-15), 26.6 (C-16), 50.0 (C-17), 17.0 (C-18), 17.4 (C-19), 36.1 (C-20), 19.8 (C-21), 34.3 (C-22), 32.6 (C-23), 150.4 (C-24), 46.9 (C-25), 177.1 (C-26), 17.6 (C-27), 111.0 (C-28), 12.4 (C-29)[3].

Camphoratin F (38): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.38, 3.23 (2H, m, H-1), 2.37 (1H, m, H-4), 1.39 (1H, m, H-5), 4.55 (1H, t, J = 7.5 Hz, H-7), 2.50 (1H, m, H-12a), 3.01 (1H, d, J = 13.8 Hz, 12b), 0.90 (1H, s, H-18), 1.61 (3H, s, H-19), 0.89 (3H, d, J = 6.0 Hz, H-21), 3.30 (1H, q, J = 7.0 Hz, H-25), 1.37 (3H, d, J = 7.1 Hz, H-27), 1.13 (3H, d, J = 6.6 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 36.6 (C-1), 38.5 (C-2), 211.8 (C-3), 44.5 (C-4), 49.0 (C-5), 34.7 (C-6), 69.7 (C-7), 156.2 (C-8),

141.3 (C-9), 37.8 (C-10), 201.7 (C-11), 58.9 (C-12),48.3 (C-13),54.0 (C-14), 25.8 (C-15), 28.6 (C-16), 55.1 (C-17), 12.9 (C-18), 18.1 (C-19), 36.4 (C-20), 19.0 (C-21), 33.9 (C-22), 31.8 (C-23), 150.4 (C-24), 46.4 (C-25), 175.2 (C-26), 17.2 (C-27), 111.3 (C-28), 12.3 (C-29), 52.1(C-30)[3].

Camphoratin G (25*R*, *S*; 39, 40): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.32, 3.32 (2H, m, H-1), 2.43 (1H, m, H-4), 2.14 (1H, m, H-5), 4.45 (1H, d, J = 3.4 Hz, H-7), 2.47 (1H, m, H-12a), 2.98 (1H, d, J = 14.2 Hz, 12b), 0.77 (1H, s, H-18), 1.47 (3H, s, H-19), 0.89 (3H, d, J = 5.4 Hz, H-21), 3.48 (1H, q, J = 7.1 Hz, H-25), 1.52 (3H, d, J = 7.1 Hz, H-27), 1.18 (3H, d, J = 6.5 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 35.7 (C-1), 38.3 (C-2), 212.3 (C-3), 44.4 (C-4), 45.5 (C-5), 32.0 (C-6), 65.8 (C-7), 156.0 (C-8), 140.3 (C-9), 37.9 (C-10), 201.2 (C-11), 58.4 (C-12), 47.6 (C-13), 52.4 (C-14), 23.8 (C-15), 28.1 (C-16), 55.6 (C-17), 12.5 (C-18), 17.0 (C-19), 36.4 (C-20), 18.8 (C-21), 34.6 (C-22), 32.2 (C-23), 150.7 (C-24), 46.9 (C-25), 177.2 (C-26), 17.4 (C-27), 110.9 (C-28), 12.5 (C-29)[3].

Camphoratin H (41): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.38, 3.40 (2H, m, H-1), 2.36 (1H, m, H-4), 1.31 (1H, m, H-5), 2.42 (1H, m, H-12a), 2.96 (1H, d, J =14.3 Hz, 12b), 0.73 (1H, s, H-18), 1.45 (3H, s, H-19), 0.89 (3H, d, J = 5.6 Hz, H-21), 1.08 (1H, d, J = 2.7 Hz, H-26), 1.06 (3H, d, J = 2.6 Hz, H-27), 4.84 (1H, s, H-28a), 4.88 (1H, s, H-28b), 1.13 (3H, d, J = 6.6 Hz, H-29). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 35.9 (C-1), 38.5 (C-2), 212.1 (C-3), 44.8 (C-4), 51.1 (C-5), 21.5 (C-6), 30.6 (C-7), 157.4

(C-8), 139.2 (C-9), 37.3 (C-10), 199.8 (C-11), 58.5 (C-12), 47.7 (C-13), 53.4 (C-14), 24.2 (C-15), 28.1 (C-16), 55.7 (C-17), 12.4 (C-18), 18.0 (C-19), 36.5 (C-20), 18.9 (C-21), 35.1 (C-22), 31.7 (C-23), 157.4 (C-24), 34.4 (C-25), 22.4 (C-26), 22.5 (C-27), 107.1 (C-28), 12.5 (C-29)[3].

15α-acetyl-dehydrosulphurenic acid (42): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 3.46 (1H, t, J = 7.8 Hz, H-3), 5.88 (1H, d, J = 6.2 Hz, H-7), 5.37 (1H, d, J = 6.2 Hz, H-11), 1.19 (3H, s, H-18), 1.32 (3H, s, H-19), 5.52 (3H, dd, J = 5.5, 9.7 Hz, H-25), 1.02 (3H, d, J = 3.3 Hz, H-26), 1.00 (3H, d, J = 3.2 Hz, H-27),4.89 (1H, s, H-28a), 4.91 (1H, s, H-28b), 1.09 (3H, s, H-29), 1.06 (3H, s, H-30), 1.12 (3H, s, H-31), 2.19 (3H, s, OAc); . ^{13}C NMR (100 MHz, pyridine-d_5) δ: 36.6 (C-1), 29.2 (C-2), 78.3 (C-3), 39.7 (C-4), 49.9 (C-5), 23.4 (C-6), 122.6 (C-7), 141.2 (C-8), 146.9 (C-9), 38.3 (C-10), 116.0 (C-11), 32.2 (C-12), 45.1(C-13), 52.0 (C-14), 77.8 (C-15), 36.7 (C-16), 46.7 (C-17), 17.0 (C-18), 23.4 (C-19), 49.2 (C-20), 181.4 (C-21), 36.9 (C-22), 33.1 (C-23), 156.2 (C-24), 34.6 (C-25), 22.3 (C-26), 22.4 (C-27), 107.4 (C-28), 16.7 (C-29), 29.1 (C-30), 16.9 (C-31), 171.4 (C-32, $\underline{C}OCH_3$), 21.7 (C-33, $CO\underline{C}H_3$)[5].

15α-acetyl-sulphurenic acid (43): 1H NMR (400 MHz, pyridine-d5) δ: 3.46 (1H, t, J = 7.9 Hz, H-3), 1.15 (3H, s, H-18), 1.02 (3H, m, H-19), 5.44 (3H, dd, J = 5.4, 9.6 Hz, H-25), 1.02 (3H, m, H-26), 1.01 (3H, d, m, H-27),4.89 (1H, s, H-28a), 4.91 (1H, s, H-28b), 1.24 (3H, s, H-29), 1.07 (3H, s, H-30), 1.26 (3H, s, H-31), 2.17 (3H, s, OAc); . 13C NMR (100 MHz, pyridine-d_5) δ: 36.4 (C-1), 29.0 (C-2), 78.3 (C-3), 39.9 (C-4),

51.0 (C-5), 19.0 (C-6), 27.2 (C-7), 133.3 (C-8), 136.5 (C-9), 37.8 (C-10), 21.4 (C-11), 29.8 (C-12), 45.6 (C-13), 51.0 (C-14), 76.4 (C-15), 36.4 (C-16), 46.9 (C-17), 16.7 (C-18), 19.7 (C-19), 49.4 (C-20), 178.8 (C-21), 32.2 (C-22), 33.0 (C-23), 156.2 (C-24), 34.6 (C-25), 22.3 (C-26), 22.4 (C-27), 107.4 (C-28), 19.3 (C-29), 29.1 (C-30), 19.0 (C-31), 171.2 (C-32, COCH3), 21.7 (C-33, COCH3)[6].

24-methylenelanosta-7,9(11)-diene-3-one (44): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 5.58 (1H, d, J = 6.5 Hz, H-7), 5.35 (1H, d, J = 6.0 Hz, H-11), 1.00 (3H, m, H-18), 1.14 (3H, s, H-19), 1.03 (3H, m, H-26), 1.03 (3H, m, H-27), 4.90 (1H, s, H-28a), 4.95 (1H, s, H-28b), 1.07 (3H, s, H-29), 1.14 (6H, m, H-30), 1.03 (3H, m, H-31). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 37.9 (C-1), 37.2 (C-2), 215.6 (C-3), 47.9 (C-4), 50.1 (C-5), 24.3 (C-6), 121.1 (C-7), 143.3 (C-8), 145.3 (C-9), 37.9 (C-10), 118.1 (C-11), 37.9 (C-12), 44.6 (C-13), 50.8 (C-14), 27.6 (C-15), 31.9 (C-16), 48.5 (C-17), 16.6 (C-18), 22.4 (C-19), 36.4 (C-20), 18.9 (C-21), 35.3 (C-22), 31.9 (C-23), 156.3 (C-24), 34.6 (C-25), 22.3 (C-26), 22.4 (C-27), 107.4 (C-28), 22.7 (C-29), 26.0 (C-30), 26.0 (C-31)[7].

Dehydroeburiconic acid (45): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 5.58 (1H, d, J = 4.4 Hz, H-7), 5.34 (1H, d, J = 4.1 Hz, H-11), 1.00 (3H, m, H-18), 1.14 (3H, m, H-19), 1.03 (6H, m, H-26, 27), 4.91 (1H, s, H-28a), 4.95 (1H, s, H-28b), 1.14 (3H, s, H-29), 1.07 (3H, s, H-30), 1.04 (3H, m, H-31). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 37.2 (C-1), 35.3 (C-2), 215.6 (C-3), 47.9 (C-4), 51.4 (C-5), 24.3 (C-6), 121.1 (C-7), 143.3

(C-8), 145.3 (C-9), 37.9 (C-10), 118.1 (C-11), 36.4 (C-12), 44.6 (C-13), 50.8 (C-14), 31.9 (C-15), 27.6 (C-16), 48.5 (C-17), 16.6 (C-18), 22.4 (C-19), 49.5 (C-20), 178.8 (C-21), 32.1 (C-22), 33.1 (C-23), 156.2 (C-24), 34.6 (C-25), 22.4 (C-26), 22.3 (C-27), 107.5 (C-28), 26.0 (C-29), 22.7 (C-30), 26.0 (C-31)[8].

24-methylenelanost-8-ene-3*β*,15*α*,21-triol (46): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 3.49 (1H, t, J = 9.6 Hz, H-3), 4.63 (1H, dd, J = 12.7, 6.4 Hz, H-15), 1.01 (3H, m, H-18), 1.12 (3H, m, H-19), 1.04 (6H, m, H-26, 27), 4.86 (1H, s, H-28a), 4.89 (1H, s, H-28b), 1.25 (3H, s, H-29), 1.10 (3H, m, H-30), 1.38 (3H, s, H-31). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 36.6 (C-1), 29.2 (C-2), 78.5 (C-3), 39.9 (C-4), 51.3 (C-5), 19.3 (C-6), 28.2 (C-7), 135.5 (C-8), 135.5 (C-9), 37.9 (C-10), 21.7 (C-11), 32.1 (C-12), 45.7 (C-13), 52.9 (C-14), 73.0 (C-15), 40.3 (C-16), 44.4 (C-17), 17.3 (C-18), 19.8 (C-19), 44.5 (C-20), 62.3 (C-21), 29.7 (C-22), 32.2 (C-23), 157.4 (C-24), 34.5 (C-25), 22.4 (C-26), 22.5 (C-27), 107.0 (C-28), 28.6 (C-29), 16.5 (C-30), 18.6 (C-31)[9].

Eburicone (24-methylenelanost-8-en-3-one) (47): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 3.49 (1H, t, J = 9.6 Hz, H-3), 4.63 (1H, dd, J = 12.7, 6.4 Hz, H-15), 1.01 (3H, m, H-18), 1.06 (3H, m, H-19), 1.03 (6H, m, H-26, 27), 4.91 (1H, s, H-28a), 4.95 (1H, s, H-28b), 1.08 (3H, s, H-29), 1.04 (3H, m, H-30), 1.38 (3H, s, H-31). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 36.6 (C-1), 34.7 (C-2), 216.6 (C-3), 47.8 (C-4), 51.7 (C-5), 20.0 (C-6), 28.9 (C-7), 135.7 (C-8), 134.1 (C-9), 37.5 (C-10), 21.7 (C-11), 27.0 (C-12), 45.3 (C-13), 50.4 (C-14), 30.8 (C-15), 31.3 (C-16), 51.7 (C-17), 16.8 (C-18), 19.1

(C-19), 35.1 (C-20), 19.1 (C-21), 33.2 (C-22), 31.3 (C-23), 156.4 (C-24), 34.7 (C-25), 22.4 (C-26), 22.5 (C-27), 107.4 (C-28), 21.7 (C-29), 26.8 (C-30), 24.9 (C-31)[10].

Methyl antcinate B (25*R*, *S*; 48, 49): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 2.56 (1H, m, H-12a), 3.02 (1H, d, J =13.7 Hz, H-12b), 0.71 (3H, s, H-18), 1.62 (3H, s, H-19), 0.88 (3H, d, J = 5.9 Hz, H-21), 3.30 (3H, m, H-25), 1.37 (3H, d, J = 7.1 Hz, H-27), 5.02 (1H, s, H-28a), 5.09 (1H, s, H-28b), 1.04 (3H, d, J = 6.6 Hz, H-29), 3.68 (3H, s, H-30). ^{13}C NMR (100 MHz, pyridine-d_5) δ:35.4 (C-1), 38.2 (C-2), 210.3 (C-3), 44.3 (C-4), 49.3 (C-5), 39.6 (C-6), 201.2 (C-7), 145.9 (C-8), 152.4 (C-9), 39.0 (C-10), 203.0 (C-11), 57.9 (C-12), 47.6 (C-13), 49.9 (C-14), 25.7 (C-15), 28.4 (C-16), 54.3 (C-17), 12.5 (C-18), 16.7 (C-19), 36.2 (C-20), 18.9 (C-21), 34.6 (C-22), 32.0 (C-23), 149.7 (C-24), 47.6 (C-25), 175.2 (C-26), 17.1 (C-27), 111.4 (C-28), 12.0 (C-29), 52.1 (C-30)[11].

Ethyl antcinate B (25*R*/*S*, 50): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 2.49 (1H, overlapped, H-12a), 2.97 (1H, d, J = 13.8 Hz, H-12b), 0.68 (3H, s, H-18), 1.58 (3H, s, H-19), 0.85 (3H, d, J = 5.8 Hz, H-21), 3.23 (3H, m, H-25), 1.33 (3H, overlapped, H-27), 4.98 (1H, s, H-28a), 5.05 (1H, s, H-28b), 1.00 (3H, d, J = 6.5 Hz, H-29), 4.14 (2H, m, H-30), 1.14 (3H, overlapped, H-31). ^{13}C NMR (100 MHz, pyridine-d_5) δ:35.2 (C-1), 38.0 (C-2), 210.2 (C-3), 44.1 (C-4), 49.1 (C-5), 39.4 (C-6), 201.0 (C-7), 145.7 (C-8), 152.2 (C-9), 38.9 (C-10), 202.9 (C-11), 57.7 (C-12), 47.5 (C-13), 49.7 (C-14), 25.5 (C-15), 28.2 (C-16), 54.1 (C-17), 12.3 (C-18), 16.9 (C-19), 36.0 (C-20), 18.7

(C-21), 34.4 (C-22), 31.8 (C-23), 150.5 (C-24), 46.2 (C-25), 174.5 (C-26), 17.0 (C-27), 111.1 (C-28), 11.8 (C-29), 60.8 (C-30), 14.5 (C-31)[5].

Methyl antcinate G (25*R*, *S*; 51, 52): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 5.60 (1H, d, J = 3.4 Hz, H-7), 2.48 (1H, d, J = 14.4 Hz, H-12a), 2.96 (1H, d, J = 14.4 Hz, H-12b), 0.71 (3H, s, H-18), 1.43 (3H, s, H-19), 0.86 (3H, d, J = 5.7 Hz, H-21), 3.29 (1H, m, H-25), 1.36 (3H, d, J = 7.1 Hz, H-27), 5.00 (1H, s, H-28a), 5.08 (1H, s, H-28b), 1.07 (3H, d, J = 6.5 Hz, H-29), 2.21 (3H, s, H-31). ^{13}C NMR (100 MHz, pyridine-d_5) δ:35.4 (C-1), 38.1 (C-2), 211.6 (C-3), 44.1 (C-4), 46.1 (C-5), 28.6 (C-6), 69.1 (C-7), 150.7 (C-8), 143.3 (C-9), 37.8 (C-10), 200.6 (C-11), 58.2 (C-12), 48.0 (C-13), 51.5 (C-14), 23.5 (C-15), 28.0 (C-16), 55.4 (C-17), 12.4 (C-18), 16.8 (C-19), 36.2 (C-20), 18.8 (C-21), 34.5 (C-22), 31.9 (C-23), 149.7 (C-24), 46.1 (C-25), 175.2 (C-26), 17.1 (C-27), 111.5 (C-28), 12.3 (C-29), 52.1 (C-30), 170.5 (C-31, $\underline{C}OCH_3$), 21.5 (C-32, $CO\underline{C}H_3$)[2].

Methyl antcinate H (53): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 3.88 (1H, d, J = 2.7 Hz, H-3), 4.51 (1H, s, H-12), 0.83 (3H, s, H-18), 1.56 (3H, s, H-19), 1.05 (3H, d, J = 2.4 Hz, H-21), 3.28 (1H, q, J = 7.0 Hz, H-25), 1.35 (3H, d, J = 7.1 Hz, H-27), 5.01 (1H, s, H-28a), 5.07 (1H, s, H-28b), 1.07 (3H, d, J = 2.2 Hz, H-29), 3.66 (3H, s, H-30). ^{13}C NMR (100 MHz, pyridine-d_5) δ:29.0 (C-1), 30.6 (C-2), 69.7 (C-3), 35.8 (C-4), 42.0 (C-5), 39.1 (C-6), 202.4 (C-7), 144.8 (C-8), 153.6 (C-9), 39.4 (C-10), 202.4 (C-11), 81.4 (C-12), 50.7 (C-13), 43.1 (C-14), 25.0 (C-15), 27.8 (C-16), 46.4 (C-17), 12.2

(C-18), 16.8 (C-19), 36.2 (C-20), 18.5 (C-21), 34.9 (C-22), 32.2 (C-23), 150.9 (C-24),46.2 (C-25), 175.2 (C-26), 17.1 (C-27), 111.4 (C-28), 16.9 (C-29) , 52.1 (C-30)[2].

3*β*,15*α*-Dihydroxylanosta-7,9(11),24-triene-21-oic acid (54): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 3.44 (1H, t, J = 7.9 Hz, H-3), 6.50 (1H, d, J = 5.8 Hz, H-7), 5.38 (1H, d, J = 5.9 Hz, H-11), 4.78 (1H, m, H-15), 1.13 (3H, s, H-18), 1.08 (3H, s, H-19), 1.58 (3H, s, H-26), 1.63 (3H, s, H-27), 1.10 (1H, s, H-28), 1.18 (3H, s, H-29), 1.43 (3H, s, H-30). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 36.8 (C-1), 29.1 (C-2), 78.4 (C-3), 40.0 (C-4), 50.1 (C-5), 23.9 (C-6), 122.7 (C-7), 142.3 (C-8), 147.4 (C-9), 38.3 (C-10), 116.7 (C-11), 37.2 (C-12), 45.3 (C-13), 52.9 (C-14), 74.1 (C-15), 39.7 (C-16), 46.9 (C-17), 17.2 (C-18), 23.5 (C-19), 49.2 (C-20), 179.1 (C-21), 33.7 (C-22), 27.1 (C-23), 125.2 (C-24), 132.1 (C-25), 18.1 (C-26), 26.2 (C-27), 17.0 (C-28) , 29.2 (C-29), 18.7 (C-30)[12,13].

Herbarulide (55): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.44 (1H, t, J = 7.9 Hz, H-3), 6.50 (1H, d, J = 5.8 Hz, H-7), 5.38 (1H, d, J = 5.9 Hz, H-11), 4.78 (1H, m, H-15), 0.63 (3H, s, H-18), 1.23 (3H, s, H-19), 1.01 (3H, d, J = 6.5 Hz, H-21), 5.13 (1H, dd, J = 8.4, 15.3 Hz, H-22), 5.24 (1H, dd, J = 8.4, 15.3 Hz, H-23), 0.83 (3H, m, H-26), 0.81 (3H, m, H-27), 0.91 (1H, d, J = 6.8 Hz, H-28). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.1 (C-1), 33.3 (C-2), 198.5 (C-3), 114.8 (C-4), 173.9 (C-5), 162.5 (C-6), 113.4 (C-7), 159.5 (C-8), 47.4 (C-9), 40.5 (C-10), 25.5 (C-11), 39.3 (C-12), 47.1 (C-13), 58.2 (C-14),

22.7 (C-15), 27.8 (C-16), 56.5 (C-17), 12.6 (C-18), 20.1 (C-19), 40.3 (C-20), 21.2(C-21), 134.8 (C-22), 133.0 (C-23), 43.0 (C-24), 33.2 (C-25), 20.1 (C-26), 19.8 (C-27), 17.7 (C-28)[14].

Calvasterol B (56): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 0.81 (3H, s, H-18), 1.38 (3H, s, H-19), 1.13 (3H, d, J = 6.5 Hz, H-21), 5.29 (1H, dd, J = 7.9, 15.3 Hz, H-22), 5.36 (1H, dd, J = 7.9, 15.3 Hz, H-23), 0.87 (3H, d, J = 2.7 Hz, H-26), 0.89 (3H, d, J = 2.7 Hz, H-27), 0.98 (3H, d, J = 6.9 Hz, H-28). ^{13}C NMR (100 MHz, pyridine-d_5) δ:28.5 (C-1), 35.0 (C-2), 199.8 (C-3), 125.1 (C-4), 156.4 (C-5), 187.8 (C-6), 128.5 (C-7), 165.5 (C-8), 74.7 (C-9), 44.8 (C-10), 28.4 (C-11), 28.5 (C-12), 47.1 (C-13),86.1 (C-14), 31.5 (C-15), 27.6 (C-16), 50.9 (C-17), 16.6 (C-18), 23.0 (C-19), 40.7 (C-20), 21.9 (C-21), 136.5 (C-22), 132.9 (C-23), 43.5 (C-24), 33.7 (C-25), 20.5 (C-26), 20.2 (C-27), 18.2 (C-28)[15].

Dankasterone A (57): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 0.94 (3H, s, H-18), 1.19 (3H, s, H-19), 1.09 (3H, d, J = 7.0 Hz, H-21), 5.31 (1H, m, H-22), 5.32 (1H, m, H-23), 0.86 (3H, m, H-26), 0.87 (3H, m, H-27), 0.97 (3H, d, J = 6.8 Hz, H-28). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 39.6 (C-1), 35.1 (C-2), 199.3 (C-3), 126.6 (C-4), 157.5 (C-5), 200.6 (C-6), 41.4 (C-7), 63.2 (C-8), 50.1 (C-9), 36.8 (C-10), 25.5 (C-11), 38.6 (C-12), 54.8 (C-13), 215.4 (C-14), 38.5 (C-15), 24.0 (C-16), 48.9 (C-17), 17.4 (C-18), 24.1 (C-19), 37.8 (C-20), 24.0 (C-21), 133.7 (C-22), 135.2 (C-23), 43.8 (C-24), 33.7 (C-25), 20.3 (C-26), 20.6 (C-27), 18.1 (C-28)[16].

Ergosta-4, 6, 8(14), 22-tetraen-3-one (58): ^{1}H NMR (400 MHz, pyridine-d_5) δ: 5.99 (1H, s, H-4), 6.11 (3H, d, J = 9.5 Hz, H-6), 6.62 (3H, d, J = 9.4 Hz, H-7), 0.94 (3H, s, H-18), 0.95 (3H, s, H-19), 1.00 (3H, d, J = 6.9 Hz, H-21), 5.30 (2H, m, H-22, H-23), 0.90 (3H, d, J = 3.3 Hz, H-26), 0.89 (3H, d, J = 3.3 Hz, H-27), 1.09 (3H, d, J = 6.6 Hz, H-28). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 34.1 (C-1), 19.0 (C-2), 197.9 (C-3), 123.0 (C-4), 163.4 (C-5), 124.6 (C-6), 133.7 (C-7), 124.6 (C-8), 44.4 (C-9), 36.7 (C-10), 25.2 (C-11), 34.3 (C-12), 43.9 (C-13), 155.4 (C-14), 35.6 (C-15), 27.8 (C-16), 55.5 (C-17), 16.4 (C-18), 18.8 (C-19), 39.3 (C-20), 21.2 (C-21), 135.0 (C-22), 132.3 (C-23), 42.9 (C-24), 33.1 (C-25), 19.9 (C-26), 17.6 (C-27), 19.6 (C-28)[17].

Ergosterol (59): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.62 (1H, m, H-3), 5.56 (1H, m, H-6), 5.37 (1H, m, H-7), 0.61 (3H, s, H-18), 0.93 (3H, s, H-19), 1.02 (3H, d, J = 6.6 Hz, H-21), 5.18 (2H, m, H-22, 23), 0.82 (6H, m, H-26, H-27), 0.90 (1H, d, J = 6.8 Hz, H-28). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 38.5 (C-1), 32.0 (C-2), 70.5 (C-3), 40.9 (C-4), 141.5 (C-5), 119.7 (C-6), 116.4 (C-7), 139.9 (C-8), 46.3 (C-9), 37.1 (C-10), 21.2 (C-11), 28.4 (C-12), 42.9 (C-13), 54.7 (C-14), 23.1 (C-15), 28.4 (C-16), 55.8 (C-17), 12.2 (C-18), 16.4 (C-19), 40.6 (C-20), 21.2 (C-21), 135.7 (C-22), 132.1 (C-23), 42.9 (C-24), 33.2 (C-25), 20.1 (C-26), 19.8 (C-27), 17.7 (C-28)[18].

Hypocrellol A (60): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.27 (1H, dd, J = 1.8, 11.3 Hz, H-3), 5.59 (1H, d, J = 6.3 Hz, H-7), 5.38 (1H, d, J = 6.3 Hz, H-11), 0.70 (3H, s, H-18),

0.93 (3H, s, H-19), 1.02 (3H, d, *J* = 6.6 Hz, H-21), 5.18 (2H, m, H-22, 23), 1.45 (3H, s, H-26), 1.48 (3H, s, H-27), 1.24 (3H, s, H-28), 1.15 (3H, s, H-29), 1.08 (3H, s, H-30). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.7 (C-1), 29.1 (C-2), 78.4 (C-3), 39.7 (C-4), 50.1 (C-5), 23.9 (C-6), 121.7 (C-7), 143.1 (C-8), 147.1 (C-9), 38.2 (C-10), 116.5 (C-11), 38.0 (C-12), 44.3 (C-13), 50.9 (C-14), 32.2 (C-15), 26.3 (C-16), 48.7 (C-17), 17.0 (C-18), 23.4 (C-19), 40.2 (C-20), 73.4 (C-21), 31.0 (C-22), 27.3 (C-23), 85.5 (C-24), 71.7 (C-25), 26.6 (C-26), 24.5 (C-27), 29.2 (C-28), 16.7 (C-29), 24.5 (C-30)[19].

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Synthesis of antcin C, G, camphoratin G methyl and ethyl esters.

Briefly, 25*R*-antcin C was prepared as an example. Antcin C (1.00 mg) and EDCI (1.5 mg) were dissolved in 1mL MeOH or EtOH. The mixture was quaked with ultrasound for 30 min and stood for 1d. The organic layer was evaporated and yielded ester of antcin C by semipreparative HPLC purification. Ester of 25*S*-antcin C was prepared according to the same procedure. The other 25*R*-antcin G, 25*S*-antcin G, 25*R*-camphoratin G and 25*S*-camphoratin G were prepared in similar procedures.

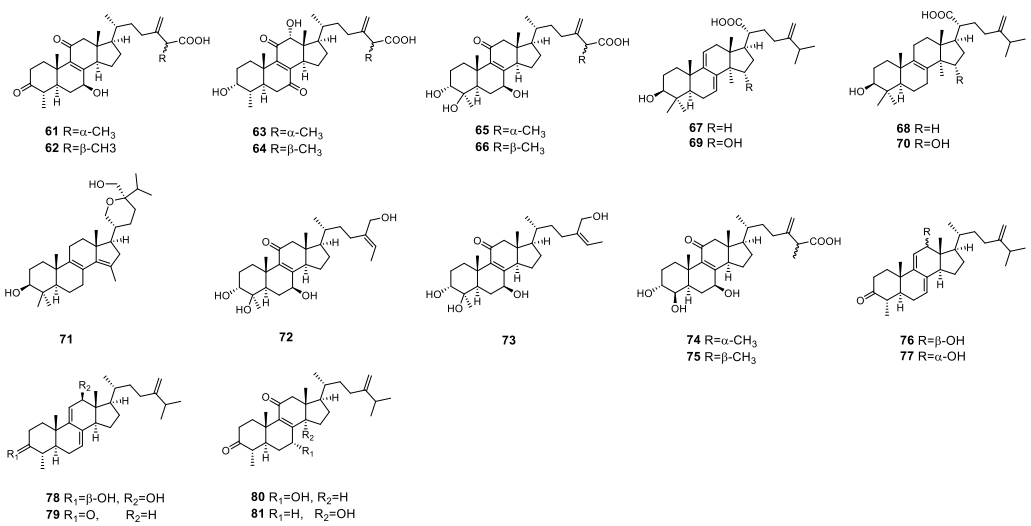


Figure S1. Structures of compounds **61**–**81**.

61/62, 25*R*/*S*-antcin C; **63/64**, 25*R*/*S*-antcin H; **65/66**, 25*R*/S-antcin K; **67**, dehydroeburicoic acid; **68**, eburicoic acid; **69**, dehydrosulphurenic acid; **70**, sulphurenic acid; **71**, antcamphorol A; **72**, antcamphorol B; **73**, antcamphorol C; **74**, antcamphorol D; **75**, antcamphorol E; **76**, antcamphorol F; **77**, antcamphorol G; **78**, antcamphorol H; **79**, antcamphorol I; **80**, antcamphorol J; **81**, antcamphorol K.

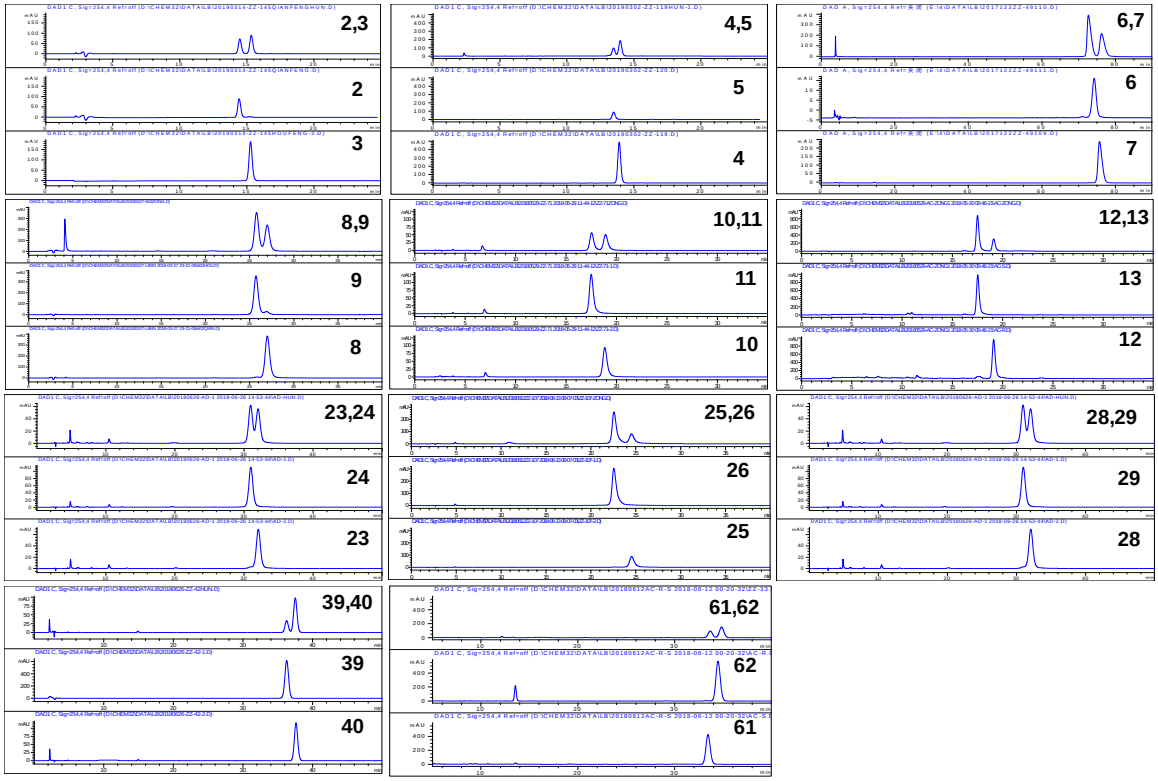


Figure S2. The epimeric pairs of ergostanoids (25*R* or *S*) were obtained as pure compounds by a YMC Pack ODS-A column (**2–9, 12, 39, 40, 13, 61, 62**) or a YMC Carotenoid column (**10, 11, 23–26, 28, 29**).

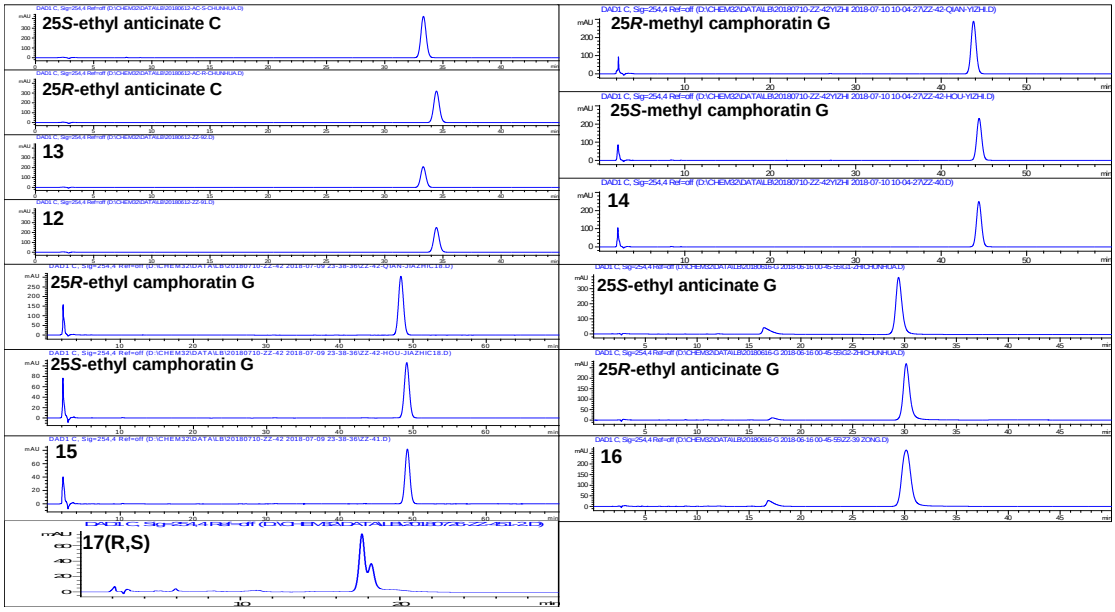


Figure S3. The absolute configurations of C-25 for **12–17** were determined by HPLC.

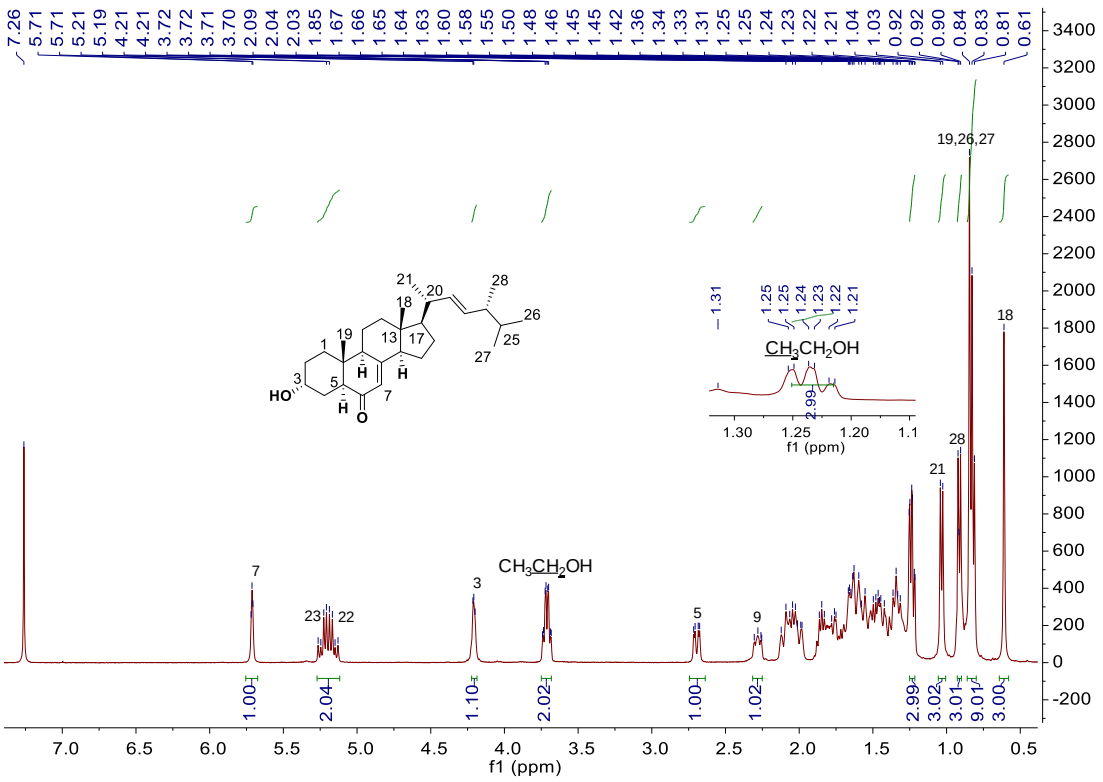


Figure S4. ^{1}H-NMR spectrum of **1** in $CDCl_3$ (400 MHz)

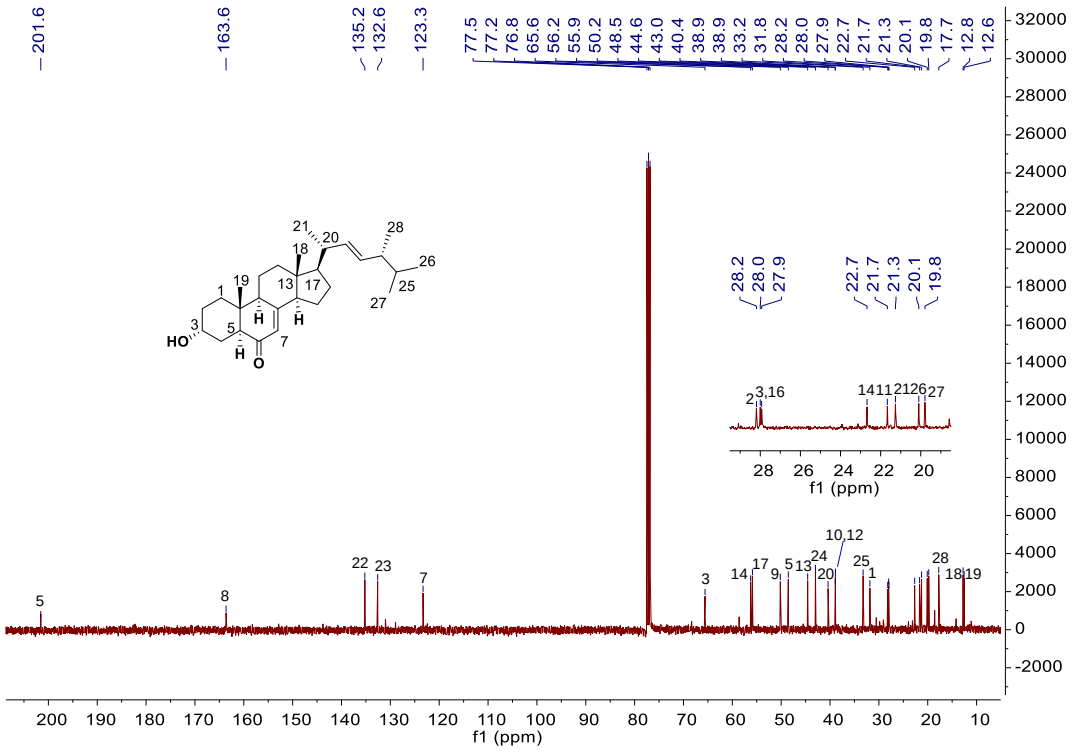


Figure S5. ^{13}C-NMR spectrum of **1** in $CDCl_3$ (100 MHz).

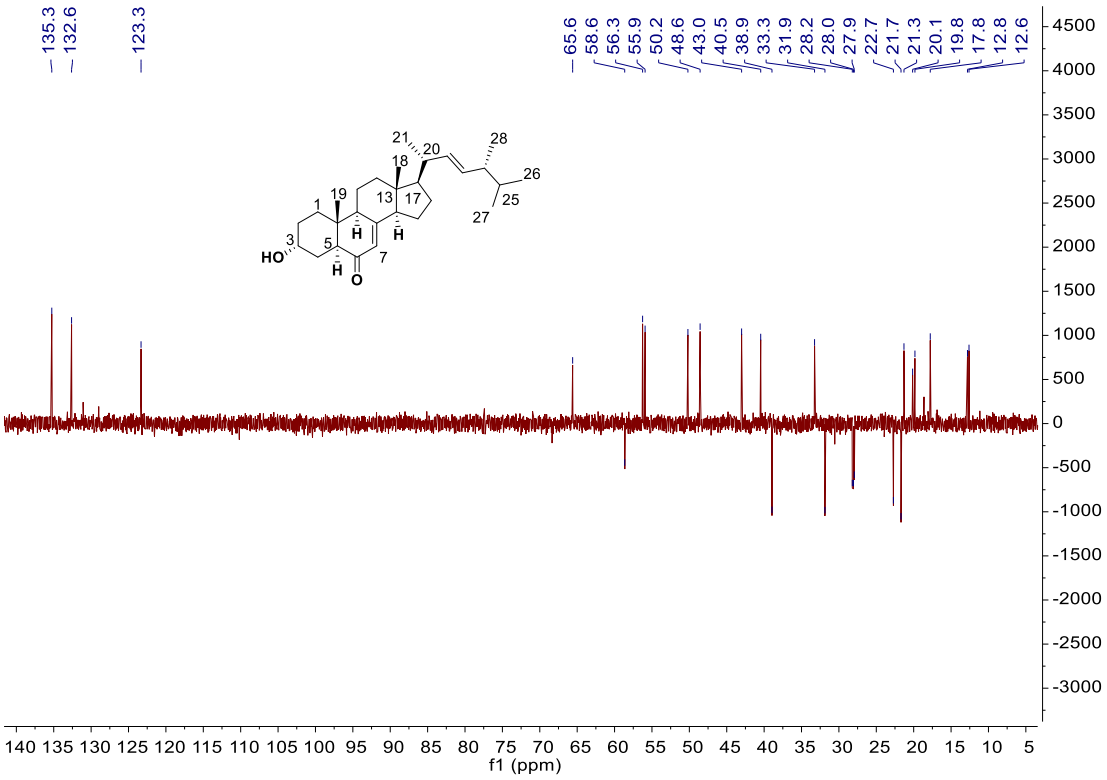


Figure S6. DEPT 135 spectrum of **1** in $CDCl_3$ (100 MHz).

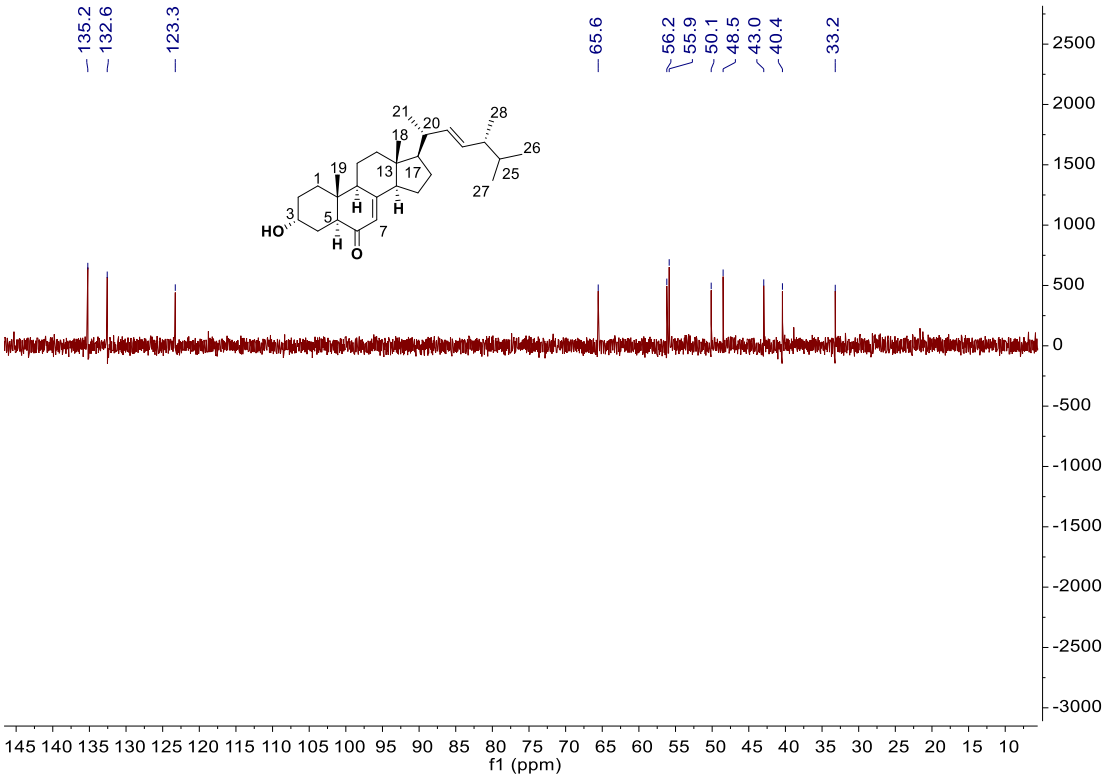


Figure S7. DEPT 90 spectrum of **1** in $CDCl_3$ (100 MHz).

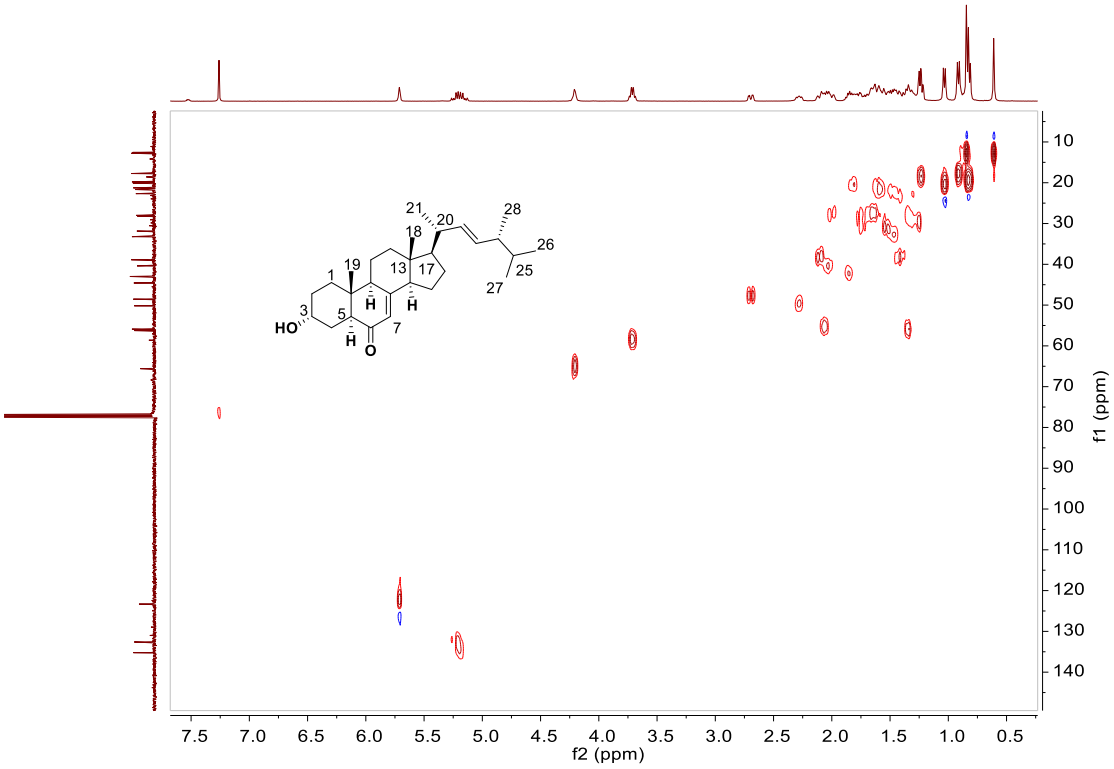


Figure S8. HSQC spectrum of **1** in $CDCl_3$ (400 MHz).

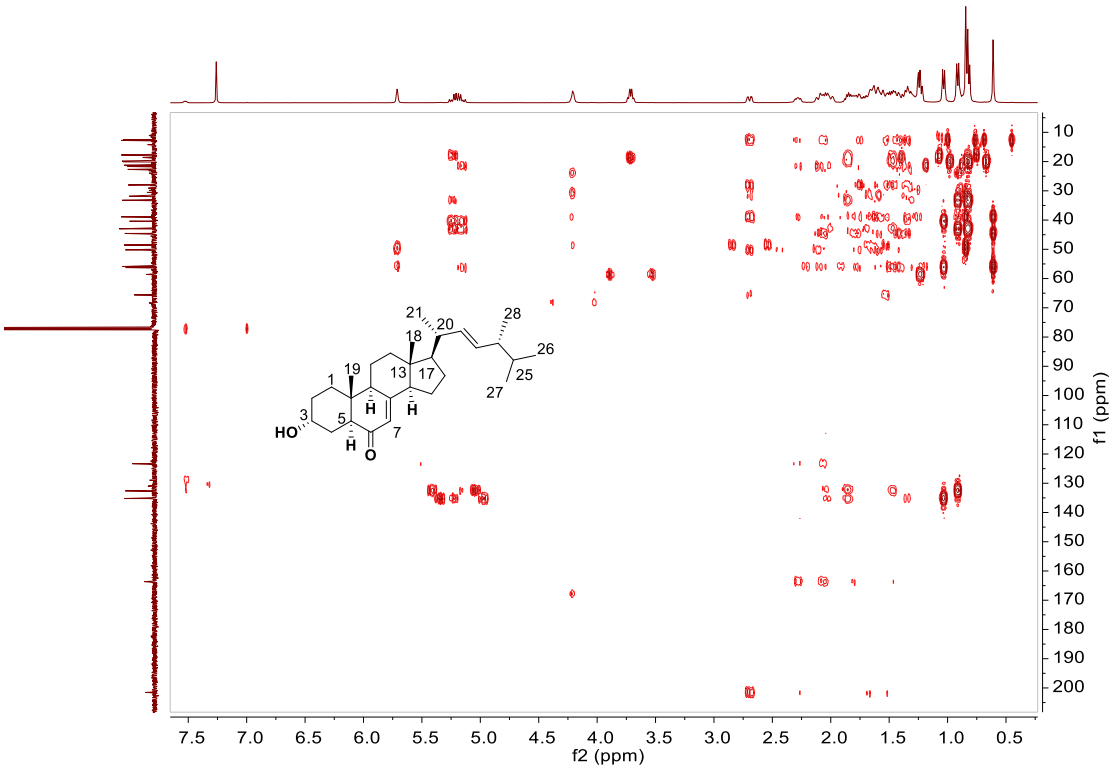


Figure S9. HMBC spectrum of **1** in $CDCl_3$ (400 MHz).

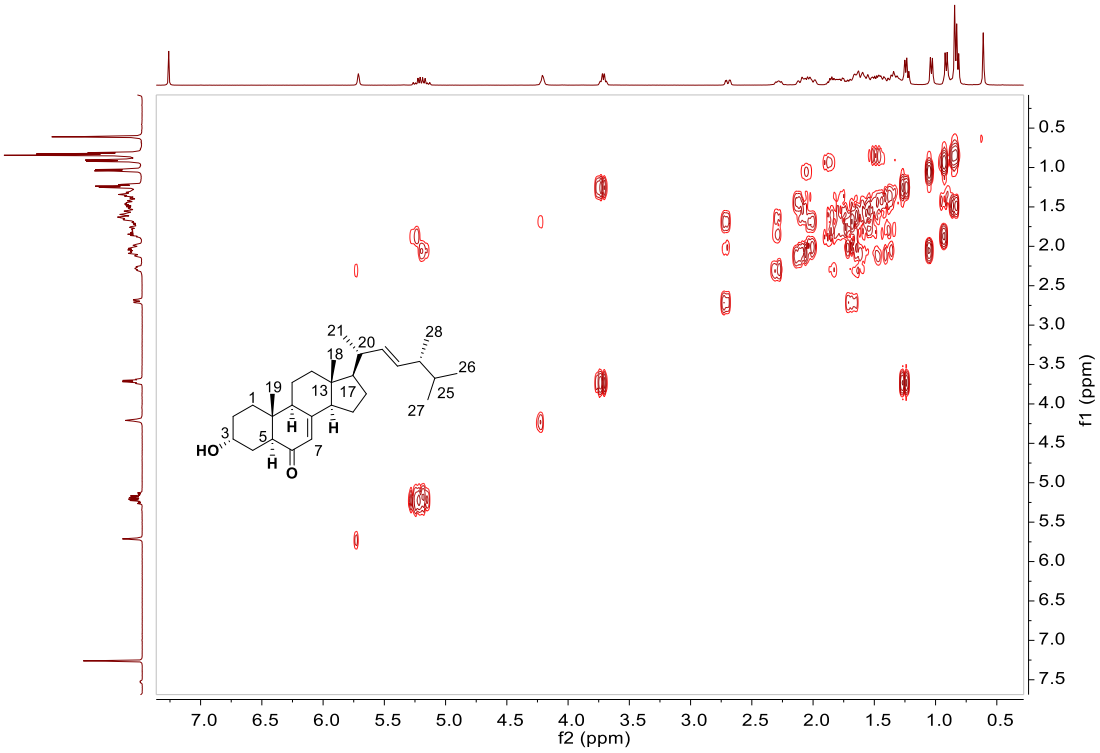


Figure S10. ^{1}H-^{1}H COSY spectrum of **1** in $CDCl_3$ (400 MHz).

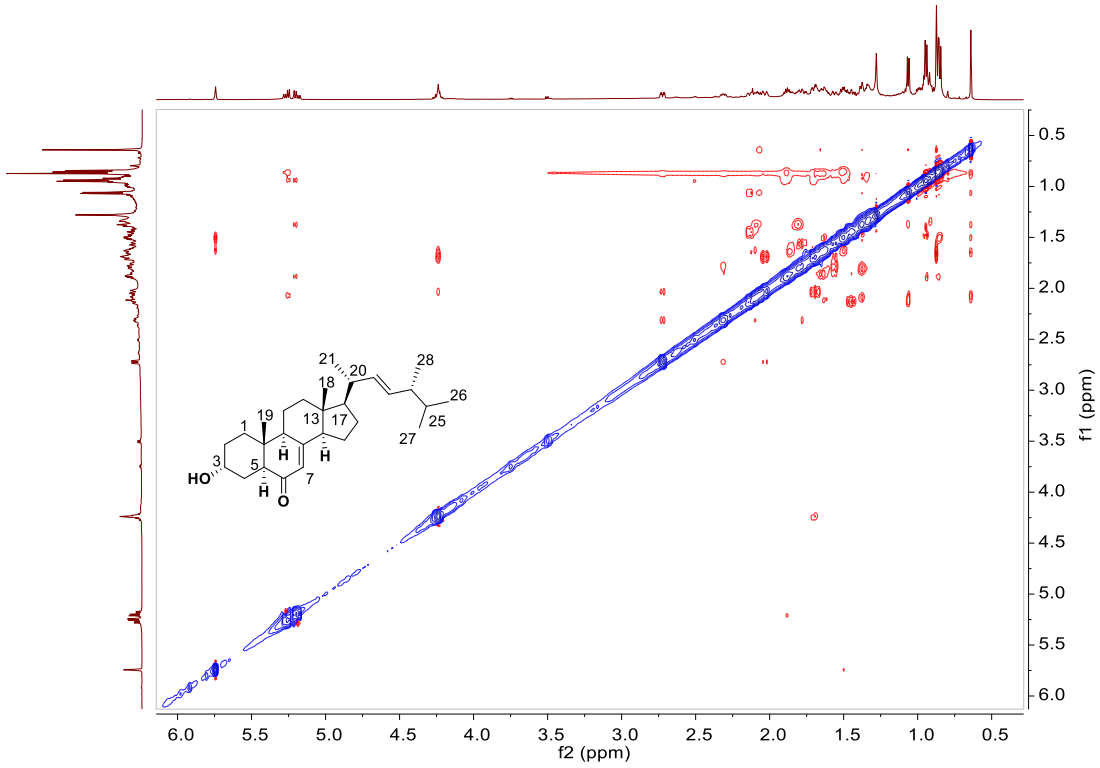


Figure S11. NOESY spectrum of **1** in $CDCl_3$ (400 MHz).

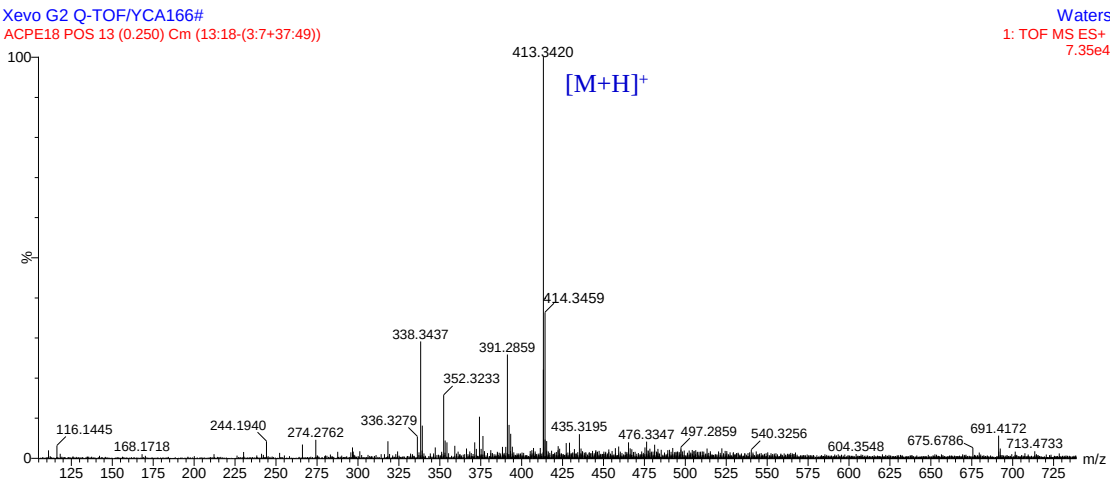


Figure S12. HR-ESI-MS spectrum of **1**.

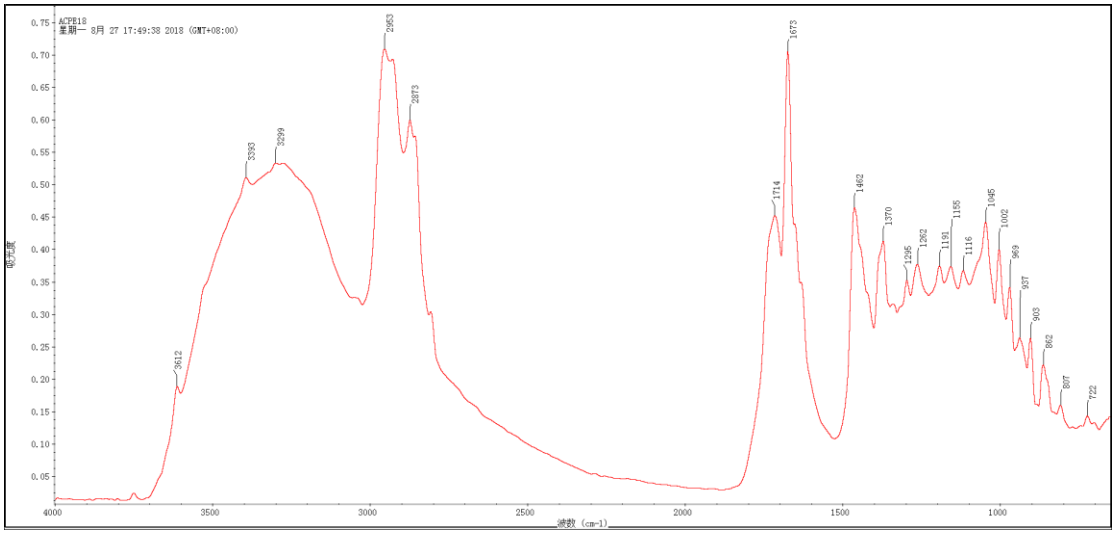


Figure S13. IR spectrum of **1**.

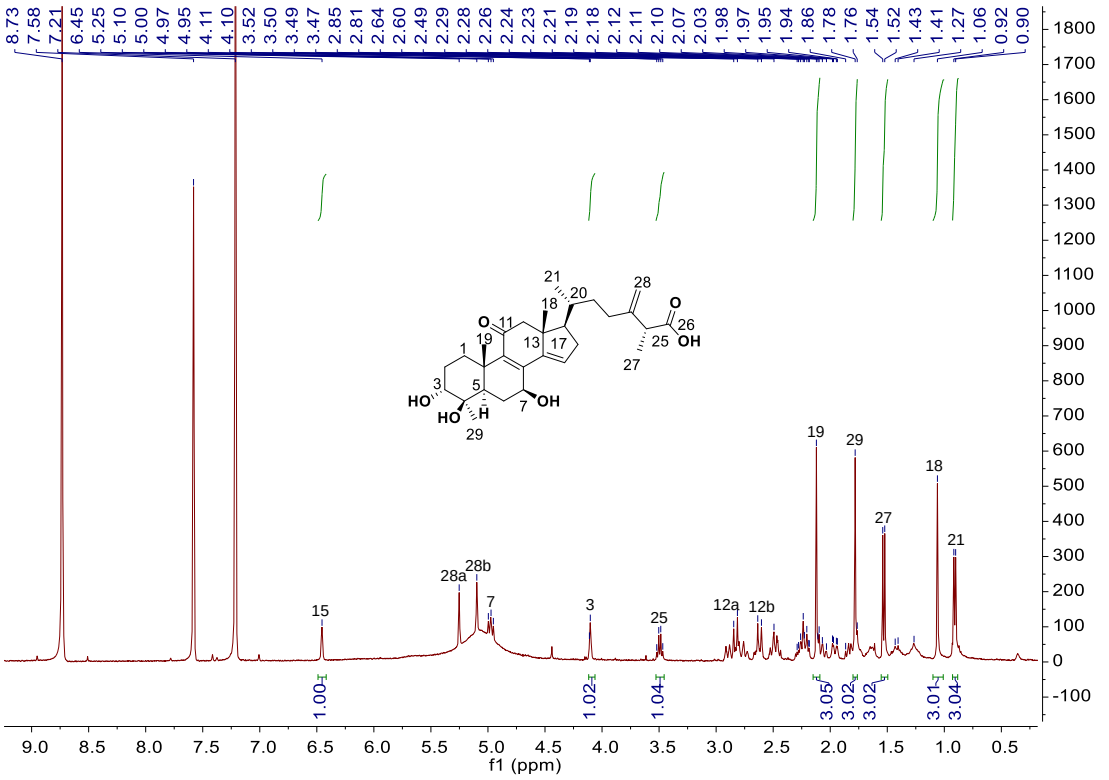


Figure S14. ^{1}H-NMR spectrum of **2** in pyridine-d_5 (400 MHz).

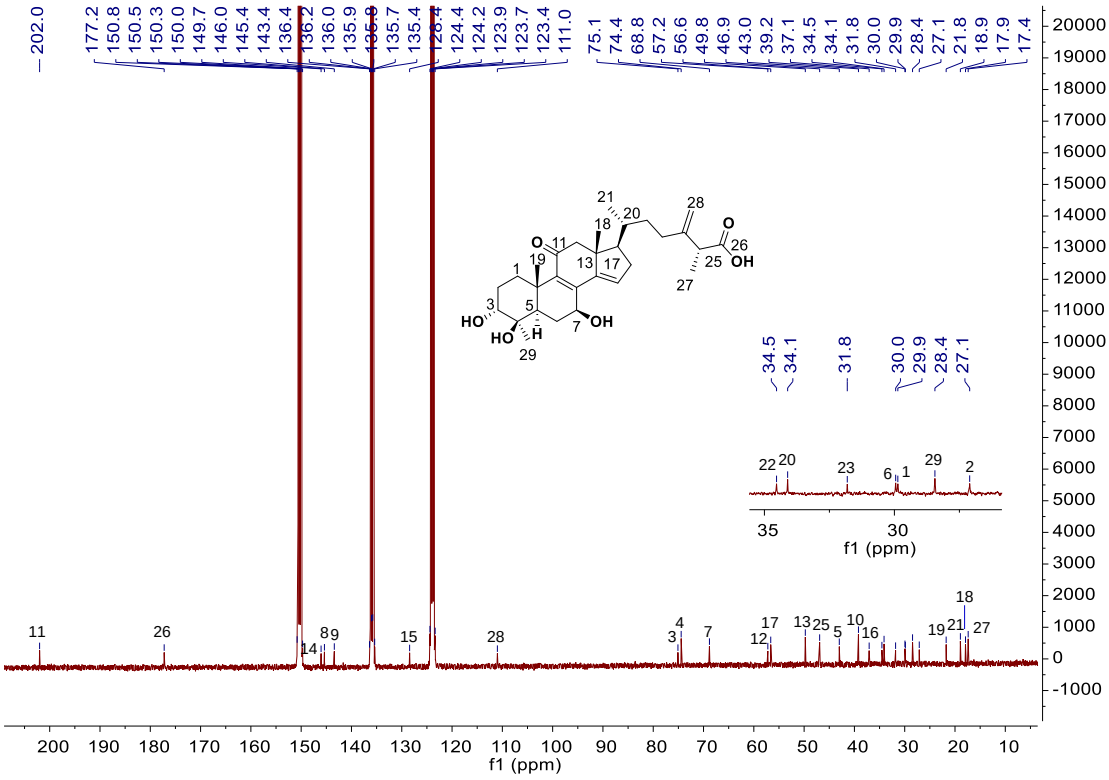


Figure S15. ^{13}C-NMR spectrum of **2** in pyridine-d_5 (100 MHz).

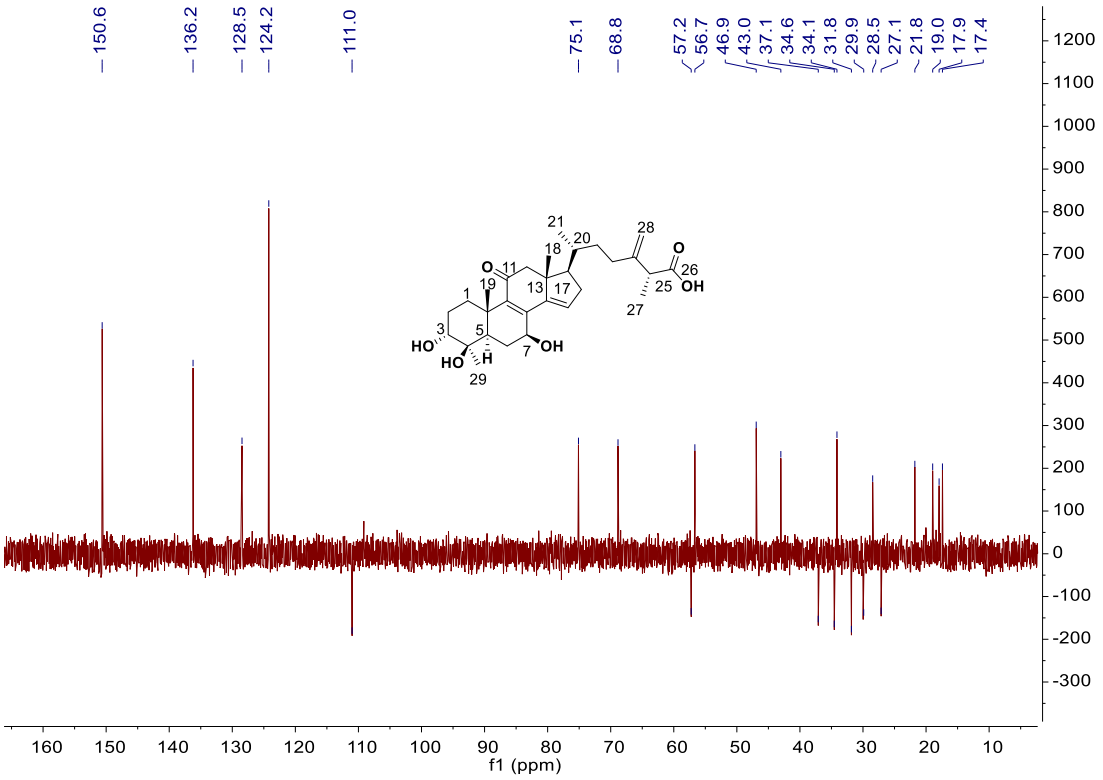


Figure S16. DEPT 135 spectrum of **2** in pyridine-d_5 (100 MHz).

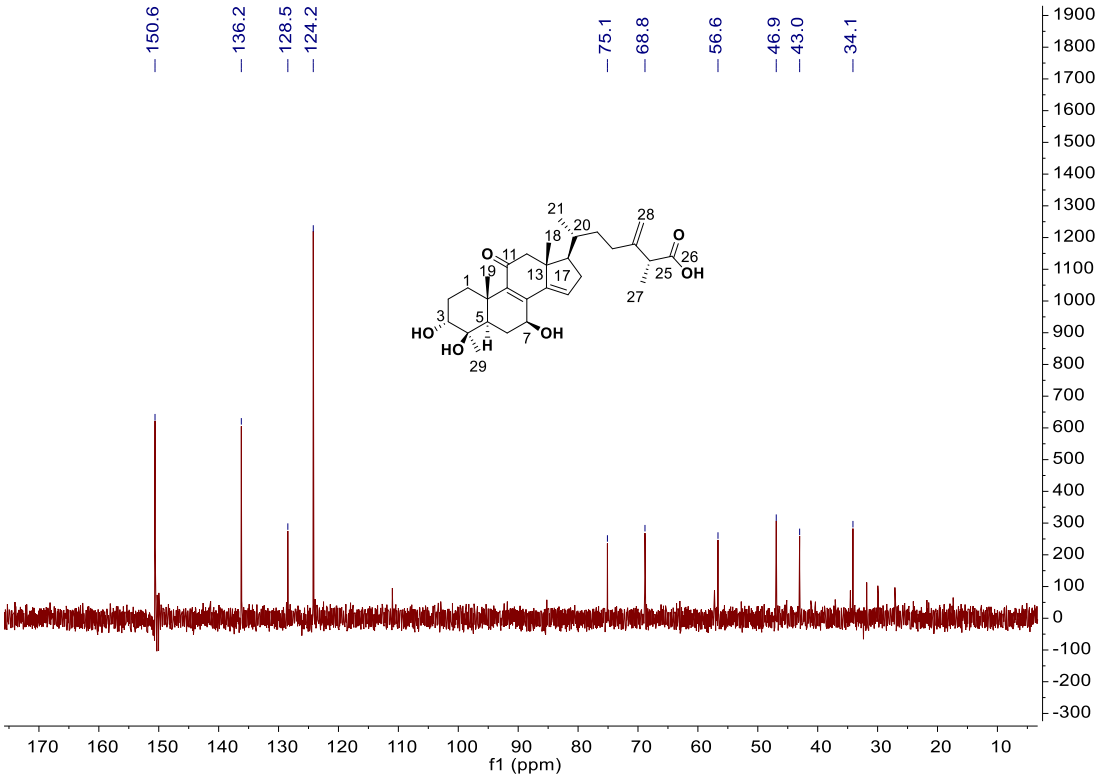


Figure S17. DEPT 90 spectrum of **2** in pyridine-d_5 (100 MHz).

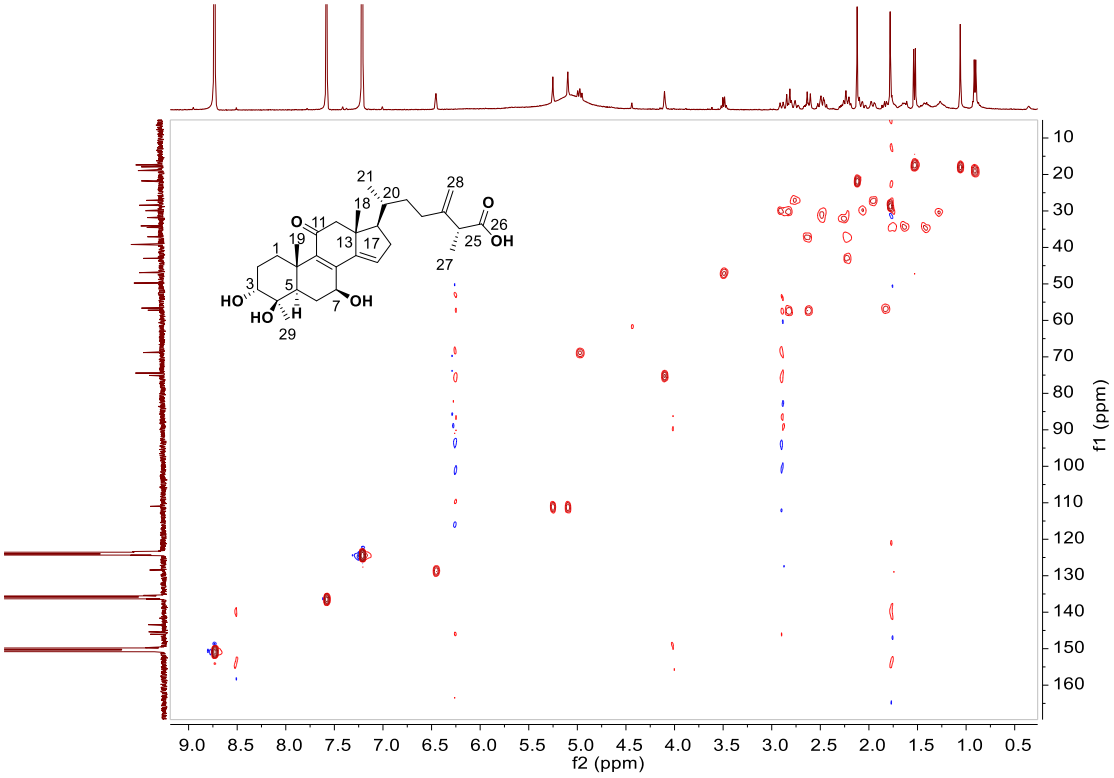


Figure S18. HSQC spectrum of **2** in pyridine-d_5 (400 MHz).

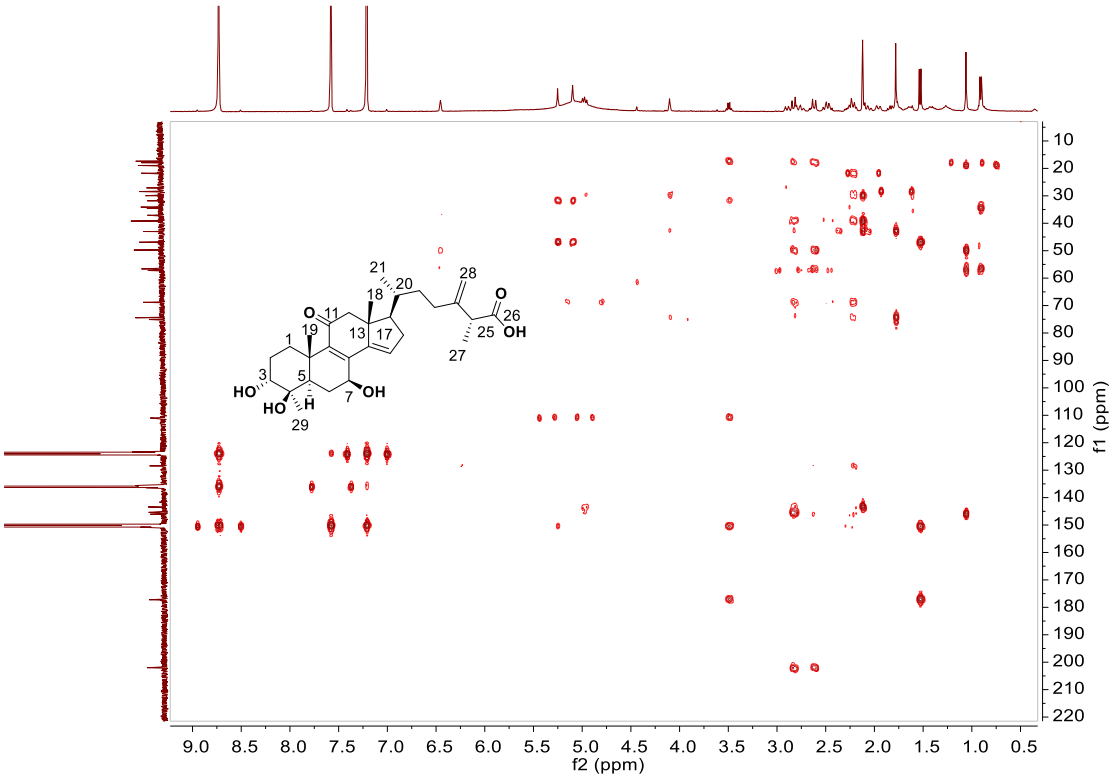


Figure S19. HMBC spectrum of **2** in pyridine-d_5 (400 MHz).

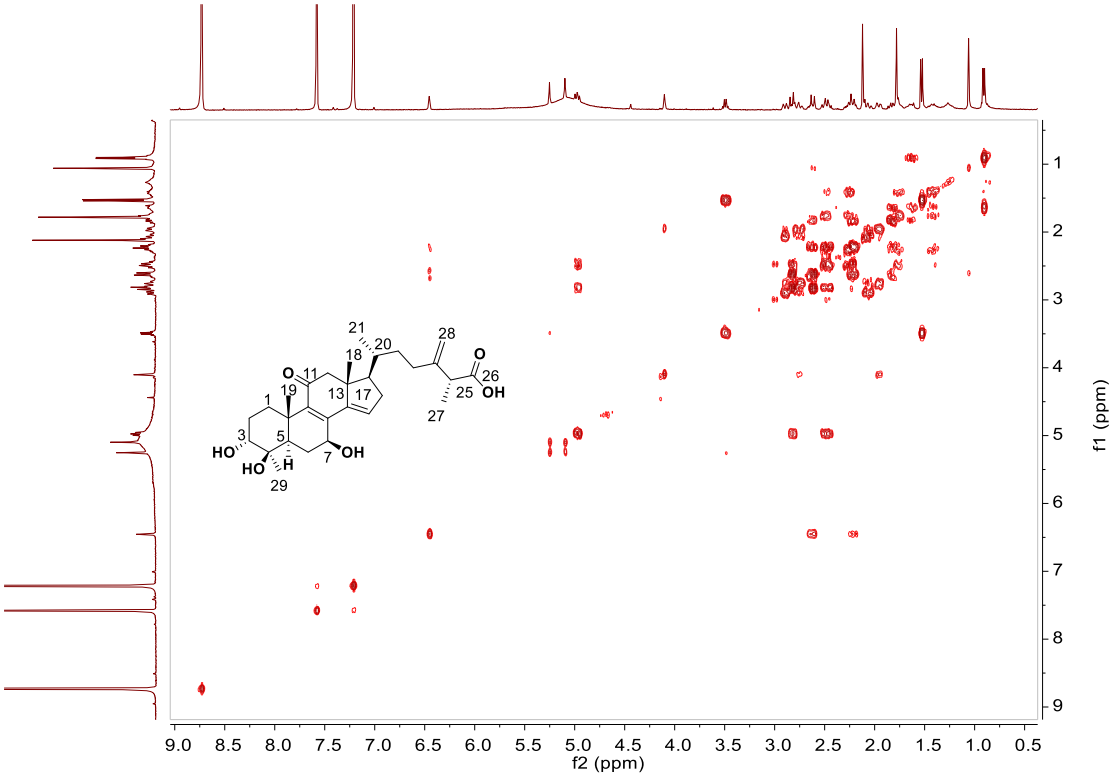


Figure S20. ^{1}H-^{1}H COSY spectrum of **2** in pyridine-d_5 (400 MHz).

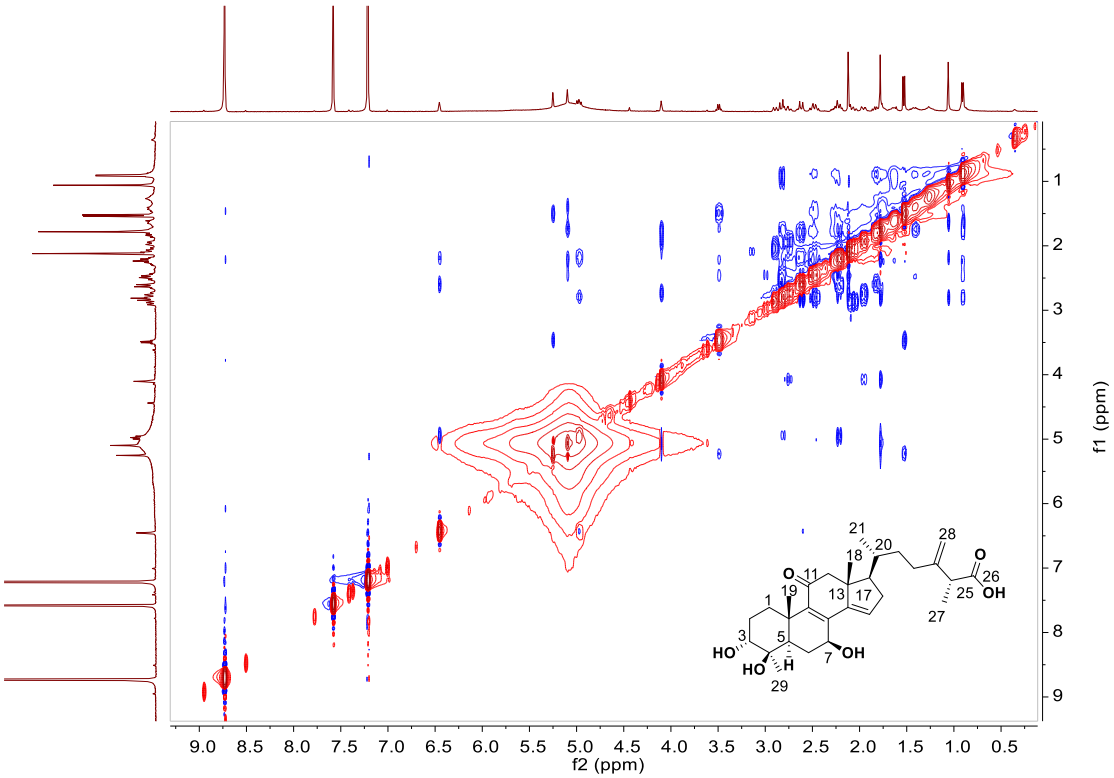


Figure S21. NOESY spectrum of **2** in pyridine-d_5 (400 MHz).

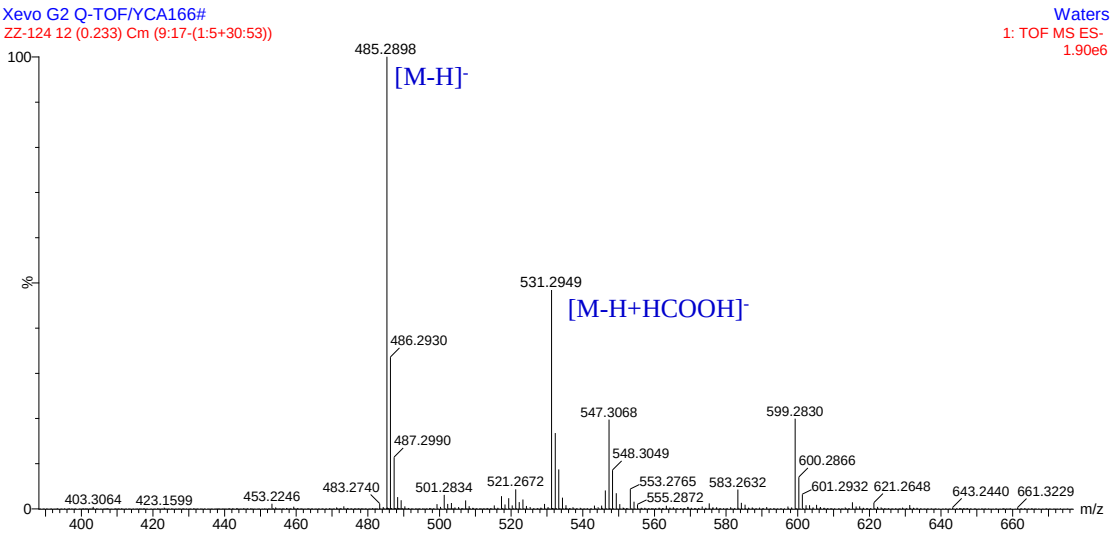


Figure S22. HR-ESI-MS spectrum of **2.**

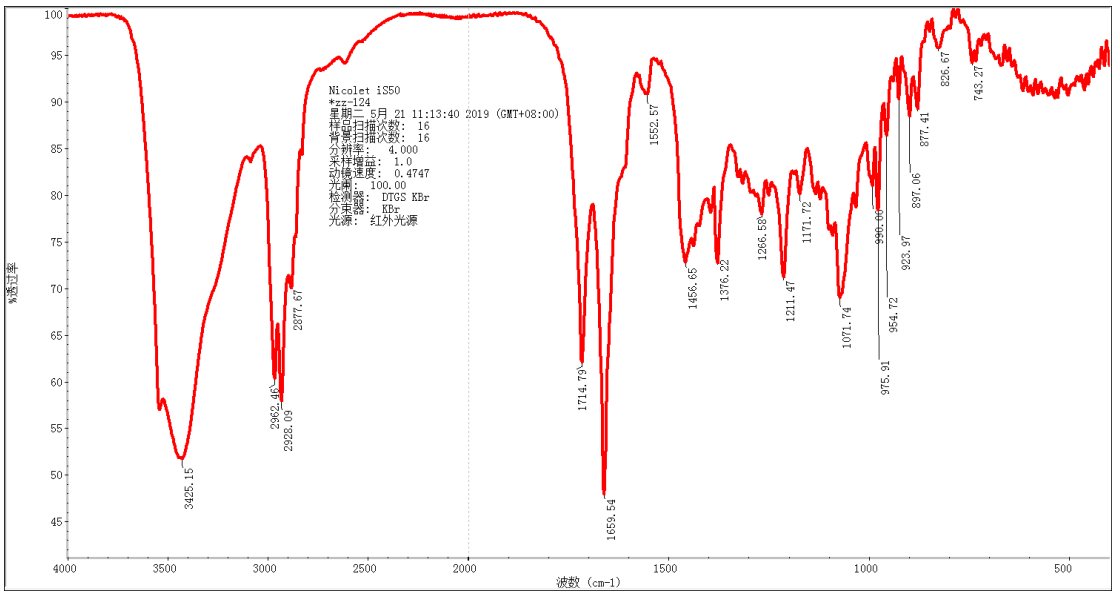


Figure S23. IR spectrum of **2.**

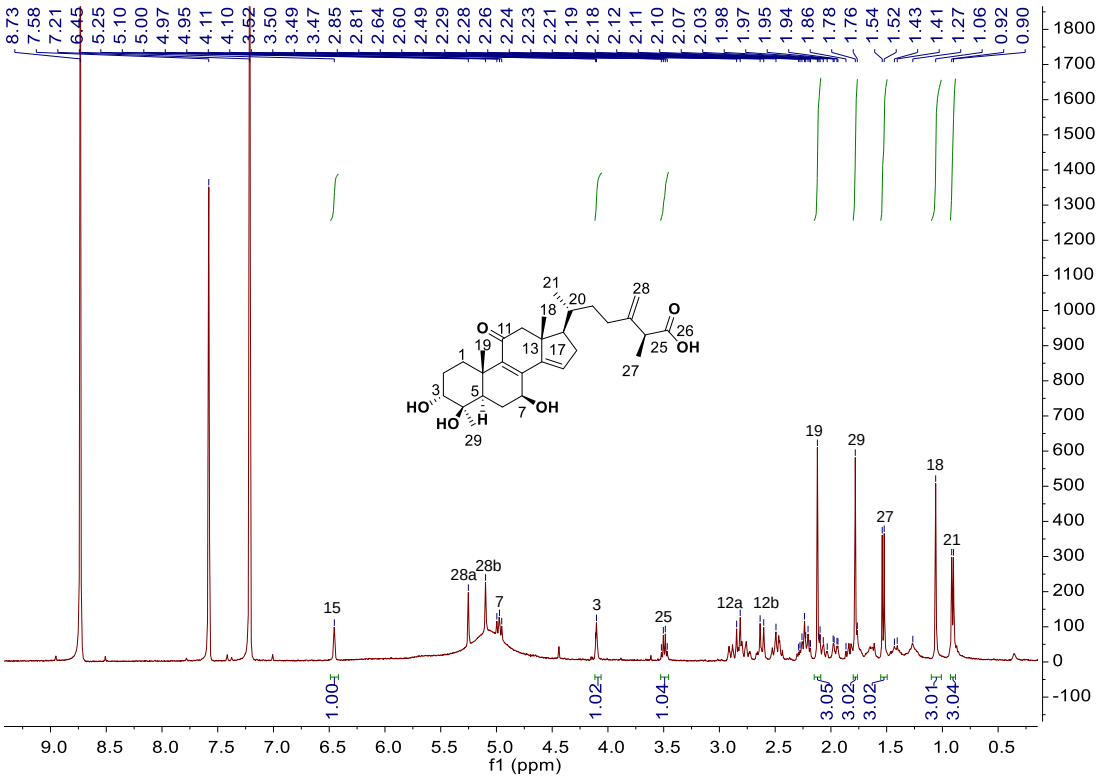


Figure S24. ^{1}H-NMR spectrum of **3** in pyridine-d_5 (400 MHz).

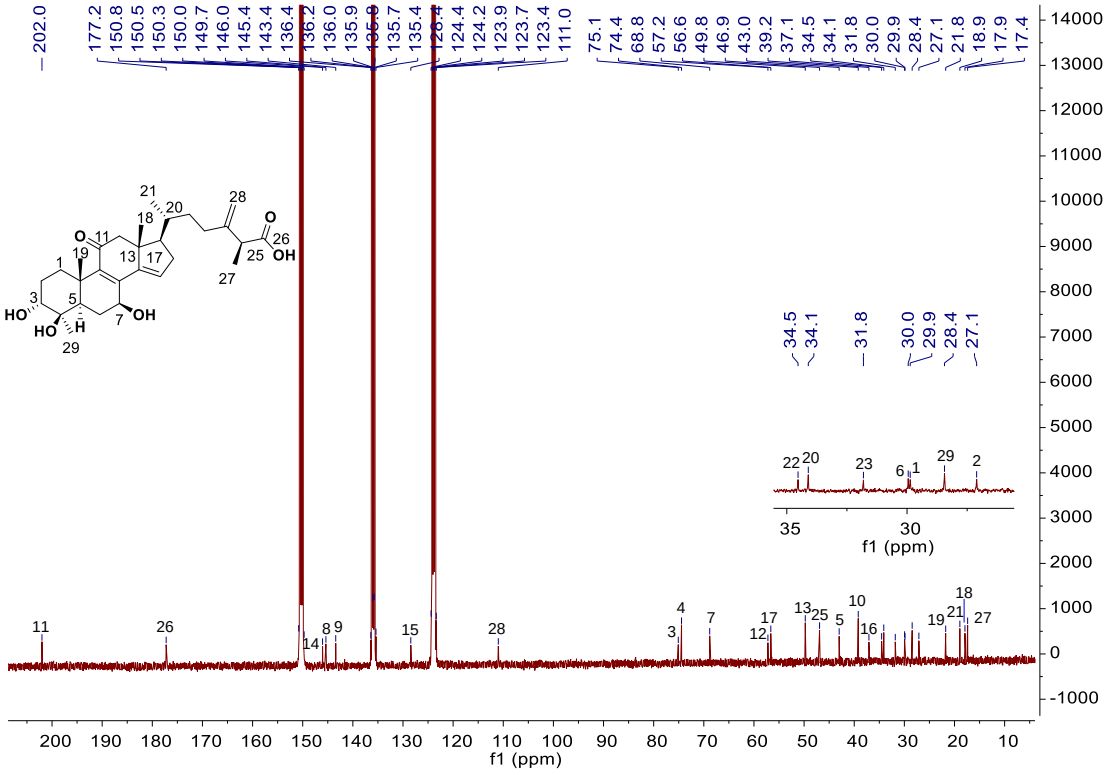


Figure S25. ^{13}C-NMR spectrum of **3** in pyridine-d_5 (100 MHz).

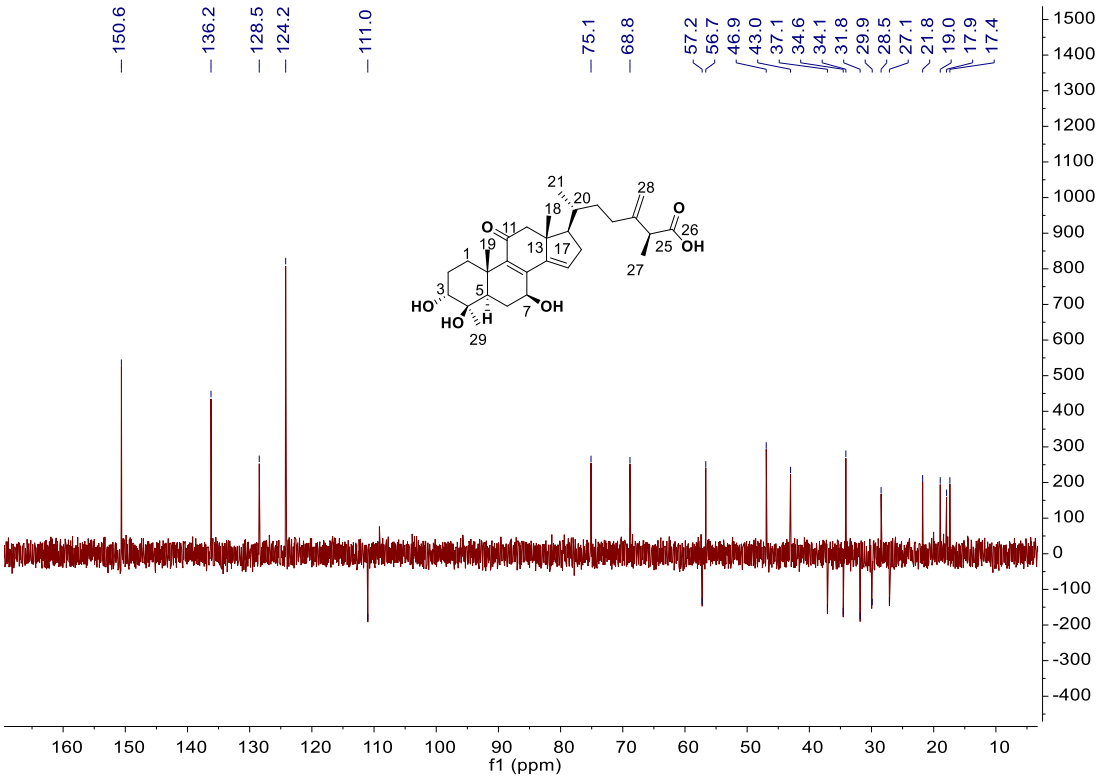


Figure S26. DEPT 135 spectrum of **3** in pyridine-d_5 (100 MHz).

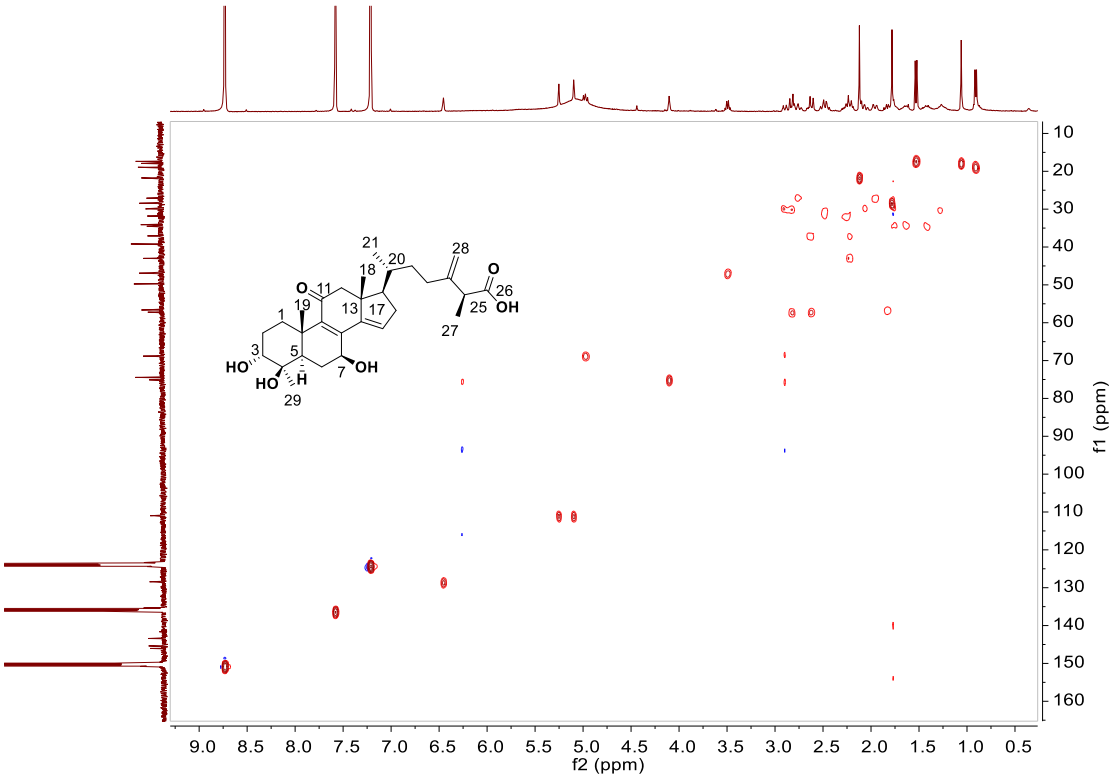


Figure S27. HSQC spectrum of **3** in pyridine-d_5 (400 MHz).

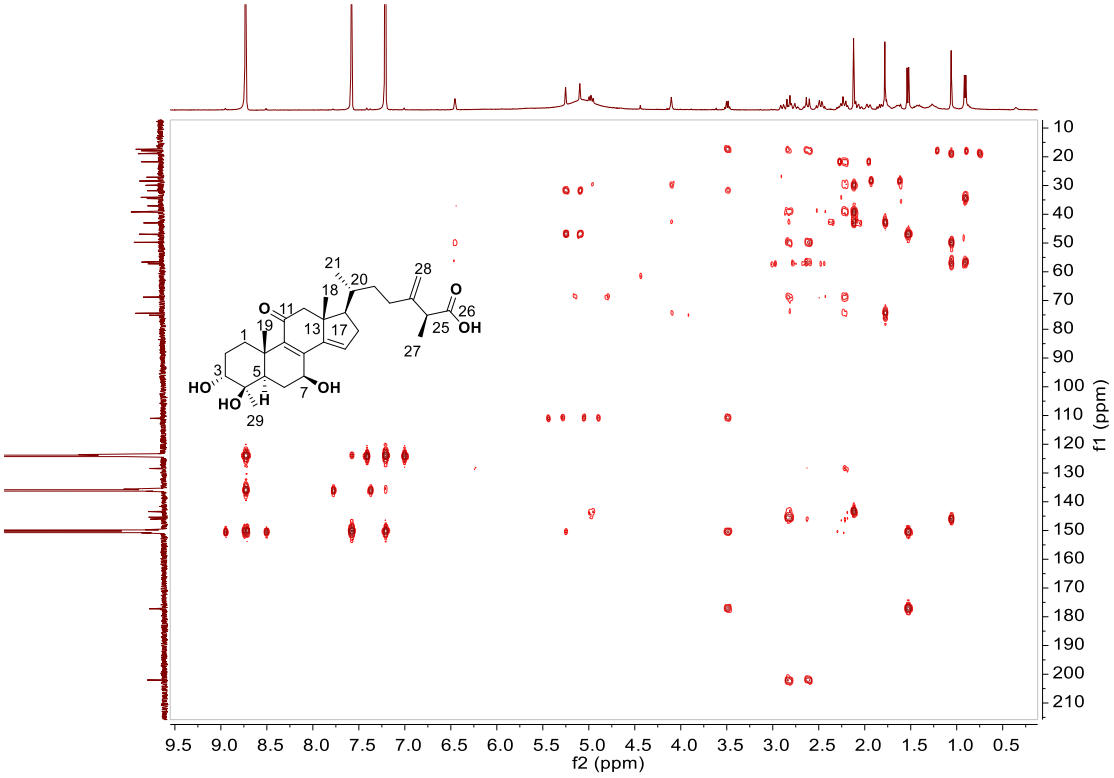


Figure S28. HMBC spectrum of **3** in pyridine-d_5 (400 MHz).

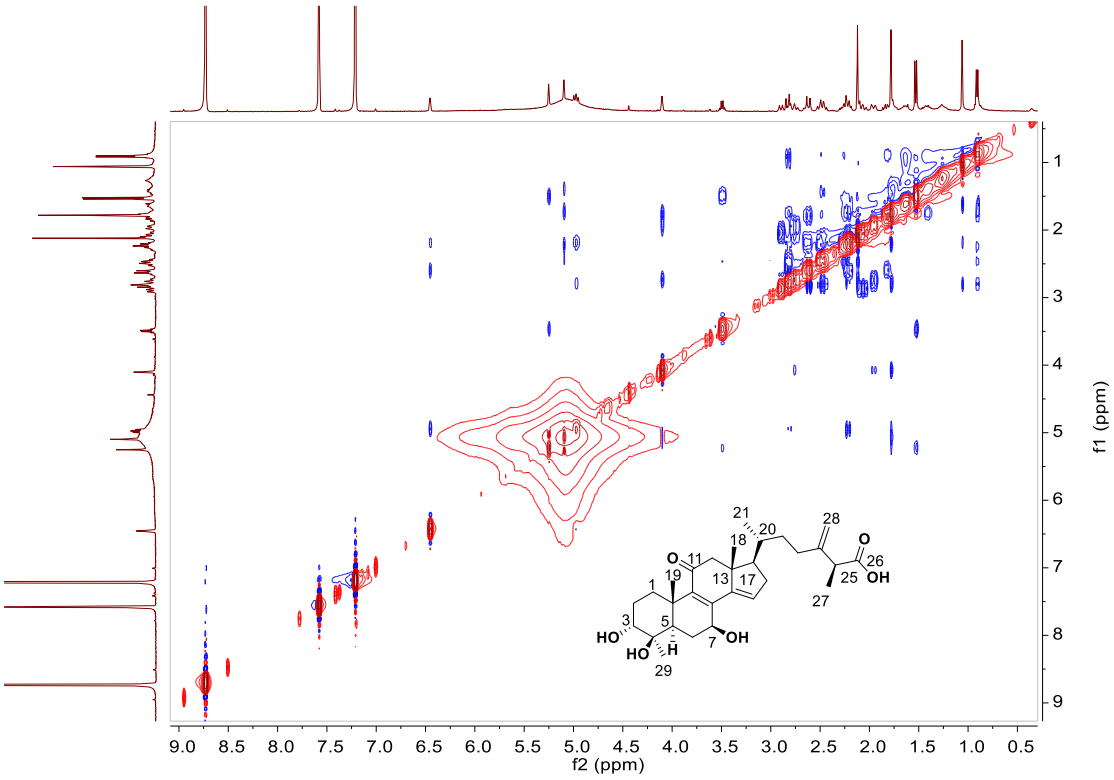


Figure S29. NOESY spectrum of **3** in pyridine-d_5 (400 MHz).

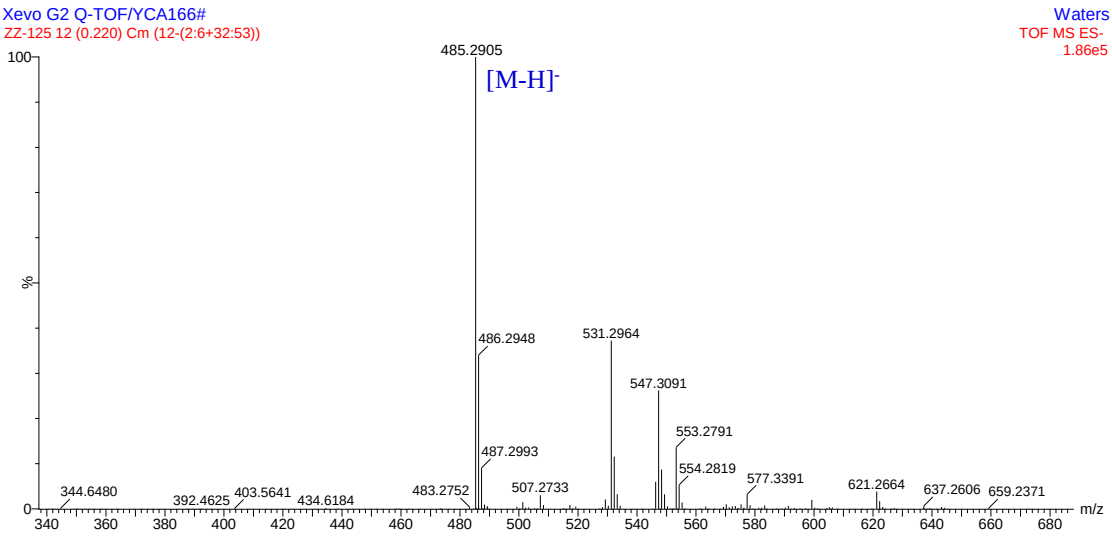


Figure S30. HR-ESI-MS spectrum of **3.**

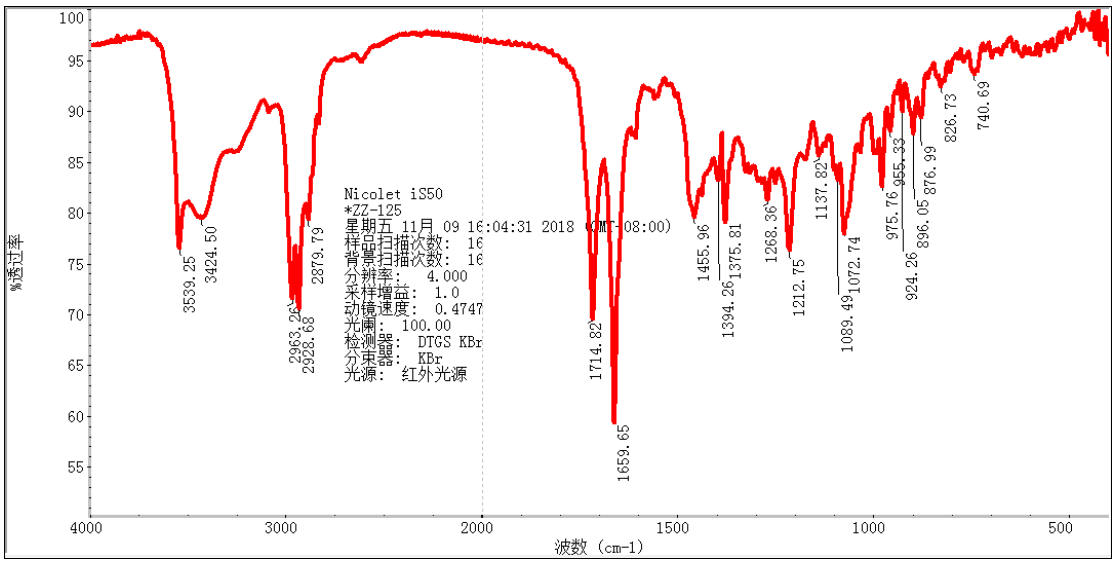


Figure S31. IR spectrum of **3**.

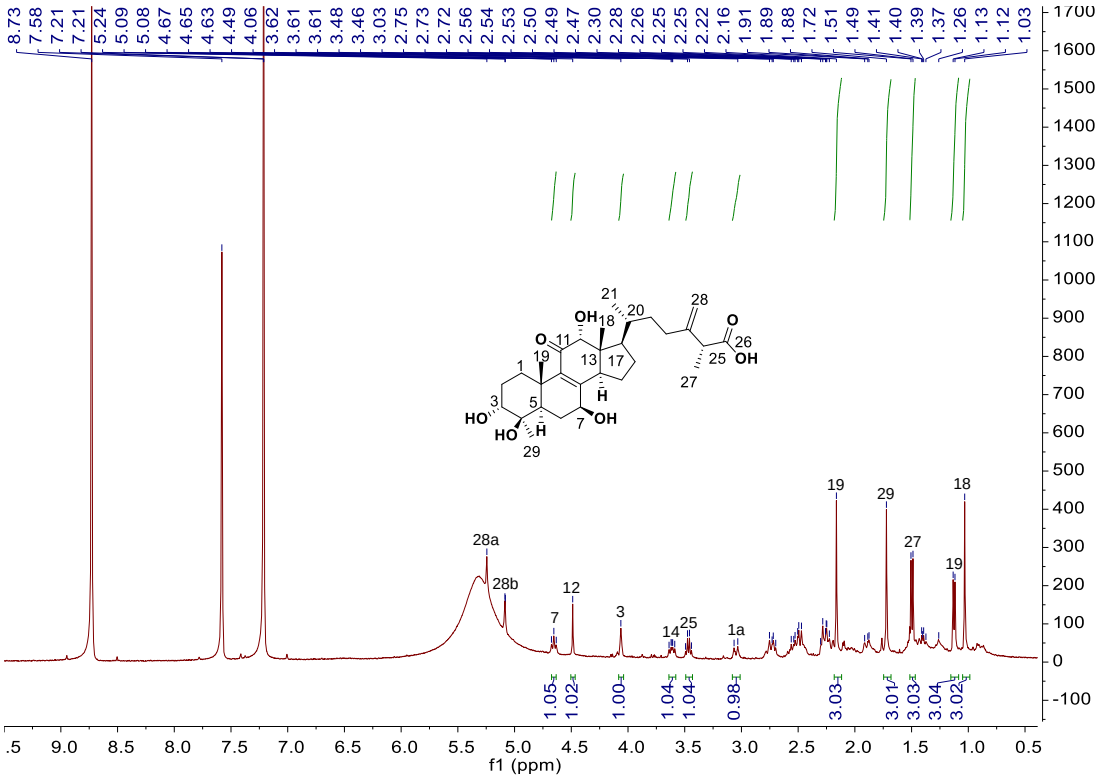


Figure S32. ^{1}H-NMR spectrum of **4** in pyridine-d_5 (400 MHz).

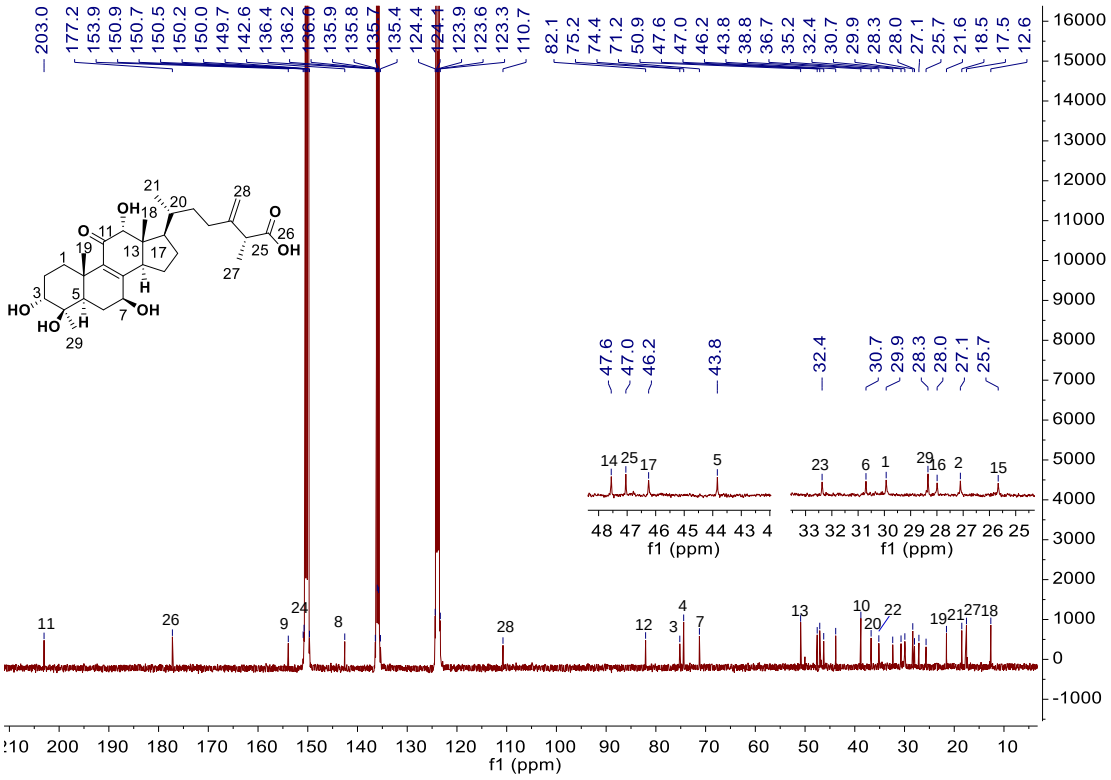


Figure S33. ^{13}C-NMR spectrum of **4** in pyridine-d_5 (100 MHz).

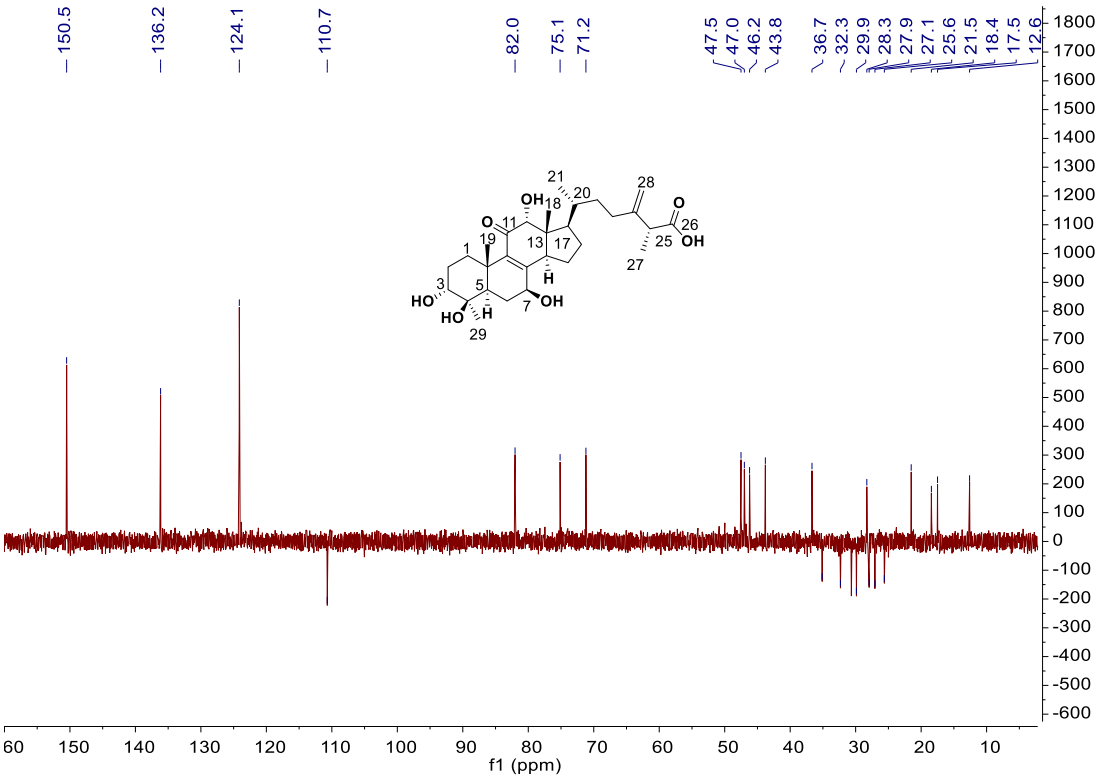


Figure S34. DEPT 135 spectrum of **4** in pyridine-d_5 (100 MHz).

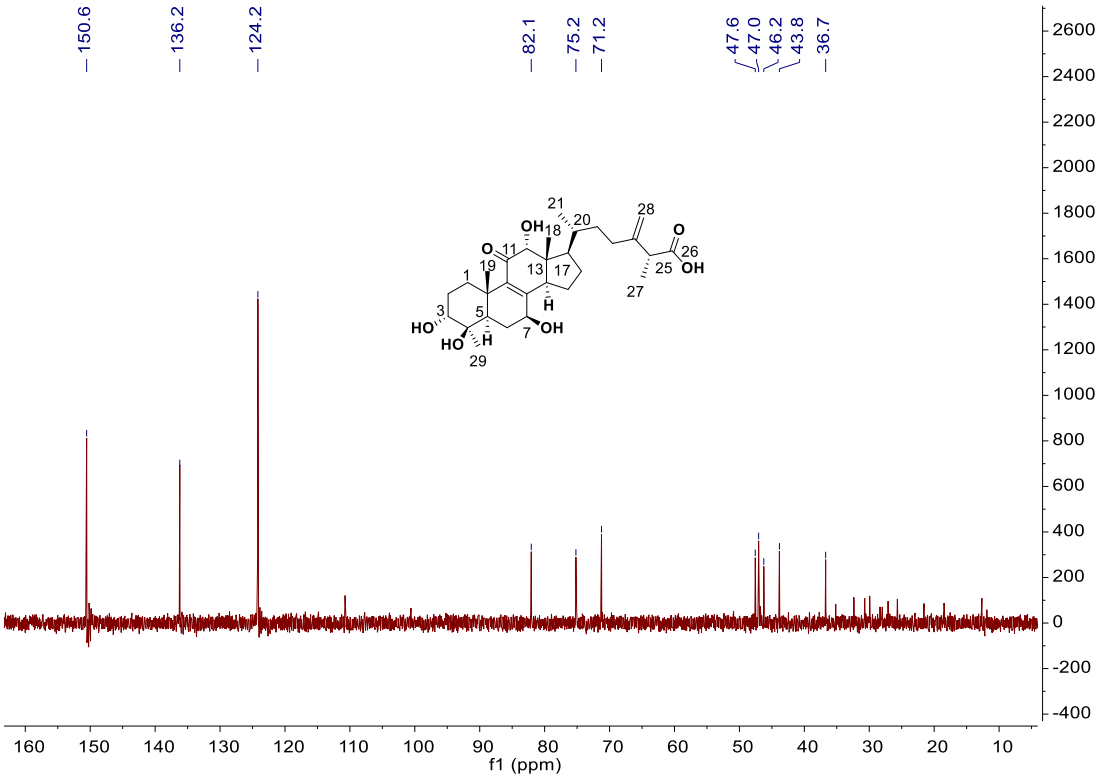


Figure S35. DEPT 90 spectrum of **4** in pyridine-d_5 (100 MHz).

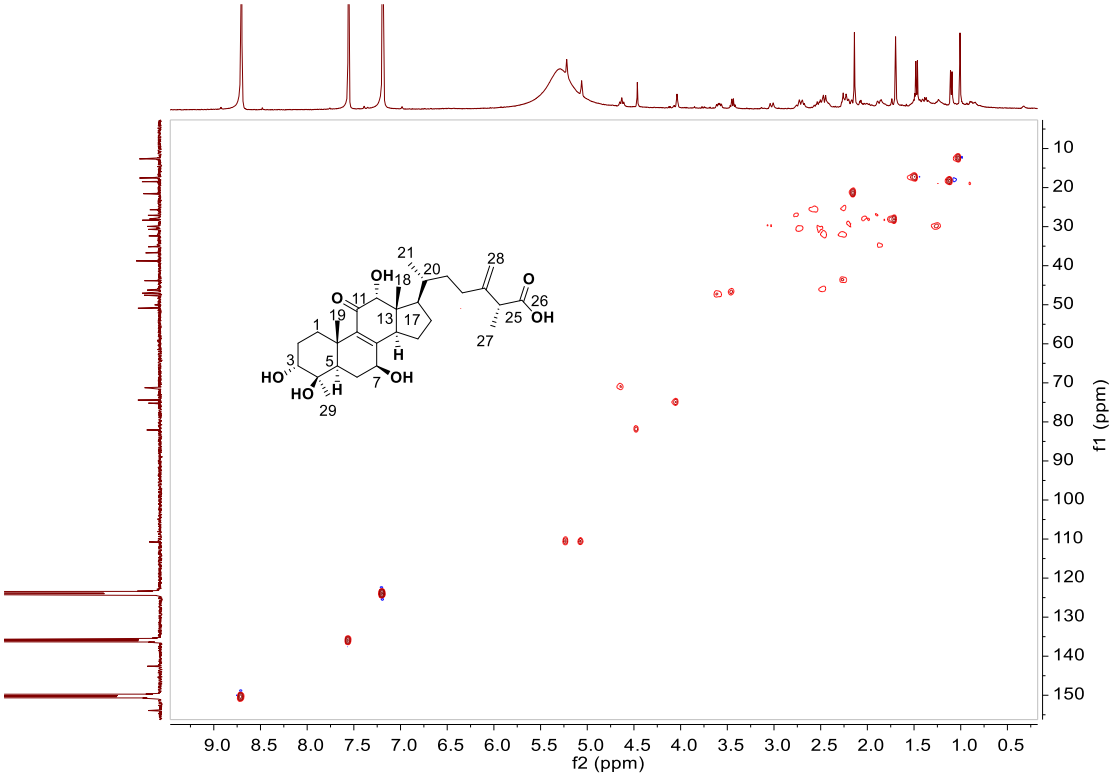


Figure S36. HSQC spectrum of **4** in pyridine-d_5 (400 MHz).

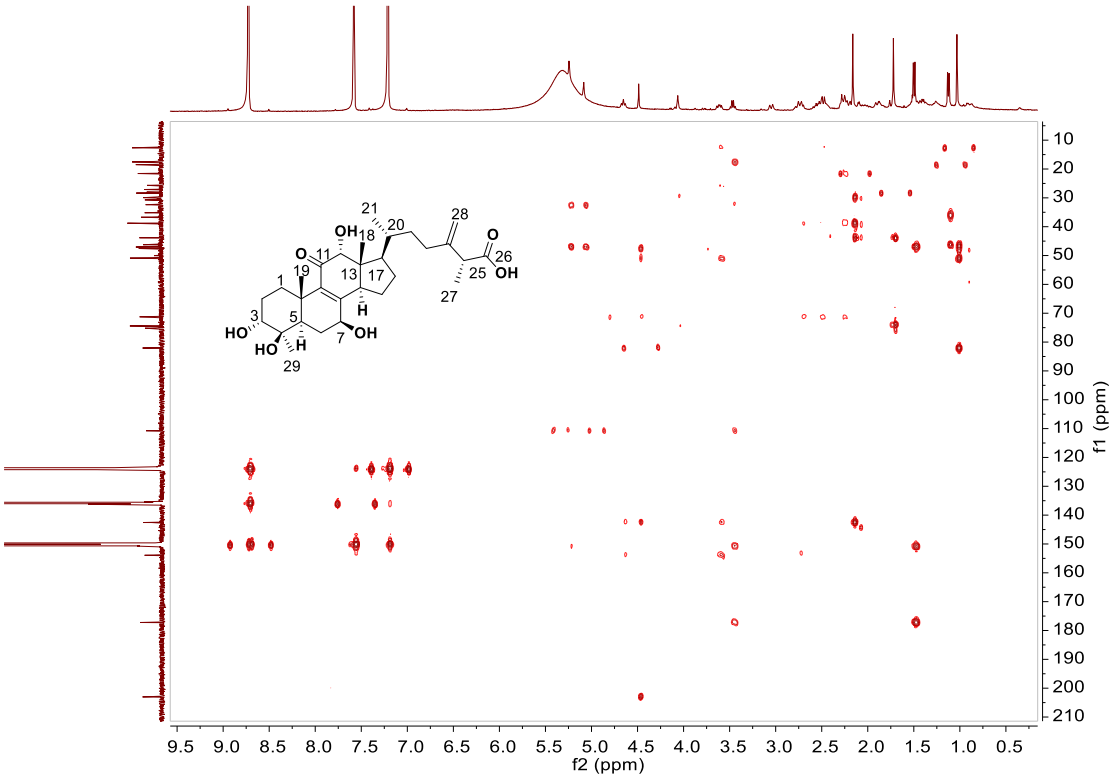


Figure S37. HMBC spectrum of **4** in pyridine-d_5 (400 MHz).

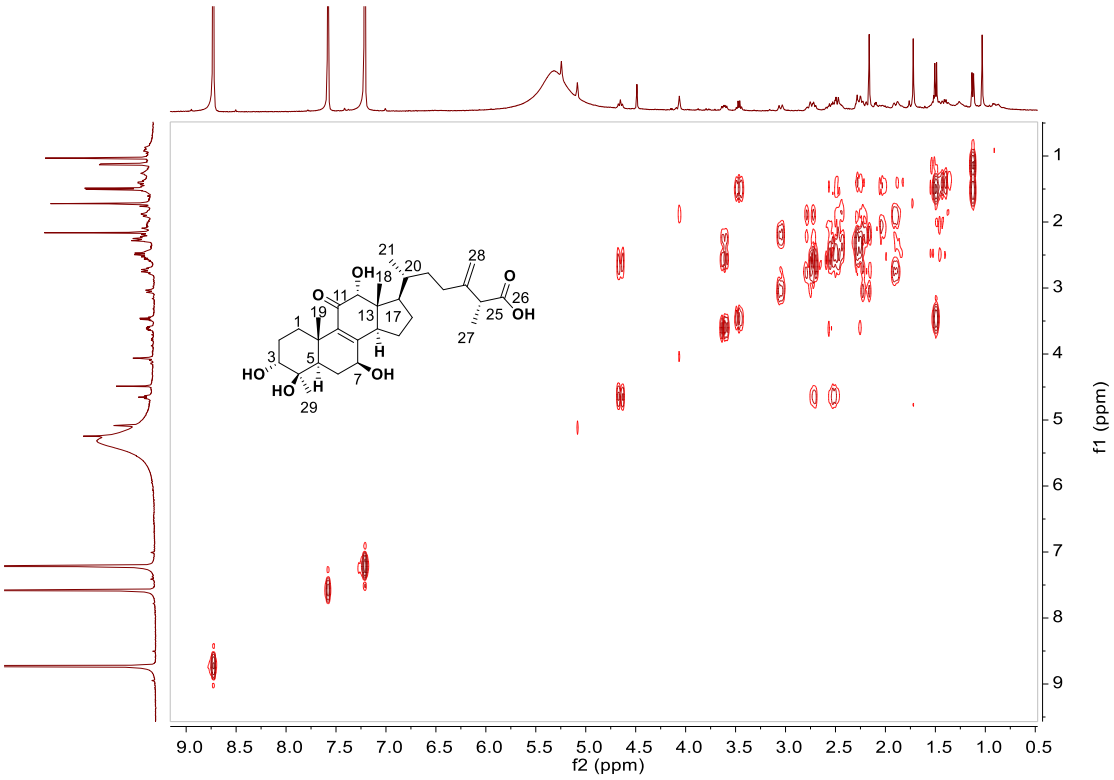


Figure S38. ^{1}H-^{1}H COSY spectrum of **4** in pyridine-d_5 (400 MHz).

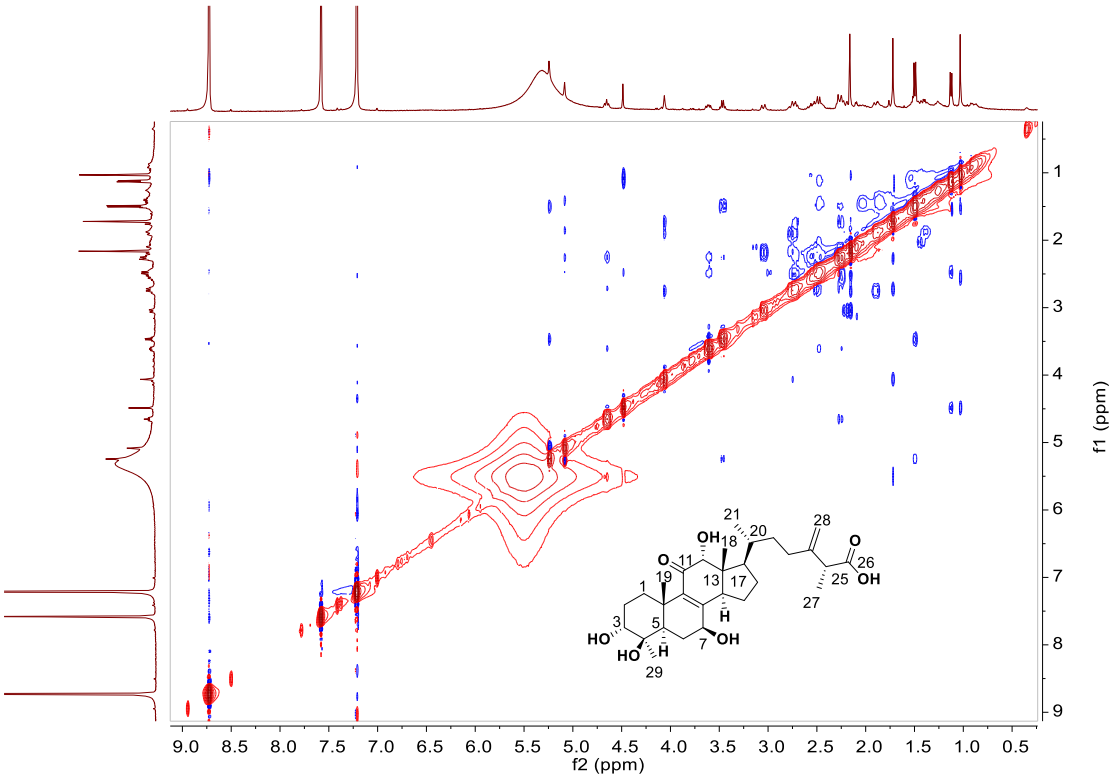


Figure S39. NOESY spectrum of **4** in pyridine-d_5 (400 MHz).

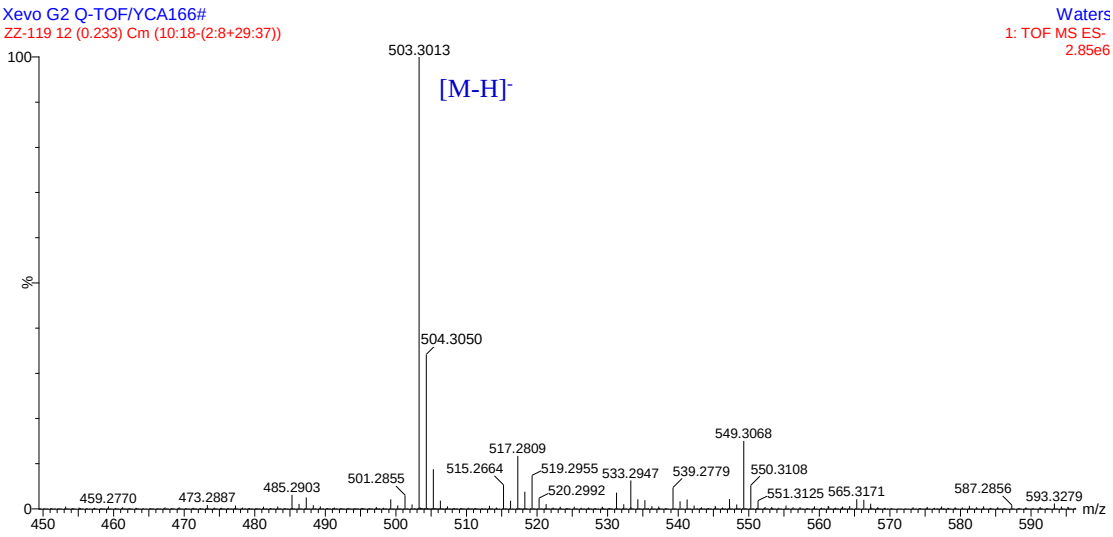


Figure S40. HR-ESI-MS spectrum of **4.**

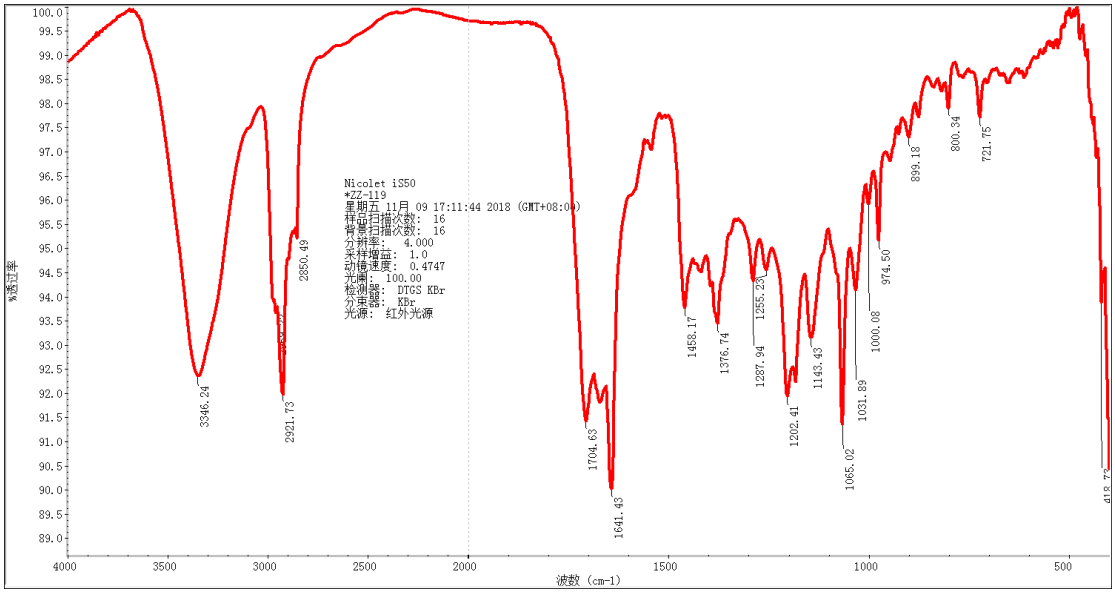


Figure S41. IR spectrum of **4**.

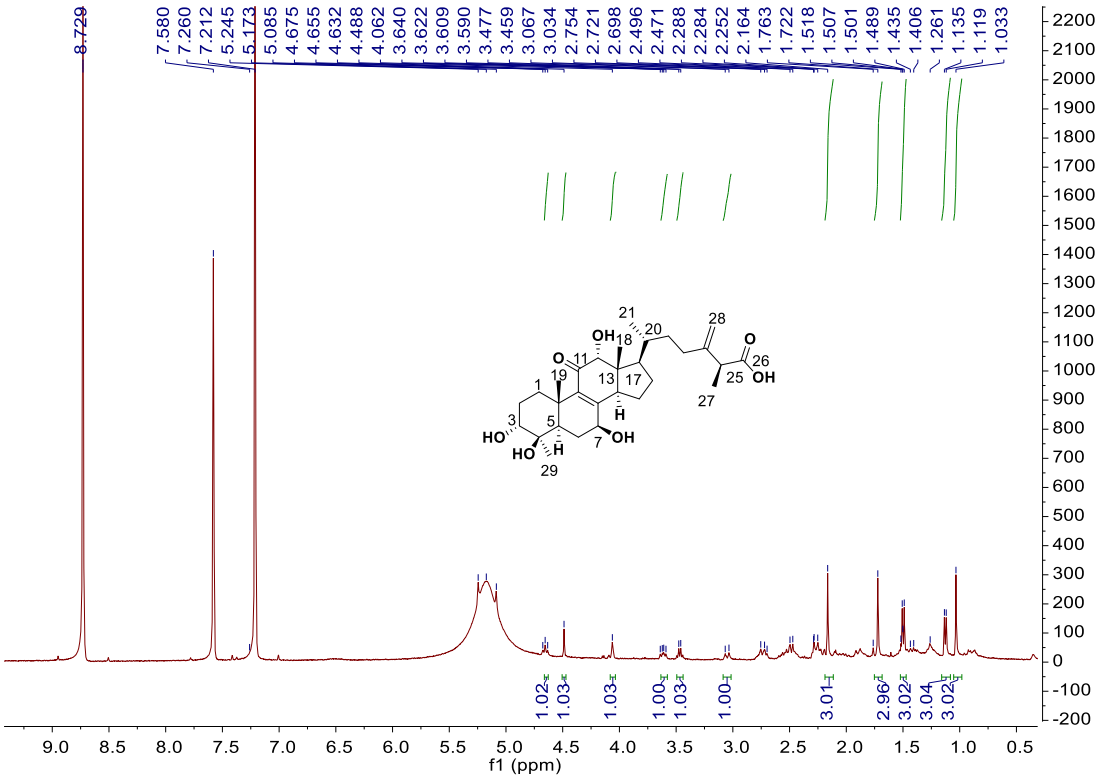


Figure S42. ^{1}H-NMR spectrum of **5** in pyridine-d_5 (400 MHz).

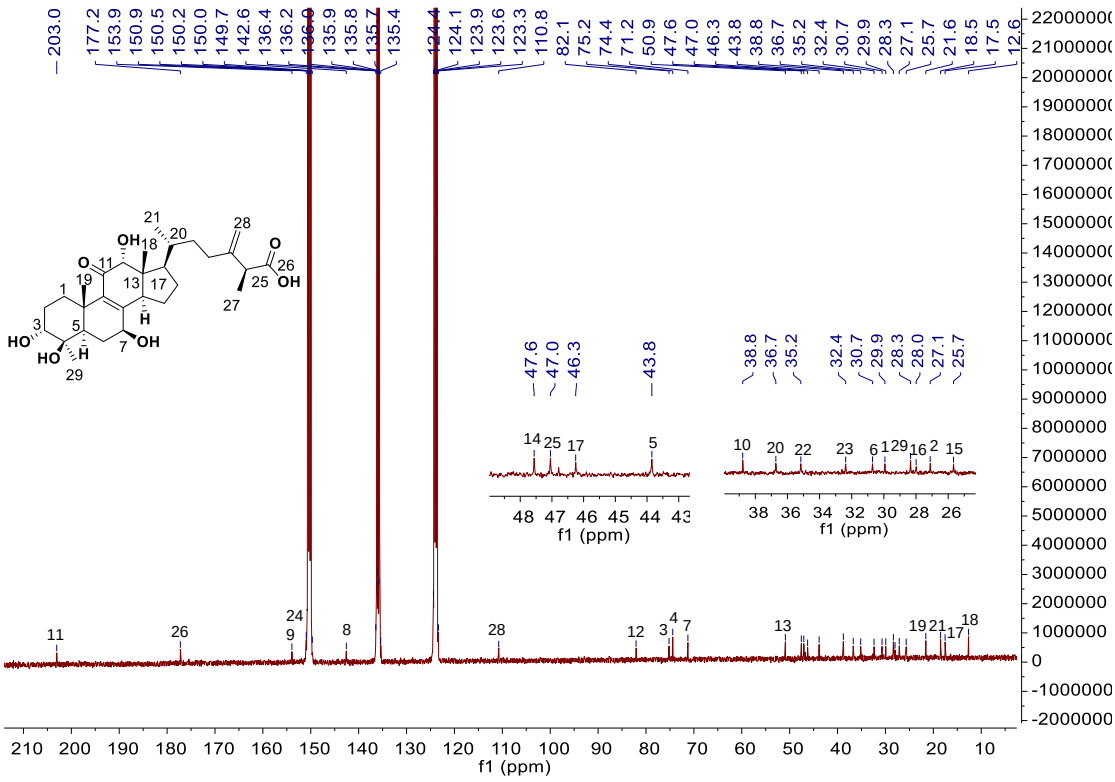


Figure S43. ^{13}C-NMR spectrum of **5** in pyridine-d_5 (100 MHz).

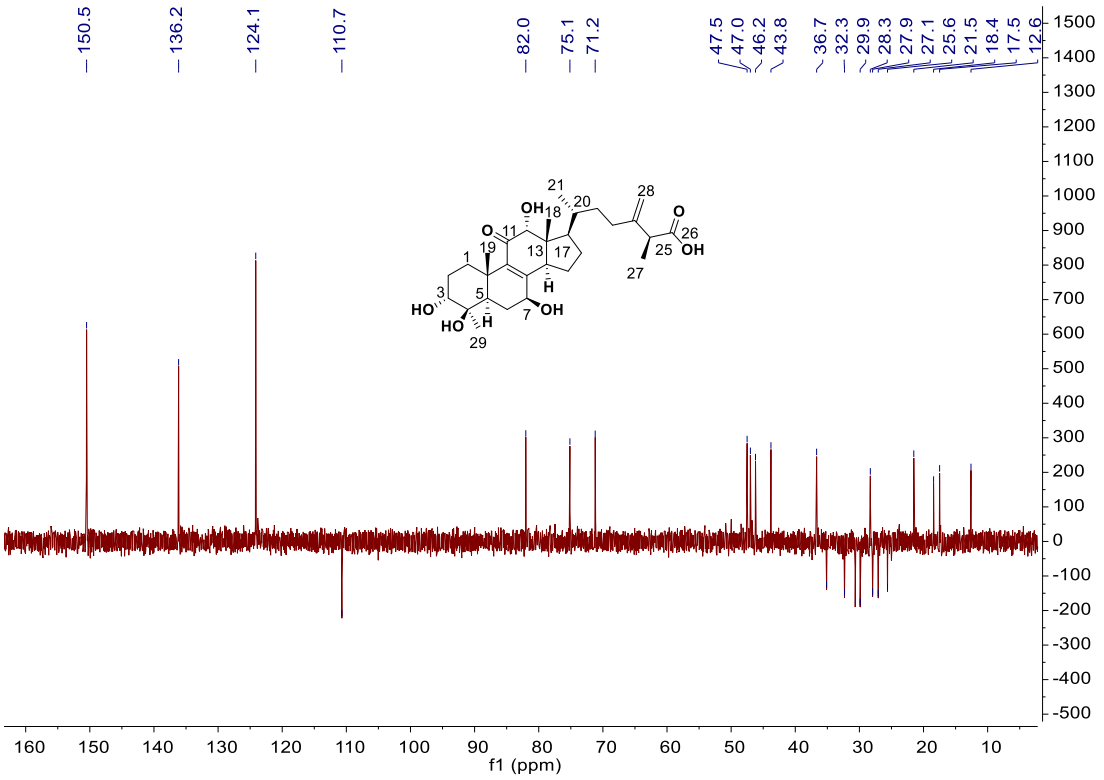


Figure S44. DEPT 135 spectrum of **5** in pyridine-d_5 (100 MHz).

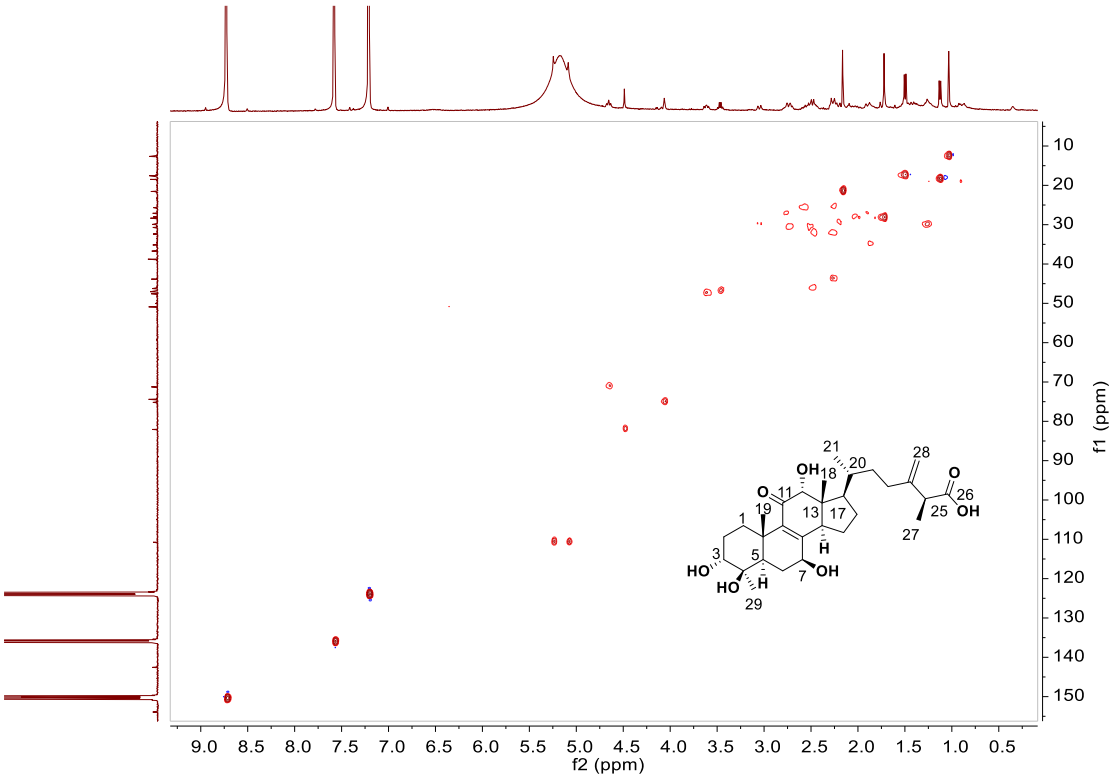


Figure S45. HSQC spectrum of **5** in pyridine-d_5 (400 MHz).

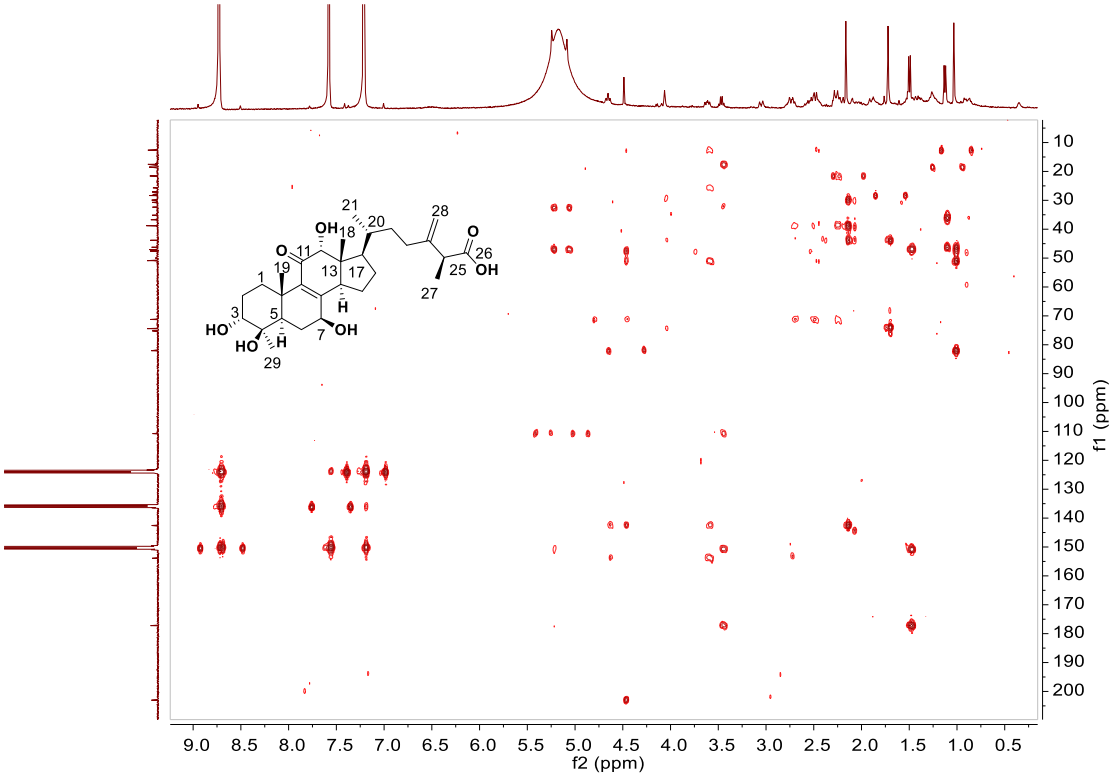


Figure S46. HMBC spectrum of **5** in pyridine-d_5 (400 MHz).

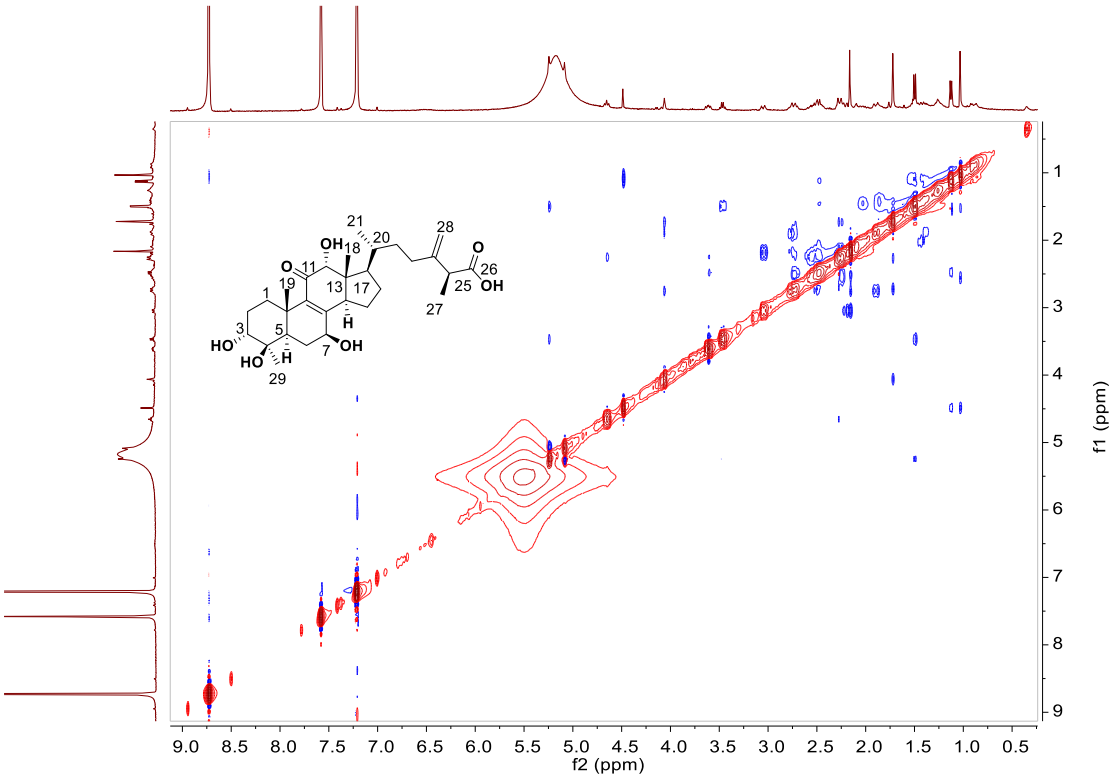


Figure S47. NOESY spectrum of **5** in pyridine-d_5 (400 MHz).

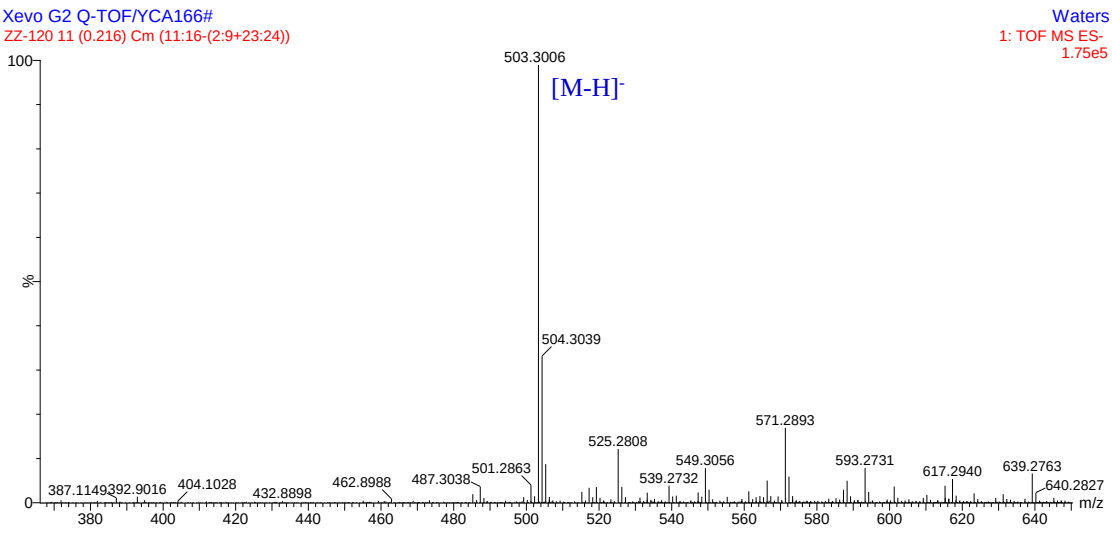


Figure S48. HR-ESI-MS spectrum of **5.**

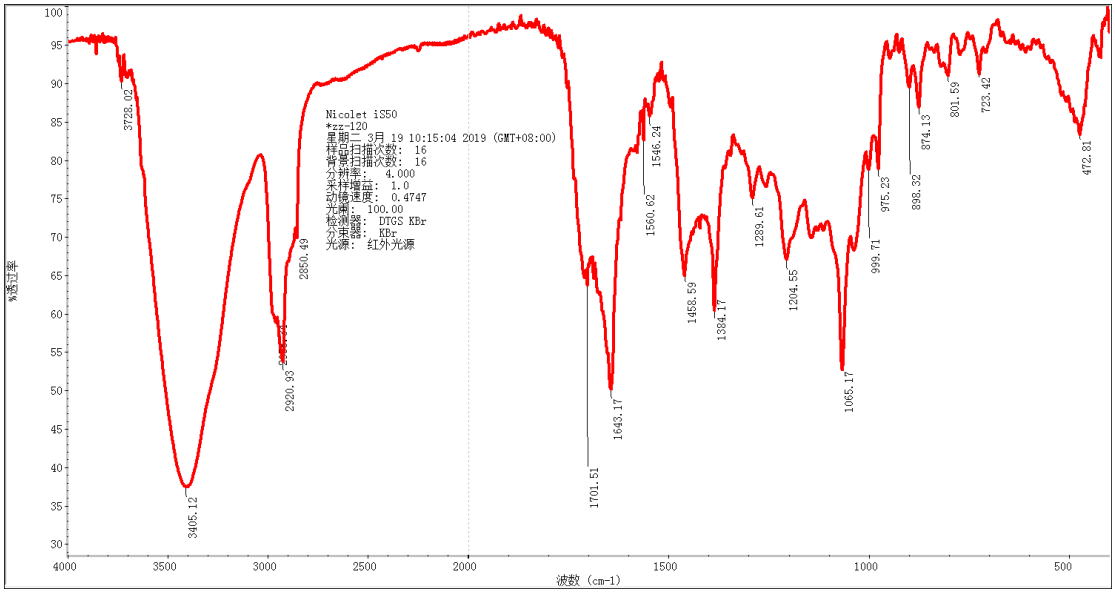


Figure S49. IR spectrum of **5**.

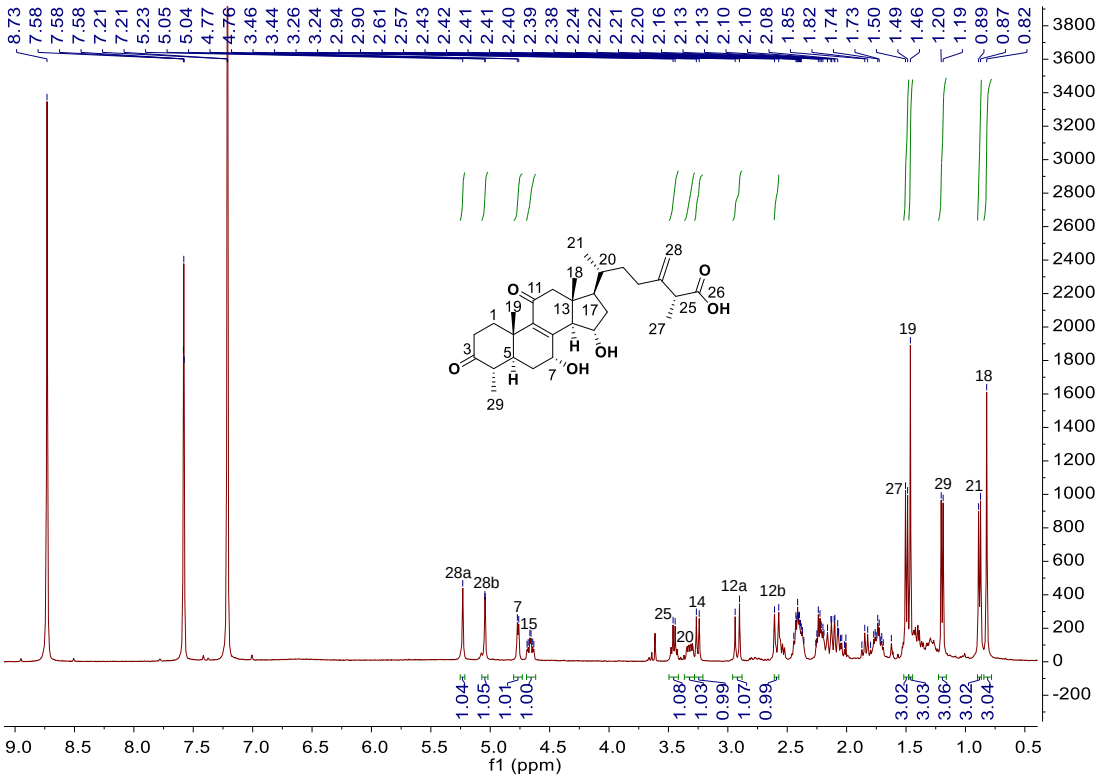


Figure S50. ^{1}H-NMR spectrum of **6** in pyridine-d_5 (400 MHz).

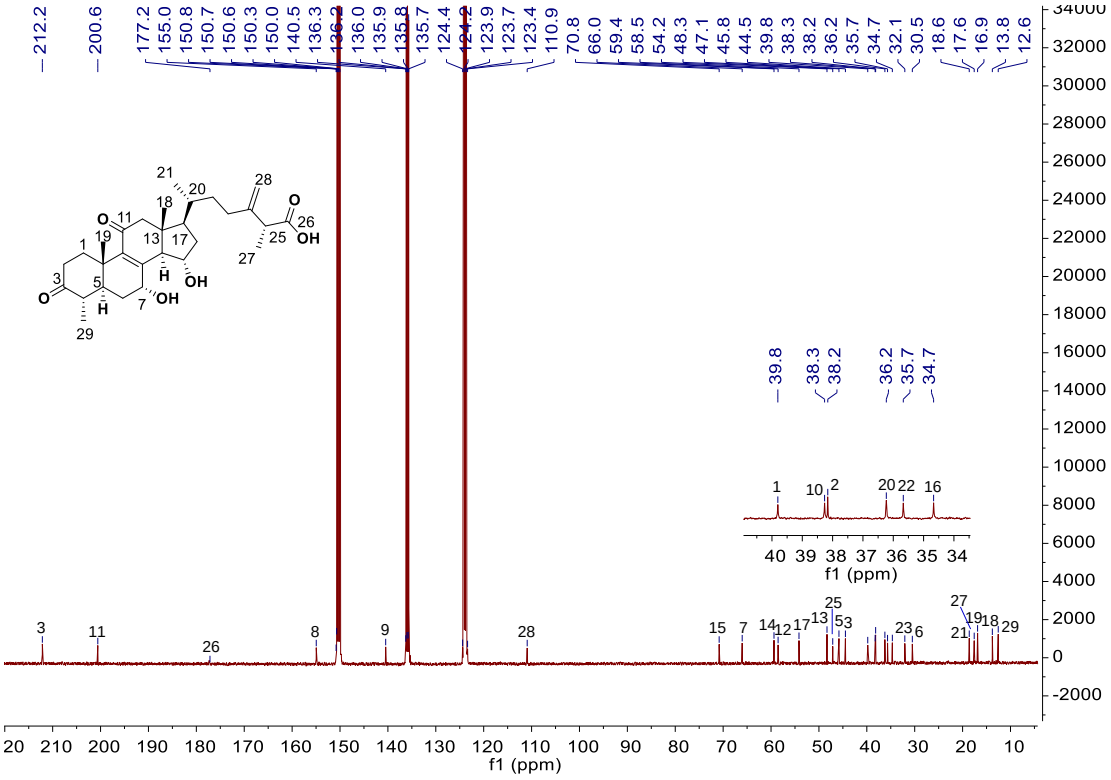


Figure S51. ^{13}C-NMR spectrum of **6** in pyridine-d_5 (100 MHz).

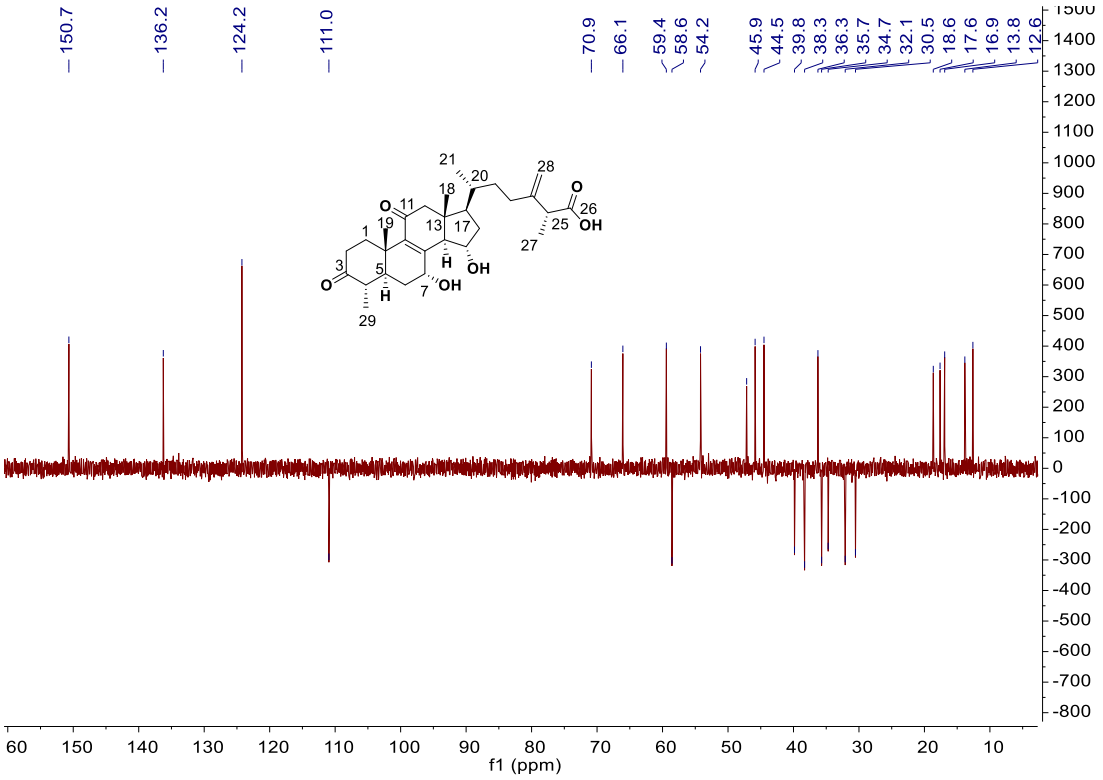


Figure S52. DEPT 135 spectrum of **6** in pyridine-d_5 (100 MHz).

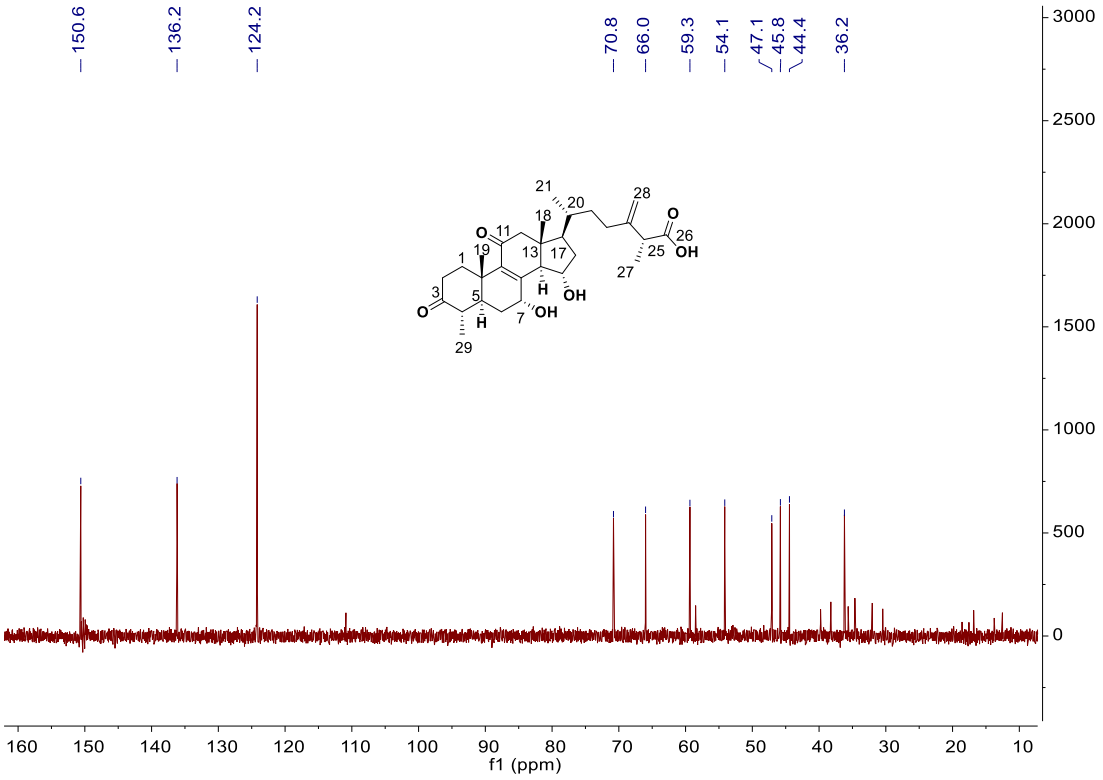


Figure S53. DEPT 90 spectrum of **6** in pyridine-d_5 (100 MHz).

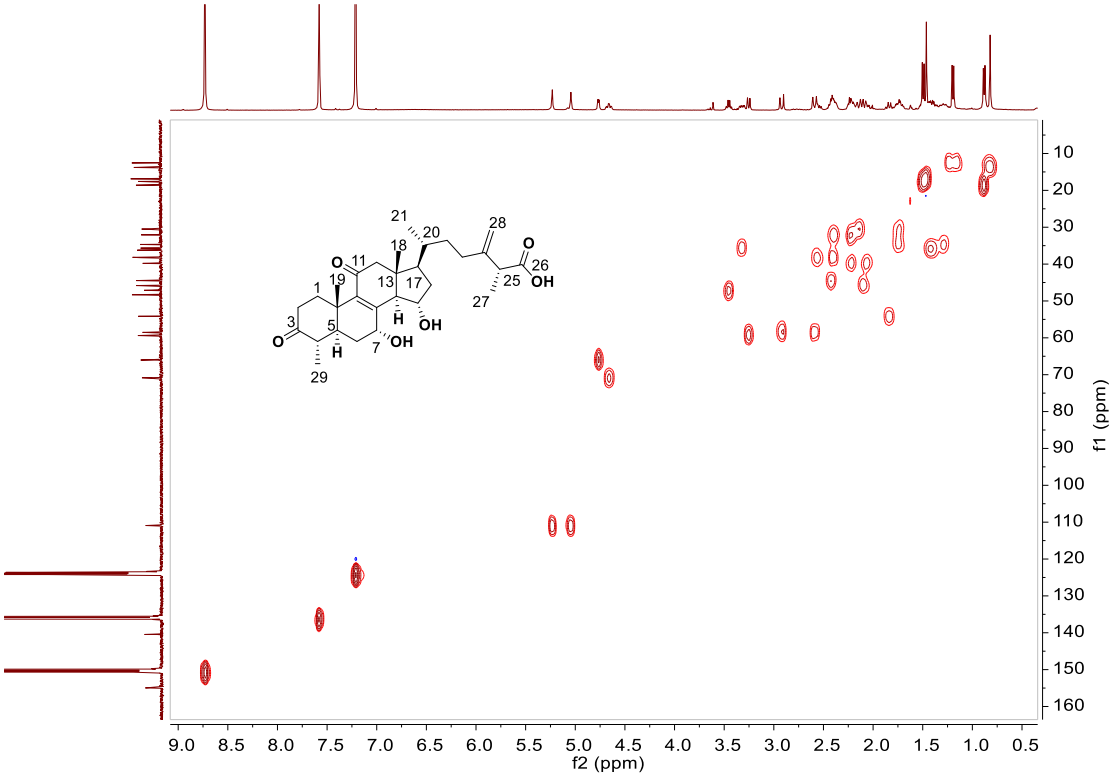


Figure S54. HSQC spectrum of **6** in pyridine-d_5 (400 MHz).

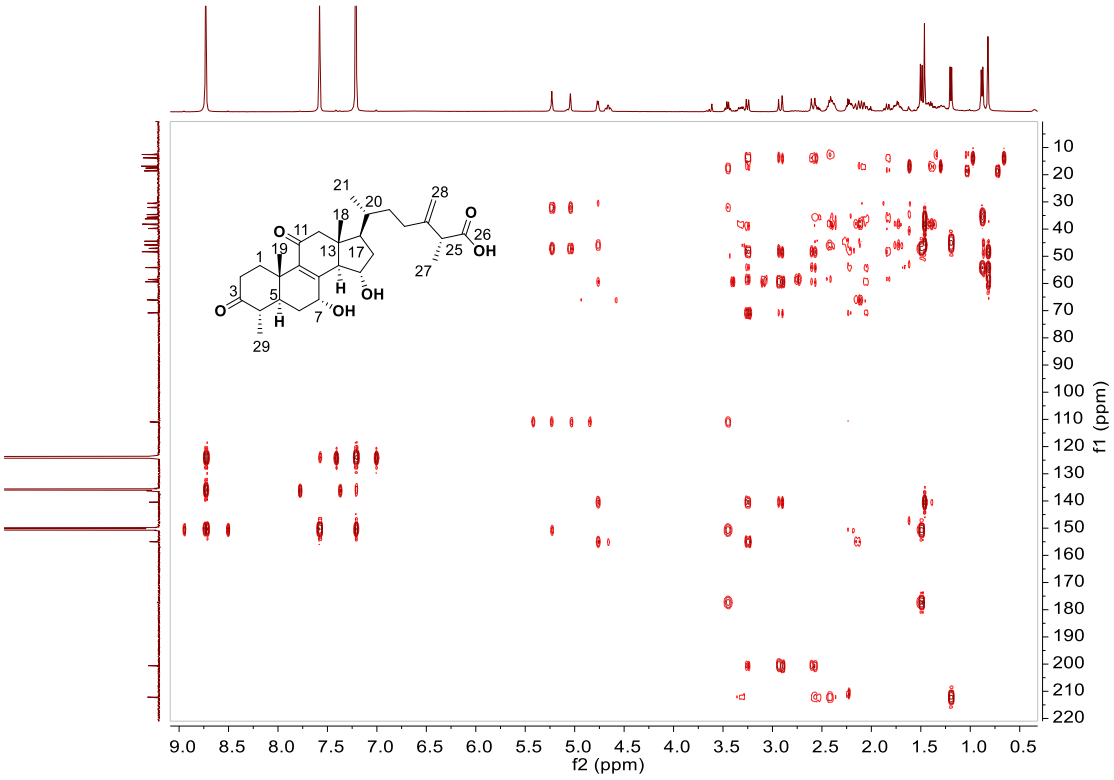


Figure S55. HMBC spectrum of **6** in pyridine-d_5 (400 MHz).

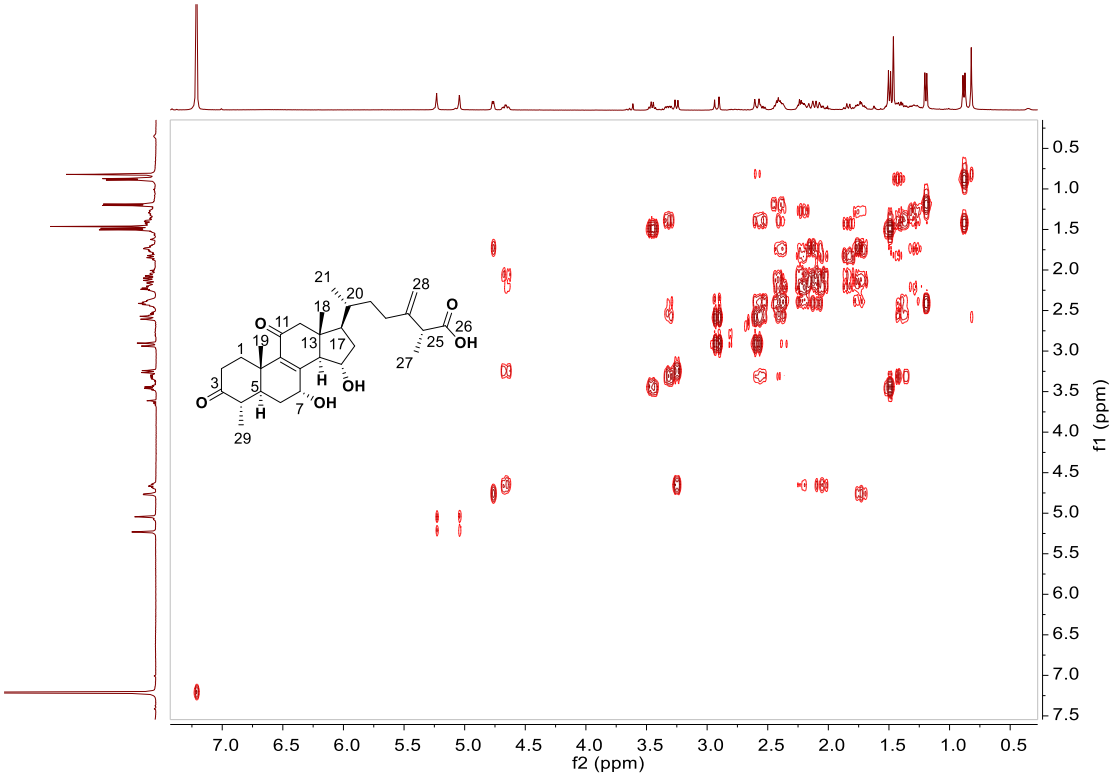


Figure S56. ^{1}H-^{1}H COSY spectrum of **6** in pyridine-d_5 (400 MHz).

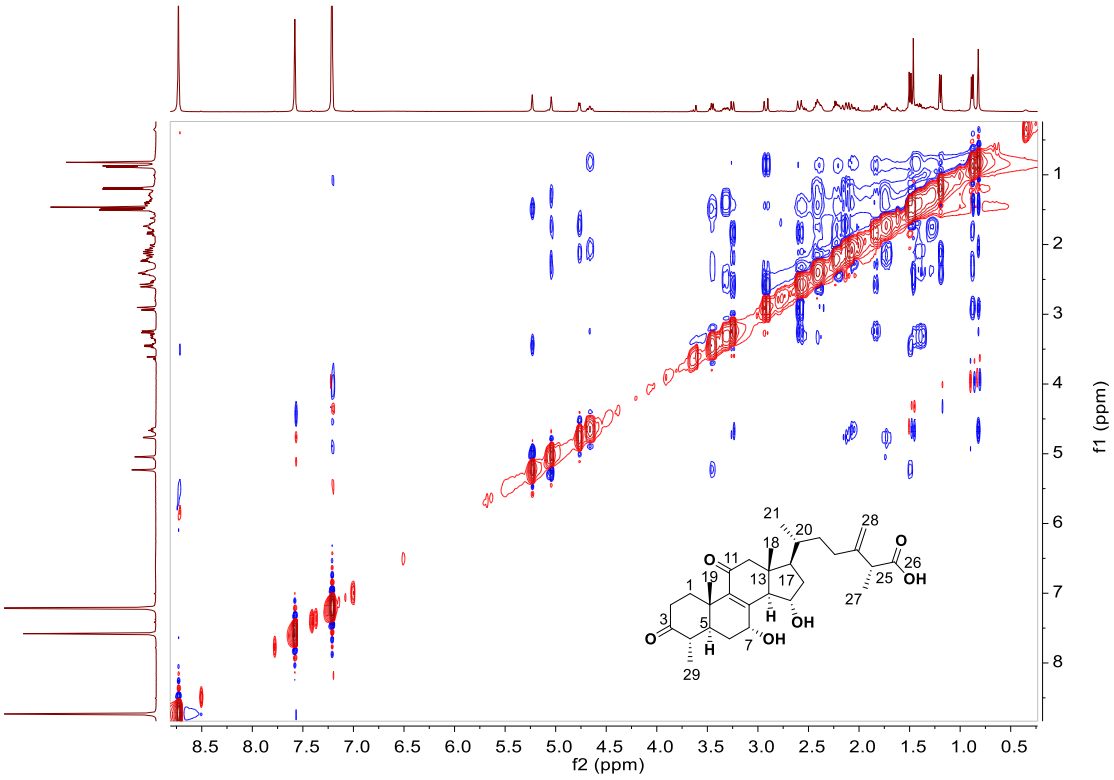


Figure S57. NOESY spectrum of **6** in pyridine-d_5 (400 MHz).

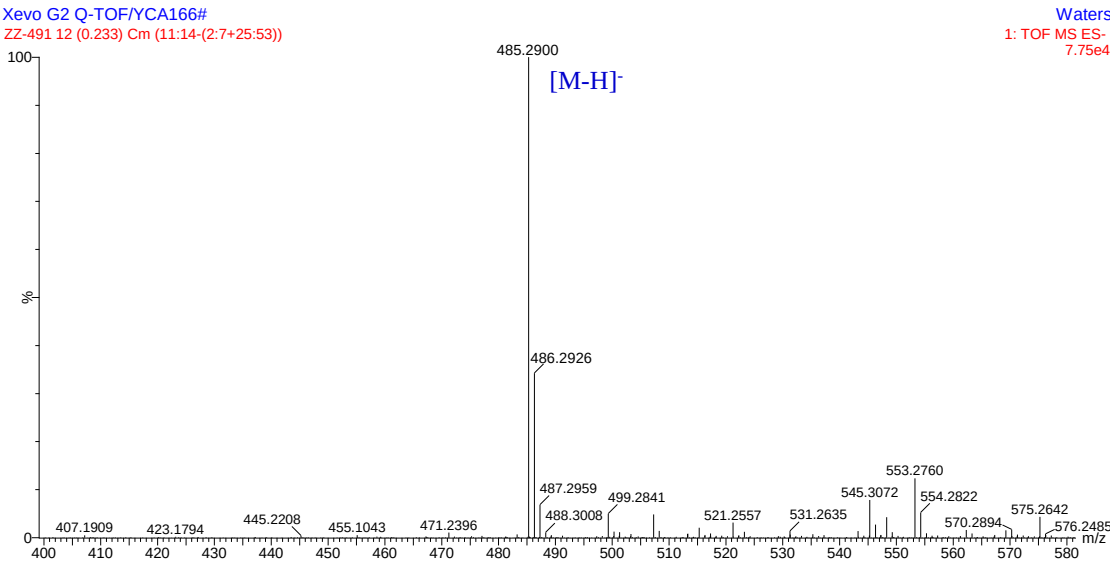


Figure S58. HR-ESI-MS spectrum of **6.**

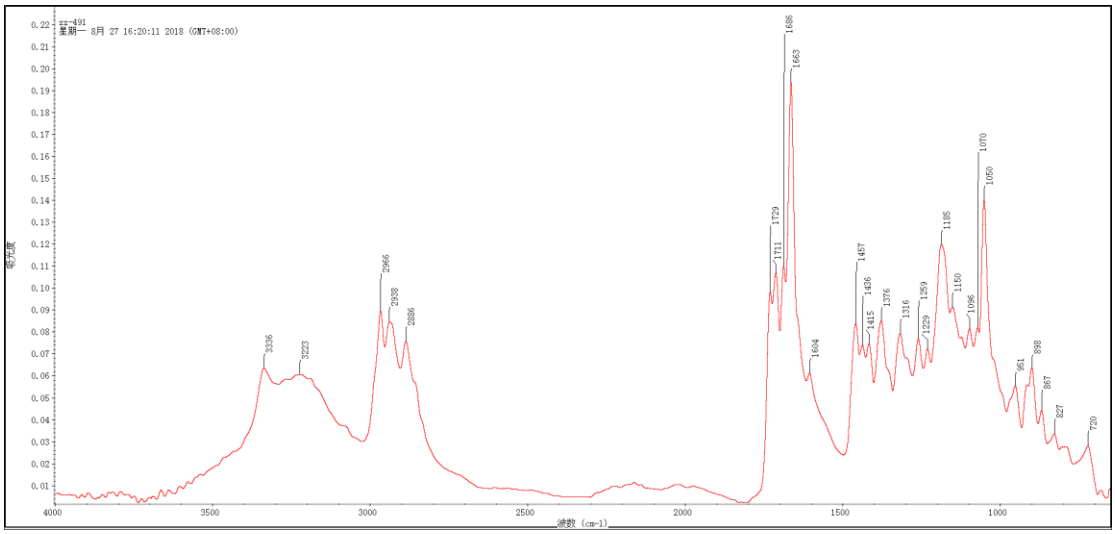


Figure S59. IR spectrum of **6**.

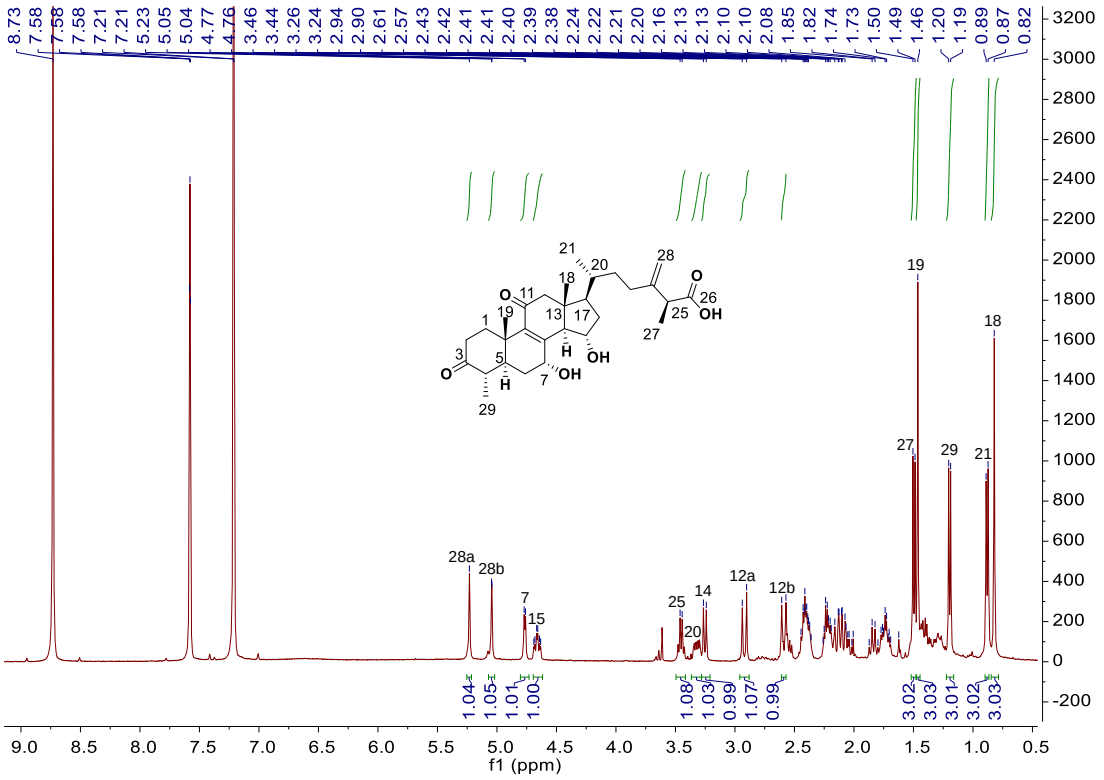


Figure S60. ^{1}H-NMR spectrum of **7** in pyridine-d_5 (400 MHz).

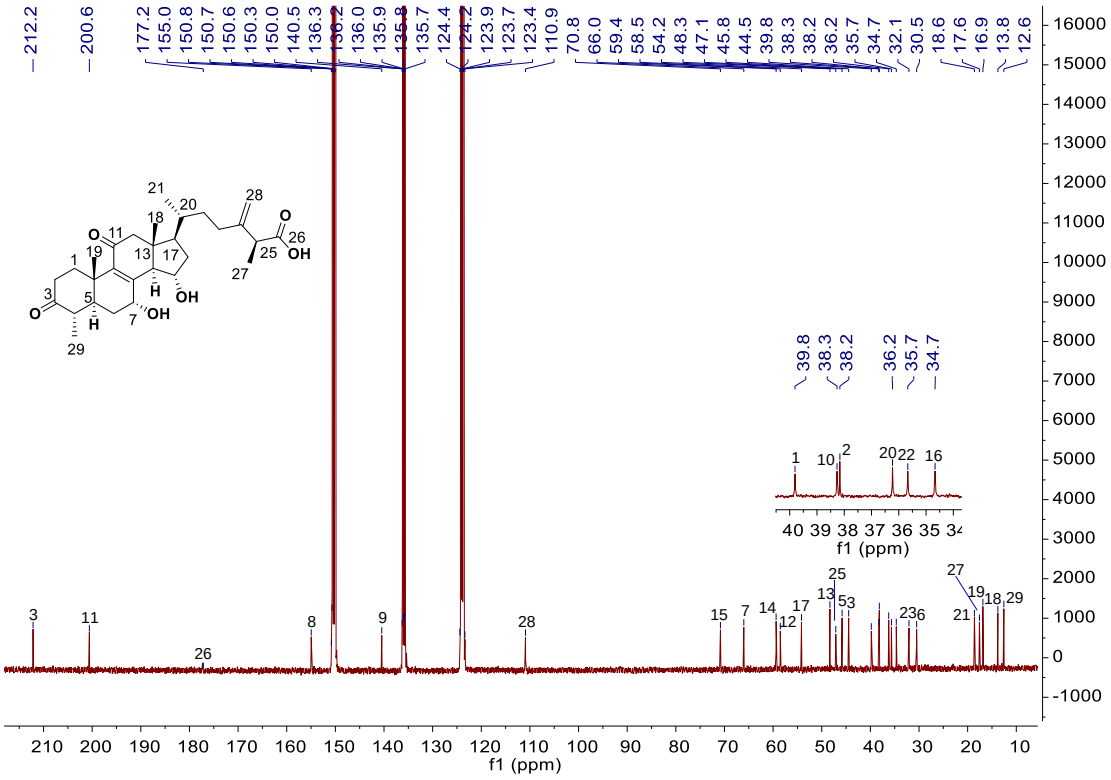


Figure S61. ^{13}C-NMR spectrum of **7** in pyridine-d_5 (100 MHz).

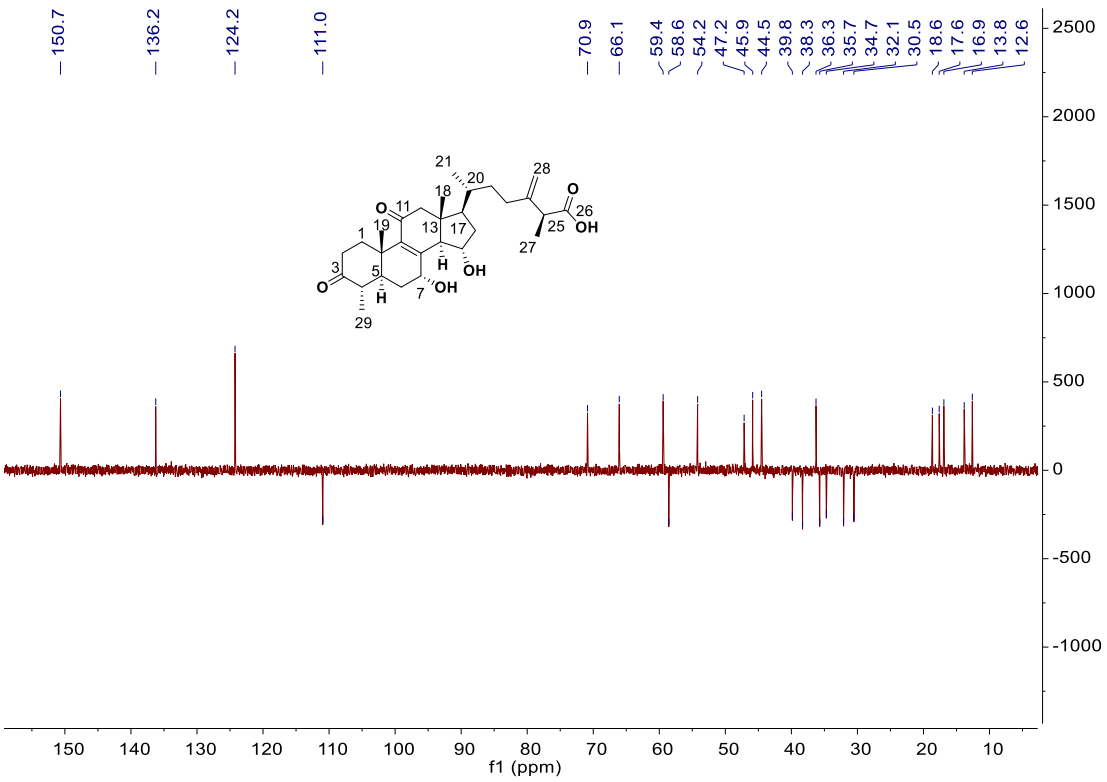


Figure S62. DEPT 135 spectrum of **7** in pyridine-d_5 (100 MHz).

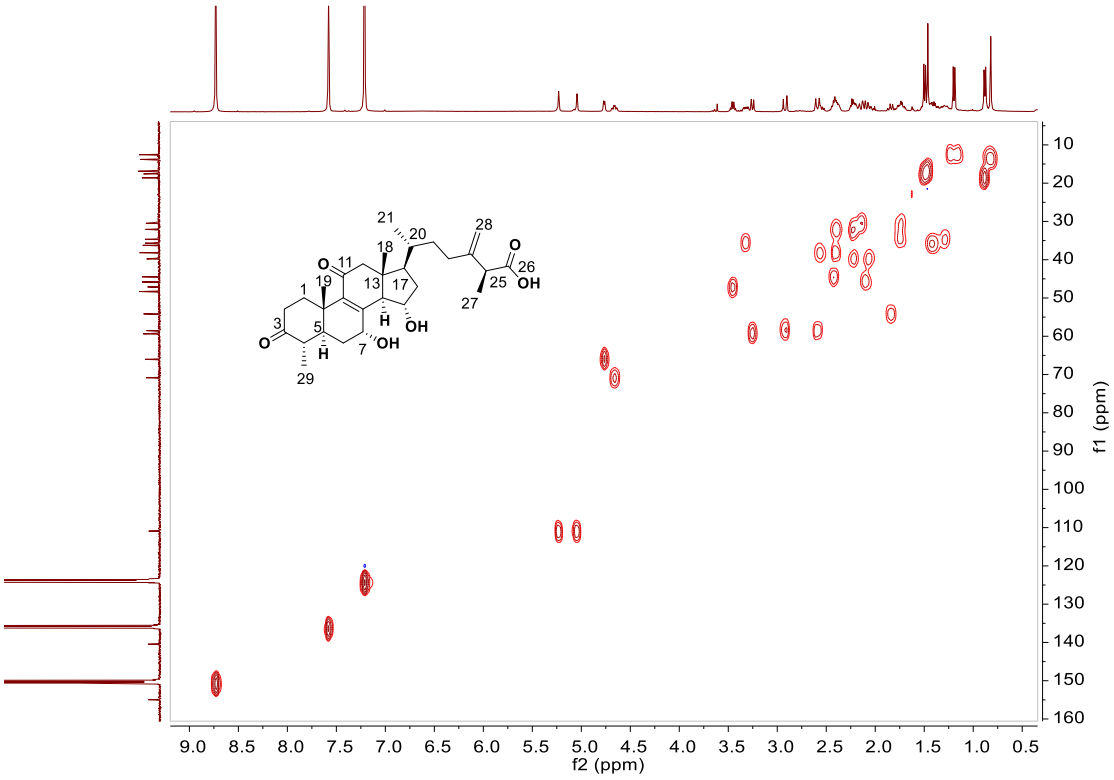


Figure S63. HSQC spectrum of **7** in pyridine-d_5 (400 MHz).

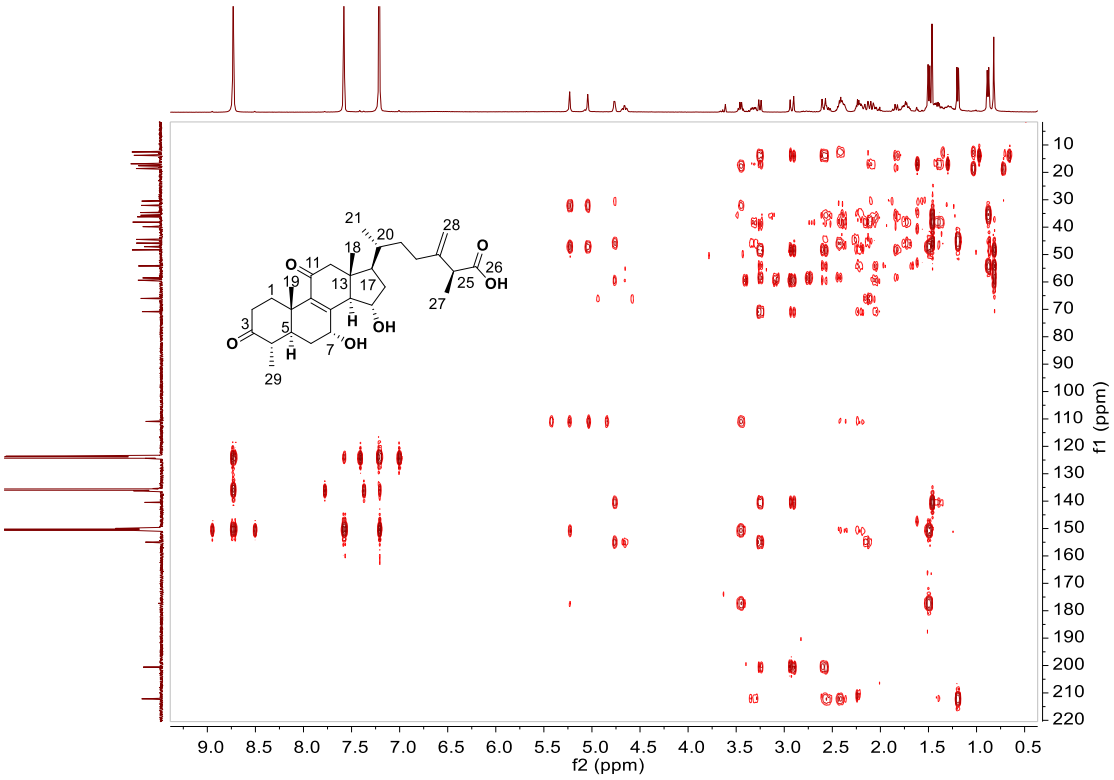


Figure S64. HMBC spectrum of **7** in pyridine-d_5 (400 MHz).

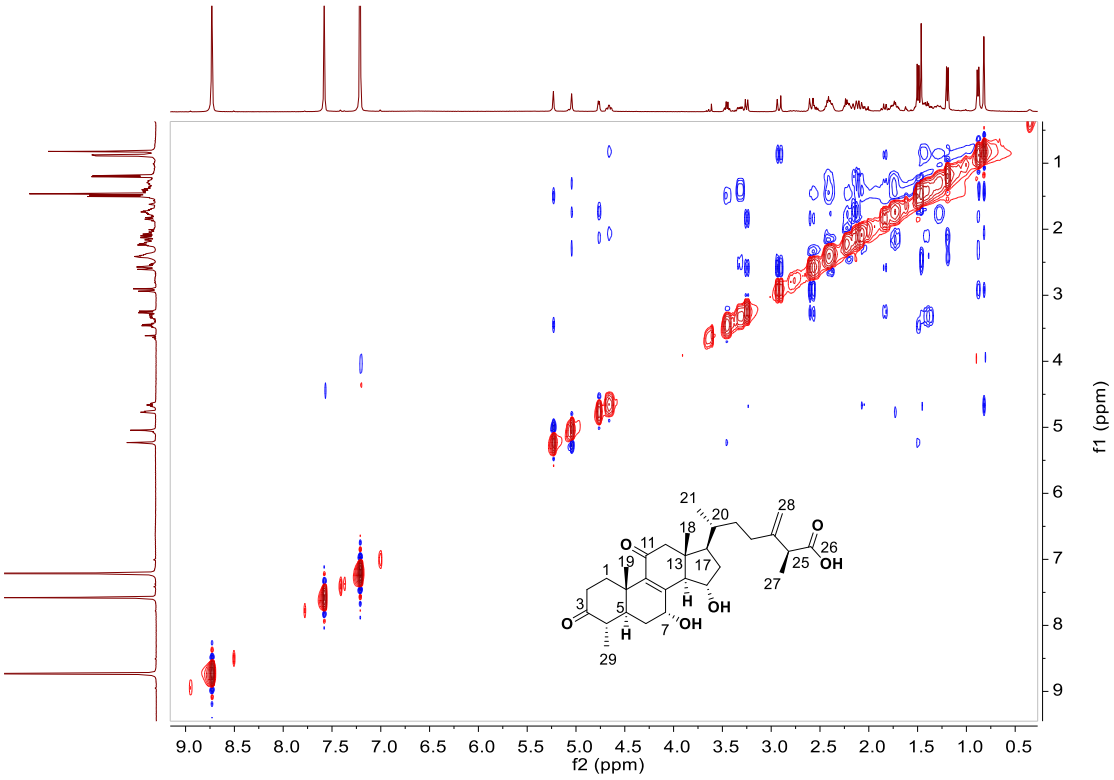


Figure S65. NOESY spectrum of **7** in pyridine-d_5 (400 MHz).

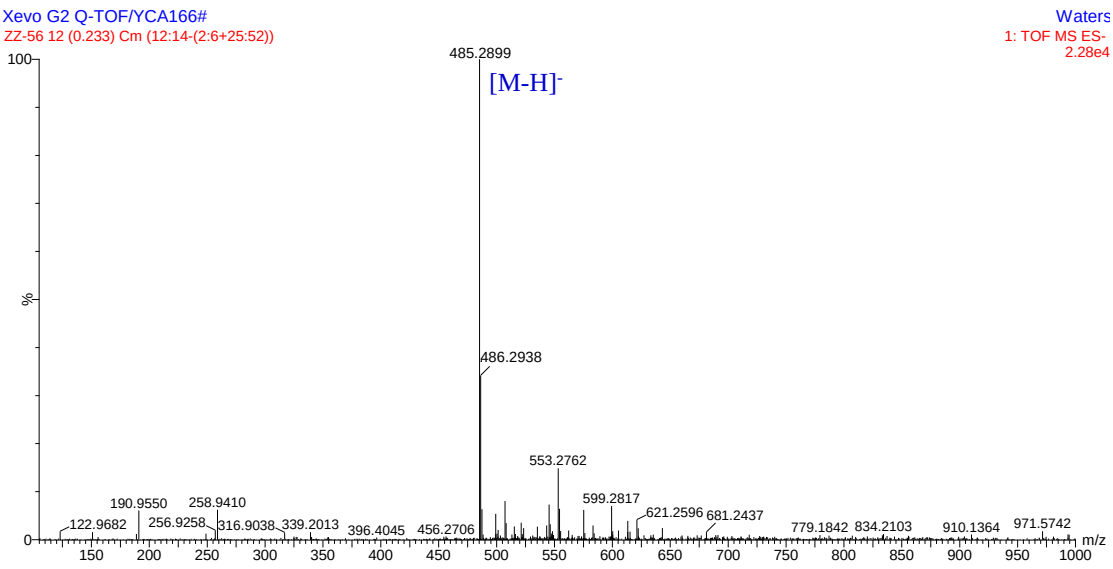


Figure S66. HR-ESI-MS spectrum of **7.**

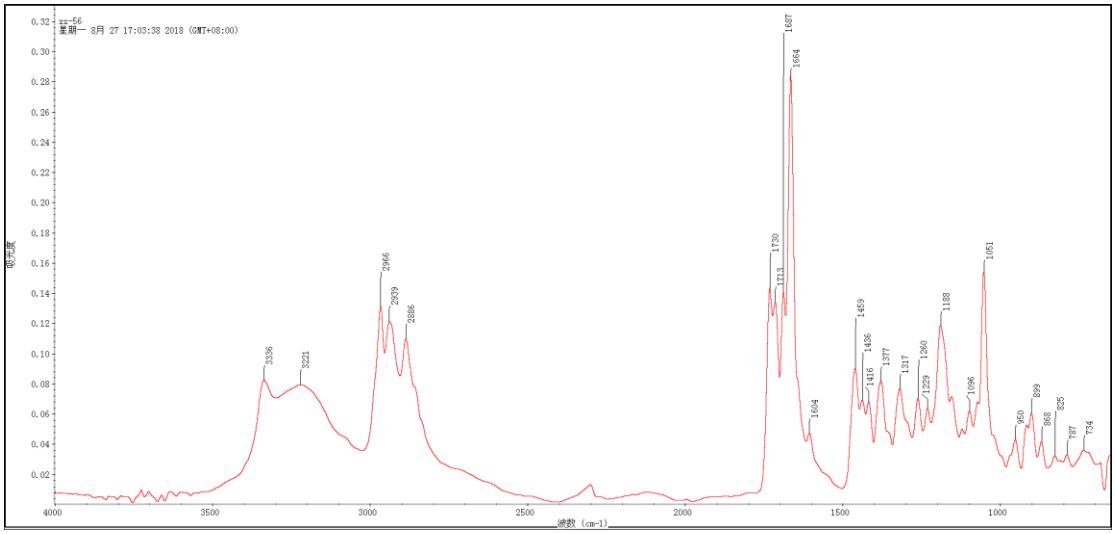


Figure S67. IR spectrum of **7**.

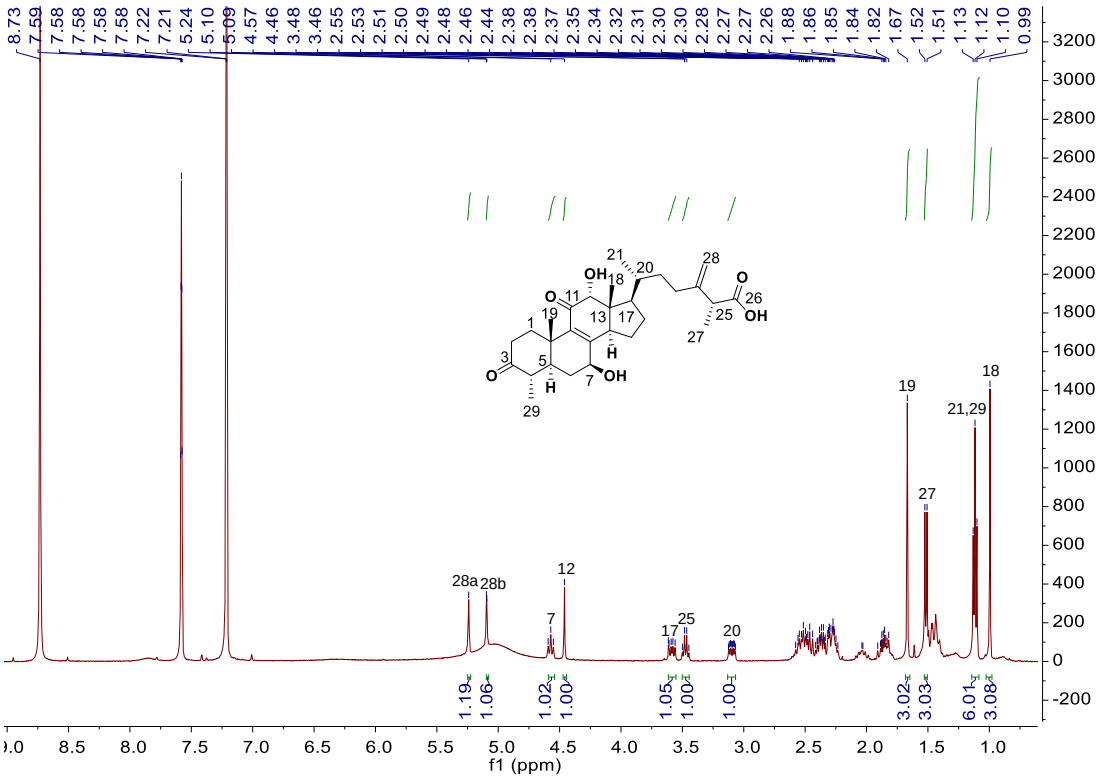


Figure S68. ^{1}H-NMR spectrum of **8** in pyridine-d_5 (400 MHz).

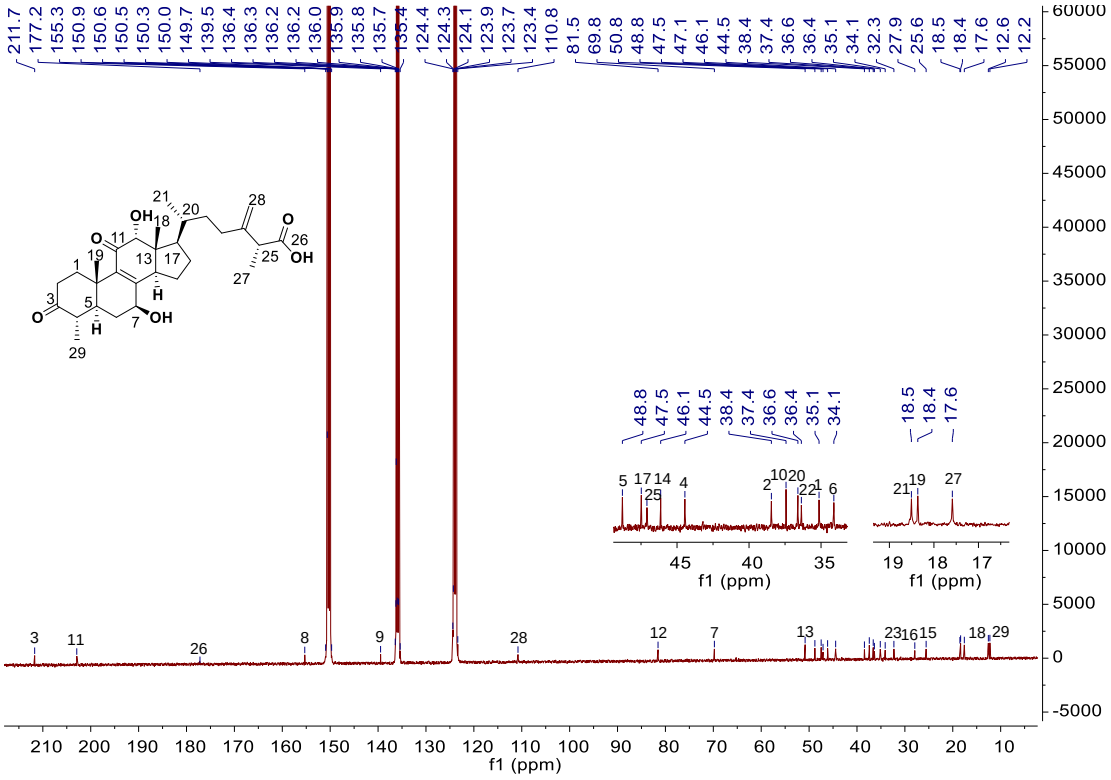


Figure S69. ^{13}C-NMR spectrum of **8** in pyridine-d_5 (100 MHz).

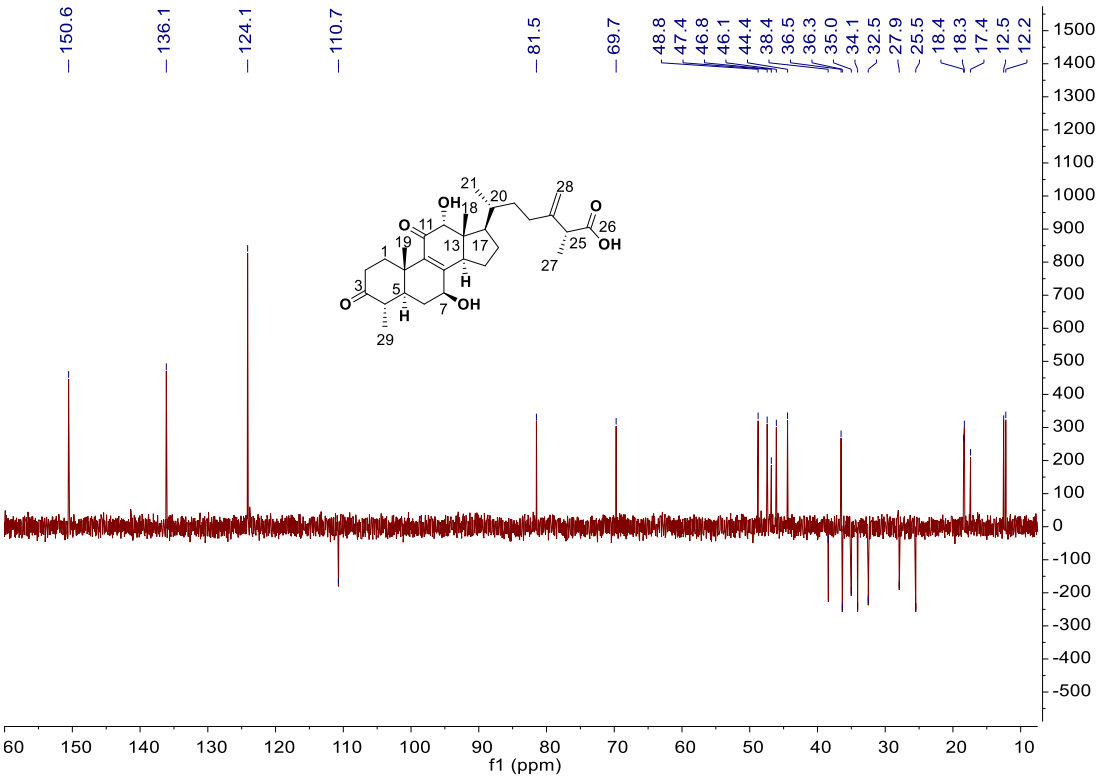


Figure S70. DEPT 135 spectrum of **8** in pyridine-d_5 (100 MHz).

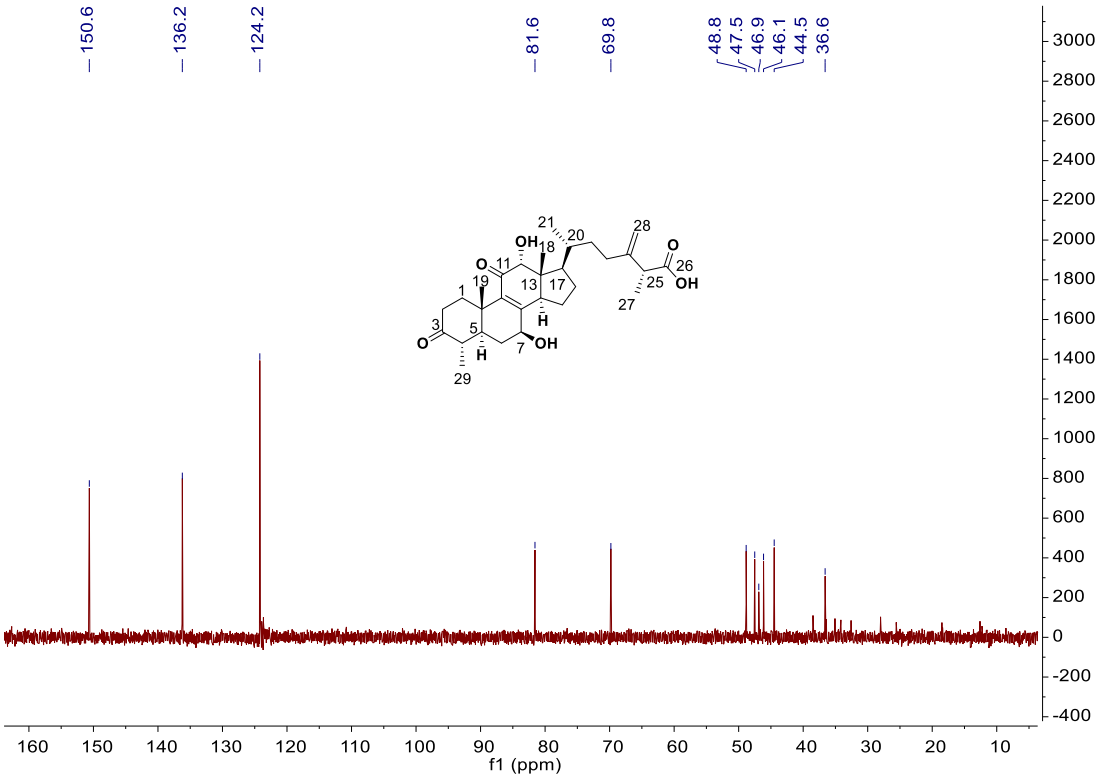


Figure S71. DEPT 90 spectrum of **8** in pyridine-d_5 (100 MHz).

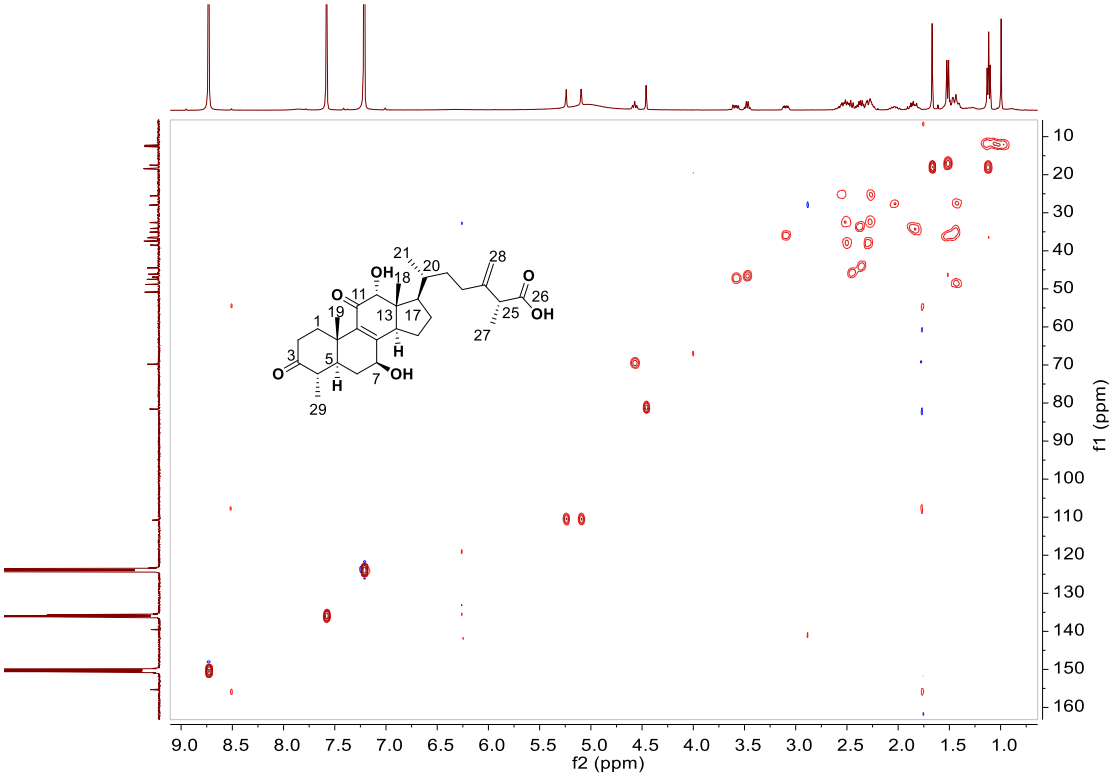


Figure S72. HSQC spectrum of **8** in pyridine-d_5 (400 MHz).

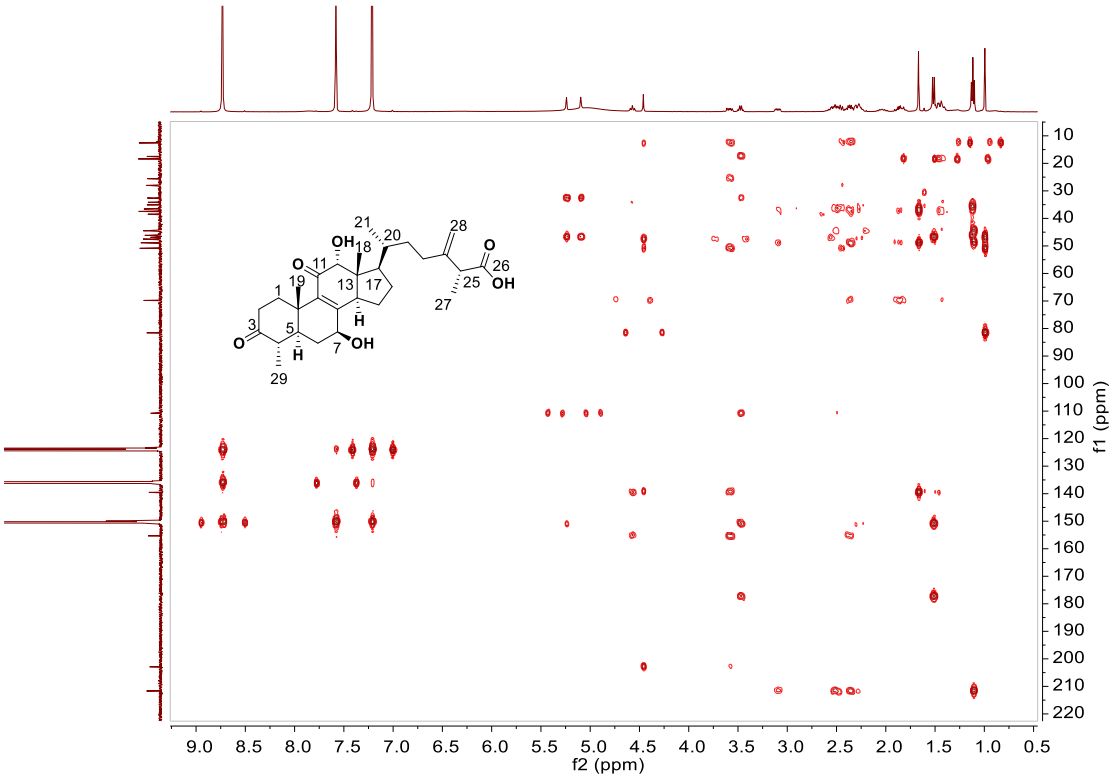


Figure S73. HMBC spectrum of **8** in pyridine-d_5 (400 MHz).

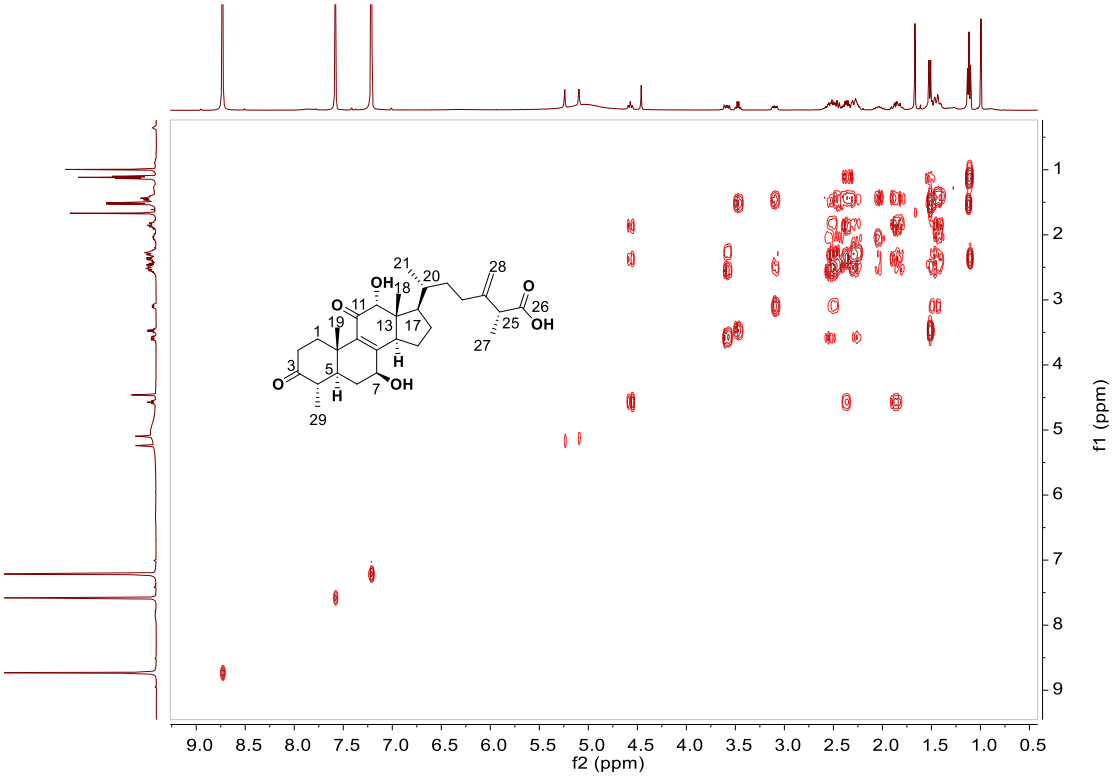


Figure S74. ^{1}H-^{1}H COSY spectrum of **8** in pyridine-d_5 (400 MHz).

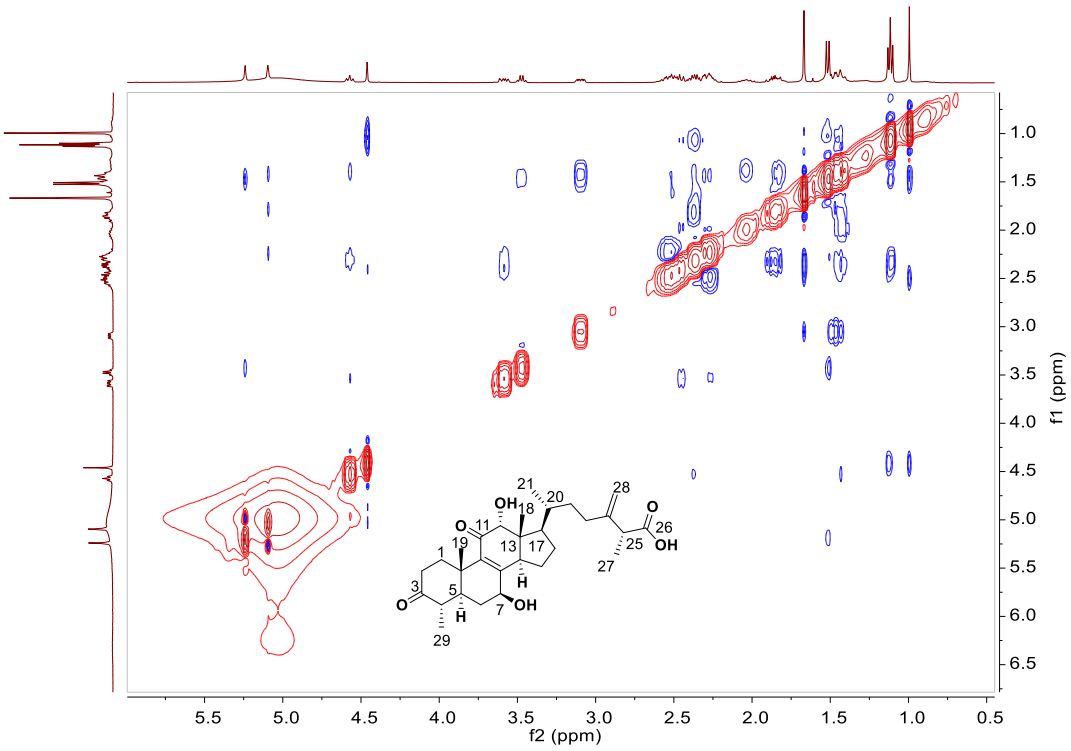


Figure S75. NOESY spectrum of **8** in pyridine-d_5 (400 MHz).

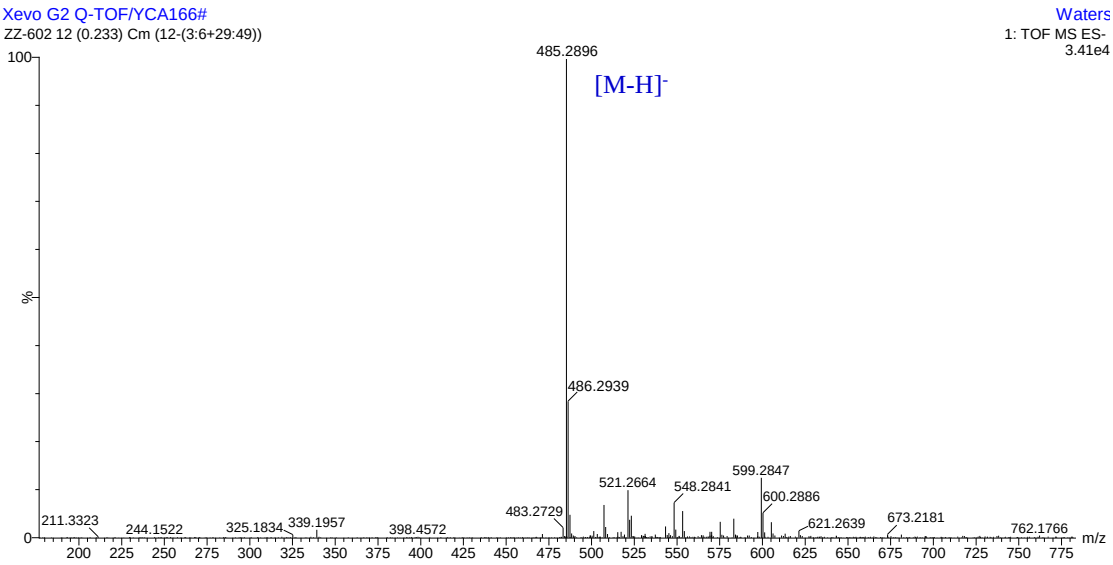


Figure S76. HR-ESI-MS spectrum of **8.**

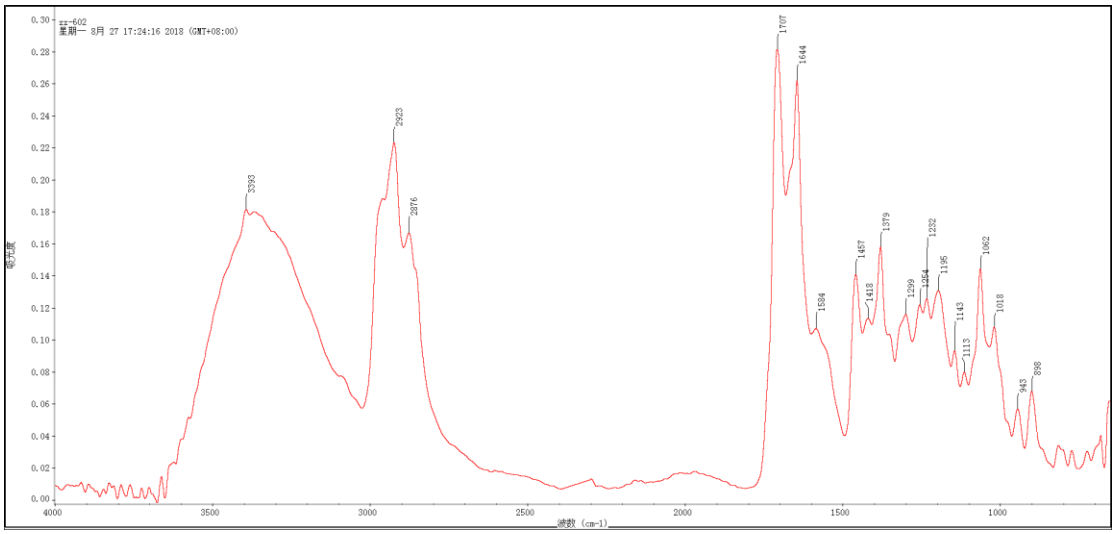


Figure S77. IR spectrum of **8**.

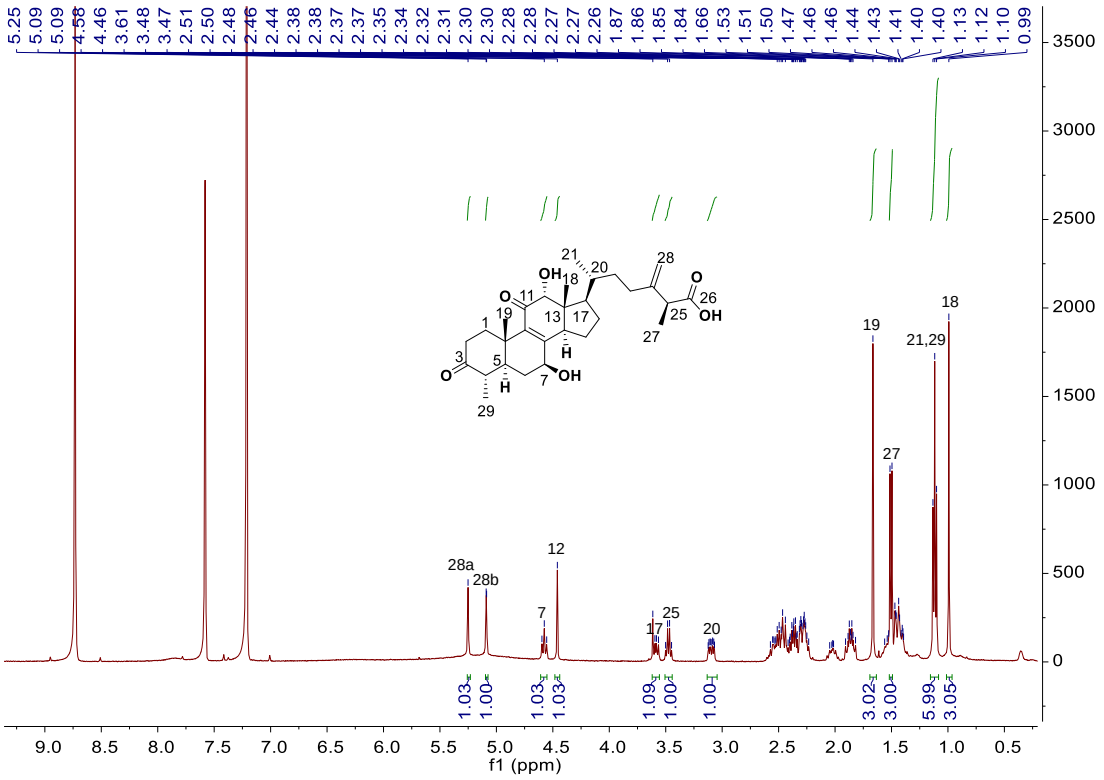


Figure S78. ^{1}H-NMR spectrum of **9** in pyridine-d_5 (400 MHz).

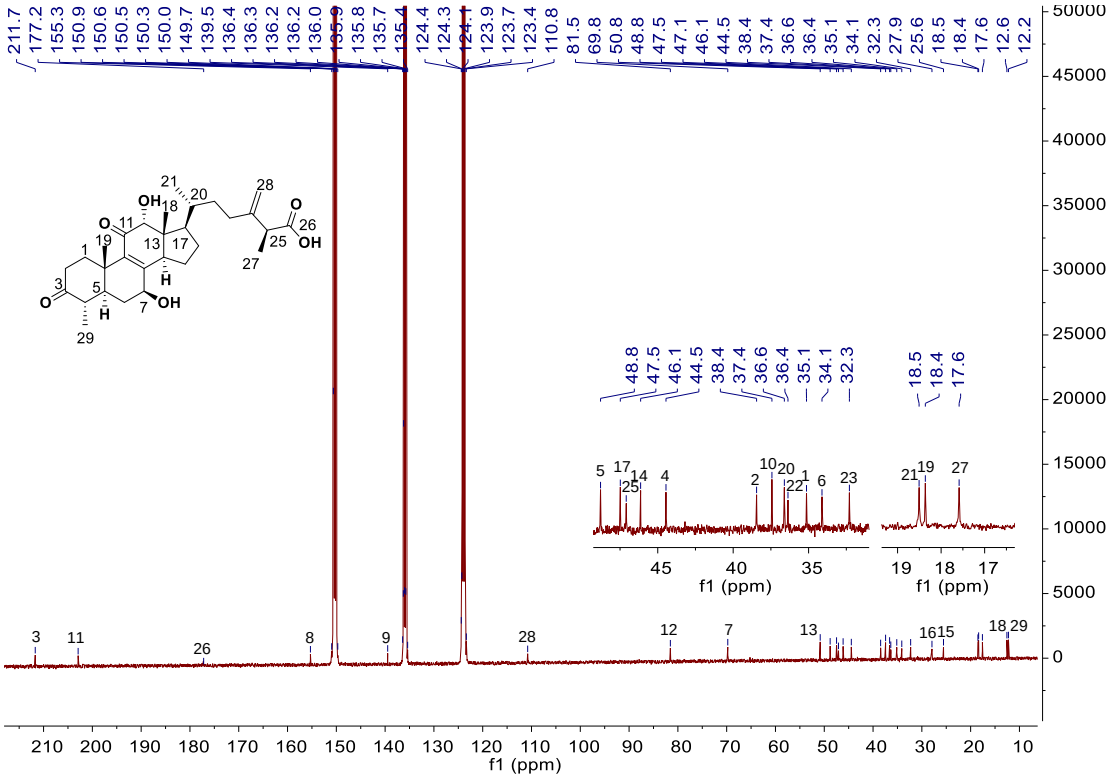


Figure S79. ^{13}C-NMR spectrum of **9** in pyridine-d_5 (100 MHz).

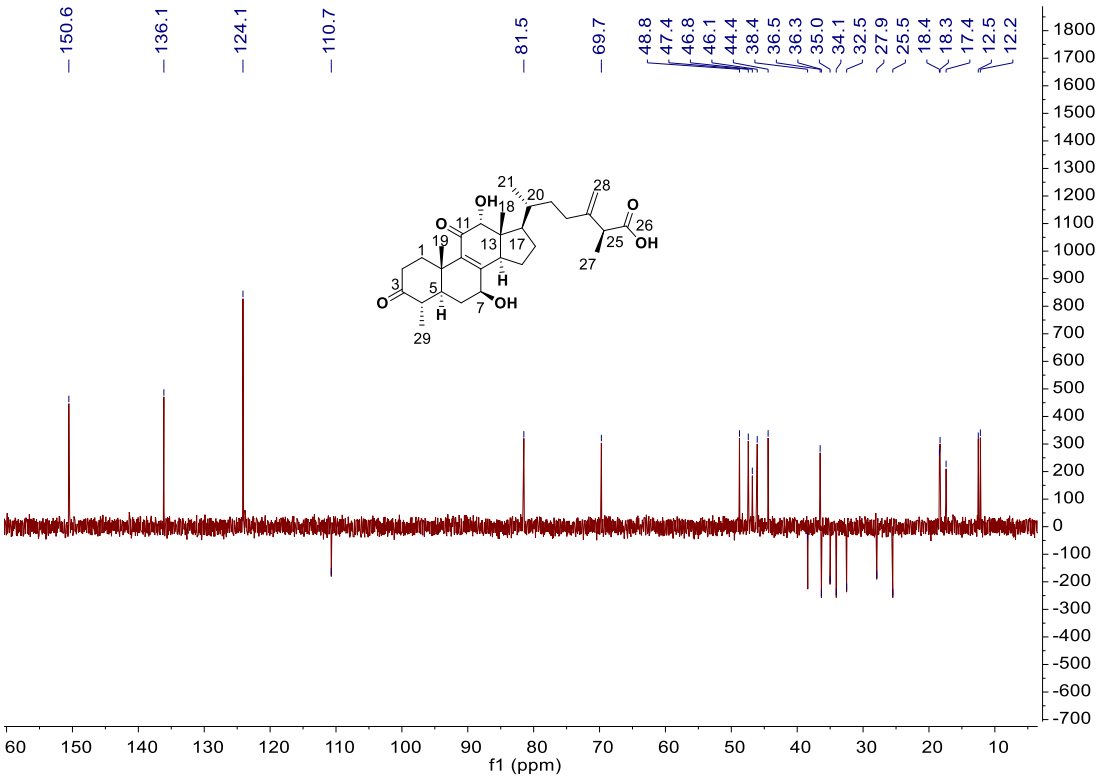


Figure S80. DEPT 135 spectrum of **9** in pyridine-d_5 (100 MHz).

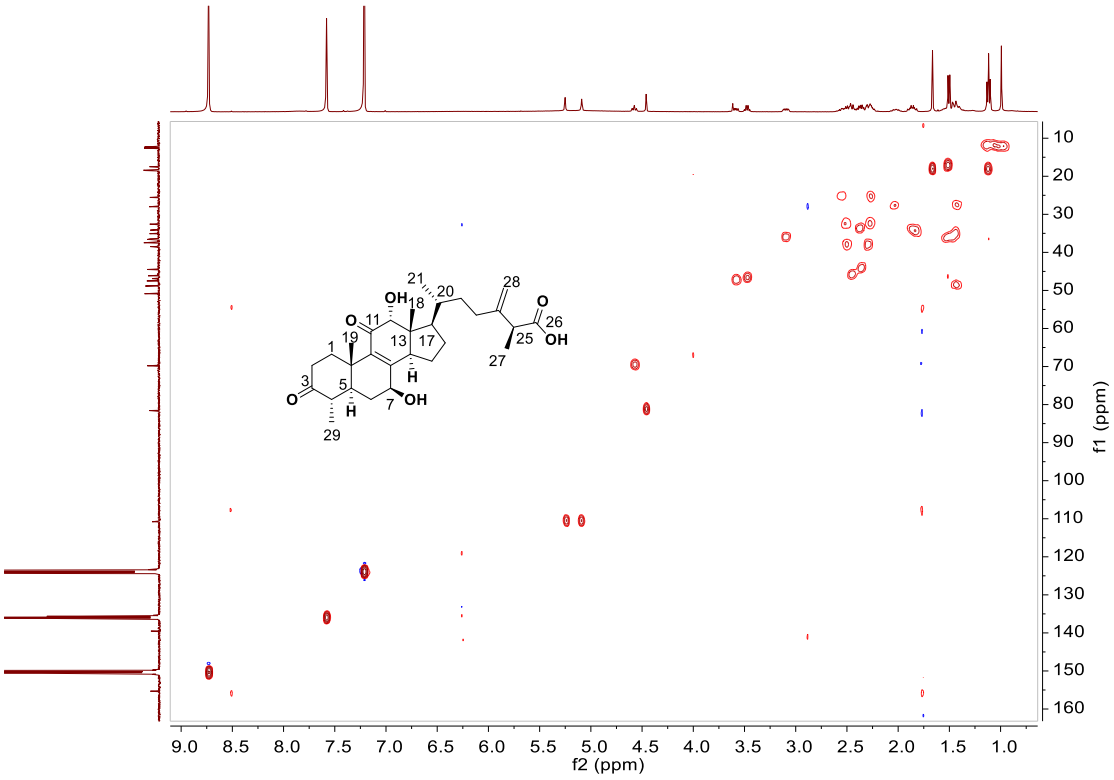


Figure S81. HSQC spectrum of **9** in pyridine-d_5 (400 MHz).

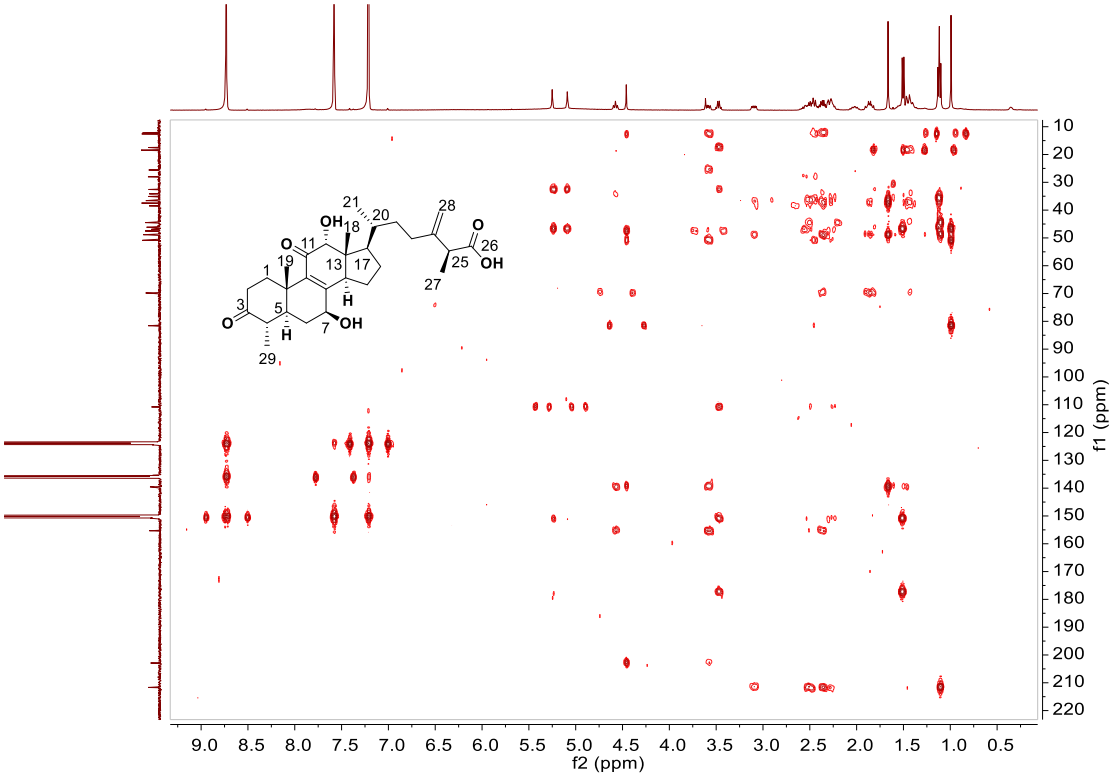


Figure S82. HMBC spectrum of **9** in pyridine-d_5 (400 MHz).

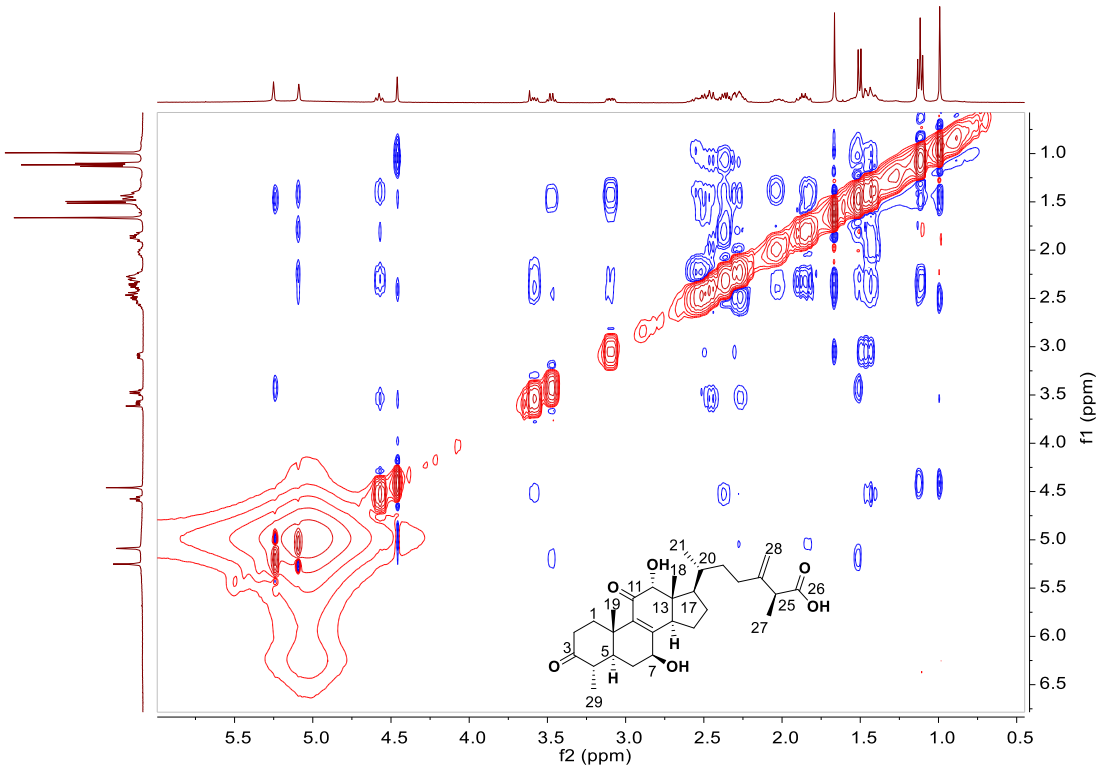


Figure S83. NOESY spectrum of **9** in pyridine-d_5 (400 MHz).

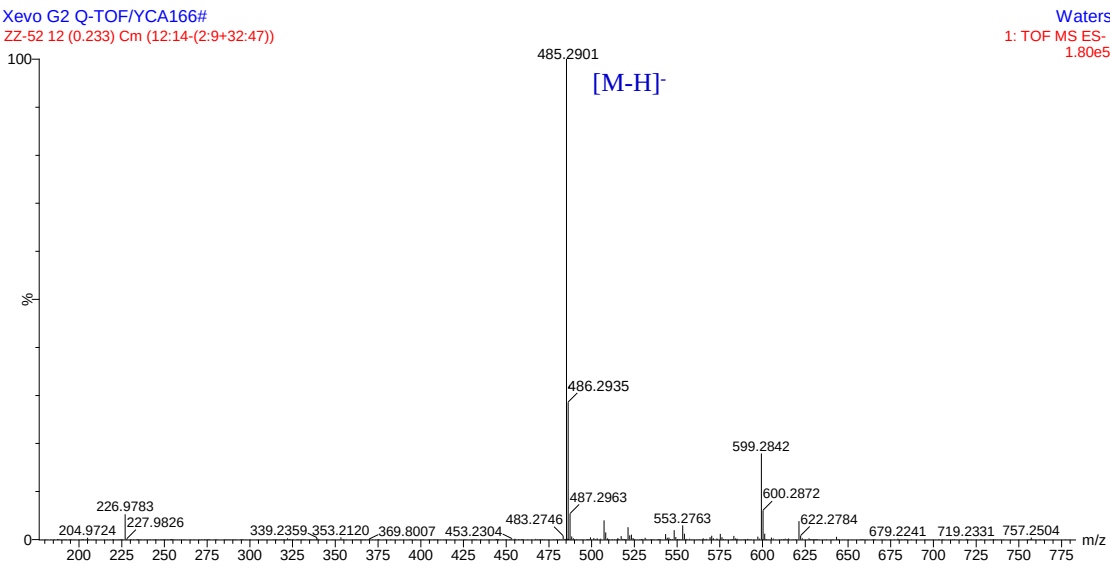


Figure S84. HR-ESI-MS spectrum of **9.**

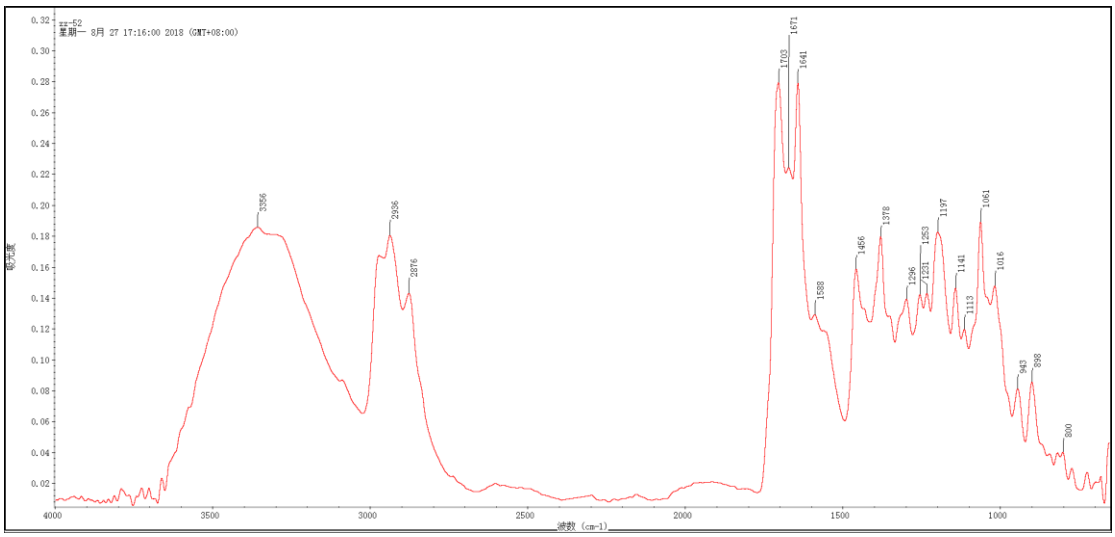


Figure S85. IR spectrum of **9**.

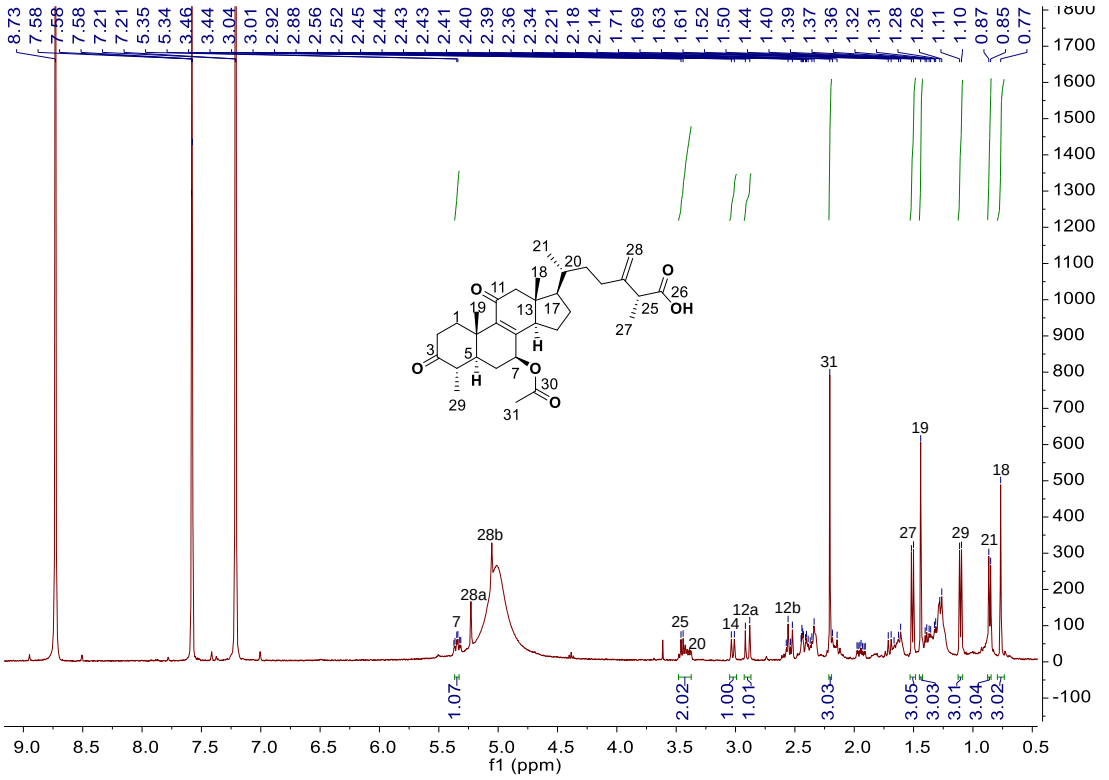


Figure S86. ^{1}H-NMR spectrum of **10** in pyridine-d_5 (400 MHz).

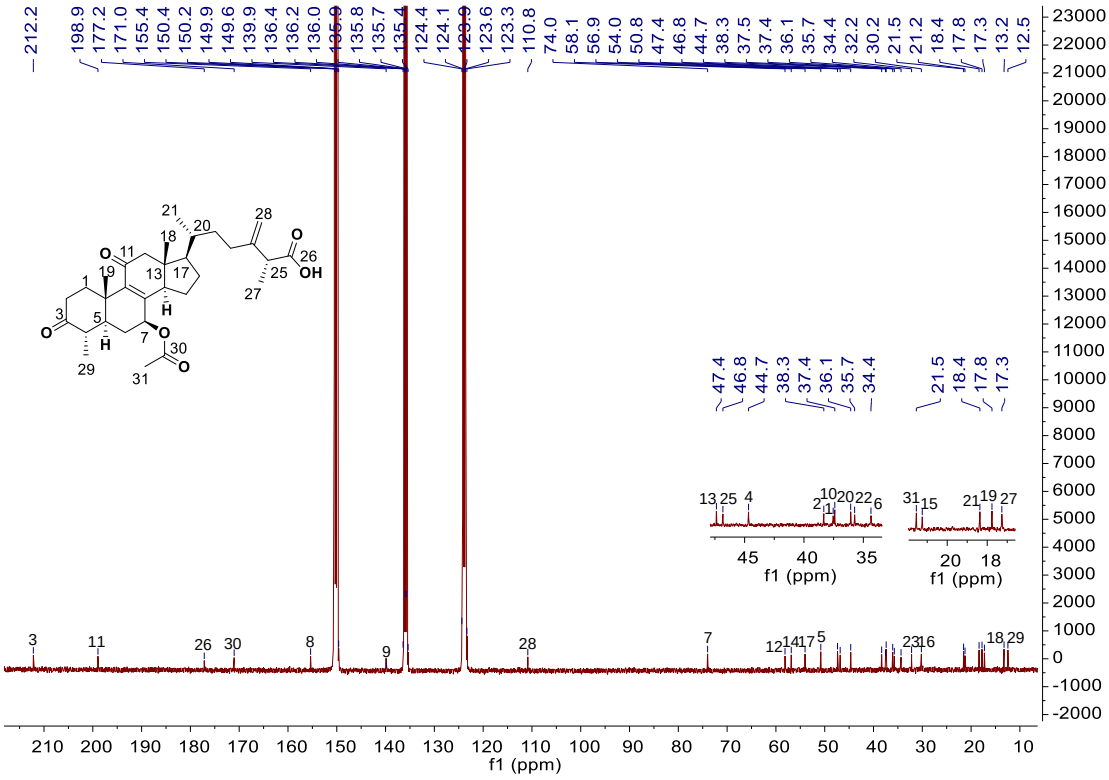


Figure S87. ^{13}C-NMR spectrum of **10** in pyridine-d_5 (100 MHz).

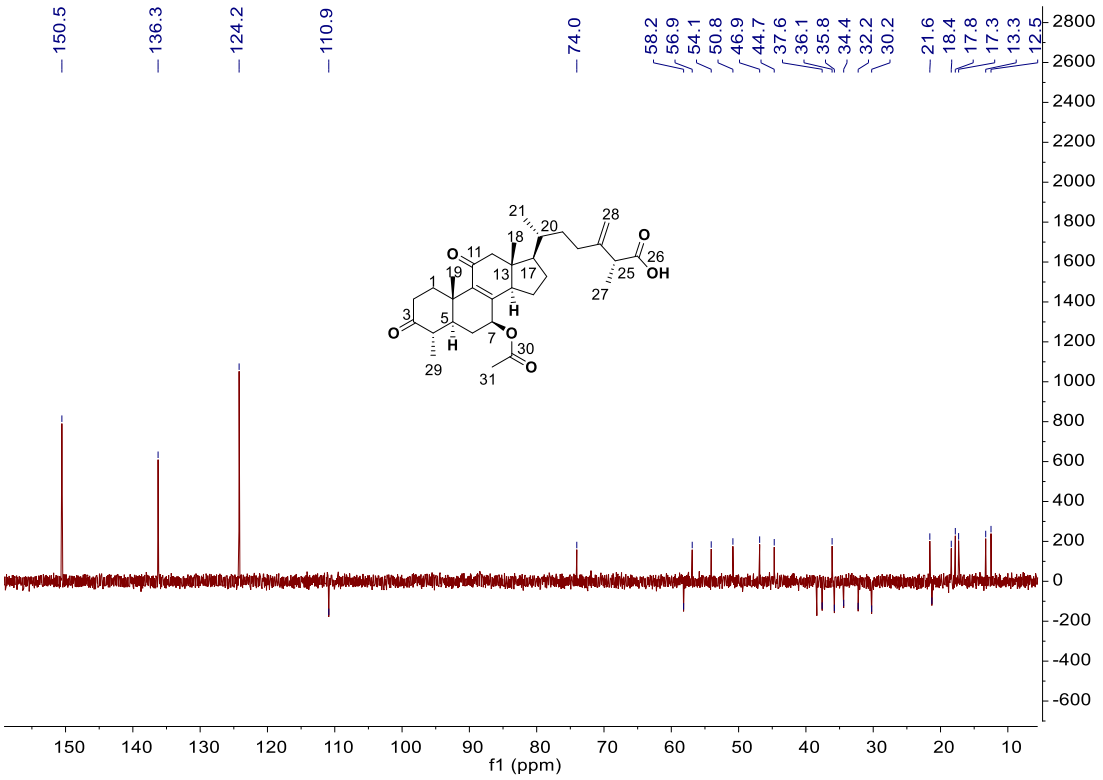


Figure S88. DEPT 135 spectrum of **10** in pyridine-d_5 (100 MHz).

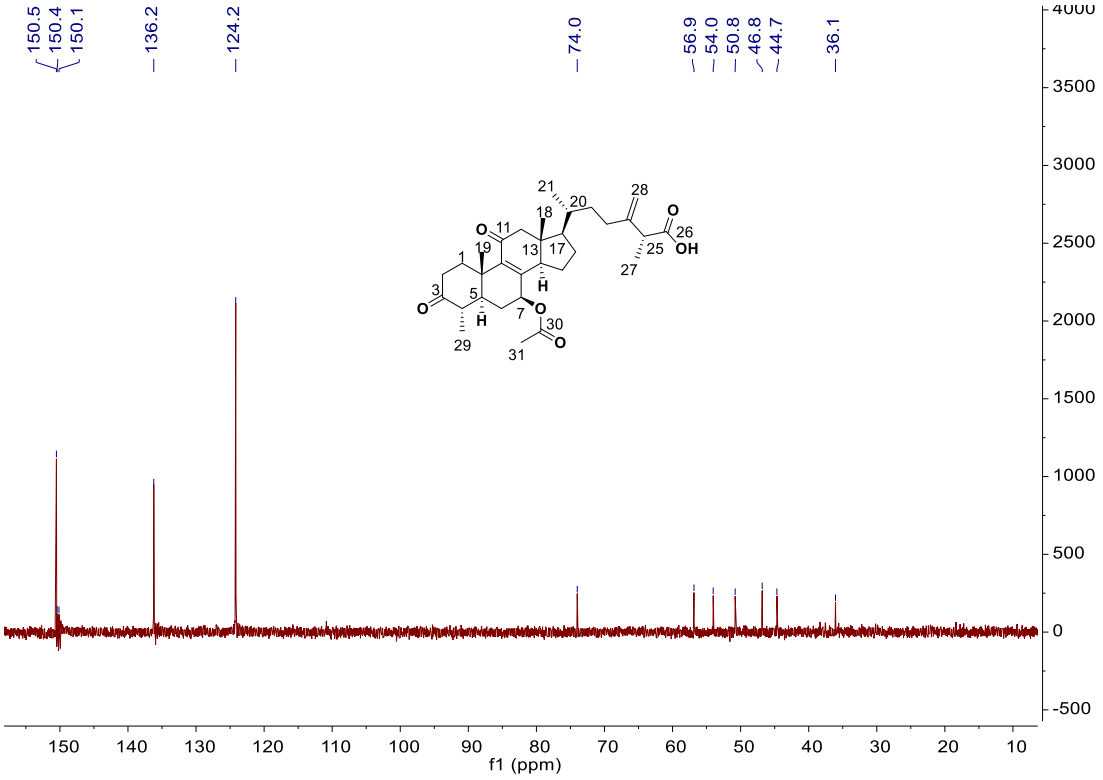


Figure S89. DEPT 90 spectrum of **10** in pyridine-d_5 (100 MHz).

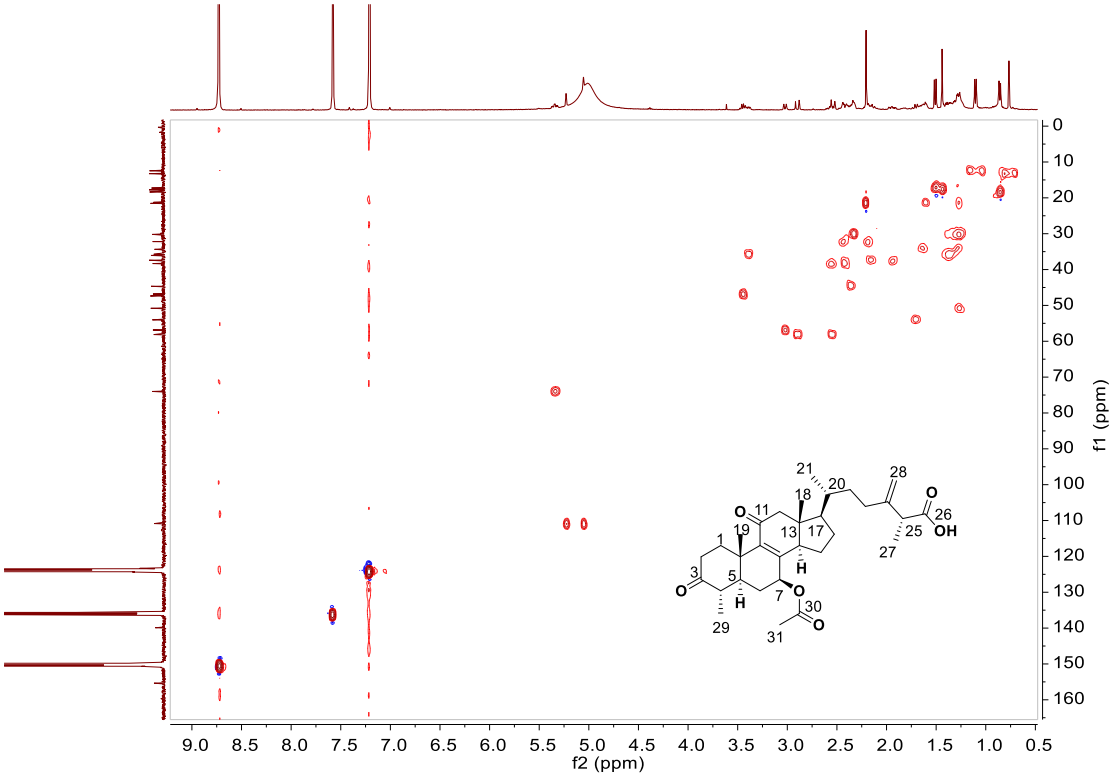


Figure S90. HSQC spectrum of **10** in pyridine-d_5 (400 MHz).

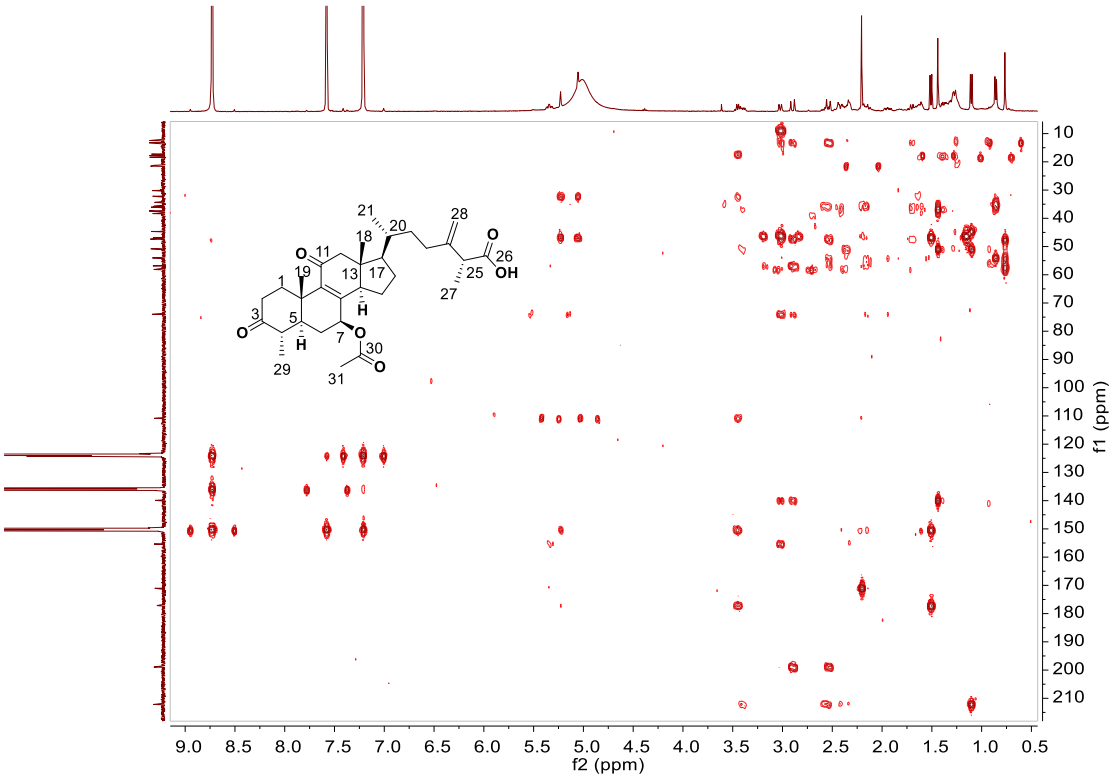


Figure S91. HMBC spectrum of **10** in pyridine-d_5 (400 MHz).

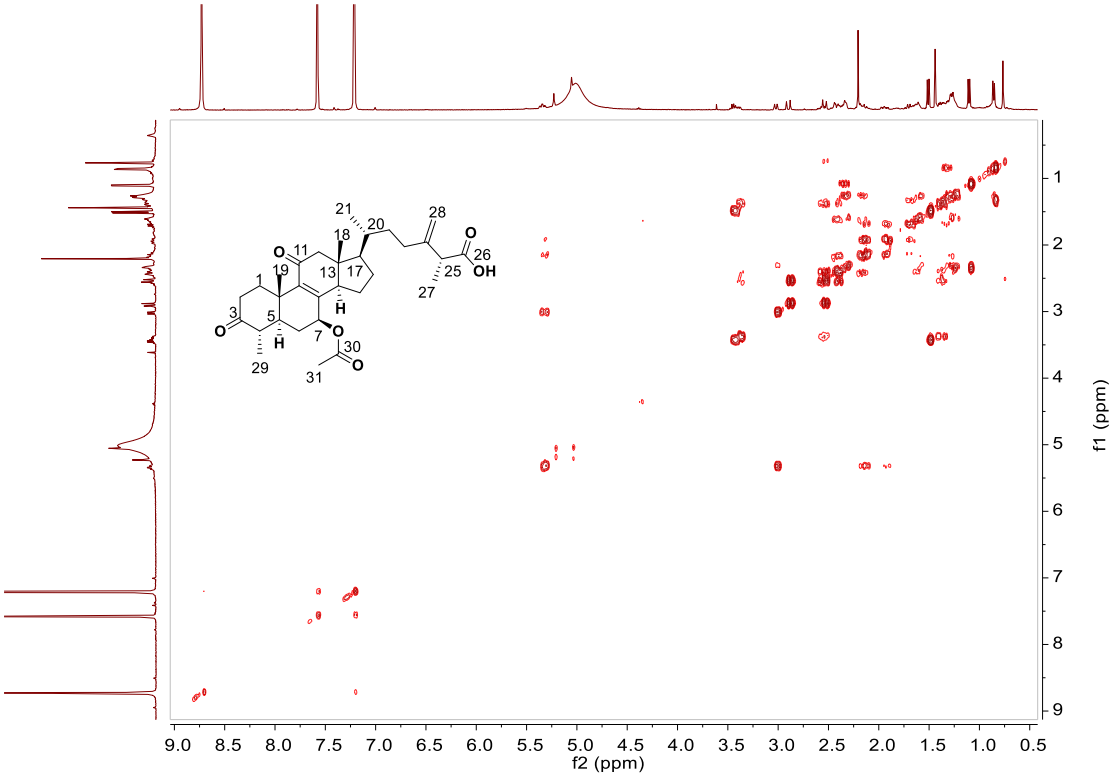


Figure S92. ^{1}H-^{1}H COSY spectrum of **10** in pyridine-d_5 (400 MHz).

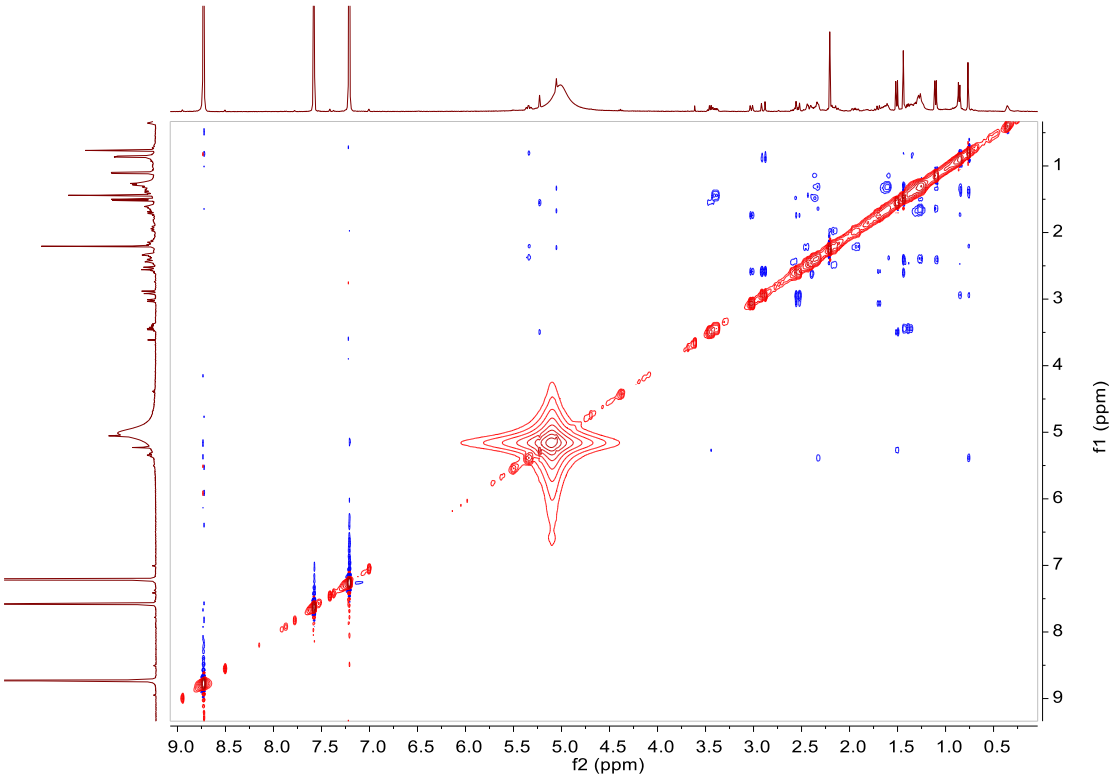


Figure S93. NOESY spectrum of **10** in pyridine-d_5 (400 MHz).

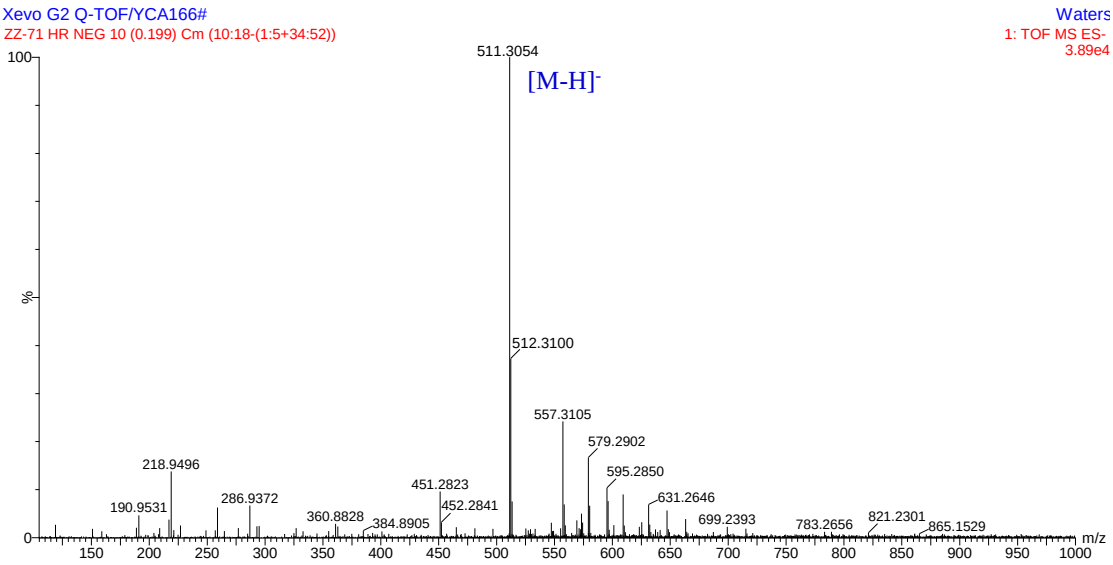


Figure S94. HR-ESI-MS spectrum of **10.**

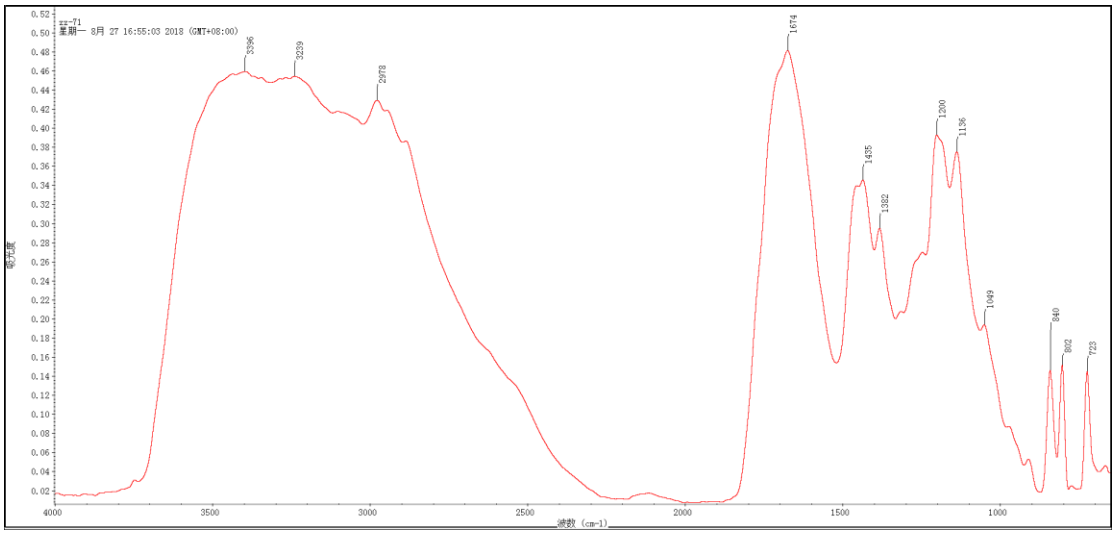


Figure S95. IR spectrum of **10**.

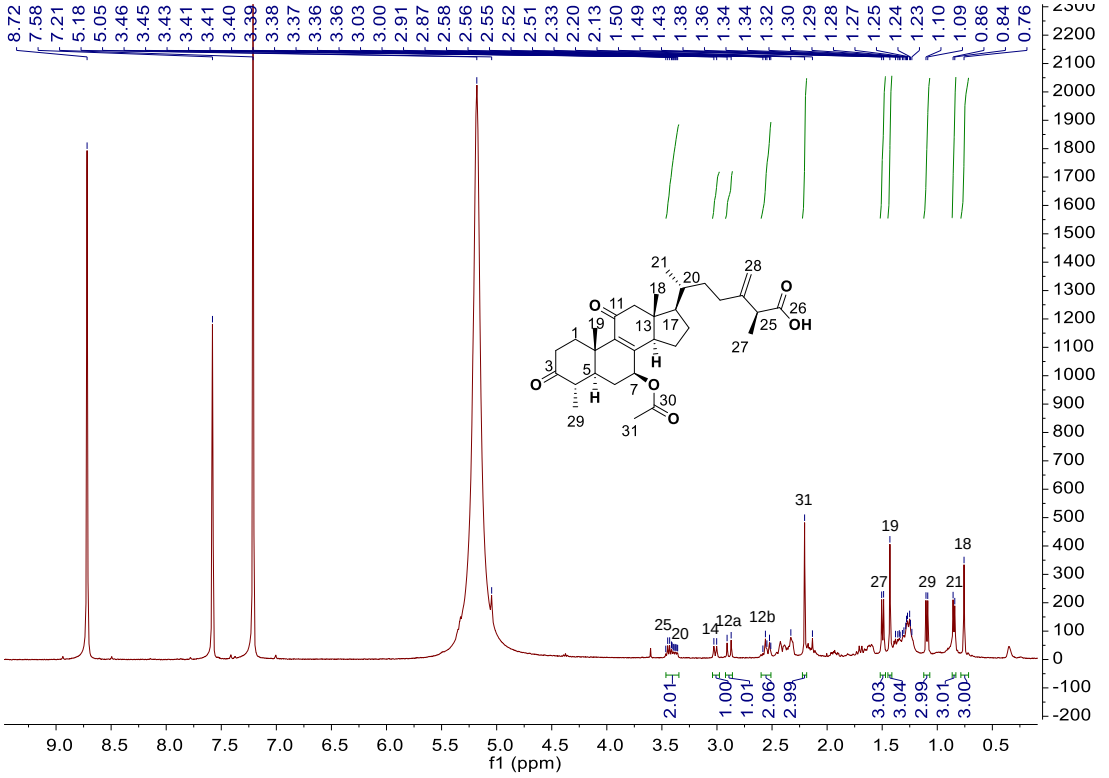


Figure S96. ^{1}H-NMR spectrum of **11** in pyridine-d_5 (400 MHz).

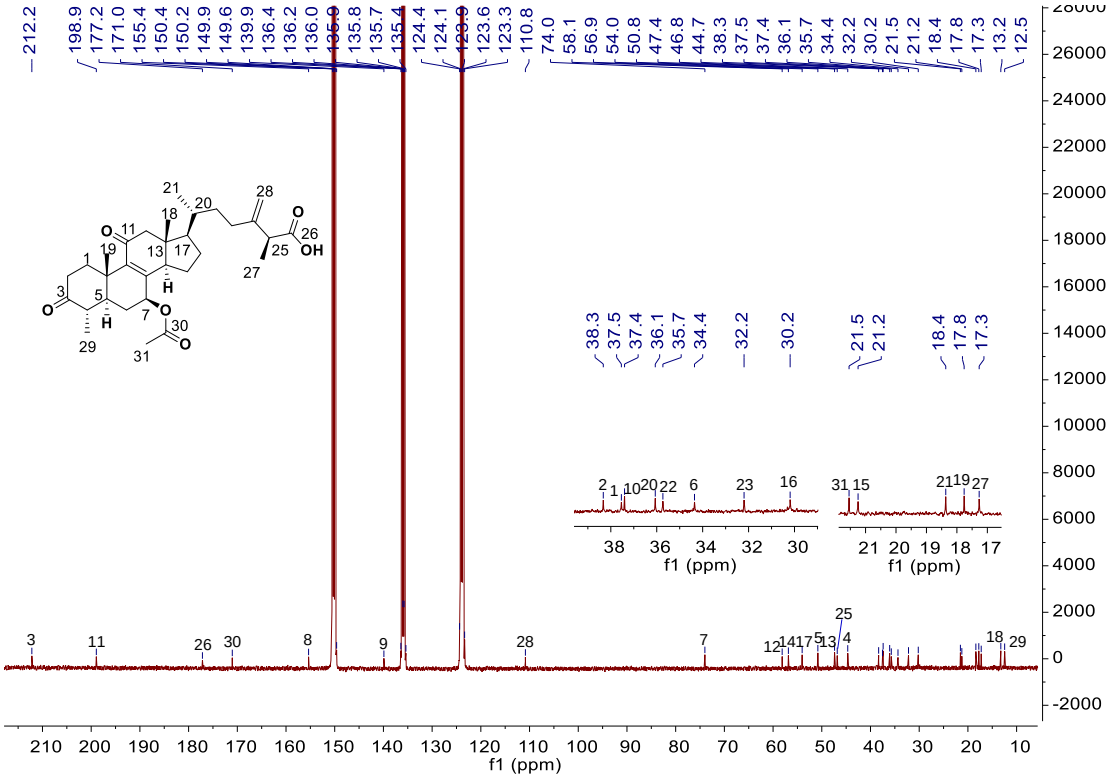


Figure S97. ^{13}C-NMR spectrum of **11** in pyridine-d_5 (100 MHz).

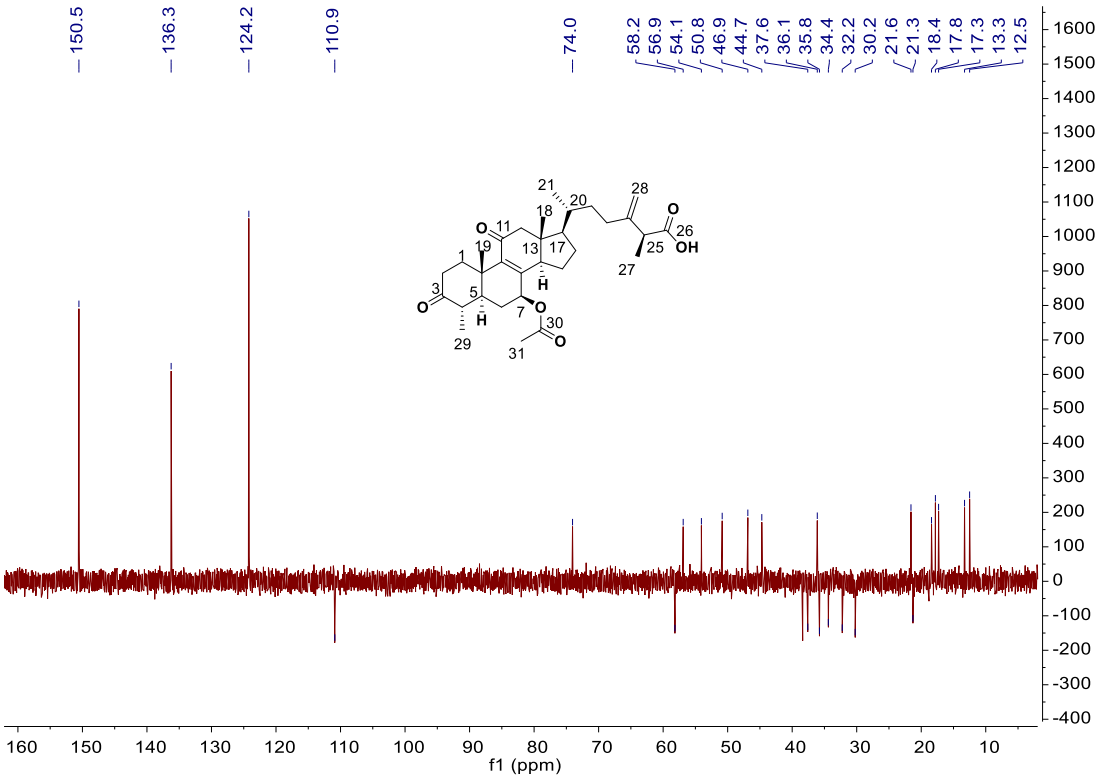


Figure S98. DEPT 135 spectrum of **11** in pyridine-d_5 (100 MHz).

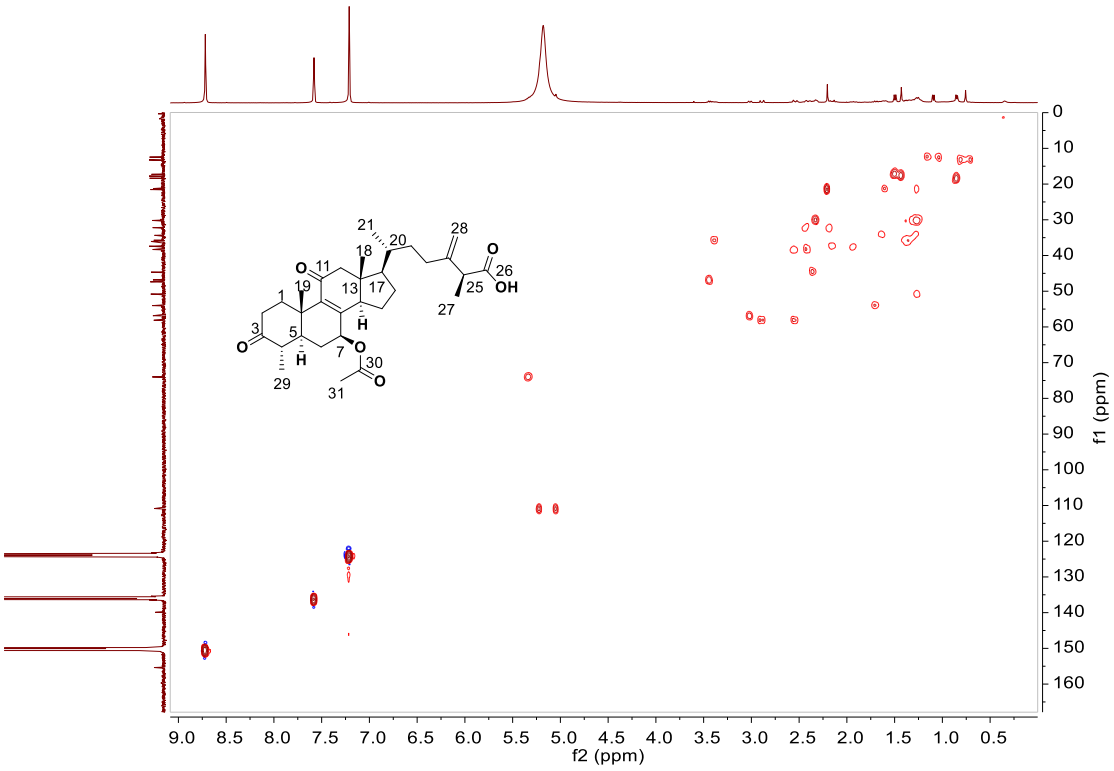


Figure S99. HSQC spectrum of **11** in pyridine-d_5 (400 MHz).

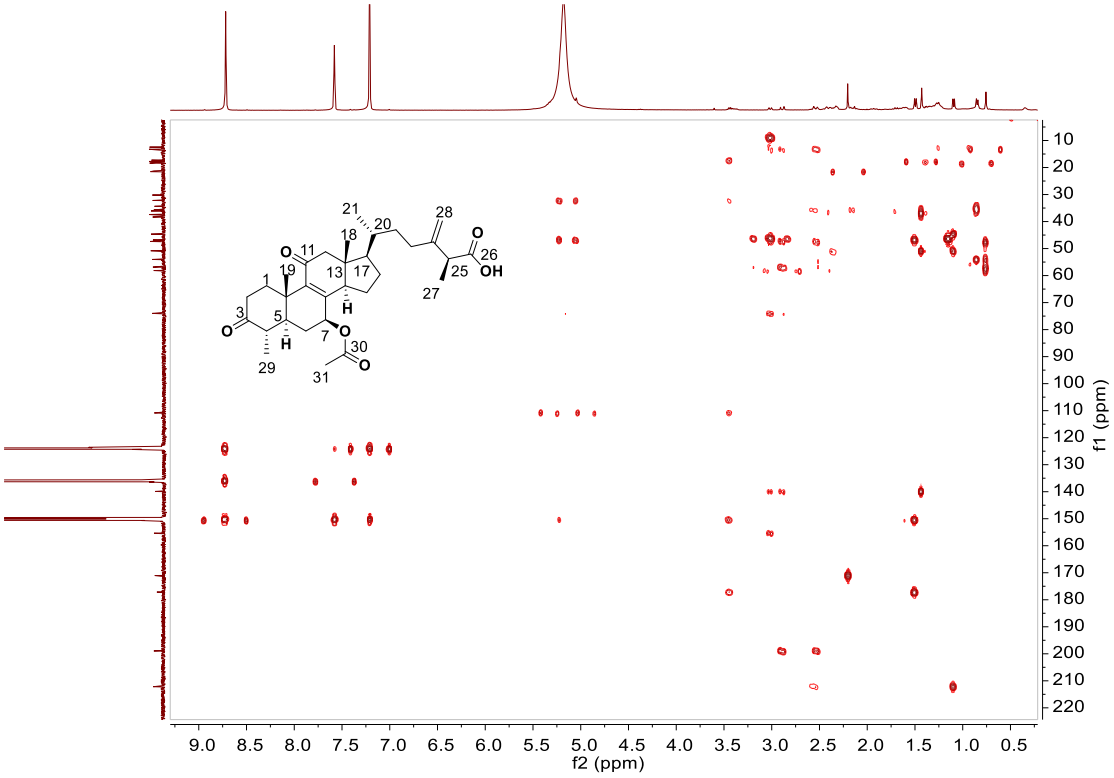


Figure S100. HMBC spectrum of **11** in pyridine-d_5 (400 MHz).

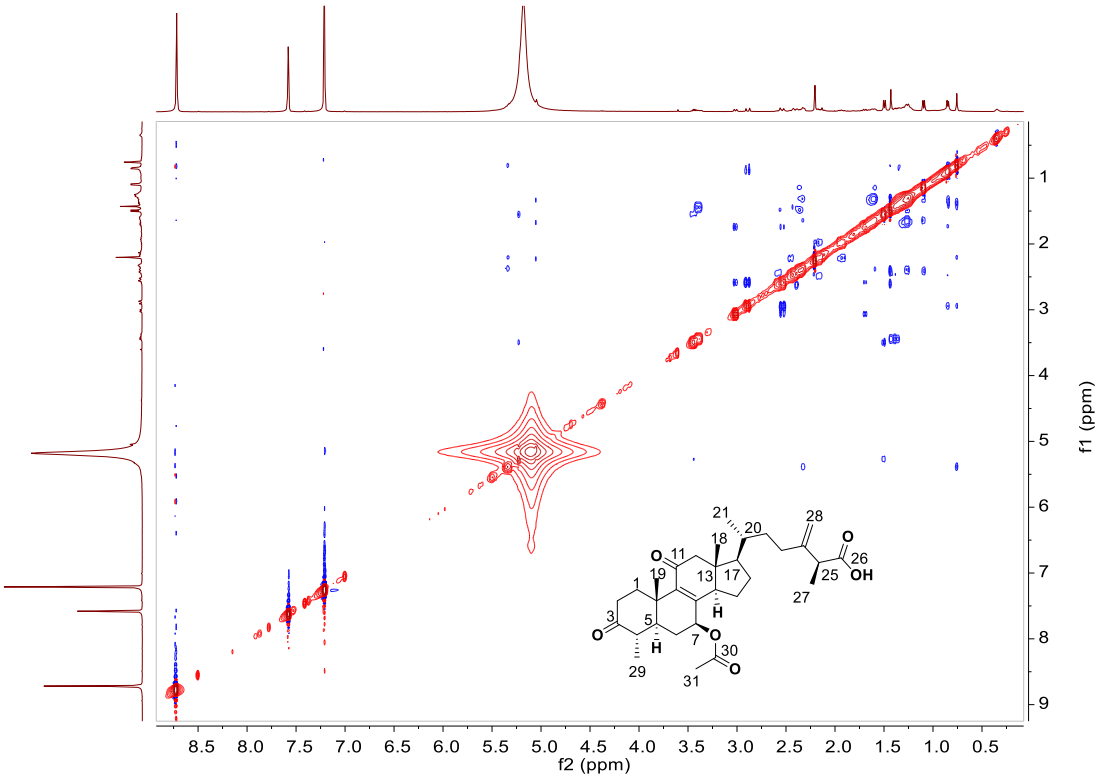


Figure S101. NOESY spectrum of **11** in pyridine-d_5 (400 MHz).

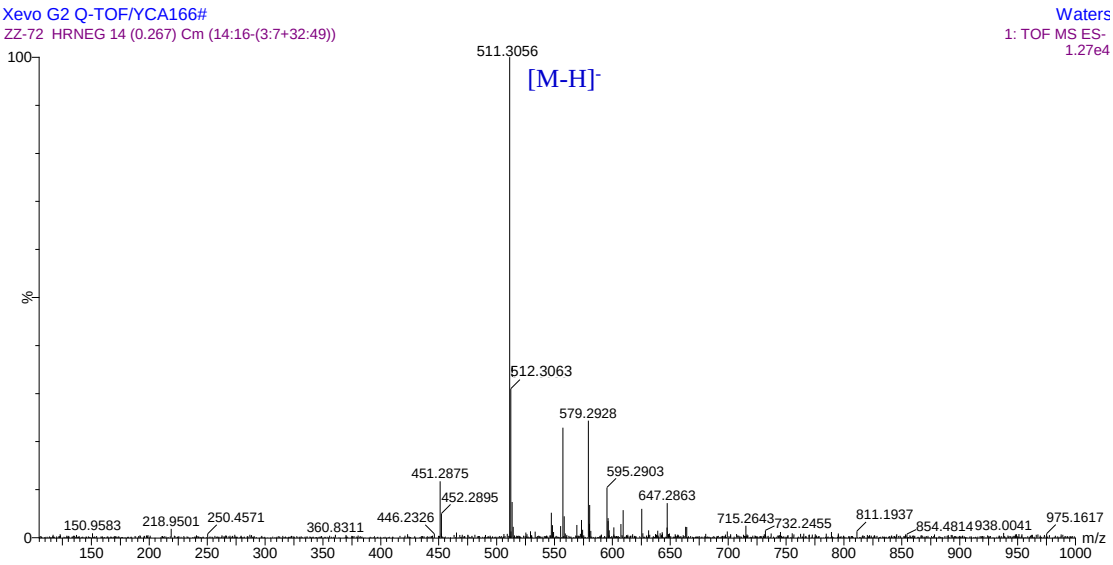


Figure S102. HR-ESI-MS spectrum of **11.**

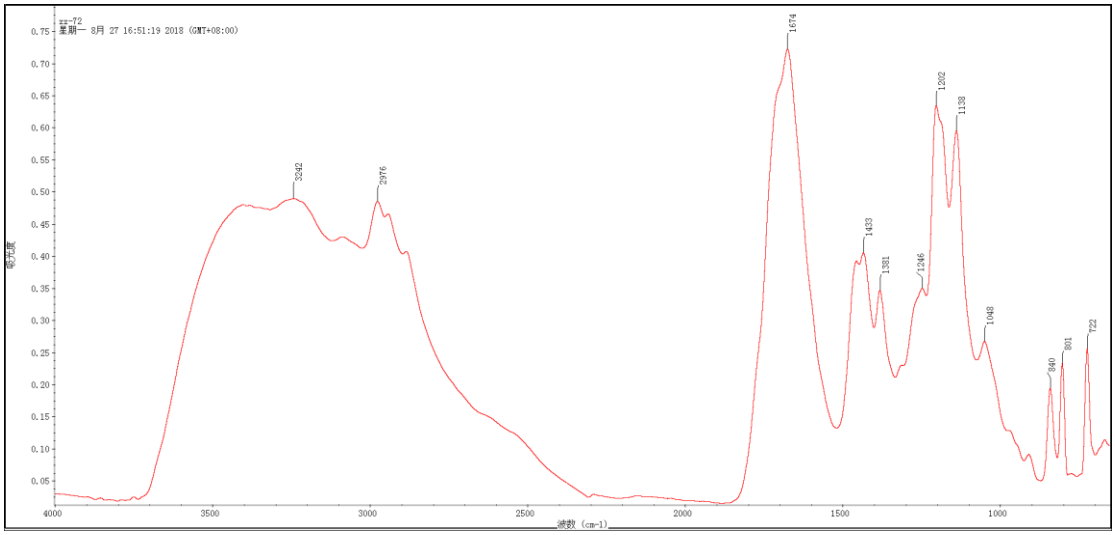


Figure S103. IR spectrum of **11**.

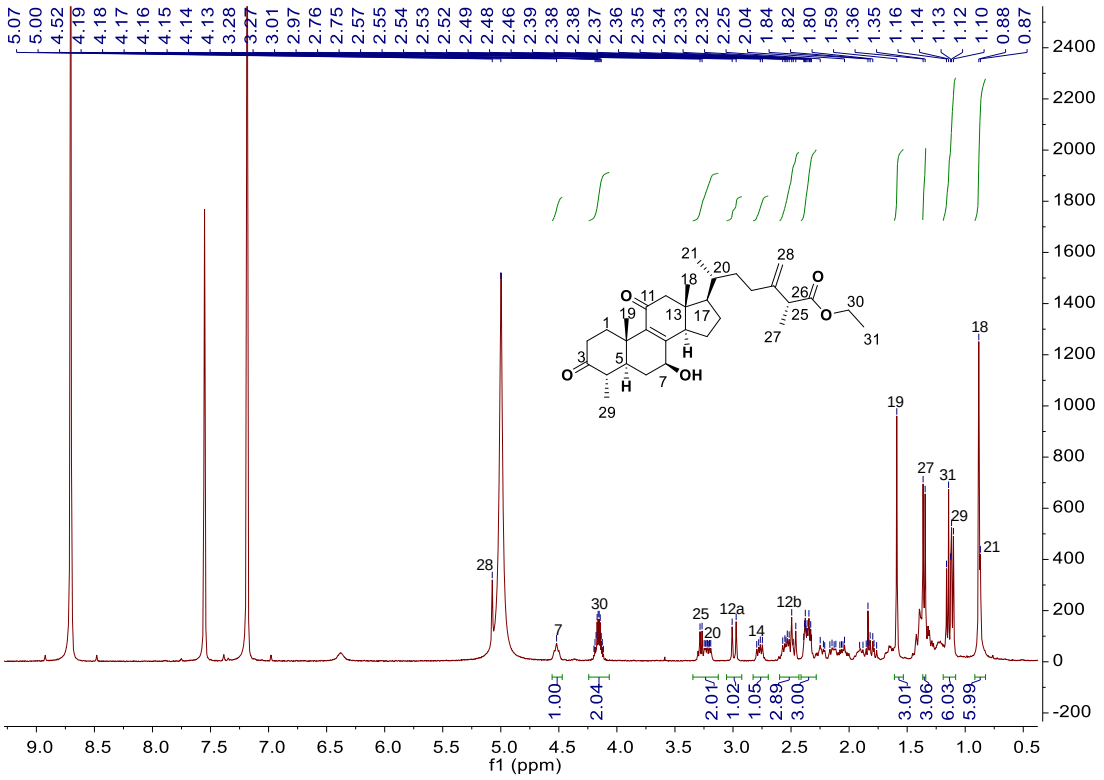


Figure S104. ^{1}H-NMR spectrum of **12** in pyridine-d_5 (400 MHz).

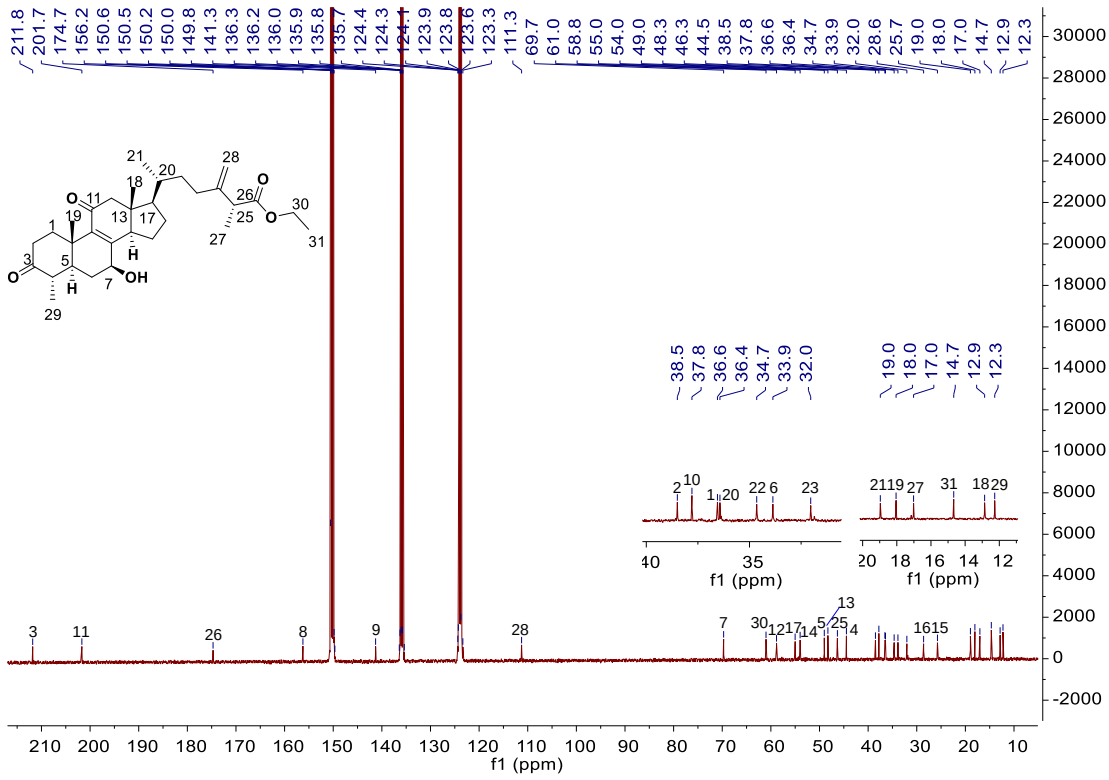


Figure S105. ^{13}C-NMR spectrum of **12** in pyridine-d_5 (100 MHz).

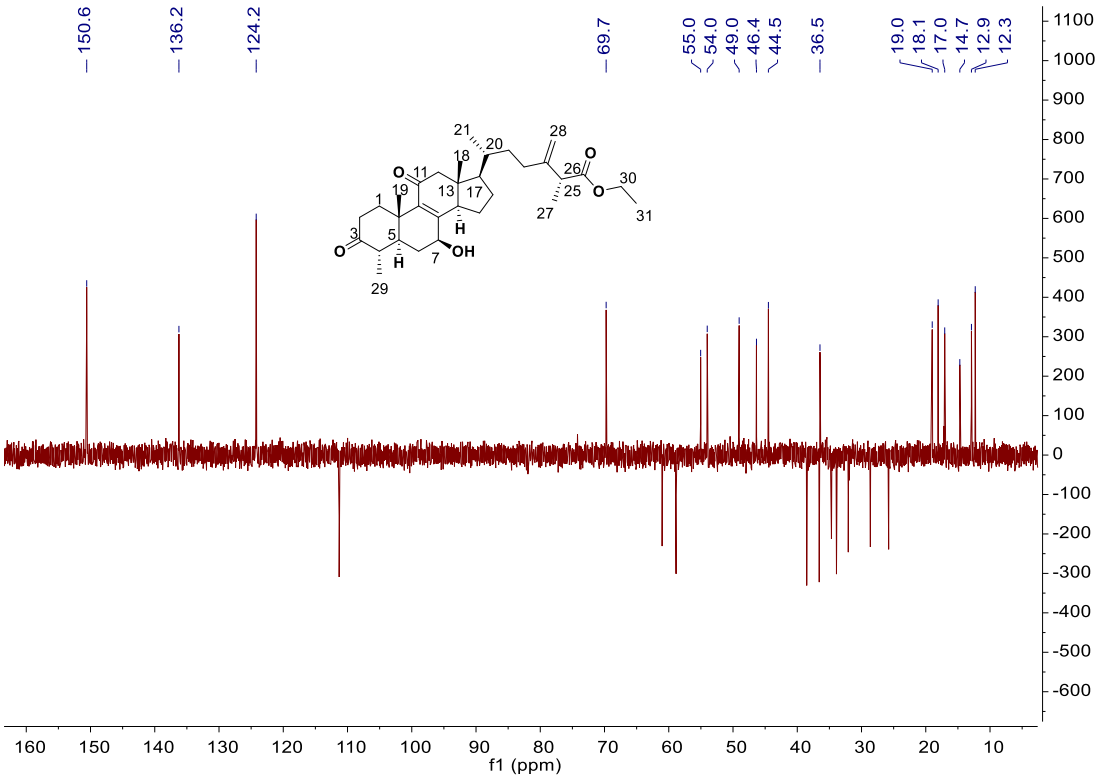


Figure S106. DEPT 135 spectrum of **12** in pyridine-d_5 (100 MHz).

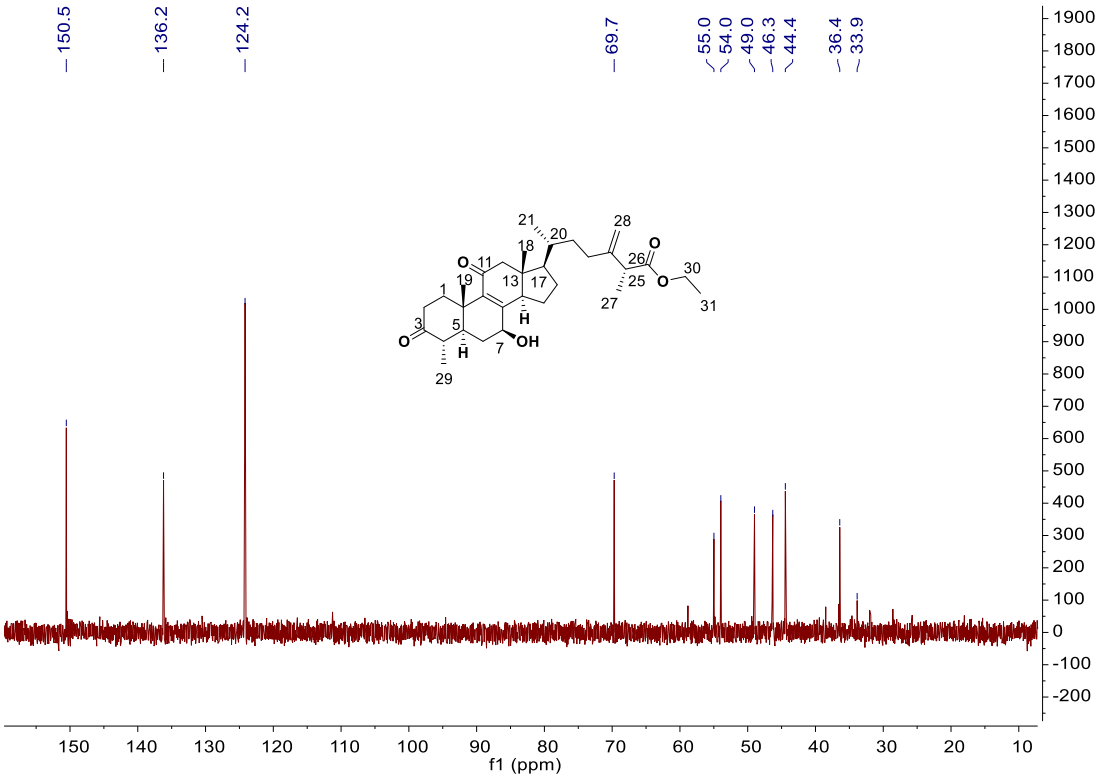


Figure S107. DEPT 90 spectrum of **12** in pyridine-d_5 (100 MHz).

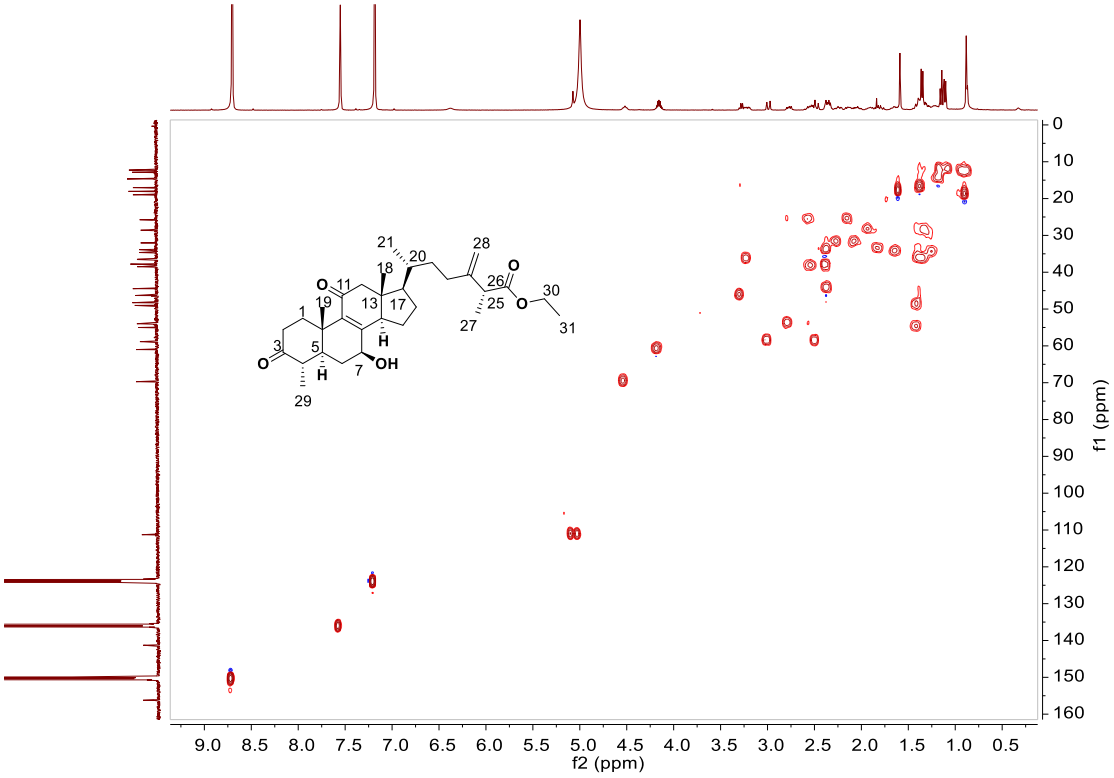


Figure S108. HSQC spectrum of **12** in pyridine-d_5 (400 MHz).

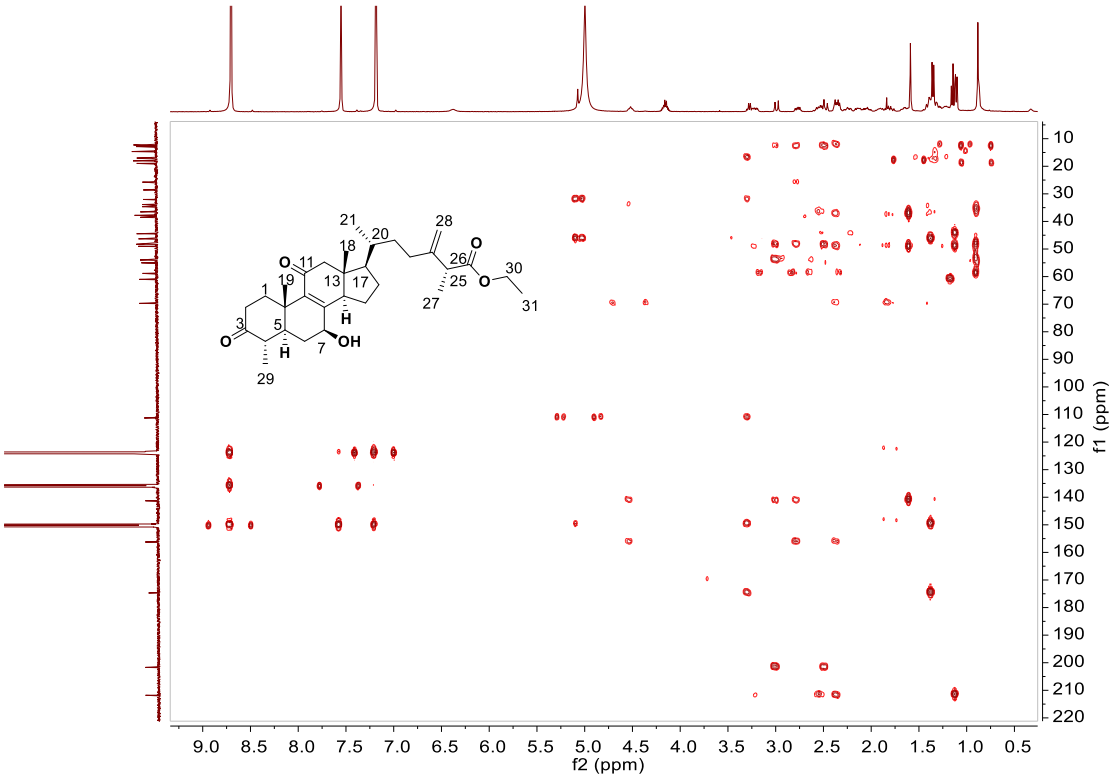


Figure S109. HMBC spectrum of **12** in pyridine-d_5 (400 MHz).

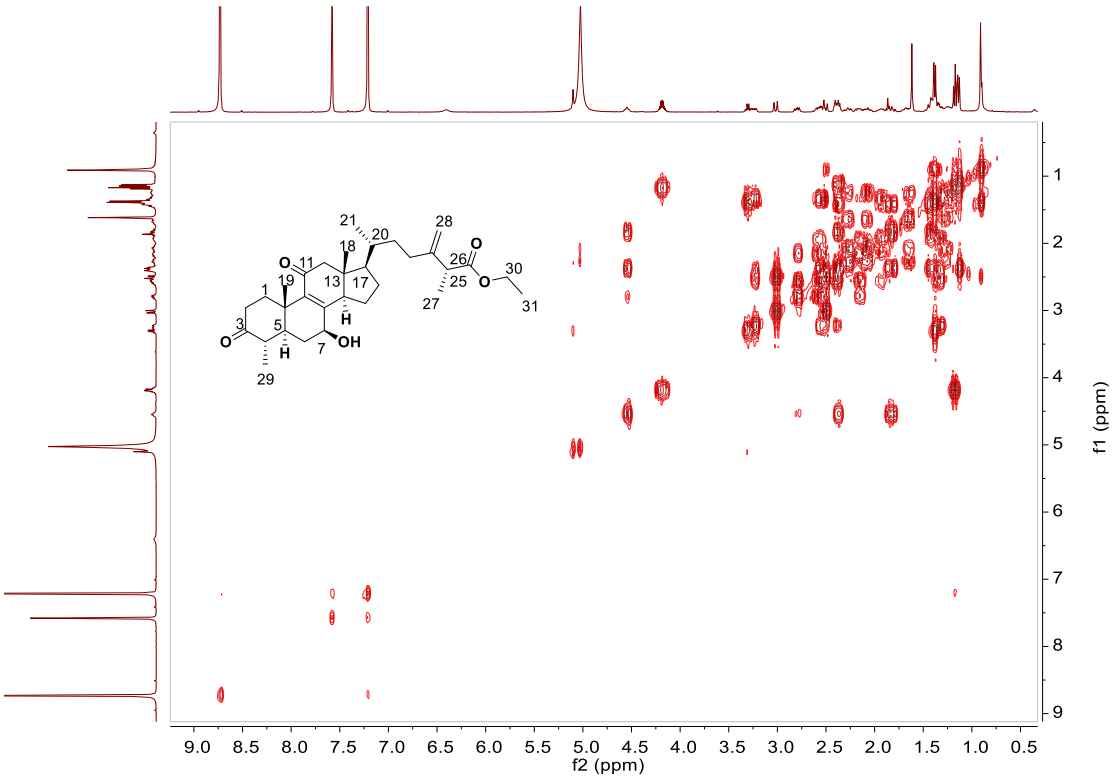


Figure S110. ^{1}H-^{1}H COSY spectrum of **12** in pyridine-d_5 (400 MHz).

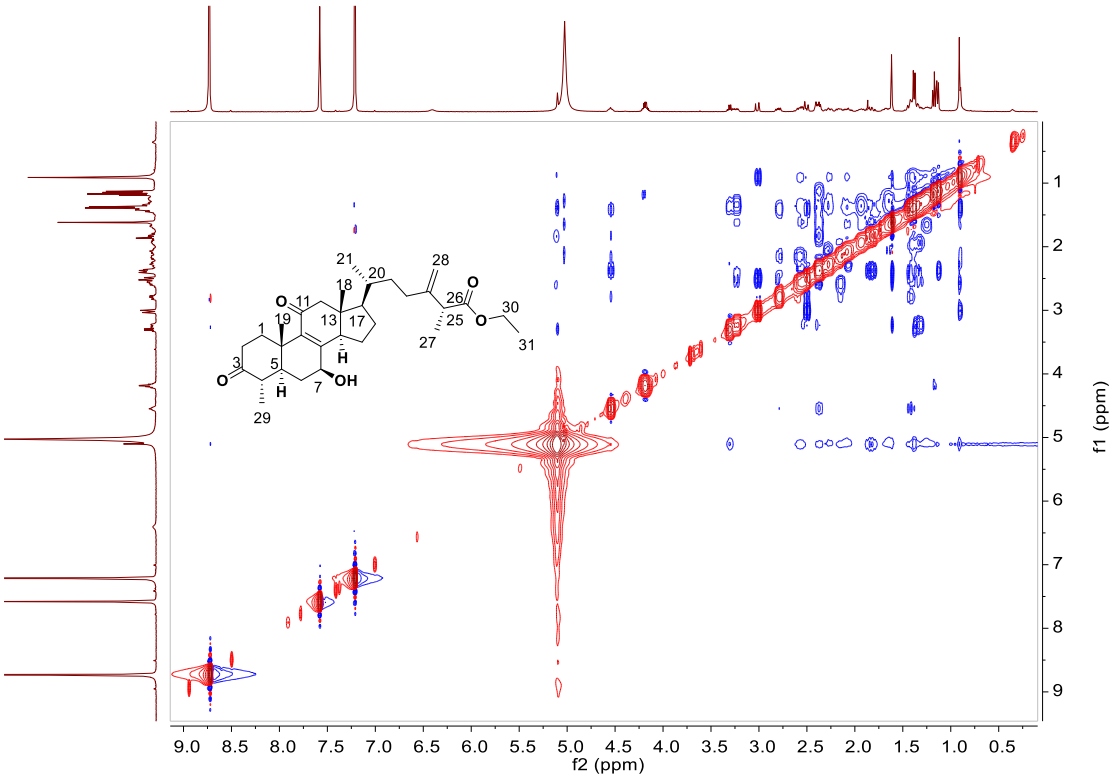


Figure S111. NOESY spectrum of **12** in pyridine-d_5 (400 MHz).

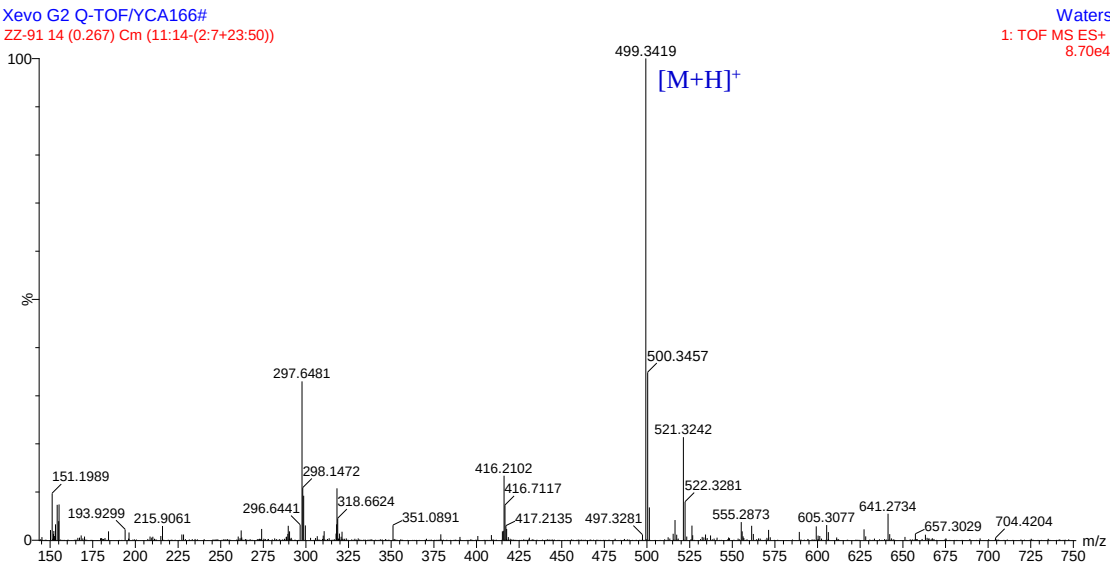


Figure S112. HR-ESI-MS spectrum of **12.**

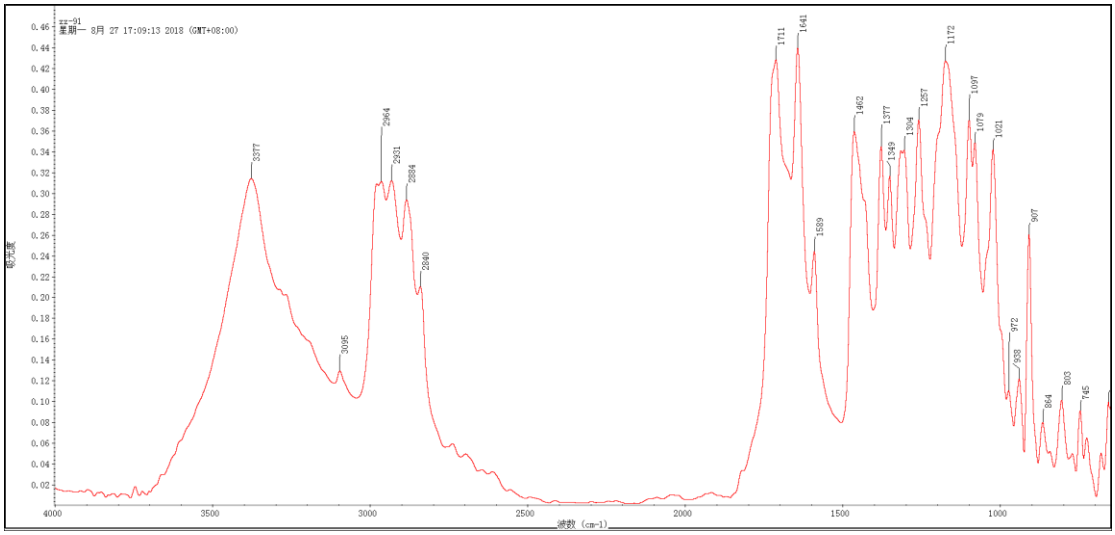


Figure S113. IR spectrum of **12**.

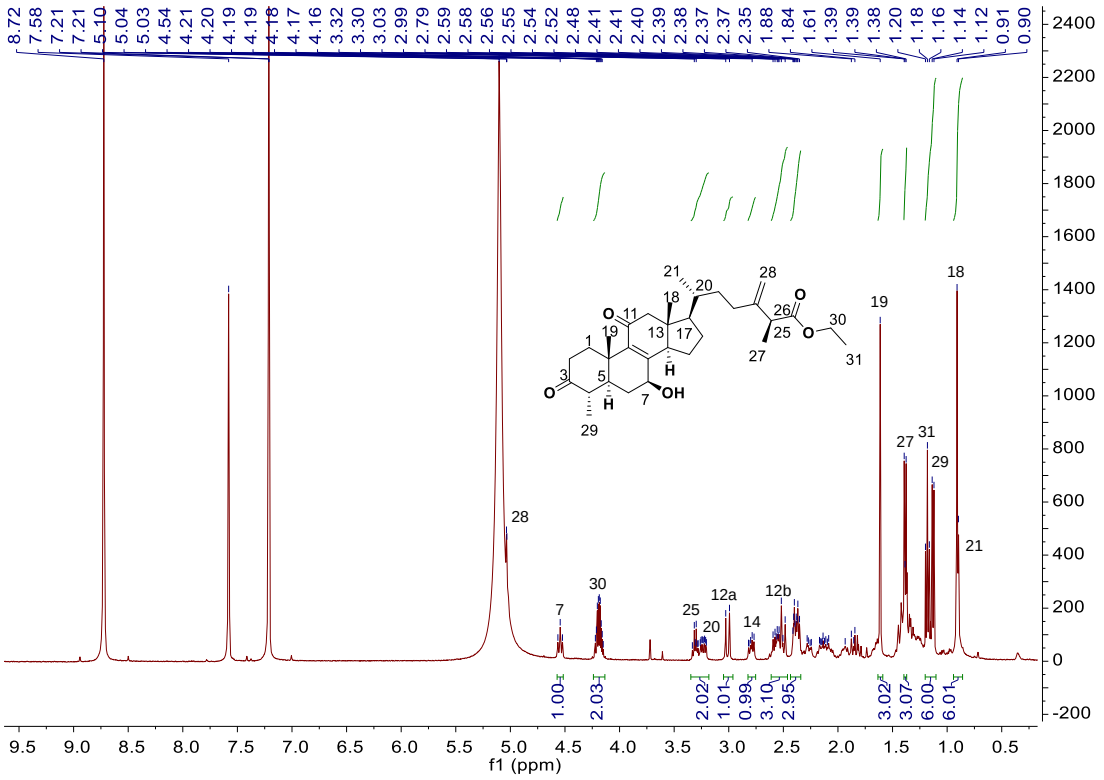


Figure S114. ^{1}H-NMR spectrum of **13** in pyridine-d_5 (400 MHz).

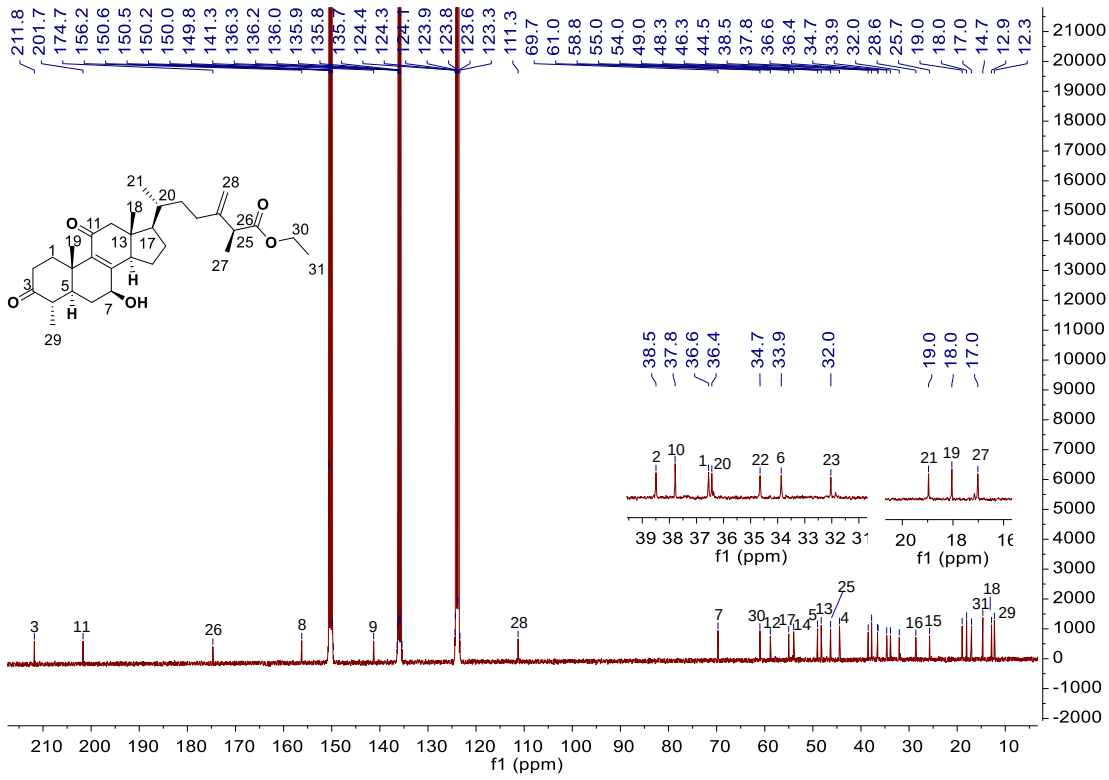


Figure S115. ^{13}C-NMR spectrum of **13** in pyridine-d_5 (100 MHz).

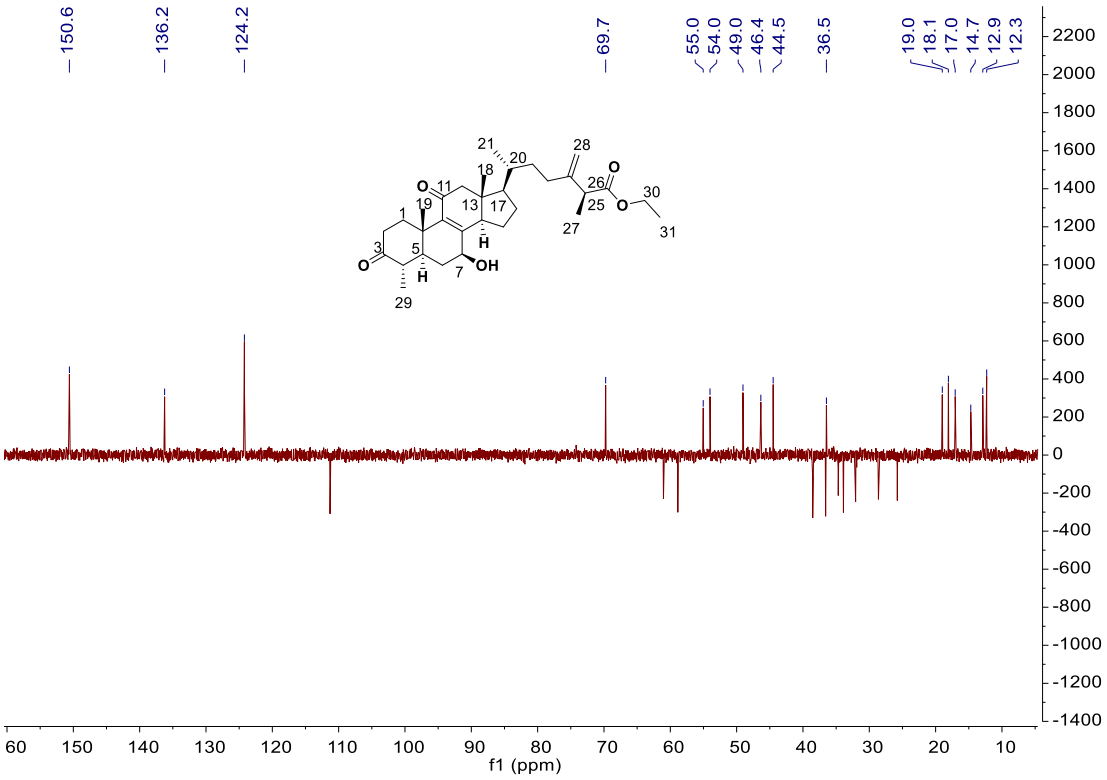


Figure S116. DEPT 135 spectrum of **13** in pyridine-d_5 (100 MHz).

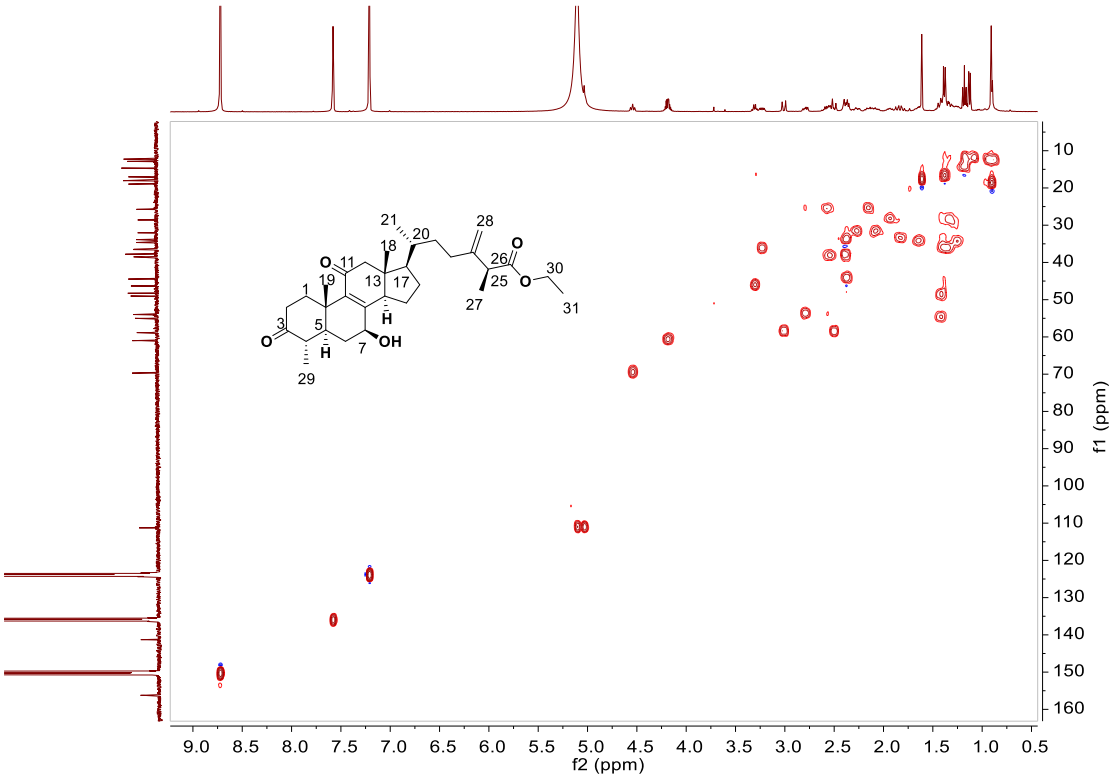


Figure S117. HSQC spectrum of **13** in pyridine-d_5 (400 MHz).

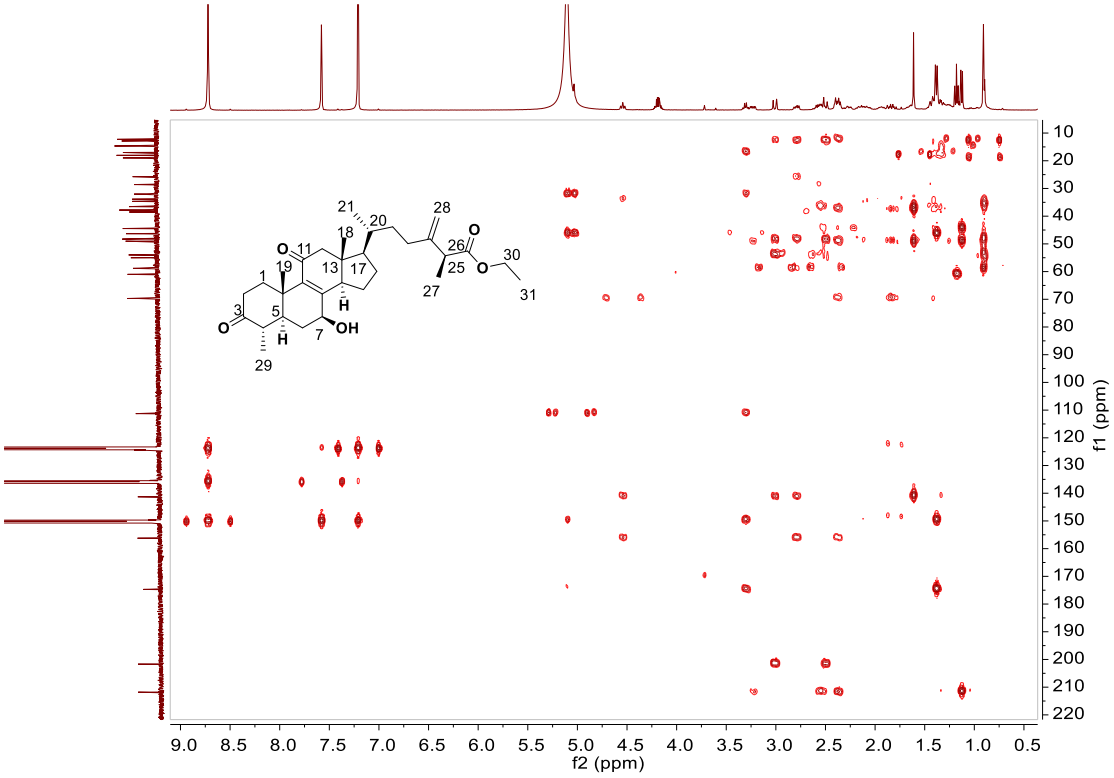


Figure S118. HMBC spectrum of **13** in pyridine-d_5 (400 MHz).

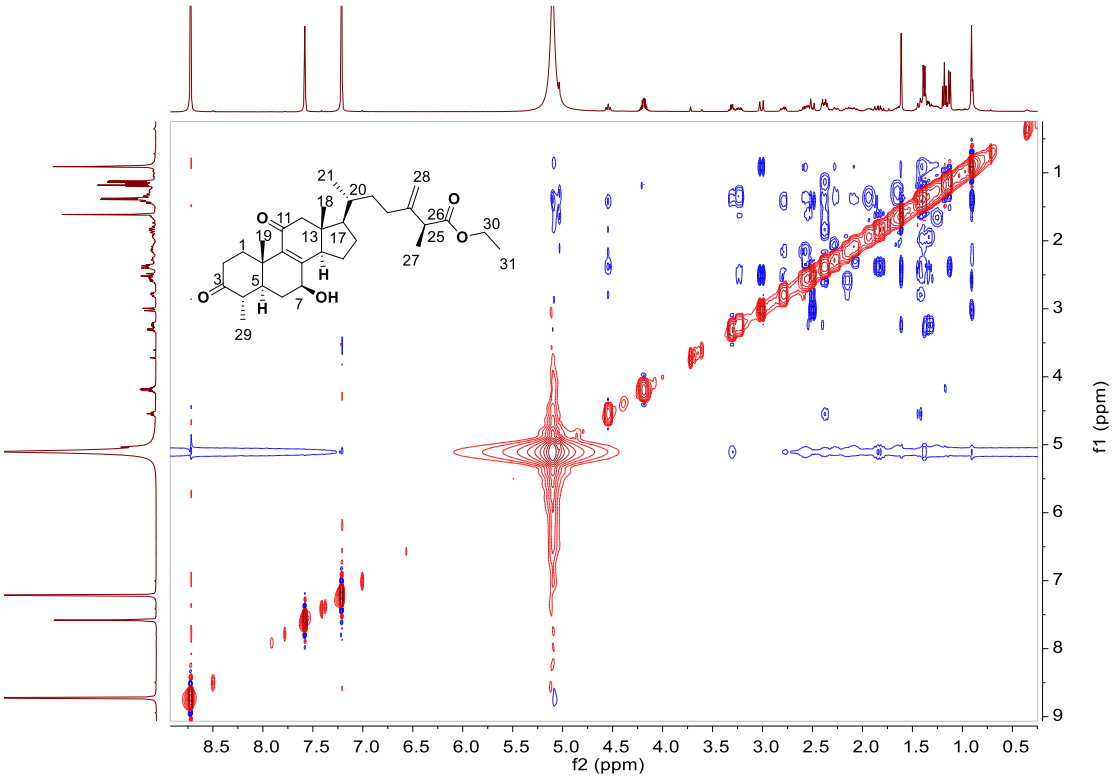


Figure S119. NOESY spectrum of **13** in pyridine-d_5 (400 MHz).

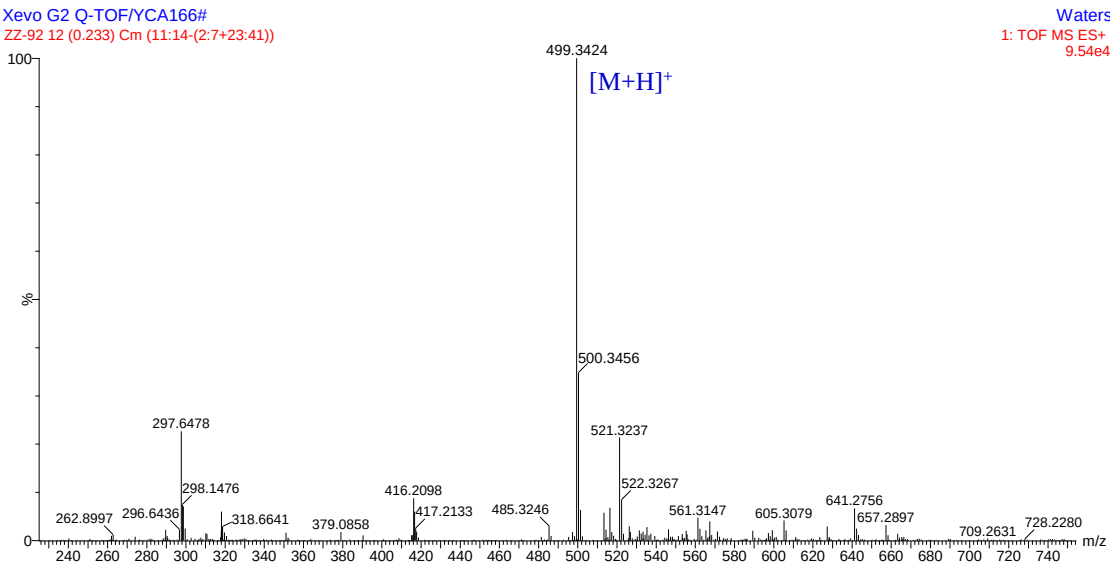


Figure S120. HR-ESI-MS spectrum of **13.**

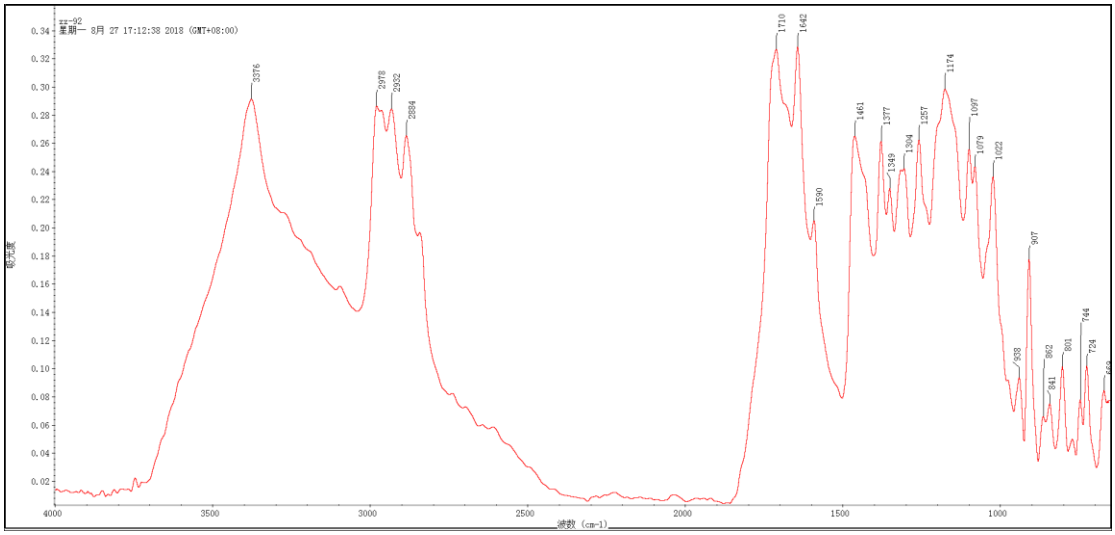


Figure S121. IR spectrum of **13**.

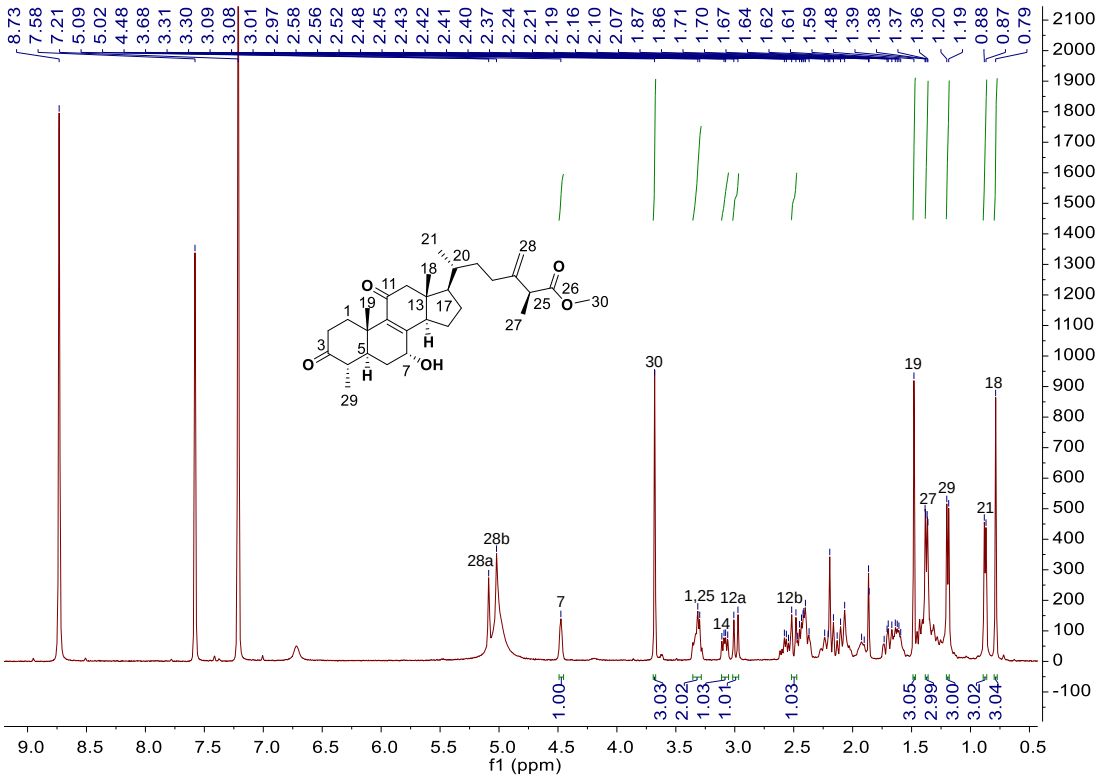


Figure S122. ^{1}H-NMR spectrum of **14** in pyridine-d_5 (400 MHz).

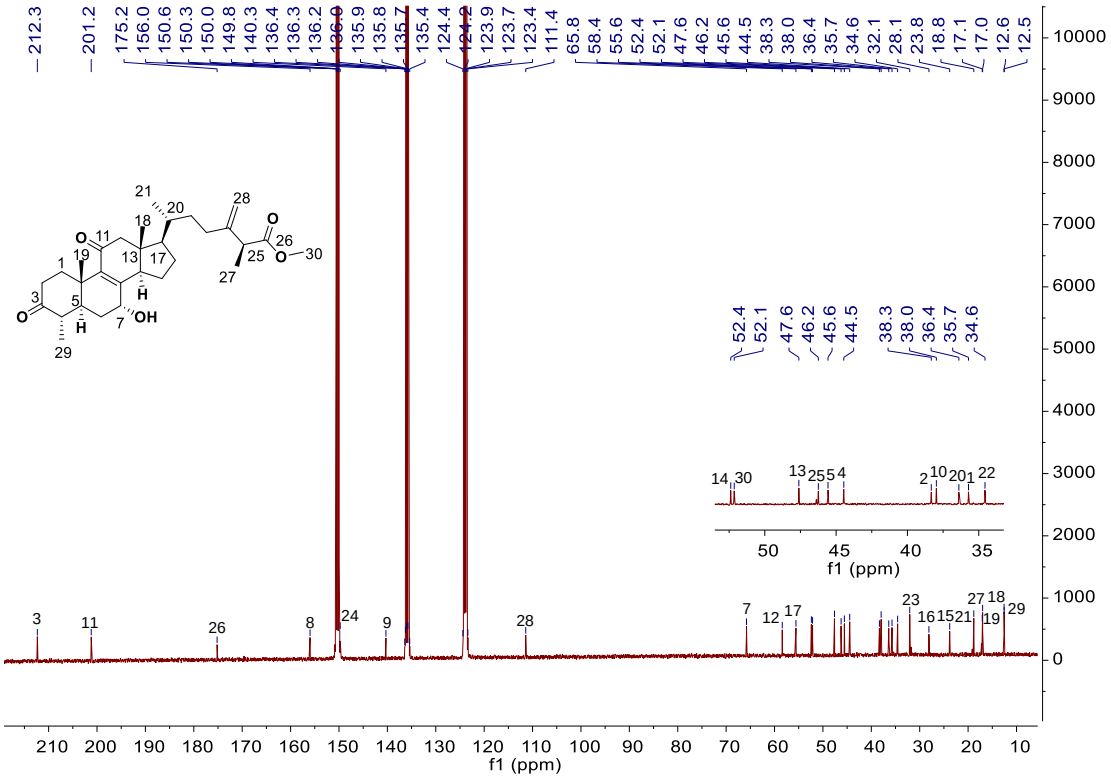


Figure S123. ^{13}C-NMR spectrum of **14** in pyridine-d_5 (100 MHz).

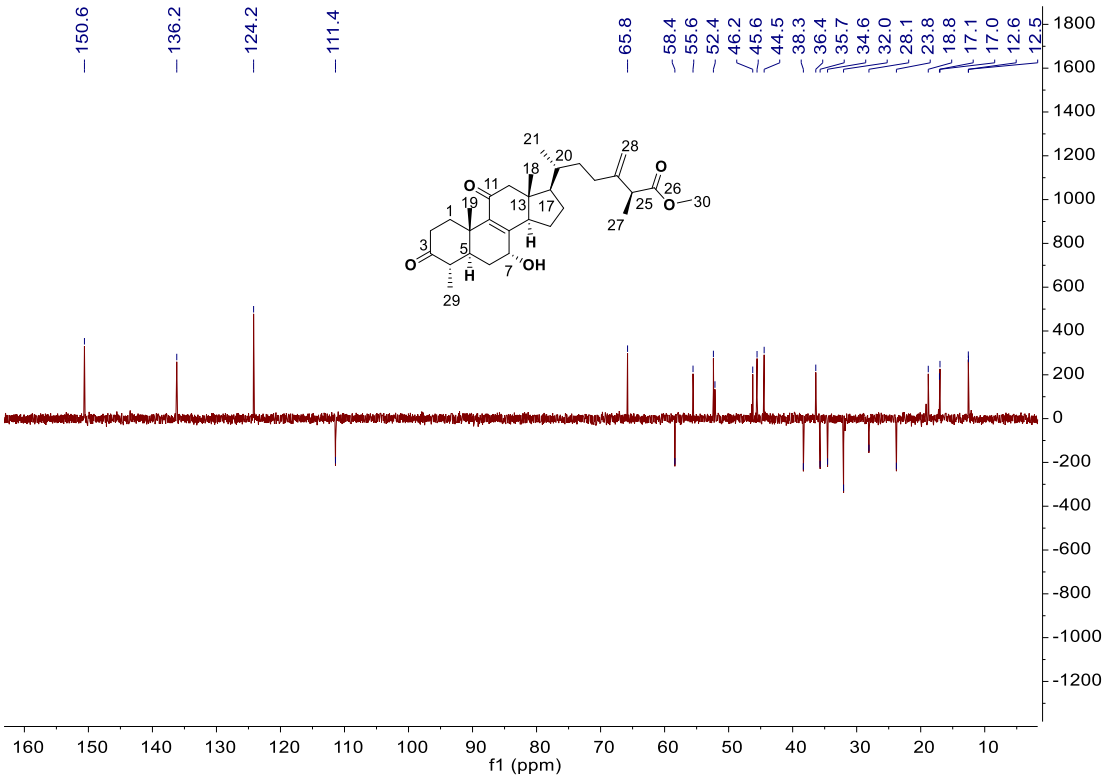


Figure S124. DEPT 135 spectrum of **14** in pyridine-d_5 (100 MHz).

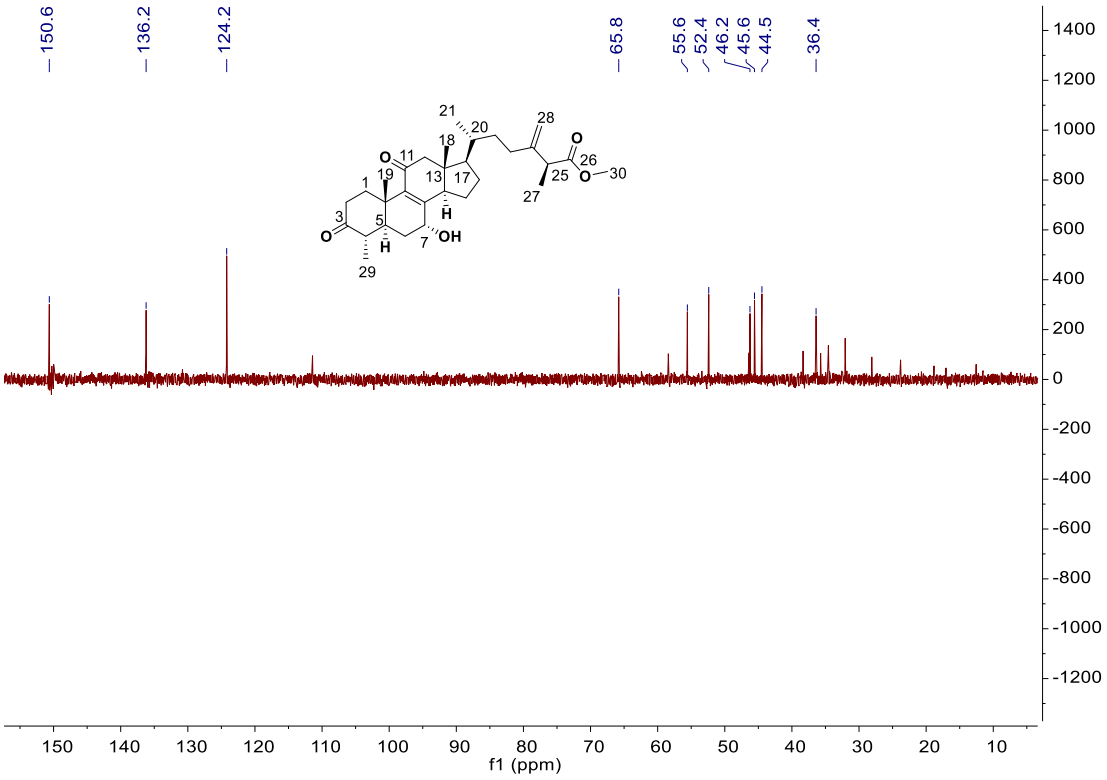


Figure S125. DEPT 90 spectrum of **14** in pyridine-d_5 (100 MHz).

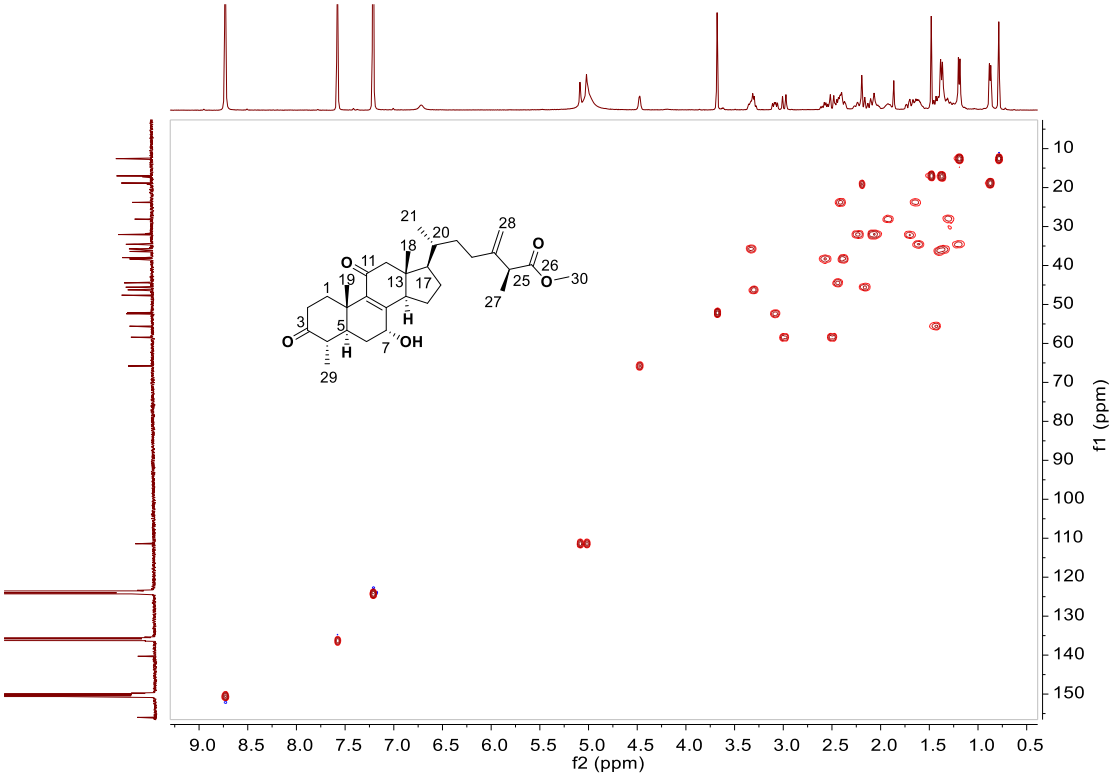


Figure S126. HSQC spectrum of **14** in pyridine-d_5 (400 MHz).

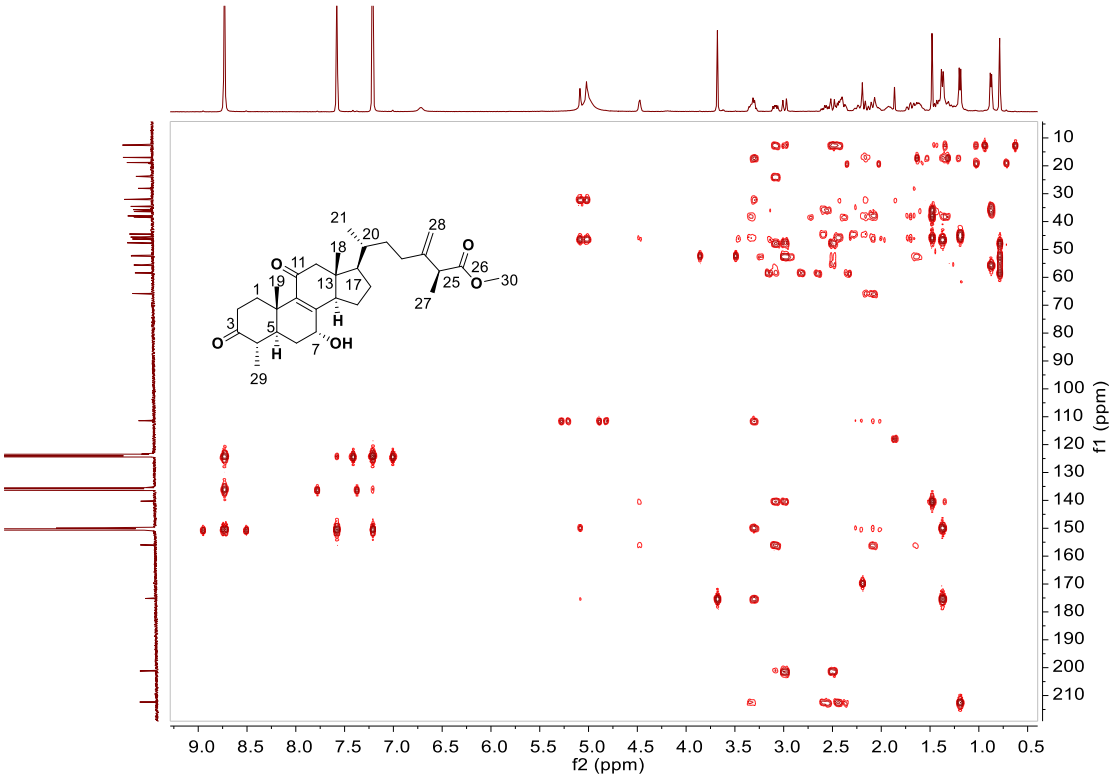


Figure S127. HMBC spectrum of **14** in pyridine-d_5 (400 MHz).

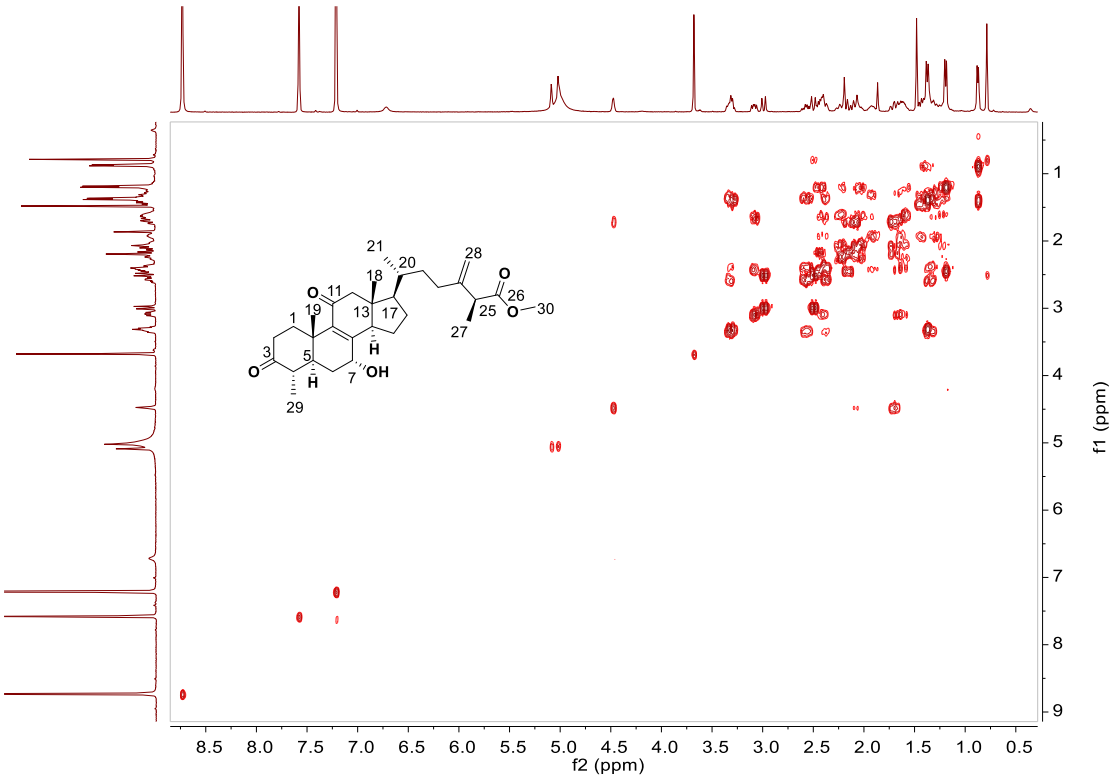


Figure S128. ^{1}H-^{1}H COSY spectrum of **14** in pyridine-d_5 (400 MHz).

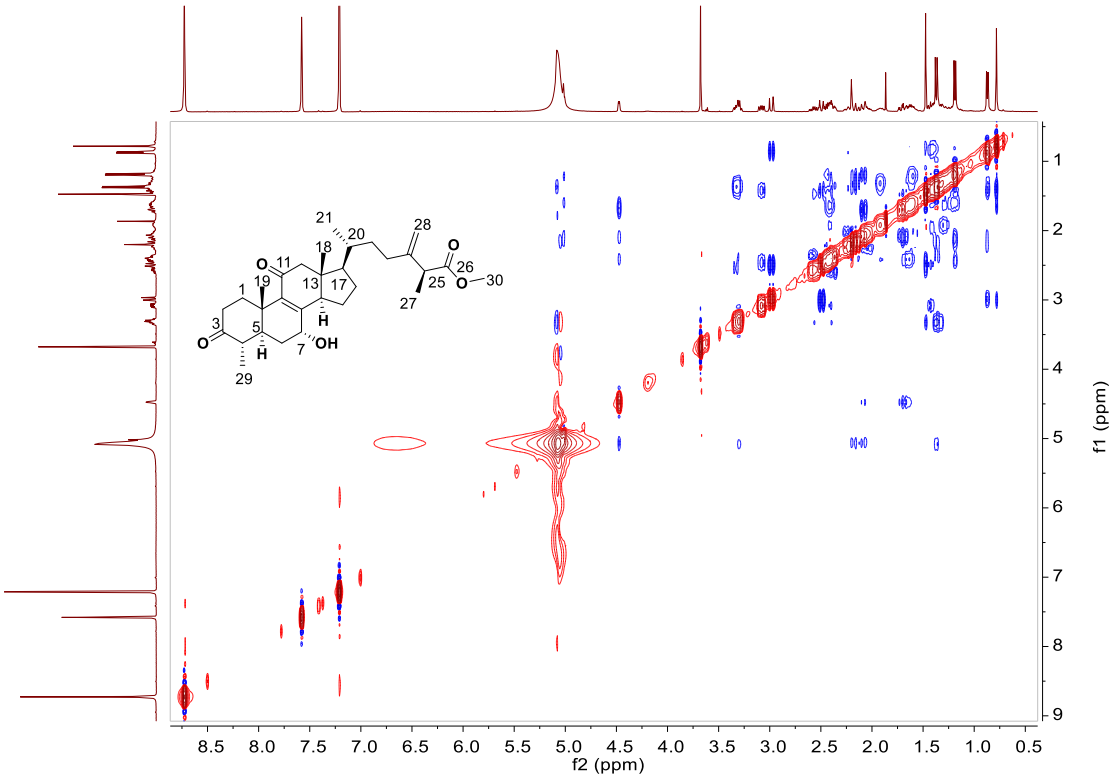


Figure S129. NOESY spectrum of **14** in pyridine-d_5 (400 MHz).

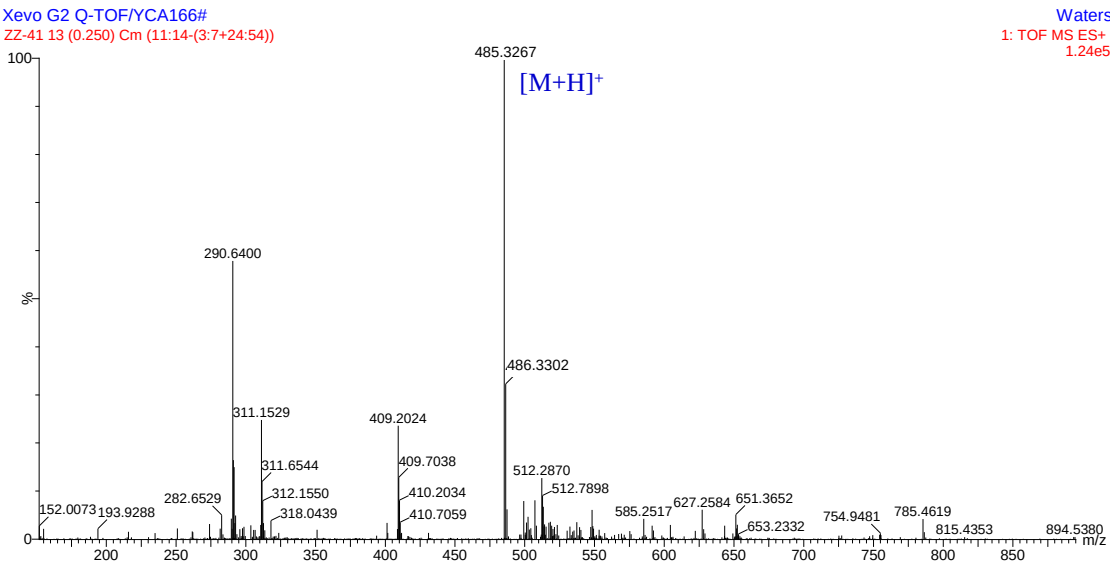


Figure S130. HR-ESI-MS spectrum of **14.**

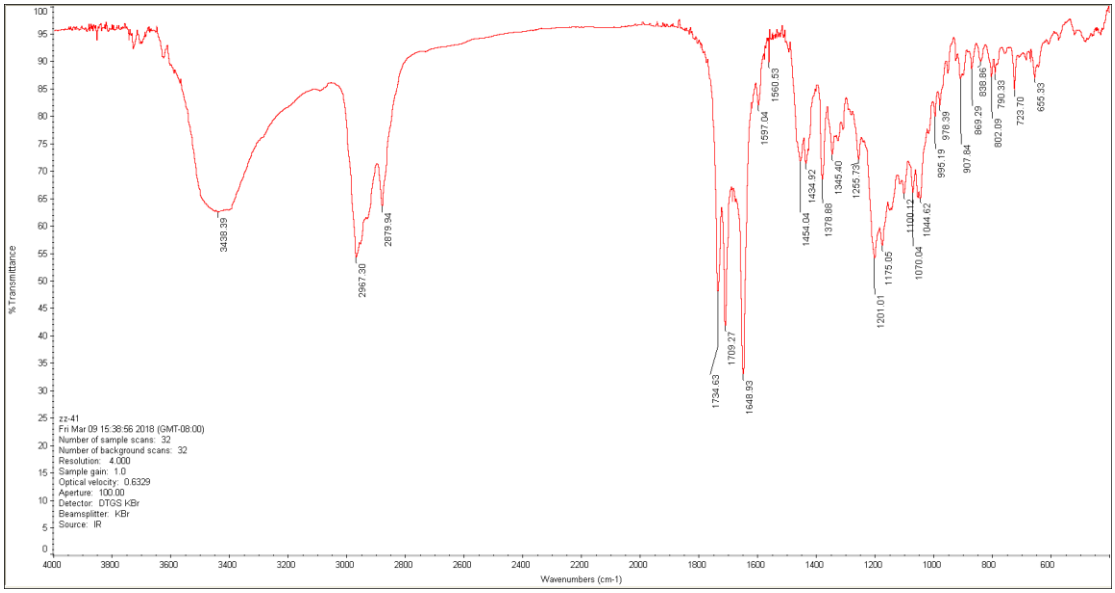


Figure S131. IR spectrum of **14**.

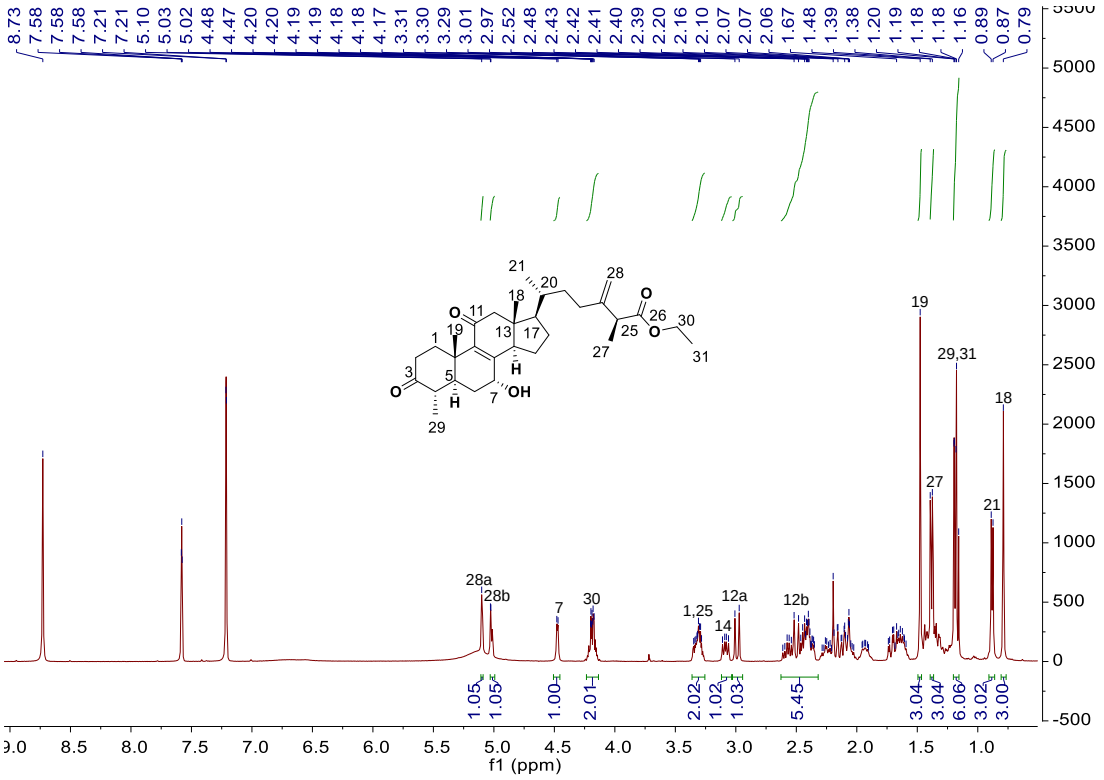


Figure S132. ^{1}H-NMR spectrum of **15** in pyridine-d_5 (400 MHz).

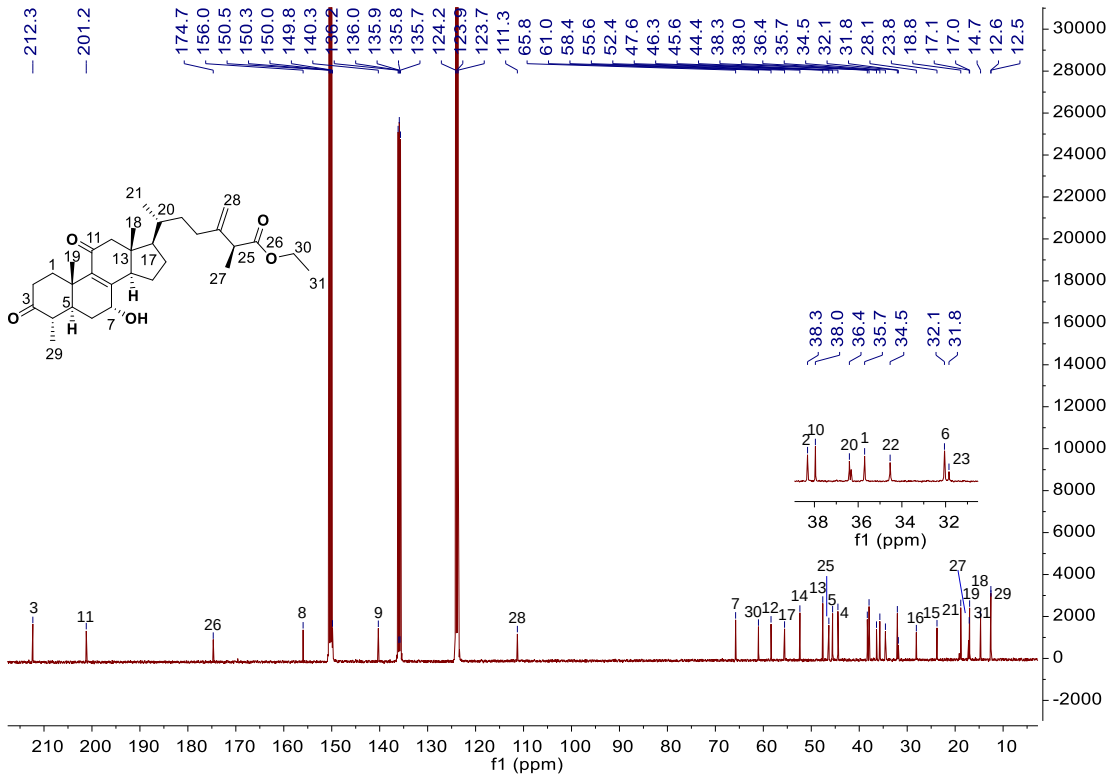


Figure S133. ^{13}C-NMR spectrum of **15** in pyridine-d_5 (100 MHz).

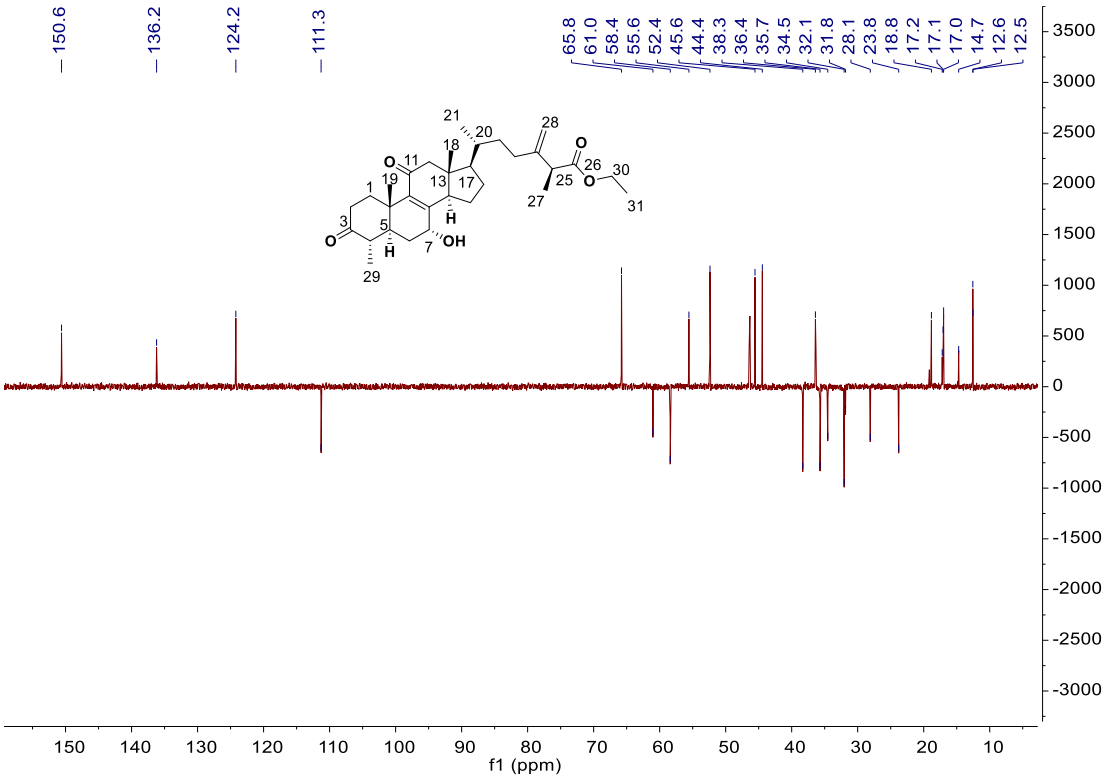


Figure S134. DEPT 135 spectrum of **15** in pyridine-d_5 (100 MHz).

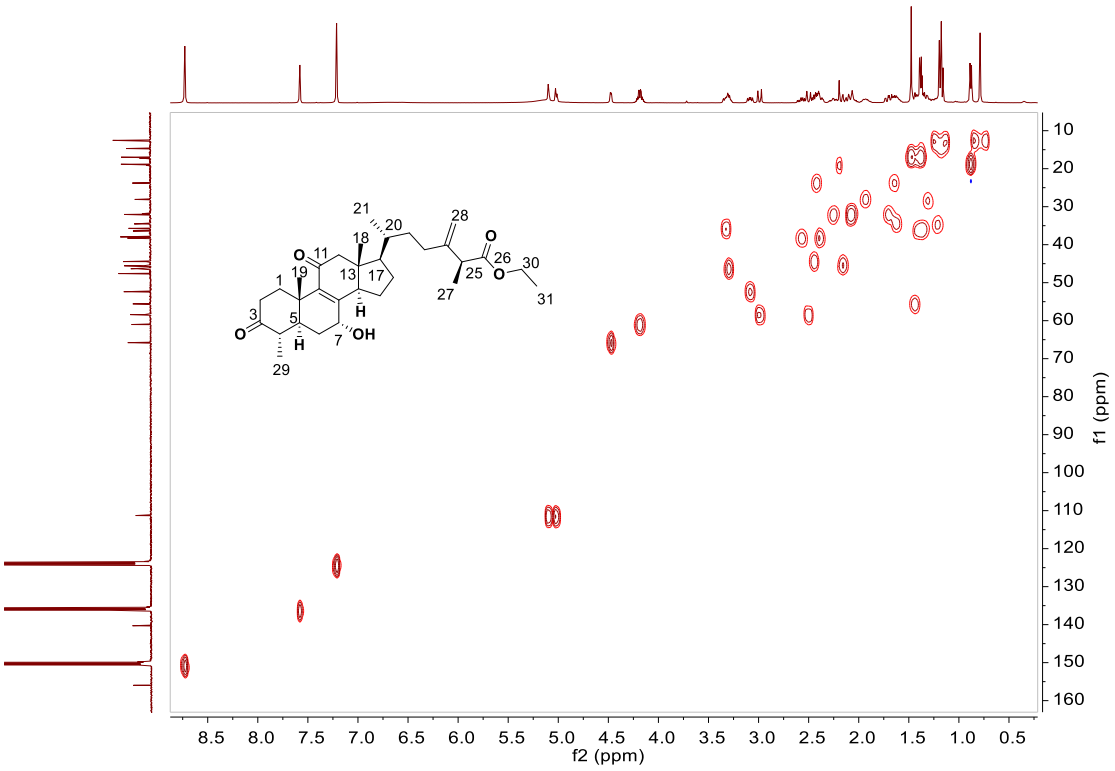


Figure S135. HSQC spectrum of **15** in pyridine-d_5 (400 MHz).

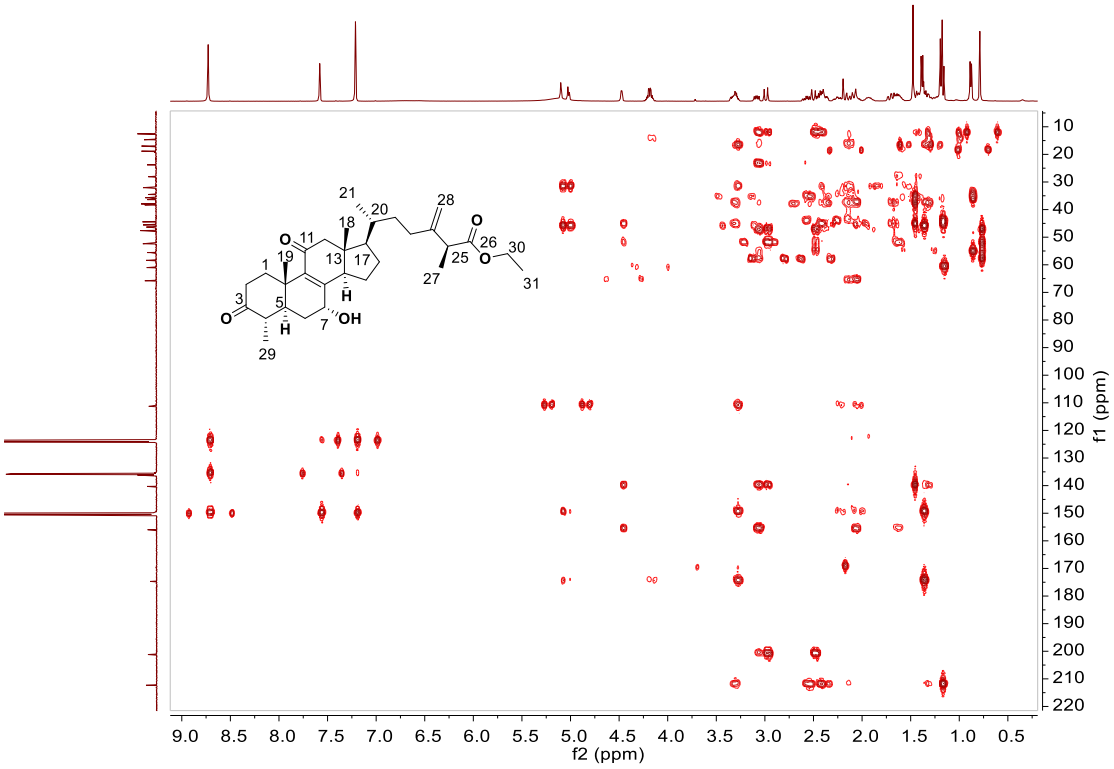


Figure S136. HMBC spectrum of **15** in pyridine-d_5 (400 MHz).

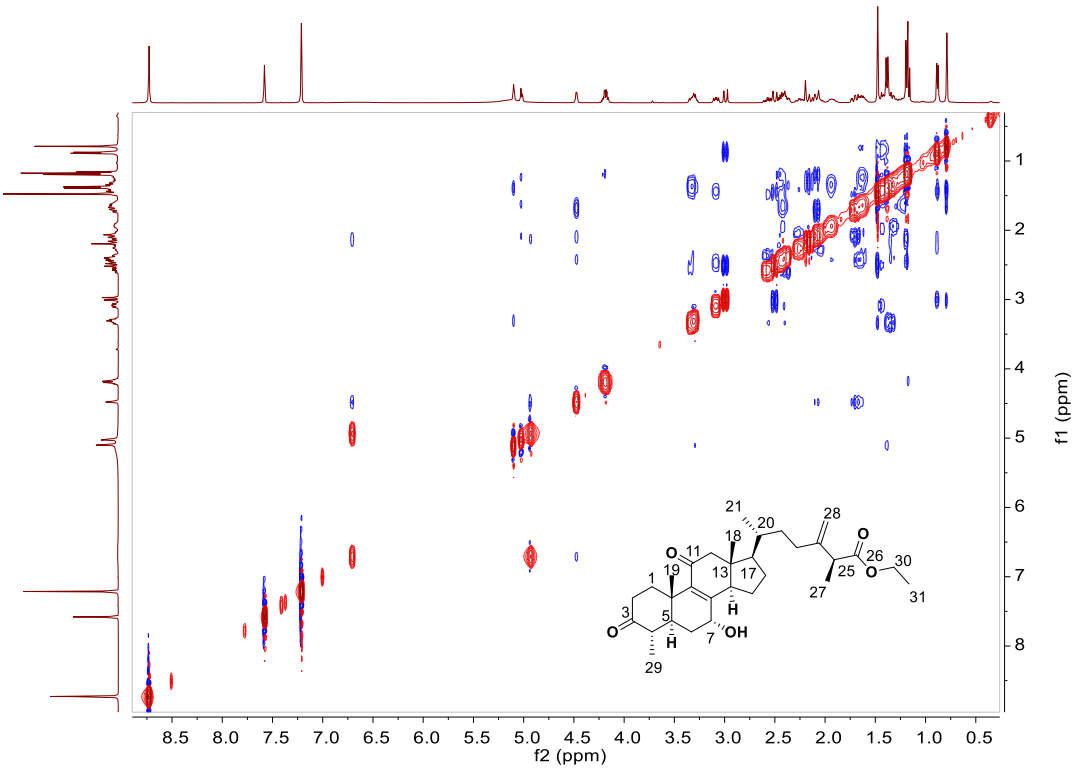


Figure S137. NOESY spectrum of **15** in pyridine-d_5 (400 MHz).

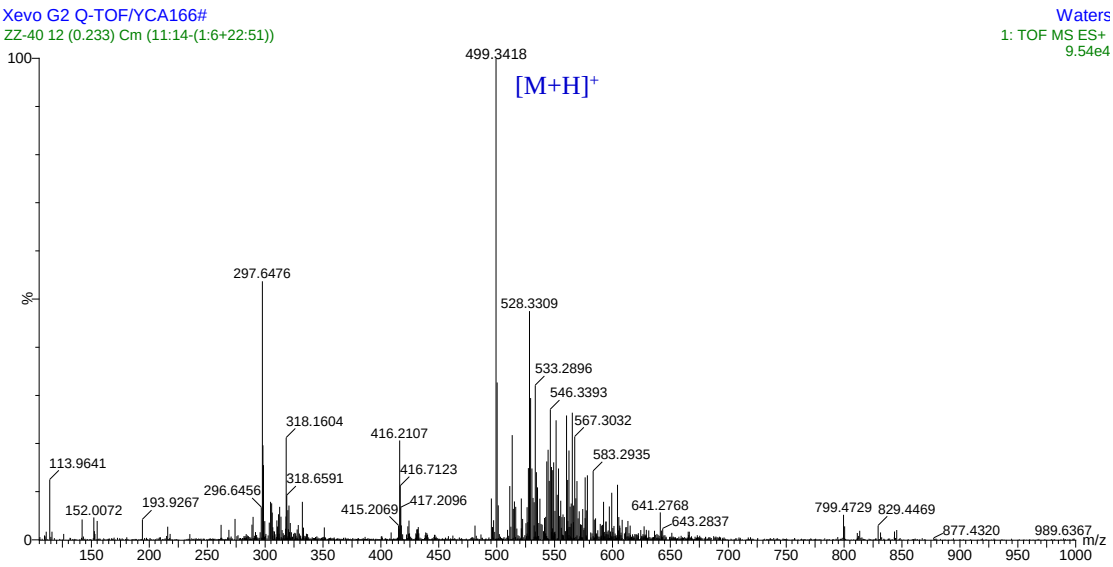


Figure S138. HR-ESI-MS spectrum of **15.**

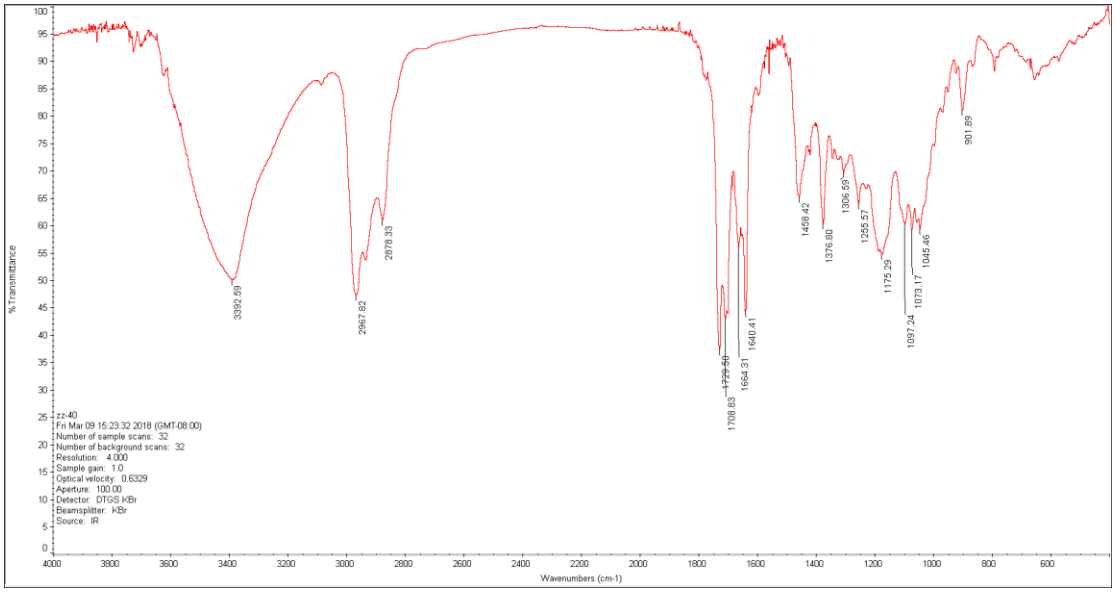


Figure S139. IR spectrum of **15**.

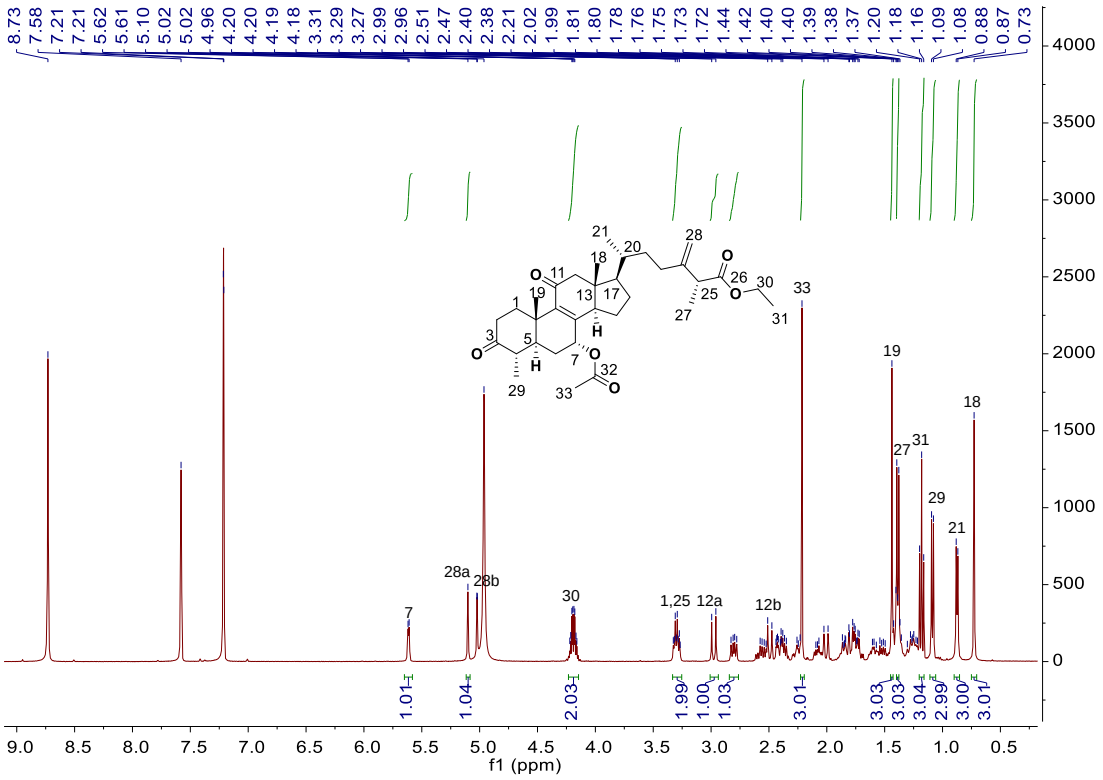


Figure S140. ^{1}H-NMR spectrum of **16** in pyridine-d_5 (400 MHz).

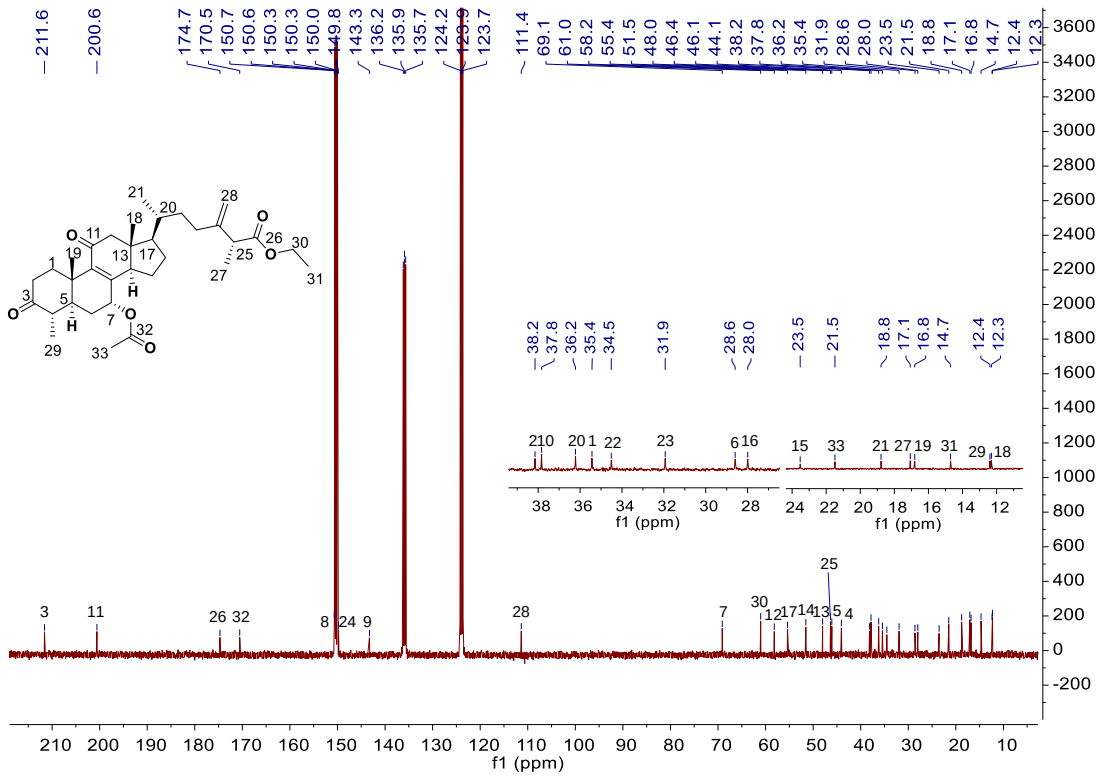


Figure S141. ^{13}C-NMR spectrum of **16** in pyridine-d_5 (100 MHz).

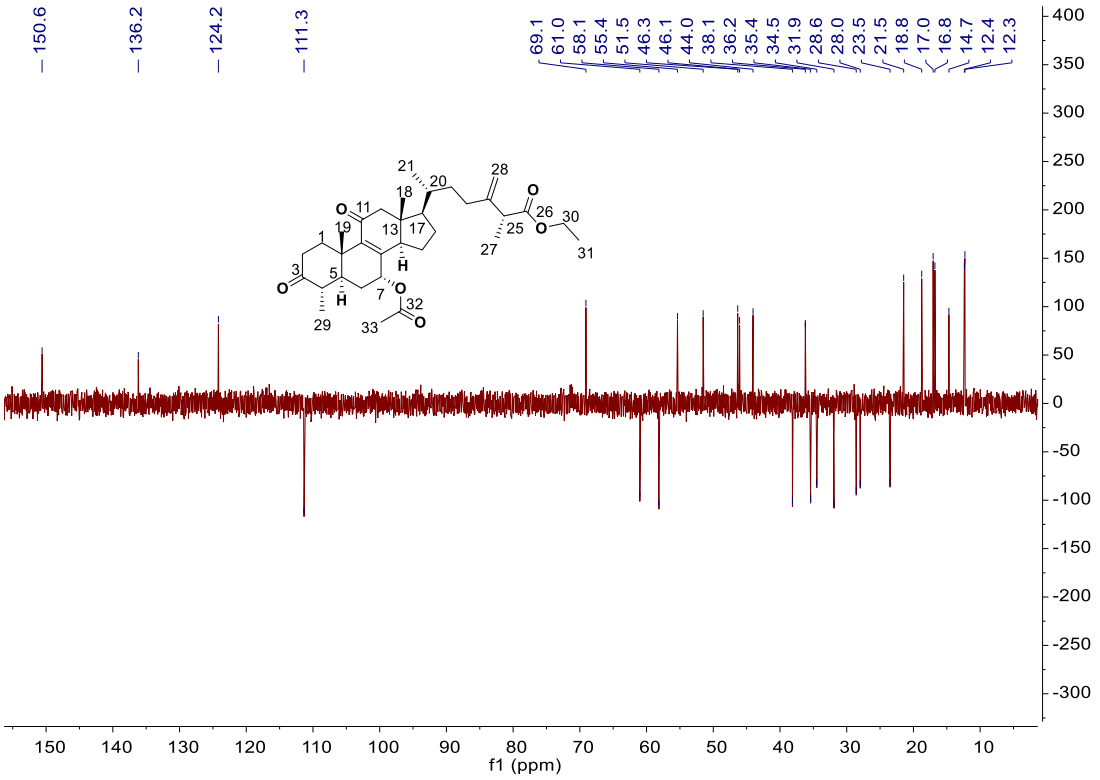


Figure S142. DEPT 135 spectrum of **16** in pyridine-d_5 (100 MHz).

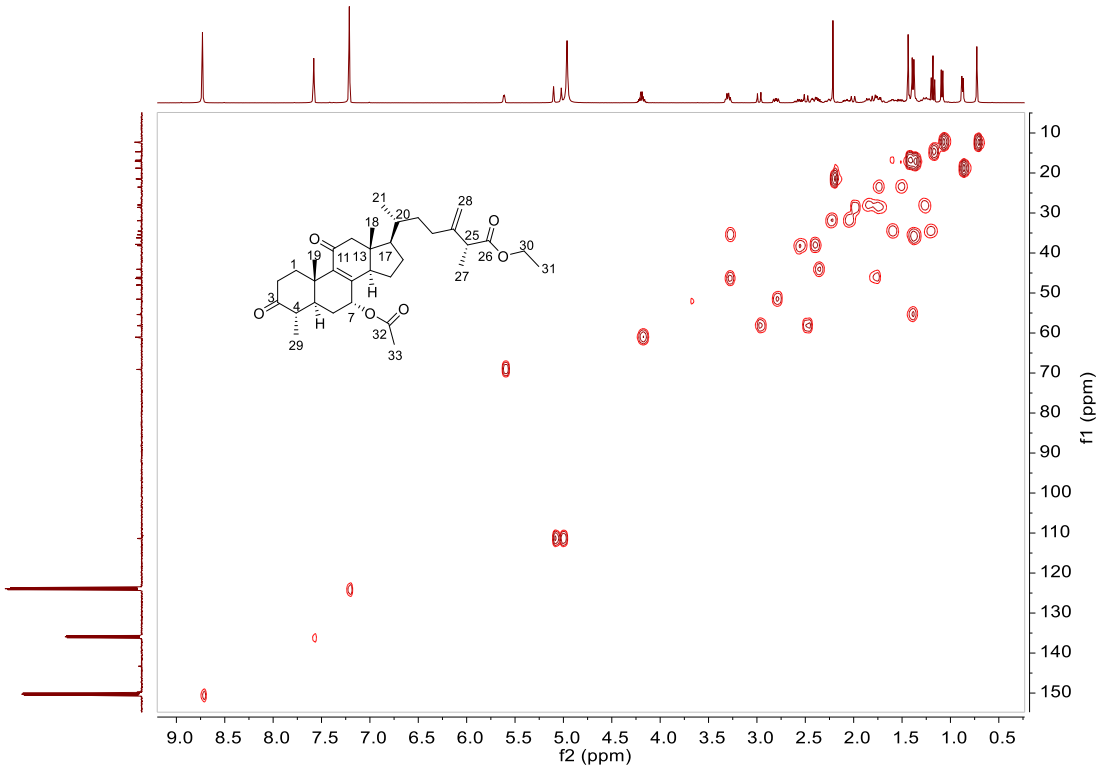


Figure S143. HSQC spectrum of **16** in pyridine-d_5 (400 MHz).

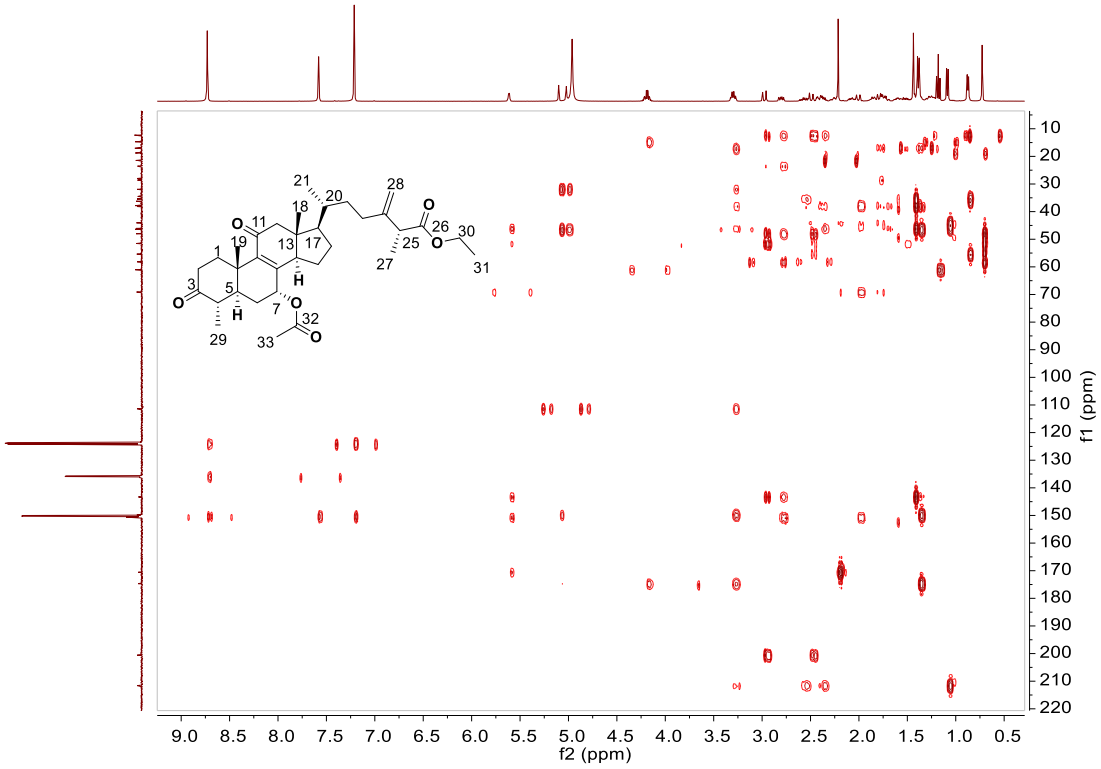


Figure S144. HMBC spectrum of **16** in pyridine-d_5 (400 MHz).

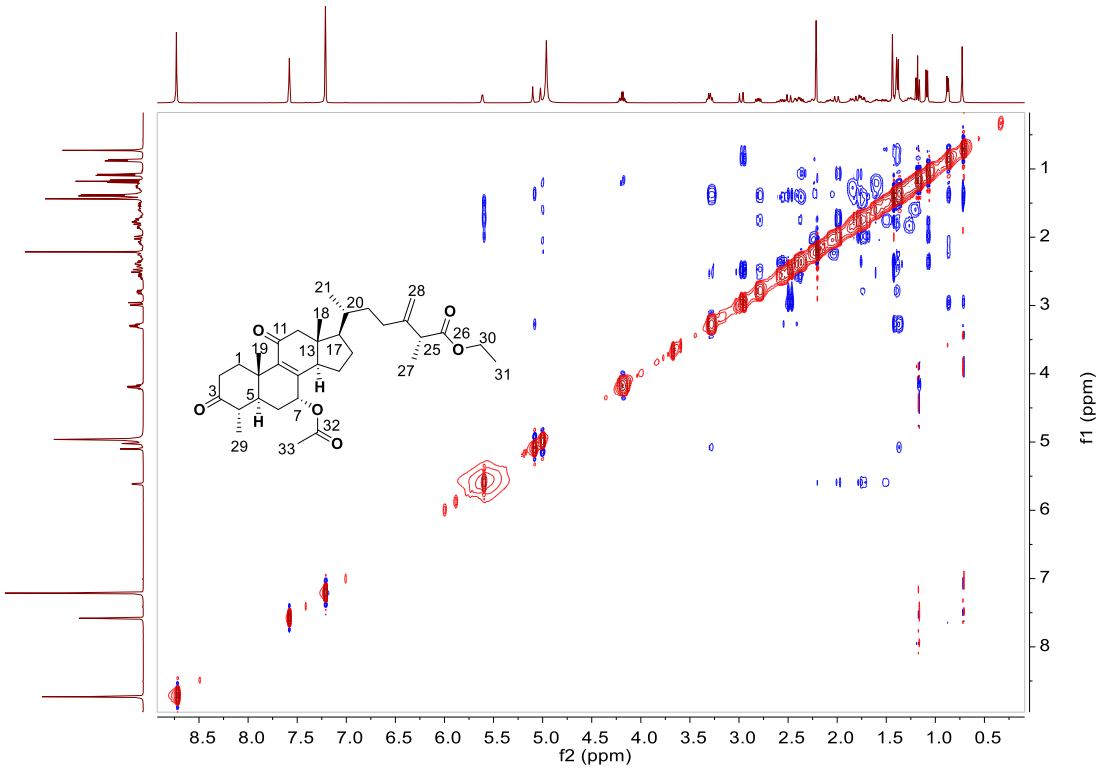


Figure S145. NOESY spectrum of **16** in pyridine-d_5 (400 MHz).

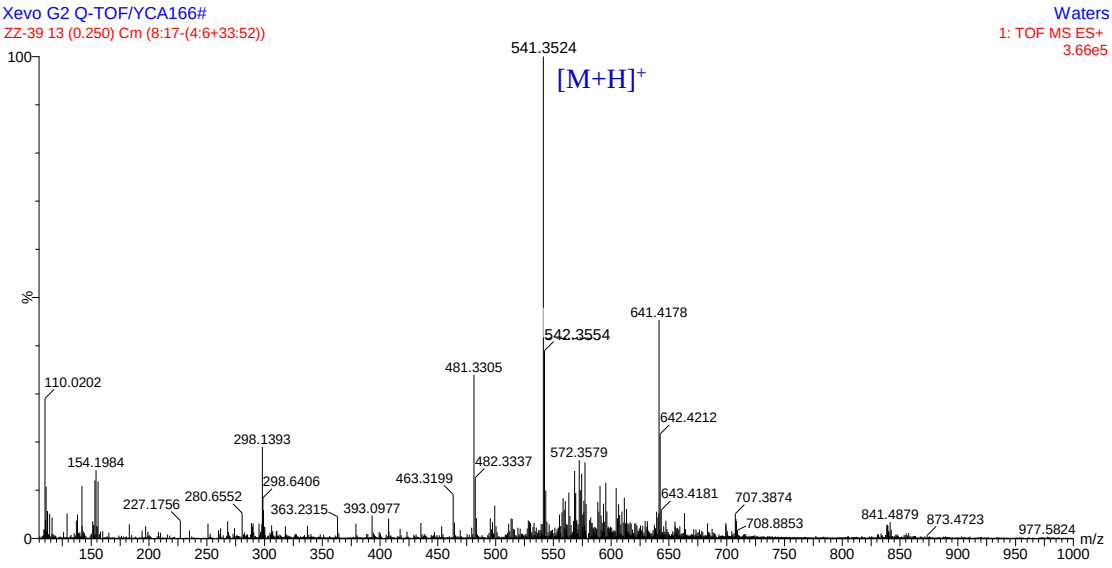


Figure S146. HR-ESI-MS spectrum of **16.**

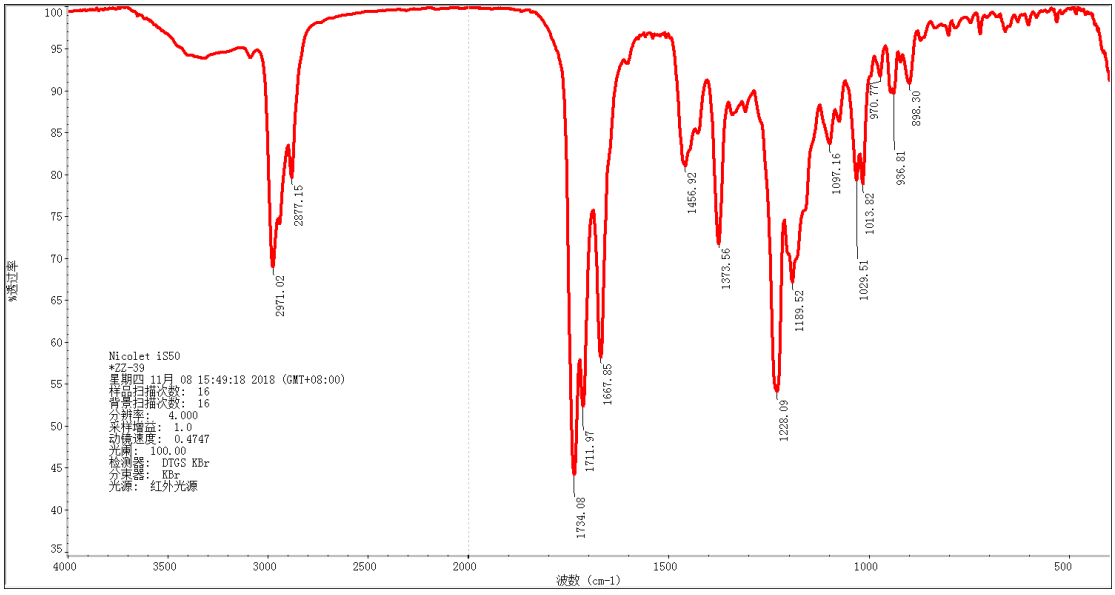


Figure S147. IR spectrum of **16**.

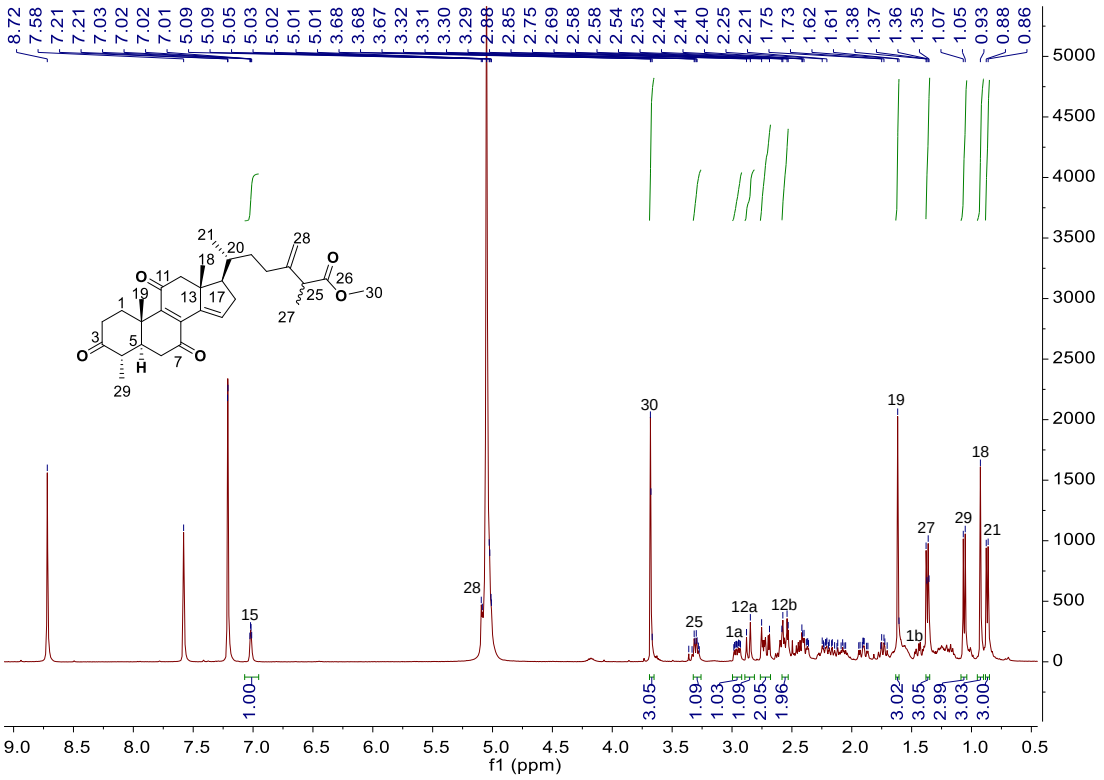


Figure S148. ^{1}H-NMR spectrum of **17** in pyridine-d_5 (400 MHz).

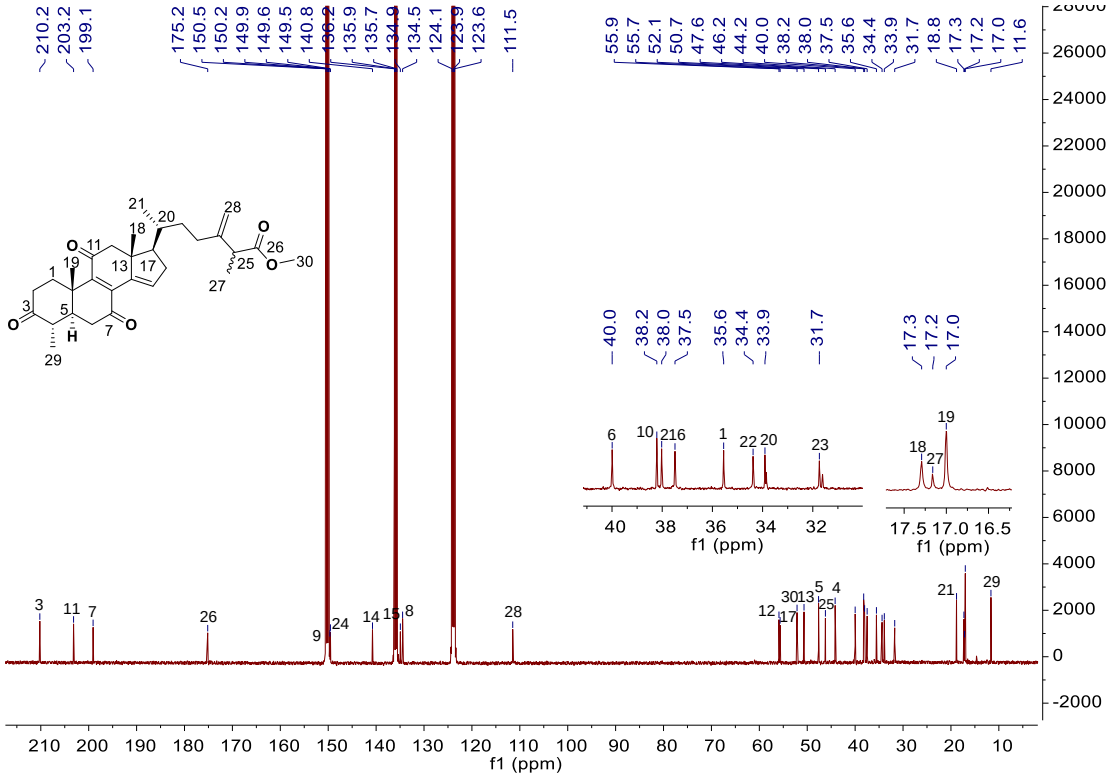


Figure S149. ^{13}C-NMR spectrum of **17** in pyridine-d_5 (100 MHz).

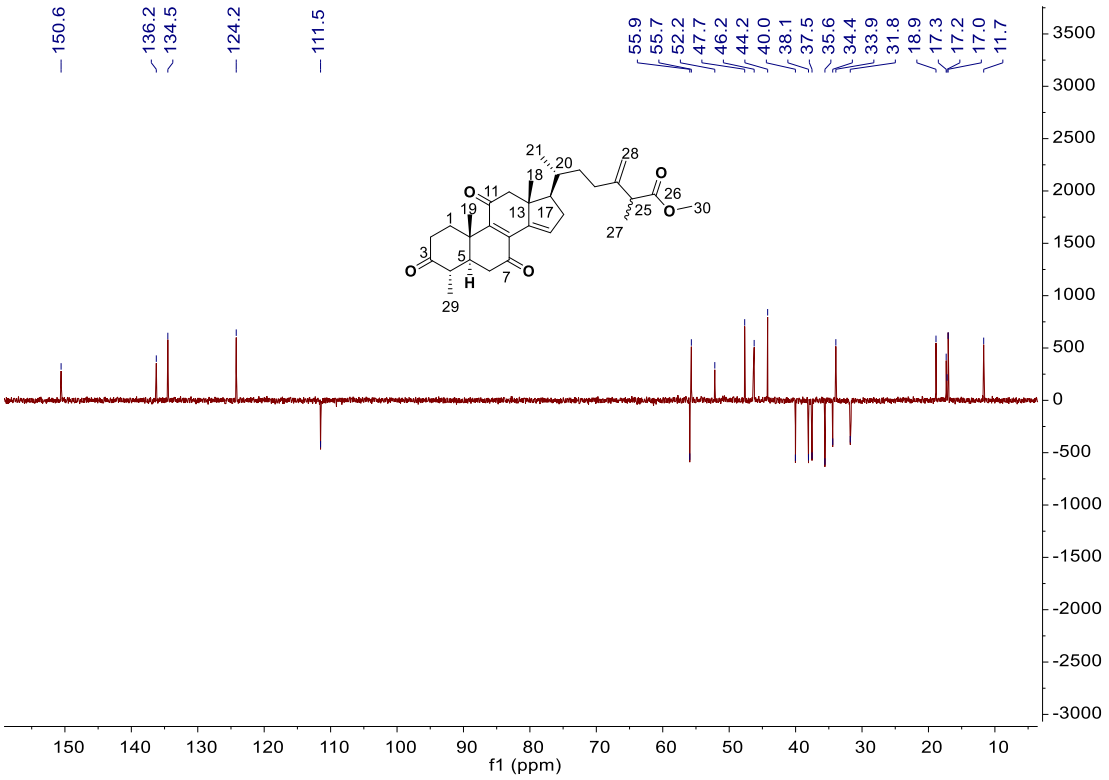


Figure S150. DEPT 135 spectrum of **17** in pyridine-d_5 (100 MHz).

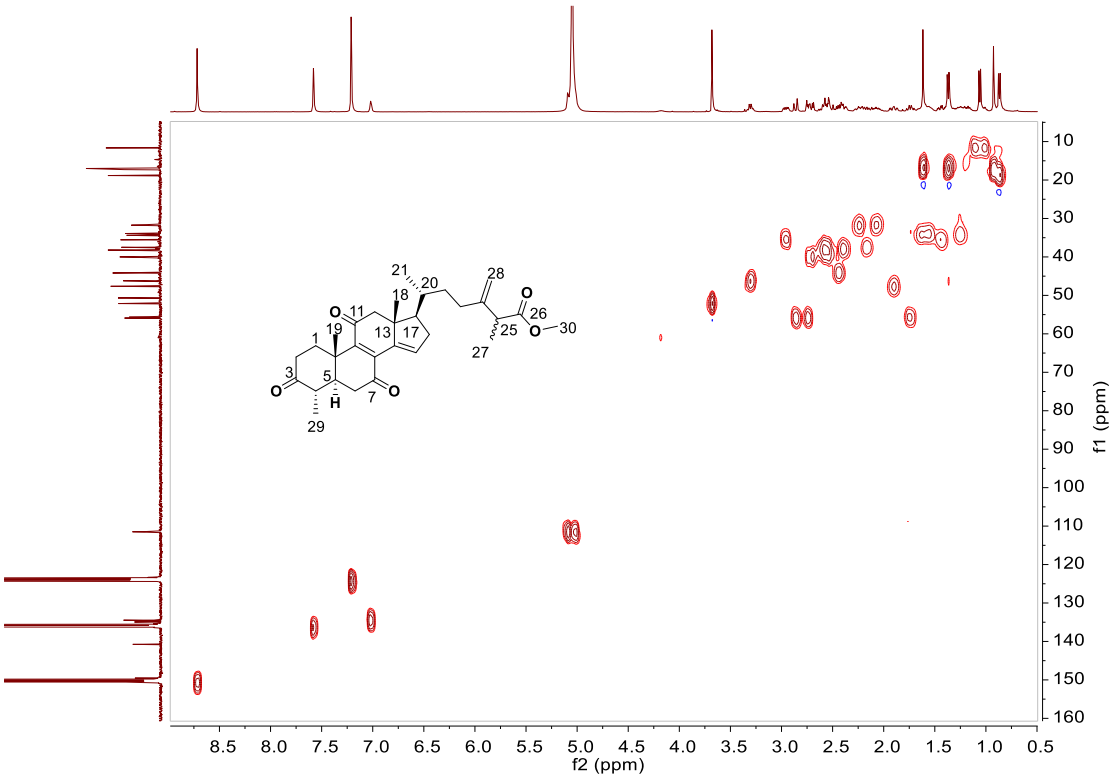


Figure S151. HSQC spectrum of **17** in pyridine-d_5 (400 MHz).

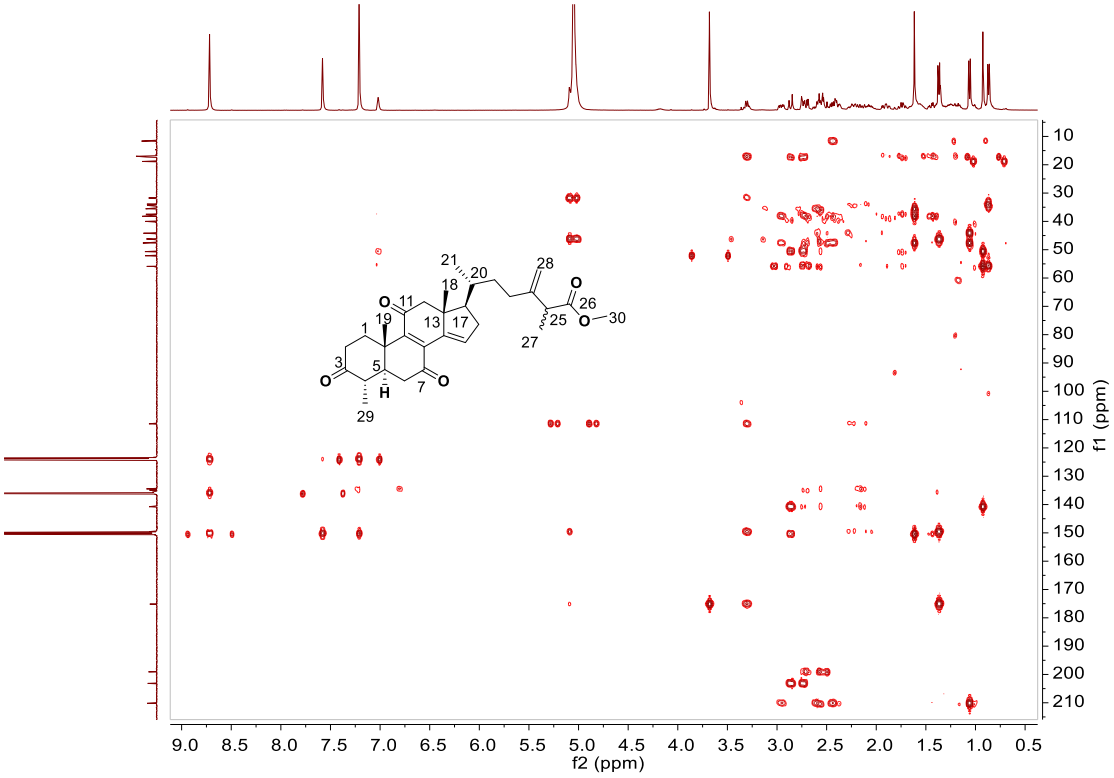


Figure S152. HMBC spectrum of **17** in pyridine-d_5 (400 MHz).

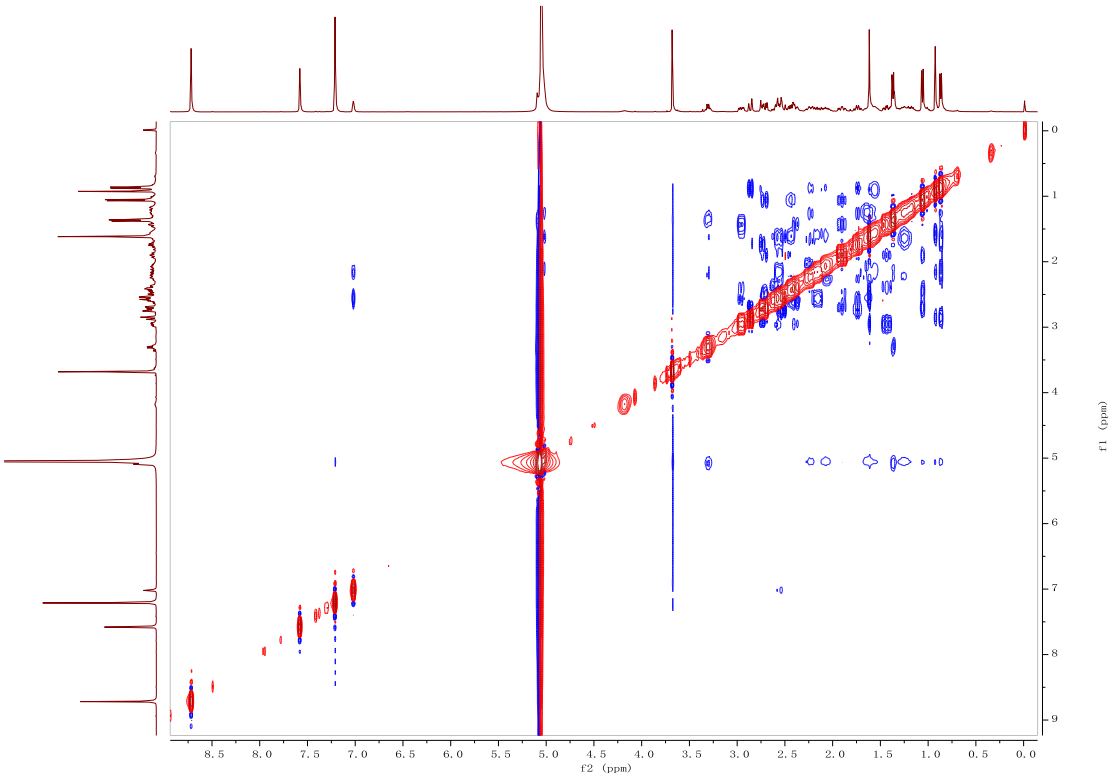


Figure S153. NOESY spectrum of **17** in pyridine-d_5 (400 MHz).

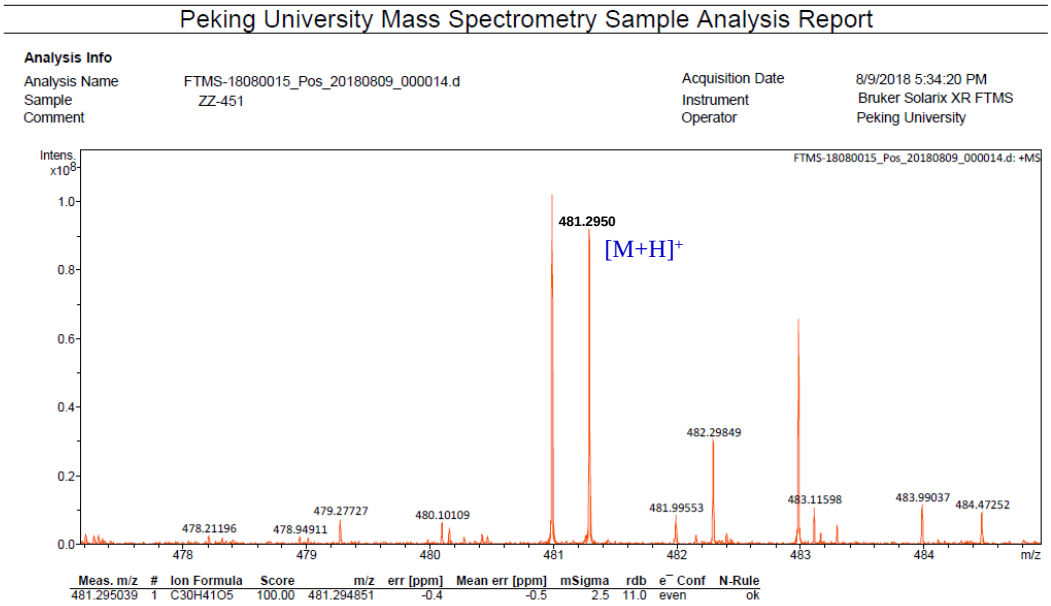


Figure S154. HR-FT-MS spectrum of **17.**

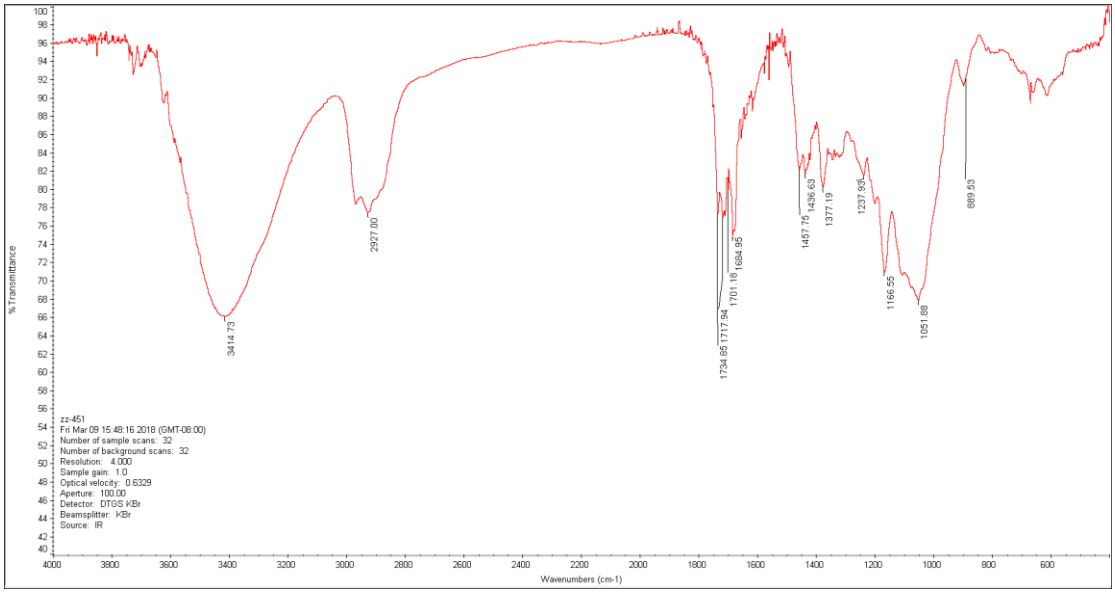


Figure S155. IR spectrum of **17**.

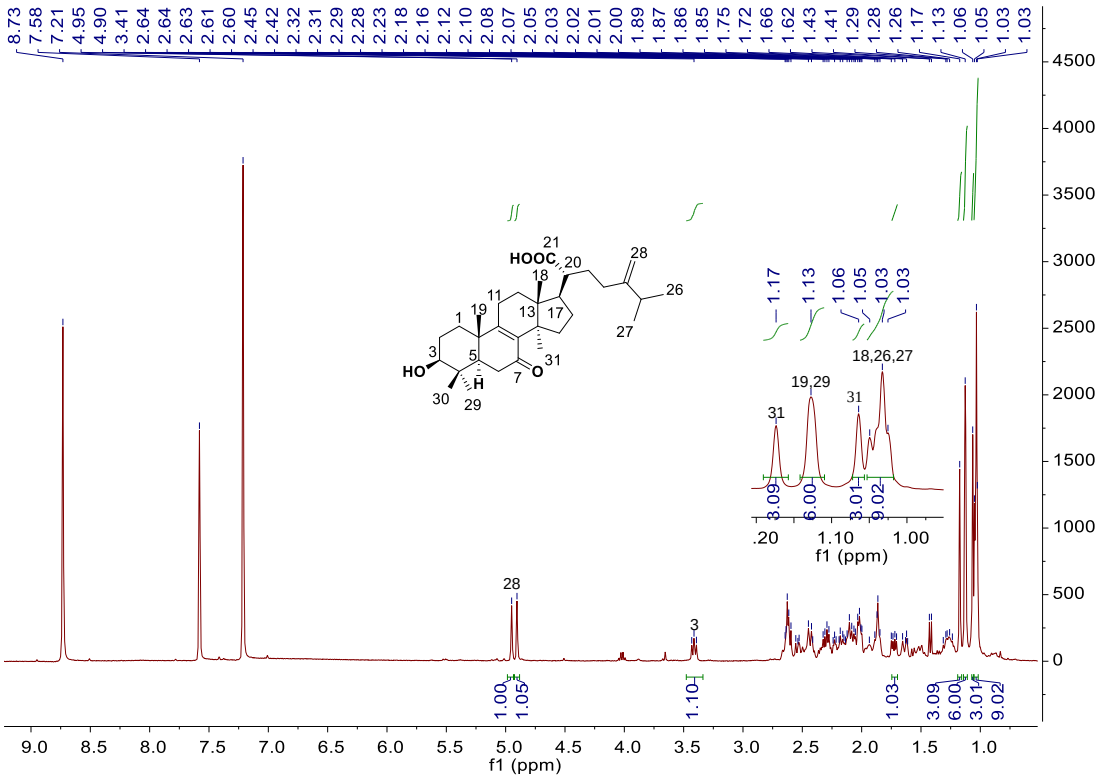


Figure S156. ^{1}H-NMR spectrum of **18** in pyridine-d_5 (400 MHz).

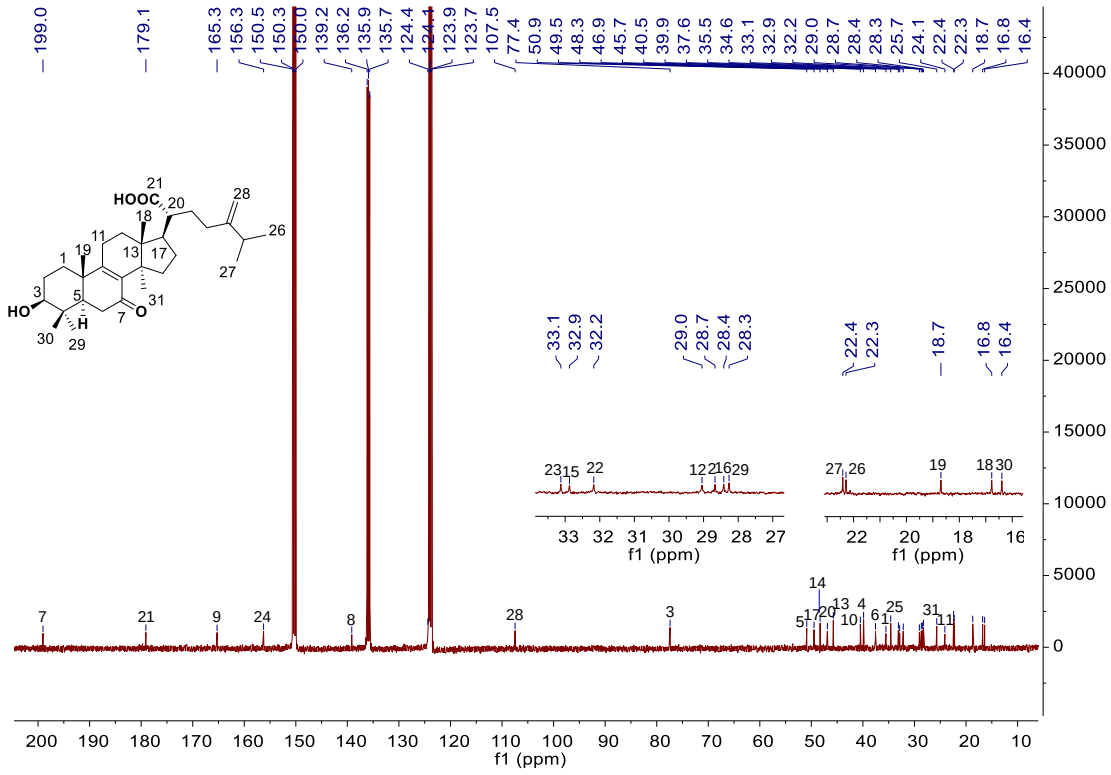


Figure S157. ^{13}C-NMR spectrum of **18** in pyridine-d_5 (100 MHz).

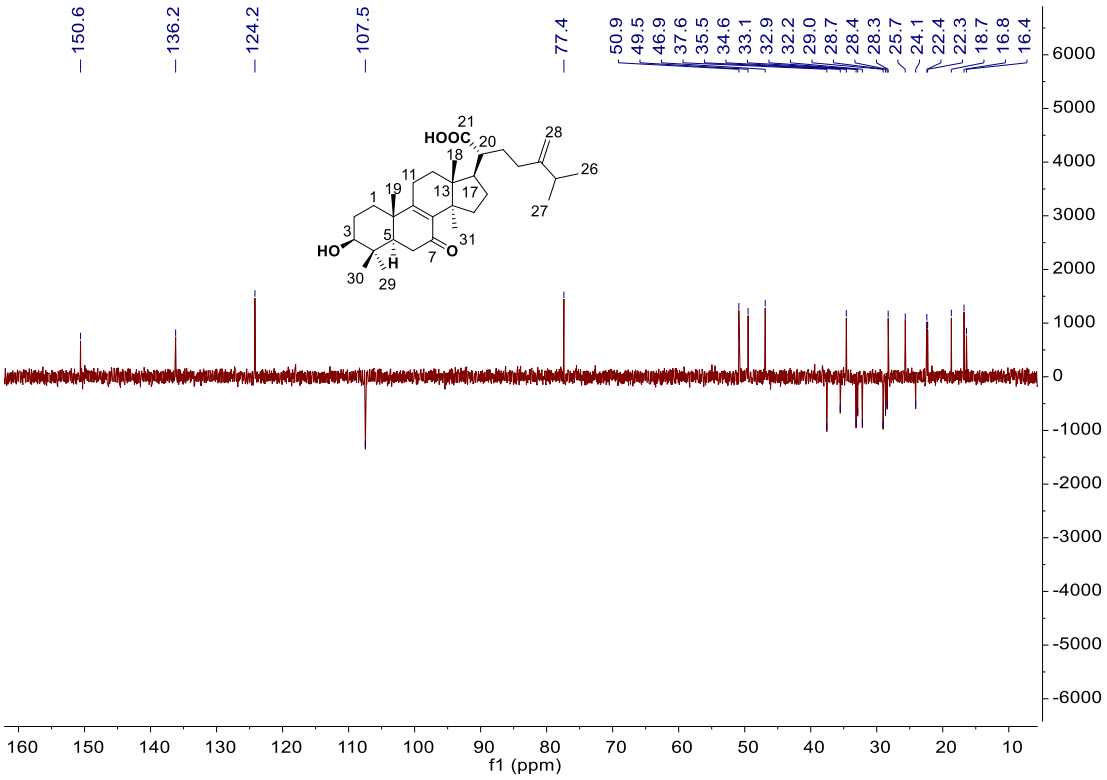


Figure S158. DEPT 135 spectrum of **18** in pyridine-d_5 (100 MHz).

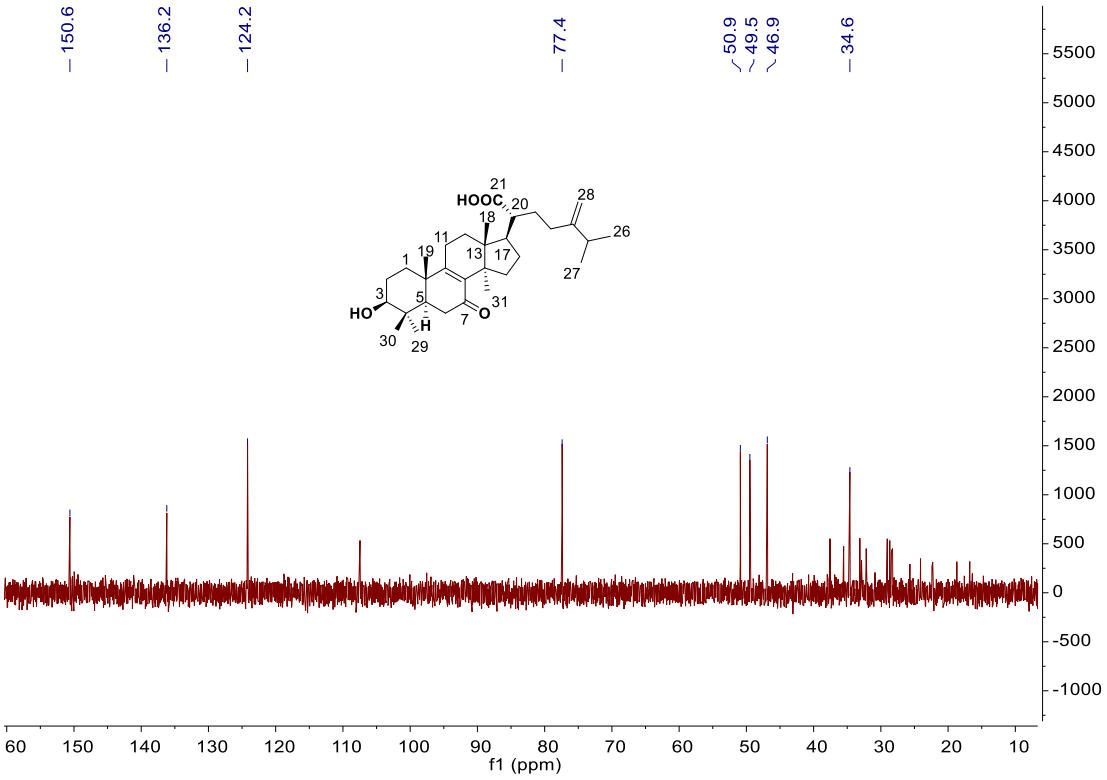


Figure S159. DEPT 90 spectrum of **18** in pyridine-d_5 (100 MHz).

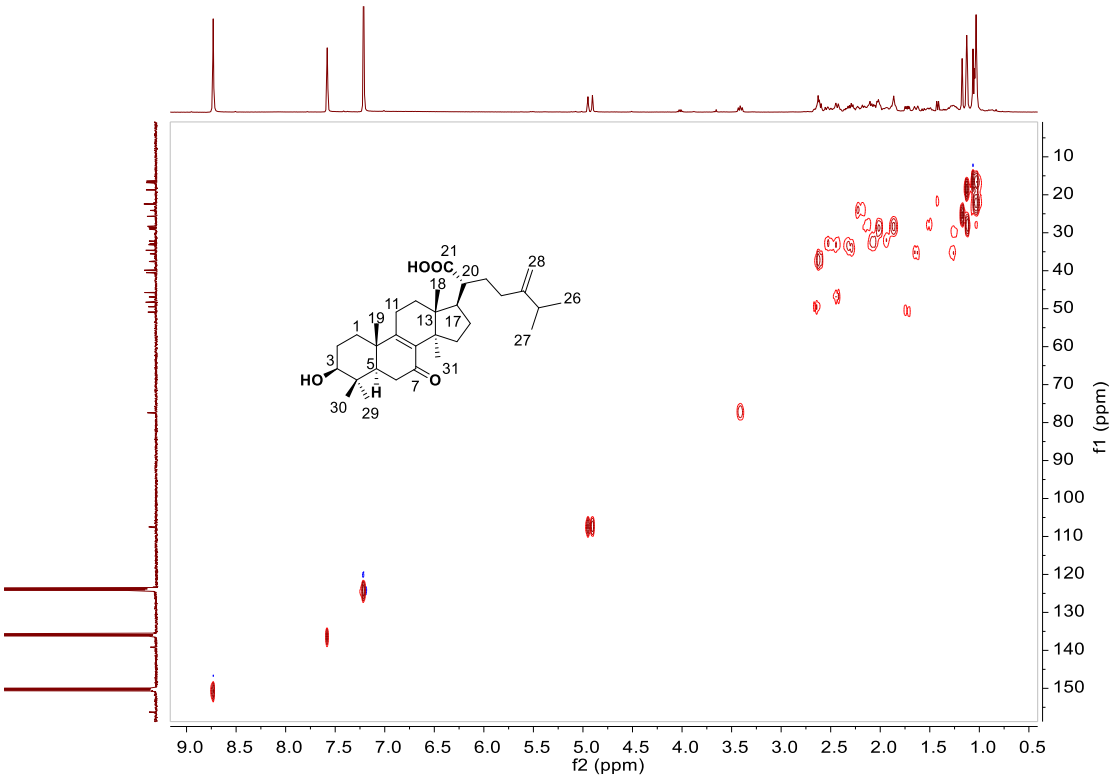


Figure S160. HSQC spectrum of **18** in pyridine-d_5 (400 MHz).

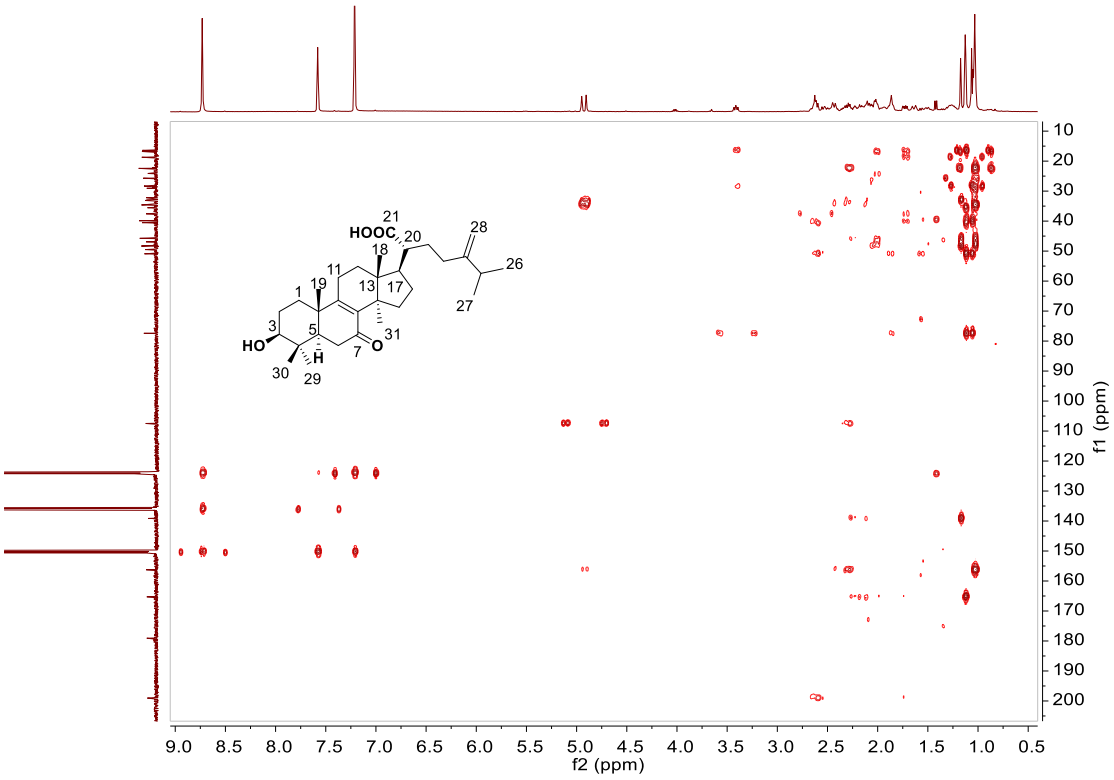


Figure S161. HMBC spectrum of **18** in pyridine-d_5 (400 MHz).

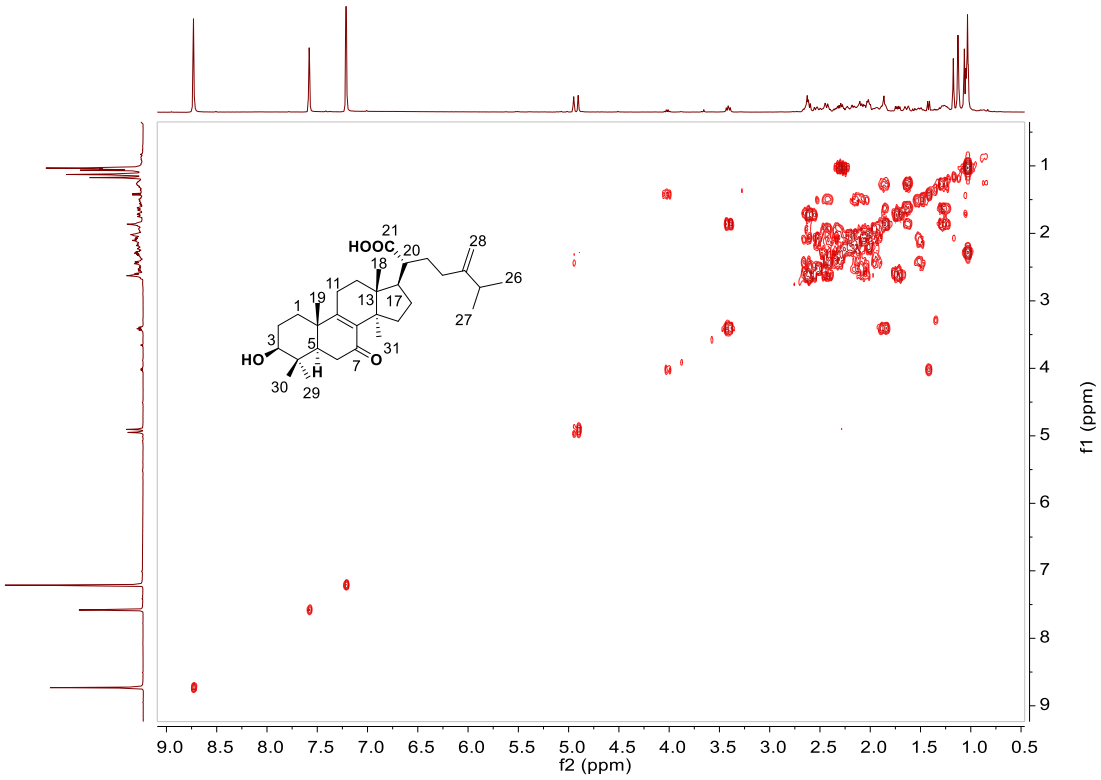


Figure S162. ^{1}H-^{1}H COSY spectrum of **18** in pyridine-d_5 (400 MHz).

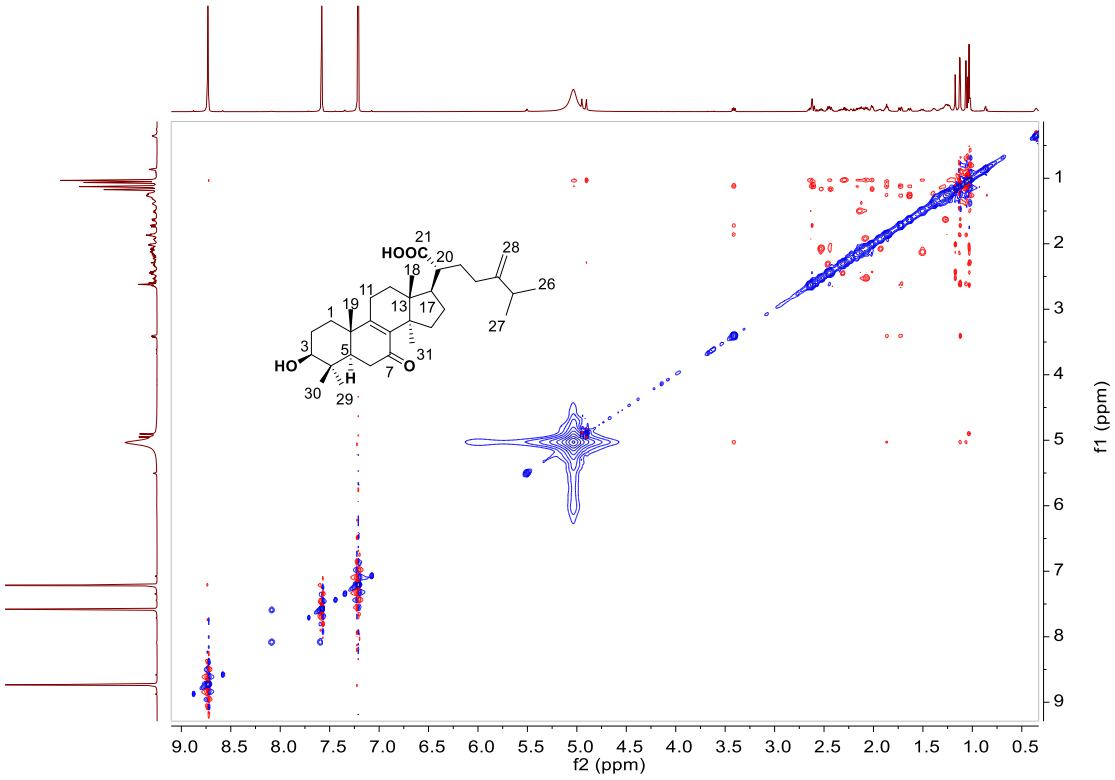


Figure S163. NOESY spectrum of **18** in pyridine-d_5 (400 MHz).

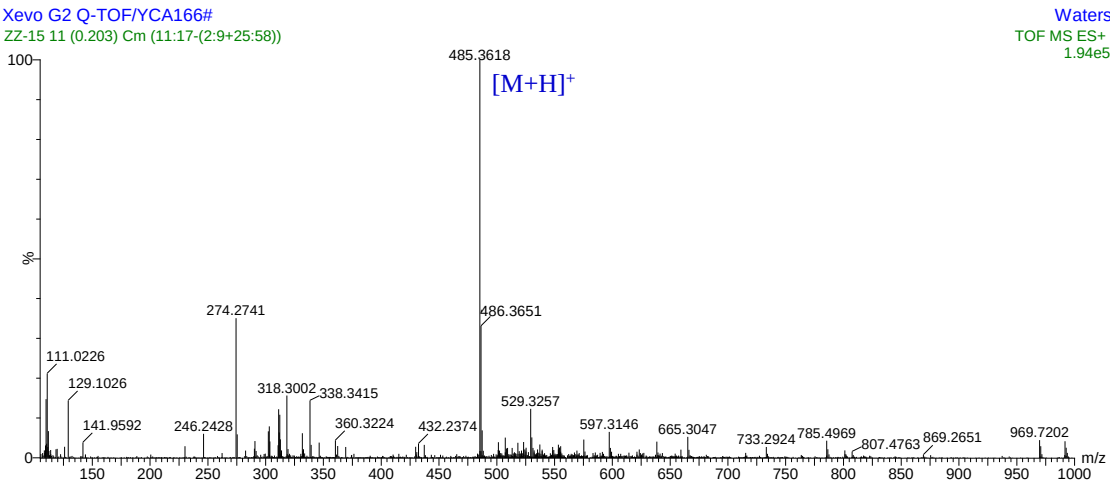


Figure S164. HR-ESI-MS spectrum of **18.**

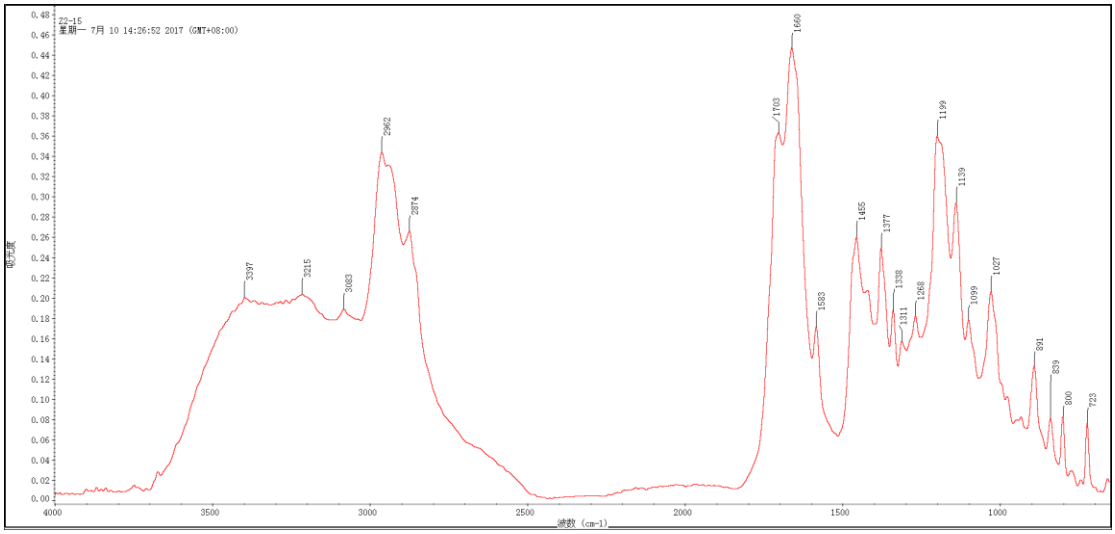


Figure S165. IR spectrum of **18**.

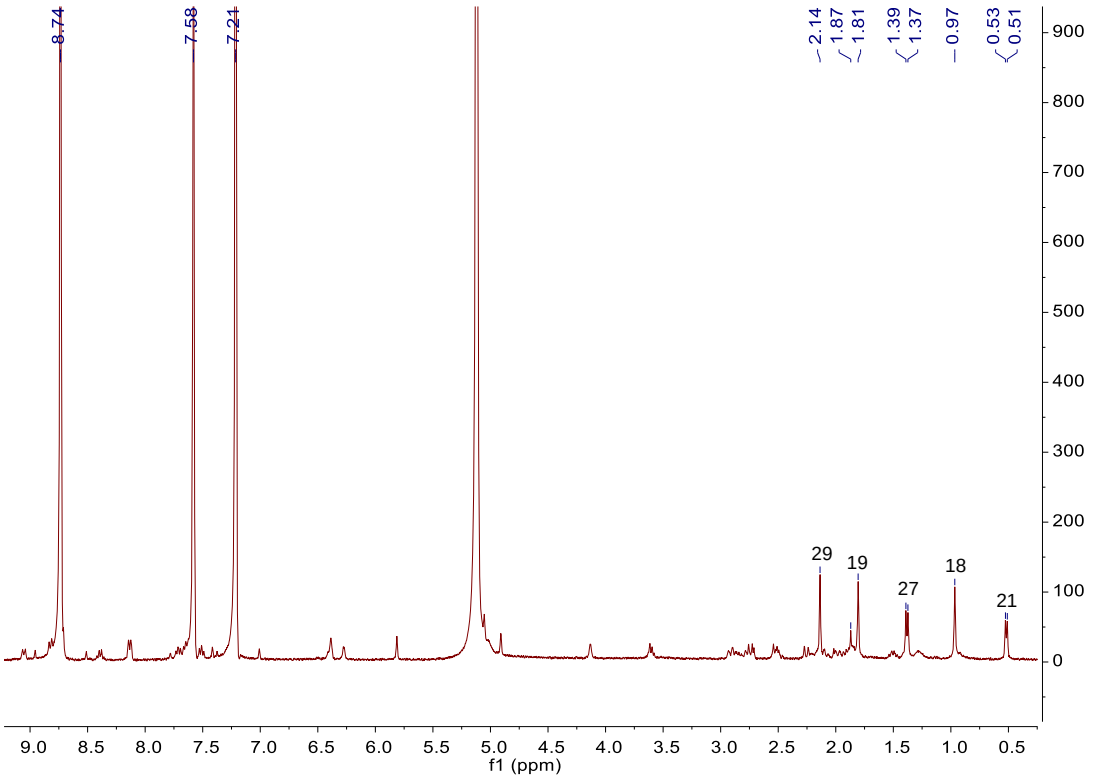


Figure S166. ^{1}H-NMR spectrum of (*R*)-AT Ester of **3** in pyridine-d_5 (400 MHz).

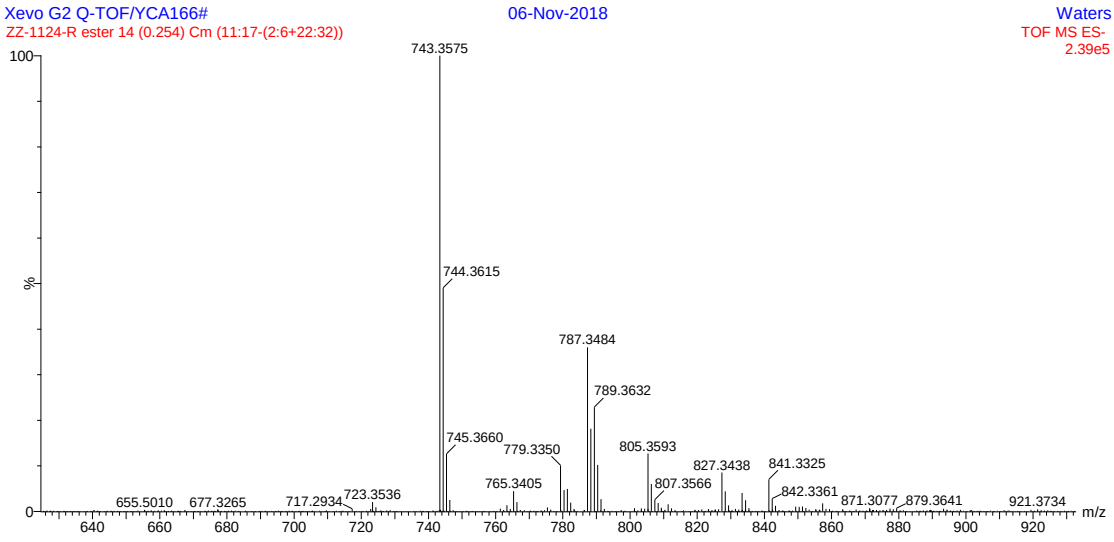


Figure S167. (-)-ESI-MS of (*R*)-AT Ester of **3**.

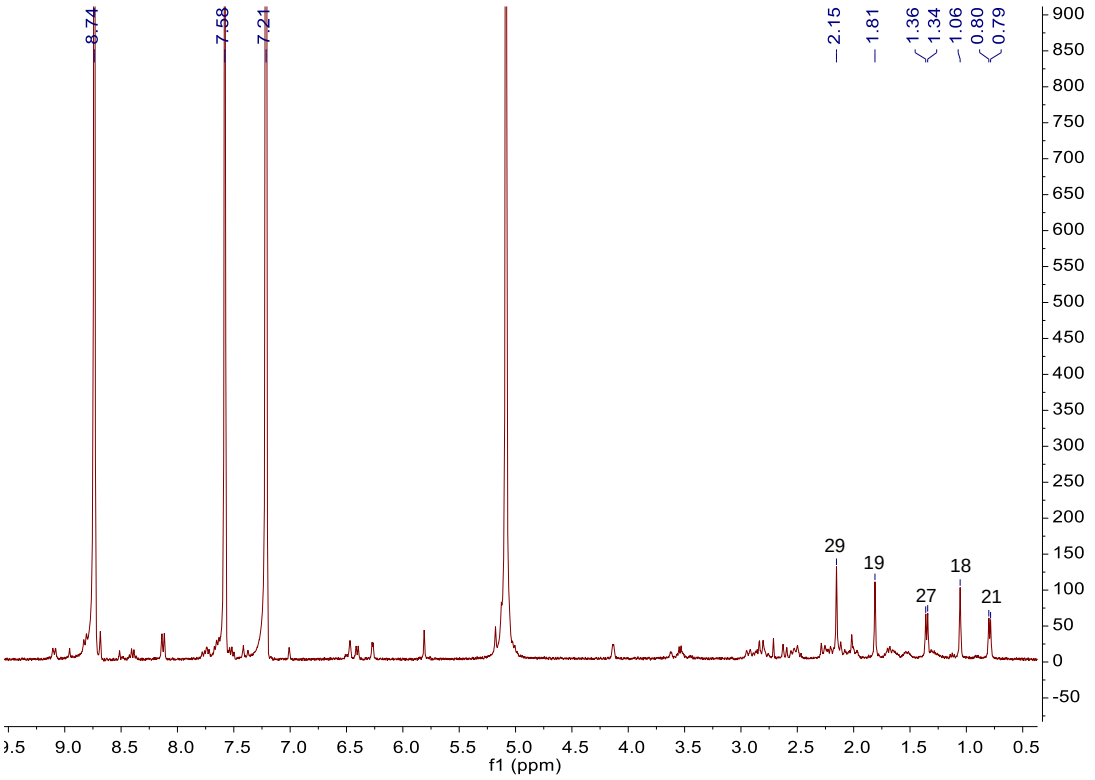


Figure S168. ^{1}H-NMR spectrum of (*S*)-AT Ester of **3** in pyridine-d_5 (400 MHz).

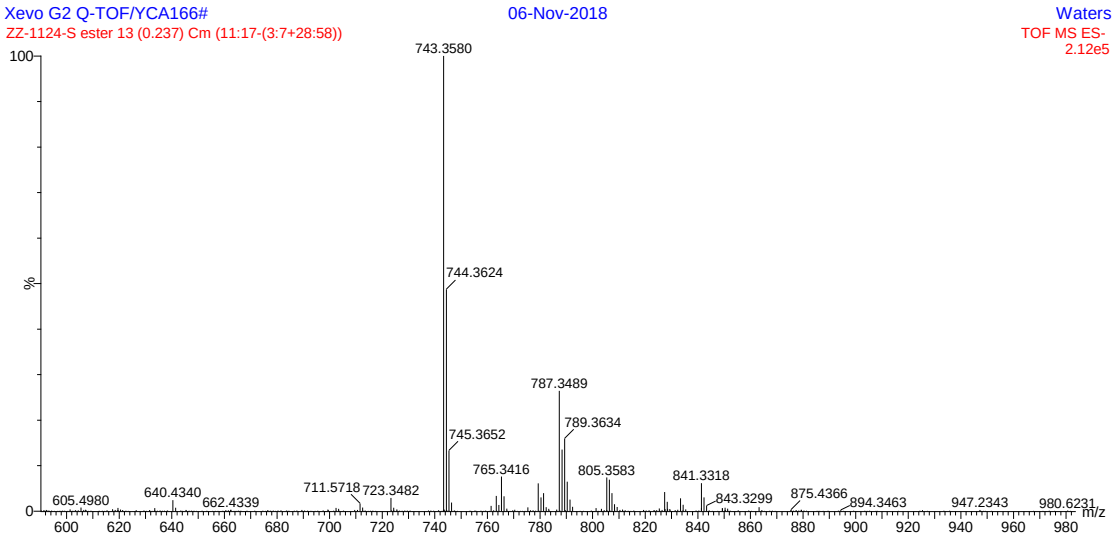


Figure S169. (-)-ESI-MS of (*S*)-AT Ester of **3**.

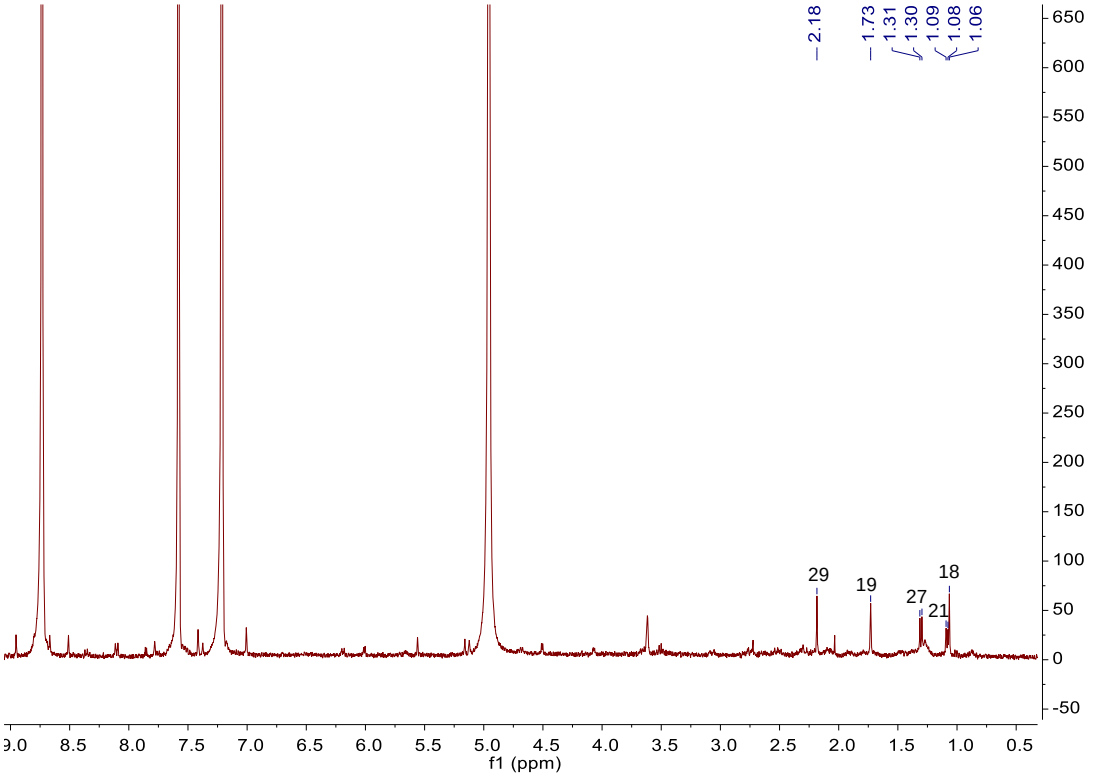


Figure S170. ^{1}H-NMR spectrum of (*R*)-AT Ester of **4** in pyridine-d_5 (400 MHz).

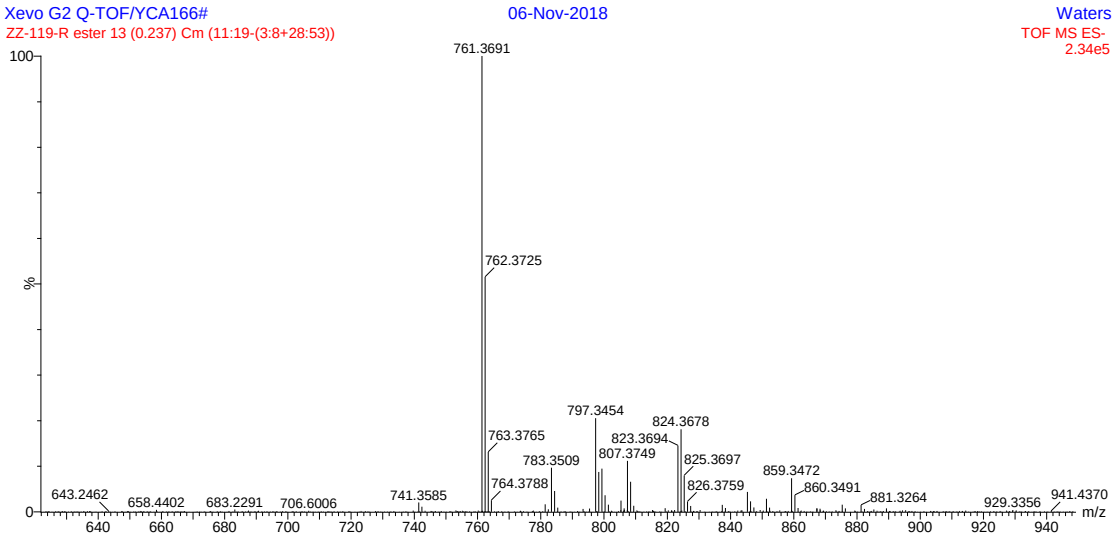


Figure S171. (-)-ESI-MS of (*R*)-AT Ester of **4**.

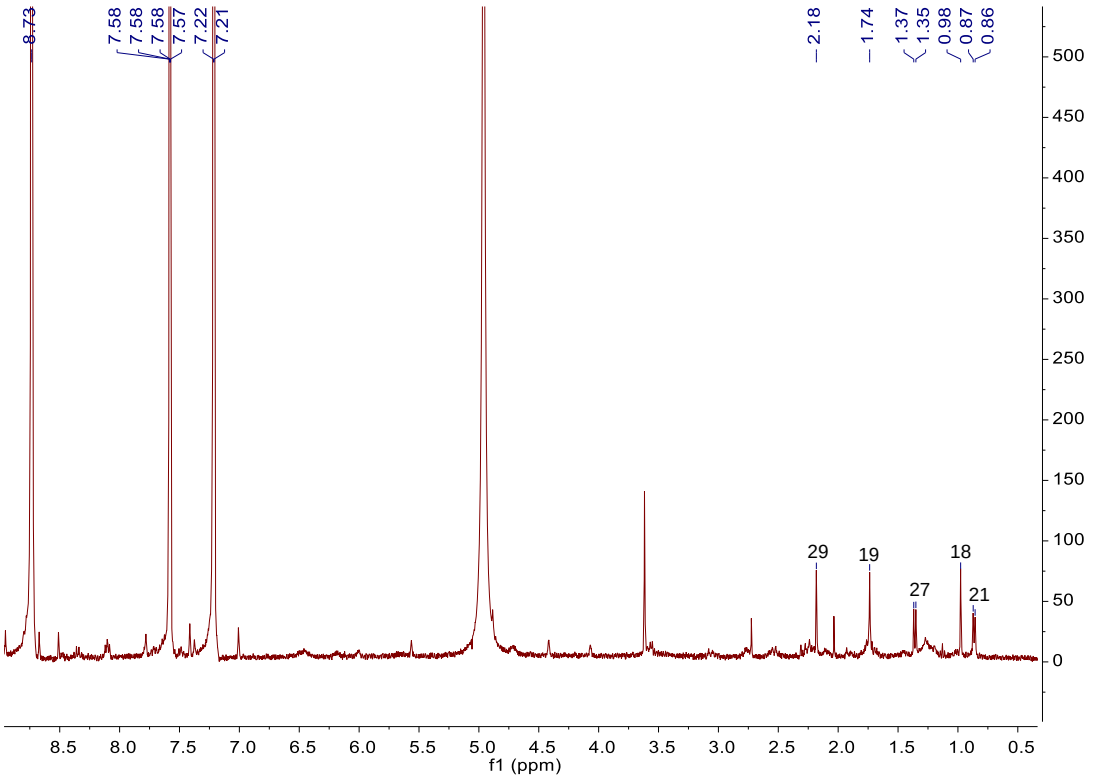


Figure S172. ^{1}H-NMR spectrum of (*S*)-AT Ester of **4** in pyridine-d_5 (400 MHz).

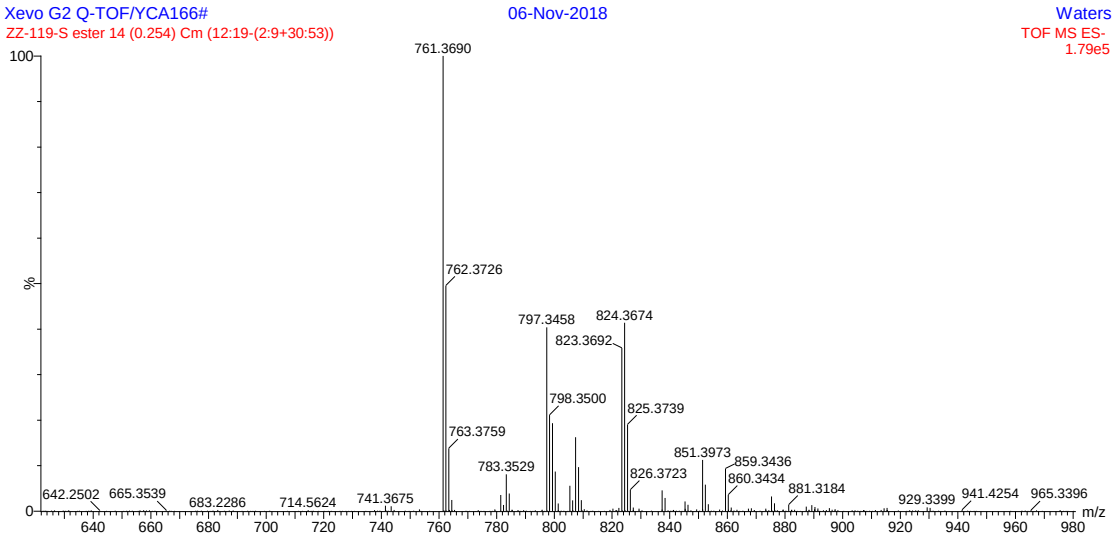


Figure S173. (-)-ESI-MS of (*S*)-AT Ester of **4**.

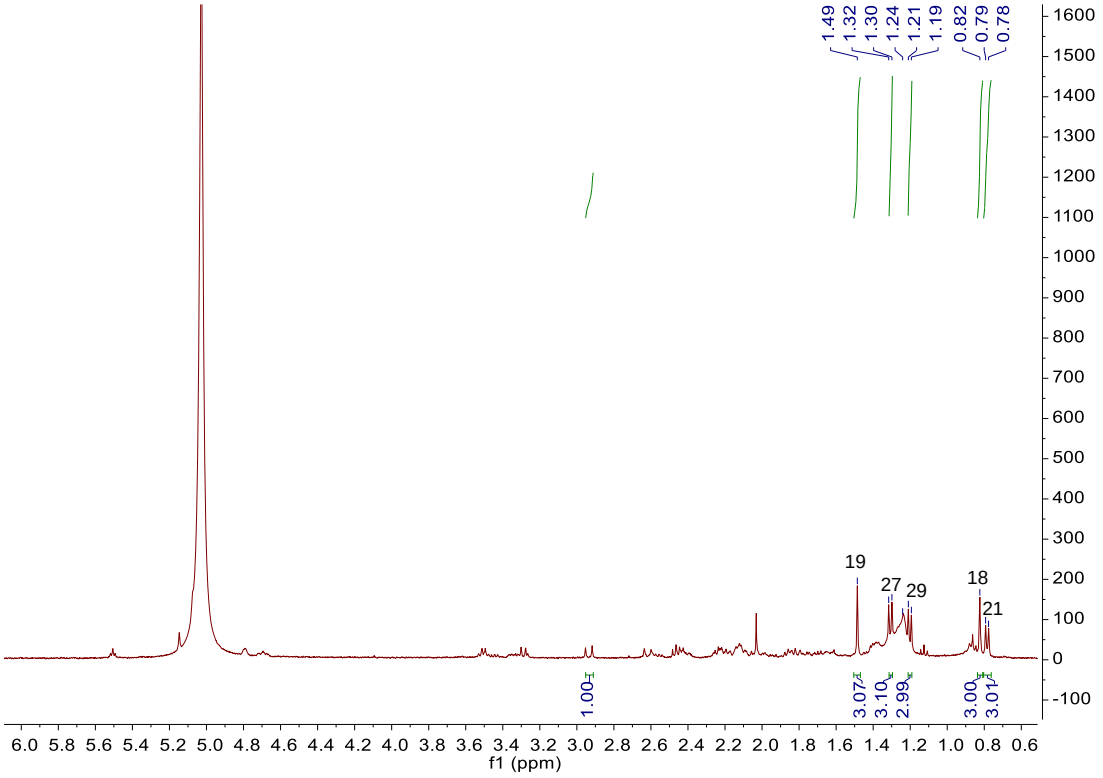


Figure S174. ^{1}H-NMR spectrum of (*R*)-AT Ester of **6** in pyridine-d_5 (400 MHz).

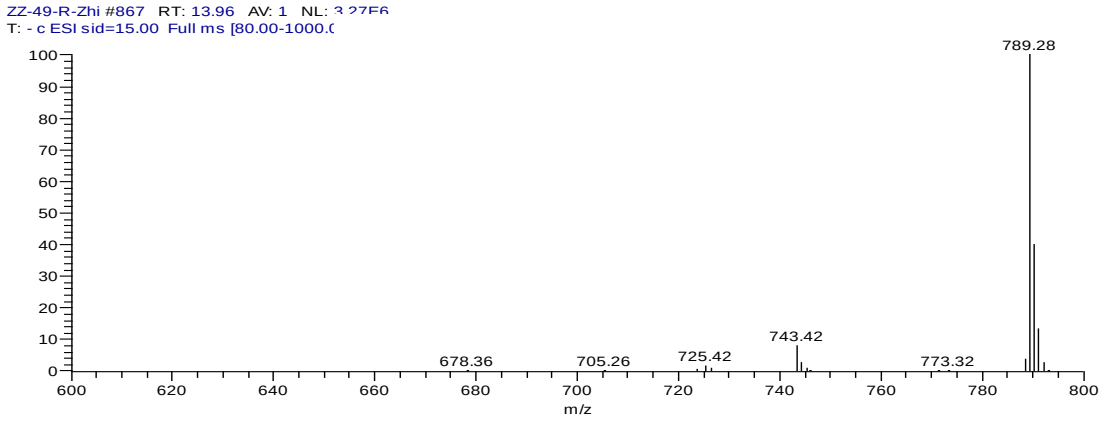


Figure S175. (-)-ESI-MS of (*R*)-AT Ester of **6**.

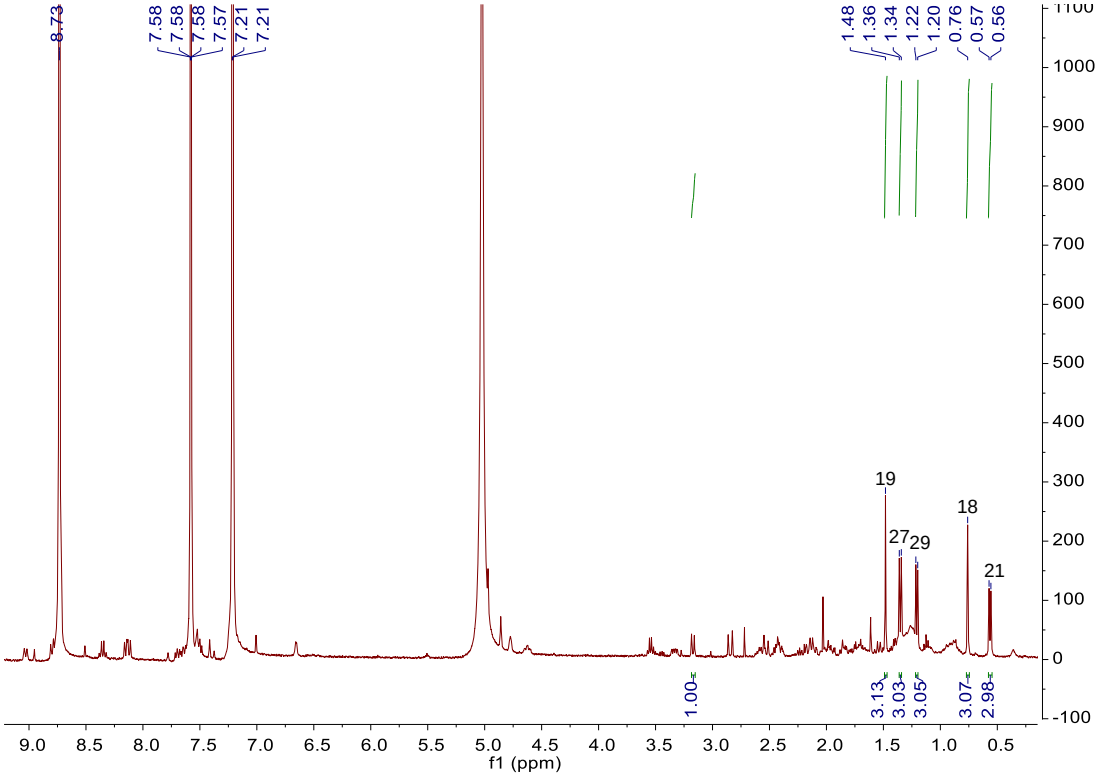


Figure S176. ^{1}H-NMR spectrum of (*S*)-AT Ester of **6** in pyridine-d_5 (400 MHz).

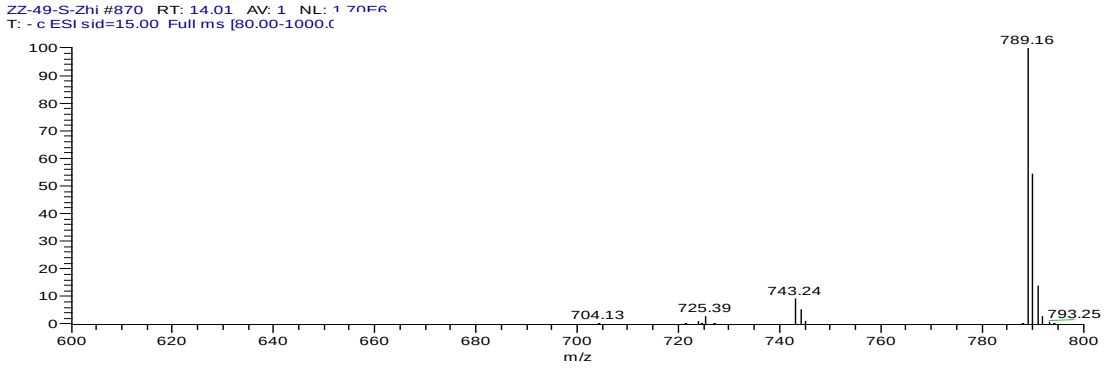


Figure S177. (-)-ESI-MS of (*S*)-AT Ester of **6**.

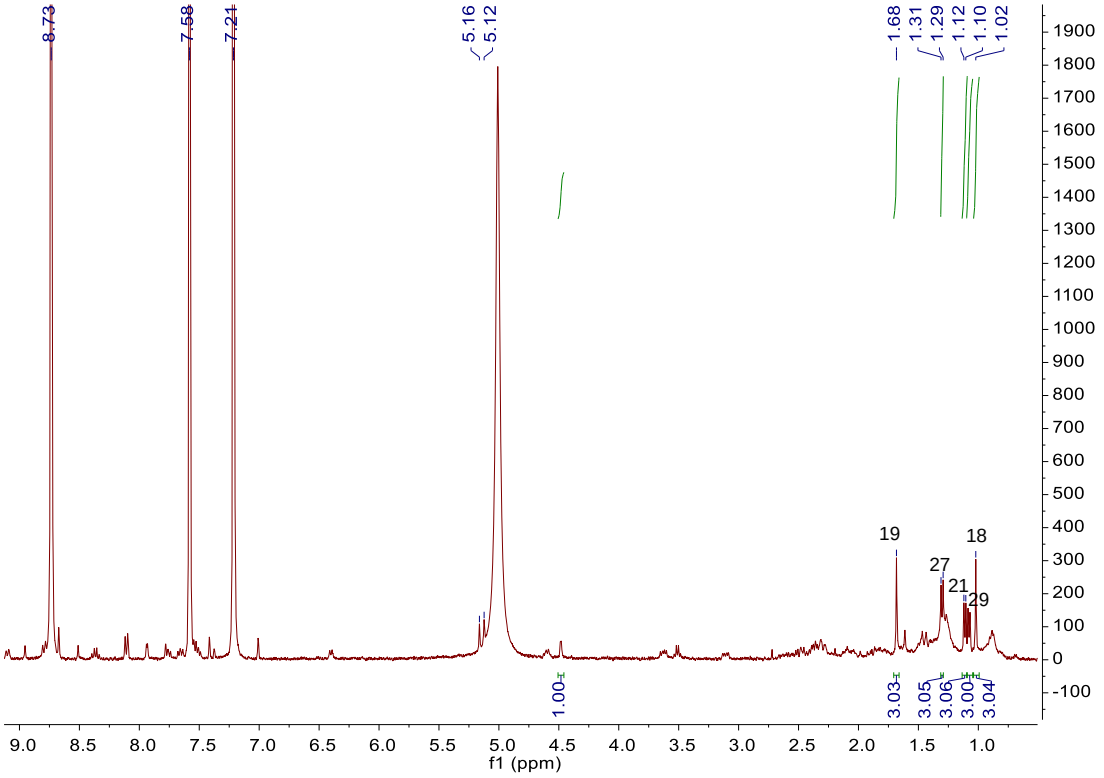


Figure S178. ^{1}H-NMR spectrum of (*R*)-AT Ester of **8** in pyridine-d_5 (400 MHz).

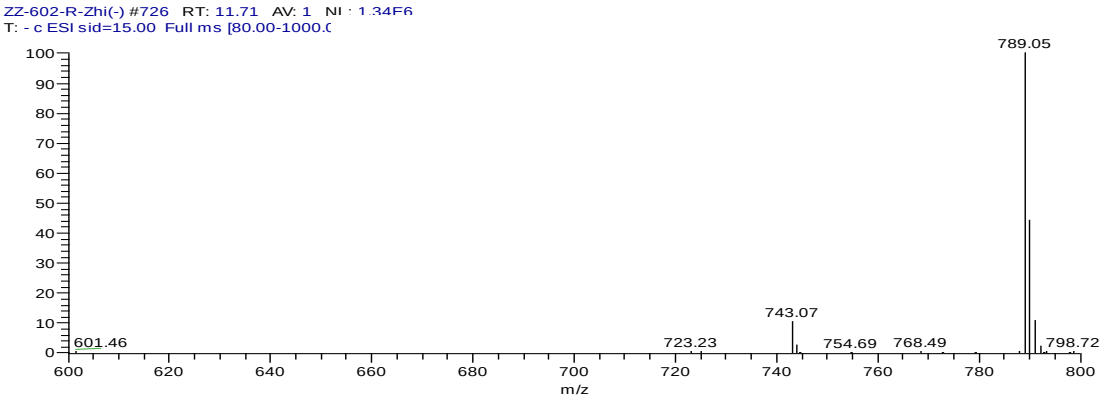


Figure S179. (-)-ESI-MS of (*R*)-AT Ester of **8**.

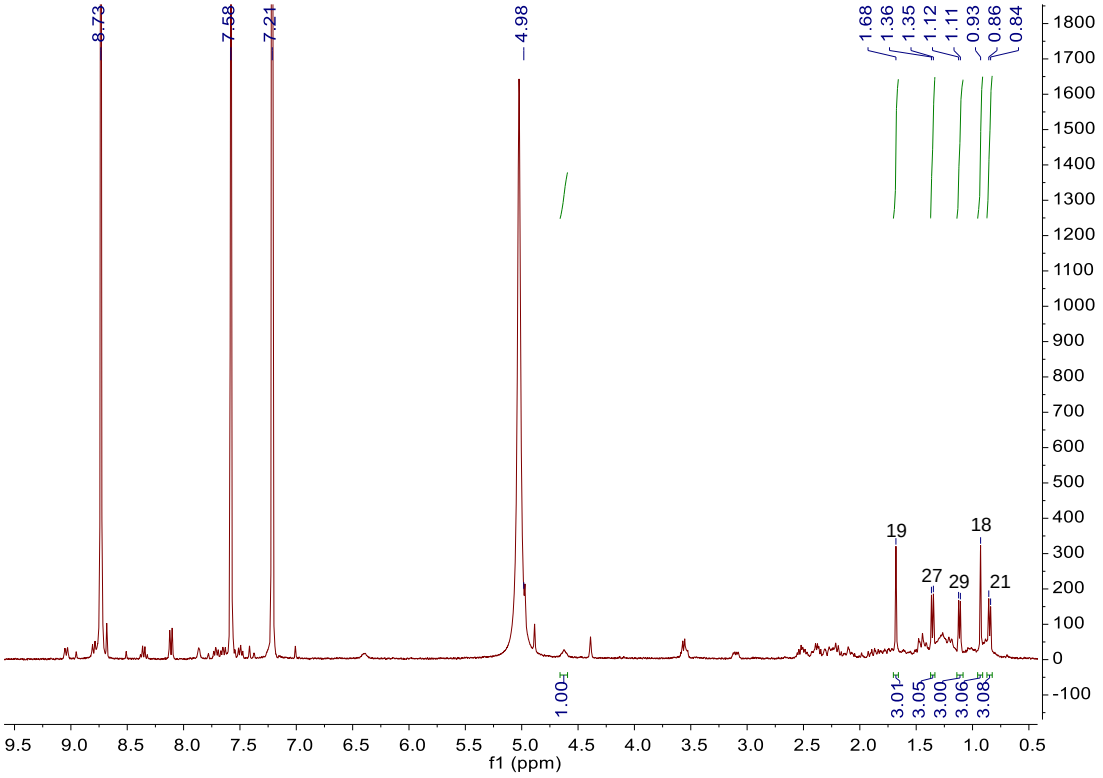


Figure S180. ^{1}H-NMR spectrum of (*S*)-AT Ester of **8** in pyridine-d_5 (400 MHz).

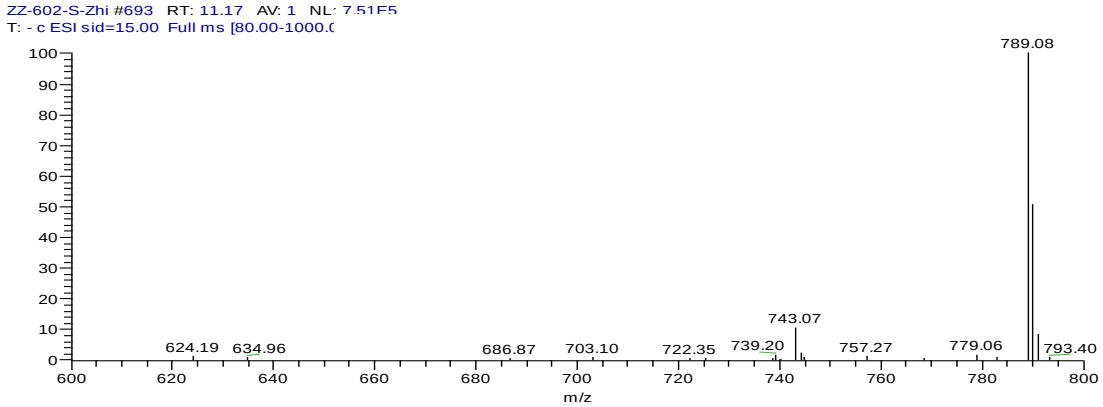


Figure S181. (-)-ESI-MS of (*S*)-AT Ester of **8**.

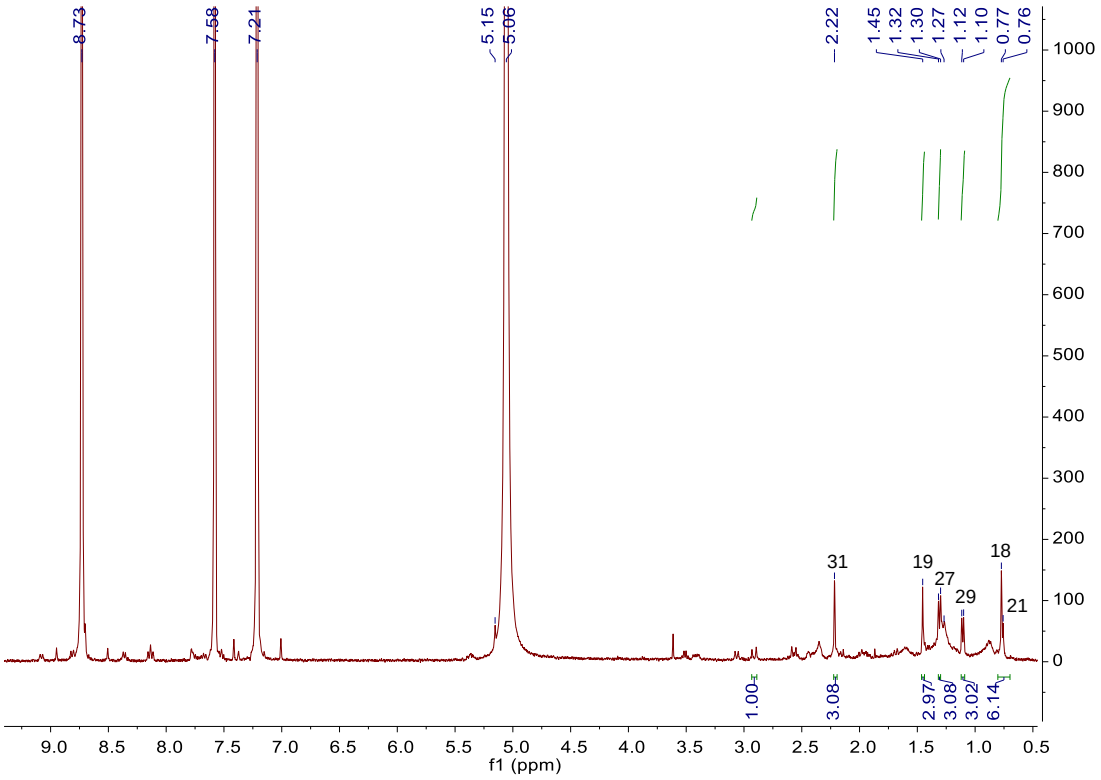


Figure S182. ^{1}H-NMR spectrum of (*R*)-AT Ester of **10** in pyridine-d_5 (400 MHz).

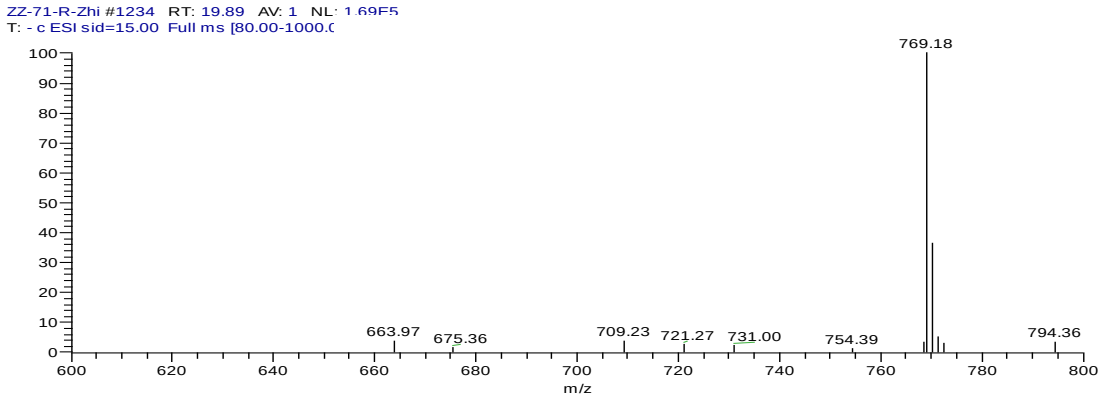


Figure S183. (-)-ESI-MS of (*R*)-AT Ester of **10**.

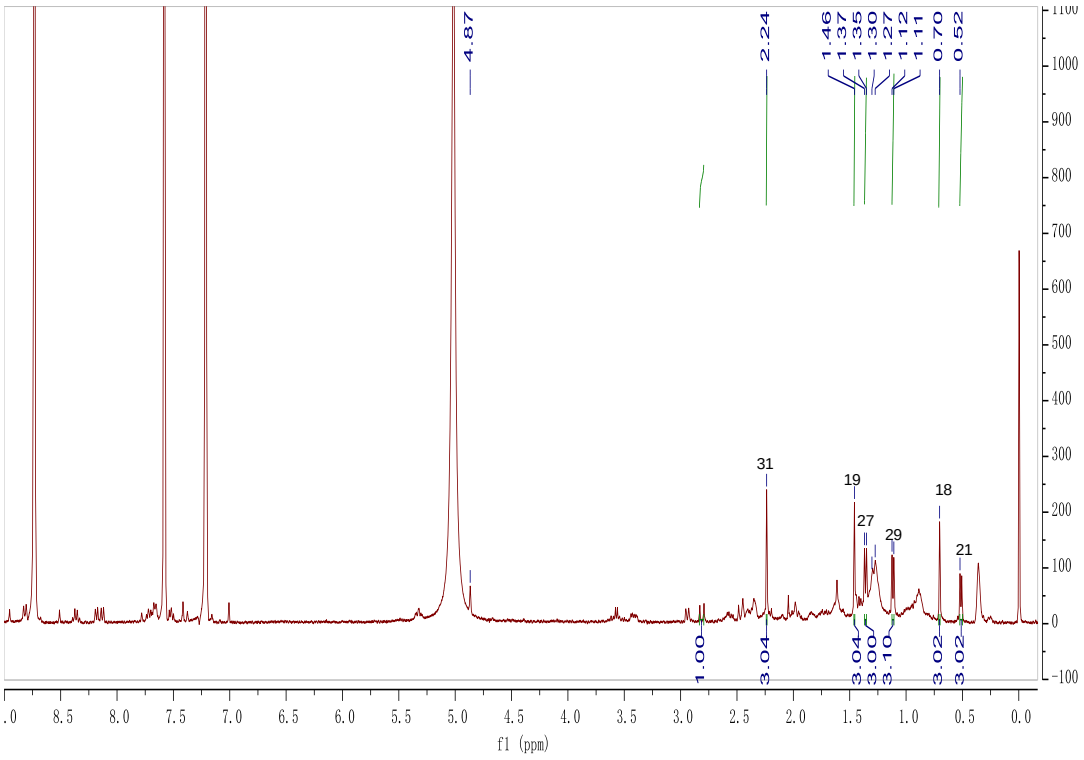


Figure S184. ^{1}H-NMR spectrum of (*S*)-AT Ester of **10** in pyridine-d_5 (400 MHz).

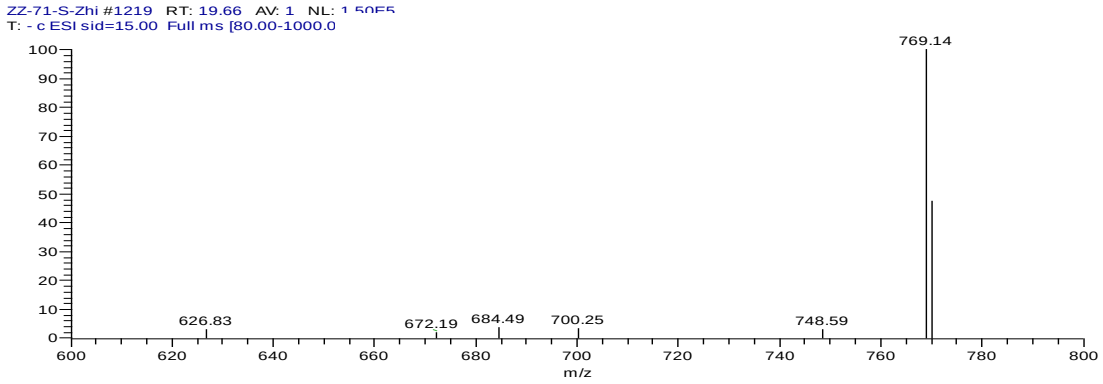


Figure S185. (-)-ESI-MS of (*S*)-AT Ester of **10**.

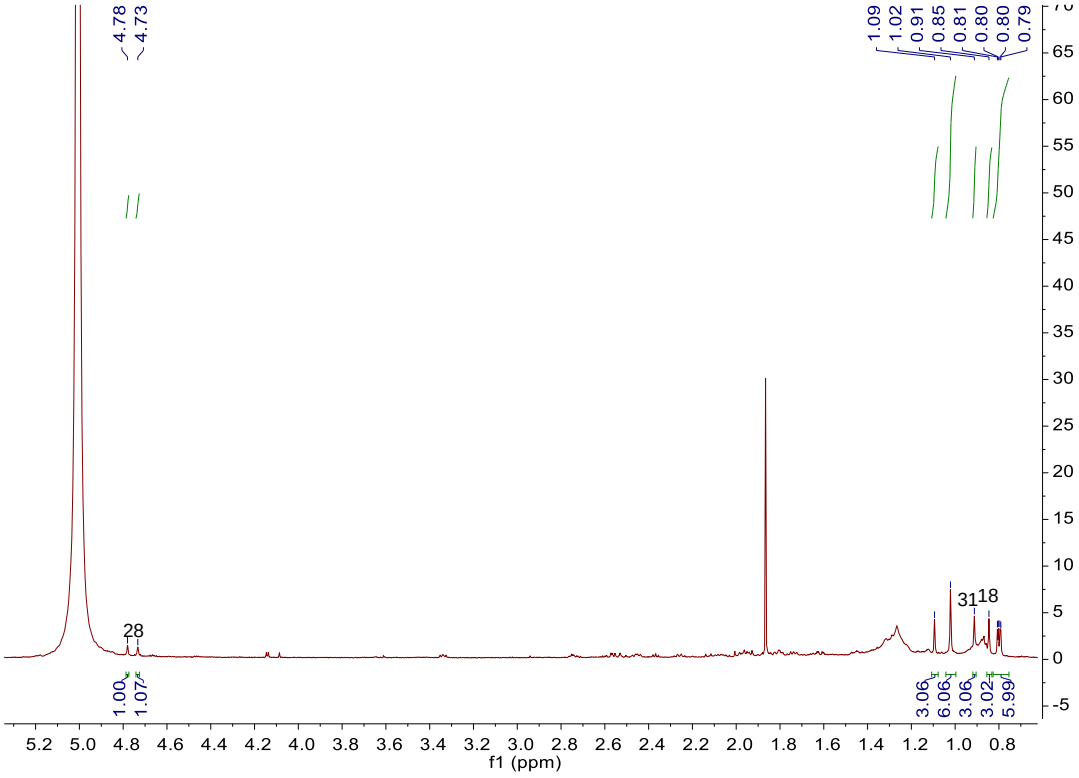


Figure S186. ^{1}H-NMR spectrum of (*R*)-AT Ester of **18** in pyridine-d_5 (600 MHz).

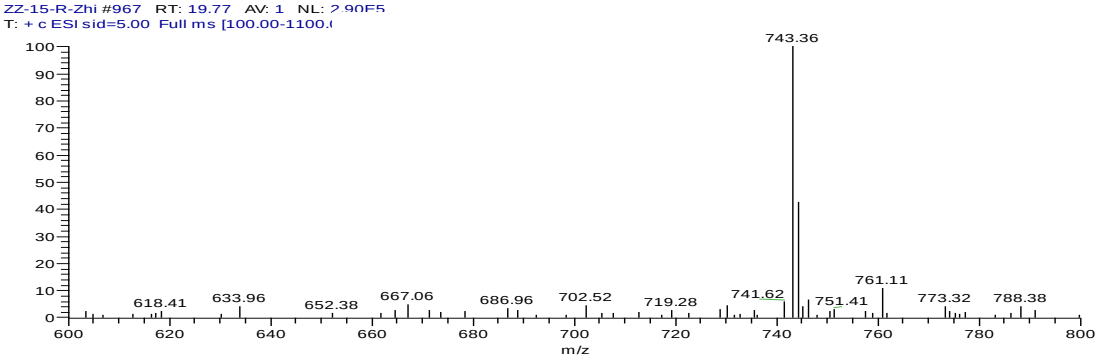


Figure S187. (-)-ESI-MS of (*R*)-AT Ester of **18**.

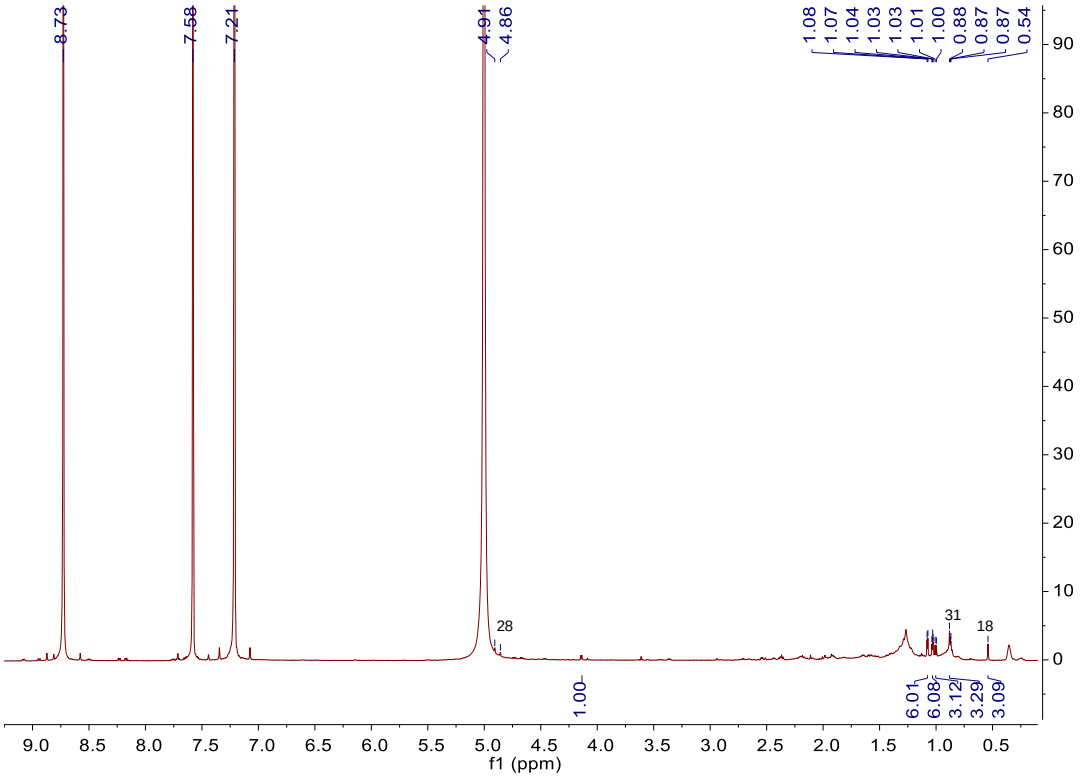


Figure S188. ^{1}H-NMR spectrum of (*S*)-AT Ester of **18** in pyridine-d_5 (400 MHz).

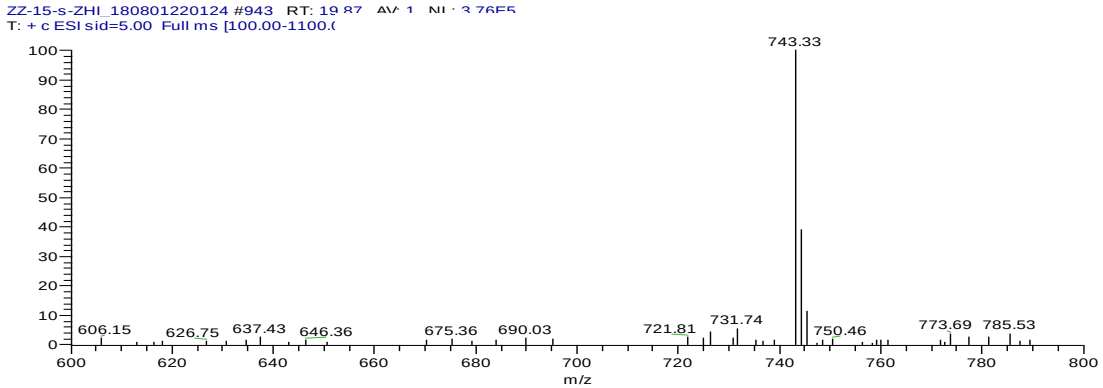


Figure S189. (-)-ESI-MS of (*S*)-AT Ester of **18**.

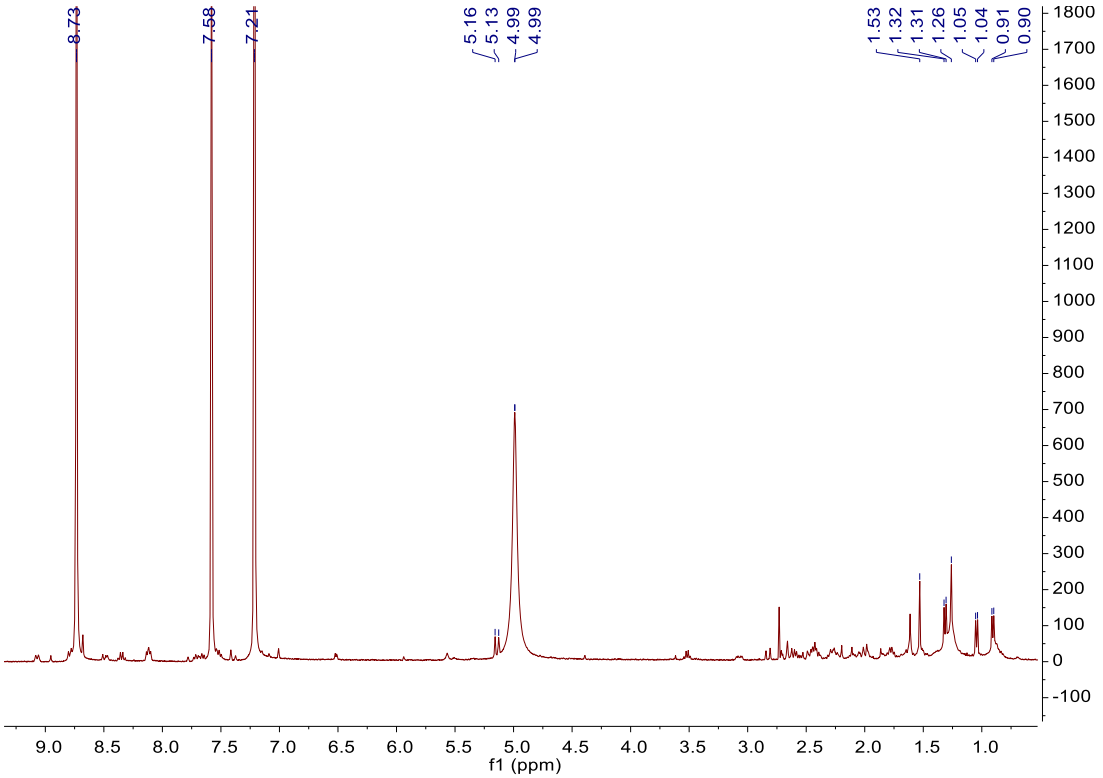


Figure S190. ^{1}H-NMR spectrum of (*R*)-AT Ester of **23** in pyridine-d_5 (400 MHz).

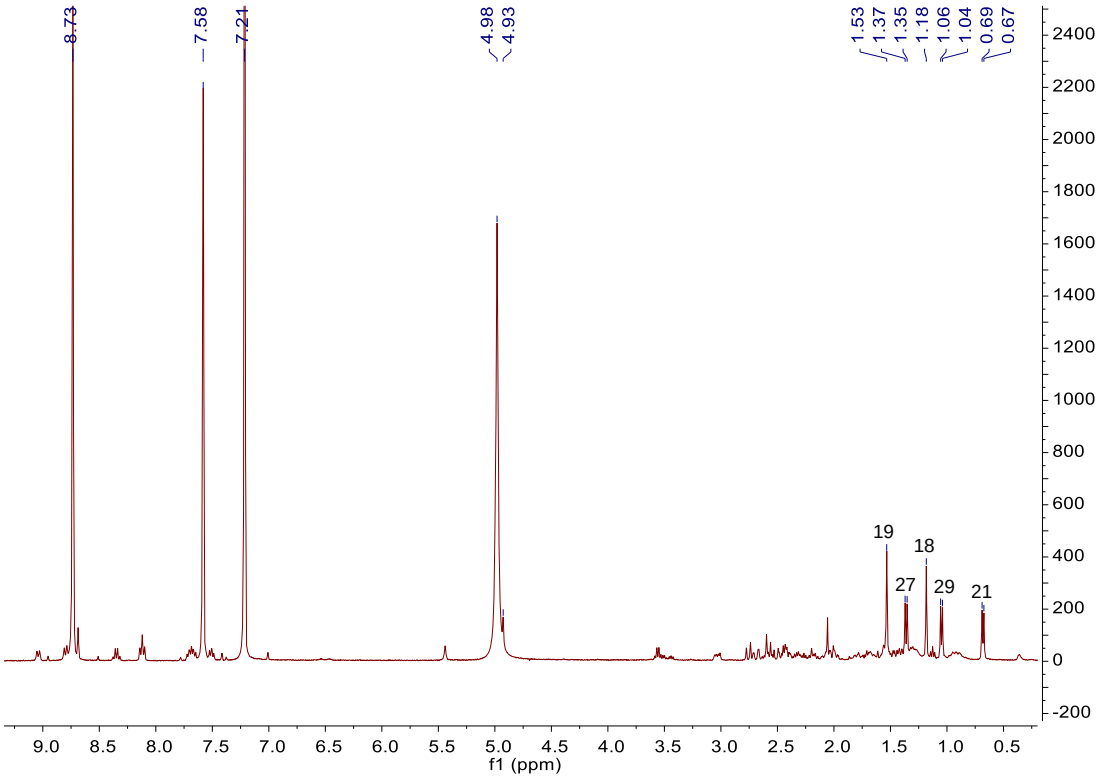


Figure S191. ^{1}H-NMR spectrum of (*S*)-AT Ester of **23** in pyridine-d_5 (400 MHz).

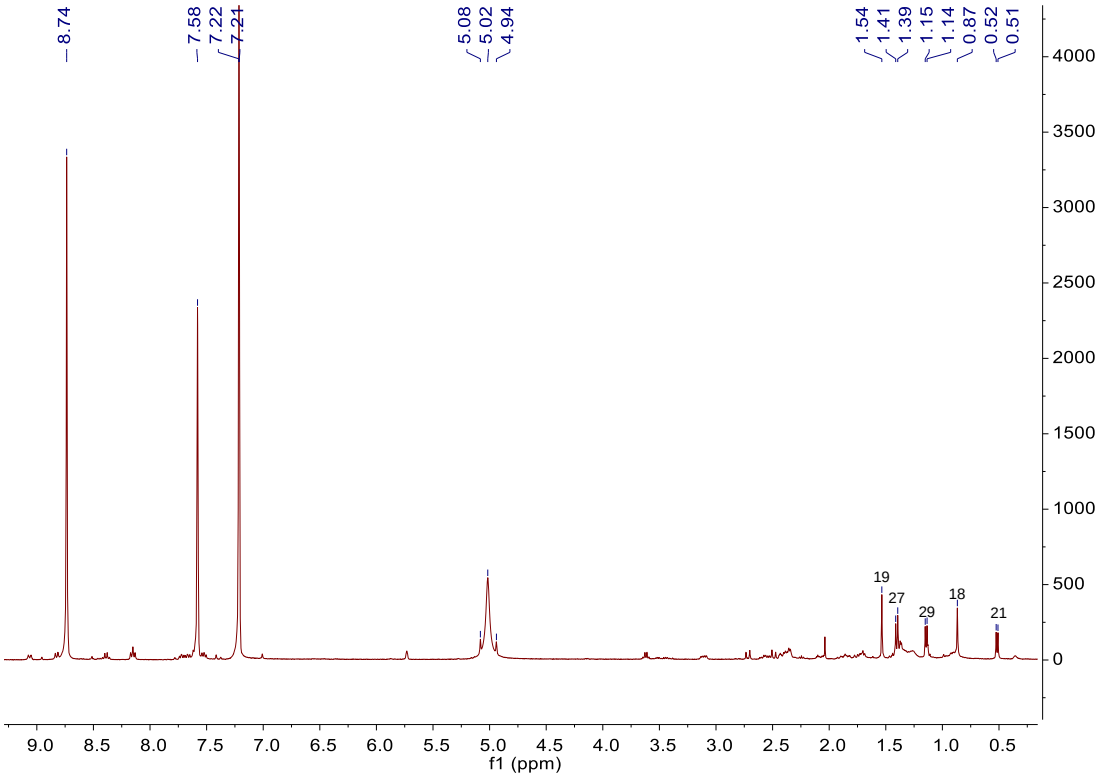


Figure S192. ^{1}H-NMR spectrum of (*R*)-AT Ester of **26** in pyridine-d_5 (400 MHz).

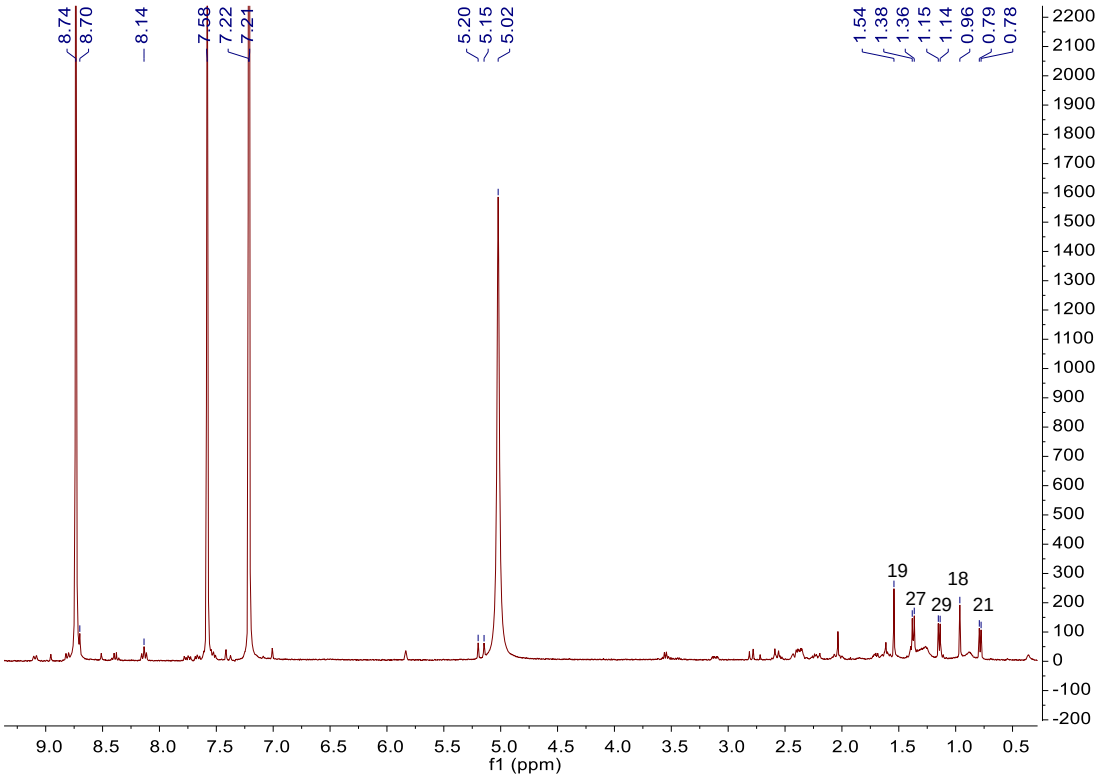


Figure S193. ^{1}H-NMR spectrum of (*S*)-AT Ester of **26** in pyridine-d_5 (400 MHz).

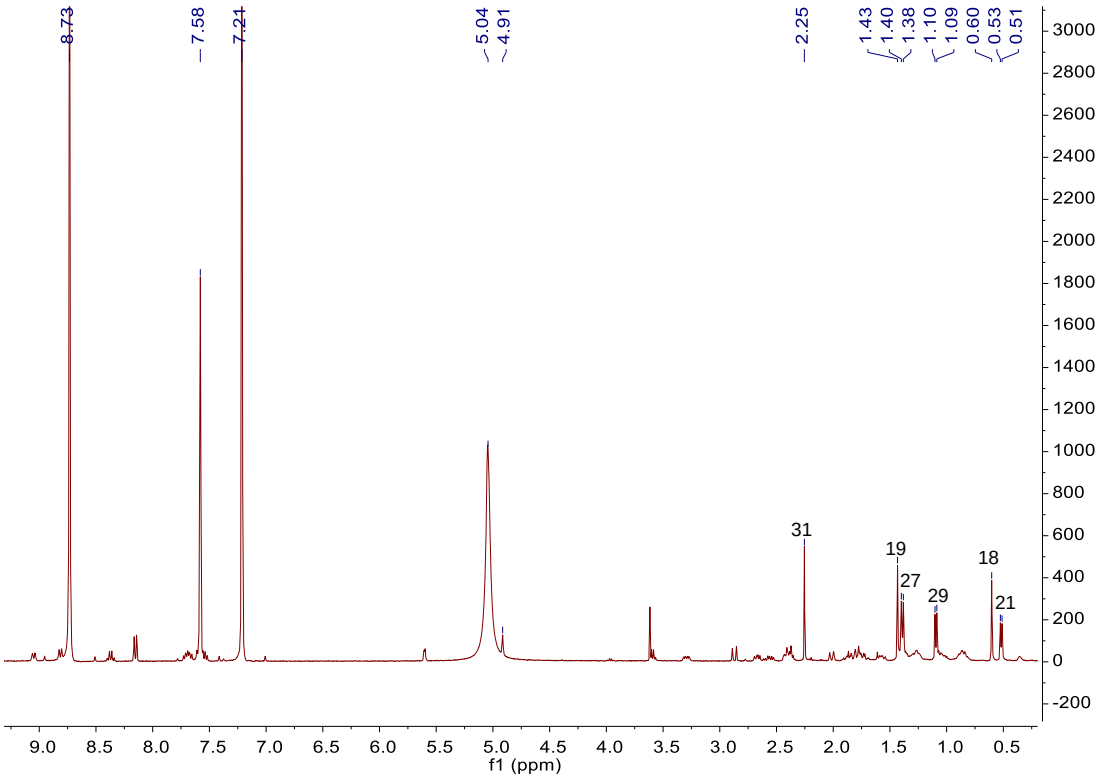


Figure S194. ^{1}H-NMR spectrum of (*R*)-AT Ester of **29** in pyridine-d_5 (400 MHz).

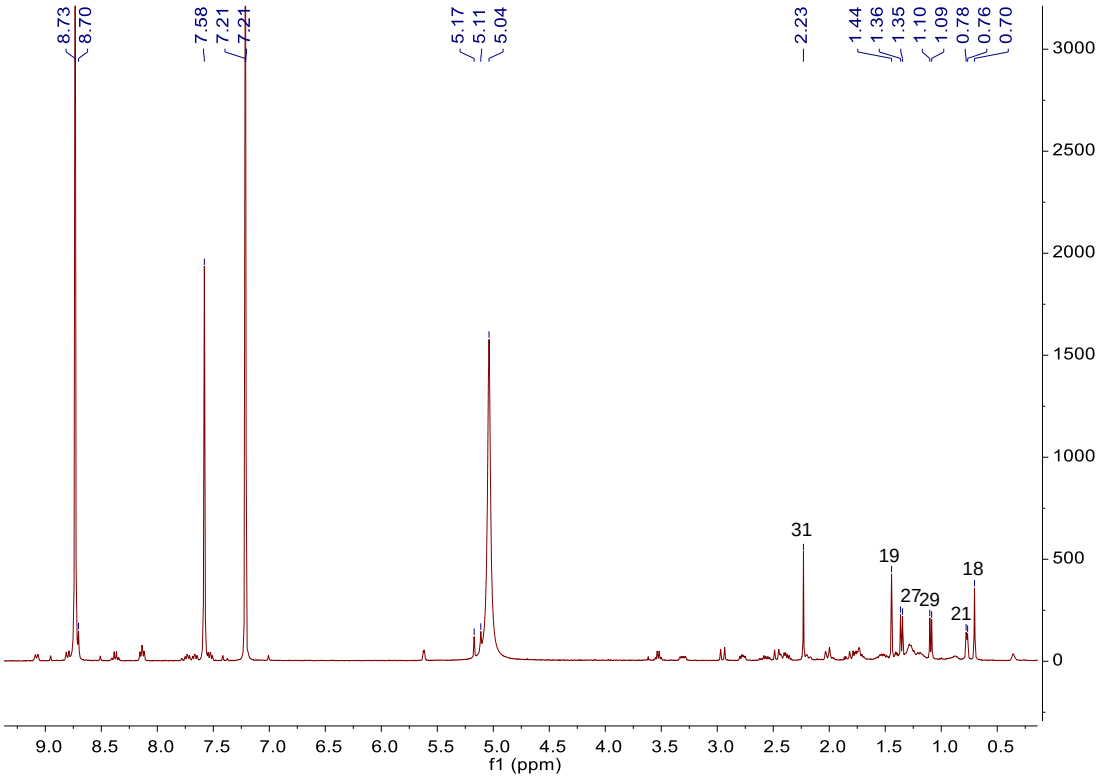


Figure S195. ^{1}H-NMR spectrum of (*S*)-AT Ester of **29** in pyridine-d_5 (400 MHz).

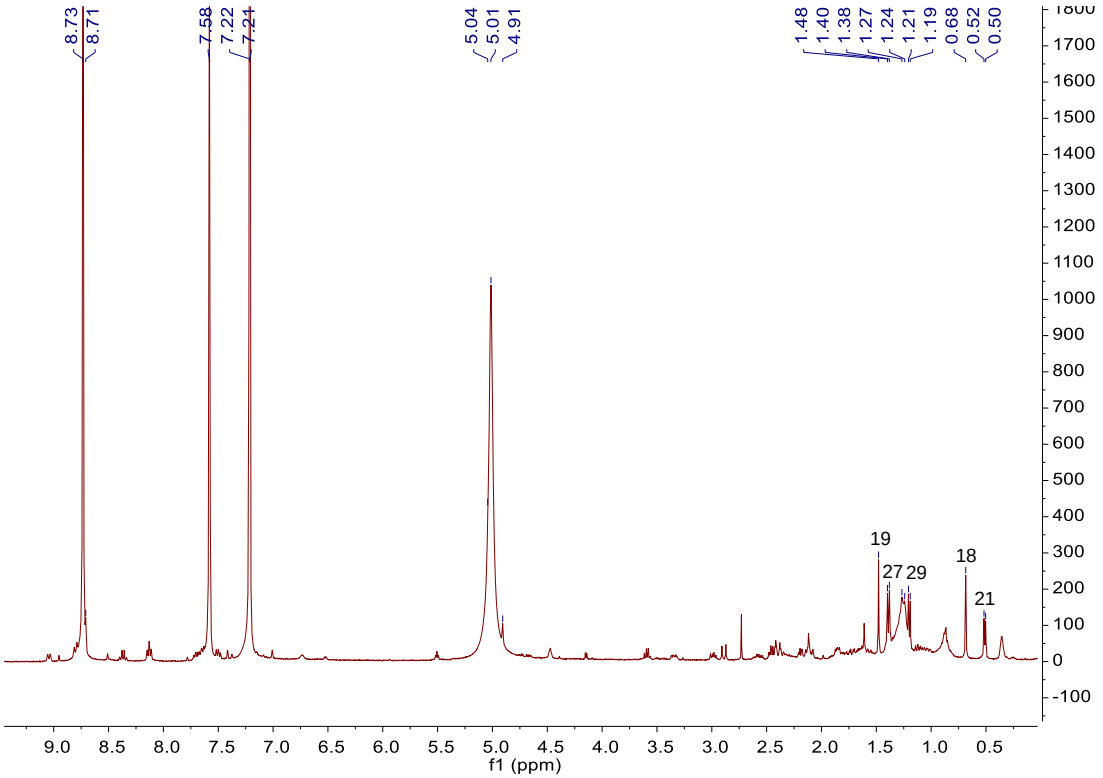


Figure S196. ^{1}H-NMR spectrum of (*R*)-AT Ester of **40** in pyridine-d_5 (400 MHz).

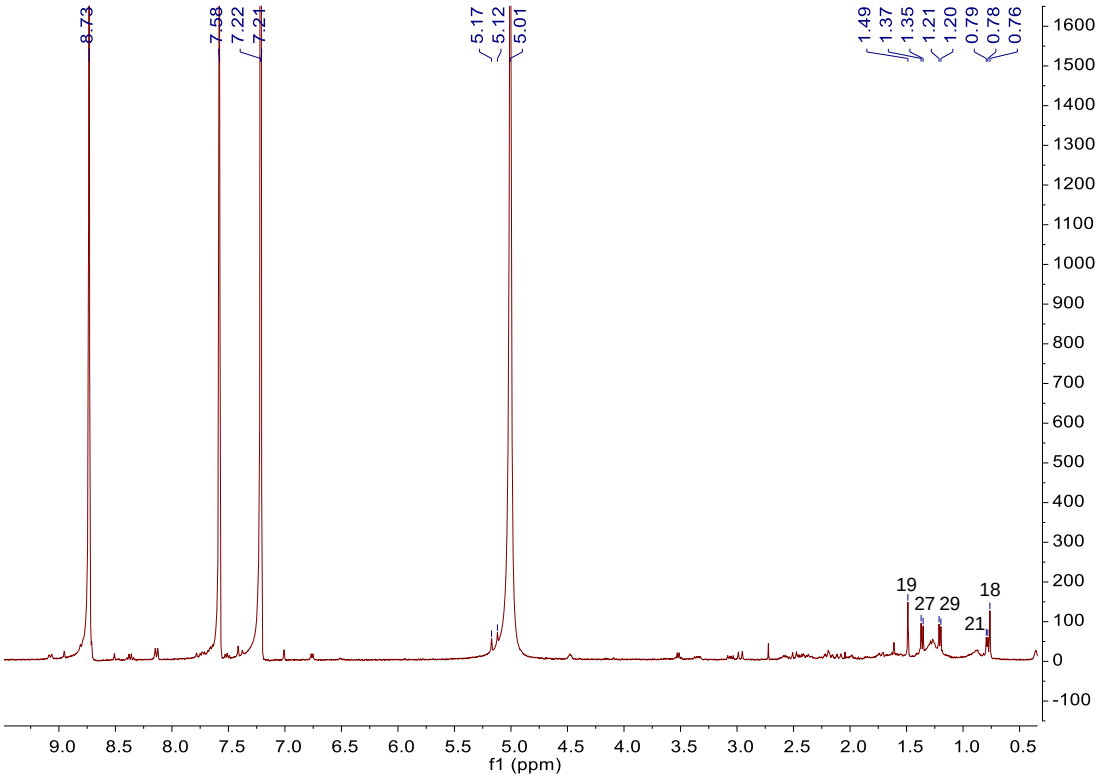


Figure S197. ^{1}H-NMR spectrum of (*S*)-AT Ester of **40** in pyridine-d_5 (400 MHz).

Detection of compounds 12–17 in *Antrodia camphorata*.

1.1 Standard solutions and sample preparation.

Preparation of mixed reference standards. The reference compounds were individually dissolved in 100% methanol to appropriate concentrations.

Preparation of Antrodia camphorata sample. In order to eliminate the interference of MeOH and EtOH, we used MeCN for extraction. 200 mg of dried fungal materials was ultrasonicated in 15 mL MeCN for 30 min. The supernatant was filtered through 0.22 μm membranes before analysis.

1.2 **Liquid chromatography.** A Vanquish UHPLC^{TM} system (Thermo Fisher Scientific Inc., USA) was used for the analysis. Samples were separated on an Acquity UPLC HSS T3 column (150 mm × 2.1 mm I.D., 1.8 μm) equipped with a VanGuard pre-column (5 mm × 2.1 mm I.D., 1.8 μm) (Waters, USA). The column temperature was 50 °C. The mobile phase, at 0.3 mL/min, consisted of water containing 0.1% formic acid (*v*/*v*, A) and acetonitrile (B). The gradient elution program was as follows: 0–5 min, 45–50% B; 5–7 min, 50-60% B; 7–11 min, 60-100% B; 11–16 min, 100% The injection volume was 2 μL.

1.3 **Mass spectrometry.** Mass spectrometry analysis was performed on a Q-Exactive hybrid quadrupole-orbitrap mass spectrometer (Thermo Scientific, San Jose, USA) equipped with a heated electrospray ionization source (HESI). The mass spectrometer was operated in both positive and negative modes. The MS parameters were set as follows: spray voltage: 3.5 kV; sheath gas flow rate: 45 arb; auxiliary gas: 10 arb; capillary temperature: 350 °C; probe heater temperature: 400 °C; S-lens RF level: 60 V; scan mode: full MS (resolution 70,000) and MS/MS (resolution 17,500); scan range: *m*/*z* 400–800. Data were processed using Xcalibur^{TM} 4.1 software (ThermoFisher).

1.4 **Detection of compounds 12–17 in *Antrodia camphorata*.** The methyl or ethyl esters (**12–17**) were tested in *Antrodia camphorata* by comparing with pure compounds. The high-resolution MS/MS spectra for **12–17** reference standards were obtained, respectively. They were identified by extracted ion chromatogram and the *m*/*z* value of the $[M+H]^+$ or $[M-H]^-$ ions. Compounds **12–14**, **16**, and **17** were detected in (+)-ESI mode. Compound **15** was detected in (-)-ESI mode.

While some of the compounds could not be detected in the total ion current (TIC) due to their low amounts in the crude extract, all the six compounds were detected in the extracted ion chromatograms (EIC) of the MeCN extract. These results confirm that compounds **12–17** are original natural products from *Antrodia camphorata*.

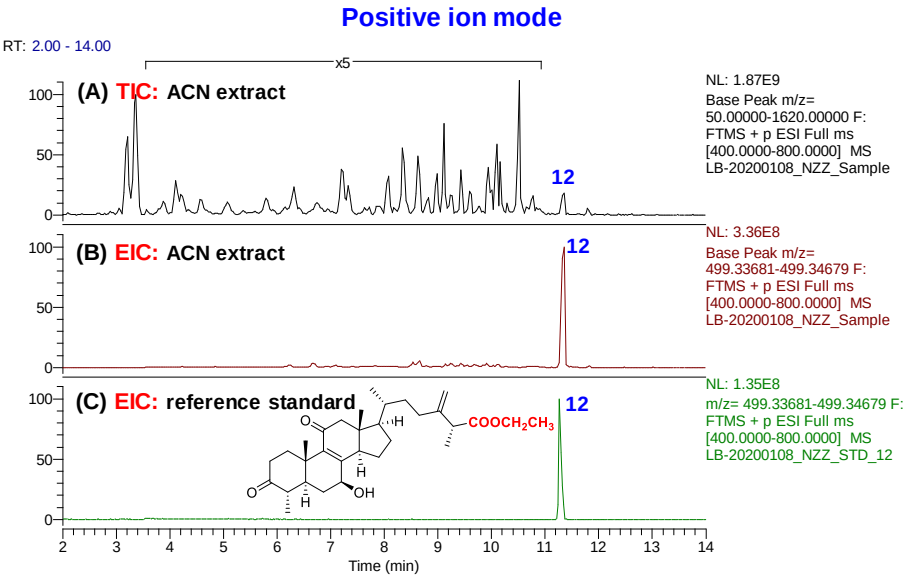


Figure S198. Detection of **12** in the MeCN extract of *Antrodia camphorata*.

(A) Total ion current (TIC) of the MeCN extract. (B) Extracted ion chromatogram (EIC) of the MeCN extract for compound **12**. (C) EIC of the pure compound **12** (reference standard).

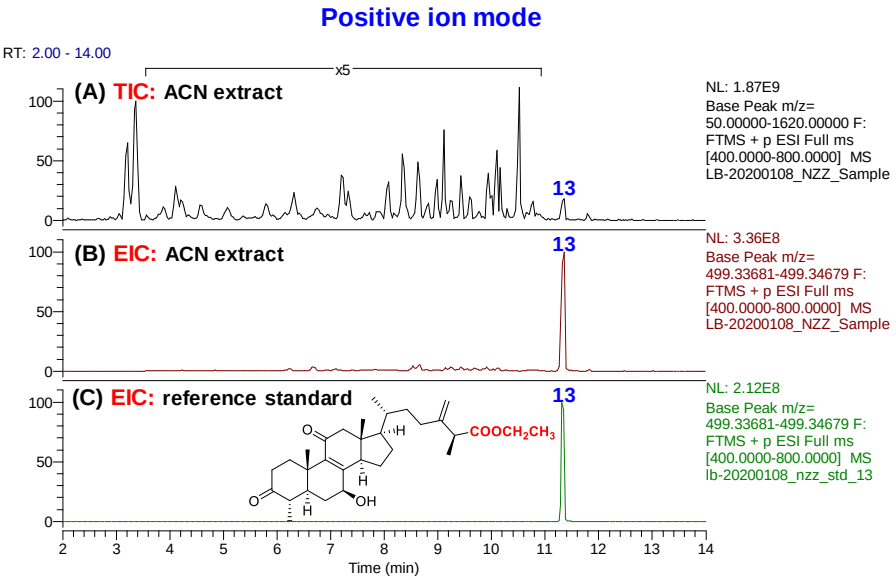


Figure S199. Detection of **13** in the MeCN extract of *Antrodia camphorata*.

(A) Total ion current (TIC) of the MeCN extract. (B) Extracted ion chromatogram (EIC) of the MeCN extract for compound **13**. (C) EIC of the pure compound **13** (reference standard).

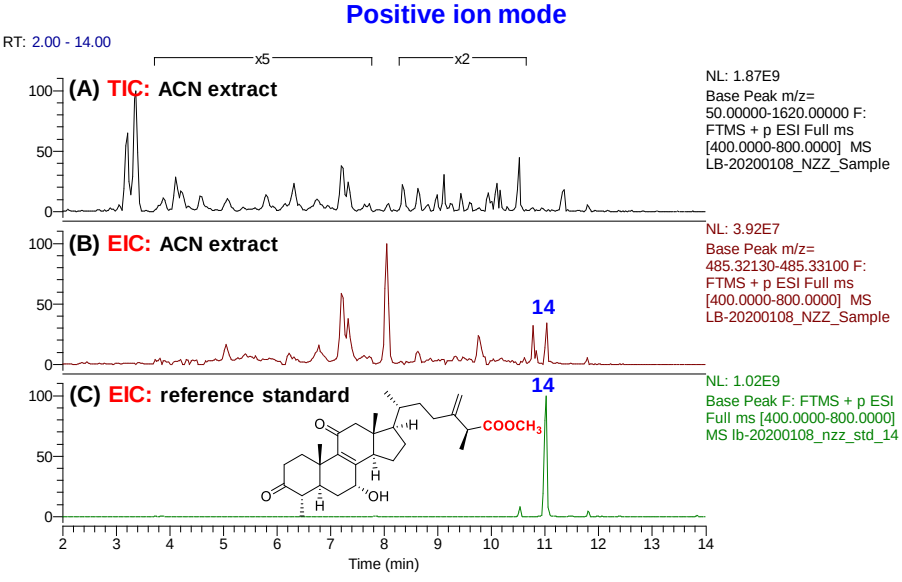


Figure S200. Detection of **14** in the MeCN extract of *Antrodia camphorata*.

(A) Total ion current (TIC) of the MeCN extract. (B) Extracted ion chromatogram (EIC) of the MeCN extract for compound **14**. (C) EIC of the pure compound **14** (reference standard).

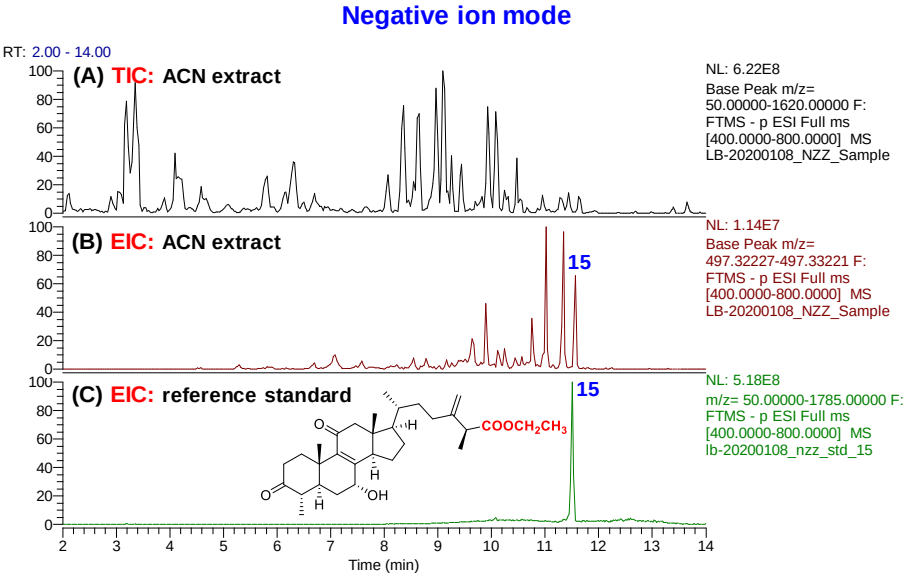


Figure S201. Detection of **15** in the MeCN extract of *Antrodia camphorata*.

(A) Total ion current (TIC) of the MeCN extract. (B) Extracted ion chromatogram (EIC) of the MeCN extract for compound **15**. (C) EIC of the pure compound **15** (reference standard).

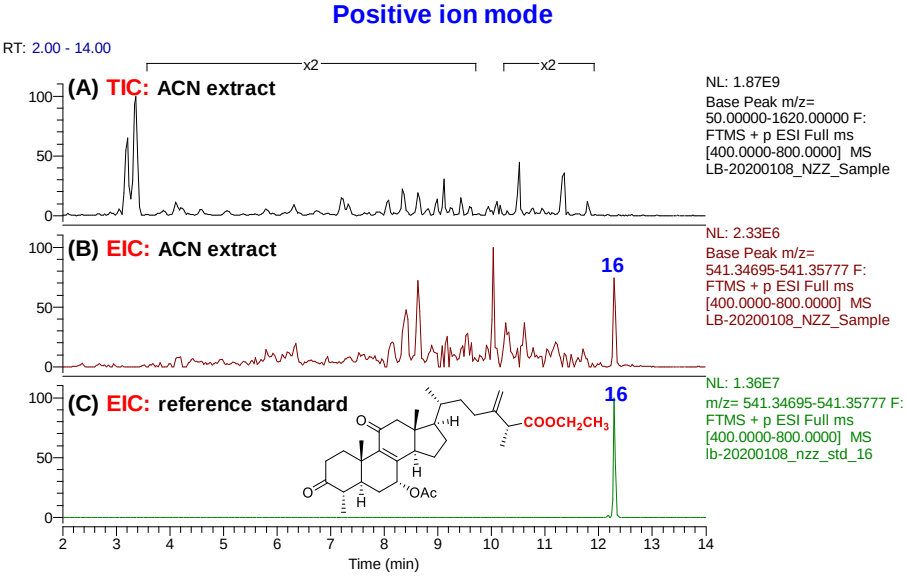


Figure S202. Detection of **16** in the MeCN extract of *Antrodia camphorata*.

(A) Total ion current (TIC) of the MeCN extract. (B) Extracted ion chromatogram (EIC) of the MeCN extract for compound **16**. (C) EIC of the pure compound **16** (reference standard).

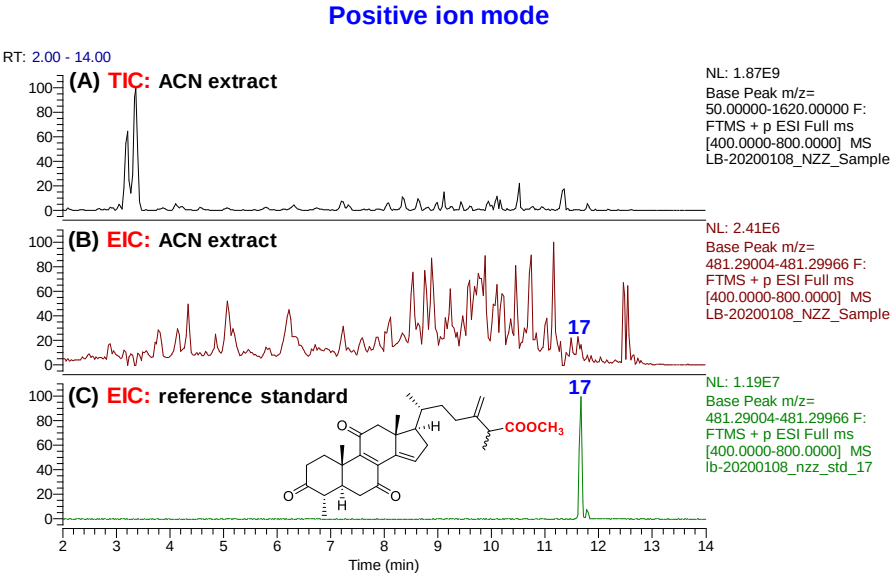
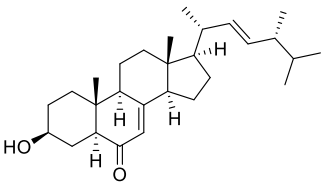
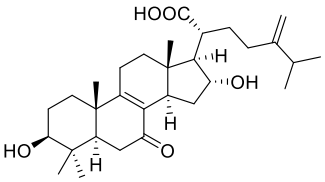


Figure S203. Detection of **17** in the MeCN extract of *Antrodia camphorata*.

(A) Total ion current (TIC) of the MeCN extract. (B) Extracted ion chromatogram (EIC) of the MeCN extract for compound **17**. (C) EIC of the pure compound **17** (reference standard).



(22*E*,24*R*)-3β-hydroxyergosta-7,22-diene-6-one



3β,16α-dihydroxy-7-oxo-24-methyllanosta-8,24(31)-dien-21-oic acid

Figure S204. Structures of (22*E*,24*R*)-3β-hydroxyergosta-7,22-diene-6-one and 3β,16α-dihydroxy-7-oxo-24-methyllanosta-8,24(31)-dien-21-oic acid.