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Electronic Supplementary Information

Spiroalanpyrroids A and B, sesquiterpene alkaloids with a unique spiro-eudesmanolide-pyrrolizidine skeleton from *Inula helenium*

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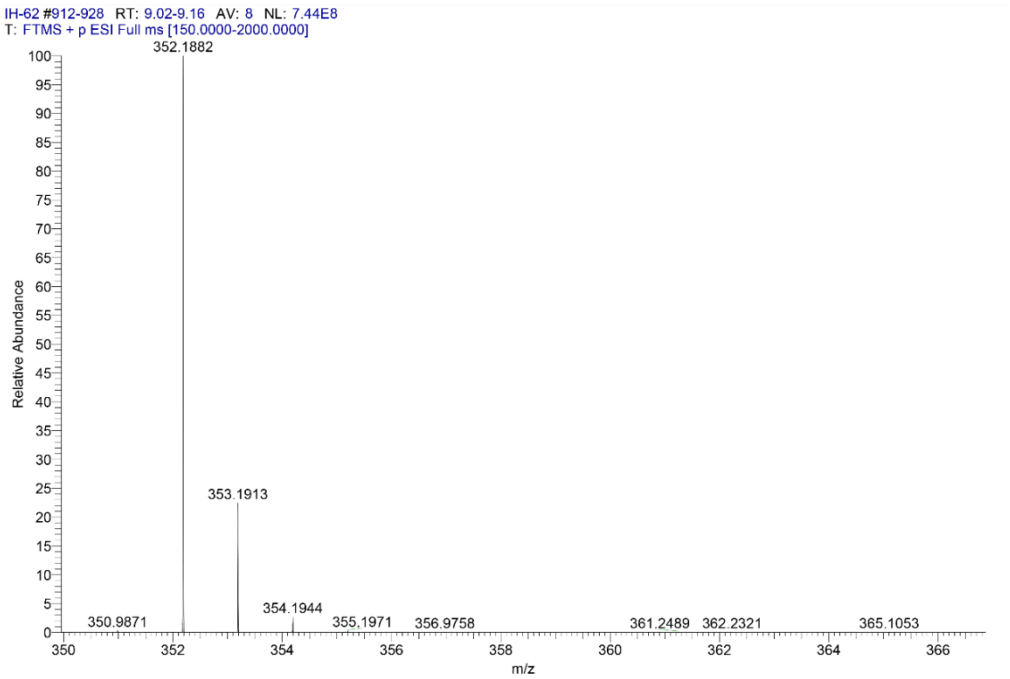

Fig. S1 HRESIMS spectrum of **1**.

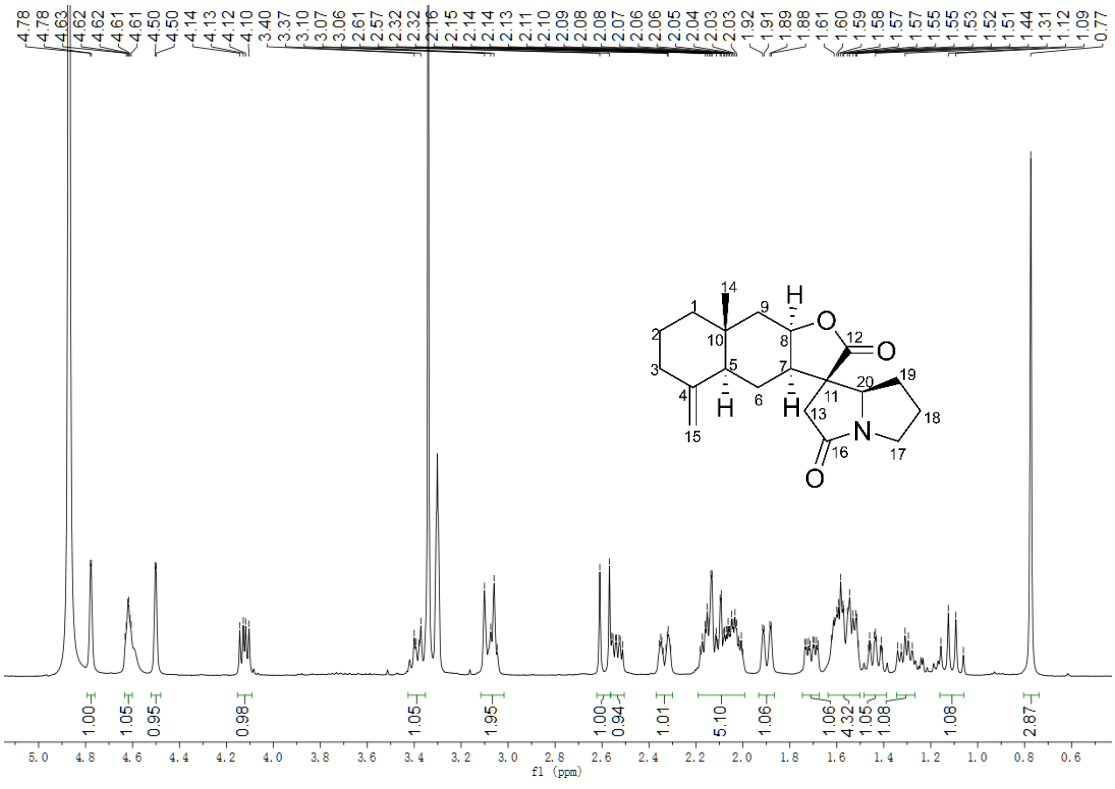

Fig. S2 ^{1}H NMR spectrum (400 MHz) of **1** in CD_3OD.

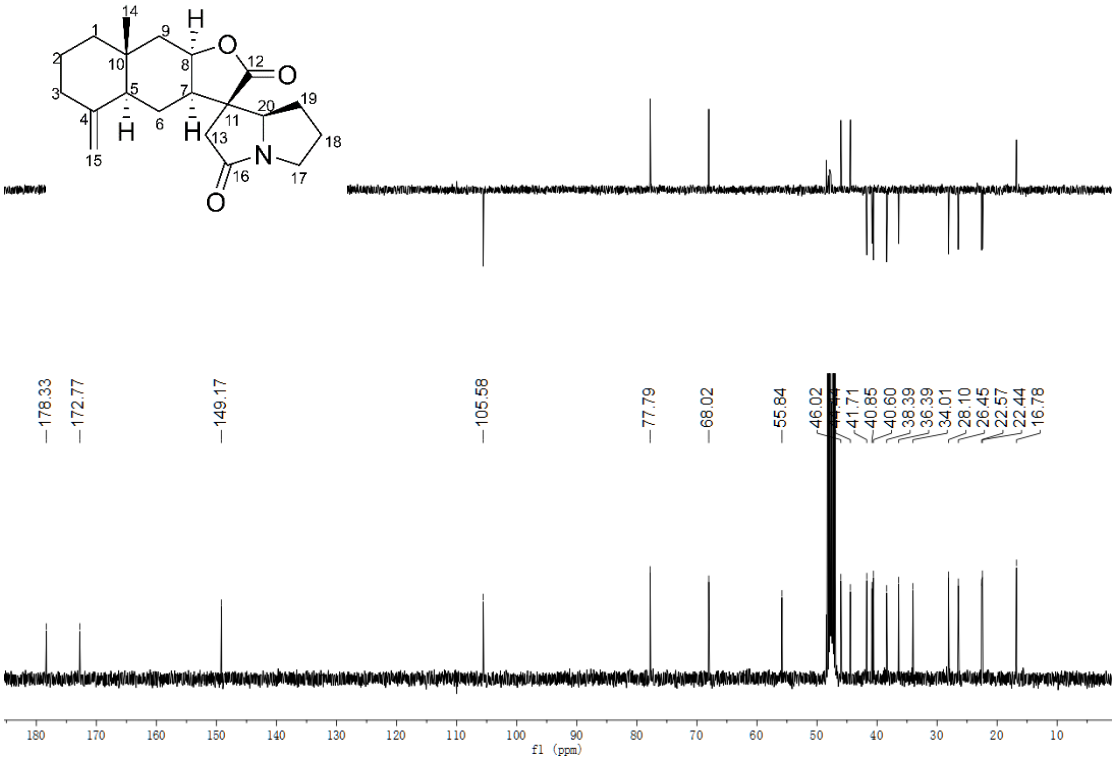

Fig. S3 ^{13}C NMR and DEPT spectra (100 MHz) of **1** in CD_3OD.

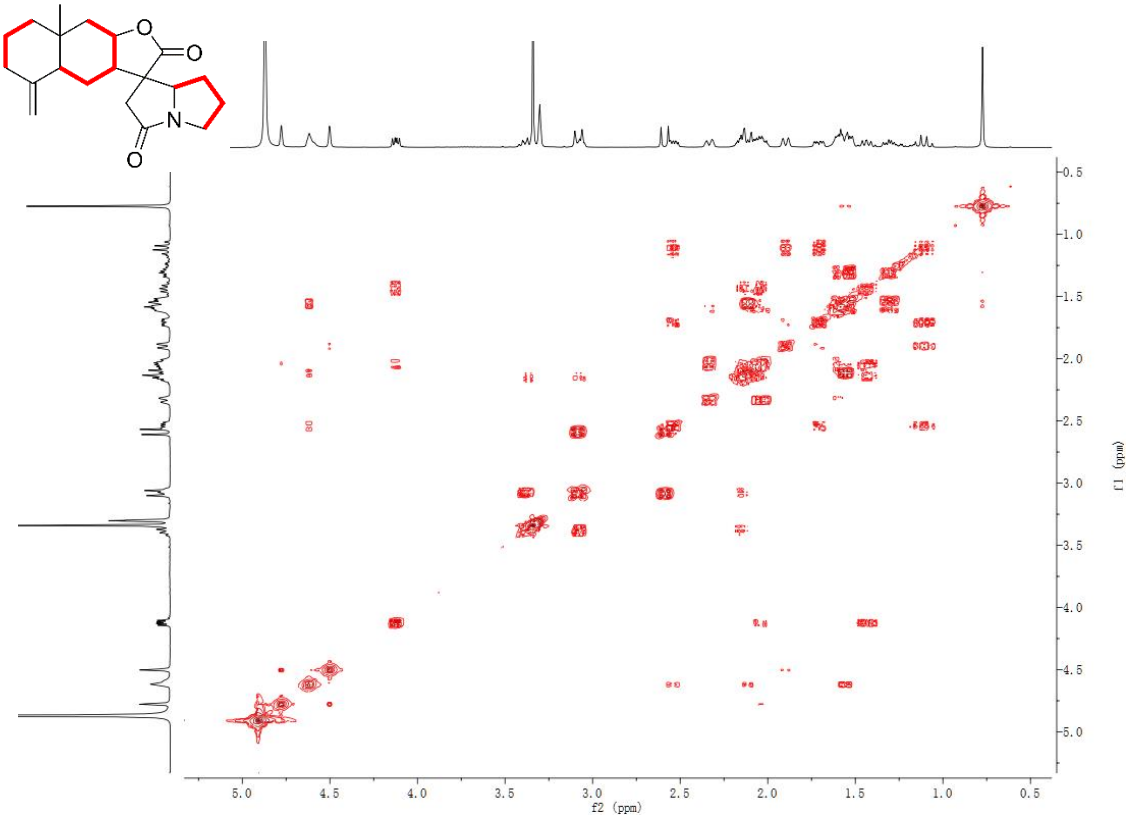

Fig. S4 ^{1}H-^{1}H COSY spectrum (400 MHz) of **1** in CD_3OD.

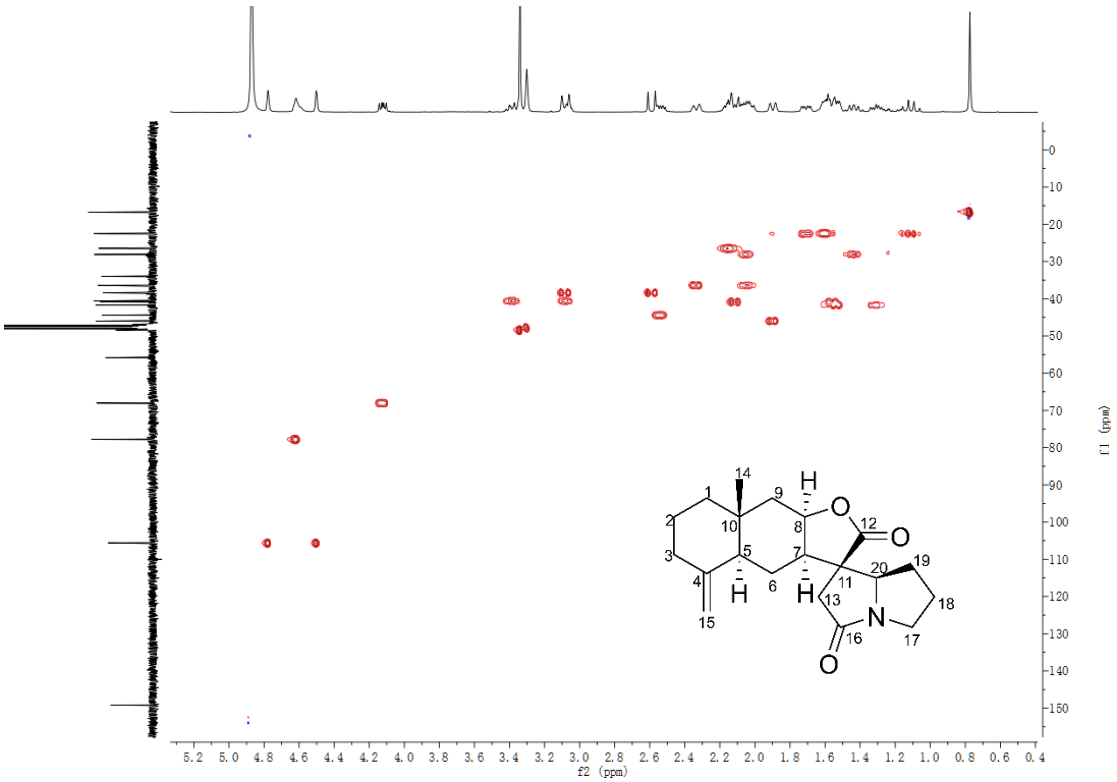

Fig. S5 HSQC spectrum (400 MHz) of **1** in CD_3OD.

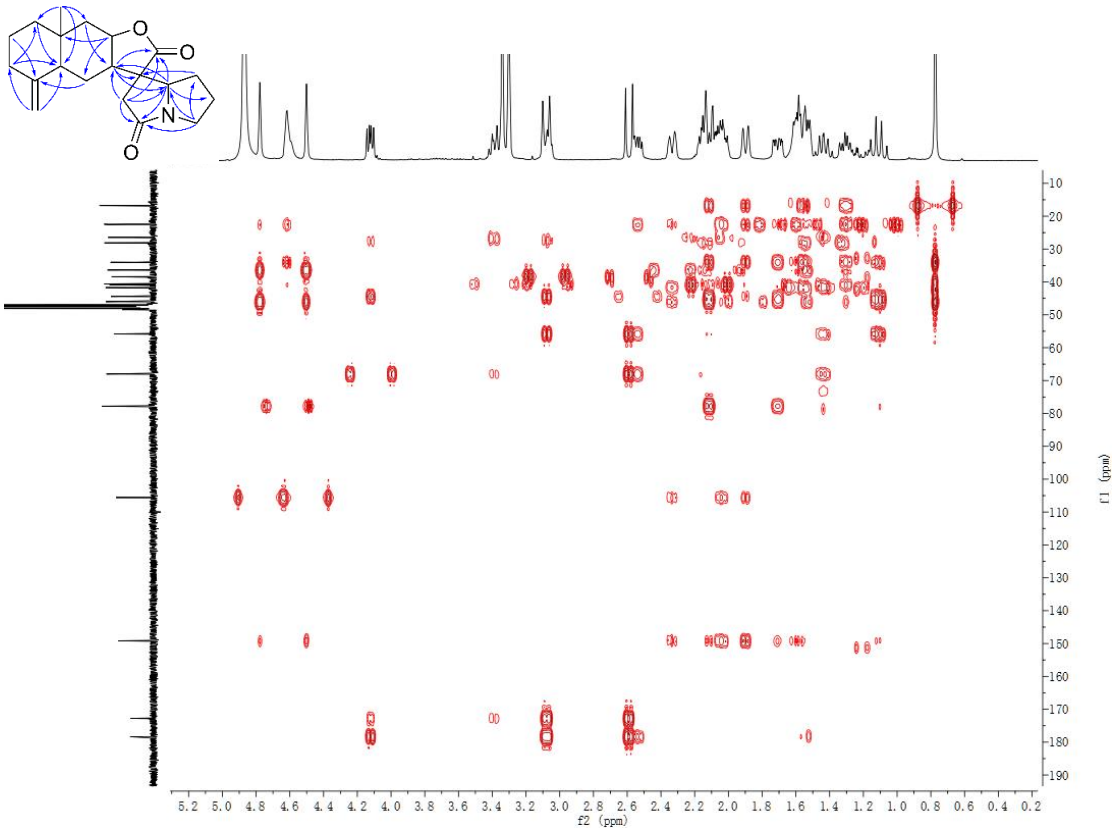

Fig. S6 HMBC spectrum (600 MHz) of **1** in CD_3OD.

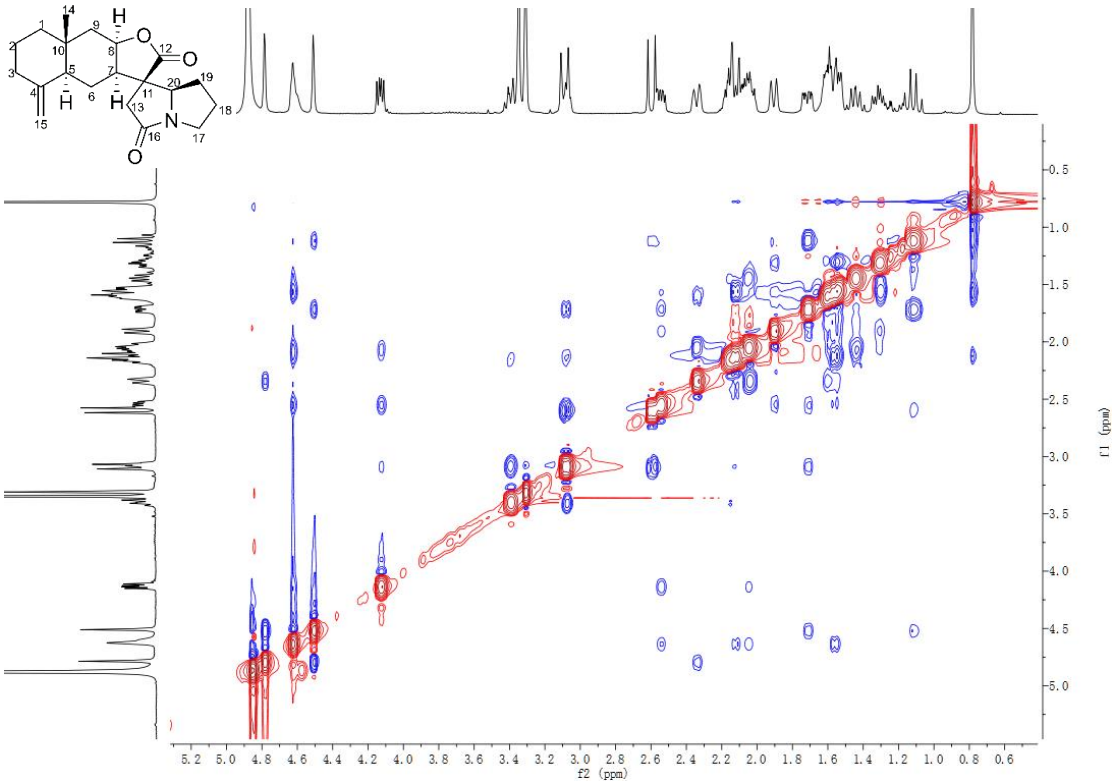

Fig. S7 NOESY spectrum (600 MHz) of **1** in CD_3OD.

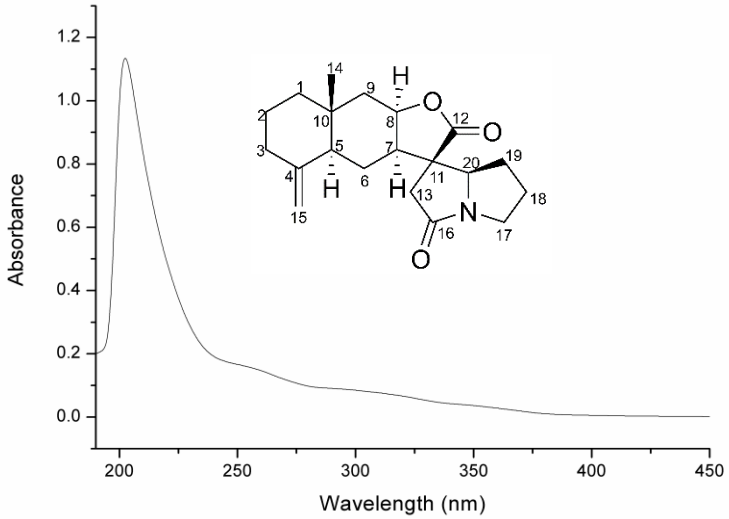

Fig. S8 UV spectrum of **1** in CH_3OH.

Table S1 Crystal data and structure refinement for **1**.

Empirical formula	$C_{20}H_{27}NO_3$	
Formula weight	329.42	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.9662(3) Å	= 90°
	b = 11.7770(3) Å	= 90°
	c = 27.0642(6) Å	= 90°
Volume	3495.31(15) $Å^3$	
Z	8	
Density (calculated)	1.252 g/m^3	
Absorption coefficient	0.664 mm^{-1}	
F(000)	1424.0	
Crystal size	0.15 × 0.12 × 0.08 mm^3	
Theta range for data collection	8.188 to 148.716°.	
Index ranges	$-10 \leq h \leq 13$, $-14 \leq k \leq 13$, $-33 \leq l \leq 33$	
Reflections collected	21237	
Independent reflections	7061 [R(int) = 0.0432]	
Data / restraints / parameters	7061 / 0 / 435	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R_1 = 0.0332, wR_2 = 0.0800	
R indices (all data)	R_1 = 0.0365, wR_2 = 0.0823	
Flack parameter	0.02(8)	
Largest diff. peak and hole	0.21 and -0.17 e.$Å^{-3}$	

Table S2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	5140.0(12)	4360.0(11)	5504.3(5)	18.8(3)
O(6)	3350.1(11)	8146.8(11)	5545.8(5)	18.1(3)
O(4)	3696.8(11)	6590.7(11)	5093.4(5)	20.5(3)
O(2)	6543.5(12)	3587.7(12)	5010.5(6)	24.1(3)
O(5)	1204.3(16)	5239.8(14)	4207.3(6)	32.5(4)
O(3)	5524.5(19)	777.8(15)	4134.3(6)	40.9(4)
N(2)	1441.4(15)	7168.6(15)	4253.2(6)	21.6(3)

N(1)	4200.6(19)	2271.5(16)	4224.6(7)	29.0(4)
C(6)	4272.1(17)	2178.4(15)	5978.5(7)	17.5(4)
C(12A)	2997.7(16)	7301.6(16)	5239.4(7)	15.1(3)
C(5)	3693.5(17)	2545.5(15)	6465.8(7)	17.6(4)
C(12)	5525.4(17)	3569.6(15)	5180.2(7)	17.7(4)
C(13A)	1066.7(16)	6275.2(15)	4995.1(7)	17.0(4)
C(7A)	1203.7(15)	8078.9(15)	5568.5(7)	14.8(3)
C(11A)	1651.7(15)	7424.4(14)	5115.6(6)	14.2(3)
C(4)	4022.9(19)	1824.6(16)	6911.0(7)	20.9(4)
C(8)	3849.1(16)	4129.4(15)	5632.4(7)	16.6(3)
C(6A)	980.7(16)	7277.2(16)	6007.6(7)	16.4(3)
C(19A)	2598.3(17)	8788.6(17)	4404.1(7)	20.9(4)
C(5A)	894.2(17)	7932.4(16)	6493.8(7)	17.3(4)
C(10A)	2105.7(17)	8565.1(16)	6613.2(7)	17.7(4)
C(7)	3738.3(17)	2853.8(16)	5544.9(7)	16.6(4)
C(10)	3956.3(18)	3816.5(16)	6584.1(7)	18.9(4)
C(20A)	1550.7(16)	8082.6(16)	4615.7(7)	16.5(3)
C(9)	3536.1(19)	4552.3(16)	6145.3(7)	20.4(4)
C(8A)	2290.5(17)	8866.7(16)	5663.5(7)	17.6(4)
C(16)	4956(2)	1451.9(18)	4391.1(8)	26.4(4)
C(9A)	2399.1(18)	9367.8(16)	6178.3(7)	20.2(4)
C(4A)	495.3(18)	7229.1(19)	6934.9(7)	22.3(4)
C(1A)	1906(2)	9294.2(18)	7080.7(7)	23.3(4)
C(2)	3449(2)	3409.8(18)	7491.6(7)	26.4(4)
C(20)	3817.2(17)	3102.2(16)	4593.3(7)	18.4(4)
C(16A)	1238.6(17)	6131.6(18)	4440.8(7)	21.9(4)
C(11)	4504.0(16)	2724.4(15)	5073.5(7)	17.1(4)
C(13)	4977.0(18)	1528.6(16)	4949.0(8)	21.6(4)
C(15)	4867(2)	1018.7(18)	6908.6(8)	27.1(4)
C(2A)	1481(2)	8597.8(18)	7523.2(7)	25.0(4)
C(19)	4093(2)	4225.4(18)	4330.9(8)	25.1(4)
C(14A)	3172.3(17)	7743.0(18)	6699.3(8)	21.3(4)
C(15A)	360(2)	6111(2)	6931.5(8)	28.3(5)
C(1)	3191(2)	4145.3(17)	7039.6(7)	24.2(4)
C(14)	5318(2)	4011.4(18)	6691.2(8)	25.2(4)
C(18A)	2381.1(19)	8687(2)	3845.1(8)	27.0(4)
C(18)	3749(2)	3948(2)	3794.0(8)	30.2(5)
C(3A)	319(2)	7931(2)	7398.1(8)	28.0(4)

C(3)	3314(2)	2142.4(18)	7368.1(7)	25.3(4)
C(17A)	1941(2)	7459(2)	3771.1(8)	30.7(5)
C(17)	4180(3)	2728(2)	3723.3(9)	45.8(7)

Table S3 Bond lengths for **1**.

Bond	lengths[Å]	Bond	lengths[Å]
O(1)-C(12)	1.347(2)	C(8)-C(7)	1.526(2)
O(1)-C(8)	1.483(2)	C(8)-C(9)	1.514(3)
O(6)-C(12A)	1.352(2)	C(6A)-C(5A)	1.528(3)
O(6)-C(8A)	1.473(2)	C(19A)-C(20A)	1.529(3)
O(4)-C((12A)	1.202(2)	C(19A)-C(18A)	1.536(3)
O(2)-C(12)	1.207(2)	C(5A)-C(10A)	1.557(3)
O(5)-C(16A)	1.226(3)	C(5A)-C(4A)	1.518(3)
O(3)-C(16)	1.226(3)	C(10A)-C(9A)	1.544(3)
N(2)-C(20A)	1.461(2)	C(10A)-C(1A)	1.545(3)
C(16A)	1.341(3)	C(10A)-C(14A)	1.536(3)
N(2)-C(17A)	1.456(3)	C(7)-C(11)	1.535(3)
N(1)-C(16)	1.349(3)	C(10)-C(9)	1.541(3)
N(1)-C(20)	1.459(3)	C(10)-C(1)	1.541(3)
N(1)-C(17)	1.459(3)	C(10)-C(14)	1.539(3)
C(6)-C(5)	1.526(3)	C(8A)-C(9A)	1.518(3)
C(6)-C(7)	1.534(3)	C(16)-C(13)	1.513(3)
C(12A)-C(11A)	1.520(2)	C(4A)-C(15A)	1.325(3)
C(5)-C(4)	1.517(3)	C(4A)-C(3A)	1.514(3)
C(5)-C(10)	1.558(3)	C(1A)-C(2A)	1.525(3)
C(12)-C(11)	1.526(3)	C(2)-C(1)	1.525(3)
C(13A)-C(11A)	1.533(2)	C(2)-C(3)	1.537(3)
C(13A)-C(16A)	1.521(3)	C(20)-C(11)	1.567(3)
C(7A)-C(11A)	1.529(2)	C(20)-C(19)	1.531(3)
C(7A)-C(6A)	1.537(2)	C(11)-C(13)	1.538(2)
C(7A)-C(8A)	1.532(2)	C(2A)-C(3A)	1.535(3)
C(11A)-C(20A)	1.563(2)	C(19)-C(18)	1.536(3)
C(4)-C(15)	1.326(3)	C(18A)-C(17A)	1.537(3)
C(4)-C(3)	1.508(3)	C(18)-C(17)	1.525(3)

Table S4 Bond angles for **1**.

Bond	angles [º]	Bond	angles [º]
C(12)-O(1)-C(8)	108.99(14)	C(8)-C(7)-C(6)	111.20(15)
C(12A)-O(6)-C(8A)	109.32(14)	C(8)-C(7)-C(11)	100.56(14)
C(16A)-N(2)-C(20A)	115.49(16)	C(9)-C(10)-C(5)	109.08(15)

C(16A)-N(2)-C(17A)	127.99(18)	C(9)-C(10)-C(1)	108.20(16)
C(17A)-N(2)-C(20A)	113.44(17)	C(1)-C(10)-C(5)	107.76(16)
C(16)-N(1)-C(20)	115.34(17)	C(14)-C(10)-C(5)	111.20(16)
C(16)-N(1)-C(17)	125.7(2)	C(14)-C(10)-C(9)	110.59(16)
C(20)-N(1)-C(17)	112.61(18)	C(14)-C(10)-C(1)	109.92(16)
C(5)-C(6)-C(7)	110.84(15)	N(2)-C(20A)-C(11A)	102.79(14)
O(6)-C(12A)-C(11A)	110.04(15)	N(2)-C(20A)-C(19A)	102.17(15)
O(4)-C(12A)-O(6)	122.15(16)	C(19A)-C(20A)-C(11A)	122.71(15)
O(4)-C(12A)-C(11A)	127.81(17)	C(8)-C(9)-C(10)	116.99(15)
C(6)-C(5)-C(10)	111.89(15)	O(6)-C(8A)-C(7A)	103.22(14)
C(4)-C(5)-C(6)	115.38(16)	O(6)-C(8A)-C(9A)	111.12(15)
C(4)-C(5)-C(10)	109.30(15)	C(9A)-C(8A)-C(7A)	116.79(16)
O(1)-C((12)-C((11)	110.10(15)	O(3)-C(16)-N(1)	125.9(2)
O(2)-C((12)-O(1)	121.71(17)	O(3)-C(16)-C((13)	126.6(2)
O(2)-C(12)-C(11)	128.19(17)	N(1)-C(16)-C(13)	107.47(17)
C(16A)-C(13A)-C(11A)	104.84(15)	C(8A)-C(9A)-C(10A)	116.45(15)
C(11A)-C(7A)-C(6A)	111.18(14)	C(15A)-C(4A)-C(5A)	124.7(2)
C(11A)-C(7A)-C(8A)	100.95(14)	C(15A)-C(4A)-C(3A)	122.3(2)
C(8A)-C(7A)-C(6A)	111.47(15)	C(3A)-C(4A)-C(5A)	112.98(18)
C(12A)-C(11A)-C(13A)	111.67(14)	C(2A)-C(1A)-C(10A)	112.81(16)
C(12A)-C(11A)-C(7A)	100.55(14)	C(1)-C(2)-C(3)	111.05(17)
C(12A)-C(11A)-C(20A)	107.86(14)	N(1)-C(20)-C(11)	103.79(15)
C(13A)-C((11A)-C((20A)	102.95(14)	N(1)-C((20)-C(19)	101.84(16)
C(7A)-C(11A)-C(13A)	118.76(15)	C(19)-C(20)-C(11)	122.37(16)
C(7A)-C(11A)-C(20A)	114.90(14)	O(5)-C(16A)-N(2)	126.15(19)
C(15)-C(4)-C(5)	124.25(19)	O(5)-C(16A)-C(13A)	126.84(19)
C(15)-C(4)-C(3)	122.79(19)	N(2)-C(16A)-C(13A)	107.01(16)
C(3)-C(4)-C(5)	112.94(17)	C(12)-C(11)-C(7)	100.34(14)
O(1)-C(8)-C(7)	102.71(14)	C(12)-C(11)-C(20)	108.93(15)
O(1)-C(8)-C(9)	111.75(15)	C(12)-C(11)-C(13)	113.02(15)
C(9)-C(8)-C(7)	116.62(16)	C(7)-C(11)-C(20)	113.48(14)
C(5A)-C(6A)-C(7A)	111.43(15)	C(7)-C(11)-C(13)	117.23(15)
C(20A)-C(19A)-C(18A)	102.10(16)	C(13)-C(11)-C(20)	103.91(15)
C(6A)-C(5A)-C(10A)	111.56(15)	C(16)-C(13)-C(11)	105.55(16)
C(4A)-C(5A)-C(6A)	114.82(16)	C(1A)-C(2A)-C(3A)	110.85(17)
C(4A)-C(5A)-C(10A)	110.11(15)	C(20)-C(19)-C(18)	101.93(17)
C(9A)-C(10A)-C(5A)	108.22(15)	C(2)-C(1)-C(10)	113.42(17)
C(9A)-C(10A)-C(1A)	108.28(15)	C(19A)-C(18A)-C(17A)	104.51(17)
C(1A)-C(10A)-C(5A)	108.38(15)	C(17)-C(18)-C(19)	104.06(18)
C(14A)-C(10A)-C(5A)	112.30(16)	C(4A)-C(3A)-C(2A)	110.84(17)

C(14A)-C(10A)-C(9A)	110.05(16)	C(4)-C(3)-C(2)	111.71(17)
C(14A)-C(10A)-C(1A)	109.51(16)	N(2)-C(17A)-C(18A)	102.85(17)
C(6)-C(7)-C(11)	112.07(15)	N(1)-C(17)-C(18)	103.59(18)

Table S5 Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	20.3(6)	13.8(6)	22.2(7)	-1.3(5)	0.9(5)	-1.8(5)
O(6)	13.4(6)	20.7(6)	20.1(6)	-1.0(5)	0.0(5)	-2.4(5)
O(4)	14.8(6)	22.5(7)	24.1(7)	0.9(5)	0.7(5)	4.3(5)
O(2)	18.1(6)	24.5(7)	29.8(7)	-0.6(6)	3.4(6)	-0.4(5)
O(5)	39.6(9)	28.8(8)	29.2(8)	-13.5(6)	5.0(7)	-5.9(7)
O(3)	64.6(12)	28.3(8)	29.8(8)	-5.6(7)	12.3(8)	15.0(8)
N(2)	22.9(7)	26.2(8)	15.8(8)	-2.8(6)	0.1(6)	-0.7(7)
N(1)	45.5(11)	23.6(9)	17.9(8)	-5.5(7)	0.1(8)	5.4(8)
C(6)	21.2(8)	12.9(8)	18.3(9)	0.9(7)	0.9(7)	-0.3(7)
C(12A)	13.8(8)	16.4(8)	15.0(8)	3.5(7)	0.0(6)	-0.8(7)
C(5)	19.6(8)	15.6(8)	17.6(9)	0.2(7)	-2.0(7)	-1.8(7)
C(12)	19.4(8)	15.1(8)	18.7(9)	1.6(7)	-1.6(7)	1.9(7)
C(13A)	14.7(7)	16.2(8)	20.2(9)	-2.3(7)	-1.0(7)	-0.2(6)
C(7A)	13.1(7)	14.5(8)	16.8(8)	-0.7(7)	0.0(6)	1.7(6)
C(11A)	11.7(7)	14.3(8)	16.4(8)	0.6(7)	-0.3(6)	1.3(6)
C(4)	27.2(9)	17.1(9)	18.4(9)	1.9(7)	-2.9(8)	-5.1(8)
C(8)	16.8(8)	14.5(8)	18.7(8)	1.3(7)	0.9(7)	1.3(7)
C(6A)	14.6(7)	18.1(8)	16.6(9)	-0.2(7)	-0.4(7)	-2.5(7)
C(19A)	18.9(8)	23.6(9)	20.4(9)	4.3(7)	2.6(7)	-0.5(7)
C(5A)	16.6(8)	20.0(9)	15.3(8)	-0.7(7)	0.6(7)	1.4(7)
C(10A)	20.4(8)	16.8(8)	16.0(8)	-0.8(7)	-1.2(7)	-2.3(7)
C(7)	18.9(8)	15.2(8)	15.7(8)	-0.4(6)	0.8(7)	-0.4(7)
C(10)	24.4(9)	14.9(8)	17.3(9)	-1.4(7)	-0.9(7)	0.7(7)
C(20A)	15.2(8)	17.9(8)	16.4(8)	0.2(7)	0.2(7)	3.0(7)
C(9)	26.9(9)	14.2(8)	20.2(9)	-0.5(7)	1.9(8)	5.1(7)
C(8A)	18.3(8)	15.7(8)	19.0(9)	1.6(7)	0.9(7)	-0.7(7)
C(16)	35.5(10)	18.9(9)	24.8(10)	-3.5(8)	5.4(9)	0.5(9)
C(9A)	27.5(9)	13.4(8)	19.8(9)	-1.3(7)	-0.8(8)	-4.8(7)
C(4A)	18.5(8)	32.1(10)	16.3(9)	0.2(8)	-0.3(7)	-4.3(8)
C(1A)	31.3(10)	19.6(9)	19.1(9)	-4.0(7)	0.2(8)	-2.3(8)
C(2)	39.7(11)	23.0(9)	16.7(9)	-0.8(8)	0.7(8)	1.0(9)
C(20)	19.0(8)	19.7(9)	16.4(8)	-2.3(7)	1.5(7)	-0.2(7)
C(16A)	17.0(8)	26.3(10)	22.3(9)	-5.6(8)	0.5(7)	-2.2(7)

C(11)	17.6(8)	15.0(8)	18.5(9)	-0.5(7)	0.2(7)	0.4(7)
C(13)	27.2(9)	14.8(8)	22.7(9)	-2.8(7)	1.0(8)	1.7(7)
C(15)	35.3(11)	22.8(10)	23.3(9)	4.8(8)	-3.7(9)	2.5(9)
C(2A)	31.2(10)	27.2(10)	16.6(9)	-3.8(8)	-0.1(8)	1.5(9)
C(19)	30.8(10)	22.1(9)	22.4(10)	5.0(8)	-3.7(8)	0.4(8)
C(14A)	18.6(8)	22.6(9)	22.6(9)	-0.9(8)	-4.6(7)	-1.0(8)
C(15A)	32.6(11)	31.5(11)	20.8(9)	5.2(8)	-1.0(8)	-12.3(9)
C(1)	34.0(11)	18.5(9)	20.2(9)	-1.3(7)	1.7(8)	3.8(8)
C(14)	28.1(10)	21.9(9)	25.6(10)	-1.1(8)	-4.1(8)	-7.5(8)
C(18A)	24.6(9)	35.4(11)	21.1(10)	7.2(8)	2.1(8)	4.1(9)
C(18)	37.4(11)	34.1(11)	19.1(10)	3.0(8)	0.4(9)	4.8(10)
C(3A)	28.4(10)	38.4(12)	17.4(9)	-1.9(9)	3.3(8)	-2.5(9)
C(3)	36.8(11)	22.4(10)	16.9(9)	3.2(7)	0.9(8)	-1.6(9)
C(17A)	36.4(11)	40.3(13)	15.3(9)	-0.4(9)	2.6(8)	-1.0(10)
C(17)	77.2(19)	43.4(14)	16.8(11)	-1.5(10)	0.1(12)	20.3(14)

Table S6 Hydrogen atom coordinates ($Å^2 \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

Atom	x	y	z	U(eq)
H(6A)	4124.79	1358.02	5925.74	21
H(6B)	5164.37	2301.32	5993.84	21
H(5)	2791.18	2476.9	6421.67	21
H(13C)	1476.49	5655.25	5177.95	20
H(13D)	189.78	6276.4	5081.98	20
H(7A)	453.19	8525.44	5489.33	18
H(8)	3316.43	4531	5388.63	20
H(6AA)	213.97	6851.37	5953.17	20
H(6AB)	1655.88	6721.28	6028.47	20
H(19C)	3400.21	8470.24	4499.17	25
H(19D)	2550.09	9588.61	4514.73	25
H(5A)	257.57	8530.06	6445.38	21
H(7)	2870.69	2634.08	5483.4	20
H(20A)	786.62	8546.07	4614.88	20
H(9A)	2639.29	4636.32	6165.96	25
H(9B)	3894.32	5318.41	6185.21	25
H(8A)	2258.7	9503.96	5419.71	21
H(9AA)	1847.37	10031.38	6199.45	24
H(9AB)	3242.45	9651.26	6221.16	24
H(1AA)	2679.45	9681.13	7166.21	28

H(1AB)	1290.97	9886.44	7008.34	28
H(2A)	2874.95	3612.58	7759.71	32
H(2B)	4287.6	3558.97	7610.52	32
H(20)	2917.99	3034.86	4647.13	22
H(13A)	5816.42	1423.38	5075.58	26
H(13B)	4444.15	941.07	5096.78	26
H(15A)	5047.19	614.12	7203.38	33
H(15B)	5292.18	845.89	6612.1	33
H(2AA)	1319.14	9110.36	7805.65	30
H(2AB)	2133.11	8062.38	7621.77	30
H(19A)	4965	4430.94	4360.1	30
H(19B)	3587.37	4851.61	4463.71	30
H(14D)	2941.13	7181.19	6949.46	32
H(14E)	3885.83	8169.02	6814.02	32
H(14F)	3370.36	7354.33	6389.36	32
H(15C)	144.27	5723.54	7226.68	34
H(15D)	477.68	5697.9	6634	34
H(1A)	3357.13	4948.48	7123.82	29
H(1B)	2315.07	4081.96	6954.65	29
H(14A)	5590.14	3480.27	6947.2	38
H(14B)	5441.29	4792.39	6805.76	38
H(14C)	5790.71	3885.71	6388.7	38
H(18C)	3144.22	8826.33	3659.38	32
H(18D)	1754.47	9235.06	3733.9	32
H(18A)	2857.32	4009.53	3743.44	36
H(18B)	4167.45	4466.29	3561.11	36
H(3AA)	107.98	7424.81	7677.43	34
H(3AB)	-366.09	8466.91	7348.76	34
H(3A)	3608.45	1684.09	7650.56	30
H(3B)	2441.18	1963.74	7316.56	30
H(17C)	1307.5	7415.58	3510.99	37
H(17D)	2625.42	6951.03	3682.01	37
H(17A)	3606.98	2296.69	3511.68	55
H(17B)	5002.1	2705.07	3572.54	55

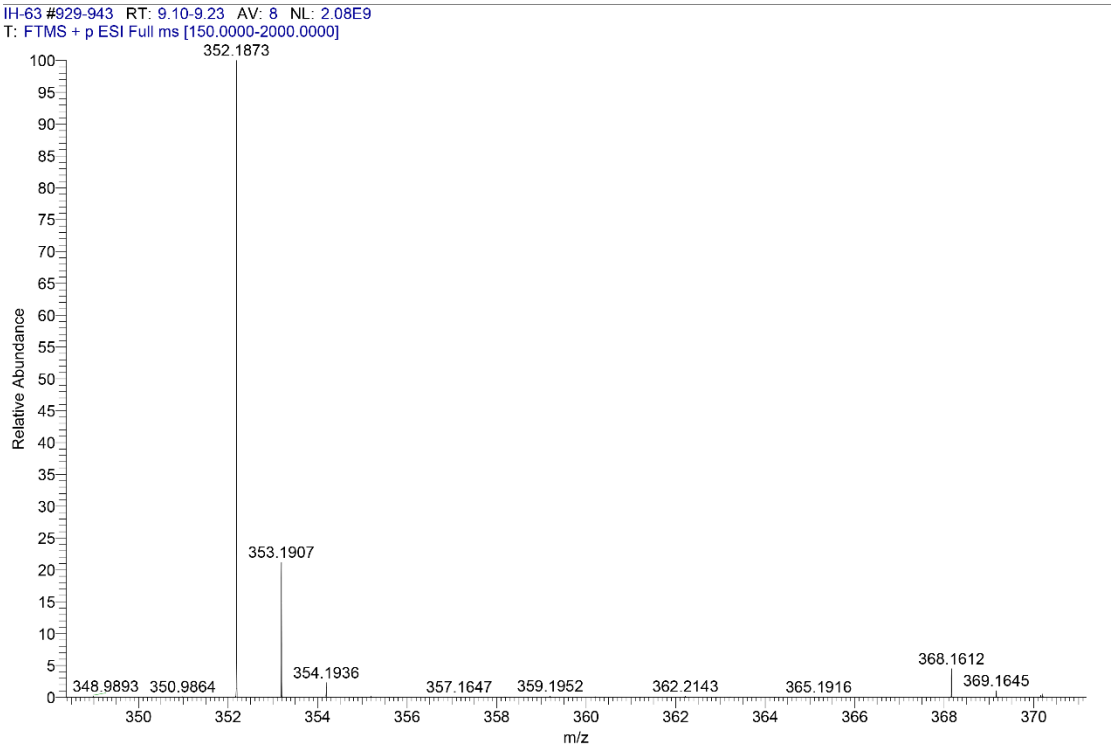

Fig. S9 HRESIMS spectrum of **2**.

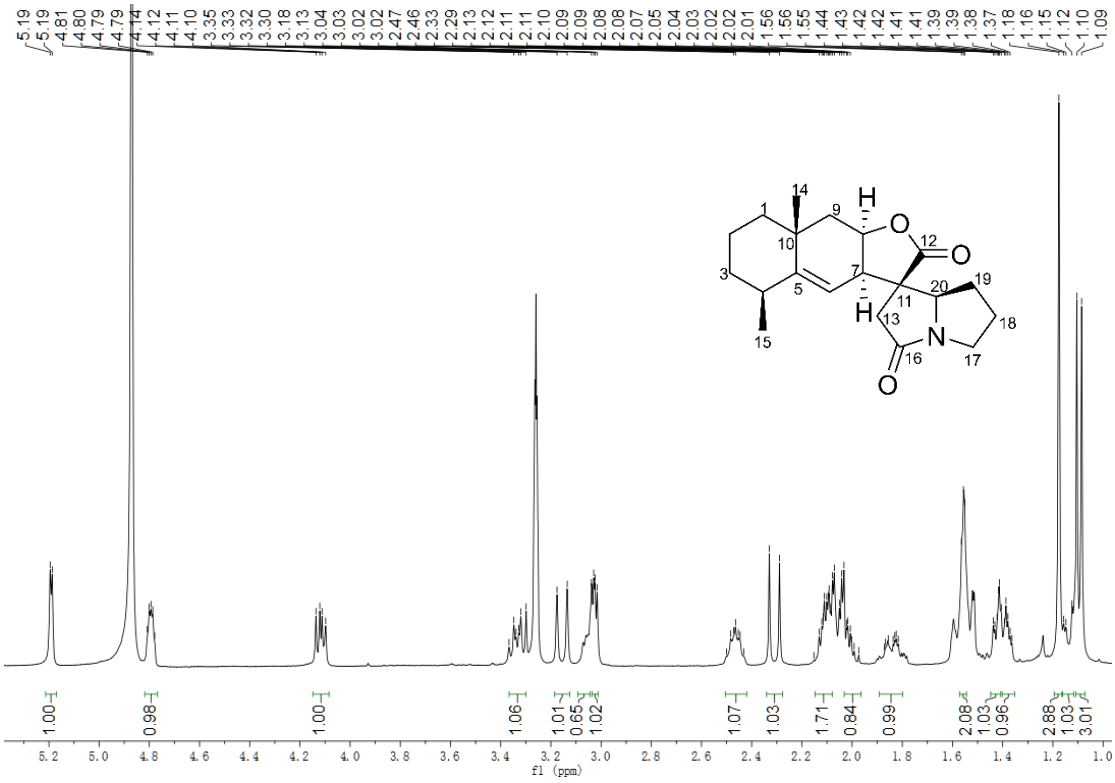

Fig. S10 ^{1}H NMR spectrum (400 MHz) of **2** in CD_3OD.

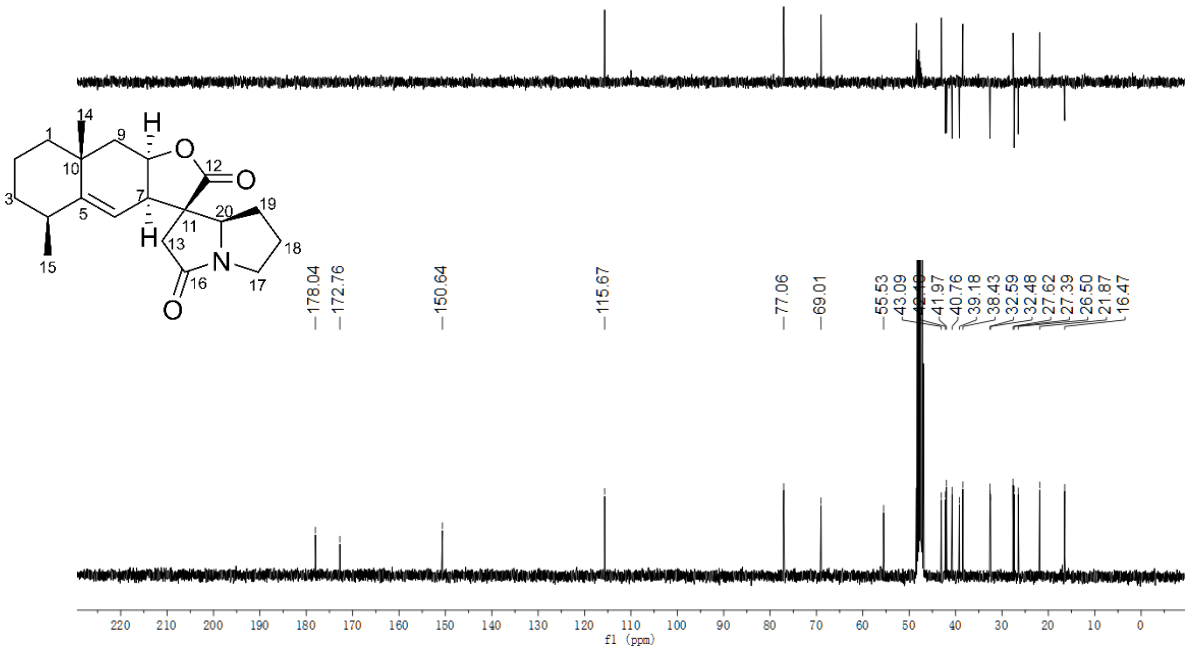

Fig. S11 ^{13}C NMR and DEPT spectra (100 MHz) of **2** in CD_3OD.

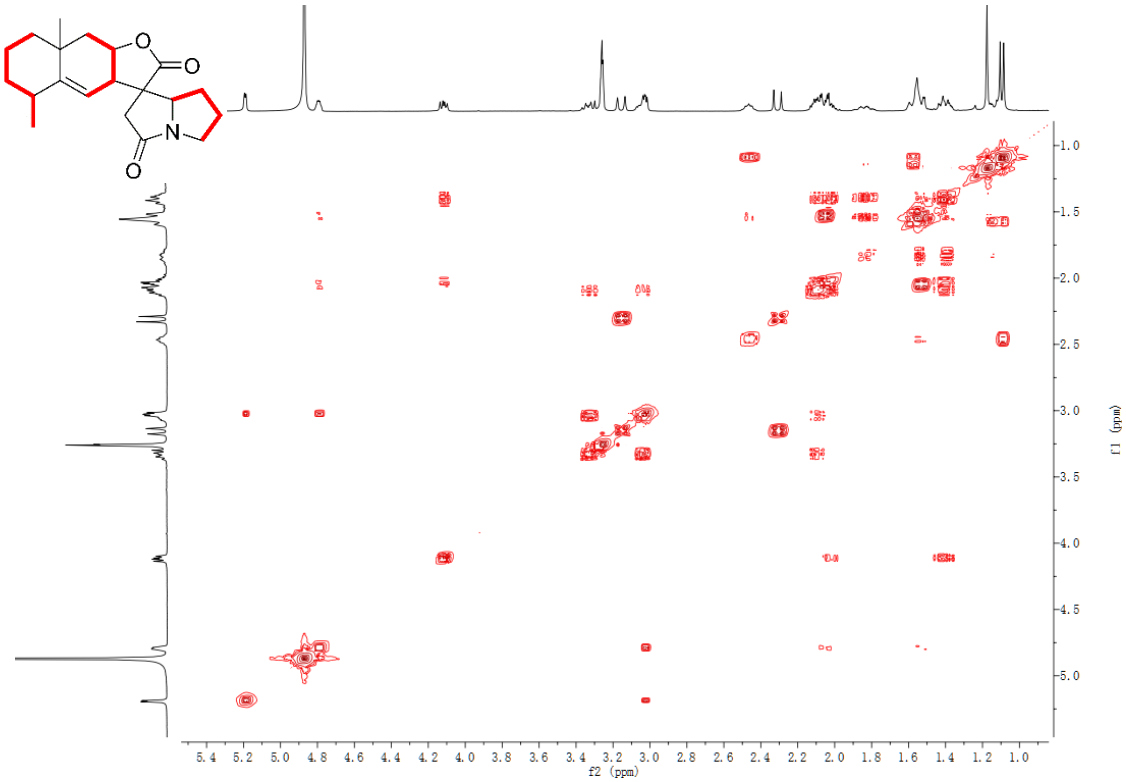

Fig. S12 ^{1}H-^{1}H COSY spectrum (400 MHz) of **2** in CD_3OD.

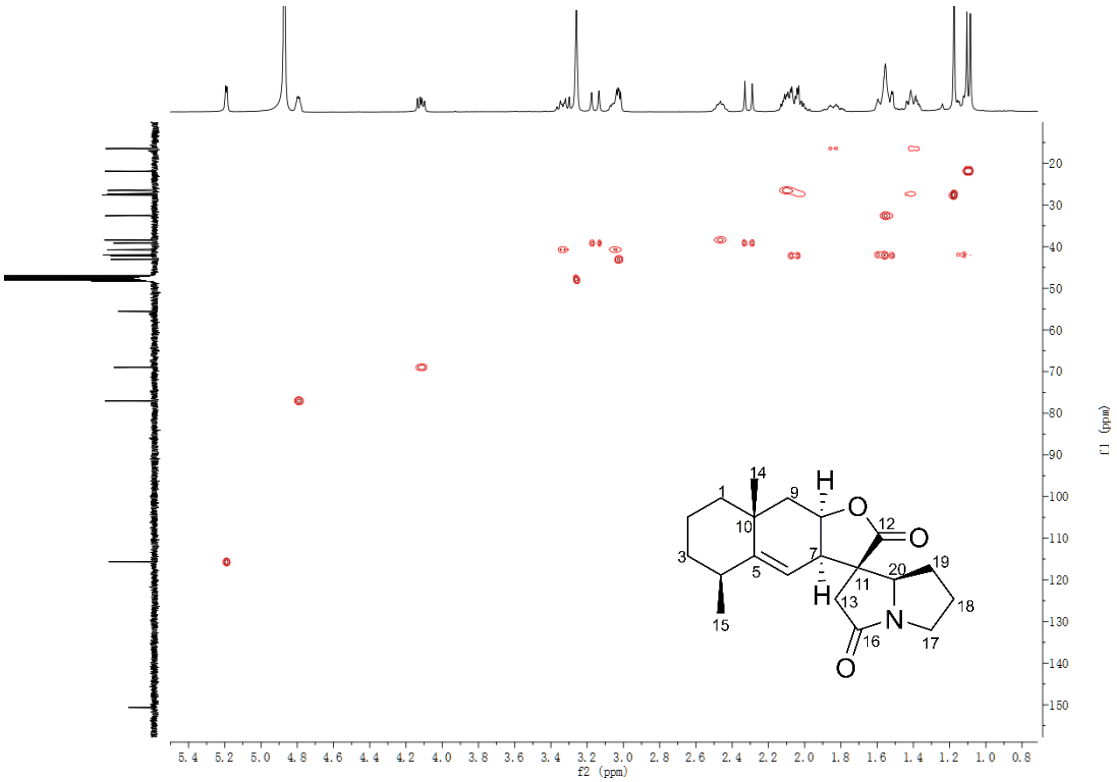

Fig. S13 HSQC spectrum (400 MHz) of **2** in CD_3OD.

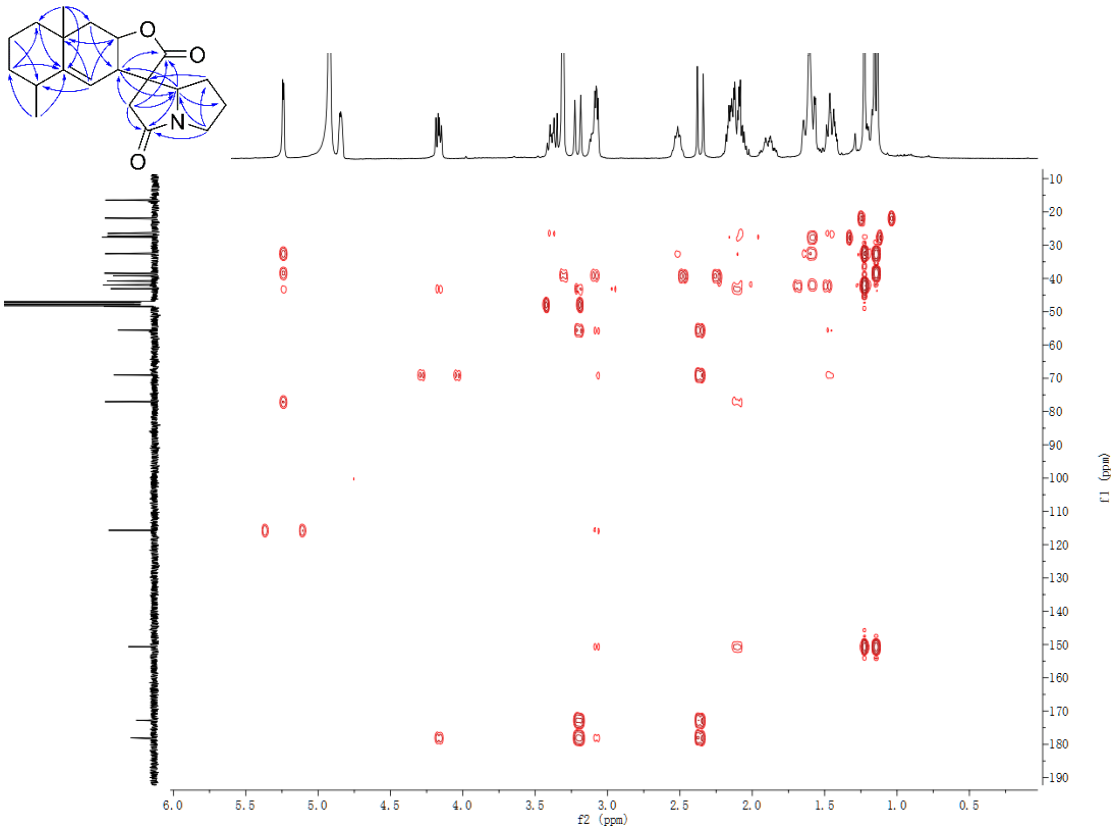

Fig. S14 HMBC spectrum (600 MHz) of **2** in CD_3OD.

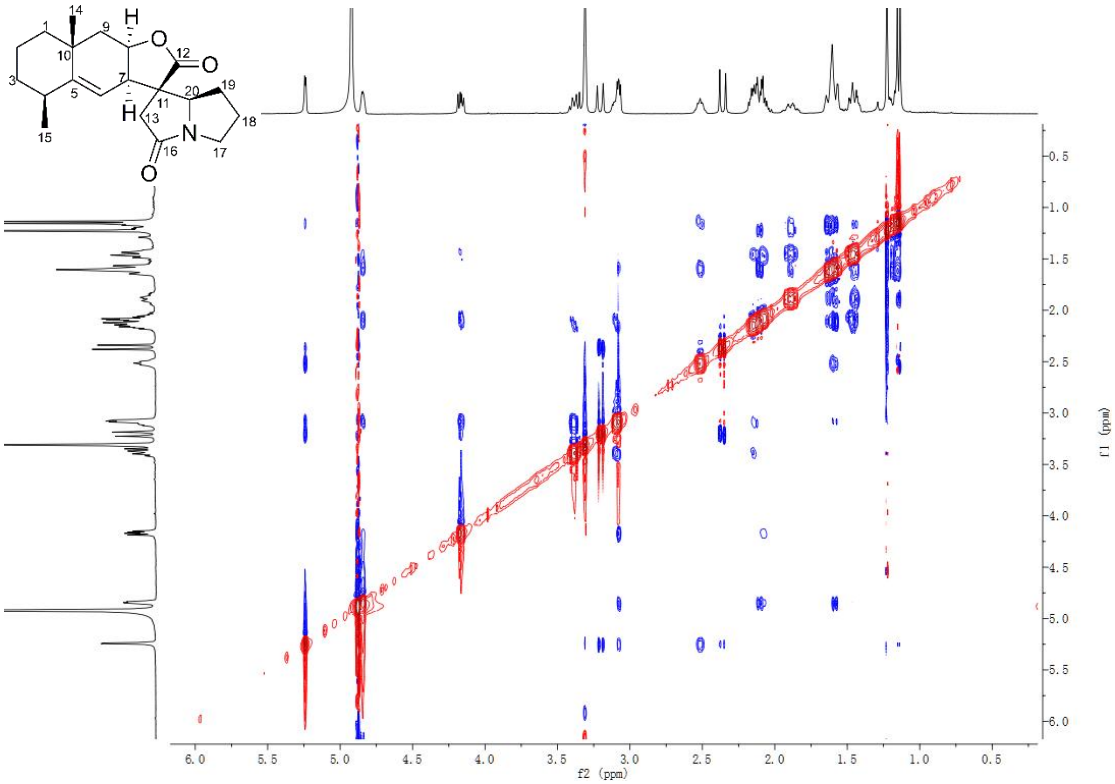

Fig. S15 NOESY spectrum (600 MHz) of **2** in CD_3OD.

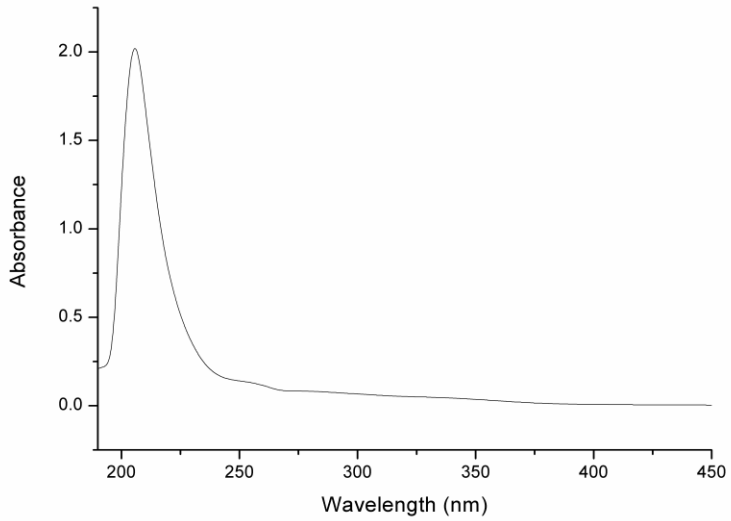

Fig. S16 UV spectrum of **2** in CH_3OH.

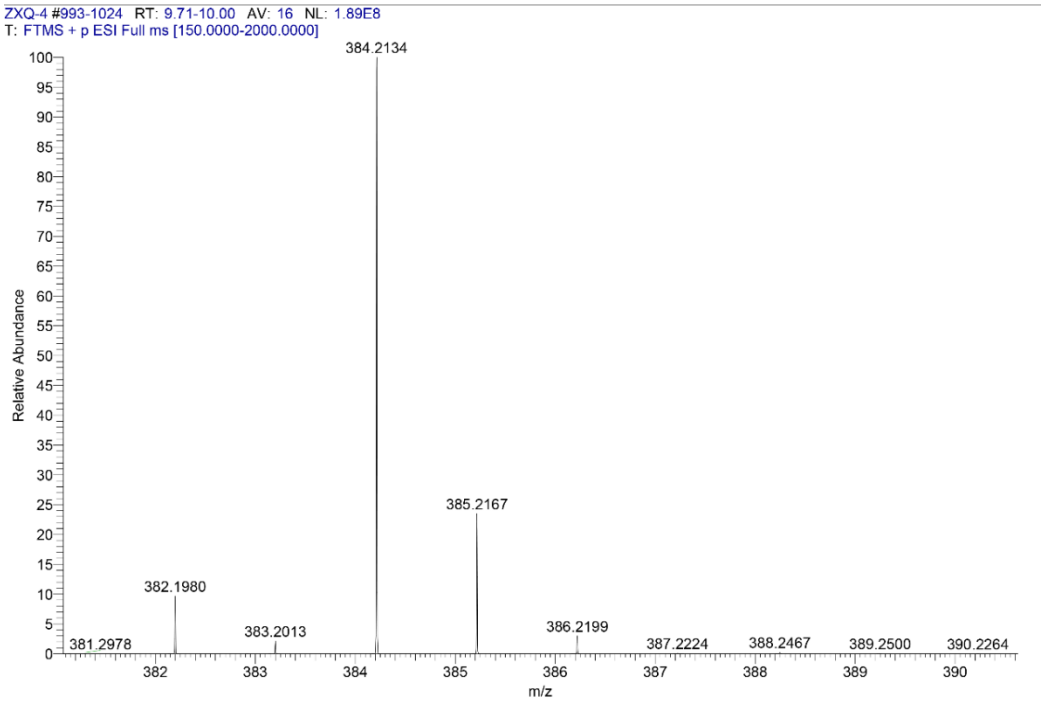

Fig. S17 HRESIMS spectrum of **3**.

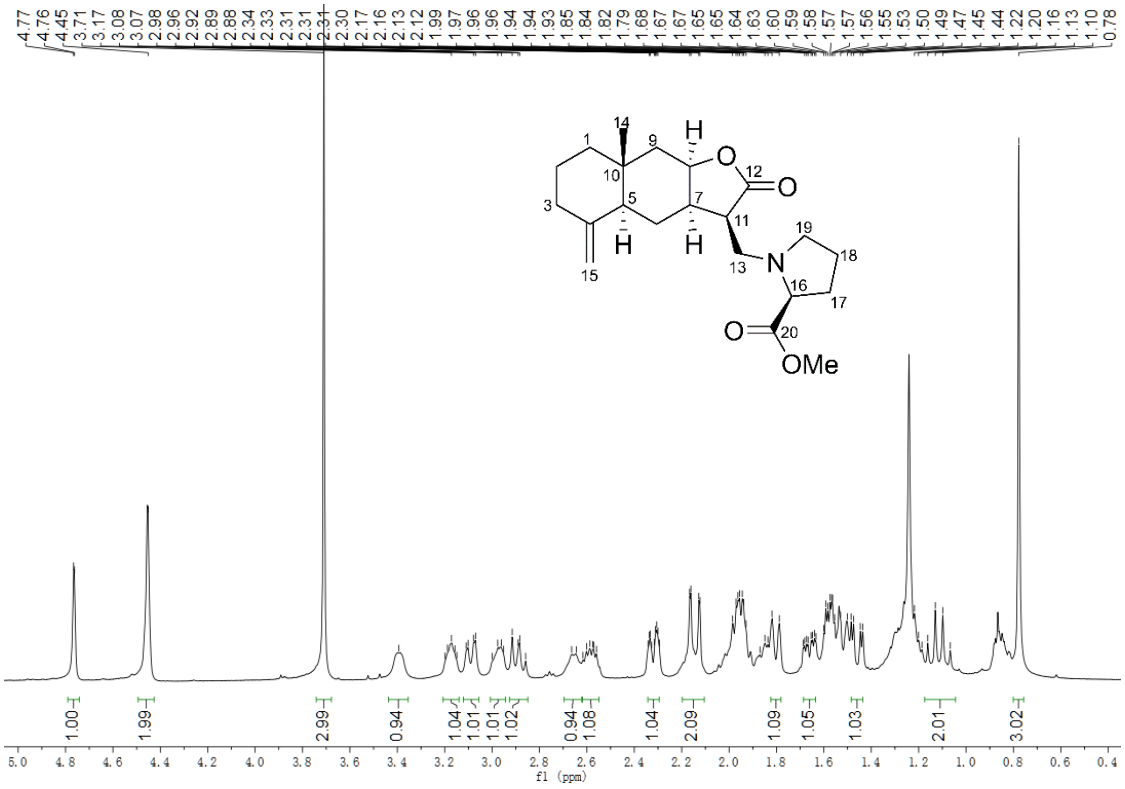

Fig. S18 ^{1}H NMR spectrum (400 MHz) of **3** in $CDCl_3$.

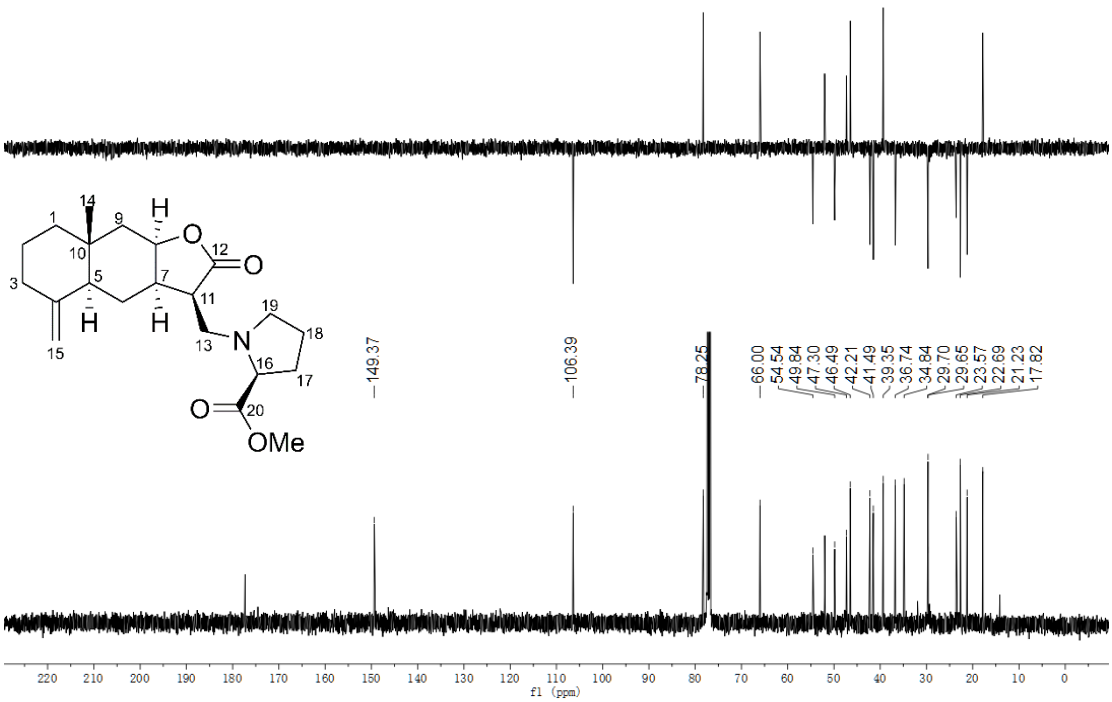

Fig. S19 ^{13}C and DEPT NMR spectra (400 MHz) of **3** in $CDCl_3$.

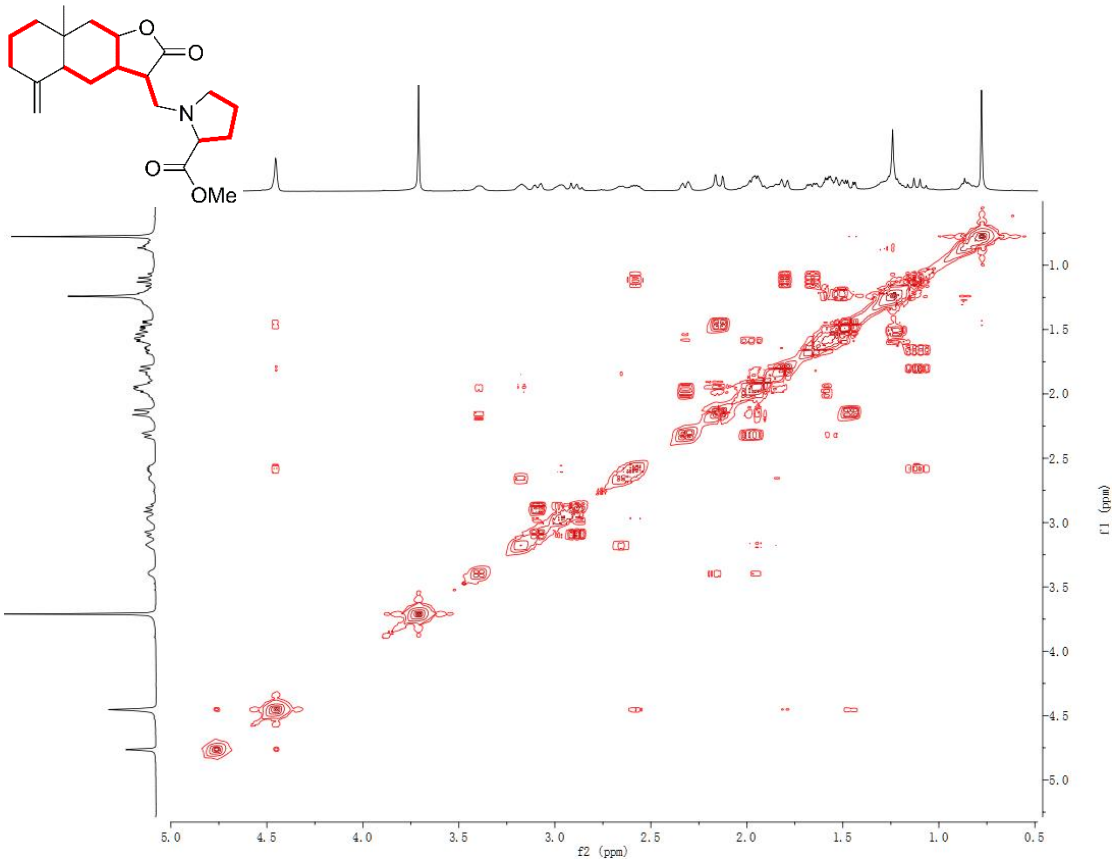

Fig. S20 ^{1}H-^{1}H COSY spectrum (400 MHz) of **3** in $CDCl_3$.

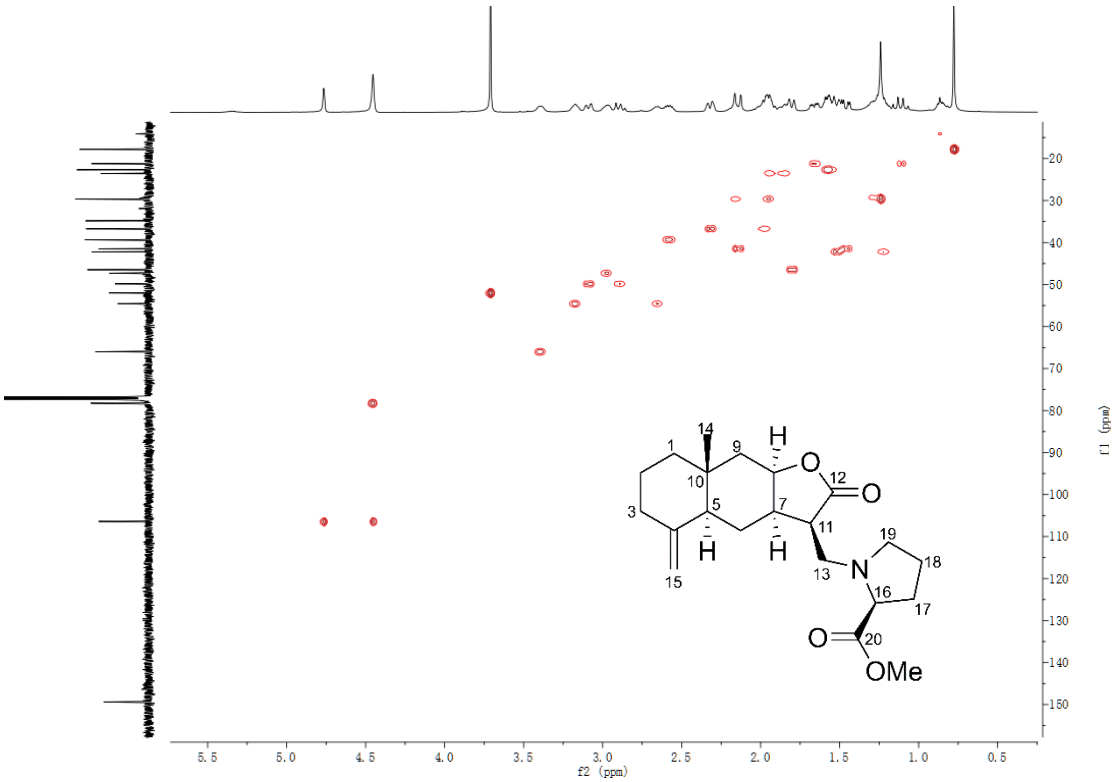

Fig. S21 HSQC spectrum (400 MHz) of **3** in $CDCl_3$.

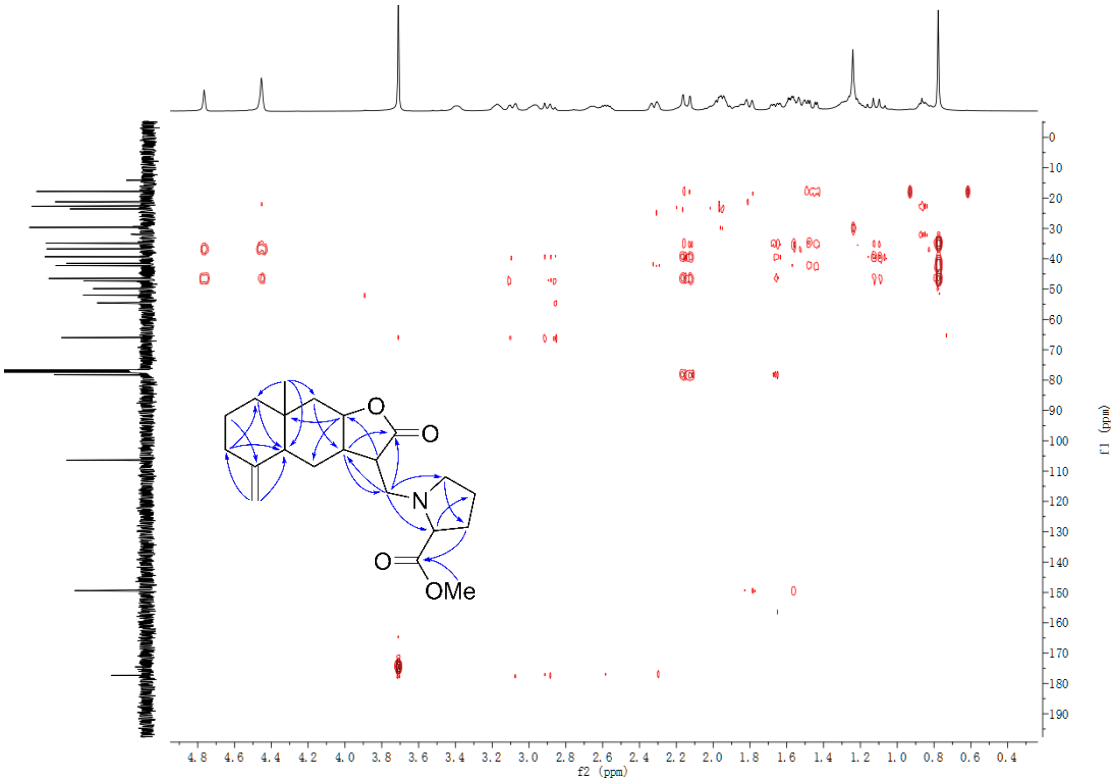

Fig. S22 HMBC spectrum (400 MHz) of **3** in $CDCl_3$.

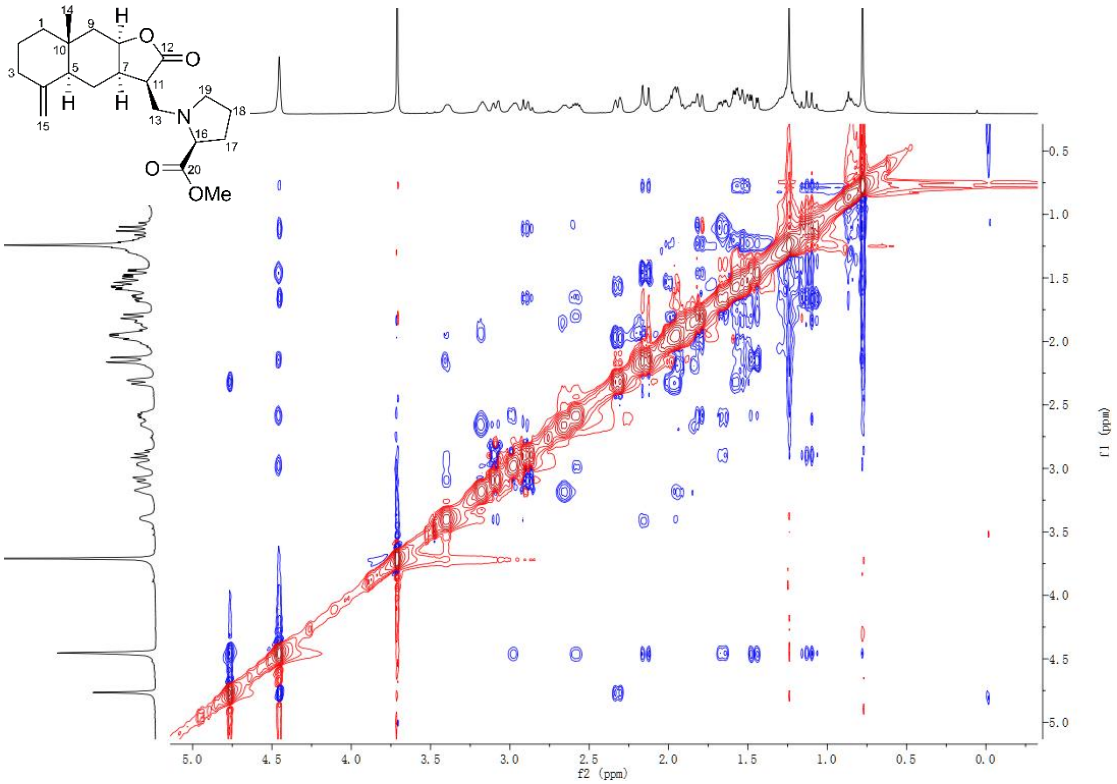

Fig. S23 NOESY spectrum (400 MHz) of **3** in $CDCl_3$.

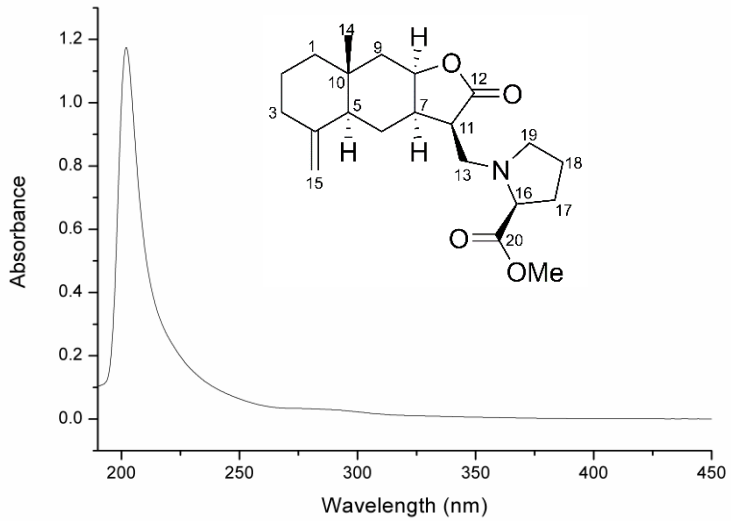

Fig. S24 UV spectrum of **3** in MeOH.

Table S7 Crystal data and structure refinement for **3**.

Empirical formula	$C_{21}H_{31}NO_4$
Formula weight	361.47
Temperature	169.98 K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 7.7456(10) Å = 90°
	b = 11.2402(9) Å = 90°
	c = 22.236(3) Å = 90°
Volume	1935.9(4) $Å^3$
Z	4
Density (calculated)	1.240 g/m^3
Absorption coefficient	0.681 mm^{-1}
F(000)	784.0
Crystal size	0.49 × 0.42 × 0.38 mm^3
Theta range for data collection	7.952 to 136.704°.
Index ranges	$-9 \le h \le 9$, $-13 \le k \le 13$, $-26 \le l \le 26$
Reflections collected	13106
Independent reflections	3543 [R(int) = 0.0252]
Data / restraints / parameters	3543 / 0 / 237
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R_1 = 0.0317, wR_2 = 0.0821
R indices (all data)	R_1 = 0.0317, wR_2 = 0.0823
Flack parameter	0.05(3)
Largest diff. peak and hole	0.16 and -0.28 e.$Å^{-3}$

Table S8 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	251.8(15)	4463.5(11)	3684.4(5)	26.0(3)
O(2)	992(2)	2770.9(13)	4138.3(6)	42.8(4)
O(3)	4369(2)	7142.7(12)	5351.2(7)	45.5(4)
O(4)	2474.7(17)	6035.8(12)	5857.6(6)	33.1(3)
N(1)	5355.1(17)	4798.1(12)	4859.5(6)	20.4(3)
N(2)	1614(3)	7050.9(18)	2140.6(9)	33.8(4)
C(1)	3013(3)	6986(2)	1659.8(9)	40.2(5)

C(2)	4819(3)	7070.0(18)	1942.2(9)	35.8(4)
C(3)	5036(2)	6182.1(16)	2445.5(8)	26.0(3)
C(4)	3655(2)	6272.2(14)	2923.2(7)	21.3(3)
C(5)	1831(2)	6111.8(15)	2640.3(7)	23.0(3)
C(6)	484(2)	6355.8(15)	3131.3(7)	26.4(4)
C(7)	750(2)	5724.2(15)	3727.2(8)	24.0(3)
C(8)	2605(2)	5682.6(14)	3963.6(7)	21.0(3)
C(9)	3915(2)	5449.2(14)	3460.1(7)	20.4(3)
C(10)	2469(2)	4627.5(15)	4400.4(7)	22.7(3)
C(11)	1199(2)	3824.7(17)	4078.2(7)	26.8(4)
C(12)	6307(2)	5394.5(18)	2450.2(8)	32.6(4)
C(13)	1593(2)	4857.8(16)	2372.4(7)	27.6(4)
C(14)	4141(2)	3992.2(14)	4568.6(7)	23.7(3)
C(15)	7138(2)	4360.4(17)	4839.2(8)	29.3(4)
C(16)	8035(2)	5100(2)	5316.8(9)	38.1(5)
C(17)	6695(3)	5148.5(19)	5817.2(9)	36.7(4)
C(18)	4939(2)	5047.8(14)	5493.4(7)	23.3(3)
C(19)	3921(2)	6198.6(15)	5546.8(7)	24.4(3)
C(20)	1465(3)	7094(2)	5972.7(10)	44.3(5)
C(21)	251.8(15)	4463.5(11)	3684.4(5)	26.0(3)

Table S9 Bond lengths for **3**.

Bond	lengths[Å]
O(1)-C(8)	1.472(2)
O(1)-C(12)	1.349(2)
O(2)-C(12)	1.203(2)
O(3)-C(20)	1.198(2)
O(4)-C(20)	1.329(2)
O(4)-C(21)	1.446(2)
N(1)-C(15)	1.457(2)
N(1)-C(16)	1.466(2)
N(1)-C(19)	1.473(2)
C(1)-C(2)	1.524(3)
C(1)-C(6)	1.542(2)
C(2)-C(3)	1.536(3)
C(3)-C(4)	1.509(2)
C(4)-C(5)	1.510(2)
C(4)-C(13)	1.324(3)
C(5)-C(6)	1.557(2)
C(5)-C(10)	1.524(2)
C(6)-C(7)	1.535(2)
C(6)-C(14)	1.541(2)
C(7)-C(8)	1.517(2)
C(8)-C(9)	1.531(2)
C(9)-C(10)	1.533(2)
C(9)-C(11)	1.537(2)
C(11)-C(12)	1.515(2)
C(11)-C(15)	1.525(2)
C(16)-C(17)	1.517(3)
C(17)-C(18)	1.523(3)
C(18)-C(19)	1.543(2)
C(19)-C(20)	1.519(2)

Table S10 Bond angles for **3**.

Bond	angles [º]	Bond	angles [º]
C(12)-O(1)-C(8)	109.14(12)	O(1)-C(8)-C(9)	103.83(12)
C(20)-O(4)-C(21)	115.76(16)	C(7)-C(8)-C(9)	116.21(14)
C(15)-N(1)-C(16)	112.67(13)	C(8)-C(9)-C(10)	112.06(13)
C(15)-N(1)-C(19)	113.69(13)	C(8)-C(9)-C(11)	100.15(13)
C(16)-N(1)-C(19)	107.44(13)	C(10)-C(9)-C(11)	112.02(13)
C(2)-C(1)-C(6)	113.28(15)	C(5)-C(10)-C(9)	112.39(13)
C(1)-C(2)-C(3)	110.95(16)	C(12)-C(11)-C(9)	101.85(12)
C(4)-C(3)-C(2)	111.32(15)	C(12)-C(11)-C(15)	112.86(14)
C(3)-C(4)-C(5)	113.49(15)	C(15)-C(11)-C(9)	117.26(13)
C(13)-C(4)-C(3)	122.06(16)	O(1)-C(12)-C(11)	110.05(15)
C(13)-C(4)-C(5)	124.45(15)	O(2)-C(12)-O(1)	121.60(16)
C(4)-C(5) -C(6)	110.52(13)	O(2)-C(12)-C(11)	128.35(16)
C(4)-C(5) -C(10)	114.64(13)	N(1)-C(15)-C(11)	111.45(13)
C(10)-C(5) -C(6)	111.47(13)	N(1)-C(16)-C(17)	103.06(15)
C(1)-C(6)-C(5)	108.09(14)	C(16)-C(17)-C(18)	102.65(15)
C(7)-C(6)-C(1)	108.45(14)	C(17)-C(18)-C(19)	104.91(14)
C(7)-C(6)-C(5)	107.98(13)	N(1)-C(19)-C(18)	105.51(14)
C(7)-C(6)-C(14)	110.93(14)	N(1)-C(19)-C(20)	110.52(13)
C(14)-C(6)-C(1)	109.55(14)	C(20)-C(19)-C(18)	111.01(14)
C(14)-C(6)-C(5)	111.73(14)	O(3)-C(20)-O(4)	123.70(17)
C(8)-C(7)-C(6)	116.45(14)	O(3)-C(20)-C(19)	125.13(16)
O(1)-C(8)-C(7)	111.00(13)	O(4)-C(20)-C(19)	111.14(15)

Table S11 Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	21.4(6)	30.6(6)	25.9(6)	1.0(5)	-1.7(5)	-6.4(5)
O(2)	50.3(8)	31.9(7)	46.0(8)	8.9(6)	-15.2(7)	-17.4(6)
O(3)	54.2(9)	23.4(6)	58.7(9)	0.6(6)	18.2(8)	2.5(6)
O(4)	27.8(6)	36.1(7)	35.5(6)	-1.9(5)	8.1(6)	6.5(6)
N(1)	20.0(7)	22.3(6)	19.0(6)	-0.6(5)	1.2(5)	0.9(5)
C(1)	29.2(9)	37.0(10)	35.2(9)	12.2(8)	-7.4(8)	1.2(8)
C(2)	39.3(11)	48.5(12)	32.7(9)	19.4(9)	-1.9(8)	-3.5(9)
C(3)	32.8(10)	38.9(10)	35.8(9)	13.8(8)	2.6(8)	-5.6(8)
C(4)	23.6(8)	28.9(8)	25.3(8)	2.7(7)	-0.6(6)	-6.3(7)
C(5)	20.3(8)	19.1(7)	24.5(7)	-0.2(6)	-2.0(6)	-2.3(6)
C(6)	20.1(7)	24.1(8)	24.7(8)	2.9(7)	-3.1(6)	-1.0(6)
C(7)	20.9(8)	27.3(8)	31.0(8)	-0.8(7)	-2.3(7)	2.4(7)

C(8)	20.3(8)	25.4(8)	26.4(8)	-4.1(6)	1.8(6)	-0.1(7)
C(9)	20.8(7)	20.5(7)	21.8(7)	-3.2(6)	-0.4(6)	-0.8(6)
C(10)	16.9(7)	22.7(8)	21.6(7)	-0.7(6)	-0.4(6)	-0.2(6)
C(11)	22.4(8)	26.6(8)	19.1(7)	-2.1(6)	1.2(6)	-2.3(7)
C(12)	26.4(8)	31.4(9)	22.7(7)	1.2(7)	1.0(7)	-6.6(7)
C(13)	26.6(9)	40.9(10)	30.4(8)	5.0(8)	7.5(7)	0.5(8)
C(14)	27.4(8)	31.3(9)	24.1(8)	-4.0(7)	-1.8(7)	-5.4(7)
C(15)	27.7(8)	21.6(7)	21.9(7)	-0.5(6)	-1.1(6)	-0.3(7)
C(16)	21.9(8)	35.4(9)	30.6(8)	4.2(7)	5.0(7)	4.6(7)
C(17)	23.0(9)	45.5(11)	45.9(11)	6.5(9)	-5.7(8)	-3.0(8)
C(18)	33.9(10)	43.9(10)	32.2(9)	-7.6(8)	-11.9(8)	6.9(9)
C(19)	26.3(8)	24.7(8)	18.9(7)	-0.2(6)	0.2(6)	1.6(7)
C(20)	26.3(8)	26.1(8)	20.8(7)	-4.1(6)	-1.2(6)	0.4(7)
C(21)	33.6(11)	50.4(12)	48.8(11)	-13.5(9)	1.9(9)	17.1(9)

Table S12 Hydrogen atom coordinates ($Å^2 \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3**.

Atom	x	y	z	U(eq)
H(1A)	473.7	6940.98	1947.53	41
H(1B)	1631.28	7852.87	2324.6	41
H(2A)	2855.16	7644.68	1369.67	48
H(2B)	2907.58	6225.98	1437.44	48
H(3A)	5702.57	6920.17	1629.53	43
H(3B)	5000.4	7883.71	2100.56	43
H(5)	3703.73	7103.66	3082.33	26
H(7A)	460.32	7223.05	3208.44	32
H(7B)	-664.28	6129.16	2973.1	32
H(8)	6.9	6115.93	4037	29
H(9)	2895.55	6431.14	4184.63	25
H(10A)	5096.78	5559.91	3620.3	24
H(10B)	3806.76	4613.22	3325.22	24
H(11)	1912.52	4916.21	4779.08	27
H(13A)	7117.84	5376.73	2129.92	39
H(13B)	6407.25	4847.18	2773.87	39
H(14A)	2515.89	4700.29	2081.53	41
H(14B)	471.64	4810.17	2169.98	41
H(14C)	1641.49	4265.7	2695.5	41
H(15A)	3876.52	3323.85	4843.62	28

H(15B)	4676.8	3658.36	4201.35	28
H(16A)	7658.59	4493.61	4438.23	35
H(16B)	7192.51	3501.83	4936.67	35
H(17A)	8310.27	5905.86	5165.5	46
H(17B)	9110.67	4711.23	5455.48	46
H(18A)	6776.99	5907.82	6040.98	44
H(18B)	6856.06	4481.32	6102.34	44
H(19)	4257.49	4374.44	5666.93	28
H(21A)	1186.46	7483.48	5590.61	66
H(21B)	2130.39	7640.7	6225.87	66
H(21C)	394.6	6873.89	6179.63	66

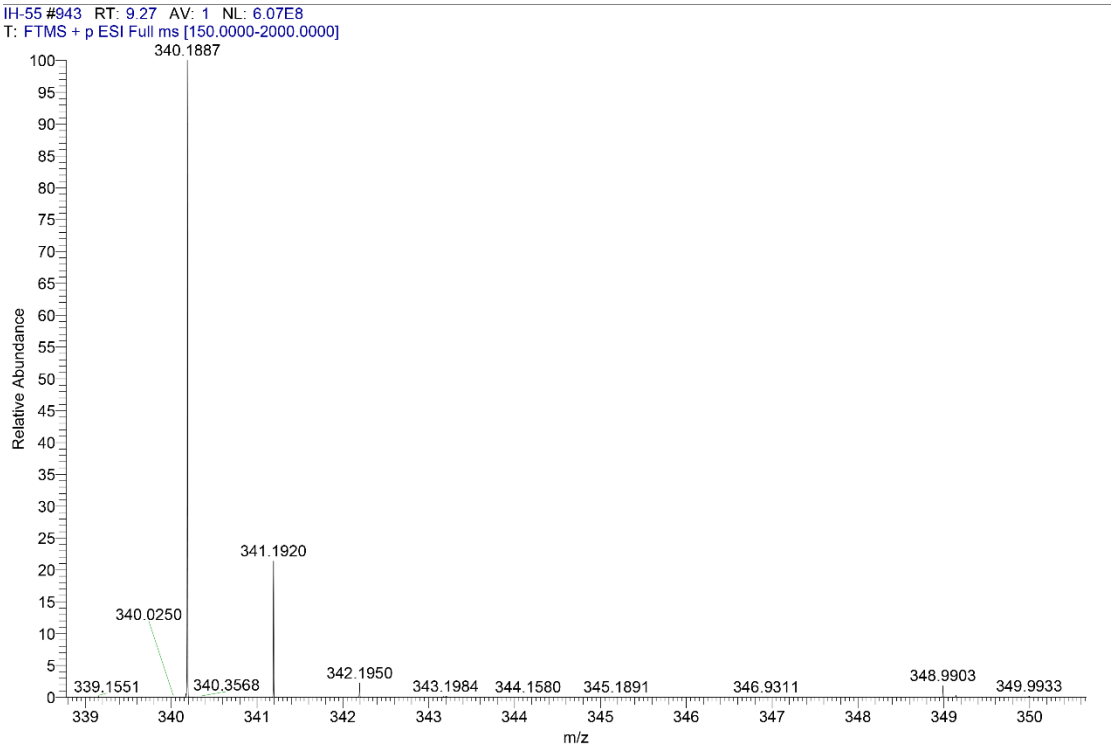

Fig. S25 HRESIMS spectrum of **4**.

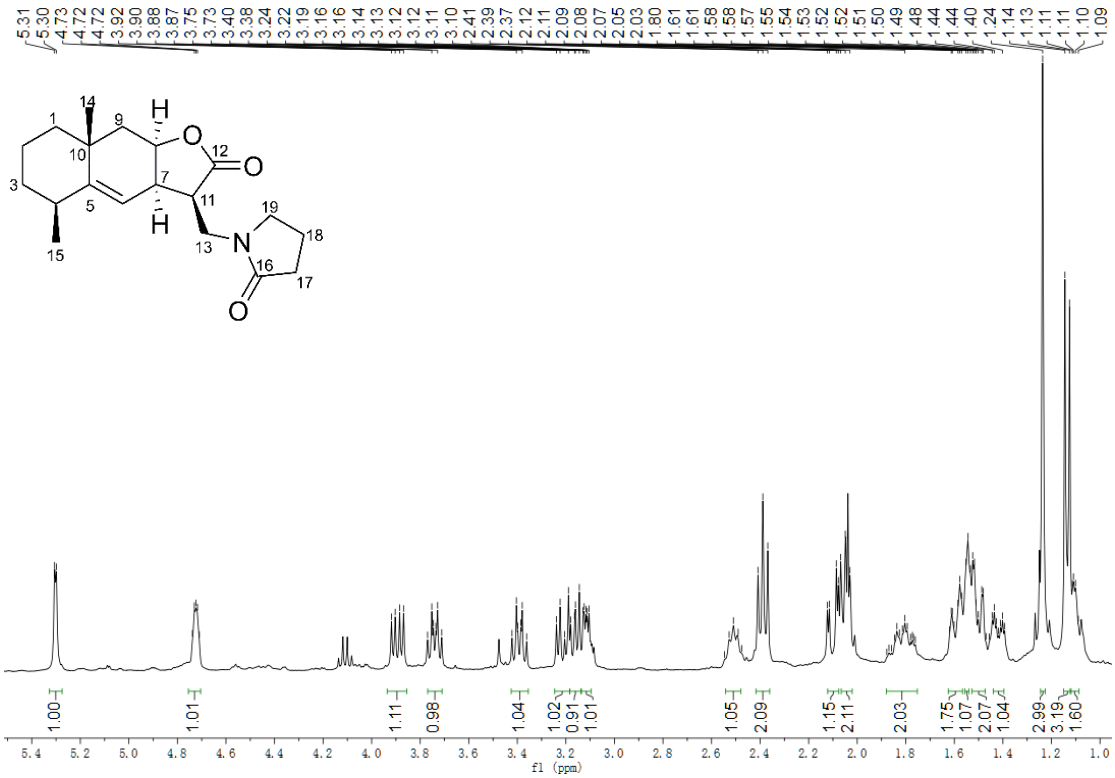

Fig. S26 ^{1}H NMR spectrum (400 MHz) of **4** in $CDCl_3$.

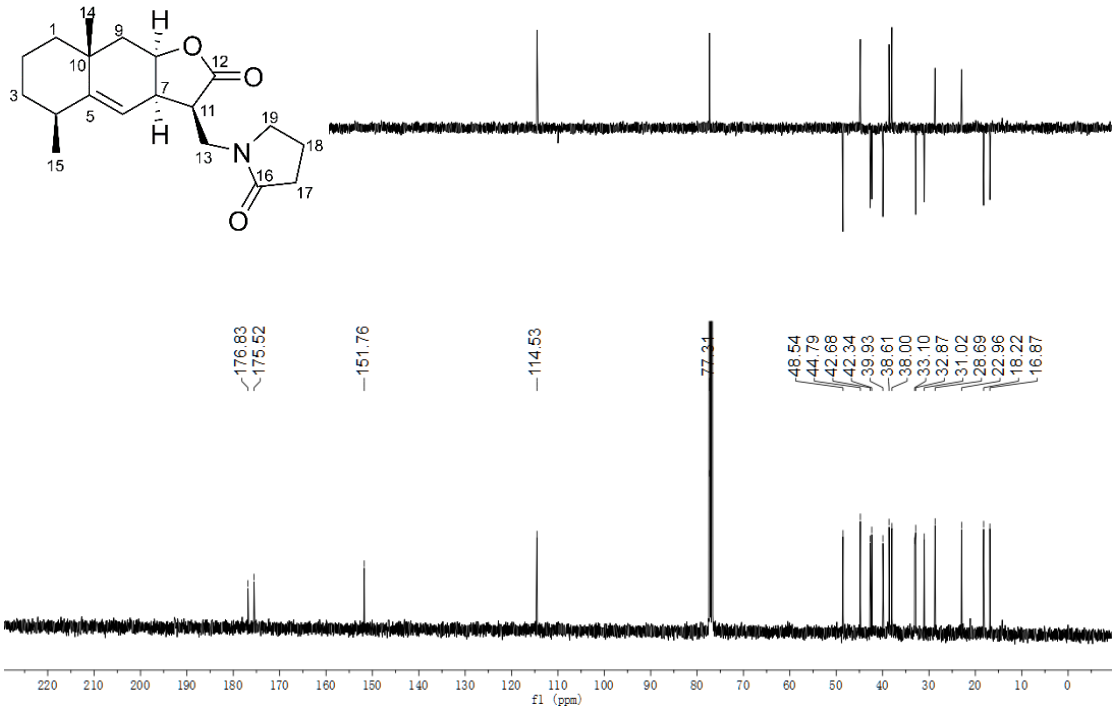

Fig. S27 ^{13}C NMR and DEPT spectra (100 MHz) of **4** in $CDCl_3$.

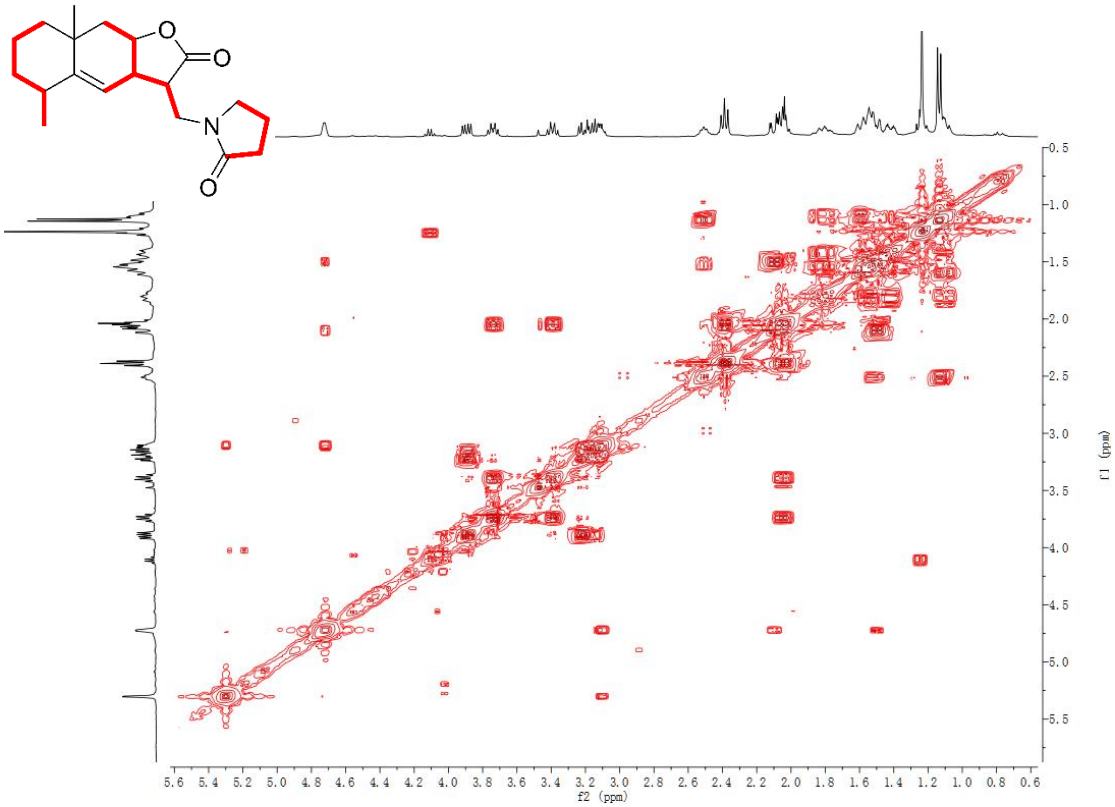

Fig. S28 ^{1}H-^{1}H COSY spectrum (400 MHz) of **4** in $CDCl_3$.

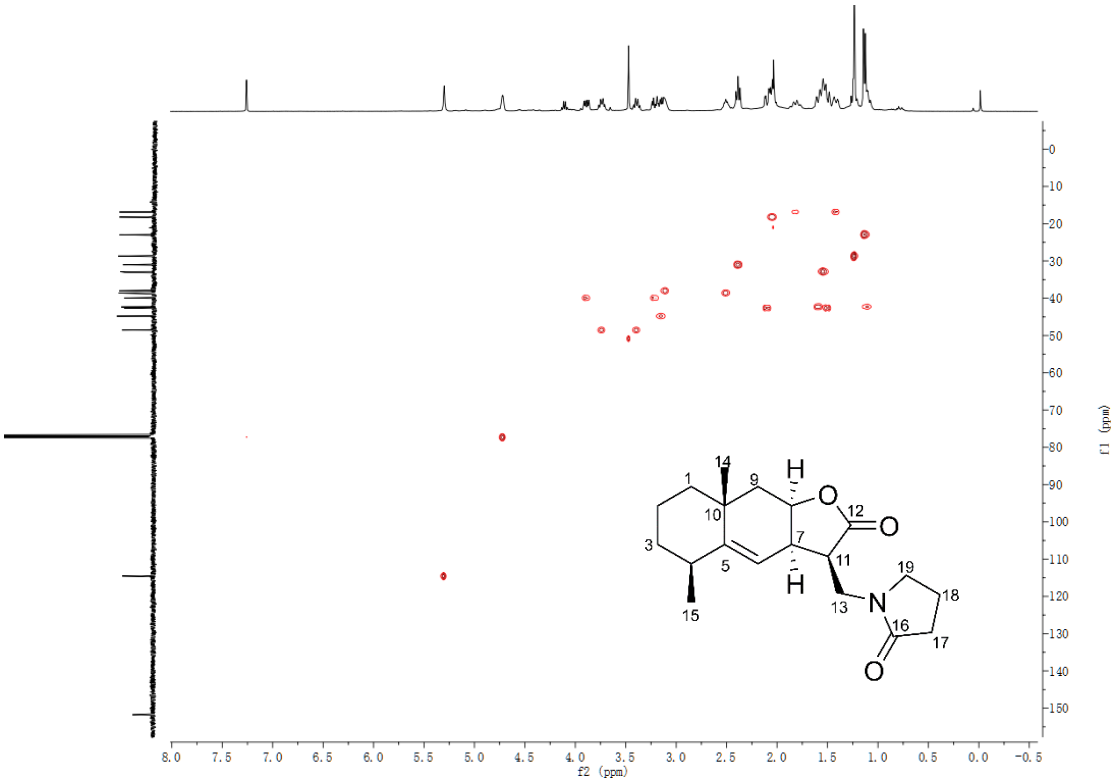

Fig. S29 HSQC spectrum (400 MHz) of **4** in $CDCl_3$.

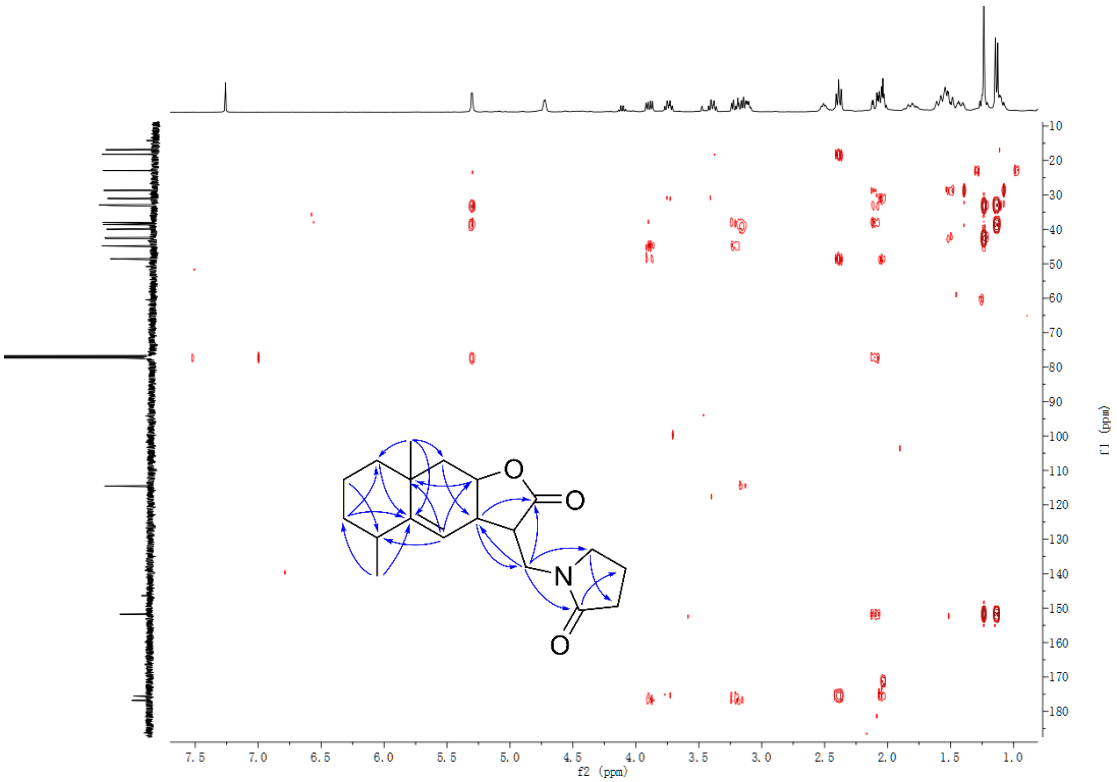

Fig. S30 HMBC spectrum (400 MHz) of **4** in $CDCl_3$.

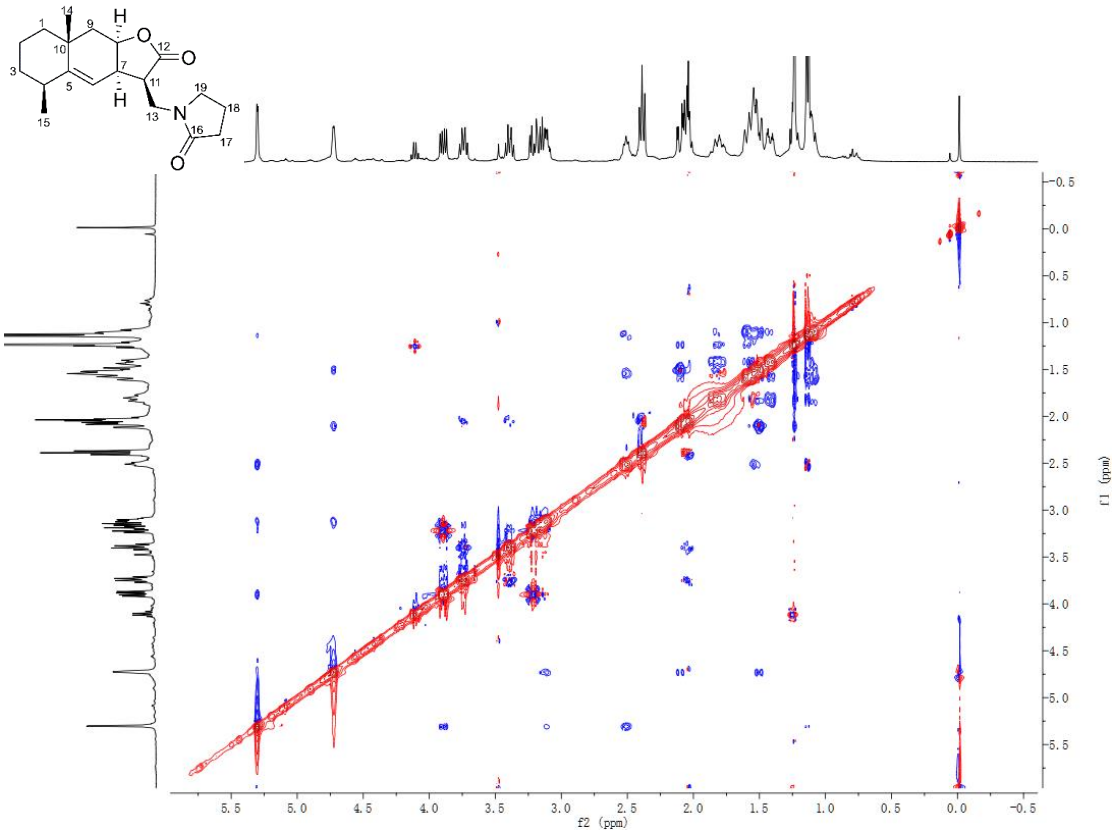

Fig. S31 NOESY spectrum (400 MHz) of **4** in $CDCl_3$.

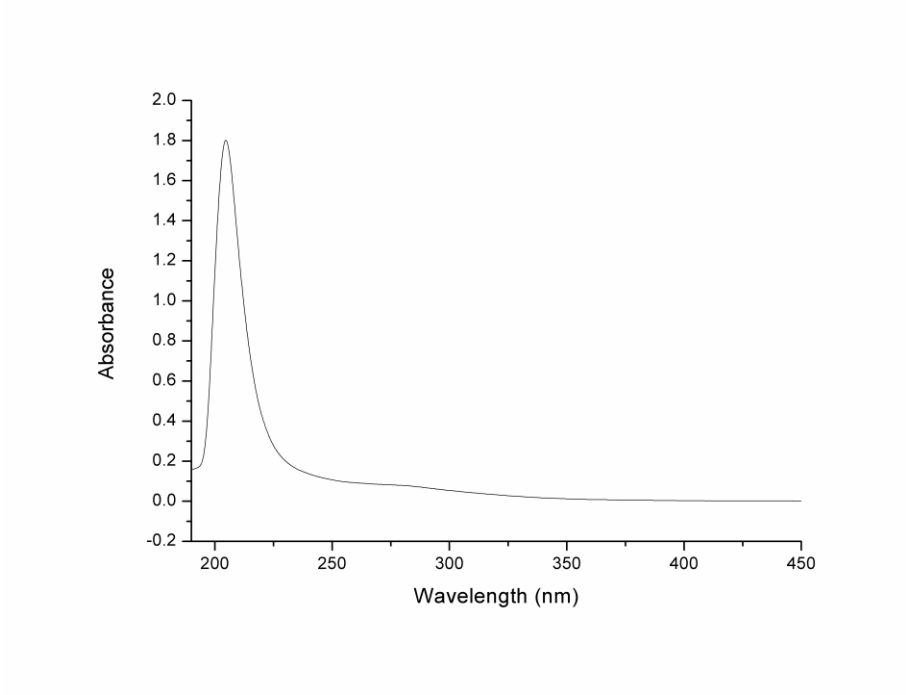

Fig. S32 UV spectrum of **4** in MeOH.

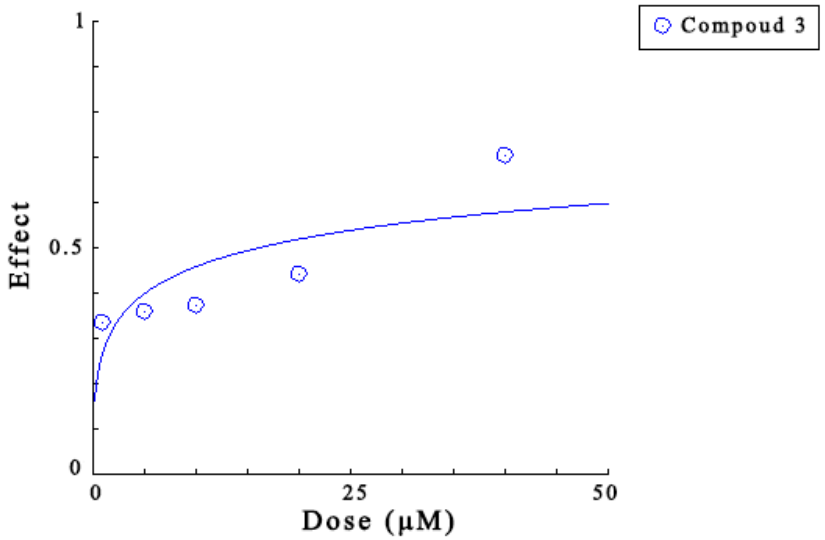

Fig. **S33** Dose-Effect Curve, showing the NO inhibition of **3**. Dose-Effect Curve is generated by Compusyn.

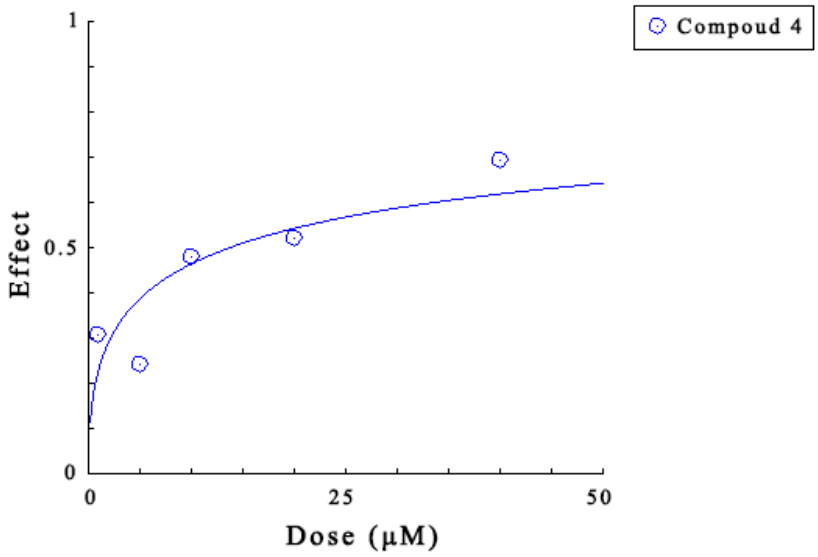

Fig. **S34** Dose-Effect Curve, showing the NO inhibition of **4**. Dose-Effect Curve is generated by Compusyn.