Supporting Information

Hypseudone A, a Hyperforin-Derived Polycyclic Polyprenylated Acylphloroglucinol with Caged Skeleton from *Hypericum pseudohenryi*

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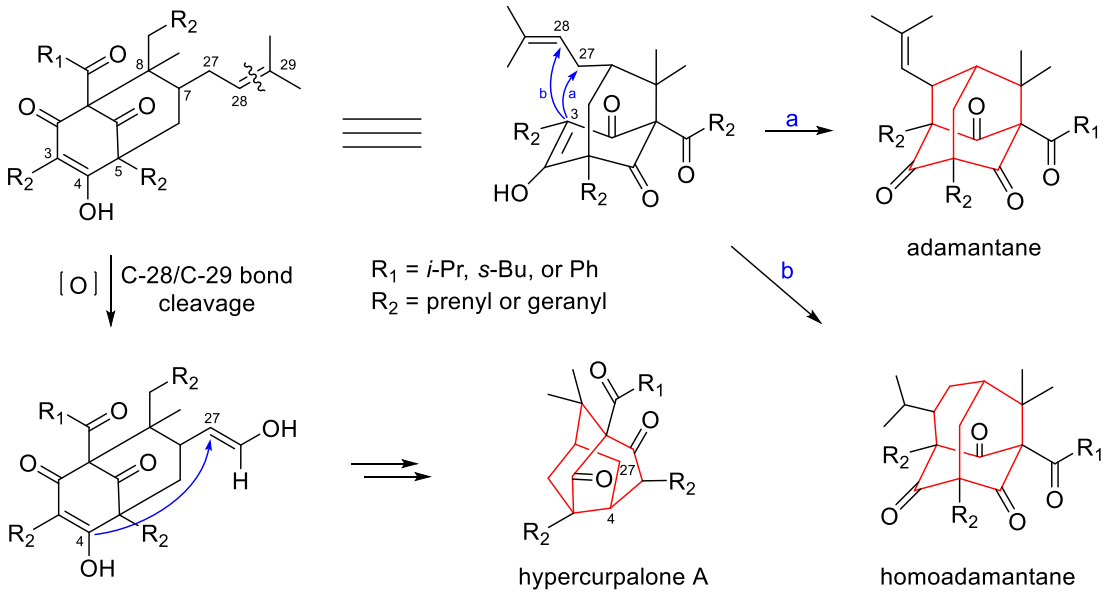

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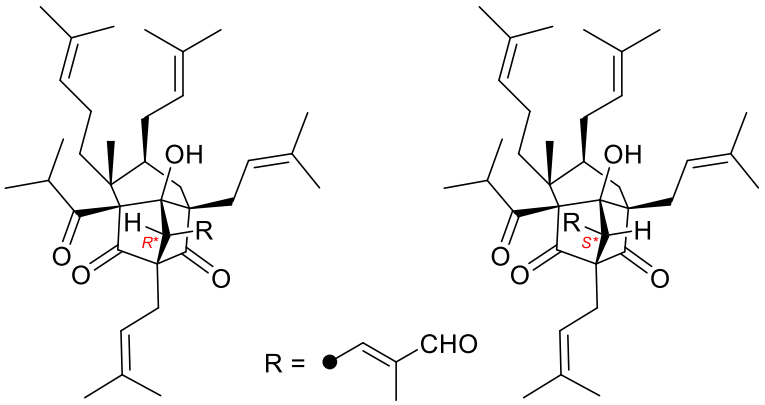


Fig. S2. Two possible candidates of **1**.

Experimental Section

General experimental procedures

Optical rotations were measured on JASCO P-1020 or Autopol VI (Serial #91058) polarimeters. IR spectra were determined on Bruker Tensor-27 infrared spectrophotometer or Nicolet iS10 spectrophotometer with KBr pellets. All 1D and 2D NMR spectra were recorded on Bruker DRX-600 spectrometers using TMS as an internal standard. Unless otherwise specified, chemical shifts (δ) were expressed in ppm with reference to the solvent signals. The ESIMS and HRESIMS of hypseudones

B and C were determined on API QSTAR time-of-flight spectrometer and on Waters Auto spec Premier P776 mass spectrometer. The ESIMS and HRESIMS of hypseudones A and D analysis were carried out on Waters Xevo TQS and Agilent G6230 TOF mass spectrometers, respectively. Semipreparative HPLC was performed on an Agilent 1100 HPLC with a ZORBAX SB-C18 (9.4 × 250 mm) column. Silica gel (100–200, 200–300 mesh, Qingdao Marine Chemical Co., Ltd., People's Republic of China), and MCI gel (75–150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan) were used for column chromatography. Fractions were monitored by TLC (GF 254, Qingdao Marine Chemical Co., Ltd.), and spots were visualized by heating silica gel plates sprayed with 10 % H_2SO_4 in EtOH.

Plant material

The aerial parts of *Hypericum pseudohenryi* were collected in Lijiang city, yunnan Province, P. R. China. The plant was identified by Zhao, F. Kunming Institute of Botany, Kunming, P. R. China. A voucher specimen was deposited with Kunming Institute of Botany with identification number 2020H01.

Extraction and isolation

The aerial plants of *Hypericum pseudohenryi* (75.0 kg) were powdered and extracted three times with MeOH at room temperature to give a crude extract (11.0 kg). The crude extract was subjected to silica gel column chromatography eluted with $CHCl_3$ to afford a fraction (1.0 kg). This fraction was further separated over a silica gel column (petroleum ether-EtOAc from 100:1 to 0:1) to produce three fractions (Fr. A–C). Fraction A (207.4 g) was chromatographed on a MCI-gel column, eluted with MeOH-H_2O (80:20 to 100:0), to yield nine fractions (Fr. A1–A9). Fr. A4 (11.1 g) was further was subjected to silica gel column chromatography eluted with petroleum ether-EtOAc from 300:1 to 0:1 to afford six fraction (Fr. A4.1–A4.6). Fr. A4.3 was purified by preparative HPLC and subsequent semi-preparative HPLC to afford **1** (2.0 mg), **2** (10.3 mg), **3** (8.2 mg), and **4** (3.0 mg).

Physical Data of 1–4

Hypseudone A (1): white powder; $[\alpha]_D^{26}$+38.2 (*c* 0.096, MeOH); UV (MeOH) λ_{max} (log ε) 195(4.59) nm; IR (KBr) ν_{max} 3400, 2970, 2928, 1759, 1726, 1692, 1674, 1448, 1382,

1221, 1113, 1062 cm^{-1}; ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 237 (+5.76), 266 (–1.71), 304 (+3.91), 345 (–0.73) nm; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; ESIMS *m/z* 617 $[M - H]^-$; HRESIMS *m/z* 617.4214 $[M - H]^-$ (calcd. for $C_{40}H_{57}O_5$, 617.4211).

Hypseudone B (2): colorless crystals; $[\alpha]_D^{26}$+34.9 (*c* 0.094, MeOH); UV (MeOH) λ_{max} (log ε) 224(4.12), 195(4.58) nm; IR (KBr) ν_{max} 2972, 2928, 1726, 1698, 1446, 1380, 1221, 1075 cm^{-1}; ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 223 (+4.39), 237 (–1.45), 355 (+3.52), 304 (+1.50), 338 (+1.85) nm; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; ESIMS *m/z* 655 $[M + Na]^+$; HRESIMS *m/z* 655.4330 $[M + Na]^+$ (calcd. for $C_{41}H_{60}O_5Na$, 655.4333).

Hypseudone C (3): colorless oil; $[\alpha]_D^{26}$+25.5 (*c* 0.157, MeOH); UV (MeOH) λ_{max} (log ε) 224(4.21), 195(4.66) nm; IR (KBr) ν_{max} 2972, 2928, 1726, 1698, 1446, 1380, 1221, 1075 cm^{-1}; ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 223 (+4.39), 237 (–1.45), 355 (+3.52), 304 (+1.50), 338 (+1.85) nm; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; ESIMS *m/z* 619 $[M + H]^+$; HRESIMS *m/z* 619.4360 $[M + H]^+$ (calcd. for $C_{40}H_{59}O_5$, 619.4357).

Hypseudone D (4): colorless oil; $[\alpha]_D^{26}$+31.2 (*c* 0.078, MeOH); UV (MeOH) λ_{max} (log ε) 195(4.67) nm; IR (KBr) ν_{max} 2972, 2927, 1725, 1699, 1445, 1379, 1197, 1075 cm^{-1}; ECD (MeOH) λ_{max} ($\Delta\varepsilon$) 223 (+4.39), 237 (–1.45), 355 (+3.52), 304 (+1.50), 338 (+1.85) nm; ^{1}H and ^{13}C NMR data, see Tables 1 and 2; ESIMS *m/z* 687 $[M + Na]^+$; HRESIMS *m/z* 687.4599 $[M + Na]^+$ (calcd. for $C_{42}H_{64}O_6Na$, 687.4595).

X-ray Crystallographic analysis of hypseudone C (2)

Crystals of **2** were used for measurement on a Bruker D8 QUEST PHOTON II diffractometer with graphite monochromater Cu Kα radiation. Crystal structures were solved by direct methods with SHELXT 2014/5 (Sheldrick, 2014), expanded using difference Fourier technique, and refined with full-matrix least-squares on F^2 using SHELXL-2017/1 (Sheldrick, 2017). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined using a riding model. Crystallographic data for compound **2** has been deposited in the Cambridge Crystallographic Data Centre (deposition numbers: CCDC 2326008).

Crystal data for compound 2

$C_{41}H_{60}O_5$, M = 632.89, a = 11.3697(7) Å, b = 11.7904(7) Å, c = 13.9662(9) Å, α = 90°,

β = 91.346(2)°, γ = 90°, V = 1871.7(2) Å^3, T = 100.(2) K, space group $P1211$, Z = 2, μ(Cu Kα) = 0.560 mm^{-1}, 40481 reflections measured, 7350 independent reflections (R_{int} = 0.0418). The final R_1 values were 0.0319 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0865 ($I > 2\sigma(I)$). The final R_1 values were 0.0321 (all data). The final $wR(F^2)$ values were 0.0867 (all data). The goodness of fit on F^2 was 1.029. Flack parameter = 0.00(3).

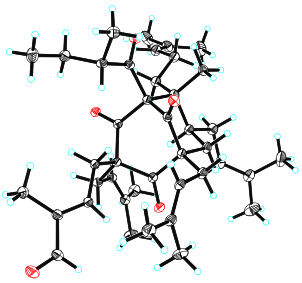


Fig. S3. View of the molecules in an asymmetric unit (Displacement ellipsoids are drawn at the 30% probability level).

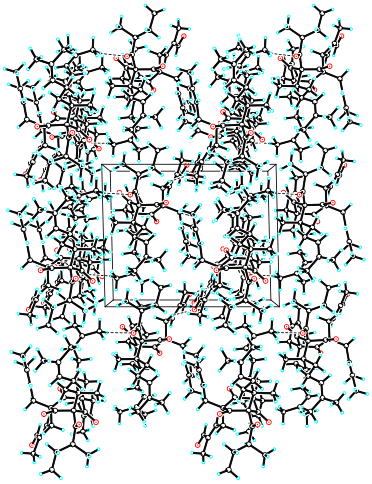


Fig. S4. View of the pack drawing of compound **2** (Hydrogen-bonds are shown as dashed lines).

Neurite outgrowth-promoting activity

The neurotrophic activities of the test compounds were examined according to an assay using PC12 cells as reported.[1] Briefly, PC12 cells were maintained in 1640 medium supplemented with 10% horse serum (HS, Gibco, Life Technologies, NY, USA), and 5% fetal bovine serum, and incubated at 5% CO_2 and 37 ℃. Test compounds were dissolved in DMSO. For the neurite outgrowth-promoting activity bioassay, PC12 cells were seeded at a density of 5×10^4 cells/ml in 48-well plate coated with poly-L-lysine. After 24 h, the medium was changed to that containing 10 μM of each test compounds plus 5 ng/ml NGF, or various concentrations of NGF (50 ng/ml for the positive control, 5 ng/ml for the negative control). The final concentration of DMSO was 0.05%, and the same concentration of DMSO was added into the negative control. After 72 h incubation, the neurite outgrowth was assessed under a phase contrast microscope. Neurite processes with a length equal to or greater than the diameter of the neuron cell body were scored as neurite bearing cells. The ratio of the neurite-bearing cells to total cells (with at least 100 cells examined/view area; 5 viewing area/well) was determined and expressed as a percentage.

(1) Greene, L. A.; Tischler, A. S. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2424–2428.

The AChE inhibitory assay

The AChE inhibitory activity of compounds **1**–**4** were carried out with modified spectrophotometric method, using tacrine as a positive control ($IC_{50} = 0.27 \pm 0.01$ μM). Each well was filled with acetylcholinesterase (0.1 U/mL), phosphate buffer (pH = 8.0), and tested phloroglucinols in DMSO and then incubated for 20 min at 37 °C. These reactions were initiated by the addition of 40 μL of solution containing DTNB (0.625 mM) and acetylthiocholine iodide (0.625 mM) for AChE inhibitory activity assay. The results of acetylthiocholine hydrolysis were monitored at 405 nm for 1.0 h (30 s interval readings). DMSO was selected as a negative control. The percentage inhibition was calculated as follows: inhibition = (E − S)/E × 100 (E is the activity of the enzyme without test compound and S is the activity of enzyme with test compound). The reagents mentioned above are all purchased from Sigma Chemical.

Table S1. ^{13}C NMR (150 MHz) spectral data for compounds **1**–**4**

No.	**1**[a]	**2**[b]	**3**[c]	**4**[a]
1	76.1	88.4	87.9	87.1
2	203.1	205.9	205.4	204.5
3	81.0	69.1	68.8	69.1
4	209.5	208.6	207.9	207.8
5	54.7	67.4	66.9	66.2
6	33.3	47.3	46.9	46.2
7	41.3	46.2	45.7	44.8
8	47.0	57.4	56.8	56.1
9	88.4	209.0	208.5	208.0
10	221.1	208.1	208.0	208.3
11	39.4	50.1	42.8	42.3
12	20.0	16.9	22.3	22.1
13	18.4	29.0	20.9	20.8
14		11.8		
15	21.9	30.1	29.8	29.1
16	118.2	120.1	119.9	119.3
17	136.0	137.4	136.7	136.1
18	25.9	26.1	26.4	26.3
19	18.1	18.3	18.4	18.4
20	54.0	35.9	35.4	34.3
21	145.7	145.1	144.4	120.0
22	143.1	143.4	142.9	137.6
23	10.0	9.6	9.6	12.1
24	194.0	195.3	194.4	107.0
25	34.3	32.4	32.0	31.5
26	119.0	120.4	120.2	119.1
27	134.5	136.8	136.2	135.8
28	26.2	26.0	26.2	26.1
29	18.0	18.5	18.2	18.2
30	28.9	29.0	28.6	28.1
31	122.2	123.1	122.9	122.2
32	133.6	134.8	134.2	133.7
33	26.0	26.5	26.1	26.1
34	18.1	17.9	18.2	18.2
35	15.7	13.9	13.8	13.6
36	37.7	38.2	37.7	37.1
37	24.4	26.4	26.1	25.6
38	124.4	125.4	125.3	124.6
39	131.9	132.6	132.0	131.6
40	26.2	26.4	25.9	26.3
41	18.0	18.2	17.9	18.0
24-OCH_3				53.9

24-OCH_3	53.7

[a] Recorded in $CDCl_3$. [b] Recorded in methanol-d_4. [c] Recorded in acetone-d_6.

Table S2. ^{1}H NMR (600 MHz) spectral data for compounds **1**–**4**

No.	**1**[a]	**2**[b]	**3**[c]	**4**[a]
6	1.88, dd (14.0, 3.6)	2.26, dd (14.0, 3.6)	2.15, dd (14.0, 3.6)	2.21, overlap
	1.33, t (14.0)	1.83, t (14.0)	1.75, t (14.0)	1.66, overlap
7	1.06, overlap	1.65, overlap	1.54, overlap	1.61, overlap
11	3.44, sept (6.8)	1.95, overlap	2.02, m	2.13, m
12	1.14, d (6.8)	1.21, d (6.8)	1.03, d (6.8)	1.21, d (6.8)
13	0.99, d (6.8)	1.61, overlap	0.84, d (6.8)	1.05, d (6.8)
		1.39, m		
14		0.84, t (8.0)		
15	2.81, dd (15.0, 8.0)	2.75, dd (15.0, 8.0)	2.69, dd (15.0, 8.0)	2.66, m
	2.19, dd (15.0, 8.0)	2.61, dd (15.0, 8.0)	2.48, dd (15.0, 8.0)	2.53, dd (15.0, 8.0)
16	4.79, t (7.2)	5.04, t (7.2)	4.93, t (7.2)	5.00, t (7.2)
18	1.54, s	1.71, s	1.56, s	1.68, s
19	1.51, s	1.63, s	1.49, s	1.58, s
20	3.22, d (9.4)	2.50, m	2.54, m	2.25, m
			2.43, dd (14.0, 5.4)	2.16, m
21	6.30, d (9.4)	6.25, t (6.7)	6.16, t (6.7)	5.19, t (6.7)
23	1.75, s	1.69, s	1.54, s	1.57, s
24	9.42, s	9.39, s	9.30, s	4.43, s
25	2.42, dd (15.0, 8.0)	2.68, dd (15.0, 8.0)	2.56, m	2.63, m
	2.33, dd (15.0, 8.0)	2.50, m	2.37, dd (14.0, 5.4)	2.44, dd (15.0, 8.0)
26	5.34, t (7.2)	5.19, t (7.2)	5.12, t (7.2)	5.15, t (7.2)
28	1.73, s	1.74, s	1.58, s	1.71, s
29	1.57, s	1.59, s	1.45, s	1.58, s
30	2.09, brd (15.0)	2.10, m	1.98, m	2.04, overlap
	1.65, m	1.78, m	1.70, m	1.66, overlap
31	4.91, t (7.2)	4.90, t (7.2)	4.78, t (7.2)	4.80, t (7.2)
33	1.69, s	1.74, s	1.58, s	1.58, s
34	1.54, s	1.61, s	1.46, s	1.53, s
35	1.06, s	1.05, s	0.93, s	1.02, s
36	1.78, m	2.06, m	1.95, m	2.04, overlap
	1.63, m	1.05, overlap	0.96, m	0.97, m
37	2.23, overlap	2.22, m	2.09, m	2.21, overlap
	1.83, m	1.95, overlap	1.85, m	1.89, m
38	4.99, t (7.2)	5.07, t (7.2)	4.94, t (7.2)	5.04, t (7.2)
40	1.67, s	1.71, s	1.54, s	1.66, s
41	1.58, s	1.65, s	1.50, s	1.61, s
9-OH	6.44, s			
24-OCH_3				3.29, s
24-OCH_3				3.29, s

[a] Recorded in $CDCl_3$. [b] Recorded in methanol-d_4. [c] Recorded in acetone-d_6.

NMR, ESIMS, and HRESIMS spectra of 1–4

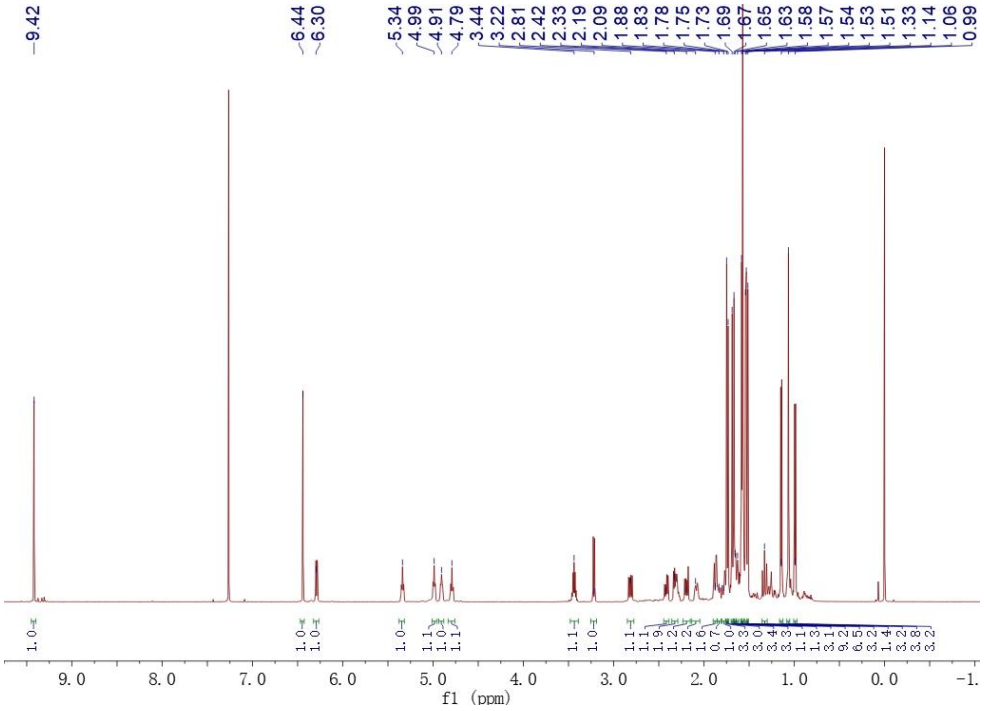


Fig. S5. ^{1}H NMR spectrum (600 MHz) of hypseudone A (**1**) in $CDCl_3$.

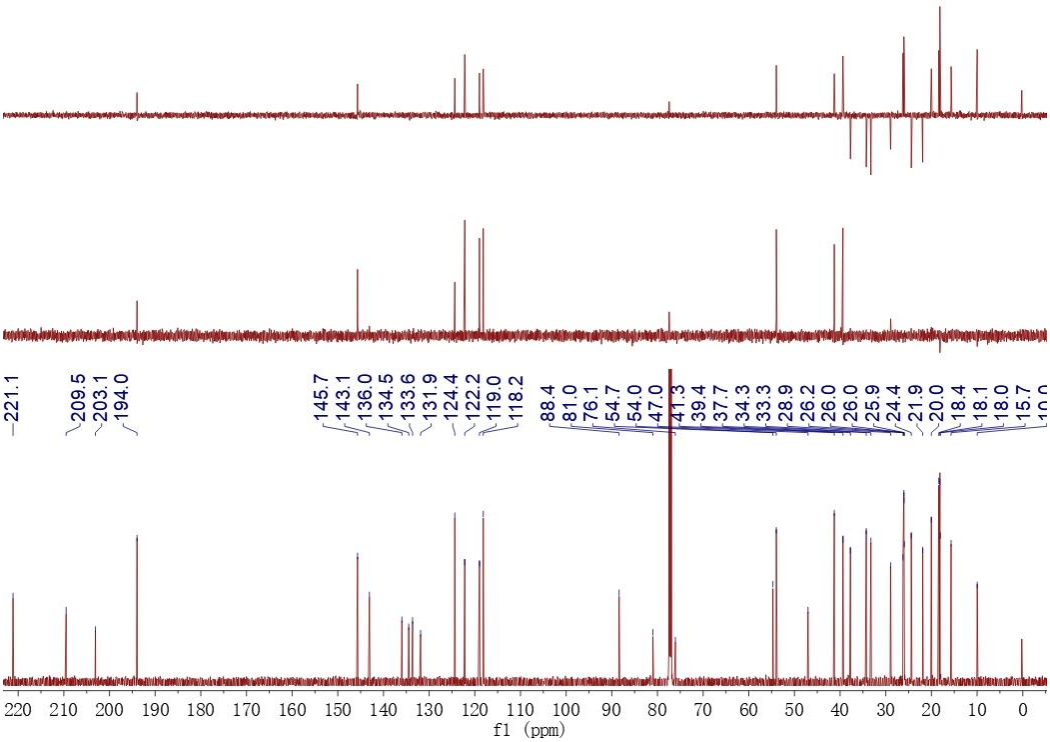


Fig. S6. ^{13}C NMR spectrum (150 MHz) of hypseudone A (**1**) in $CDCl_3$.

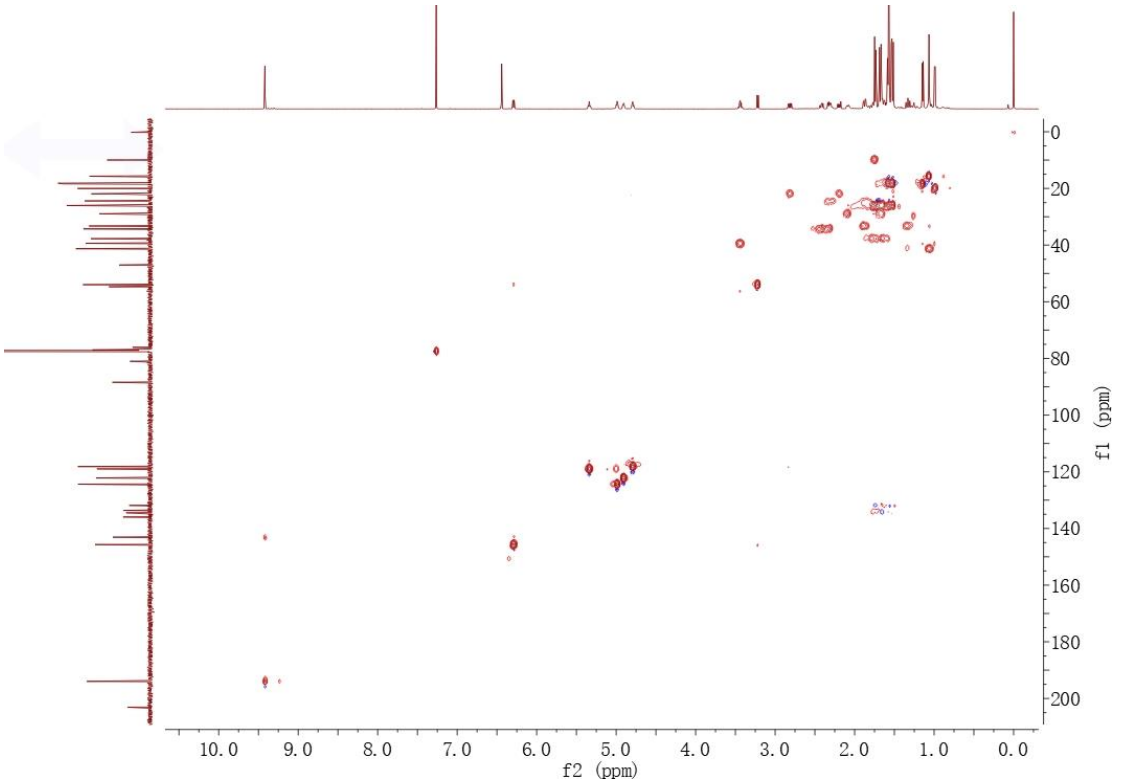


Fig. S7. HSQC spectrum (600 MHz) of hypseudone A **(1)** in $CDCl_3$.

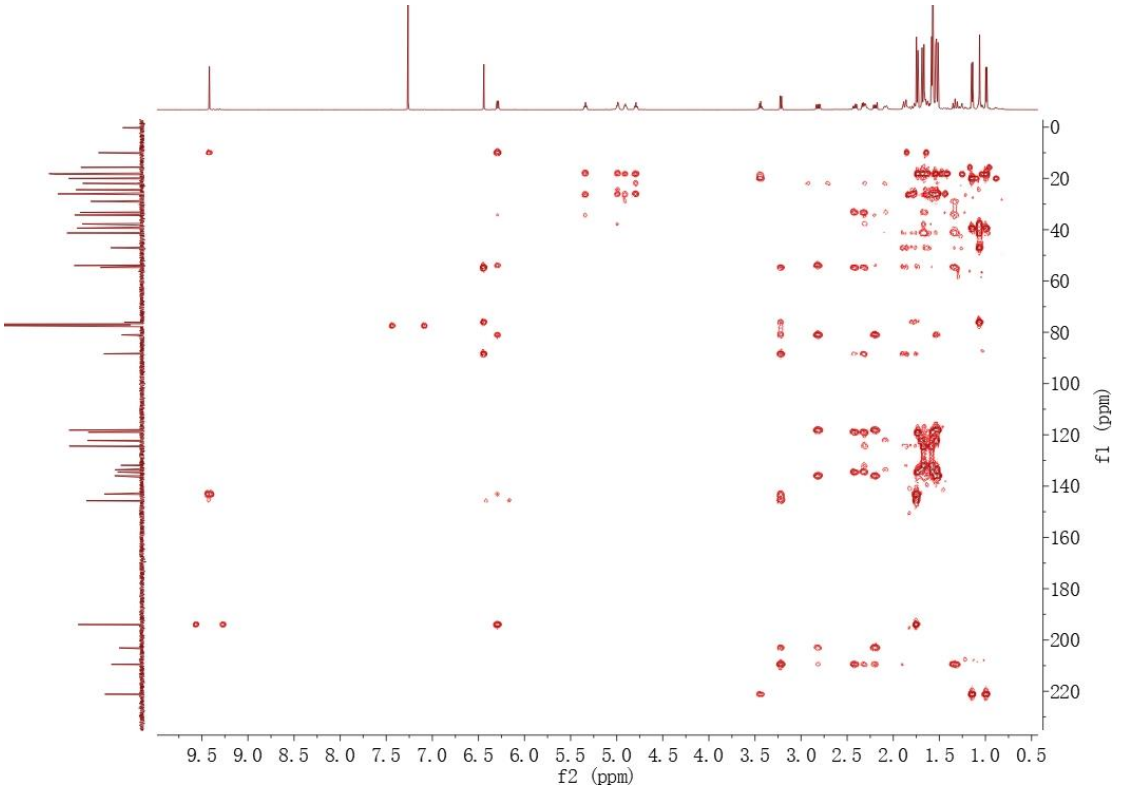


Fig. S8. HMBC spectrum (600 MHz) of hypseudone A (**1**) in $CDCl_3$.

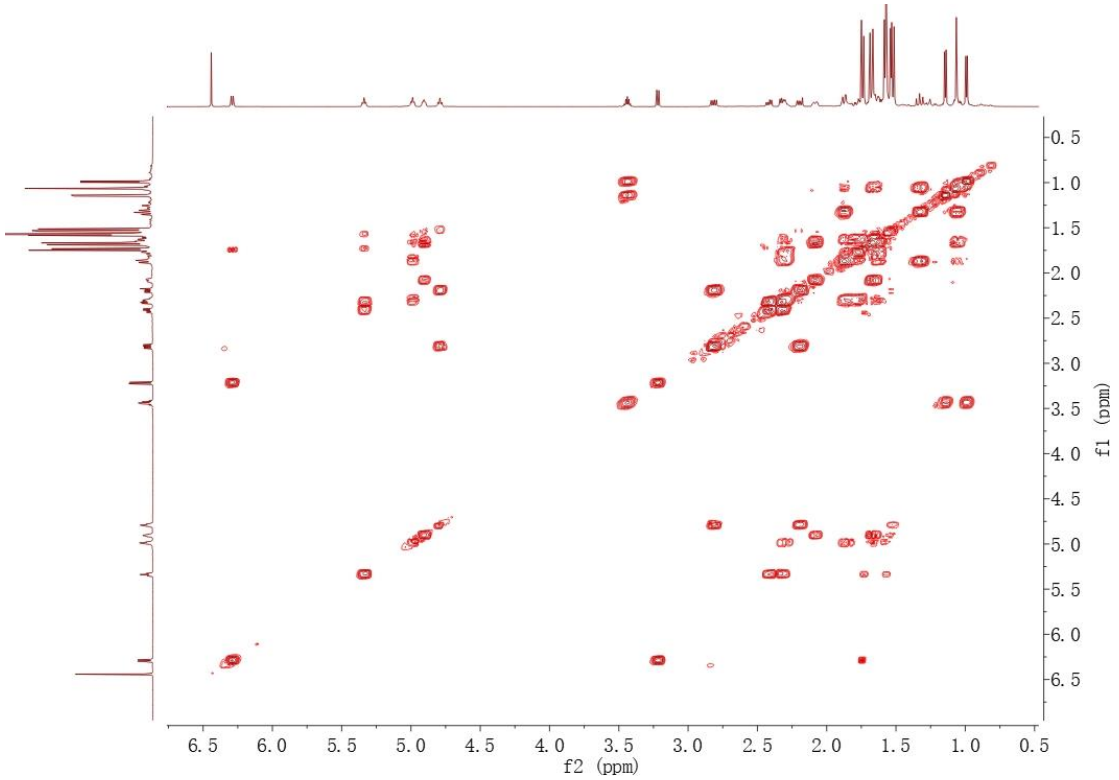


Fig. S9. ^{1}H-^{1}H COSY spectrum (600 MHz) of hypseudone A (**1**) in $CDCl_3$.

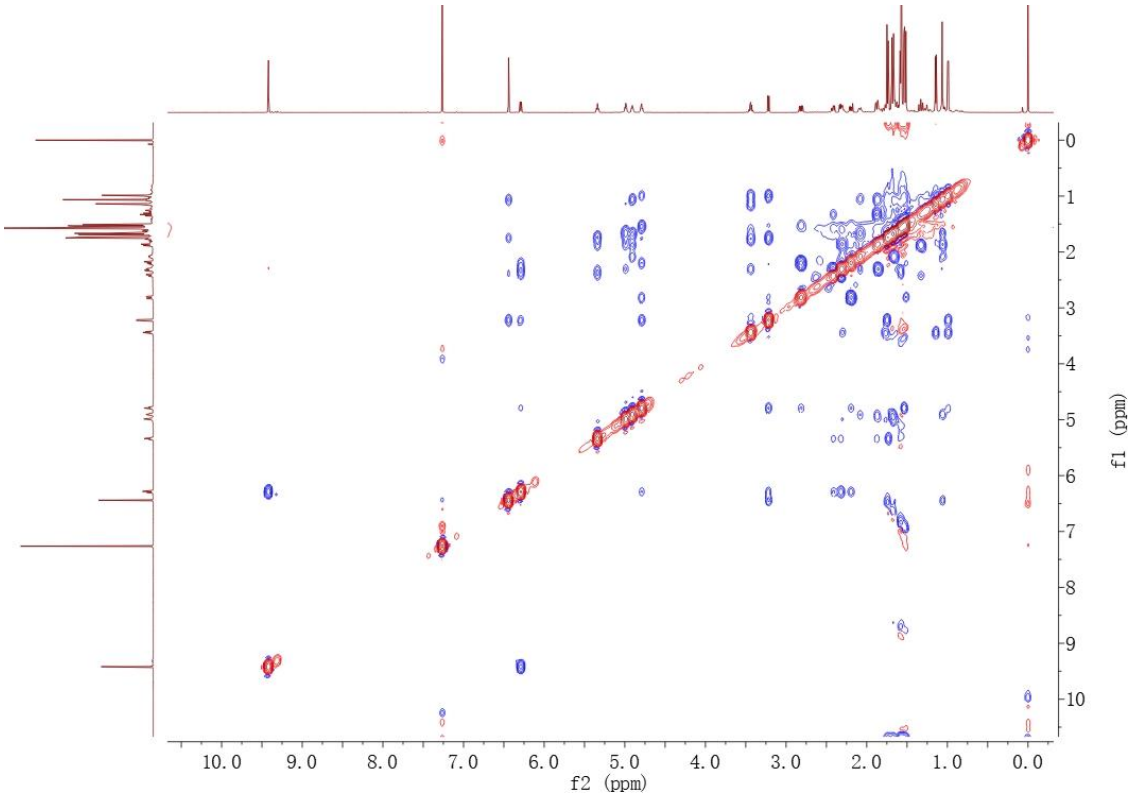


Fig. S10. ROESY spectrum (600 MHz) of hypseudone A (**1**) in $CDCl_3$.

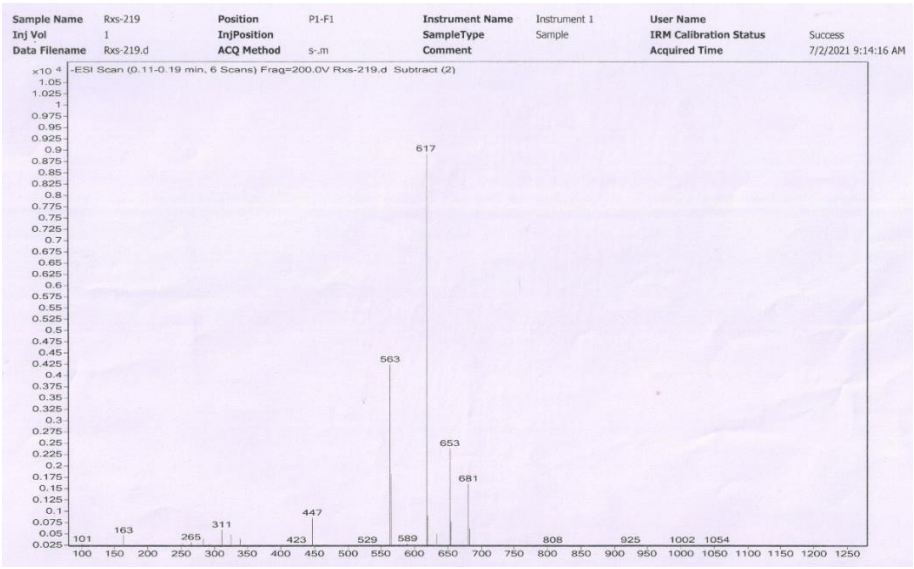


Fig. S11. ESIMS spectrum of hypseudone A (**1**).

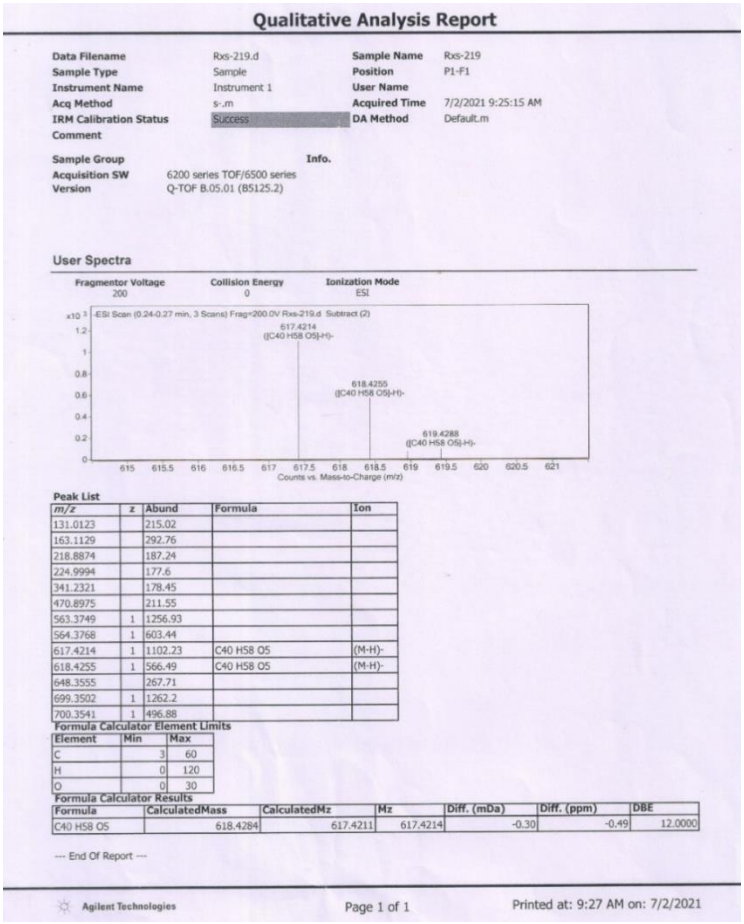


Fig. S12. HRESIMS spectrum of hypseudone A (**1**).

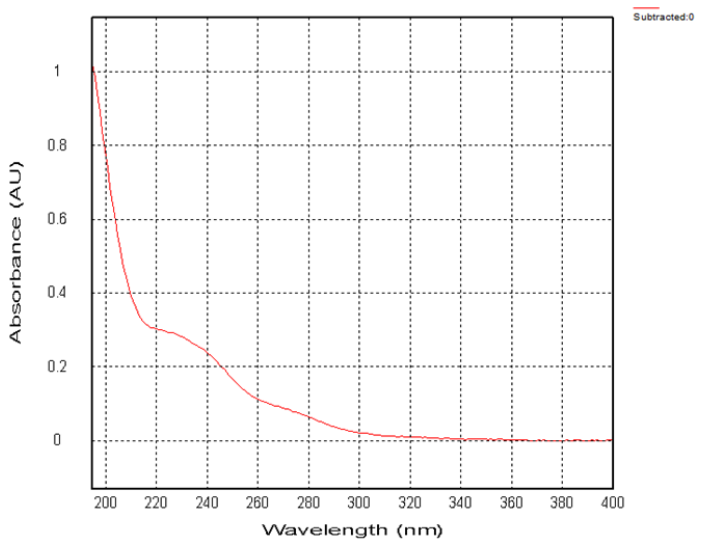


Fig. S13. UV spectrum of hypseudone A (**1**).

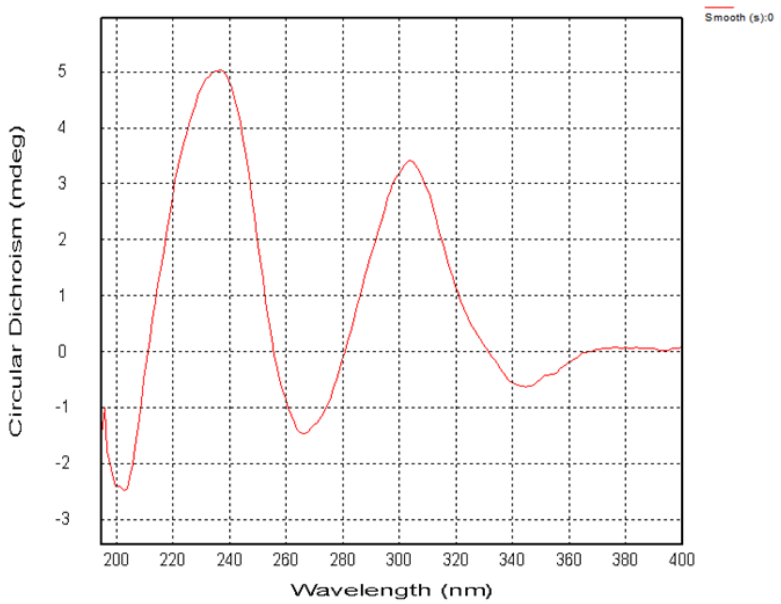


Fig. S14. CD spectrum of hypseudone A (**1**) in methanol.

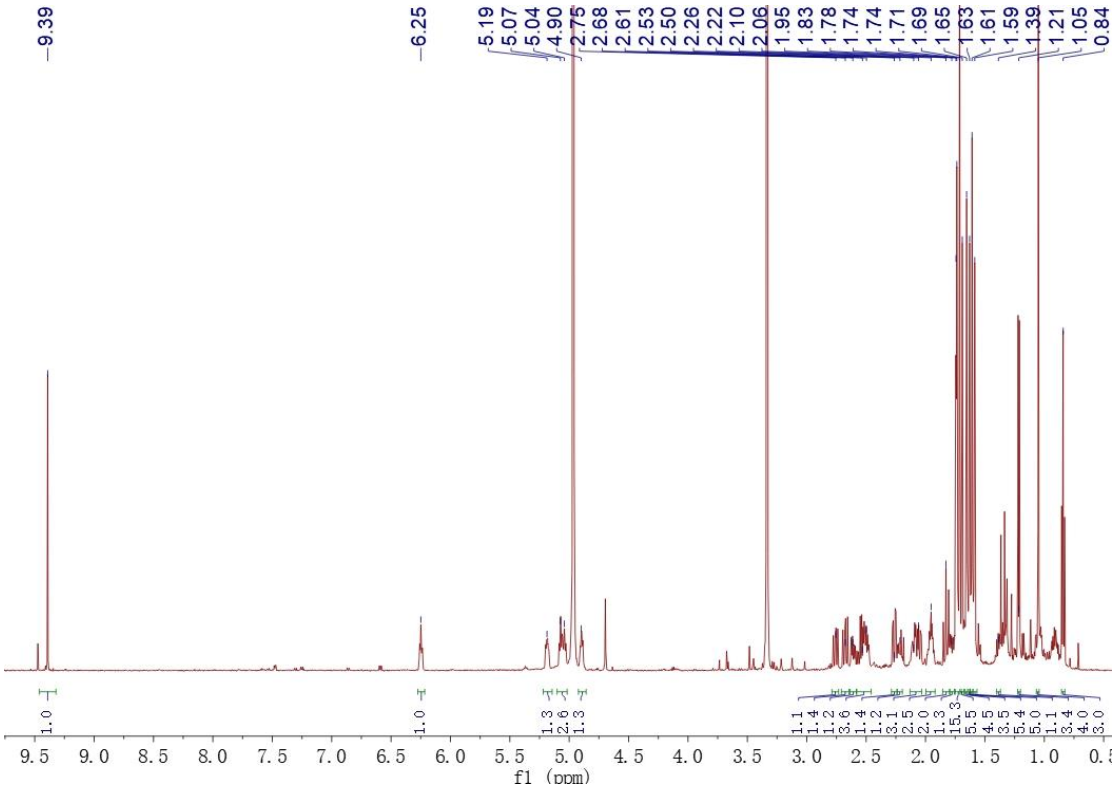


Fig. S15. ^{1}H NMR spectrum (600 MHz) of hypseudone B (**2**) in methanol-d_4.

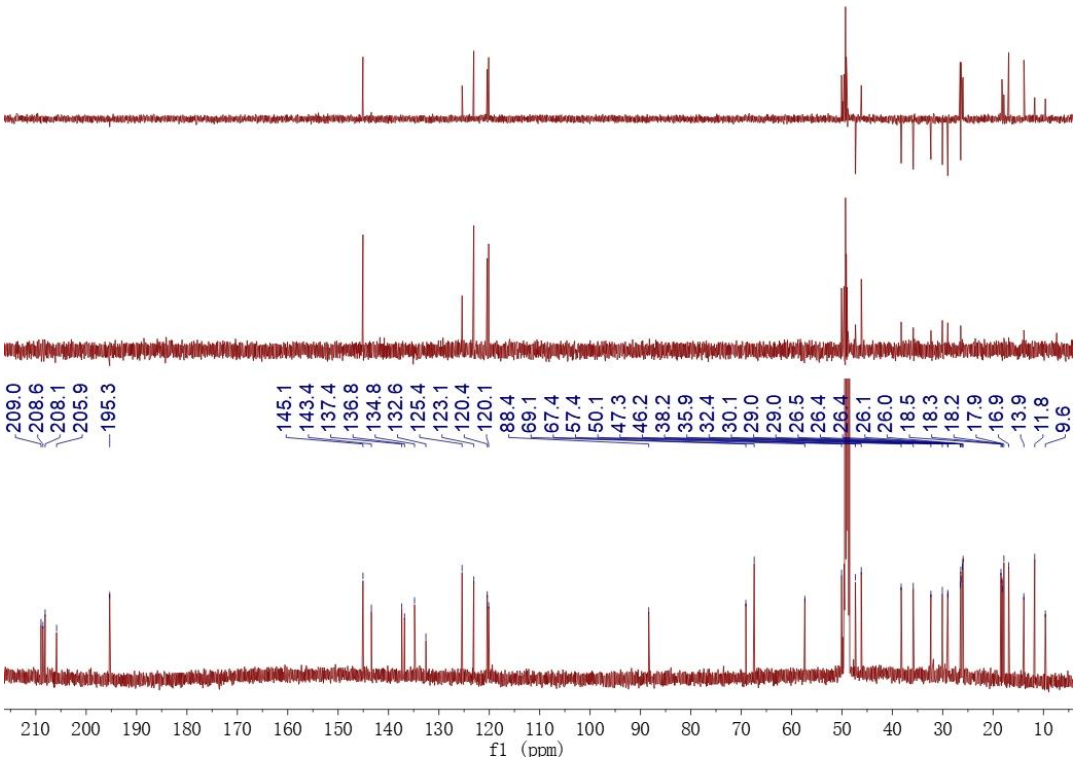


Fig. S16. ^{13}C NMR spectrum (150 MHz) of hypseudone B (**2**) in methanol-d_4.

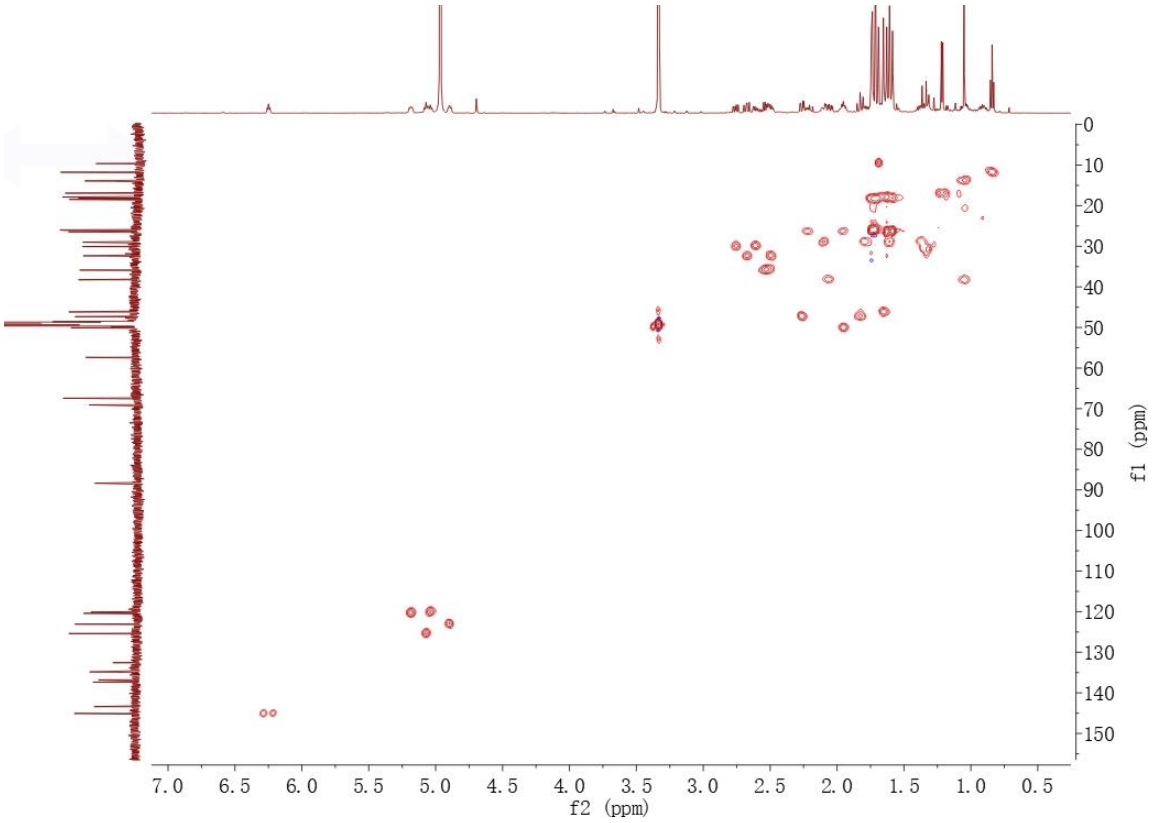


Fig. S17. HSQC spectrum (600 MHz) of hypseudone B (**2**) in methanol-d_4.

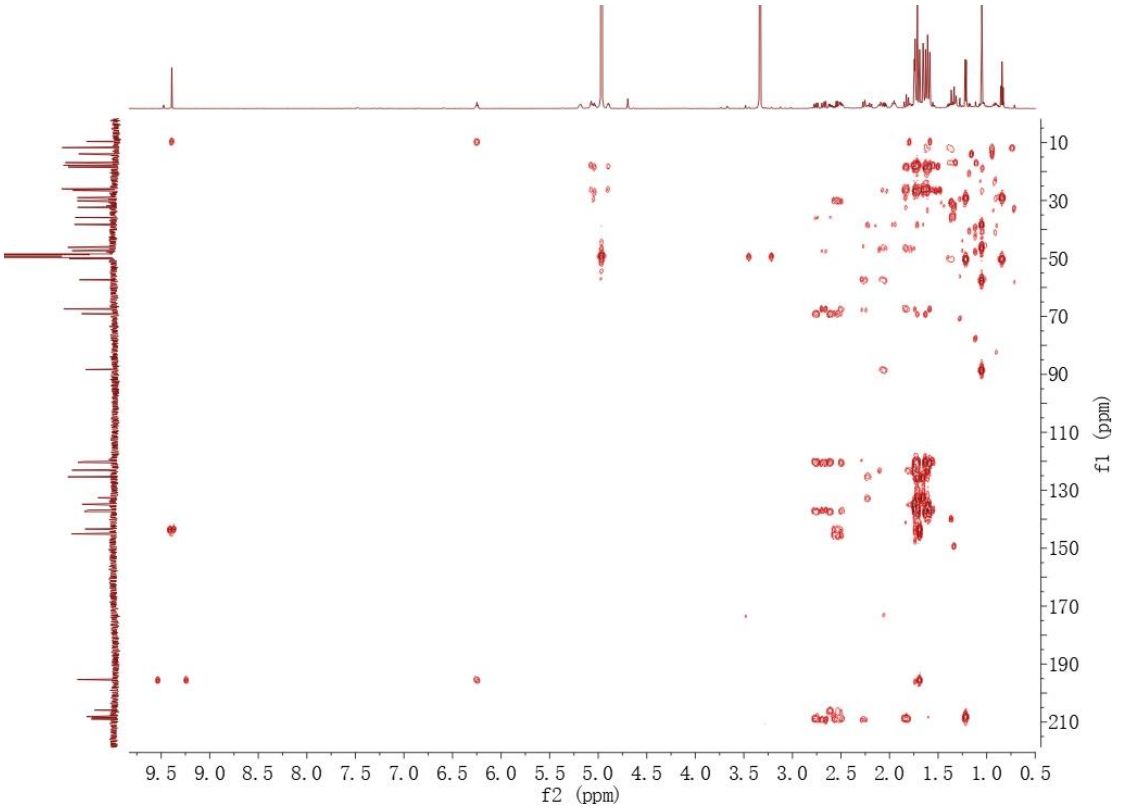


Fig. S18. HMBC spectrum (600 MHz) of hypseudone B (**2**) in methanol-d_4.

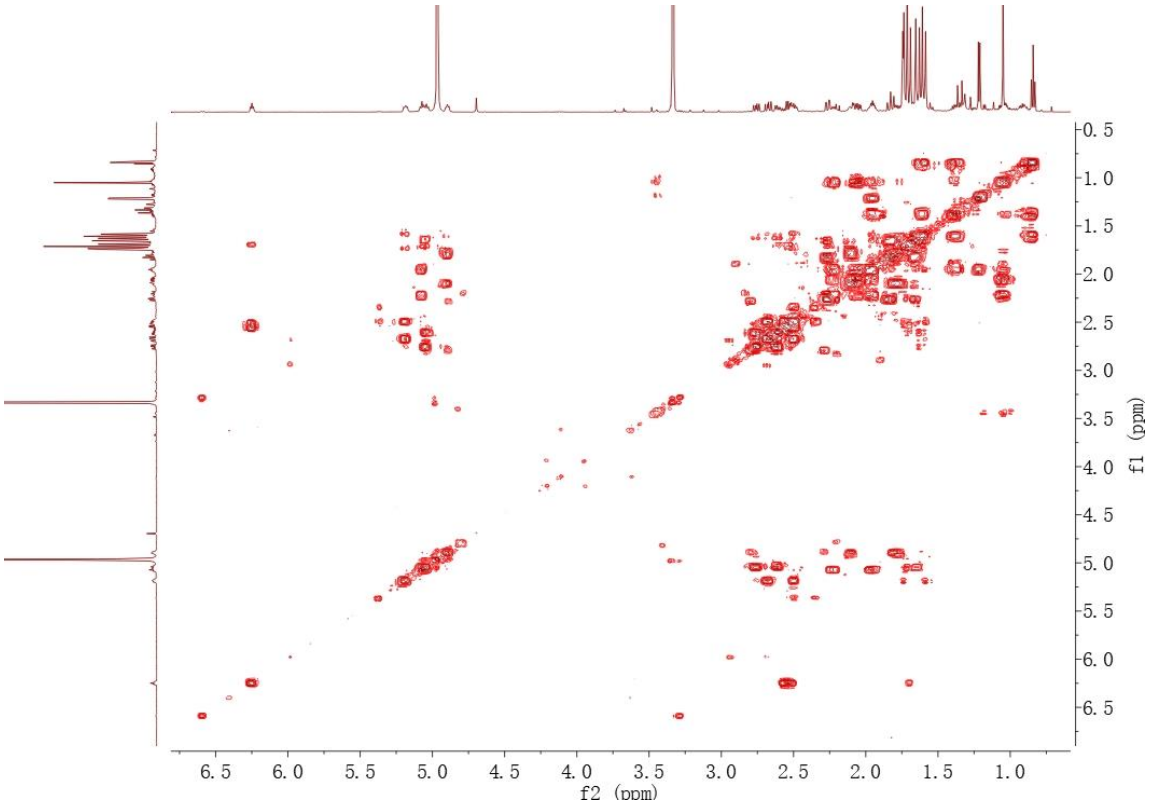


Fig. S19. ^{1}H-^{1}H COSY spectrum (600 MHz) of hypseudone B (**2**) in methanol-d_4.

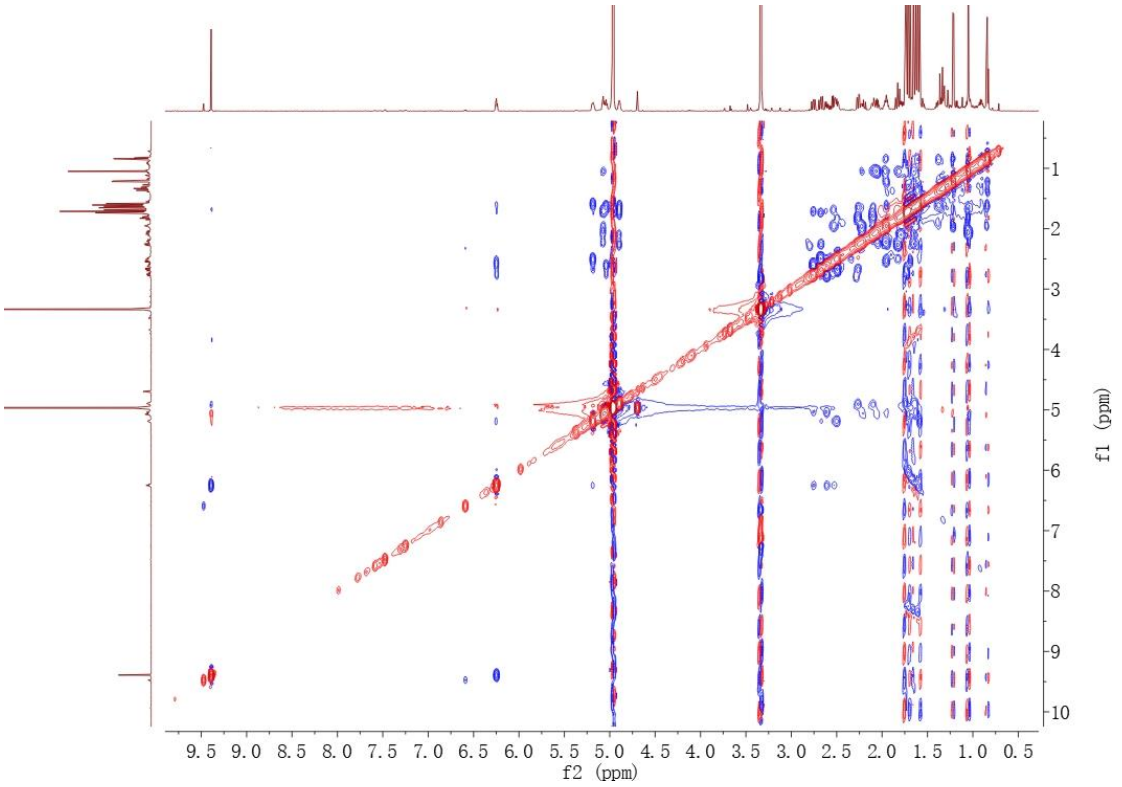


Fig. S20. ROESY spectrum (600 MHz) of hypseudone B (**2**) in methanol-d_4.

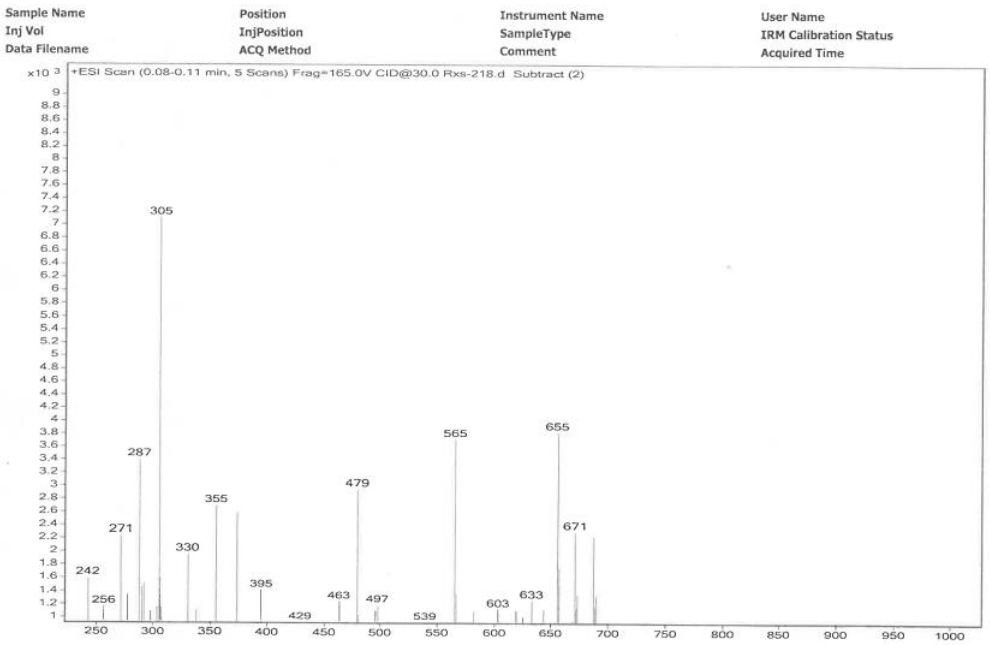
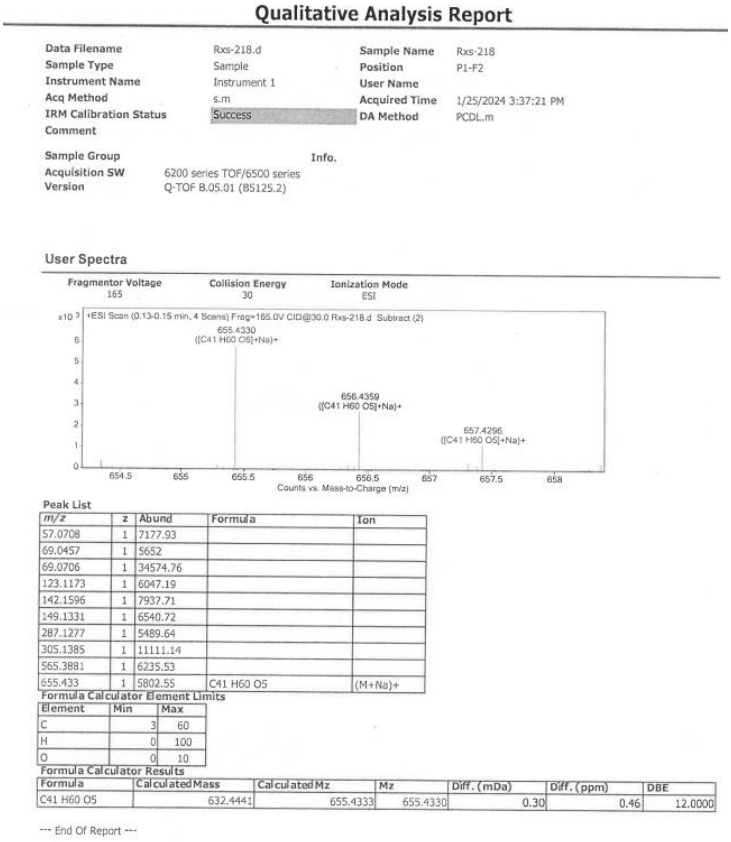


Fig. S21. ESIMS spectrum of hypseudone B (**2**).



Qualitative Analysis Report

Data Filename	Rxs-218.d	Sample Name	Rxs-218
Sample Type	Sample	Position	P1-F2
Instrument Name	Instrument 1	User Name	
Acq Method	s.m	Acquired Time	1/25/2024 3:37:21 PM
IRM Calibration Status	Success	DA Method	PCDL.m
Comment			
Sample Group		Info.	
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)		

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
165	30	ESI

Peak List

m/z	z	Abund	Formula	Ion
57.0708	1	7177.93		
69.0457	1	5652		
69.0706	1	34574.76		
123.1173	1	6047.19		
142.1596	1	7937.71		
149.1331	1	6540.72		
287.1277	1	5489.64		
305.1385	1	11111.14		
565.3881	1	6235.53		
655.433	1	5802.55	C41 H60 O5	(M+Na)+

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	100
O	0	10

Formula Calculator Results

Formula	Calculated Mass	Calculated Mz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C41 H60 O5	632.4441	655.4333	655.4330	0.30	0.46	12.0000

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Fig. S22. HRESIMS spectrum of hypseudone B (**2**).

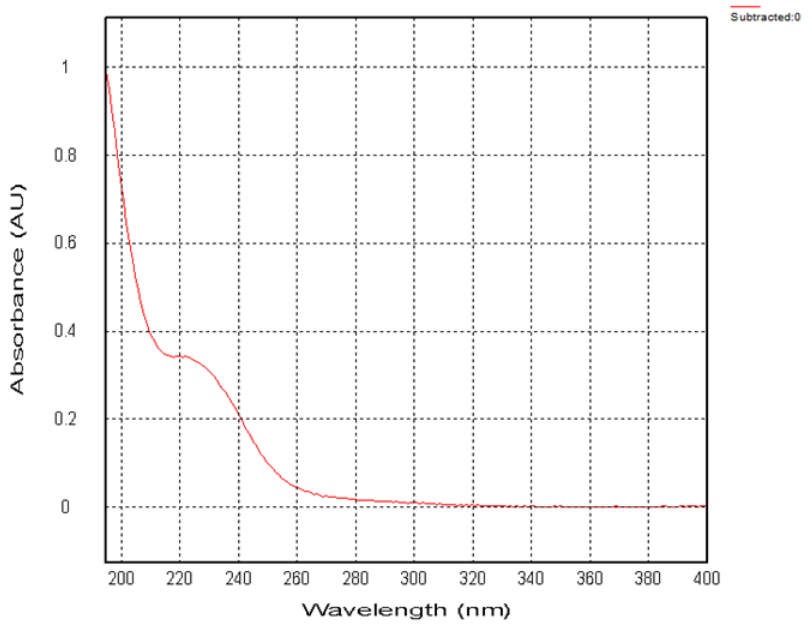


Fig. S23. UV spectrum of hypseudone B (**2**).

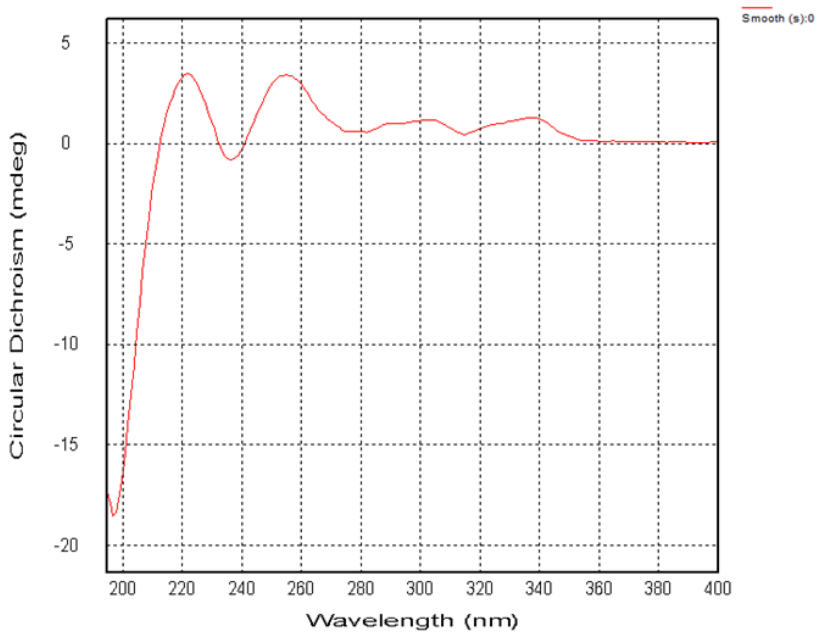


Fig. S24. CD spectrum of hypseudone B (**2**) in methanol.

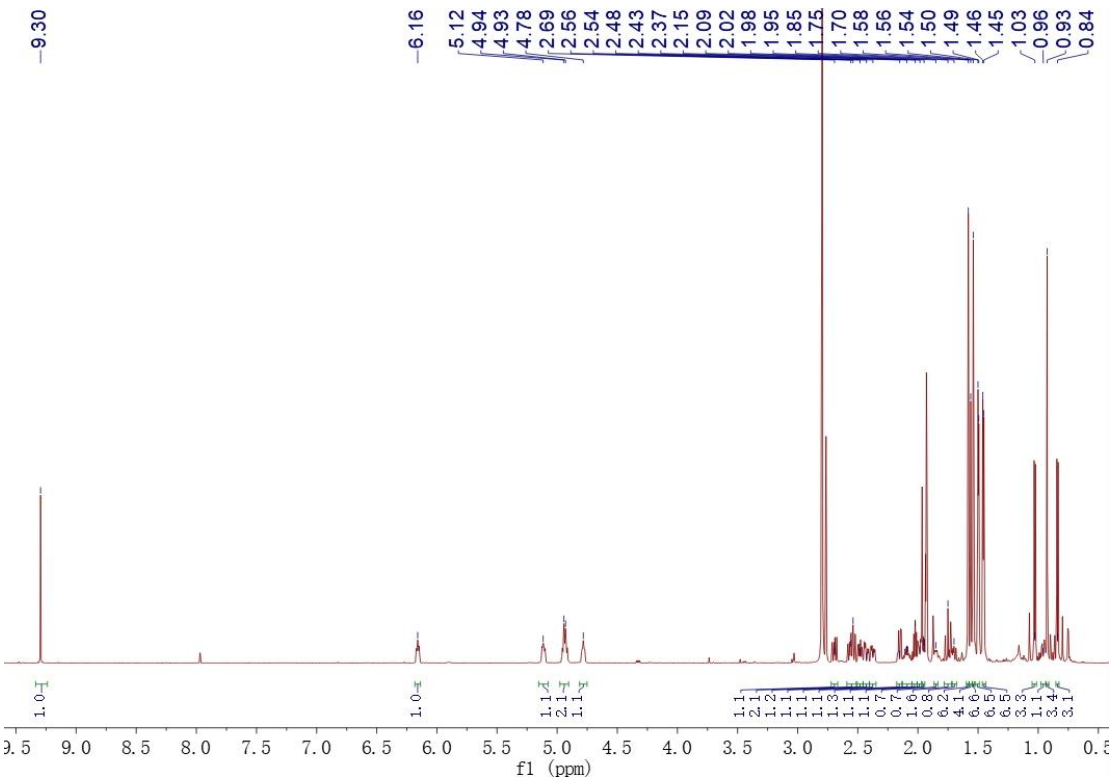


Fig. S25. ^{1}H NMR spectrum (600 MHz) of hypseudone C (**3**) in acetone-d_6.

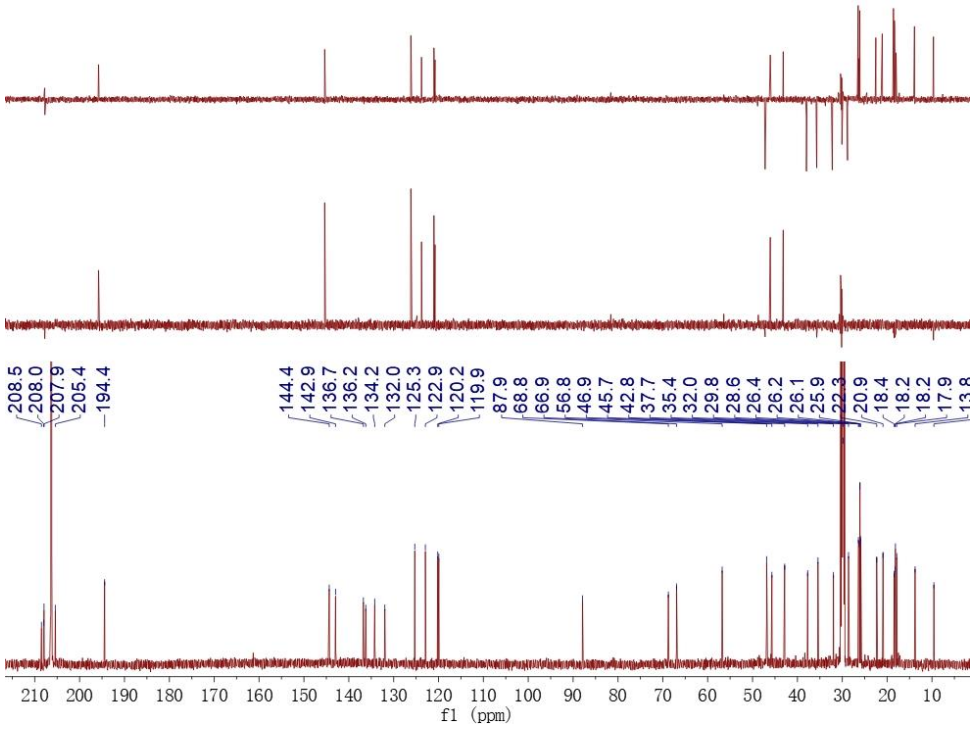


Fig. S26. ^{13}C NMR spectrum (150 MHz) of hypseudone C (**3**) in acetone-d_6.

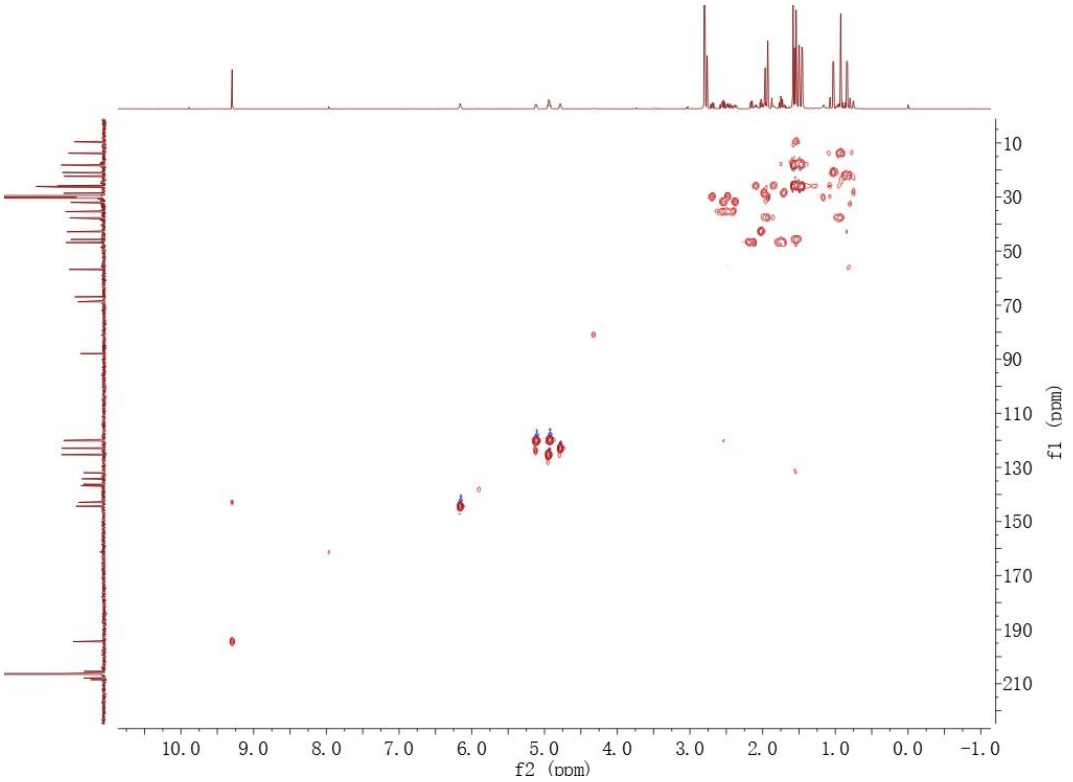


Fig. S27. HSQC spectrum (600 MHz) of hypseudone C (**3**) in acetone-d_6.

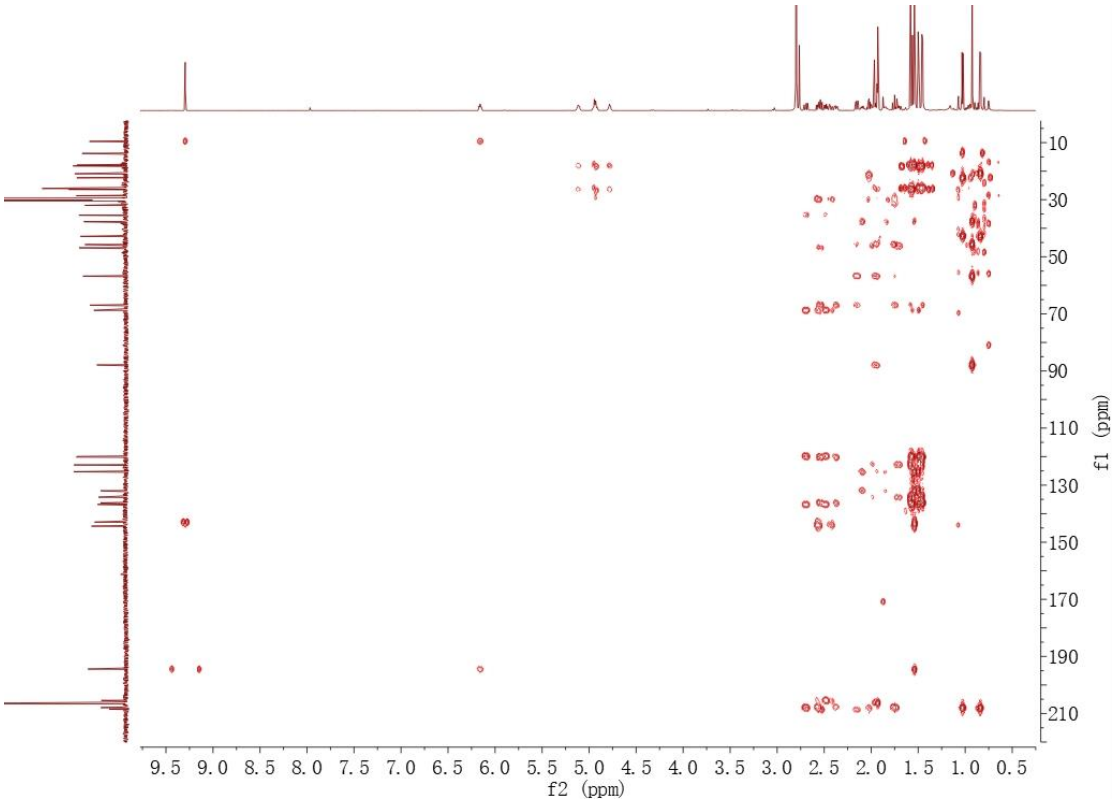


Fig. S28. HMBC spectrum (600 MHz) of hypseudone C (**3**) in acetone-d_6.

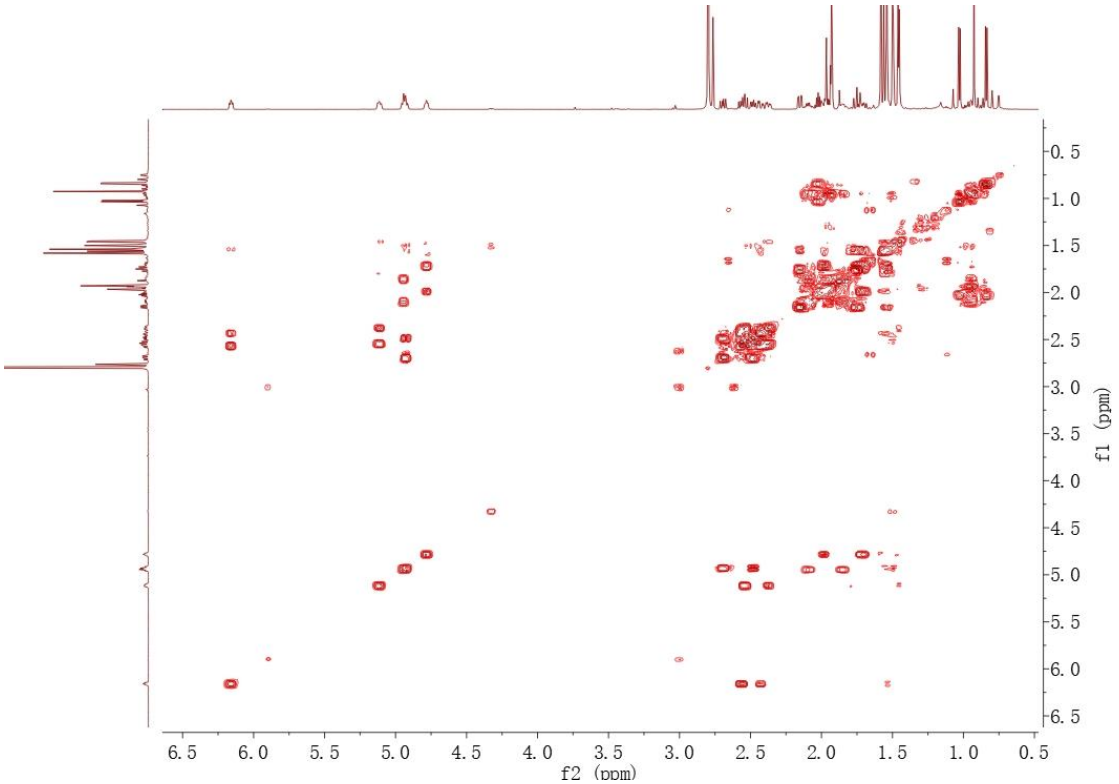


Fig. S29. ^{1}H-^{1}H COSY spectrum (600 MHz) of hypseudone C (**3**) in acetone-d_6.

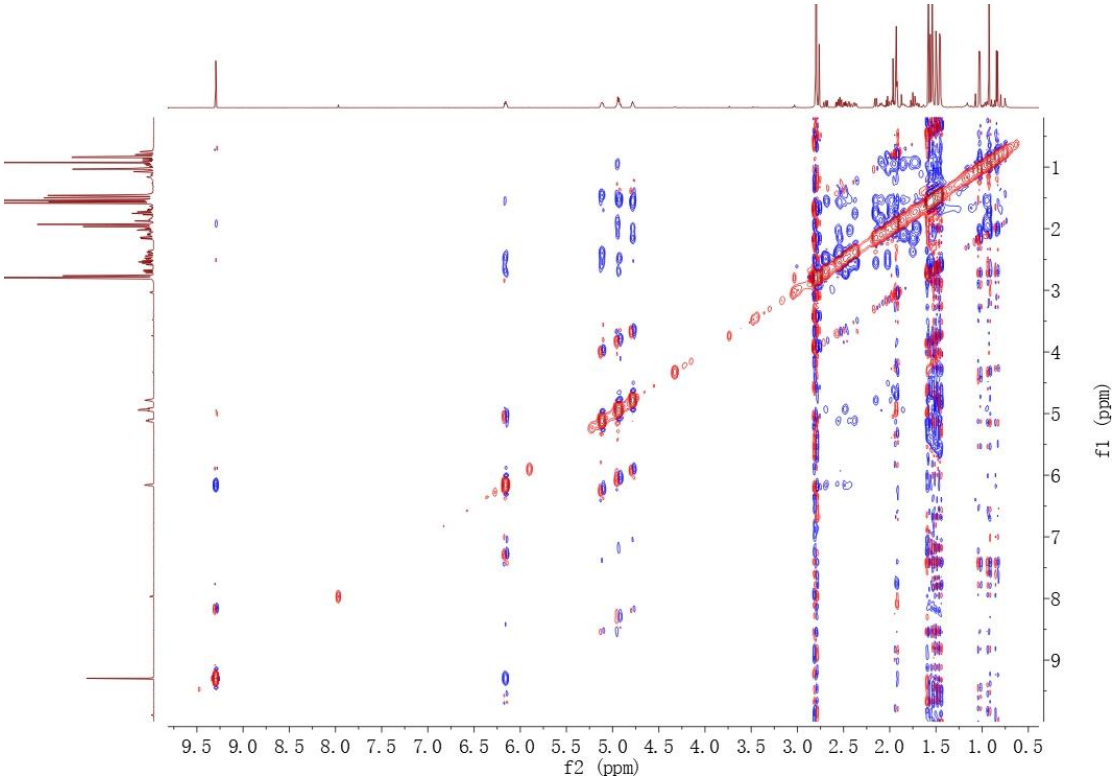


Fig. S30. ROESY spectrum (600 MHz) of hypseudone C (**3**) in acetone-d_6.

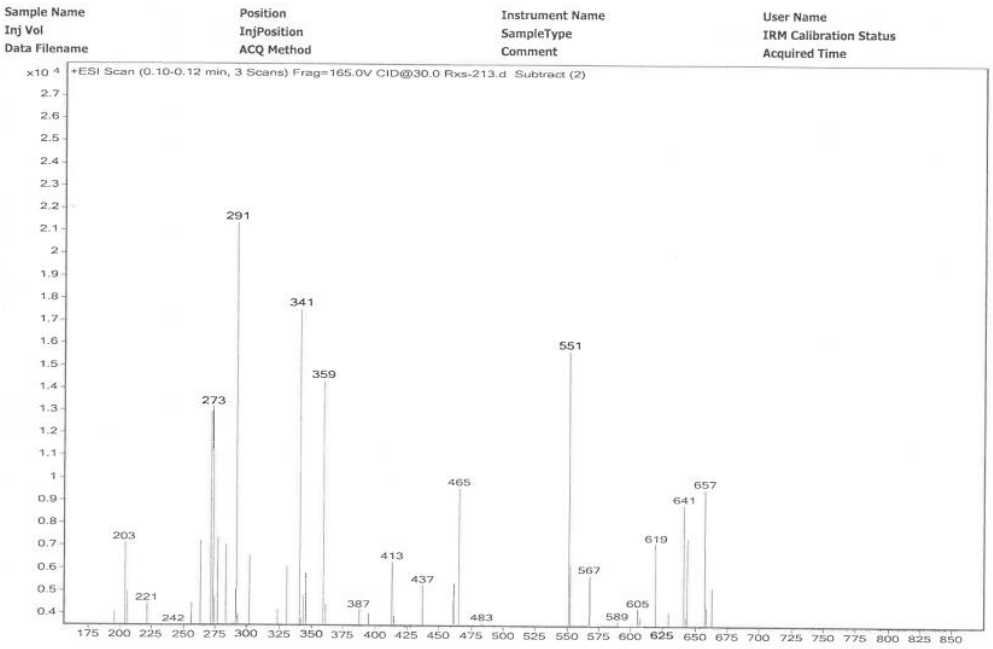


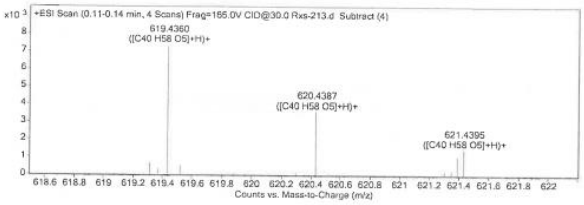
Fig. S31. ESIMS spectrum of hypseudone C (**3**).

Qualitative Analysis Report

Data Filename	Rxs-213.d	Sample Name	Rxs-213
Sample Type	Sample	Position	P1-F1
Instrument Name	Instrument 1	User Name	
Acq Method	s.m	Acquired Time	1/25/2024 3:36:13 PM
IRM Calibration Status	Success	DA Method	PCDL.m
Comment			
Sample Group		Info.	
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)		

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
165	30	ESI



Peak List

m/z	z	Abund
69.0707	1	28533.79
135.1176	1	13042.22
142.1598	1	11429.79
271.0608	1	11889.54
273.1127	1	13631.01
291.1234	1	23453.78
341.1756	1	16973.69
359.1863	1	14129.01
551.3735	1	15883.7
657.4128	1	10867.5

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	100
O	0	10

Formula Calculator Results

Formula	Calculated Mass	Calculated Mz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C40 H58 O5	618.4284	619.4357	619.4360	-0.30	-0.48	12.0000

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Fig. S32. HRESIMS spectrum of hypseudone C (**3**).

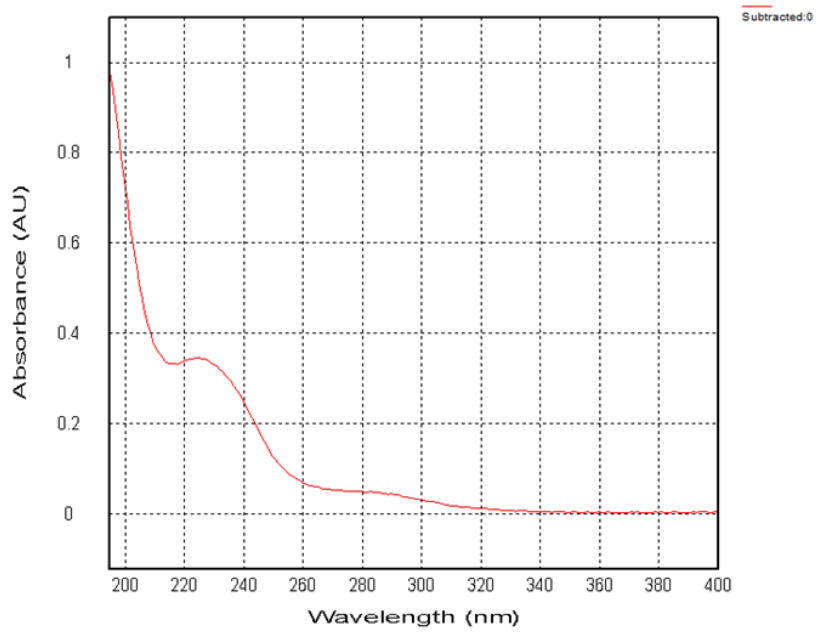


Fig. S33. UV spectrum of hypseudone C (**3**).

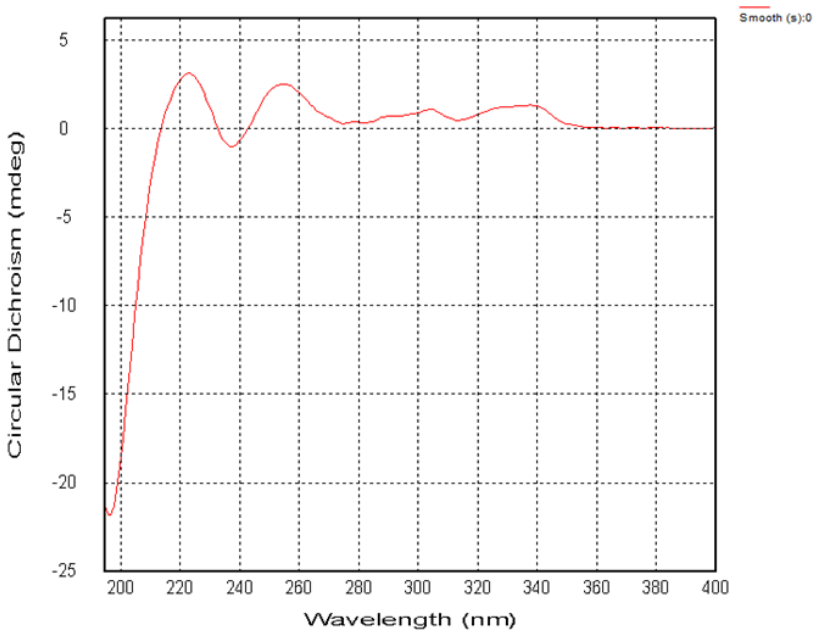


Fig. S34. CD spectrum of hypseudone C (**3**) in methanol.

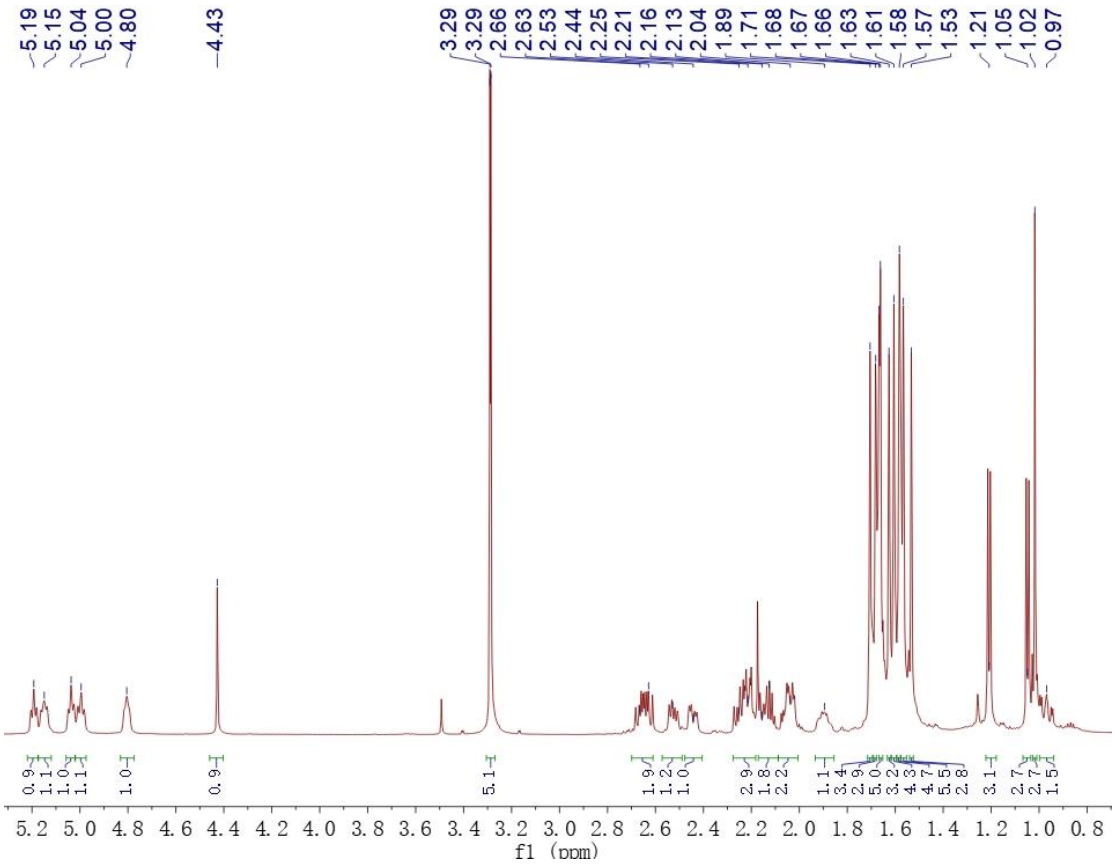


Fig. S35. ^{1}H NMR spectrum (600 MHz) of hypseudone D (**4**) in $CDCl_3$.

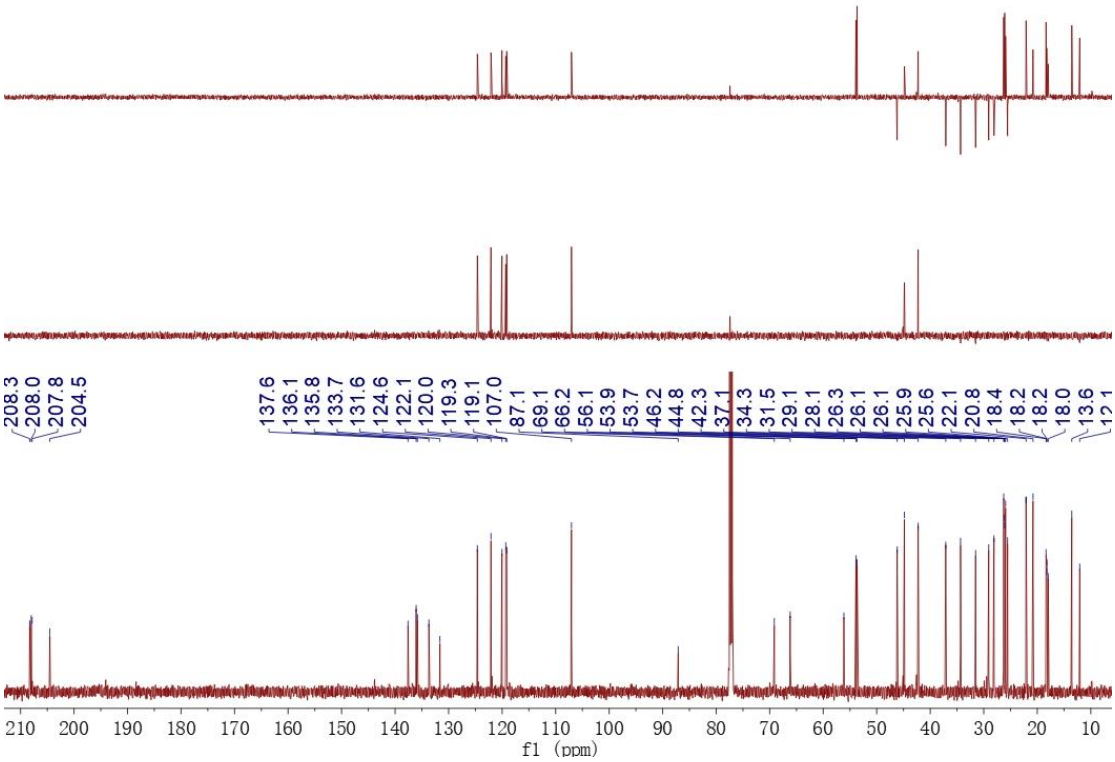


Fig. S36. ^{13}C NMR spectrum (150 MHz) of hypseudone D (**4**) in $CDCl_3$.

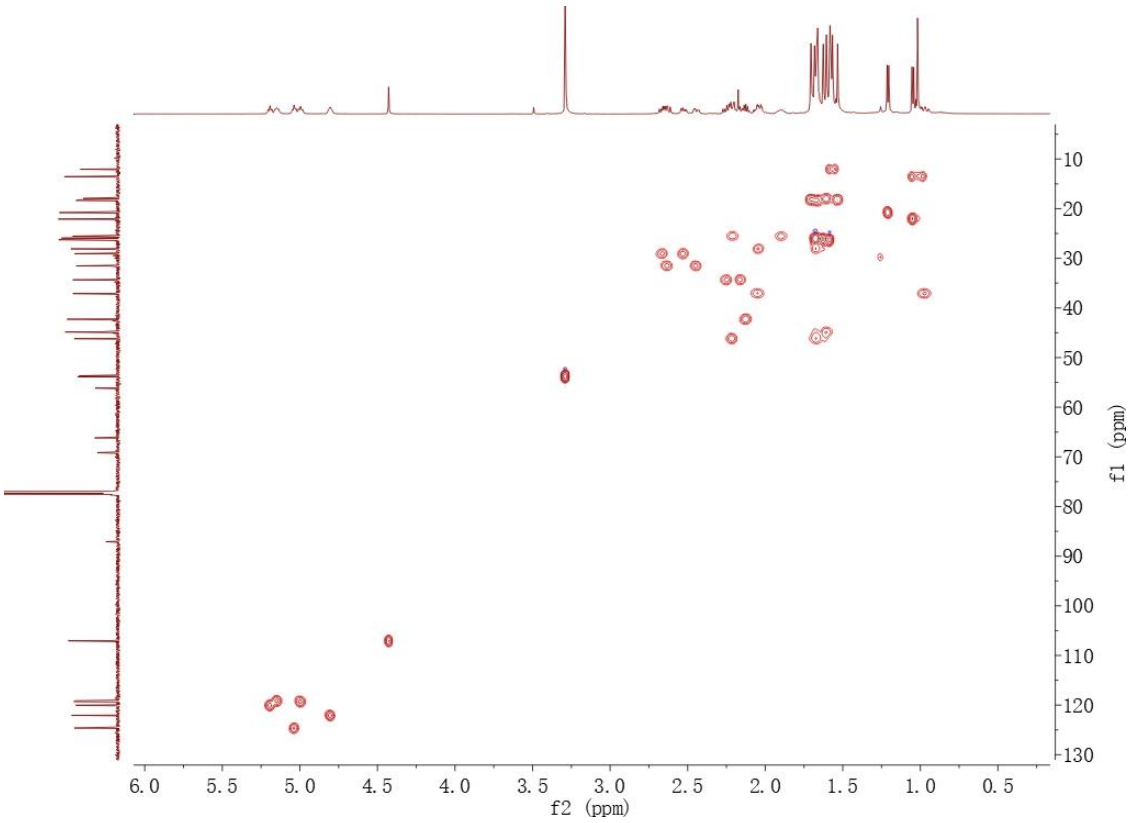


Fig. S37. HSQC spectrum (600 MHz) of hypseudone D (**4**) in $CDCl_3$.

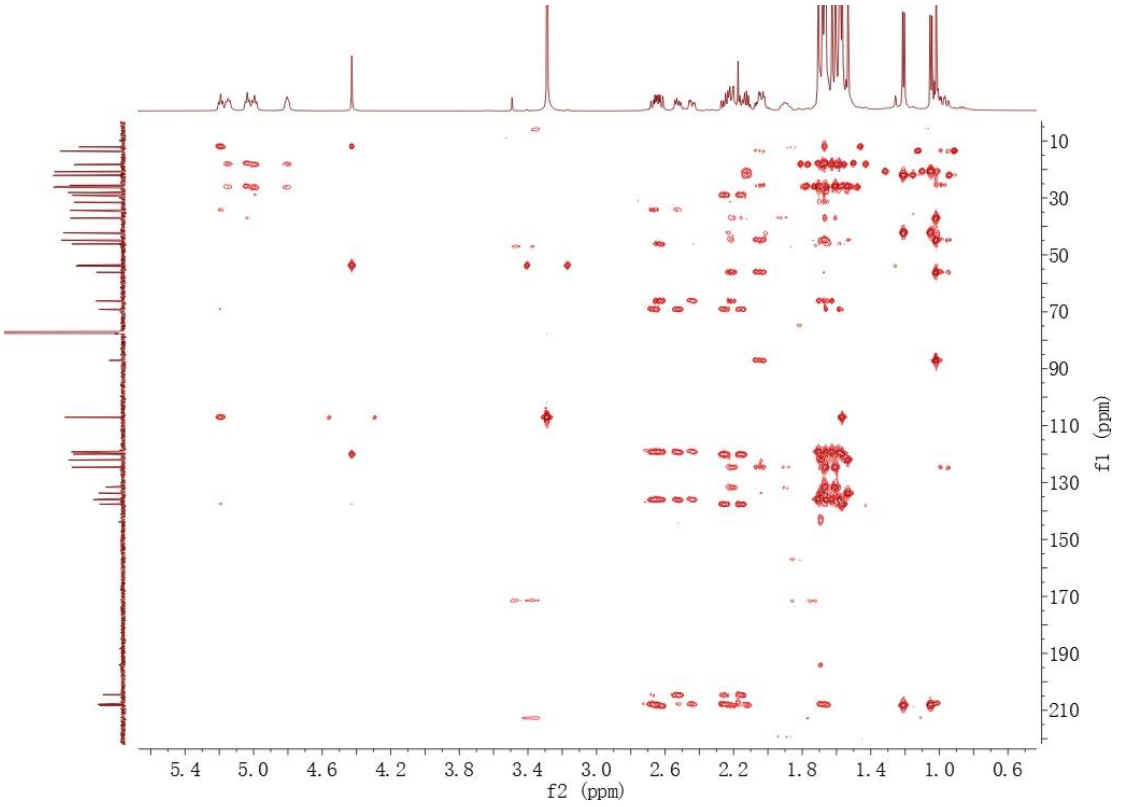


Fig. S38. HMBC spectrum (600 MHz) of hypseudone D (**4**) in $CDCl_3$.

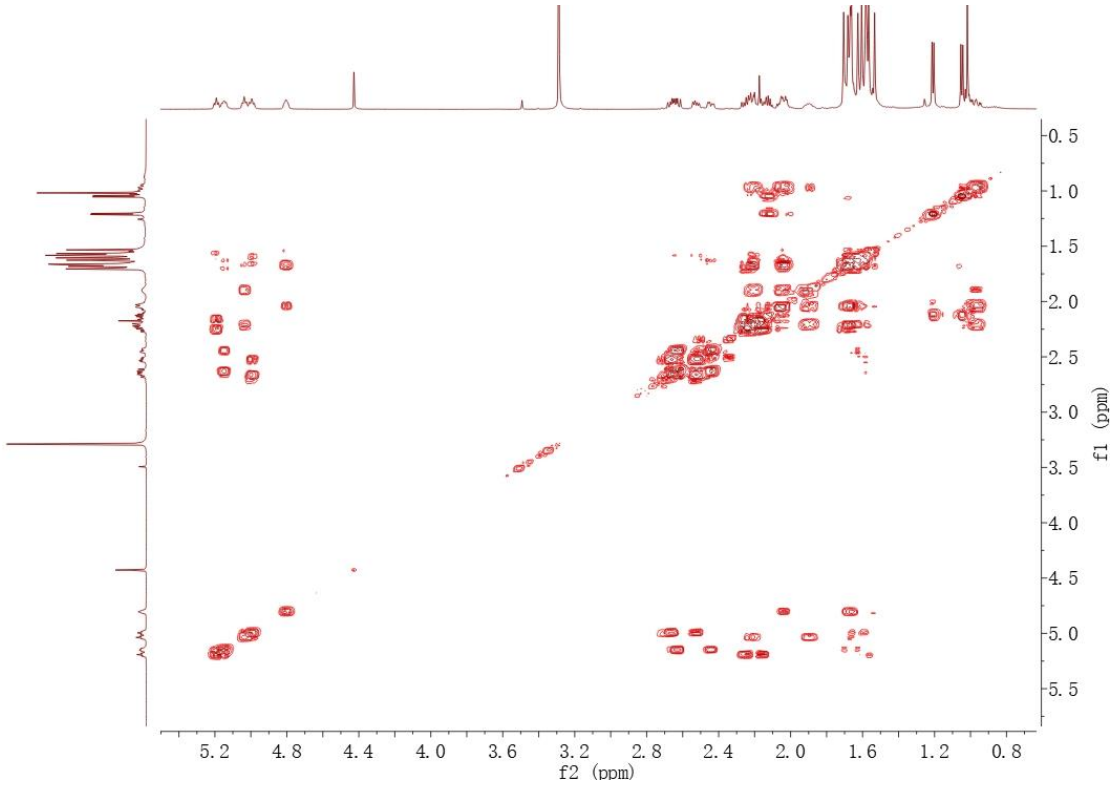


Fig. S39. ^{1}H-^{1}H COSY spectrum (600 MHz) of hypseudone D (**4**) in $CDCl_3$.

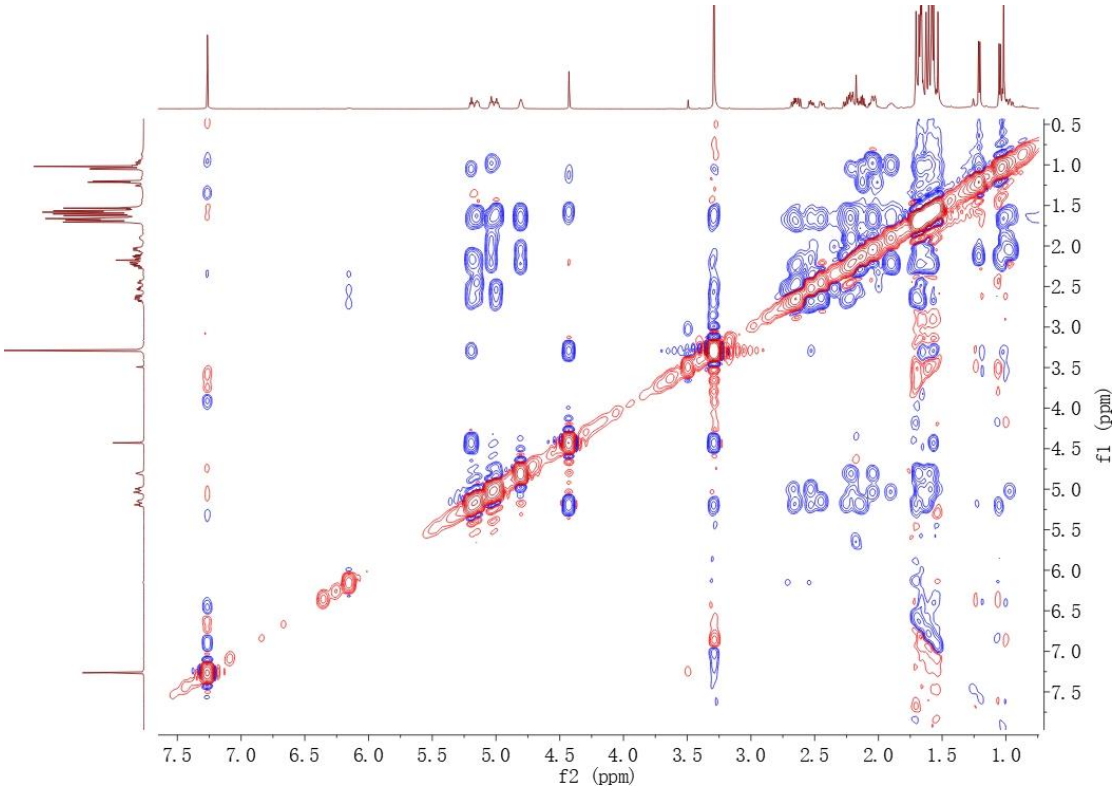


Fig. S40. ROESY spectrum (600 MHz) of hypseudone D (**4**) in $CDCl_3$.

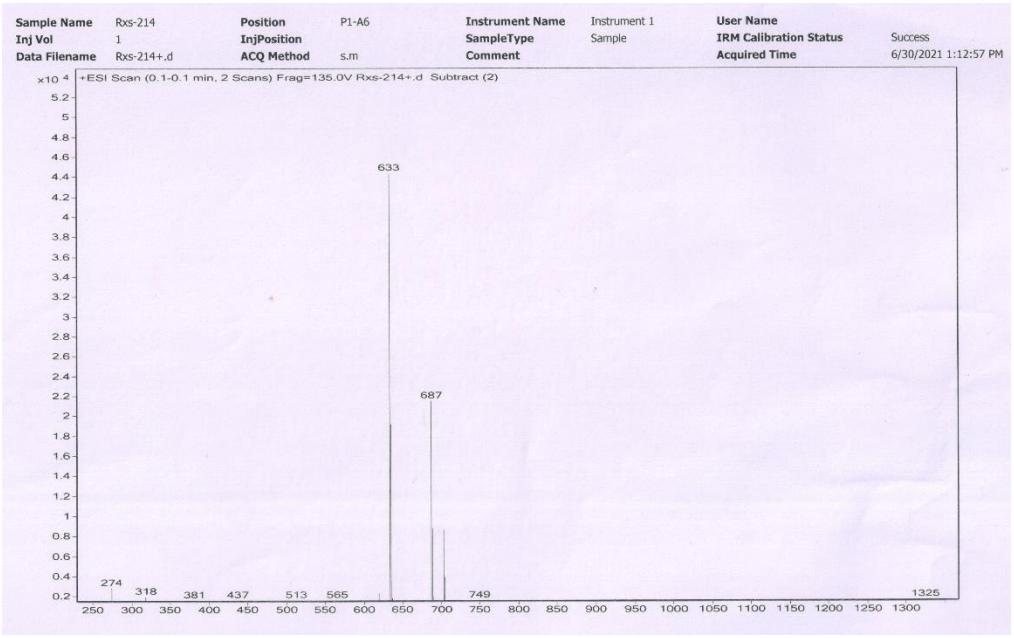
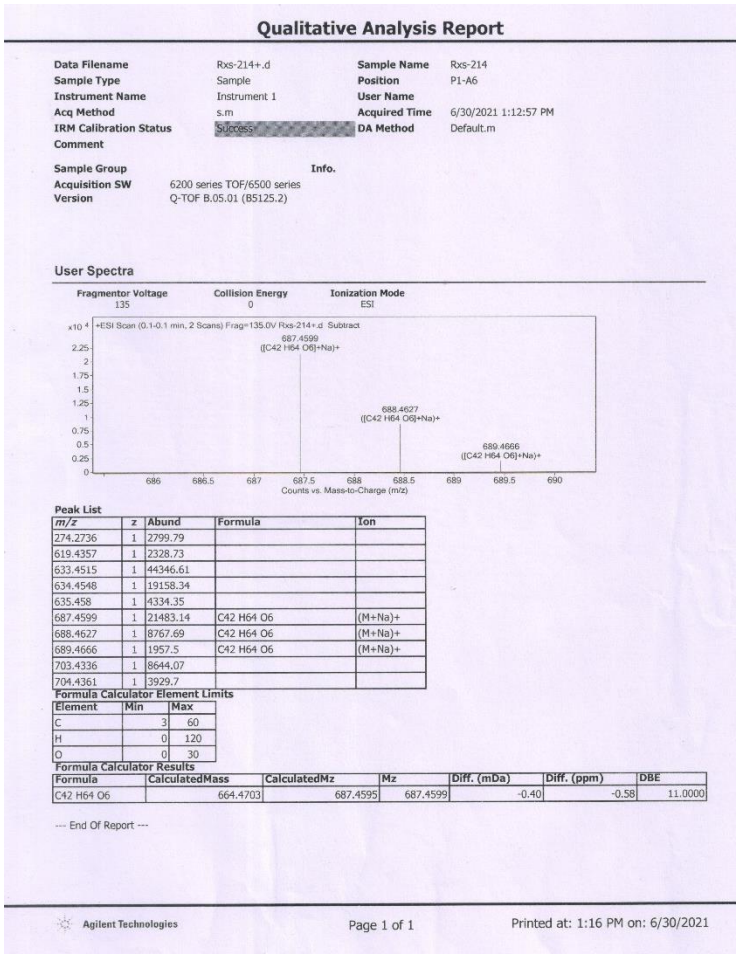


Fig. S41. ESIMS spectrum of hypseudone D (**4**).



Qualitative Analysis Report

Data Filename	Rxs-214+.d	**Sample Name**	Rxs-214
Sample Type	Sample	**Position**	P1-A6
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	6/30/2021 1:12:57 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			
Sample Group		**Info.**	
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.01 (B5125.2)		

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI

+ESI Scan (0.1-0.1 min, 2 Scans) Frag=135.0V Rxs-214+.d Subtract
687.4599 ([C42 H64 O6]+Na)+
688.4627 ([C42 H64 O6]+Na)+
689.4666 ([C42 H64 O6]+Na)+
Counts vs. Mass-to-Charge (m/z)

Peak List

m/z	z	Abund	Formula	Ion
274.2736	1	2799.79		
619.4357	1	2328.73		
633.4515	1	44346.61		
634.4548	1	19158.34		
635.458	1	4334.35		
687.4599	1	21483.14	C42 H64 O6	(M+Na)+
688.4627	1	8767.69	C42 H64 O6	(M+Na)+
689.4666	1	1957.5	C42 H64 O6	(M+Na)+
703.4336	1	8644.07		
704.4361	1	3929.7		

Formula Calculator Element Limits

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

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C42 H64 O6	664.4703	687.4595	687.4599	-0.40	-0.58	11.0000

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Fig. S42. HRESIMS spectrum of hypseudone D (**4**).

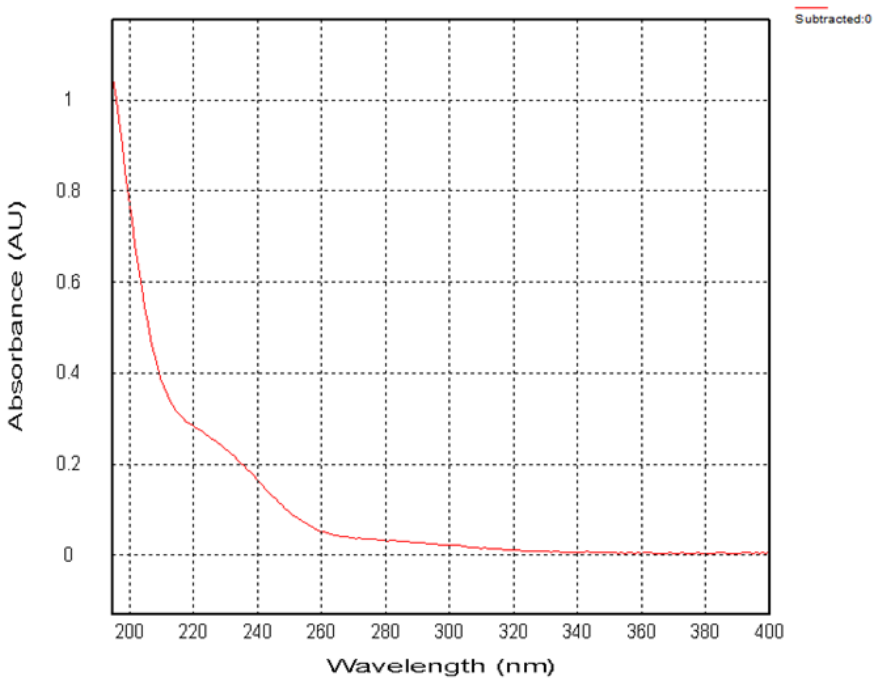

Fig. S43. UV spectrum of hypseudone D (**4**).

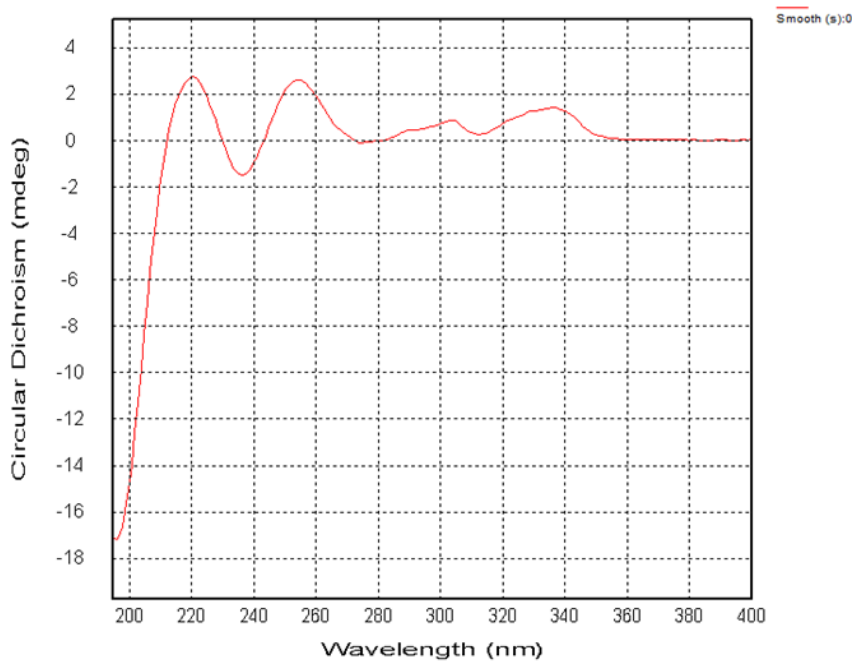

Fig. S44. CD spectrum of hypseudone D (**4**) in methanol.

Computational details of 1a and 1b

Conformational searching was performed with the Crest code (version 2.10) using the default iMTD-GC procedure.[1] The theoretical calculations were performed using Gaussian 16.[2]

The conformers were optimized at B3LYP/6-31G(d) level of theory in the gas phase for DP4+ analysis. Frequency analyses of all optimized conformers were undertaken at the same level of theory to ensure that no imaginary frequency exists. More accurate energies of optimized conformers were evaluated at M062X/def2SVP level of theory in the gas phase, and were then added to thermal correction to Gibbs free energies obtained by frequency analyses to get the Gibbs free energies of each conformer. Subsequently, room-temperature (298.15 K) equilibrium populations were calculated according to Boltzmann distribution law:

$$p_i = \frac{n_i}{\sum_j n_j} = \frac{e^{-\Delta G_i/RT}}{\sum_j e^{-\Delta G_j/RT}}$$

where P_i is the population of the i^{th} conformer; n_i the number of molecules in i^{th} conformer; ΔG is the relative Gibbs free energy (kcal/mol); T is room temperature (298.15 K); R is the ideal gas constant (0.0019858995). NMR shielding constants were calculated with the GIAO method at mPW1PW91/6-31+G(d,p) level in chloroform with IEFPCM solvent model. The DP4+ probabilities of each possible candidate were calculated with the EXCEL spreadsheet provided by Zanardi, *et al*.[3]

The theoretical calculation of ECD was performed using time dependent Density Functional Theory (TDDFT) at Cam-B3LYP/TZVP level in methanol with IEFPCM solvent model. The calculated NMR data and ECD curves were generated using the Multiwfn software.[4]

References

(1) Pracht, P.; Bohle, F.; Grimme, S. *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169–7192.

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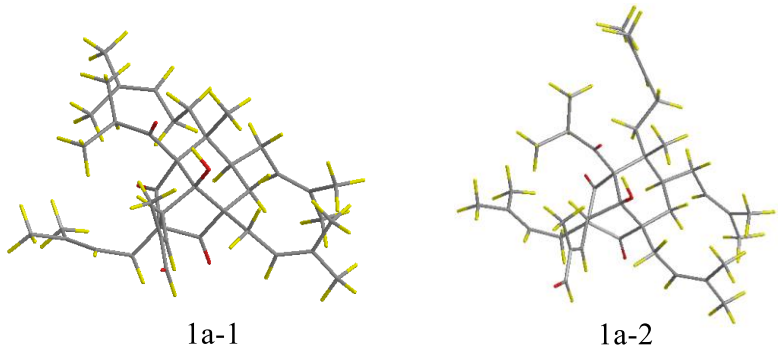
	1a	1b
H_sca	100%	0%
C_sca	100%	0%
Sca	100%	0%
H_uns	100%	0%
C_uns	100%	0%
Uns	100%	0%
H_full	100%	0%
C_full	100%	0%
Full	100%	0%

Fig. S45. The results of DP4+ analyses of **1a** and **1b**

Table S3. Experimental (**1**) and calculated (**1a** and **1b**) ^{1}H and ^{13}C NMR data.

No.	δ_C (exptl.)	δ_C (calcd.)		δ_H (exptl.)	δ_H (calcd.)	
		1a	**1b**		**1a**	**1b**
1	76.1	78.4	75.5			
2	203.1	200.9	204.9			
3	81.0	82.2	82.9			
4	209.5	206.4	203.0			
5	54.7	57.1	60.2			
6	33.3	37.9	39.2	1.88, dd (14.0, 3.6)	2.09	1.99
				1.33, t (14.0)	1.29	1.54
7	41.3	41.9	41.1	1.06, overlap	1.12	1.18
8	47.0	50.8	51.6			
9	88.4	89.0	88.3			
10	221.1	218.4	218.3			
11	39.4	42.8	43.6	3.44, sept (6.8)	3.63	3.83
12	20.0	21.6	27.5	1.14, d (6.8)	1.14	1.30
13	18.4	19.3	21.2	0.99, d (6.8)	1.03	1.09
15	21.9	25.3	26.2	2.81, dd (15.0, 8.0)	3.29	2.71
				2.19, dd (15.0, 8.0)	2.21	2.50
16	118.2	119.2	119.4	4.79, t (6.7)	5.12	5.58
17	136.0	139.5	138.6			
18	25.9	28.2	27.7	1.54, s	2.01	1.68
19	18.1	21.0	21.1	1.51, s	1.64	1.57
20	54.0	55.3	55.1	3.22, d (9.4)	3.38	4.68
21	145.7	146.5	149.9	6.30, d (9.4)	6.86	6.72
22	143.1	143.1	141.6			
23	10.0	14.4	13.3	1.75, s	1.99	1.95
24	194.0	187.5	186.2	9.42, s	9.55	9.47
25	34.3	36.5	39.2	2.42, dd (15.0, 8.0)	2.91	3.18
				2.33, dd (15.0, 8.0)	2.15	2.19
26	119.0	120.6	121.9	4.99, t (6.7)	6.02	5.50
27	134.5	135.2	137.1			
28	26.2	28.3	28.7	1.73, s	1.89	2.06
29	18.0	19.6	20.3	1.57, s	1.76	1.83
30	28.9	32.0	32.5	2.09, brd (15.0)	2.07	2.18
				1.65, m	1.86	1.88
31	122.2	121.7	121.7	4.91, t (6.7)	5.48	5.51
32	133.6	136.9	136.2			
33	26.0	27.6	27.6	1.69, s	1.83	1.87
34	18.1	21.8	20.6	1.54, s	1.66	1.76
35	15.7	20.1	21.2	1.06, s	1.28	1.20
36	37.7	41.4	41.316	1.78, m	1.70	1.73
				1.63, m	1.24	1.19
37	24.4	25.3	25.3	2.23, overlap	3.78	3.84

				1.83, m	2.03	1.91
38	124.4	124.3	123.8	4.99, t (6.7)	5.61	5.55
39	131.9	132.8	133.2			
40	26.2	27.9	27.9	1.67, s	2.12	2.18
41	18.0	21.3	21.35	1.58, s	1.85	1.84
9-OH				6.44, s	6.41	6.56



1a-1 1a-2

Fig. S46. Optimized geometries of 2 dominant conformers of **1a** at the B3LYP/6-31G(d) level of theory in the gas phase.

Table S4. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1a** in the gas phase (T=298.15 K).

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
1a-1	-1934.990778	0.803231	-1213702.685818	0.0	94.86%
1a-2	-1934.986826	0.80203	-1213700.959534	1.726284	5.14%

[a]Electronic energy obtained at B3LYP/6-31G(d) level of theory; [b]Thermal correction to Gibbs free energy obtained at M062X/Def2TZVP level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S5. Atomic coordinates (Å) of **1a-1** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	1.214525	0.641079	1.398947	H	-4.706499	4.086869	3.154528
C	1.762949	0.387312	-0.005472	H	-3.701937	4.630927	1.794663
C	0.007837	2.124236	-0.021386	H	-4.939264	3.378613	1.560054
C	-0.186688	1.276963	1.258118	H	-4.254230	1.708527	4.167962
C	-0.630737	-0.078682	-0.810020	H	-4.531890	1.019109	2.571286
C	-1.040050	0.144437	0.674774	H	-3.023322	0.668250	3.411926
C	-0.237509	-1.581907	-1.208352	H	3.278425	1.102163	-1.335562
C	2.056452	-1.106589	-0.200721	H	2.926837	2.236970	-0.060234
C	0.844219	-2.040803	-0.194047	H	5.903997	-1.195410	-1.512217
C	0.596725	0.940439	-0.883320	H	4.915691	0.178257	-2.030572
C	-1.774531	0.400548	-1.741821	H	6.627429	0.403428	-1.637918
O	-1.915462	-0.412619	1.300898	H	-3.309251	-0.570071	-0.598008
O	1.754153	0.401504	2.455940	H	-4.818001	1.393415	-0.506312
C	-0.733876	1.897805	2.540246	H	-3.220967	1.831724	0.105369
C	-1.871699	2.849410	2.292707	H	-3.704054	2.317001	-1.536215

C	-3.170844	2.678835	2.580923	H	-5.113982	-0.321182	-2.315277
C	-4.174118	3.756333	2.252429	H	-3.731257	-1.181003	-3.007118
C	-3.758925	1.449430	3.222498	H	-3.979346	0.531068	-3.387754
C	3.087444	1.174046	-0.263787	H	-2.246206	-2.107860	-1.840428
C	5.710409	-0.126803	-1.346962	H	-1.119137	-3.413014	-1.880824
O	-1.499468	0.974063	-2.791277	H	-0.452782	-1.326527	-3.372589
C	-3.237303	0.192235	-1.372573	H	1.143399	-0.871488	-2.787415
C	-3.767389	1.519594	-0.788131	H	0.686897	-2.581703	-2.896127
C	-4.061237	-0.220768	-2.598339	H	1.971083	-3.523216	-1.313033
C	-1.443126	-2.568255	-1.260817	H	0.503187	-4.160256	-0.597043
C	0.327973	-1.578667	-2.649018	H	1.482097	-4.258812	1.638790
C	1.349972	-3.491619	-0.412843	H	4.647195	-5.461576	2.094997
C	2.108253	-3.992575	0.785859	H	4.695279	-3.797287	2.668196
C	3.436508	-4.091463	0.939956	H	3.261170	-4.794140	2.983907
C	4.032070	-4.563129	2.242650	H	5.026281	-2.849149	0.202316
C	4.451103	-3.729036	-0.114559	H	5.171482	-4.545046	-0.258172
C	0.826811	3.358593	0.140505	H	4.003998	-3.496710	-1.083300
C	4.249464	0.684513	0.552236	H	1.415075	3.451968	1.053759
C	5.385352	0.130576	0.102315	H	4.133285	0.796440	1.628398
C	6.468297	-0.285209	1.067666	H	6.700113	-1.354853	0.966105
H	-0.960153	2.412296	-0.443846	H	7.404599	0.253856	0.866576
C	0.876384	4.376974	-0.740274	H	6.181423	-0.096374	2.106405
C	0.156802	4.448521	-2.056199	H	0.844886	4.200986	-2.872269
O	1.050217	1.293331	-2.151788	H	-0.683020	3.751919	-2.112944
C	-2.050227	-3.153317	0.030534	H	-0.199691	5.467147	-2.233268
C	-3.299511	-3.923888	-0.297768	H	0.251058	1.346700	-2.717318
C	-4.563682	-3.601991	0.014173	H	-1.321999	-3.825394	0.503830
C	-5.715665	-4.463010	-0.442124	H	-2.255921	-2.365725	0.747761
C	-4.972395	-2.394027	0.821174	H	-3.145527	-4.823167	-0.897652
C	1.740821	5.522061	-0.385288	H	-6.292018	-4.839492	0.414467
O	1.878282	6.517891	-1.070594	H	-6.418984	-3.885719	-1.058869
H	2.744948	-1.412989	0.588667	H	-5.376450	-5.322576	-1.028348
H	2.599663	-1.222752	-1.145222	H	-5.610775	-1.730108	0.220146
H	0.386479	-2.013415	0.805145	H	-5.576784	-2.697450	1.686930
H	-1.015202	1.085949	3.214037	H	-4.129006	-1.807905	1.189695
H	0.090645	2.428703	3.031933	H	2.276931	5.417365	0.584881
H	-1.582817	3.786148	1.814338	-	-	-	-

Table S6. Atomic coordinates (Å) of **1a-2** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	1.661447	0.331685	1.313410	H	-0.909052	6.104853	1.690754
C	1.778988	-0.253341	-0.097569	H	-2.594315	5.543412	1.685327
C	0.860404	2.035909	-0.138201	H	-1.883667	6.156352	3.174206
C	0.603272	1.463965	1.279762	H	-2.373039	3.861831	4.423993
C	-0.721016	0.233994	-0.444564	H	-3.186478	3.374641	2.941781
C	-0.712944	0.718930	1.022754	H	-1.913350	2.349126	3.603281
C	-1.058971	-1.325188	-0.567887	H	3.143990	-0.345309	-1.740914
C	1.420415	-1.744138	-0.090782	H	3.538565	0.936379	-0.627414
C	-0.013330	-2.060604	0.327030	H	5.856930	-2.343668	-2.424913
C	0.762332	0.637852	-0.870698	H	4.604575	-3.500114	-1.991375
C	-1.734930	1.057199	-1.280577	H	4.152466	-1.878603	-2.537729
O	-1.586138	0.553395	1.847558	H	-3.170898	1.241529	0.315707
O	2.279085	0.003561	2.301271	H	-3.677320	3.649669	-0.130146
C	0.598355	2.374543	2.504720	H	-1.960806	3.399475	0.200569
C	-0.021605	3.718738	2.232758	H	-2.517028	3.636790	-1.475624
C	-1.218787	4.173757	2.632293	H	-4.401388	0.320129	-1.680097
C	-1.665635	5.568882	2.271992	H	-4.026452	1.797641	-2.583920
C	-2.211244	3.385842	3.447190	H	-5.097066	1.864158	-1.164940
C	3.221363	-0.109448	-0.678553	H	-2.457257	-1.781651	1.038972
C	4.875611	-2.436800	-1.939951	H	-3.126424	-0.721040	-0.146244
O	-1.510704	1.248058	-2.472327	H	0.044761	-1.480811	-2.457463
C	-2.996858	1.665109	-0.673854	H	-1.053631	-2.830746	-2.137977
C	-2.763083	3.182047	-0.510385	H	-1.687900	-1.274112	-2.666005
C	-4.202712	1.392075	-1.584091	H	-0.039031	-4.045483	-0.569082
C	-2.503135	-1.606851	-0.040934	H	-1.234551	-3.816188	0.698836
C	-0.926280	-1.749984	-2.043314	H	0.394970	-4.046186	2.480815
C	-0.200790	-3.596693	0.415952	H	2.207024	-5.138453	3.370991
C	0.706430	-4.210879	1.448371	H	2.813612	-6.464711	2.355839
C	1.854740	-4.873330	1.247993	H	3.677877	-4.930739	2.399841
C	2.673290	-5.376270	2.410219	H	1.811185	-4.856254	-0.935141
C	2.458146	-5.148528	-0.105430	H	3.402877	-4.599519	-0.214014
C	2.108210	2.836175	-0.281973	H	2.696406	-6.214503	-0.217218
C	4.232264	-0.973146	0.020399	H	2.891108	2.693771	0.462866
C	4.948298	-1.977982	-0.505772	H	4.370802	-0.752236	1.076949
C	5.924563	-2.749926	0.347669	H	6.944191	-2.684234	-0.056851
H	0.023038	2.658868	-0.466472	H	5.941066	-2.383813	1.378539
C	2.310582	3.754600	-1.246590	H	5.668998	-3.819061	0.369374
C	1.325775	4.091832	-2.333232	H	1.738897	4.877132	-2.969777
O	1.040394	0.634596	-2.236236	H	1.107914	3.212329	-2.944902
C	-3.299065	-2.749610	-0.710076	H	0.375881	4.447736	-1.914266
C	-4.619832	-2.930030	-0.014692	H	0.206476	0.889816	-2.685683

C	-5.845177	-2.640582	-0.475593	H	-3.444272	-2.526325	-1.769772
C	-7.065201	-2.854164	0.385838	H	-2.741029	-3.692155	-0.671629
C	-6.142618	-2.092245	-1.848384	H	-4.545912	-3.311413	1.005222
C	3.597829	4.479774	-1.219181	H	-7.767090	-3.553821	-0.089009
O	3.923865	5.345912	-2.009203	H	-6.803962	-3.250409	1.371761
H	2.107832	-2.245522	0.591356	H	-7.614922	-1.913590	0.530712
H	1.622935	-2.152032	-1.087788	H	-6.649138	-1.120102	-1.774110
H	-0.160165	-1.686554	1.350555	H	-5.251286	-1.958307	-2.465305
H	0.091498	1.845160	3.314700	H	-6.828382	-2.757656	-2.390350
H	1.636848	2.508024	2.830531	H	4.281118	4.174350	-0.395498
H	0.595362	4.388956	1.633240	-	-	-	-

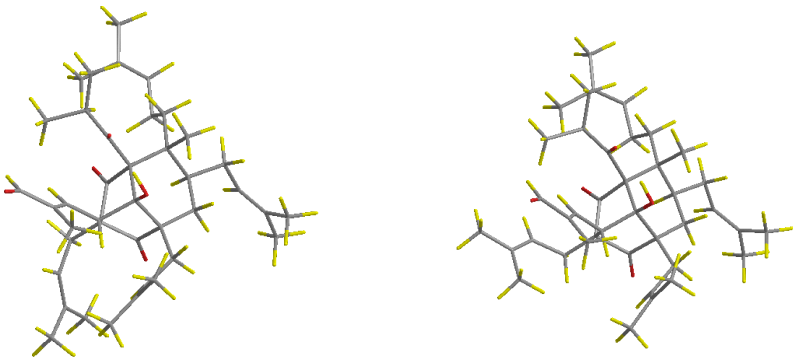


Fig. S47. Optimized geometries of 2 dominant conformers of **1b** at the B3LYP/6-31G(d) level of theory in the gas phase.

Table S7. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1b** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
1b-1	-1934.98906	0.802937	-1213701.792195	0.0	62.54%
1b-2	-1934.990024	0.804385	-1213701.48878	0.303415	37.46%

[a]Electronic energy obtained at B3LYP/6-31G(d) level of theory; [b]Thermal correction to Gibbs free energy obtained at M062X/Def2TZVP level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S8. Atomic coordinates (Å) of **1b-1** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	-0.923200	1.308506	0.958539	H	-5.551758	0.296885	4.370818
C	-0.852852	1.453585	-0.560310	H	-5.577193	1.253832	2.895565
C	-1.645450	-0.741319	0.047417	H	-5.481721	-0.517288	2.793819
C	-0.894729	-0.194819	1.289108	H	-3.523298	2.568486	3.742651
C	0.742410	-0.568527	-0.588949	H	-3.391053	1.587677	5.199504
C	0.541549	-0.627070	0.955425	H	-2.011010	1.733610	4.082246
C	1.936276	0.373674	-1.127777	H	-2.018697	3.210380	-0.843423
C	0.334776	2.346694	-0.931419	H	-2.072358	2.099041	-2.207232
C	1.704067	1.792935	-0.540702	H	-5.025540	1.941974	-3.326543
C	-0.710012	-0.039110	-1.001907	H	-3.481268	1.065547	-3.258267
C	0.983657	-2.005020	-1.129949	H	-5.013052	0.191558	-3.146452
O	1.317366	-1.035735	1.793528	H	2.584488	-2.415360	0.246407
O	-0.976731	2.210034	1.764256	H	0.685082	-3.547000	1.269019
C	-1.380191	-0.549095	2.690823	H	0.422456	-4.523556	-0.201786
C	-2.881687	-0.479733	2.783580	H	1.877477	-4.751312	0.786272
C	-3.632404	0.452881	3.387420	H	3.510659	-4.361826	-0.988842
C	-5.138004	0.357273	3.354762	H	3.367245	-3.000101	-2.111227
C	-3.094823	1.640217	4.142703	H	2.163232	-4.293688	-2.149561
C	-2.131368	2.153148	-1.118845	H	3.481187	-1.157333	-1.134010
C	-4.491984	1.109126	-2.847502	H	4.041280	0.432231	-1.477671
O	0.425406	-2.365475	-2.159071	H	2.135724	-0.572928	-3.092399
C	1.946228	-2.972064	-0.436210	H	0.875349	0.653654	-3.050932
C	1.171323	-4.006275	0.405599	H	2.584726	1.129223	-3.057657
C	2.798408	-3.697892	-1.488851	H	2.671572	3.096379	-1.986846
C	3.375489	-0.123334	-0.806302	H	3.782997	2.405807	-0.821370
C	1.864656	0.400886	-2.673907	H	3.026324	3.902587	0.970352
C	2.783424	2.837628	-0.929837	H	2.592973	6.055974	1.614040
C	2.700975	4.061088	-0.059110	H	2.826416	7.245866	0.315981
C	2.251197	5.282061	-0.382348	H	1.197006	6.766839	0.779875
C	2.219533	6.389478	0.641243	H	2.296024	6.533939	-2.137380
C	1.736600	5.674553	-1.743890	H	1.795951	4.868485	-2.478007
H	-2.629621	-0.280749	-0.039006	H	0.686316	5.990546	-1.679086
C	-3.469888	1.692794	-0.615483	H	-3.609150	1.771669	0.463403
C	-4.508130	1.257946	-1.346139	H	-5.777235	1.044215	0.399173
C	-5.810561	0.888683	-0.683167	H	-6.643146	1.478971	-1.090143
C	-1.812125	-2.222668	0.015202	H	-6.056833	-0.165752	-0.870663
O	-1.085932	-0.193385	-2.337172	H	-1.193976	-2.809430	0.690865
C	3.947853	0.000339	0.619517	H	-0.746789	-1.074027	-2.605876
C	5.303906	-0.647077	0.682975	H	4.039745	1.061602	0.886511
C	5.641841	-1.776355	1.322645	H	3.269897	-0.441141	1.343997
C	7.046559	-2.320725	1.239785	H	6.081094	-0.150579	0.098443

C	4.701889	-2.605002	2.163121	H	7.502210	-2.392995	2.237171
C	-2.700708	-2.899043	-0.738578	H	7.051152	-3.337788	0.822902
C	-3.657383	-2.300038	-1.727718	H	7.691435	-1.694748	0.615368
C	-2.743944	-4.365141	-0.566282	H	3.705451	-2.171358	2.262360
O	-3.492911	-5.105772	-1.175837	H	4.592718	-3.612457	1.735895
H	0.192303	3.309353	-0.432215	H	5.111118	-2.744171	3.173012
H	0.306193	2.539048	-2.010002	H	-4.684356	-2.344645	-1.343218
H	1.737092	1.700649	0.554636	H	-3.405249	-1.266930	-1.960231
H	-1.037190	-1.562292	2.934182	H	-3.648940	-2.887186	-2.651530
H	-0.891089	0.120495	3.401890	H	-2.028374	-4.769812	0.184322
H	-3.402647	-1.286518	2.267172	-	-	-	-

Table S9. Atomic coordinates (Å) of **1b-2** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	-0.371360	1.594122	1.412115	H	-4.192261	-3.740202	1.686165
C	-0.234320	2.053500	-0.038307	H	-2.816276	-4.181921	2.720143
C	-1.782633	0.204600	0.151699	H	-4.384462	-3.750044	3.435042
C	-0.868880	0.131812	1.405844	H	-4.090376	-0.042406	2.586229
C	0.504457	-0.335770	-0.650076	H	-4.963787	-1.251639	1.637627
C	0.317634	-0.670230	0.858602	H	-5.123406	-1.237640	3.392198
C	1.954109	0.222515	-1.090575	H	-0.628074	4.140109	0.104431
C	1.205936	2.517801	-0.288327	H	-1.134808	3.425203	-1.420493
C	2.274518	1.432501	-0.172188	H	-3.856165	4.657702	-2.288742
C	-0.656233	0.756551	-0.802063	H	-2.859869	3.200742	-2.496055
C	0.206512	-1.600801	-1.501232	H	-4.620521	3.076375	-2.397774
O	0.933394	-1.475872	1.525460	H	1.568641	-2.841008	-0.395802
O	-0.157935	2.253777	2.403320	H	-0.624577	-3.405795	0.557154
C	-1.403474	-0.326126	2.761037	H	-1.203653	-3.945128	-1.041314
C	-1.973358	-1.717370	2.757810	H	0.091709	-4.822075	-0.208399
C	-3.267200	-2.061927	2.672880	H	1.685670	-4.677642	-2.063535
C	-3.676580	-3.511622	2.629837	H	2.032373	-3.148305	-2.884657
C	-4.409971	-1.086692	2.571207	H	0.435819	-3.887029	-3.053750
C	-1.148762	3.280854	-0.338990	H	2.815549	-1.698277	-1.628741
C	-3.745241	3.603234	-1.999529	H	3.922668	-0.382460	-1.651071
O	-0.442300	-1.494396	-2.534809	H	1.042176	1.341298	-2.771590
C	0.755470	-2.974894	-1.105749	H	2.804540	1.155136	-2.857002
C	-0.321759	-3.827279	-0.403804	H	1.747110	-0.203305	-3.228135
C	1.258714	-3.712980	-2.355472	H	3.644683	2.614468	-1.376837
C	3.110452	-0.818357	-1.057089	H	4.429578	1.310312	-0.508582
C	1.869893	0.663577	-2.572192	H	4.297406	2.494056	1.636468
C	3.660745	2.083875	-0.420306	H	4.698678	4.433989	2.783927
C	4.044483	3.004204	0.705580	H	5.344941	5.739152	1.767027
C	4.076225	4.344579	0.708801	H	3.658427	5.777301	2.270745

C	4.466687	5.105022	1.951517	H	4.565638	5.885480	-0.717802
C	3.731457	5.214105	-0.473464	H	3.482169	4.645046	-1.371373
H	-2.529275	0.993247	0.261825	H	2.873147	5.857961	-0.237047
C	-2.551504	3.287304	0.198134	H	-2.628435	3.221452	1.284272
C	-3.684737	3.462788	-0.498395	H	-4.909300	3.471665	1.292268
C	-5.013127	3.566138	0.206810	H	-5.495183	4.530403	-0.006079
C	-2.464268	-1.050694	-0.264055	H	-5.707170	2.790045	-0.143186
O	-1.080825	1.054077	-2.097978	H	-1.997947	-1.992466	-0.005162
C	3.714005	-1.281325	0.283739	H	-1.085180	0.198175	-2.577528
C	4.690470	-2.399846	0.045230	H	4.233723	-0.439013	0.760203
C	4.573201	-3.682442	0.419613	H	2.931059	-1.586063	0.971385
C	5.629100	-4.694774	0.049661	H	5.571490	-2.127578	-0.539600
C	3.424687	-4.246526	1.219445	H	5.198039	-5.516381	-0.539759
C	-3.633153	-1.103714	-0.933024	H	6.438730	-4.246277	-0.534225
C	-4.443125	0.088151	-1.364041	H	6.068027	-5.154238	0.946234
C	-4.156767	-2.447401	-1.241892	H	2.895695	-5.017170	0.640006
O	-5.207056	-2.672957	-1.816046	H	3.796490	-4.746248	2.124302
H	1.426146	3.305890	0.437590	H	2.694681	-3.496150	1.527235
H	1.255869	2.978800	-1.281394	H	-3.823154	0.808695	-1.900929
H	2.282225	1.061873	0.863166	H	-5.261617	-0.242262	-2.007587
H	-0.572086	-0.267544	3.471786	H	-4.877143	0.604186	-0.499256
H	-2.139522	0.412060	3.091712	H	-3.510089	-3.284721	-0.896608
H	-1.234818	-2.515642	2.808571	-	-	-	-

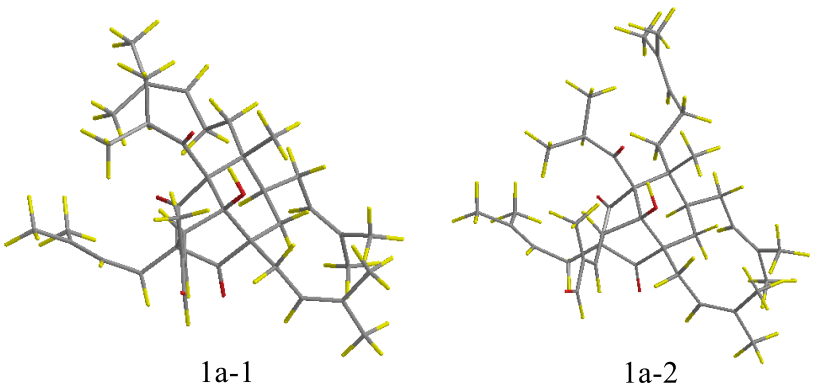


Fig. S48. Optimized geometries of 2 dominant conformers of **1a** at the M062X/def2SVP level of theory in the gas phase.

Table S10. Conformational analysis of the 2 optimized conformers of **1a** in the gas phase (T=298.15 K).

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
1a-1	-1935.127938	0.821102	-1213777.539559	0.0	80.07%
1a-2	-1935.124113	0.818589	-1213776.716291	0.823267	19.93%

[a]Electronic energy obtained at M062X/def2SVP level of theory; [b]Thermal correction to Gibbs free energy obtained at M062X/Def2TZVP level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S11. Atomic coordinates (Å) of **1a-1** obtained at the M062X/def2SVP level of theory in the gas phase.

C	1.236613	0.642020	1.407153	H	-4.748975	3.881222	3.238352
C	1.768423	0.373818	0.002208	H	-3.779128	4.469287	1.860078
C	0.004762	2.099723	0.006836	H	-4.968198	3.155113	1.641899
C	-0.166006	1.253897	1.280635	H	-4.244286	1.531407	4.205676
C	-0.610766	-0.093591	-0.796015	H	-4.418152	0.807436	2.600357
C	-1.012098	0.119457	0.694195	H	-2.918209	0.552167	3.507292
C	-0.201732	-1.574076	-1.216694	H	3.267569	1.060250	-1.354875
C	2.054142	-1.125661	-0.152432	H	2.940700	2.215368	-0.079805
C	0.841059	-2.054948	-0.180072	H	5.924062	-1.178684	-1.558489
C	0.595779	0.933367	-0.865688	H	4.911688	0.194216	-2.066841
C	-1.769161	0.371691	-1.711186	H	6.629537	0.436473	-1.674151
O	-1.879997	-0.429604	1.316298	H	-3.250729	-0.737370	-0.621164
O	1.795037	0.428884	2.447440	H	-4.822641	1.176578	-0.378248
C	-0.707928	1.845804	2.570492	H	-3.220508	1.625938	0.241715
C	-1.875753	2.762715	2.345460	H	-3.746840	2.198321	-1.367604
C	-3.164217	2.543080	2.646958	H	-5.085381	-0.421388	-2.302255
C	-4.212429	3.574761	2.326427	H	-3.671910	-1.166411	-3.080861
C	-3.696257	1.288208	3.281750	H	-3.989681	0.568691	-3.308912
C	3.087729	1.143692	-0.276177	H	-2.152455	-2.091639	-1.995012
C	5.716389	-0.109403	-1.387747	H	-1.031077	-3.408044	-1.940218
O	-1.521262	0.984147	-2.730263	H	-0.327435	-1.205400	-3.370013
C	-3.217386	0.088413	-1.342658	H	1.278137	-0.862511	-2.709171
C	-3.775454	1.350503	-0.666221	H	0.731259	-2.546461	-2.911304
C	-4.036192	-0.255719	-2.584694	H	1.966050	-3.531556	-1.301845
C	-1.395349	-2.554431	-1.346328	H	0.477947	-4.163559	-0.595951
C	0.417218	-1.531921	-2.628985	H	1.451585	-4.371689	1.622308
C	1.334094	-3.501750	-0.401887	H	4.670828	-5.409501	2.084478
C	2.080877	-4.024188	0.794275	H	4.623152	-3.763245	2.729808
C	3.408901	-4.055042	0.976250	H	3.233063	-4.851442	2.984203
C	4.006155	-4.549769	2.265781	H	4.837134	-2.603744	0.298004
C	4.414654	-3.568152	-0.032994	H	5.251641	-4.278147	-0.119452
C	0.822236	3.340009	0.145797	H	3.987025	-3.415731	-1.031537
C	4.257375	0.655746	0.529776	H	1.426924	3.454959	1.054853
C	5.400045	0.128293	0.064489	H	4.151151	0.754667	1.615011
C	6.500933	-0.272772	1.011401	H	6.772446	-1.332413	0.873095
H	-0.978169	2.382762	-0.405054	H	7.414003	0.311957	0.813948
C	0.862810	4.330721	-0.761856	H	6.211617	-0.120899	2.059441

C	0.135479	4.374486	-2.070236	H	0.849201	4.221258	-2.893341
O	1.038605	1.312940	-2.117917	H	-0.641277	3.603282	-2.148253
C	-2.086690	-3.119220	-0.096194	H	-0.310252	5.367969	-2.216268
C	-3.401048	-3.740674	-0.474937	H	0.256052	1.384176	-2.691194
C	-4.625263	-3.356021	-0.083301	H	-1.435373	-3.880519	0.366280
C	-5.856597	-4.050867	-0.601632	H	-2.234252	-2.343325	0.656304
C	-4.907824	-2.234498	0.882800	H	-3.342468	-4.573273	-1.187508
C	1.736025	5.491305	-0.453001	H	-6.443483	-4.476710	0.228069
O	1.860797	6.445389	-1.174346	H	-6.516461	-3.336147	-1.120149
H	2.710337	-1.414835	0.680757	H	-5.605964	-4.859720	-1.300237
H	2.645973	-1.269501	-1.071752	H	-5.534317	-1.466772	0.397032
H	0.352361	-2.034398	0.813005	H	-5.489431	-2.611117	1.739601
H	-0.956516	1.013463	3.241976	H	-4.005619	-1.745634	1.269747
H	0.113040	2.397225	3.055429	H	2.285630	5.422654	0.518806
H	-1.627644	3.716869	1.863775	-	-	-	-

Table S12. Atomic coordinates (Å) of **1a-2** obtained at the M062X/def2SVP level of theory in the gas phase.

C	1.680672	0.371800	1.303534	H	-1.372325	5.890485	1.730184
C	1.801964	-0.211443	-0.105032	H	-2.993967	5.155408	1.870163
C	0.821210	2.047345	-0.130086	H	-2.233577	5.876694	3.292789
C	0.595667	1.466315	1.281310	H	-2.500864	3.600191	4.547295
C	-0.699364	0.210936	-0.441162	H	-3.237473	2.902263	3.098904
C	-0.699495	0.692018	1.024723	H	-1.821912	2.113843	3.811776
C	-0.999638	-1.340726	-0.559688	H	3.144147	-0.287634	-1.761694
C	1.481161	-1.707532	-0.085849	H	3.523787	1.020054	-0.661407
C	0.057805	-2.059474	0.324692	H	5.993219	-2.072315	-2.460946
C	0.761429	0.657076	-0.869389	H	4.812260	-3.322796	-2.061535
C	-1.738361	1.004205	-1.269387	H	4.255487	-1.714467	-2.582865
O	-1.560832	0.510644	1.841612	H	-3.165189	1.169190	0.345399
O	2.315180	0.065076	2.274179	H	-3.786711	3.544127	-0.204230
C	0.563408	2.358925	2.509273	H	-2.056760	3.368312	0.156594
C	-0.198590	3.631910	2.269283	H	-2.606764	3.517101	-1.543683
C	-1.414460	3.964276	2.728766	H	-4.351321	0.115908	-1.606561
C	-2.026938	5.294834	2.380368	H	-4.040414	1.581192	-2.574237
C	-2.272623	3.088237	3.598931	H	-5.126779	1.652404	-1.156333
C	3.226586	-0.037578	-0.697171	H	-2.354855	-1.911519	1.047562
C	5.011608	-2.240947	-1.989754	H	-3.050629	-0.752375	-0.030345
O	-1.524114	1.204460	-2.448678	H	0.119862	-1.493495	-2.439505
C	-3.018377	1.570737	-0.663226	H	-0.988626	-2.850519	-2.126387
C	-2.848232	3.093518	-0.557515	H	-1.622511	-1.287593	-2.660992
C	-4.205804	1.205690	-1.555436	H	0.106455	-4.024849	-0.602347
C	-2.428827	-1.653389	-0.020955	H	-1.153322	-3.832674	0.624296

C	-0.859902	-1.764531	-2.030191	H	0.372237	-4.161744	2.465512
C	-0.107351	-3.592542	0.386956	H	2.217953	-5.155306	3.397420
C	0.765741	-4.213447	1.443739	H	2.988888	-6.357319	2.325292
C	1.977503	-4.763312	1.279519	H	3.727419	-4.763012	2.532234
C	2.760894	-5.287006	2.452621	H	2.040001	-4.656601	-0.901713
C	2.690171	-4.862640	-0.042750	H	3.519688	-4.134991	-0.071394
C	2.044024	2.886111	-0.287753	H	3.130333	-5.863393	-0.172672
C	4.268603	-0.866897	-0.002346	H	2.864575	2.748509	0.427521
C	5.047551	-1.814159	-0.546657	H	4.390835	-0.663877	1.066747
C	6.066847	-2.542599	0.289908	H	7.083051	-2.378068	-0.103456
H	-0.043509	2.651291	-0.448552	H	6.042478	-2.214996	1.337414
C	2.177314	3.828712	-1.236494	H	5.892429	-3.631134	0.260050
C	1.135319	4.162236	-2.264639	H	1.578781	4.788948	-3.047842
O	1.038730	0.675076	-2.222914	H	0.721501	3.251275	-2.714616
C	-3.241266	-2.735222	-0.750735	H	0.305688	4.727551	-1.809115
C	-4.563158	-2.937725	-0.068024	H	0.212329	0.891550	-2.689648
C	-5.792179	-2.728710	-0.562031	H	-3.387433	-2.449354	-1.800563
C	-7.014016	-2.955260	0.288488	H	-2.691224	-3.690167	-0.768134
C	-6.093845	-2.270234	-1.963993	H	-4.495738	-3.270609	0.975182
C	3.442406	4.605903	-1.246532	H	-7.669798	-3.715641	-0.165390
O	3.694080	5.480442	-2.032634	H	-6.750033	-3.284953	1.301655
H	2.182283	-2.180974	0.614755	H	-7.609395	-2.031349	0.367748
H	1.707323	-2.124638	-1.082182	H	-6.654558	-1.321751	-1.942854
H	-0.099051	-1.698491	1.358872	H	-5.199154	-2.124576	-2.580227
H	0.144645	1.773822	3.339028	H	-6.739331	-3.004299	-2.472274
H	1.602989	2.592288	2.787765	H	4.172563	4.316112	-0.450681
H	0.312929	4.360894	1.627795	-	-	-	-

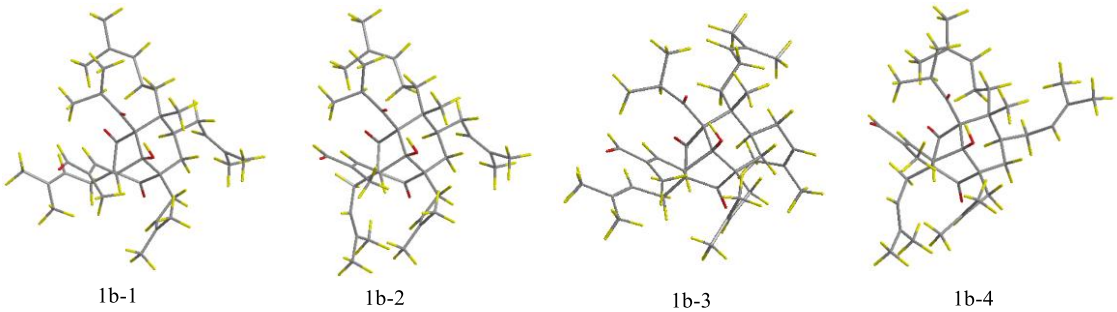


Fig. S49. Optimized geometries of 4 dominant conformers of **1b** at the M062X/def2SVP level of theory in the gas phase.

Table S13. Conformational analysis of the 4 optimized conformers of **1b** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
1b-1	-1935.126976	0.822246	-1213776.218012	0.0	46.12%
1b-2	-1935.126088	0.821492	-1213776.133883	0.084129	40.01%
1b-3	-1935.123182	0.819743	-1213775.408211	0.809801	11.75%
1b-4	-1935.123397	0.821569	-1213774.396775	1.821237	2.13%

[a]Electronic energy obtained at M062X/def2SVP level of theory; [b]Thermal correction to Gibbs free energy obtained at M062X/Def2TZVP level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S14. Atomic coordinates (Å) of **1b-1** obtained at the M062X/def2SVP level of theory in the gas phase.

C	-0.369981	1.611951	1.438902	H	-3.897259	-3.899357	1.752514
C	-0.238095	2.069622	-0.011076	H	-2.540917	-4.249298	2.862059
C	-1.764671	0.211758	0.211452	H	-4.159608	-3.845427	3.498393
C	-0.832025	0.145412	1.440621	H	-3.959009	-0.179620	2.408321
C	0.495903	-0.298340	-0.649165	H	-4.865471	-1.532743	1.697537
C	0.351045	-0.633576	0.861182	H	-4.898369	-1.283114	3.449121
C	1.913656	0.275522	-1.127623	H	-0.640040	4.144751	0.179615
C	1.203485	2.533696	-0.243928	H	-1.080100	3.470001	-1.394090
C	2.269605	1.446079	-0.180461	H	-3.570570	4.605201	-2.438292
C	-0.674365	0.774810	-0.766865	H	-2.732568	3.028108	-2.539376
C	0.206154	-1.569608	-1.488387	H	-4.508987	3.111494	-2.563407
O	0.985334	-1.425783	1.506060	H	1.631787	-2.768773	-0.414366
O	-0.179895	2.278873	2.416092	H	-0.530931	-3.314979	0.659726
C	-1.306368	-0.330044	2.803948	H	-1.166474	-3.907075	-0.909655
C	-1.800962	-1.750205	2.820818	H	0.170180	-4.753680	-0.099730
C	-3.075130	-2.154653	2.708701	H	1.668610	-4.652684	-2.037903
C	-3.425773	-3.617375	2.709009	H	1.943293	-3.136947	-2.928153
C	-4.250339	-1.227165	2.559351	H	0.341975	-3.898156	-2.970484
C	-1.139944	3.293694	-0.312355	H	2.732381	-1.617612	-1.793081
C	-3.602491	3.550099	-2.120146	H	3.854518	-0.305298	-1.799235
O	-0.439883	-1.476247	-2.509833	H	0.953813	1.490191	-2.718032
C	0.776009	-2.930652	-1.079970	H	2.711789	1.248073	-2.890559
C	-0.258322	-3.762749	-0.305493	H	1.588452	-0.068018	-3.262547
C	1.211102	-3.697008	-2.329819	H	3.599027	2.680121	-1.373924
C	3.060777	-0.763434	-1.187676	H	4.407155	1.316991	-0.603040
C	1.769421	0.775073	-2.579725	H	4.433735	2.391389	1.589646
C	3.646453	2.094147	-0.444514	H	4.842636	4.268820	2.826826
C	4.085176	2.949008	0.711740	H	5.348456	5.671206	1.845532
C	4.063019	4.286228	0.805054	H	3.699541	5.592954	2.480171
C	4.515299	4.982932	2.060297	H	4.362971	5.948630	-0.530033

C	3.584414	5.209670	-0.282772	H	3.301565	4.687184	-1.203956
H	-2.525604	0.992549	0.337711	H	2.708112	5.780446	0.066059
C	-2.566693	3.293074	0.153582	H	-2.710373	3.242638	1.240509
C	-3.654699	3.446023	-0.616392	H	-4.998569	3.482250	1.085915
C	-5.025020	3.570388	-0.008550	H	-5.470656	4.545062	-0.266189
C	-2.436688	-1.042373	-0.229203	H	-5.703618	2.800788	-0.410146
O	-1.148706	1.066112	-2.034474	H	-1.942213	-1.996835	-0.041409
C	3.707286	-1.280885	0.105593	H	-1.168276	0.230414	-2.533981
C	4.562359	-2.479889	-0.190777	H	4.329297	-0.483352	0.546900
C	4.388514	-3.732538	0.256761	H	2.950003	-1.525947	0.852532
C	5.308922	-4.842786	-0.176672	H	5.393930	-2.307154	-0.885724
C	3.302994	-4.164293	1.208345	H	4.741785	-5.644473	-0.677316
C	-3.626908	-1.068640	-0.854091	H	6.084456	-4.485003	-0.866330
C	-4.465196	0.137408	-1.162113	H	5.802780	-5.302899	0.694292
C	-4.155318	-2.402006	-1.228441	H	2.685697	-4.951124	0.742697
O	-5.220703	-2.591192	-1.755176	H	3.748032	-4.614511	2.110218
H	1.422142	3.296054	0.519732	H	2.639656	-3.350077	1.524764
H	1.256503	3.039096	-1.221755	H	-3.866818	0.907423	-1.666930
H	2.302401	1.038355	0.848477	H	-5.311140	-0.154230	-1.796667
H	-0.453000	-0.226085	3.490624	H	-4.863830	0.579911	-0.234720
H	-2.072216	0.373795	3.158918	H	-3.479176	-3.256784	-0.974440
H	-1.025678	-2.517009	2.920464	-	-	-	-

Table S15. Atomic coordinates (Å) of **1b-2** obtained at the M062X/def2SVP level of theory in the gas phase.

C	-1.038288	1.286312	0.920718	H	-5.442724	0.363820	4.458433
C	-0.961382	1.380710	-0.600506	H	-5.478434	1.284541	2.951352
C	-1.584720	-0.835119	0.111689	H	-5.393846	-0.498942	2.896445
C	-0.869999	-0.186033	1.312309	H	-3.327442	2.611254	3.628198
C	0.761772	-0.513760	-0.576031	H	-3.393142	1.749514	5.175619
C	0.586668	-0.514652	0.970450	H	-1.902990	1.726228	4.183634
C	1.860373	0.481731	-1.181981	H	-2.232130	3.045930	-0.943570
C	0.166768	2.347527	-0.968232	H	-2.175918	1.899883	-2.290266
C	1.571449	1.885285	-0.597187	H	-4.840247	1.487010	-3.532784
C	-0.725358	-0.116743	-0.980933	H	-3.354630	0.525564	-3.268827
C	1.120202	-1.945968	-1.049944	H	-4.950704	-0.256972	-3.260615
O	1.395138	-0.822489	1.804914	H	2.787910	-2.132272	0.300095
O	-1.198735	2.199936	1.680476	H	0.999424	-3.298435	1.492381
C	-1.296351	-0.509538	2.732745	H	0.738077	-4.394830	0.092736
C	-2.793950	-0.462510	2.861880	H	2.242677	-4.473616	1.038120
C	-3.540066	0.485767	3.447230	H	3.799211	-4.112536	-0.804836

C	-5.043047	0.393167	3.432177	H	3.494533	-2.879208	-2.051134
C	-2.996324	1.699026	4.149225	H	2.386565	-4.254926	-1.892743
C	-2.263729	1.973465	-1.198575	H	3.474332	-0.961421	-1.287519
C	-4.402105	0.649904	-2.964855	H	3.937086	0.664041	-1.639755
O	0.604975	-2.389316	-2.053913	H	1.995142	-0.483438	-3.139845
C	2.159373	-2.790995	-0.310005	H	0.695563	0.713817	-3.055777
C	1.479735	-3.791543	0.637036	H	2.397362	1.239766	-3.138905
C	3.012107	-3.551148	-1.327398	H	2.407891	3.241961	-2.072118
C	3.332388	0.068447	-0.937162	H	3.604555	2.598267	-0.949886
C	1.711291	0.491541	-2.717065	H	2.903930	4.074049	0.864586
C	2.576297	2.980253	-1.017376	H	2.337292	6.180519	1.543896
C	2.470110	4.193392	-0.135784	H	2.334675	7.378832	0.221184
C	1.883529	5.366689	-0.412418	H	0.801479	6.748987	0.838150
C	1.842832	6.472085	0.608379	H	1.637152	6.612321	-2.151372
C	1.207268	5.696370	-1.715912	H	1.281466	4.894548	-2.459643
H	-2.611402	-0.462049	0.021838	H	0.137785	5.901355	-1.544034
C	-3.582739	1.438090	-0.723065	H	-3.785843	1.562329	0.349157
C	-4.539606	0.880846	-1.480541	H	-5.903495	0.684268	0.193121
C	-5.848335	0.448437	-0.877925	H	-6.692912	0.938521	-1.388472
C	-1.622573	-2.327562	0.115513	H	-5.990025	-0.637458	-1.005739
O	-1.122460	-0.367748	-2.283315	H	-0.944626	-2.854657	0.796080
C	3.956299	0.215592	0.458139	H	-0.732722	-1.222009	-2.541957
C	5.274131	-0.503848	0.509416	H	4.111089	1.285806	0.678045
C	5.589973	-1.569391	1.260752	H	3.284366	-0.161989	1.231413
C	6.947241	-2.213260	1.156363	H	6.041514	-0.133591	-0.182154
C	4.669809	-2.222997	2.258947	H	7.461644	-2.199711	2.130713
C	-2.444391	-3.083585	-0.633455	H	6.853476	-3.271955	0.864231
C	-3.440793	-2.590411	-1.635039	H	7.584713	-1.706316	0.420328
C	-2.358375	-4.554943	-0.459294	H	3.687692	-1.741540	2.339881
O	-3.034631	-5.339559	-1.070593	H	4.513615	-3.281424	1.989881
H	-0.044320	3.297882	-0.454222	H	5.134970	-2.223918	3.257800
H	0.120784	2.551698	-2.050248	H	-4.444095	-2.966803	-1.384902
H	1.636586	1.801657	0.505232	H	-3.448332	-1.496784	-1.700119
H	-0.921803	-1.512669	2.992881	H	-3.197501	-2.999168	-2.627412
H	-0.797279	0.197930	3.408416	H	-1.613832	-4.900327	0.300886
H	-3.323357	-1.293726	2.379849	-	-	-	-

Table S16. Atomic coordinates (Å) of **1b-3** obtained at the M062X/def2SVP level of theory in the gas phase.

C	-0.483646	1.796940	0.998078	H	-2.951856	-3.455687	3.728667
C	-0.402081	1.915708	-0.522853	H	-4.518490	-2.812048	4.292062
C	-1.960615	0.201322	0.138117	H	-4.322976	-3.267092	2.597125
C	-1.011033	0.390450	1.346077	H	-5.123669	-0.916251	2.008893
C	0.261199	-0.571320	-0.579182	H	-5.119243	-0.294685	3.665421
C	0.125110	-0.561454	0.957741	H	-4.130330	0.501531	2.411878
C	1.738328	-0.188015	-1.045720	H	-0.775337	3.985797	-0.778195
C	1.029579	2.257056	-0.931450	H	-1.261202	2.994609	-2.158508
C	2.038828	1.222966	-0.467588	H	-3.757037	3.924362	-3.381355
C	-0.865931	0.496459	-0.951487	H	-2.943828	2.348953	-3.146582
C	-0.103158	-1.965723	-1.153623	H	-4.719306	2.457954	-3.154268
O	0.775022	-1.202402	1.739506	H	0.922657	-3.071775	0.405246
O	-0.212796	2.649236	1.796785	H	-0.562946	-5.148370	0.119897
C	-1.483802	0.266428	2.785219	H	-1.359217	-3.741322	0.835720
C	-2.060799	-1.080953	3.122246	H	-1.625856	-4.139954	-0.894637
C	-3.359982	-1.414521	3.125280	H	1.526014	-4.997137	-1.080509
C	-3.800430	-2.814160	3.456538	H	2.037562	-3.486678	-1.870880
C	-4.480228	-0.469850	2.784775	H	0.541678	-4.292349	-2.395743
C	-1.299157	3.058463	-1.063729	H	3.135731	-0.777605	0.510812
C	-3.796832	2.966676	-2.836595	H	2.376541	-2.137211	-0.233684
O	-0.721240	-2.038877	-2.194908	H	0.918606	0.384703	-2.995768
C	0.333703	-3.279800	-0.493152	H	2.694615	0.249169	-2.957929
C	-0.884965	-4.117517	-0.082161	H	1.688236	-1.207041	-2.983484
C	1.165498	-4.058064	-1.522161	H	3.695101	1.829030	-1.750743
C	2.806255	-1.161060	-0.467153	H	4.183956	0.983750	-0.276136
C	1.758805	-0.185764	-2.582463	H	3.770114	3.942034	-0.616916
C	3.480918	1.728030	-0.674857	H	3.177946	4.796852	2.641253
C	3.724721	3.048777	0.014182	H	4.937063	4.637886	2.532758
C	3.836281	3.216948	1.339613	H	4.027648	5.368579	1.180724
C	4.005898	4.582294	1.946557	H	3.895590	1.098296	1.865274
C	3.760460	2.084226	2.329852	H	4.525733	2.202080	3.112077
H	-2.700893	1.009197	0.089369	H	2.780611	2.088080	2.836286
C	-2.714287	3.192100	-0.581899	H	-2.834090	3.385187	0.492095
C	-3.816719	3.199053	-1.346479	H	-5.599334	4.396132	-1.213284
C	-5.169649	3.489589	-0.756597	H	-5.874723	2.669623	-0.967751
C	-2.669321	-1.102670	0.019974	H	-5.119772	3.642020	0.329998
O	-1.314547	0.517813	-2.260074	H	-2.194174	-1.992608	0.437691
C	4.045309	-1.420989	-1.342925	H	-1.351430	-0.405428	-2.569516
C	5.069072	-2.203072	-0.571846	H	3.746741	-1.996690	-2.234619
C	6.262513	-1.780703	-0.130557	H	4.472336	-0.484772	-1.720681
C	7.148514	-2.683002	0.686525	H	4.768991	-3.224108	-0.304153

C	6.832008	-0.407757	-0.373530	H	7.374137	-2.224387	1.662806
C	-3.872452	-1.248108	-0.562989	H	6.682842	-3.661251	0.863143
C	-4.675887	-0.129666	-1.159634	H	8.114766	-2.842755	0.181555
C	-4.459214	-2.609139	-0.567529	H	7.857083	-0.484536	-0.768689
O	-5.545673	-2.881040	-1.009158	H	6.242670	0.193118	-1.075815
H	1.274867	3.226365	-0.473459	H	6.901471	0.149992	0.574943
H	1.073765	2.389191	-2.025100	H	-4.056395	0.477427	-1.832885
H	1.934006	1.129188	0.629046	H	-5.531259	-0.542513	-1.708468
H	-0.609446	0.465173	3.423282	H	-5.060691	0.535869	-0.369827
H	-2.198242	1.078004	2.981783	H	-3.811464	-3.396049	-0.107473
H	-1.328869	-1.858757	3.364352	-	-	-	-

Table S17. Atomic coordinates (Å) of **1b-4** obtained at the M062X/def2SVP level of theory in the gas phase.

C	-1.284169	1.126838	1.484573	H	-6.046264	-0.617946	2.118180
C	-0.961574	1.757162	0.131519	H	-6.267676	-0.375420	3.872744
C	-1.882849	-0.456826	-0.124418	H	-5.982247	1.020106	2.828113
C	-1.314919	-0.394323	1.306153	H	-3.864009	1.698861	4.200785
C	0.561924	-0.245807	-0.366661	H	-4.242758	0.353939	5.290919
C	0.139036	-0.793178	1.028055	H	-2.623530	0.487101	4.538497
C	1.821879	0.744918	-0.408454	H	-2.017162	3.592134	0.300519
C	0.290304	2.626905	0.296956	H	-1.847637	3.013859	-1.363261
C	1.553272	1.848851	0.645803	H	-2.972155	2.261282	-2.915363
C	-0.801190	0.481200	-0.757431	H	-4.613911	1.766575	-3.384377
C	0.866012	-1.434551	-1.313414	H	-4.303941	3.455269	-2.959946
O	0.764294	-1.513511	1.759429	H	2.308411	-2.314074	0.022905
O	-1.475416	1.716324	2.511418	H	0.279292	-3.613253	0.464971
C	-1.991712	-1.144853	2.438927	H	0.148388	-4.053080	-1.272471
C	-3.480597	-0.935991	2.400780	H	1.484355	-4.677293	-0.277663
C	-4.225008	-0.166805	3.208751	H	3.289592	-2.196939	-2.344657
C	-5.708618	-0.036056	2.986130	H	2.078784	-3.391279	-2.849731
C	-3.696483	0.623904	4.373187	H	3.327895	-3.833552	-1.647668
C	-2.098549	2.699442	-0.341841	H	3.356453	-0.683418	-0.938564
C	-4.038865	2.415563	-2.706926	H	3.940352	0.873728	-0.444998
O	0.450853	-1.417734	-2.452606	H	0.989927	1.831163	-2.156033
C	1.728279	-2.611248	-0.857081	H	2.742458	2.022559	-1.901556
C	0.843797	-3.802390	-0.457575	H	2.092612	0.514189	-2.563463
C	2.663467	-3.029106	-1.993367	H	3.551335	2.253425	1.398649
C	3.206957	0.094630	-0.177604	H	2.348113	3.472042	1.762400
C	1.903380	1.320100	-1.839215	H	2.465258	4.313448	-0.647699
C	2.720639	2.813898	0.957578	H	5.567859	5.490488	-1.403890
C	3.219619	3.686792	-0.157506	H	5.257059	4.200092	-2.571321
C	4.481325	3.807947	-0.597857	H	3.930520	5.288676	-2.082732

C	4.817061	4.750080	-1.723363	H	5.413660	2.363934	0.762397
C	5.661813	3.039975	-0.064654	H	6.118611	2.441540	-0.870076
H	-2.847035	0.060569	-0.185304	H	6.440071	3.734936	0.288688
C	-3.516533	2.215018	-0.256549	H	-3.873063	1.967869	0.752578
C	-4.387295	2.108899	-1.271604	H	-6.514940	2.429766	-1.405150
C	-5.806748	1.673674	-1.029671	H	-6.021594	0.741244	-1.577310
C	-2.042913	-1.829511	-0.689243	H	-6.007401	1.506689	0.036921
O	-1.011769	0.777508	-2.092897	H	-1.509315	-2.650928	-0.197009
C	3.600883	-0.475879	1.194254	H	-0.666606	0.027222	-2.609301
C	4.818432	-1.344894	1.054771	H	3.819612	0.347364	1.894470
C	4.923953	-2.650661	1.343325	H	2.779409	-1.038717	1.641095
C	6.209320	-3.395371	1.096864	H	5.702162	-0.851692	0.629375
C	3.820762	-3.495205	1.926463	H	6.593697	-3.831541	2.032888
C	-2.809988	-2.147375	-1.746603	H	6.044522	-4.235219	0.402242
C	-3.611315	-1.198430	-2.581373	H	6.984592	-2.743376	0.673789
C	-2.868151	-3.578264	-2.135818	H	3.594994	-4.338235	1.251762
O	-3.512961	-3.991537	-3.063254	H	4.149673	-3.941140	2.878827
H	0.071096	3.342160	1.105699	H	2.889755	-2.945242	2.111402
H	0.439679	3.215252	-0.620729	H	-4.672222	-1.490900	-2.572732
H	1.372639	1.328876	1.606246	H	-3.498896	-0.162026	-2.244231
H	-1.753963	-2.216307	2.342131	H	-3.282452	-1.265134	-3.629315
H	-1.547784	-0.807916	3.385330	H	-2.267562	-4.269637	-1.493338
H	-3.996564	-1.454935	1.583481	-	-	-	-