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Supplementary Information

Caged Polycyclic Polyprenylated Acylphloroglucinols as $Ca_v3.2$ Low Voltage-Gated Ca^{2+} Channel Inhibitors from *Hypericum curvisepalum*

Yan-Song Ye,‡[a] Rui Liu,‡[ac] Na-Na Jiang,‡[ab] Song-Yu Li,[a] Yin Nian*[a] and Gang Xu*[a]

1. Experimental Section

1.1 General experimental procedures

Optical rotations were measured on a Jasco P-1020 polarimeter. UV spectra were detected on a Shmadzu UV-2401PC spectrometer. IR spectra were determined on a Bruker FT-IR Tensor-27 infrared spectrophotometer with KBr disks. All 1D and 2D NMR spectra were recorded on Bruker AV-600 and 800 MHz spectrometers using TMS as an internal standard. Unless otherwise specified, chemical shifts (δ) were expressed in ppm with reference to the solvent signals. ESIMS and HRESIMS analysis were carried out on and Aglient G6200 TOF mass spectrometers, respectively. Semipreparative HPLC was performed on a waters 1525 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.

1.2 Plant material

The aerial parts of *Hypericum curvisepalum* were collected in Puan County, Guizhou 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 2018H02.

1.3 Extraction and isolation

The aerial plants of *H. curvisepalum* (25.0 kg) were powdered and extracted three times with MeOH at room temperature to give a crude extract (3.7 kg). The crude extract was subjected to silica gel column chromatography eluted with $CHCl_3$ to afford a fraction (811.6 g). This fraction was separated over an MCI-gel column (MeOH-H_2O from 70:30 to 100:0) to produce five fractions (Fr. A–E). Fraction A (15.9 g) was chromatographed on a silica gel column eluted with petroleum ether-acetone (400:1 to 0:1) to yield six fractions (Fr. A1–A6). Fr. A1 (4.2 g) was purified silica gel column chromatography and semipreparative HPLC (MeOH-H_2O, 95:5) to afford **5** (1.8 mg). Fraction B (47.0 g) was chromatographed on a silica gel column, eluted with petroleum ether-acetone (400:1 to 0:1), to yield eight fractions (Fr. B1–B8). Fr. B6 (697.4 mg) was further purified by preparative and semipreparative HPLC (MeOH-H_2O, 95:5) to afford **1** (2.5 mg) and **3** (2.7 mg). Fr. B5 (7.3 g) was further purified silica gel column chromatography and semipreparative HPLC (MeOH-H_2O, 90:10) to afford **4** (3.2 mg). Fraction C (11.7 g) was chromatographed on a silica gel column eluted with petroleum ether-ethyl acetate (300:1 to 0:1) to yield seven fractions (Fr. C1–C7). Fr. C4 (1.6 g) was purified silica gel column chromatography and semipreparative HPLC (MeOH-H_2O, 90:10) to afford **2** (24.5 mg).

1.4 Compounds properties

Hypercurpalone A (**1**): yellow gum; [α] −17.9 (*c* 0.13, MeOH); UV (MeOH) λ_{max} (log ε) 393 (2.88), 245 (5.41), 225 (5.22), 197 (5.94) nm; IR (KBr) ν_{max} 2966, 2925, 1727, 1697, 1446, 1389, 1223, 1185, 1109, 1003, 842, 803, 755, 688 cm^{-1}; ECD λ_{max} ($\Delta\varepsilon$) 200 (15.13), 223 (2.01), 230 (1.47), 257 (-5.20), 278 (-0.96), 298 (-1.97) nm; ^{1}H and ^{13}C NMR data, see Table 1; ESIMS *m/z* 501 $[M + H]^+$; HRESIMS *m/z* 501.3359 $[M + H]^+$ (calcd for $C_{34}H_{45}O_3$, 501.3363).

Hypercurpalone B (**3**): colorless gum; [α] +1.94 (*c* 0.10, MeOH); UV (MeOH) λ_{max} (log ε) 244 (3.40), 224 (3.76), 196 (3.25) nm; IR (KBr) ν_{max} 3428, 2954, 2926, 1737, 1703, 1685, 1448, 1390, 1370, 1233, 1260, 1075 cm^{-1}; ^{1}H and ^{13}C NMR data, see Table S1; ESIMS *m/z* 571 $[M + Na]^+$; HRESIMS *m/z* 571.3031 $[M + Na]^+$ (calcd for $C_{34}H_{44}O_6Na$, 571.3030).

1.5 Details for the structural elucidations of 3

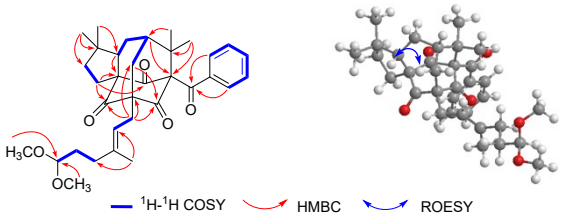

Fig. S1. Key ^{1}H-^{1}H COSY, HMBC, and ROESY correlations of **3.**

Hypercurpalone B (**3**) was assigned the molecular formula of $C_{34}H_{44}O_6$ from its ^{13}C NMR and HRESIMS data, suggesting 13 degrees of unsaturation. Its IR spectrum showed absorption attributable to carbonyl groups (1721 and 1689 cm^{-1}), and the UV spectrum exhibited characteristic maximum absorption of benzoyl group at 246 nm. The ^{13}C NMR and DEPT spectra exhibited 34 carbon signals, which were assigned as seven methyls (two methoxy groups), seven methylenes, four methines (one olefinic one), nine quaternary carbons (three carbonyls), and other seven signals assignable to a benzoyl group. These data indicated the presence of characteristic signals for a homoadamantane-type core skeleton (δ_C 82.8, C-1; 206.6, C-2; 76.3, C-3; 204.8, C-4; 69.0, C-5; 36.5, C-6; 43.4, C-7; 49.0, C-8; 204.3, C-9; 24.5, C-32; 56.5, C-33).[1] Detailed analysis of the NMR spectroscopic data showed **3** resembled to those of sampsonione H.[1] However, in addition to the two methoxyl signals (δ_C 53.4; δ_H 3.21, s), 32 carbon atoms indicated this structure must be a PPAP with losing three carbons. The key ^{1}H-^{1}H COSY correlations of H-28/H-27/H_2-26 and HMBC correlations from two methoxyl to C-28 confirmed that the geranyl of sampsonione H was oxidized to be a structure of hemiketal in **3** (Fig. S1). Finally, the relative configurations of **3** and 23*E* of the

geometry in the geranyl were defined by the rigid caged skeleton and correlations of H-33 with H-6 (δ_H 2.30) and Me-25 with H_2-22 in the ROESY spectrum (Fig. S1).

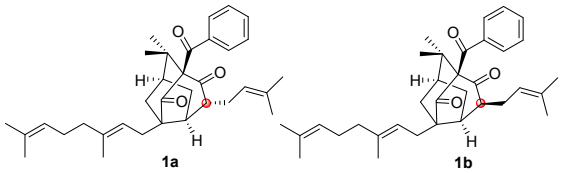

Fig. S2 Two possible isomers of **1.**

Table S1. The ^{1}H NMR and ^{13}C NMR data for 1 and 3.

No	1[a]		3[b]	
	δ_C	δ_H, mult, (*J*, Hz)	δ_C	δ_H, mult, (*J*, Hz)
1	84.2		82.8	
2	207.1		206.6	
3	54.6	2.67, m	76.3	
4	38.8	2.45, brd (10.5)	204.8	
5	60.0		69.0	
6	45.8	2.16 dd (12.0, 3.8)	36.5	2.41, dd (14.1, 7.0)
		1.88 dd (12.0, 3.8)		2.30, overlap
7	51.1	1.77, brs	43.4	2.09, t (7.6)
8	50.3		49.0	
9	211.3		204.3	
10	193.8		194.2	
11	137.5		136.4	
12	128.3	7.38, t (7.3)	129.6	6.93, d (6.9)
13	128.0	7.27, t (7.3)	129.2	7.22, t (6.9)
14	131.9	7.39, overlap	133.4	7.35, t (6.9)
15	128.0	7.27, t (7.3)	129.2	7.22, t (6.9)
16	128.3	7.38, t (7.3)	129.6	6.93, d (6.9)
17	26.0	2.64, m; 2.09, m	28.9	2.30, overlap
				2.25, m
18	120.7	5.03, t (7.2)	43.6	1.65, overlap
				1.59, overlap
19	134.3			
20	25.9	1.71, s		
21	17.7	1.59, s		
22	30.7	2.79, dd (14.2, 7.5)	30.3	2.49, dd (14.6, 7.5)
		2.22, dd (14.2, 7.5)		2.44, dd (14.6, 7.5)
23	119.1	5.25, t (7.2)	120.8	5.22, t (6.8)
24	138.6		139.0	
25	16.5	1.67, s	16.5	1.61, s
26	40.1	2.05, m	35.9	1.98, t (6.6)
27	26.6	2.13, overlap	32.1	1.59, overlap

28	123.9	5.11, t (7.2)	105.7	4.25, t (5.3)
29	131.8			
30	25.7	1.67, s		
31	17.8	1.61, s		
32	31.3	1.90, m; 1.58, m	24.5	1.83, t (14.9)
				1.74, m
33			56.5	1.93, dd (12.5, 7.2)
34			45.3	
35			28.6	0.94, s
36			21.0	0.86, s
37	25.0	1.30, s	25.6	1.30, s
38	23.3	1.24, s	22.8	1.27, s
28-OCH_3			53.4	3.21, s
28-OCH_3			53.4	3.21, s

[a]Recorded in $CDCl_3$ (600 MH_Z for ^1H NMR; 150 MH_Z for ^{13}C NMR).

[b]Recorded in MeOD (800 MH_Z for ^1H NMR; 200 MH_Z for ^{13}C NMR).

Reference

(1) Hu, L. H.; Sim, K. Y. *Tetrahedron Lett.* **1999**, *40*, 759–762.

(2) Max, J.; Heilmann, J. *Planta Med.* **2021**, *87*, 1167–1183.

1.6 Cell preparation and expression

Human embryonic kidney (HEK) 293T cells were grown in DMEM (HyClone) plus 10% newborn calf serum (Gibco) and penicillin (100 U/ml)/streptomycin (0.1 mg/ml) (Biological Industries). HEK 293T cells were transiently transfected with pCDNA3.1-T-type (Ca_v3.1-3.3) and pCDNA3.1-hERG, together with pCDNA3.1-EGFP plasmids using LipoD293™ (SignaGen Laboratories) and used in 48 hours.

1.7 Electrophysiology

All experiments were performed at room temperature (~22 °C). Pipettes were fabricated from borosilicate glass (World Precision Instru-ments) using a micropipette puller (P-1000, Sutter Instrument), and were fire-polished to resistances of 2~4 M for whole-cell recording. Currents were amplified by Double IPA (Sutter Instrument, USA), which is integrated patch clamp amplifiers with data acquisition system. Currents were low-pass filtered at 2 kHz and sampled at 10 kHz. SutterPatch2.1 software (Sutter Instrument) were used for data acquisition and analysis.

For T-type (Ca_v3.1-3.3) measurement, the extracellular solutions contained (in mM) 142 CsCl, 1 $MgCl_2$, 2 $CaCl_2$, 10 Glucose and 10 HEPES (pH 7.4 adjusted with CsOH). The intracellular solutions contained (in mM) 142 CsCl, 2 $MgCl_2$, 11 EGTA, 5 Na-ATP, 10 HEPES (pH 7.4 adjusted with CsOH). Peak currents of Ca_v3.1 and Ca_v3.2 were elicited by 150 ms depolarization to -40 mV at 4 s intervals from a holding potential (HP) of -100 mV. For Ca_v3.3, 400 ms depolarization to -40 mV was used to stimulate peak current. Family of currents (for I-V curve) for Ca_v3.1

and $Ca_v3.2$ were evoked from a HP of -100 mV by 150 ms depolarization from -80 mV to + 60 mV in 10 mV increasement at 4 s intervals. For $Ca_v3.3$, each step depolarization was 400 ms.

For hERG measurement, the extracellular solutions contained (in mM) NaCl 140, KCl 4, $MgCl_2 \cdot 6H_2O$ 1, $CaCl_2$ 2, Glucose 10, HEPES 10, (pH 7.4 adjusted with NaOH). The intracellular solutions contained (in mM) KCl 130, $MgCl_2 \cdot 6H_2O$ 1, EGTA 5, Na-ATP 5, HEPES 10 (pH 7.4 adjusted with KOH). I-V curves of hERG were evoked from a HP of -80 mV by 2000 ms incrementally increased voltage steps (in 10 mV) from -60 to +60 mV then repolarized to -50 by 2000 ms to evoke tail currents at 8 s intervals.

1.8 Animals and ethics

C57 mice weighing 18–22 g and aged 6–8 weeks were purchased from SKbex Biotechnology Co., Ltd. Generally, mice, half male and half femal, were randomly divided into 4 to 8 per group. Each animal was housed in a single cage to prevent fighting and freely ate food and water. The mice were maintained at a constant temperature (24 °C) and humidity (55％) with a 12 h light–dark cycle and were acclimatized to the environment for at least one week before the experiments. All the procedures and care and handling of the animals were approved by the Animal Care and Use Committee at Kunming Institute of Botany, Chinese Academy of Sciences.

1.9 Acetic acid induced writhing test in mice

Acetic acid-induced writhing test was performed as reported previously. Briefly, 0.9% (v/v) saline was used as the solvent in present study. Mice were intraperitoneally (i.p.) injected with vehicle (10 ml/kg; saline), Z944 (10 mg/kg), and **2** (20 mg/kg) 30 min before i.p. injection of 0.6%, 10 ml/kg body weight acetic acid. Number of abdominal writhes were counted for each group of mice once after the injection of acetic acid up to 30 minutes and expressed as percent protection. The percentage of protection against acetic acid was calculated using the following formula:

$$\text{Protection (\%)} = (Nc - Nt)/Nc \times 100\%$$

Nc: Number of writhing in model group; Nt: Number of writhing in test group. A writhe was defined as a contraction of the abdominal muscles following by body elongation and hind limbs' extension.

1.10 Data analysis and statistics

Data fitting and statistical analyses were per-formed using GraphPad Prism 8.0.1 (GraphPad Software Company, San Diego, CA, USA). IC_{50} value and Hill coefficient were determined by fitting the data points to a Hill equation with the form of $Y = I_{Min} + (I_{Max} - I_{Min})/[1 + 10(LogIC_{50} - C) \times Hillslope]$. Where IC_{50} is the concentration at which half-maximal currents were inhibited, C is the concentration of compounds, I_{Min} is the minimum inhibition ratio,

I_{Max} is the maximum inhibition ratio, and Hillslope is the Hill coefficient. Statistical significance was determined by $^{ns}P > 0.05$, $^{*}P < 0.05$, $^{**}P < 0.01$, $^{***}P < 0.001$; and using Student's t-test for comparing two groups. All the data were presented as mean ± SEM.

Table S2. Dose-related effects of compounds 1, 2, and mibefradil on peak currents of $Ca_v3.2$.

Cmp	Concentration (μM)	Inhibition Ratio (%)					Mean ± SEM
		Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	
1	0.3	7.3	5.7	6.9			6.6 ± 0.5 %
	1	11.4	12.1	11.8			11.7 ± 0.2 %
	3	22.9	25.6	35.6			28.0 ± 3.9 %
	10	61.4	48.5	52.2			54.0 ± 3.8 %
	30	83.6	84.5	75.2			81.1 ± 2.9 %
2	1	2.4	4.2	4.3	4.9	4.1	3.9 ± 0.4 %
	3	13.2	15.4	20.3	13.7	21.2	16.8 ± 1.7 %
	10	51.1	61.1	51.8	52	53.1	53.8 ± 1.8 %
	30	79.1	80.1	82.5	80.7	82.7	81.0 ± 0.7 %
Mibefradil	0.3	7.4	14.9	10.5			10.9 ± 3.8 %
	1	44.2	46.4	49.3			46.6 ± 2.6 %
	2	68.2	70.2	69.1			69.2 ± 1.0 %
	5	95.7	93.9	96.1			95.2 ± 1.2 %
	10	95.5	92.8	94.2			94.2 ± 1.4 %

Table S3. Dose-related effects of compound 2 on peak currents of $Ca_v3.3$.

Cmp	Concentration (μM)	Inhibition Ratio (%)					Mean ± SEM
		Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	
2	3	6.5	9.6	6.7	7.6	9.6	8.0 ± 0.7 %
	10	34.6	37.4	35.8	39.6	37.8	37.0 ± 1.0 %
	30	69.4	74.1	71.8	74.5	70	71.9 ± 1.0 %
	50	92.7	85.3	88	87.5	90.3	88.8 ± 1.3 %

Table S4. Inhibitions of compounds 2–5 on $Ca_v3.1$ peak currents.

Cmd	CONC (μM)	Stimulation ratio (%)			Mean ± SEM
		Exp. 1	Exp. 2	Exp. 3	
2	10	26.7	24.7	24.9	25.4 ± 0.6 %
3	10	9.1	11.3	8.7	9.7 ± 0.8 %
4	10	8.4	8.0	14.1	10.2 ± 2.0 %
5	10	31.4	46.8	37.9	38.7 ± 4.5 %

Cmd: Compound. CONC: Concentration

Table S5. Inhibitions of compounds 3–5 $Ca_v3.2$ peak currents.

Cmd	CONC (μM)	Stimulation ratio (%)			Mean ± SEM
		Exp. 1	Exp. 2	Exp. 3	
3	10	8.20	10.30	7.60	8.7 ± 0.8 %
4	10	34.00	24.30	31.00	29.8 ± 2.9 %
5	10	2.60	4.90	7.90	5.1 ± 1.5 %

Cmd: Compound. CONC: Concentration

Table S6. Inhibitions of compounds 3–5 on $Ca_v3.3$ peak currents.

Cmd	CONC (μM)	Stimulation ratio (%)			Mean ± SEM
		Exp. 1	Exp. 2	Exp. 3	
3	10	11.10	10.90	12.80	11.6 ± 0.6 %
4	10	14.30	20.50	22.00	18.9 ± 2.4 %
5	10	10.70	10.80	13.30	11.6 ± 0.9 %

Cmd: Compound. CONC: Concentration

Table S7. Protective effect of compound 2 and Z944 on writhing induced by acetic acid in mice

Groups	Dose	No. of writhes	% Protection
Acetic acid (n = 8)	10 ul/g, i.p.	28.1 ± 1.2	-
Saline (n = 4)	10 ul/g, i.p.	0	-
2 (n = 8)	20 mg/kg, i.p.	14.1 ± 1.1***	49.8 %
Z944 (n = 8)	10 mg/kg, i.p.	7.4 ± 0.7***	73.8 %

Data are represented as mean ± SEM. $^{**}P < 0.01$ / $^{***}P < 0.001$ *vs* acetic acid. Intraperitoneal injection: i.p.

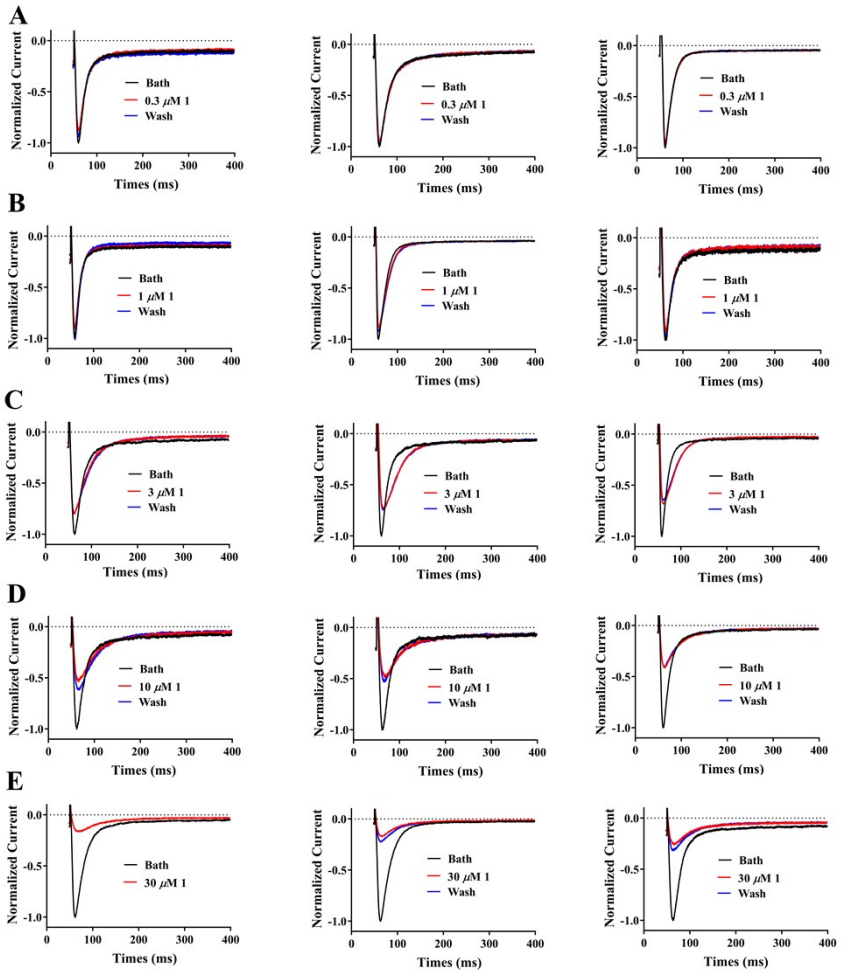

Fig. S3 Inhibitory effect of **1** on $Ca_v3.2$ at indicated concentrations. Representative $Ca_v3.2$ peak current traces were elicited by 150 ms depolarization to −40 mV at 4 s intervals from a HP of −100 mV, normalized by the peak current before drug exposure.

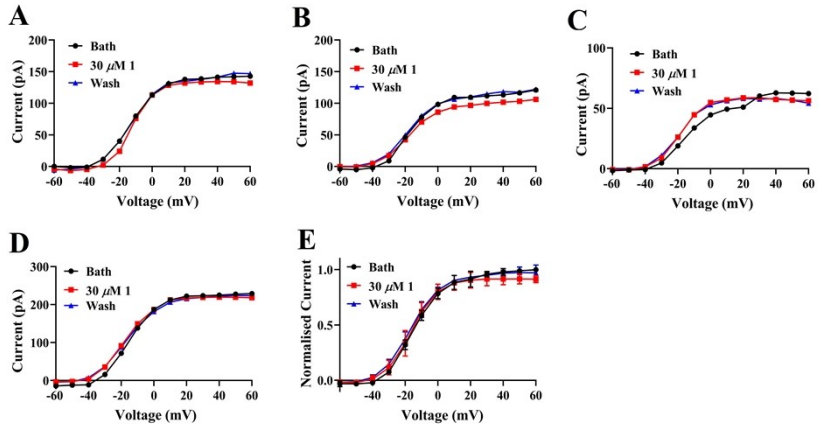

Fig. S4 Effect of **1** on hERG. **A-D** stand for four parallel experiments of I-V curves of hERG in the absence or presence of 30 μM **1.** I-V curves of hERG were evoked from a HP of -80 mV by 2000 ms incrementally increased voltage steps (in 10 mV) from -60 to +60 mV then repolarized to -50 by 2000 ms to evoke tail currents at 8 s intervals. **E** stands for the normalized I-V curves of hERG in the absence or presence of 30 μM **1**. All the data were represented as mean ± SEM (n = 4).

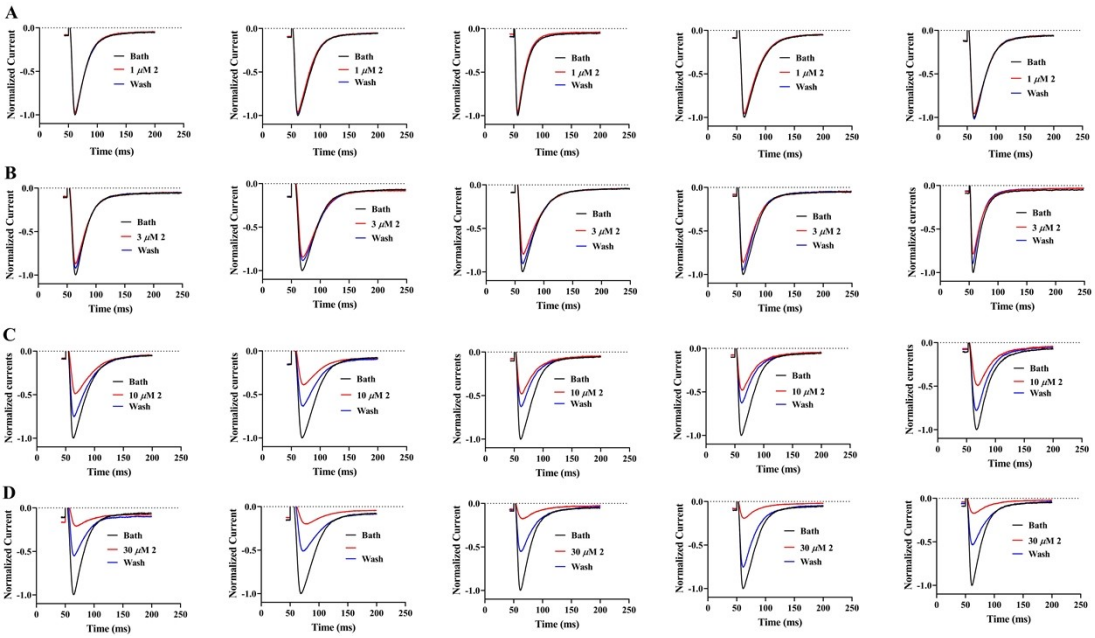

Fig. S5 Inhibitory effect of **2** on $Ca_v3.2$ at indicated concentrations. Representative $Ca_v3.2$ peak current traces were elicited by 150 ms depolarization to −40 mV at 4 s intervals from a HP of −100 mV, normalized by the peak current before drug exposure.

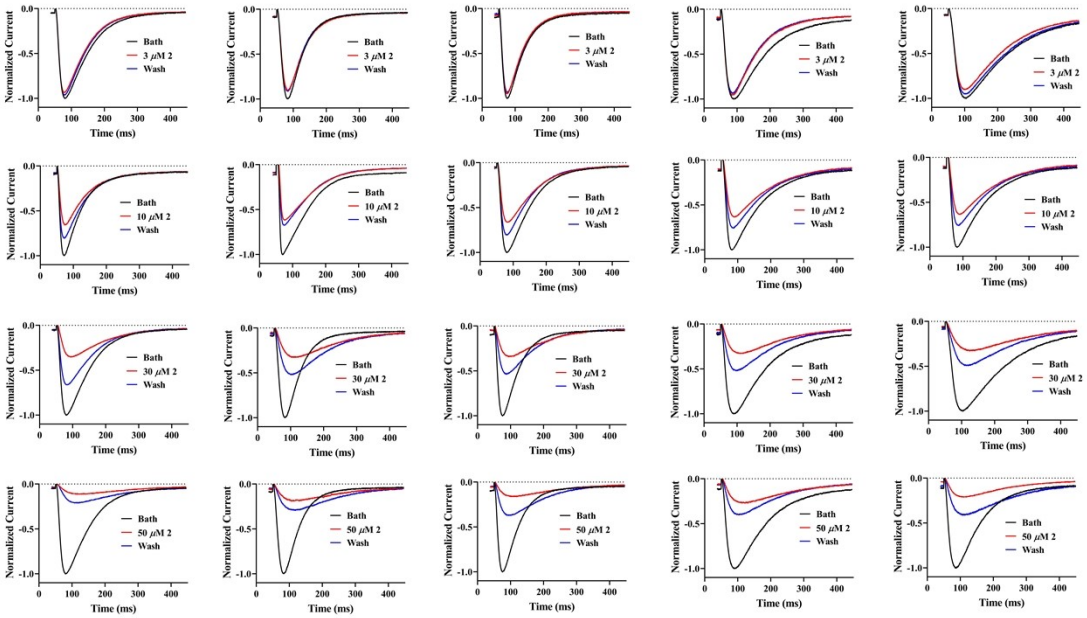

Fig. S6 Inhibitory effect of **2** on $Ca_v3.3$ at indicated concentrations. Representative $Ca_v3.3$ peak current traces were elicited by 150 ms depolarization to −40 mV at 4 s intervals from a HP of −100 mV, normalized by the peak current before drug exposure.

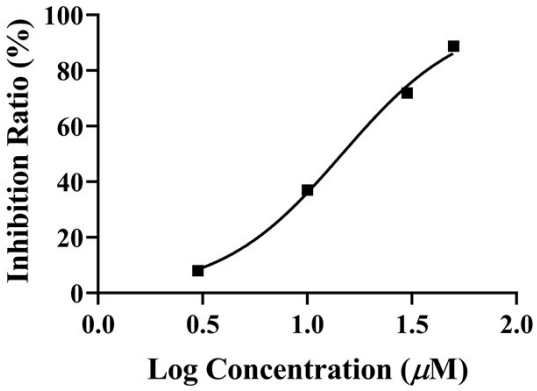

Fig. S7 Dose-response relationships of **2** for $Ca_v3.3$ at HP of −100 mV. Data points represent mean ± SEM of five measurements. The solid curves represent fit to the Hill equation. The IC_{50} value of **2** is 14.7 ± 0.8 μM. While, the Hill coefficient of **2** is 1.5.

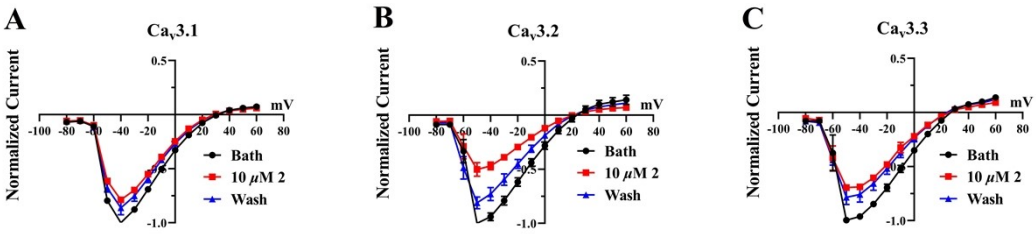

Fig. S8 Normalized current-voltage (I-V) curves of $Ca_v3.1$, $Ca_v3.2$, and $Ca_v3.3$ in the absence or presence of **2** at the concentration of 10 μM. $Ca_v3.1$ and $Ca_v3.2$ Currents were evoked from a HP of -100 mV by 150 ms depolarization from -80 mV to + 60 mV in 10 mV increasement at 4 s intervals. 400 ms depolarization stimuli were used to evoke $Ca_v3.3$ currents. Each concentration with 3 parallel tests.

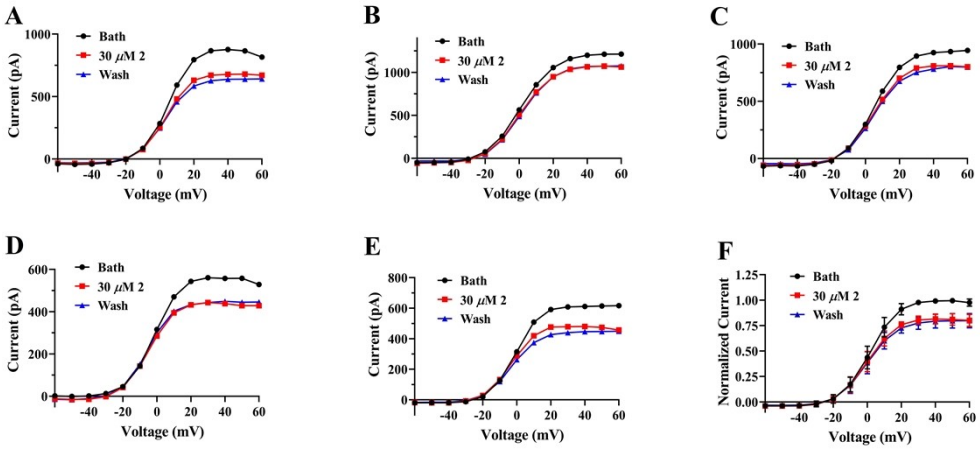

Fig. S9 Effect of **2** on hERG. **A-E** stand for five parallel experiments of I-V curves of hERG in the absence or presence of 30 μM **1.** I-V curves of hERG were evoked from a HP of -80 mV by 2000 ms incrementally increased voltage steps (in 10 mV) from -60 to +60 mV then repolarized to -50 by 2000 ms to evoke tail currents at 8 s intervals. **F** stands for the normalized I-V curves of hERG in the absence or presence of 30 μM **2**. All the data were represented as mean ± SEM (n = 5).

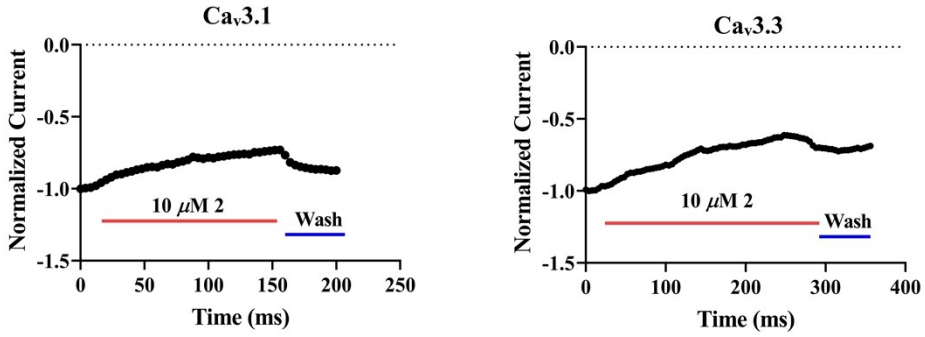

Fig. S10 Time courses of $Ca_v3.1$ and $Ca_v3.3$ peak currents inhibited by 10 μM **2**, respectively. Ordinate axis, peak current during steady-state exposure to indicated compound and washout, normalized by the peak current before drug exposure.

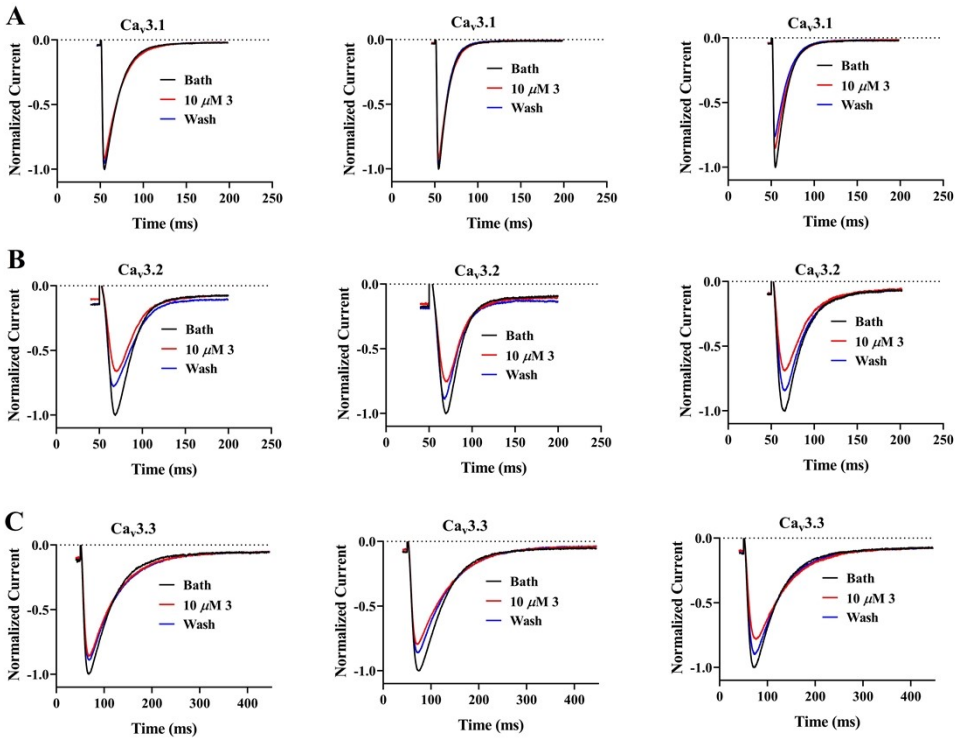

Fig. S11 Inhibitory effect of **3** on peak currents of $Ca_v3.1$, $Ca_v3.2$, and $Ca_v3.3$ at 10 μM. Representative $Ca_v3.1$ and $Ca_v3.2$ peak current traces were elicited by 150 ms depolarization to −40 mV at 4 s intervals from a HP of −100 mV, normalized by the peak current before drug exposure. 400 ms depolarization stimuli were used to evoke $Ca_v3.3$ peak currents.

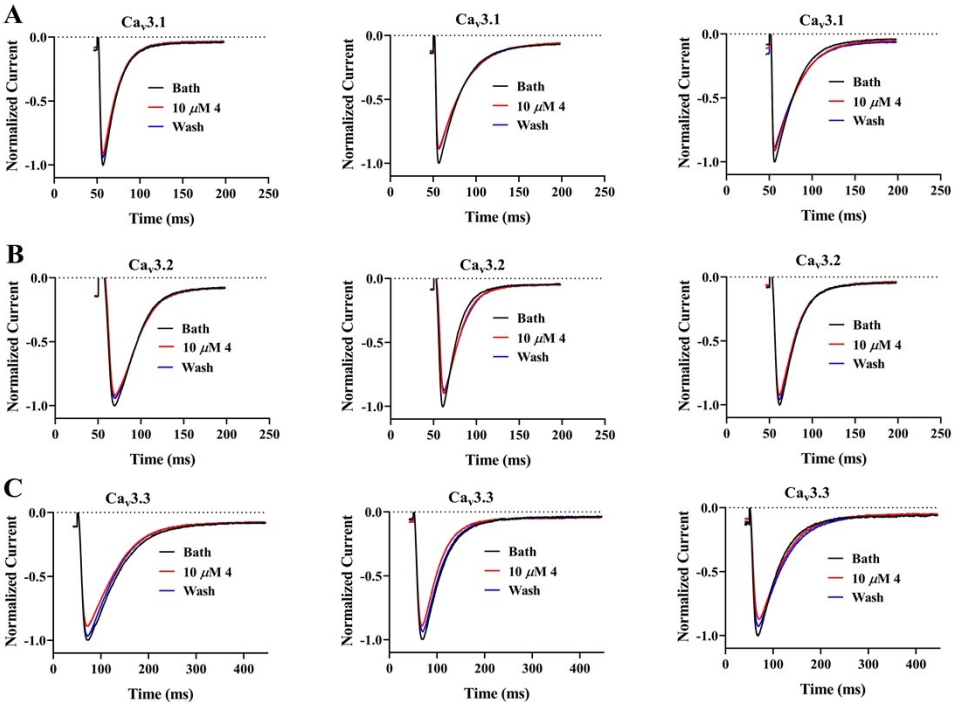

Fig. S12 Inhibitory effect of **4** on peak currents of $Ca_v3.1$, $Ca_v3.2$, and $Ca_v3.3$ at 10 μM. Representative $Ca_v3.1$ and $Ca_v3.2$ peak current traces were elicited by 150 ms depolarization to −40 mV at 4 s intervals from a HP of −100 mV, normalized by the peak current before drug exposure. 400 ms depolarization stimuli were used to evoke $Ca_v3.3$ peak currents.

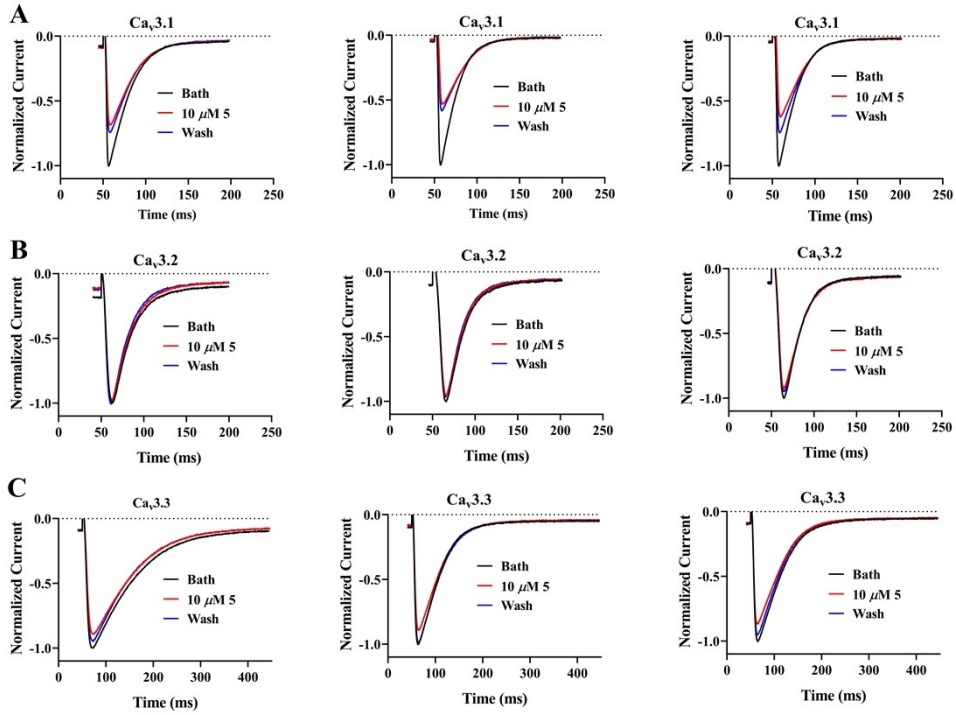

Fig. S13 Inhibitory effect of **5** on peak currents of $Ca_v3.1$, $Ca_v3.2$, and $Ca_v3.3$ at 10 μM. Representative $Ca_v3.1$ and $Ca_v3.2$ peak current traces were elicited by 150 ms depolarization to −40 mV at 4 s intervals from a HP of −100 mV, normalized by the peak current before drug exposure. 400 ms depolarization stimuli were used to evoke $Ca_v3.3$ peak currents.

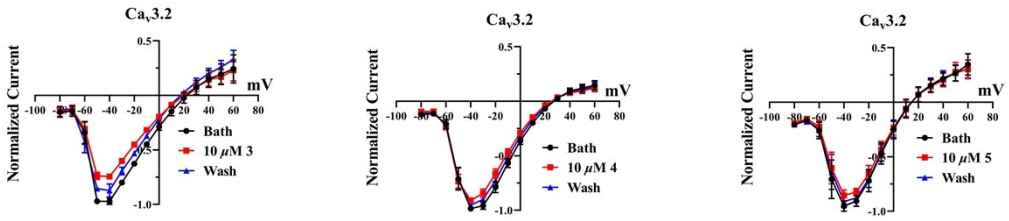

Fig. S14 Normalized current-voltage (I-V) curves of $Ca_v3.2$ in the absence or presence of **3-5** at the concentration of 10 μM. $Ca_v3.2$ Currents were evoked from a HP of -100 mV by 150 ms depolarization from -80 mV to + 60 mV in 10 mV increasement at 4 s intervals. Each concentration with 3 parallel tests.

2. Computational details of 1a and 1b

2.1 Computational method

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,p) level of theory in the gas phase. 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/6-311+G(2d,p) 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 Sarotti, *et al*.[3]

To provide more accurate calculated data, optimized conformers were reoptimized at M06-2X-D3/def2-SVP level, and energy of optimized conformers were evaluated at M06-2X-D3/def2-TZVP level. NMR shielding constants were calculated with the GIAO method at mPW1PW91/6-31+G(d,p) level in chloroform with IEFPCM solvent model. 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]

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

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(3) Grimblat, N.; Zanardi, M. M.; Sarotti, A. M. *J. Org. Chem.* **2015**, *80*, 12526−12534.

(4) Lu T.; Chen, F. W. *J. Comput. Chem.* **2012**, *33*, 580–592.

2.2 General computational data and results

Functional	Solvent?	Basis Set	Type of Data
mPW1PW91	PCM	6-31+G(d,p)	Shielding Tensors

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	100.00%	0.00%	–	–	–	–
sDP4+ (C data)	100.00%	0.00%	–	–	–	–
sDP4+ (all data)	100.00%	0.00%	–	–	–	–
uDP4+ (H data)	100.00%	0.00%	–	–	–	–
uDP4+ (C data)	100.00%	0.00%	–	–	–	–
uDP4+ (all data)	100.00%	0.00%	–	–	–	–
DP4+ (H data)	100.00%	0.00%	–	–	–	–
DP4+ (C data)	100.00%	0.00%	–	–	–	–
DP4+ (all data)	100.00%	0.00%	–	–	–	–

Fig. S15 The results of DP4+ analyses of **1a** (Isomer 1) and **1b** (Isomer 2).

Table S8. Experimental and calculated ^{13}C NMR chemical shifts of 1a and 1b.

No	δ_C (exptl.)	δ_C (calcd.)		No	δ_C (exptl.)	δ_C (calcd.)	
		1a	**1b**			**1a**	**1b**
1	84.2	85.777	88.007	19	134.3	135.809	135.89
2	207.1	206.059	208.361	20	25.9	28.29	27.559
3	54.6	58.211	59.533	21	17.7	20.731	21.094
4	38.8	40.906	39.394	22	30.7	35.093	34.064
5	60.0	63.243	58.79	23	119.1	123.118	120.574
6	45.8	49.638	48.845	24	138.6	140.006	140.105
7	51.1	53.542	52.381	25	16.5	19.161	19.902
8	50.3	53.474	52.978	26	40.1	43.912	43.654
9	211.3	210.224	210.896	27	26.6	28.609	29.632
10	193.8	190.168	197.054	28	123.9	125.084	125.237
11	137.5	133.653	138.585	29	131.8	135.09	133.289
12	128.3	129.071	128.859	30	25.7	28.815	29.382
13	128.0	125.977	125.183	31	17.8	20.809	20.467
14	131.9	130.582	128.775	32	31.3	34.782	39.267
15	128.0	125.977	125.183	37	25.0	27.091	26.643
16	128.3	129.071	128.859	38	23.3	24.45	24.754
17	26.0	29.346	33.709	**CMAE**		**1.2**	**1.6**
18	120.7	123.99	120.164	**CMaxErr**		**4.2**	**5.1**

Table S9. Experimental and calculated ^{1}H NMR chemical shifts of 1a and 1b.

No	δ_C (exptl.)	δ_C (calcd.)		No	δ_C (exptl.)	δ_C (calcd.)	
		1a	**1b**			**1a**	**1b**
3	2.67	3.19	2.33	22a	2.79	3.25	2.66
4	2.45	2.56	2.63	22b	2.22	1.83	2.42
6a	2.16	2.28	2.21	23	5.25	5.85	5.56
6b	1.88	1.86	2.09	25	1.67	1.89	1.76
7	1.77	1.63	1.53	26	2.05	2.22	2.26
12	7.38	8.01	7.65	27	2.13	2.46	2.29
13	7.27	7.71	7.57	28	5.11	5.52	5.34
14	7.39	7.78	7.59	30	1.67	1.67	1.60
15	7.27	7.71	7.57	31	1.61	1.36	1.56
16	7.38	8.01	7.65	32a	1.9	1.92	2.05
17a	2.64	2.59	2.15	32b	1.58	1.84	1.51
17b	2.09	2.03	1.89	37	1.30	1.36	1.41
18	5.03	5.43	4.75	38	1.24	1.29	1.23
20	1.71	1.83	1.43	**CMAE**		**0.13**	**0.19**
21	1.59	1.70	1.42	**CMaxErr**		**0.46**	**0.58**

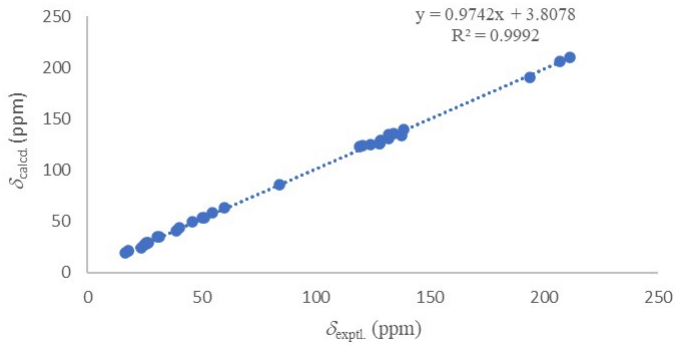


Fig. S16 Regression analysis of experimental versus calculated ^{13}C NMR chemical shifts of **1a**.

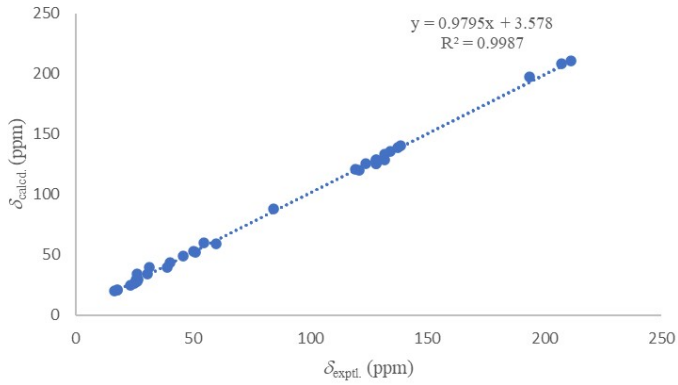


Fig. S17 Regression analysis of experimental versus calculated ^{13}C NMR chemical shifts of **1b**.

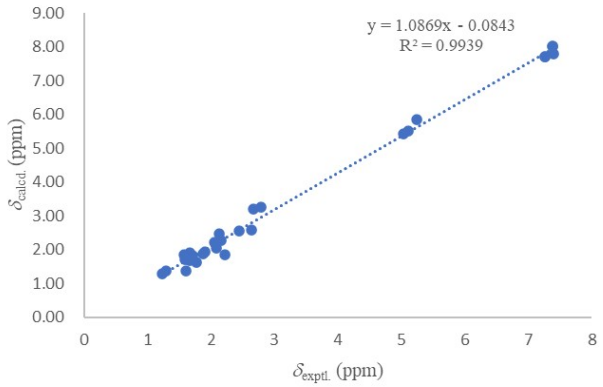


Fig. S18 Regression analysis of experimental versus calculated ^{1}H NMR chemical shifts of **1a**

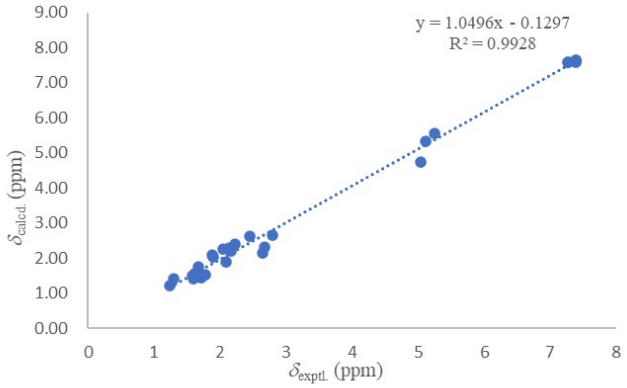


Fig. S19 Regression analysis of experimental versus calculated ^{1}H NMR chemical shifts of **1b**

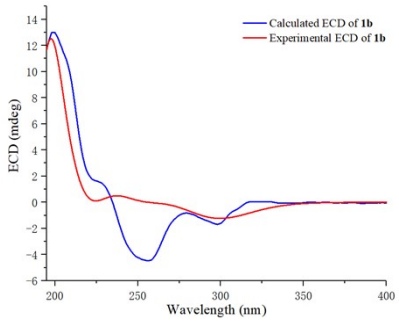


Fig. S20 Experimental and calculated ECD spectra of **1b**

2.3 Computational data of 1a

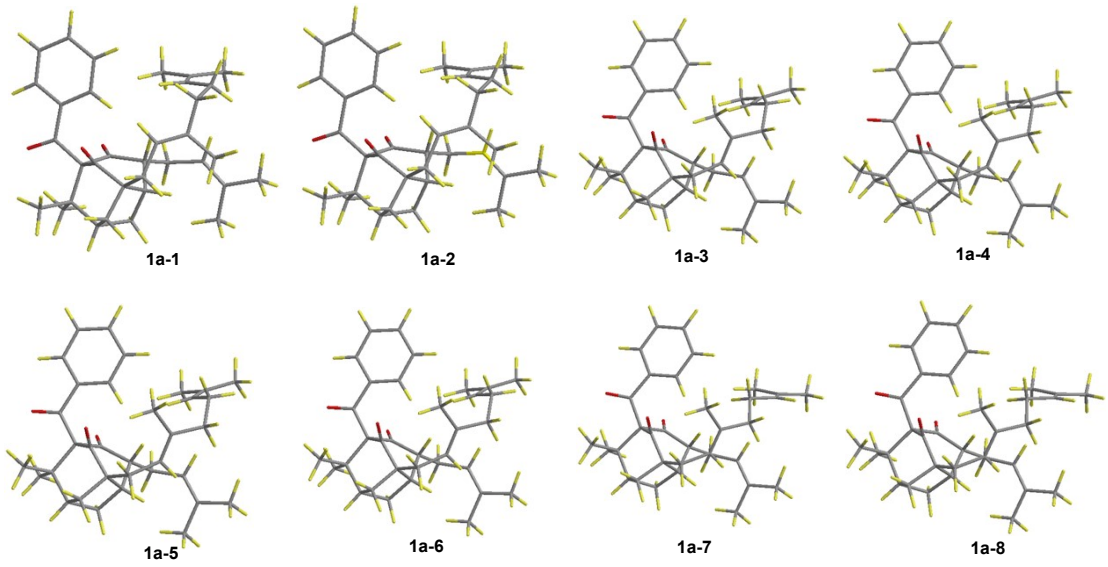


Fig. S21 Optimized geometries of 8 dominant conformers of **1a** at the B3LYP/6-31G(d) level of theory in the gas phase.

Table S10. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1a** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	ΔG (kcal/mol)[d]	Population[e]
1a-1	-1547.558482	0.626954	-970699.533864	0.0	27.82%
1a-2	-1547.55848	0.626965	-970699.525725	0.008139	27.44%
1a-3	-1547.557261	0.626756	-970698.892145	0.641719	9.41%
1a-4	-1547.557259	0.626767	-970698.883793	0.650071	9.28%
1a-5	-1547.557257	0.626766	-970698.883115	0.650749	9.27%
1a-6	-1547.557257	0.626771	-970698.88026	0.653604	9.22%
1a-7	-1547.556478	0.626833	-970698.352269	1.181595	3.78%
1a-8	-1547.55648	0.626838	-970698.350236	1.183628	3.77%

[a]Electronic energy obtained at M062X/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP/6-31G(d) 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 B3LYP/6-31G(d) level of theory in the gas phase.

C	0.482591	-0.664273	-0.695145	H	0.562277	-4.022934	-0.299925
C	1.469778	-0.727136	-1.876268	H	-0.094779	-3.024519	-1.583225
C	0.521409	-1.891620	0.222911	H	-1.818390	-4.354646	-0.021011
C	-0.945749	-0.464866	-1.174253	H	-0.379896	-3.842625	1.981290
C	-2.071996	-0.825212	-0.171662	H	-1.933195	-3.058175	2.303261
C	-1.533806	-0.770354	1.257201	H	-3.947672	-3.704516	0.591881
C	-0.359828	-1.713553	1.507962	H	-3.777205	-2.169010	1.456168
C	-0.057500	-3.141950	-0.497349	H	-4.702637	-2.227000	-0.038765
C	-1.438299	-3.340669	0.144902	H	-3.239475	-3.682892	-1.926801
C	-2.545201	-2.359980	-0.371170	H	-3.615653	-1.974309	-2.222338
C	-1.084391	-3.084420	1.616111	H	-1.978206	-2.576278	-2.491594
O	-1.227980	-0.033844	-2.274664	H	-0.907134	1.559910	0.530970
O	-2.080901	-0.145612	2.147445	H	-0.637461	3.974425	0.788198
C	-3.822323	-2.623168	0.462462	H	-2.513036	5.513448	0.247487
C	-2.855246	-2.659146	-1.846263	H	-4.667484	4.586388	-0.584972
C	-3.206407	0.207089	-0.419392	H	-4.923359	2.124702	-0.868294
C	-2.944230	1.668572	-0.196780	H	-0.275260	-1.385846	3.622320
O	-4.295578	-0.143475	-0.837873	H	1.194763	-2.075056	2.934262
C	-1.736702	2.202974	0.271290	H	0.259967	0.859188	2.905292
C	-1.582422	3.578192	0.428938	H	1.806384	2.496912	2.915294
C	-2.635068	4.441169	0.122931	H	3.434281	2.013912	3.382547
C	-3.843933	3.920630	-0.343397	H	4.277433	-0.270243	2.895198
C	-3.994579	2.547310	-0.502732	H	3.131191	-1.566442	2.515188
C	0.416520	-1.321382	2.774347	H	3.709925	-0.501241	1.240259
C	0.991476	0.070206	2.738307	H	3.659307	3.456105	1.506402
C	2.269002	0.433326	2.545539	H	4.067730	1.849612	0.945571
C	2.667286	1.892539	2.603861	H	1.148544	2.497746	0.553497
C	3.399543	-0.531403	2.290382	H	0.269879	2.776658	-1.607017
C	3.228124	2.468158	1.287608	H	1.195539	4.027869	-2.455856
C	2.177022	2.596121	0.210387	H	1.366545	2.343725	-2.929015
C	2.380992	2.851550	-1.090418	H	3.840723	3.998023	-2.185320
C	1.237341	3.002967	-2.060994	H	4.555270	2.941340	-0.956785
C	3.752184	3.019915	-1.693507	H	3.926887	2.262793	-2.470392
H	0.738839	0.218687	-0.090644	H	3.227088	0.292283	-1.070164
C	2.904566	-0.679918	-1.436663	H	5.462873	-2.072179	-0.099359
C	3.801238	-1.677675	-1.429012	H	5.938817	-1.690347	-1.750885
C	5.216101	-1.438288	-0.962571	H	5.378401	-0.394481	-0.675819
C	3.516210	-3.092659	-1.863238	H	4.184336	-3.392085	-2.682158
H	1.260497	-1.618757	-2.474301	H	3.706780	-3.791957	-1.037236
H	1.254700	0.124920	-2.527766	H	2.487076	-3.242184	-2.195093
H	1.558259	-2.055761	0.524432	-	-	-	-

Table S12. Atomic coordinates (Å) of **1a-2** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	0.482185	-0.664290	-0.695120	H	0.561066	-4.023031	-0.300374
C	1.469300	-0.727297	-1.876277	H	-0.095790	-3.024246	-1.583487
C	0.520740	-1.891781	0.222798	H	-1.819686	-4.354187	-0.021418
C	-0.946114	-0.464566	-1.174160	H	-0.380957	-3.842800	1.980938
C	-2.072415	-0.824674	-0.171516	H	-1.934069	-3.058055	2.303071
C	-1.534148	-0.770127	1.257315	H	-4.703400	-2.225825	-0.038622
C	-0.360410	-1.713679	1.507906	H	-3.948747	-3.703612	0.591776
C	-0.058501	-3.141858	-0.497628	H	-3.777867	-2.168259	1.456265
C	-1.439322	-3.340338	0.144651	H	-3.616464	-1.973028	-2.222261
C	-2.546030	-2.359290	-0.371192	H	-1.979245	-2.575567	-2.491680
C	-1.085299	-3.084393	1.615883	H	-3.240892	-3.681773	-1.926912
O	-1.228316	-0.033539	-2.274576	H	-0.907015	1.559958	0.532032
O	-2.081035	-0.145338	2.147655	H	-0.636275	3.974401	0.788682
C	-3.823153	-2.622273	0.462501	H	-2.510804	5.514213	0.246560
C	-2.856277	-2.658178	-1.846301	H	-4.665319	4.587962	-0.586693
C	-3.206512	0.207981	-0.419083	H	-4.922294	2.126323	-0.869336
C	-2.943705	1.669408	-0.196767	H	-0.275731	-1.386403	3.622319
O	-4.295912	-0.142214	-0.837274	H	1.194161	-2.075765	2.934068
C	-1.736134	2.203351	0.271719	H	0.260028	0.858681	2.905854
C	-1.581252	3.578538	0.429053	H	1.806866	2.496057	2.915777
C	-2.633318	4.441957	0.122268	H	3.434562	2.012493	3.383204
C	-3.842215	3.921877	-0.344494	H	4.277814	-0.270952	2.893634
C	-3.993470	2.548583	-0.503475	H	3.130972	-1.567439	2.516485
C	0.416053	-1.321901	2.774352	H	3.708139	-0.503637	1.239653
C	0.991330	0.069559	2.738604	H	3.660339	3.454863	1.507301
C	2.268934	0.432392	2.545811	H	4.068333	1.848295	0.946342
C	2.667638	1.891473	2.604390	H	1.149432	2.497623	0.553816
C	3.399130	-0.532655	2.290222	H	1.197570	4.027936	-2.455320
C	3.228874	2.467083	1.288305	H	1.367923	2.343782	-2.928689
C	2.178020	2.595557	0.210902	H	0.271264	2.777012	-1.606762
C	2.382328	2.850942	-1.089866	H	3.842992	3.997074	-2.183899
C	1.238880	3.002957	-2.060594	H	4.556649	2.939089	-0.955968
C	3.753693	3.018710	-1.692723	H	3.927922	2.261954	-2.470066
H	0.738660	0.218537	-0.090520	H	3.226729	0.291574	-1.069820
C	2.904111	-0.680442	-1.436725	H	5.378002	-0.395504	-0.675953
C	3.800705	-1.678274	-1.429586	H	5.462434	-2.073467	-0.100244
C	5.215622	-1.439176	-0.963151	H	5.938254	-1.690926	-1.751644
C	3.515524	-3.093047	-1.864398	H	2.486225	-3.242445	-2.195810
H	1.259781	-1.618821	-2.474374	H	4.183248	-3.392033	-2.683812
H	1.254421	0.124855	-2.527730	H	3.706553	-3.792753	-1.038849
H	1.557563	-2.056197	0.524267	-	-	-	-

Table S13. Atomic coordinates (Å) of **1a-3** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	0.173793	-1.046359	-0.813215	H	-0.994768	-4.197224	-0.367025
C	1.098200	-1.437931	-1.976718	H	-1.316845	-3.015621	-1.624205
C	-0.194287	-2.213884	0.110389	H	-3.293815	-3.613096	0.100573
C	-1.112291	-0.372734	-1.256146	H	-1.633418	-3.658560	1.987703
C	-2.216841	-0.255282	-0.172867	H	-2.752476	-2.344746	2.376354
C	-1.580364	-0.380220	1.215172	H	-4.950750	-2.206594	0.873200
C	-0.842609	-1.704873	1.440406	H	-4.165296	-0.809646	1.624728
C	-1.250436	-3.146533	-0.540430	H	-5.178762	-0.577443	0.206850
C	-2.553179	-2.812556	0.203591	H	-2.988128	-1.940602	-2.414606
C	-3.250266	-1.495467	-0.270136	H	-4.518878	-2.480759	-1.707997
C	-2.023889	-2.693497	1.640950	H	-4.252305	-0.762014	-2.054858
O	-1.290218	0.077854	-2.369854	H	-3.810449	3.503587	-0.977693
O	-1.770347	0.433427	2.100145	H	-2.630658	5.697089	-0.964080
C	-4.458075	-1.249155	0.667152	H	-0.230497	5.800890	-0.314232
C	-3.773755	-1.676401	-1.703840	H	0.965792	3.713556	0.318852
C	-2.905324	1.122097	-0.399772	H	-0.220726	1.576117	0.355525
C	-2.104147	2.388058	-0.326652	H	-0.360566	-1.080585	3.439757
O	-4.085311	1.187276	-0.696648	H	0.295260	-2.650219	2.983173
C	-2.768191	3.570826	-0.688094	H	2.134891	-1.686351	1.730985
C	-2.102352	4.791427	-0.680224	H	3.973992	0.613556	3.224043
C	-0.755590	4.849744	-0.315331	H	3.855940	-0.328530	1.737239
C	-0.084229	3.681766	0.046821	H	0.200341	0.914315	3.655182
C	-0.756258	2.461708	0.044959	H	1.747390	1.540927	4.282065
C	0.130364	-1.623156	2.628747	H	1.085978	2.138067	2.763945
C	1.475601	-1.027714	2.296303	H	3.257239	2.657906	2.066750
C	1.969743	0.175542	2.627739	H	4.687068	1.964319	1.329726
C	3.409103	0.509460	2.285044	H	1.842528	1.485679	0.237969
C	1.204285	1.235501	3.377312	H	2.780525	1.276067	-3.000279
C	3.613240	1.805650	1.469183	H	1.395357	1.750260	-1.994617
C	2.885266	1.781407	0.156742	H	2.390245	2.979505	-2.787669
C	3.338281	2.074580	-1.071668	H	5.188429	1.820105	-2.141282
C	2.420877	2.012137	-2.268164	H	4.770838	3.498531	-1.821192
C	4.752224	2.489408	-1.387434	H	5.408136	2.488409	-0.514169
H	0.707825	-0.304289	-0.200264	H	3.026149	-0.758132	-1.195491
C	2.496334	-1.668652	-1.475101	H	4.897995	-1.863992	-0.501445
C	3.121209	-2.837308	-1.270258	H	4.552960	-3.443856	0.232848
C	4.519650	-2.870790	-0.704398	H	5.216649	-3.365498	-1.395158
C	2.528132	-4.191604	-1.566084	H	1.516786	-4.138193	-1.974929
H	0.690385	-2.316490	-2.486628	H	3.153627	-4.742601	-2.281612
H	1.088128	-0.626129	-2.710560	H	2.489905	-4.803620	-0.654169
H	0.719678	-2.763729	0.343677	-	-	-	-

Table S14. Atomic coordinates (Å) of **1a-4** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	0.174360	-1.046447	-0.813026	H	-0.993106	-4.197666	-0.366325
C	1.099045	-1.437879	-1.976360	H	-1.315435	-3.016452	-1.623816
C	-0.193395	-2.213938	0.110747	H	-3.292403	-3.614287	0.100853
C	-1.111919	-0.373320	-1.256222	H	-1.632277	-3.658736	1.988250
C	-2.216627	-0.256086	-0.173115	H	-2.751834	-2.345205	2.376413
C	-1.580247	-0.380518	1.215032	H	-4.165137	-0.810767	1.624272
C	-0.842064	-1.704896	1.440593	H	-5.178511	-0.579348	0.206199
C	-1.249125	-3.147103	-0.540002	H	-4.949954	-2.208227	0.873010
C	-2.552074	-2.813450	0.203794	H	-4.517699	-2.482716	-1.708114
C	-3.249583	-1.496724	-0.270302	H	-4.251539	-0.763994	-2.055386
C	-2.023012	-2.693884	1.641204	H	-2.986983	-1.942341	-2.414610
O	-1.289845	0.076990	-2.370048	H	-3.812202	3.502361	-0.976762
O	-1.770467	0.433318	2.099775	H	-2.633448	5.696424	-0.962371
C	-4.457616	-1.250653	0.666776	H	-0.233128	5.801028	-0.313223
C	-3.772794	-1.678151	-1.704042	H	0.964350	3.713948	0.318440
C	-2.905690	1.120969	-0.400341	H	-0.221172	1.575897	0.354376
C	-2.105184	2.387324	-0.326734	H	-0.360333	-1.079853	3.439790
O	-4.085585	1.185594	-0.697704	H	0.295915	-2.649493	2.983743
C	-2.769896	3.569947	-0.687410	H	2.135388	-1.685487	1.731348
C	-2.104627	4.790867	-0.679132	H	3.973683	0.615503	3.223757
C	-0.757777	4.849635	-0.314630	H	3.855992	-0.326965	1.737151
C	-0.085745	3.681787	0.046729	H	1.746613	1.542520	4.281373
C	-0.757214	2.461425	0.044494	H	1.085176	2.138928	2.762975
C	0.130785	-1.622578	2.628997	H	0.199827	0.915188	3.654506
C	1.475872	-1.026869	2.296428	H	3.256261	2.659338	2.066011
C	1.969595	0.176656	2.627517	H	4.686313	1.966098	1.329083
C	3.408855	0.510989	2.284768	H	1.841835	1.486467	0.237589
C	1.203708	1.236602	3.376666	H	2.779765	1.277067	-3.001061
C	3.612542	1.807085	1.468612	H	1.394481	1.750240	-1.995080
C	2.884506	1.782384	0.156211	H	2.388591	2.980241	-2.787910
C	3.337369	2.075387	-1.072296	H	5.187324	1.821390	-2.142370
C	2.419829	2.012734	-2.268685	H	4.769638	3.499698	-1.821735
C	4.751218	2.490450	-1.388254	H	5.407311	2.489270	-0.515122
H	0.708089	-0.304099	-0.200146	H	3.026656	-0.757272	-1.194992
C	2.497205	-1.668029	-1.474522	H	4.554067	-3.441977	0.234256
C	3.122449	-2.836437	-1.269375	H	5.218041	-3.364230	-1.393670
C	4.520808	-2.869353	-0.703265	H	4.898894	-1.862378	-0.500703
C	2.529914	-4.190989	-1.565169	H	2.492457	-4.803213	-0.653366
H	0.691613	-2.316653	-2.486208	H	1.518344	-4.138013	-1.973516
H	1.088786	-0.626175	-2.710310	H	3.155347	-4.741506	-2.281127
H	0.720753	-2.763390	0.344238	-	-	-	-

Table S15. Atomic coordinates (Å) of **1a-5** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	0.173961	-1.046510	-0.813053	H	-0.994542	-4.197326	-0.366600
C	1.098536	-1.438185	-1.976403	H	-1.316493	-3.015886	-1.623979
C	-0.194192	-2.213888	0.110664	H	-3.293659	-3.613242	0.100636
C	-1.112070	-0.372916	-1.256228	H	-1.633495	-3.658366	1.987982
C	-2.216775	-0.255377	-0.173132	H	-2.752661	-2.344523	2.376314
C	-1.580578	-0.380159	1.215026	H	-4.950831	-2.206641	0.872797
C	-0.842706	-1.704697	1.440500	H	-4.165409	-0.809675	1.624331
C	-1.250225	-3.146667	-0.540178	H	-5.178693	-0.577522	0.206312
C	-2.553085	-2.812639	0.203632	H	-4.252158	-0.762434	-2.055205
C	-3.250173	-1.495659	-0.270372	H	-2.987722	-1.940780	-2.414818
C	-2.023975	-2.693371	1.641054	H	-4.518436	-2.481241	-1.708358
O	-1.289785	0.077650	-2.369982	H	-3.810593	3.503566	-0.977521
O	-1.770752	0.433583	2.099885	H	-2.630948	5.697150	-0.963311
C	-4.458089	-1.249234	0.666744	H	-0.230765	5.800918	-0.313494
C	-3.773471	-1.676732	-1.704131	H	0.965663	3.713484	0.318985
C	-2.905292	1.121954	-0.400291	H	-0.220679	1.575955	0.355065
C	-2.104209	2.387958	-0.326818	H	-0.360879	-1.080015	3.439780
O	-4.085177	1.187048	-0.697586	H	0.295077	-2.649713	2.983529
C	-2.768333	3.570792	-0.687922	H	2.134839	-1.685993	1.731471
C	-2.102576	4.791440	-0.679723	H	3.973299	0.614918	3.224281
C	-0.755803	4.849739	-0.314845	H	3.855847	-0.327889	1.737885
C	-0.084360	3.681695	0.046956	H	0.199484	0.915085	3.654316
C	-0.756313	2.461590	0.044783	H	1.746326	1.541799	4.281732
C	0.130144	-1.622720	2.628915	H	1.085511	2.138683	2.763258
C	1.475389	-1.027251	2.296490	H	3.256563	2.658605	2.065832
C	1.969310	0.176158	2.627697	H	4.686697	1.964868	1.329567
C	3.408682	0.510263	2.285181	H	1.842568	1.485314	0.237136
C	1.203553	1.236214	3.376830	H	2.391160	2.978513	-2.789023
C	3.612838	1.806105	1.468773	H	2.781080	1.274850	-3.000532
C	2.885260	1.781293	0.156124	H	1.395774	1.749961	-1.995487
C	3.338520	2.074377	-1.072217	H	4.771048	3.498765	-1.821040
C	2.421424	2.011444	-2.268944	H	5.408197	2.488290	-0.514206
C	4.752464	2.489498	-1.387617	H	5.188896	1.820471	-2.141576
H	0.707901	-0.304330	-0.200152	H	3.026398	-0.758303	-1.194978
C	2.496600	-1.668850	-1.474536	H	4.898134	-1.864138	-0.500508
C	3.121393	-2.837499	-1.269386	H	4.552778	-3.443747	0.234188
C	4.519727	-2.870959	-0.703240	H	5.216813	-3.365950	-1.393712
C	2.528343	-4.191829	-1.565173	H	1.516942	-4.138464	-1.973892
H	0.690814	-2.316795	-2.486297	H	3.153782	-4.742762	-2.280804
H	1.088550	-0.626421	-2.710283	H	2.490270	-4.803874	-0.653272
H	0.719758	-2.763677	0.344160	-	-	-	-

Table S16. Atomic coordinates (Å) of **1a-6** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	0.173538	-1.046688	-0.813319	H	-0.996241	-4.197047	-0.366886
C	1.097902	-1.438640	-1.976764	H	-1.317805	-3.015458	-1.624206
C	-0.195031	-2.213977	0.110372	H	-3.295099	-3.611997	0.100501
C	-1.112226	-0.372493	-1.256342	H	-1.634800	-3.657940	1.987738
C	-2.216828	-0.254609	-0.173141	H	-2.753375	-2.343642	2.376221
C	-1.580521	-0.379737	1.214968	H	-4.951714	-2.204748	0.872681
C	-0.843204	-1.704589	1.440299	H	-4.165530	-0.808372	1.624496
C	-1.251491	-3.146271	-0.540411	H	-5.178710	-0.575369	0.206523
C	-2.554157	-2.811741	0.203507	H	-4.252595	-0.760801	-2.055101
C	-3.250715	-1.494417	-0.270371	H	-2.988609	-1.939586	-2.414847
C	-2.024896	-2.692763	1.640887	H	-4.519447	-2.479539	-1.708274
O	-1.289879	0.078180	-2.370059	H	-3.809162	3.505244	-0.976289
O	-1.770308	0.433993	2.099911	H	-2.628557	5.698296	-0.961629
C	-4.458469	-1.247557	0.666823	H	-0.228112	5.800761	-0.312557
C	-3.774214	-1.675281	-1.704100	H	0.967529	3.712574	0.318987
C	-2.904736	1.123036	-0.400143	H	-0.219845	1.575644	0.354972
C	-2.103135	2.388673	-0.326302	H	-0.360971	-1.080318	3.439622
O	-4.084577	1.188678	-0.697537	H	0.294201	-2.650279	2.983177
C	-2.766811	3.571917	-0.686898	H	2.134542	-1.687437	1.731516
C	-2.100507	4.792260	-0.678480	H	3.973859	0.612655	3.223925
C	-0.753602	4.849835	-0.313982	H	3.855925	-0.329942	1.737438
C	-0.082602	3.681381	0.047304	H	1.747109	1.541127	4.280921
C	-0.755121	2.461599	0.044998	H	1.086523	2.137872	2.762292
C	0.129758	-1.623169	2.628678	H	0.200067	0.914789	3.653647
C	1.475284	-1.028309	2.296299	H	3.258400	2.656861	2.065733
C	1.969635	0.174992	2.627250	H	4.687893	1.962315	1.329025
C	3.409209	0.508398	2.284807	H	1.843582	1.483140	0.237117
C	1.204250	1.235509	3.376076	H	2.781423	1.275946	-3.001128
C	3.613978	1.804190	1.468497	H	1.396008	1.748985	-1.995242
C	2.886050	1.779828	0.156010	H	2.390135	2.979092	-2.787887
C	3.338767	2.074118	-1.072242	H	4.770050	3.500783	-1.819124
C	2.421364	2.011546	-2.268744	H	5.408604	2.488035	-0.514765
C	4.752294	2.490622	-1.387732	H	5.188604	1.823388	-2.143341
H	0.707820	-0.304783	-0.200416	H	3.026236	-0.759553	-1.195799
C	2.495906	-1.669902	-1.474978	H	4.551043	-3.445308	0.234396
C	3.120046	-2.838828	-1.269435	H	5.215164	-3.368551	-1.393519
C	4.518354	-2.872878	-0.703263	H	4.897331	-1.866195	-0.500917
C	2.526241	-4.192931	-1.564747	H	2.487371	-4.804474	-0.652543
H	0.689798	-2.317038	-2.486714	H	1.515055	-4.139122	-1.973933
H	1.088205	-0.626800	-2.710561	H	3.151636	-4.744644	-2.279813
H	0.718720	-2.764126	0.343778	-	-	-	-

Table S17. Atomic coordinates (Å) of **1a-7** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	0.036134	-0.983792	-0.780175	H	-1.444911	-4.034820	-0.713784
C	1.046249	-1.348162	-1.877980	H	-1.553154	-2.724992	-1.877558
C	-0.512563	-2.185504	0.004239	H	-3.713757	-3.278986	-0.367163
C	-1.154520	-0.192302	-1.282873	H	-2.226623	-3.635500	1.628275
C	-2.320361	-0.034579	-0.272000	H	-3.256058	-2.259414	2.047680
C	-1.816823	-0.321626	1.145746	H	-5.298378	-1.774669	0.421822
C	-1.227801	-1.726335	1.320779	H	-4.441209	-0.530433	1.344615
C	-1.590536	-2.953536	-0.808469	H	-5.317609	-0.081322	-0.111101
C	-2.918237	-2.561860	-0.137155	H	-4.719343	-1.877926	-2.127928
C	-3.457763	-1.149803	-0.539772	H	-4.249280	-0.178976	-2.317411
C	-2.501538	-2.612705	1.341249	H	-3.094356	-1.460064	-2.693764
O	-1.223345	0.307871	-2.386953	H	-0.208173	1.553360	0.629205
O	-1.999017	0.444978	2.073358	H	1.228104	3.531176	0.710013
C	-4.701850	-0.858873	0.334814	H	0.405840	5.719937	-0.123556
C	-3.894888	-1.164332	-2.013110	H	-1.894324	5.898143	-1.058914
C	-2.835816	1.422339	-0.438359	H	-3.342965	3.875138	-1.159251
C	-1.881583	2.573186	-0.295374	H	-0.858396	-1.299080	3.398888
O	-3.990014	1.647743	-0.755612	H	-0.288115	-2.880674	2.863098
C	-0.585994	2.485205	0.232539	H	1.672686	-1.945777	1.752518
C	0.229563	3.613394	0.294523	H	3.633016	0.435825	3.127846
C	-0.234933	4.843907	-0.170824	H	3.414018	-0.667980	1.770519
C	-1.525171	4.943935	-0.694201	H	-0.123383	0.630465	3.852794
C	-2.339634	3.818342	-0.753195	H	1.469075	1.140791	4.468756
C	-0.351345	-1.820134	2.583541	H	0.799033	1.865334	3.010697
C	1.040880	-1.294594	2.355805	H	2.140601	1.328770	0.627414
C	1.581939	-0.126829	2.735059	H	2.887729	2.334742	1.857550
C	2.983086	0.205957	2.270902	H	5.190988	1.304475	1.051937
C	0.886577	0.921420	3.563489	H	5.946417	2.531587	-2.039728
C	3.008865	1.401886	1.287889	H	6.550488	1.423264	-0.790075
C	4.273110	1.446437	0.478504	H	5.793222	0.792992	-2.267502
C	4.390451	1.615882	-0.847775	H	3.361848	2.821897	-2.302373
C	5.744848	1.589290	-1.511860	H	3.220945	1.091155	-2.581518
C	3.240101	1.855948	-1.793728	H	2.262206	1.865355	-1.308209
H	0.549339	-0.331469	-0.057532	H	2.939760	-0.785717	-0.926751
C	2.388899	-1.658131	-1.276402	H	4.707471	-1.973291	-0.158921
C	2.955054	-2.856838	-1.074730	H	4.253253	-3.556661	0.507993
C	4.307612	-2.959828	-0.413340	H	5.031485	-3.465027	-1.067850
C	2.337538	-4.174699	-1.467672	H	1.360664	-4.066190	-1.944348
H	0.656300	-2.179967	-2.473673	H	2.993155	-4.720740	-2.159604
H	1.128290	-0.495090	-2.560235	H	2.212186	-4.819961	-0.587081
H	0.323619	-2.840424	0.257369	-	-	-	-

Table S18. Atomic coordinates (Å) of **1a-8** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	0.035931	-0.983557	-0.780424	H	-1.445468	-4.034425	-0.714766
C	1.045913	-1.347730	-1.878428	H	-1.553716	-2.724227	-1.878122
C	-0.512842	-2.185422	0.003722	H	-3.714201	-3.278442	-0.367638
C	-1.154697	-0.191821	-1.282795	H	-2.226915	-3.635664	1.627533
C	-2.320439	-0.034238	-0.271744	H	-3.256142	-2.259571	2.047427
C	-1.816739	-0.321704	1.145850	H	-5.298598	-1.774143	0.421876
C	-1.227892	-1.726533	1.320466	H	-4.441227	-0.530222	1.344903
C	-1.590994	-2.953097	-0.809097	H	-5.317694	-0.080662	-0.110626
C	-2.918580	-2.561465	-0.137526	H	-4.719680	-1.876913	-2.127984
C	-3.457978	-1.149231	-0.539718	H	-4.249641	-0.177904	-2.317010
C	-2.501736	-2.612754	1.340821	H	-3.094740	-1.458870	-2.693834
O	-1.223601	0.308635	-2.386743	H	-0.208271	1.553475	0.630423
O	-1.998776	0.444676	2.073687	H	1.228548	3.530954	0.710820
C	-4.701977	-0.858390	0.335041	H	0.407034	5.719637	-0.123646
C	-3.895219	-1.163348	-2.013025	H	-1.892930	5.898172	-1.059461
C	-2.835707	1.422814	-0.437657	H	-3.342092	3.875507	-1.159414
C	-1.881192	2.573452	-0.294877	H	-0.858251	-1.299816	3.398637
O	-3.989931	1.648481	-0.754629	H	-0.288225	-2.881367	2.862466
C	-0.585723	2.485286	0.233318	H	1.672504	-1.946417	1.751684
C	0.230105	3.613285	0.295105	H	3.633540	0.434134	3.127728
C	-0.233974	4.843769	-0.170742	H	3.414062	-0.668907	1.769853
C	-1.524091	4.943979	-0.694388	H	-0.122759	0.629249	3.853265
C	-2.338845	3.818580	-0.753166	H	1.469852	1.139012	4.469292
C	-0.351338	-1.820759	2.583135	H	0.799815	1.864350	3.011632
C	1.040923	-1.295361	2.355350	H	2.140814	1.328814	0.628105
C	1.582283	-0.127866	2.735005	H	2.888525	2.333879	1.858612
C	2.983409	0.204855	2.270779	H	5.191350	1.304119	1.051886
C	0.887217	0.920168	3.563981	H	5.945618	2.531077	-2.040565
C	3.009277	1.401318	1.288382	H	6.550451	1.423834	-0.790323
C	4.273305	1.446022	0.478709	H	5.793047	0.792268	-2.267127
C	4.390308	1.615545	-0.847598	H	2.261815	1.863356	-1.307871
C	5.744556	1.589059	-1.512010	H	3.360474	2.822577	-2.300496
C	3.239773	1.855732	-1.793292	H	3.221524	1.092082	-2.582204
H	0.549240	-0.331450	-0.057666	H	2.939755	-0.785548	-0.927656
C	2.388630	-1.657883	-1.277086	H	4.707173	-1.973440	-0.159625
C	2.954541	-2.856694	-1.075322	H	4.252850	-3.556816	0.507182
C	4.307167	-2.959903	-0.414104	H	5.030910	-3.465126	-1.068741
C	2.336644	-4.174482	-1.467917	H	1.360290	-4.065759	-1.945610
H	0.655857	-2.179404	-2.474241	H	2.992621	-4.721393	-2.158813
H	1.127897	-0.494521	-2.560511	H	2.210060	-4.819053	-0.586987
H	0.323262	-2.840531	0.256609	-	-	-	-

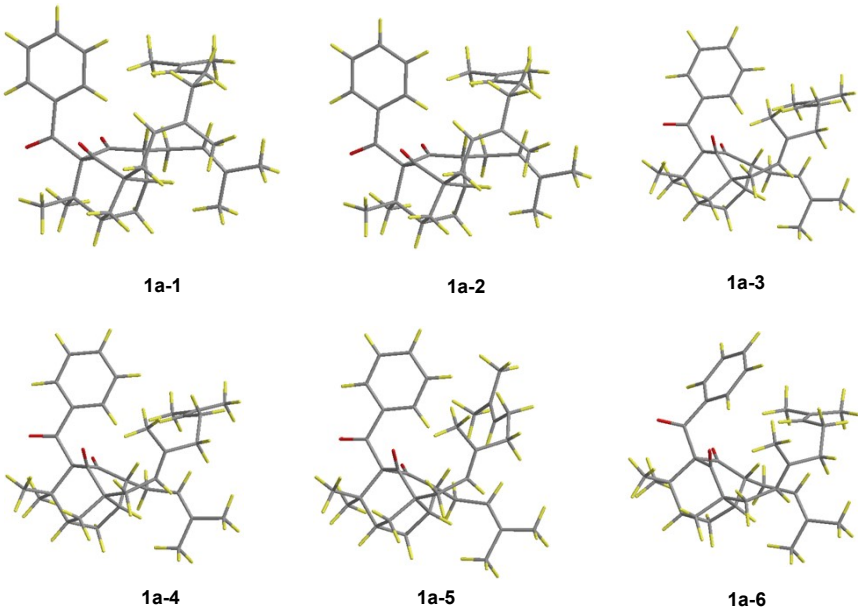


Fig. S22 Optimized geometries of 6 dominant conformers of **1a** at the M062X/def2SVP level of theory in the gas phase.

Table S19. Conformational analysis of the M062X/def2SVP optimized conformers of **1a** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	ΔG (kcal/mol)[d]	Population[e]
1a-1	-1547.669338	0.641787	-970759.788566	0.0	25.42%
1a-2	-1547.669337	0.641846	-970759.750352	0.038215	23.83%
1a-3	-1547.668058	0.640749	-970759.636134	0.152432	19.65%
1a-4	-1547.668056	0.640751	-970759.633957	0.15461	19.58%
1a-5	-1547.66798	0.641568	-970759.073762	0.714804	7.60%
1a-6	-1547.667169	0.641383	-970758.680652	1.107914	3.91%

[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 S20. Atomic coordinates (Å) of **1a-1** obtained at the M062X/def2SVP level of theory in the gas phase.

C	0.564229	-0.572298	-0.663343	H	0.896682	-3.919211	-0.317052
C	1.566881	-0.526720	-1.823040	H	0.179191	-2.940988	-1.598699
C	0.684098	-1.803486	0.237213	H	-1.453688	-4.433556	-0.077894
C	-0.865028	-0.482390	-1.167669	H	-0.086738	-3.838001	1.954865
C	-1.972491	-0.944290	-0.191215	H	-1.710745	-3.171776	2.259405
C	-1.461330	-0.859000	1.244090	H	-3.588308	-3.947702	0.580055
C	-0.224310	-1.712265	1.504190	H	-3.610295	-2.356942	1.379077
C	0.214695	-3.078584	-0.508632	H	-4.488569	-2.587340	-0.138478
C	-1.152162	-3.391828	0.108900	H	-2.898963	-3.851913	-1.980958
C	-2.319405	-2.495213	-0.411487	H	-3.381725	-2.161817	-2.278619
C	-0.844337	-3.128078	1.585864	H	-1.694952	-2.656947	-2.520338
O	-1.157929	-0.068310	-2.259313	H	-0.992035	1.506099	0.528479
O	-2.059741	-0.293298	2.124198	H	-0.944779	3.934488	0.884452
C	-3.578612	-2.861430	0.402291	H	-2.964377	5.312465	0.425755
C	-2.581473	-2.801810	-1.889634	H	-5.037931	4.224914	-0.424929
C	-3.180912	-0.012573	-0.439550	H	-5.072372	1.754426	-0.805255
C	-3.048327	1.465296	-0.168188	H	-0.231227	-1.344062	3.609729
O	-4.216274	-0.436609	-0.887587	H	1.307594	-1.965500	2.980598
C	-1.888992	2.085639	0.308265	H	0.204462	0.921604	2.856945
C	-1.858372	3.462514	0.518203	H	1.678445	2.634348	2.828782
C	-2.989405	4.234642	0.257974	H	3.350321	2.246711	3.260323
C	-4.150577	3.625274	-0.217685	H	4.271748	-0.000275	2.924857
C	-4.177340	2.250993	-0.430533	H	3.199886	-1.372540	2.552244
C	0.487946	-1.260098	2.780881	H	3.749247	-0.298208	1.256922
C	0.981628	0.160531	2.718058	H	3.476503	3.604568	1.311092
C	2.239662	0.585140	2.517850	H	3.875003	1.977689	0.781015
C	2.563442	2.061963	2.509926	H	0.918749	2.573639	0.532665
C	3.420053	-0.326143	2.307372	H	-0.063228	2.749609	-1.594068
C	3.044419	2.601399	1.154696	H	0.744239	4.118550	-2.399506
C	1.934713	2.687122	0.135642	H	0.994621	2.477695	-3.000842
C	2.062772	2.934834	-1.176657	H	3.437404	4.113563	-2.337553
C	0.867204	3.070065	-2.081280	H	4.240536	3.055549	-1.151800
C	3.395199	3.127420	-1.847695	H	3.533992	2.374536	-2.641406
H	0.729425	0.324116	-0.035596	H	3.306140	0.523320	-0.984599
C	2.993761	-0.456271	-1.362905	H	5.521841	-1.829540	0.032694
C	3.901867	-1.443417	-1.341844	H	6.042993	-1.449375	-1.614428
C	5.300032	-1.195207	-0.841520	H	5.447733	-0.144738	-0.554372
C	3.633797	-2.857993	-1.778403	H	4.342305	-3.161730	-2.565367
H	1.396857	-1.388678	-2.484736	H	3.788412	-3.549368	-0.933280
H	1.329815	0.362598	-2.423969	H	2.615449	-3.007258	-2.155753
H	1.731951	-1.889713	0.560361	-	-	-	-

Table S21. Atomic coordinates (Å) of **1a-2** obtained at the M062X/def2SVP level of theory in the gas phase.

C	0.564240	-0.572371	-0.663328	H	0.896492	-3.919348	-0.317280
C	1.566990	-0.526696	-1.822929	H	0.179060	-2.940995	-1.598877
C	0.684026	-1.803646	0.237119	H	-1.453882	-4.433594	-0.078162
C	-0.864990	-0.482370	-1.167706	H	-0.086930	-3.838231	1.954640
C	-1.972506	-0.944272	-0.191306	H	-1.710907	-3.171922	2.259215
C	-1.461394	-0.859158	1.244019	H	-4.488688	-2.587200	-0.138723
C	-0.224390	-1.712453	1.504094	H	-3.588530	-3.947670	0.579746
C	0.214556	-3.078666	-0.508814	H	-3.610431	-2.356961	1.378872
C	-1.152320	-3.391885	0.108693	H	-3.381799	-2.161716	-2.278811
C	-2.319507	-2.495196	-0.411676	H	-1.695005	-2.656783	-2.520534
C	-0.844489	-3.128240	1.585683	H	-2.898988	-3.851821	-1.981238
O	-1.157838	-0.068248	-2.259349	H	-0.991972	1.506030	0.528641
O	-2.059783	-0.293484	2.124165	H	-0.944706	3.934373	0.885035
C	-3.578757	-2.861385	0.402049	H	-2.964251	5.312459	0.426410
C	-2.581532	-2.801708	-1.889849	H	-5.037765	4.225088	-0.424590
C	-3.180870	-0.012467	-0.439612	H	-5.072243	1.754630	-0.805262
C	-3.048242	1.465373	-0.168112	H	-0.231280	-1.344278	3.609645
O	-4.216243	-0.436423	-0.887699	H	1.307524	-1.965752	2.980507
C	-1.888911	2.085622	0.308487	H	0.204399	0.921377	2.856742
C	-1.858283	3.462467	0.518646	H	1.678415	2.634127	2.828666
C	-2.989285	4.234659	0.258459	H	3.350293	2.246496	3.260170
C	-4.150439	3.625388	-0.217377	H	4.271321	-0.001007	2.925864
C	-4.177223	2.251134	-0.430421	H	3.199620	-1.372909	2.551378
C	0.487889	-1.260332	2.780792	H	3.750043	-0.297631	1.257305
C	0.981583	0.160299	2.717935	H	3.476623	3.604349	1.311051
C	2.239620	0.584918	2.517737	H	3.874831	1.977489	0.780741
C	2.563407	2.061749	2.509777	H	0.918632	2.574276	0.532641
C	3.420062	-0.326341	2.307486	H	0.745389	4.118968	-2.400667
C	3.044362	2.601269	1.154560	H	0.993638	2.477135	-3.000239
C	1.934625	2.687356	0.135569	H	-0.063570	2.751885	-1.593539
C	2.062697	2.935025	-1.176745	H	3.437866	4.113314	-2.337474
C	0.867138	3.070687	-2.081305	H	4.240541	3.054549	-1.152084
C	3.395166	3.127062	-1.847873	H	3.533477	2.374300	-2.641788
H	0.729403	0.323980	-0.035476	H	3.306137	0.523441	-0.984339
C	2.993832	-0.456169	-1.362665	H	5.447843	-0.144457	-0.554250
C	3.901995	-1.443267	-1.341554	H	5.521757	-1.829097	0.033313
C	5.300111	-1.195002	-0.841119	H	6.043167	-1.449443	-1.613850
C	3.634063	-2.857808	-1.778322	H	2.615372	-3.007359	-2.154639
H	1.397088	-1.388630	-2.484695	H	4.341860	-3.160957	-2.566162
H	1.329947	0.362649	-2.423825	H	3.789884	-3.549424	-0.933621
H	1.731880	-1.889948	0.560261	-	-	-	-

Table S22. Atomic coordinates (Å) of **1a-3** obtained at the M062X/def2SVP level of theory in the gas phase.

C	0.226162	-1.029011	-0.818401	H	-0.809517	-4.216927	-0.332348
C	1.142970	-1.400977	-1.985748	H	-1.181184	-3.051307	-1.605672
C	-0.088505	-2.195517	0.122240	H	-3.128041	-3.720311	0.131537
C	-1.090096	-0.414492	-1.259292	H	-1.461200	-3.678929	2.015145
C	-2.190685	-0.336548	-0.174478	H	-2.636813	-2.396228	2.392650
C	-1.535377	-0.411646	1.207377	H	-4.781560	-2.384409	0.965370
C	-0.752358	-1.705092	1.445533	H	-4.094751	-0.876324	1.615144
C	-1.105021	-3.173816	-0.515256	H	-5.154868	-0.817136	0.202251
C	-2.415634	-2.887052	0.227026	H	-2.887587	-2.084642	-2.389679
C	-3.164073	-1.608156	-0.254348	H	-4.409933	-2.653807	-1.664345
C	-1.891812	-2.729998	1.657937	H	-4.189902	-0.928072	-2.048889
O	-1.292458	0.010540	-2.366452	H	-3.994050	3.342775	-0.892594
O	-1.736011	0.405779	2.069981	H	-2.920593	5.599733	-0.863988
C	-4.369681	-1.401761	0.688722	H	-0.502998	5.807978	-0.300303
C	-3.683407	-1.826908	-1.679344	H	0.823613	3.769241	0.234189
C	-2.944773	0.997113	-0.406035	H	-0.257574	1.559717	0.250041
C	-2.203663	2.306997	-0.334653	H	-0.303720	-1.020869	3.432298
O	-4.114282	1.004579	-0.697547	H	0.409813	-2.584756	3.006088
C	-2.940100	3.458398	-0.640131	H	2.230165	-1.585448	1.743287
C	-2.335463	4.710800	-0.624424	H	3.960658	0.790174	3.203475
C	-0.981723	4.827545	-0.308615	H	3.879182	-0.153425	1.703775
C	-0.238549	3.687821	-0.004449	H	0.176221	0.984758	3.597557
C	-0.849830	2.435783	-0.012790	H	1.703267	1.738640	4.164872
C	0.209514	-1.567784	2.630199	H	0.987342	2.204252	2.615902
C	1.533436	-0.935897	2.287884	H	3.181179	2.816918	2.047771
C	1.979062	0.293769	2.590139	H	4.626211	2.167948	1.280418
C	3.406051	0.673905	2.255507	H	1.746791	1.650324	0.264209
C	1.162658	1.346999	3.288000	H	2.666038	1.260186	-2.993670
C	3.558300	1.971615	1.445732	H	1.281542	1.723271	-1.961193
C	2.804115	1.912529	0.151984	H	2.232965	2.964878	-2.810435
C	3.239869	2.119904	-1.099550	H	5.069337	1.702964	-2.143856
C	2.298694	2.006771	-2.269639	H	4.684811	3.421871	-2.016815
C	4.656483	2.468130	-1.466429	H	5.321162	2.554195	-0.599387
H	0.740190	-0.251320	-0.219174	H	3.099612	-0.643472	-1.320682
C	2.556931	-1.578255	-1.508999	H	4.997957	-1.703278	-0.620000
C	3.187669	-2.726809	-1.223267	H	4.647417	-3.194872	0.295809
C	4.599216	-2.723577	-0.699666	H	5.263638	-3.306737	-1.357430
C	2.575260	-4.093469	-1.377801	H	1.538463	-4.063507	-1.735359
H	0.757077	-2.304583	-2.480968	H	3.164835	-4.704887	-2.079659
H	1.091831	-0.596848	-2.732935	H	2.587188	-4.626190	-0.412484
H	0.853950	-2.706612	0.362425	-	-	-	-

Table S23. Atomic coordinates (Å) of **1a-4** obtained at the M062X/def2SVP level of theory in the gas phase.

C	0.226328	-1.029199	-0.818352	H	-0.809286	-4.217083	-0.331833
C	1.143224	-1.401254	-1.985608	H	-1.180861	-3.051698	-1.605403
C	-0.088348	-2.195573	0.122440	H	-3.127852	-3.720421	0.131757
C	-1.089883	-0.414660	-1.259371	H	-1.461176	-3.678720	2.015515
C	-2.190554	-0.336663	-0.174652	H	-2.636824	-2.395953	2.392702
C	-1.535332	-0.411579	1.207256	H	-4.781615	-2.384428	0.965013
C	-0.752288	-1.704968	1.445623	H	-4.094781	-0.876377	1.614854
C	-1.104786	-3.174007	-0.514958	H	-5.154675	-0.817150	0.201784
C	-2.415459	-2.887141	0.227178	H	-4.189509	-0.928627	-2.049273
C	-3.163875	-1.608337	-0.254469	H	-2.887060	-2.085153	-2.389688
C	-1.891762	-2.729852	1.658110	H	-4.409459	-2.654318	-1.664473
O	-1.292128	0.010388	-2.366548	H	-3.994298	3.342686	-0.892026
O	-1.736088	0.405905	2.069771	H	-2.921023	5.599732	-0.862742
C	-4.369612	-1.401821	0.688405	H	-0.503366	5.807981	-0.299351
C	-3.683001	-1.827360	-1.679506	H	0.823517	3.769138	0.234188
C	-2.944701	0.996930	-0.406385	H	-0.257505	1.559545	0.249433
C	-2.203749	2.306873	-0.334672	H	-0.303758	-1.020420	3.432306
O	-4.114130	1.004297	-0.698234	H	0.409800	-2.584381	3.006388
C	-2.940325	3.458312	-0.639656	H	2.230243	-1.585267	1.743574
C	-2.335783	4.710760	-0.623586	H	3.960576	0.790771	3.203208
C	-0.982005	4.827508	-0.307937	H	3.879169	-0.153130	1.703683
C	-0.238684	3.687734	-0.004292	H	1.703205	1.739706	4.164065
C	-0.849879	2.435658	-0.012969	H	0.986911	2.204427	2.614985
C	0.209516	-1.567470	2.630325	H	0.176218	0.985239	3.597386
C	1.533457	-0.935623	2.287991	H	3.180906	2.817217	2.047157
C	1.979013	0.294140	2.589969	H	4.626028	2.168284	1.279922
C	3.405986	0.674275	2.255262	H	1.746775	1.649756	0.263736
C	1.162522	1.347537	3.287473	H	2.665870	1.260090	-2.994034
C	3.558135	1.971857	1.445258	H	1.281308	1.722914	-1.961533
C	2.803972	1.912477	0.151512	H	2.232343	2.964686	-2.810962
C	3.239567	2.120167	-1.100028	H	4.683793	3.423529	-2.016415
C	2.298369	2.006658	-2.270063	H	5.320801	2.554775	-0.599946
C	4.655963	2.469254	-1.466923	H	5.068962	1.704890	-2.145158
H	0.740334	-0.251432	-0.219201	H	3.099902	-0.643779	-1.320581
C	2.557140	-1.578549	-1.508720	H	4.647356	-3.195169	0.296537
C	3.187737	-2.727103	-1.222663	H	5.263706	-3.307088	-1.356651
C	4.599244	-2.723896	-0.698953	H	4.998004	-1.703604	-0.619280
C	2.575218	-4.093739	-1.376993	H	2.586979	-4.626288	-0.411581
H	0.757352	-2.304871	-2.480828	H	1.538470	-4.063748	-1.734694
H	1.092171	-0.597146	-2.732824	H	3.164830	-4.705332	-2.078671
H	0.854112	-2.706589	0.362767	-	-	-	-

Table S24. Atomic coordinates (Å) of **1a-5** obtained at the M062X/def2SVP level of theory in the gas phase.

C	0.299342	-1.218984	-0.839628	H	-0.789995	-4.324720	-0.044504
C	1.138025	-1.727921	-2.017031	H	-1.166917	-3.267520	-1.407760
C	-0.008618	-2.289762	0.210084	H	-3.084963	-3.725267	0.419538
C	-1.005078	-0.577718	-1.275886	H	-1.363766	-3.588812	2.250279
C	-2.068390	-0.397206	-0.170389	H	-2.492293	-2.245496	2.558753
C	-1.398910	-0.401105	1.204243	H	-4.714911	-2.279455	1.128945
C	-0.621944	-1.681544	1.507812	H	-3.950106	-0.772930	1.690321
C	-1.064319	-3.294415	-0.313375	H	-5.016917	-0.742206	0.279171
C	-2.347146	-2.908941	0.431938	H	-4.109746	-1.090743	-1.966421
C	-3.071627	-1.651015	-0.139025	H	-2.836617	-2.296734	-2.235098
C	-1.779130	-2.657959	1.832459	H	-4.357624	-2.778268	-1.446923
O	-1.220049	-0.200362	-2.397857	H	-3.846345	3.282286	-0.874303
O	-1.610649	0.445145	2.035717	H	-2.815584	5.550629	-0.694792
C	-4.257398	-1.335143	0.796391	H	-0.413881	5.763552	-0.056401
C	-3.616468	-1.969126	-1.535864	H	0.939181	3.710289	0.351525
C	-2.790231	0.935416	-0.478419	H	-0.056858	1.498937	0.147592
C	-2.043970	2.240914	-0.369361	H	-0.135817	-0.918156	3.452960
O	-3.940824	0.946594	-0.838055	H	0.622865	-2.468137	3.052619
C	-2.795454	3.399290	-0.610148	H	2.370829	-1.435368	1.712145
C	-2.216097	4.658824	-0.507051	H	3.982329	1.194948	3.045726
C	-0.871704	4.777605	-0.153809	H	3.995268	0.056467	1.689114
C	-0.112875	3.631499	0.076383	H	0.250013	1.100497	3.547513
C	-0.690376	2.368275	-0.039922	H	1.756447	1.943174	4.039218
C	0.372719	-1.471561	2.652259	H	0.968192	2.318895	2.498639
C	1.658633	-0.796290	2.250421	H	3.001172	2.963267	1.581759
C	2.053514	0.462565	2.504766	H	4.553777	2.380711	0.998882
C	3.448748	0.908558	2.123391	H	2.545112	0.683903	-0.276657
C	1.207498	1.497599	3.194186	H	1.054771	2.621418	-2.637076
C	3.500993	2.083487	1.138850	H	2.613713	2.201363	-3.371444
C	2.874146	1.724470	-0.183703	H	1.721647	0.989379	-2.408787
C	2.682588	2.532476	-1.235902	H	2.260863	4.623641	-1.516140
C	1.986287	2.052943	-2.478022	H	3.522101	4.306754	-0.290940
C	3.111494	3.973689	-1.252967	H	3.880359	4.133328	-2.026269
H	0.856472	-0.407996	-0.331701	H	3.190247	-1.011968	-1.632878
C	2.576743	-1.921192	-1.626691	H	5.074284	-2.076761	-0.902348
C	3.172854	-3.058528	-1.238571	H	4.732795	-3.436711	0.201490
C	4.622557	-3.075126	-0.833843	H	5.199533	-3.763430	-1.472059
C	2.484678	-4.395639	-1.167317	H	1.433091	-4.357463	-1.477369
H	0.693149	-2.658315	-2.400318	H	3.005304	-5.129234	-1.803373
H	1.060420	-1.000220	-2.837005	H	2.522866	-4.790328	-0.138467
H	0.931226	-2.798829	0.466846	-	-	-	-

Table S25. Atomic coordinates (Å) of **1a-6** obtained at the M062X/def2SVP level of theory in the gas phase.

C	0.072793	-0.964037	-0.892257	H	-1.416180	-4.008223	-0.790841
C	0.916173	-1.291094	-2.124546	H	-1.656778	-2.627322	-1.864428
C	-0.376947	-2.200710	-0.103288	H	-3.613379	-3.263310	-0.118569
C	-1.170621	-0.164824	-1.203001	H	-1.882297	-3.729656	1.646509
C	-2.185644	-0.049083	-0.039993	H	-2.836313	-2.361099	2.268270
C	-1.494466	-0.403723	1.277620	H	-4.047595	-0.550998	1.813132
C	-0.912433	-1.816051	1.307763	H	-5.136449	-0.084687	0.501683
C	-1.557340	-2.918126	-0.808095	H	-5.028880	-1.794146	0.999276
C	-2.782756	-2.560507	0.046496	H	-4.838794	-1.768531	-1.623885
C	-3.352462	-1.131229	-0.205932	H	-4.353137	-0.066959	-1.820771
C	-2.181744	-2.688064	1.449352	H	-3.287846	-1.364682	-2.398496
O	-1.391207	0.365645	-2.260657	H	-2.527218	3.157372	-2.029561
O	-1.539350	0.303835	2.254139	H	-1.005039	5.110108	-2.286558
C	-4.454013	-0.868456	0.841912	H	0.679920	5.609964	-0.516889
C	-3.983874	-1.075548	-1.601281	H	0.830118	4.150639	1.489195
C	-2.692085	1.414090	-0.099844	H	-0.677221	2.201614	1.733326
C	-1.684890	2.541503	-0.147213	H	-0.315487	-1.538288	3.354474
O	-3.854650	1.674833	-0.266270	H	0.208561	-3.065741	2.624437
C	-1.781962	3.383083	-1.265898	H	2.034768	-1.995993	1.379725
C	-0.930630	4.472831	-1.404165	H	4.128599	-0.058862	3.059918
C	0.013940	4.751750	-0.413556	H	3.803193	-0.719774	1.444736
C	0.100275	3.932549	0.707453	H	2.073933	0.740031	4.485842
C	-0.738410	2.823017	0.842351	H	1.295713	1.610464	3.159349
C	0.102462	-1.983322	2.441910	H	0.430846	0.278836	3.935786
C	1.460895	-1.423265	2.119313	H	3.396536	2.178533	2.370281
C	2.053966	-0.327196	2.615590	H	4.658124	1.586189	1.298575
C	3.460951	0.021490	2.183835	H	1.616149	1.588708	0.676202
C	1.421611	0.610439	3.607115	H	2.059881	1.492031	-2.744864
C	3.609626	1.431218	1.586257	H	0.898642	1.972355	-1.468007
C	2.681858	1.659390	0.429914	H	1.936172	3.184271	-2.252799
C	2.986970	1.934062	-0.847373	H	4.550994	1.314546	-2.183033
C	1.906354	2.149412	-1.873285	H	4.529447	3.048453	-1.851359
C	4.386251	2.059646	-1.387067	H	5.162883	1.923668	-0.625820
H	0.673227	-0.320347	-0.215990	H	2.939027	-0.762649	-1.445673
C	2.323418	-1.628270	-1.720788	H	4.325487	-3.581229	-0.173108
C	2.872005	-2.844891	-1.588153	H	4.892354	-3.562490	-1.847913
C	4.291422	-3.004355	-1.112052	H	4.771364	-2.031734	-0.938753
C	2.156459	-4.137549	-1.877850	H	2.146408	-4.775991	-0.979038
H	0.439192	-2.107680	-2.687492	H	1.118793	-3.993224	-2.203457
H	0.908641	-0.415598	-2.788187	H	2.686459	-4.705793	-2.659014
H	0.485914	-2.872364	0.008633	-	-	-	-

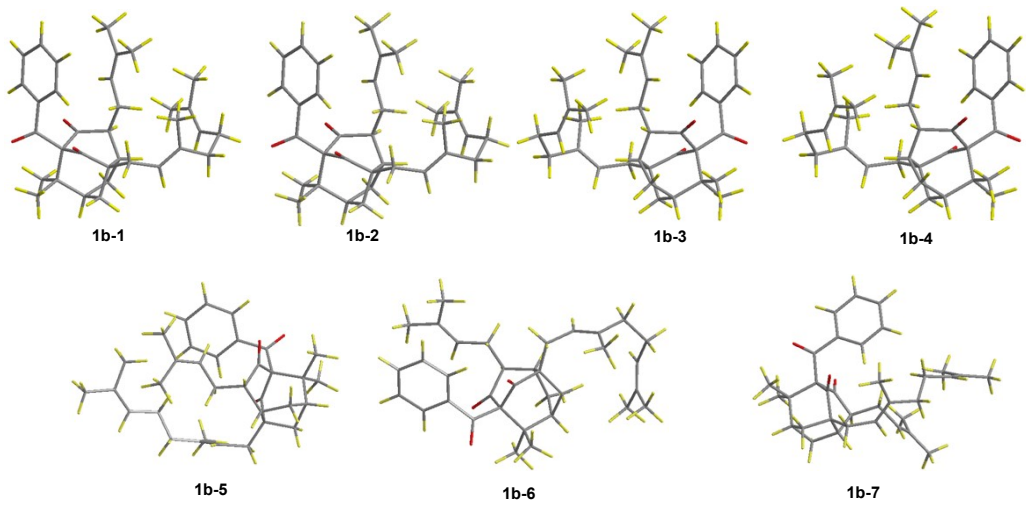


Fig. S23 Optimized geometries of 7 dominant conformers of **1b** at the B3LYP/6-31G(d) level of theory in the gas phase.

Table S26. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1b** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	ΔG (kcal/mol)[d]	Population[e]
Rxnb23-1	-1547.550741	0.627364	-970694.419174	0.0	21.38%
Rxnb23-2	-1547.550741	0.627364	-970694.419124	0.000050	21.38%
Rxnb23-3	-1547.55074	0.627364	-970694.418597	0.000577	21.36%
Rxnb23-4	-1547.550741	0.627368	-970694.416332	0.002843	21.28%
Rxnb23-5	-1547.549632	0.627463	-970693.660947	0.758227	5.94%
Rxnb23-6	-1547.547937	0.625787	-970693.649119	0.770055	5.82%
Rxnb23-7	-1547.546649	0.625173	-970693.226454	1.192721	2.85%

[a]Electronic energy obtained at @@@ level of theory; [b]Thermal correction to Gibbs free energy obtained at M062X/6-311+G(2d,p) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S27. Atomic coordinates (Å) of **1b-1** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	0.168882	-0.273543	-1.111068	H	-1.231212	-4.436174	-1.133562
C	0.666706	-1.643837	-0.648262	H	0.624056	-4.150599	0.540006
C	-1.340576	-0.326196	-1.195632	H	-0.869336	-3.871185	1.445410
C	-2.064987	-1.155843	-0.104735	H	-4.289219	-3.082708	0.236775
C	-1.158625	-1.351295	1.106958	H	-3.195561	-4.479953	0.152464
C	0.171712	-2.029466	0.792312	H	-2.973546	-3.236225	1.393349
C	0.104901	-2.755310	-1.580620	H	-2.402935	-2.217293	-2.806270
C	-0.986756	-3.442487	-0.742279	H	-3.275812	-3.671275	-2.297885
C	-2.338348	-2.655208	-0.644886	H	-3.953965	-2.065351	-1.975871
C	-0.264834	-3.511023	0.609641	H	-4.645970	1.569360	-1.000556
O	-1.979788	0.232267	-2.065700	H	-4.535027	4.027987	-0.666749
O	-1.519126	-1.119784	2.248417	H	-3.055866	4.971143	1.098753
C	-3.255677	-3.403298	0.350445	H	-1.704326	3.441202	2.516352
C	-3.028233	-2.640600	-2.017988	H	-1.805474	1.005033	2.163346
C	-3.353712	-0.341182	0.211216	H	1.012845	-0.809170	2.366612
C	-3.214929	1.124182	0.536401	H	0.893256	-2.500736	2.762263
O	-4.464872	-0.806412	0.048359	H	2.831346	-2.969349	1.100782
C	-4.002525	1.991700	-0.236848	H	5.706723	-1.480907	1.960131
C	-3.935241	3.367735	-0.046839	H	4.967686	-2.460979	0.693873
C	-3.102204	3.896960	0.941839	H	4.292254	0.417243	3.005474
C	-2.338187	3.039649	1.730935	H	3.553666	1.031761	1.530465
C	-2.381776	1.660156	1.525985	H	2.534455	0.387432	2.821906
C	1.168611	-1.808311	1.955843	H	5.661564	0.525763	0.556180
C	2.601155	-2.006036	1.559424	H	6.474329	-0.790079	-0.264341
C	3.605230	-1.123132	1.668162	H	4.316029	-1.258271	-1.583479
C	4.979613	-1.456571	1.134649	H	2.249494	1.289779	-2.721789
C	3.477070	0.244678	2.290480	H	3.695598	1.241779	-3.719085
C	5.488753	-0.444108	0.080731	H	2.964097	-0.278438	-3.169450
C	4.568797	-0.311839	-1.100987	H	4.801469	2.813269	-1.867840
C	4.053251	0.805993	-1.635768	H	3.318534	2.696086	-0.928125
C	3.192829	0.750487	-2.874098	H	4.869976	2.235872	-0.196946
C	4.281223	2.203492	-1.116275	H	0.227300	0.779366	0.793280
C	0.644721	0.888547	-0.215572	H	1.730046	0.775066	-0.104686
C	0.283850	2.241193	-0.779549	H	-0.277258	2.234137	-1.712101
C	0.556045	3.422506	-0.210489	H	0.963840	5.387112	-1.019452
C	0.112611	4.715193	-0.842440	H	-0.396646	4.544691	-1.795439
C	1.285178	3.560236	1.100616	H	-0.581710	5.250354	-0.180504
H	0.527606	-0.084777	-2.127516	H	0.663301	4.094777	1.831357
H	1.758184	-1.629913	-0.656927	H	1.562789	2.597205	1.535293
H	0.884424	-3.487965	-1.816348	H	2.202948	4.152062	0.979652
H	-0.250838	-2.356230	-2.535224	-	-	-	-

Table S28. Atomic coordinates (Å) of **1b-2** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	0.168861	-0.273525	-1.111054	H	-1.231269	-4.436143	-1.133582
C	0.666674	-1.643828	-0.648270	H	0.624007	-4.150600	0.539979
C	-1.340597	-0.326165	-1.195613	H	-0.869377	-3.871180	1.445396
C	-2.065011	-1.155810	-0.104716	H	-4.289250	-3.082657	0.236792
C	-1.158645	-1.351283	1.106966	H	-3.195621	-4.479922	0.152426
C	0.171685	-2.029465	0.792305	H	-2.973562	-3.236233	1.393341
C	0.104854	-2.755286	-1.580635	H	-3.275852	-3.671214	-2.297899
C	-0.986801	-3.442462	-0.742292	H	-3.953992	-2.065289	-1.975869
C	-2.338385	-2.655174	-0.644888	H	-2.402961	-2.217235	-2.806266
C	-0.264877	-3.511016	0.609626	H	-1.805445	1.005075	2.163329
O	-1.979811	0.232302	-2.065679	H	-1.704229	3.441249	2.516265
O	-1.519133	-1.119777	2.248431	H	-3.055771	4.971182	1.098658
C	-3.255714	-3.403271	0.350438	H	-4.535017	4.028009	-0.666762
C	-3.028265	-2.640544	-2.017991	H	-4.646031	1.569373	-1.000492
C	-3.353736	-0.341150	0.211233	H	1.012843	-0.809191	2.366611
C	-3.214953	1.124207	0.536433	H	0.893224	-2.500757	2.762252
O	-4.464897	-0.806381	0.048370	H	2.831296	-2.969400	1.100765
C	-2.381753	1.660192	1.525971	H	5.706723	-1.481044	1.960056
C	-2.338124	3.039689	1.730881	H	4.967625	-2.461071	0.693796
C	-3.102147	3.896995	0.941784	H	3.553668	1.031690	1.530447
C	-3.935228	3.367761	-0.046850	H	2.534515	0.387357	2.821937
C	-4.002551	1.991722	-0.236817	H	4.292323	0.417164	3.005420
C	1.168592	-1.808332	1.955835	H	5.661568	0.525658	0.556147
C	2.601131	-2.006085	1.559411	H	6.474285	-0.790182	-0.264426
C	3.605228	-1.123205	1.668142	H	4.315879	-1.258312	-1.583466
C	4.979591	-1.456672	1.134592	H	2.249459	1.289860	-2.721724
C	3.477105	0.244604	2.290464	H	3.695514	1.241725	-3.719087
C	5.488723	-0.444200	0.080683	H	2.963926	-0.278422	-3.169378
C	4.568731	-0.311890	-1.101002	H	4.801675	2.813160	-1.867870
C	4.053228	0.805967	-1.635775	H	3.318679	2.696159	-0.928226
C	3.192747	0.750493	-2.874063	H	4.870034	2.235802	-0.196959
C	4.281323	2.203458	-1.116317	H	0.227313	0.779346	0.793314
C	0.644725	0.888543	-0.215541	H	1.730049	0.775042	-0.104671
C	0.283865	2.241206	-0.779487	H	-0.277330	2.234176	-1.711986
C	0.556145	3.422506	-0.210440	H	-0.581483	5.250433	-0.180313
C	0.112703	4.715212	-0.842344	H	0.963950	5.387072	-1.019494
C	1.285391	3.560197	1.100607	H	-0.396708	4.544727	-1.795263
H	0.527578	-0.084744	-2.127501	H	2.203176	4.151989	0.979574
H	1.758152	-1.629915	-0.656944	H	0.663598	4.094763	1.831400
H	0.884371	-3.487943	-1.816375	H	1.562998	2.597153	1.535253
H	-0.250887	-2.356192	-2.535232	-	-	-	-

Table S29. Atomic coordinates (Å) of **1b-3** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	-0.168964	-0.273637	1.111137	H	1.231453	-4.436135	1.133657
C	-0.666678	-1.643964	0.648325	H	-0.623836	-4.150728	-0.539926
C	1.340516	-0.326088	1.195572	H	0.869546	-3.871211	-1.445318
C	2.064980	-1.155742	0.104738	H	4.289330	-3.082639	-0.236672
C	1.158620	-1.351276	-1.106939	H	3.195600	-4.479838	-0.152454
C	-0.171658	-2.029566	-0.792253	H	2.973689	-3.236044	-1.393289
C	-0.104799	-2.755386	1.580691	H	3.275977	-3.671020	2.297984
C	0.986911	-3.442473	0.742363	H	3.954016	-2.065067	1.975897
C	2.338435	-2.655093	0.644945	H	2.402995	-2.217078	2.806302
C	0.265007	-3.511085	-0.609559	H	4.647472	1.569163	0.999309
O	1.979713	0.232563	2.065537	H	4.536786	4.027814	0.665508
O	1.519080	-1.119730	-2.248403	H	3.056385	4.971221	-1.098820
C	3.255779	-3.403177	-0.350383	H	1.703386	3.441507	-2.515278
C	3.028324	-2.640375	2.018039	H	1.804321	1.005375	-2.162303
C	3.353730	-0.341104	-0.211206	H	-1.012845	-0.809438	-2.366663
C	3.215088	1.124237	-0.536453	H	-0.893222	-2.501037	-2.762144
O	4.464866	-0.806406	-0.048322	H	-2.831290	-2.969552	-1.100643
C	4.003494	1.991626	0.236119	H	-5.706702	-1.481301	-1.959941
C	3.936361	3.367664	0.046108	H	-4.967564	-2.461161	-0.693575
C	3.102628	3.897032	-0.941910	H	-4.292314	0.416924	-3.005439
C	2.337797	3.039854	-1.730360	H	-3.553645	1.031527	-1.530505
C	2.381256	1.660363	-1.525385	H	-2.534502	0.387127	-2.821967
C	-1.168585	-1.808540	-1.955784	H	-5.661550	0.525577	-0.556315
C	-2.601118	-2.006261	-1.559337	H	-6.474247	-0.790142	0.264460
C	-3.605207	-1.123372	-1.668088	H	-4.315720	-1.258069	1.583476
C	-4.979561	-1.456816	-1.134490	H	-2.249473	1.290299	2.721405
C	-3.477090	0.244402	-2.290481	H	-3.695480	1.242346	3.718839
C	-5.488691	-0.444211	-0.080713	H	-2.963935	-0.277904	3.169354
C	-4.568678	-0.311713	1.100937	H	-4.870214	2.235857	0.196652
C	-4.053288	0.806242	1.635617	H	-4.801895	2.813411	1.867499
C	-3.192758	0.750965	2.873876	H	-3.318893	2.696407	0.927864
C	-4.281502	2.203662	1.116015	H	-0.228014	0.779244	-0.793209
C	-0.645127	0.888413	0.215770	H	-1.730477	0.774839	0.105207
C	-0.284195	2.241090	0.779630	H	0.277050	2.234094	1.712097
C	-0.556469	3.422360	0.210522	H	-0.963922	5.387229	1.019042
C	-0.112826	4.715090	0.842238	H	0.396332	4.544689	1.795308
C	-1.285887	3.559980	-1.100438	H	0.581663	5.249952	0.180232
H	-0.527602	-0.084970	2.127636	H	-1.563138	2.596893	-1.535229
H	-1.758158	-1.630122	0.656985	H	-2.203918	4.151350	-0.979198
H	-0.884269	-3.488098	1.816415	H	-0.664420	4.094952	-1.831210
H	0.250898	-2.356268	2.535294	-	-	-	-

Table S30. Atomic coordinates (Å) of **1b-4** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	-0.168816	-0.273635	1.111085	H	1.231830	-4.436092	1.133608
C	-0.666458	-1.644001	0.648315	H	-0.623520	-4.150776	-0.539910
C	1.340649	-0.326087	1.195642	H	0.869809	-3.871180	-1.445369
C	2.065149	-1.155653	0.104733	H	3.196213	-4.479604	-0.152434
C	1.158802	-1.351261	-1.106940	H	2.973951	-3.235947	-1.393346
C	-0.171448	-2.029585	-0.792260	H	4.289639	-3.082176	-0.236813
C	-0.104480	-2.755388	1.580680	H	2.403293	-2.217042	2.806277
C	0.987244	-3.442439	0.742318	H	3.276323	-3.670931	2.297887
C	2.338727	-2.654981	0.644896	H	3.954295	-2.064930	1.975856
C	0.265287	-3.511088	-0.609583	H	1.805322	1.005128	-2.163441
O	1.979808	0.232445	2.065703	H	1.703773	3.441278	-2.516466
O	1.519255	-1.119724	-2.248410	H	3.055005	4.971461	-1.098836
C	3.256146	-3.402943	-0.350447	H	4.534286	4.028566	0.666713
C	3.028630	-2.640282	2.017991	H	4.645657	1.569955	1.000516
C	3.353754	-0.340804	-0.211232	H	-1.012709	-0.809419	-2.366586
C	3.214732	1.124523	-0.536475	H	-0.893024	-2.500997	-2.762169
O	4.464984	-0.805856	-0.048343	H	-2.831054	-2.969653	-1.100613
C	2.381497	1.660353	-1.526070	H	-5.706511	-1.481485	-1.960125
C	2.337677	3.039838	-1.731026	H	-4.967475	-2.461352	-0.693713
C	3.101527	3.897286	-0.941915	H	-3.553752	1.031354	-1.530447
C	3.934631	3.368209	0.046786	H	-2.534382	0.387165	-2.821838
C	4.002154	1.992185	0.236795	H	-4.292180	0.416746	-3.005500
C	-1.168398	-1.808551	-1.955772	H	-5.661474	0.525387	-0.556389
C	-2.600925	-2.006352	-1.559311	H	-6.474288	-0.790401	0.264175
C	-3.605061	-1.123532	-1.668126	H	-4.316001	-1.258486	1.583441
C	-4.979435	-1.456997	-1.134615	H	-3.695939	1.241377	3.719122
C	-3.477008	0.244285	-2.290467	H	-2.963993	-0.278557	3.169295
C	-5.488688	-0.444438	-0.080840	H	-2.249790	1.289919	2.721906
C	-4.568817	-0.312072	1.100937	H	-4.801996	2.812921	1.867725
C	-4.053353	0.805801	1.635710	H	-3.318858	2.696079	0.928285
C	-3.192986	0.750353	2.874087	H	-4.870077	2.235582	0.196797
C	-4.281480	2.203280	1.116230	H	-0.227386	0.779262	-0.793283
C	-0.644809	0.888388	0.215574	H	-1.730123	0.774757	0.104704
C	-0.284112	2.241075	0.779571	H	0.276974	2.234077	1.712138
C	-0.556442	3.422362	0.210520	H	-0.964332	5.387112	1.019102
C	-0.113112	4.715093	0.842451	H	0.395840	4.544665	1.795627
C	-1.285578	3.559983	-1.100601	H	0.581477	5.250095	0.180663
H	-0.527565	-0.084884	2.127525	H	-1.563024	2.596902	-1.535270
H	-1.757939	-1.630227	0.657012	H	-2.203445	4.151657	-0.979655
H	-0.883904	-3.488136	1.816447	H	-0.663763	4.094606	-1.831332
H	0.251235	-2.356244	2.535266	-	-	-	-

Table S31. Atomic coordinates (Å) of **1b-5** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	1.089037	-0.191637	1.860368	H	5.280172	-1.202503	1.077565
C	1.930508	-1.475215	1.714618	H	3.839576	-3.218648	0.674668
C	1.796257	0.907583	1.101394	H	3.953126	-2.408888	-0.893056
C	2.476025	0.498941	-0.227575	H	5.759976	-0.413673	-1.101437
C	1.946661	-0.839280	-0.746919	H	4.242140	-0.549370	-2.004687
C	2.091532	-1.992719	0.238327	H	4.963487	1.034027	-1.753565
C	3.387651	-1.163808	2.182669	H	4.313398	1.515570	1.833614
C	4.208783	-1.085275	0.880887	H	5.772106	1.223662	0.874531
C	4.044393	0.235193	0.055697	H	4.529477	2.344169	0.288963
C	3.619413	-2.286538	0.139680	H	1.285477	4.081646	-0.701859
O	1.844154	2.060723	1.481601	H	-1.030387	4.971158	-0.826048
O	1.617042	-1.001387	-1.909505	H	-2.884887	3.492551	-1.586634
C	4.791640	0.065625	-1.287472	H	-2.394656	1.149401	-2.246762
C	4.692215	1.403395	0.816246	H	-0.097985	0.266310	-2.092033
C	2.181485	1.679817	-1.196780	H	1.535002	-3.477025	-1.199040
C	0.745189	2.110829	-1.361791	H	1.643452	-4.065376	0.454788
O	3.065809	2.354849	-1.684274	H	-0.556809	-3.188505	1.037828
C	0.471439	3.448591	-1.036961	H	-3.190537	-3.663688	-1.038631
C	-0.828989	3.940584	-1.104142	H	-2.715230	-3.048562	0.542164
C	-1.869085	3.111610	-1.531310	H	-1.485745	-3.664109	-2.951470
C	-1.596250	1.793009	-1.891358	H	-1.169849	-1.937020	-2.826327
C	-0.299966	1.286001	-1.796605	H	0.166037	-3.062308	-2.666211
C	1.273693	-3.236760	-0.165513	H	-2.705164	-0.711579	-0.382215
C	-0.215239	-3.137658	0.004283	H	-3.150729	-1.333614	-1.960448
C	-1.157336	-2.985059	-0.938359	H	-5.208271	-2.449618	-0.442910
C	-2.612024	-2.873323	-0.535694	H	-7.270022	-1.547966	0.054838
C	-0.884571	-2.914668	-2.418866	H	-7.167571	-0.047869	1.000797
C	-3.258061	-1.515783	-0.880831	H	-7.550229	0.026706	-0.715347
C	-4.718545	-1.476567	-0.508331	H	-3.863253	1.084249	-0.287683
C	-5.470931	-0.388001	-0.293973	H	-5.212496	1.463420	-1.371278
C	-6.939447	-0.505018	0.027845	H	-5.402717	1.664376	0.365631
C	-4.947772	1.022838	-0.398689	H	-0.403091	-0.533004	0.316570
C	-0.383237	-0.287342	1.384243	H	-0.835722	-1.143537	1.889134
C	-1.169900	0.967960	1.627938	H	-0.718941	1.880359	1.246207
C	-2.354295	1.077014	2.247761	H	-3.067728	2.698436	3.481810
C	-2.996340	2.431702	2.417957	H	-2.428603	3.213526	1.905059
C	-3.148061	-0.073068	2.813837	H	-4.020958	2.438616	2.025306
H	1.079508	0.109176	2.913278	H	-3.471219	0.146748	3.839933
H	1.480227	-2.265405	2.323884	H	-4.056711	-0.242008	2.220786
H	3.778342	-1.984972	2.792919	H	-2.593536	-1.014600	2.830326
H	3.440271	-0.261557	2.798999	-	-	-	-

Table S32. Atomic coordinates (Å) of **1b-6** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	-0.773861	0.481201	-1.620587	H	2.274889	-2.554371	-0.739444
C	0.706890	0.436787	-1.220348	H	2.989214	-0.316886	0.158384
C	-1.408276	-0.822835	-1.184617	H	2.124394	-1.104142	1.488863
C	-0.933653	-1.396087	0.173319	H	-0.221692	-3.972211	1.456846
C	-0.259645	-0.310802	1.012841	H	1.511210	-3.731273	1.149673
C	0.929665	0.359489	0.329943	H	0.593641	-2.552444	2.100341
C	1.365825	-0.855424	-1.784745	H	-0.330774	-3.113341	-2.122087
C	1.533691	-1.768295	-0.556084	H	0.586280	-4.303249	-1.186138
C	0.228980	-2.490049	-0.080955	H	-1.126980	-4.017908	-0.830912
C	2.025683	-0.736018	0.465033	H	-2.582222	0.484322	2.177578
O	-2.244007	-1.411302	-1.841908	H	-4.675023	1.783531	2.312165
O	-0.538920	-0.114888	2.183596	H	-6.726404	0.978093	1.163772
C	0.541852	-3.227174	1.241890	H	-6.665795	-1.158555	-0.110552
C	-0.194128	-3.535559	-1.124873	H	-4.563682	-2.476404	-0.211475
C	-2.223594	-1.971703	0.826052	H	0.463854	2.402406	0.845590
C	-3.429088	-1.074895	0.955092	H	1.302696	1.512010	2.094833
O	-2.340046	-3.153311	1.085083	H	2.517178	2.835861	-0.411228
C	-3.463856	0.134545	1.659393	H	4.691055	3.370767	-0.433153
C	-4.653245	0.859956	1.740811	H	5.436168	3.562429	1.154120
C	-5.805424	0.404721	1.103207	H	4.685490	2.069801	3.066654
C	-5.773159	-0.796865	0.391774	H	3.117380	1.251034	2.960590
C	-4.598669	-1.539438	0.333091	H	4.548962	0.523418	2.233864
C	1.283453	1.693772	1.017960	H	6.943965	2.360154	-0.313976
C	2.572959	2.292942	0.532491	H	6.458966	1.309574	1.002154
C	3.777653	2.200880	1.115096	H	5.286520	1.235458	-1.860476
C	4.992671	2.824622	0.469080	H	4.818116	-0.782269	-2.835738
C	4.034435	1.475932	2.412294	H	5.956123	-2.047593	-2.334546
C	6.091161	1.799807	0.096140	H	4.317632	-2.050507	-1.696925
C	5.631571	0.795766	-0.922547	H	5.173931	-1.922555	0.767237
C	5.602581	-0.541862	-0.826799	H	6.810223	-2.049155	0.132112
C	5.146063	-1.391081	-1.987494	H	6.385695	-0.707903	1.205875
C	6.019135	-1.331509	0.388037	H	-1.576740	1.628492	0.049359
C	-1.567685	1.675899	-1.047085	H	-1.011346	2.589382	-1.301624
C	-2.983517	1.729687	-1.572517	H	-3.255877	0.950838	-2.281504
C	-3.916392	2.620845	-1.217656	H	-6.051339	2.435764	-0.999767
C	-5.306091	2.567410	-1.795179	H	-5.557786	3.502499	-2.315001
C	-3.671383	3.729737	-0.228359	H	-5.418208	1.739636	-2.501535
H	-0.853020	0.516895	-2.712928	H	-2.666510	3.702843	0.200814
H	1.204081	1.329611	-1.609343	H	-3.811526	4.712494	-0.699636
H	2.355475	-0.629176	-2.191637	H	-4.391749	3.673096	0.598075
H	0.781709	-1.300880	-2.595638	-	-	-	-

Table S33. Atomic coordinates (Å) of **1b-7** obtained at the B3LYP/6-31G(d) level of theory in the gas phase.

C	-0.597090	-1.405934	-1.121200	H	-4.675259	-2.429976	-0.013886
C	-1.264361	-2.324671	-0.085627	H	-3.125917	-3.141226	1.833274
C	-1.469572	-0.191863	-1.379347	H	-3.634711	-1.501081	2.254651
C	-2.399968	0.279879	-0.244563	H	-4.404051	0.453321	1.563391
C	-1.833629	-0.131785	1.116855	H	-5.275001	1.069918	0.167275
C	-1.645045	-1.637618	1.282791	H	-5.657863	-0.541487	0.806623
C	-2.624723	-2.800899	-0.677491	H	-4.460017	0.625858	-2.114203
C	-3.680180	-1.981291	0.079312	H	-3.760722	-0.947617	-2.510111
C	-3.826434	-0.484617	-0.355484	H	-5.380673	-0.857598	-1.802832
C	-3.120024	-2.096906	1.497556	H	-2.407623	4.273098	-1.283481
O	-1.426472	0.415705	-2.431986	H	-0.485385	5.850750	-1.375776
O	-1.709673	0.658702	2.034587	H	1.735721	5.139245	-0.504154
C	-4.849026	0.170701	0.605398	H	2.007689	2.868010	0.459528
C	-4.379447	-0.411290	-1.786883	H	0.110736	1.326299	0.553902
C	-2.518917	1.824443	-0.410327	H	-1.193008	-1.451334	3.365999
C	-1.288792	2.687561	-0.380591	H	-0.936437	-3.062611	2.704423
O	-3.594424	2.343428	-0.650538	H	1.213365	-2.461174	1.741850
C	-1.433831	3.980360	-0.908446	H	3.502292	-0.691253	3.479550
C	-0.355571	4.857145	-0.956451	H	3.197514	-1.527139	1.957166
C	0.890309	4.457746	-0.469383	H	1.534709	0.445853	4.679057
C	1.045418	3.179141	0.066403	H	0.896878	1.307131	3.277752
C	-0.034203	2.298672	0.108384	H	-0.129707	0.158857	4.114378
C	-0.781395	-1.992180	2.510136	H	2.561536	0.736260	0.947086
C	0.691184	-1.738362	2.367640	H	3.114713	1.494448	2.432546
C	1.428485	-0.748178	2.895119	H	5.433736	0.470748	2.053981
C	2.901068	-0.660474	2.558562	H	7.185063	0.436973	0.580055
C	0.895737	0.338438	3.792433	H	6.772406	-0.262383	-0.998914
C	3.263679	0.625183	1.776529	H	6.928168	1.482589	-0.832666
C	4.678460	0.598221	1.276062	H	4.556745	1.698882	-1.804639
C	5.105473	0.673993	0.007067	H	4.257965	-0.038404	-1.841068
C	6.575758	0.577836	-0.318016	H	3.167783	1.021850	-0.945719
C	4.215254	0.849801	-1.197433	H	1.062308	-0.078231	-1.467926
C	0.855676	-0.940155	-0.827435	H	0.926513	-0.596340	0.205329
C	1.876803	-2.020552	-1.058854	H	2.175047	-2.602456	-0.188598
C	2.444506	-2.318234	-2.236915	H	3.166305	-4.184247	-3.056953
C	3.482092	-3.405426	-2.349231	H	4.430171	-3.003271	-2.732888
C	2.121404	-1.606466	-3.526774	H	3.681404	-3.879856	-1.383476
H	-0.556106	-1.943761	-2.074009	H	1.318221	-0.872798	-3.429077
H	-0.602323	-3.173316	0.111327	H	3.009280	-1.089155	-3.916237
H	-2.788187	-3.863218	-0.465889	H	1.822389	-2.329473	-4.297568
H	-2.665697	-2.686675	-1.764365	-	-	-	-

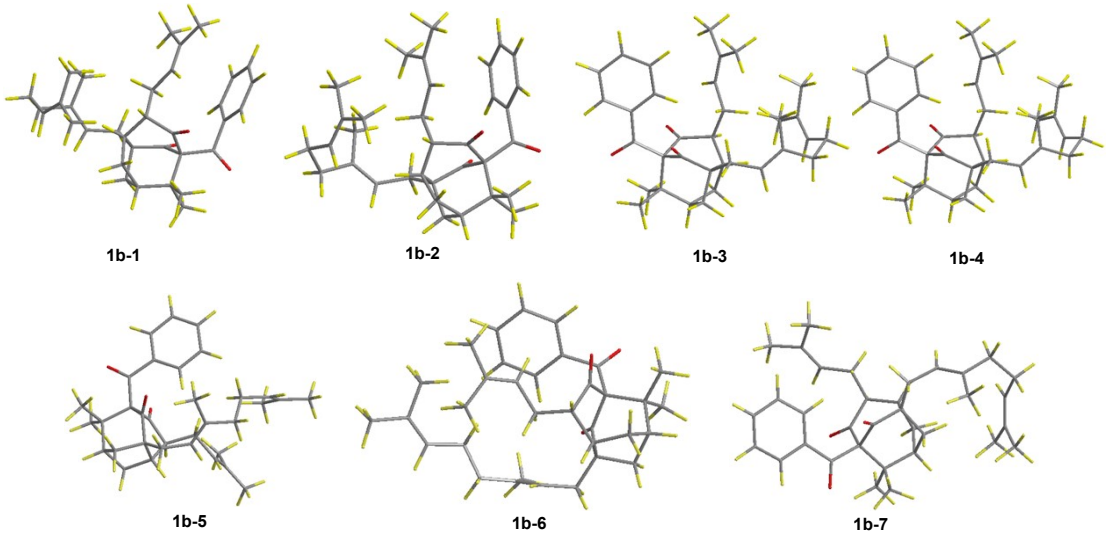


Fig. S24 Optimized geometries of 7 dominant conformers of **1b** at the M062X/def2SVP level of theory in the gas phase.

Table S34. Conformational analysis of the M062X/def2SVP optimized conformers of **1b** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	ΔG (kcal/mol)[d]	Population[e]
1b-1	-1547.66034	0.640413	-970755.004149	0.0	37.99%
1b-2	-1547.66161	0.642125	-970754.726524	0.277625	23.77%
1b-3	-1547.661069	0.642212	-970754.332818	0.671331	12.23%
1b-4	-1547.661068	0.642229	-970754.321755	0.682394	12.00%
1b-5	-1547.657008	0.638823	-970753.911257	1.092892	6.00%
1b-6	-1547.660213	0.642032	-970753.908665	1.095483	5.97%
1b-7	-1547.657086	0.639919	-970753.272587	1.731561	2.04%

[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 S35. Atomic coordinates (Å) of **1b-1** obtained at the M062X/def2SVP level of theory in the gas phase.

C	-0.185972	0.113896	0.993923	H	-0.851730	-4.216186	0.688922
C	-1.218063	-0.834346	0.378955	H	-2.212883	-3.006384	-1.034497
C	1.088064	-0.672940	1.186933	H	-0.669828	-3.380531	-1.842167
C	1.456518	-1.643693	0.042833	H	0.961354	-5.053036	-0.559249
C	0.681061	-1.311523	-1.229612	H	1.503013	-3.739836	-1.634351
C	-0.831702	-1.317097	-1.055473	H	2.592669	-4.351588	-0.383383
C	-1.304282	-2.135572	1.222959	H	1.009399	-2.959508	2.624893
C	-0.577090	-3.195879	0.380578	H	1.234426	-4.598539	1.969112
C	0.982440	-3.122397	0.425301	H	2.562750	-3.413389	1.892286
C	-1.125491	-2.838500	-1.002521	H	2.755358	0.271674	-2.348133
O	1.797545	-0.575755	2.155142	H	3.762647	2.523985	-2.547001
O	1.208113	-1.217847	-2.311363	H	5.093976	3.474442	-0.671594
C	1.545996	-4.121183	-0.604261	H	5.414860	2.145440	1.412524
C	1.475475	-3.535594	1.816003	H	4.415113	-0.125498	1.599861
C	2.983590	-1.471545	-0.134972	H	-1.064095	0.415484	-2.318614
C	3.508833	-0.065691	-0.352079	H	-1.227890	-1.123436	-3.148222
O	3.757104	-2.374191	0.042273	H	-3.535898	-1.460622	-2.146348
C	3.320510	0.686745	-1.516665	H	-5.745101	1.071630	-2.440311
C	3.894706	1.954659	-1.625194	H	-5.542680	-0.549394	-1.752147
C	4.644373	2.484014	-0.578138	H	-3.102964	2.287348	-0.696712
C	4.829135	1.738274	0.586812	H	-2.161978	2.078642	-2.190877
C	4.275186	0.466762	0.694511	H	-3.822654	2.709460	-2.256568
C	-1.505900	-0.586366	-2.228095	H	-5.435672	2.120863	-0.222075
C	-2.996912	-0.507495	-2.091959	H	-6.753117	0.954078	-0.209602
C	-3.730774	0.593084	-1.870523	H	-5.247290	-0.778080	0.873640
C	-5.221235	0.499269	-1.655414	H	-4.006260	0.189792	3.893929
C	-3.163596	1.983607	-1.755204	H	-4.028048	-1.184134	2.756671
C	-5.656724	1.045806	-0.281685	H	-2.586087	-0.141388	2.896426
C	-5.025547	0.297027	0.856035	H	-4.026101	2.572320	2.979566
C	-4.228218	0.766487	1.827607	H	-2.692295	2.273929	1.862098
C	-3.689026	-0.148873	2.894571	H	-4.252273	2.874717	1.242613
C	-3.788325	2.199421	1.970918	H	0.557032	1.103022	-0.803220
C	0.109335	1.376537	0.170308	H	-0.857746	1.852566	-0.067461
C	1.025711	2.328858	0.899616	H	1.396052	1.993864	1.874986
C	1.425785	3.522539	0.444018	H	1.821593	5.359632	1.499225
C	2.326573	4.410319	1.256209	H	2.632141	3.926521	2.193290
C	1.008207	4.074797	-0.890843	H	3.233842	4.667662	0.686930
H	-0.515513	0.424485	1.997993	H	0.370112	3.384923	-1.458028
H	-2.192524	-0.325289	0.333687	H	0.462928	5.024349	-0.764717
H	-2.352870	-2.442962	1.343160	H	1.897343	4.297732	-1.502320
H	-0.891060	-2.006852	2.234665	-	-	-	-

Table S36. Atomic coordinates (Å) of **1b-2** obtained at the M062X/def2SVP level of theory in the gas phase.

C	-0.138429	-0.303778	1.145449	H	1.380481	-4.425919	1.089117
C	-0.606848	-1.681368	0.680880	H	-0.515705	-4.165507	-0.544355
C	1.367413	-0.347132	1.240283	H	0.960120	-3.819737	-1.478507
C	2.093801	-1.120557	0.117353	H	4.375278	-2.964143	-0.301458
C	1.178299	-1.316993	-1.085006	H	3.293062	-4.382585	-0.281147
C	-0.129226	-2.030260	-0.767261	H	3.047185	-3.072974	-1.463621
C	0.009116	-2.783945	1.583491	H	3.453246	-3.639574	2.190386
C	1.100290	-3.429186	0.715738	H	4.040430	-1.979130	1.921425
C	2.425054	-2.606778	0.607369	H	2.511081	-2.250364	2.782611
C	0.355804	-3.495457	-0.620547	H	4.003149	1.774641	1.311777
O	1.997324	0.173259	2.125315	H	3.728829	4.217471	0.928521
O	1.523893	-1.079445	-2.216845	H	2.667176	5.032702	-1.174137
C	3.338935	-3.292263	-0.426770	H	1.880273	3.393028	-2.873314
C	3.143188	-2.608743	1.960787	H	2.139052	0.963643	-2.478353
C	3.325641	-0.246643	-0.217127	H	-1.003861	-0.789036	-2.303404
C	3.074315	1.212518	-0.547403	H	-0.831946	-2.473032	-2.745002
O	4.452405	-0.640509	-0.077461	H	-2.770046	-3.040120	-1.092596
C	3.535105	2.140915	0.397068	H	-5.662808	-1.612291	-1.938345
C	3.375568	3.505873	0.180551	H	-4.908169	-2.569776	-0.652886
C	2.776013	3.961442	-0.994410	H	-4.313944	0.388295	-2.877774
C	2.330144	3.044046	-1.942073	H	-3.550985	0.947760	-1.383181
C	2.469792	1.672304	-1.722560	H	-2.542881	0.376038	-2.733502
C	-1.130559	-1.808345	-1.917784	H	-5.684925	0.405098	-0.549348
C	-2.555938	-2.056400	-1.529995	H	-6.452302	-0.927592	0.303518
C	-3.578921	-1.193624	-1.619921	H	-4.281302	-1.315727	1.620822
C	-4.946716	-1.564035	-1.099622	H	-2.189477	1.305993	2.586440
C	-3.476585	0.197202	-2.187842	H	-3.610362	1.252433	3.632463
C	-5.479561	-0.558297	-0.062262	H	-2.857491	-0.275790	3.104226
C	-4.546787	-0.385020	1.101976	H	-4.933183	2.139896	0.155883
C	-4.011877	0.750412	1.577251	H	-4.634891	2.798126	1.780868
C	-3.116567	0.744341	2.787940	H	-3.275031	2.553816	0.681068
C	-4.239050	2.124186	1.004349	H	-0.145591	0.742373	-0.768843
C	-0.592498	0.848275	0.237220	H	-1.684343	0.737909	0.094321
C	-0.239256	2.199300	0.809395	H	0.313316	2.195718	1.756427
C	-0.523862	3.380976	0.245407	H	-1.032931	5.270707	1.146605
C	-0.137154	4.677893	0.898793	H	0.438367	4.511091	1.818820
C	-1.241490	3.508325	-1.070079	H	0.471787	5.289830	0.214510
H	-0.504890	-0.110907	2.164000	H	-1.562805	2.540045	-1.475510
H	-1.704894	-1.697281	0.713933	H	-2.130231	4.152698	-0.968569
H	-0.742679	-3.547466	1.828354	H	-0.584286	3.989708	-1.812718
H	0.377233	-2.381595	2.538575	-	-	-	-

Table S37. Atomic coordinates (Å) of **1b-3** obtained at the M062X/def2SVP level of theory in the gas phase.

C	0.285386	-0.259756	-1.158140	H	-0.917188	-4.465455	-0.933780
C	0.799444	-1.556987	-0.545503	H	0.764936	-3.949146	0.867563
C	-1.231754	-0.330789	-1.289056	H	-0.827562	-3.655701	1.605524
C	-1.994557	-1.169649	-0.236605	H	-4.118550	-3.332151	-0.043388
C	-1.164608	-1.190492	1.047645	H	-2.828336	-4.526842	0.247855
C	0.210117	-1.840544	0.880592	H	-2.991835	-3.099679	1.297663
C	0.382409	-2.768354	-1.410745	H	-1.981334	-2.374792	-2.871917
C	-0.743077	-3.427639	-0.612108	H	-2.805101	-3.871767	-2.374904
C	-2.121628	-2.704746	-0.697949	H	-3.628733	-2.299979	-2.214481
C	-0.153097	-3.344056	0.796335	H	-5.640885	0.792809	0.255774
O	-1.832226	0.222250	-2.174071	H	-6.025528	3.157115	0.963598
O	-1.587449	-0.823885	2.114357	H	-4.080022	4.620853	1.489995
C	-3.075803	-3.454410	0.259575	H	-1.764162	3.706383	1.316633
C	-2.661901	-2.808602	-2.127718	H	-1.406913	1.378980	0.656988
C	-3.386475	-0.502046	-0.060292	H	0.918994	-0.440227	2.371193
C	-3.506197	0.925218	0.406602	H	0.738644	-2.081120	2.943628
O	-4.392698	-1.101590	-0.346574	H	2.819860	-2.763558	1.557664
C	-4.803785	1.446170	0.501063	H	5.614275	-1.169545	2.430155
C	-5.010307	2.764287	0.892582	H	4.974925	-2.307610	1.232868
C	-3.920016	3.584657	1.187607	H	3.534579	1.243245	1.384347
C	-2.626372	3.075998	1.092937	H	2.408091	0.831090	2.700590
C	-2.424175	1.752190	0.710824	H	4.158012	0.899273	3.003860
C	1.098494	-1.485334	2.088825	H	5.726495	0.641705	0.786654
C	2.555396	-1.738726	1.848570	H	6.567481	-0.778537	0.179977
C	3.555954	-0.846976	1.901631	H	4.485618	-1.381406	-1.215053
C	4.965561	-1.250451	1.540699	H	2.482597	1.066604	-2.695642
C	3.390650	0.602874	2.270975	H	3.966864	0.851868	-3.626073
C	5.566773	-0.381844	0.420060	H	3.163167	-0.576204	-2.921254
C	4.721798	-0.383760	-0.821555	H	4.892000	2.662950	-1.948137
C	4.229876	0.667841	-1.494994	H	3.447636	2.586571	-0.935203
C	3.414854	0.479618	-2.747610	H	5.053651	2.251380	-0.225687
C	4.427917	2.111359	-1.114956	H	0.484543	0.917867	0.666727
C	0.798357	0.969627	-0.391145	H	1.898564	0.867550	-0.355063
C	0.393361	2.278574	-1.020600	H	-0.170775	2.207899	-1.957497
C	0.636901	3.496329	-0.515714	H	1.010081	5.410140	-1.439047
C	0.163940	4.742279	-1.211127	H	-0.361029	4.508647	-2.146028
C	1.375515	3.716235	0.776557	H	-0.523244	5.309789	-0.562340
H	0.650531	-0.172835	-2.192939	H	0.744794	4.263581	1.496648
H	1.892906	-1.479917	-0.470309	H	1.700334	2.779748	1.247099
H	1.214471	-3.480762	-1.506366	H	2.267600	4.341882	0.608860
H	0.094832	-2.473464	-2.430015	-	-	-	-

Table S38. Atomic coordinates (Å) of **1b-4** obtained at the M062X/def2SVP level of theory in the gas phase.

C	0.285303	-0.259730	-1.157978	H	-0.917114	-4.465508	-0.934066
C	0.799465	-1.557034	-0.545546	H	0.765204	-3.949374	0.867187
C	-1.231816	-0.330855	-1.288776	H	-0.827239	-3.656123	1.605347
C	-1.994480	-1.169846	-0.236309	H	-4.118397	-3.332420	-0.043005
C	-1.164406	-1.190811	1.047845	H	-2.828090	-4.527109	0.247905
C	0.210297	-1.840816	0.880569	H	-2.991498	-3.100067	1.297894
C	0.382365	-2.768284	-1.410930	H	-2.805459	-3.871732	-2.374707
C	-0.743003	-3.427734	-0.612257	H	-3.628892	-2.299865	-2.214094
C	-2.121592	-2.704874	-0.697813	H	-1.981601	-2.374828	-2.871792
C	-0.152875	-3.344328	0.796130	H	-1.406717	1.378225	0.658689
O	-1.832407	0.222127	-2.173740	H	-1.763728	3.705936	1.317581
O	-1.587158	-0.824335	2.114641	H	-4.079403	4.621246	1.488801
C	-3.075596	-3.454687	0.259778	H	-6.024980	3.158075	0.961089
C	-2.662097	-2.808595	-2.127503	H	-5.640574	0.793469	0.254164
C	-3.386369	-0.502235	-0.059810	H	0.919042	-0.440817	2.371557
C	-3.505957	0.925205	0.406599	H	0.739126	-2.081932	2.943465
O	-4.392655	-1.101875	-0.345647	H	2.820385	-2.763603	1.557539
C	-2.423888	1.751861	0.711534	H	5.614422	-1.168861	2.429896
C	-2.625961	3.075810	1.093252	H	4.975397	-2.307112	1.232615
C	-3.919506	3.584936	1.186745	H	3.534233	1.243362	1.383910
C	-5.009836	2.764884	0.890993	H	2.407808	0.831067	2.700140
C	-4.803445	1.446612	0.499941	H	4.157722	0.899610	3.003455
C	1.098746	-1.485787	2.088814	H	5.726222	0.642394	0.786403
C	2.555690	-1.738814	1.848388	H	6.567552	-0.777619	0.179662
C	3.556036	-0.846823	1.901333	H	4.485607	-1.381066	-1.215102
C	4.965756	-1.249949	1.540421	H	2.482292	1.066172	-2.695972
C	3.390428	0.603015	2.270581	H	3.966560	0.852121	-3.626540
C	5.566749	-0.381189	0.419791	H	3.163537	-0.576333	-2.921687
C	4.721749	-0.383330	-0.821807	H	4.891679	2.663237	-1.949022
C	4.229837	0.668114	-1.495495	H	3.447472	2.586822	-0.935880
C	3.414800	0.479587	-2.748043	H	5.053634	2.251897	-0.226546
C	4.427786	2.111695	-1.115705	H	0.484808	0.917618	0.667036
C	0.798312	0.969596	-0.390922	H	1.898539	0.867638	-0.355172
C	0.393041	2.278565	-1.020123	H	-0.170975	2.207917	-1.957096
C	0.636232	3.496299	-0.515036	H	-0.525592	5.308650	-0.561867
C	0.162861	4.742206	-1.210252	H	1.008585	5.411029	-1.436870
C	1.374747	3.716220	0.777290	H	-0.360913	4.508614	-2.145833
H	0.650370	-0.172690	-2.192796	H	2.267567	4.340781	0.609433
H	1.892930	-1.479936	-0.470456	H	0.744457	4.264698	1.496886
H	1.214437	-3.480649	-1.506769	H	1.698453	2.779673	1.248482
H	0.094649	-2.473236	-2.430117	-	-	-	-

Table S39. Atomic coordinates (Å) of **1b-5** obtained at the M062X/def2SVP level of theory in the gas phase.

C	-0.619158	-1.528261	-0.998749	H	-4.723897	-2.298636	0.184927
C	-1.313831	-2.323023	0.114409	H	-3.199804	-2.886274	2.099650
C	-1.443757	-0.307527	-1.366756	H	-3.645625	-1.182967	2.355296
C	-2.361234	0.288358	-0.284521	H	-4.311714	0.763362	1.460451
C	-1.787985	-0.013761	1.102786	H	-5.255118	1.166779	0.022857
C	-1.667959	-1.503446	1.409362	H	-5.584566	-0.348730	0.902187
C	-2.686010	-2.804685	-0.428959	H	-4.380880	0.529975	-2.192328
C	-3.707344	-1.880798	0.240309	H	-3.742965	-1.111744	-2.423905
C	-3.798275	-0.431537	-0.329231	H	-5.367134	-0.882221	-1.734667
C	-3.153616	-1.877231	1.660922	H	-2.361789	4.284660	-1.377787
O	-1.370169	0.204203	-2.454475	H	-0.422773	5.849726	-1.529595
O	-1.599308	0.845256	1.926931	H	1.841531	5.078777	-0.827383
C	-4.793387	0.339253	0.567102	H	2.147074	2.771345	0.036324
C	-4.344135	-0.476728	-1.759602	H	0.227389	1.243897	0.213464
C	-2.449281	1.808168	-0.580619	H	-1.231647	-1.134047	3.468658
C	-1.204705	2.662998	-0.589959	H	-0.999187	-2.813729	2.954132
O	-3.501731	2.314517	-0.878544	H	1.176009	-2.318907	1.940529
C	-1.365434	3.969760	-1.068472	H	3.459074	-0.361866	3.490282
C	-0.280611	4.836102	-1.152293	H	3.153193	-1.350082	2.050284
C	0.985896	4.405147	-0.759711	H	-0.134947	0.465718	4.156532
C	1.157744	3.108617	-0.276703	H	1.552304	0.945918	4.510295
C	0.068236	2.243337	-0.187876	H	0.718298	1.544381	3.058882
C	-0.824364	-1.763962	2.665808	H	2.490305	0.751149	0.805577
C	0.648685	-1.540370	2.504061	H	2.934041	1.705223	2.222231
C	1.383370	-0.501886	2.932158	H	5.330378	0.925514	2.041218
C	2.848536	-0.429811	2.572490	H	7.139070	0.834122	0.651908
C	0.845893	0.666817	3.712860	H	6.888978	-0.223469	-0.763414
C	3.166254	0.777212	1.672512	H	6.823376	1.531856	-0.959825
C	4.599325	0.808118	1.231671	H	4.459754	1.293007	-1.980752
C	5.080706	0.680937	-0.013749	H	4.483711	-0.460740	-1.734911
C	6.563492	0.709019	-0.274484	H	3.162146	0.505243	-1.051182
C	4.240307	0.498692	-1.249295	H	1.085970	-0.309691	-1.475872
C	0.845878	-1.104587	-0.753445	H	0.941275	-0.671215	0.251160
C	1.822182	-2.240472	-0.895119	H	2.121689	-2.766070	0.018088
C	2.354831	-2.650390	-2.056036	H	2.991090	-4.592100	-2.748731
C	3.353805	-3.773181	-2.107313	H	4.302453	-3.424413	-2.547342
C	2.029095	-2.021775	-3.385097	H	3.564098	-4.177818	-1.108743
H	-0.608489	-2.149278	-1.907614	H	1.207098	-1.296370	-3.336863
H	-0.674345	-3.174927	0.391224	H	2.916874	-1.510472	-3.793338
H	-2.891167	-3.837057	-0.112206	H	1.753676	-2.799549	-4.114601
H	-2.724042	-2.794708	-1.527164	-	-	-	-

Table S40. Atomic coordinates (Å) of 1b-6 obtained at the M062X/def2SVP level of theory in the gas phase.

C	1.109046	-0.157173	1.856062	H	5.296810	-1.153283	1.040171
C	1.958788	-1.434493	1.734868	H	3.861286	-3.189856	0.713898
C	1.821641	0.924554	1.078541	H	3.941672	-2.412383	-0.884493
C	2.471224	0.488252	-0.252899	H	5.689458	-0.506829	-1.185826
C	1.924547	-0.859032	-0.728709	H	4.140060	-0.561036	-2.064126
C	2.103523	-1.988198	0.276409	H	4.958341	0.987284	-1.831643
C	3.415874	-1.095795	2.168218	H	4.357677	1.548263	1.742280
C	4.216604	-1.049800	0.856166	H	5.782650	1.255800	0.717290
C	4.031644	0.239365	-0.003333	H	4.497361	2.360154	0.168332
C	3.624784	-2.269475	0.157114	H	1.292863	4.034109	-0.674526
O	1.895069	2.071226	1.437255	H	-1.026208	4.941316	-0.709756
O	1.549663	-1.043750	-1.861354	H	-2.916928	3.484198	-1.434209
C	4.741259	0.026455	-1.355744	H	-2.463280	1.149307	-2.160235
C	4.695148	1.424796	0.705817	H	-0.161474	0.247180	-2.104036
C	2.155969	1.638307	-1.240570	H	1.541056	-3.488319	-1.136310
C	0.712327	2.078338	-1.357261	H	1.681410	-4.060228	0.532293
O	3.019543	2.281411	-1.775054	H	-0.527877	-3.196400	1.137749
C	0.458900	3.409094	-0.996585	H	-3.164162	-3.675347	-0.931457
C	-0.839284	3.910337	-1.013992	H	-2.688417	-3.046251	0.652155
C	-1.897043	3.095028	-1.420378	H	-1.563601	-3.581101	-2.860397
C	-1.644629	1.783820	-1.816478	H	-1.050232	-1.894725	-2.697194
C	-0.348190	1.268568	-1.778898	H	0.156854	-3.171563	-2.583184
C	1.294678	-3.239789	-0.094947	H	-2.711473	-0.713890	-0.255643
C	-0.189658	-3.144936	0.096405	H	-3.081230	-1.333604	-1.866933
C	-1.138116	-2.991745	-0.839531	H	-5.194834	-2.496309	-0.455761
C	-2.587967	-2.875730	-0.431817	H	-7.289670	-1.608800	-0.082837
C	-0.873721	-2.914222	-2.319340	H	-7.230811	-0.129533	0.914127
C	-3.232172	-1.529237	-0.789754	H	-7.530648	-0.003447	-0.823274
C	-4.708031	-1.513919	-0.490332	H	-3.877568	1.040512	-0.186428
C	-5.481630	-0.434993	-0.309131	H	-5.160983	1.416812	-1.363587
C	-6.960507	-0.561689	-0.063062	H	-5.476490	1.612162	0.364062
C	-4.959723	0.976166	-0.371636	H	-0.361267	-0.510422	0.291743
C	-0.350355	-0.253429	1.365581	H	-0.823631	-1.103321	1.874747
C	-1.124119	1.014831	1.583883	H	-0.640015	1.932587	1.230639
C	-2.330842	1.143703	2.156061	H	-3.090355	2.740414	3.387642
C	-2.948227	2.507271	2.319782	H	-2.320710	3.289433	1.872223
C	-3.170895	0.007620	2.673895	H	-3.944480	2.546312	1.851789
H	1.095676	0.170799	2.906075	H	-3.464052	0.191181	3.719774
H	1.523447	-2.217112	2.374250	H	-4.102596	-0.071797	2.088820
H	3.828352	-1.895805	2.798623	H	-2.668991	-0.966442	2.623361
H	3.467733	-0.168215	2.756595	-	-	-	-

Table S41. Atomic coordinates (Å) of **1b-7** obtained at the M062X/def2SVP level of theory in the gas phase.

C	-0.674529	0.737044	-1.656985	H	2.226128	-2.475461	-1.028339
C	0.763529	0.591887	-1.160230	H	2.924025	-0.421011	0.250126
C	-1.435085	-0.555867	-1.377260	H	1.928112	-1.379511	1.383122
C	-1.010035	-1.375583	-0.138494	H	-0.302983	-4.230021	0.643191
C	-0.385831	-0.421821	0.883852	H	1.418234	-3.767743	0.616588
C	0.870197	0.287710	0.373947	H	0.262207	-2.884628	1.640390
C	1.449816	-0.604675	-1.859019	H	-0.317838	-2.631810	-2.664468
C	1.493741	-1.690865	-0.782508	H	0.546418	-4.002670	-1.930696
C	0.146059	-2.425615	-0.520584	H	-1.188689	-3.760657	-1.606026
C	1.922728	-0.849913	0.419836	H	-2.711876	0.690053	0.576133
O	-2.327784	-0.946259	-2.084338	H	-4.763614	1.813882	1.291894
O	-0.776079	-0.328255	2.019866	H	-6.741473	0.476006	2.015108
C	0.387868	-3.383737	0.668031	H	-6.624490	-2.012387	1.984111
C	-0.233718	-3.245315	-1.757947	H	-4.532707	-3.143768	1.221422
C	-2.286187	-2.094305	0.382098	H	0.394670	2.218042	1.220037
C	-3.484865	-1.310471	0.847648	H	1.215926	1.120542	2.311983
O	-2.354675	-3.298118	0.370082	H	2.469337	2.903276	0.121806
C	-3.559994	0.082317	0.873548	H	4.663794	3.337049	0.178923
C	-4.725796	0.723452	1.285939	H	5.336697	3.272825	1.816553
C	-5.829044	-0.025646	1.688576	H	4.611750	1.328585	3.340383
C	-5.763315	-1.420182	1.671563	H	3.021185	0.578439	3.047880
C	-4.601226	-2.056525	1.250869	H	4.449978	0.020653	2.156913
C	1.213508	1.483729	1.275745	H	6.911013	2.322914	0.195415
C	2.509767	2.155385	0.922000	H	6.418466	1.102683	1.363426
C	3.709253	1.921089	1.475107	H	5.256775	1.381948	-1.502696
C	4.939249	2.651383	0.995329	H	4.858840	-0.502189	-2.729922
C	3.947579	0.912664	2.566300	H	5.976240	-1.840152	-2.356012
C	6.056365	1.705554	0.518940	H	4.323968	-1.885033	-1.732458
C	5.621864	0.834769	-0.623784	H	5.228048	-2.066978	0.722789
C	5.624571	-0.504647	-0.699868	H	6.852036	-2.114338	0.028808
C	5.168657	-1.210208	-1.949681	H	6.464999	-0.911481	1.278898
C	6.070309	-1.432341	0.398936	H	-1.349741	1.971341	0.005536
C	-1.374981	1.986873	-1.097466	H	-0.747840	2.850066	-1.382821
C	-2.785026	2.164930	-1.602245	H	-3.115042	1.457980	-2.370632
C	-3.655659	3.086511	-1.170309	H	-5.791994	2.983959	-0.926470
C	-5.051480	3.162812	-1.723462	H	-5.258732	4.164678	-2.132509
C	-3.323691	4.106261	-0.114691	H	-5.213826	2.419676	-2.514402
H	-0.673944	0.830780	-2.754271	H	-2.340034	3.946587	0.344766
H	1.301431	1.526424	-1.373636	H	-3.334940	5.120160	-0.546961
H	2.481477	-0.345310	-2.134367	H	-4.082865	4.102449	0.684199
H	0.931581	-0.904709	-2.780977	-	-	-	-

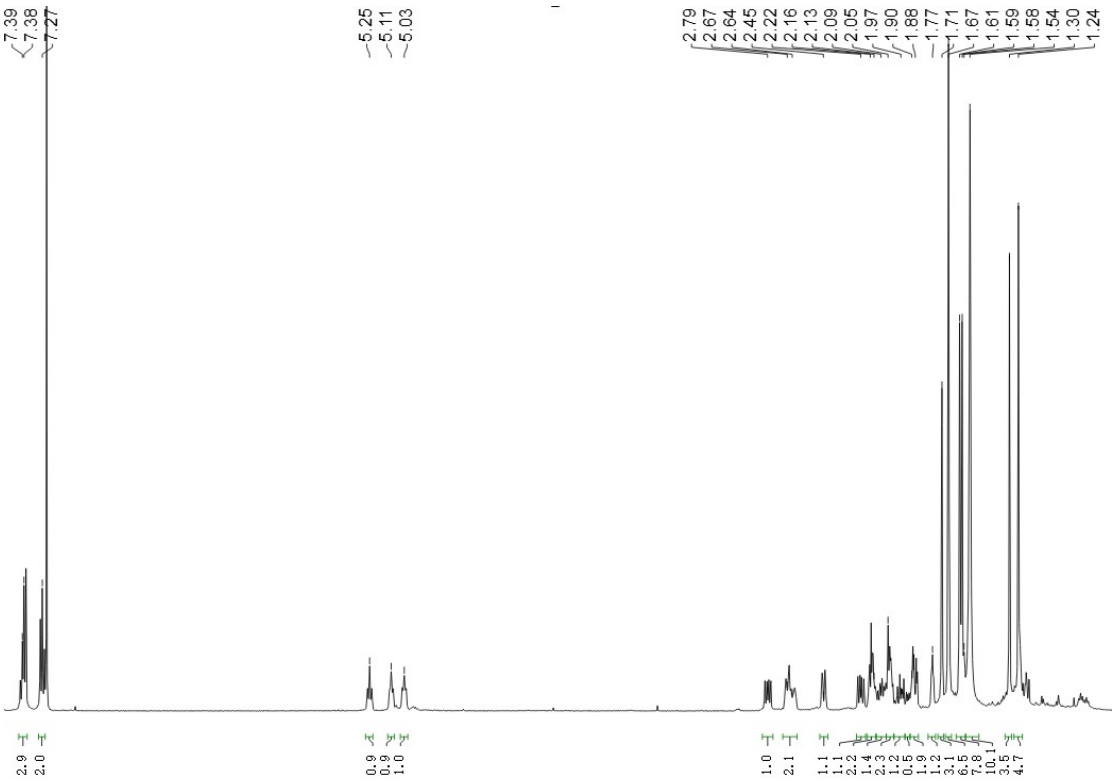


Fig. S25 ^{1}H NMR (600 MHz) spectrum of **1** in $CDCl_3$.

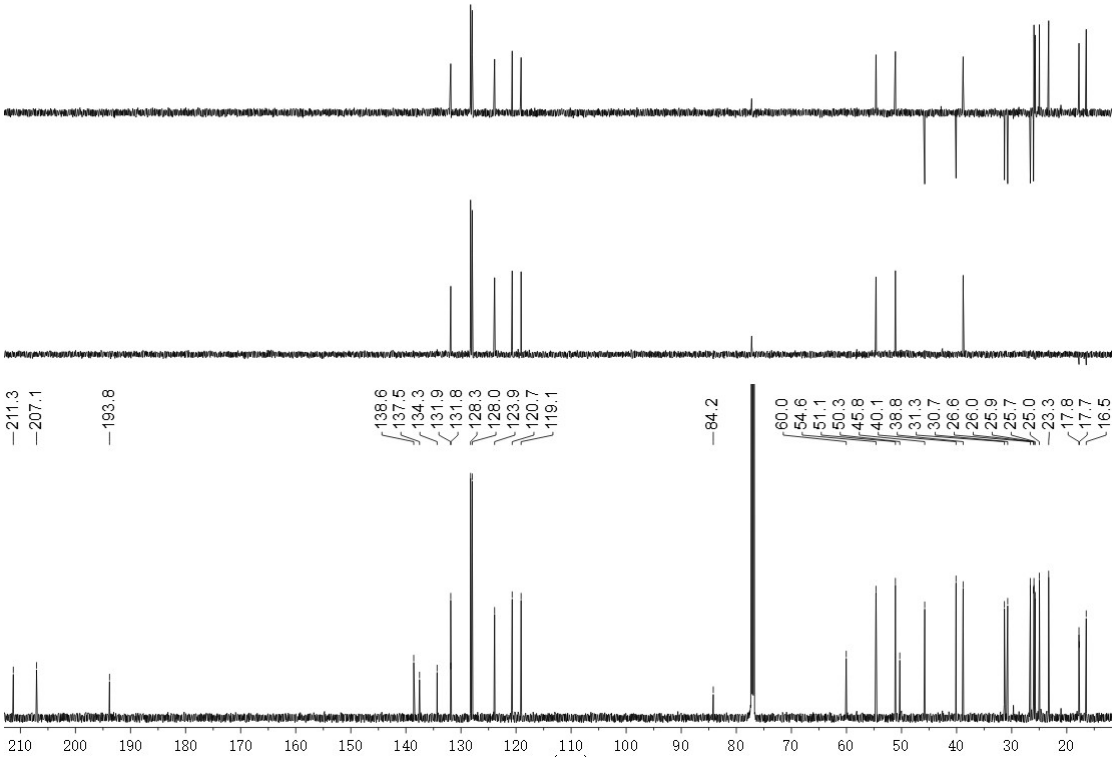


Fig. S26 ^{13}C NMR and DEPT (150 MHz) spectra of **1** in $CDCl_3$.

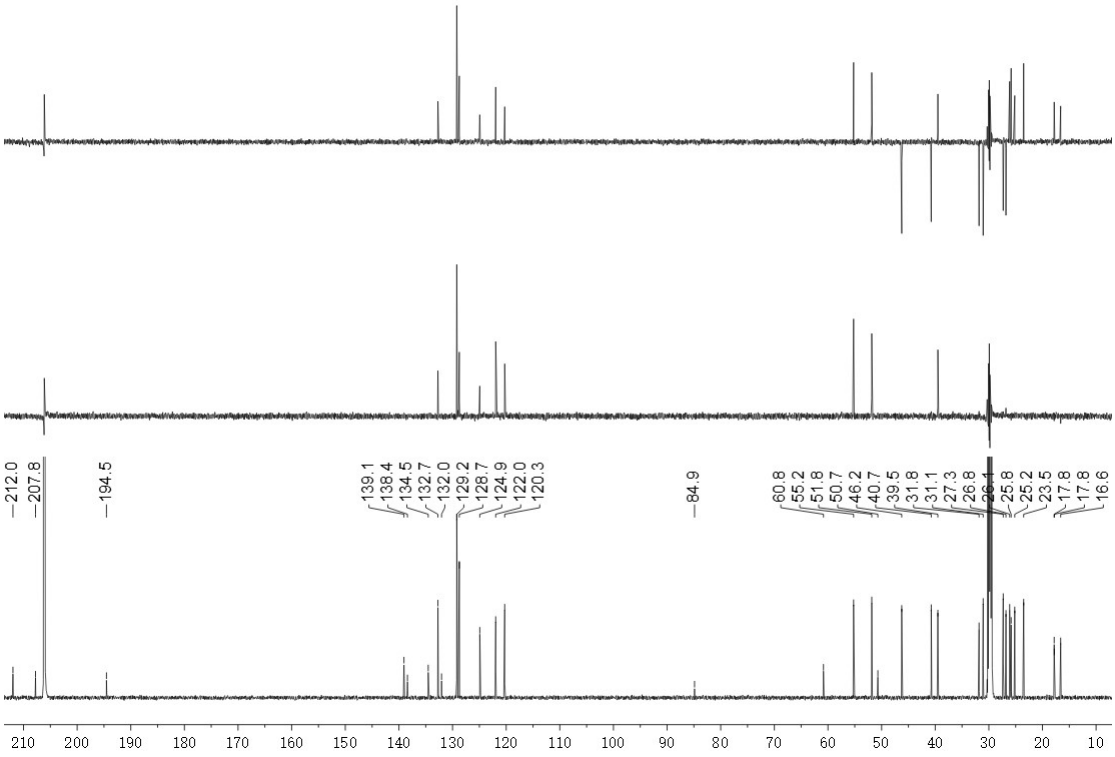


Fig. S27 ^{13}C NMR and DEPT (150 MHz) spectra of **1** in Acetone-d_6.

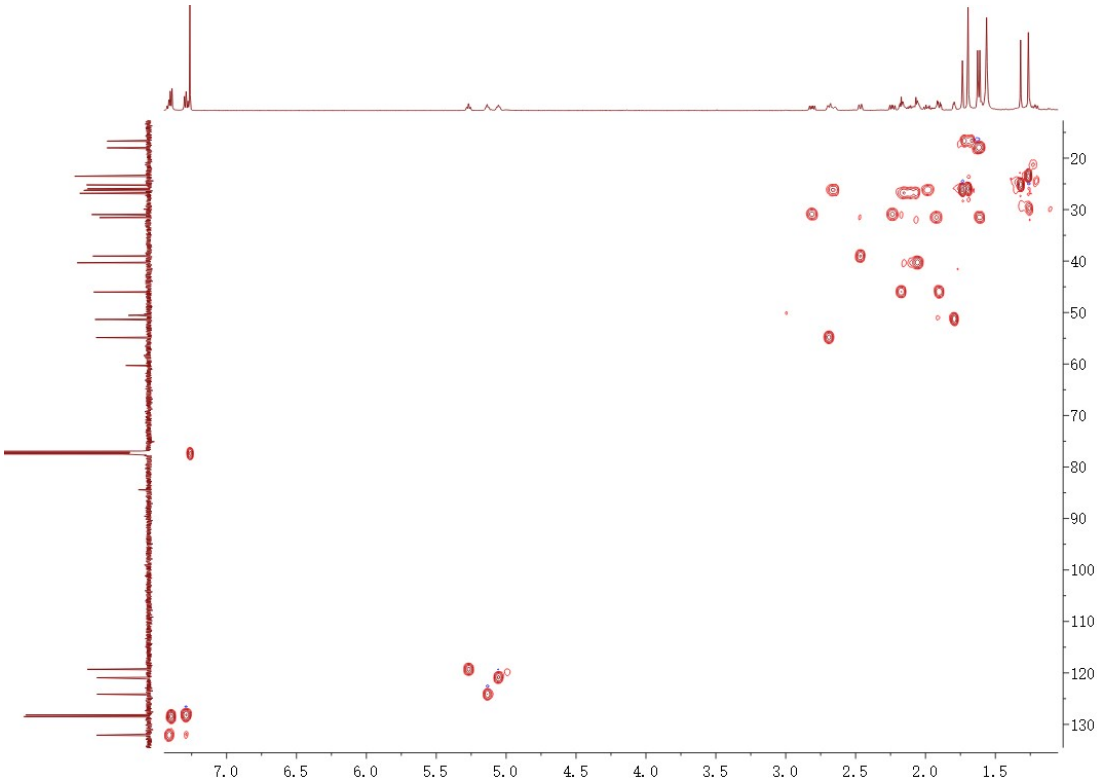


Fig. S28 HSQC (600 MHz) spectrum of **1** in $CDCl_3$.

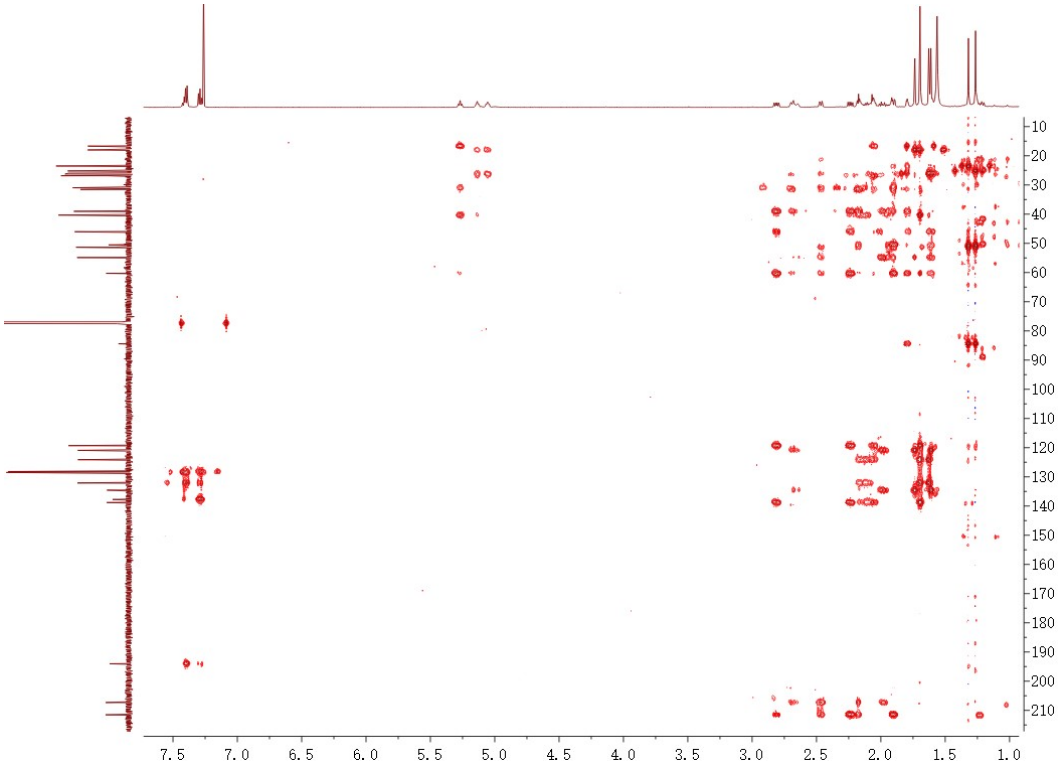


Fig. S29 HMBC (600 MHz) spectrum of **1** in $CDCl_3$.

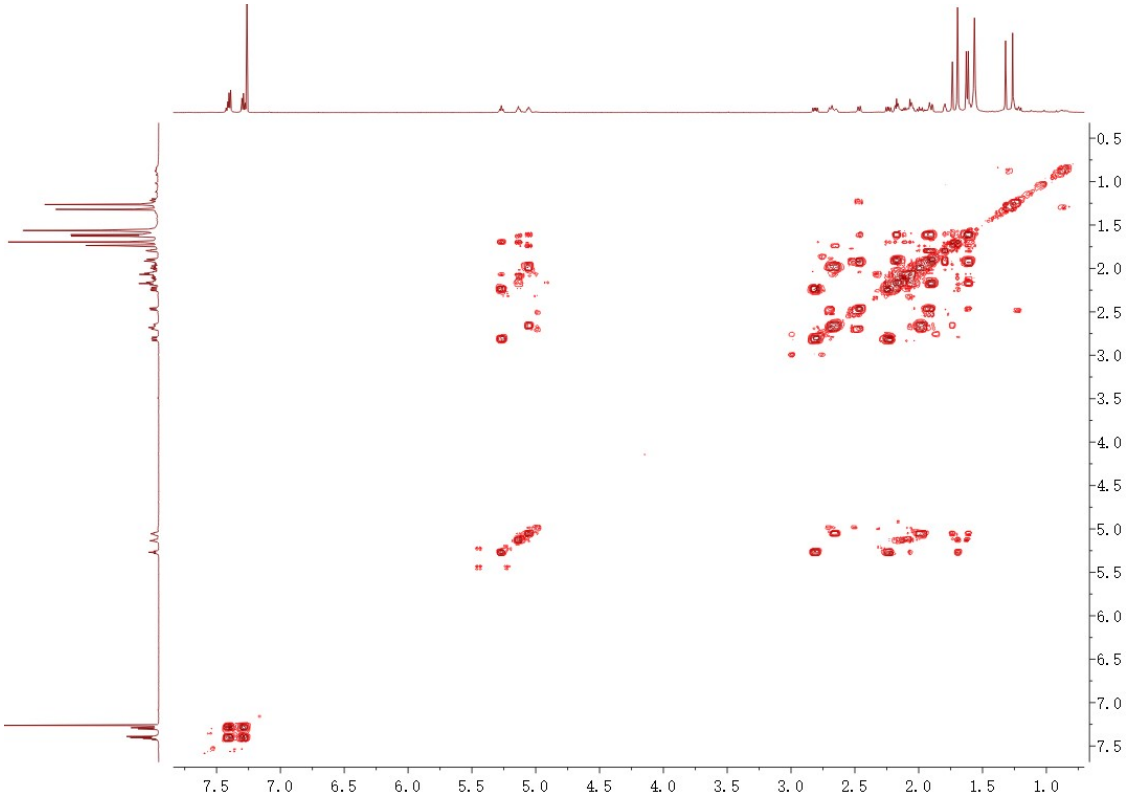


Fig. S30 ^{1}H-^{1}H COSY (600 MHz) spectrum of **1** in $CDCl_3$.

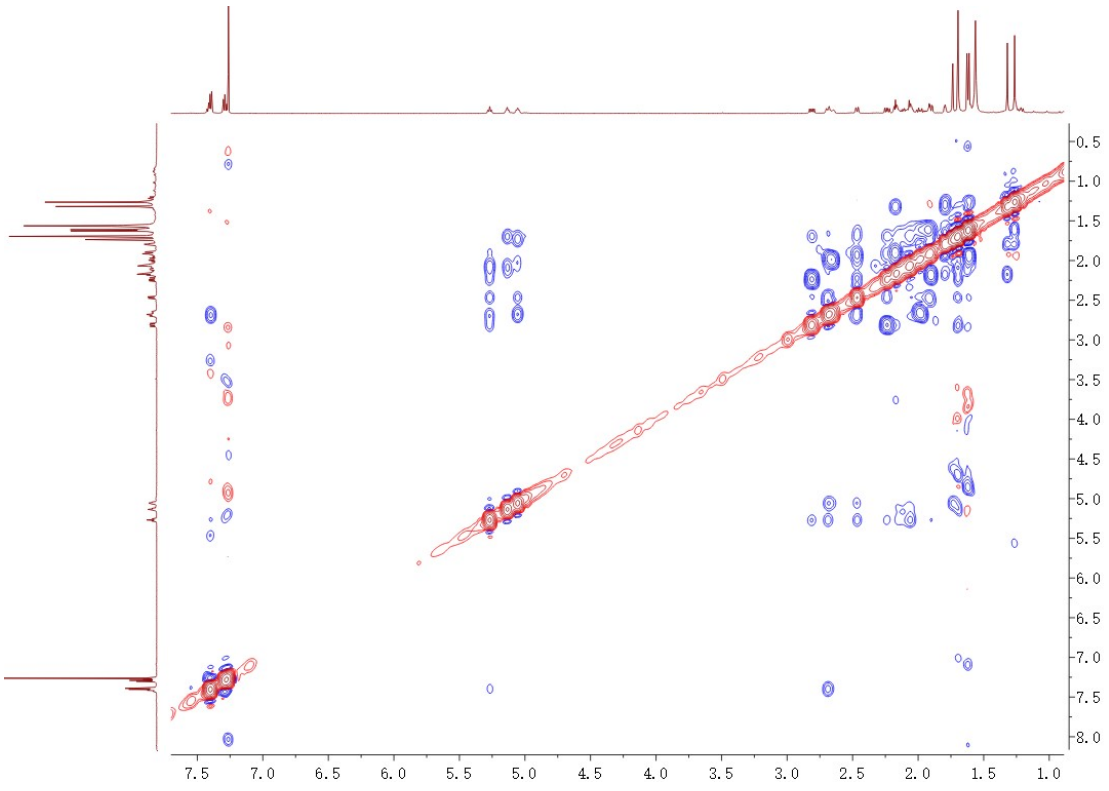


Fig. S31 ROESY (600 MHz) spectrum of **1** in $CDCl_3$.

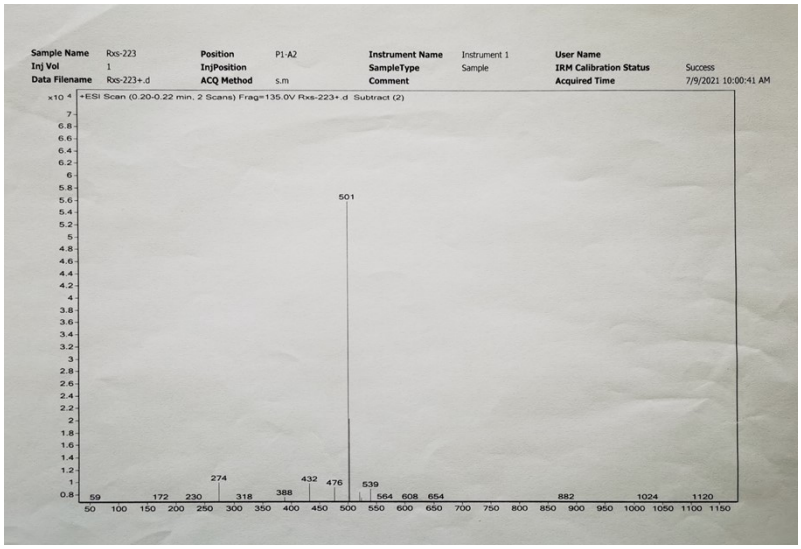
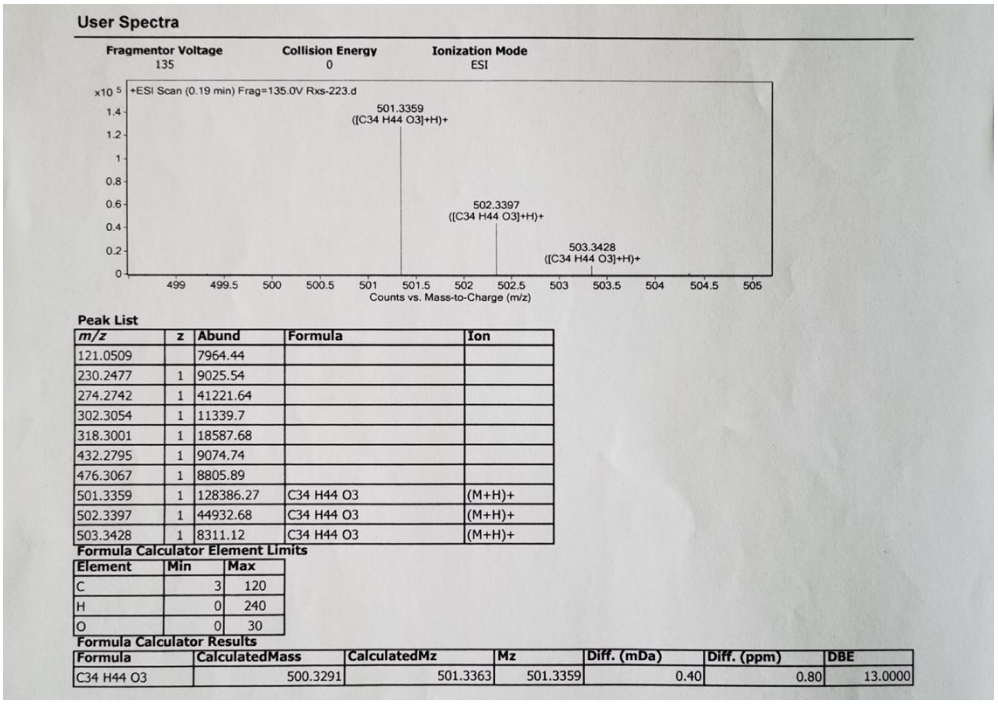


Fig. S32 ESIMS spectrum of **1**.



User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI

Peak List

m/z	z	Abund	Formula	Ion
121.0509		7964.44		
230.2477	1	9025.54		
274.2742	1	41221.64		
302.3054	1	11339.7		
318.3001	1	18587.68		
432.2795	1	9074.74		
476.3067	1	8805.89		
501.3359	1	128386.27	C34 H44 O3	(M+H)+
502.3397	1	44932.68	C34 H44 O3	(M+H)+
503.3428	1	8311.12	C34 H44 O3	(M+H)+

Formula Calculator Element Limits

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

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C34 H44 O3	500.3291	501.3363	501.3359	0.40	0.80	13.0000

Fig. S33 HRESIMS spectrum of **1**.

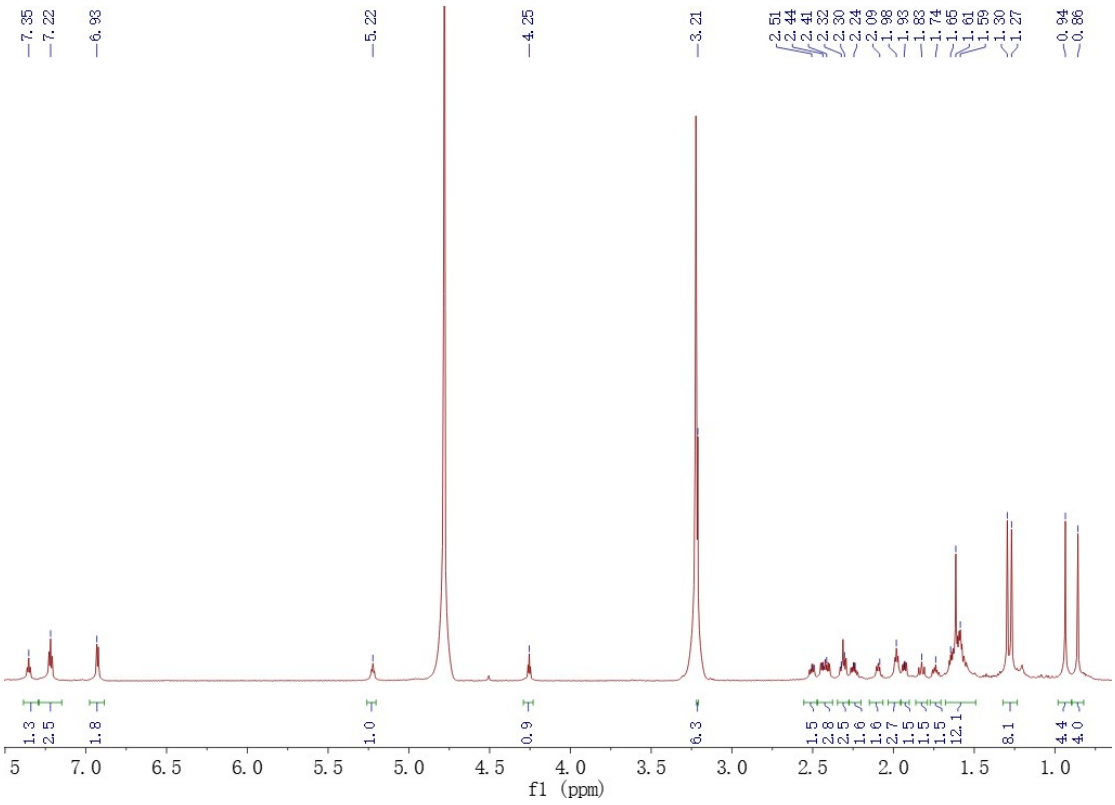


Fig. S34 ^{1}H NMR (800 MHz) spectrum of **3** in MeOD.

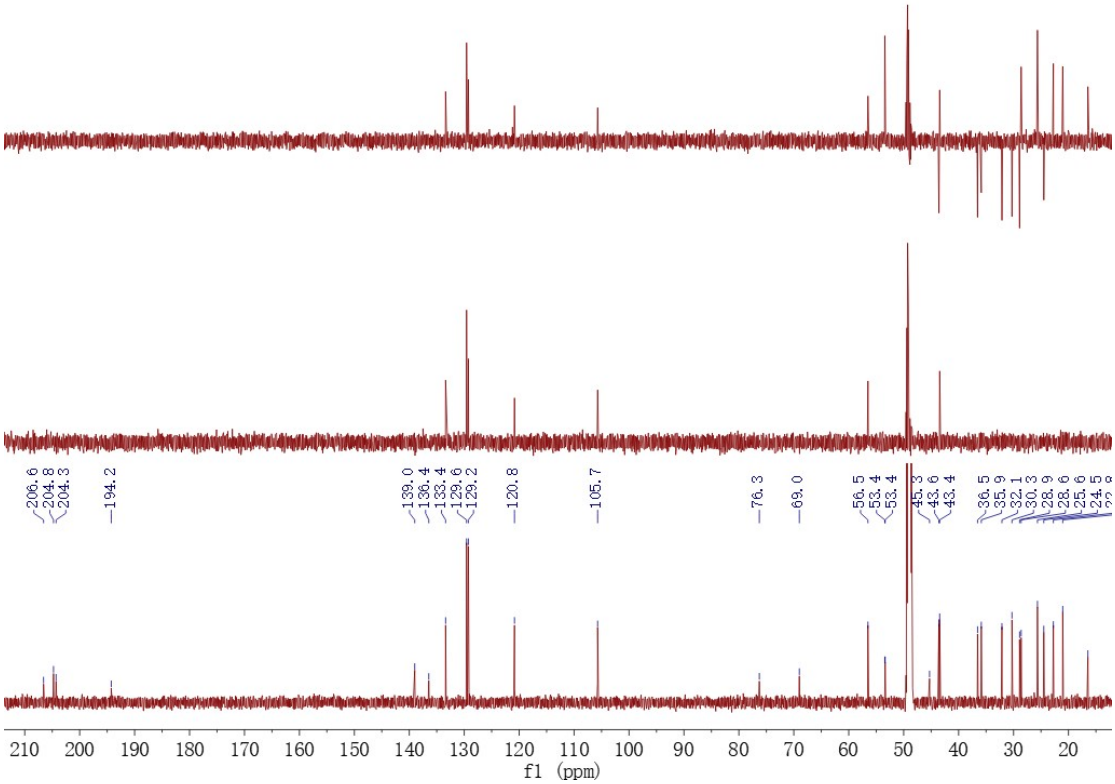


Fig. S35 ^{13}C NMR and DEPT (200 MHz) spectra of **3** in MeOD.

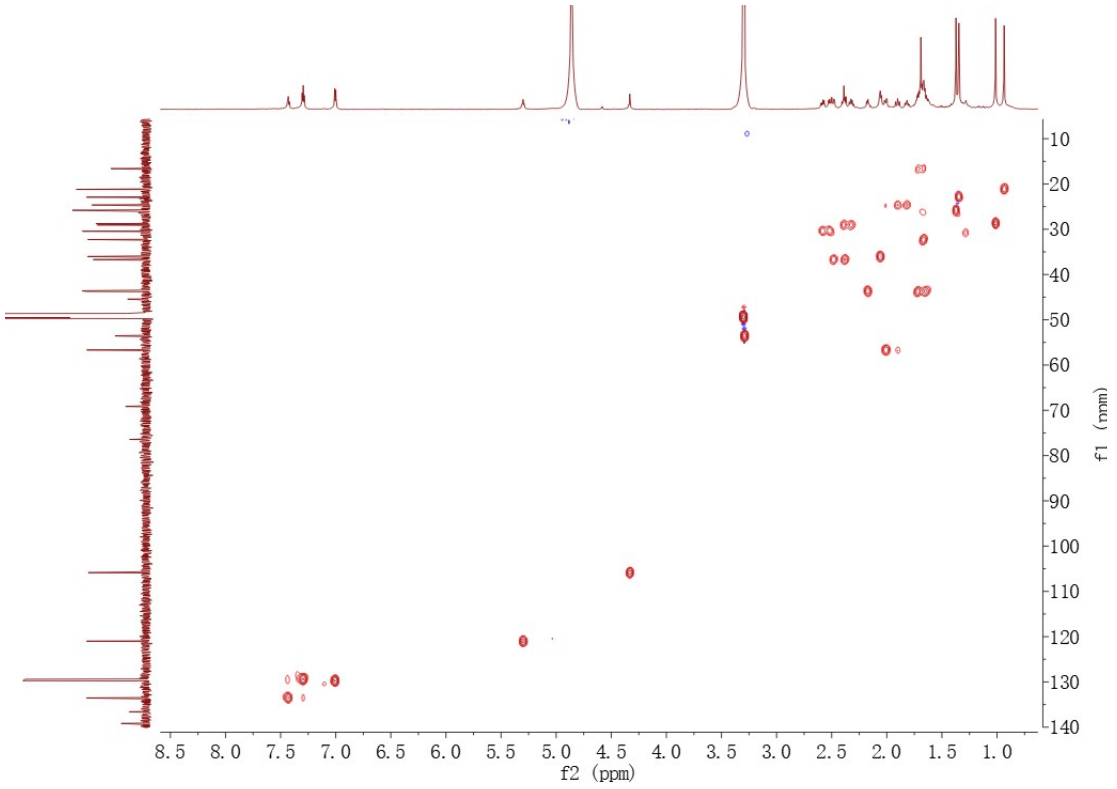


Fig. S36 HSQC (800 MHz) spectrum of **3** in MeOD.

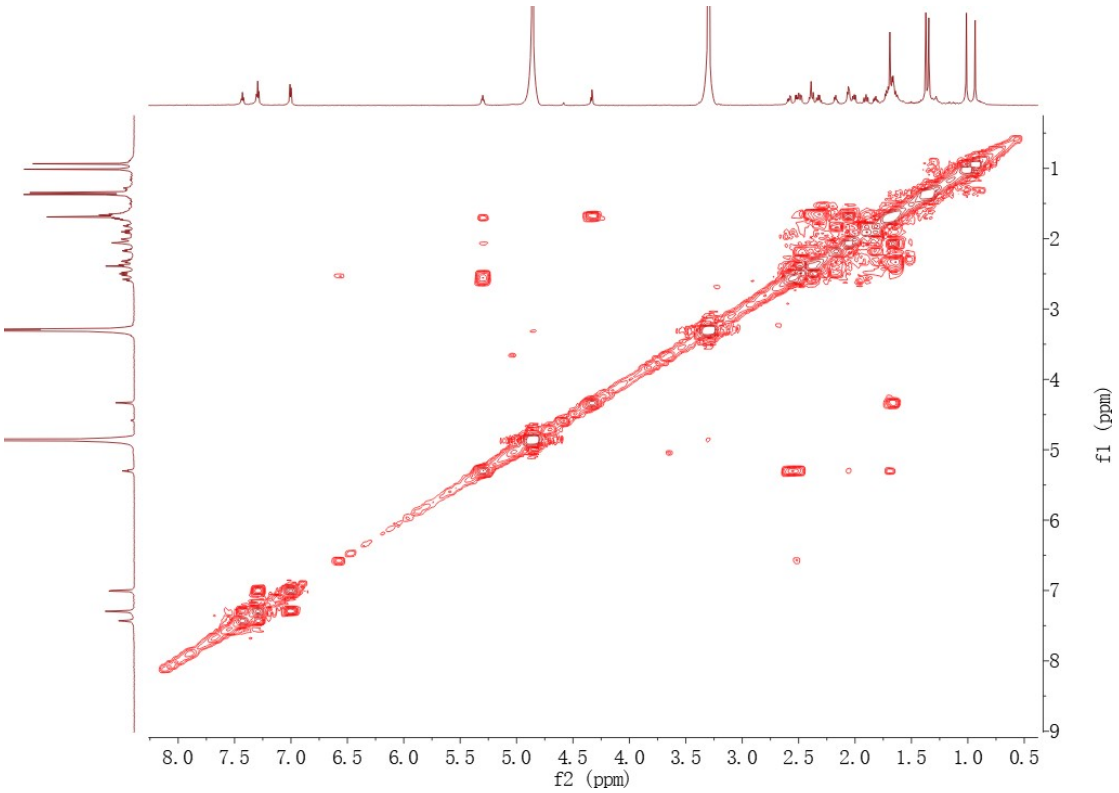


Fig. S37 ^{1}H-^{1}H COSY (800 MHz) spectrum of **3** in MeOD.

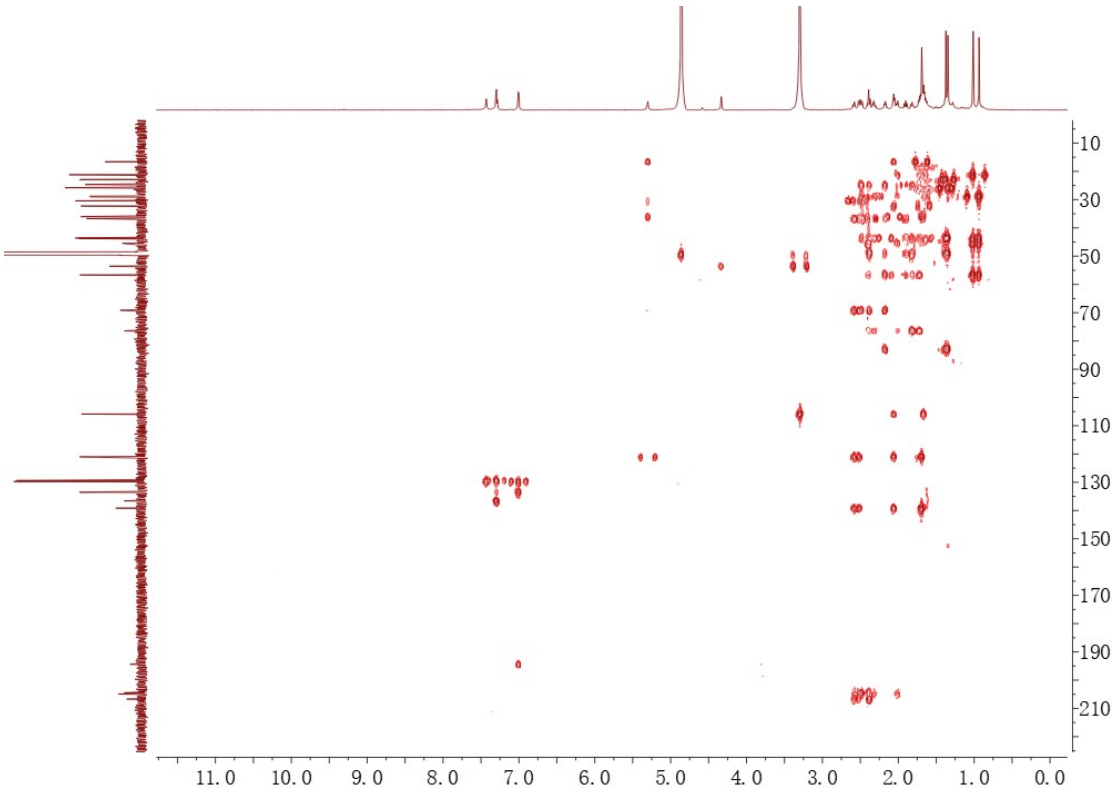


Fig. S38 HMBC (800 MHz) spectrum of **3** in MeOD.

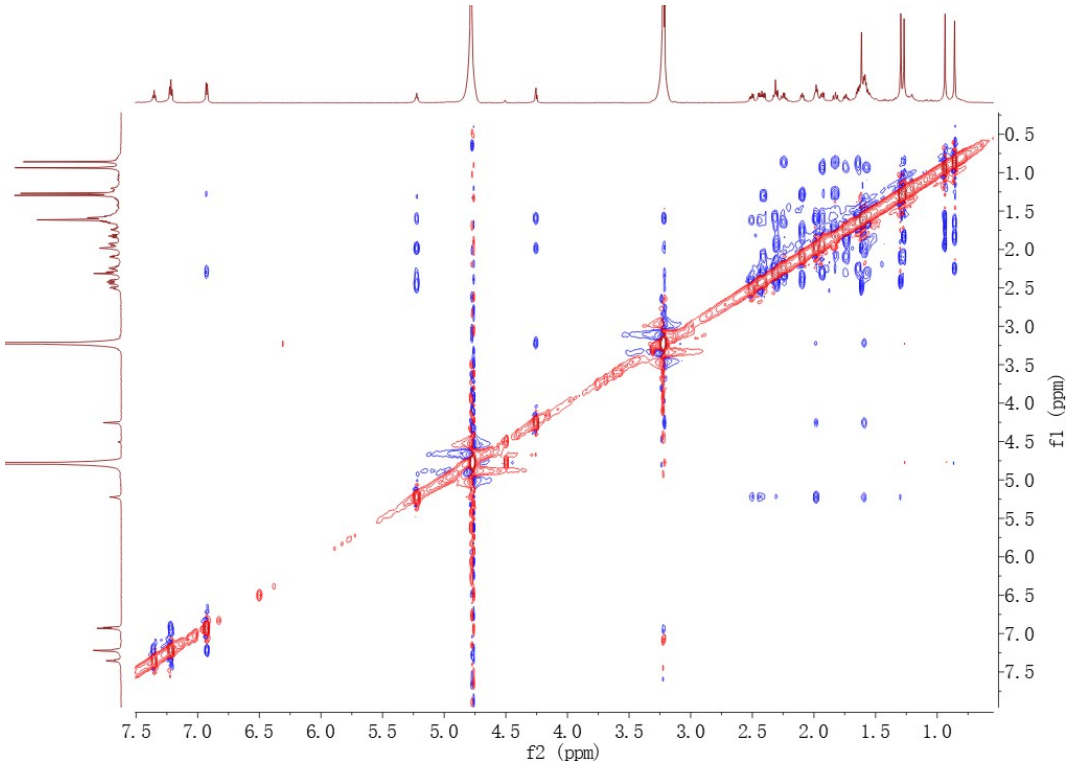


Fig. S39 ROESY (800 MHz) spectrum of **3** in MeOD.

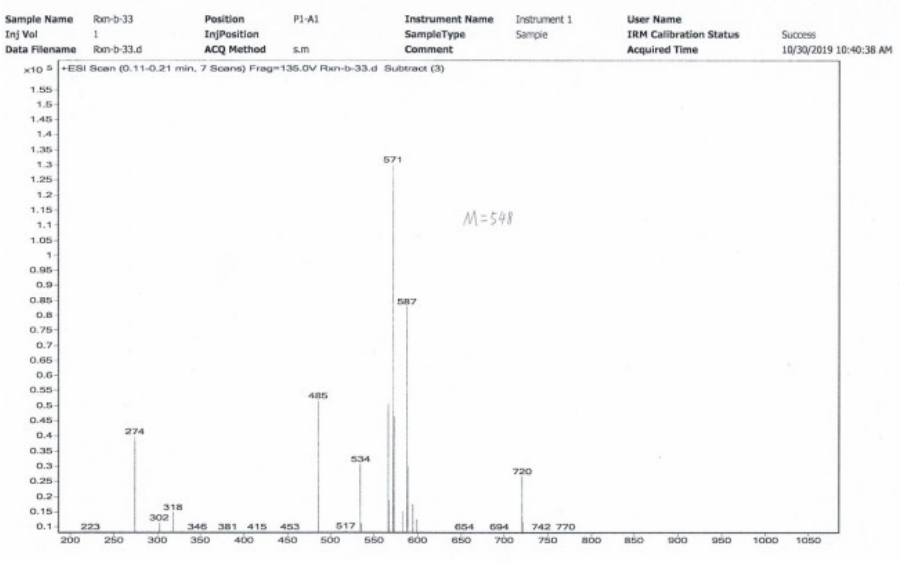


Fig. S40 ESIMS spectrum of **3**.

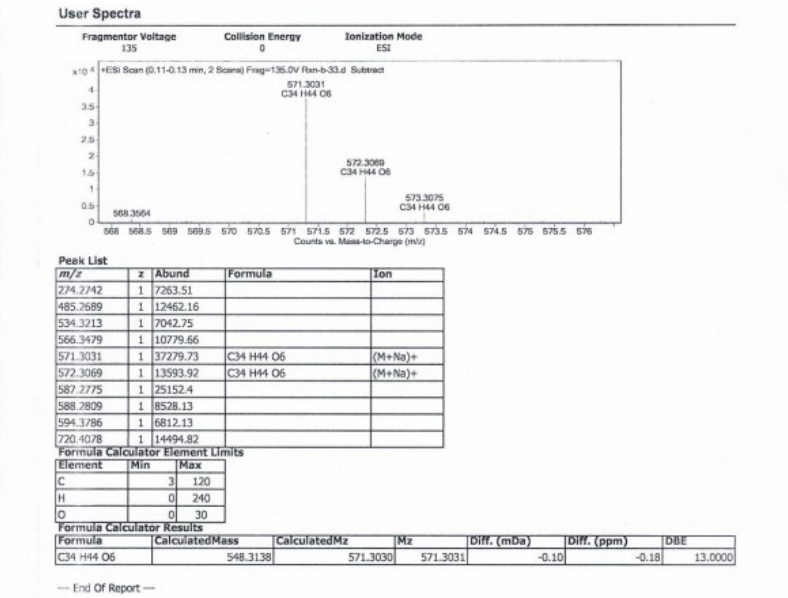


Fig. S41 HRESIMS spectrum of **3**.