Supplementary Information for

Surmounting Challenges of Structure and Configuration Assignment for Trace Novel Flexible Hetero-Tetra/Trimeric Furancarboxylic Acid

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Contents of Supporting Information

Part S1. NMR data 1–3, key 2D NMR correlations of pentrifuranone B (3), summary for NMR computation of pentetrafuranone A (1), and proposed biosynthetic pathway.

Table S1.1. NMR data (δ in ppm, J in Hz) of pentetrafuranone A (**1**).

No.	**1** in methanol-d_4			**1** in DMSO-d_6	
	δ_H, mult (J)	δ_C, type	RDCs	δ_H, mult (J)	δ_C, type
2		200.6 C			197.4 C
2′		199.8 C			197.2 C
2″		200.5 C			197.5 C
3		107.9 C			106.4 C
3′		108.0 C			106.5 C
3″		107.1 C			105.7 C
4		200.6 C			197.1 C
4′		200.9 C			196.9 C
4″		200.4 C			196.8 C
5		92.6 C			90.6 C
5′		92.9 C			90.5 C
5″		92.7 C			90.5 C
6	5.62 (d, 15.5)	126.9 CH	6.0	5.55 (d, 15.5)	126.0 CH
6′	5.55 (d, 15.5)	126.6 CH	12.4	5.56 (d, 15.5)	126.0 CH
6″	5.41 (d, 15.5)	127.1 CH	15.2	5.41 (d, 15.5)	126.1 CH
7	6.32 (dd, 15.5, 10.3)	133.5 CH	6.1	6.25 (dd, 15.5, 10.4)	131.5 CH
7′	6.28 (dd, 15.5, 10.4)	133.6 CH	12.2	6.23 (dd, 15.5, 10.4)	131.5 CH
7″	6.13 (dd, 15.5, 10.4)	132.5 CH	15.5	6.10 (dd, 15.5, 10.4)	130.9 CH
8	6.09 (dd, 15.5, 10.3)	129.3 CH	5.0	6.04 (overlapped)	127.8 CH
8′	6.04 (dd, 15.5, 10.4)	128.9 CH	12.2	6.01 (overlapped)	127.7 CH
8″	5.58 (dd, 15.2, 10.3)	129.1 CH	17.0	5.71 (dd, 15.3, 10.4)	127.6 CH
9	5.92 (dt, 15.5, 6.6)	140.6 CH	5.0	5.88 (dt, 15.2, 6.6)	138.9 CH
9′	5.85 (dt, 15.5, 6.6)	140.6 CH	11.6	5.85 (dt, 15.2, 6.6)	138.9 CH
9″	5.37 (dt, 15.2, 6.5)	139.9 CH	14.1	5.49 (dt, 14.2, 6.9)	138.3 CH
10	2.12 (overlapped)	26.7 CH_2		2.06 (overlapped)	25.1 CH_2
10′	2.11 (overlapped)	26.6 CH_2		2.06 (overlapped)	25.1 CH_2
10″	1.86 (m)	26.4 CH_2		1.90 (m)	24.9 CH_2
11	1.01 (t, 7.6)	13.8 CH_3		0.94 (t, 7.4)	13.2 CH_3
11′	1.00 (t, 7.7)	13.7 CH_3		0.94 (t, 7.4)	13.2 CH_3
11″	0.83 (t, 7.4)	13.5 CH_3		0.83 (t, 7.4)	13.0 CH_3
12		164.1 C			162.1 C
12′		164.1 C			162.2 C
12″		164.4 C			162.5 C

No.	**1** in methanol-d_4			**1** in DMSO-d_6	
	δ_H, mult (*J*)	δ_C, type	RDCs	δ_H, mult (*J*)	δ_C, type
12-OCH_3	3.72 (s)	51.7 CH_3		3.61 (s)	50.9 CH_3
12′-OCH_3	3.70 (s)	51.7 CH_3		3.58 (s)	50.9 CH_3
12″-OCH_3	3.80 (s)	51.7 CH_3		3.67 (s)	50.9 CH_3
13	1.50 (s)	22.5 CH_3	0.4	1.40 (s)	21.4 CH_3
13′	1.53 (s)	22.4 CH_3	1.5	1.43 (s)	21.3 CH_3
13″	1.46 (s)	23.0 CH_3	0.7	1.37 (s)	21.7 CH_3
14	b 2.67 (dd, 13.0, 3.3)	34.2 CH_2	−10.0	b 2.65 (t, 11.6)	31.9 CH_2
	a 2.48 (dd, 13.0, 10.3)		−20.4	a 2.56 (overlapped)	
14′	b 3.07 (dd, 13.6, 4.0)	33.7 CH_2	−23.0	b 2.95 (dd, 13.6, 3.5)	31.8 CH_2
	a 2.55 (dd, 13.6, 10.0)		−9.5	a 2.50 (overlapped)	
14″	b 3.47 (dd, 12.4, 5.2)	40.4 CH_2	−18.1	b 3.25 (dd, 12.7, 6.3)	38.1 CH_2
	a 2.76 (dd, 12.4, 9.6)		2.6	a 2.87 (dd, 12.7, 8.6)	
15	2.86 (m)	38.4 CH	−21.5	2.72 (m)	36.7 CH
15′	2.93 (m)	39.3 CH	−17.0	2.81 (m)	37.2 CH
15″	3.52 (m)	31.4 CH	2.6	3.30 (overlapped)	29.7 CH
16	0.96 (d, 6.7)	13.6 CH_3	1.3	0.84 (d, 6.7)	12.8 CH_3
16′	1.06 (d, 7.0)	14.5 CH_3	4.7	0.91 (d, 7.0)	13.7 CH_3
16″	1.25 (d, 6.8)	23.0 CH_3	−4.6	1.14 (d, 6.8)	21.6 CH_3
17		95.9 C			94.1 C
18		135.5 C			131.7 C
19	6.58 (s)	98.4 CH	−13.1	6.52 (s)	96.9 CH
20		150.5 C			149.1 C
20-OCH_3	3.98 (s)	56.8 CH_3		3.87 (s)	56.1 CH_3
21		133.4 C			133.7 C
22		142.2 C			141.0C
23		116.9 C			115.0 C
24		155.1 C			153.3 C
25	5.20 (d, 9.5)	102.0 CH		5.05 (d, 9.0)	100.1 CH
21-OH				8.82 (s)	
22-OH				9.29 (s)	

Table S1.2. NMR data (δ in ppm, J in Hz) of pentrifuranone A (**2**) in methanol-d_4.

No.	δ_H, mult (J)	δ_C, type	RDCs
2		199.0 C	
3		109.3 C	
4		200.8 C	
5		92.6 C	
6	5.63 (d, 15.5)	126.9 CH	21.6
7	6.34 (dd, 15.5, 10.4)	133.2 CH	24.0
8	6.08 (overlapped)	129.1CH	
9	5.83 (dt, 15.2, 6.7)	140.5 CH	22.0
10	2.12 (m)	26.6 CH_2	
11	1.01 (t, 7.5)	13.7 CH_3	
12		164.3 C	
12-OCH_3	3.77 (s)	51.9 CH_3	
13	1.60 (s)	22.9 CH_3	3.8
14	3.57 (d, 4.7)	57.0 CH	−28.5
15	3.02 (qd, 6.9, 4.7)	45.0 CH	9
16		94.9 C	
17		136.1 C	
18		128.0 C	
19		88.9 C	
20		140.7 C	
21		135.1 C	
22		148.9 C	
22-OCH_3	3.92 (s)	57.0 CH_3	
23	6.82 (s)	98.8 CH	−2.4
24	0.67 (d, 6.9)	15.9 CH_3	4.5
25	1.81 (s)	16.9 CH_3	−0.6
2′		200.4 C	
3′		108.2 C	
4′		200.7 C	
5′		92.8 C	
6′	5.52 (d, 15.5)	126.4 CH	0.1
7′	6.34 (dd, 15.5, 10.4)	133.8 CH	2.3
8′	6.07 (overlapped)	129.1 CH	
9′	5.87 (dt, 15.2, 6.6)	140.6 CH	3.8
10′	2.12 (m)	26.7 CH_2	
11′	1.02 (t, 7.5)	13.7 CH_3	
12′		164.4 C	

No.	δ_H, mult (*J*)	δ_C, type	RDCs
12′-OCH_3	3.79 (s)	51.8 CH_3	
13′	1.57 (s)	22.3 CH_3	−6.5
14′	b 3.42 (dd, 9.4, 9.4)	35.8 CH_2	9.0
	a 3.12 (overlapped)		−11.4
15′	3.13 (overlapped)	31.4 CH	−0.5
16′	1.27 (d, 5.7)	14.3 CH_3	−3.7

Table S1.3. NMR data (δ in ppm, *J* in Hz) of pentrifuranone B (**3**).

No.	**3** in methanol-d_4			**3** in DMSO-d_6		
	δ_H, mult (*J*)	δ_C, type	RDCs	δ_H, mult (*J*)	δ_C, type	RDCs
2		196.6 C			193.8 C	
3		108.5 C			106.7 C	
4		200.9 C			196.9 C	
5		92.3 C			90.1 C	
6	5.31 (d, 15.2)	126.8 CH	5.0	5.35 (d, 14.4)	126.1 CH	−6.9
7	5.96 (overlapped)	133.1 CH	5.1	5.95 (overlapped)	131.4 CH	−6.1
8	5.93 (overlapped)	129.0 CH	3.8	5.93 (overlapped)	127.6 CH	−7.2
9	5.76 (dt, 14.5, 6.6)	140.4 CH	5.5	5.81 (dt, 13.8, 6.8)	138.9 CH	−4.8
10	2.07 (m)	26.7 CH_2		2.03 (m)	25.0 CH_2	
11	0.98 (t, 7.5)	13.7 CH_3		0.92 (t, 7.5)	13.1 CH_3	
12		164.3 C			162.7 C	
12-OCH_3	3.81 (s)	51.8 CH_3		3.72 (s)	51.1 CH_3	
13	1.18 (s)	21.3 CH_3	9.0	1.07 (s)	19.8 CH_3	3.0
14	4.08 (d, 4.0)	60.2 CH	−12.8	3.97 (d, 4.1)	58.1 CH	
15	2.50 (m)	46.7 CH	17.2	2.40 (m)	44.2 CH	5.3
16		94.4 C			92.2 C	
17		138.2 C			136.3 C	
18		125.9 C			124.3 C	
19		91.0 C			88.9 C	
20		142.0 C			141.0 C	
21		134.4 C			133.0 C	
22		149.0 C			147.3 C	
22-OCH_3	3.92 (s)	57.2 CH_3	−3.8	3.82 (s)	56.5 CH_3	−1.9
23	6.72 (s)	97.7 CH	8.0	6.62 (s)	96.4 CH	6.3
24	1.27 (d, 6.9)	17.6 CH_3	8.7	1.19 (d, 6.9)	17.2 CH_3	4.3
25	1.82 (s)	19.8 CH_3	−5.9	1.74 (s)	19.1 CH_3	−5.1
2′		199.8 C			197.1 C	

No.	**3** in methanol-d_4			**3** in DMSO-d_6		
	δ_H, mult (J)	δ_C, type	RDCs	δ_H, mult (J)	δ_C, type	RDCs
3′		108.3 C			106.8 C	
4′		201.1 C			197.1 C	
5′		92.6 C			90.5 C	
6′	5.58 (d, 15.5)	126.9 CH	14.0	5.61 (d, 15.5)	126.1 CH	4.3
7′	6.32(dd, 15.5, 10.4)	133.4 CH	13.1	6.28(dd, 15.2, 10.5)	131.6 CH	4.8
8′	6.06 (dd, 15.2, 10.4)	129.1CH	12.4	6.07 (dd, 15.2, 10.5)	127.8CH	7.5
9′	5.86 (dt, 15.0, 6.6)	140.5 CH	13.4	5.88 (dt, 15.2, 6.5)	138.9 CH	2.3
10′	2.12 (m)	26.6 CH_2		2.07 (m)	25.1 CH_2	
11′	1.02 (t, 7.5)	13.7 CH_3		0.97 (t, 7.5)	13.1 CH_3	
12′		164.6 C			162.4 C	
12′-OCH_3	3.60 (s)	51.6 CH_3		3.60 (s)	50.9 CH_3	
13′	1.55 (s)	22.0 CH_3	−0.5	1.48 (s)	21.1 CH_3	−1.6
14′	b 3.47 (dd, 14.0, 7.1)	35.2 CH_2	−18.2	b 3.36 (dd, 14.2, 9.0)	33.5 CH_2	−4.4
	a 3.28 (dd, 14.0, 7.9)		−4.9	a 3.12 (dd, 14.2, 5.4)		9.7
15′	2.89 (m)	33.7 CH	−21.4	2.73 (m)	31.3 CH	−12.1
16′	1.51 (d, 7.2)	15.7 CH_3	−4.5	1.39 (d, 7.2)	14.5 CH_3	−5.1

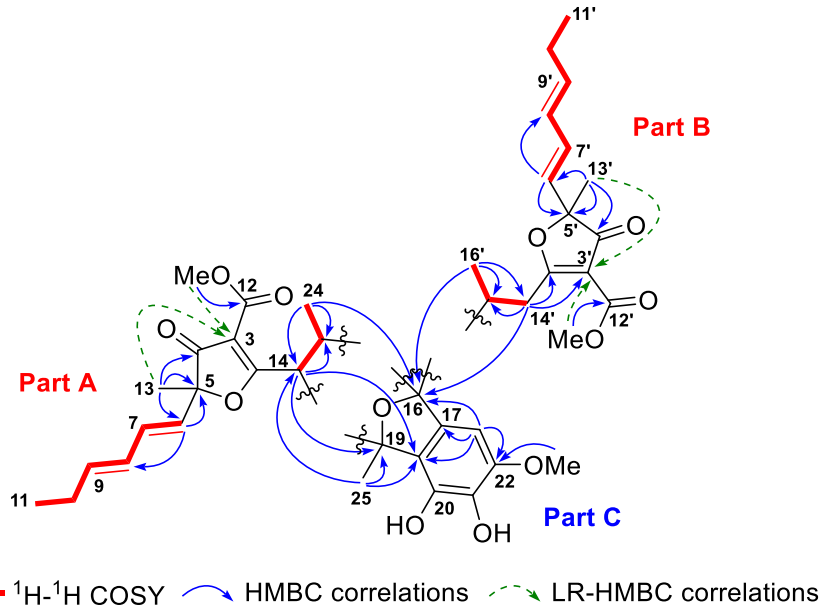

Figure S1.1. ^{1}H–^{1}H COSY, selected HMBC, and LR-HSQMBC correlations of pentrifuranone B (**3**).

Proposed biosynthetic pathway

The hetero-dimeric/trimeric/tetrameric FcAs originated from the same precursors, SPE and gregatin A, and with a similar mechanism through Michael addition and intermolecular nucleophilic attack, but in different mole ratios. Specifically, the Michael reaction from carbanion of SPE to the *α*,*β*,*γ*,*δ*-unsaturated carbonyl system of gregatin A generates intermediate 1, and it affords heterodimeric FcA, penicilfuranone A, with a subsequent intramolecular vinylogous aldol condensation, which has been proposed in previous study[18] (Figure 6). The intermediate 1 is able to adopt a proton in the environment through another pathway to yield intermediate 2.

Later, the general base in the environment deprives the proton at CH_2-16 to generate the carbanion, then it attacks the unsaturated carbonyl system of gregatin A to give intermediate 3 or adopts a proton to give intermediate 4. Intermediate 3 is further subjected to dehydration, oxidation, and intermolecular nucleophilic attack to provide heterotrimeric FcA, compounds **2** and **3**. Intermediate 4 through another round of proton deprivation and Michael addition to gregatin A, and with subsequent oxidation and intermolecular nucleophilic attack to finally generate heterotetrameric FcA, compound **1**.

The Michael addition reaction in biosynthesis of hetero-dimeric/trimeric/tetrameric FcAs worth to be further investigated in future study. There are two prior things need to be addressed: 1) the biosynthesis of SPE; 2) what kind of factor (enzyme, organic, or inorganic molecules) ignites SPE to become a reactive nucleophile? To the best of our knowledge, Michael addition is wildly involved in biosynthesis of NPs, yet, there are only several study cases, like dialkylresorcinol (DarB)[S1], lumiquinone A[S2], rifamycin B (Rif-Orf19)[S3], and rhizoxin (RhiE)[S4] have been reported as enzymatic Michael addition for C–C bond formation. Obviously, hetero-dimeric/trimeric/tetrameric FcAs, are dissimilar to the reported cases, which require an intermolecular reaction between metabolites from two independent BGCs with an uncharacterized mechanism.

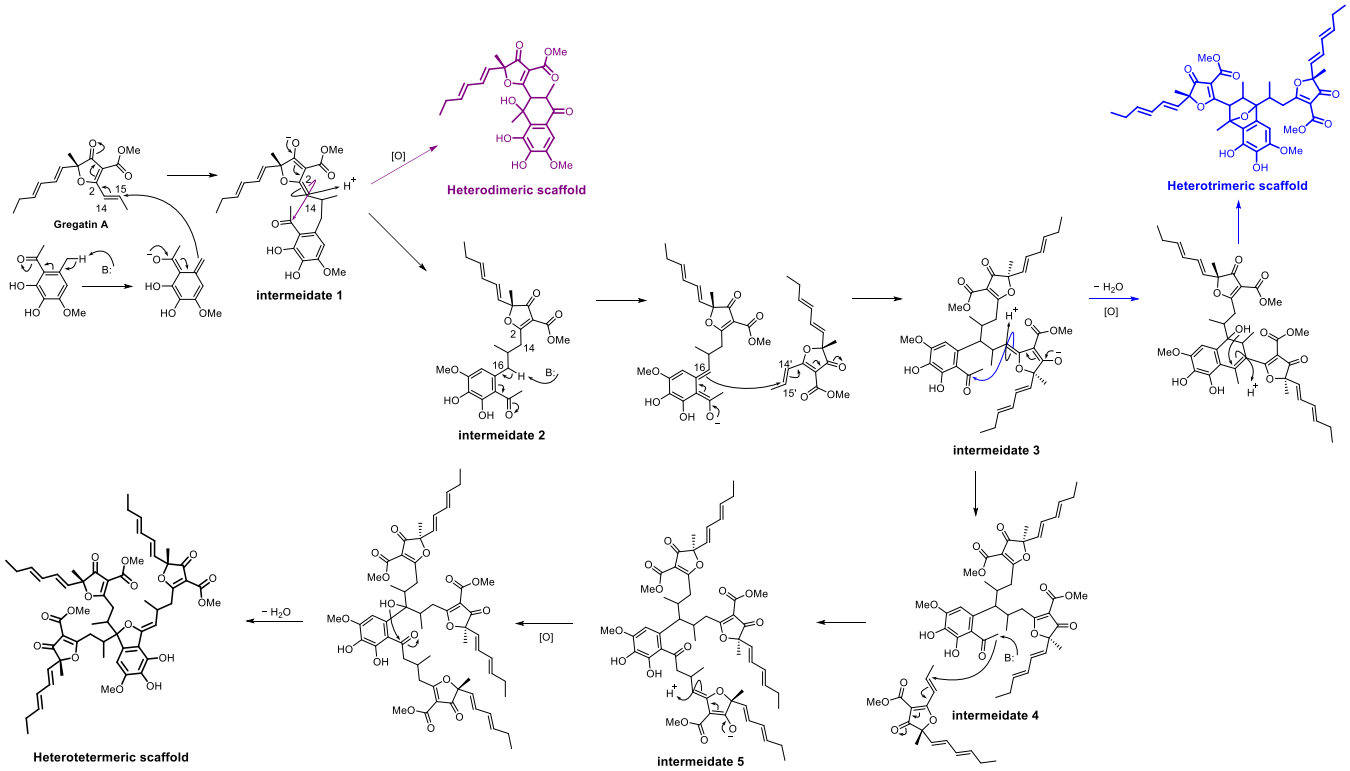

Figure S1.2. proposed biosynthetic pathway of heterodimeric FcA (penicilfuranone A[18]), heterotrimeric FcA (**2** and **3**) and heterotetrameric FcA (**1**).

Table S1.4. A summary for quantum chemical NMR calculation of pentetrafuranone A (**1**).

Analysis on NMR computational data of 1 using data 1 as the experimental chemical shifts									
Diastereomers		**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**
C data	**R^2**	0.9980	0.9991	0.9992	0.9978	0.9983	0.9988	0.9979	0.9984
	MAE	3.0	2.7	2.6	2.8	2.7	2.5	2.9	2.8
	CMAE	2.0	2.1	1.4	2.2	2.0	1.6	2.2	1.7
	DP4+ possibility	0.00%	88.04%	11.96%	0.00%	0.00%	0.00%	0.00%	0.00%
H data	**R^2**	0.9449	0.9732	0.9499	0.9305	0.9605	0.9667	0.9623	0.9512
	MAE	0.37	0.26	0.40	0.42	0.26	0.24	0.30	0.37
	CMAE	0.32	0.23	0.34	0.40	0.24	0.20	0.28	0.29
	DP4+ possibility	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
DP4+ all data		0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
Analysis on NMR computational data of 1 using data 2 as the experimental chemical shifts									
Diastereomers		**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**
C data	**R^2**	0.9980	0.9990	0.9991	0.9978	0.9983	0.9988	0.9978	0.9984
	MAE	3.0	2.7	2.6	2.8	2.7	2.6	2.9	2.8
	CMAE	2.1	1.5	1.5	2.2	2.0	1.7	2.2	1.7
	DP4+ possibility	0.00%	98.64%	1.36%	0.00%	0.00%	0.01%	0.00%	0.00%
H data	**R^2**	0.9309	0.9634	0.9381	0.9173	0.9556	0.9567	0.9639	0.9344
	MAE	0.39	0.29	0.43	0.44	0.28	0.25	0.30	0.39
	CMAE	0.34	0.25	0.36	0.41	0.26	0.22	0.28	0.32
	DP4+ possibility	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
DP4+ all data		0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%

Note: the best value for each parameter was highlighted in orange.

Reference

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Part S2. Experimental section

General experimental procedure

Optical rotations were measured in MeOH using a digital polarimeter. UV data were recorded from 195 to 400 nm in MeOH using a spectrophotometer, UV spectra are plotted in absorbance units (AU). Experimental ECD spectra were measured from 195 to 400 nm in MeOH on a spectrophotometer. IR spectra were recorded on a spectrophotometer in KBr discs. 1D and 2D NMR spectra were recorded on 800 MHz NMR spectrometers for ^{1}H, and 200 MHz for ^{13}C. Chemical shifts (δ) were given on parts per million (ppm) scale with reference to the solvent signals and coupling constants were expressed in Hertz. Structural assignments were made with additional information from COSY, HSQC, and HMBC experiments. ESIMS and HRESIMS were performed on triple quadrupole mass spectrometer. HREIMS were performed on a double focusing mass spectrometer. LC-MS/MS was performed on Agilent 6530 Accurate-Mass Q-TOF spectrometer coupled to an Agilent 1290 LC system with Zorbax SB-C18 (9.4 mm × 250mm) column. Column chromatography was performed with silica gel (100–200 mesh), Lichroprep RP-18 gel (40–63 mm). Preparative HPLC with dual wavelength detector was performed using an ODS column (7 μm, 20 mm × 25 cm, 10 mL/min; 7 μm, 40 mm × 25 cm, 50 mL/min). Semipreparative HPLC with a DAD detector was performed using an ODS column (5 μm, 9.4 mm × 25 cm, 3 mL/min). Chiral separation was performed on Agilent 1260 liquid chromatograph with a DAICEL AD-H (4.6mm × 250mm) chiral chromatographic column. Fractions were monitored by TLC and spots were visualized by heating silica gel plates sprayed with 10% H_2SO_4 in EtOH. All solvents were distilled prior to use.

Fungal material and fermentation

The fungal strain of *Penicillium* sp. sh18 was isolated from the fresh stems of *Isodon eriocalyx var. laxiflora* that was collected from Kunming Botanical Garden, Kunming, People's Republic of China, in December 2012. The large-scale fermentation procedure was as following: Twenty flasks of the inoculated media were incubated at 28 °C on a rotary shaker at 170 rpm for 5 days to prepare the seed. Fermentation was carried out on solid rice medium in 360 Fernbach flasks (500 mL, 110 mL distilled water was added to 100 g rice and kept overnight before autoclaving). Each flask was inoculated with 5.0 mL of the spore inoculum and incubated for 40 days at 28 °C in a static incubator.

Extraction and purification of compounds 1–3

The culture medium was overlaid and extracted with EtOAc, then the solvent was evaporated in vacuo to afford a crude extract (600 g). The extraction was subjected to column chromatography on silica gel with a $CHCl_3/Me_2CO$ gradient system (1:0, 9:1, 8:2, 7:3, 6:4, 0:1) to yield six fractions, A-G. Fraction B ($CHCl_3/Me_2CO$ 9:1, 101 g) was chromatographed on a

silica gel column with a petroleum ether/ Me_2CO gradient system (from 100:1 to 0:1) to afford fractions B1-B7. Fraction B3 (petroleum ether/ Me_2CO 10:1) was purified by preparative HPLC (15 ml/min, detector UV λ_{max} = 202 nm, MeCN/H_2O 80:20) to yield subfractions B3/6-9, subfraction B3-9 was purified by semipreparative HPLC (3 ml/min, detector UV λ_{max} = 202 nm, MeCN/H_2O 90:10) to yield **1** (4.6 mg, retention time = 7.5 min). The subfraction B3-7 was purified by semipreparative HPLC (3 ml/min, detector UV λ_{max} = 202 nm, MeOH/H_2O 80:20) to yield **2** (2.3 mg, retention time = 9.5 min), **3** (1.3 mg, retention time = 7.8 min).

Pentetrafuranone A (**1**): brown gum; $[\alpha]_D^{20}$: −43.28 (MeOH, *c* 0.055); ECD (MeOH) λ_{max} ($\Delta\varepsilon$): 205 (−11.56), 220 (9.62), 230 (3.53), 246 (15.38), 272 (17.86), 308 (−11.03) nm; UV (MeOH) λ_{max} (log ε): 229 (3.86) and 272 (3.43) nm; HRESIMS ion peak at *m/z* 1045.4568 ([M+Na]$^+$, calcd for 1045.4556). ^{1}H and ^{13}C NMR data, see Table S1.1.

Pentrifuranone A (**2**): yellow gum; ECD (MeOH) λ_{max} ($\Delta\varepsilon$): 203 (−23.49), 217 (26.23), 228 (7.84), 245 (39.84), 260 (9.71), 277 (19.42), and 315 (−20.93) nm; UV (MeOH) λ_{max} (log ε): 208 (3.92), 230 (3.88), and 272 (3.42) nm; HRESIMS ion peak at *m/z* 769.3213 ([M+Na]$^+$, calcd for 769.3194). ^{1}H and ^{13}C NMR data, see Table S1.2.

Pentrifuranone B (**3**): yellow gum; $[\alpha]_D^{25.2}$: 9.15 (MeOH, *c* 0.090); ECD (MeOH) λ_{max} ($\Delta\varepsilon$): 222 (-22.52), 246 (24.20), 282 (14.82), and 322 (−8.28) nm; UV (MeOH) λ_{max} (log ε): 210 (3.78), 231 (3.74), and 272 (3.28) nm; HRESIMS ion peak at *m/z* 769.3196 ([M+Na]$^+$, calcd for 769.3194). ^{1}H and ^{13}C NMR data, see Table S1.3.

Results of DP4+ analysis

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

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6	Isomer 7	Isomer 8
sDP4+ (H data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
sDP4+ (C data)	0.00%	31.69%	68.31%	0.00%	0.00%	0.00%	0.00%	0.00%
sDP4+ (all data)	0.00%	2.10%	0.00%	0.00%	0.00%	97.90%	0.00%	0.00%
uDP4+ (H data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
uDP4+ (C data)	0.00%	24.55%	1.55%	0.00%	0.02%	44.16%	0.00%	29.72%
uDP4+ (all data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
DP4+ (H data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
DP4+ (C data)	0.00%	88.04%	11.96%	0.00%	0.00%	0.00%	0.00%	0.00%
DP4+ (all data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%

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

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6	Isomer 7	Isomer 8
sDP4+ (H data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
sDP4+ (C data)	0.00%	47.29%	52.71%	0.00%	0.00%	0.00%	0.00%	0.00%
sDP4+ (all data)	0.00%	11.46%	0.00%	0.00%	0.00%	88.54%	0.00%	0.00%
uDP4+ (H data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
uDP4+ (C data)	0.00%	28.29%	0.35%	0.00%	0.03%	34.43%	0.00%	36.90%
uDP4+ (all data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
DP4+ (H data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
DP4+ (C data)	0.00%	98.64%	1.36%	0.00%	0.00%	0.01%	0.00%	0.00%
DP4+ (all data)	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%

Figure S2.1. DP4+ results of **1** fitted with data 1 (above) and data2 (down), respectively (isomers 1–8 corresponded to **1a**-**1h**, respectively).

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

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	0.00%	93.17%	1.41%	5.42%	–	–
sDP4+ (C data)	0.00%	100.00%	0.00%	0.00%	–	–
sDP4+ (all data)	0.00%	100.00%	0.00%	0.00%	–	–
uDP4+ (H data)	0.03%	68.85%	8.04%	23.08%	–	–
uDP4+ (C data)	0.00%	100.00%	0.00%	0.00%	–	–
uDP4+ (all data)	0.00%	100.00%	0.00%	0.00%	–	–
DP4+ (H data)	0.00%	97.92%	0.17%	1.91%	–	–
DP4+ (C data)	0.00%	100.00%	0.00%	0.00%	–	–
DP4+ (all data)	0.00%	100.00%	0.00%	0.00%	–	–

Figure S2.2. DP4+ results of **2** (isomers 1–4 corresponded to **2a**–**2d**, respectively).

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

	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
sDP4+ (H data)	0.00%	100.00%	0.00%	0.00%	–	–
sDP4+ (C data)	0.00%	93.87%	0.65%	5.48%	–	–
sDP4+ (all data)	0.00%	100.00%	0.00%	0.00%	–	–
uDP4+ (H data)	0.00%	100.00%	0.00%	0.00%	–	–
uDP4+ (C data)	0.00%	9.33%	4.44%	86.23%	–	–
uDP4+ (all data)	0.00%	100.00%	0.00%	0.00%	–	–
DP4+ (H data)	0.00%	100.00%	0.00%	0.00%	–	–
DP4+ (C data)	0.00%	64.84%	0.21%	34.94%	–	–
DP4+ (all data)	0.00%	100.00%	0.00%	0.00%	–	–

Figure S2.3. DP4+ results of **3** (isomers 1–4 corresponded to **3em**–**3hm**, respectively).

RDC results

Table S2.1. Results for RDC analysis of compound **1** when using energy-based population and population fitted method, respectively.

	energy based				**energy based core region**			
	data1		**data2**		**data1**		**data2**	
diastereomers	Q value	SVD condition number	Q value	SVD condition number	Q value	SVD condition number	Q value	SVD condition number
a	0.64	4.43	0.60	4.43	0.27	4.22	0.25	4.22
b	0.58	6.33	0.40	6.33	0.17	5.18	0.18	5.18
c	0.71	3.45	0.73	3.45	0.64	5.00	0.66	5.00
d	0.52	4.25	0.41	4.25	0.16	9.90	0.21	9.90
e	0.77	4.71	0.60	4.71	0.57	4.97	0.49	4.97
f	0.75	7.05	0.77	7.05	0.82	15.69	0.80	15.69
g	0.51	6.05	0.60	6.05	0.57	14.40	0.61	14.40
h	0.76	6.08	0.70	6.08	0.45	16.33	0.42	16.33
	population fitted				**population fitted (10 conformers)**			
	data1		**data2**		**data1**		**data2**	
diastereomers	Q value	SVD condition number	Q value	SVD condition number	Q value	SVD condition number	Q value	SVD condition number
a	0.43	3.30	0.45	3.78	0.41	3.50	0.39	3.72
b	0.26	9.99	0.17	6.68	0.17	5.98	0.17	6.68
c	0.71	3.45	0.73	3.45	0.46	4.60	0.45	4.88
d	0.40	6.64	0.35	4.66	0.29	5.64	0.25	5.13
e	0.60	4.52	0.51	4.05	0.60	4.52	0.51	4.05
f	0.42	8.26	0.41	7.69	0.42	8.26	0.41	7.69
g	0.32	16.36	0.34	17.19	0.32	16.36	0.34	17.19
h	0.43	15.17	0.42	3.96	0.43	15.17	0.42	3.96

Table S2.2. In-depth RDC analysis of **1** fitting with diastereomers **b** and **d** (data 1 and data 2).

data1				data2			
No. of D_{CH}	**Exptl.**	**b**	**d**	**No. of D_{CH}**	**Exptl.**	**b**	**d**
19	-13.1	-10.80	0.93	19	-13.1	-8.89	-12.09
6	6	7.31	3.26	6	12.4	11.49	13.45
6'	12.4	12.13	0.27	6'	6	8.16	5.36
6"	15.2	16.53	0.93	6"	15.2	18.30	18.7
7	6.1	7.20	3.26	7	12.2	12.09	13.1
7'	12.2	12.22	0.27	7'	6.1	7.94	5.64
7"	15.5	15.98	0.93	7"	15.5	17.65	17.96
8	5	7.41	3.26	8	12.2	12.33	13.7
8'	12.2	9.20	0.27	8'	5	3.89	3.71
8"	17	11.03	0.93	8"	17	14.01	13.68
9	5	7.12	3.26	9	11.6	12.49	13.6
9'	11.6	8.76	0.27	9'	5	3.38	3.31
9"	14.1	10.60	0.93	9"	14.1	13.89	13.42
14a	-10	-14.95	3.26	14a	-23	-22.26	-21.19
14b	-20.4	-22.05	0.27	14b	-9.5	-10.24	-8.64
14'a	-23	-24.56	0.93	14'a	-10	-8.59	-3.94
14'b	-9.5	-6.00	3.26	14'b	-20.4	-21.96	-17.46
14"a	-18.1	-14.90	0.27	14"a	-18.1	-13.61	-15.5
14"b	2.6	-0.27	0.93	14"b	2.6	0.68	6.59
13	0.4	3.28	3.26	13	1.5	3.27	6.48
13'	1.5	-4.01	0.27	13'	0.4	-4.74	1.94
13"	0.7	2.78	0.93	13"	0.7	1.54	5.15
16	1.3	4.58	3.26	16	4.7	4.96	-2
16'	4.7	3.86	0.27	16'	1.3	3.51	5.89
16"	-4.6	-7.13	0.93	16"	-4.6	-4.58	-5.59
15	-21.5	-17.90	3.26	15	-17	-17.27	-12.78
15'	-17	-25.21	0.27	15'	-21.5	-22.75	7.33
15"	2.6	-0.63	0.93	15"	2.6	0.67	-9.14
R^2		0.93	0.75	R^2		0.97	0.73
MRSD		3.26	6.51	MRSD		2.11	6.59
Q		0.27	0.54	Q		0.17	0.54

Table S2.3. Results for RDC analysis of compound **2** when using energy-based population and population fitted method, respectively.

	energy based		population fitted		population fitted (Top 4 conformers)		energy based core region	
diastereomer	**Q value**	**SVD numb**	**Q value**	**SVD numb**	**Q value**	**SVD numb**	**Q value**	**SVD numb**
a	0.27	3.50	0.26	3.67			0.27	7.08
b	0.24	3.88	0.20	5.13			0.15	10.08
c	0.34	2.51	0.21	42.53	0.32	2.59	0.17	3.26
d	0.42	5.16	0.20	12.30	0.28	40.02	0.30	4.60

Table S2.4. Results for RDC analysis of compound **3** when using energy-based population and population fitted method, respectively (data in methanol-d_4 and DMSO-d_6).

	energy based		population fitted		energy based		population fitted	
diastereomer	**Q value**	**SVD numb**	**Q value**	**SVD numb**	**Q value**	**SVD numb**	**Q value**	**SVD numb**
e	0.54	4.35	0.16	4.43	0.41	6.24	0.40	6.05
f	0.16	3.37	0.06	4.71	0.12	4.10	0.06	4.73
g	0.35	5.39	0.29	5.72	0.35	5.38	0.29	5.71
h	0.56	2.34	0.24	4.75	0.24	4.77	0.24	4.75

QID results

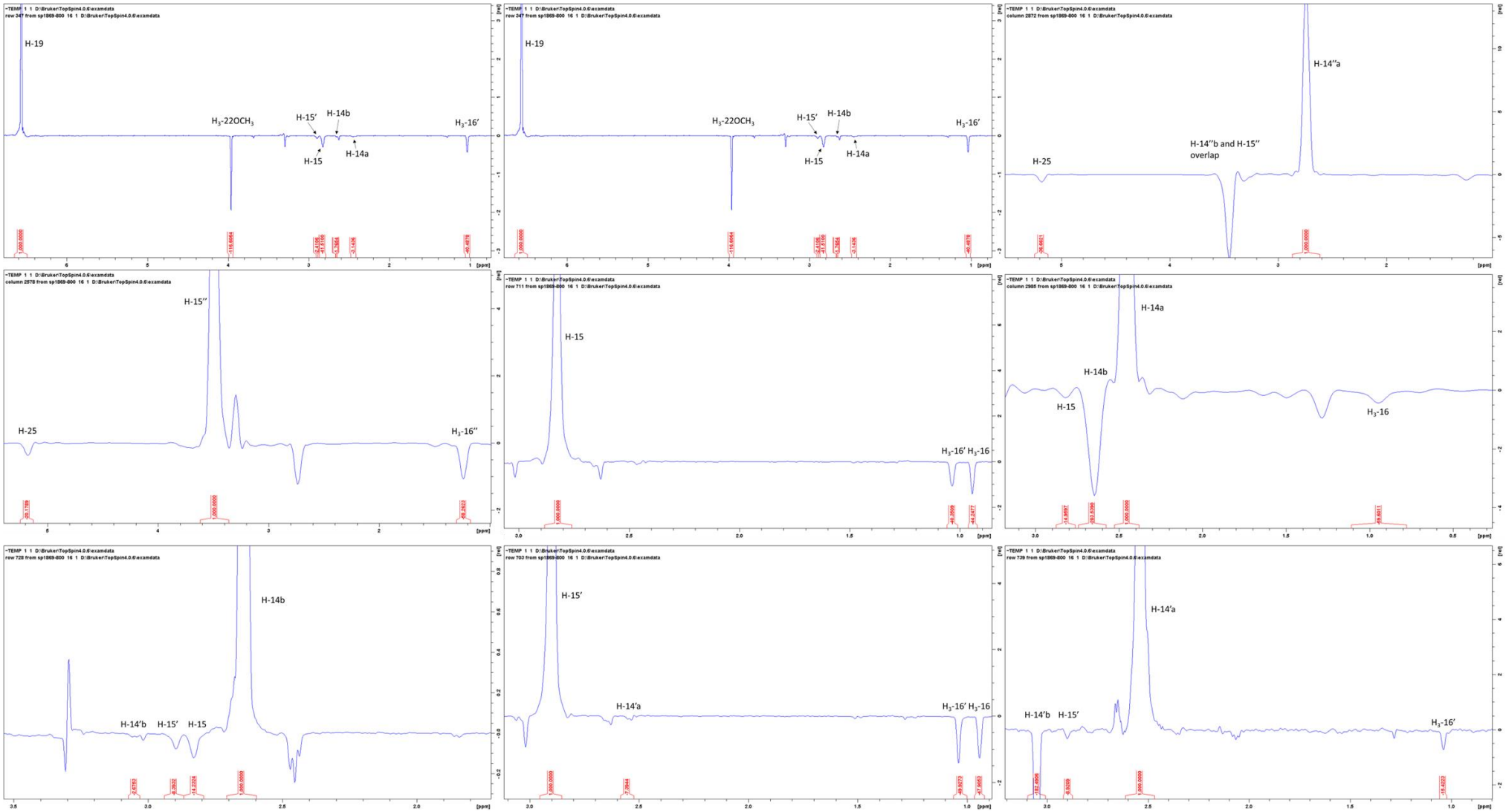


Figure S2.4. NOE intensities extracted from 2D ROESY of **1**.

Table S2.5. QID analysis of **1** using data 1. (X represent ', Y represent " for atom number)

proton pairs		exptl. distance	a	b	c	d	e	f	g	h
H-14a	H-14b	1.75	1.77	1.78	1.78	1.75	1.77	1.77	1.77	1.77
H-14a	H-16	2.73	3.00	2.96	2.89	2.57	2.89	2.87	2.67	2.97
H-14a	H-16X	5.25	5.25	5.23	5.33	5.26	5.58	5.62	4.35	5.18
H-14a	H-14Xb	5.17	5.17	5.20	5.17	5.97	4.96	4.93	5.87	5.96
H-14b	H-14Xa	6.07	6.07	5.74	6.13	5.91	5.46	5.67	5.57	4.41
H-14b	H-14Xb	3.75	4.99	4.56	5.23	4.88	3.96	4.56	4.82	5.45
H-14b	H-16	4.00	3.76	3.90	3.86	3.15	3.90	3.90	2.86	3.87
H-14b	H-16X	4.85	4.85	4.60	4.80	5.26	5.24	5.22	4.73	4.08
H-14Xa	H-14Xb	1.87	1.76	1.76	1.76	1.75	1.77	1.76	1.77	1.75
H-14Xa	H-16	5.15	5.15	5.25	4.89	4.87	4.76	4.16	5.38	4.89
H-14Xa	H-16X	3.45	2.62	2.60	2.89	2.84	2.58	2.80	2.84	3.01
H-14Xb	H-16	5.22	5.22	5.20	4.63	4.57	4.36	2.72	5.34	4.82
H-14Xb	H-16X	4.00	3.28	3.20	3.92	3.88	3.21	3.91	3.89	2.65
H-14Ya	H-14Yb	1.78	1.75	1.79	1.79	1.75	1.73	1.76	1.79	1.79
H-14Ya	H-16Y	3.08	2.84	2.85	2.80	2.96	2.85	2.88	3.05	2.86
H-14Yb	H-16Y	2.87	2.91	2.94	3.00	2.86	2.87	3.18	2.76	2.92
H-15	H-14a	2.86	2.97	3.04	3.03	2.65	3.05	3.05	2.42	3.03
H-15	H-14b	2.86	2.45	2.44	2.51	3.03	2.47	2.50	3.05	2.44
H-15	H-14Xa	4.83	4.83	4.54	4.93	3.86	3.71	3.67	4.30	3.11
H-15	H-14Xb	4.42	4.42	3.26	4.74	4.64	2.41	2.23	4.61	3.93
H-15	H-16	2.87	2.60	2.61	2.63	2.60	2.61	2.60	2.58	2.62
H-15	H-16X	2.90	2.57	2.47	2.55	2.58	4.60	4.55	2.40	3.57
H-15X	H-14a	4.25	4.25	4.21	4.38	4.66	4.56	4.51	4.02	3.56

proton pairs		exptl. distance	a	b	c	d	e	f	g	h
H-15X	H-14b	3.12	4.61	3.21	4.64	4.22	4.68	4.68	3.36	3.02
H-15X	H-14Xa	3.12	2.68	2.65	2.34	2.36	2.65	2.39	3.04	3.07
H-15X	H-14Xb	2.47	3.03	3.02	2.42	2.37	3.04	2.40	2.56	2.53
H-15X	H-16	2.85	2.49	2.57	2.48	2.43	2.64	2.62	4.81	2.57
H-15X	H-16X	2.82	2.61	2.61	2.59	2.59	2.58	2.58	2.64	2.60
H-15Y	H-14Ya	2.44	2.44	3.06	3.04	2.44	2.48	2.63	3.06	3.04
H-15Y	H-16Y	2.74	2.61	2.61	2.62	2.60	2.61	2.60	2.62	2.61
H-19	H-15	2.40	4.31	3.93	2.61	2.54	4.29	4.30	4.32	2.88
H-19	H-14a	3.71	3.03	3.44	4.60	4.56	3.81	3.61	3.99	2.87
H-19	H-14b	3.86	4.32	4.66	3.21	4.03	4.83	4.69	2.40	2.91
H-19	H-16	4.00	2.60	2.60	5.01	4.95	2.67	2.64	4.49	4.76
H-19	H-15X	3.87	2.83	2.79	4.34	4.26	2.59	2.49	2.57	3.88
H-19	H-14Xa	4.86	4.86	3.76	4.89	5.04	5.19	4.87	4.64	2.20
H-19	H-14Xb	4.24	4.24	3.42	4.78	5.06	5.19	4.37	3.28	3.92
H-19	H-16X	2.89	5.15	5.02	2.60	2.69	3.78	3.81	4.97	4.27
H-25	H-15Y	2.73	2.42	3.08	3.09	2.35	2.33	3.05	3.09	3.09
H-25	H-16Y	2.86	3.16	3.22	3.10	3.72	3.67	2.97	3.03	3.13
H-25	H-14Ya	2.44	4.22	2.74	2.89	4.10	4.19	2.94	2.56	2.81
H-25	H-14Yb	4.00	3.96	3.85	3.93	3.73	3.83	3.72	3.79	3.91
MAD			**0.43**	**0.40**	**0.27**	**0.28**	**0.55**	**0.46**	**0.39**	**0.36**
$\boldsymbol{R^2}$			**0.62**	**0.67**	**0.85**	**0.84**	**0.49**	**0.57**	**0.62**	**0.66**

Table S2.6. QID analysis of **1** using data 2. (X represent ', Y represent " for atom number)

proton pairs		exptl. distance	a	b	c	d	e	f	g	h
H-14a	H-14b	1.75	1.76	1.76	1.76	1.75	1.77	1.76	1.77	1.75
H-14a	H-16	2.73	2.62	2.60	2.89	2.84	2.58	2.80	2.84	2.65
H-14a	H-16X	5.15	5.15	5.25	4.89	4.87	4.76	4.16	5.38	4.82
H-14a	H-14Xb	6.07	6.07	5.74	6.13	5.91	5.46	5.67	6.17	5.45
H-14b	H-14Xa	5.17	5.17	5.20	5.17	5.97	4.96	4.93	4.82	5.21
H-14b	H-14Xb	3.75	4.99	4.56	5.23	4.88	3.96	4.56	5.87	4.41
H-14b	H-16	4.00	3.28	3.20	3.92	3.88	3.21	3.91	3.89	3.01
H-14b	H-16X	5.22	5.22	5.20	4.63	4.57	4.36	2.72	5.34	4.89
H-14Xa	H-14Xb	1.87	1.77	1.78	1.78	1.75	1.77	1.77	1.77	1.77
H-14Xa	H-16	5.25	5.25	5.23	5.33	5.26	5.58	5.62	4.73	5.18
H-14Xa	H-16X	3.45	3.00	2.96	2.89	2.57	2.89	2.87	2.86	2.97
H-14Xb	H-16	4.85	4.85	4.60	4.80	5.26	5.24	5.22	4.35	4.08
H-14Xb	H-16X	4.00	3.76	3.90	3.86	3.15	3.90	3.90	2.67	3.87
H-14Ya	H-14Yb	1.78	1.75	1.79	1.79	1.75	1.73	1.76	1.79	1.79
H-14Ya	H-16Y	3.08	2.84	2.85	2.80	2.96	2.85	2.88	3.05	2.86
H-14Yb	H-16Y	2.87	2.91	2.94	3.00	2.86	2.87	3.18	2.76	2.92
H-15	H-14a	2.86	2.68	2.65	2.34	2.36	2.65	2.39	3.04	2.53
H-15	H-14b	2.86	3.03	3.02	2.42	2.37	3.04	2.40	2.56	3.07
H-15	H-14Xa	4.25	4.25	4.21	4.38	4.66	4.56	4.51	3.36	3.56
H-15	H-14Xb	4.61	4.61	3.21	4.64	4.22	4.68	4.68	4.02	3.02
H-15	H-16	2.87	2.61	2.61	2.59	2.59	2.58	2.58	2.64	2.60
H-15	H-16X	2.90	2.49	2.57	2.48	2.43	2.64	2.62	4.81	2.57
H-15X	H-14a	4.83	4.83	4.54	4.93	3.86	3.71	3.67	4.30	3.93

proton pairs		exptl. distance	a	b	c	d	e	f	g	h
H-15X	H-14b	3.12	4.42	3.26	4.74	4.64	2.41	2.23	4.61	3.11
H-15X	H-14Xa	3.12	2.97	3.04	3.03	2.65	3.05	3.05	3.05	3.03
H-15X	H-14Xb	2.47	2.45	2.44	2.51	3.03	2.47	2.50	2.42	2.44
H-15X	H-16	2.85	2.57	2.47	2.55	2.58	4.60	4.55	2.40	3.57
H-15X	H-16X	2.82	2.60	2.61	2.63	2.60	2.61	2.60	2.58	2.62
H-15Y	H-14Ya	2.44	2.44	3.06	3.04	2.44	2.48	2.63	3.06	3.04
H-15Y	H-16Y	2.74	2.61	2.61	2.62	2.60	2.61	2.60	2.62	2.61
H-19	H-15	2.40	2.83	2.79	4.34	4.26	2.59	2.49	2.57	3.88
H-19	H-14a	3.71	4.86	3.76	4.89	5.04	5.19	4.87	4.64	3.92
H-19	H-14b	3.86	4.24	3.42	4.78	5.06	5.19	4.37	3.28	2.20
H-19	H-16	5.15	5.15	5.02	2.60	2.69	3.78	3.81	4.97	4.27
H-19	H-15X	3.87	4.31	3.93	2.61	2.54	4.29	4.30	4.32	2.88
H-19	H-14Xa	4.00	3.03	3.44	4.60	4.56	3.81	3.61	2.40	2.87
H-19	H-14Xb	4.32	4.32	4.66	3.21	4.03	4.83	4.69	3.99	2.91
H-19	H-16X	2.89	2.60	2.60	5.01	4.95	2.67	2.64	4.49	4.76
H-25	H-15Y	2.73	2.42	3.08	3.09	2.35	2.33	3.05	3.09	3.09
H-25	H-16Y	2.86	3.16	3.22	3.10	3.72	3.67	2.97	3.03	3.13
H-25	H-14Ya	2.44	4.22	2.74	2.89	4.10	4.19	2.94	2.56	2.81
H-25	H-14Yb	4.00	3.96	3.85	3.93	3.73	3.83	3.72	3.79	3.91
MAD			**0.29**	**0.21**	**0.44**	**0.49**	**0.32**	**0.31**	**0.41**	**0.40**
R^2			**0.81**	**0.91**	**0.63**	**0.60**	**0.74**	**0.79**	**0.63**	**0.60**

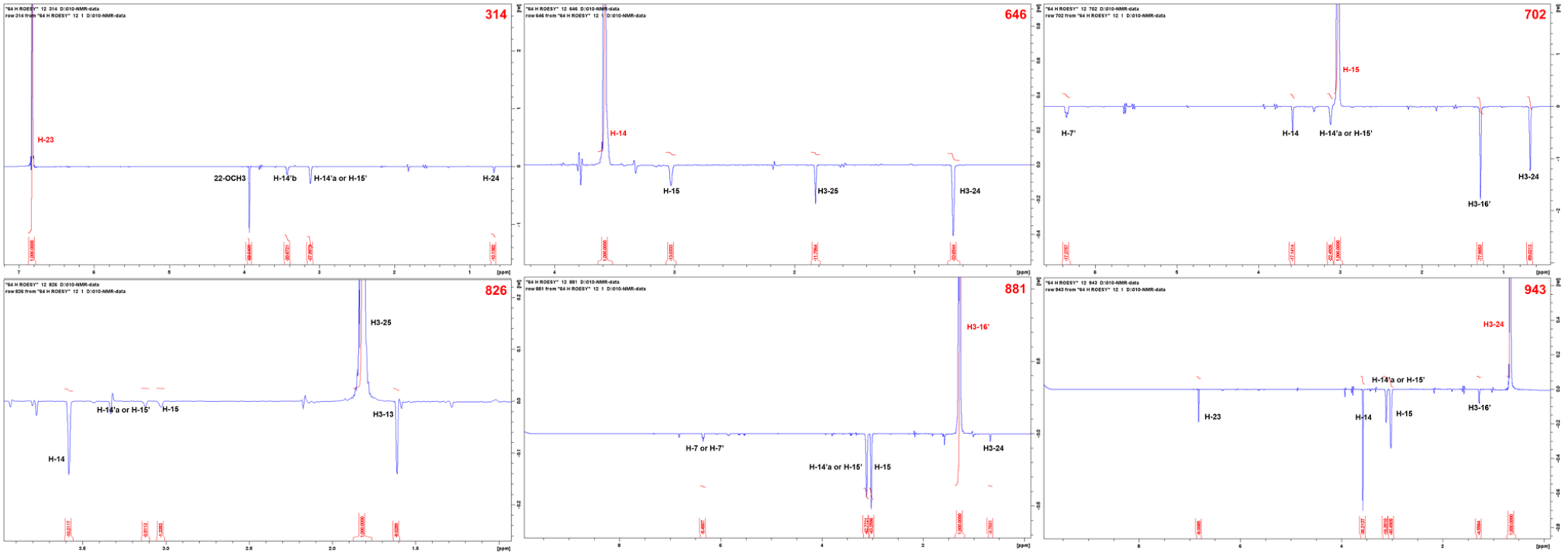


Figure S2.5. 1D slices extracted from the 2D ROESY spectrum of **2**.

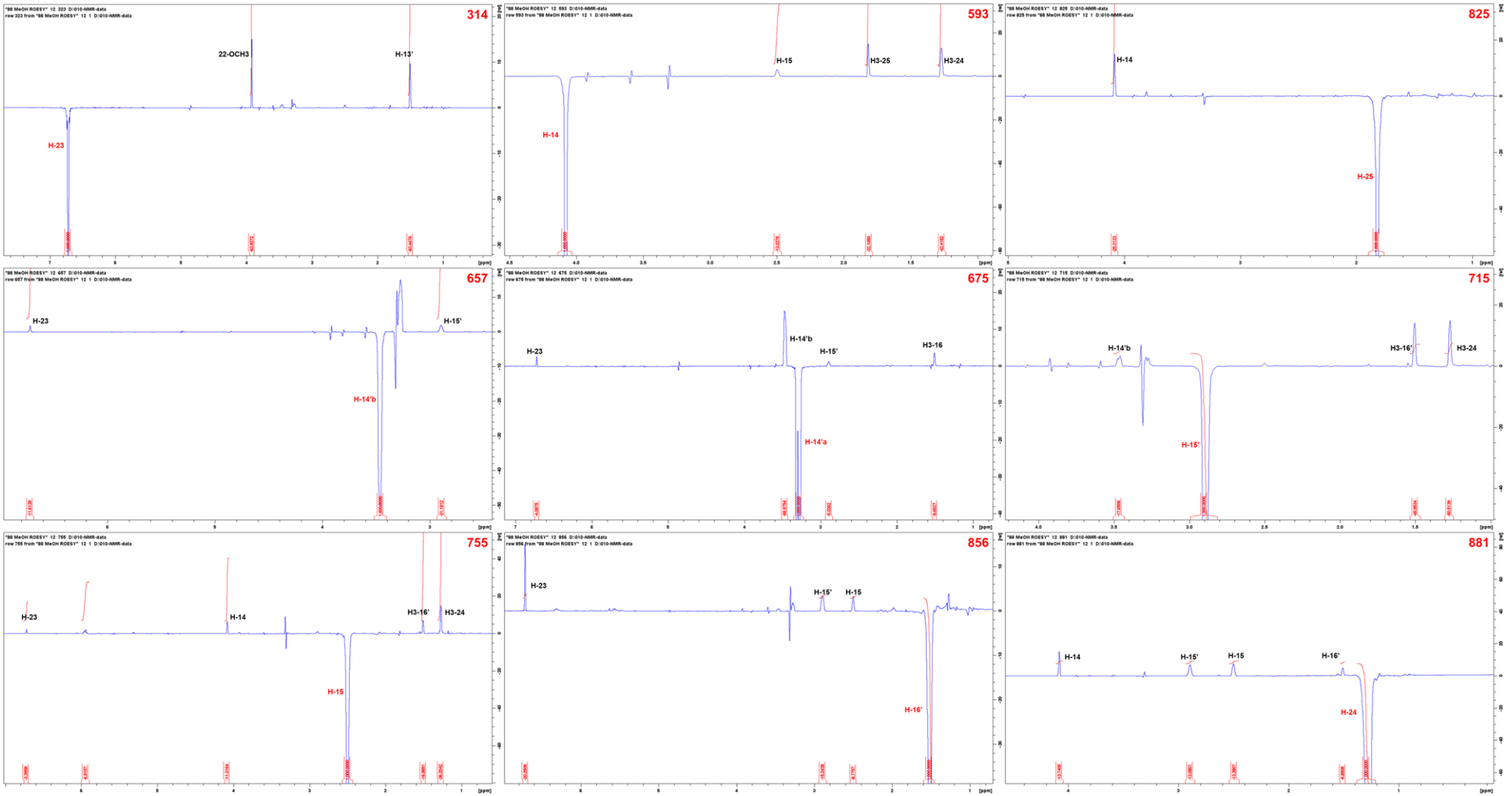


Figure S2.6. 1D slices extracted from the 2D ROESY spectrum of **3**.

fc-rDG/DDD results

Table S2.7. The input data used for fc-rDG/DDD calculation of compound **1**. (X represent ', Y represent '' for atom number)

#Type	Atoms		Exp.	Error	Weight	
RDC	C6	H6	6	0.5	1	
RDC	C7	H7	6.1	0.5	1	
RDC	C8	H8	5	0.5	1	
RDC	C9	H9	5	0.5	1	
RDC	C13	H13	0.4	0.5	1	
RDC	C14	H14a	-10	0.5	1	
RDC	C14	H14b	-20.4	0.5	1	
RDC	C15	H15	-21.5	0.5	1	
RDC	C16	H16	1.3	0.5	1	
RDC	C19	H19	-13.1	0.5	1	
RDC	C6X	H6X	12.4	0.5	1	
RDC	C7X	H7X	12.2	0.5	1	
RDC	C8X	H8X	12.2	0.5	1	
RDC	C9X	H9X	11.6	0.5	1	
RDC	C13X	H13X	1.5	0.5	1	
RDC	C14X	H14Xa	-23	0.5	1	
RDC	C14X	H14Xb	-9.5	0.5	1	
RDC	C15X	H15X	-17	0.5	1	
RDC	C16X	H16X	4.7	0.5	1	
RDC	C6Y	H6Y	15.2	0.5	1	
RDC	C7Y	H7Y	15.5	0.5	1	
RDC	C8Y	H8Y	17	0.5	1	
RDC	C9Y	H9Y	14.1	0.5	1	
RDC	C13Y	H13Y	0.7	0.5	1	
RDC	C14Y	H14Ya	-18.1	0.5	1	
RDC	C14Y	H14Yb	2.6	0.5	1	
RDC	C15Y	H15Y	2.6	0.5	1	
RDC	C16Y	H16Y	-4.6	0.5	1	
#Type	Atoms		dist(min)	dist(max)	Weight	
NOE	H15	H14a	2.715373	3.001201	1	
NOE	H19	H14a	3.523327	3.894203	1	
NOE	H14a	H14b	1.662957	1.838006	1	
NOE	H15	H14b	2.721452	3.007921	1	
NOE	H15X	H14b	2.96273	3.274596	1	
NOE	H19	H14b	3.671213	4.057657	1	
NOE	H15X	H14Xa	2.964527	3.276582	1	
NOE	H14b	H14Xb	3.566543	3.941968	1	
NOE	H14Xa	H14Xb	1.778241	1.965424	1	

NOE	H15X	H14Xb	2.349336	2.596634	1	
NOE	H15Y	H14Ya	2.321474	2.56584	1	
NOE	H25	H14Ya	2.321435	2.565796	1	
NOE	H14Ya	H14Yb	1.691	1.869	1	
NOE	H19	H15	2.277415	2.517143	1	
NOE	H19	H15X	3.680971	4.068442	1	
NOE	H25	H15Y	2.596662	2.869995	1	
NOE	H14a	H16a|H16b|H16c	2.589968	2.862596	1	
NOE	H15	H16a|H16b|H16c	2.722822	3.009435	1	
NOE	H15X	H16a|H16b|H16c	2.709424	2.994626	1	
NOE	H14Xa	H16Xa|H16Xb|H16Xc	3.2761	3.620953	1	
NOE	H15	H16Xa|H16Xb|H16Xc	2.75295	3.042734	1	
NOE	H15X	H16Xa|H16Xb|H16Xc	2.683706	2.966202	1	
NOE	H19	H16Xa|H16Xb|H16Xc	2.741832	3.030446	1	
NOE	H14Ya	H16Ya|H16Yb|H16Yc	2.92856	3.236829	1	
NOE	H14Yb	H16Ya|H16Yb|H16Yc	2.723686	3.010389	1	
NOE	H15Y	H16Ya|H16Yb|H16Yc	2.598966	2.872541	1	
NOE	H25	H16Ya|H16Yb|H16Yc	2.718565	3.00473	1	
NOE	H19	H27a|H27b|H27c	2.306818	2.54964	1	
NOE	H14a	H16Xa|H16Xb|H16Xc	4	10	1	
NOE	H14a	H14Xb	4	10	1	
NOE	H14b	H14Xa	4	10	1	
NOE	H14b	H16a|H16b|H16c	4	10	1	
NOE	H14b	H16Xa|H16Xb|H16Xc	4	10	1	
NOE	H14Xa	H16a|H16b|H16c	4	10	1	
NOE	H14Xb	H16a|H16b|H16c	4	10	1	
NOE	H14Xb	H16Xa|H16Xb|H16Xc	4	10	1	
NOE	H15	H14Xa	4	10	1	
NOE	H15	H14Xb	4	10	1	
NOE	H15X	H14a	4	10	1	
NOE	H19	H16a|H16b|H16c	4	10	1	
NOE	H19	H14Xb	4	10	1	
NOE	H25	H14Yb	4	10	1	
NOE	H19	H14Xa	4	10	1	
Double Bond Restraints:						
#Type	Atoms				Weight	Force Constant
CIS	O1	C2	C3	C4	1	K=100.00
CIS	C2	C3	C4	C5	1	K=100.00
TRANS	C2	C3	C12	O26	1	K=100.00
TRANS	C5	C6	C7	C8	1	K=100.00
TRANS	C6	C7	C8	C9	1	K=100.00
TRANS	C7	C8	C9	C10	1	K=100.00
CIS	C23	C18	C19	C20	1	K=100.00

CIS	C17	C18	C23	C24	1	K=100.00
CIS	C18	C19	C20	C21	1	K=100.00
CIS	C19	C20	C21	C22	1	K=100.00
CIS	C20	C21	C22	C23	1	K=100.00
CIS	C21	C22	C23	C18	1	K=100.00
CIS	C18	C23	C24	O17	1	K=100.00
CIS	O17	C24	C25	C15Y	1	K=100.00
CIS	O1X	C2X	C3X	C4X	1	K=100.00
CIS	C2X	C3X	C4X	C5X	1	K=100.00
TRANS	C2X	C3X	C12X	O17X	1	K=100.00
TRANS	C5X	C6X	C7X	C8X	1	K=100.00
TRANS	C6X	C7X	C8X	C9X	1	K=100.00
TRANS	C7X	C8X	C9X	C10X	1	K=100.00
CIS	O1Y	C2Y	C3Y	C4Y	1	K=100.00
CIS	C2Y	C3Y	C4Y	C5Y	1	K=100.00
TRANS	C2Y	C3Y	C12Y	O17Y	1	K=100.00
TRANS	C5Y	C6Y	C7Y	C8Y	1	K=100.00
TRANS	C6Y	C7Y	C8Y	C9Y	1	K=100.00
TRANS	C7Y	C8Y	C9Y	C10Y	1	K=100.00

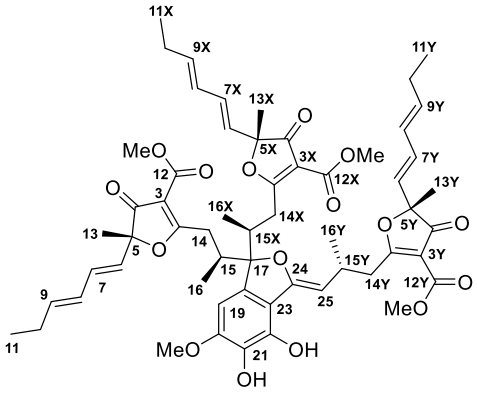


Figure S2.7. The initial guess structure for fc-rDG/DDD calculation of compound **1** (X represent ', Y represent " for atom number).

Table S2.8. Key computational results extracted from the section "Configurational Families (Excluding Methylene Assignments)" in the "shake2.out" output file of compound **1**. (X represent ', Y represent " for atom number)

Family No.	rDG/DDD Energies			Bayesian Weights (i)	[H0]	[H0]	[H0]	[H0]	[H1]	[H1]	[H1]
	dE(min)	E(min)	E(max)		C5	C17	C5X	C5Y	C15	C15X	C15Y
1	38.8133	275.6057	424.4952	6.20E-17	(lk)	(lk)	(lk)	(lk)	(lk)	(lk)	(lk)
2	39.8713	276.6637	445.3886	1.41E-17	(lk)	(lk)	(lk)	(lk)	(lk)	(lk)	(ul)
3	45.1217	281.9141	407.8738	1.37E-20	(lk)	(lk)	(lk)	(lk)	(lk)	(ul)	(lk)
4	44.7912	281.5836	416.2892	5.31E-20	(lk)	(lk)	(lk)	(lk)	(lk)	(ul)	(ul)
5	26.9419	263.7342	372.5456	9.09E-14	(lk)	(lk)	(lk)	(lk)	(ul)	(lk)	(lk)
6	28.8289	265.6213	370.6427	7.91E-15	(lk)	(lk)	(lk)	(lk)	(ul)	(lk)	(ul)
7	2.4607	239.253	513.0293	3.82E-01	(lk)	(lk)	(lk)	(lk)	(ul)	(ul)	(lk)
8	3.0708	239.8632	440.5303	7.68E-02	(lk)	(lk)	(lk)	(lk)	(ul)	(ul)	(ul)
9	2.9791	239.7715	449.2403	8.97E-02	(lk)	(ul)	(lk)	(lk)	(lk)	(lk)	(lk)
10	0	236.7924	404.5657	4.52E-01	(lk)	(ul)	(lk)	(lk)	(lk)	(lk)	(ul)
11	30.0002	266.7926	295.418	4.53E-15	(lk)	(ul)	(lk)	(lk)	(lk)	(ul)	(lk)
12	27.3079	264.1003	388.1598	3.26E-14	(lk)	(ul)	(lk)	(lk)	(lk)	(ul)	(ul)
13	44.7676	281.56	415.4186	4.02E-20	(lk)	(ul)	(lk)	(lk)	(ul)	(lk)	(lk)
14	45.1466	281.939	447.07	1.80E-20	(lk)	(ul)	(lk)	(lk)	(ul)	(lk)	(ul)
15	40.3805	277.1728	518.3178	1.07E-17	(lk)	(ul)	(lk)	(lk)	(ul)	(ul)	(lk)
16	38.7737	275.5661	429.1418	4.76E-17	(lk)	(ul)	(lk)	(lk)	(ul)	(ul)	(ul)

Table S2.9. The input data used for fc-rDG/DDD calculation of compound **2**.

#Type	Atoms		Exp.	Error	Weight	
RDC	C6	H6	21.6	0.5	1	
RDC	C13	H13	3.8	0.5	1	
RDC	C14	H14	-28.5	0.5	1	
RDC	C15	H15	9	0.5	1	
RDC	C27	H27	-0.2	0.5	1	
RDC	C23	H23	-2.4	0.5	1	
RDC	C24	H24	4.5	0.5	1	
RDC	C25	H25	-0.6	0.5	1	
RDC	C6'	H6'	0.1	0.5	1	
RDC	C13'	H13'	-6.5	0.5	1	
RDC	C14'	H14'a	9	0.5	1	
RDC	C14'	H14'b	-11.4	0.5	1	
RDC	C15'	H15'	-0.5	0.5	1	
RDC	C16'	H16'	-3.7	0.5	1	
#Type	Atoms		NOE (volume)	Error	Weight	
NOE	H23	H14'b	79332000	+/-10%	1	
NOE	H14	H15	58708000	+/-10%	1	
NOE	H16'a|H16'b|H16'c	H15	2.21E+08	+/-25%	1	
NOE	H24a|H24b|H24c	H15'	74851000	+/-25%	1	
NOE	H13a|H13b|H13c	H6	36359000	+/-25%	1	
NOE	H13'a|H13'b|H13'c	H6'	31765000	+/-25%	1	
NOE	H13a|H13b|H13c	H7	18523000	+/-25%	1	
NOE	H13'a|H13'b|H13'c	H7'	33893000	+/-25%	1	
NOE	H25a|H25b|H25c	H13a|H13b|H13c	63272000	+/-25%	1	
NOE	H15	H16'a|H16'b|H16'c	2.66E+08	+/-25%	1	
NOE	H14	H24a|H24b|H24c	1.79E+08	+/-25%	1	
NOE	H23	H24a|H24b|H24c	39980000	+/-25%	1	
NOE	H15	H24a|H24b|H24c	2E+08	+/-25%	1	
NOE	H14	H25a|H25b|H25c	61446000	+/-25%	1	
NOE	H23	H27a|H27b|H27c	2.04E+08	+/-25%	1	
#Double Bond Restraints:						
#Type	Atoms				Weight	Force Constant
CIS	O1	C2	C3	C4	1	K=100.00
CIS	C2	C3	C4	C5	1	K=100.00
TRANS	C5	C6	C7	C8	1	K=100.00
TRANS	C6	C7	C8	C9	1	K=100.00
TRANS	C7	C8	C9	C10	1	K=100.00
CIS	O1'	C2'	C3'	C4'	1	K=100.00
CIS	C2'	C3'	C4'	C5'	1	K=100.00
TRANS	C5'	C6'	C7'	C8'	1	K=100.00

TRANS	C6'	C7'	C8'	C9'	1	K=100.00
TRANS	C7'	C8'	C9'	C10'	1	K=100.00
CIS	C16	C17	C18	C19	1	K=100.00
CIS	C18	C17	C23	C22	1	K=100.00
CIS	C17	C18	C20	C21	1	K=100.00
CIS	C18	C20	C21	C22	1	K=100.00
CIS	C20	C21	C22	C23	1	K=100.00
CIS	C21	C22	C23	C17	1	K=100.00

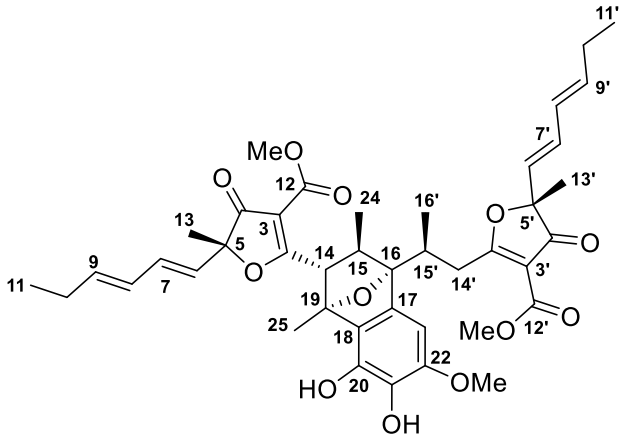


Figure S2.8. The initial guess structure for fc-rDG/DDD calculation of compound **2**.

Table S2.10. Key computational results extracted from the section "Configurational Families (Excluding Methylene Assignments)" in the "shake2.out" output file of compound **2**. (X represent ', Y represent " for atom number)

Family No.	rDG/DDD Energies			Bayesian Weights (i)	[H0]	[H0]	[H0]	[H0]	[H1]	[H1]	[H1]
	dE(min)	E(min)	E(max)		C5	C16	C19	C5'	C14	C15	C15'
1	3.1811	3.4003	114.4289	4.44E-05	(lk)	(lk)	(lk)	(lk)	(lk)	(lk)	(lk)
2	0	0.2192	141.1332	5.51E-01	(lk)	(lk)	(lk)	(lk)	(lk)	(lk)	(ul)
3	15.0784	15.2976	17.8191	3.95E-10	(lk)	(lk)	(lk)	(lk)	(lk)	(ul)	(lk)
4	11.9916	12.2108	21.5592	2.41E-08	(lk)	(lk)	(lk)	(lk)	(ul)	(lk)	(ul)
5	7.8446	8.0638	114.5752	8.05E-06	(lk)	(lk)	(lk)	(lk)	(ul)	(ul)	(lk)
6	18.2409	18.4601	121.0578	6.55E-12	(lk)	(lk)	(lk)	(lk)	(ul)	(ul)	(ul)
7	18.8602	19.0794	26.0871	2.72E-12	(lk)	(ul)	(ul)	(lk)	(lk)	(lk)	(lk)
8	7.5661	7.7853	109.2965	7.07E-06	(lk)	(ul)	(ul)	(lk)	(lk)	(lk)	(ul)
9	12.1859	12.4051	25.7626	1.85E-08	(lk)	(ul)	(ul)	(lk)	(lk)	(ul)	(lk)
10	19.6014	19.8206	25.8494	1.58E-12	(lk)	(ul)	(ul)	(lk)	(ul)	(lk)	(ul)
11	0.1566	0.3758	122.3863	4.49E-01	(lk)	(ul)	(ul)	(lk)	(ul)	(ul)	(lk)
12	3.4525	3.6717	113.6037	3.01E-05	(lk)	(ul)	(ul)	(lk)	(ul)	(ul)	(ul)

Table S2.11. The input data used for fc-rDG/DDD calculation of compound **3**.

#Type	Atoms		Exp.	Error	Weigh	
RDC	C6	H6	5	0.5	1	
RDC	C7	H7	5.1	0.5	1	
RDC	C8	H8	3.8	0.5	1	
RDC	C9	H9	5.5	0.5	1	
RDC	C13	H13a	9	0.5	1	
RDC	C14	H14	-12.8	0.5	1	
RDC	C15	H15	17.2	0.5	1	
RDC	C27	H27a	-3.8	0.5	1	
RDC	C23	H23	8	0.5	1	
RDC	C24	H24a	8.7	0.5	1	
RDC	C25	H25a	-5.9	0.5	1	
RDC	C6'	H6'	14	0.5	1	
RDC	C7'	H7'	13.1	0.5	1	
RDC	C8'	H8'	12.4	0.5	1	
RDC	C9'	H9'	13.4	0.5	1	
RDC	C13'	H13'a	-0.5	0.5	1	
RDC	C14'	H14'a	-18.2	0.5	1	
RDC	C14'	H14'b	-4.9	0.5	1	
RDC	C15'	H15'	-21.4	0.5	1	
RDC	C16'	H16'a	-4.5	0.5	1	
#Type	Atoms		NOE (volume)	Error	Weight	
NOE	H23	H14'a	12061000	+/-10%	1	
NOE	H16'a|H16'b|H16'c	H14'a	27737000	+/-25%	1	
NOE	H23	H14'b	9088200	+/-10%	1	
NOE	H15'	H14'b	21292000	+/-10%	1	
NOE	H14	H15	12994000	+/-10%	1	
NOE	H13a|H13b|H13c	H6	9810500	+/-25%	1	
NOE	H13'a|H13'b|H13'c	H6'	10077000	+/-25%	1	
NOE	H13a|H13b|H13c	H7	9160400	+/-25%	1	
NOE	H13'a|H13'b|H13'c	H7'	8327700	+/-25%	1	
NOE	H23	H16'a|H16'b|H16'c	20383667	+/-25%	1	
NOE	H24a|H24b|H24c	H16'a|H16'b|H16'c	3809000	+/-25%	1	
NOE	H15'	H16'a|H16'b|H16'c	18081667	+/-25%	1	
NOE	H15	H16'a|H16'b|H16'c	11402667	+/-25%	1	
NOE	H14	H24a|H24b|H24c	19014667	+/-25%	1	
NOE	H15	H24a|H24b|H24c	23346000	+/-10%	1	
NOE	H15'	H24a|H24b|H24c	20694333	+/-25%	1	
NOE	H14	H25a|H25b|H25c	14145000	+/-10%	1	
NOE	H23	H27a|H27b|H27c	17673667	+/-25%	1	
#Double Bond Restraints:						

#Type	Atoms				Weight	Force Constant
CIS	O1	C2	C3	C4	1	K=100.00
CIS	C2	C3	C4	C5	1	K=100.00
TRANS	C5	C6	C7	C8	1	K=100.00
TRANS	C6	C7	C8	C9	1	K=100.00
TRANS	C7	C8	C9	C10	1	K=100.00
CIS	O1'	C2'	C3'	C4'	1	K=100.00
CIS	C2'	C3'	C4'	C5'	1	K=100.00
TRANS	C5'	C6'	C7'	C8'	1	K=100.00
TRANS	C6'	C7'	C8'	C9'	1	K=100.00
TRANS	C7'	C8'	C9'	C10'	1	K=100.00
CIS	C16	C17	C18	C19	1	K=100.00
CIS	C18	C17	C23	C22	1	K=100.00
CIS	C17	C18	C20	C21	1	K=100.00
CIS	C18	C20	C21	C22	1	K=100.00
CIS	C20	C21	C22	C23	1	K=100.00
CIS	C21	C22	C23	C17	1	K=100.00

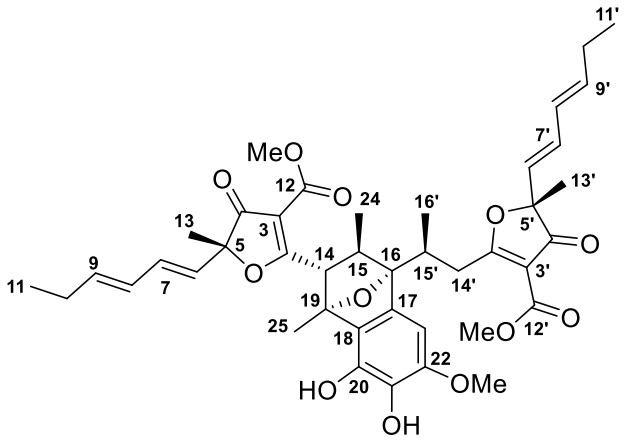
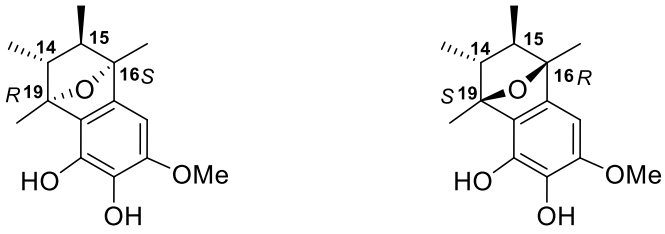


Figure S2.9. The initial guess structure for fc-rDG/DDD calculation of compound **3**.

Table S2.12. Key computational results extracted from the section “Configurational Families (Excluding Methylene Assignments)” in the “shake2.out” output file of compound **3**. (X represent ', Y represent " for atom number)

Family No.	rDG/DDD Energies			Bayesian Weights (i)	[H0]	[H0]	[H0]	[H0]	[H1]	[H1]	[H1]
	dE(min)	E(min)	E(max)		C5	C16	C19	C5'	C14	C15	C15'
1	27.5503	28.5498	84.9952	6.91E-16	(lk)	(lk)	(lk)	(lk)	(lk)	(lk)	(lk)
2	24.955	25.9544	75.1912	9.14E-15	(lk)	(lk)	(lk)	(lk)	(lk)	(lk)	(ul)
3	3.4548	4.4543	39.8852	3.52E-04	(lk)	(lk)	(lk)	(lk)	(lk)	(ul)	(lk)
4	87.3684	88.3679	102.1087	6.23E-42	(lk)	(lk)	(lk)	(lk)	(lk)	(ul)	(ul)
5	31.9442	32.9437	142.9812	5.99E-16	(lk)	(lk)	(lk)	(lk)	(ul)	(lk)	(ul)
6	0.1864	1.1858	116.5178	4.62E-01	(lk)	(lk)	(lk)	(lk)	(ul)	(ul)	(lk)
7	27.8255	28.825	68.7871	3.61E-15	(lk)	(lk)	(lk)	(lk)	(ul)	(ul)	(ul)
8	26.001	27.0005	62.8188	1.55E-14	(lk)	(ul)	(ul)	(lk)	(lk)	(lk)	(lk)
9	0	0.9995	117.7324	5.37E-01	(lk)	(ul)	(ul)	(lk)	(lk)	(lk)	(ul)
10	31.8335	32.833	138.0569	6.24E-16	(lk)	(ul)	(ul)	(lk)	(lk)	(ul)	(lk)
11	48.3891	49.3886	108.3121	5.28E-25	(lk)	(ul)	(ul)	(lk)	(ul)	(lk)	(lk)
12	4.0464	5.0459	25.5588	1.14E-04	(lk)	(ul)	(ul)	(lk)	(ul)	(lk)	(ul)
13	26.0707	27.0701	76.0847	3.37E-15	(lk)	(ul)	(ul)	(lk)	(ul)	(ul)	(lk)
14	28.8572	29.8567	31.3115	3.40E-16	(lk)	(ul)	(ul)	(lk)	(ul)	(ul)	(ul)



truncated 16*S*, 19*R* truncated 16*R*, 19*S*

Figure S2.10. Truncated models used for assigning the configuration of C-16 and C-19 in **2** and **3**.

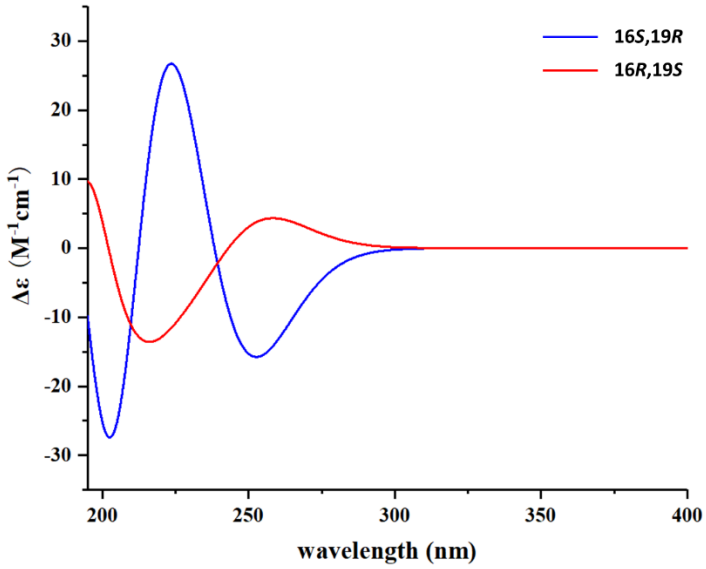
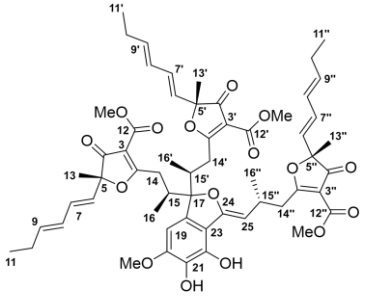


Figure S2.11. Calculated ECD of truncated 16*S*, 19*R* and truncated 16*R*, 19*S*.

Part S3. Experimental spectra of 1–3



pentetrafuranone A (1)

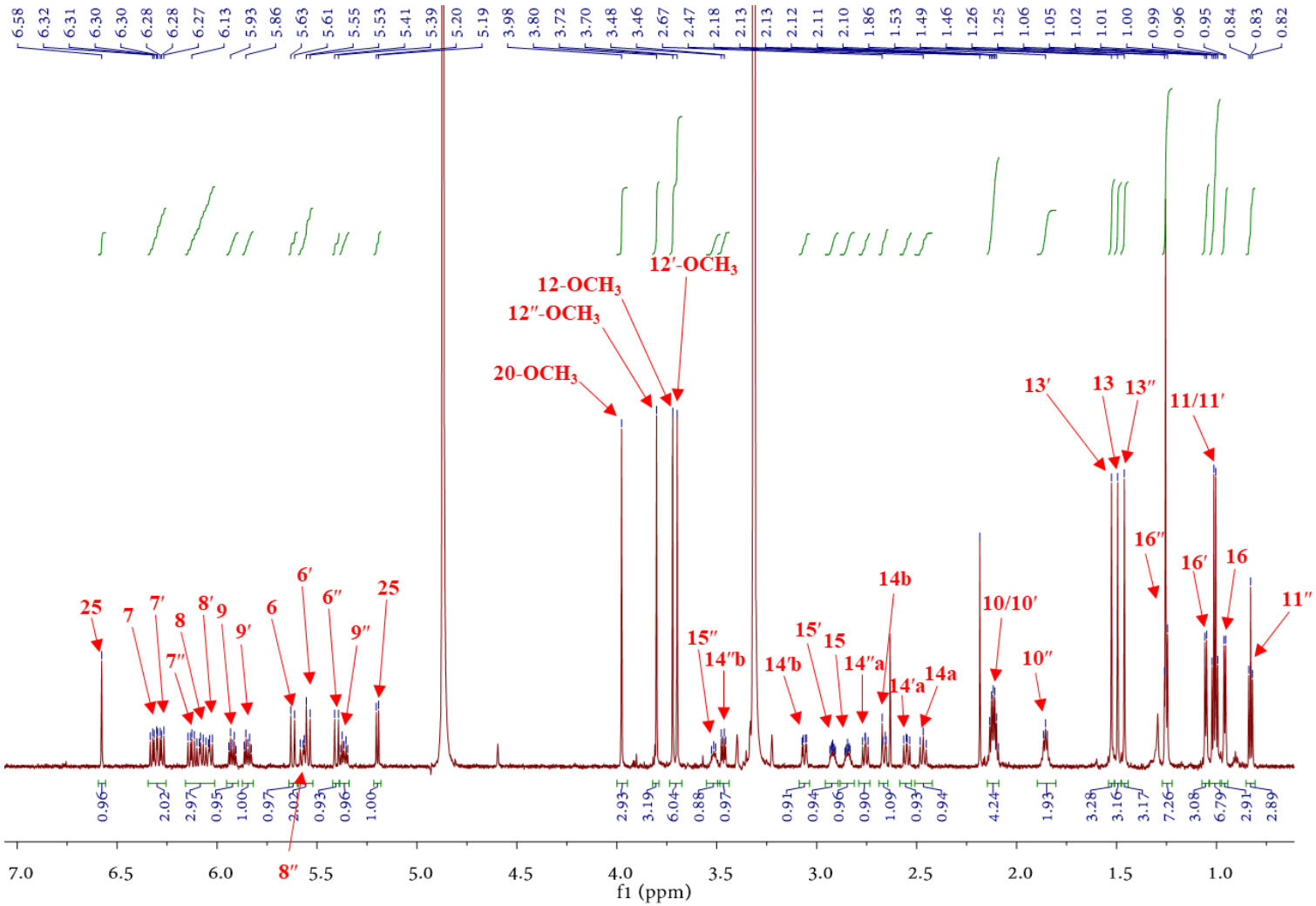
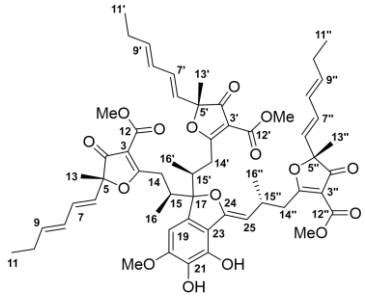


Figure S3.1. ^{1}H NMR of pentetrafuranone A (**1**) in CD_3OD.



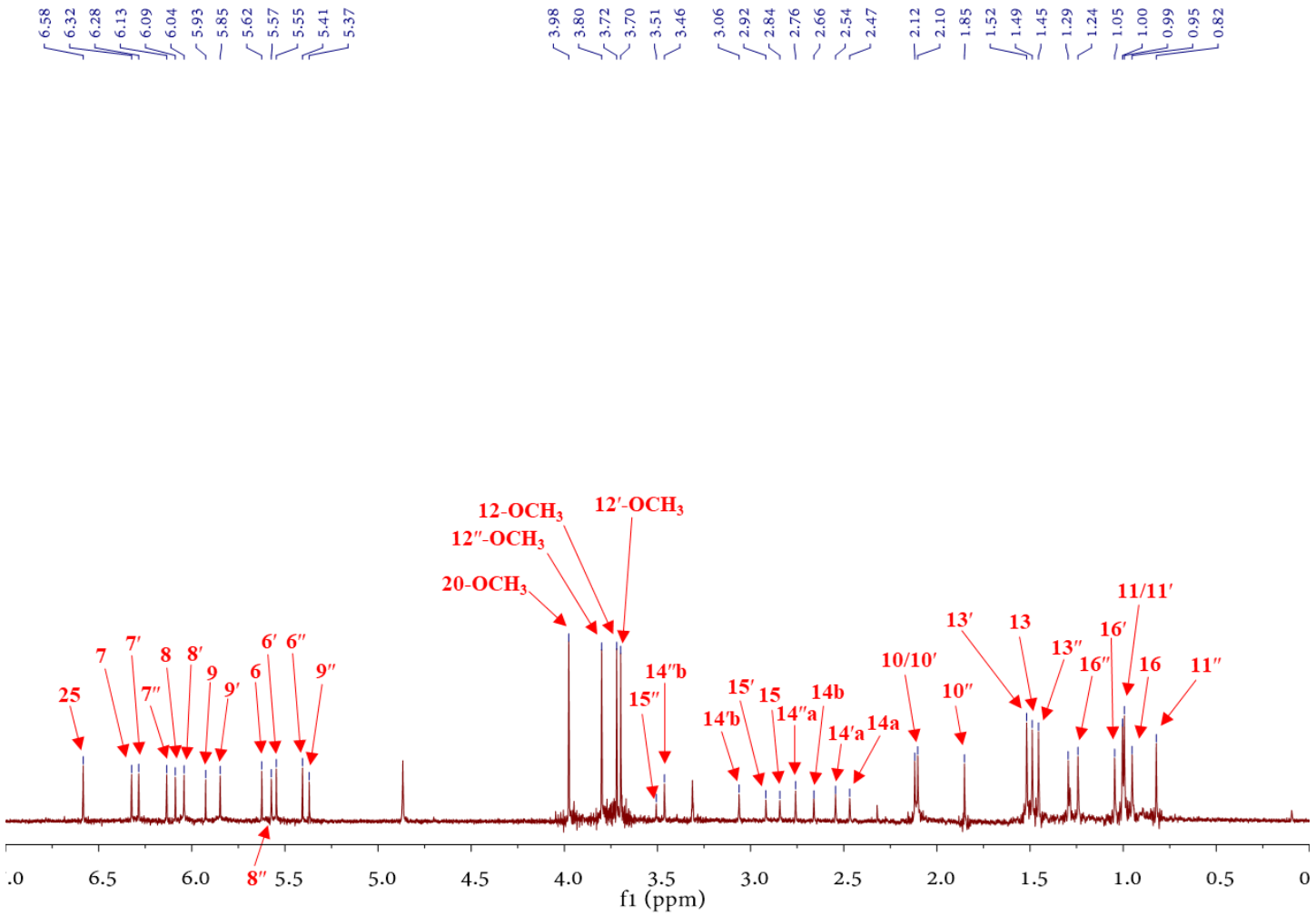


Figure S3.2. Pure shift ^{1}H NMR of pentetrafuranone A (**1**) in CD_3OD.

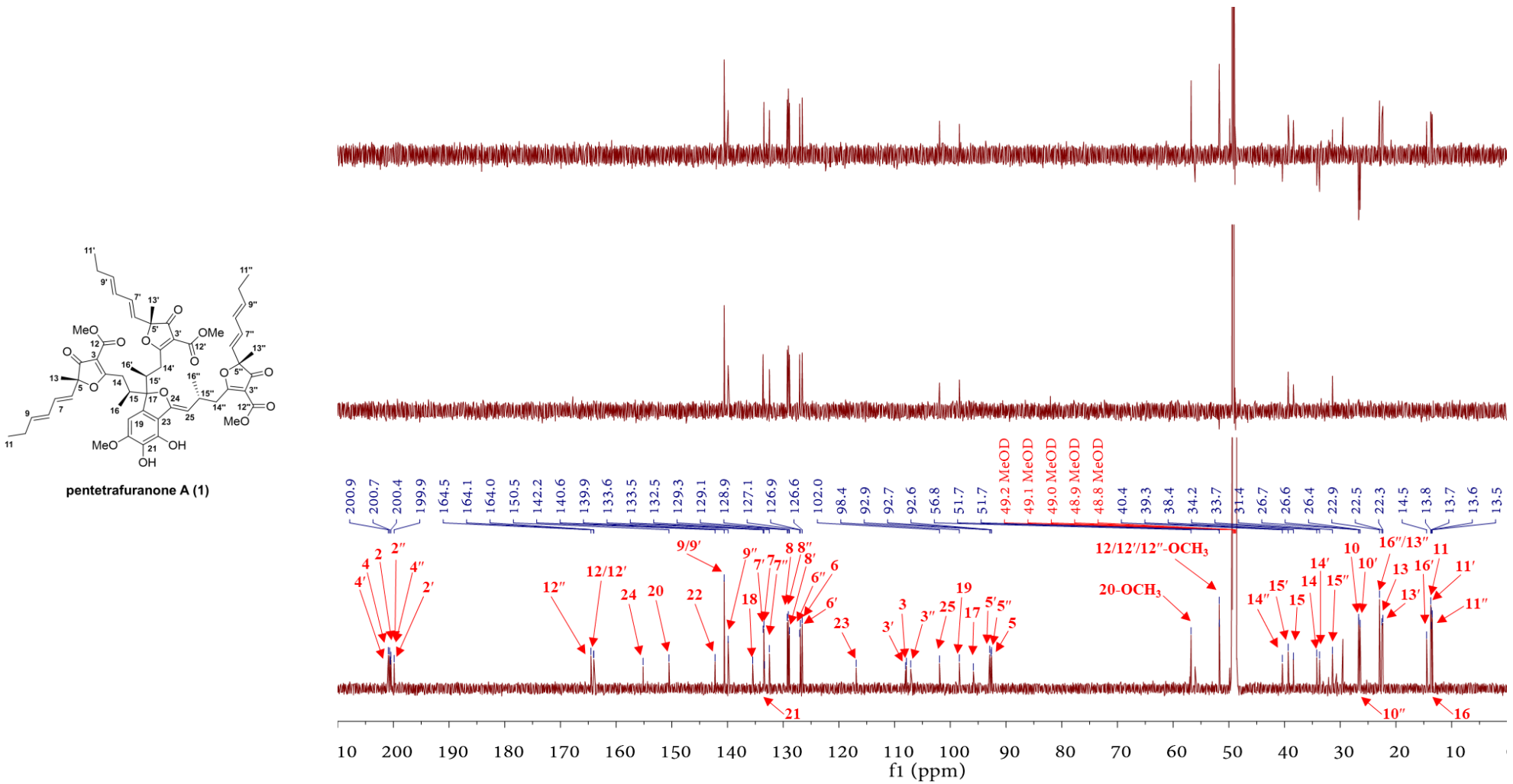


Figure S3.3. ^{13}C NMR, DEPT90, and DEPT135 of pentetrafuranone A (**1**) in CD_3OD.

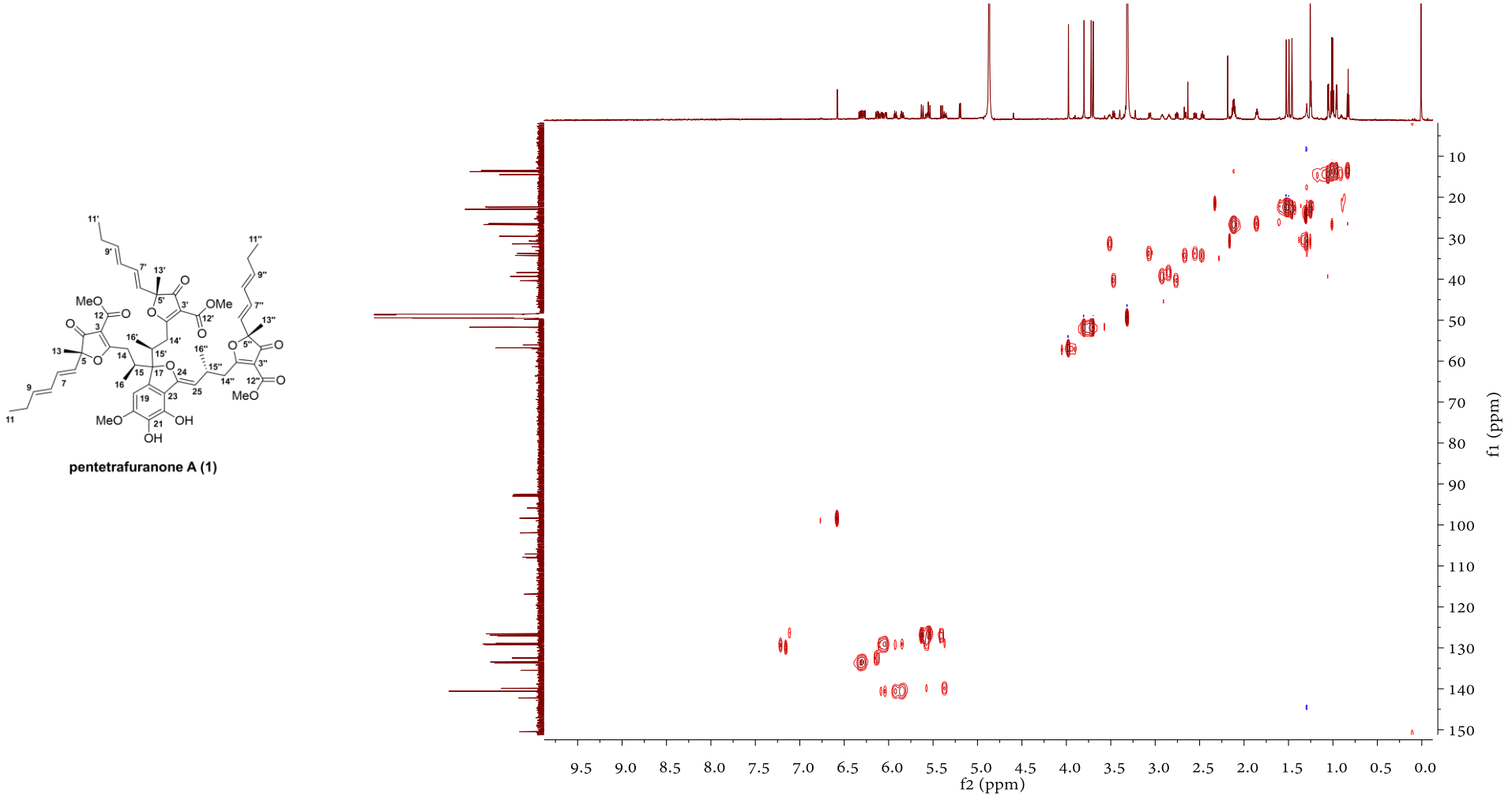


Figure S3.4. HSQC spectrum of pentetrafuranone A (**1**) in CD_3OD.

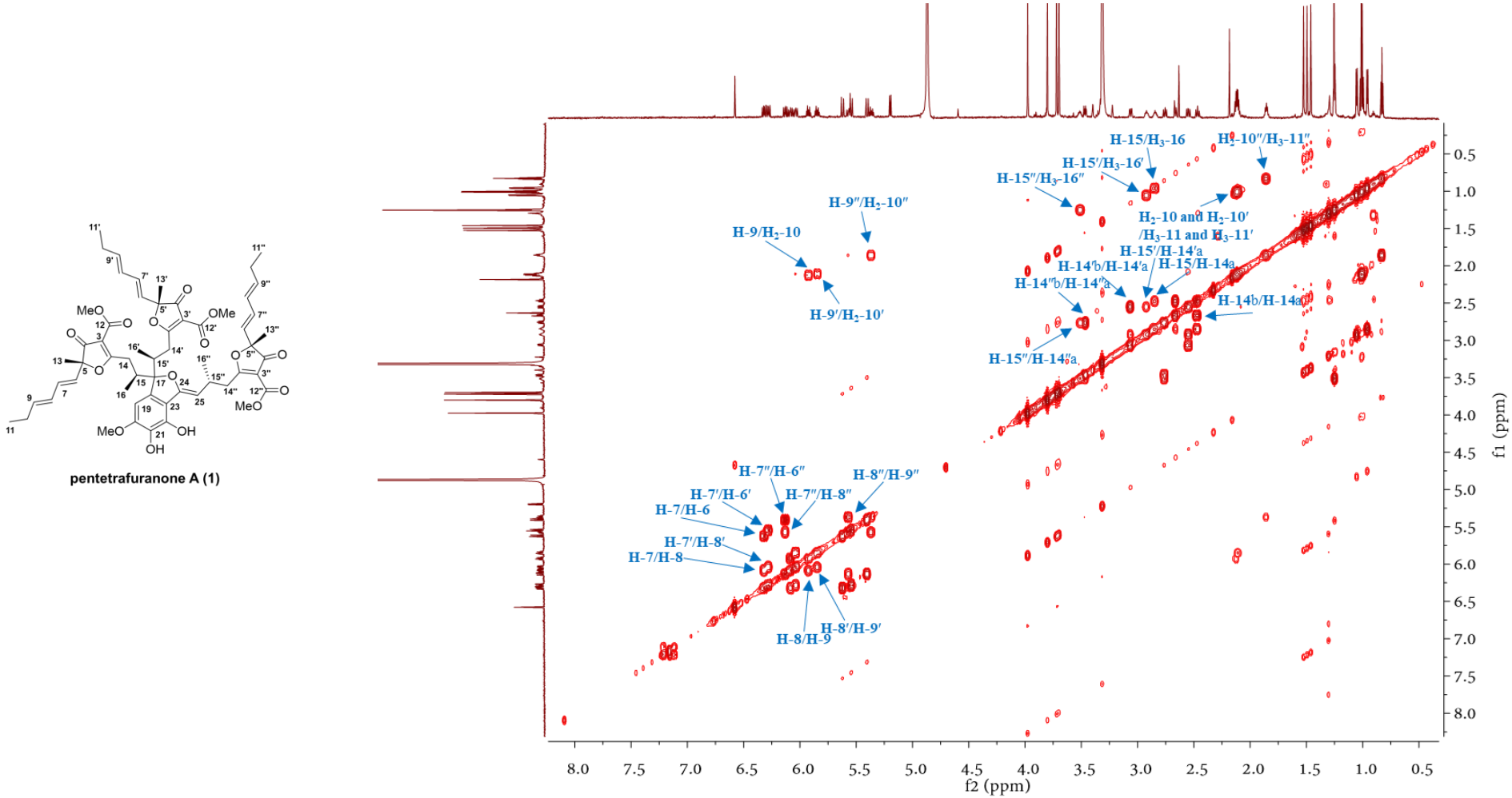


Figure S3.5. ^{1}H-^{1}H COSY spectrum of pentetrafuranone A (**1**) in CD_3OD.

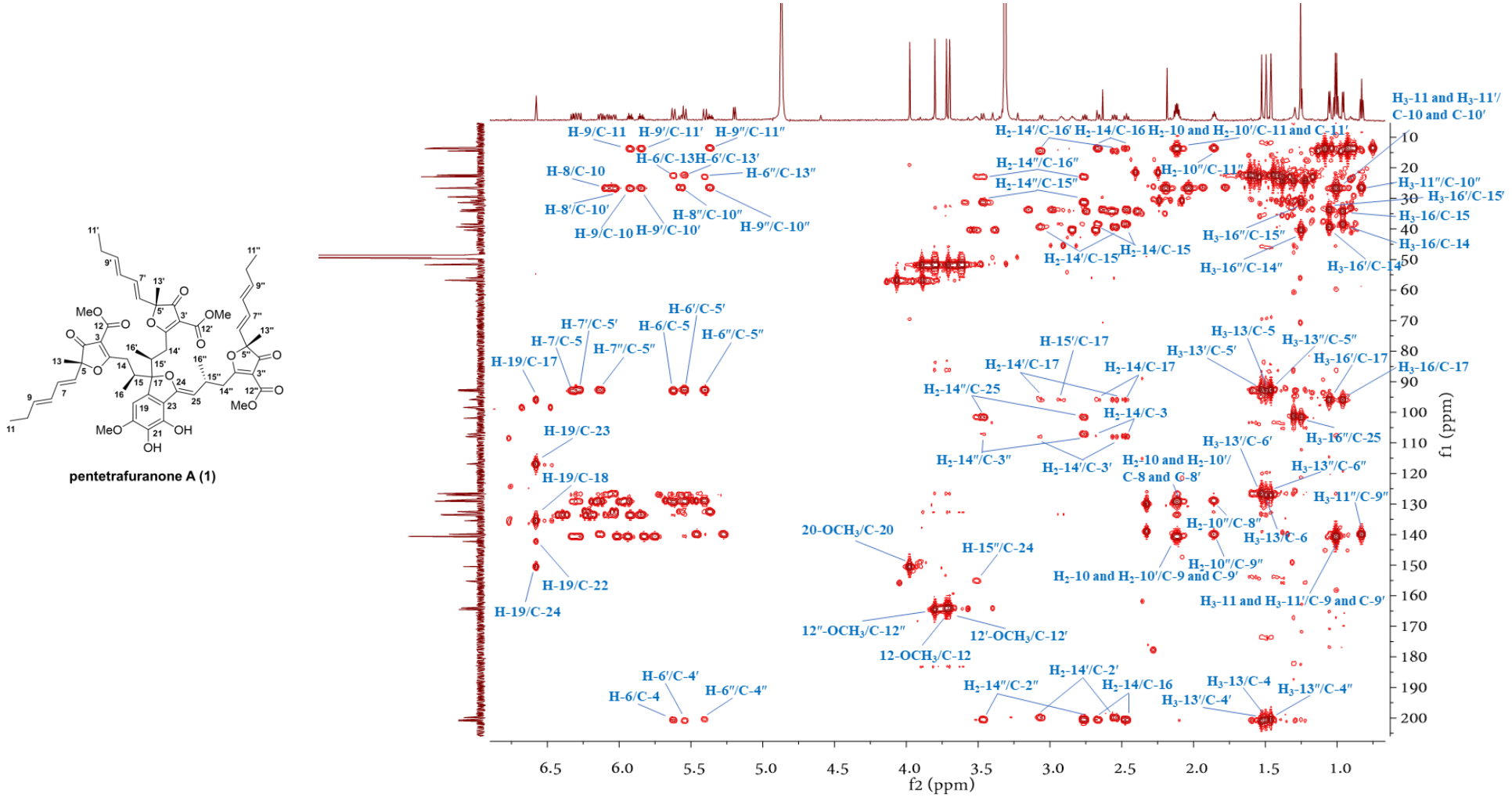


Figure S3.6. HMBC spectrum of pentetrafuranone A (**1**) in CD_3OD.

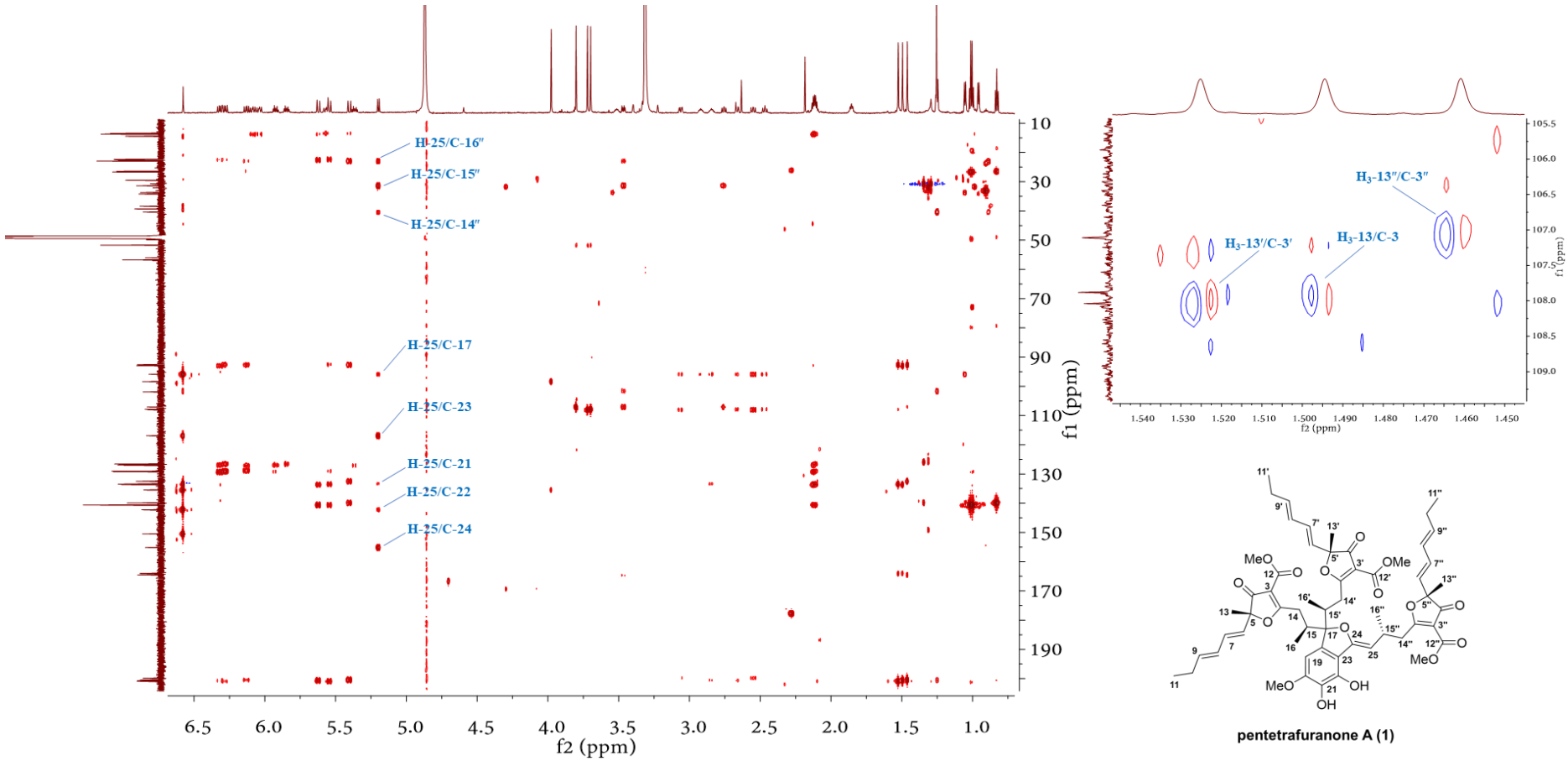


Figure S3.7. LR-HSQMBC spectrum of pentetrafuranone A (**1**) in CD_3OD.

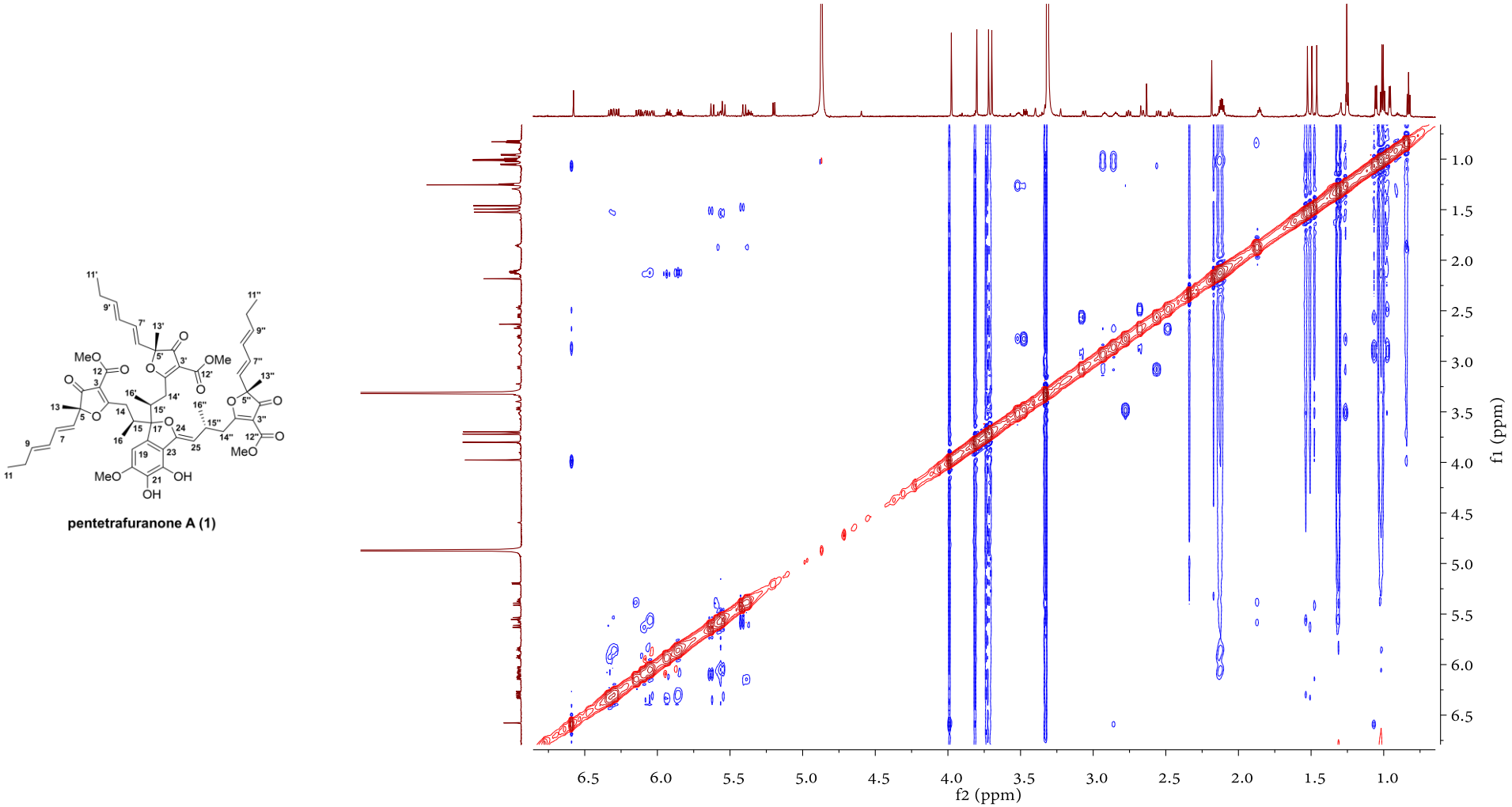


Figure S3.8. ROESY spectrum of pentetrafuranone A (**1**) in CD_3OD.

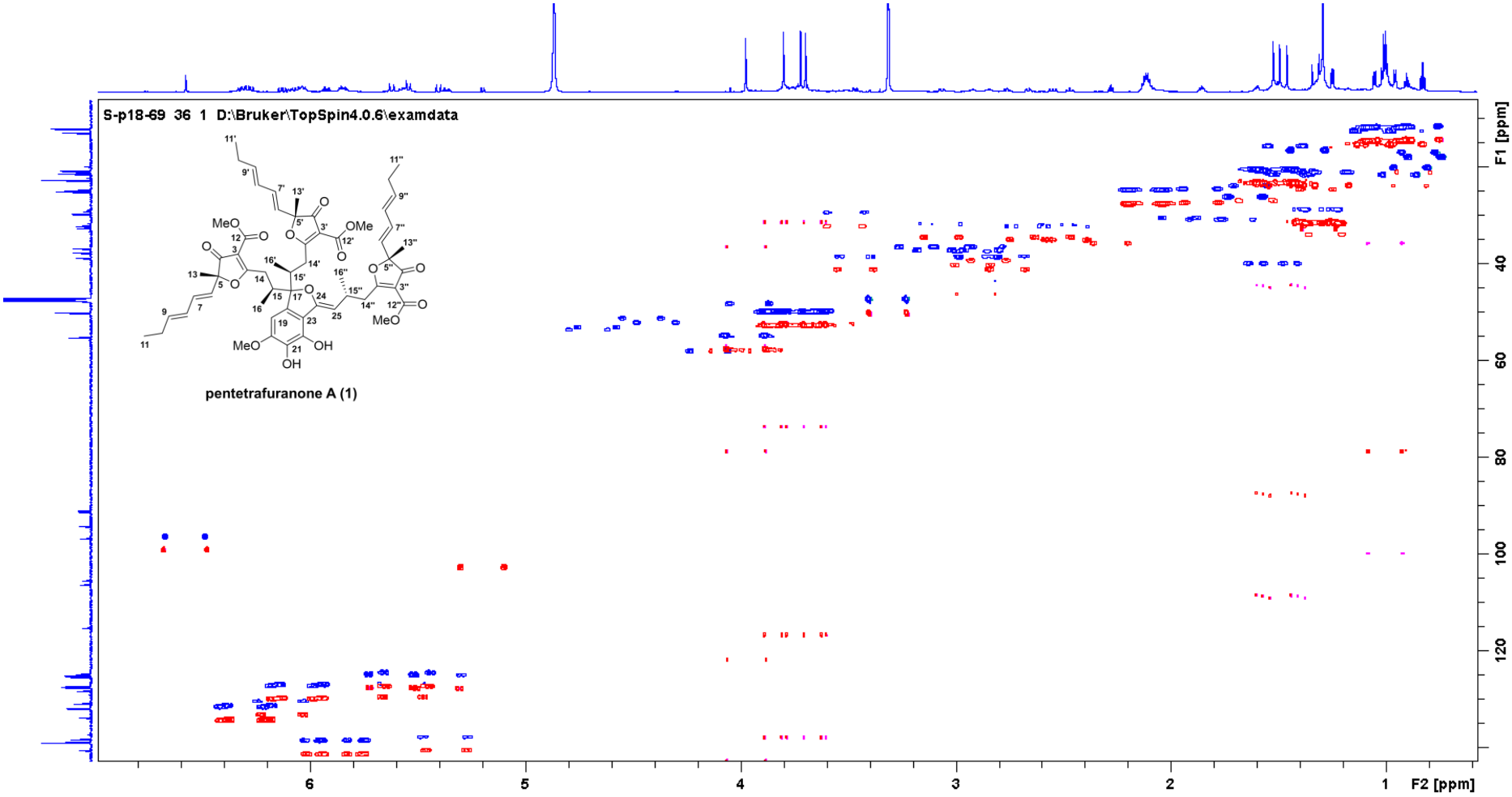


Figure S3.9. Clip-HSQC spectra in isotropic (blue) and anisotropic (red) conditions of pentetrafuranone A (**1**) in CD_3OD.

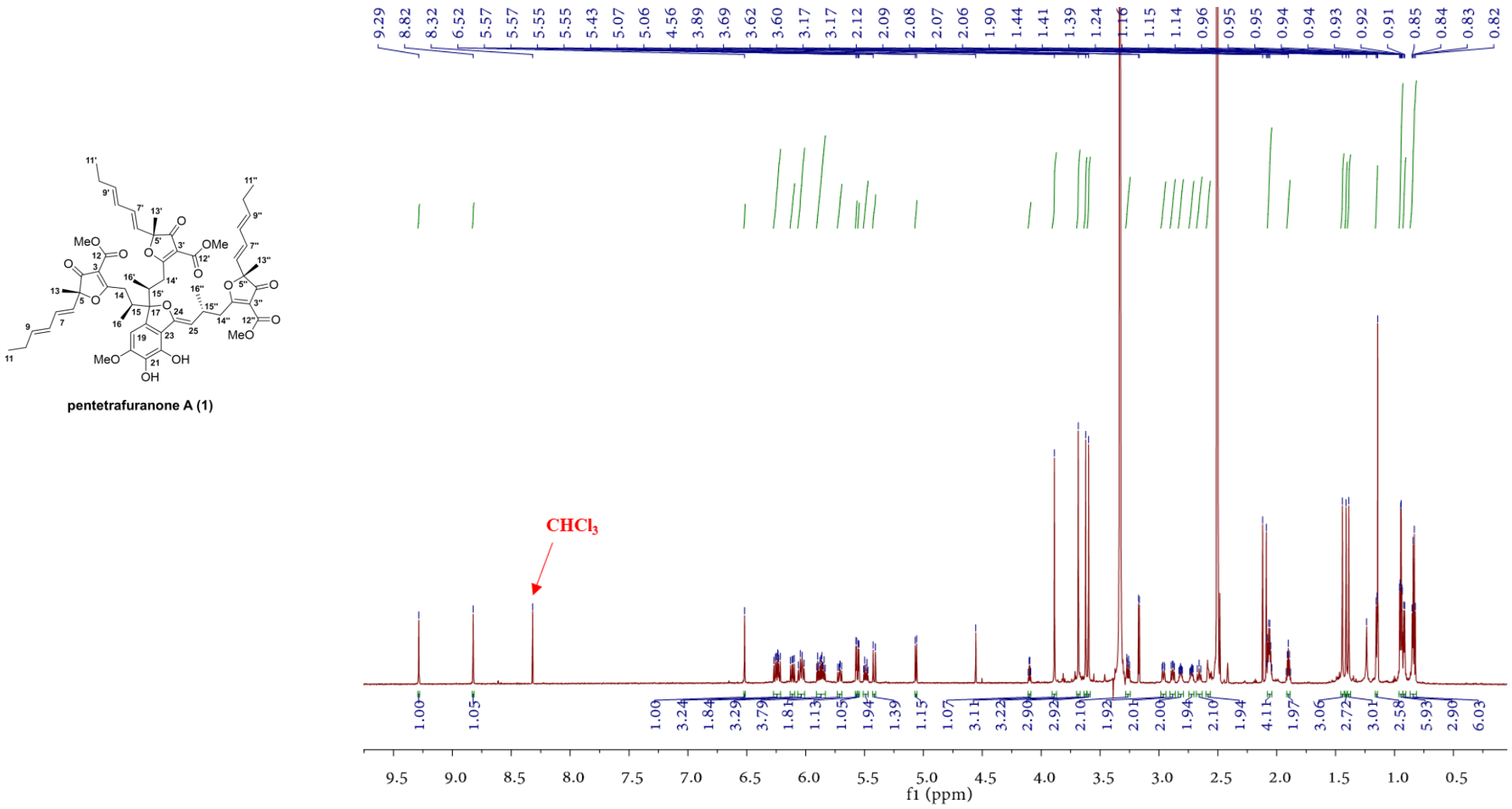


Figure S3.10. ^{1}H NMR of pentetrafuranone A (**1**) in DMSO-d_6.

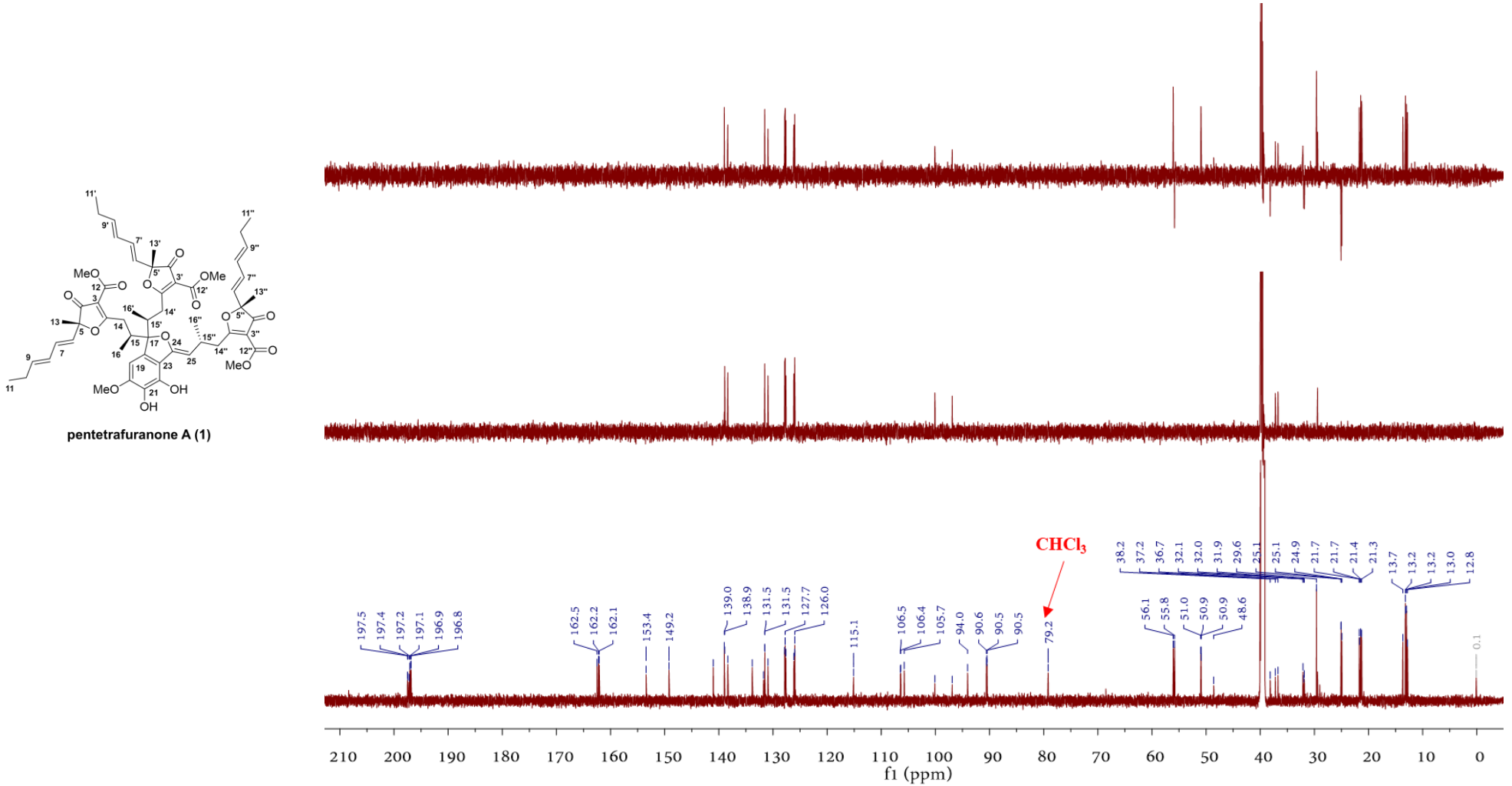


Figure S3.11. ^{13}C NMR of pentetrafuranone A (**1**) in DMSO-d_6.

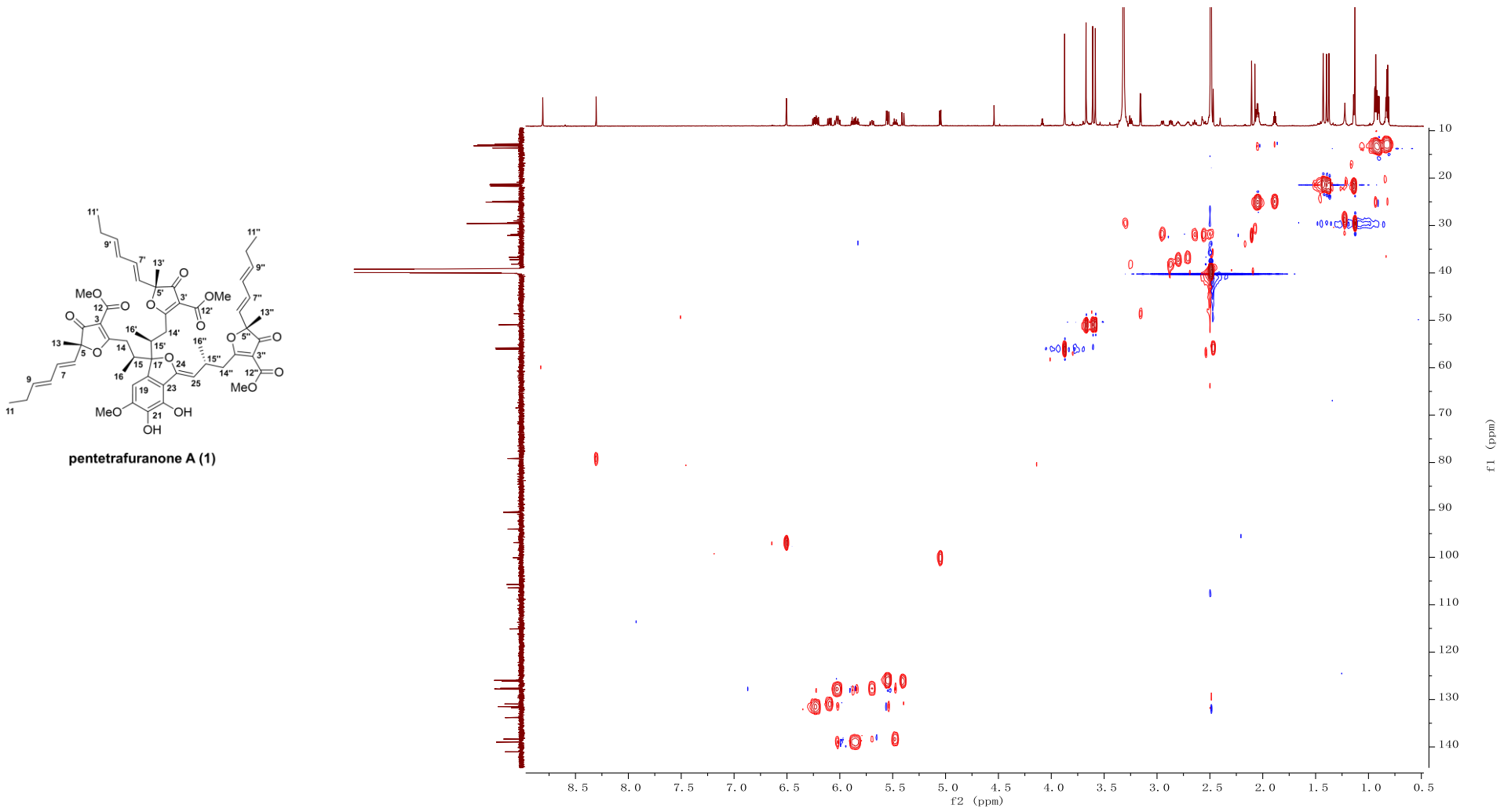


Figure S3.12. HSQC spectrum of pentetrafuranone A (**1**) in DMSO-d_6.

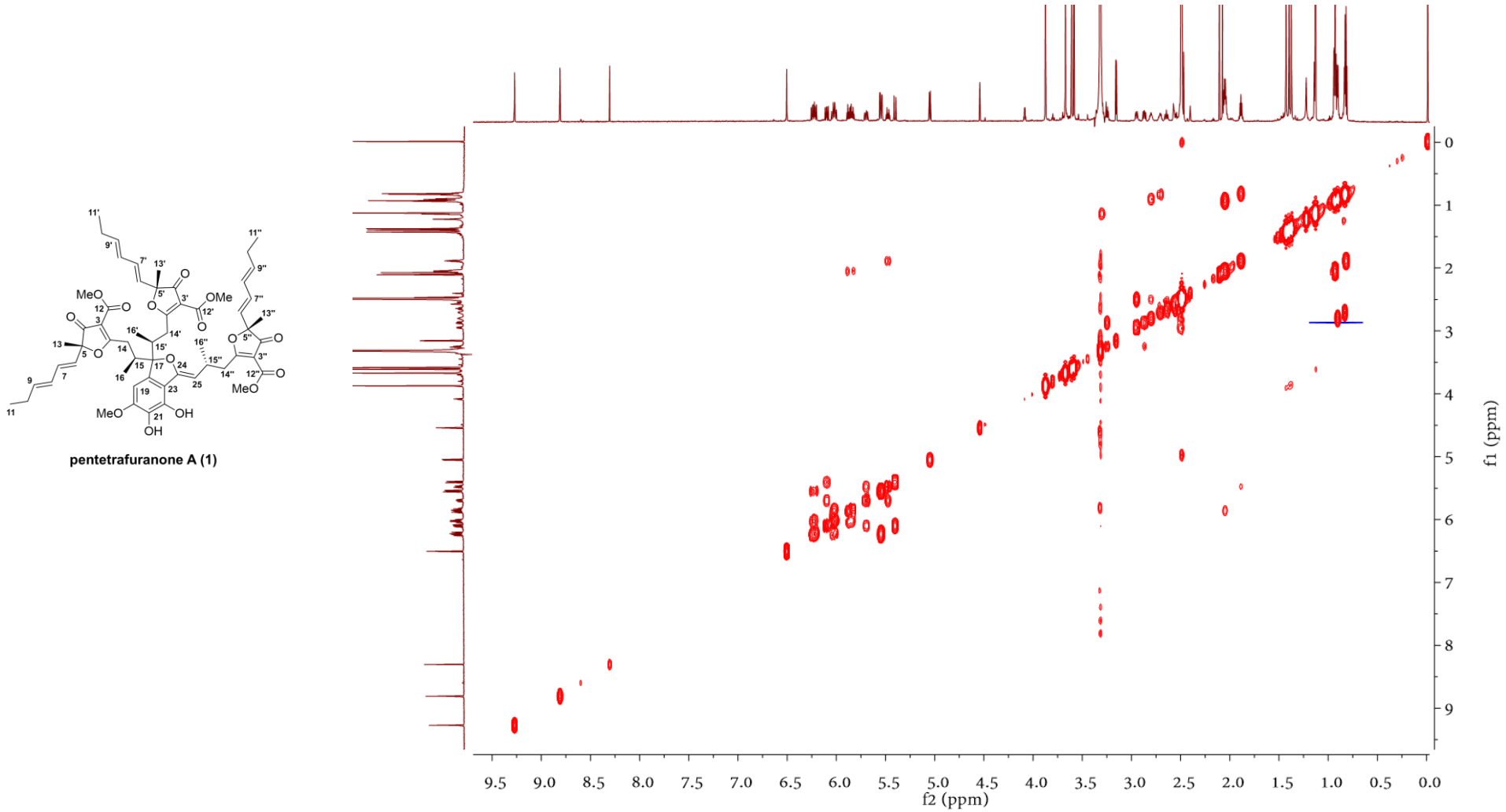


Figure S3.13. ^{1}H–^{1}H COSY spectrum of pentetrafuranone A (**1**) in DMSO-d_6.

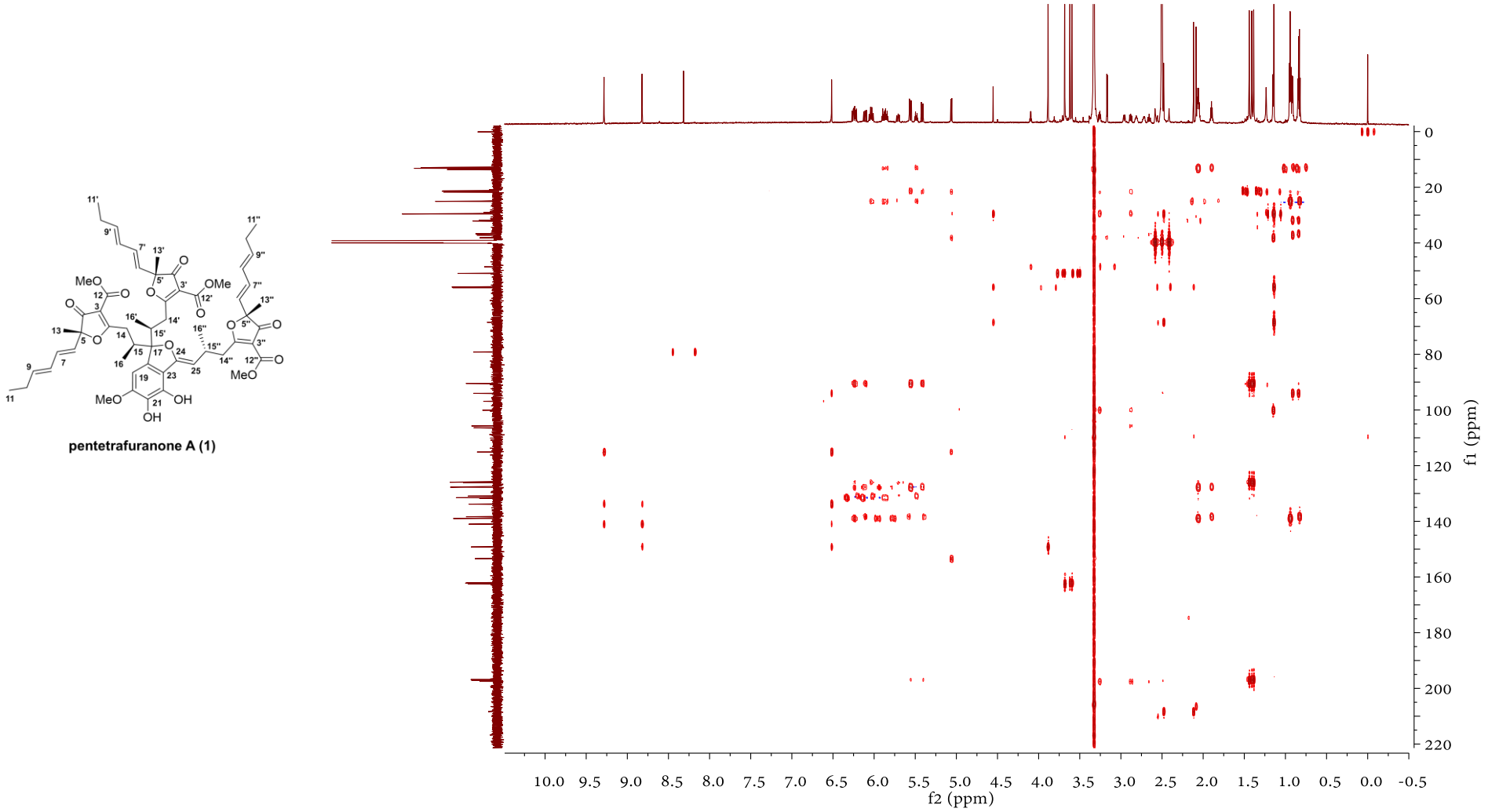


Figure S3.14. HMBC spectrum of pentetrafuranone A (**1**) in DMSO-d_6.

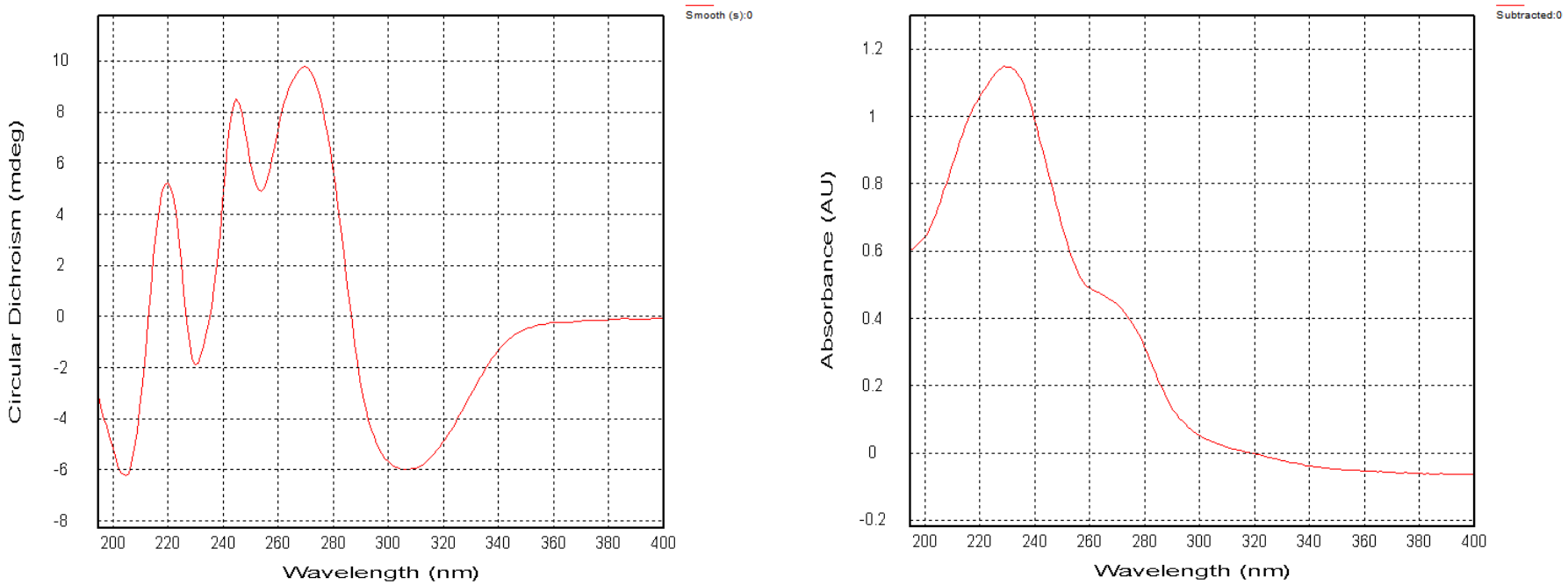
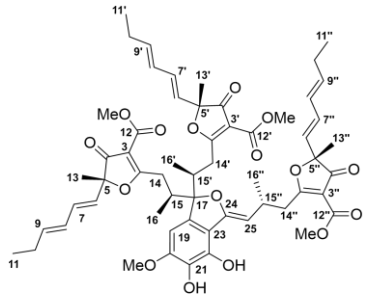


Figure S3.15. Circular dichroism (CD) spectrum and UV spectrum of pentetrafuranone A (**1**) in MeOH.



pentetrafuranone A (1)

Rudolph Research Analytical

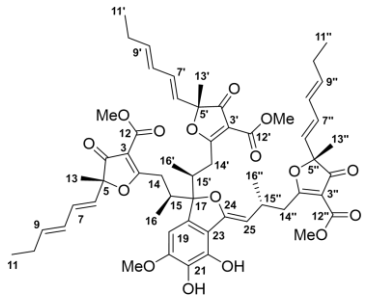
This sample was measured on an Autopol VI, Serial #91058
Manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

Measurement Date : Wednesday, 28-DEC-2022

Set Temperature : 20.0

Time Delay : Disabled

Delay between Measurement : Disabled



pentetrafuranone A (1)

n	Average	Std.Dev.	% RSD	Maximum	Minimum
5	-43.28	0.81	-1.87	-41.82	-43.64

S.No	Sample ID	Time	Result	Scale	OR °Arc	WLG.nm	Lg.mm	Conc.g/100ml	Temp.
1	sp18-69	02:16:40 PM	-43.64	SR	-0.024	589	100.00	0.055	20.0
2	sp18-69	02:16:46 PM	-43.64	SR	-0.024	589	100.00	0.055	20.0
3	sp18-69	02:16:52 PM	-43.64	SR	-0.024	589	100.00	0.055	20.0
4	sp18-69	02:16:59 PM	-43.64	SR	-0.024	589	100.00	0.055	20.0
5	sp18-69	02:17:05 PM	-41.82	SR	-0.023	589	100.00	0.055	20.0

Figure S3.16. Optical rotation of pentetrafuranone A (**1**) in MeOH.

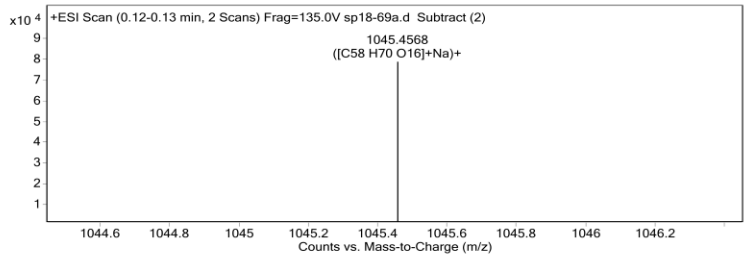
Qualitative Analysis Report

Data Filename	sp18-69a.d	**Sample Name**	sp18-69a
Sample Type	Sample	**Position**	P1-A5
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	4/9/2018 4:48:39 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

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

User Spectra

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



Peak List

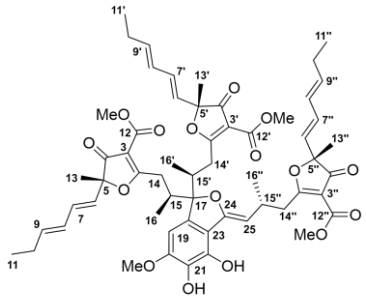
m/z	z	Abund	Formula	Ion
534.224	2	9754.46		
534.7263	2	7094.7		
1045.4568	1	79069.37	C58 H70 O16	(M+Na)+
1046.4592	1	48922.13	C58 H70 O16	(M+Na)+
1047.4616	1	16305.91	C58 H70 O16	(M+Na)+
1061.4355	1	21883.7		
1062.4392	1	13301.22		
1063.4365	1	5892.33		

Formula Calculator Element Limits

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

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C58 H70 O16	1022.4664	1045.4556	1045.4568	-1.20	-1.15	24.0000



pentetrafuranone A (1)

--- End Of Report ---

Figure S3.17. HRESIMS spectrum of pentetrafuranone A (**1**).

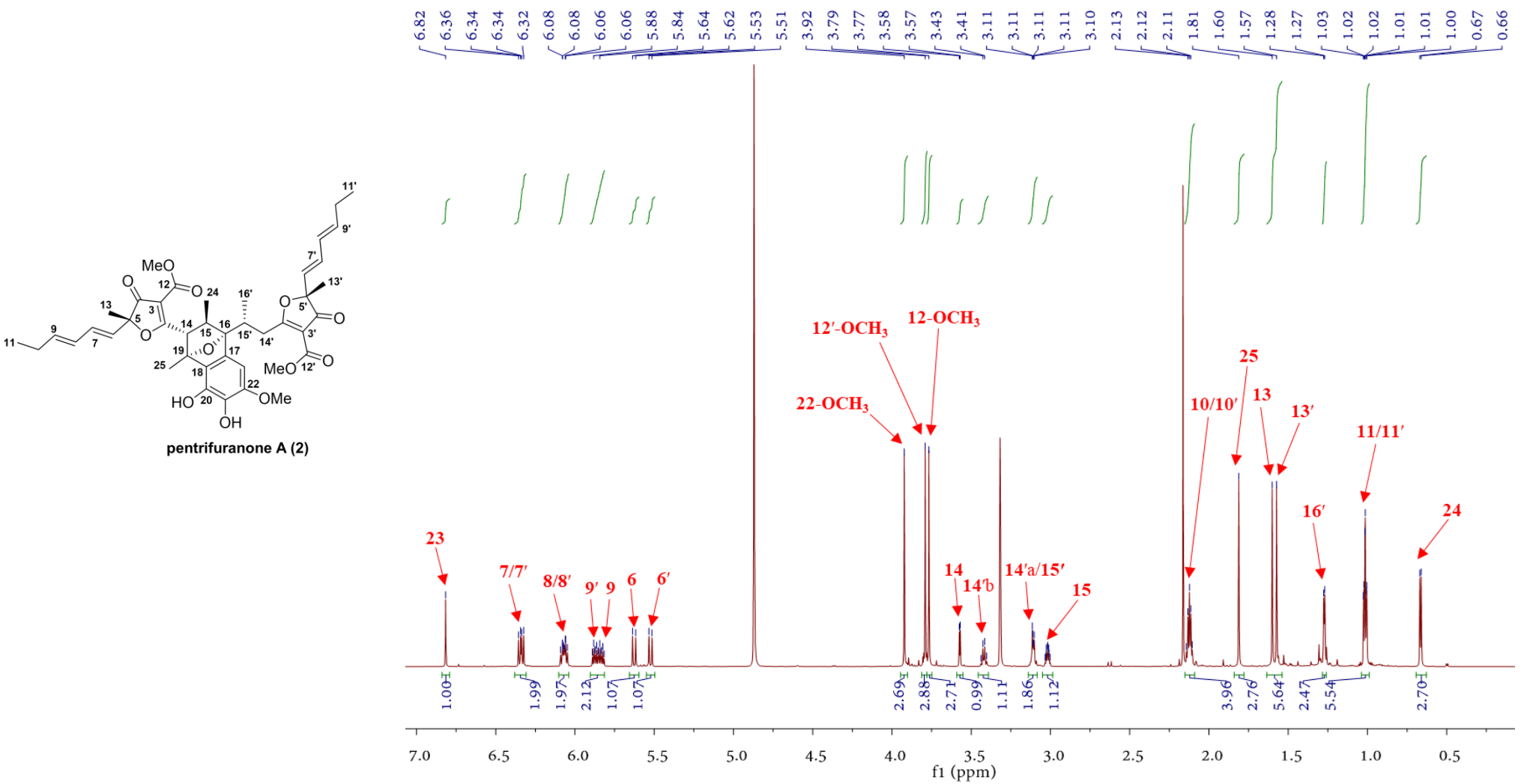


Figure S3.18. ^{1}H NMR of pentrifuranone A (**2**) in CD_3OD.

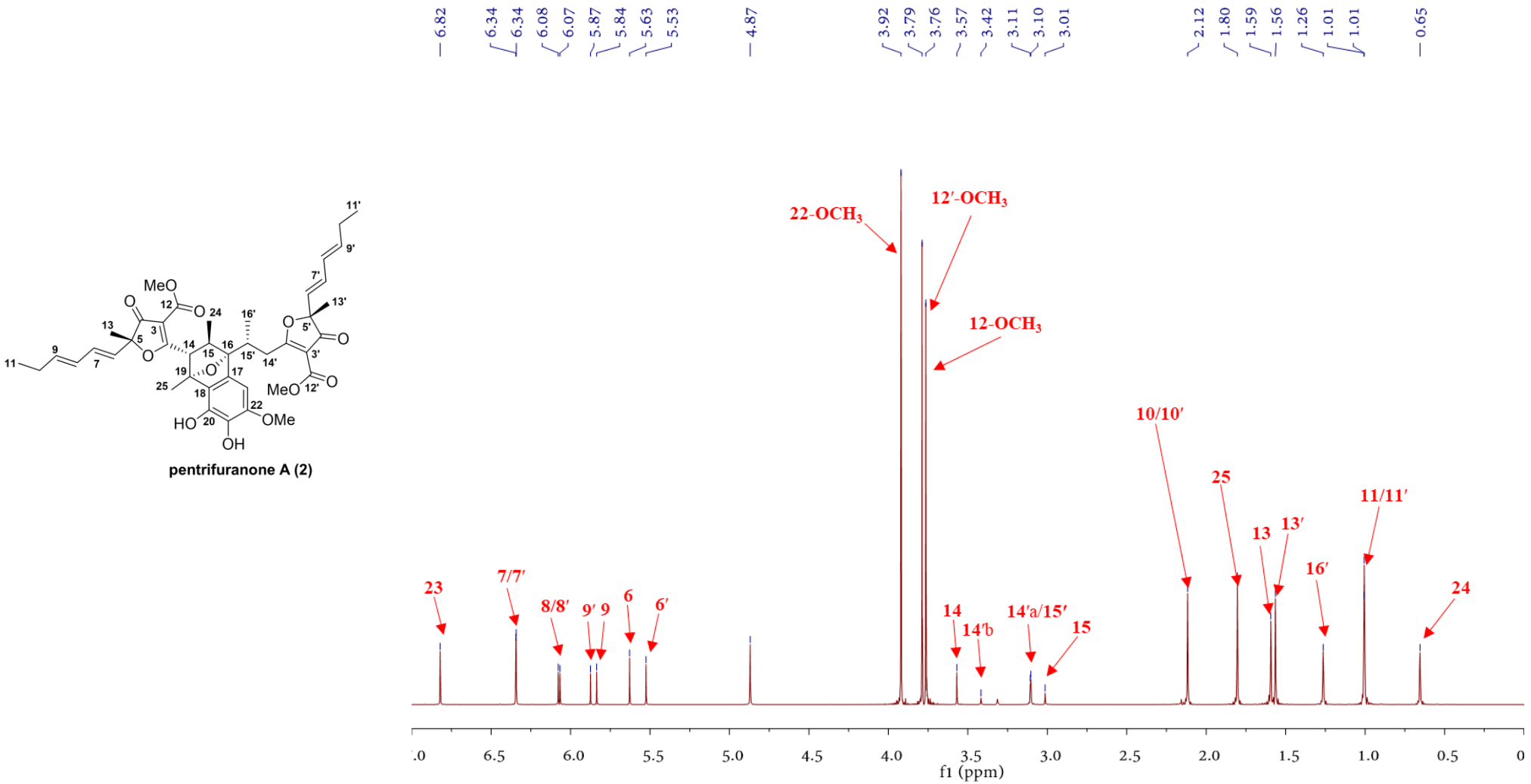


Figure S3.19. Pure shift ^{1}H NMR of pentrifuranone A (**2**) in CD_3OD.

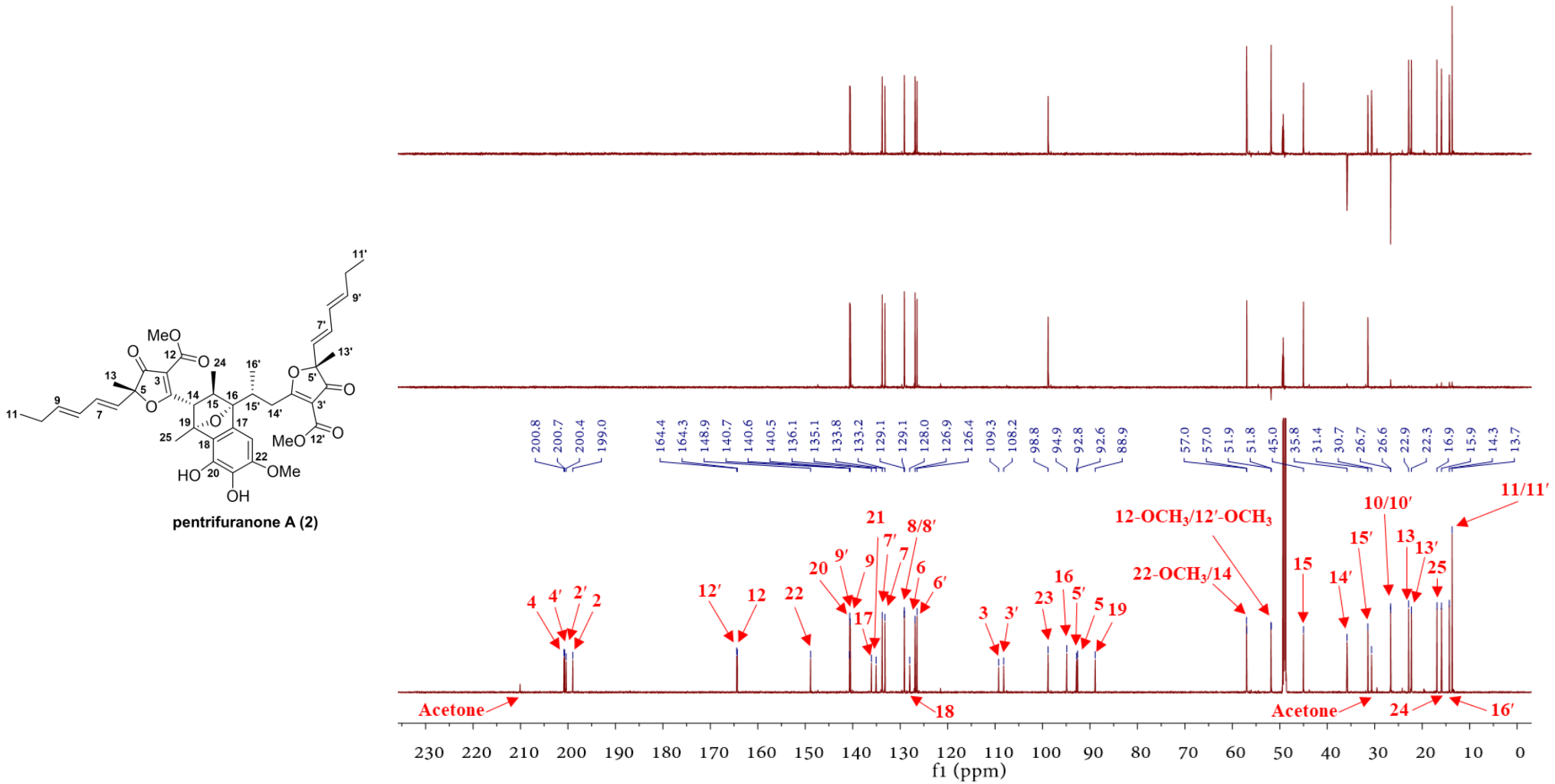


Figure S3.20. ^{13}C NMR, DEPT90, and DEPT135 of pentrifuranone A (**2**) in CD_3OD.

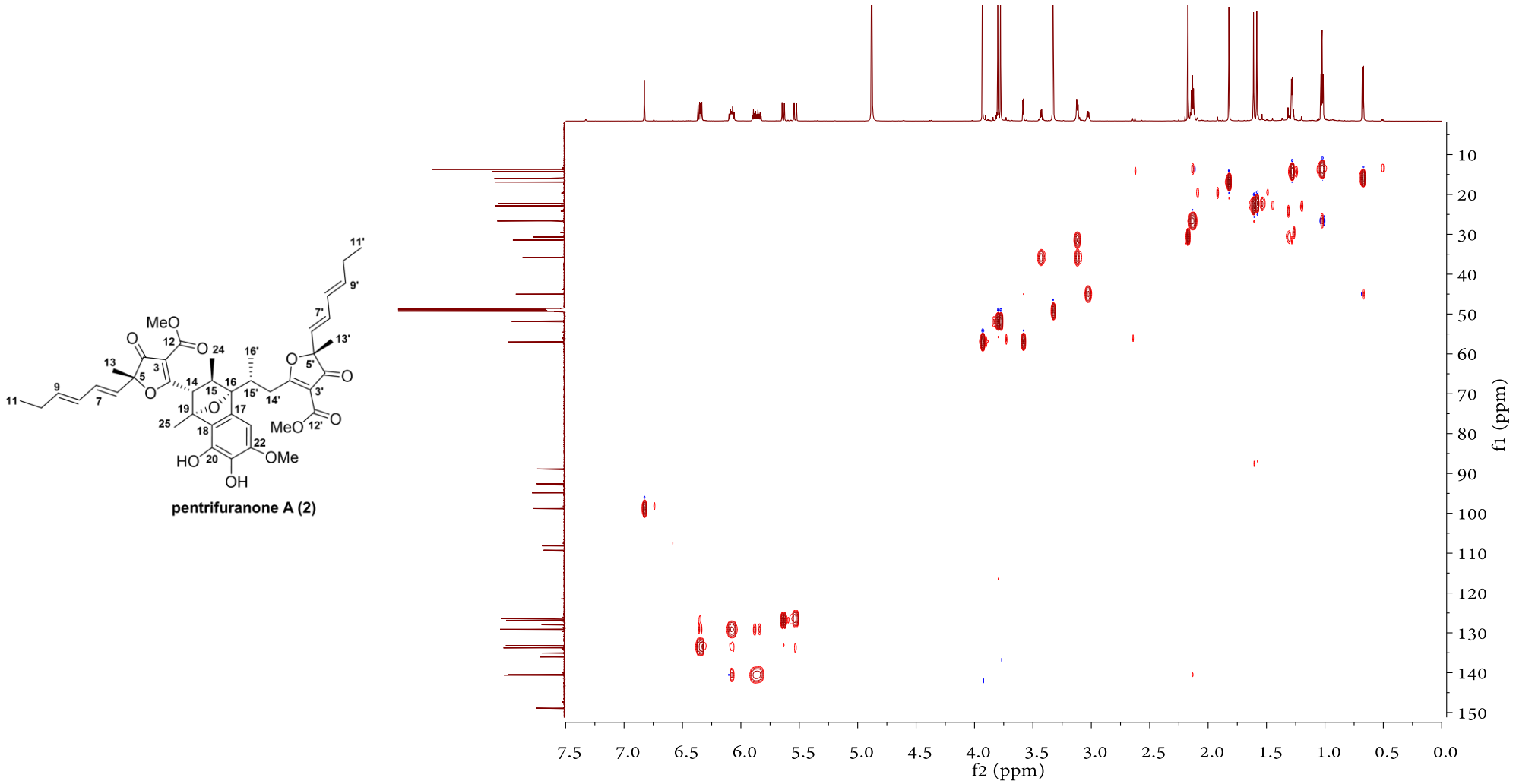


Figure S3.21. HSQC spectrum of pentrifuranone A (**2**) in CD_3OD.

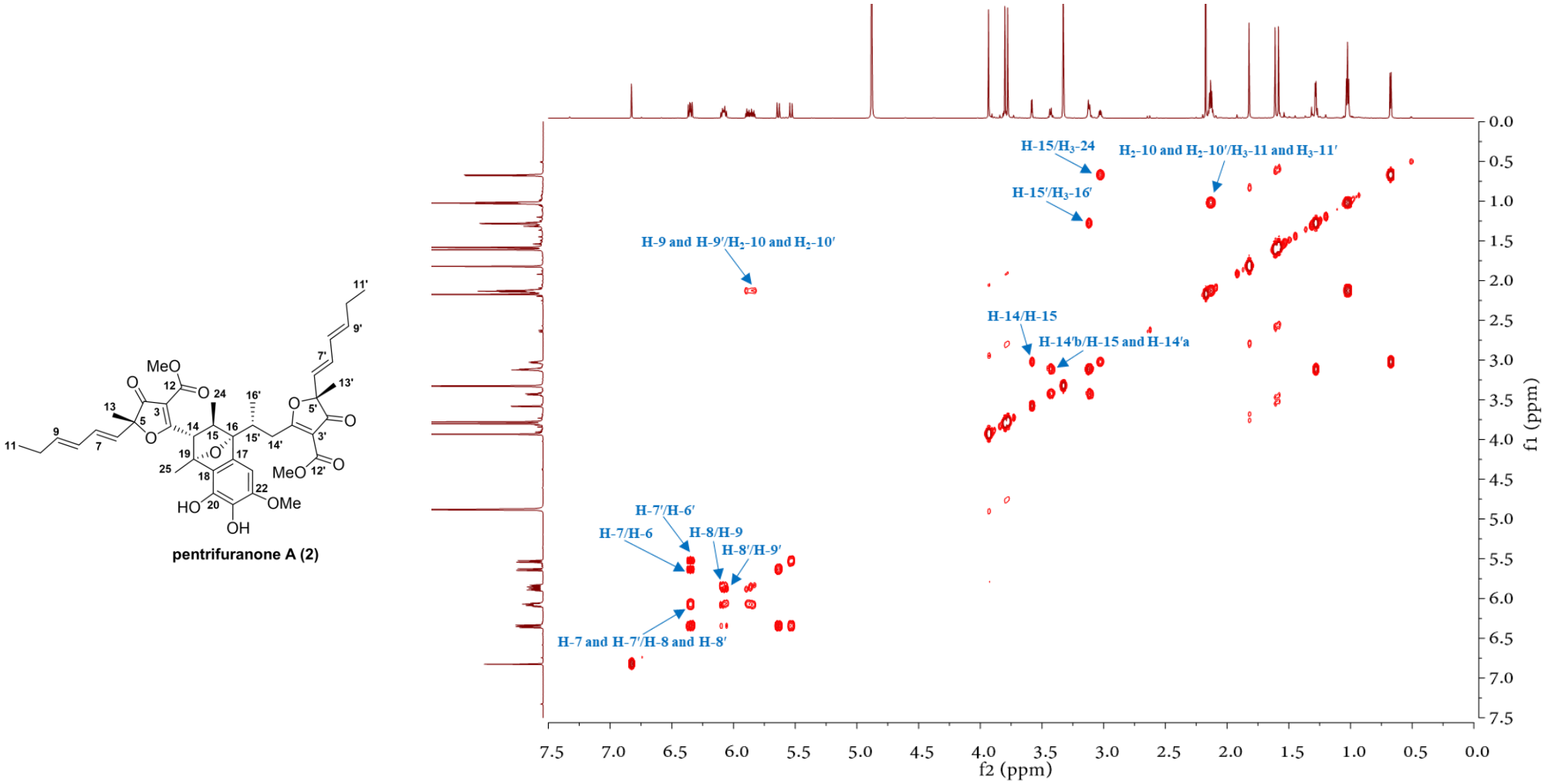


Figure S3.22. ^{1}H–^{1}H COSY spectrum of pentrifuranone A (**2**) in CD_3OD.

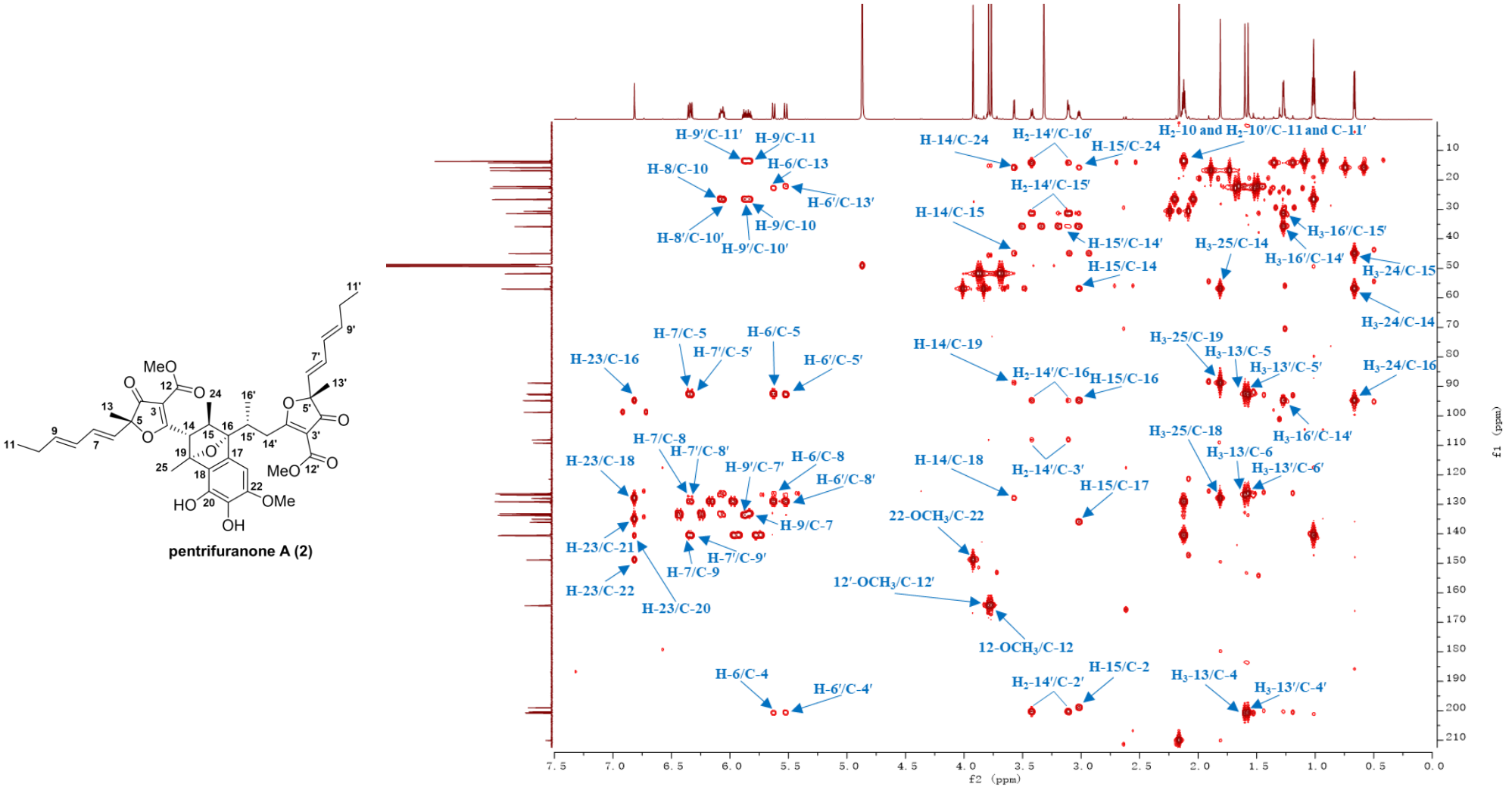


Figure S3.23. HMBC spectrum of pentrifuranone A (**2**) in CD_3OD.

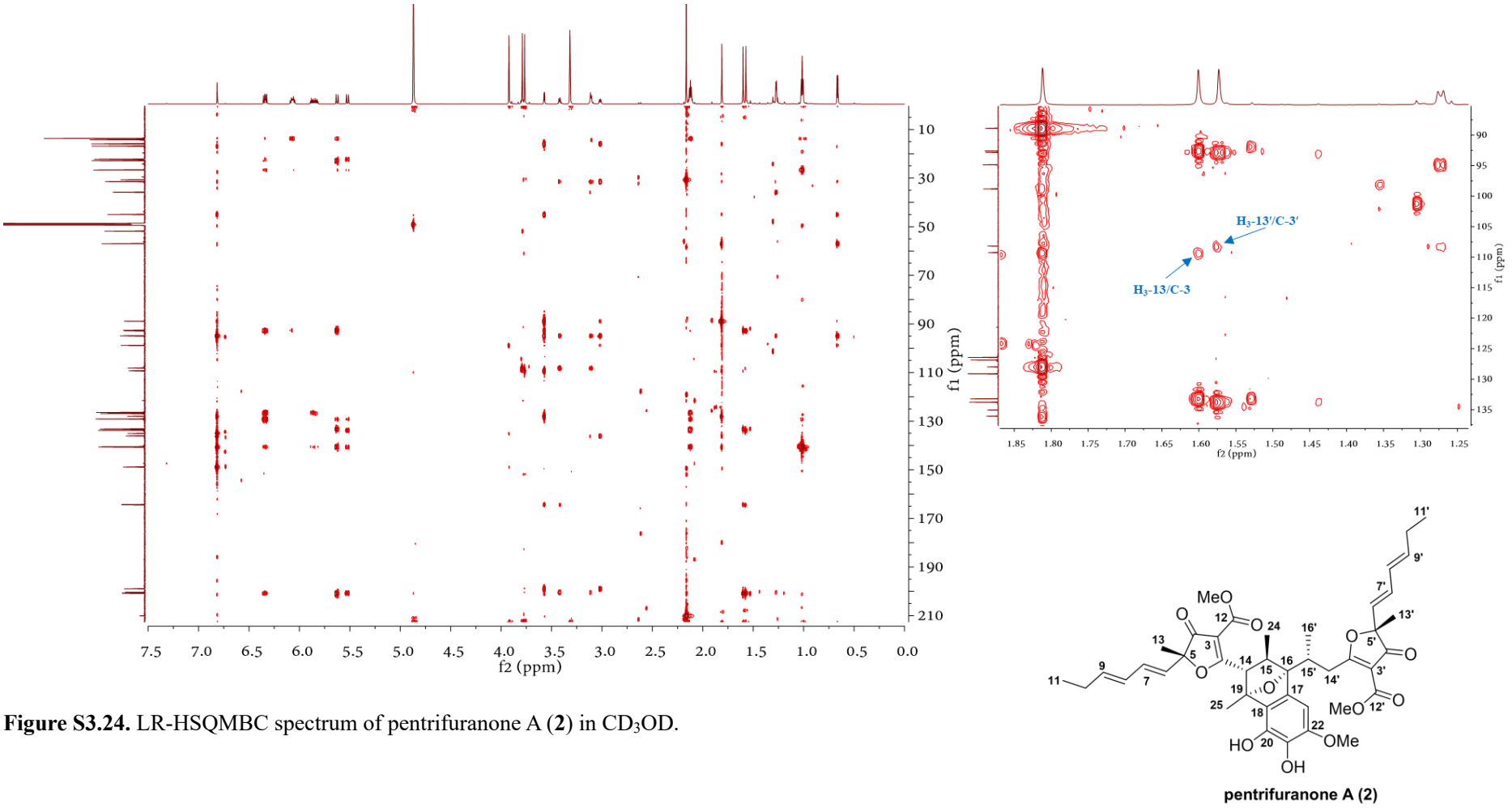


Figure S3.24. LR-HSQMBC spectrum of pentrifuranone A (**2**) in CD_3OD.

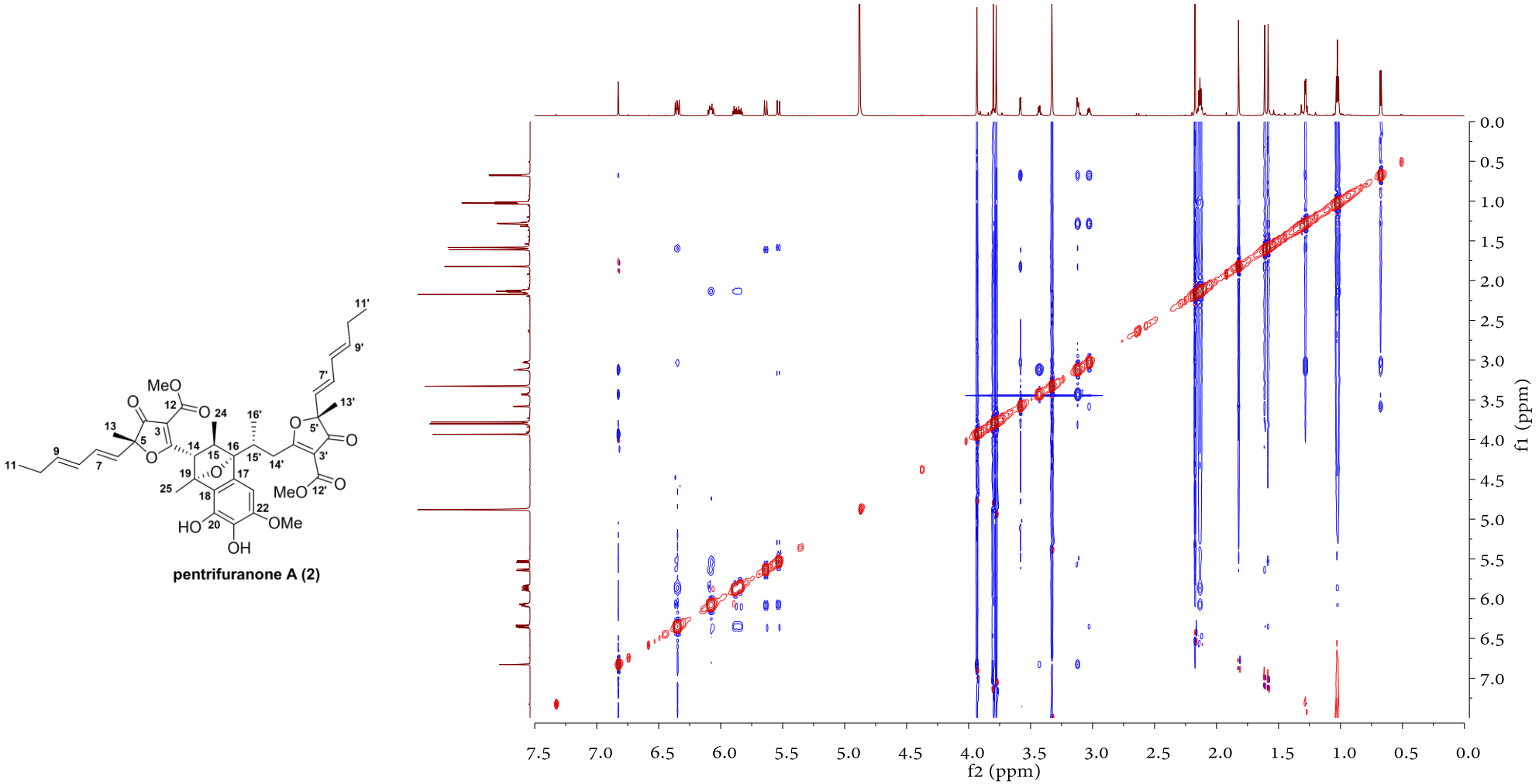


Figure S3.25. ROESY spectrum of pentrifuranone A (**2**) in CD_3OD.

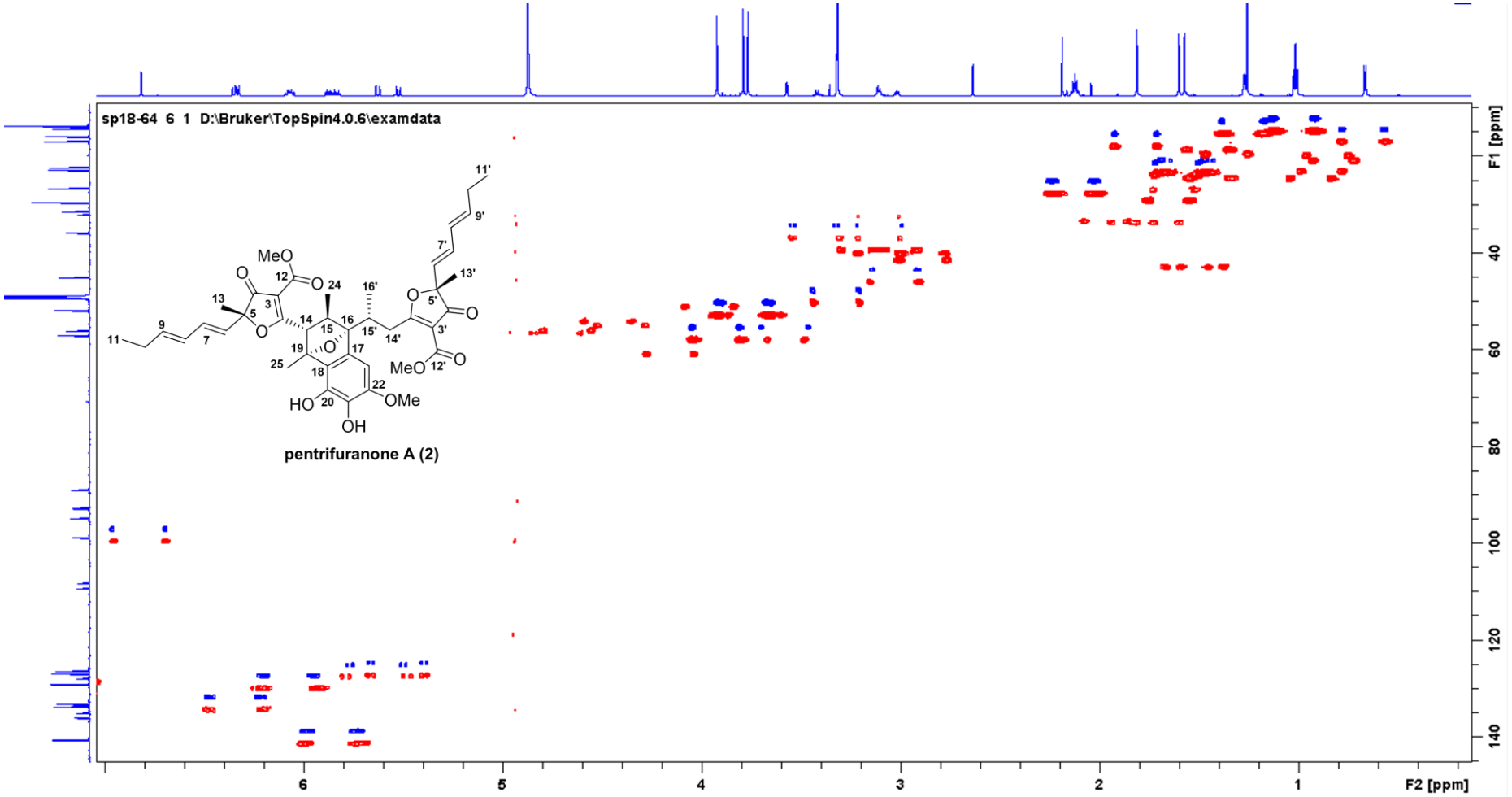
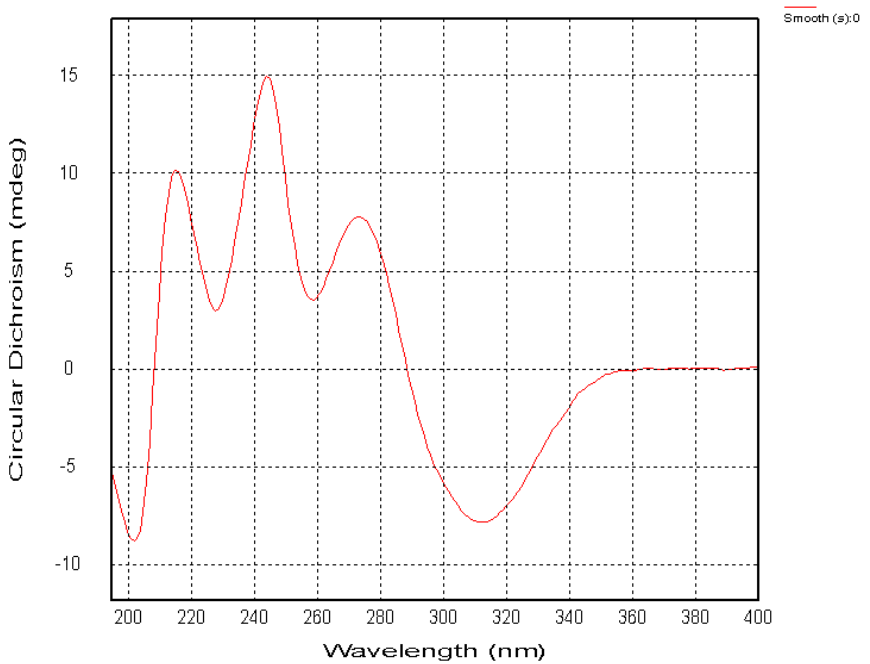


Figure S3.26. Clip-HSQC spectra in isotropic (blue) and anisotropic (red) conditions of pentrifuranone A (**2**) in CD_3OD.



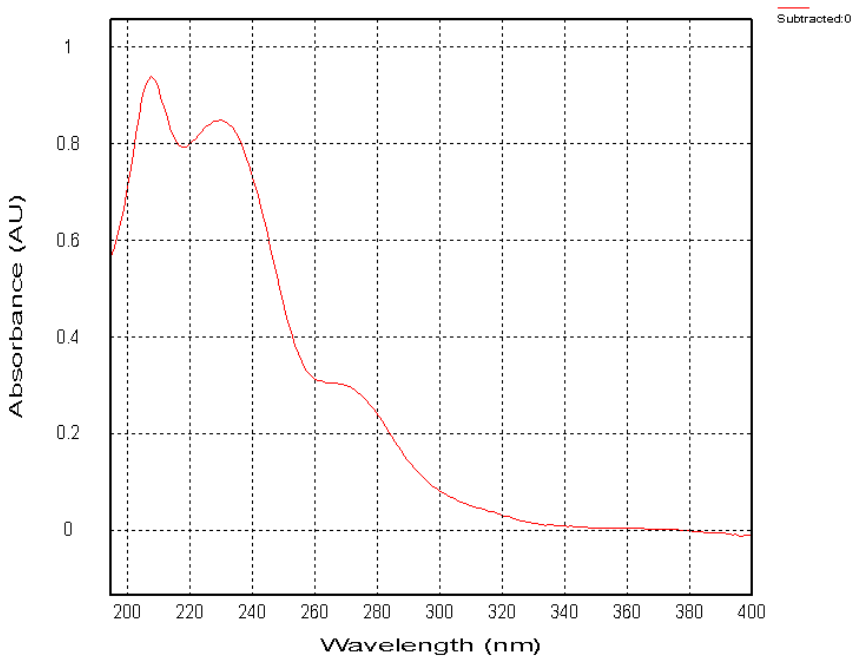
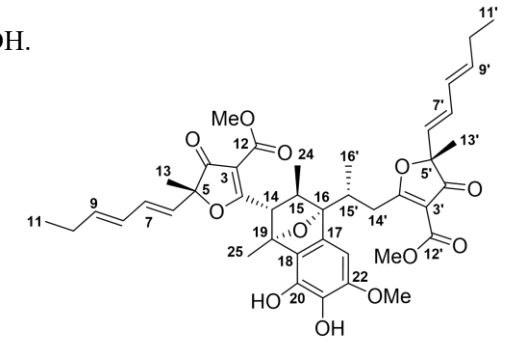


Figure S3.27. Circular dichroism (CD) spectrum and UV spectrum of pentrifuranone A (**2**) in MeOH.



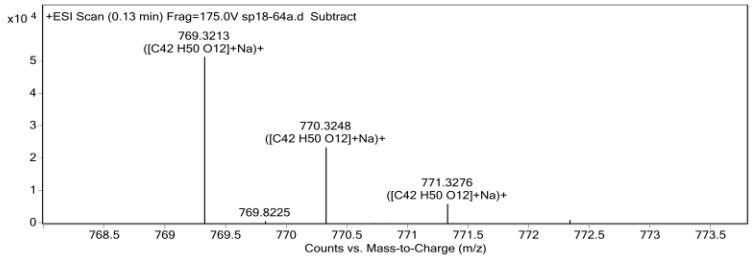
Qualitative Analysis Report

Data Filename	sp18-64a.d	**Sample Name**	sp18-64a
Sample Type	Sample	**Position**	P1-B8
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	3/20/2019 4:40:27 PM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

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

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

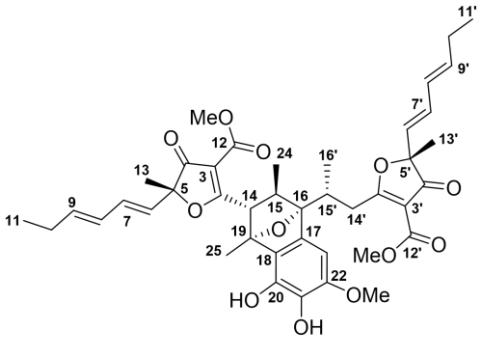


Peak List

m/z	z	Abund	Formula	Ion
221.0805	1	32919.37		
245.1175	1	7641.58		
299.1262	1	27163.46		
471.2026	1	8670.3		
565.2124	1	10440.33		
769.3213	1	51486.25	C42 H50 O12	(M+Na)+
770.3248	1	23667.18	C42 H50 O12	(M+Na)+
771.3276	1	6167.58	C42 H50 O12	(M+Na)+
785.2964	1	12749.9		
786.3009	1	4904.68		

Formula Calculator Element Limits

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



Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C42 H50 O12	746.3302	769.3194	769.3213	-1.90	-2.47	18.0000

--- End Of Report ---

Figure S3.28. HRESIMS spectrum of pentrifuranone A (**2**).

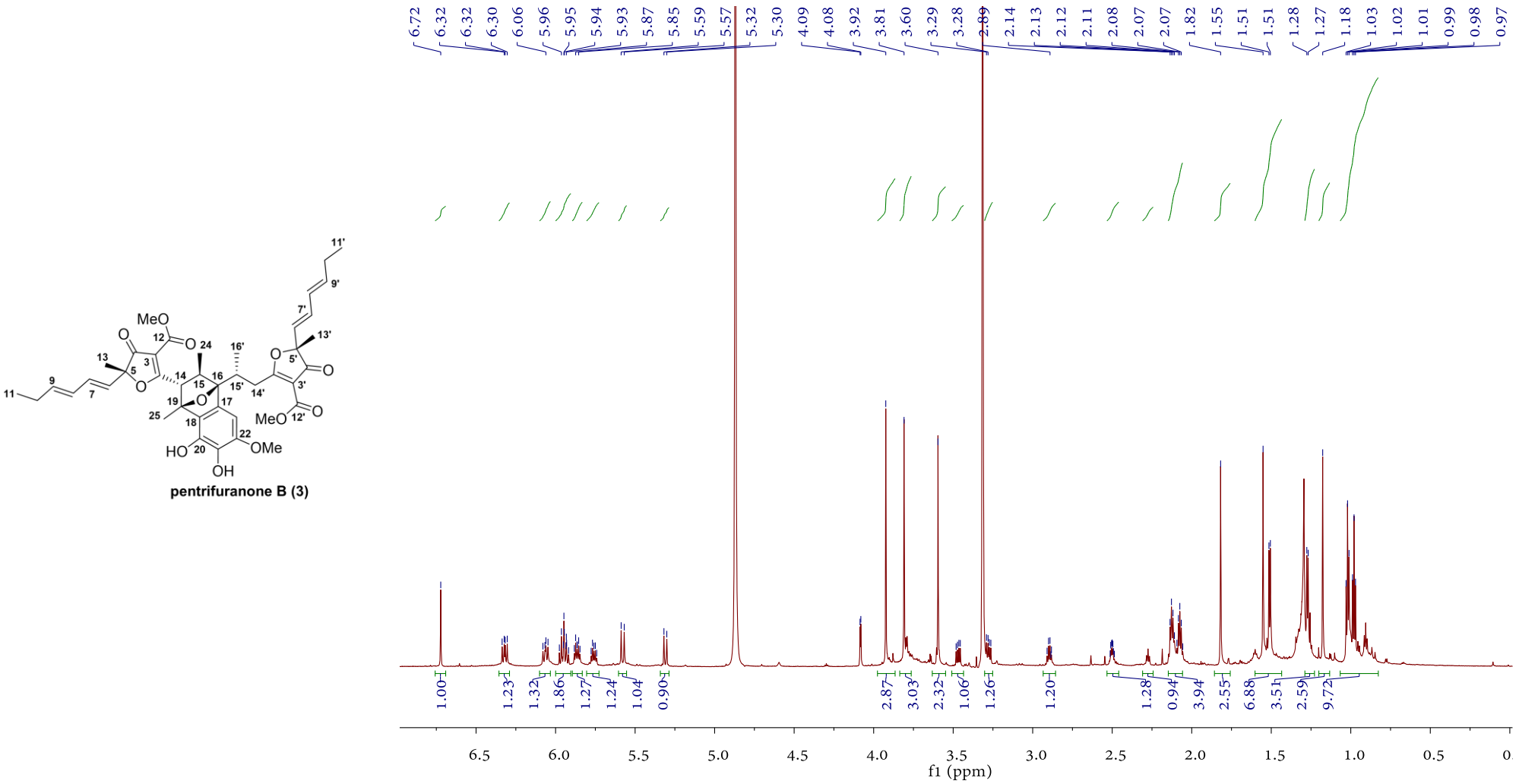
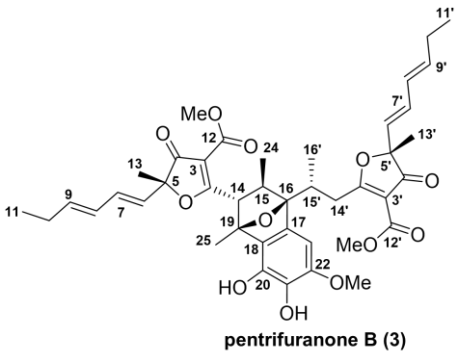


Figure S3.29. ^{1}H NMR of pentrifuranone B (**3**) in CD_3OD.



pentrifuranone B (3)

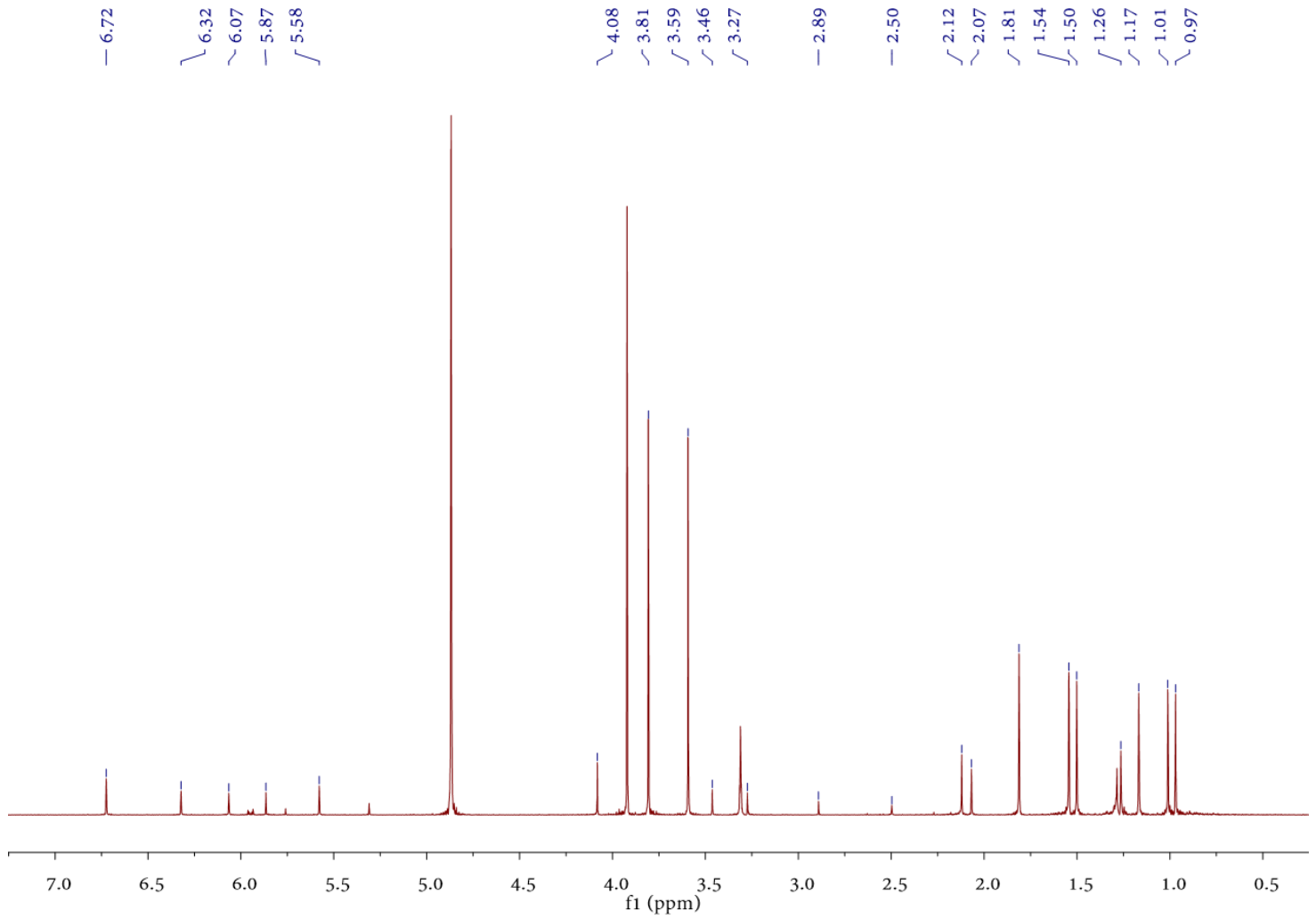


Figure S3.30. Pure shift ^{1}H NMR of pentrifuranone B (**3**) in CD_3OD.

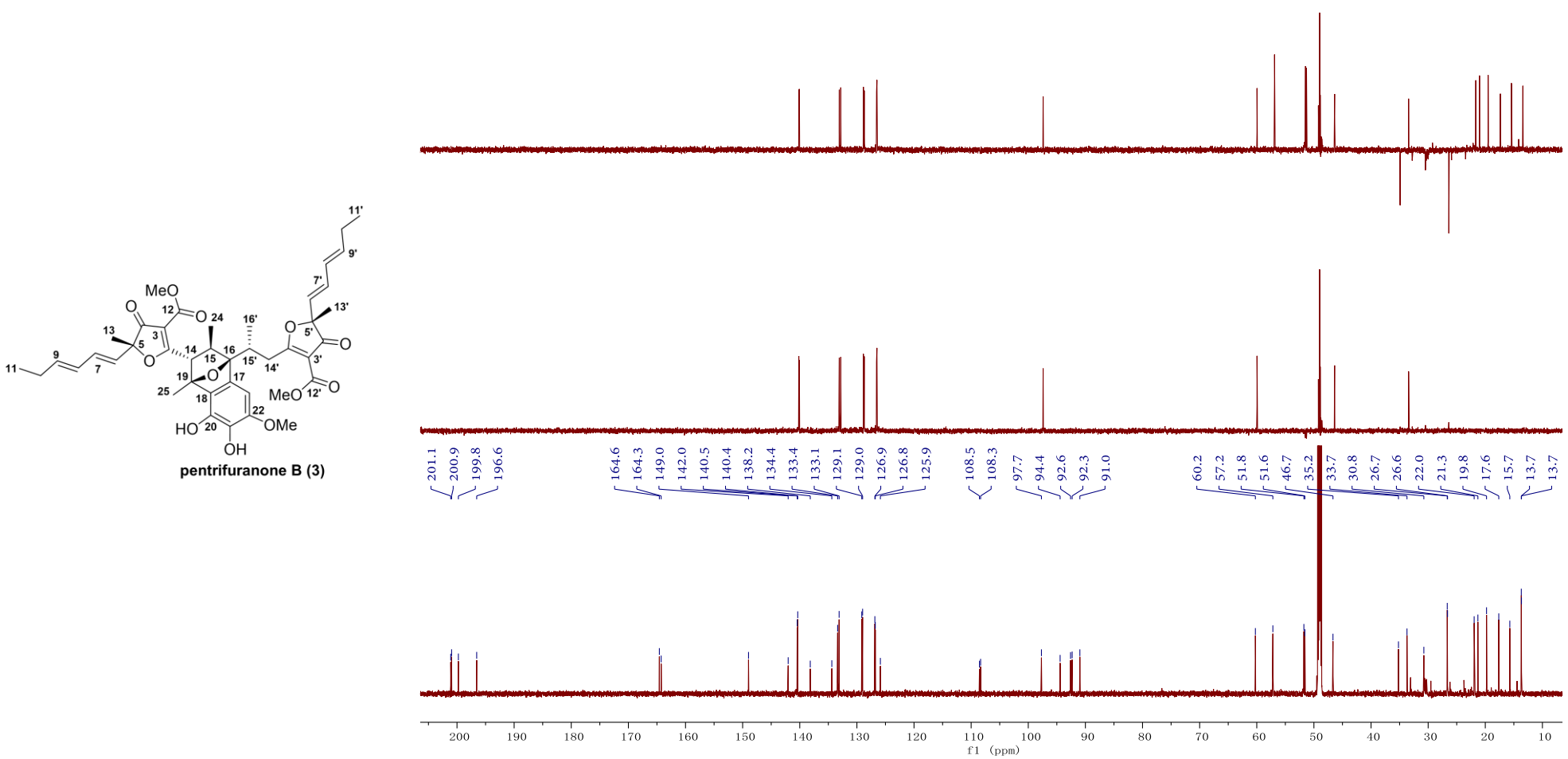


Figure S3.31. ^{13}C NMR, DEPT90, and DEPT135 of pentrifuranone B (**3**) in CD_3OD.

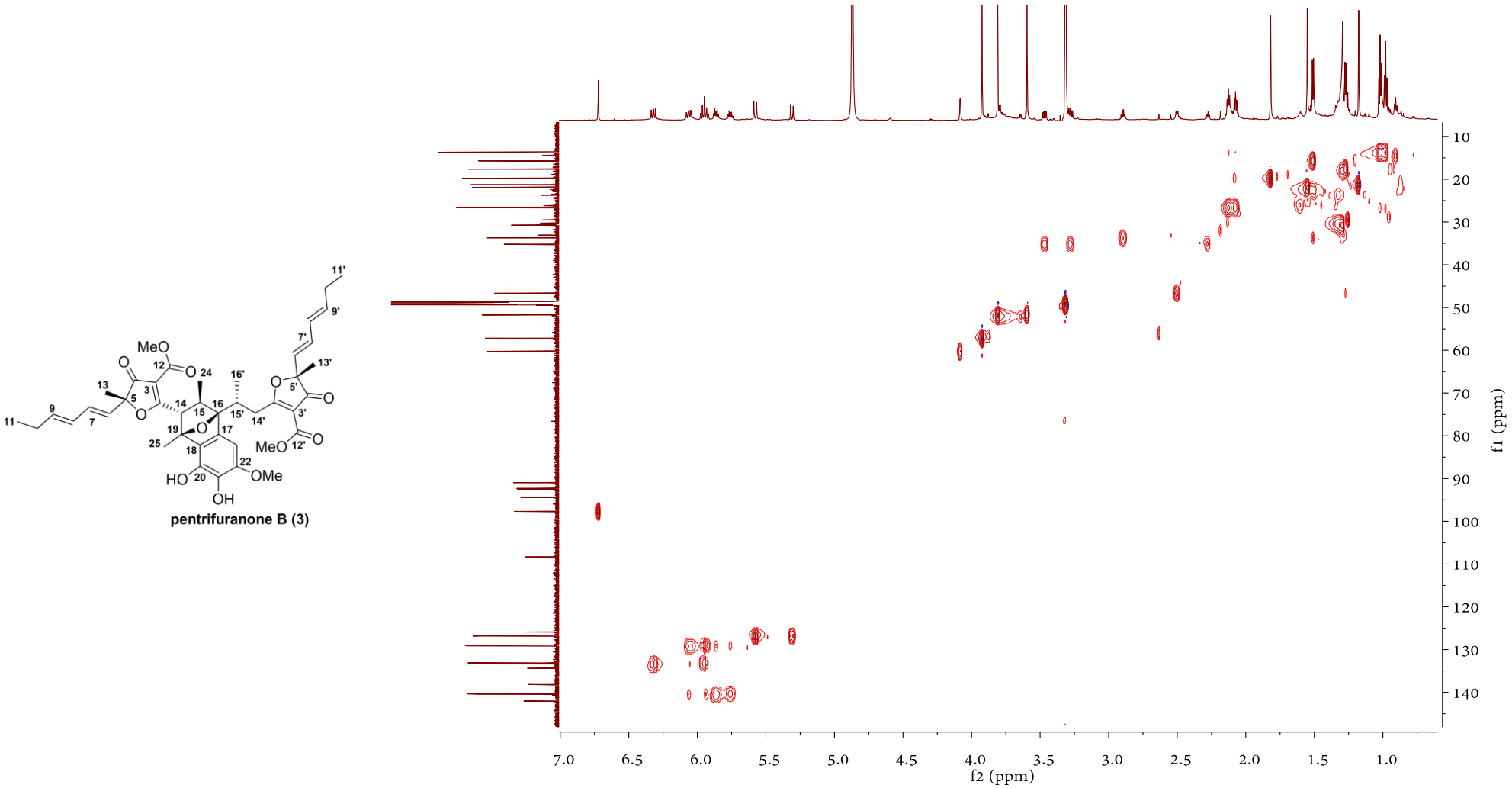


Figure S3.32. HSQC spectrum of pentrifuranone B (**3**) in CD_3OD.

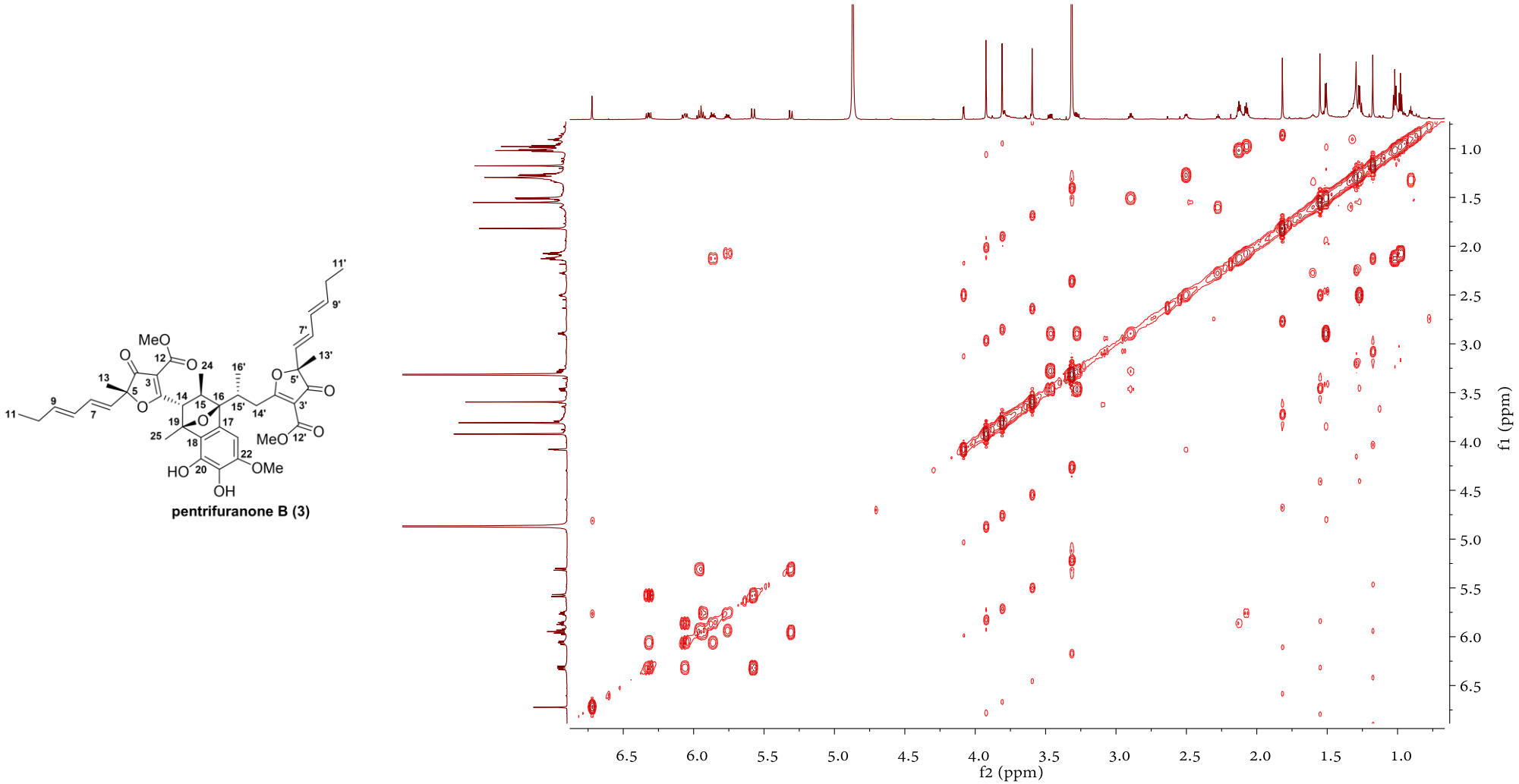


Figure S3.33. ^{1}H–^{1}H COSY spectrum of pentrifuranone B (**3**) in CD_3OD.

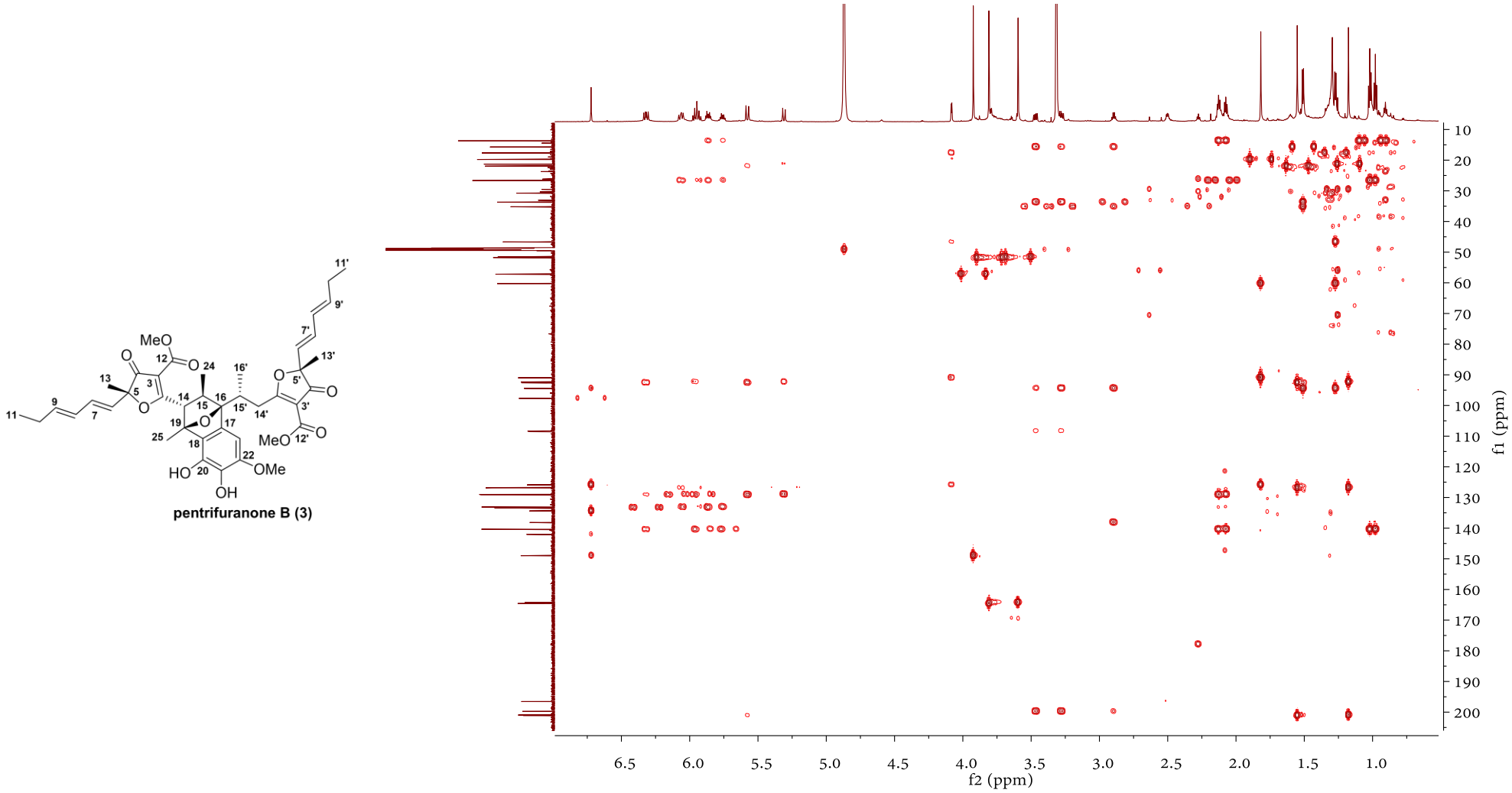


Figure S3.34. HMBC spectrum of pentrifuranone B (**3**) in CD_3OD.

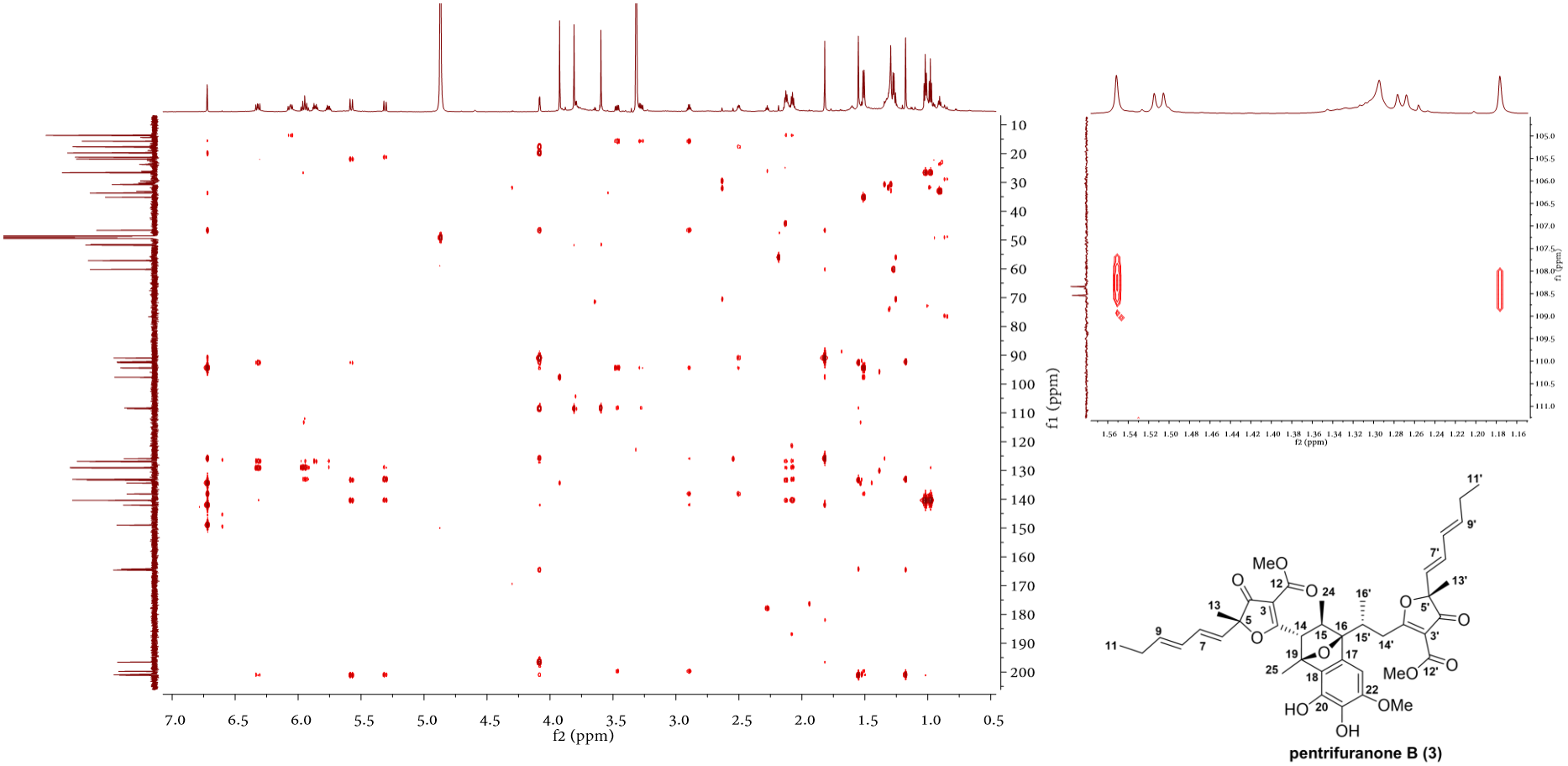


Figure S3.35. LR-HSQMBC spectrum of pentrifuranone B (**3**) in CD_3OD.

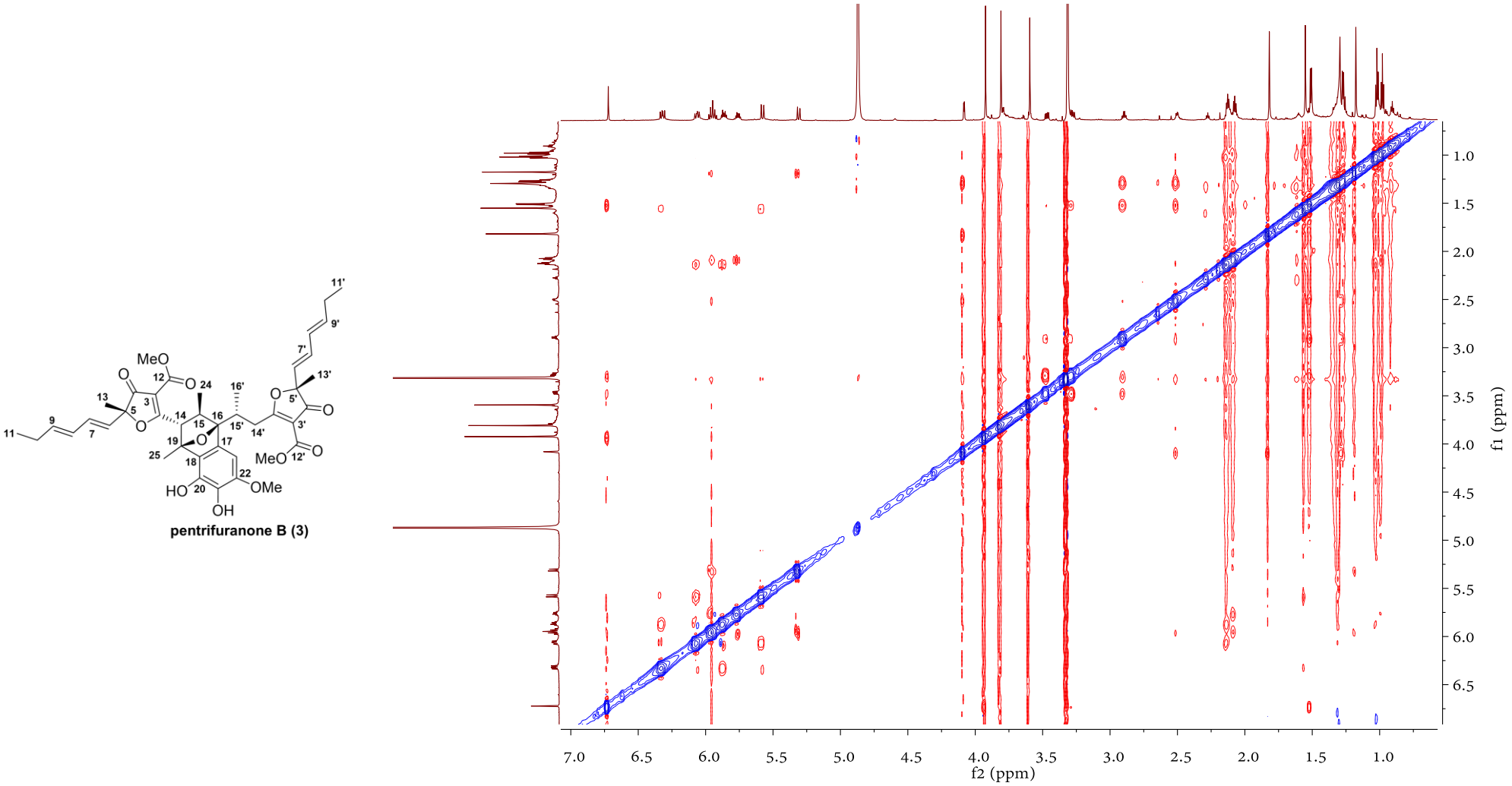


Figure S3.36. ROESY spectrum of pentrifuranone B (**3**) in CD_3OD.

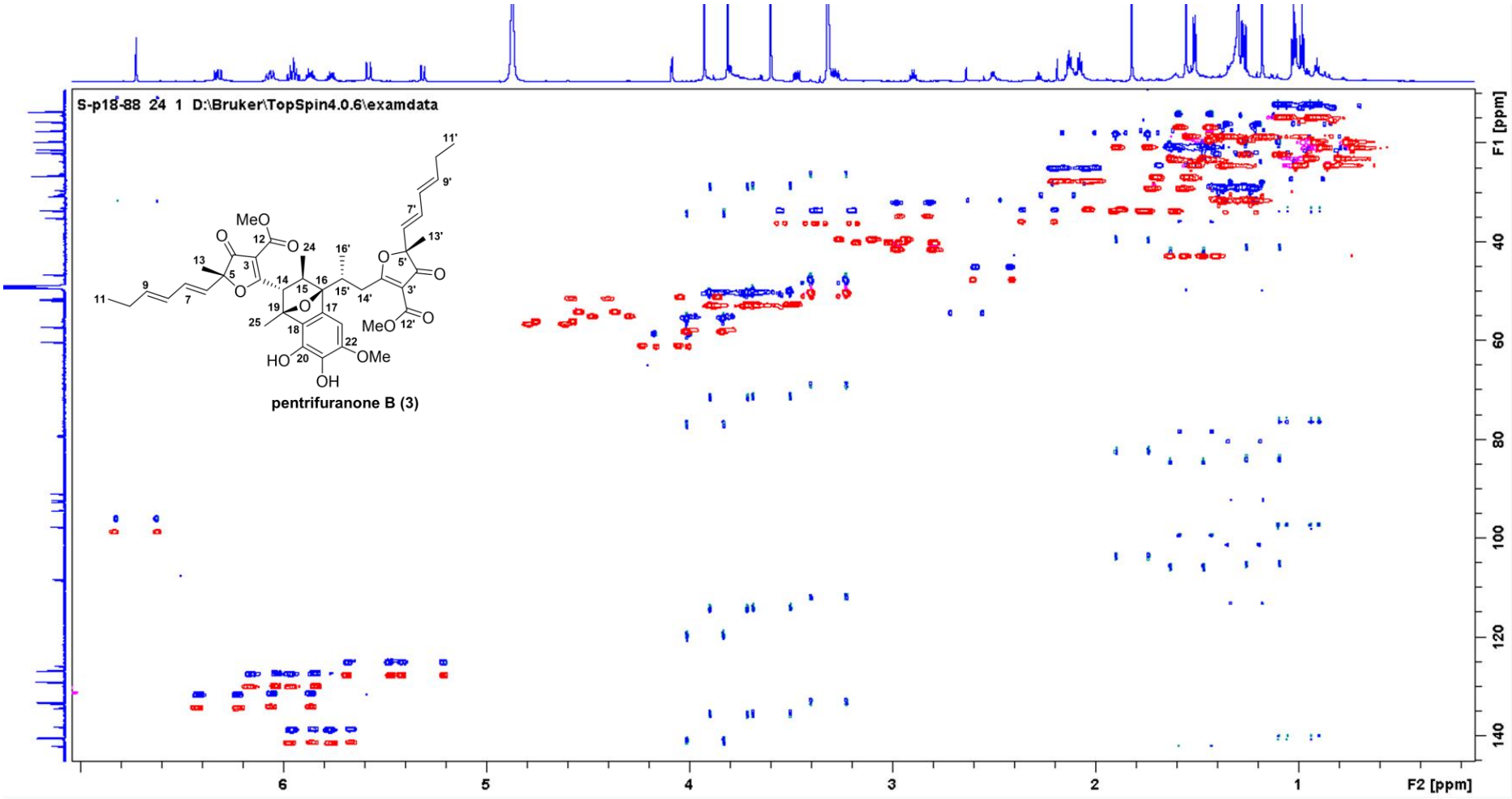


Figure S3.37. Clip-HSQC spectra in isotropic (blue) and anisotropic (red) conditions of pentrifuranone B (**3**) in CD_3OD.

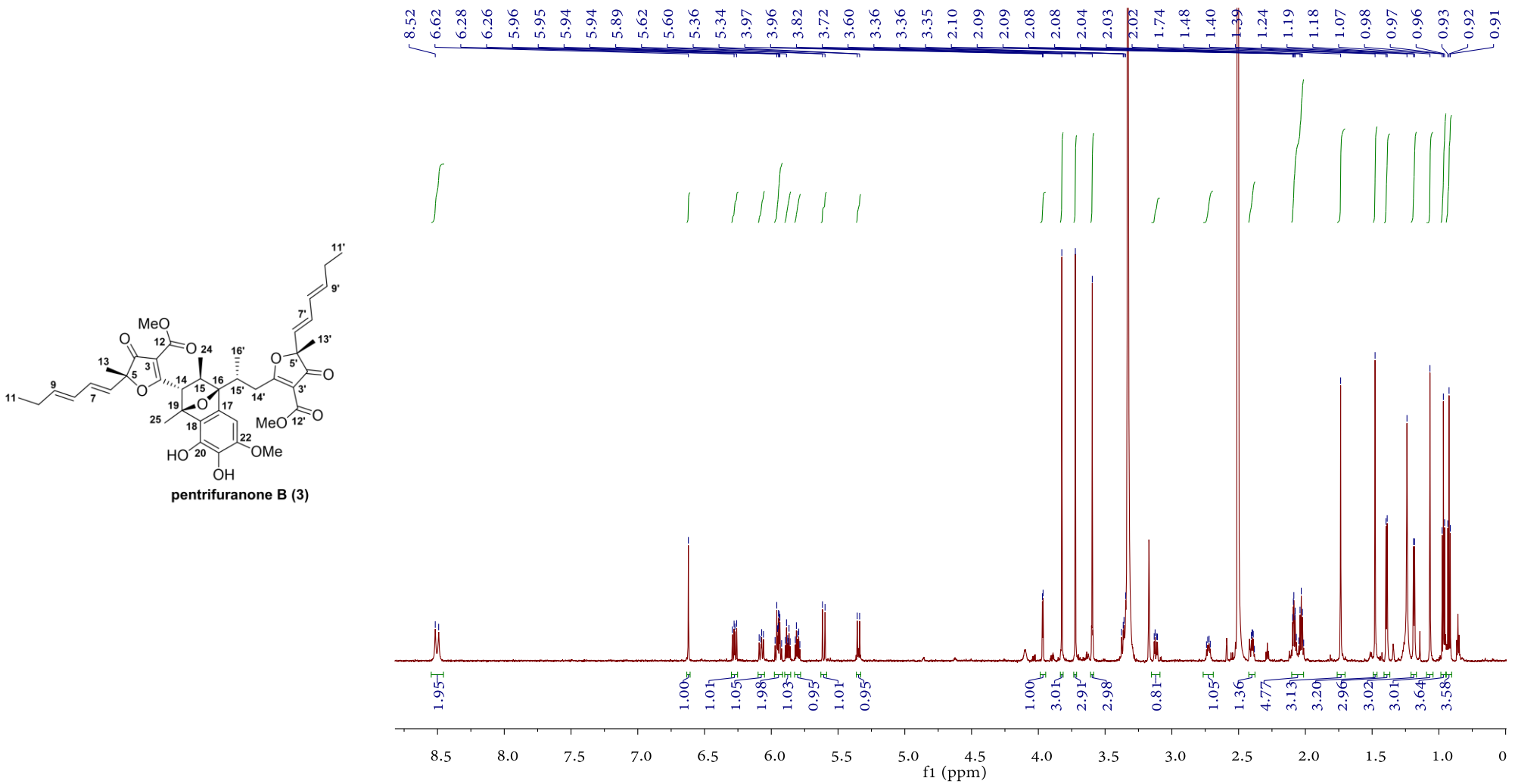


Figure S3.38. 1H NMR of pentrifuranone B (**3**) in DMSO-d_6.

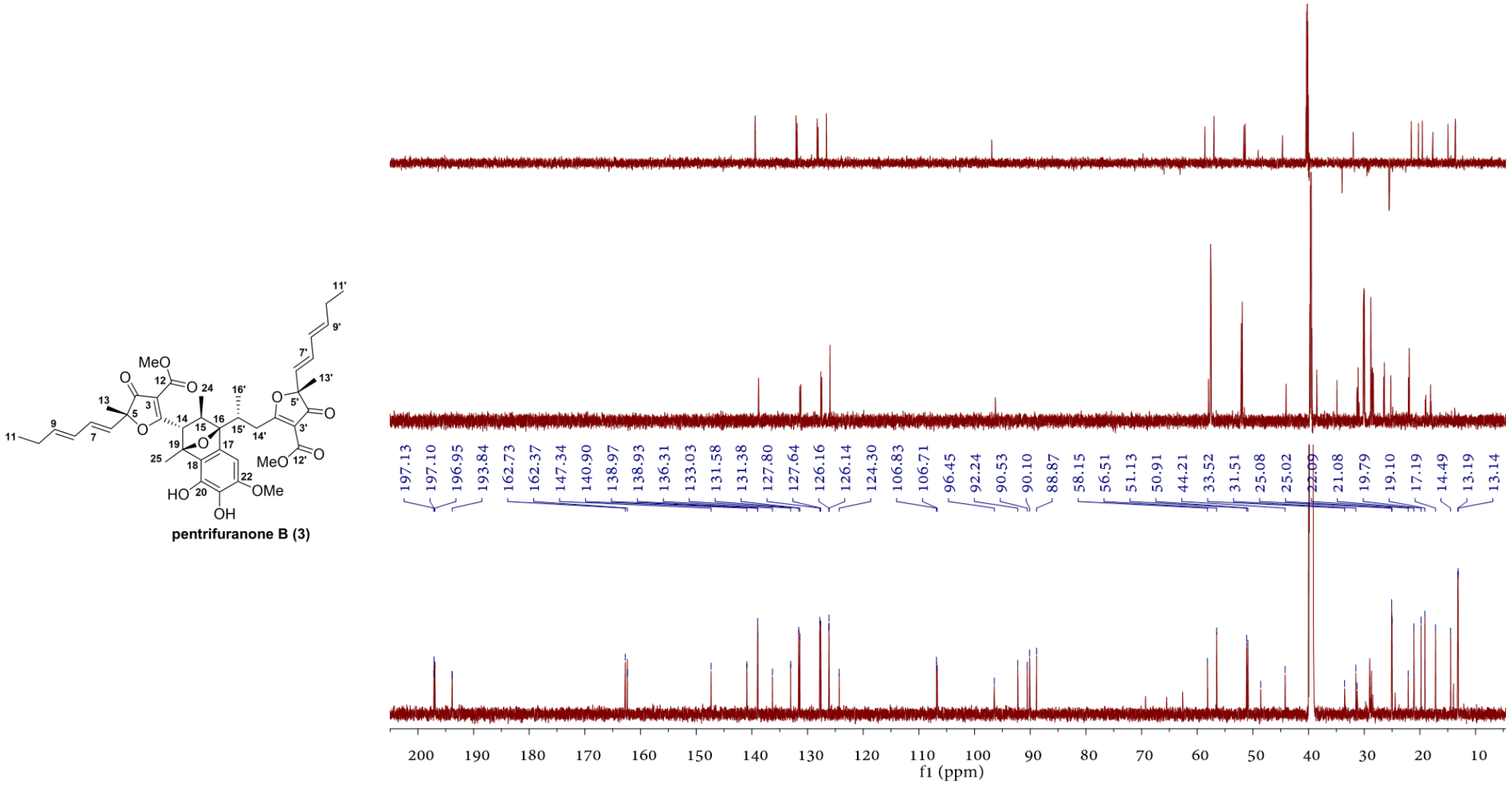


Figure S3.39. ^{13}C NMR, DEPT90, and DEPT135 of pentrifuranone B (**3**) in DMSO-d_6.

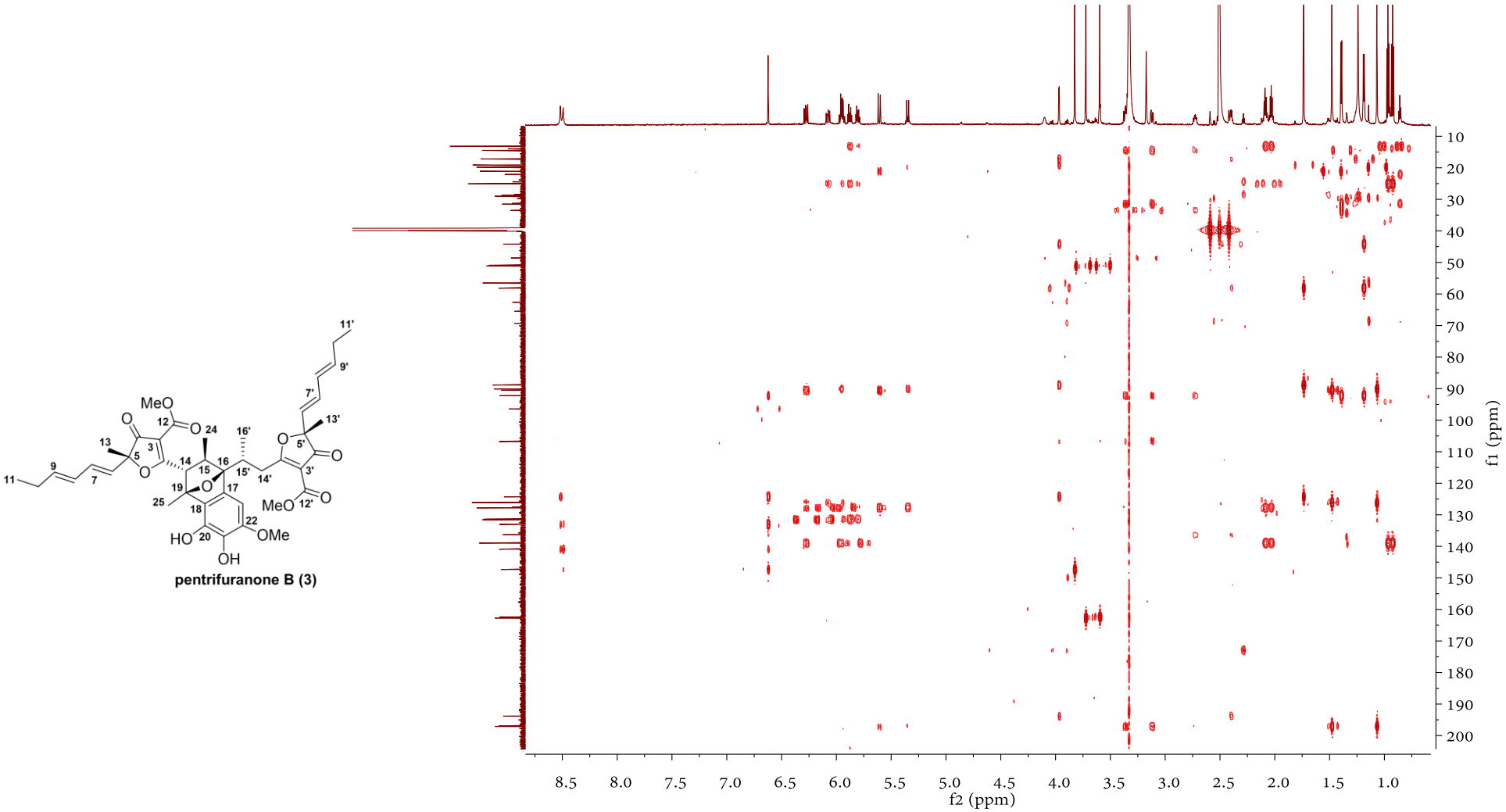


Figure S3.40. HMBC spectrum of pentrifuranone B (**3**) in DMSO-d_6.

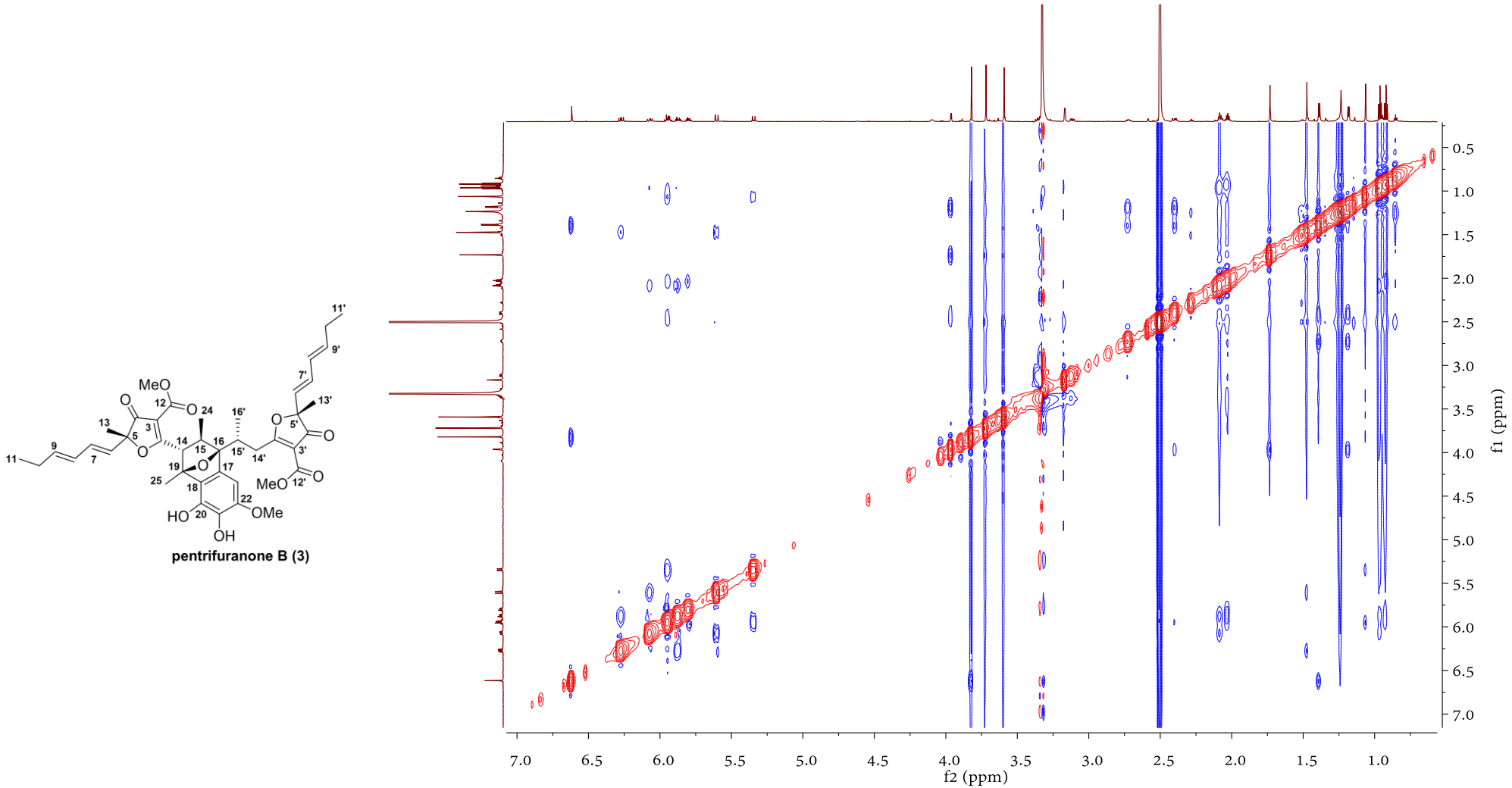


Figure S3.41. ROESY spectrum of pentrifuranone B (**3**) in DMSO-d_6.

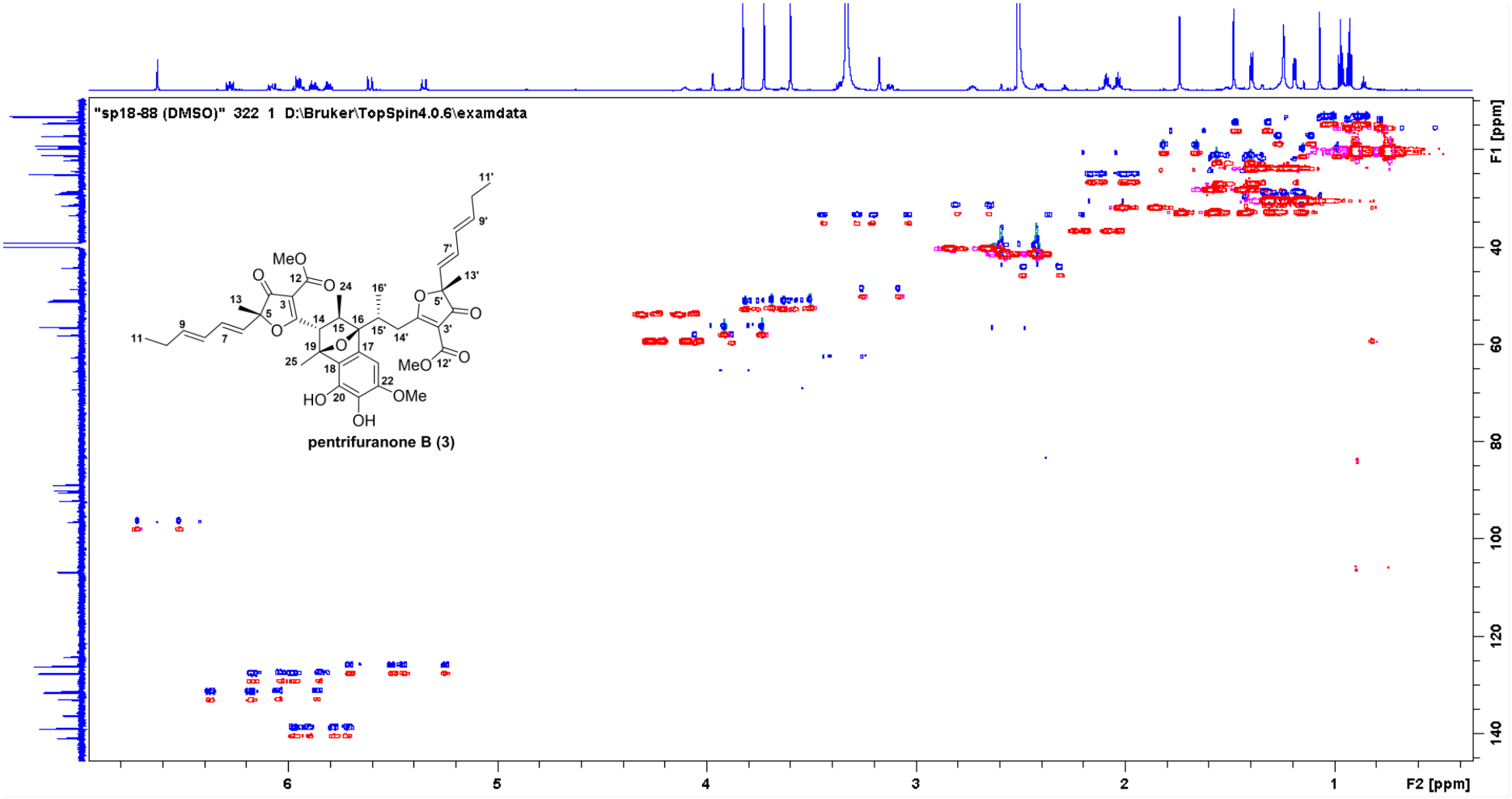
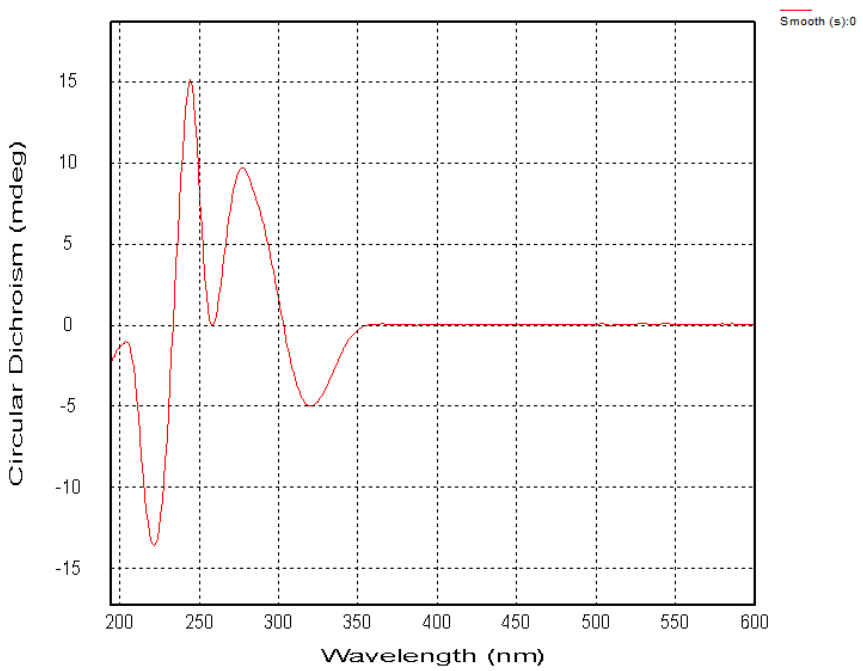


Figure S3.42. Clip-HSQC spectra in isotropic (blue) and anisotropic (red) conditions of pentrifuranone B (**3**) in DMSO-d_6.



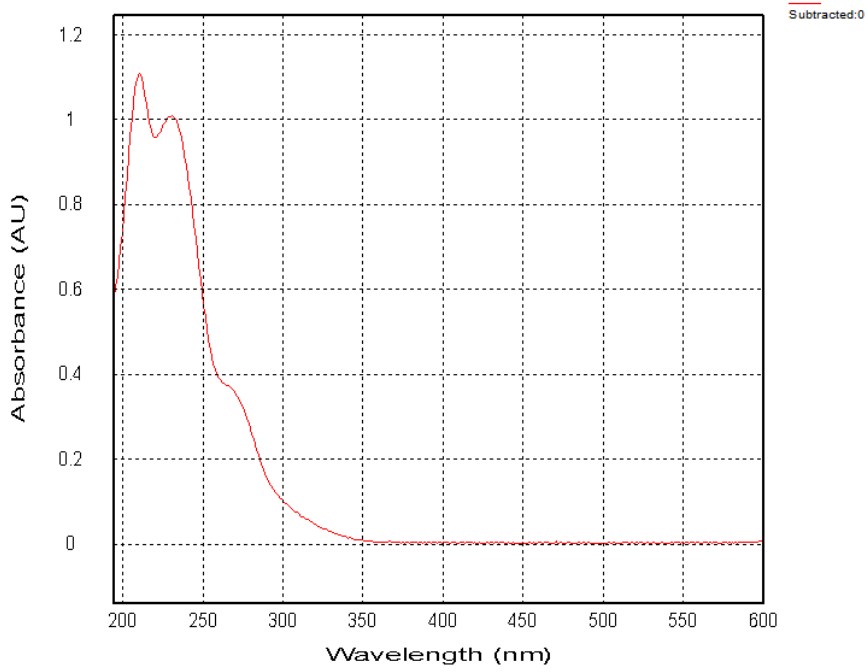
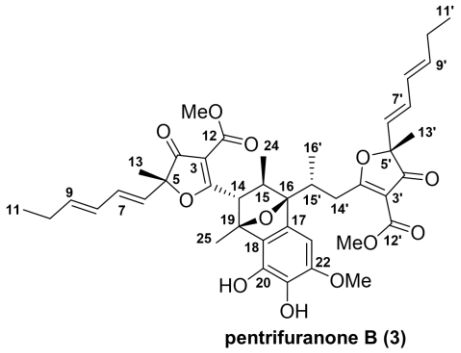


Figure S3.43. Circular dichroism (CD) spectrum and UV spectrum of pentrifuranone B (**3**) in MeOH.



Rudolph Research Analytical

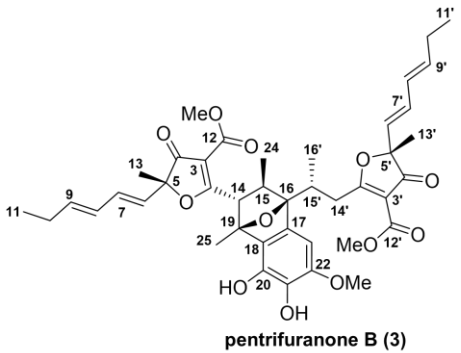
This sample was measured on an Autopol VI, Serial #91058
Manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

Measurement Date : Sunday, 26-SEP-2021

Set Temperature : OFF

Time Delay : Disabled

Delay between Measurement : Disabled



pentrifuranone B (3)

n	Average	Std.Dev.	% RSD	Maximum	Minimum
5	9.15	0.18	1.96	9.44	9.00

S.No	Sample ID	Time	Result	Scale	OR °Arc	WLG.nm	Lg.mm	Conc.g/100ml	Temp.
1	sp18-88	10:48:49 AM	9.11	SR	0.0082	589	100.00	0.090	25.2
2	sp18-88	10:48:57 AM	9.44	SR	0.0085	589	100.00	0.090	25.2
3	sp18-88	10:49:05 AM	9.22	SR	0.0083	589	100.00	0.090	25.2
4	sp18-88	10:49:14 AM	9.00	SR	0.0081	589	100.00	0.090	25.2
5	sp18-88	10:49:22 AM	9.00	SR	0.0081	589	100.00	0.090	25.2

Figure S3.44. Optical rotation of pentrifuranone B (**3**) in MeOH.

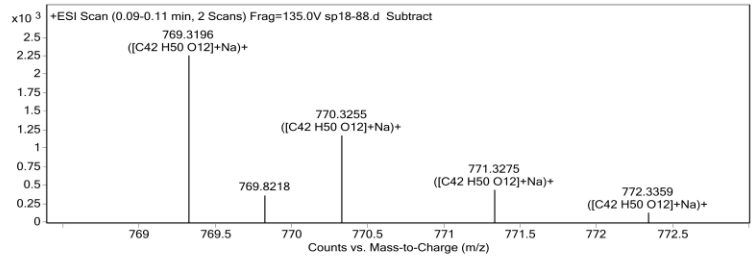
Qualitative Analysis Report

Data Filename	sp18-88.d	**Sample Name**	sp18-88
Sample Type	Sample	**Position**	P1-A2
Instrument Name	Instrument 1	**User Name**	
Acq Method	s.m	**Acquired Time**	10/17/2022 4:45:24 PM
IRM Calibration Status	Success	**DA Method**	PCDL.m
Comment			

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

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI

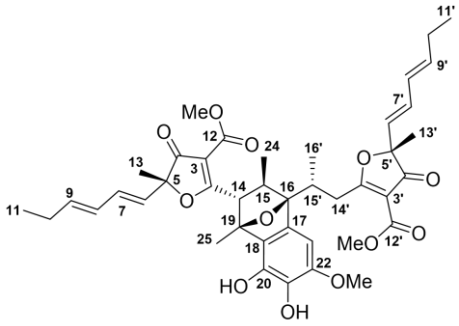


Peak List

m/z	z	Abund
346.2804	1	24973.32
346.6146	1	15175.44
518.9164	1	122814.29
519.4176	1	84589.9
519.9188	1	29158.68
1036.8261	1	115671.23
1037.8286	1	71414.46
1038.8303	1	23430.19
1058.8076	1	59475.55
1059.81	1	38056.43

Formula Calculator Element Limits

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



Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C42 H50 O12	746.3302	769.3194	769.3196	-0.20	-0.26	18.0000

--- End Of Report ---

Figure S3.45. HRESIMS spectrum of pentrifuranone B (**3**).

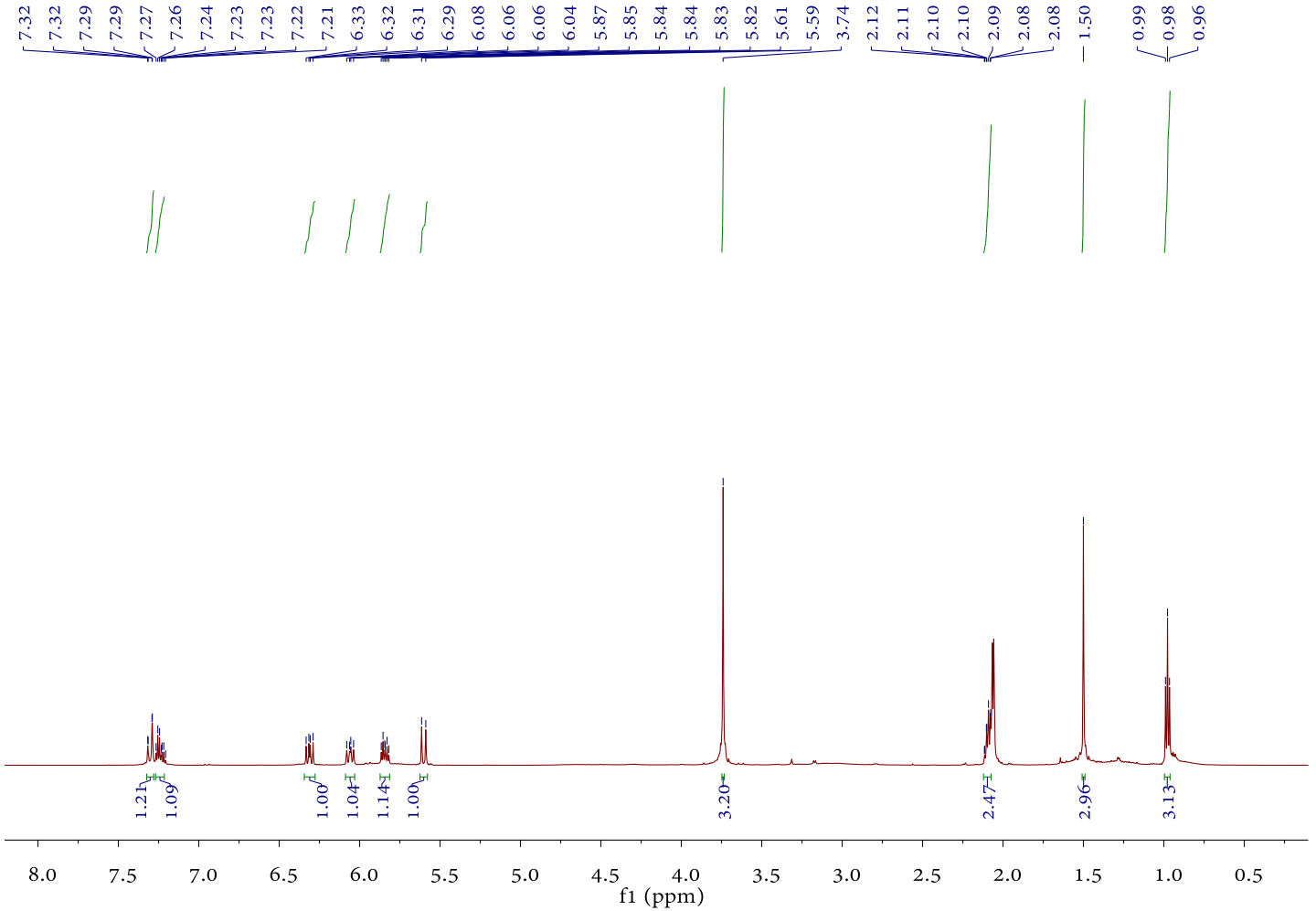


Figure S3.46. ^{1}H NMR of gregatin A in Acetone-d_6.

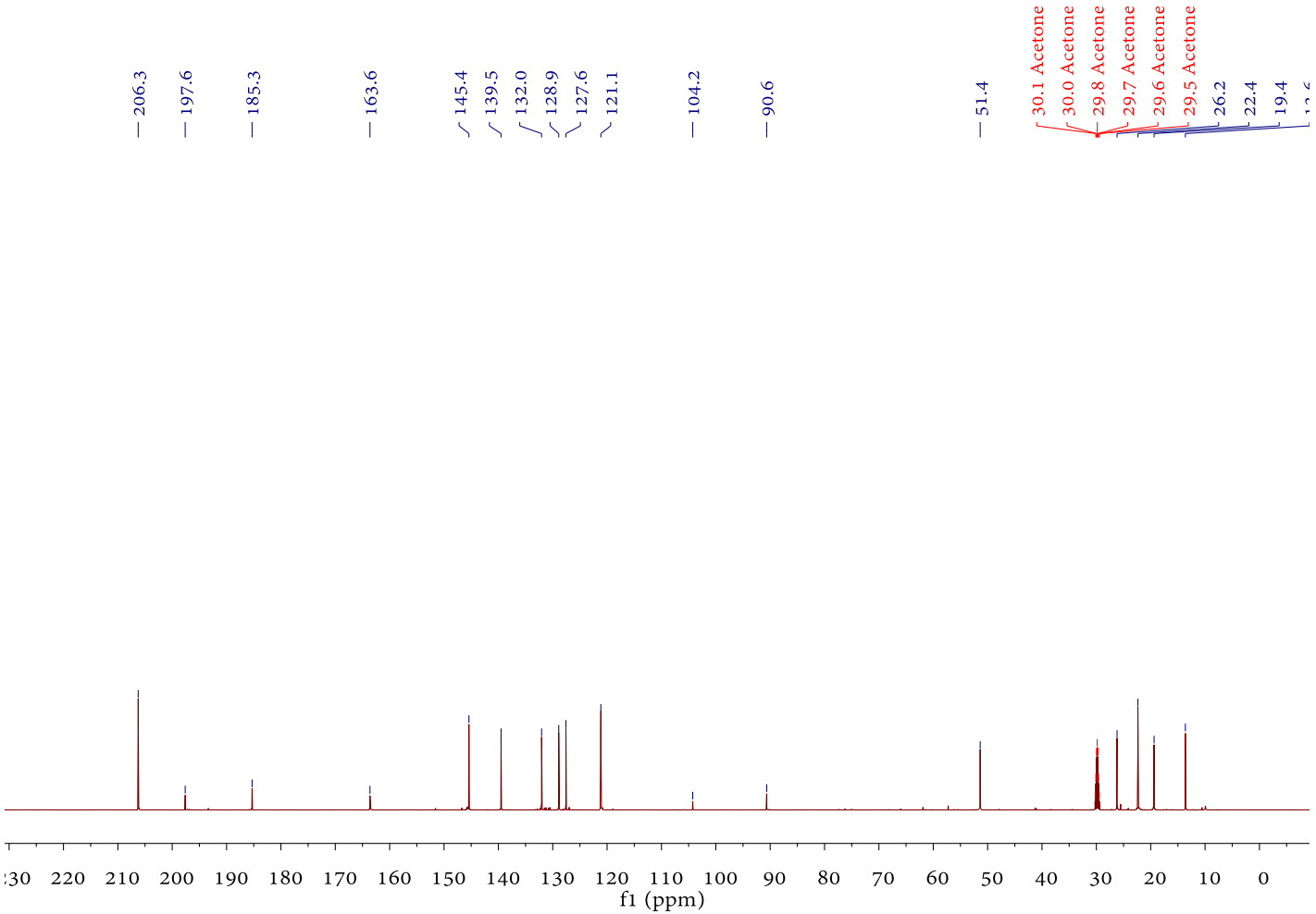


Figure S3.47. ^{13}C NMR of gregatin A in Acetone-d_6.

Optical rotation measurement

Model : P-1020 (A060460638)

No.	Sample	Mode	Data	Monitor Blank	Temp. Cell Temp Point	Date Comment Sample Name	Light Filter Operator	Cycle Time Integ Time
No.1	19 (1/3)	Sp.Rot	-186.8270	-0.3503 0.0000	26.3 50.00 Cell	Fri Aug 03 17:06:55 2018 0.00375g/mL MeOH SP18-52	Na 589nm	2 sec 2 sec
No.2	19 (2/3)	Sp.Rot	-185.4400	-0.3477 0.0000	26.3 50.00 Cell	Fri Aug 03 17:07:00 2018 0.00375g/mL MeOH SP18-52	Na 589nm	2 sec 2 sec
No.3	19 (3/3)	Sp.Rot	-184.5870	-0.3461 0.0000	26.3 50.00 Cell	Fri Aug 03 17:07:05 2018 0.00375g/mL MeOH SP18-52	Na 589nm	2 sec 2 sec

Figure S3.48. Optical rotation of gregatin A in MeOH.

Optical rotation measurement

Model : P-1020 (A060460638)

No.	Sample	Mode	Data	Monitor Blank	Temp. Cell Temp Point	Date Comment Sample Name	Light Filter Operator	Cycle Time Integ Time
No.1	7 (1/3)	Sp.Rot	-154.3000	-0.1543 0.0000	22.9 50.00 Cell	Fri Sep 28 20:44:23 2018 0.00199g/mL CHCl3 SP18-52	Na 589nm	2 sec 2 sec
No.2	7 (2/3)	Sp.Rot	-155.6000	-0.1556 0.0000	22.9 50.00 Cell	Fri Sep 28 20:44:28 2018 0.00199g/mL CHCl3 SP18-52	Na 589nm	2 sec 2 sec
No.3	7 (3/3)	Sp.Rot	-157.3000	-0.1573 0.0000	22.9 50.00 Cell	Fri Sep 28 20:44:34 2018 0.00199g/mL CHCl3 SP18-52	Na 589nm	2 sec 2 sec

Figure S3.49. Optical rotation of gregatin A in $CHCl_3$.

Part S4. Computational data of 1

Table S4.1. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1a** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **1a.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1a-1	-3455.505897	-3455.506994	-3455.581190	1.055196	-2167712.483213	0.000000	6.397E-01
1a-2	-3455.507443	-3455.509461	-3455.583335	1.057268	-2167711.950810	0.532402	2.603E-01
1a-3	-3455.501957	-3455.502765	-3455.578588	1.055047	-2167711.125139	1.358073	6.455E-02
1a-4	-3455.503766	-3455.503492	-3455.580291	1.059486	-2167710.087041	2.396172	1.118E-02
1a-5	-3455.501830	-3455.502295	-3455.577329	1.056140	-2167709.864335	2.618878	7.675E-03
1a-6	-3455.501313	-3455.502462	-3455.577695	1.056146	-2167709.661213	2.821999	5.446E-03
1a-7	-3455.500923	-3455.500926	-3455.576098	1.055777	-2167709.609984	2.873228	4.995E-03
1a-8	-3455.498482	-3455.500044	-3455.576110	1.054812	-2167709.244315	3.238898	2.693E-03
1a-9	-3455.508936	-3455.507498	-3455.577378	1.060051	-2167708.634862	3.848351	9.622E-04
1a-10	-3455.506970	-3455.506862	-3455.576848	1.058291	-2167708.572338	3.910875	8.658E-04
1a-11	-3455.497397	-3455.498639	-3455.574328	1.054435	-2167708.563810	3.919403	8.534E-04
1a-12	-3455.500048	-3455.501332	-3455.575320	1.055799	-2167708.303510	4.179702	5.498E-04
1a-13	-3455.506944	-3455.505866	-3455.575314	1.059661	-2167707.359123	5.124090	1.116E-04
1a-14	-3455.509865	-3455.510398	-3455.577270	1.061643	-2167706.331090	6.152123	1.966E-05
1a-15	-3455.505478	-3455.506359	-3455.573605	1.058145	-2167706.008843	6.474369	1.141E-05
1a-16	-3455.507761	-3455.508248	-3455.575043	1.060011	-2167705.986900	6.496313	1.099E-05
1a-17	-3455.498160	-3455.501628	-3455.572021	1.054116	-2167705.918785	6.564428	9.797E-06
1a-18	-3455.498151	-3455.501625	-3455.572014	1.054117	-2167705.911010	6.572203	9.669E-06
1a-19	-3455.505524	-3455.507517	-3455.576258	1.060605	-2167705.431719	7.051494	4.303E-06
1a-20	-3455.499441	-3455.502692	-3455.571972	1.055122	-2167705.393580	7.089633	4.035E-06
1a-21	-3455.505615	-3455.506823	-3455.573847	1.059075	-2167705.371291	7.111922	3.886E-06
1a-22	-3455.499741	-3455.500552	-3455.570821	1.056663	-2167705.235173	7.248039	3.088E-06
1a-23	-3455.504069	-3455.505429	-3455.574408	1.059891	-2167705.115578	7.367634	2.523E-06
1a-24	-3455.505903	-3455.507637	-3455.576511	1.061700	-2167705.065956	7.417257	2.320E-06
1a-25	-3455.505281	-3455.506428	-3455.575651	1.061473	-2167705.037103	7.446110	2.210E-06
1a-26	-3455.506364	-3455.507437	-3455.574862	1.060991	-2167704.890651	7.592562	1.726E-06
1a-27	-3455.502164	-3455.504029	-3455.573507	1.059034	-2167704.771476	7.711737	1.411E-06
1a-28	-3455.505272	-3455.506936	-3455.575801	1.062226	-2167704.334196	8.149016	6.742E-07
1a-29	-3455.495747	-3455.497470	-3455.568594	1.055111	-2167704.239306	8.243907	5.744E-07
1a-30	-3455.497852	-3455.500886	-3455.570229	1.055679	-2167704.086466	8.396747	4.437E-07
1a-31	-3455.496087	-3455.496652	-3455.567947	1.055933	-2167704.043676	8.439536	4.128E-07
1a-32	-3455.498734	-3455.500791	-3455.570898	1.057525	-2167703.960884	8.522329	3.589E-07
1a-33	-3455.502609	-3455.504827	-3455.573101	1.059597	-2167703.942241	8.540972	3.478E-07
1a-34	-3455.498738	-3455.500795	-3455.570906	1.057566	-2167703.939944	8.543268	3.464E-07
1a-35	-3455.495352	-3455.496896	-3455.568289	1.055482	-2167703.927796	8.555417	3.394E-07

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1a-36	-3455.492087	-3455.493120	-3455.565153	1.053182	-2167703.723382	8.759831	2.403E-07
1a-37	-3455.503237	-3455.505298	-3455.572504	1.059813	-2167703.530112	8.953101	1.734E-07
1a-38	-3455.493274	-3455.494342	-3455.566255	1.054716	-2167703.430477	9.052735	1.465E-07
1a-39	-3455.494038	-3455.496141	-3455.564826	1.052514	-2167703.265784	9.217429	1.110E-07
1a-40	-3455.493436	-3455.496153	-3455.567396	1.054497	-2167703.248898	9.234315	1.078E-07
1a-41	-3455.495208	-3455.497595	-3455.568876	1.056745	-2167702.974435	9.508777	6.783E-08
1a-42	-3455.497698	-3455.499444	-3455.568427	1.057181	-2167702.821212	9.662000	5.237E-08
1a-43	-3455.497407	-3455.497366	-3455.567319	1.058018	-2167702.721867	9.761346	4.428E-08
1a-44	-3455.494857	-3455.496348	-3455.566149	1.055557	-2167702.571122	9.912090	3.432E-08
1a-45	-3455.493255	-3455.496198	-3455.567192	1.055303	-2167702.473490	10.009723	2.911E-08
1a-46	-3455.494693	-3455.496345	-3455.569247	1.058759	-2167702.404609	10.078604	2.591E-08
1a-47	-3455.495850	-3455.498555	-3455.568894	1.057886	-2167702.070384	10.412829	1.473E-08
1a-48	-3455.486633	-3455.490239	-3455.563114	1.051270	-2167702.028931	10.454282	1.374E-08
1a-49	-3455.497222	-3455.497411	-3455.567032	1.058730	-2167701.950970	10.532242	1.204E-08
1a-50	-3455.496026	-3455.495911	-3455.565637	1.057679	-2167701.924929	10.558284	1.152E-08
1a-51	-3455.490611	-3455.493423	-3455.564393	1.053571	-2167701.885930	10.597283	1.079E-08
1a-52	-3455.494338	-3455.496340	-3455.565876	1.055981	-2167701.812544	10.670669	9.532E-09
1a-53	-3455.494890	-3455.498327	-3455.567963	1.056801	-2167701.707212	10.776001	7.979E-09
1a-54	-3455.492320	-3455.495786	-3455.567199	1.056034	-2167701.691261	10.791952	7.767E-09
1a-55	-3455.494888	-3455.498330	-3455.567979	1.056844	-2167701.687314	10.795899	7.715E-09
1a-56	-3455.487555	-3455.490875	-3455.562990	1.052038	-2167701.648823	10.834390	7.230E-09
1a-57	-3455.490822	-3455.494028	-3455.563849	1.053061	-2167701.617561	10.865652	6.858E-09
1a-58	-3455.493369	-3455.494496	-3455.565312	1.056668	-2167701.576597	10.906615	6.399E-09
1a-59	-3455.499124	-3455.501712	-3455.570145	1.060076	-2167701.553826	10.929387	6.158E-09
1a-60	-3455.492200	-3455.494718	-3455.564257	1.054489	-2167701.409538	11.073674	4.826E-09
1a-61	-3455.492209	-3455.494721	-3455.564264	1.054508	-2167701.405635	11.077578	4.794E-09
1a-62	-3455.492208	-3455.494720	-3455.564261	1.054520	-2167701.396009	11.087203	4.717E-09
1a-63	-3455.492208	-3455.494720	-3455.564260	1.054535	-2167701.386377	11.096835	4.641E-09
1a-64	-3455.490975	-3455.493678	-3455.563582	1.054018	-2167701.165510	11.317703	3.196E-09
1a-65	-3455.495482	-3455.497632	-3455.565691	1.056723	-2167701.138326	11.344886	3.053E-09
1a-66	-3455.492896	-3455.495463	-3455.565270	1.056377	-2167700.829766	11.653447	1.813E-09
1a-67	-3455.491312	-3455.494104	-3455.563569	1.054580	-2167700.748461	11.734752	1.580E-09
1a-68	-3455.491851	-3455.495818	-3455.566049	1.056246	-2167700.522159	11.961054	1.078E-09
1a-69	-3455.491849	-3455.495818	-3455.566051	1.056249	-2167700.520239	11.962974	1.075E-09
1a-70	-3455.493656	-3455.497445	-3455.566800	1.057206	-2167700.502525	11.980688	1.043E-09
1a-71	-3455.489356	-3455.493054	-3455.563989	1.054509	-2167700.488236	11.994976	1.018E-09
1a-72	-3455.494595	-3455.496036	-3455.564165	1.057100	-2167700.388884	12.094328	8.609E-10
1a-73	-3455.488929	-3455.493692	-3455.565860	1.055727	-2167700.229970	12.253243	6.583E-10
1a-74	-3455.495409	-3455.497294	-3455.565353	1.058139	-2167700.204562	12.278650	6.306E-10

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1a-75	-3455.491272	-3455.494495	-3455.565031	1.056568	-2167700.147849	12.335364	5.730E-10
1a-76	-3455.487887	-3455.491089	-3455.561959	1.053528	-2167700.141078	12.342134	5.665E-10
1a-77	-3455.493878	-3455.496105	-3455.563871	1.056773	-2167699.916327	12.566886	3.876E-10
1a-78	-3455.493884	-3455.498294	-3455.565852	1.057078	-2167699.597914	12.885298	2.264E-10
1a-79	-3455.491126	-3455.493770	-3455.562779	1.056484	-2167699.150877	13.332336	1.064E-10
1a-80	-3455.491733	-3455.495322	-3455.564333	1.057438	-2167698.934929	13.548283	7.388E-11
1a-81	-3455.491730	-3455.495320	-3455.564331	1.057439	-2167698.932080	13.551132	7.352E-11

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at B3LYP/6-31G(d) level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S4.2. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1b** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **1b.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1b-1	-3455.512636	-3455.513457	-3455.586820	1.060232	-2167713.029000	0.000000	3.759E-01
1b-2	-3455.510888	-3455.512568	-3455.586494	1.059660	-2167712.644000	0.385454	1.960E-01
1b-3	-3455.503893	-3455.504482	-3455.581181	1.055539	-2167712.581000	0.448104	1.763E-01
1b-4	-3455.509152	-3455.508963	-3455.582314	1.057515	-2167712.540000	0.489130	1.645E-01
1b-5	-3455.501648	-3455.502578	-3455.579262	1.054919	-2167711.552000	1.477813	3.098E-02
1b-6	-3455.508409	-3455.509941	-3455.581386	1.057093	-2167711.142000	1.887238	1.552E-02
1b-7	-3455.507298	-3455.508677	-3455.580228	1.056208	-2167711.067000	1.962305	1.367E-02
1b-8	-3455.507721	-3455.509751	-3455.580939	1.056677	-2167710.811000	2.218300	8.871E-03
1b-9	-3455.503496	-3455.502936	-3455.577698	1.056153	-2167710.731000	2.298614	7.745E-03
1b-10	-3455.503150	-3455.506048	-3455.575785	1.051820	-2167710.079000	2.950518	2.576E-03
1b-11	-3455.507652	-3455.508376	-3455.578787	1.057095	-2167710.018000	3.011774	2.322E-03
1b-12	-3455.501171	-3455.501642	-3455.577080	1.056570	-2167709.435000	3.594602	8.679E-04
1b-13	-3455.503618	-3455.504684	-3455.575054	1.054215	-2167709.267000	3.762145	6.540E-04
1b-14	-3455.504576	-3455.508343	-3455.578130	1.054904	-2167709.070000	3.958985	4.690E-04
1b-15	-3455.507435	-3455.507922	-3455.578415	1.058506	-2167709.047000	3.982203	4.510E-04
1b-16	-3455.506461	-3455.507077	-3455.578170	1.058392	-2167708.884000	4.145717	3.422E-04
1b-17	-3455.507748	-3455.508636	-3455.579086	1.059157	-2167708.808000	4.221456	3.011E-04
1b-18	-3455.505148	-3455.509173	-3455.578228	1.055187	-2167708.793000	4.236867	2.933E-04
1b-19	-3455.507741	-3455.508632	-3455.579079	1.059175	-2167708.791000	4.238800	2.924E-04

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1b-20	-3455.505240	-3455.505611	-3455.576741	1.057362	-2167708.788000	4.241768	2.909E-04
1b-21	-3455.503909	-3455.505892	-3455.576147	1.055172	-2167708.777000	4.252222	2.858E-04
1b-22	-3455.504505	-3455.506233	-3455.576334	1.055934	-2167708.577000	4.452916	2.037E-04
1b-23	-3455.503984	-3455.507410	-3455.577694	1.055755	-2167708.477000	4.552757	1.721E-04
1b-24	-3455.503511	-3455.503746	-3455.575842	1.057128	-2167708.456000	4.573910	1.660E-04
1b-25	-3455.504135	-3455.508169	-3455.577851	1.055750	-2167708.197000	4.832610	1.072E-04
1b-26	-3455.505045	-3455.507434	-3455.577263	1.056887	-2167708.147000	4.882414	9.860E-05
1b-27	-3455.503795	-3455.504126	-3455.576397	1.058511	-2167707.876000	5.153802	6.235E-05
1b-28	-3455.504955	-3455.505057	-3455.576257	1.058606	-2167707.872000	5.157385	6.197E-05
1b-29	-3455.498566	-3455.499643	-3455.572066	1.053463	-2167707.858000	5.171447	6.051E-05
1b-30	-3455.498566	-3455.499641	-3455.572065	1.053469	-2167707.855000	5.174785	6.017E-05
1b-31	-3455.510175	-3455.510661	-3455.577304	1.059442	-2167707.763000	5.266375	5.155E-05
1b-32	-3455.509479	-3455.508488	-3455.576772	1.060545	-2167707.664000	5.365370	4.361E-05
1b-33	-3455.505690	-3455.507856	-3455.577377	1.058497	-2167707.348000	5.681222	2.558E-05
1b-34	-3455.508435	-3455.509945	-3455.576869	1.059024	-2167707.110000	5.919490	1.711E-05
1b-35	-3455.504931	-3455.507421	-3455.576925	1.058193	-2167707.052000	5.977245	1.552E-05
1b-36	-3455.504930	-3455.507418	-3455.576921	1.058215	-2167707.037000	5.992355	1.513E-05
1b-37	-3455.504929	-3455.507417	-3455.576916	1.058215	-2167707.034000	5.995499	1.505E-05
1b-38	-3455.504935	-3455.507417	-3455.576904	1.058276	-2167706.991000	6.038081	1.400E-05
1b-39	-3455.510262	-3455.510449	-3455.575822	1.060069	-2167706.627000	6.402345	7.569E-06
1b-40	-3455.502229	-3455.504223	-3455.574456	1.056980	-2167706.575000	6.454496	6.930E-06
1b-41	-3455.506206	-3455.507671	-3455.574637	1.057732	-2167706.549000	6.480902	6.628E-06
1b-42	-3455.502423	-3455.504356	-3455.574517	1.057247	-2167706.484000	6.545446	5.944E-06
1b-43	-3455.505002	-3455.506673	-3455.575545	1.058735	-2167706.360000	6.669177	4.823E-06
1b-44	-3455.507009	-3455.508784	-3455.576341	1.059441	-2167706.351000	6.678859	4.745E-06
1b-45	-3455.506843	-3455.508901	-3455.576067	1.059092	-2167706.221000	6.808532	3.811E-06
1b-46	-3455.506841	-3455.508901	-3455.576076	1.059103	-2167706.218000	6.811318	3.793E-06
1b-47	-3455.508441	-3455.510262	-3455.577497	1.060852	-2167706.162000	6.867504	3.450E-06
1b-48	-3455.501923	-3455.503300	-3455.572939	1.056793	-2167706.128000	6.901471	3.258E-06
1b-49	-3455.501204	-3455.502793	-3455.573423	1.057228	-2167706.026000	7.003866	2.740E-06
1b-50	-3455.503675	-3455.506918	-3455.576927	1.059097	-2167706.013000	7.015977	2.685E-06
1b-51	-3455.501433	-3455.503917	-3455.573977	1.057018	-2167705.943000	7.086747	2.382E-06
1b-52	-3455.502153	-3455.504020	-3455.573616	1.057401	-2167705.863000	7.166213	2.083E-06
1b-53	-3455.502462	-3455.504802	-3455.573911	1.057246	-2167705.849000	7.180796	2.033E-06
1b-54	-3455.500540	-3455.501269	-3455.568287	1.053283	-2167705.818000	7.211525	1.930E-06
1b-55	-3455.500906	-3455.503126	-3455.572674	1.056284	-2167705.752000	7.277933	1.725E-06
1b-56	-3455.500003	-3455.502472	-3455.573690	1.057149	-2167705.690000	7.339008	1.556E-06
1b-57	-3455.497717	-3455.500151	-3455.571782	1.055293	-2167705.680000	7.349751	1.528E-06
1b-58	-3455.500773	-3455.502410	-3455.572227	1.056574	-2167705.655000	7.374223	1.466E-06

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1b-59	-3455.502261	-3455.503578	-3455.573180	1.057849	-2167705.654000	7.375779	1.462E-06
1b-60	-3455.506747	-3455.509175	-3455.574393	1.058015	-2167705.614000	7.415544	1.367E-06
1b-61	-3455.501764	-3455.504093	-3455.574138	1.057963	-2167705.549000	7.480710	1.225E-06
1b-62	-3455.501038	-3455.503364	-3455.573029	1.056876	-2167705.536000	7.493580	1.198E-06
1b-63	-3455.501047	-3455.502334	-3455.572372	1.057631	-2167705.302000	7.726979	8.080E-07
1b-64	-3455.499463	-3455.502074	-3455.571993	1.056019	-2167705.245000	7.784633	7.330E-07
1b-65	-3455.498386	-3455.500279	-3455.571006	1.056089	-2167705.032000	7.997318	5.118E-07
1b-66	-3455.499188	-3455.501487	-3455.572387	1.057394	-2167704.825000	8.204644	3.606E-07
1b-67	-3455.499709	-3455.501761	-3455.571638	1.056926	-2167704.804000	8.225326	3.482E-07
1b-68	-3455.501004	-3455.502732	-3455.571862	1.057497	-2167704.790000	8.239677	3.399E-07
1b-69	-3455.501003	-3455.502726	-3455.571847	1.057541	-2167704.755000	8.274027	3.207E-07
1b-70	-3455.507676	-3455.510400	-3455.575525	1.060344	-2167704.677000	8.352784	2.808E-07
1b-71	-3455.507677	-3455.510401	-3455.575526	1.060347	-2167704.676000	8.353933	2.803E-07
1b-72	-3455.501068	-3455.503965	-3455.573826	1.058517	-2167704.648000	8.381078	2.677E-07
1b-73	-3455.506431	-3455.508362	-3455.575001	1.061163	-2167704.332000	8.697476	1.569E-07
1b-74	-3455.499851	-3455.503354	-3455.573029	1.057666	-2167704.302000	8.727565	1.491E-07
1b-75	-3455.500334	-3455.503470	-3455.573206	1.058220	-2167704.296000	8.733545	1.476E-07
1b-76	-3455.496118	-3455.498456	-3455.569998	1.056366	-2167703.947000	9.082021	8.194E-08
1b-77	-3455.499223	-3455.501398	-3455.571014	1.057685	-2167703.859000	9.170549	7.056E-08
1b-78	-3455.498314	-3455.500582	-3455.570080	1.056913	-2167703.699000	9.330718	5.384E-08
1b-79	-3455.498425	-3455.500485	-3455.570806	1.058030	-2167703.584000	9.445350	4.436E-08
1b-80	-3455.501987	-3455.505047	-3455.573961	1.060318	-2167703.501000	9.528870	3.853E-08

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at B3LYP/6-31G(d) level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S4.3. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **1b-5** (with a population of 65.7% obtained in population-fitted RDC analysis) at the PBE0/TZVP (methanol, IEFPCM solvent model) level of theory.

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
1	273->274	0.65795	3.3589	369.12	0.0025	8.8095	8.8042
2	273->275	0.68613	3.3746	367.40	0.0174	16.035	16.5782
3	273->276	0.67236	3.6737	337.49	0.0049	-4.8605	-5.0316
4	270->274	0.43749	3.8431	322.61	0.0065	-19.7928	-21.3558
	270->275	-0.35715					
5	271->274	-0.36423	3.8795	319.59	0.0079	-27.3428	-28.243
	271->276	0.49112					
6	269->275	0.22826	3.8837	319.24	0.0072	-27.9616	-27.3091
	272->274	0.31244					
	272->275	0.39463					
7	273->277	0.6631	3.9750	311.91	0.0031	1.5734	1.6915
8	269->274	0.31373	4.0046	309.60	0.0229	-9.9916	-10.3712
	269->275	0.3832					
	272->274	-0.28276					
	272->275	-0.33009					
9	272->274	0.50522	4.2006	295.16	0.0005	-1.8803	-2.019
	272->275	-0.4039					
10	273->279	0.67675	4.2231	293.59	0.0413	13.2076	12.803
11	270->274	-0.36031	4.2501	291.72	0.0002	1.9715	2.0427
	270->276	0.5194					
12	271->274	0.44633	4.2709	290.30	0.0008	-1.8421	-1.9341
	271->275	-0.4163					
	271->276	0.32555					
13	273->278	0.50756	4.2952	288.66	0.0266	-9.4777	-9.0666
	273->280	0.29845					
14	265->275	0.23016	4.3058	287.94	0.0030	0.5778	1.2058
	273->278	0.39416					
15	273->280	0.55358	4.3319	286.21	0.1067	79.8167	81.6854
16	269->276	-0.26639	4.3525	284.86	0.0052	1.2428	1.0977
	272->276	0.60334					
17	270->274	0.25049	4.3999	281.79	0.0013	2.114	2.024
	270->275	0.54111					
	270->276	0.23398					
18	264->274	0.231	4.4288	279.95	0.0176	35.2666	35.7051
	270->274	0.25155					
	270->276	0.25817					

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
19	269->274	0.47423	4.4697	277.39	0.0068	12.3167	12.6052
	269->275	-0.38298					
20	263->276	0.31245	4.4819	276.63	0.0201	-16.2913	-15.8716
	271->274	0.24749					
	271->275	0.25607					
	271->276	-0.2281					
21	272->280	-0.35197	4.4946	275.85	0.0321	33.8443	36.0019
	273->281	0.39443					
	273->284	0.29723					
22	271->274	0.31168	4.5252	273.99	0.0028	-1.1373	-0.943
	271->275	0.49545					
	271->276	0.29812					
23	272->277	0.58731	4.5900	270.12	0.0048	4.0968	4.3242
24	269->276	0.59712	4.6031	269.35	0.0014	-4.6312	-4.8856
25	270->277	0.27624	4.6598	266.07	0.0196	36.795	36.3274
	273->281	0.36466					
26	268->274	0.31001	4.7055	263.49	0.1513	353.6029	366.4241
	268->275	0.39513					
	270->277	-0.34631					
27	273->281	0.25727	4.7253	262.39	0.0616	14.3804	15.3597
	273->282	0.56549					
28	271->277	0.46506	4.7336	261.93	0.5129	125.0664	127.3684
	271->278	-0.29693					
29	270->277	0.28956	4.7431	261.40	0.0892	-251.6336	-258.6517
	272->279	0.38612					
30	272->279	0.42061	4.7706	259.89	0.1249	-135.1978	-135.8617
	272->280	0.26811					
31	271->277	0.44541	4.8086	257.84	0.1300	-16.1102	-16.944
	271->278	0.47935					
32	270->278	0.59133	4.8516	255.55	0.0127	-52.05	-53.5045
	272->278	0.25873					
33	268->274	0.51011	4.8782	254.16	0.0009	-1.9035	-1.6189
	268->275	-0.40786					
34	269->277	0.25659	4.9024	252.91	0.0037	4.0112	3.9621
	269->280	0.36674					
	272->280	0.31795					
35	269->277	0.46189	4.9326	251.36	0.0120	-6.2199	-6.005
	272->277	0.25692					
36	269->277	0.268	4.9393	251.01	0.0031	-0.3031	-0.2132

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	272->278	0.52275					

[a]Number of the excited states; [b]Only transitions with contribution over 10.0% were listed; [c]Configuration-interaction coefficient; [d]Excitation energy; [e]Wavelength;[f]Oscillator strength; [g]Rotatory strength in velocity form (10^{-40} cgs); [h]Rotatory strength in length form (10^{-40} cgs).

Table S4.4. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **1b-4** (with a population of 32.5% obtained in population-fitted RDC analysis) at the PBE0/TZVP (methanol, IEFPCM solvent model) level of theory.

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
1	273->274	0.60815	3.3053	375.10	0.0028	12.2952	12.308
	273->276	-0.32817					
2	273->275	0.69661	3.3471	370.42	0.0191	7.1677	7.7747
3	273->274	0.33601	3.5873	345.62	0.0075	-10.0965	-10.363
	273->276	0.61249					
4	271->274	0.5399	3.7154	333.70	0.0174	-10.8219	-10.1986
	271->276	0.35259					
5	270->274	-0.28918	3.7840	327.66	0.0232	-15.4192	-16.2967
	272->274	0.44337					
	272->276	-0.22985					
6	270->275	0.28073	3.8684	320.51	0.0028	-17.0838	-16.9174
	272->274	0.22363					
	272->275	0.52899					
7	263->275	0.24761	4.0154	308.77	0.0168	13.9521	14.2171
	269->275	0.40806					
	273->277	0.30595					
8	272->274	0.35755	4.0365	307.16	0.0200	12.627	12.45
	272->276	0.29502					
	273->277	0.45692					
9	272->274	-0.24987	4.0516	306.01	0.0424	-25.4978	-26.0996
	272->276	-0.25472					
	273->277	0.41318					
10	270->274	0.39189	4.1054	302.00	0.0005	-2.9172	-3.0082
	272->276	-0.33109					
	273->279	-0.36237					
11	270->274	0.30882	4.1408	299.42	0.0069	-6.1813	-6.1073
	273->278	0.23986					
	273->279	0.50149					
12	271->274	-0.37036	4.1693	297.38	0.0011	-3.5069	-3.8669

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	271->275	0.26778					
	271->276	0.52026					
13	270->274	0.29994	4.2359	292.70	0.0015	6.7866	6.8704
	270->275	0.32919					
	270->276	0.24692					
	272->276	0.33071					
14	270->275	0.37798	4.2647	290.72	0.0032	-5.0585	-4.2143
	270->276	-0.37003					
	272->275	-0.2469					
15	273->278	0.62736	4.3299	286.34	0.0001	-1.0539	-0.9725
	273->279	-0.29595					
16	270->276	0.23926	4.3388	285.76	0.0318	-25.1754	-24.923
	273->280	0.55178					
17	264->274	-0.24496	4.3553	284.67	0.0089	6.3563	6.2117
	270->276	0.34995					
18	263->275	-0.31678	4.3969	281.98	0.0226	35.6284	36.7032
	269->275	0.36677					
19	262->274	-0.31254	4.4221	280.37	0.0101	23.486	26.6114
	262->276	-0.25457					
	271->275	0.32322					
20	271->275	0.55833	4.4540	278.37	0.0029	12.049	13.0064
	271->276	-0.28184					
21	270->277	0.24155	4.4695	277.40	0.0139	2.8122	3.2491
	272->277	0.43861					
	273->282	0.23245					
	273->284	0.24904					
22	269->274	0.59236	4.5209	274.25	0.0005	1.169	1.2303
	269->275	-0.27698					
23	272->277	-0.37055	4.5476	272.64	0.0548	-10.3731	-10.9536
	273->282	0.40963					
24	273->281	0.65006	4.5780	270.83	0.0002	0.4507	0.4792
25	269->276	0.57603	4.6627	265.91	0.0213	-31.8291	-33.0109
26	269->276	-0.28687	4.6740	265.26	0.0385	-125.3985	-124.4648
	273->282	0.33773					
27	271->278	0.27574	4.7051	263.51	0.0591	-306.2939	-312.9769
	272->278	0.37002					
	272->279	0.29504					
28	271->278	0.4661	4.7288	262.19	0.2496	334.9438	343.815
	272->279	-0.28546					

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
29	268->274	0.27261	4.7347	261.86	0.0144	-0.2855	2.9731
	268->275	0.49193					
30	270->278	-0.24409	4.7700	259.93	0.0075	-11.884	-12.3386
	272->278	0.50137					
	272->279	-0.35611					
31	270->277	0.43535	4.7950	258.57	0.0328	0.1828	0.7147
	270->279	0.30017					
	272->280	0.30031					
32	268->274	0.5163	4.8369	256.33	0.0118	32.3178	33.4102
	268->275	-0.27899					
33	268->274	0.23642	4.8482	255.73	0.0732	36.8518	38.9675
	270->277	-0.25287					
	270->279	0.33906					
34	271->279	0.64562	4.9026	252.89	0.0067	-8.7575	-9.5584
35	273->283	0.57765	4.9234	251.83	0.0059	2.7323	2.8016
36	270->277	-0.25961	4.9262	251.68	0.0059	-5.2069	-5.1327
	272->280	0.36251					
	273->283	-0.34449					
	273->284	0.23757					

[a]Number of the excited states; [b]Only transitions with contribution over 10.0% were listed; [c]Configuration-interaction coefficient; [d]Excitation energy; [e]Wavelength;[f]Oscillator strength; [g]Rotatory strength in velocity form (10^{-40} cgs); [h]Rotatory strength in length form (10^{-40} cgs).

Table S4.5. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **1b-3** (with a population of 1.7% obtained in population-fitted RDC analysis) at the PBE0/TZVP (methanol, IEFPCM solvent model) level of theory.

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
1	273->274	0.63434	3.3253	372.85	0.0019	5.7498	5.3373
	273->276	-0.25708					
2	273->275	0.68972	3.3891	365.83	0.0186	23.231	24.1126
3	273->274	0.26411	3.6628	338.50	0.0059	-14.382	-14.5994
	273->276	0.6394					
4	272->274	0.50932	3.7286	332.52	0.0135	-2.1567	-1.7293
	272->276	0.39726					
5	269->274	0.47359	3.8588	321.30	0.0067	-12.6018	-13.8295
6	270->275	0.48493	3.8990	317.99	0.0148	-31.809	-31.6032
	271->275	0.26921					
7	273->277	0.69675	3.9189	316.38	0.0028	2.0447	2.3454
8	270->275	-0.26222	4.0061	309.49	0.0203	-9.2344	-9.3845

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	271->274	0.23719					
	271->275	0.53779					
9	272->274	-0.43422	4.1549	298.40	0.0015	-2.1054	-2.4798
	272->275	0.24319					
	272->276	0.47843					
10	271->274	0.5716	4.1778	296.77	0.0004	-0.9792	-1.0661
	271->275	-0.24208					
11	269->274	0.39121	4.2813	289.60	0.0025	-0.3371	-0.4396
	269->276	0.3729					
	271->276	0.26465					
12	273->279	0.60006	4.2899	289.02	0.0322	8.8699	9.0472
13	265->275	0.32291	4.3072	287.85	0.0037	-12.4933	-12.4663
	266->275	0.23267					
	270->275	-0.2518					
	273->279	-0.26377					
14	273->280	0.59564	4.3437	285.44	0.1124	37.4463	39.1246
15	269->276	-0.25431	4.3685	283.81	0.0027	1.7476	1.5132
	271->276	0.50974					
16	270->274	0.52543	4.3891	282.48	0.0027	15.2696	15.6985
	270->275	-0.24584					
17	273->278	0.66191	4.3925	282.27	0.0017	1.6251	1.7181
18	269->275	0.38779	4.4184	280.61	0.0191	22.1923	23.066
	269->276	0.22464					
19	272->275	0.58626	4.4281	279.99	0.0040	7.5875	8.5443
20	269->275	0.47003	4.4411	279.18	0.0067	1.769	1.8978
	269->276	-0.3865					
21	263->274	0.26982	4.4645	277.71	0.0075	21.7852	24.198
	263->276	0.28266					
	272->275	-0.29152					
	272->276	0.31754					
22	271->280	0.27402	4.4834	276.54	0.0512	39.4692	41.9519
	273->281	0.47034					
	273->284	0.24495					
23	271->277	0.61482	4.5528	272.33	0.0056	1.6471	1.8572
24	270->276	0.60913	4.5745	271.03	0.0015	-3.3126	-3.4786
	271->276	0.25018					
25	272->277	0.6908	4.6158	268.61	0.0050	1.8789	1.8121
26	269->277	0.38731	4.6657	265.73	0.0602	15.4416	15.0728
	271->280	-0.24713					

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	273->281	0.24374					
27	268->275	-0.28925	4.7142	263.00	0.0792	-71.8293	-71.2319
	269->277	0.23458					
	273->282	0.34349					
	273->283	-0.29265					
28	268->275	0.36316	4.7198	262.69	0.0277	-17.2492	-17.9195
	273->282	0.39292					
	273->283	-0.28942					
29	268->275	-0.23726	4.7518	260.92	0.0810	-384.1222	-386.9449
	272->278	0.4419					
30	272->278	0.3375	4.7670	260.09	0.4888	452.1279	462.6235
	273->281	-0.23551					
31	268->274	0.57926	4.8362	256.37	0.0009	-2.6051	-2.5145
	268->275	-0.26692					
32	271->279	0.53942	4.8474	255.78	0.0035	-9.2524	-8.5304
	271->280	-0.24337					
33	270->277	0.57865	4.8532	255.47	0.0054	-6.954	-7.1106
	271->277	0.23962					
34	273->282	0.38847	4.9178	252.11	0.0019	-2.7378	-2.4311
	273->283	0.53821					
35	270->280	0.5123	4.9257	251.71	0.0119	-18.2626	-18.5265
	271->280	0.26489					
36	269->278	0.49689	4.9636	249.79	0.0091	6.2357	6.8496
	270->278	-0.24637					
	271->278	0.38116					

[a]Number of the excited states; [b]Only transitions with contribution over 10.0% were listed; [c]Configuration-interaction coefficient; [d]Excitation energy; [e]Wavelength;[f]Oscillator strength; [g]Rotatory strength in velocity form (10^{-40} cgs); [h]Rotatory strength in length form (10^{-40} cgs).

Table S4.6. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1c** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **1c.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1c-1	-3455.509925	-3455.508763	-3455.584420	1.056665	-2167715.006000	0.000000	7.607E-01
1c-2	-3455.510424	-3455.510258	-3455.583897	1.057988	-2167713.222000	1.783487	3.741E-02
1c-3	-3455.507677	-3455.505608	-3455.580885	1.057246	-2167712.992000	2.013566	2.537E-02
1c-4	-3455.508807	-3455.506749	-3455.584164	1.060521	-2167712.988000	2.017776	2.519E-02
1c-5	-3455.505563	-3455.505554	-3455.581449	1.055761	-2167712.985000	2.021165	2.504E-02
1c-6	-3455.501476	-3455.504828	-3455.580482	1.052022	-2167712.615000	2.390411	1.342E-02
1c-7	-3455.508662	-3455.507905	-3455.581387	1.057112	-2167712.568000	2.438239	1.238E-02
1c-8	-3455.506461	-3455.506773	-3455.582147	1.057043	-2167712.416000	2.589404	9.592E-03
1c-9	-3455.504555	-3455.505132	-3455.581115	1.055786	-2167712.392000	2.613895	9.203E-03
1c-10	-3455.503379	-3455.504693	-3455.580226	1.054422	-2167712.228000	2.777936	6.976E-03
1c-11	-3455.503380	-3455.504692	-3455.580224	1.054424	-2167712.226000	2.779549	6.957E-03
1c-12	-3455.508571	-3455.508564	-3455.581726	1.057318	-2167712.180000	2.825520	6.437E-03
1c-13	-3455.509475	-3455.510416	-3455.583307	1.058187	-2167712.033000	2.973277	5.016E-03
1c-14	-3455.506871	-3455.506756	-3455.582093	1.058049	-2167712.019000	2.986574	4.904E-03
1c-15	-3455.508196	-3455.507614	-3455.580505	1.056984	-2167711.984000	3.021670	4.622E-03
1c-16	-3455.507908	-3455.507460	-3455.581049	1.057537	-2167711.895000	3.110580	3.978E-03
1c-17	-3455.507855	-3455.506073	-3455.580940	1.058931	-2167711.789000	3.216370	3.327E-03
1c-18	-3455.503895	-3455.504718	-3455.580279	1.055753	-2167711.733000	3.272676	3.025E-03
1c-19	-3455.505013	-3455.505878	-3455.579098	1.054555	-2167711.718000	3.287761	2.949E-03
1c-20	-3455.506104	-3455.505060	-3455.578140	1.055607	-2167711.654000	3.351735	2.647E-03
1c-21	-3455.507846	-3455.507339	-3455.580115	1.057057	-2167711.647000	3.358637	2.616E-03
1c-22	-3455.501999	-3455.502857	-3455.579246	1.054991	-2167711.541000	3.464679	2.187E-03
1c-23	-3455.500434	-3455.500312	-3455.578061	1.054793	-2167711.537000	3.468977	2.171E-03
1c-24	-3455.504443	-3455.504178	-3455.579367	1.056258	-2167711.527000	3.478421	2.137E-03
1c-25	-3455.505746	-3455.508106	-3455.581438	1.055968	-2167711.361000	3.644376	1.615E-03
1c-26	-3455.505749	-3455.508107	-3455.581438	1.056012	-2167711.336000	3.670128	1.546E-03
1c-27	-3455.505747	-3455.508106	-3455.581434	1.056020	-2167711.327000	3.678418	1.524E-03
1c-28	-3455.508443	-3455.509710	-3455.582228	1.057974	-2167711.285000	3.721238	1.418E-03
1c-29	-3455.505935	-3455.504880	-3455.577609	1.055756	-2167711.235000	3.770641	1.305E-03
1c-30	-3455.503312	-3455.501115	-3455.578917	1.058293	-2167711.180000	3.825717	1.189E-03
1c-31	-3455.508960	-3455.509116	-3455.581358	1.058448	-2167711.138000	3.868224	1.106E-03
1c-32	-3455.505868	-3455.503325	-3455.578188	1.058101	-2167711.061000	3.945293	9.713E-04
1c-33	-3455.507430	-3455.507768	-3455.580453	1.057531	-2167711.032000	3.974284	9.249E-04
1c-34	-3455.504800	-3455.501935	-3455.576971	1.057257	-2167711.028000	3.977980	9.192E-04
1c-35	-3455.508148	-3455.509284	-3455.582428	1.058881	-2167710.923000	4.082892	7.699E-04
1c-36	-3455.508145	-3455.509283	-3455.582423	1.058893	-2167710.911000	4.095222	7.541E-04

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1c-37	-3455.508145	-3455.509283	-3455.582423	1.058896	-2167710.910000	4.095843	7.533E-04
1c-38	-3455.508146	-3455.509283	-3455.582426	1.058916	-2167710.899000	4.107251	7.389E-04
1c-39	-3455.505808	-3455.506612	-3455.580753	1.057694	-2167710.825000	4.181334	6.520E-04
1c-40	-3455.507876	-3455.509551	-3455.582228	1.058346	-2167710.795000	4.211309	6.198E-04
1c-41	-3455.503078	-3455.505686	-3455.580149	1.055340	-2167710.791000	4.214535	6.164E-04
1c-42	-3455.504577	-3455.502053	-3455.577150	1.057622	-2167710.697000	4.308465	5.260E-04
1c-43	-3455.504291	-3455.502892	-3455.576003	1.055359	-2167710.692000	4.313529	5.215E-04
1c-44	-3455.506055	-3455.506984	-3455.580312	1.057418	-2167710.643000	4.362876	4.798E-04
1c-45	-3455.504909	-3455.505800	-3455.580968	1.058421	-2167710.449000	4.556886	3.458E-04
1c-46	-3455.505393	-3455.503991	-3455.576173	1.056274	-2167710.227000	4.779153	2.375E-04
1c-47	-3455.504725	-3455.504239	-3455.576170	1.055567	-2167710.093000	4.912603	1.896E-04
1c-48	-3455.506474	-3455.506485	-3455.578665	1.057630	-2167710.052000	4.953347	1.770E-04
1c-49	-3455.506639	-3455.507128	-3455.579994	1.058523	-2167710.027000	4.979325	1.694E-04
1c-50	-3455.505126	-3455.505908	-3455.578874	1.057275	-2167709.923000	5.083070	1.422E-04
1c-51	-3455.505564	-3455.508987	-3455.582972	1.058811	-2167709.873000	5.132862	1.307E-04
1c-52	-3455.505272	-3455.506695	-3455.579813	1.057832	-2167709.760000	5.245781	1.080E-04
1c-53	-3455.505274	-3455.506697	-3455.579815	1.057849	-2167709.751000	5.254823	1.064E-04
1c-54	-3455.505272	-3455.506695	-3455.579814	1.057859	-2167709.744000	5.262196	1.051E-04
1c-55	-3455.507985	-3455.508043	-3455.579738	1.059151	-2167709.742000	5.263564	1.048E-04
1c-56	-3455.507406	-3455.507250	-3455.579239	1.058867	-2167709.741000	5.264549	1.046E-04
1c-57	-3455.503495	-3455.506264	-3455.578513	1.055461	-2167709.588000	5.418293	8.071E-05
1c-58	-3455.505618	-3455.504755	-3455.576650	1.057252	-2167709.574000	5.431640	7.891E-05
1c-59	-3455.506253	-3455.508074	-3455.579310	1.057305	-2167709.526000	5.480265	7.269E-05
1c-60	-3455.502968	-3455.504052	-3455.577146	1.055897	-2167709.514000	5.492043	7.126E-05
1c-61	-3455.502968	-3455.504052	-3455.577147	1.055904	-2167709.510000	5.495388	7.086E-05
1c-62	-3455.502967	-3455.504051	-3455.577144	1.055900	-2167709.510000	5.495651	7.083E-05
1c-63	-3455.502966	-3455.504048	-3455.577144	1.055904	-2167709.509000	5.496429	7.073E-05
1c-64	-3455.504727	-3455.507859	-3455.579727	1.056495	-2167709.473000	5.533031	6.649E-05
1c-65	-3455.504734	-3455.507863	-3455.579737	1.056588	-2167709.423000	5.583225	6.109E-05
1c-66	-3455.504302	-3455.504115	-3455.576365	1.057097	-2167709.067000	5.938685	3.352E-05
1c-67	-3455.504295	-3455.504110	-3455.576363	1.057099	-2167709.065000	5.941201	3.337E-05
1c-68	-3455.503588	-3455.503319	-3455.575374	1.056232	-2167709.041000	5.965128	3.205E-05
1c-69	-3455.503587	-3455.503319	-3455.575371	1.056247	-2167709.028000	5.977665	3.138E-05
1c-70	-3455.504459	-3455.505505	-3455.578056	1.057695	-2167708.980000	6.025588	2.894E-05
1c-71	-3455.505648	-3455.505397	-3455.576921	1.058098	-2167708.829000	6.177060	2.241E-05
1c-72	-3455.503266	-3455.505310	-3455.578506	1.057562	-2167708.719000	6.286421	1.863E-05
1c-73	-3455.503268	-3455.505308	-3455.578501	1.057568	-2167708.715000	6.290637	1.850E-05
1c-74	-3455.503267	-3455.505308	-3455.578504	1.057578	-2167708.711000	6.295218	1.835E-05
1c-75	-3455.503041	-3455.503159	-3455.574580	1.055620	-2167708.684000	6.322276	1.753E-05

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1c-76	-3455.500166	-3455.500919	-3455.574966	1.056935	-2167707.702000	7.304175	3.339E-06
1c-77	-3455.504290	-3455.504698	-3455.575263	1.057911	-2167707.492000	7.513867	2.344E-06
1c-78	-3455.504292	-3455.504698	-3455.575262	1.057944	-2167707.472000	7.533489	2.267E-06
1c-79	-3455.504853	-3455.505398	-3455.576146	1.058988	-2167707.285000	7.721049	1.652E-06
1c-80	-3455.501848	-3455.503894	-3455.574579	1.057025	-2167706.591000	8.414436	5.121E-07
1c-81	-3455.497136	-3455.498222	-3455.571157	1.055105	-2167706.251000	8.754742	2.882E-07
1c-82	-3455.503141	-3455.501590	-3455.572090	1.060222	-2167705.281000	9.725121	5.597E-08

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at B3LYP/6-31G(d) level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S4.7. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1d** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **1d.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1d-1	-3455.505712	-3455.502823	-3455.578187	1.058644	-2167710.936000	0.000000	9.887E-01
1d-2	-3455.503382	-3455.504106	-3455.578178	1.059418	-2167708.177000	2.759074	9.361E-03
1d-3	-3455.504321	-3455.506197	-3455.576933	1.058721	-2167707.111000	3.825052	1.547E-03
1d-4	-3455.494322	-3455.495103	-3455.566919	1.052451	-2167705.449000	5.487607	9.332E-05
1d-5	-3455.495585	-3455.498795	-3455.568846	1.052081	-2167705.366000	5.570274	8.116E-05
1d-6	-3455.493681	-3455.494041	-3455.565711	1.053040	-2167704.585000	6.351649	2.169E-05
1d-7	-3455.492041	-3455.493644	-3455.566094	1.052197	-2167704.574000	6.362053	2.131E-05
1d-8	-3455.496600	-3455.498609	-3455.568126	1.053890	-2167704.532000	6.404001	1.985E-05
1d-9	-3455.491049	-3455.493267	-3455.566026	1.051728	-2167704.441000	6.495729	1.700E-05
1d-10	-3455.489612	-3455.491246	-3455.564335	1.050904	-2167704.262000	6.673839	1.259E-05
1d-11	-3455.489610	-3455.491245	-3455.564339	1.050950	-2167704.236000	6.700407	1.203E-05
1d-12	-3455.494244	-3455.497183	-3455.566691	1.052008	-2167704.229000	6.707084	1.190E-05
1d-13	-3455.487005	-3455.489580	-3455.562315	1.048016	-2167704.217000	6.719326	1.166E-05
1d-14	-3455.491297	-3455.494311	-3455.563295	1.048864	-2167704.024000	6.912371	8.413E-06
1d-15	-3455.494459	-3455.496434	-3455.566629	1.053459	-2167703.885000	7.051519	6.651E-06
1d-16	-3455.494456	-3455.496432	-3455.566625	1.053473	-2167703.873000	7.063046	6.522E-06
1d-17	-3455.496273	-3455.498714	-3455.567816	1.054247	-2167703.843000	7.092902	6.202E-06
1d-18	-3455.488936	-3455.490925	-3455.564577	1.051540	-2167703.792000	7.143906	5.690E-06
1d-19	-3455.491506	-3455.493482	-3455.565957	1.053051	-2167703.719000	7.217668	5.023E-06

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1d-20	-3455.491503	-3455.493479	-3455.565955	1.053059	-2167703.712000	7.224069	4.969E-06
1d-21	-3455.489441	-3455.491311	-3455.564125	1.051391	-2167703.678000	7.258675	4.687E-06
1d-22	-3455.495262	-3455.496628	-3455.565700	1.053608	-2167703.591000	7.345295	4.049E-06
1d-23	-3455.491323	-3455.493596	-3455.566696	1.053766	-2167703.547000	7.389038	3.761E-06
1d-24	-3455.490403	-3455.492308	-3455.564124	1.051740	-2167703.435000	7.500834	3.114E-06
1d-25	-3455.490786	-3455.493553	-3455.562623	1.049488	-2167703.366000	7.570216	2.770E-06
1d-26	-3455.493754	-3455.495402	-3455.566546	1.054569	-2167703.341000	7.594808	2.657E-06
1d-27	-3455.493754	-3455.495402	-3455.566547	1.054574	-2167703.339000	7.597444	2.645E-06
1d-28	-3455.493220	-3455.495463	-3455.564987	1.052651	-2167703.194000	7.742704	2.070E-06
1d-29	-3455.494004	-3455.495946	-3455.564813	1.052782	-2167703.191000	7.745276	2.061E-06
1d-30	-3455.491331	-3455.492853	-3455.564656	1.053083	-2167703.166000	7.770050	1.976E-06
1d-31	-3455.493104	-3455.494977	-3455.563933	1.052092	-2167703.115000	7.821304	1.812E-06
1d-32	-3455.491135	-3455.491687	-3455.564021	1.053681	-2167703.001000	7.934913	1.496E-06
1d-33	-3455.492405	-3455.494032	-3455.562738	1.051573	-2167702.845000	8.091261	1.149E-06
1d-34	-3455.490477	-3455.492883	-3455.564972	1.053048	-2167702.832000	8.104012	1.124E-06
1d-35	-3455.485498	-3455.488565	-3455.561262	1.048716	-2167702.808000	8.128083	1.080E-06
1d-36	-3455.490884	-3455.493175	-3455.561705	1.050012	-2167702.760000	8.176576	9.946E-07
1d-37	-3455.490849	-3455.493442	-3455.561887	1.049945	-2167702.726000	8.210041	9.400E-07
1d-38	-3455.490617	-3455.492959	-3455.565097	1.053408	-2167702.725000	8.211578	9.375E-07
1d-39	-3455.491613	-3455.493729	-3455.562233	1.050772	-2167702.724000	8.211936	9.370E-07
1d-40	-3455.492985	-3455.495422	-3455.563205	1.051483	-2167702.686000	8.250056	8.785E-07
1d-41	-3455.498849	-3455.500271	-3455.569132	1.058489	-2167702.646000	8.290317	8.208E-07
1d-42	-3455.491059	-3455.493649	-3455.562049	1.050264	-2167702.630000	8.306356	7.988E-07
1d-43	-3455.491910	-3455.494849	-3455.562278	1.050195	-2167702.598000	8.338659	7.564E-07
1d-44	-3455.494229	-3455.496861	-3455.565113	1.053400	-2167702.558000	8.378085	7.077E-07
1d-45	-3455.493226	-3455.494711	-3455.565924	1.055385	-2167702.541000	8.394839	6.880E-07
1d-46	-3455.489841	-3455.492341	-3455.564475	1.053015	-2167702.482000	8.454063	6.225E-07
1d-47	-3455.490701	-3455.492018	-3455.563779	1.053557	-2167702.448000	8.488544	5.873E-07
1d-48	-3455.493132	-3455.494988	-3455.563797	1.053073	-2167702.425000	8.511454	5.650E-07
1d-49	-3455.489870	-3455.491530	-3455.562917	1.052416	-2167702.408000	8.528359	5.491E-07
1d-50	-3455.490473	-3455.492103	-3455.561799	1.051423	-2167702.348000	8.588021	4.964E-07
1d-51	-3455.493439	-3455.495998	-3455.564112	1.052831	-2167702.333000	8.603050	4.840E-07
1d-52	-3455.490568	-3455.494495	-3455.564167	1.051633	-2167702.261000	8.675464	4.283E-07
1d-53	-3455.498118	-3455.499722	-3455.568462	1.058252	-2167702.260000	8.676035	4.279E-07
1d-54	-3455.494338	-3455.495704	-3455.564411	1.054544	-2167702.195000	8.741608	3.830E-07
1d-55	-3455.490538	-3455.494530	-3455.563839	1.051359	-2167702.186000	8.749929	3.777E-07
1d-56	-3455.485416	-3455.488822	-3455.561040	1.049220	-2167702.139000	8.796853	3.489E-07
1d-57	-3455.494101	-3455.495589	-3455.563933	1.054164	-2167702.057000	8.879765	3.033E-07
1d-58	-3455.488535	-3455.490828	-3455.562151	1.051791	-2167701.922000	9.014772	2.415E-07

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1d-59	-3455.486609	-3455.489538	-3455.560564	1.049582	-2167701.914000	9.022785	2.382E-07
1d-60	-3455.488120	-3455.492941	-3455.563264	1.050416	-2167701.897000	9.038968	2.318E-07
1d-61	-3455.487213	-3455.489759	-3455.562807	1.052397	-2167701.795000	9.141269	1.950E-07
1d-62	-3455.489480	-3455.490803	-3455.561892	1.052727	-2167701.781000	9.154874	1.906E-07
1d-63	-3455.489831	-3455.490944	-3455.562428	1.053517	-2167701.753000	9.182841	1.818E-07
1d-64	-3455.491244	-3455.493043	-3455.561216	1.051632	-2167701.745000	9.191463	1.792E-07
1d-65	-3455.490571	-3455.493282	-3455.562611	1.052420	-2167701.554000	9.382675	1.297E-07
1d-66	-3455.493335	-3455.496858	-3455.565018	1.054047	-2167701.534000	9.402416	1.255E-07
1d-67	-3455.493364	-3455.496910	-3455.565038	1.054270	-2167701.392000	9.544313	9.873E-08
1d-68	-3455.495630	-3455.498063	-3455.566380	1.057007	-2167701.215000	9.721475	7.320E-08
1d-69	-3455.488981	-3455.491172	-3455.560591	1.051613	-2167701.119000	9.817093	6.228E-08
1d-70	-3455.489611	-3455.493567	-3455.562759	1.052054	-2167701.095000	9.840901	5.983E-08
1d-71	-3455.488248	-3455.491171	-3455.561674	1.052089	-2167701.041000	9.895531	5.455E-08
1d-72	-3455.486791	-3455.489174	-3455.561819	1.052791	-2167701.030000	9.906236	5.358E-08
1d-73	-3455.486610	-3455.489390	-3455.558832	1.050073	-2167700.612000	10.324339	2.644E-08
1d-74	-3455.487635	-3455.490335	-3455.559425	1.051032	-2167700.432000	10.503911	1.952E-08
1d-75	-3455.486909	-3455.491746	-3455.561826	1.051473	-2167700.322000	10.614752	1.619E-08
1d-76	-3455.489801	-3455.493696	-3455.561682	1.052546	-2167700.149000	10.787597	1.209E-08
1d-77	-3455.487597	-3455.489837	-3455.558566	1.051356	-2167699.979000	10.957022	9.083E-09
1d-78	-3455.490249	-3455.492259	-3455.561321	1.055417	-2167699.303000	11.633072	2.900E-09
1d-79	-3455.487383	-3455.489967	-3455.559909	1.053527	-2167699.243000	11.692935	2.621E-09
1d-80	-3455.484024	-3455.489118	-3455.557834	1.051046	-2167697.923000	13.013754	2.816E-10
1d-81	-3455.486131	-3455.491303	-3455.558970	1.053001	-2167697.360000	13.576421	1.089E-10

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at B3LYP/6-31G(d) level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S4.8. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1e** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **1e.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1e-1	-3455.509977	-3455.509536	-3455.582765	1.058923	-2167712.097000	0.000000	1.435E-01
1e-2	-3455.509988	-3455.509484	-3455.582903	1.059385	-2167711.934000	0.163545	1.088E-01
1e-3	-3455.510023	-3455.509887	-3455.582896	1.059178	-2167711.829000	0.268539	9.116E-02

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1e-4	-3455.503346	-3455.503464	-3455.579651	1.056252	-2167711.469000	0.628240	4.965E-02
1e-5	-3455.503346	-3455.503468	-3455.579663	1.056321	-2167711.430000	0.666694	4.653E-02
1e-6	-3455.504560	-3455.503383	-3455.580734	1.058766	-2167711.384000	0.713493	4.299E-02
1e-7	-3455.504155	-3455.503898	-3455.580954	1.058106	-2167711.358000	0.738888	4.119E-02
1e-8	-3455.504154	-3455.503896	-3455.580947	1.058118	-2167711.347000	0.749806	4.044E-02
1e-9	-3455.502519	-3455.502594	-3455.580723	1.057608	-2167711.318000	0.779085	3.849E-02
1e-10	-3455.502858	-3455.502431	-3455.578832	1.056256	-2167711.294000	0.803137	3.695E-02
1e-11	-3455.502860	-3455.502433	-3455.578832	1.056258	-2167711.294000	0.803413	3.694E-02
1e-12	-3455.502416	-3455.503141	-3455.580859	1.057152	-2167711.281000	0.815932	3.616E-02
1e-13	-3455.509997	-3455.510036	-3455.583246	1.060338	-2167711.210000	0.887272	3.206E-02
1e-14	-3455.500939	-3455.501217	-3455.579081	1.056101	-2167711.106000	0.991362	2.689E-02
1e-15	-3455.507036	-3455.507544	-3455.580549	1.057447	-2167711.038000	1.059245	2.398E-02
1e-16	-3455.507034	-3455.507544	-3455.580544	1.057456	-2167711.028000	1.068953	2.359E-02
1e-17	-3455.507522	-3455.507109	-3455.580104	1.057951	-2167711.020000	1.077066	2.327E-02
1e-18	-3455.510460	-3455.510376	-3455.583078	1.060600	-2167711.017000	1.079833	2.316E-02
1e-19	-3455.510982	-3455.510818	-3455.583454	1.061211	-2167710.921000	1.176569	1.967E-02
1e-20	-3455.505274	-3455.505203	-3455.579040	1.056919	-2167710.785000	1.312033	1.565E-02
1e-21	-3455.511049	-3455.510558	-3455.583368	1.061700	-2167710.765000	1.332302	1.512E-02
1e-22	-3455.501194	-3455.501222	-3455.579236	1.057332	-2167710.587000	1.509840	1.120E-02
1e-23	-3455.507828	-3455.507429	-3455.580675	1.059249	-2167710.555000	1.542044	1.061E-02
1e-24	-3455.503520	-3455.504169	-3455.576793	1.054550	-2167710.410000	1.687398	8.300E-03
1e-25	-3455.510315	-3455.510778	-3455.583074	1.061283	-2167710.243000	1.853861	6.266E-03
1e-26	-3455.505466	-3455.505133	-3455.577632	1.056646	-2167710.238000	1.859496	6.206E-03
1e-27	-3455.501068	-3455.500907	-3455.579138	1.057992	-2167710.230000	1.866957	6.129E-03
1e-28	-3455.506256	-3455.506946	-3455.582878	1.061059	-2167710.118000	1.979047	5.072E-03
1e-29	-3455.506092	-3455.506711	-3455.582791	1.061341	-2167709.932000	2.165346	3.703E-03
1e-30	-3455.506090	-3455.506709	-3455.582791	1.061350	-2167709.926000	2.171181	3.666E-03
1e-31	-3455.505324	-3455.505638	-3455.577979	1.057083	-2167709.775000	2.322120	2.841E-03
1e-32	-3455.503172	-3455.503462	-3455.581156	1.060501	-2167709.639000	2.457936	2.259E-03
1e-33	-3455.507918	-3455.507960	-3455.580158	1.059808	-2167709.603000	2.494538	2.123E-03
1e-34	-3455.504869	-3455.504913	-3455.578603	1.058300	-2167709.572000	2.524953	2.017E-03
1e-35	-3455.504858	-3455.504513	-3455.577014	1.057163	-2167709.533000	2.563796	1.889E-03
1e-36	-3455.507927	-3455.508141	-3455.579813	1.059709	-2167709.341000	2.756093	1.365E-03
1e-37	-3455.507920	-3455.508138	-3455.579814	1.059724	-2167709.329000	2.767752	1.339E-03
1e-38	-3455.505124	-3455.505091	-3455.577258	1.058223	-2167708.825000	3.271898	5.713E-04
1e-39	-3455.507296	-3455.508559	-3455.581491	1.061175	-2167708.816000	3.281449	5.622E-04
1e-40	-3455.504597	-3455.504979	-3455.577421	1.057994	-2167708.811000	3.286205	5.577E-04
1e-41	-3455.507566	-3455.506918	-3455.578782	1.060390	-2167708.807000	3.289813	5.543E-04
1e-42	-3455.504594	-3455.504978	-3455.577419	1.058001	-2167708.804000	3.293233	5.511E-04

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1e-43	-3455.508833	-3455.508445	-3455.580029	1.061436	-2167708.771000	3.326597	5.209E-04
1e-44	-3455.508827	-3455.508442	-3455.580026	1.061432	-2167708.769000	3.327877	5.198E-04
1e-45	-3455.502985	-3455.503701	-3455.576293	1.056612	-2167708.760000	3.336957	5.118E-04
1e-46	-3455.502984	-3455.503701	-3455.576291	1.056612	-2167708.759000	3.338244	5.107E-04
1e-47	-3455.503445	-3455.503269	-3455.574239	1.055507	-2167708.725000	3.372191	4.823E-04
1e-48	-3455.504294	-3455.505857	-3455.578879	1.058624	-2167708.590000	3.507530	3.837E-04
1e-49	-3455.504299	-3455.505854	-3455.578873	1.058625	-2167708.589000	3.507869	3.835E-04
1e-50	-3455.503165	-3455.503395	-3455.574221	1.055398	-2167708.527000	3.570080	3.453E-04
1e-51	-3455.503695	-3455.503829	-3455.575836	1.057116	-2167708.523000	3.574027	3.430E-04
1e-52	-3455.503892	-3455.504765	-3455.577040	1.057681	-2167708.460000	3.636890	3.084E-04
1e-53	-3455.505487	-3455.505600	-3455.577403	1.058890	-2167708.405000	3.691846	2.811E-04
1e-54	-3455.501555	-3455.501371	-3455.574854	1.056741	-2167708.342000	3.755230	2.525E-04
1e-55	-3455.506623	-3455.505887	-3455.577262	1.059721	-2167708.329000	3.767924	2.472E-04
1e-56	-3455.504226	-3455.504150	-3455.576496	1.058393	-2167708.267000	3.829927	2.226E-04
1e-57	-3455.501738	-3455.501974	-3455.575831	1.057764	-2167708.049000	4.048285	1.540E-04
1e-58	-3455.505814	-3455.506118	-3455.578529	1.060511	-2167707.975000	4.121928	1.359E-04
1e-59	-3455.506319	-3455.506374	-3455.577726	1.060005	-2167707.946000	4.151527	1.293E-04
1e-60	-3455.504662	-3455.504589	-3455.576907	1.059404	-2167707.889000	4.208028	1.175E-04
1e-61	-3455.502794	-3455.503132	-3455.573915	1.056334	-2167707.680000	4.417211	8.256E-05
1e-62	-3455.503656	-3455.503774	-3455.574446	1.057631	-2167707.337000	4.759820	4.629E-05
1e-63	-3455.503522	-3455.502217	-3455.574118	1.059542	-2167706.826000	5.271414	1.951E-05
1e-64	-3455.503443	-3455.503573	-3455.573377	1.058528	-2167706.096000	6.000688	5.693E-06
1e-65	-3455.503444	-3455.503570	-3455.573373	1.058539	-2167706.089000	6.007898	5.624E-06
1e-66	-3455.505096	-3455.504650	-3455.574371	1.060257	-2167705.996000	6.101314	4.803E-06
1e-67	-3455.502345	-3455.505718	-3455.577515	1.059604	-2167705.983000	6.114555	4.697E-06
1e-68	-3455.504474	-3455.504318	-3455.573761	1.059430	-2167705.951000	6.146457	4.450E-06
1e-69	-3455.504473	-3455.504318	-3455.573756	1.059424	-2167705.950000	6.146996	4.446E-06
1e-70	-3455.501512	-3455.500982	-3455.570825	1.057402	-2167705.615000	6.482000	2.525E-06
1e-71	-3455.503069	-3455.502819	-3455.572923	1.059336	-2167705.543000	6.554043	2.236E-06
1e-72	-3455.494346	-3455.495073	-3455.569372	1.055154	-2167705.325000	6.771685	1.548E-06
1e-73	-3455.500029	-3455.498691	-3455.569561	1.058564	-2167704.600000	7.496962	4.548E-07
1e-74	-3455.493709	-3455.495344	-3455.564402	1.053323	-2167702.786000	9.311008	2.124E-08
1e-75	-3455.500121	-3455.500204	-3455.569684	1.061466	-2167701.964000	10.132826	5.302E-09
1e-76	-3455.498866	-3455.498639	-3455.565624	1.058593	-2167701.414000	10.683068	2.093E-09
1e-77	-3455.498858	-3455.498635	-3455.565612	1.058603	-2167701.398000	10.699534	2.036E-09
1e-78	-3455.498041	-3455.498081	-3455.565336	1.058217	-2167701.302000	10.795240	1.732E-09
1e-79	-3455.496967	-3455.498219	-3455.565363	1.057803	-2167700.818000	11.279024	7.651E-10
1e-80	-3455.497686	-3455.498632	-3455.565865	1.059362	-2167700.347000	11.750082	3.453E-10

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at B3LYP/6-31G(d) level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S4.9. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1f** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **1f.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1f-1	-3455.509707	-3455.507974	-3455.579867	1.056549	-2167712.580000	0.000000	1.510E-01
1f-2	-3455.506558	-3455.507231	-3455.581561	1.056099	-2167712.415000	0.164443	1.144E-01
1f-3	-3455.504572	-3455.503862	-3455.581149	1.057162	-2167712.357000	0.222486	1.037E-01
1f-4	-3455.512037	-3455.511645	-3455.583528	1.059489	-2167712.190000	0.389709	7.819E-02
1f-5	-3455.513120	-3455.513388	-3455.584684	1.060031	-2167712.161000	0.418292	7.451E-02
1f-6	-3455.504058	-3455.503221	-3455.580225	1.056763	-2167712.107000	0.472244	6.802E-02
1f-7	-3455.501506	-3455.503527	-3455.579619	1.053331	-2167712.088000	0.492016	6.578E-02
1f-8	-3455.507333	-3455.505836	-3455.579629	1.057334	-2167711.789000	0.790368	3.975E-02
1f-9	-3455.510831	-3455.510186	-3455.582182	1.059061	-2167711.773000	0.806777	3.866E-02
1f-10	-3455.510438	-3455.509040	-3455.581851	1.059551	-2167711.730000	0.849585	3.596E-02
1f-11	-3455.508342	-3455.506063	-3455.579160	1.057818	-2167711.682000	0.897463	3.317E-02
1f-12	-3455.511808	-3455.511441	-3455.582589	1.059363	-2167711.665000	0.914995	3.220E-02
1f-13	-3455.511256	-3455.510986	-3455.581917	1.059449	-2167711.128000	1.451790	1.301E-02
1f-14	-3455.511773	-3455.511054	-3455.582086	1.060092	-2167711.112000	1.467352	1.267E-02
1f-15	-3455.513675	-3455.514367	-3455.584134	1.060850	-2167711.037000	1.542947	1.115E-02
1f-16	-3455.513674	-3455.514366	-3455.584132	1.060848	-2167711.037000	1.543179	1.115E-02
1f-17	-3455.510021	-3455.508909	-3455.580946	1.059736	-2167710.867000	1.712906	8.368E-03
1f-18	-3455.509683	-3455.509030	-3455.580521	1.058880	-2167710.849000	1.730250	8.126E-03
1f-19	-3455.512279	-3455.512604	-3455.582636	1.060034	-2167710.839000	1.740666	7.985E-03
1f-20	-3455.507205	-3455.504902	-3455.579445	1.059503	-2167710.818000	1.761248	7.712E-03
1f-21	-3455.507490	-3455.505425	-3455.578618	1.058599	-2167710.718000	1.862037	6.505E-03
1f-22	-3455.506113	-3455.504683	-3455.578090	1.057461	-2167710.702000	1.877725	6.335E-03
1f-23	-3455.506109	-3455.504683	-3455.578091	1.057466	-2167710.698000	1.881979	6.289E-03
1f-24	-3455.503405	-3455.505209	-3455.580797	1.056986	-2167710.669000	1.910505	5.994E-03
1f-25	-3455.506108	-3455.505771	-3455.580918	1.059269	-2167710.656000	1.923237	5.866E-03
1f-26	-3455.503053	-3455.504316	-3455.579886	1.056743	-2167710.590000	1.990041	5.240E-03
1f-27	-3455.507324	-3455.505719	-3455.578300	1.058145	-2167710.515000	2.064826	4.618E-03

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1f-28	-3455.504143	-3455.503412	-3455.578427	1.057434	-2167710.491000	2.088301	4.439E-03
1f-29	-3455.508324	-3455.507565	-3455.580681	1.059920	-2167710.364000	2.216092	3.577E-03
1f-30	-3455.506528	-3455.504741	-3455.578879	1.059193	-2167710.334000	2.245277	3.405E-03
1f-31	-3455.506049	-3455.504903	-3455.577642	1.057642	-2167710.129000	2.450551	2.408E-03
1f-32	-3455.512503	-3455.512649	-3455.582662	1.061377	-2167710.125000	2.454774	2.390E-03
1f-33	-3455.512505	-3455.512647	-3455.582659	1.061389	-2167710.118000	2.461645	2.363E-03
1f-34	-3455.506523	-3455.505175	-3455.578283	1.058507	-2167710.115000	2.464506	2.351E-03
1f-35	-3455.506134	-3455.507563	-3455.580289	1.057838	-2167710.051000	2.528612	2.110E-03
1f-36	-3455.510284	-3455.509139	-3455.580727	1.060984	-2167709.967000	2.612929	1.830E-03
1f-37	-3455.512750	-3455.512554	-3455.582263	1.061636	-2167709.926000	2.653227	1.710E-03
1f-38	-3455.503483	-3455.502881	-3455.577302	1.057194	-2167709.856000	2.723858	1.517E-03
1f-39	-3455.507940	-3455.506768	-3455.579474	1.059993	-2167709.820000	2.759864	1.428E-03
1f-40	-3455.503962	-3455.503204	-3455.577299	1.057418	-2167709.810000	2.769327	1.405E-03
1f-41	-3455.508903	-3455.507851	-3455.579062	1.059663	-2167709.693000	2.886826	1.152E-03
1f-42	-3455.504661	-3455.504555	-3455.576499	1.056389	-2167709.546000	3.034013	8.987E-04
1f-43	-3455.510533	-3455.510865	-3455.581471	1.060982	-2167709.508000	3.071725	8.432E-04
1f-44	-3455.512100	-3455.512509	-3455.582102	1.061618	-2167709.457000	3.123130	7.731E-04
1f-45	-3455.512110	-3455.512512	-3455.582108	1.061645	-2167709.448000	3.131250	7.626E-04
1f-46	-3455.507418	-3455.506318	-3455.579345	1.060399	-2167709.439000	3.141033	7.501E-04
1f-47	-3455.506921	-3455.506756	-3455.580342	1.060524	-2167709.399000	3.180779	7.014E-04
1f-48	-3455.502964	-3455.504544	-3455.579795	1.058263	-2167709.380000	3.199447	6.796E-04
1f-49	-3455.502962	-3455.504543	-3455.579793	1.058260	-2167709.379000	3.200225	6.787E-04
1f-50	-3455.506858	-3455.506825	-3455.579440	1.059684	-2167709.278000	3.301849	5.717E-04
1f-51	-3455.506664	-3455.506929	-3455.579706	1.059818	-2167709.174000	3.406183	4.793E-04
1f-52	-3455.503904	-3455.503322	-3455.575240	1.056224	-2167709.158000	3.422084	4.666E-04
1f-53	-3455.505475	-3455.503958	-3455.576968	1.058966	-2167709.108000	3.472190	4.288E-04
1f-54	-3455.507904	-3455.507039	-3455.578077	1.059467	-2167709.081000	3.498971	4.098E-04
1f-55	-3455.508775	-3455.508889	-3455.580326	1.060927	-2167708.961000	3.618416	3.349E-04
1f-56	-3455.511287	-3455.512185	-3455.582973	1.062827	-2167708.938000	3.641226	3.223E-04
1f-57	-3455.502836	-3455.502843	-3455.577045	1.057851	-2167708.900000	3.679967	3.019E-04
1f-58	-3455.500670	-3455.502142	-3455.575800	1.055264	-2167708.823000	3.757125	2.650E-04
1f-59	-3455.508179	-3455.506794	-3455.580409	1.062744	-2167708.814000	3.765979	2.610E-04
1f-60	-3455.500668	-3455.502140	-3455.575790	1.055272	-2167708.811000	3.768307	2.600E-04
1f-61	-3455.511813	-3455.512638	-3455.583329	1.063651	-2167708.690000	3.889245	2.120E-04
1f-62	-3455.508772	-3455.509194	-3455.579793	1.060846	-2167708.484000	4.095536	1.496E-04
1f-63	-3455.504246	-3455.503721	-3455.575945	1.057946	-2167708.484000	4.095623	1.496E-04
1f-64	-3455.506200	-3455.506753	-3455.579060	1.060150	-2167708.379000	4.200548	1.253E-04
1f-65	-3455.505652	-3455.505758	-3455.578054	1.059650	-2167708.342000	4.237677	1.177E-04
1f-66	-3455.506660	-3455.506187	-3455.579251	1.061615	-2167708.223000	4.356218	9.634E-05

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1f-67	-3455.511810	-3455.512624	-3455.582673	1.063901	-2167708.129000	4.450864	8.210E-05
1f-68	-3455.503641	-3455.503155	-3455.574302	1.056866	-2167708.106000	4.473548	7.902E-05
1f-69	-3455.505262	-3455.505619	-3455.577630	1.059747	-2167707.857000	4.722565	5.189E-05
1f-70	-3455.504541	-3455.504845	-3455.576638	1.059165	-2167707.633000	4.946463	3.555E-05
1f-71	-3455.509611	-3455.510211	-3455.579650	1.061895	-2167707.624000	4.955211	3.503E-05
1f-72	-3455.501967	-3455.501103	-3455.574774	1.058511	-2167707.607000	4.972498	3.402E-05
1f-73	-3455.505109	-3455.505583	-3455.577568	1.059983	-2167707.597000	4.982821	3.343E-05
1f-74	-3455.504515	-3455.504580	-3455.576799	1.059819	-2167707.474000	5.105359	2.718E-05
1f-75	-3455.504514	-3455.504579	-3455.576795	1.059822	-2167707.470000	5.109908	2.698E-05
1f-76	-3455.505119	-3455.504072	-3455.574999	1.059192	-2167707.436000	5.143862	2.547E-05
1f-77	-3455.504472	-3455.504494	-3455.576625	1.059804	-2167707.401000	5.178657	2.402E-05
1f-78	-3455.508976	-3455.509726	-3455.579439	1.061893	-2167707.400000	5.179937	2.397E-05
1f-79	-3455.508978	-3455.509729	-3455.579441	1.061899	-2167707.396000	5.183382	2.383E-05
1f-80	-3455.501370	-3455.500337	-3455.570753	1.057678	-2167705.713000	6.866707	1.388E-06
1f-81	-3455.500733	-3455.501795	-3455.572614	1.057560	-2167705.640000	6.939817	1.227E-06
1f-82	-3455.500261	-3455.499850	-3455.571835	1.058879	-2167705.248000	7.332080	6.325E-07
1f-83	-3455.500811	-3455.499678	-3455.571533	1.059314	-2167705.238000	7.341210	6.228E-07

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at B3LYP/6-31G(d) level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S4.10. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1g** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **1g.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1g-1	-3455.514017	-3455.513006	-3455.585927	1.061919	-2167712.560000	0.000000	3.878E-01
1g-2	-3455.511775	-3455.512058	-3455.584922	1.060952	-2167711.724000	0.835824	9.453E-02
1g-3	-3455.510486	-3455.511378	-3455.583745	1.059448	-2167711.547000	1.013074	7.007E-02
1g-4	-3455.510480	-3455.511378	-3455.583749	1.059466	-2167711.534000	1.025454	6.862E-02
1g-5	-3455.510477	-3455.511374	-3455.583745	1.059490	-2167711.518000	1.042102	6.672E-02
1g-6	-3455.511843	-3455.513832	-3455.585454	1.060254	-2167711.424000	1.135373	5.700E-02
1g-7	-3455.510624	-3455.512254	-3455.583878	1.059179	-2167711.335000	1.224416	4.904E-02
1g-8	-3455.503015	-3455.503293	-3455.575478	1.052478	-2167711.118000	1.441587	3.398E-02
1g-9	-3455.510077	-3455.512035	-3455.583862	1.059252	-2167711.074000	1.485713	3.154E-02

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1g-10	-3455.509076	-3455.510073	-3455.581533	1.057929	-2167711.046000	1.514013	3.007E-02
1g-11	-3455.507854	-3455.509689	-3455.580709	1.056931	-2167710.629000	1.930284	1.489E-02
1g-12	-3455.507852	-3455.509685	-3455.580706	1.056941	-2167710.622000	1.937344	1.471E-02
1g-13	-3455.509200	-3455.510132	-3455.582813	1.060462	-2167710.300000	2.259471	8.538E-03
1g-14	-3455.505653	-3455.506180	-3455.577040	1.055293	-2167710.175000	2.384331	6.915E-03
1g-15	-3455.505328	-3455.506841	-3455.576771	1.054125	-2167710.121000	2.439074	6.304E-03
1g-16	-3455.511906	-3455.511521	-3455.583502	1.062865	-2167710.051000	2.508481	5.607E-03
1g-17	-3455.507473	-3455.508372	-3455.581265	1.059380	-2167710.028000	2.531178	5.396E-03
1g-18	-3455.504492	-3455.506406	-3455.576320	1.053584	-2167709.926000	2.633618	4.539E-03
1g-19	-3455.504492	-3455.506408	-3455.576325	1.053590	-2167709.924000	2.635305	4.526E-03
1g-20	-3455.506442	-3455.507003	-3455.576703	1.055343	-2167709.912000	2.647868	4.431E-03
1g-21	-3455.511955	-3455.512347	-3455.582372	1.061245	-2167709.871000	2.688869	4.134E-03
1g-22	-3455.508893	-3455.509931	-3455.581251	1.059798	-2167709.670000	2.889430	2.946E-03
1g-23	-3455.503450	-3455.504693	-3455.578077	1.056468	-2167709.640000	2.919758	2.799E-03
1g-24	-3455.503452	-3455.504693	-3455.578077	1.056470	-2167709.639000	2.920404	2.796E-03
1g-25	-3455.506431	-3455.506787	-3455.577962	1.057367	-2167709.560000	2.999607	2.446E-03
1g-26	-3455.506732	-3455.507269	-3455.580894	1.060249	-2167709.477000	3.082475	2.127E-03
1g-27	-3455.506741	-3455.507272	-3455.580885	1.060257	-2167709.471000	3.089088	2.103E-03
1g-28	-3455.509794	-3455.509902	-3455.581990	1.061825	-2167709.446000	3.113611	2.018E-03
1g-29	-3455.506822	-3455.507891	-3455.578773	1.057716	-2167709.403000	3.156683	1.876E-03
1g-30	-3455.504692	-3455.506137	-3455.578216	1.057149	-2167709.173000	3.386718	1.272E-03
1g-31	-3455.505268	-3455.505315	-3455.576652	1.057053	-2167709.129000	3.430699	1.181E-03
1g-32	-3455.506136	-3455.507600	-3455.579193	1.058326	-2167709.036000	3.523802	1.009E-03
1g-33	-3455.502860	-3455.503950	-3455.577706	1.057217	-2167709.033000	3.526983	1.004E-03
1g-34	-3455.506133	-3455.507598	-3455.579188	1.058328	-2167709.030000	3.529361	9.998E-04
1g-35	-3455.506090	-3455.508012	-3455.580055	1.058754	-2167709.021000	3.539044	9.836E-04
1g-36	-3455.503965	-3455.504178	-3455.578452	1.059198	-2167708.808000	3.751471	6.870E-04
1g-37	-3455.501286	-3455.502925	-3455.576478	1.056346	-2167708.464000	4.095630	3.842E-04
1g-38	-3455.503525	-3455.505521	-3455.575135	1.054724	-2167708.416000	4.144123	3.540E-04
1g-39	-3455.503075	-3455.504207	-3455.578306	1.058992	-2167708.269000	4.290625	2.764E-04
1g-40	-3455.501463	-3455.502699	-3455.575779	1.056433	-2167708.224000	4.335900	2.560E-04
1g-41	-3455.509429	-3455.511044	-3455.580094	1.060376	-2167708.220000	4.340135	2.542E-04
1g-42	-3455.501458	-3455.502691	-3455.575770	1.056469	-2167708.197000	4.362280	2.449E-04
1g-43	-3455.496654	-3455.498397	-3455.571177	1.051435	-2167708.154000	4.405853	2.275E-04
1g-44	-3455.504309	-3455.506088	-3455.578920	1.059175	-2167708.134000	4.425676	2.200E-04
1g-45	-3455.504307	-3455.506084	-3455.578914	1.059175	-2167708.131000	4.428694	2.189E-04
1g-46	-3455.504432	-3455.505130	-3455.576443	1.057909	-2167708.052000	4.507508	1.916E-04
1g-47	-3455.506635	-3455.508212	-3455.579391	1.060038	-2167708.015000	4.545058	1.798E-04
1g-48	-3455.504677	-3455.506257	-3455.576315	1.057012	-2167707.981000	4.578340	1.700E-04

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1g-49	-3455.501051	-3455.502365	-3455.576849	1.057826	-2167707.973000	4.587050	1.675E-04
1g-50	-3455.501847	-3455.503492	-3455.576194	1.056982	-2167707.883000	4.676682	1.440E-04
1g-51	-3455.505311	-3455.505552	-3455.577038	1.059283	-2167707.850000	4.709651	1.362E-04
1g-52	-3455.501794	-3455.502020	-3455.575462	1.057770	-2167707.820000	4.740022	1.294E-04
1g-53	-3455.500983	-3455.502732	-3455.576215	1.057278	-2167707.645000	4.914436	9.638E-05
1g-54	-3455.503380	-3455.504593	-3455.576546	1.058409	-2167707.479000	5.080202	7.284E-05
1g-55	-3455.508259	-3455.508877	-3455.574104	1.056803	-2167707.328000	5.231417	5.642E-05
1g-56	-3455.502626	-3455.503958	-3455.574816	1.056962	-2167707.227000	5.332834	4.754E-05
1g-57	-3455.500588	-3455.501228	-3455.574554	1.057414	-2167707.214000	5.345434	4.654E-05
1g-58	-3455.502432	-3455.502269	-3455.571307	1.054974	-2167707.211000	5.348377	4.631E-05
1g-59	-3455.498654	-3455.498218	-3455.574302	1.058264	-2167707.197000	5.362433	4.522E-05
1g-60	-3455.508406	-3455.509494	-3455.578210	1.060722	-2167707.151000	5.408504	4.184E-05
1g-61	-3455.500878	-3455.502507	-3455.572027	1.054016	-2167707.139000	5.420345	4.101E-05
1g-62	-3455.505493	-3455.505823	-3455.571478	1.054820	-2167707.106000	5.453527	3.877E-05
1g-63	-3455.503227	-3455.503976	-3455.575536	1.058466	-2167707.102000	5.457826	3.849E-05
1g-64	-3455.502507	-3455.504971	-3455.576650	1.057928	-2167707.063000	5.496988	3.603E-05
1g-65	-3455.502506	-3455.504972	-3455.576653	1.057931	-2167707.061000	5.498575	3.593E-05
1g-66	-3455.508943	-3455.507971	-3455.573533	1.058270	-2167707.048000	5.512155	3.512E-05
1g-67	-3455.499953	-3455.502193	-3455.574904	1.056733	-2167706.857000	5.702808	2.545E-05
1g-68	-3455.499601	-3455.502076	-3455.574359	1.056021	-2167706.814000	5.745346	2.369E-05
1g-69	-3455.506379	-3455.507435	-3455.575618	1.058843	-2167706.723000	5.836221	2.032E-05
1g-70	-3455.506828	-3455.507414	-3455.572800	1.056634	-2167706.636000	5.923198	1.754E-05
1g-71	-3455.498249	-3455.500230	-3455.572688	1.055427	-2167706.448000	6.111373	1.277E-05
1g-72	-3455.507650	-3455.508913	-3455.580386	1.064238	-2167706.200000	6.359204	8.399E-06
1g-73	-3455.504516	-3455.505609	-3455.573625	1.057760	-2167706.130000	6.429917	7.454E-06
1g-74	-3455.507105	-3455.507820	-3455.572702	1.058178	-2167705.525000	7.034438	2.685E-06
1g-75	-3455.501781	-3455.503162	-3455.571048	1.056648	-2167705.030000	7.530126	1.163E-06
1g-76	-3455.500393	-3455.502479	-3455.572459	1.057452	-2167704.968000	7.592141	1.047E-06
1g-77	-3455.504088	-3455.503466	-3455.570923	1.058916	-2167704.784000	7.775240	7.684E-07
1g-78	-3455.497809	-3455.500533	-3455.567992	1.054056	-2167703.895000	8.664263	1.712E-07
1g-79	-3455.502241	-3455.502701	-3455.568619	1.057101	-2167703.799000	8.761168	1.454E-07
1g-80	-3455.501844	-3455.502740	-3455.567924	1.056158	-2167703.681000	8.878786	1.192E-07
1g-81	-3455.501721	-3455.501966	-3455.568556	1.057937	-2167703.370000	9.189606	7.050E-08
1g-82	-3455.501912	-3455.503003	-3455.567849	1.057724	-2167702.529000	10.030769	1.703E-08
1g-83	-3455.498329	-3455.500736	-3455.570034	1.059338	-2167702.061000	10.498640	7.727E-09

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at B3LYP/6-31G(d) level of theory; [e]Gibbs free energy

(G = E_{M06} + T + ($E_{M05\text{-}Sol}$ – E_{M05}) + 1.89 kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S4.11. Conformational analysis of the B3LYP/6-31G(d) optimized conformers of **1h** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **1h.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1h-1	-3455.521553	-3455.524040	-3455.590791	1.059745	-2167714.781000	0.000000	1.500E-01
1h-2	-3455.520485	-3455.523194	-3455.590229	1.059168	-2167714.651000	0.129503	1.206E-01
1h-3	-3455.520487	-3455.523191	-3455.590218	1.059223	-2167714.613000	0.167994	1.130E-01
1h-4	-3455.514744	-3455.515650	-3455.586491	1.057295	-2167714.612000	0.168396	1.129E-01
1h-5	-3455.513315	-3455.512185	-3455.586566	1.059492	-2167714.558000	0.222693	1.030E-01
1h-6	-3455.519530	-3455.520559	-3455.588428	1.059635	-2167714.282000	0.498649	6.464E-02
1h-7	-3455.514438	-3455.515272	-3455.586137	1.057797	-2167714.120000	0.661134	4.912E-02
1h-8	-3455.514581	-3455.516414	-3455.586539	1.057495	-2167713.935000	0.845901	3.596E-02
1h-9	-3455.517756	-3455.520683	-3455.588202	1.058203	-2167713.848000	0.932302	3.107E-02
1h-10	-3455.516624	-3455.518350	-3455.587293	1.058626	-2167713.765000	1.015533	2.700E-02
1h-11	-3455.516617	-3455.518348	-3455.587286	1.058647	-2167713.745000	1.035839	2.609E-02
1h-12	-3455.520703	-3455.522415	-3455.590023	1.061419	-2167713.734000	1.046300	2.563E-02
1h-13	-3455.520704	-3455.522415	-3455.590022	1.061422	-2167713.733000	1.048214	2.555E-02
1h-14	-3455.518355	-3455.518357	-3455.586887	1.060230	-2167713.586000	1.194829	1.995E-02
1h-15	-3455.518490	-3455.520605	-3455.589224	1.060859	-2167713.332000	1.449136	1.298E-02
1h-16	-3455.513274	-3455.515041	-3455.585334	1.057599	-2167713.155000	1.626066	9.628E-03
1h-17	-3455.513453	-3455.515507	-3455.585563	1.057663	-2167713.079000	1.702238	8.466E-03
1h-18	-3455.516406	-3455.517755	-3455.586484	1.059525	-2167712.930000	1.850265	6.593E-03
1h-19	-3455.516386	-3455.517746	-3455.586479	1.059526	-2167712.920000	1.861146	6.473E-03
1h-20	-3455.517251	-3455.519389	-3455.588136	1.060423	-2167712.908000	1.872473	6.350E-03
1h-21	-3455.517000	-3455.518848	-3455.587637	1.060530	-2167712.710000	2.070380	4.546E-03
1h-22	-3455.517002	-3455.518850	-3455.587639	1.060535	-2167712.708000	2.072494	4.530E-03
1h-23	-3455.516045	-3455.516707	-3455.585337	1.059443	-2167712.693000	2.087661	4.415E-03
1h-24	-3455.516716	-3455.514600	-3455.583843	1.060764	-2167712.670000	2.110728	4.247E-03
1h-25	-3455.518861	-3455.522031	-3455.590148	1.061911	-2167712.589000	2.191318	3.706E-03
1h-26	-3455.514931	-3455.517357	-3455.587230	1.059789	-2167712.557000	2.223979	3.507E-03
1h-27	-3455.514770	-3455.516366	-3455.585106	1.058879	-2167712.316000	2.465090	2.334E-03
1h-28	-3455.516636	-3455.517459	-3455.585933	1.060639	-2167712.215000	2.565320	1.971E-03
1h-29	-3455.511601	-3455.515073	-3455.584906	1.056983	-2167712.203000	2.578115	1.928E-03
1h-30	-3455.516502	-3455.519259	-3455.587924	1.060753	-2167712.180000	2.600724	1.856E-03
1h-31	-3455.514880	-3455.515368	-3455.584030	1.059275	-2167712.087000	2.693286	1.588E-03
1h-32	-3455.513077	-3455.516525	-3455.586543	1.058907	-2167712.038000	2.742715	1.460E-03

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1h-33	-3455.514454	-3455.516834	-3455.584807	1.058678	-2167711.762000	3.018275	9.170E-04
1h-34	-3455.514500	-3455.516751	-3455.584609	1.058740	-2167711.680000	3.100528	7.981E-04
1h-35	-3455.516446	-3455.515780	-3455.583661	1.060869	-2167711.580000	3.200313	6.743E-04
1h-36	-3455.513251	-3455.516407	-3455.586242	1.059692	-2167711.540000	3.240492	6.300E-04
1h-37	-3455.516628	-3455.516978	-3455.585105	1.061408	-2167711.510000	3.270681	5.987E-04
1h-38	-3455.513463	-3455.515287	-3455.583301	1.058134	-2167711.508000	3.272845	5.965E-04
1h-39	-3455.515226	-3455.517008	-3455.586039	1.061001	-2167711.453000	3.327595	5.439E-04
1h-40	-3455.516144	-3455.514983	-3455.583252	1.061198	-2167711.428000	3.352883	5.211E-04
1h-41	-3455.517314	-3455.517944	-3455.586012	1.062299	-2167711.344000	3.436692	4.523E-04
1h-42	-3455.517317	-3455.517944	-3455.586009	1.062301	-2167711.344000	3.437069	4.520E-04
1h-43	-3455.510281	-3455.514181	-3455.584356	1.057670	-2167711.158000	3.622551	3.305E-04
1h-44	-3455.510671	-3455.512783	-3455.581052	1.056194	-2167711.133000	3.647839	3.167E-04
1h-45	-3455.516594	-3455.518719	-3455.587438	1.062605	-2167711.110000	3.671063	3.045E-04
1h-46	-3455.515619	-3455.519519	-3455.586336	1.059802	-2167711.063000	3.718025	2.813E-04
1h-47	-3455.513974	-3455.516234	-3455.584023	1.059363	-2167710.916000	3.865067	2.194E-04
1h-48	-3455.515265	-3455.518385	-3455.585654	1.060153	-2167710.905000	3.876199	2.153E-04
1h-49	-3455.515240	-3455.517747	-3455.584684	1.059990	-2167710.783000	3.997984	1.753E-04
1h-50	-3455.513553	-3455.517523	-3455.585785	1.059695	-2167710.741000	4.040190	1.632E-04
1h-51	-3455.516094	-3455.515425	-3455.583504	1.062164	-2167710.671000	4.110175	1.450E-04
1h-52	-3455.514255	-3455.515255	-3455.584004	1.061308	-2167710.475000	4.306100	1.042E-04
1h-53	-3455.511369	-3455.515785	-3455.585644	1.059831	-2167710.286000	4.494381	7.580E-05
1h-54	-3455.515185	-3455.514147	-3455.582094	1.061876	-2167710.198000	4.582294	6.534E-05
1h-55	-3455.512192	-3455.515437	-3455.584281	1.059842	-2167710.160000	4.621092	6.120E-05
1h-56	-3455.512191	-3455.515436	-3455.584278	1.059861	-2167710.146000	4.635085	5.977E-05
1h-57	-3455.515660	-3455.516798	-3455.583959	1.061852	-2167710.018000	4.762794	4.817E-05
1h-58	-3455.513306	-3455.517384	-3455.585438	1.060954	-2167709.665000	5.115556	2.655E-05
1h-59	-3455.513978	-3455.516248	-3455.584299	1.061654	-2167709.645000	5.135567	2.567E-05
1h-60	-3455.509824	-3455.513276	-3455.580945	1.057394	-2167709.472000	5.308637	1.916E-05
1h-61	-3455.510814	-3455.513911	-3455.582344	1.059403	-2167709.312000	5.468964	1.462E-05
1h-62	-3455.512796	-3455.516616	-3455.584478	1.060899	-2167709.259000	5.521969	1.336E-05
1h-63	-3455.508458	-3455.510429	-3455.580201	1.058901	-2167708.989000	5.791863	8.472E-06
1h-64	-3455.505759	-3455.508676	-3455.578516	1.056413	-2167708.900000	5.881043	7.287E-06
1h-65	-3455.512861	-3455.515360	-3455.583180	1.061565	-2167708.855000	5.925319	6.762E-06
1h-66	-3455.510483	-3455.512577	-3455.581780	1.060737	-2167708.751000	6.029760	5.669E-06
1h-67	-3455.510118	-3455.511672	-3455.579859	1.059493	-2167708.665000	6.116249	4.898E-06
1h-68	-3455.510755	-3455.511424	-3455.580088	1.060919	-2167708.469000	6.312066	3.519E-06
1h-69	-3455.513651	-3455.515458	-3455.582475	1.062327	-2167708.369000	6.411814	2.973E-06
1h-70	-3455.508978	-3455.510838	-3455.580210	1.060063	-2167708.335000	6.445454	2.809E-06
1h-71	-3455.513688	-3455.513765	-3455.580397	1.062387	-2167708.113000	6.667966	1.929E-06

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
1h-72	-3455.506921	-3455.509355	-3455.578634	1.058402	-2167708.028000	6.752716	1.672E-06
1h-73	-3455.508675	-3455.510796	-3455.580414	1.060614	-2167707.954000	6.826817	1.475E-06
1h-74	-3455.504987	-3455.506883	-3455.576876	1.057412	-2167707.884000	6.897160	1.310E-06
1h-75	-3455.504753	-3455.508009	-3455.576793	1.056005	-2167707.862000	6.919028	1.262E-06
1h-76	-3455.505692	-3455.509324	-3455.577631	1.056675	-2167707.731000	7.049793	1.012E-06
1h-77	-3455.507391	-3455.509517	-3455.578142	1.059272	-2167707.367000	7.413693	5.475E-07
1h-78	-3455.507320	-3455.509180	-3455.578435	1.060053	-2167707.227000	7.553387	4.324E-07
1h-79	-3455.511097	-3455.510229	-3455.578544	1.062958	-2167707.185000	7.595417	4.028E-07
1h-80	-3455.506983	-3455.509422	-3455.578047	1.060004	-2167706.652000	8.129187	1.635E-07
1h-81	-3455.505338	-3455.507181	-3455.575506	1.059088	-2167706.006000	8.775098	5.493E-08

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at B3LYP/6-31G(d) level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Part S5. Computational data of 2

Table S5.1. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **2a** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **2a.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
2a-1	-2533.187372	-2532.961202	-2533.013985	0.772557	-1589121.527337	0.000000	93.83%
2a-2	-2533.187242	-2532.961141	-2533.014809	0.776519	-1589119.514775	2.012562	3.13%
2a-3	-2533.182796	-2532.957704	-2533.009961	0.771299	-1589119.115484	2.411853	1.60%
2a-4	-2533.184471	-2532.958113	-2533.010671	0.773372	-1589119.055031	2.472306	1.44%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S5.2. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **2b** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **2b.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
2b-1	-2533.181622	-2532.953477	-2533.008827	0.769325	-1589121.558028	0.000000	88.70%
2b-2	-2533.182021	-2532.956093	-2533.012475	0.772908	-1589120.207786	1.350242	9.07%
2b-3	-2533.179015	-2532.953032	-2533.008274	0.770680	-1589119.004279	2.553749	1.19%
2b-4	-2533.178350	-2532.951993	-2533.007290	0.770195	-1589118.926042	2.631986	1.04%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S5.3. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **2b-1** at the PBE0/TZVP (methanol, IEFPCM solvent model) level of theory.

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
1	199->200	0.53065	3.6525	339.45	0.0076	-24.8912	-25.3821
	199->201	-0.45229					
2	199->200	0.43327	3.8153	324.96	0.0427	-19.5702	-18.6454
	199->201	0.47473					
3	196->200	0.49701	3.8443	322.51	0.0287	8.3264	9.77
	196->201	0.28269					
4	198->200	-0.3754	3.8513	321.93	0.0305	-20.9729	-21.8613
	198->201	0.48983					
5	197->200	0.54835	4.0106	309.14	0.0114	-17.4629	-17.8695
	197->201	-0.40215					
6	197->200	0.3771	4.1568	298.27	0.0557	12.5934	13.0077
	197->201	0.55663					
7	198->200	0.5698	4.2701	290.35	0.0009	-2.8337	-2.9612
	198->201	0.3928					
8	199->203	0.68401	4.3684	283.82	0.0092	-3.6129	-4.1752
9	193->200	-0.3211	4.4019	281.66	0.0019	0.8196	1.1915
	193->201	0.46804					
	198->201	-0.27631					
10	192->200	0.44513	4.4664	277.60	0.0027	21.2057	22.1777
	192->201	0.26825					
	196->200	0.36176					
11	196->201	0.61937	4.5277	273.83	0.0013	1.6324	1.6138
12	199->202	0.69689	4.6607	266.02	0.0014	-1.873	-1.9203
13	197->203	0.66516	4.7633	260.29	0.0327	5.4571	6.7351
14	198->203	0.51652	4.8289	256.75	0.1157	43.7457	47.4817
	199->204	-0.33367					
15	195->200	0.42023	4.8429	256.01	0.2534	-131.3267	-129.8471
	196->202	0.40123					
16	198->203	0.27287	4.8800	254.06	0.0090	-38.0385	-40.9884
	199->204	0.54612					
17	195->200	0.43179	4.9637	249.78	0.4314	217.0745	219.5648
	196->202	-0.32131					
18	196->202	0.23538	5.0184	247.06	0.0145	25.2058	26.2211
	197->202	0.6013					
19	197->206	0.26465	5.0614	244.96	0.0071	-33.4116	-32.2727
	198->202	0.31586					

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	199->207	0.36671					
20	198->202	0.62549	5.0692	244.58	0.0066	-12.1841	-11.8838
21	194->200	-0.37986	5.1011	243.05	0.0929	51.012	55.8162
	194->201	0.40486					
	197->206	0.23218					
	199->207	0.22453					
22	195->200	-0.22503	5.2196	237.54	0.0082	-9.999	-10.316
	195->201	0.5424					
23	197->204	0.64323	5.2461	236.33	0.0126	-7.4445	-7.3265
24	198->203	0.30521	5.2582	235.79	0.3461	-88.1224	-85.1235
	198->204	0.37499					
25	199->205	0.69632	5.2774	234.93	0.0038	8.1349	8.5188
26	190->200	0.34622	5.2935	234.22	0.3380	-171.0857	-171.7192
	196->202	-0.28579					
27	196->203	0.69187	5.3056	233.69	0.0088	-3.5028	-3.5337
28	189->201	-0.2251	5.3816	230.39	0.1005	47.3909	48.116
	193->203	0.31988					
	198->204	0.46586					
29	191->200	0.24589	5.3918	229.95	0.0292	42.935	41.8219
	194->200	0.42554					
	194->201	0.38392					
30	191->200	0.54259	5.4097	229.19	0.0295	-8.4559	-10.324
	191->201	0.23724					
	194->200	-0.25715					
31	197->207	-0.23695	5.4369	228.04	0.0961	0.2789	0.9331
	199->206	0.58836					
32	193->200	0.57123	5.4947	225.64	0.0002	-0.3292	-0.3899
	193->201	0.38994					
33	190->200	0.26312	5.5136	224.87	0.3466	119.3537	117.8788
	196->205	0.53112					
34	191->201	0.2272	5.5537	223.25	0.0007	0.4872	0.5514
	192->200	-0.31088					
	192->201	0.51622					
35	198->206	0.64874	5.5985	221.46	0.0039	16.1425	17.247
36	190->200	0.24443	5.6070	221.12	0.0338	-18.7263	-19.4625
	192->202	0.39596					
	195->202	0.3415					

[a]Number of the excited states; [b]Only transitions with contribution over 10.0% were listed; [c]Configuration-interaction coefficient; [d]Excitation energy; [e]Wavelength;[f]Oscillator strength; [g]Rotatory strength in velocity form (10^{-40} cgs); [h]Rotatory strength in length form (10^{-40} cgs).

Table S5.4. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **2b-2** at the PBE0/TZVP (methanol, IEFPCM solvent model) level of theory.

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
1	192->200	-0.23439	3.8295	323.76	0.0238	-35.8705	-35.1096
	196->200	0.36896					
	198->200	0.45657					
2	199->200	0.55516	3.8762	319.86	0.0309	-26.4341	-26.9412
	199->201	0.41594					
3	198->201	0.52028	3.9358	315.02	0.0186	11.3877	11.12
4	199->200	-0.41052	3.9751	311.90	0.0290	16.4491	17.3952
	199->201	0.56408					
5	197->200	0.57628	4.1753	296.94	0.0123	-6.7074	-6.7816
	198->200	0.27323					
6	196->200	0.41558	4.2053	294.83	0.0031	6.1969	6.3945
	197->201	0.29951					
	198->200	-0.3783					
7	197->200	-0.27575	4.2762	289.94	0.0086	7.1835	7.9073
	197->201	0.57923					
8	193->201	0.33445	4.4431	279.05	0.0023	-3.7593	-3.8856
	194->201	0.29931					
	198->201	0.37999					
9	192->200	0.47216	4.5102	274.90	0.0031	20.4974	21.0277
	196->200	0.28002					
10	196->201	0.57402	4.5624	271.75	0.0014	-2.8955	-2.6216
11	199->202	0.59055	4.6352	267.48	0.0086	5.1845	5.1297
	199->203	-0.30445					
12	198->202	0.61872	4.6897	264.37	0.0658	-143.9978	-150.2044
13	199->202	0.36742	4.7600	260.47	0.0369	16.7998	18.1399
	199->203	0.50677					
14	196->202	0.48908	4.8538	255.44	0.0874	-168.2104	-172.5123
	197->202	-0.24609					
	198->203	-0.23928					
15	195->200	0.49943	4.8911	253.49	0.1529	241.8605	249.0366
	195->201	0.33286					
16	198->203	0.53705	4.9266	251.66	0.3068	234.7257	242.7492
17	197->202	-0.23904	4.9440	250.78	0.0128	25.2189	26.6428
	197->203	0.30274					
	197->204	0.27281					
	199->207	0.33308					

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
18	197->202	0.48243	4.9778	249.08	0.0054	-2.748	-2.5745
	199->204	0.22473					
19	195->201	0.52286	4.9967	248.13	0.1104	66.667	73.5232
20	196->203	0.47965	5.0133	247.31	0.0863	7.8955	8.6368
	198->204	-0.29627					
21	197->202	-0.24352	5.0728	244.41	0.0313	39.8949	40.1492
	197->203	-0.30731					
	199->204	0.44816					
22	193->200	-0.34172	5.1314	241.62	0.0713	-30.5141	-31.0764
	194->200	0.3874					
	195->200	-0.26158					
23	197->203	0.40164	5.1389	241.27	0.0177	28.6168	29.6316
	197->206	-0.24431					
	199->204	0.25751					
	199->207	-0.32476					
24	198->203	0.27417	5.2869	234.51	0.4244	389.7867	402.4854
	198->204	-0.23284					
25	199->205	0.66363	5.3219	232.97	0.0132	5.288	5.512
26	196->203	0.30035	5.3255	232.81	0.4815	-484.0703	-497.5062
	198->204	0.23943					
27	191->200	-0.25203	5.3346	232.42	0.0808	114.1319	118.6088
	191->201	-0.28456					
	193->201	-0.31411					
	194->201	0.34975					
28	193->200	0.49795	5.3728	230.76	0.0057	-14.8925	-15.3392
	194->200	0.39399					
	194->201	-0.23272					
29	189->200	-0.23911	5.3997	229.61	0.0404	-8.0384	-10.6966
	191->200	0.28495					
	198->204	-0.2776					
	198->205	-0.23775					
30	197->204	0.51544	5.4093	229.21	0.0291	-23.823	-24.4273
	199->206	-0.23863					
31	190->201	0.27494	5.4417	227.84	0.1091	55.0634	56.7171
	198->204	0.33943					
	198->205	-0.27429					
32	191->200	0.33261	5.4867	225.97	0.0213	-24.0313	-24.7068
	198->205	0.32035					
33	197->207	-0.25375	5.4904	225.82	0.0333	53.566	57.4619

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	199->206	0.56635					
34	195->202	0.23001	5.5549	223.20	0.0266	-24.5556	-25.7166
	196->205	0.37044					
	198->205	-0.28522					
35	191->201	0.33783	5.5938	221.65	0.0205	-13.2109	-13.4642
	192->201	0.46502					
36	195->202	0.42668	5.6035	221.26	0.0089	32.2831	32.9709
	195->203	-0.40215					

[a]Number of the excited states; [b]Only transitions with contribution over 10.0% were listed; [c]Configuration-interaction coefficient; [d]Excitation energy; [e]Wavelength; [f]Oscillator strength; [g]Rotatory strength in velocity form (10^{-40} cgs); [h]Rotatory strength in length form (10^{-40} cgs).

Table S5.5. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **2c** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **2c.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
2c-1	-2533.185017	-2532.960487	-2533.016703	0.773922	-1589121.347552	0.000000	25.41%
2c-2	-2533.186626	-2532.961993	-2533.016525	0.773979	-1589121.264973	0.082579	22.10%
2c-3	-2533.188794	-2532.963675	-2533.017910	0.775870	-1589121.252517	0.095035	21.64%
2c-4	-2533.186688	-2532.961040	-2533.016156	0.775396	-1589120.781334	0.566218	9.77%
2c-5	-2533.187527	-2532.961946	-2533.017202	0.776730	-1589120.558540	0.789012	6.70%
2c-6	-2533.188251	-2532.962446	-2533.016534	0.776882	-1589120.184079	1.163473	3.56%
2c-7	-2533.188762	-2532.962538	-2533.017972	0.778758	-1589120.172853	1.174699	3.49%
2c-8	-2533.188226	-2532.961697	-2533.017131	0.778490	-1589120.004257	1.343296	2.63%
2c-9	-2533.181093	-2532.954794	-2533.011306	0.772495	-1589119.966939	1.380613	2.47%
2c-10	-2533.188746	-2532.961710	-2533.017363	0.779387	-1589119.904879	1.442673	2.22%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S5.6. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **2d** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **2d.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
2d-1	-2533.180397	-2532.953312	-2533.010297	0.770145	-1589121.301236	0.000000	63.29%
2d-2	-2533.178580	-2532.952446	-2533.010870	0.771284	-1589120.348949	0.952288	12.67%
2d-3	-2533.181295	-2532.954534	-2533.011206	0.772317	-1589120.304879	0.996357	11.76%
2d-4	-2533.182196	-2532.956196	-2533.008464	0.769602	-1589119.810717	1.490520	5.11%
2d-5	-2533.182183	-2532.956136	-2533.010241	0.771673	-1589119.655567	1.645669	3.93%
2d-6	-2533.180913	-2532.955243	-2533.011922	0.773162	-1589119.540082	1.761154	3.23%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Part S6. Computational data of 3 in methanol

Table S6.1. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **3em** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **3em.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
3em-1	-2533.178093	-2532.951003	-2533.006638	0.771773	-1589117.986894	0.000000	91.01%
3em-2	-2533.185035	-2532.959512	-2533.011002	0.777395	-1589116.214113	1.772782	4.56%
3em-3	-2533.187386	-2532.961440	-2533.012625	0.780044	-1589115.835554	2.151340	2.41%
3em-4	-2533.185749	-2532.960022	-2533.011354	0.778718	-1589115.732720	2.254175	2.02%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S6.2. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **3fm** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **3fm.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
3fm-1	-2533.178430	-2532.950060	-2533.006644	0.772195	-1589118.528853	0.000000	53.34%
3fm-2	-2533.181936	-2532.952790	-2533.009088	0.776077	-1589118.113618	0.415236	26.45%
3fm-3	-2533.173389	-2532.945240	-2533.002428	0.768998	-1589117.750873	0.777981	14.34%
3fm-4	-2533.179990	-2532.951246	-2533.007855	0.775863	-1589117.222009	1.306844	5.87%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S6.3. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **3fm-1** at the PBE0/TZVP (methanol, IEFPCM solvent model) level of theory.

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
1	199->200	0.70131	3.7341	332.03	0.0159	1.1893	0.9805
2	192->200	-0.25336	3.8316	323.58	0.0278	-11.3351	-10.6382
	196->200	-0.23557					
	197->200	0.56441					
3	193->201	0.251	3.8925	318.52	0.0588	-12.6447	-11.9435
	198->200	0.23753					
	198->201	0.5532					
4	199->201	0.68392	3.9509	313.81	0.0031	4.9679	4.8004
5	196->200	0.62679	3.9978	310.13	0.0088	1.9442	1.4969
	197->200	0.26416					
6	196->201	0.61777	4.2715	290.26	0.0052	-4.2838	-4.4496
	197->201	0.27414					
7	198->200	0.63797	4.4501	278.61	0.0005	2.7852	2.9175
8	192->200	0.50922	4.4686	277.46	0.0007	9.3368	9.7862
	197->200	0.28934					
9	193->201	0.46306	4.5580	272.01	0.0053	-0.0224	0.3428
	198->201	-0.33824					
10	196->201	-0.28367	4.6377	267.34	0.0009	-0.1668	-0.2152
	197->201	0.62583					
11	199->202	0.67333	4.6490	266.69	0.0118	7.081	7.4404
12	199->203	0.60393	4.6597	266.08	0.0566	-11.4978	-10.9173
	199->204	0.23638					
13	194->200	0.25674	4.8541	255.42	0.4322	-462.92	-465.8164
	195->200	0.2771					
	197->202	0.3774					
	198->203	0.24834					
14	195->201	0.2752	4.8861	253.75	0.1753	102.5766	103.2913
	197->202	-0.29674					
	198->203	0.40285					
15	196->203	-0.26633	4.9368	251.14	0.0025	-6.8944	-7.612
	196->204	-0.27822					
	196->206	0.2311					
	199->207	0.35132					
16	196->202	0.6106	4.9484	250.56	0.0007	-6.0416	-6.3026
	197->202	0.26562					
17	195->200	0.45126	4.9747	249.23	0.0614	419.1996	419.6573

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	198->203	-0.2584					
18	196->203	0.51884	5.0366	246.17	0.0038	0.6281	0.0813
	197->203	0.23532					
19	194->200	-0.27975	5.0562	245.21	0.3703	-123.5573	-127.6322
	195->201	0.50509					
20	194->200	0.42543	5.1690	239.86	0.0894	97.7911	97.4792
	195->200	-0.38213					
	195->201	0.26764					
21	199->204	0.56693	5.2133	237.82	0.0060	14.7113	15.46
22	198->202	0.67688	5.2262	237.24	0.0001	-0.1237	-0.1237
23	199->205	0.56279	5.2707	235.23	0.0916	-76.3342	-75.8344
24	189->200	-0.31317	5.2903	234.36	0.1721	-91.2324	-90.9173
	197->202	0.24213					
	199->205	0.41163					
25	196->203	-0.2914	5.3132	233.35	0.0012	-1.0368	-1.0761
	197->203	0.63565					
26	190->201	-0.22622	5.3579	231.41	0.5019	87.9387	92.6981
	198->203	0.31971					
	198->204	-0.30465					
27	193->200	-0.25733	5.4064	229.33	0.0376	29.0277	28.8124
	193->201	0.22888					
	194->201	0.43199					
28	193->200	0.52704	5.4207	228.72	0.0851	32.0874	32.3061
	194->201	0.30728					
29	199->206	0.4826	5.4574	227.19	0.0161	47.623	46.661
	199->207	0.30393					
30	189->200	-0.28148	5.4828	226.13	0.4243	103.8628	101.377
	197->205	0.47655					
31	190->201	-0.3029	5.4942	225.66	0.0989	-6.2741	-8.7804
	198->204	0.46575					
32	196->205	0.57459	5.5552	223.19	0.0046	0.4446	0.3881
	197->205	0.27875					
33	196->204	0.51705	5.5765	222.33	0.0408	11.4949	10.5698
	197->204	0.24026					
34	191->200	0.48183	5.5891	221.83	0.0091	7.0176	7.668
	192->202	0.23706					
	196->205	-0.23403					
35	191->200	-0.2587	5.6111	220.96	0.0302	40.8734	42.7376
	192->202	0.36726					

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	194->202	0.26406					
36	195->203	0.553	5.6167	220.74	0.0180	-33.2477	-33.4563

[a]Number of the excited states; [b]Only transitions with contribution over 10.0% were listed; [c]Configuration-interaction coefficient; [d]Excitation energy; [e]Wavelength;[f]Oscillator strength; [g]Rotatory strength in velocity form (10^{-40} cgs); [h]Rotatory strength in length form (10^{-40} cgs).

Table S6.4. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **3fm-2** at the PBE0/TZVP (methanol, IEFPCM solvent model) level of theory.

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
1	199->200	0.68418	3.7342	332.03	0.0153	15.9958	15.7703
2	197->200	-0.29437	3.7864	327.45	0.0100	20.6998	21.6084
	197->201	-0.25599					
	198->200	0.38117					
	199->201	0.27316					
3	196->200	-0.24783	3.8332	323.45	0.0179	-22.5825	-22.6561
	199->201	0.52247					
4	196->200	0.33225	3.8758	319.89	0.0143	-17.7829	-16.3803
	196->201	-0.31339					
	199->201	0.37929					
5	197->200	0.40208	3.9743	311.96	0.0089	-0.1669	-0.849
	198->200	0.49299					
6	197->201	0.29297	4.0654	304.97	0.0043	3.0484	4.1698
	198->201	0.57694					
7	197->200	0.46442	4.3931	282.22	0.0009	4.2517	4.2988
	197->201	-0.4262					
8	193->200	0.33186	4.4620	277.87	0.0007	7.4461	7.269
	193->201	0.24879					
	196->200	-0.26429					
	197->201	-0.30572					
9	192->200	0.32282	4.4711	277.30	0.0020	10.0223	11.4442
	192->201	-0.26297					
	193->201	-0.24961					
	196->200	-0.29997					
10	199->202	0.60612	4.4921	276.01	0.0026	-10.3233	-10.7343
	199->203	0.30619					
11	196->200	0.32217	4.5333	273.49	0.0021	7.7704	7.7758
	196->201	0.54758					

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
12	199->202	-0.30381	4.5641	271.65	0.0169	6.9148	7.4328
	199->203	0.61844					
13	198->202	0.62958	4.7279	262.24	0.0083	13.1333	13.5344
14	198->203	0.59166	4.7764	259.58	0.0063	-2.4067	-2.6046
15	195->200	0.27435	4.8432	256.00	0.0339	-141.3447	-133.9526
	197->202	0.41744					
	197->203	0.32074					
16	198->207	-0.30848	4.9246	251.77	0.0207	-21.3561	-22.334
	199->206	0.47612					
17	195->200	0.44287	4.9569	250.13	0.4037	162.3736	169.7797
	195->201	0.26458					
18	196->202	0.40015	4.9723	249.35	0.3076	79.2458	77.5199
	196->203	-0.25921					
19	197->202	-0.4393	5.0348	246.26	0.0063	-0.5631	-0.4682
	197->203	0.46828					
20	194->200	-0.31826	5.0959	243.30	0.1040	62.1432	70.6494
	196->202	0.32293					
	199->205	0.33365					
21	196->202	0.32538	5.1105	242.61	0.0154	-1.8175	-1.8048
	196->203	0.43262					
	199->205	-0.38922					
22	194->200	0.25992	5.1304	241.67	0.1291	14.3919	18.0652
	196->203	0.32505					
	199->205	0.3975					
23	191->200	0.24455	5.2369	236.75	0.0014	-1.7063	-1.4026
	195->200	-0.34524					
	195->201	0.49032					
24	199->204	0.6724	5.2507	236.13	0.0299	-13.6344	-13.357
25	189->200	0.26524	5.2998	233.94	0.2087	178.2915	182.9906
	189->201	0.23001					
26	198->205	0.38189	5.3229	232.93	0.1679	-20.8046	-24.7411
27	194->200	0.3064	5.3594	231.34	0.1516	69.8573	72.2056
	194->201	0.34419					
28	191->200	0.27277	5.3757	230.64	0.0652	-45.9825	-47.9249
	194->200	0.26047					
	194->201	0.40559					
29	198->205	-0.28125	5.3927	229.91	0.0882	-70.9951	-72.9857
	199->207	0.36683					
30	198->205	0.24714	5.4208	228.72	0.0520	-40.881	-41.3764

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	198->206	0.24861					
	199->207	0.44092					
31	191->200	0.26804	5.4525	227.39	0.0063	6.7097	6.5318
	198->204	0.48117					
32	193->200	-0.392	5.4974	225.53	0.0137	7.4723	7.6597
	193->201	0.44982					
33	197->204	0.53129	5.5217	224.54	0.0525	-7.2265	-7.8268
	198->204	0.25134					
34	192->200	0.44232	5.5685	222.65	0.0026	-0.9236	-1.1256
	192->201	0.47568					
35	196->205	0.50797	5.5828	222.08	0.1418	-58.3296	-58.6142
	197->205	0.28601					
36	195->202	0.28976	5.6015	221.34	0.0627	-124.0437	-128.227
	195->203	0.26242					
	197->205	0.26418					

[a]Number of the excited states; [b]Only transitions with contribution over 10.0% were listed; [c]Configuration-interaction coefficient; [d]Excitation energy; [e]Wavelength;[f]Oscillator strength; [g]Rotatory strength in velocity form (10^{-40} cgs); [h]Rotatory strength in length form (10^{-40} cgs).

Table S6.5. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **3fm-3** at the PBE0/TZVP (methanol, IEFPCM solvent model) level of theory.

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
1	199->200	0.69602	3.7374	331.74	0.0119	-3.2014	-3.3192
2	192->200	0.2602	3.8213	324.45	0.0260	-0.1973	0.4913
	197->200	0.61164					
3	194->201	-0.28258	3.9609	313.02	0.0393	-55.6198	-55.8969
	198->200	0.28835					
	198->201	0.50592					
4	196->200	0.57197	4.0526	305.93	0.0090	-3.5468	-4.3836
	198->200	0.26612					
	199->201	-0.29213					
5	196->200	0.2717	4.0539	305.84	0.0006	-1.3461	-1.4407
	199->201	0.61926					
6	196->200	-0.28985	4.3103	287.65	0.0009	-0.2217	-0.1832
	198->200	0.57825					
	198->201	-0.22599					
7	196->201	0.58433	4.4086	281.24	0.0031	9.1484	9.0229

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	198->201	0.29846					
8	192->200	0.53647	4.4690	277.43	0.0006	8.2152	8.6719
	197->200	-0.31063					
9	194->201	0.47207	4.5400	273.09	0.0062	18.6461	18.8761
	196->201	-0.34338					
	198->201	0.25748					
10	199->202	0.69429	4.6638	265.84	0.0051	7.6037	7.7552
11	199->203	0.69067	4.6721	265.37	0.0168	-8.3284	-9.1407
12	197->201	0.68221	4.6741	265.26	0.0024	-0.9979	-1.0413
13	193->200	0.31583	4.8485	255.72	0.3820	-74.3114	-74.1099
	195->200	0.34293					
	197->202	0.41037					
14	195->200	0.23294	4.9099	252.52	0.0241	-145.0334	-148.0275
	197->202	-0.2857					
	198->203	0.42425					
15	195->200	-0.26015	4.9307	251.45	0.2171	12.1762	12.5718
	196->203	0.22868					
	198->203	0.30649					
	199->207	-0.2359					
16	195->200	-0.23165	4.9573	250.10	0.1885	33.3267	34.9282
	196->206	-0.24308					
	198->203	0.24285					
	199->207	0.31578					
17	196->202	0.54246	5.0057	247.69	0.0029	7.5874	8.2239
	198->202	0.38302					
18	193->200	-0.30601	5.0280	246.59	0.1711	154.0249	157.8406
	195->201	0.4519					
19	195->201	0.22537	5.0336	246.31	0.0674	68.6315	71.8235
	196->203	0.55387					
20	196->202	-0.40251	5.1476	240.86	0.0014	1.3553	1.3938
	198->202	0.56893					
21	193->200	0.45754	5.1747	239.60	0.0643	20.9228	20.5934
	195->200	-0.38656					
	195->201	0.26603					
22	197->203	0.51707	5.2666	235.42	0.2072	-16.6528	-16.9065
	198->204	-0.23238					
	199->204	-0.24341					
23	197->203	0.46832	5.2676	235.37	0.1364	7.031	7.8003
	199->204	0.27202					

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
24	190->200	0.30629	5.2752	235.03	0.2937	-109.8419	-111.6745
	197->202	-0.22704					
	199->205	0.37981					
25	190->200	-0.23191	5.2923	234.27	0.0809	-50.4178	-50.1562
	199->205	0.50843					
26	199->204	0.51176	5.3031	233.79	0.0215	-9.5354	-9.3696
	199->205	-0.2965					
27	194->200	0.62383	5.3479	231.84	0.0228	-9.1727	-9.2923
	194->201	-0.26737					
28	193->201	0.37413	5.3973	229.71	0.0062	1.5098	2.5481
	199->206	0.34876					
29	193->201	-0.33897	5.4119	229.10	0.0069	21.6101	20.9677
	199->206	0.39044					
30	189->201	0.25024	5.4471	227.62	0.0060	1.2689	1.0447
	194->203	-0.34181					
	198->204	0.40079					
31	190->200	-0.28739	5.4694	226.69	0.4159	104.04	102.3333
	197->205	0.47859					
32	191->200	0.56125	5.5203	224.60	0.0166	12.6055	12.4537
	193->201	-0.27168					
33	195->203	0.61356	5.5687	222.64	0.0940	-30.3521	-29.3602
34	192->202	-0.28743	5.6009	221.36	0.0067	10.6864	11.165
	196->205	0.40474					
	198->205	0.34124					
35	192->202	0.399	5.6193	220.64	0.0137	-18.4398	-18.5418
	196->205	0.30465					
	198->205	0.2463					
36	194->203	0.25485	5.6577	219.14	0.0504	2.8593	2.2537
	198->206	0.43548					
	199->208	-0.24881					

[a]Number of the excited states; [b]Only transitions with contribution over 10.0% were listed; [c]Configuration-interaction coefficient; [d]Excitation energy; [e]Wavelength;[f]Oscillator strength; [g]Rotatory strength in velocity form (10^{-40} cgs); [h]Rotatory strength in length form (10^{-40} cgs).

Table S6.6. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **3fm-4** at the PBE0/TZVP (methanol, IEFPCM solvent model) level of theory.

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
1	199->200	0.6886	3.6891	336.08	0.0107	7.0771	6.5978
2	197->200	0.27019	3.7740	328.52	0.0061	10.4941	10.7836
	197->201	0.24475					
	198->200	0.43713					
	199->201	0.27492					
3	199->201	0.59213	3.7847	327.59	0.0121	-16.2823	-16.3436
4	196->201	0.29523	3.8863	319.03	0.0218	-33.3969	-31.2421
	197->200	-0.24978					
	198->200	0.28256					
	198->201	-0.27698					
	199->201	-0.24912					
5	196->200	0.38625	3.9594	313.14	0.0185	30.3912	29.6825
	197->200	-0.25986					
	197->201	-0.24699					
	198->200	0.4138					
6	196->201	0.32476	4.0444	306.56	0.0045	-5.0635	-3.9835
	198->201	0.56956					
7	197->200	0.41255	4.4253	280.17	0.0018	7.0958	7.4811
	197->201	-0.40807					
8	199->202	0.65606	4.4378	279.38	0.0009	0.0047	-0.0121
	199->203	0.23869					
9	192->201	0.30068	4.4730	277.19	0.0006	3.338	3.3733
	193->200	-0.23689					
	196->200	0.37379					
10	193->200	0.27412	4.4852	276.43	0.0039	12.8697	14.2523
	193->201	0.29039					
	197->201	0.31619					
11	199->202	-0.23391	4.5008	275.47	0.0217	5.7837	5.682
	199->203	0.61342					
12	196->200	0.2754	4.5312	273.62	0.0026	6.4047	6.3488
	196->201	0.48024					
13	198->202	0.62699	4.6717	265.40	0.0139	2.9322	3.2537
	198->203	0.25288					
14	198->202	-0.23955	4.7101	263.23	0.0080	-1.7072	-1.6135
	198->203	0.59418					
15	195->200	0.31951	4.8440	255.96	0.0340	-241.5655	-236.199

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
	197->202	0.4614					
16	198->206	0.22637	4.9087	252.58	0.0210	-27.4027	-27.898
	199->204	-0.23354					
	199->206	0.36087					
	199->207	-0.23012					
17	195->200	0.41511	4.9648	249.73	0.3857	276.8392	287.6869
18	195->200	0.24996	4.9749	249.22	0.3418	44.193	39.3635
	196->203	0.41399					
19	196->203	-0.23128	5.0322	246.38	0.0015	0.8935	0.8586
	197->202	-0.22691					
	197->203	0.59549					
20	196->202	0.5521	5.0678	244.65	0.0071	-2.7731	-2.459
21	196->202	0.26716	5.0710	244.49	0.0477	-19.0806	-17.5401
	199->204	-0.25005					
	199->205	0.40491					
22	194->200	0.35532	5.1137	242.45	0.1551	51.7709	61.0089
	194->201	-0.28727					
	196->203	0.2257					
23	199->204	0.55169	5.1972	238.56	0.0054	-12.4226	-12.4922
	199->205	0.42226					
24	191->200	0.24855	5.2506	236.13	0.0022	0.7784	1.3874
	195->200	-0.29008					
	195->201	0.50846					
25	198->205	0.38246	5.2738	235.09	0.1399	166.536	167.8399
26	189->200	0.24445	5.3034	233.78	0.3235	-13.9774	-13.6243
	197->202	0.24332					
	198->204	0.24559					
27	191->200	-0.26505	5.3381	232.26	0.0519	83.4201	84.4502
	198->204	0.33944					
28	194->200	0.34837	5.3560	231.49	0.0107	-14.6086	-15.2909
	194->201	0.44964					
29	198->205	0.25867	5.3696	230.90	0.1448	-87.3071	-89.3768
	199->207	-0.24924					
30	198->205	0.27714	5.4116	229.11	0.0460	-19.1791	-18.8672
	199->206	0.34393					
	199->207	0.34779					
31	191->200	0.32641	5.4279	228.42	0.0461	-11.1444	-9.6349
	198->204	0.36567					
	198->205	0.2337					

Num[a]	Transition[b]	CI-coeff[c]	ΔE (eV)[d]	λ (nm)[e]	f[f]	R_{vel}[g]	R_{len}[h]
32	193->201	-0.31054	5.5047	225.23	0.0411	16.7372	16.5155
	197->204	0.38604					
33	192->201	0.30337	5.5145	224.83	0.0049	-7.1825	-7.3756
	193->200	0.31847					
	193->201	-0.30734					
34	192->200	0.42658	5.5367	223.93	0.0029	4.3663	4.2353
	192->201	0.33577					
35	196->204	-0.34779	5.5685	222.65	0.2082	-118.9297	-122.1837
	196->205	0.42093					
36	193->202	0.29741	5.5868	221.92	0.0499	-30.204	-31.0625
	195->202	0.47008					

[a]Number of the excited states; [b]Only transitions with contribution over 10.0% were listed; [c]Configuration-interaction coefficient; [d]Excitation energy; [e]Wavelength;[f]Oscillator strength; [g]Rotatory strength in velocity form (10^{-40} cgs); [h]Rotatory strength in length form (10^{-40} cgs).

Table S6.7. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **3gm** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **3gm.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
3gm-1	-2533.185543	-2532.958620	-2533.013336	0.773302	-1589121.125229	0.000000	58.59%
3gm-2	-2533.185720	-2532.958932	-2533.012694	0.774035	-1589120.178444	0.946785	11.84%
3gm-3	-2533.185485	-2532.958737	-2533.013088	0.774528	-1589120.090287	1.034942	10.20%
3gm-4	-2533.186738	-2532.958960	-2533.013462	0.776351	-1589119.828011	1.297218	6.55%
3gm-5	-2533.185272	-2532.957611	-2533.012053	0.775029	-1589119.700019	1.425209	5.28%
3gm-6	-2533.183919	-2532.957592	-2533.012603	0.774351	-1589119.633109	1.492120	4.71%
3gm-7	-2533.183255	-2532.956531	-2533.010819	0.773450	-1589119.328477	1.796752	2.82%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S6.8. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **3hm** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **3hm.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
3hm-1	-2533.179966	-2532.951142	-2533.003704	0.770884	-1589117.791999	0.000000	43.39%
3hm-2	-2533.178857	-2532.951799	-2533.006687	0.772699	-1589117.417018	0.374981	23.03%
3hm-3	-2533.178607	-2532.951670	-2533.006934	0.773472	-1589117.011063	0.780936	11.60%
3hm-4	-2533.179799	-2532.954086	-2533.007896	0.773260	-1589116.978690	0.813309	10.99%
3hm-5	-2533.178909	-2532.951451	-2533.005637	0.772853	-1589116.911824	0.880175	9.81%
3hm-6	-2533.179594	-2532.953531	-2533.007611	0.775441	-1589115.651565	2.140434	1.17%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent=Methanol)) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Part S7. Computational data of 3 in dimethyl sulfoxide

Table S7.1. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **3ed** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **3ed.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
3ed-1	-2533.178093	-2532.951003	-2532.990043	0.771773	-1589107.573312	0.000000	96.04%
3ed-2	-2533.185749	-2532.960022	-2532.994441	0.778718	-1589105.119919	2.453393	1.52%
3ed-3	-2533.185035	-2532.959512	-2532.993124	0.777395	-1589104.995981	2.577331	1.24%
3ed-4	-2533.187386	-2532.961440	-2532.995320	0.780044	-1589104.976749	2.596564	1.20%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent= DimethylSulfoxide) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S7.2. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **3fd** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **3fd.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
3fd-1	-2533.178430	-2532.950060	-2532.989242	0.772195	-1589107.608960	0.000000	63.11%
3fd-2	-2533.173389	-2532.945240	-2532.985495	0.768998	-1589107.124888	0.484072	27.86%
3fd-3	-2533.181936	-2532.952790	-2532.990312	0.776077	-1589106.331998	1.276963	7.30%
3fd-4	-2533.179990	-2532.951246	-2532.989141	0.775863	-1589105.478723	2.130237	1.73%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent= DimethylSulfoxide) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S7.3. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **3gd** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **3gd.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
3gd-1	-2533.185543	-2532.958620	-2532.995099	0.773302	-1589109.681900	0.000000	60.57%
3gd-2	-2533.185720	-2532.958932	-2532.994708	0.774035	-1589108.892098	0.789803	15.96%
3gd-3	-2533.185485	-2532.958737	-2532.994818	0.774528	-1589108.625661	1.056239	10.17%
3gd-4	-2533.185272	-2532.957611	-2532.993967	0.775029	-1589108.351054	1.330846	6.40%
3gd-5	-2533.183919	-2532.957592	-2532.994239	0.774351	-1589108.109825	1.572076	4.26%
3gd-6	-2533.183255	-2532.956531	-2532.992492	0.773450	-1589107.827933	1.853968	2.64%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent= DimethylSulfoxide) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.

Table S7.4. Conformational analysis of the M06-2X-D3/def2-SVP optimized conformers of **3hd** (T=298.15 K) (coordinates (Å) for all conformer are arranged in **3hd.xyz**)

Conformer	E_{M06}[a]	E_{M05}[b]	$E_{M05\text{-}Sol}$[c]	T[d]	G[e]	*rel*-G[f]	P[g]
3hd-1	-2533.179966	-2532.951142	-2532.988571	0.770884	-1589108.295634	0.000000	92.58%
3hd-2	-2533.179799	-2532.954086	-2532.991059	0.773260	-1589106.413673	1.881960	3.86%
3hd-3	-2533.178857	-2532.951799	-2532.988646	0.772699	-1589106.096202	2.199431	2.26%
3hd-4	-2533.178909	-2532.951451	-2532.987886	0.772853	-1589105.772626	2.523008	1.31%

[a]Electronic energy (A.U.) obtained at M06-2X-D3/6-311G(2d,p) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3/6-31G(d) level of theory; [b]Electronic energy (A.U.) obtained at M05-2X-D3-SCRF/6-31G(d) (SMD, Solvent= DimethylSulfoxide) level of theory; [d]Thermal correction to Gibbs free energy (A.U.) obtained at M06-2X-D3/def2-SVP level of theory; [e]Gibbs free energy ($G = E_{M06} + T + (E_{M05\text{-}Sol} - E_{M05}) + 1.89$ kcal/mol); [f]The relative Gibbs free energy (kcal/mol); [f]The Boltzmann distribution of each conformer.