Supporting Information

Phomoidrides E–G, Three Dimeric Anhydrides from the Fungus *Pleosporales* sp. Give New Insight to the Biosynthesis of Phomoidrides

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Table **S1**. Predicted functions of genes in the *phi* gene cluster.

Gene	Size (protein)	Predicted functions	Identities(%) /positives(%)	BlastP Homolog
phiP	508	MFS tansporter	100/76	XP_018070357.1
phiQ	507	FMN binding Oxidoreductase	100/82	XP_018031531.1
phiR	159	hypothetical protein	50/37	Q96S38.2
phiS	614	Sulfatase/Arylsulfatase	90/43	KXH36502.1
phiT	326	hypothetical protein	18/47	XP_023065433.1
phiU	403	methyltransferase	98/56	ORY13414.1
phiA	2591	PKS [KS, AT, DH, MT, ER, KR, ACP]	99/71	ADA79525.1
phiB	208	PEBP superfamily	98/63	XP_002485358.1
phiC	226	ketosteroid isomerase-like protein	89/40	ANF07278.1
phiD	659	MFS multidrug transporter	81/60	XP_002485360.1
phiE	300	methyltransferase	95/61	XP_002485361.1
phiF	301	DUF1115 domain protein	96/44	XP_001259206.1
phiG	336	alpha/beta-hydrolase	89/64	XP_001800751.1
phiH	279	hypothetical protein	87/37	OTA92757.1
phiI	504	2-methylcitrate dehydratase	96/62	EDP54866.1
phiJ	457	citrate synthase	94/59	XP_002485362.1
phiK	276	alpha-ketoglutarate-dependent taurine dioxygenase (α-KGD)	100/63	XP_002485367.1
phiL	423	MFS transporter	97/61	XP_002485366.1
phiM	224	FSH1/DUF341 family hydrolase	99/48	XP_002485365.1
phiN	259	PEBP superfamily	55/45	ANF07283.1
phiO	342	C6 transcription factor	97/29	ANF07281.1

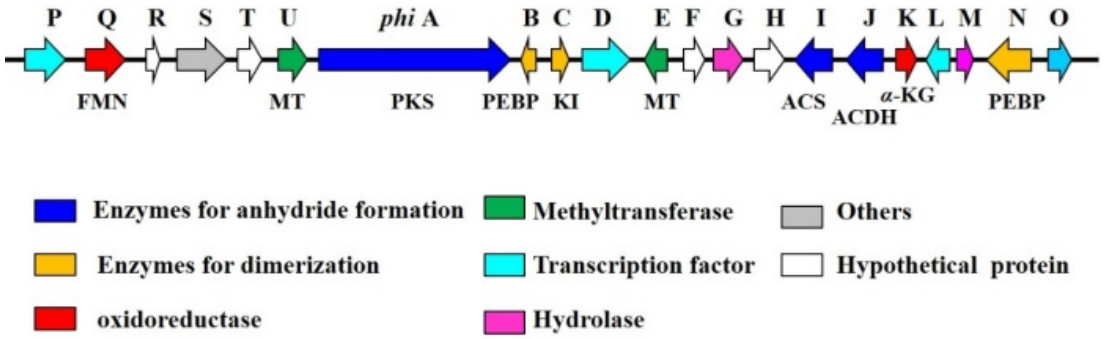


Table **S2**. Energies of conformers for **1** and **2** at MMFF94 force field.

Compound	Conformer	Energy (kcal/mol)	Population (%)
1	1	38.85	56.2
1	2	39.77	11.9
1	3	39.78	11.7
1	4	40.34	4.5
1	5	40.43	3.9
1	6	40.57	3.1
1	7	40.62	2.8
1	8	41.05	1.4
1	9	41.29	0.9
1	10	41.31	0.9
1	11	41.57	0.6
1	12	41.64	0.5
1	13	41.72	0.4
1	14	42.1	0.2
1	15	42.34	0.2
1	16	42.38	0.2
1	17	42.43	0.1
1	18	42.63	0.1
1	19	42.72	0.1
1	20	42.72	0.1
2	1	103.1	25.7
2	2	103.11	25.3
2	3	103.25	19.9
2	4	103.94	6.2
2	5	104.19	4.1
2	6	104.34	3.2
2	7	104.35	3.1
2	8	104.48	2.5
2	9	104.84	1.4
2	10	104.87	1.3
2	11	104.94	1.2
2	12	105.15	0.8
2	13	105.24	0.7
2	14	105.46	0.5
2	15	105.55	0.4
2	16	105.59	0.4
2	17	105.65	0.4
2	18	105.7	0.3
2	19	105.75	0.3
2	20	105.81	0.3
2	21	105.89	0.2
2	22	105.94	0.2

2	23	105.98	0.2
2	24	106.07	0.2
2	25	106.1	0.2
2	26	106.15	0.2

AAGGATCATTACCAATTGCGGGCGAGGCCTAGCCTCCCCGCGAACCTTCTC
ATCCCTTTATGGTGTACCTTTGTTTCCTCGGCAGGCTTGCCTGCCAGCGAGG
ACCCCCAACAAACCTTTTTGCAGTAAGAAGTATACGTCTTATCAAAAACAA
ATCGTTTACAACTTTCAACAATGGATCTCTTGGTTCTGGCATCGATGAAGAA
CGCAGCGAAATGCGATAAGTAGTGTGAATTGCAGAATTTAGCGAATCATCG
AATCTTTGAACGCACATTGCGCCTCTTGGTATTCCATGGGGCACGCCTGTTC
GAGCGTCATTTCAACCCTCAAGCACTGCTTGGTGTTGGGCGTCTGTCCCGC
CTCTGCGCGTGGACTCGCCTCAAAGTCATTGGCGGCTGTTCCCCTTCGGCT
CGTAAGCGCAGCACAGTCAGCGCCCGGAGCTCTGGTGGATGGCGTCCAGC
AAGCTATATTTCTAGTCTTGACCTCGGATCAGGTGGGGATACCCGCTGAACT
TAAG

Fig. **S1**. The internal transcribed spacer identification of *Pleosporales* sp.

Image coloured by rainbow N → C terminus

Model dimensions (Å): **X**:51.978 **Y**:52.485 **Z**:40.563

Model (left) based on template c3gjbA

Top template information

PDB header:biosynthetic protein **Chain:** A: **PDB Molecule:**cytc3; **PDBTitle:** cytc3 with fe(ii) and alpha-ketoglutarate

Confidence and coverage

Confidence: 56.4% Coverage: 50%

138 residues (50% of your sequence) have been modelled with 56.4% confidence by the single highest scoring template.

Phyre alarm

You may wish to submit your sequence to Phyrealarm. This will automatically scan your sequence every week for new potential templates as they appear in the Phyre2 library.

Please note: You must be registered and logged in to use Phyrealarm.

3D viewing

Interactive 3D view in JSmol

For other options to view your downloaded structure offline see the FAQ

Fig. **S2**. Structure analysis of PhiK by Phyre2 showed PhiK is close to CytC3 with Fe^{II} and α-ketoglutarate

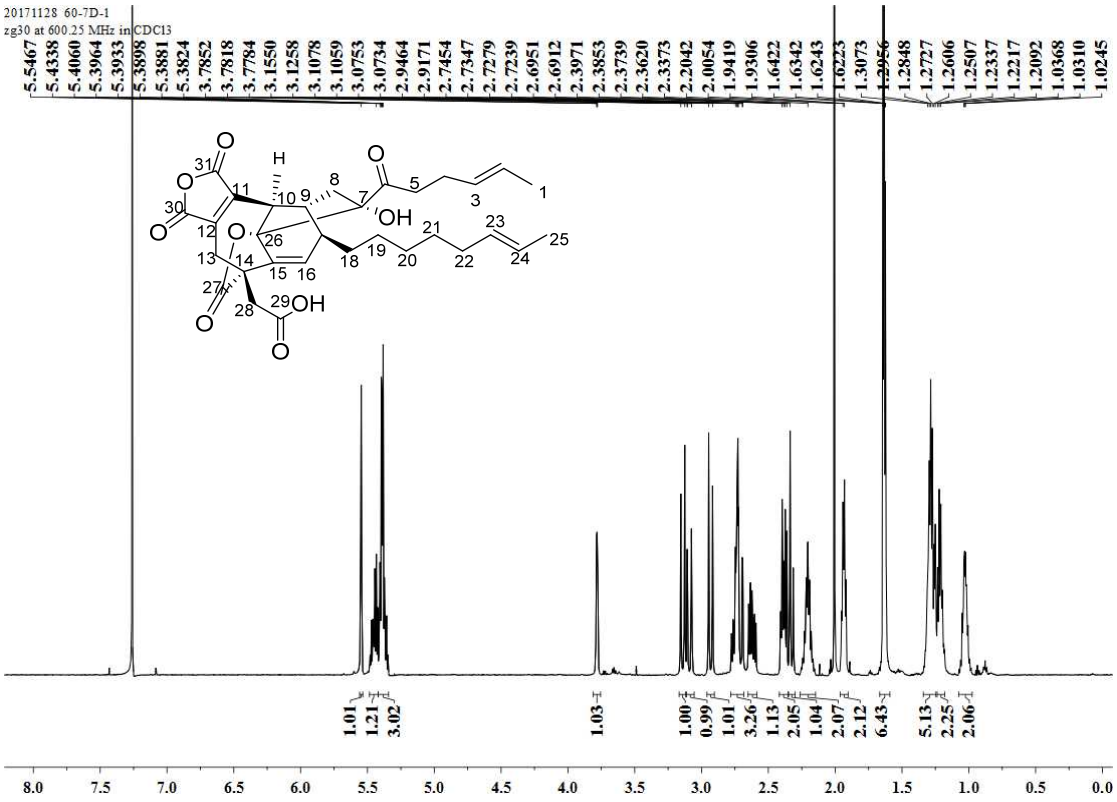


Fig. **S3**. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **1**

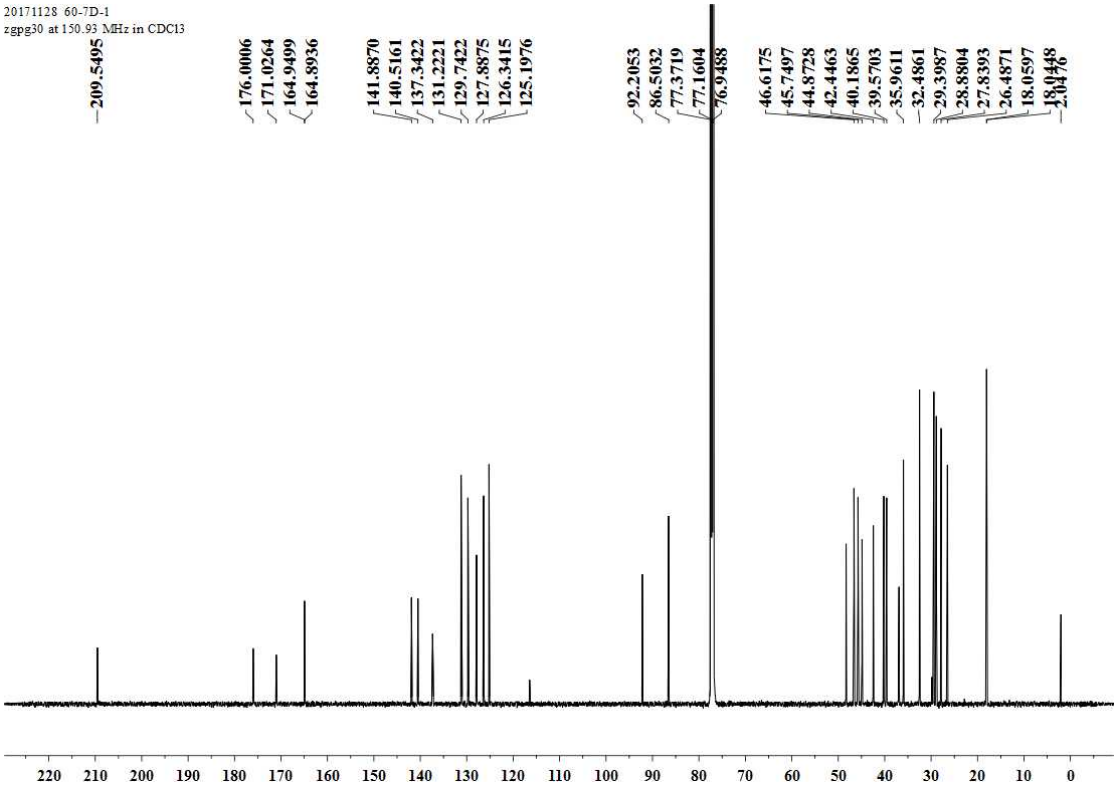


Fig. **S4**. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **1**

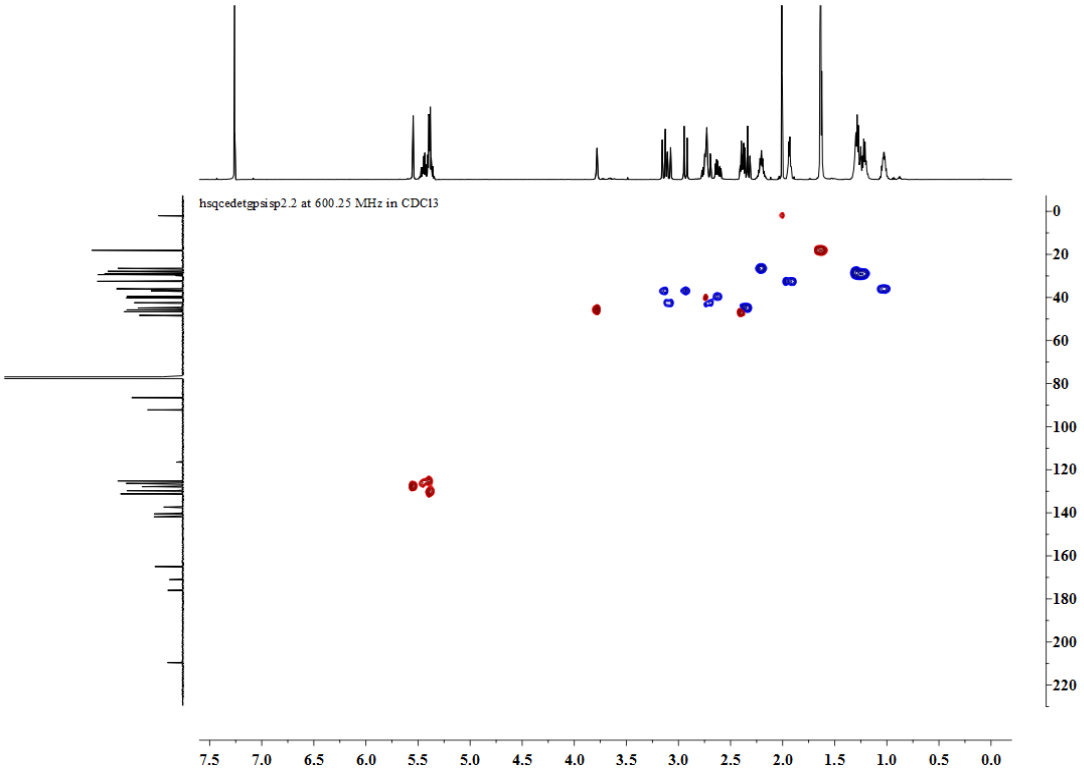


Fig. **S5**. HSQC (600 MHz, $CDCl_3$) spectrum for **1**

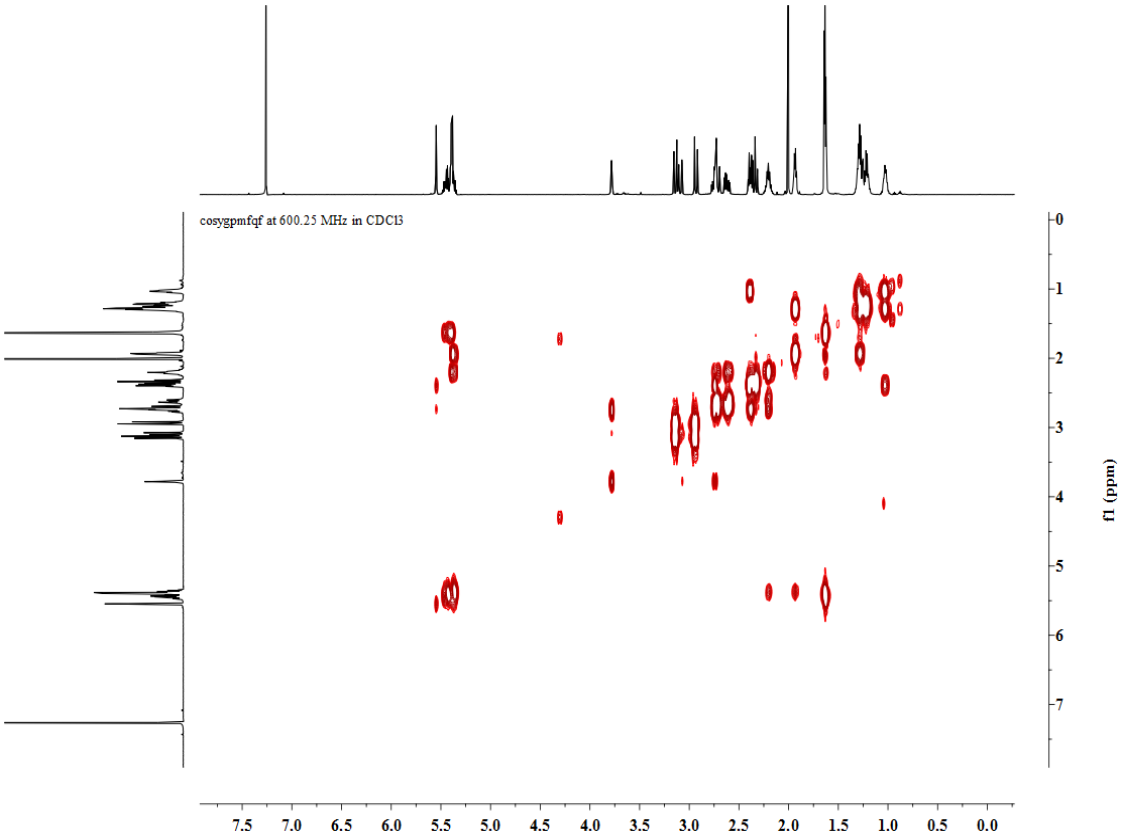


Fig. **S6**. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum for **1**

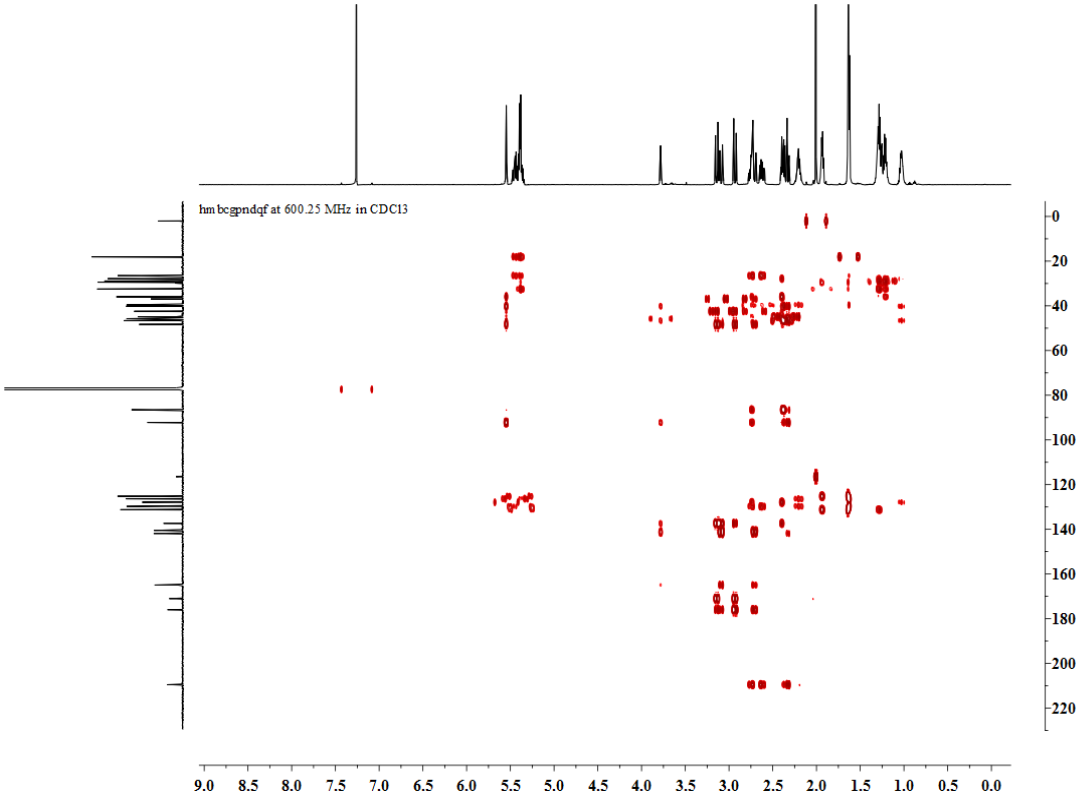


Fig. **S7**. HMBC (600 MHz, $CDCl_3$) spectrum for **1**

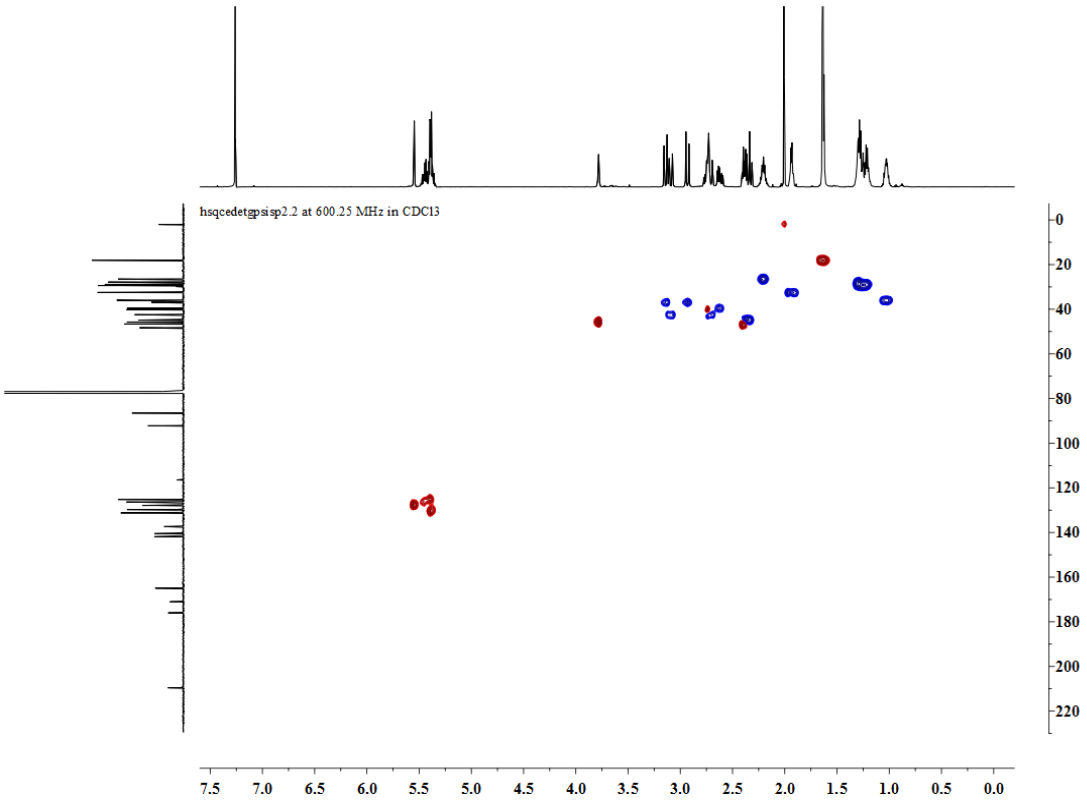
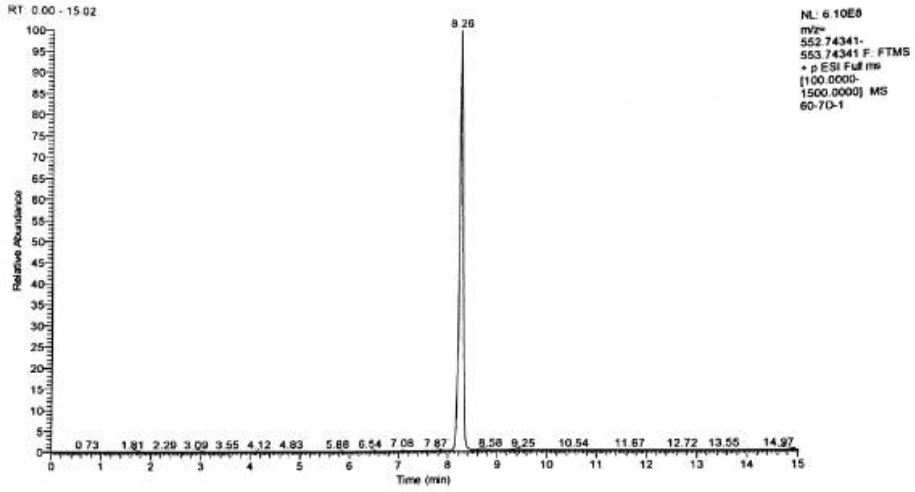


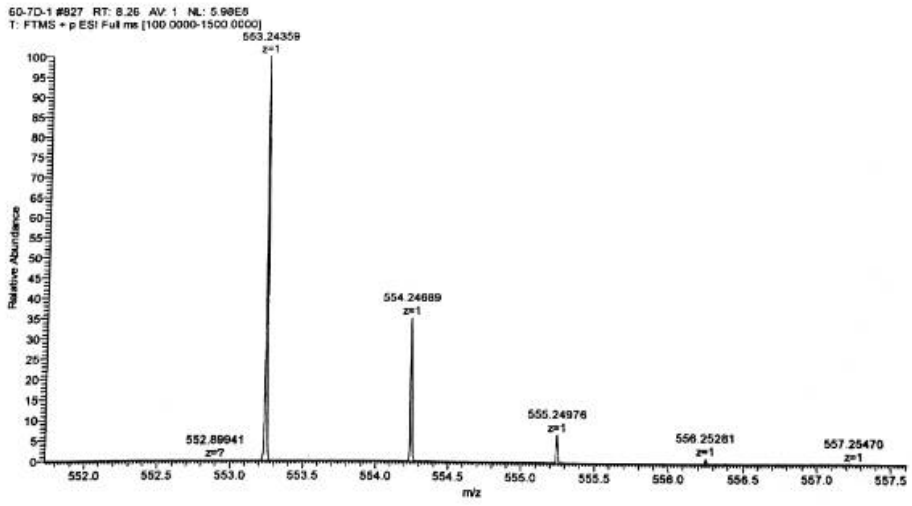
Fig. **S8**. NOESY (600 MHz, $CDCl_3$) spectrum for **1**

Thermo Qexactive Focus Report

compound NO. : 60-7D-1

Method : LCMS(compound)-low





m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
553.24359	553.24321	0.69	13.5	C31 H37 O9	M+H

Fig. **S9**. HR-ESI-MS spectrum for **1**

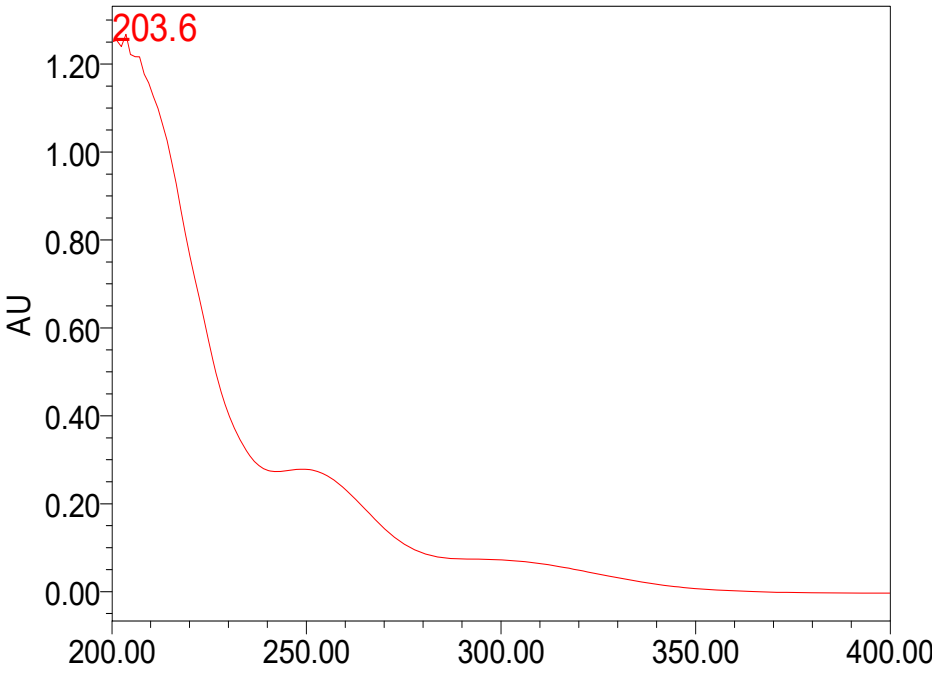


Fig. **S10**. UV spectrum for **1** in CH_3CN

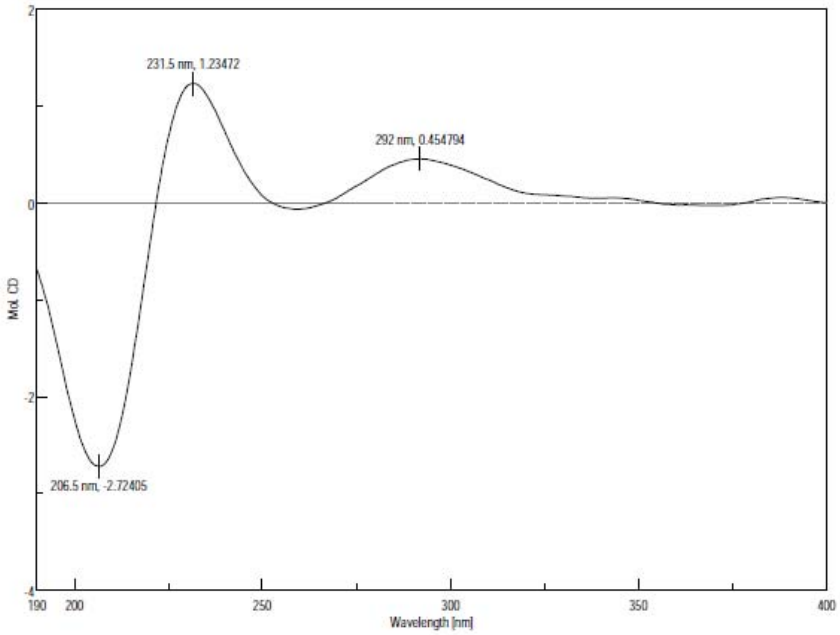


Fig. **S11**. CD spectrum for **1** in CH_3CN

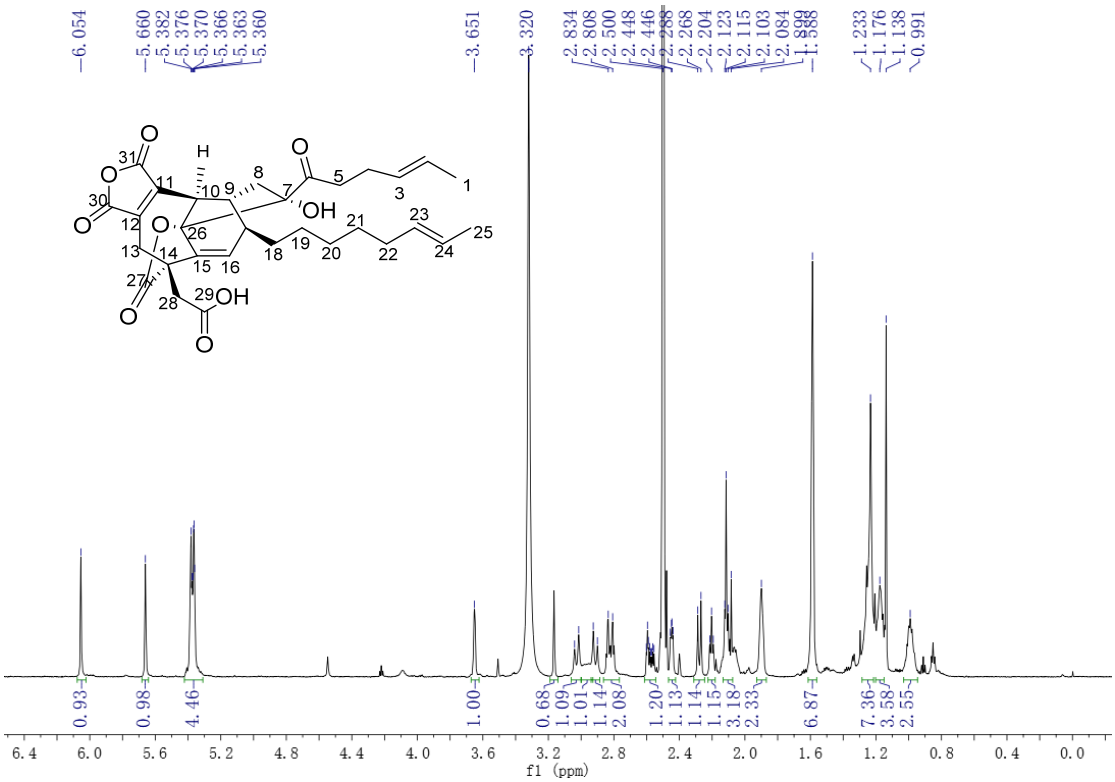


Fig. **S12**. ^{1}H NMR (700 MHz, DMSO-d_6) spectrum for **1**.

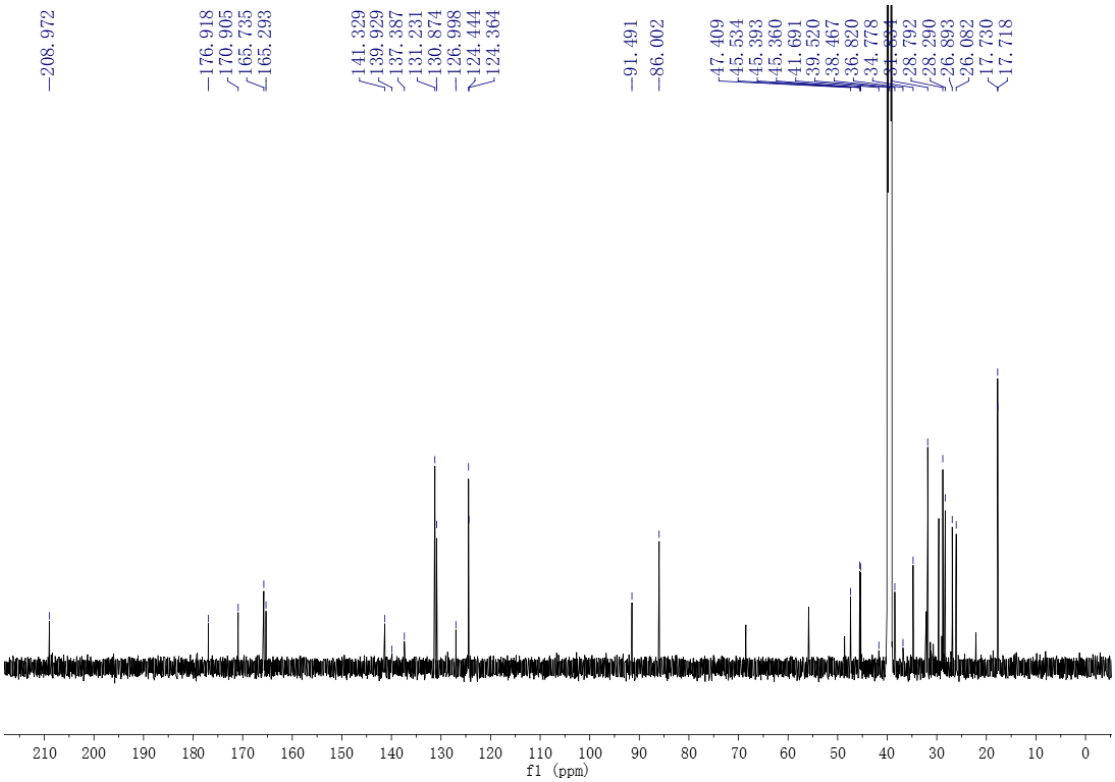


Fig. **S13**. ^{13}C NMR (175 MHz, DMSO-d_6) spectrum for **1**.

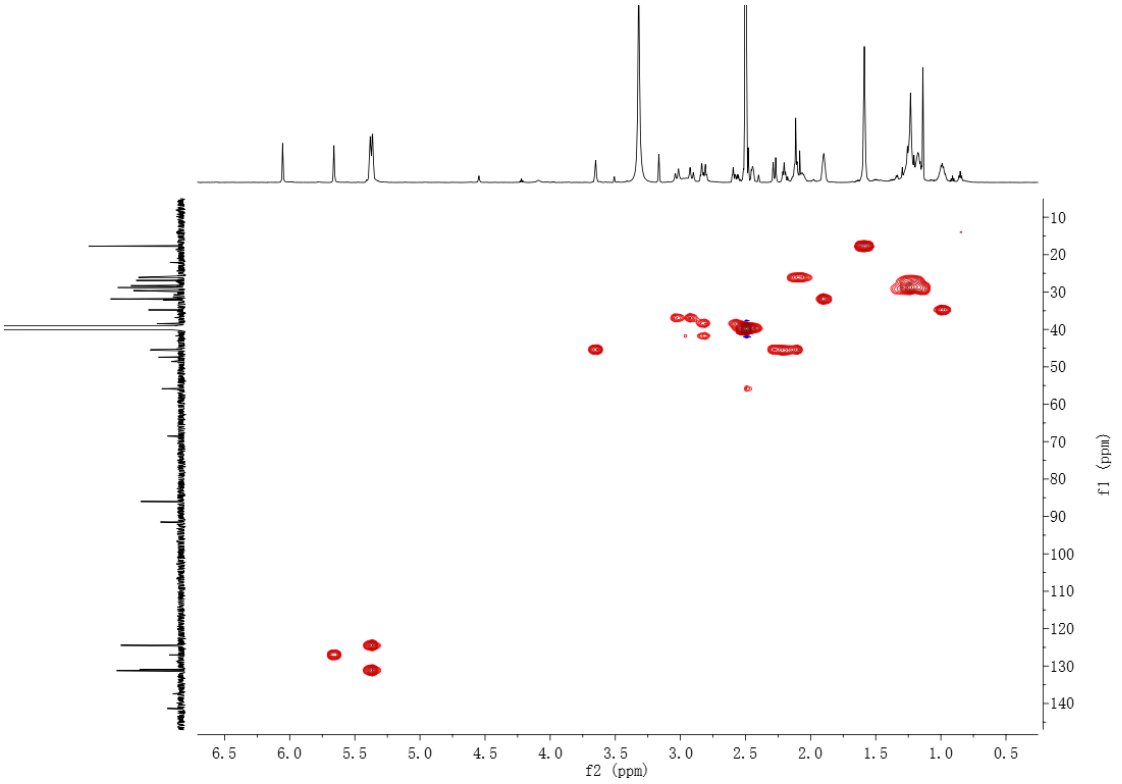


Fig. **S14**. HSQC (700 MHz, DMSO-d_6) spectrum for **1**.

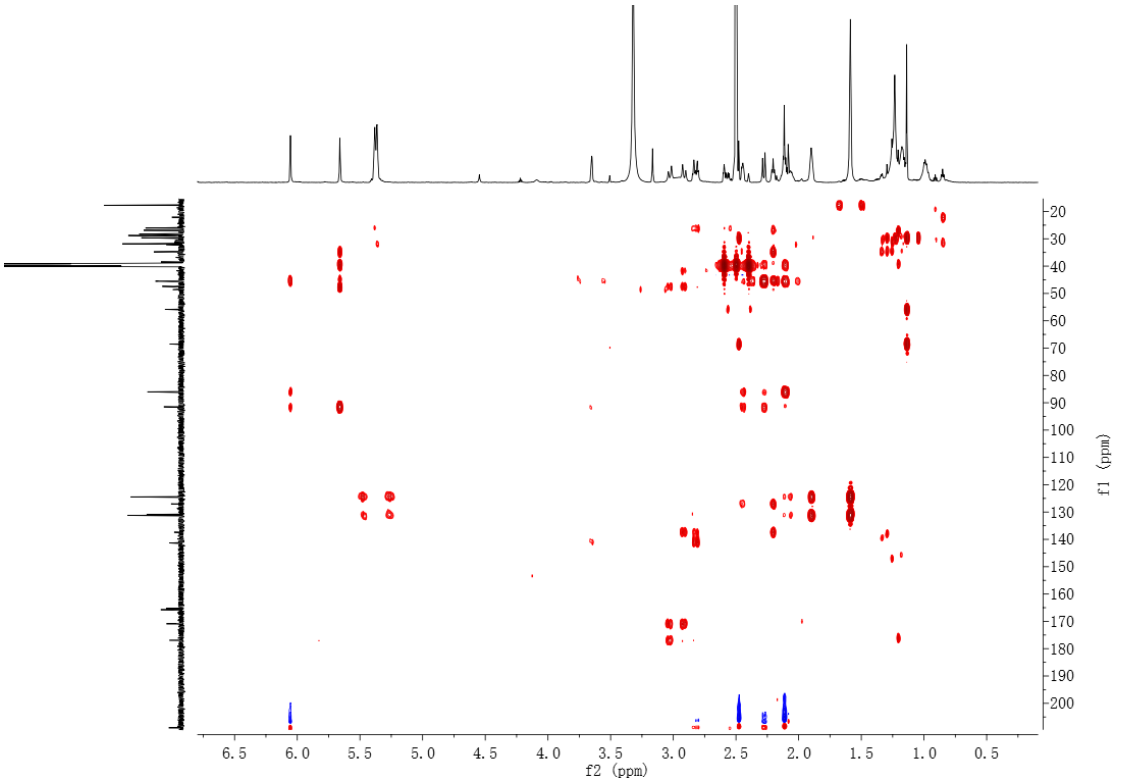


Fig. **S15**. HMBC (700 MHz, DMSO-d_6) spectrum for **1**

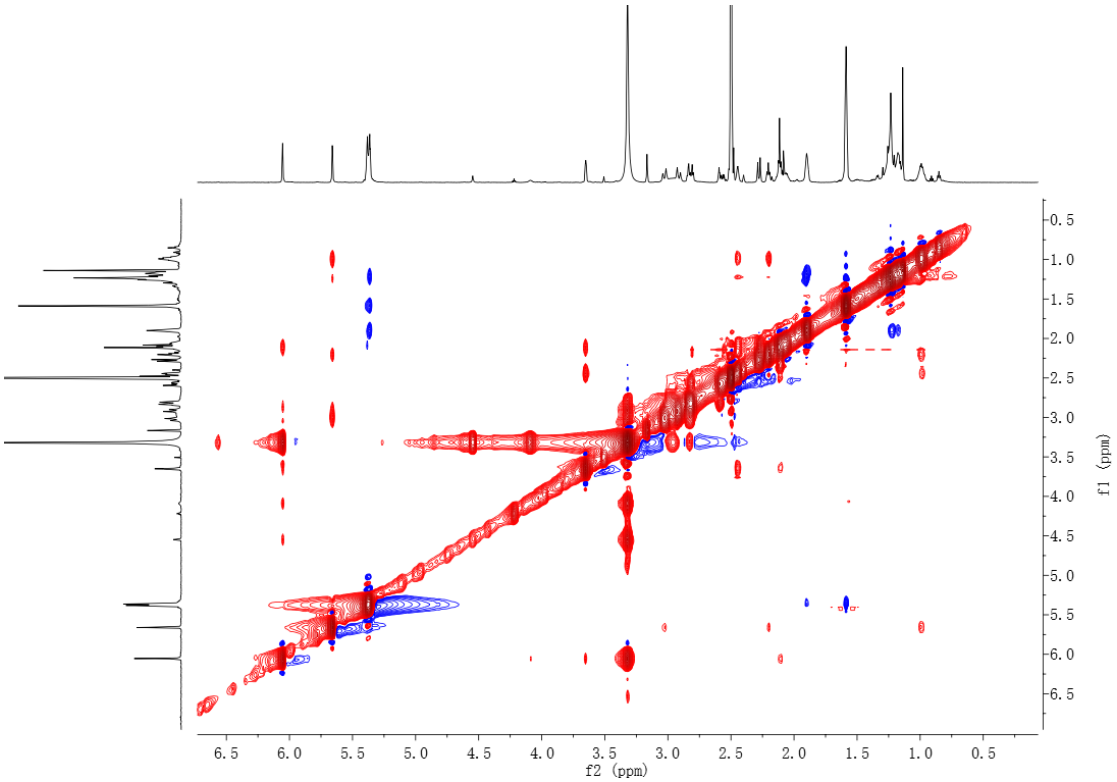


Fig. **S16**. NOESY (700 MHz, DMSO-d_6) spectrum for **1**

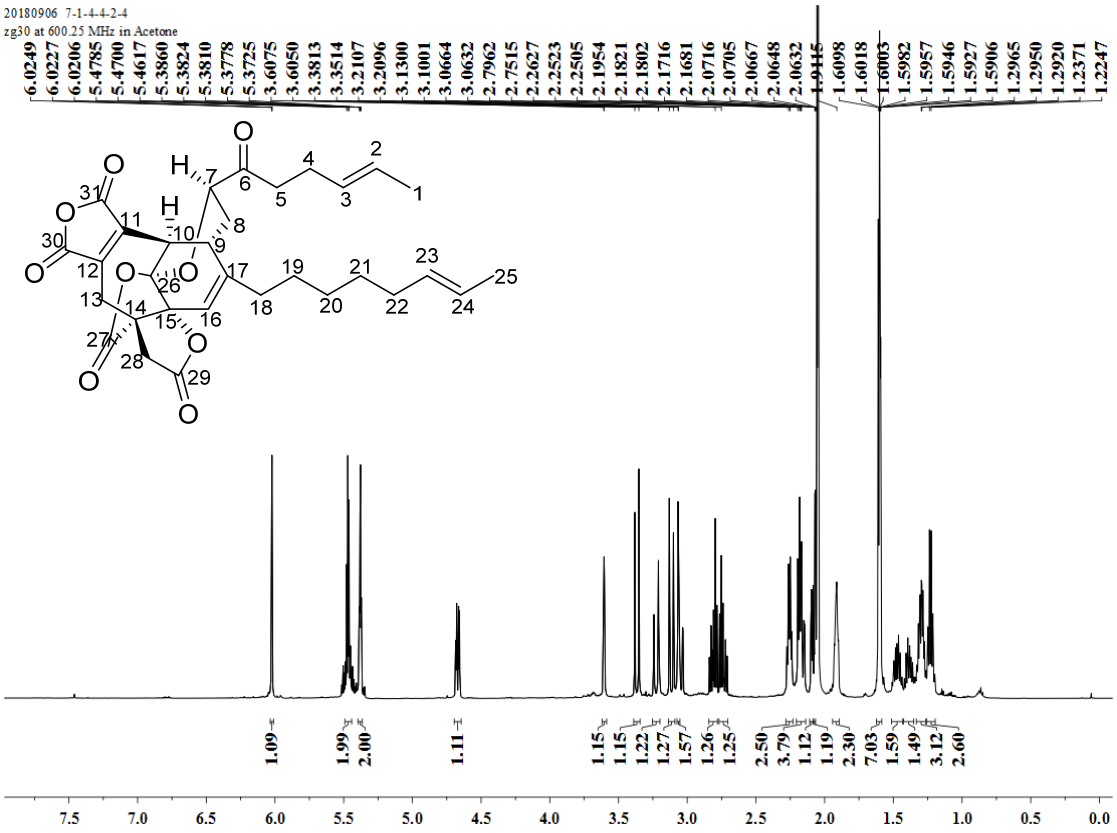


Fig. **S17**. ^{1}H NMR (600 MHz, Acetone-d_6) spectrum for **2**

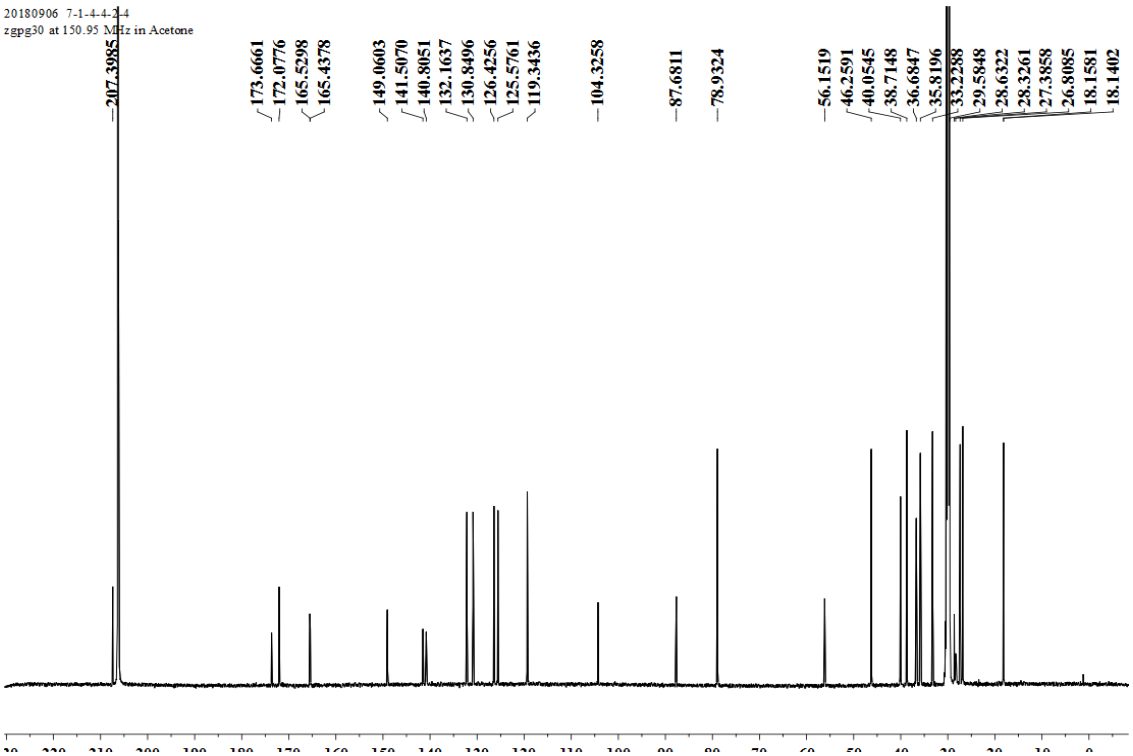


Fig. **S18**. ^{13}C NMR (150 MHz, Acetone-d_6) spectrum for **2**

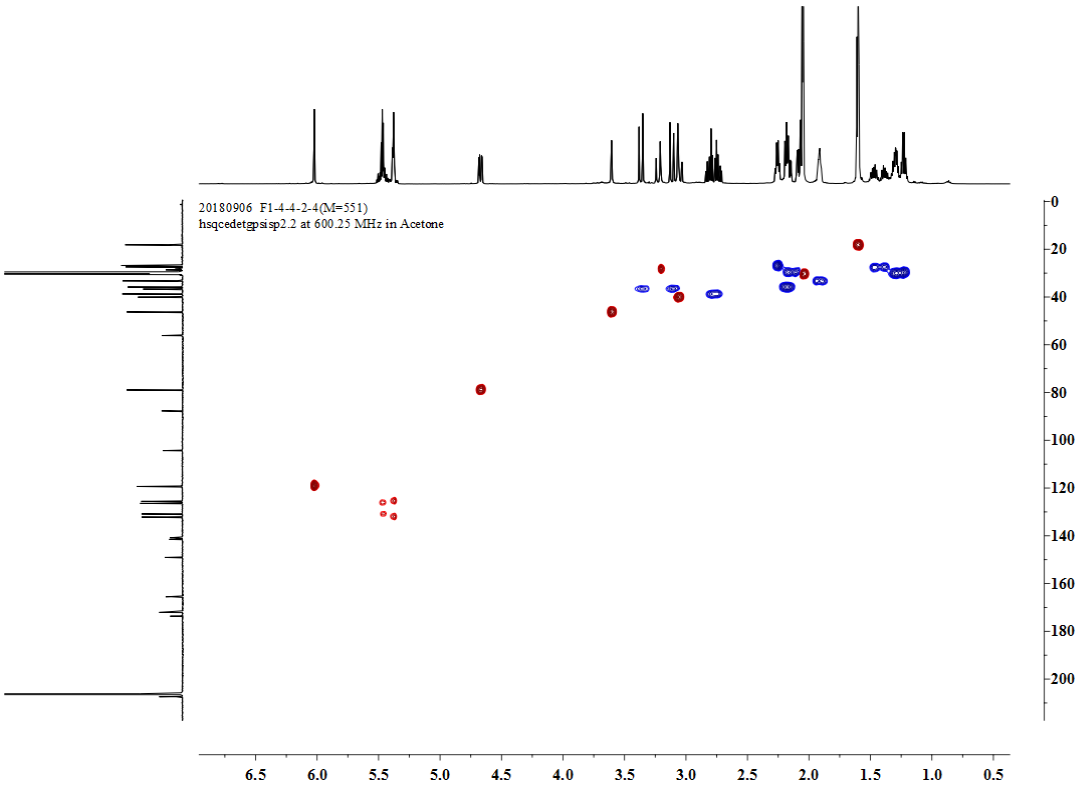


Fig. **S19**. HSQC (600 MHz, Acetone-d_6) spectrum for **2**

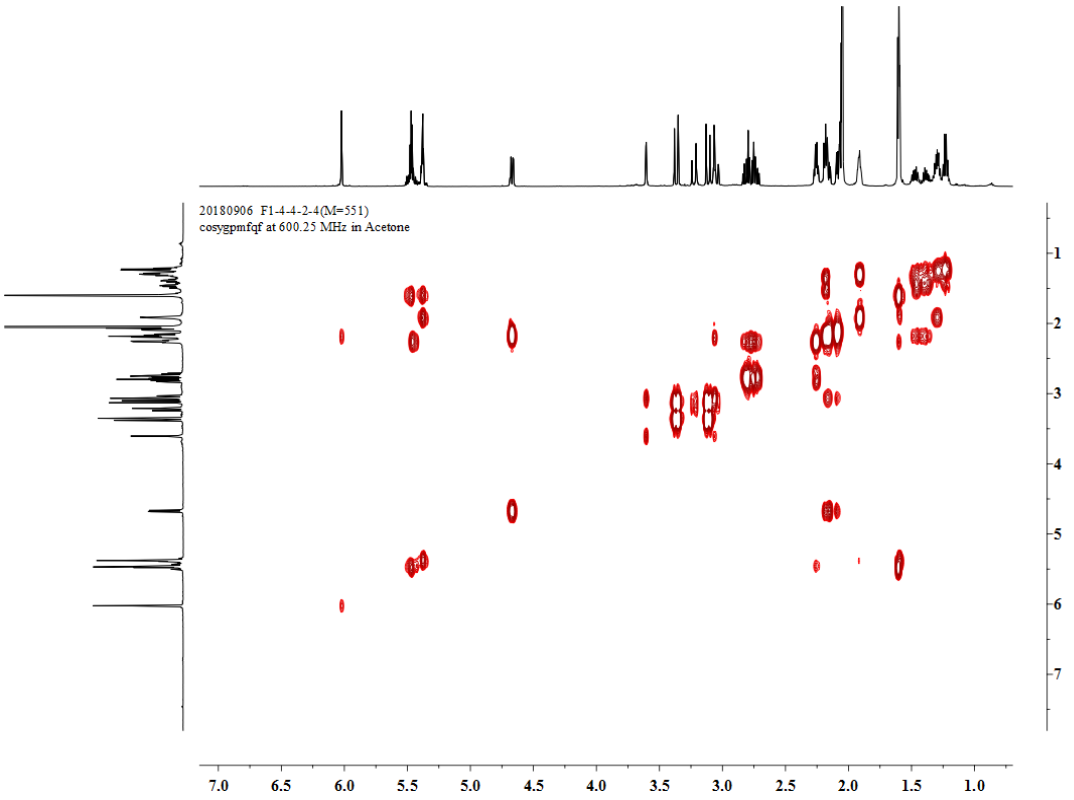


Fig. **S20**. ^{1}H-^{1}H COSY (600 MHz, Acetone-d_6) spectrum for **2**

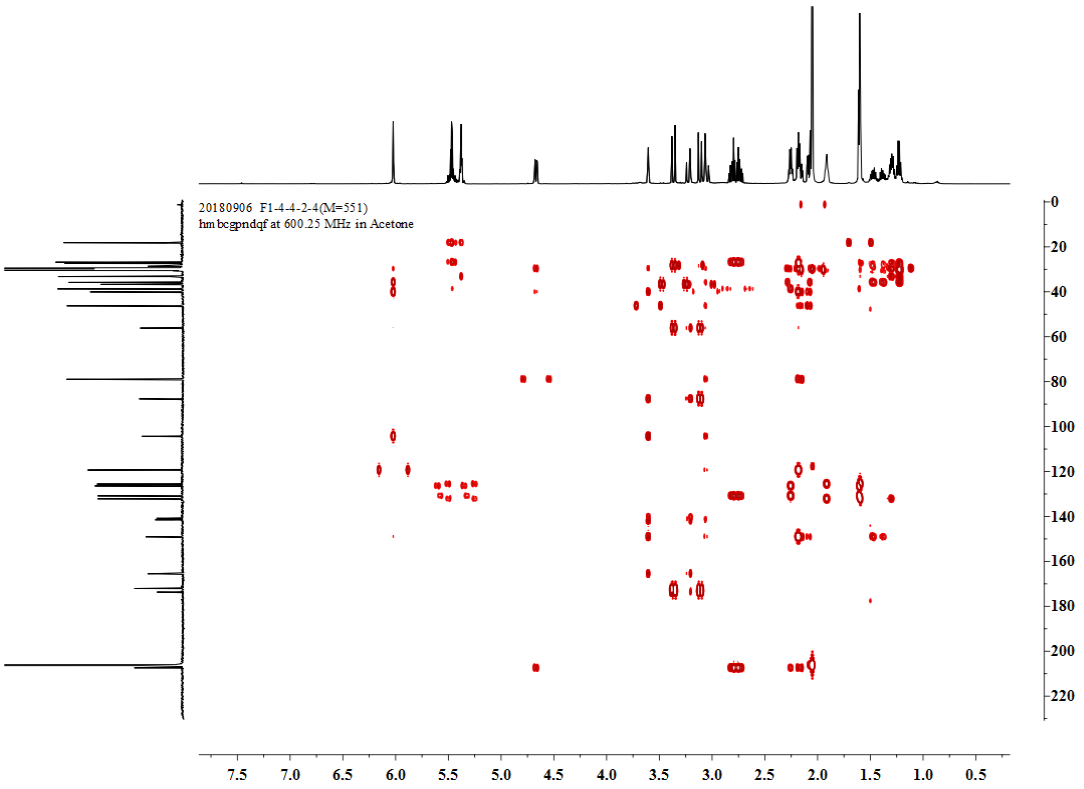


Fig. **S21**. HMBC (600 MHz, Acetone-d_6) spectrum for **2**

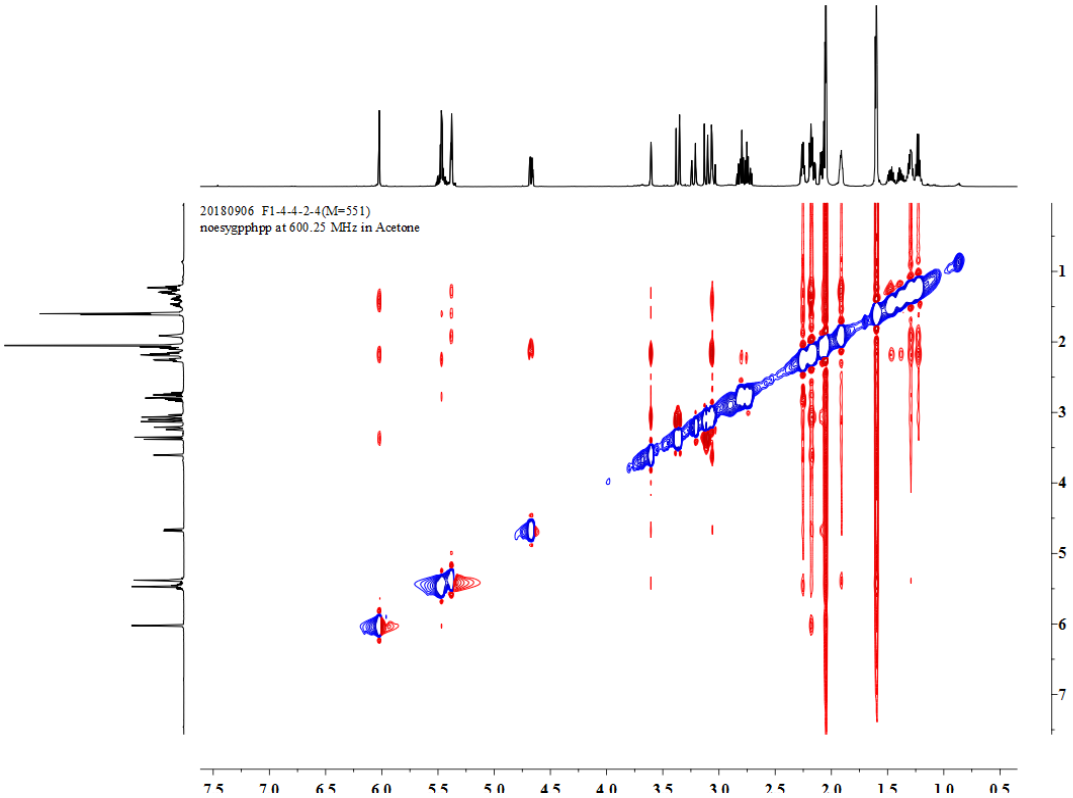
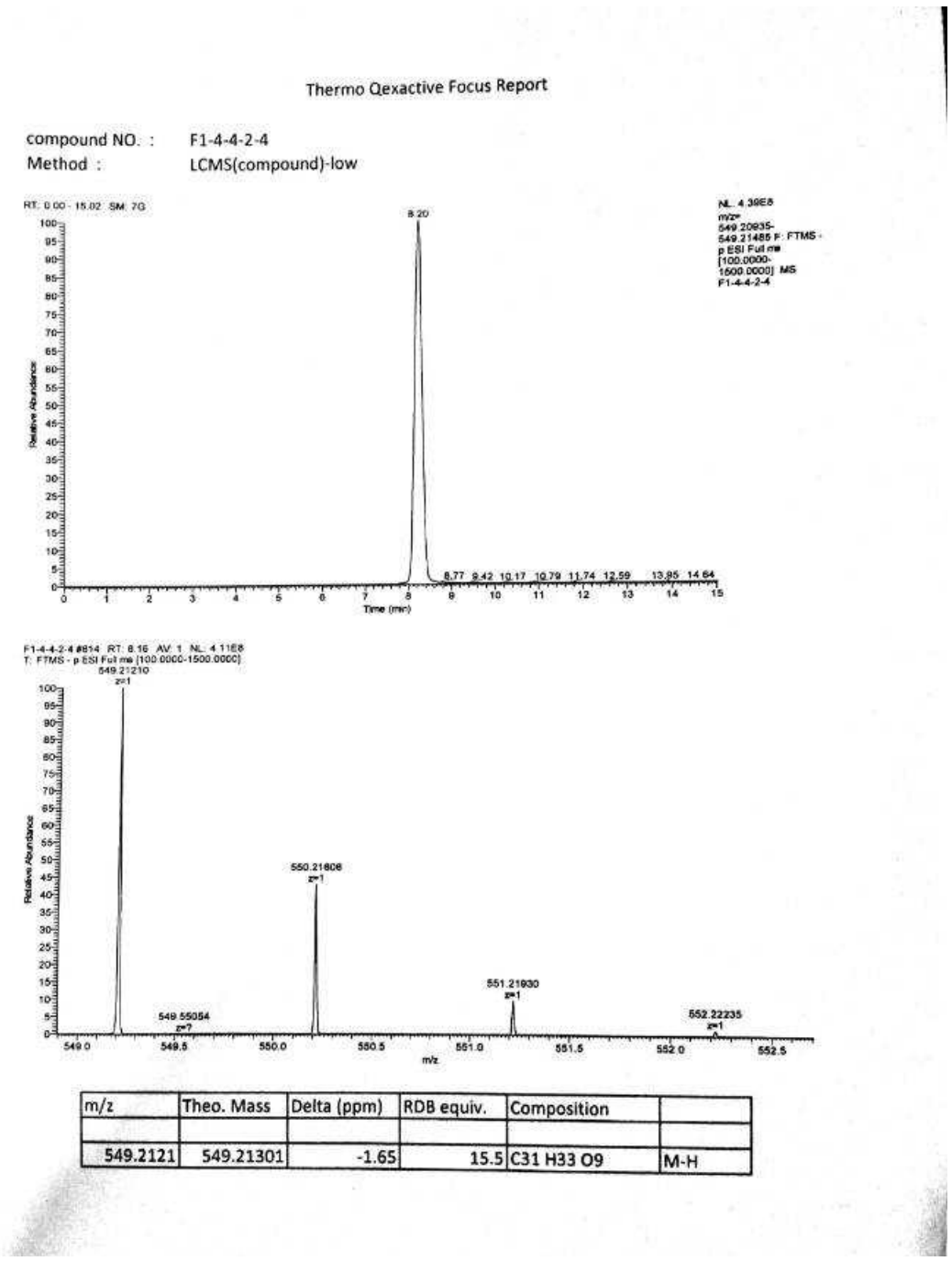


Fig. **S22**. NOESY (600 MHz, Acetone-d_6) spectrum for **2**



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
549.2121	549.21301	-1.65	15.5	C31 H33 O9	M-H

Fig. **S23**. HR-ESI-MS spectrum for **2**

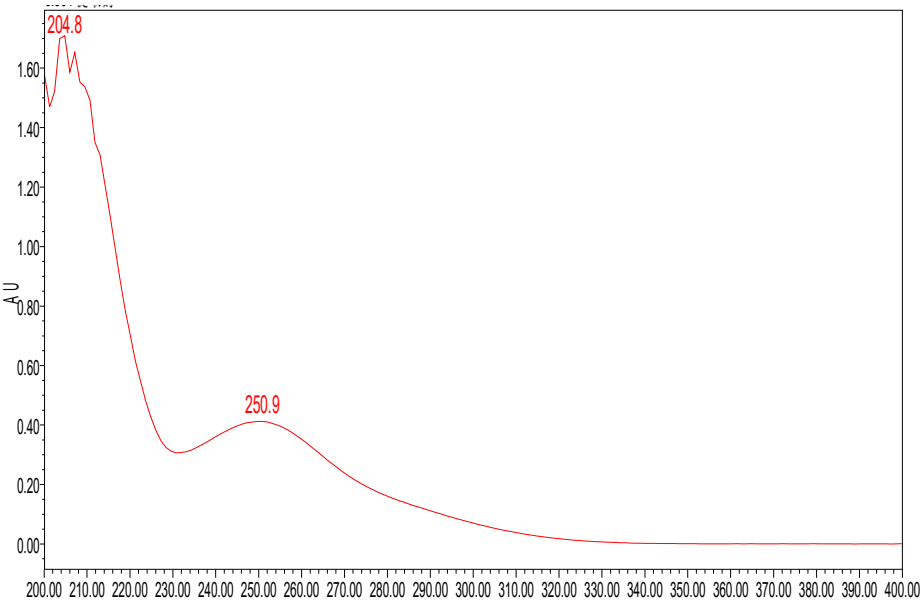


Fig. **S24**. UV spectrum for **2** in CH_3CN

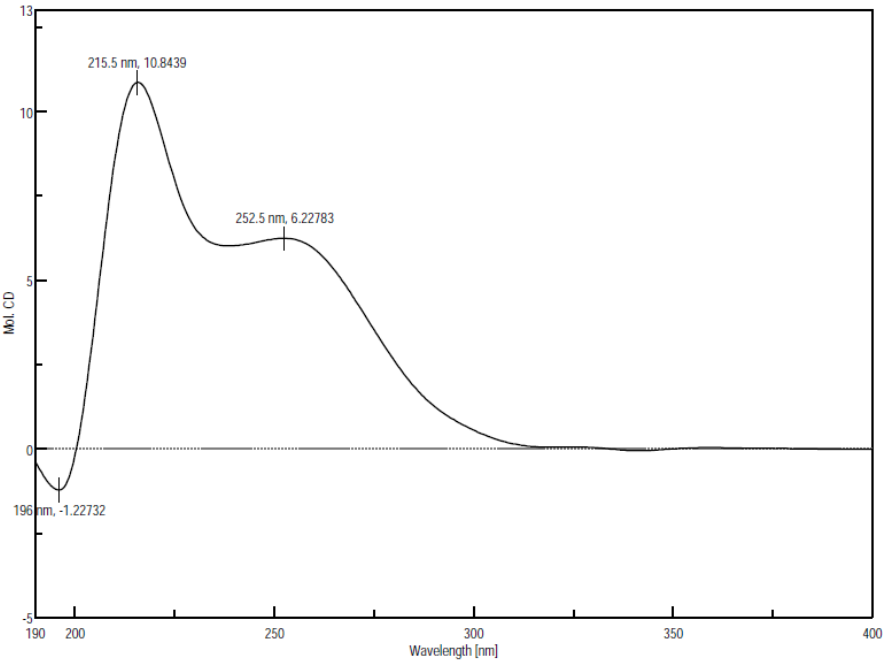


Fig. **S25**. CD spectrum for **2** in CH_3CN

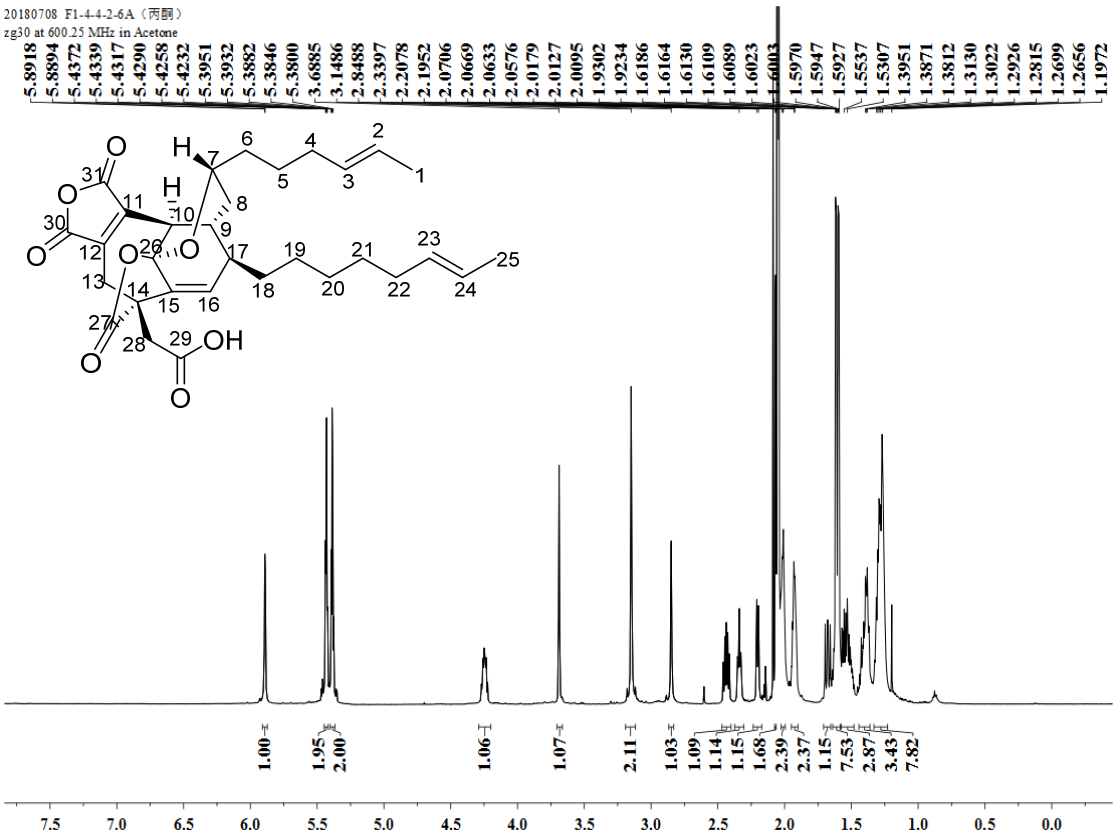


Fig. **S26**. ^{1}H NMR (600 MHz, Acetone-d_6) spectrum for **3**

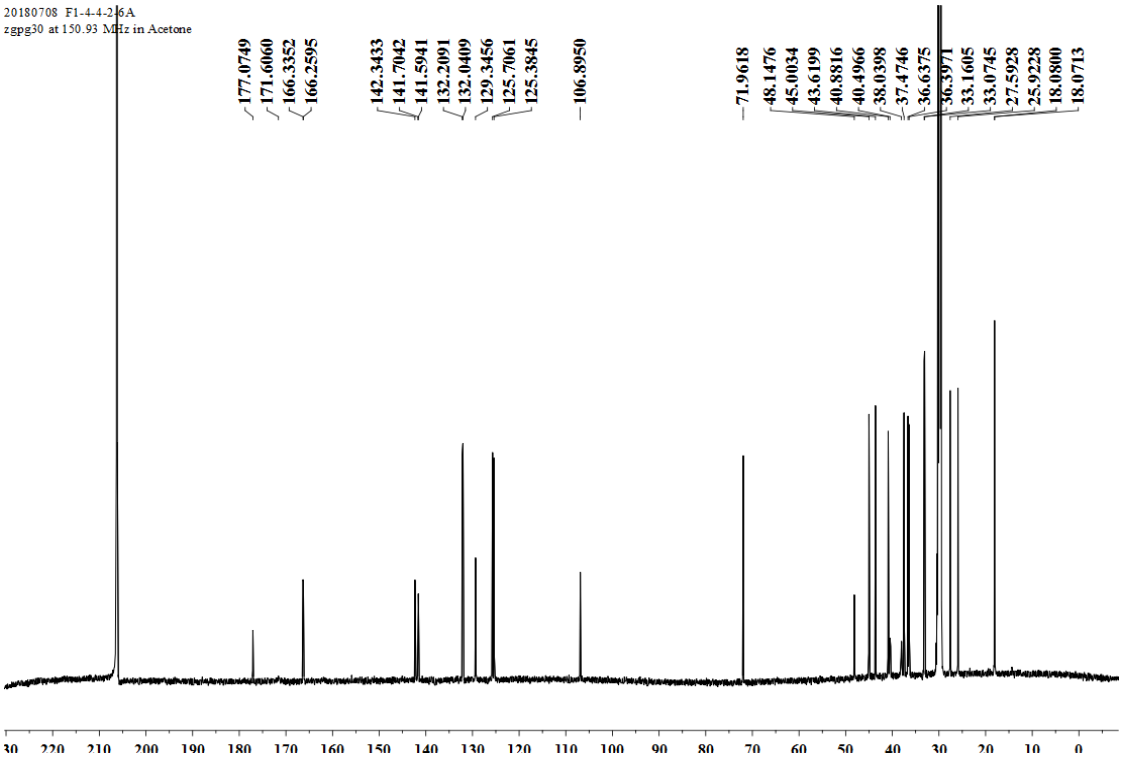


Fig. **S27**. ^{13}C NMR (150 MHz, Acetone-d_6) spectrum for **3**

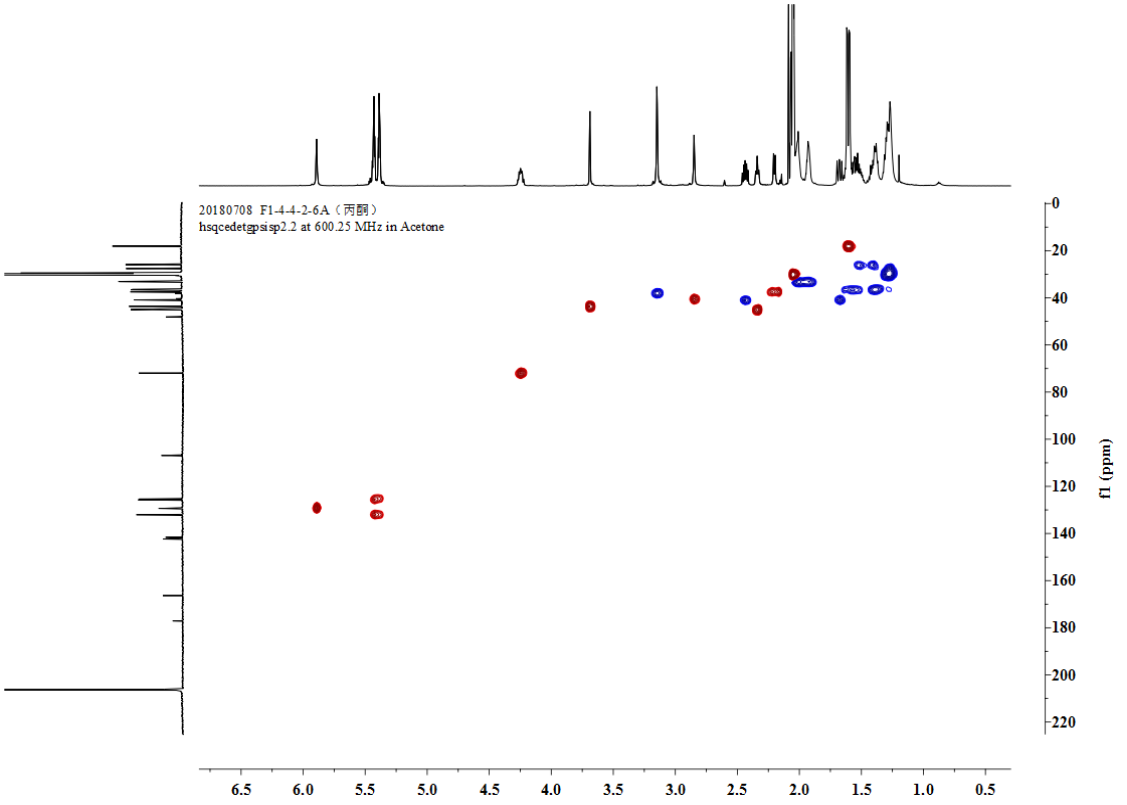


Fig. **S28** HSQC (600 MHz, Acetone-d_6) spectrum for **3**

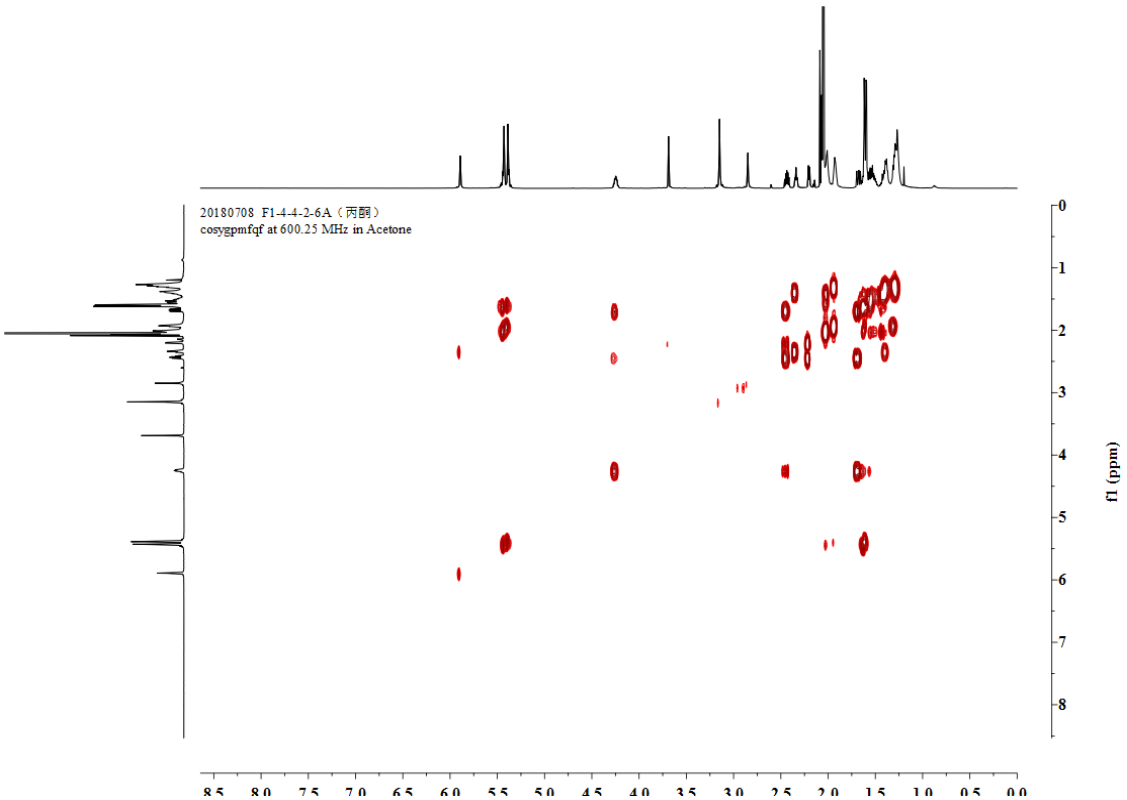


Fig. **S29**. ^{1}H-^{1}H COSY (600 MHz, Acetone-d_6) spectrum for **3**

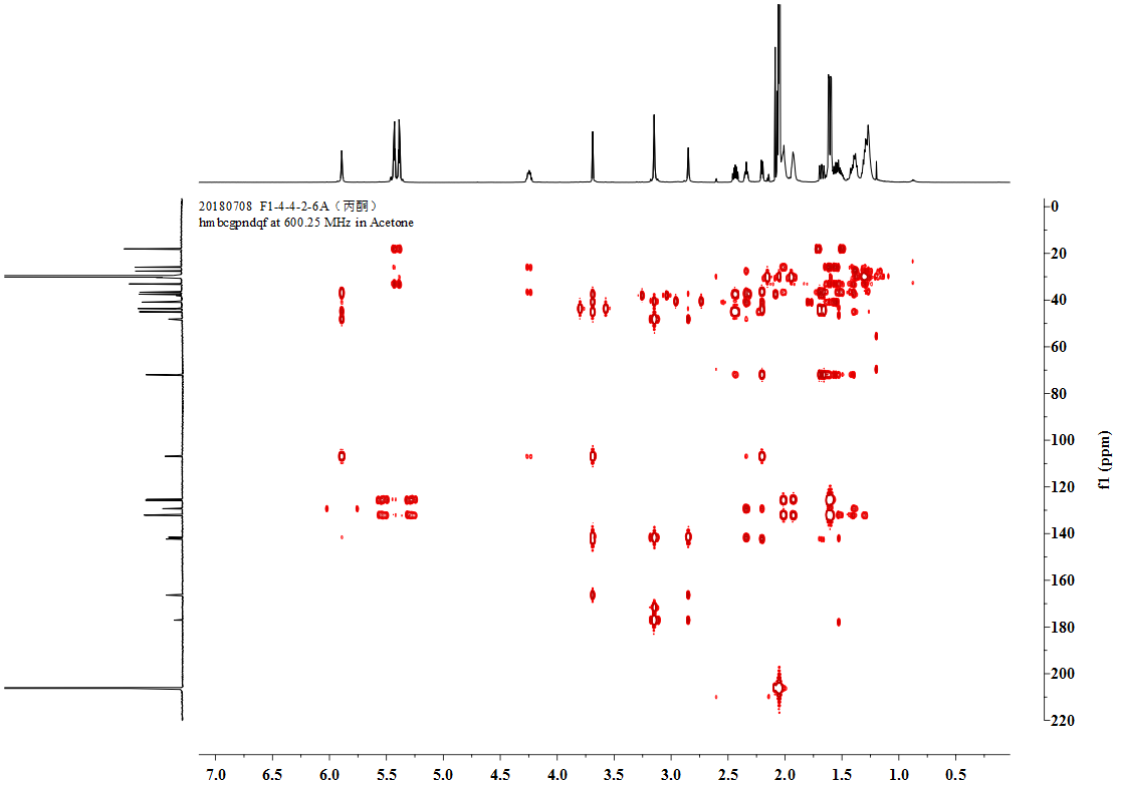


Fig. **S30**. HMBC (600 MHz, Acetone-d_6) spectrum for **3**

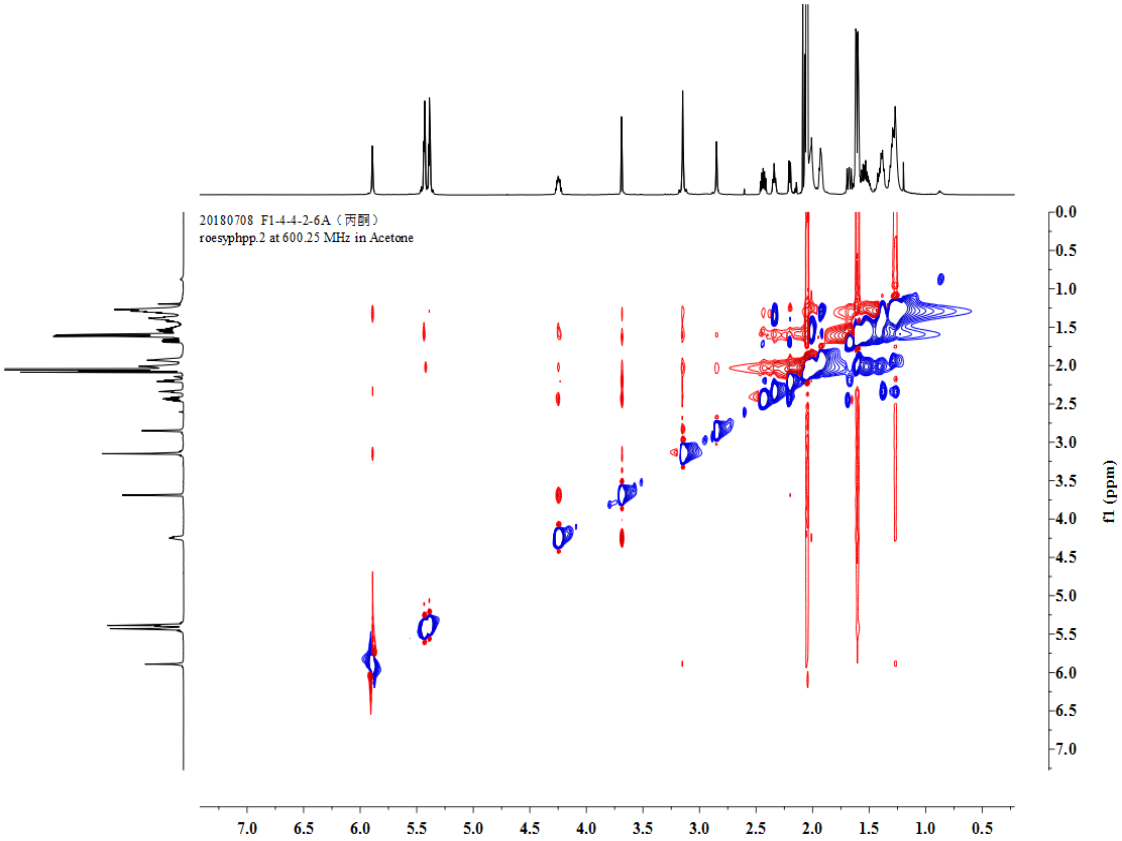
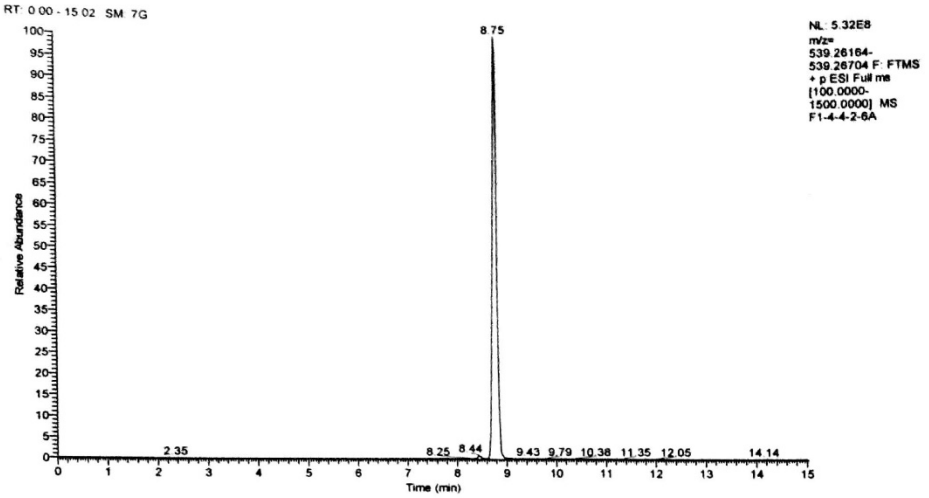


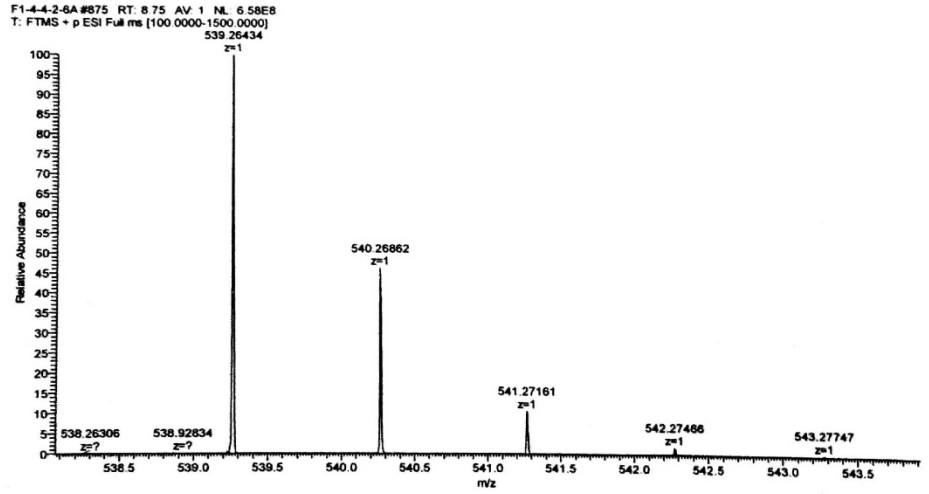
Fig. **S31**. NOESY (600 MHz, Acetone-d_6) spectrum for **3**

Thermo Qexactive Focus Report

compound NO. : F1-4-4-2-6A

Method : LCMS(compound)-low





m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition	
539.26434	539.26394	0.73	12.5	C31 H39 O8	M+H

Fig. **S32**. HR-ESI-MS spectrum for **3**

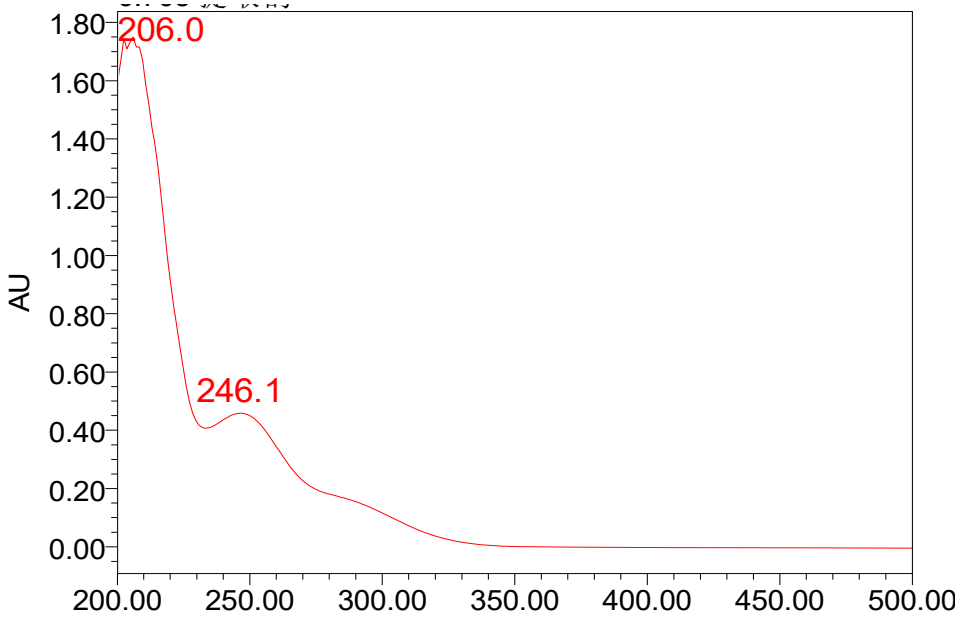


Fig. **S33**. UV spectrum for **3** in CH_3CN

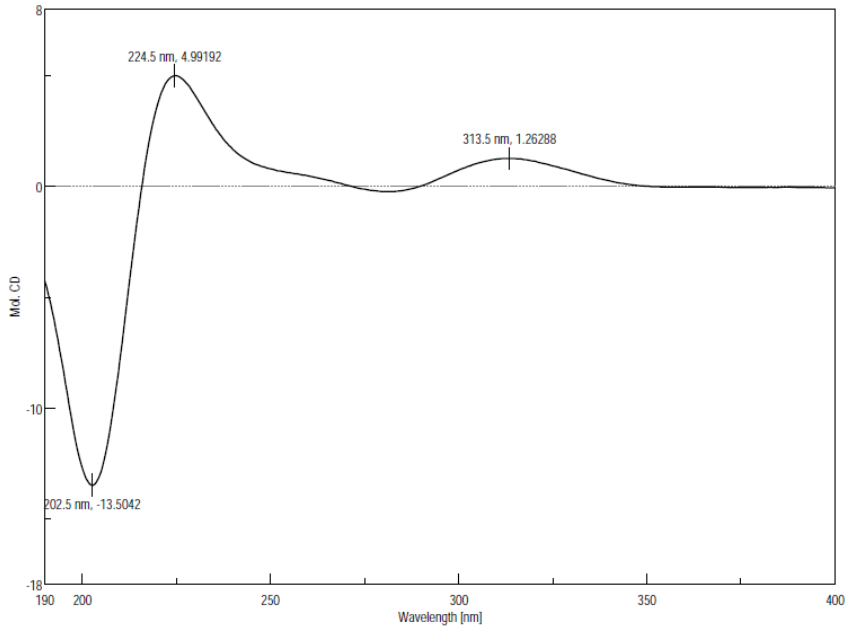


Fig. **S34**. CD spectrum for **3** in CH_3CN

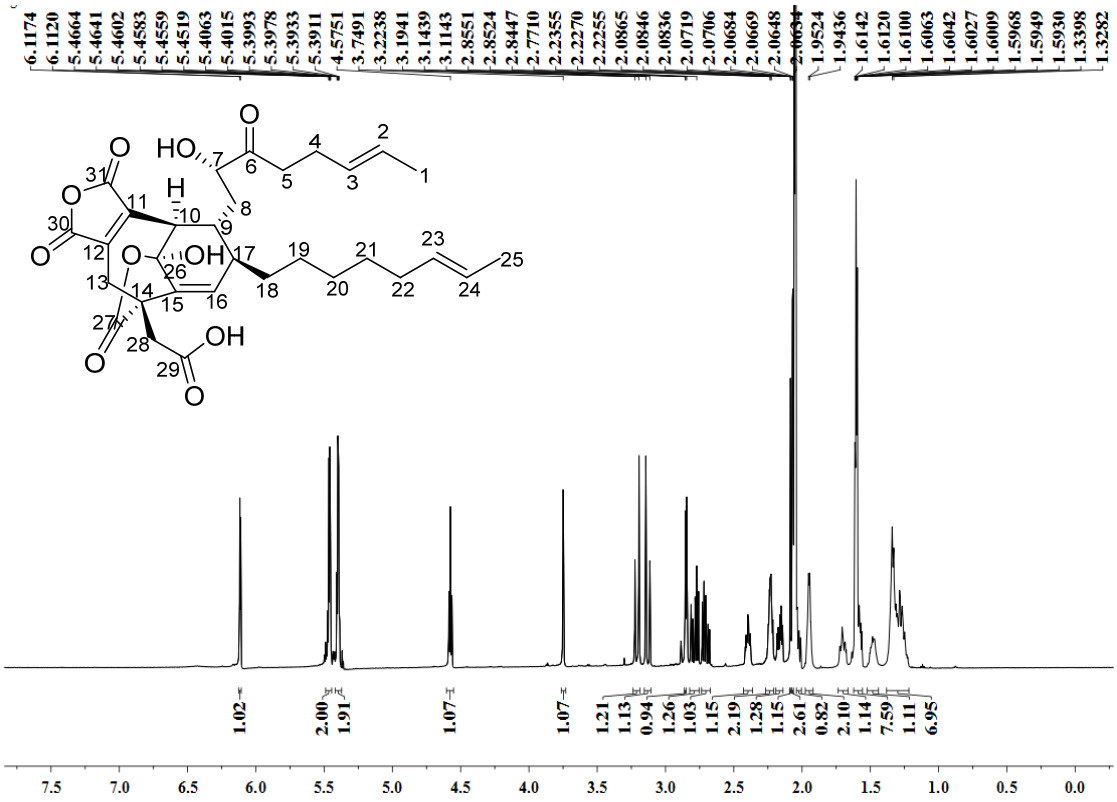


Fig. **S35**. ^{1}H NMR (600 MHz, Aceton-d_6) spectrum for Phomoidride A

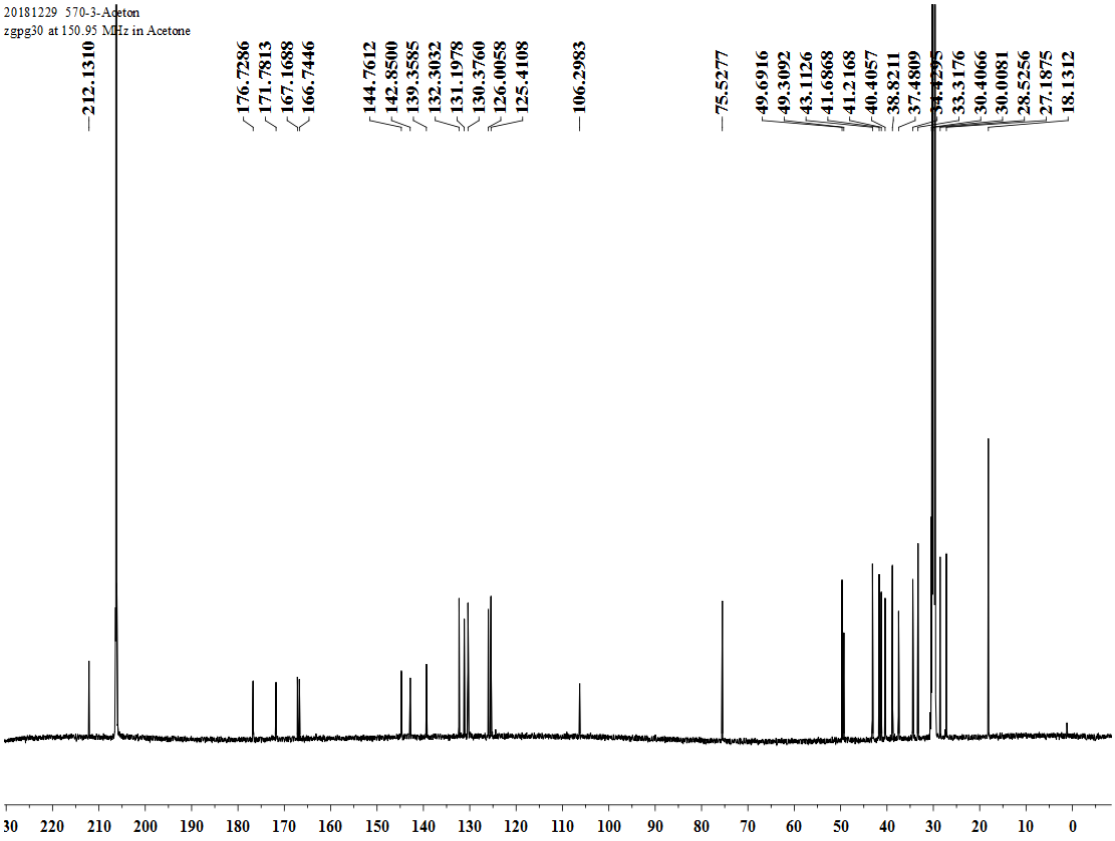


Fig. **S37**. ^{13}C NMR (150 MHz, Aceton-d_6) spectrum for Phomoidride A

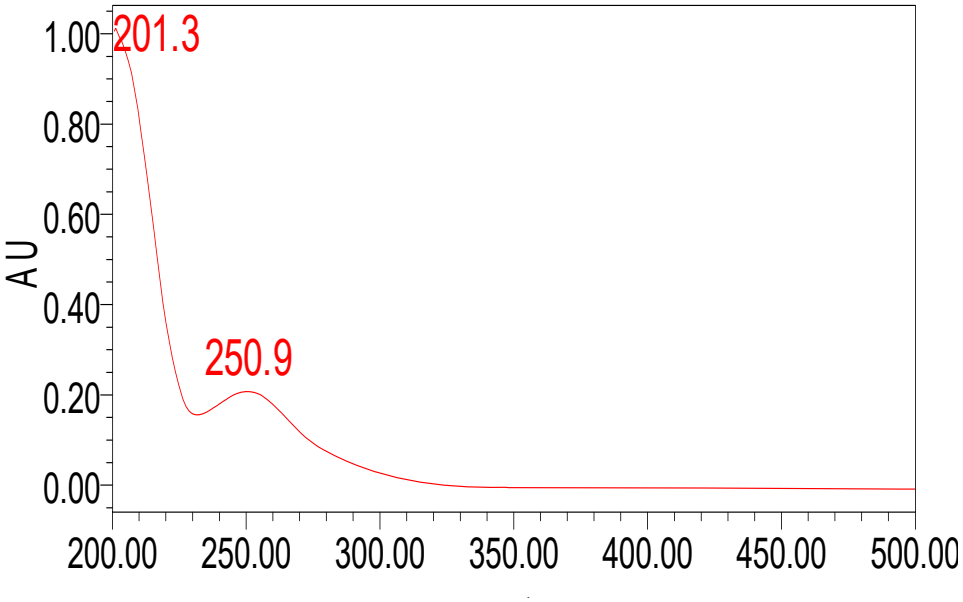


Fig. **S38**. UV spectrum for Phomoidride A in CH_3CN

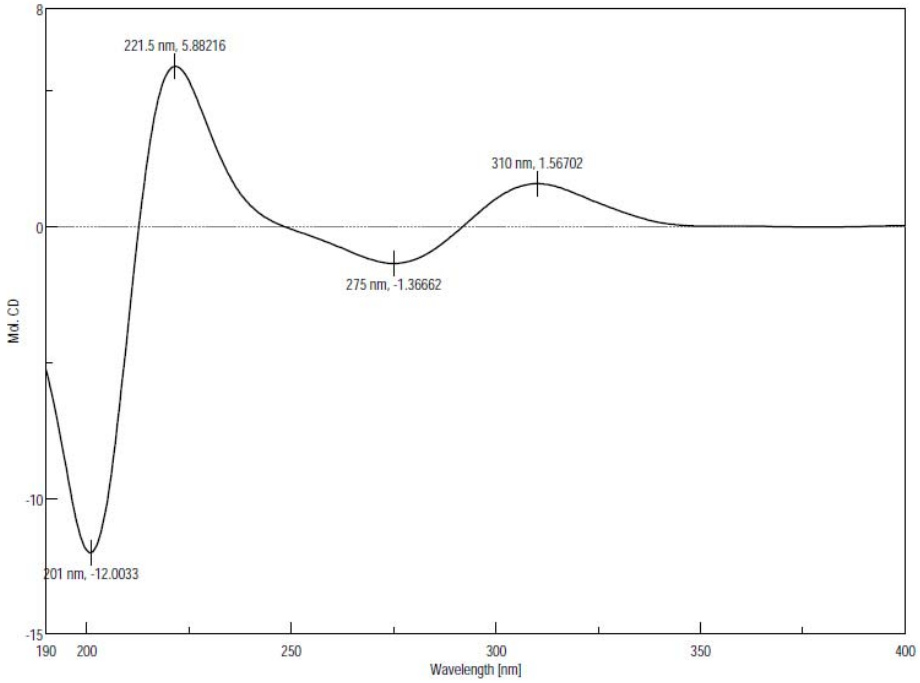


Fig. **S39**. CD spectrum for Phomoidride A in CH_3CN

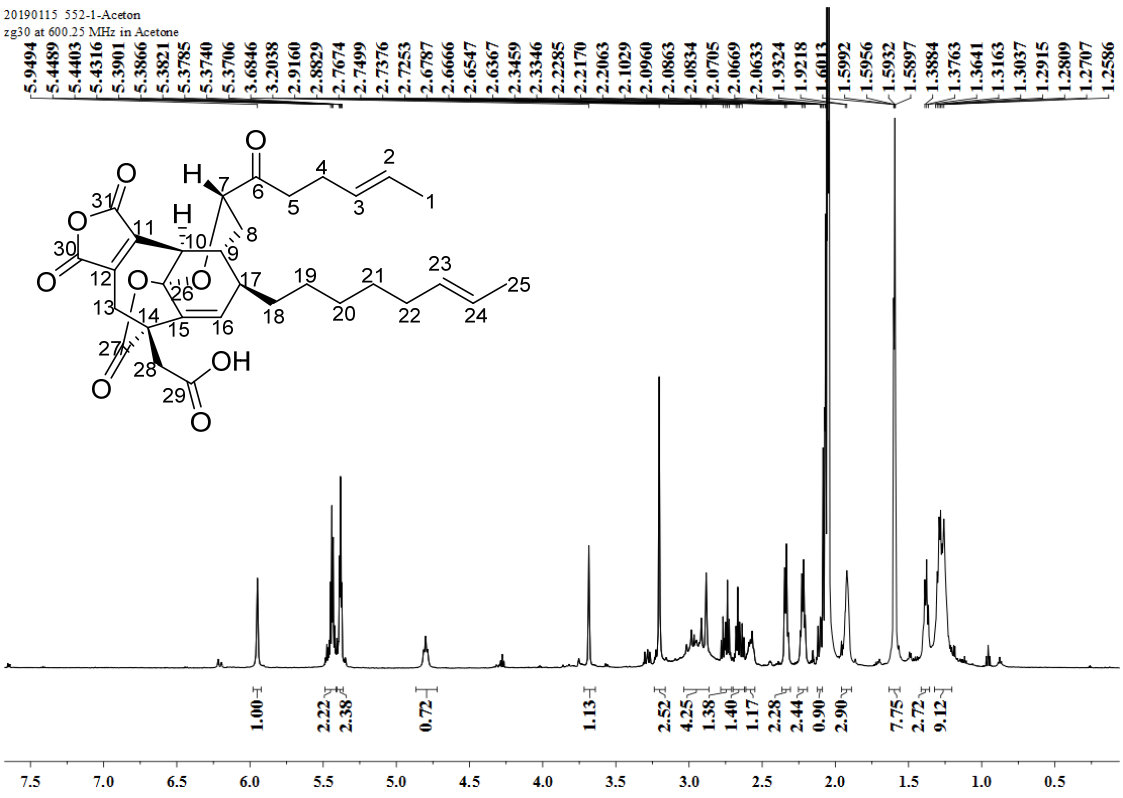


Fig. **S40**. ^{1}H NMR (600 MHz, Aceton-d_6) spectrum for Phomoidride B

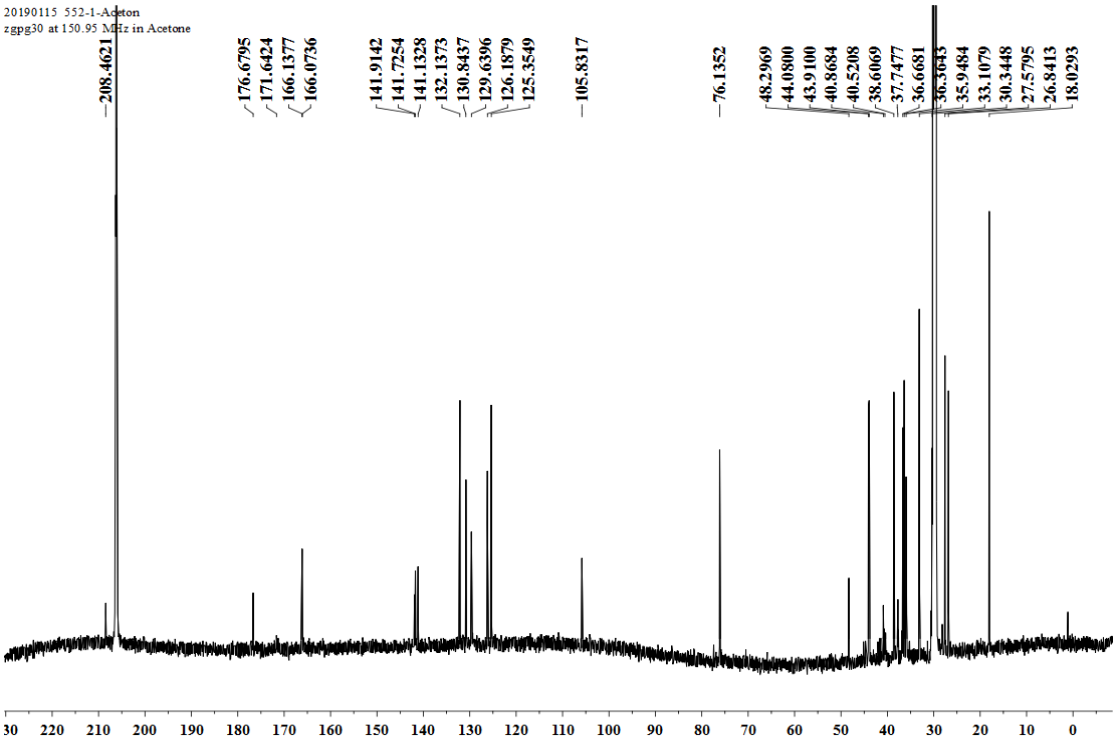


Fig. **S41**. ^{13}C NMR (150 MHz, Aceton-d_6) spectrum for Phomoidride B

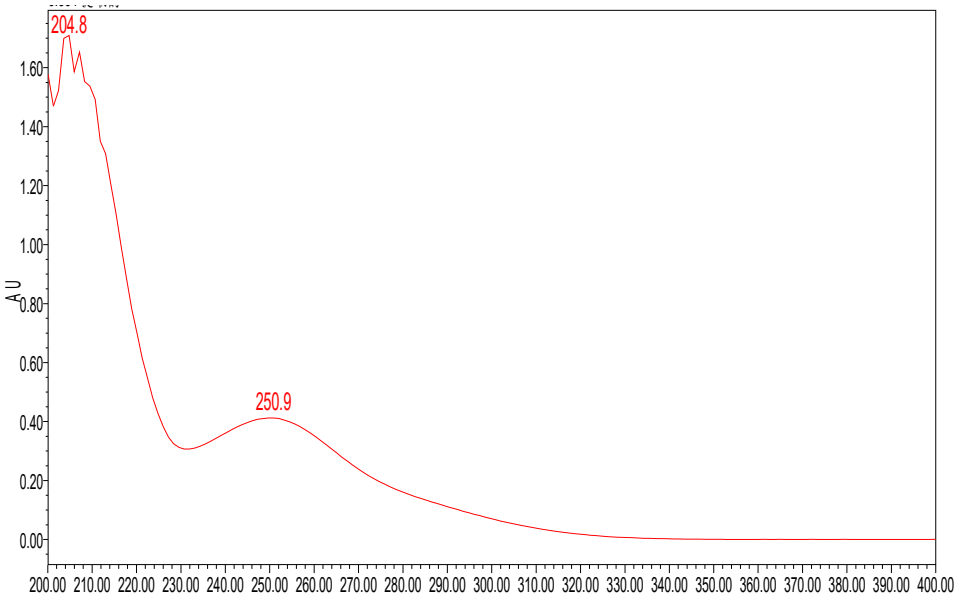


Fig. **S42**. UV spectrum for Phomoidride B in CH_3CN

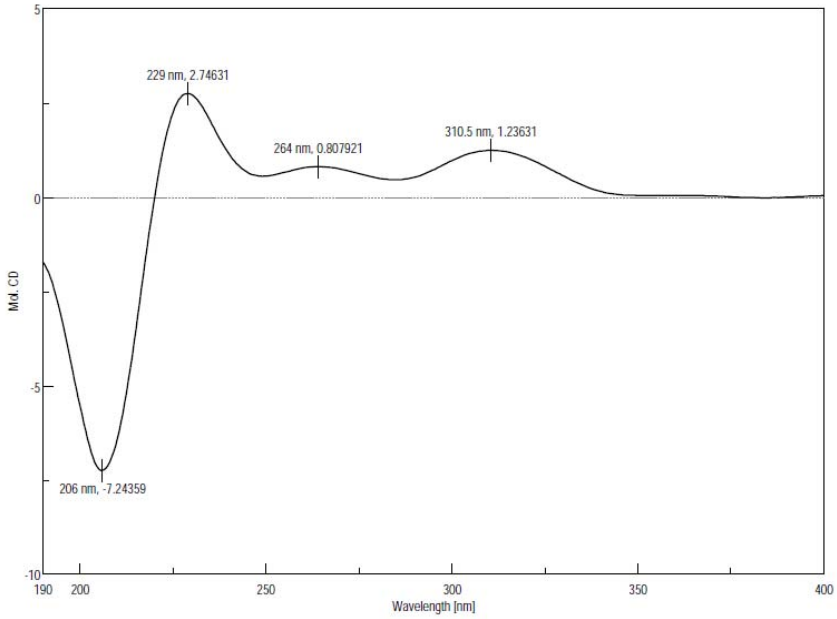


Fig. **S43**. CD spectrum for Phomoidride B in CH_3CN

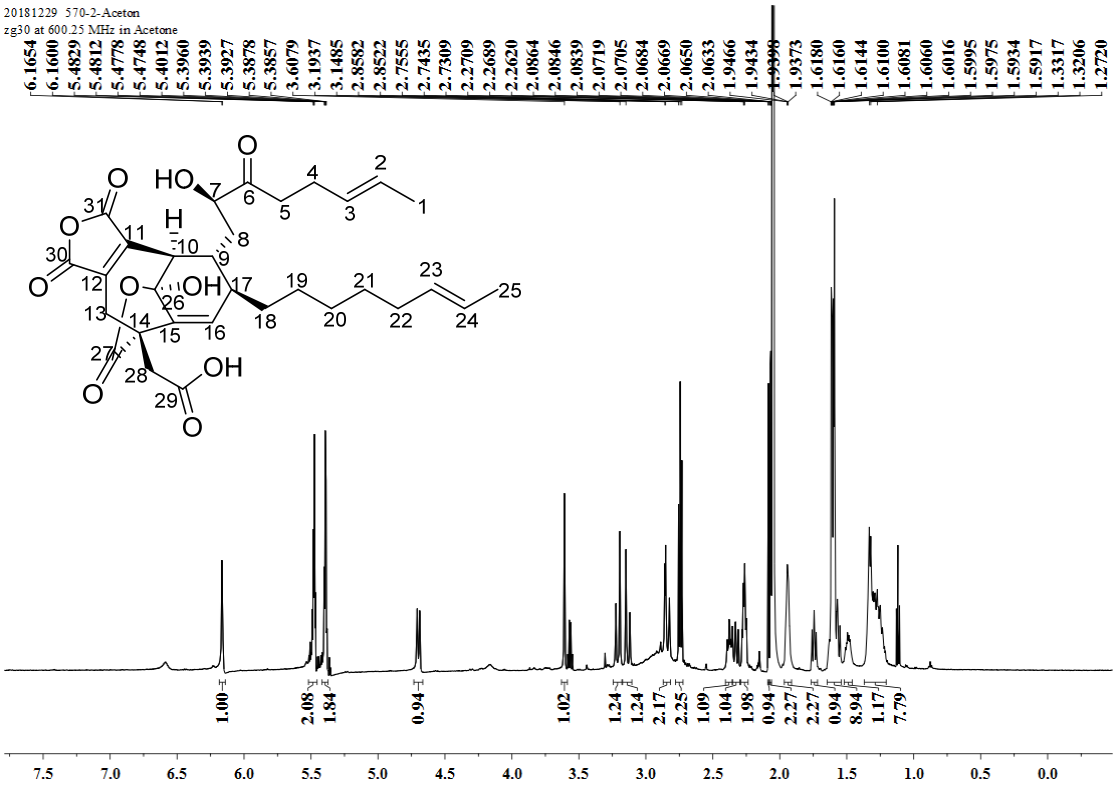


Fig. **S44**. ^{1}H NMR (600 MHz, Aceton-d_6) spectrum for Phomoidride C

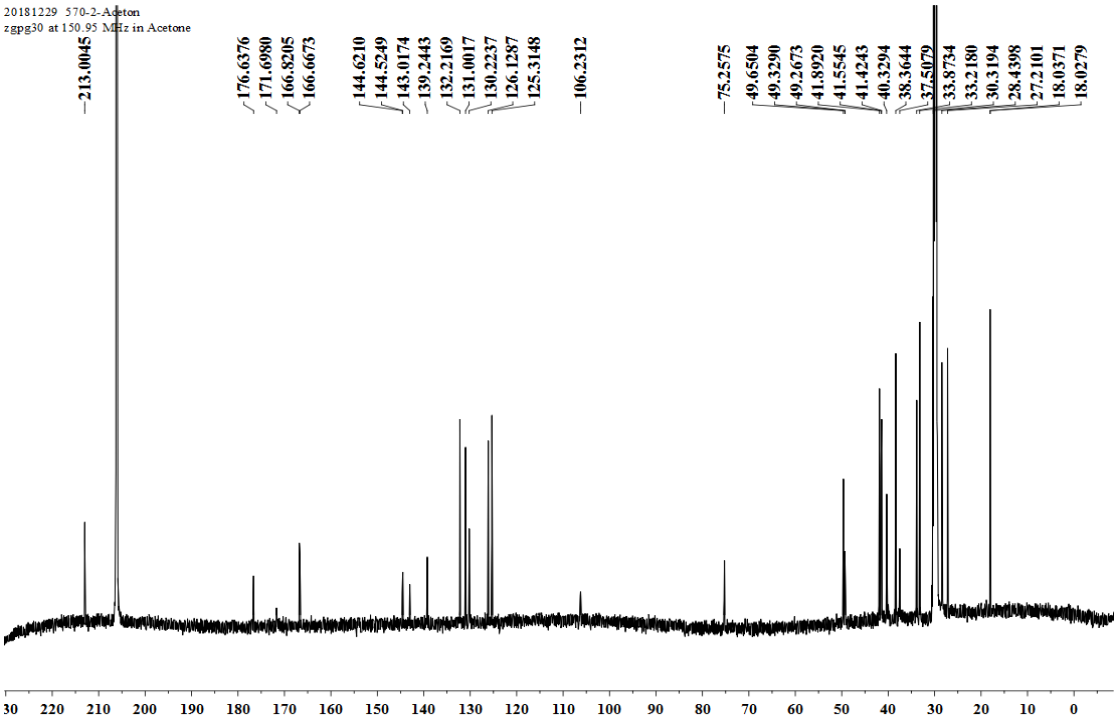


Fig. **S45**. ^{13}C NMR (150 MHz, Aceton-d_6) spectrum for Phomoidride C

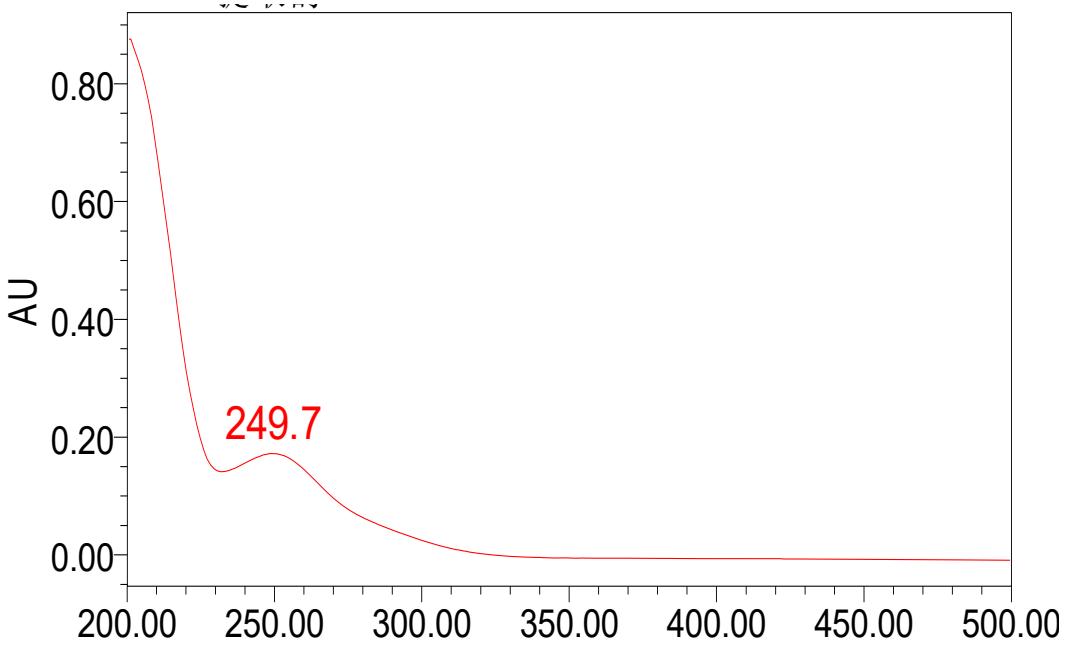


Fig. **S46**. UV spectrum for Phomoidride C in CH_3CN

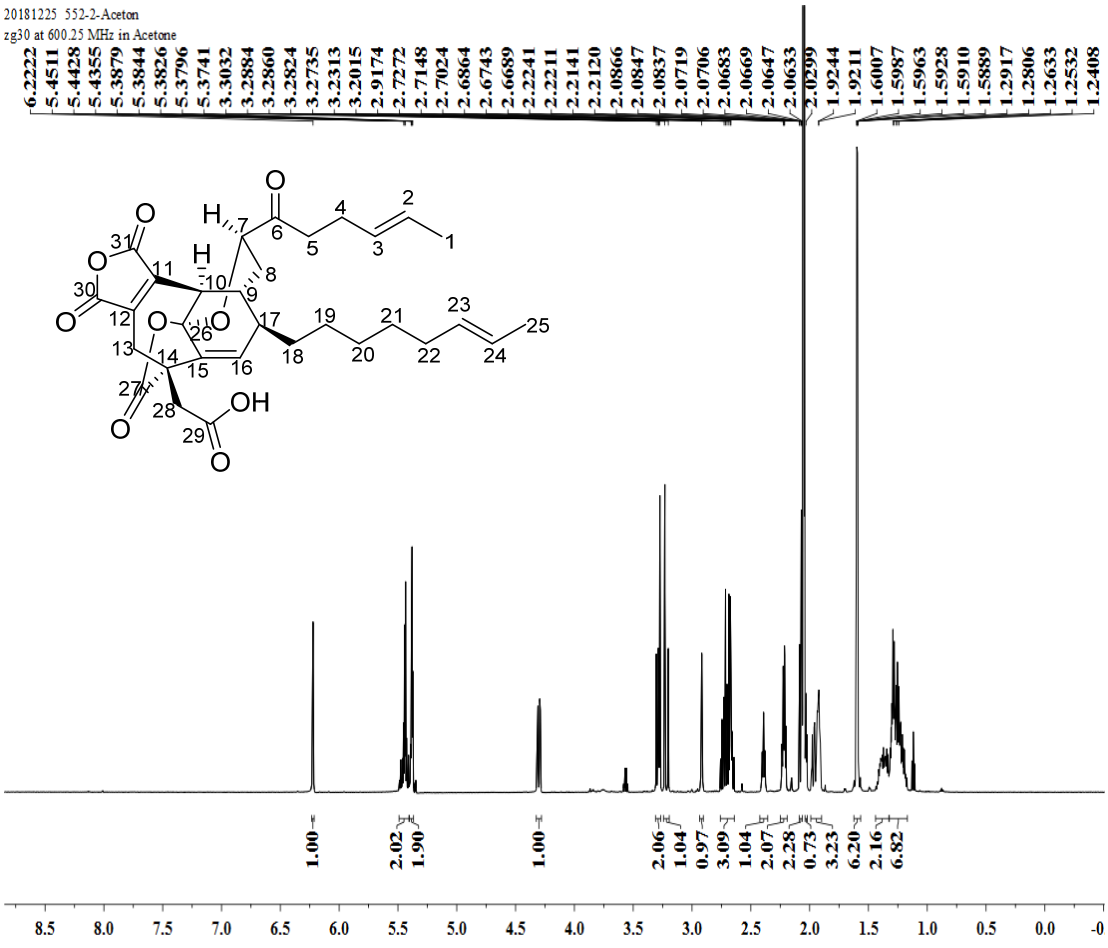


Fig. **S47**. ^{1}H NMR (600 MHz, Aceton-d_6) spectrum for Phomoidride D

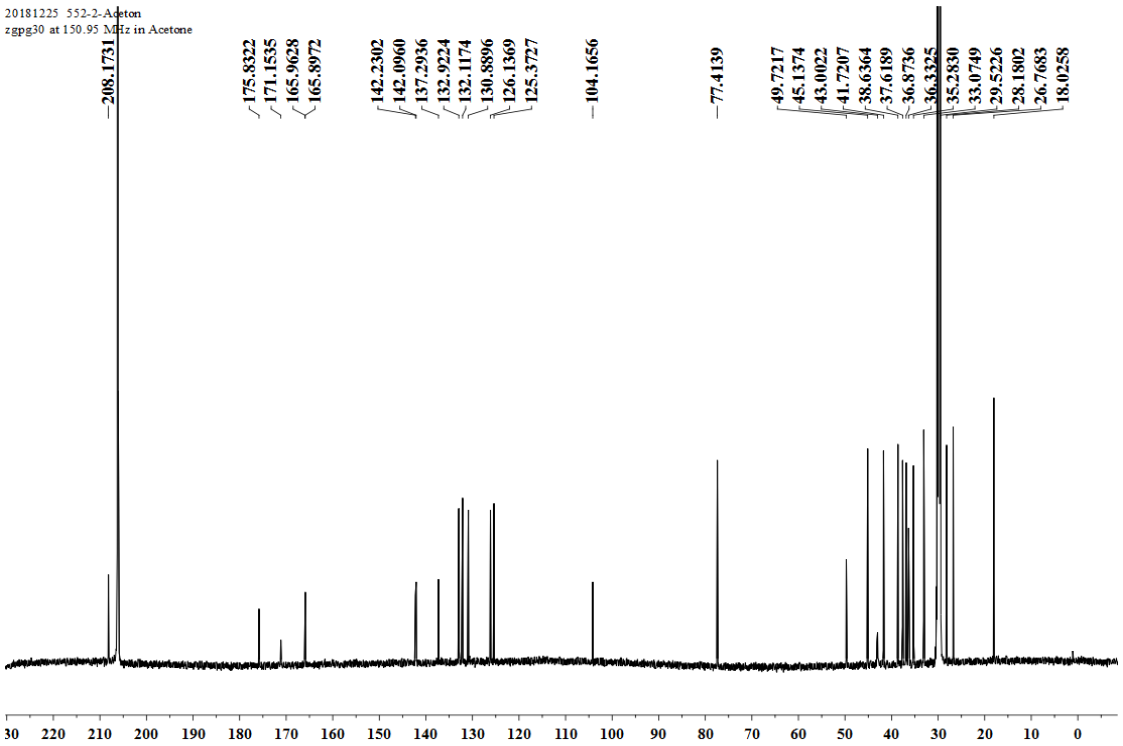


Fig. **S48**. ^{13}C NMR (150 MHz, Aceton-d_6) spectrum for Phomoidride D

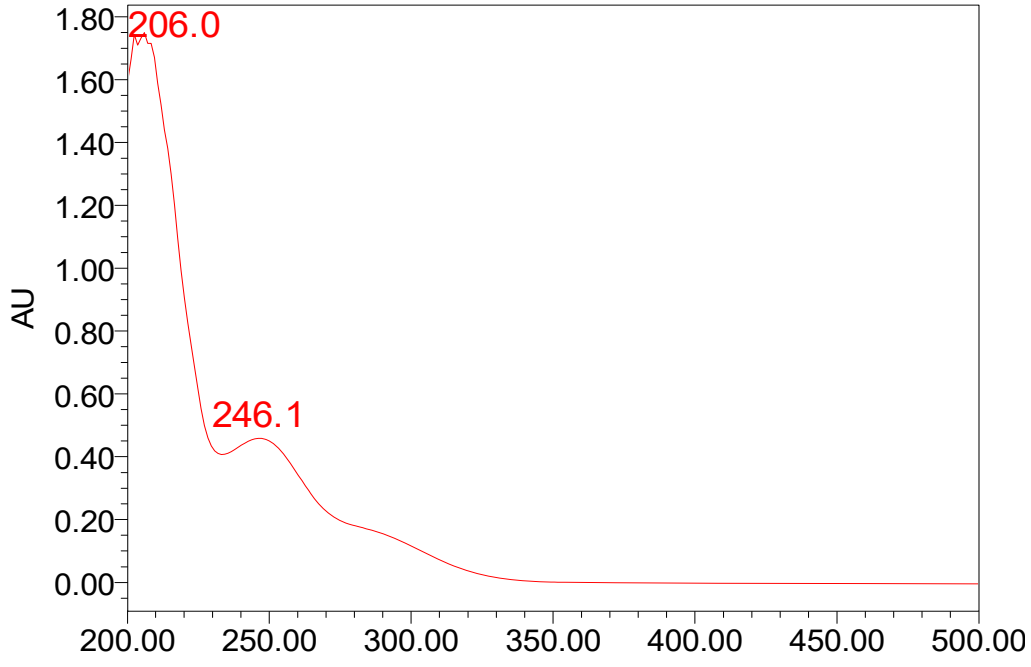
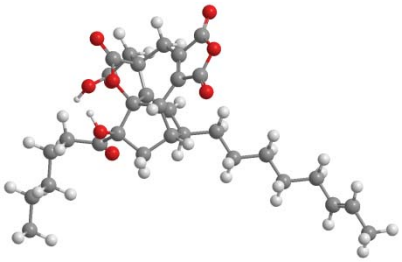
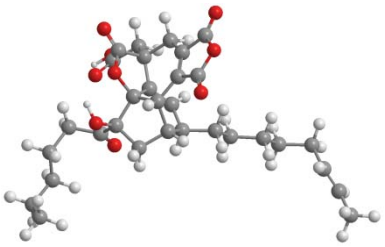


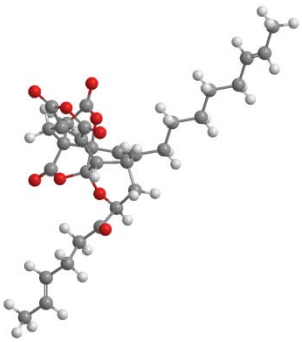
Fig. **S49**. UV spectrum for Phomoidride D in CH_3CN



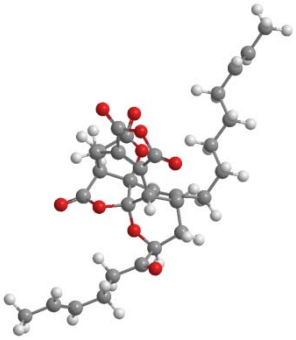
Conformer: 1-2 (82.8%)
Energy: -1180468.90 kcal/mol



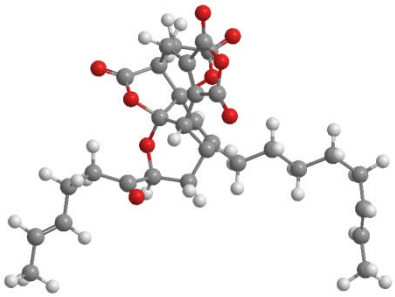
1-13 (17.2%)
-1180467.97 kcal/mol



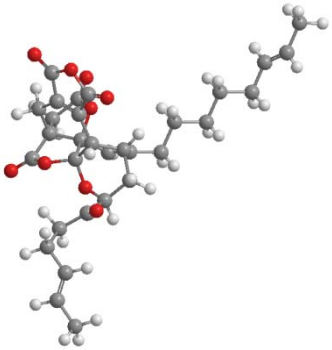
Conformer: 2-20 (82.8%)
Energy: -1178860.03 kcal/mol



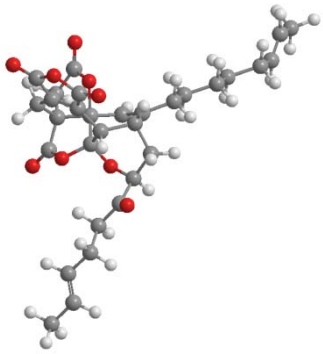
2-2 (24.3%)
-1178859.95 kcal/mol



Conformer: 2-13 (18.3%)
Energy: -1178859.78 kcal/mol



2-14 (21.6%)
-1178859.88 kcal/mol



2-19 (8.0%)
-1178859.29 kcal/mol

Fig. **S50**. 3D conformers and energies of **1** and **2** at B3LYP/6-31G(d) level in gas phase.