Supplementary Information for

8,14-*seco*-*ent*-Kaurane Diterpenoids from *Isodon glutinosus*: Enol-Enol Tautomerism and Antitumor Activity

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1. General Experimental Procedures

Optical rotation was measured with Jasco P-1020 polarimeters. UV spectra and IR spectra were obtained from Shimadzu UV-2401A spectrophotometer and Tenor 27 spectrophotometer respectively. 1D and 2D NMR spectra were recorded on Bruker Avance III 500 and Bruker Avance III 600 spectrometers with TMS as internal standard. The chemical shifts (δ) were expressed in ppm with reference to the solvent signals. HRESIMS was performed on an Agilent 6200 QSTAR TOF time-of-flight mass spectrometer. Melting point was measured by melting-point apparatus HMX-1B+. Crystal X-ray diffraction data was recorded on the Bruker D8 Quest diffractometer using a copper target (Cu Kα) as a light source. Semipreparative HPLC was performed on an Agilent 1260 liquid chromatograph with a Zorbax SB-C18 (9.4 mm × 25 cm) column. Column chromatography (CC) was performed using silica gel (80–100 mesh and 100–200 mesh, Qingdao Marine Chemical, Inc., Qingdao, P. R. China), MCI gel (CHP20P, 75–150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan) and LH-20. Fractions were monitored by thin layer chromatography (TLC), which was carried out on silica gel 60 F254 on glass plate (Qingdao Marine Chemical, Inc.). Spots were visualized by UV light (254 nm and 365 nm) and by heating silica gel plates sprayed with 10% H_2SO_4 in ethanol. DMEM, RPMI 1640, PBS and FBS were purchased from VivaCell. 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium (MTS) was bought from Promega. All of cell plates were obtained from NEST. The apoptosis kit and Cell cycle kit were bought from BD and Beyotime respectively.

2. Bioactivity Investigation of Glutinosasins A−E

2.1 Cytotoxicity assay

MTS assay was used to evaluated the cytotoxic activity. The human tumor cell lines: leukemia cell line (HL-60), lung cancer cell line (A549), breast cancer cell line (MDA-MB-231), and colorectal carcinoma cell line (SW480) were used in the cytotoxic assay, which obtained from ATCC (Manassas, VA, USA). Cells were cultured in RPMI 1640 or DMEM medium supplemented with 10% fetal bovine serum at 37 ℃ in a humidified atmosphere with 5% CO_2. Briefly, cells were seeded into 96-well plates at suitable density. After incubated at 37 ℃ overnight, the cells were cultured with compounds at concentrations of 0.064, 0.32, 1.6, 8, and 40 μM (in triplicate) or Taxol for another 48 h. The data were analyzed displayed as mean ± SD by GraphPad Prism 9.0.

2.2 Cell apoptosis

Cell apoptosis was measured by Annexin V-PE/7-AAD method. Briefly, SW480 cells were plated in 6-well plates with a density of 3×10^5 cells/2 ml and incubated for 24 h. After incubation, SW480 cells were then incubated with or without compound **4** (5 μM、10 μM、20 μM) or doxorubicin (5 μM) as positive control. Incubated after 24 h, the treated cells were washed with cold PBS which were digested by trypsin and collected cells. After centrifuged, 5 μL Annexin V-PE and 5 μL 7-AAD were added and incubated in the dark at room temperature for 15 min before quantification by Flow Cytometer (BD, FACSymphony, America).

2.3 Cell cycle

Propidium Iodide (PI) method was used to measure cell arrest. SW480 cells were seeded in 6-well plates at the density of 3×10^5 cells/2 ml and incubated for 24 h. After incubated, SW480 cells were then nurtured with or without compound **4** (1 μM、2 μM、4 μM) for 24 h. Incubated after 24 h, the treated cells were washed with cold PBS which were digested by trypsin and collected cells. After centrifuged, adding 75% ethanol into centrifugation tube incubated at 4 ℃ overnight. In the following day,100 μL RNase A was added and incubated in the 37 ℃ for 30 min. The addition of 400 μL PI was continuously incubated in the dark at room temperature for 30 min before quantification Flow Cytometer (BD, FACSymphony, America).

3. NMR, MS, UV, ECD, IR Spectra, and OR of Glutinosasin A

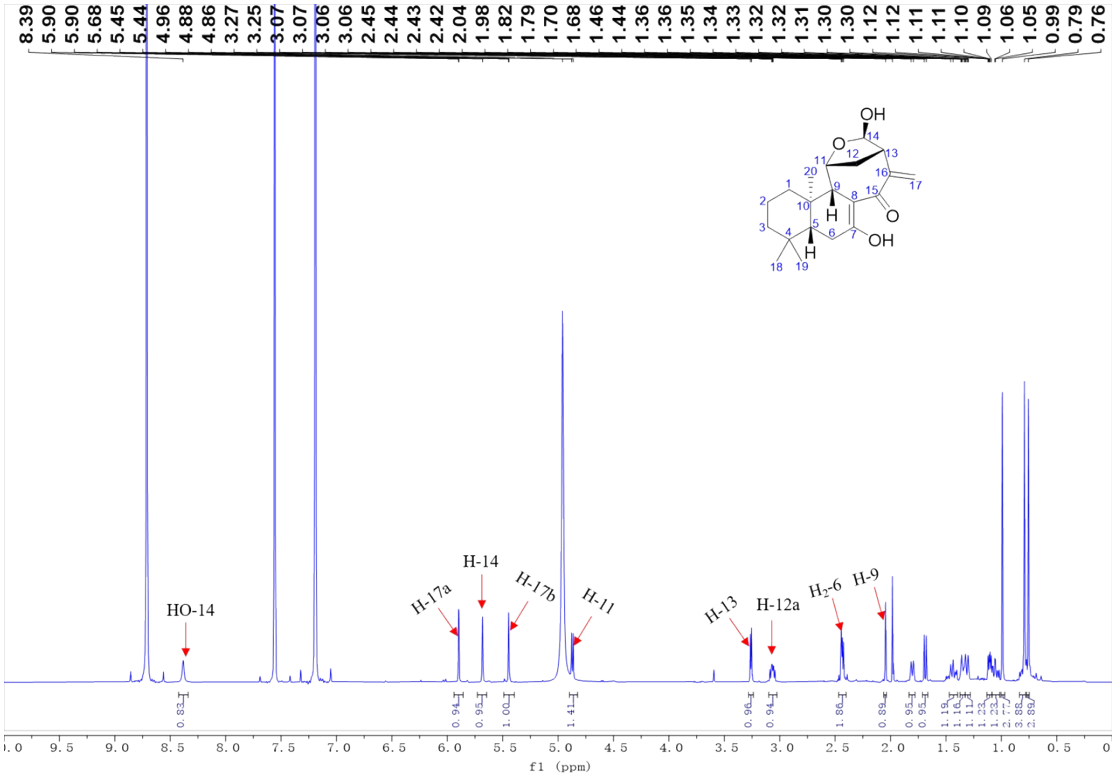


Figure S1. ^{1}H NMR spectrum of glutinosasin A (**1**) (600 MHz, pyridine-d_5)

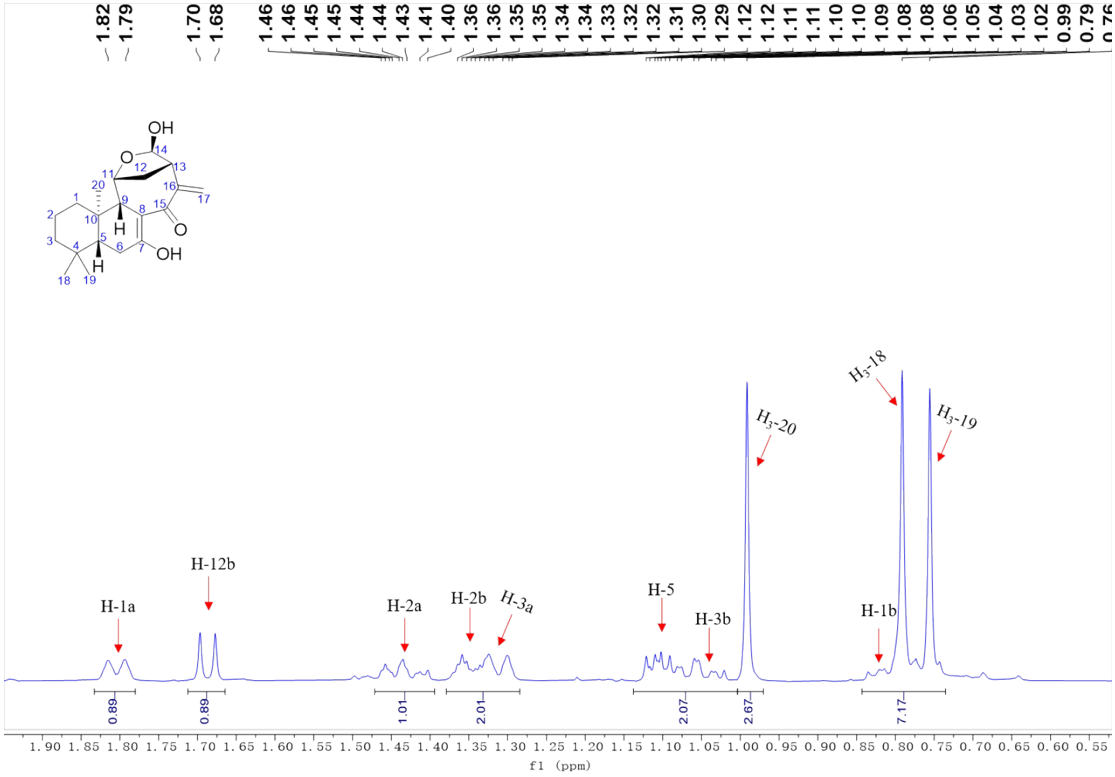


Figure S2. ^{1}H NMR spectrum of glutinosasin A (**1**) (600 MHz, pyridine-d_5) (amplified)

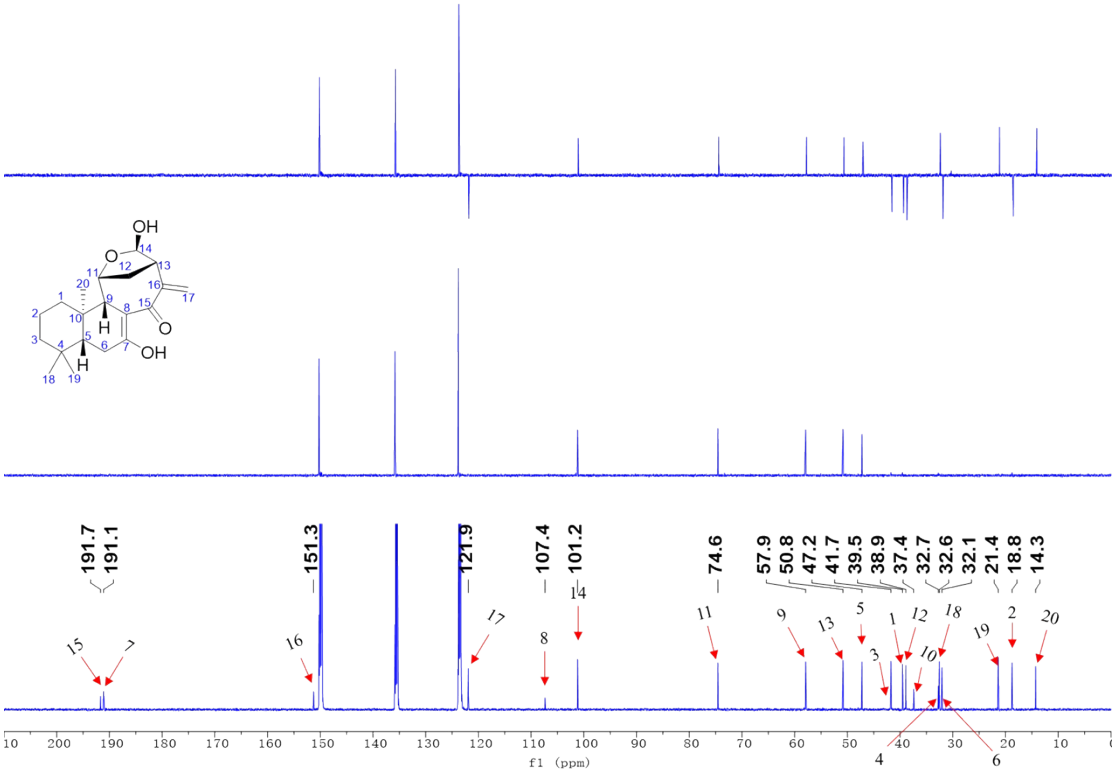


Figure S3. ^{13}C NMR spectrum of glutinosasin A (**1**) (150 MHz, pyridine-d_5)

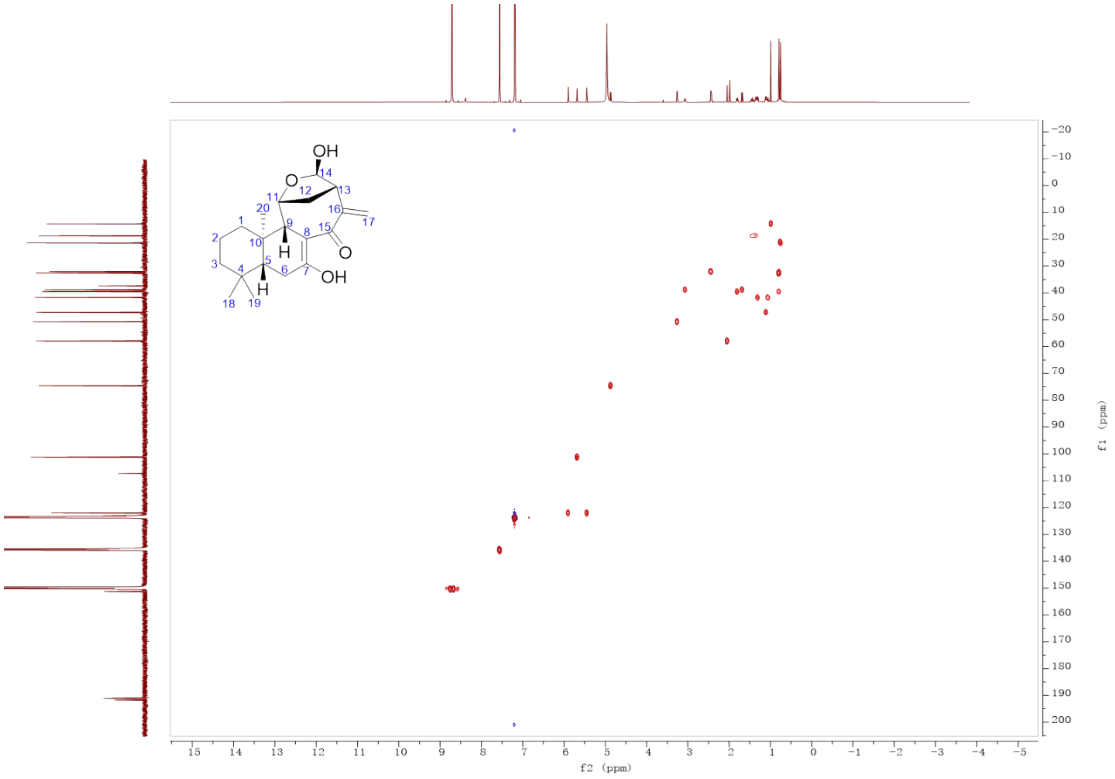


Figure S4. HSQC spectrum of glutinosasin A (**1**) (^{1}H: 600 MHz, ^{13}C: 150 MHz, pyridine-d_5)

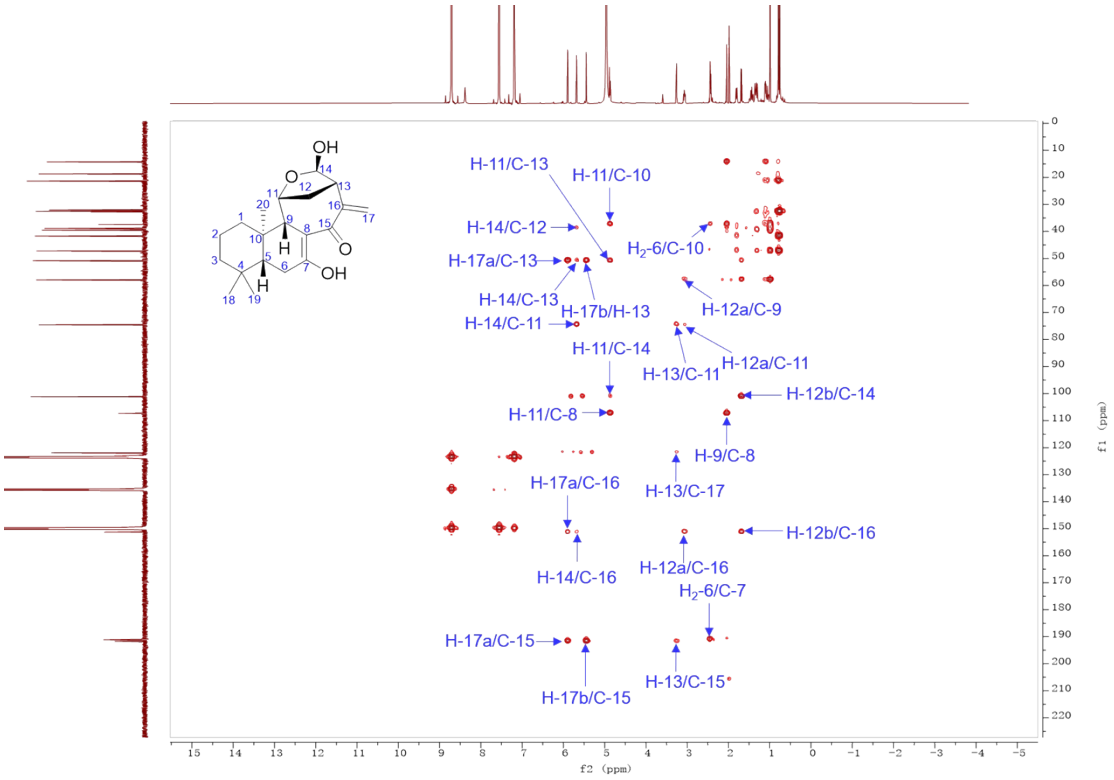


Figure S5. HMBC spectrum of glutinosasin A (**1**) (^{1}H: 600 MHz, ^{13}C: 150 MHz, pyridine-d_5)

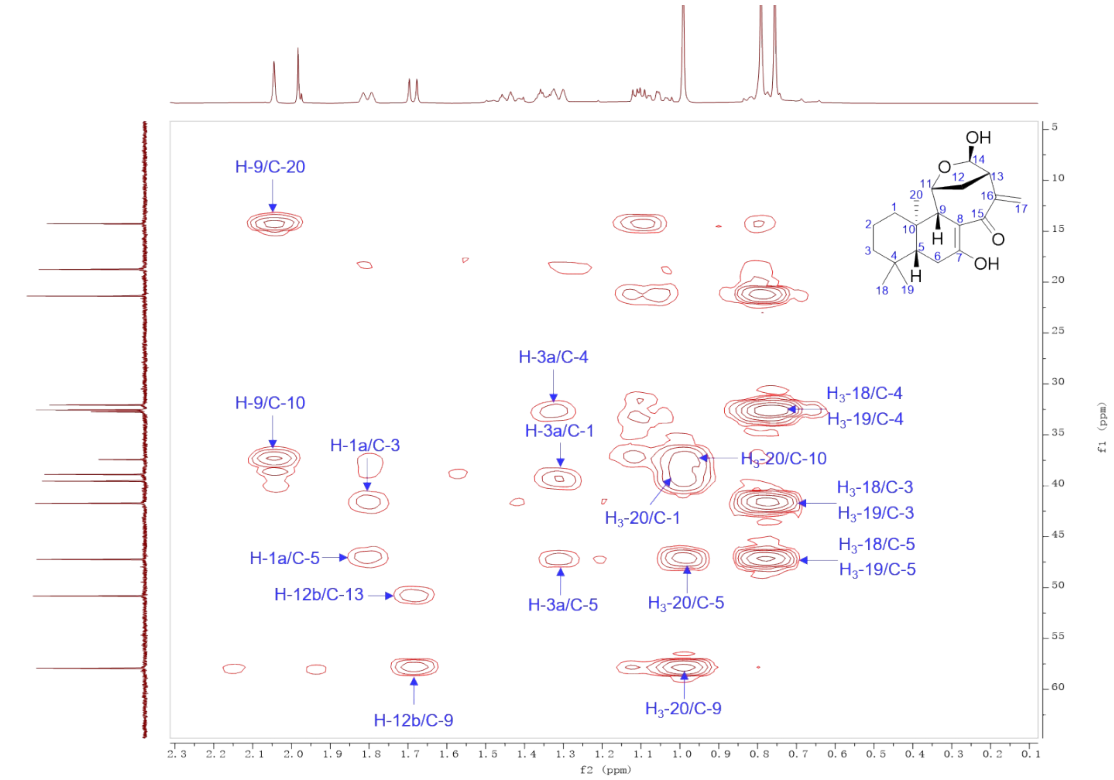


Figure S6. HMBC spectrum of glutinosasin A (**1**) (^{1}H: 600 MHz, ^{13}C: 150 MHz, pyridine-d_5) (amplified)

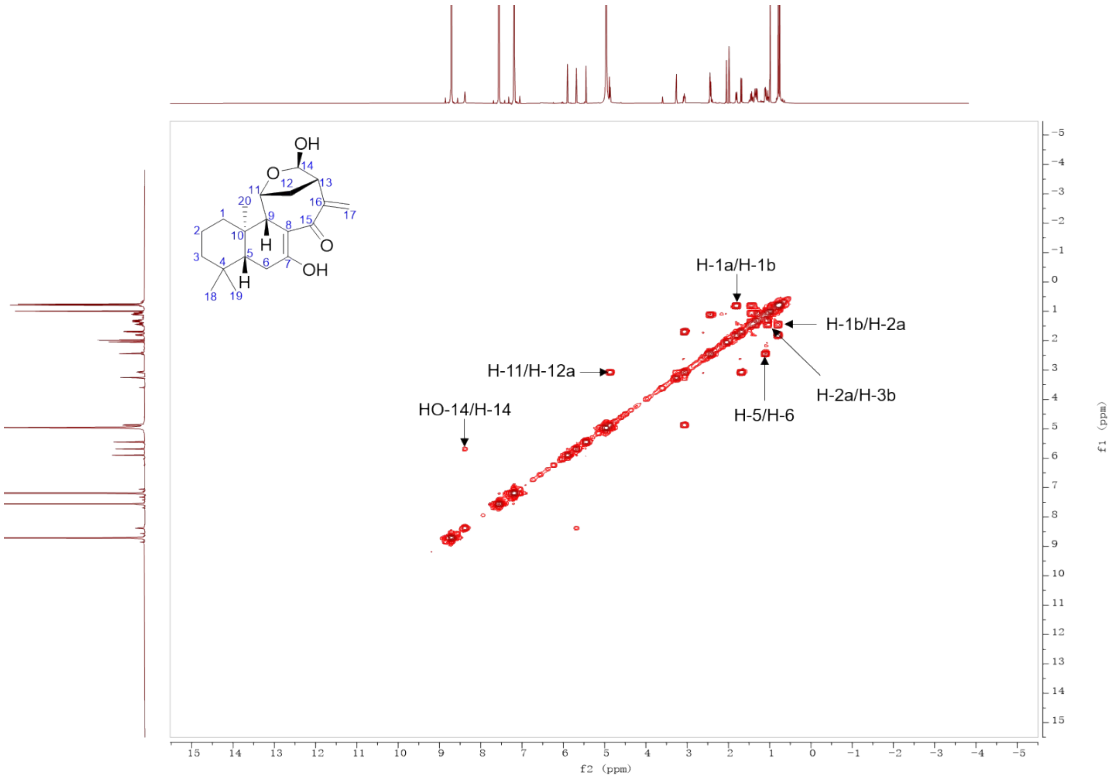


Figure S7. ^{1}H–^{1}H COSY spectrum of glutinosasin A (**1**) (600 MHz, pyridine-d_5)

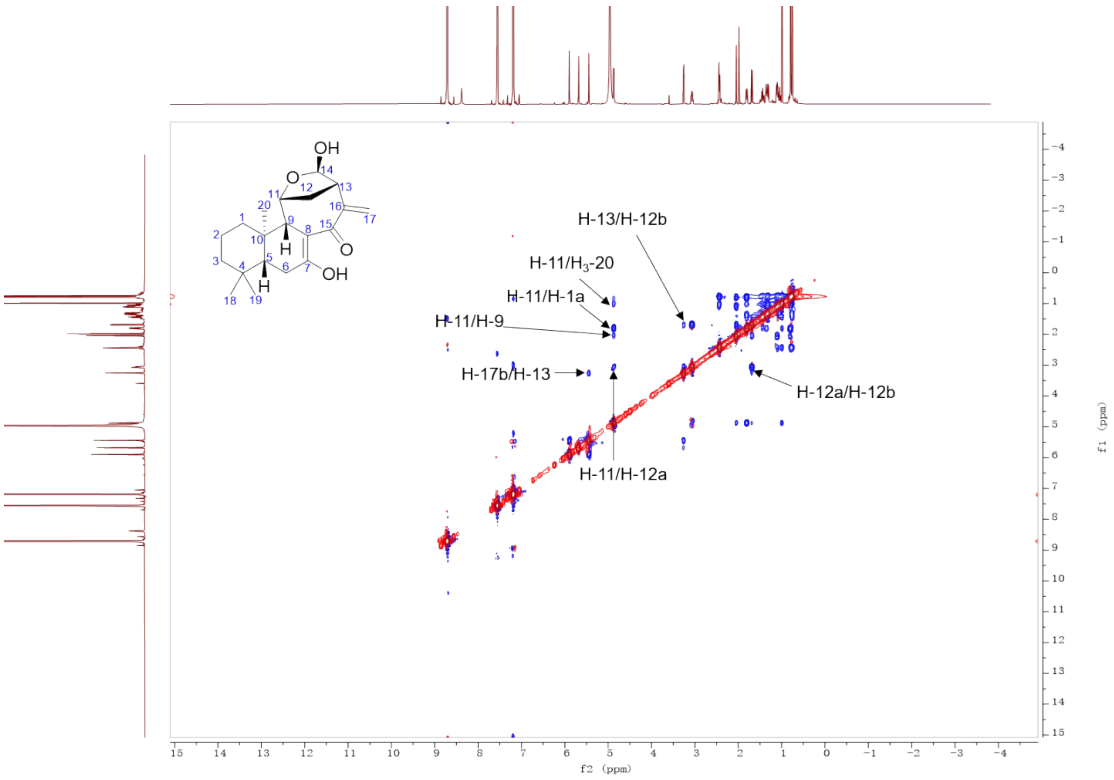


Figure S8. ROESY spectrum of glutinosasin A (**1**) (600 MHz, pyridine-d_5)

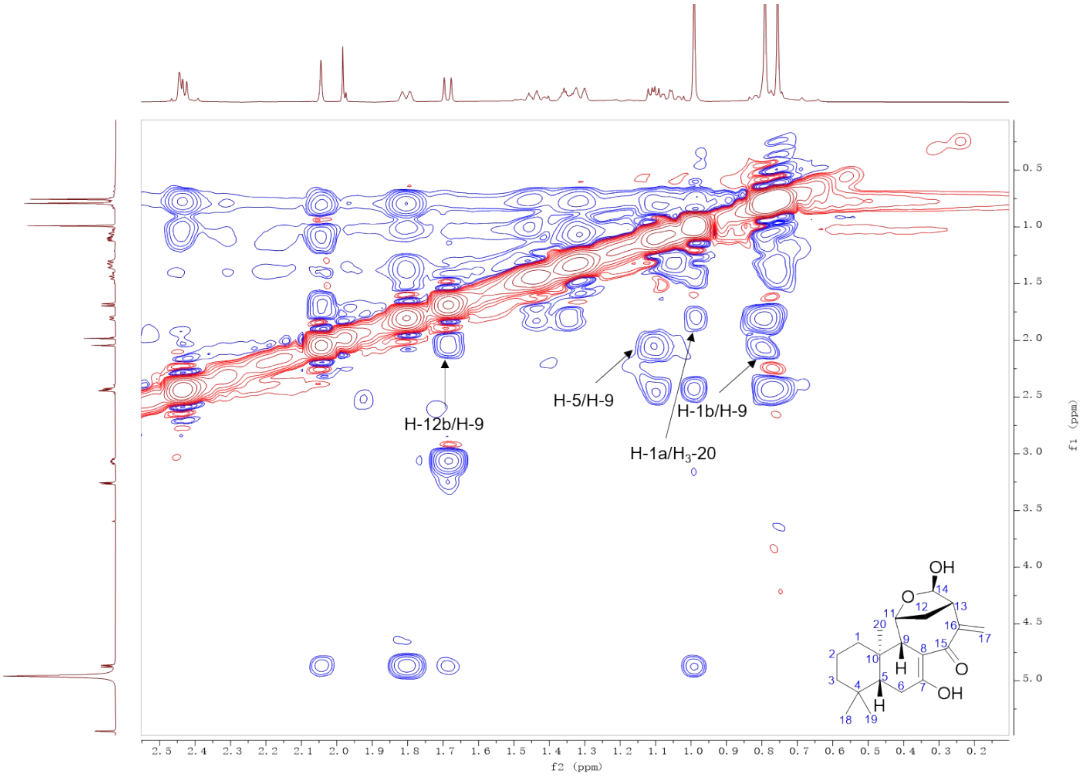
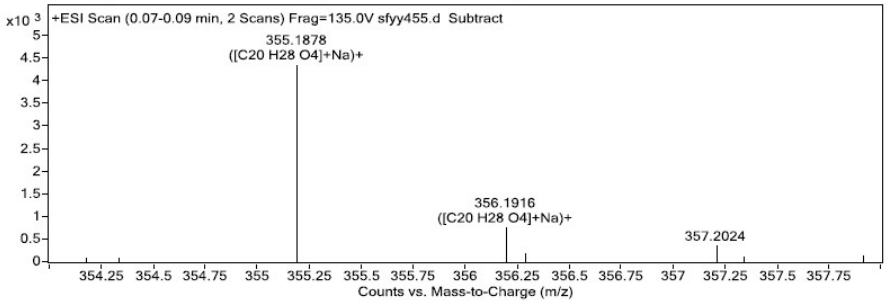


Figure S9. ROESY spectrum of glutinosasin A (**1**) (600 MHz, pyridine-d_5)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
242.2845	1	2376.21		
355.1878	1	4365.42	C20 H28 O4	(M+Na)+
417.2805	1	1897.56		
433.2746	1	2783.81		
687.3861	1	1910.53		
841.5199	1	6409.75		
842.5242	1	3855.49		
857.4951	1	8287.35		
858.4977	1	5095.1		
859.4992	1	2372.38		

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
C20 H28 O4	332.1988	355.1880	355.1878	0.20	0.56	7.0000

Figure S10. The HRESIMS spectrum of glutinosasin 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 : Monday, 12-DEC-2022

Set Temperature : 20.0

Time Delay : Disabled

Delay between Measurement : Disabled

n	Average	Std.Dev.	% RSD	Maximum	Minimum
5	-9.56	0.82	-8.57	-8.96	-10.45

S.No	Sample ID	Time	Result	Scale	OR °Arc	WLG.nm	Lg.mm	Conc.g/100ml	Temp.
1	SFYY455	04:26:57 PM	-10.45	SR	-0.007	589	100.00	0.067	20.0
2	SFYY455	04:27:03 PM	-8.96	SR	-0.006	589	100.00	0.067	20.0
3	SFYY455	04:27:10 PM	-8.96	SR	-0.006	589	100.00	0.067	20.0
4	SFYY455	04:27:17 PM	-10.45	SR	-0.007	589	100.00	0.067	20.0
5	SFYY455	04:27:24 PM	-8.96	SR	-0.006	589	100.00	0.067	20.0

Figure S11. OR of glutinosasin A (**1**)

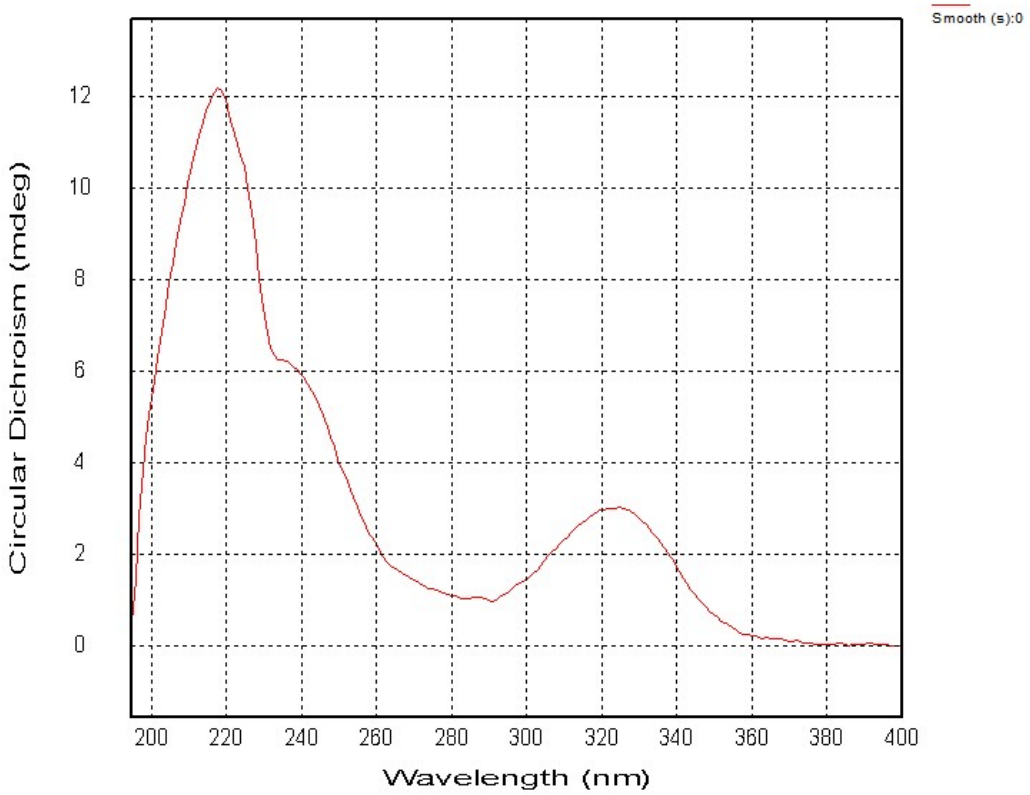


Figure S12. CD spectrum of glutinosasin A (**1**)

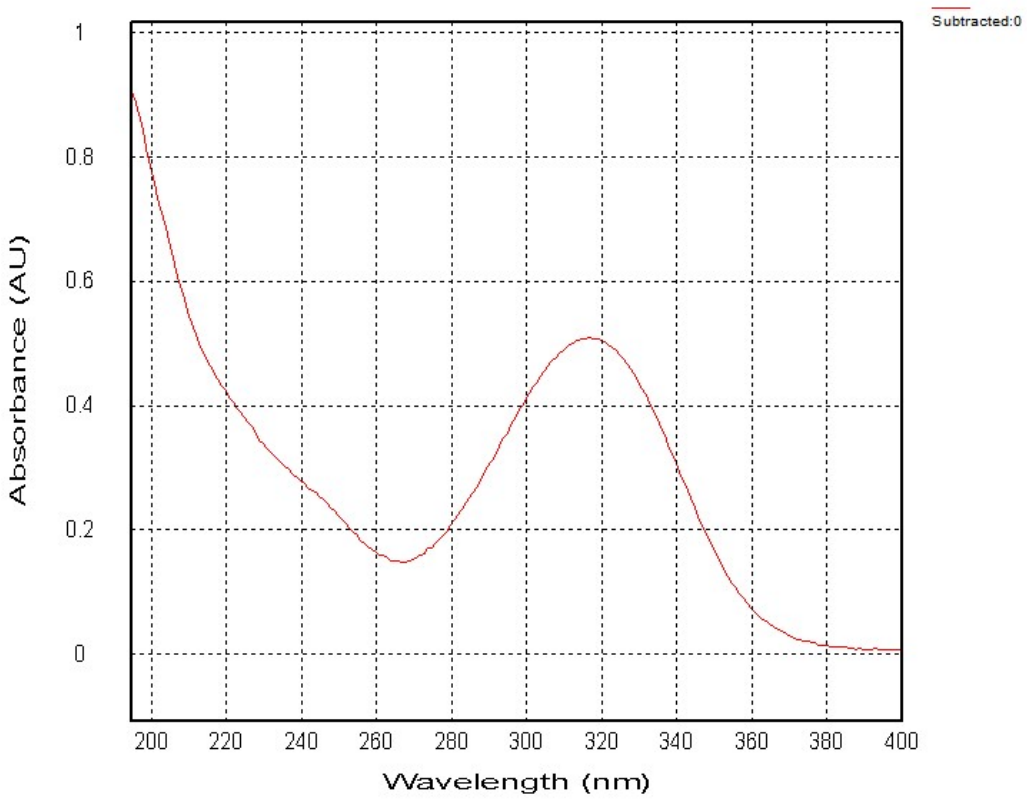


Figure S13. The UV spectrum of glutinosasin A (**1**)

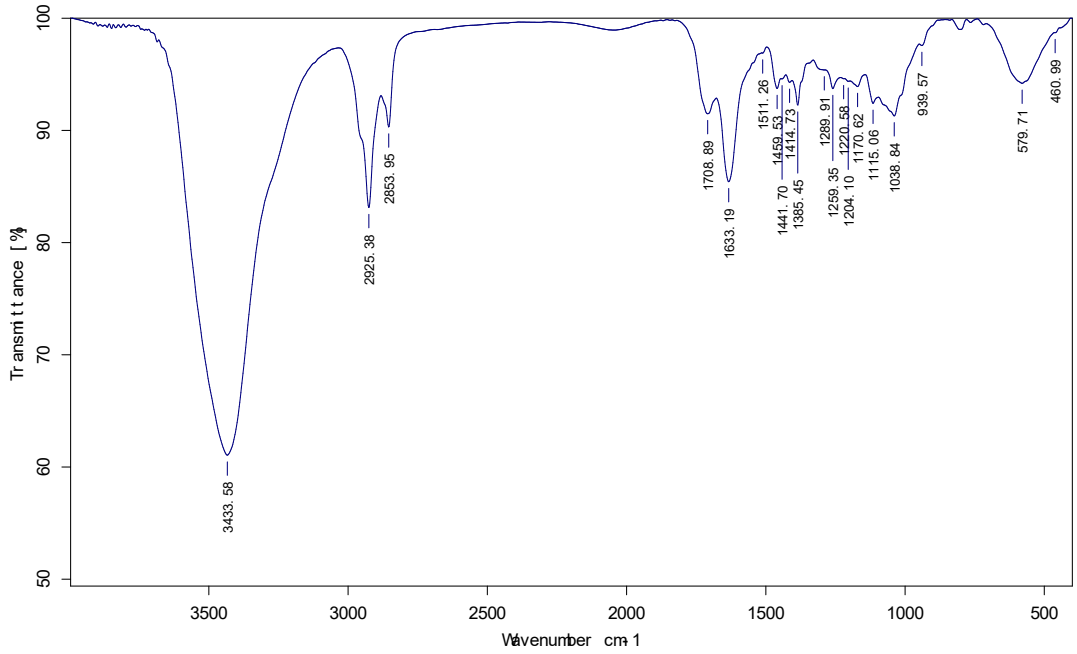


Figure S14. The IR spectrum of glutinosasin A (**1**)

4. NMR, MS, UV, ECD, IR Spectra, and OR of Glutinosasin B

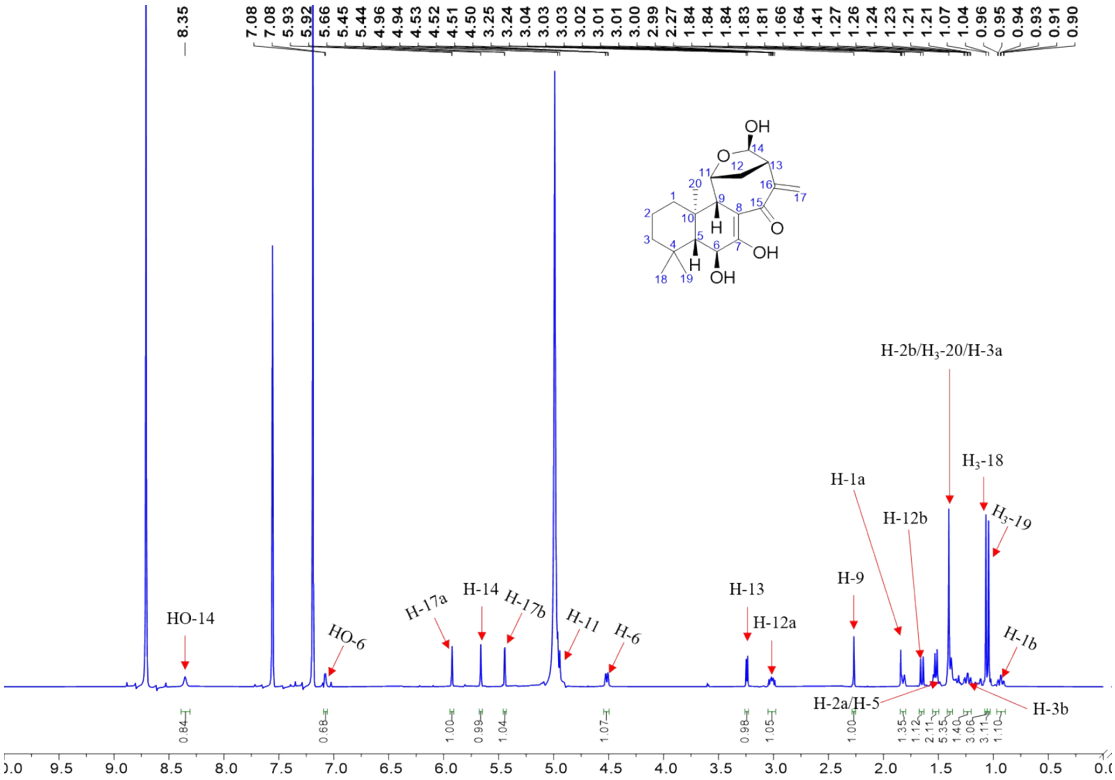


Figure S15. ^{1}H NMR spectrum of glutinosasin B (**2**) (600 MHz, pyridine-d_5)

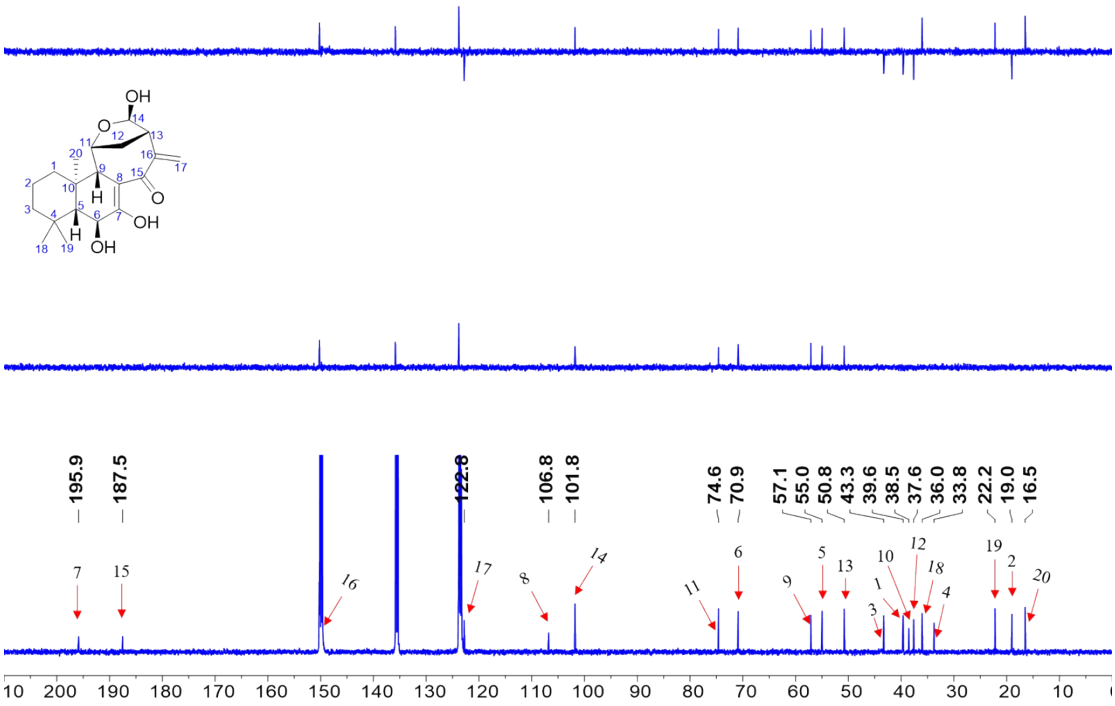


Figure S16. ^{13}C NMR spectrum of glutinosasin B (**2**) (150 MHz, pyridine-d_5)

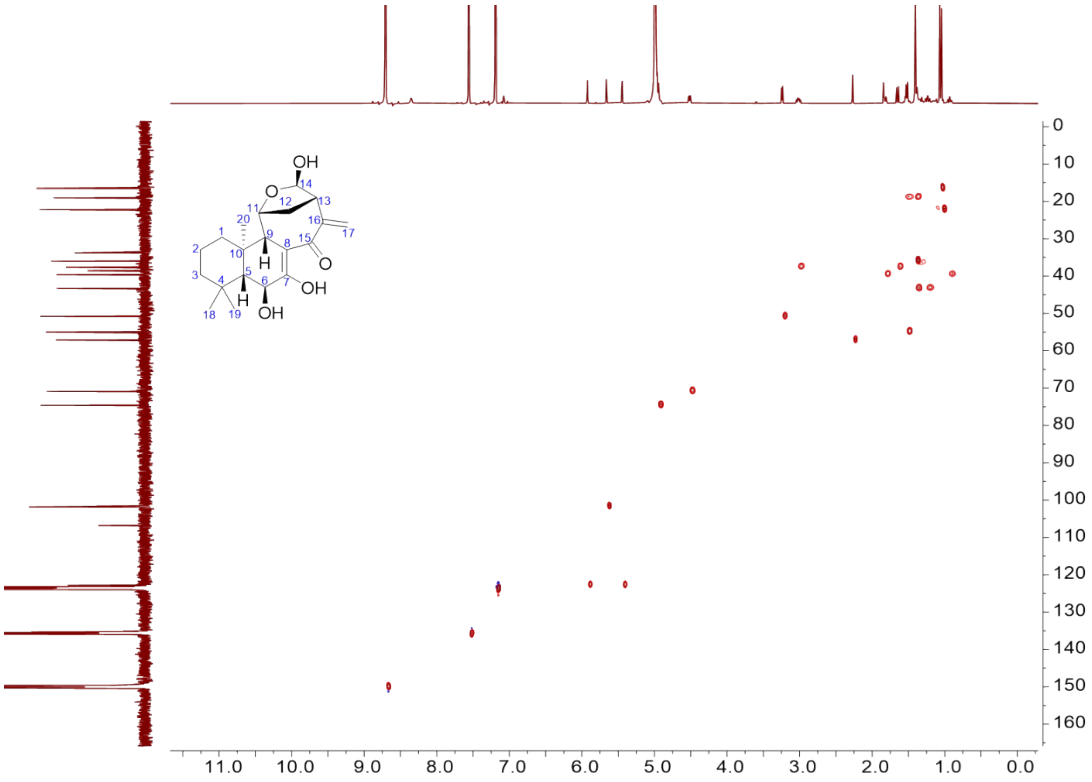


Figure S17. HSQC spectrum of glutinosasin B (**2**) (150 MHz, pyridine-d_5)

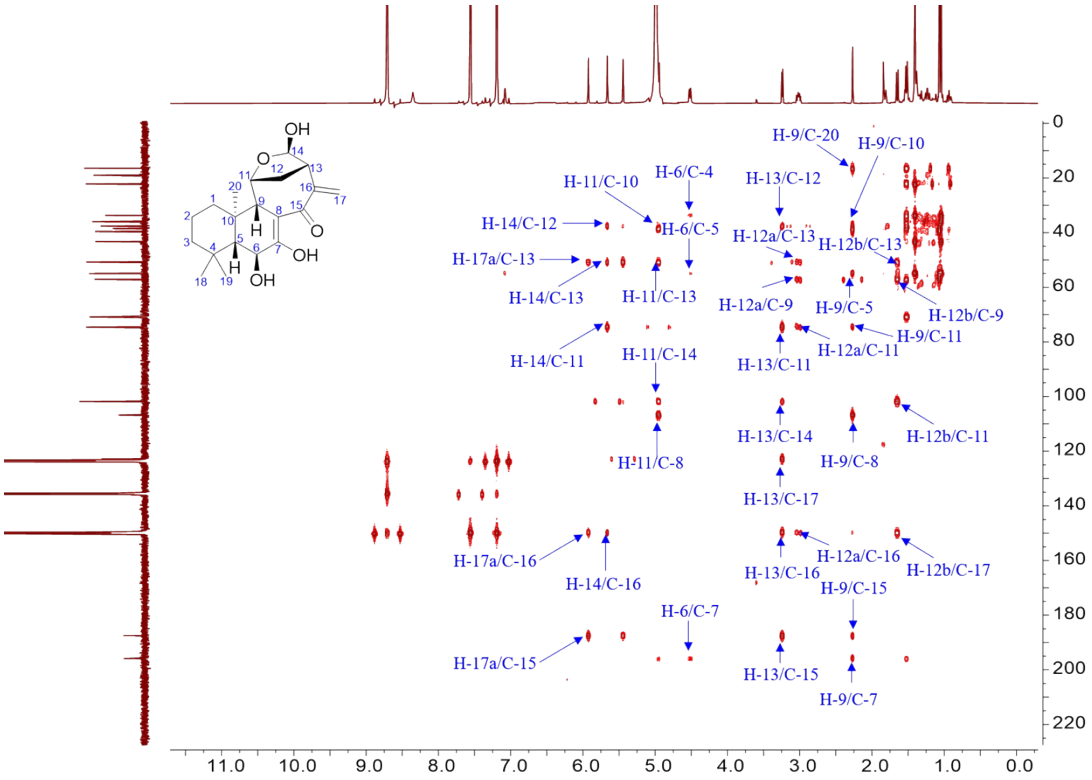


Figure S18. HMBC spectrum of glutinosasin B (**2**) (^{1}H: 600 MHz, ^{13}C: 150 MHz, pyridine-d_5)

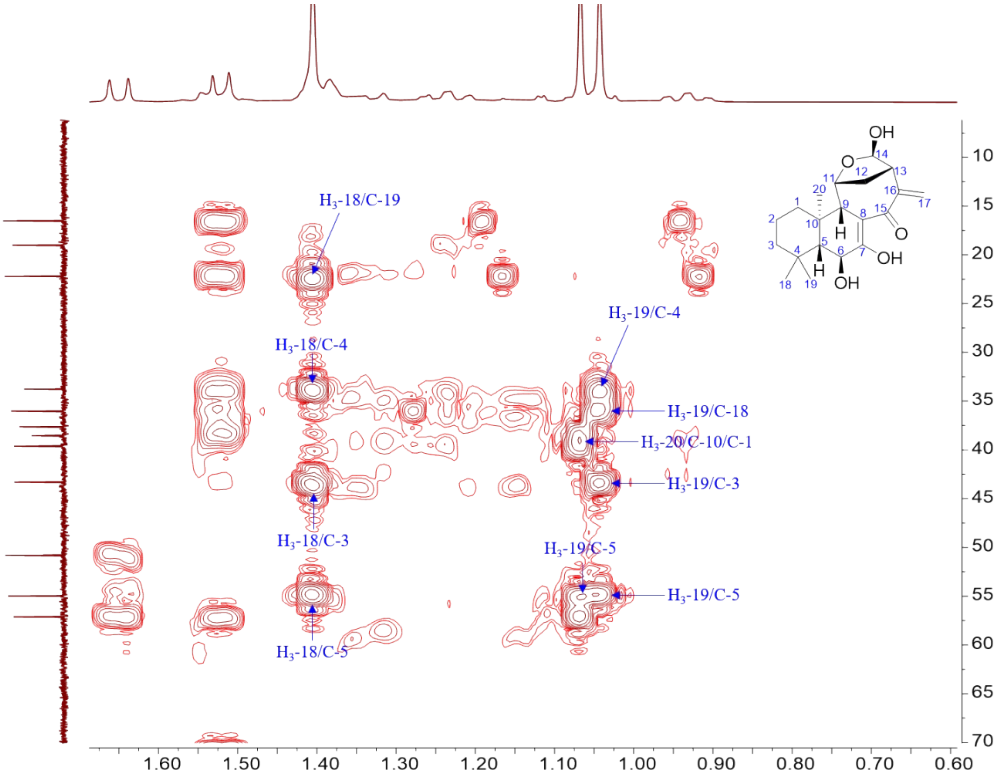


Figure S19. HMBC spectrum of glutinosasin B (**2**) (^{1}H: 600 MHz, ^{13}C: 150 MHz, pyridine-d_5) (amplified)

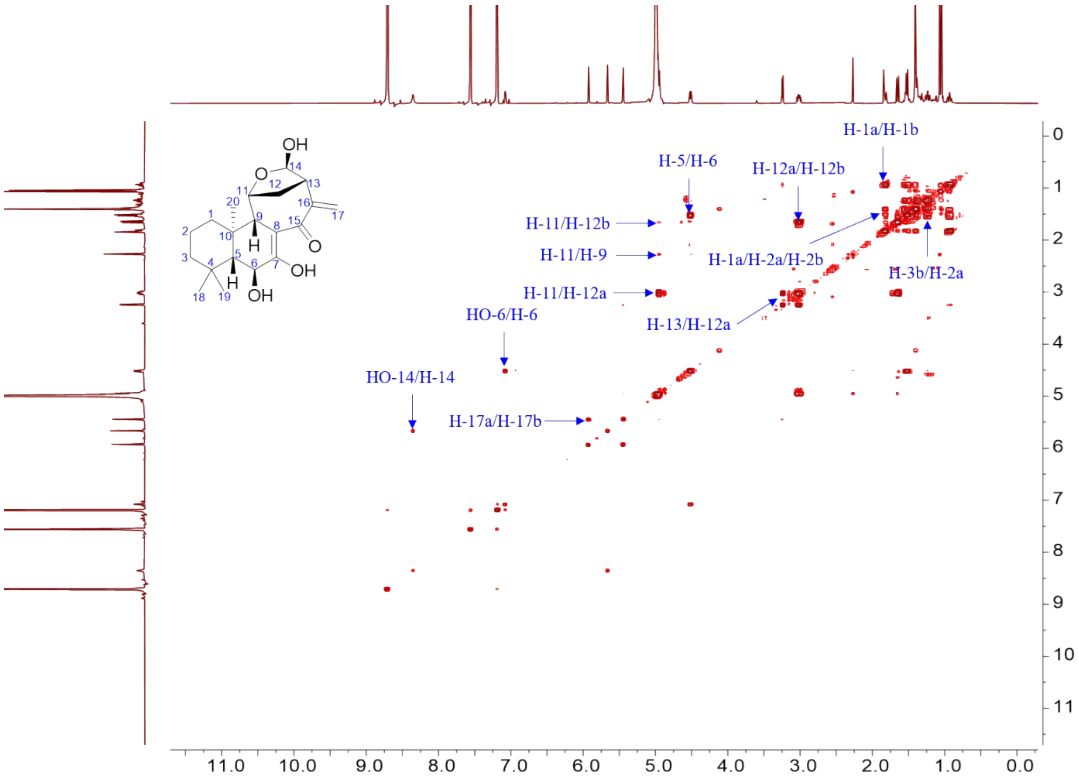


Figure S20. ^{1}H–^{1}HCOSY spectrum of glutinosasin B (**2**) (600 MHz, pyridine-d_5)

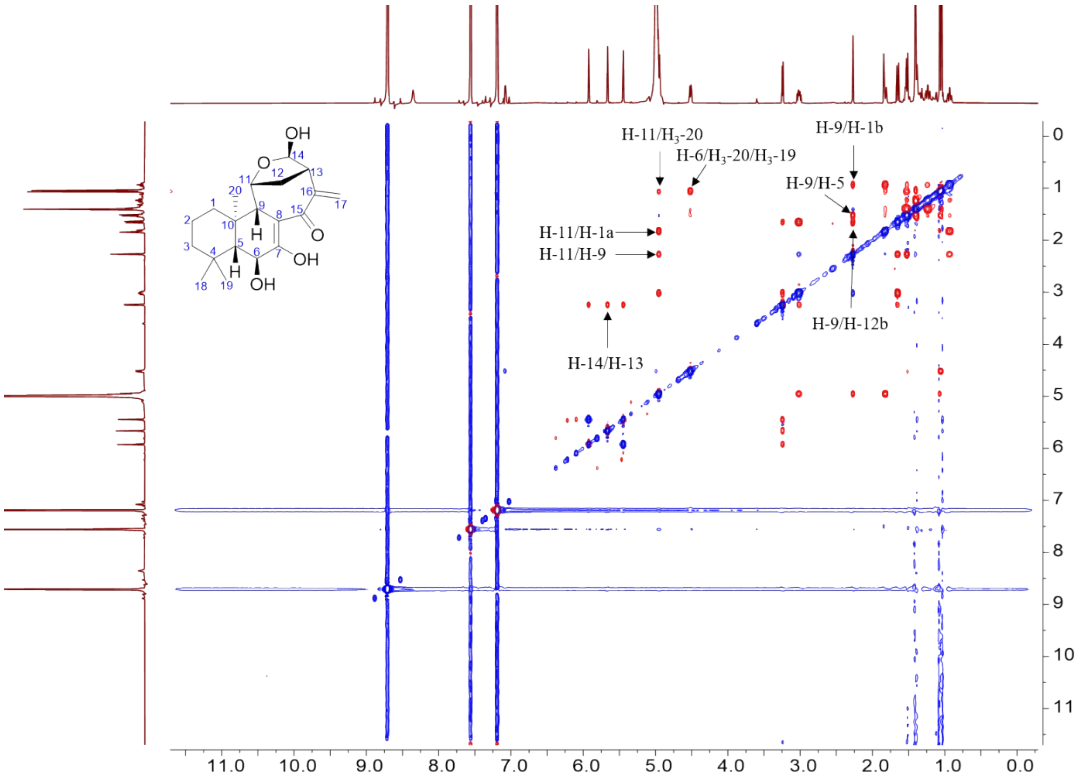
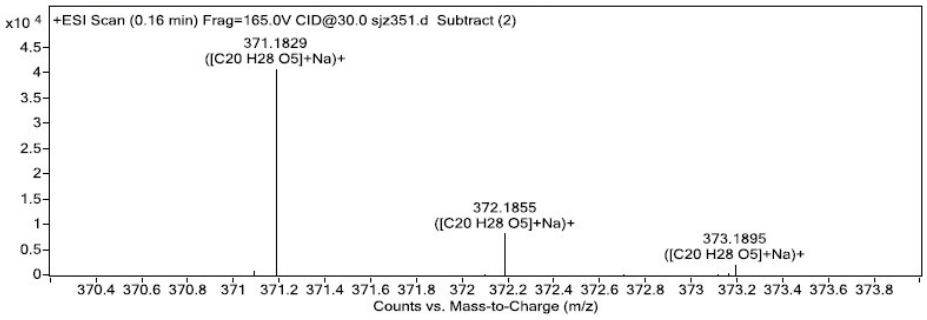


Figure S21. ROESY spectrum of glutinosasin B (**2**) (600 MHz, pyridine-d_5)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
165	30	ESI



Peak List

m/z	z	Abund	Formula	Ion
90.0464	1	22218.45		
166.0496	1	66122.46		
233.089	1	18957.18		
272.1175	1	45317.4		
285.1846	1	22922.72		
313.1795	1	33082.21		
331.1902	1	20975.09		
371.1829	1	40775.77	C20 H28 O5	(M+Na)+
403.2088	1	24531.2		
719.3743	1	16480.02		

Formula Calculator Element Limits

Element	Min	Max
C	3	45
H	0	120
O	0	20

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C20 H28 O5	348.1937	371.1829	371.1829	0.00	0.00	7.0000

Figure S22. The HRESIMS spectrum glutinosasin B (**2**)

Rudolph Research Analytical

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

Measurement Date : Thursday, 18-JAN-2024

Set Temperature : 20.0

Time Delay : Disabled

Delay between Measurement : Disabled

n	Average	Std.Dev.	% RSD	Maximum	Minimum
5	-14.49	0.46	-3.17	-14.29	-15.31

S.No	Sample ID	Time	Result	Scale	OR °Arc	WLG.nm	Lg.mm	Conc.g/100ml	Temp.
1	SJZ351	01:05:22 PM	-14.29	SR	-0.014	589	100.00	0.098	20.1
2	SJZ351	01:05:28 PM	-14.29	SR	-0.014	589	100.00	0.098	20.1
3	SJZ351	01:05:35 PM	-14.29	SR	-0.014	589	100.00	0.098	20.0
4	SJZ351	01:05:41 PM	-15.31	SR	-0.015	589	100.00	0.098	20.0
5	SJZ351	01:05:48 PM	-14.29	SR	-0.014	589	100.00	0.098	20.0

Figure S23. OR of glutinosasin B (**2**)

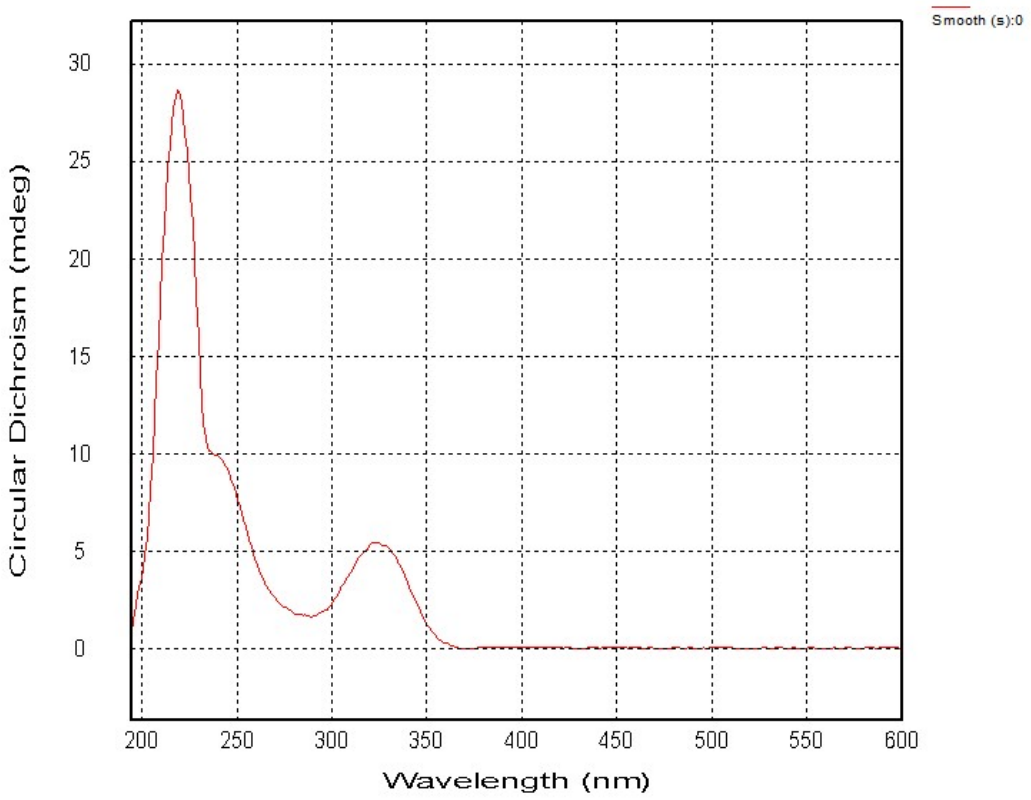


Figure S24. CD spectrum of glutinosasin B (**2**)

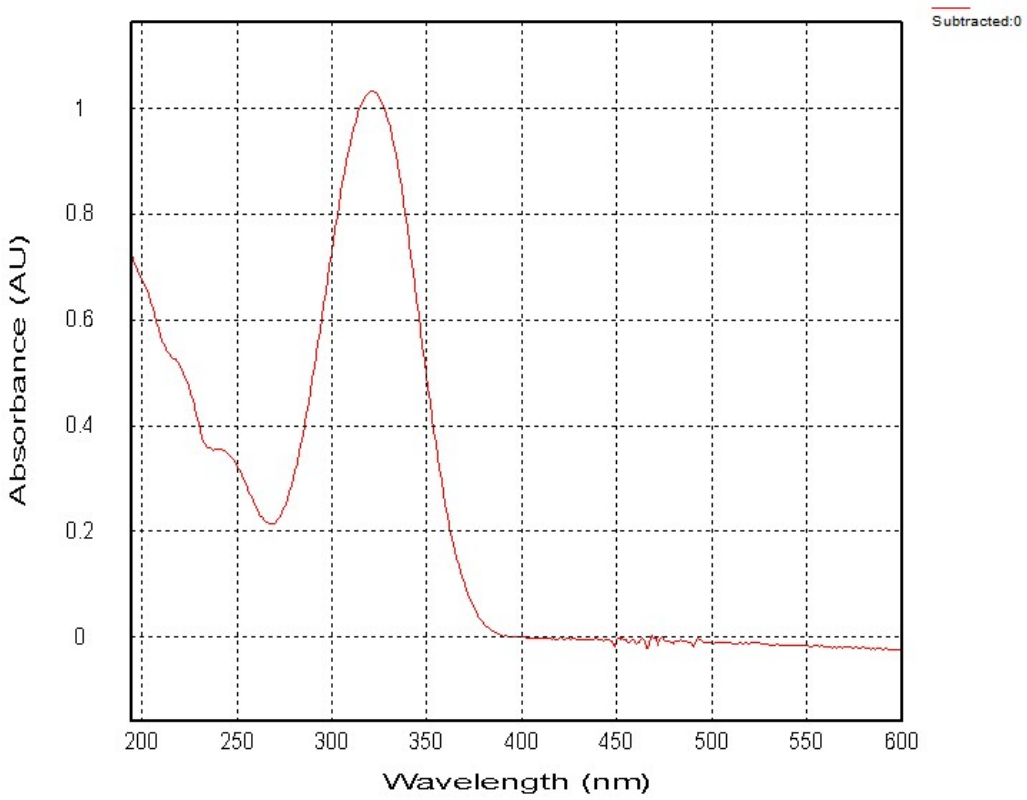


Figure S25. The UV spectrum of glutinosasin B (**2**)

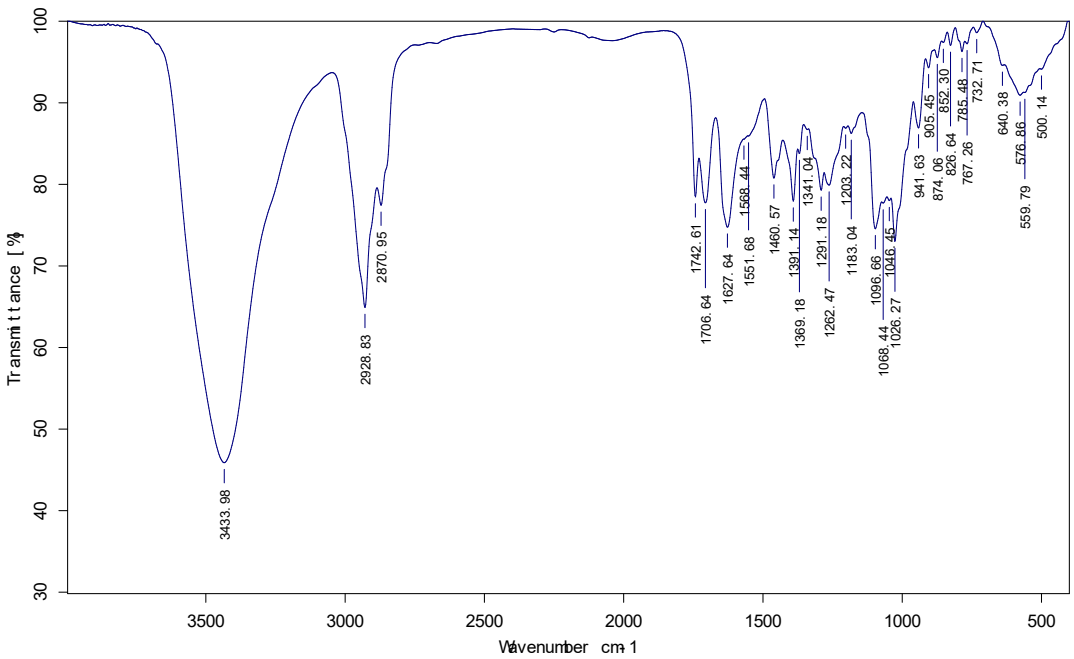


Figure S26. The IR spectrum of glutinosasin B (**2**)

5. NMR, MS, UV, ECD, IR Spectra, and OR of Glutinosasin C

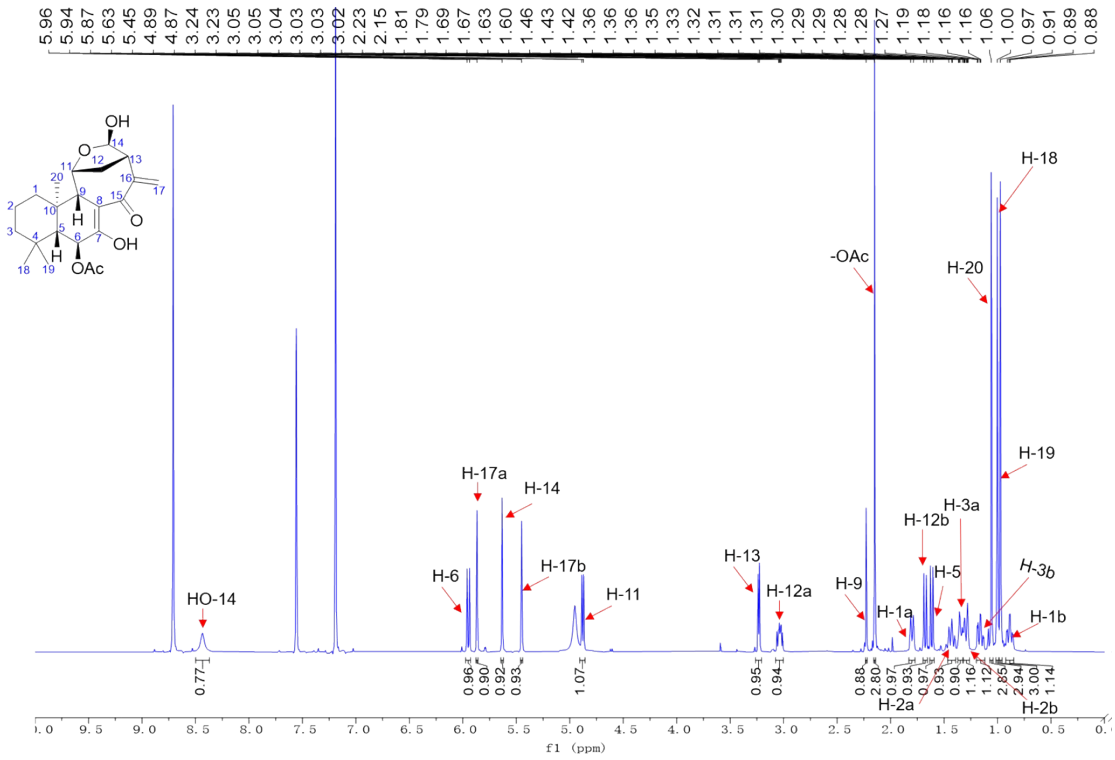


Figure S27. ^{1}H NMR spectrum of glutinosasin C (**3**) (500 MHz, pyridine-d_5)

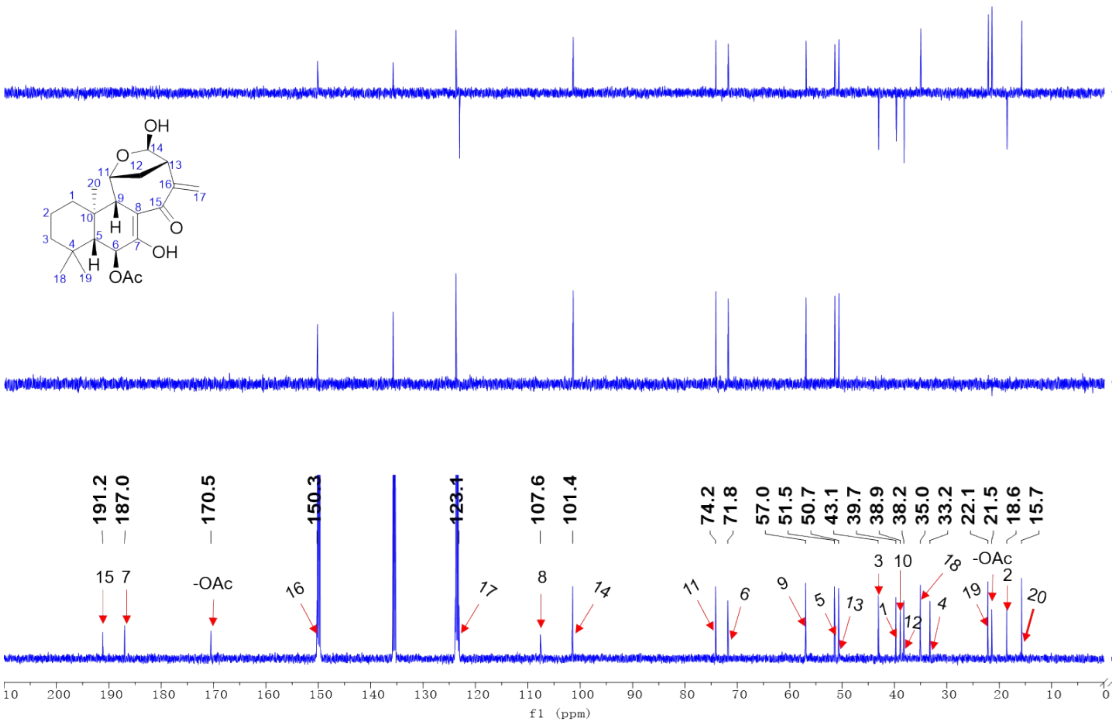


Figure S28. ^{13}C NMR spectrum of glutinosasin C (**3**) (125 MHz, pyridine-d_5)

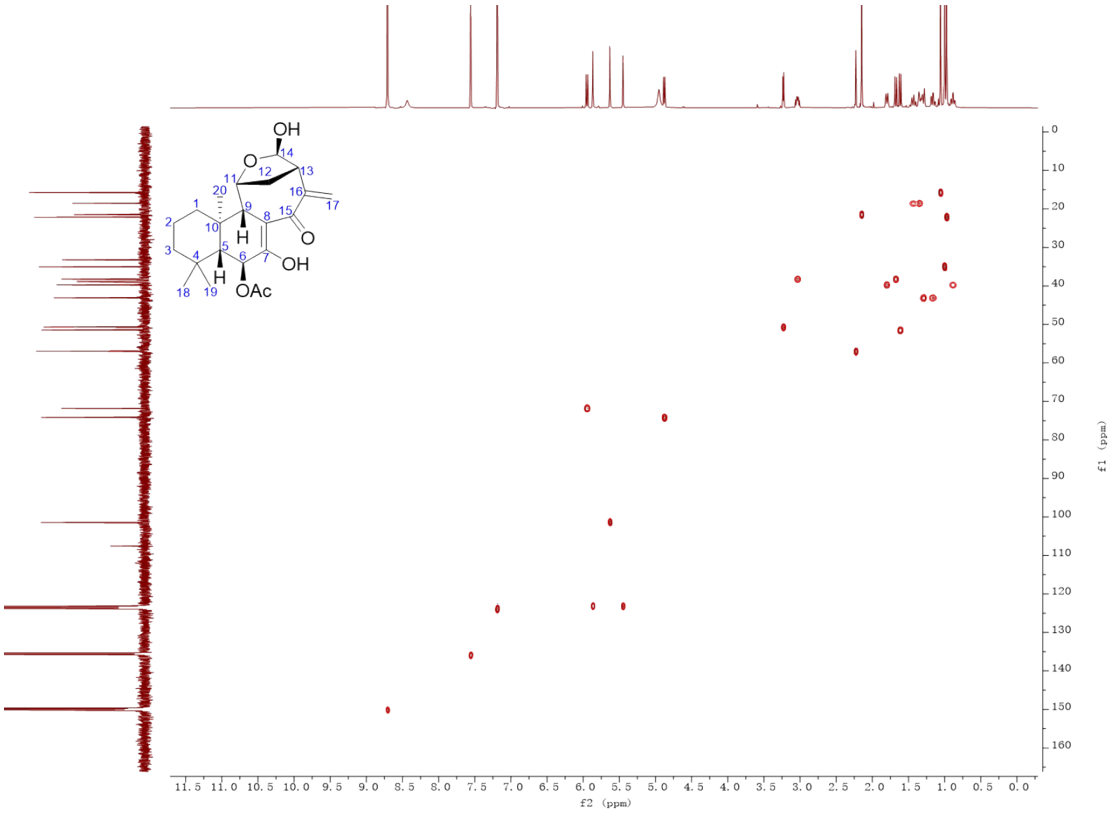


Figure S29. HSQC spectrum of glutinosasin C (**3**) (^{1}H: 500 MHz, ^{13}C: 125 MHz, pyridine-d_5)

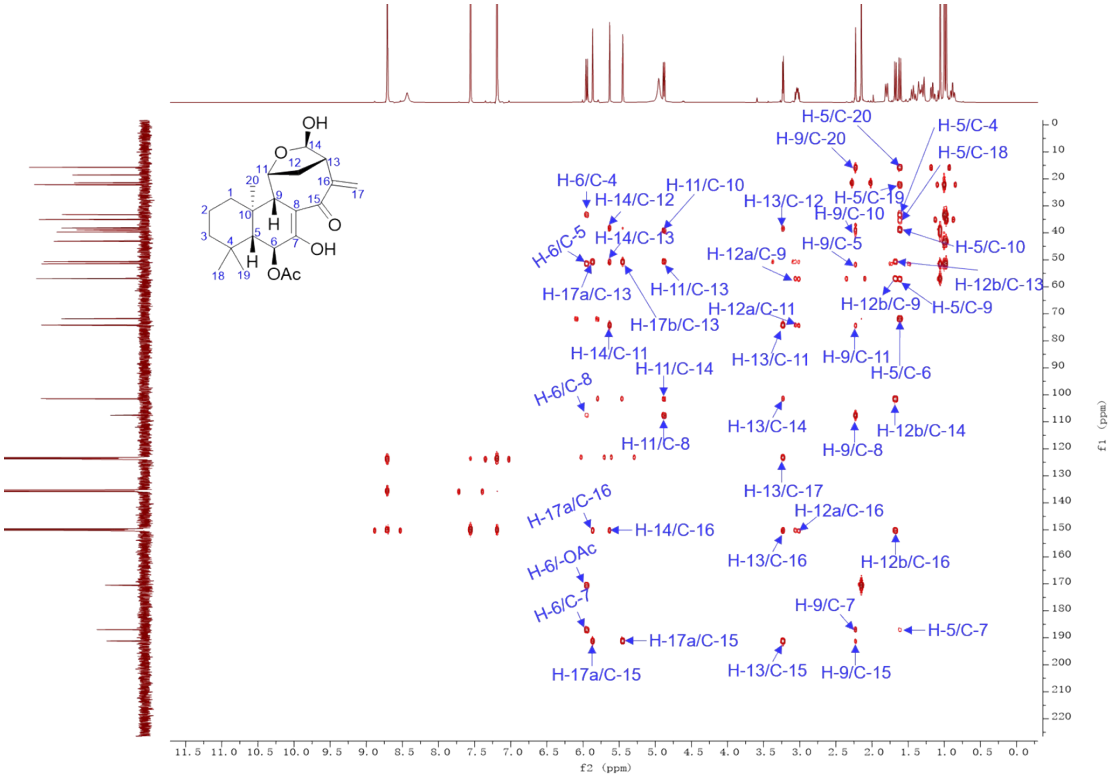


Figure S30. HMBC spectrum of glutinosasin C (**3**) (^{1}H: 500 MHz, ^{13}C: 125 MHz, pyridine-d_5)

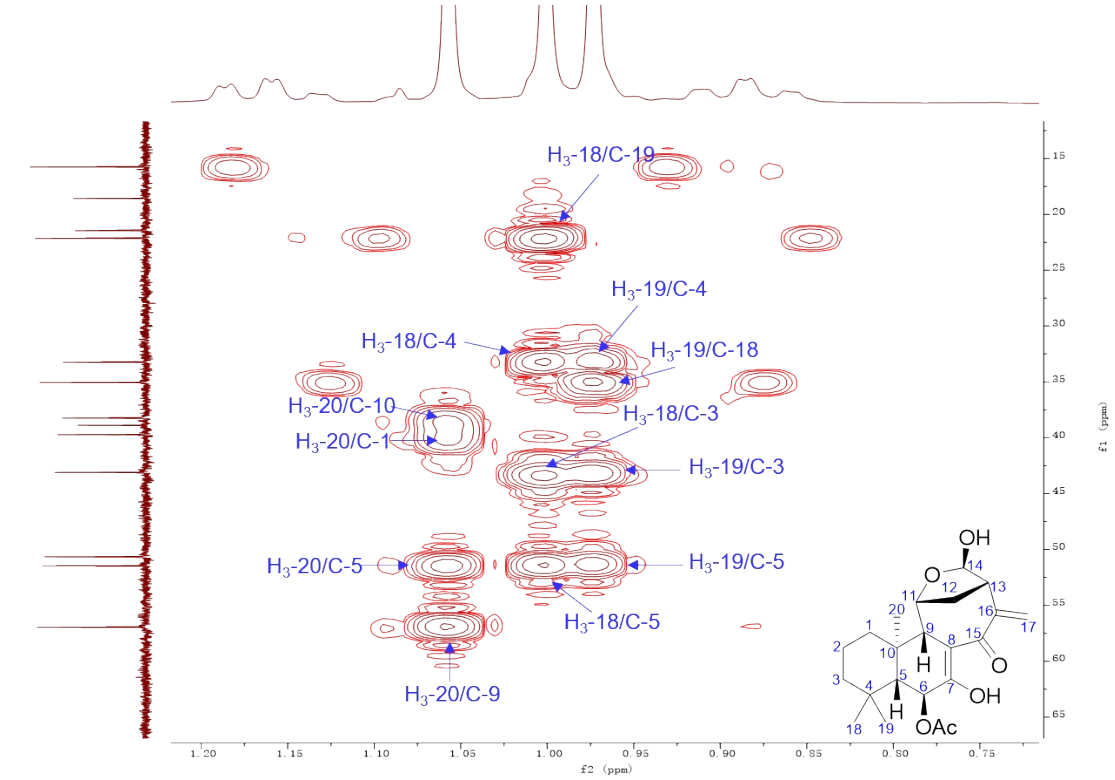


Figure S31. HMBC spectrum of glutinosasin C (**3**) (^{1}H: 500 MHz, ^{13}C: 125 MHz, pyridine-d_5) (amplified)

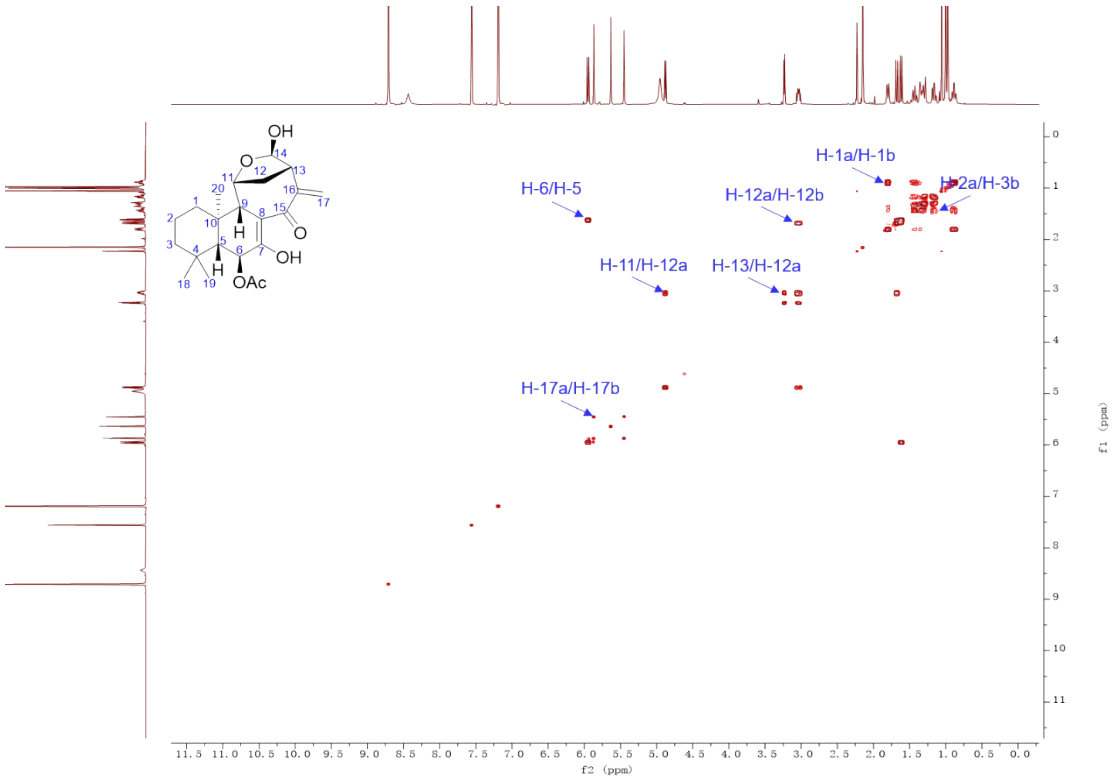


Figure S32. ^{1}H–^{1}H COSY spectrum of glutinosasin C (**3**) (500 MHz, pyridine-d_5)

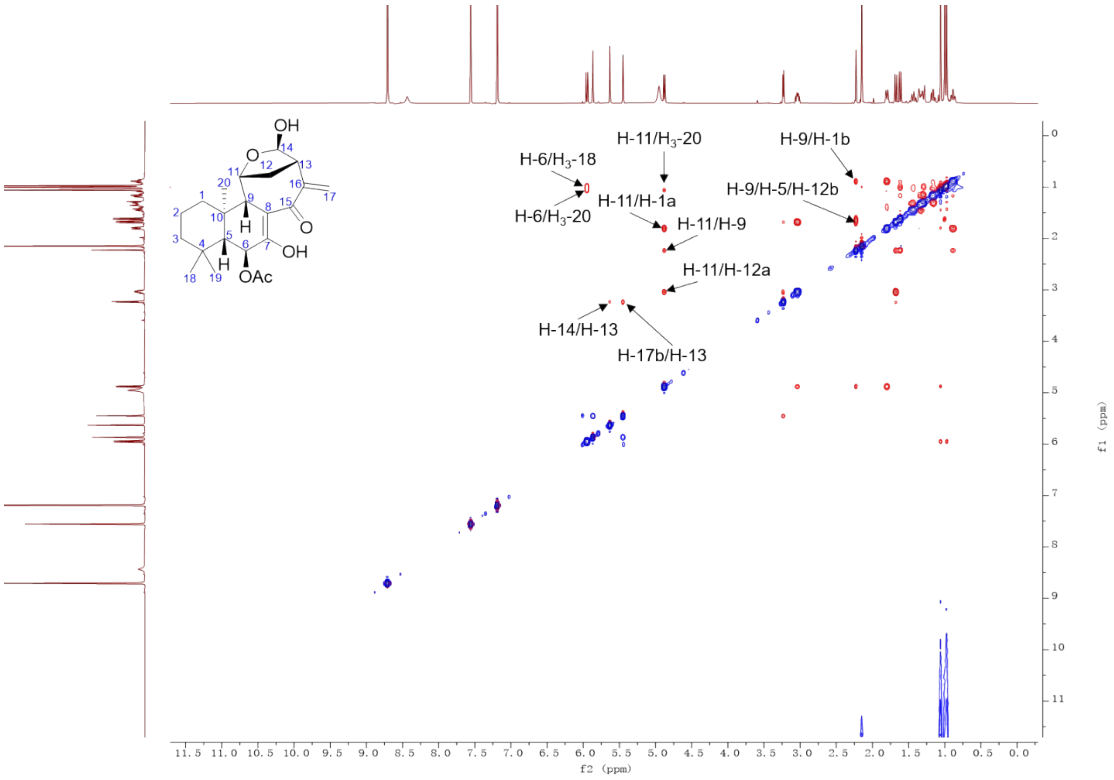
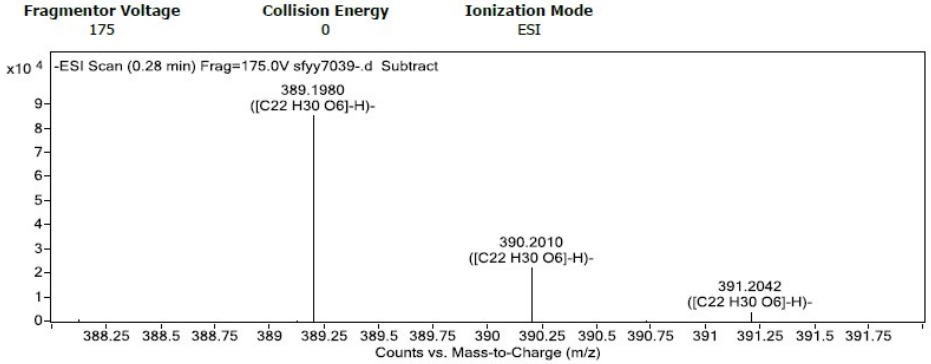


Figure S33. ROESY spectrum of glutinosasin C (**3**) (500 MHz, pyridine-d_5)



Peak List

m/z	z	Abund	Formula	Ion
112.9853	1	28540.06		
119.0364	1	24627.23		
389.198	1	85620.61	C22 H30 O6	(M-H)-
390.201	1	22350.04	C22 H30 O6	(M-H)-
779.4015	1	29826.58		
780.4039	1	15421.73		
825.4071	1	57409.65		
826.4101	1	28129.92		
966.0016	1	55598.63		
1033.9888	1	46150.76		

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
C22 H30 O6	390.2042	389.1970	389.1980	-1.00	-2.57	8.0000

Figure S34. The HRESIMS spectrum of glutinosasin C (**3**)

Rudolph Research Analytical

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

Measurement Date : Monday, 25-APR-2022

Set Temperature : OFF

Time Delay : Disabled

Delay between Measurement : Disabled

n	Average	Std.Dev.	% RSD	Maximum	Minimum
5	-54.23	0.21	-0.38	-53.85	-54.33

S.No	Sample ID	Time	Result	Scale	OR °Arc	WLG.nm	Lg.mm	Conc.g/100ml	Temp.
1	SFYY7039	05:25:26 PM	-54.33	SR	-0.113	589	100.00	0.208	25.2
2	SFYY7039	05:25:32 PM	-54.33	SR	-0.113	589	100.00	0.208	25.2
3	SFYY7039	05:25:38 PM	-54.33	SR	-0.113	589	100.00	0.208	25.2
4	SFYY7039	05:25:45 PM	-54.33	SR	-0.113	589	100.00	0.208	25.2
5	SFYY7039	05:25:51 PM	-53.85	SR	-0.112	589	100.00	0.208	25.2

Figure S35. OR of glutinosasin C (**3**)

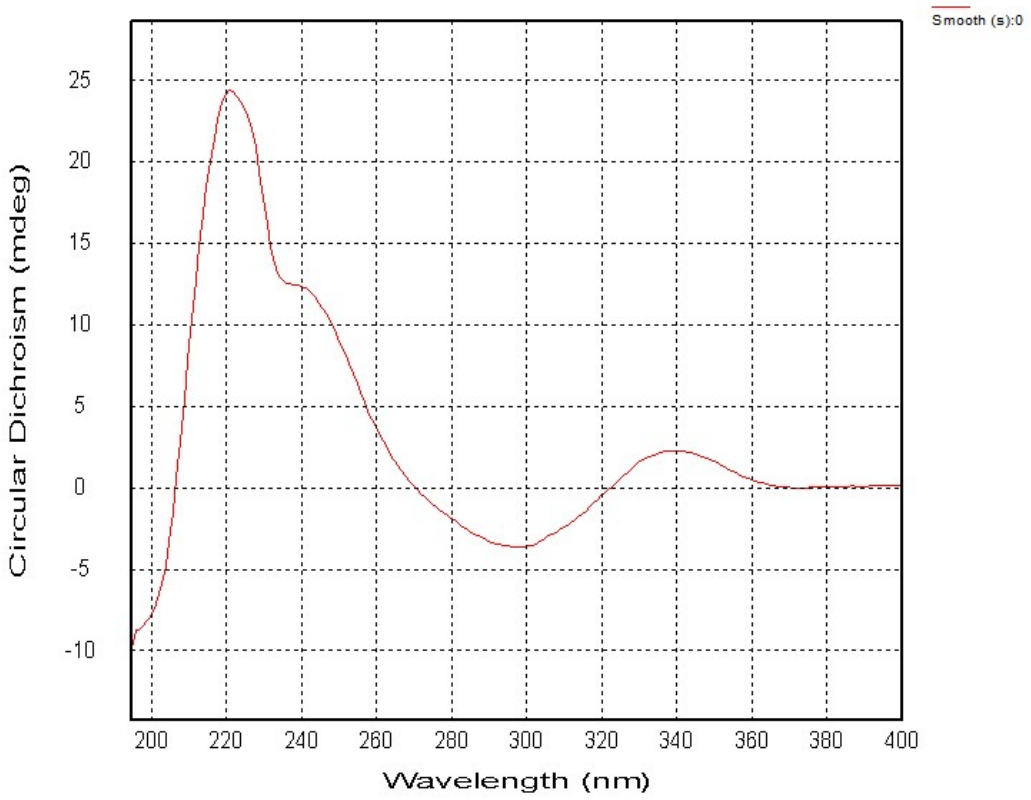


Figure S36. CD spectrum of glutinosasin C (**3**)

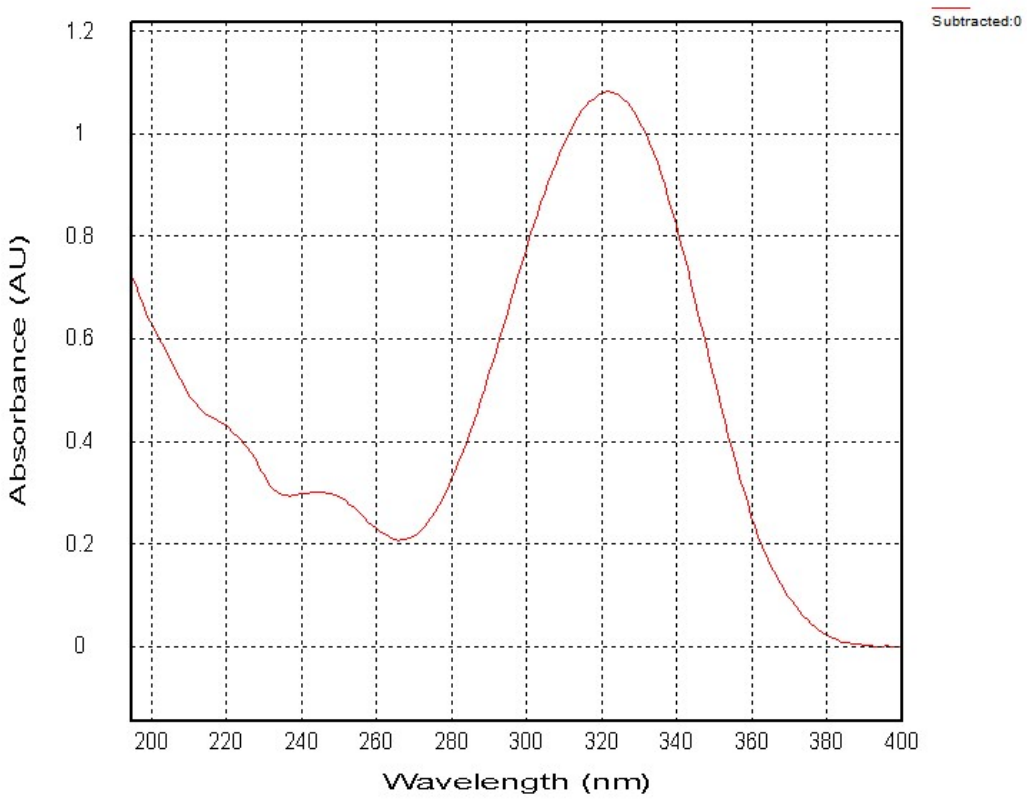


Figure S37. The UV spectrum of glutinosasin C (**3**)

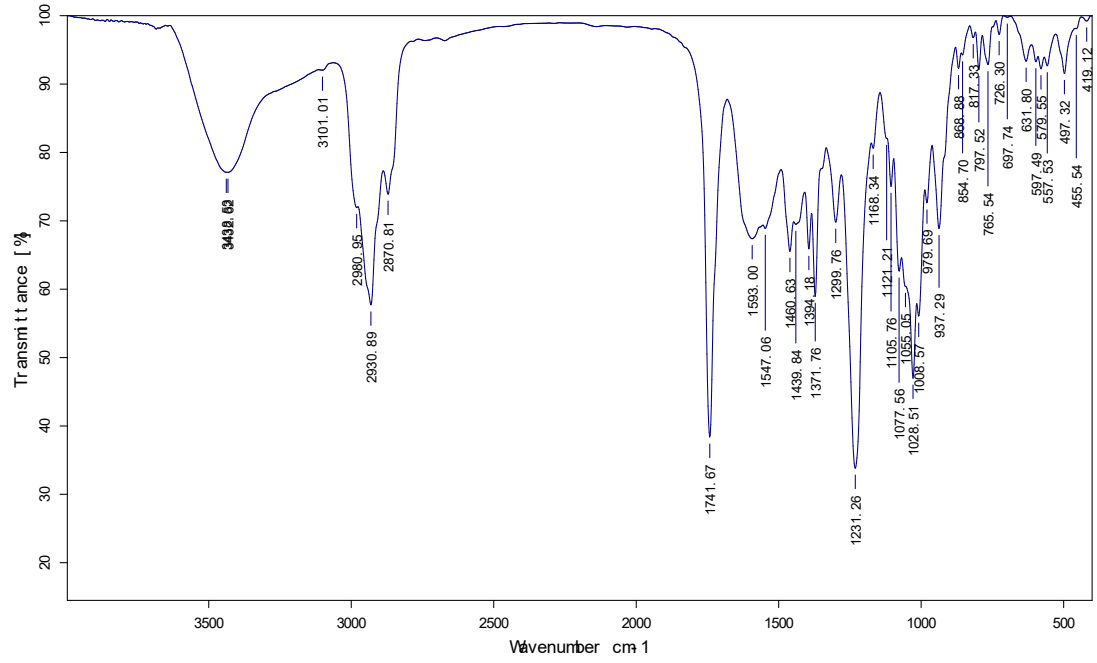


Figure S38. The IR spectrum of glutinosasin C (**3**)

6. NMR, MS, UV, ECD, IR Spectra, and OR of Glutinosasin D

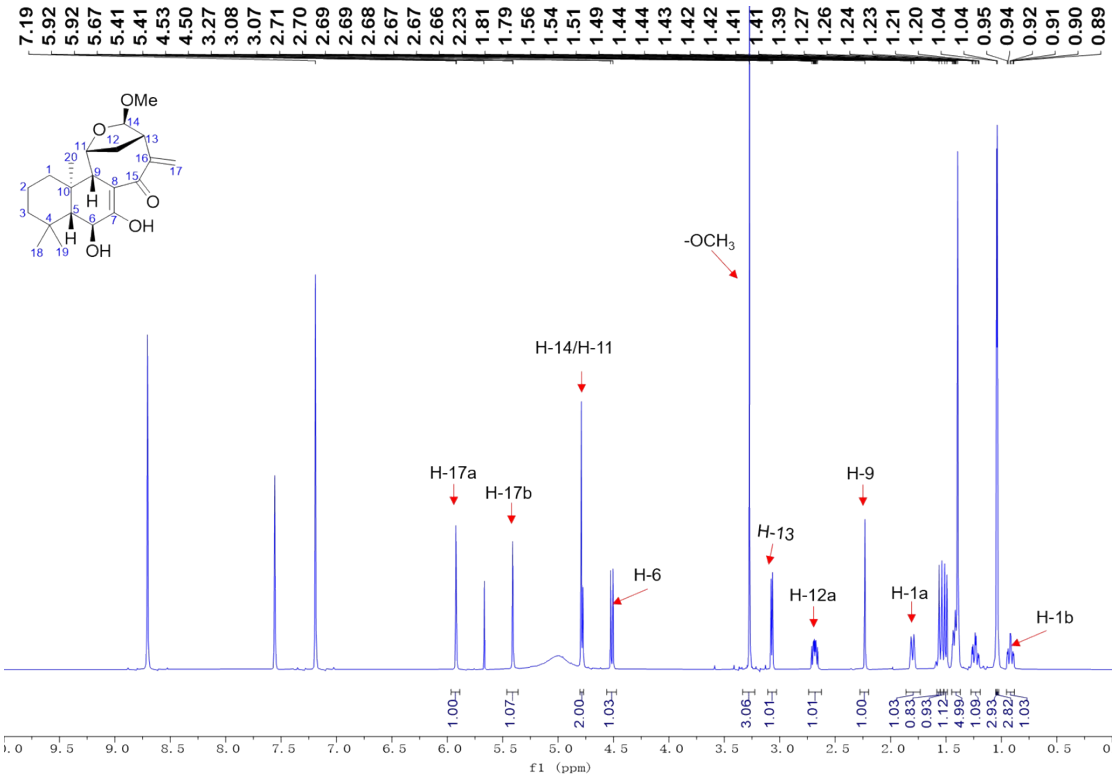


Figure S39. ^{1}H NMR spectrum of glutinosasin D (**4**) (500 MHz, pyridine-d_5)

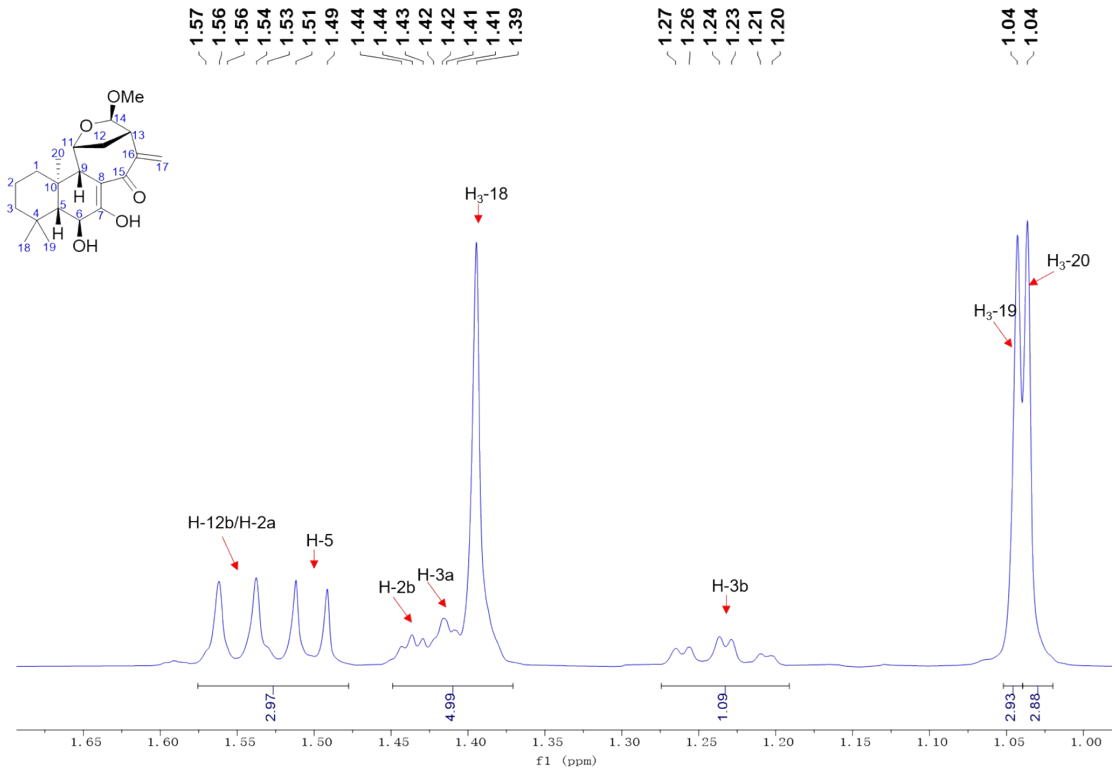


Figure S40. ^{1}H NMR spectrum of glutinosasin D (**4**) (500 MHz, pyridine-d_5) (amplified)

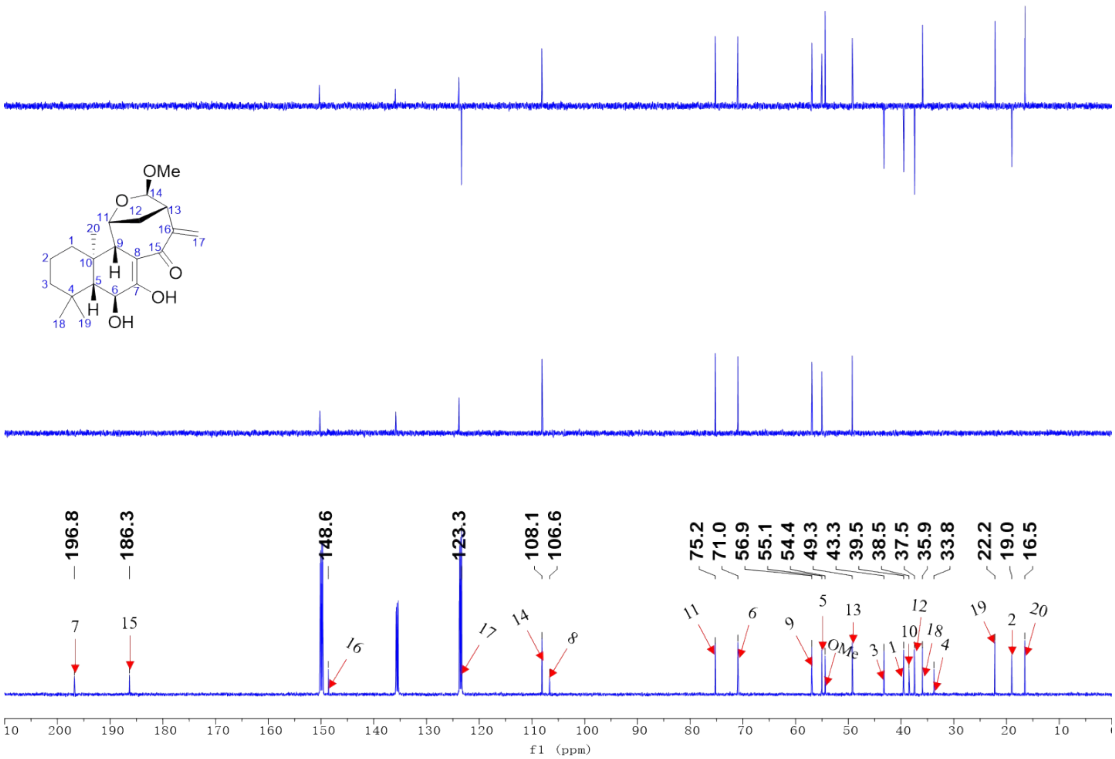


Figure S41. ^{13}C NMR spectrum of glutinosasin D (**4**) (125 MHz, pyridine-d_5)

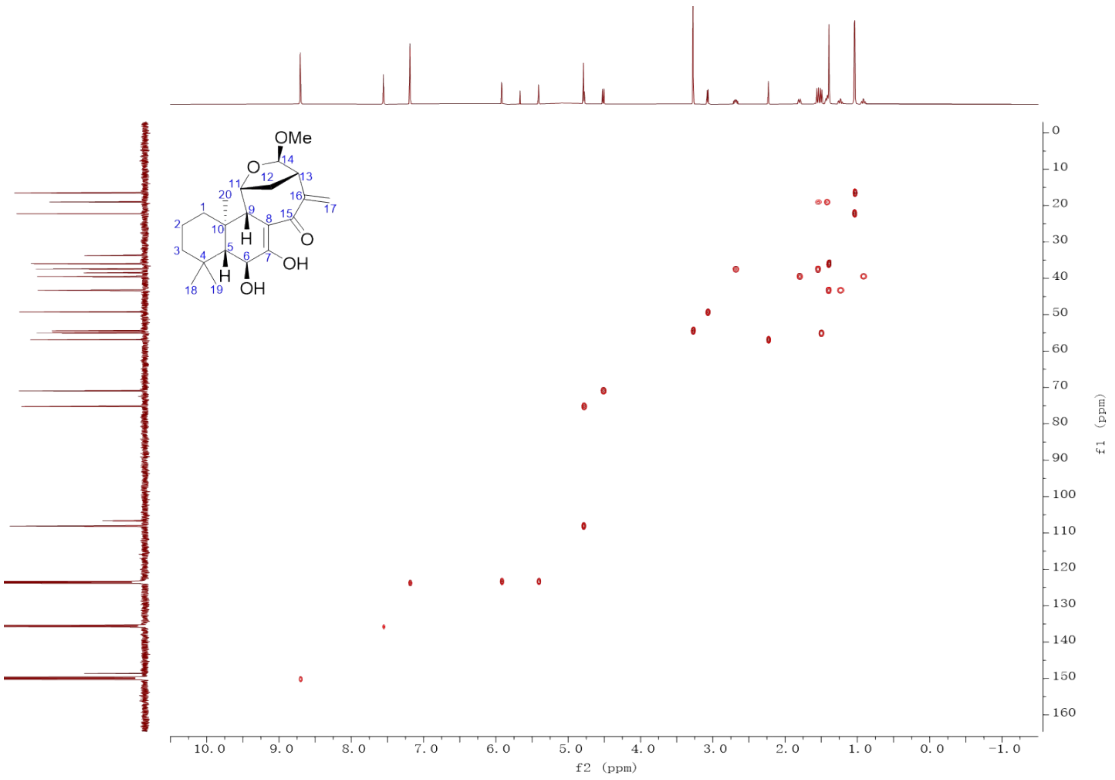


Figure S42. HSQC spectrum of glutinosasin D (**4**) (^{1}H: 500 MHz, 13C: 125 MHz, pyridine-d_5)

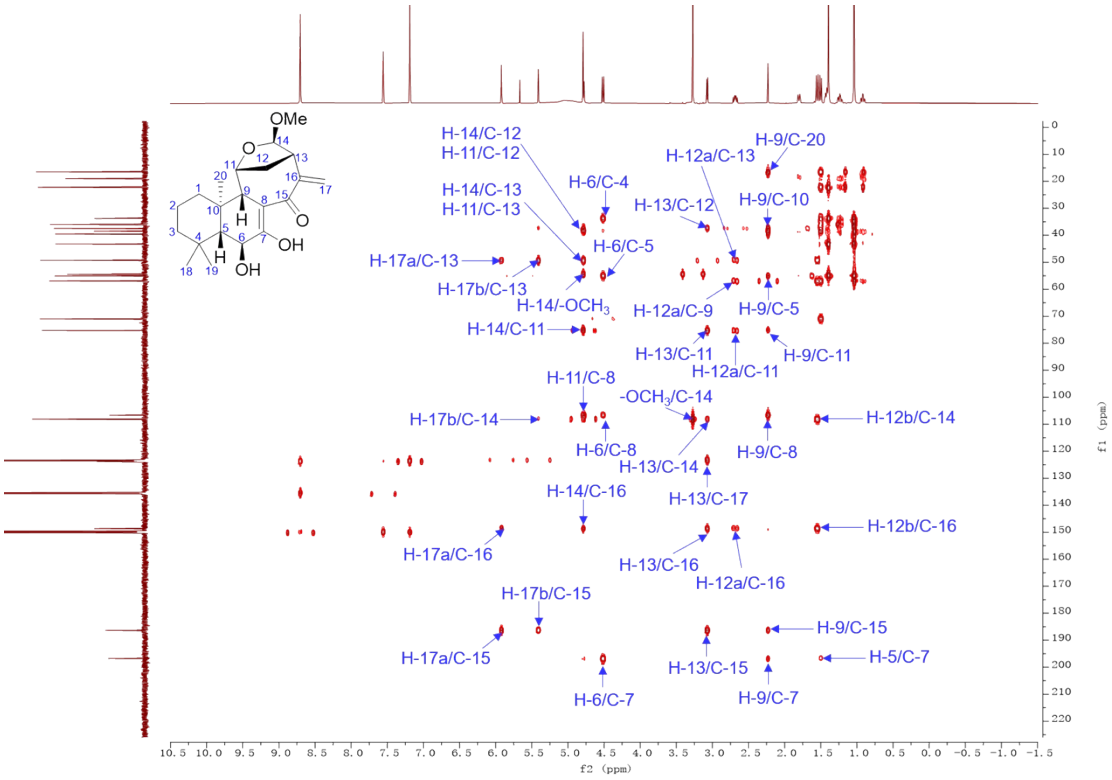


Figure S43. HMBC spectrum of glutinosasin D (**4**) (^{1}H: 500 MHz, 13C: 125 MHz, pyridine-d_5)

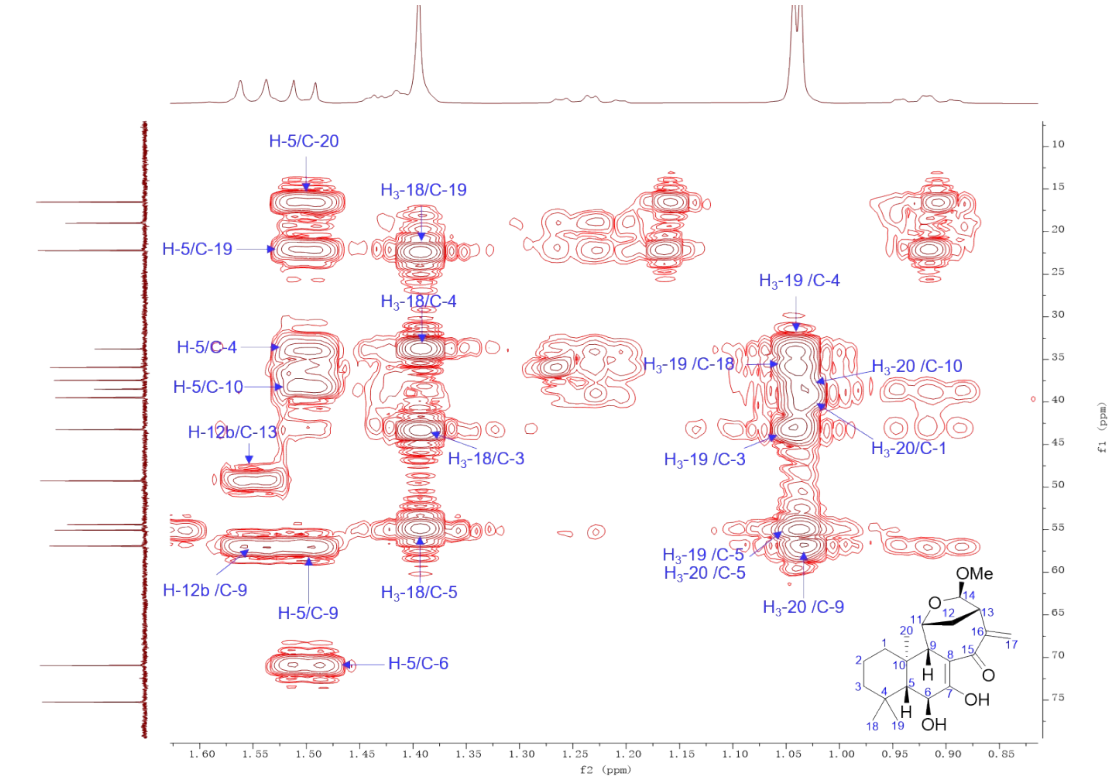


Figure S44. HMBC spectrum of glutinosasin D (**4**) (^{1}H: 500 MHz, 13C: 125 MHz, pyridine-d_5) (amplified)

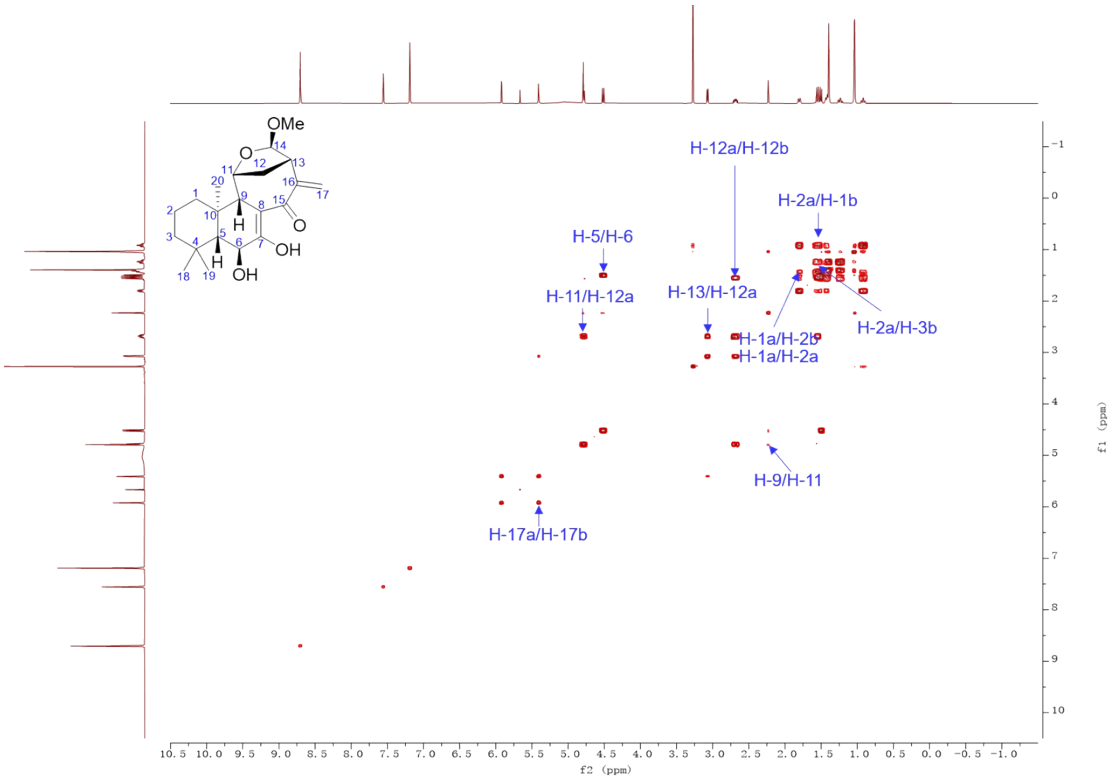


Figure S45. ^{1}H–^{1}H COSY spectrum of glutinosasin D (**4**) (500 MHz, pyridine-d_5)

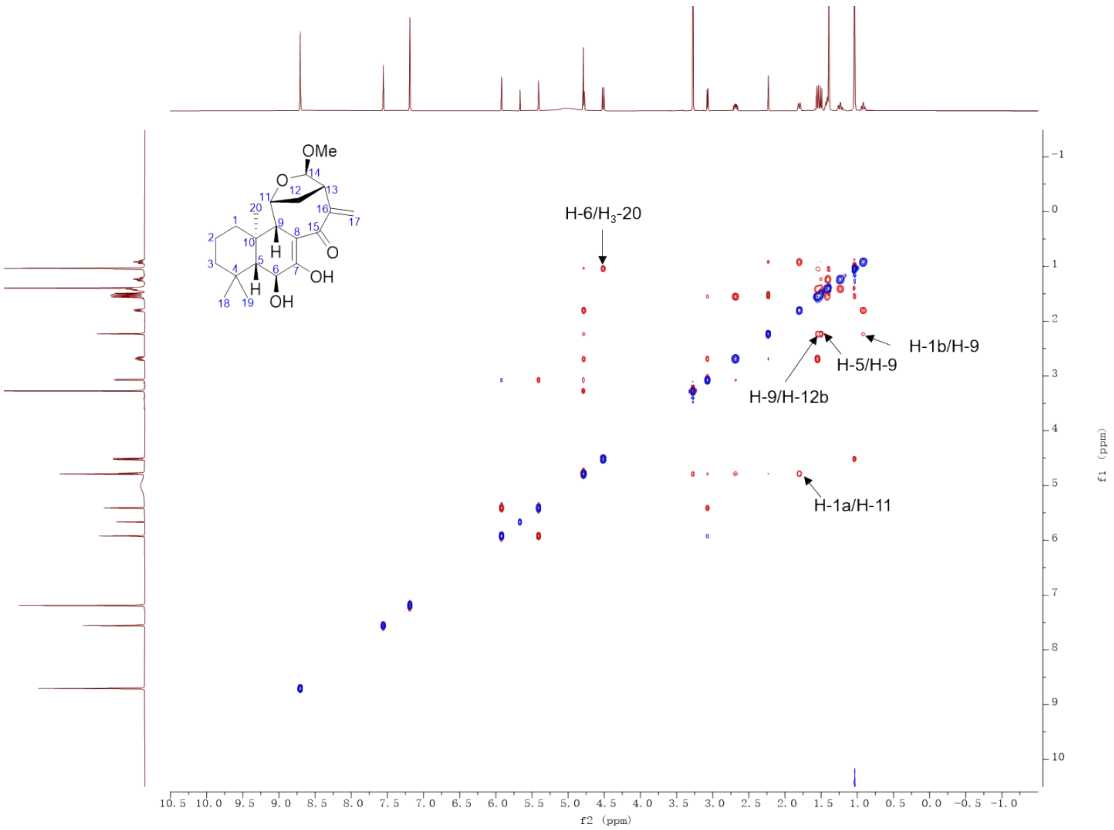
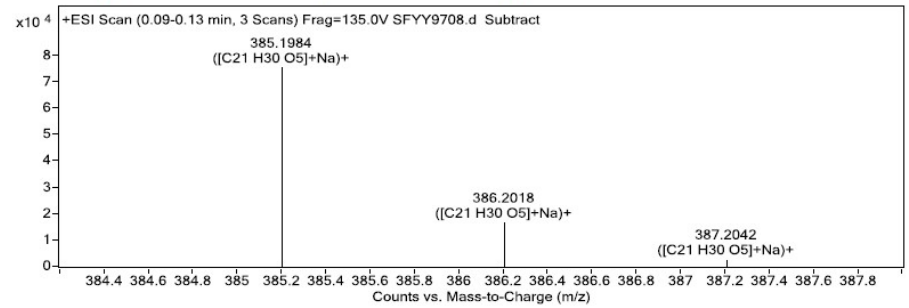


Figure S46. ROESY spectrum of glutinosasin D (**4**) (500 MHz, pyridine-d_5)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
85.0807	1	97043.7		
313.1794	1	16746.24		
345.2058	1	24652.92		
363.2157	1	8858.25		
385.1984	1	75528.97	C21 H30 O5	(M+Na)+
386.2018	1	16732.49	C21 H30 O5	(M+Na)+
447.2898	1	20270.91		
747.4086	1	67219.77		
748.4119	1	30245.09		
749.4092	1	9852.04		

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
C21 H30 O5	362.2093	385.1985	385.1984	0.10	0.26	7.0000

Figure S47. The HRESIMS spectrum of glutinosasin D (**4**)

Rudolph Research Analytical

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

Measurement Date : Thursday, 24-NOV-2022

Set Temperature : OFF

Time Delay : Disabled

Delay between Measurement : Disabled

n	Average	Std.Dev.	% RSD	Maximum	Minimum
5	-83.92	0.88	-1.04	-82.35	-84.31

S.No	Sample ID	Time	Result	Scale	OR °Arc	WLG.nm	Lg.mm	Conc.g/100ml	Temp.
1	SFYY9708	08:09:40 PM	-84.31	SR	-0.086	589	100.00	0.102	20.3
2	SFYY9708	08:09:46 PM	-84.31	SR	-0.086	589	100.00	0.102	20.3
3	SFYY9708	08:09:52 PM	-84.31	SR	-0.086	589	100.00	0.102	20.2
4	SFYY9708	08:09:59 PM	-84.31	SR	-0.086	589	100.00	0.102	20.2
5	SFYY9708	08:10:05 PM	-82.35	SR	-0.084	589	100.00	0.102	20.2

Figure S48. OR of glutinosasin D (**4**)

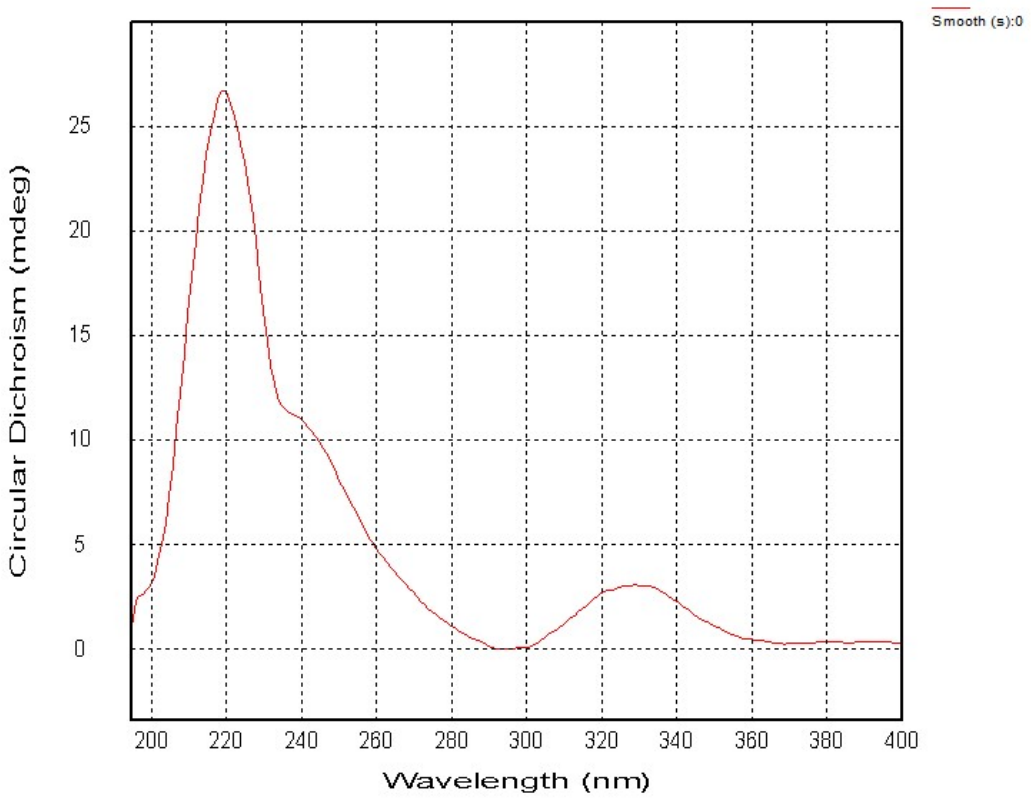


Figure S49. CD spectrum of glutinosasin D (**4**)

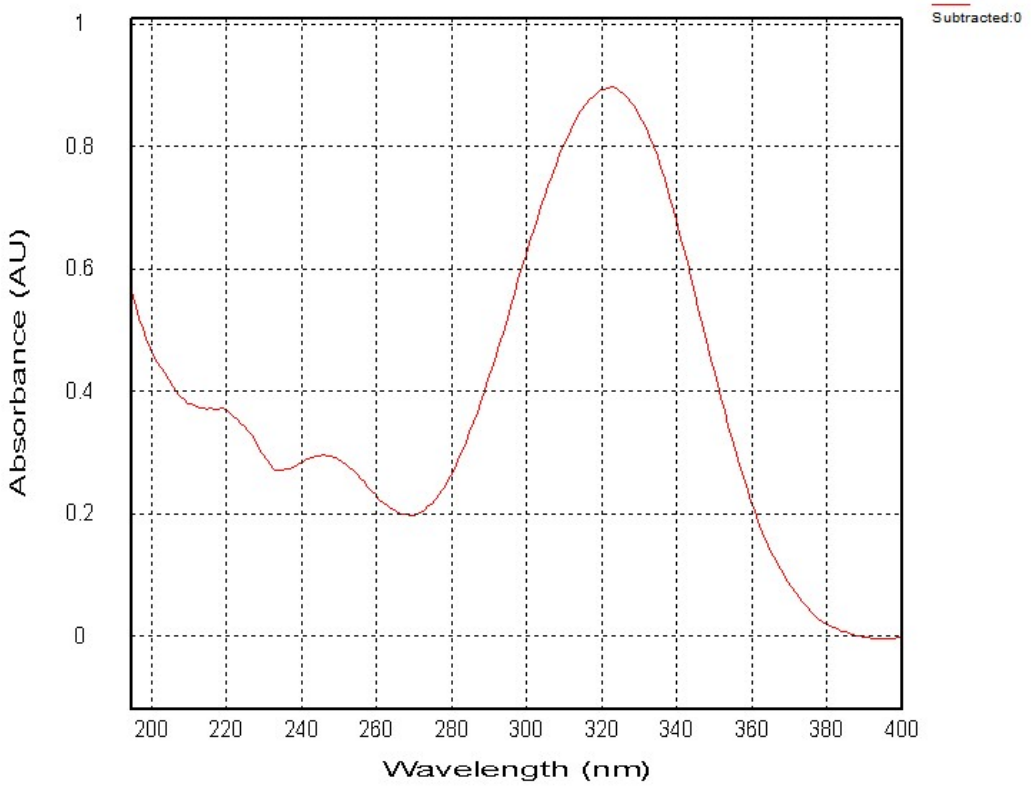


Figure S50. The UV spectrum of glutinosasin D (**4**)

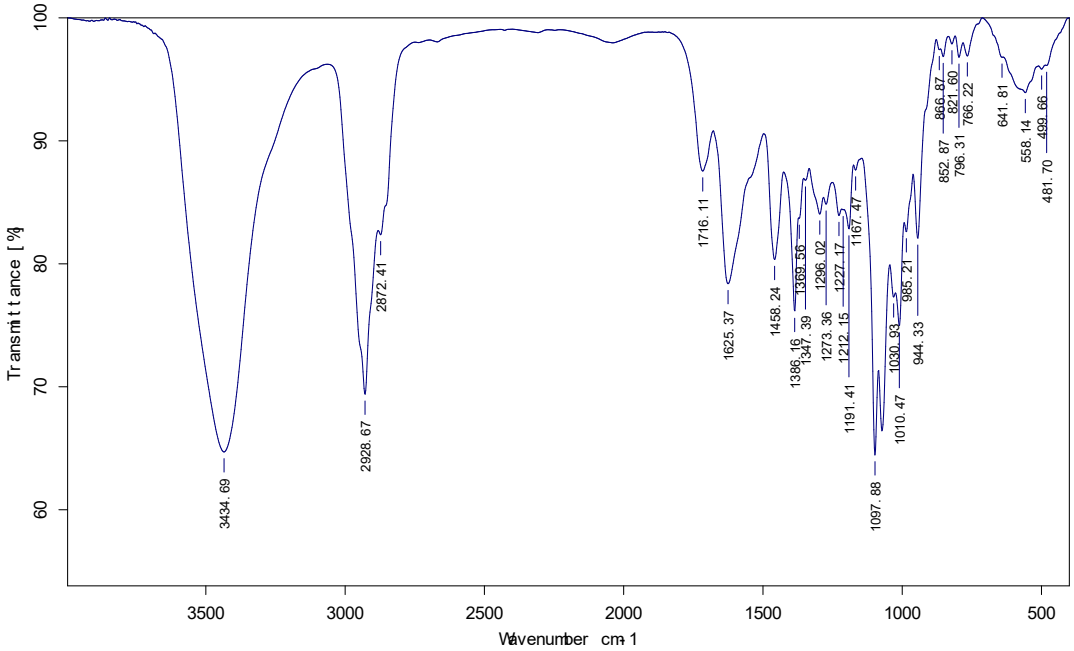


Figure S51. The IR spectrum of glutinosasin D (**4**)

7. NMR, MS, UV, ECD, IR Spectra, and OR of Glutinosasin E

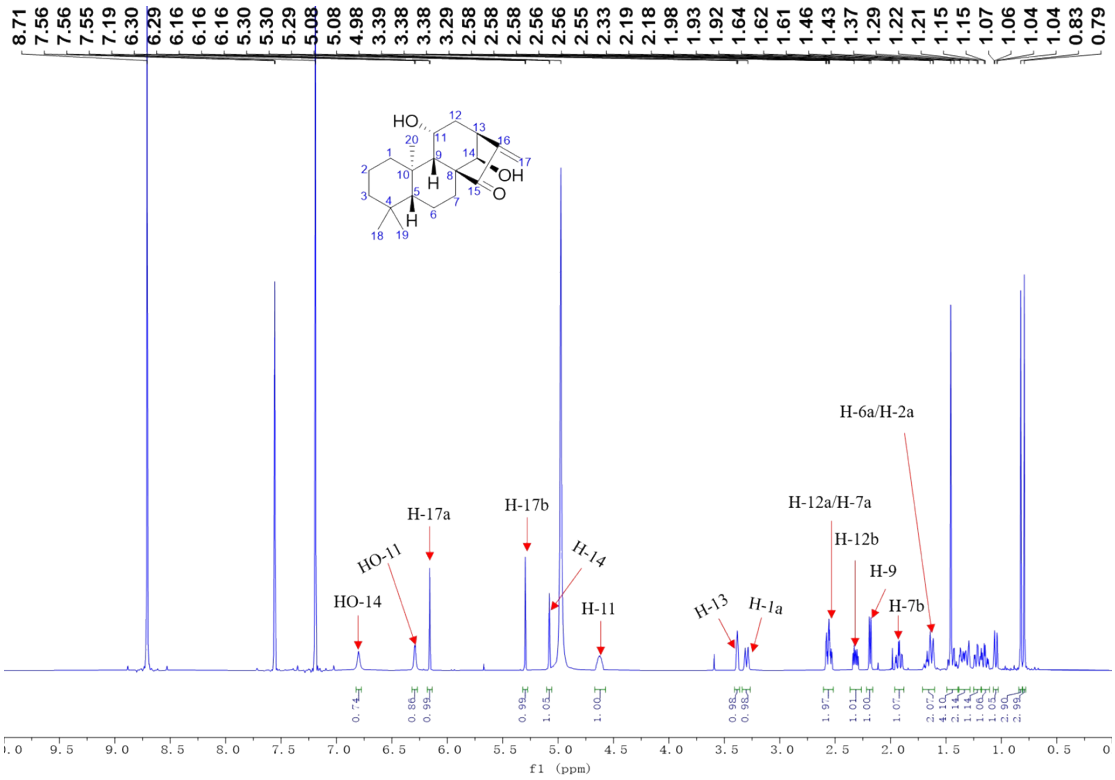


Figure S52. ^{1}H NMR spectrum of glutinosasin E (**5**) (600 MHz, pyridine-d_5)

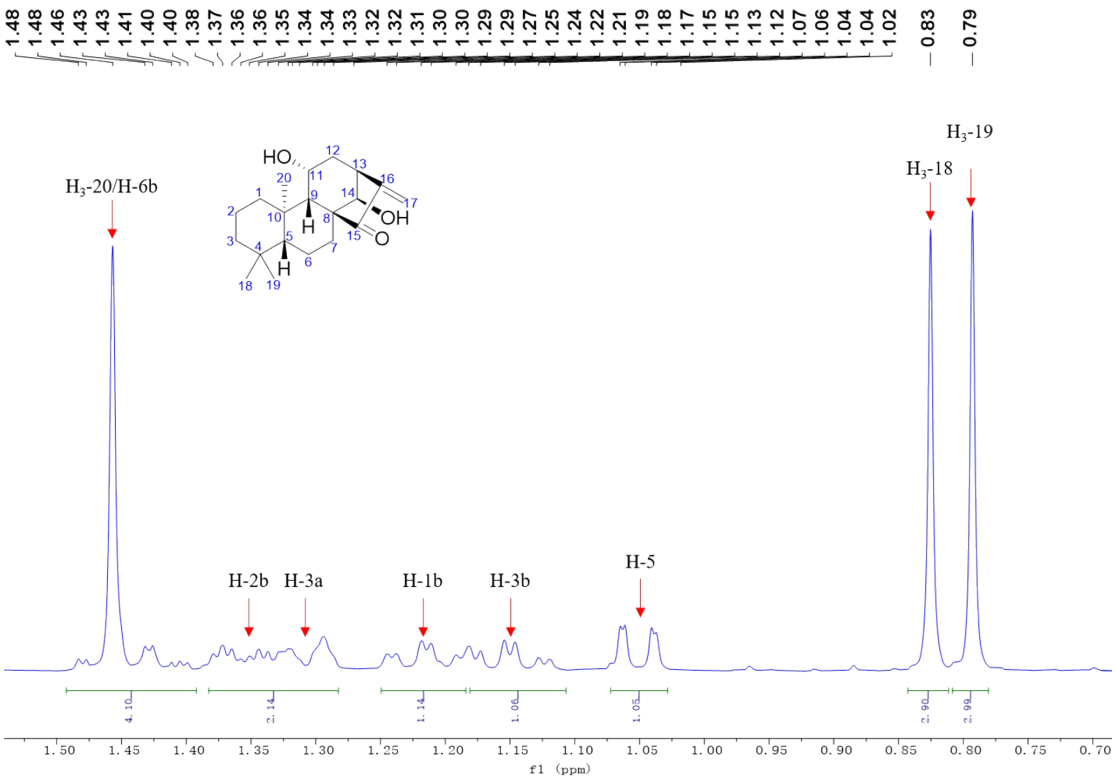


Figure S53. ^{1}H NMR spectrum of glutinosasin E (**5**) (600 MHz, pyridine-d_5) (amplified)

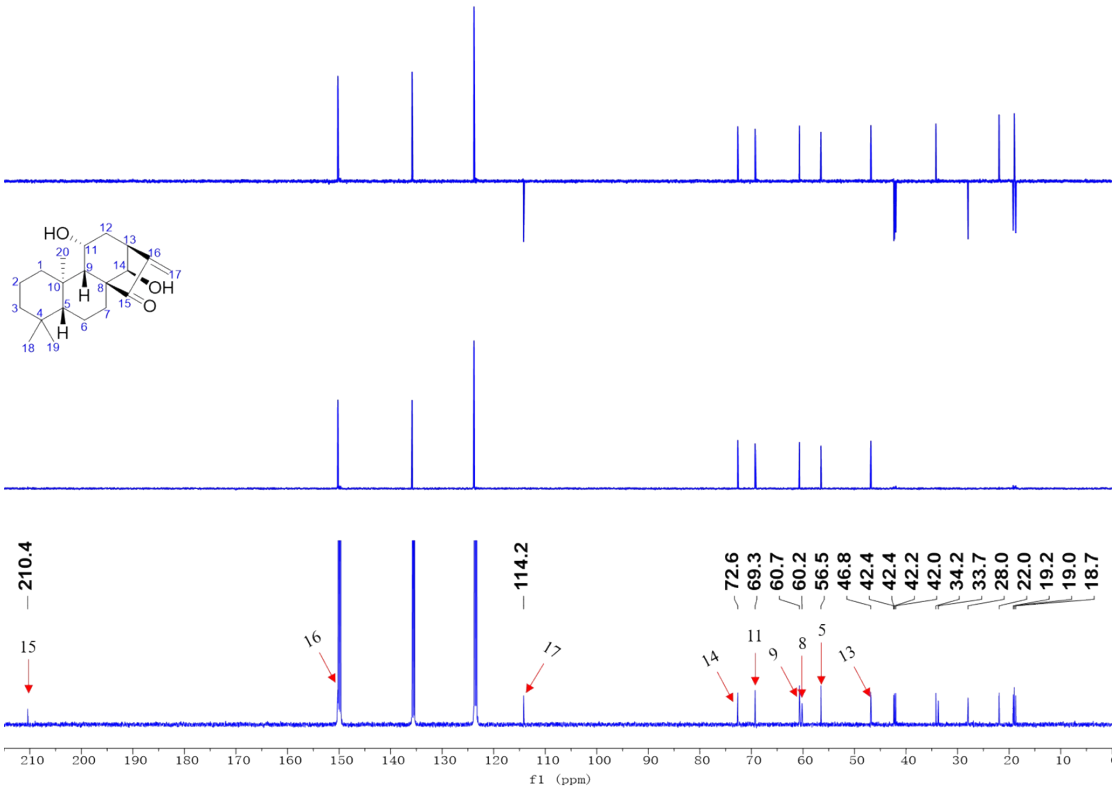


Figure S54. ^{13}C NMR spectrum of glutinosasin E (**5**) (150 MHz, pyridine-d_5)

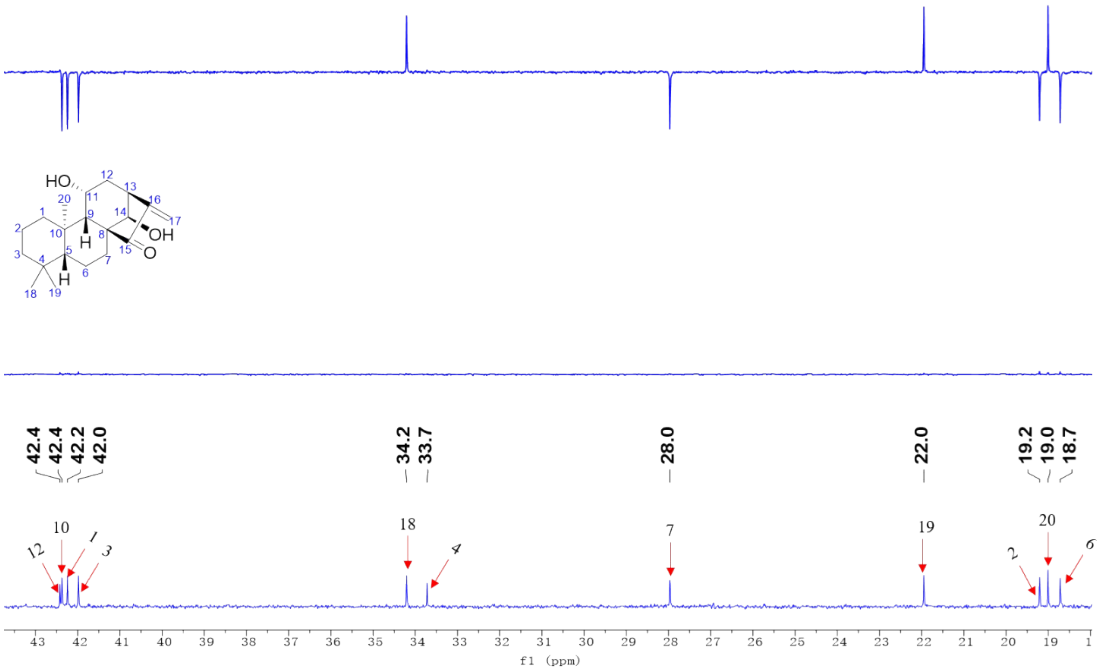


Figure S55. ^{13}C NMR spectrum of glutinosasin E (**5**) (150 MHz, pyridine-d_5) (amplified)

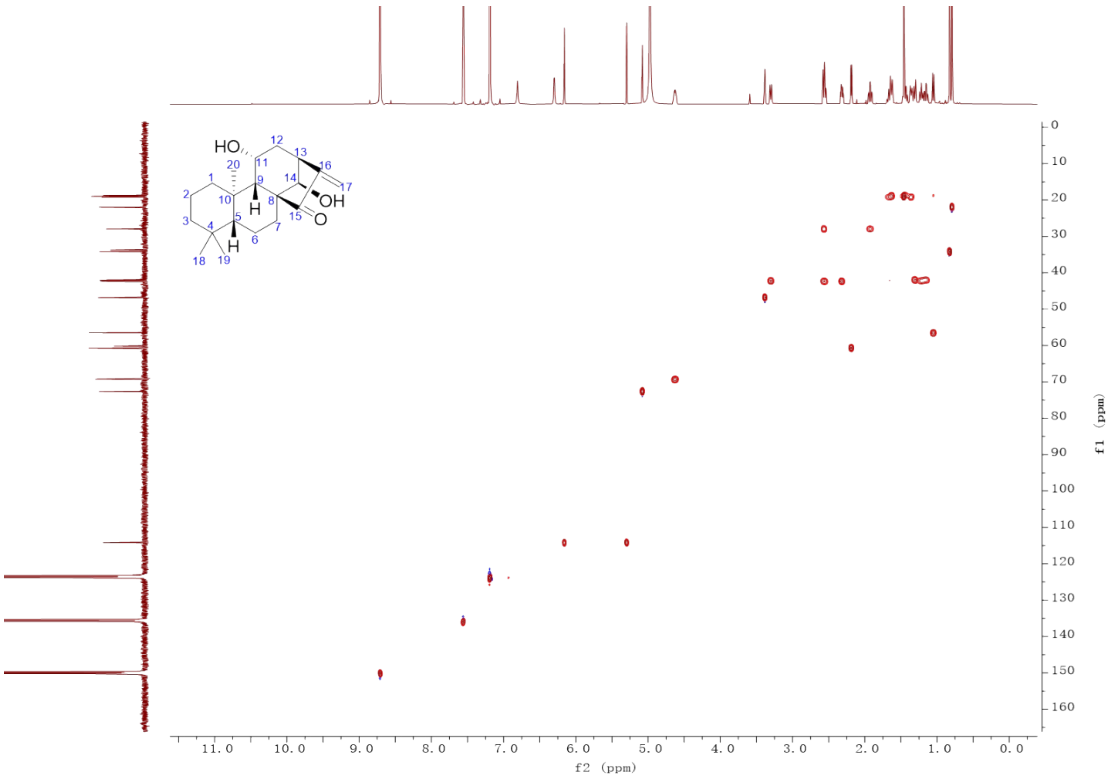


Figure S56. HSQC spectrum of glutinosasin E (**5**) (^{1}H: 600 MHz, ^{13}C: 150 MHz, pyridine-d_5)

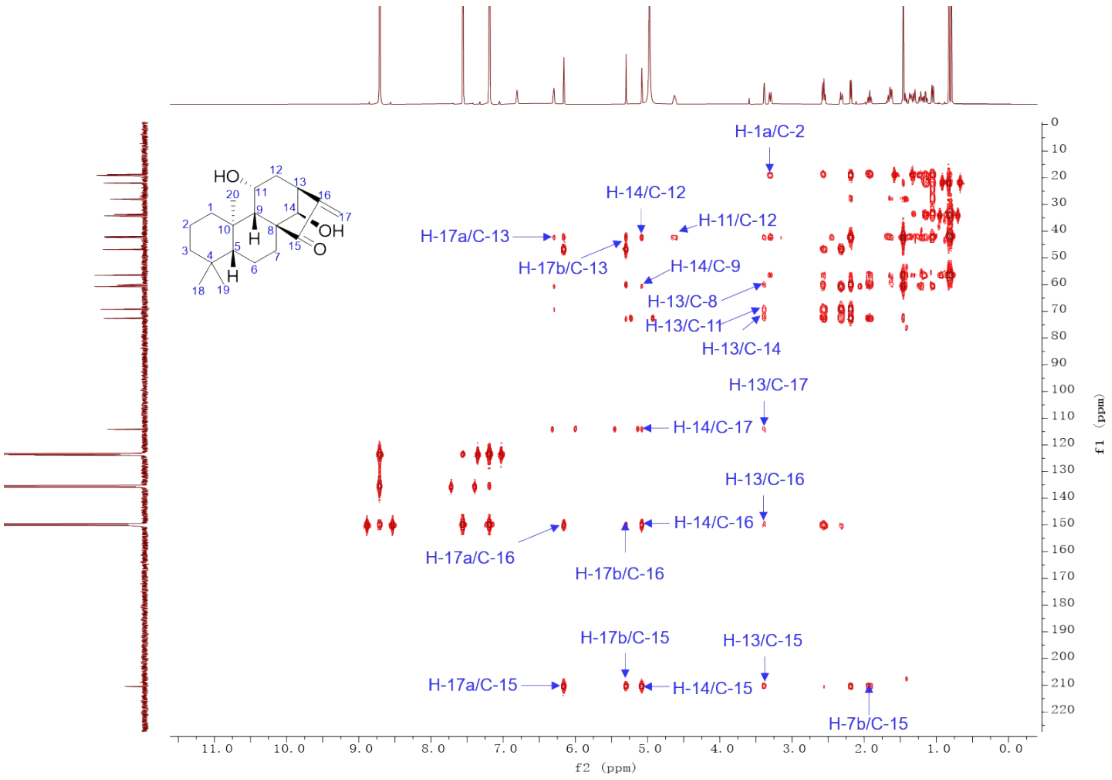


Figure S57. HMBC spectrum of glutinosasin E (**5**) (^{1}H: 600 MHz, ^{13}C: 150 MHz, pyridine-d_5)

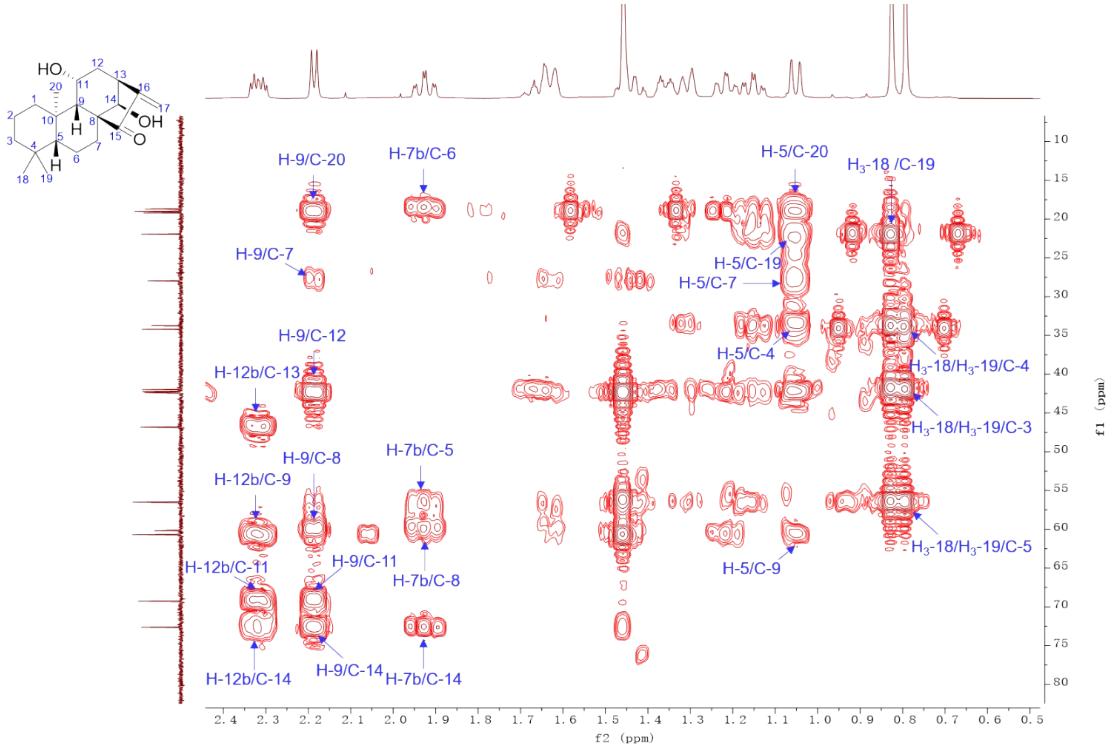


Figure S58. HMBC spectrum of glutinosasin E (**5**) (^{1}H: 600 MHz, ^{13}C: 150 MHz, pyridine-d_5) (amplified)

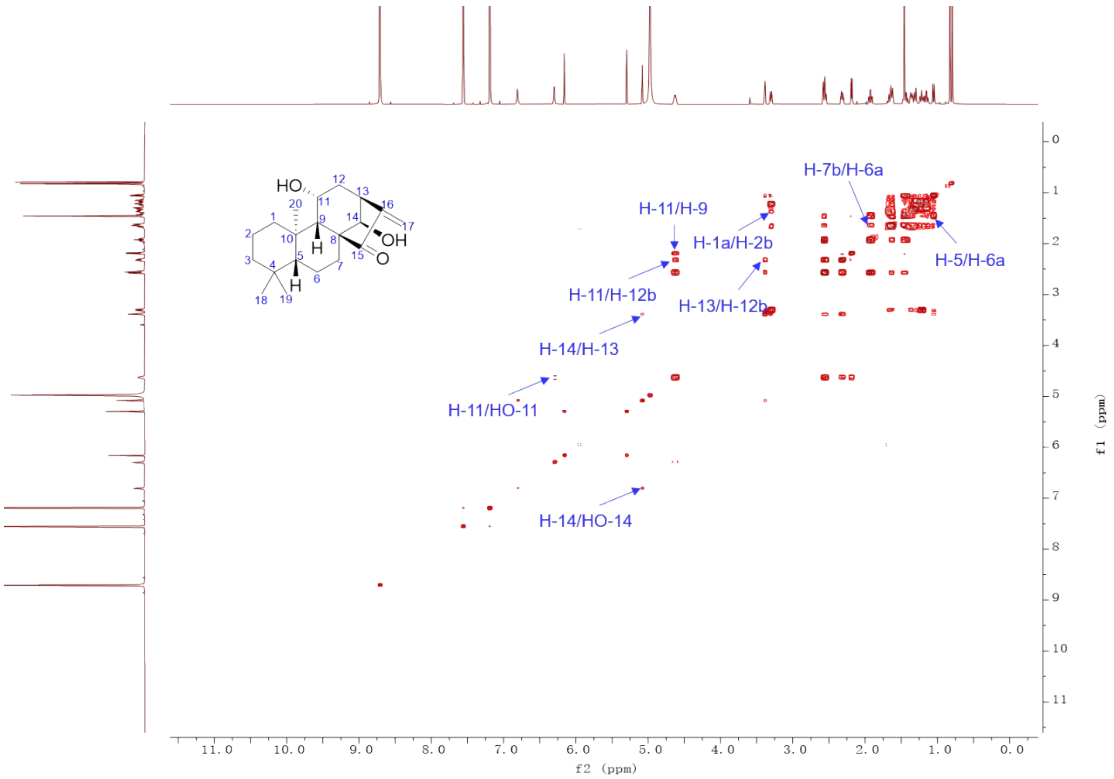


Figure S59. ^{1}H–^{1}H COSY spectrum of glutinosasin E (**5**) (600 MHz, pyridine-d_5)

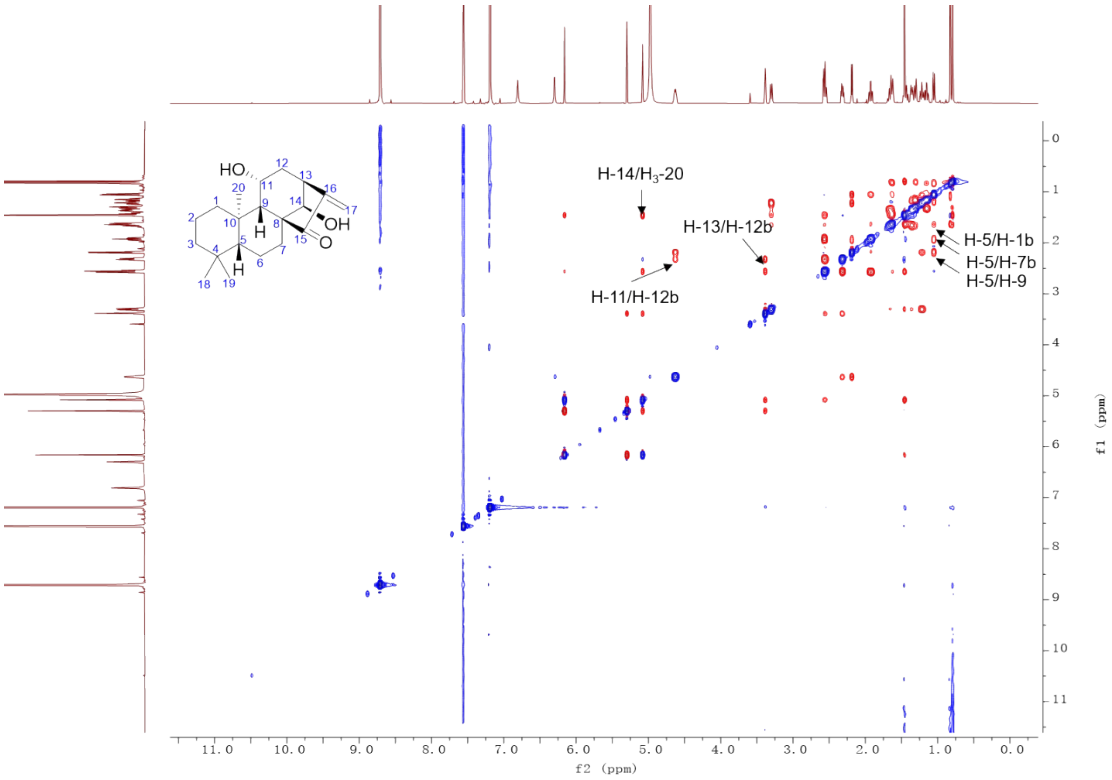
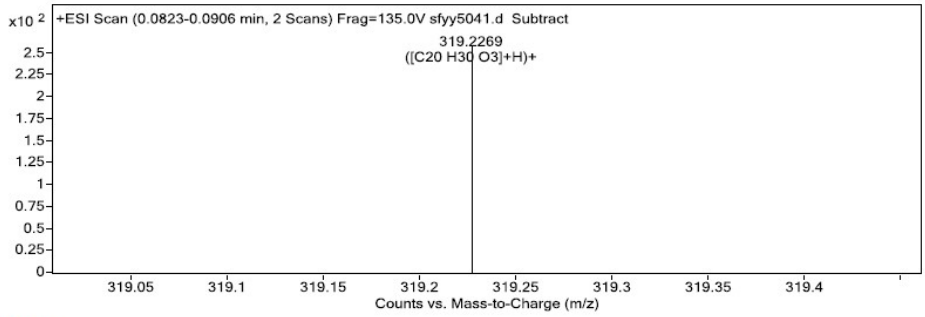


Figure S60. ROESY spectrum of glutinosasin E (**5**) (600 MHz, pyridine-d_5)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Peak List

m/z	z	Abund
79.0216	1	11522.56
97.9953	1	6452.65
101.0035	1	8927.42
105.9817	1	6167.73
137.0022	1	7250.06
144.9886	1	5059.48
150.1126	1	7335.72
172.0953	1	2597.32
240.988	1	4060.02
256.9602	1	3726.16

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	100
O	0	20

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C20 H30 O3	318.2195	319.2268	319.2269	-0.10	-0.31	6.0000

Figure S61. The HRESIMS spectrum of glutinosasin E (**5**)

Rudolph Research Analytical

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

Measurement Date : Wednesday, 30-OCT-2024

Set Temperature : 20.0

Time Delay : Disabled

Delay between Measurement : Disabled

n	Average	Std.Dev.	% RSD	Maximum	Minimum
5	-72.77	0.66	-0.90	-72.29	-73.49

S.No	Sample ID	Time	Result	Scale	OR °Arc	WLG.nm	Lg.mm	Conc.g/100ml	Temp.
1	SFYY5041	04:09:28 PM	-72.29	SR	-0.120	589	100.00	0.166	20.0
2	SFYY5041	04:09:35 PM	-72.29	SR	-0.120	589	100.00	0.166	20.0
3	SFYY5041	04:09:42 PM	-73.49	SR	-0.122	589	100.00	0.166	20.0
4	SFYY5041	04:09:48 PM	-72.29	SR	-0.120	589	100.00	0.166	20.0
5	SFYY5041	04:09:55 PM	-73.49	SR	-0.122	589	100.00	0.166	20.0

Figure S62. OR of glutinosasin E (**5**)

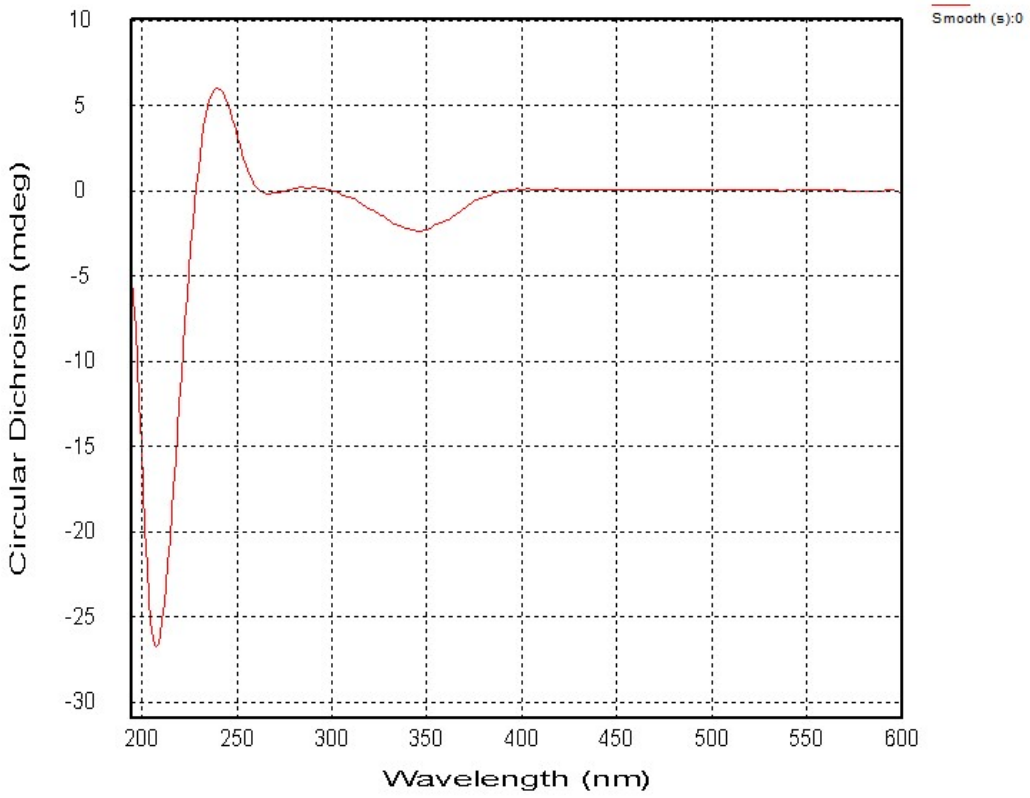


Figure S63. CD spectrum of glutinosasin E (**5**)

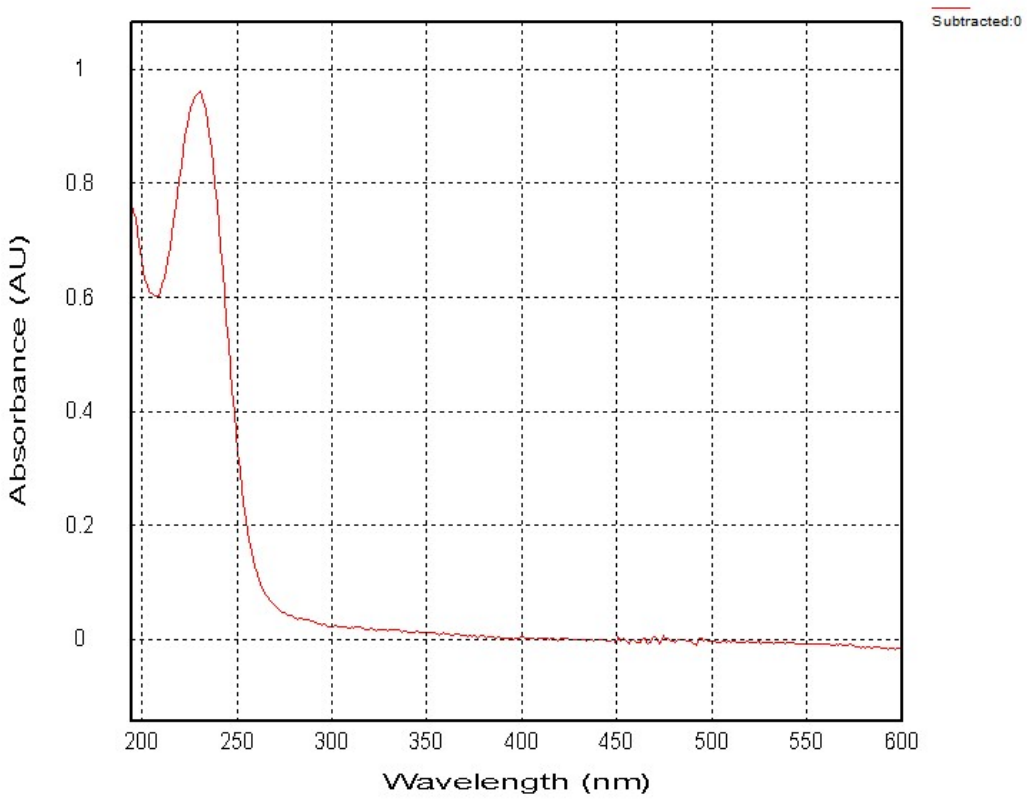


Figure S64. UV spectrum of glutinosasin E (**5**)

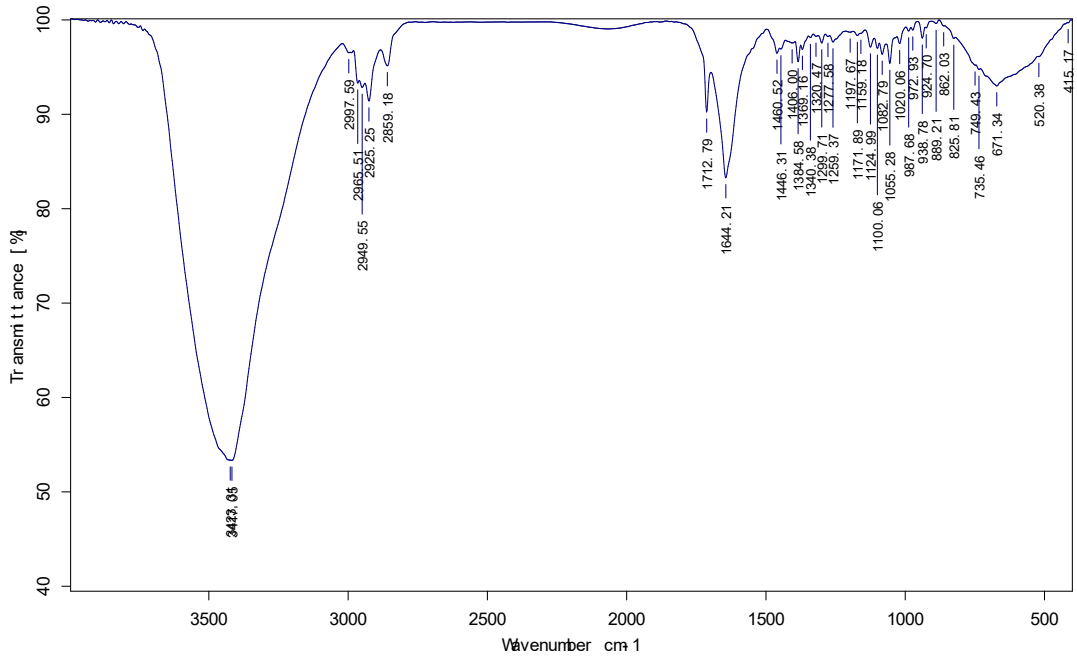


Figure S65. IR spectrum of glutinosasin E (**5**)

Table S1. Cytotoxicity of **1**–**5** against four tumor cell lines

No.	HL-60	A549	MDA-MB-231	SW480
		$IC_{50} \pm$ SD (μM)		
1	19.97±0.28	14.93±0.63	18.05±0.27	7.45±0.33
2	>20	>20	15.91±1.40	18.00±0.52
3	6.06±0.41	8.95±0.15	5.97±0.11	4.50±0.31
4	2.55±0.10	3.23±0.03	4.15±0.18	2.33±0.14
5	>20	>20	>20	>20
Taxol		<0.008		

8. Computational Methods

8.1. Conformational analysis

Conformational searches for the four tautomers of glutinosasins A−D (**C1**−**C4**): **T1** (HO–C(7)=C(8)–C(15)=O), **T2** (O=C(7)–C(8)=C(15)–OH), **T3** (O=C(7)–C(8, α-H)–C(15)=O), and **T4** (O=C(7)–C(8, β-H)–C(15)=O) were performed using the Crest program (version 3.0.1)[1]. The default workflow was applied to identify conformations within an energy cut-off of 4 kcal/mol from the global minimum for further optimization at the B3LYP-D3BJ/6-31G(d) level in the gas phase. Frequency calculations confirmed that each optimized structure was a true minimum on the potential energy surface. Single-point energy calculations were then conducted at the M06-2X/6-311+G(2d,p) level in the gas phase. Gibbs free energies were obtained by adding "thermal correction to Gibbs free energies" from frequency calculations to these single-point energies. Two geometries with an RMSD below 0.25 Å and an energy difference less than 0.25 kcal/mol were considered as duplicates, removing the higher energy conformer. Subsequently, room temperature (298.15 K) equilibrium populations were calculated according to Boltzmann distribution law:

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

Where P_i is the population of the i^{th} conformer; n_i the number of molecules in i^{th} conformer; ΔG is the relative Gibbs free energy (kcal/mol); T is room temperature (298.15 K); R is the ideal gas constant (0.0019858995). Only conformers with a population greater than 2% were used for subsequent NMR and ECD computations.

8.2. NMR calculations

The ^{13}C NMR shielding tensors for the conformers of **T1**, **T2**, and their combination (**T1**+**T2**) for each compound were calculated using the GIAO method at the mPW1PW91-SCRF/6-31+G(d,p) level employing the pyridine IEFPCM solvent model. The calculated ^{13}C NMR shielding tensors were converted into chemical shifts by referencing them to the shielding tensor of tetramethylsilane (TMS) computed under identical theoretical conditions. Statistical parameters, including the linear regression $\delta_{\text{cal}} = a\delta_{exp} + b$; the coefficient of determination, R^2; the mean absolute error (*MAE*) defined as $\Sigma_n |\delta_{cal} - \delta_{exp}|/n$; the corrected mean absolute error, *CMAE*, defined as $\Sigma_n |\delta_{\text{corr}} - \delta_{exp}|/n$, where $\delta_{corr} = (\delta_{cal} - b)/a$ were determined for comparison between experimental and calculated chemical shifts[2]. Spin-spin coupling constants were calculated at the B972/pcJ-1 level under the same solvent conditions.

8.3. ECD calculations

Time-dependent density functional theory (TDDFT) calculations for the ECD spectra of compounds **C1**−**C4** were carried out at the CAM-B3LYP/6-31G(2d,p) level using the methanol IEFPCM solvent model. Thirty-six excited states were calculated for each conformer, and the resulting ECD curves were generated using Multiwfn software (version 3.8)[3]. These curves were then ploted using Origin software.

8.4. Weak interaction analysis

Intramolecular noncovalent interactions in the lowest-energy conformers of **T1** and **T2** (**C1**–**C4**) were analyzed using the Interaction Region Indicator (IRI) method[4] in Multiwfn software (version 3.8)[3]. Checkpoint files obtained in single-point energy calculations at the M06-2X/6-311+G(2d,p) level in the gas phase were used to generate the cub files, and IRI isosurfaces were visualized in VMD 1.9.3 using the *IRIfill.vmd* script.

8.5. Transition state (TS) calculations

Transition state (TS) calculations were performed using the #p Opt=(Calcfc,ts,noeigen) Freq B3LYP/6-31G(d) keyword set, incorporating D3BJ empirical dispersion corrections and solvation effects via the IEFPCM model in pyridine. Intrinsic Reaction Coordinate (IRC) analyses were conducted to confirm the connectivity between **T1** and **T2** tautomers, utilizing the specified Maxpoints=50. Geometry optimization and frequency analysis for the IRC endpoints were executed using the B3LYP-D3BJ/6-31G(d) method, ensuring that all structures were true minima by confirming the absence of imaginary frequencies. Single-point energy calculations for the TS and optimized IRC endpoints were then computed at the M06-2X/6-311+G(2d,p) level with the IEFPCM model for pyridine. The relative electronic energies of the TS and optimized IRC endpoints were subsequently used to plot the energy diagram illustrating the energetic relationship between **T1**, **T2**, and the transition state.

The geometry optimization, frequency analysis, single-point energy calculation, NMR calculation, TS, and IRC calculation were all completed in the Gaussian 16 program.

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9. Computational Data for ^{13}C NMR and Spin-Spin Coupling Constant Calculation of Glutinosasins A−D (C1−C4)

9.1. NMR computational data of glutinosasin A (1, C1)

Table S2. Experimental and calculated ^{13}C NMR chemical shifts of **C1**

No.	$\delta_{exptl.}$	C1-T1-$\delta_{calcd.}$	C1-T2-$\delta_{calcd.}$	C1-$\delta_{calcd.}$
1	39.5	40.3	40.0	40.2
2	18.8	21.6	21.7	21.6
3	41.7	42.0	41.9	42.0
4	32.7	35.2	35.5	35.3
5	47.2	47.9	49.2	48.4
6	32.1	31.8	38.0	34.2
7	191.1	179.7	201.8	188.3
8	107.4	106.3	107.1	106.6
9	57.9	58.9	59.1	59.0
10	37.4	40.2	40.6	40.3
11	74.6	76.2	77.0	76.6
12	38.9	40.8	37.7	39.5
13	50.8	52.4	52.4	52.3
14	101.2	101.9	103.3	102.4
15	191.7	194.9	173.0	186.4
16	151.3	153.7	146.9	151.0
17	121.9	122.1	124.8	123.2
18	32.6	32.6	32.2	32.5
19	21.4	22.3	21.8	22.1
20	14.3	15.4	16.4	15.8
R^2	/	**0.9974**	**0.9909**	**0.9995**
MAE	/	**1.9**	**3.3**	**1.6**
CMAE	/	**1.7**	**3**	**1**

Table S3. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C1-T1** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	*Δ*G (kcal/mol)[d]	Population[e]
C1-T1-1	-1079.761636	0.399628	-677299.660208	0.0	96.44%
C1-T1-2	-1079.757907	0.399012	-677297.706920	1.953288	3.56%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S4. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C1-T2** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	*Δ*G (kcal/mol)	Population
C1-T2-1	-1079.760639	0.399366	-677299.198538	0.0	66.77%
C1-T2-2	-1079.758754	0.398243	-677298.720452	0.478086	29.78%
C1-T2-3	-1079.757188	0.398713	-677297.443357	1.75518	3.45%

Table S5. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C1** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	*Δ*G (kcal/mol)	Population
C1-1 (T1-1)	-1079.761636	0.399628	-677299.660208	0.0	58.82%
C1-2 (T2-1)	-1079.760639	0.399366	-677299.198538	0.461671	26.97%
C1-3 (T2-2)	-1079.758754	0.398243	-677298.720452	0.939757	12.03%
C1-4 (T1-2)	-1079.757907	0.399012	-677297.706920	1.953288	2.17%

Table S6. Cartesian coordinates (Å) of **C1-T1-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.661531	-2.002522	0.691020	H	3.419806	-3.185229	1.098601
C	3.153308	-2.293799	0.517703	H	3.376098	-2.534786	-0.528903
C	3.986950	-1.101487	0.982196	H	5.059652	-1.317847	0.894634
C	3.667993	0.196481	0.211110	H	3.789505	-0.934146	2.051381
C	2.121755	0.440141	0.248731	H	1.911941	0.671703	1.304898
C	1.695880	1.662257	-0.559333	H	2.203907	2.570276	-0.219812
C	0.226657	1.936711	-0.478814	H	1.957805	1.553337	-1.618883
C	-0.707006	1.033532	0.003462	H	-0.148955	-0.351360	1.545812
C	-0.248608	-0.359375	0.449704	H	-0.773484	-2.422084	0.018016
C	1.176051	-0.754010	-0.085076	H	-2.790708	-2.616604	1.200694
C	-1.287582	-1.468193	0.134675	H	-2.082101	-1.312251	2.182610
C	-2.402233	-1.595084	1.177312	H	-4.472072	-0.892981	0.965191
C	-3.470529	-0.656689	0.599977	H	-3.670235	-0.199538	-1.564432
C	-3.346438	-1.000262	-0.887724	H	-3.724153	2.560811	1.895092
C	-2.065534	1.536025	0.154102	H	-4.752019	1.056351	2.250360
C	-3.172648	0.798056	0.864837	H	5.434594	1.143990	1.062505
C	-3.922063	1.509947	1.714917	H	3.943069	1.511905	1.944054
C	4.366447	1.360535	0.943995	H	4.285117	2.304547	0.395171
C	4.275584	0.118936	-1.203601	H	4.039684	1.005891	-1.799777
C	1.095061	-1.066673	-1.592799	H	5.367720	0.062975	-1.125191
O	-1.962260	-1.192010	-1.114355	H	3.947346	-0.757209	-1.765946
O	-0.071757	3.157065	-0.894956	H	2.073096	-1.297486	-2.016728
O	-4.081978	-2.182788	-1.115617	H	0.449241	-1.930633	-1.770887
O	-2.381534	2.689438	-0.244148	H	0.665878	-0.236509	-2.158733
H	1.085525	-2.885512	0.393562	H	-1.080196	3.242063	-0.764923
H	1.464818	-1.848902	1.762515	H	-3.828097	-2.501572	-1.996638

Table S7. Cartesian coordinates (Å) of **C1-T1-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.672540	-1.989220	0.728435	H	3.439295	-3.153825	1.151293
C	3.165111	-2.275513	0.554243	H	3.384610	-2.535324	-0.488494
C	3.992813	-1.069231	0.992361	H	5.066503	-1.280653	0.905379
C	3.663460	0.211109	0.196659	H	3.797869	-0.882157	2.058737
C	2.115495	0.445749	0.231122	H	1.905699	0.702541	1.281466
C	1.680432	1.644338	-0.607025	H	2.195241	2.561093	-0.303818
C	0.213722	1.922135	-0.503990	H	1.923592	1.501523	-1.666892
C	-0.712888	1.022557	0.000308	H	-0.156599	-0.350129	1.552134
C	-0.251926	-0.366338	0.455415	H	-0.747111	-2.434969	0.051251
C	1.176202	-0.761266	-0.073383	H	-2.791334	-2.644421	1.192116
C	-1.279544	-1.488260	0.143796	H	-2.095836	-1.356762	2.188180
C	-2.404269	-1.617812	1.173546	H	-4.466762	-0.894894	0.931293
C	-3.454158	-0.663556	0.593827	H	-3.585802	-0.105525	-1.544132
C	-3.320873	-0.960197	-0.916629	H	-3.687366	2.515815	1.990823
C	-2.061860	1.533121	0.188281	H	-4.708205	1.001739	2.324971
C	-3.151508	0.781203	0.907135	H	3.930925	1.561824	1.903696
C	-3.887053	1.469331	1.787870	H	4.266171	2.326767	0.339454
C	4.354356	1.394085	0.906278	H	5.424061	1.187159	1.027690
C	4.270751	0.110485	-1.216776	H	4.022453	0.980682	-1.832272
C	1.096322	-1.105038	-1.574819	H	5.363578	0.070916	-1.138252
O	-1.947256	-1.264468	-1.113510	H	3.954231	-0.782448	-1.759160
O	-0.091836	3.141221	-0.915484	H	0.639110	-0.299173	-2.153580
O	-4.148203	-2.008220	-1.356968	H	2.078894	-1.313669	-1.999452
O	-2.383770	2.691419	-0.189950	H	0.476126	-1.990680	-1.735740
H	1.101016	-2.882591	0.453635	H	-1.095632	3.233137	-0.756066
H	1.480419	-1.812697	1.797282	H	-3.809380	-2.828981	-0.964166

Table S8. Cartesian coordinates (Å) of **C1-T2-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.670558	-1.995461	0.690193	H	3.430402	-3.175273	1.094339
C	3.162703	-2.282703	0.515716	H	3.385192	-2.520880	-0.531634
C	3.993268	-1.089983	0.982170	H	5.066627	-1.303995	0.896641
C	3.671818	0.205757	0.209605	H	3.793374	-0.922987	2.050985
C	2.124178	0.448197	0.241169	H	1.912568	0.688464	1.295465
C	1.703843	1.658710	-0.584211	H	2.236360	2.566342	-0.287378
C	0.234438	1.991535	-0.500780	H	1.936111	1.510917	-1.645506
C	-0.724228	1.032895	0.009129	H	-0.123920	-0.328302	1.552388
C	-0.244165	-0.354782	0.458475	H	-0.750820	-2.436732	0.126523
C	1.178523	-0.748196	-0.085710	H	-2.787877	-2.583104	1.282156
C	-1.272686	-1.482318	0.185662	H	-2.093419	-1.235780	2.214323
C	-2.400143	-1.563041	1.218174	H	-4.467919	-0.885644	0.938852
C	-3.461336	-0.654144	0.585769	H	-3.612509	-0.270581	-1.596711
C	-3.312863	-1.052010	-0.886882	H	-3.851212	2.606389	1.722375
C	-2.030067	1.505961	0.173118	H	-4.887231	1.099273	2.033565
C	-3.188211	0.811957	0.808117	H	4.281644	2.316076	0.395559
C	-4.018801	1.548209	1.559770	H	5.435928	1.158372	1.059783
C	4.366933	1.371612	0.942645	H	3.944163	1.520010	1.943409
C	4.280235	0.128082	-1.204628	H	4.049110	1.017989	-1.798123
C	1.086597	-1.068646	-1.591127	H	5.372013	0.065632	-1.126050
O	-1.931144	-1.279622	-1.083878	H	3.946842	-0.744817	-1.769311
O	-0.081786	3.150562	-0.880415	H	0.453832	-1.944689	-1.756345
O	-4.066875	-2.229196	-1.084443	H	0.634998	-0.250334	-2.157244
O	-2.366004	2.735726	-0.190966	H	2.064028	-1.282316	-2.025930
H	1.100639	-2.881747	0.392011	H	-1.507124	3.164426	-0.564850
H	1.473810	-1.843971	1.762067	H	-3.792711	-2.592289	-1.941973

Table S9. Cartesian coordinates (Å) of **C1-T2-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-1.498466	-2.066154	-0.161393	H	-3.155081	-3.440599	-0.007806
C	-2.930554	-2.403015	0.268650	H	-3.020985	-2.356784	1.360363
C	-3.944585	-1.462919	-0.385439	H	-4.964832	-1.718927	-0.070853
C	-3.675709	0.028141	-0.085640	H	-3.908655	-1.611260	-1.474893
C	-2.191712	0.328155	-0.468197	H	-2.159179	0.119354	-1.548236
C	-1.811388	1.802770	-0.286928	H	-2.181430	2.407291	-1.123080
C	-0.343204	2.158633	-0.124965	H	-2.288044	2.231489	0.600569
C	0.713868	1.164252	-0.256842	H	-0.109237	-0.145666	-1.718072
C	0.211953	-0.223853	-0.665761	H	0.757422	-2.235659	-1.127929
C	-1.097919	-0.602526	0.129101	H	2.855965	-1.878876	-2.085260
C	1.244301	-1.345824	-0.726929	H	2.276090	-0.213338	-2.304845
C	2.478749	-0.994315	-1.567525	H	4.512917	-0.714662	-0.812463
C	3.479785	-0.560409	-0.495826	H	3.411346	-1.205021	1.626688
C	3.141222	-1.552232	0.622342	H	4.394930	2.562079	0.674234
C	2.019921	1.605548	-0.004303	H	5.397346	1.049550	0.291110
C	3.321136	0.873393	-0.047744	H	-4.520666	1.942096	-0.763394
C	4.427827	1.538235	0.327336	H	-5.641787	0.579207	-0.847324
C	-4.595083	0.872961	-0.989479	H	-4.349132	0.732400	-2.049162
C	-4.049264	0.341512	1.376021	H	-3.537294	-0.298010	2.095784
C	-0.868761	-0.417499	1.645317	H	-3.831561	1.380427	1.643478
O	1.738333	-1.677861	0.592376	H	-5.127020	0.193744	1.513006
O	-0.135052	3.366191	0.155401	H	-0.906915	0.631236	1.952365
O	3.783928	-2.772765	0.316457	H	-1.617989	-0.953565	2.231089
O	2.227011	2.877481	0.324654	H	0.111950	-0.810239	1.916538
H	-0.794306	-2.747312	0.329303	H	1.314421	3.341414	0.321452
H	-1.420092	-2.248951	-1.243762	H	3.395357	-3.444913	0.899226

Table S10. Cartesian coordinates (Å) of **C1-T2-3** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.682642	-1.981919	0.728690	H	3.451939	-3.141412	1.150264
C	3.175971	-2.262798	0.554443	H	3.396126	-2.520562	-0.488685
C	3.999047	-1.054784	0.993903	H	5.073644	-1.262761	0.909555
C	3.666252	0.222412	0.195702	H	3.800959	-0.867468	2.059681
C	2.116675	0.454179	0.223154	H	1.904128	0.719780	1.271220
C	1.686953	1.640375	-0.632744	H	2.225218	2.555602	-0.372437
C	0.220080	1.975918	-0.529221	H	1.901069	1.458679	-1.692526
C	-0.730337	1.020098	0.004446	H	-0.131560	-0.328145	1.557721
C	-0.247480	-0.363359	0.463330	H	-0.725217	-2.449418	0.155949
C	1.179013	-0.756351	-0.074153	H	-2.787191	-2.614814	1.272881
C	-1.264758	-1.503613	0.194888	H	-2.103633	-1.285800	2.222544
C	-2.400468	-1.589779	1.216226	H	-4.460879	-0.891256	0.909685
C	-3.443928	-0.663078	0.584643	H	-3.522539	-0.164800	-1.569776
C	-3.286180	-1.007347	-0.914667	H	-3.805541	2.563789	1.832568
C	-2.027114	1.498982	0.204043	H	-4.836131	1.049928	2.129000
C	-3.165446	0.793907	0.857918	H	3.929186	1.573131	1.902937
C	-3.977666	1.509848	1.647472	H	4.259052	2.341081	0.339332
C	4.352318	1.408345	0.904899	H	5.423076	1.206053	1.025109
C	4.274818	0.121333	-1.217030	H	4.031264	0.994387	-1.830222
C	1.089431	-1.109503	-1.572717	H	5.367359	0.075450	-1.137894
O	-1.919440	-1.352664	-1.078610	H	3.953303	-0.768639	-1.761653
O	-0.104442	3.132221	-0.906534	H	2.070838	-1.304988	-2.006874
O	-4.128023	-2.051138	-1.338664	H	0.480022	-2.004837	-1.720386
O	-2.373000	2.729814	-0.146800	H	0.613720	-0.315311	-2.153044
H	1.118236	-2.879318	0.453544	H	-1.526728	3.156211	-0.547301
H	1.489712	-1.806908	1.797712	H	-3.789127	-2.870722	-0.943384

Table S11. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C1-T3** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	ΔG (kcal/mol)[d]	Population[e]
C1-T3-1	-1079.750833	0.398704	-677293.460904	0.0	52.67%
C1-T3-2	-1079.750467	0.398512	-677293.351875	0.109028	43.81%
C1-T3-3	-1079.748088	0.398510	-677291.860069	1.600834	3.53%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S12. Cartesian coordinates (Å) of **C1-T3-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-1.630114	-2.029258	-0.648162	H	-3.399164	-3.181978	-1.093263
C	-3.132362	-2.296551	-0.503405	H	-3.370943	-2.546391	0.537308
C	-3.964575	-1.098608	-0.961558	H	-5.035309	-1.308008	-0.839599
C	-3.612103	0.211299	-0.222913	H	-3.798325	-0.946151	-2.038080
C	-2.071784	0.429350	-0.342627	H	-1.907771	0.487557	-1.428358
C	-1.615308	1.790645	0.246271	H	-1.536162	2.532760	-0.559333
C	-0.266177	1.792480	0.925295	H	-2.324607	2.197970	0.969996
C	0.814084	0.853894	0.390842	H	0.136168	-0.059069	-1.454717
C	0.273017	-0.361592	-0.407672	H	0.872275	-2.441660	-0.661846
C	-1.153114	-0.760551	0.096311	H	2.965202	-2.133535	-1.712188
C	1.341060	-1.482978	-0.437220	H	2.170086	-0.664170	-2.312678
C	2.491395	-1.194948	-1.412841	H	4.510569	-0.541218	-0.875338
C	3.480165	-0.384250	-0.550301	H	3.432492	-0.441346	1.675873
C	3.310406	-1.099290	0.805012	H	3.976170	3.056576	-0.814698
C	1.812616	1.653137	-0.440586	H	5.231235	1.685487	-0.857792
C	3.209838	1.106786	-0.575351	H	-3.953610	1.485646	-1.972369
C	4.194098	1.995040	-0.760881	H	-4.188521	2.324786	-0.428814
C	-4.325484	1.370104	-0.947035	H	-5.403168	1.176301	-1.001213
C	-4.142606	0.161702	1.222401	H	-3.825785	-0.731780	1.762136
C	-1.118312	-1.037257	1.614955	H	-3.823520	1.030170	1.807352
O	1.986536	-1.617262	0.847333	H	-5.238811	0.164216	1.208838
O	-0.022913	2.509516	1.876329	H	-1.091679	-0.122919	2.214694
O	4.251092	-2.147543	0.834047	H	-1.990476	-1.606366	1.940808
O	1.485221	2.701719	-0.972375	H	-0.228034	-1.620294	1.867168
H	-1.076714	-2.904270	-0.288578	H	3.997499	-2.729727	1.568543
H	-1.393702	-1.923533	-1.717768	H	1.326674	0.474578	1.278037

Table S13. Cartesian coordinates (Å) of **C1-T3-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.599904	-1.941759	0.744620	H	3.319154	-3.107843	1.328058
C	3.090187	-2.281841	0.643808	H	3.326706	-2.650790	-0.361509
C	3.963524	-1.074634	0.980782	H	5.026251	-1.332921	0.886527
C	3.666202	0.171145	0.115846	H	3.801310	-0.808386	2.035518
C	2.130831	0.448374	0.183163	H	1.945762	0.647804	1.250772
C	1.712356	1.741077	-0.555809	H	2.322582	2.591275	-0.248038
C	0.270324	2.066771	-0.237424	H	1.820256	1.616924	-1.640407
C	-0.699247	0.940280	-0.585974	H	-0.204577	0.021275	1.294632
C	-0.267966	-0.295903	0.245390	H	-0.870960	-2.397849	0.136664
C	1.177410	-0.751769	-0.151338	H	-2.756526	-2.325951	1.576199
C	-1.344312	-1.417246	0.191680	H	-1.882275	-0.942357	2.277395
C	-2.330937	-1.341573	1.365766	H	-4.373598	-0.519719	1.322255
C	-3.427981	-0.430157	0.783170	H	-3.931038	-0.357038	-1.380964
C	-3.522694	-1.033445	-0.621629	H	-3.021953	2.969660	1.522845
C	-2.134819	1.445280	-0.448820	H	-4.013147	1.697439	2.445347
C	-2.998928	1.022408	0.714190	H	4.008505	1.625849	1.722571
C	-3.368622	1.944326	1.604689	H	4.408395	2.247412	0.110981
C	4.426992	1.356036	0.745638	H	5.478727	1.085649	0.895150
C	4.207811	-0.020296	-1.312517	H	5.302081	-0.080581	-1.284120
C	1.182898	-1.193684	-1.631974	H	3.843139	-0.929788	-1.792142
O	-2.168306	-1.280005	-0.994377	H	3.945903	0.825324	-1.957364
O	-0.072993	3.089214	0.323271	H	1.265936	-0.353647	-2.326616
O	-4.270043	-2.221728	-0.539206	H	2.008163	-1.872899	-1.851818
O	-2.565804	2.216485	-1.284847	H	0.254794	-1.721476	-1.874070
H	1.014832	-2.833372	0.494119	H	-4.202040	-2.660251	-1.402321
H	1.363595	-1.695258	1.790463	H	-0.580399	0.709445	-1.648391

Table S14. Cartesian coordinates (Å) of **C1-T3-3** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-1.639935	-2.020891	-0.665337	H	-3.417217	-3.161836	-1.107424
C	-3.142424	-2.282306	-0.512456	H	-3.374693	-2.539331	0.527840
C	-3.972222	-1.077009	-0.955206	H	-5.042980	-1.282681	-0.827558
C	-3.608749	0.225026	-0.208129	H	-3.812742	-0.916401	-2.031595
C	-2.068346	0.437194	-0.337036	H	-1.911884	0.503959	-1.423442
C	-1.601942	1.791397	0.260290	H	-1.523396	2.539780	-0.539524
C	-0.249649	1.781162	0.932359	H	-2.305262	2.196205	0.991164
C	0.824005	0.841390	0.384338	H	0.130077	-0.045845	-1.466902
C	0.272902	-0.362111	-0.424409	H	0.846651	-2.435255	-0.731981
C	-1.151985	-0.760350	0.085895	H	2.950432	-2.133573	-1.764215
C	1.330040	-1.491199	-0.478005	H	2.177005	-0.651490	-2.338938
C	2.487491	-1.193825	-1.442289	H	4.506104	-0.562054	-0.854366
C	3.467639	-0.399276	-0.558320	H	3.327599	-0.381642	1.656583
C	3.268130	-1.088858	0.824153	H	3.986511	3.037719	-0.848734
C	1.818485	1.644754	-0.449327	H	5.233969	1.659871	-0.896820
C	3.210900	1.093059	-0.600166	H	-4.176911	2.342804	-0.392543
C	4.199142	1.975155	-0.794372	H	-5.400750	1.204586	-0.965550
C	-4.321848	1.393051	-0.917595	H	-3.956856	1.515394	-1.944628
C	-4.129279	0.165735	1.240446	H	-3.803076	1.028358	1.830091
C	-1.107656	-1.049806	1.602042	H	-5.225517	0.172341	1.234476
O	1.976045	-1.691607	0.793622	H	-3.811922	-0.733035	1.770944
O	0.003569	2.489531	1.886912	H	-1.979107	-1.619726	1.928288
O	4.241251	-2.059472	1.102505	H	-0.217225	-1.636816	1.843994
O	1.488258	2.696343	-0.972963	H	-1.076157	-0.140598	2.209308
H	-1.088959	-2.901420	-0.315449	H	4.059371	-2.817681	0.522988
H	-1.410490	-1.908206	-1.735892	H	1.336248	0.454483	1.268020

Table S15. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C1-T4** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	ΔG (kcal/mol)[d]	Population[e]
C1-T4-1	-1079.751916	0.399916	-677293.379793	0.0	100.00%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S16. Cartesian coordinates (Å) of **C1-T4-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-1.478073	-2.082603	-0.463533	H	-3.145468	-3.448554	-0.322014
C	-2.869123	-2.455665	0.053494	H	-2.857900	-2.535849	1.147089
C	-3.903885	-1.425855	-0.399108	H	-4.906798	-1.705939	-0.051235
C	-3.594675	0.014386	0.068302	H	-3.943620	-1.435463	-1.498466
C	-2.117323	0.364422	-0.316053	H	-2.144470	0.409350	-1.416847
C	-1.682913	1.762250	0.171022	H	-2.444053	2.523435	-0.009872
C	-0.429205	2.202468	-0.538041	H	-1.471835	1.746352	1.246186
C	0.715759	1.187892	-0.647511	H	-0.131562	-0.304382	-1.892130
C	0.235355	-0.280277	-0.855009	H	1.085523	-2.208974	-1.307724
C	-1.005581	-0.689984	0.013468	H	3.198456	-1.550779	-2.078560
C	1.417298	-1.266226	-0.864076	H	2.448788	0.028418	-2.342438
C	2.671143	-0.729467	-1.589481	H	4.609231	-0.207684	-0.687865
C	3.549094	-0.220939	-0.425124	H	3.446081	-1.046349	1.633987
C	3.257737	-1.331318	0.592865	H	3.768010	2.956929	1.003490
C	1.715405	1.415356	0.493423	H	5.120942	1.904024	0.289609
C	3.159525	1.107998	0.185646	H	-4.478266	1.992958	-0.343836
C	4.065202	2.035805	0.512592	H	-5.576292	0.633250	-0.585440
C	-4.537120	0.961308	-0.704857	H	-4.307931	0.964306	-1.777034
C	-3.928631	0.165299	1.565770	H	-3.497590	-0.623963	2.184682
C	-0.683280	-0.752338	1.522085	H	-3.588613	1.126513	1.964207
O	1.865943	-1.547481	0.484651	H	-5.015754	0.121464	1.700910
O	-0.309508	3.297952	-1.051311	H	-1.589610	-0.895313	2.109655
O	4.006615	-2.467740	0.227127	H	-0.010012	-1.583073	1.729488
O	1.386542	1.934593	1.546427	H	-0.195541	0.152769	1.884763
H	-0.749081	-2.840600	-0.155203	H	3.694871	-3.201859	0.780485
H	-1.505377	-2.096825	-1.563991	H	1.250871	1.492173	-1.552285

9.2. NMR computational data of glutinosasin B (2, C2)

Table S17. Experimental and calculated ^{13}C NMR chemical shifts of **C2**

No.	$\delta_{exptl.}$	C2-T1-$\delta_{calcd.}$	C2-T2-$\delta_{calcd.}$	C2-$\delta_{calcd.}$
1	39.6	41.0	42.0	41.6
2	19.0	21.2	21.3	21.2
3	43.3	43.6	43.5	43.6
4	33.8	36.1	36.4	36.3
5	55.0	52.6	52.3	52.4
6	70.9	70.6	73.3	72.3
7	195.9	178.0	200.7	192.1
8	106.8	105.8	105.1	105.4
9	57.1	58.6	59.6	59.2
10	38.5	40.4	40.2	40.3
11	74.6	75.8	76.0	76.0
12	37.6	40.6	39.8	40.1
13	50.8	52.3	52.4	52.4
14	101.8	101.8	102.1	102.0
15	187.5	196.4	177.0	184.4
16	149.7	152.6	147.2	149.2
17	122.8	123.8	125.4	124.8
18	36.0	35.7	35.5	35.6
19	22.2	22.6	22.7	22.7
20	16.5	17.2	18.4	17.9
R^2		**0.9924**	**0.9969**	**0.9993**
MAE		**2.6**	**2.4**	**1.7**
CMAE		**2.5**	**1.9**	**1.2**

Table S18. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C2-T1** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	⊿G (kcal/mol)[d]	Population[e]
C2-T1-1	-1154.980313	0.403003	-724497.262232	0	100.00%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S19. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C2-T2** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
C2-T2-1	-1154.981575	0.403844	-724497.526435	0.0	95.01%
C2-T2-2	-1154.978105	0.403155	-724495.781326	1.745109	4.99%

Table S20. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C2** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
C2-1 (T2-1)	-1154.981575	0.403844	-724497.526435	0.0	59.08%
C2-2 (T1-1)	-1154.980313	0.403003	-724497.262232	0.264203	37.82%
C2-3 (T2-2)	-1154.978105	0.403155	-724495.781326	1.745109	3.10%

Table S21. Cartesian coordinates (Å) of **C2-T1-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-1.438974	-2.217366	-0.643374	H	-4.865137	-1.786993	-0.780564
C	-2.892443	-2.610738	-0.391819	H	-3.649942	-1.420295	-1.996584
C	-3.810623	-1.512794	-0.912420	H	-1.824031	0.490120	-1.321157
C	-3.579686	-0.129643	-0.262354	H	-0.781930	-3.041517	-0.346528
C	-2.045562	0.220772	-0.278009	H	-1.299809	-2.079929	-1.726093
C	-1.687703	1.444070	0.565992	H	-1.890342	1.227575	1.626613
C	-0.215226	1.782738	0.459328	H	0.278037	-0.482432	-1.557529
C	0.762260	0.942155	-0.029256	H	-4.371862	1.877490	-0.687444
C	0.377780	-0.472315	-0.461850	H	-5.396695	0.535884	-1.246546
C	-1.025398	-0.917799	0.084335	H	-3.922124	0.960923	-2.130579
C	1.478162	-1.514166	-0.127475	H	-4.074430	0.874186	1.619092
C	2.599939	-1.587074	-1.168600	H	-5.279483	-0.290438	1.069944
C	3.614596	-0.585070	-0.600222	H	-3.790101	-0.864233	1.816646
C	3.506196	-0.919472	0.891066	H	-0.445045	-0.372935	2.139363
C	2.088421	1.527150	-0.186583	H	-1.895627	-1.379238	2.052658
C	3.241624	0.850020	-0.878482	H	-0.303625	-2.080907	1.781181
C	3.959405	1.598847	-1.724617	H	4.627977	-0.770419	-0.961938
C	-4.362104	0.882273	-1.129277	H	3.046160	-2.584719	-1.182719
C	-4.201812	-0.104628	1.147146	H	2.265014	-1.332574	-2.176607
C	-0.920286	-1.195690	1.600830	H	1.023575	-2.495208	0.005001
O	0.013965	3.023807	0.869314	H	3.788973	-0.097123	1.560299
O	2.323238	2.706416	0.194726	H	4.063791	-2.382746	2.015629
O	-2.442147	2.581960	0.169925	H	3.704727	2.635766	-1.913879
O	2.132397	-1.175050	1.117530	H	4.818241	1.188978	-2.249381
O	4.298403	-2.061462	1.130144	H	-1.969581	3.350826	0.532798
H	-3.111211	-3.557276	-0.901210	H	1.018966	3.174573	0.703412
H	-3.062724	-2.790326	0.676850	-	-	-	-

Table S22. Cartesian coordinates (Å) of **C2-T2-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.440518	-2.194590	0.709763	H	4.866594	-1.760467	0.824301
C	2.892783	-2.595712	0.463902	H	3.655323	-1.365994	2.035635
C	3.812169	-1.484514	0.953459	H	1.816447	0.530580	1.302301
C	3.575774	-0.119359	0.268800	H	0.782620	-3.029809	0.448018
C	2.041195	0.228939	0.268012	H	1.308176	-2.017263	1.787529
C	1.682448	1.411640	-0.632657	H	1.778746	1.093837	-1.683027
C	0.228513	1.841261	-0.453344	H	-0.292439	-0.473913	1.558684
C	-0.783027	0.945760	0.038968	H	4.329626	1.908594	0.655359
C	-0.386974	-0.472983	0.462515	H	5.385617	0.597669	1.231537
C	1.023418	-0.921665	-0.063000	H	3.907413	1.005299	2.116927
C	-1.472794	-1.531882	0.133302	H	5.283772	-0.284841	-1.052288
C	-2.611762	-1.590599	1.154357	H	3.812467	-0.922181	-1.780919
C	-3.607423	-0.585474	0.560671	H	4.050862	0.830710	-1.644444
C	-3.473719	-0.924738	-0.928516	H	0.372912	-2.185649	-1.717360
C	-2.051462	1.499664	0.243235	H	0.382064	-0.484481	-2.127091
C	-3.244981	0.849406	0.853353	H	1.904995	-1.376581	-2.030852
C	-4.023339	1.598332	1.647726	H	-4.629351	-0.767772	0.897986
C	4.343670	0.921198	1.114061	H	-3.065573	-2.584939	1.164728
C	4.202287	-0.127330	-1.139343	H	-2.293674	-1.333816	2.167389
C	0.924296	-1.252272	-1.570724	H	-1.005689	-2.510585	0.033782
O	0.012267	3.050399	-0.749624	H	-3.715153	-0.093484	-1.603326
O	-2.310673	2.765327	-0.058601	H	-4.046121	-2.381833	-2.053360
O	2.505122	2.542773	-0.420257	H	-3.788425	2.634180	1.862660
O	-2.108157	-1.234933	-1.129246	H	-4.915064	1.181205	2.106877
O	-4.302534	-2.037804	-1.182526	H	1.945094	3.300019	-0.679735
H	3.112464	-3.528871	0.997041	H	-1.440217	3.166756	-0.403053
H	3.058790	-2.802967	-0.600508	-	-	-	-

Table S23. Cartesian coordinates (Å) of **C2-T2-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.453697	-2.184013	0.740935	H	4.876127	-1.722730	0.838322
C	2.907911	-2.578578	0.496372	H	3.665407	-1.319923	2.047340
C	3.820003	-1.453087	0.966526	H	1.808537	0.553397	1.287709
C	3.571227	-0.100114	0.262305	H	0.801214	-3.028870	0.496254
C	2.033856	0.236223	0.258120	H	1.324294	-1.988984	1.816032
C	1.664015	1.401170	-0.662687	H	1.745680	1.061755	-1.707225
C	0.212849	1.830334	-0.465919	H	-0.301419	-0.483382	1.563813
C	-0.790611	0.932903	0.042375	H	3.894716	1.052724	2.094391
C	-0.390651	-0.484161	0.466929	H	4.305830	1.940038	0.619679
C	1.024753	-0.927762	-0.052490	H	5.375465	0.647636	1.212293
C	-1.464557	-1.555273	0.133898	H	5.280596	-0.265151	-1.056695
C	-2.612801	-1.625116	1.142134	H	3.818209	-0.935089	-1.773288
C	-3.589906	-0.600942	0.555355	H	4.032607	0.823163	-1.667646
C	-3.441432	-0.877345	-0.959369	H	1.912753	-1.389583	-2.015367
C	-2.049813	1.488541	0.283291	H	0.401887	-2.231411	-1.689297
C	-3.224607	0.820705	0.906171	H	0.367863	-0.537365	-2.121830
C	-3.987911	1.541616	1.739356	H	-4.621895	-0.780652	0.862561
C	4.330278	0.959319	1.091986	H	-3.065260	-2.624252	1.138705
C	4.197099	-0.123707	-1.146040	H	-2.306874	-1.397008	2.165550
C	0.930035	-1.282905	-1.555411	H	-0.978924	-2.526458	0.048839
O	-0.011231	3.038633	-0.754881	H	-3.617915	0.011536	-1.571059
O	-2.318885	2.756776	0.001827	H	-4.044851	-2.704217	-1.109777
O	2.488110	2.536791	-0.485741	H	-3.750256	2.570995	1.981464
O	-2.098419	-1.301797	-1.134122	H	-4.870346	1.109230	2.202465
O	-4.344683	-1.841742	-1.439832	H	1.919065	3.290199	-0.736915
H	3.136211	-3.501856	1.042893	H	-1.460323	3.160792	-0.364947
H	3.071840	-2.800662	-0.565300	-	-	-	-

Table S24. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C2-T3** in the gas phase (T=298.15 K)

Conformer	**E (Hartree)[a]**	**C (Hartree)[b]**	**G (kcal/mol)[c]**	**⊿G (kcal/mol)[d]**	**Population[e]**
C2-T3-1	-1154.971335	0.401294	-724492.700589	0.0	51.72%
C2-T3-2	-1154.971663	0.401985	-724492.472882	0.227707	35.21%
C2-T3-3	-1154.970492	0.402223	-724491.588954	1.111635	7.91%
C2-T3-4	-1154.971052	0.403188	-724491.334829	1.365760	5.15%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S25. Cartesian coordinates (Å) of **C2-T3-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.369567	-2.160047	0.698426	H	4.816198	-1.802009	0.837207
C	2.824212	-2.608286	0.558949	H	3.629693	-1.264336	2.017173
C	3.772433	-1.481766	0.948511	H	1.866020	0.450112	1.273236
C	3.577542	-0.162934	0.161930	H	0.713119	-2.993199	0.425788
C	2.058574	0.226476	0.212197	H	1.168245	-1.932859	1.755938
C	1.710254	1.539850	-0.554958	H	1.779537	1.353313	-1.635901
C	0.268919	1.907191	-0.226667	H	-0.313222	-0.104396	1.314306
C	-0.773072	0.863808	-0.553186	H	4.536523	1.812685	0.334675
C	-0.394939	-0.399862	0.260298	H	5.451530	0.465176	1.048026
C	1.027654	-0.913548	-0.152725	H	4.031809	1.124290	1.878481
C	-1.529279	-1.460442	0.185226	H	3.665792	-1.111401	-1.836218
C	-2.520987	-1.343495	1.351556	H	3.976766	0.630682	-1.836049
C	-3.572601	-0.382563	0.766611	H	5.201336	-0.486914	-1.235130
C	-3.676660	-0.964842	-0.646625	H	1.076411	-0.475020	-2.329004
C	-2.171577	1.473515	-0.395415	H	1.820521	-2.001344	-1.892436
C	-3.097347	1.055236	0.718969	H	0.067986	-1.843686	-1.874858
C	-3.493830	1.986677	1.589203	H	-4.527578	-0.442440	1.292998
C	4.448705	0.883284	0.893675	H	-2.991884	-2.308397	1.554916
C	4.122456	-0.296158	-1.271521	H	-2.061582	-0.969530	2.268557
C	1.003397	-1.323251	-1.644207	H	-1.111016	-2.464561	0.124120
O	0.030517	2.955973	0.349396	H	-4.047916	-0.262612	-1.402043
O	-2.510736	2.335555	-1.183441	H	-4.413656	-2.554948	-1.451200
O	2.533433	2.631426	-0.231504	H	-3.129228	3.006741	1.521146
O	-2.330581	-1.263895	-1.007927	H	-4.181545	1.752844	2.398496
O	-4.474337	-2.120375	-0.585442	H	1.937279	3.276545	0.201355
H	2.997746	-3.481420	1.199814	H	-0.690735	0.626349	-1.617473
H	3.024950	-2.942196	-0.466063	-	-	-	-

Table S26. Cartesian coordinates (Å) of **C2-T3-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.436767	-2.098661	0.924547	H	4.865061	-1.652762	0.900968
C	2.886563	-2.528209	0.711894	H	3.686381	-1.094259	2.078865
C	3.814074	-1.359686	1.019250	H	1.836102	0.655300	1.174171
C	3.561031	-0.095928	0.164298	H	0.774435	-2.958277	0.776002
C	2.028343	0.253785	0.167300	H	1.317047	-1.784485	1.972021
C	1.641213	1.358851	-0.841352	H	1.593158	0.902902	-1.842929
C	0.241822	1.881550	-0.533037	H	-0.253824	-0.186799	1.558111
C	-0.856109	0.888759	-0.205273	H	4.341751	1.956318	0.260247
C	-0.384999	-0.418499	0.493044	H	5.397287	0.720734	0.985628
C	1.006655	-0.936946	-0.001887	H	3.942930	1.262081	1.838004
C	-1.525403	-1.466725	0.403232	H	3.747330	-1.172668	-1.760953
C	-2.741099	-1.177219	1.302979	H	3.955301	0.585082	-1.878131
C	-3.679499	-0.374522	0.378996	H	5.228194	-0.418483	-1.179549
C	-3.416191	-1.086548	-0.957370	H	1.864240	-1.731051	-1.863162
C	-1.957342	1.551614	0.637762	H	0.275568	-2.380950	-1.456476
C	-3.376736	1.110028	0.404504	H	0.410809	-0.772293	-2.127839
C	-4.326026	2.045834	0.314301	H	-4.729940	-0.516761	0.641319
C	4.356594	1.039597	0.846751	H	-3.225662	-2.116338	1.579865
C	4.141643	-0.290395	-1.249780	H	-2.477633	-0.640104	2.217808
C	0.890406	-1.476776	-1.444741	H	-1.125874	-2.458827	0.616385
O	0.032921	3.079337	-0.619715	H	-3.546369	-0.446649	-1.839788
O	-1.682895	2.365039	1.497883	H	-3.969618	-2.762221	-1.734957
O	2.523562	2.454901	-0.887125	H	-4.079689	3.100649	0.384095
O	-2.058948	-1.496021	-0.941596	H	-5.370616	1.784479	0.164017
O	-4.280158	-2.198871	-1.007683	H	1.940809	3.241967	-0.890797
H	3.118610	-3.374921	1.369455	H	-1.275858	0.591278	-1.175144
H	3.033966	-2.887438	-0.313861	-	-	-	-

Table S27. Cartesian coordinates (Å) of **C2-T3-3** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.331901	-2.169008	0.774845	H	3.595978	-2.278966	-0.768607
C	2.796419	-2.283488	1.232092	H	4.794113	-1.940161	0.461776
C	3.753971	-1.742900	0.175183	H	1.972420	0.387173	1.283405
C	3.579766	-0.213645	-0.023439	H	1.061959	-3.070920	0.212706
C	2.074489	0.193711	0.205610	H	0.689157	-2.161459	1.663915
C	1.713561	1.543517	-0.476149	H	1.763055	1.420677	-1.567386
C	0.282917	1.912814	-0.118614	H	-0.322949	-0.119408	1.349499
C	-0.765597	0.888906	-0.496764	H	4.303686	1.580999	0.987713
C	-0.396859	-0.393547	0.288821	H	5.507395	0.275825	0.865934
C	1.020671	-0.919452	-0.113479	H	4.192672	0.164798	2.047046
C	-1.514354	-1.465595	0.180966	H	3.496353	-0.251303	-2.222489
C	-2.553675	-1.357248	1.304490	H	4.138578	1.259747	-1.544542
C	-3.593823	-0.411915	0.676776	H	5.124048	-0.208197	-1.540645
C	-3.625016	-0.986147	-0.743729	H	0.158152	-1.981881	-1.813219
C	-2.161791	1.511299	-0.356458	H	0.962025	-0.488627	-2.284745
C	-3.158692	1.038206	0.669621	H	1.918339	-1.899888	-1.856883
C	-3.661201	1.948643	1.508233	H	-4.571542	-0.499069	1.155422
C	4.447345	0.501091	1.034317	H	-3.019757	-2.327829	1.491543
C	4.103813	0.174062	-1.417118	H	-2.136534	-0.975528	2.238502
C	1.018491	-1.339449	-1.600021	H	-1.074895	-2.463160	0.145230
O	0.057563	2.934215	0.508115	H	-3.964341	-0.281020	-1.511887
O	-2.438392	2.440297	-1.092210	H	-4.306523	-2.582968	-1.583140
O	2.570347	2.594025	-0.094774	H	-3.332414	2.982259	1.472883
O	-2.265455	-1.283243	-1.045485	H	-4.402549	1.683059	2.257995
O	-4.422987	-2.143973	-0.725315	H	1.989739	3.239158	0.358425
H	2.939910	-1.723733	2.164659	H	-0.663094	0.679893	-1.565354
H	3.024390	-3.329161	1.468484	-	-	-	-

Table S28. Cartesian coordinates (Å) of **C2-T3-4** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-1.556837	-2.134302	-0.736809	H	-4.996128	-1.530347	-0.548848
C	-3.037161	-2.458155	-0.484222	H	-3.932072	-1.088850	-1.877880
C	-3.957127	-1.274203	-0.794380	H	-1.987517	0.318206	-1.437430
C	-3.571030	0.042614	-0.078568	H	-0.951688	-3.007017	-0.464230
C	-2.057994	0.276625	-0.342952	H	-1.404840	-1.963259	-1.812897
C	-1.531688	1.678580	0.069799	H	-2.292913	2.270728	0.589015
C	-0.330861	1.585050	0.993690	H	0.166500	-0.000587	-1.460663
C	0.827608	0.738403	0.467919	H	-5.442520	0.932851	-0.740097
C	0.325746	-0.409499	-0.456183	H	-4.062990	1.328020	-1.785691
C	-1.081783	-0.888580	0.044099	H	-4.255040	2.132653	-0.222900
C	1.417979	-1.489892	-0.599309	H	-3.540224	0.859818	1.953989
C	2.582941	-1.054412	-1.500464	H	-5.048259	0.050782	1.511896
C	3.546084	-0.363084	-0.514531	H	-3.622494	-0.902917	1.916623
C	3.355516	-1.254161	0.728547	H	-0.080274	-1.799505	1.744951
C	1.868574	1.639489	-0.183977	H	-1.023835	-0.382352	2.207495
C	3.268354	1.115556	-0.336880	H	-1.835242	-1.892045	1.847511
C	4.256857	2.019516	-0.347962	H	4.584062	-0.467985	-0.836057
C	-4.373994	1.178610	-0.745872	H	3.075645	-1.934854	-1.920884
C	-3.957541	0.003962	1.411055	H	2.269038	-0.405701	-2.322337
C	-1.005512	-1.251879	1.547131	H	0.976017	-2.420879	-0.957656
O	-0.276638	2.141801	2.071519	H	3.460061	-0.719392	1.682230
O	1.587053	2.778914	-0.538141	H	4.034798	-2.973916	1.272065
O	-1.117694	2.330122	-1.136296	H	4.040225	3.078320	-0.253928
O	2.034488	-1.771298	0.677535	H	5.297448	1.722488	-0.445406
O	4.300906	-2.294368	0.631578	H	-0.370770	2.924766	-0.931169
H	-3.327160	-3.317693	-1.100896	H	1.291933	0.283779	1.347600
H	-3.175474	-2.777900	0.555260	-	-	-	-

Table S29. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C2-T4** in the gas phase (T=298.15 K)

Conformer	**E (Hartree)**[a]	**C (Hartree)**[b]	**G (kcal/mol)**[c]	**⊿G (kcal/mol)**[d]	**Population**[e]
C2-T4-1	-1154.974186	0.403541	-724493.079424	0.0	100.00%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S30. Cartesian coordinates (Å) of **C2-T4-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-1.204570	-2.278670	-0.436629	H	-4.630477	-2.176180	0.030666
C	-2.538851	-2.752422	0.135757	H	-3.707615	-1.904520	-1.440003
C	-3.657121	-1.833621	-0.343476	H	-2.044137	0.211885	-1.418817
C	-3.485472	-0.344413	0.042694	H	-0.402597	-2.964350	-0.141399
C	-2.031191	0.130127	-0.320596	H	-1.266989	-2.312221	-1.535212
C	-1.665757	1.539522	0.233320	H	-1.382786	1.441750	1.288689
C	-0.446922	2.026948	-0.523992	H	0.006565	-0.417978	-1.897505
C	0.765188	1.122278	-0.652584	H	-4.256585	0.371789	-1.878123
C	0.372981	-0.371371	-0.861453	H	-4.550934	1.486761	-0.534277
C	-0.838222	-0.846892	0.013300	H	-5.505202	-0.008590	-0.682161
C	1.612639	-1.281171	-0.865389	H	-3.680556	0.896241	1.837213
C	2.832010	-0.672121	-1.592900	H	-4.932719	-0.333844	1.651946
C	3.680643	-0.114124	-0.430279	H	-3.329061	-0.803549	2.202694
C	3.450276	-1.235235	0.592044	H	0.141242	-1.729778	1.746624
C	1.760129	1.427676	0.478618	H	0.016165	0.012163	1.867582
C	3.217409	1.193371	0.174128	H	-1.411758	-0.978271	2.120879
C	4.070326	2.170316	0.501255	H	4.738412	-0.042677	-0.692781
C	-4.510132	0.435034	-0.812504	H	3.404679	-1.460722	-2.084531
C	-3.862335	-0.134980	1.522266	H	2.564803	0.072235	-2.345052
C	-0.505180	-0.880828	1.524477	H	1.340847	-2.244356	-1.304889
O	-0.473979	3.113471	-1.079933	H	3.625101	-0.937641	1.631961
O	1.403390	1.960370	1.515272	H	3.989610	-3.078587	0.785420
O	-2.684942	2.504191	0.122043	H	3.722141	3.075570	0.988028
O	2.071126	-1.523002	0.486831	H	5.132496	2.094017	0.283615
O	4.256643	-2.330830	0.226890	H	-2.286831	3.232863	-0.396094
H	-2.735742	-3.781345	-0.189709	H	1.264634	1.468697	-1.563041
H	-2.495702	-2.779496	1.231110	-	-	-	-

9.3. NMR computational data of glutinosasin C (3, C3)

Table S31. Experimental and calculated ^{13}C NMR chemical shifts of **C3**

No.	$\delta_{exptl.}$	C3-T1-$\delta_{calcd.}$	C3-T2-$\delta_{calcd.}$	C3-$\delta_{calcd.}$
1	39.7	40.7	40.2	40.4
2	18.6	21.4	21.7	21.6
3	43.1	43.5	42.8	43.1
4	33.2	36.3	36.3	36.3
5	51.5	50.8	52.1	51.5
6	71.8	73.0	77.2	75.5
7	187.0	174.5	196.7	187.6
8	107.6	107.4	108.1	107.8
9	57.0	58.3	57.9	58.1
10	38.9	41.6	41.9	41.7
11	74.2	75.6	76.7	76.2
12	38.2	40.6	37.4	38.7
13	50.7	52.3	52.2	52.2
14	101.4	101.9	103.5	102.9
15	191.2	195.9	173.0	182.4
16	150.3	153.1	146.4	149.2
17	123.1	123.1	125.8	124.6
18	35.0	35.4	34.3	34.8
19	22.1	22.4	22.0	22.2
20	15.7	16.5	17.9	17.3
21	170.5	170.7	170.1	170.4
22	21.5	23.1	22.9	23.0
R^2		**0.997**	**0.9927**	**0.9986**
MAE		**1.9**	**2.9**	**1.6**
CMAE		**1.7**	**2.8**	**1.5**

Table S32. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C3-T1** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	⊿G (kcal/mol)[d]	Population[e]
C3-T1-1	-1307.627136	0.434511	-820263.372338	0.0	63.27%
C3-T1-2	-1307.627147	0.435035	-820263.050286	0.322052	36.73%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S33. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C3-T2** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
C3-T2-1	-1307.627387	0.434792	-820263.353061	0.0	42.45%
C3-T2-2	-1307.627068	0.434993	-820263.027207	0.325854	24.48%
C3-T2-3	-1307.627863	0.435986	-820262.902617	0.450445	19.84%
C3-T2-4	-1307.624882	0.433388	-820262.662592	0.69047	13.23%

Table S34. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C3** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
C3-1 (T1-1)	-1307.627136	0.434511	-820263.372338	0.0	25.90%
C3-2 (T2-1)	-1307.627387	0.434792	-820263.353061	0.019277	25.07%
C3-3 (T1-2)	-1307.627147	0.435035	-820263.050286	0.322052	15.04%
C3-4 (T2-2)	-1307.627068	0.434993	-820263.027207	0.345131	14.46%
C3-5 (T2-3)	-1307.627863	0.435986	-820262.902617	0.469721	11.72%
C3-6 (T2-4)	-1307.624882	0.433388	-820262.662592	0.709746	7.81%

Table S35. Cartesian coordinates (Å) of **C3-T1-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-0.289684	2.880272	0.509870	H	-1.779029	3.785569	-0.781787
C	-1.593357	3.642534	0.289577	H	-3.686408	3.438896	0.829207
C	-2.743937	2.888294	0.942375	H	-2.548229	2.828881	2.023378
C	-2.947277	1.455843	0.398224	H	-1.377184	0.493958	1.493206
C	-1.570957	0.691023	0.428484	H	0.541134	3.457520	0.091800
C	-1.600055	-0.665462	-0.271231	H	-0.108735	2.810373	1.592837
C	-0.277259	-1.397829	-0.205517	H	-1.883831	-0.566775	-1.321468
C	0.916963	-0.811807	0.164624	H	0.920318	0.823016	1.556400
C	0.955086	0.685400	0.465174	H	-4.796052	1.474396	1.534131
C	-0.298503	1.453515	-0.087212	H	-3.502971	0.557723	2.325479
C	2.278267	1.350964	-0.001248	H	-4.374006	-0.138060	0.954729
C	3.430310	1.210053	0.999214	H	-3.747207	0.527152	-1.430537
C	4.108865	-0.075861	0.507479	H	-4.597111	1.978372	-0.899715
C	4.019544	0.142516	-1.006165	H	-3.041082	2.123250	-1.709008
C	2.050308	-1.716229	0.323864	H	-1.108307	1.989480	-2.060757
C	3.372465	-1.322262	0.930879	H	0.640848	2.146311	-1.927239
C	3.894695	-2.161335	1.833236	H	-0.075500	0.556917	-2.087712
C	-3.960440	0.786622	1.356352	H	5.150903	-0.144501	0.826219
C	-3.605584	1.519996	-0.994436	H	4.126556	2.047064	0.902907
C	-0.216209	1.537298	-1.626962	H	3.091665	1.145875	2.035696
C	-3.384477	-2.242151	-0.466273	H	2.099405	2.402553	-0.221196
C	-4.149989	-3.268968	0.326800	H	4.040029	-0.781057	-1.598010
O	-0.412727	-2.674499	-0.514984	H	4.892900	1.288372	-2.287486
O	1.951288	-2.937087	0.030733	H	3.376357	-3.067969	2.125409
O	-2.557799	-1.543670	0.353506	H	4.854419	-1.958995	2.301311
O	-3.488843	-2.049216	-1.656570	H	-3.453340	-4.039874	0.673191
O	2.751362	0.735089	-1.220958	H	-4.601716	-2.811554	1.212279
O	5.071544	1.005210	-1.376321	H	-4.917550	-3.721186	-0.301625
H	-1.508627	4.646632	0.722769	H	0.521114	-3.073526	-0.400319

Table S36. Cartesian coordinates (Å) of **C3-T1-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-0.613540	-2.710168	-0.815454	H	-2.009936	-3.825150	0.415084
C	-1.931958	-3.452892	-0.613775	H	-4.055580	-3.060750	-0.840665
C	-3.099046	-2.532712	-0.944945	H	-3.020131	-2.240477	-2.002410
C	-3.149754	-1.250037	-0.085226	H	-1.649417	-0.147285	-1.143132
C	-1.741117	-0.549116	-0.128201	H	0.216138	-3.398961	-0.628322
C	-1.613589	0.637426	0.829295	H	-0.541673	-2.411274	-1.871622
C	-0.256034	1.307384	0.792372	H	-1.778289	0.306554	1.858028
C	0.863059	0.759465	0.198827	H	0.584449	-0.484607	-1.526882
C	0.761502	-0.619704	-0.449490	H	-3.867599	0.085495	-1.676553
C	-0.469060	-1.449320	0.069248	H	-4.532412	0.464439	-0.075784
C	2.079625	-1.429488	-0.333767	H	-5.114589	-0.948093	-0.961511
C	3.121122	-1.079900	-1.402342	H	-3.030580	-2.336791	1.840969
C	3.944045	0.001358	-0.689118	H	-3.696295	-0.702434	1.968472
C	4.003846	-0.597675	0.718869	H	-4.662568	-1.999446	1.270248
C	2.033507	1.625639	0.138174	H	-0.000576	-1.023594	2.180334
C	3.260720	1.345297	-0.690407	H	-1.073260	-2.410897	1.954096
C	3.749745	2.367094	-1.403216	H	0.645216	-2.537860	1.590023
C	-4.225050	-0.347871	-0.735590	H	4.947484	0.103891	-1.107217
C	-3.646583	-1.592131	1.332605	H	3.758745	-1.942303	-1.613058
C	-0.222299	-1.874965	1.532426	H	2.674538	-0.730078	-2.335670
C	-2.582327	2.439161	-0.420633	H	1.857614	-2.495159	-0.364303
C	-3.664606	3.486483	-0.366055	H	4.159603	0.138973	1.516917
O	-0.276922	2.477142	1.404630	H	4.917575	-2.078515	1.549318
O	2.044999	2.741482	0.724603	H	3.268811	3.338833	-1.396475
O	-2.640508	1.644634	0.673837	H	4.641471	2.251670	-2.013678
O	-1.771212	2.310021	-1.311169	H	-3.540370	4.096536	0.534060
O	2.725773	-1.166667	0.934239	H	-3.607047	4.114666	-1.255224
O	5.021402	-1.574787	0.726075	H	-4.648528	3.009478	-0.309291
H	-1.956060	-4.337675	-1.261592	H	0.671752	2.846263	1.286545

Table S37. Cartesian coordinates (Å) of **C3-T2-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	0.629880	-2.718918	0.755236	H	2.051333	-3.796720	-0.478629
C	1.956973	-3.447108	0.556826	H	4.074669	-3.052312	0.825316
C	3.114496	-2.529507	0.922540	H	3.017634	-2.253207	1.982886
C	3.169488	-1.236073	0.081329	H	1.661994	-0.150542	1.143788
C	1.759011	-0.537711	0.123494	H	-0.185123	-3.412419	0.527707
C	1.640187	0.655119	-0.823390	H	0.533445	-2.455738	1.819108
C	0.275082	1.349621	-0.845240	H	1.827492	0.332190	-1.849927
C	-0.880265	0.764290	-0.213330	H	-0.515662	-0.447847	1.518696
C	-0.739039	-0.606442	0.452939	H	3.876602	0.071597	1.699410
C	0.485678	-1.432364	-0.093823	H	4.540794	0.487447	0.107763
C	-2.045416	-1.436997	0.423182	H	5.131313	-0.939394	0.966331
C	-3.077976	-1.013462	1.472839	H	3.746032	-0.656518	-1.954617
C	-3.924969	-0.006022	0.686461	H	4.680636	-1.986926	-1.276393
C	-3.983163	-0.704777	-0.675739	H	3.046566	-2.279014	-1.867986
C	-2.013088	1.582812	-0.152579	H	0.024167	-0.960783	-2.200465
C	-3.281279	1.353280	0.597478	H	1.071291	-2.369320	-1.996294
C	-3.862323	2.414856	1.174630	H	-0.651802	-2.468220	-1.629694
C	4.238450	-0.340394	0.750181	H	-4.929868	0.101699	1.098723
C	3.673401	-1.558349	-1.338474	H	-3.700037	-1.864545	1.761661
C	0.229880	-1.825431	-1.564331	H	-2.624881	-0.583623	2.369128
C	2.535459	2.453754	0.460617	H	-1.806819	-2.491506	0.545633
C	3.623595	3.495658	0.483337	H	-4.137951	-0.025940	-1.523912
O	0.265526	2.448597	-1.453077	H	-4.896722	-2.246736	-1.386753
O	-2.033147	2.771708	-0.740498	H	-3.423496	3.403844	1.118989
O	2.655591	1.665260	-0.630486	H	-4.792443	2.308221	1.725608
O	1.668033	2.322392	1.297794	H	4.606254	3.012901	0.503276
O	-2.712213	-1.298042	-0.851822	H	3.571052	4.101943	-0.426221
O	-5.007366	-1.674114	-0.610746	H	3.503159	4.128070	1.363165
H	1.975296	-4.345961	1.185235	H	-1.110695	2.897953	-1.165949

Table S38. Cartesian coordinates (Å) of **C3-T2-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	0.309679	-2.888785	0.481567	H	1.822175	-3.742973	-0.816572
C	1.620456	-3.636624	0.256246	H	3.703171	-3.436691	0.838168
C	2.754634	-2.896487	0.951440	H	2.539600	-2.872300	2.030029
C	2.955742	-1.447207	0.453976	H	1.360815	-0.501195	1.528903
C	1.575023	-0.688647	0.465990	H	-0.511700	-3.463614	0.042743
C	1.607114	0.663529	-0.239592	H	0.118226	-2.844855	1.564135
C	0.304448	1.454262	-0.117240	H	1.814425	0.539331	-1.304946
C	-0.936661	0.804815	0.226047	H	-0.933310	-0.875949	1.553088
C	-0.957218	-0.707088	0.465886	H	4.310519	0.167525	1.112611
C	0.313911	-1.448635	-0.083973	H	4.790987	-1.459880	1.612722
C	-2.262146	-1.384436	-0.033118	H	3.453710	-0.636457	2.431205
C	-3.438969	-1.253070	0.937516	H	3.769474	-0.468516	-1.345692
C	-4.097819	0.042383	0.446446	H	4.647322	-1.904394	-0.815969
C	-3.962689	-0.146102	-1.068984	H	3.112440	-2.077089	-1.659150
C	-2.029894	1.650920	0.438505	H	-0.554708	-2.165842	-1.949268
C	-3.389028	1.283375	0.928301	H	0.036035	-0.523291	-2.065639
C	-3.990274	2.121337	1.784476	H	1.178802	-1.870230	-2.064987
C	3.933237	-0.794030	1.458032	H	-5.150891	0.103239	0.727023
C	3.646561	-1.469858	-0.924240	H	-4.135947	-2.085094	0.808186
C	0.251116	-1.500538	-1.627058	H	-3.129245	-1.207541	1.984157
C	3.333514	2.261642	-0.591843	H	-2.067013	-2.434316	-0.245364
C	4.139011	3.308719	0.131070	H	-3.936768	0.791293	-1.638965
O	0.415190	2.690840	-0.308105	H	-4.824096	-1.251701	-2.392680
O	-1.931002	2.962198	0.270283	H	-3.503984	3.025331	2.132077
O	2.625673	1.519990	0.298986	H	-4.987973	1.912797	2.160248
O	3.318797	2.084935	-1.789178	H	3.452025	4.064453	0.526868
O	-2.713140	-0.780763	-1.264228	H	4.672194	2.870056	0.979896
O	-5.032713	-0.963717	-1.489368	H	4.840901	3.775951	-0.560160
H	1.534984	-4.654804	0.655046	H	-0.963116	3.142050	-0.011532

Table S39. Cartesian coordinates (Å) of **C3-T2-3** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	0.538086	2.612477	-0.533665	H	1.662831	3.745423	0.940038
C	1.745560	3.454059	-0.113764	H	3.911634	3.304798	-0.058072
C	3.048641	2.694270	-0.354060	H	3.152787	2.513472	-1.434136
C	3.124064	1.332923	0.374733	H	1.921856	0.363922	-1.085387
C	1.837913	0.521579	-0.003708	H	-0.388226	3.167833	-0.351898
C	1.773993	-0.870919	0.634873	H	0.605201	2.443096	-1.618590
C	0.410225	-1.579710	0.737656	H	2.115325	-0.823190	1.670678
C	-0.815882	-0.954685	0.282769	H	-0.089148	-0.028973	-1.458986
C	-0.582182	0.311205	-0.536522	H	5.254216	1.266337	-0.044500
C	0.464990	1.245656	0.181074	H	4.280859	0.359021	-1.213597
C	-1.815102	1.038323	-1.062211	H	4.585389	-0.314944	0.393763
C	-2.820780	0.103589	-1.748304	H	2.545476	2.169585	2.339159
C	-3.835308	-0.143928	-0.630305	H	3.372868	0.613810	2.438735
C	-3.877294	1.243305	0.019564	H	4.281688	2.069300	2.049334
C	-2.007530	-1.602622	0.620255	H	-1.023910	1.645131	1.700867
C	-3.421592	-1.212715	0.357035	H	0.267885	0.599027	2.291282
C	-4.387847	-1.863664	1.026834	H	0.555496	2.323183	2.094735
C	4.382085	0.609883	-0.150793	H	-4.824874	-0.392235	-1.019048
C	3.325926	1.557945	1.885575	H	-3.311694	0.611251	-2.581163
C	0.050224	1.461443	1.655165	H	-2.353975	-0.812755	-2.117704
C	2.414283	-2.305373	-1.160662	H	-1.484736	1.813962	-1.754800
C	3.500498	-3.231273	-1.644327	H	-4.204516	1.237790	1.066078
O	0.473704	-2.686269	1.321572	H	-4.555172	2.976178	-0.489640
O	-1.966986	-2.749371	1.298255	H	-4.165735	-2.632671	1.754678
O	2.727372	-1.792394	0.045215	H	-5.432879	-1.624027	0.850642
O	1.390486	-2.046947	-1.760396	H	3.236689	-3.621072	-2.627620
O	-2.542806	1.694307	0.006440	H	4.454053	-2.695745	-1.694663
O	-4.715964	2.060997	-0.770602	H	3.623533	-4.056049	-0.935272
H	1.751525	4.390173	-0.685619	H	-0.988716	-2.984815	1.433569

Table S40. Cartesian coordinates (Å) of **C3-T2-4** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-0.212480	2.782470	0.448325	H	-1.374195	3.863091	-1.034430
C	-1.401476	3.659957	0.042568	H	-3.571351	3.646709	0.119879
C	-2.731188	3.008629	0.422993	H	-2.782483	2.927777	1.518929
C	-2.923706	1.598481	-0.177722	H	-1.686006	0.722865	1.302818
C	-1.667215	0.753397	0.204654	H	0.723244	3.266078	0.146455
C	-1.749521	-0.710110	-0.241514	H	-0.200017	2.713700	1.546446
C	-0.441183	-1.426193	-0.599895	H	-2.403056	-0.847059	-1.102543
C	0.844533	-0.926950	-0.152644	H	0.318449	0.210249	1.577720
C	0.758791	0.409040	0.586932	H	-5.025793	1.659677	0.366953
C	-0.273526	1.356475	-0.142354	H	-4.021365	0.793283	1.542006
C	2.082005	1.086549	0.931174	H	-4.454706	0.030637	-0.002052
C	3.031880	0.198155	1.743690	H	-2.433568	2.264728	-2.228570
C	3.950127	-0.368834	0.657932	H	-3.270132	0.711406	-2.158537
C	4.075774	0.845750	-0.268795	H	-4.154766	2.202803	-1.852475
C	1.959060	-1.722662	-0.451893	H	-0.392535	2.307084	-2.116704
C	3.388393	-1.577539	-0.048138	H	1.118093	1.452300	-1.805275
C	4.222205	-2.596960	-0.319293	H	-0.348210	0.553820	-2.208215
C	-4.175449	0.975309	0.471958	H	4.936725	-0.622630	1.049199
C	-3.194899	1.698517	-1.691006	H	3.618336	0.801018	2.440653
C	0.038095	1.415844	-1.656966	H	2.505100	-0.577440	2.305585
C	-3.332943	-2.335626	0.562324	H	1.866644	2.004273	1.479255
C	-3.652568	-3.189988	1.763477	H	4.310879	0.594333	-1.310062
O	-0.607591	-2.481868	-1.256118	H	4.987946	2.544120	-0.181453
O	1.794052	-2.834256	-1.162833	H	3.891348	-3.490633	-0.830957
O	-2.293106	-1.507030	0.846662	H	5.265515	-2.544062	-0.022480
O	-3.920609	-2.361280	-0.494123	H	-3.790337	-2.562357	2.649218
O	2.802823	1.451533	-0.268780	H	-4.554539	-3.770192	1.567655
O	5.059609	1.695000	0.283615	H	-2.814607	-3.865567	1.965297
H	-1.312039	4.636283	0.534592	H	0.797745	-2.925338	-1.361152

Table S41. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C3-T3** in the gas phase (T=298.15 K)

Conformer	**E (Hartree)[a]**	**C (Hartree)[b]**	**G (kcal/mol)[c]**	**⊿G (kcal/mol)[d]**	**Population[e]**
C3-T3-1	-1307.616924	0.433235	-820257.764998	0.0	37.91%
C3-T3-2	-1307.616393	0.432896	-820257.644104	0.120894	30.91%
C3-T3-3	-1307.617438	0.434112	-820257.537347	0.227651	25.81%
C3-T3-4	-1307.615436	0.433589	-820256.608905	1.156093	5.38%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S42. Cartesian coordinates (Å) of **C3-T3-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-0.329837	-2.874610	-0.550430	H	-1.839230	-3.779391	0.717481
C	-1.647540	-3.618387	-0.350190	H	-3.735251	-3.370305	-0.886741
C	-2.783436	-2.834584	-0.992870	H	-2.586458	-2.766631	-2.072909
C	-2.965645	-1.403357	-0.436358	H	-1.374600	-0.452720	-1.506472
C	-1.579579	-0.656755	-0.445150	H	0.487750	-3.468026	-0.128498
C	-1.600873	0.691593	0.286256	H	-0.136923	-2.792473	-1.630478
C	-0.316639	1.510247	0.117428	H	-1.737054	0.533319	1.360031
C	1.011343	0.776649	-0.012721	H	0.841461	-0.709379	-1.563201
C	0.940526	-0.703020	-0.469627	H	-3.490381	-0.515182	-2.373290
C	-0.319426	-1.458143	0.071003	H	-4.329148	0.235303	-1.012765
C	2.294529	-1.390344	-0.148767	H	-4.815537	-1.372425	-1.570020
C	3.460840	-0.957286	-1.054907	H	-4.636511	-1.883257	0.854082
C	4.085542	0.223230	-0.283965	H	-3.085870	-2.100159	1.658556
C	3.908655	-0.271442	1.161357	H	-3.729077	-0.475474	1.408696
C	1.952829	1.563926	-0.938516	H	0.626372	-2.190820	1.885934
C	3.423074	1.543409	-0.620442	H	-0.130825	-0.629304	2.114852
C	4.105384	2.687846	-0.724730	H	-1.130130	-2.073768	2.017903
C	-3.956852	-0.711341	-1.400916	H	5.155469	0.316421	-0.481346
C	-3.628075	-1.465097	0.953930	H	4.190631	-1.767209	-1.126750
C	-0.243226	-1.590399	1.607140	H	3.141064	-0.688102	-2.064989
C	-3.254548	2.314594	0.783516	H	2.175064	-2.473460	-0.180809
C	-4.121021	3.358025	0.131193	H	3.785981	0.532909	1.898315
O	-0.359516	2.720491	0.169850	H	4.823962	-1.546457	2.281350
O	1.526183	2.147262	-1.916007	H	3.608643	3.608852	-1.012645
O	-2.662603	1.538056	-0.162448	H	5.171864	2.735772	-0.519245
O	-3.100873	2.163047	1.974703	H	-3.471090	4.090940	-0.358715
O	2.718807	-1.043969	1.189599	H	-4.753764	2.909705	-0.640706
O	5.032324	-1.066224	1.463639	H	-4.732379	3.853580	0.885783
H	-1.576958	-4.615391	-0.801802	H	1.432210	0.775304	1.000309

Table S43. Cartesian coordinates (Å) of **C3-T3-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-0.260724	2.863072	0.517142	H	-1.679014	3.960691	-0.703240
C	-1.532996	3.692812	0.349932	H	-3.656762	3.529656	0.741539
C	-2.743936	2.936541	0.879678	H	-2.623357	2.805477	1.965089
C	-2.969040	1.539249	0.251880	H	-1.446510	0.605583	1.419196
C	-1.620147	0.738894	0.340713	H	0.589300	3.436738	0.134119
C	-1.672749	-0.685098	-0.259439	H	-0.076710	2.705187	1.590271
C	-0.384708	-1.450277	0.057145	H	-1.788845	-0.650921	-1.346325
C	0.874918	-0.757838	-0.427028	H	0.797098	0.473308	1.335109
C	0.908904	0.631578	0.254531	H	-3.697837	0.572642	2.088198
C	-0.329277	1.485996	-0.184454	H	-4.522052	0.016198	0.629724
C	2.292234	1.316262	0.052409	H	-4.874790	1.622379	1.279499
C	3.251909	1.051469	1.221995	H	-3.641088	0.680871	-1.647425
C	3.961566	-0.231496	0.749090	H	-4.495864	2.144660	-1.160393
C	4.184201	0.142281	-0.719619	H	-2.871897	2.260617	-1.837031
C	2.070438	-1.695695	-0.241624	H	0.759665	1.864074	-2.033278
C	3.076729	-1.457751	0.857801	H	-0.655477	0.849308	-2.286133
C	3.165866	-2.348256	1.847073	H	-0.850651	2.572966	-2.026281
C	-4.078694	0.887045	1.110467	H	4.907416	-0.400111	1.268349
C	-3.510692	1.664537	-1.183318	H	3.985796	1.856585	1.308166
C	-0.275283	1.700122	-1.715764	H	2.739313	0.929807	2.178141
C	-3.165374	-2.502715	-0.426896	H	2.170883	2.384616	-0.122938
C	-4.139253	-3.327908	0.370926	H	4.315146	-0.712530	-1.392469
O	-0.389474	-2.481759	0.694269	H	5.324794	1.348587	-1.700558
O	2.185108	-2.650577	-0.984389	H	2.501390	-3.205625	1.888220
O	-2.756966	-1.424361	0.295774	H	3.894496	-2.239032	2.647149
O	-2.782728	-2.737896	-1.549792	H	-3.592883	-3.826482	1.178784
O	2.965860	0.773725	-1.111377	H	-4.902777	-2.692989	0.830198
O	5.278318	1.021635	-0.787939	H	-4.601429	-4.075463	-0.274266
H	-1.421692	4.641376	0.889167	H	0.790051	-0.621244	-1.508785

Table S44. Cartesian coordinates (Å) of **C3-T3-3** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-0.905999	-2.702141	-0.953441	H	-2.364862	-3.806076	0.211940
C	-2.294445	-3.333165	-0.774639	H	-4.395377	-2.791425	-0.776492
C	-3.422378	-2.313497	-0.949047	H	-3.425786	-1.972607	-1.994569
C	-3.293952	-1.069590	-0.039941	H	-1.797067	-0.281632	-1.293635
C	-1.853319	-0.513328	-0.222160	H	-0.143488	-3.472632	-0.791727
C	-1.632689	0.856439	0.455521	H	-0.799904	-2.361844	-1.994483
C	-0.352132	0.931700	1.282574	H	-2.452626	1.171404	1.098266
C	0.916651	0.399295	0.620988	H	0.343901	-0.203329	-1.384581
C	0.609180	-0.695335	-0.440214	H	-4.046447	0.313450	-1.564500
C	-0.662793	-1.506335	-0.004707	H	-4.324763	0.876125	0.090560
C	1.877180	-1.524389	-0.737664	H	-5.307393	-0.435406	-0.567762
C	2.905774	-0.773110	-1.594353	H	-4.733384	-1.611629	1.489930
C	3.764258	-0.043315	-0.543342	H	-3.133321	-2.286206	1.794681
C	3.790394	-1.101310	0.576398	H	-3.438035	-0.573276	2.091263
C	1.762188	1.562941	0.101359	H	-0.643265	-1.288971	2.205368
C	3.226065	1.320971	-0.167335	H	-1.169293	-2.863724	1.644644
C	4.034392	2.386065	-0.086656	H	0.535725	-2.429327	1.555810
C	-4.296256	-0.012504	-0.548198	H	4.790041	0.088600	-0.892929
C	-3.658848	-1.407992	1.416593	H	3.532041	-1.488380	-2.133749
C	-0.480426	-2.045028	1.433953	H	2.446600	-0.096296	-2.319616
C	-1.858563	3.102349	-0.355150	H	1.601247	-2.470308	-1.205506
C	-1.426881	4.006826	-1.478487	H	3.837572	-0.679501	1.589223
O	-0.343524	1.356088	2.417675	H	4.794323	-2.717202	0.888403
O	1.281359	2.676059	-0.039185	H	3.634793	3.365022	0.155546
O	-1.479584	1.818253	-0.617732	H	5.104494	2.302249	-0.255262
O	-2.449548	3.435753	0.644118	H	-1.917953	4.975317	-1.378466
O	2.580491	-1.839684	0.483958	H	-0.340984	4.130893	-1.413105
O	4.900291	-1.932298	0.326742	H	-1.656846	3.558399	-2.449205
H	-2.416487	-4.143786	-1.503296	H	1.486250	-0.074562	1.426336

Table S45. Cartesian coordinates (Å) of **C3-T3-4** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-0.221598	2.851804	0.620520	H	-1.484414	4.510212	1.211904
C	-1.573128	3.426039	1.079116	H	-2.415548	3.468306	-0.903096
C	-2.684308	3.089907	0.090060	H	-3.612985	3.604118	0.365408
C	-2.963598	1.563151	0.039782	H	-1.540714	0.660963	1.390676
C	-1.628507	0.762957	0.299904	H	0.276116	3.583390	-0.026548
C	-1.669716	-0.680375	-0.246344	H	0.423906	2.733989	1.499535
C	-0.390036	-1.442749	0.099219	H	-1.776865	-0.685523	-1.334663
C	0.869517	-0.765730	-0.413880	H	0.802721	0.455773	1.349454
C	0.909763	0.620968	0.269102	H	-4.916458	1.759986	0.982720
C	-0.316546	1.494564	-0.149683	H	-3.589502	1.582296	2.140681
C	2.281663	1.323282	0.061098	H	-4.162605	0.173245	1.241372
C	3.268809	1.040213	1.201700	H	-2.942245	1.382534	-2.152591
C	3.974797	-0.228310	0.687491	H	-3.974947	0.190308	-1.346387
C	4.155738	0.171527	-0.780553	H	-4.490578	1.874121	-1.462446
C	2.060174	-1.713862	-0.245409	H	-0.512798	0.879398	-2.267263
C	3.112658	-1.468968	0.807252	H	-0.954754	2.554028	-1.963781
C	3.263480	-2.376857	1.773706	H	0.741285	2.076440	-1.965099
C	-3.967419	1.243322	1.168660	H	4.937744	-0.393749	1.175418
C	-3.620900	1.224445	-1.309330	H	4.000025	1.847938	1.287048
C	-0.264983	1.761520	-1.670609	H	2.779297	0.896307	2.166924
C	-3.177342	-2.495592	-0.336560	H	2.139349	2.395031	-0.082289
C	-4.178341	-3.262968	0.485192	H	4.266883	-0.671842	-1.471650
O	-0.396699	-2.448775	0.775078	H	5.266510	1.401925	-1.765651
O	2.128148	-2.691103	-0.965134	H	2.618564	-3.248281	1.826756
O	-2.773607	-1.378315	0.330512	H	4.024088	-2.267617	2.543374
O	-2.771712	-2.799058	-1.434104	H	-4.621732	-4.052686	-0.121770
O	2.932254	0.815555	-1.130218	H	-3.661187	-3.704766	1.343641
O	5.251831	1.048104	-0.861978	H	-4.955265	-2.596846	0.872180
H	-1.835052	3.021159	2.064670	H	0.768382	-0.631149	-1.494382

Table S46. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C3-T4** in the gas phase (T=298.15 K)

Conformer	**E (Hartree)[a]**	**C (Hartree)[b]**	**G (kcal/mol)[c]**	**⊿G (kcal/mol)[d]**	**Population[e]**
C3-T4-1	-1307.619868	0.435786	-820258.01143	0.0	73.11%
C3-T4-2	-1307.617787	0.434649	-820257.419076	0.592354	26.89%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S47. Cartesian coordinates (Å) of **C3-T4-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-0.412278	-2.583094	-0.609352	H	-1.464944	-3.728561	0.904569
C	-1.574077	-3.465332	-0.154162	H	-3.743831	-3.395874	-0.096722
C	-2.903497	-2.756303	-0.396181	H	-3.014022	-2.586755	-1.477573
C	-3.036309	-1.394940	0.325496	H	-1.895682	-0.318463	-1.109755
C	-1.780716	-0.521405	-0.039226	H	0.541018	-3.095543	-0.440202
C	-1.753620	0.848224	0.663521	H	-0.506079	-2.429713	-1.695166
C	-0.450105	1.675181	0.596533	H	-1.956721	0.730459	1.729805
C	0.817306	1.095596	-0.018093	H	0.100906	-0.052030	-1.647990
C	0.610267	-0.278992	-0.702243	H	-4.599734	0.158506	0.338172
C	-0.373323	-1.206541	0.089480	H	-5.152609	-1.448338	-0.159808
C	1.938002	-0.910221	-1.145780	H	-4.205482	-0.454258	-1.276920
C	2.915584	0.097988	-1.788138	H	-3.336464	-0.679312	2.383391
C	3.883939	0.421311	-0.631332	H	-4.204375	-2.156210	1.980594
C	3.983962	-0.972955	0.001854	H	-2.473525	-2.217557	2.302862
C	1.982594	1.193803	0.987733	H	1.106088	-1.743423	1.581877
C	3.360139	1.390336	0.402797	H	0.041651	-0.464576	2.133967
C	4.087044	2.410932	0.867299	H	-0.545196	-2.123154	2.069988
C	-4.321605	-0.735494	-0.223052	H	4.860097	0.754465	-0.990823
C	-3.258034	-1.622810	1.833223	H	3.480219	-0.384467	-2.588306
C	0.075749	-1.389929	1.554846	H	2.417674	0.976763	-2.202731
C	-2.679979	2.267019	-0.995536	H	1.726903	-1.731533	-1.834493
C	-3.871165	3.115605	-1.352547	H	4.299928	-0.968085	1.051066
O	-0.458104	2.802780	1.040389	H	4.779828	-2.665925	-0.472413
O	1.803833	1.219473	2.189933	H	3.704156	3.060963	1.647597
O	-2.831355	1.711423	0.222562	H	5.076642	2.629226	0.473672
O	-1.703217	2.090807	-1.698155	H	-4.777869	2.501693	-1.357276
O	2.656525	-1.460308	-0.012180	H	-4.005878	3.897169	-0.598393
O	4.847295	-1.752301	-0.793440	H	-3.718937	3.564721	-2.334092
H	-1.552121	-4.412852	-0.706392	H	1.059266	1.819804	-0.804216

Table S48. Cartesian coordinates (Å) of **C3-T4-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	0.007200	2.841687	-0.259282	H	1.179820	3.566893	1.413337
C	1.164304	3.651188	0.320366	H	3.321270	3.762928	0.103343
C	2.480183	3.171691	-0.280750	H	2.446645	3.353401	-1.365221
C	2.794852	1.673795	-0.046186	H	1.515853	0.855841	-1.543728
C	1.539480	0.810381	-0.444547	H	-0.945028	3.206696	0.140274
C	1.644334	-0.677558	-0.053813	H	-0.018192	3.004264	-1.347870
C	0.543062	-1.521524	-0.691614	H	1.560417	-0.801012	1.029410
C	-0.874770	-0.957723	-0.753039	H	-0.622607	0.809972	-1.899999
C	-0.927544	0.590661	-0.865857	H	3.669290	1.353220	-2.034696
C	0.125833	1.329282	0.028943	H	4.436941	0.387972	-0.770413
C	-2.371972	1.114744	-0.792648	H	4.751917	2.127456	-0.866755
C	-3.391984	0.240279	-1.555448	H	3.394924	0.402385	1.649989
C	-4.020902	-0.611506	-0.432221	H	4.255804	1.938279	1.528965
C	-4.083427	0.454154	0.670236	H	2.608876	1.903626	2.145738
C	-1.725253	-1.597686	0.358727	H	-1.021256	1.597034	1.856547
C	-3.193098	-1.775599	0.064829	H	-0.223816	0.038790	1.792414
C	-3.722191	-2.979863	0.304831	H	0.719226	1.481492	2.128793
C	3.982905	1.354235	-0.984171	H	-5.023874	-0.957100	-0.692136
C	3.276684	1.461466	1.403036	H	-4.173253	0.869342	-1.986232
C	-0.109645	1.092366	1.538452	H	-2.946549	-0.347411	-2.360194
C	3.422225	-2.201340	0.326465	H	-2.393619	2.143034	-1.162273
C	4.554391	-2.898084	-0.381073	H	-4.138105	0.047040	1.685917
O	0.782872	-2.612177	-1.164983	H	-5.114071	2.050318	1.012004
O	-1.220015	-2.052575	1.368692	H	-3.118897	-3.782902	0.715826
O	2.884016	-1.247197	-0.478558	H	-4.765412	-3.195649	0.088676
O	3.037313	-2.432964	1.449367	H	5.247439	-2.169448	-0.812956
O	-2.842491	1.124964	0.576773	H	5.077440	-3.551639	0.317453
O	-5.173164	1.303100	0.395154	H	4.140891	-3.489471	-1.204787
H	1.019124	4.715221	0.096944	H	-1.277462	-1.376050	-1.681354

9.4. NMR computational data of glutinosasin D (4, C4)

Table S49. Experimental and calculated ^{13}C NMR chemical shifts of **C4**

No.	$\delta_{exptl.}$	C4-T1-$\delta_{calcd.}$	C4-T2-$\delta_{calcd.}$	C4-$\delta_{calcd.}$
1	39.5	40.8	41.8	41.4
2	19.0	21.6	21.5	21.5
3	43.3	43.7	43.6	43.7
4	33.7	36.2	36.4	36.3
5	55.1	52.6	52.0	52.3
6	71.0	70.8	73.6	72.4
7	196.8	177.9	200.4	191.0
8	106.6	105.7	104.9	105.2
9	56.9	58.6	59.5	59.2
10	38.5	41.0	40.8	40.9
11	75.2	75.5	75.7	75.6
12	37.5	41.2	40.5	40.8
13	49.3	52.5	52.5	52.5
14	108.1	106.2	106.4	106.3
15	186.3	196.9	177.5	185.6
16	148.6	152.7	147.2	149.5
17	123.3	123.5	125.1	124.5
18	36.0	35.8	35.6	35.7
19	22.2	22.8	22.7	22.8
20	16.5	17.1	18.3	17.8
21	54.4	53.4	53.3	53.4
R^2		**0.9907**	**0.9975**	**0.9988**
MAE		**2.9**	**2.3**	**1.8**
CMAE		**2.8**	**1.9**	**1.5**

Table S50. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C4-T1** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	⊿G (kcal/mol)[d]	Population[e]
C4-T1-1	-1194.271027	0.428725	-749136.0448	0	100.00%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S51. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C4-T2** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
C4-T2-1	-1194.272288	0.429673	-749136.241113	0	100.00%

Table S52. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C4** in the gas phase (T=298.15 K)

Conformer	E (Hartree)	C (Hartree)	G (kcal/mol)	ΔG (kcal/mol)	Population
C4-1 (T2-1)	-1194.272288	0.429673	-749136.241113	0.0	58.21%
C4-2 (T1-1)	-1194.271027	0.428725	-749136.0448	0.196313	41.79%

Table S53. Cartesian coordinates (Å) of **C4-T1-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.473579	-2.149511	0.915048	H	4.925648	-2.022398	0.814220
C	2.869323	-2.701168	0.635370	H	3.826390	-1.405066	2.039179
C	3.908837	-1.638791	0.967560	H	2.131228	0.571427	1.236375
C	3.754622	-0.326282	0.166050	H	2.069343	0.953176	-1.778196
C	2.260303	0.163475	0.223115	H	-0.025105	-0.167270	1.704477
C	1.953365	1.308243	-0.742183	H	-1.040824	-2.271527	0.441778
C	0.524588	1.790198	-0.599338	H	-2.979426	-2.036413	1.742457
C	-0.486465	1.106341	0.041356	H	-2.033688	-0.751175	2.529904
C	-0.195511	-0.276577	0.623012	H	-4.415708	-0.125003	1.384249
C	1.125523	-0.910650	0.058537	O	-4.334448	-1.671496	-0.544939
C	-1.400121	-1.243752	0.478494	H	-3.697517	0.156744	-1.250717
C	-2.453709	-1.091705	1.580827	H	-3.151296	3.272128	1.852997
C	-3.415872	-0.077028	0.948545	H	-4.358157	1.982906	2.424917
C	-3.434763	-0.595139	-0.493387	H	5.682717	0.279753	0.958781
C	-1.746654	1.823194	0.194232	H	4.311240	0.939598	1.864492
C	-2.906309	1.340857	1.024941	H	4.740320	1.635206	0.297112
C	-3.503424	2.247508	1.808153	H	3.762346	-1.314282	-1.816360
C	4.675713	0.703806	0.857554	H	4.211399	0.399972	-1.848285
C	4.282554	-0.524818	-1.267907	H	5.342412	-0.802284	-1.227656
C	0.897137	-1.352219	-1.404696	H	0.464106	-0.555897	-2.013880
C	-4.398656	-2.284581	-1.823997	H	1.820327	-1.681752	-1.882498
O	-1.906393	2.964689	-0.318254	H	0.192234	-2.187768	-1.441761
O	2.824521	2.411045	-0.526925	H	2.396998	3.171993	-0.956237
O	-2.100154	-0.990908	-0.760277	O	0.374610	2.989502	-1.147363
H	0.731254	-2.938576	0.755862	H	-5.146586	-3.077492	-1.755677
H	1.416394	-1.875370	1.979052	H	-4.707197	-1.561807	-2.594714
H	3.039719	-3.597825	1.243858	H	-3.430638	-2.712247	-2.109146
H	2.954449	-3.019009	-0.411042	H	-0.601818	3.249187	-0.949196

Table S54. Cartesian coordinates (Å) of **C4-T2-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.483093	-2.117961	0.981130	H	4.933533	-1.988787	0.852612
C	2.876972	-2.676243	0.706022	H	3.841419	-1.344847	2.070340
C	3.916818	-1.604092	1.004094	H	2.126711	0.612477	1.212244
C	3.752060	-0.313434	0.170273	H	1.938172	0.821219	-1.812835
C	2.255808	0.171856	0.212017	H	-0.037159	-0.155601	1.708344
C	1.939064	1.268113	-0.805921	H	-1.020551	-2.284117	0.488118
C	0.541595	1.847429	-0.600446	H	-2.997434	-2.036180	1.734277
C	-0.507015	1.112718	0.053835	H	-2.060659	-0.747673	2.527321
C	-0.204275	-0.275881	0.627537	H	-4.420473	-0.130999	1.326004
C	1.124573	-0.911336	0.082761	O	-4.340118	-1.657468	-0.591067
C	-1.395152	-1.261497	0.491537	H	-3.628236	0.143848	-1.293503
C	-2.465141	-1.094890	1.573755	H	-3.241417	3.272758	1.805435
C	-3.411092	-0.083849	0.913801	H	-4.466740	1.967343	2.289861
C	-3.405771	-0.611162	-0.526044	H	4.699078	1.667695	0.260398
C	-1.709640	1.798840	0.254018	H	5.675931	0.342503	0.935226
C	-2.912376	1.337143	1.002459	H	4.299455	0.986750	1.843754
C	-3.574415	2.243905	1.735542	H	3.783366	-1.371170	-1.774474
C	4.659687	0.744541	0.836419	H	4.178870	0.355853	-1.869366
C	4.281014	-0.545568	-1.258647	H	5.348553	-0.791142	-1.212721
C	0.896251	-1.405881	-1.364986	H	0.382495	-0.662867	-1.978940
C	-4.390188	-2.282821	-1.864850	H	1.829650	-1.671166	-1.862318
O	-1.881396	3.037646	-0.189187	H	0.260384	-2.296054	-1.364149
O	2.866534	2.336176	-0.780534	H	-1.004057	3.314862	-0.626015
O	-2.081828	-1.056363	-0.760421	H	2.356493	3.105467	-1.100548
H	0.741270	-2.914139	0.860059	O	0.408754	3.027603	-1.031883
H	1.437470	-1.804656	2.034842	H	-4.651987	-1.558740	-2.651554
H	3.052173	-3.556900	1.336138	H	-3.430243	-2.747062	-2.117963
H	2.954163	-3.020551	-0.332690	H	-5.167015	-3.048459	-1.809003

Table S55. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C4-T3** in the gas phase (T=298.15 K)

Conformer	E (Hartree)[a]	C (Hartree)[b]	G (kcal/mol)[c]	ΔG (kcal/mol)[d]	Population[e]
C4-T3-1	-1194.262164	0.427348	-749131.346795	0.0	46.70%
C4-T3-2	-1194.262419	0.42779	-749131.229534	0.117261	38.31%
C4-T3-3	-1194.261322	0.428029	-749130.391646	0.955149	9.31%
C4-T3-4	-1194.261801	0.428973	-749130.09967	1.247125	5.68%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S56 Cartesian coordinates (Å) of **C4-T3-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.389574	-2.113078	0.904734	H	4.857158	-2.099553	0.864663
C	2.783942	-2.719209	0.748345	H	3.790990	-1.337720	2.036062
C	3.856929	-1.665148	0.988126	H	2.169262	0.474108	1.205300
C	3.752673	-0.410524	0.087500	H	2.022116	1.111841	-1.770784
C	2.284029	0.135847	0.163508	H	-0.047555	0.152688	1.392151
C	2.027255	1.402407	-0.710809	H	-1.135013	-2.212038	0.466821
C	0.647582	1.944240	-0.359391	H	-2.913049	-1.735751	1.956885
C	-0.507110	0.987668	-0.538771	H	-1.818777	-0.441349	2.499894
C	-0.212825	-0.228109	0.375953	H	-4.269102	0.246698	1.585529
C	1.128622	-0.920649	-0.046488	O	-4.483244	-1.582677	-0.125272
C	-1.448377	-1.168655	0.450677	H	-3.925203	0.122784	-1.137505
C	-2.360597	-0.846492	1.643057	H	-2.529688	3.540925	1.418720
C	-3.341832	0.160150	1.015348	H	-3.650861	2.486835	2.458508
C	-3.579429	-0.534966	-0.329186	H	4.419082	0.973804	1.652490
C	-1.829538	1.748303	-0.380801	H	4.908088	1.464000	0.030014
C	-2.730860	1.530943	0.808418	H	5.722538	0.100264	0.829360
C	-2.987781	2.573969	1.601002	H	5.262786	-1.027779	-1.337960
C	4.758833	0.603028	0.678408	H	3.643965	-1.540923	-1.812576
C	4.207925	-0.729690	-1.347938	H	4.127256	0.151892	-1.992389
C	0.986170	-1.459374	-1.489512	H	-0.006325	-1.900639	-1.628587
C	-4.751747	-2.330116	-1.303613	H	1.104921	-0.688326	-2.254470
O	-2.125521	2.563195	-1.233656	H	1.719496	-2.236505	-1.707252
O	2.969166	2.428763	-0.528380	H	2.461761	3.168956	-0.136398
O	-2.286025	-0.997577	-0.719338	O	0.543321	3.060848	0.121289
H	0.641186	-2.895619	0.740576	H	-5.492379	-3.085777	-1.033982
H	1.265827	-1.771210	1.943152	H	-5.162667	-1.685804	-2.095132
H	2.903384	-3.543249	1.462425	H	-3.845022	-2.817957	-1.679208
H	2.898105	-3.164521	-0.247237	H	-0.504481	0.646238	-1.577629

Table S57. Cartesian coordinates (Å) of **C4-T3-2** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.456097	-1.997163	1.182231	H	4.904917	-1.924855	0.948382
C	2.840902	-2.600468	0.958248	H	3.858939	-1.110726	2.102404
C	3.897320	-1.509639	1.078218	H	2.143786	0.708176	1.077339
C	3.723154	-0.334093	0.088353	H	1.752949	0.629396	-1.933321
C	2.236118	0.174763	0.118741	H	0.004124	0.145481	1.653556
C	1.904039	1.190682	-0.997734	H	-1.142269	-2.116455	1.035862
C	0.584007	1.891119	-0.691724	H	-3.138336	-1.445401	2.042640
C	-0.587233	1.063726	-0.200528	H	-2.215647	0.011227	2.458736
C	-0.209898	-0.194392	0.631844	H	-4.529901	0.177880	0.977942
C	1.092218	-0.911927	0.141603	O	-4.343903	-1.716675	-0.471003
C	-1.452225	-1.119589	0.720117	H	-3.492976	-0.180981	-1.547560
C	-2.581102	-0.600943	1.630139	H	-3.543151	3.649622	0.234448
C	-3.486910	0.177281	0.655084	H	-4.966556	2.457593	0.234865
C	-3.371603	-0.712772	-0.592918	H	4.710912	1.620006	-0.102440
C	-1.572279	1.930883	0.599433	H	5.676606	0.371868	0.720046
C	-3.038643	1.614215	0.479634	H	4.335765	1.161497	1.564697
C	-3.894915	2.625477	0.309037	H	3.688186	-1.640582	-1.698409
C	4.667052	0.781768	0.590397	H	4.065152	0.059239	-2.037470
C	4.198374	-0.752304	-1.316583	H	5.268740	-0.986788	-1.280774
C	0.839535	-1.600529	-1.218206	H	0.136123	-2.428222	-1.092506
C	-4.320946	-2.653837	-1.538040	H	0.395663	-0.932991	-1.960019
O	-1.175210	2.806564	1.342620	H	1.757048	-2.005022	-1.645580
O	2.887355	2.174234	-1.216142	H	2.387025	3.013271	-1.285643
O	-2.057005	-1.248480	-0.586023	O	0.492344	3.086868	-0.910273
H	0.703437	-2.792726	1.169238	H	-4.475764	-2.154351	-2.506640
H	1.428822	-1.552256	2.188017	H	-3.370766	-3.198838	-1.569165
H	3.024455	-3.384500	1.703088	H	-5.140982	-3.352445	-1.359327
H	2.892002	-3.090653	-0.021577	H	-1.085339	0.698902	-1.108328

Table S58. Cartesian coordinates (Å) of **C4-T3-3** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	1.355943	-2.096734	1.010019	H	3.511097	-2.595131	-0.609972
C	2.825138	-2.312331	1.412591	H	4.801887	-2.255638	0.522662
C	3.771636	-1.983792	0.262594	H	2.267861	0.419669	1.210920
C	3.735757	-0.473397	-0.092345	H	2.005664	1.169617	-1.722958
C	2.291916	0.106672	0.156935	H	-0.057052	0.160908	1.432152
C	2.027184	1.408841	-0.650234	H	-1.099864	-2.205739	0.518684
C	0.660285	1.957564	-0.273723	H	-2.941846	-1.736842	1.933022
C	-0.500850	1.011937	-0.491504	H	-1.889361	-0.414715	2.491153
C	-0.215655	-0.212872	0.411955	H	-4.323786	0.199626	1.477655
C	1.119456	-0.919906	0.006600	O	-4.447216	-1.627507	-0.221736
C	-1.436774	-1.169488	0.469569	H	-3.861144	0.071678	-1.228345
C	-2.394459	-0.843022	1.623060	H	-2.729959	3.547882	1.357796
C	-3.371351	0.135646	0.947430	H	-3.873667	2.454766	2.330658
C	-3.542334	-0.574929	-0.399755	H	4.494132	0.052758	1.896015
C	-1.821401	1.782500	-0.357136	H	4.684818	1.332661	0.685417
C	-2.796703	1.524109	0.762241	H	5.747327	-0.094685	0.653586
C	-3.156071	2.563230	1.520963	H	5.188525	-0.782003	-1.667474
C	4.724959	0.254385	0.842624	H	3.529490	-0.730260	-2.268414
C	4.218055	-0.287421	-1.541533	H	4.350080	0.770054	-1.787590
C	0.994482	-1.488625	-1.424240	H	1.818757	-2.163780	-1.658042
C	-4.656867	-2.393317	-1.400055	H	0.064002	-2.055835	-1.528725
O	-2.052117	2.650045	-1.178636	H	0.985532	-0.711855	-2.193940
O	3.001061	2.400065	-0.421816	H	2.510481	3.145278	-0.018449
O	-2.233066	-1.033165	-0.732316	O	0.568830	3.057080	0.245582
H	0.969992	-3.019323	0.560418	H	-3.730112	-2.876925	-1.729270
H	0.765930	-1.932567	1.920265	H	-5.401341	-3.152735	-1.152421
H	3.072392	-1.677348	2.272425	H	-5.039219	-1.763930	-2.217587
H	2.963353	-3.345963	1.749943	H	-0.477991	0.683916	-1.534534

Table S59. Cartesian coordinates (Å) of **C4-T3-4** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-1.530109	-2.094962	-0.960051	H	-5.002294	-1.923215	-0.583600
C	-2.949883	-2.615356	-0.689471	H	-4.060417	-1.225513	-1.894924
C	-4.012048	-1.522689	-0.837423	H	-2.269890	0.349338	-1.376562
C	-3.743661	-0.250122	0.001452	H	-2.695361	2.032294	0.859597
C	-2.281678	0.187114	-0.291142	H	-0.097412	0.289701	-1.514616
C	-1.898474	1.591269	0.251134	H	1.005413	-2.057358	-1.302312
C	-0.650262	1.546153	1.113686	H	2.986297	-1.233059	-2.284097
C	0.568956	0.900188	0.457069	H	1.993341	0.223511	-2.490831
C	0.155983	-0.198041	-0.566240	H	4.369888	0.281373	-1.102087
C	-1.161619	-0.888279	-0.068203	O	4.374791	-1.685044	0.188282
C	1.355698	-1.122148	-0.862537	H	3.402246	-0.355475	1.419385
C	2.418220	-0.463668	-1.754505	H	3.457193	3.663072	-0.131601
C	3.342904	0.231323	-0.735911	H	4.848459	2.490783	-0.513308
C	3.315422	-0.794975	0.414475	H	-4.666179	1.748390	0.108292
C	1.468129	1.979266	-0.131995	H	-5.734317	0.476517	-0.490651
C	2.908974	1.641585	-0.392354	H	-4.461570	1.136580	-1.538041
C	3.787175	2.652003	-0.345290	H	-3.589117	-1.394728	1.883925
C	-4.702071	0.845701	-0.509539	H	-3.707539	0.351955	2.107675
C	-4.050143	-0.487196	1.491368	H	-5.132837	-0.581101	1.636344
C	-0.970106	-1.392101	1.383164	H	-1.705946	-2.153103	1.643718
C	4.447561	-2.727563	1.150813	H	0.020106	-1.843777	1.486120
O	1.042882	3.108013	-0.351348	H	-1.054307	-0.602974	2.133325
O	-1.621796	2.408676	-0.891705	H	-0.936914	3.062061	-0.651717
O	2.058366	-1.456389	0.353016	O	-0.605652	1.993141	2.241917
H	-0.817061	-2.913203	-0.804803	H	5.332003	-3.319057	0.905134
H	-1.451399	-1.798222	-2.016514	H	4.555437	-2.319821	2.167497
H	-3.170214	-3.435741	-1.383470	H	3.555850	-3.363156	1.116681
H	-3.000176	-3.053379	0.314268	H	1.124170	0.415128	1.264882

Table S60. Conformational analysis of the B3LYP-D3BJ/6-31G(d) optimized conformers of **C4-T4** in the gas phase (T=298.15 K)

Conformer	**E (Hartree)[a]**	**C (Hartree)[b]**	**G (kcal/mol)[c]**	**⊿G (kcal/mol)[d]**	**Population[e]**
C4-T4-1	-1194.265023	0.429312	-749131.908376	0.0	100.00%

[a]Electronic energy obtained at M06-2X-D3/6-311+G(2d,p) level of theory; [b]Thermal correction to Gibbs free energy obtained at B3LYP-D3BJ/6-31G(d) level of theory; [c]Gibbs free energy (E + C); [d]The relative Gibbs free energy; [e]The Boltzmann distribution of each conformer.

Table S61. Cartesian coordinates (Å) of **C4-T4-1** obtained at the B3LYP-D3BJ/6-31G(d) level of theory in the gas phase.

C	-1.110580	-2.254176	-0.589080	H	-4.507290	-2.610782	-0.040370
C	-2.358129	-2.925322	-0.018494	H	-3.669622	-2.137595	-1.511017
C	-3.595492	-2.126964	-0.413589	H	-2.281543	0.166221	-1.392560
C	-3.598217	-0.653795	0.062115	H	-1.696866	1.303447	1.372259
C	-2.225679	0.020508	-0.302361	H	-0.183909	-0.172822	-1.956653
C	-2.021217	1.428482	0.331729	H	1.384673	-1.850333	-1.502511
C	-0.895449	2.110145	-0.419991	H	3.308898	-0.770618	-2.283581
C	0.414666	1.373942	-0.634125	H	2.278720	0.658085	-2.430387
C	0.204259	-0.141798	-0.928005	H	4.499794	0.719235	-0.838110
C	-0.911356	-0.817257	-0.057854	O	4.330328	-1.656008	-0.046162
C	1.546567	-0.886202	-1.013433	H	3.584115	-0.452035	1.454592
C	2.658770	-0.089187	-1.731467	H	3.156089	3.582681	1.054141
C	3.467279	0.501365	-0.556815	H	4.654762	2.829290	0.257212
C	3.409258	-0.697630	0.399353	H	-4.508916	0.074450	-1.791932
C	1.399053	1.733108	0.490635	H	-4.899158	1.060327	-0.373674
C	2.864081	1.702421	0.138010	H	-5.664683	-0.531329	-0.595543
C	3.598690	2.758366	0.504368	H	-4.987020	-0.923517	1.699847
C	-4.736619	0.040822	-0.719158	H	-3.321588	-1.218098	2.184775
C	-3.954298	-0.582920	1.559872	H	-3.894136	0.442181	1.935768
C	-0.531076	-0.899955	1.440328	H	-1.400696	-1.143658	2.049800
C	4.329493	-2.840094	0.739668	H	0.220394	-1.674343	1.594033
O	1.011539	2.154085	1.566822	H	-0.111824	0.028300	1.827033
O	-3.155015	2.262567	0.304652	H	-2.865588	3.065770	-0.173903
O	2.068351	-1.140630	0.311524	O	-1.073579	3.216669	-0.903973
H	-0.221221	-2.849996	-0.355493	H	4.573442	-2.618113	1.789352
H	-1.201006	-2.229604	-1.685968	H	3.355691	-3.341771	0.702034
H	-2.435686	-3.949346	-0.404171	H	5.097654	-3.494368	0.322428
H	-2.279255	-3.012687	1.071699	H	0.838751	1.834405	-1.532257

Table S62. Experimental and calculated spin-spin coupling constant calculation of glutinosasins A−D (**C1**−**C4**)

Proton pairs	**C1-*exp***	**C1-*cal***	**C2-*exp***	**C2-*cal***	**C3-*exp***	**C3-*cal***	**C4-*exp***	**C4-*cal***
H-5/H-6a	/	/	/	/	/	/	/	/
H-5/H-6b	/	/	10.3	11.3	11.8	11.0	10.1	11.3
H-9/H-11	≈0	0.8	≈0	0.4	≈0	1.0	≈0	0.4
H-12b/H-11	≈0	0.6	≈0	0.5	≈0	0.6	≈0	0.5
H-12a/H-11	8.8	8.8	9.0	8.7	8.9	8.9	8.9	8.7
H-13/H-12b	≈0	0.6	≈0	0.6	≈0	0.6	≈0	0.6
H-13/H-12a	6.2	6.4	6.5	6.4	6.0	6.4	6.4	6.4
H-13/H-14	≈0	0.1	≈0	0.1	≈0	0.2	≈0	0.2

Note: calculated spin-spin coupling constant were obtained at B972-SCRF/pcJ-1(IEFPCM, methanol)//B3LYP-D3BJ/6-31G(d) level of theory.

10. Computational Data for TDDFT ECD Calculation of Glutinosasins A−D (C1−C4)

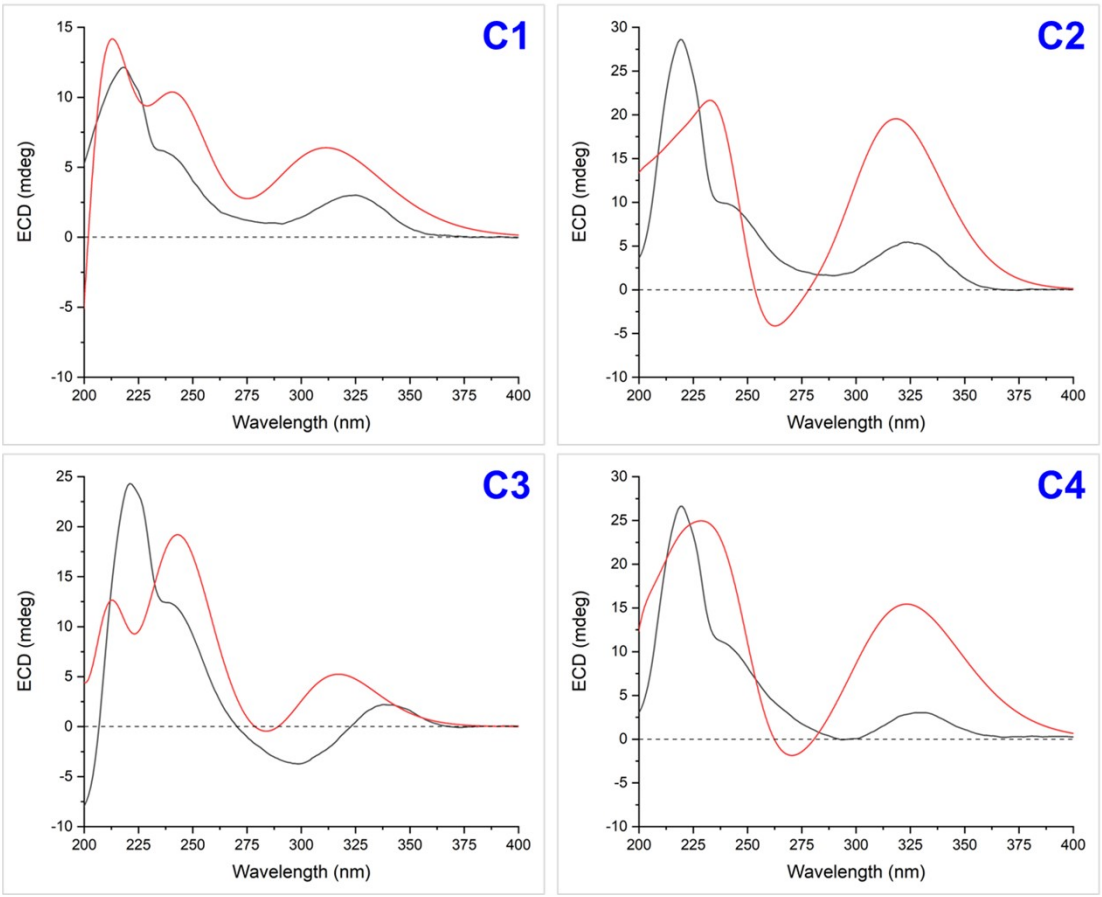

Figure S66. Experimental ECD spectra (black) of glutinosasins A−D **(C1−C4)**. Calculated ECD spectra (red) obtained at CAM-B3LYP-SCRF/6-31+G(2d,p)(IEFPCM, methanol)//B3LYP-D3BJ/6-31G(d) level of theory. **C1**: FWHM: 0.8; shift: 13 nm. **C2**: FWHM: 0.66667; shift: 22 nm. **C3**: FWHM: 0.66667; shift: 15 nm. **C4**: FWHM: 0.8; shift: 25 nm.

Table S63. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **C1-T1-1** at the CAM/6-31+G(2d,p) level of theory in MeOH with IEFPCM solvent model.

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
1	86->91	0.19607	4.1374	299.66	0.0275	5.4647	5.6742
	87->91	-0.20688					
	89->91	0.56554					
2	90->91	0.68394	4.3876	282.58	0.3114	-1.7808	-2.6617
3	86->91	-0.1807	5.4490	227.54	0.0955	17.0461	16.6274
	87->91	0.39972					
	88->91	0.39708					
	89->91	0.35568					
4	86->91	0.22135	5.9165	209.56	0.0128	-8.3806	-8.2742
	87->91	-0.38701					
	88->91	0.52368					
5	90->92	0.324	6.1732	200.84	0.0065	5.3415	6.3494
	90->93	0.44537					
	90->94	0.34555					
6	90->92	0.41186	6.4032	193.63	0.0630	14.7516	15.6078
	90->93	-0.27026					
	90->96	0.28044					
	90->98	0.31575					
7	85->91	0.43882	6.5791	188.45	0.0066	6.6197	7.1689
	86->91	0.31541					
	87->91	0.19879					
	89->93	0.18258					
8	85->91	-0.257	6.6246	187.16	0.0076	8.4129	8.4554
	86->91	0.43678					
	87->91	0.22774					
9	85->91	0.38629	6.6675	185.95	0.0417	-27.7627	-26.9719
	89->93	-0.32743					
	89->96	0.24674					
10	90->94	0.18159	6.8103	182.05	0.0017	-7.7199	-7.4609
	90->95	0.49291					
	90->100	-0.27316					
	90->101	-0.18555					
11	89->92	0.39701	6.9694	177.90	0.0145	1.1864	3.6093
	89->94	0.34541					
12	83->91	0.36047	7.0536	175.77	0.0354	-22.398	-22.6769
13	83->91	0.22283	7.0860	174.97	0.0053	-1.4716	-1.2037
	90->92	-0.21893					
	90->93	0.23696					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	90->96	0.3387					
14	81->91	0.33623	7.1494	173.42	0.0163	-22.4866	-22.399
	84->91	0.49896					
15	90->92	-0.20368	7.1694	172.94	0.0015	8.6187	7.9614
	90->94	0.34414					
	90->95	-0.20025					
	90->99	-0.27055					
16	80->91	-0.201	7.1870	172.51	0.0392	-19.9065	-20.2345
	83->91	0.26907					
	88->92	0.35096					
	88->93	-0.2111					
17	74->91	-0.19598	7.2396	171.26	0.0102	17.0423	16.8029
	80->91	0.17363					
	84->91	-0.22745					
	88->92	0.32427					
18	87->93	0.25879	7.2821	170.26	0.0980	-2.0909	-3.8163
	88->93	0.17408					
19	87->92	0.17423	7.3107	169.59	0.0377	18.1934	16.7038
	90->92	-0.179					
	90->98	0.32534					
20	78->91	0.22457	7.3692	168.25	0.0006	-9.0908	-9.6299
	79->91	-0.26525					
	83->91	0.27736					
21	87->92	-0.1856	7.4477	166.47	0.0876	36.851	37.3351
	90->100	0.18593					
	90->101	-0.18354					
22	90->94	0.21982	7.5473	164.28	0.0077	-7.9783	-7.9186
	90->95	0.21639					
	90->96	0.17606					
	90->97	0.36802					
	90->100	0.29765					
23	76->91	0.17834	7.5722	163.74	0.0231	8.787	7.4973
	77->91	0.22467					
	80->91	-0.21276					
	81->91	-0.19905					
	82->91	0.31719					
24	88->92	0.23485	7.6089	162.95	0.0035	14.635	14.7252
	88->93	0.18871					
	89->92	-0.19906					
	90->99	0.23823					
25	83->92	0.26677	7.6265	162.57	0.0033	-5.6782	-5.8703
	83->93	-0.214					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	87->92	0.1809					
26	89->92	-0.18233	7.6605	161.85	0.0185	23.6401	23.1912
	90->97	0.37395					
	90->98	0.19695					
	90->100	-0.28255					
27	90->96	-0.30267	7.6763	161.52	0.0063	-10.8792	-11.0805
	90->100	0.1923					
	90->101	0.41732					
28	88->93	-0.2187	7.6981	161.06	0.0028	7.1308	6.8317
	90->94	0.2005					
	90->99	0.36485					
29	86->92	-0.19865	7.7327	160.34	0.0017	10.4721	10.9802
	87->93	-0.21057					
	88->93	0.26917					
30	88->94	0.25001	7.7648	159.68	0.0037	-3.2485	-2.7701
	89->97	0.18295					
31	88->94	0.24291	7.7877	159.21	0.0349	-5.548	-5.4887
	88->95	0.19554					
	89->93	0.22984					
	89->96	0.17378					
	89->98	0.17732					
	89->101	0.22932					
32	76->91	0.32843	7.8312	158.32	0.0337	2.9304	2.8068
	80->91	-0.28411					
	82->91	-0.18925					
33	87->93	0.17375	7.8654	157.63	0.0050	-1.1753	-1.2678
	87->94	0.18998					
	89->97	0.17616					
34	69->91	-0.18105	7.8726	157.49	0.0047	15.7761	15.0841
	70->91	0.20219					
	73->91	-0.17441					
35	86->92	0.18332	7.9161	156.62	0.0089	-17.2416	-17.2438
	87->92	0.20883					
	87->94	-0.20354					
36	88->94	0.1848	7.9774	155.42	0.0279	19.224	19.2343
	88->95	-0.17739					
	88->96	0.21082					
	89->95	0.21404					

[a]Number of the excited states; [b]Only transitions with contribution over 6.0% 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 S64. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **C1-T2-1** at the CAM/6-31+G(2d,p) level of theory in MeOH with IEFPCM solvent model.

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
1	86->91	-0.17978	4.1719	297.19	0.0008	-2.9812	-2.8947
	89->91	0.60189					
2	90->91	0.69942	4.2445	292.11	0.4120	18.0569	16.7823
3	87->91	0.32518	5.4891	225.87	0.0742	-7.628	-7.6814
	88->91	0.60844					
4	86->91	-0.23882	5.8171	213.14	0.0198	6.7305	6.8745
	87->91	0.51376					
	88->91	-0.29694					
	89->91	-0.26002					
5	90->92	-0.18123	6.1081	202.98	0.0229	9.5525	11.2813
	90->93	0.4712					
	90->94	0.34207					
	90->96	-0.24172					
6	90->92	0.4825	6.2619	198.00	0.0552	12.6434	13.0103
	90->96	-0.23831					
	90->97	-0.29984					
	90->98	0.16129					
7	85->91	0.30873	6.3543	195.12	0.0017	-5.6219	-5.9021
	86->91	0.46837					
	87->91	0.20668					
	89->91	0.16808					
8	85->91	0.54462	6.5015	190.70	0.0021	2.2509	2.2593
	86->91	-0.32668					
9	74->91	-0.19024	6.7950	182.46	0.0024	17.7821	18.9359
	76->91	-0.17271					
	85->91	-0.16478					
	89->93	0.1961					
	89->96	-0.18097					
	90->95	0.24054					
10	90->94	0.16722	6.8015	182.29	0.0034	13.1326	13.3714
	90->95	0.42152					
	90->100	-0.22993					
11	81->91	-0.30999	6.9427	178.58	0.0299	-4.6039	-4.5698
	84->91	0.55064					
12	89->92	-0.22217	6.9762	177.72	0.0168	-15.2755	-14.1317
	89->93	0.20832					
	89->94	0.18166					
	90->93	0.2699					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	90->94	-0.23742					
	90->97	0.20366					
	90->99	0.16889					
13	78->91	0.17483	6.9999	177.12	0.0029	8.7004	8.3054
	80->91	0.19096					
	82->91	-0.21277					
	83->91	0.52932					
	84->91	0.17011					
14	89->92	0.3145	7.0240	176.52	0.0044	3.422	2.8793
	89->93	-0.21869					
	89->94	-0.18508					
	90->92	0.16456					
	90->93	0.2261					
	90->97	0.17524					
15	90->92	-0.2783	7.0726	175.30	0.0162	26.5763	25.8021
	90->94	-0.24156					
	90->96	-0.26873					
	90->98	0.31628					
	90->101	-0.17771					
16	78->91	0.2069	7.1741	172.82	0.0322	-19.1147	-19.3494
	83->91	-0.1594					
	88->92	0.31572					
	88->93	0.18322					
	89->92	0.16967					
	89->93	0.19066					
17	83->91	0.23008	7.2414	171.22	0.0175	-23.9588	-24.3076
	88->92	0.2002					
	88->93	0.17451					
	90->97	0.23905					
18	78->91	-0.20629	7.2645	170.67	0.0195	-16.0585	-15.957
	88->92	0.21887					
	90->97	-0.17191					
19	88->93	-0.20548	7.2738	170.45	0.0742	-19.2287	-20.1298
	90->97	0.2631					
	90->99	-0.20136					
20	73->91	0.17314	7.3777	168.05	0.0419	21.9892	21.7277
	74->91	0.16441					
	88->94	0.16867					
21	76->91	0.21521	7.4385	166.68	0.0033	12.8029	12.76
	77->91	0.25937					
	80->91	-0.23949					
	81->91	0.23535					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	82->91	0.34368					
22	90->95	0.17267	7.4893	165.55	0.0431	-23.619	-23.6231
	90->96	0.17957					
	90->100	0.372					
	90->101	-0.1756					
23	90->94	0.18591	7.4944	165.44	0.0784	33.7737	33.3432
	90->98	0.40929					
	90->101	0.2141					
	90->102	0.17858					
24	89->92	0.16597	7.5618	163.96	0.0019	12.376	12.7452
	89->93	-0.1682					
	89->94	0.17144					
	89->95	0.24751					
	90->99	0.26594					
25	87->92	-0.16797	7.5956	163.23	0.0133	5.678	5.6126
	89->95	0.20491					
	90->94	-0.19499					
	90->99	-0.18858					
26	83->92	0.23807	7.6268	162.56	0.0095	-35.8461	-35.4507
	83->93	0.21094					
	90->101	-0.17419					
27	75->91	-0.18689	7.6399	162.29	0.0393	-27.2677	-27.1077
	76->91	-0.21562					
	77->91	0.17124					
	80->91	0.25366					
28	90->96	-0.21206	7.6637	161.78	0.0035	9.2826	9.47
	90->98	-0.18689					
	90->100	0.29001					
	90->101	0.2651					
29	86->92	-0.16686	7.6855	161.32	0.0292	32.3752	31.9439
	88->92	0.24427					
	90->97	-0.2281					
	90->99	-0.2084					
30	69->91	-0.22443	7.7389	160.21	0.0004	2.9817	2.9542
	73->91	-0.17989					
	76->91	0.17113					
	79->91	0.27585					
	87->92	0.17946					
	89->94	0.16374					
31	86->92	0.22948	7.7541	159.89	0.0080	-7.8102	-7.9719
	87->92	0.27617					
	88->94	-0.2419					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
32	87->93	-0.17216	7.7902	159.15	0.0042	-5.495	-5.1192
	88->93	0.20133					
	88->94	0.21338					
	88->95	0.17346					
	89->94	0.17657					
33	89->94	-0.26457	7.8160	158.63	0.0107	-9.3876	-9.6315
	89->95	0.28462					
	89->97	-0.18345					
34	89->96	0.25653	7.8612	157.72	0.0077	7.2583	6.8859
	90->103	-0.19331					
	90->107	-0.16698					
35	80->91	0.22927	7.8827	157.29	0.0093	8.1792	8.6252
	82->91	0.24056					
	89->93	0.17961					
	90->107	0.16096					
36	77->91	0.16376	7.9111	156.72	0.0087	8.1124	8.1767
	81->91	0.20946					
	82->91	-0.27502					
	89->96	0.27846					

[a]Number of the excited states; [b]Only transitions with contribution over 5.0% 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 S65. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **C2-T2-1** at the CAM/6-31+G(2d,p) level of theory in MeOH with IEFPCM solvent model.

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
1	93->95	-0.18981	4.1803	296.59	0.3699	18.5703	17.5021
	94->95	0.65434					
2	92->95	-0.2477	4.2961	288.60	0.0594	4.6552	4.2853
	93->95	0.48901					
	94->95	0.24937					
3	90->95	-0.26177	5.3564	231.47	0.0632	-22.2166	-22.2229
	92->95	0.59013					
	93->95	0.22349					
4	90->95	0.55596	5.6929	217.79	0.0194	13.4129	13.4919
	93->95	0.32801					
5	86->95	-0.20922	5.7205	216.74	0.0144	17.458	17.6573
	91->95	0.59415					
6	86->95	0.30277	6.1872	200.39	0.0025	-10.04	-10.1781
	88->95	0.43456					
	91->95	0.18608					
	92->95	0.1951					
7	94->97	0.59533	6.2134	199.54	0.0373	21.6414	23.4716
	94->100	0.23288					
8	94->96	0.53428	6.3385	195.60	0.0462	-0.6542	-0.5504
	94->99	0.17436					
	94->100	-0.22383					
9	85->95	-0.20242	6.5096	190.46	0.0006	-0.369	-0.2898
	88->95	0.26083					
	89->95	0.52887					
10	82->95	-0.19609	6.8145	181.94	0.0081	21.0443	21.029
	85->95	-0.20535					
	86->95	0.28487					
	87->95	0.31386					
	88->95	-0.23068					
11	84->95	0.17563	6.8262	181.63	0.0021	16.1331	17.2853
	87->95	0.31577					
	88->95	-0.25541					
12	83->95	-0.23661	6.9044	179.57	0.0021	2.5036	2.8263
	85->95	0.17388					
	86->95	0.22651					
	87->95	-0.23925					
	89->95	0.26789					
	94->99	0.26053					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
13	94->99	0.42429	6.9253	179.03	0.0057	-10.9271	-10.7774
	94->100	0.17793					
	94->104	-0.2464					
14	93->96	0.34524	7.0768	175.20	0.0088	14.0346	13.906
	94->98	0.21329					
15	71->95	-0.18074	7.0954	174.74	0.0060	-23.2154	-23.0969
	78->95	0.21451					
	81->95	0.25125					
	84->95	0.34478					
16	92->96	0.17966	7.1406	173.63	0.0047	-7.6203	-6.7136
	93->97	-0.18542					
	94->98	0.27292					
	94->101	-0.25198					
17	85->95	0.26359	7.1747	172.81	0.0104	19.6201	18.9929
	87->95	0.23005					
	93->97	0.29054					
18	94->96	0.2649	7.1961	172.29	0.0007	4.6668	4.9523
	94->100	0.37244					
	94->103	0.19729					
19	91->96	0.20441	7.2430	171.18	0.0726	5.0349	4.4758
	92->96	-0.25606					
	92->97	0.26499					
	93->96	-0.21714					
20	84->95	-0.19192	7.3236	169.29	0.0964	-13.5549	-14.7327
	90->97	0.26216					
	92->97	-0.24582					
21	79->95	-0.26123	7.3515	168.65	0.0337	4.7369	4.647
	84->95	0.27933					
	85->95	-0.24118					
	92->97	-0.23459					
22	94->96	0.17334	7.3949	167.66	0.0111	-0.2408	-0.5135
	94->101	-0.20725					
	94->102	0.29959					
	94->103	0.30425					
	94->104	-0.2412					
	94->107	-0.17515					
23	91->96	0.21951	7.5430	164.37	0.0164	-44.988	-45.2475
	92->96	0.23005					
24	80->95	0.20694	7.5654	163.88	0.0189	-3.0929	-3.2814
	92->96	0.24028					
	94->104	0.18317					
25	80->95	0.19532	7.5781	163.61	0.0350	10.9855	10.0889

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	94->104	-0.17868					
26	77->95	0.18847	7.6071	162.99	0.0294	-8.663	-8.4703
	82->95	0.30976					
	84->95	-0.19221					
	85->95	-0.30614					
27	87->96	0.24912	7.6320	162.45	0.0006	5.197	5.0049
	88->96	-0.20604					
28	94->99	-0.22072	7.6670	161.71	0.0253	-9.4013	-9.4666
	94->102	0.30192					
	94->105	-0.28355					
29	91->96	0.1889	7.6851	161.33	0.0028	4.5221	4.5269
	92->98	-0.18253					
	94->98	0.30921					
	94->103	0.31902					
30	88->96	0.17451	7.7155	160.69	0.0119	14.4189	16.3375
	93->97	-0.22368					
	93->98	0.19348					
	93->99	0.28366					
	93->104	-0.18096					
31	94->100	0.19412	7.7434	160.12	0.0090	-16.5567	-15.9772
	94->102	0.28466					
	94->104	0.2237					
	94->105	0.23523					
32	83->95	0.3212	7.7934	159.09	0.0067	4.888	4.8277
33	79->95	-0.17508	7.8107	158.74	0.0077	-1.4024	-1.5403
	80->95	0.29572					
	83->95	0.26369					
	90->97	-0.20672					
34	83->95	0.18511	7.8298	158.35	0.0325	-2.0128	-2.7131
35	91->96	-0.19564	7.8627	157.69	0.0074	21.3773	20.4248
	93->100	-0.17436					
	94->101	0.31708					
	94->108	-0.18897					
36	77->95	-0.22086	7.8917	157.11	0.0109	3.1076	3.2493
	78->95	0.26873					
	92->99	-0.17982					

[a]Number of the excited states; [b]Only transitions with contribution over 6.0% 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 S66. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **C2-T1-1** at the CAM/6-31+G(2d,p) level of theory in MeOH with IEFPCM solvent model.

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
1	88->95	0.23865	4.1098	301.68	0.0362	7.1828	7.4626
	92->95	-0.20196					
	93->95	0.53169					
2	94->95	0.67214	4.3875	282.58	0.3037	-1.4872	-2.3328
3	91->95	0.33243	5.3156	233.24	0.0887	13.3343	13.0256
	92->95	0.41864					
	93->95	0.38032					
4	90->95	0.21333	5.7803	214.49	0.0175	-2.4186	-2.3432
	91->95	-0.3739					
	92->95	0.48523					
5	88->95	-0.32417	6.0183	206.01	0.0020	3.8001	3.7785
	90->95	0.53776					
6	94->96	0.33345	6.3567	195.04	0.0044	-0.9779	-0.3582
	94->97	0.48905					
	94->98	0.25616					
7	88->95	0.39864	6.3631	194.85	0.0046	4.2731	4.3118
	89->95	0.25514					
	90->95	0.21464					
	91->95	0.33018					
8	94->96	0.41469	6.4876	191.11	0.0668	15.3967	16.2551
	94->97	-0.30981					
	94->99	0.25544					
	94->100	-0.29162					
9	85->95	-0.20365	6.6769	185.69	0.0040	-7.8525	-7.709
	87->95	-0.24469					
	89->95	0.52017					
	91->95	-0.21709					
10	93->97	0.43429	6.7319	184.17	0.0658	-18.3008	-16.7376
	93->100	0.27999					
11	86->95	-0.36122	6.9233	179.08	0.0041	5.2926	5.0979
	87->95	0.3732					
12	94->99	0.4935	6.9528	178.32	0.0045	-8.5495	-8.2645
	94->100	0.21266					
	94->104	-0.27861					
13	86->95	0.32591	7.0597	175.62	0.0062	1.8247	2.4748
	93->96	-0.23362					
14	93->96	0.33999	7.0863	174.96	0.0074	-27.9241	-25.0171
	93->98	0.26638					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
15	78->95	0.22389	7.1656	173.03	0.0075	-29.0717	-29.1275
	84->95	0.28661					
	87->95	0.23455					
16	92->96	0.3541	7.1947	172.33	0.0408	67.1237	66.605
	94->100	-0.2485					
17	81->95	0.20699	7.2240	171.63	0.0349	-6.3297	-6.4455
	86->95	0.23869					
	94->100	0.24579					
18	92->96	0.29252	7.2444	171.15	0.0154	9.6341	9.594
	94->100	0.29053					
19	92->97	0.26841	7.3099	169.61	0.0582	-36.4016	-37.3438
	94->98	-0.25143					
20	90->96	0.20593	7.3312	169.12	0.0577	38.9655	38.0453
	94->98	0.25455					
21	91->96	-0.20407	7.4276	166.92	0.0340	2.3181	2.0931
	94->98	-0.20652					
	94->103	0.22979					
22	79->95	-0.30407	7.4806	165.74	0.0199	21.5434	20.5301
	84->95	0.3444					
	85->95	-0.2552					
23	94->102	0.2031	7.5110	165.07	0.0169	34.7752	32.5518
	94->104	0.23579					
24	94->104	0.3175	7.5955	163.23	0.0403	-48.4608	-48.4707
25	86->96	0.30708	7.6418	162.25	0.0003	3.5222	3.48
26	93->96	0.21279	7.6961	161.10	0.0026	9.6342	9.4678
27	85->95	0.20533	7.7190	160.62	0.0096	-7.2406	-6.7886
28	94->105	0.26549	7.7239	160.52	0.0404	-14.6123	-15.3227
29	92->97	0.32103	7.7678	159.61	0.0134	7.0992	6.9616
30	94->101	0.2213	7.7835	159.29	0.0093	-0.9885	-0.4095
31	72->95	0.23988	7.8128	158.69	0.0108	-2.1404	-2.1186
	83->95	0.28643					
32	92->100	-0.21482	7.8288	158.37	0.0024	0.2271	0.1397
	94->101	0.32653					
	94->102	-0.21036					
33	94->98	0.24121	7.8494	157.95	0.0026	13.7606	13.6237
	94->103	0.30425					
34	93->100	0.27061	7.8690	157.56	0.0594	-39.302	-39.5064
	93->105	0.20725					
	94->102	0.22875					
35	94->101	0.31077	7.9217	156.51	0.0086	-1.511	-1.3708
	94->102	0.31815					
36	93->102	0.26946	7.9228	156.49	0.0099	8.6092	8.4105

[a]Number of the excited states; [b]Only transitions with contribution over 8.0% 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 S67. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **C3-T1-1** at the CAM/6-31+G(2d,p) level of theory in MeOH with IEFPCM solvent model.

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
1	101->106	-0.24842	4.0937	302.86	0.0301	4.3571	4.6081
	103->106	0.2206					
	104->106	0.53694					
2	105->106	0.67967	4.3828	282.89	0.3342	-8.4855	-9.1396
3	101->106	0.23097	5.3507	231.72	0.0881	16.339	16.0202
	102->106	-0.36333					
	103->106	-0.37253					
	104->106	0.3882					
4	101->106	0.25081	5.8289	212.70	0.0137	-0.2956	-0.1527
	102->106	-0.38326					
	103->106	0.51449					
5	100->112	0.38516	5.9773	207.42	0.0012	-5.1461	-5.1107
	100->115	0.23373					
6	99->106	0.31422	6.3308	195.84	0.0011	4.1495	4.141
	101->106	0.34829					
	102->106	0.33293					
7	105->107	-0.24775	6.3620	194.88	0.0075	5.483	6.3244
	105->108	0.4622					
	105->109	0.3369					
8	105->107	0.45821	6.4676	191.70	0.0840	12.5429	13.1095
	105->108	0.23185					
	105->110	-0.30068					
	105->115	-0.20175					
9	99->106	0.46862	6.6111	187.54	0.0031	-15.8733	-15.5948
	101->106	-0.28143					
10	99->106	0.27296	6.6834	185.51	0.0542	-30.404	-29.2653
	104->108	0.34984					
	104->110	-0.28752					
11	96->106	0.3713	6.7967	182.42	0.0235	8.7182	8.9405
	98->106	-0.20729					
12	100->106	0.41984	6.9505	178.38	0.0099	7.2129	7.2256
	105->110	0.22553					
	105->111	0.22886					
13	100->106	0.3779	6.9816	177.59	0.0100	-12.7407	-12.5665
	105->110	-0.24674					
	105->111	-0.28802					
14	94->106	-0.2512	7.0454	175.98	0.0024	6.033	6.8387
	97->106	0.33367					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	98->106	0.25395					
	104->107	0.21509					
15	104->107	0.35299	7.0700	175.37	0.0091	-25.0139	-22.4911
	104->109	-0.30199					
	105->111	0.3197					
16	105->112	0.42124	7.1261	173.99	0.0035	-2.064	-2.0088
	105->115	0.22445					
	97->106	0.20811					
17	103->107	0.35735	7.2192	171.74	0.0727	36.6595	35.9693
	103->108	0.26313					
18	92->106	0.23137	7.2311	171.46	0.0176	6.0924	5.9856
	97->106	0.29337					
	97->106	-0.25841					
19	98->106	0.26474	7.2557	170.88	0.0124	3.5268	3.0395
	105->111	-0.21682					
20	91->106	-0.20914	7.2686	170.57	0.0223	-1.7954	-1.5078
	98->106	0.36016					
	101->108	0.20784					
21	102->108	-0.21896	7.3267	169.22	0.0817	-40.0785	-41.6605
	103->107	0.24595					
22	105->108	-0.20383	7.3722	168.18	0.0290	13.4834	11.5214
	105->109	0.29741					
	87->106	-0.29311					
23	90->106	0.27625	7.4413	166.62	0.0061	-11.1304	-11.8099
	95->106	0.34444					
24	105->109	-0.23581	7.4691	166.00	0.0086	-6.86	-6.6574
	105->114	0.28201					
	105->107	-0.20151					
25	105->114	0.28302	7.5357	164.53	0.0288	-38.0309	-38.3573
	105->115	-0.2134					
	89->106	-0.20379					
26	94->106	0.29903	7.5796	163.58	0.0598	100.3185	100.6804
	96->106	0.22988					
27	97->107	0.22869	7.6476	162.12	0.0042	-19.4046	-19.3855
	105->114	-0.22017					
28	105->116	0.22027	7.6845	161.34	0.0369	3.5526	3.2311
	105->117	0.24392					
29	104->107	0.24042	7.7004	161.01	0.0128	28.779	28.6124
30	89->106	0.25836	7.7288	160.42	0.0053	1.6063	0.9599
31	102->112	0.20529	7.7626	159.72	0.0688	-25.4695	-25.4093
32	105->113	0.31951	7.7749	159.47	0.0087	-10.733	-10.536
33	102->107	-0.2045	7.8024	158.91	0.0304	-0.8365	-0.6625

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	102->108	0.23971					
	103->108	-0.22689					
34	105->112	0.25169	7.8176	158.60	0.0273	22.2597	21.4939
	105->116	0.2154					
	103->111	0.20812					
35	104->111	-0.23032	7.8418	158.11	0.0215	13.6799	13.9684
	105->113	0.2602					
36	105->114	0.22257	7.8675	157.59	0.0100	-11.8851	-12.2174

[a]Number of the excited states; [b]Only transitions with contribution over 8.0% 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 S68. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **C3-T2-1** at the CAM/6-31+G(2d,p) level of theory in MeOH with IEFPCM solvent model.

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
1	104->106	0.36607	4.1727	297.13	0.2749	-4.5842	-5.1787
	105->106	0.55488					
2	104->106	0.4664	4.1954	295.52	0.1512	18.111	18.1897
	105->106	-0.42629					
3	102->106	-0.32758	5.4327	228.22	0.0652	-7.9549	-7.8977
	103->106	0.6043					
4	102->106	0.50747	5.7706	214.85	0.0268	29.4559	29.5692
	103->106	0.29707					
	104->106	-0.23958					
5	100->106	-0.23376	5.8481	212.01	0.0020	-15.4795	-15.6385
	100->112	0.23477					
	101->106	-0.20033					
	101->112	0.28933					
6	101->106	0.49011	6.1476	201.68	0.0109	-13.3806	-12.7863
7	105->108	0.34926	6.1740	200.82	0.0633	22.8071	24.1506
	105->110	0.31321					
	105->111	-0.27234					
8	100->106	0.43836	6.2255	199.15	0.0153	8.4817	8.5381
	101->106	0.33148					
9	105->107	0.47771	6.3400	195.56	0.0323	-13.4017	-13.8956
	105->109	0.38343					
	105->114	-0.21863					
10	99->106	0.58088	6.4888	191.07	0.0023	2.6904	2.6303
11	96->106	0.23258	6.7567	183.50	0.0052	34.4566	35.2275
12	105->107	-0.21091	6.8221	181.74	0.0058	-10.015	-10.0674
	105->109	0.33503					
	105->110	0.36857					
	105->112	0.20628					
13	96->106	-0.25794	6.8932	179.86	0.0008	4.5656	4.6179
	98->106	0.46321					
14	105->110	-0.24404	6.9403	178.64	0.0036	-5.8941	-5.5881
	105->112	0.49088					
	105->117	-0.21229					
15	94->106	-0.20405	7.0051	176.99	0.0050	-11.8084	-11.6529
	95->106	-0.24842					
	97->106	0.46097					
16	103->107	0.2287	7.0859	174.97	0.0093	-12.2448	-11.8614
	105->108	0.34902					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	105->114	0.22955					
17	105->109	-0.20695	7.1064	174.47	0.0098	39.74	39.4873
	105->111	0.24088					
	105->113	0.30187					
	105->116	-0.28224					
18	91->106	0.20559	7.1502	173.40	0.0002	-2.5653	-2.3073
	96->106	0.31221					
	98->106	0.32154					
19	93->106	0.25622	7.1607	173.15	0.0206	-23.3482	-23.6387
	94->106	0.24498					
	97->106	0.26965					
20	104->107	0.23402	7.2392	171.27	0.0239	64.6351	64.5045
	104->109	0.35012					
21	103->107	0.32947	7.2628	170.71	0.0375	-30.2952	-30.3322
	104->109	0.26561					
	104->112	0.2192					
22	103->110	0.25854	7.3323	169.09	0.0459	-31.7983	-33.2163
23	105->114	0.38303	7.3391	168.94	0.0139	4.0837	4.1547
	105->115	0.20881					
24	104->107	-0.22441	7.3688	168.26	0.0479	-8.6159	-9.3338
	104->108	0.27934					
	104->112	0.33024					
25	89->106	-0.30584	7.4128	167.26	0.0067	14.7666	14.7355
	92->106	0.20898					
	94->106	0.35201					
	96->106	-0.27112					
26	87->106	-0.21467	7.4690	166.00	0.0127	0.3163	-0.3789
	90->106	-0.22713					
	95->106	0.24239					
27	90->106	0.2127	7.4947	165.43	0.0955	33.5688	33.5817
	105->113	0.22354					
28	105->110	-0.20025	7.5761	163.65	0.0068	-8.7944	-8.7639
	105->116	0.31141					
	105->117	0.28799					
29	98->107	0.24975	7.6259	162.58	0.0013	7.6106	7.5824
30	105->111	0.23347	7.6436	162.21	0.0037	12.4112	13.0941
	105->116	0.20796					
31	90->106	0.24013	7.6624	161.81	0.0192	-23.5357	-23.5198
	92->106	-0.22772					
	93->106	0.25506					
32	105->111	0.25296	7.6928	161.17	0.0096	-11.9352	-11.3371
	105->113	-0.20306					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	105->115	0.3246					
33	102->109	0.20023	7.7296	160.40	0.0208	12.7336	11.2432
34	103->107	0.21833	7.7445	160.09	0.0183	14.1142	13.9435
	105->114	-0.21663					
35	104->110	0.26181	7.7716	159.53	0.0121	-1.1203	-1.419
36	104->112	0.22748	7.8052	158.85	0.0293	9.0468	8.882

[a]Number of the excited states; [b]Only transitions with contribution over 8.0% 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 S69. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **C4-T1-1** at the CAM/6-31+G(2d,p) level of theory in MeOH with IEFPCM solvent model.

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
1	98->99	0.65717	4.1784	296.73	0.3716	16.7066	15.468
2	95->99	0.21247	4.2954	288.65	0.0557	3.4005	3.0469
	96->99	-0.22499					
	97->99	0.47973					
	98->99	-0.24178					
3	94->99	-0.21967	5.3477	231.85	0.0630	-22.8135	-22.9004
	96->99	0.60556					
	97->99	0.20401					
4	93->99	0.28514	5.6553	219.24	0.0182	12.9678	13.0101
	94->99	-0.2217					
	95->99	0.44243					
	97->99	-0.35999					
5	90->99	-0.20748	5.7227	216.65	0.0151	18.6957	18.8376
	94->99	0.45933					
	95->99	0.36736					
6	90->99	0.25193	6.1679	201.02	0.0021	-8.4308	-8.5698
	91->99	0.40638					
	93->99	-0.3023					
	96->99	0.20031					
7	98->101	0.61075	6.2121	199.59	0.0353	20.2726	21.7848
8	98->100	0.51727	6.3427	195.48	0.0512	2.0129	2.1675
	98->103	0.26344					
	98->104	-0.23197					
9	92->99	-0.34544	6.4035	193.62	0.0007	0.6221	0.8089
	93->99	0.37303					
	94->99	0.30969					
10	91->99	0.25525	6.5657	188.84	0.0019	-0.6518	-0.6948
	92->99	0.43791					
	93->99	0.36342					
11	86->99	0.24981	6.8218	181.75	0.0089	39.1867	40.0418
12	89->99	-0.20064	6.8982	179.73	0.0023	2.5427	2.8704
	90->99	-0.23346					
	91->99	0.22142					
	92->99	-0.24011					
	98->103	0.2982					
13	90->99	0.2086	6.9175	179.23	0.0056	-10.6783	-10.6112
	98->103	0.39585					
	98->108	-0.23268					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
14	87->99	-0.25742	6.9820	177.58	0.0015	-6.5752	-6.547
	88->99	0.43688					
	91->99	-0.2169					
15	97->100	0.33627	7.0869	174.95	0.0093	4.7148	4.8384
16	82->99	0.21713	7.1319	173.84	0.0047	-8.0018	-7.6416
	89->99	0.26502					
	98->102	0.21955					
17	96->101	0.20862	7.1427	173.58	0.0075	9.2592	9.9274
	97->101	-0.20174					
	98->102	0.33716					
	98->105	0.25327					
18	98->100	0.30601	7.2095	171.97	0.0082	3.5729	3.2581
	98->101	-0.20118					
	98->104	0.42139					
	98->109	-0.22108					
19	83->99	-0.23707	7.2820	170.26	0.0677	-13.7519	-15.3675
	88->99	0.24139					
	97->101	0.25107					
20	96->101	0.37305	7.3252	169.26	0.0978	3.6487	3.2988
21	95->100	0.32089	7.3446	168.81	0.0069	13.3777	12.6463
	97->100	-0.29598					
22	98->105	-0.23914	7.3919	167.73	0.0173	10.3219	9.7108
	98->107	0.35012					
	98->108	-0.21249					
23	93->100	-0.23914	7.4844	165.66	0.0122	-21.8084	-21.1844
	96->100	0.26722					
24	84->99	0.32429	7.5224	164.82	0.0007	2.414	2.5398
	96->100	0.26067					
25	97->101	0.20699	7.5411	164.41	0.0131	-23.0471	-23.3049
26	86->99	0.26446	7.5824	163.52	0.0122	6.2252	5.8976
	88->99	0.22697					
	89->99	0.30523					
27	98->108	0.32341	7.6230	162.64	0.0400	-31.8406	-31.6879
28	94->100	0.20871	7.6628	161.80	0.0036	-5.5068	-5.2492
	98->102	0.26187					
	98->107	-0.25859					
	98->109	0.28331					
29	84->99	0.21205	7.7182	160.64	0.0017	13.4696	13.3545
	97->103	0.22878					
30	98->104	0.22059	7.7229	160.54	0.0445	5.1939	5.5906
	98->109	0.3024					
31	97->103	0.25425	7.7472	160.04	0.0183	19.9926	20.7465

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	97->104	0.27567					
	98->106	-0.2151					
32	85->99	0.22276	7.7629	159.71	0.0041	0.9331	0.9416
	87->99	0.39683					
33	97->104	0.2206	7.8043	158.87	0.0129	10.3135	9.7753
	98->106	0.37996					
34	98->105	-0.20424	7.8179	158.59	0.0503	-5.1252	-5.7897
	98->106	0.21905					
35	94->100	0.25699	7.8512	157.92	0.0027	-3.9149	-4.3238
	98->105	0.22296					
36	96->103	0.20516	7.8736	157.47	0.0265	-34.6788	-34.8989
	97->103	0.22829					

[a]Number of the excited states; [b]Only transitions with contribution over 8.0% 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 S70. Key transitions, oscillator strengths, and rotatory strengths in the ECD spectrum of conformer **C4-T2-1** at the CAM/6-31+G(2d,p) level of theory in MeOH with IEFPCM solvent model.

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
1	91->99	0.25485	4.1101	301.65	0.0363	7.2201	7.3527
	95->99	-0.24573					
	97->99	0.52658					
	98->99	-0.19097					
2	98->99	0.67187	4.3872	282.61	0.3023	-4.0891	-4.9687
3	95->99	0.38425	5.3104	233.47	0.0884	13.129	12.841
	96->99	0.38793					
	97->99	0.38339					
4	93->99	0.18688	5.7537	215.49	0.0169	-1.8175	-1.7271
	95->99	-0.33839					
	96->99	0.52499					
5	91->99	-0.32352	6.0168	206.06	0.0023	3.8656	3.8365
	93->99	0.35856					
	94->99	0.40624					
6	91->99	0.33221	6.3329	195.78	0.0024	3.6771	3.5942
	92->99	0.2616					
	93->99	-0.19177					
	94->99	0.42772					
7	98->100	0.38675	6.3497	195.26	0.0060	-2.1522	-1.3252
	98->101	0.52562					
8	98->100	0.35422	6.5004	190.73	0.0683	17.1234	17.8166
	98->101	-0.33123					
	98->103	-0.34455					
	98->104	-0.23998					
9	91->99	0.24474	6.5672	188.79	0.0012	1.2688	1.2877
	92->99	-0.18225					
	93->99	0.44413					
	95->99	0.34897					
10	89->99	-0.20007	6.7238	184.40	0.0121	-6.406	-6.0471
	92->99	0.44159					
	93->99	0.21806					
	94->99	-0.25771					
	97->101	0.18239					
11	92->99	-0.19626	6.7381	184.00	0.0614	-16.9099	-15.9306
	97->101	0.42629					
	97->103	0.24644					
	97->104	0.19964					
12	98->103	0.47726	6.9446	178.53	0.0037	-11.6295	-11.4027

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	98->104	-0.24818					
	98->108	-0.27946					
13	86->99	0.25781	7.0300	176.36	0.0166	7.273	7.473
	87->99	-0.22155					
	90->99	0.32497					
	97->100	-0.18304					
	97->101	-0.23183					
14	83->99	0.1787	7.0690	175.39	0.0014	5.1255	5.2907
	85->99	0.20305					
	88->99	0.37742					
	89->99	-0.32922					
	92->99	-0.23608					
15	90->99	0.25809	7.0835	175.03	0.0022	-10.7376	-7.5405
	97->100	0.37379					
	97->101	0.20778					
	97->102	-0.2442					
16	82->99	0.24382	7.1672	172.99	0.0052	-27.4455	-27.5026
	86->99	-0.19029					
	88->99	0.26436					
	90->99	0.24323					
17	98->100	0.22523	7.2484	171.05	0.0228	26.1167	26.2117
	98->104	0.4088					
	98->108	-0.17359					
	98->110	-0.19562					
18	95->101	0.18811	7.2624	170.72	0.0890	41.615	40.1678
	96->100	-0.18785					
	96->101	0.19547					
	98->104	-0.19502					
19	95->101	0.27367	7.2988	169.87	0.0551	-44.1962	-44.9973
	96->100	0.17607					
	96->101	0.22313					
	97->103	0.19659					
	98->102	0.23983					
20	95->100	-0.22921	7.3531	168.62	0.0151	35.8011	34.5738
	96->100	0.38396					
21	83->99	0.26735	7.3960	167.64	0.0257	21.6236	20.4403
	88->99	-0.19501					
	98->102	-0.19255					
	98->107	-0.19934					
22	83->99	0.2196	7.4284	166.91	0.0101	6.6507	6.309
	88->99	-0.1862					
	95->100	-0.19857					

Num[a]	*Transition*[b]	*CI-coeff*[b]	*ΔE (eV)*[d]	*λ (nm)*[e]	*f*[f]	R_{vel}[g]	R_{len}[h]
	98->107	0.22241					
23	94->100	0.18586	7.5027	165.25	0.0192	-18.2041	-18.7673
	98->102	0.25773					
	98->105	0.22978					
	98->108	-0.1973					
24	93->100	0.31406	7.5530	164.15	0.0084	33.2678	32.3528
25	98->100	0.183	7.6102	162.92	0.0499	-45.9559	-45.7314
	98->108	0.32336					
26	86->99	0.18185	7.6644	161.77	0.0024	4.7342	4.6861
	88->99	0.2586					
	89->99	0.30985					
27	94->100	0.19252	7.7025	160.97	0.0056	-3.8347	-3.6631
	96->101	0.22433					
	97->103	-0.19561					
	98->107	0.19109					
28	98->108	0.22587	7.7159	160.69	0.0387	-14.2062	-14.4655
	98->109	0.30379					
	98->117	0.20447					
29	95->101	-0.20657	7.7471	160.04	0.0150	9.8582	9.6273
	96->101	0.33683					
30	97->100	0.18132	7.7911	159.14	0.0107	5.907	5.8914
31	75->99	-0.25792	7.8070	158.81	0.0197	-18.0871	-17.9294
	78->99	0.19016					
	84->99	0.27098					
	87->99	-0.25008					
32	96->104	0.20366	7.8427	158.09	0.0350	11.8742	11.2266
	98->105	0.30657					
33	96->103	0.35215	7.8800	157.34	0.0249	-29.9843	-29.4712
34	97->103	-0.17485	7.8849	157.24	0.0189	-1.6276	-1.2576
	97->104	0.27351					
	97->109	0.21042					
	98->106	-0.22418					
35	84->99	0.19841	7.9076	156.79	0.0034	2.6402	2.8859
	96->104	-0.19122					
	97->105	0.19465					
36	84->99	-0.18626	7.9233	156.48	0.0070	14.5203	13.8565
	98->105	0.28795					
	98->106	-0.21234					
	98->113	0.19189					

[a]Number of the excited states; [b]Only transitions with contribution over 6.0% 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).

11. Geometry Analysis of Glutinosasins A−D (C1−C4)

Table S71. Bond length of selected bonds in the lowest-energy conformers of **C1−C4** tautomers.

Bond	C-6/C-7	C-7/C-8	C-8/C-15	C-15/C-16	C-16/C-17	C-7/O	C-15/O
C1-T1-1	1.50	1.39	1.46	1.51	1.34	1.32	1.26
C1-T2-1	1.51	1.45	1.40	1.49	1.34	1.26	1.33
C1-T3-1	1.51	1.53	1.53	1.51	1.34	1.22	1.22
C1-T4-1	1.51	1.53	1.53	1.51	1.34	1.22	1.22
C2-T1-1	1.51	1.38	1.46	1.51	1.34	1.33	1.26
C2-T2-1	1.53	1.44	1.40	1.49	1.34	1.26	1.33
C3-T1-1	1.51	1.38	1.46	1.51	1.34	1.32	1.26
C3-T2-1	1.53	1.44	1.40	1.49	1.34	1.26	1.33
C4-T1-1	1.51	1.38	1.46	1.51	1.34	1.33	1.26
C4-T2-1	1.53	1.44	1.40	1.49	1.34	1.26	1.33

Table S72. Mayer bond order of selected bonds in the lowest-energy conformers of **C1−C4** tautomers.

Bond order	C-6/C-7	C-7/C-8	C-8/C-15	C-15/C-16	C-16/C-17	C-7/O	C-15/O
C1-T1-1	1.08	1.16	0.83	1.02	1.34	1.30	1.77
C1-T2-1	1.29	1.07	1.11	0.96	1.36	1.74	1.44
C1-T3-1	1.00	0.83	0.82	0.89	0.85	1.73	2.01
C1-T4-1	0.88	0.97	0.79	0.83	1.00	1.80	2.02
C2-T1-1	1.17	1.28	0.85	0.95	1.30	1.29	1.85
C2-T2-1	1.11	1.15	1.15	0.91	1.29	1.69	1.45
C3-T1-1	1.09	1.46	0.90	0.81	1.26	1.49	1.78
C3-T2-1	1.15	1.21	1.10	1.03	1.29	2.56	1.21
C4-T1-1	1.14	1.31	0.88	0.93	1.29	1.26	1.89
C4-T2-1	1.08	1.15	1.17	0.90	1.29	1.63	1.44

Table S73. Selected dihedrals in lowest-energy conformers of **C1−C4** tautomers.

Dihedral	**C-6/C-7/C-8/C-15**	**C-16/C-15/C-8/C-7**	**C-17/C-16/C-15/C-8**
C1-T1-1	172.89	-169.61	134.60
C1-T2-1	173.32	-172.80	141.26
C1-T3-1	102.74	154.85	-151.51
C1-T4-1	-95.55	-147.91	131.07
C2-T1-1	173.10	-171.02	135.58
C2-T2-1	175.60	-174.07	141.74
C3-T1-1	172.81	-169.72	133.94
C3-T2-1	171.73	-170.33	141.71
C4-T1-1	173.20	-171.04	135.54
C4-T2-1	175.83	-174.14	141.81

12. Weak Interaction Analysis of Glutinosasins A−D (C1−C4)

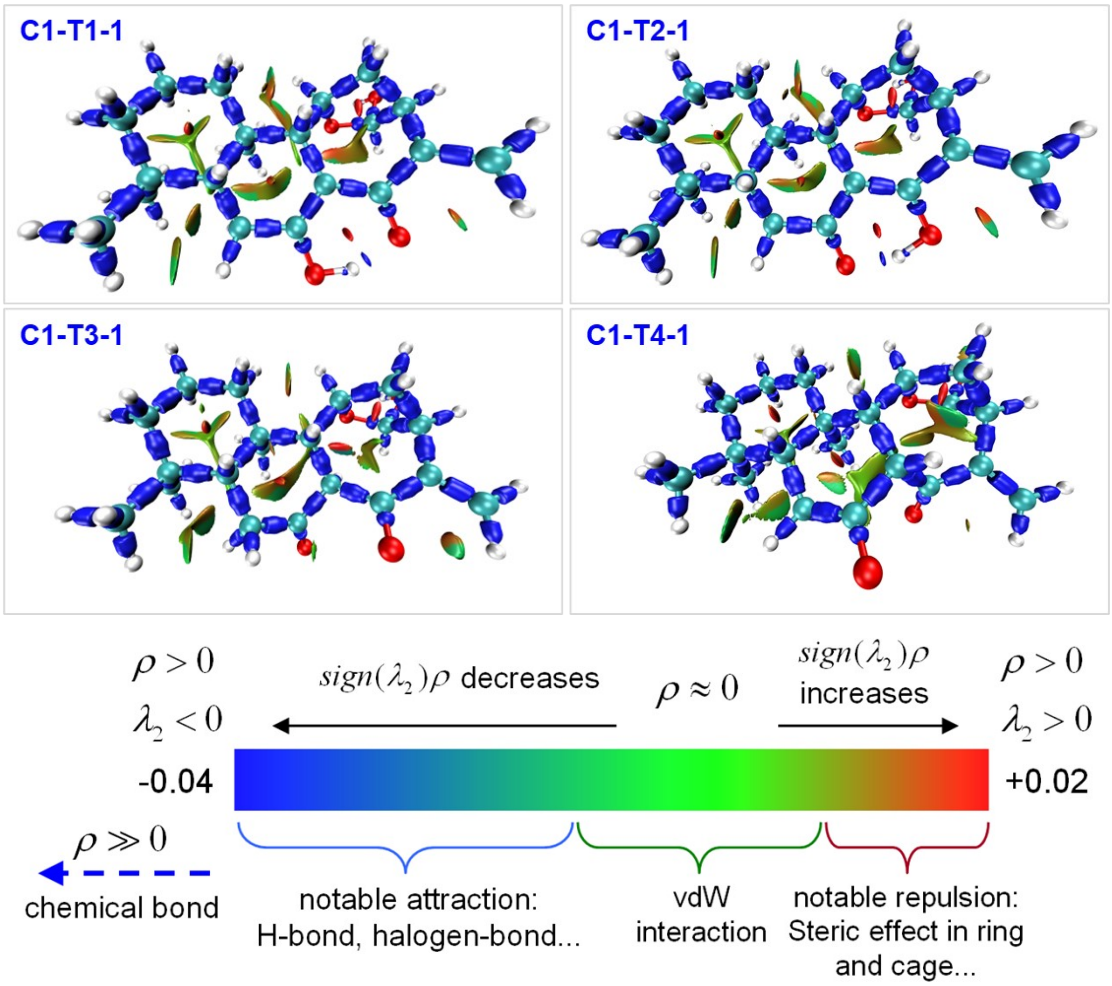

Figure S67. Weak interaction analysis of **T1**–**T4** of **C1** using the Interaction Region Indicator (IRI) method and the lowest-energy conformers. Note: the color bar used in this figure was copied from the Multiwfn software package (version 3.8).

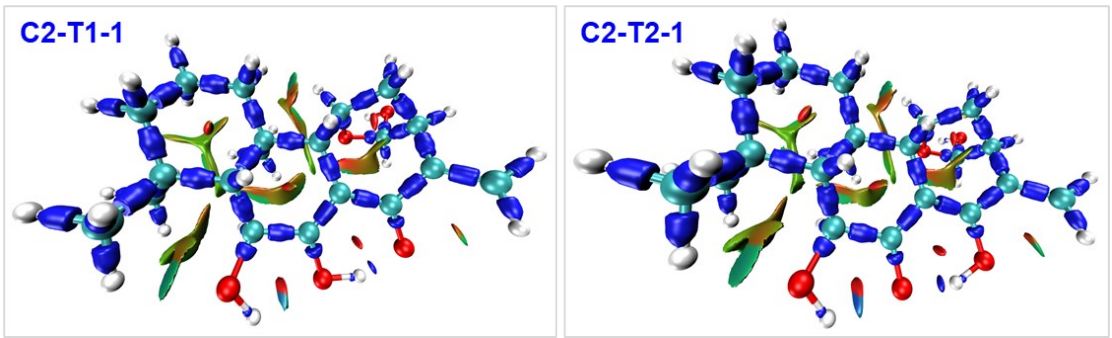

Figure S68. Weak interaction analysis of **T1**–**T2** of **C2** using the IRI method and the lowest-energy conformers.

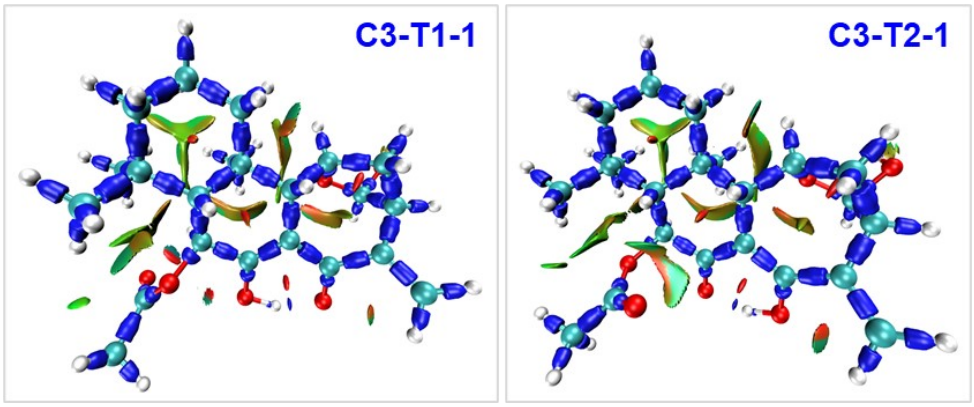

Figure S69. Weak interaction analysis of **T1**–**T2** of **C3** using the IRI method and the lowest-energy conformers.

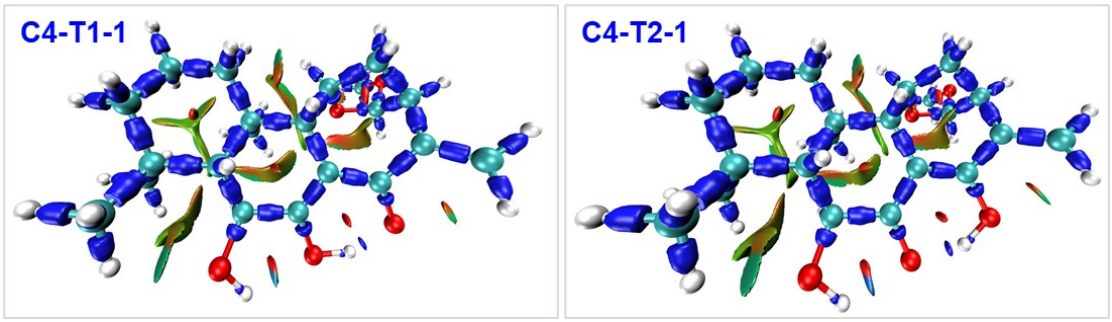

Figure S70. Weak interaction analysis of **T1**–**T2** of **C4** using the IRI method and the lowest-energy conformers.

13. Computational Data for Transition State Analysis of Proton Transfer in Glutinosasins A–D (C1−C4)

Table S74. Energy profile for proton transfer in **C1**–**C4** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level of theory.

Name	E (Hartree)[a]	⊿E (kcal/mol)[b]
C1-TS	-1079.769751	1.35
C1-T1	-1079.771908	0.00
C1-T2	-1079.770980	0.58
C2-TS	-1154.989270	1.37
C2-T1	-1154.990614	0.53
C2-T2	-1154.991456	0.00
C3-TS	-1307.638932	1.16
C3-T1	-1307.640783	0.00
C3-T2	-1307.640699	0.05
C4-TS	-1194.278516	1.38
C-T1	-1194.279812	0.56
C4-T2	-1194.280712	0.00

[a]Electronic energy obtained at M06-2X-D3-SCRF/6-311+G(2d,p) (Solvent=Pyridine) level of theory; [b]The relative electronic energy.

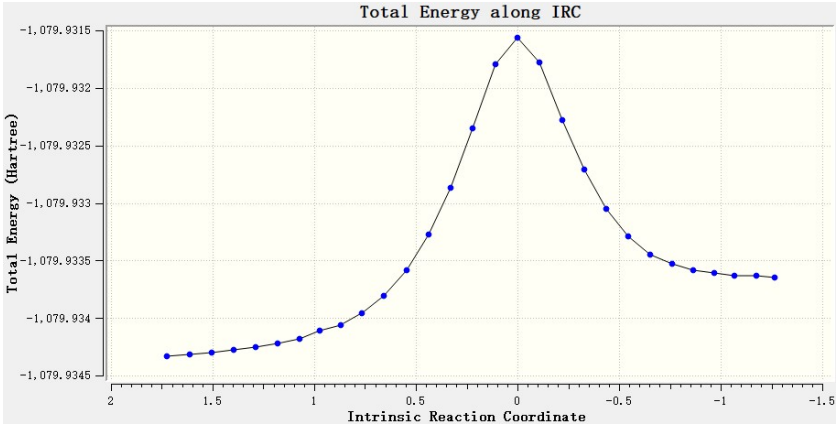

Figure S71. IRC profile for proton transfer in **C1** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level of theory (left: **C1-T1**; top: **C1-TS**; right: **C1-T2**).

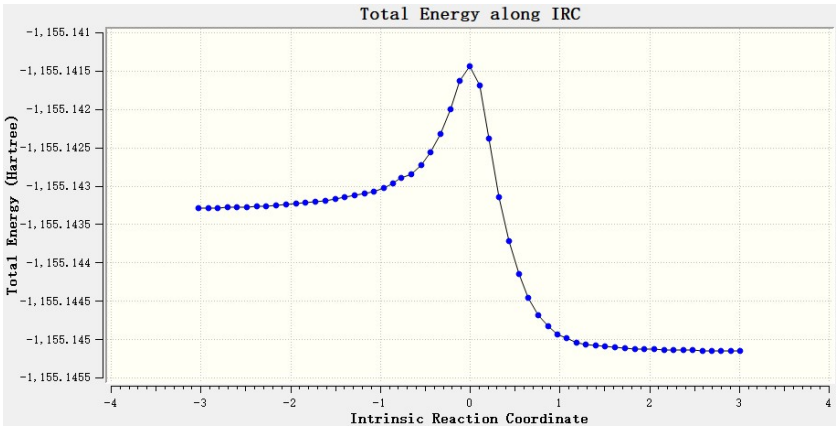

Figure S72. IRC profile for proton transfer in **C2** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level of theory (left: **C2-T1**; top: **C2-TS**; right: **C2-T2**).

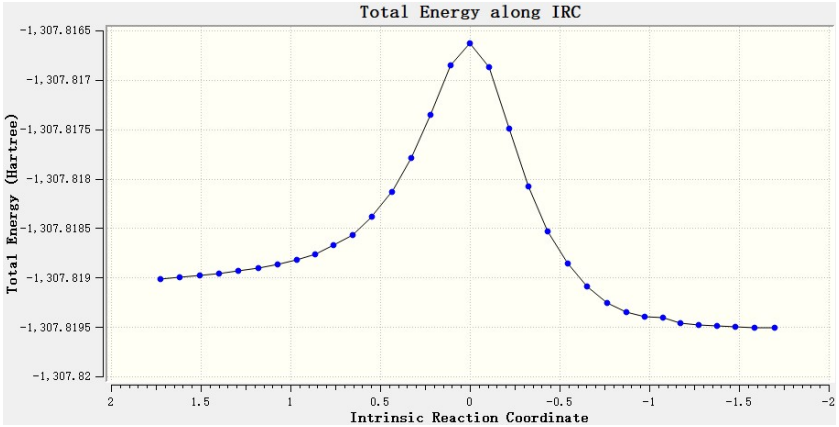

Figure S73. IRC profile for proton transfer in **C3** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level of theory (left: **C3-T1**; top: C3-TS; right: **C3-T2**).

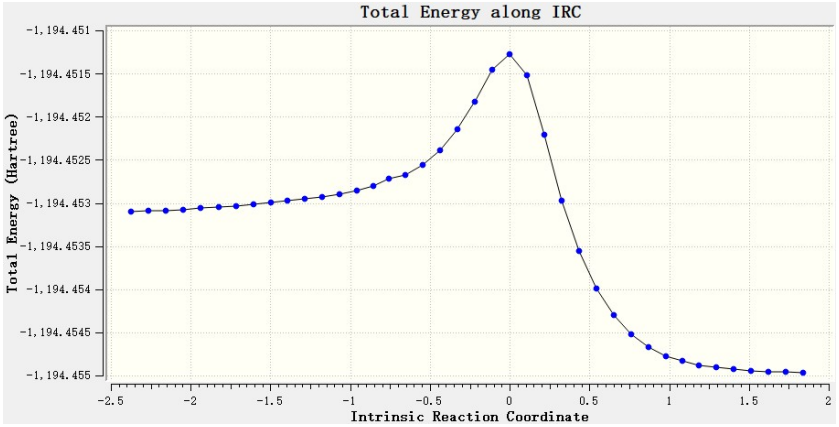

Figure S74. IRC profile for proton transfer in **C4** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level of theory (left: **C4-T1**; top: **C4-TS**; right: **C4-T2**).

Table S75. Cartesian coordinates (Å) of the proton transfer transition state in **C1** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level. (Imaginary frequency: −1049.49 cm^{-1})

C	-1.676130	-2.001575	-0.689669	H	-3.440012	-3.174212	-1.092953
C	-3.168950	-2.284498	-0.511645	H	-3.390262	-2.525208	0.535359
C	-3.998317	-1.088541	-0.973490	H	-5.071759	-1.299383	-0.882043
C	-3.671216	0.206902	-0.202016	H	-3.802309	-0.920881	-2.042755
C	-2.124083	0.444635	-0.246329	H	-1.918197	0.676077	-1.302933
C	-1.695168	1.665811	0.563049	H	-2.214636	2.572573	0.239341
C	-0.227066	1.957697	0.475137	H	-1.940307	1.545132	1.625367
C	0.713791	1.020227	-0.013339	H	0.123202	-0.341914	-1.557878
C	0.241000	-0.365603	-0.464596	H	0.767184	-2.441344	-0.123030
C	-1.181095	-0.754089	0.083022	H	2.792732	-2.572476	-1.297356
C	1.278878	-1.481836	-0.187909	H	2.095102	-1.221097	-2.215872
C	2.405193	-1.553221	-1.222909	H	4.473934	-0.873008	-0.950798
C	3.469180	-0.647259	-0.589121	H	3.633814	-0.274815	1.595247
C	3.325712	-1.049638	0.882735	H	3.823015	2.617700	-1.733399
C	2.039010	1.517870	-0.155053	H	4.865256	1.119319	-2.064480
C	3.193289	0.820580	-0.802619	H	-5.437852	1.159210	-1.044238
C	4.004894	1.561411	-1.570245	H	-3.948513	1.524107	-1.932536
C	-4.368788	1.374129	-0.930963	H	-4.282716	2.317368	-0.381382
C	-4.270787	0.130332	1.216128	H	-4.030745	1.017690	1.810304
C	-1.091974	-1.071068	1.588901	H	-5.363300	0.074961	1.142634
O	1.940299	-1.262536	1.081740	H	-3.940027	-0.746113	1.776599
O	0.113691	3.145061	0.857573	H	-2.067246	-1.308716	2.015322
O	4.072709	-2.232097	1.077444	H	-0.441662	-1.933645	1.757311
O	2.326982	2.722240	0.235709	H	-0.668132	-0.240369	2.159257
H	-1.105872	-2.887055	-0.389713	H	1.286333	3.143307	0.629422
H	-1.480504	-1.851702	-1.761472	H	3.869802	-2.550444	1.972534

Table S76. Cartesian coordinates (Å) of **C1-T1** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level.

C	-1.656237	-2.006264	-0.685418	H	-3.411447	-3.187298	-1.104948
C	-3.149075	-2.297317	-0.520098	H	-3.378258	-2.540435	0.524645
C	-3.980337	-1.104330	-0.987878	H	-5.053426	-1.320303	-0.904908
C	-3.666053	0.193356	-0.214114	H	-3.776825	-0.935725	-2.055575
C	-2.120030	0.437019	-0.246166	H	-1.905523	0.667559	-1.301105
C	-1.698565	1.661306	0.562641	H	-2.205326	2.567475	0.215933
C	-0.229872	1.932934	0.489606	H	-1.968060	1.555978	1.620718
C	0.704780	1.030914	0.007925	H	0.155759	-0.356098	-1.531461
C	0.249853	-0.363584	-0.435937	H	0.780020	-2.419830	0.022987
C	-1.176566	-0.757128	0.093274	H	2.787414	-2.628010	-1.177115
C	1.292054	-1.468036	-0.113520	H	2.064743	-1.343433	-2.170921
C	2.396116	-1.607426	-1.164669	H	4.463139	-0.883292	-0.993649
C	3.465802	-0.655156	-0.612748	H	3.692526	-0.167645	1.543002
C	3.365122	-0.978676	0.881284	H	3.641792	2.540387	-1.982535
C	2.059918	1.530828	-0.154503	H	4.671815	1.039875	-2.340594
C	3.149420	0.794486	-0.890261	H	-5.428790	1.139356	-1.072125
C	3.860063	1.497016	-1.781277	H	-3.932893	1.509236	-1.947377
C	-4.361473	1.357766	-0.949559	H	-4.283190	2.301255	-0.399094
C	-4.279145	0.114756	1.198239	H	-4.045088	1.001079	1.796339
C	-1.105663	-1.069863	1.601357	H	-5.370875	0.059559	1.113799
O	1.982444	-1.173069	1.126275	H	-3.954306	-0.762684	1.760549
O	0.076304	3.154927	0.907803	H	-2.084639	-1.315138	2.014282
O	4.113406	-2.150931	1.120650	H	-0.451813	-1.927060	1.783791
O	2.387282	2.682048	0.253210	H	-0.698075	-0.233132	2.174368
H	-1.080741	-2.888248	-0.384163	H	1.085085	3.231202	0.776935
H	-1.453481	-1.851706	-1.755172	H	3.944301	-2.412334	2.040820

Table S77. Cartesian coordinates (Å) of **C1-T2** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level.

C	-1.667212	-1.997708	-0.691078	H	-3.425318	-3.172995	-1.110275
C	-3.160660	-2.283816	-0.525207	H	-3.389738	-2.526737	0.519653
C	-3.987548	-1.088198	-0.991677	H	-5.061548	-1.300843	-0.911474
C	-3.669555	0.204827	-0.212761	H	-3.781215	-0.917176	-2.058472
C	-2.121853	0.445488	-0.237903	H	-1.905084	0.687965	-1.290044
C	-1.704245	1.654698	0.592052	H	-2.235838	2.561839	0.291154
C	-0.235450	1.984045	0.516646	H	-1.944078	1.506902	1.651856
C	0.721097	1.029469	0.001705	H	0.131492	-0.333809	-1.539614
C	0.244735	-0.359869	-0.446063	H	0.755889	-2.436723	-0.086806
C	-1.179811	-0.752643	0.091173	H	2.784343	-2.596420	-1.257706
C	1.276376	-1.483375	-0.164670	H	2.078092	-1.267631	-2.203405
C	2.394660	-1.576529	-1.204988	H	4.460917	-0.877810	-0.961985
C	3.457547	-0.653357	-0.596100	H	3.630571	-0.236063	1.579092
C	3.329222	-1.029506	0.884280	H	3.782412	2.588257	-1.814421
C	2.024517	1.501785	-0.177766	H	4.822443	1.085012	-2.123670
C	3.168939	0.808295	-0.834864	H	-5.428600	1.159798	-1.067893
C	3.967576	1.536439	-1.628575	H	-3.931595	1.525057	-1.943061
C	-4.360351	1.373758	-0.945290	H	-4.278059	2.316024	-0.393544
C	-4.284181	0.122643	1.198607	H	-4.054131	1.009814	1.796919
C	-1.098159	-1.077268	1.596239	H	-5.375600	0.062513	1.113315
O	1.948626	-1.261944	1.097674	H	-3.955492	-0.753652	1.760756
O	0.086327	3.143614	0.905545	H	-2.077602	-1.300842	2.020894
O	4.096128	-2.195956	1.096759	H	-0.462076	-1.950901	1.762510
O	2.366144	2.732044	0.191367	H	-0.661723	-0.256185	2.171105
H	-1.098357	-2.884292	-0.392040	H	1.508500	3.153857	0.575322
H	-1.464513	-1.842172	-1.760749	H	3.904245	-2.499923	1.999249

Table S78. Cartesian coordinates (Å) of the proton transfer transition state in **C2** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level. (Imaginary frequency: −1057.38 cm^{-1})

C	1.450403	-2.212923	0.658555	H	4.875404	-1.767367	0.786414
C	2.904982	-2.602236	0.408200	H	3.659270	-1.394905	2.001737
C	3.819838	-1.496980	0.918514	H	1.828356	0.497593	1.319454
C	3.581762	-0.121395	0.255326	H	0.797481	-3.041379	0.366401
C	2.047089	0.226484	0.276117	H	1.310893	-2.069024	1.739892
C	1.682304	1.441555	-0.578325	H	1.856283	1.202716	-1.638699
C	0.212893	1.797431	-0.449521	H	-0.266770	-0.481145	1.566904
C	-0.769842	0.928693	0.037618	H	4.378285	1.889532	0.652957
C	-0.375081	-0.481116	0.472722	H	5.401156	0.554600	1.227479
C	1.029079	-0.919888	-0.077147	H	3.928544	0.990495	2.109950
C	-1.473223	-1.529820	0.160557	H	4.052519	0.856840	-1.647669
C	-2.603665	-1.563496	1.193576	H	5.276822	-0.282087	-1.082515
C	-3.612551	-0.579045	0.585730	H	3.790967	-0.887425	-1.810855
C	-3.490276	-0.948392	-0.896917	H	0.442953	-0.392882	-2.136455
C	-2.067259	1.511493	0.196965	H	1.895360	-1.393613	-2.044905
C	-3.253700	0.865196	0.837308	H	0.308211	-2.099873	-1.758905
C	-4.013890	1.633155	1.630453	H	-4.628913	-0.755723	0.942006
C	4.366544	0.900187	1.108551	H	-3.050966	-2.559619	1.239195
C	4.196492	-0.110951	-1.157693	H	-2.276138	-1.278670	2.195517
C	0.921161	-1.209745	-1.590926	H	-1.020308	-2.515526	0.065298
O	-0.044007	3.022046	-0.809029	H	-3.753898	-0.138650	-1.588042
O	-2.274822	2.731822	-0.169138	H	-4.119438	-2.382451	-2.029614
O	2.446973	2.590223	-0.230386	H	-3.767680	2.672309	1.817955
O	-2.117067	-1.229925	-1.101409	H	-4.894627	1.230494	2.122357
O	-4.299540	-2.082013	-1.123497	H	1.943216	3.345665	-0.584273
H	3.127293	-3.542818	0.926708	H	-1.180401	3.107545	-0.569772
H	3.075473	-2.791090	-0.658830				

Table S79. Cartesian coordinates (Å) of **C2-T1** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level.

C	1.433526	-2.219548	0.631373	H	4.859402	-1.791364	0.791336
C	2.888423	-2.613857	0.390579	H	3.634986	-1.420928	1.998895
C	3.804181	-1.516426	0.916372	H	1.822178	0.480579	1.321886
C	3.579200	-0.134514	0.261347	H	0.778203	-3.041190	0.325242
C	2.045871	0.220304	0.277004	H	1.284961	-2.085810	1.712788
C	1.690888	1.450628	-0.558393	H	1.915916	1.254313	-1.617387
C	0.215052	1.780849	-0.471776	H	-0.280716	-0.483330	1.545813
C	-0.761085	0.941238	0.018393	H	4.394753	1.865941	0.673601
C	-0.377750	-0.472746	0.450831	H	5.397292	0.517259	1.251819
C	1.026164	-0.916444	-0.093956	H	3.922266	0.967344	2.123335
C	-1.480222	-1.512215	0.112343	H	4.074935	0.856632	-1.628854
C	-2.592340	-1.596302	1.161907	H	5.280513	-0.303017	-1.067318
C	-3.610247	-0.586187	0.613816	H	3.791877	-0.881789	-1.811851
C	-3.521775	-0.904493	-0.882223	H	0.484481	-0.350427	-2.154971
C	-2.087623	1.521024	0.180647	H	1.902594	-1.397738	-2.054289
C	-3.222366	0.844446	0.900116	H	0.291561	-2.057228	-1.798168
C	-3.903057	1.582972	1.785670	H	-4.618814	-0.765183	0.991116
C	4.367722	0.875041	1.125510	H	-3.037765	-2.594280	1.170006
C	4.202889	-0.117883	-1.147564	H	-2.248615	-1.354895	2.169623
C	0.928496	-1.187855	-1.611738	H	-1.026937	-2.491014	-0.036136
O	-0.018696	3.019351	-0.893912	H	-3.809773	-0.075438	-1.539762
O	-2.335274	2.694661	-0.217176	H	-4.165041	-2.301591	-2.052446
O	2.426765	2.593823	-0.129228	H	-3.630005	2.612167	1.992658
O	-2.147889	-1.158300	-1.124427	H	-4.743453	1.168922	2.335913
O	-4.320703	-2.040170	-1.129893	H	1.988392	3.358677	-0.540832
H	3.102145	-3.558995	0.904380	H	-1.022201	3.165353	-0.734696
H	3.067582	-2.796073	-0.676155				

Table S80. Cartesian coordinates (Å) of **C2-T2** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level.

C	1.437095	-2.198554	0.693254	H	4.862846	-1.765406	0.831517
C	2.890801	-2.599073	0.456321	H	3.642043	-1.371628	2.035411
C	3.807508	-1.489712	0.954579	H	1.815414	0.520814	1.305240
C	3.576453	-0.123812	0.269463	H	0.781425	-3.030980	0.419325
C	2.042629	0.228725	0.269066	H	1.295466	-2.028782	1.770539
C	1.686503	1.418483	-0.622621	H	1.806113	1.118967	-1.675151
C	0.226463	1.838311	-0.465161	H	-0.291301	-0.474041	1.548703
C	-0.781205	0.944146	0.029121	H	4.355858	1.896058	0.649922
C	-0.385085	-0.473614	0.453369	H	5.386980	0.574989	1.243355
C	1.025198	-0.919765	-0.073000	H	3.906582	1.007748	2.114115
C	-1.472996	-1.531040	0.123742	H	4.050751	0.817957	-1.650517
C	-2.602882	-1.595971	1.153579	H	5.286710	-0.290516	-1.048286
C	-3.603979	-0.588208	0.573641	H	3.817262	-0.934190	-1.775658
C	-3.487187	-0.917324	-0.919153	H	0.415406	-0.454326	-2.141095
C	-2.050842	1.494419	0.238526	H	1.912233	-1.385724	-2.035779
C	-3.232863	0.844896	0.868514	H	0.359937	-2.159149	-1.737277
C	-3.988022	1.588693	1.690335	H	-4.621495	-0.765517	0.925754
C	4.350380	0.911464	1.115677	H	-3.053690	-2.591568	1.164668
C	4.204907	-0.135988	-1.137746	H	-2.276669	-1.344984	2.164951
C	0.931265	-1.239270	-1.582950	H	-1.007224	-2.508710	0.013432
O	0.005486	3.045374	-0.778098	H	-3.734376	-0.082463	-1.586212
O	-2.316129	2.757725	-0.076101	H	-4.143443	-2.307193	-2.090976
O	2.493739	2.560774	-0.378452	H	-3.740913	2.619538	1.916896
O	-2.120594	-1.224757	-1.132972	H	-4.868320	1.169725	2.168887
O	-4.320492	-2.026507	-1.177955	H	1.937432	3.309408	-0.670159
H	3.106036	-3.532447	0.990596	H	-1.447251	3.156020	-0.427998
H	3.065275	-2.805307	-0.606920				

Table S81. Cartesian coordinates (Å) of the proton transfer transition state in **C3** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level. (Imaginary frequency: −1078.96 cm^{-1})

C	-0.306210	-2.893775	-0.489843	H	-1.803449	-3.763920	0.817703
C	-1.614761	-3.643169	-0.255955	H	-3.705290	-3.436420	-0.806792
C	-2.758206	-2.895553	-0.927885	H	-2.557198	-2.858828	-2.008517
C	-2.954729	-1.450697	-0.414724	H	-1.373361	-0.503790	-1.507651
C	-1.574102	-0.693500	-0.443437	H	0.520075	-3.469014	-0.061376
C	-1.597805	0.663101	0.257859	H	-0.124880	-2.841781	-1.573179
C	-0.282909	1.414005	0.153841	H	-1.837036	0.553641	1.317816
C	0.926700	0.792905	-0.201061	H	0.912996	-0.857991	-1.565557
C	0.954469	-0.708692	-0.476974	H	-4.799617	-1.470565	-1.555699
C	-0.305649	-1.458300	0.085905	H	-3.484079	-0.610471	-2.372287
C	2.275515	-1.376226	-0.014277	H	-4.345924	0.153588	-1.031051
C	3.432047	-1.204556	-1.003902	H	-3.761687	-0.481227	1.389770
C	4.103007	0.073058	-0.481377	H	-4.619167	-1.935504	0.879352
C	3.997712	-0.164890	1.029069	H	-3.069503	-2.076298	1.703467
C	2.029371	1.683660	-0.374825	H	-1.129004	-1.945565	2.067433
C	3.382526	1.330134	-0.902785	H	0.614093	-2.155102	1.930867
C	3.952803	2.195687	-1.752658	H	-0.057042	-0.542297	2.076728
C	-3.951398	-0.793585	-1.397898	H	5.148344	0.146530	-0.786409
C	-3.624869	-1.483490	0.973114	H	4.130944	-2.040896	-0.924170
C	-0.225262	-1.523900	1.626710	H	3.099561	-1.121670	-2.040678
C	-3.346775	2.269639	0.524538	H	2.101045	-2.433199	0.179773
C	-4.210857	3.229894	-0.248155	H	3.996283	0.750747	1.632560
O	-0.378071	2.680685	0.391710	H	4.919713	-1.252617	2.333872
O	1.883926	2.946383	-0.133896	H	3.446906	3.103235	-2.062561
O	-2.591915	1.531335	-0.321693	H	4.937582	2.004553	-2.169088
O	-3.329904	2.151176	1.732920	H	-3.572836	3.954980	-0.763963
O	2.738155	-0.784022	1.222981	H	-4.785165	2.695763	-1.011378
O	5.063529	-1.009921	1.404306	H	-4.885038	3.750313	0.432185
H	-1.534802	-4.655601	-0.669693	H	0.728064	3.043802	0.186216

Table S82. Cartesian coordinates (Å) of **C3-T1** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level.

C	-0.282707	-2.883761	-0.493470	H	-1.773326	-3.786597	0.800259
C	-1.585586	-3.646768	-0.271206	H	-3.678145	-3.447676	-0.816273
C	-2.735654	-2.897443	-0.930464	H	-2.536478	-2.842813	-2.010707
C	-2.943456	-1.461651	-0.396125	H	-1.369577	-0.497595	-1.484165
C	-1.568070	-0.695261	-0.421065	H	0.548910	-3.456908	-0.072093
C	-1.600620	0.660474	0.281012	H	-0.100843	-2.815858	-1.575809
C	-0.278626	1.393624	0.219570	H	-1.887841	0.560473	1.329706
C	0.913938	0.809923	-0.153797	H	0.921668	-0.823281	-1.543217
C	0.956094	-0.687060	-0.452959	H	-4.787824	-1.487718	-1.537462
C	-0.295965	-1.455752	0.100039	H	-3.487957	-0.587351	-2.335953
C	2.282942	-1.345388	0.014382	H	-4.363711	0.130975	-0.978300
C	3.426286	-1.215009	-0.996433	H	-3.763128	-0.520716	1.416248
C	4.105529	0.078721	-0.526252	H	-4.596089	-1.985928	0.897172
C	4.035026	-0.120435	0.990960	H	-3.042849	-2.106254	1.717966
C	2.046759	1.712271	-0.322112	H	-1.104833	-2.004603	2.069996
C	3.354223	1.315992	-0.954075	H	0.644911	-2.138078	1.941429
C	3.845768	2.136842	-1.890667	H	-0.095973	-0.556482	2.104257
C	-3.950820	-0.800298	-1.365708	H	5.141018	0.152789	-0.863710
C	-3.609426	-1.517825	0.992954	H	4.123849	-2.050304	-0.896591
C	-0.218202	-1.538237	1.640092	H	3.079860	-1.166056	-2.030607
C	-3.380343	2.253815	0.455890	H	2.107116	-2.393453	0.250495
C	-4.209221	3.208899	-0.360753	H	4.060976	0.809008	1.572182
O	-0.411570	2.673212	0.534276	H	4.970347	-1.184436	2.305492
O	1.954957	2.933489	-0.016392	H	3.311518	3.029524	-2.198002
O	-2.561898	1.536664	-0.348518	H	4.791407	1.926743	-2.382743
O	-3.436849	2.124169	1.661839	H	-3.551539	3.943884	-0.836251
O	2.766173	-0.710072	1.223703	H	-4.732304	2.671776	-1.157938
O	5.092423	-0.975039	1.364815	H	-4.927572	3.717684	0.282143
H	-1.498326	-4.651711	-0.701389	H	0.523626	3.067557	0.417189

Table S83. Cartesian coordinates (Å) of **C3-T2** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level.

C	-0.301602	-2.888932	-0.472906	H	-1.815936	-3.748124	0.821597
C	-1.612028	-3.638122	-0.250488	H	-3.694089	-3.438616	-0.836366
C	-2.745506	-2.898040	-0.946957	H	-2.527196	-2.870609	-2.024474
C	-2.950438	-1.449434	-0.448427	H	-1.353191	-0.499361	-1.516888
C	-1.570241	-0.689694	-0.455802	H	0.520027	-3.462019	-0.033032
C	-1.603931	0.660787	0.253599	H	-0.108364	-2.841946	-1.554398
C	-0.300017	1.450963	0.143181	H	-1.821160	0.535282	1.316285
C	0.935454	0.804705	-0.210854	H	0.936872	-0.871472	-1.539824
C	0.959760	-0.706308	-0.453189	H	-4.779101	-1.469666	-1.615693
C	-0.309540	-1.449979	0.095282	H	-3.443481	-0.633729	-2.424429
C	2.268287	-1.378093	0.045893	H	-4.316253	0.158533	-1.106686
C	3.436428	-1.257264	-0.935373	H	-3.779809	-0.471930	1.342894
C	4.097151	0.045203	-0.465417	H	-4.641201	-1.918744	0.817272
C	3.980226	-0.123622	1.053827	H	-3.106981	-2.072822	1.667000
C	2.028241	1.649095	-0.435576	H	-1.172899	-1.891180	2.072519
C	3.374886	1.277840	-0.951986	H	0.562752	-2.163515	1.958404
C	3.948855	2.098647	-1.843487	H	-0.051826	-0.526893	2.082283
C	-3.927283	-0.797937	-1.454547	H	5.144621	0.110622	-0.764343
C	-3.644961	-1.474830	0.927651	H	4.134212	-2.088047	-0.803351
C	-0.249961	-1.505787	1.638210	H	3.118608	-1.226078	-1.979554
C	-3.342594	2.263632	0.572042	H	2.074832	-2.424719	0.272907
C	-4.217666	3.234903	-0.174286	H	3.958172	0.819779	1.612720
O	-0.408915	2.688797	0.351092	H	4.907488	-1.133996	2.416023
O	1.933805	2.961256	-0.255432	H	3.448033	2.989914	-2.204149
O	-2.621563	1.517768	-0.295627	H	4.935017	1.883576	-2.244447
O	-3.294333	2.142760	1.779572	H	-3.585304	3.962308	-0.693928
O	2.730683	-0.757554	1.267655	H	-4.808794	2.711947	-0.932331
O	5.057192	-0.930530	1.478007	H	-4.876216	3.751986	0.523754
H	-1.524622	-4.654518	-0.652837	H	0.969719	3.137657	0.038596

Table S84. Cartesian coordinates (Å) of the proton transfer transition state in **C4** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level. (Imaginary frequency: −1057.27 cm^{-1})

C	1.482845	-2.145427	0.928696	H	4.934546	-2.008161	0.819098
C	2.879588	-2.694464	0.649943	H	3.834635	-1.385112	2.042530
C	3.916715	-1.627198	0.972845	H	2.134845	0.577706	1.233206
C	3.756064	-0.322215	0.160502	H	2.030113	0.925263	-1.786076
C	2.261714	0.167132	0.220700	H	-0.016041	-0.166465	1.711823
C	1.948297	1.302408	-0.755175	H	-1.038057	-2.282052	0.510063
C	0.527071	1.807557	-0.589580	H	-2.985006	-2.000756	1.787330
C	-0.493379	1.096977	0.052004	H	-2.042964	-0.695159	2.538994
C	-0.194325	-0.283469	0.633189	H	-4.418066	-0.106721	1.356388
C	1.127953	-0.912716	0.065444	O	-4.337482	-1.682399	-0.543178
C	-1.396567	-1.253822	0.509662	H	-3.665087	0.119280	-1.278605
C	-2.457317	-1.062516	1.597928	H	-3.214637	3.306749	1.760561
C	-3.414703	-0.066743	0.929197	H	-4.439297	2.020608	2.296152
C	-3.420692	-0.617595	-0.501089	H	5.685973	0.291012	0.942774
C	-1.723087	1.812331	0.208094	H	4.316457	0.959820	1.845205
C	-2.918438	1.357575	0.982627	H	4.744918	1.639284	0.267902
C	-3.559754	2.279963	1.713970	H	3.763893	-1.339622	-1.805242
C	4.678960	0.714446	0.839620	H	4.186905	0.379124	-1.869894
C	4.277048	-0.534277	-1.274127	H	5.340874	-0.796858	-1.236689
C	0.896664	-1.365708	-1.393609	H	0.457621	-0.576695	-2.008610
C	-4.408477	-2.308237	-1.819252	H	1.819152	-1.693402	-1.873875
O	-1.847512	2.996098	-0.291374	H	0.197946	-2.206818	-1.417909
O	2.831380	2.406710	-0.594702	H	2.371775	3.159890	-1.008440
O	-2.089843	-1.041900	-0.743224	O	0.354262	3.001025	-1.080129
H	0.743855	-2.937798	0.773669	H	-5.176903	-3.080934	-1.750002
H	1.425493	-1.865494	1.990679	H	-4.690752	-1.584826	-2.598136
H	3.053187	-3.585323	1.265720	H	-3.450734	-2.765887	-2.091185
H	2.964305	-3.020315	-0.394017	H	-0.752463	3.219394	-0.792080

Table S85. Cartesian coordinates (Å) of **C4-T1** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level.

C	1.470536	-2.154772	0.898263	H	4.923765	-2.024753	0.820980
C	2.868972	-2.704507	0.629156	H	3.814890	-1.405335	2.038173
C	3.905751	-1.641687	0.967891	H	2.132162	0.559010	1.238912
C	3.756224	-0.331146	0.162212	H	2.104860	0.987255	-1.771326
C	2.263005	0.162520	0.221454	H	-0.022719	-0.168212	1.692279
C	1.959726	1.318357	-0.732087	H	-1.040969	-2.273061	0.420634
C	0.524038	1.786357	-0.611605	H	-2.966781	-2.046556	1.741566
C	-0.485687	1.102295	0.029085	H	-2.013762	-0.769762	2.529437
C	-0.193263	-0.279136	0.611945	H	-4.401224	-0.120412	1.416814
C	1.128411	-0.910654	0.046367	O	-4.349191	-1.661242	-0.534199
C	-1.399001	-1.246006	0.469589	H	-3.715972	0.170756	-1.227981
C	-2.442344	-1.101032	1.581534	H	-3.082299	3.254553	1.916497
C	-3.408135	-0.079434	0.965831	H	-4.285472	1.968901	2.500169
C	-3.446009	-0.586484	-0.479120	H	5.686016	0.260963	0.959826
C	-1.747390	1.813774	0.185794	H	4.317128	0.944378	1.852627
C	-2.887055	1.335096	1.043311	H	4.764416	1.619774	0.279305
C	-3.449921	2.235669	1.858966	H	3.762163	-1.329961	-1.813808
C	4.684355	0.695194	0.849812	H	4.210310	0.382232	-1.859816
C	4.282911	-0.537536	-1.271113	H	5.342827	-0.814779	-1.229454
C	0.907333	-1.344097	-1.419844	H	0.515728	-0.533185	-2.038462
C	-4.442352	-2.247190	-1.827781	H	1.825412	-1.706843	-1.882842
O	-1.921694	2.947797	-0.343797	H	0.176081	-2.156153	-1.465412
O	2.810552	2.433189	-0.474138	H	2.414504	3.182413	-0.952017
O	-2.113556	-0.983361	-0.763133	O	0.367889	2.981489	-1.172069
H	0.731035	-2.943255	0.726089	H	-5.198776	-3.032178	-1.765351
H	1.401937	-1.886952	1.962689	H	-4.752367	-1.503369	-2.576235
H	3.035054	-3.599481	1.241024	H	-3.485375	-2.682716	-2.136279
H	2.963233	-3.024255	-0.415828	H	-0.608431	3.234527	-0.981483

Table S86. Cartesian coordinates (Å) of **C4-T2** at B3LYP-D3BJ-SCRF/6-31G(d) (Solvent=Pyridine) level.

C	1.483238	-2.121188	0.970252	H	4.934436	-1.986888	0.858783
C	2.879306	-2.677282	0.703130	H	3.834066	-1.341495	2.070196
C	3.916310	-1.603728	1.005303	H	2.127647	0.605983	1.213782
C	3.753994	-0.315351	0.167344	H	1.963046	0.842358	-1.812210
C	2.258427	0.172808	0.210879	H	-0.035611	-0.158077	1.699733
C	1.942169	1.275139	-0.800168	H	-1.018540	-2.287591	0.469205
C	0.536699	1.842290	-0.611099	H	-2.984786	-2.049591	1.731920
C	-0.506484	1.107834	0.045729	H	-2.044196	-0.767866	2.526949
C	-0.201625	-0.279464	0.619801	H	-4.409431	-0.133389	1.352550
C	1.128195	-0.911364	0.074370	O	-4.350545	-1.650695	-0.587658
C	-1.392730	-1.265505	0.483777	H	-3.642099	0.156003	-1.274788
C	-2.454987	-1.106689	1.573673	H	-3.193124	3.254352	1.865770
C	-3.405182	-0.090123	0.928220	H	-4.417159	1.951285	2.355890
C	-3.413823	-0.604958	-0.515621	H	5.678715	0.327014	0.940206
C	-1.710211	1.790617	0.254263	H	4.302563	0.997443	1.831196
C	-2.899479	1.328927	1.021417	H	4.724888	1.655170	0.242533
C	-3.537769	2.229997	1.782789	H	3.787046	-1.386420	-1.769018
C	4.667935	0.739528	0.829665	H	4.174088	0.339203	-1.880909
C	4.282101	-0.555362	-1.260576	H	5.350812	-0.795962	-1.213925
C	0.905539	-1.400274	-1.375668	H	0.417948	-0.645500	-1.997191
C	-4.425437	-2.245383	-1.878292	H	1.837827	-1.686952	-1.862886
O	-1.889859	3.026685	-0.198635	H	0.251859	-2.277295	-1.379665
O	2.856762	2.359884	-0.748181	H	2.345392	3.116412	-1.096351
O	-2.090954	-1.050930	-0.764172	O	0.396753	3.019438	-1.056658
H	0.743679	-2.917433	0.840151	H	-5.209353	-3.004106	-1.831657
H	1.429024	-1.811693	2.024140	H	-4.688331	-1.498768	-2.641953
H	3.052121	-3.555621	1.336854	H	-3.475086	-2.715516	-2.154776
H	2.963640	-3.024063	-0.334170	H	-1.015461	3.301129	-0.643053