Supporting information for

Pardinumones A–D, Antibacterial Polyketide-Amino Acid Derivatives from the Mushroom *Tricholoma pardinum*

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Content

Sections S1 Computational details

S1.1. Computational details for pardinumones A and B (1 and 2) (ECD).

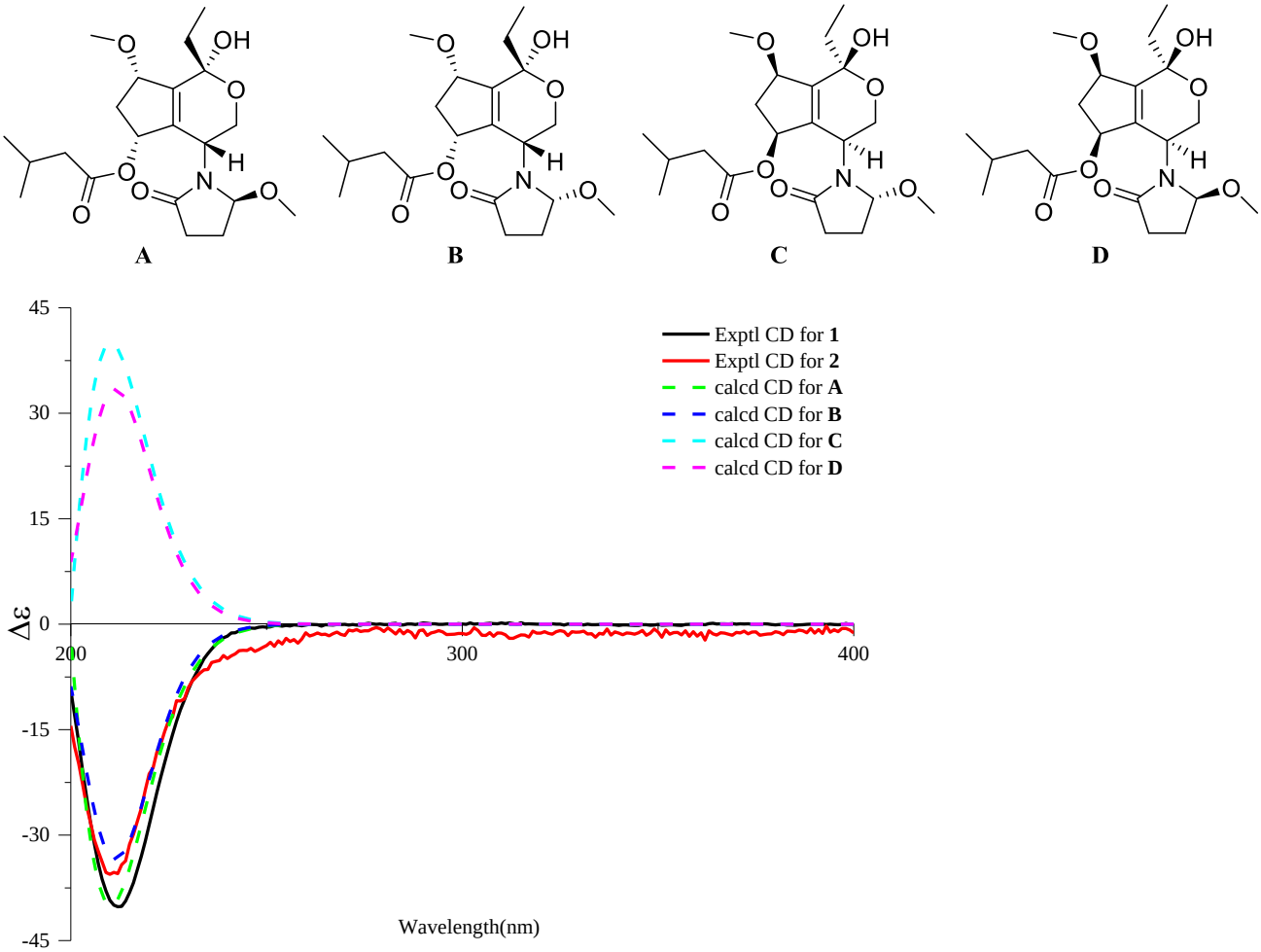


Figure S1. Calculated ECD spectra for **A-D** at the mPW1PW91/TZVP level in methanol with PCM model (A and C: σ = 0.3 eV, UV shift -15 nm; B and D: σ = 0.3 eV, UV shift -8 nm). Experimental CD spectra of **1** (black line) and **2** (red line) in MeOH.

Table S1. Energy analysis for conformers of **AA-AE** at B3LYP/6-31G* level in the gas phase

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
AA	-1401.017501	-1400.987370	-1400.986426	-1401.079190	0.001642	1.030371	13.25%
AB	-1401.017659	-1400.987708	-1400.986764	-1401.078470	0.002362	1.482177	6.18%
AC	-1401.019029	-1400.988809	-1400.987865	-1401.080832	0.000000	0.000000	75.53%
AD	-1401.016194	-1400.986170	-1400.985226	-1401.077592	0.003240	2.033131	2.44%
AE	-1401.016616	-1400.986650	-1400.985706	-1401.077651	0.003181	1.996108	2.59%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S2. Main conformers of **A**.

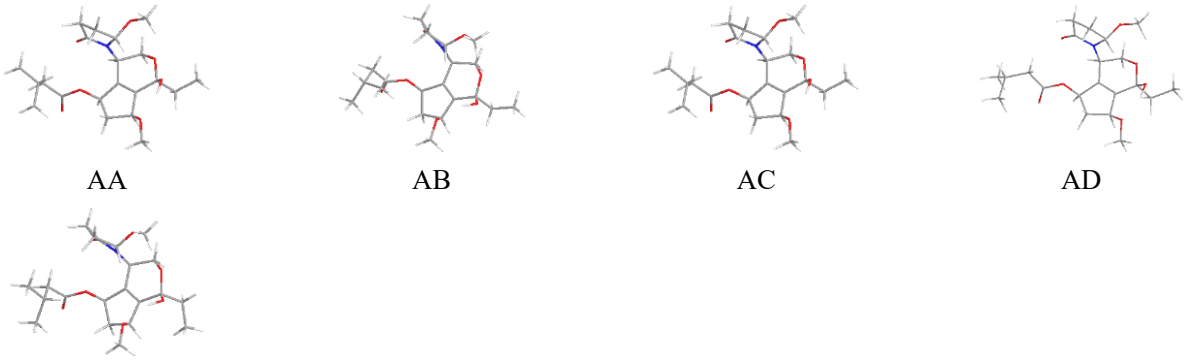


Table S2. Energy analysis for conformers of **BA-BG** at B3LYP/6-31G* level in the gas phase

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
BA	-1401.020210	-1400.990059	-1400.989115	-1401.082105	0.000000	0.000000	80.45%
BB	-1401.017843	-1400.987860	-1400.986916	-1401.078552	0.003553	2.229541	1.86%
BC	-1401.018112	-1400.988030	-1400.987086	-1401.079390	0.002715	1.703688	4.53%
BD	-1401.018179	-1400.988002	-1400.987058	-1401.079800	0.002305	1.446409	6.99%
BE	-1401.017574	-1400.987744	-1400.986800	-1401.077597	0.004508	2.828813	0.68%
BF	-1401.017253	-1400.987154	-1400.986210	-1401.078882	0.003223	2.022463	2.64%
BG	-1401.016860	-1400.986730	-1400.985786	-1401.078952	0.003153	1.978537	2.85%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S3. Main conformers of **B**

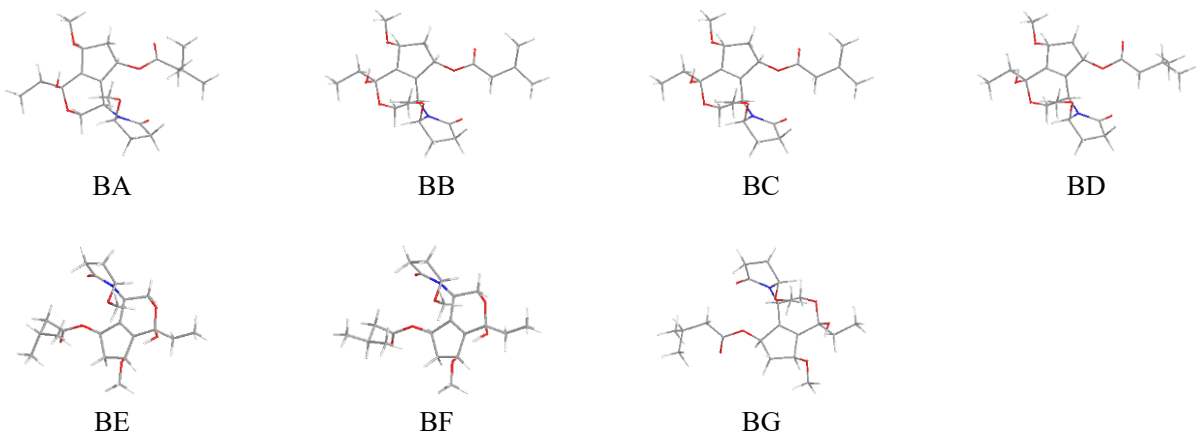


Table S3. Energy analysis for conformers of **CA-CF** at B3LYP/6-31G* level in the gas phase

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
CA	-1401.0175000	-1400.9873700	-1400.9864260	-1401.0791870	0.0016460	1.0328806	7.99%
CB	-1401.0175450	-1400.9873920	-1400.9864480	-1401.0795420	0.0012910	0.8101148	11.64%
CC	-1401.0176590	-1400.9877080	-1400.9867640	-1401.0784700	0.0023630	1.4828049	3.74%
CD	-1401.0190300	-1400.9888090	-1400.9878650	-1401.0808330	0.0000000	0.0000000	45.72%
CE	-1401.0180470	-1400.9877290	-1400.9867850	-1401.0804150	0.0004180	0.2622990	29.35%
CF	-1401.0166160	-1400.9866500	-1400.9857060	-1401.0776510	0.0031820	1.9967352	1.57%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S4. Main conformers of **C**

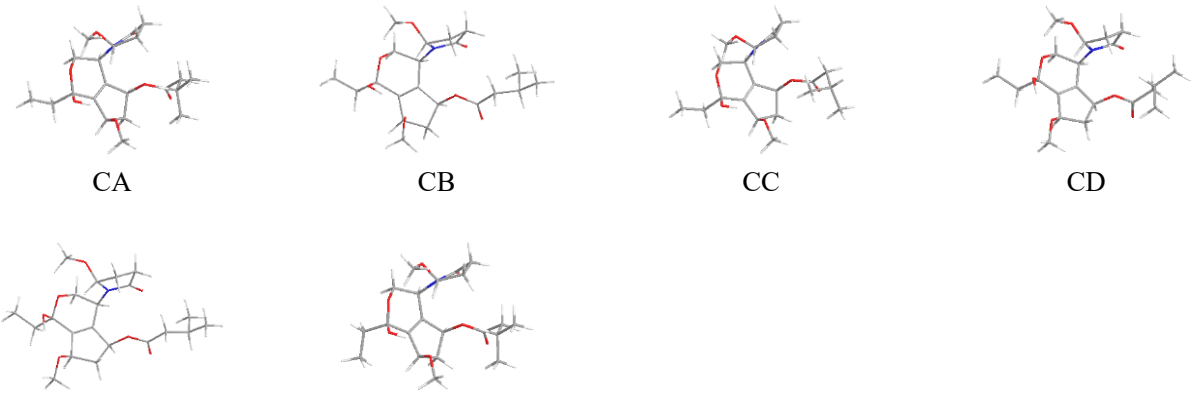
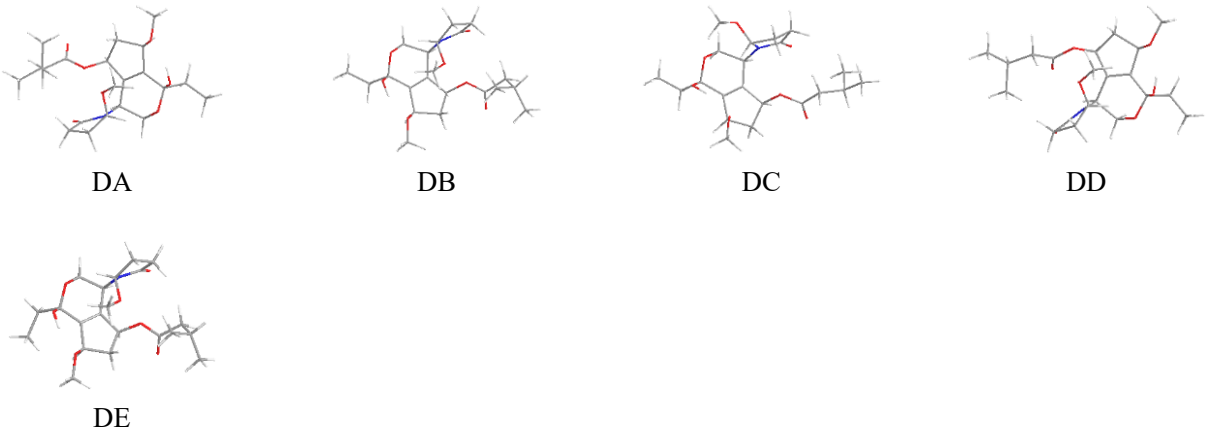


Table S4. Energy analysis for conformers of **DA-DE** at B3LYP/6-31G* level in the gas phase

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
DA	-1401.020210	-1400.990059	-1400.989115	-1401.082104	0.000000	0.000000	84.81%
DB	-1401.018112	-1400.988030	-1400.987086	-1401.079390	0.002714	1.703061	4.78%
DC	-1401.016597	-1400.986479	-1400.985535	-1401.078461	0.003643	2.286017	1.79%
DD	-1401.018590	-1400.988376	-1400.987432	-1401.079897	0.002207	1.384913	8.18%
DE	-1401.016415	-1400.986507	-1400.985562	-1401.077147	0.004957	3.110565	0.44%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S5. Main conformers of **D**



S1.2. Computational details for pardinumones A and B (1 and 2) (NMR).

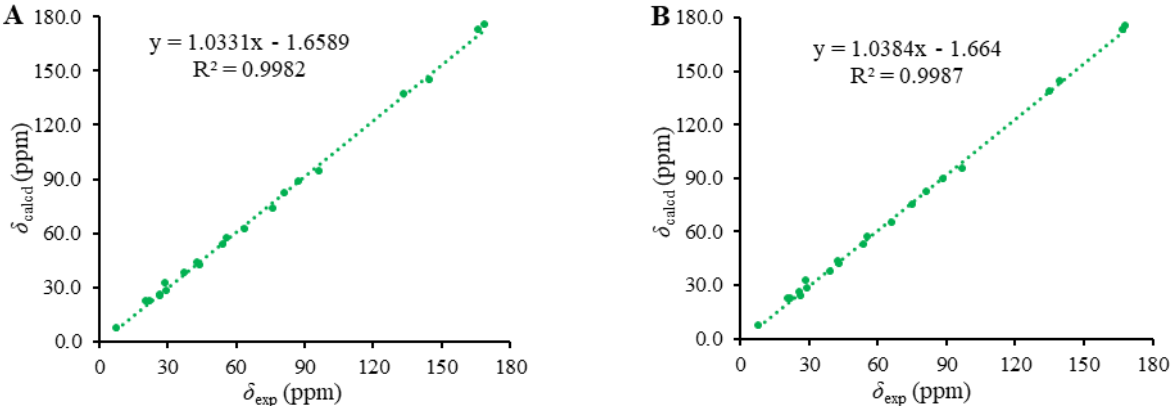


Figure S6. Regression analysis of experimental versus calculated ^{13}C NMR chemical shifts of **1**(**A**) and **2**(**B**).

Table S5. Experimental and calculated ^{13}C NMR data of **1** and **2**

No.	**1**				**2**			
	δ_{Exp}	δ_{Calcd}[a]	δ_{Corr}[b]	Relative errors[c]	δ_{Exp}	δ_{Calcd}[a]	δ_{Corr}[b]	Relative errors[c]
1	7.5	7.9	6.5	1.0	7.5	7.8	6.5	1.0
2	32.4	28.8	28.1	4.3	32.5	29.0	28.4	4.1
3	94.6	96.3	97.8	-3.2	95.0	97.0	99.0	-4.0
4	145.2	144.8	147.9	-2.7	144.2	139.5	143.2	1.0
5	82.3	81.5	82.5	-0.2	82.5	81.4	82.9	-0.4
6	37.7	37.8	37.4	0.3	37.7	39.4	39.3	-1.6
7	73.3	76.3	77.2	-3.9	74.9	75.0	76.3	-1.4
8	137.1	133.6	136.3	0.8	138.6	135.3	138.9	-0.3
9	42.3	44.0	43.8	-1.5	42.0	43.2	43.2	-1.2
10	62.2	64.1	64.6	-2.4	65.3	66.4	67.3	-2.0
1′	173.1	166.2	170.0	3.1	173.0	166.9	171.6	1.4
2′	43.4	43.0	42.7	0.7	43.5	42.6	42.6	0.9
3′	25.7	26.9	26.2	-0.5	25.8	26.2	25.5	0.3
4′	22.5	20.7	19.7	2.8	22.5	21.0	20.1	2.4
5′	22.6	22.5	21.5	1.1	22.6	22.2	21.4	1.2
1″	175.3	168.6	172.5	2.8	175.2	168.4	173.2	2.0
2″	28.3	29.8	29.1	-0.8	28.4	29.5	29.0	-0.6
3″	24.9	26.8	26.0	-1.1	24.1	26.4	25.7	-1.6
4″	88.5	87.5	88.7	-0.2	89.7	88.7	90.5	-0.8
5-OCH_3	57.0	55.9	56.1	0.9	57.0	55.7	56.2	0.8
4″-OCH_3	53.4	54.2	54.4	-1.0	53.0	53.9	54.3	-1.3
			RMSD	2.09			RMSD	1.34

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta\text{exp} - \delta\text{corr}$.

Figure S7. Calculated ^{13}C chemical shifts of **A**–**B** fitting with the experimental data of compound **1**(**A**) following STS protocol.

Note:
Pmean > 5% is the confidence interval

Note:
sp carbons include C≡N
sp2-CH/C for double bonds except carbonyl group
C=O includes only ketones and aldehydes

	A	B
MAE	1.53	1.57
RMS	1.80	1.88
P_{mean}	14.97%	12.86%
Prel	96.05%	3.95%

Heavy atom bear	Type of carbon	Carbon no.	Exptl δ	Shielding tenso	Corr Shielding	Calcd δ	Calcd δ (S	abs dev	P	Shielding t	Corr Shield	Calcd δ	Calcd δ (S	abs dev	P
	sp3-CH3	1	7.5	187.3	187.33	7.74	6.65	0.85	0.41	187.4	187.44	7.63	6.41	1.09	0.29
	sp3-CH2/CH/C	2	32.4	166.4	166.44	29.95	28.65	3.75	0.00	166.3	166.29	30.10	28.75	3.65	0.00
	sp3-CH2/CH/C	3	94.6	99.0	98.96	98.43	96.48	1.88	0.09	98.3	98.28	99.12	97.33	2.73	0.01
	sp2-C	4	145.2	50.5	50.46	150.35	147.92	2.72	0.16	55.7	55.73	145.10	143.03	2.17	0.26
	sp3-CH2/CH/C	5	82.3	113.8	113.76	83.41	81.60	0.70	0.53	113.8	113.84	83.33	81.64	0.66	0.55
	sp3-CH2/CH/C	6	37.7	157.5	157.50	39.02	37.64	0.06	0.95	155.8	155.82	40.73	39.31	1.61	0.15
	sp3-CH2/CH/C	7	73.3	118.9	118.92	78.17	76.41	3.11	0.01	120.2	120.21	76.86	75.21	1.91	0.09
	sp2-C	8	137.1	61.7	61.71	139.14	136.81	0.29	0.88	59.9	59.93	140.91	138.87	1.77	0.36
	sp3-CH2/CH/C	9	42.3	151.3	151.28	45.33	43.88	1.58	0.15	152.1	152.09	44.51	43.06	0.76	0.49
	sp3-CH2/CH/C	10	62.2	131.1	131.14	65.77	64.14	1.94	0.08	128.8	128.84	68.10	66.51	4.31	0.00
	X-C=O	1'	173.1	29.1	29.06	173.69	171.03	2.07	0.20	28.4	28.38	174.31	172.05	1.05	0.52
	sp3-CH2/CH/C	2'	43.4	152.3	152.30	44.30	42.86	0.54	0.63	152.6	152.62	43.97	42.53	0.87	0.43
	sp3-CH2/CH/C	3'	25.7	168.3	168.33	28.03	26.75	1.05	0.35	169.1	169.10	27.25	25.91	0.21	0.85
	sp3-CH3	4'	22.5	174.5	174.55	20.99	19.77	2.73	0.01	174.3	174.26	21.29	19.99	2.51	0.02
	sp3-CH3	5'	22.6	172.8	172.81	22.80	21.57	1.03	0.32	173.0	173.04	22.56	21.25	1.35	0.19
	X-C=O	1''	175.3	26.7	26.67	175.85	173.18	2.12	0.19	26.9	26.91	175.64	173.38	1.92	0.23
	sp3-CH2/CH/C	2''	28.3	165.5	165.46	30.94	29.63	1.33	0.23	165.7	165.71	30.69	29.33	1.03	0.35
	sp3-CH2/CH/C	3''	24.9	168.5	168.48	27.87	26.59	1.69	0.13	168.9	168.90	27.45	26.11	1.21	0.27
	sp3-CH2/CH/C	4''	88.5	107.8	107.80	89.46	87.60	0.90	0.42	106.5	106.54	90.74	89.00	0.50	0.65
	sp3-CH3	5-OMe	57.0	139.3	139.34	57.51	55.95	1.05	0.31	139.5	139.54	57.30	55.77	1.23	0.23
	sp3-CH3	4''-OMe	53.4	141.0	141.03	55.75	54.21	0.81	0.43	141.4	141.40	55.37	53.86	0.46	0.66

Figure S8. Calculated ^{13}C chemical shifts of **A**–**B** fitting with the experimental data of compound **2**(**B**) following STS protocol.

Note:
Pmean > 5% is the confidence interval

Note:
sp carbons include C≡N
sp2-CH/C for double bonds except carbonyl group
C=O includes only ketones and aldehydes

	A	B
MAE	1.59	1.26
RMS	1.87	1.50
P_{mean}	14.78%	20.97%
Prel	0.06%	99.94%

Heavy atom bear	Type of carbon	Carbon no.	Exptl δ	Shielding tenso	Corr Shielding	Calcd δ	Calcd δ (S	abs dev	P	Shielding t	Corr Shield	Calcd δ	Calcd δ (S	abs dev	P
	sp3-CH3	1	7.5	187.3	187.329689	7.74	6.83	0.67	0.52	187.4	187.44	7.63	6.58	0.92	0.37
	sp3-CH2/CH/C	2	32.5	166.4	166.4375169	29.95	28.86	3.64	0.00	166.3	166.29	30.10	28.95	3.55	0.00
	sp3-CH2/CH/C	3	95.0	99.0	98.95746973	98.43	96.79	1.79	0.11	98.3	98.28	99.12	97.66	2.66	0.02
	sp2-C	4	144.2	50.5	50.46089109	150.35	148.30	4.10	0.03	55.7	55.73	145.10	143.43	0.77	0.69
	sp3-CH2/CH/C	5	82.5	113.8	113.7586664	83.41	81.89	0.61	0.58	113.8	113.84	83.33	81.94	0.56	0.61
	sp3-CH2/CH/C	6	37.7	157.5	157.4965865	39.02	37.86	0.16	0.88	155.8	155.82	40.73	39.53	1.83	0.10
	sp3-CH2/CH/C	7	74.9	118.9	118.9230598	78.17	76.69	1.79	0.11	120.2	120.21	76.86	75.49	0.59	0.59
	sp2-C	8	138.6	61.7	61.70819481	139.14	137.18	1.42	0.46	59.9	59.93	140.91	139.26	0.66	0.73
	sp3-CH2/CH/C	9	42.0	151.3	151.27958	45.33	44.12	2.12	0.06	152.1	152.09	44.51	43.29	1.29	0.24
	sp3-CH2/CH/C	10	65.3	131.1	131.1350364	65.77	64.40	0.90	0.42	128.8	128.84	68.10	66.78	1.48	0.18
	X-C=O	1'	173.0	29.1	29.05811477	173.69	171.45	1.55	0.34	28.4	28.38	174.31	172.50	0.50	0.76
	sp3-CH2/CH/C	2'	43.5	152.3	152.3006551	44.30	43.09	0.41	0.71	152.6	152.62	43.97	42.75	0.75	0.50
	sp3-CH2/CH/C	3'	25.8	168.3	168.3297007	28.03	26.96	1.16	0.30	169.1	169.10	27.25	26.11	0.31	0.78
	sp3-CH3	4'	22.5	174.5	174.5492479	20.99	19.98	2.52	0.02	174.3	174.26	21.29	20.18	2.32	0.03
	sp3-CH3	5'	22.6	172.8	172.8065182	22.80	21.77	0.83	0.42	173.0	173.04	22.56	21.44	1.16	0.26
	X-C=O	1''	175.2	26.7	26.66916236	175.85	173.60	1.60	0.32	26.9	26.91	175.64	173.83	1.37	0.40
	sp3-CH2/CH/C	2''	28.4	165.5	165.4576354	30.94	29.85	1.45	0.19	165.7	165.71	30.69	29.53	1.13	0.31
	sp3-CH2/CH/C	3''	24.1	168.5	168.4845208	27.87	26.80	2.70	0.02	168.9	168.90	27.45	26.31	2.21	0.05
	sp3-CH2/CH/C	4''	89.7	107.8	107.7951799	89.46	87.90	1.80	0.10	106.5	106.54	90.74	89.31	0.39	0.73
	sp3-CH3	5-OMe	57.0	139.3	139.3351354	57.51	56.20	0.80	0.44	139.5	139.54	57.30	56.02	0.98	0.34
	sp3-CH3	4''-OMe	53.0	141.0	141.0276343	55.75	54.46	1.46	0.16	141.4	141.40	55.37	54.11	1.11	0.28

Table S6. Energy analysis for conformers of **AA-AE** at B3LYP/TZVP level in methanol with IEFPCM model

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
AA	-1401.528089	-1401.497559	-1401.496615	-1401.590853	0.000437	0.274222	35.76%
AB	-1401.526354	-1401.496060	-1401.495116	-1401.587923	0.003367	2.112824	1.60%
AC	-1401.528104	-1401.497542	-1401.496597	-1401.591290	0.000000	0.000000	56.82%
AD	-1401.524348	-1401.493939	-1401.492994	-1401.586702	0.004588	2.879014	0.44%
AE	-1401.526867	-1401.496542	-1401.495598	-1401.589065	0.002225	1.396209	5.38%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S9. Main conformers of **A**.

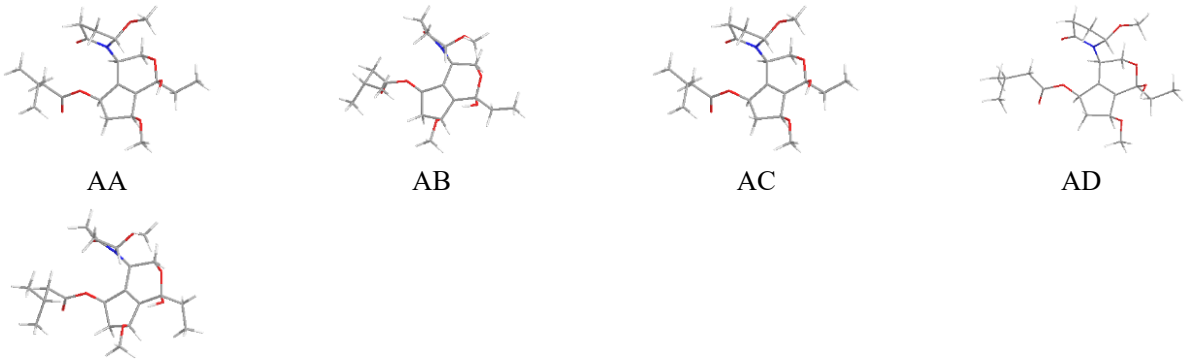
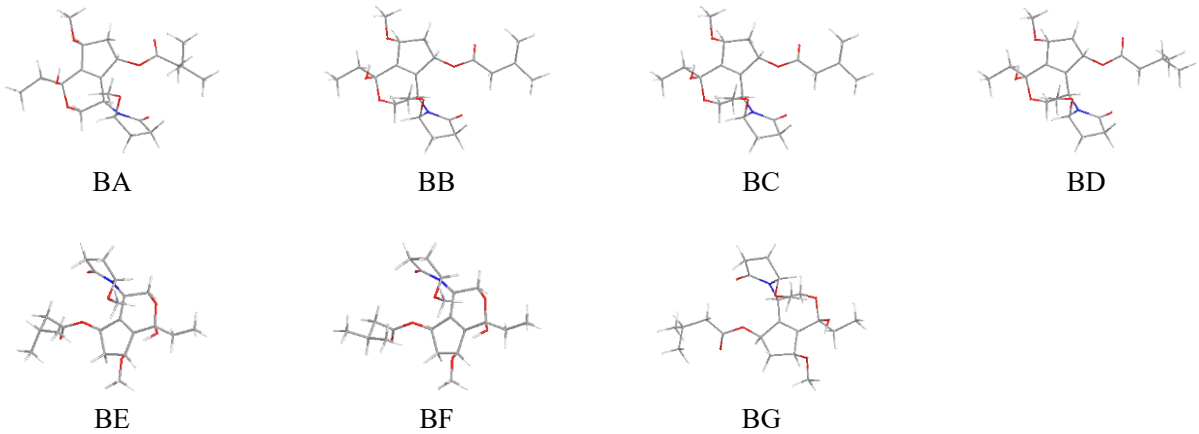


Table S7. Energy analysis for conformers of **BA-BG** at B3LYP/TZVP level in methanol with IEFPCM model

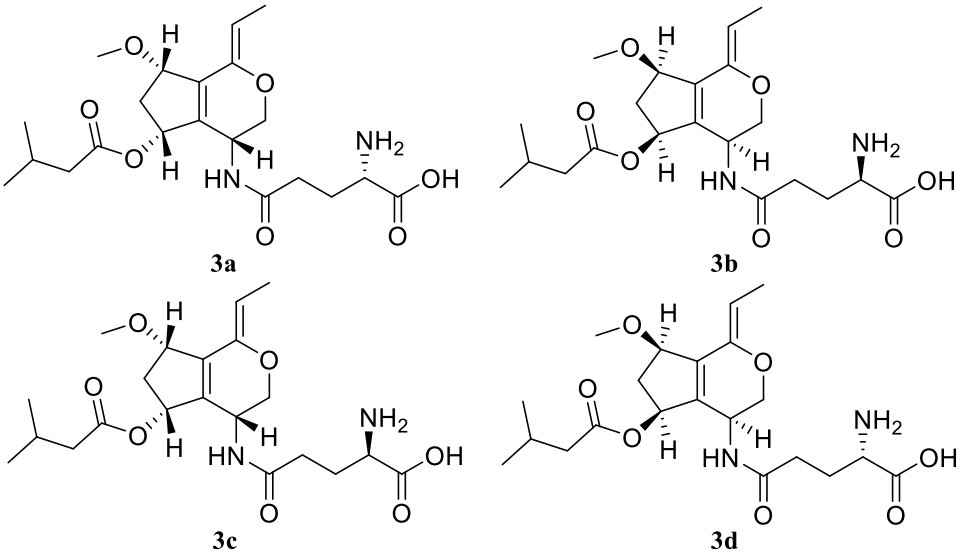
Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
BA	-1401.527661	-1401.497219	-1401.496275	-1401.589834	0.000000	0.000000	62.03%
BB	-1401.525616	-1401.495174	-1401.494230	-1401.587716	0.002118	1.329065	6.57%
BC	-1401.524747	-1401.494328	-1401.493383	-1401.587131	0.002703	1.696158	3.54%
BD	-1401.525719	-1401.495139	-1401.494195	-1401.588828	0.001006	0.631275	21.36%
BE	-1401.524291	-1401.494022	-1401.493078	-1401.585600	0.004234	2.656875	0.70%
BF	-1401.524855	-1401.494433	-1401.493489	-1401.586750	0.003084	1.935239	2.36%
BG	-1401.523860	-1401.493276	-1401.492331	-1401.587106	0.002728	1.711846	3.44%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S10. Main conformers of **B**



S1.3. Computational details for pardinumone C (3) (ECD).



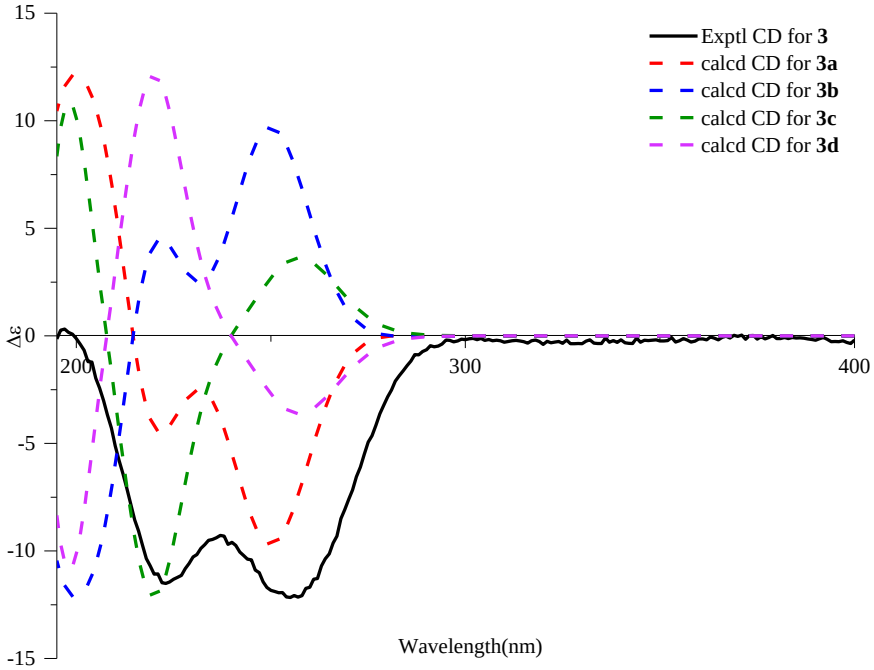


Figure S11. Calculated ECD spectra for **3a-3d** at the mPW1PW91/TZVP level in methanol with PCM model (**3a** and **3b**: $\sigma = 0.25$ eV, UV shift -10 nm; **3c** and **3d**: $\sigma = 0.25$ eV, UV shift -5 nm). Experimental CD spectra of **3** (black line) in MeOH.

Table S8. Energy analysis for conformers of **3aA-3aG** at B3LYP/6-31G* level in the gas phase

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
3aA	-1455.181361	-1455.149429	-1455.148485	-1455.248826	0.000633	0.397214	14.66%
3aB	-1455.181198	-1455.149448	-1455.148504	-1455.246757	0.002702	1.695531	1.64%
3aC	-1455.182776	-1455.151141	-1455.150197	-1455.249362	0.000097	0.060868	25.87%
3aD	-1455.184197	-1455.152720	-1455.151776	-1455.249459	0.000000	0.000000	28.67%
3aE	-1455.179584	-1455.147725	-1455.146781	-1455.247439	0.002020	1.267569	3.37%
3aF	-1455.182941	-1455.151427	-1455.150482	-1455.248705	0.000754	0.473142	12.90%
3aG	-1455.182941	-1455.151427	-1455.150482	-1455.248705	0.000754	0.473142	12.90%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S12. Main conformers of 3a

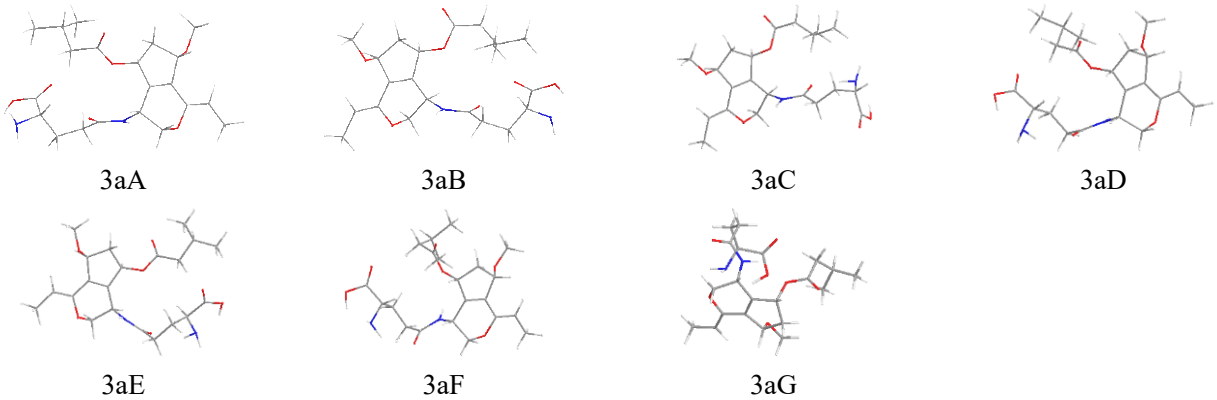


Table S9. Energy analysis for conformers of **3bA-3bE** at B3LYP/6-31G* level in the gas phase

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
3bA	-1455.189273	-1455.158156	-1455.157212	-1455.251935	0.002097	1.315887	8.71%
3bB	-1455.193011	-1455.162360	-1455.161416	-1455.254032	0.000000	0.000000	80.37%
3bC	-1455.189094	-1455.157926	-1455.156982	-1455.251781	0.002251	1.412524	7.40%
3bD	-1455.187282	-1455.156140	-1455.155196	-1455.249902	0.004130	2.591614	1.01%
3bE	-1455.185902	-1455.154285	-1455.153341	-1455.250763	0.003269	2.051329	2.51%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S13. Main conformers of 3b

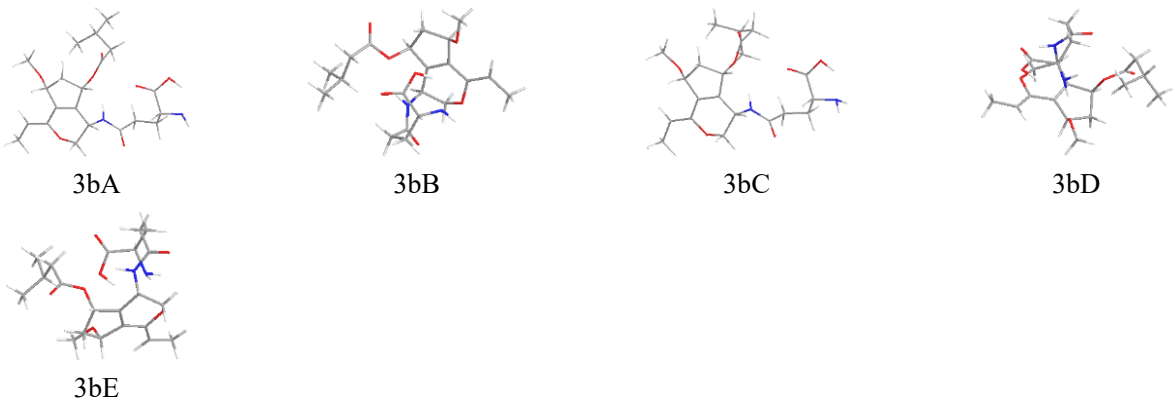


Table S10. Energy analysis for conformers of **3cA-3cH** at B3LYP/6-31G* level in the gas phase

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
3cA	-1455.185992	-1455.154694	-1455.153750	-1455.250442	0.002635	1.653488	2.61%
3cB	-1455.185993	-1455.154694	-1455.153750	-1455.250449	0.002628	1.649095	2.63%
3cC	-1455.188742	-1455.157369	-1455.156424	-1455.253077	0.000000	0.000000	42.58%
3cD	-1455.186708	-1455.155295	-1455.154350	-1455.251218	0.001859	1.166540	5.94%
3cE	-1455.187019	-1455.155442	-1455.154498	-1455.252417	0.000660	0.414156	21.15%
3cF	-1455.187019	-1455.155442	-1455.154498	-1455.252418	0.000659	0.413529	21.18%
3cG	-1455.185587	-1455.154318	-1455.153373	-1455.250173	0.002904	1.822288	1.96%
3cH	-1455.185587	-1455.154318	-1455.153373	-1455.250173	0.002904	1.822288	1.96%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S14. Main conformers of 3c

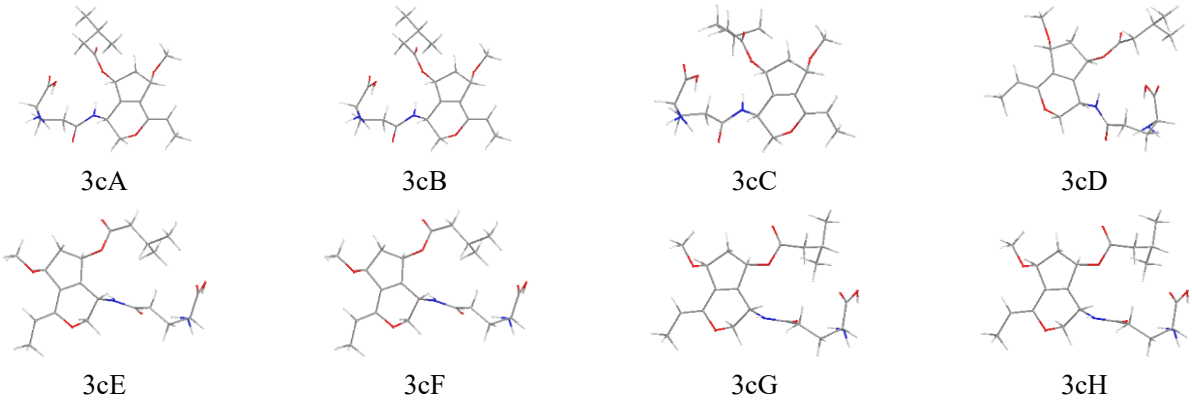
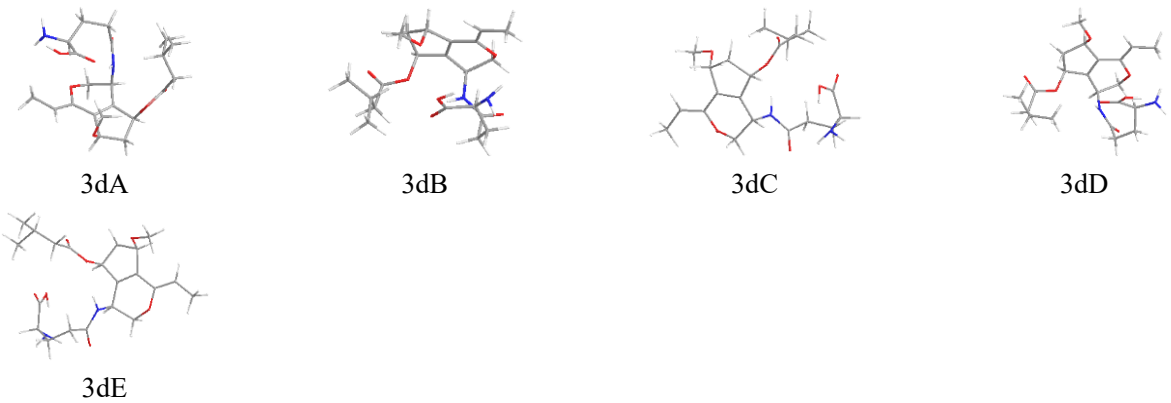


Table S11. Energy analysis for conformers of **3dA-3dE** at B3LYP/6-31G* level in the gas phase

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
3dA	-1455.194240	-1455.163267	-1455.162323	-1455.256525	0.000000	0.000000	84.42%
3dB	-1455.190270	-1455.159035	-1455.158091	-1455.254119	0.002406	1.509788	6.59%
3dC	-1455.189211	-1455.157943	-1455.156999	-1455.253464	0.003061	1.920807	3.29%
3dD	-1455.189211	-1455.157943	-1455.156999	-1455.253464	0.003061	1.920807	3.29%
3dE	-1455.189795	-1455.158650	-1455.157706	-1455.253165	0.003360	2.108432	2.40%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S15. Main conformers of 3d



S1.4. Computational details for pardinumone C (3) (NMR).

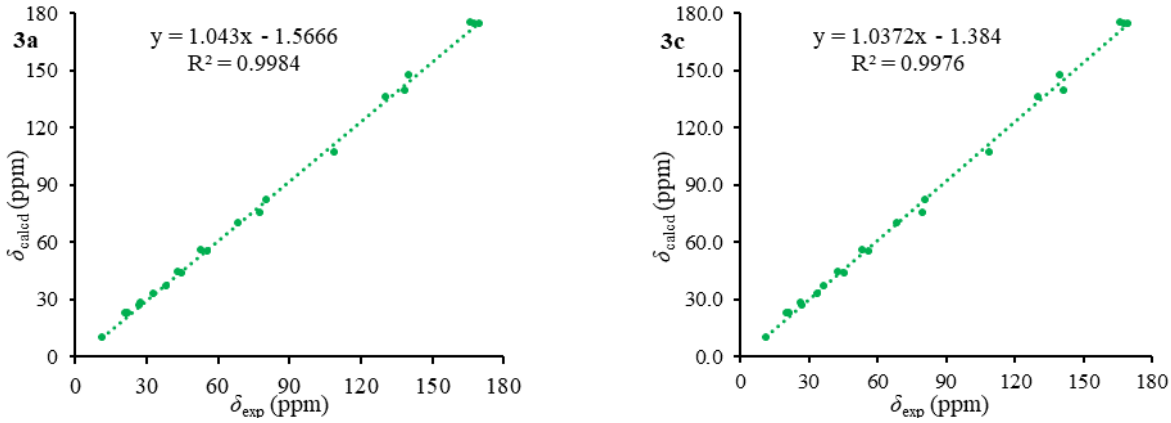


Figure S16. Regression analysis of experimental versus calculated ^{13}C NMR chemical shifts of **3**.

Table S12. Experimental and calculated ^{13}C NMR data of **3**.

No.	δ_{Exp}	3a			3c		
		δ_{Calcd}[a]	δ_{Corr}[b]	Relative errors[c]	δ_{Calcd}[a]	δ_{Corr}[b]	Relative errors[c]
1	10.1	11.4	10.3	-0.2	11.4	10.5	-0.4
2	106.9	108.9	112.0	-5.1	108.9	111.5	-4.6
3	147.4	140.3	144.7	2.7	140.1	144.0	3.4
4	139.5	138.4	142.8	-3.3	141.4	145.2	-5.7
5	82.5	80.1	82.0	0.5	80.9	82.5	0.0
6	37.1	38.4	38.5	-1.4	36.5	36.5	0.6
7	75.2	77.7	79.5	-4.3	79.6	81.2	-6.0
8	135.9	130.4	134.4	1.5	130.1	133.6	2.3
9	43.5	44.6	45.0	-1.5	45.8	46.1	-2.6
10	70.0	68.7	70.0	0.0	68.7	69.9	0.1
1′	174.4	167.5	173.1	1.3	167.8	172.6	1.8
2′	44.3	43.0	43.3	1.0	43.0	43.2	1.1
3′	27.0	26.8	26.4	0.6	27.3	26.9	0.1
4′	22.7	22.2	21.6	1.1	20.4	19.8	2.9
5′	22.8	20.9	20.2	2.6	21.7	21.1	1.7
1″	175.0	165.8	171.4	3.6	166.3	171.1	3.9
2″	33.1	32.9	32.8	0.3	33.6	33.4	-0.3
3″	28.0	27.4	27.0	1.0	26.4	26.0	2.0
4″	55.7	53.1	53.8	1.9	53.6	54.2	1.5
5″	174.4	169.6	175.3	-0.9	169.6	174.6	-0.2
5-OCH_3	55.1	55.7	56.5	-1.4	56.0	56.7	-1.6
			RMSD	2.19		RMSD	2.72

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta$exp − δcorr.

Figure S17. Calculated ^{13}C chemical shifts of **3a** and **3c** fitting with the experimental data of compound **3** following STS protocol.

Note:
Pmean > 5% is the confidence interval

Note:
sp carbons include C≡N
sp2-CH/C for double bonds except carbonyl group
C=O includes only ketones and aldehydes

MAE	1.77
RMS	2.35
P_{mean}	12.01%
Prel	100.00%

MAE	2.14
RMS	2.75
P_{mean}	6.39%
Prel	0.00%

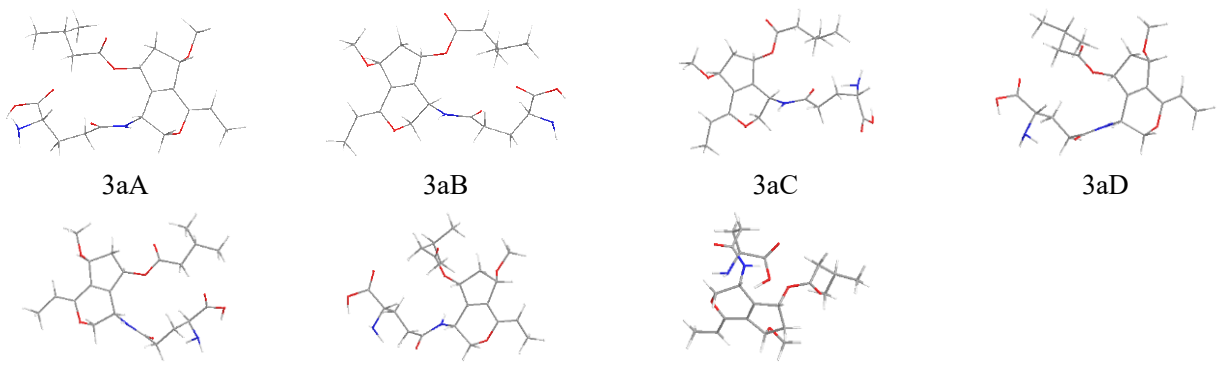
				3a						3c					
Heavy atom bear	Type of carbon	Carbon no.	Exptl δ	Shielding tenso	Corr Shielding	Calcd δ	Calcd δ (Sl	abs dev	P	Shielding t	Corr Shield	Calcd δ	Calcd δ (Sl	abs dev	P
	sp3-CH3	1	10.1	183.9	183.86	11.34	10.47	0.37	0.72	183.8	183.83	11.37	10.60	0.50	0.63
	sp2-CH	2	106.9	86.4	86.36	115.31	113.97	7.07	0.00	86.4	86.38	115.29	113.53	6.63	0.00
	sp2-C	3	147.4	55.0	54.98	145.85	144.37	3.03	0.12	55.1	55.12	145.71	143.65	3.75	0.05
	sp2-C	4	139.5	56.9	56.89	143.95	142.48	2.98	0.12	53.9	53.90	146.92	144.85	5.35	0.01
	sp3-CH2/CH/C	5	82.5	115.1	115.14	82.01	80.82	1.68	0.13	114.4	114.41	82.75	81.29	1.21	0.28
	sp3-CH2/CH/C	6	37.1	156.9	156.89	39.64	38.64	1.54	0.16	158.8	158.77	37.73	36.71	0.39	0.72
	sp3-CH2/CH/C	7	75.2	117.5	117.55	79.56	78.39	3.19	0.00	115.6	115.64	81.49	80.05	4.85	0.00
	sp2-C	8	135.9	64.9	64.89	135.97	134.54	1.36	0.48	65.2	65.16	135.69	133.74	2.16	0.26
	sp3-CH2/CH/C	9	43.5	150.7	150.66	45.96	44.94	1.44	0.20	149.4	149.44	47.20	46.08	2.58	0.02
	sp3-CH2/CH/C	10	70.0	126.6	126.60	70.38	69.24	0.76	0.49	126.6	126.58	70.40	69.06	0.94	0.40
	X-C=O	1'	174.4	27.8	27.77	174.85	173.25	1.15	0.48	27.5	27.47	175.13	172.79	1.61	0.32
	sp3-CH2/CH/C	2'	44.3	152.3	152.26	44.34	43.32	0.98	0.38	152.3	152.28	44.32	43.23	1.07	0.34
	sp3-CH2/CH/C	3'	27.0	168.4	168.44	27.91	26.97	0.03	0.98	168.0	167.95	28.41	27.48	0.48	0.67
	sp3-CH3	4'	22.7	173.0	173.03	22.56	21.64	1.06	0.30	174.9	174.87	20.66	19.79	2.91	0.01
	sp3-CH3	5'	22.8	174.4	174.39	21.15	20.24	2.56	0.01	173.5	173.54	22.04	21.16	1.64	0.11
	X-C=O	1"	175.0	29.5	29.47	173.31	171.72	3.28	0.05	29.0	29.01	173.73	171.41	3.59	0.03
	sp3-CH2/CH/C	2"	33.1	162.3	162.33	34.11	33.14	0.04	0.97	161.7	161.70	34.76	33.76	0.66	0.55
	sp3-CH2/CH/C	3"	28.0	167.9	167.87	28.49	27.55	0.45	0.68	168.8	168.83	27.52	26.59	1.41	0.21
	sp3-CH2/CH/C	4"	55.7	142.2	142.20	54.55	53.48	2.22	0.05	141.6	141.64	55.12	53.93	1.77	0.11
	C=O	5"	174.4	25.7	25.65	176.85	175.24	0.84	0.59	25.6	25.63	176.88	174.53	0.13	0.94
	sp3-CH3	5-OMe	55.1	139.6	139.58	57.26	56.18	1.08	0.29	139.3	139.27	57.58	56.37	1.27	0.22

Table S13. Energy analysis for conformers of **3aA-3aG** at B3LYP/TZVP level in methanol with IEFPCM model

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
3aA	-1455.734973	-1455.702995	-1455.702051	-1455.801873	0.001164	0.730421	10.51%
3aB	-1455.733972	-1455.701850	-1455.700906	-1455.800667	0.002370	1.487198	2.93%
3aC	-1455.735535	-1455.703518	-1455.702574	-1455.803037	0.000000	0.000000	36.07%
3aD	-1455.733907	-1455.701867	-1455.700923	-1455.801899	0.001138	0.714106	10.80%
3aE	-1455.735661	-1455.703811	-1455.702867	-1455.802531	0.000506	0.317520	21.10%
3aF	-1455.734941	-1455.703103	-1455.702159	-1455.801760	0.001277	0.801330	9.32%
3aG	-1455.734940	-1455.703102	-1455.702158	-1455.801755	0.001282	0.804467	9.27%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S18. Main conformers of 3a



3aA 3aB 3aC 3aD

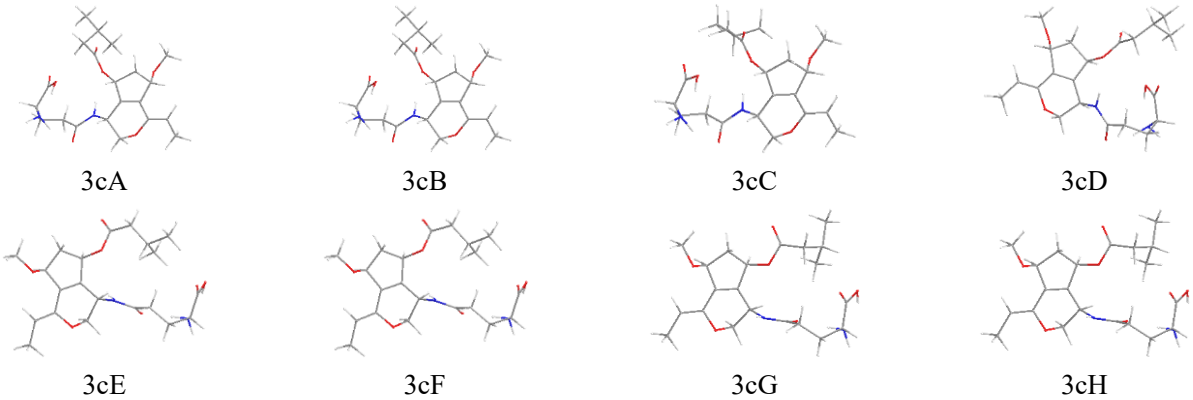
3aE 3aF 3aG

Table S14. Energy analysis for conformers of **3cA-3cH** at B3LYP/TZVP level in methanol with IEFPCM model

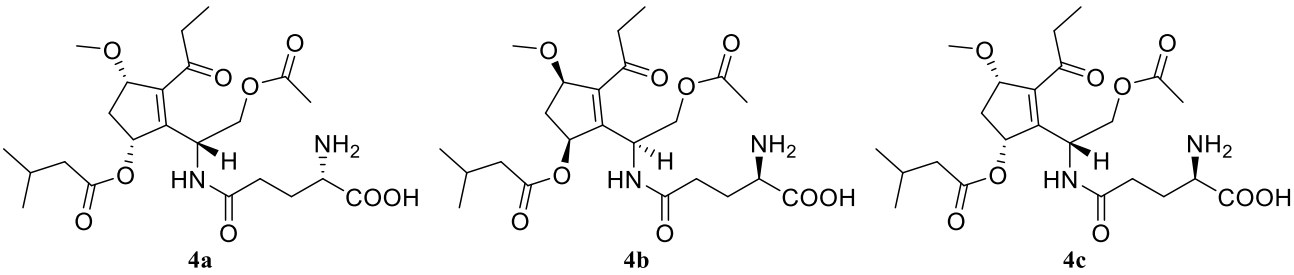
Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
3cA	-1455.733742	-1455.701894	-1455.700950	-1455.800406	0.002816	1.767067	1.89%
3cB	-1455.735152	-1455.703326	-1455.702382	-1455.801205	0.002017	1.265687	4.42%
3cC	-1455.735154	-1455.703327	-1455.702382	-1455.801214	0.002008	1.260039	4.46%
3cD	-1455.736023	-1455.704273	-1455.703329	-1455.801240	0.001982	1.243724	4.58%
3cE	-1455.734110	-1455.702106	-1455.701162	-1455.801751	0.001471	0.923066	7.88%
3cF	-1455.736341	-1455.704388	-1455.703443	-1455.803222	0.000000	0.000000	37.44%
3cG	-1455.736342	-1455.704388	-1455.703444	-1455.803222	0.000000	0.000000	37.44%
3cH	-1455.733743	-1455.701894	-1455.700950	-1455.800406	0.002816	1.767067	1.89%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S19. Main conformers of 3c



S1.5. Computational details for pardinumone D (4) (ECD).



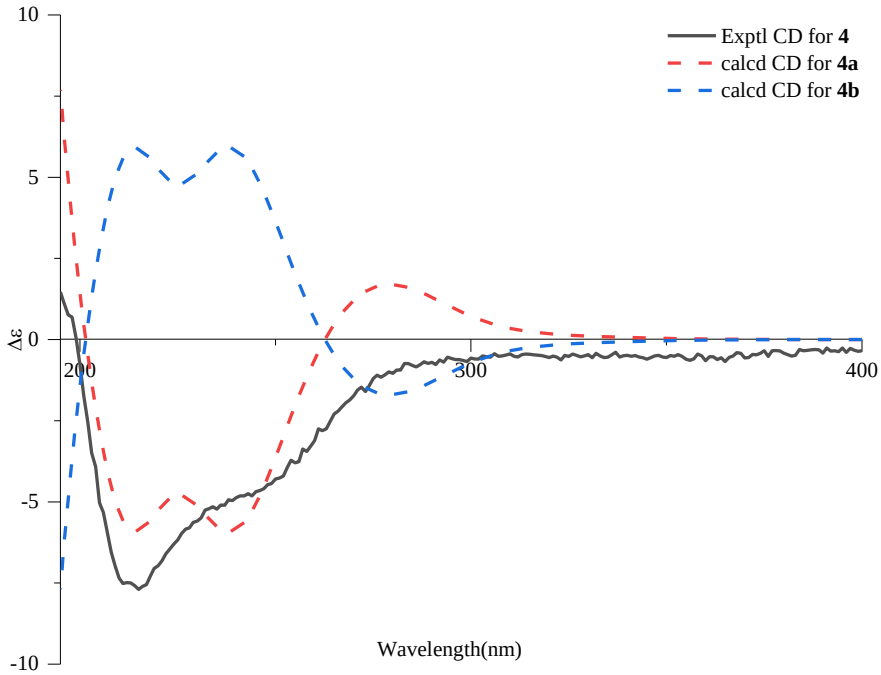


Figure S20. Calculated ECD spectra for **4a-4b** at the mPW1PW91/TZVP level in methanol with PCM model (**4a** and **4b**: σ = 0.30 eV, UV shift -8 nm). Experimental CD spectra of **4** (black line) in MeOH.

Table S15. Energy analysis for conformers of **4aA-4aH** at B3LYP/6-31G* level in the gas phase

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
4aA	-1684.242603	-1684.205529	-1684.204585	-1684.316163	0.004148	2.602909	0.51%
4aB	-1684.243094	-1684.206076	-1684.205132	-1684.316685	0.003626	2.275349	0.88%
4aC	-1684.241609	-1684.204468	-1684.203523	-1684.314148	0.006163	3.867341	0.06%
4aD	-1684.248454	-1684.211586	-1684.210642	-1684.320311	0.000000	0.000000	41.13%
4aE	-1684.248450	-1684.211583	-1684.210639	-1684.320298	0.000013	0.008158	40.57%
4aF	-1684.248580	-1684.211776	-1684.210832	-1684.319053	0.001258	0.789407	10.84%
4aG	-1684.245044	-1684.207891	-1684.206947	-1684.318485	0.001826	1.145832	5.94%
4aH	-1684.241863	-1684.205016	-1684.204072	-1684.314195	0.006116	3.837848	0.06%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S21. Main conformers of 4a

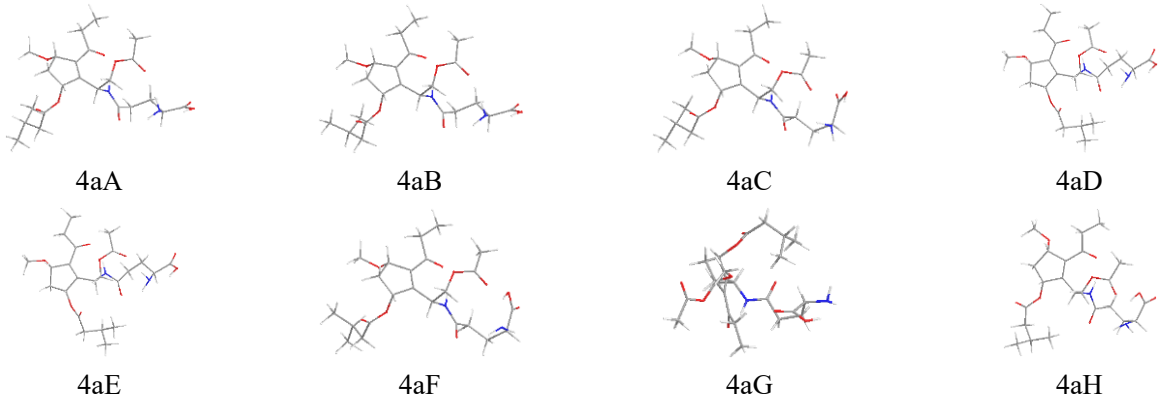
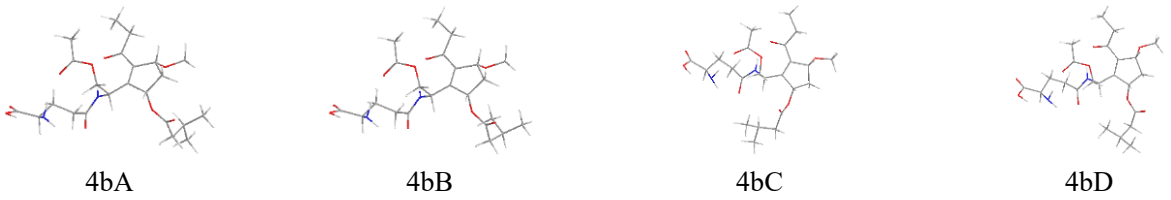


Table S16. Energy analysis for conformers of **4bA-4bH** at B3LYP/6-31G* level in the gas phase

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
4bA	-1684.243094	-1684.206076	-1684.205132	-1684.316682	0.003629	2.277232	1.01%
4bB	-1684.248453	-1684.211585	-1684.210641	-1684.320311	0.000000	0.000000	47.09%
4bC	-1684.245603	-1684.208711	-1684.207767	-1684.318560	0.001751	1.098769	7.36%
4bD	-1684.242437	-1684.205171	-1684.204227	-1684.316447	0.003864	2.424697	0.78%
4bE	-1684.245008	-1684.207897	-1684.206953	-1684.317833	0.002478	1.554969	3.41%
4bF	-1684.249103	-1684.212258	-1684.211314	-1684.319974	0.000337	0.211471	32.95%
4bG	-1684.246654	-1684.209763	-1684.208819	-1684.318405	0.001906	1.196033	6.25%
4bH	-1684.244172	-1684.207364	-1684.206420	-1684.316810	0.003501	2.196911	1.15%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S22. Main conformers of 4b



4bE 4bF 4bG 4bH

S1.6. Computational details for pardinumone D (4) (NMR).

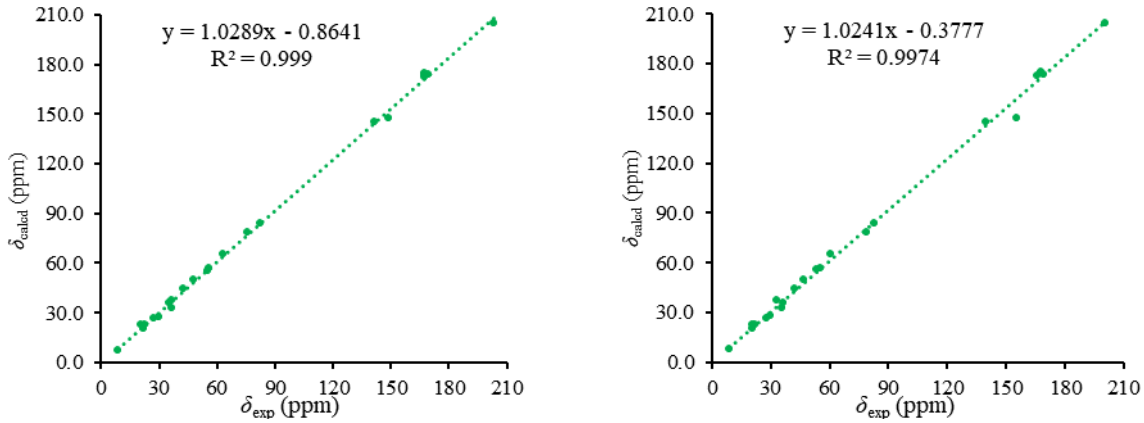


Figure S23. Regression analysis of experimental versus calculated ^{13}C NMR chemical shifts of **4**.

Table S17. Experimental and calculated ^{13}C NMR data of **4**.

No.	δ_{Exp}	4a			4c		
		δ_{Calcd}[a]	δ_{Corr}[b]	Relative errors[c]	δ_{Calcd}[a]	δ_{Corr}[b]	Relative errors[c]
1	7.6	8.9	8.2	-0.6	8.7	8.6	-1.0
2	35.8	35.5	35.7	0.1	36.5	37.0	-1.2
3	204.5	203.1	208.1	-3.6	200.4	204.8	-0.3
4	145.2	141.3	144.5	0.7	139.8	142.8	2.4
5	83.8	82.1	83.7	0.1	83.1	84.7	-0.9
6	37.4	36.5	36.7	0.7	33.3	33.7	3.7
7	78.4	76.0	77.4	1.0	78.9	80.5	-2.1
8	147.3	148.9	152.3	-5.0	155.6	158.9	-11.6
9	49.6	47.7	48.2	1.4	47.2	48.0	1.6
10	65.2	63.3	64.2	1.0	60.5	61.6	3.6
1′	173.9	167.6	171.5	2.4	167.8	171.4	2.5
2′	44.1	42.7	43.0	1.1	42.1	42.8	1.3
3′	26.9	27.3	27.2	-0.3	28.0	28.3	-1.4
4′	22.7	20.6	20.3	2.4	20.9	21.0	1.7
5′	22.7	22.4	22.2	0.5	22.2	22.3	0.4

1″	174.7	167.2	171.1	3.6	167.7	171.4	3.3
2″	32.7	36.8	37.0	-4.3	36.0	36.5	-3.8
3″	27.7	29.9	29.9	-2.2	30.2	30.5	-2.8
4″	55.7	55.0	55.7	0.0	53.5	54.4	1.3
5″	173.8	169.2	173.2	0.6	169.4	173.1	0.7
5-OCH_3	56.7	55.7	56.4	0.3	55.3	56.3	0.4
-OOC*CH_3*	20.7	21.8	21.5	-0.8	20.7	20.8	-0.1
-OO*C*CH_3	172.3	167.4	171.3	1.0	166.2	169.8	2.5
			RMSD	2.02		RMSD	3.17

[a]Weighted average from the calculated shifts; [b]Obtained by linear fit δexp versus δcalcd; [c]$\Delta\delta = \delta\text{exp} - \delta\text{corr}$.

Figure S24. Calculated ^{13}C chemical shifts of **4a** and **4c** fitting with the experimental data of compound **4** following STS protocol.

Note:
Pmean > 5% is the confidence interval

Note:
sp carbons include C=N
sp2-CH/C for double bonds except carbonyl group
C=O includes only ketones and aldehydes

	4a	4c
MAE	1.41	2.21
RMS	1.89	3.10
P_{mean}	17.20%	4.66%
Prel	100.00%	0.00%

Heavy atom bearin	Type of carbon	Carbon no.	Exptl δ	Shielding tensors	Corr Shielding	Calcd δ	Calcd δ (SC	abs dev	P	Shielding te	Corr Shield	Calcd δ	Calcd δ (SC	abs dev	P
	sp3-CH3	1	7.6	186.4	186.41	8.69	8.22	0.62	0.55	186.5	186.52	8.57	8.56	0.96	0.35
	sp3-CH2/CH/C	2	35.8	159.8	159.75	36.73	35.91	0.11	0.92	158.8	158.77	37.73	37.21	1.41	0.21
	C=O	3	204.5	-7.8	-7.79	207.74	204.77	0.27	0.86	-5.1	-5.11	205.26	201.83	2.67	0.09
	sp2-C	4	145.2	54.0	53.99	146.83	144.63	0.57	0.77	55.4	55.42	145.41	143.02	2.18	0.26
	sp3-CH2/CH/C	5	83.8	113.1	113.10	84.07	82.66	1.14	0.30	112.1	112.15	85.04	83.70	0.10	0.93
	sp3-CH2/CH/C	6	37.4	158.7	158.74	37.76	36.93	0.47	0.67	162.0	161.97	34.48	34.02	3.38	0.00
	sp3-CH2/CH/C	7	78.4	119.2	119.21	77.88	76.54	1.86	0.09	116.3	116.32	80.81	79.54	1.14	0.30
	sp2-C	8	147.3	46.4	46.38	154.42	152.12	4.82	0.01	39.7	39.70	161.08	158.41	11.11	0.00
	sp3-CH2/CH/C	9	49.6	147.6	147.59	49.08	48.10	1.50	0.18	148.0	148.03	48.63	47.92	1.68	0.13
	sp3-CH2/CH/C	10	65.2	132.0	132.01	64.88	63.71	1.49	0.18	134.7	134.74	62.11	61.17	4.03	0.00
	X-C=O	1'	173.9	27.7	27.70	174.92	172.37	1.53	0.34	27.5	27.49	175.11	172.21	1.69	0.30
	sp3-CH2/CH/C	2'	44.1	152.6	152.59	44.00	43.09	1.01	0.36	153.1	153.13	43.46	42.84	1.26	0.26
	sp3-CH2/CH/C	3'	26.9	168.0	168.00	28.37	27.65	0.75	0.50	167.2	167.24	29.14	28.77	1.87	0.09
	sp3-CH3	4'	22.7	174.7	174.65	20.89	20.27	2.43	0.02	174.4	174.39	21.16	20.92	1.78	0.09
	sp3-CH3	5'	22.7	172.9	172.88	22.72	22.08	0.62	0.55	173.1	173.09	22.51	22.25	0.45	0.66
	X-C=O	1''	174.7	28.1	28.11	174.55	172.00	2.70	0.10	27.5	27.52	175.08	172.17	2.53	0.12
	sp3-CH2/CH/C	2''	32.7	158.5	158.46	38.04	37.20	4.50	0.00	159.3	159.30	37.19	36.68	3.98	0.00
	sp3-CH2/CH/C	3''	27.7	165.4	165.38	31.02	30.27	2.57	0.02	165.1	165.08	31.32	30.91	3.21	0.00
	sp3-CH2/CH/C	4''	55.7	140.3	140.28	56.50	55.43	0.27	0.81	141.7	141.72	55.03	54.21	1.49	0.18
	COOH	5''	173.8	26.1	26.06	178.24	175.64	1.84	0.07	25.9	25.86	178.42	175.46	1.66	0.10
	sp3-CH3	5-OMe	56.7	139.6	139.61	57.23	56.15	0.55	0.60	139.9	139.91	56.91	56.06	0.64	0.53
	sp3-CH3	OOCMe	20.7	173.5	173.49	22.09	21.46	0.76	0.46	174.6	174.57	20.97	20.74	0.04	0.97
	X-C=O	OOCMe	172.3	27.9	27.91	174.73	172.18	0.12	0.94	29.1	29.07	173.68	170.79	1.51	0.35

Table S18. Energy analysis for conformers of **4aA-4aH** at B3LYP/TZVP level in methanol with IEFPCM model

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
4aA	-1684.885665	-1684.848000	-1684.847056	-1684.961755	0.001005	0.630647	12.29%
4aB	-1684.885035	-1684.847427	-1684.846483	-1684.961041	0.001719	1.078689	5.77%
4aC	-1684.882606	-1684.844750	-1684.843806	-1684.958920	0.003840	2.409636	0.61%
4aD	-1684.887791	-1684.850231	-1684.849287	-1684.962760	0.000000	0.000000	35.65%
4aE	-1684.887791	-1684.850231	-1684.849287	-1684.962744	0.000016	0.010040	35.05%
4aF	-1684.885573	-1684.847816	-1684.846871	-1684.960997	0.001763	1.106299	5.50%
4aG	-1684.885410	-1684.847786	-1684.846841	-1684.959581	0.003179	1.994853	1.23%
4aH	-1684.883409	-1684.845463	-1684.844519	-1684.960672	0.002088	1.310240	3.90%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

Figure S25. Main conformers of 4a

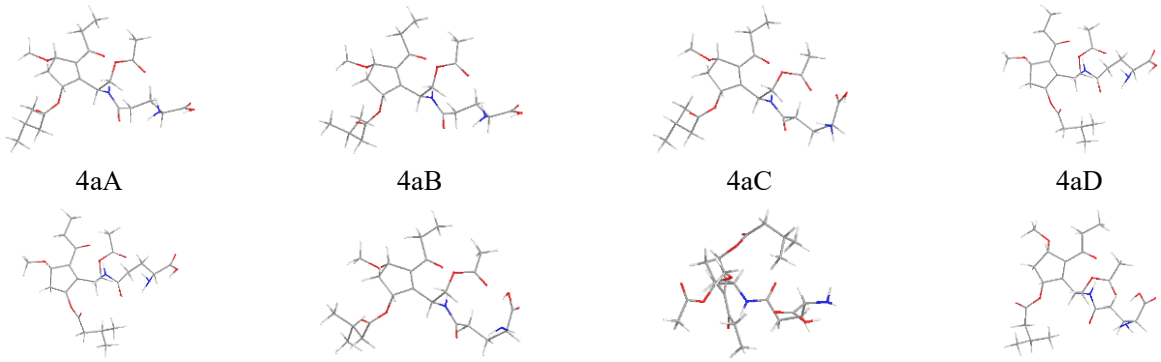
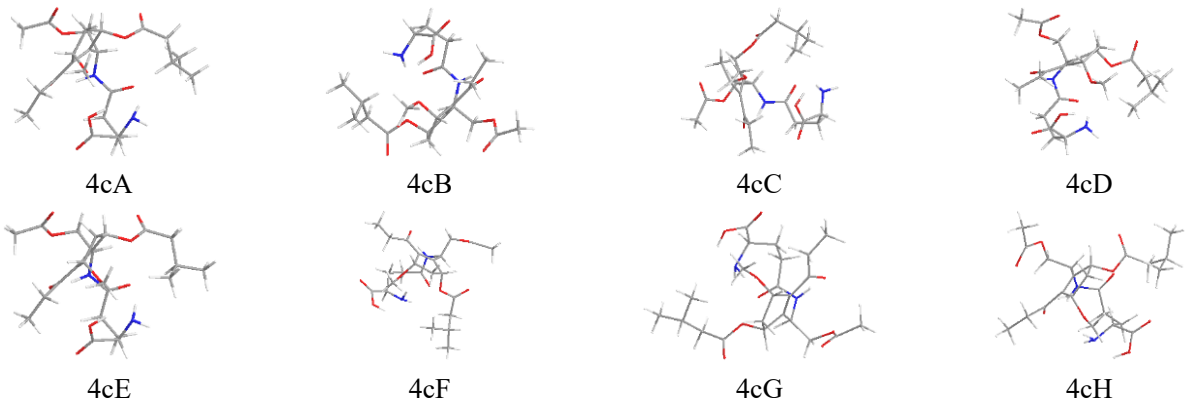


Table S19. Energy analysis for conformers of **4cA-4cH** at B3LYP/TZVP level in methanol with IEFPCM model

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔG*	*ΔE*(kcal/mol)	*PE*%
4bA	-1684.888557	-1684.851106	-1684.850162	-1684.961220	0.002513	1.576931	2.96%
4bB	-1684.887855	-1684.850385	-1684.849441	-1684.960546	0.003187	1.999873	1.45%
4bC	-1684.886834	-1684.849489	-1684.848545	-1684.960051	0.003682	2.310490	0.86%
4bD	-1684.888168	-1684.850460	-1684.849516	-1684.963733	0.000000	0.000000	42.46%
4bE	-1684.887633	-1684.850103	-1684.849158	-1684.962433	0.001300	0.815762	10.71%
4bF	-1684.889956	-1684.852411	-1684.851467	-1684.963275	0.000458	0.287399	26.13%
4bG	-1684.885596	-1684.848093	-1684.847149	-1684.959440	0.004293	2.693898	0.45%
4bH	-1684.888261	-1684.850735	-1684.849791	-1684.962750	0.000983	0.616842	14.98%

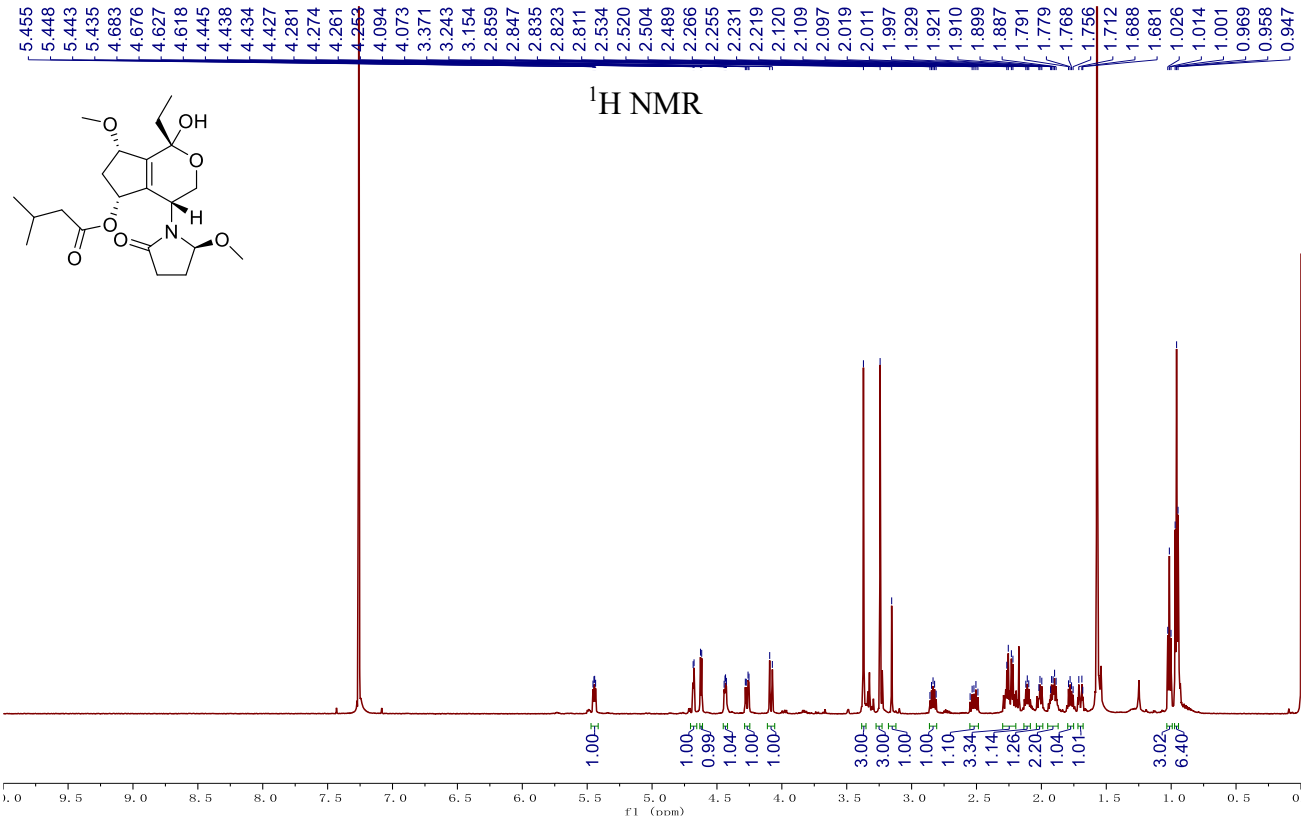
E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

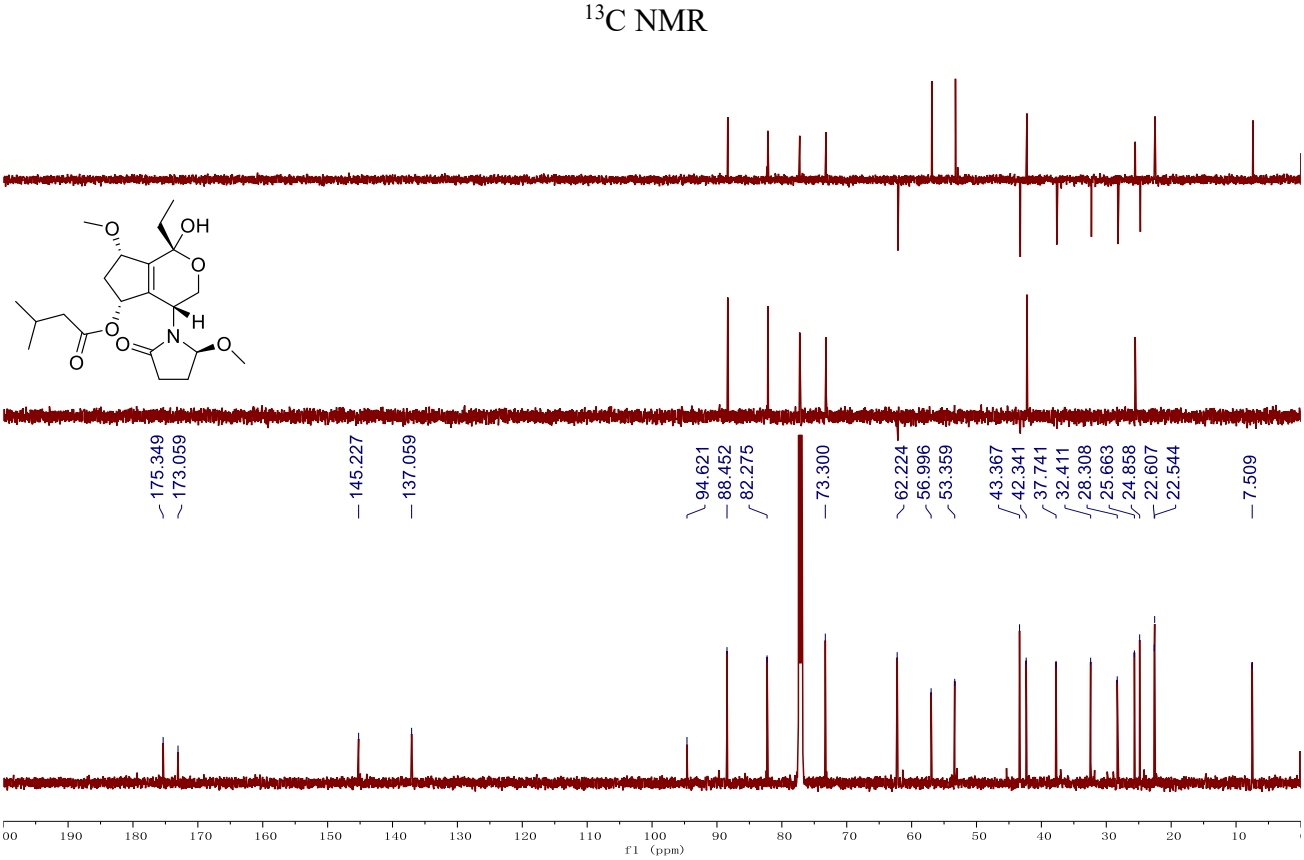
Figure S26. Main conformers of 4c

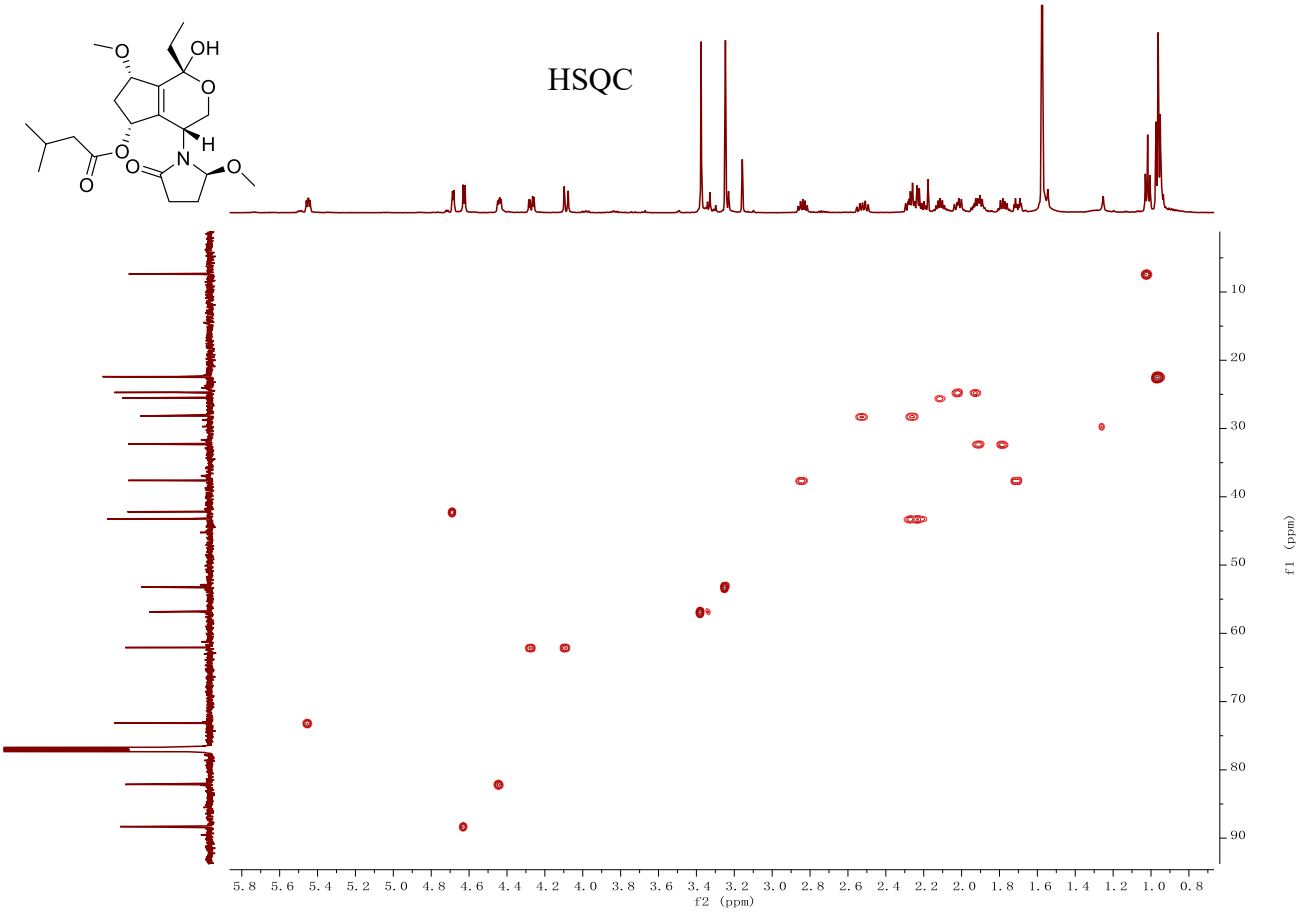


Sections S2 Supplementary of NMR and HRESIMS

S2.1 NMR and HRESIMS spectra of pardinumone A (1)



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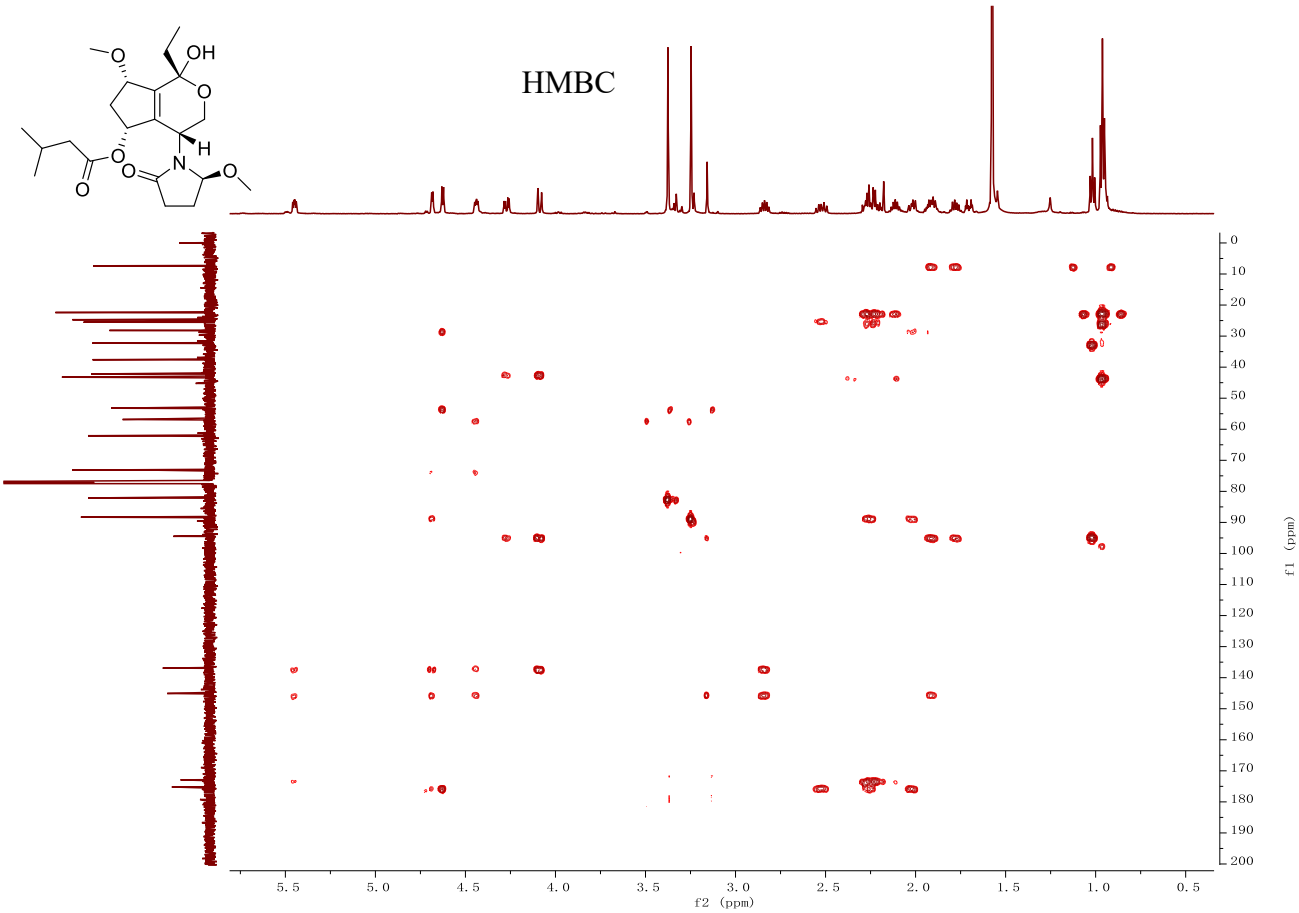
f2 (ppm)
f1 (ppm)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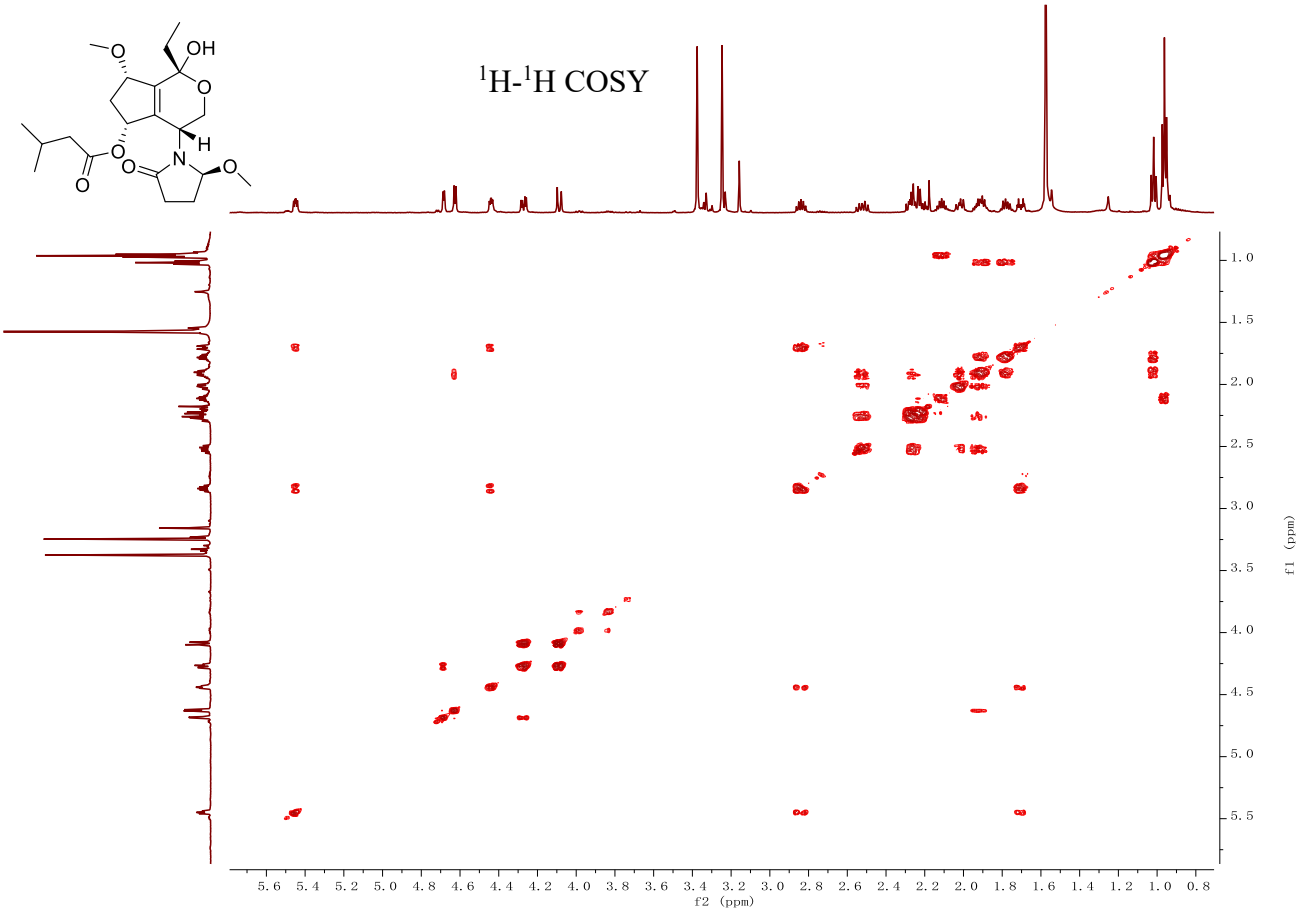
^{1}H-^{1}H COSY
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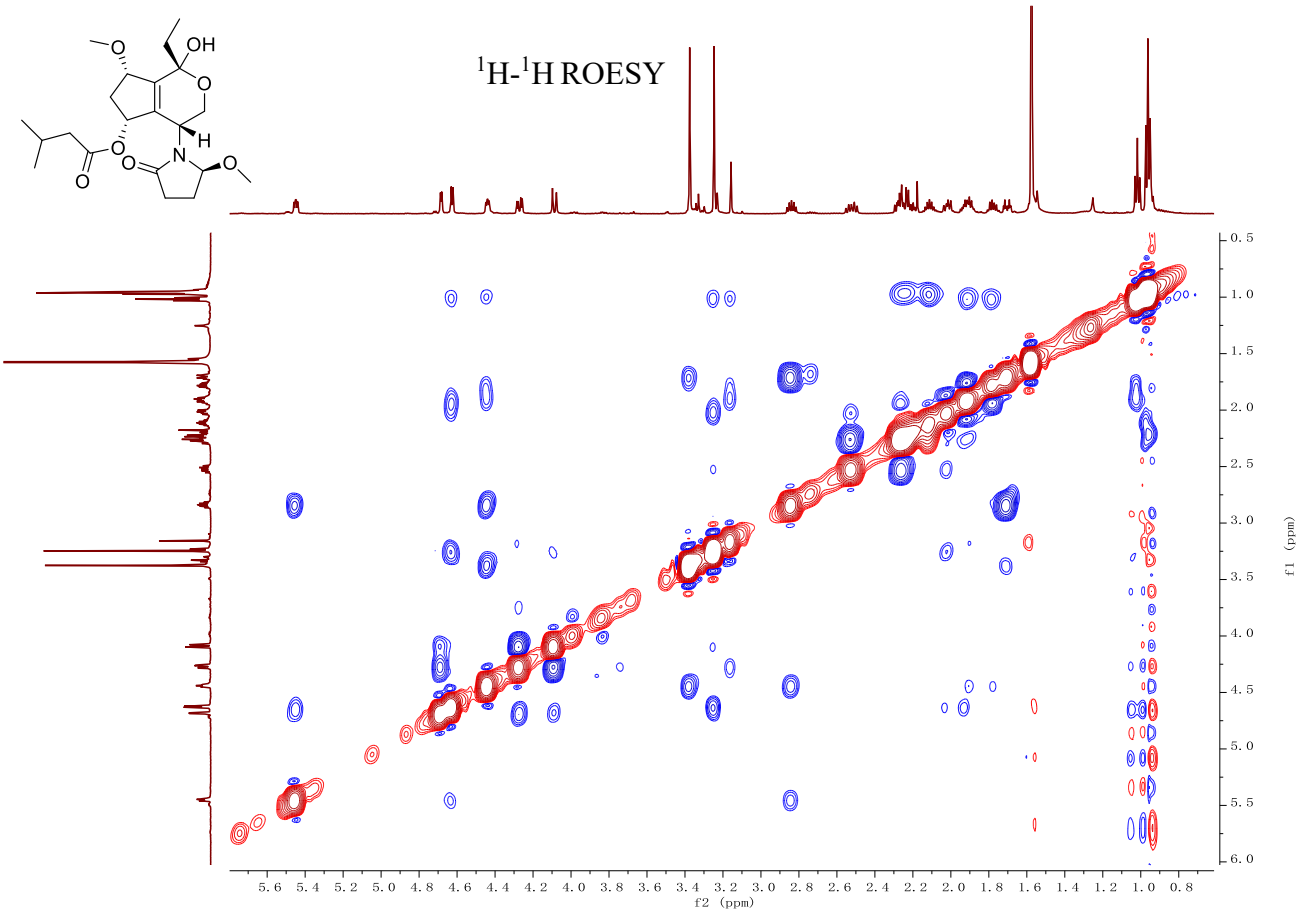
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f2 (ppm)
f1 (ppm)

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
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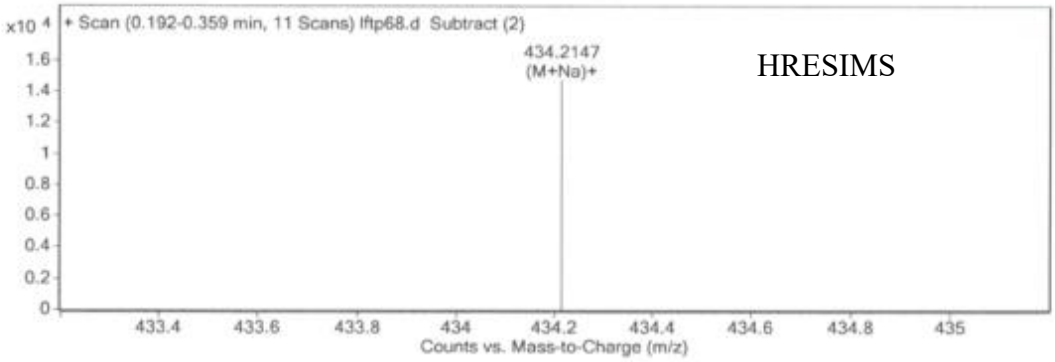
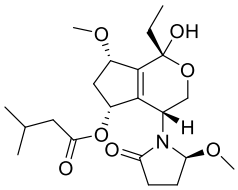


Peak List

m/z	z	Abund	Formula	Ion
274.274	1	32532.61		
275.2772	1	6295.54		
292.1543		5933.59		
302.3051	1	8636.97		
318.3002	1	13053.87		
434.2147	1	14808.72	C21 H33 N O7	(M+Na)+
448.2303	1	7691.22		
450.1885	1	10356.26		



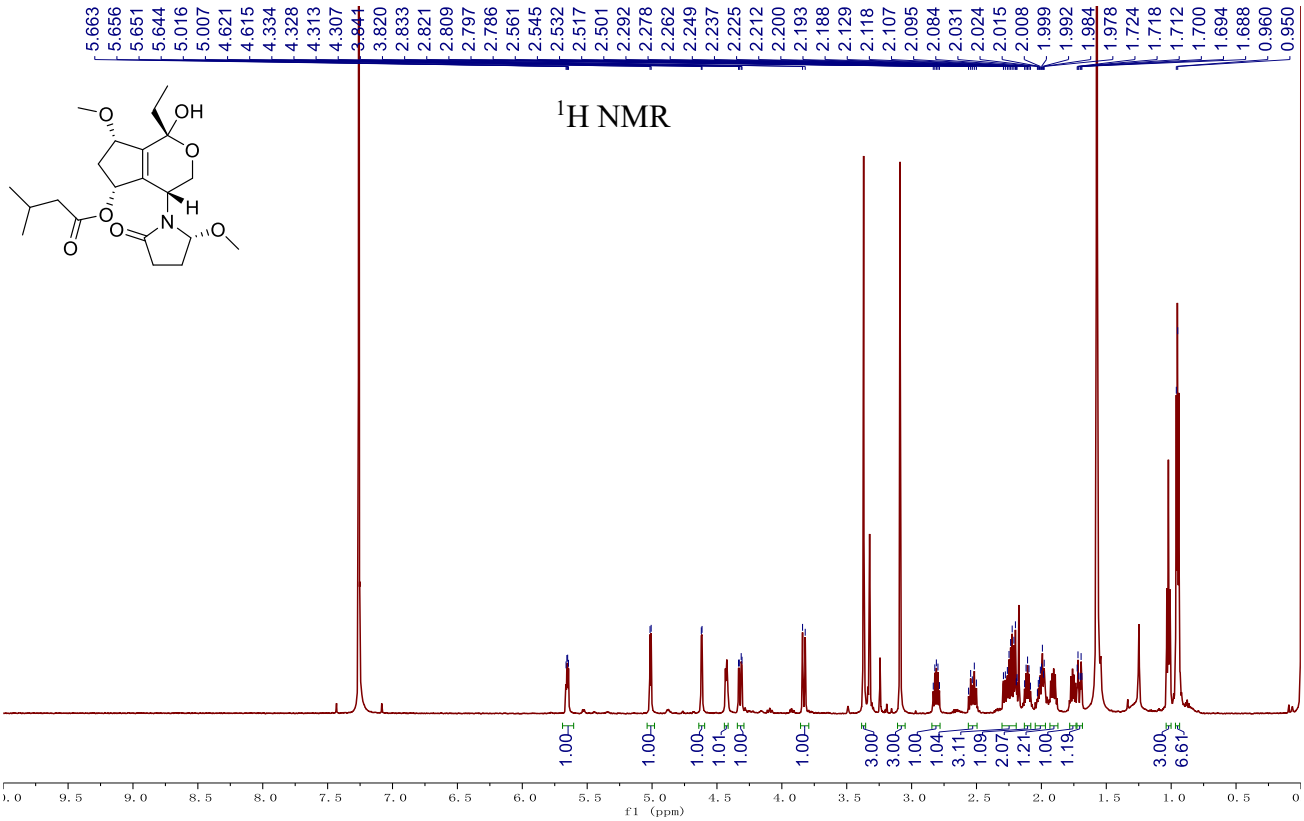
Formula Calculator Element Limits

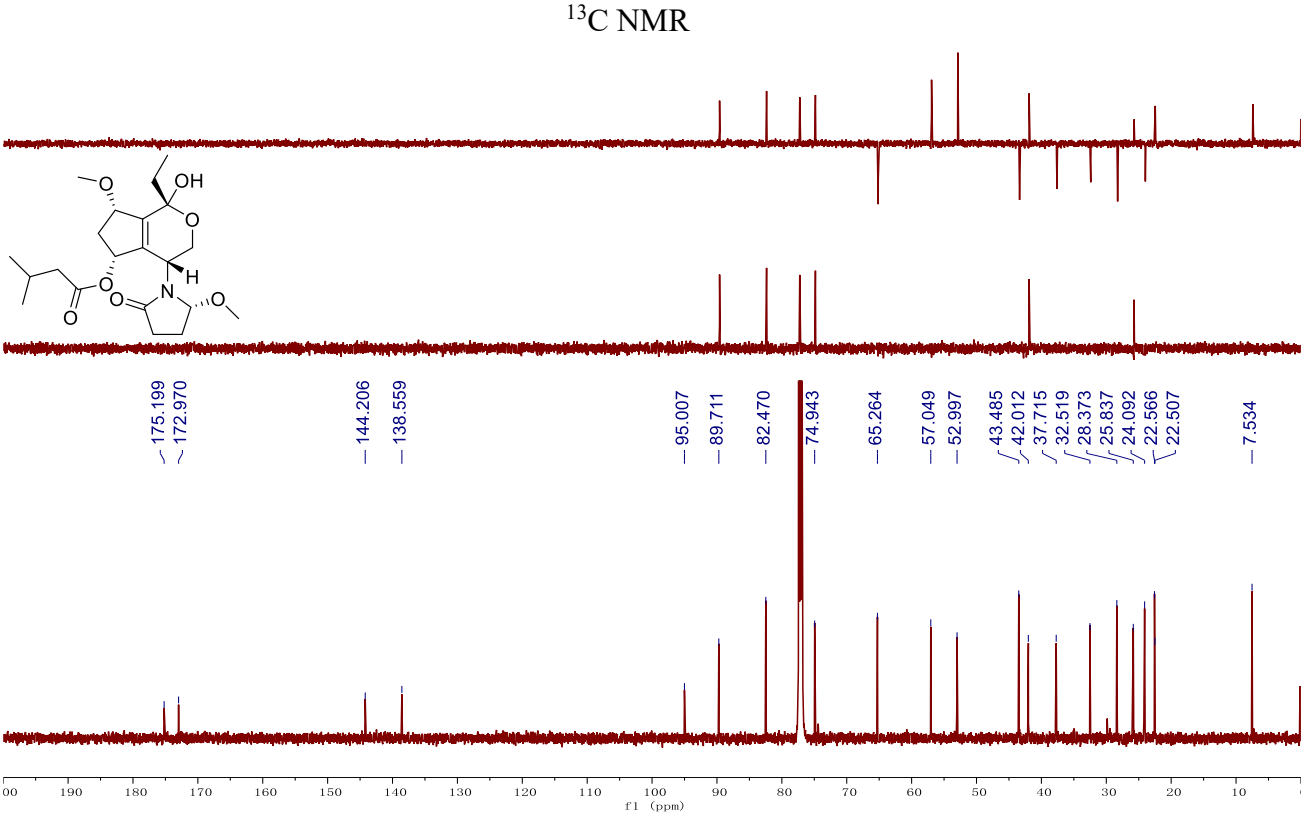
Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	30

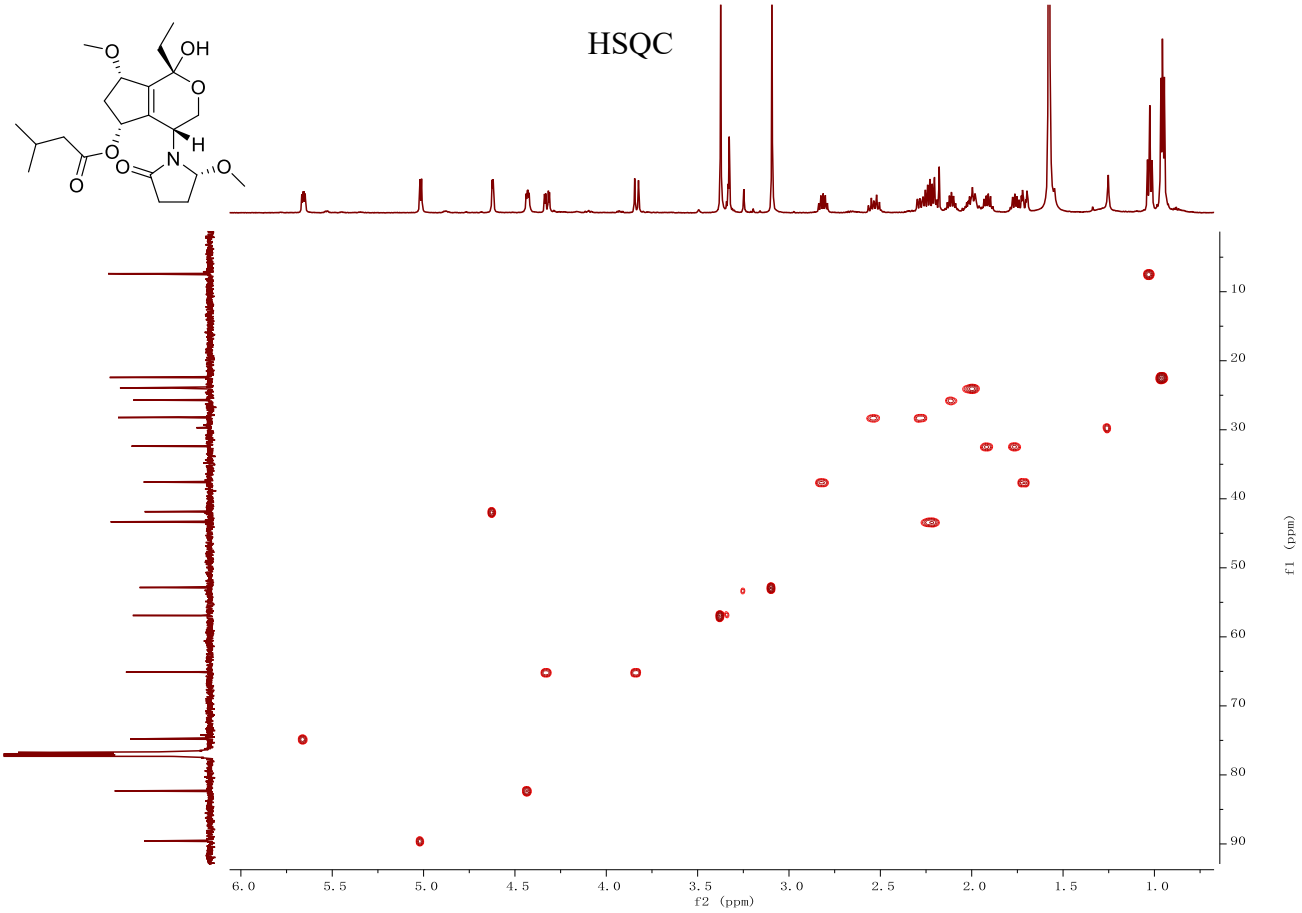
Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C21 H33 N O7	411.2257	434.2149	434.2147	0.2	0.6	6.0000

S2.2 NMR and HRESIMS spectra of pardinumone B (2)



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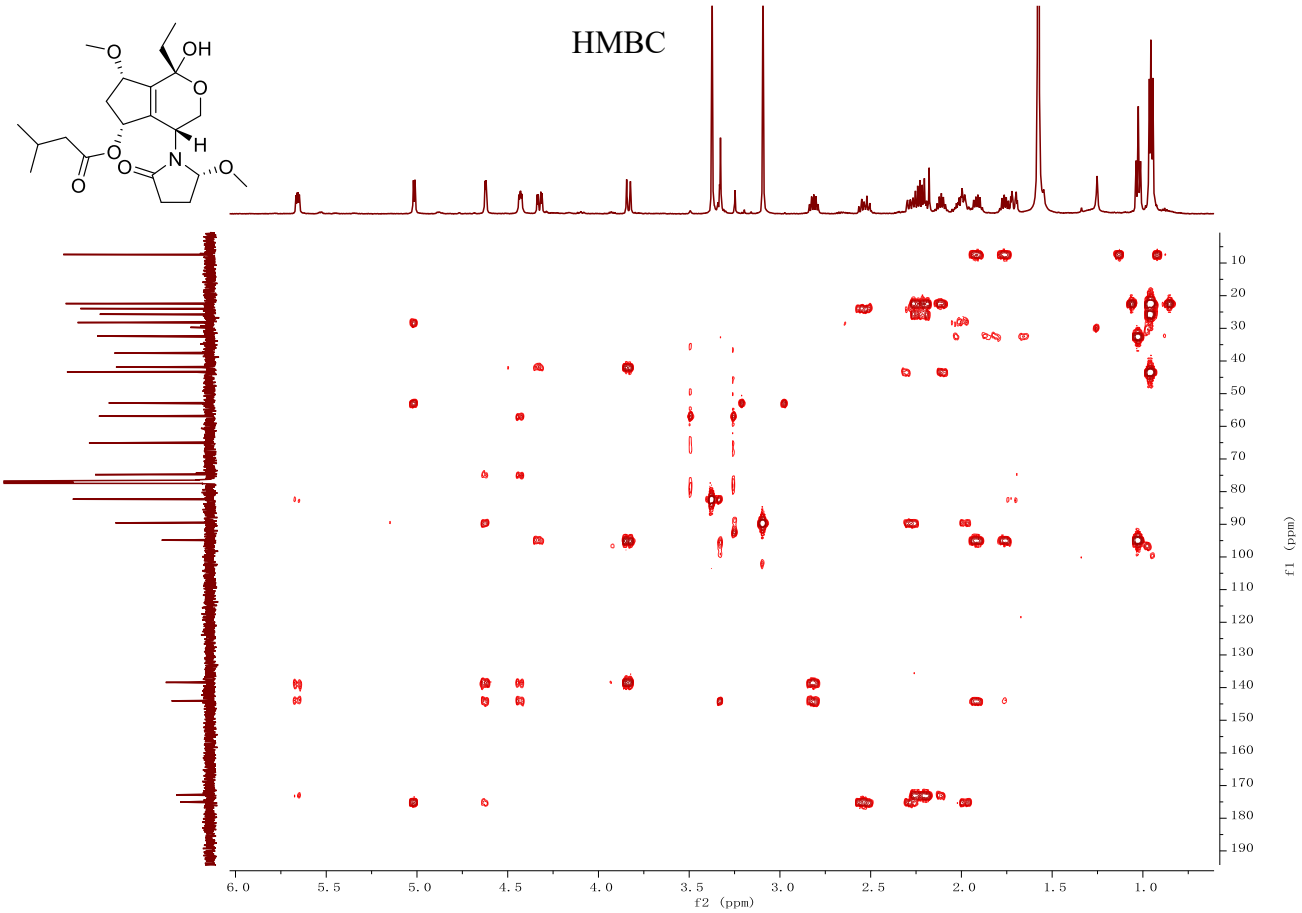
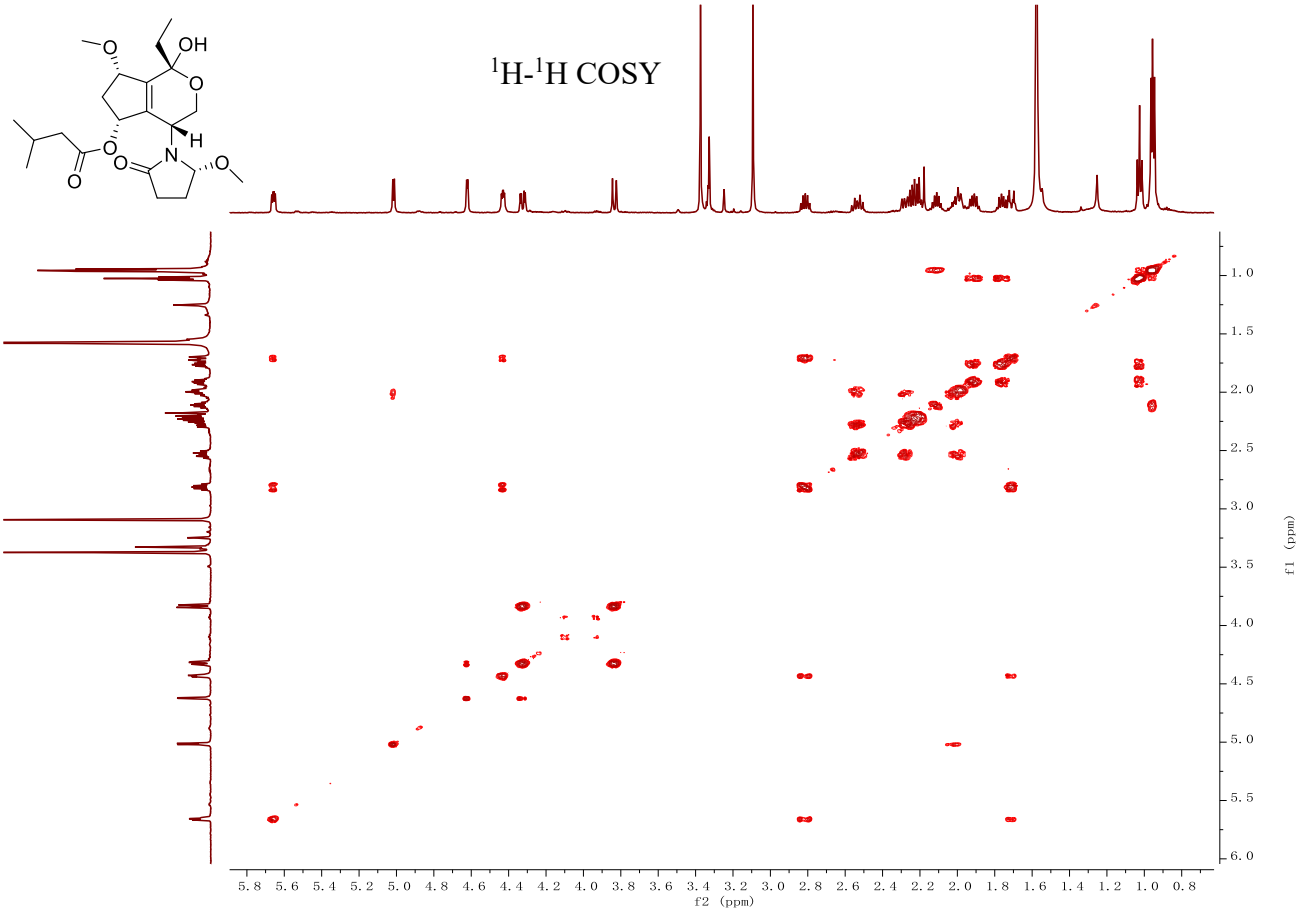
f2 (ppm)
f1 (ppm)


HMBC
f2 (ppm)
f1 (ppm)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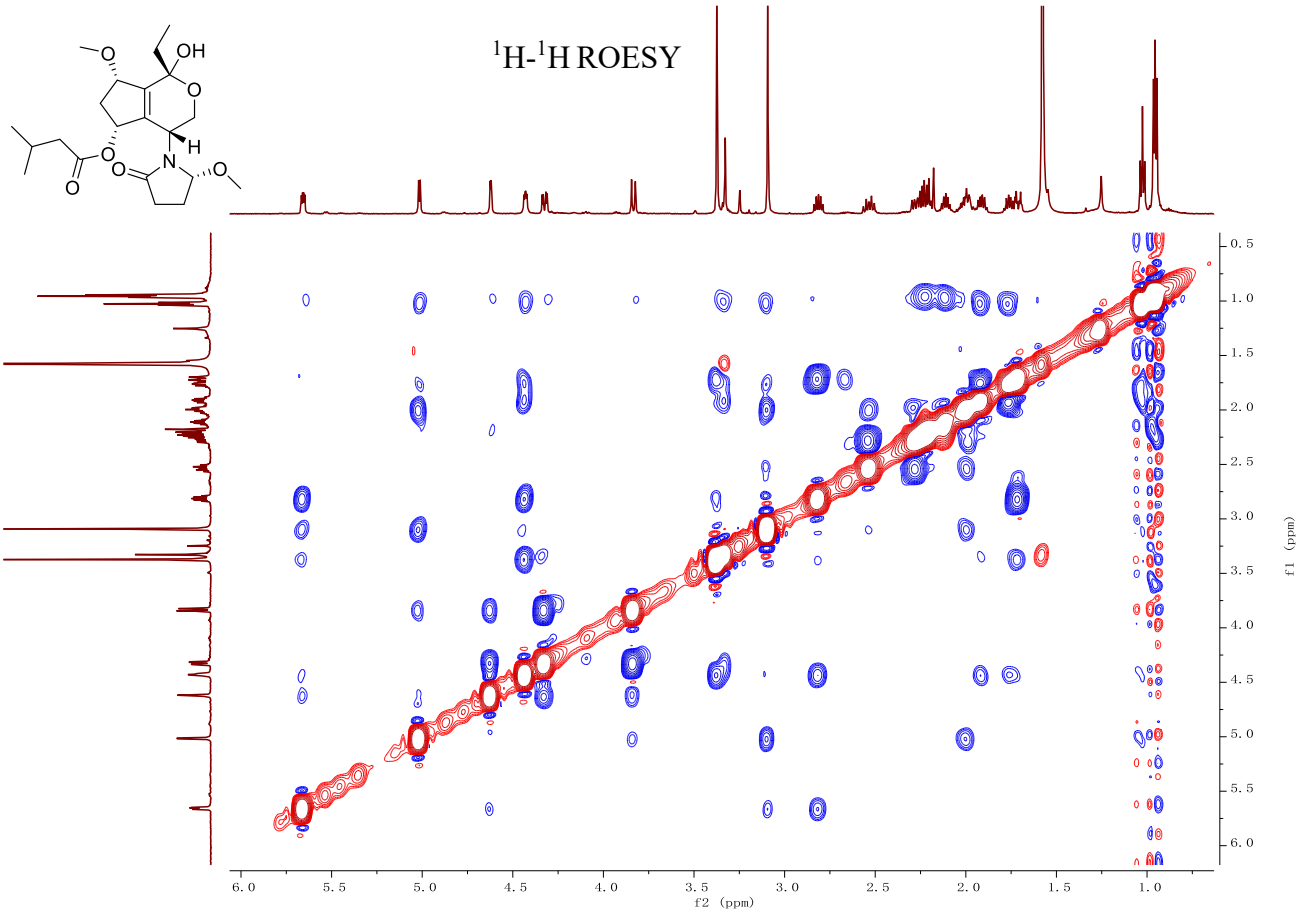
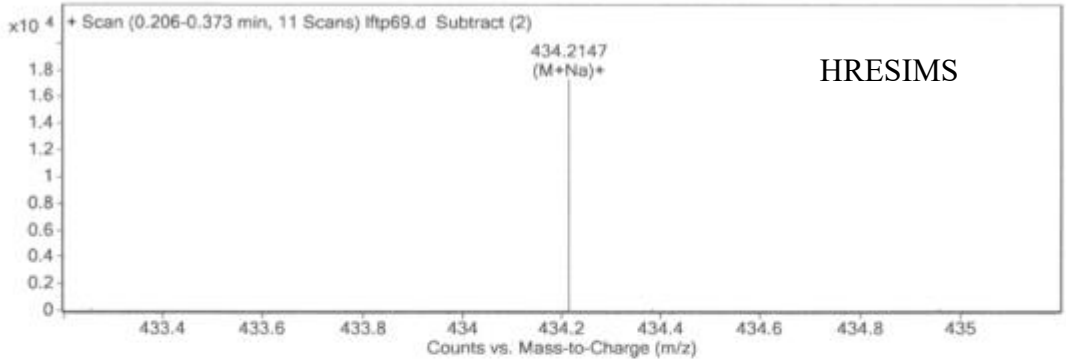
f2 (ppm)
f1 (ppm)


^{1}H-^{1}H ROESY
f2 (ppm)
f1 (ppm)

User Spectra

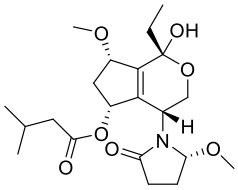
Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



HRESIMS

Peak List

m/z	z	Abund	Formula	Ion
249.1959	1	5534.32		
274.274	1	31321.89		
292.1544	1	13335.53		
302.3052	1	9321		
318.3001	1	12674.19		
434.2147	1	17397.4	C21 H33 N O7	(M+Na)+
448.2302	1	11541		
450.1885	1	10958.54		



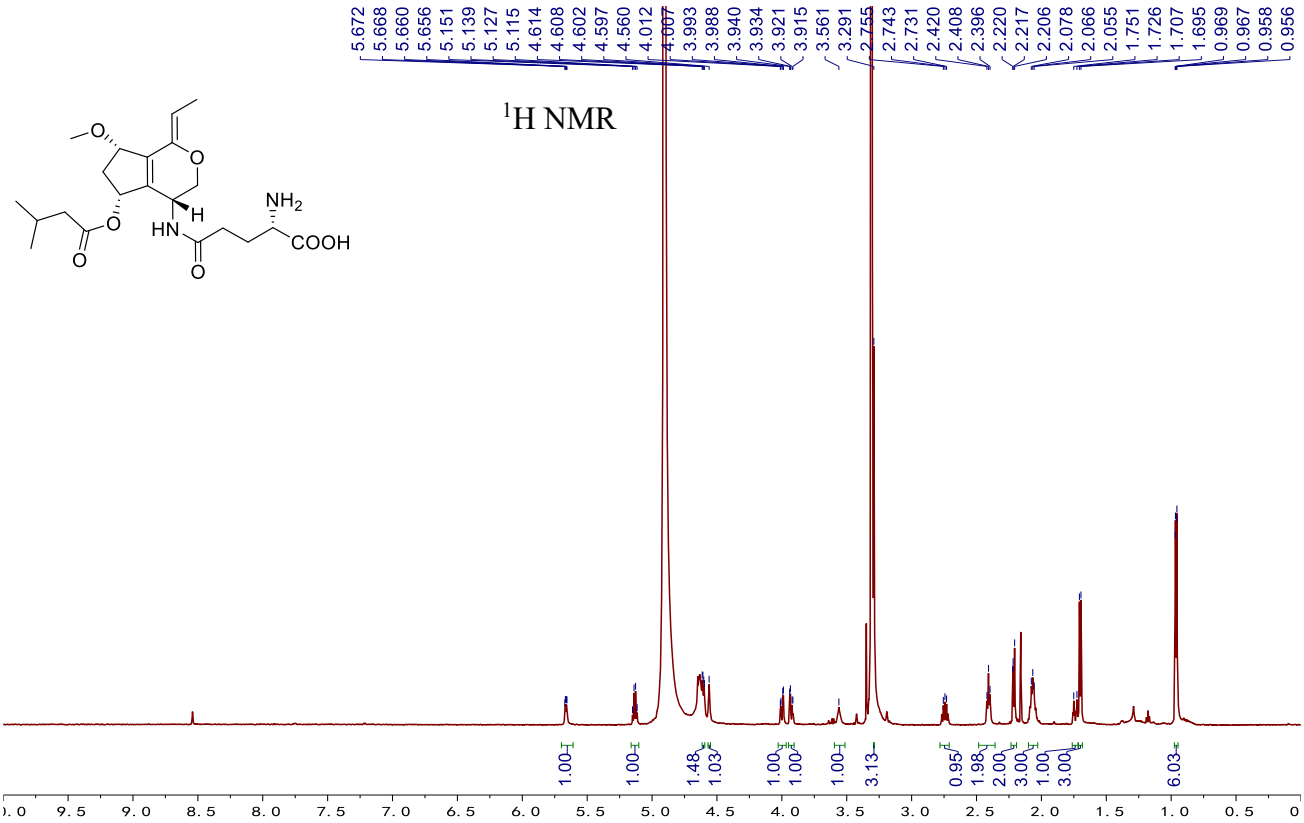
Formula Calculator Element Limits

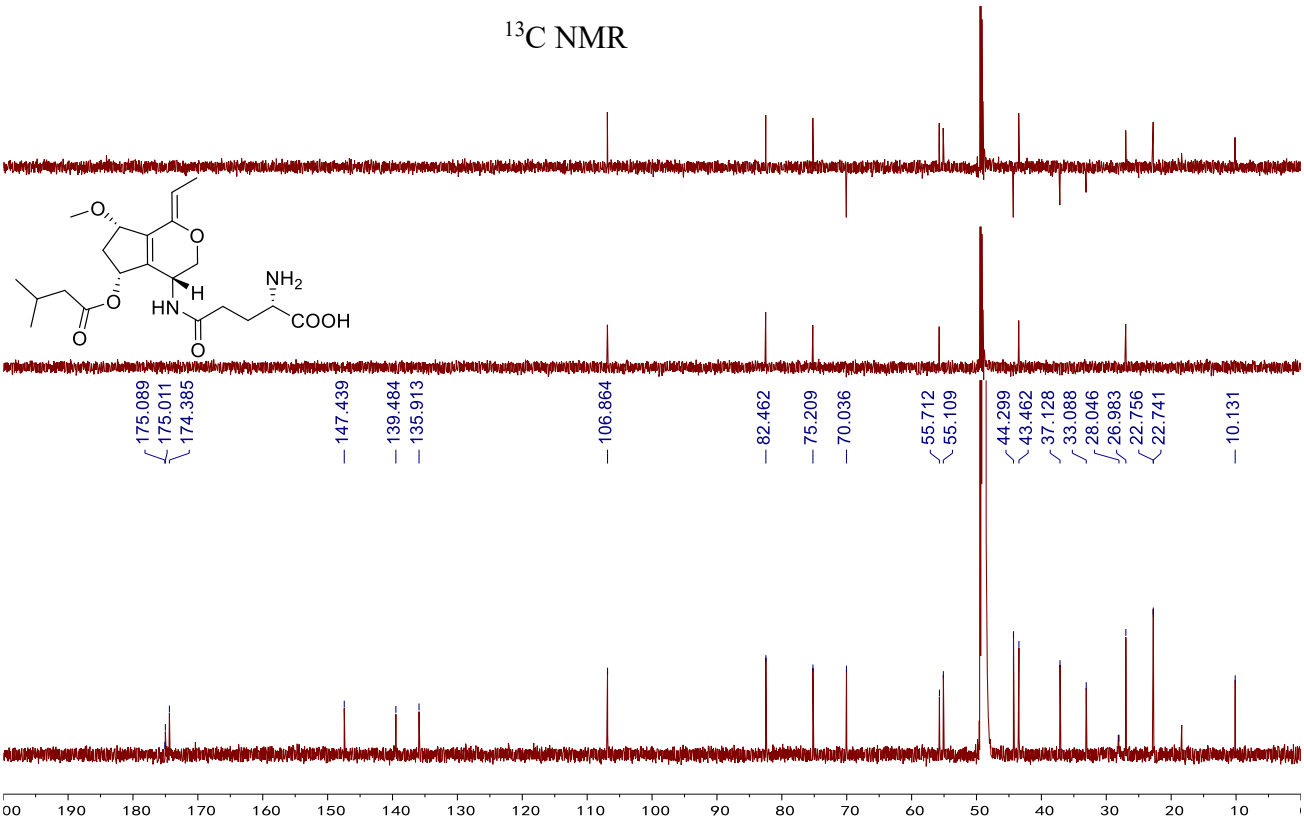
Element	Min	Max
C	3	60
H	0	120
O	0	30
N	0	30

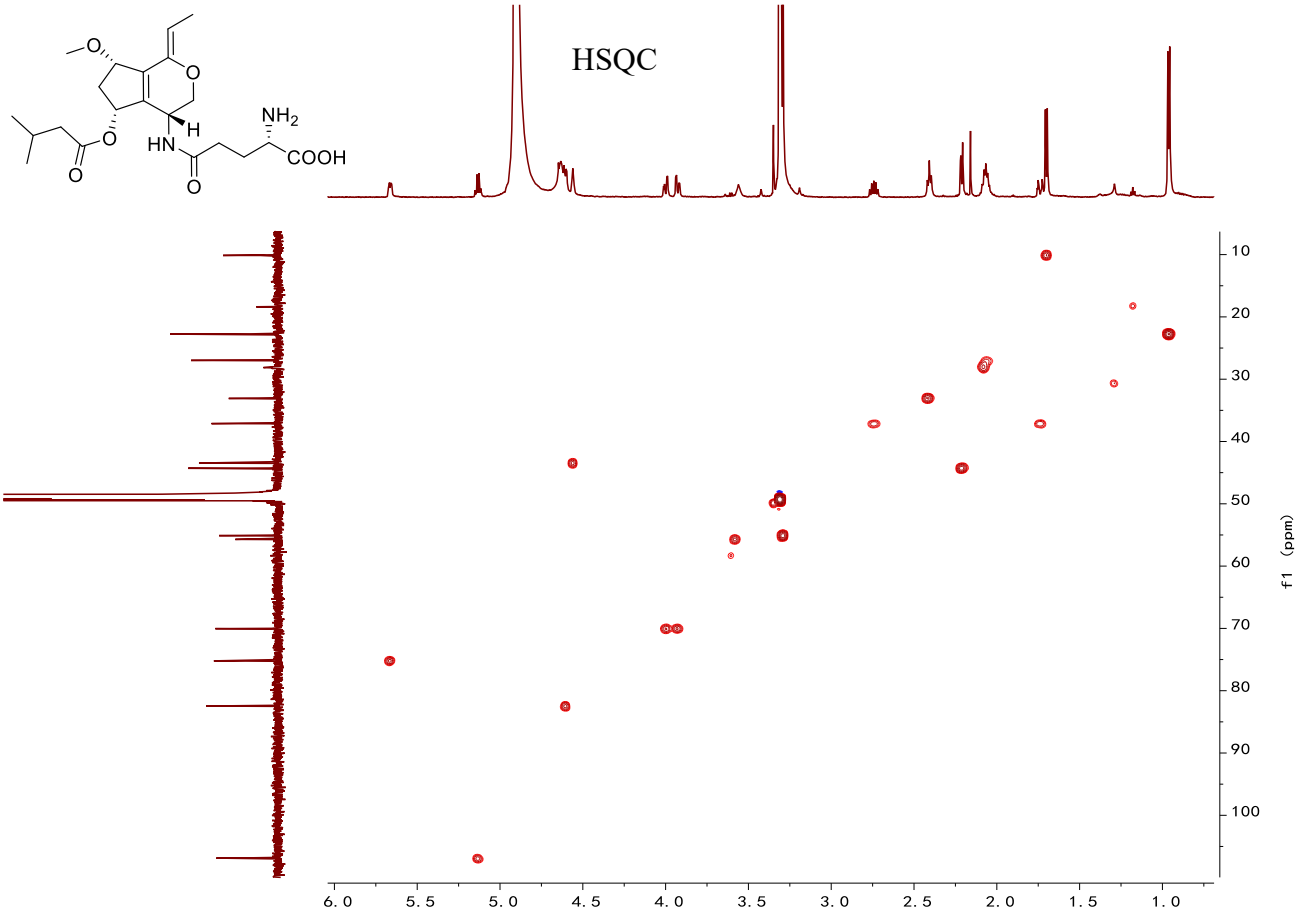
Formula Calculator Results

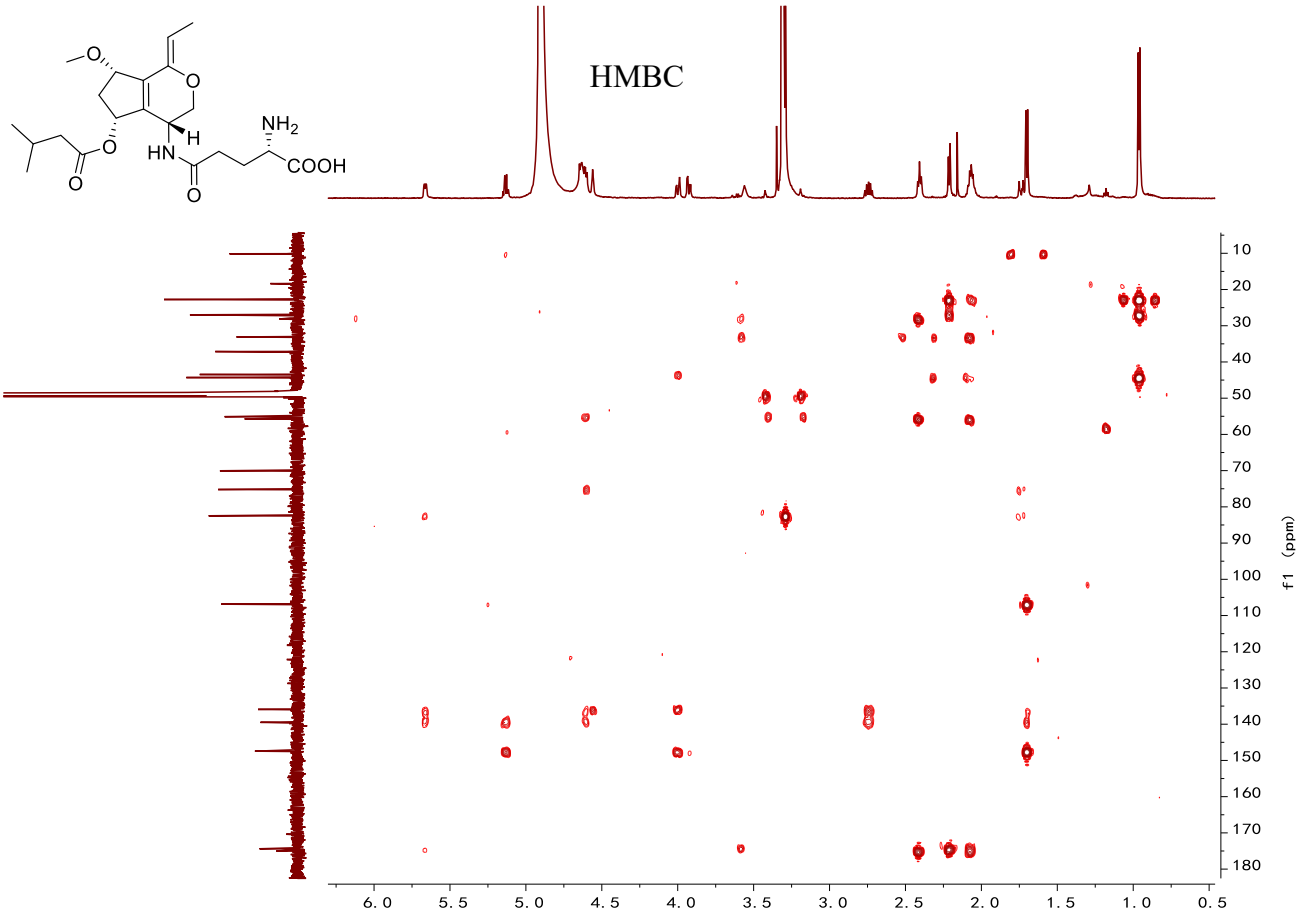
Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C21 H33 N O7	411.2257	434.2149	434.2147	0.3	0.6	6.0000

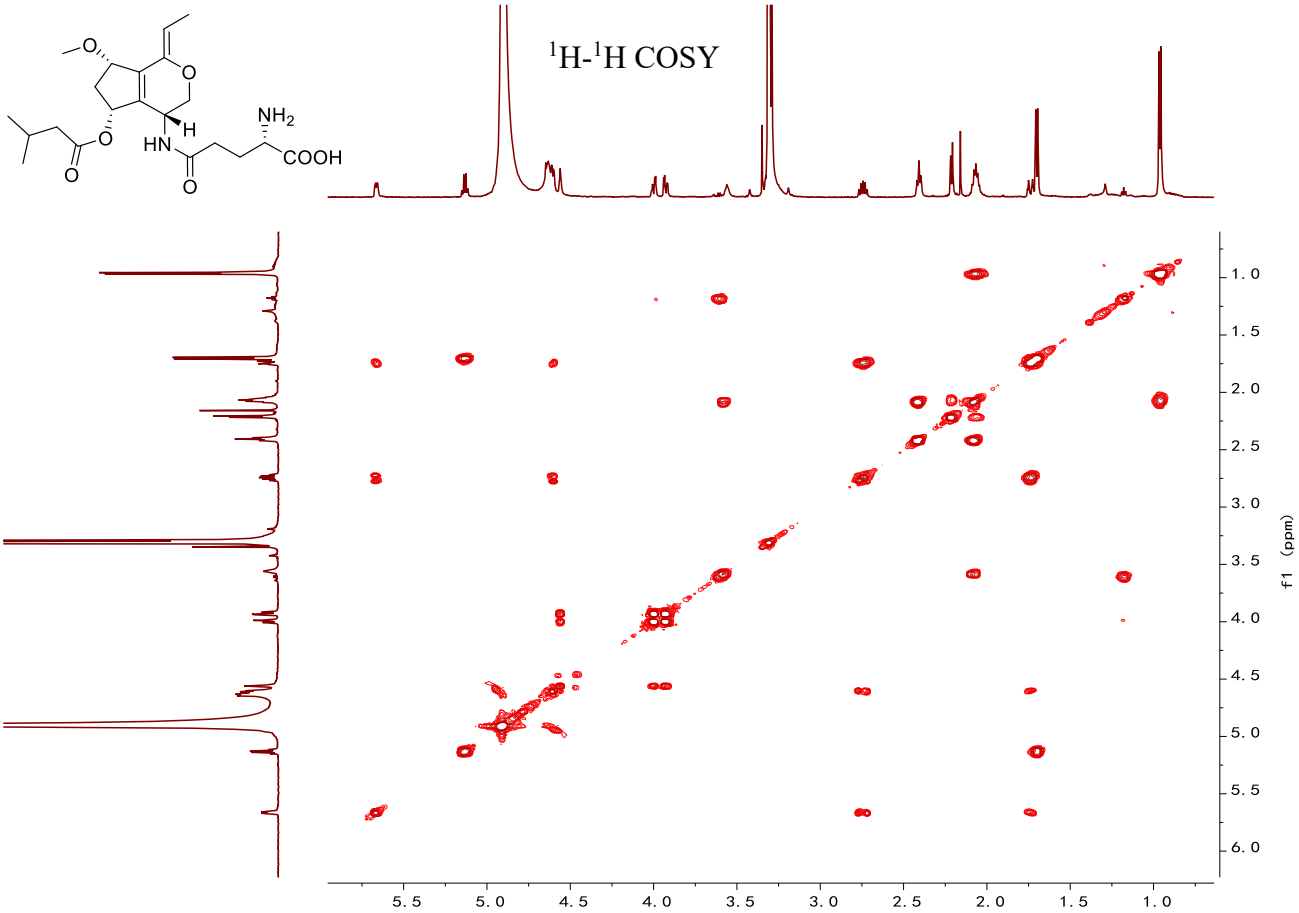
S2.3 NMR and HRESIMS spectra of pardinumone C (3)

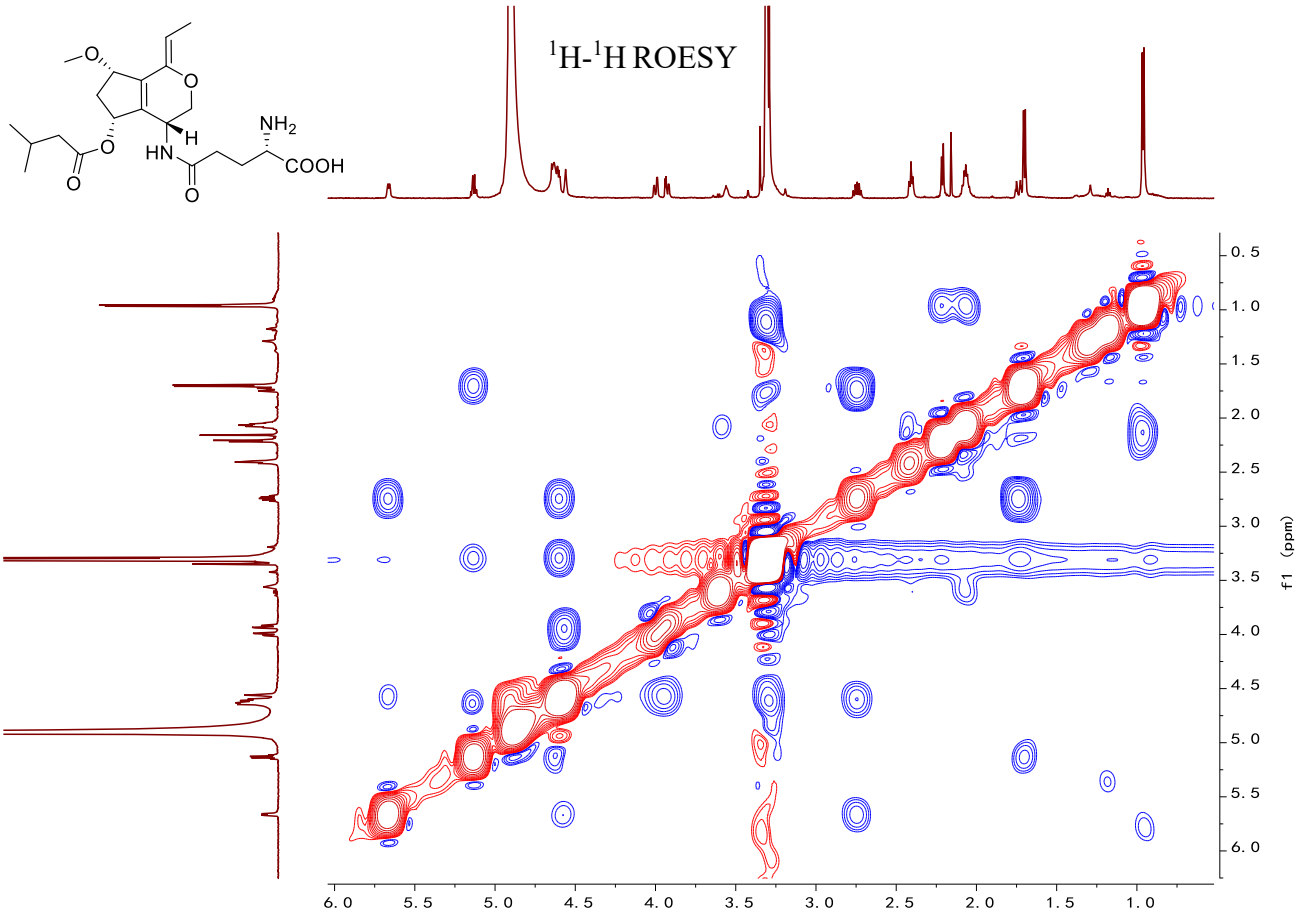





HSQC
NH2
COOH
HN
H
O
f1 (ppm)

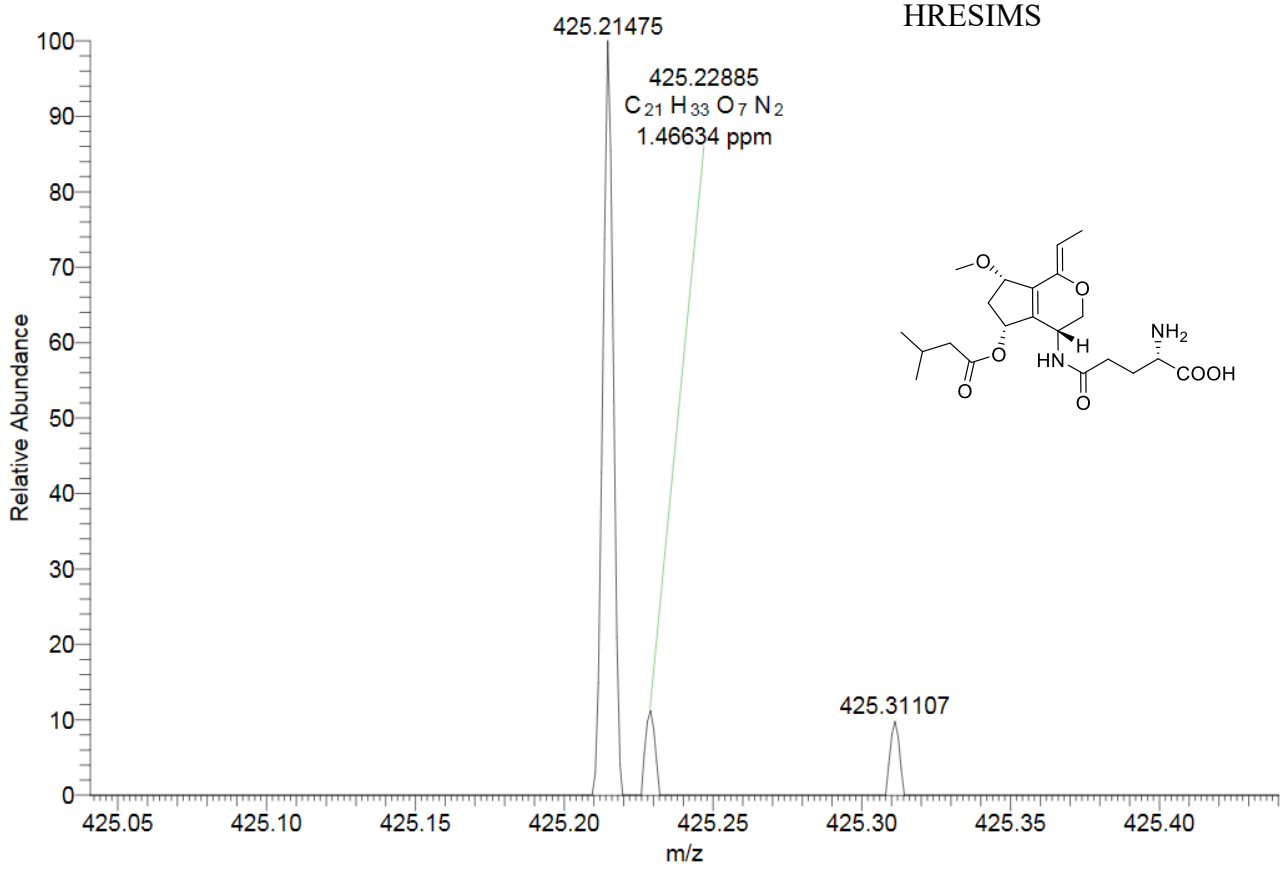

HMBC
NH2
COOH
HN
H
O
f1 (ppm)


^{1}H-^{1}H COSY
NH2
COOH
HN
H
O
f1 (ppm)

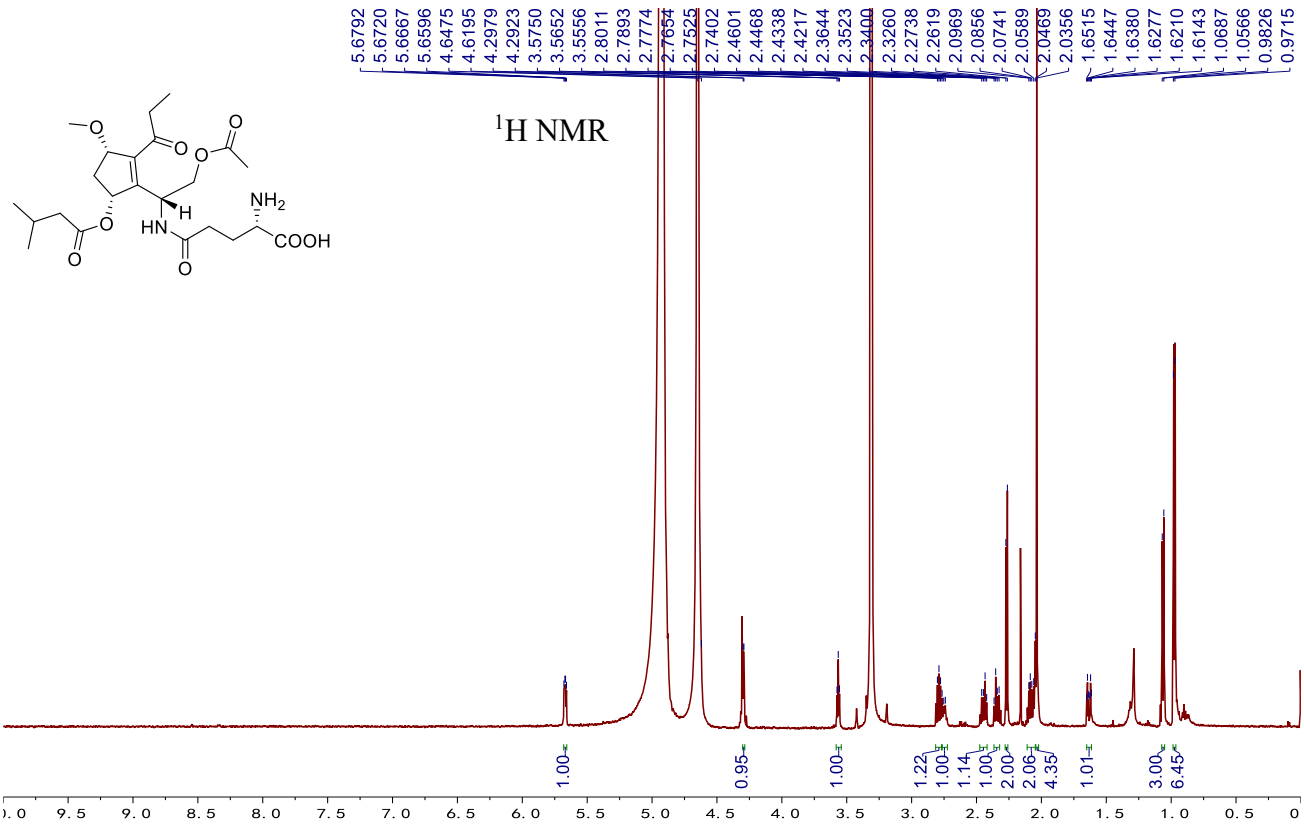

^{1}H-^{1}H ROESY
NH2
COOH
HN
H
O
f1 (ppm)

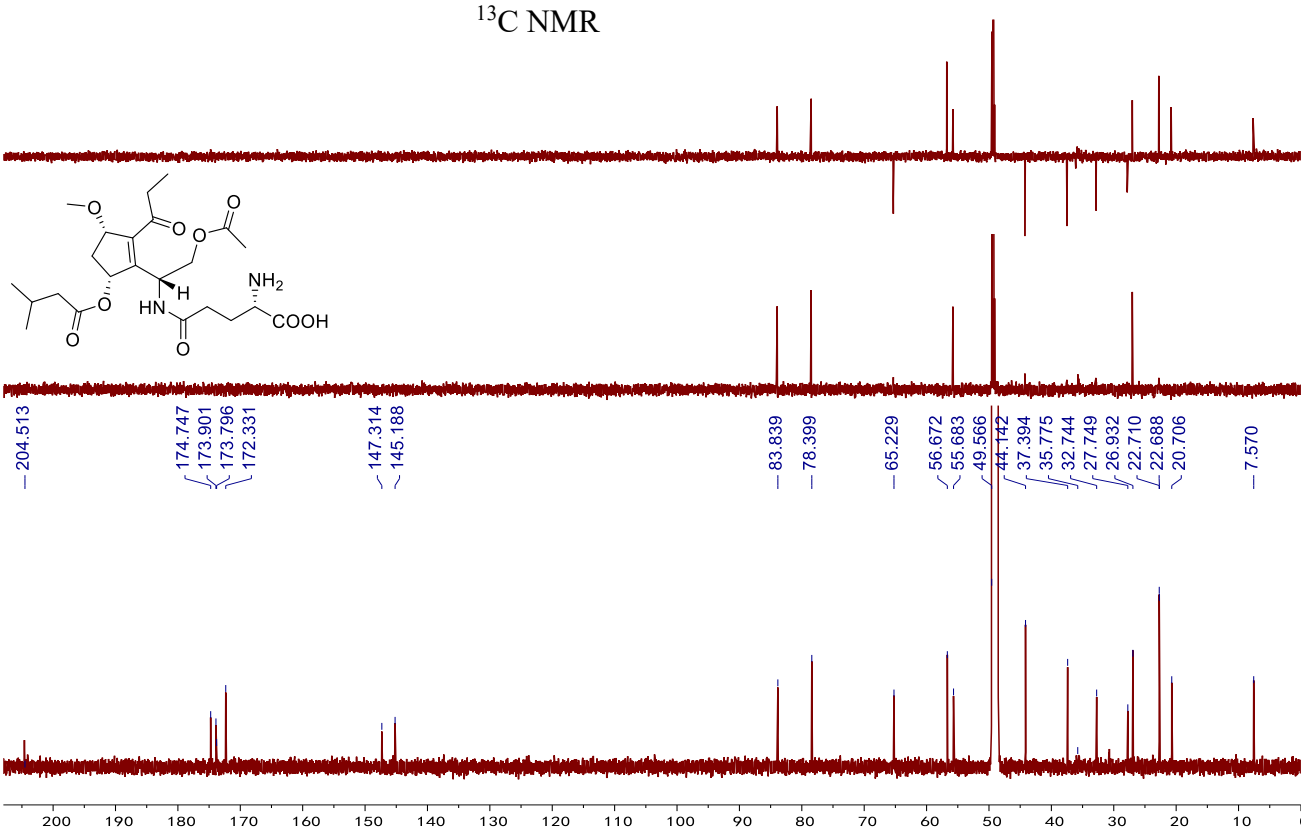
T: FTMS + p ESI Full lock ms [150.0000-1100.0000]

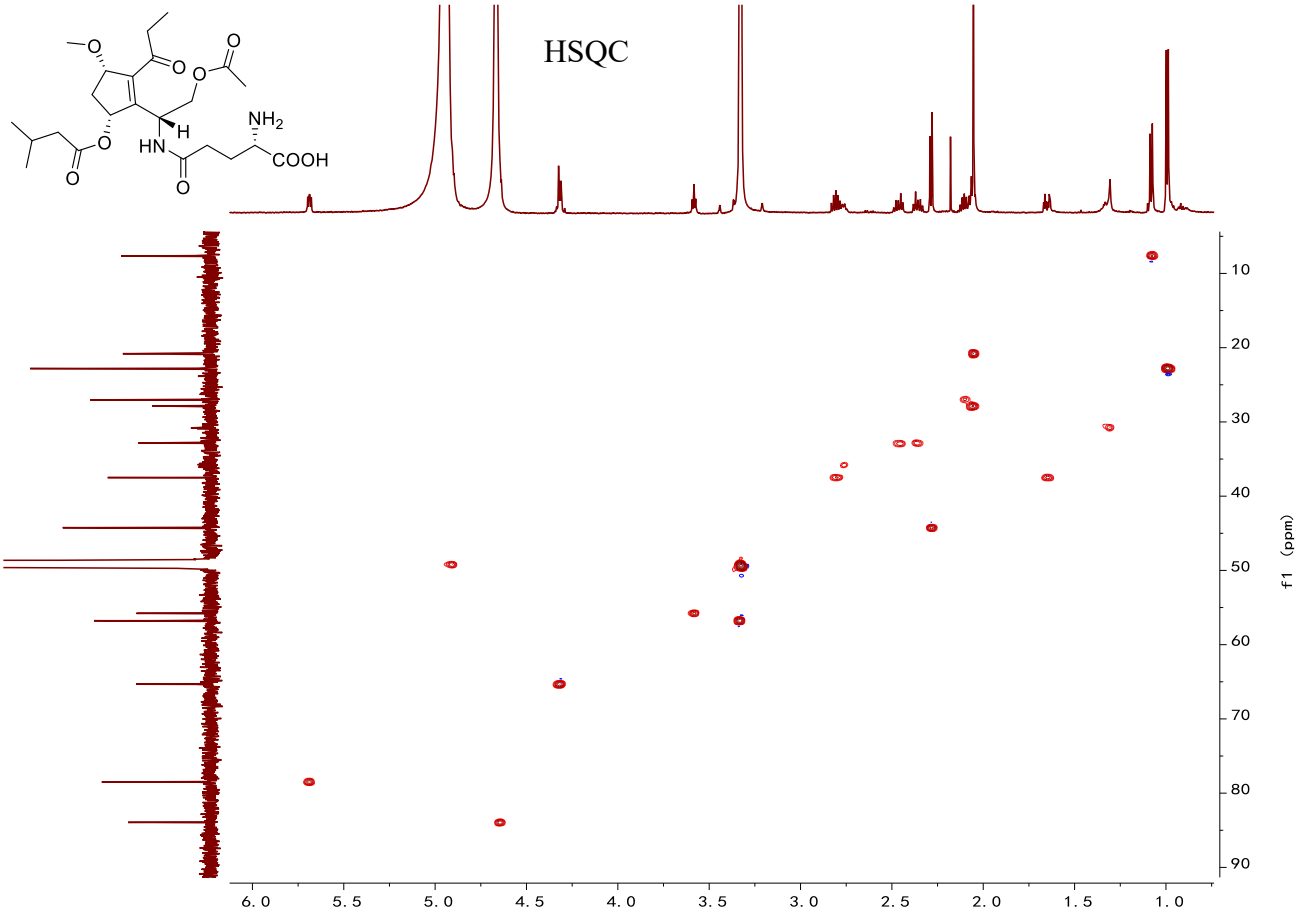
HRESIMS

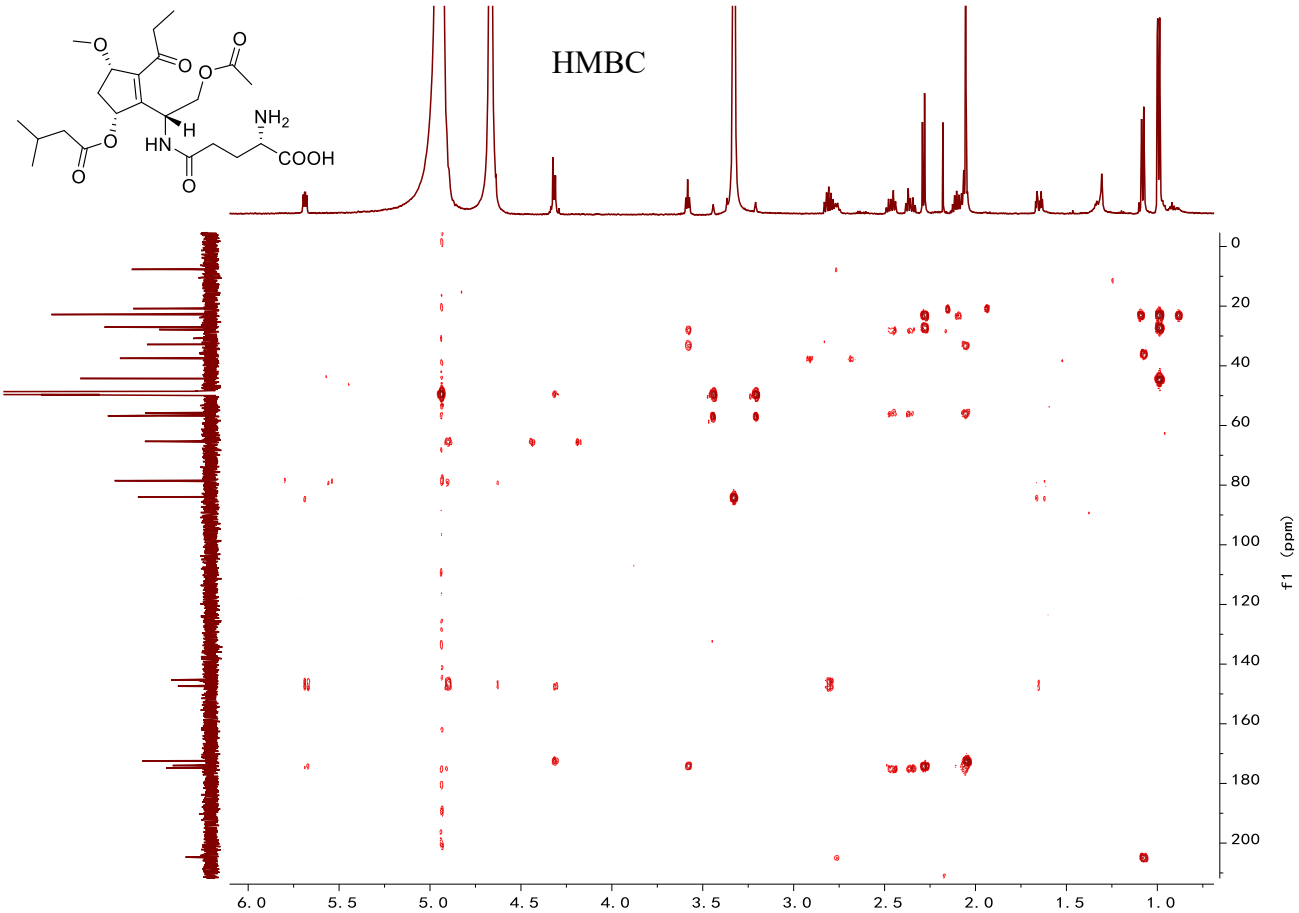


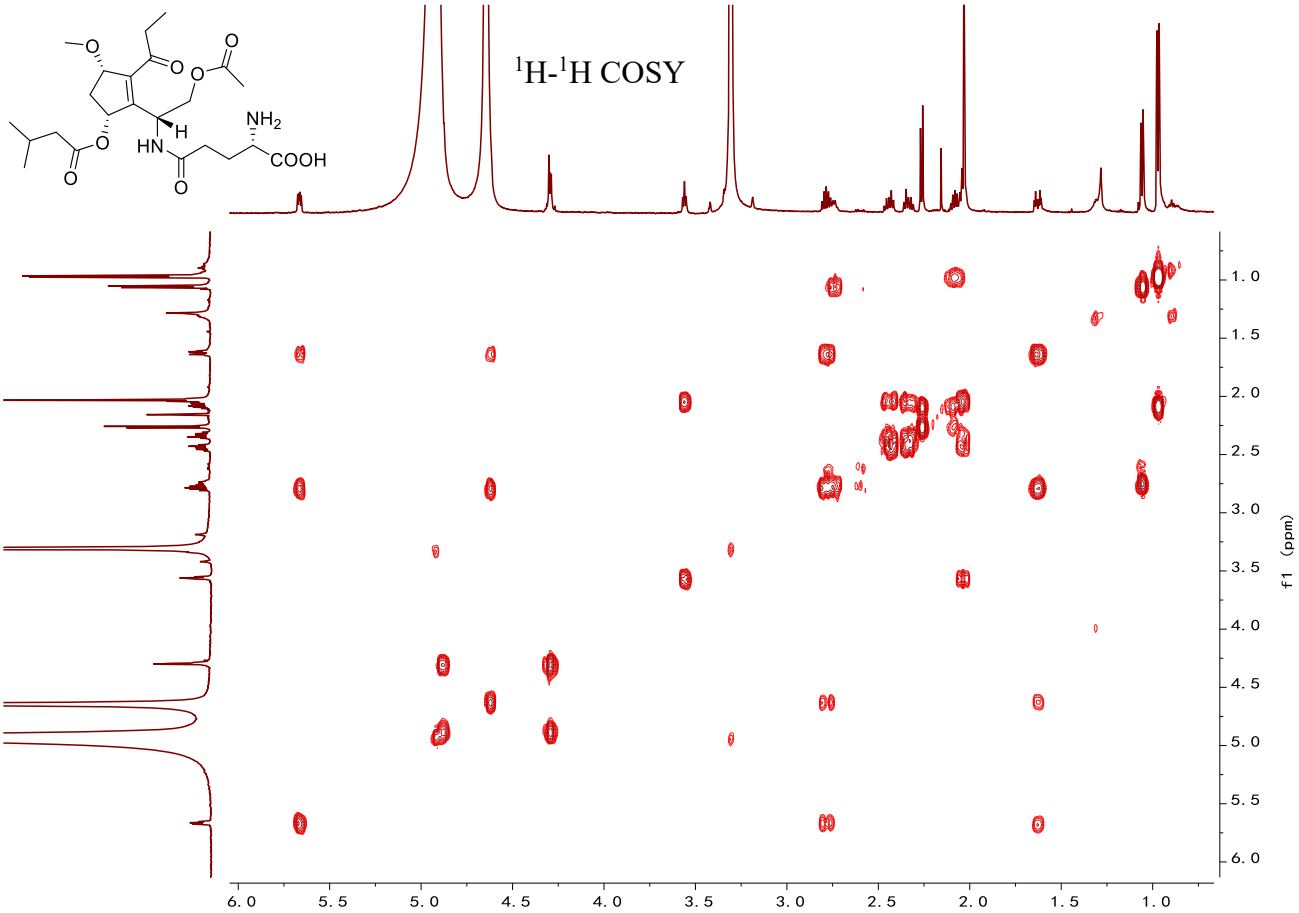
S2.4 NMR and HRESIMS spectra of pardinumone D (4)

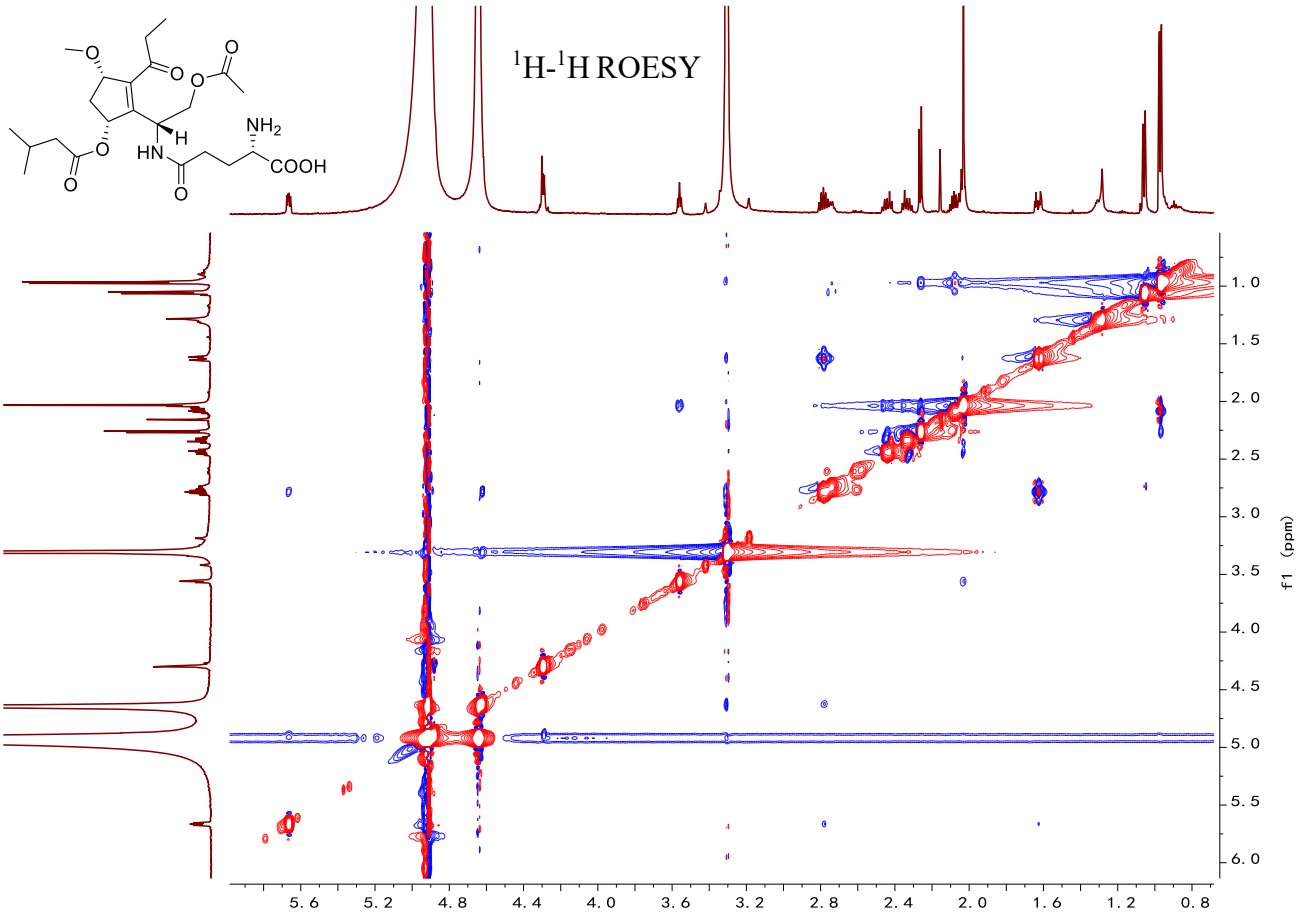


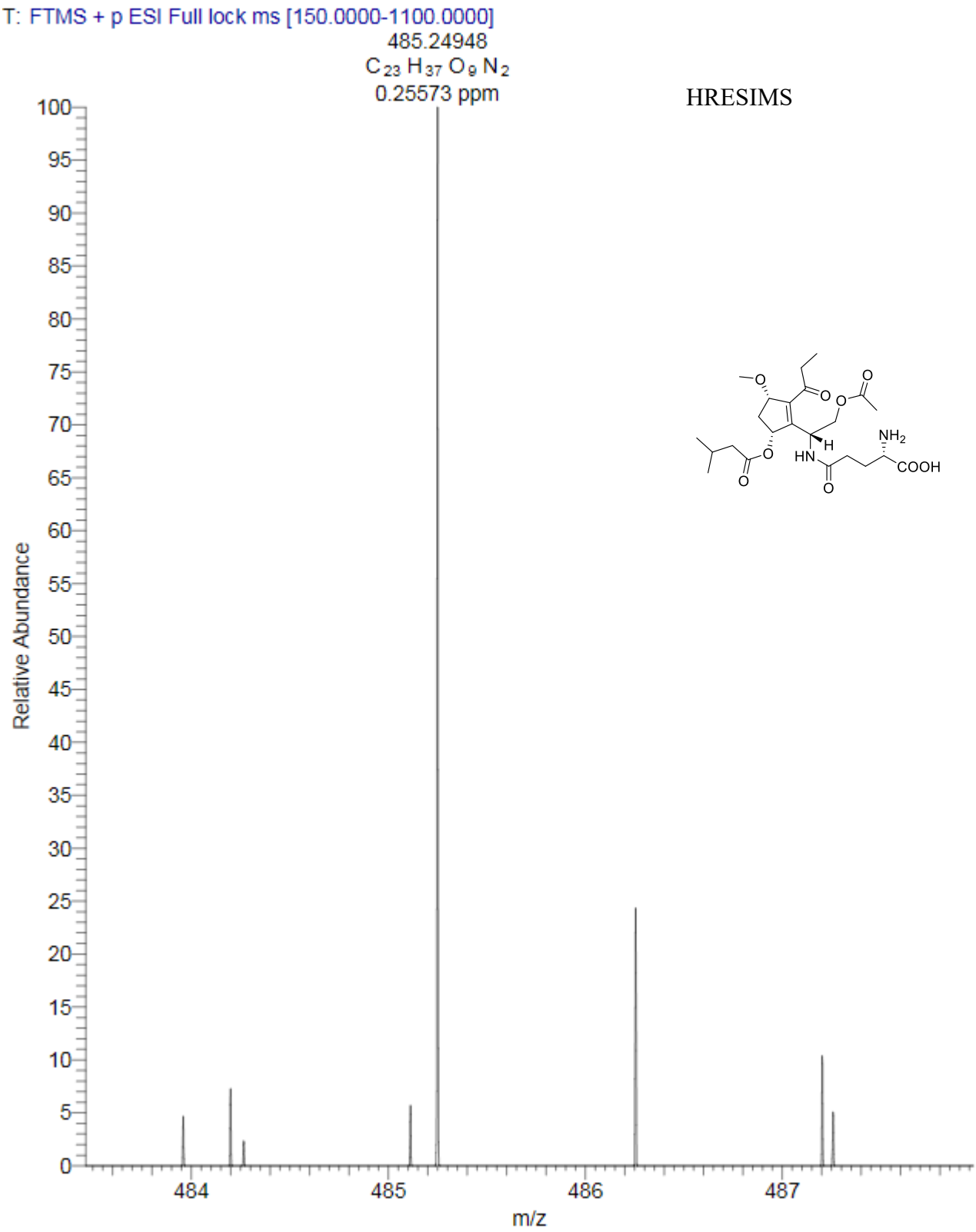



HSQC
NH2
COOH
HN
H
O
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
10
20
30
40
50
60
70
80
90


HMBC
NH2
COOH
HN
H
O
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
20
40
60
80
100
120
140
160
180
200


^{1}H-^{1}H COSY
NH2
COOH
HN
H
f1 (ppm)


^{1}H-^{1}H ROESY
NH2
COOH
HN
H
f1 (ppm)


T: FTMS + p ESI Full lock ms [150.0000-1100.0000]
485.24948
C23 H37 O9 N2
0.25573 ppm
HRESIMS
Relative Abundance
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
484
485
486
487
O
O
O
O
O
O
H
HN
NH2
COOH