Supporting Information

for

Cycloheximide congeners produced by *Streptomyces* sp. SC0581 and photoinduced interconversion between (*E*)- and (*Z*)-2,3-dehydroanhydrocycloheximides

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HRESIMS, 1D and 2D NMR spectra of compounds 1–3; energies, populations, and key torsion angles of low-energy conformers of compounds 1–3 by theoretical computations

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1. Theoretical computations

Table S1. Relative thermal energies (ΔE, kcal/mol)[a], and relative free energies (ΔG, kcal/mol)[a], equilibrium populations (P, %)[b], and key torsion angles (ϕ, degree) of low-energy conformers of **1** in MeOH

conformer	$\phi_{C3\text{-}C4\text{-}C5\text{-}C6}$	$\phi_{H6\text{-}C6\text{-}C\alpha\text{-}H\alpha}$	ΔE	ΔG	P
(4*R*,6*R*,α*S*)-**1**					
S-**1a1**	-49.45	-60.90	0.00	0.02	25.8
S-**1a2**	-49.48	-61.12	0.65	0.58	10.1
S-**1a3**	-49.75	-62.98	0.76	0.78	7.2
S-**1a4**	-49.77	-64.17	1.34	1.15	3.9
S-**1a5** [c]	-49.79	-61.51	1.50	2.11	0.8
S-**1b1**	-46.27	55.65	0.56	0.00	26.9
S-**1b2**	-46.25	54.89	0.89	0.68	8.6
S-**1b3**	-46.31	55.31	1.16	0.99	5.1
S-**1b4**	-46.50	54.46	0.79	1.03	4.7
S-**1b5** [c]	-46.26	56.72	1.94	1.67	1.6
S-**1b6** [c]	-46.26	55.23	1.45	1.78	1.3
S-**1c1** [c]	-48.10	159.61	2.28	1.61	1.8
S-**1c2** [c]	-47.98	163.21	2.42	1.92	1.1
S-**1c3** [c]	-47.60	164.54	3.08	2.08	0.8
(4*R*,6*R*,α*R*)-**1**					
R-**1a1**	-48.24	174.44	0.00	0.00	58.1
R-**1a2**	-48.11	174.07	1.06	1.02	10.3
R-**1a3**	-48.46	173.83	1.06	1.20	7.7
R-**1a4**	-48.13	174.97	1.35	1.84	2.6
R-**1a5**	-48.29	173.22	2.06	1.97	2.1
R-**1a6** [c]	-48.55	173.01	1.99	2.37	1.1
R-**1b1**	-46.12	-81.43	1.42	1.26	6.9
R-**1b2** [c]	-46.04	-79.73	2.17	2.10	1.7
R-**1b3** [c]	-46.10	-80.46	2.56	2.39	1.0
R-**1c1**	-48.81	63.24	2.27	1.42	5.3
R-**1c2**	-48.89	63.88	2.55	1.89	2.4

[a] At the B3LYP-D3/def2-TZVP level, in kcal/mol. [b] From ΔG values at 298.15 K.

[c]Conformer not used for ECD/ TDDFT calculations.

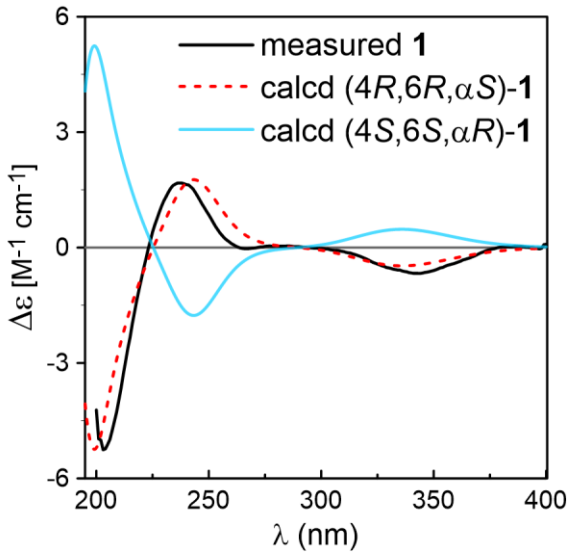


Figure S1. Comparison of the experimental ECD spectrum of **1** with the M11/TZVP calculated spectra of (4*R*,6*R*,α*S*)-**1** and (4*S*,6*S*,α*R*)-**1** in MeOH (σ = 0.38 eV, shift = +15, scaling factor = 0.50).

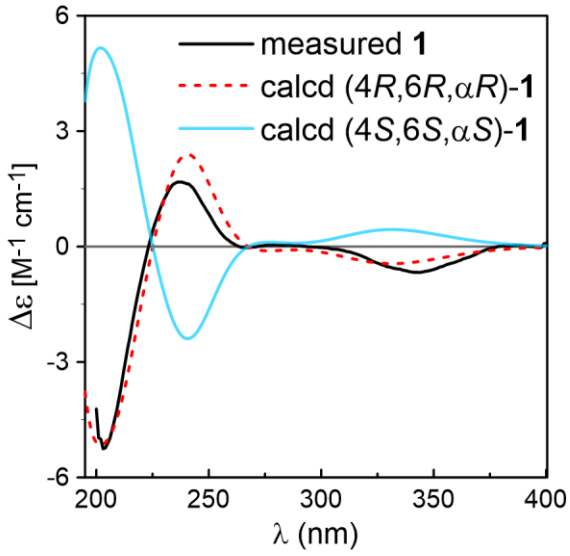


Figure S2. Comparison of the experimental ECD spectrum of **1** with the M11/TZVP calculated spectra of (4*R*,6*R*,α*R*)-**1** and (4*S*,6*S*,α*S*)-**1** in MeOH (σ = 0.38 eV, shift = +10 nm, scaling factor = 1.0).

Table S2. Relative thermal energies (ΔE, kcal/mol)[a], and relative free energies (ΔG, kcal/mol)[a], equilibrium populations (P, %)[b], and key dihedral angles (ϕ, degree) of low-energy conformers of **2** and **3** in MeOH

conformer	$\phi_{C3\text{-}C4\text{-}C5\text{-}C6}$	$\phi_{C6\text{-}C\alpha\text{-}C\beta\text{-}C4'}$	ΔE	ΔG	P
(4*R*)-**2**					
2a	-48.32	105.45	0.00	0.00	15.8
2b	-47.27	-104.97	0.26	0.11	13.1
2c	-48.11	85.29	0.80	0.27	10.0
2d	48.39	105.10	0.55	0.28	9.9
2e	48.55	-118.48	0.15	0.54	6.3
2f	48.05	-108.81	0.95	0.59	5.9
2g	-46.85	-84.15	0.87	0.64	5.3
2h	-48.01	99.43	0.55	0.72	4.7
2i	-46.91	-97.81	0.80	0.80	4.1
2j	48.15	81.99	1.18	0.85	3.7
2k	49.08	-83.30	0.83	1.16	2.2
2l [c]	48.27	98.62	1.11	1.32	1.7
(4*R*)-**3**					
3a	48.77	121.83	0.44	0.00	39.5
3b	-47.64	106.80	0.00	0.79	10.4
3c	-47.75	-95.66	0.53	0.89	8.7
3d	-47.63	86.64	0.38	1.02	7.0
3e	48.74	-106.18	0.50	1.33	4.2
3f	48.63	-85.95	0.85	1.47	3.3
3g	-48.50	-72.80	1.26	1.64	2.5
3h	-47.58	-91.79	1.13	1.66	2.4
3i	-47.66	104.16	0.81	1.67	2.3
3j [c]	50.03	72.24	1.39	2.01	1.3
3k [c]	48.71	-103.76	1.24	2.27	0.9
3l [c]	48.15	92.15	1.26	2.29	0.8

[a] At the B3LYP-D3/def2-TZVP level, in kcal/mol. [b]From ΔG values at 298.15 K. [c]Conformer not used for ECD/ TDDFT calculations.

2. NMR spectra and HRESIMS

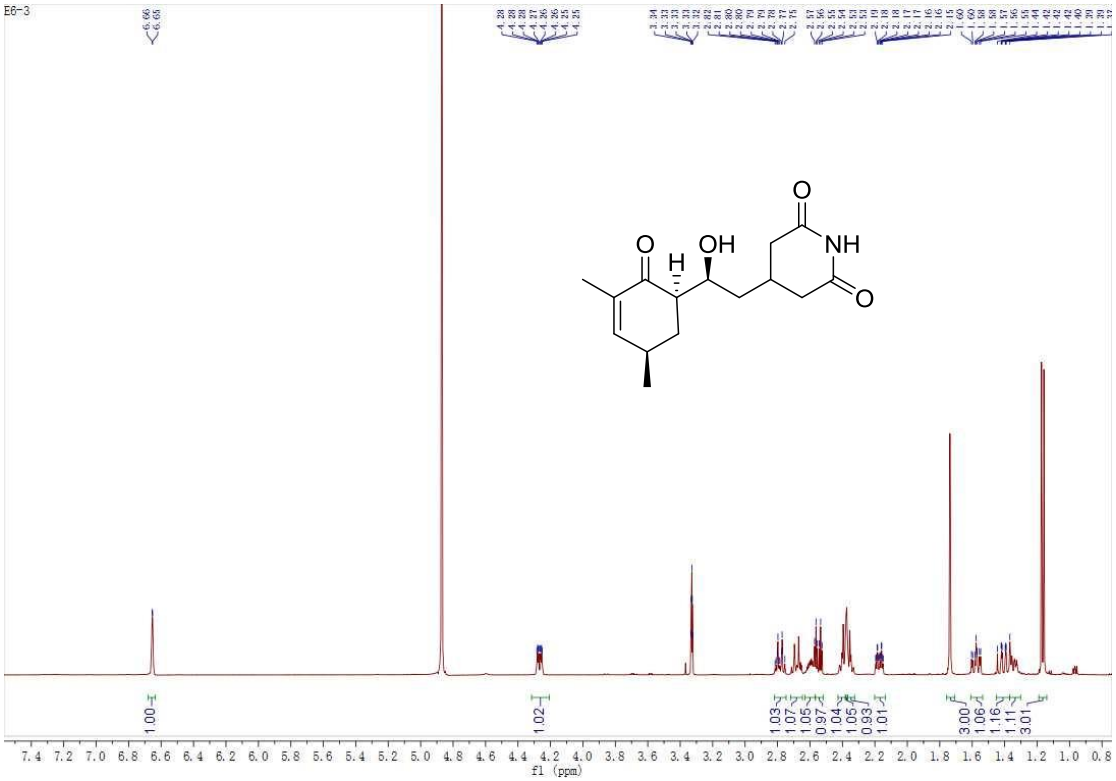


Figure S3. ^{1}H NMR (500 Hz) spectrum of compound **1** in CD_3OD.

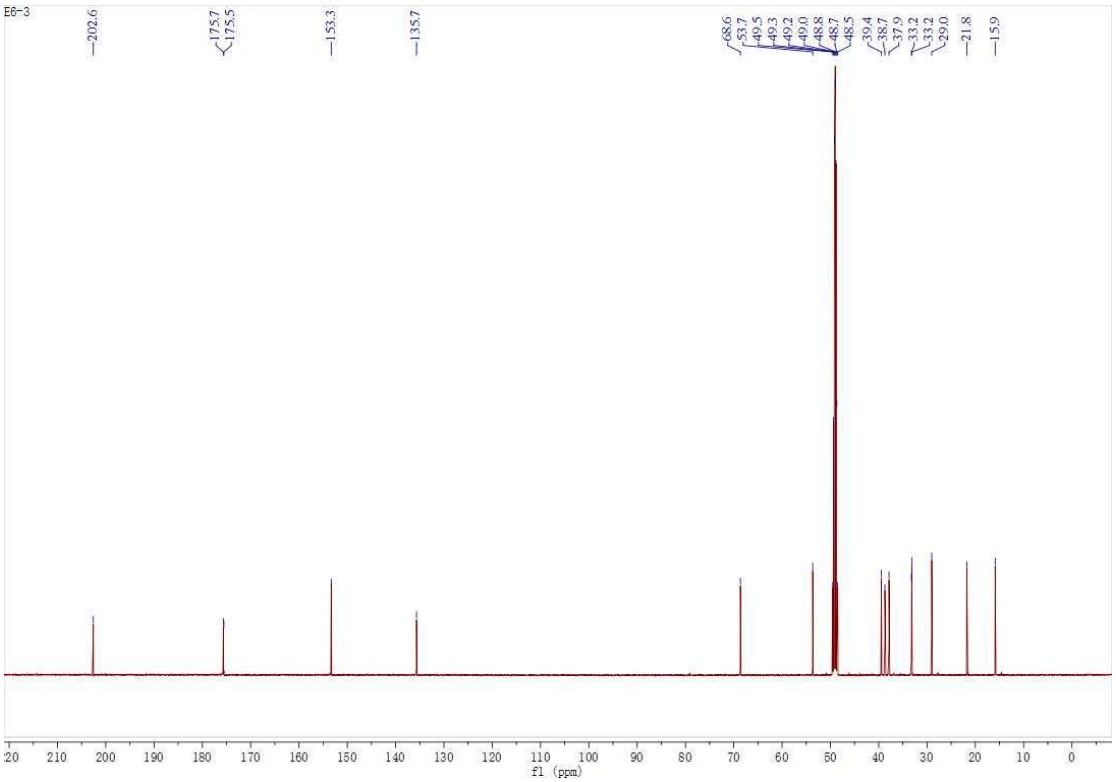


Figure S4. ^{13}C NMR (125 Hz) spectrum of compound **1** in CD_3OD.

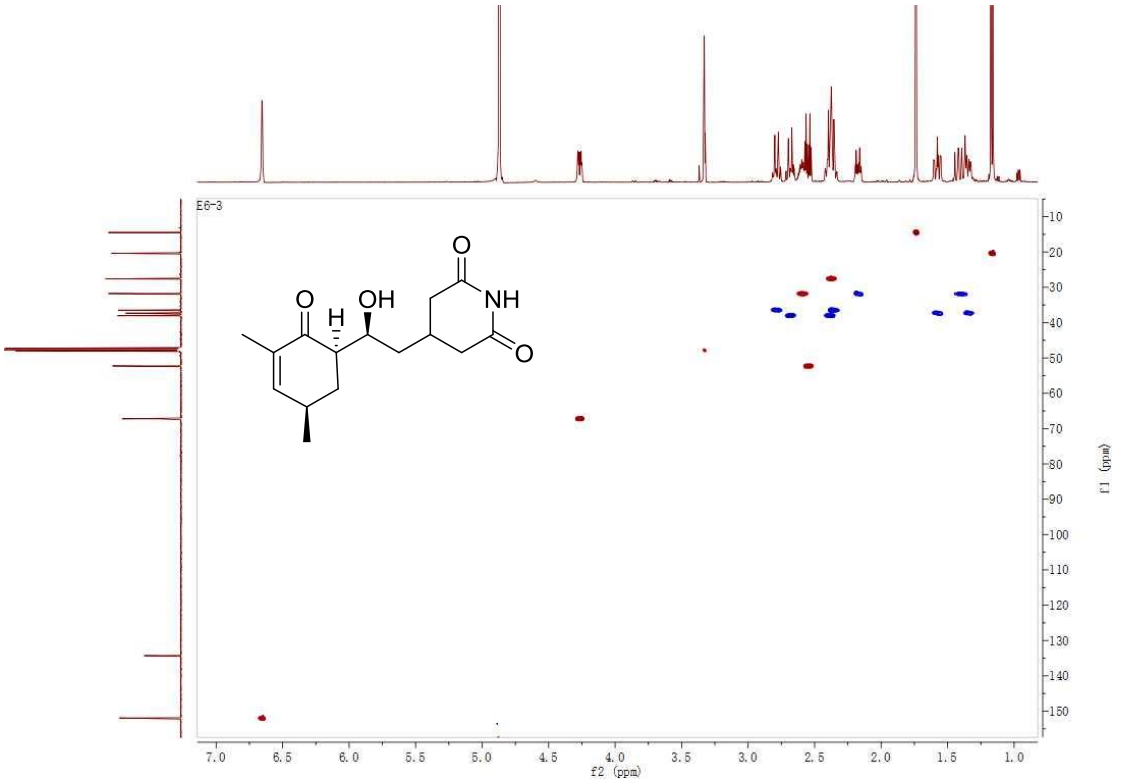


Figure S5. HSQC spectrum of compound **1** in CD_3OD.

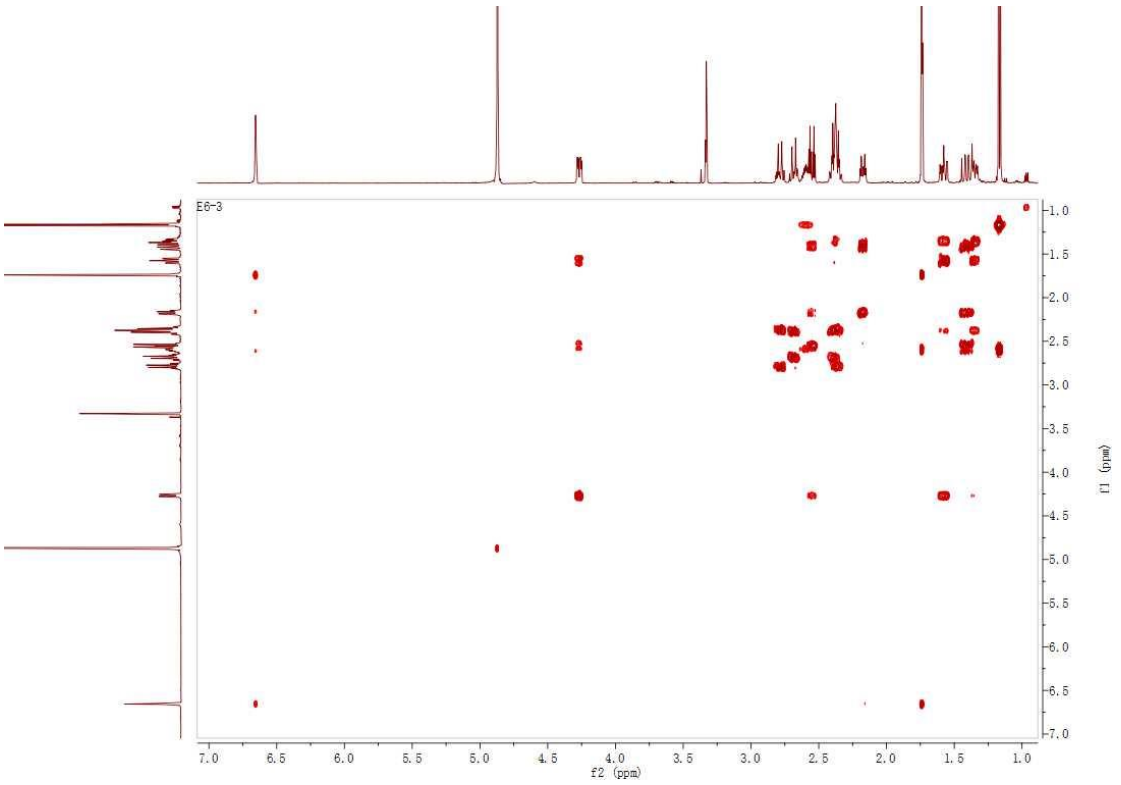


Figure S6. ^{1}H-^{1}H COSY spectrum of compound **1** in CD_3OD.

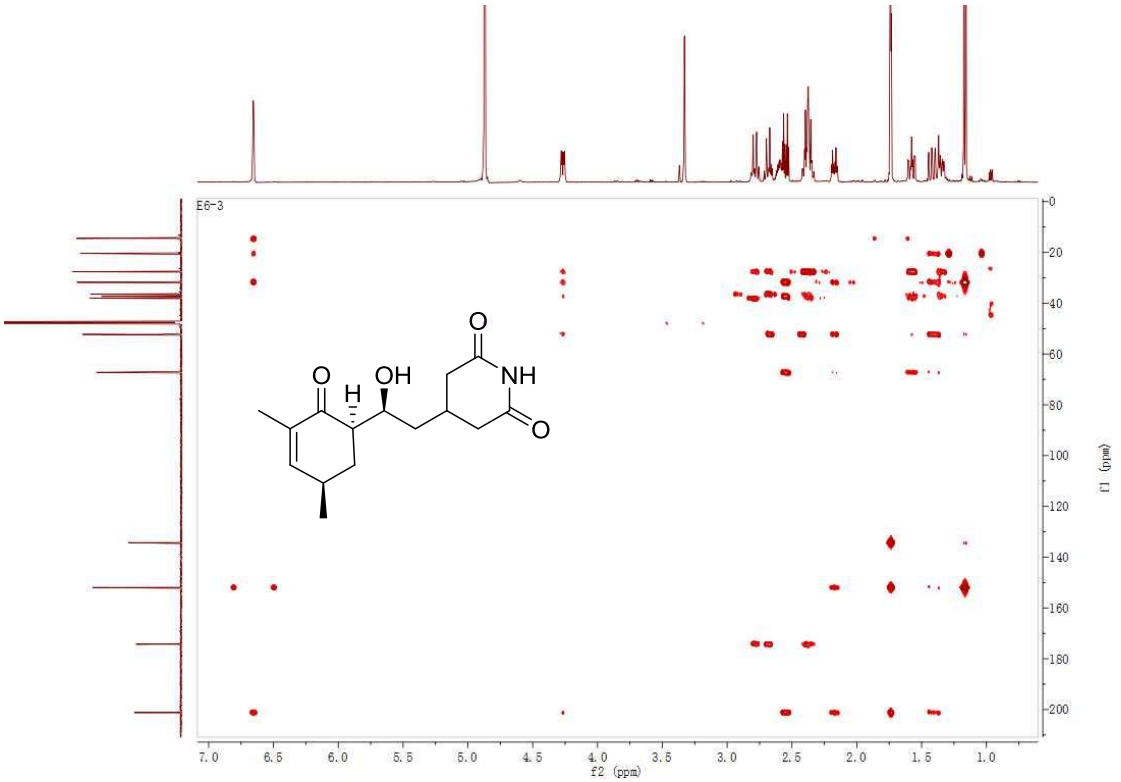


Figure S7. HMBC spectrum of compound **1** in CD_3OD.

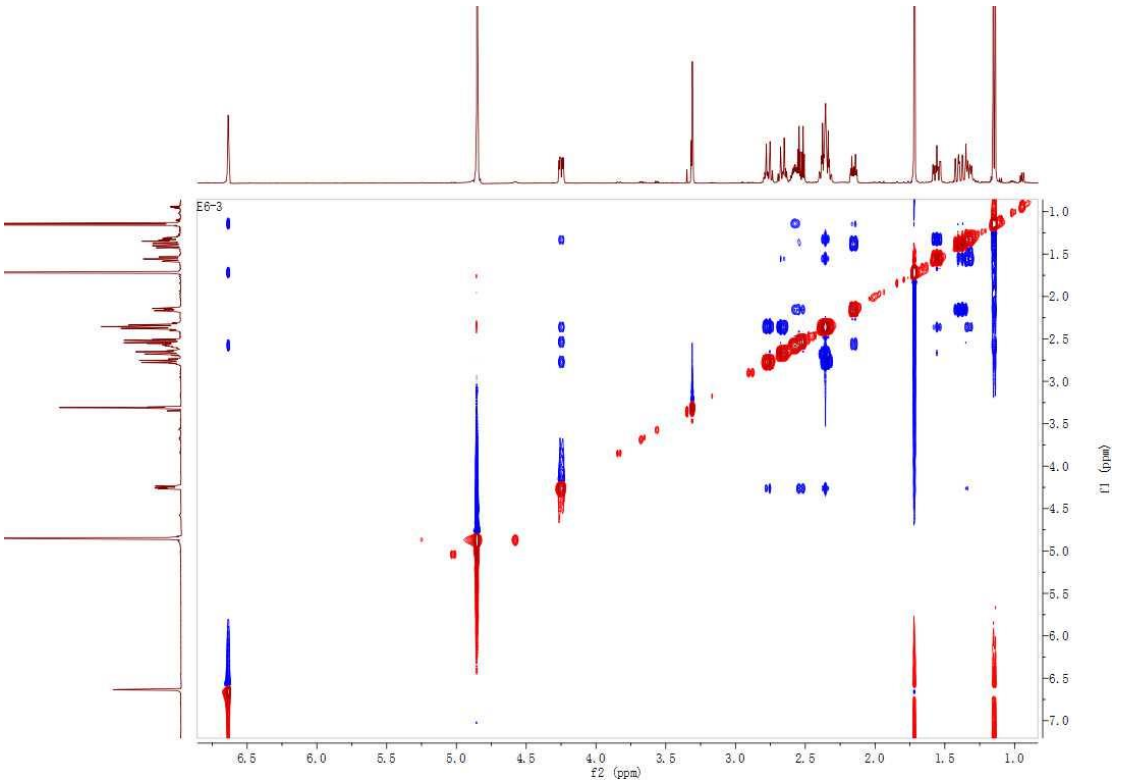
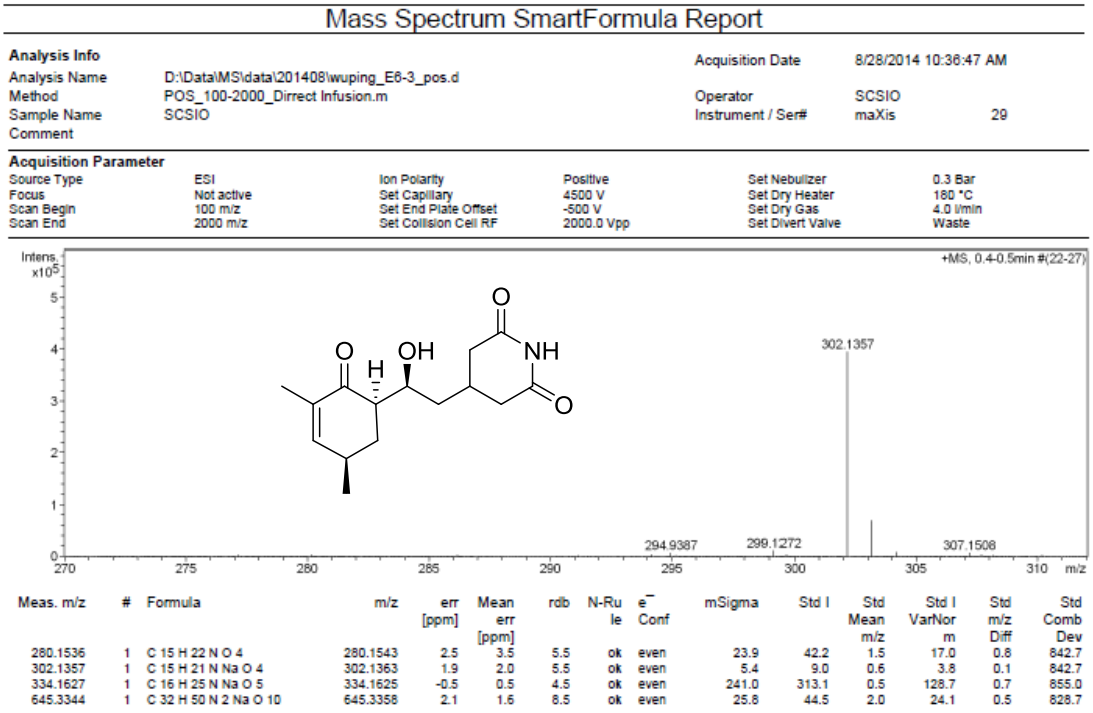


Figure S8. NOESY spectrum of compound **1** in CD_3OD.



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
280.1536	1	C 15 H 22 N O 4	280.1543	2.5	3.5	5.5	ok	even	23.9	42.2	1.5	17.0	0.8	842.7
302.1357	1	C 15 H 21 N Na O 4	302.1363	1.9	2.0	5.5	ok	even	5.4	9.0	0.6	3.8	0.1	842.7
334.1627	1	C 16 H 25 N Na O 5	334.1625	-0.5	0.5	4.5	ok	even	241.0	313.1	0.5	128.7	0.7	855.0
645.3344	1	C 32 H 50 N 2 Na O 10	645.3358	2.1	1.6	8.5	ok	even	25.8	44.5	2.0	24.1	0.5	828.7

Figure S9. HRESIMS of compound **1.**

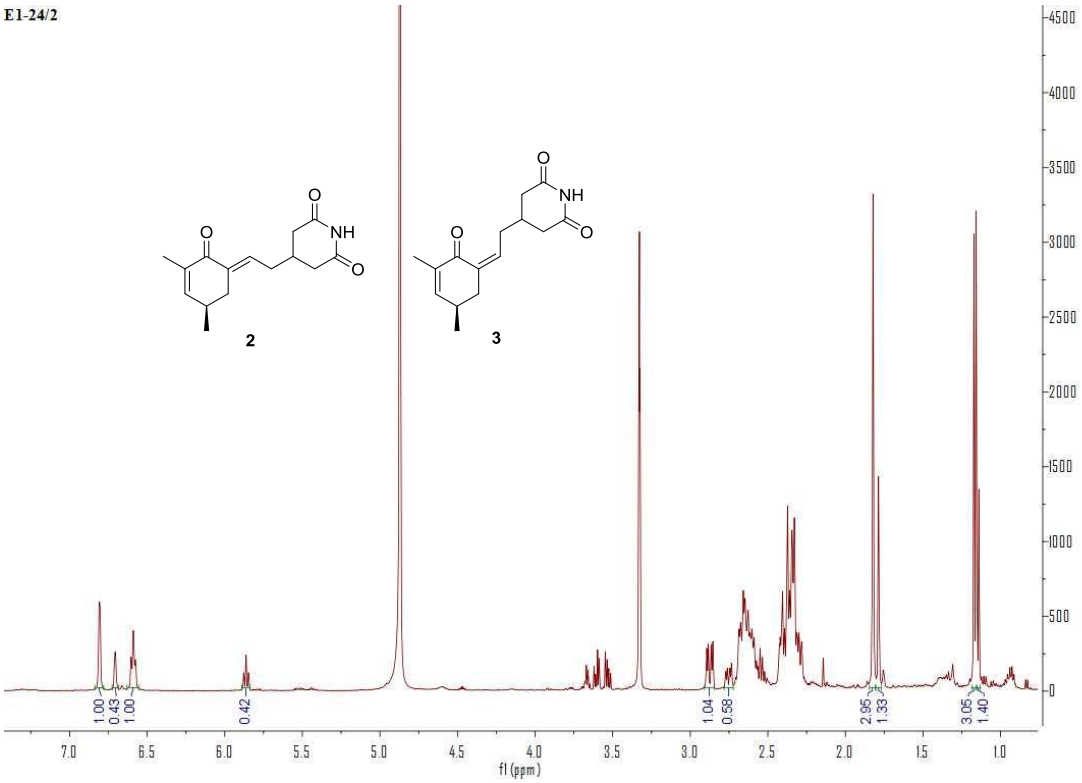


Figure S10. ^{1}H NMR (500 MHz) spectrum of compounds **2**/**3** in CD_3OD.

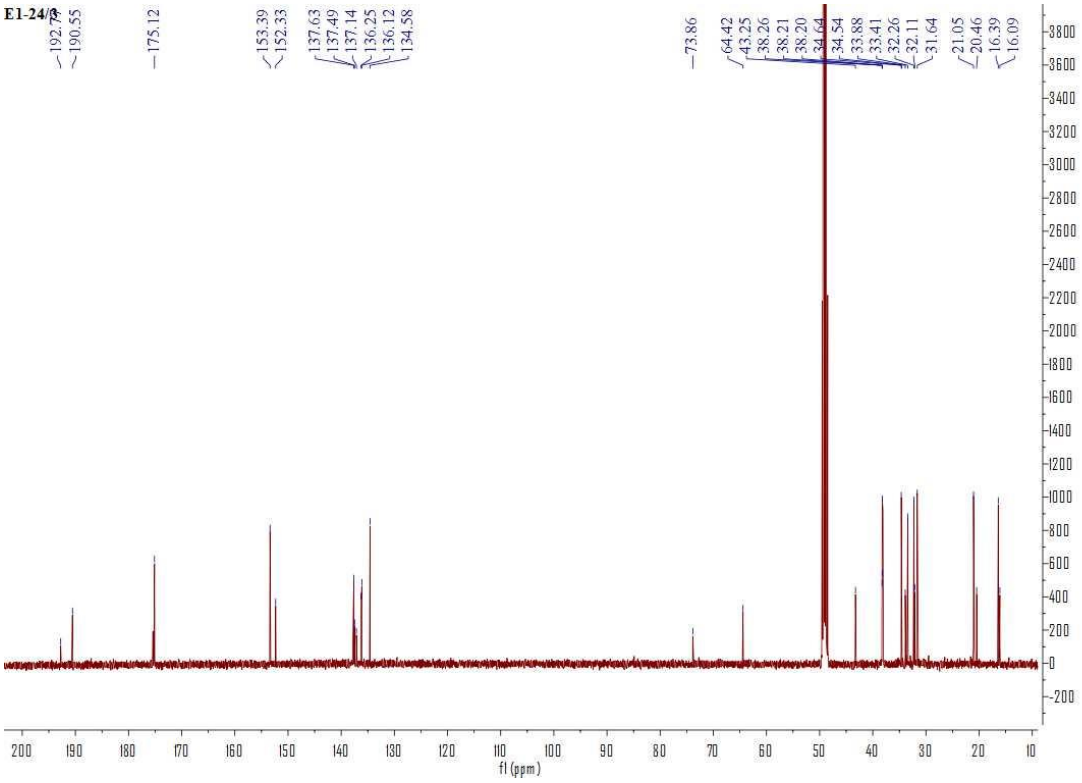


Figure S11. ^{13}C NMR (125 MHz) spectrum of compounds **2**/**3** in CD_3OD.

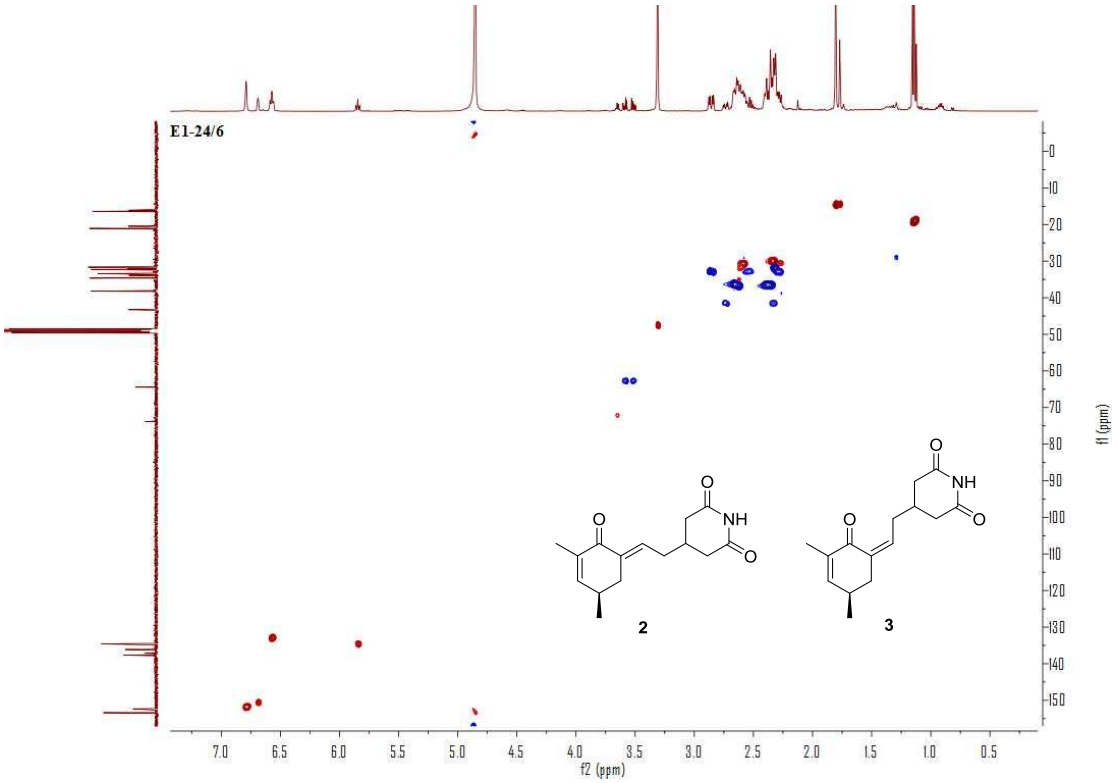


Figure S12. HSQC spectrum of compounds **2**/**3** in CD_3OD.

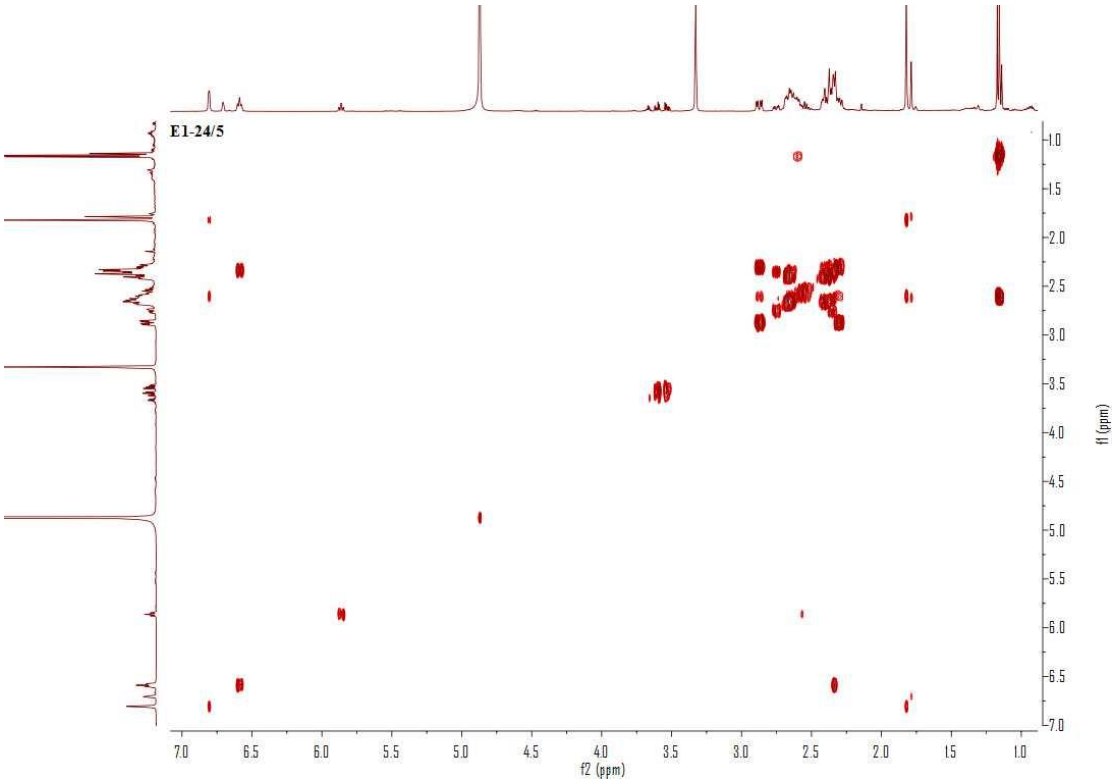


Figure S13. $^{1}H,^{1}H$ COSY spectrum of compounds **2**/**3** in CD_3OD.

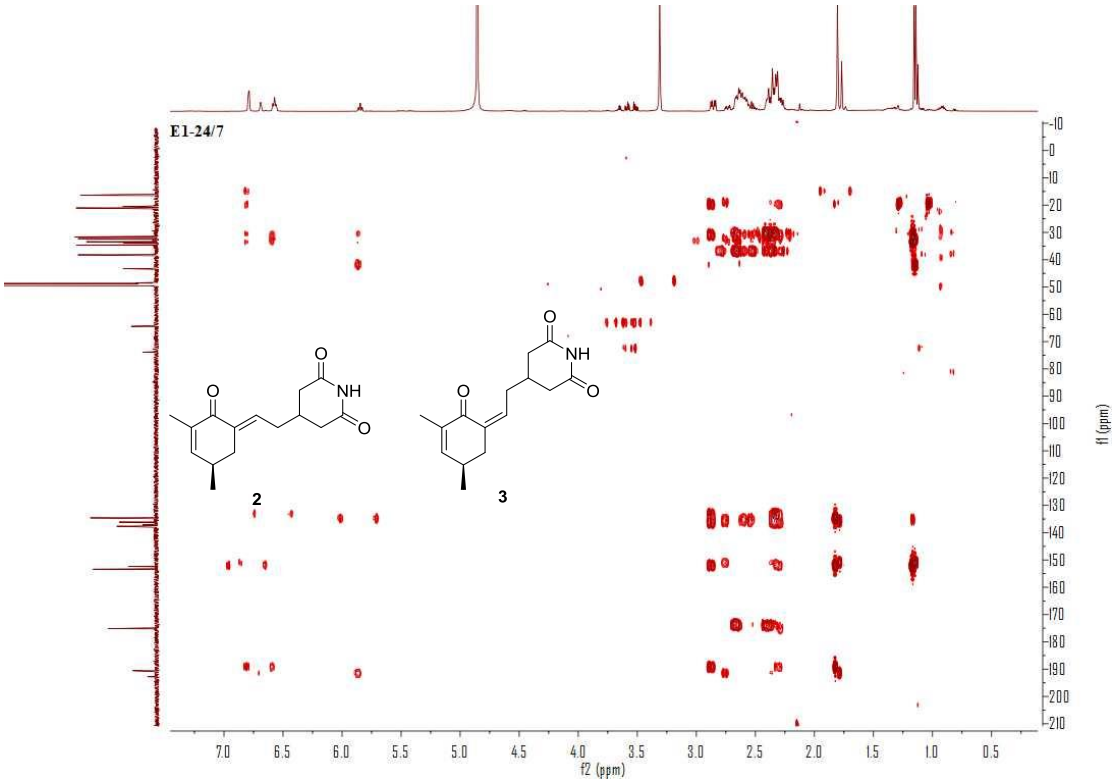


Figure S14. HMBC spectrum of compounds **2/3** in CD_3OD.

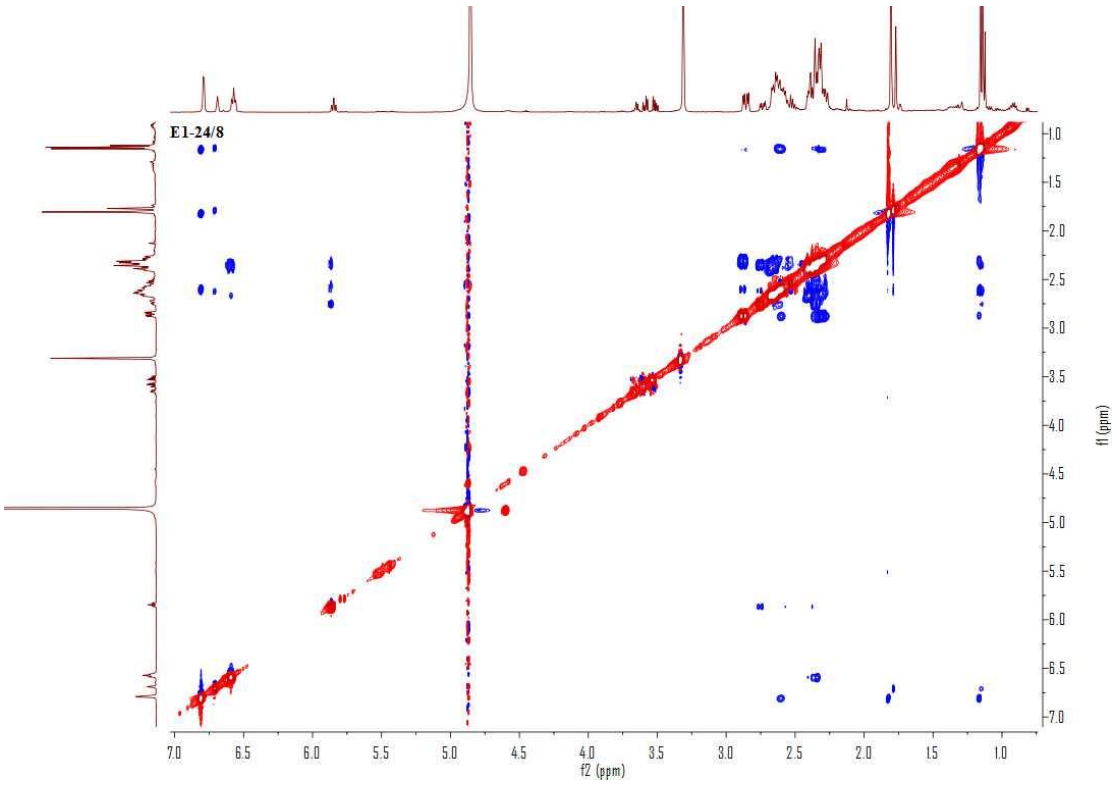


Figure S15. NOESY spectrum of compounds **2/3** in CD_3OD.

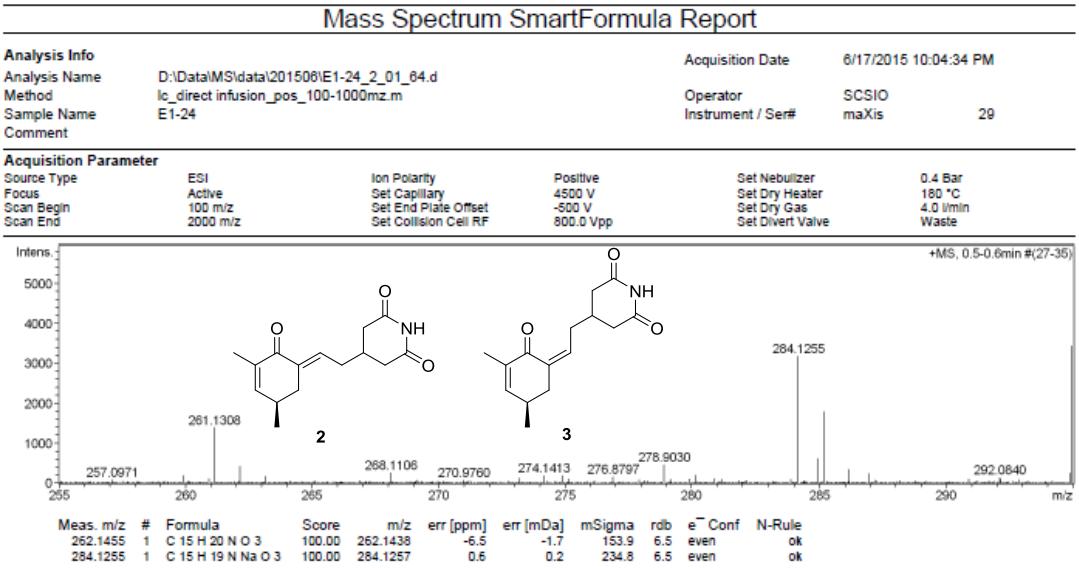


Figure S16. HRESIMS of compounds **2**/**3**.