Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Roquefornine A, a sesterterpenoid with a 5/6/5/5/6-fused ring system from the fungus *Penicillium roqueforti* YJ-14

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Contents

NMR Computational Methods

Table S1. Energy (298.15 K) analysis for **a**-**d**.

Conf.	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
a			
a1	-1165.963094	0.368975527	0.110192264
a2	-1165.963406	0.173192594	0.153367203
a3	-1165.962458	0.768071506	0.056165026
a4	-1165.963079	0.378388168	0.108454644
a5	-1165.963319	0.227785912	0.139860597
a6	-1165.963682	0.00	0.205469236
a7	-1165.962966	0.44929673	0.096215695
a8	-1165.963252	0.269829042	0.130275334
b			
b1	-1165.940225	0.01066766	0.339364246
b2	-1165.940242	0.00	0.345532919
b3	-1165.940155	0.054593318	0.315102835
c			
c1	-1165.936847	0.00	0.51818103
c2	-1165.936087	0.476907144	0.231596487
c3	-1165.93616	0.431098958	0.250222484
d			
d1	-1165.964736	0.063378449	0.194322391
d2	-1165.963033	1.132026958	0.031974794
d3	-1165.964591	0.154367312	0.166645777
d4	-1165.963073	1.106926582	0.033359199
d5	-1165.962993	1.157127334	0.030647841
d6	-1165.964837	0.00	0.216273206
d7	-1165.964016	0.515185217	0.090611052
d8	-1165.962837	1.2550188	0.025978208
d9	-1165.962843	1.251253744	0.026143899
d10	-1165.963881	0.599898986	0.078533438
d11	-1165.962815	1.268824007	0.025379605
d12	-1165.9639	0.587976308	0.080130591

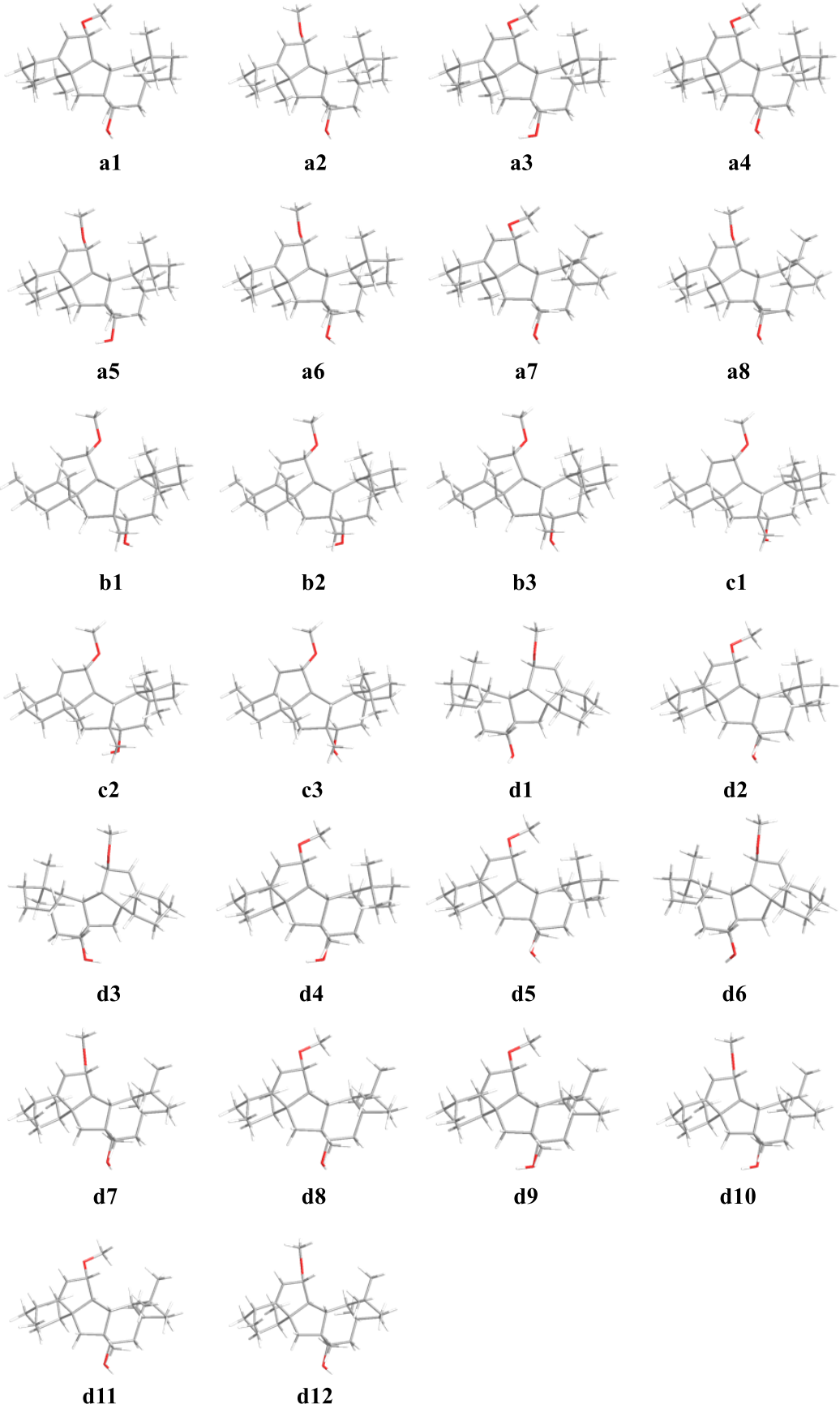

Figure S1. mPW1PW91/6-311+G(d,p) (chloroform) optimized lowest energy conformers for **a**-**d**.

	A	B	C	D	E	F	G	H
3								
12			DP4+	100.00%	0.00%	0.00%	0.00%	-
14	Nuclei	sp2?	xperimenta	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
15	C		41.3	43.51	51.46	43.32	53.59	
16	C		59.4	64.09	63.11	62.95	62.38	
17	C		43.1	46.35	41.88	45.06	42.57	
18	C		28	31.31	32.68	36.45	28.81	
19	C		34.8	38.38	37.52	42.76	30.80	
20	C		33.4	38.71	37.91	37.29	38.50	
21	C	x	162.5	174.36	164.99	175.04	169.49	
22	C	x	118.6	125.68	130.44	127.21	126.63	
23	C		90.2	92.39	84.97	85.69	94.37	
24	C		62.2	67.53	65.78	67.56	68.54	
25	C		45.8	49.30	52.36	52.58	49.78	
26	C		69.3	70.49	78.46	77.64	71.07	
27	C		44.1	47.07	47.71	48.18	46.28	
28	C		49.8	52.87	46.26	47.22	55.76	
29	C		43.2	47.16	46.44	46.31	47.53	
30	C		41.7	44.58	44.63	45.49	44.91	
31	C		40.5	42.99	42.80	42.74	42.77	
32	C		56.2	59.14	56.28	55.86	59.00	
33	C		43.3	47.04	47.99	47.79	47.09	
34	C		18.5	20.19	16.05	23.88	16.66	
35	C		19.5	21.28	19.17	19.20	21.88	
36	C		22.1	23.34	23.33	20.13	22.60	
37	C		33.4	33.89	33.29	33.95	34.38	
38	C		31.7	32.35	31.10	31.05	32.54	
39	C		25.4	26.52	24.58	25.22	27.05	
40	C		56.3	56.96	57.22	57.70	57.17	
41								
42	H		2.22	2.353	1.750	1.907	2.388	
43	H		1.57	1.459	1.701	1.511	1.502	
44	H		1.42	1.488	2.089	1.587	1.843	
45	H		1.3	1.321	2.085	1.535	1.362	
46	H		1.43	1.713	1.239	1.339	2.309	
47	H		1.55	1.743	1.642	1.965	1.878	
48	H		1.66	1.714	1.204	0.973	1.274	
49	H		2.85	3.172	2.333	2.354	2.555	
50	H	x	5.28	5.746	5.912	5.620	5.871	
51	H		3.85	3.880	4.072	4.097	3.907	
52	H		2.25	2.393	2.335	2.428	2.356	
53	H		3.84	3.975	3.724	3.776	3.922	
54	H		1.55	1.403	1.392	1.370	1.431	
55	H		1.55	1.501	1.539	1.586	1.540	
56	H		1.48	1.581	1.853	2.178	1.624	
57	H		1.57	1.545	1.540	1.546	1.672	
58	H		1.45	1.547	1.665	1.685	1.568	
59	H		1.45	1.547	1.594	1.504	1.515	
60	H		1.45	1.434	1.345	1.255	1.394	
61	H		1.4	1.331	1.831	2.129	1.537	
62	H		0.99	1.056	0.927	1.205	0.887	
63	H		1.16	1.234	1.085	1.117	1.212	
64	H		0.98	0.904	1.230	1.174	0.932	
65	H		1.28	1.321	1.153	1.126	1.295	
66	H		1.02	1.025	1.007	1.006	1.043	
67	H		0.9	0.991	1.024	0.905	0.991	
68	H		3.29	3.290	2.496	2.807	3.389	

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Unscaled Shifts	
3								
4			Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
5	sDP4+ (H data)		100.00%	0.00%	0.00%	0.00%	-	-
6	sDP4+ (C data)		100.00%	0.00%	0.00%	0.00%	-	-
7	sDP4+ (all data)		100.00%	0.00%	0.00%	0.00%	-	-
8	uDP4+ (H data)		100.00%	0.00%	0.00%	0.00%	-	-
9	uDP4+ (C data)		100.00%	0.00%	0.00%	0.00%	-	-
10	uDP4+ (all data)		100.00%	0.00%	0.00%	0.00%	-	-
11	DP4+ (H data)		100.00%	0.00%	0.00%	0.00%	-	-
12	DP4+ (C data)		100.00%	0.00%	0.00%	0.00%	-	-
13	DP4+ (all data)		100.00%	0.00%	0.00%	0.00%	-	-

Figure S2. DP4+ evaluation of theoretical and experimental data.

Table S2. Calculated (calc.) and experimental (exp.) ^{13}C NMR chemical shift values of **a**-**d** at the mPW1PW91/6-311+G(d,p) level in chloroform and total absolute deviation (TAD) and mean absolute error (MAE).

no.	exp.	calc. **a**	|calc. **a** – exp.|	calc. **b**	|calc. **b** – exp.|	calc. **c**	|calc. **c** – exp.|	calc. **d**	|calc. **d** – exp.|
1	41.3	43.51	2.21	51.46	10.16	43.32	2.02	53.59	12.29
2	59.4	64.09	4.69	63.11	3.71	62.95	3.55	62.38	2.98
3	43.1	46.35	3.25	41.88	1.22	45.06	1.96	42.57	0.53
4	28.0	31.31	3.31	32.68	4.68	36.45	8.45	28.81	0.81
5	34.8	38.38	3.58	37.52	2.72	42.76	7.96	30.80	4.00
6	33.4	38.71	5.31	37.91	4.51	37.29	3.89	38.50	5.10
7	162.5	174.36	11.86	164.99	2.49	175.04	12.54	169.49	6.99
8	118.6	125.68	7.08	130.44	11.84	127.21	8.61	126.63	8.03
9	90.2	92.39	2.19	84.97	5.23	85.69	4.51	94.37	4.17
10	62.2	67.53	5.33	65.78	3.58	67.56	5.36	68.54	6.34
11	45.8	49.30	3.5	52.36	6.56	52.58	6.78	49.78	3.98
12	69.3	70.49	1.19	78.46	9.16	77.64	8.34	71.07	1.77
13	44.1	47.07	2.97	47.71	3.61	48.18	4.08	46.28	2.18
14	49.8	52.87	3.07	46.26	3.54	47.22	2.58	55.76	5.96
15	43.2	47.16	3.96	46.44	3.24	46.31	3.11	47.53	4.33
16	41.7	44.58	2.88	44.63	2.93	45.49	3.79	44.91	3.21
17	40.5	42.99	2.49	42.80	2.30	42.74	2.24	42.77	2.27
18	56.2	59.14	2.94	56.28	0.08	55.86	0.34	59.00	2.80
19	43.3	47.04	3.74	47.99	4.69	47.79	4.49	47.09	3.79
20	18.5	20.19	1.69	16.05	2.45	23.88	5.38	16.66	1.84
21	19.5	21.28	1.78	19.17	0.33	19.20	0.30	21.88	2.38
22	22.1	23.34	1.24	23.33	1.23	20.13	1.97	22.60	0.50
23	33.4	33.89	0.49	33.29	0.11	33.95	0.55	34.38	0.98
24	31.7	32.35	0.65	31.10	0.60	31.05	0.65	32.54	0.84
25	25.4	26.52	1.12	24.58	0.82	25.22	0.18	27.05	1.65
26	56.3	56.96	0.66	57.22	0.92	57.70	1.40	57.17	0.87
TAD			83.17		92.72		105.02		90.60
MAE			3.20		3.57		4.04		3.48

Table S3. Calculated (calc.) and experimental (exp.) ^{1}H NMR chemical shift values of **a**-**d** at the mPW1PW91/6-311+G(d,p) level in chloroform and total absolute deviation (TAD) and mean absolute error (MAE).

no.	exp.	calc. **a**	|calc. **a** – exp.|	calc. **b**	|calc. **b** – exp.|	calc. **c**	|calc. **c** – exp.|	calc. **d**	|calc. **d** – exp.|
1α	2.22	2.35	0.13	1.75	0.47	1.91	0.31	2.39	0.17
1β	1.58	1.46	0.12	1.70	0.12	1.51	0.07	1.50	0.08
3	1.42	1.49	0.07	2.09	0.67	1.59	0.17	1.84	0.42
4α	1.30	1.32	0.02	2.09	0.79	1.54	0.24	1.36	0.06
4β	1.43	1.71	0.28	1.24	0.19	1.34	0.09	2.31	0.88
5α	1.55	1.74	0.20	1.64	0.09	1.96	0.41	1.88	0.33
5β	1.66	1.71	0.05	1.20	0.46	0.97	0.69	1.27	0.39
6	2.85	3.17	0.29	2.33	0.52	2.35	0.50	2.56	0.29
8	5.28	5.75	0.45	5.91	0.63	5.62	0.34	5.87	0.59
9	3.85	3.88	0.02	4.07	0.22	4.10	0.25	3.91	0.06
10	2.25	2.39	0.15	2.34	0.09	2.43	0.18	2.36	0.11
12	3.84	3.98	0.14	3.72	0.12	3.78	0.06	3.92	0.08
13α	1.55	1.40	0.19	1.39	0.16	1.37	0.18	1.43	0.12
13β	1.55	1.50	0.02	1.54	0.01	1.59	0.04	1.54	0.01
14	1.49	1.58	0.11	1.85	0.36	2.18	0.69	1.62	0.13
16α	1.57	1.54	0.01	1.54	0.03	1.55	0.02	1.67	0.10
16β	1.45	1.55	0.05	1.66	0.21	1.68	0.23	1.57	0.12
17α	1.45	1.55	0.05	1.59	0.14	1.50	0.05	1.52	0.07
17β	1.45	1.43	0.04	1.34	0.11	1.25	0.20	1.39	0.06
18	1.40	1.33	0.05	1.83	0.43	2.13	0.73	1.54	0.14
20	0.99	1.06	0.06	0.93	0.06	1.20	0.21	0.89	0.10
21	1.16	1.23	0.07	1.08	0.08	1.12	0.04	1.21	0.05
22	0.98	0.90	0.07	1.23	0.25	1.17	0.19	0.93	0.05
23	1.28	1.32	0.05	1.15	0.13	1.13	0.15	1.30	0.02
24	1.02	1.01	0.01	1.01	0.01	1.01	0.01	1.04	0.02
25	0.90	0.99	0.10	1.02	0.12	0.90	0.00	0.99	0.09
26	3.29	3.29	0.00	2.50	0.79	2.81	0.48	3.39	0.10
TAD			2.88		7.29		6.58		4.60
MAE			0.11		0.28		0.25		0.18

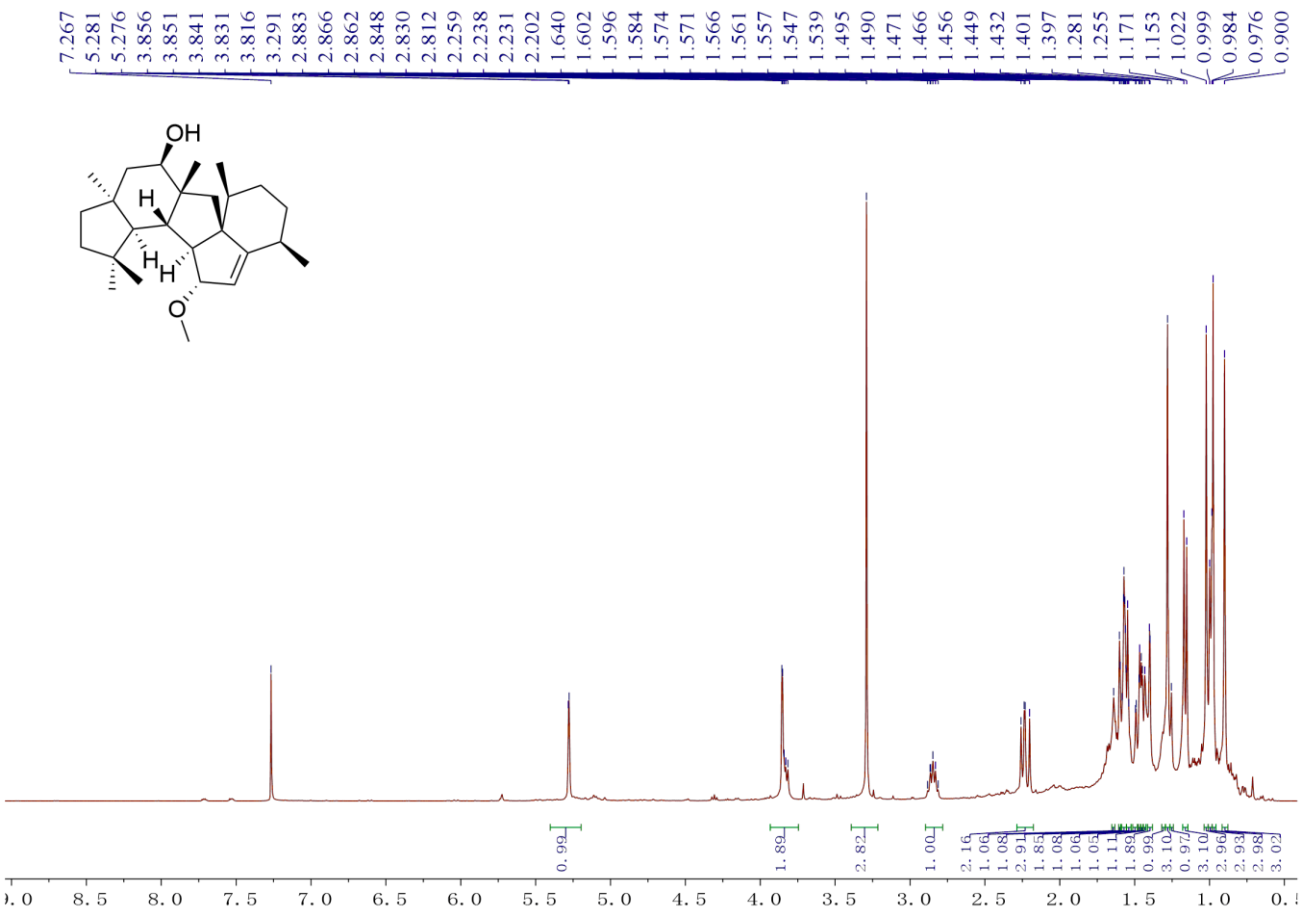

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of roquefornine A (**1**).

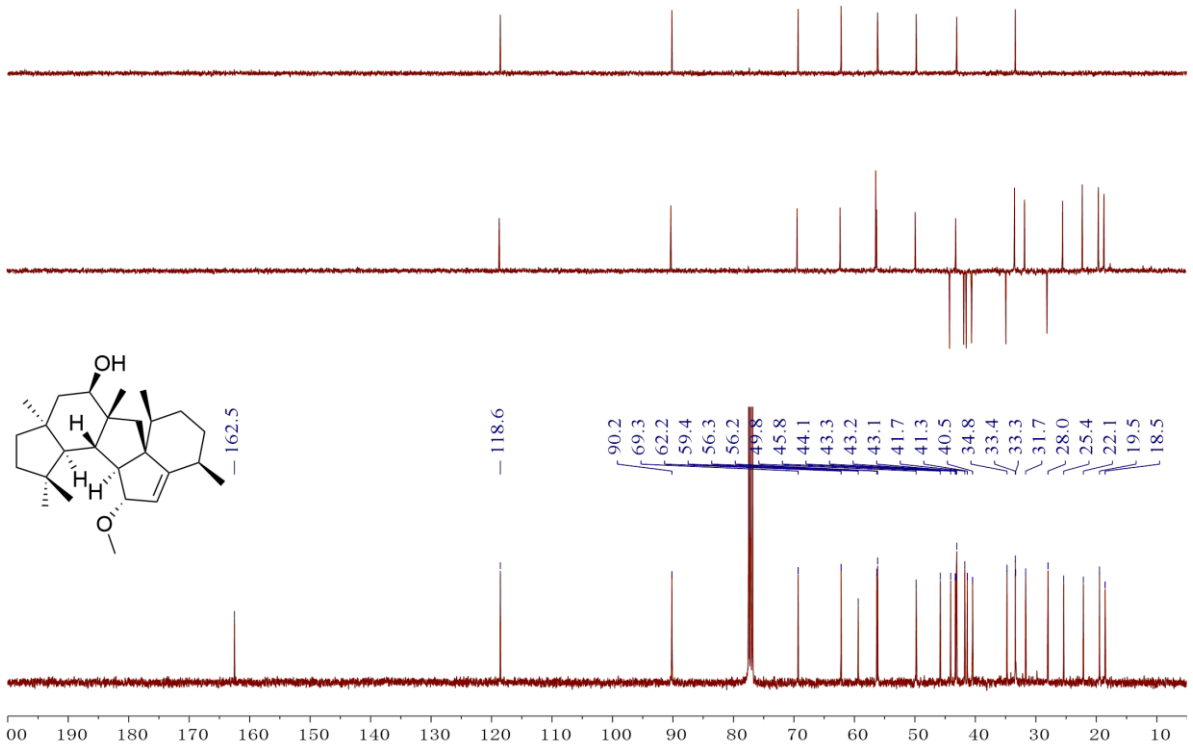

Figure S4. ^{13}C NMR spectrum ($CDCl_3$, 150 MHz) of roquefornine A (**1**).

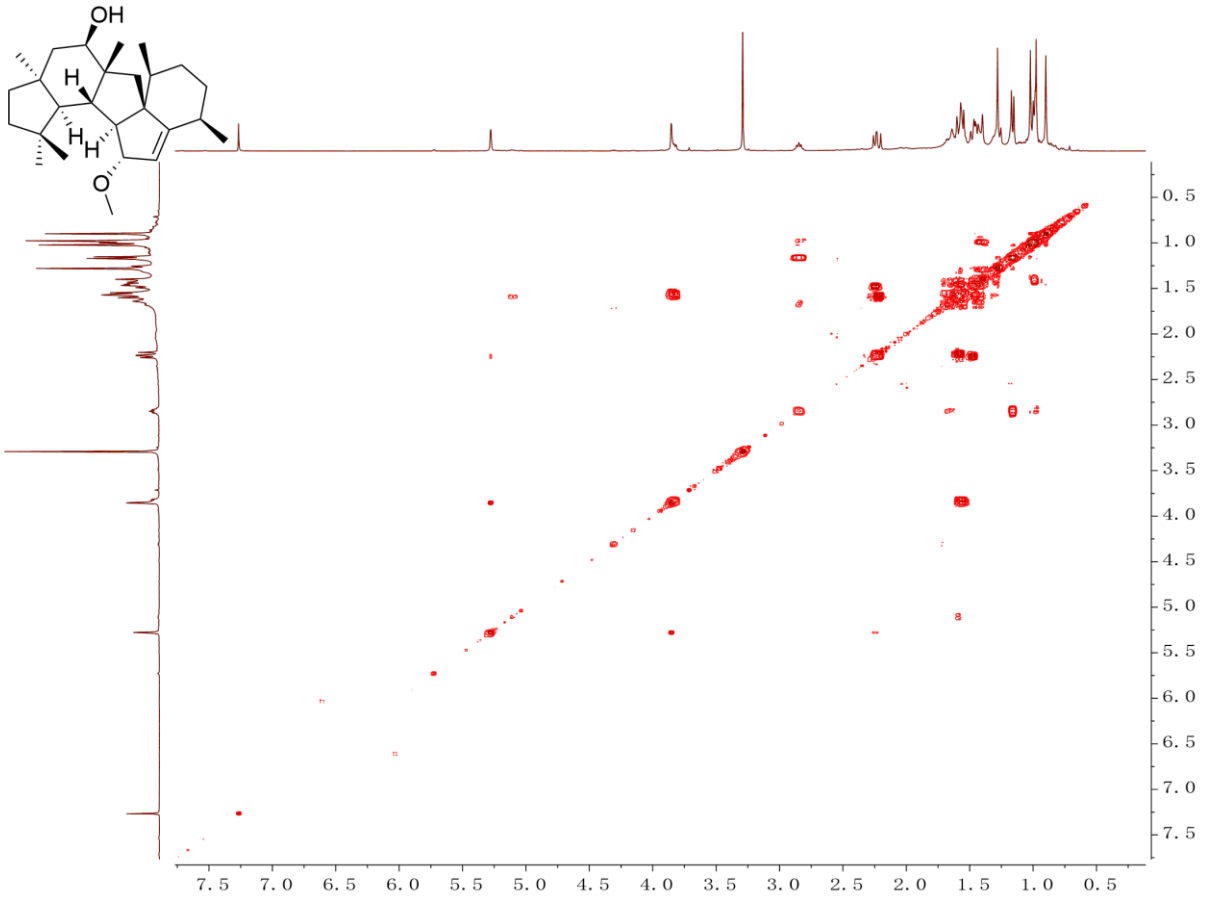

Figure S5. ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 600 MHz) of roquefornine A (**1**).

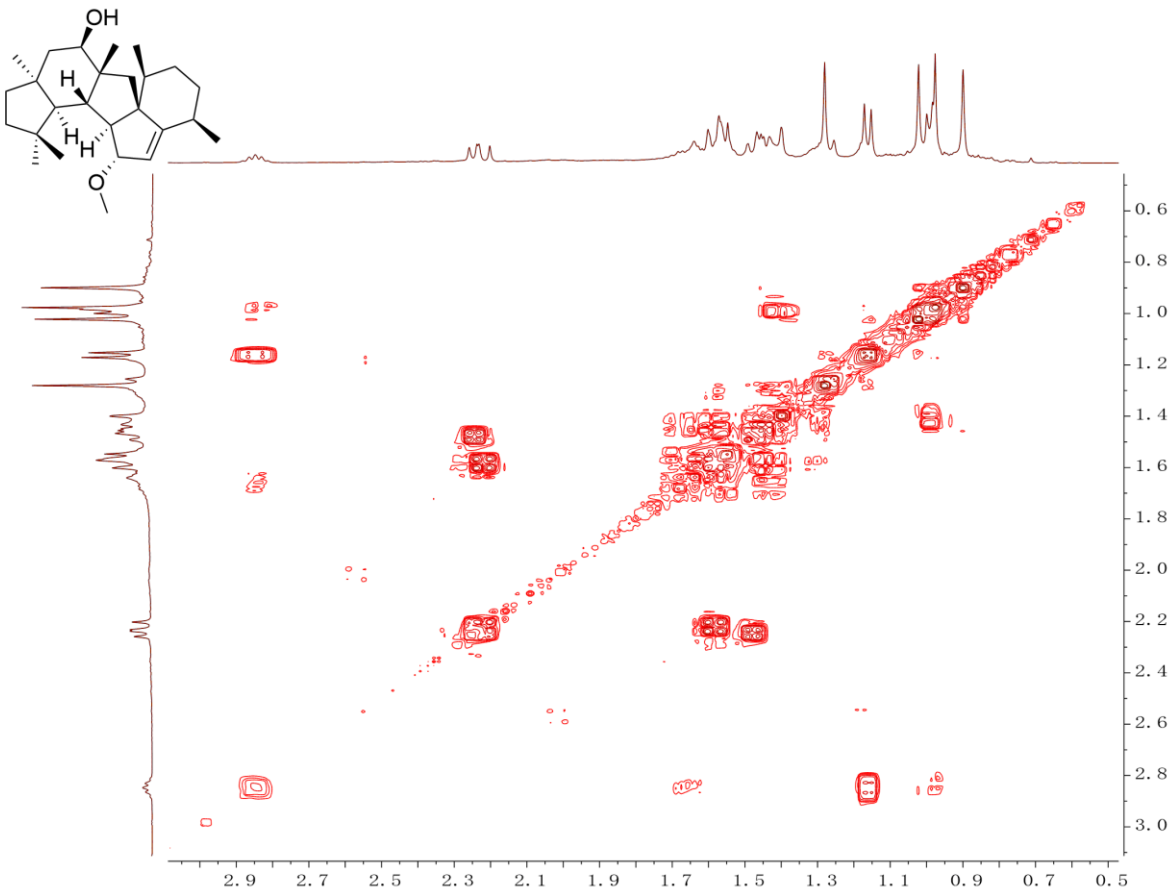

Figure S6. Enlarged ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 600 MHz) of roquefornine A (**1**).

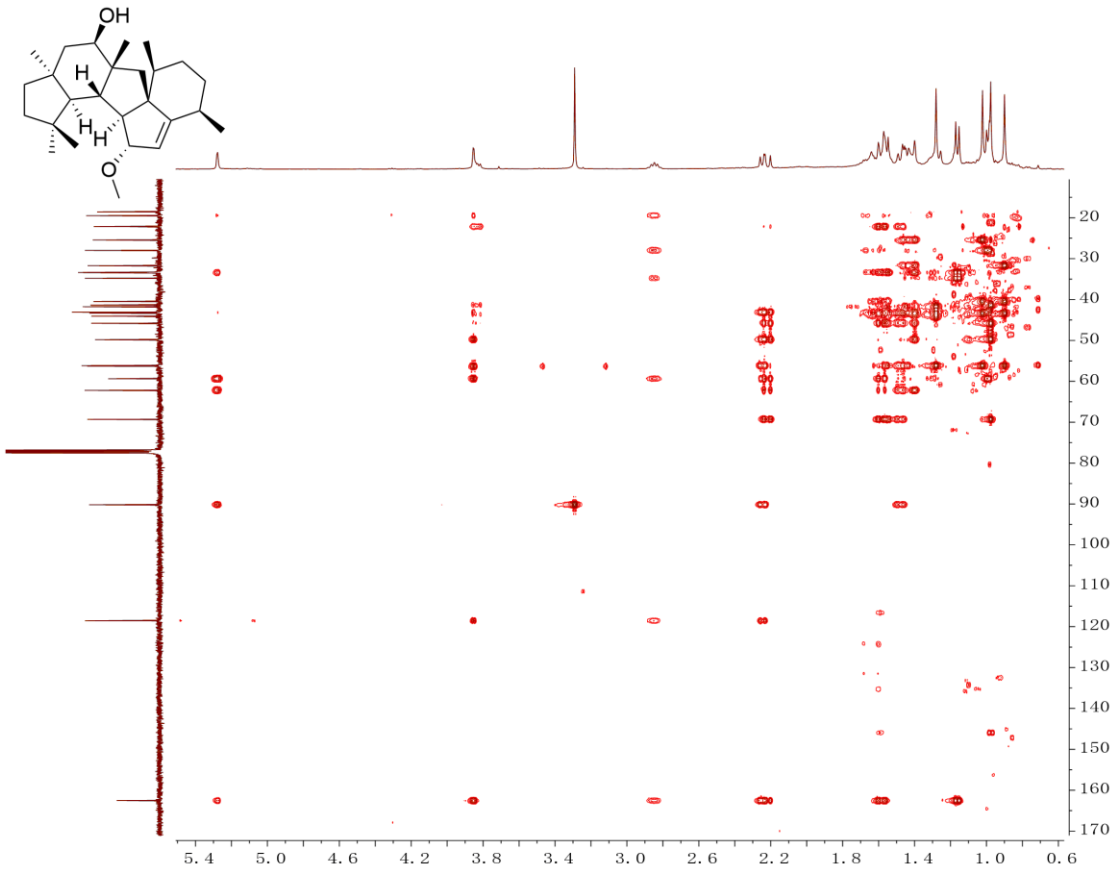

Figure S7. HMBC spectrum ($CDCl_3$, 600 MHz) of roquefornine A (**1**).

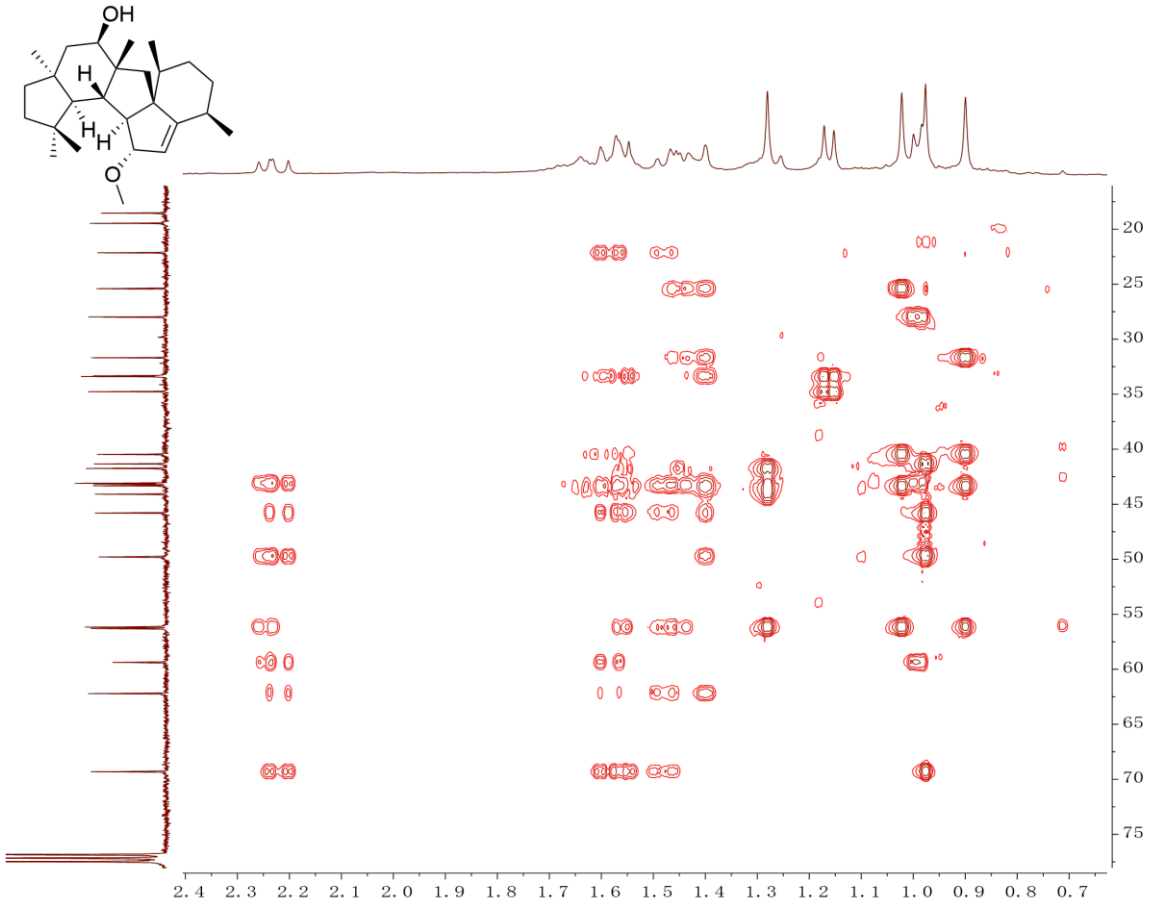

Figure S8. Enlarged HMBC spectrum ($CDCl_3$, 600 MHz) of roquefornine A (**1**).

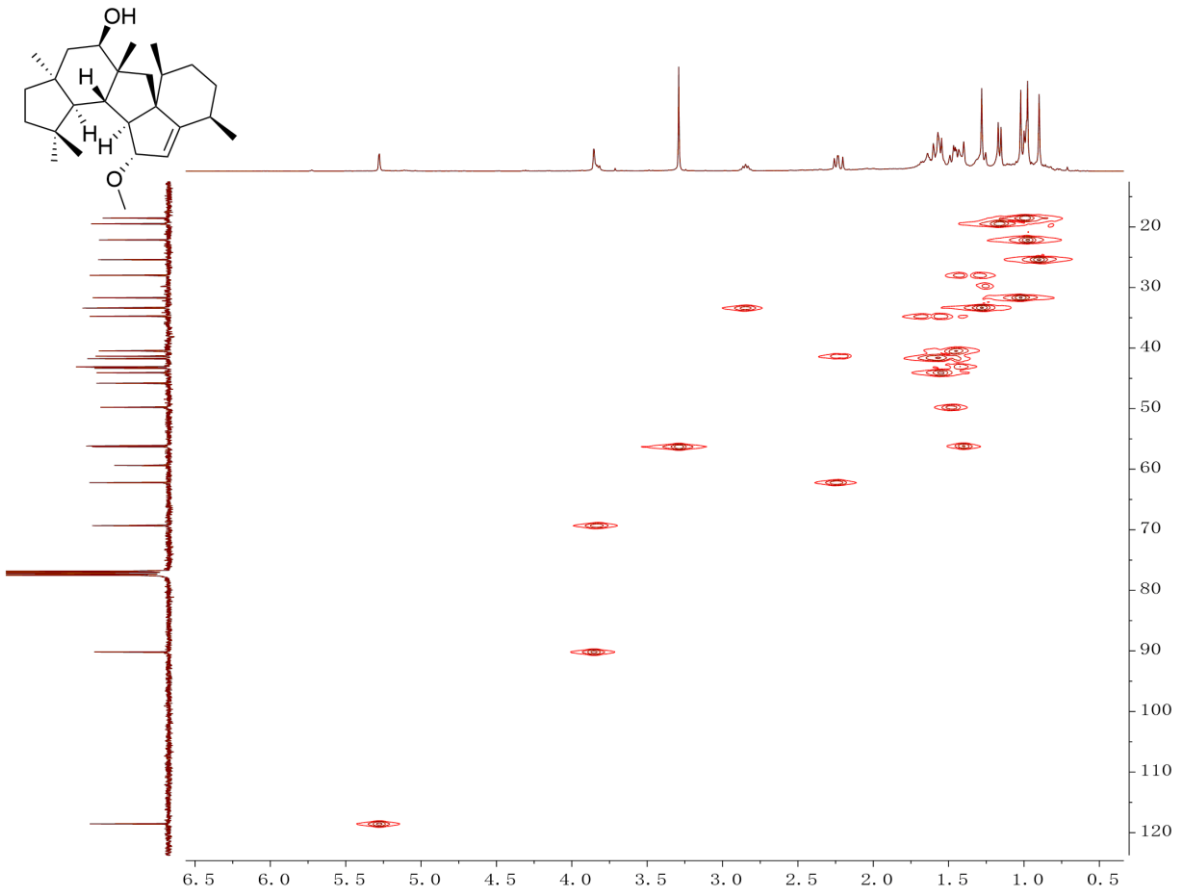

Figure S9. HSQC spectrum ($CDCl_3$, 600 MHz) of roquefornine A (**1**).

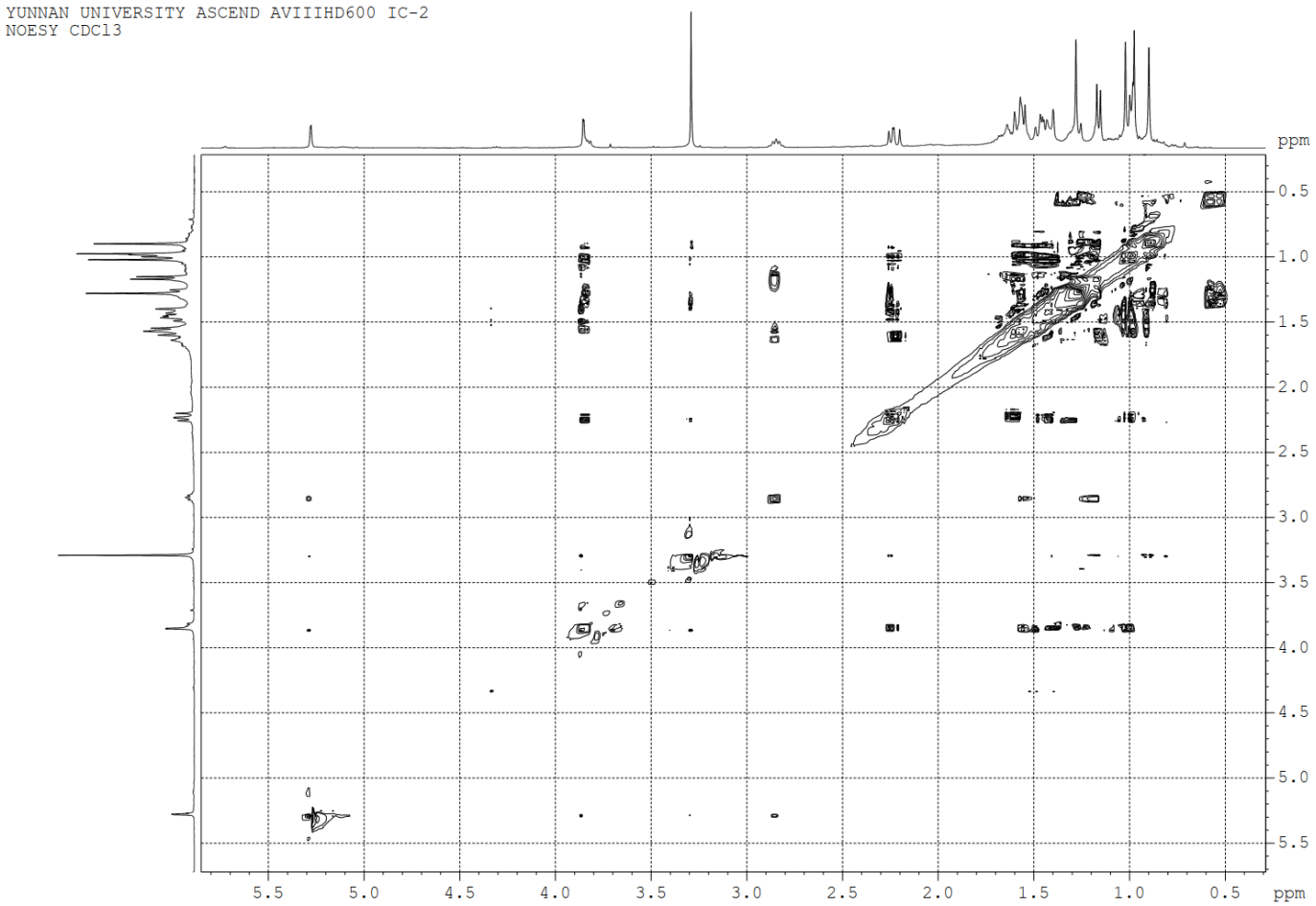

Figure S10. NOESY spectrum ($CDCl_3$, 600 MHz) of roquefornine A (**1**).

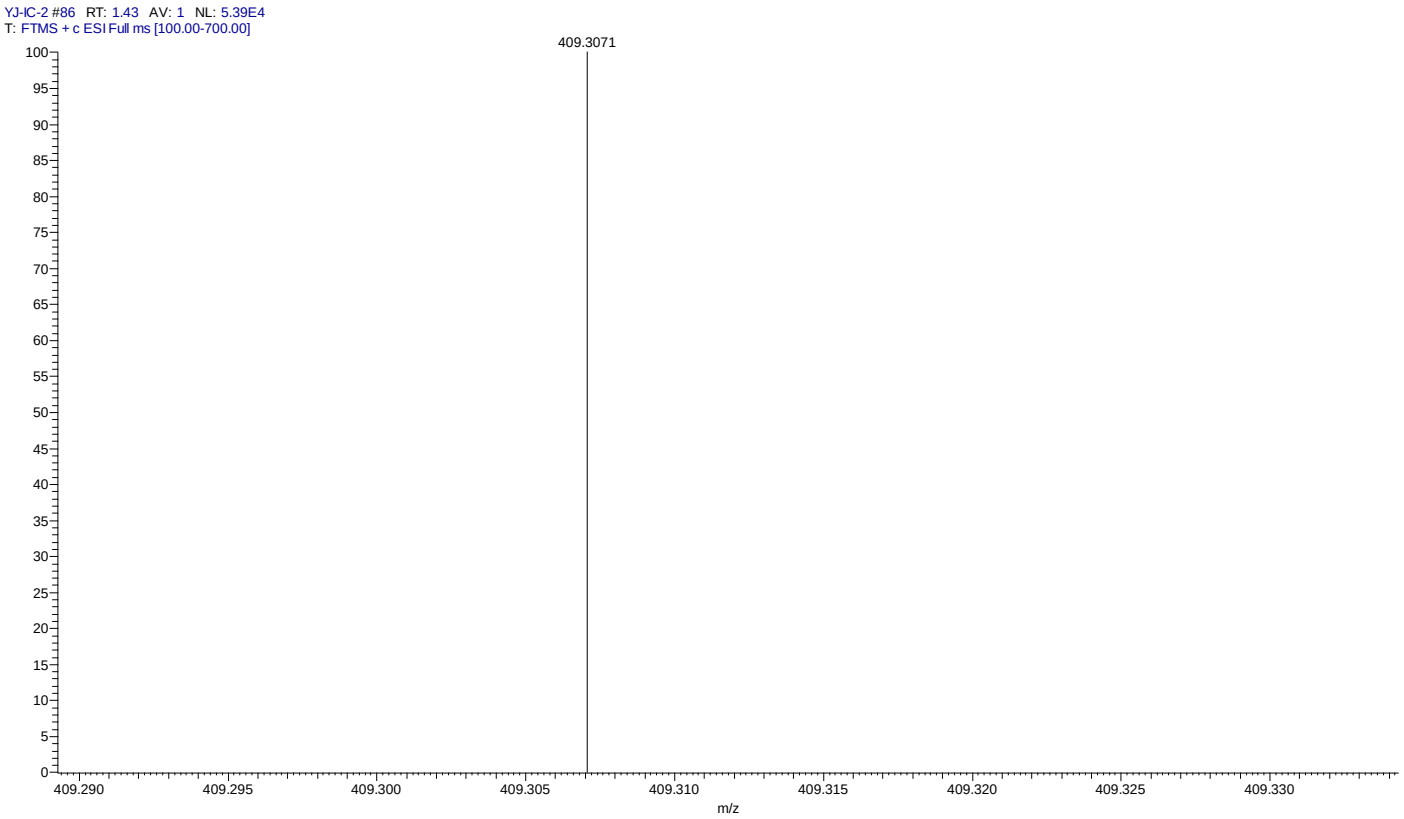

Figure S11. (+)-HR-ESI-MS $[M + Na]^+$ of roquefornine A (**1**).