

Supporting Information for
Lycopalhine A, a novel sterically congested *Lycopodium*
alkaloid with an unprecedented skeleton from *Palhinhaea*
cernua

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Detailed experimental procedures

General Experimental Procedures. Optical rotation was measured at 15°C using a Jasco P-1020 polarimeter equipped with a 1 dm pathlength cell. IR spectrum was obtained over the frequency range of 399.3-3996.3 cm^{-1} using a Tensor 27 spectrometer with KBr pellets. UV spectrum was recorded using a Shimadzu UV-2401A spectrophotometer equipped with a DAD and a 1 cm pathlength cell. Samples in methanol solution (0.032mg/ml) were scanned from 190-400 nm in 1 nm steps. ECD spectrum was recorded using an Applied Photophysics Chirascan spectrometer equipped with a 1 cm pathlength cell. Samples in methanol solution (0.32mg/ml) were scanned from 195-400 nm in 1 nm steps. 1D and 2D NMR spectra were performed on a Bruker DRX-500 spectrometer with TMS as an internal standard. Mass spectra were obtained on a Bruker Esquire HCT 3D ion trap mass spectrometer (ESI mode) and an API-Qstar-Pulsar instrument (HRESI mode). Column chromatography (CC) was performed using silica gel (200–300 mesh, Qingdao Marine Chemical Co. Ltd., Qingdao, People's Republic of China) and MCI gel (75–150 μm ; Mitsubishi Chemical Corporation, Japan).

Computational Methods. The theoretical ^{13}C NMR and ECD spectra were performed by density functional theory (DFT) and time-dependent DFT (TD-DFT), respectively, using Gaussian 09¹ and analyzed using GUIs *GaussView* (version 5.0). A conformational search using molecular mechanics calculations was performed in Discovery Studio 3.1 Client.² The corresponding minimum geometries were fully optimized by DFT at the B3LYP/6-31G(d) level, followed then optimized at the

B3LYP/6-31+G(d, p) level of theory in three systems (the gas phase, methanol, and pyridine). Frequency calculations (at 298.15 K) at the same level of theory were used to confirm the nature of all stationary points as minima and also provided values for computed free energies.³ Boltzmann statistics based on relative free energies at 298.15 K was used in the computations.⁴ The relative energies, relative free energies in three systems (the gas phase, methanol, and pyridine), together with their Boltzmann-calculated distributions are given in Table S1.

The ¹³C NMR shielding constants were computed using GIAO technique at the mPW1PW91-SCRF/6-311+G(2d,p) level of theory in PCM solvent continuum model with pyridine as a solvent.⁵ The ¹³C NMR chemical shifts were calculated as $\delta = \sigma_{\text{ref.}} - \sigma$, where $\sigma_{\text{ref.}}$ was the shielding constant of TMS calculated at the same level of theory (187.1160 ppm).⁶ Calibration of the ¹³C NMR chemical shifts was effected by plotting experimental values against calculated values and performing linear regression analysis. The resulting equation was then used for calibrating the calculated ¹³C NMR chemical shifts (see Figure S19).⁶

Time-dependent DFT (TD-DFT) with the basis set B3LYP/6-31+G(d,p) was used to calculate the excitation energies (E), oscillator strength (f), rotatory strength in velocity form (R_{vel}) and rotatory strength in length form (R_{len}) of the lowest 30 excited states.⁷ The calculations were performed in the gas phase and in methanol using the COSMO solvent continuum model. The peak intensity, $\Delta\varepsilon(E)$, was calculated with the Gaussian function:

$$\Delta\varepsilon(E) = \frac{1}{2.297 \times 10^{-39}} \frac{1}{\sqrt{2\pi}\sigma} \sum_i^A \Delta E_i R_i e^{-[(E - \Delta E_i)/(2\sigma)]^2}$$

where σ is the width of the band at $1/e$ height and ΔE_i and R_i are the excitation energies and rotatory strengths for transition i , respectively, $\sigma = 0.20$ eV and R_{vel} were used.⁷

Extraction and Isolation. The whole plant of *P. cernua* was collected in Guizhou Province, People's Republic of China, and was identified by one of the authors (X. C) (voucher no. 201105P). The air-dried and powdered sample (60 kg) was extracted with pure MeOH for three times (4, 3, and 3 h). The extracts were partitioned between EtOAc and 1% HCl/H₂O. The water-soluble portion was adjusted to pH 9 with saturated aqueous Na₂CO₃ solution, and then was extracted with CHCl₃ to afford an alkaloidal extract (51.5 g). The latter was chromatographed on MPLC (MCI gel) eluting with a gradient of MeOH–H₂O (3:7, 6:4, 8:2, and 1:0) to give four fractions (F01–F04). F01 (6 g) and F02 (12 g) were submitted to repeated silica gel CC to yield lycopalhine A (**1**, 1.5 mg), and a known compound obscurinine (**2**, 10 mg)⁸, respectively.

Lycopalhine A (1): colorless gum; $[\alpha]_D^{25} + 89.1$ (c 0.17, CH₃OH); UV (CH₃OH) λ_{max} (log ϵ) 203 (2.61) nm; IR (KBr) ν_{max} 3431, 2921, 1716, 1631, 1417, 1261, 1097, 1026, 802, 581 cm⁻¹; ¹H and ¹³C NMR data, see Table 1; positive ESIMS m/z 289 [M + H]⁺; positive HRESIMS m/z 2891920 [M + H]⁺ (calcd for C₁₇H₂₅N₂O₂, 289.1916).

Acetylcholinesterase (AChE)/Butrylcholinesterase(BuChE) Inhibitory Activity

Assay. AChE/BuChE inhibitory activity of the compounds isolated was assayed by the spectrophotometric method developed by Ellman et.al with slightly modification.⁹

S-acetylthiocholine iodide, *S*-butyrylthiocholine iodide, 5,5'-dithio-bis-(2-nitrobenzoic) acid (DTNB, Ellman's reagent), AChE and BuChE derived from human erythrocytes were purchased from Sigma Chemical Company. Compounds were dissolved in DMSO. The reaction mixture contained 110 μ L of phosphate buffer (pH 8.0), 10 μ L of test compound (50 μ M), and 40 μ L of AChE or BuChE (0.04 U/100 μ L), and the mixture was incubated for 20 min (30 °C). The reaction was initiated by the addition of 20 μ L of DTNB (6.25 mM) and 20 μ L of acetylthiocholine or butyrylthiocholine for AChE or BuChE inhibitory activity, respectively. The hydrolysis of acetylthiocholine or butyrylthiocholine was monitored at 405 nm after 30 min. Tacrine was used as positive control. All the reactions were performed in triplicate. The percentage inhibition was calculated as follows: % inhibition = $(E - S)/E \times 100$ (E is the activity of the enzyme without test compound and S is the activity of enzyme with test compound).

Notes and references

- 1 Gaussian 09 package citation: Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
- 2 Reference 7 in the manuscript.
- 3 T. Oja, P. Tähtinen, N. Dreijack, P. Mäntsälä, J. Niemi, M. Metsä-Ketelä and K. D. Klika, *Tetrahedron: Asymmetry*, 2012, **23**, 670–682.
- 4 (a) M. W. Lodewyk and D. J. Tantillo, *J. Nat. Prod.*, 2011, **74**, 1339–1343. (b) P. Tähtinen, T. Oja, N. Dreijack, P. Mäntsälä, J. Niemi, M. Metsä-Ketelä and K. D. Klika, *RSC Adv.*, 2012, **2**, 5098–5100.

- 5 Reference 8 in the manuscript.
- 6 Reference 9 in the manuscript.
- 7 References 10 and 11 in the manuscript.
- 8 Reference 12 in the manuscript.
- 9 Reference 14 in the manuscript.

Figure S1. ^1H NMR spectrum (full spectrum) of lycopalhine A (**1**) in pyridine- d_5 (500 MHz)

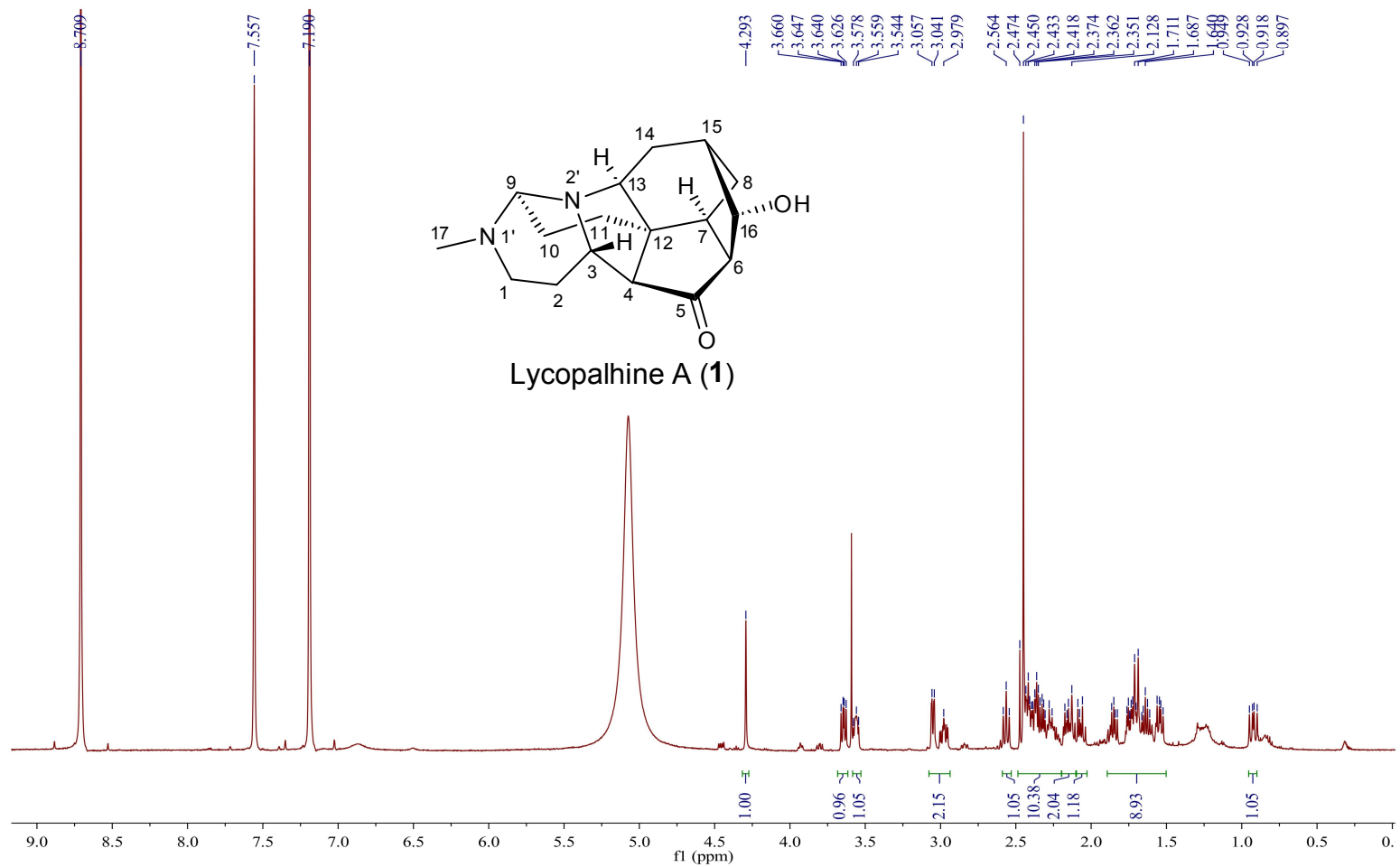


Figure S2. ^1H NMR spectrum (0–4.5 ppm) of lycopalhine A (**1**) in pyridine- d_5 (500 MHz)

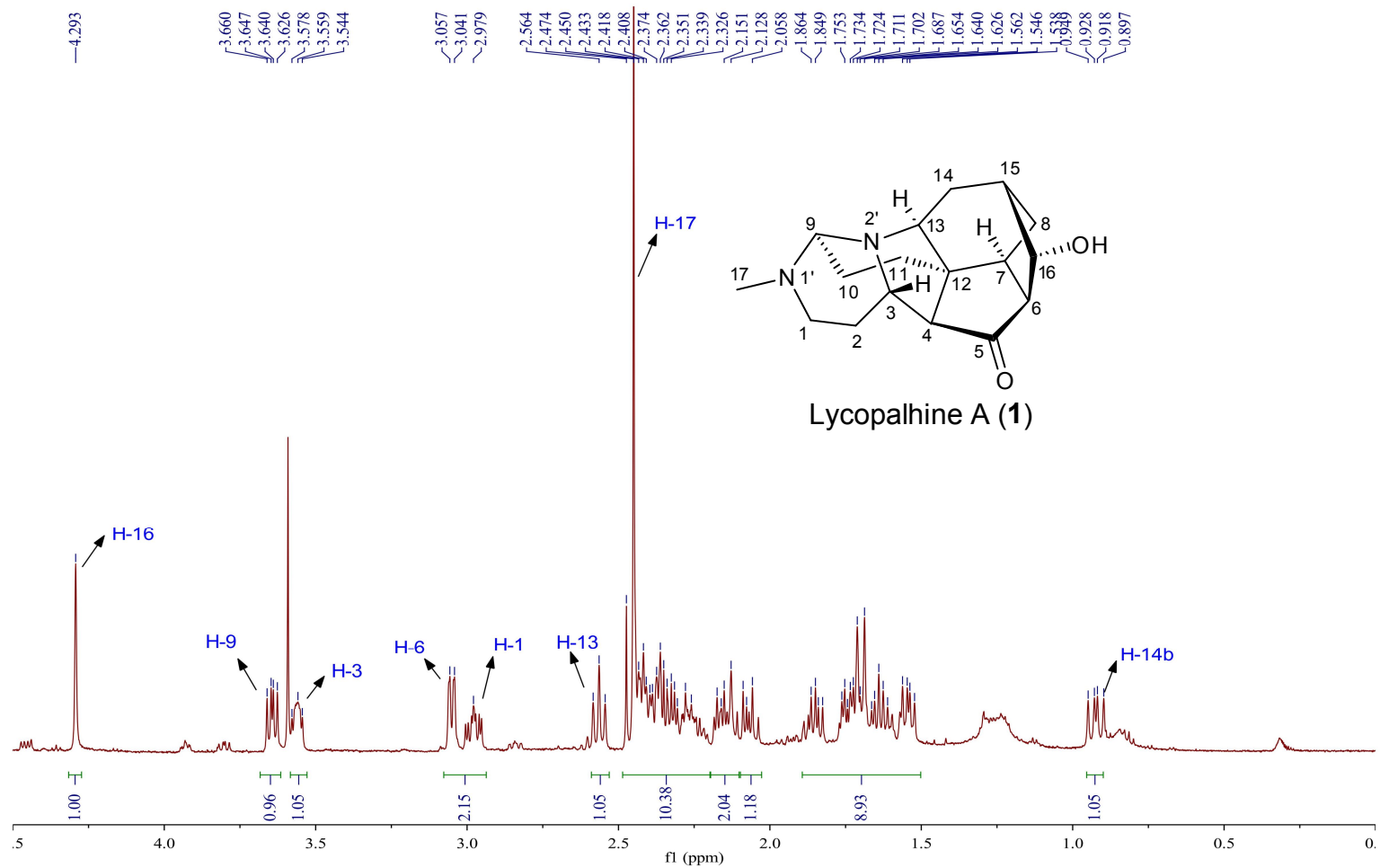


Figure S3. ^1H NMR spectrum (1.5–2.5 ppm) of lycopalhine A (1) in pyridine- d_5 (500 MHz)

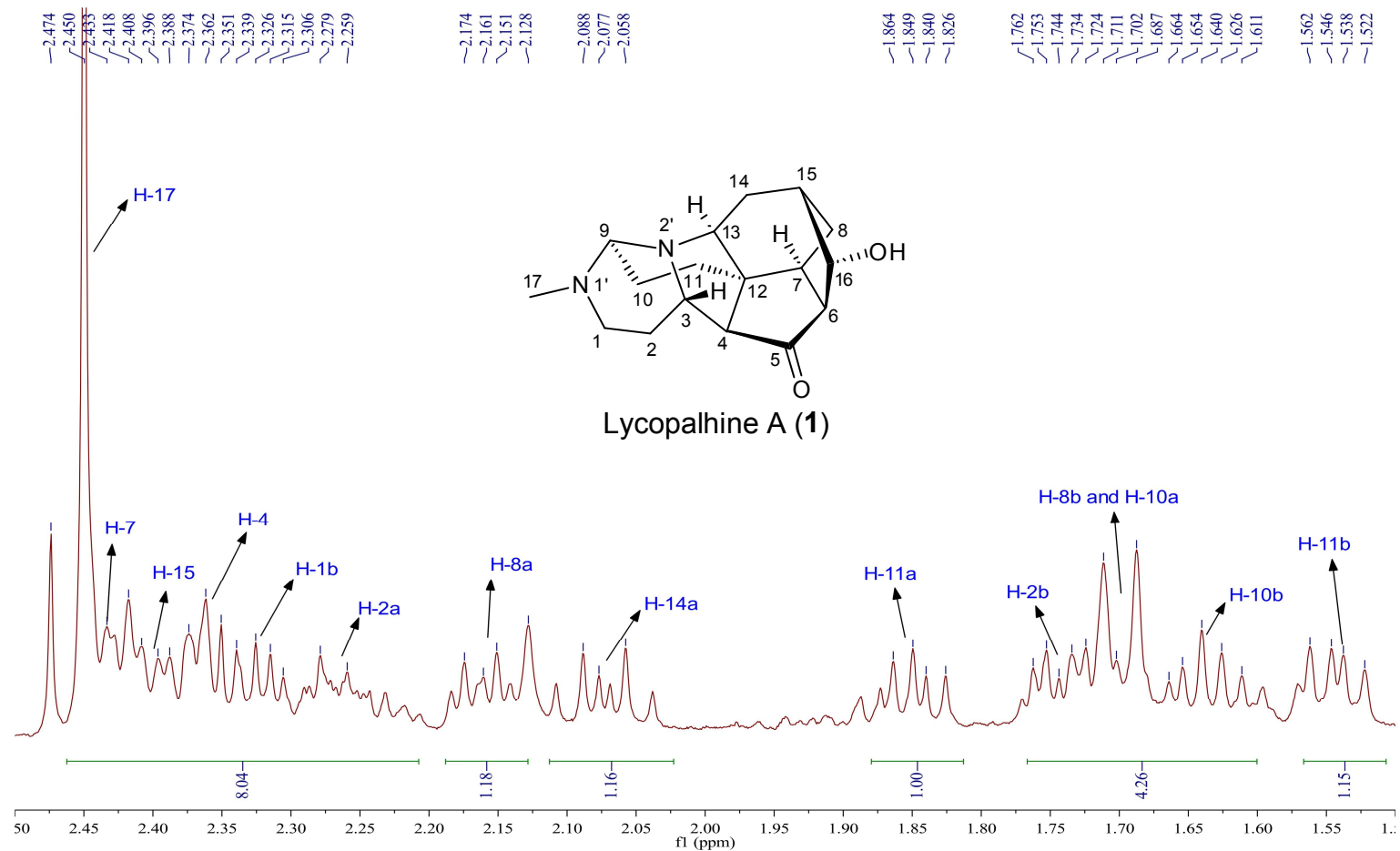


Figure S4. ^{13}C and DEPT NMR spectra (full spectra) of lycopalhine A (**1**) in pyridine- d_5 (125 MHz)

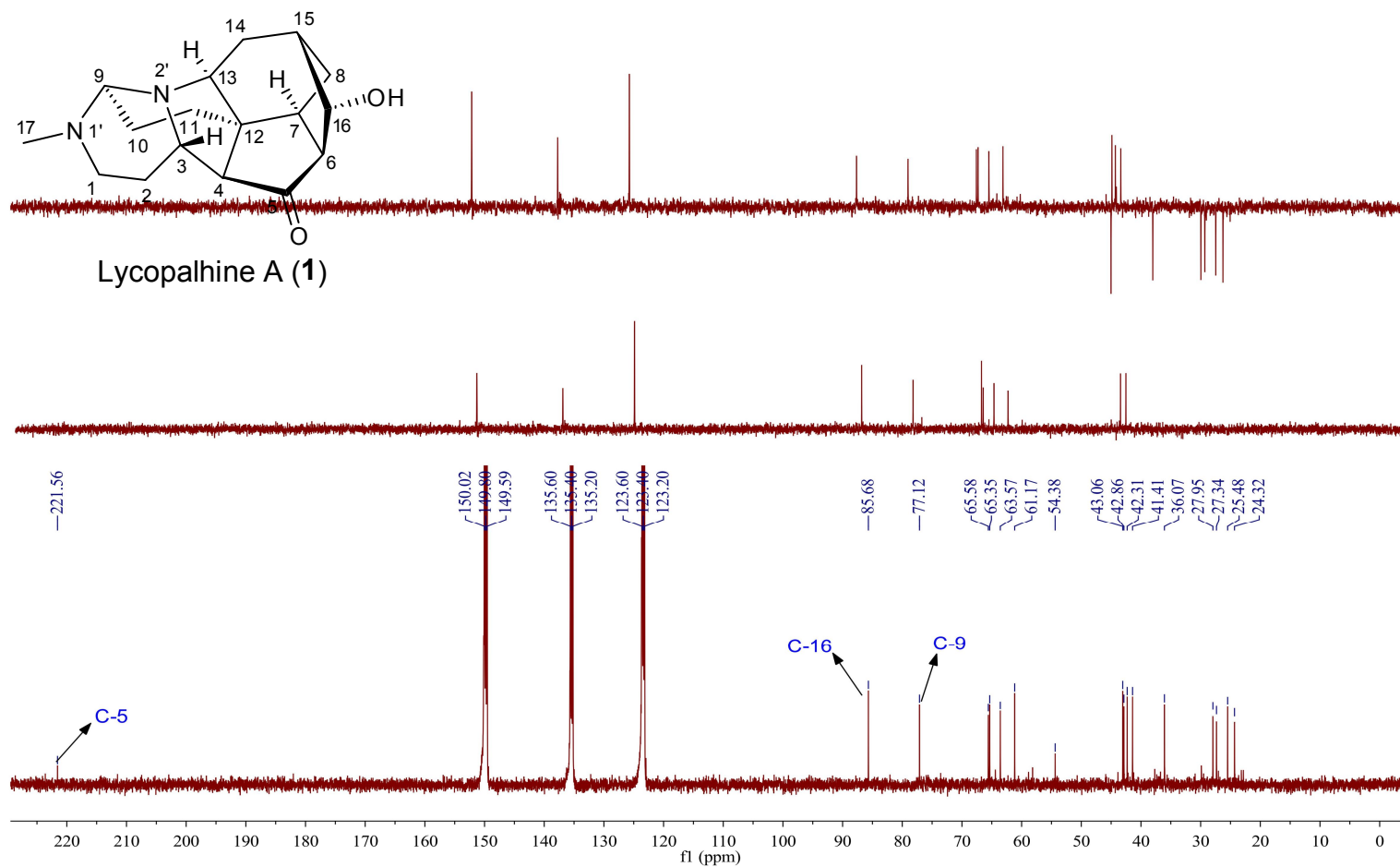


Figure S5. ^{13}C and DEPT NMR spectra (20–70 ppm) of lycopalhine A (**1**) in pyridine- d_5 (125 MHz)

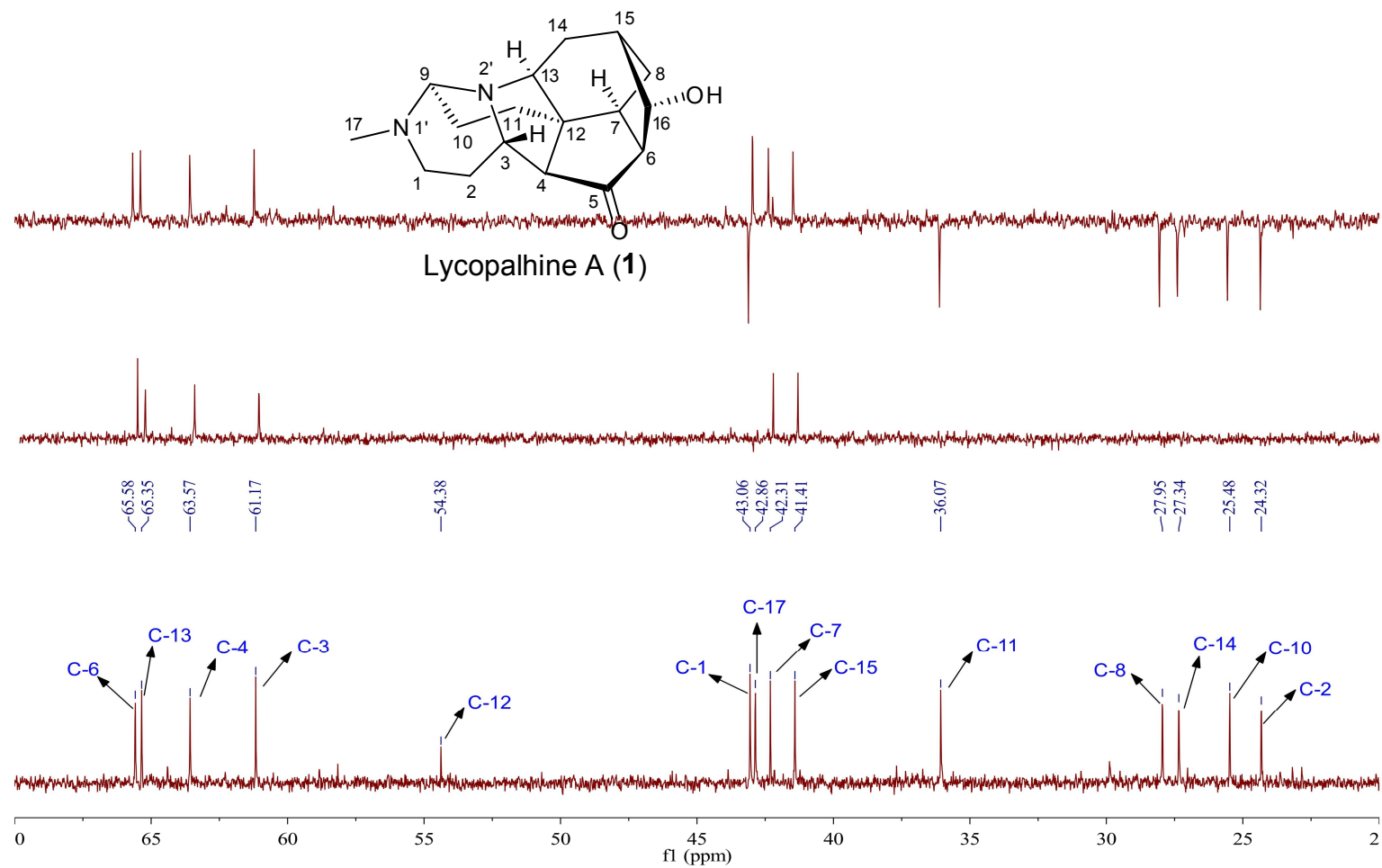


Figure S6. HSQC spectrum (δ_{H} 0–4.5 ppm and δ_{C} 15–90 ppm) of lycopalhine A (**1**) in pyridine- d_5

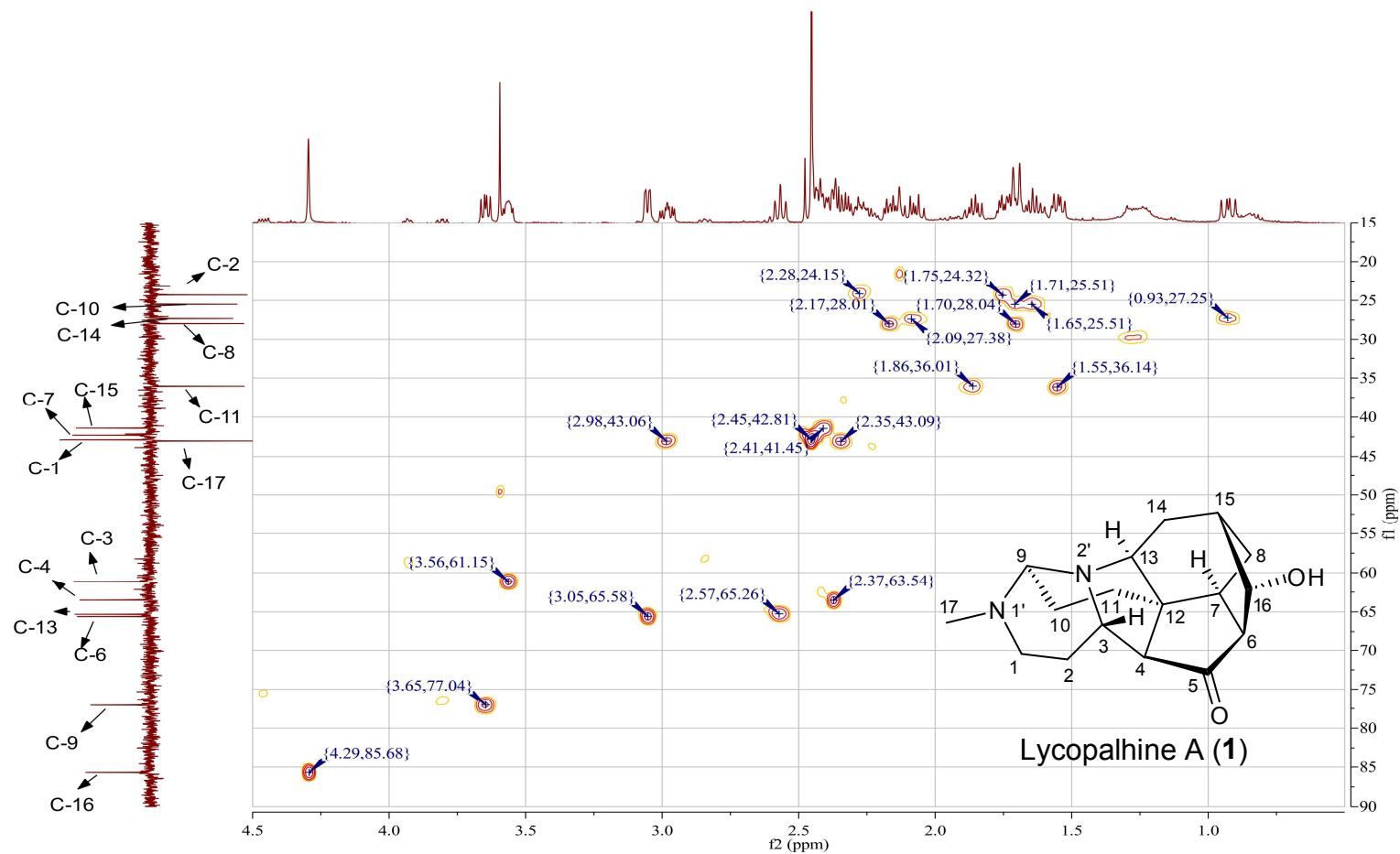


Figure S7. ^1H - ^1H COSY spectrum (0.5–4.5 ppm) of lycopalhine A (**1**) in pyridine- d_5

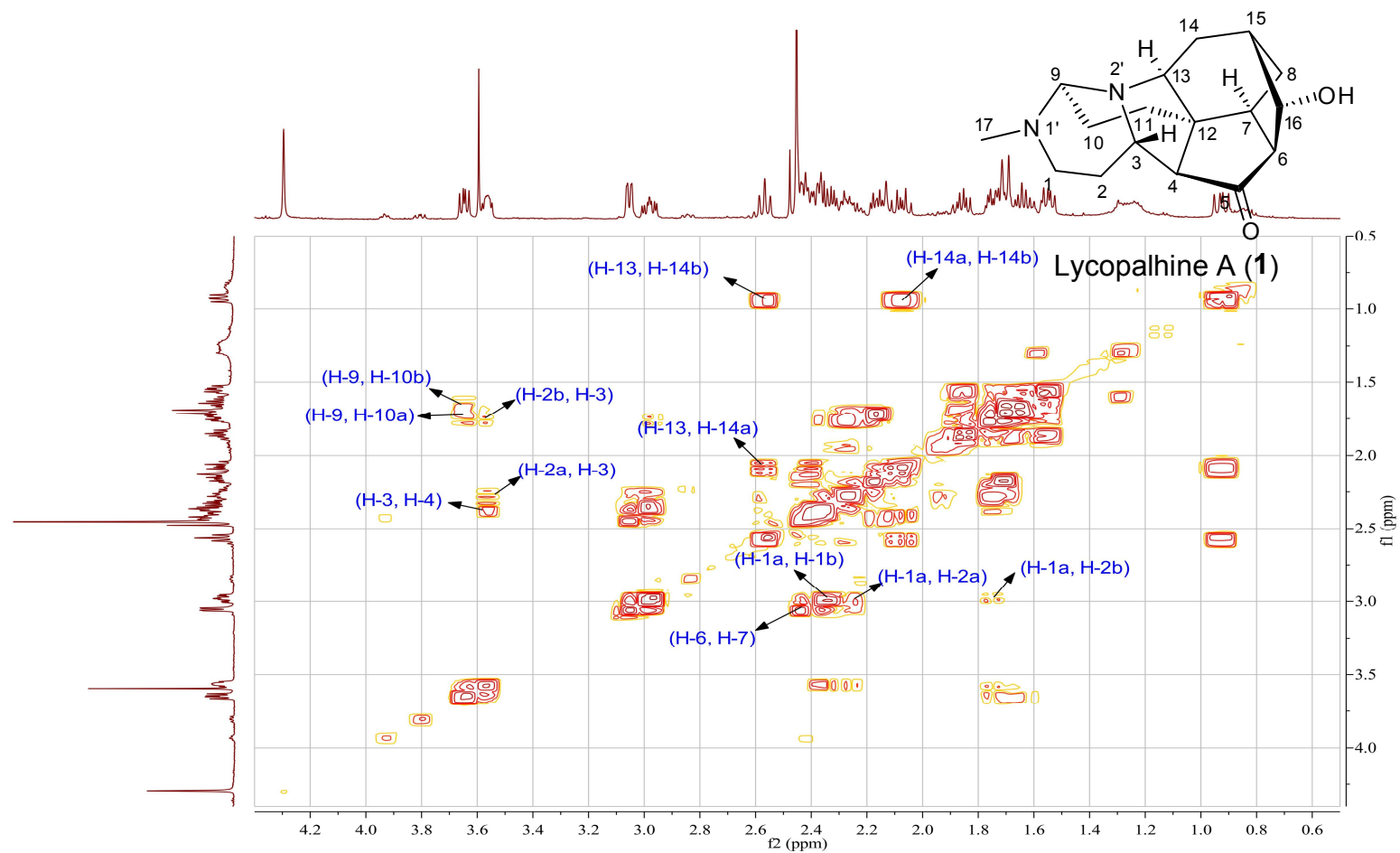


Figure S8. ^1H - ^1H COSY spectrum (1.4–2.5 ppm) of lycopalhine A (**1**) in pyridine- d_5

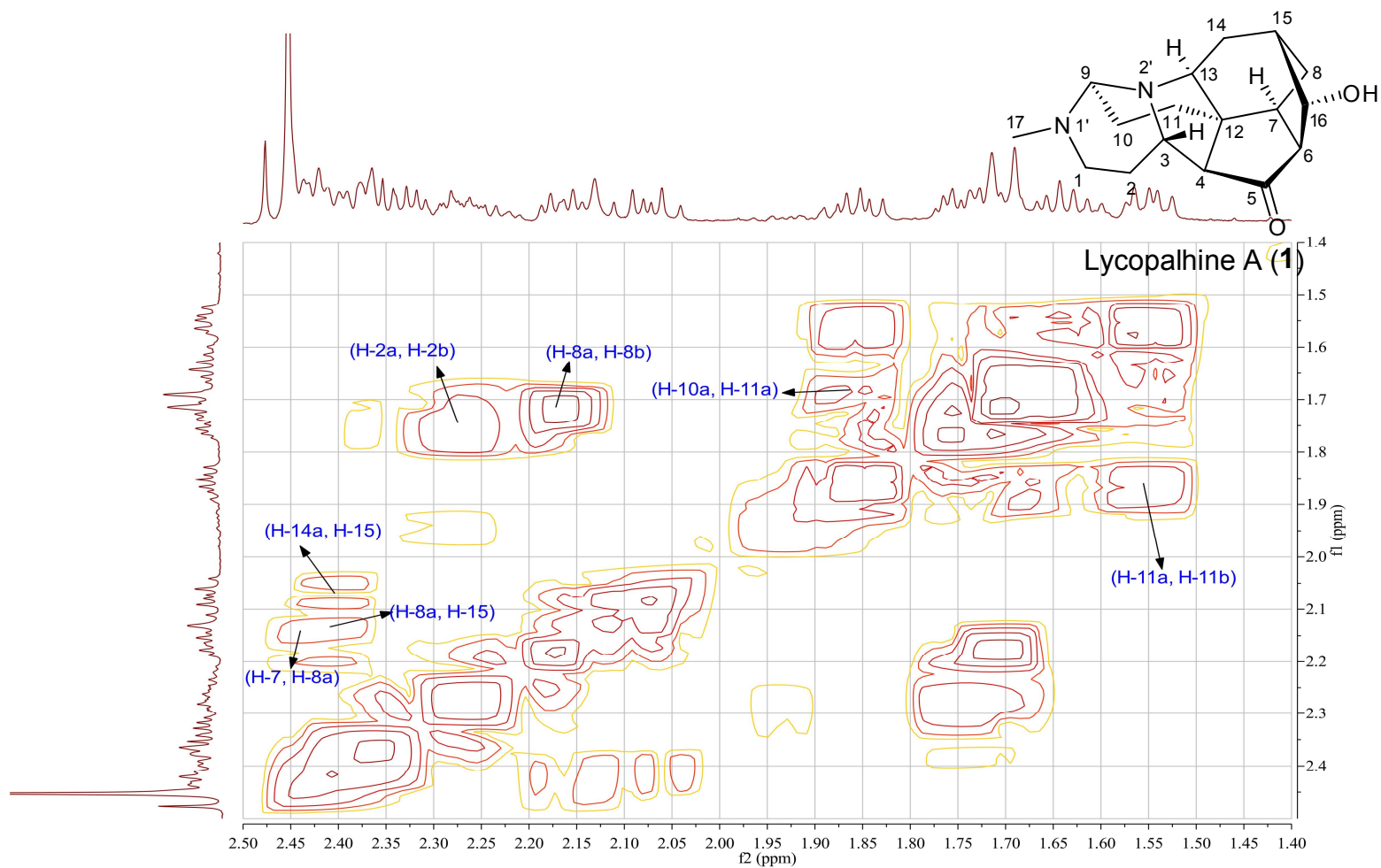


Figure S9. HMBC spectrum (δ_{H} 0.5–4.8 ppm and δ_{C} 15–225 ppm) of lycopalhine A (**1**) in pyridine- d_5

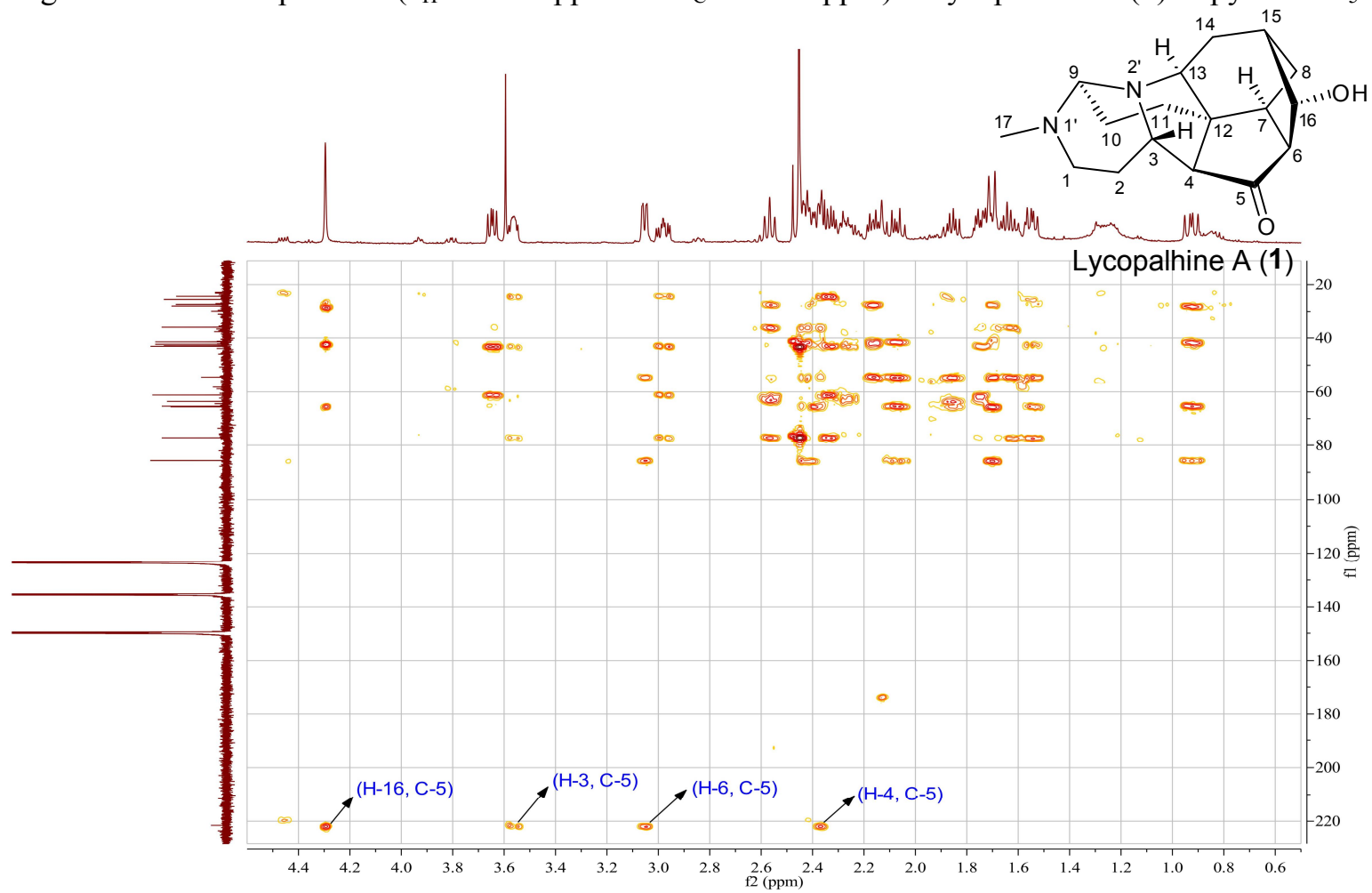


Figure S10. HMBC spectrum (δ_{H} 2.7–4.5 ppm and δ_{C} 15–95 ppm) of lycopalhine A (**1**) in pyridine- d_5

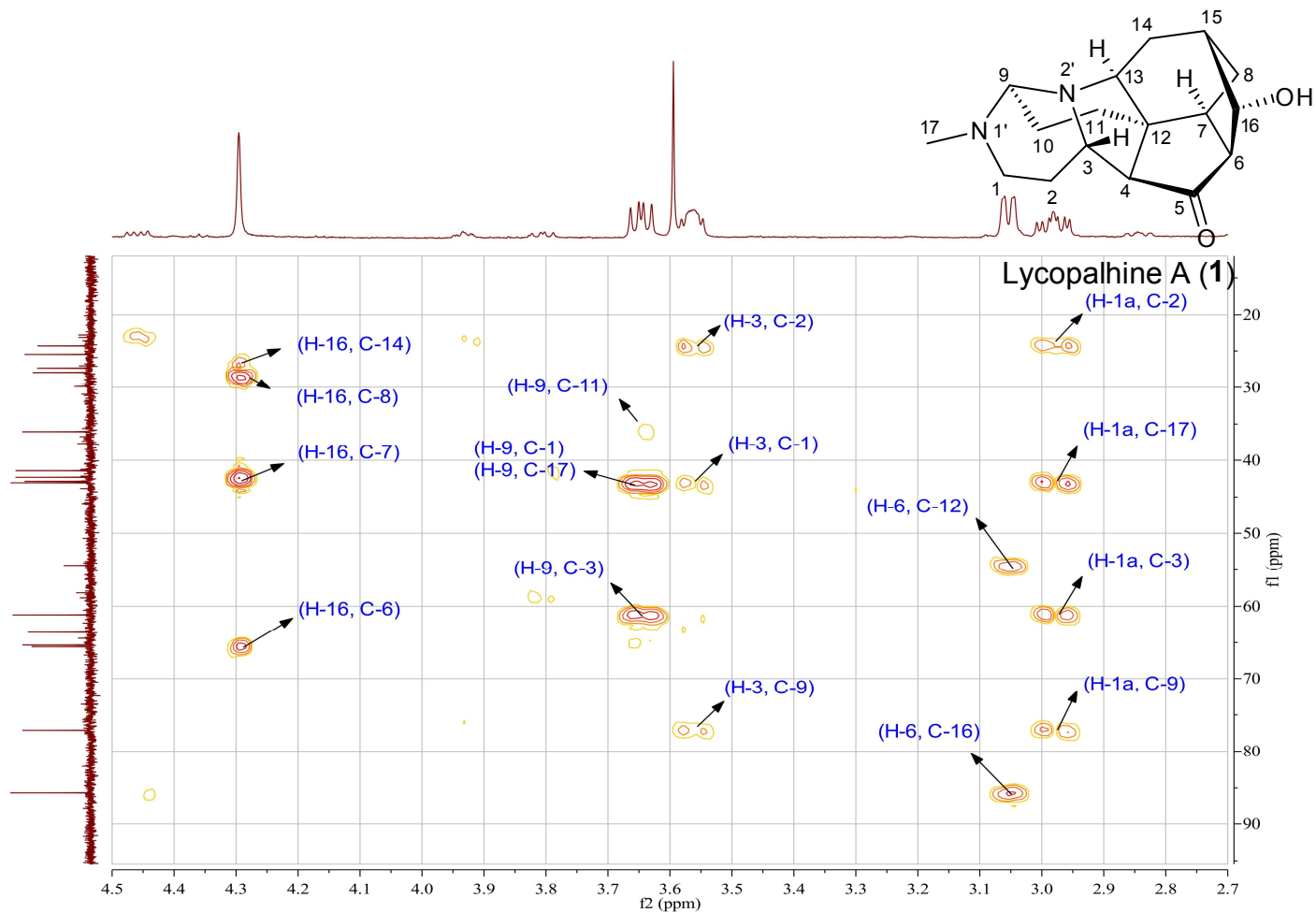


Figure S11. HMBC spectrum (δ_{H} 0.6–2.9 ppm and δ_{C} 15–95 ppm) of lycopalhine A (**1**) in pyridine- d_5

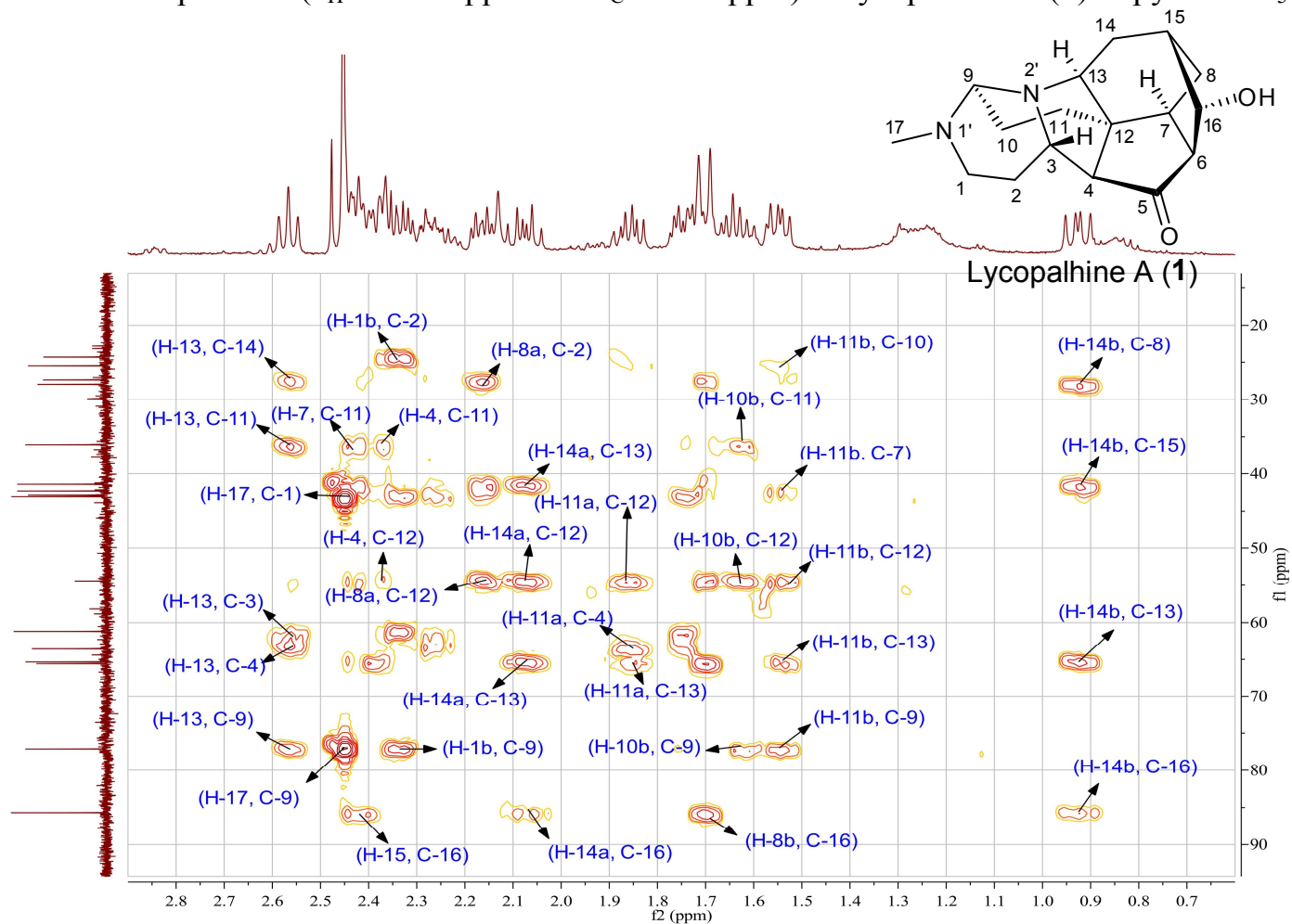


Figure S12. ROESY spectrum (0.5–4.5 ppm) of lycopalhine A (**1**) in pyridine-*d*₅

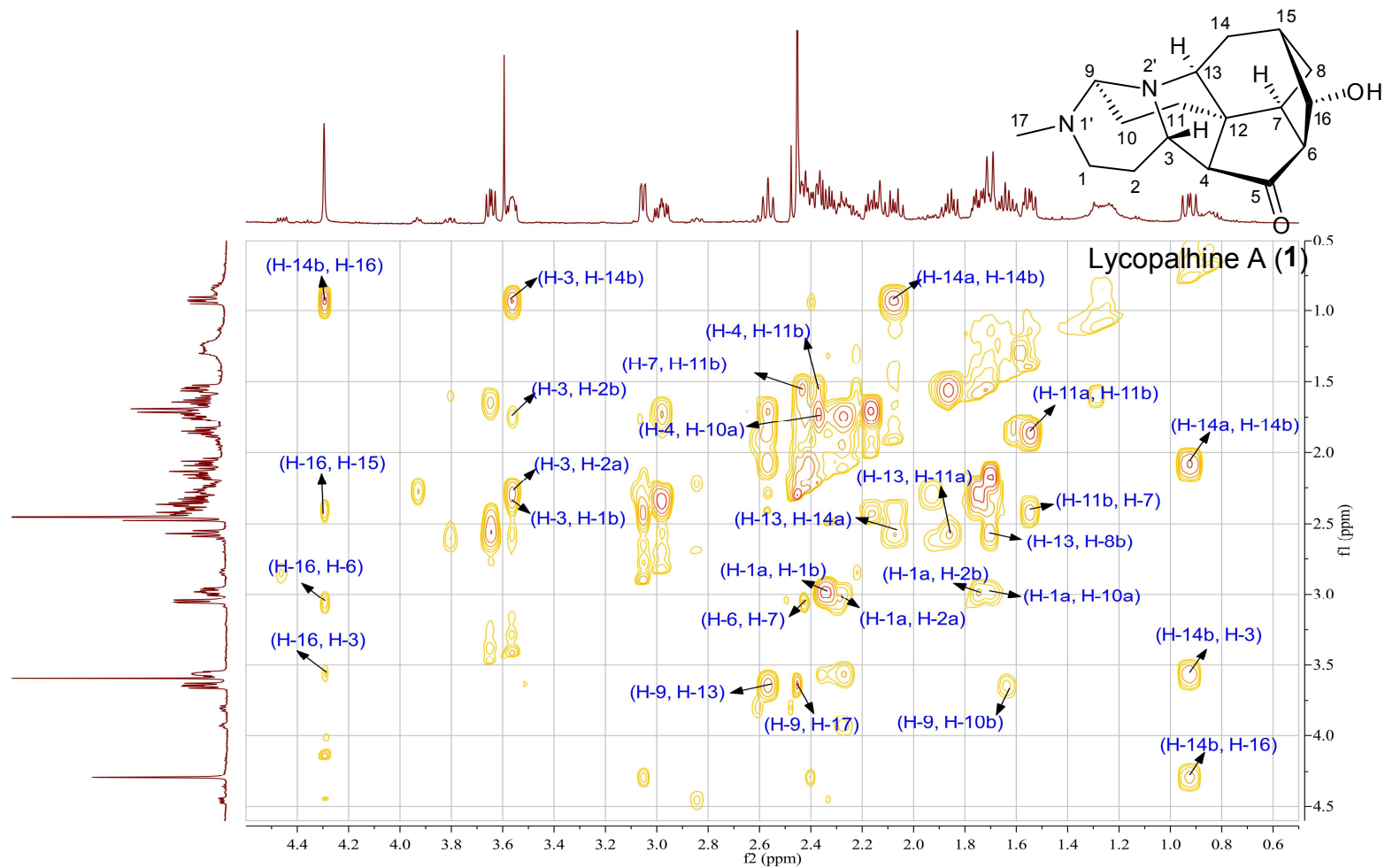


Figure S13. Positive ESIMS spectrum of lycopalhine A (1)

Mass Spectrum List Report					
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Analysis Name	D:\DATA\2011file\110622\fax-16000.d		Operator	QUYAN	
Method	ms_ptservice.m		Instrument	HCT	
Sample Name	fax-16		Comment		
Acquisition Parameter					
Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Std/Enhanced	Scan Begin	100 m/z	Scan End	800 m/z
Capillary Exit	200.0 Volt	Skimmer	40.0 Volt	Trap Drive	50.2
Accumulation Time	200 µs	Averages	7 Spectra	Auto MS/MS	off

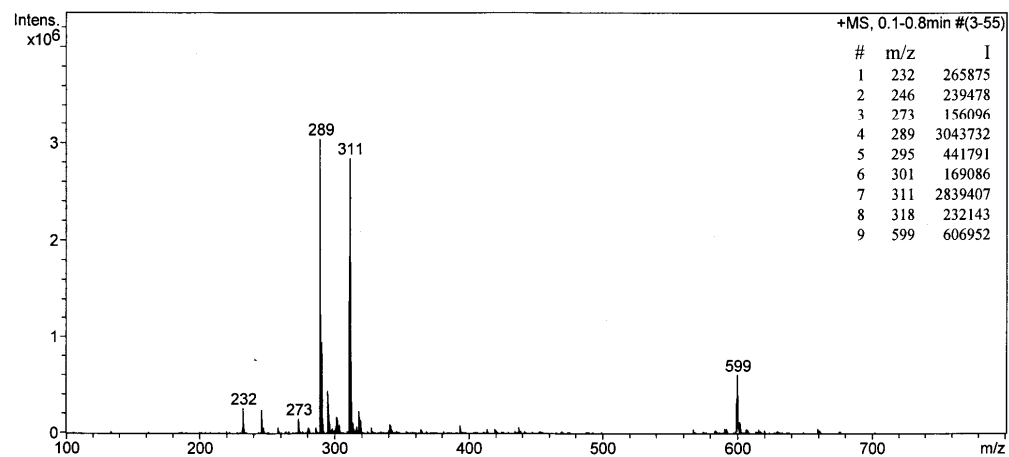
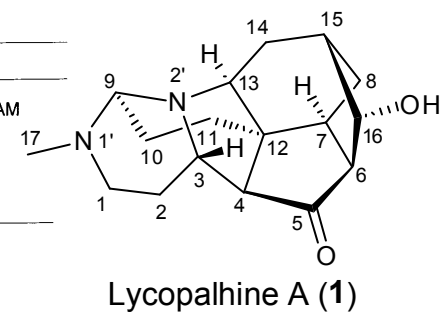


Figure S14. HRESIMS spectrum of lycopalhine A (1)

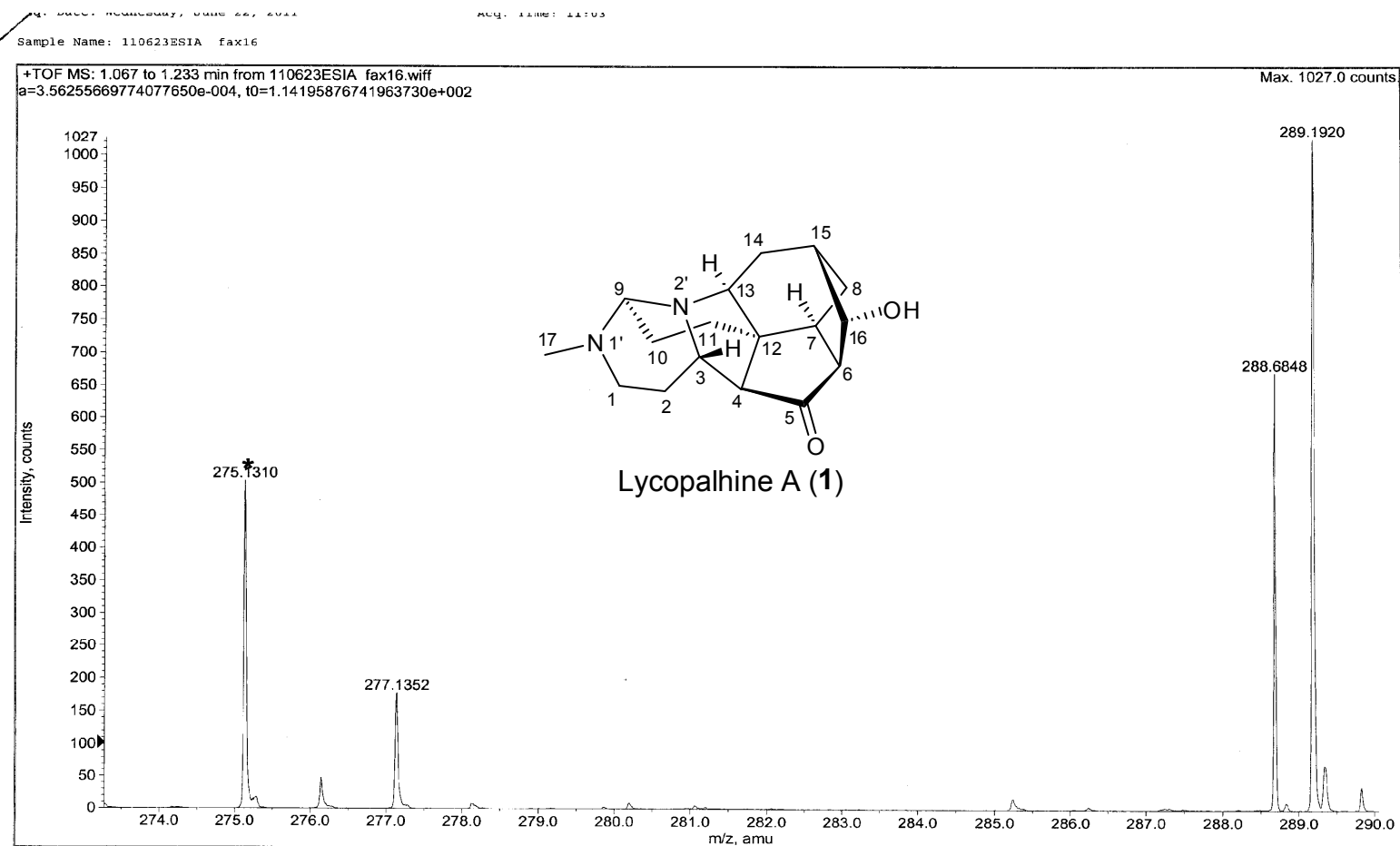


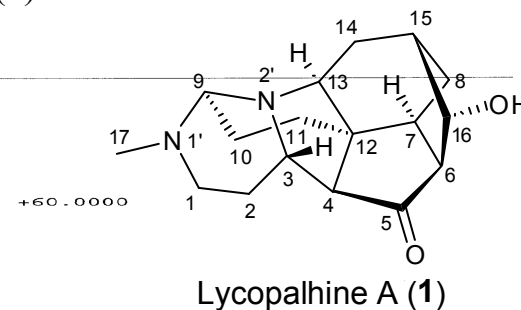
Figure S15. HRESIMS report of lycopalhine A (1)

Acq. Date: Wednesday, June 22, 2011
 Sample Name: 110623ESIA fax16

Acq. Time: 11:03

Elemental composition calculator

Target m/z: +289.1920 amu
 Tolerance: +10.0000 ppm
 Result type: Elemental
 Max num of results: 1000
 Min DBE: -10.0000 Max DBE: +60.0000
 Electron state: OddAndEven
 Num of charges: 0
 Add water: N/A
 Add proton: N/A
 File Name: 110623ESIA fax16.wiff



	Elements	Min Number	Max Number
1	Br	0	0
2	C	0	200
3	Cl	0	0
4	F	0	0
5	H	0	400
6	K	0	0
7	N	2	2
8	Na	0	0
9	O	0	2
10	P	0	0

Sample Name: 110623ESIA fax16

Acq. Time: 11:03

	Elements	Min Number	Max Number
11	Pt	0	0
12	S	0	0
13	Si	0	0

	Formula	Calculated m/z (amu)	mDa Error	PPM Error	DBE
1	C17 H25 N2 O2	289.1916	0.3967	1.3717	6.5

Figure S16. ECD and UV spectra of lycopalhine A (1) in methanol

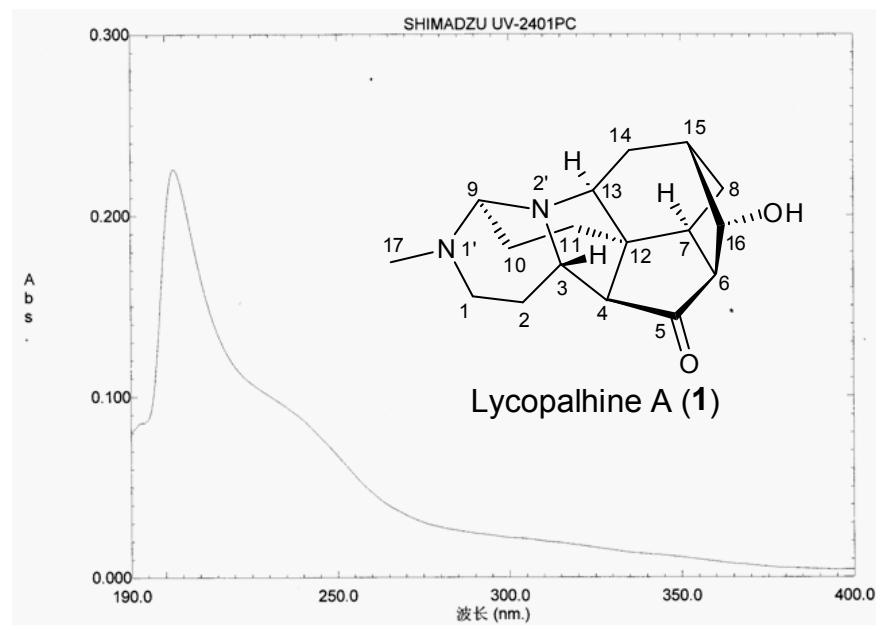
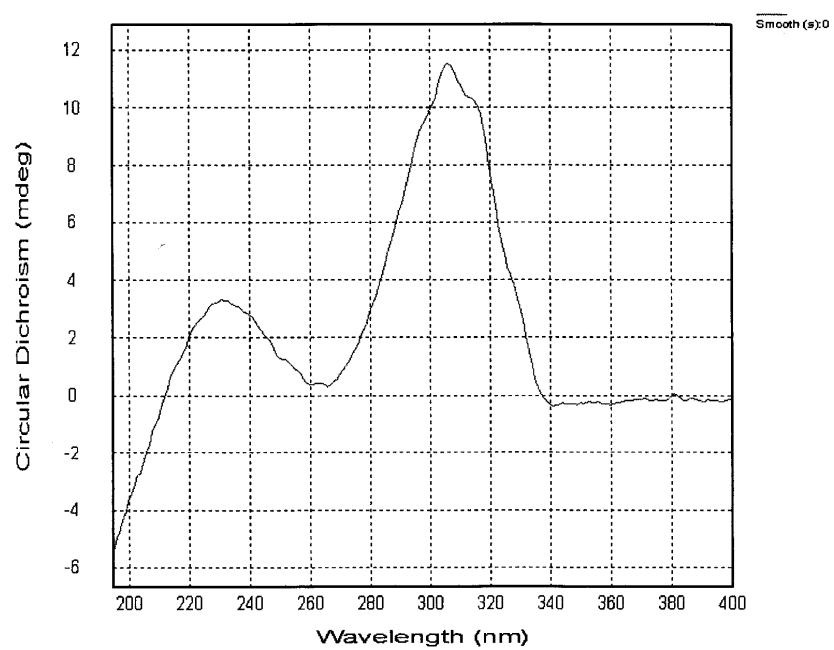
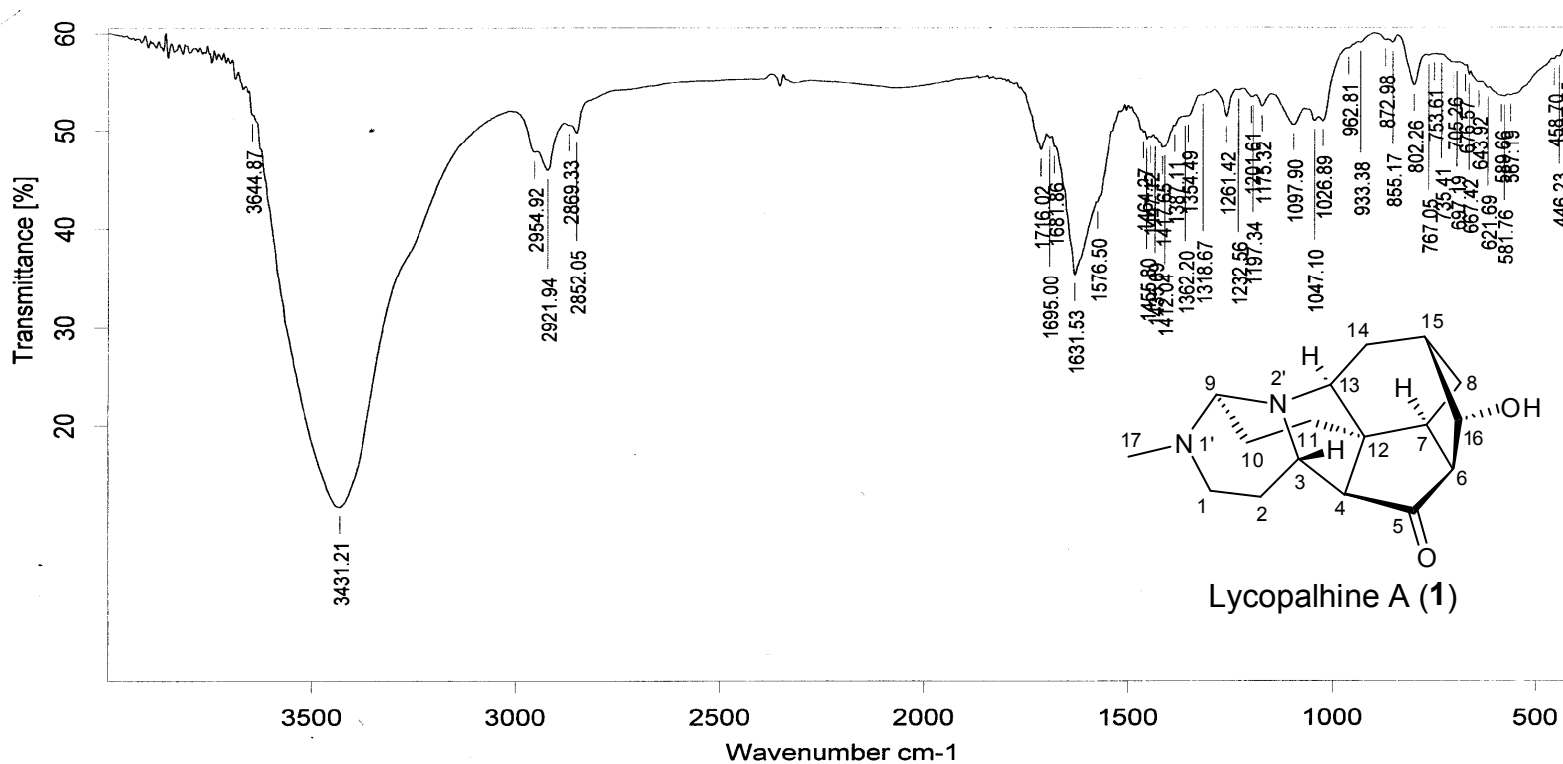


Figure S17. IR spectrum of lycopalhine A (1)



Sample : fax16a	Frequency Range : 399.246 - 3996.32	Measured on : 21/12/2011
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Customer : 111221IR2	Zerofilling : 2	Sample Scans : 16
	Acquisition : Double Sided,For	

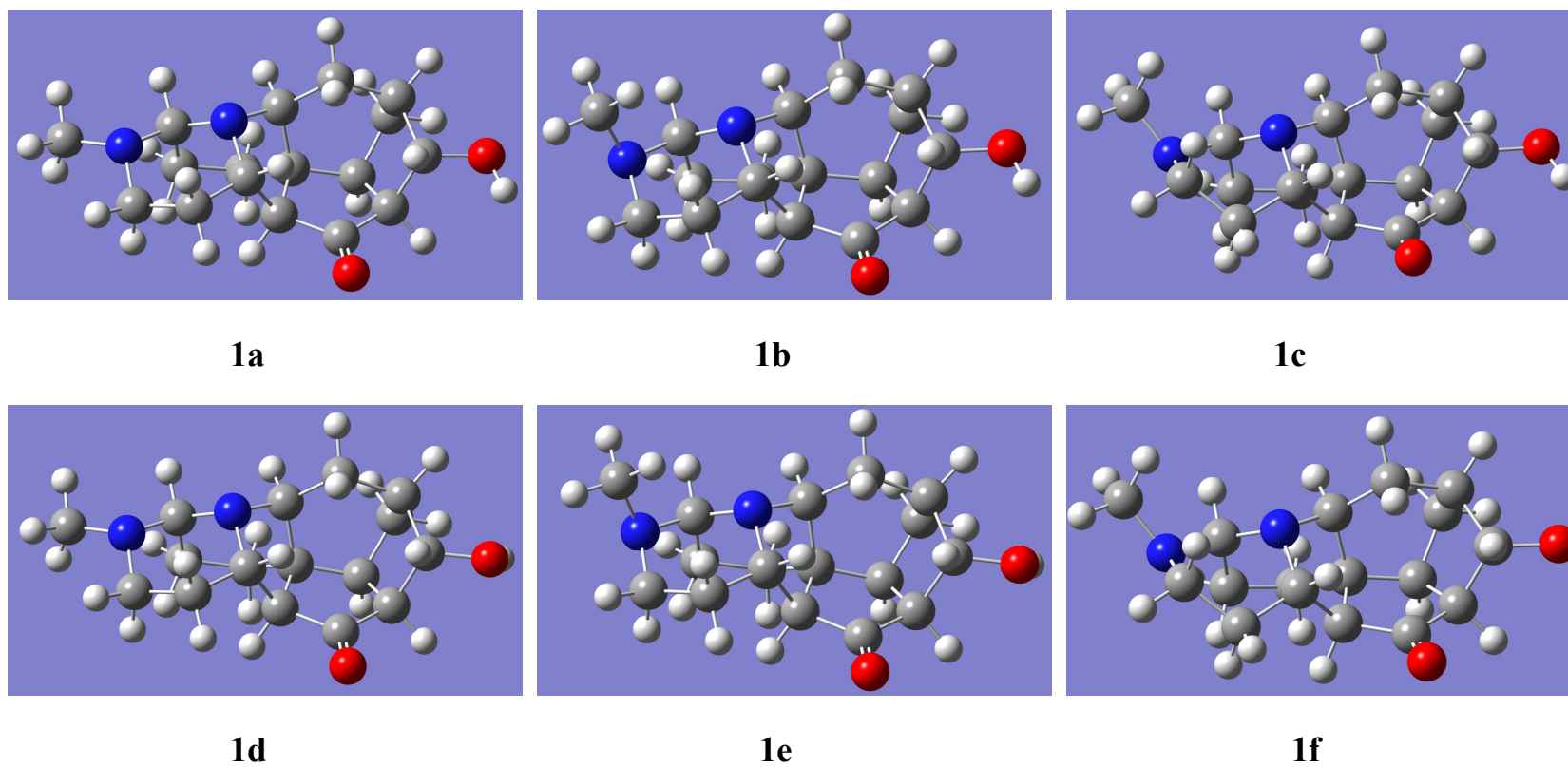


Figure S18. Optimized geometries of lycopalhine A (**1**) at the B3LYP/6-31+g (d,p) level in the gas phase.

Table S1. Conformational analysis of lycopalhine A (**1**) at the B3LYP/6-31+G(d,p) level of theory (kcal/mol).

Conformers	In the gas phase				In methanol (PCM model)				In pyridine (PCM model)			
	ΔE	P_E (%)	ΔG	P_G (%)	ΔE	P_E (%)	ΔG	P_G (%)	ΔE	P_E (%)	ΔG	P_G (%)
1a	0.88	10.4	1.03	9.5	0	27.9	0.02	26.9	0.09	26.0	0.09	26.2
1b	0	45.3	0.30	31.7	0.03	26.5	0.21	19.4	0	30.2	0.21	21.3
1c	0.08	39.4	0	52.8	0.23	18.9	0	27.7	0.20	21.5	0	30.5
1d	2.66	0.5	2.75	0.5	0.59	10.3	0.62	9.7	0.82	7.6	0.85	7.3
1e	1.77	2.3	1.91	2.1	0.6	10	0.89	6.1	0.71	9.1	1.03	5.5
1f	1.83	2.1	1.63	3.4	0.86	6.4	0.59	10.2	0.97	5.7	0.71	9.2

Table S2. Calculated, experimental chemical shifts, and the relative errors of lycopalhine A (**1**) at the mPW1PW91-SCRF/6-311+G(2d,p) level of theory in PCM solvent continuum model with pyridine as a solvent

NO.	<i>Exptl.</i> ^a	<i>Calcd.</i> ^b	<i>Corr.</i> ^c	$\Delta\delta^d$	No.	<i>Exptl.</i> ^a	<i>Calcd.</i> ^b	<i>Corr.</i> ^c	$\Delta\delta^d$
1	43.06 (t)	45.68	42.09	0.97	10	25.48 (t)	27.3	24.74	0.74
2	24.32 (t)	28.36	25.75	1.43	11	36.07 (t)	38.96	35.74	0.33
3	61.17 (d)	65.66	60.94	0.23	12	54.38 (s)	60.63	56.20	1.82
4	63.57 (d)	69.2	64.28	0.71	13	65.35 (d)	69.49	64.56	0.79
5	221.56 (s)	236.16	221.82	0.26	14	27.34 (t)	30.56	27.82	0.48
6	65.58 (d)	72.22	67.13	1.55	15	41.41 (d)	45.38	41.80	0.39
7	42.31 (d)	47.15	43.48	1.17	16	85.68 (d)	91.67	85.48	0.20
8	27.95 (t)	30.77	28.02	0.07	17	42.86 (q)	43.6	40.13	2.73
9	77.12 (d)	81.1	75.51	1.61					

^a in 125 MHz. ^b Boltzmann-calculated population-weighted averages of **1a–1f**. ^c $\delta_{\text{corr.}} = (\delta_{\text{calcd.}} - \text{intercept})/\text{slope}$ (see Figure S19). ^d $\Delta\delta = |\delta_{\text{corr.}} - \delta_{\text{exptl.}}|$. (see ref. 9 in the manuscript).

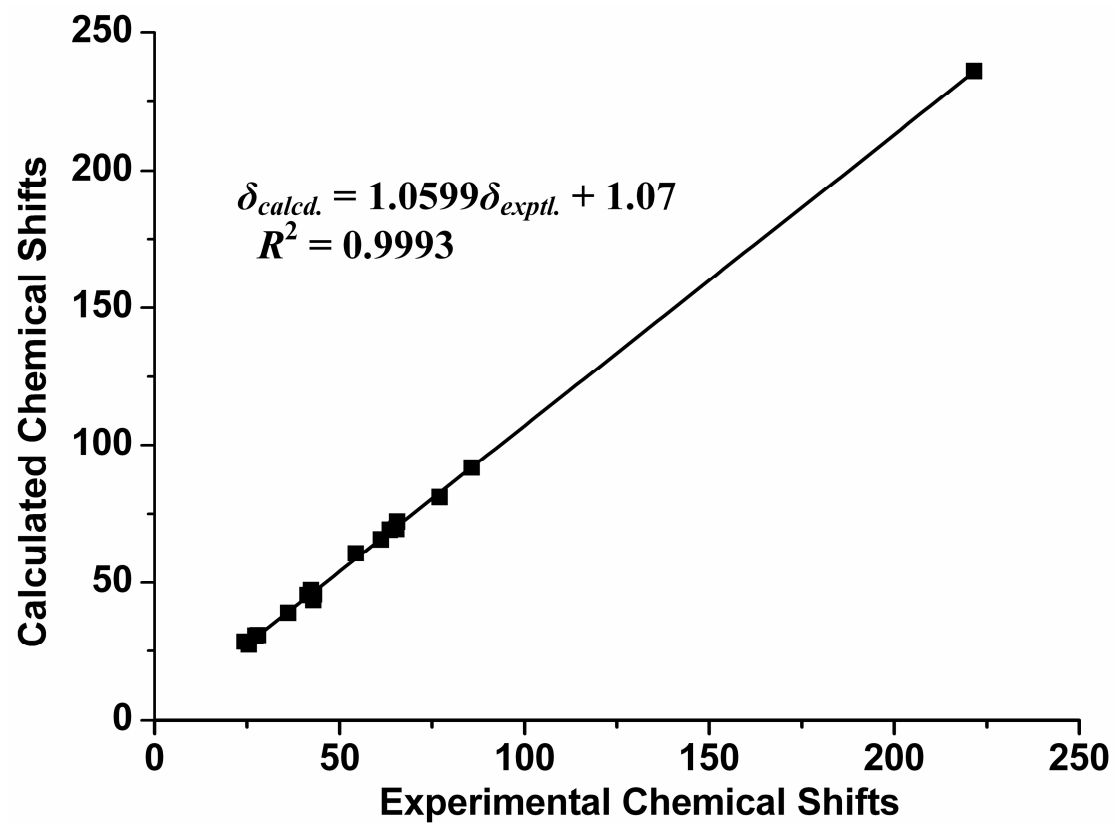


Figure S19. Regression analysis of experimental vs. calculated ^{13}C NMR chemical shifts (ppm). The general correlation is very satisfactory ($R^2 = 0.9993$) (see ref. 9 in the manuscript).

Table S2. Optimized Z-Matrixes of lycopalhine A (**1**) at the B3LYP/6-31+G(d,p) level of theory in the gas phase (Å)

1a				1b				1c			
C	2.622511	-0.98174	-1.080471	C	2.530778	-0.975266	-1.147374	C	2.491854	-1.018059	-1.183777
C	1.213495	-0.868698	-1.726106	C	1.072836	-0.925774	-1.683815	C	1.035268	-0.732592	-1.661714
C	0.046795	-1.078142	-0.726518	C	-0.005296	-1.129169	-0.588453	C	-0.027937	-0.985582	-0.568142
C	0.334881	-0.659787	0.75617	C	0.3823	-0.640524	0.849329	C	0.401669	-0.567402	0.872303
C	1.831558	-0.797776	1.154036	C	1.909762	-0.718833	1.132951	C	1.926551	-0.756379	1.112383
C	2.559842	-1.793697	0.23089	C	2.594929	-1.73245	0.196015	C	2.49831	-1.811478	0.141995
C	-0.021729	0.851265	0.748883	C	-0.020309	0.859022	0.808926	C	0.107269	0.951795	0.845594
C	1.309865	1.58374	0.769207	C	1.284963	1.62819	0.689663	C	1.449124	1.6146	0.572084
C	2.458146	0.58046	0.811485	C	2.464208	0.660698	0.686258	C	2.57273	0.583383	0.651082
C	-0.831052	1.065833	-0.592545	C	-0.945816	0.991029	-0.466834	C	-0.973099	1.145008	-0.281688
C	-0.641813	-1.485482	1.603391	C	-0.498519	-1.454483	1.807896	C	-0.527364	-1.324211	1.836681
C	-2.10064	-1.202749	1.17579	C	-1.994445	-1.211259	1.505556	C	-2.009437	-0.98151	1.55411
C	-2.058404	1.983389	-0.589169	C	-2.204961	1.86805	-0.395027	C	-2.264714	1.888346	0.118258

C	-2.326694	-0.878619	-0.349257	C	-2.350725	-0.991418	-0.000126	C	-2.356059	-0.857302	0.040531
N	-3.485949	-0.009406	-0.574629	N	-3.581547	-0.218448	-0.10151	N	-3.635049	-0.15441	-0.147199
C	-3.317533	1.330016	-0.016199	C	-3.386587	1.181439	0.309934	C	-3.475103	1.247712	-0.560486
O	1.448057	2.794136	0.721776	O	1.381191	2.838378	0.577266	O	1.609221	2.790645	0.296316
C	3.143693	0.382936	-0.588601	C	3.048055	0.421914	-0.753051	C	3.190403	0.285689	-0.758483
O	4.564405	0.278191	-0.464413	O	4.476571	0.359239	-0.733274	O	4.593018	0.021218	-0.676381
C	-4.757328	-0.620893	-0.216326	C	-4.24807	-0.35358	-1.39851	C	-4.563368	-0.854156	-1.028095
N	-1.156644	-0.296649	-1.057387	N	-1.258981	-0.402537	-0.846223	N	-1.276775	-0.230198	-0.768043
H	3.333016	-1.390968	-1.804449	H	3.194831	-1.395721	-1.908132	H	3.068705	-1.502623	-1.976518
H	1.111917	0.094379	-2.237717	H	0.937801	-1.713224	-2.432464	H	0.95998	0.296114	-2.03285
H	1.115638	-1.624906	-2.511694	H	0.90379	0.014992	-2.219179	H	0.791984	-1.367603	-2.519453
H	-0.219675	-2.140306	-0.753963	H	-0.235471	-2.199787	-0.552598	H	-0.269544	-2.053759	-0.584866
H	1.926901	-1.045776	2.217293	H	2.094656	-0.918463	2.194463	H	2.131543	-0.980499	2.164878
H	3.569976	-2.001486	0.596721	H	3.636312	-1.896725	0.488867	H	3.524101	-2.079898	0.409875
H	2.036479	-2.750907	0.128032	H	2.094462	-2.707005	0.172941	H	1.907201	-2.73309	0.109411

H	-0.608368	1.170391	1.618925	H	-0.541789	1.198754	1.712231	H	-0.258499	1.336047	1.806887
H	3.211379	0.926693	1.525298	H	3.257606	1.059342	1.325368	H	3.357702	0.961498	1.313432
H	-0.134979	1.496132	-1.319228	H	-0.327211	1.412995	-1.265673	H	-0.513988	1.690725	-1.11225
H	-0.397423	-2.550263	1.489429	H	-0.242703	-2.518201	1.708836	H	-0.349665	-2.403301	1.729025
H	-0.521693	-1.252588	2.670019	H	-0.289113	-1.18175	2.850763	H	-0.285782	-1.072276	2.877986
H	-2.740606	-2.05015	1.445326	H	-2.605655	-2.04314	1.870558	H	-2.674376	-1.730881	1.998481
H	-2.465302	-0.35876	1.768892	H	-2.317045	-0.339012	2.077644	H	-2.263599	-0.038155	2.044867
H	-2.261522	2.254966	-1.630589	H	-2.491189	2.111232	-1.424771	H	-2.190157	2.939599	-0.175804
H	-1.822115	2.906212	-0.048602	H	-1.961359	2.817372	0.095365	H	-2.409738	1.876817	1.203832
H	-2.535811	-1.818765	-0.873454	H	-2.544223	-1.972285	-0.449316	H	-2.468033	-1.868792	-0.366644
H	-4.19407	1.924087	-0.298266	H	-4.314109	1.726359	0.106622	H	-3.351503	1.326235	-1.656363
H	-3.292382	1.330827	1.091252	H	-3.250119	1.21676	1.395998	H	-4.391277	1.790253	-0.297469
H	2.897533	1.197316	-1.282273	H	2.727383	1.199646	-1.458256	H	3.01082	1.109388	-1.460351
H	4.918881	1.138147	-0.202354	H	4.824237	1.237486	-0.529142	H	5.055508	0.847248	-0.483495
H	-5.574688	0.003205	-0.59298	H	-3.67028	0.040996	-2.248595	H	-4.199776	-0.929674	-2.070058

H	-4.90807	-0.749373	0.872104	H	-5.21251	0.163125	-1.359039	H	-5.519565	-0.319919	-1.041548
H	-4.840117	-1.604666	-0.690466	H	-4.44532	-1.413298	-1.590338	H	-4.75378	-1.863286	-0.649611
1d				1e				1f			
C	2.624904	-0.974964	-1.084707	C	2.534192	-0.965233	-1.152948	C	2.49548	-1.008094	-1.189625
C	1.21406	-0.857843	-1.72743	C	1.074599	-0.90507	-1.686635	C	1.037669	-0.717189	-1.663434
C	0.04842	-1.074191	-0.728979	C	-0.002801	-1.121304	-0.593772	C	-0.026039	-0.979941	-0.573024
C	0.33598	-0.656641	0.754106	C	0.3831	-0.636518	0.845765	C	0.4022	-0.567981	0.869982
C	1.833324	-0.788649	1.151335	C	1.910812	-0.709185	1.128683	C	1.92781	-0.75219	1.109073
C	2.554259	-1.78911	0.225898	C	2.586999	-1.727714	0.188933	C	2.490441	-1.80826	0.1329
C	-0.023233	0.852118	0.748504	C	-0.022382	0.860509	0.809144	C	0.105978	0.949401	0.850527
C	1.306607	1.590358	0.768911	C	1.280875	1.635084	0.685682	C	1.445975	1.617709	0.575031
C	2.461499	0.589687	0.807394	C	2.467118	0.670832	0.681801	C	2.575932	0.589078	0.65046
C	-0.834585	1.067006	-0.591228	C	-0.952451	0.993927	-0.462841	C	-0.975985	1.146556	-0.274204
C	-0.637145	-1.486857	1.60106	C	-0.492927	-1.458063	1.802099	C	-0.524243	-1.332941	1.830356
C	-2.096921	-1.207724	1.174263	C	-1.989956	-1.220778	1.50124	C	-2.007214	-0.99288	1.548783
C	-2.064593	1.980874	-0.5849	C	-2.215744	1.864461	-0.384248	C	-2.269424	1.883568	0.131337

C	-2.324949	-0.882351	-0.350433	C	-2.348187	-0.997295	-0.003453	C	-2.354065	-0.861559	0.035699
N	-3.486413	-3.486413	-0.57381	N	-3.58234	-0.229863	-0.100641	N	-3.634547	-0.161309	-0.148306
C	-3.321656	1.322829	-0.012867	C	-3.39387	1.169019	0.317706	C	-3.478277	1.244469	-0.551472
O	1.433485	2.800643	0.732248	O	1.366221	2.844833	0.578575	O	1.595631	2.794443	0.303416
C	3.154429	0.393627	-0.590072	C	3.064666	0.433127	-0.752688	C	3.200363	0.298687	-0.757951
O	4.57762	0.428315	-0.493654	O	4.48997	0.500475	-0.758243	O	4.620801	0.179329	-0.712734
C	-4.756194	-0.631932	-0.217078	C	-4.249148	-0.362051	-1.397855	C	-4.559886	-0.857316	-1.03547
N	-1.156791	-0.296052	-1.058347	N	-1.259523	-0.399923	-0.847976	N	-1.276062	-0.226893	-0.769
H	3.328753	-1.387128	-1.814264	H	3.190341	-1.389722	-1.918971	H	3.06624	-1.492257	-1.987585
H	1.114318	-1.605493	-2.520974	H	0.935364	-1.678514	-2.449007	H	0.966743	0.316442	-2.021015
H	1.115458	0.110873	-2.228559	H	0.911097	0.045886	-2.205173	H	0.793172	-1.340513	-2.529342
H	-0.214694	-2.137295	-0.758816	H	-0.227483	-2.193432	-0.563966	H	-0.265545	-2.048654	-0.596605
H	1.92905	-1.038328	-1.038328	H	2.095943	-0.911784	2.18963	H	2.132473	-0.981902	2.160538
H	3.557852	-2.025787	0.603566	H	2.079939	-2.69835	0.163206	H	3.506842	-2.113786	0.413672
H	2.027565	-2.743957	0.12232	H	3.622605	-1.925404	0.495331	H	1.893748	-2.725577	0.095476

H	-0.609087	1.168787	1.619859	H	-0.540347	1.197598	1.715392	H	-0.258107	1.328945	1.814206
H	3.214293	0.949726	1.514444	H	3.256158	1.084299	1.316485	H	3.361387	0.976508	1.306222
H	-0.140945	1.501152	-1.317808	H	-0.33849	1.423294	-1.261121	H	-0.51924	1.699084	-1.101441
H	-0.39018	-2.551065	1.485738	H	-0.232579	-2.520515	1.699359	H	-0.343991	-2.41123	1.717336
H	-0.517314	-1.254787	2.667885	H	-0.284302	-1.187855	2.845763	H	-0.283948	-1.085517	2.873016
H	-2.734311	-2.057201	1.443251	H	-2.596988	-2.056763	1.863745	H	-2.670071	-1.746361	1.989162
H	-2.463305	-0.365363	1.768476	H	-2.315892	-0.352058	2.07664	H	-2.263644	-0.052789	2.044309
H	-2.26893	2.254512	-1.625495	H	-2.504025	2.112482	-1.412211	H	-2.197443	2.936855	-0.155773
H	-1.83015	2.902959	-0.042387	H	-1.975424	2.81197	0.111113	H	-2.41393	1.864645	1.216869
H	-2.531753	-1.822477	-0.875641	H	-2.53735	-1.977434	-0.456174	H	-2.463246	-1.871178	-0.376918
H	-4.199909	1.914833	-0.293751	H	-4.323978	1.710427	0.11708	H	-3.355173	1.330884	-1.646732
H	-3.296539	1.32153	1.094542	H	-3.25768	1.199809	1.403906	H	-4.39582	1.782597	-0.284467
H	2.917963	1.206608	-1.281227	H	2.761699	1.212374	-1.456645	H	3.024635	1.122632	-1.453505
H	4.878433	-0.278584	0.09326	H	4.846853	-0.170162	-0.160238	H	4.867763	-0.548986	-0.127374
H	-5.575094	-0.009125	-0.592409	H	-4.440932	-1.421832	-1.594857	H	-4.194711	-0.924313	-2.077409

H	-4.906775	-0.763255	0.871026	H	-3.674134	0.039962	-2.24628	H	-5.517359	-0.32541	-1.04637
H	-4.836336	-1.614793	-0.693569	H	-5.216254	0.149283	-1.355009	H	-4.748263	-1.869578	-0.664396

Table S3. Frequencies of lycopalhine A (**1**) at the B3LYP/6-31+G(d,p) level of theory in the gas phase (cm⁻¹)

1a			1b			1c		
50.0778	101.3007	119.1174	55.1878	97.2967	112.439	61.246	84.386	122.9415
143.2619	169.1197	206.4965	143.0156	163.1421	197.5896	148.9511	177.1694	193.2592
222.9624	245.1599	255.4839	211.1203	232.0296	252.4292	224.5381	239.9286	253.2009
262.9668	286.2146	305.285	259.8041	292.5528	307.739	259.843	293.7625	297.2044
316.5272	325.1429	349.6246	317.9594	329.5456	342.4811	301.3691	318.6557	345.4349
361.7338	380.1985	426.2788	376.8606	390.3797	447.521	360.0108	384.122	420.7534
452.6821	466.2931	476.7852	458.333	469.989	486.4657	445.6639	465.1739	483.3966
491.5965	527.7659	532.6762	492.6789	527.3047	547.7016	496.2528	510.7187	542.1854
552.7407	582.0758	593.4899	550.8348	578.4474	595.2947	550.9085	560.89	606.8395
631.2065	649.9605	670.1366	627.9775	647.8478	677.7333	626.2148	651.1942	669.5292
712.3567	742.877	769.0116	708.3236	742.9055	764.9494	698.9034	752.2866	783.478

789.1115	809.4857	828.9803	790.0862	807.892	816.359	792.0422	816.4247	827.4757
849.3289	863.0992	876.0453	849.4448	862.2985	884.4493	854.3084	867.4043	870.9316
892.6894	897.5338	919.2179	889.5498	898.6591	913.8897	895.0702	916.4459	925.0465
937.3829	955.8637	962.4005	940.1599	940.855	956.0363	934.7292	955.3035	965.7802
970.677	987.8648	994.5889	964.3017	987.1445	993.8662	974.5327	985.1551	998.568
1011.9998	1024.6628	1027.827	1008.7902	1018.0772	1031.3442	1011.1817	1024.7303	1034.6043
1041.4138	1057.4978	1062.0073	1039.7633	1051.0627	1058.9508	1039.3796	1054.49	1069.4373
1076.2554	1081.7672	1097.388	1065.3629	1071.5893	1086.7085	1071.5246	1081.4642	1097.4567
1106.5771	1119.622	1126.3191	1105.5558	1117.3152	1123.5735	1109.2768	1115.305	1121.6127
1139.1481	1148.6145	1156.7407	1138.7107	1146.0436	1151.7394	1129.5408	1140.7141	1148.3876
1170.6946	1175.7355	1191.9813	1159.2272	1169.8437	1189.7159	1166.2707	1168.8817	1177.1493
1193.2964	1199.0369	1214.5337	1190.9446	1196.3138	1214.4285	1188.8026	1194.2766	1208.2417
1220.9909	1234.0879	1239.3231	1221.2636	1232.6536	1237.6541	1214.4911	1225.8203	1237.7214
1251.8339	1264.5053	1266.2108	1251.224	1260.3416	1267.9647	1240.7074	1247.7696	1259.6032
1277.611	1284.9588	1304.1624	1275.5039	1285.8482	1304.6178	1278.5298	1282.3637	1301.5038

1316.0172	1323.191	1327.2865	1318.3013	1323.2253	1327.8636	1309.7839	1317.8776	1324.3216
1335.362	1342.9022	1345.0726	1335.4984	1341.0178	1343.8932	1327.5066	1329.1319	1337.5367
1347.7285	1350.697	1364.6508	1348.3199	1350.155	1363.2126	1341.3468	1345.6574	1354.3401
1368.1576	1375.1605	1380.1927	1370.8864	1375.8936	1376.6776	1359.9163	1367.0275	1373.1481
1382.9527	1405.3104	1417.7418	1386.5822	1402.9189	1415.2147	1390.7988	1399.333	1410.6938
1423.3013	1429.5204	1464.0088	1421.5845	1427.0196	1464.1834	1424.7395	1430.5031	1466.7257
1483.1583	1488.3436	1496.6853	1483.4123	1487.285	1492.1321	1486.5509	1493.7105	1498.9809
1500.0521	1507.8805	1511.0293	1503.3902	1506.1795	1510.9597	1501.257	1507.217	1510.0931
1518.4311	1525.861	1785.501	1513.9709	1519.4435	1785.5924	1512.4218	1517.7006	1787.9628
2913.1843	2937.0813	3016.4419	2992.086	3017.4866	3035.5007	2938.6524	2944.2852	3015.385
3036.18	3038.5918	3047.3559	3042.0365	3042.9284	3049.3399	3041.3548	3044.4428	3045.7342
3047.8856	3051.8251	3055.1753	3050.8173	3052.8376	3053.5602	3047.0491	3049.9971	3051.7371
3056.4047	3057.1063	3058.755	3056.896	3057.3025	3063.0946	3055.8915	3058.0604	3061.6366
3061.1454	3063.8194	3064.9919	3065.3476	3070.7838	3071.8495	3062.6445	3062.9669	3066.2827
3069.6587	3088.7091	3091.6668	3084.9212	3087.4625	3091.5461	3069.4904	3086.4202	3087.7982

3097.0223	3098.3062	3101.2636	3095.6041	3096.8153	3105.9612	3099.0413	3100.855	3107.8379
3105.3181	3106.4466	3821.965	3108.5487	3120.0934	3822.1907	3109.5551	3111.8008	3825.137
1d			1e			1f		
50.9119	101.5257	120.6019	51.7741	96.8384	112.6101	60.9602	83.9672	123.0519
142.8992	172.1104	206.8943	142.3717	164.905	197.1088	147.9686	177.1155	195.5582
221.4385	243.7557	255.7829	211.5416	228.7665	252.3441	224.3339	238.3936	251.7206
262.9039	267.2755	287.8471	258.1254	262.9207	297.3616	253.9818	263.104	296.7614
315.6028	331.4382	350.9904	317.5052	330.1993	346.1448	309.6763	320.1287	347.6021
363.8218	382.7383	427.3444	383.9983	391.5046	447.7066	362.3341	389.6557	421.1459
452.7309	466.6234	476.8548	458.8411	470.374	485.6521	446.4179	465.3802	483.2696
489.7728	526.8221	531.3155	492.408	525.4668	547.1947	495.6342	509.1725	541.2596
552.5417	582.3827	593.1423	550.1825	578.7635	594.4288	550.399	560.3268	606.1185
630.5053	649.1154	670.0698	627.101	646.383	677.7707	625.3367	649.4711	669.3788
712.1819	741.3716	768.8349	708.0823	740.9789	764.4381	699.3171	749.8079	782.3922
785.0223	807.9682	828.7735	785.8841	806.9186	815.4042	787.8485	815.1605	827.0798
844.2686	860.529	874.1612	842.1296	860.4033	881.7331	846.8687	864.5646	870.4057

890.2227	895.5988	917.9136	889.0226	895.4184	913.0976	889.9111	915.1461	923.8989
934.8553	954.9979	961.1577	937.6103	938.7511	956.2179	932.3216	954.1034	965.465
971.2364	982.9935	993.951	962.9005	982.1641	994.1893	971.4335	979.9912	996.6776
1008.8559	1024.6076	1037.755	1004.8543	1021.1762	1035.89	1010.5176	1028.5181	1037.538
1039.7413	1057.4885	1058.7516	1039.2508	1052.3272	1057.1399	1041.7066	1054.2918	1066.3334
1076.1541	1082.8878	1094.6721	1063.2165	1073.4423	1083.1759	1069.6773	1082.7259	1095.415
1101.5729	1120.052	1127.4501	1102.343	1117.4625	1123.5625	1105.5141	1115.6587	1120.3449
1136.8408	1148.4151	1156.7409	1136.1424	1146.4868	1150.6732	1128.1435	1139.0001	1147.4412
1172.3272	1176.8227	1185.8182	1159.0309	1173.0227	1183.8992	1166.4184	1167.2223	1182.3302
1195.2226	1200.2234	1214.4904	1193.6917	1196.3699	1213.0856	1187.9762	1194.0772	1208.7046
1218.6458	1230.7509	1244.6933	1218.9778	1229.8954	1242.5192	1212.7518	1225.0271	1235.8373
1253.5171	1266.0137	1274.3982	1251.6395	1265.9745	1272.8307	1242.7979	1251.0378	1272.723
1276.9337	1287.5867	1291.8743	1277.0018	1287.259	1291.4382	1278.0831	1281.0108	1291.946
1313.5463	1317.7011	1327.13	1312.3791	1320.8701	1328.2281	1307.7572	1310.6164	1323.0926
1333.2907	1337.6381	1345.7884	1333.6325	1336.2944	1343.3888	1325.4842	1328.2852	1333.0486

1348.1376	1350.9088	1363.5257	1347.7358	1351.0689	1362.0457	1339.9405	1343.9463	1353.6833
1369.016	1374.9509	1380.2584	1371.5757	1375.8156	1376.9271	1357.8885	1366.6147	1373.3579
1383.1743	1405.7969	1417.7487	1387.0036	1403.1016	1415.4698	1391.0915	1399.8964	1411.1402
1424.6267	1438.0808	1464.0657	1424.7642	1433.7285	1464.3357	1425.4443	1439.6161	1466.8306
1483.25	1488.3609	1496.7546	1483.5628	1487.1643	1492.3701	1486.4572	1493.6471	1499.0961
1500.9533	1509.6624	1517.1805	1502.9862	1506.9727	1513.7074	1501.3533	1507.3719	1513.369
1518.8843	1526.0021	1791.4361	1519.4223	1520.568	1791.3944	1518.1026	1518.3685	1793.6383
2913.7899	2937.2386	3015.5467	2992.5398	3016.3232	3034.1557	2939.4932	2945.1235	3014.193
3031.2528	3038.1686	3046.8987	3042.0552	3043.2942	3048.8027	3034.8672	3040.8846	3045.5981
3048.294	3052.8786	3056.6163	3051.0818	3053.6747	3054.2041	3047.9983	3049.597	3051.8798
3057.2686	3058.3309	3061.0052	3057.4236	3062.2344	3064.1103	3056.675	3059.0228	3063.332
3061.48	3064.6324	3070.2657	3071.1503	3072.1907	3082.617	3064.1686	3065.3152	3066.7999
3083.2176	3084.643	3084.643	3084.3822	3085.7086	3094.5421	3083.5599	3088.374	3094.0963
3097.4787	3098.4969	3102.0781	3096.3235	3096.7033	3105.1715	3097.1243	3101.9535	3108.3151
3105.4164	3106.6764	3813.9795	3108.8192	3120.8909	3811.1385	3110.751	3111.9921	3814.0607

Table S4. Frequencies of lycopalhine A (**1**) at the B3LYP/6-31+G(d,p) level of theory (PCM model) in methanol (cm⁻¹)

1a			1b			1c		
49.7061	100.8710	118.6045	55.5385	100.5125	112.8665	59.7552	85.1208	123.5317
142.3682	171.5259	206.6186	143.6161	165.0003	207.7756	149.0304	178.2845	194.0047
222.6192	245.6595	253.3811	214.6641	234.7734	252.3097	225.2606	242.3147	253.8842
263.0531	283.2370	296.2774	255.8066	286.5738	300.4661	259.8545	292.4582	298.1314
311.1340	323.5513	351.5816	308.9970	329.7799	342.9111	300.6867	317.6778	345.9431
362.2594	381.1983	425.3165	376.8473	389.5038	447.3188	361.4332	385.9774	420.6736
451.6451	467.8060	479.0656	457.1977	469.8156	486.3777	445.2969	465.7263	483.5271
492.3370	527.6796	532.7054	492.8625	526.6674	548.4906	496.5479	510.9922	541.3371
552.6517	581.7951	593.4879	550.5324	578.6917	595.2850	551.8025	560.2022	607.1066
631.2472	650.7406	670.3141	628.8848	649.2880	677.8837	628.6958	650.7544	668.8007
714.2261	742.5217	768.1349	709.5539	741.8586	763.2183	700.5004	753.2620	781.2918
789.0939	808.2663	826.5640	790.3076	806.5958	813.7755	791.8185	815.6357	825.7061
849.1611	861.6691	876.4331	848.6569	860.2521	884.1723	853.8724	865.2713	871.4607

892.1882	895.7483	918.2844	888.0782	897.6567	913.1782	895.5187	915.5371	923.2827
937.9106	955.7712	960.6285	939.5772	940.5165	955.7039	935.4862	954.1457	964.1925
968.7350	987.0829	993.2720	962.9060	986.1852	993.3165	973.3836	984.0578	997.8357
1010.2828	1021.6986	1025.5853	1006.6228	1014.7853	1024.6558	1010.1817	1021.7134	1029.2376
1036.5321	1054.4158	1057.3745	1039.0569	1047.3011	1055.0841	1037.5723	1051.4562	1064.6991
1072.3459	1078.8146	1094.4025	1062.4562	1069.0248	1082.4968	1067.5100	1079.9958	1094.6273
1105.1485	1114.4973	1124.6809	1102.9625	1116.2386	1120.3746	1107.6563	1110.9910	1119.5328
1135.7422	1146.7539	1155.0147	1135.6019	1144.0693	1149.6557	1126.0082	1139.7851	1146.4408
1168.9309	1171.5344	1190.2142	1158.6279	1169.9269	1187.3454	1164.3549	1168.0887	1178.2623
1194.6487	1195.3856	1211.7210	1191.6633	1195.4114	1212.1418	1186.0154	1190.8469	1205.8094
1217.5720	1233.0245	1240.3089	1218.1753	1231.0981	1239.4521	1212.4296	1224.9973	1238.8185
1253.6477	1261.5824	1266.4445	1251.8488	1257.8251	1266.0676	1240.0931	1248.2536	1258.3671
1279.5054	1284.7572	1303.3012	1278.6147	1285.3794	1304.5154	1279.9999	1282.2773	1301.9016
1310.1143	1322.2150	1326.5755	1317.0166	1322.6585	1326.3252	1304.6541	1317.8349	1325.3755
1334.6313	1342.6116	1344.3902	1334.4061	1341.9869	1343.7399	1326.7661	1329.6082	1337.4484

1349.6235	1351.5262	1364.9330	1349.8334	1350.9070	1363.8383	1340.6315	1346.0803	1354.2760
1367.2288	1374.8571	1380.5569	1371.2370	1376.0409	1377.3531	1360.6111	1367.5995	1374.4792
1382.4613	1403.2593	1415.3227	1387.5323	1402.5277	1413.1631	1388.6339	1396.3749	1410.3916
1422.4401	1428.9827	1459.9636	1421.8683	1427.9954	1460.5327	1424.9058	1428.7006	1462.2968
1476.1253	1482.5958	1490.2042	1477.1818	1482.6610	1485.5929	1481.6732	1485.8070	1492.7278
1495.0750	1502.0669	1504.8980	1498.7094	1500.4272	1504.9334	1497.0290	1498.1001	1504.9950
1510.1691	1521.4567	1750.7814	1509.5211	1511.5749	1750.2818	1505.8306	1509.2412	1753.8687
2939.1806	2953.9042	3023.2509	2991.5893	3023.8066	3042.5283	2938.6668	2942.2151	3022.3651
3044.7888	3045.1766	3045.6417	3044.0389	3051.2917	3052.9086	3045.4989	3048.9390	3049.9311
3053.2469	3057.1215	3058.4750	3056.1295	3056.5105	3059.0733	3051.8262	3053.8205	3054.7359
3060.0868	3063.8900	3064.7932	3059.2307	3063.9787	3064.4187	3059.1363	3061.0793	3062.8295
3065.5940	3067.1081	3071.8592	3069.4790	3071.5801	3073.0306	3064.3436	3067.4172	3069.6261
3072.9155	3086.0607	3094.2459	3084.9443	3086.4857	3093.8751	3076.6540	3085.5630	3091.4622
3096.3483	3097.0970	3103.9360	3096.3806	3098.7469	3103.7532	3097.4421	3099.1894	3106.7473
3105.0174	3110.0392	3810.4605	3110.1390	3119.7426	3808.8981	3110.3311	3112.2028	3815.9223

1d			1e			1f		
48.1554	100.5549	118.4369	55.5365	100.8613	113.0934	57.1490	83.7234	122.9048
142.0037	170.4364	206.3271	143.6586	165.7102	208.1333	148.7120	177.3238	193.9951
221.7146	245.9734	255.7986	213.9810	233.0038	252.2050	225.2641	241.9534	255.1546
263.0921	280.4205	288.2021	263.0560	280.9760	302.6433	256.9180	271.3673	298.4264
315.4859	332.8350	353.2954	323.1301	330.7684	348.8385	310.5649	319.1748	348.8089
364.2921	384.1614	426.7793	384.0275	390.1505	447.7373	363.8845	392.2664	421.3743
452.1483	467.8624	478.9192	457.5125	470.3443	485.6220	446.0281	465.7869	483.2759
490.8808	526.8085	531.9662	492.9061	525.7922	548.2337	496.1380	509.8760	540.0664
552.9485	582.5328	593.5067	550.2940	579.7550	595.1031	553.2810	559.8151	606.8849
631.3175	649.6470	669.9385	628.8785	648.7285	678.0139	629.5769	648.3480	668.1640
713.7111	740.9427	767.8296	709.1031	740.4781	762.5704	700.2964	750.7112	780.8279
784.9272	806.7273	826.6542	786.4516	805.7418	813.0427	787.5124	814.7381	825.5813
844.3159	860.0532	875.0618	842.1067	860.2420	882.0125	847.0151	864.6358	870.8130
891.8577	893.1958	917.6212	888.1360	895.2433	912.8811	892.3650	915.6292	922.6330
936.6288	954.3214	960.6938	938.6583	939.4493	955.5380	933.6931	953.1398	964.1023

969.1736	982.9465	993.4802	962.7117	982.2963	994.6107	971.5745	979.4492	997.4093
1008.2139	1024.3508	1032.1523	1004.8692	1017.8709	1029.4515	1009.6935	1025.3288	1032.0087
1035.9378	1050.9865	1055.8548	1038.6281	1049.0977	1051.6461	1039.3279	1050.9072	1062.0990
1071.2333	1080.4819	1090.8391	1061.6623	1070.5454	1079.4877	1064.4221	1081.5793	1091.7273
1101.6700	1115.0930	1125.2243	1100.0281	1116.3772	1121.2922	1105.0326	1110.9912	1118.9021
1134.7527	1147.8462	1154.7935	1134.3497	1145.0558	1148.8448	1125.7527	1139.5448	1145.6726
1169.1476	1175.0466	1187.4507	1158.5354	1175.3562	1187.3863	1165.3916	1168.0657	1181.3665
1194.3624	1197.1706	1214.2030	1192.7412	1195.5112	1214.4483	1187.6242	1191.5371	1208.2340
1216.2619	1231.2779	1243.8623	1217.1104	1231.5697	1241.6771	1211.3258	1225.0748	1236.0744
1254.5988	1262.4154	1273.3127	1251.5826	1262.2137	1273.4472	1242.4817	1250.5522	1272.3722
1279.5854	1287.7236	1293.6514	1279.8546	1288.6359	1294.7086	1279.4253	1283.2550	1292.7061
1309.6692	1315.6670	1326.6093	1313.0923	1319.5214	1327.3215	1304.2907	1310.2238	1323.5961
1331.8288	1338.0655	1346.3374	1333.4926	1337.9612	1344.4205	1326.3749	1330.4125	1332.3521
1349.5497	1351.4839	1363.8443	1348.6605	1351.9398	1362.5144	1339.7585	1344.5559	1353.1080
1367.8311	1375.1937	1380.5557	1372.1859	1376.1304	1377.4866	1358.8116	1367.5875	1374.5467

1382.5325	1403.6416	1415.3037	1387.6048	1402.7561	1413.1113	1388.7147	1396.5835	1410.9270
1423.9826	1438.9937	1459.9961	1426.5644	1432.9525	1460.6239	1426.8561	1438.6341	1462.5425
1476.1784	1482.6226	1490.3706	1477.2251	1482.6146	1485.6233	1481.6797	1485.8664	1493.0464
1496.1976	1504.0112	1510.1404	1499.2244	1501.3698	1509.4603	1497.7995	1498.3297	1505.6805
1515.6202	1521.4466	1751.7200	1511.5885	1518.4890	1751.0736	1509.2640	1522.2490	1754.9393
2939.4442	2954.2625	3023.6736	2991.7687	3024.0586	3042.8086	2938.5552	2942.1332	3022.7654
3042.8787	3045.1509	3045.9571	3044.5374	3051.3751	3053.0133	3045.9957	3047.1820	3049.5323
3052.9984	3057.5458	3059.4180	3056.5486	3057.2019	3059.4634	3050.4053	3054.1288	3055.1752
3064.1140	3065.0963	3065.8354	3063.6003	3064.9378	3069.8092	3059.4330	3061.5406	3063.6242
3067.1868	3072.4978	3073.6508	3071.7881	3074.7559	3082.8245	3067.1318	3068.6849	3078.0480
3083.3727	3092.9822	3095.7680	3086.7815	3092.0594	3094.6358	3084.3344	3094.2460	3095.5291
3096.8216	3099.0356	3100.3892	3098.0450	3098.9727	3099.3953	3098.4327	3099.6951	3104.2144
3104.2739	3110.0983	3797.8176	3110.2657	3119.9517	3799.6688	3107.0327	3112.4008	3802.8049

Table S5. Frequencies of lycopalhine A (**1**) at the B3LYP/6-31+G(d,p) level of theory (PCM model) in pyridine (cm⁻¹)

1a			1b			1c		
49.1702	100.2543	118.2652	55.5543	100.5155	113.3700	60.2170	85.6224	123.5293
142.2452	171.1631	206.3746	143.7252	165.4286	208.1078	149.1667	178.9097	193.9989
222.5983	245.7265	253.6090	215.2384	234.9800	252.6178	225.1538	241.7302	253.8361
262.7364	283.9480	297.5732	256.1339	287.8682	301.3201	259.7745	293.2360	298.4112
311.1932	323.4516	350.8958	309.1846	329.8339	342.9919	302.6704	317.7580	345.9662
361.9858	381.2412	425.2071	376.7671	389.5319	447.3414	361.3058	385.7893	420.6551
451.7446	467.5130	478.5768	457.3174	469.9030	486.5381	445.3057	465.7089	483.5732
492.1965	527.6115	532.4729	492.8907	526.7314	548.6039	496.6126	510.9412	541.4340
552.7421	581.7384	593.4397	550.5330	578.6852	595.3298	551.8943	560.2440	607.1104
631.2954	650.8108	670.2589	628.8636	649.2412	677.8592	628.6742	650.8408	668.8301
713.7392	742.4751	768.0463	709.3872	741.8669	763.2881	700.3534	753.1504	781.5403
789.0029	808.2569	826.5128	790.2545	806.6649	814.0164	791.8159	815.7174	825.9518
849.0928	861.6973	875.9822	848.7358	860.4922	884.1804	853.9395	865.4542	871.3844

892.2006	895.8323	918.4388	888.2402	897.7466	913.2249	895.5950	915.6304	923.5057
937.8373	955.6910	960.6076	939.6291	940.5035	955.6697	935.4086	954.1832	964.3711
968.8574	987.1632	993.3511	963.0989	986.2650	993.3491	973.3841	984.1228	997.8722
1010.4338	1022.1550	1025.4687	1006.8641	1015.1905	1025.2248	1010.2717	1021.9877	1029.7564
1036.9376	1054.7001	1057.7215	1039.1736	1047.6344	1055.4254	1037.6674	1051.7414	1065.1760
1072.6696	1079.0367	1094.5101	1062.7174	1069.2921	1082.8653	1067.8303	1080.2209	1094.8194
1105.3140	1115.0391	1124.5488	1103.2623	1116.3577	1120.6259	1107.8653	1111.4027	1119.7751
1136.1231	1147.0037	1155.0661	1135.9029	1144.4149	1149.8620	1126.3629	1139.9995	1146.8340
1169.2249	1171.8719	1190.3993	1159.1930	1170.0717	1187.5567	1164.6445	1168.2239	1178.4809
1194.7033	1195.7191	1211.8741	1191.7488	1195.4836	1212.3752	1186.3301	1191.0637	1205.9899
1217.9376	1233.0359	1240.3143	1218.4486	1231.2676	1239.5190	1212.6825	1225.1665	1238.9344
1253.3382	1261.7856	1266.4459	1251.8677	1258.1329	1266.4065	1240.2819	1248.2299	1258.6161
1279.2658	1284.6542	1303.3473	1278.3706	1285.3986	1304.4990	1280.0903	1282.3022	1301.8953
1310.6746	1322.2929	1326.7783	1317.1578	1322.7813	1326.5440	1305.1665	1317.7264	1325.1550
1334.6405	1342.5684	1344.2463	1334.5120	1341.8465	1343.7435	1326.8638	1329.5849	1337.4488

1349.4748	1351.3259	1364.7886	1349.7024	1350.7862	1363.7378	1340.6789	1345.9829	1354.3003
1367.2061	1374.8374	1380.5520	1371.2212	1376.1767	1377.3238	1360.4662	1367.5403	1374.3962
1382.0125	1403.3216	1415.5380	1387.4585	1402.4560	1413.3133	1388.8070	1396.5185	1410.5265
1422.6014	1429.1901	1460.2097	1421.9122	1427.8912	1461.1208	1425.1421	1429.0660	1462.9194
1476.6789	1482.9814	1490.6107	1477.9042	1483.1429	1486.3888	1482.1432	1486.5029	1493.4468
1495.6111	1502.4774	1505.3041	1498.9476	1500.8888	1505.4969	1497.2061	1498.8521	1505.3967
1510.7679	1521.4339	1753.5204	1509.8152	1512.6861	1753.0843	1506.2841	1510.0921	1756.5205
2935.6357	2951.6773	3022.4006	2991.8387	3023.2993	3042.6896	2938.7745	2942.6135	3021.6047
3044.5174	3044.8152	3046.0295	3043.4105	3050.7803	3052.8791	3045.7931	3048.6786	3049.6210
3053.7250	3056.1747	3058.0955	3055.7074	3056.1783	3058.4493	3051.8215	3052.7160	3054.6950
3059.8164	3063.2820	3064.4753	3059.1691	3063.3327	3064.2013	3059.5722	3060.5899	3062.4181
3065.1772	3066.6259	3071.2190	3069.7604	3071.5645	3072.3305	3064.0627	3067.1978	3068.9592
3072.4163	3086.6659	3094.2073	3085.3483	3086.5334	3093.8220	3075.7976	3085.6850	3091.1999
3096.9823	3097.4323	3103.2650	3096.3270	3098.4566	3103.8812	3097.5648	3099.4395	3106.9154
3104.8646	3109.8643	3811.4190	3110.0729	3119.8623	3809.7871	3110.5887	3111.7818	3816.8891

1d			1e			1f		
48.3953	100.1442	118.3355	55.1272	100.7467	113.5961	57.8137	84.3785	123.0001
141.8629	170.8826	206.2457	143.7394	166.2486	208.4113	148.7598	178.0416	194.3201
221.8807	245.8890	255.8831	214.6290	233.3969	252.5106	225.1987	241.3146	255.1186
262.8631	285.3242	288.0979	262.2493	284.2666	303.5468	256.5675	270.5991	298.5152
315.6931	332.6977	352.7930	323.6658	330.9303	348.5608	310.3745	319.0929	348.7516
364.3259	384.6099	426.7035	384.1393	390.1838	447.7317	363.8291	392.3166	421.4231
452.2563	467.7166	478.4783	457.5670	470.4419	485.7407	446.0468	465.8570	483.3293
490.7305	526.7662	531.7194	492.8916	525.7718	548.3525	496.2208	509.7957	540.2333
552.9447	582.4769	593.4293	550.2118	579.7035	595.0522	553.2229	559.8019	606.8741
631.3081	649.8052	669.9322	628.7766	648.5279	677.9824	629.4686	648.6795	668.2233
713.2881	740.9407	767.7666	708.9523	740.4959	762.6633	700.2155	750.5821	781.0552
784.8703	806.7763	826.5415	786.3559	805.8442	813.2845	787.5012	814.8076	825.7993
844.2372	860.0271	874.6444	842.0964	860.3893	882.0137	847.0288	864.6356	870.7583
891.6990	893.3462	917.7037	888.2238	895.2893	912.8897	892.2284	915.6036	922.8352
936.4204	954.3482	960.5627	938.6105	939.3168	955.6021	933.6048	953.1656	964.2473

969.3067	982.9282	993.5779	962.7829	982.3096	994.6346	971.5034	979.5156	997.2917
1008.2204	1024.2530	1032.6105	1004.9735	1018.3216	1030.0852	1009.8201	1025.6475	1032.5718
1036.2877	1051.5615	1055.9530	1038.7650	1049.3954	1052.0293	1039.4320	1051.2001	1062.4532
1071.6870	1080.6659	1091.0073	1061.8811	1070.8160	1079.7631	1064.8532	1081.7900	1091.9690
1101.7449	1115.5826	1125.1196	1100.2757	1116.4853	1121.4873	1105.0957	1111.4339	1119.0775
1134.9764	1147.9034	1154.9214	1134.5630	1145.3819	1148.9608	1126.0285	1139.5649	1146.0333
1169.4885	1175.1185	1187.3787	1159.1366	1175.3672	1187.3022	1165.6031	1168.2106	1181.4916
1194.6869	1197.4017	1214.2153	1192.9455	1195.6521	1214.2512	1187.6482	1191.7387	1208.2944
1216.3400	1231.3468	1243.9728	1217.3915	1231.7729	1241.8099	1211.5003	1225.2106	1236.1172
1254.4062	1262.6526	1273.4636	1251.6715	1262.8410	1273.6050	1242.6694	1250.7121	1272.4767
1279.3435	1287.6745	1293.8183	1279.7174	1288.8259	1294.4923	1279.4779	1283.2527	1292.8083
1310.1122	1315.7266	1326.8199	1313.1025	1319.6801	1327.5682	1304.8171	1310.1921	1323.6408
1331.9572	1337.9068	1346.0613	1333.6283	1337.7601	1344.3189	1326.1374	1330.2841	1332.3603
1349.3892	1351.3295	1363.6352	1348.6244	1351.8119	1362.4409	1339.7833	1344.5310	1353.2041
1367.8009	1375.1137	1380.5671	1372.1937	1376.2975	1377.4601	1358.7210	1367.5494	1374.4843

1382.1231	1403.7041	1415.4943	1387.5620	1402.6551	1413.3112	1388.9280	1396.7426	1411.0866
1424.1429	1439.3743	1460.2264	1426.3269	1433.1056	1461.2136	1427.0493	1439.0479	1463.1428
1476.7084	1483.0103	1490.8026	1477.9686	1483.0753	1486.4484	1482.1566	1486.5552	1493.7668
1496.7040	1504.2195	1510.7150	1499.3027	1501.7534	1509.7656	1497.9666	1498.9901	1506.1981
1516.2114	1521.4716	1755.2935	1512.6973	1519.0103	1754.6363	1510.1529	1522.0355	1758.2898
2936.0736	2952.1169	3022.6306	2992.0860	3023.3675	3043.0946	2938.7804	2942.6665	3021.8255
3041.2999	3044.9119	3046.4003	3043.4734	3050.9977	3052.9118	3045.4381	3047.3151	3049.3150
3053.6123	3056.4050	3059.3916	3056.3387	3056.5820	3059.0416	3050.2801	3052.9248	3055.1258
3063.4507	3064.8072	3065.3996	3062.8767	3064.6880	3070.1250	3059.9853	3061.0260	3063.4033
3066.7345	3071.7462	3072.6717	3071.8796	3073.4886	3083.0089	3066.6469	3068.1203	3076.6417
3083.5433	3092.1147	3095.9450	3086.8899	3091.3746	3094.7342	3084.3254	3094.2867	3095.1064
3097.6387	3099.3939	3101.4390	3098.5536	3098.7327	3100.2122	3098.2749	3099.9747	3105.3093
3103.6652	3109.9540	3799.2577	3110.1876	3120.1543	3800.8197	3107.2867	3111.9613	3804.1314