Supporting Information

(±)-Pheharmines A-B, two pairs of racemic alkaloids with a morpholino[4,3,2-*hi*]β-carboline core, from the roots of *Peganum harmala*

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1. Experimental section

HPLC analyses of the crude ethanol extracts of different parts of *P.* harmala

HPLC analysis was performed on a Cosmosil 5C_{18}-MS-II column (150 × 4.6 mm I. D., 5 μm) equipped with a LC-6AD pump and a Shimadzu SPD-20A UV-Vis detector (Shimadzu Co. Ltd., Japan). The mobile phase with a flow rate of 0.5 mL/min consisted of solvent A (methanol with 0.1% diethylamine) and solvent B (H_2O with 0.1% diethylamine). A binary gradient elution was performed as follows:

Time (min)	A%	B%
0.00	10	90
90.00	90	10

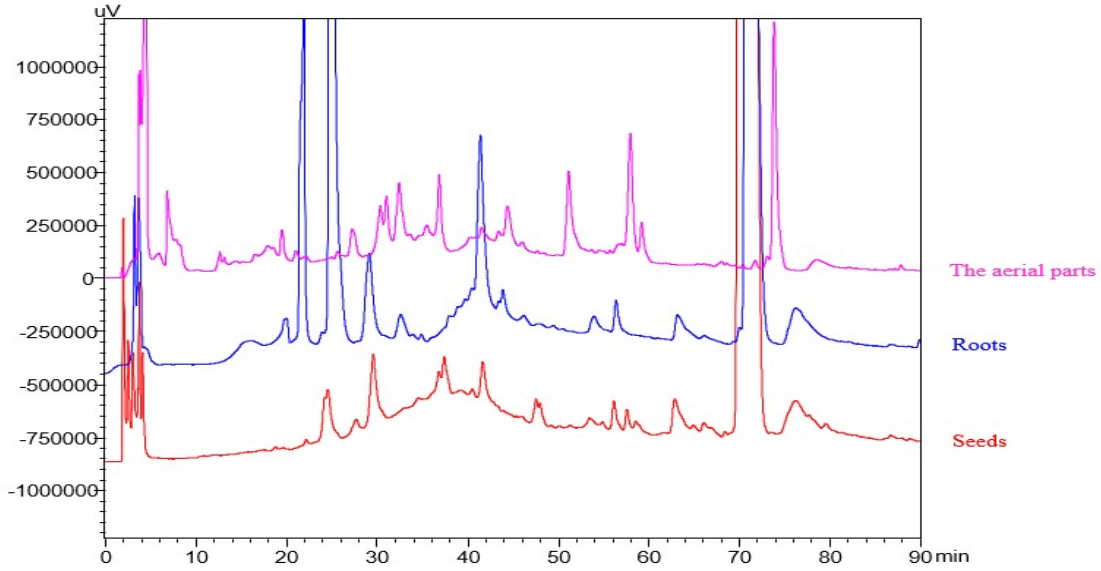
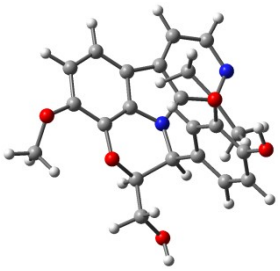
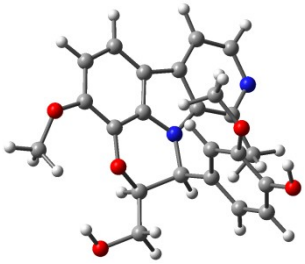
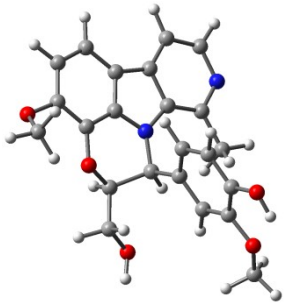


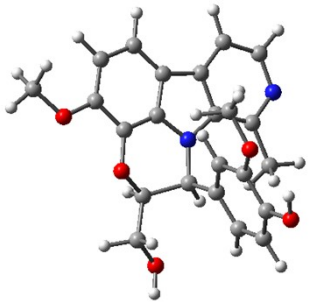
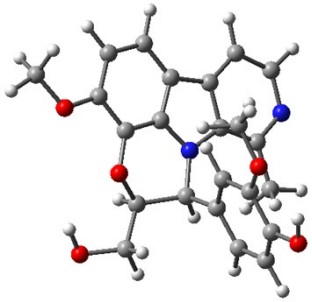
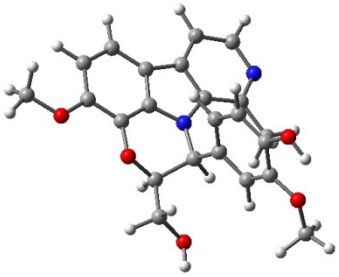
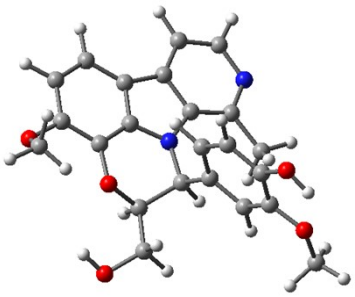
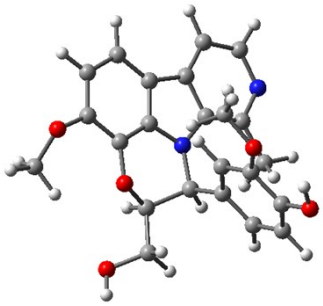
Figure S1 HPLC chromatogram of the ethanolic extracts of aerial parts, roots, and seeds of *P. harmala*

2 Computational methods

Conformational searches for (7′*S*,8′*S*)-pheharmine A and (7′*S*,8′*R*)-pheharmine B were carried out by CONFLEX using molecular mechanics MMFF94s. Their low-energy conformers separately accounting for more than 1% Boltzmann distribution were optimized at the B3LYP/6-31G(d) level in MeOH using the polarizable continuum model (PCM) with the Gaussian 09 program package.[1] ECD calculations of all the conformers were run by the time-dependent density functional theory (TDDFT) method at B3LYP/6-311G+(d,p) level with the PCM in the methanol solvent. The overall calculated ECD spectra were generated by Boltzmann weighting using SpecDis 1.51.[2]

Table S1 Gibbs free energy changes[a] and equilibrium populations[b] of B3LYP/6-31G(d) optimized low-energy 3D conformers of (7′*S*,8′*S*)-pheharmine A in ECD calculations

label	conformer	ΔG (kcal/mol)[a]	P(%)[b]
A-c1		0	0.07
A-c2		-0.37525	0.13
A-c3		-0.98912	0.36

A-c4		-3.25110	16.43
A-c5		-4.07944	66.58
A-c6		-3.18512	14.7
A-c7		-1.85825	1.56
A-c8		-0.53338	0.17

[a]B3LYP/6-311G+(d,p); [b]ΔG values at 298.15K

Table S2 Cartesian coordinates for the low-energy 3D conformers of (7′*S*,8′*S*)-pheharmine A at the B3LYP/6-31G(d) level of theory in methanol.

A-c1				**A-c2**			
Atom	X	Y	Z	Atom	X	Y	Z
C	1.586	-4.5401	0.1616	C	1.3888	-4.4745	-0.3388
O	2.577	-3.796	-0.5308	O	2.4482	-3.7082	-0.8904
C	2.5103	-2.4292	-0.4815	C	2.4138	-2.3489	-0.7303
C	3.532	-1.8057	-1.2162	C	3.4303	-1.6903	-1.441
C	3.6444	-0.4064	-1.3076	C	3.5701	-0.2909	-1.4269
C	2.6907	0.3914	-0.6526	C	2.6507	0.4713	-0.6864
C	1.7036	-0.2509	0.0618	C	1.6708	-0.2054	0.0061
C	1.5808	-1.6367	0.1992	C	1.5242	-1.5952	0.0418
O	0.5293	-2.1374	0.9288	O	0.4919	-2.1329	0.7725
C	0.0801	-1.1914	1.9372	C	0.0896	-1.2526	1.8648
H	0.9155	-1.051	2.6422	H	0.9494	-1.2087	2.5518
C	-1.0507	-1.853	2.7296	C	-1.0547	-1.9506	2.6077
O	-1.4894	-1.0082	3.7867	O	-0.5774	-3.148	3.2244
C	-0.2956	0.2201	1.365	C	-0.271	0.2019	1.4089
H	-0.3733	0.9061	2.216	H	-0.3032	0.8178	2.315
C	-1.6096	0.2368	0.5858	C	-1.6145	0.3031	0.6929
C	-2.775	0.7138	1.2142	C	-2.74	0.7671	1.3992
C	-3.9961	0.7206	0.5423	C	-3.9862	0.8456	0.7799
C	-4.0565	0.2471	-0.7601	C	-4.1121	0.4577	-0.5461
O	-5.2672	0.2621	-1.3977	O	-5.3467	0.5439	-1.1293
C	-2.9214	-0.2375	-1.4161	C	-3.0182	-0.0111	-1.2785
O	-3.1351	-0.675	-2.6983	O	-3.295	-0.36	-2.5753
C	-1.989	-1.1143	-3.4202	C	-2.1935	-0.7866	-3.3703
C	-1.7022	-0.2452	-0.7358	C	-1.7732	-0.0908	-0.6517
N	0.8601	0.7008	0.5859	N	0.8643	0.719	0.6272
C	1.2898	1.9699	0.2724	C	1.3097	2.0004	0.3966
C	2.4462	1.7946	-0.5128	C	2.4401	1.864	-0.4331
C	3.1172	2.9258	-0.9981	C	3.1216	3.0158	-0.8504
C	2.5885	4.1546	-0.6612	C	2.6287	4.2251	-0.4066
N	1.4842	4.3278	0.0891	N	1.5485	4.3611	0.3853
C	0.7993	3.2535	0.5759	C	0.8542	3.2666	0.8083
C	-0.4211	3.5689	1.3805	C	-0.3399	3.5458	1.664
H	1.6343	-4.3588	1.2399	H	1.4149	-4.451	0.7548
H	0.5877	-4.3451	-0.2427	H	0.4173	-4.1576	-0.7318
H	1.7987	-5.6019	0.0016	H	1.5391	-5.5147	-0.6445
H	4.263	-2.4242	-1.7345	H	4.1336	-2.2805	-2.0266
H	4.4481	0.0411	-1.8841	H	4.3677	0.1845	-1.9896
H	-1.9009	-2.1037	2.0864	H	-1.4591	-1.3141	3.4001
H	-0.6957	-2.7955	3.1622	H	-1.8631	-2.2411	1.9294

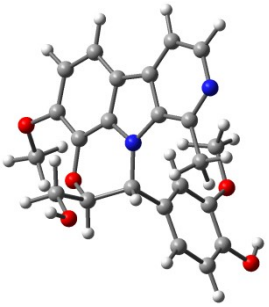
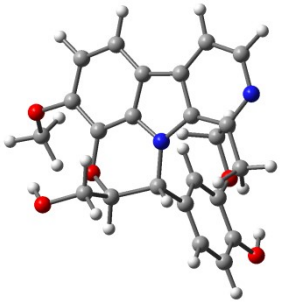
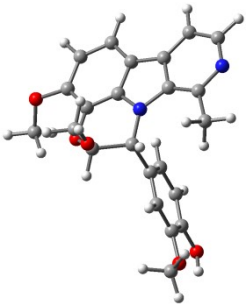
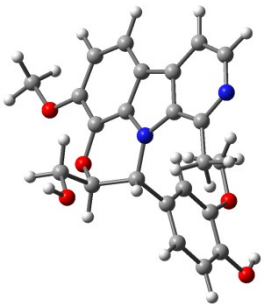
H	-2.1892	-1.4927	4.2616	H	-0.1552	-3.673	2.5195
H	-2.7403	1.0804	2.2391	H	-2.6592	1.0749	2.4402
H	-4.8936	1.0911	1.0285	H	-4.8544	1.2063	1.324
H	-5.0844	-0.0934	-2.2895	H	-5.2134	0.2364	-2.0473
H	-2.3165	-1.3959	-4.4256	H	-2.5702	-0.9975	-4.3758
H	-1.2532	-0.3098	-3.5227	H	-1.4385	0.0021	-3.4561
H	-1.5465	-2.0008	-2.954	H	-1.7591	-1.7115	-2.9767
H	-0.8099	-0.6265	-1.2211	H	-0.9117	-0.4608	-1.1982
H	4.0092	2.847	-1.6069	H	3.9949	2.9666	-1.4889
H	3.0592	5.0726	-1.0019	H	3.1094	5.1573	-0.6901
H	-1.315	3.2088	0.8669	H	-1.2535	3.2518	1.143
H	-0.3551	3.1219	2.3755	H	-0.2657	3.0175	2.6176
H	-0.5287	4.6508	1.513	H	-0.4155	4.6156	1.8867
	A-c3				**A-c4**		
Atom	X	Y	Z	Atom	X	Y	Z
C	2.7022	-4.2328	-0.264	C	3.9328	-4.1035	-0.5278
O	3.6886	-3.2458	-0.5259	O	2.8578	-3.3686	0.0401
C	3.3216	-1.9302	-0.4254	C	2.8246	-2.0195	-0.196
C	4.31	-1.0483	-0.8916	C	3.763	-1.3079	-0.9558
C	4.1337	0.3472	-0.8845	C	3.6496	0.0852	-1.1544
C	2.922	0.8722	-0.4032	C	2.561	0.7748	-0.5881
C	1.9764	-0.0193	0.0536	C	1.6625	0.0414	0.1516
C	2.131	-1.408	0.0894	C	1.7606	-1.3265	0.3897
O	1.0987	-2.1765	0.5714	O	0.7865	-1.96	1.1301
C	0.2785	-1.4388	1.5172	C	0.1482	-1.0337	2.0511
H	0.9188	-1.2029	2.3826	H	0.9199	-0.7124	2.7693
C	-0.811	-2.3861	2.0277	C	-0.894	-1.8165	2.8541
O	-1.622	-1.7502	3.0095	O	-1.5096	-0.9856	3.8322
C	-0.2783	-0.0816	0.9615	C	-0.4263	0.2622	1.3712
H	-0.6442	0.4912	1.8211	H	-0.6382	0.9804	2.1713
C	-1.4131	-0.2483	-0.0468	C	-1.7015	0.0191	0.5658
C	-1.1782	-0.6361	-1.3767	C	-2.9445	0.3765	1.1204
C	-2.2392	-0.8053	-2.2657	C	-4.1291	0.1494	0.4221
C	-3.5377	-0.5907	-1.827	C	-4.0749	-0.4423	-0.8313
O	-4.5593	-0.7661	-2.7204	O	-5.2516	-0.6572	-1.4962
C	-3.8109	-0.2075	-0.5114	C	-2.8601	-0.8188	-1.4111
O	-5.1397	-0.0355	-0.2209	O	-2.9639	-1.3977	-2.6502
C	-5.4522	0.4305	1.0868	C	-1.7441	-1.7778	-3.2784
C	-2.7452	-0.044	0.3749	C	-1.6773	-0.5891	-0.7056
N	0.8664	0.6907	0.4466	N	0.6607	0.8744	0.5839
C	1.0668	2.0445	0.3	C	0.8953	2.1701	0.1838
C	2.361	2.1788	-0.2401	C	2.0915	2.1266	-0.5621
C	2.8551	3.4621	-0.5123	C	2.5898	3.3131	-1.1179
C	2.0236	4.5235	-0.2211	C	1.8618	4.4619	-0.8868

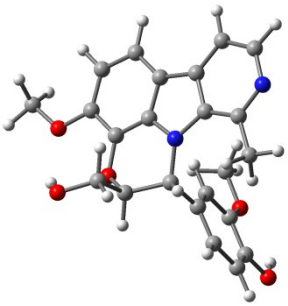
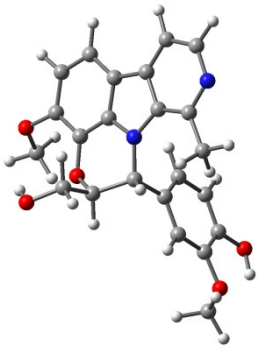
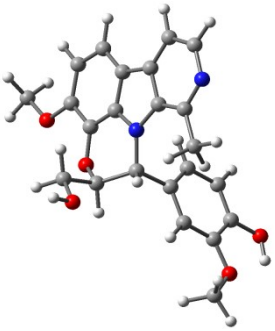
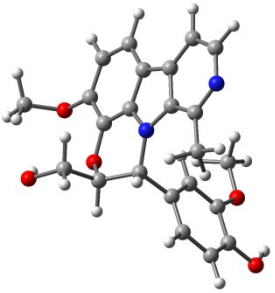
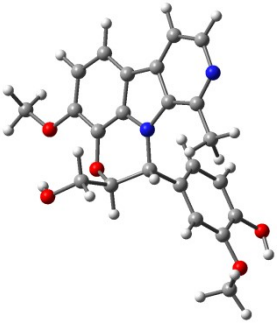
N	0.7868	4.4014	0.2967	N	0.7203	4.5093	-0.1748
C	0.2666	3.1704	0.569	C	0.1989	3.3769	0.3788
C	-1.124	3.1599	1.1186	C	-1.0819	3.549	1.1313
H	2.4371	-4.2516	0.7976	H	3.9129	-4.0512	-1.6214
H	1.823	-4.1025	-0.9033	H	4.8958	-3.7644	-0.1321
H	3.1379	-5.2073	-0.5062	H	3.8078	-5.1527	-0.2433
H	5.2432	-1.4562	-1.2764	H	4.6103	-1.8056	-1.4175
H	4.9186	0.9993	-1.2549	H	4.3916	0.6133	-1.7462
H	-1.4457	-2.7476	1.2117	H	-1.6644	-2.2452	2.2044
H	-0.347	-3.2704	2.4796	H	-0.4112	-2.6567	3.3662
H	-2.2418	-2.427	3.3379	H	-2.1389	-1.5487	4.3187
H	-0.1684	-0.8129	-1.7417	H	-2.9987	0.8319	2.1082
H	-2.0538	-1.1018	-3.294	H	-5.0867	0.4289	0.851
H	-5.3709	-0.554	-2.2201	H	-4.9875	-1.0658	-2.3436
H	-6.5378	0.554	1.1465	H	-1.9917	-2.2088	-4.2532
H	-5.1582	-0.302	1.8456	H	-1.1016	-0.9083	-3.4527
H	-4.9947	1.4067	1.2792	H	-1.224	-2.5465	-2.6973
H	-2.9226	0.2367	1.4094	H	-0.7226	-0.8816	-1.1301
H	3.8417	3.6203	-0.9295	H	3.5025	3.3355	-1.7
H	2.3441	5.545	-0.4058	H	2.1915	5.4167	-1.2867
H	-1.8074	2.6944	0.4053	H	-1.8932	3.0295	0.6172
H	-1.1603	2.6301	2.0735	H	-0.9849	3.1743	2.1531
H	-1.4775	4.1812	1.2971	H	-1.3542	4.608	1.1947
	A-c5				**A-c6**		
Atom	X	Y	Z	Atom	X	Y	Z
C	3.9963	-3.8266	-1.0299	C	4.7741	-3.6137	-0.7672
O	2.9192	-3.1827	-0.3634	O	3.5692	-3.0934	-0.2238
C	2.8331	-1.8205	-0.4803	C	3.3835	-1.7377	-0.2926
C	3.7149	-1.0124	-1.21	C	4.3193	-0.8175	-0.7843
C	3.5475	0.3877	-1.2797	C	4.0462	0.5671	-0.8188
C	2.4618	0.9857	-0.6125	C	2.8	1.0344	-0.3609
C	1.6188	0.1589	0.0933	C	1.909	0.1003	0.1146
C	1.7724	-1.2196	0.2041	C	2.1578	-1.2671	0.1887
O	0.8523	-1.9506	0.9219	O	1.1809	-2.1124	0.6673
C	0.2233	-1.1321	1.9525	C	0.2864	-1.4153	1.5755
H	1.0218	-0.8797	2.6679	H	0.8857	-1.122	2.4526
C	-0.7769	-2.0335	2.6831	C	-0.7496	-2.4262	2.0746
O	-0.0803	-3.095	3.3401	O	-1.6293	-1.8315	3.0239
C	-0.4148	0.1988	1.4181	C	-0.3482	-0.1038	0.9853
H	-0.6032	0.8303	2.2941	H	-0.7657	0.4568	1.8294
C	-1.7261	-0.0113	0.6676	C	-1.453	-0.3594	-0.0379
C	-2.9448	0.2728	1.3114	C	-1.1708	-0.7695	-1.3518
C	-4.1589	0.0687	0.6581	C	-2.2029	-1.0164	-2.2565
C	-4.1587	-0.4261	-0.638	C	-3.5196	-0.8589	-1.8489

O	-5.3643	-0.6184	-1.2558	O	-4.5123	-1.1092	-2.757
C	-2.9689	-0.7281	-1.306	C	-3.8395	-0.4591	-0.5487
O	-3.1259	-1.2147	-2.5784	O	-5.1813	-0.351	-0.2884
C	-1.9346	-1.5303	-3.2913	C	-5.5446	0.1112	1.0075
C	-1.7559	-0.5214	-0.6464	C	-2.8022	-0.2169	0.3532
N	0.6111	0.9143	0.6387	N	0.7487	0.7387	0.4744
C	0.7862	2.2476	0.3459	C	0.8623	2.0987	0.2951
C	1.9511	2.3122	-0.4472	C	2.1516	2.3045	-0.2381
C	2.3884	3.5597	-0.9138	C	2.5615	3.6103	-0.5414
C	1.6353	4.6576	-0.5531	C	1.6582	4.6211	-0.2855
N	0.5233	4.6016	0.2036	N	0.4275	4.4309	0.2262
C	0.0607	3.4079	0.6731	C	-0.0126	3.1757	0.5282
C	-1.1956	3.4707	1.4815	C	-1.404	3.0865	1.0681
H	3.9325	-3.6831	-2.1135	H	4.8614	-3.3808	-1.8337
H	4.9616	-3.4861	-0.641	H	5.6451	-3.2533	-0.2102
H	3.9183	-4.9	-0.8317	H	4.7435	-4.7029	-0.6667
H	4.5581	-1.4371	-1.7463	H	5.2879	-1.1398	-1.1537
H	4.2467	0.9918	-1.8507	H	4.7893	1.2594	-1.2036
H	-1.3279	-1.4777	3.4472	H	-1.3363	-2.8428	1.2491
H	-1.4868	-2.4986	1.9922	H	-0.2396	-3.2694	2.5546
H	0.4781	-3.5162	2.6571	H	-2.2077	-2.5464	3.3468
H	-2.9627	0.6588	2.329	H	-0.1456	-0.9057	-1.6902
H	-5.0996	0.2919	1.1532	H	-1.9808	-1.3306	-3.2722
H	-5.1395	-0.9621	-2.1425	H	-5.3435	-0.932	-2.2758
H	-2.2255	-1.898	-4.28	H	-6.6364	0.1725	1.0459
H	-1.3138	-0.64	-3.4366	H	-5.2234	-0.5942	1.7809
H	-1.375	-2.3277	-2.791	H	-5.1477	1.1144	1.1955
H	-0.8189	-0.7565	-1.1411	H	-3.0148	0.0788	1.3767
H	3.2749	3.6652	-1.5266	H	3.5392	3.8234	-0.9549
H	1.9181	5.6549	-0.8785	H	1.9116	5.6564	-0.4956
H	-2.0128	2.9852	0.9437	H	-2.0518	2.5717	0.3554
H	-1.0548	2.9976	2.4562	H	-1.4156	2.5664	2.029
H	-1.4888	4.5106	1.6613	H	-1.8205	4.0862	1.2318
	A-c7				**A-c8**		
Atom	X	Y	Z	Atom	X	Y	Z
C	-2.6552	-4.0556	0.6959	C	1.8315	-4.4237	-0.0617
O	-3.6841	-3.0758	0.6841	O	2.5802	-3.6067	-0.9522
C	-3.301	-1.769	0.538	C	2.5002	-2.2496	-0.785
C	-4.2675	-0.8525	0.9796	C	3.4774	-1.5441	-1.5046
C	-4.0604	0.5377	0.9218	C	3.5645	-0.1402	-1.4709
C	-2.8429	1.0191	0.4097	C	2.6272	0.5769	-0.7069
C	-1.9235	0.0922	-0.03	C	1.676	-0.1453	-0.0213
C	-2.1104	-1.2921	-0.018	C	1.5791	-1.5386	-0.0108
O	-1.1132	-2.1025	-0.5052	O	0.5455	-2.1207	0.6801

C	-0.292	-1.4087	-1.4908	C	0.119	-1.2972	1.8046
H	-0.9524	-1.2088	-2.3493	H	0.975	-1.2506	2.4959
C	0.7798	-2.3991	-1.9582	C	-1.0171	-2.0406	2.5209
O	0.1696	-3.4848	-2.6586	O	-0.4953	-3.1832	3.2025
C	0.3051	-0.0511	-0.9847	C	-0.279	0.1622	1.3881
H	0.6625	0.4829	-1.8728	H	-0.3253	0.7506	2.3117
C	1.4657	-0.2171	-0.0086	C	-1.628	0.2448	0.6787
C	1.2582	-0.576	1.3341	C	-2.7563	0.7005	1.3857
C	2.3379	-0.748	2.1992	C	-4.0057	0.7576	0.7707
C	3.6283	-0.5656	1.7243	C	-4.132	0.355	-0.5509
O	4.668	-0.743	2.5956	O	-5.3702	0.4185	-1.1294
C	3.8748	-0.2121	0.395	C	-3.0353	-0.1072	-1.2834
O	5.1988	-0.0684	0.0708	O	-3.3134	-0.4739	-2.575
C	5.4953	0.3354	-1.2607	C	-2.2133	-0.9211	-3.3612
C	2.7902	-0.0439	-0.4681	C	-1.7868	-0.1632	-0.6616
N	-0.8061	0.7633	-0.4662	N	0.8368	0.7364	0.6173
C	-0.9722	2.1252	-0.3579	C	1.2393	2.0368	0.4133
C	-2.2554	2.3064	0.1954	C	2.3691	1.9559	-0.4253
C	-2.7173	3.6088	0.4316	C	3.0078	3.1384	-0.8241
C	-1.8668	4.6411	0.0948	C	2.4774	4.3211	-0.3529
N	-0.6399	4.4738	-0.4339	N	1.3995	4.4045	0.4493
C	-0.1507	3.2237	-0.672	C	0.7458	3.2786	0.8548
C	1.2338	3.1659	-1.2334	C	-0.4504	3.5016	1.7236
H	-2.307	-4.2634	-0.3201	H	2.0362	-4.1761	0.9851
H	-1.8292	-3.7745	1.3579	H	0.7629	-4.3753	-0.2922
H	-3.0862	-4.9825	1.0874	H	2.1499	-5.4592	-0.2187
H	-5.2046	-1.227	1.3882	H	4.1959	-2.1001	-2.1045
H	-4.827	1.2194	1.2773	H	4.3375	0.3728	-2.0347
H	1.486	-1.924	-2.6453	H	-1.4935	-1.4048	3.273
H	1.3298	-2.8308	-1.1163	H	-1.7663	-2.399	1.8075
H	-0.5215	-3.8411	-2.069	H	-1.2562	-3.7103	3.5029
H	0.2553	-0.7272	1.7291	H	-2.6742	1.0202	2.4228
H	2.1739	-1.022	3.2376	H	-4.8761	1.114	1.3141
H	5.4725	-0.5623	2.0718	H	-5.2349	0.108	-2.0463
H	6.5823	0.4255	-1.3483	H	-2.5921	-1.1569	-4.3603
H	5.1638	-0.4178	-1.9831	H	-1.4585	-0.1349	-3.4682
H	5.0603	1.3156	-1.4823	H	-1.7783	-1.8361	-2.9456
H	2.9518	0.2247	-1.5077	H	-0.9217	-0.5276	-1.2068
H	-3.6944	3.8028	0.8563	H	3.8778	3.1313	-1.4688
H	-2.1621	5.6751	0.2498	H	2.9241	5.2745	-0.6209
H	1.915	2.7149	-0.5086	H	-1.3597	3.2132	1.1919
H	1.2512	2.5994	-2.1675	H	-0.3653	2.9373	2.6553
H	1.6049	4.1726	-1.4541	H	-0.544	4.56	1.9896

Table S3 Gibbs free energies changes[a] and equilibrium populations[b] of B3LYP/6-31G(d) optimized low-energy 3D conformers of (7′*S*,8′*R*)-pheharmine B in ECD calculations

Label	Conformer	ΔG (kcal/mol)[a]	P(%)[b]
B-c1		0	0.41
B-c2		-0.66232	1.24
B-c3		-0.07569	0.46
B-c4		-2.35507	21.64

B-c5		-2.5383	29.49
B-c6		-0.61793	1.15
B-c7		-2.33512	20.92
B-c8		0.49335	0.18
B-c9		-2.42898	24.52

[a]B3LYP/6-311G+(d,p); [b]ΔG values at 298.15K

Table S4 Cartesian coordinates for the low-energy 3D conformers of (7′*S*,8′*S*)-pheharmine B at the B3LYP/6-31G(d) level of theory in methanol.

	B-c1				B-c2		
Atom	X	Y	Z	Atom	X	Y	Z
C	-1.9558	-4.3858	-0.0536	C	-2.1132	-4.1	-0.6991
O	-2.8812	-3.5368	-0.7175	O	-3.0817	-3.1321	-1.0823
C	-2.6253	-2.1913	-0.724	C	-2.7303	-1.814	-0.9595
C	-3.4607	-1.4785	-1.5986	C	-3.4966	-0.9539	-1.7602
C	-3.3616	-0.085	-1.7591	C	-3.2864	0.4367	-1.7744
C	-2.387	0.6109	-1.0237	C	-2.2733	0.9753	-0.962
C	-1.59	-0.1181	-0.1677	C	-1.5515	0.1027	-0.1767
C	-1.6797	-1.4956	0.0364	C	-1.7531	-1.2758	-0.117
O	-0.8298	-2.0954	0.9307	O	-0.9871	-2.0307	0.7346
C	-0.2915	-1.1864	1.9296	C	-0.3984	-1.2694	1.8304
H	0.5409	-1.7274	2.3995	H	0.3613	-1.9396	2.2539
C	-1.3389	-0.9648	3.0366	C	-1.4627	-1.0609	2.9251
O	-0.7731	-0.2396	4.123	O	-1.9369	-2.3231	3.3935
C	0.2711	0.1625	1.3646	C	0.2791	0.078	1.4133
H	0.3466	0.8843	2.1845	H	0.3782	0.6997	2.3106
C	1.6731	-0.0397	0.7902	C	1.6785	-0.1755	0.8575
C	2.7846	0.1368	1.6357	C	2.7772	-0.1509	1.7369
C	4.0793	-0.0582	1.1582	C	4.0668	-0.399	1.27
C	4.2656	-0.4371	-0.1633	C	4.2606	-0.679	-0.0749
O	5.5465	-0.6226	-0.6078	O	5.5366	-0.9188	-0.5068
C	3.1852	-0.6314	-1.0291	C	3.1926	-0.7214	-0.9755
O	3.5244	-1.0101	-2.3029	O	3.5373	-1.0157	-2.2697
C	2.4521	-1.1755	-3.2248	C	2.4822	-1.0207	-3.2256
C	1.8902	-0.4372	-0.5446	C	1.9024	-0.475	-0.5019
N	-0.6983	0.7397	0.4266	N	-0.6123	0.822	0.5181
C	-0.9019	2.0351	0.0097	C	-0.7019	2.1642	0.2303
C	-1.967	1.9742	-0.9091	C	-1.751	2.2821	-0.702
C	-2.408	3.1573	-1.5181	C	-2.0871	3.5523	-1.1905
C	-1.755	4.3198	-1.1634	C	-1.3515	4.617	-0.7121
N	-0.7356	4.3829	-0.286	N	-0.3448	4.5084	0.1756
C	-0.2726	3.254	0.3231	C	0.0175	3.2908	0.67
C	0.8728	3.4418	1.2668	C	1.1629	3.291	1.632
H	-0.9362	-4.2397	-0.4248	H	-1.1224	-3.8721	-1.1066
H	-2.0183	-4.2606	1.0316	H	-2.0879	-4.2122	0.3888
H	-2.2378	-5.4196	-0.2771	H	-2.4249	-5.0622	-1.1177
H	-4.208	-2.0208	-2.1757	H	-4.2745	-1.3742	-2.3955
H	-4.0223	0.4347	-2.4462	H	-3.894	1.0747	-2.4089
H	-2.2113	-0.4154	2.6687	H	-1.0387	-0.5291	3.7823

H	-1.6968	-1.9312	3.4089	H	-2.3297	-0.4986	2.5658
H	-1.4637	-0.1711	4.8074	H	-2.2728	-2.7986	2.6098
H	2.6491	0.4285	2.676	H	2.6406	0.0633	2.7952
H	4.9369	0.0819	1.8096	H	4.9158	-0.3763	1.9471
H	5.4506	-0.8766	-1.5465	H	5.4497	-1.0875	-1.4654
H	2.8837	-1.4521	-4.1916	H	2.9195	-1.2447	-4.2033
H	1.7865	-1.9872	-2.9131	H	1.7511	-1.8042	-3.0005
H	1.9005	-0.2395	-3.3621	H	2.0038	-0.0379	-3.2919
H	1.0352	-0.5948	-1.1938	H	1.0563	-0.5153	-1.1803
H	-3.222	3.167	-2.2321	H	-2.885	3.6995	-1.9077
H	-2.0466	5.2731	-1.5955	H	-1.56	5.6295	-1.0466
H	0.6021	3.107	2.2714	H	0.8591	2.8679	2.5929
H	1.7492	2.8933	0.9146	H	2.0016	2.7231	1.2231
H	1.1495	4.4994	1.3345	H	1.5134	4.312	1.8173
	B-c3				**B-c4**		
Atom	X	Y	Z	Atom	X	Y	Z
C	-2.4997	-4.2766	-0.4767	C	-4.1013	-3.8947	-0.7037
O	-3.5383	-3.3158	-0.611	O	-3.0721	-3.1896	-0.0242
C	-3.1839	-1.9938	-0.5545	C	-2.8665	-1.8817	-0.3766
C	-4.1661	-1.1345	-1.0708	C	-3.6377	-1.164	-1.3005
C	-3.9952	0.2608	-1.1037	C	-3.36	0.1862	-1.6016
C	-2.799	0.8064	-0.6065	C	-2.2768	0.8231	-0.9679
C	-1.8614	-0.0655	-0.0963	C	-1.544	0.0841	-0.0672
C	-2.0098	-1.4505	-0.0228	C	-1.8047	-1.2388	0.2693
O	-1.0077	-2.2037	0.5345	O	-1.0016	-1.8879	1.1781
C	-0.145	-1.4575	1.4345	C	-0.2945	-0.9806	2.0675
H	0.7348	-2.0957	1.5926	H	0.4891	-1.5861	2.5428
C	-0.8304	-1.3255	2.807	C	-1.2422	-0.5406	3.1985
O	0.072	-0.7838	3.7665	O	-0.5361	0.2002	4.1886
C	0.3562	-0.0767	0.8878	C	0.4031	0.2404	1.3681
H	0.697	0.5316	1.7322	H	0.5994	1.0113	2.1205
C	1.5443	-0.2708	-0.0531	C	1.7449	-0.1798	0.7688
C	1.3806	-0.5183	-1.4263	C	2.9143	-0.0156	1.5346
C	2.4899	-0.7125	-2.2486	C	4.1544	-0.4034	1.0308
C	3.7631	-0.6678	-1.699	C	4.2269	-0.9658	-0.2355
O	4.8329	-0.8628	-2.5298	O	5.4561	-1.3389	-0.7077
C	3.964	-0.4348	-0.3355	C	3.0845	-1.158	-1.0183
O	5.2757	-0.4235	0.0632	O	3.3115	-1.7325	-2.2431
C	5.5239	-0.1647	1.4401	C	2.1702	-1.9438	-3.0673
C	2.8504	-0.2427	0.4839	C	1.8449	-0.7675	-0.5084
N	-0.7727	0.6625	0.3129	N	-0.5231	0.8613	0.4133
C	-0.9733	2.0097	0.1159	C	-0.5787	2.129	-0.1196
C	-2.2501	2.1209	-0.4672	C	-1.6806	2.1238	-0.9985
C	-2.7403	3.3931	-0.7927	C	-1.9906	3.293	-1.7068

C	-1.9214	4.4665	-0.5081	C	-1.1806	4.3877	-1.4845
N	-0.7002	4.3656	0.0503	N	-0.1276	4.3979	-0.6456
C	-0.1834	3.1455	0.3727	C	0.2116	3.2794	0.0574
C	1.1895	3.1533	0.9664	C	1.4089	3.4022	0.9456
H	-1.6539	-4.0579	-1.1371	H	-5.0834	-3.4604	-0.49
H	-2.1877	-4.3682	0.568	H	-3.9108	-3.9329	-1.7814
H	-2.9067	-5.2466	-0.7795	H	-4.1048	-4.9233	-0.3303
H	-5.0874	-1.5601	-1.465	H	-4.4778	-1.6229	-1.8128
H	-4.7729	0.8974	-1.5143	H	-3.9741	0.7217	-2.3198
H	-1.7155	-0.683	2.7603	H	-2.0639	0.078	2.8233
H	-1.1611	-2.3106	3.1546	H	-1.6893	-1.4216	3.6725
H	-0.4032	-0.7633	4.6175	H	-1.1696	0.3863	4.9053
H	0.3912	-0.5655	-1.8768	H	2.8672	0.4175	2.5325
H	2.3618	-0.8991	-3.3109	H	5.0572	-0.2719	1.6197
H	5.6171	-0.7883	-1.9523	H	5.2804	-1.7041	-1.5968
H	6.6076	-0.1755	1.5917	H	2.5134	-2.4006	-4.0006
H	5.157	0.826	1.7281	H	1.4663	-2.638	-2.5964
H	5.0914	-0.9472	2.0722	H	1.6845	-0.9954	-3.3201
H	2.9688	-0.0686	1.5496	H	0.9415	-0.9176	-1.0905
H	-3.7141	3.5348	-1.2446	H	-2.8245	3.3436	-2.3955
H	-2.2396	5.4807	-0.7328	H	-1.3647	5.3268	-1.9989
H	1.1814	2.7009	1.9614	H	1.1456	3.1736	1.9814
H	1.8865	2.6171	0.3186	H	2.2028	2.7334	0.6059
H	1.5595	4.1786	1.0734	H	1.8041	4.4234	0.9238
		B-c5				**B-c6**	
Atom	X	Y	Z	Atom	X	Y	Z
C	-4.323	-3.3591	-1.2938	C	-2.5662	-4.0198	-0.964
O	-3.249	-2.8391	-0.5222	O	-3.6008	-3.049	-0.8579
C	-2.9325	-1.5175	-0.696	C	-3.2036	-1.7451	-0.721
C	-3.6147	-0.6254	-1.5332	C	-4.1412	-0.8146	-1.1914
C	-3.2262	0.7269	-1.6415	C	-3.9095	0.5713	-1.1291
C	-2.1226	1.1875	-0.8992	C	-2.6999	1.0311	-0.5787
C	-1.4775	0.2796	-0.0907	C	-1.8102	0.088	-0.1115
C	-1.847	-1.052	0.0533	C	-2.0205	-1.2898	-0.132
O	-1.1296	-1.8778	0.887	O	-1.0734	-2.1246	0.4051
C	-0.395	-1.1545	1.9181	C	-0.1962	-1.4735	1.37
H	0.3068	-1.8935	2.3269	H	0.6346	-2.1784	1.5064
C	-1.37	-0.7957	3.0557	C	-0.9241	-1.3826	2.7252
O	-1.9727	-1.9813	3.575	O	-1.2745	-2.6894	3.18
C	0.4082	0.0961	1.4195	C	0.3753	-0.0867	0.9225
H	0.6082	0.7357	2.2869	H	0.7144	0.4434	1.82
C	1.7482	-0.3323	0.8264	C	1.5803	-0.2741	0.0038
C	2.8949	-0.321	1.6422	C	1.4388	-0.4566	-1.3823
C	4.1299	-0.7242	1.1373	C	2.5584	-0.6477	-2.1909

C	4.2194	-1.1492	-0.1804	C	3.8206	-0.6649	-1.6156
O	5.4435	-1.5401	-0.6509	O	4.9006	-0.8553	-2.4338
C	3.099	-1.188	-1.0153	C	3.9998	-0.4974	-0.2397
O	3.3403	-1.6384	-2.288	O	5.3029	-0.5421	0.1833
C	2.2214	-1.6949	-3.1663	C	5.5344	-0.3565	1.5746
C	1.8646	-0.7827	-0.5044	C	2.8755	-0.3079	0.5664
N	-0.4247	0.9052	0.5231	N	-0.702	0.7383	0.3683
C	-0.3663	2.2328	0.1652	C	-0.8379	2.1026	0.2523
C	-1.4335	2.4307	-0.7347	C	-2.0978	2.308	-0.3429
C	-1.6332	3.7052	-1.2831	C	-2.5268	3.6192	-0.5913
C	-0.7548	4.6947	-0.8927	C	-1.6674	4.6344	-0.2248
N	0.267	4.5101	-0.0356	N	-0.461	4.443	0.342
C	0.5	3.2849	0.5152	C	-0.003	3.1835	0.591
C	1.6775	3.1958	1.4332	C	1.3619	3.0937	1.196
H	-5.2673	-2.8689	-1.0352	H	-1.7562	-3.6901	-1.6237
H	-4.1152	-3.2789	-2.366	H	-2.1923	-4.2932	0.027
H	-4.4236	-4.4218	-1.0533	H	-3.003	-4.9204	-1.4069
H	-4.4689	-0.9441	-2.1228	H	-5.0732	-1.1736	-1.6246
H	-3.774	1.4001	-2.2946	H	-4.6527	1.2669	-1.507
H	-0.8442	-0.3025	3.8789	H	-0.2769	-0.9323	3.4841
H	-2.1785	-0.139	2.721	H	-1.8466	-0.7972	2.6679
H	-2.3192	-2.4715	2.8028	H	-1.8176	-3.089	2.4732
H	2.8393	0.0046	2.6792	H	0.4585	-0.4543	-1.855
H	5.0166	-0.7105	1.7642	H	2.4471	-0.7839	-3.2629
H	5.2837	-1.7971	-1.5801	H	5.676	-0.831	-1.8403
H	2.5747	-2.0682	-4.1324	H	6.6142	-0.4083	1.7435
H	1.4641	-2.3939	-2.7962	H	5.1924	0.6304	1.9034
H	1.797	-0.6987	-3.3296	H	5.0665	-1.1539	2.1614
H	0.9774	-0.8151	-1.1287	H	2.9819	-0.1818	1.6396
H	-2.4369	3.9119	-1.9788	H	-3.4855	3.833	-1.0472
H	-0.8528	5.7061	-1.2772	H	-1.9378	5.6742	-0.3866
H	1.3749	2.8267	2.4162	H	1.326	2.567	2.1529
H	2.44	2.5406	1.0064	H	2.0455	2.5827	0.5143
H	2.1313	4.1821	1.5779	H	1.7686	4.0929	1.385
	B-c7				**B-c8**		
Atom	X	Y	Z	Atom	X	Y	Z
C	-4.6369	-3.6769	-0.9199	C	-4.2849	-3.0959	-0.2652
O	-3.4771	-3.1354	-0.3035	O	-3.1666	-2.837	-1.1135
C	-3.2765	-1.7851	-0.4213	C	-2.8195	-1.5137	-1.0406
C	-4.1949	-0.8785	-0.9675	C	-3.4529	-0.5968	-1.8844
C	-3.9134	0.5021	-1.0402	C	-3.103	0.7656	-1.8613
C	-2.6779	0.9778	-0.5628	C	-2.0772	1.1937	-0.9941
C	-1.8032	0.0554	-0.0347	C	-1.4693	0.2446	-0.2006
C	-2.0587	-1.3062	0.0739	C	-1.8065	-1.1024	-0.1765

O	-1.1105	-2.1431	0.6144	O	-1.1357	-1.975	0.6441
C	-0.1642	-1.4558	1.4765	C	-0.458	-1.3145	1.7558
H	0.6707	-2.1564	1.6134	H	0.2443	-2.0676	2.137
C	-0.795	-1.2649	2.8679	C	-1.489	-1.0661	2.8731
O	0.1688	-0.7726	3.7946	O	-2.0573	-2.3055	3.2983
C	0.4237	-0.1163	0.905	C	0.3351	-0.0109	1.3934
H	0.8218	0.4738	1.7372	H	0.479	0.5628	2.316
C	1.5791	-0.4019	-0.0535	C	1.7117	-0.3636	0.8348
C	1.3709	-0.6761	-1.4155	C	2.8208	-0.3792	1.7009
C	2.449	-0.9504	-2.2562	C	4.0873	-0.7172	1.2273
C	3.735	-0.9606	-1.7354	C	4.2463	-1.0506	-0.1101
O	4.774	-1.233	-2.5836	O	5.5	-1.3793	-0.5488
C	3.979	-0.7064	-0.3827	C	3.1652	-1.0605	-0.996
O	5.2982	-0.7572	-0.0124	O	3.4741	-1.419	-2.2831
C	5.5887	-0.4974	1.356	C	2.395	-1.4535	-3.2113
C	2.8964	-0.4333	0.455	C	1.8991	-0.7199	-0.5164
N	-0.6554	0.7019	0.3401	N	-0.4744	0.8472	0.5225
C	-0.7576	2.0558	0.1144	C	-0.4332	2.1993	0.2708
C	-2.0295	2.2497	-0.461	C	-1.4387	2.4378	-0.688
C	-2.4243	3.5472	-0.8151	C	-1.6345	3.744	-1.1577
C	-1.5233	4.5616	-0.5637	C	-0.8165	4.7228	-0.6323
N	-0.3083	4.382	-0.0118	N	0.1446	4.5	0.2839
C	0.1177	3.1344	0.3376	C	0.3741	3.2431	0.7593
C	1.4923	3.0521	0.9211	C	1.4833	3.1147	1.7543
H	-5.5468	-3.3137	-0.4313	H	-4.0718	-2.8204	0.7736
H	-4.6524	-3.4648	-1.9942	H	-5.1789	-2.573	-0.6218
H	-4.605	-4.7637	-0.7961	H	-4.4868	-4.1708	-0.2956
H	-5.1565	-1.2088	-1.348	H	-4.2239	-0.939	-2.5701
H	-4.6425	1.1851	-1.4662	H	-3.6071	1.4701	-2.5161
H	-1.6375	-0.5663	2.8397	H	-1.0187	-0.6017	3.7451
H	-1.1786	-2.2225	3.2375	H	-2.3134	-0.4272	2.5428
H	-0.2732	-0.7354	4.6626	H	-2.2859	-2.7969	2.4858
H	0.3695	-0.6841	-1.8413	H	2.7113	-0.1255	2.7536
H	2.2864	-1.1581	-3.3097	H	4.9451	-0.7237	1.8934
H	5.5729	-1.1913	-2.0232	H	5.3886	-1.5761	-1.4996
H	6.6727	-0.5695	1.4865	H	2.7999	-1.7564	-4.1817
H	5.2859	0.5165	1.6381	H	1.6451	-2.1954	-2.9173
H	5.1244	-1.2458	2.0066	H	1.9469	-0.4617	-3.3325
H	3.0477	-0.2401	1.5132	H	1.0423	-0.7308	-1.1825
H	-3.3886	3.7519	-1.2631	H	-2.3905	3.982	-1.8956
H	-1.7655	5.5913	-0.8117	H	-0.9157	5.7572	-0.9496
H	1.4619	2.6064	1.9186	H	1.1192	2.6696	2.6836
H	2.1459	2.4665	0.2707	H	2.2925	2.5081	1.3417
H	1.9318	4.0504	1.0197	H	1.8985	4.0977	2.0009

B-c9			
Atom	X	Y	Z
C	-4.7585	-3.2877	-1.2586
O	-3.5692	-2.8596	-0.6093
C	-3.297	-1.5168	-0.6217
C	-4.1537	-0.5227	-1.1119
C	-3.7994	0.8425	-1.0681
C	-2.5535	1.2132	-0.5282
C	-1.7393	0.2068	-0.0604
C	-2.0672	-1.1433	-0.07
O	-1.1786	-2.0704	0.4228
C	-0.2241	-1.5044	1.367
H	0.5534	-2.2733	1.4684
C	-0.9077	-1.385	2.7425
O	-1.3628	-2.6675	3.1744
C	0.4425	-0.1553	0.9271
H	0.8309	0.3357	1.8269
C	1.6186	-0.4191	-0.0101
C	1.4387	-0.614	-1.39
C	2.5298	-0.8721	-2.2186
C	3.8014	-0.9452	-1.6689
O	4.8535	-1.1998	-2.5061
C	4.0174	-0.7705	-0.2991
O	5.3253	-0.8761	0.098
C	5.5926	-0.6988	1.4839
C	2.9214	-0.5134	0.527
N	-0.5725	0.76	0.3957
C	-0.5989	2.1309	0.2765
C	-1.845	2.4368	-0.3076
C	-2.1661	3.7775	-0.5613
C	-1.2221	4.7202	-0.2095
N	-0.0305	4.4331	0.3482
C	0.3244	3.1415	0.6019
C	1.683	2.9436	1.1948
H	-5.6462	-2.9046	-0.7449
H	-4.7585	-3.0027	-2.316
H	-4.7918	-4.3803	-1.2089
H	-5.1222	-0.77	-1.5357
H	-4.4828	1.5948	-1.4512
H	-0.2069	-1.0114	3.4952
H	-1.7767	-0.7207	2.7208
H	-1.8839	-3.0348	2.4323
H	0.4488	-0.5717	-1.8406
H	2.3886	-1.0184	-3.2856

H	5.6402	-1.2114	-1.9274
H	6.6712	-0.8076	1.6327
H	5.3102	0.3062	1.8146
H	5.0942	-1.468	2.083
H	3.0562	-0.3796	1.5959
H	-3.1081	4.0675	-1.0097
H	-1.4068	5.7778	-0.3761
H	1.6173	2.3998	2.1404
H	2.3247	2.4019	0.4963
H	2.1593	3.9077	1.4026

References

[1] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al., *Gaussian 09*, Wallingford CT, 2010.

[2] T. Bruhn, Y. Hemberger, A. Schaumlöffel, et al., *SpecDis*, version 1.51; Germany, 2010.

3 NMR, HRESIMS, UV, and ECD spectra

Spectra of pheharmine A

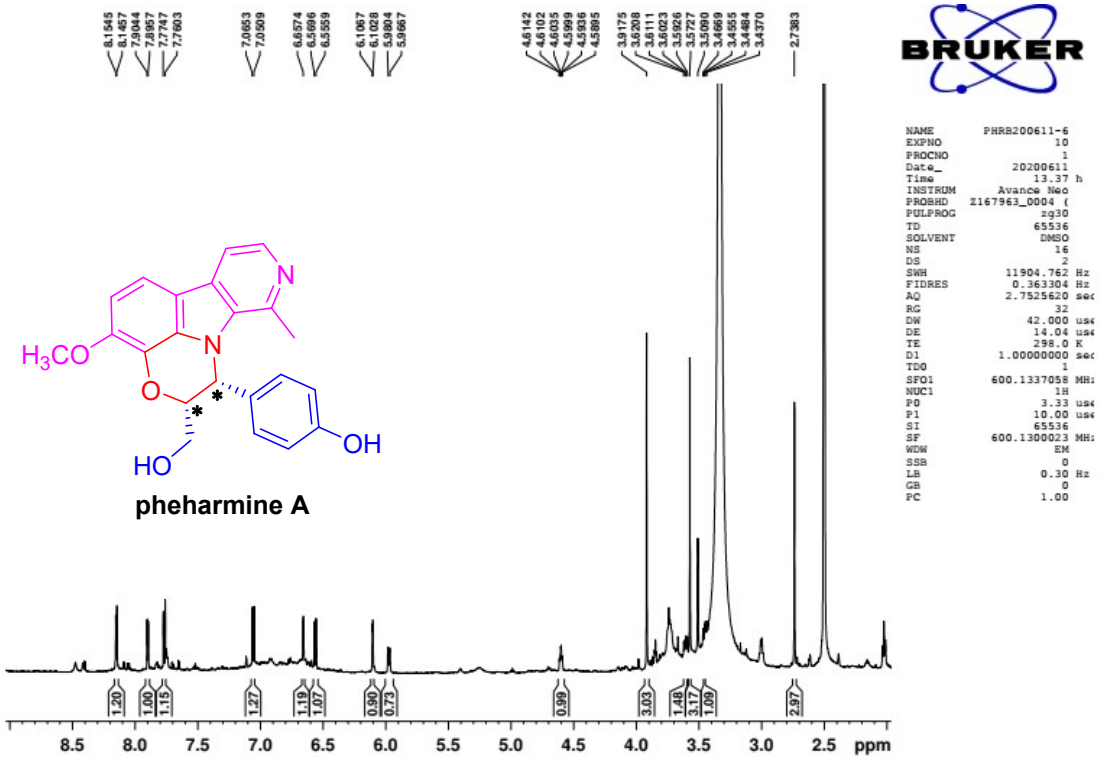


Figure S2 ^{1}H NMR spectrum (600 MHz) of pheharmine A in DMSO-d_6

Figure S3 ^{13}C NMR (150 MHz) spectrum of pheharmine A in DMSO-d_6

Figure S4 HSQC spectrum of pheharmine A in DMSO-d_6

Figure S5 HMBC spectrum of pheharmine A in DMSO-d_6

Figure S6 ^{1}H-^{1}H COSY spectrum of pheharmine A in DMSO-d_6

Figure S7 NOESY spectrum of pheharmine A in DMSO-d_6

Figure S8 HRESIMS spectrum of pheharmine A

Figure S9 UV spectrum of pheharmine A in MeOH

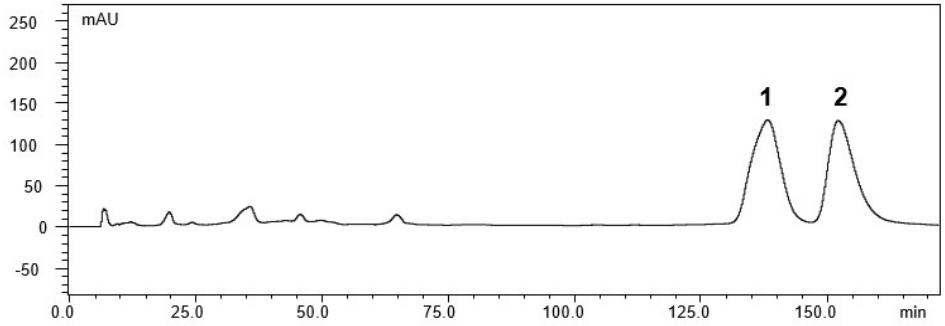


Figure S10 Chiral HPLC separation profile of **1**/**2**

Figure S11 Experimental ECD spectrum of (+)-pheharmine A (**1**) in MeOH

Figure S12 Experimental ECD spectrum of (−)-pheharmine A (**2**) in MeOH

Spectra of pheharmine B

Figure S13 ^{1}H NMR spectrum (600 MHz) of pheharmine B in DMSO-d_6

Figure S14 ^{13}C NMR spectrum (150 MHz) of pheharmine B in DMSO-d_6

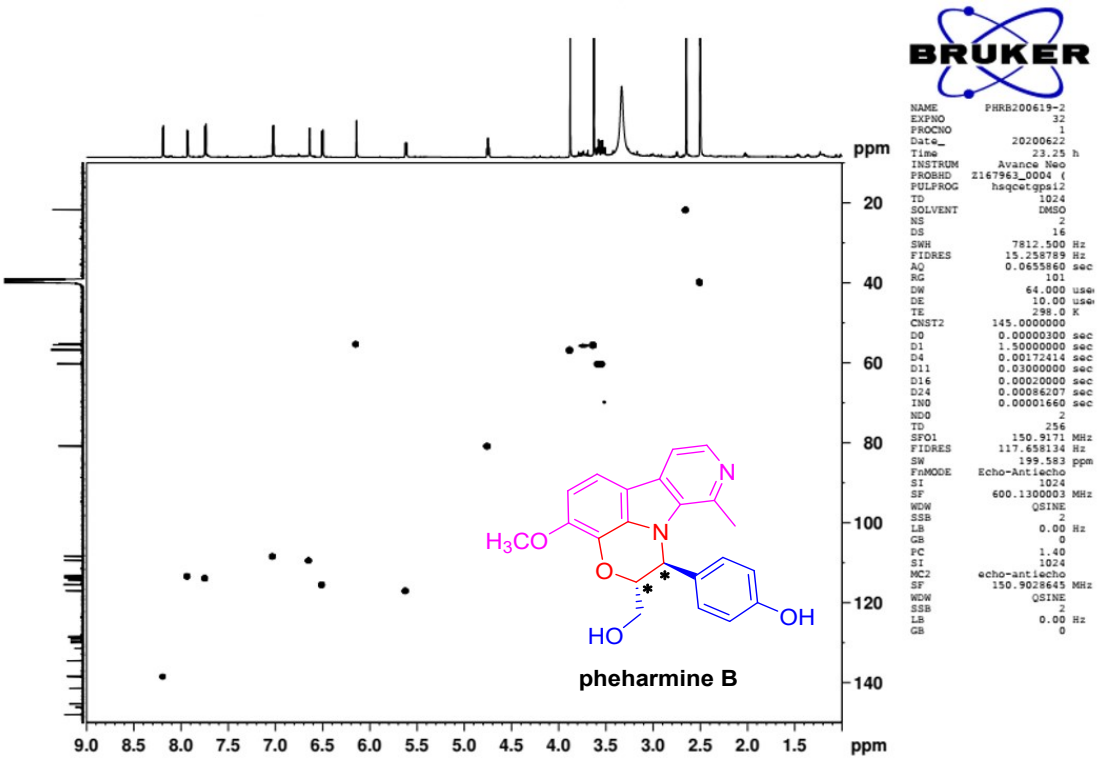


Figure S15 HSQC spectrum of pheharmine B in DMSO-d_6

Figure S16 HMBC spectrum of pheharmine B in DMSO-d_6

Figure S17 ^{1}H-^{1}H COSY spectrum of pheharmine B in DMSO-d_6

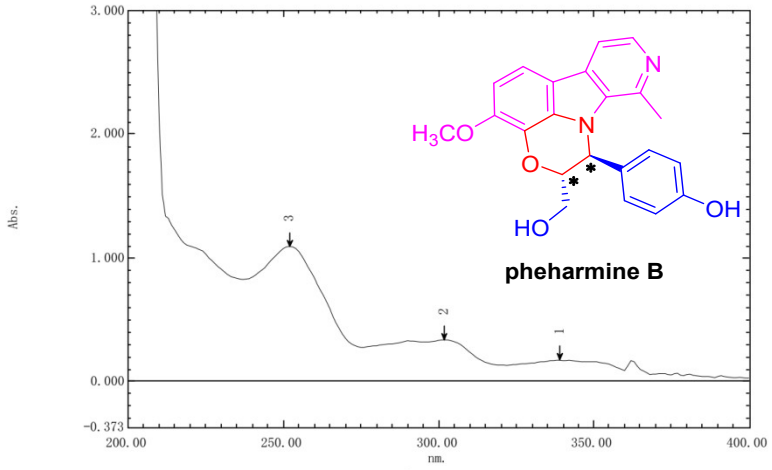
Figure S18 NOESY spectrum of pheharmine B in DMSO-d_6

Figure S19 HRESIMS spectrum of pheharmine B

Spectrum Peak Pick Report

FIELD FIELD TEXT

Data Set: 没有



测定属性
波长范围（nm.）： 200.00到400.00
扫描速度： 中速
采样间隔： 1.0
自动采样间隔: 停用
扫描模式： 单一的

试样准备属性
重量:
体积 :
稀释:
光程长:
附加信息:

仪器属性
仪器类型： UV-1700
测定方式： 吸收值
狭缝宽： 1.0 nm
光源改变波长: 360.0 nm
S/R 转换： 标准

附件属性
附件： 无

No.	P/V	Wavelength	Abs.	描述
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2	↑	302.00	.333	
3	↑	252.00	1.091	
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5	↓	275.00	.272	
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FIELD TEXT

Figure S20 UV spectrum of pheharmine B in MeOH

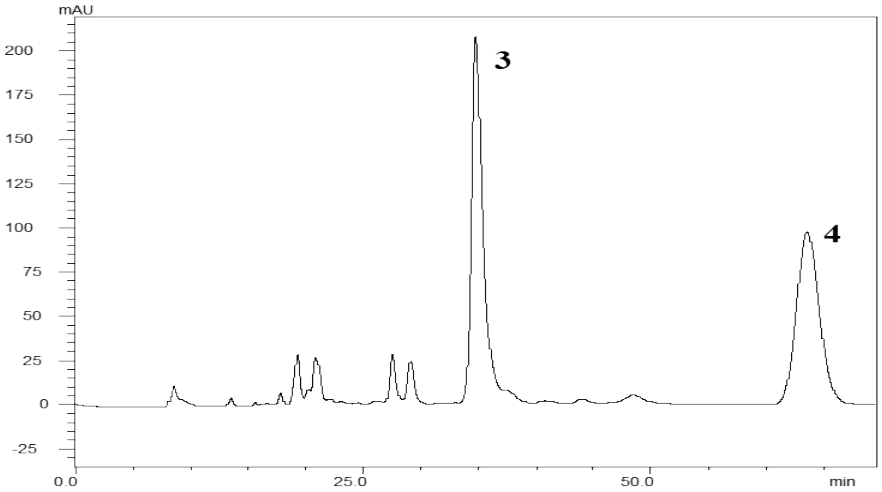

Figure S21 Chiral HPLC separation profile of **3**/**4**

Figure S22 Experimental ECD spectrum of (−)-pheharmine B (**3**) in MeOH

Figure S23 Experimental ECD spectrum of (+)-pheharmine B (**4**) in MeOH