Supporting information

Rotational Energy Barrier Around the C1–C11 Single Bond in Lamellarins: a Study by Variable-Temperature NMR

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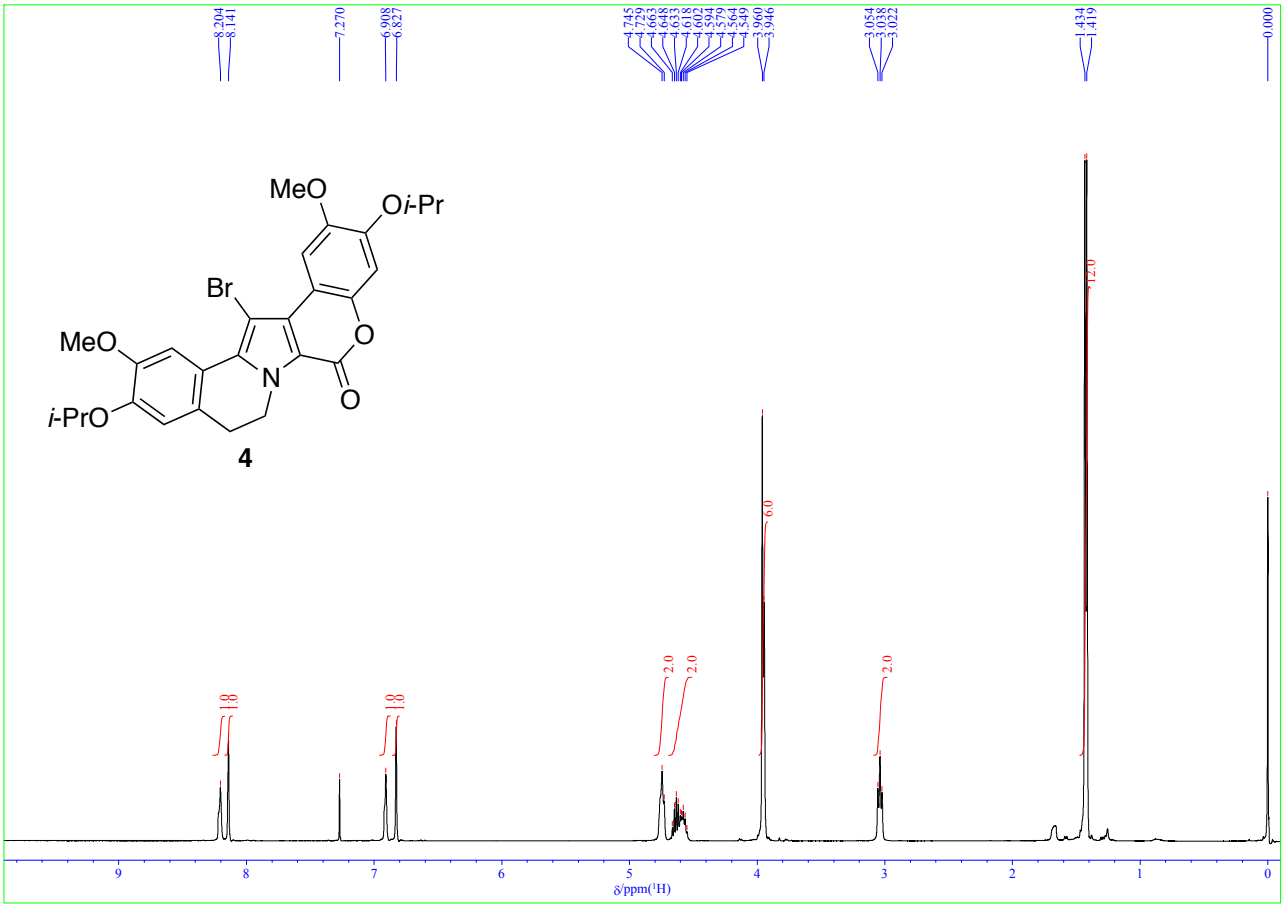

Figure S1. ^{1}H NMR spectrum of compound (**4**) (400 MHz, $CDCl_3$).

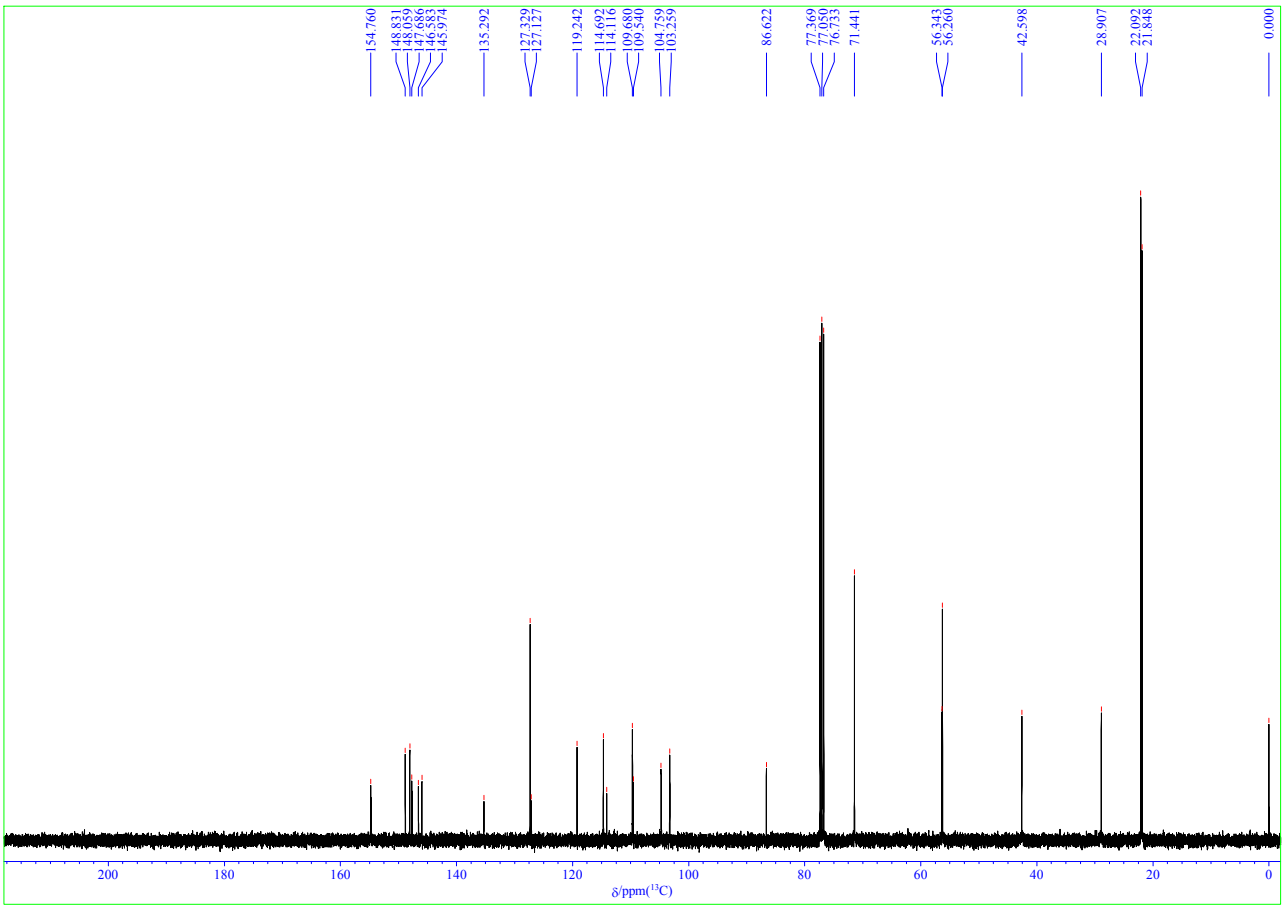

Figure S2. ^{13}C NMR spectrum of compound (**4**) (100 MHz, $CDCl_3$).

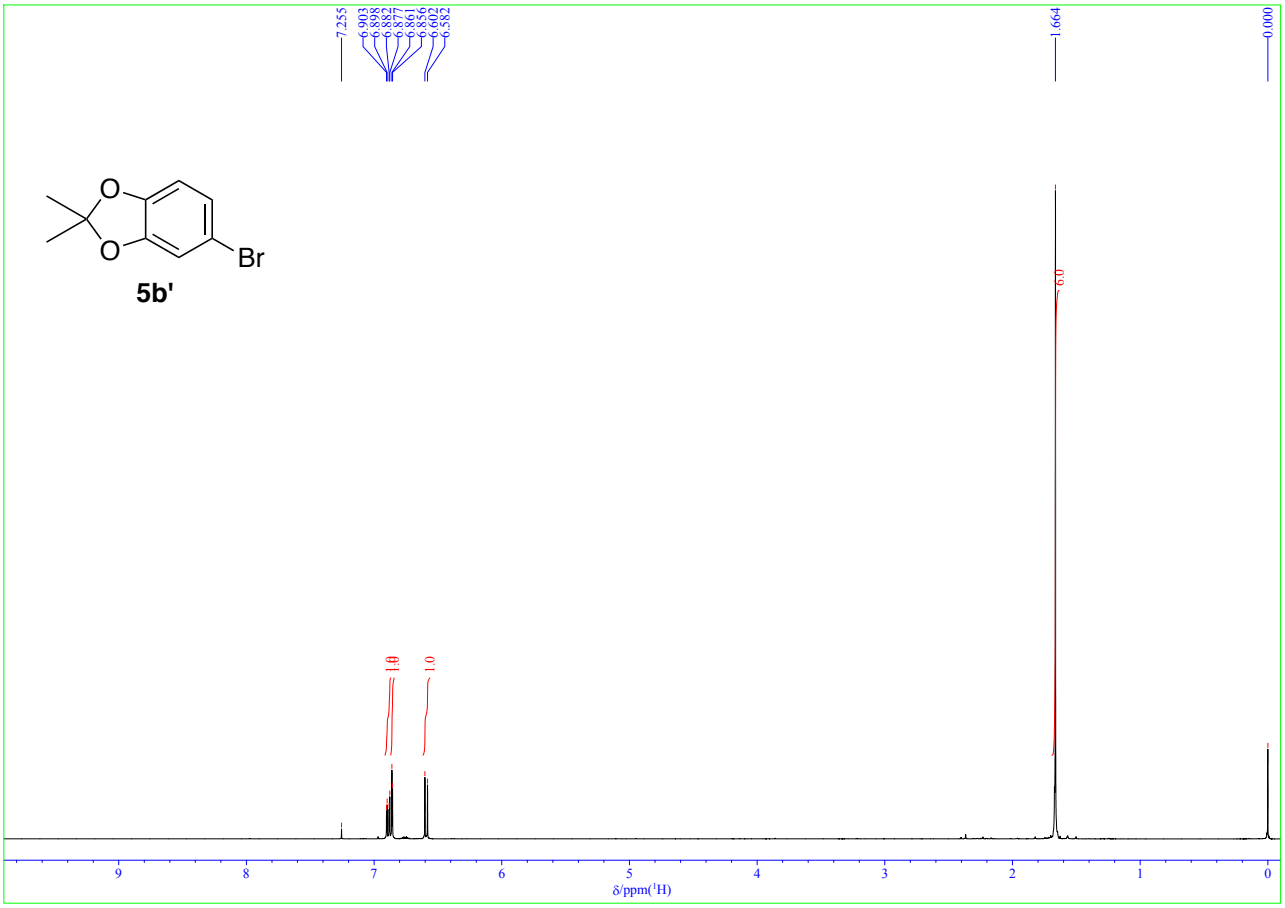

Figure S3. ^{1}H NMR spectrum of compound (**5b'**) (400 MHz, $CDCl_3$).

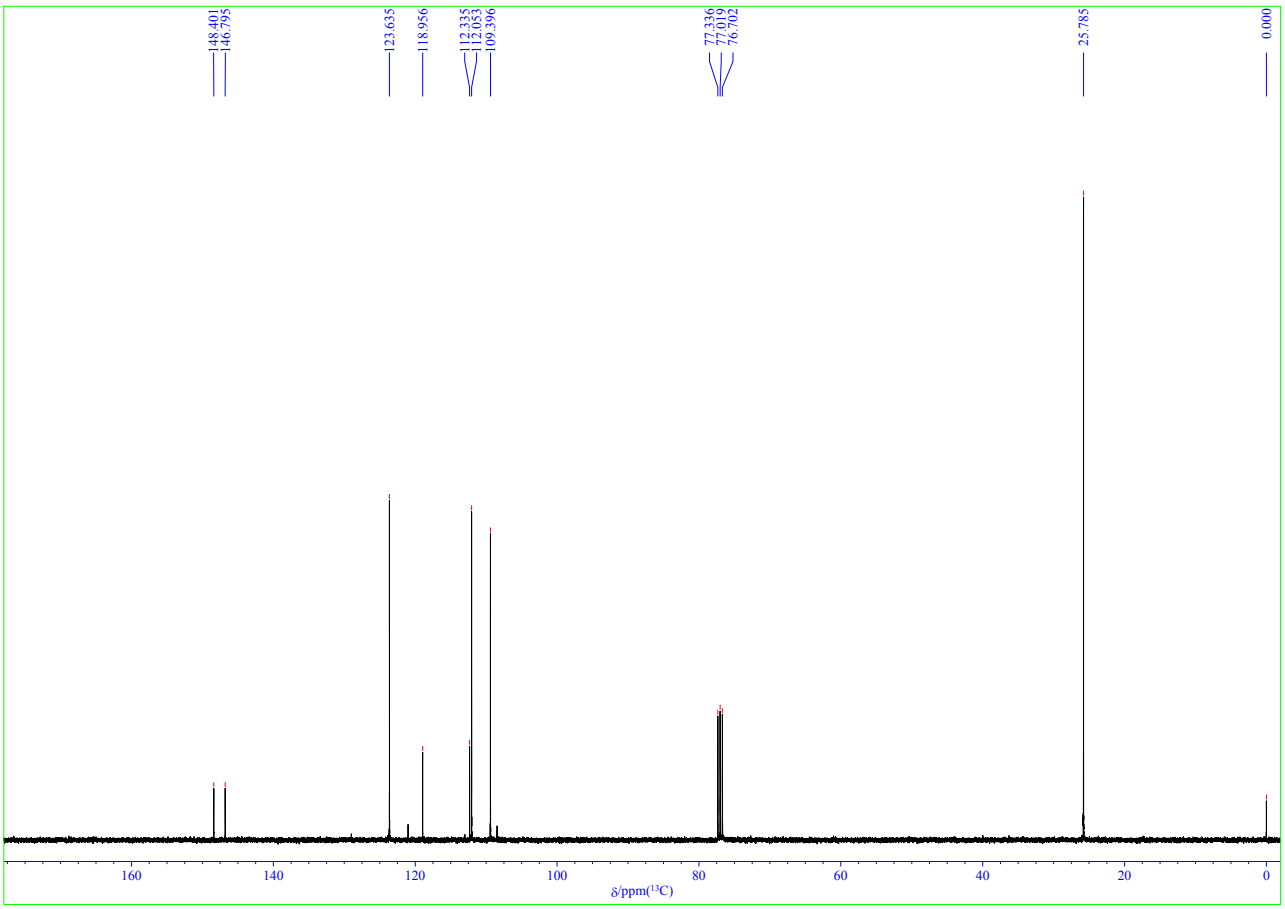

Figure S4. ^{13}C NMR spectrum of compound (**5b'**) (100 MHz, $CDCl_3$).

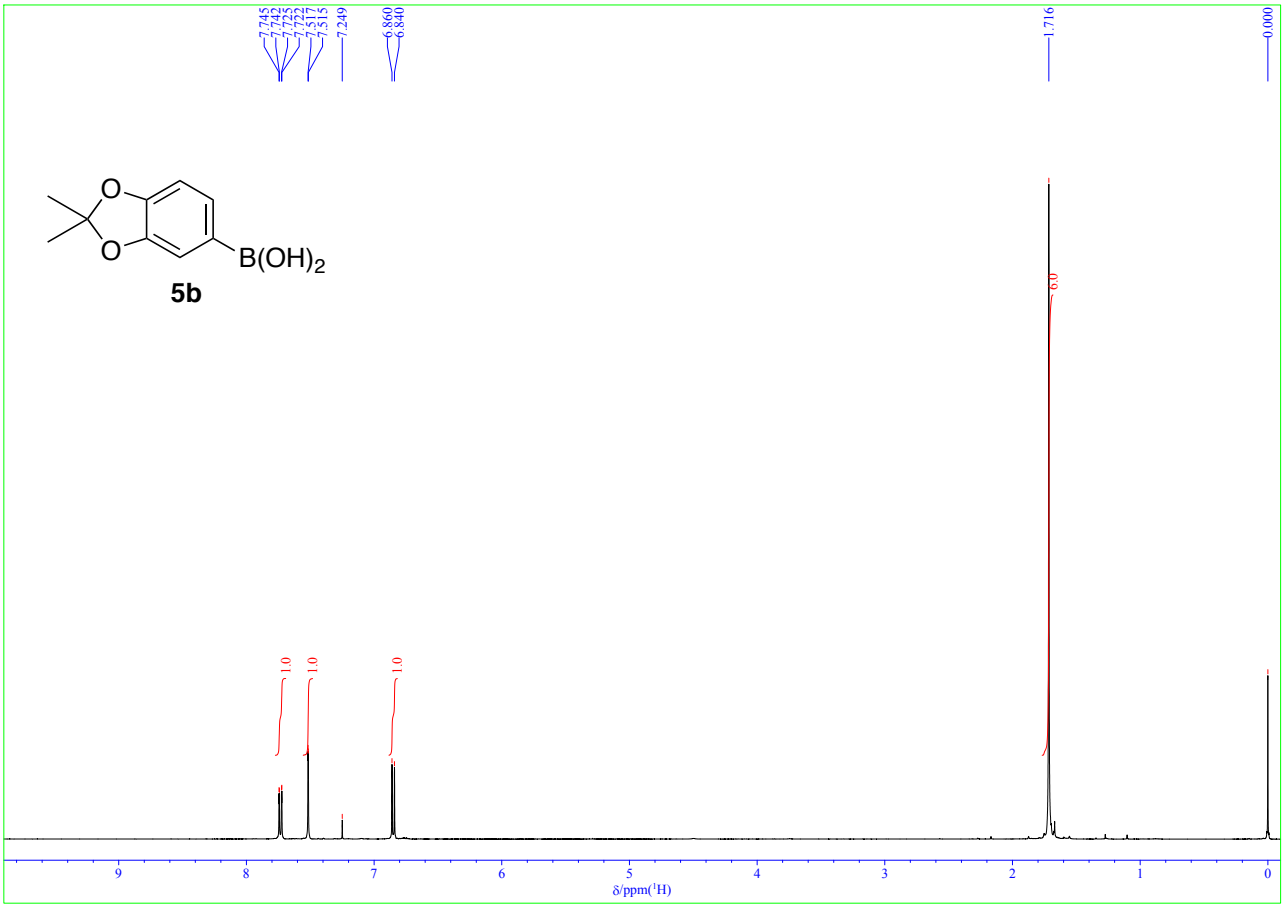

Figure S5. ^{1}H NMR spectrum of compound (**5b**) (400 MHz, $CDCl_3$).

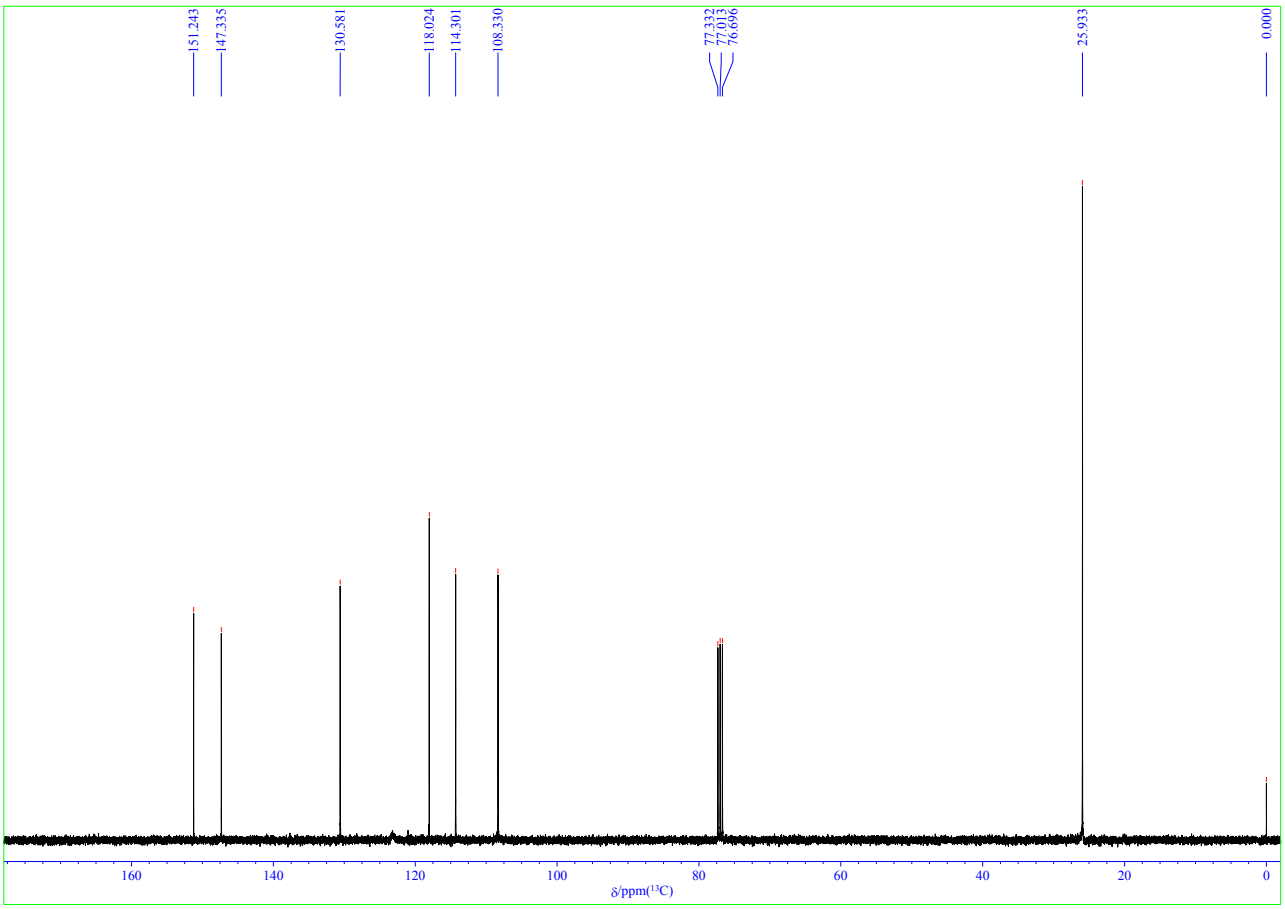

Figure S6. ^{13}C NMR spectrum of compound (**5b**) (100 MHz, $CDCl_3$).

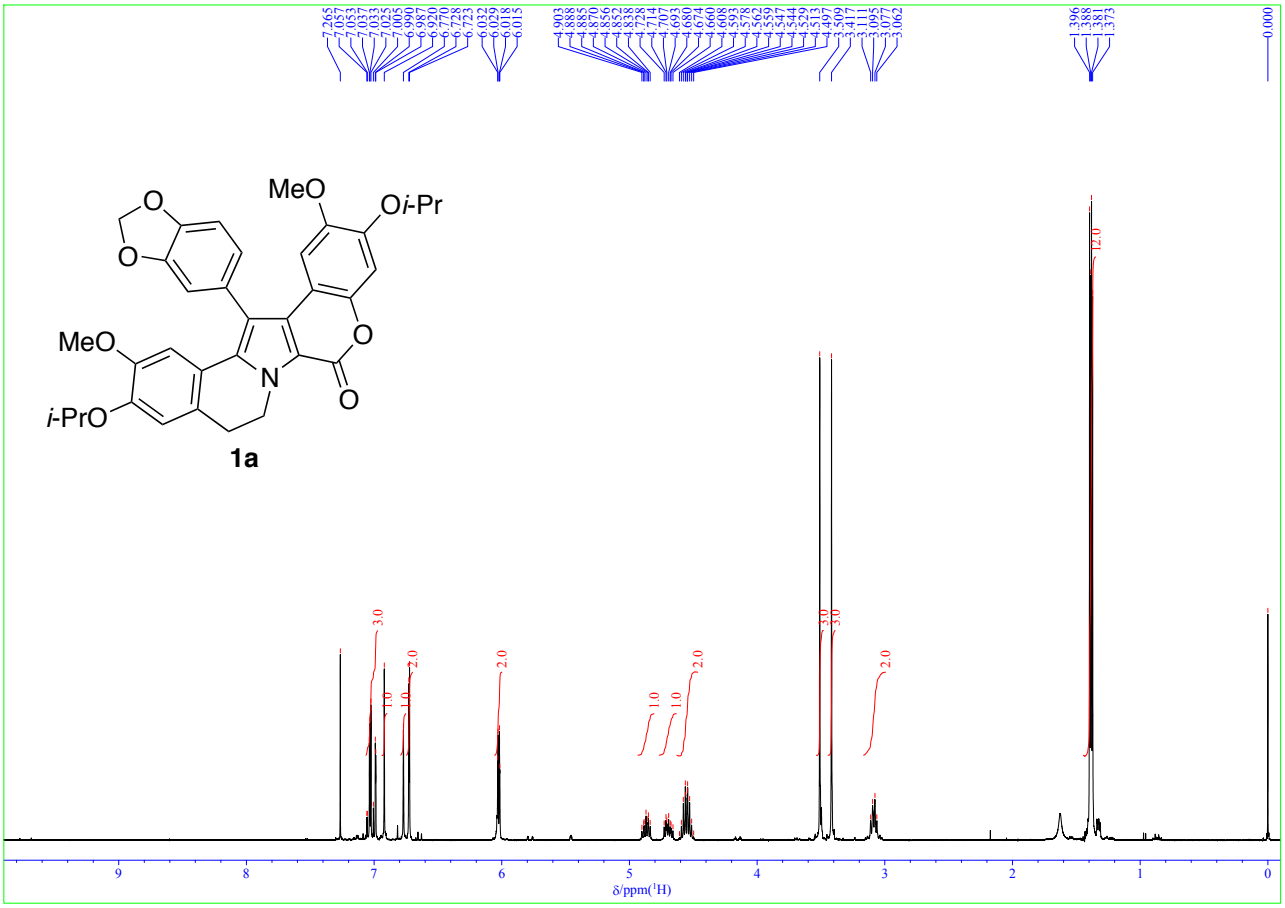

Figure S7. ^{1}H NMR spectrum of compound (**1a**) (400 MHz, $CDCl_3$).

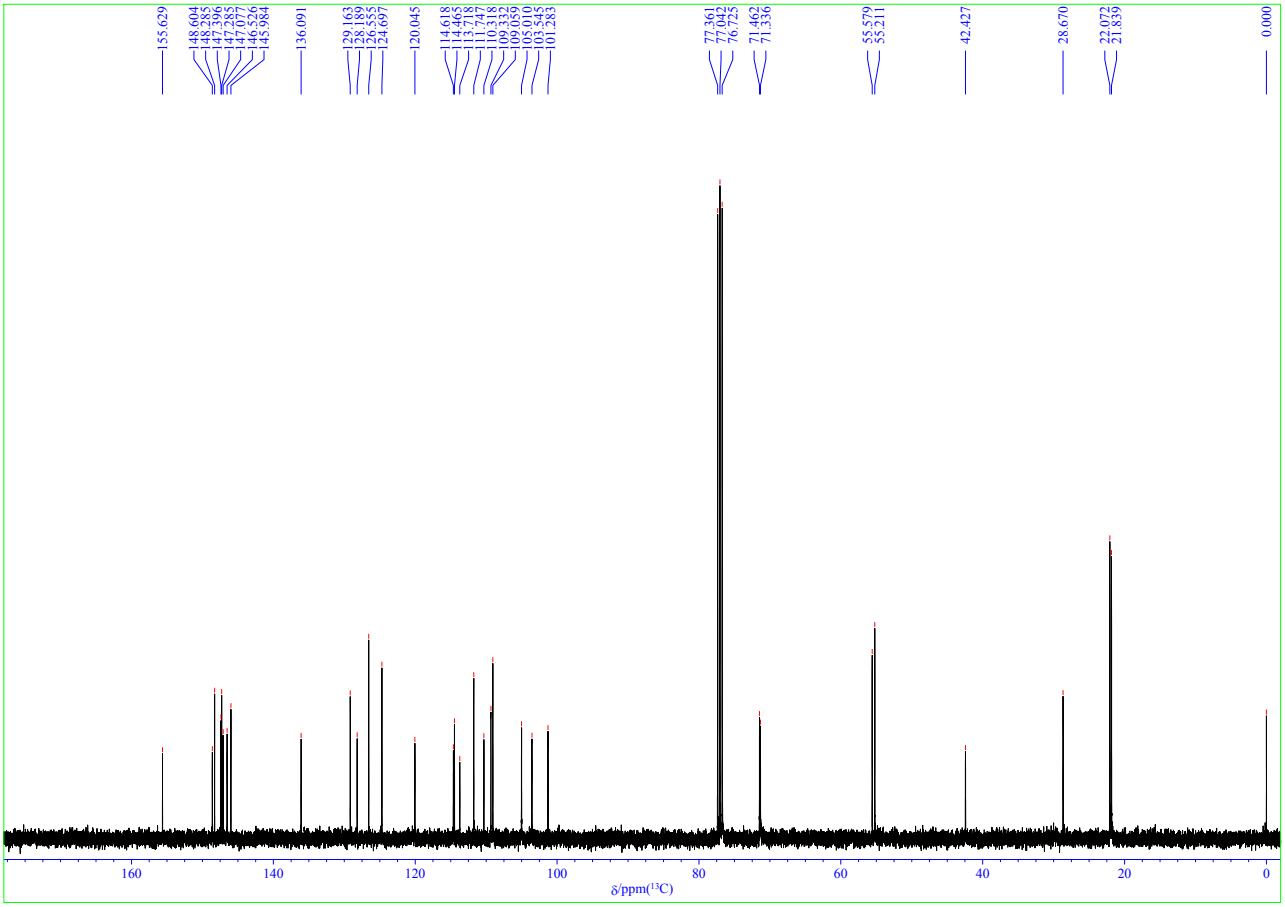

Figure S8. ^{13}C NMR spectrum of compound (**1a**) (100 MHz, $CDCl_3$).

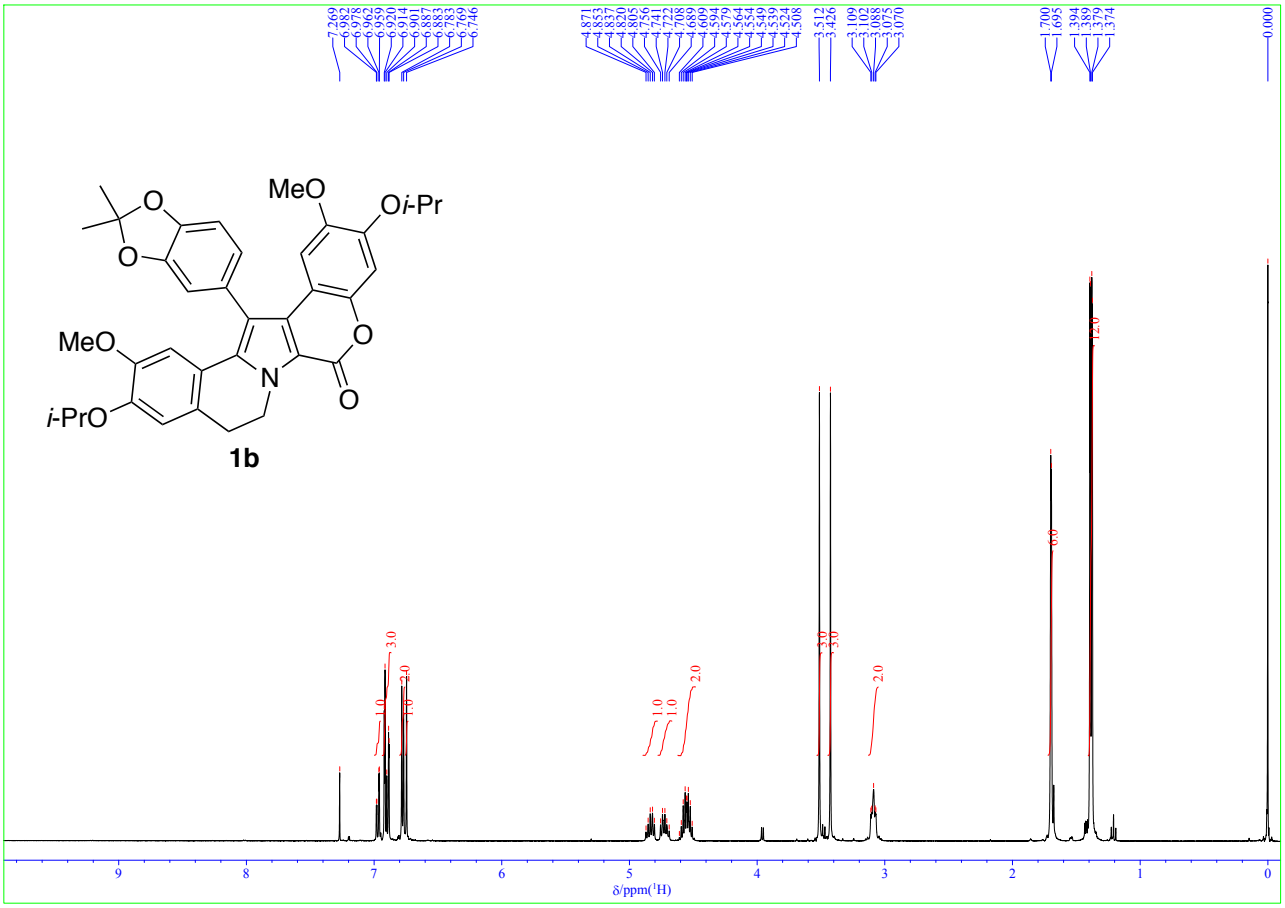

Figure S9. ^{1}H NMR spectrum of compound (**1b**) (400 MHz, $CDCl_3$).

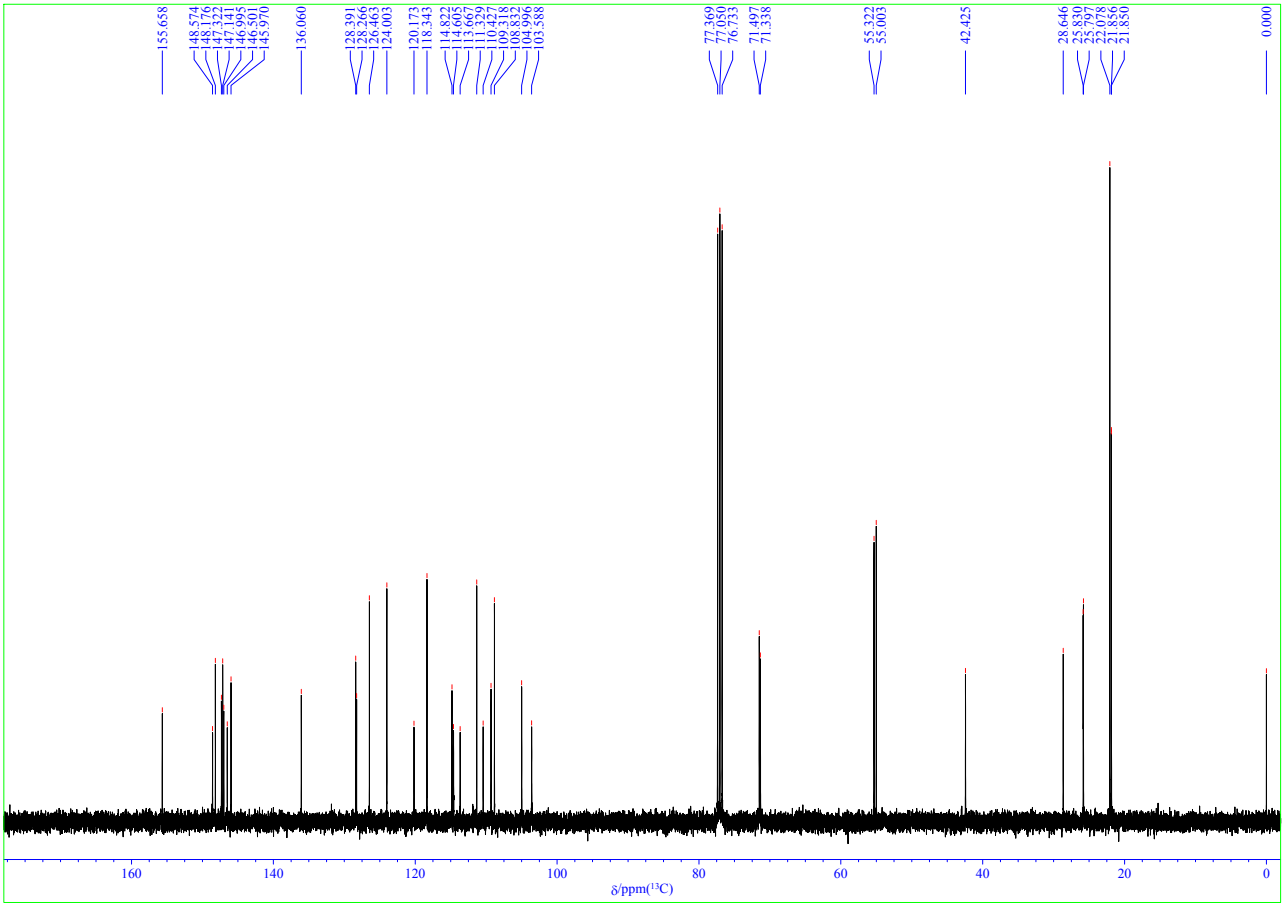

Figure S10. ^{13}C NMR spectrum of compound (**1b**) (100 MHz, $CDCl_3$).

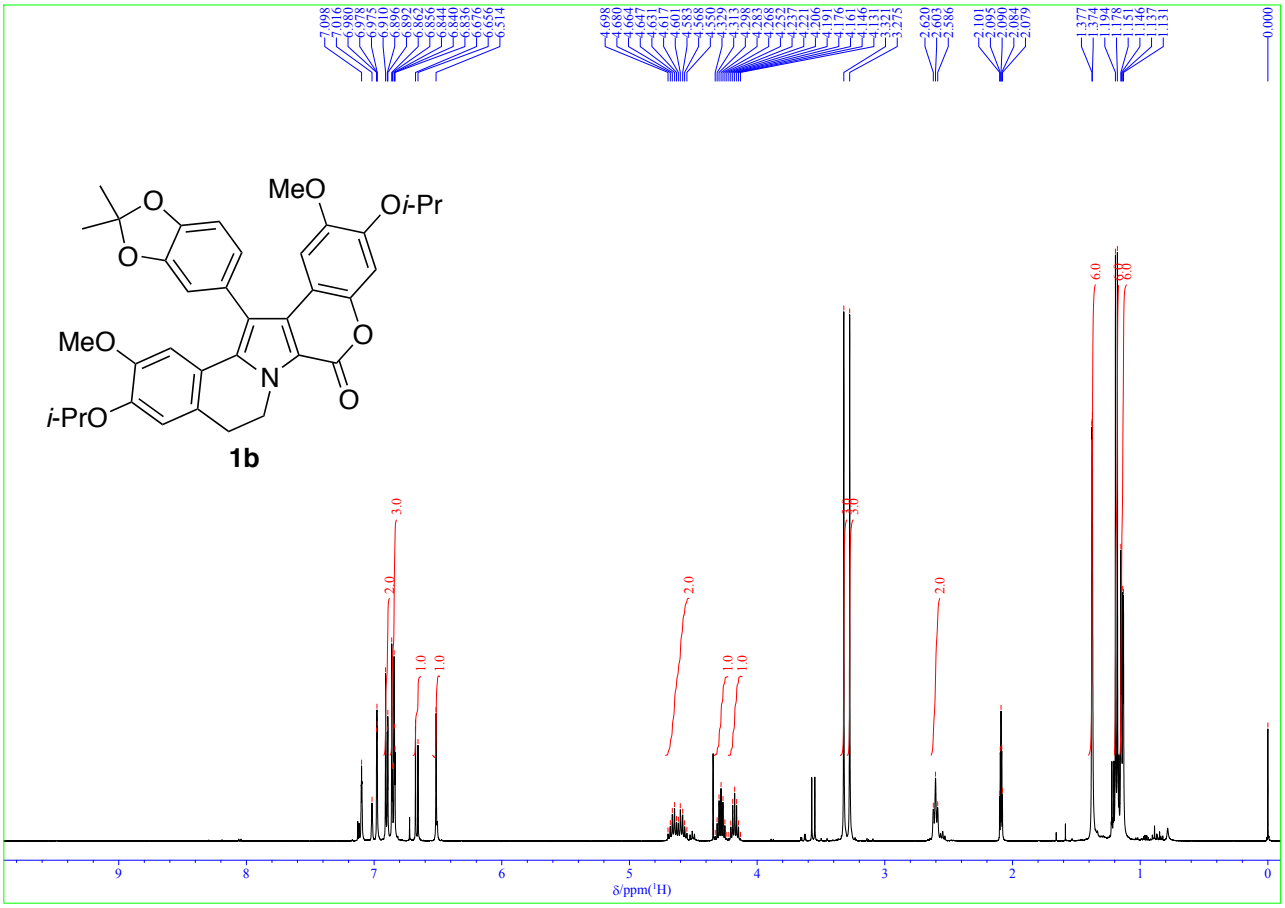

Figure S11. ^{1}H NMR spectrum of compound (**1b**) (400 MHz, toluene-d_8).

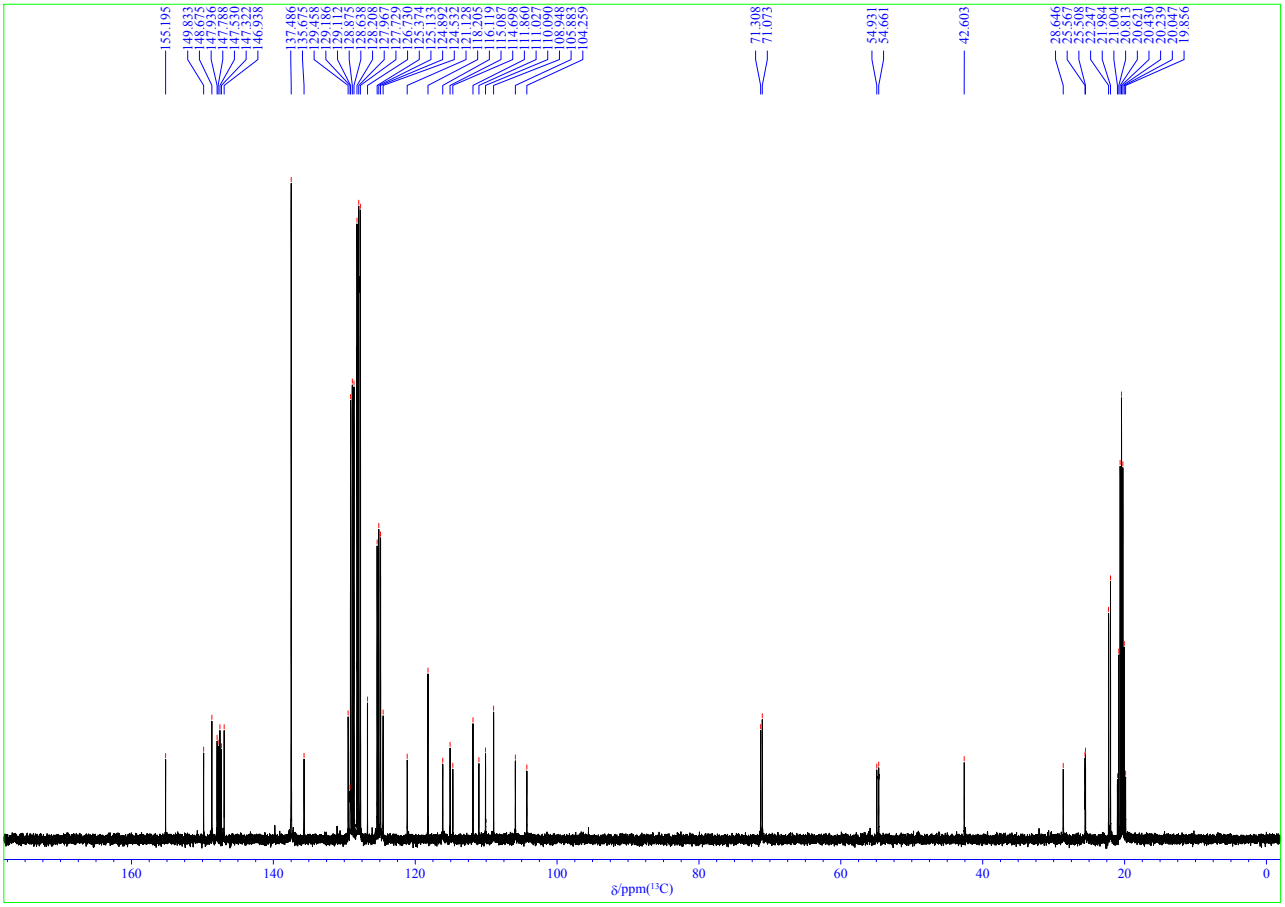

Figure S12. ^{13}C NMR spectrum of compound (**1b**) (100 MHz, toluene-d_8).

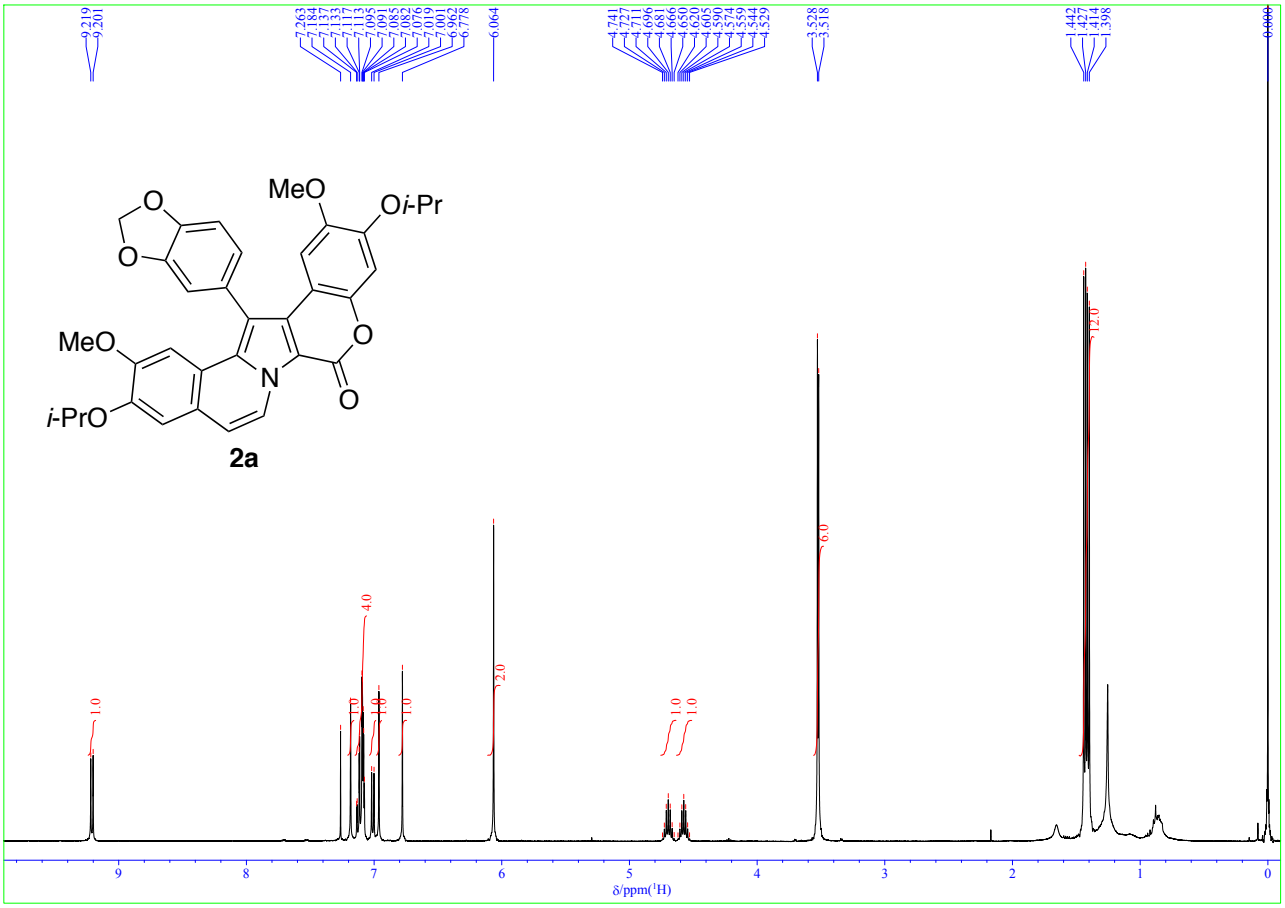

Figure S13. ^{1}H NMR spectrum of compound (**2a**) (400 MHz, $CDCl_3$).

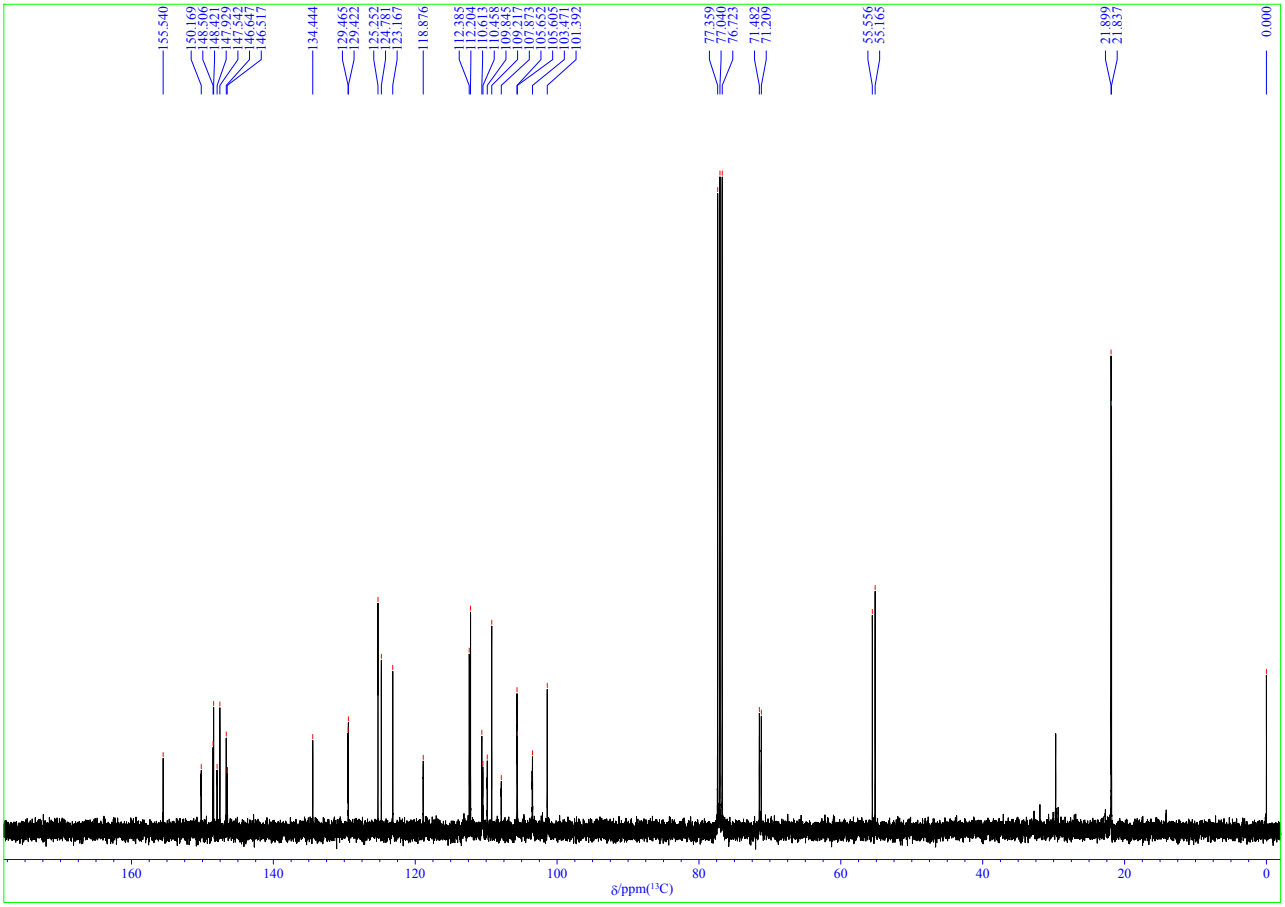

Figure S14. ^{13}C NMR spectrum of compound (**2a**) (100 MHz, $CDCl_3$).

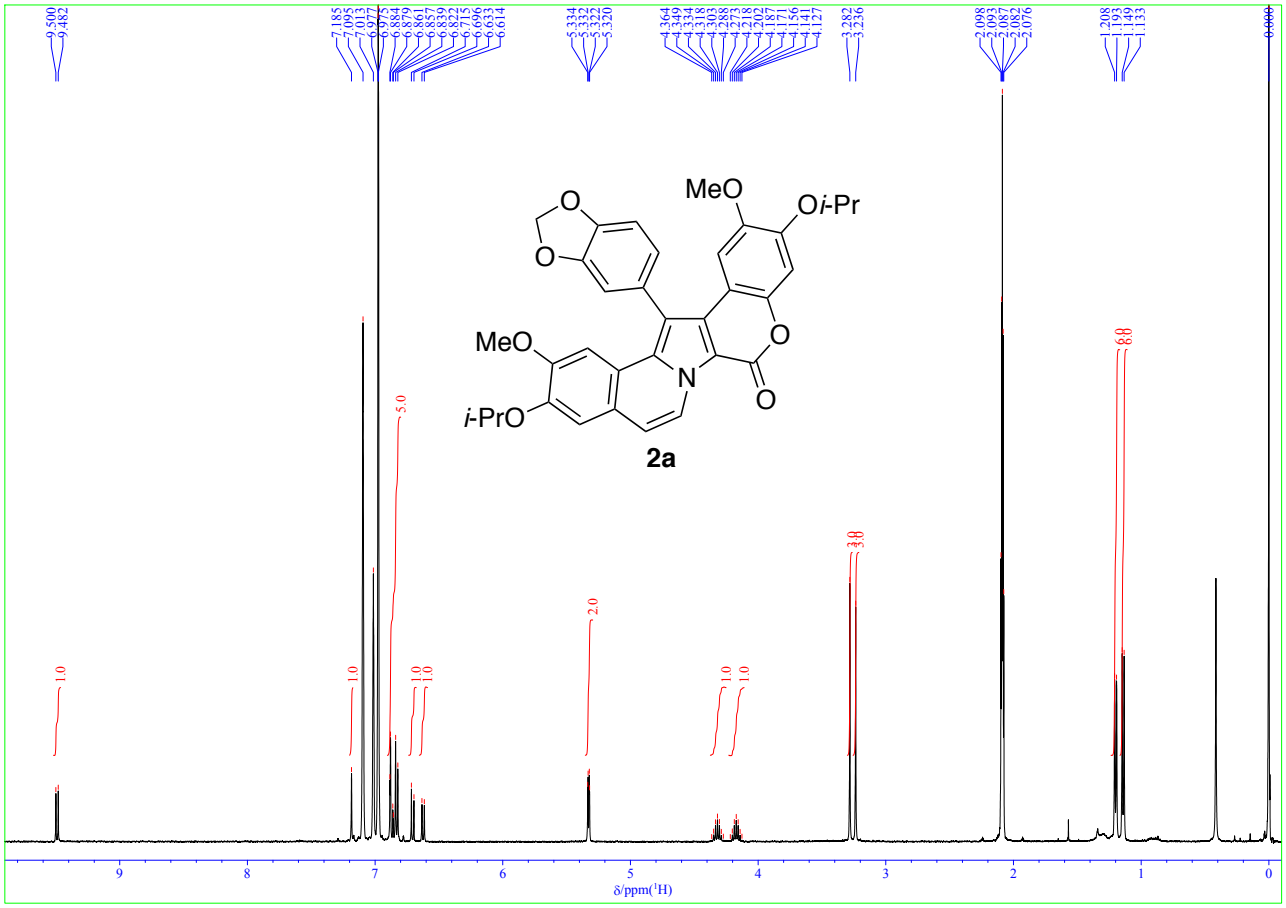

Figure S15. ^{1}H NMR spectrum of compound (**2a**) (400 MHz, toluene-d_8).

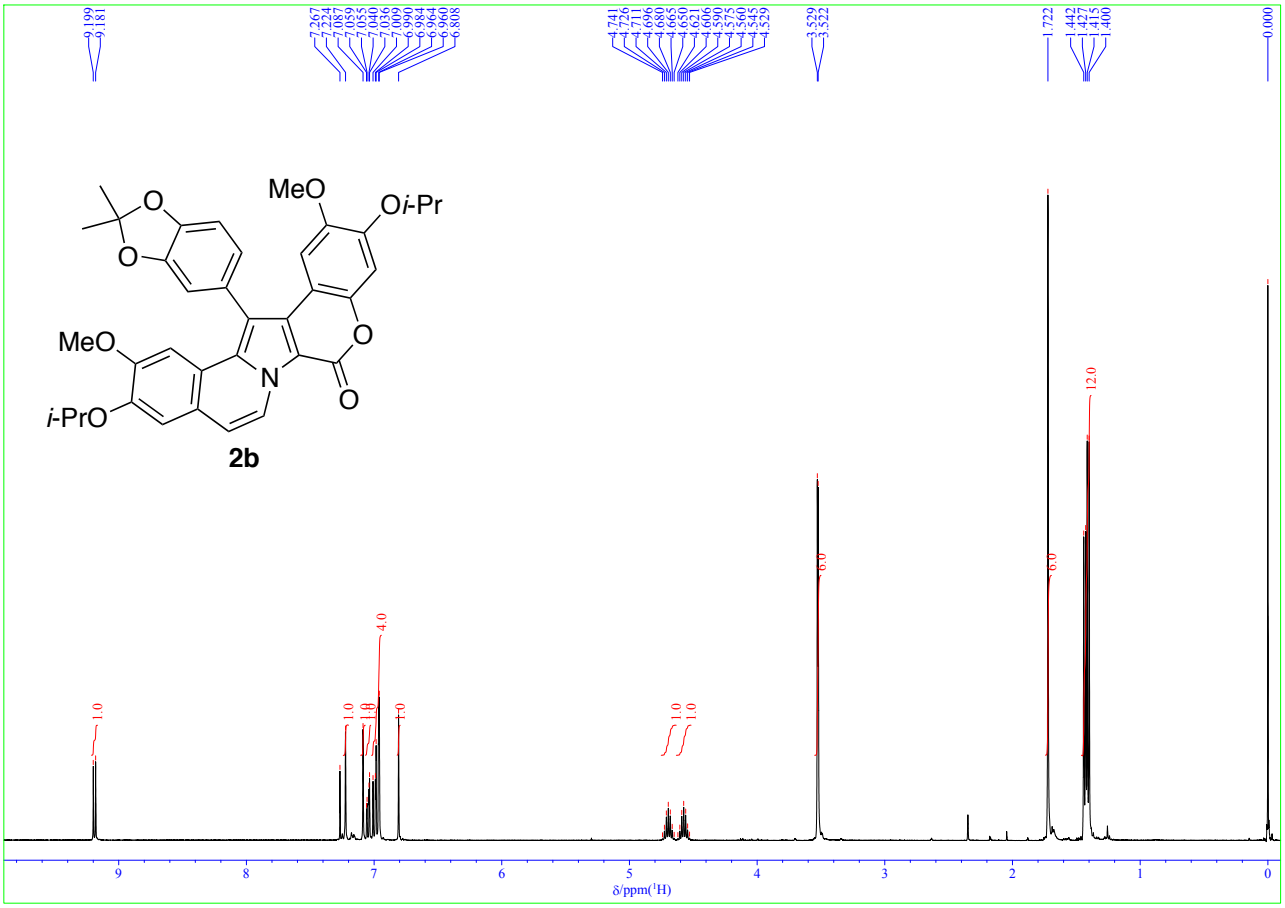

Figure S16. ^{1}H NMR spectrum of compound (**2b**) (400 MHz, $CDCl_3$).

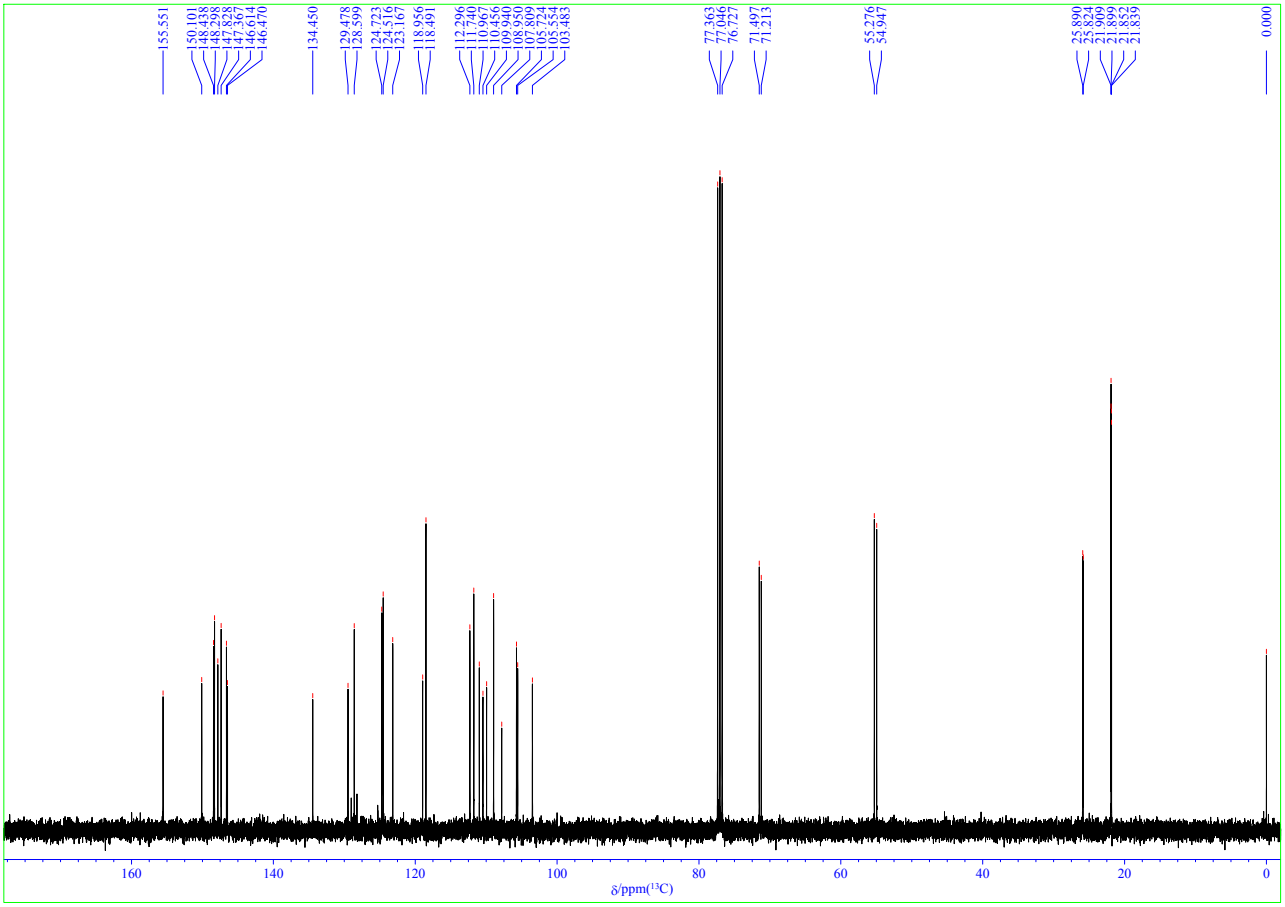

Figure S17. ^{13}C NMR spectrum of compound (**2b**) (100 MHz, $CDCl_3$).

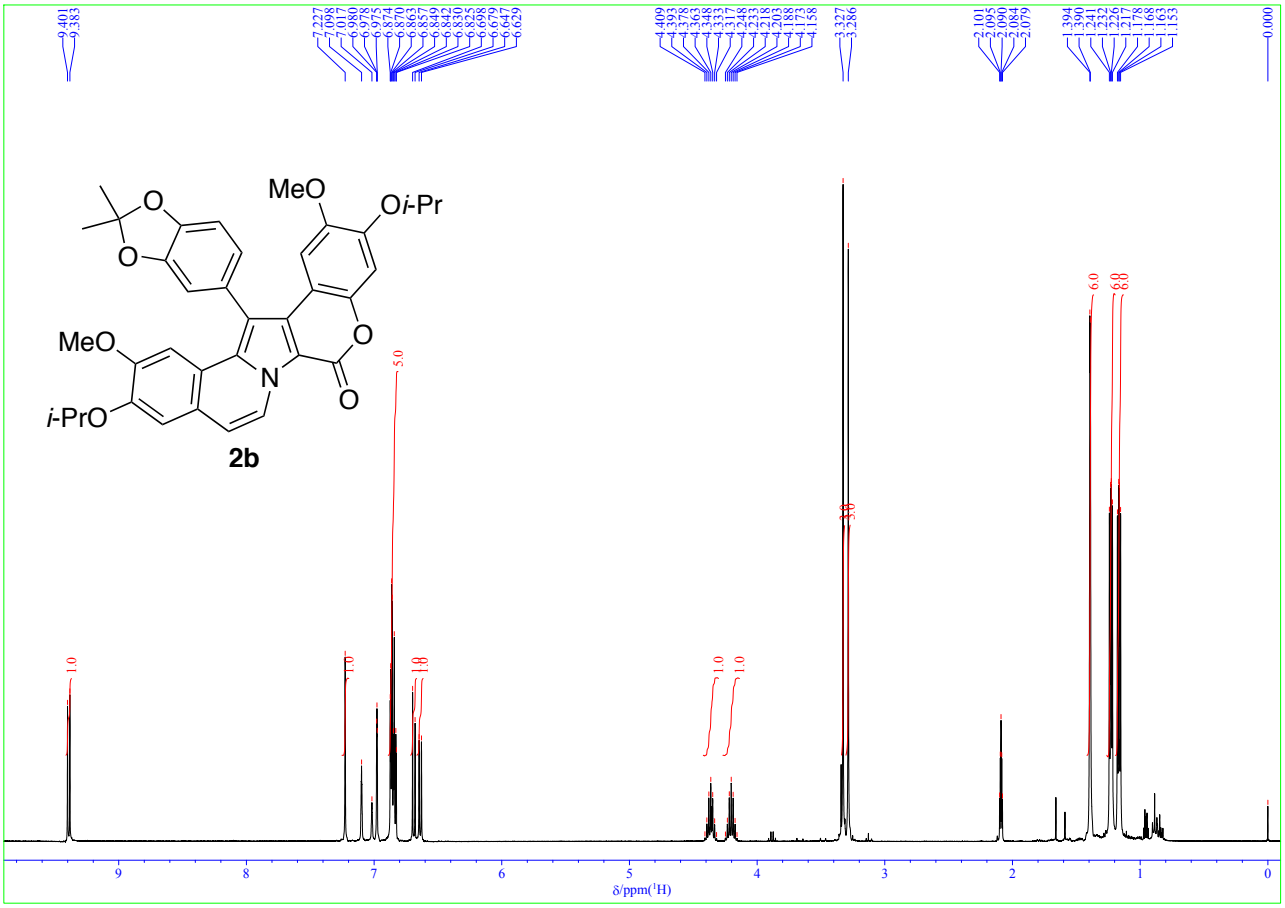

Figure S18. ^{1}H NMR spectrum of compound (**2b**) (400 MHz, toluene-d_8).

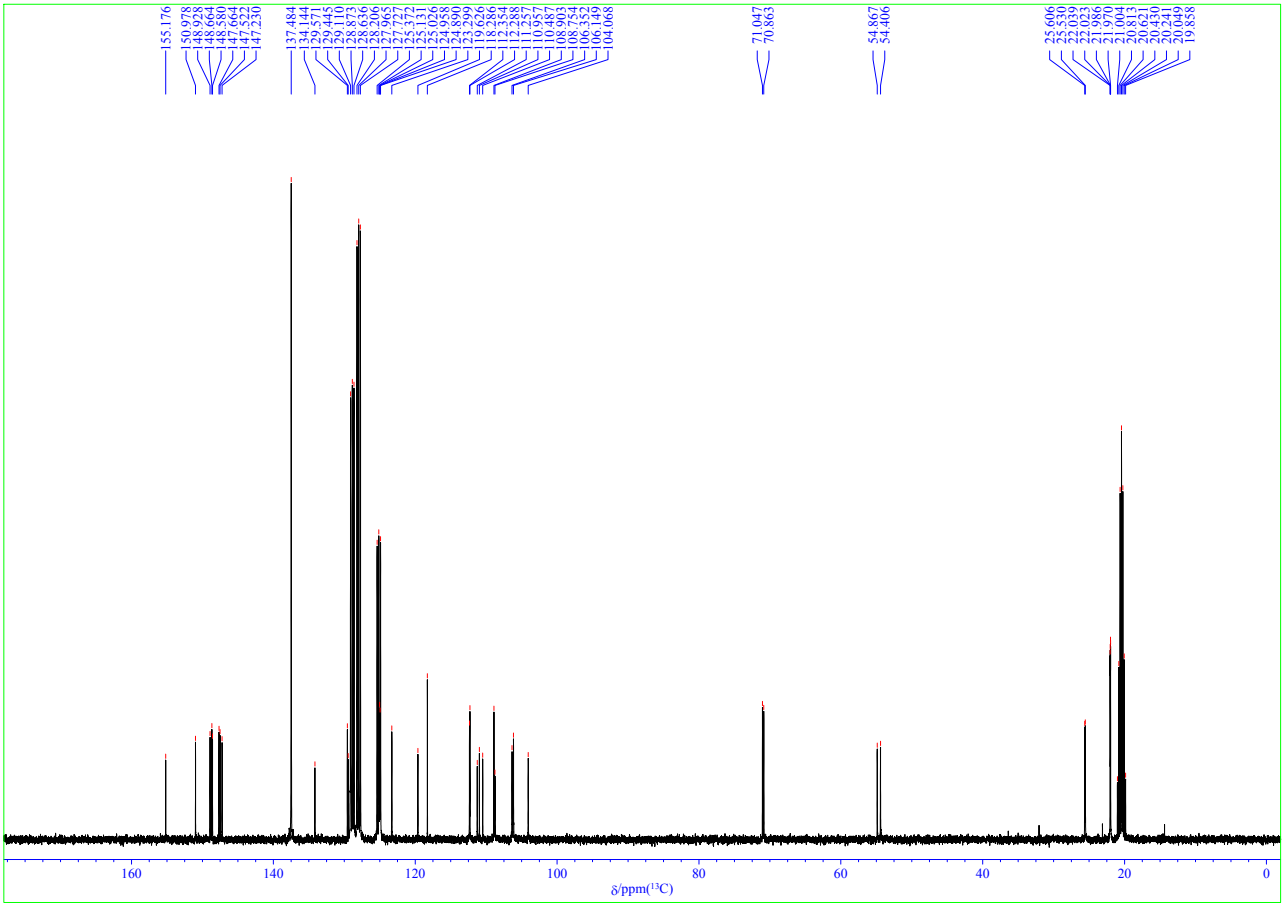

Figure S19. ^{13}C NMR spectrum of compound (**2b**) (100 MHz, toluene-d_8).

Theoretical calculations

All calculations were performed with Spartan '10 for Windows program package.[1] Equilibrium and transition state structures involved in the enantiomerization process of **1a** and **2a** were optimized using B3LYP DFT theory level[2] with the 6-31G(d) basis set. The nature of the obtained stationary points (minimum or first order saddle point) was confirmed through analysis of vibrational frequencies. Thermodynamic properties (enthalpies, Gibbs free energies, and entropies) were computed for a standard pressure of 0.1 MPa (1 atm) and for the coalescence temperatures T_c as determined in the VT-NMR experiment and a temperature of 20 °C (293 K). For the calculation of the partition functions, the vibrational frequencies were scaled by a factor of 0.9806.[3]

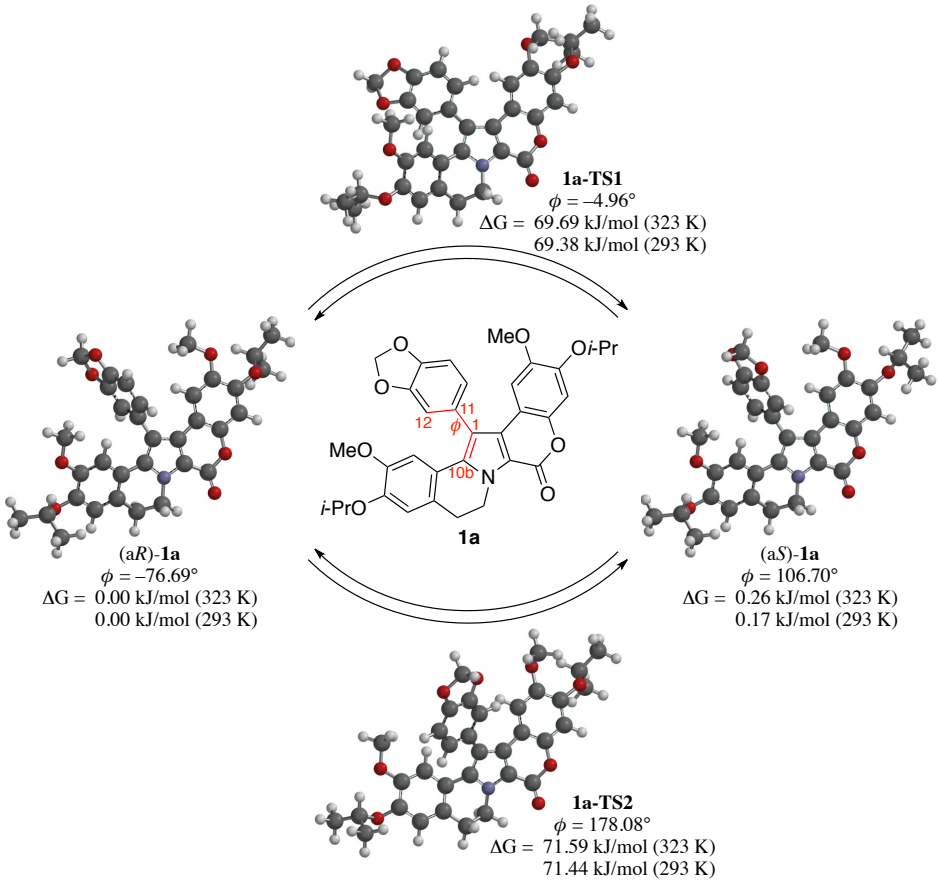

Figure S20. DFT-optimized structures for the ground states and transition states of the enantiomerization of 5,6-saturated lamellarin analogue (**1a**)

Table S1. Calculated enthalpies (ΔH), entropy contributions (–TΔS), and Gibbs free energies (ΔG) for ground state and transition state structures of 5,6-saturated lamellarin analogue (**1a**)[a]

species	ϕ^b	T_c (323 K)			20 °C (293 K)		
		ΔH	–TΔS	ΔG	ΔH	–TΔS	ΔG
(a*R*)-**1a**	–76.69	0.00	0.00	0.00	0.00	0.00	0.00
1a-TS1	–4.96	69.83	–0.14	69.69	69.83	–0.45	69.38
(a*S*)-**1a**	106.70	0.24	0.02	0.26	0.24	–0.07	0.17
1a-TS2	178.08	71.79	–0.20	71.59	71.79	–0.35	71.44

[a] Values for enthalpies (ΔH), entropy contributions (–TΔS), and Gibbs free energies (ΔG) were given in kJ/mol.
[b] Values for torsion angle C10b–C1–C11–C12 was given in degree (°).

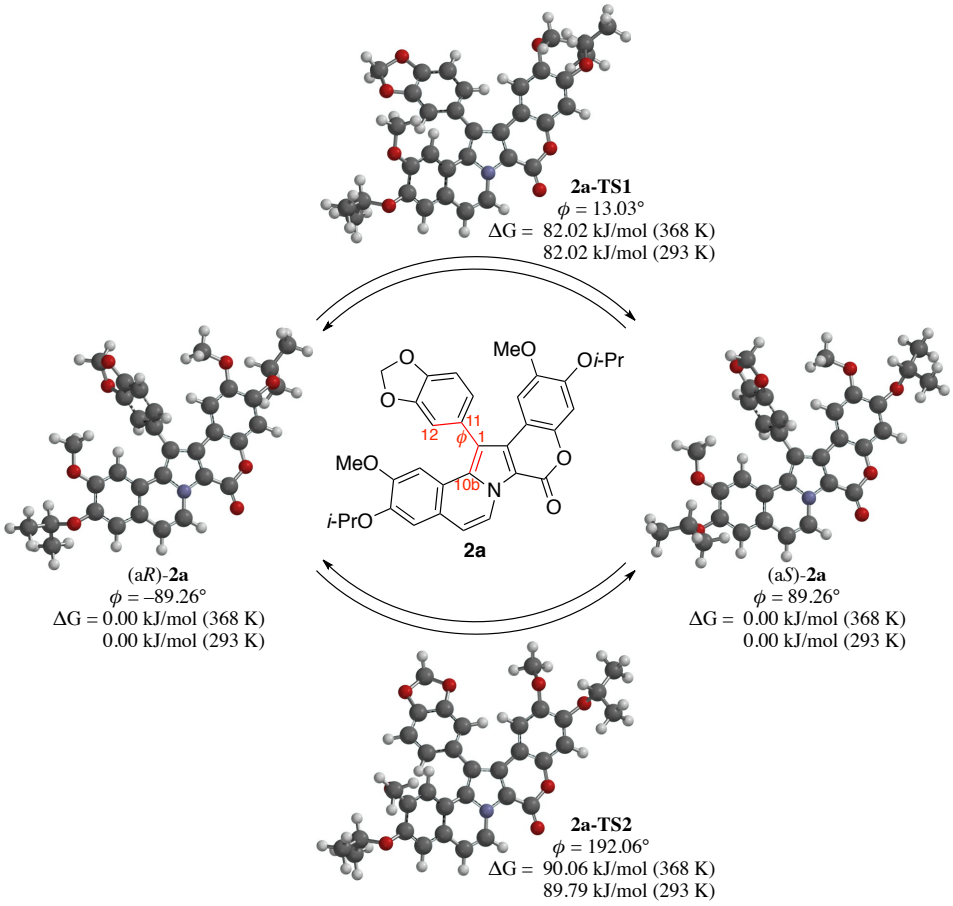

Figure S21. DFT-optimized structures for the ground states and transition states of the enantiomerization of 5,6-unsaturated lamellarin analogue (**2a**)

Table S2. Calculated enthalpies (ΔH), entropy contributions (–TΔS), and Gibbs free energies (ΔG) for ground state and transition state structures of 5,6-unsaturated lamellarin analogue (**2a**)[a]

species	ϕ^b	T_c (368 K)			20 °C (293 K)		
		ΔH	–TΔS	ΔG	ΔH	–TΔS	ΔG
(a*R*)-**2a**	–89.26	0.00	0.00	0.00	0.00	0.00	0.00
2a-TS1	13.03	82.24	–0.22	82.02	82.32	–0.30	82.02
(a*S*)-**2a**	89.26	0.00	0.00	0.00	0.00	0.00	0.00
2a-TS2	192.06	90.44	–0.38	90.06	90.57	–0.78	89.79

[a] Values for enthalpies (ΔH), entropy contributions (–TΔS), and Gibbs free energies (ΔG) were given in kJ/mol.
[b] Values for torsion angle C10b–C1–C11–C12 was given in degree (°).

Cartesian coordinates (in Å, 1 Å = 100 pm) of the DFT-optimized geometry of (a*R*)-1a.

N	0.644411	-2.555420	0.123483
C	-0.722054	-2.547751	-0.026826
C	1.108887	-1.260964	0.075293
C	-1.148525	-1.220952	-0.150910
C	0.012719	-0.396769	-0.089741
C	-2.571087	-0.968002	-0.272466
C	-5.379751	-0.716448	-0.492730
C	-3.176575	0.302364	-0.372564
C	-3.407030	-2.097456	-0.286256
C	-4.793476	-1.970828	-0.393193
C	-4.554199	0.439270	-0.490162
H	-2.541618	1.176753	-0.367752
H	-5.418383	-2.856427	-0.406021
C	0.054570	1.089204	-0.134612
C	0.115666	3.864458	-0.246907
C	-0.065025	1.770115	-1.355477
C	0.207964	1.823965	1.065799
C	0.236389	3.200644	0.972901
C	-0.039526	3.175474	-1.433994
H	-0.180470	1.192455	-2.267459
H	0.295412	1.320396	2.021991
H	-0.136092	3.695636	-2.381069
C	2.553462	-1.034832	0.188362
C	5.338591	-0.677630	0.423756
C	3.356728	-2.071184	0.704608
C	3.156172	0.172314	-0.212091
C	4.529642	0.366030	-0.084976
C	4.734409	-1.872309	0.808422
H	2.536752	0.957047	-0.622475
H	5.375812	-2.654437	1.205025
O	-2.928547	-3.385579	-0.183120
C	-1.589606	-3.696933	-0.024828
O	-1.280560	-4.868263	0.094334
O	-6.731827	-0.624992	-0.677991
O	-5.204661	1.635960	-0.618278
O	6.682261	-0.516497	0.626070
O	5.178618	1.520898	-0.422089
O	0.145087	5.222974	-0.040237
O	0.342260	4.120640	1.989084
C	-4.421661	2.818962	-0.639006
H	-3.710843	2.817191	-1.475429
H	-3.867588	2.953661	0.299442
H	-5.127828	3.641840	-0.764662
C	4.403675	2.607023	-0.907154
H	3.902878	2.357669	-1.851785
H	5.108712	3.423085	-1.075908
H	3.648824	2.920818	-0.174939
C	0.467428	5.393324	1.346068
H	-0.233557	6.100428	1.798016
H	1.502354	5.752067	1.439500
C	-7.517724	-0.023089	0.386440
H	-6.959895	0.828359	0.790043
C	7.532666	-0.360666	-0.542373
H	7.040134	0.323044	-1.241261
C	7.756858	-1.715041	-1.210966
H	6.806482	-2.162661	-1.520608
H	8.256184	-2.406211	-0.522349
H	8.384124	-1.601603	-2.102865
C	8.817790	0.274592	-0.030764
H	8.603841	1.239665	0.438135
H	9.522430	0.432216	-0.854649
H	9.294321	-0.373392	0.713393
C	-8.794957	0.475355	-0.274506
H	-9.450659	0.948329	0.464878
H	-9.337211	-0.358178	-0.734967
H	-8.557516	1.205916	-1.053438
C	-7.769764	-1.049807	1.488197
H	-8.348092	-0.601880	2.304889
H	-6.826314	-1.418697	1.904411
H	-8.330800	-1.904955	1.094740
C	1.535342	-3.715567	0.215405
H	1.902774	-3.961782	-0.790121
H	0.948818	-4.559172	0.576473
C	2.701015	-3.363863	1.138370
H	3.425638	-4.185131	1.135181
H	2.325361	-3.273263	2.168369

Cartesian coordinates (in Å, 1 Å = 100 pm) of the DFT-optimized geometry of 1a-TS1.

N	0.445260	-2.383680	0.582268
C	-0.921180	-2.283030	0.579761
C	0.985814	-1.147800	0.314122
C	-1.278790	-0.956601	0.298540
C	-0.058774	-0.184035	0.264919
C	-2.695292	-0.736750	0.015530
C	-5.496173	-0.579709	-0.493834
C	-3.250533	0.296539	-0.766973
C	-3.586758	-1.763076	0.399517
C	-4.962280	-1.666694	0.191069
C	-4.612588	0.387874	-1.020965
H	-2.612695	1.030111	-1.242857
H	-5.614084	-2.460157	0.538817
C	0.123076	1.276126	0.496967
C	0.449013	4.005274	1.118745
C	-0.950660	2.186268	0.498118
C	1.395175	1.779430	0.896560
C	1.520334	3.120317	1.174464
C	-0.811333	3.552972	0.797075
H	-1.951635	1.835489	0.315070
H	2.254326	1.137087	1.013845
H	-1.669828	4.215753	0.785444
C	2.424143	-1.118351	0.008943
C	5.165515	-1.207975	-0.639364
C	3.242703	-2.134305	0.537252
C	2.976553	-0.193280	-0.898341
C	4.330151	-0.222721	-1.222083
C	4.600515	-2.153763	0.212400
H	2.325646	0.540621	-1.355283
H	5.252139	-2.927219	0.608997
O	-3.163202	-2.936533	0.977981
C	-1.835277	-3.320115	0.990484
O	-1.565818	-4.440557	1.380307
O	-6.845698	-0.537703	-0.729045
O	-5.075862	1.444031	-1.778476
O	6.484502	-1.323226	-0.979167
O	4.931779	0.630519	-2.102491
O	0.873459	5.275137	1.432753
O	2.661945	3.803998	1.537141
C	-5.500477	1.081311	-3.097479
H	-5.856758	2.001329	-3.566767
H	-6.308772	0.343231	-3.066642
H	-4.659879	0.678588	-3.677556
C	4.133458	1.634791	-2.713220
H	4.810406	2.203757	-3.352806
H	3.686083	2.303262	-1.966484
H	3.337508	1.194962	-3.327913
C	2.219240	5.116183	1.897446
H	2.243062	5.224919	2.991515
H	2.859260	5.861148	1.416737
C	-7.585218	0.566844	-0.131677
H	-7.042500	1.494402	-0.344294
C	7.383436	-0.250042	-0.585316
H	6.874665	0.705379	-0.748412
C	8.581653	-0.353645	-1.517859
H	8.263592	-0.240396	-2.558475
H	9.067788	-1.329582	-1.408522
H	9.315592	0.426287	-1.287090
C	7.752495	-0.398955	0.888788
H	6.859543	-0.369074	1.522297
H	8.416356	0.415486	1.201487
H	8.267249	-1.350926	1.061701
C	-8.934640	0.584488	-0.836020
H	-8.810569	0.734747	-1.912982
H	-9.558081	1.394641	-0.442694
H	-9.459990	-0.364107	-0.678989
C	-7.706807	0.366595	1.376805
H	-8.246154	-0.561035	1.599595
H	-8.254430	1.202682	1.826776
H	-6.721220	0.314888	1.850574
C	1.254461	-3.593753	0.766401
H	1.414762	-4.069222	-0.210570
H	0.681804	-4.279723	1.388836
C	2.592671	-3.196474	1.391671
H	3.234311	-4.080031	1.470875
H	2.415097	-2.830486	2.413212

Cartesian coordinates (in Å, 1 Å = 100 pm) of the DFT-optimized geometry of (a*S*)-1a.

N	0.711690	-2.575472	0.101931
C	-0.662351	-2.573127	0.061160
C	1.160575	-1.278554	0.201401
C	-1.108478	-1.250742	0.160251
C	0.047482	-0.420866	0.248097
C	-2.538607	-1.012210	0.191220
C	-5.359031	-0.789006	0.220155
C	-3.162535	0.244838	0.336927
C	-3.362989	-2.145212	0.082866
C	-4.754563	-2.031819	0.089301
C	-4.546461	0.367419	0.360069
H	-2.538476	1.120145	0.446822
H	-5.370131	-2.920054	0.005073
C	0.075911	1.057623	0.397107
C	0.141787	3.818204	0.705132
C	0.395945	1.643879	1.629584
C	-0.222534	1.883481	-0.715508
C	-0.183108	3.250128	-0.525478
C	0.437205	3.039230	1.806664
H	0.622074	0.998268	2.472075
H	-0.475199	1.453822	-1.678788
H	0.680656	3.484822	2.765192
C	2.608260	-1.043915	0.230943
C	5.400948	-0.671764	0.304487
C	3.457353	-2.127576	0.531719
C	3.169554	0.218127	-0.040418
C	4.547046	0.417715	0.010243
C	4.837538	-1.919823	0.558699
H	2.515578	1.042077	-0.287911
H	5.513559	-2.737818	0.791779
O	-2.866680	-3.424843	-0.038746
C	-1.516796	-3.728297	-0.033759
O	-1.188725	-4.897953	-0.111417
O	-6.722342	-0.718364	0.305244
O	-5.215454	1.549376	0.524173
O	6.754151	-0.514048	0.429952
O	5.159123	1.620704	-0.206124
O	0.078186	5.188733	0.613598
O	-0.461929	4.245608	-1.433521
C	-4.447462	2.727158	0.713945
H	-5.169188	3.536277	0.840758
H	-3.809940	2.939729	-0.154585
H	-3.818460	2.655890	1.610797
C	4.339507	2.753193	-0.454514
H	3.766392	2.641074	-1.384441
H	5.023041	3.598820	-0.550907
H	3.644851	2.936051	0.375061
C	-0.120437	5.471462	-0.776467
H	0.809361	5.871322	-1.205844
H	-0.940725	6.185670	-0.888944
C	-7.431205	-0.042498	-0.768549
H	-6.874135	0.861448	-1.036110
C	7.513253	-0.174494	-0.762160
H	6.948596	0.569746	-1.332823
C	7.733895	-1.424296	-1.611200
H	6.778901	-1.868774	-1.911203
H	8.302881	-2.174327	-1.050004
H	8.292374	-1.175677	-2.521287
C	8.809214	0.446344	-0.260505
H	8.596176	1.336181	0.339328
H	9.448671	0.734196	-1.102263
H	9.358437	-0.267855	0.363197
C	-7.541703	-0.963857	-1.981123
H	-8.058595	-0.454529	-2.802963
H	-8.104419	-1.869125	-1.726279
H	-6.550829	-1.263519	-2.338462
C	-8.782173	0.347984	-0.186170
H	-9.388126	0.867206	-0.936889
H	-8.646937	1.008491	0.675442
H	-9.327801	-0.543298	0.143233
C	1.615265	-3.719879	-0.043880
H	1.902634	-3.813107	-1.100041
H	1.065483	-4.617063	0.236795
C	2.848984	-3.481377	0.825514
H	3.577596	-4.279320	0.646562
H	2.557507	-3.547029	1.884307

Cartesian coordinates (in Å, 1 Å = 100 pm) of the DFT-optimized geometry of 1a-TS2.

N	0.693668	-2.316043	-0.750605
C	-0.673614	-2.237944	-0.802162
C	1.202192	-1.078037	-0.436385
C	-1.064236	-0.924314	-0.505235
C	0.139472	-0.133126	-0.407882
C	-2.495295	-0.733770	-0.279260
C	-5.319693	-0.640757	0.113327
C	-3.103980	0.269038	0.501932
C	-3.353005	-1.753732	-0.748420
C	-4.736497	-1.692684	-0.587771
C	-4.479517	0.339460	0.683093
H	-2.502946	0.995477	1.033368
H	-5.356731	-2.487468	-0.986368
C	0.302505	1.334083	-0.607124
C	0.668803	4.069507	-1.178969
C	1.555972	1.873630	-0.971076
C	-0.803342	2.224293	-0.607206
C	-0.585638	3.556361	-0.880841
C	1.764936	3.233993	-1.245343
H	2.405743	1.217266	-1.084683
H	-1.812372	1.887389	-0.447384
H	2.746137	3.603806	-1.523585
C	2.627619	-1.029033	-0.077496
C	5.343729	-1.081598	0.673571
C	3.483002	-2.023195	-0.588322
C	3.129705	-0.105790	0.860125
C	4.469664	-0.117949	1.235998
C	4.827953	-2.024080	-0.212360
H	2.450052	0.613724	1.297498
H	5.507345	-2.781042	-0.593903
O	-2.882911	-2.901703	-1.343021
C	-1.552245	-3.273338	-1.288150
O	-1.249151	-4.380526	-1.690815
O	-6.684389	-0.571770	0.205800
O	-5.002267	1.349039	1.466338
O	6.649778	-1.182626	1.064083
O	5.021713	0.734145	2.149960
O	0.585109	5.426554	-1.385067
O	-1.516024	4.573695	-0.896954
C	-5.531684	2.447778	0.716357
H	-5.935722	3.151501	1.447946
H	-6.329441	2.118061	0.041083
H	-4.741240	2.940854	0.135172
C	4.177617	1.703086	2.756317
H	4.817932	2.274248	3.430700
H	3.373756	1.228533	3.333649
H	3.736482	2.377407	2.010971
C	-0.818305	5.718155	-1.399485
H	-1.138342	5.919858	-2.431902
H	-1.016425	6.578068	-0.753576
C	-7.275102	-0.754513	1.525826
H	-6.710888	-0.143830	2.238230
C	7.547924	-0.088522	0.731626
H	7.018844	0.856035	0.893215
C	7.981523	-0.200372	-0.728097
H	7.115973	-0.169699	-1.398637
H	8.517210	-1.141112	-0.898695
H	8.646172	0.629673	-0.994864
C	8.706905	-0.195954	1.712198
H	8.343057	-0.110235	2.740356
H	9.438636	0.598859	1.530274
H	9.211345	-1.162519	1.602757
C	-8.700123	-0.231478	1.411957
H	-9.220012	-0.332926	2.370755
H	-9.255504	-0.796877	0.655375
H	-8.704559	0.824541	1.124610
C	-7.213510	-2.224860	1.931593
H	-7.642090	-2.360833	2.931300
H	-6.180187	-2.585836	1.956539
H	-7.778951	-2.843431	1.225283
C	1.529102	-3.510185	-0.920970
H	0.993498	-4.193984	-1.577926
H	1.656184	-3.999374	0.054102
C	2.885257	-3.082497	-1.483742
H	2.744233	-2.703521	-2.506266
H	3.543727	-3.954705	-1.549500

Cartesian coordinates (in Å, 1 Å = 100 pm) of the DFT-optimized geometry of (a*R*)-2a.

N	0.679671	-2.651010	-0.143946
C	-0.703064	-2.617129	-0.145702
C	1.160852	-1.342157	-0.223852
C	-1.111362	-1.281339	-0.226930
C	0.052594	-0.470526	-0.276496
C	-2.536086	-1.010969	-0.242312
C	-5.348090	-0.718617	-0.254111
C	-3.128489	0.266533	-0.328993
C	-3.385708	-2.128811	-0.172639
C	-4.774241	-1.980214	-0.173120
C	-4.508391	0.423619	-0.345098
H	-2.482097	1.129766	-0.397859
H	-5.411752	-2.855296	-0.121110
C	0.088182	1.015139	-0.349831
C	0.106890	3.788018	-0.514297
C	0.076535	1.669257	-1.590326
C	0.110354	1.776355	0.844830
C	0.118731	3.151607	0.726013
C	0.087453	3.073079	-1.695854
H	0.055286	1.071317	-2.496018
H	0.120344	1.292491	1.815222
H	0.080888	3.572564	-2.658771
C	2.592334	-1.148808	-0.239151
C	5.408432	-0.864178	-0.252665
C	3.432040	-2.295026	-0.167908
C	3.186869	0.130861	-0.330375
C	4.564442	0.281906	-0.347140
C	4.831974	-2.116376	-0.171454
H	2.550103	0.999680	-0.402914
H	5.489425	-2.979210	-0.121408
O	-2.922126	-3.423059	-0.091844
C	-1.575589	-3.752533	-0.072411
O	-1.270949	-4.929228	0.003291
C	2.842849	-3.602569	-0.086758
H	3.483573	-4.476375	-0.034067
C	1.499575	-3.765673	-0.076594
H	0.976995	-4.710469	-0.019352
O	-6.708282	-0.611314	-0.336261
O	-5.149183	1.627253	-0.457311
O	6.767807	-0.749903	-0.337637
O	5.207595	1.478578	-0.463524
O	0.145864	5.150326	-0.336209
O	0.166521	4.093931	1.726565
C	-4.353195	2.792319	-0.602959
H	-3.713059	2.957684	0.274032
H	-5.055009	3.622621	-0.701408
H	-3.722434	2.738847	-1.499734
C	4.418441	2.652946	-0.595732
H	5.127052	3.477031	-0.694435
H	3.787922	2.815381	0.287852
H	3.781220	2.608596	-1.487722
C	-0.001402	5.357375	1.074153
H	-1.007310	5.748059	1.283728
H	0.767894	6.052186	1.421952
C	-7.402816	0.039036	0.763206
H	-6.808395	0.899169	1.088147
C	7.462206	-0.099330	0.762260
H	6.856329	0.746438	1.103392
C	8.769839	0.416115	0.178777
H	8.570190	1.123943	-0.631084
H	9.361310	-0.413562	-0.224435
H	9.362125	0.920326	0.950276
C	7.660381	-1.091705	1.905514
H	6.698819	-1.475477	2.262859
H	8.166909	-0.608490	2.749192
H	8.270028	-1.940478	1.575616
C	-8.724530	0.524830	0.185796
H	-8.544758	1.226310	-0.634257
H	-9.318359	1.027989	0.956851
H	-9.305104	-0.319686	-0.202096
C	-7.574138	-0.942634	1.919981
H	-8.081192	-0.457317	2.762230
H	-6.603476	-1.306509	2.273282
H	-8.172349	-1.805537	1.606181

Cartesian coordinates (in Å, 1 Å = 100 pm) of the DFT-optimized geometry of 2a-TS1.

N	0.527599	-2.410033	0.693612
C	-0.849308	-2.321551	0.679248
C	1.060259	-1.162040	0.351773
C	-1.209549	-1.006473	0.367604
C	-0.008085	-0.213638	0.317529
C	-2.619007	-0.793924	0.053604
C	-5.389617	-0.655448	-0.575296
C	-3.157360	0.290960	-0.668935
C	-3.504543	-1.852938	0.349551
C	-4.869566	-1.770928	0.072584
C	-4.505628	0.370157	-0.984618
H	-2.514144	1.090959	-1.014503
H	-5.522769	-2.592400	0.343997
C	0.080019	1.247925	0.582080
C	0.151569	3.976116	1.298091
C	-1.072675	1.965952	0.968778
C	1.318068	1.945270	0.649252
C	1.311622	3.279600	0.986954
C	-1.064370	3.326412	1.314775
H	-2.015914	1.449657	1.058764
H	2.265393	1.457575	0.491107
H	-1.978848	3.834043	1.602043
C	2.464967	-1.155974	-0.000525
C	5.228922	-1.230004	-0.639809
C	3.271166	-2.263084	0.391593
C	3.044977	-0.174879	-0.841130
C	4.394121	-0.196139	-1.159604
C	4.650813	-2.246731	0.094574
H	2.403755	0.570193	-1.290179
H	5.283401	-3.070290	0.411930
O	-3.090299	-3.036242	0.912889
C	-1.753808	-3.380555	1.027068
O	-1.479942	-4.497870	1.424839
C	2.648735	-3.413799	0.981339
H	3.255235	-4.261535	1.281194
C	1.300189	-3.499643	1.057520
H	0.739024	-4.363505	1.385106
O	-6.724192	-0.627561	-0.881336
O	-4.965411	1.470917	-1.677691
O	6.551069	-1.307058	-0.970749
O	5.008808	0.699684	-1.981727
O	0.451692	5.291086	1.569035
O	2.394020	4.131918	1.059140
C	-5.283457	1.210145	-3.049491
H	-4.388849	0.892498	-3.600835
H	-5.648106	2.153450	-3.462685
H	-6.058757	0.441786	-3.139218
C	4.229633	1.754235	-2.532663
H	4.920435	2.350960	-3.130442
H	3.788390	2.381085	-1.747368
H	3.432396	1.366069	-3.179202
C	1.881978	5.343753	1.624526
H	2.204560	5.424641	2.672783
H	2.236626	6.196470	1.039212
C	-7.527135	0.416903	-0.256868
H	-6.997183	1.368312	-0.372537
C	7.435308	-0.263771	-0.473987
H	6.915150	0.696508	-0.550750
C	8.639213	-0.265624	-1.404789
H	8.325199	-0.058990	-2.432179
H	9.136414	-1.241797	-1.383885
H	9.362150	0.497735	-1.096977
C	7.797632	-0.545601	0.982093
H	6.900676	-0.590791	1.609028
H	8.445868	0.246261	1.375135
H	8.327347	-1.501140	1.067997
C	-8.832157	0.452147	-1.039897
H	-9.340251	-0.516581	-0.978444
H	-8.648080	0.678072	-2.094785
H	-9.499199	1.219410	-0.632361
C	-7.733344	0.108545	1.223869
H	-8.325302	0.900791	1.696434
H	-6.776772	0.041406	1.752056
H	-8.264518	-0.841887	1.348337

Cartesian coordinates (in Å, 1 Å = 100 pm) of the DFT-optimized geometry of (a*S*)-2a.

N	0.679684	-2.651007	0.143935
C	-0.703051	-2.617131	0.145686
C	1.160861	-1.342151	0.223833
C	-1.111354	-1.281341	0.226905
C	0.052599	-0.470523	0.276470
C	-2.536078	-1.010976	0.242291
C	-5.348083	-0.718634	0.254111
C	-3.128485	0.266524	0.328970
C	-3.385697	-2.128821	0.172629
C	-4.774231	-1.980229	0.173120
C	-4.508387	0.423606	0.345086
H	-2.482095	1.129760	0.397827
H	-5.411739	-2.855314	0.121119
C	0.088181	1.015141	0.349819
C	0.106882	3.788017	0.514319
C	0.076582	1.669243	1.590322
C	0.110299	1.776373	-0.844834
C	0.118672	3.151623	-0.726000
C	0.087499	3.073064	1.695868
H	0.055372	1.071292	2.496008
H	0.120251	1.292521	-1.815233
H	0.080970	3.572536	2.658792
C	2.592342	-1.148797	0.239133
C	5.408440	-0.864159	0.252672
C	3.432051	-2.295014	0.167921
C	3.186873	0.130876	0.330330
C	4.564444	0.281925	0.347106
C	4.831985	-2.116361	0.171480
H	2.550103	0.999695	0.402837
H	5.489439	-2.979194	0.121459
O	-2.922110	-3.423068	0.091838
C	-1.575573	-3.752538	0.072405
O	-1.270929	-4.929233	-0.003288
C	2.842866	-3.602560	0.086784
H	3.483592	-4.476366	0.034111
C	1.499592	-3.765668	0.076603
H	0.977015	-4.710466	0.019366
O	-6.708275	-0.611335	0.336275
O	-5.149182	1.627238	0.457300
O	6.767813	-0.749882	0.337661
O	5.207591	1.478603	0.463466
O	0.145841	5.150328	0.336247
O	0.166412	4.093960	-1.726542
C	-4.353196	2.792307	0.602936
H	-3.722428	2.738842	1.499706
H	-5.055012	3.622608	0.701386
H	-3.713068	2.957669	-0.274061
C	4.418432	2.652972	0.595624
H	5.127037	3.477062	0.694316
H	3.781194	2.608648	1.487604
H	3.787928	2.815378	-0.287976
C	-0.001472	5.357397	-1.074106
H	0.767820	6.052204	-1.421924
H	-1.007382	5.748098	-1.283642
C	-7.402823	0.039013	-0.763184
H	-6.808401	0.899136	-1.088145
C	7.462230	-0.099329	-0.762235
H	6.856374	0.746452	-1.103372
C	7.660392	-1.091710	-1.905485
H	6.698825	-1.475464	-2.262837
H	8.270019	-1.940496	-1.575581
H	8.166936	-0.608509	-2.749160
C	8.769873	0.416089	-0.178747
H	8.570237	1.123924	0.631111
H	9.362174	0.920283	-0.950245
H	9.361322	-0.413601	0.224471
C	-7.574177	-0.942667	-1.919946
H	-8.081247	-0.457356	-2.762188
H	-8.172386	-1.805563	-1.606124
H	-6.603526	-1.306552	-2.273264
C	-8.724523	0.524825	-0.185754
H	-9.318360	1.027983	-0.956803
H	-8.544728	1.226309	0.634291
H	-9.305098	-0.319683	0.202155

Cartesian coordinates (in Å, 1 Å = 100 pm) of the DFT-optimized geometry of 2a-TS2.

N	0.757892	-2.205242	0.984708
C	-0.619762	-2.149267	1.024095
C	1.243320	-0.979297	0.518432
C	-1.027214	-0.879846	0.598184
C	0.149375	-0.065292	0.435038
C	-2.454435	-0.742091	0.323494
C	-5.258940	-0.745486	-0.170723
C	-3.056103	0.207751	-0.526741
C	-3.300455	-1.755141	0.826506
C	-4.677904	-1.741527	0.609377
C	-4.424107	0.230525	-0.759605
H	-2.451707	0.940714	-1.046667
H	-5.294648	-2.526812	1.031342
C	0.226869	1.415901	0.555873
C	0.385001	4.195828	1.003167
C	1.454996	2.090735	0.721329
C	-0.954866	2.192615	0.709057
C	-0.839912	3.548977	0.907967
C	1.558209	3.475000	0.932916
H	2.377471	1.531820	0.736583
H	-1.935636	1.747956	0.725190
H	2.526392	3.949372	1.051516
C	2.634916	-0.962914	0.114855
C	5.373042	-1.028927	-0.640818
C	3.481480	-2.036747	0.525315
C	3.168569	-0.014856	-0.787605
C	4.498688	-0.039481	-1.166533
C	4.845711	-2.019868	0.168986
H	2.536280	0.744334	-1.231384
H	5.504502	-2.812999	0.510193
O	-2.825008	-2.844722	1.517796
C	-1.479384	-3.169831	1.554649
O	-1.157555	-4.233574	2.051396
C	2.910726	-3.155574	1.221789
H	3.547304	-3.971971	1.545141
C	1.571143	-3.251384	1.384592
H	1.045660	-4.095304	1.809565
O	-6.619512	-0.718901	-0.311029
O	-4.948479	1.190908	-1.600658
O	6.694951	-1.080628	-0.996902
O	4.958760	0.921936	-2.037374
O	0.191078	5.544995	1.184219
O	-1.858933	4.468328	1.038629
C	-5.494926	2.323002	-0.914190
H	-5.898013	2.983266	-1.685641
H	-4.715040	2.853188	-0.351867
H	-6.296884	2.021148	-0.230593
C	5.256141	0.439960	-3.354406
H	5.631888	1.299449	-3.913856
H	4.348068	0.058593	-3.838591
H	6.015941	-0.347727	-3.327637
C	-1.218247	5.698797	1.393384
H	-1.594137	6.502448	0.753834
H	-1.408014	5.919079	2.453672
C	-7.164811	-0.954803	-1.642760
H	-6.595747	-0.349302	-2.355285
C	7.544767	0.012502	-0.538605
H	7.028891	0.955742	-0.748853
C	8.815800	-0.077414	-1.371202
H	8.592105	0.025897	-2.437476
H	9.308405	-1.043439	-1.214310
H	9.513430	0.717109	-1.085443
C	7.806454	-0.117659	0.959670
H	6.871075	-0.098116	1.528211
H	8.431287	0.712384	1.308641
H	8.325062	-1.057802	1.179330
C	-7.051269	-2.433910	-2.001938
H	-7.449465	-2.610887	-3.007748
H	-7.617641	-3.047538	-1.292122
H	-6.007857	-2.765357	-1.989581
C	-8.605776	-0.467743	-1.584698
H	-9.094060	-0.606806	-2.555339
H	-8.646224	0.594704	-1.325206
H	-9.168907	-1.028391	-0.830315

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