Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material

UV-induced radical formation and isomerization of 4-methoxyindole and 5-methoxyindole

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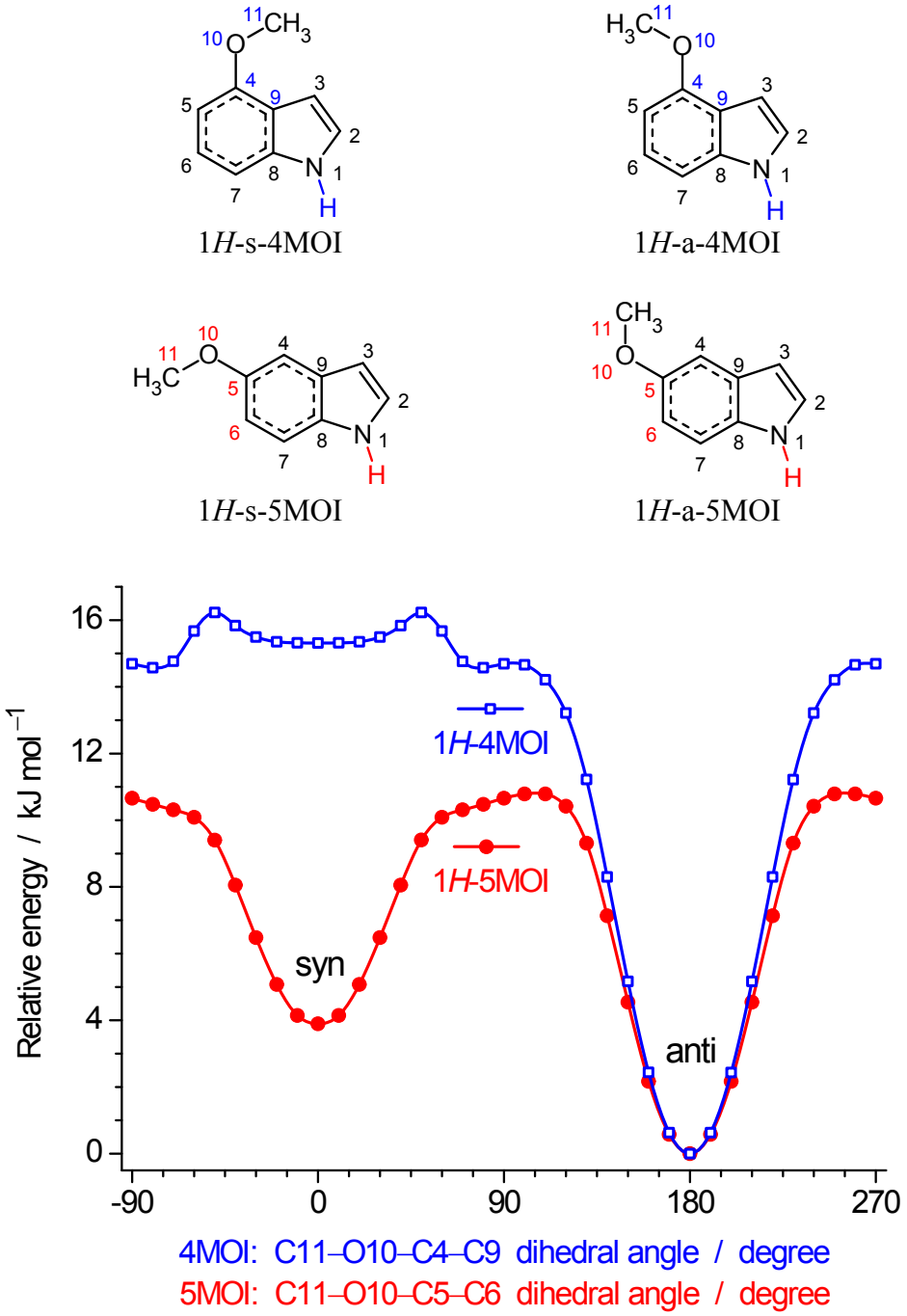


Fig. S1. Relaxed potential energy scans computed at the B3LYP/6-311++G(3df,3pd) level for 1*H*-4MOI (blue, squares) and 1*H*-5MOI (red, circles) as functions of the internal rotation of the methoxy group. Energies of the most stable conformers (1*H*-a-4MOI and 1*H*-a-5MOI) were chosen as relative zeroes. Structures of the main local minima, including the atom numbering, are shown above the scans. The four atoms defining the reaction coordinates, as well as the labile protons, are shown in blue (4MOI) and in red (5MOI).

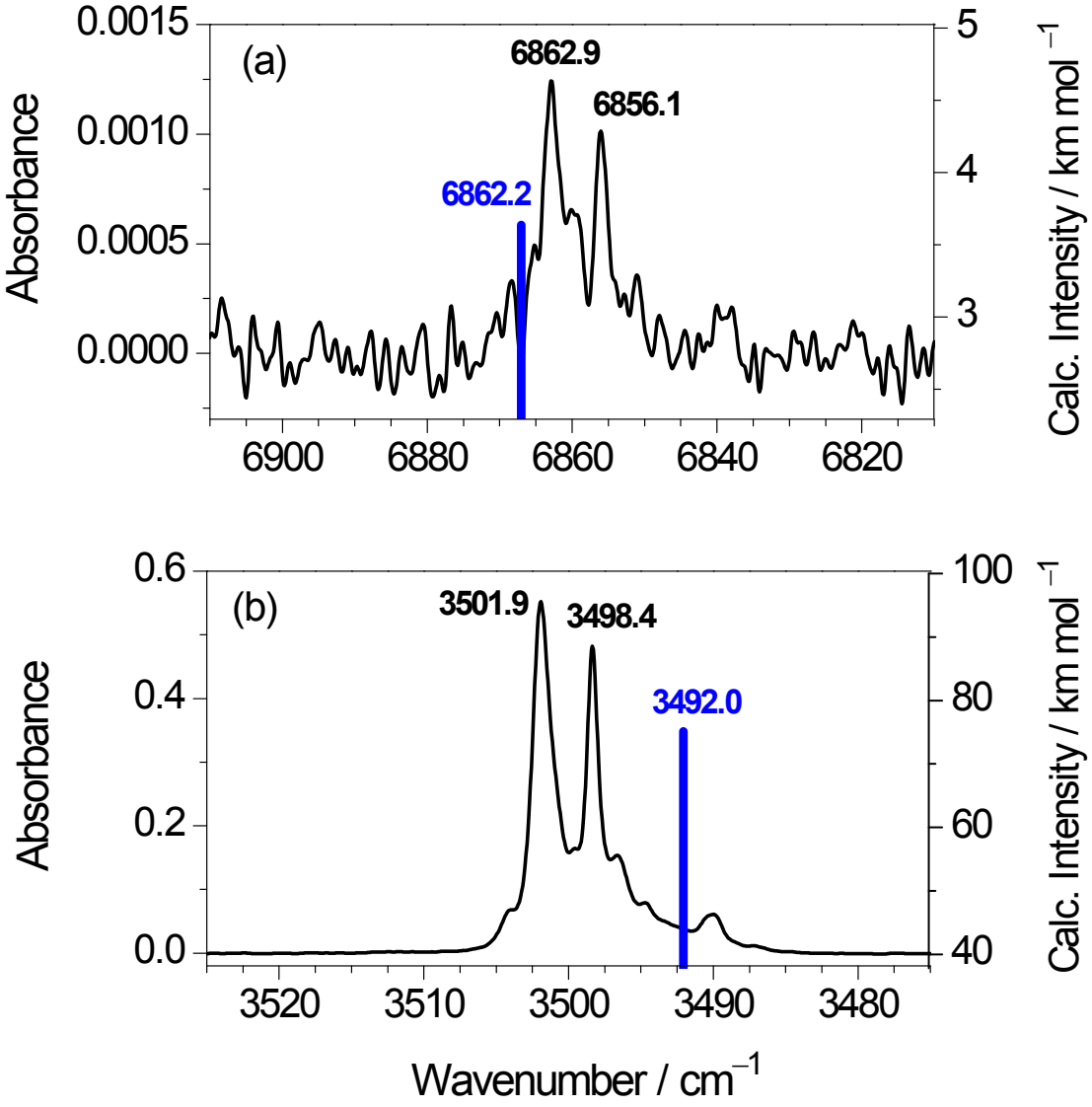


Fig. S2. Fragments of the near-IR (a) and mid-IR (b) experimental spectra of 4MOI isolated in a xenon matrix at 15 K, showing the bands assigned, respectively, to the first overtone and fundamental vibration of the N_1H stretching mode. Blue sticks represent the wavenumbers and IR intensities calculated for the $2\nu N_1H$ (anharmonic approximation, unscaled wavenumber) and νN_1H modes (harmonic approximation, scaled wavenumber) of 1*H*-a-4MOI at the B3LYP/6-311++G(d,p) level.

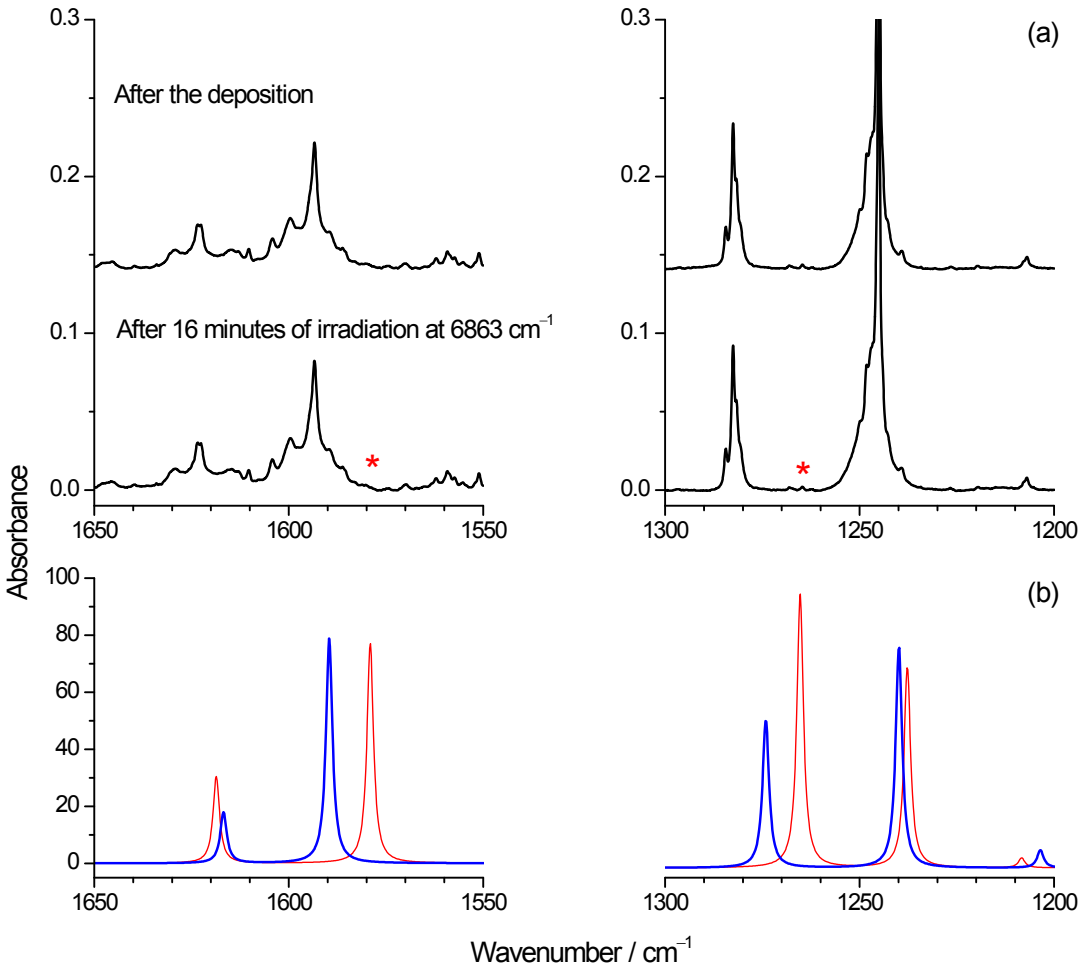


Fig. S3. (a) Selected fragments of the mid-IR spectrum of 1*H*-4MOI isolated in a xenon matrix at 15 K, after the matrix deposition and after subjecting the matrix to 15 minutes of near-IR irradiation at 6863 cm^{-1}. Asterisks (*) correspond to spectral positions where the minor 1*H*-s conformer was expected to absorb. (b) B3LYP/6-311++G(d,p) simulated spectra for the 1*H*-a (blue line) and 1*H*-s (red line) conformers of 4MOI.

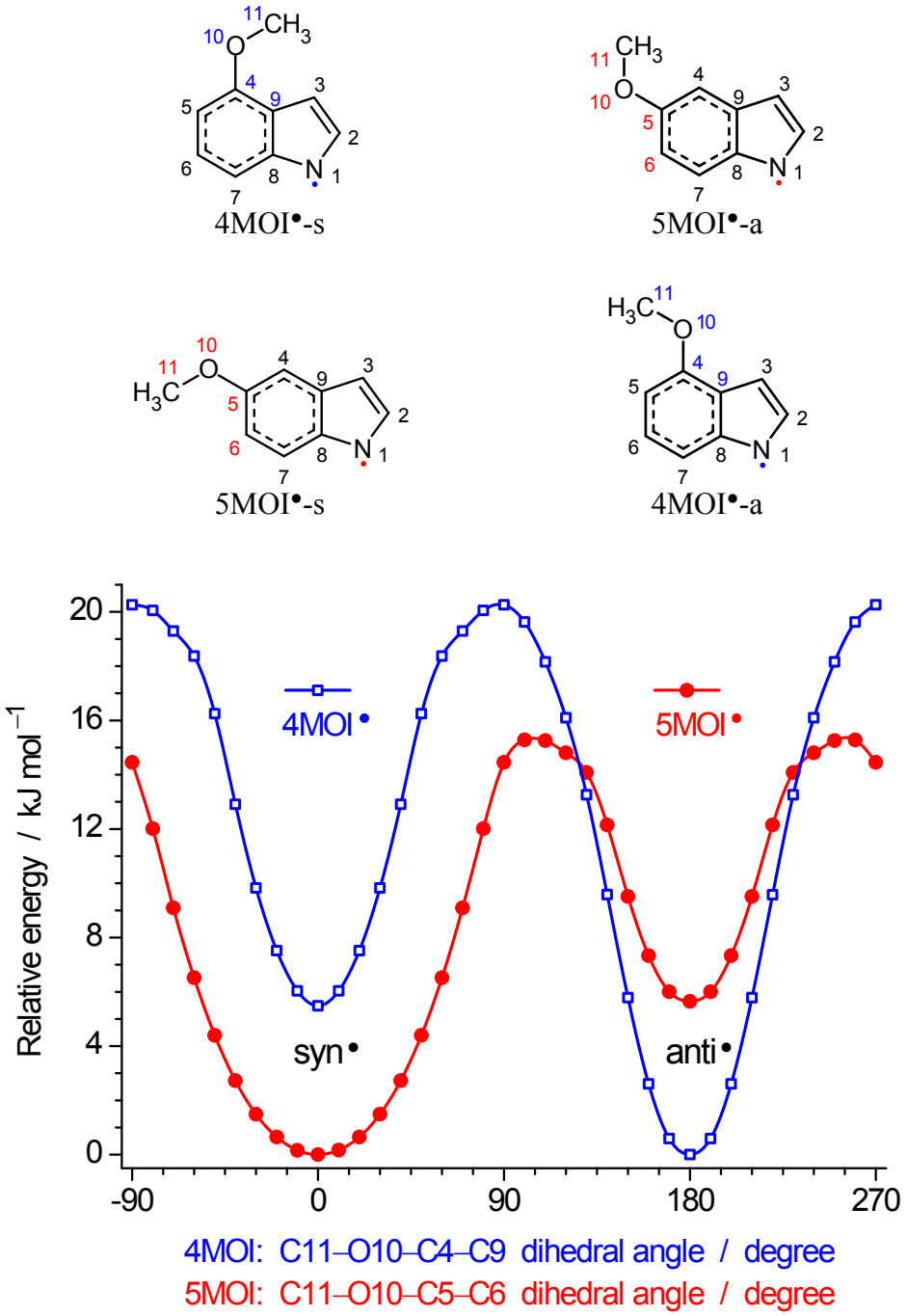


Fig. S4. Relaxed potential energy scans computed at the B3LYP/6-311++G(d,p) level for 4MOI• (blue, squares) and 5MOI• (red, circles) radicals as functions of the internal rotation of the methoxy group. Energies of the most stable conformers (4MOI•-a and 5MOI•-s) were chosen as relative zeroes. Structures of the local minima, including the atom numbering, are shown above the scans. The four atoms defining the reaction coordinates are shown in blue (4MOI•) and in red (5MOI•).

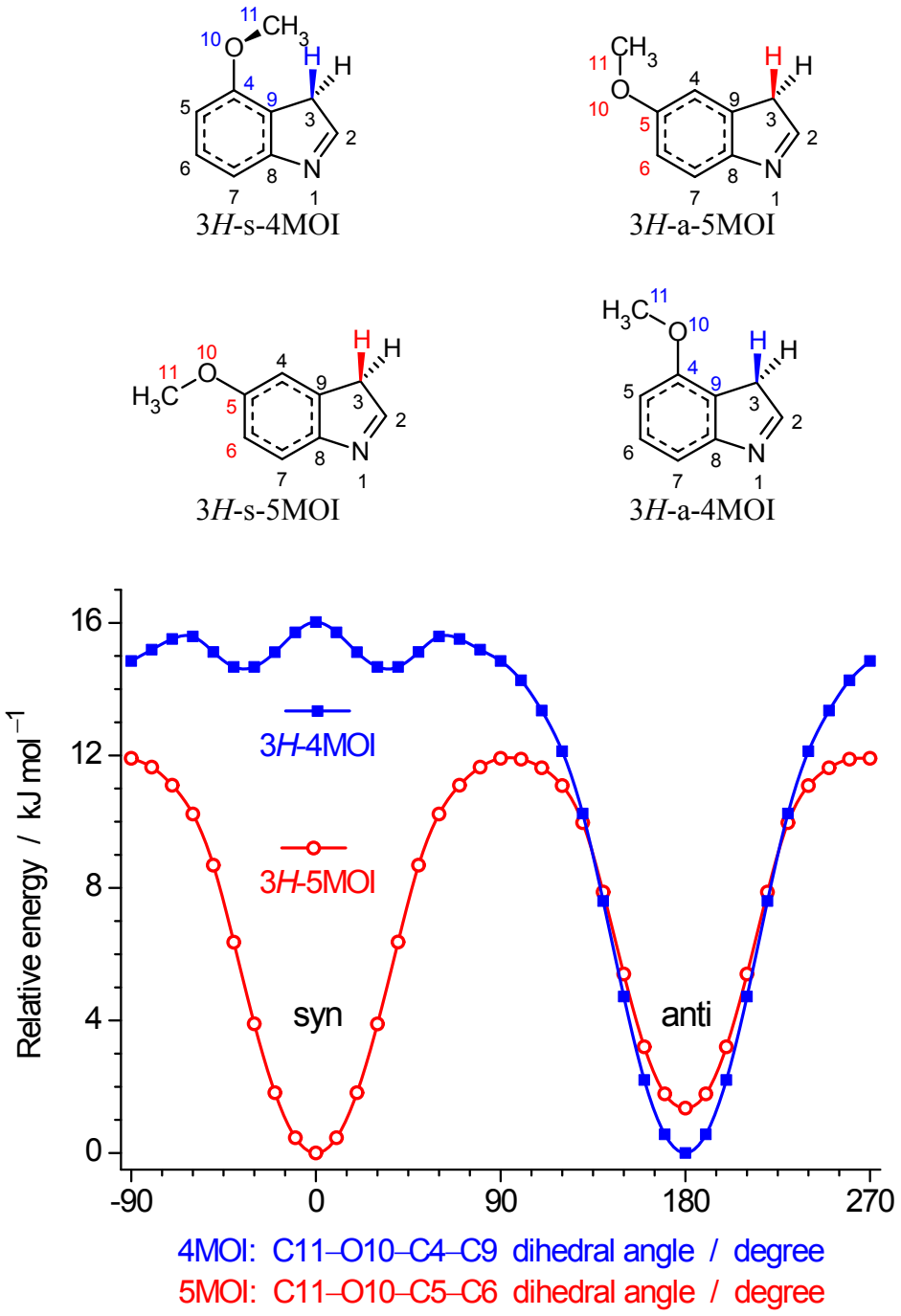


Fig. S5. Relaxed potential energy scans computed at the B3LYP/6-311++G(d,p) level for 3*H*-4MOI (blue, squares) and 3*H*-5MOI (red, circles) as functions of the internal rotation of the methoxy group. Energies of the most stable conformers (3*H*-a-4MOI and 3*H*-s-5MOI) were chosen as relative zeroes. Structures of the local minima, including the atom numbering, are shown above the scans. The four atoms defining the reaction coordinates, as well as the labile protons, are shown in blue (4MOI) and in red (5MOI).

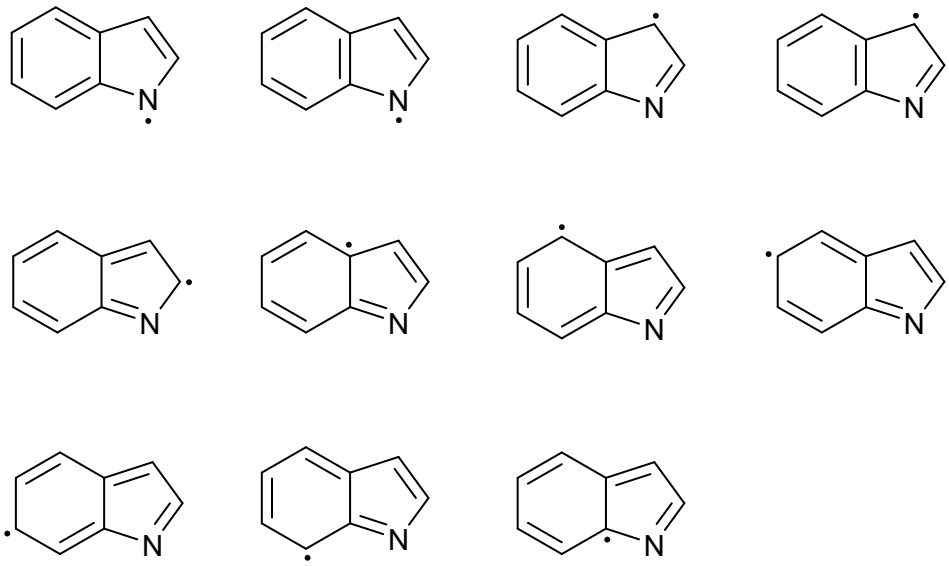


Fig. S6. Eleven reference structures selected for the NRT analysis of indolyl and methoxyindolyl isomers, corresponding to all non-ionic structures with a single unpaired electron in the indole ring system.

Table S1. Optimized geometries (Cartesian coordinates, Å) of all prototropic tautomers of 4-methoxyindole (4MOI) optimized at the B3LYP/6-311++G(d,p) level.

	1*H*-s (C_1)			**1*H*-a (C_s)**		
N	2.276053	-0.846773	0.041793	1.967907	1.669258	0.000000
C	1.598760	-2.045704	-0.040314	0.966370	2.624259	0.000000
C	0.254972	-1.805497	-0.095595	-0.252967	2.003285	0.000000
C	-1.028597	0.518866	-0.077598	-0.832417	-0.546616	0.000000
C	-0.787844	1.889162	-0.041880	-0.248587	-1.808200	0.000000
C	0.513041	2.406118	0.028347	1.156159	-1.948827	0.000000
C	1.619142	1.571133	0.071677	2.004472	-0.855587	0.000000
C	1.373673	0.196972	0.034874	1.403502	0.410398	0.000000
C	0.068830	-0.373596	-0.045600	0.000000	0.591542	0.000000
O	-2.346881	0.163114	-0.177201	-2.174552	-0.301007	0.000000
C	-2.774186	-1.138125	0.205703	-3.063255	-1.409145	0.000000
H	3.275789	-0.744310	0.081543	2.954834	1.863026	0.000000
H	2.133058	-2.982443	-0.052894	1.210827	3.674753	0.000000
H	-0.496970	-2.571390	-0.165973	-1.215536	2.487375	0.000000
H	-1.643382	2.552731	-0.068308	-0.859900	-2.700229	0.000000
H	0.650082	3.481110	0.054207	1.575108	-2.948723	0.000000
H	2.626936	1.965579	0.127999	3.081371	-0.976888	0.000000
H	-3.856377	-1.073233	0.317473	-4.066991	-0.986763	0.000000
H	-2.329454	-1.441549	1.157787	-2.929155	-2.027979	0.893912
H	-2.543755	-1.879961	-0.564449	-2.929155	-2.027979	-0.893912
	2*H*-s (C_1)			**2*H*-a (C_s)**		
N	-2.482408	-0.410422	-0.160514	-2.115918	1.568369	0.000000
C	-2.010480	-1.770943	0.034996	-1.097483	2.606700	0.000000
C	-0.526159	-1.717235	0.223094	0.240772	1.934559	0.000000
C	1.080945	0.303916	0.249642	0.859315	-0.559106	0.000000
C	1.062697	1.659747	0.168536	0.280344	-1.794691	0.000000
C	-0.167467	2.392174	-0.051800	-1.161025	-1.940926	0.000000
C	-1.372313	1.783563	-0.192720	-2.024804	-0.893657	0.000000
C	-1.424994	0.345165	-0.095573	-1.471514	0.437469	0.000000
C	-0.169875	-0.411570	0.134402	0.000000	0.602572	0.000000
O	2.249246	-0.367542	0.510674	2.187738	-0.290021	0.000000
C	2.798566	-1.107081	-0.585945	3.095000	-1.387720	0.000000
H	-2.299634	-2.391812	-0.824837	-1.232656	3.257689	0.875286
H	-2.520464	-2.214163	0.902118	-1.232656	3.257689	-0.875286
H	0.109515	-2.570704	0.412381	1.199568	2.433052	0.000000
H	1.993895	2.203273	0.276497	0.881082	-2.693987	0.000000
H	-0.101827	3.473401	-0.108718	-1.550897	-2.953452	0.000000
H	-2.286312	2.339210	-0.360159	-3.098758	-1.028574	0.000000
H	3.100284	-0.429675	-1.392040	2.964148	-2.005492	-0.894368
H	3.675106	-1.623430	-0.196713	4.091918	-0.951054	0.000000
H	2.086797	-1.839228	-0.978115	2.964148	-2.005492	0.894368

Table S1. Continued. [B3LYP/6-311++G(d,p) optimized geometries of all prototropic tautomers of 4MOI].

	3*H*-s (C_1)			**3*H*-a (C_s)**		
N	2.401193	-0.763426	-0.080686	-1.999761	1.764265	0.000000
C	1.820637	-1.900708	0.039491	-1.043307	2.622321	0.000000
C	0.313958	-1.836852	0.151169	0.347001	2.026299	0.000000
C	-1.013132	0.491136	0.122037	0.782313	-0.583236	0.000000
C	-0.810999	1.879603	0.072652	0.134224	-1.826935	0.000000
C	0.466291	2.419835	-0.041522	-1.264402	-1.895580	0.000000
C	1.592210	1.597099	-0.116011	-2.055962	-0.749745	0.000000
C	1.383259	0.227132	-0.061403	-1.396228	0.476199	0.000000
C	0.099402	-0.345504	0.057966	0.000000	0.567485	0.000000
O	-2.315043	0.089973	0.279033	2.137035	-0.406385	0.000000
C	-2.742444	-1.127896	-0.322956	2.971940	-1.558202	0.000000
H	2.387235	-2.827218	0.054847	-1.245341	3.689495	0.000000
H	-0.026872	-2.265579	1.101684	0.924488	2.339887	0.878107
H	-0.161559	-2.417809	-0.646459	0.924488	2.339887	-0.878107
H	-1.683574	2.519411	0.124966	0.705053	-2.745733	0.000000
H	0.581681	3.497201	-0.077786	-1.734884	-2.872494	0.000000
H	2.593781	1.998191	-0.203918	-3.137295	-0.799438	0.000000
H	-3.831191	-1.113358	-0.283433	3.994461	-1.184156	0.000000
H	-2.420057	-1.184570	-1.367772	2.808799	-2.168925	0.894239
H	-2.382547	-2.005135	0.221873	2.808799	-2.168925	-0.894239
	5*H*-s (C_s)			**5*H*-a (C_s)**		
N	2.175372	1.217694	0.000000	2.649597	-0.044984	0.000148
C	1.277780	2.285319	0.000000	2.439532	-1.428445	-0.000094
C	-0.032139	1.896644	0.000000	1.116703	-1.779881	-0.000236
C	-0.893901	-0.587491	0.000000	-0.908507	-0.167705	-0.000086
C	-0.430059	-2.016503	0.000000	-1.299263	1.283399	0.000132
C	1.050855	-2.242748	0.000000	-0.167001	2.271779	0.000365
C	1.925893	-1.224792	0.000000	1.123636	1.895163	0.000375
C	1.437588	0.131268	0.000000	1.450479	0.493061	0.000162
C	0.000000	0.444797	0.000000	0.402889	-0.528225	-0.000073
O	-2.233771	-0.533010	0.000000	-1.853394	-1.127576	-0.000313
C	-2.911069	0.728492	0.000000	-3.242036	-0.790068	-0.000283
H	1.657021	3.298361	0.000000	3.294348	-2.091303	-0.000150
H	-0.888348	2.549701	0.000000	0.693842	-2.772073	-0.000422
H	-0.885194	-2.513712	0.867851	-1.943583	1.478579	-0.869556
H	1.385927	-3.273881	0.000000	-0.447171	3.319113	0.000525
H	-2.658568	1.300176	-0.895207	-3.516228	-0.224585	-0.895053
H	-3.972025	0.487456	0.000000	-3.770163	-1.741202	-0.000504
H	-2.658568	1.300176	0.895207	-3.516282	-0.224972	0.894715
H	-0.885194	-2.513712	-0.867851	-1.943696	1.478293	0.869799
H	2.997828	-1.384252	0.000000	1.930325	2.619165	0.000542

Table S1. Continued. [B3LYP/6-311++G(d,p) optimized geometries of all prototropic tautomers of 4MOI].

	6*H*-s (C_1)			**6*H*-a (C_s)**		
N	-2.494681	-0.688130	-0.157249	2.094721	1.725299	0.000000
C	-1.926876	-1.851396	0.039031	1.115050	2.594473	0.000000
C	-0.486171	-1.788824	0.232111	-0.213496	1.999309	0.000000
C	1.050563	0.310117	0.246424	-0.860210	-0.507184	0.000000
C	0.994619	1.654734	0.159330	-0.310753	-1.744741	0.000000
C	-0.285268	2.402833	-0.052222	1.174676	-1.963104	0.000000
C	-1.516729	1.571580	-0.187109	2.027439	-0.739686	0.000000
C	-1.441613	0.231291	-0.097293	1.457673	0.478795	0.000000
C	-0.165421	-0.463995	0.138967	0.000000	0.652184	0.000000
O	2.247709	-0.317174	0.507333	-2.189852	-0.216954	0.000000
C	2.800784	-1.060083	-0.583465	-3.110129	-1.300384	0.000000
H	-2.518017	-2.761280	0.051927	1.320662	3.659957	0.000000
H	0.166357	-2.627150	0.425080	-1.156242	2.524923	0.000000
H	1.909615	2.227392	0.260260	-0.927526	-2.633687	0.000000
H	-0.433835	3.120026	0.771298	1.455943	-2.584078	0.865801
H	-0.189744	3.047637	-0.940306	1.455943	-2.584078	-0.865801
H	-2.471537	2.062707	-0.342465	3.106944	-0.848017	0.000000
H	3.061078	-0.390861	-1.411111	-2.989869	-1.921619	0.894224
H	3.704115	-1.534851	-0.202348	-4.101723	-0.851222	0.000000
H	2.109742	-1.826864	-0.944892	-2.989869	-1.921619	-0.894224
	7*H*-s (C_s)			**7*H*-a (C_s)**		
N	2.199889	1.114802	0.000000	2.094721	1.725299	0.000000
C	1.351657	2.225594	0.000000	1.115050	2.594473	0.000000
C	0.025980	1.892427	0.000000	-0.213496	1.999309	0.000000
C	-0.940846	-0.560436	0.000000	-0.860210	-0.507184	0.000000
C	-0.533599	-1.962011	0.000000	-0.310753	-1.744741	0.000000
C	0.755307	-2.336090	0.000000	1.174676	-1.963104	0.000000
C	1.875809	-1.349509	0.000000	2.027439	-0.739686	0.000000
C	1.414685	0.069267	0.000000	1.457673	0.478795	0.000000
C	0.000000	0.444483	0.000000	0.000000	0.652184	0.000000
O	-2.276441	-0.443378	0.000000	-2.189852	-0.216954	0.000000
C	-2.895949	0.846976	0.000000	-3.110129	-1.300384	0.000000
H	1.777044	3.219890	0.000000	1.320662	3.659957	0.000000
H	-0.802020	2.580523	0.000000	-1.156242	2.524923	0.000000
H	-1.335912	-2.690284	0.000000	-0.927526	-2.633687	0.000000
H	1.009230	-3.390841	0.000000	1.455943	-2.584078	0.865801
H	2.523786	-1.533282	0.868328	1.455943	-2.584078	-0.865801
H	2.523786	-1.533282	-0.868328	3.106944	-0.848017	0.000000
H	-2.617691	1.406703	-0.895004	-2.989869	-1.921619	0.894224
H	-3.966495	0.653065	0.000000	-4.101723	-0.851222	0.000000
H	-2.617691	1.406703	0.895004	-2.989869	-1.921619	-0.894224

Table S1. Continued. [B3LYP/6-311++G(d,p) optimized geometries of all prototropic tautomers of 4MOI].[a]

	4*H*-sc' (C_1)			**4*H*-ac (C_1)**		
N	2.531966	0.092213	0.333477	-2.705833	-0.215370	-0.068634
C	2.423757	-1.180484	0.054182	-2.388327	-1.483395	-0.051191
C	1.088306	-1.574774	-0.398791	-0.951128	-1.732341	0.082248
C	-1.069908	-0.110858	-0.755667	1.029302	-0.031155	0.325435
C	-1.453856	1.304589	-0.383015	1.172535	1.454436	0.076396
C	-0.567606	2.215170	0.062372	0.115033	2.276582	-0.059824
C	0.825251	1.876260	0.309963	-1.252552	1.781206	-0.072218
C	1.256715	0.611551	0.087809	-1.480058	0.450866	0.035924
C	0.350217	-0.433598	-0.383996	-0.379378	-0.503102	0.151549
O	-2.035447	-1.074797	-0.336982	1.912801	-0.828684	-0.462153
C	-2.160678	-1.221959	1.074990	3.257318	-0.846448	-0.010456
H	-1.138156	-0.148994	-1.853989	1.293146	-0.177208	1.392149
H	3.270491	-1.849959	0.162369	-3.150452	-2.250940	-0.134648
H	0.775807	-2.572298	-0.673328	-0.467897	-2.698248	0.099341
H	-2.491989	1.571292	-0.551400	2.179594	1.855670	0.065418
H	-0.889862	3.231831	0.259996	0.273587	3.341643	-0.189903
H	1.506718	2.626685	0.695113	-2.078900	2.469225	-0.211658
H	-2.936101	-1.970972	1.233764	3.788882	-1.553780	-0.646967
H	-2.464506	-0.282754	1.552950	3.321060	-1.182740	1.033646
H	-1.225784	-1.567322	1.528961	3.742934	0.133554	-0.096893

	4*H*- sc'' (C_1)		
N	-2.510494	-0.696436	-0.138083
C	-1.927887	-1.860650	-0.032722
C	-0.480523	-1.777856	0.166510
C	1.078521	0.354638	0.352666
C	0.857219	1.833329	0.154093
C	-0.356052	2.385176	-0.022800
C	-1.559017	1.575205	-0.114690
C	-1.467466	0.227493	-0.023580
C	-0.183499	-0.449020	0.167326
O	2.178161	-0.013527	-0.479327
C	2.879948	-1.180785	-0.081743
H	1.392227	0.240045	1.408939
H	-2.498821	-2.781154	-0.091814
H	0.179882	-2.623925	0.284987
H	1.753404	2.442261	0.182411
H	-0.450330	3.460407	-0.125495
H	-2.521800	2.045619	-0.280394
H	3.786289	-1.217589	-0.686552
H	2.301569	-2.092998	-0.261478
H	3.158291	-1.134570	0.980230

[a] Abbreviations sc', sc'' and ac stand for synclinal and anticlinal orientations around the C11−O10−C4−C9 dihedral angle (see Table. S9)

Table S2. Optimized geometries (Cartesian coordinates, Å) of all prototropic tautomers of 4-methoxyindole (4MOI) optimized at the B3LYP/6-311++G(3df,3pd) level.

	1*H*-s (C_s)			**1*H*-a (C_s)**		
N	-2.093037	1.216696	0.000000	1.965538	1.662807	0.000000
C	-1.221898	2.281027	0.000000	0.968842	2.616933	0.000000
C	0.059462	1.818347	0.000000	-0.249047	2.000590	0.000000
C	0.924817	-0.691546	0.000000	-0.832086	-0.543669	0.000000
C	0.447606	-1.996733	0.000000	-0.250415	-1.802606	0.000000
C	-0.920447	-2.280126	0.000000	1.150658	-1.944363	0.000000
C	-1.863910	-1.269352	0.000000	1.998110	-0.855293	0.000000
C	-1.383648	0.037817	0.000000	1.400233	0.408303	0.000000
C	0.000000	0.376401	0.000000	0.000000	0.591179	0.000000
O	2.284128	-0.583552	0.000000	-2.170454	-0.300083	0.000000
C	2.922512	0.680114	0.000000	-3.057048	-1.404704	0.000000
H	-3.093988	1.284518	0.000000	2.950423	1.854158	0.000000
H	-1.586721	3.293498	0.000000	1.214226	3.664866	0.000000
H	0.928676	2.447170	0.000000	-1.207971	2.486748	0.000000
H	1.173013	-2.797675	0.000000	-0.861973	-2.691282	0.000000
H	-1.241093	-3.313001	0.000000	1.567425	-2.942439	0.000000
H	-2.924010	-1.481728	0.000000	3.072425	-0.977186	0.000000
H	3.989184	0.470862	0.000000	-4.059698	-0.986210	0.000000
H	2.673108	1.256103	0.892794	-2.922740	-2.022929	0.891067
H	2.673108	1.256103	-0.892794	-2.922740	-2.022929	-0.891067
	2*H*-s (C_1)			**2*H*-a (C_s)**		
N	2.476584	-0.411504	0.159188	2.110621	-1.564717	0.000000
C	2.005363	-1.769215	-0.033825	1.095993	-2.602056	0.000000
C	0.524556	-1.712894	-0.221188	-0.238819	-1.930928	0.000000
C	-1.077738	0.303883	-0.248817	-0.858066	0.556982	0.000000
C	-1.058669	1.656226	-0.167263	-0.280594	1.789515	0.000000
C	0.169429	2.385918	0.052339	1.157314	1.935630	0.000000
C	1.371071	1.779149	0.191394	2.019578	0.892040	0.000000
C	1.423048	0.344264	0.094294	1.468349	-0.436117	0.000000
C	0.170221	-0.410451	-0.134348	0.000000	-0.602167	0.000000
O	-2.243611	-0.364946	-0.508543	-2.183102	0.291176	0.000000
C	-2.797402	-1.10262	0.581673	-3.086913	1.386331	0.000000
H	2.292917	-2.387746	0.824889	1.231112	-3.251719	0.873001
H	2.513869	-2.213906	-0.897715	1.231112	-3.251719	-0.873001
H	-0.111377	-2.5637	-0.407144	-1.194724	-2.429612	0.000000
H	-1.987225	2.199947	-0.272265	-0.881194	2.685748	0.000000
H	0.104313	3.464654	0.109906	1.545947	2.945991	0.000000
H	2.282744	2.334091	0.357977	3.090948	1.027978	0.000000
H	-3.10489	-0.427064	1.383647	-2.955250	2.003459	-0.891508
H	-3.668463	-1.621107	0.190012	-4.083283	0.954655	0.000000
H	-2.088363	-1.830638	0.979177	-2.955250	2.003459	0.891508

Table S2. Continued. [B3LYP/6-311++G(3df,3pd) optimized geometries of all prototropic tautomers of 4MOI].

	3*H*-s (C_1)			**3*H*-a (C_s)**		
N	-2.389362	-0.777258	0.076097	-1.994566	1.760539	0.000000
C	-1.802390	-1.908043	-0.037600	-1.041563	2.617234	0.000000
C	-0.299756	-1.833905	-0.143781	0.345588	2.023244	0.000000
C	1.008313	0.499078	-0.114244	0.780845	-0.581072	0.000000
C	0.795615	1.883157	-0.068636	0.134390	-1.822004	0.000000
C	-0.482572	2.412397	0.039418	-1.260375	-1.890600	0.000000
C	-1.600231	1.584305	0.109979	-2.050646	-0.748246	0.000000
C	-1.381283	0.219631	0.058146	-1.392914	0.474522	0.000000
C	-0.096158	-0.343438	-0.054994	0.000000	0.566854	0.000000
O	2.310485	0.109824	-0.262170	2.131986	-0.407348	0.000000
C	2.740907	-1.119052	0.303960	2.963648	-1.556415	0.000000
H	-2.360188	-2.837087	-0.052277	-1.242491	3.682137	0.000000
H	0.046384	-2.263093	-1.088878	0.922060	2.336971	0.875395
H	0.177348	-2.407693	0.654152	0.922060	2.336971	-0.875395
H	1.660828	2.529101	-0.117229	0.704885	-2.737891	0.000000
H	-0.605432	3.486494	0.073592	-1.729448	-2.865421	0.000000
H	-2.602489	1.977871	0.193206	-3.129468	-0.798733	0.000000
H	3.827375	-1.096988	0.276756	3.985329	-1.187345	0.000000
H	2.409990	-1.211361	1.340735	2.799653	-2.166387	0.891359
H	2.393172	-1.979806	-0.268875	2.799653	-2.166387	-0.891359
	5*H*-s (C_s)			**5*H*-a (C_s)**		
N	2.168351	1.216573	0.000000	2.074138	1.639055	0.000000
C	1.271805	2.281469	0.000000	1.071406	2.610465	0.000000
C	-0.033826	1.891405	0.000000	-0.190302	2.089158	0.000000
C	-0.891633	-0.587018	0.000000	-0.822469	-0.415582	0.000000
C	-0.426564	-2.012650	0.000000	-0.254394	-1.803168	0.000000
C	1.050950	-2.237010	0.000000	1.241272	-1.902720	0.000000
C	1.922314	-1.221127	0.000000	2.036737	-0.823736	0.000000
C	1.434003	0.131194	0.000000	1.448224	0.486396	0.000000
C	0.000000	0.442898	0.000000	0.000000	0.663940	0.000000
O	-2.227460	-0.531538	0.000000	-2.152009	-0.229392	0.000000
C	-2.904496	0.725322	0.000000	-3.048233	-1.337126	0.000000
H	1.647859	3.293168	0.000000	1.347789	3.653815	0.000000
H	-0.889652	2.540935	0.000000	-1.125572	2.621609	0.000000
H	-0.880404	-2.510003	0.865096	-0.648764	-2.347768	0.866870
H	1.385899	-3.265546	0.000000	1.652594	-2.903132	0.000000
H	-2.652940	1.297061	-0.892238	-2.921986	-1.952053	0.892048
H	-3.963419	0.486496	0.000000	-4.044433	-0.906216	0.000000
H	-2.652940	1.297061	0.892238	-2.921986	-1.952053	-0.892048
H	-0.880404	-2.510003	-0.865096	-0.648764	-2.347768	-0.866870
H	2.991907	-1.379778	0.000000	3.114775	-0.910447	0.000000

Table S2. Continued. [B3LYP/6-311++G(3df,3pd) optimized geometries of all prototropic tautomers of 4MOI].

	6*H*-s (C_1)			**6*H*-a (C_s)**		
N	2.488954	-0.688619	0.155725	-2.089322	-1.722005	0.000000
C	1.921781	-1.849097	-0.037247	-1.112766	-2.589747	0.000000
C	0.484439	-1.784769	-0.229483	0.212460	-1.995659	0.000000
C	-1.047041	0.309841	-0.245750	0.858490	0.505165	0.000000
C	-0.990305	1.650962	-0.158389	0.310053	1.739404	0.000000
C	0.286541	2.396827	0.053190	-1.171458	1.957867	0.000000
C	1.514664	1.567114	0.185602	-2.021876	0.737623	0.000000
C	1.439531	0.230751	0.095200	-1.454255	-0.477676	0.000000
C	0.166026	-0.462982	-0.139352	0.000000	-0.651802	0.000000
O	-2.241569	-0.315317	-0.505574	2.185165	0.218704	0.000000
C	-2.799943	-1.054985	0.579266	3.101507	1.300060	0.000000
H	2.510133	-2.757979	-0.048319	-1.317529	-3.652965	0.000000
H	-0.168876	-2.620254	-0.418502	1.152981	-2.520414	0.000000
H	-1.902597	2.223824	-0.256266	0.926359	2.625507	0.000000
H	0.434284	3.114929	-0.766108	-1.452540	2.578153	0.862986
H	0.191926	3.038821	0.940121	-1.452540	2.578153	-0.862986
H	2.466885	2.057899	0.340551	-3.098774	0.847000	0.000000
H	-3.068224	-0.386390	1.401451	2.980103	1.920589	0.891368
H	-3.696825	-1.533667	0.194970	4.092842	0.856386	0.000000
H	-2.110981	-1.816289	0.948399	2.980103	1.920589	-0.891368
	7*H*-s (C_s)			**7*H*-a (C_s)**		
N	2.193040	1.113868	0.000000	-2.092776	-1.572322	0.000000
C	1.345987	2.221666	0.000000	-1.113609	-2.573719	0.000000
C	0.024322	1.887083	0.000000	0.160086	-2.081452	0.000000
C	-0.938625	-0.559986	0.000000	0.853505	0.413054	0.000000
C	-0.530237	-1.958379	0.000000	0.318832	1.767090	0.000000
C	0.755135	-2.330355	0.000000	-1.003666	2.004160	0.000000
C	1.872461	-1.345847	0.000000	-2.026649	0.921373	0.000000
C	1.411165	0.069220	0.000000	-1.437082	-0.443909	0.000000
C	0.000000	0.442562	0.000000	0.000000	-0.657008	0.000000
O	-2.270028	-0.441908	0.000000	2.173747	0.177809	0.000000
C	-2.889287	0.844069	0.000000	3.115639	1.248635	0.000000
H	1.768147	3.214769	0.000000	-1.418209	-3.608972	0.000000
H	-0.803327	2.571769	0.000000	1.083676	-2.633646	0.000000
H	-1.329093	-2.686872	0.000000	1.004291	2.600624	0.000000
H	1.009743	-3.382316	0.000000	-1.358621	3.026767	0.000000
H	2.519649	-1.529633	0.865537	-2.687980	1.051839	0.865097
H	2.519649	-1.529633	-0.865537	-2.687980	1.051839	-0.865097
H	-2.611802	1.403697	-0.892062	3.014959	1.865852	0.893437
H	-3.957745	0.652509	0.000000	4.092029	0.774279	0.000000
H	-2.611802	1.403697	0.892062	3.014959	1.865852	-0.893437

Table S2. Continued. [B3LYP/6-311++G(3df,3pd) optimized geometries of all prototropic tautomers of 4MOI].[a]

	4*H*-sc' (C_1)			**4*H*-ac (C_1)**		
N	2.527078	0.087080	0.332381	-2.700402	-0.212477	-0.068977
C	2.416481	-1.182467	0.055076	-2.385943	-1.477893	-0.051024
C	1.083002	-1.572162	-0.396626	-0.952361	-1.727350	0.082240
C	-1.067561	-0.107988	-0.752843	1.026821	-0.033701	0.324131
C	-1.447198	1.305224	-0.379863	1.170906	1.449287	0.077024
C	-0.561685	2.211182	0.063814	0.117664	2.270130	-0.059649
C	0.827839	1.870898	0.308629	-1.247486	1.777853	-0.072459
C	1.255973	0.609215	0.086964	-1.476683	0.451715	0.034952
C	0.350028	-0.432240	-0.384014	-0.380379	-0.502284	0.150957
O	-2.032258	-1.067902	-0.337766	1.908984	-0.830181	-0.458049
C	-2.162526	-1.219294	1.068937	3.251227	-0.843723	-0.012446
H	-1.133834	-0.141569	-1.849548	1.287481	-0.177313	1.389644
H	3.259101	-1.853160	0.163916	-3.146862	-2.243293	-0.134093
H	0.768136	-2.566962	-0.668841	-0.471133	-2.691607	0.100541
H	-2.482966	1.572596	-0.545064	2.176083	1.848257	0.066392
H	-0.881539	3.225742	0.262261	0.277421	3.332620	-0.188070
H	1.508796	2.618379	0.693466	-2.070721	2.465764	-0.211835
H	-2.938528	-1.964591	1.225091	3.783131	-1.551291	-0.644141
H	-2.464034	-0.283455	1.548864	3.319221	-1.172856	1.030871
H	-1.232729	-1.567540	1.524869	3.733733	0.134303	-0.104438

	4*H*-sc'' (C_1)		
N	-2.506366	-0.700891	-0.126103
C	-1.920567	-1.861251	-0.036927
C	-0.475225	-1.774806	0.149320
C	1.074913	0.356207	0.341604
C	0.849438	1.831010	0.140413
C	-0.362992	2.378565	-0.024928
C	-1.562458	1.568160	-0.104187
C	-1.468140	0.224487	-0.014108
C	-0.183718	-0.448806	0.161317
O	2.174214	-0.016828	-0.480249
C	2.887421	-1.165232	-0.063151
H	1.382572	0.249666	1.398281
H	-2.486841	-2.781588	-0.099860
H	0.188605	-2.617220	0.251142
H	1.742031	2.441173	0.161687
H	-0.460084	3.451088	-0.126588
H	-2.525051	2.035915	-0.262278
H	3.788644	-1.210054	-0.670546
H	2.317405	-2.084457	-0.216295
H	3.171541	-1.093665	0.993057

[a] Abbreviations sc', sc'' and ac stand for synclinal and anticlinal orientations around the C11−O10−C4−C9 dihedral angle (see Table. S9)

Table S3. Optimized geometries (Cartesian coordinates, Å) of the syn and anti conformers of 1*H*-4MOI calculated at the MP2/6-311++G(3df,3pd) level.

	1*H*-s (C_s)			**1*H*-a (C_s)**		
N	-2.123053	1.143754	0.000000	1.974566	1.646079	0.000000
C	-1.297855	2.235603	0.000000	0.993246	2.607347	0.000000
C	0.010134	1.816779	0.000000	-0.240304	1.998024	0.000000
C	0.956768	-0.664262	0.000000	-0.843930	-0.532862	0.000000
C	0.518261	-1.982469	0.000000	-0.274391	-1.798567	0.000000
C	-0.843547	-2.312972	0.000000	1.129296	-1.954443	0.000000
C	-1.818644	-1.330372	0.000000	1.990409	-0.872009	0.000000
C	-1.374526	-0.007719	0.000000	1.401345	0.397510	0.000000
C	0.000000	0.380360	0.000000	0.000000	0.594554	0.000000
O	2.311626	-0.514539	0.000000	-2.177541	-0.268633	0.000000
C	2.854271	0.791567	0.000000	-3.039719	-1.390691	0.000000
H	-3.127391	1.173875	0.000000	2.962570	1.828773	0.000000
H	-1.700344	3.234882	0.000000	1.251186	3.653443	0.000000
H	0.851210	2.484136	0.000000	-1.195522	2.493704	0.000000
H	1.271920	-2.758275	0.000000	-0.894031	-2.682579	0.000000
H	-1.131152	-3.356037	0.000000	1.536646	-2.957057	0.000000
H	-2.873153	-1.572634	0.000000	3.064193	-1.004909	0.000000
H	3.931786	0.660551	0.000000	-4.048972	-0.993080	0.000000
H	2.558157	1.342221	0.892712	-2.886707	-2.002482	0.890668
H	2.558157	1.342221	-0.892712	-2.886707	-2.002482	-0.890668

Table S4. Optimized geometries (Cartesian coordinates, Å) of all prototropic tautomers of 5-methoxyindole (5MOI) optimized at the B3LYP/6-311++G(d,p) level.

	1*H*-s (C_s)			**1*H*-a (C_s)**		
N	2.226173	1.595869	0.000000	-2.141862	1.721655	0.000000
C	1.584078	2.818221	0.000000	-1.331919	2.838464	0.000000
C	0.228430	2.627878	0.000000	-0.017370	2.449922	0.000000
C	-1.150376	0.410731	0.000000	1.033186	0.055747	0.000000
C	-1.013588	-0.973081	0.000000	0.689025	-1.288580	0.000000
C	0.261820	-1.575692	0.000000	-0.665444	-1.695509	0.000000
C	1.416292	-0.797748	0.000000	-1.691318	-0.768403	0.000000
C	1.278288	0.586673	0.000000	-1.349946	0.587419	0.000000
C	0.000000	1.208764	0.000000	0.000000	1.014698	0.000000
O	-2.188512	-1.686762	0.000000	1.593215	-2.321458	0.000000
C	-2.127459	-3.102728	0.000000	2.974459	-2.003001	0.000000
H	3.222907	1.463563	0.000000	-3.147426	1.733407	0.000000
H	2.153068	3.734886	0.000000	-1.761444	3.827985	0.000000
H	-0.517913	3.406589	0.000000	0.834756	3.111584	0.000000
H	-2.144150	0.842245	0.000000	2.065959	0.377674	0.000000
H	0.360011	-2.652461	0.000000	-0.875863	-2.757846	0.000000
H	2.391758	-1.271719	0.000000	-2.725893	-1.093869	0.000000
H	-3.161432	-3.445571	0.000000	3.502184	-2.955835	0.000000
H	-1.622135	-3.486316	0.894048	3.255499	-1.433780	0.893785
H	-1.622135	-3.486316	-0.894048	3.255499	-1.433780	-0.893785
	2*H*-s (C_s)			**2*H*-a (C_s)**		
N	-2.329118	1.432535	0.000000	-2.277635	1.557368	0.000000
C	-1.719207	2.754056	0.000000	-1.493336	2.784486	0.000000
C	-0.233290	2.571943	0.000000	-0.046042	2.396701	0.000000
C	1.182668	0.423822	0.000000	1.069935	0.077612	0.000000
C	1.048237	-0.932767	0.000000	0.736407	-1.243633	0.000000
C	-0.263029	-1.566014	0.000000	-0.650045	-1.691791	0.000000
C	-1.412697	-0.846029	0.000000	-1.689456	-0.827906	0.000000
C	-1.334285	0.594050	0.000000	-1.409624	0.590457	0.000000
C	0.000000	1.231426	0.000000	0.000000	1.039482	0.000000
O	2.198608	-1.671432	0.000000	1.612860	-2.284190	0.000000
C	2.139309	-3.092497	0.000000	3.003942	-1.989011	0.000000
H	-2.074354	3.316923	0.874933	-1.767425	3.389892	0.875418
H	-2.074354	3.316923	-0.874933	-1.767425	3.389892	-0.875418
H	0.493483	3.372769	0.000000	0.784345	3.089836	0.000000
H	2.171923	0.865005	0.000000	2.098114	0.413170	0.000000
H	-0.321143	-2.646608	0.000000	-0.806680	-2.764367	0.000000
H	-2.383562	-1.326561	0.000000	-2.717876	-1.167996	0.000000
H	3.175643	-3.426524	0.000000	3.514203	-2.950422	0.000000
H	1.640547	-3.478081	-0.895339	3.286313	-1.423218	0.894221
H	1.640547	-3.478081	0.895339	3.286313	-1.423218	-0.894221

Table S4. Continued. [B3LYP/6-311++G(d,p) optimized geometries of all prototropic tautomers of 5MOI].

	3*H*-s (C_s)			**3*H*-a (C_s)**		
N	-2.305923	1.583458	0.000000	-2.210187	1.744857	0.000000
C	-1.722558	2.728108	0.000000	-1.457600	2.786000	0.000000
C	-0.207973	2.668484	0.000000	0.028500	2.489451	0.000000
C	1.133296	0.389350	0.000000	1.009910	0.029368	0.000000
C	0.976050	-1.007938	0.000000	0.634060	-1.321843	0.000000
C	-0.300296	-1.584685	0.000000	-0.721415	-1.689597	0.000000
C	-1.442705	-0.776814	0.000000	-1.722910	-0.726899	0.000000
C	-1.283667	0.599198	0.000000	-1.350441	0.615106	0.000000
C	0.000000	1.177099	0.000000	0.000000	0.984210	0.000000
O	2.141434	-1.722478	0.000000	1.521049	-2.362007	0.000000
C	2.073341	-3.141368	0.000000	2.911165	-2.073292	0.000000
H	-2.292568	3.652345	0.000000	-1.876638	3.787637	0.000000
H	0.214231	3.167543	0.880192	0.523062	2.916913	0.880411
H	0.214231	3.167543	-0.880192	0.523062	2.916913	-0.880411
H	2.135957	0.801009	0.000000	2.051387	0.323391	0.000000
H	-0.417397	-2.659796	0.000000	-0.961056	-2.745986	0.000000
H	-2.432442	-1.217561	0.000000	-2.769019	-1.008759	0.000000
H	3.105460	-3.488256	0.000000	3.415601	-3.038245	0.000000
H	1.564793	-3.517909	-0.894254	3.204451	-1.512407	0.894510
H	1.564793	-3.517909	0.894254	3.204451	-1.512407	-0.894510
	4*H*-s (C_s)			**4*H*-a (C_s)**		
N	-2.319032	1.657771	0.000000	-1.965316	-2.094301	0.000000
C	-1.663840	2.795462	0.000000	-2.934121	-1.204418	0.000000
C	-0.216447	2.638248	0.000000	-2.463707	0.169644	0.000000
C	1.227108	0.435393	0.000000	0.000000	1.097489	0.000000
C	0.930700	-1.040785	0.000000	1.379158	0.486509	0.000000
C	-0.333263	-1.544630	0.000000	1.585820	-0.858414	0.000000
C	-1.475065	-0.665794	0.000000	0.489709	-1.781183	0.000000
C	-1.321551	0.685819	0.000000	-0.800508	-1.337481	0.000000
C	0.000000	1.290882	0.000000	-1.099379	0.081592	0.000000
O	2.066473	-1.767352	0.000000	2.471449	1.286621	0.000000
C	1.974063	-3.191822	0.000000	2.334585	2.706692	0.000000
H	-2.191754	3.743024	0.000000	-3.974045	-1.512219	0.000000
H	0.510646	3.438671	0.000000	-3.083711	1.055768	0.000000
H	1.860182	0.646583	0.871310	-0.090279	1.758493	0.872507
H	1.860182	0.646583	-0.871310	-0.090279	1.758493	-0.872507
H	-0.506341	-2.611967	0.000000	2.604734	-1.225235	0.000000
H	-2.471904	-1.093851	0.000000	0.691994	-2.847012	0.000000
H	2.999647	-3.554897	0.000000	3.350886	3.095433	0.000000
H	1.455271	-3.548179	-0.894810	1.813489	3.060425	0.894317
H	1.455271	-3.548179	0.894810	1.813489	3.060425	-0.894317

Table S4. Continued. [B3LYP/6-311++G(d,p) optimized geometries of all prototropic tautomers of 5MOI].[a]

	6*H*-s (C_1)			**6*H*-a (C_s)**		
N	-2.697205	0.952877	0.030155	1.993933	-2.072179	0.000000
C	-3.230325	-0.243631	0.050551	2.932466	-1.160206	0.000000
C	-2.269692	-1.335057	0.032198	2.442100	0.210628	0.000000
C	0.311413	-1.208852	-0.029772	0.000000	1.059275	0.000000
C	1.328660	-0.316522	-0.061537	-1.274064	0.597512	0.000000
C	1.106088	1.172881	-0.068321	-1.618474	-0.865021	0.000000
C	-0.324158	1.615418	-0.032550	-0.458244	-1.808619	0.000000
C	-1.316974	0.713188	-0.005146	0.798743	-1.338014	0.000000
C	-1.039774	-0.736860	-0.003834	1.078909	0.109731	0.000000
O	2.600680	-0.801665	-0.152184	-2.397637	1.356996	0.000000
C	3.706677	0.033902	0.176361	-2.256281	2.774687	0.000000
H	-4.308708	-0.365182	0.078942	3.979766	-1.445874	0.000000
H	-2.501737	-2.390144	0.045842	3.048819	1.104894	0.000000
H	0.536247	-2.269142	-0.032702	0.220837	2.118720	0.000000
H	1.636236	1.634368	0.777333	-2.261616	-1.069434	0.867791
H	1.587232	1.601460	-0.960458	-2.261616	-1.069434	-0.867791
H	-0.533312	2.679760	-0.025060	-0.655585	-2.875298	0.000000
H	4.590293	-0.591473	0.061663	-3.268129	3.175321	0.000000
H	3.648475	0.385633	1.211951	-1.724920	3.115276	-0.894353
H	3.788778	0.891111	-0.498835	-1.724920	3.115276	0.894353
	7*H*-s (C_s)			**7*H*-a (C_1)**		
N	2.335369	-1.481100	0.000000	-2.667926	0.675427	-0.190999
C	3.211650	-0.366324	0.000000	-3.072283	-0.680206	-0.109286
C	2.564328	0.831193	0.000000	-2.035027	-1.544565	0.070095
C	0.000000	1.193256	0.000000	0.474181	-0.922092	0.259783
C	-1.281418	0.504414	0.000000	1.405493	0.194977	0.244205
C	-1.371905	-0.845056	0.000000	0.991173	1.469473	0.093637
C	-0.154388	-1.724753	0.000000	-0.452883	1.832041	-0.067065
C	1.136860	-0.979790	0.000000	-1.374321	0.659127	-0.070450
C	1.158960	0.493192	0.000000	-0.856691	-0.709720	0.101476
O	-2.329585	1.381800	0.000000	2.738802	-0.074210	0.476000
C	-3.645322	0.846312	0.000000	3.406393	-0.792227	-0.563004
H	4.278370	-0.543291	0.000000	-4.124571	-0.915327	-0.190365
H	2.997984	1.819286	0.000000	-2.076921	-2.618944	0.162484
H	-0.026927	2.278376	0.000000	0.874430	-1.918417	0.422217
H	-2.333388	-1.340832	0.000000	1.727250	2.265005	0.107924
H	-0.185650	-2.397573	0.868536	-0.748741	2.529883	0.729367
H	-0.185650	-2.397573	-0.868536	-0.583615	2.408093	-0.993991
H	-4.317990	1.702094	0.000000	4.423124	-0.965792	-0.212960
H	-3.825112	0.239079	0.894101	3.430467	-0.202934	-1.486464
H	-3.825112	0.239079	-0.894101	2.927432	-1.756729	-0.765565

Table S4. Continued. [B3LYP/6-311++G(d,p) optimized geometries of all prototropic tautomers of 5MOI].[a]

	5*H*-sc' (C_1)			**5*H*-ac (C_1)**		
N	2.456921	0.874988	0.376032	-2.602116	0.952543	-0.115247
C	3.019111	-0.423772	0.306674	-3.210938	-0.326909	-0.116060
C	2.128742	-1.383332	-0.057284	-2.324555	-1.350769	-0.006076
C	-0.382452	-1.036265	-0.580201	0.247716	-1.147789	0.178387
C	-1.454644	0.007277	-0.764344	1.379135	-0.172625	0.335839
C	-1.072423	1.405336	-0.344355	1.017726	1.276938	0.119401
C	0.181244	1.748644	0.001073	-0.253820	1.698547	0.002444
C	1.202878	0.731232	0.050893	-1.323195	0.730732	0.003590
C	0.871179	-0.680477	-0.251217	-1.020514	-0.715403	0.084828
O	-2.720333	-0.407247	-0.251045	2.462686	-0.623770	-0.475261
C	-2.772492	-0.540616	1.167237	3.742509	-0.159562	-0.075171
H	-1.630275	0.055218	-1.852406	1.687577	-0.257000	1.399605
H	4.067774	-0.548483	0.539210	-4.286902	-0.389776	-0.203259
H	2.308575	-2.440139	-0.181874	-2.534839	-2.409017	0.016971
H	-0.670821	-2.065061	-0.777637	0.518970	-2.198726	0.188175
H	-1.869694	2.139866	-0.386217	1.837450	1.986017	0.109252
H	0.448827	2.767363	0.258935	-0.501668	2.747065	-0.119290
H	-3.788722	-0.853226	1.405336	4.468413	-0.666569	-0.710550
H	-2.559354	0.409051	1.670785	3.945097	-0.411323	0.974903
H	-2.068953	-1.299692	1.529148	3.854850	0.922727	-0.210071

	5*H*-sc'' (C_1)		
N	-2.697954	0.690249	-0.105910
C	-3.093527	-0.670811	-0.110496
C	-2.054463	-1.539512	-0.006535
C	0.452900	-0.929535	0.176239
C	1.415595	0.221395	0.323929
C	0.823310	1.587062	0.108104
C	-0.498929	1.802891	0.002997
C	-1.399922	0.676654	0.007904
C	-0.868238	-0.703511	0.083633
O	2.570247	0.096208	-0.505618
C	3.538885	-0.832968	-0.045605
H	1.746933	0.198919	1.383338
H	-4.145824	-0.905076	-0.194762
H	-2.092828	-2.617883	0.013424
H	0.864312	-1.933927	0.197521
H	1.539239	2.400093	0.075678
H	-0.909429	2.798997	-0.116774
H	4.388136	-0.756845	-0.724344
H	3.170364	-1.866110	-0.062284
H	3.869127	-0.589560	0.973503

[a] Abbreviations sc', sc'' and ac stand for synclinal and anticlinal orientations around the C11−O10−C5−C6 dihedral angle (see Table S10).

Table S5. Optimized geometries (Cartesian coordinates, Å) of all prototropic tautomers of 5-methoxyindole (5MOI) optimized at the B3LYP/6-311++G(3df,3pd) level.

	1*H*-s (C_s)			**1*H*-a (C_s)**		
N	2.221458	1.590960	0.000000	-2.137281	1.716748	0.000000
C	1.582291	2.810125	0.000000	-1.329913	2.830358	0.000000
C	0.229545	2.622218	0.000000	-0.018184	2.443884	0.000000
C	-1.147718	0.410644	0.000000	1.030214	0.055019	0.000000
C	-1.012984	-0.970110	0.000000	0.687859	-1.286356	0.000000
C	0.259795	-1.571127	0.000000	-0.664072	-1.691422	0.000000
C	1.411392	-0.795843	0.000000	-1.687211	-0.766726	0.000000
C	1.274985	0.585222	0.000000	-1.347006	0.585656	0.000000
C	0.000000	1.206759	0.000000	0.000000	1.012033	0.000000
O	-2.183092	-1.683312	0.000000	1.590975	-2.314555	0.000000
C	-2.122600	-3.095420	0.000000	2.968299	-1.996502	0.000000
H	3.215638	1.458216	0.000000	-3.140366	1.728368	0.000000
H	2.150468	3.724611	0.000000	-1.758417	3.817844	0.000000
H	-0.514195	3.400140	0.000000	0.831675	3.104567	0.000000
H	-2.138632	0.842920	0.000000	2.060975	0.374902	0.000000
H	0.356406	-2.645412	0.000000	-0.875577	-2.751119	0.000000
H	2.384582	-1.268842	0.000000	-2.719549	-1.091011	0.000000
H	-3.153205	-3.440493	0.000000	3.498188	-2.945272	0.000000
H	-1.617383	-3.478090	0.891210	3.248160	-1.427367	0.890943
H	-1.617383	-3.478090	-0.891210	3.248160	-1.427367	-0.890943
	2*H*-s (C_s)			**2*H*-a (C_s)**		
N	-2.322867	1.429666	0.000000	-2.271254	1.554768	0.000000
C	-1.715453	2.748809	0.000000	-1.488761	2.779316	0.000000
C	-0.233113	2.565845	0.000000	-0.045442	2.390078	0.000000
C	1.179758	0.423062	0.000000	1.066590	0.075970	0.000000
C	1.046965	-0.930273	0.000000	0.734406	-1.241973	0.000000
C	-0.261868	-1.561747	0.000000	-0.649874	-1.687602	0.000000
C	-1.408427	-0.844273	0.000000	-1.686175	-0.825935	0.000000
C	-1.331046	0.592446	0.000000	-1.406634	0.588943	0.000000
C	0.000000	1.229054	0.000000	0.000000	1.036500	0.000000
O	2.192309	-1.668856	0.000000	1.609552	-2.278656	0.000000
C	2.133565	-3.086089	0.000000	2.996659	-1.983758	0.000000
H	-2.069919	3.310516	0.872645	-1.761903	3.383618	0.873154
H	-2.069919	3.310516	-0.872645	-1.761903	3.383618	-0.873154
H	0.492099	3.364727	0.000000	0.783653	3.080851	0.000000
H	2.166368	0.864594	0.000000	2.093055	0.408772	0.000000
H	-0.318743	-2.639788	0.000000	-0.808104	-2.757556	0.000000
H	-2.376686	-1.324595	0.000000	-2.712264	-1.165354	0.000000
H	3.166526	-3.422444	0.000000	3.509108	-2.941197	0.000000
H	1.634793	-3.470673	-0.892450	3.278048	-1.418056	0.891356
H	1.634793	-3.470673	0.892450	3.278048	-1.418056	-0.891356

Table S5. Continued. [B3LYP/6-311++G(3df,3pd) optimized geometries of all prototropic tautomers of 5MOI].

	3*H*-s (C_s)			**3*H*-a (C_s)**		
N	-2.299273	1.581829	0.000000	-2.203027	1.743347	0.000000
C	-1.717463	2.723430	0.000000	-1.451530	2.781092	0.000000
C	-0.206563	2.662942	0.000000	0.030507	2.483115	0.000000
C	1.130082	0.388216	0.000000	1.006033	0.027488	0.000000
C	0.974530	-1.006087	0.000000	0.631317	-1.320677	0.000000
C	-0.299247	-1.580327	0.000000	-0.721545	-1.685398	0.000000
C	-1.438722	-0.774572	0.000000	-1.719884	-0.724311	0.000000
C	-1.280411	0.597798	0.000000	-1.347480	0.613710	0.000000
C	0.000000	1.174368	0.000000	0.000000	0.980928	0.000000
O	2.135048	-1.720814	0.000000	1.516907	-2.356734	0.000000
C	2.066132	-3.135630	0.000000	2.903113	-2.068816	0.000000
H	-2.284866	3.646410	0.000000	-1.867433	3.781408	0.000000
H	0.215807	3.160691	0.877434	0.525565	2.908623	0.877650
H	0.215807	3.160691	-0.877434	0.525565	2.908623	-0.877650
H	2.129992	0.800479	0.000000	2.045595	0.318996	0.000000
H	-0.415353	-2.652932	0.000000	-0.963209	-2.738897	0.000000
H	-2.426014	-1.214846	0.000000	-2.763715	-1.005244	0.000000
H	3.094530	-3.485788	0.000000	3.409582	-3.029892	0.000000
H	1.557295	-3.510919	-0.891379	3.195399	-1.507980	0.891619
H	1.557295	-3.510919	0.891379	3.195399	-1.507980	-0.891619
	4*H*-s (C_s)			**4*H*-a (C_s)**		
N	-2.312396	1.655530	0.000000	-1.959291	-2.090569	0.000000
C	-1.658861	2.790573	0.000000	-2.926653	-1.203632	0.000000
C	-0.215213	2.632406	0.000000	-2.457252	0.166912	0.000000
C	1.224177	0.434554	0.000000	0.000000	1.093761	0.000000
C	0.929185	-1.039101	0.000000	1.376741	0.486165	0.000000
C	-0.332010	-1.540555	0.000000	1.583365	-0.855540	0.000000
C	-1.470622	-0.663450	0.000000	0.490316	-1.776550	0.000000
C	-1.317952	0.684509	0.000000	-0.796753	-1.335385	0.000000
C	0.000000	1.288474	0.000000	-1.096416	0.079757	0.000000
O	2.060113	-1.765658	0.000000	2.462996	1.286761	0.000000
C	1.966579	-3.185865	0.000000	2.325295	2.702631	0.000000
H	-2.184574	3.736612	0.000000	-3.964353	-1.510531	0.000000
H	0.511381	3.430034	0.000000	-3.075400	1.051393	0.000000
H	1.856515	0.645638	0.868441	-0.089778	1.754064	0.869603
H	1.856515	0.645638	-0.868441	-0.089778	1.754064	-0.869603
H	-0.503825	-2.605411	0.000000	2.599812	-1.222064	0.000000
H	-2.465240	-1.090603	0.000000	0.693011	-2.839855	0.000000
H	2.988347	-3.552271	0.000000	3.337699	3.094562	0.000000
H	1.447524	-3.541177	-0.891907	1.803995	3.054774	0.891561
H	1.447524	-3.541177	0.891907	1.803995	3.054774	-0.891561

Table S5. Continued. [B3LYP/6-311++G(3df,3pd) optimized geometries of all prototropic tautomers of 5MOI].

	6*H*-s (C_s)			**6*H*-a (C_s)**		
N	2.376760	-1.580108	0.000000	1.987950	-2.068788	0.000000
C	3.186986	-0.554319	0.000000	2.924777	-1.159824	0.000000
C	2.526494	0.736591	0.000000	2.435484	0.207869	0.000000
C	0.000000	1.249370	0.000000	0.000000	1.055523	0.000000
C	-1.204961	0.638078	0.000000	-1.271643	0.597162	0.000000
C	-1.355620	-0.856036	0.000000	-1.615750	-0.862387	0.000000
C	-0.081996	-1.636230	0.000000	-0.458936	-1.804469	0.000000
C	1.100111	-1.009596	0.000000	0.794742	-1.336402	0.000000
C	1.189612	0.461051	0.000000	1.075897	0.107921	0.000000
O	-2.315087	1.422617	0.000000	-2.389876	1.357618	0.000000
C	-3.611021	0.844117	0.000000	-2.246241	2.770959	0.000000
H	4.260168	-0.701576	0.000000	3.969849	-1.444672	0.000000
H	3.009892	1.700090	0.000000	3.040474	1.100395	0.000000
H	0.044976	2.330012	0.000000	0.219679	2.112636	0.000000
H	-1.955382	-1.162041	0.866280	-2.258099	-1.066565	0.865050
H	-1.955382	-1.162041	-0.866280	-2.258099	-1.066565	-0.865050
H	-0.143643	-2.716707	0.000000	-0.657885	-2.868334	0.000000
H	-4.305954	1.678695	0.000000	-3.253805	3.175637	0.000000
H	-3.784469	0.237613	0.891496	-1.714361	3.109966	-0.891464
H	-3.784469	0.237613	-0.891496	-1.714361	3.109966	0.891464
	7*H*-s (C_s)			**7*H*-a (C_1)**		
N	2.331306	-1.474928	0.000000	2.663743	0.669747	0.187742
C	3.205325	-0.362081	0.000000	3.064436	-0.684005	0.106142
C	2.558183	0.831363	0.000000	2.027106	-1.543043	-0.070196
C	0.000000	1.190036	0.000000	-0.474414	-0.916157	-0.255249
C	-1.279198	0.503093	0.000000	-1.402438	0.199899	-0.240003
C	-1.367955	-0.842795	0.000000	-0.985835	1.469853	-0.089691
C	-0.153212	-1.720307	0.000000	0.455724	1.829317	0.068352
C	1.134809	-0.976528	0.000000	1.372880	0.657347	0.069820
C	1.156357	0.493096	0.000000	0.853432	-0.707308	-0.100327
O	-2.326554	1.375624	0.000000	-2.733269	-0.064948	-0.469740
C	-3.637705	0.839556	0.000000	-3.400965	-0.798997	0.552239
H	4.270044	-0.536543	0.000000	4.113731	-0.922267	0.185105
H	2.989769	1.817781	0.000000	2.065752	-2.615205	-0.162109
H	-0.025863	2.272826	0.000000	-0.875638	-1.909779	-0.414665
H	-2.327175	-1.337244	0.000000	-1.717289	2.266285	-0.101201
H	-0.184252	-2.392385	0.865690	0.750910	2.525989	-0.725604
H	-0.184252	-2.392385	-0.865690	0.588718	2.404016	0.992574
H	-4.312905	1.690199	0.000000	-4.416457	-0.962949	0.201739
H	-3.815847	0.232328	0.891230	-3.422718	-0.229774	1.485255
H	-3.815847	0.232328	-0.891230	-2.926607	-1.766396	0.736115

Table S5. Continued. [B3LYP/6-311++G(3df,3pd) optimized geometries of all prototropic tautomers of 5MOI].

	5*H*-sc' (C_1)			**5*H*-ac (C_1)**		
N	2.452351	0.872130	0.374620	-2.595448	0.950658	-0.117332
C	3.013272	-0.424254	0.305252	-3.204053	-0.326074	-0.117680
C	2.123953	-1.380308	-0.056246	-2.320084	-1.346711	-0.005949
C	-0.380176	-1.032339	-0.579709	0.245350	-1.145084	0.181419
C	-1.450930	0.008334	-0.762200	1.376713	-0.173712	0.335884
C	-1.068443	1.402965	-0.342604	1.015248	1.273428	0.123411
C	0.181283	1.744628	0.003186	-0.252055	1.694399	0.003362
C	1.200757	0.729969	0.051426	-1.319602	0.729798	0.002771
C	0.869256	-0.678455	-0.248966	-1.018648	-0.713150	0.085267
O	-2.713489	-0.405098	-0.251735	2.456596	-0.621329	-0.474733
C	-2.771465	-0.541476	1.161745	3.734361	-0.160219	-0.078857
H	-1.623149	0.057888	-1.848808	1.685330	-0.258277	1.397165
H	4.059663	-0.550407	0.536173	-4.277477	-0.389790	-0.206042
H	2.302396	-2.434998	-0.180346	-2.529913	-2.402629	0.017563
H	-0.668434	-2.058568	-0.776551	0.513749	-2.194257	0.193300
H	-1.864192	2.135512	-0.381908	1.833386	1.980491	0.114084
H	0.447651	2.760976	0.261455	-0.497953	2.740979	-0.117200
H	-3.785738	-0.853754	1.397163	4.458581	-0.662593	-0.715602
H	-2.560488	0.404077	1.668206	3.940128	-0.413960	0.967311
H	-2.071296	-1.299240	1.524851	3.846147	0.920018	-0.209165

	5*H*-sc'' (C_1)		
N	-2.691170	0.687520	-0.110024
C	-3.085860	-0.671150	-0.112570
C	-2.048965	-1.535969	-0.004778
C	0.451179	-0.925790	0.182763
C	1.413576	0.222354	0.324959
C	0.820408	1.584909	0.111080
C	-0.497815	1.799209	0.002737
C	-1.396392	0.675551	0.006224
C	-0.865839	-0.700974	0.085560
O	2.563001	0.095453	-0.504496
C	3.529950	-0.832694	-0.051372
H	1.745895	0.201093	1.381645
H	-4.135250	-0.906815	-0.198588
H	-2.086225	-2.611976	0.017028
H	0.861673	-1.927764	0.206892
H	1.533243	2.397549	0.080812
H	-0.907207	2.793220	-0.116292
H	4.375736	-0.759198	-0.730758
H	3.160933	-1.862835	-0.066541
H	3.863933	-0.592211	0.964327

[a] Abbreviations sc', sc'' and ac stand for synclinal and anticlinal orientations around the C11−O10−C5−C6 dihedral angle (see Table S10).

Table S6. Optimized geometries (Cartesian coordinates, Å) of the syn and anti conformers of 1*H*-5MOI calculated at the MP2/6-311++G(3df,3pd) level.

	1*H*-s (C_s)			**1*H*-a (C_s)**		
N	1.947171	-1.981163	0.000000	-2.141861	1.693777	0.000000
C	2.965589	-0.997984	0.000000	-1.349735	2.816196	0.000000
C	2.486666	0.278482	0.000000	-0.026924	2.436737	0.000000
C	0.000000	0.997691	0.000000	1.039125	0.059293	0.000000
C	-1.364318	0.499674	0.000000	0.698856	-1.285599	0.000000
C	-1.628160	-0.828570	0.000000	-0.652661	-1.699745	0.000000
C	-0.555368	-1.870322	0.000000	-1.686599	-0.783357	0.000000
C	0.827777	-1.319052	0.000000	-1.347951	0.573473	0.000000
C	1.050659	0.134854	0.000000	0.000000	1.010957	0.000000
O	-2.440237	1.353726	0.000000	1.601951	-2.310576	0.000000
C	-2.230579	2.759232	0.000000	2.965678	-1.942412	0.000000
H	3.998618	-1.317620	0.000000	-3.146524	1.694963	0.000000
H	3.052412	1.197569	0.000000	-1.791192	3.798979	0.000000
H	0.176553	2.066903	0.000000	0.817039	3.106400	0.000000
H	-2.662448	-1.151951	0.000000	2.068646	0.385889	0.000000
H	-0.686590	-2.533653	0.867318	-0.853641	-2.762570	0.000000
H	-0.686590	-2.533653	-0.867318	-2.717851	-1.113245	0.000000
H	-3.225386	3.202005	0.000000	3.527707	-2.870347	0.000000
H	-1.694233	3.092352	-0.895463	3.217257	-1.362580	0.890364
H	-1.694233	3.092352	0.895463	3.217257	-1.362580	-0.890364

Table S7. Optimized geometries (Cartesian coordinates, Å) of the syn and anti conformers of 3*H*-5MOI optimized at the MP2 and CBS-QB3 levels.

MP2/6-311++G(d,p)

	3*H*-s (C_s)			**3*H*-a (C_s)**		
N	-2.318556	1.569796	0.000000	-2.224972	1.731972	0.000000
C	-1.725258	2.725128	0.000000	-1.459153	2.781055	0.000000
C	-0.212375	2.670188	0.000000	0.025383	2.487562	0.000000
C	1.143562	0.393960	0.000000	1.020667	0.029684	0.000000
C	0.990647	-1.005765	0.000000	0.644997	-1.325024	0.000000
C	-0.290411	-1.591754	0.000000	-0.715731	-1.698714	0.000000
C	-1.440127	-0.787122	0.000000	-1.726322	-0.738917	0.000000
C	-1.282262	0.596249	0.000000	-1.351928	0.609145	0.000000
C	0.000000	1.181606	0.000000	0.000000	0.984493	0.000000
O	2.159576	-1.714350	0.000000	1.528105	-2.367838	0.000000
C	2.050412	-3.129670	0.000000	2.907240	-2.034206	0.000000
H	-2.301006	3.648202	0.000000	-1.883395	3.782590	0.000000
H	0.202877	3.166461	0.886329	0.512957	2.913128	0.886501
H	0.202877	3.166461	-0.886329	0.512957	2.913128	-0.886501
H	2.147596	0.810354	0.000000	2.062006	0.333313	0.000000
H	-0.405347	-2.669487	0.000000	-0.947768	-2.759792	0.000000
H	-2.431256	-1.232107	0.000000	-2.774438	-1.024174	0.000000
H	3.073292	-3.505012	0.000000	3.441264	-2.983894	0.000000
H	1.529558	-3.487784	-0.895283	3.177731	-1.462935	0.895575
H	1.529558	-3.487784	0.895283	3.177731	-1.462935	-0.895575

MP2/6-311++G(3df,3pd)

	3*H*-s (C_s)			**3*H*-a (C_s)**		
N	1.947171	-1.981163	0.000000	-2.141861	1.693777	0.000000
C	2.965589	-0.997984	0.000000	-1.349735	2.816196	0.000000
C	2.486666	0.278482	0.000000	-0.026924	2.436737	0.000000
C	0.000000	0.997691	0.000000	1.039125	0.059293	0.000000
C	-1.364318	0.499674	0.000000	0.698856	-1.285599	0.000000
C	-1.628160	-0.828570	0.000000	-0.652661	-1.699745	0.000000
C	-0.555368	-1.870322	0.000000	-1.686599	-0.783357	0.000000
C	0.827777	-1.319052	0.000000	-1.347951	0.573473	0.000000
C	1.050659	0.134854	0.000000	0.000000	1.010957	0.000000
O	-2.440237	1.353726	0.000000	1.601951	-2.310576	0.000000
C	-2.230579	2.759232	0.000000	2.965678	-1.942412	0.000000
H	3.998618	-1.317620	0.000000	-3.146524	1.694963	0.000000
H	3.052412	1.197569	0.000000	-1.791192	3.798979	0.000000
H	0.176553	2.066903	0.000000	0.817039	3.106400	0.000000
H	-2.662448	-1.151951	0.000000	2.068646	0.385889	0.000000
H	-0.686590	-2.533653	0.867318	-0.853641	-2.762570	0.000000
H	-0.686590	-2.533653	-0.867318	-2.717851	-1.113245	0.000000
H	-3.225386	3.202005	0.000000	3.527707	-2.870347	0.000000
H	-1.694233	3.092352	-0.895463	3.217257	-1.362580	0.890364
H	-1.694233	3.092352	0.895463	3.217257	-1.362580	-0.890364

Table S7. Continued. Optimized geometries (Cartesian coordinates, Å) of the syn and anti conformers of 3*H*-5MOI optimized at the MP2 and CBS-QB3 levels.

CBS-QB3

	3*H*-s (C_s)			**3*H*-a (C_s)**		
N	-2.307154	1.581793	0.000000	-2.211796	1.743179	0.000000
C	-1.723064	2.725459	0.000000	-1.458939	2.783417	0.000000
C	-0.207879	2.668121	0.000000	0.028169	2.489479	0.000000
C	1.132519	0.388903	0.000000	1.009993	0.030292	0.000000
C	0.976330	-1.008471	0.000000	0.635885	-1.321170	0.000000
C	-0.300447	-1.584703	0.000000	-0.719988	-1.688775	0.000000
C	-1.441587	-0.776882	0.000000	-1.721269	-0.727297	0.000000
C	-1.283463	0.599169	0.000000	-1.350169	0.615026	0.000000
C	0.000000	1.176690	0.000000	0.000000	0.984100	0.000000
O	2.141866	-1.720028	0.000000	1.520363	-2.361607	0.000000
C	2.073622	-3.138259	0.000000	2.909758	-2.071882	0.000000
H	-2.294031	3.649296	0.000000	-1.879351	3.784664	0.000000
H	0.214867	3.166745	0.880146	0.523266	2.916384	0.880352
H	0.214867	3.166745	-0.880146	0.523266	2.916384	-0.880352
H	2.136197	0.797656	0.000000	2.051167	0.325171	0.000000
H	-0.417131	-2.659787	0.000000	-0.955195	-2.746018	0.000000
H	-2.432483	-1.214592	0.000000	-2.767785	-1.006914	0.000000
H	3.105840	-3.484821	0.000000	3.414447	-3.036662	0.000000
H	1.565421	-3.516865	-0.893988	3.204607	-1.510778	0.894233
H	1.565421	-3.516865	0.893988	3.204607	-1.510778	-0.894233

Table S8. Optimized geometries (Cartesian coordinates, Å) of the methoxy-indolyl radicals (4MOI• and 5MOI•) optimized at the UB3LYP/6-311++G(d,p) level.

4-methoxy-indolyl (4MOI•) radical

	4MOI•-s (C_s)			**4MOI•-a (C_s)**		
N	-2.152574	1.320037	0.000000	2.040650	1.753643	0.000000
C	-1.257137	2.293349	0.000000	1.052013	2.622441	0.000000
C	0.088372	1.823185	0.000000	-0.250346	2.006357	0.000000
C	0.883120	-0.696911	0.000000	-0.812585	-0.531518	0.000000
C	0.347792	-2.010045	0.000000	-0.188071	-1.793609	0.000000
C	-1.014580	-2.226393	0.000000	1.202081	-1.886872	0.000000
C	-1.926952	-1.144693	0.000000	2.033368	-0.746329	0.000000
C	-1.416637	0.133480	0.000000	1.424581	0.489384	0.000000
C	0.000000	0.399547	0.000000	0.000000	0.618731	0.000000
O	2.233169	-0.657538	0.000000	-2.149575	-0.337167	0.000000
C	2.925684	0.587818	0.000000	-3.018908	-1.468874	0.000000
H	-1.562069	3.332750	0.000000	1.245356	3.688556	0.000000
H	0.966196	2.448924	0.000000	-1.207749	2.506350	0.000000
H	1.048494	-2.835532	0.000000	-0.777393	-2.700012	0.000000
H	-1.389879	-3.243113	0.000000	1.655545	-2.871681	0.000000
H	-2.997606	-1.307611	0.000000	3.112534	-0.836883	0.000000
H	3.983860	0.333495	0.000000	-4.028578	-1.063047	0.000000
H	2.687852	1.167556	0.895834	2.040650	1.753643	0.000000
H	-2.152574	1.320037	0.000000	1.052013	2.622441	0.000000

5-methoxy-indolyl (5MOI•) radical

	5MOI•-s (C_s)			**5MOI•-a (C_s)**		
N	2.334060	-1.559187	0.000000	-1.933524	-2.072995	0.000000
C	3.197547	-0.529775	0.000000	-2.924117	-1.186662	0.000000
C	2.561959	0.724721	0.000000	-2.463423	0.157856	0.000000
C	0.000000	1.207728	0.000000	0.000000	1.013193	0.000000
C	-1.258836	0.545672	0.000000	1.331349	0.539615	0.000000
C	-1.337895	-0.844995	0.000000	1.598881	-0.831535	0.000000
C	-0.160780	-1.621697	0.000000	0.558135	-1.772812	0.000000
C	1.066223	-0.987137	0.000000	-0.747747	-1.318431	0.000000
C	1.145198	0.438206	0.000000	-1.025754	0.071476	0.000000
O	-2.330566	1.382671	0.000000	2.423776	1.356817	0.000000
C	-3.638588	0.821837	0.000000	2.232666	2.765470	0.000000
H	4.264576	-0.710145	0.000000	-3.957526	-1.508717	0.000000
H	3.034498	1.696902	0.000000	-3.069483	1.053633	0.000000
H	0.014530	2.291472	0.000000	-0.218985	2.072867	0.000000
H	-2.296911	-1.343740	0.000000	2.634296	-1.148883	0.000000
H	-0.219249	-2.704048	0.000000	0.774599	-2.834727	0.000000
H	-4.323676	1.667530	0.000000	3.231159	3.199126	0.000000
H	-3.808312	0.213807	0.894559	1.695227	3.097054	0.895034
H	-3.808312	0.213807	-0.894559	1.695227	3.097054	-0.895034
H	2.334060	-1.559187	0.000000	-1.933524	-2.072995	0.000000

Table S9. Structures and relative electronic energies (ΔE, kJ mol^{-1}) of 4MOI isomers optimized at the B3LYP/6-311++G(d,p) level.

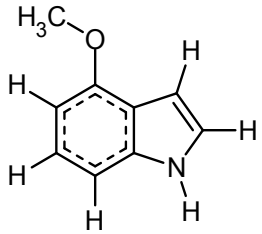
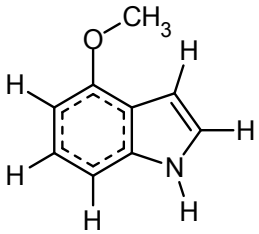
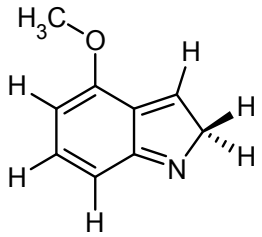
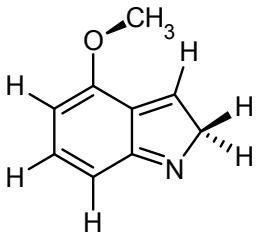
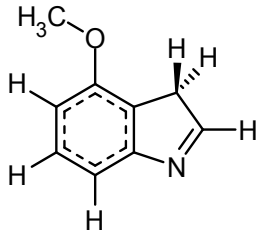
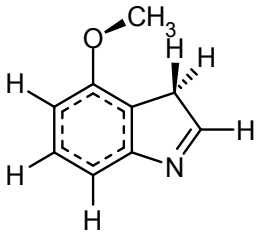
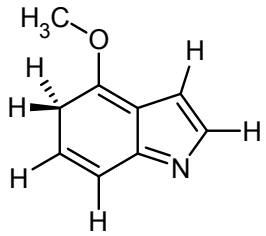
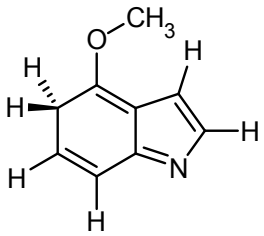
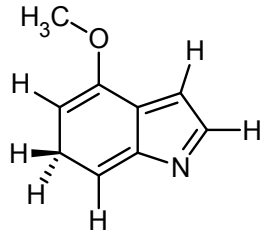
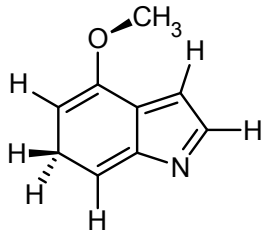
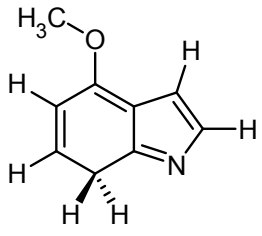
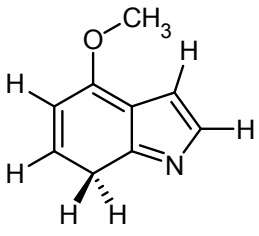
Name	Structure	ΔE	Name	Structure	ΔE
1*H*-a		0.00	**1*H*-s**		15.24
2*H*-a		112.59	**2*H*-s**		131.40
3*H*-a		40.45	**3*H*-s**		54.80
5*H*-a		126.86	**5*H*-s**		117.62
6*H*-a		128.00	**6*H*-s**		142.91
7*H*-a		133.17	**7*H*-s**		123.52

Table S9. Continued.

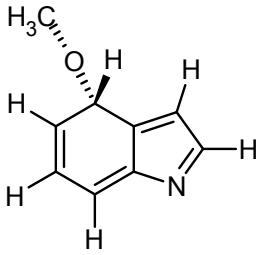
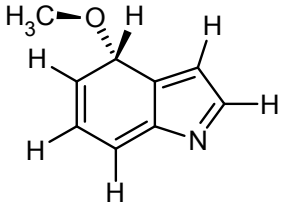
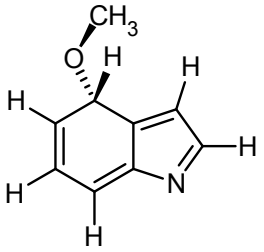
Name	Structure	ΔE
4*H*-sc' C11-O10-C4-C9 = 64.0°		173.55
4*H*-ac C11-O10-C4-C9 = −156.5°		177.27
4*H*-sc'' C11-O10-C4-C9 = −77.4°		178.74

Table S10. Structures and relative electronic energies (ΔE, kJ mol^{-1}) of 5MOI isomers optimized at the B3LYP/6-311++G(d,p) level.

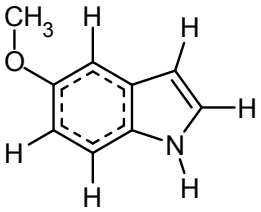
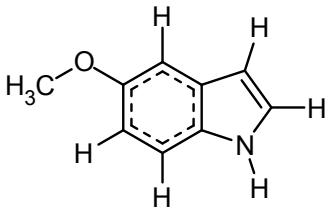
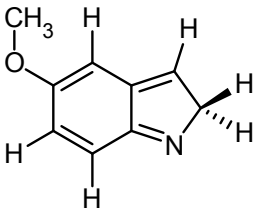
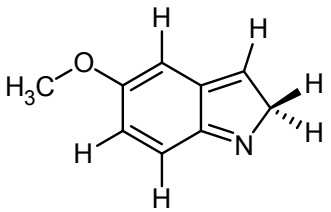
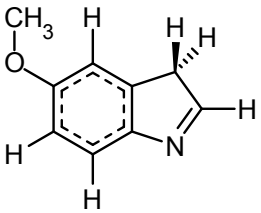
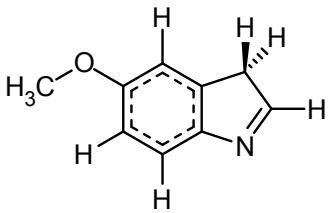
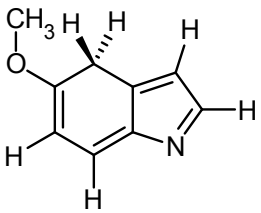
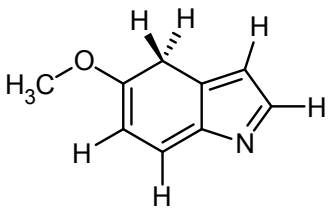
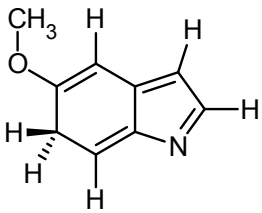
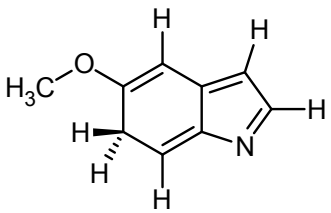
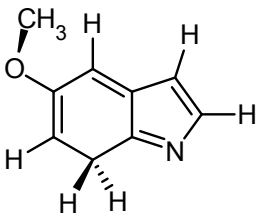
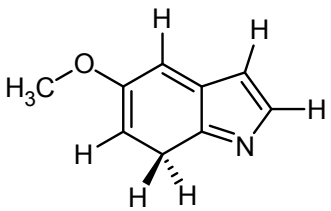
Name	Structure	ΔE	Name	Structure	ΔE
1*H*-a		0.00	**1*H*-s**		3.58
2*H*-a		106.14	**2*H*-s**		120.38
3*H*-a		38.85	**3*H*-s**		37.87
4*H*-a		130.22	**4*H*-s**		116.31
6*H*-a		112.94	**6*H*-s**		129.71
7*H*-a		153.07	**7*H*-s**		139.36

Table S10. Continued.

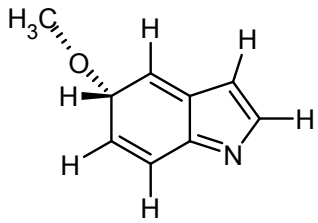
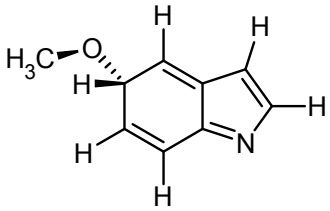
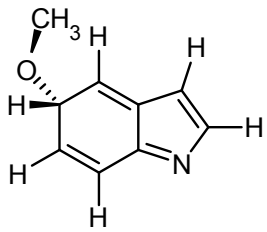
Name	Structure	ΔE
5*H*-sc'' C11-O10-C4-C6 = −65.6°		167.90
5*H*-sc' C11-O10-C4-C6 = 74.0°		170.74
5*H*-ac C11-O10-C4-C6 = 154.5°		171.37

Table S11. Structures and relative electronic energies (ΔE, kJ mol^{-1}) of 4MOI$^{\bullet}$ radicals optimized at the B3LYP/6-311++G(d,p) level and at the B3LYP/6-311++G(3df,3pd) level (in parentheses).

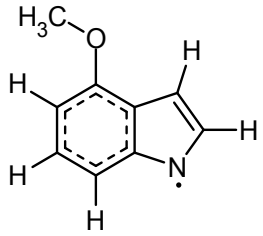
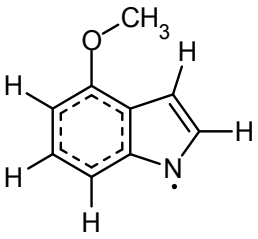
Name	Structure	ΔE
4MOI$^{\bullet}$-a		0.00 (0.00)
4MOI$^{\bullet}$-s		5.48 (5.47)

Table S12. Structures and relative electronic energies (ΔE, kJ mol^{-1}) of 5MOI$^{\bullet}$ radicals optimized at the B3LYP/6-311++G(d,p) level and at the B3LYP/6-311++G(3df,3pd) level (in parentheses).

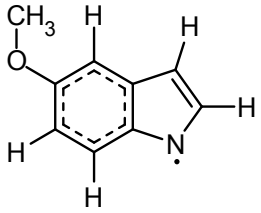
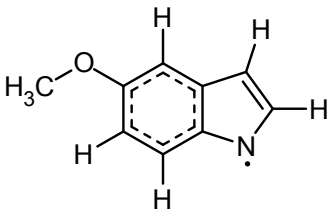
Name	Structure	ΔE
5MOI$^{\bullet}$-a		5.53 (5.40)
5MOI$^{\bullet}$-s		0.00 (0.00)

Table S13. Results of the harmonic vibrational calculations carried out at the B3LYP/6-31++G(d,p) level for the most relevant isomers of 4-methoxyindole (1*H*-a and 3*H*-a) and for the 4-methoxyindolyl radical (4MOI•-a) [ν = wavenumber, cm^{-1}; A^{th} = infrared intensity, km mol^{-1}].

1*H*-a		3*H*-a		4MOI•-a	
ν	A^{th}	ν	A^{th}	ν	A^{th}
3492.0	75.1	3142.1	6.6	3171.4	6.2
3199.8	2.0	3137.1	7.3	3147.4	7.2
3179.4	0.0	3108.1	9.4	3135.5	6.6
3143.1	8.9	3101.1	14.1	3127.4	14.2
3121.4	19.7	3071.2	20.3	3111.2	7.4
3104.7	2.8	3005.8	35.8	3080.4	15.8
3068.1	22.5	2988.8	3.8	3022.0	28.2
3000.2	38.7	2965.1	7.4	2958.3	59.1
2943.6	63.6	2947.4	56.6	1592.1	64.7
1616.8	17.9	1616.6	34.9	1565.7	145.0
1589.6	78.8	1598.6	92.5	1479.3	112.5
1510.3	22.7	1576.8	14.4	1472.2	47.0
1505.6	80.0	1487.3	66.0	1462.7	10.2
1474.3	43.8	1474.6	57.7	1448.7	6.0
1459.2	8.7	1462.0	9.0	1440.9	24.4
1444.5	0.5	1444.7	8.0	1386.7	3.3
1430.0	18.2	1429.8	11.3	1350.3	4.8
1412.7	16.3	1395.9	12.2	1315.4	31.1
1360.5	89.8	1345.8	13.8	1289.1	174.9
1345.8	5.8	1303.0	20.3	1266.3	133.5
1274.1	76.5	1263.2	208.3	1193.0	105.2
1239.9	114.6	1257.0	14.3	1175.9	16.3
1203.5	9.1	1208.8	15.3	1165.3	3.2
1179.9	1.2	1180.8	1.1	1155.5	22.5
1166.9	8.8	1168.1	5.2	1141.2	0.7
1143.4	0.7	1151.6	0.3	1073.5	48.5
1128.3	59.3	1144.7	0.7	1041.7	1.5
1079.0	107.5	1109.1	0.8	965.0	6.3
1062.4	8.9	1081.2	114.5	934.3	30.2
1057.3	5.5	1059.0	5.9	925.2	1.6
962.3	7.3	952.2	4.1	884.4	7.2
917.0	0.6	945.5	4.0	872.9	2.8
895.9	9.0	941.0	1.8	860.4	1.1
849.5	2.1	916.6	6.8	829.7	8.7
826.5	3.6	859.4	1.8	769.9	19.9
820.0	1.7	857.8	0.4	751.7	39.9
783.0	1.5	812.5	0.5	723.7	29.3
724.5	138.0	784.7	41.2	672.6	16.2
704.6	10.9	761.5	7.5	629.0	0.2
680.1	7.6	709.1	24.7	611.8	1.3
622.4	0.8	667.4	8.7	543.1	0.1
620.2	3.1	619.3	3.7	502.4	10.7
589.7	0.5	617.7	0.0	485.1	0.5
528.8	0.3	517.6	0.2	460.0	1.8
502.2	5.7	500.0	4.3	344.0	1.0
470.7	1.6	473.5	5.0	268.1	1.9
375.4	64.9	400.4	0.1	222.1	0.6
341.4	0.1	338.7	0.7	208.2	3.1
280.5	4.1	271.4	0.6	202.0	1.7
224.3	0.0	218.7	4.5	157.7	7.2
218.5	7.8	197.8	2.6	82.6	2.0
198.7	4.2	197.5	0.0		
165.8	2.6	166.3	8.9		
77.0	7.9	77.0	2.3		

Table S14. Results of the harmonic vibrational calculations carried out at the B3LYP/6-31++G(d,p) level for the most relevant isomers of 5-methoxyindole (1*H*-a, 1*H*-s, 3*H*-a and 3*H*-s) and for the 5-methoxyindolyl radical (5MOI•-a and 5MOI•-s) [ν = wavenumber, cm^{-1}; A^{th} = infrared intensity, km mol^{-1}].

1*H*-a		1*H*-s		3*H*-a		3*H*-s		5MOI•-a		5MOI•-s	
ν	A^{th}	ν	A^{th}	ν	A^{th}	ν	A^{th}	ν	A^{th}	ν	A^{th}
3493.1	76.9	3494.4	75.4	3134.4	5.5	3144.5	8.1	3155.9	13.2	3162.6	12.6
3189.5	2.1	3189.2	2.7	3131.7	7.9	3124.2	3.2	3136.6	8.4	3149.3	8.8
3169.4	2.2	3171.0	1.2	3120.3	4.0	3119.9	6.5	3135.9	5.0	3139.3	8.5
3137.1	7.6	3144.5	6.5	3103.9	10.7	3102.4	11.0	3135.1	3.9	3124.4	1.0
3132.3	5.2	3125.1	4.1	3069.7	22.8	3069.7	22.6	3121.7	3.9	3122.1	7.2
3105.3	10.4	3105.8	11.6	2996.7	40.6	3000.7	38.8	3073.2	21.1	3077.0	19.7
3064.5	26.9	3062.5	27.3	2992.7	3.8	2993.9	3.8	3002.7	37.0	3010.4	32.3
2989.3	43.8	2988.8	45.5	2965.4	7.8	2966.8	7.6	2944.3	58.1	2950.4	64.3
2935.9	56.6	2935.3	69.4	2940.6	55.5	2943.5	63.8	1594.4	16.7	1594.3	17.0
1627.2	42.7	1635.9	31.9	1618.5	57.4	1631.0	40.8	1563.9	73.9	1580.4	66.5
1587.9	28.7	1583.0	51.8	1592.3	11.3	1589.9	48.3	1473.3	29.5	1475.1	0.7
1513.2	19.5	1519.4	21.3	1573.3	55.6	1576.3	42.7	1470.5	117.2	1464.7	169.6
1481.6	74.0	1481.1	6.5	1475.6	2.3	1478.0	0.1	1463.7	9.7	1463.0	10.2
1475.2	1.4	1472.4	103.9	1473.0	123.1	1468.2	125.2	1451.5	0.8	1440.5	20.1
1459.2	8.6	1460.5	8.2	1461.9	9.3	1461.5	9.1	1430.4	84.1	1434.1	143.5
1455.8	72.4	1454.9	20.5	1449.3	16.6	1440.6	34.0	1374.9	14.8	1373.2	61.7
1440.8	38.4	1438.4	47.8	1432.4	23.5	1439.7	6.2	1344.9	11.0	1351.8	10.0
1415.1	7.0	1417.1	6.2	1395.3	20.4	1396.9	21.3	1325.2	14.3	1346.6	21.6
1343.0	12.0	1345.5	21.2	1323.6	3.1	1338.9	40.0	1270.7	176.0	1269.8	105.1
1324.3	12.6	1315.8	45.9	1300.2	10.4	1301.8	11.2	1237.2	155.1	1220.1	165.9
1281.4	60.9	1273.7	62.6	1281.9	72.9	1279.0	46.8	1178.8	1.5	1186.1	6.2
1239.3	10.1	1239.2	25.3	1255.6	172.4	1239.3	186.2	1158.5	9.7	1162.3	23.6
1218.6	136.0	1214.2	113.8	1209.5	10.8	1209.2	2.2	1143.4	0.6	1144.0	0.7
1188.2	16.3	1184.2	10.5	1184.4	23.0	1185.4	8.5	1141.0	24.8	1142.6	24.9
1152.8	97.3	1151.0	126.4	1176.4	21.7	1175.5	25.4	1123.5	23.9	1113.3	0.2
1145.1	0.7	1141.9	0.7	1144.8	0.7	1142.8	0.8	1055.8	90.3	1060.5	126.7
1120.5	27.7	1134.3	17.5	1130.8	24.9	1131.3	29.2	1027.7	35.5	1025.6	33.8
1085.3	4.4	1088.2	26.9	1114.3	1.4	1117.7	1.5	931.1	1.9	932.9	77.3
1066.3	11.0	1065.9	5.1	1084.5	35.1	1097.4	49.1	931.0	2.4	916.7	6.9
1035.7	40.0	1037.9	40.8	1032.2	35.7	1032.6	38.0	890.6	58.6	899.1	99.5
935.2	8.5	924.1	1.5	946.0	1.1	950.6	0.7	867.3	4.3	878.4	0.0
912.9	0.0	889.2	10.8	940.6	1.0	923.1	2.8	856.3	59.4	870.3	33.0
893.1	12.1	886.7	1.5	920.1	2.1	916.9	8.7	838.0	43.1	863.1	27.1
842.3	15.8	857.1	25.8	913.2	14.6	907.9	1.9	818.2	17.8	791.2	32.4
826.4	17.5	840.6	2.3	862.9	0.7	863.9	32.0	763.5	16.2	766.7	24.9
791.9	21.8	781.2	7.5	843.0	54.5	859.3	2.0	731.7	7.3	735.3	2.6
789.6	25.2	771.8	19.1	820.0	11.3	806.1	32.7	726.5	11.2	731.3	22.8
745.5	10.4	744.9	26.1	770.9	11.9	765.6	0.0	691.9	4.1	710.6	18.9
738.9	5.1	732.7	10.6	764.5	0.6	762.4	2.4	580.3	1.7	593.3	0.7
704.4	67.5	706.9	60.9	733.6	3.1	730.3	0.0	549.8	14.2	568.9	112.9
617.1	0.4	620.6	8.0	726.7	0.0	730.1	10.0	536.0	0.2	547.3	0.0
597.4	1.5	617.1	0.2	597.6	5.9	622.3	13.6	454.8	2.3	538.5	5.5
591.0	6.9	585.3	6.5	589.3	3.5	591.7	3.2	433.0	104.1	421.8	6.1
515.6	2.1	535.9	4.2	514.6	3.1	535.8	5.4	415.7	6.3	384.9	24.8
450.8	3.3	423.0	5.9	445.7	7.6	451.7	2.3	352.7	4.4	359.1	2.8
420.2	7.3	412.1	0.2	445.7	2.3	419.1	2.8	335.4	0.7	329.5	1.2
361.6	4.3	358.7	2.4	420.0	3.2	413.8	0.1	227.3	1.9	246.1	3.7
360.9	30.2	352.1	11.2	362.9	5.0	355.0	0.5	209.1	9.3	220.4	6.4
348.1	41.5	330.1	58.8	306.2	1.1	303.2	1.9	206.0	0.0	205.3	4.8
233.6	0.1	243.6	4.1	226.5	0.1	232.7	1.5	138.4	0.8	156.5	3.0
216.8	9.0	220.3	3.4	207.2	0.5	219.2	4.7	69.8	1.4	78.6	2.6
207.9	3.6	206.2	8.7	203.0	10.6	201.6	6.1				
144.8	0.3	145.6	0.4	139.0	1.2	145.0	3.5				
77.6	6.9	51.8	5.7	75.6	1.2	66.3	4.0				

Table S15. Second-order perturbation energies [$\Delta E^{(2)}$, kcal mol^{-1}] corresponding to the conjugative donor-acceptor interactions within the indole ring, calculated for the different tautomers of 4MOI at the B3LYP/6-311++G(d,p) level.[a]

Donor	Acceptor	- $\Delta E^{(2)}$	Donor	Acceptor	- $\Delta E^{(2)}$
		4MOI			
1*H*-a			2*H*-a		
BD (2) C2 - C3	BD*(2) C8 - C9	14.54	BD (2) N1 - C8	BD*(2) C3 - C9	10.48
BD (2) C4 - C5	BD*(2) C6 - C7	20.78	BD (2) N1 - C8	BD*(2) C6 - C7	10.15
BD (2) C4 - C5	BD*(2) C8 - C9	13.24	BD (2) C3 - C9	BD*(2) N1 - C8	21.04
BD (2) C6 - C7	BD*(2) C4 - C5	14.26	BD (2) C3 - C9	BD*(2) C4 - C5	17.00
BD (2) C6 - C7	BD*(2) C8 - C9	18.78	BD (2) C4 - C5	BD*(2) C3 - C9	15.16
BD (2) C8 - C9	BD*(2) C2 - C3	18.60	BD (2) C4 - C5	BD*(2) C6 - C7	16.45
BD (2) C8 - C9	BD*(2) C4 - C5	23.25	BD (2) C6 - C7	BD*(2) N1 - C8	20.81
BD (2) C8 - C9	BD*(2) C6 - C7	16.48	BD (2) C6 - C7	BD*(2) C4 - C5	10.75
LP (1) N1	BD*(2) C2 - C3	34.04			
LP (1) N1	BD*(2) C8 - C9	33.20			
		207.17			**121.84**
3*H*-a			4*H*-a		
BD (2) N1 - C2	BD*(2) C8 - C9	13.94	BD (2) N1 - C2	BD*(2) C7 - C8	21.28
BD (2) C4 - C5	BD*(2) C6 - C7	21.45	BD (2) N1 - C2	BD*(2) C3 - C9	9.90
BD (2) C4 - C5	BD*(2) C8 - C9	16.98	BD (2) C3 - C9	BD*(2) N1 - C2	21.68
BD (2) C6 - C7	BD*(2) C4 - C5	17.28	BD (2) C3 - C9	BD*(2) C7 - C8	16.49
BD (2) C6 - C7	BD*(2) C8 - C9	21.43	BD (2) C5 - C6	BD*(2) C7 - C8	13.86
BD (2) C8 - C9	BD*(2) N1 - C2	10.47	BD (2) C7 - C8	BD*(2) N1 - C2	12.39
BD (2) C8 - C9	BD*(2) C4 - C5	24.12	BD (2) C7 - C8	BD*(2) C3 - C9	15.25
BD (2) C8 - C9	BD*(2) C6 - C7	17.16	BD (2) C7 - C8	BD*(2) C5 - C6	11.72
		142.83			**122.57**
5*H*-s			6*H*-s		
BD (2) N1 - C 8	BD*(2) C2 - C3	21.61	BD (2) N1 - C2	BD*(2) C3 - C9	9.64
BD (2) N1 - C 8	BD*(2) C4 - C9	9.61	BD (2) N1 - C2	BD*(2) C7 - C8	21.87
BD (2) N1 - C 8	BD*(2) C6 - C7	11.72	BD (2) C3 - C9	BD*(2) N1 - C2	23.95
BD (2) C2 - C 3	BD*(2) N1 - C8	11.03	BD (2) C3 - C9	BD*(2) C4 - C5	15.54
BD (2) C2 - C 3	BD*(2) C4 - C9	19.41	BD (2) C3 - C9	BD*(2) C7 - C8	14.9
BD (2) C4 - C 9	BD*(2) N1 - C8	19.43	BD (2) C4 - C5	BD*(2) C3 - C9	15.61
BD (2) C4 - C 9	BD*(2) C2 - C3	12.96	BD (2) C7 - C8	BD*(2) N1 - C2	12.31
BD (2) C6 - C 7	BD*(2) N1 - C8	17.21	BD (2) C7 - C8	BD*(2) C3 - C9	15.18
		122.98			**129.00**
7*H*-s					
BD (2) N1 - C8	BD*(2) C2 - C3	20.54			
BD (2) N1 - C8	BD*(2) C4 - C9	9.45			
BD (2) C2 - C3	BD*(2) N1 - C8	11.06			
BD (2) C2 - C3	BD*(2) C4 - C9	19.41			
BD (2) C4 - C9	BD*(2) N1 - C8	21.2			
BD (2) C4 - C9	BD*(2) C2 - C3	13.16			
BD (2) C4 - C9	BD*(2) C5 - C6	9.03			
BD (2) C5 - C6	BD*(2) C4 - C9	15.17			
		119.02			

[a] The values displayed for each tautomer refer the most stable conformer (see Table S9). BD (2) and BD*(2) stands, respectively, for π bonding and π* antibonding orbitals, while LP stands for a valence lone pair. Values in bold correspond to the sum of the individual values of $\Delta E^{(2)}$ calculated for each tautomer.

Table S16. Second-order perturbation energies [$\Delta E^{(2)}$, kcal mol^{-1}] corresponding to the conjugative donor-acceptor interactions within the indole ring, calculated for the different tautomers of 5MOI at the B3LYP/6-311++G(d,p) level.[a]

Donor	Acceptor	- $\Delta E^{(2)}$	Donor	Acceptor	- $\Delta E^{(2)}$
		5MOI			
1*H*-a			2*H*-a		
BD (2) C2 - C3	BD*(2) C8 - C9	16.30	BD (2) N1 - C8	BD*(2) C3 - C9	10.48
BD (2) C4 - C5	BD*(2) C6 - C7	16.10	BD (2) N1 - C8	BD*(2) C6 - C7	10.15
BD (2) C4 - C5	BD*(2) C8 - C9	18.14	BD (2) C3 - C9	BD*(2) N1 - C8	21.04
BD (2) C6 - C7	BD*(2) C4 - C5	18.31	BD (2) C3 - C9	BD*(2) C4 - C5	17.00
BD (2) C6 - C7	BD*(2) C8 - C9	16.63	BD (2) C4 - C5	BD*(2) C3 - C9	15.16
BD (2) C8 - C9	BD*(2) C2 - C3	17.72	BD (2) C4 - C5	BD*(2) C6 - C7	16.45
BD (2) C8 - C9	BD*(2) C4 - C5	17.27	BD (2) C6 - C7	BD*(2) N1 - C8	20.81
BD (2) C8 - C9	BD*(2) C6 - C7	20.19	BD (2) C6 - C7	BD*(2) C4 - C5	10.75
LP (1) N1	BD*(2) C2 - C3	36.25			
LP (1) N1	BD*(2) C8 - C9	32.70			
		209.61			**121.16**
3*H*-s			4*H*-s		
BD (2) N1 - C2	BD*(2) C7 - C8	15.39	BD (2) N1 - C2	BD*(2) C7 - C8	21.29
BD (2) C4 - C9	BD*(2) C5 - C6	21.42	BD (2) N1 - C2	BD*(2) C3 - C9	10.21
BD (2) C4 - C9	BD*(2) C7 - C8	16.92	BD (2) C3 - C9	BD*(2) N1 - C2	22.52
BD (2) C5 - C6	BD*(2) C4 - C9	16.92	BD (2) C3 - C9	BD*(2) C7 - C8	15.88
BD (2) C5 - C6	BD*(2) C7 - C8	20.37	BD (2) C5 - C6	BD*(2) C7 - C8	17.28
BD (2) C7 - C8	BD*(2) N1 - C2	11.38	BD (2) C7 - C8	BD*(2) N1 - C2	13.5
BD (2) C7 - C8	BD*(2) C4 - C9	21.49	BD (2) C7 - C8	BD*(2) C3 - C9	17.02
BD (2) C7 - C8	BD*(2) C5 - C6	18.14	BD (2) C7 - C8	BD*(2) C5 - C6	11.66
		142.03			**129.36**
5*H*-a			6*H*-a		
BD (2) N1 - C8	BD*(2) C2 - C3	19.22	BD (2) N1 - C2	BD*(2) C7 - C8	22.33
BD (2) N1 - C8	BD*(2) C4 - C9	9.98	BD (2) N1 - C2	BD*(2) C3 - C9	8.9
BD (2) N1 - C8	BD*(2) C6 - C7	11.14	BD (2) C3 - C9	BD*(2) N1 - C2	24.92
BD (2) C2 - C3	BD*(2) N1 - C8	10.11	BD (2) C3 - C9	BD*(2) C4 - C5	13.55
BD (2) C2 - C3	BD*(2) C4 - C9	20.25	BD (2) C3 - C9	BD*(2) C7 - C8	14.18
BD (2) C4 - C9	BD*(2) N1 - C8	16.45	BD (2) C4 - C5	BD*(2) C3 - C9	19.48
BD (2) C4 - C9	BD*(2) C2 - C3	11.59	BD (2) C7 - C8	BD*(2) N1 - C2	11.24
BD (2) C6 - C7	BD*(2) N1 - C8	18.35	BD (2) C7 - C8	BD*(2) C3 - C9	14.57
		117.09			**129.17**
7*H*-s					
BD (2) N1 - C8	BD*(2) C2 - C3	18.86			
BD (2) N1 - C8	BD*(2) C4 - C9	10.06			
BD (2) C2 - C3	BD*(2) N1 - C8	9.97			
BD (2) C2 - C3	BD*(2) C4 - C9	21.38			
BD (2) C4 - C9	BD*(2) N1 - C8	17.85			
BD (2) C4 - C9	BD*(2) C2 - C3	11.97			
BD (2) C4 - C9	BD*(2) C5 - C6	13.44			
BD (2) C5 - C6	BD*(2) C4 - C9	12.77			
		116.30			

[a] The values displayed for each tautomer refer the most stable conformer (see Table S10) are displayed. BD (2) and BD*(2) stands, respectively, for π bonding and π* antibonding orbitals, while LP stands for a valence lone pair. Values in bold correspond to the sum of the individual values of $\Delta E^{(2)}$ calculated for each tautomer.

Table S17. Vertical excitation energies (*E* / nm) and oscillator strengths (*f*) calculated at the TD-DFT(B3LYP)/6-311++G(3df,3pd) level for the twelve lowest energy excited singlet states of the anti-conformer of 1*H*-4MOI (1*H*-a) and for the syn and anti conformers of 1*H*-5MOI (1*H*-s and 1*H*-a).

Excited state	1*H*-a-4MOI		1*H*-s-5MOI		1*H*-a-5MOI	
	E / nm	*f*	*E / nm*	*f*	*E / nm*	*f*
S_1 (^1L_b)	279.23	0.0020	286.5	0.051	278.92	0.0471
S_2 (^1L_a)	266.78	0.1396	276.6	0.000	268.46	0.0004
S_3	262.72	0.0015	261.5	0.107	260.66	0.0045
S_4	251.73	0.0268	259.3	0.004	259.73	0.1279
S_5	249.66	0.0000	255.1	0.002	253.82	0.0034
S_6	238.00	0.0035	243.6	0.000	240.59	0.0014
S_7	233.55	0.0164	238.4	0.002	238.23	0.0007
S_8	231.73	0.0000	231.3	0.002	233.16	0.0014
S_9	225.20	0.0024	228.2	0.007	225.28	0.0026
S_{10}	219.00	0.0198	224.5	0.000	222.18	0.0001
S_{11}	216.74	0.0021	219.2	0.093	218.44	0.0116
S_{12}	214.26	0.0001	215.3	0.000	216.60	0.0188

Table S18. Experimental absorptions appearing in the IR spectra recorded after exposing the matrix-isolated 4MOI (Xe, 15 K) to a series of monochromatic UV-irradiations ($\lambda = 290$, and $\lambda = 285$ nm), compared with the corresponding wavenumbers (ν / cm^{-1}) and absolute IR intensities (A^{th} / km mol^{-1}) calculated at the B3LYP/6-311++G(d,p) level for the *anti*-conformer of the 4-methoxyindolyl radical (4MOI•-a) and of the 3*H*-tautomer of 4MOI (3*H*-a).

Exp. ν / cm^{-1}	Photoproduct	Calculated [a]		Sym.	Approximate description [b]
		ν	A^{th}		
1493	3*H*-a	1487	65.9	A'	νCC; νC_4O_{10}; δC_5H; δC_6H
1480	4MOI•-a	1479	112.5	A'	νCC; νC_4O_{10}; δC_5H; δC_6H
1461	3*H*-a	1475	57.7	A'	δCH_3 as
1461	4MOI•-a	1472	46.9	A'	δCH_3 as
1435	4MOI•-a	1441	24.3	A'	δCH_3 s
1343	3*H*-a	1346	13.8	A'	νCC
1315	4MOI•-a	1315	31.1	A'	δC_2H; δC_3H; νC_2C_3
1305	3*H*-a	1303	20.3	A'	δC_2H; νN_1C_2; νN_1C_8
1270	4MOI•-a	1266	133.5	A'	νC_4O_{10}; δCH
1266	3*H*-a	1263	208.3	A'	νC_4O_{10}; δCH
1259	3*H*-a	1257	14.3	A'	ωCH_2; δCH; νN_1C_8
1217	3*H*-a	1209	15.2	A'	νN_1C_8; νCC
1200	4MOI•-a	1193	105.2	A'	νCC; νN_1C_8
1183	4MOI•-a	1170	16.3	A'	ρCH_3
1152	4MOI•-a	1155	22.5	A'	νCC; νN_1C_2; δCH
939	4MOI•-a	934	30.2	A'	$\nu O_{10}C_{11}$; νN_1C_8
785	3*H*-a	785	41.2	A"	γ ind; γCH
774	4MOI•-a	770	19.9	A"	γ ind; γCH
750	4MOI•-a	752	39.9	A"	γ py; γC_2H; γC_3H
727	4MOI•-a	724	29.3	A"	γ ind; γCH

[a] Calculated harmonic wavenumbers are scaled by 0.980. Some strong absorptions of the photoproducts appear in a close proximity with bands of the precursor, and could not be unequivocally identified in the experimental difference spectrum. All harmonic vibrations computed for 4MOI•-a and 3*H*-a-4MOI are listed in Table S13.

[b] Based on the results provided by the "vibAnalysis" software [F. Teixeira and M. N. D. S. Cordeiro, *J. Chem. Theory Comput.*, 2019, **15**, 456-470], supported by ChemCraft animation of the vibrations. Abbreviations: ν, stretching; δ, in-plane deformation; γ, out-of-plane deformation; ρ, rocking; ω, wagging; s, symmetric; as, antisymmetric; ind, indole ring; py, pyrrole fragment (5-membered ring); benz, benzene fragment (6-membered ring).

Table S19. Experimental absorptions appearing in the IR spectra recorded after exposing the matrix-isolated 5MOI (Xe, 16 K) to a series of monochromatic UV-irradiations (from λ = 310 nm to λ = 238 nm), compared with the corresponding wavenumbers (ν / cm^{-1}) and absolute IR intensities (A^{th} / km mol^{-1}) calculated at the B3LYP/6-311++G(d,p) level for the two conformers of 5-methoxy indolyl radical (5MOI•-a, 5MOI•-s) and of 3*H*-tautomer (3*H*-a, 3*H*-s) of 5MOI.

Exp. $\tilde{\nu}$/cm^{-1}	Photoproduct	Calculated [a]		Sym.	Approximate description [b]
		ν	A^{th}		
1614	3*H*-a	1618	57.4	A'	νCC
1429	5MOI•-s	1434	143.5	A'	δCH_3 s; νCC
1429	5MOI•-a	1430	84.1	A'	δCH_3 s; νCC
1382	3*H*-a	1395	20.4	A'	δCH_2
1382	3*H*-s	1397	21.3	A'	δCH_2
1364	5MOI•-a	1375	14.8	A'	νCC; νN_1C_2; δCH
1364	5MOI•-s	1373	61.7	A'	νCC; δCH
1336	3*H*-s	1339	40.0	A'	νCC
1301	3*H*-a	1282	72.9	A'	δCH; νCC; νC_5O_{10}
1301	3*H*-s	1279	46.8	A'	δCH; νC_5C_{10}
1268	5MOI•-a	1271	176.0	A'	νC_5O_{10}; νCC; δCH
1268	5MOI•-s	1270	105.1	A'	νC_5O_{10}; νCC; δCH
1258	3*H*-a	1255	172.4	A'	νC_5O_{10}; νCC; νN_1C_8; ωCH_2
1240	3*H*-s	1239	186.2	A'	νC_5O_{10}; νCC; ωCH_2; $\nu O_{10}C_{11}$
1234	5MOI•-a	1237	155.1	A'	νC_5O_{10}; δCH; νCC
1221	5MOI•-s	1220	165.9	A'	νC_5O_{10}; δCH; νCC
1134	3*H*-a	1131	24.9	A’	νCC; δCH; $\nu O_{10}C_{11}$
1134	3*H*-s	1131	29.2	A’	νCC; δCH; $\nu O_{10}C_{11}$
1181	3*H*-a	1184	23.0	A’	ρCH_3; νN_1C_8; νCC
1174	3*H*-a	1176	21.7	A’	νN_1C_8; ρCH_3; δCH
1174	3*H*-s	1175	25.3	A’	νCC; νN_1C_8; ρCH_3; δCH
1104	3*H*-s	1097	49.1	A’	δ benz; $\nu O_{10}C_{11}$; νN_1C_8
1091	3*H*-a	1084	35.1	A’	δ benz; $\nu O_{10}C_{11}$; νN_1C_8
933	5MOI•-s	933	77.3	A’	δ ind
883	5MOI•-s	899	99.4	A’	νC_2C_3; νC_3C_9; δ ind
880	5MOI•-a	890	58.6	A’	δ py; νN_1C_2; νC_8C_9
865	3*H*-s	864	32.0	A"	γC_4H; γ benz
865	5MOI•-s	860	33.0	A'	δ py; νN_1C_2; νC_8C_9
865	5MOI•-s	863	27.1	A"	γCH
860	5MOI•-a	856	59.4	A'	δ py
842	3*H*-a	843	54.5	A"	γC_4H; γ benz
837	5MOI•-a	838	43.1	A"	γCH
819	5MOI•-a	818	17.8	A"	γCH
809	3*H*-a	820	11.3	A"	γCH
565	5MOI•-s	569	112.9	A'	δ py

[a] Calculated harmonic wavenumbers are scaled by 0.980. Some strong absorptions of the photoproducts appear in a close proximity with bands of the precursor, and could not be unequivocally identified in the experimental difference spectrum. All harmonic vibrations computed for 4MOI•-a and 3*H*-a-4MOI are listed in Table S14.

[b] Based on the results provided by the “vibAnalysis” software [F. Teixeira and M. N. D. S. Cordeiro, *J. Chem. Theory Comput.*, 2019, **15**, 456-470]. Abbreviations: ν, stretching; δ, in-plane deformation; γ, out-of-plane deformation; ρ, rocking; s, symmetric; ind, indole ring; py, pyrrole fragment (5-membered ring); benz, benzene fragment (6-membered ring).

Table S20. Zero-point corrected energies (kJ mol^{-1}) and dipole moments (Debye, values in parentheses) calculated for the two conformers of 3*H*-5MOI at different levels of theory. [a]

Level of theory	3*H*-s	3*H*-a
B3LYP/6-311++G(d,p)	0.000 (1.93)	0.982 (3.95)
B3LYP/6-311++G(3df,3pd)	0.000 (1.94)	0.922 (3.65)
MP2/6-311++G(d,p)	–0.055 (1.60)	0.000 (3.95)
MP2/6-311++G(3df,3pd)	0.000 (1.62)	0.228 (3.78)
CBS-QB3	0.000 (1.65)	0.497 (3.79)
QCISD/6-311++G(d,p)	0.000 (1.62)	0.510 (3.78)

[a] The B3LYP, CBS-QB3 and MP2 energies were obtained after full geometry optimizations, while the QCISD/6-311++G(d,p) energies were obtained by single-point calculations on geometries optimized at the MP2/6-311++G(d,p) level by adding zero-point corrected energies calculated at the same level.

Table S21. Natural bond orders calculated for indolyl and methoxy-substituted indolyl radicals at the UB3LYP/6-311++G(d,p) level of theory [a]

	N_1C_2	C_2C_3	C_3C_9	C_9C_4	C_4C_5	C_5C_6	C_6C_7	C_7C_8	C_8C_9
Indolyl	1.602	1.287	1.239	1.380	1.427	1.466	1.385	1.451	1.210
2MOI•-s	1.583	1.194	1.357	1.290	1.503	1.394	1.427	1.430	1.198
2MOI•-a	1.586	1.201	1.366	1.286	1.493	1.402	1.424	1.435	1.184
3MOI•-s	1.555	1.299	1.165	1.405	1.453	1.451	1.435	1.428	1.251
3MOI•-a	1.594	1.267	1.201	1.377	1.468	1.433	1.427	1.430	1.235
4MOI•-s	1.549	1.333	1.261	1.362	1.341	1.499	1.356	1.455	1.172
4MOI•-a	1.595	1.289	1.323	1.300	1.395	1.461	1.382	1.441	1.182
5MOI•-s	1.475	1.404	1.180	1.453	1.334	1.454	1.393	1.435	1.193
5MOI•-a	1.545	1.348	1.188	1.409	1.394	1.423	1.425	1.420	1.239
6MOI•-s	1.616	1.264	1.341	1.289	1.520	1.344	1.364	1.457	1.191
6MOI•-a	1.602	1.281	1.322	1.331	1.467	1.392	1.338	1.472	1.171
7MOI•-s	1.492	1.393	1.228	1.409	1.375	1.509	1.307	1.395	1.176
7MOI•-a	1.505	1.386	1.207	1.404	1.398	1.485	1.350	1.384	1.200

[a] See Fig. S1 for the atom numbering scheme.