

Supplement of Magn. Reson., 2, 281–290, 2021
<https://doi.org/10.5194/mr-2-281-2021-supplement>
© Author(s) 2021. CC BY 4.0 License.



Supplement of

Non-classical disproportionation revealed by photo-chemically induced dynamic nuclear polarization NMR

Jakob Wörner et al.

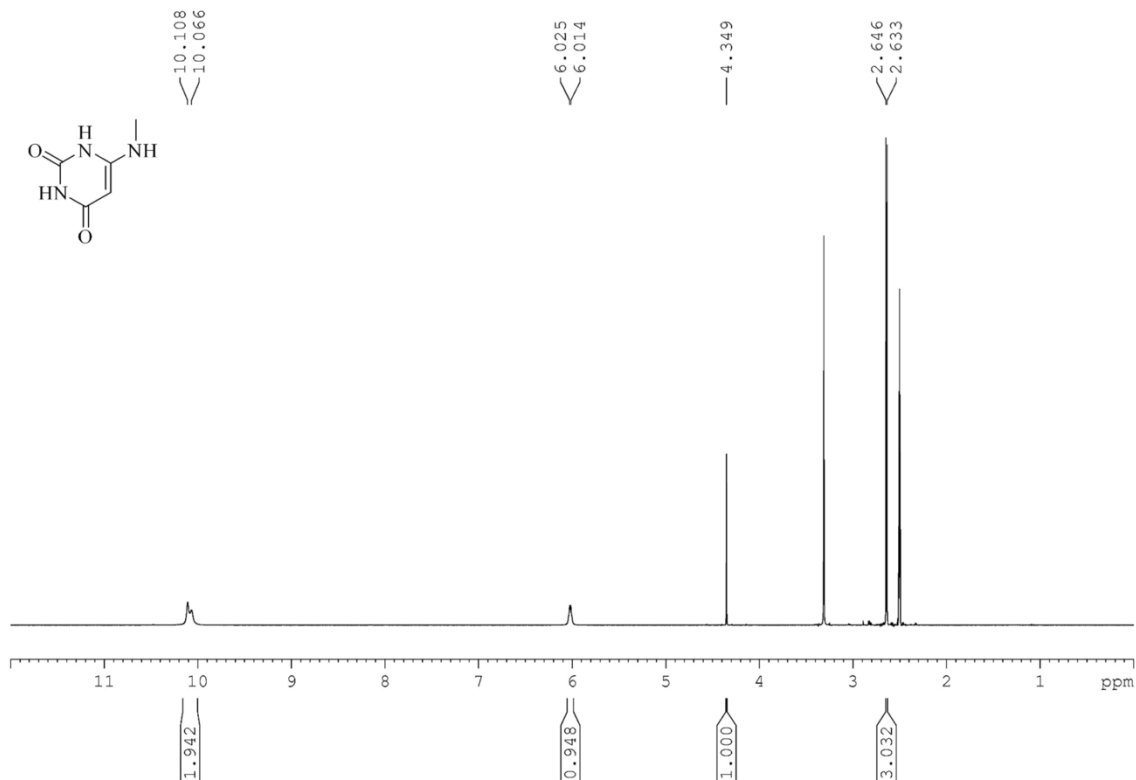
Correspondence to: Stefan Weber (stefan.weber@physchem.uni-freiburg.de)

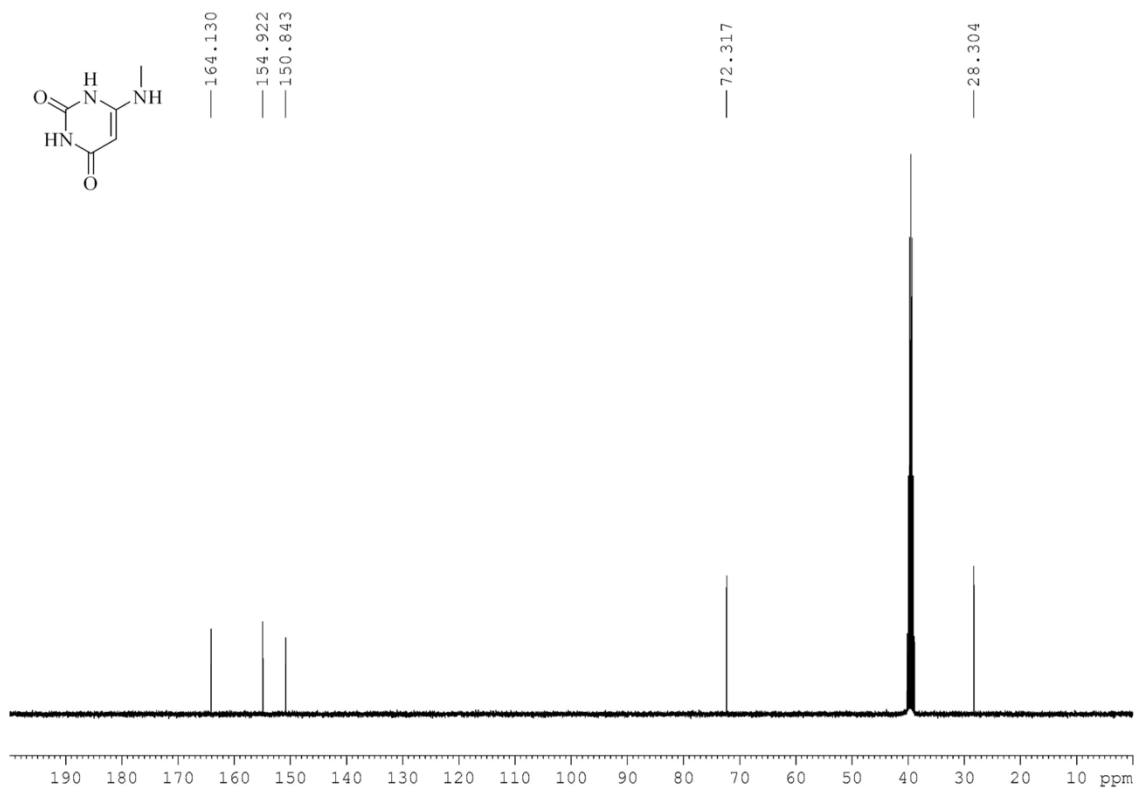
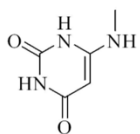
The copyright of individual parts of the supplement might differ from the article licence.

Preparation of 6,7,8-trimethylumazine

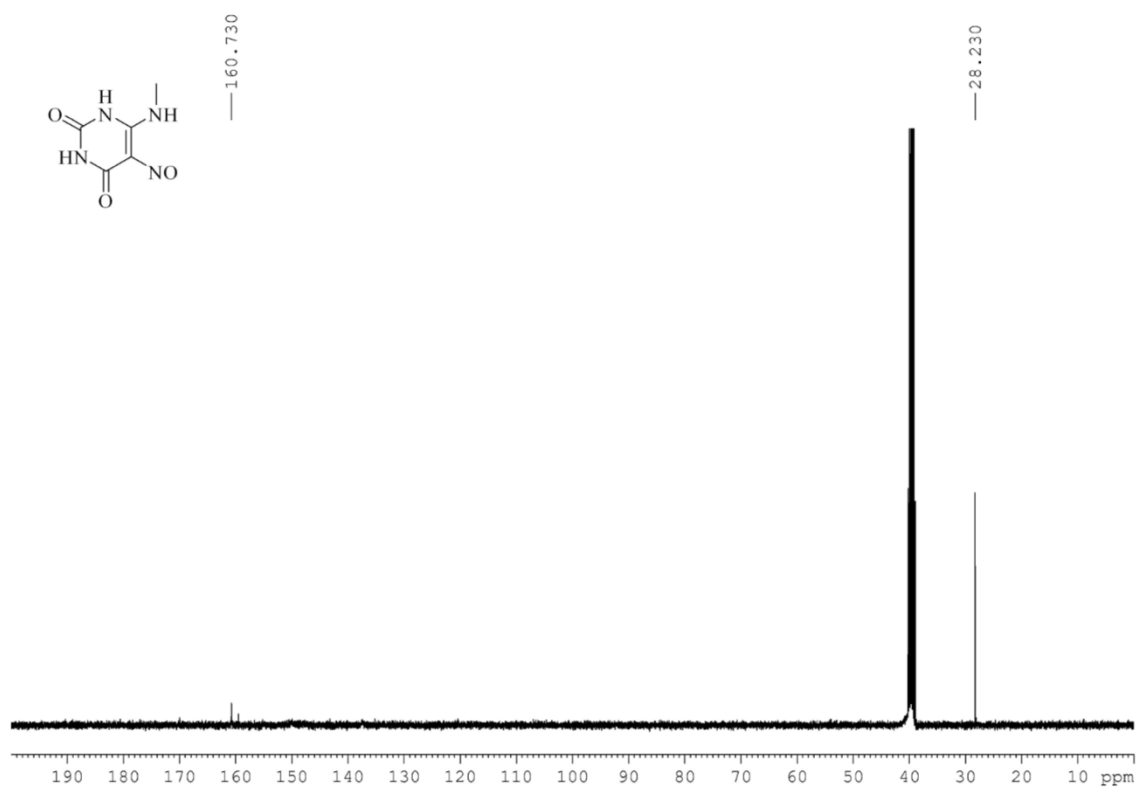
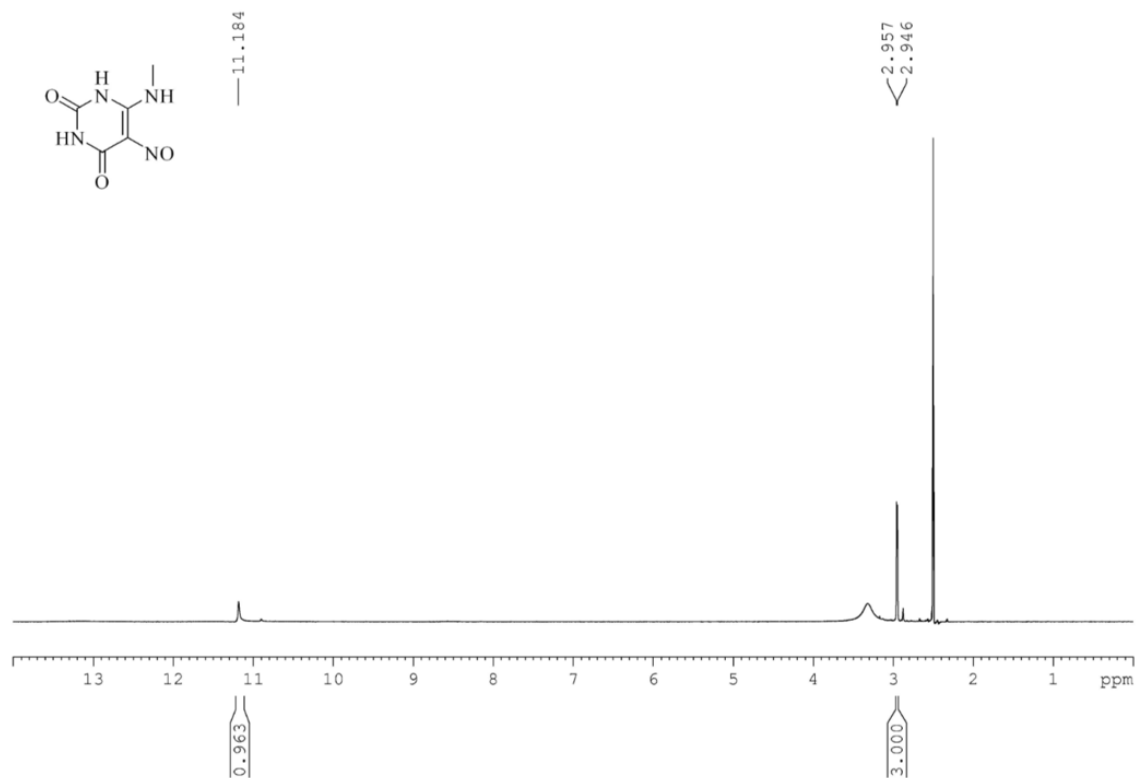
6,7,8-Trimethylumazine was synthesized along a route described previously starting out with the preparation of 6-methylaminouracil (Masuda, 1957).

6-Methylaminouracil. A mixture of 6-chlorouracil (3 mmol, 0.44 g) and methylamine (40 wt. % in H₂O, 5 ml) was stirred under reflux overnight. The white solid (0.37 g, 88%) was harvested by filtration, washed with water (5 ml), methanol (10 ml), and Et₂O (20 ml), and dried over P₂O₅; ¹H NMR (DMSO-6d, 400 MHz): δ [ppm] = 10.11–10.07 (m, 2H), 6.03–6.01 (m, 1H), 4.35 (s, 1H), 2.64 (d, 3H, *J* = 1.22 Hz); ¹³C NMR (DMSO-6d, 100 MHz): δ [ppm] = 164.1, 154.9, 150.8, 72.3, 28.3; HRMS (ESI): *m/z* for C₅H₆O₂N₃ [M-H]⁻ calculated: 140.0485, found: 140.0466.

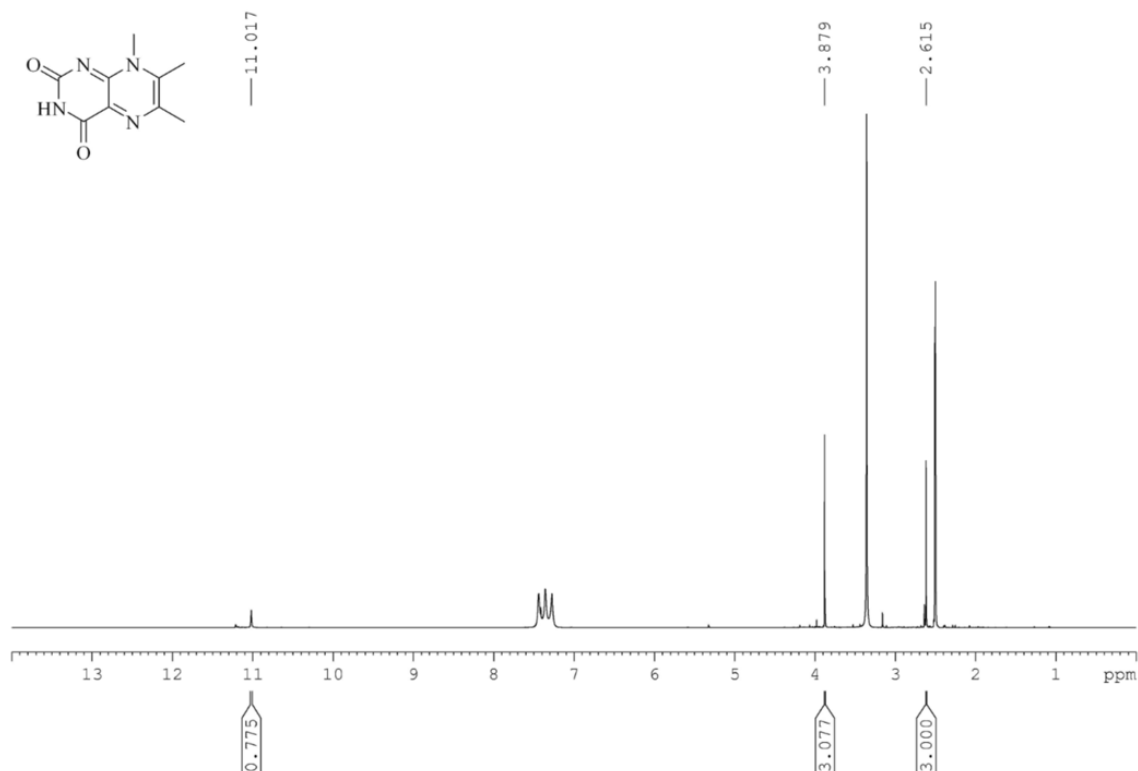


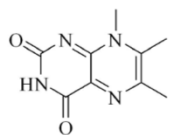


5-Nitroso-6-methylaminouracil. 6-Methylaminouracil (2.5 mmol, 0.35 g) was suspended in 6 ml of water, and NaNO_2 (0.35 g, 5 mmol) was added. Acetic acid (3.5 M) was added slowly until pH 4 was reached. Then the mixture was stirred for 30 min at room temperature. A red solid (0.39 g, 92%) was obtained by filtration, washed with water, and dried over P_2O_5 ; ^1H NMR (DMSO- d_6 , 400 MHz): δ [ppm] = 11.18, 2.95 (d, 3H, J = 1.07 Hz); ^{13}C NMR (DMSO- d_6 , 100 MHz): δ [ppm] = 160.7, 28.2.

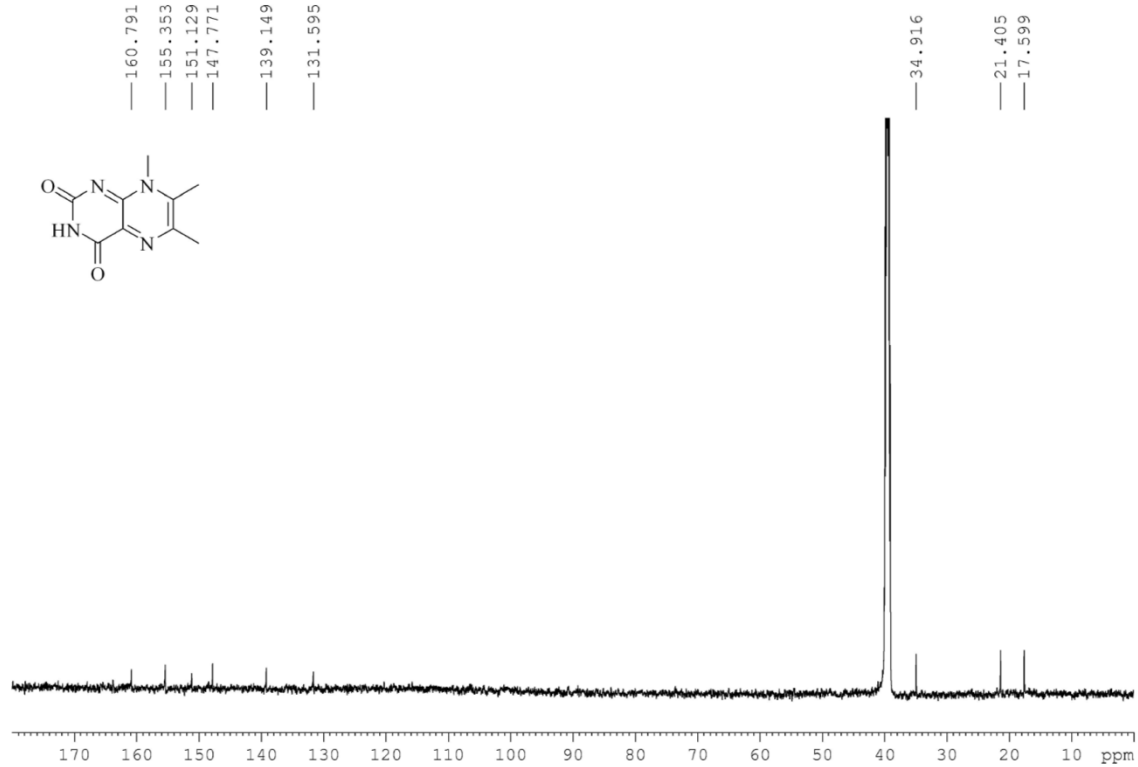


6,7,8-Trimethyllumazine. 5-Nitroso-6-methylaminouracil (0.34 g, 2 mmol) was suspended in 7 ml of water, and the mixture was heated to 100 °C. Na₂S₂O₄ was added in portions until the color of the solution changed from red to yellow. Butane-2,3-dione (0.77 ml) was added, and the mixture was stirred for 20 min at 75 °C. The mixture was then kept at 0 °C. A yellow solid (0.15 g, 36.4 %) was obtained by filtration, washed with cold methanol and Et₂O, and dried over P₂O₅; ¹H NMR (DMSO-6d, 600 MHz): δ [ppm] = 11.02 (s, 1H), 3.88 (s, 3H), 2.62 (s, 3H); ¹³C NMR (DMSO-6d, 150 MHz): δ [ppm] = 160.8, 155.4, 151.1, 147.8, 139.1, 131.6, 34.9, 21.4, 17.6; HRMS (ESI): *m/z* for C₉H₁₁O₂N₄ [M+H]⁺ calculated: 207.0877, found: 207.0876.





— 160.791
— 155.353
— 151.129
— 147.771
— 139.149
— 131.595



Magnetic-resonance parameters obtained from density functional theory

Table S1: Principal values and isotropic g-values for various oxidized and reduced TML radicals.

	g_{xx}	g_{yy}	g_{zz}	g_{iso}
TMLH ^{red•-}	2.00221	2.00377	2.00421	2.00340
TMLH ₂ ^{red•} (H(5))	2.00222	2.00343	2.00419	2.00328
TMLH ₂ ^{red•} (H(1))	2.00223	2.00383	2.00422	2.00342
TML ^{ox•}	2.00235	2.00316	2.00372	2.00308

Table S2: Hyperfine couplings of TMLH^{red•-} in MHz.

atom	A_{xx}	A_{yy}	A_{zz}	A_{iso}
N(1)	0.058	-0.152	-2.105	-0.733
C(2)	-0.216	-1.137	2.766	0.471
O(2)	0.598	0.739	-4.501	-1.055
N(3)	0.448	-0.987	-1.238	-0.593
H(3)	1.181	-2.197	-2.496	-1.170
C(4)	-6.275	-7.695	13.813	-0.052
O(4)	3.460	3.983	-21.205	-4.587
C(4a)	2.839	-14.542	-16.874	-9.526
N(5)	-0.743	-0.953	50.019	16.108
C(6)	-20.257	-24.640	-39.781	-28.226
C(6 α)	0.152	0.506	1.420	0.692
H(6 α)	-3.461	-7.306	-8.136	-6.301
H(6 α)	-5.281	-8.843	-9.816	-7.980
H(6 α)	1.783	-3.134	-3.585	-1.645
C(7)	-2.181	-2.841	86.224	27.067
C(7 α)	-13.314	-14.182	-15.089	-14.195
H(7 α)	0.838	1.236	7.755	3.276
H(7 α)	49.406	49.668	56.044	51.706
H(7 α)	29.148	30.011	35.893	31.684
N(8)	-1.142	-1.394	28.585	8.683
C(8 α)	-6.495	-8.181	-8.401	-7.692
H(8 α)	7.543	8.394	14.070	10.002
H(8 α)	3.541	3.764	9.419	5.575
H(8 α)	28.043	28.269	33.892	30.068
C(8a)	-8.331	-9.948	-13.709	-10.663

Table S3: Hyperfine couplings of TMLH₂^{red}•(H(5)) in MHz.

atom	A_{xx}	A_{yy}	A_{zz}	A_{iso}
N(1)	-0.052	0.190	-2.310	-0.724
C(2)	-0.377	0.505	-1.409	-0.427
O(2)	0.528	0.711	-3.955	-0.905
N(3)	-0.687	-0.995	1.697	0.005
H(3)	1.014	-3.094	-3.201	-1.760
C(4)	4.974	-8.136	-9.990	-4.384
O(4)	3.479	3.849	-20.170	-4.281
C(4a)	-12.725	-14.401	24.858	-0.756
N(5)	-0.915	-1.221	44.747	14.204
H(5)	-1.964	-30.261	-43.507	-25.244
C(6)	-9.055	-17.334	-19.952	-15.447
C(6 α)	-0.736	-1.629	-1.986	-1.450
H(6 α)	0.571	1.383	5.843	2.599
H(6 α)	1.419	2.312	6.501	3.411
H(6 α)	2.091	-2.743	-3.288	-1.313
C(7)	-8.226	-8.867	54.308	12.405
C(7 α)	-9.026	-9.635	-10.616	-9.759
H(7 α)	0.039	0.323	6.327	2.230
H(7 α)	36.595	36.894	42.648	38.712
H(7 α)	21.039	22.088	27.164	23.430
N(8)	-0.069	-0.392	34.395	11.311
C(8 α)	-7.542	-8.615	-9.478	-8.545
H(8 α)	11.083	12.121	17.650	13.618
H(8 α)	3.991	4.313	10.185	6.163
H(8 α)	34.827	35.036	40.919	36.927
C(8a)	-11.124	-12.891	-19.000	-14.338

Table S4: Hyperfine couplings of TMLH₂^{red}(H(1)) in MHz.

atom	A_{XX}	A_{YY}	A_{ZZ}	A_{iso}
N(1)	-0.048	0.152	-1.815	-0.570
H(1)	-0.817	-1.227	2.738	0.231
C(2)	-0.003	-0.904	4.051	1.048
O(2)	0.861	0.960	-5.818	-1.332
N(3)	-0.709	-1.019	-1.237	-0.988
H(3)	-1.141	1.294	-1.769	-0.539
C(4)	-5.621	-6.919	11.529	-0.337
O(4)	3.637	4.183	-21.161	-4.447
C(4a)	0.911	-14.200	-16.659	-9.983
N(5)	-0.914	-1.145	50.909	16.283
C(6)	-20.607	-25.140	-40.620	-28.789
C(6 α)	0.417	0.878	1.842	1.046
H(6 α)	-3.070	-7.161	-7.965	-6.065
H(6 α)	-5.455	-9.060	-10.086	-8.200
H(6 α)	1.600	-3.349	-3.834	-1.861
C(7)	-1.273	-2.106	93.036	29.886
C(7 α)	-13.686	-14.535	-15.586	-14.602
H(7 α)	2.183	2.627	9.374	4.728
H(7 α)	52.044	52.242	58.968	54.418
H(7 α)	28.591	29.563	35.580	31.245
N(8)	-1.515	-1.776	27.273	7.994
C(8 α)	-5.450	-7.068	-7.414	-6.644
H(8 α)	1.635	2.503	8.237	4.125
H(8 α)	9.826	10.295	15.582	11.901
H(8 α)	25.169	25.435	31.043	27.216
C(8a)	-8.071	-9.664	-14.358	-10.698

Table S5: Hyperfine couplings of TML^{ox•} in MHz.

atom	A_{XX}	A_{YY}	A_{ZZ}	A_{iso}
N(1)	-0.108	0.146	0.608	0.215
C(2)	-0.993	-2.086	-2.454	-1.844
O(2)	1.559	1.693	-8.491	-1.746
N(3)	0.529	-0.547	-0.871	-0.296
H(3)	0.517	-2.244	-2.577	-1.435
C(4)	-14.500	-16.279	-16.714	-15.831
O(4)	4.965	5.421	-23.891	-4.502
C(4a)	-0.275	1.364	87.743	29.611
N(5)	-2.687	-3.299	-8.157	-4.714
C(6)	6.479	7.392	59.385	24.419
C(6 α)	1.085	2.163	113.923	39.057
H(6 α)	-0.521	-0.892	3.460	0.682
H(6 α)	19.964	21.808	24.983	22.252
H(6 α)	19.608	21.465	24.521	21.865
C(7)	-22.443	-26.582	-53.291	-34.105
C(7 α)	-7.560	-8.087	-8.204	-7.950
H(7 α)	-14.145	-35.627	-52.780	-34.184
H(7 α)	-14.233	-35.831	-53.653	-34.572
N(8)	1.277	1.418	15.268	5.988
C(8 α)	-2.975	-3.618	-3.921	-3.505
H(8 α)	2.667	4.201	8.431	5.100
H(8 α)	10.378	11.454	14.771	12.201
H(8 α)	0.586	1.324	4.002	1.971
C(8a)	-13.510	-15.186	-20.552	-16.416

References

Masuda, T.: Application of chromatography. XXXI. Structure of a green fluorescent substance produced by *Eremothecium ashbyii*, Pharm. Bull., 5, 28-30, 1957.