Electronic Supplementary Information

CYMANTRENE DERIVATIVES CONTAINING IMINO GROUPS: SPECTRAL AND PHOTOCHEMICAL PROPERTIES

L. N. Telegina,* Yu. A. Borisov, and E. S. Kelbysheva

Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia

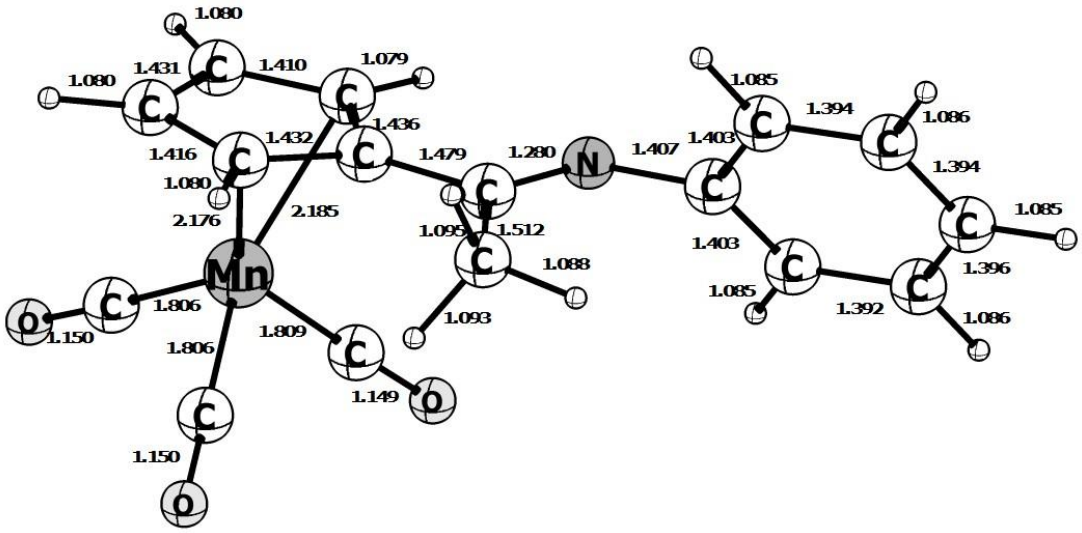

Figure S1. Optimized structure of compound **1** in benzene.

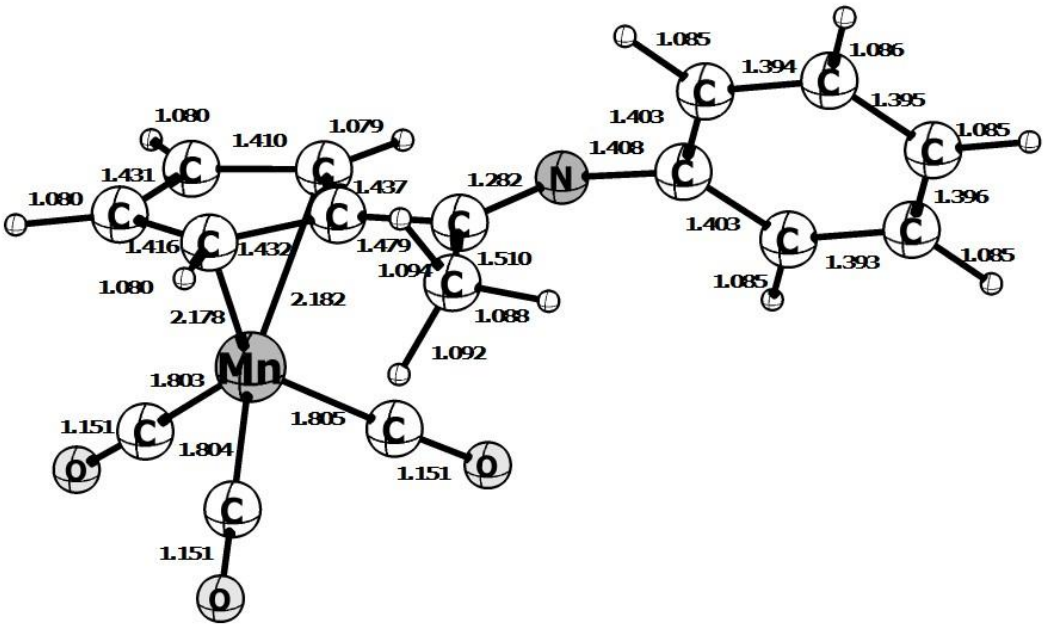

Figure S2. Optimized structure of compound **1** in acetonitrile.

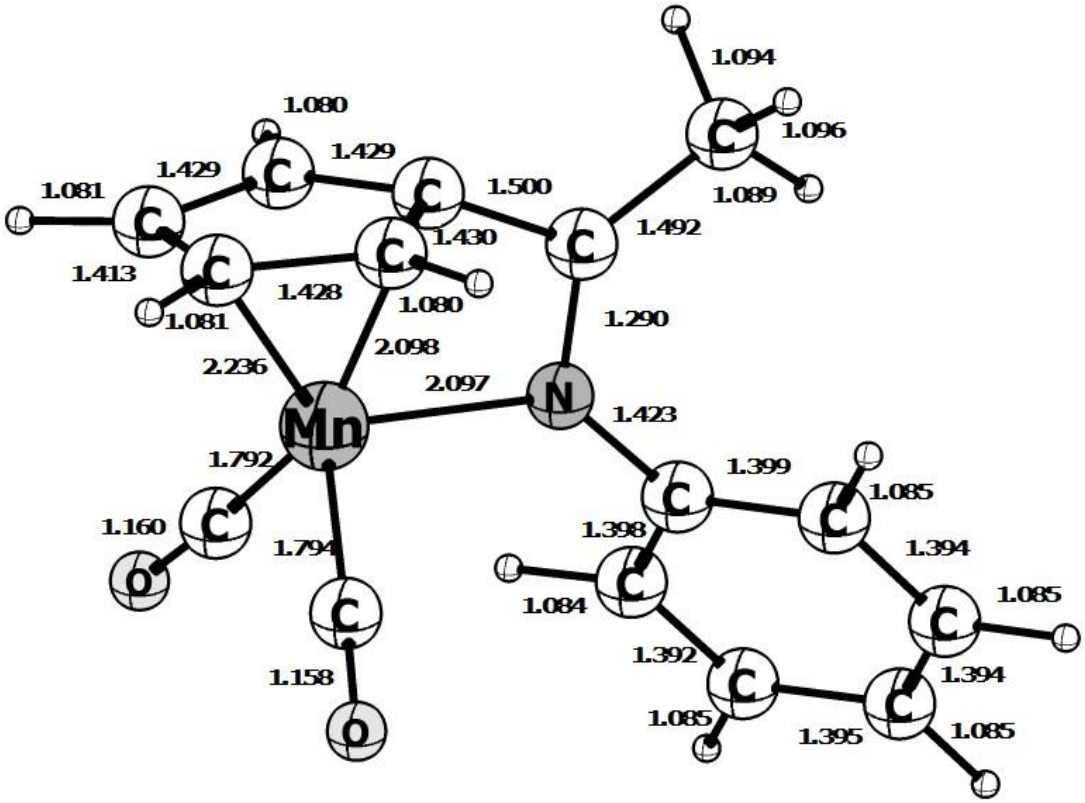

Figure S3. Optimized structure of compound **3** in benzene.

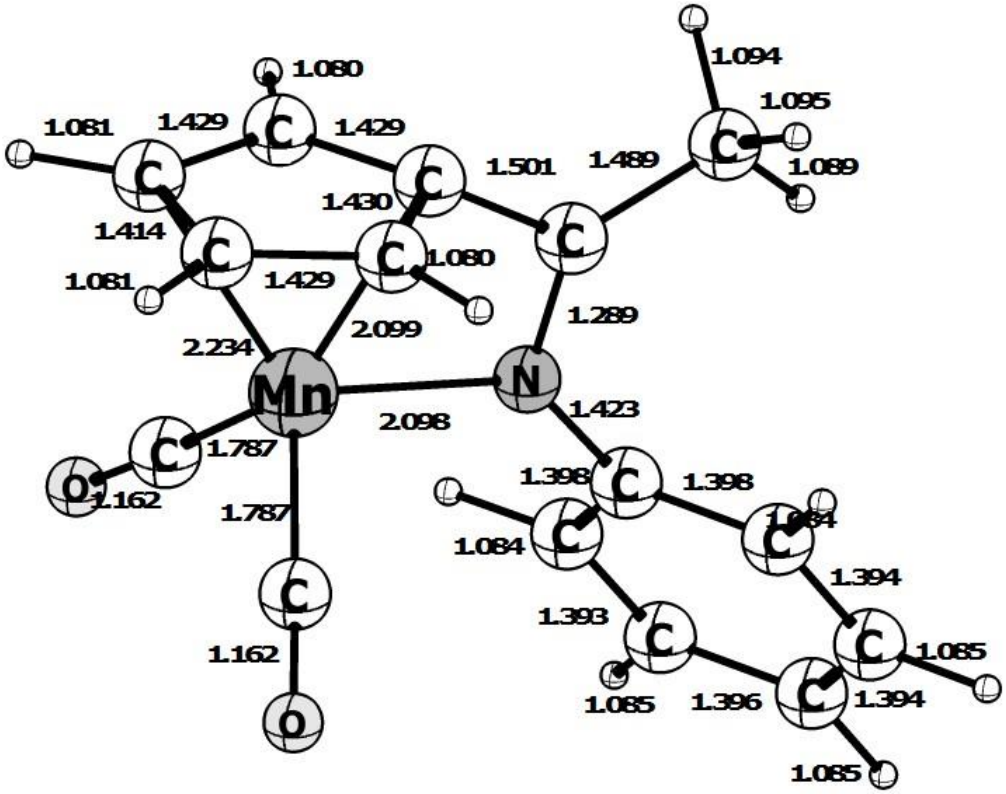

Figure S4. Optimized structure of compound **3** in acetonitrile.

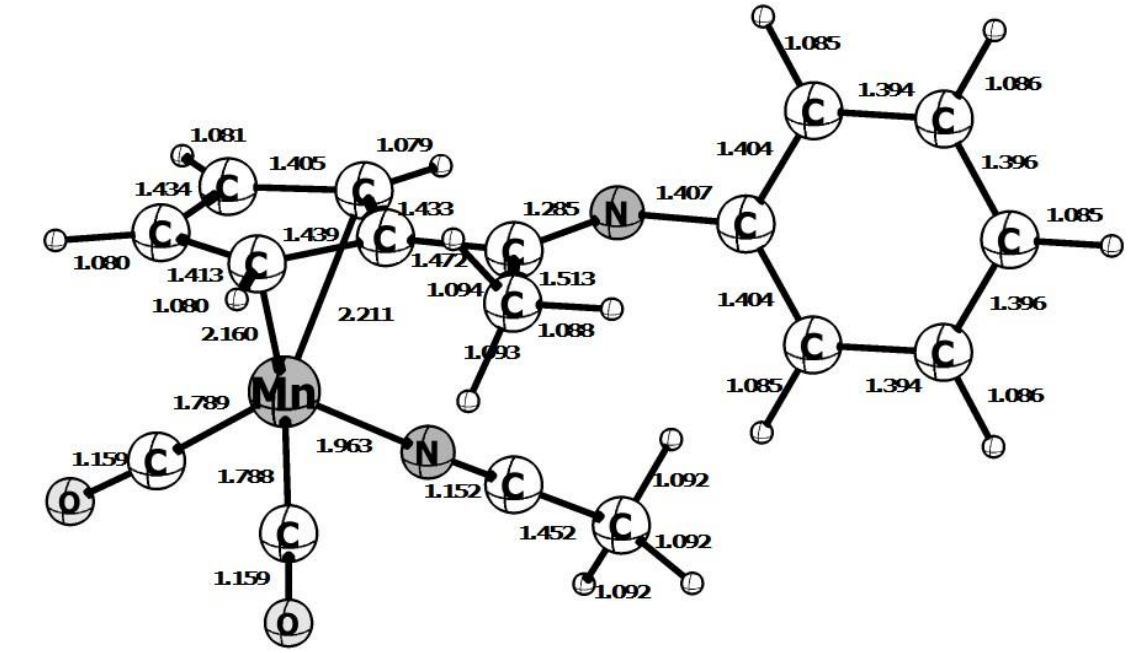

Figure S4. Optimized structure of compound **5** in acetonitrile.

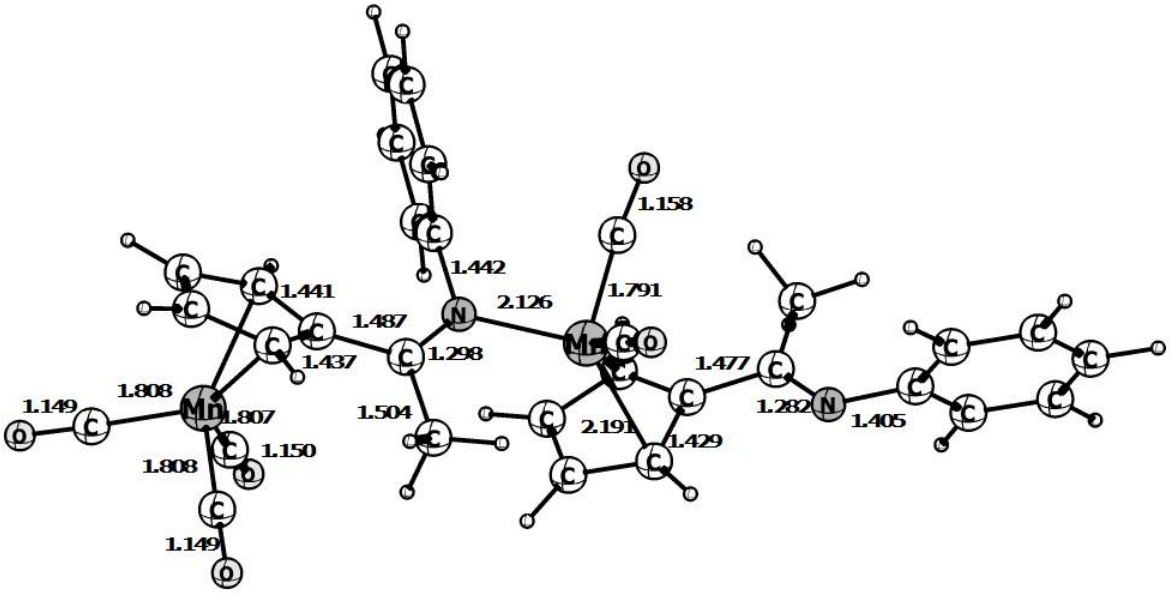

Figure S5. Optimized structure of compound **D** in benzene where the Mn atom of the dicarbonyl complex is coordinated with the imino group of the tricarbonyl complex.

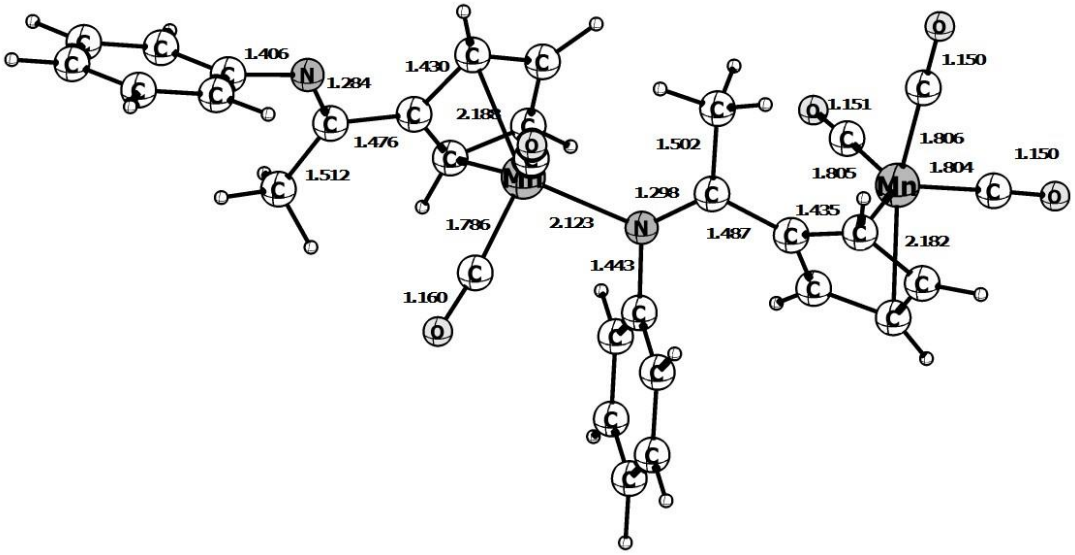

Figure S6. Optimized structure of compound **D** in acetonitrile where the Mn atom of the dicarbonyl complex is coordinated with the imino group of the tricarbonyl complex.

Table S1. Main energy parameters for the intermediates (T = 298 K, P = 1 bar)

Intermediate	E_{tot}, a.u.	E_{ZPVE}, a.u. E_H, a.u.	E_G, a.u.	S, cal/mol
		Reaction in benzene		
1	–2048.6382795	–2048.398272	–2048.449099	150.175
		–2048.377746		
1* [a]	–1935.2127264	–1934.982495	–1935.029409	136.306
		–1934.964645		
3	–1935.2265105	–1934.995439	–1935.041481	134.975
		–1934.977350		
1*Bz [a]	–2167.5240055	–2167.191943	–2167.248487	170.515
		–2167.167469		
D	–3983.87758342	–3983.404692	–3983.476473	230.280
		–3983.367059		
		Reaction in acetonitrile		
1	–2048.6440318	–2048.404228	–2048.455049	150.156
		–2048.383705		
1* [a]	–1935.2222602	–1934.992249	–1935.039099	136.189
		–1934.974392		
3	–1935.2330118	–1935.002130	–1935.048819	136.433
		–1934.983995		
5	–2068.0626865	–2067.784890	–2067.839312	161.729
		–2067.762470		
D	–3983.88959310	–3983.4168041	–3983.4885841	230.058
		–3983.378601		

[a] **1***—complex **1** after CO elimination due to photolysis; **1*Bz**—dicarbonyl complex in which the Mn atom interacts with the benzene molecule;

E_{tot}—total energy; $E_{ZPVE} = E_{tot}$ + ZPVE; $E_H = E_{tot}$ + ZPVE + E_{vib} + E_{rot} + E_{trans}; $E_G = E_H - T \cdot S$; ZPVE—zero point vibration energy, E_{vib}—vibration energy, E_{rot}—rotational energy, E_{trans}—translational energy, S—entropy, T—temperature (K).

Free Gibbs energies $\Delta G°$ (enthalpies $\Delta H°$) and equilibrium constants (K_p) for the reactions explored:

In benzene:

(S1) **1*** ↔ **3** –7.58 kcal/mol (–7.97 58 kcal/mol), $K_p = 3.6 \cdot 10^5$
(S2) **1*** + PhH ↔ **1*Bz** +5.63 kcal/mol (–4.76 kcal/mol), $K_p = 7.5 \cdot 10^{-5}$
(S3) **1*** + **1** ↔ **D** +1.28 58 kcal/mol (–15.48 kcal/mol), $K_p = 1.2 \cdot 10^{-1}$

In acetonitrile:

(S4) **1*** ↔ **3** –6.10 58 kcal/mol (–6.03 kcal/mol), $K_p = 3.4 \cdot 10^4$
(S5) **1*** + MeCN ↔ **5** –18.58 kcal/mol (–28.89 kcal/mol), $K_p = 4.2 \cdot 10^{13}$
(S6) **1*** + **1** ↔ **D** +3.49 kcal/mol (–12.87 kcal/mol), $K_p = 2.8 \cdot 10^{-3}$