Supporting Information

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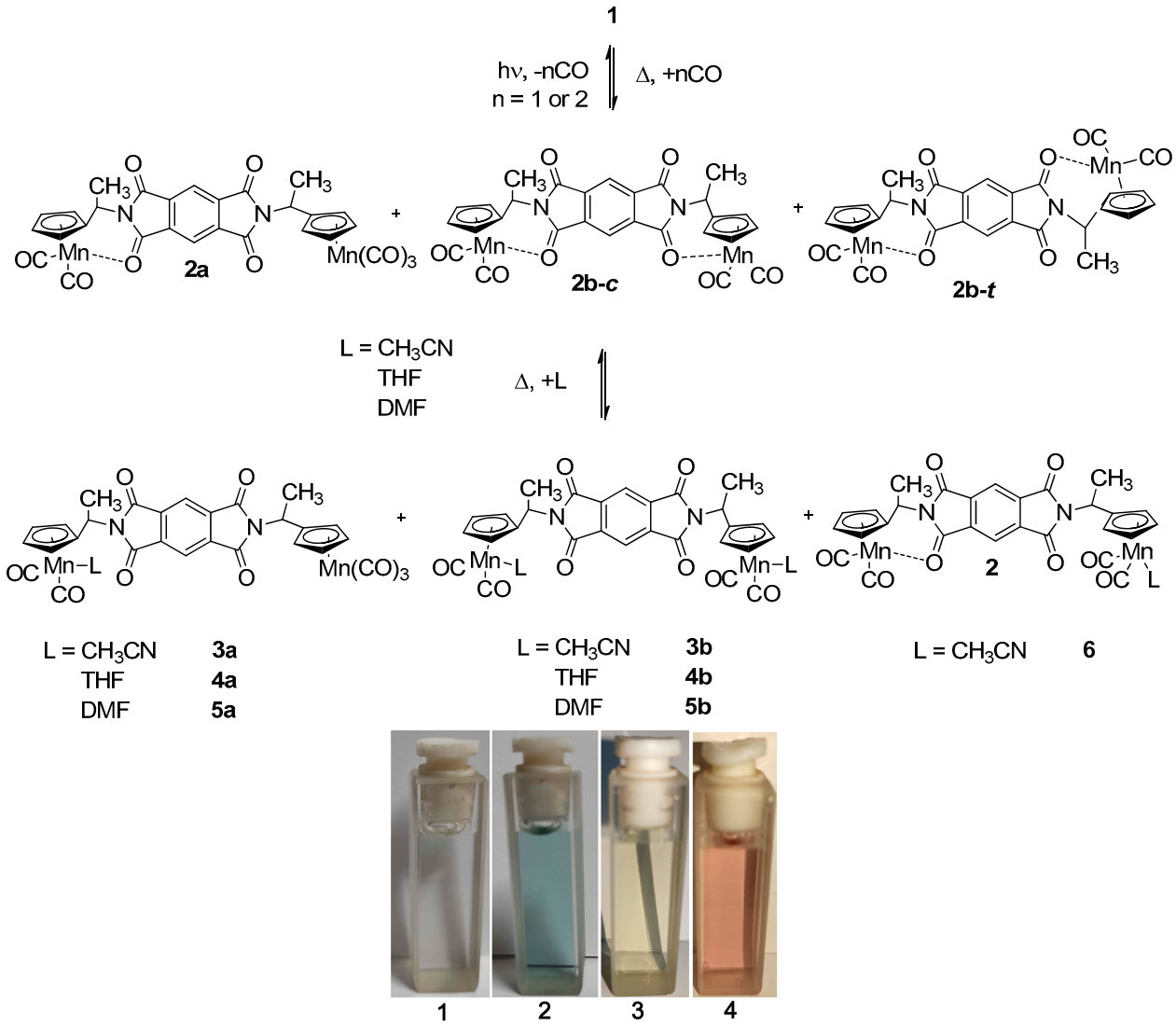


Scheme S1. Stage 1 – photolysis of compound **1** in benzene. Stage 2 – thermal reaction of compound **1** in the presence of donor ligands. Color of benzene solutions for compounds **1-2**, color of acetonitrile solutions for compound **3**, color of THF solutions for compound **4**.

IR spectra.

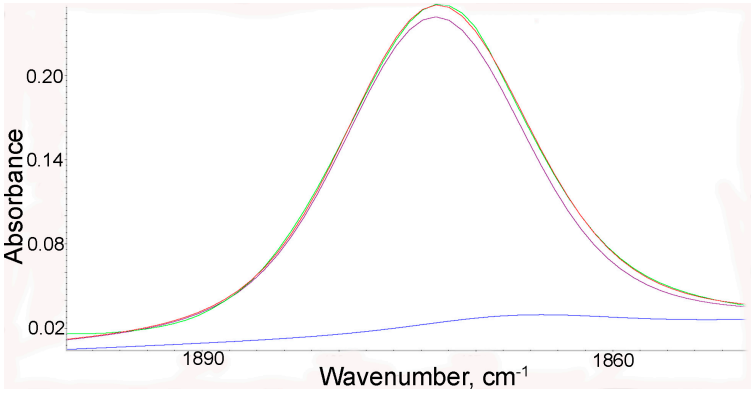


Figure S1. Curve fitting of the ν(CO) band of dicarbonyl complexes in the IR spectrum of benzene solution after irradiation of **1** with CH_3CN (4 eq.) for 4 min

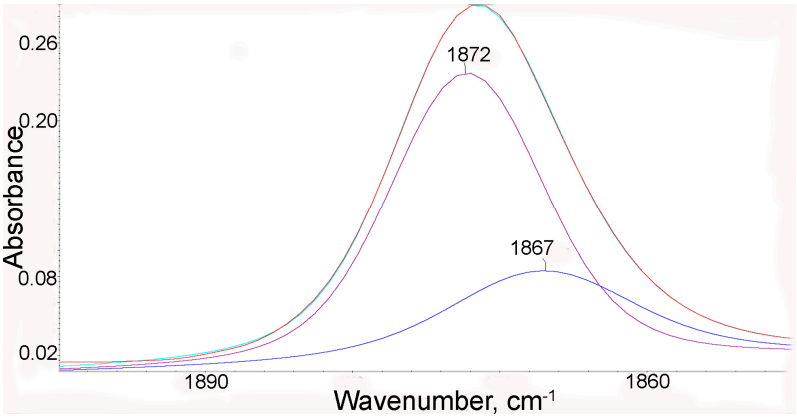


Figure S2. Curve fitting of the ν(CO) band of dicarbonyl complexes in the IR spectrum of benzene solution after irradiation of **1** and the subsequent thermal reaction for 90 min in closed IR cell at room temperature.

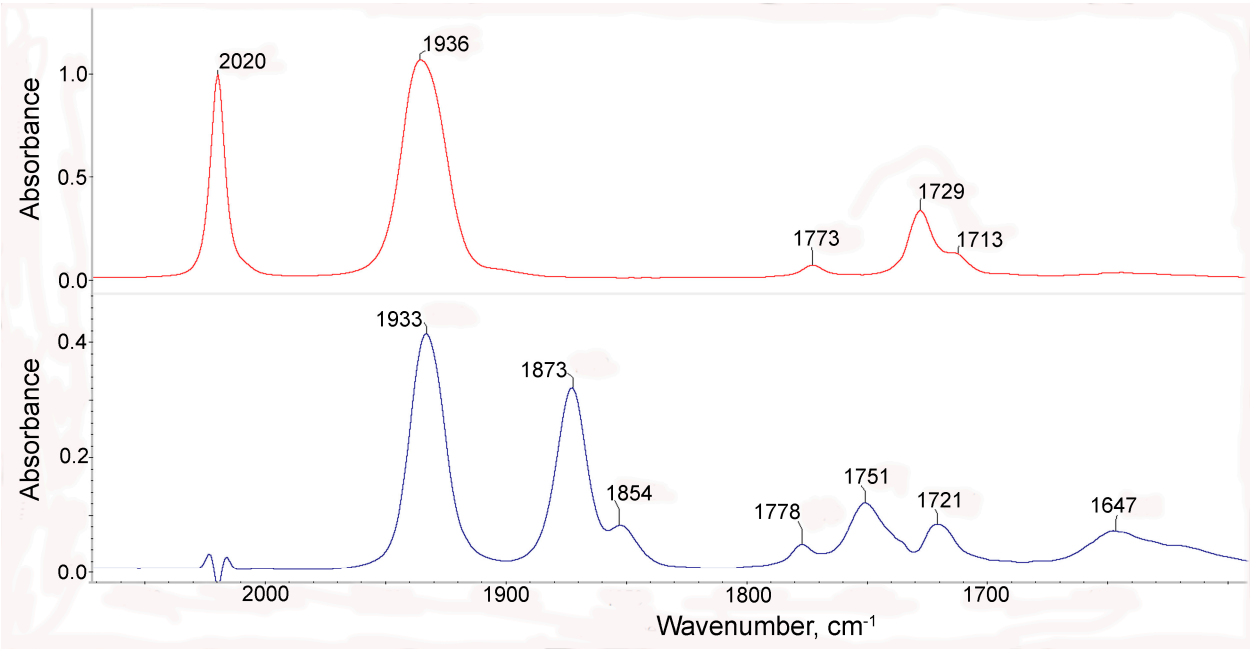


Figure S3. IR spectra in the ν(CO) range of a THF solution of **1** (red line) and the photolysis products (blue line) The latter was obtained by the subtraction of the spectrum of **1** from the spectrum of the reaction mixture after irradiation of **1** and represents the spectrum of the photolysis products.

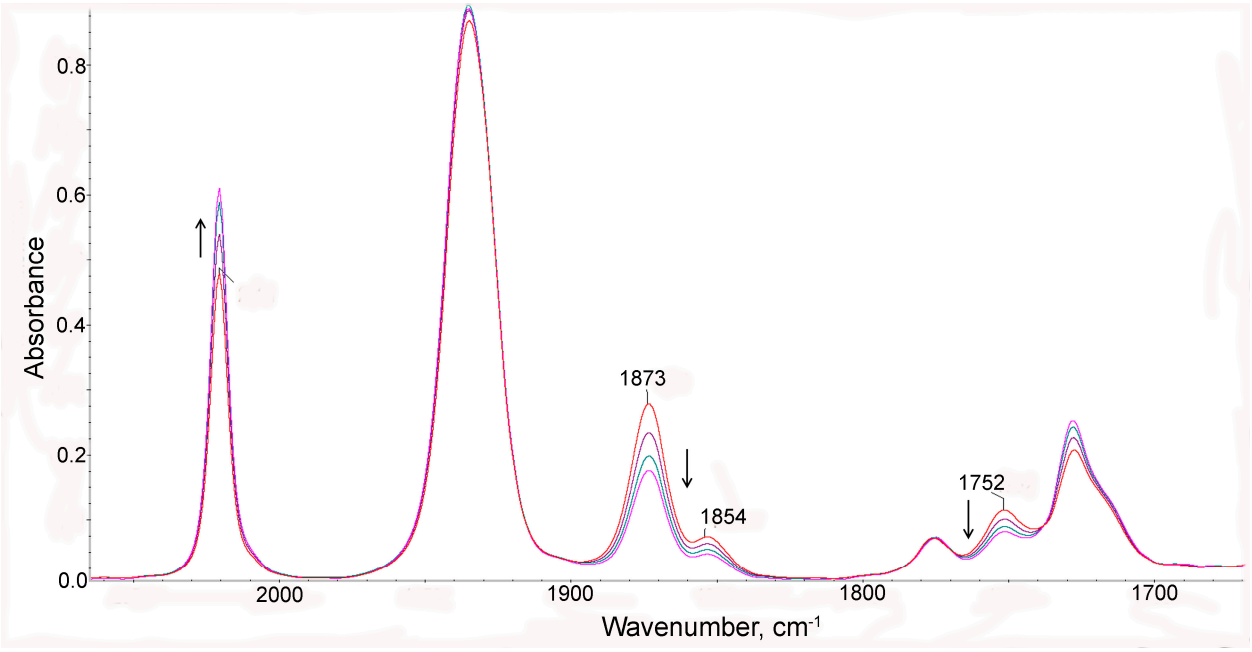


Figure S4. IR monitoring of the transformation **2** and **4** to **1** in the region of ν(CO) stretches after irradiation of **1** for 4 min at room temperature. The spectra were recorded every 5 min in a sealed IR cell.

NMR spectra.

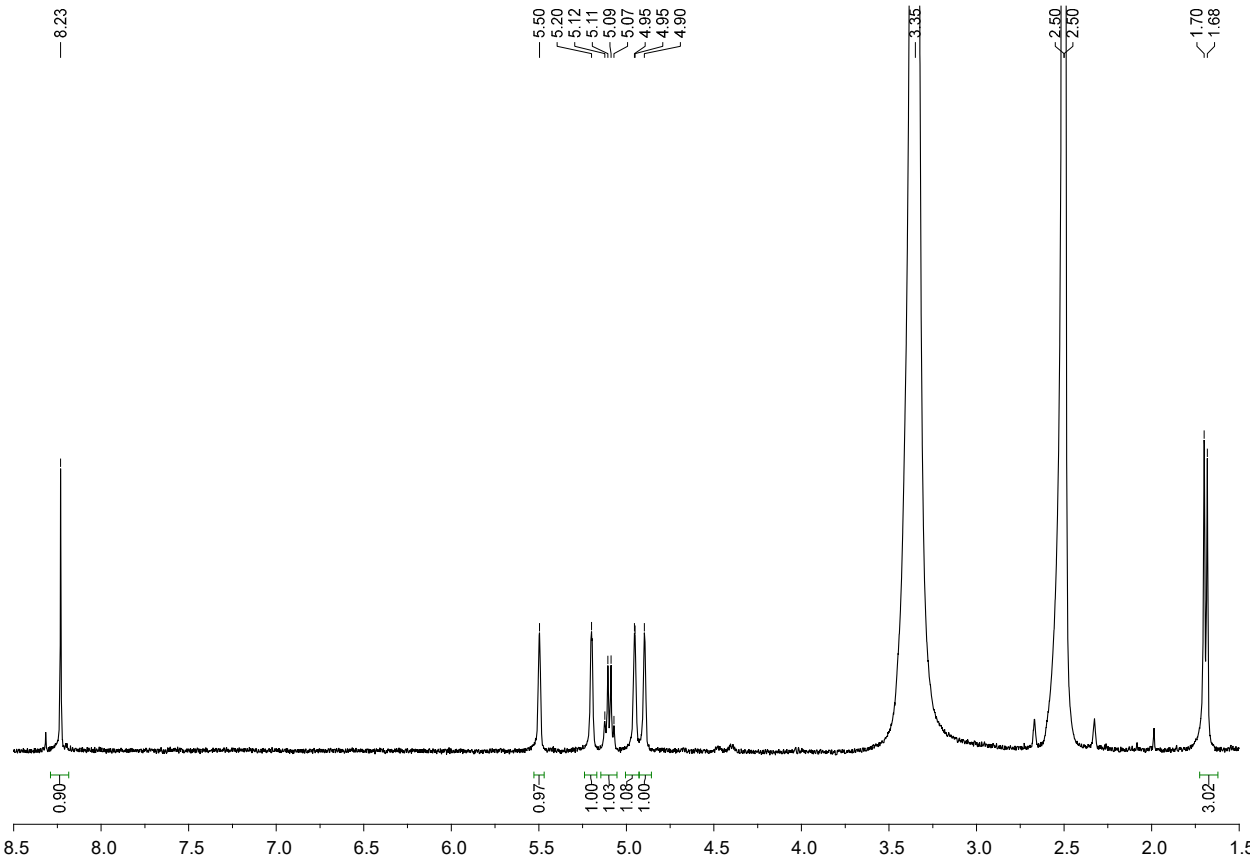


Figure S5. ^{1}H NMR spectrum of compound **1** in DMSO-d_6.

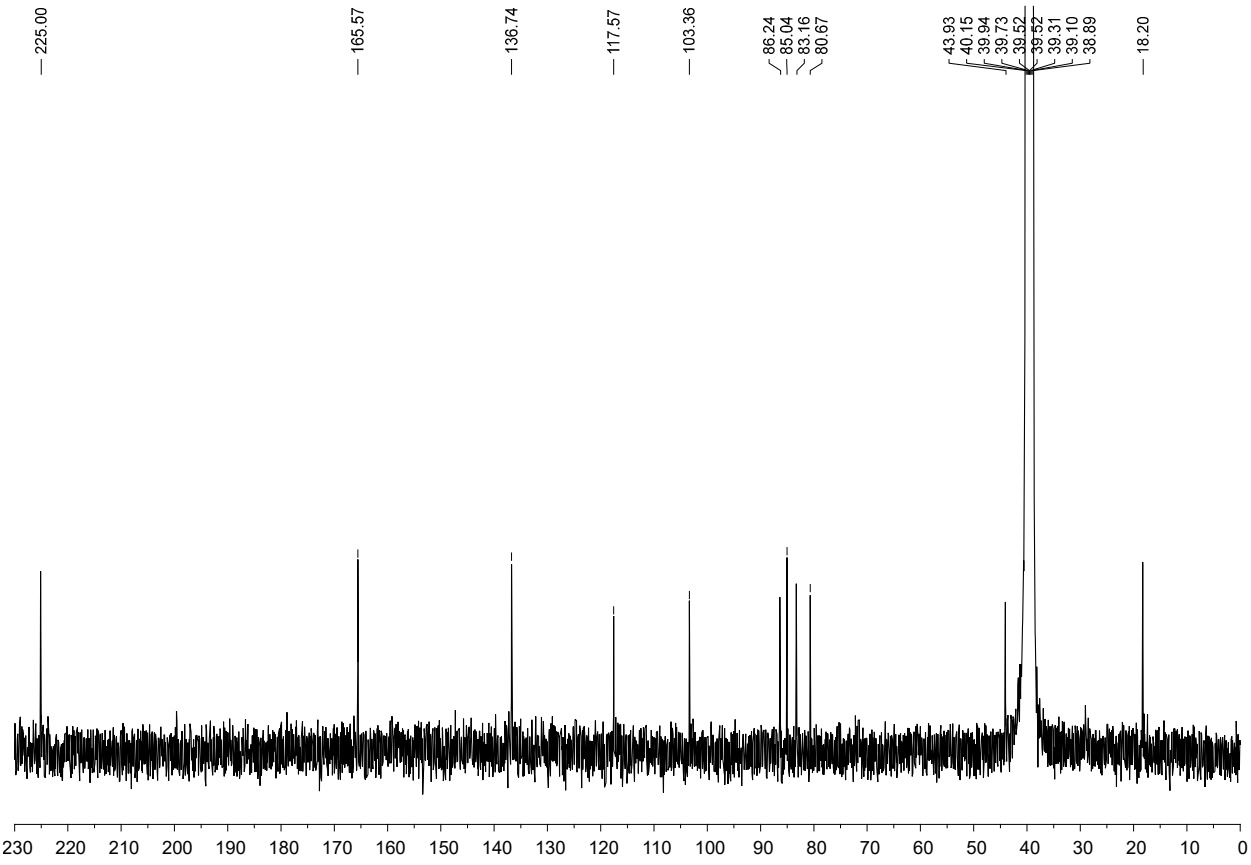


Figure S6. ^{13}C NMR spectrum of compound **1** in DMSO-d_6.

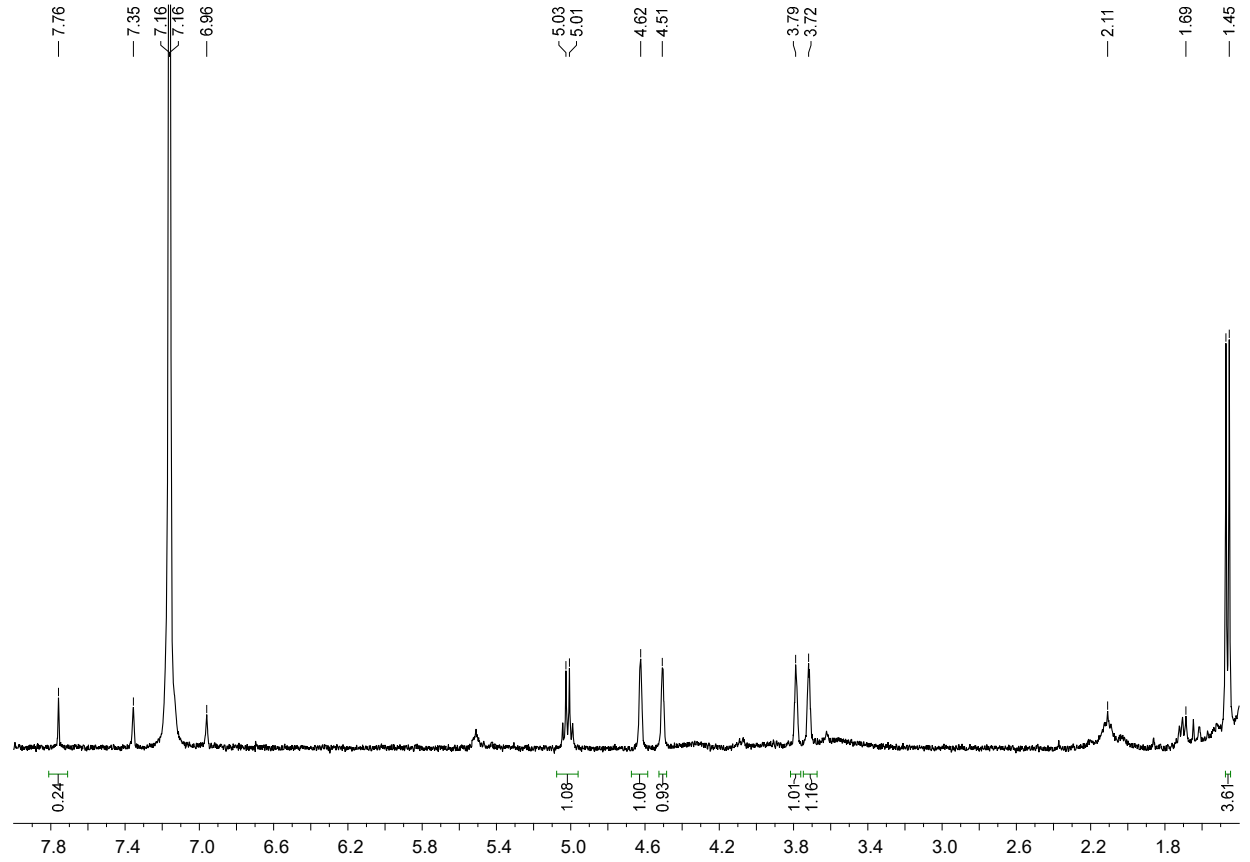


Figure S7. ^{1}H NMR spectrum of compound **1** in benzene-d_6 (256 scans).

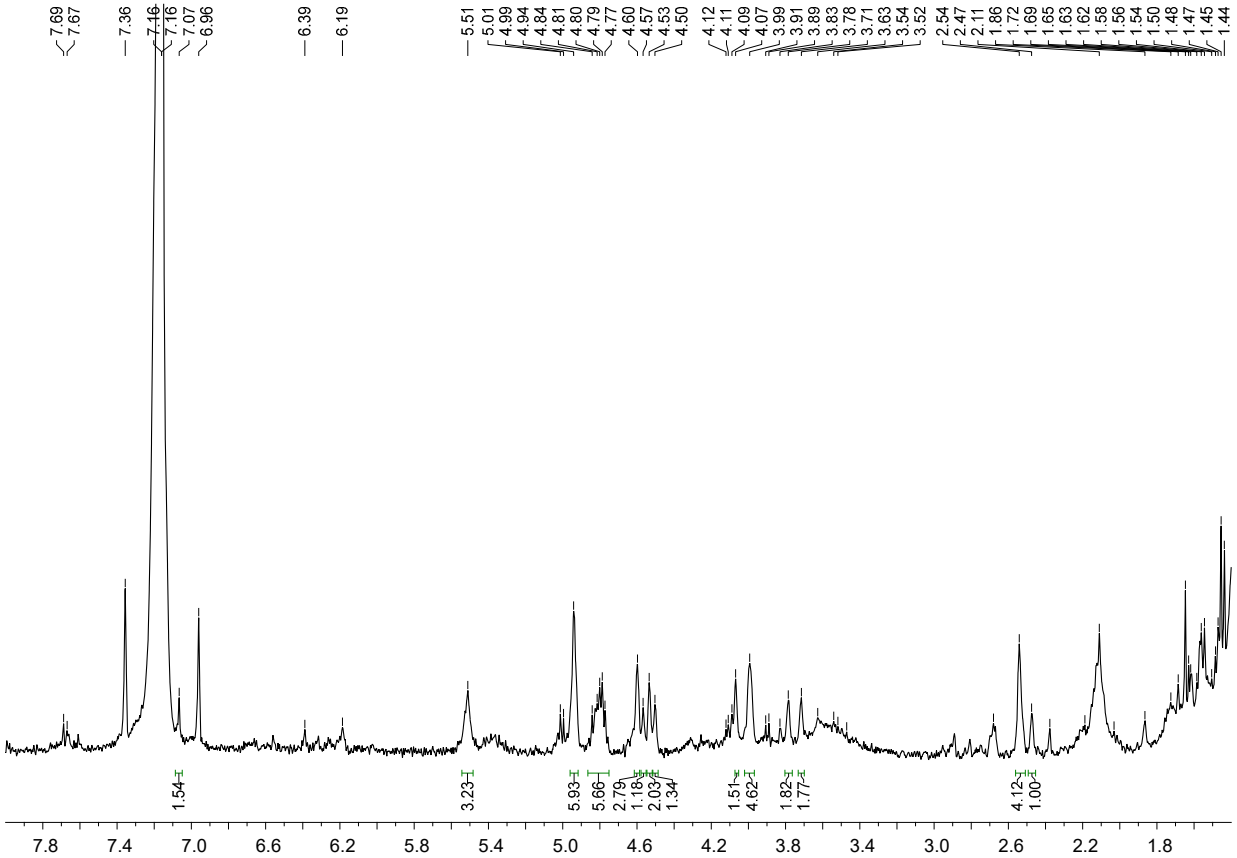


Figure S8. ^{1}H NMR spectrum of compound **1** in benzene-d_6 after irradiation for 30 sec (256 scans).

MS spectra.

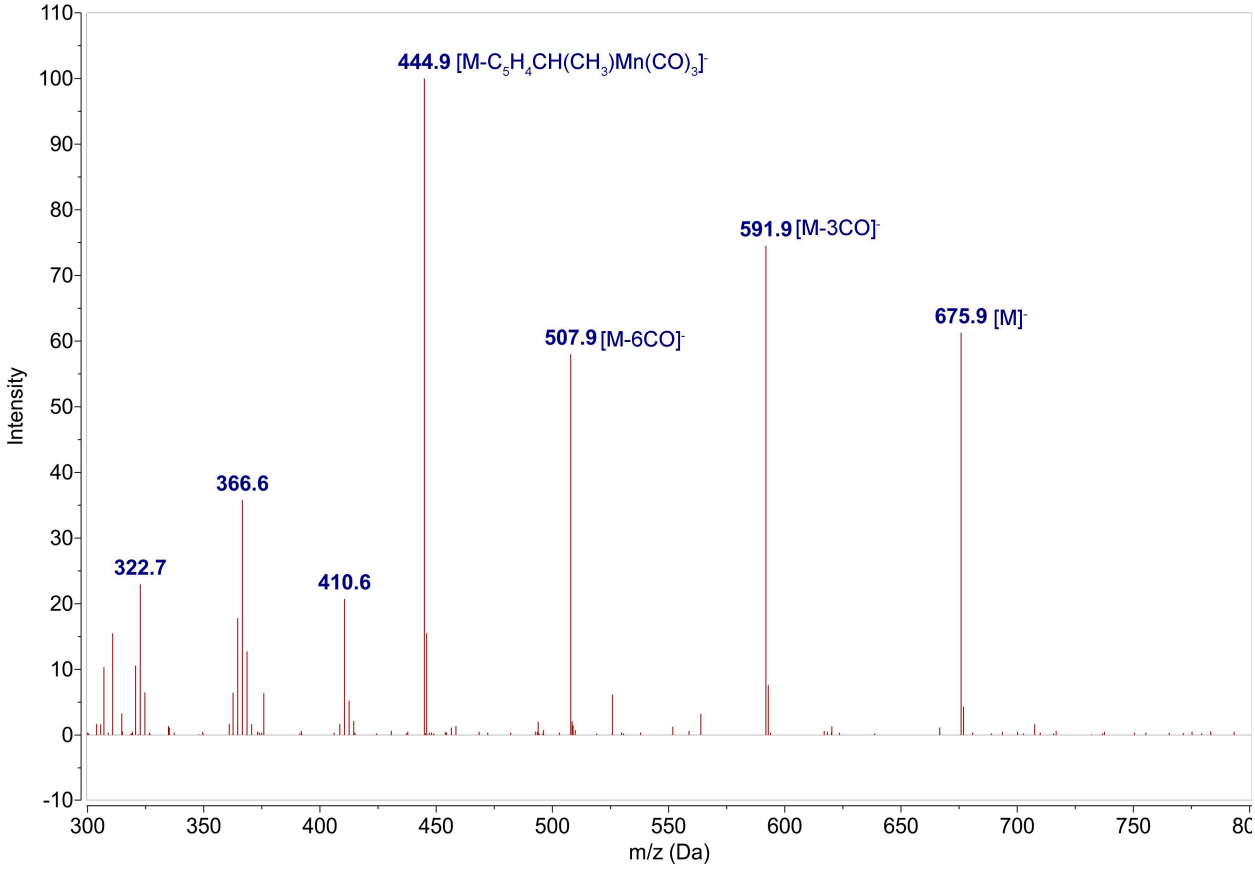


Figure S9. MALDI mass-spectrum of compound **1** (monitoring of photolysis of **1** in benzene).

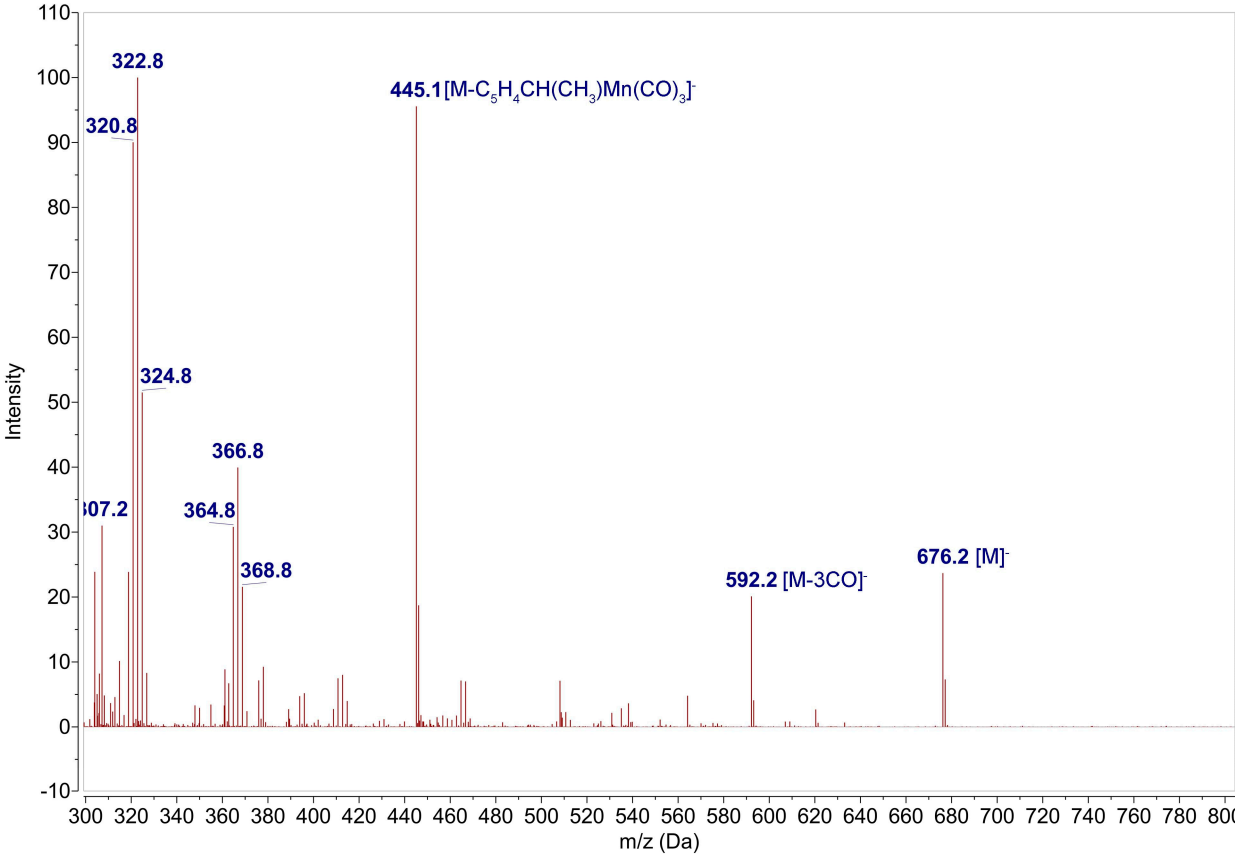


Figure S10. MALDI mass-spectrum of compound **1** after irradiation for 45 s in benzene.

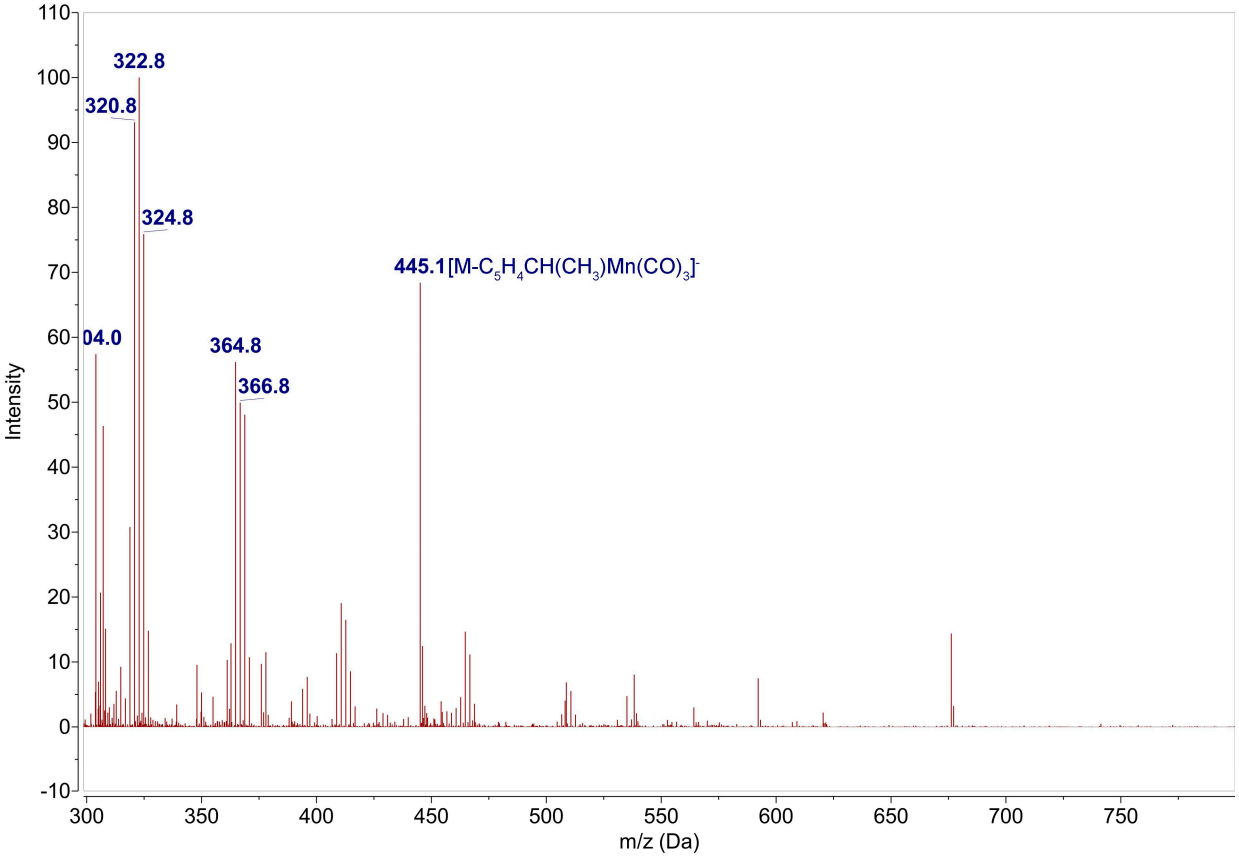


Figure S11. MALDI mass-spectrum of compound **1** after irradiation for 135 s in benzene.

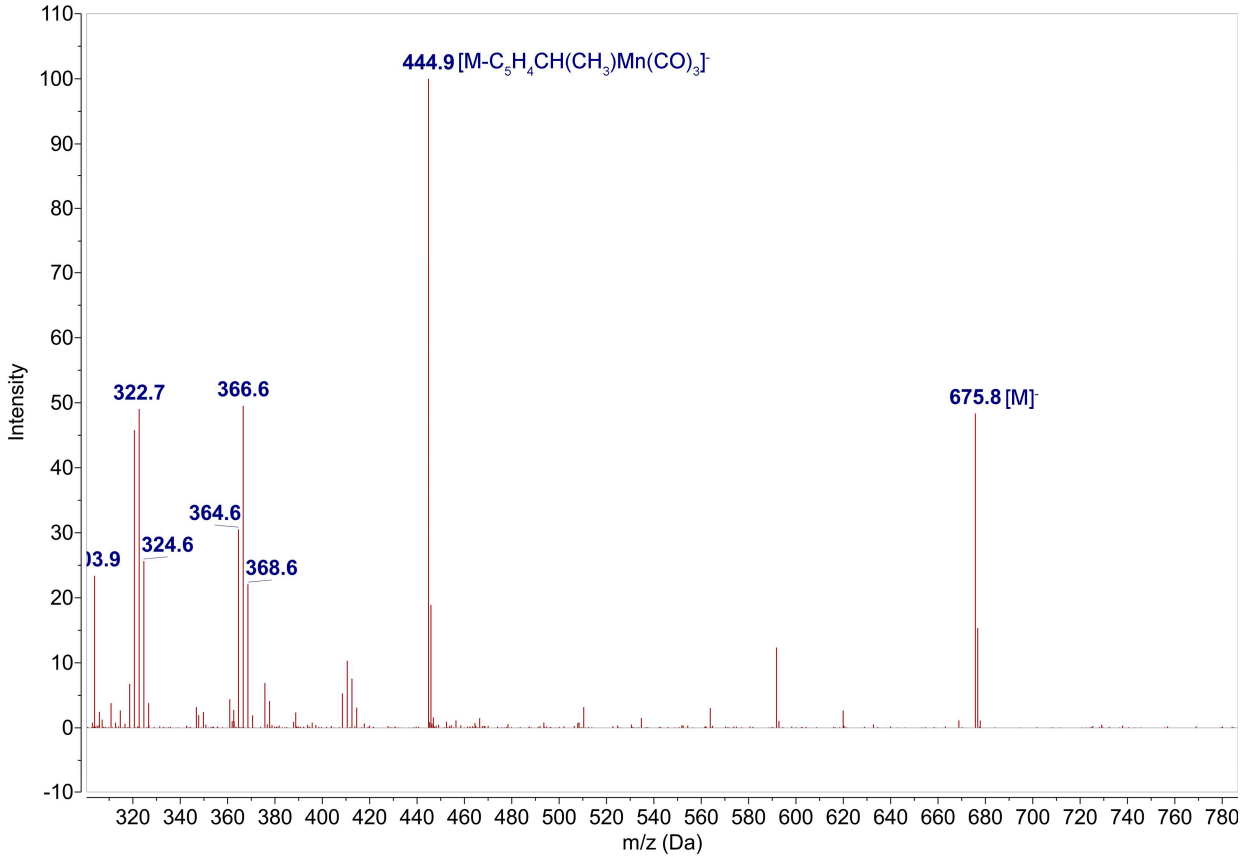


Figure S12. MALDII mass-spectrum of compound **1** (monitoring of photolysis of **1** in benzene : acetonitrile).

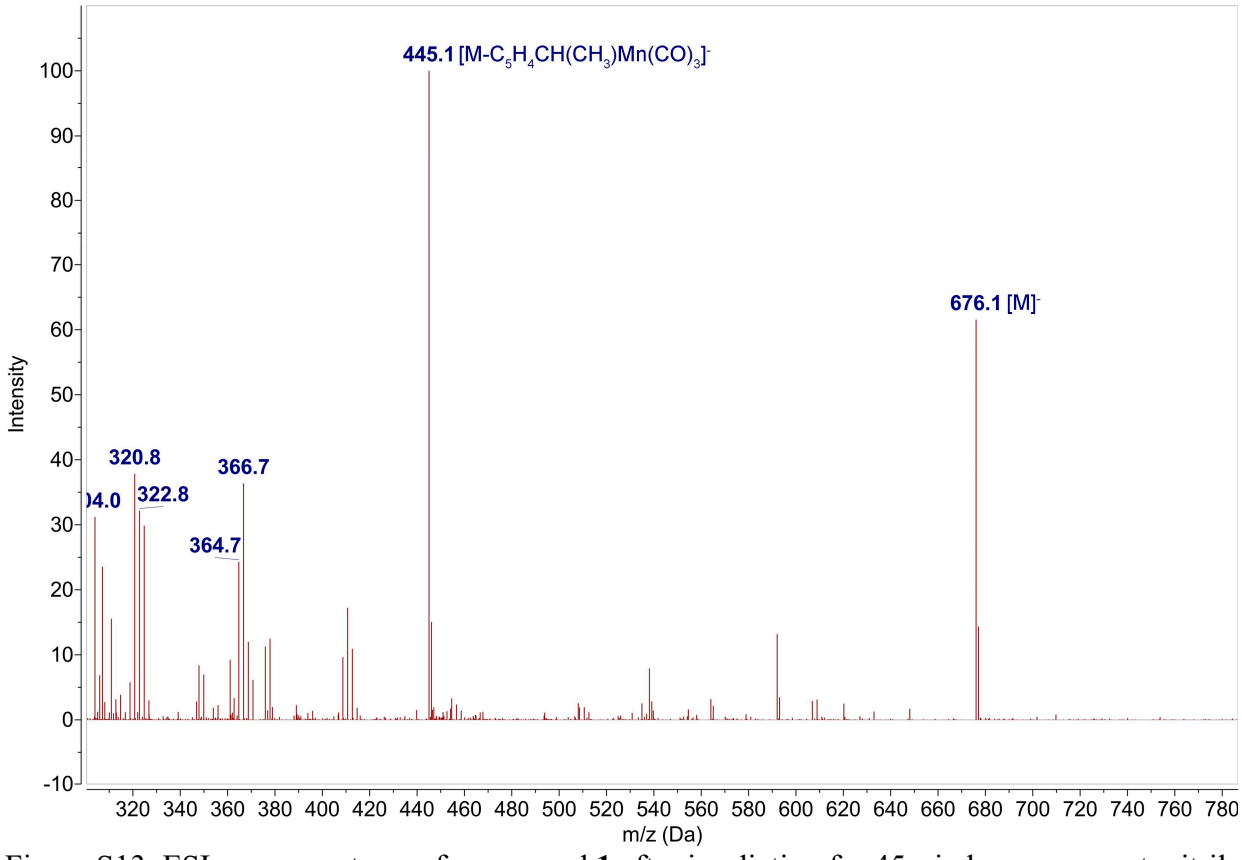


Figure S13. ESI mass-spectrum of compound **1** after irradiation for 45 s in benzene : acetonitrile.

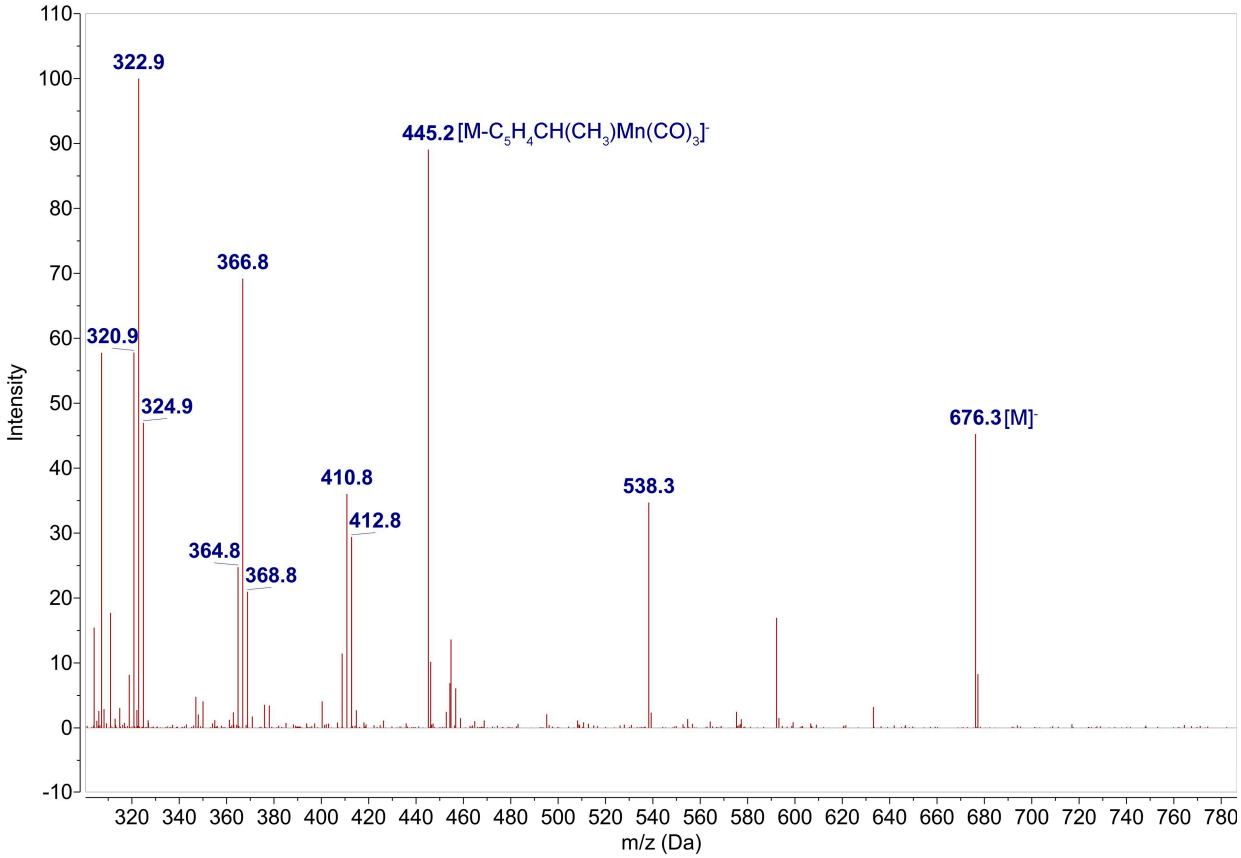


Figure S14. MALDI mass-spectrum of compound **1** after irradiation for 135 s in benzene : acetonitrile.

UV-vis spectra.

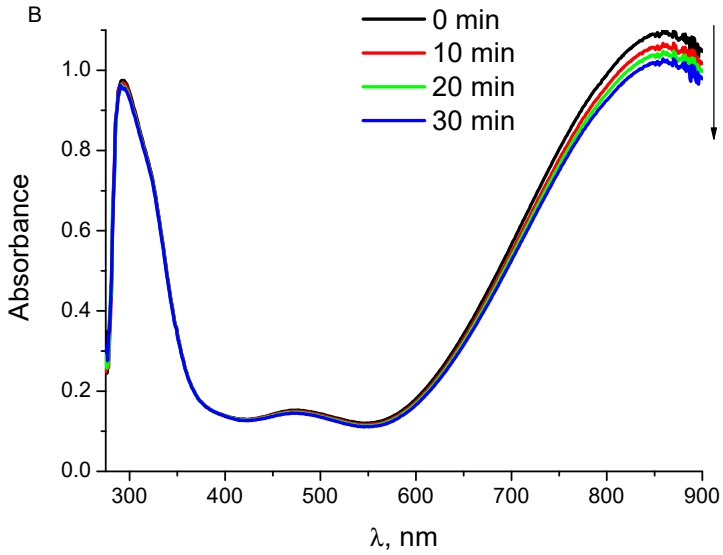


Figure S15. UV-vis monitoring of the thermal reversible reaction after irradiation of **1** in benzene during 30 min.

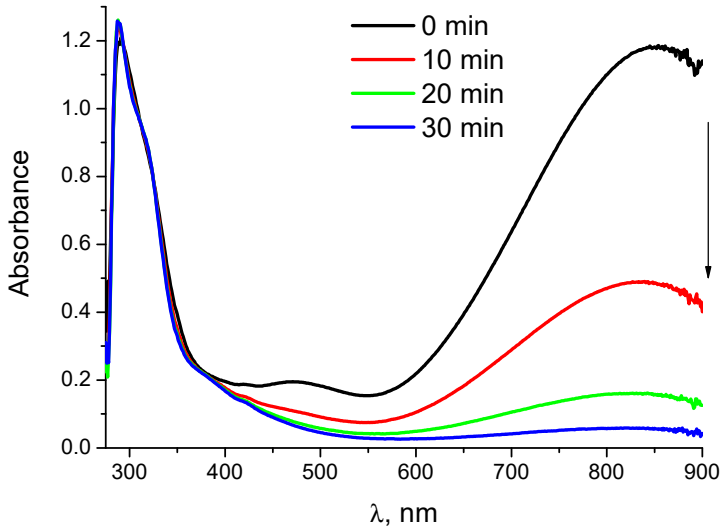


Figure S16. UV-vis monitoring of the thermal reaction after irradiation of **1** in acetonitrile during 30 min.

Kinetic study.

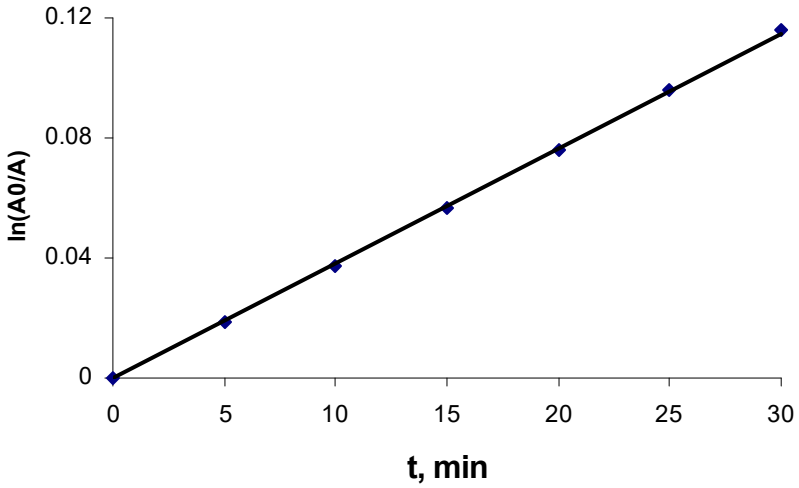


Figure S17. The kinetic curve for thermal transformation of chelates **2** to **1** (C 1 мМ) in benzene at 24 ºC (R = 0.9997) by IR monitoring.

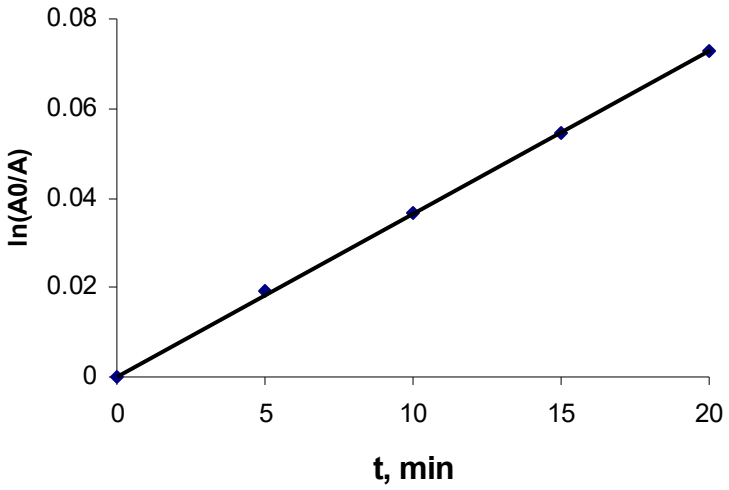


Figure S18. The kinetic curve for thermal transformation of chelates **2** to **1** (C 1 мМ) in benzene at 24 ºC (R = 0.9991) at 859 nm by UV-vis monitoring.

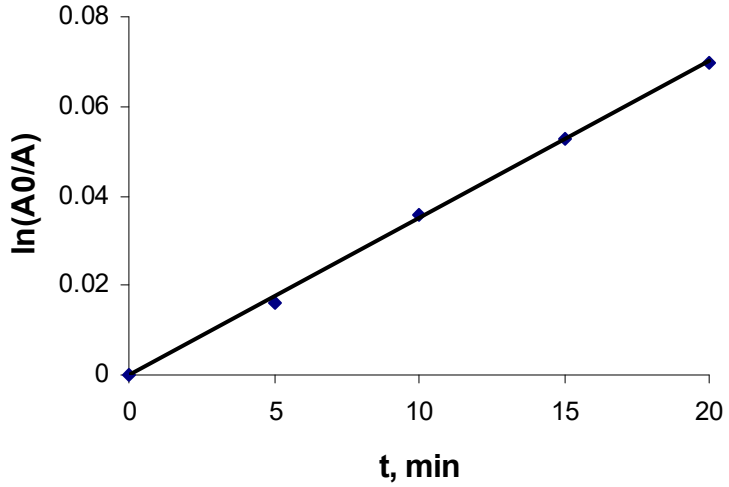


Figure S19. The kinetic curve for thermal transformation of chelates **2** to **1** (C 1 мМ) in benzene at 24 ºC (R = 0.9995) at 475 nm by UV-vis monitoring.

Cyclic voltammograms.

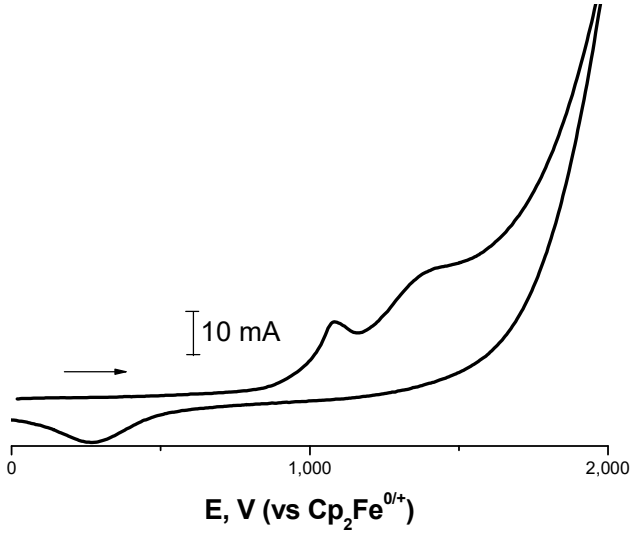


Figure S20. Cyclic voltammogram of compound **7** in 0.1 M tetraethylammonium tetrafluoroborate solution (relative to $Fc^{0/+}$). Scanning speed 100 mV/s.

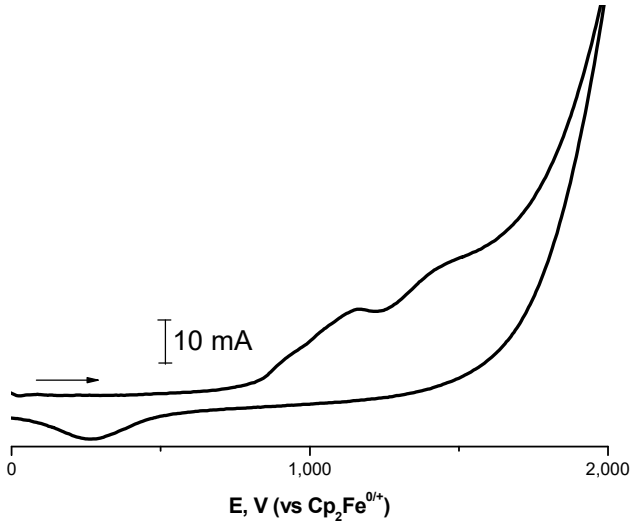


Figure S21. Cyclic voltammogram of compound **7** after irradiation for 2 min in 0.1 M tetraethylammonium tetrafluoroborate solution (relative to $Fc^{0/+}$). Scanning speed 100 mV/s.

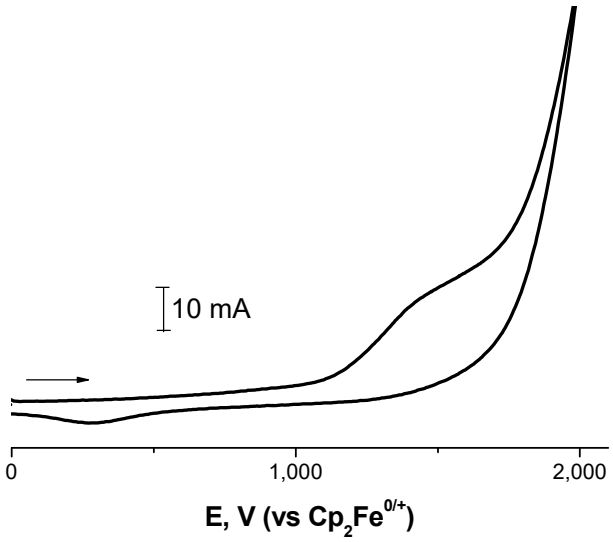


Figure S22. Cyclic voltammogram of compound **1** in 0.1 M tetraethylammonium tetrafluoroborate solution (relative to $Fc^{0/+}$). Scanning speed 100 mV/s.

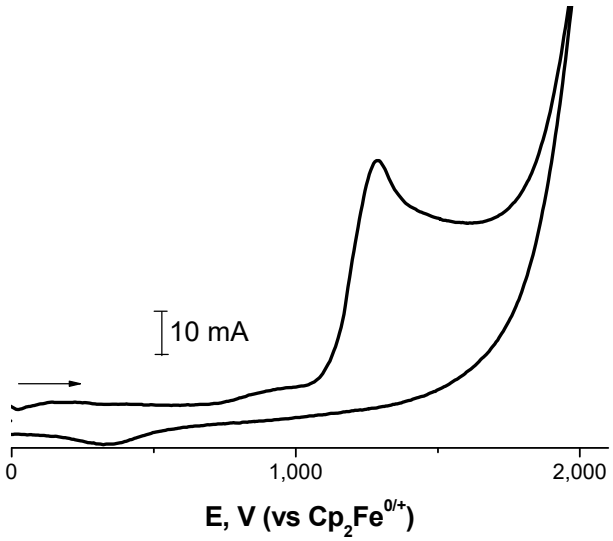
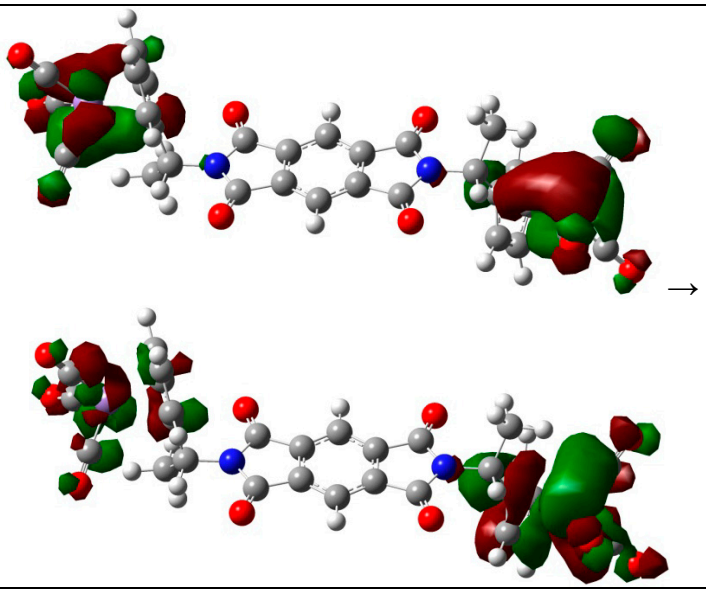
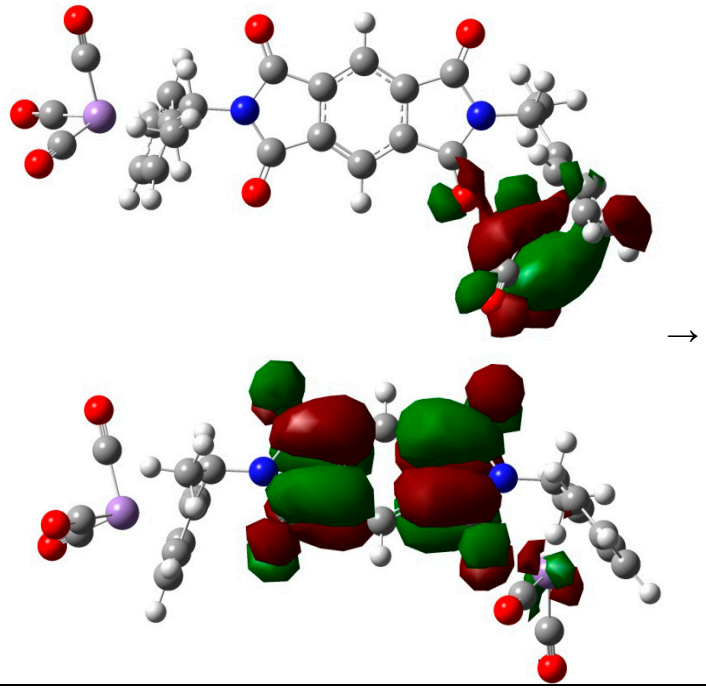
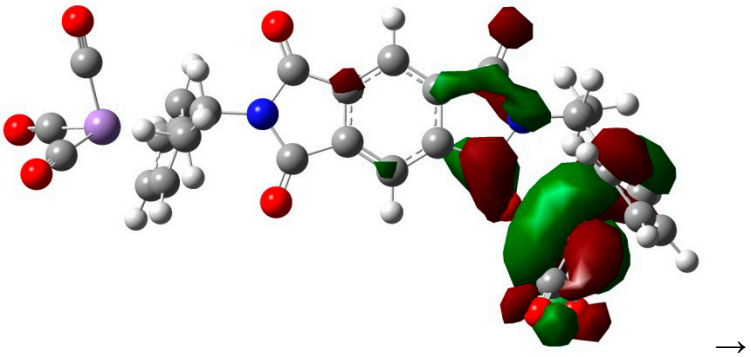


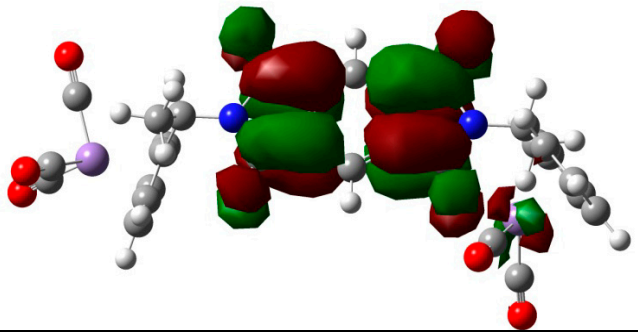
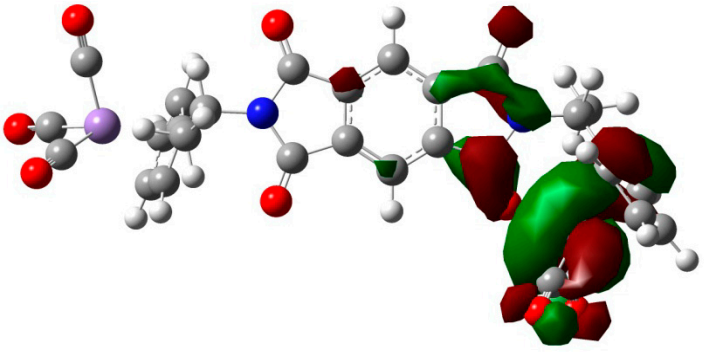
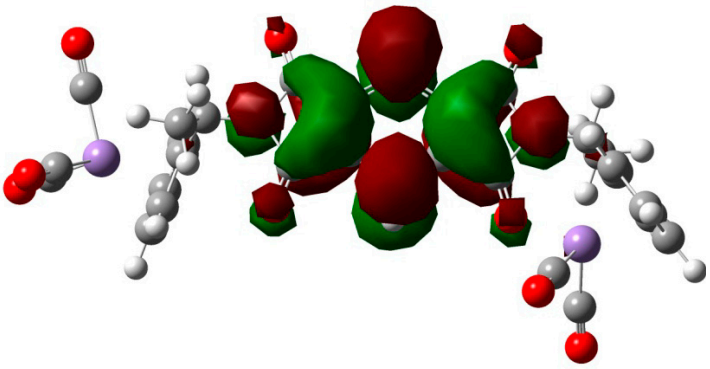
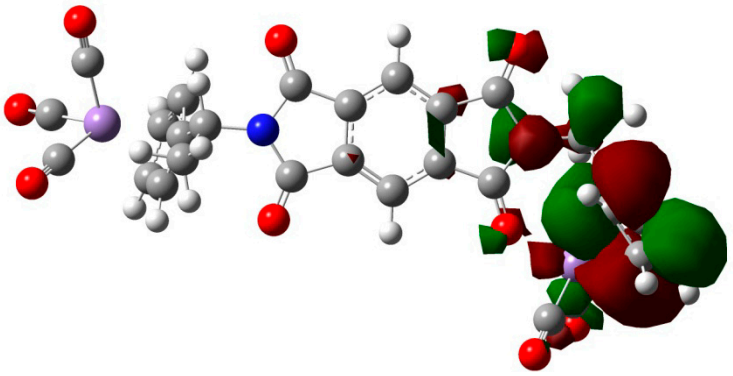
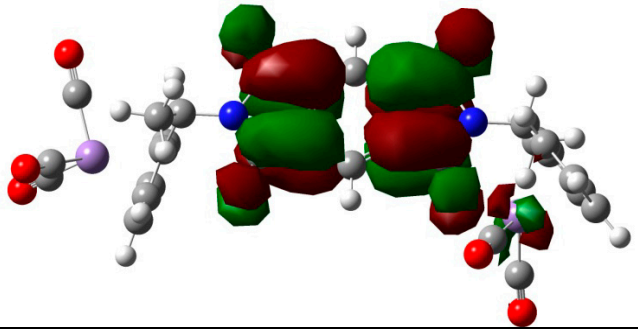
Figure S23. Cyclic voltammogram of compound **1** after irradiation for 2 min in 0.1 M tetraethylammonium tetrafluoroborate solution (relative to $Fc^{0/+}$). Scanning speed 100 mV/s.

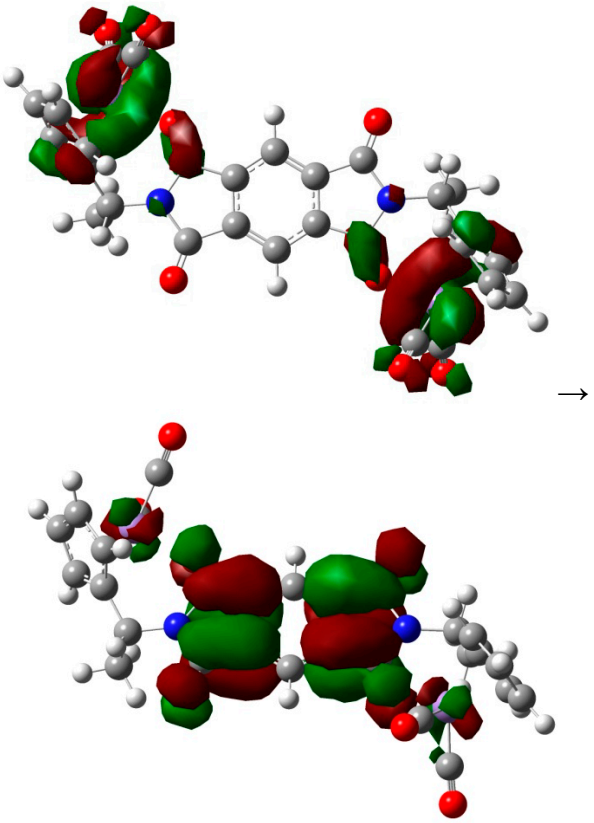
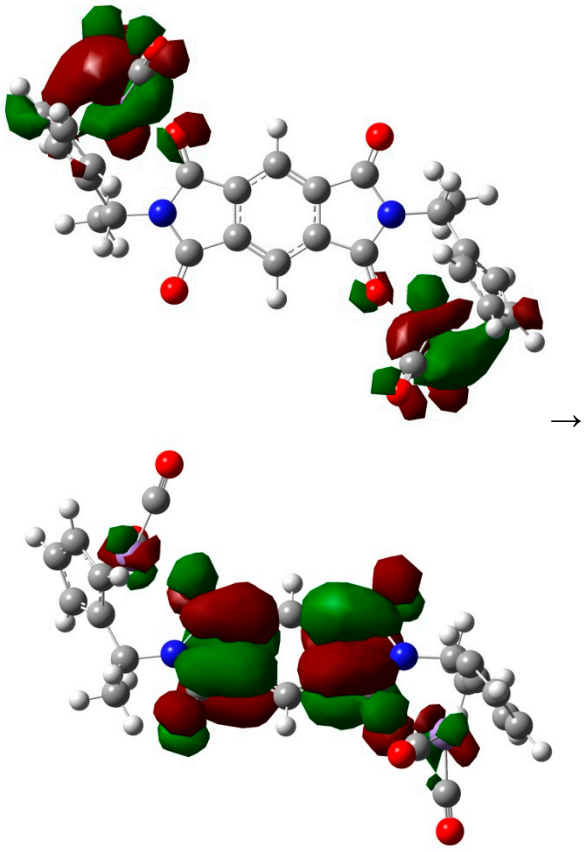
DFT study.

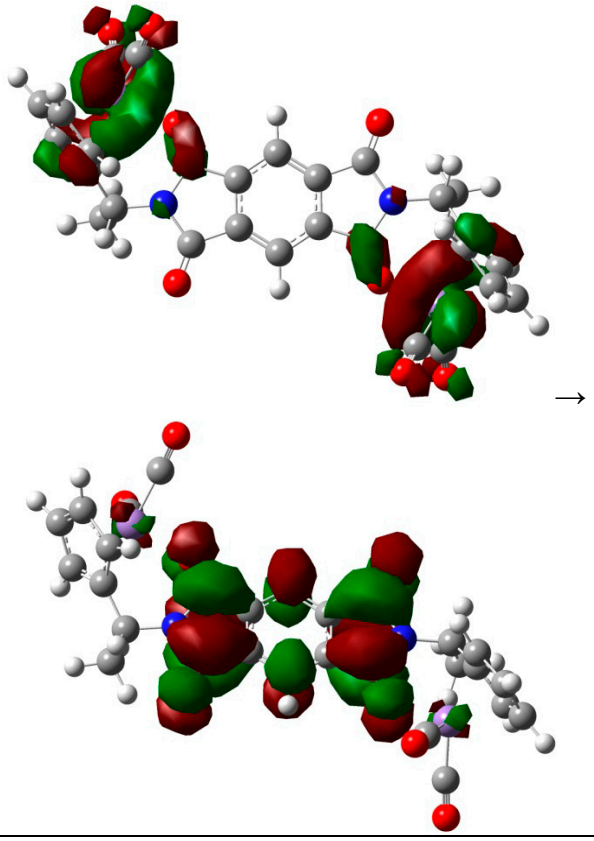
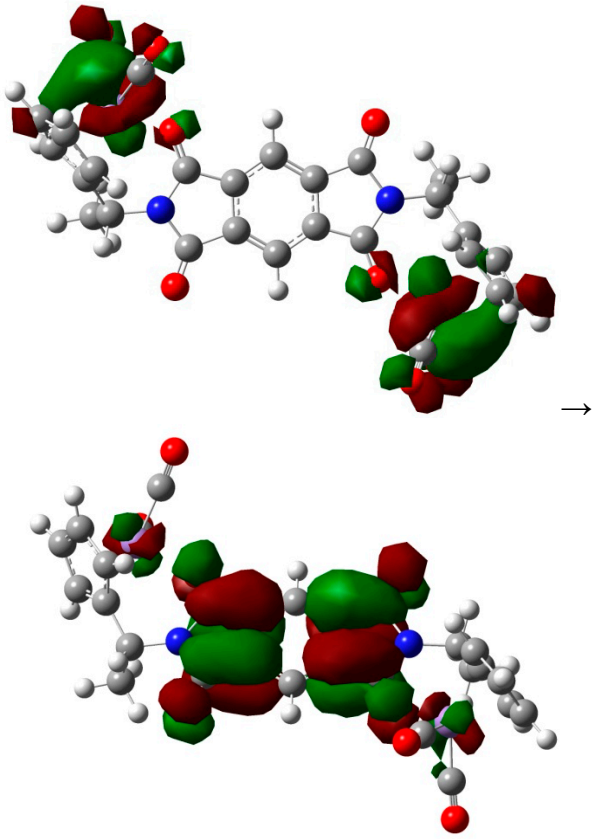
Table S1. Selected TD-DFT results at B3lYB/Def2-TZVP level

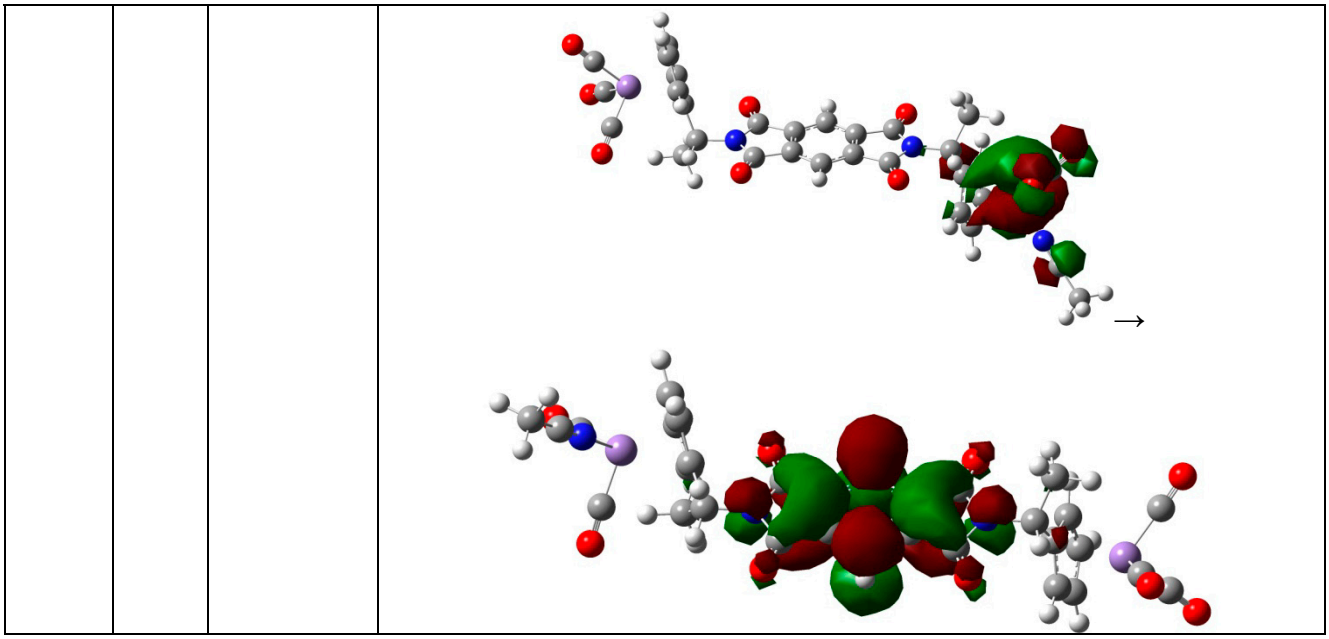
Number of transition	L, nm	Oscillator strength	Transition orbitals
1			
10	352	0.03899	169→174

			
2a			
1	832	0.02049	162→164 
2	750	0.20162	163→164 

			
7	484	0.02409	163→165  → 
13	397	0.01203	157-164  → 
2b-*t*			

1	873	0.16781	156 (HOMO) →157 (LUMO) 
3	826	0.28189	154→157 
11	501	0.04114	156→159

			
20	399	0.01508	153→157 
3a			
9	402	0.013651	173→176



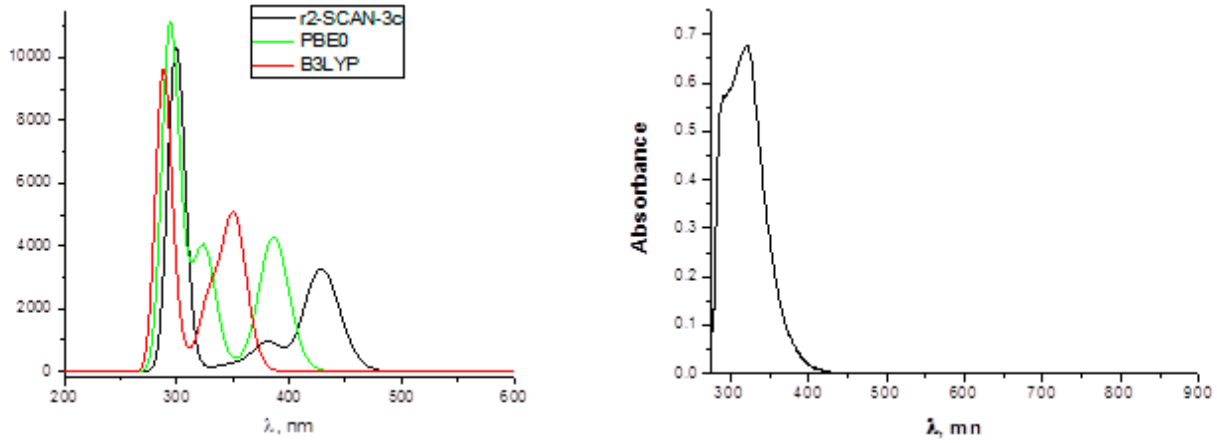


Figure S24. Comparison for TD-DFT simulated absrobtion spectra for **1** using B3LYP, r2-SCAN-3c, and PBE0 functionals (right graph); experimental absorbtion spectrum of **1** in benzene (left graph).

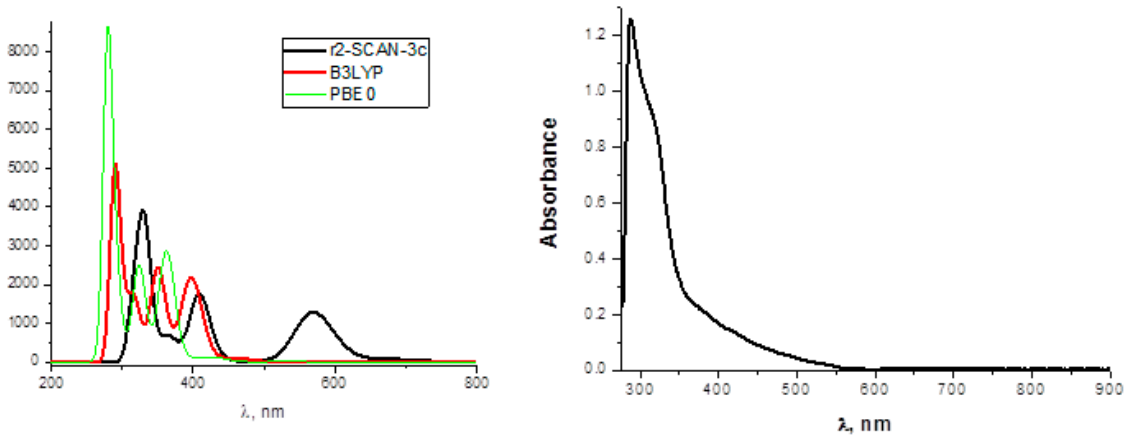


Figure S25. Comparison for TD-DFT simulated absorbtion spectra for **3a** using B3LYP, r2-SCAN-3c, and PBE0 functionals (right graph); experimental absorbtion spectrum for **3** in a mixture of benzene: acetonitrile (left graph).

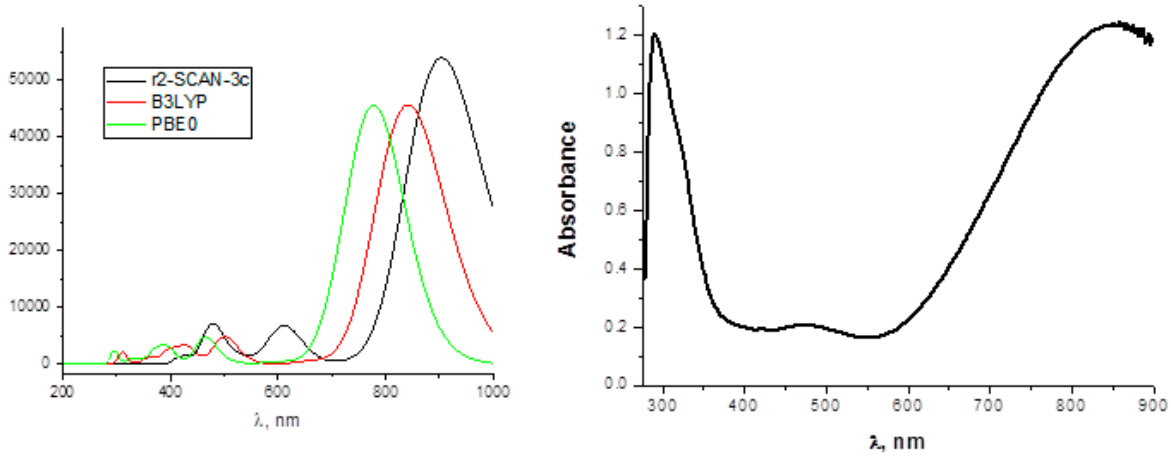


Figure S26. Comparison for TD-DFT simulated absorbtion spectra for **2a** using B3LYP, r2-SCAN-3c, and PBE0 functionals (right graph); experimental absorbtion spectrum for **2** in benzene (left graph).

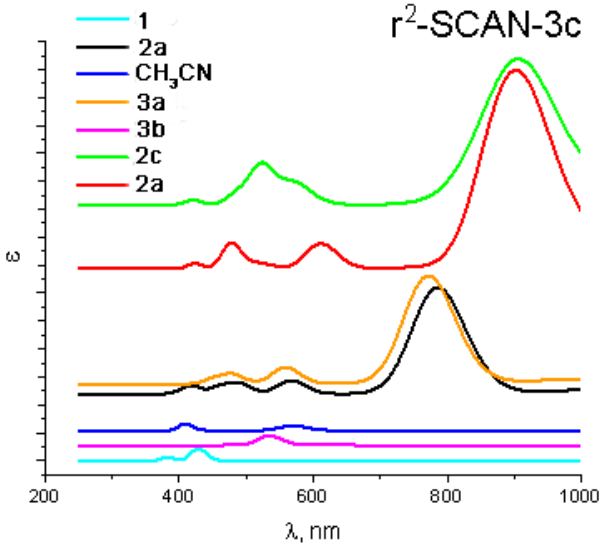


Figure S27. TD-DFT simulated absorbtion r2-SCAN-3c/Def2-TZVP level.