Electronic Supplementary Material (ESI) for RSC Advances.

Photoinduced and Ground State Conversions in a Cyclic β-Thioxoketone

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Supplementary materials

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Table S1. Results of calculations (B3LYP/6311++G(d,p)).

		E (S_0) [a] [kcal/mol]	S_0-S_1 [b] [nm/cm^{-1}/*f*]	S_0-S_2 [b] [nm/cm^{-1}/*f*]	μ(S_0) [c] [D]	^{1}H [ppm]	IR Freq [d] [cm^{-1}]
1	vac	0.0 (0.0)	455/22.0/0.0004	325/30.8/0.23	4.04	16.94	2777 (OHs) 1575 (OHb)
	DCM	0.0 (0.0)	443/22.6/0.0005	335/29.8/0.30	5.61	16.93	2754 (OHs) 1558 (OHb)
	exp		475/21.1	376/26.6		16.8	
2	vac	4.66 (2.68)	353/28.3/0.0008	309/32.3/0.21	3.66	14.20	2259 (SHs) 1631 (COs) 1489 (def, SHb)
	DCM	4.40 (2.50)	347/28.8/0.0014	315/31.7/0.27	4.92	13.58	2303 (SHs) 1611 (COs) 1474 (def, SHb)
	exp						
2a	vac	6.88 (5.30)	351/28.5/0.0002	294/34.0/0.21	4.24	3.92	2601 (SHs) 1694 (COs) 1530 (def, SHb)
	DCM	4.77 (3.35)	345/29.0/0.0007	308/32.5/0.35	5.76	4.35	2624 (SHs) 1665 (COs) 1515 (def, SHb)
	exp			286/35.0			
3	vac	6.40 (4.38)	339/29.5/0.0018	283/35.3/0.24	2.04	3.72	2697 (SHs, vw) 1720(COs) 1585 (def)
	DCM	5.50 (3.55)	328/30.5/0.0078	299/33.4/0.38	2.87	3.99	2695 (SHs, vw) 1695(COs) 1580 (def)
	exp			286/35.0		3.25	

4	vac	10.65 (8.27)	266/37.6/0.0044	257/38.9/0.096	1.20	4.80(OH) 2.47(SH)	3731 (OHs) 2668 (SHs,vw) 1706 (def COH)
	DCM	10.92 (8.49)	261/38.2/0.0073	256/39.0/0.18	1.61	5.02(OH) 2.76(SH)	3720 (OHs) 2672 (SHs,vw) 1704 (def COH)
	exp			268/37.3		5.0 (OH) 2.6 (SH)	
5	vac	7.51 (5.09)	301/33.2/0.0029	234/42.7/0.077	3.78	3.99	2653 (SH, w) 1768 (COs)
	DCM	6.21 (3.88)	295/33.9/0.0043	231/43.2/0.10	5.08	3.96	2662 (SH, w) 1737 (COs)
	exp					3.62 (CH) 2.6 (SH)	
6	vac	5.75 (5.69)	499/20.0/0.0	302/33.1/0.014	3.66		1774 (COs) 1040 (CSs)
	DCM	4.16 (4.18)	491/20.4/0.0	317/31.6/0.021	5.91		1743 (COs) 1032 (CSs)
7	vac	6.32 (5.05)	271/36.9/0.0056	251/39.8/0.087	2.01	4.06 (CH) 1.96 (SH)	2668 (SH)
	DCM	6.27 (5.09)	263/38.0/0.016	251/39.8/0.18	2.78	4.20	2671 (SH)

						(CH) 2.37 (SH)	
1anti	vac	11.46 (11.70)	543/18.4/0.0008	330/30.3/0.27	2.85	5.80	3814 (OH)
	DCM	10.85 (11.16)	523/19.1/0.0012	343/29.2/0.38	4.55	6.26	3801(OH)

[a] in parentheses, zero-point energy-corrected values; [b] calculated transition wavelength in nm, wavenumbers/10^3, oscillator strength; [c] ground state dipole moment [d] b: bend, s: stretch.

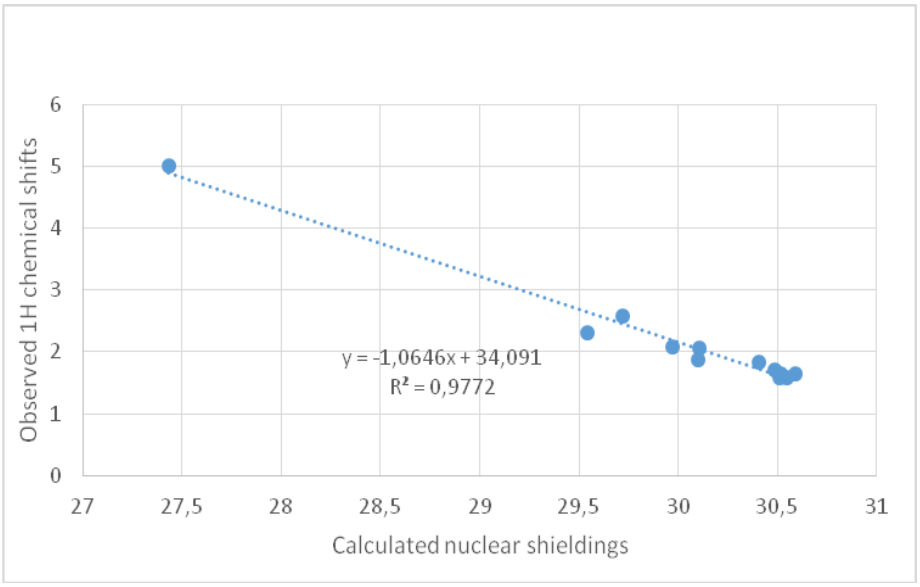

Figure S1. Plot of ^{1}H chemical shifts of **MTPO** vs. calculated nuclear shieldings.

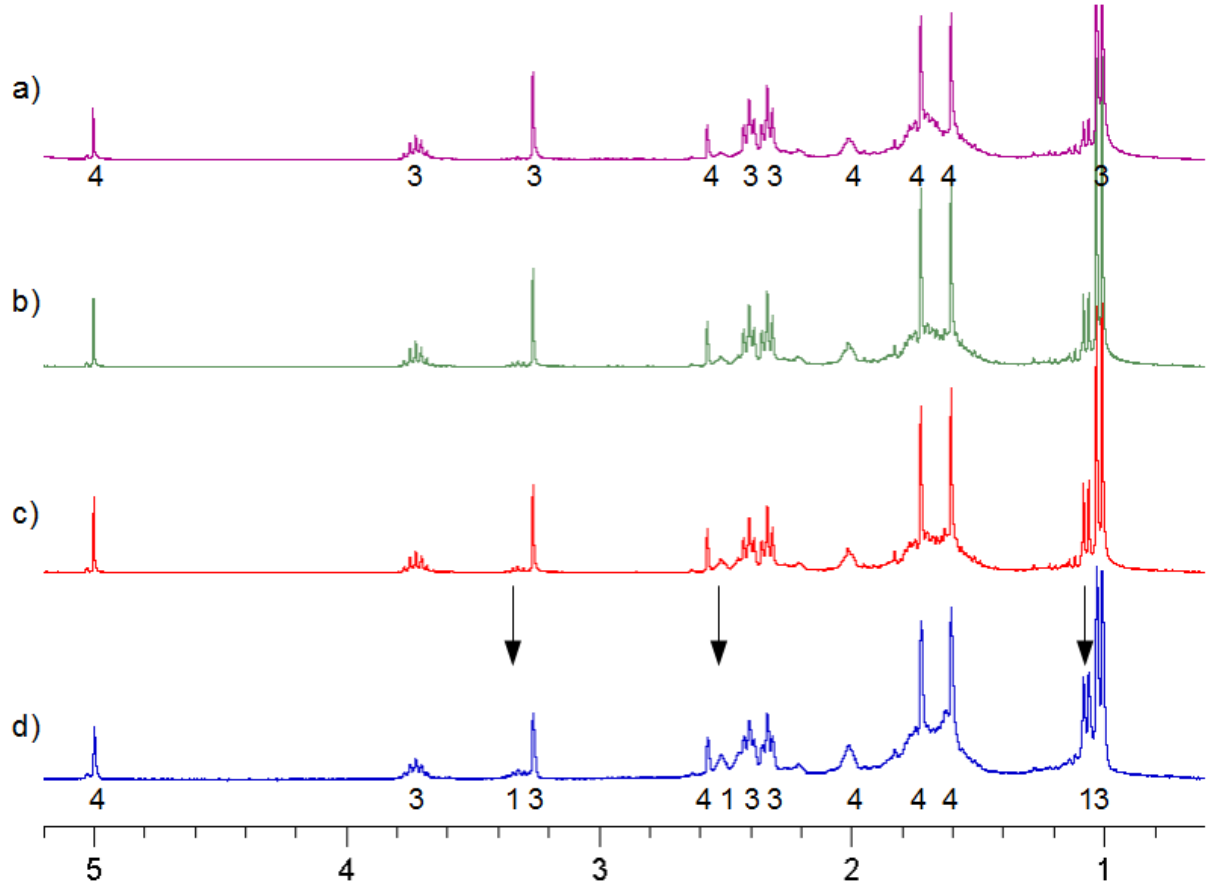

Figure S2. ^{1}H NMR spectra of **MTPO** (3.0 mg in 0.6 ml CD_2Cl_2) after irradiation at 198 K for 2 hours resulting in a mixture of **3** and **4** measured at 198 K in the dark. a) just after irradiation; b) after 4 hours in the dark; c) after 8 hours in the dark; d) after 12 hours in the dark. The arrows indicate appearing signals of **MTPO.**

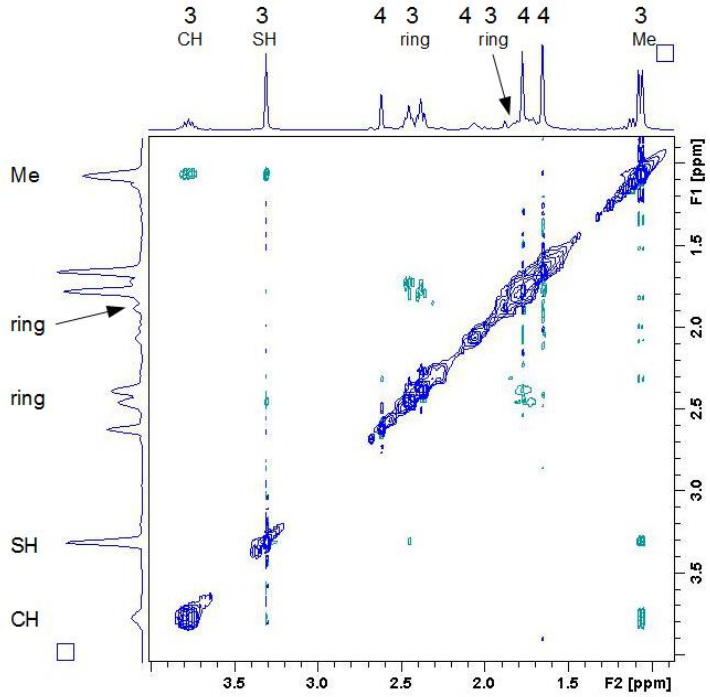

Figure S3. ^{1}H-NOESY spectrum of compound **MTPO** (3.0 mg in 0.6 ml CD_2Cl_2) after irradiation for 2 hours with UV-light at 198 K resulting in **3** and **4** mixture. The line assignment is shown with numbers and arrows. Mixing time was 0.7 s.

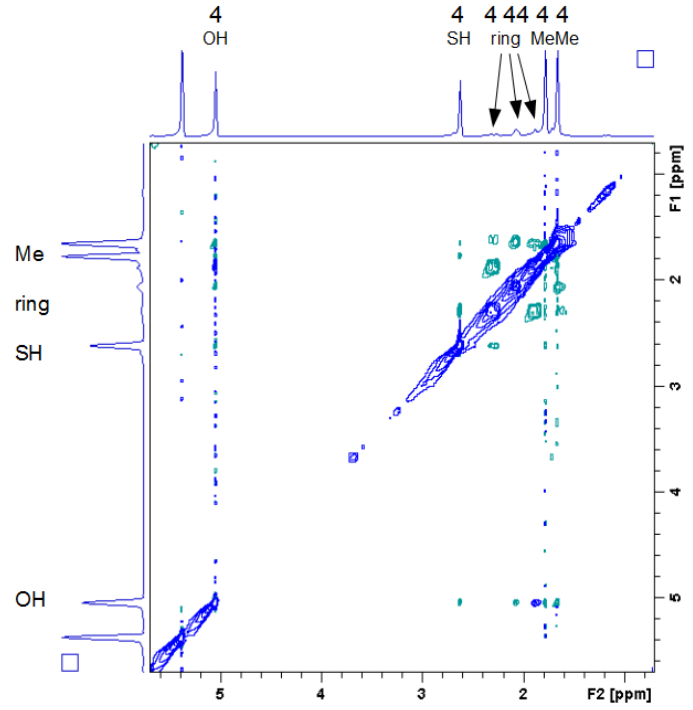

Figure S4. ^{1}H-NOESY spectrum of compound **MTPO** (3.0 mg in 0.6 ml CD_2Cl_2) after irradiation for 4 hours with UV-light at 198 K resulting in almost pure **4**. The line assignment is shown with numbers and arrows. Mixing time was 1.2 s.

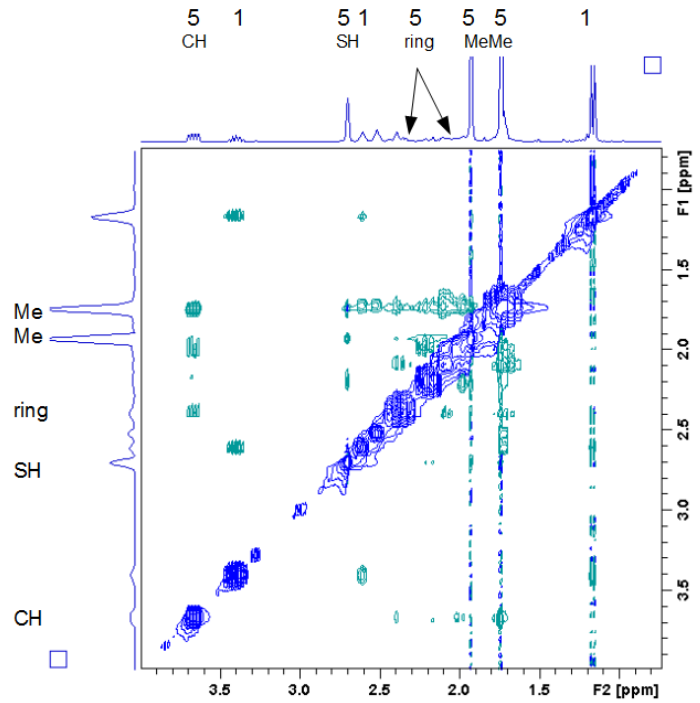

Figure S5. ^{1}H-NOESY spectrum of compound **MTPO** (6.0 mg in 0.6 ml CD_2Cl_2) after irradiating for 16 hours with UV-light at 198 K and storing at room temperature for 2 hours resulting in **5** and **MTPO** mixture measured at 238 K. The quartz rod was fixed above the meniscus during irradiation. The line assignment is shown with numbers and arrows. Mixing time was 1.5 s.

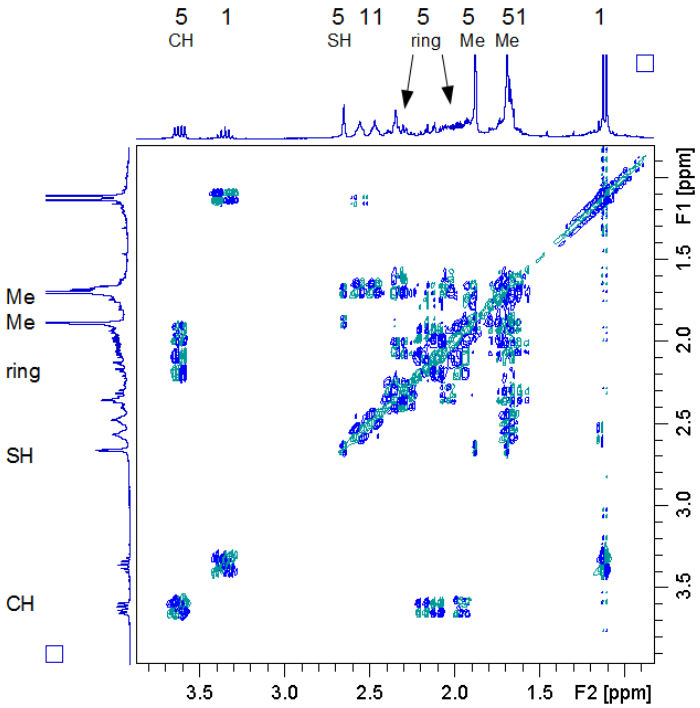

Figure S6. ^{1}H-COSY spectrum of compound **MTPO** (6.0 mg in 0.6 ml CD_2Cl_2) after irradiating for 16 hours with UV-light at 198 K and storing at room temperature for 2 hours resulting in **5** and **MTPO** mixture measured at 238 K.

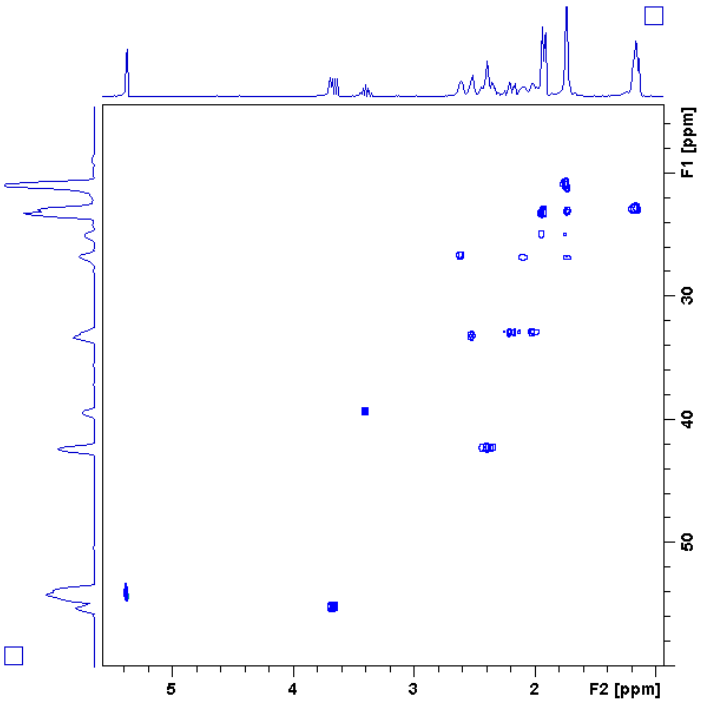

Figure S7. ^{1}H-^{13}C HSQC spectrum of compound **MTPO** (6.0 mg in 0.6 ml CD_2Cl_2) after irradiating for 16 hours with UV-light at 198 K and storing at room temperature for 2 hours resulting with **5** and **MTPO** mixture measured at 238 K. Optimized for J = 130 Hz.

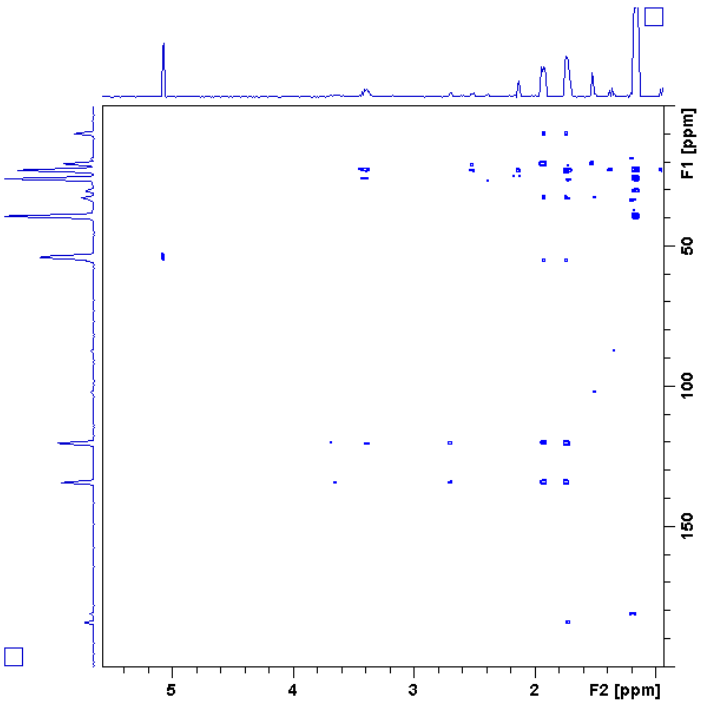

Figure S8. ^{1}H-^{13}C HMBC spectrum of compound **MTPO** (6.0 mg in 0.6 ml CD_2Cl_2) after irradiating for 16 hours with UV-light at 198 K and storing at room temperature for 2 hours resulting with **5** and **MTPO** mixture measured at 238 K. Optimized for J = 4 Hz.

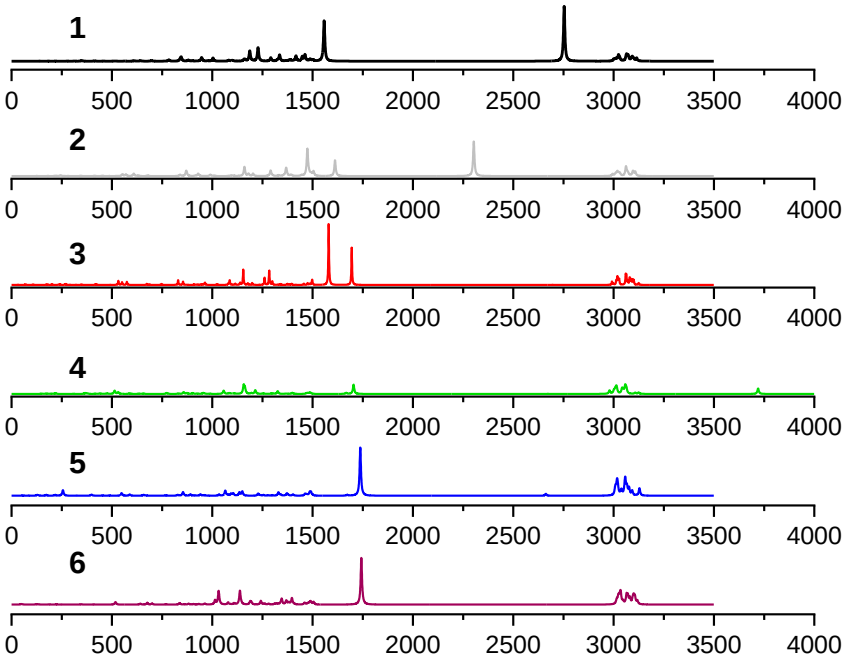

Figure S9. Simulated IR spectra for **1** – **6** in CH_2Cl_2, with the same intensity scale for each form.

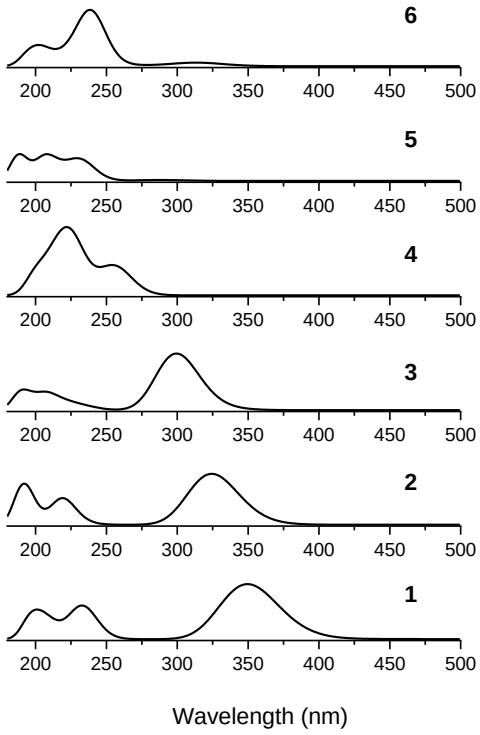

Figure S10. Simulated electronic absorption spectra for **1** – **6** in CH_2Cl_2, with the same intensity scale for each form. Half-width at half-height of 2000 cm^{-1} was assumed.