Supplementary Material (ESI) for Chemical Communications

Efficient Ultraviolet-Light Energy Dissipation by an Aromatic Ketone

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Electronic Supplementary Information

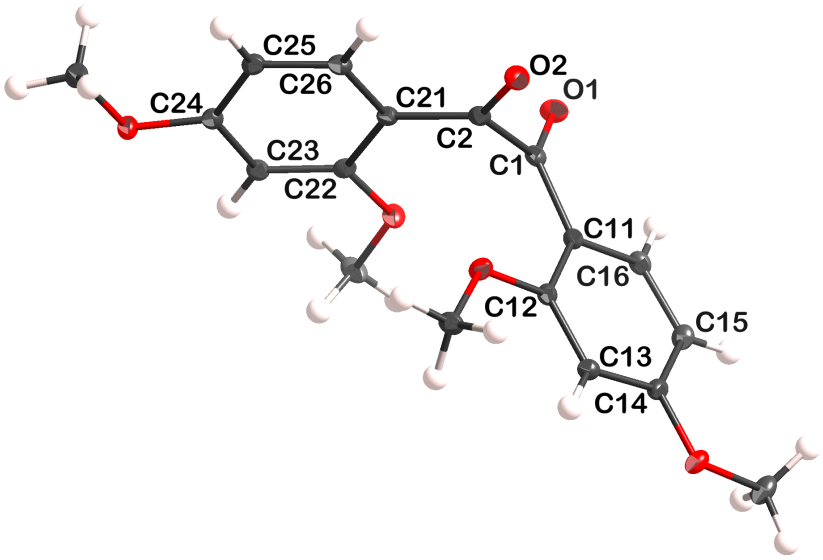


Figure S1. X-ray ellipsoid plot of **TMBZ** (50% probability level) with the labeling scheme (red oxygen, grey carbon and white hydrogen atoms).

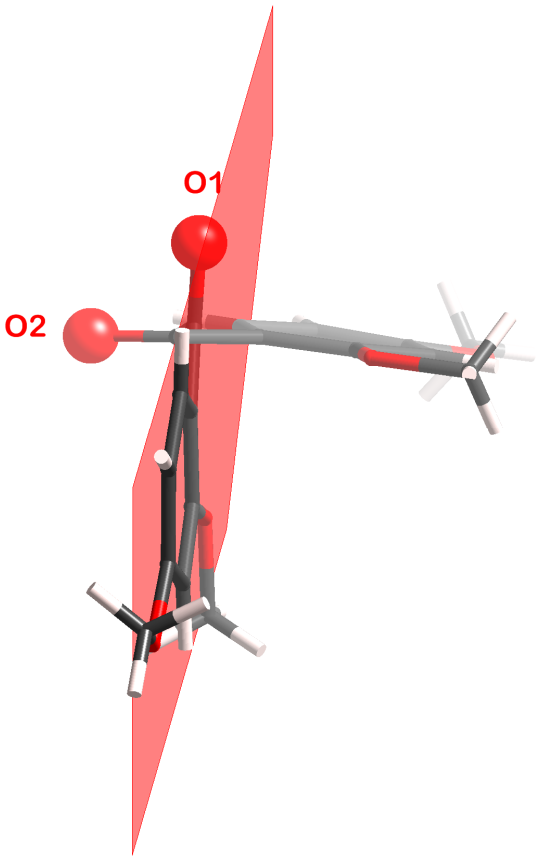


Figure S2. X-ray view of **TMBZ** showing molecular planes arrangement (red oxygen, grey carbon and white hydrogen atoms).

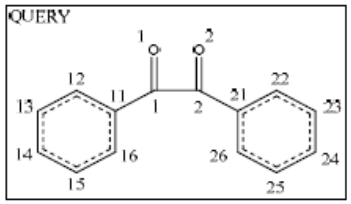
Single crystal X-ray diffraction analysis for **TMBZ** shows a non planar structure with both carbonyl group planes almost perpendicular (dihedral angle 85.27(5)º). In the **TMBZ** structure, every CO group is almost coplanar to its bonded aromatic ring (C11-C1-O1-C2 and C11-C16 dihedral angle 13.53(6)º and C1-C2-O2-C21 and C21-C26 dihedral angle 11.25(6)º). The structures of other benzil derivatives with acyclic carbonyl groups have been reported in the CSD (Cambridge Crystallographic Data Base, version 5.30; 456637 entries). Molecular planes arrangement similar to that of **TMBZ** has been found for most benzyl derivatives structures containing at least one non-substituted ortho position (34 out of 36 structures reported in the CSD, see table 1). However, when all the rings ortho positions are substituted the co-planarity of aromatic ring-carbonyl group is lost while the carbonyl groups torsion angle decreases considerably. **TMBZ** long C(1)-C(2) observed distance of 1.5329(15) Å̊ is similar to the 1.54 Å̊ observed mean value for other C(O)-C(O) bonds.

CSD version 5.30 (November 2008)

Structures that match query with acyclic CO

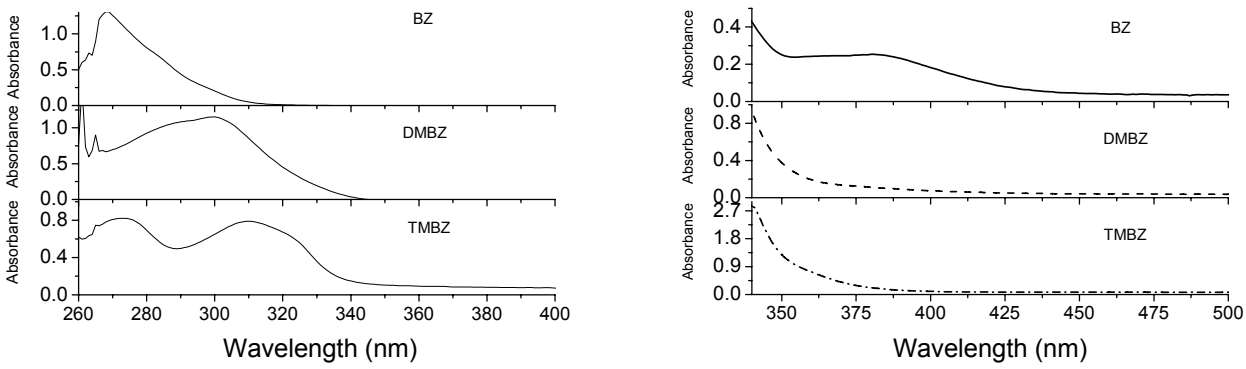
ANG1: Plane1 and Plane2 dihedral angle
ANG2: Plane3 and Plane4 dihedral angle
ANG3: Plane2 and Plane3 dihedral angle

Plane1: C11-C12-C13-C14-C15-C16
Plane2: C11-C1-O1-C2
Plane3: C1-C2-O2-C21
Plane4: C21-C22-C23-C24-C25-C26



CSD Refcode	C1-C2 (Angstrom)	ANG1 (°)	ANG2 (°)	ANG3 (°)	C11-C16 o-subs	C11-C16 m-subs	C11-C16 p-subs	C21-C26 o-subs	C21-C26 m-subs	C21-C26 p-subs	Publication Year	Compound Name
BENZIL	1,522	6,744	6,744	68,405	0	0	0	0	0	0	1965	Benzil
BENZIL02	1,542	6,559	6,559	68,389	0	0	0	0	0	0	1981	Benzil
BENZIL03	1,548	6,693	6,92	73,486	0	0	0	0	0	0	1987	Benzil
BENZIL03	1,526	7,958	7,585	62,225	0	0	0	0	0	0	1987	Benzil
BENZIL03	1,532	8,789	6,284	68,287	0	0	0	0	0	0	1987	Benzil
BENZIL04	1,521	6,566	6,566	68,448	0	0	0	0	0	0	1987	Benzil
BENZIL05	1,529	7,218	7,218	68,202	0	0	0	0	0	0	1987	Benzil
CASGOS	1,528	7,17	0,622	79,536	0	0	1	0	0	0	1983	4-Ethoxybenzil
CIJFIK	1,53	4,843	4,581	67,483	0	0	1	0	0	0	1984	2,2'-Diphenyl-1,1'-(1,4-phenylene)-diethanedione
CIJFIK	1,526	10,802	5,607	63,76	0	0	1	0	0	0	1984	2,2'-Diphenyl-1,1'-(1,4-phenylene)-diethanedione
KOWVEX	1,534	3,559	14,908	70,749	0	0	1	0	0	0	1991	bis(4-(2-Phenyl-1,2-dioxoethyl)phenyl) ether
KOWVEX	1,52	7,541	16,528	53,707	0	0	1	0	0	0	1991	bis(4-(2-Phenyl-1,2-dioxoethyl)phenyl) ether
CASGEI	1,536	5,932	5,932	52,33	0	0	1	0	0	1	1983	4,4'-Dimethoxybenzil
CASGEI01	1,534	5,803	5,803	52,459	0	0	1	0	0	1	1989	4,4'-Dimethoxybenzil
CASGIM	1,535	4,996	4,996	81,042	0	0	1	0	0	1	1983	4,4'-Diethoxybenzil
CASGIM01	1,544	5,007	5,007	80,947	0	0	1	0	0	1	1989	4,4'-Diethoxybenzil
CASGUY	1,527	4,169	4,169	89,467	0	0	1	0	0	1	1983	rac-bis(4-Oxyphenyl-2',2'-dimethyl-1',3'-dioxacyclopentyl-4'-methyl)-ethane-1,2-dic
CASHAF	1,562	5,022	2,549	75,611	0	0	1	0	0	1	1983	rac-bis(4-Oxyphenyl-2',2'-dimethyl-1',3'-dioxacyclopentyl-4'-methyl)-ethane-1,2-dic
CASHEJ	1,562	2,568	9,149	85,153	0	0	1	0	0	1	1983	(S,S)-bis(4-Oxyphenyl-2',2'-dimethyl-1',3'-dioxacyclopentyl-4'-methyl)-ethane-1,2-d
DNBZIL	1,532	3,513	1,954	65,415	0	0	1	0	0	1	1979	4,4'-Dinitrobenzil
JAVLUN	1,528	2,32	16,243	48,311	0	0	1	0	0	1	1989	4,4'-Dibenzyloxybenzil
YODPIR	1,535	4,915	14,405	66,454	0	0	1	0	0	1	2008	(E)-1,2-bis(4-methylphenyl)ethane-1,2-dione
YODPOX	1,536	3,83	9,094	64,643	0	0	1	0	0	1	2008	(E)-1,2-bis(4-fluorophenyl)ethane-1,2-dione
CIJFEG	1,524	6,161	3,288	81,818	0	1	0	0	0	0	1984	2,2'-Diphenyl-1,1'-(1,3-phenylene)-diethanedione
CIJFEG	1,535	4,823	24,648	35,714	0	1	0	0	0	0	1984	2,2'-Diphenyl-1,1'-(1,3-phenylene)-diethanedione
OCUNIK	1,536	11,141	11,141	74,65	0	1	0	0	1	0	2005	3,3'-Dimethoxybenzil
LOLWAK	1,533	42,511	12,741	58,407	1	0	0	0	0	0	2000	3-(2-(Phenyldicarbonyl)phenyl)imino-2-phenyl-3H-indole
QAXPUB	1,529	1,968	0,56	74,027	1	0	0	0	0	1	2005	2,4'-Dihydroxybenzil
JAVLEX	1,519	22,614	14,831	68,634	1	0	0	1	0	0	1989	2,2'-Dimethoxybenzil
WETVIA	1,521	4,803	2,401	86,877	1	0	1	1	0	1	1994	2,2'-Dihydroxy-4,4'-bis(octyloxy)benzil
DACJAS	1,542	6,525	3,654	87,288	1	1	0	1	1	0	1985	alpha-Naphthil
DACJAS10	1,541	6,344	3,624	87,197	1	1	0	1	1	0	1986	alpha-Naphthil
XIQNER	1,54	6,154	5,883	65,593	1	1	0	1	1	0	2007	bis(5-Bromo-2-hydroxyphenyl)ethanedione
MIPCEU	1,558	74,611	74,611	0	2	0	0	2	0	0	2007	bis(2,6-Di-isopropylphenyl)glyoxal
BOLCUA	1,52	80,963	80,963	0,02	2	0	1	2	0	1	1983	Mesitil
BOLCUA	1,535	86,705	86,705	0,02	2	0	1	2	0	1	1983	Mesitil
BOLCUA1	1,533	78,263	75,343	1,696	2	0	1	2	0	1	1985	2,2',4,4',6,6'-Hexamethylbenzil
HXBZLA	1,535	74,861	72,105	54,96	2	0	1	2	0	1	1981	2,2',4,4',6,6'-Hexa-t-butylbenzil
ZIXCAK	1,535	76,221	76,221	0	2	0	1	2	0	1	1995	2,2',4,4',6,6'-Hexaisopropylbenzil
SIWDEH	1,564	52,542	53,938	43,874	2	2	0	2	2	0	1991	Di(9-anthryl)ethane-1,2-dione
SIWDEH01	1,555	86,811	86,84	0,923	2	2	0	2	2	0	1991	Di(9-anthryl)ethane-1,2-dione
KOWVAT	1,542	72,65	20,299	29,318	2	2	1	0	0	0	1991	3,6-bis(2-Phenyl-1,2-dioxoethyl)durene

(A)



(B)

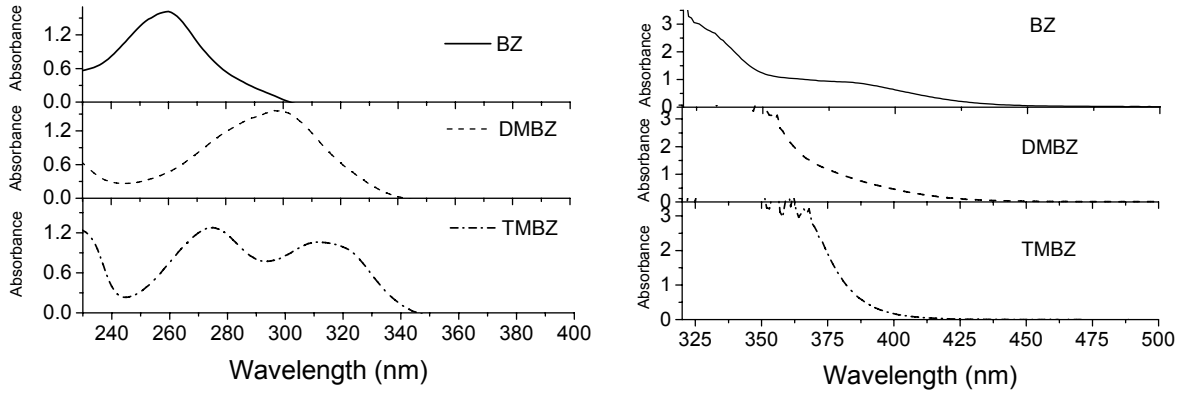


Figure S3. Absorption spectra of BZ, DMBZ, and TMBZ in DMF (A) and MeOH (B).

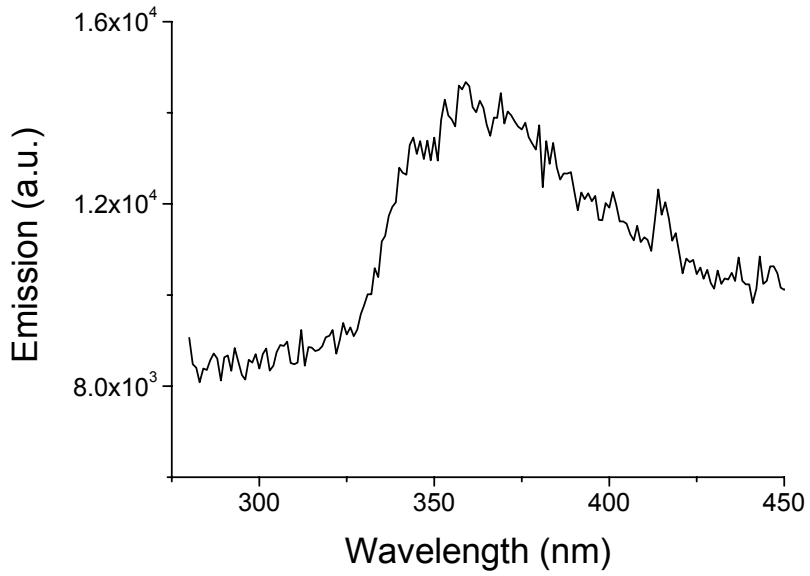


Figure S4. Excitation spectrum (λ_{em}=550 nm) of an deaerated acetonitrile solution of TMBZ

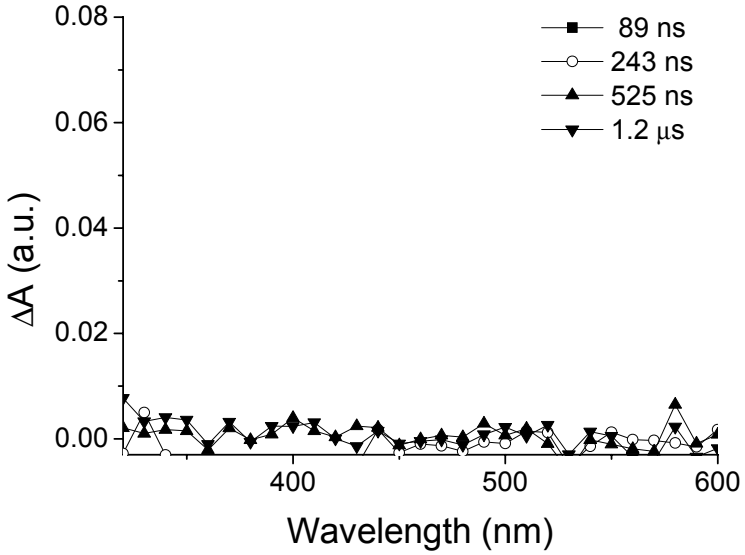
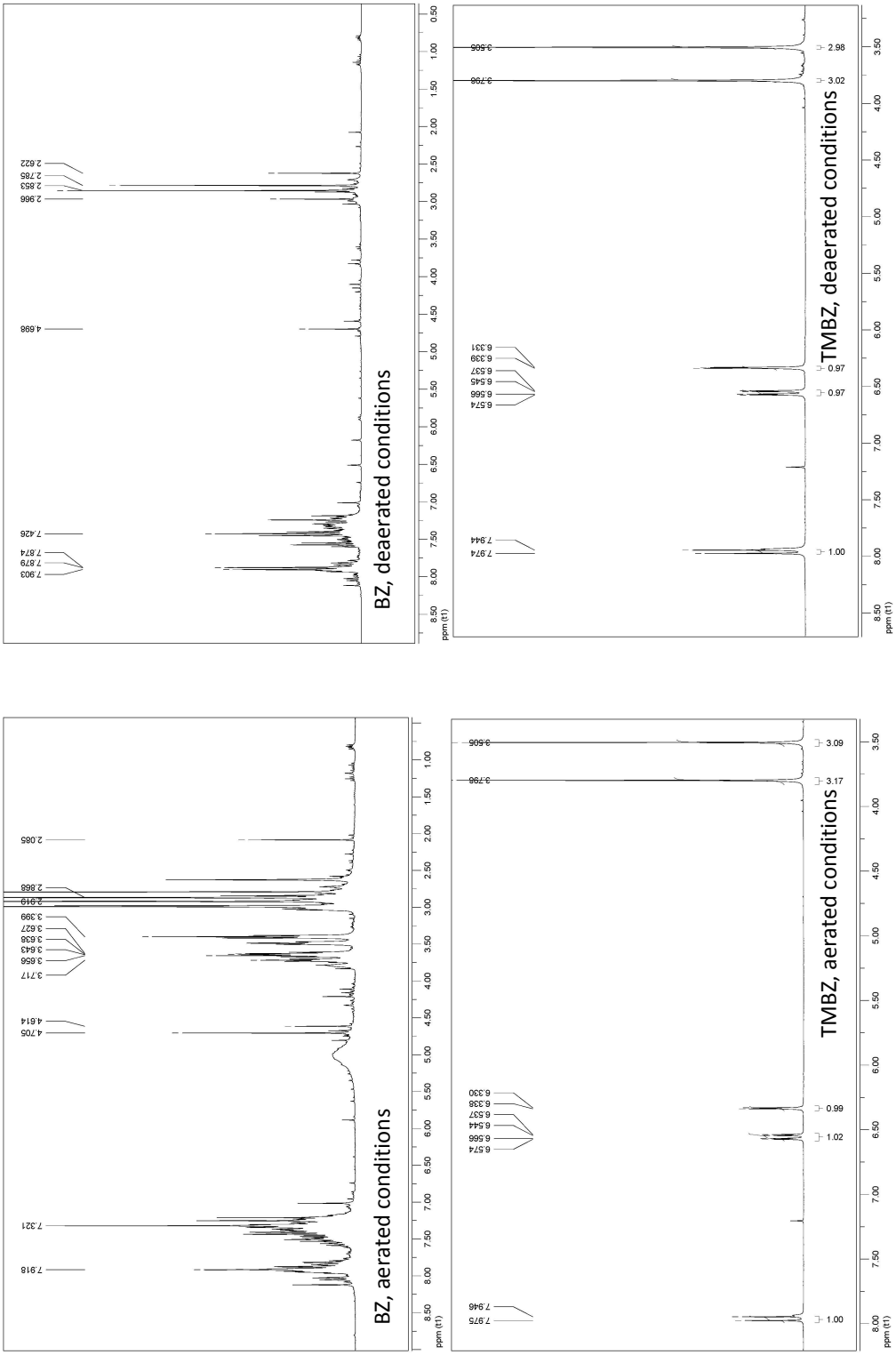


Figure S5. Transient absorption spectra of TMBZ in CH_3CN recorded 89 ns (!), 243 ns (–), 525 ns (7), and 1.2 μs (B) after the laser pulse (355 nm).



FigureS6. NMR spectra of the photolysates (3h of irradiation, pyrex filter) of BZ (10 mM) and TMBZ (10 mM) in DMF in the presence or in the absence of oxygen.

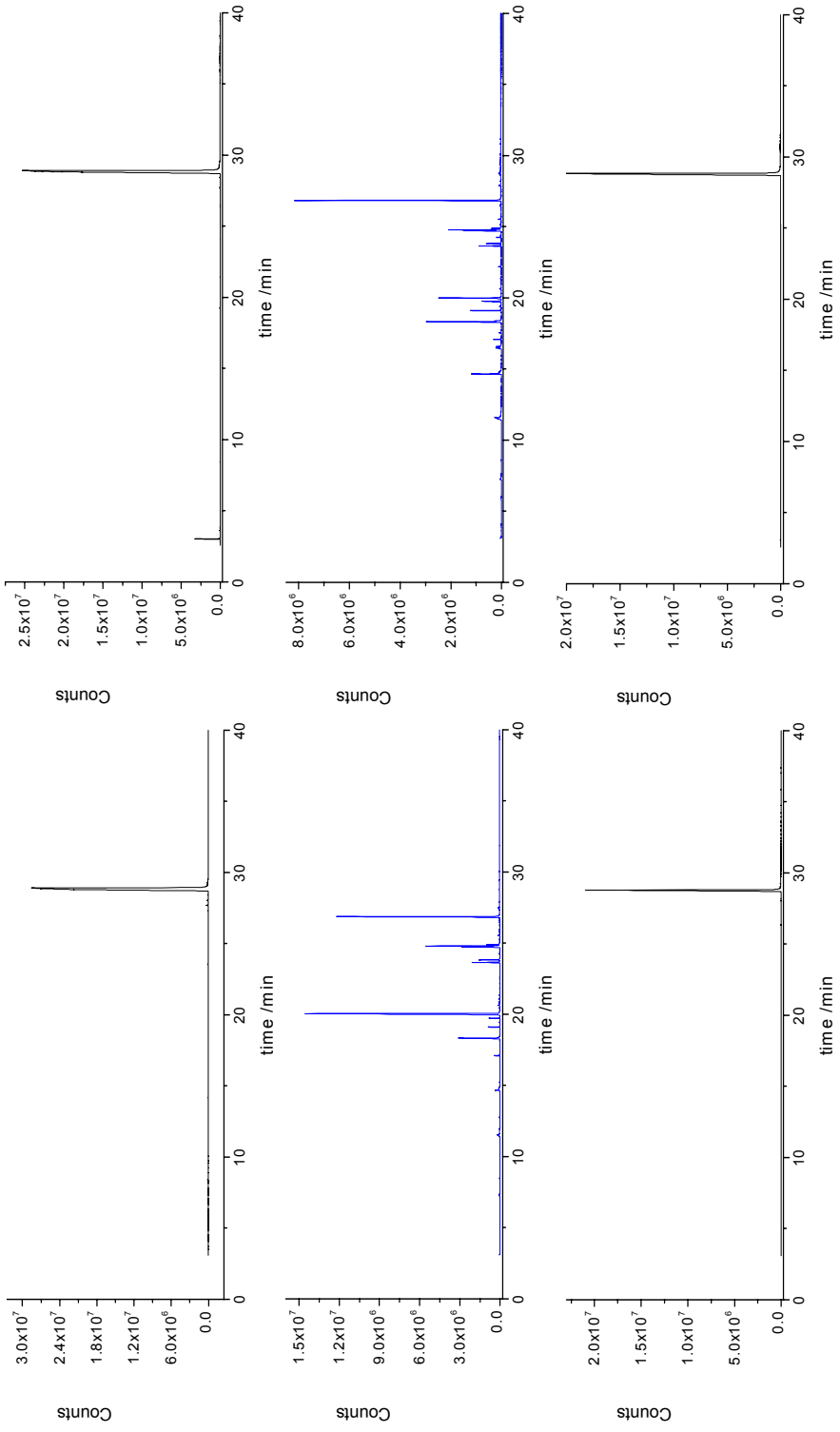


Figure S7. GC-MS chromatograms of the photolysates of BZ and TMZ shown in Figure S6.

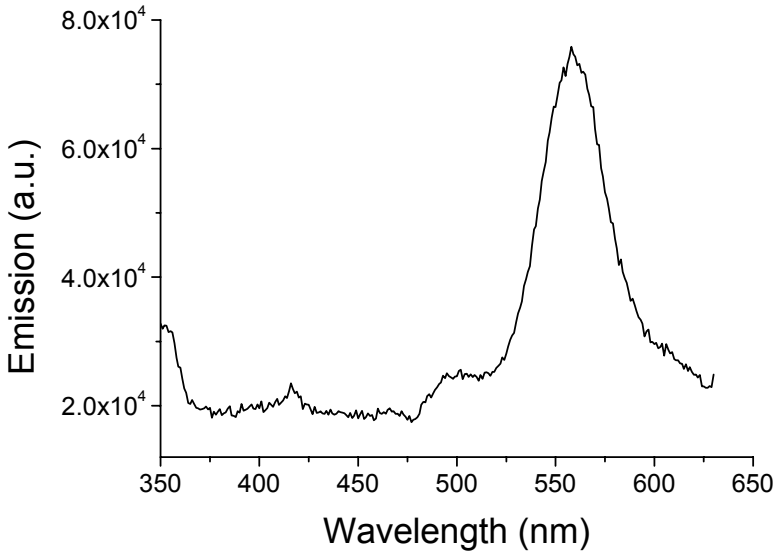


Figure S8. Emission spectrum (λ_{exc} = 320 nm) of a deaerated mixture of BZ (A_{320}=0.1) and acetophenone (A_{320}=0.8).

Experimental details

Irradiations:

Testing the stability of the samples

Solutions of BZ, DMBZ and TMBZ (10 mM) were irradiated (pyrex filter, 380<λ<320 nm or 360<λ<300 nm) in different solvents (DMF, MeOH, ACN and toluene) under aerated and deaerated conditions for 1 or 3 h. The samples were analysed by NMR and GC/MS after solvent evaporation.

Testing TMBZ as photosensitiser

After laser flash photolysis (excimer laser, λ_{exc}=308 nm) of an deaerated (bubbling N_2 for 15 minutes) acetonitrile containing pyrene (A_{308}=0.1) and TMBZ (A_{308}=0.2) no transient absorption was detected in the range 320 to 700 nm.