Supporting Information for

Substituent Effect on the Photoreduction Kinetics of Benzophenone

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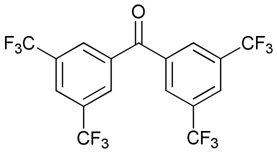
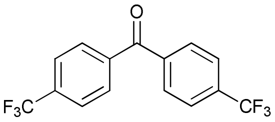
General procedure for preparation of the trifluoromethylated benzophenone derivatives. To the mixture of 30 ml dry THF and 1.58 g (66.0 mmol) magnesium granules isopropyl bromide (5.55 ml, 59.0 mmol) was added dropwise over 1 h at a rate that maintained vigorous boiling. After completion of the reaction the mixture was cooled to room temperature and 2.79 g (66.0 mmol) lithium chloride was added, and then further stirred for 1 h. This "Super" Grignard solution was transferred via cannula into a dry THF solution (30ml) of trifluoromethyl substituted bromobenzene (66.0 mmol) at -10° C, at such a rate that the reaction temperature never exceeded -5°C. Then the reaction mixture was stirred at 0° C for an additional 2h and ethyl formate (2.44 g, 33.0 mmol) was added. After stirring the reaction mixture for 5 h at room temperature, the reaction was quenched and the reaction mixture was partitioned between 100 ml of CH_2Cl_2 and 100 ml of brine saturated with NH_4Cl. After separating the organic layer, the aqueous phase was extracted with additional CH_2Cl_2. The combined organic phase was dried over Na_2SO_4, the solvent was removed by a rotary evaporator and the residue was recrystallized from hexane.

To a stirred acetone solution (100 ml) of the corresponding substituted trifluoromethylated diphenylmethanol (4.4 mmol) Jones' reagent (13.2 mmol, 3.4 ml) was added dropwise at 0°C. Then the resulting mixture was allowed to reach room temperature and stirred until the reaction reached completion (3h) as detected by the absence of starting material by thin-layer chromatography. Isopropyl alcohol (10 ml) was added to quench the excess of the Jones' reagent. The mixture was filtered through cellite then was poured into separatory funnel and 150 ml diethyl ether was added. The organic phase was washed with water (3x50 ml) and then with brine (2x50 ml). The organic layer was then dried over Na_2SO_4 and the solvent was removed to provide the corresponding benzophenone derivative.



3,3',5,5'-Tetrakis(trifluoromethyl)benzophenone, bis[3,5-bis(trifluoromethyl)phenyl]methanone (CFBp)**.** Prepared according to general procedure, to provide the title compound as a white solid in 40 % yield. MP:139 °C ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.23 (bs, 4H), 8.17 (bs, 2H) ^{13}C-NMR (300 MHz, $CDCl_3$) δ 191.0, 138.0, 133.8, 133.3, 132.9, 132.4, 130.1, 129.9, 128.3, 127.1, 127.0, 126.9, 124.7, 121.1, 117.5, ^{19}F-NMR (300 MHz, $CDCl_3$) δ -63.6



4,4'-Di(trifluoromethyl)benzophenone (dpCFBp). Prepared according to general procedure, to provide the title compound as a white solid in 39 % yield. MP:110 °C ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.90 (d, 4H, *J*=8.4 Hz), 7.78 (d, 4H, *J*=8.2 Hz),)^{13}C-NMR (300 MHz, $CDCl_3$) δ 194.2, 139.6, 134.3, 130.2, 125.6, 121.6 ^{19}F-NMR (300 MHz, $CDCl_3$) δ -63.5

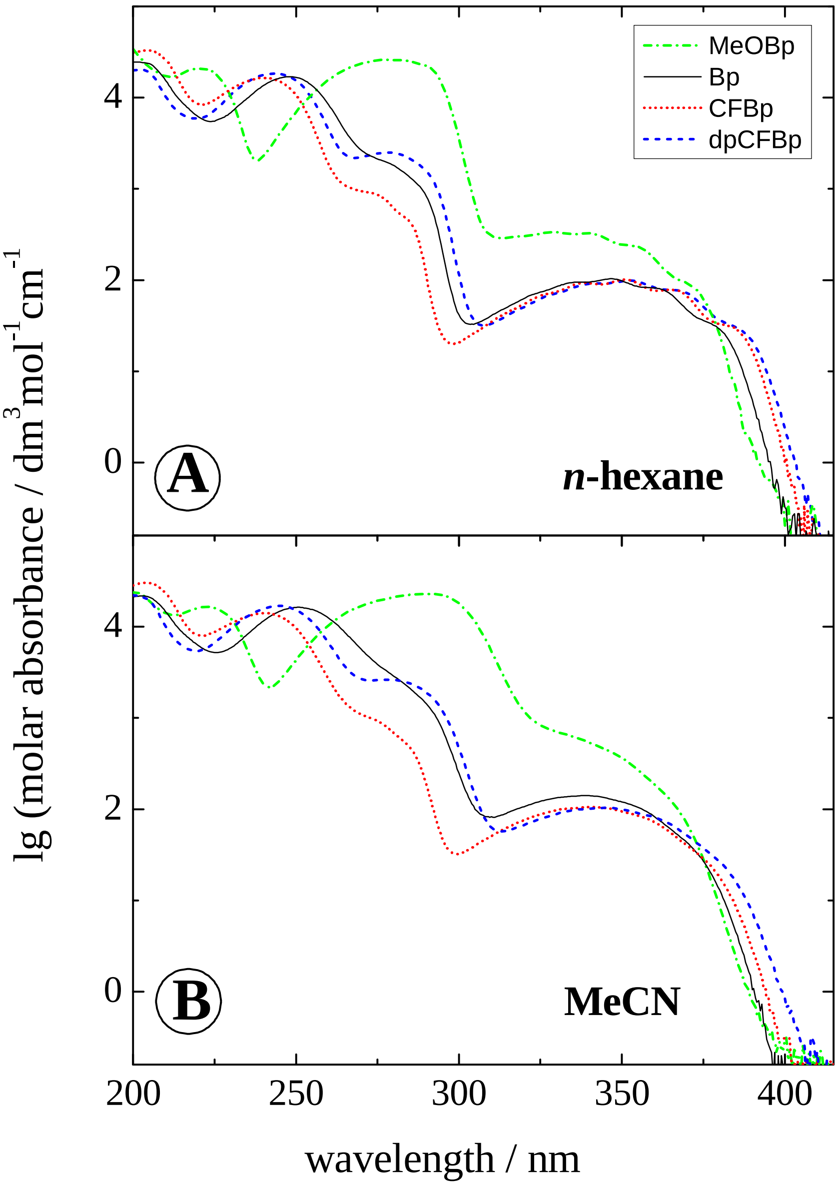


Figure S1. Absorption spectra of the four benzophenone derivatives (Bp: black solid, CFBp: red dotted, dpCFBp: blue dashed and MeOBp: green dash-dotted line) in *n*-hexane (A) and acetonitrile (B) at room temperature.

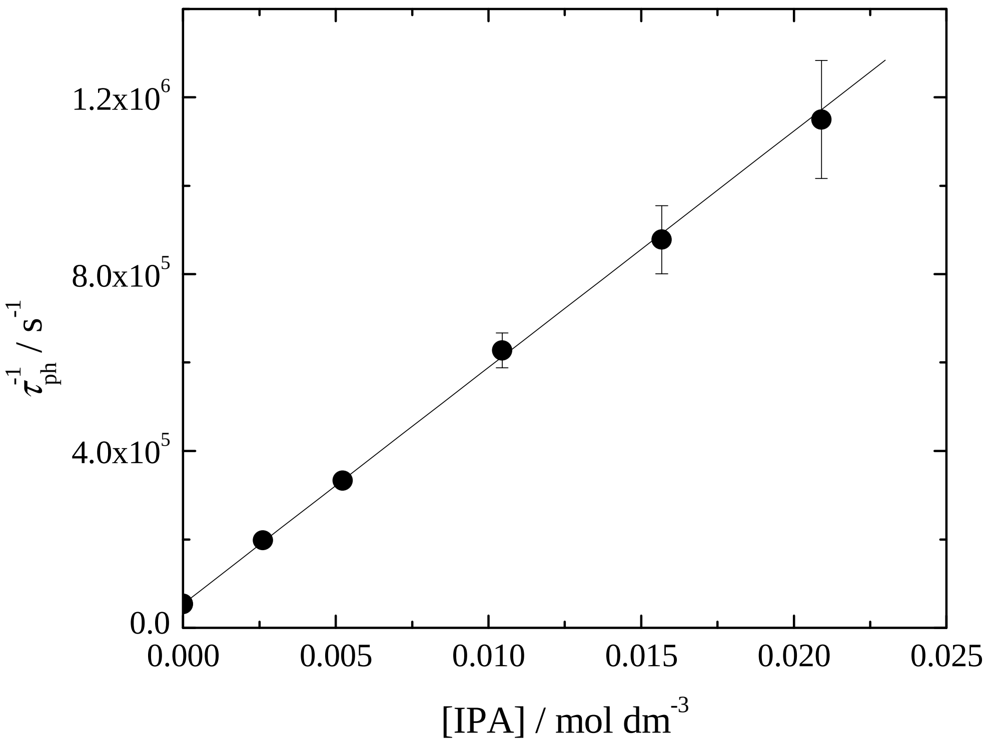


Figure S2. Pseudo first-order plots of the rate coefficient of the photoreduction of triplet CFBp by 2-propanol in acetonitrile at 23 °C. The pseudo-first order rate coefficient k'_2 is equal of the inverse of τ_{ph} at the given alcohol concentration.

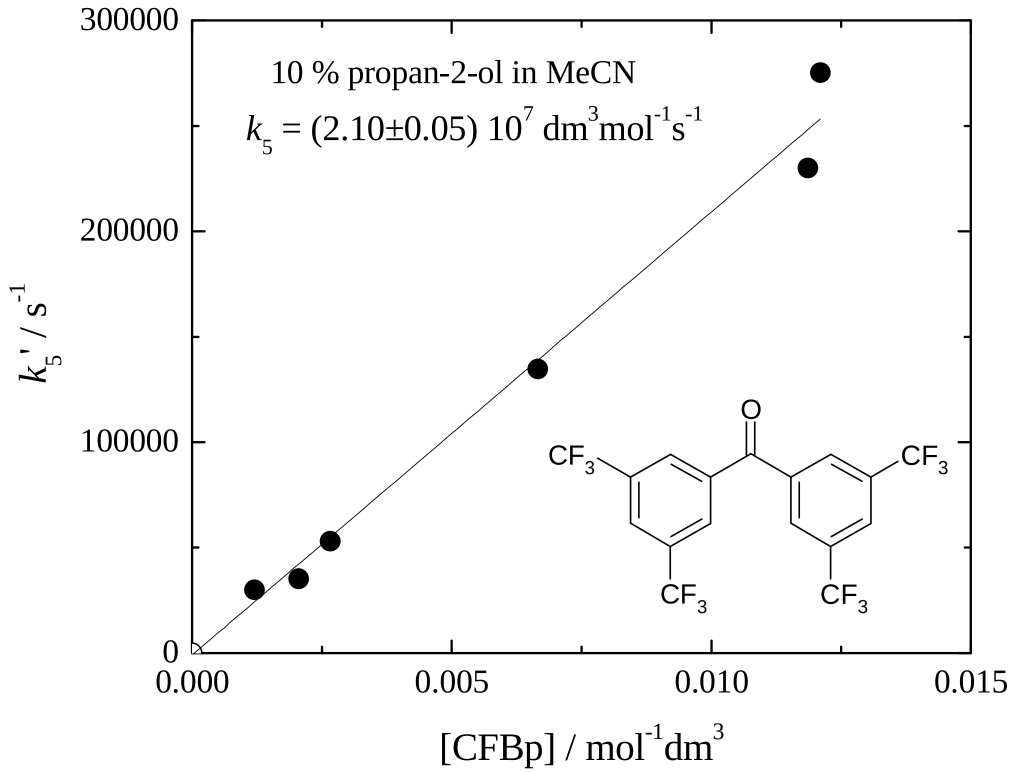


Figure S3. Pseudo first-order plots of the rate coefficient of the secondary photoreduction step (5) of triplet CFBp in 1.31 mol dm^{-3} 2-propanol – acetonitrile at 23 ^{o}C. The k'_5 pseudo first-order rate coefficient was fitted by model simulation (see text).

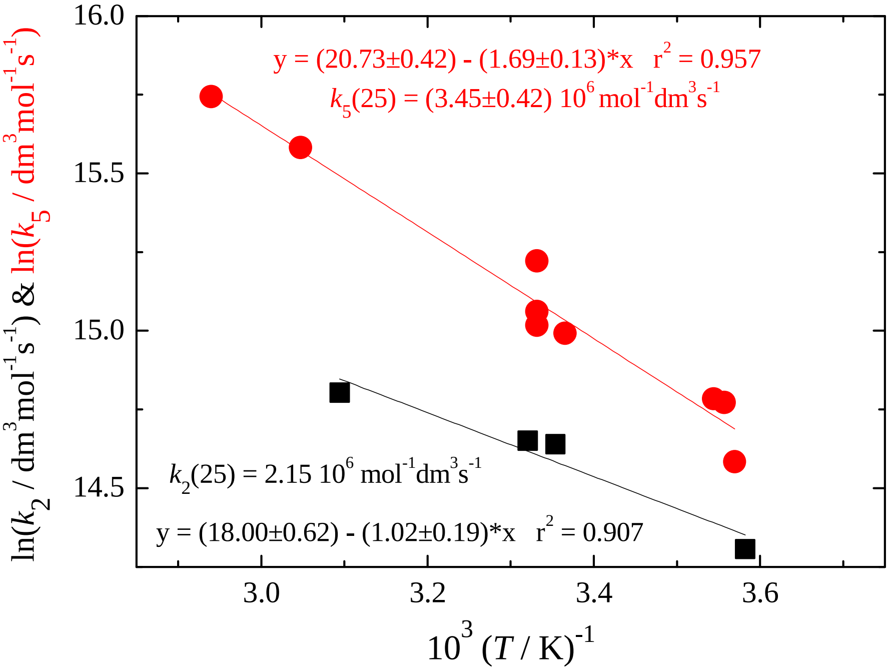


Figure S4. Arrhenius plot of the reaction rate coefficients of the primary photoreduction reaction (2) (black square) and the secondary hydrogen transfer (5) (red circle) by benzophenone photoreduction by 2-propanol in benzene.

Table S1. The TD-DFT B3LYP/6-31G* vertical excitation energies and oscillator strengths of the five lowest energy bands for the four benzophenone derivatives in vacuum, *n*-hexane and MeCN.

Compound	Sym.	Abs^{max} / eV		Abs^{max} / nm			Oscillator strength		
		n-hexane	MeCN	vacuum	*n*-hexane	MeCN	vacuum	*n*-hexane	MeCN
MeOBp	A	3.653	3.754	344.4	339.4	330.3	0.0019	0.0033	0.0045
	B	4.109	4.020	294.1	301.7	308.4	0.5074	0.6233	0.6441
	A	4.460	4.405	273.8	278.0	281.5	0.0296	0.0439	0.0452
	A	4.721	4.663	260.8	262.6	265.9	0.0007	0.0022	0.0055
	B	4.777	4.727	258.2	259.6	262.3	0.0006	0.0009	0.0015
Bp	A	3.582	3.679	351.0	346.1	337.0	0.0009	0.0013	0.0013
	A	4.530	4.458	270.8	273.7	278.1	0.0126	0.0206	0.0226
	B	4.596	4.528	266.9	269.8	273.8	0.0410	0.0879	0.0700
	B	4.670	4.597	261.0	265.5	269.7	0.2500	0.3010	0.3396
	A	4.970	4.860	250.4	253.2	255.1	0.0377	0.0566	0.0588
CFBp	A	3.566	3.652	352.0	347.7	339.5	0.0010	0.0015	0.0016
	A	4.669	4.651	264.7	265.6	266.6	0.0094	0.0151	0.0153
	B	4.725	4.709	261.7	262.4	263.3	0.0143	0.0318	0.0463
	B	4.807	4.772	255.2	257.9	259.8	0.2267	0.3151	0.3240
	A	4.973	4.960	247.8	249.3	250.0	0.0169	0.0314	0.0355
dpCFBp	A	3.520	3.580	356.3	352.2	346.4	0.0010	0.0014	0.0013
	A	4.472	4.425	274.4	277.3	280.2	0.0147	0.0239	0.0251
	A	4.536	4.490	270.6	273.3	276.1	0.0294	0.0413	0.0287
	A	4.668	4.639	262.2	265.6	267.3	0.3138	0.3973	0.4186
	A	4.880	4.870	251.8	254.1	254.6	0.0453	0.0646	0.0638

Table S2. Calculated bond lengths (in Å) for the reactant ketone, the transition structure TS and the product ketyl radical involved in reaction (5) for the examined ketones.

distancey	acetone	MeOBp	Bp	dpCFBp	CFBp
C=O					
ketone	1.210	1.230	1.215	1.208	1.206
TS, aromatic	N/A	1.274	1.266	1.256	1.245
TS, aliphatic	1.276	1.281	1.284	1.302	1.306
ketyl	1.366	1.359	1.354	1.349	1.347
>C-C(=O)					
ketone	1.497	1.496	1.486	1.490	1.490
TS, aromatic	N/A	1.453	1.458	1.470	1.468
TS, aliphatic	1.477	1.478	1.476	1.490	1.472
ketyl	1.482	1.427	1.430	1.429	1.430
O-H					
TS, aromatic	N/A	1.300	1.361	1.428	1.556
TS, aliphatic	1.192	1.102	1.064	1.059	0.998
ketyl	0.958	0.960	0.960	0.960	0.960
TS imaginary frequency / cm^{-1}	2349i	2434i	1905i	1138i	642i

Table S3. Calculated reaction enthalpies of the formation of hydrogen-bonded complexes in the unsubstituted benzophenone – 2-propanol – acetonitrile system.

reaction	ΔH^{o} / kJ mol^{-1}	
	vacuum	MeCN
(5*i*)	-26.7	-13.,2
-(5*iii*)	-27.5	-17.3
(7)	-25.0	-8.4
(8*i*)	-17.8	-10.0
(8*ii*)	-28.8	-21.6
(8*iii*)	-37.6	-26.9
(9)	-15.7	-9.4
(10)	-24.3	-17.7