Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Electronic Supplementary Material:

Triplet- *vs.* Singlet-State Imposed Photochemistry. The Role of Substituent Effects on the Photo-Fries and Photodissociation Reaction of Triphenylmethyl Silanes

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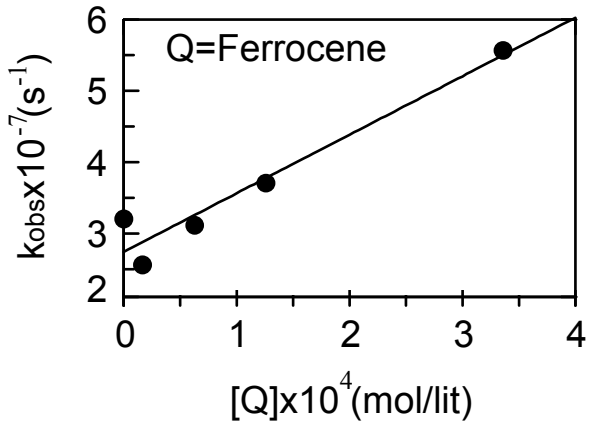


Figure A. Plot of the quenching of the triplet state of **1** (at 520 nm) by ferrocene, using 308-nm laser light (MeCN).

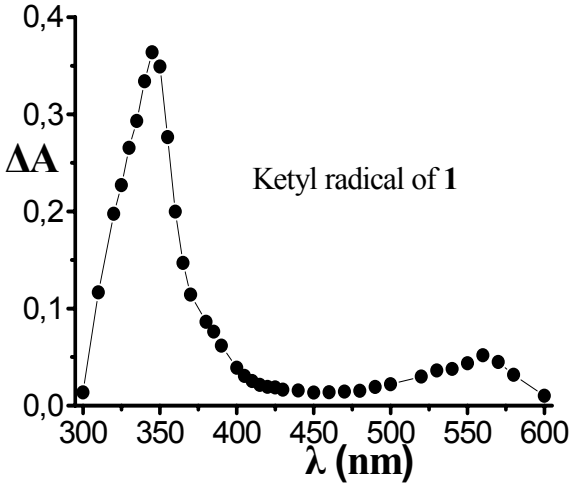


Figure B. Transient absorption spectrum observed 1.62 μs after the pulsing (266-nm) of a solution of **1** in cyclohexan in the presence of 0.01 mM Et_3N under nitrogen. It corresponds to the ketyl radical *p*-(Ph_2CSiMe_3)-C_6H_4-C(•)(OH)Ph.

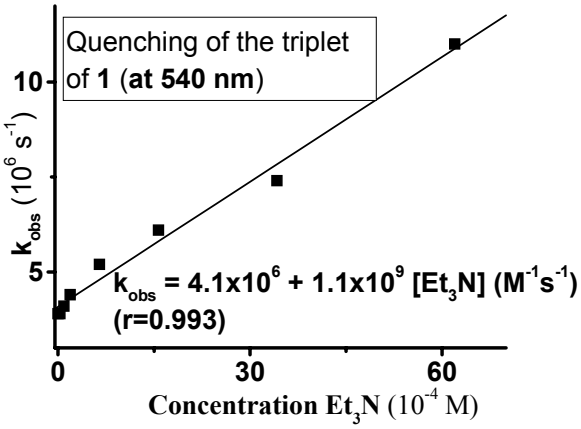


Figure C. Plot of the quenching rate constant of the triplet state of **1** (at 540 nm) by Et_3N, using 266-nm laser light (hexane).

Absorption Coeffiecient of 6.

The absorption coeffiecient value ε_6 of the photo-Fries product **6** (10300 $M^{-1}cm^{-1}$) was derived using a linear correlation we found between the ε values of structurally similar 1,3-exocyclic cyclohexatriens reported in the literature (see structures bellow, Figure D) and the oscillator strength values (f) we calculated using the semiempirical method CNDO/S (see Table A); (a) J. Del Bene, H. H. Jaffe, J. Am. Chem. Soc., 1985, 107, 7767:

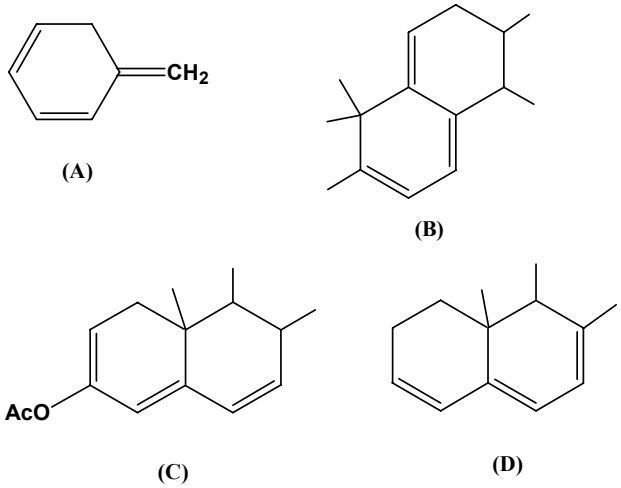
ε = 25748 x f, (r=0.977)

For compound **1** we calculated f = 0.4 and therefore ε = 10300 $M^{-1}cm^{-1}$.

Table A. Absorption Data of Compounds **A, B, C, D** (see the structures and the plot bellow)

Comp.	Experimental		Calculated[c]	
	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	λ_{max} (nm)	f *oscillator strength*
A	**303**	**4400**[a]	**304**	**0.380**
B	**324**	**11800**[b]	**317**	**0.464**
C	**306**	**14500**[b]	**302**	**0.538**
D	**315**	**19800**[b]	**307**	**0.666**

[a)] W. J. Bailey, R. A. Baylouny, *J.Org.Chem*. 1962, **27**, 3476; [b)] H. H. Jaffé, M. Orchin, *'Theory and Applications of Ultraviolet Spectroscopy'*, Wiley, NY, 1964, p. 200; [c)] Calculated using CNDO/S.



(A) **(B)** **(C)** **(D)**

Figure D. See for details in **Table A**.