Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Photochemistry of Tris(2,3,5,6-tetrathiaaryl)methyl Radicals in Various Solutions

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1. $R3H^+$ cation: Synthesis and conversion back to R3H radical

R3H Methanol (0.0105 g, 1.20 x 10^{-2} mmol) and $CDCl_3$ (0.250 mL) were charged into Pyrex-glass vial (2.0 mL). Trifluoroacetic acid (TFA, 0.250 mL) was added, and the color of solution was immediately changed from pale-yellow to deep green. The solution was left standing at room temperature for 30 min, after which 0.040 mL of solution was sampled and then diluted with anhydrous chloroform (0.960 mL) to give a 0.967 mM solution of $R3H^+$ cation in a mixed $CHCl_3/CF_3CO_2H$ (50:1, v/v) solvent. UV spectrum shows a characteristic absorption at 748 nm.

To solution of diamagnetic $R3H^+$ cation (100 μL) obtained above was added a 5mM solution (50 μL) of anhydrous tin(II) chloride in anhydrous tetrahydrofurane to cause the immediate formation of TAM radical, which demonstrates a very characteristic quartet splitting in ESR spectrum (Figure S1).

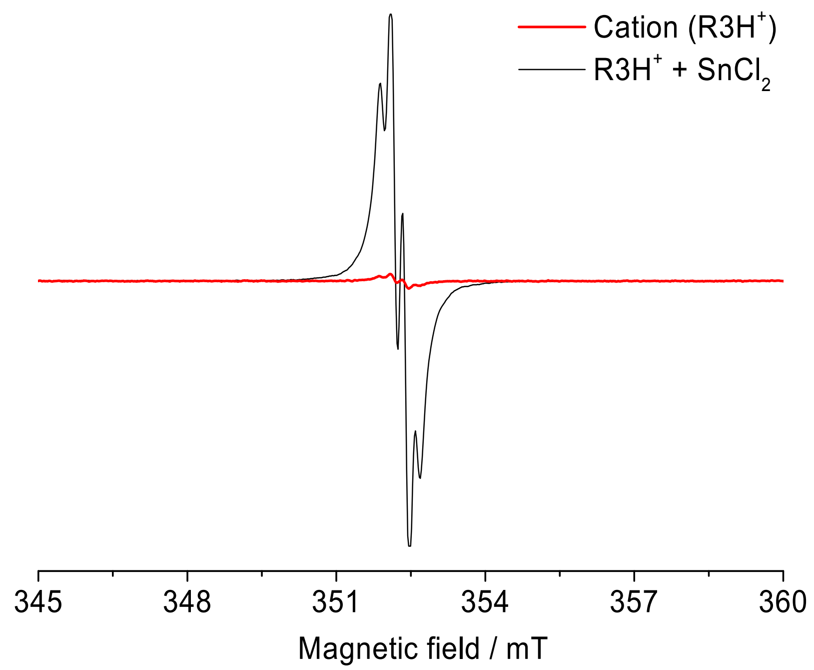

Fig. S1. Room temperature X-band CW EPR spectra of $R3H^+$ carbocation in $CHCl_3/CF_3CO_2H$ (50:1, v/v, red line) and that after addition of $SnCl_2$ (black line).

2. Steady-state photolysis of Trityl radicals in various solvents

Table S1. Molar absorption coefficients for R3H trityl radicals and its quinone-methides and cation forms in chloroform and for carbocation of Finland trityl in CF_3COOH.

Substance	Solvent	ε / $M^{-1}cm^{-1}$			
R3H	$CHCl_3$	$\varepsilon^{326} = 23550$	$\varepsilon^{444} = 20500$	$\varepsilon^{610} = 1650$	$\varepsilon^{760} = 1125$
R3H-QM	$CHCl_3$	$\varepsilon^{520} = 21950$			
$R3H^+$	$CHCl_3$	$\varepsilon^{366} = 16100$	$\varepsilon^{750} = 10800$		
Finland trityl	H_2O	$\varepsilon^{467} = 18320$			

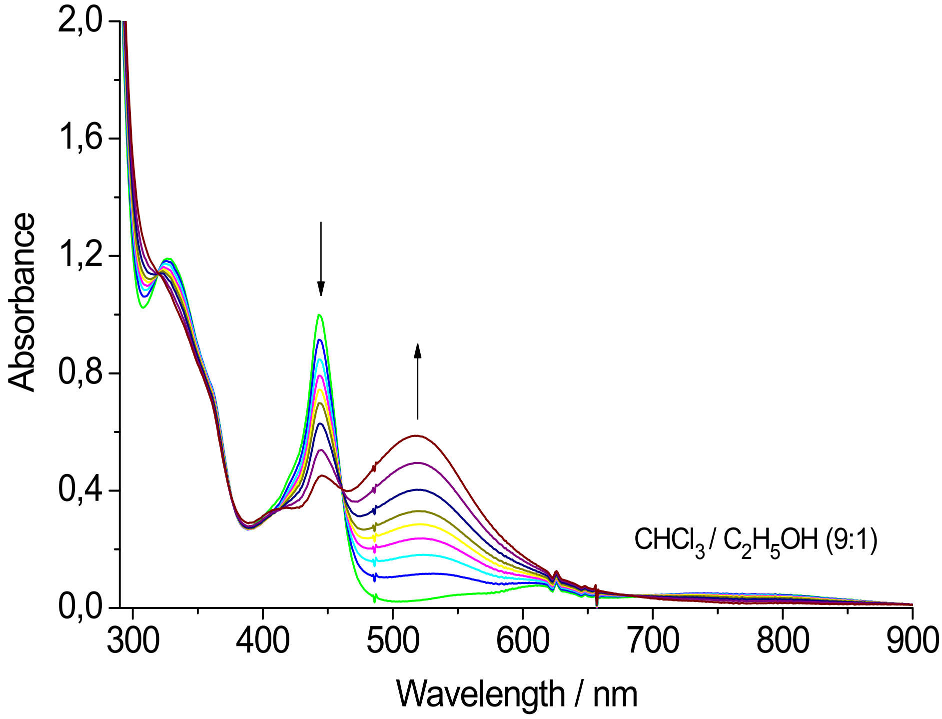

Fig. S2. Steady-state photolysis (308 nm) of R3H trityl radical in chloroform/ethanol (9:1) mixed solvent in the presence of oxygen. Spectra were recorded every 15-30 min, from 0 to 120 min in cuvette with pathlength 1 cm.

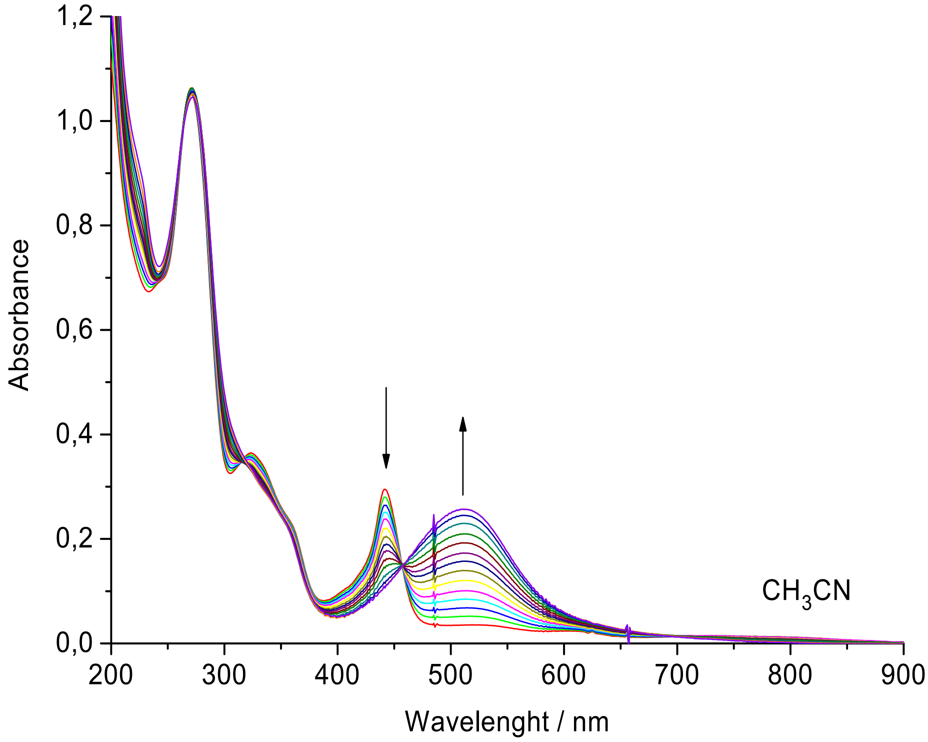

Fig. S3. Steady-state photolysis (308 nm) of R3H trityl radical in acetonitrile in the presence of oxygen. Spectra were recorded every 5-20 min, from 0 to 150 min in cuvette with pathlength 1 cm.

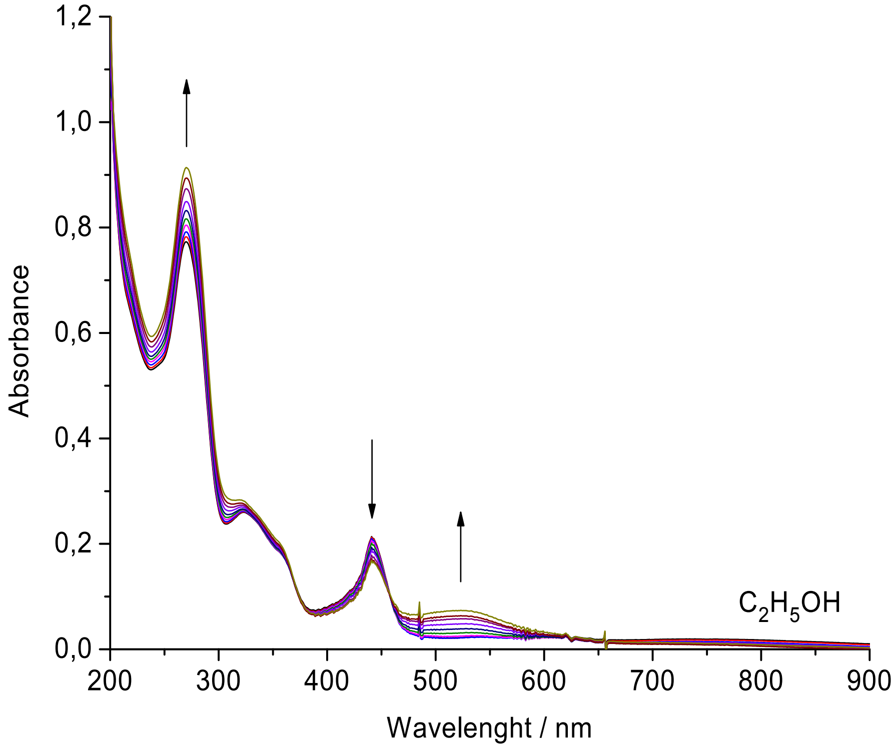

Fig. S4. Steady-state photolysis (308 nm) of R3H trityl radical in ethanol in the presence of oxygen. Spectra were recorded every 5-25 min, from 0 to 150 min in cuvette with pathlength 1 cm.

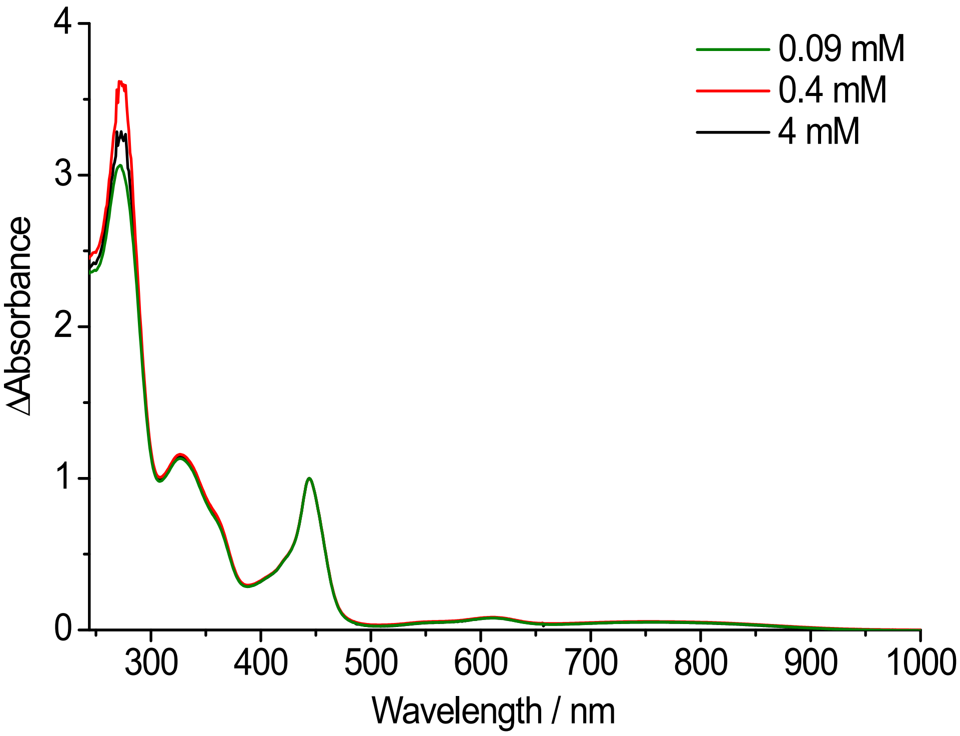

Fig. S5. UV absorption spectra for R3H trityl with different concentration (0.09, 0.4 and 4 mM) in chloroform. The spectra were normalized at the maximum at 444 nm.

3. Gel permeation chromatography

Figure S6 reveals UV absorption spectrum of trimers of carbocation and TAM radical formed after photolysis of TAM radicals.

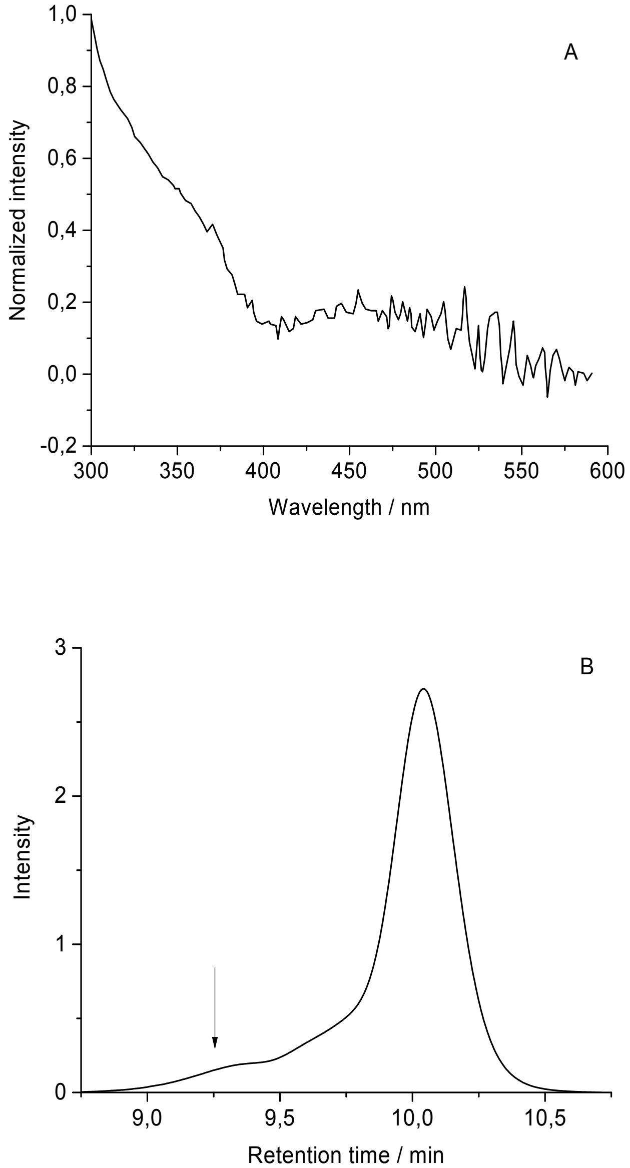

Fig. S6. GPC trace (B) and UV absorption spectrum (A, the position of retention time indicated in figure) for R3H trityl after irradiation at 308 nm during 30 min in the absence of oxygen and after the adding of oxygen.

4. High-resolution mass spectrometry (HRMS/ESI)

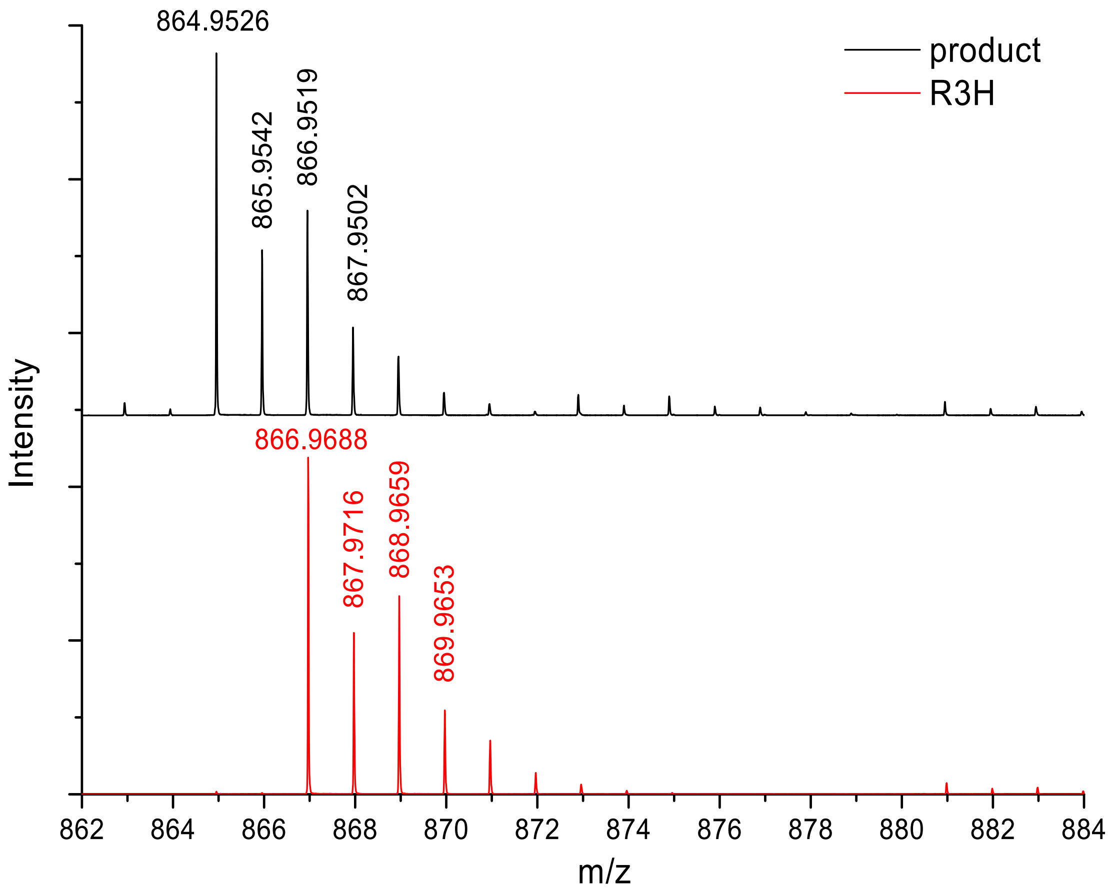

Fig. S7. HRMS spectrum of R3H trityl radical (red line, calculated for $C_{37}H_{39}S_{12}$: 866.9700; observed 866.9688) and product of its photolysis in chloroform in the absence of oxygen (black line, calculated for $C_{37}H_{37}S_{12}$: 864.9545; observed 864.9526).

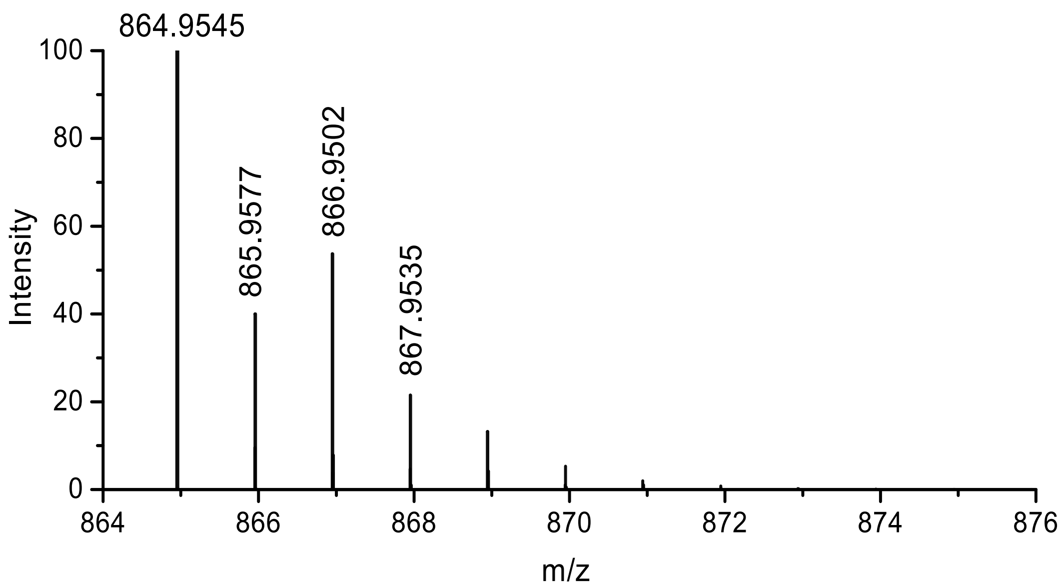

Fig. S8. Calculated HRMS spectrum for cation $[R3H\text{-}2H]^+$.

5. The possible scheme of TAM radical's photolysis in chloroform in the presence of oxygen

$$R^\bullet \xrightarrow{h\nu} R^+ + e^-$$

$$CHCl_3 + e^- \rightarrow {}^\bullet CHCl_2 + Cl^-$$

$$O_2 + e^- \rightarrow O_2^{\bullet -}$$

$$O_2 + CHCl_2^\bullet \rightarrow CHCl_2O_2^\bullet$$

$$CHCl_2^\bullet + CHCl_2^\bullet \rightarrow C_2H_2Cl_4$$

$$R^\bullet + CHCl_2O_2^\bullet \rightarrow R\text{-}QM + \underline{CHCl_2OH} \rightarrow CO + 2HCl$$

$$R^+ + CHCl_2O_2^\bullet \rightarrow R\text{-}QM + CHCl_2O^\bullet + H^+$$

$$R^\bullet + O_2^{\bullet -} \rightarrow R\text{-}QM + OH^-$$

$$R^+ + O_2^{\bullet -} \rightarrow R\text{-}QM + OH^\bullet$$

$$OH^\bullet + CHCl_3 \rightarrow H_2O + {}^\bullet CCl_3$$

$$CCl_3^\bullet + CCl_3^\bullet \rightarrow C_2Cl_6$$

$$CCl_3^\bullet + O_2 \rightarrow CCl_3O_2^\bullet$$

$$R^\bullet + CCl_3O_2^\bullet \rightarrow R\text{-}QM + \underline{CCl_3OH} \rightarrow COCl_2 + HCl$$