Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Photochemical reactivity of phenyl (methyl-tetrazolyl) ketone- Hydrogen atom transfer *vs* electron transfer

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Table SI-1: Spectral characteristics of **1** in the different solvents

Solvent	λ_{max} /nm	$\varepsilon/M^{-1}cm^{-1}$
MeCN	265	13800
cyclohexane	268	15640
n-heptane	268	15160
i-PrOH	268	13500

Figure SI-1: UV spectrum of **1** at 7.3×10^{-5} M in MeCN. Inset: UV spectrum of **1** at 9.5×10^{-4} M in MeCN

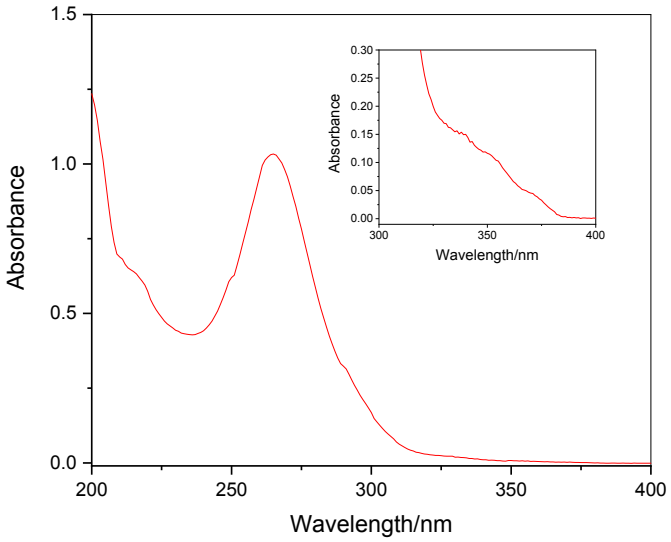
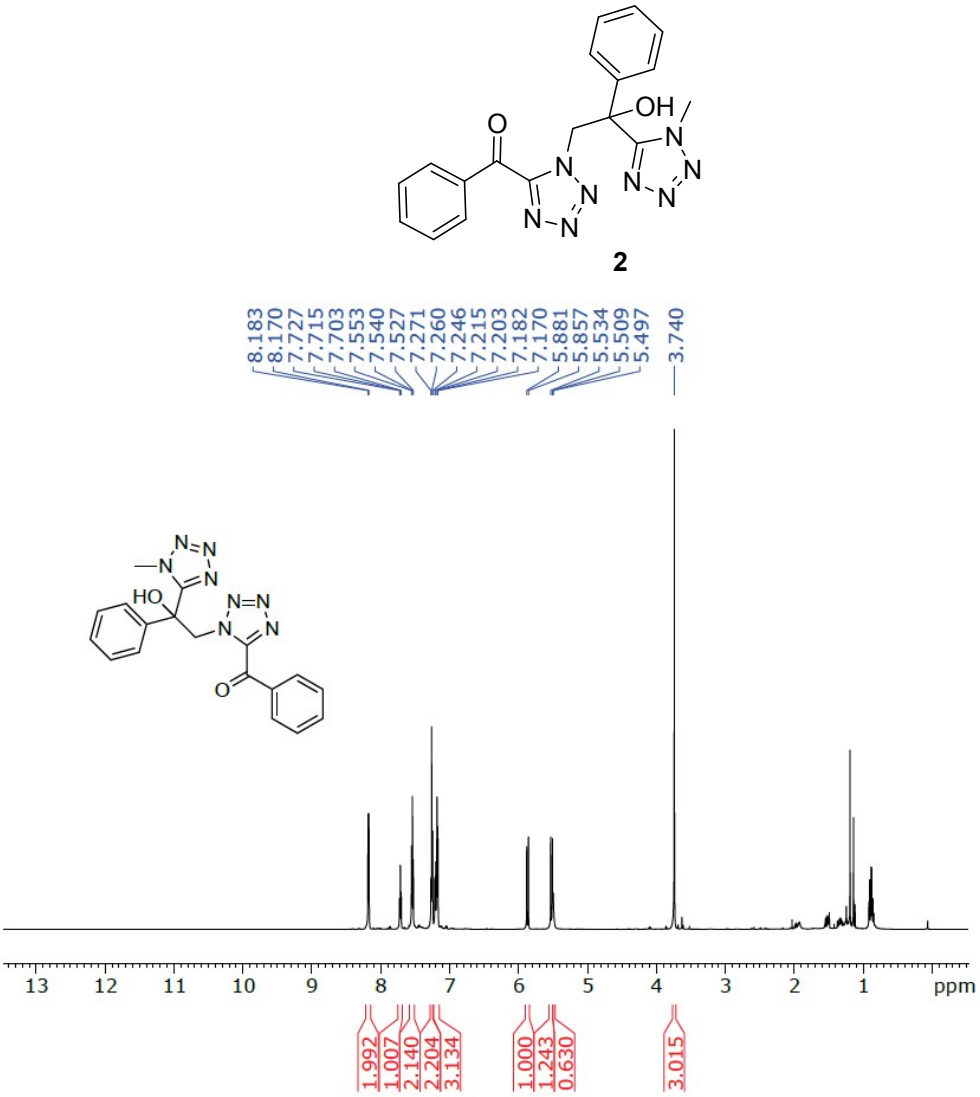
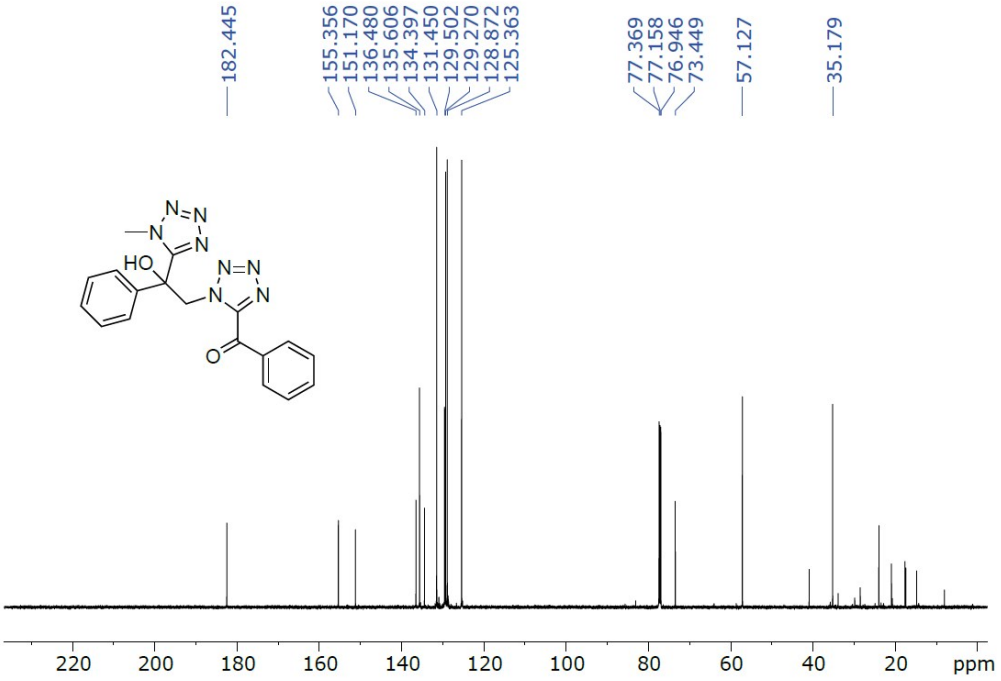


Figure SI-2: ^{1}H and ^{13}C-NMR spectra of photoproduct **2** and UHPLC-MS (ESI positive mode) spectrum




182.445
155.356
151.170
136.480
135.606
134.397
131.450
129.502
129.270
128.872
125.363
77.369
77.158
76.946
73.449
57.127
35.179
HO
O
220
200
180
160
140
120
100
80
60
40
20
ppm

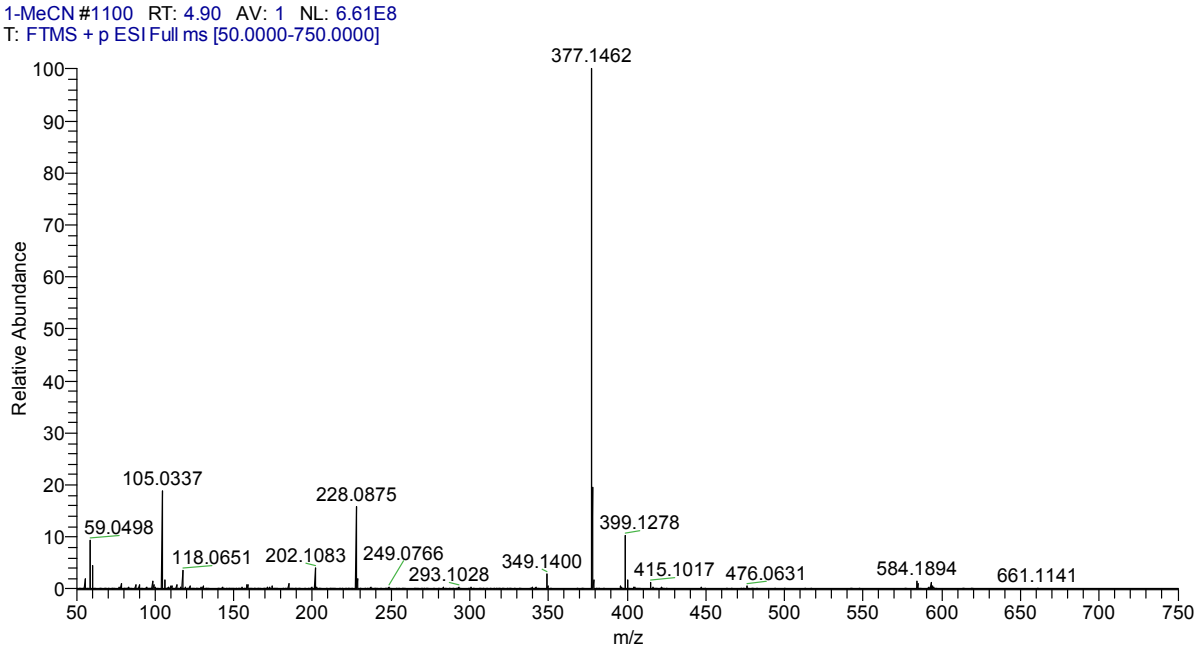
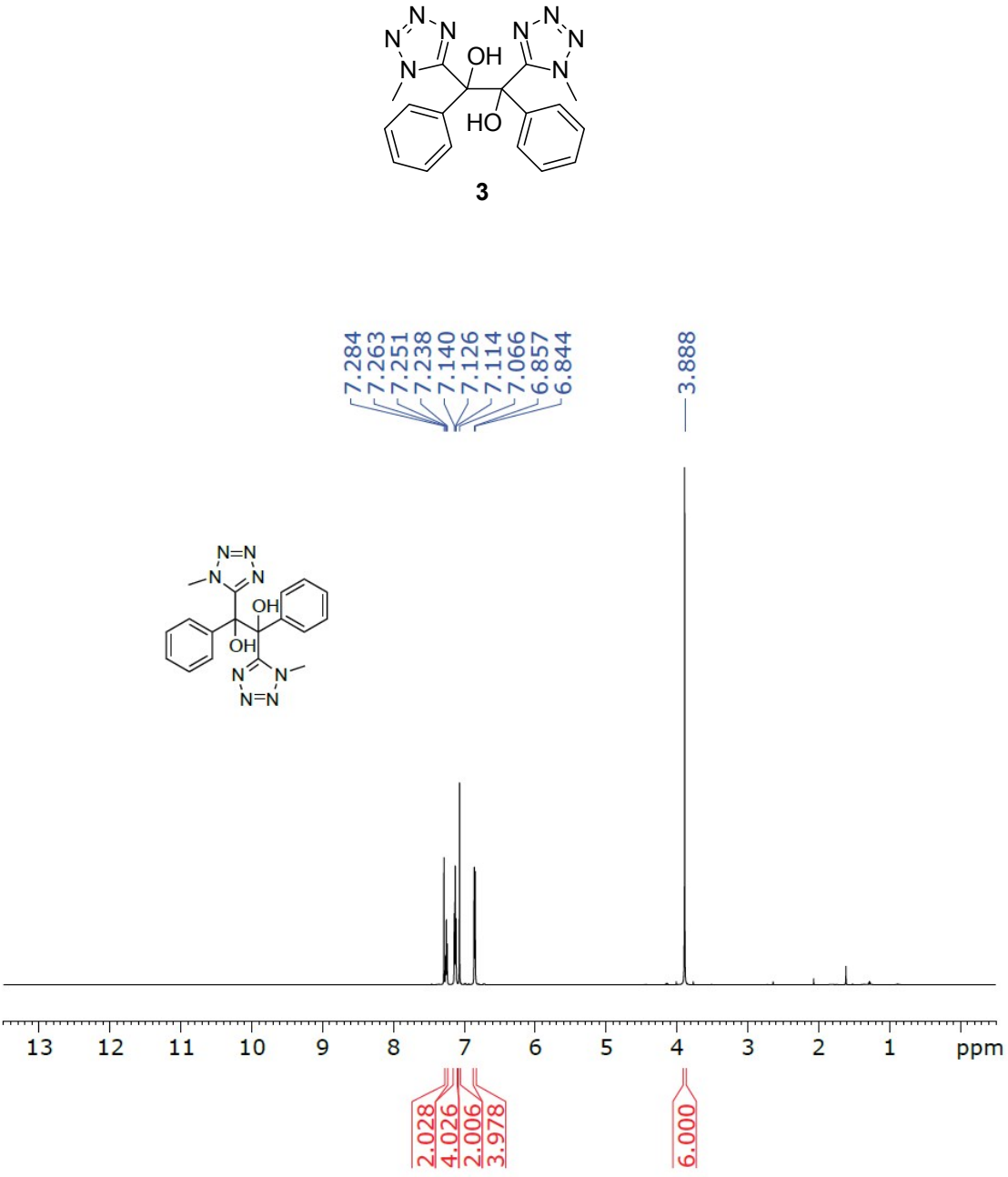
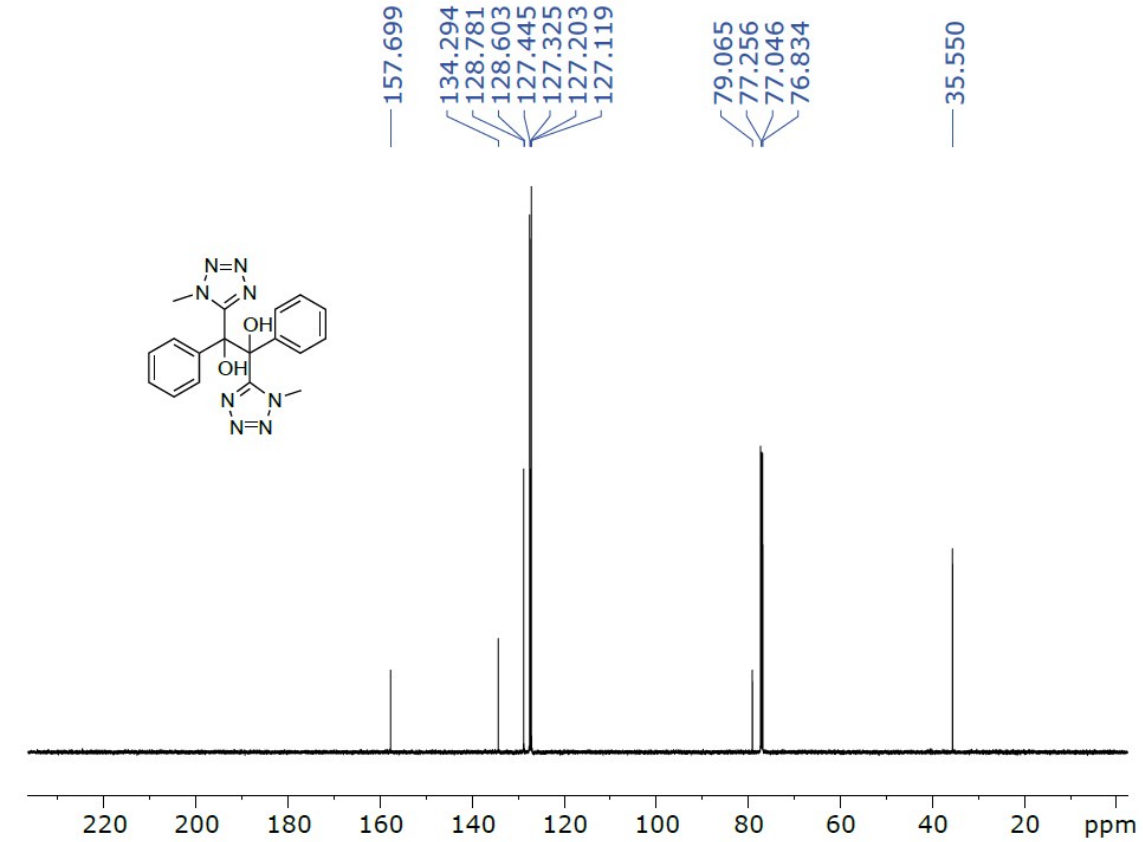

1-MeCN #1100 RT: 4.90 AV: 1 NL: 6.61E8
T: FTMS + p ESI Full ms [50.0000-750.0000]
Relative Abundance
m/z
377.1462
105.0337
228.0875
59.0498
399.1278
118.0651
202.1083
249.0766
293.1028
349.1400
415.1017
476.0631
584.1894
661.1141

Figure SI-3: ^{1}H and ^{13}C-NMR spectra of photoproduct **3** and UHPLC-MS (ESI positive mode) spectrum




157.699
134.294
128.781
128.603
127.445
127.325
127.203
127.119
79.065
77.256
77.046
76.834
35.550
N=N
N
N
OH
OH
N
N
N=N
220
200
180
160
140
120
100
80
60
40
20
ppm

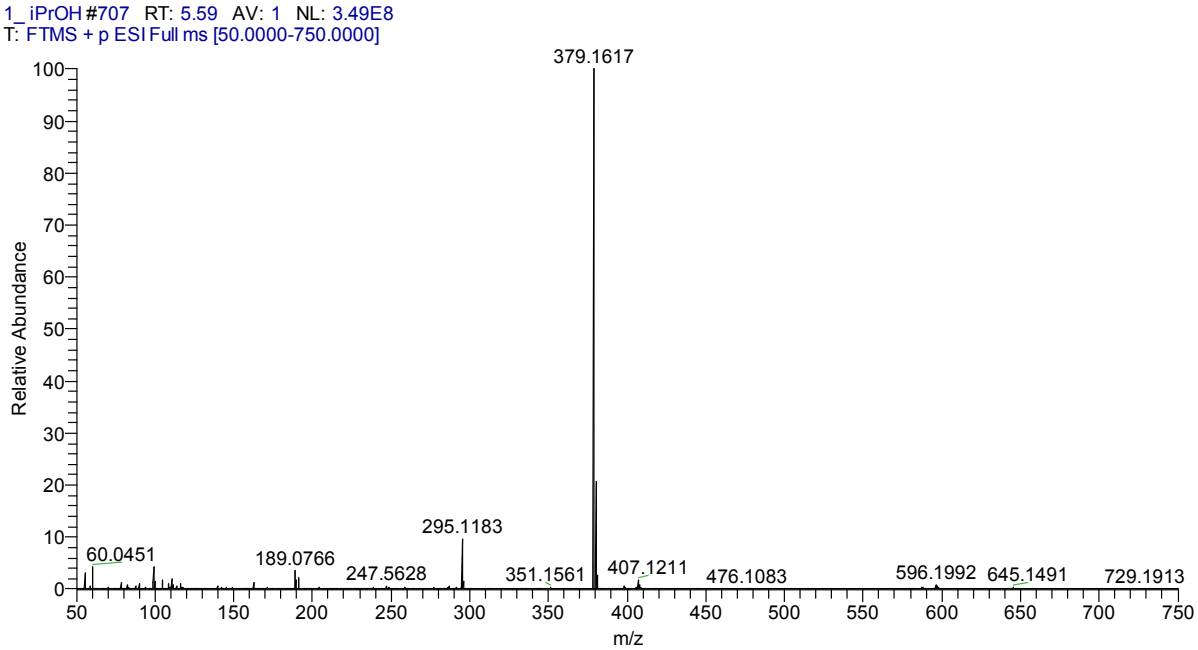
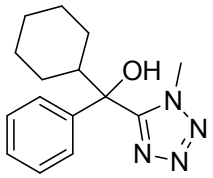
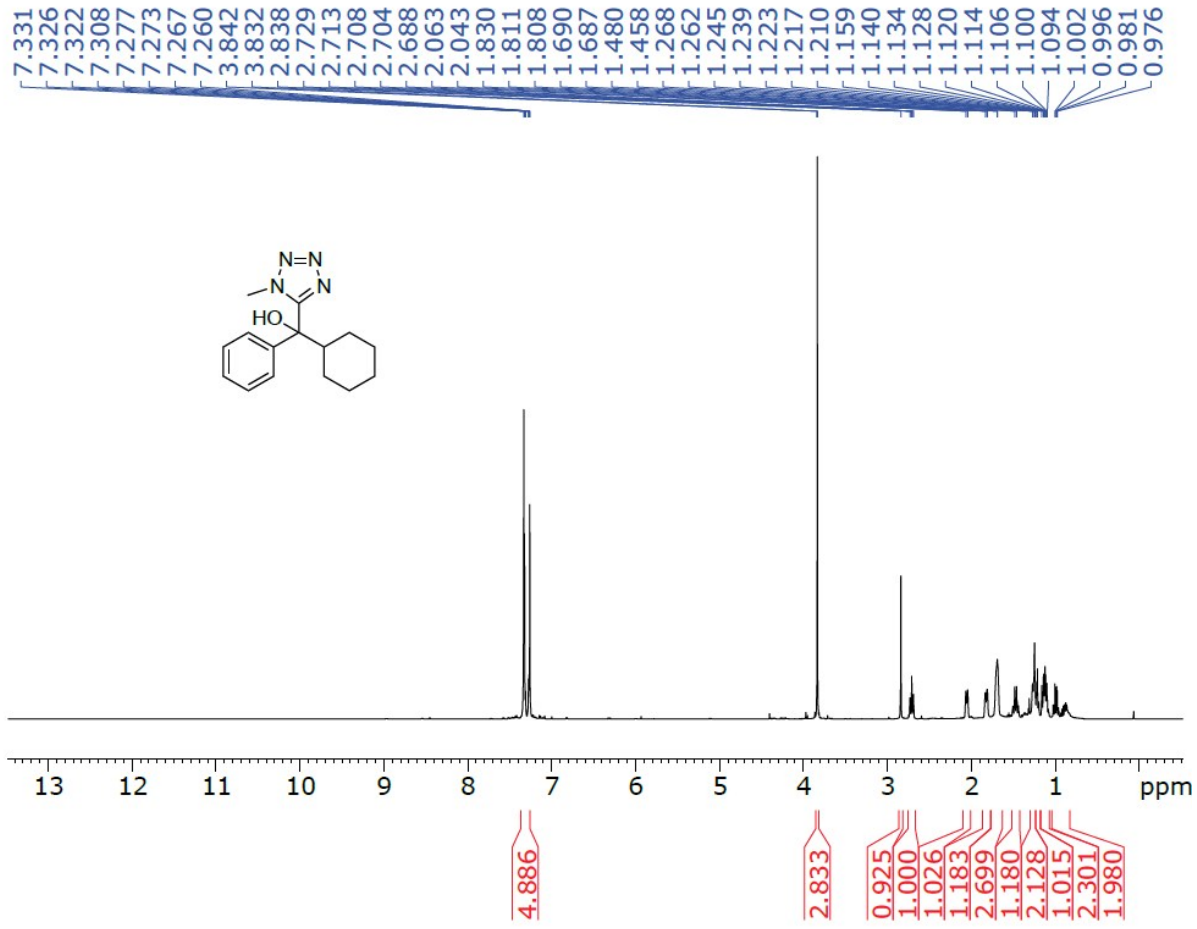
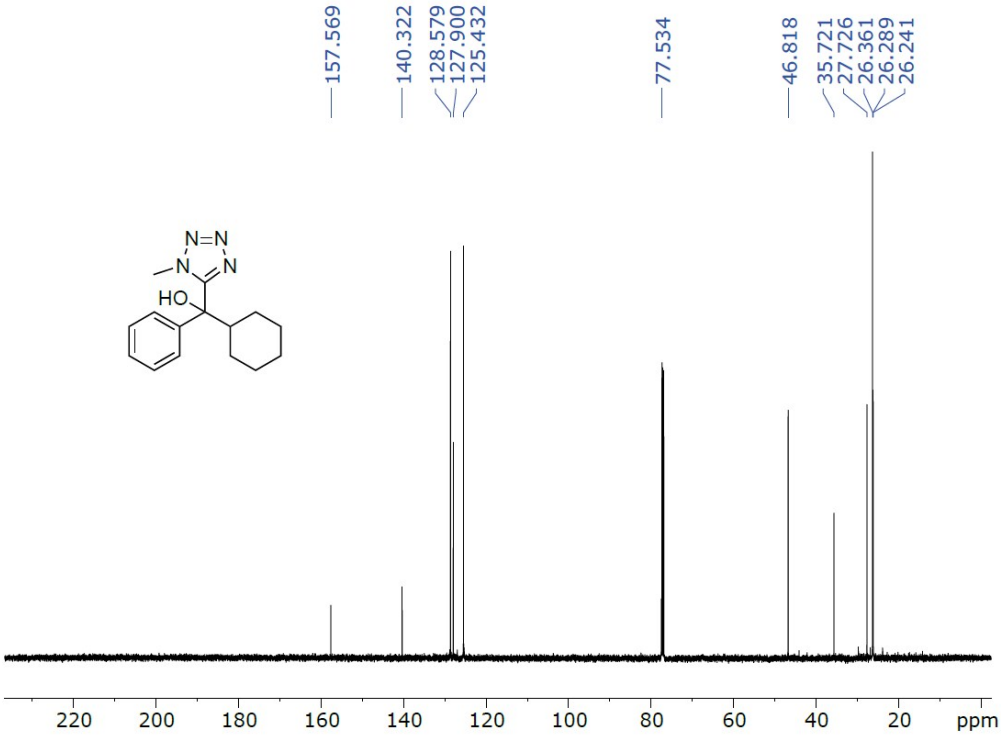

1_ iPrOH #707 RT: 5.59 AV: 1 NL: 3.49E8
T: FTMS + p ESI Full ms [50.0000-750.0000]
379.1617
295.1183
60.0451
189.0766
247.5628
351.1561
407.1211
476.1083
596.1992
645.1491
729.1913
Relative Abundance
m/z

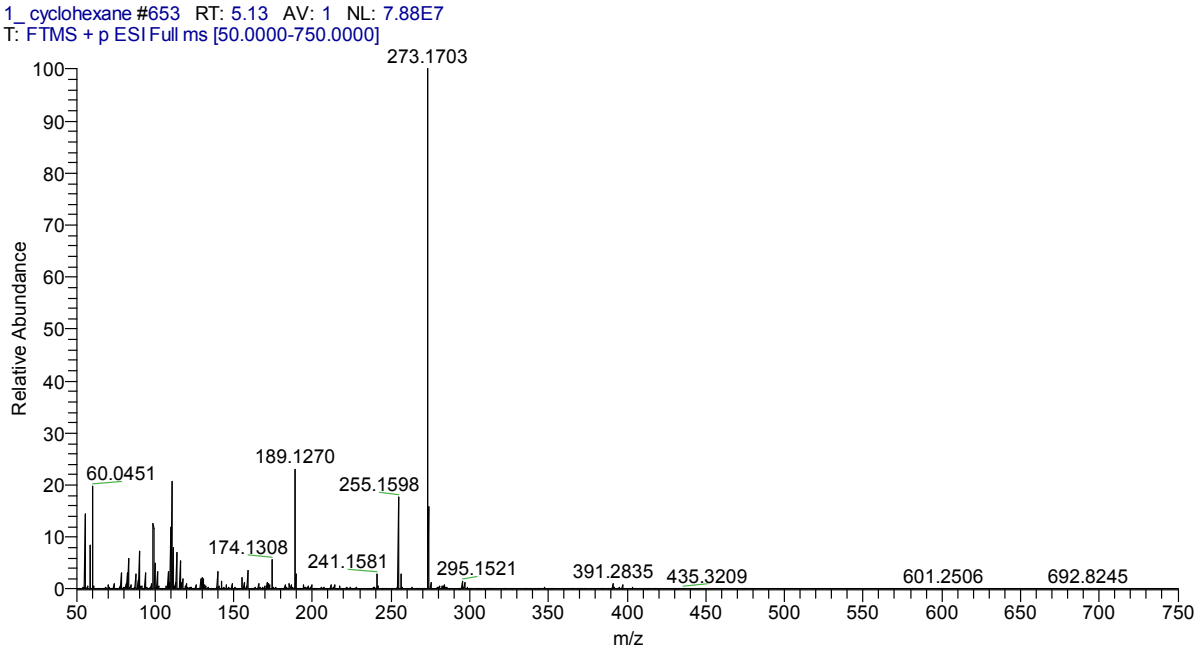
Figure SI-4: ^{1}H and ^{13}C-NMR spectra of photoproduct **4** and UHPLC-MS (ESI positive mode) spectrum



4



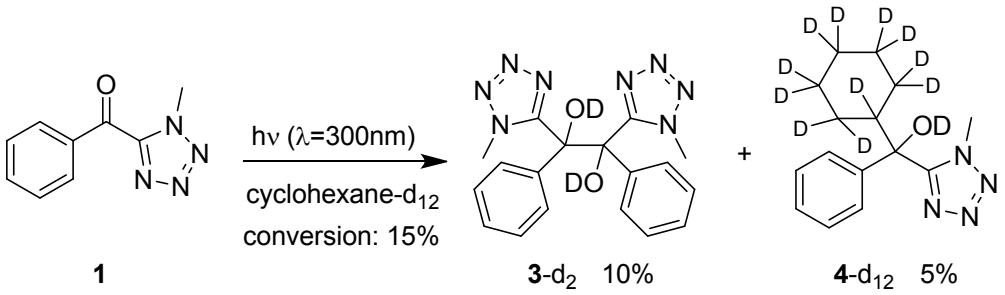

157.569
140.322
128.579
127.900
125.432
77.534
46.818
35.721
27.726
26.361
26.289
26.241
N=N
N
N
HO
220
200
180
160
140
120
100
80
60
40
20
ppm


1_ cyclohexane #653 RT: 5.13 AV: 1 NL: 7.88E7
T: FTMS + p ESI Full ms [50.0000-750.0000]
273.1703
189.1270
60.0451
255.1598
174.1308
241.1581
295.1521
391.2835
435.3209
601.2506
692.8245
Relative Abundance
m/z

Irradiation of compound 1 in deuterated cyclohexane C_6D_{12}.

In a NMR quartz tube is dissolved 10.0 mg of compound **1** in 0.75 mL of deuterated cyclohexane (C_6D_{12}). The reaction mixture is bubbled with argon during 5 min. Irradiation at 300 nm is carried out during 15 min. 1H NMR is then performed. The conversion was 15% (Scheme S-1).

Scheme S-1: Reaction of compound **1** in C_6D_{12}, 1H-NMR spectrum of the reaction mixture.



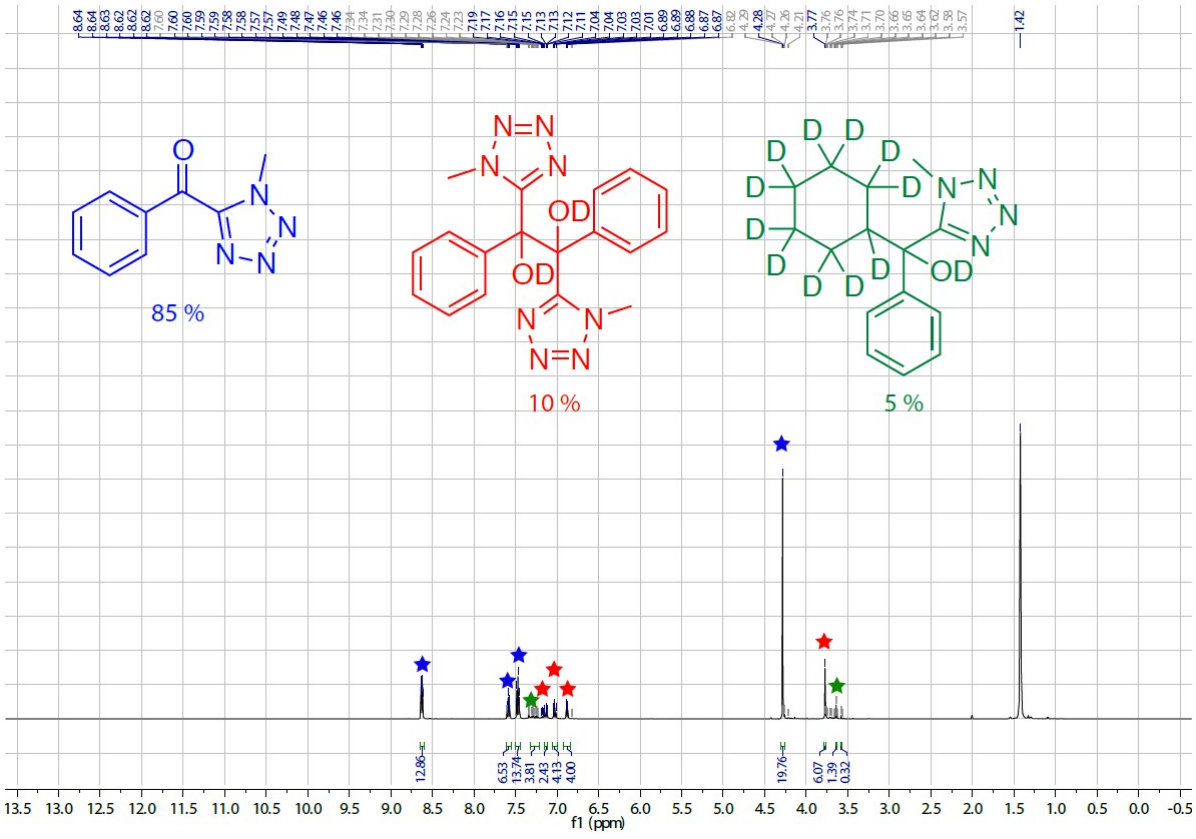


Figure SI-5: Transient absorption spectrum of ^{3}1* measured in MeCN, n-heptane, cyclohexane and iPrOH. A_{266} around 0.8.

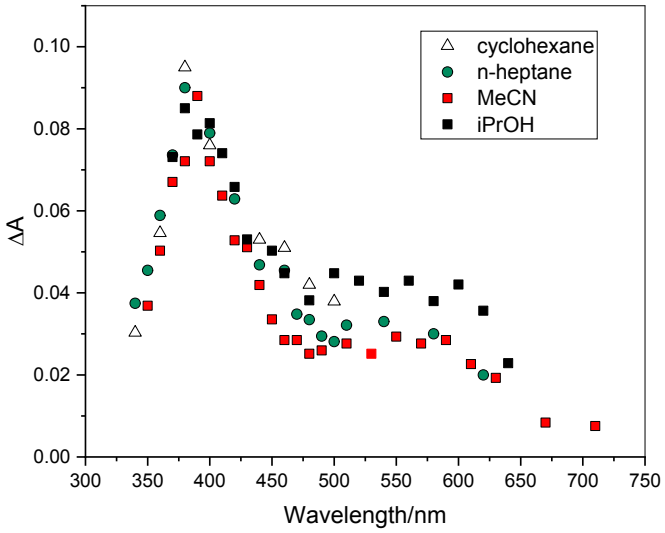


Figure SI-6: Formation of the triplet of anthracene at 420 nm after excitation of anthracene alone (curve 1) and after excitation of anthracene in the presence of **1** at 266 nm in argon-saturated MeCN. A part of the anthracene triplets are formed immediately after the pulse by direct excitation, and the other part is formed in 0.7 □s by energy transfer from $^{3}\mathbf{1}^{*}$ to ground state anthracene. At the concentration of 1.5×10^{-4} M, anthracene trapped about 60% of $^{3}\mathbf{1}^{*}$. (R. Bensasson and E. J. Land, Triplet-Triplet Extinction Coefficients via Energy Transfer, *Trans. Faraday Soc.* 1971, **67**, 1904-1915. G. Grabner, G. Koehler, G. Marconi, S. Monti and E. Venuti**,** Photophysical properties of methylated phenols in non-polar solvents, *J. Phys. Chem.* 1990, **94**, 3609-3613.)

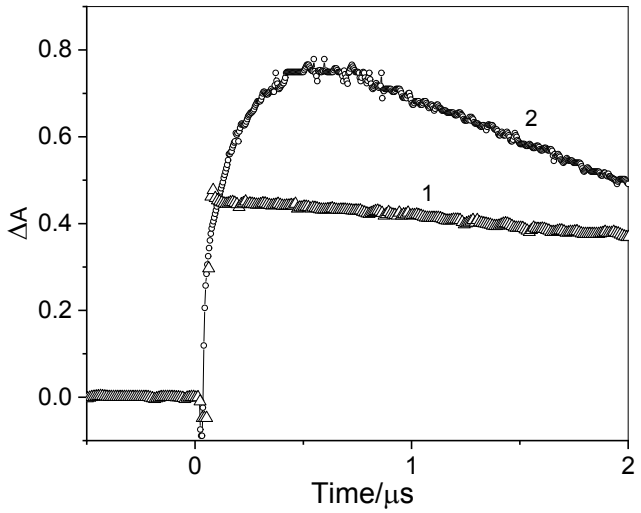


Figure SI-7: Effect of i-PrOH on the decay of $^{3}\mathbf{1}^{*}$ in air-saturated MeCN. Plot of the apparent first-order decay rate constant against i-PrOH concentration. The other experimental conditions are the same as those given in Figure 1.

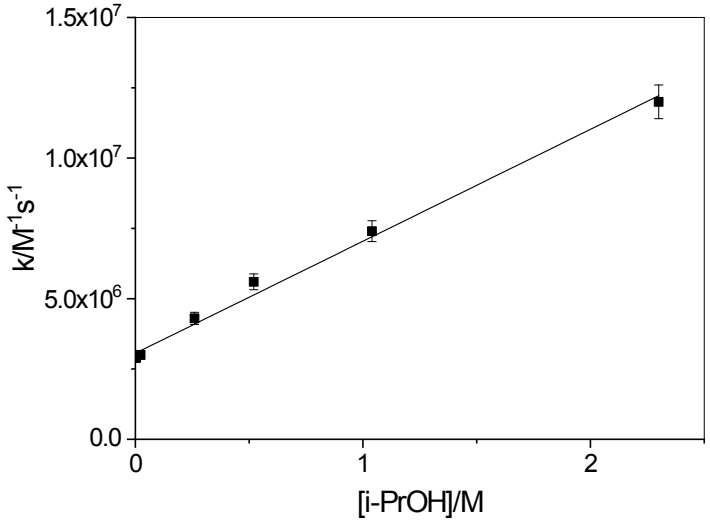


Figure SI-8: Influence of **1** concentration on the decay of ^{3}**1***. Excitation in MeCN at 355 nm. Argon – saturated medium. Detection at 550 nm.

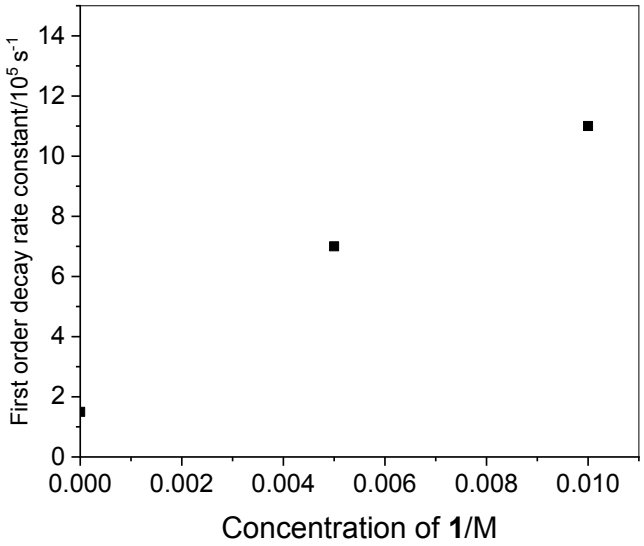


Figure SI-9 : Monitoring of the transient absorbance at 480 nm after excitation of **1** in deoxygenated cyclohexane. Following the fast decay of $^{3}\mathbf{1}^{*}$ a long-life secondary transient is observed.

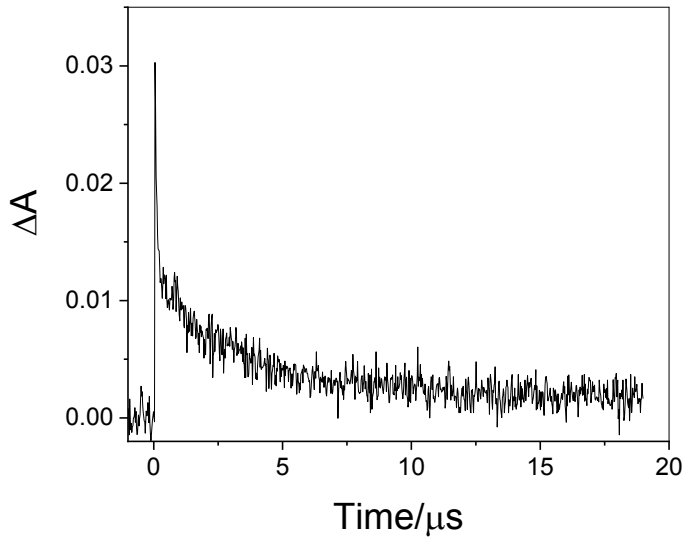


Figure SI-10: Plot of 1/A vs time, where A is the transient absorbance measured at 330 nm in i-PrOH. The linearity of the plot shows that the transient disappears by a bimolecular recombination.

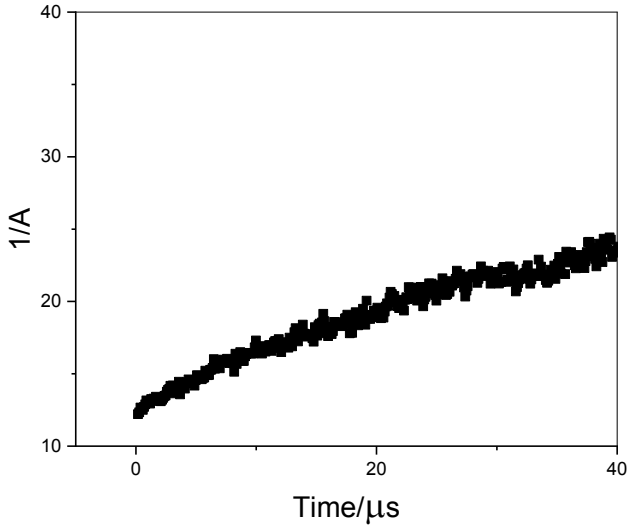


Figure SI-11: Absorbance decay of the secondary transient formed in cyclohexane at 330 nm. Experimental data and fitting postulating a mixture of first order decay and second order decay. The red line corresponds to the sum of first order (weight of 80%) with a rate constant of 2.5×10^5 s^{-1} and second order (weight of 20%) with $2k/\varepsilon=6.5\times10^5$ $cm^{-1}s^{-1}$

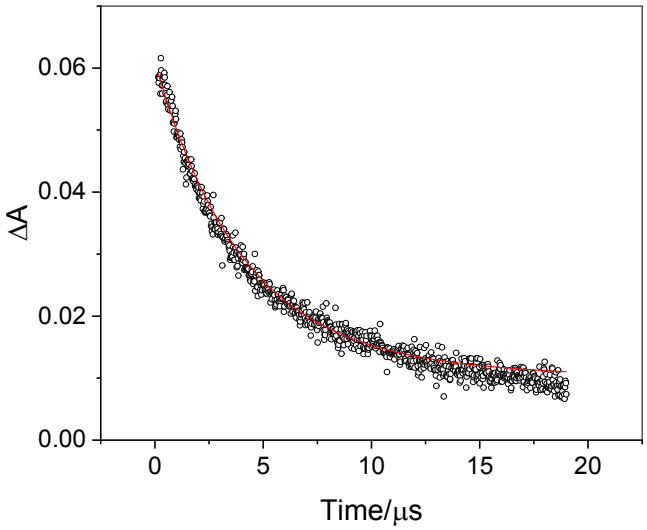


Figure SI-12: Effect of oxygen on the formation and the decay of the secondary transient formed in MeCN at 460 nm, (a) deoxygenated medium, (b) air-saturated medium, (c) oxygen-saturated medium.