Electronic supplementary information to "The Photoformation of a Phthalide: A Ketene Intermediate Traced by FSRS"

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1 Additonal spectroscopic and computational data

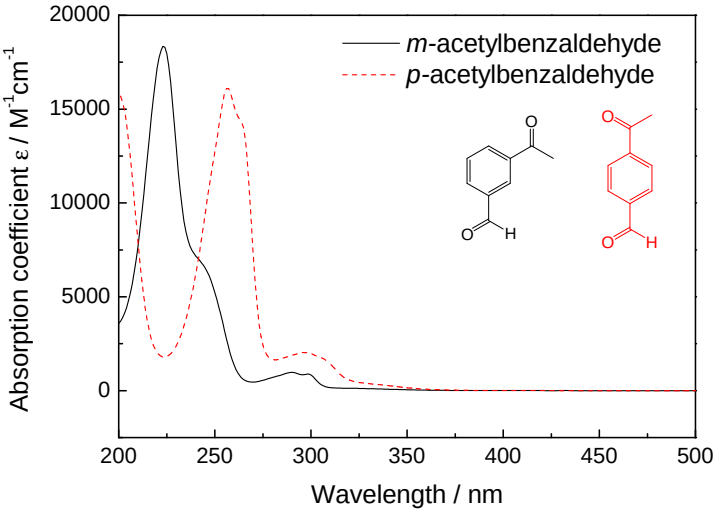

Fig. S 1 UV/Vis absorption spectra of mABA and pABA dissolved in acetonitrile.

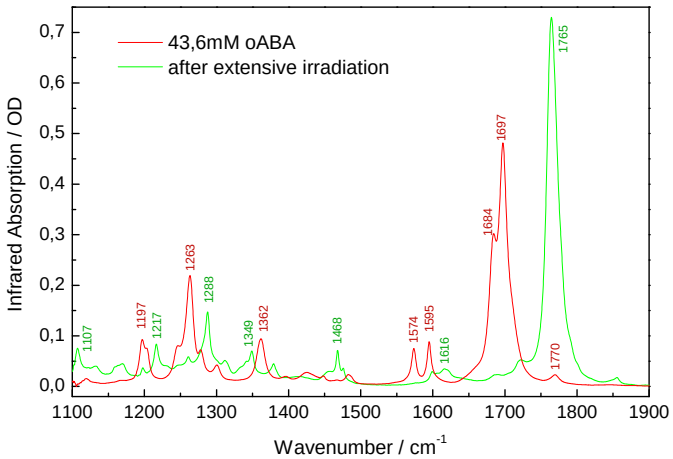

Fig. S 2 Infrared absorption spectrum of oABA in acetonitrile (43.6 mM, 200 μm CaF_2 cuvette) before (red) and after (green) extensive illumination at 266 nm.

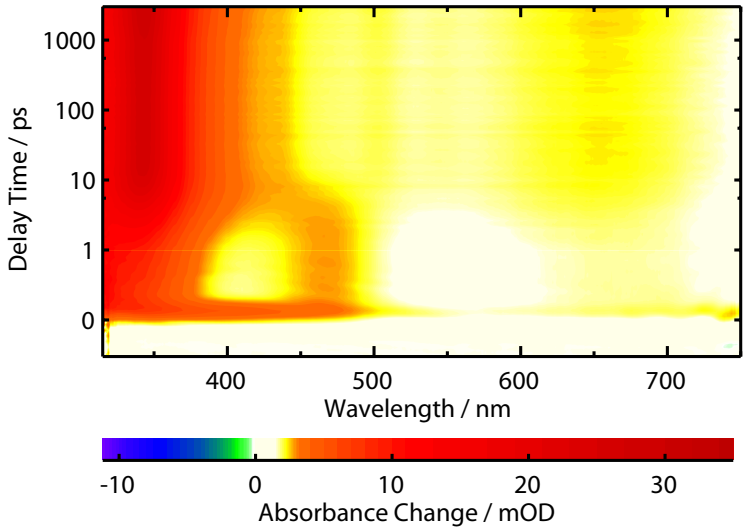

Fig. S 3 fs-UV/Vis data for mABA dissolved in acetonitrile (63 mM) upon excitation at 266 nm. Note that the time axis is linear until 1 ps and logarithmic thereafter.

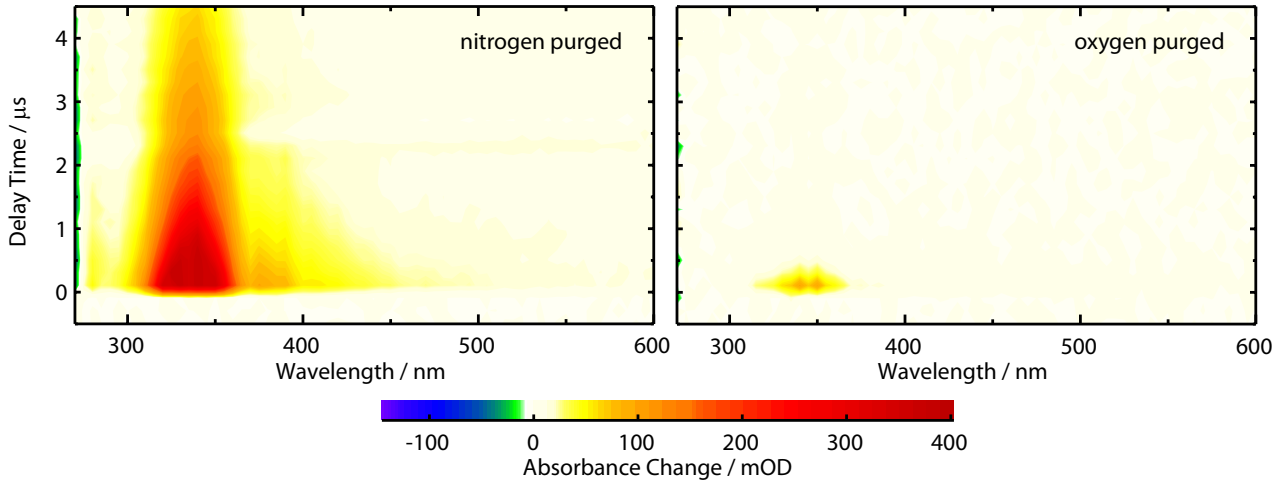

Fig. S 4 Nanosecond transient absorption data for pABA dissolved in acetonitrile (0.14 mM) under oxygen-free conditions (left) and with oxygen saturation (right).

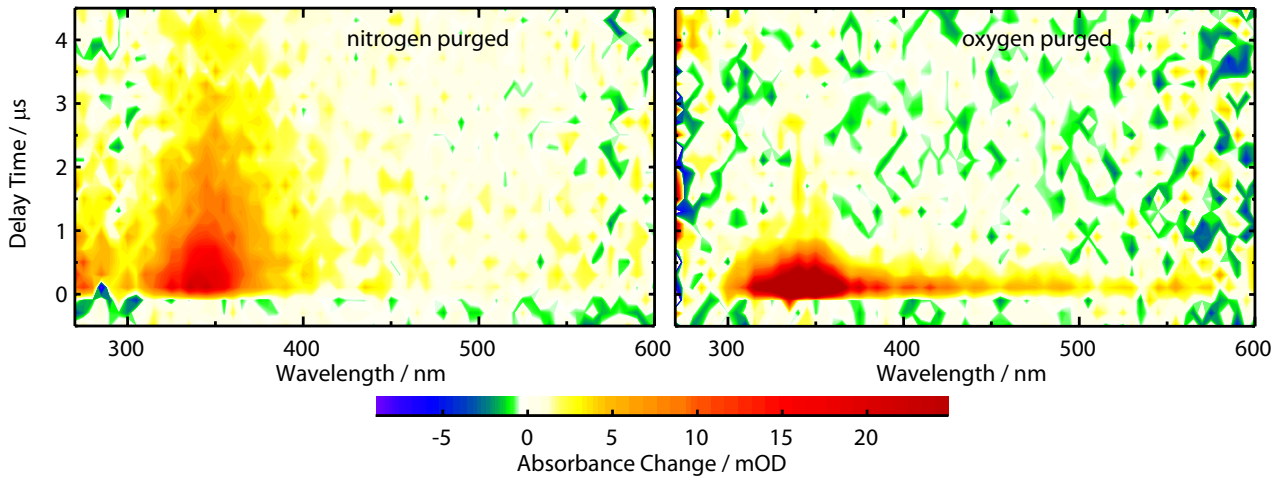

Fig. S 5 Nanosecond transient absorption data for mABA dissolved in acetonitrile (3 mM) under oxygen-free conditions (left) and with oxygen saturation (right).

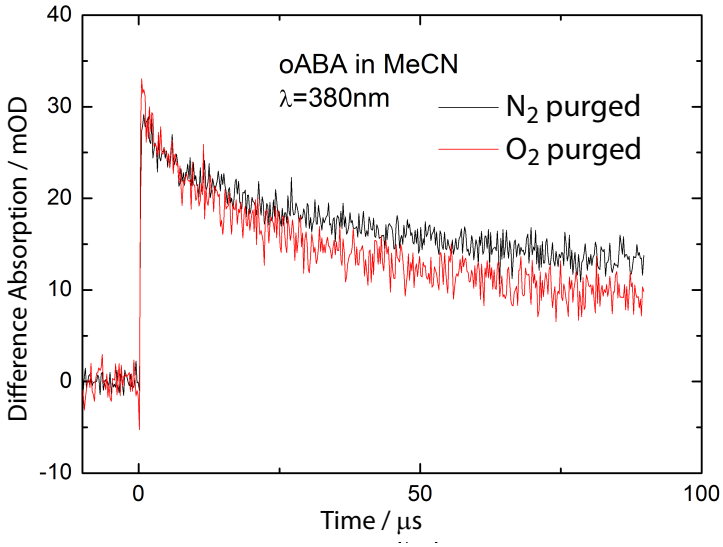

Fig. S 6 Nanosecond transient absorption time traces at λ = 380 nm for oABA dissolved in acetonitrile (0.12 mM) under oxygen-free conditions (black line) and with oxygen saturation (red line).

Table S 1 Cartesian coordinates and selected energy and enthalpy values of the optimized oABA structure in acetonitrile (DFT B3LYP/TZVP).

ZPE corrected energy: -498.248933 Hartree
Free energy: -498.284990 Hartree
Enthalpy: -498.238042 Hartree

C	0.161793	-0.488458	0.157466
C	-0.588535	0.688116	0.092957
C	-1.990883	0.598170	-0.050700
C	-2.597751	-0.657827	-0.097857
C	-1.839611	-1.818729	-0.012493
C	-0.457103	-1.733023	0.112819
C	0.078436	2.016748	0.272115
O	-0.549051	2.961445	0.726715
C	-2.859709	1.789913	-0.251945
O	-4.043694	1.802366	0.026017
C	1.532386	2.159903	-0.105323
H	-3.671297	-0.711101	-0.223887
H	-2.324381	-2.785834	-0.051802
H	0.141079	-2.632813	0.177987
H	1.235736	-0.439845	0.273284
H	1.726155	1.758501	-1.101280
H	1.808336	3.211213	-0.066227
H	2.161809	1.608014	0.597347
H	-2.392312	2.664459	-0.723715

Table S 2 Cartesian coordinates and selected energy and enthalpy values of the optimized *Z*-ketene-enol structure in acetonitrile (DFT B3LYP/TZVP).

ZPE corrected energy: -498.193789 Hartree
Free energy: -498.229226 Hartree
Enthalpy: -498.182557 Hartree

C	-0.736985	-1.723299	0.021223
C	0.152842	-0.576323	-0.002542
C	-0.511906	0.755674	-0.011237
C	-1.969316	0.828318	-0.032177
C	-2.711703	-0.296469	-0.013475
C	-2.080979	-1.598600	0.015463
C	1.507001	-0.653280	-0.012411
O	2.149883	0.565099	0.063935
C	0.131241	1.924526	0.002471
O	0.506490	3.027106	0.013035
C	2.391851	-1.852061	-0.019814
H	-2.435935	1.804837	-0.036611
H	-3.791876	-0.228842	-0.004844
H	-2.706825	-2.482102	0.043804
H	-0.295684	-2.710043	0.057303
H	3.043515	0.522983	-0.305288
H	1.827087	-2.777791	-0.118091
H	3.107122	-1.814028	-0.846086
H	2.969342	-1.903569	0.909042

Table S 3 Cartesian coordinates and selected energy and enthalpy values of the optimized biradical structure in acetonitrile (DFT B3LYP/TZVP).

ZPE corrected energy: -498.178148 Hartree
Free energy: -498.214638 Hartree
Enthalpy: -498.167255 Hartree

C	-0.642047	-1.658342	-0.057456
C	0.166813	-0.482703	-0.014422
C	-0.526651	0.783405	0.016016
C	-1.939937	0.814227	0.002559
C	-2.676887	-0.345748	-0.039285
C	-2.011867	-1.591416	-0.069405
C	1.570398	-0.609772	-0.003924
O	2.380674	0.455041	0.035820
C	0.187671	2.030866	0.060210
O	-0.179237	3.173741	0.090333
C	2.303081	-1.911386	-0.035024
H	-2.431563	1.778577	0.026116
H	-3.758428	-0.306066	-0.049111
H	-2.590157	-2.506265	-0.102375
H	-0.163397	-2.627196	-0.081277
H	1.833845	1.292415	0.055039
H	2.050263	-2.536063	0.825249
H	2.068329	-2.483814	-0.935819
H	3.374198	-1.720595	-0.018381

Table S 4 Cartesian coordinates and selected energy and enthalpy values of the optimized cyclic enol structure in acetonitrile (DFT B3LYP/TZVP).

ZPE corrected energy: -498.221396 Hartree
Free energy: -498.255315 Hartree
Enthalpy: -498.211546 Hartree

C	0.662348	1.277396	0.045836
C	-0.441742	0.464164	0.020257
C	0.092155	-0.893372	-0.008236
C	1.457866	-0.797979	0.002289
O	1.790728	0.549326	0.035706
C	-1.850288	0.686052	0.016833
C	-2.678846	-0.395876	-0.013445
C	-2.159674	-1.737487	-0.041585
C	-0.821220	-1.993391	-0.039444
C	2.579275	-1.764917	-0.013749
O	0.876297	2.604674	0.078171
H	-2.255796	1.690709	0.037752
H	-3.752260	-0.253674	-0.016685
H	-2.862679	-2.561428	-0.065062
H	-0.451420	-3.011311	-0.060976
H	0.033025	3.075913	0.083559
H	2.182136	-2.779616	-0.039147
H	3.210587	-1.674061	0.875301
H	3.220214	-1.633644	-0.890794

Table S 5 Cartesian coordinates and selected energy and enthalpy values of the optimized *E*-ketene-enol structure in acetonitrile (DFT B3LYP/TZVP).

ZPE corrected energy: -498.186972 Hartree
Free energy: -498.222853 Hartree
Enthalpy: -498.175649 Hartree

C	0.821529	-1.601601	-0.304702
C	2.151860	-1.430618	-0.140941
C	2.707020	-0.158091	0.260648
C	1.907133	0.937147	0.348216
C	0.465191	0.864222	0.049102
C	-0.133778	-0.526064	-0.060930
C	-1.455789	-0.770815	0.079936
C	-0.108681	1.832123	-0.186338
C	-2.507524	0.208751	0.484763
O	-1.900611	-2.054253	-0.187325
O	-0.752012	3.008895	-0.470293
H	0.423382	-2.572099	-0.568790
H	2.824449	-2.266141	-0.291065
H	3.768181	-0.073039	0.468249
H	2.322236	1.901533	0.598216
H	-2.085531	1.007361	1.088276
H	-3.017817	0.663429	-0.367454
H	-3.273501	-0.279860	1.088741
H	-2.823765	-2.140710	0.078944