Photochemistry of 2-diphenylmethoxyacetophenone. Direct Detection of a Long Lived Enol From a Norrish Type II Photoreaction.

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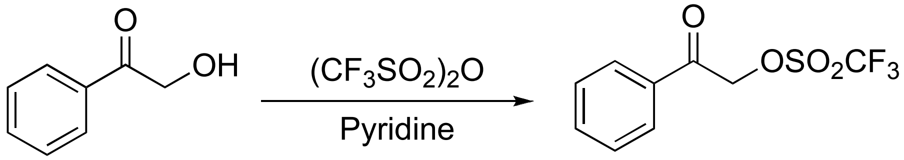
Electronic Supplementary Information.

***General*:** Compound **1** was synthesized from 2-hydroxyacetone and benzhydrol following the procedure given below. Acetophenone, butyrophenone and valerophenone were purchased from Sigma Aldrich. Acetonitrile was purchased from Fisher Chemicals (spectrophotomertic grade) and CD_3CN from Cambridge Isotope Laboratories. NMR spectra were recorded using Bruker Avance 400 MHz or 500 MHz spectrometers at 300 K. GC analysis was performed on a Varian 3900 GC on a CP-SIL 5 CB column (25 m x 0.25 mm, 0.25 μ). The absorption spectrum of **1** (Fig. S1) was recorded on an Agilent 8453 spectrometer at room temperature (295 K) under argon saturated conditions. Emission spectra (Fig. S1) were recorded on a HORIBA Fluorolog-3 spectrometer at 77 K in ethanol and methylcyclohexane. The phosphorescence lifetime was measured on an Edinburgh Analytical Instruments OB920 fluorometer using a pulsed Xe-lamp at excitation source and multi channel scaling for time-resolved signal detection. Laser flash photolysis experiments employed the pulses from a Spectra Physics GCR-150-30 Nd:YAG laser (266 nm, ca. 5 mJ/pulse, 5 ns pulse length) and a computer-controlled system that has been described elsewhere [Y. Yagci, S. Jockusch, N. J. Turro, *Macromolecules* 2007, **40**, 4481-4485].

***Photolysis experiments*:** Typically, 3 to 5 mM solution of the substrate in acetonitrile in a quartz tube was degassed by six freeze – pump – thaw cycles and sealed. The solution was irradiated at 254 nm until about 20 - 30 % conversion was obtained (~ 30 s to 1 min). The tube was then transferred to an NMR spectrometer and the spectra were recorded in 2 minute intervals until ~ 80 % of the enol formed was converted to the ketone. The relative amount of enol present in the sample was calculated by integrating the enol signals and were normalized to an internal standard, such as unreacted starting material. Quantum yields of formation of benzophenone and acetophenone were calculated by irradiating equimolar solutions of **1** and valerophenone at 254 nm and analyzing the products by gas chromatography.

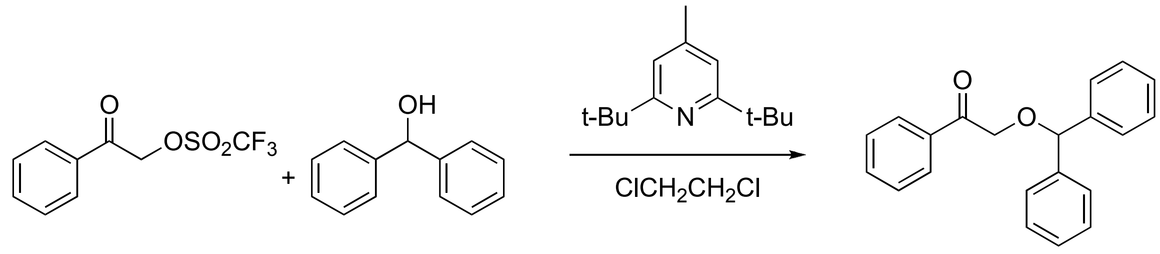
To ensure that possible trace amounts of water in commercial butyrophenone were not responsible for the short lifetime of the generated acetophenone enol, control experiments were performed with dried butyrophenone (dried over sodium sulfate prior to use). However, after photolysis, the same lifetime (6 min) of the acetophenone enol was observed compared to butyrophenone, which was not dried with sodium sulfate.

Synthesis of phenacyl triflate:



Trifluoromethanesulfonic anhydride (10 g, 35.5 mmol, 1 equiv) was stirred in dichloromethane (20 mL) and a solution of pyridine (3.5 g, 44 mmol, 1.25 equiv) in dichloromethane (10 mL) was added at -20 °C. To this solution, phenacyl alcohol (2-hydroxyacetophenone, (4.8 g, 35.5 mmol, 1 equiv.)) in dichloromethane (10 mL) was added over a period of 10 to 15 min. The cooling bath was removed and the mixture was stirred to room temperature. After 30 min, it was cooled in an ice-salt bath held at -10 °C and filtered. The white solid was washed with three portions of cold hexane (25 mL each). The filtrates were combined and concentrated. To the oily residue, 500 mL of hexanes was added and stirred overnight. The slurry was concentrated to ~ 100 mL and cooled to 0 °C and filtered to get 4.7 g of white solid (50 %). Column purification was carried out on neutral alumina with hexane and ethyl acetate as eluent.

Synthesis of 1:



A solution of phenacyl triflate (1 g, 3.73 mmol, 1 equiv), benzhydrol (500 mg, 2.72 mmol, 0.7 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (1.1 g, 5.36 mmol, 1.45 equiv) in 25 mL 1,2-dichloroethane was refluxed for 36 hours. The solution was cooled to ~50 °C and concentrated under vacuum. The residue was re-dissolved in 50 mL chloroform and washed with aqueous bicarbonate (20 mL), water (20 mL) and brine. The chloroform layer was dried over sodium sulfate and concentrated. Column purification (silica gel, hexanes, ethyl acetate) afforded 300 mg of **1** as white solid (36 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.84 (m, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.38 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.22 (m, 1H), 5.61 (s, 1H), 4.75 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.25, 141.22, 135.09, 133.46, 128.66, 128.49, 127.99, 127.79, 127.36, 83.78, 71.35. EI-MS m/z (%) 303 (M+H, 1), 105 (75), 120 (15), 167 (100), 183 (80).

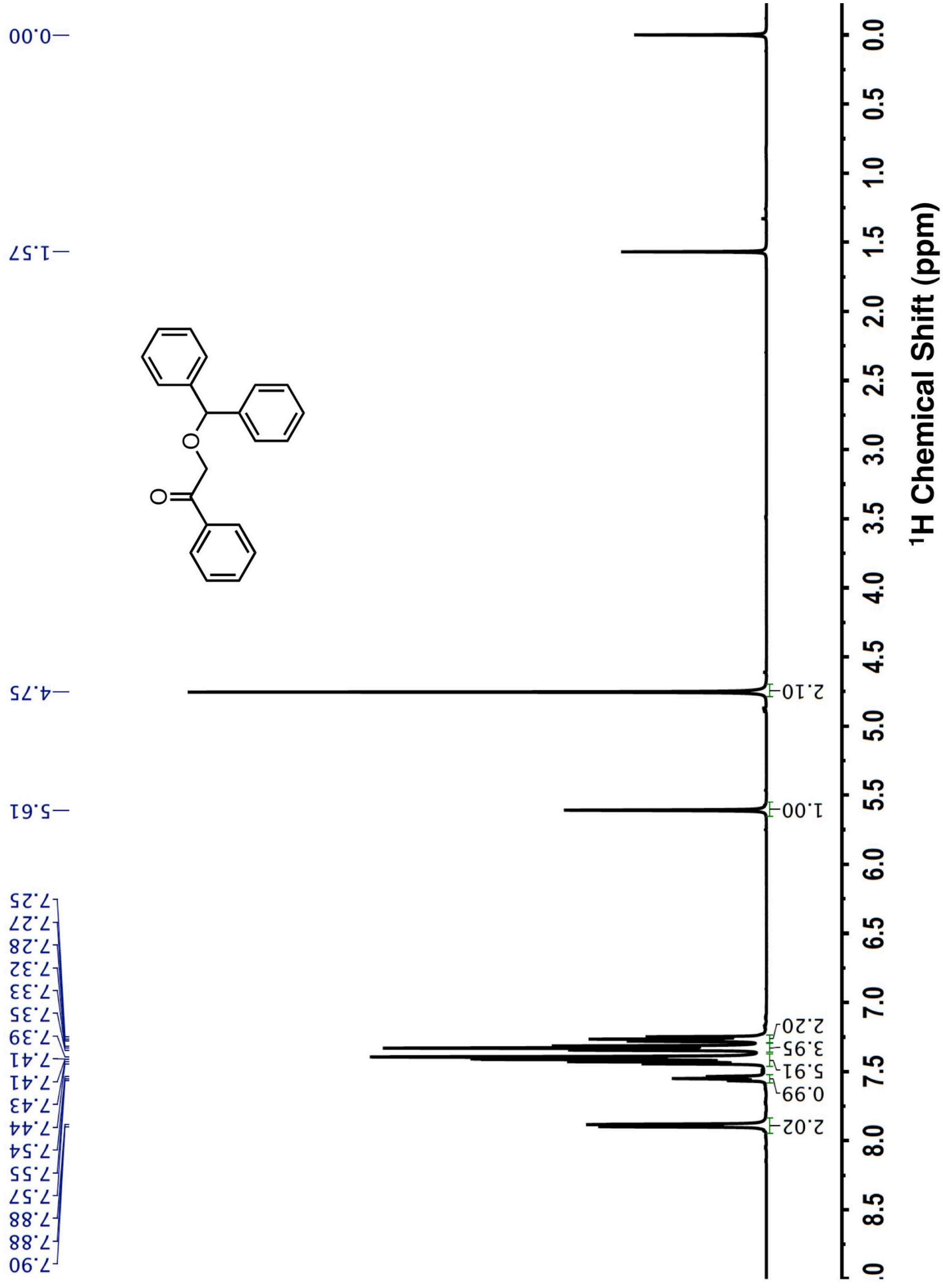


Fig. S1. ^{1}H NMR spectrum of **1** in $CDCl_3$ (500 MHz).

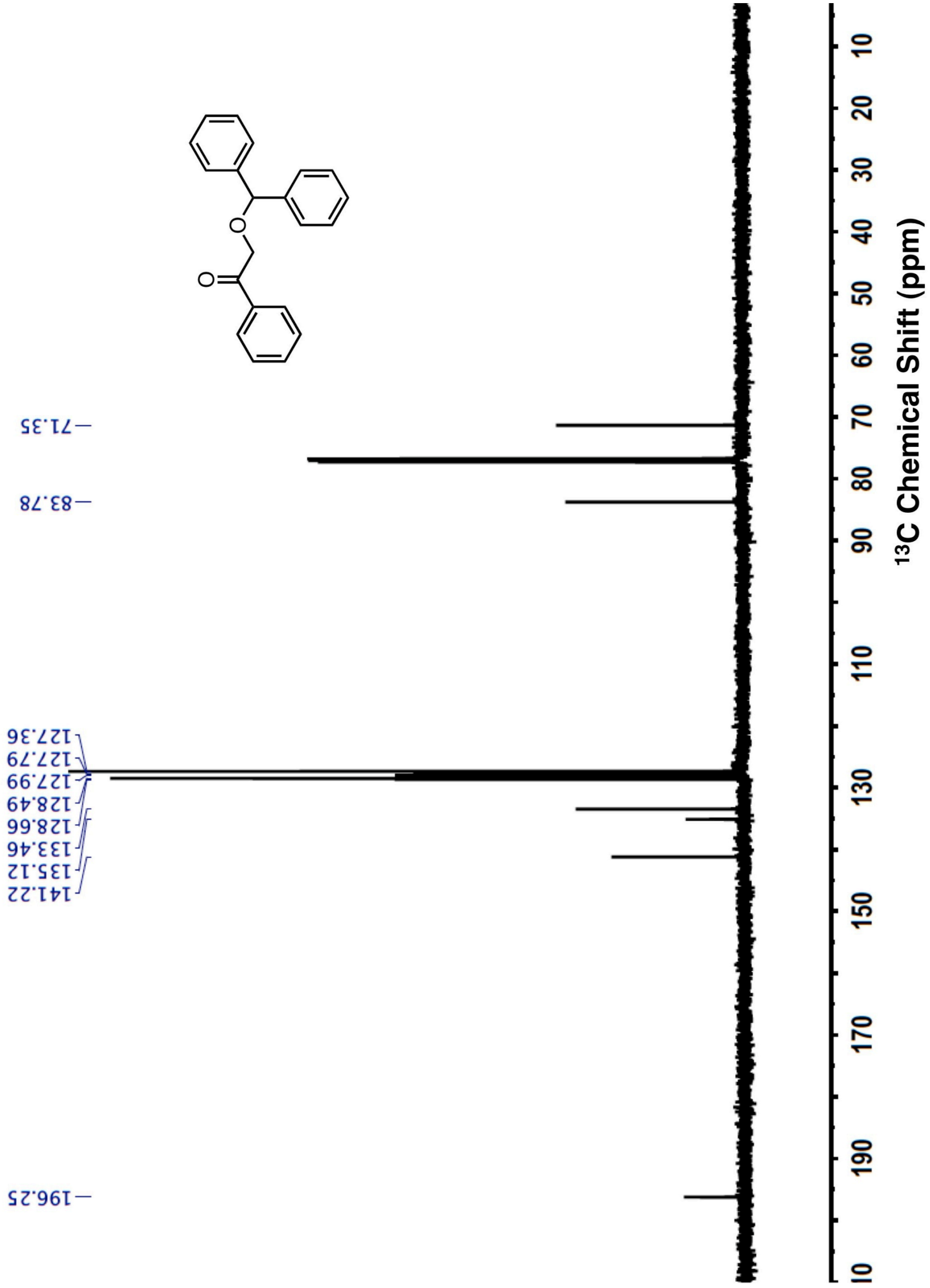


Fig. S2. ^{13}C NMR spectrum of **1** in $CDCl_3$ (125 MHz).

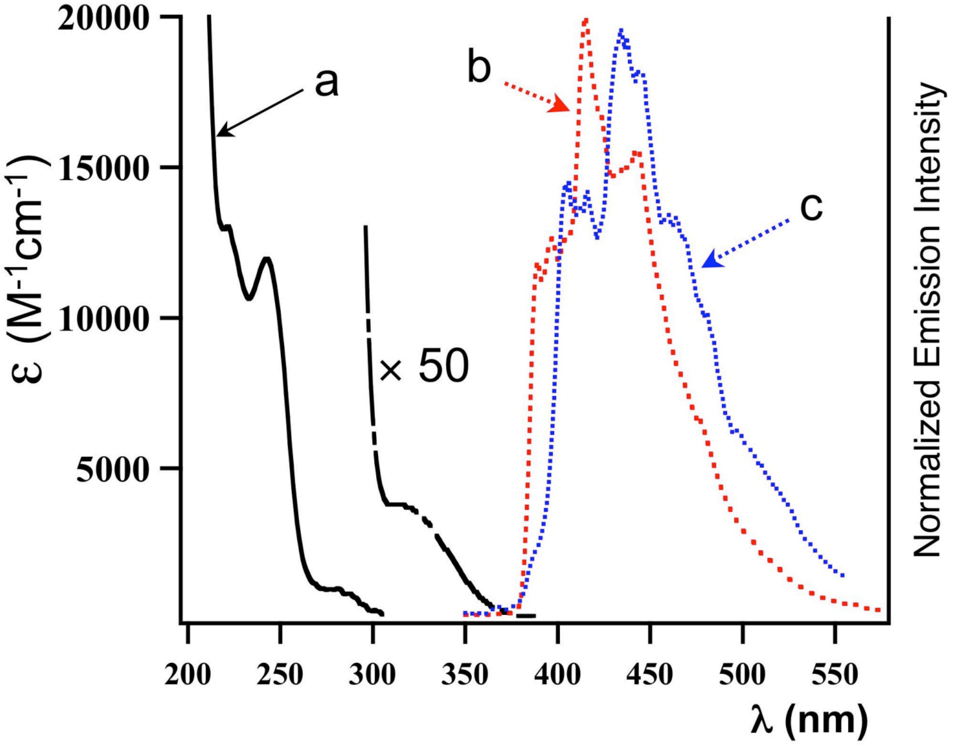


Fig. S3. Absorption (a, acetonitrile, 298 K) and emission spectra of **1** recorded at 77 K in ethanol (b) and in methylcyclohexane (c).

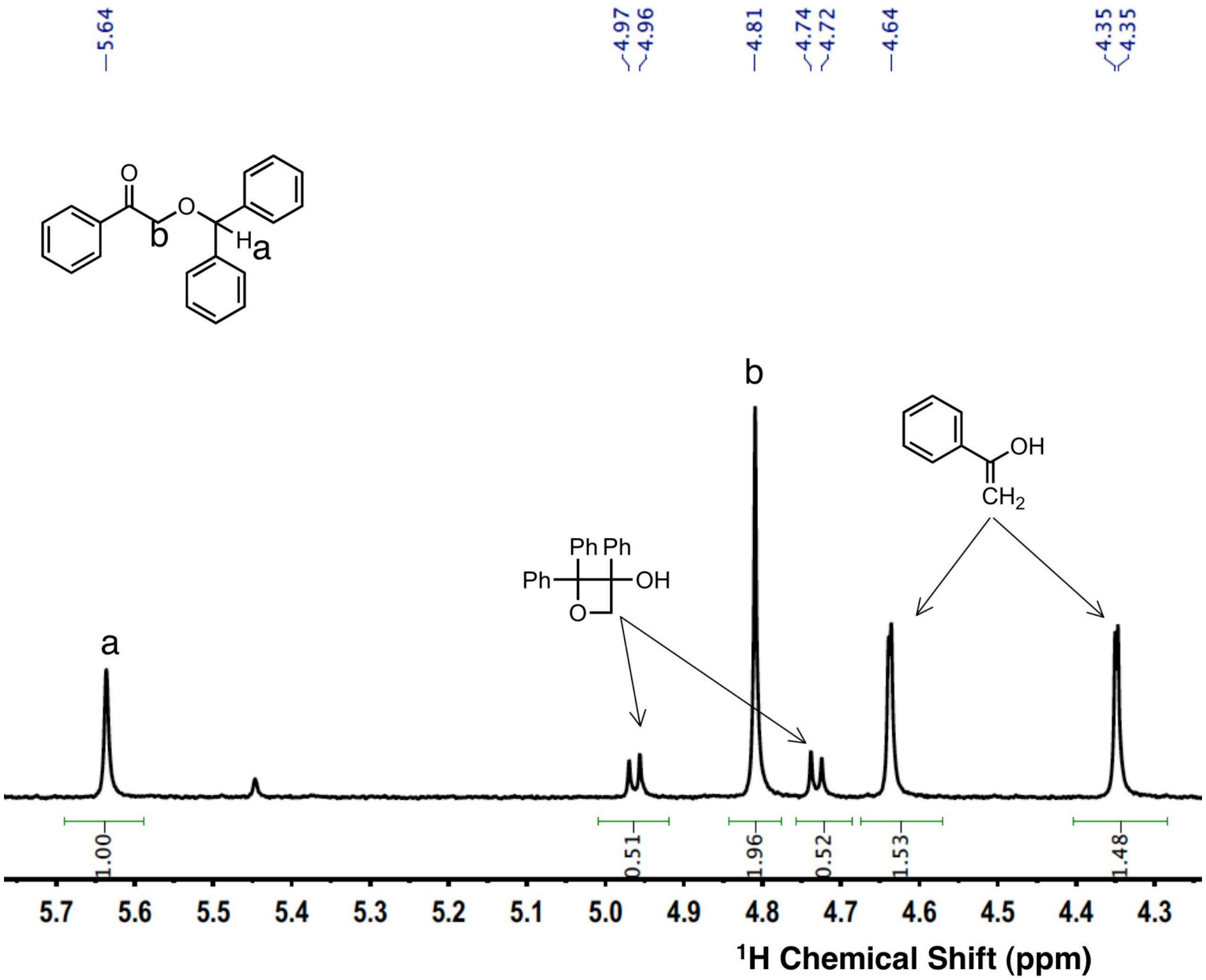


Fig. S4. Partial ^{1}H NMR spectrum (500 MHz, CD_3CN) of irradiated **1** (conversion ~75 %) showing the aliphatic signals of **1** (marked a and b), oxetanol (**5**) and enol (**3**) signals. Based on integration of product signals, relative yields of the products from β-bond cleavage to form **3**, **4** and **5** is 86 %, and from cyclization to form **5** is ~14 %.

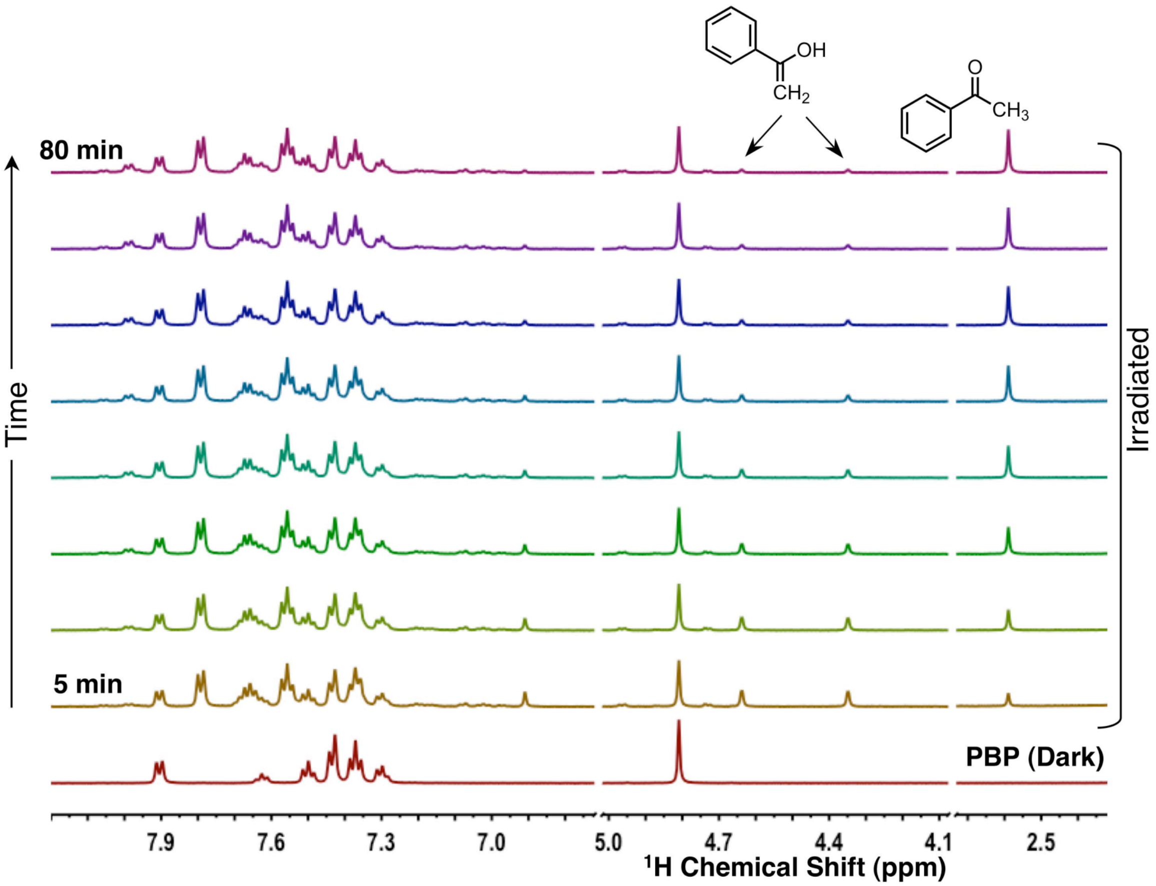
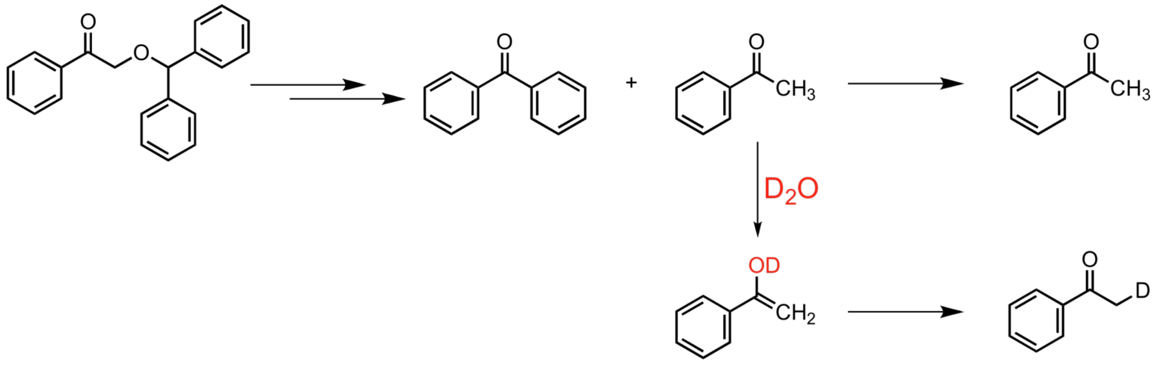


Fig. S5. ^{1}H NMR spectra (500 MHz, CD_3CN) of irradiated **1** showing the enol-keto conversion. Spectra recorded in about 4 minute intervals are shown.



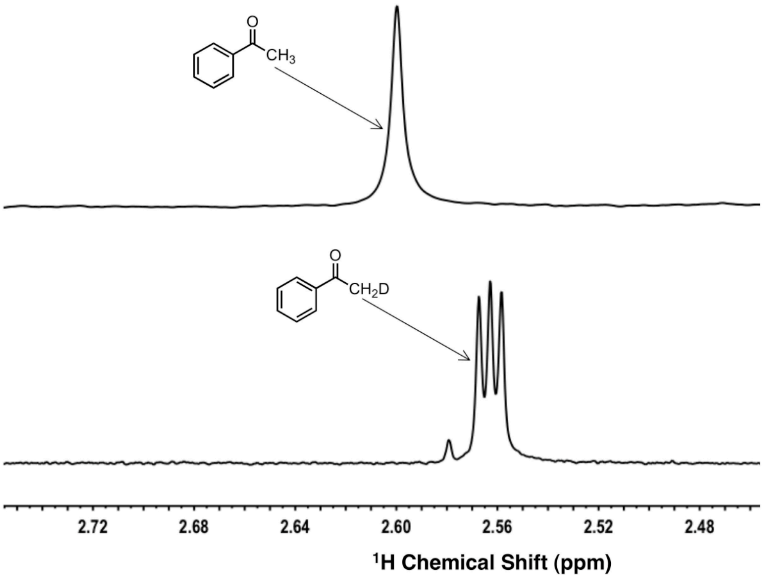


Fig. S6. ^{1}H NMR spectrum (500 MHz, CD_3CN + 20 % D_2O) of irradiated **1** showing the methyl signals of acetophenone.

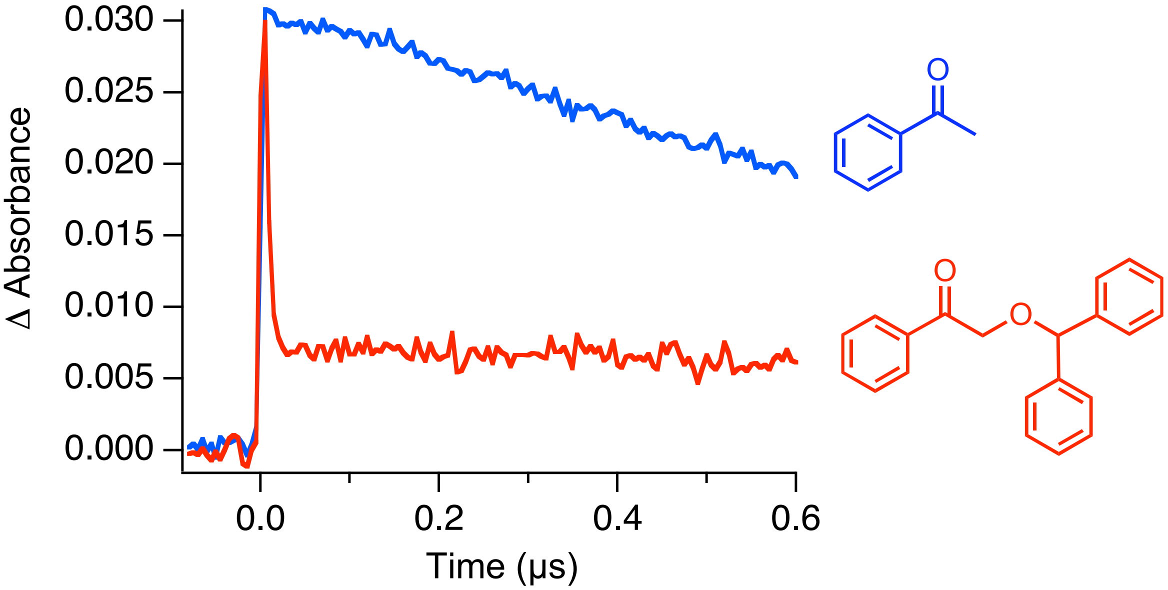


Fig. S7. Kinetic transient absorption traces of argon saturated acetonitrile solutions of **1** and acetophenone observed at 320 nm after pulsed laser excitation (266 nm, 5 ns pulse width). The blue decay trace at 320 nm is assigned to the known triplet-triplet absorption of acetophenone. Solutions of **1** with the same absorbance at the excitation wavelength compared to the acetophenone solution (A_{266nm} = 0.3) showed a similar ΔA at 320 nm directly after the laser pulse (red decay trace), which indicates that similar amounts of triplet states of **1** are formed. However, ^{3}(**1**)* decayed rapidly with a lifetime shorter than 20 ns (shorter than the time resolution of our experimental setup). The fast decay of the triplet absorption indicates a fast reaction from the triplet state, such as the Norrish Type II reaction.

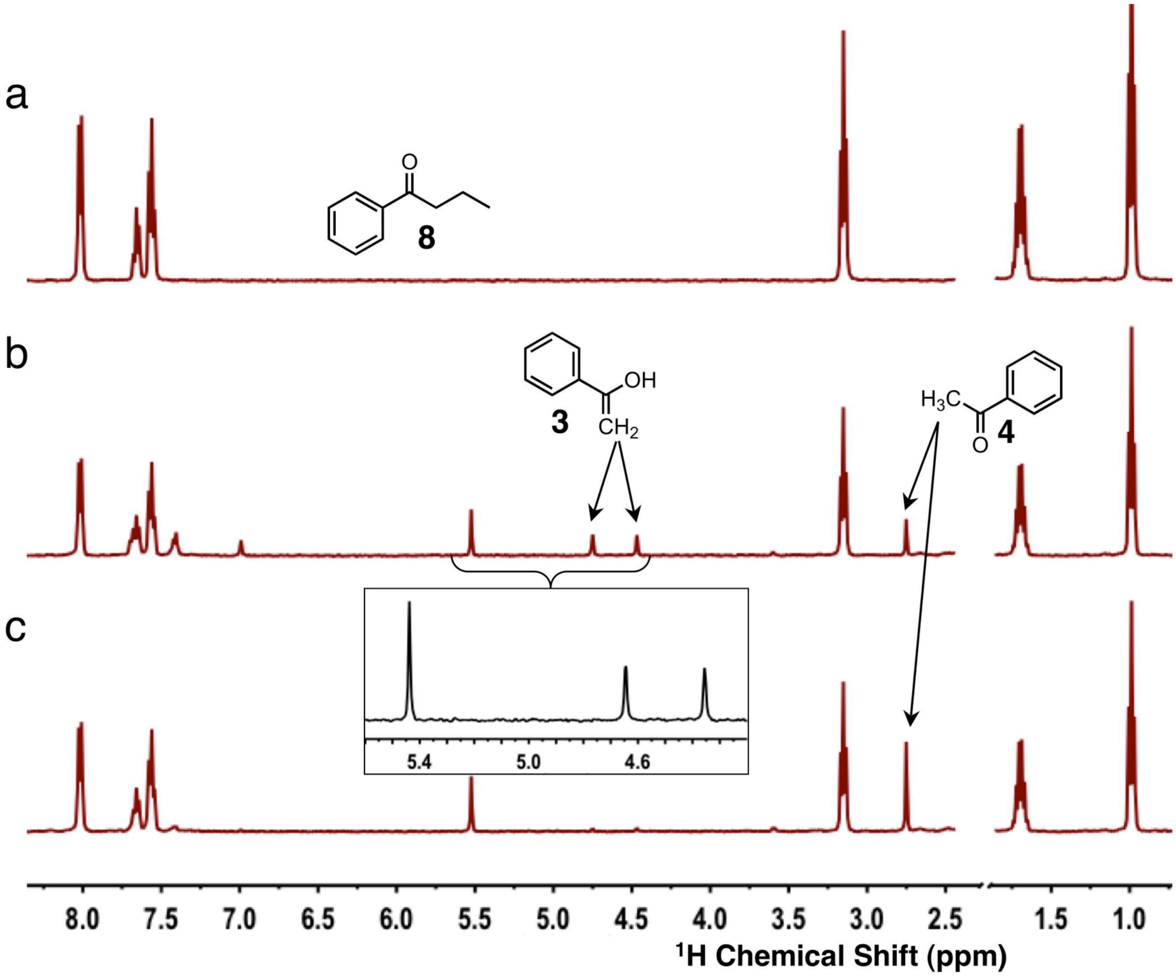


Fig. S8. ^{1}H NMR spectra (400 MHz, CD_3CN) of butyrophenone **8** (a) prior to photolysis, (b) 3 min after photolysis at 254 nm (~20 % conversion) and (c) sample b after 30 min to complete enol to keto tautomerization. Solvent signals are omitted.

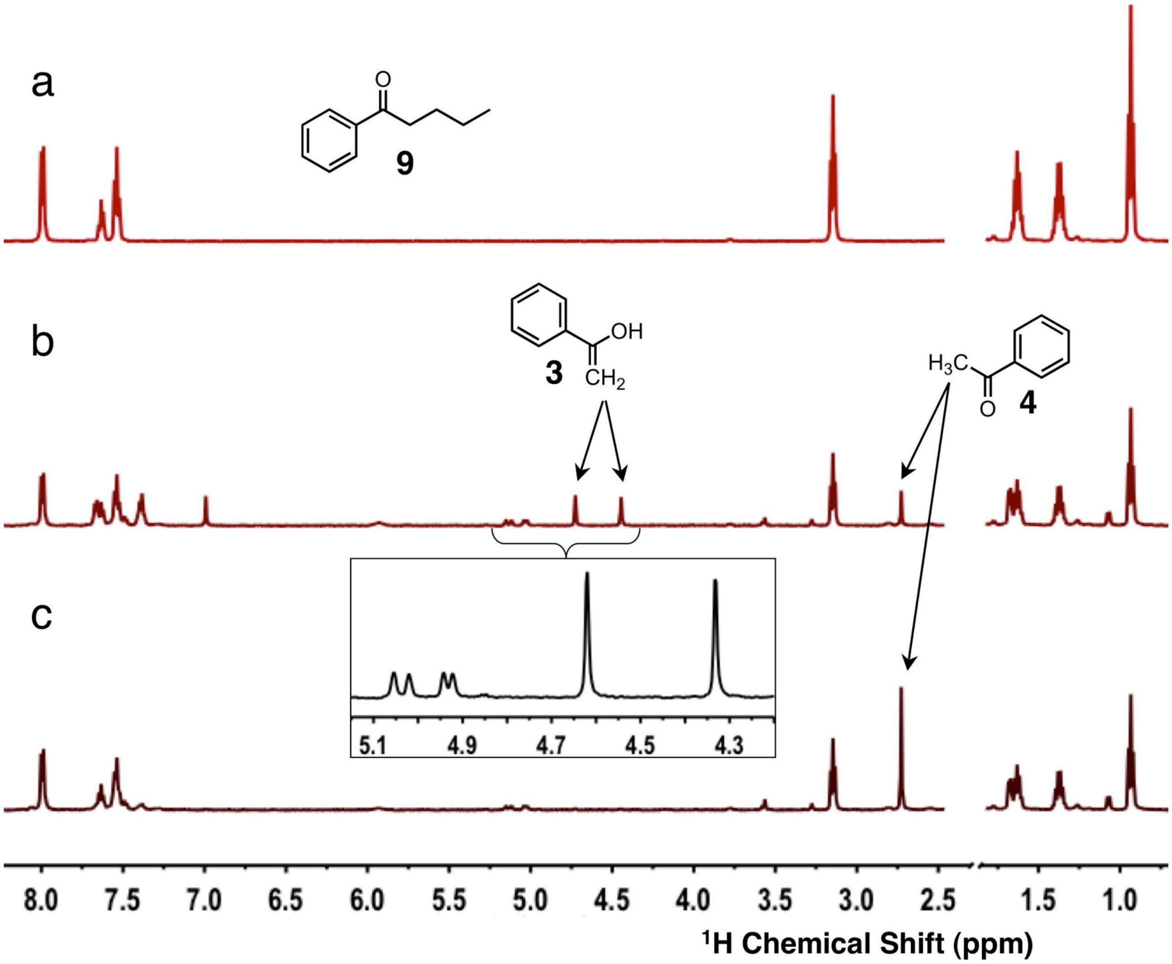


Fig. S8. ^{1}H NMR spectra (400 MHz, CD_3CN) of valerophenone **9** (a) prior to photolysis, (b) 3 min after photolysis at 254 nm (~ 40 % conversion) and (c) sample b after 30 min to complete enol to keto tautomerization. Solvent signals are omitted.