

## Supplementary Information

### Mechanism of the Photorelease of Alcohols from the 9-Phenyl-9-tritylone Protecting Group

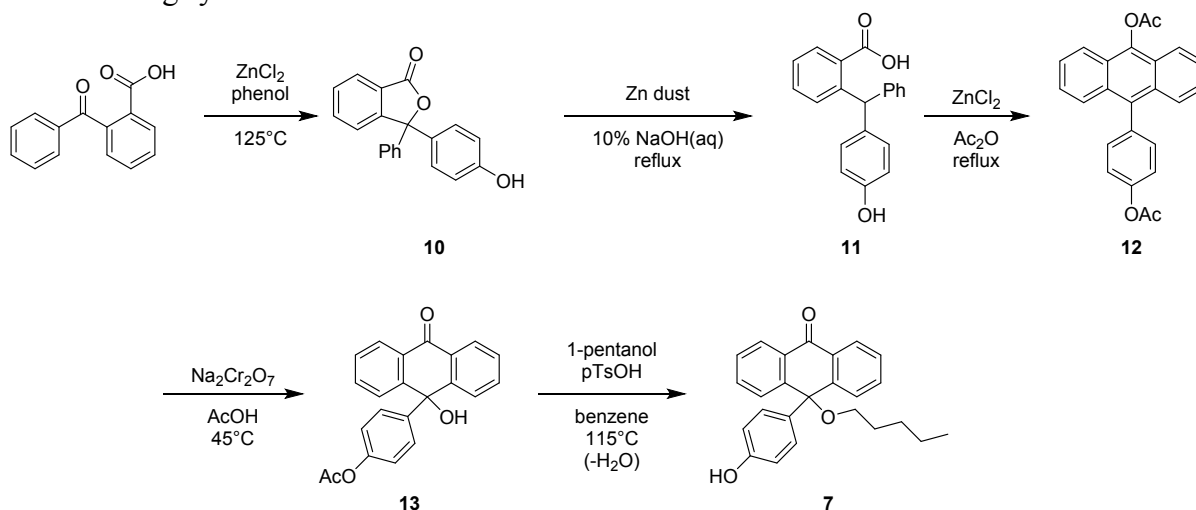
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#### Synthesis:

**9-benzyloxy-9-phenylanthrone (5)** was synthesized following a literature procedure.<sup>1</sup>

**10-(4-hydroxyphenyl)-10-(pentyloxy)-9(10*H*)-anthracenone (7)** was synthesized using the following synthetic route:



**3-Phenyl-3-(4-hydroxyphenyl)phthalide (10)**: Following modified literature procedures,<sup>2,3</sup> in a 250 mL round bottom flask equipped with a stir bar was added 2-benzoylbenzoic acid (6.9367 g, 30.7 mmol), phenol (3.0873 g, 32.8 mmol), and zinc chloride (4.2408 g, 31.1 mmol). The solid mixture was heated to 125°C and stirred in the melt for 8 hours. Upon completion of the reaction, boiling acetic acid was added until dissolved. Once dissolved, the reaction mixture was poured into approximately 200 mL of deionized water and a white precipitate formed. The water was decanted off and the precipitate was dissolved in ethyl acetate and washed with 15% sodium carbonate. The organic layer was dried with magnesium sulfate and the solvent was removed under reduced pressure to yield 5.5278 g (60%) of phthalide.

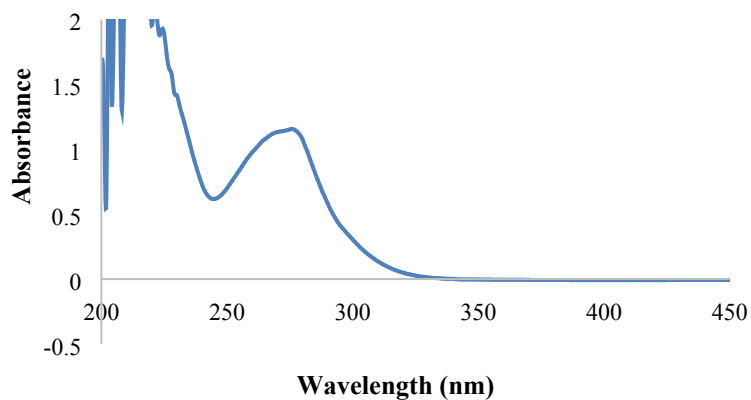
**2-(4'-hydroxybenzhydryl)benzoic acid (11)** was synthesized following a literature procedure.<sup>3</sup>

**9-acetoxy-10-(4-acetoxyphenyl)anthracene (12):** Following a modified literature procedure,<sup>4</sup> in a 10 mL round bottom flask equipped with a stir bar was added 2-(4'-hydroxybenzhydryl)benzoic acid (1.6283 g, 5.35 mmol) and zinc chloride (0.5 g). To this, acetic anhydride (3.26 mL, 34.5 mmol) was added and the reaction mixture was heated at 99°C for 15 minutes. (Note: this reaction is very time and temperature sensitive). Upon completion of the reaction, the mixture was poured into pH 4 deionized water (acidified with HCl) and a precipitate formed. The water was decanted off and the precipitate was dissolved in dichloromethane, then dried over magnesium sulfate, and then the solvent was removed under reduced pressure to yield 1.9393 g (98%) of 9-acetoxy-10-(4-acetoxyphenyl)anthracene.

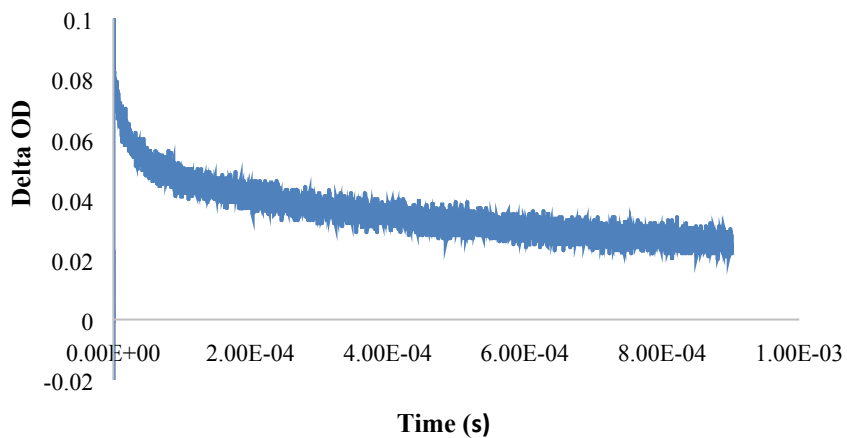
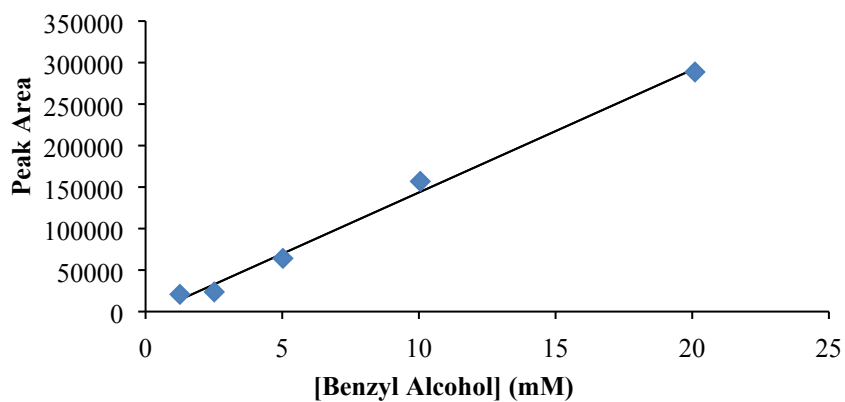
**10-(4-(acetyloxy)phenyl)-10-hydroxy-9-anthracenone (13):** Following a literature procedure for the oxidation of 9-phenylanthracene,<sup>1</sup> to a 50 mL round bottom flask equipped with a stir bar, 9-acetoxy-10-(4-acetoxyphenyl)anthracene (1.9534 g, 5.27 mmol) was added to 20 mL of glacial acetic acid. To the slurry solution, sodium dichromate dihydrate (2.3663 g, 7.94 mmol) was added and the mixture was heated at 45°C for 90 minutes with stirring. Soon after the addition of sodium dichromate the solution goes from a tan/brownish color to dark green. After 90 minutes, the solution was poured into 40 mL of deionized water and vacuum filtered. The precipitate was washed with generous portions of deionized water and placed under vacuum to dry, yielding 1.5935 g (88%) of 10-(4-(acetyloxy)phenyl)-10-hydroxy-9-anthracenone.

**10-(4-hydroxyphenyl)-10-(pentyloxy)-9(10*H*)-anthracenone (7):** Following a literature procedure for synthesizing PTO-ethers,<sup>1</sup> in a 50 mL round bottom flask equipped with a stir bar, 10-(4-acetoxyphenyl)-10-hydroxy-9(10*H*)-anthracenone (0.2303 g, 0.669 mmol), *p*-toluenesulfonic acid monohydrate (48.8 mg, 0.257 mmol) and 1-pentanol (0.20 mL, 1.85 mmol) was added to 25 mL of benzene. The solution was heated at 115°C for 18 hours under reflux equipped with a Dean-Stark trap for the removal of water. Upon completion of the reaction, the solution was left to cool to room temperature and the solvent was removed under reduced pressure. The resulting crude solid was purified using flash chromatography with silica gel and a mobile phase of 80:20 hexanes:ethyl acetate to yield 0.0823 g (33%) of 10-(4-hydroxyphenyl)-10-(pentyloxy)-9(10*H*)-anthracenone. m.p. = 168-172 °C, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 9.33 (1H, s), 8.19-8.17 (2H, dd), 7.71-7.67 (2H, dt), 7.54-7.50 (2H, dt), 7.47-7.45 (2H, d), 7.03-7.01 (2H, d), 6.62-6.60 (2H, d), 2.95-2.92 (2H, t), 1.56-1.49 (2H, m), 1.35-1.27 (2H, m), 1.24-1.15 (2H, m), 0.85-0.82 (3H, t). <sup>13</sup>C NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ = 183.43, 156.82, 146.42, 137.65, 135.14, 131.74, 129.09, 127.23, 127.18, 115.93, 78.12, 63.87, 29.87, 28.69, 22.68, 14.70 (1 peak not accounted for and could be overlapping with previous peaks). HRMS (ESI-) Calcd for C<sub>25</sub>H<sub>24</sub>O<sub>3</sub> [M-H]<sup>-</sup>: 371.1653, Found: 371.1643

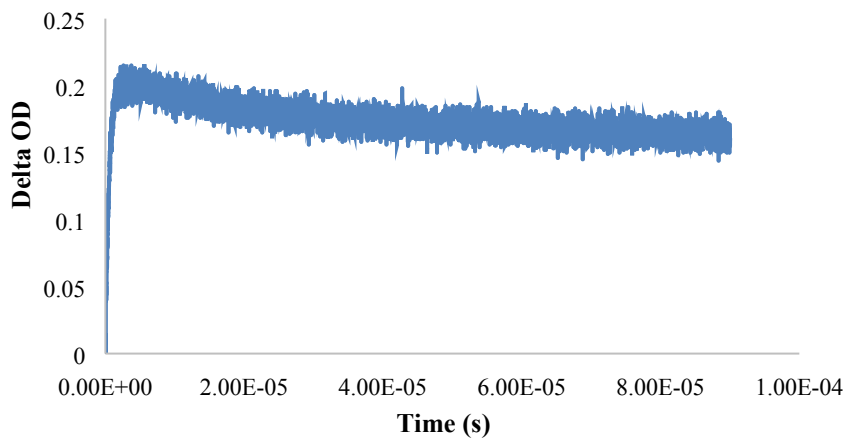
### UV-Vis Spectrum of Benzyl Ether 5 in 3:1 methanol: 1,4-dioxane



### GC calibration curve for benzyl alcohol 6

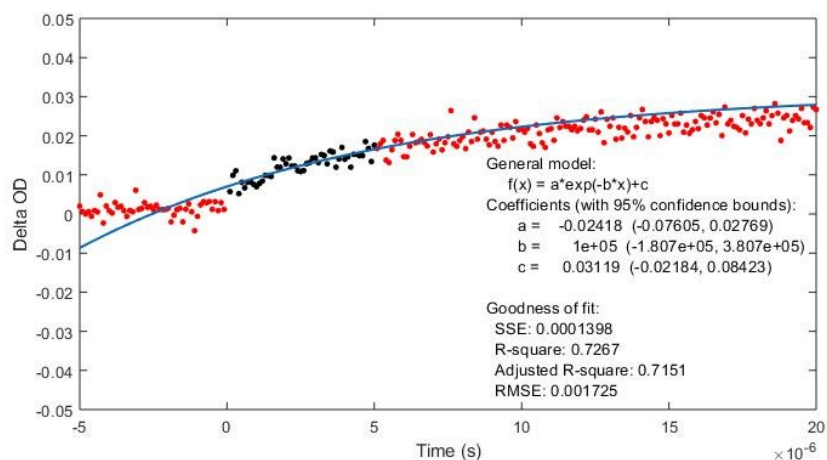


Benzyl Ether 5 in 3:1 methanol: 1,4-dioxane monitored at 540 nm (ketyl radical 3) at long times

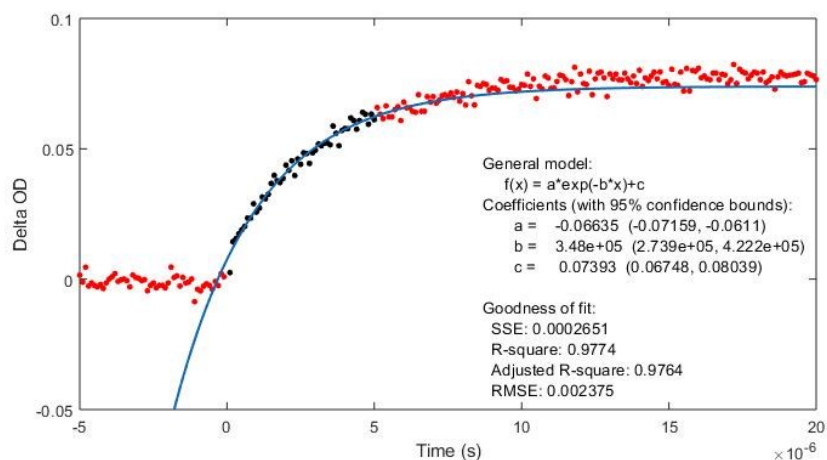


Benzyl Ether **5** in 3:1 methanol: 1,4-dioxane with 1 mM NaOH monitored at 620 nm (anion radical **2**) at long times

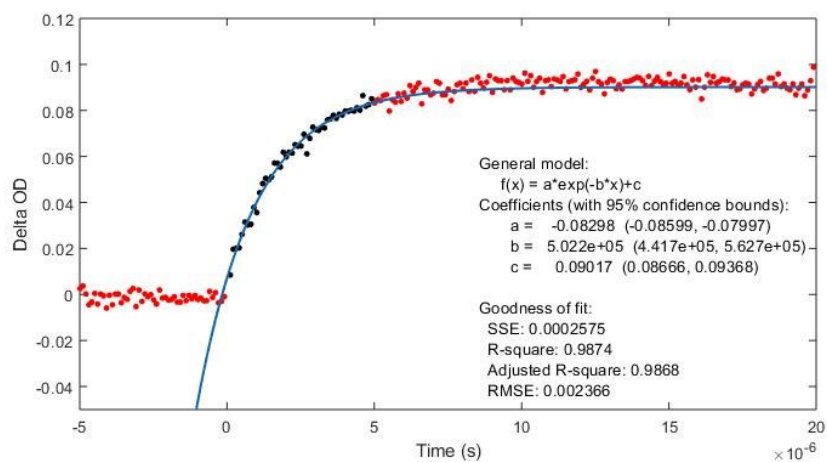
### Pseudo-First Order Analysis for Rate of Proton Transfer Between **2** and **3**



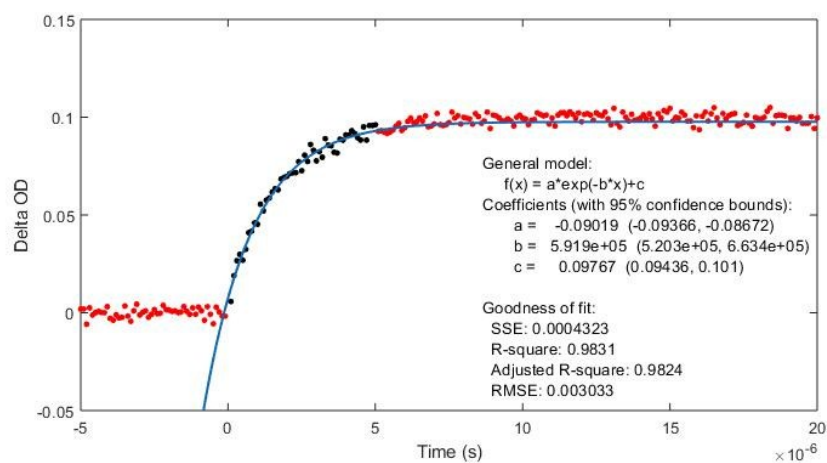
Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0 mM NaOH monitored at 620 nm



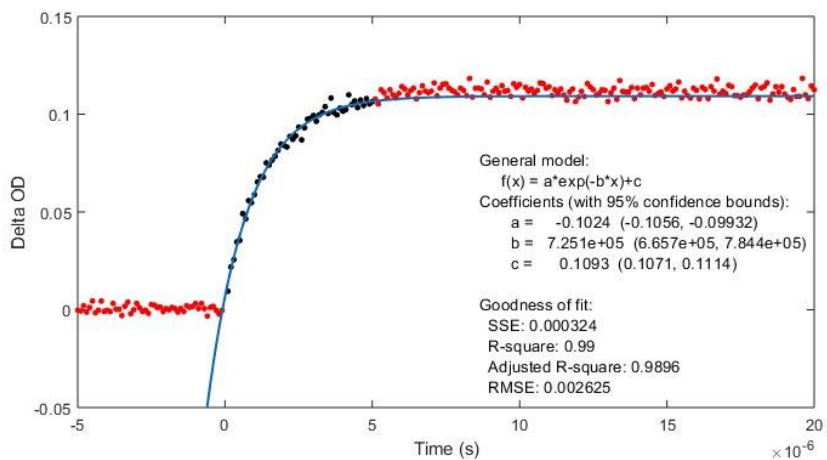
Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0.1 mM NaOH monitored at 620 nm



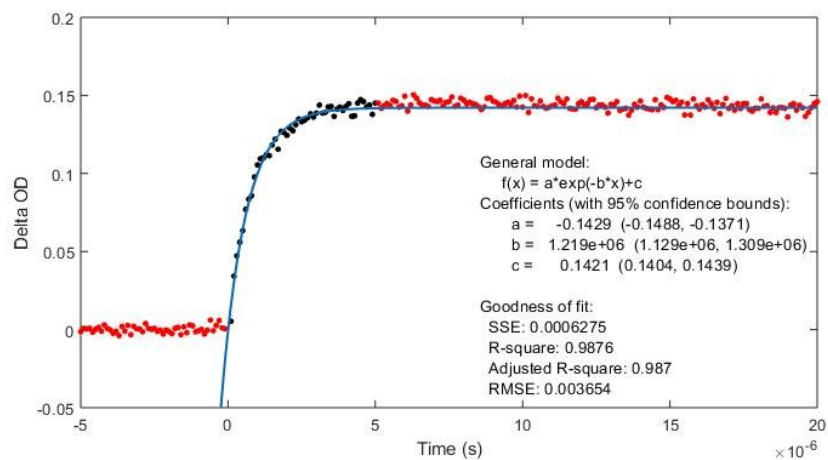
Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0.2 mM NaOH monitored at 620 nm



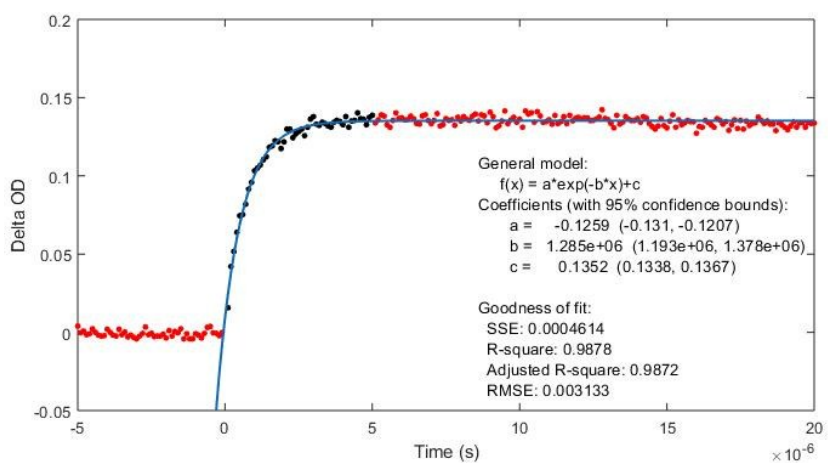
Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0.3 mM NaOH monitored at 620 nm



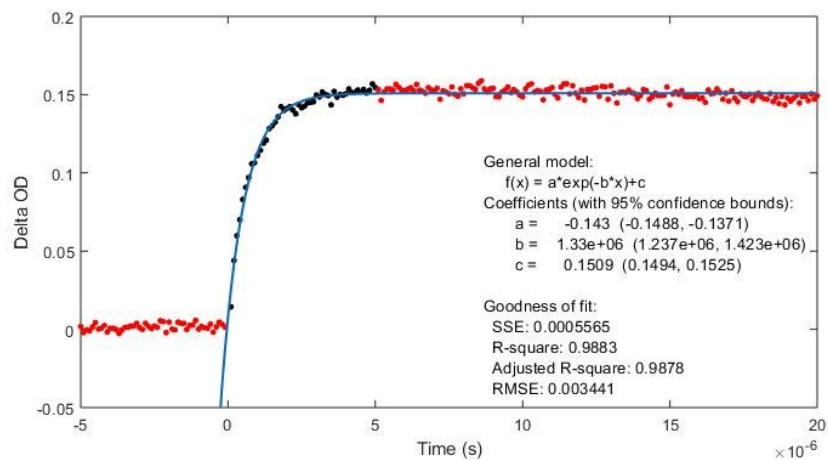
Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0.4 mM NaOH monitored at 620 nm



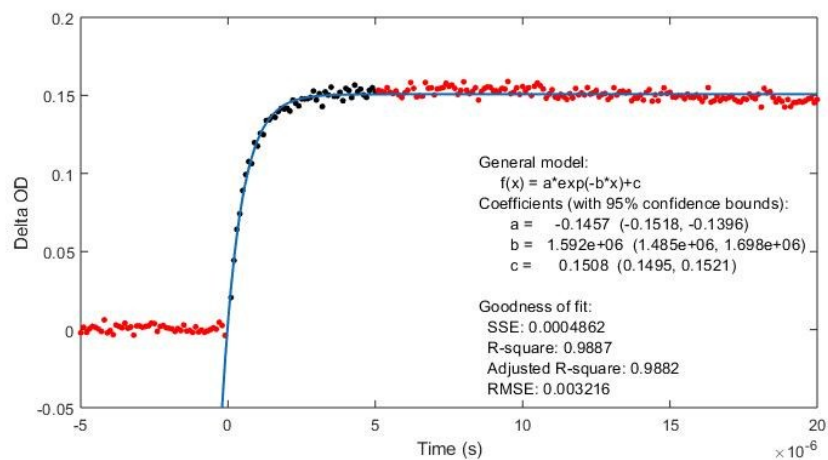
Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0.5 mM NaOH monitored at 620 nm



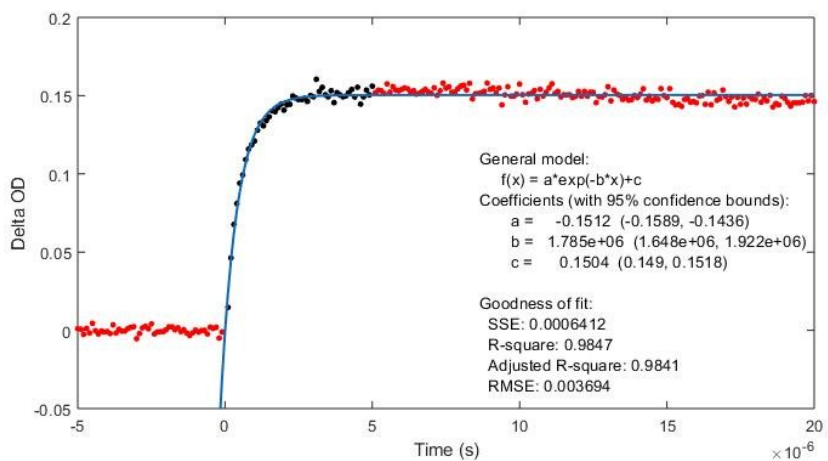
Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0.6 mM NaOH monitored at 620 nm



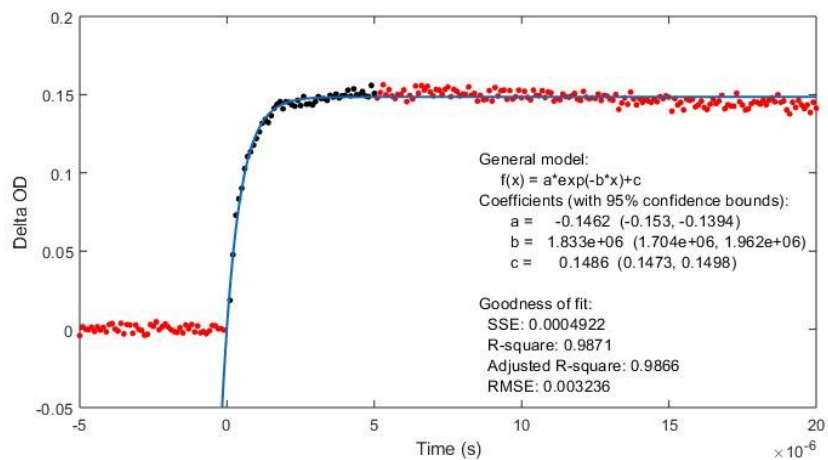
Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0.7 mM NaOH monitored at 620 nm



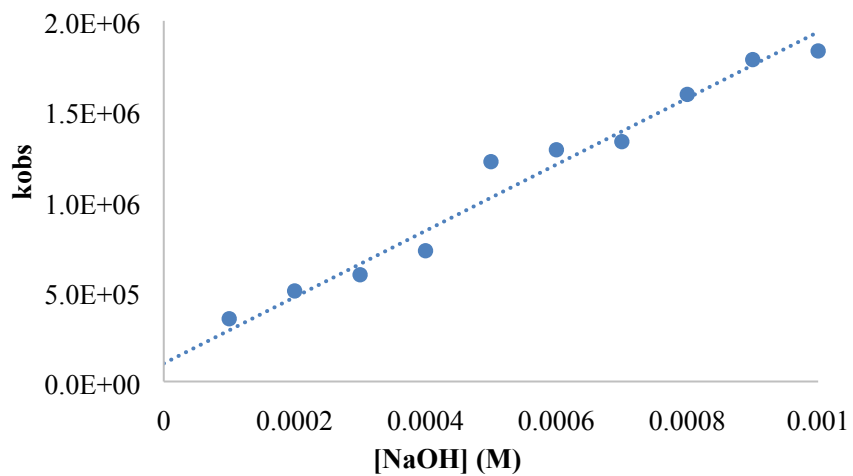
Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0.8 mM NaOH monitored at 620 nm



Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 0.9 mM NaOH monitored at 620 nm

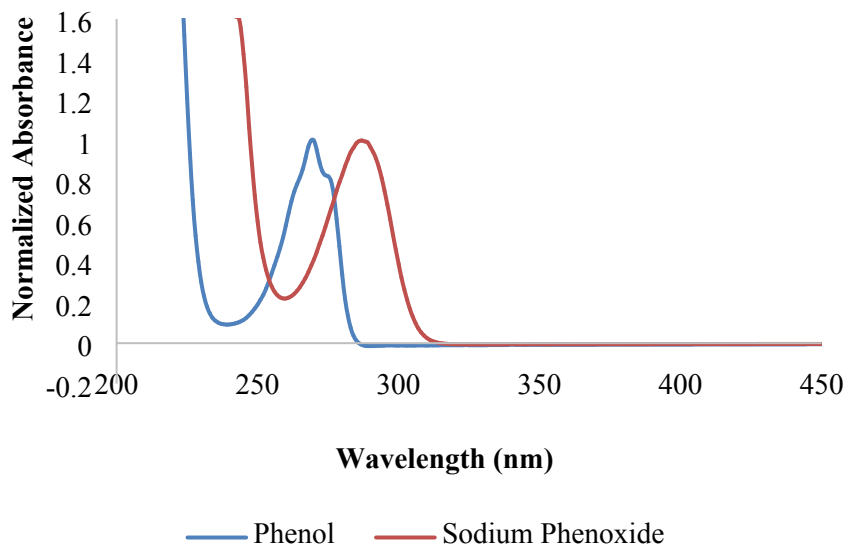


Benzyl ether **5** in 3:1 methanol: 1,4-dioxane with 1.0 mM NaOH monitored at 620 nm



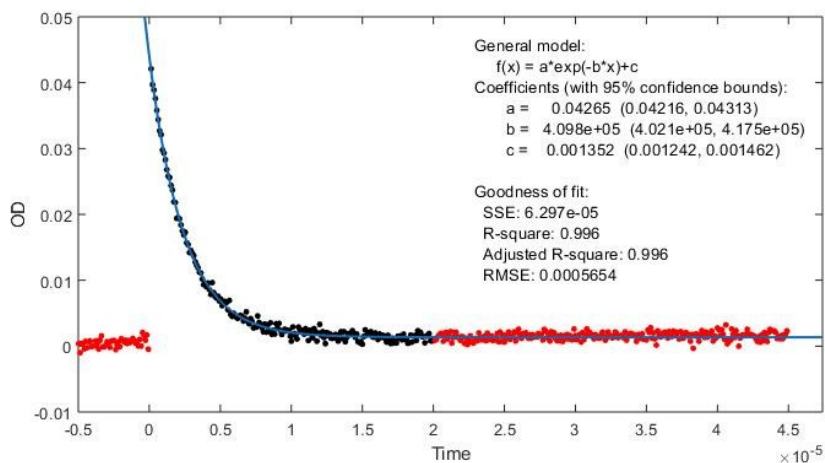
Determination of second-order rate constant for proton transfer

### UV-Vis Spectra of Phenol and Sodium Phenoxide in Water





## Determination of Lifetime of Anion Diradical **9**



Pentyl Ether **7** in basic acetonitrile monitored at 510 nm (anion diradical **9**)

### References

1. D. M. Denning, N. J. Pedowitz, M. D. Thum and D. E. Falvey, *Organic Letters*, 2015, **17**, 5986-5989.
2. J. Gronowska and P. Miecznik, *Pol. J. Chem.*, 1987, **61**, 621-622.
3. J. Gronowska, A. Dzielendziak and J. Heldt, *Acta Phys. Chem.*, 1983, **29**, 145-156.
4. F. F. Blicke and R. J. Warzynski, *Journal of the American Chemical Society*, 1940, **62**, 3191-3194.