

Flash-Photolytic Generation of Dienols and Dienolates from α,β -Unsaturated Esters and Kinetics of their Amine-Catalyzed Ketonization in Nonaqueous Media

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SUPPLEMENTARY INFORMATION

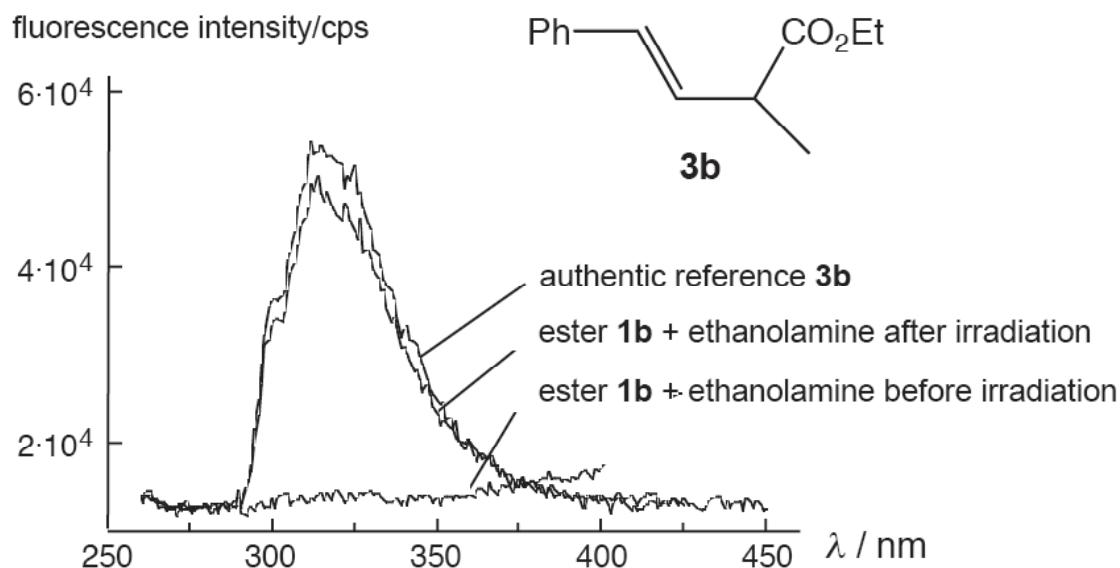


Fig. S1 Comparison of the fluorescence spectra (uncorrected) of the deconjugated ester **3b** and an irradiated sample of the conjugated ester **1b**.

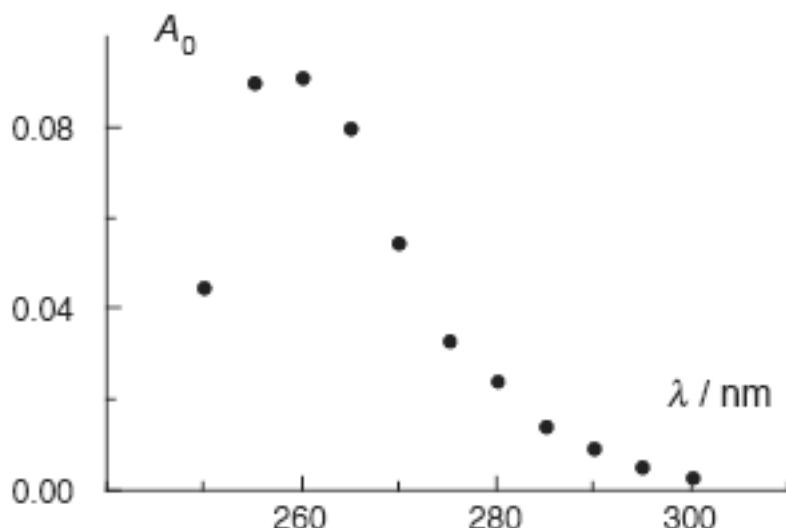


Fig. S2 Transient absorption generated by CFP of **1a** with ethanolamine (1×10^{-3} M) in acetonitrile.

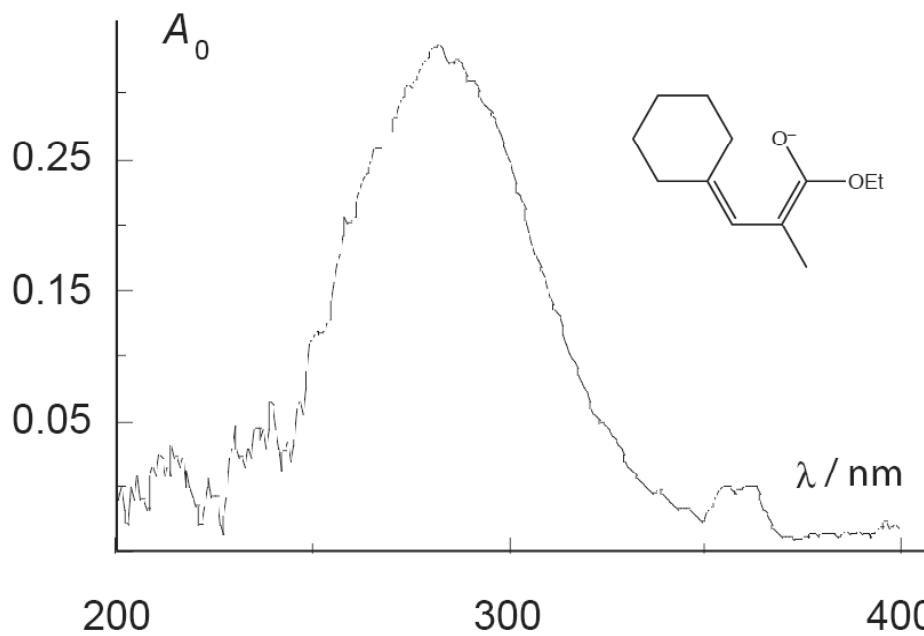


Fig. S3 Transient absorption generated by LFP of ester **1a** in aqueous base (pH 10).

Table S1: Rate data for the decay of **1b** in acetonitrile in the presence of ethanolamine (**I**) at various temperatures.

| [I] ₀ /M | <i>k</i> _{obs} × 10 ⁻⁶ /s ⁻¹ | | | |
|------------------------|---|---|--|--|
| | 8.3 °C | 16.6 °C | 26.8 °C | 38.3 °C |
| 0 | 0.00211 | 0.0023 | 0.0025 | 0.0026 |
| 0.0003 | 0.51 | 0.52 | | |
| 0.0005 | 0.83 | 0.85 | 0.77 | 0.71 |
| 0.0007 | 1.15 | 1.14 | 1.08 | 0.97 |
| 0.001 | 1.55 | 1.58 | 1.48 | 1.33 |
| 0.003 | 4.13 | 4.22 | 3.95 | 3.63 |
| 0.005 | 6.3 | 6.47 | 5.6 | 5.14 |
| 0.007 | 7.87 | 8.72 | 7.51 | 6.67 |
| 0.01 | 9.21 | 10.25 | 10.85 | 9.55 |
| 0.015 | 12.45 | 13.6 | 14.3 | 14.8 |
| 0.02 | 14.95 | 16.65 | 17.5 | 19.1 |
| 0.025 | 15.55 | 19.0 | 21.0 | 22.0 |
| 0.03 | 16.8 | 20.0 | 23.6 | 23.5 |
| 0.035 | 16.8 | | | |
| 0.04 | 16.0 | | | |
| limiting rate constant | <i>k</i> /s ⁻¹ | <i>k</i> /s ⁻¹ | <i>k</i> /s ⁻¹ | <i>k</i> /s ⁻¹ |
| | 2.35 × 10 ⁷ /s ⁻¹ | 3.59 × 10 ⁷ /s ⁻¹ | 6.2 × 10 ⁷ /s ⁻¹ | 8.0 × 10 ⁷ /s ⁻¹ |
| dissociation constant | <i>K</i> _{diss} /M | <i>K</i> _{diss} /M | <i>K</i> _{diss} /M | <i>K</i> _{diss} /M |
| | 0.013 | 0.023 | 0.049 | 0.068 |