

Supporting Information

Kinetic measurements used to determine the electrophilicity of 9(10*H*)-phenanthrenone- and 1-acenaphthenone- derived α,β -unsaturated ketones

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Data storage system:

Folder and file names CGxxx refer to individual experiments and are identical to those in this Supporting Information.

The folders contain

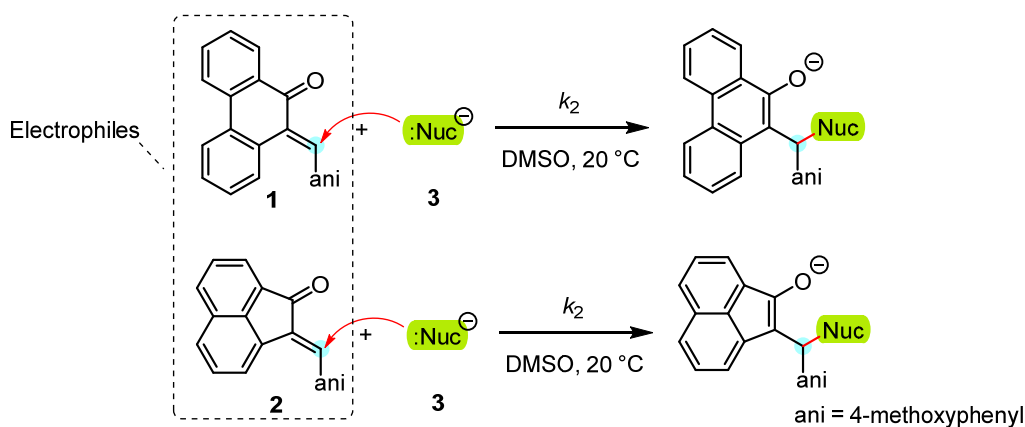
- txt files with absorbance vs. time data [raw data]
- exp files used for the k_{obs} determination [evaluated data]
- pdf files with results of the k_{obs} determination [evaluated data].

Kinetics of the Reactions of Carbanions (Reference Nucleophiles) with **1** and **2**

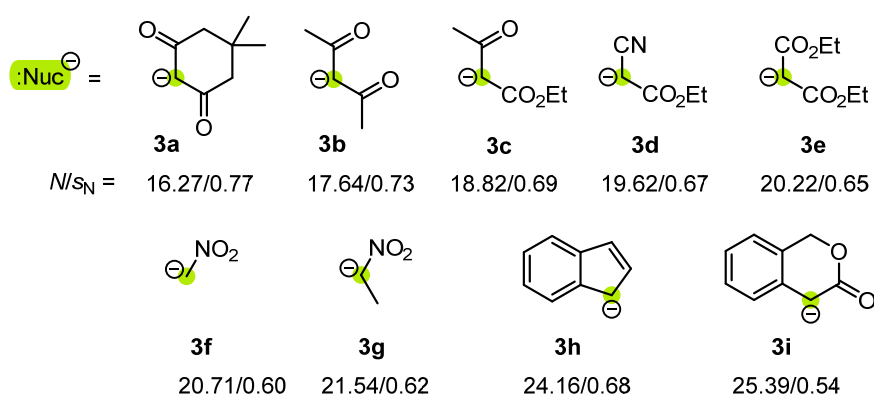
Kinetic measurements were performed by harnessing UV/Vis photometry on AppliedPhotophysics SX.20 stopped-flow instruments. The kinetic measurements were initiated by mixing equal volumes of DMSO solutions of the nucleophiles (**3**) and electrophiles (**1** derived from 9(10*H*)-phenanthrenone or **2** derived from 1-acenaphthenone). The temperature (20.0 ± 0.2 °C) was maintained constant by using circulating bath cryostats.

All solutions were prepared by using dry DMSO (ThermoScientific, DMSO 99.7+%, extra dry, over molecular sieve, AcroSeal) and kept under an atmosphere of dry nitrogen. The kinetic measurements for each electrophile/nucleophile combination were performed with or without added 18-crown-6 ether (18-c-6) for **3a–3h**. The nucleophile **3i** was generated from the conjugate acid 3-isochromanone by mixing it with NaH as a base as described in [1].

Nucleophile concentrations were at least ten times higher than electrophile concentrations to achieve pseudo-first order kinetics. The first-order rate constants k_{obs} (s^{-1}) could be obtained from the decay of the absorbance at or close to the absorption maximum of the reaction partner used in lower concentration by least squares fitting of the equation $A_t = A_0 \exp(-k_{\text{obs}}t) + C$ to the exponential absorption decay curve. Plots of k_{obs} (s^{-1}) versus the nucleophile concentration gave the second-order rate constants k_2 ($\text{M}^{-1} \text{s}^{-1}$) as slopes of the linear correlations.



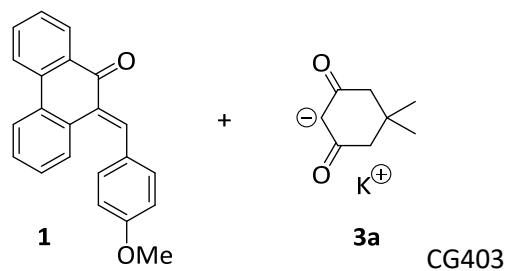
Reference nucleophiles:



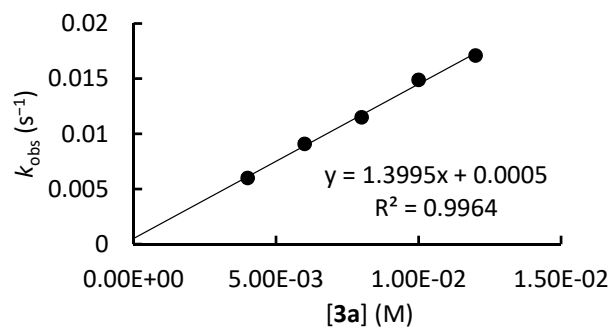
counterion for **3a–3h**: K^+ ; counterion for **3i**: Na^+

[1] M. S. Mousavi, A. Di Mola, G. Pierri, C. Tedesco, M. J. Hensinger, A. Sun, Y. Wang, P. Mayer, A. R. Ofial, A. Massa, *J. Org. Chem.* **2024**, *89*, 6915-6928.

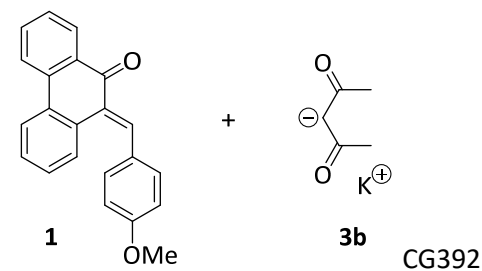
1 + 3a in DMSO (stopped-flow method, absorption decay@415 nm)



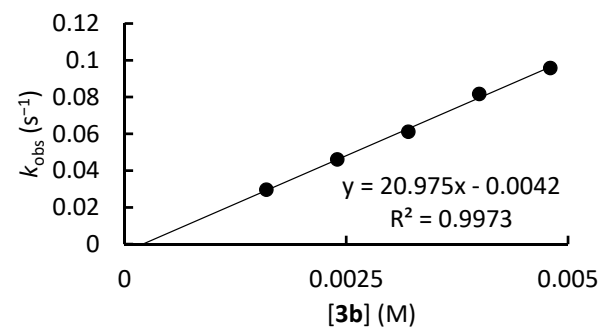
[1] ₀ (M)	[3a] ₀ (M)	[18-c-6] (M)	<i>k</i> _{obs} (s ⁻¹)
4.73 × 10 ⁻⁵	4.00 × 10 ⁻³		6.01 × 10 ⁻³
4.73 × 10 ⁻⁵	6.00 × 10 ⁻³	6.60 × 10 ⁻³	9.09 × 10 ⁻³
4.73 × 10 ⁻⁵	8.00 × 10 ⁻³		1.15 × 10 ⁻²
4.73 × 10 ⁻⁵	1.00 × 10 ⁻²	1.10 × 10 ⁻²	1.49 × 10 ⁻²
4.73 × 10 ⁻⁵	1.20 × 10 ⁻²		1.71 × 10 ⁻²



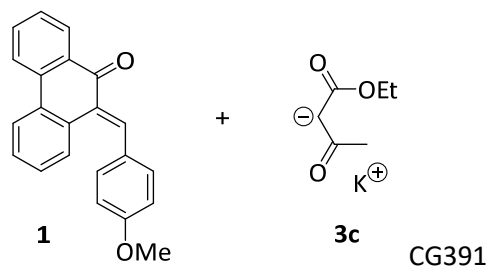
1 + 3b in DMSO (stopped-flow method, absorption decay@415 nm)



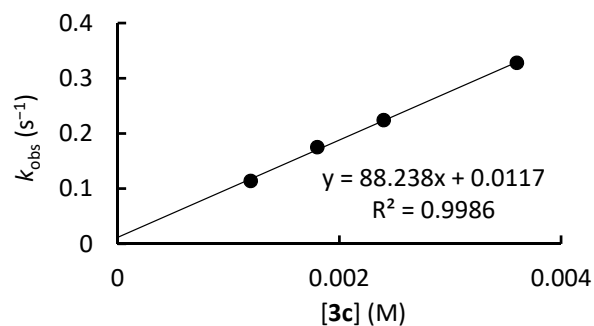
[1] ₀ (M)	[3b] ₀ (M)	[18-c-6] (M)	<i>k</i> _{obs} (s ⁻¹)
4.81 × 10 ⁻⁵	1.60 × 10 ⁻³		2.97 × 10 ⁻²
4.81 × 10 ⁻⁵	2.40 × 10 ⁻³	2.64 × 10 ⁻³	4.61 × 10 ⁻²
4.81 × 10 ⁻⁵	3.20 × 10 ⁻³		6.12 × 10 ⁻²
4.81 × 10 ⁻⁵	4.00 × 10 ⁻³	4.40 × 10 ⁻³	8.17 × 10 ⁻²
4.81 × 10 ⁻⁵	4.80 × 10 ⁻³		9.58 × 10 ⁻²



1 + 3c in DMSO (stopped-flow method, absorption decay@415 nm)

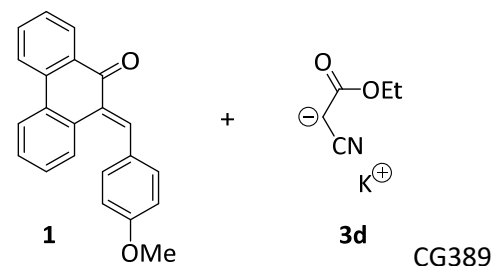


[1] ₀ (M)	[3c] ₀ (M)	[18-c-6] (M)	<i>k</i> _{obs} (s ⁻¹)
5.04 × 10 ⁻⁵	1.20 × 10 ⁻³		1.14 × 10 ⁻¹
5.04 × 10 ⁻⁵	1.80 × 10 ⁻³	1.98 × 10 ⁻³	1.75 × 10 ⁻¹
5.04 × 10 ⁻⁵	2.40 × 10 ⁻³		2.24 × 10 ⁻¹
5.04 × 10 ⁻⁵	3.60 × 10 ⁻³		3.28 × 10 ⁻¹

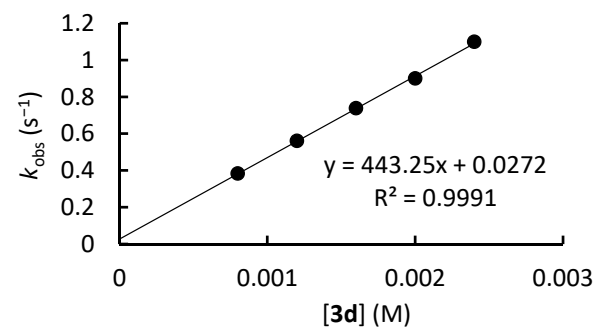


$$k_2 = (8.82 \pm 0.24) \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$$

1 + 3d in DMSO (stopped-flow method, absorption decay@415 nm)

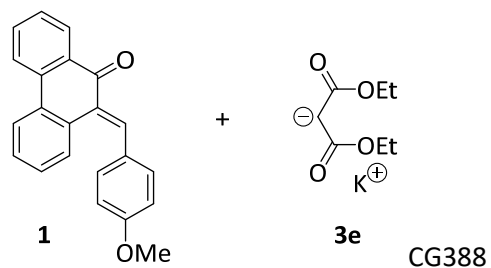


[1] ₀ (M)	[3d] ₀ (M)	[18-c-6] (M)	<i>k</i> _{obs} (s ⁻¹)
3.82 × 10 ⁻⁵	8.00 × 10 ⁻⁴		3.83 × 10 ⁻¹
3.82 × 10 ⁻⁵	1.20 × 10 ⁻³	1.32 × 10 ⁻³	5.61 × 10 ⁻¹
3.82 × 10 ⁻⁵	1.60 × 10 ⁻³		7.38 × 10 ⁻¹
3.82 × 10 ⁻⁵	2.00 × 10 ⁻³	2.20 × 10 ⁻³	9.00 × 10 ⁻¹
3.82 × 10 ⁻⁵	2.40 × 10 ⁻³		1.10

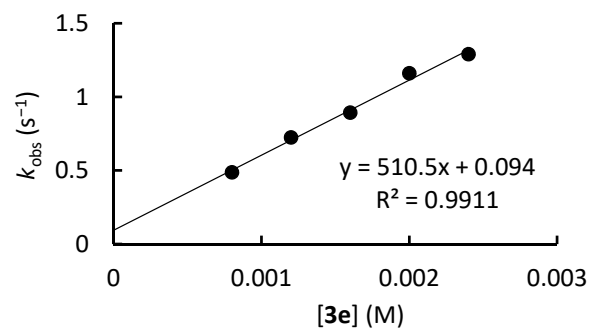


$$k_2 = (4.43 \pm 0.08) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$$

1 + 3e in DMSO (stopped-flow method, absorption decay@415 nm)

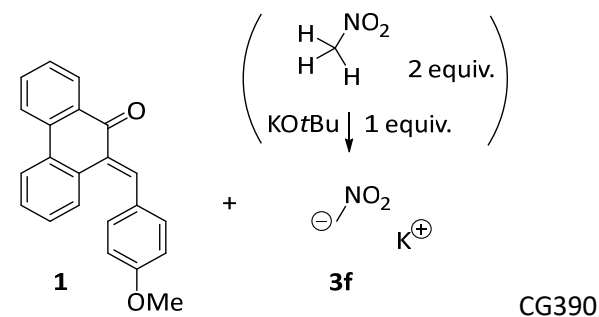


[1] ₀ (M)	[3e] ₀ (M)	[18-c-6] (M)	<i>k</i> _{obs} (s ⁻¹)
4.27 × 10 ⁻⁵	8.00 × 10 ⁻⁴		4.87 × 10 ⁻¹
4.27 × 10 ⁻⁵	1.20 × 10 ⁻³	1.32 × 10 ⁻³	7.24 × 10 ⁻¹
4.27 × 10 ⁻⁵	1.60 × 10 ⁻³		8.93 × 10 ⁻¹
4.27 × 10 ⁻⁵	2.00 × 10 ⁻³	2.20 × 10 ⁻³	1.16
4.27 × 10 ⁻⁵	2.40 × 10 ⁻³		1.29

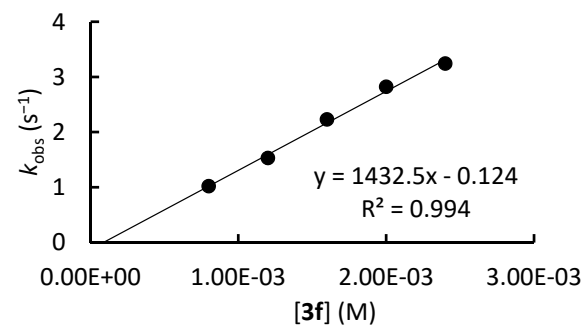


$$k_2 = (5.11 \pm 0.28) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$$

1 + 3f in DMSO (stopped-flow method, absorption decay@415 nm)

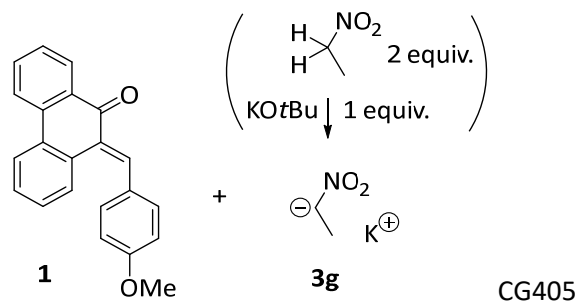


[1] ₀ (M)	[3f] ₀ (M)	[18-c-6] (M)	<i>k</i> _{obs} (s ⁻¹)
3.64 × 10 ⁻⁵	8.00 × 10 ⁻⁴		1.02
3.64 × 10 ⁻⁵	1.20 × 10 ⁻³	1.32 × 10 ⁻³	1.53
3.64 × 10 ⁻⁵	1.60 × 10 ⁻³		2.23
3.64 × 10 ⁻⁵	2.00 × 10 ⁻³	2.20 × 10 ⁻³	2.82
3.64 × 10 ⁻⁵	2.40 × 10 ⁻³		3.24

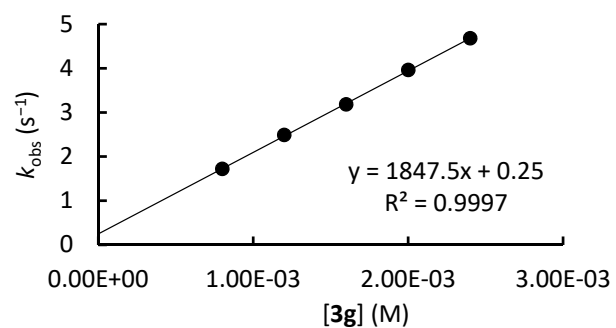


$$k_2 = (1.43 \pm 0.07) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

1 + 3g in DMSO (stopped-flow method, absorption decay@415 nm)

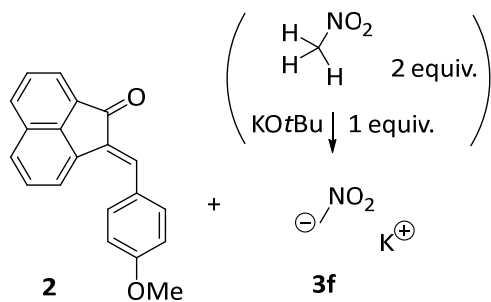


$[1]_0$ (M)	$[3g]_0$ (M)	$[18\text{-c-}6]$ (M)	k_{obs} (s^{-1})
3.59×10^{-5}	8.00×10^{-4}		1.72
3.59×10^{-5}	1.20×10^{-3}	1.32×10^{-3}	2.49
3.59×10^{-5}	1.60×10^{-3}		3.18
3.59×10^{-5}	2.00×10^{-3}	2.20×10^{-3}	3.96
3.59×10^{-5}	2.40×10^{-3}		4.68

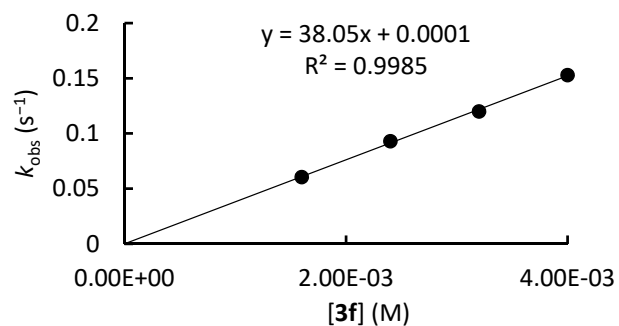


$$k_2 = (1.85 \pm 0.02) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

2 + 3f in DMSO (stopped-flow method, absorption decay@338 nm)

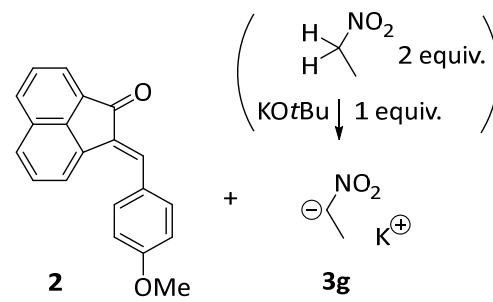


$[2]_0$ (M)	$[3f]_0$ (M)	$[18\text{-c-}6]$ (M)	k_{obs} (s^{-1})
2.66×10^{-5}	1.60×10^{-3}		6.05×10^{-2}
2.79×10^{-5}	2.40×10^{-3}	2.64×10^{-3}	9.31×10^{-2}
2.90×10^{-5}	3.20×10^{-3}		1.20×10^{-1}
2.95×10^{-5}	4.00×10^{-3}	4.40×10^{-3}	1.53×10^{-1}

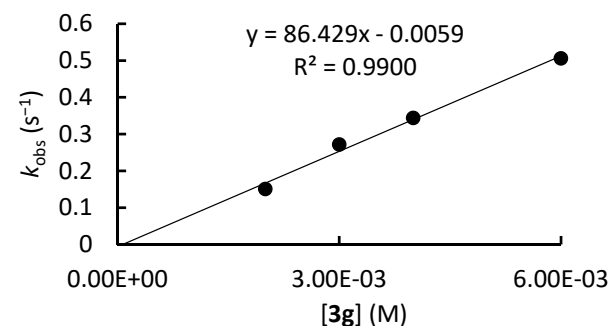


$$k_2 = (3.81 \pm 0.11) \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$$

2 + 3g in DMSO (stopped-flow method, absorption decay@338 nm)

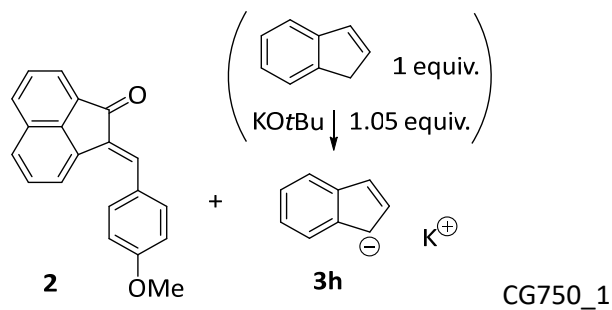


$[2]_0$ (M)	$[3g]_0$ (M)	$[18\text{-c-}6]$ (M)	k_{obs} (s^{-1})
2.01×10^{-5}	2.00×10^{-3}		1.51×10^{-1}
2.13×10^{-5}	3.00×10^{-3}	3.30×10^{-3}	2.72×10^{-1}
2.17×10^{-5}	4.00×10^{-3}		3.44×10^{-1}
2.21×10^{-5}	6.00×10^{-3}		5.06×10^{-1}

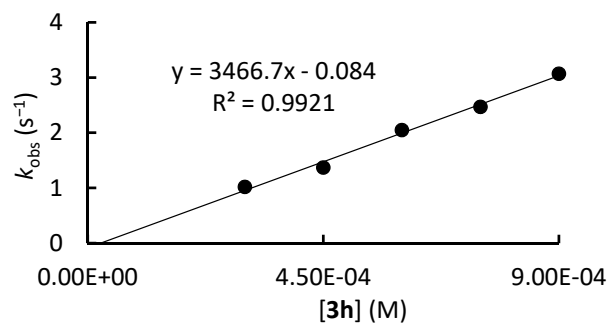


$$k_2 = (8.64 \pm 0.62) \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$$

2 + 3h in DMSO (stopped-flow method, absorption decay@338 nm)

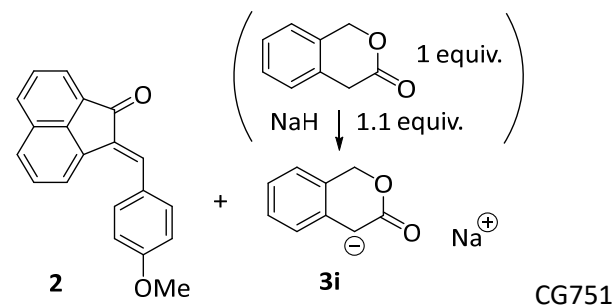


[2] ₀ (M)	[3h] ₀ (M)	[18-c-6] (M)	<i>k</i> _{obs} (s ⁻¹)
3.00 × 10 ⁻⁵	3.00 × 10 ⁻⁴		1.02
3.00 × 10 ⁻⁵	4.50 × 10 ⁻⁴	5.20 × 10 ⁻⁴	1.37
3.00 × 10 ⁻⁵	6.00 × 10 ⁻⁴		2.05
3.00 × 10 ⁻⁵	7.50 × 10 ⁻⁴	8.66 × 10 ⁻⁴	2.47
3.00 × 10 ⁻⁵	9.00 × 10 ⁻⁴		3.07

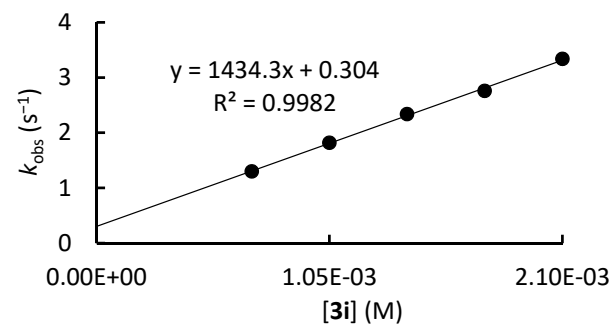


$$k_2 = (3.47 \pm 0.18) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

2 + 3i in DMSO (stopped-flow method, absorption decay@420 nm)



[2] ₀ (M)	[3i] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
7.00 × 10 ⁻⁵	7.00 × 10 ⁻⁴	1.30
7.00 × 10 ⁻⁵	1.05 × 10 ⁻³	1.82
7.00 × 10 ⁻⁵	1.40 × 10 ⁻³	2.34
7.00 × 10 ⁻⁵	1.75 × 10 ⁻³	2.76
7.00 × 10 ⁻⁵	2.10 × 10 ⁻³	3.34



$$k_2 = (1.43 \pm 0.04) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$