

Supporting Information

Kinetic measurements used to determine the nucleophilicity of mesoionic N-heterocyclic olefins in THF

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Data storage system:

Folder and file names AE-xxx 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

The kinetics of reactions of mNHOs **1a** with electrophiles **5**, **8**, **14**, **15** and **16** (structures are shown in Figure S1) in anhydrous THF (dried over Na and degassed with 2-3 freeze pump thawing cycles) were monitored by employing stopped-flow UV/vis photometry on an Applied Photophysics SX.20 instrument. The temperature of drive syringes, the flow circuit, and the observation cell was maintained constant at 20 °C (± 0.2 °C) by use of a circulating bath cryostat. All solutions were prepared in flame-dried Schlenk tubes under an atmosphere of dry argon.

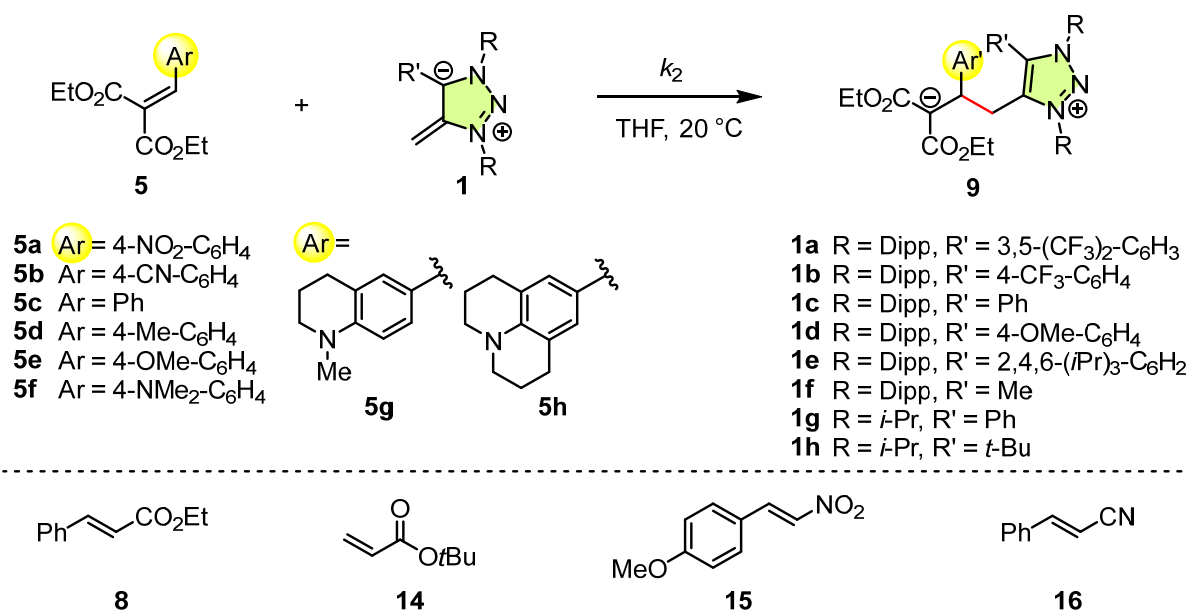


Figure S1. Nucleophiles and electrophiles employed in kinetic measurements.

The time-dependent absorptions were followed at the respective absorption maxima (λ_{max}) of either the mNHO or the electrophile. In all measurements, one component was used in at least 4-fold higher concentration over the other, resulting in pseudo-first order kinetics and monoexponential decay of the concentration of the minor compound. First-order rate constants k_{obs} (s⁻¹) were obtained by least-squares fitting of the exponential function $A_t = A_0 \exp(-k_{\text{obs}}t) + C$ to the experimentally observed decay of the time-dependent absorbances (typically averaged from four to eight runs). For each combination of mNHO and electrophile, k_{obs} was determined at four different concentrations, which allowed us to calculate the second order rate constants k_2 (M⁻¹ s⁻¹) from the slope of the linear correlations of k_{obs} with the concentration of the excess component.

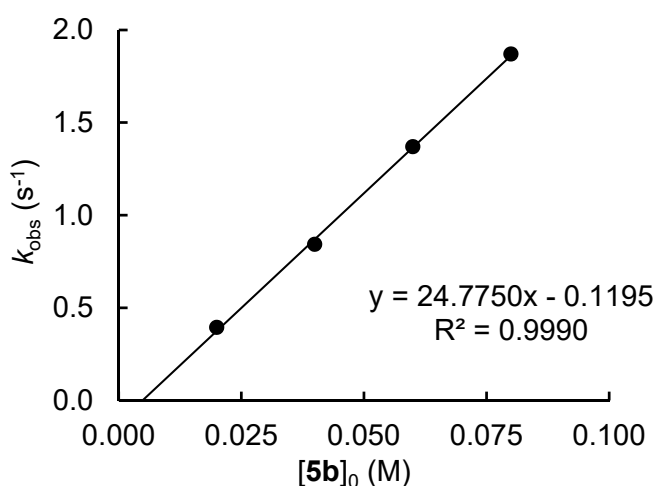
By plotting the decadic logarithm of the second order rate constants k_2 ($\lg k_2$) against the electrophilicity parameters E of the reference electrophiles **5** (and **8**), nucleophilicity parameters N and the nucleophile-specific sensitivity parameters s_N of mNHOs **1** were determined from the linear correlations according to equation (1). For the determination of N and s_N of mNHOs **1** only rate constants with diethyl arylidene malonates **5** were considered, except for **1h** for which data of the reaction with **8** was included in the correlation.

$$\lg k_2(20^\circ\text{C}) = s_N (N + E) \quad (1)$$

1a + diethyl 2-(4-cyanobenzylidene)malonate (**5b**) in THF (20 °C, stopped flow, 590 nm)

AEM-399

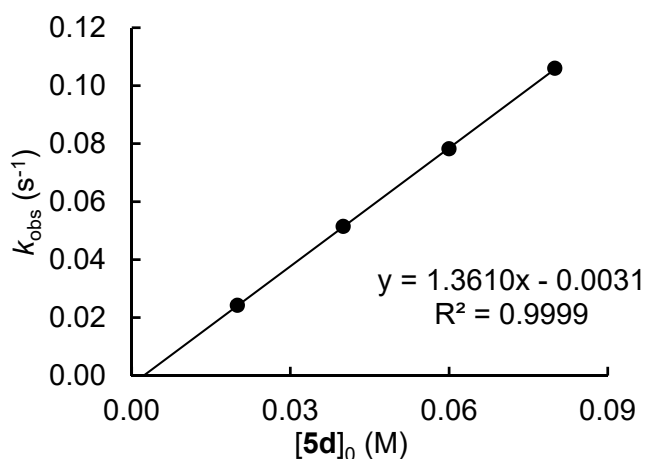
[1a] ₀ (M)	[5b] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.00 × 10 ⁻⁴	2.00 × 10 ⁻²	3.94 × 10 ⁻¹
2.00 × 10 ⁻⁴	4.00 × 10 ⁻²	8.43 × 10 ⁻¹
2.00 × 10 ⁻⁴	6.00 × 10 ⁻²	1.37
2.00 × 10 ⁻⁴	8.00 × 10 ⁻²	1.87
<i>k</i> ₂ = 2.48 × 10 ¹ M ⁻¹ s ⁻¹		



1a + diethyl 2-(4-methylbenzylidene)malonate (**5d**) in THF (20 °C, stopped flow, 590 nm)

AEM-395

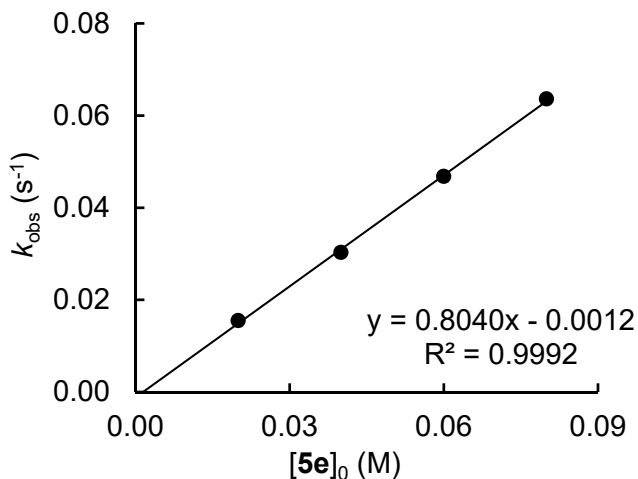
[1a] ₀ (M)	[5d] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.00 × 10 ⁻⁴	2.00 × 10 ⁻²	2.42 × 10 ⁻²
2.00 × 10 ⁻⁴	4.00 × 10 ⁻²	5.14 × 10 ⁻²
2.00 × 10 ⁻⁴	6.00 × 10 ⁻²	7.82 × 10 ⁻²
2.00 × 10 ⁻⁴	8.00 × 10 ⁻²	1.06 × 10 ⁻¹
<i>k</i> ₂ = 1.36 M ⁻¹ s ⁻¹		



1a + diethyl 2-(4-methoxybenzylidene)malonate (**5e**) in THF (20 °C, stopped flow, 590 nm)

AEM-393

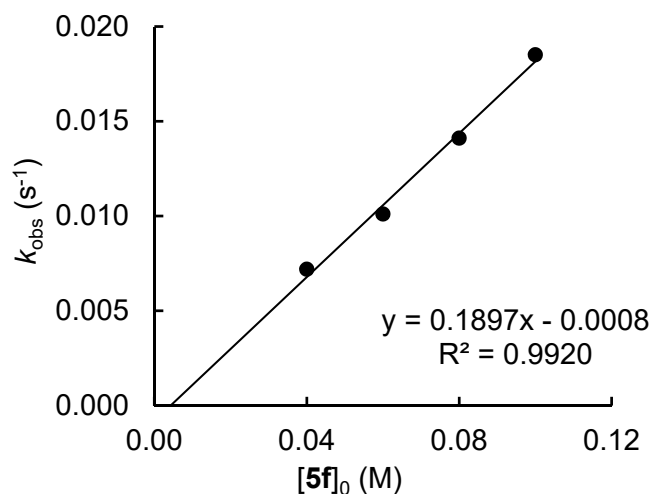
[1a] ₀ (M)	[5e] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.00 × 10 ⁻⁴	2.00 × 10 ⁻²	1.55 × 10 ⁻²
2.00 × 10 ⁻⁴	4.00 × 10 ⁻²	3.03 × 10 ⁻²
2.00 × 10 ⁻⁴	6.00 × 10 ⁻²	4.68 × 10 ⁻²
2.00 × 10 ⁻⁴	8.00 × 10 ⁻²	6.36 × 10 ⁻²
<i>k</i> ₂ = 8.04 × 10 ⁻¹ M ⁻¹ s ⁻¹		



1a + diethyl 2-(4-(dimethylamino)benzylidene)malonate (**5f**) in THF (20 °C, stopped flow, 590 nm)

AEM-391

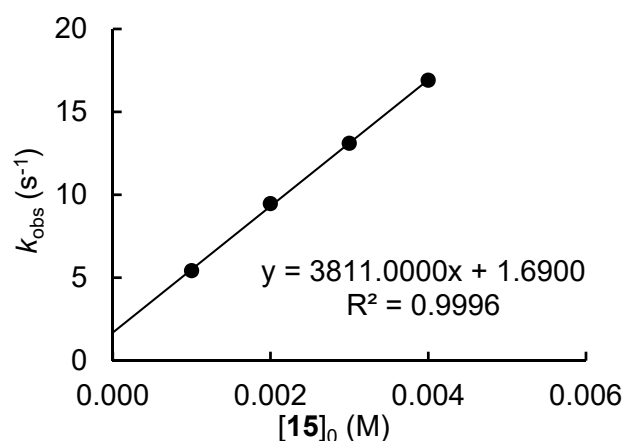
[1a] ₀ (M)	[5f] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.00 × 10 ⁻⁴	4.00 × 10 ⁻²	7.19 × 10 ⁻³
2.00 × 10 ⁻⁴	6.00 × 10 ⁻²	1.01 × 10 ⁻²
2.00 × 10 ⁻⁴	8.00 × 10 ⁻²	1.41 × 10 ⁻²
2.00 × 10 ⁻⁴	1.00 × 10 ⁻¹	1.85 × 10 ⁻²
<i>k</i> ₂ = 1.90 × 10 ⁻¹ M ⁻¹ s ⁻¹		



1a + *p*-anisyl-β-nitrostyrene (**15**) in THF (20 °C, stopped flow, 590 nm)

AEM-441

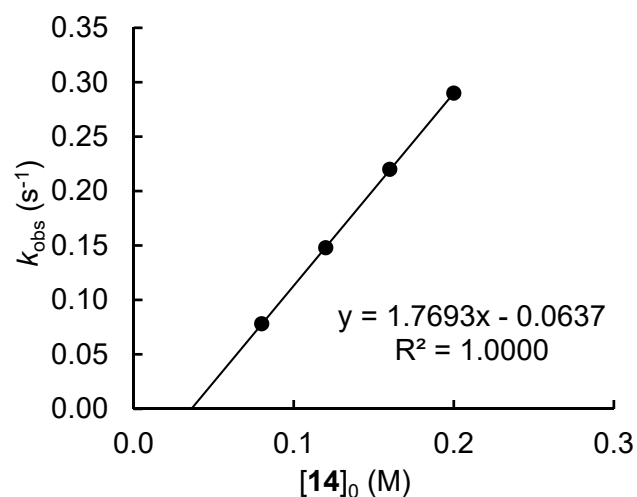
[1a] ₀ (M)	[15] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.00 × 10 ⁻⁴	1.00 × 10 ⁻³	5.41
2.00 × 10 ⁻⁴	2.00 × 10 ⁻³	9.46
2.00 × 10 ⁻⁴	3.00 × 10 ⁻³	1.31 × 10 ¹
2.00 × 10 ⁻⁴	4.00 × 10 ⁻³	1.69 × 10 ¹
<i>k</i> ₂ = 3.81 × 10 ³ M ⁻¹ s ⁻¹		



1a + *tert*-butyl acrylate (**14**) in THF (20 °C, stopped flow, increase at 590 nm)

AEM-404

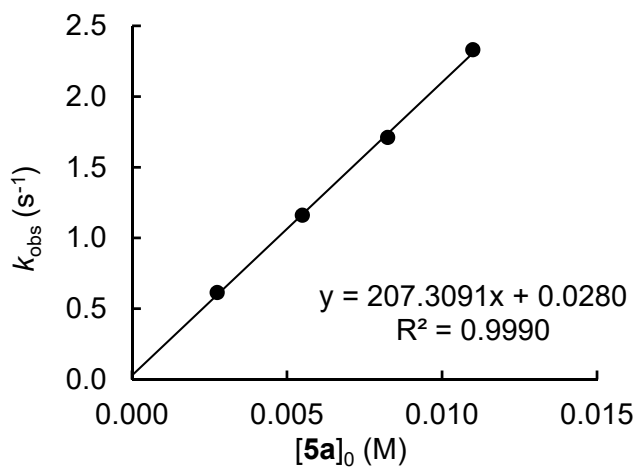
[1a] ₀ (M)	[14] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.00 × 10 ⁻⁴	8.00 × 10 ⁻²	7.81 × 10 ⁻²
2.00 × 10 ⁻⁴	1.20 × 10 ⁻¹	1.48 × 10 ⁻¹
2.00 × 10 ⁻⁴	1.60 × 10 ⁻¹	2.20 × 10 ⁻¹
2.00 × 10 ⁻⁴	2.00 × 10 ⁻¹	2.90 × 10 ⁻¹
<i>k</i> ₂ = 1.77 M ⁻¹ s ⁻¹		



1b + diethyl 2-(4-nitrobenzylidene)malonate (**5a**) in THF (20 °C, stopped flow, 578 nm)

AEM-309

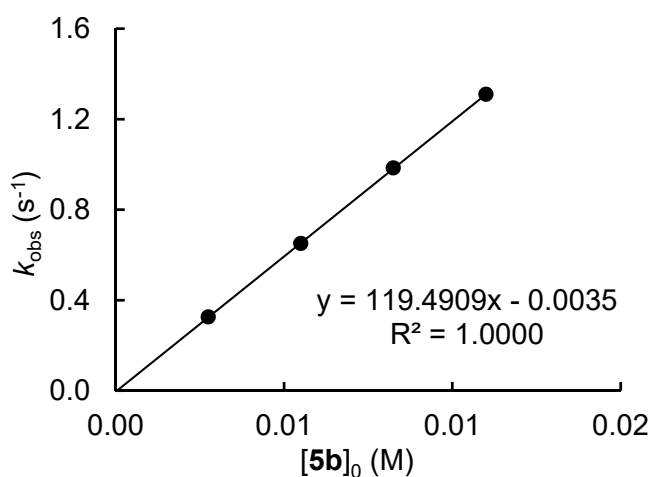
[1b] ₀ (M)	[5a] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.75 × 10 ⁻⁴	2.75 × 10 ⁻³	6.13 × 10 ⁻¹
2.75 × 10 ⁻⁴	5.50 × 10 ⁻³	1.16 × 10 ⁰
2.75 × 10 ⁻⁴	8.25 × 10 ⁻³	1.71 × 10 ⁰
2.75 × 10 ⁻⁴	1.10 × 10 ⁻²	2.33 × 10 ⁰
<i>k</i> ₂ = 2.07 × 10 ² M ⁻¹ s ⁻¹		



1b + diethyl 2-(4-cyanobenzylidene)malonate (**5b**) in THF (20 °C, stopped flow, 578 nm)

AEM-308

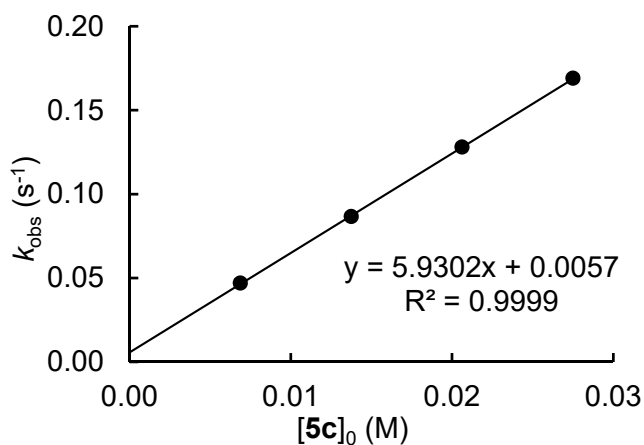
[1b] ₀ (M)	[5b] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.75 × 10 ⁻⁴	2.75 × 10 ⁻³	3.26 × 10 ⁻¹
2.75 × 10 ⁻⁴	5.50 × 10 ⁻³	6.51 × 10 ⁻¹
2.75 × 10 ⁻⁴	8.25 × 10 ⁻³	9.85 × 10 ⁻¹
2.75 × 10 ⁻⁴	1.10 × 10 ⁻²	1.31
<i>k</i> ₂ = 1.19 × 10 ² M ⁻¹ s ⁻¹		



1b + diethyl 2-benzylidenemalonate (**5c**) in THF (20 °C, stopped flow, 578 nm)

AEM-306

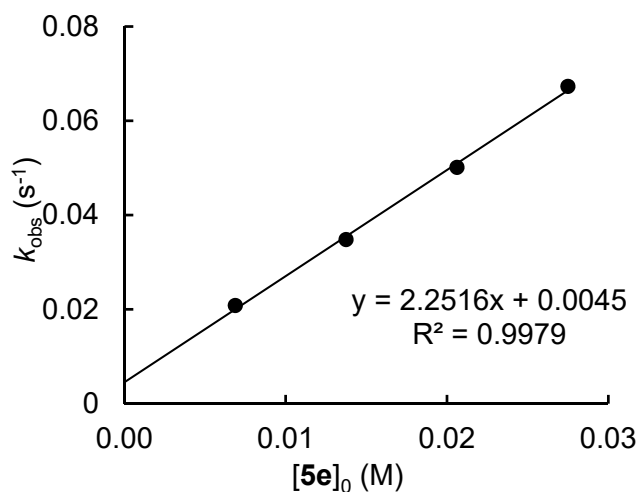
[1c] ₀ (M)	[5c] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.75 × 10 ⁻⁴	6.88 × 10 ⁻³	4.69 × 10 ⁻²
2.75 × 10 ⁻⁴	1.38 × 10 ⁻²	8.66 × 10 ⁻²
2.75 × 10 ⁻⁴	2.06 × 10 ⁻²	1.28 × 10 ⁻¹
2.75 × 10 ⁻⁴	2.75 × 10 ⁻²	1.69 × 10 ⁻¹
<i>k</i> ₂ = 5.93 M ⁻¹ s ⁻¹		



1b + diethyl 2-(4-methoxybenzylidene)malonate (**5e**) in THF (20 °C, stopped flow, 578 nm)

AEM-305

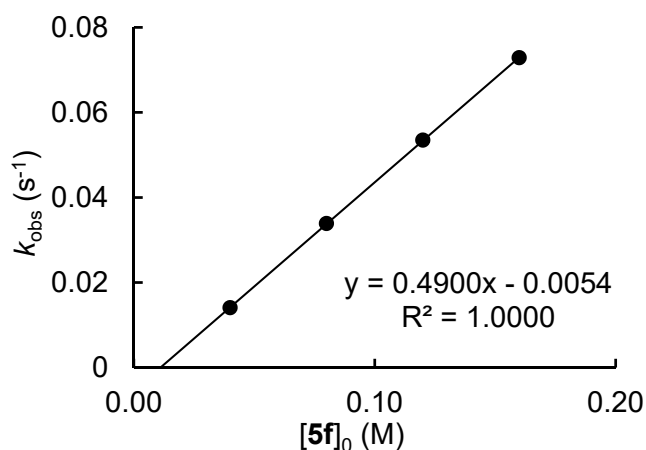
[1b] ₀ (M)	[5e] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.75 × 10 ⁻⁴	6.88 × 10 ⁻³	2.08 × 10 ⁻²
2.75 × 10 ⁻⁴	1.38 × 10 ⁻²	3.48 × 10 ⁻²
2.75 × 10 ⁻⁴	2.06 × 10 ⁻²	5.01 × 10 ⁻²
2.75 × 10 ⁻⁴	2.75 × 10 ⁻²	6.73 × 10 ⁻²
<i>k</i> ₂ = 2.25 M ⁻¹ s ⁻¹		



1b + diethyl 2-(4-(dimethylamino)benzylidene)malonate (**5f**) in THF (20 °C, stopped flow, 578 nm)

AEM-304

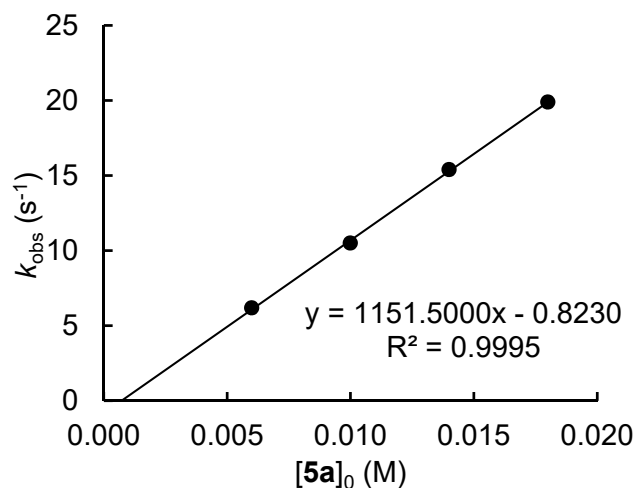
[1b] ₀ (M)	[5f] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.75 × 10 ⁻⁴	4.00 × 10 ⁻²	1.41 × 10 ⁻²
2.75 × 10 ⁻⁴	8.00 × 10 ⁻²	3.39 × 10 ⁻²
2.75 × 10 ⁻⁴	1.20 × 10 ⁻¹	5.35 × 10 ⁻²
2.75 × 10 ⁻⁴	1.60 × 10 ⁻¹	7.29 × 10 ⁻²
<i>k</i> ₂ = 4.90 × 10 ⁻¹ M ⁻¹ s ⁻¹		



1c + diethyl 2-(4-nitrobenzylidene)malonate (**5a**) in THF (20 °C, stopped flow, 535 nm)

AEM-120

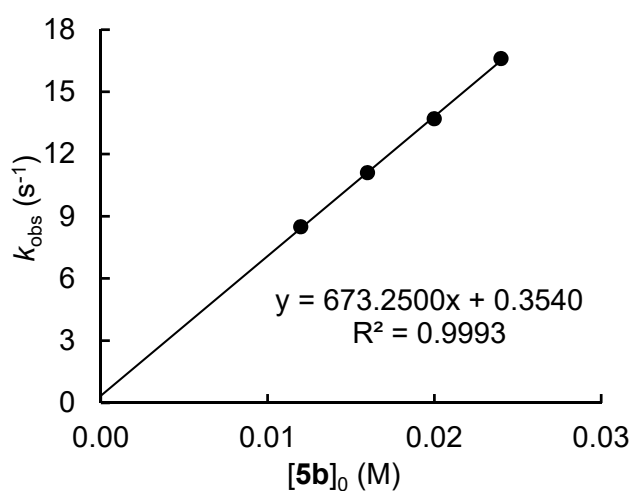
[1c] ₀ (M)	[5a] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
4.00 × 10 ⁻⁴	6.00 × 10 ⁻³	6.18 × 10 ⁰
4.00 × 10 ⁻⁴	1.00 × 10 ⁻²	1.05 × 10 ¹
4.00 × 10 ⁻⁴	1.40 × 10 ⁻²	1.54 × 10 ¹
4.00 × 10 ⁻⁴	1.80 × 10 ⁻²	1.99 × 10 ¹
<i>k</i> ₂ = 1.15 × 10 ³ M ⁻¹ s ⁻¹		



1c + diethyl 2-(4-cyanobenzylidene)malonate (**5b**) in THF (20 °C, stopped flow, 535 nm)

AEM-119

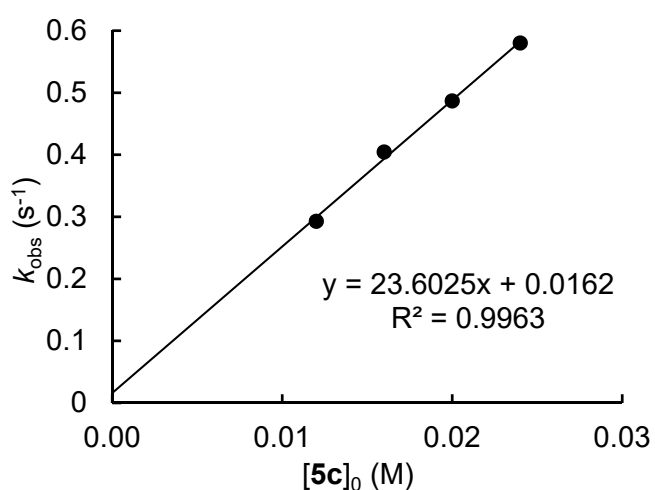
[1a] ₀ (M)	[5b] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
4.00 × 10 ⁻⁴	1.20 × 10 ⁻²	8.49
4.00 × 10 ⁻⁴	1.60 × 10 ⁻²	1.11 × 10 ¹
4.00 × 10 ⁻⁴	2.00 × 10 ⁻²	1.37 × 10 ¹
4.00 × 10 ⁻⁴	2.40 × 10 ⁻²	1.66 × 10 ¹
<i>k</i> ₂ = 6.73 × 10 ² M ⁻¹ s ⁻¹		



1c + diethyl benzylidenemalonate (**5c**) in THF (20 °C, stopped flow, 535 nm)

AEM-118

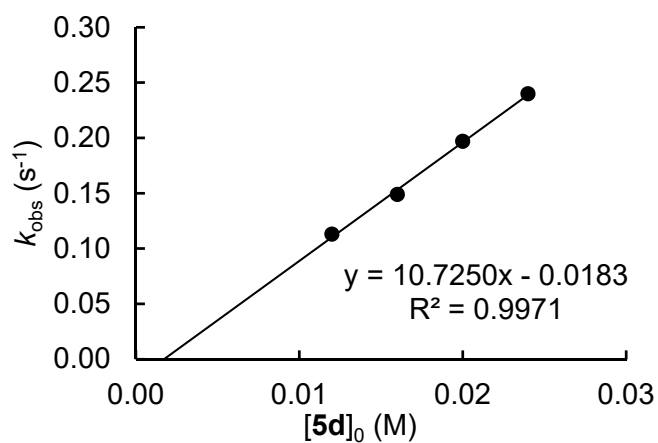
[1c] ₀ (M)	[5c] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
4.00 × 10 ⁻⁴	1.20 × 10 ⁻²	2.93 × 10 ⁻¹
4.00 × 10 ⁻⁴	1.60 × 10 ⁻²	4.05 × 10 ⁻¹
4.00 × 10 ⁻⁴	2.00 × 10 ⁻²	4.87 × 10 ⁻¹
4.00 × 10 ⁻⁴	2.40 × 10 ⁻²	5.80 × 10 ⁻¹
<i>k</i> ₂ = 2.36 × 10 ¹ M ⁻¹ s ⁻¹		



1c + diethyl 2-(4-methylbenzylidene)malonate (**5d**) in THF (20 °C, stopped flow, 535 nm)

AEM-116

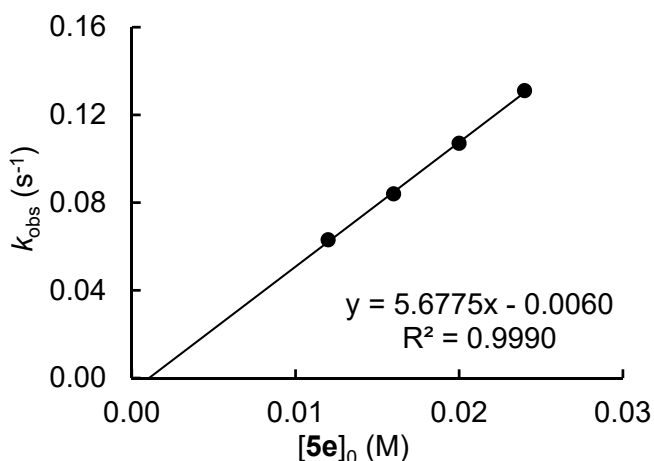
[1c] ₀ (M)	[5d] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
4.00 × 10 ⁻⁴	1.20 × 10 ⁻²	1.13 × 10 ⁻¹
4.00 × 10 ⁻⁴	1.60 × 10 ⁻²	1.49 × 10 ⁻¹
4.00 × 10 ⁻⁴	2.00 × 10 ⁻²	1.97 × 10 ⁻¹
4.00 × 10 ⁻⁴	2.40 × 10 ⁻²	2.40 × 10 ⁻¹
<i>k</i> ₂ = 1.07 × 10 ¹ M ⁻¹ s ⁻¹		



1c + diethyl 2-(4-methoxybenzylidene)malonate (**5e**) in THF (20 °C, stopped flow, 535 nm)

AEM-114

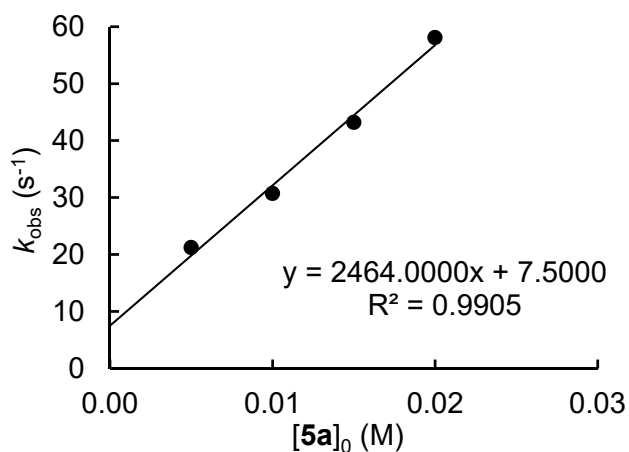
[1a] ₀ (M)	[5e] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
4.00 × 10 ⁻⁴	1.20 × 10 ⁻²	6.30 × 10 ⁻²
4.00 × 10 ⁻⁴	1.60 × 10 ⁻²	8.39 × 10 ⁻²
4.00 × 10 ⁻⁴	2.00 × 10 ⁻²	1.07 × 10 ⁻¹
4.00 × 10 ⁻⁴	2.40 × 10 ⁻²	1.31 × 10 ⁻¹
<i>k</i> ₂ = 5.68 M ⁻¹ s ⁻¹		



1d + diethyl 2-(4-nitrobenzylidene)malonate (**5a**) in THF (20 °C, stopped flow, 519 nm)

AEM-217

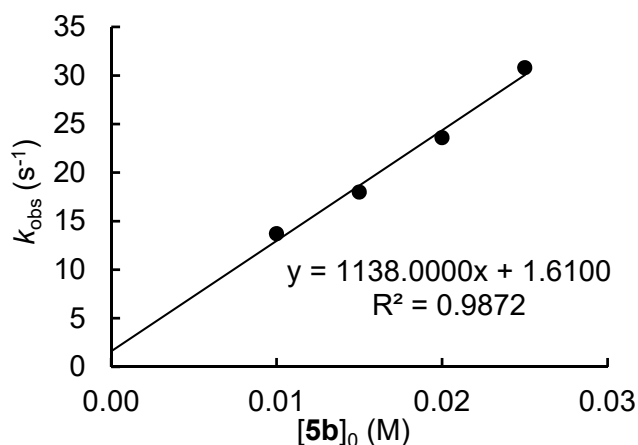
[1d] ₀ (M)	[5a] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
5.00 × 10 ⁻⁴	5.00 × 10 ⁻³	2.12 × 10 ¹
5.00 × 10 ⁻⁴	1.00 × 10 ⁻²	3.07 × 10 ¹
5.00 × 10 ⁻⁴	1.50 × 10 ⁻²	4.32 × 10 ¹
5.00 × 10 ⁻⁴	2.00 × 10 ⁻²	5.81 × 10 ¹
<i>k</i> ₂ = 2.46 × 10 ³ M ⁻¹ s ⁻¹		



1d + diethyl 2-(4-cyanobenzylidene)malonate (**5b**) in THF (20 °C, stopped flow, 519 nm)

AEM-219

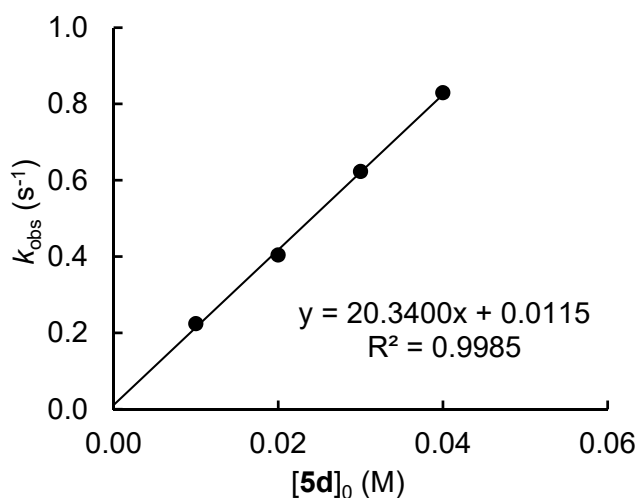
[1d] ₀ (M)	[5b] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
5.00 × 10 ⁻⁴	1.00 × 10 ⁻²	1.37 × 10 ¹
5.00 × 10 ⁻⁴	1.50 × 10 ⁻²	1.80 × 10 ¹
5.00 × 10 ⁻⁴	2.00 × 10 ⁻²	2.36 × 10 ¹
5.00 × 10 ⁻⁴	2.50 × 10 ⁻²	3.08 × 10 ¹
<i>k</i> ₂ = 1.14 × 10 ³ M ⁻¹ s ⁻¹		



1d + diethyl 2-(4-methylbenzylidene)malonate (**5d**) in THF (20 °C, stopped flow, 519 nm)

AEM-215

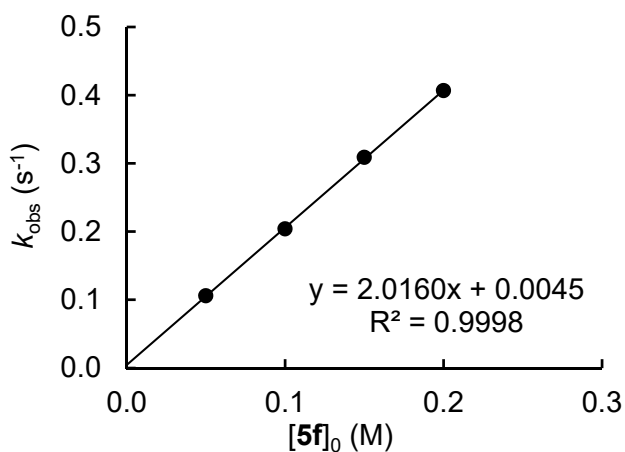
[1d] ₀ (M)	[5d] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
5.00 × 10 ⁻⁴	1.00 × 10 ⁻²	2.24 × 10 ⁻¹
5.00 × 10 ⁻⁴	2.00 × 10 ⁻²	4.04 × 10 ⁻¹
5.00 × 10 ⁻⁴	3.00 × 10 ⁻²	6.23 × 10 ⁻¹
5.00 × 10 ⁻⁴	4.00 × 10 ⁻²	8.29 × 10 ⁻¹
<i>k</i> ₂ = 2.03 × 10 ¹ M ⁻¹ s ⁻¹		



1d + diethyl 2-(4-(dimethylamino)benzylidene)malonate (**5f**) in THF (20 °C, stopped flow, 519 nm)

AEM-216

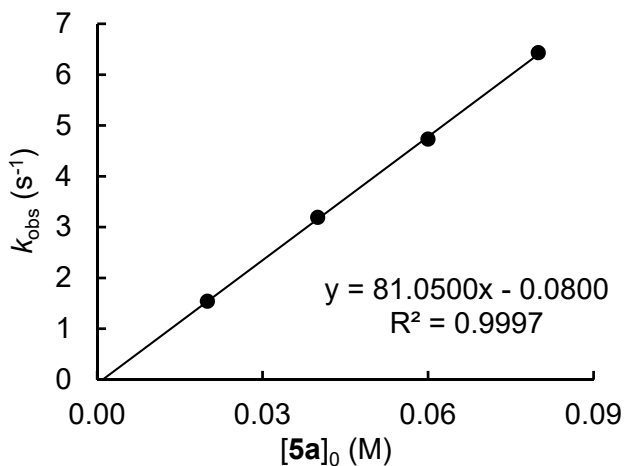
[1d] ₀ (M)	[5f] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
5.00 × 10 ⁻⁴	5.00 × 10 ⁻²	1.06 × 10 ⁻¹
5.00 × 10 ⁻⁴	1.00 × 10 ⁻¹	2.04 × 10 ⁻¹
5.00 × 10 ⁻⁴	1.50 × 10 ⁻¹	3.09 × 10 ⁻¹
5.00 × 10 ⁻⁴	2.00 × 10 ⁻¹	4.07 × 10 ⁻¹
<i>k</i> ₂ = 2.02 M ⁻¹ s ⁻¹		



1e + diethyl 2-(4-nitrobenzylidene)malonate (**5a**) in THF (20 °C, stopped flow, 515 nm)

AEM-402

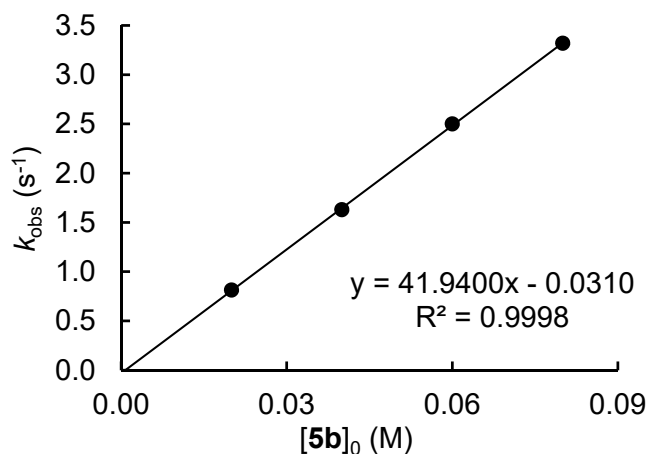
[1e] ₀ (M)	[5a] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
4.00 × 10 ⁻⁴	2.00 × 10 ⁻²	1.54
4.00 × 10 ⁻⁴	4.00 × 10 ⁻²	3.19
4.00 × 10 ⁻⁴	6.00 × 10 ⁻²	4.73
4.00 × 10 ⁻⁴	8.00 × 10 ⁻²	6.43
<i>k</i> ₂ = 8.11 × 10 ¹ M ⁻¹ s ⁻¹		



1e + diethyl 2-(4-cyanobenzylidene)malonate (**5b**) in THF (20 °C, stopped flow, 515 nm)

AEM-400

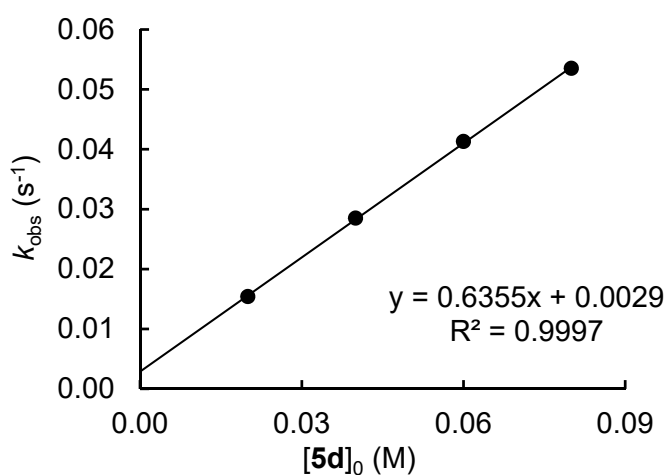
[1e] ₀ (M)	[5b] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
4.00 × 10 ⁻⁴	2.00 × 10 ⁻²	8.14 × 10 ⁻¹
4.00 × 10 ⁻⁴	4.00 × 10 ⁻²	1.63
4.00 × 10 ⁻⁴	6.00 × 10 ⁻²	2.50
4.00 × 10 ⁻⁴	8.00 × 10 ⁻²	3.32
<i>k</i> ₂ = 4.19 × 10 ¹ M ⁻¹ s ⁻¹		



1e + diethyl 2-(4-methylbenzylidene)malonate (**5d**) in THF (20 °C, stopped flow, 515 nm)

AEM-396

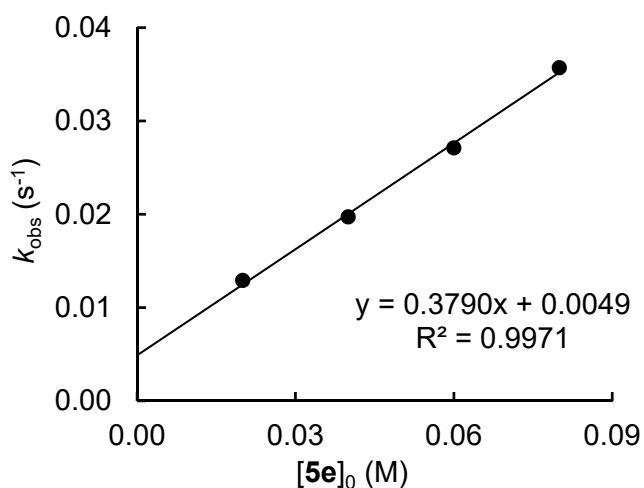
[1e] ₀ (M)	[5d] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
4.00 × 10 ⁻⁴	2.00 × 10 ⁻²	1.55 × 10 ⁻²
4.00 × 10 ⁻⁴	4.00 × 10 ⁻²	2.85 × 10 ⁻²
4.00 × 10 ⁻⁴	6.00 × 10 ⁻²	4.13 × 10 ⁻²
4.00 × 10 ⁻⁴	8.00 × 10 ⁻²	5.35 × 10 ⁻²
<i>k</i> ₂ = 6.36 × 10 ⁻¹ M ⁻¹ s ⁻¹		



1e + diethyl 2-(4-methoxybenzylidene)malonate (**5e**) in THF (20 °C, stopped flow, 590 nm)

AEM-394

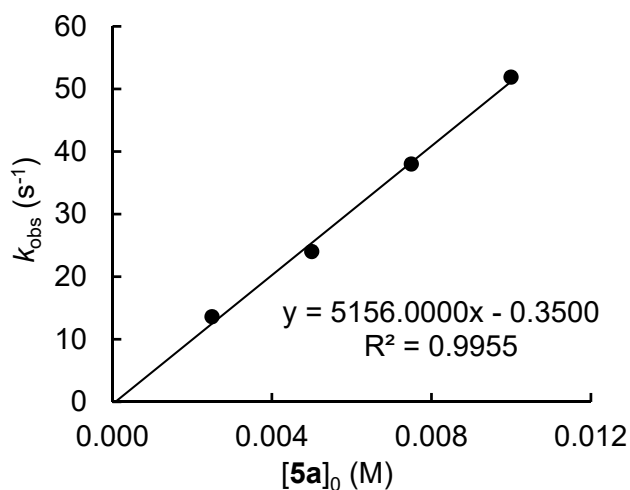
[1e] ₀ (M)	[5e] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.00 × 10 ⁻⁴	2.00 × 10 ⁻²	1.29 × 10 ⁻²
2.00 × 10 ⁻⁴	4.00 × 10 ⁻²	1.97 × 10 ⁻²
2.00 × 10 ⁻⁴	6.00 × 10 ⁻²	2.71 × 10 ⁻²
2.00 × 10 ⁻⁴	8.00 × 10 ⁻²	3.57 × 10 ⁻²
<i>k</i> ₂ = 3.79 × 10 ⁻¹ M ⁻¹ s ⁻¹		



1f + diethyl 2-(4-nitrobenzylidene)malonate (**5a**) in THF (20 °C, stopped flow, 468 nm)

AEM-554

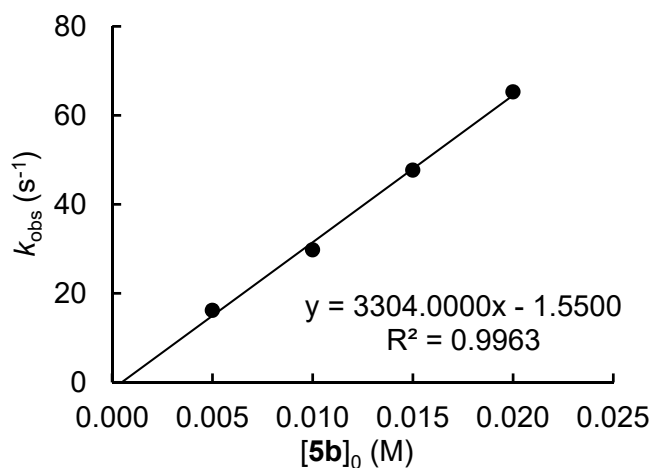
[1f] ₀ (M)	[5a] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
7.18 × 10 ⁻⁴	2.50 × 10 ⁻³	1.36 × 10 ¹
7.18 × 10 ⁻⁴	5.00 × 10 ⁻³	2.40 × 10 ¹
7.18 × 10 ⁻⁴	7.50 × 10 ⁻³	3.80 × 10 ¹
7.18 × 10 ⁻⁴	1.00 × 10 ⁻²	5.19 × 10 ¹
<i>k</i> ₂ = 5.16 × 10 ³ M ⁻¹ s ⁻¹		



1f + diethyl 2-(4-cyanobenzylidene)malonate (**5b**) in THF (20 °C, stopped flow, 468 nm)

AEM-555

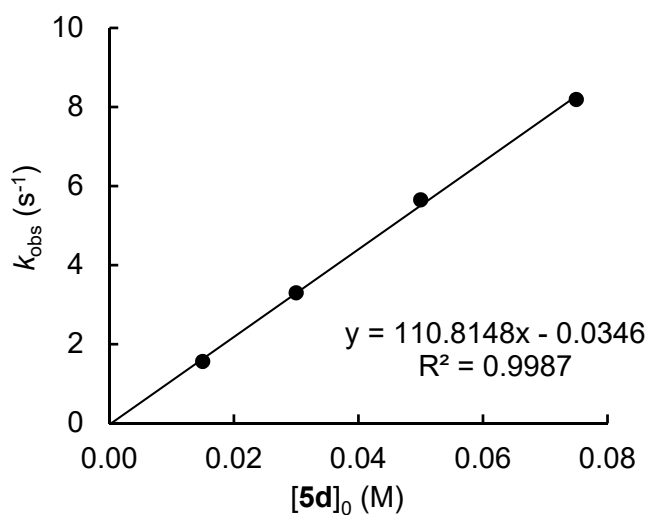
[1f] ₀ (M)	[5b] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
7.18 × 10 ⁻⁴	5.00 × 10 ⁻³	1.62 × 10 ¹
7.18 × 10 ⁻⁴	1.00 × 10 ⁻²	2.98 × 10 ¹
7.18 × 10 ⁻⁴	1.50 × 10 ⁻²	4.77 × 10 ¹
7.18 × 10 ⁻⁴	2.00 × 10 ⁻²	6.53 × 10 ¹
<i>k</i> ₂ = 3.30 × 10 ³ M ⁻¹ s ⁻¹		



1f + diethyl 2-(4-methylbenzylidene)malonate (**5d**) in THF (20 °C, stopped flow, 468 nm)

AEM-556

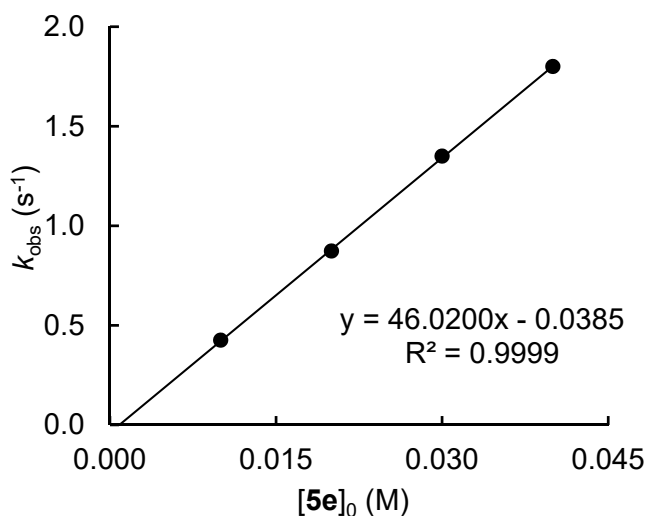
[1f] ₀ (M)	[5d] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
7.18 × 10 ⁻⁴	1.50 × 10 ⁻²	1.56
7.18 × 10 ⁻⁴	3.00 × 10 ⁻²	3.30
7.18 × 10 ⁻⁴	5.00 × 10 ⁻²	5.65
7.18 × 10 ⁻⁴	7.50 × 10 ⁻²	8.19
<i>k</i> ₂ = 1.11 × 10 ² M ⁻¹ s ⁻¹		



1f + diethyl 2-(4-methoxybenzylidene)malonate (**5e**) in THF (20 °C, stopped flow, 468 nm)

AEM-552

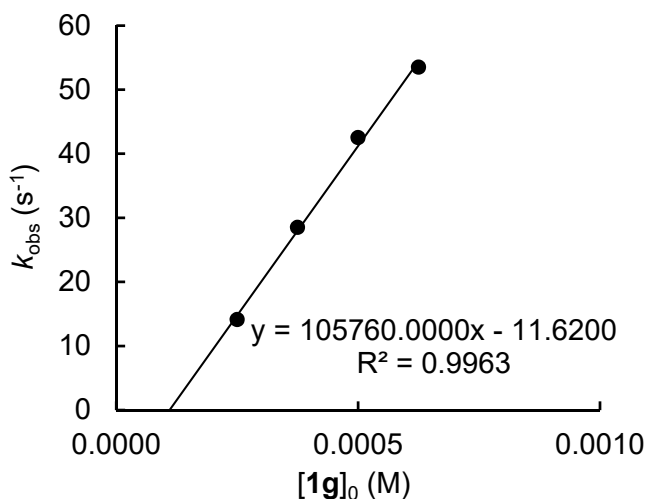
[1f] ₀ (M)	[5e] ₀ (M)	k _{obs} (s ⁻¹)
7.18 × 10 ⁻⁴	1.00 × 10 ⁻²	4.25 × 10 ⁻¹
7.18 × 10 ⁻⁴	2.00 × 10 ⁻²	8.73 × 10 ⁻¹
7.18 × 10 ⁻⁴	3.00 × 10 ⁻²	1.35
7.18 × 10 ⁻⁴	4.00 × 10 ⁻²	1.80
$k_2 = 4.60 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$		



1g + diethyl 2-(4-methylbenzylidene)malonate (**5d**) in THF (20 °C, stopped flow, 295 nm)

AEM-124

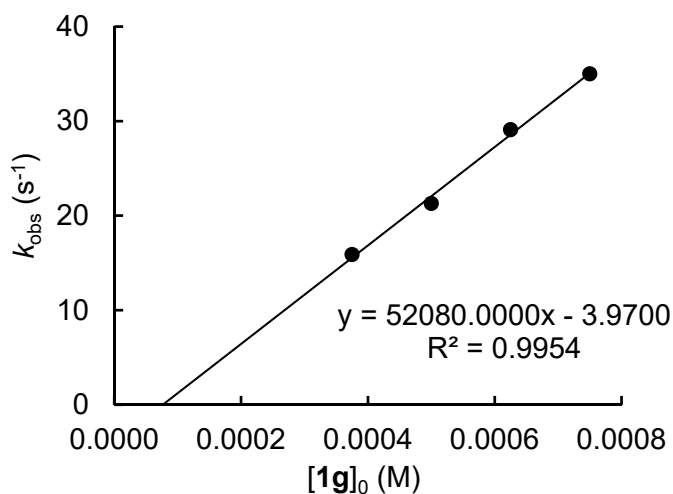
[5d] ₀ (M)	[1g] ₀ (M)	k _{obs} (s ⁻¹)
2.50 × 10 ⁻⁵	2.50 × 10 ⁻⁴	1.41 × 10 ¹
2.50 × 10 ⁻⁵	3.75 × 10 ⁻⁴	2.85 × 10 ¹
2.50 × 10 ⁻⁵	5.00 × 10 ⁻⁴	4.25 × 10 ¹
2.50 × 10 ⁻⁵	6.25 × 10 ⁻⁴	5.35 × 10 ¹
$k_2 = 1.06 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$		



1g + diethyl 2-(4-methoxybenzylidene)malonate (**5e**) in THF (20 °C, stopped flow, 310 nm)

AEM-123

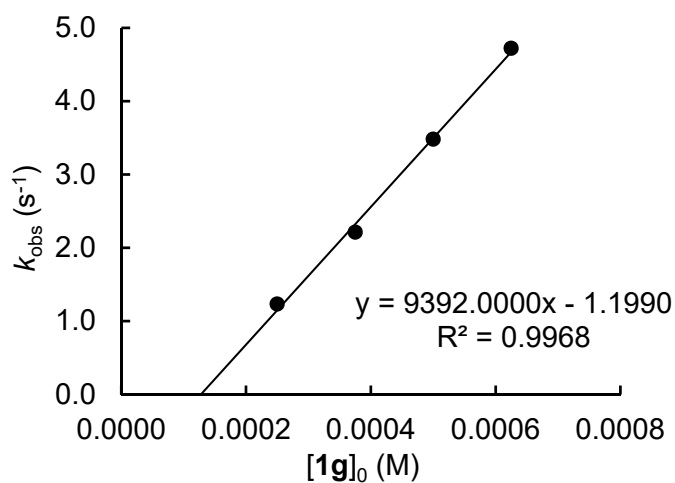
[5e] ₀ (M)	[1g] ₀ (M)	k _{obs} (s ⁻¹)
2.50 × 10 ⁻⁵	3.75 × 10 ⁻⁴	1.59 × 10 ¹
2.50 × 10 ⁻⁵	5.00 × 10 ⁻⁴	2.13 × 10 ¹
2.50 × 10 ⁻⁵	6.25 × 10 ⁻⁴	2.91 × 10 ¹
2.50 × 10 ⁻⁵	7.50 × 10 ⁻⁴	3.50 × 10 ¹
$k_2 = 5.21 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$		



1g + diethyl 2-(4-(dimethylamino)benzylidene)malonate (**5f**) in THF (20 °C, stopped flow, 368 nm)

AEM-125

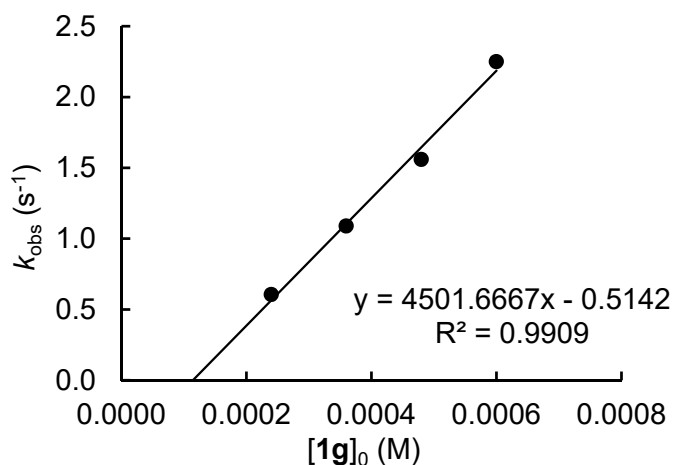
[5f] ₀ (M)	[1g] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.50 × 10 ⁻⁵	2.50 × 10 ⁻⁴	1.23
2.50 × 10 ⁻⁵	3.80 × 10 ⁻⁴	2.21
2.50 × 10 ⁻⁵	5.00 × 10 ⁻⁴	3.48
2.50 × 10 ⁻⁵	6.30 × 10 ⁻⁴	4.72
<i>k</i> ₂ = 9.39 × 10 ³ M ⁻¹ s ⁻¹		



1g + diethyl 2-((1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)methylene)malonate (**5g**) in THF (20 °C, stopped flow, 380 nm)

AEM-126

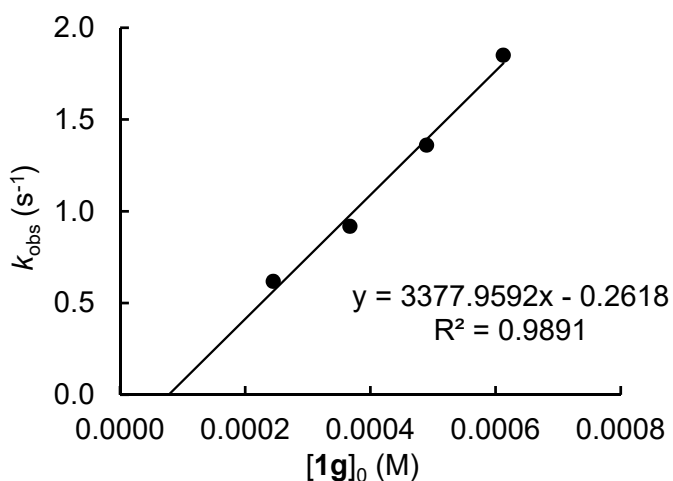
[5g] ₀ (M)	[1g] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.40 × 10 ⁻⁵	2.40 × 10 ⁻⁴	6.06 × 10 ⁻¹
2.40 × 10 ⁻⁵	3.60 × 10 ⁻⁴	1.09
2.40 × 10 ⁻⁵	4.80 × 10 ⁻⁴	1.56
2.40 × 10 ⁻⁵	6.00 × 10 ⁻⁴	2.25
<i>k</i> ₂ = 4.50 × 10 ³ M ⁻¹ s ⁻¹		



1g + diethyl 2-((julolidin-9-yl)methylene)malonate (**5h**) in THF (20 °C, stopped flow, 390 nm)

AEM-127

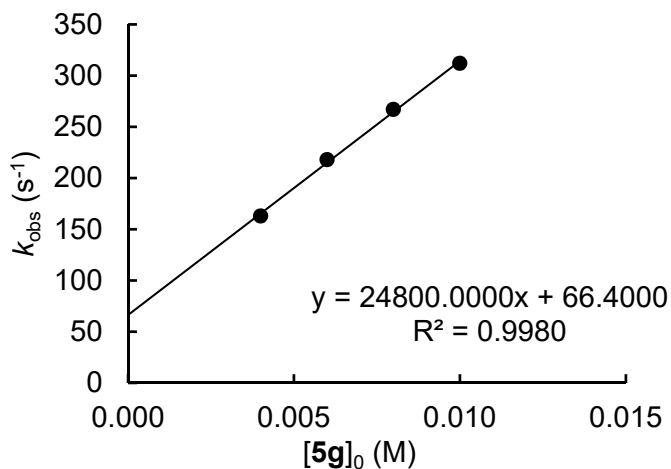
[5h] ₀ (M)	[1g] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
2.45 × 10 ⁻⁵	2.45 × 10 ⁻⁴	6.18 × 10 ⁻¹
2.45 × 10 ⁻⁵	3.68 × 10 ⁻⁴	9.18 × 10 ⁻¹
2.45 × 10 ⁻⁵	4.90 × 10 ⁻⁴	1.36
2.45 × 10 ⁻⁵	6.13 × 10 ⁻⁴	1.85
<i>k</i> ₂ = 3.38 × 10 ³ M ⁻¹ s ⁻¹		



1h + diethyl 2-((1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)methylene)malonate (**5g**) in THF (20 °C, stopped flow, 500 nm)

AEM-419

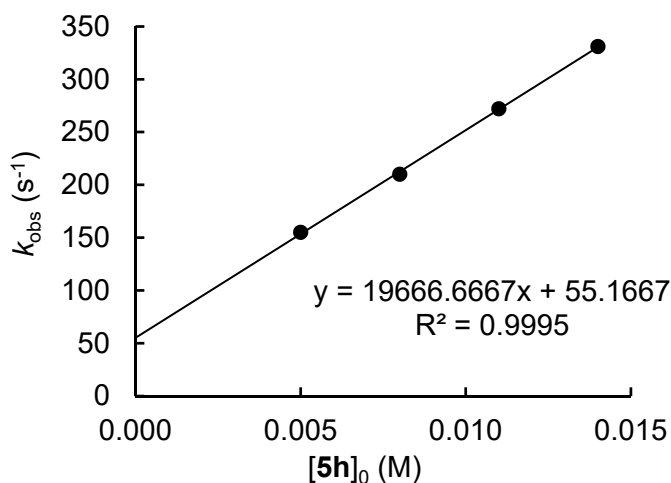
[1h] ₀ (M)	[5g] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
8.00 × 10 ⁻⁴	4.00 × 10 ⁻³	1.63 × 10 ²
8.00 × 10 ⁻⁴	6.00 × 10 ⁻³	2.18 × 10 ²
8.00 × 10 ⁻⁴	8.00 × 10 ⁻³	2.67 × 10 ²
8.00 × 10 ⁻⁴	1.00 × 10 ⁻²	3.12 × 10 ²
<i>k</i> ₂ = 2.48 × 10 ⁴ M ⁻¹ s ⁻¹		



1h + diethyl 2-((julolidin-9-yl)methylene)malonate (**5h**) in THF (20 °C, stopped flow, 500 nm)

AEM-418

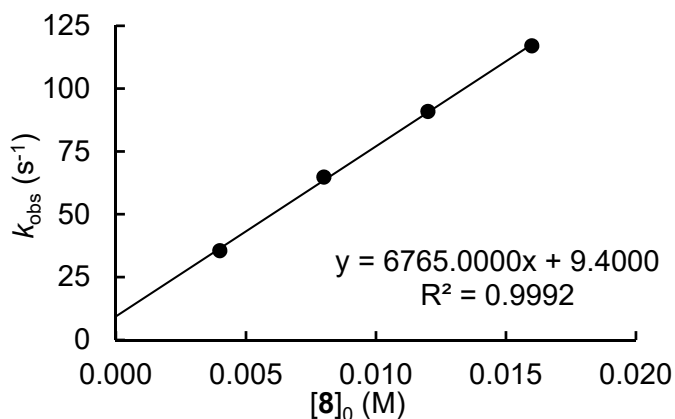
[1h] ₀ (M)	[5h] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
1.00 × 10 ⁻³	5.00 × 10 ⁻³	1.55 × 10 ²
1.00 × 10 ⁻³	8.00 × 10 ⁻³	2.10 × 10 ²
1.00 × 10 ⁻³	1.10 × 10 ⁻²	2.72 × 10 ²
1.00 × 10 ⁻³	1.40 × 10 ⁻²	3.31 × 10 ²
<i>k</i> ₂ = 1.97 × 10 ⁴ M ⁻¹ s ⁻¹		



1h + ethyl cinnamate (**8**) in THF (20 °C, stopped flow, 464 nm)

AEM-435

[1h] ₀ (M)	[8] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
8.00 × 10 ⁻⁴	4.00 × 10 ⁻³	3.55 × 10 ¹
8.00 × 10 ⁻⁴	8.00 × 10 ⁻³	6.48 × 10 ¹
8.00 × 10 ⁻⁴	1.20 × 10 ⁻²	9.09 × 10 ¹
8.00 × 10 ⁻⁴	1.60 × 10 ⁻²	1.17 × 10 ²
<i>k</i> ₂ = 6.77 × 10 ³ M ⁻¹ s ⁻¹		



1h + cinnamonnitrile (**16**) in THF (20 °C, stopped flow, 464 nm)

AEM-436

$[\mathbf{1h}]_0$ (M)	$[\mathbf{16}]_0$ (M)	k_{obs} (s^{-1})
8.00×10^{-4}	4.00×10^{-3}	5.86×10^1
8.00×10^{-4}	8.00×10^{-3}	8.95×10^1
8.00×10^{-4}	1.20×10^{-2}	1.32×10^2
8.00×10^{-4}	1.60×10^{-2}	1.62×10^2
$k_2 = 8.82 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		

