
Supporting Information

**Kinetic measurements used to determine the nucleophilicity
of mesoionic pyridine-derived olefins in THF**

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Data storage system:

Folder and file names AEM-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 **1a** with different electrophiles (structures are shown in Figure S1) in anhydrous THF were monitored by stopped-flow UV/vis spectrophotometry on an Applied Photophysics SX.20 instrument. In all measurements, the decrease of the absorption of **1a** at 625 nm was followed. The temperature of the 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.

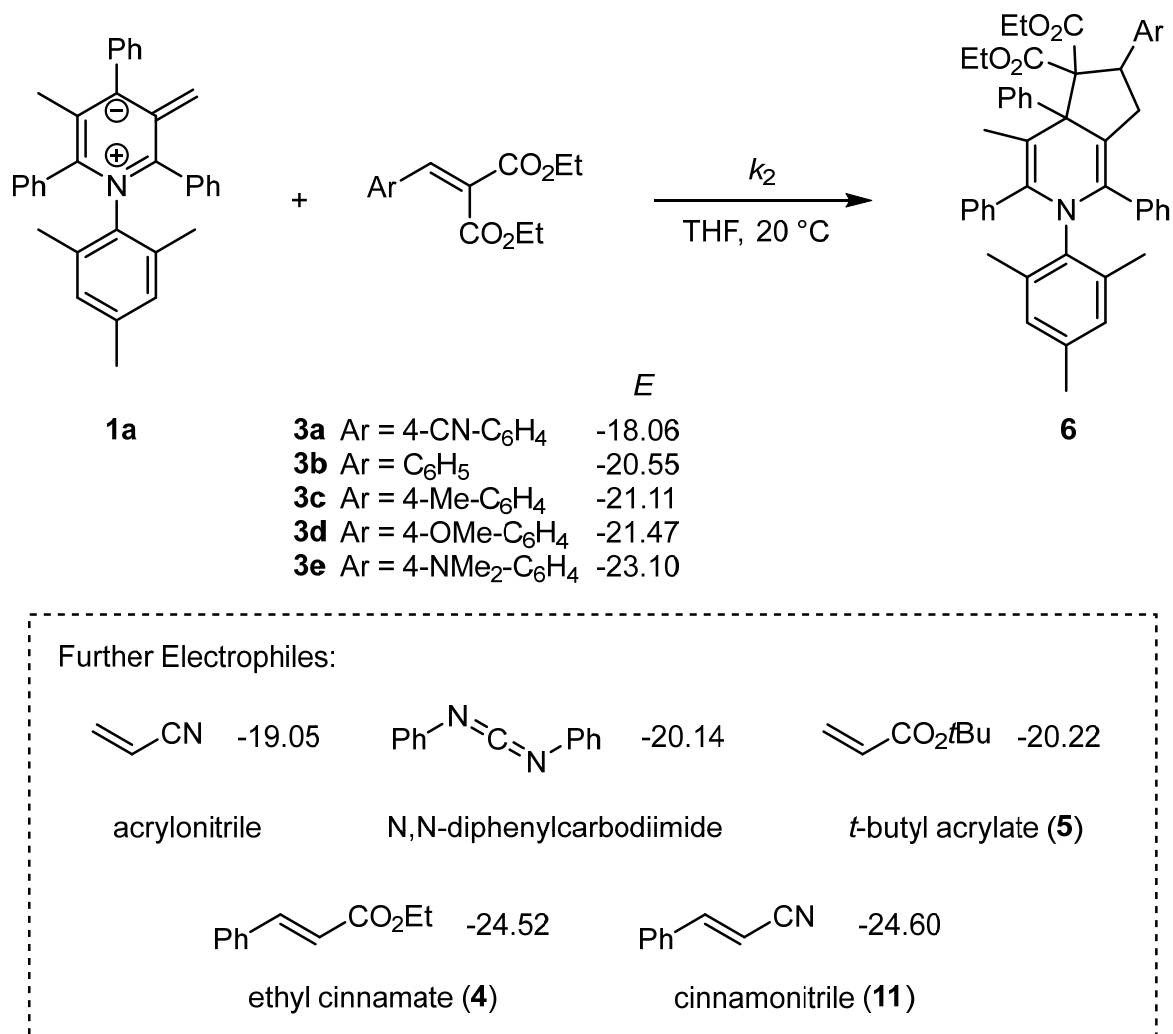
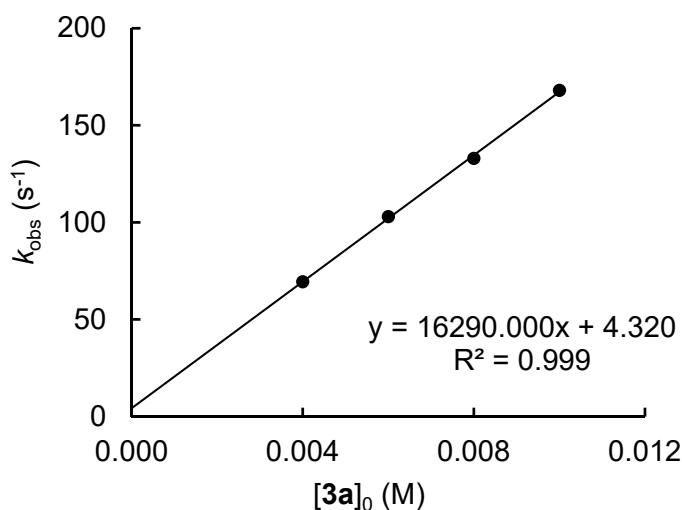


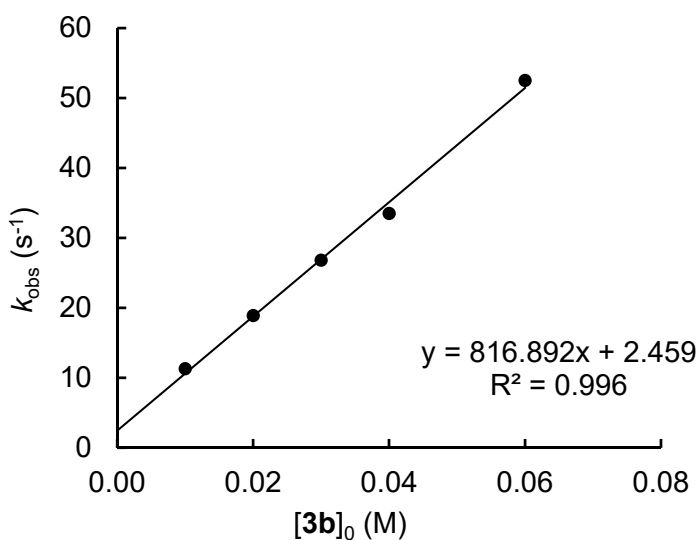
Figure S1. Electrophiles employed in the kinetic studies.

1a + diethyl 2-(4-cyanobenzylidene)malonate (3a)*AEM-643*

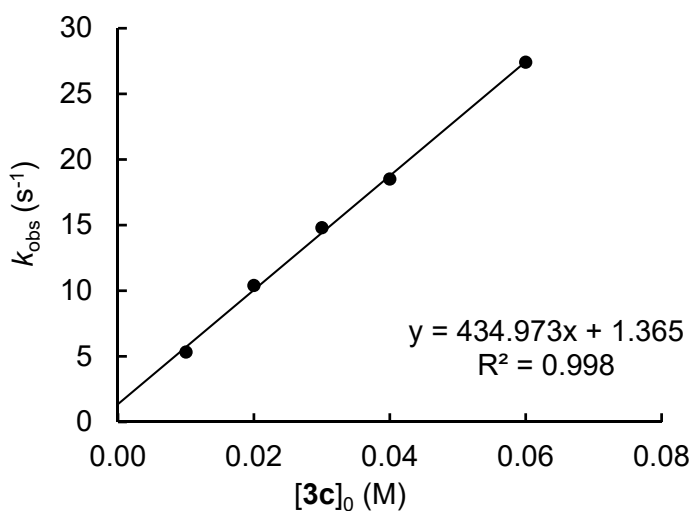
[1a] ₀ (M)	[3a] ₀ (M)	k _{obs} (s ⁻¹)
1.00 × 10 ⁻³	4.00 × 10 ⁻³	6.94 × 10 ¹
1.00 × 10 ⁻³	6.00 × 10 ⁻³	1.03 × 10 ²
1.00 × 10 ⁻³	8.00 × 10 ⁻³	1.33 × 10 ²
1.00 × 10 ⁻³	1.00 × 10 ⁻²	1.68 × 10 ²
$k_2 = 1.63 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$		

**1a + diethyl 2-benzylidenemalonate (3b)***AEM-513*

[1a] ₀ (M)	[3b] ₀ (M)	k _{obs} (s ⁻¹)
1.00 × 10 ⁻³	1.00 × 10 ⁻²	1.13 × 10 ¹
1.00 × 10 ⁻³	2.00 × 10 ⁻²	1.89 × 10 ¹
1.00 × 10 ⁻³	3.00 × 10 ⁻²	2.68 × 10 ¹
1.00 × 10 ⁻³	4.00 × 10 ⁻²	3.35 × 10 ¹
1.00 × 10 ⁻³	6.00 × 10 ⁻²	5.25 × 10 ¹
$k_2 = 8.17 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$		

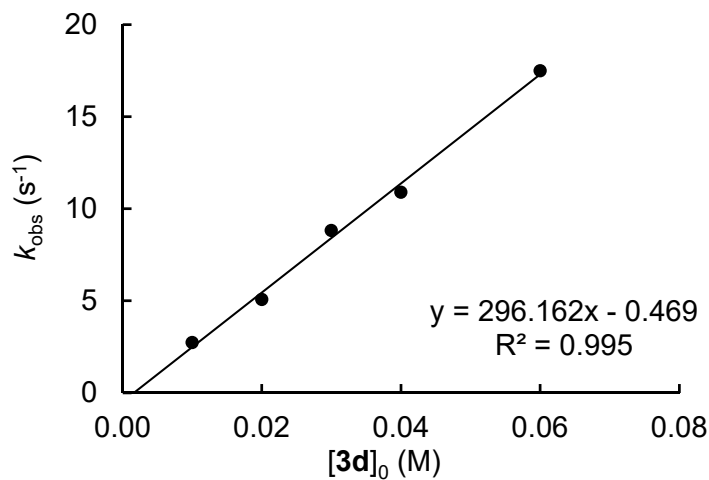
**1a + diethyl 2-(4-methylbenzylidene)malonate (3c)***AEM-512*

[1a] ₀ (M)	[3c] ₀ (M)	k _{obs} (s ⁻¹)
1.00 × 10 ⁻³	1.00 × 10 ⁻²	5.32 × 10 ⁰
1.00 × 10 ⁻³	2.00 × 10 ⁻²	1.04 × 10 ¹
1.00 × 10 ⁻³	3.00 × 10 ⁻²	1.48 × 10 ¹
1.00 × 10 ⁻³	4.00 × 10 ⁻²	1.85 × 10 ¹
1.00 × 10 ⁻³	6.00 × 10 ⁻²	2.74 × 10 ¹
$k_2 = 4.35 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$		

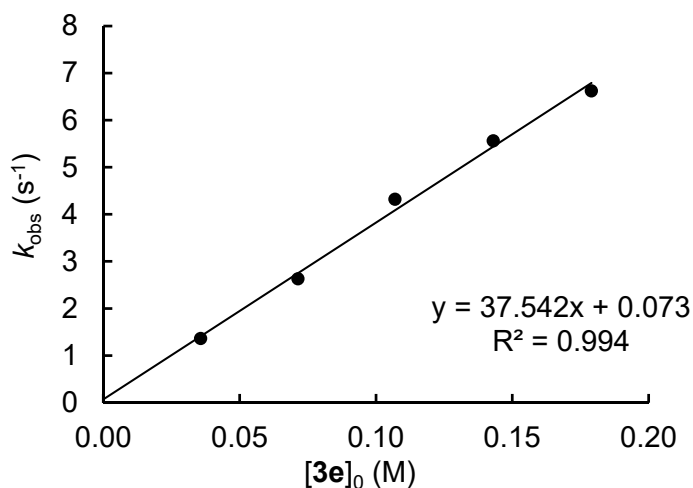


1a + diethyl 2-(4-methoxybenzylidene)malonate (3d)*AEM-509*

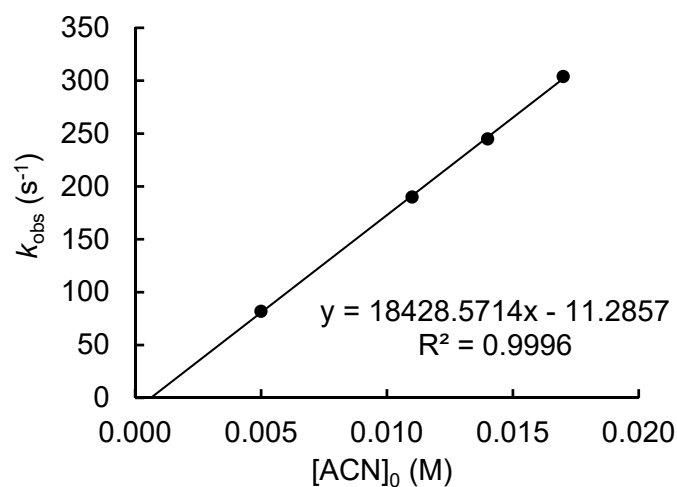
[1a] ₀ (M)	[3d] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
1.00 × 10 ⁻³	1.00 × 10 ⁻²	2.74 × 10 ⁰
1.00 × 10 ⁻³	2.00 × 10 ⁻²	5.08 × 10 ⁰
1.00 × 10 ⁻³	3.00 × 10 ⁻²	8.82 × 10 ⁰
1.00 × 10 ⁻³	4.00 × 10 ⁻²	1.09 × 10 ¹
1.00 × 10 ⁻³	6.00 × 10 ⁻²	1.75 × 10 ¹
<i>k</i> ₂ = 2.96 × 10 ² M ⁻¹ s ⁻¹		

**1a + diethyl 2-(4-dimethylaminobenzylidene)malonate (3e)***AEM-631*

[1a] ₀ (M)	[3e] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
1.00 × 10 ⁻³	3.57 × 10 ⁻²	1.36 × 10 ⁰
1.00 × 10 ⁻³	7.14 × 10 ⁻²	2.63 × 10 ⁰
1.00 × 10 ⁻³	1.07 × 10 ⁻¹	4.32 × 10 ⁰
1.00 × 10 ⁻³	1.43 × 10 ⁻¹	5.56 × 10 ⁰
1.00 × 10 ⁻³	1.79 × 10 ⁻¹	6.62 × 10 ⁰
<i>k</i> ₂ = 3.75 × 10 ¹ M ⁻¹ s ⁻¹		

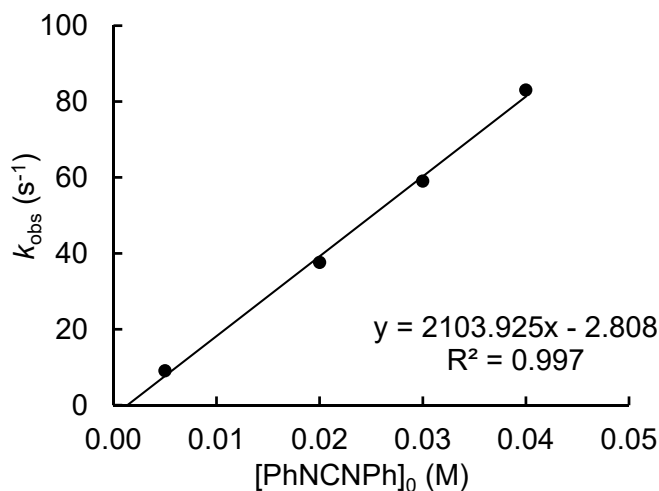
**1a + acrylonitrile (ACN)***AEM-629; [a] only one kinetic run each.*

[1a] ₀ (M)	[ACN] ₀ (M)	<i>k</i> _{obs} (s ⁻¹) ^[a]
1.00 × 10 ⁻³	5.00 × 10 ⁻³	8.20 × 10 ¹
1.00 × 10 ⁻³	1.10 × 10 ⁻²	1.90 × 10 ²
1.00 × 10 ⁻³	1.40 × 10 ⁻²	2.45 × 10 ²
1.00 × 10 ⁻³	1.70 × 10 ⁻²	3.04 × 10 ²
<i>k</i> ₂ = 1.84 × 10 ⁴ M ⁻¹ s ⁻¹		

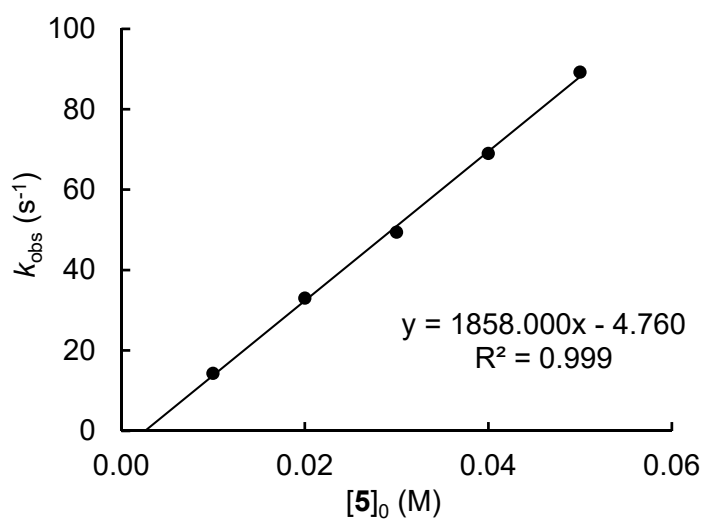


1a + *N,N*-diphenylcarbodiimide (PhNCNPh)*AEM-528*

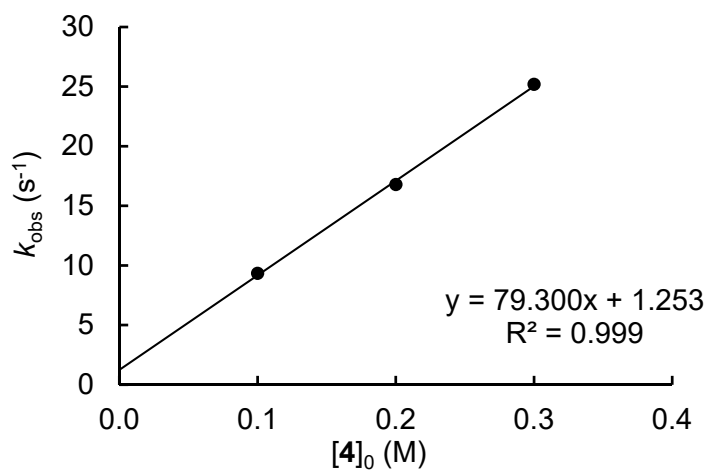
[1a] ₀ (M)	[PhNCNPh] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
1.00 × 10 ⁻³	5.00 × 10 ⁻³	9.04 × 10 ⁰
1.00 × 10 ⁻³	2.00 × 10 ⁻²	3.76 × 10 ¹
1.00 × 10 ⁻³	3.00 × 10 ⁻²	5.90 × 10 ¹
1.00 × 10 ⁻³	4.00 × 10 ⁻²	8.30 × 10 ¹
<i>k</i> ₂ = 2.10 × 10 ³ M ⁻¹ s ⁻¹		

**1a + *tert*-butyl acrylate (5)***AEM-525*

[1a] ₀ (M)	[5] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
1.00 × 10 ⁻³	1.00 × 10 ⁻²	1.43 × 10 ¹
1.00 × 10 ⁻³	2.00 × 10 ⁻²	3.30 × 10 ¹
1.00 × 10 ⁻³	3.00 × 10 ⁻²	4.94 × 10 ¹
1.00 × 10 ⁻³	4.00 × 10 ⁻²	6.90 × 10 ¹
1.00 × 10 ⁻³	5.00 × 10 ⁻²	8.92 × 10 ¹
<i>k</i> ₂ = 1.86 × 10 ³ M ⁻¹ s ⁻¹		

**1a + ethyl cinnamate (4)***AEM-515*

[1a] ₀ (M)	[4] ₀ (M)	<i>k</i> _{obs} (s ⁻¹)
1.00 × 10 ⁻³	1.00 × 10 ⁻¹	9.34 × 10 ⁰
1.00 × 10 ⁻³	2.00 × 10 ⁻¹	1.68 × 10 ¹
1.00 × 10 ⁻³	3.00 × 10 ⁻¹	2.52 × 10 ¹
<i>k</i> ₂ = 7.93 × 10 ¹ M ⁻¹ s ⁻¹		



1a + cinnamonnitrile (11)*AEM-630*

$[1a]_0$ (M)	$[CMN]_0$ (M)	k_{obs} (s^{-1})
1.00×10^{-3}	1.20×10^{-1}	8.04×10^0
1.00×10^{-3}	2.40×10^{-1}	1.64×10^1
1.00×10^{-3}	3.60×10^{-1}	2.45×10^1
1.00×10^{-3}	4.80×10^{-1}	3.29×10^1
1.00×10^{-3}	6.00×10^{-1}	3.89×10^1
$k_2 = 6.52 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$		

