

## Supporting Information

### **Kinetic measurements used to determine the nucleophilicity of 2-methylene-1,2-dihydropyridines in different solvents**

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#### **Data storage system:**

Main folders refer to the solvents used for the kinetic measurements (that is, DMSO, MeCN, DCM, and THF).

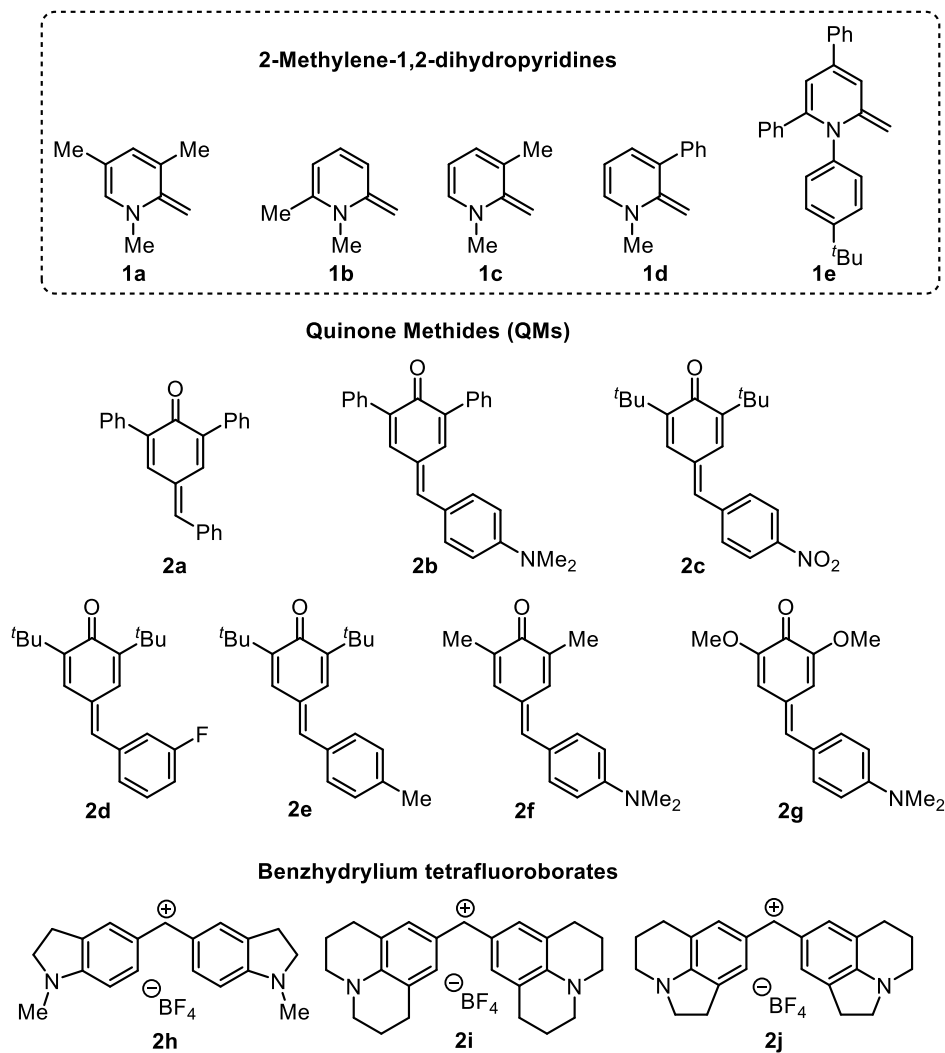
Subfolders and file names AB-xx and AEM-xxx refer to individual experiments and are identical to those in this Supporting Information.

The folders contain

- txt files with absorbance vs. time data [raw data]
- exp files used for the  $k_{\text{obs}}$  determination [evaluated data]
- pdf files with results of the  $k_{\text{obs}}$  determination [evaluated data]
- xlsx files (MS Excel) with experimental details (concentrations, volumes, wavelengths, in German).

## Kinetics

The kinetics of reactions of **1** with electrophiles **2** (structures are shown in Figure S1) in DMSO, MeCN, THF or dichloromethane were monitored by UV/vis photometry on an Applied Photophysics SX.20 stopped-flow instrument. The temperature of the drive syringes, the flow circuit, and the observation cell was maintained constant at 20 °C ( $\pm 0.2$  °C) by use of a circulating bath cryostat. All solutions were prepared in dry glassware under an atmosphere of dry argon.



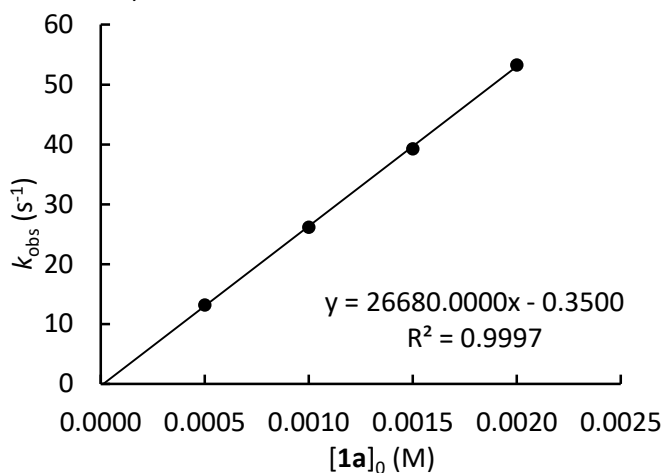
**Figure S1:** Nucleophiles and electrophiles employed in the kinetic studies.

## Kinetics of Reactions of 1a with Electrophiles 2 in DMSO

**1a + 2b** in DMSO (20 °C, stopped flow, decrease at 533 nm)

AB-24

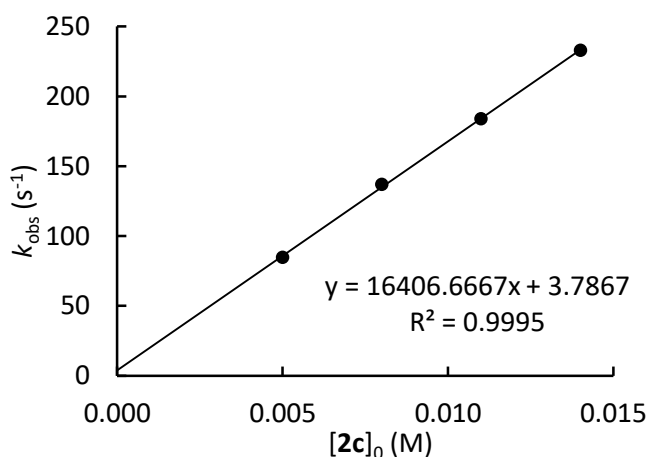
[2b] <sub>0</sub> (M)	[1a] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	5.00 × 10 <sup>-4</sup>	1.32 × 10 <sup>1</sup>
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	2.62 × 10 <sup>1</sup>
2.00 × 10 <sup>-5</sup>	1.50 × 10 <sup>-3</sup>	3.93 × 10 <sup>1</sup>
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-3</sup>	5.33 × 10 <sup>1</sup>
$k_2 = 2.67 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$		



**1a + 2c** in DMSO (20 °C, stopped flow, increase at 575 nm)

AB-56

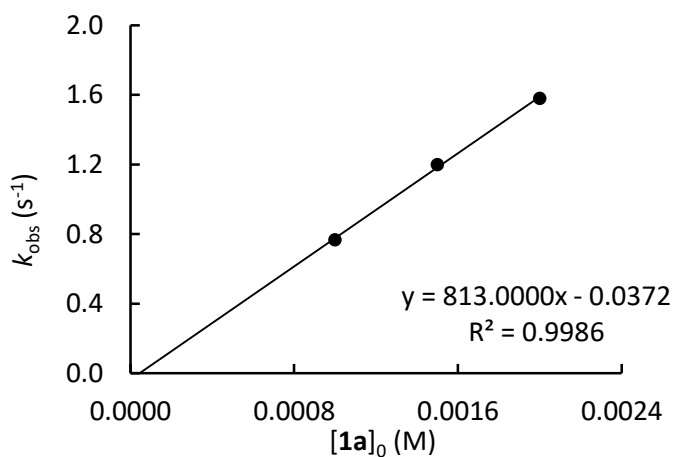
[1a] <sub>0</sub> (M)	[2c] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
1.00 × 10 <sup>-3</sup>	5.00 × 10 <sup>-3</sup>	8.46 × 10 <sup>1</sup>
1.00 × 10 <sup>-3</sup>	8.00 × 10 <sup>-3</sup>	1.37 × 10 <sup>2</sup>
1.00 × 10 <sup>-3</sup>	1.10 × 10 <sup>-2</sup>	1.84 × 10 <sup>2</sup>
1.00 × 10 <sup>-3</sup>	1.40 × 10 <sup>-2</sup>	2.33 × 10 <sup>2</sup>
$k_2 = 1.64 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$		



**1a + 2f** in DMSO (20 °C, stopped flow, decrease at 500 nm)

AB-54

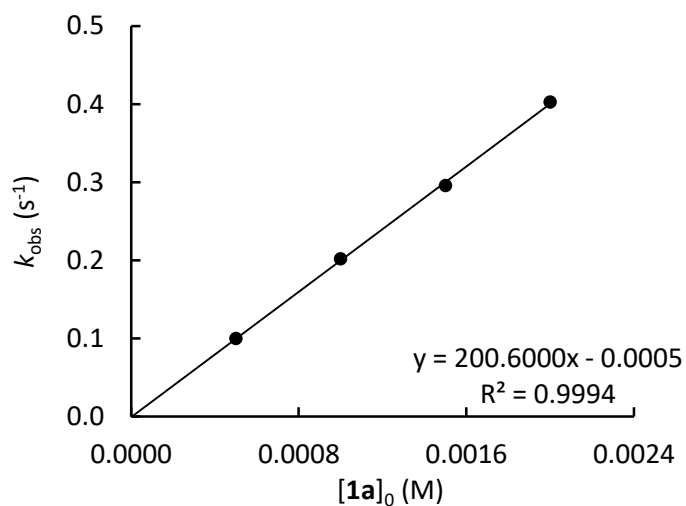
[2f] <sub>0</sub> (M)	[1a] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	7.67 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	1.50 × 10 <sup>-3</sup>	1.20
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-3</sup>	1.58
$k_2 = 8.13 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$		



**1a + 2g** in DMSO (20 °C, stopped flow, decrease at 500 nm)

AB-53

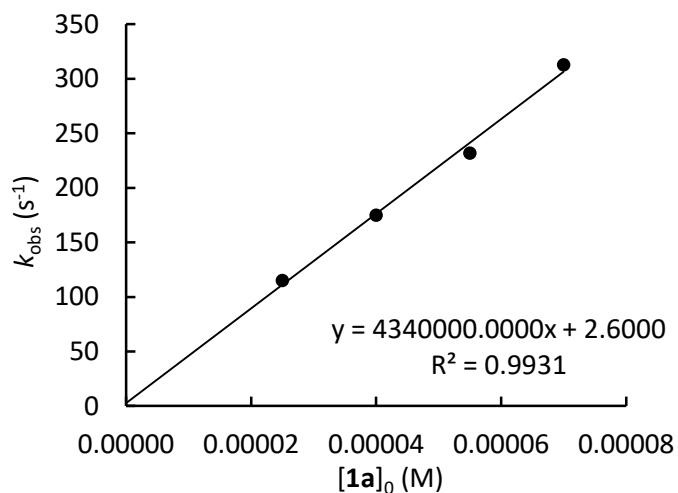
$[2g]_0$ (M)	$[1a]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$2.00 \times 10^{-5}$	$5.00 \times 10^{-4}$	$1.00 \times 10^{-1}$
$2.00 \times 10^{-5}$	$1.00 \times 10^{-3}$	$2.02 \times 10^{-1}$
$2.00 \times 10^{-5}$	$1.50 \times 10^{-3}$	$2.96 \times 10^{-1}$
$2.00 \times 10^{-5}$	$2.00 \times 10^{-3}$	$4.03 \times 10^{-1}$
$k_2 = 2.01 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$		



**1a + 2j** in DMSO (20 °C, stopped flow, decrease at 639 nm)

AB-55

$[2j]_0$ (M)	$[1a]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$5.00 \times 10^{-6}$	$2.50 \times 10^{-5}$	$1.15 \times 10^2$
$5.00 \times 10^{-6}$	$4.00 \times 10^{-5}$	$1.75 \times 10^2$
$5.00 \times 10^{-6}$	$5.50 \times 10^{-5}$	$2.32 \times 10^2$
$5.00 \times 10^{-6}$	$7.00 \times 10^{-5}$	$3.13 \times 10^2$
$k_2 = 4.34 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$		

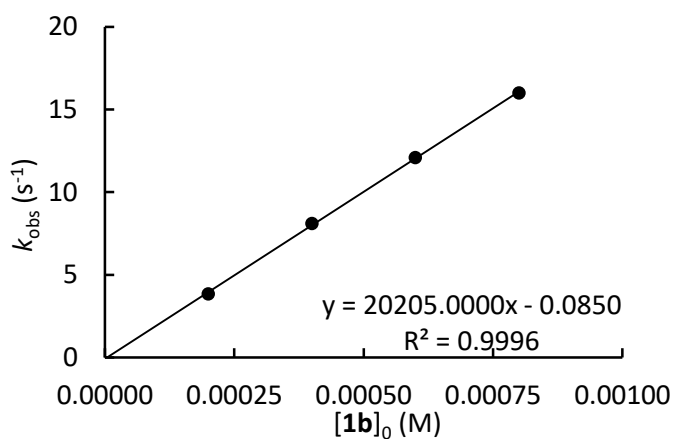


## Kinetics of Reactions of **1b** with Electrophiles **2** in DMSO

**1b + 2b** in DMSO (20 °C, stopped flow, decrease at 533 nm)

AB-25

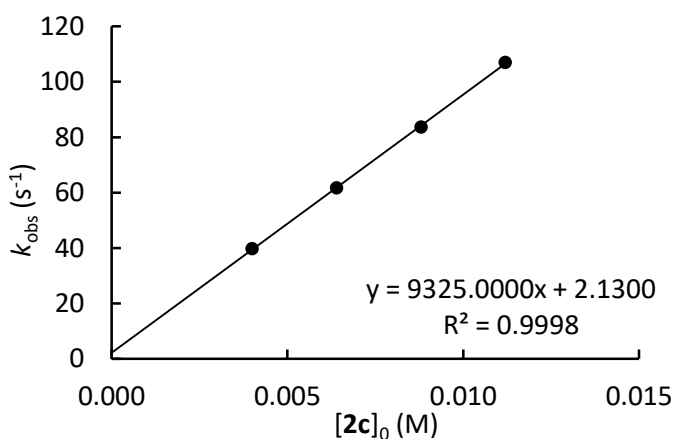
$[2b]_0$ (M)	$[1b]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$2.00 \times 10^{-5}$	$2.00 \times 10^{-4}$	3.86
$2.00 \times 10^{-5}$	$4.00 \times 10^{-4}$	8.11
$2.00 \times 10^{-5}$	$6.00 \times 10^{-4}$	$1.21 \times 10^1$
$2.00 \times 10^{-5}$	$8.00 \times 10^{-4}$	$1.60 \times 10^1$
$k_2 = 2.02 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$		



**1b + 2c** in DMSO (20 °C, stopped flow, increase at 575 nm)

AB-66

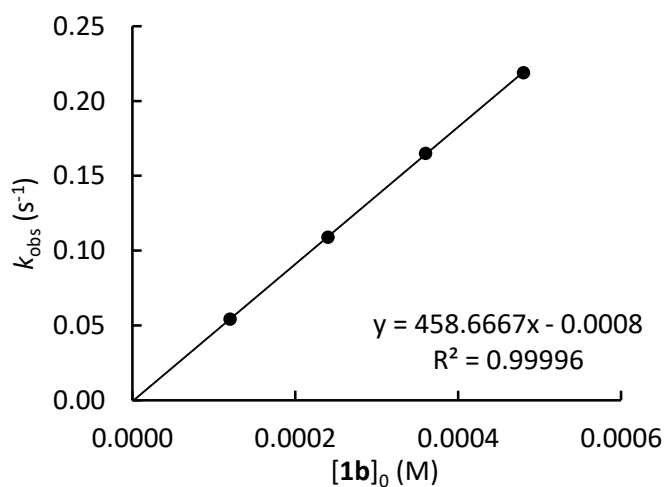
$[1b]_0$ (M)	$[2c]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$8.00 \times 10^{-4}$	$4.00 \times 10^{-3}$	$3.97 \times 10^1$
$8.00 \times 10^{-4}$	$6.40 \times 10^{-3}$	$6.17 \times 10^1$
$8.00 \times 10^{-4}$	$8.80 \times 10^{-3}$	$8.36 \times 10^1$
$8.00 \times 10^{-4}$	$1.12 \times 10^{-2}$	$1.07 \times 10^2$
$k_2 = 9.33 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		



**1b + 2f** in DMSO (20 °C, stopped flow, decrease at 510 nm)

AB-69

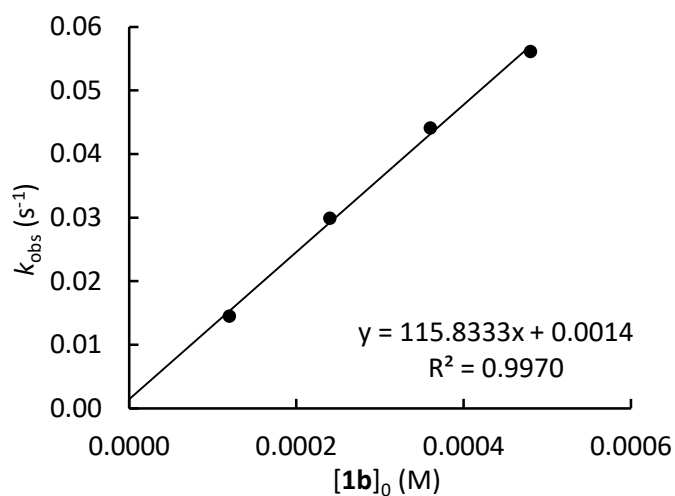
$[2f]_0$ (M)	$[1b]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$2.00 \times 10^{-5}$	$1.20 \times 10^{-4}$	$5.42 \times 10^{-2}$
$2.00 \times 10^{-5}$	$2.40 \times 10^{-4}$	$1.09 \times 10^{-1}$
$2.00 \times 10^{-5}$	$3.60 \times 10^{-4}$	$1.65 \times 10^{-1}$
$2.00 \times 10^{-5}$	$4.80 \times 10^{-4}$	$2.19 \times 10^{-1}$
$k_2 = 4.59 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$		



**1b + 2g** in DMSO (20 °C, stopped flow, decrease at 510 nm)

AB-68

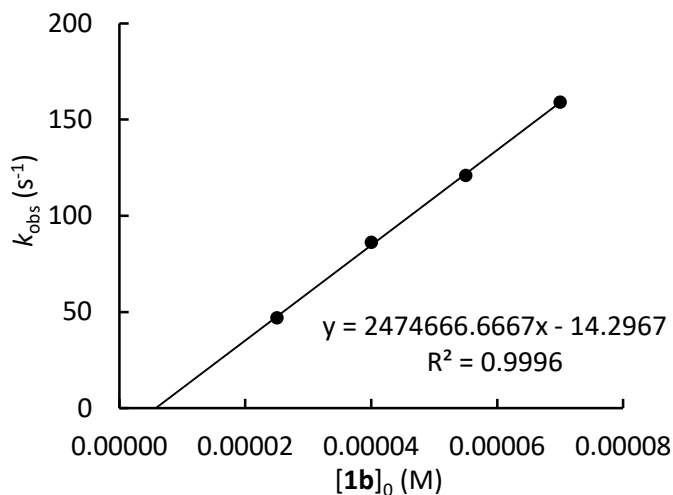
$[2g]_0$ (M)	$[1b]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$2.00 \times 10^{-5}$	$1.20 \times 10^{-4}$	$1.45 \times 10^{-2}$
$2.00 \times 10^{-5}$	$2.40 \times 10^{-4}$	$2.99 \times 10^{-2}$
$2.00 \times 10^{-5}$	$3.60 \times 10^{-4}$	$4.41 \times 10^{-2}$
$2.00 \times 10^{-5}$	$4.80 \times 10^{-4}$	$5.61 \times 10^{-2}$
$k_2 = 1.16 \times 10^2 M^{-1} s^{-1}$		



**1b + 2j** in DMSO (20 °C, stopped flow, decrease at 639 nm)

AB-67

$[2j]_0$ (M)	$[1b]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$5.00 \times 10^{-6}$	$2.50 \times 10^{-5}$	$4.69 \times 10^1$
$5.00 \times 10^{-6}$	$4.00 \times 10^{-5}$	$8.61 \times 10^1$
$5.00 \times 10^{-6}$	$5.50 \times 10^{-5}$	$1.21 \times 10^2$
$5.00 \times 10^{-6}$	$7.00 \times 10^{-5}$	$1.59 \times 10^2$
$k_2 = 2.47 \times 10^6 M^{-1} s^{-1}$		

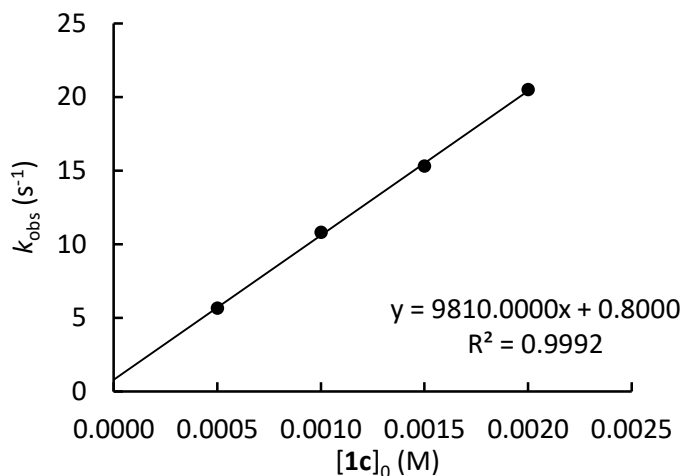


## Kinetics of Reactions of 1c with Electrophiles 2 in DMSO

**1c + 2b** in DMSO (20 °C, stopped flow, decrease at 533 nm)

AB-21

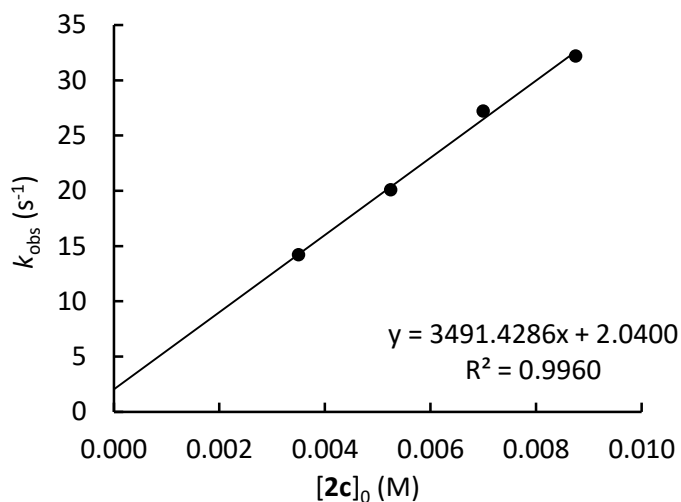
[2b] <sub>0</sub> (M)	[1c] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	5.00 × 10 <sup>-4</sup>	5.65
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	1.08 × 10 <sup>1</sup>
2.00 × 10 <sup>-5</sup>	1.50 × 10 <sup>-3</sup>	1.53 × 10 <sup>1</sup>
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-3</sup>	2.05 × 10 <sup>1</sup>
$k_2 = 9.81 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		



**1c + 2c** in DMSO (20 °C, stopped flow, increase at 575 nm)

AB-19

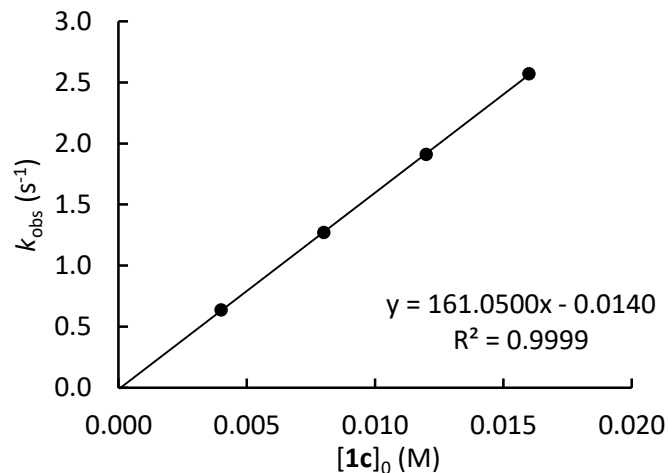
[1c] <sub>0</sub> (M)	[2c] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
3.50 × 10 <sup>-4</sup>	3.50 × 10 <sup>-3</sup>	1.42 × 10 <sup>1</sup>
3.50 × 10 <sup>-4</sup>	5.25 × 10 <sup>-3</sup>	2.01 × 10 <sup>1</sup>
3.50 × 10 <sup>-4</sup>	7.00 × 10 <sup>-3</sup>	2.72 × 10 <sup>1</sup>
3.50 × 10 <sup>-4</sup>	8.75 × 10 <sup>-3</sup>	3.22 × 10 <sup>1</sup>
$k_2 = 3.49 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		



**1c + 2f** in DMSO (20 °C, stopped flow, decrease at 500 nm)

AB-20

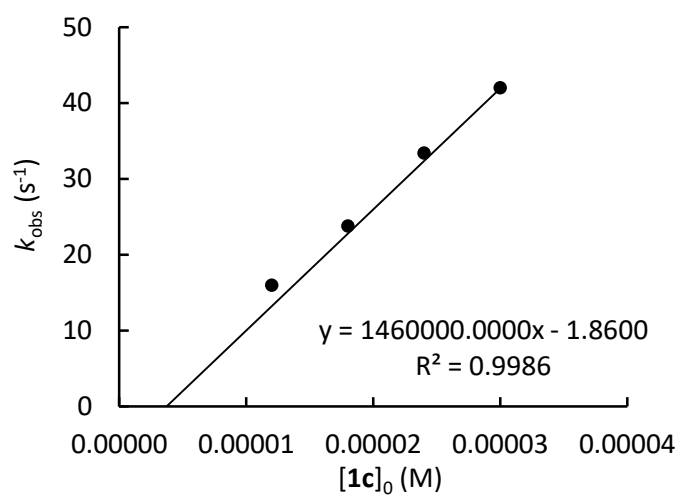
[2f] <sub>0</sub> (M)	[1c] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	4.00 × 10 <sup>-3</sup>	6.36 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	8.00 × 10 <sup>-3</sup>	1.27
2.00 × 10 <sup>-5</sup>	1.20 × 10 <sup>-2</sup>	1.91
2.00 × 10 <sup>-5</sup>	1.60 × 10 <sup>-2</sup>	2.57
$k_2 = 1.61 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$		



**1c + 2j** in DMSO (20 °C, stopped flow, decrease at 639 nm)

AB-22

$[2j]_0$ (M)	$[1c]_0$ (M)	$k_{\text{obs}}$ ( $s^{-1}$ )
$3.00 \times 10^{-6}$	$1.20 \times 10^{-5}$	$1.60 \times 10^1$
$3.00 \times 10^{-6}$	$1.80 \times 10^{-5}$	$2.38 \times 10^1$
$3.00 \times 10^{-6}$	$2.40 \times 10^{-5}$	$3.34 \times 10^1$
$3.00 \times 10^{-6}$	$3.00 \times 10^{-5}$	$4.20 \times 10^1$
$k_2 = 1.46 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$		



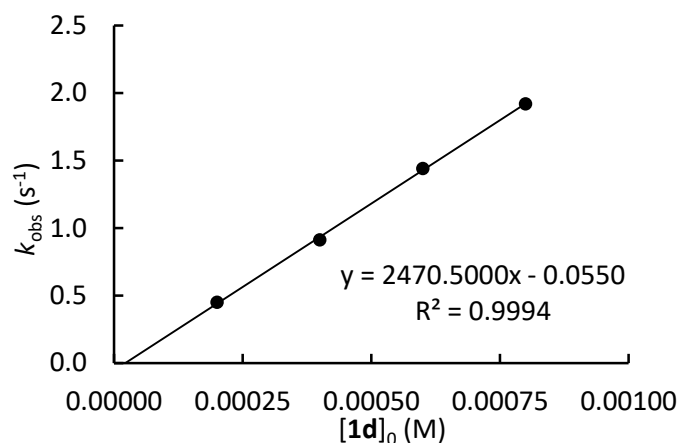


## Kinetics of Reactions of 1d with Electrophiles 2 in DMSO

**1d + 2b** in DMSO (20 °C, stopped flow, decrease at 533 nm)

AB-26

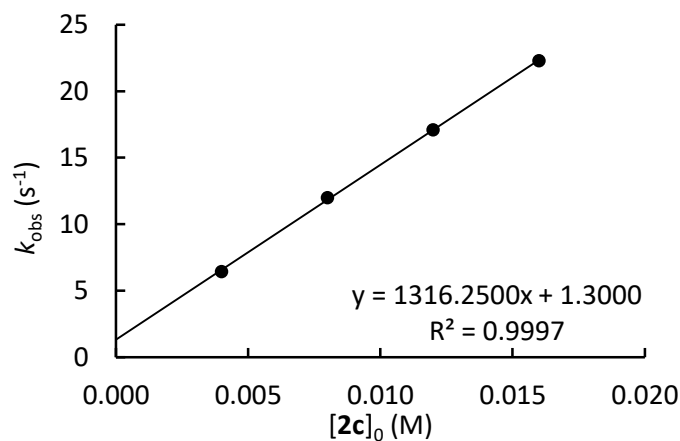
[2b] <sub>0</sub> (M)	[1d] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-4</sup>	4.49 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	4.00 × 10 <sup>-4</sup>	9.12 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	6.00 × 10 <sup>-4</sup>	1.44
2.00 × 10 <sup>-5</sup>	8.00 × 10 <sup>-4</sup>	1.92
$k_2 = 2.47 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		



**1d + 2c** in DMSO (20 °C, stopped flow, increase at 575 nm)

AB-60

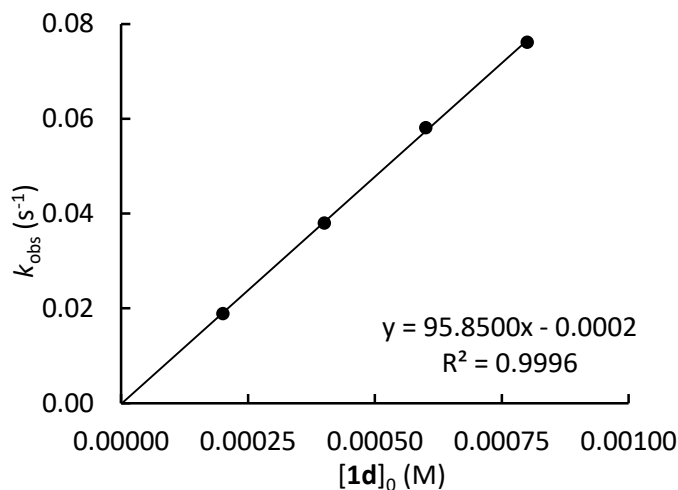
[1d] <sub>0</sub> (M)	[2c] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
8.00 × 10 <sup>-4</sup>	4.00 × 10 <sup>-3</sup>	6.45
8.00 × 10 <sup>-4</sup>	8.00 × 10 <sup>-3</sup>	1.20 × 10 <sup>1</sup>
8.00 × 10 <sup>-4</sup>	1.20 × 10 <sup>-2</sup>	1.71 × 10 <sup>1</sup>
8.00 × 10 <sup>-4</sup>	1.60 × 10 <sup>-2</sup>	2.23 × 10 <sup>1</sup>
$k_2 = 1.32 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		



**1d + 2f** in DMSO (20 °C, stopped flow, decrease at 510 nm)

AB-58

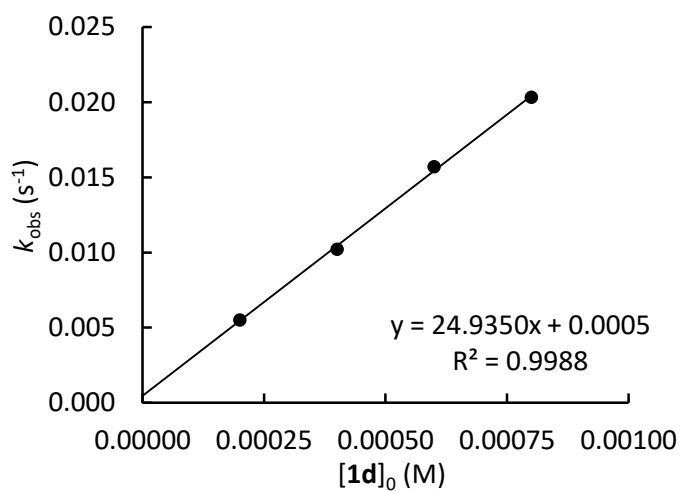
[2f] <sub>0</sub> (M)	[1d] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-4</sup>	1.89 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	4.00 × 10 <sup>-4</sup>	3.80 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	6.00 × 10 <sup>-4</sup>	5.81 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	8.00 × 10 <sup>-4</sup>	7.61 × 10 <sup>-2</sup>
$k_2 = 9.59 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$		



**1d + 2g** in DMSO (20 °C, stopped flow, decrease at 510 nm)

AB-57

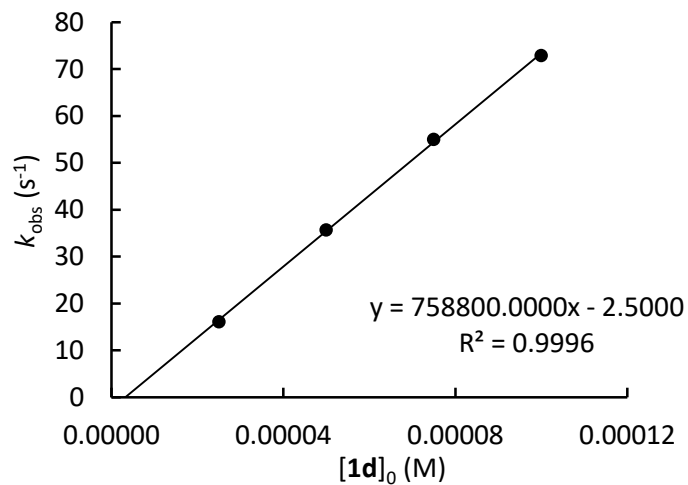
$[2g]_0$ (M)	$[1d]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$2.00 \times 10^{-5}$	$2.00 \times 10^{-4}$	$5.51 \times 10^{-3}$
$2.00 \times 10^{-5}$	$4.00 \times 10^{-4}$	$1.02 \times 10^{-2}$
$2.00 \times 10^{-5}$	$6.00 \times 10^{-4}$	$1.57 \times 10^{-2}$
$2.00 \times 10^{-5}$	$8.00 \times 10^{-4}$	$2.03 \times 10^{-2}$
$k_2 = 2.49 \times 10^1 M^{-1} s^{-1}$		



**1d + 2j** in DMSO (20 °C, stopped flow, decrease at 639 nm)

AB-59

$[2j]_0$ (M)	$[1d]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$5.00 \times 10^{-6}$	$2.50 \times 10^{-5}$	$1.61 \times 10^1$
$5.00 \times 10^{-6}$	$5.00 \times 10^{-5}$	$3.57 \times 10^1$
$5.00 \times 10^{-6}$	$7.50 \times 10^{-5}$	$5.50 \times 10^1$
$5.00 \times 10^{-6}$	$1.00 \times 10^{-4}$	$7.29 \times 10^1$
$k_2 = 7.59 \times 10^5 M^{-1} s^{-1}$		

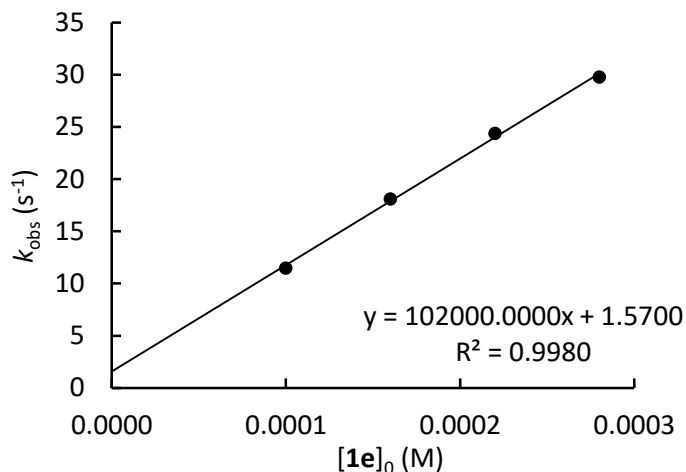


## Kinetics of Reactions of **1e** with Electrophiles **2** in DMSO

**1e** + **2a** in DMSO (20 °C, stopped flow, decrease at 384 nm)

AB-64

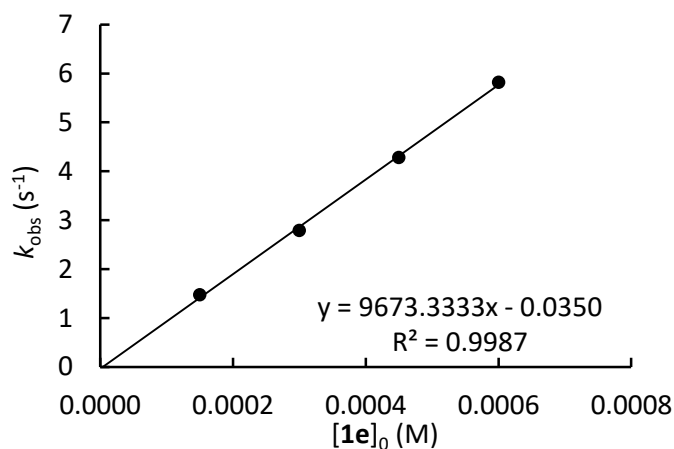
[ <b>2a</b> ] <sub>0</sub> (M)	[ <b>1e</b> ] <sub>0</sub> (M)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-4</sup>	1.15 × 10 <sup>1</sup>
2.00 × 10 <sup>-5</sup>	1.60 × 10 <sup>-4</sup>	1.81 × 10 <sup>1</sup>
2.00 × 10 <sup>-5</sup>	2.20 × 10 <sup>-4</sup>	2.44 × 10 <sup>1</sup>
2.00 × 10 <sup>-5</sup>	2.80 × 10 <sup>-4</sup>	2.98 × 10 <sup>1</sup>
<i>k</i> <sub>2</sub> = 1.02 × 10 <sup>5</sup> M <sup>-1</sup> s <sup>-1</sup>		



**1e** + **2b** in DMSO (20 °C, stopped flow, decrease at 533 nm)

AB-28

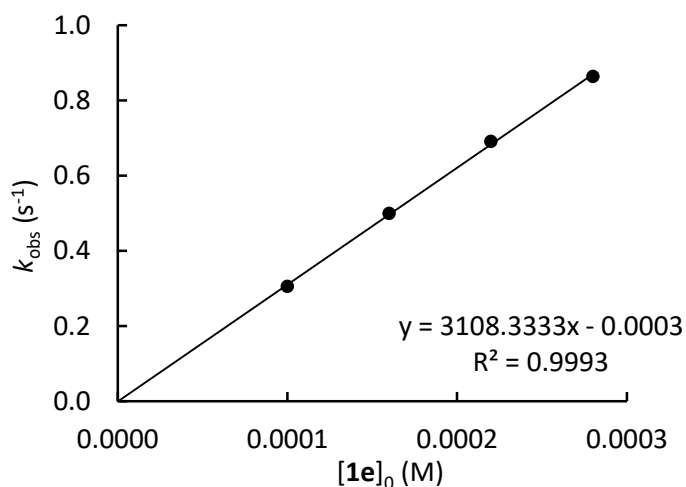
[ <b>2b</b> ] <sub>0</sub> (M)	[ <b>1e</b> ] <sub>0</sub> (M)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )
3.00 × 10 <sup>-5</sup>	1.50 × 10 <sup>-4</sup>	1.48
3.00 × 10 <sup>-5</sup>	3.00 × 10 <sup>-4</sup>	2.79
3.00 × 10 <sup>-5</sup>	4.50 × 10 <sup>-4</sup>	4.28
3.00 × 10 <sup>-5</sup>	6.00 × 10 <sup>-4</sup>	5.82
<i>k</i> <sub>2</sub> = 9.67 × 10 <sup>3</sup> M <sup>-1</sup> s <sup>-1</sup>		



**1e** + **2c** in DMSO (20 °C, stopped flow, decrease at 374 nm)

AB-65

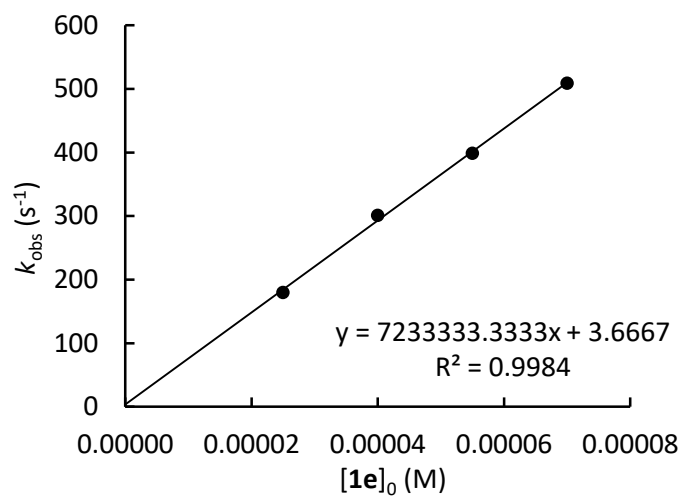
[ <b>2c</b> ] <sub>0</sub> (M)	[ <b>1e</b> ] <sub>0</sub> (M)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-4</sup>	3.06 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	1.60 × 10 <sup>-4</sup>	5.00 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	2.20 × 10 <sup>-4</sup>	6.91 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	2.80 × 10 <sup>-4</sup>	8.64 × 10 <sup>-1</sup>
<i>k</i> <sub>2</sub> = 3.11 × 10 <sup>3</sup> M <sup>-1</sup> s <sup>-1</sup>		



**1e + 2i** in DMSO (20 °C, stopped flow, decrease at 642 nm)

AB-62

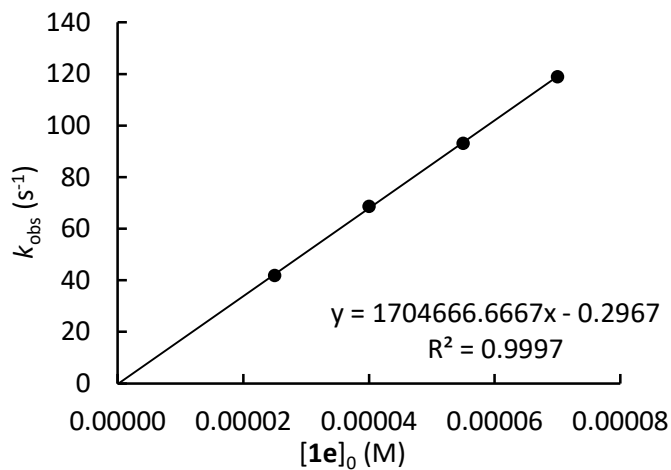
$[2i]_0$ (M)	$[1e]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$5.00 \times 10^{-6}$	$2.50 \times 10^{-5}$	$1.80 \times 10^2$
$5.00 \times 10^{-6}$	$4.00 \times 10^{-5}$	$3.01 \times 10^2$
$5.00 \times 10^{-6}$	$5.50 \times 10^{-5}$	$3.99 \times 10^2$
$5.00 \times 10^{-6}$	$7.00 \times 10^{-5}$	$5.09 \times 10^2$
$k_2 = 7.23 \times 10^6 M^{-1} s^{-1}$		



**1e + 2j** in DMSO (20 °C, stopped flow, decrease at 639 nm)

AB-61

$[2j]_0$ (M)	$[1e]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$5.00 \times 10^{-6}$	$2.50 \times 10^{-5}$	$4.19 \times 10^1$
$5.00 \times 10^{-6}$	$4.00 \times 10^{-5}$	$6.87 \times 10^1$
$5.00 \times 10^{-6}$	$5.50 \times 10^{-5}$	$9.31 \times 10^1$
$5.00 \times 10^{-6}$	$7.00 \times 10^{-5}$	$1.19 \times 10^2$
$k_2 = 1.70 \times 10^6 M^{-1} s^{-1}$		

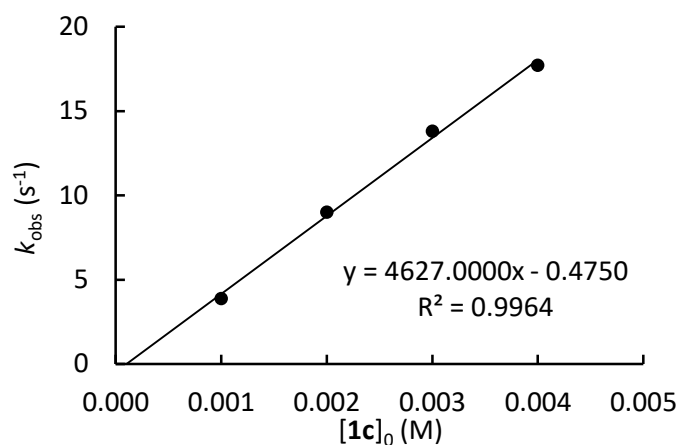


# Kinetics of Reactions of 1c with Electrophiles 2 in MeCN

1c + 2b in MeCN (20 °C, stopped flow, decrease at 533 nm)

AB-49

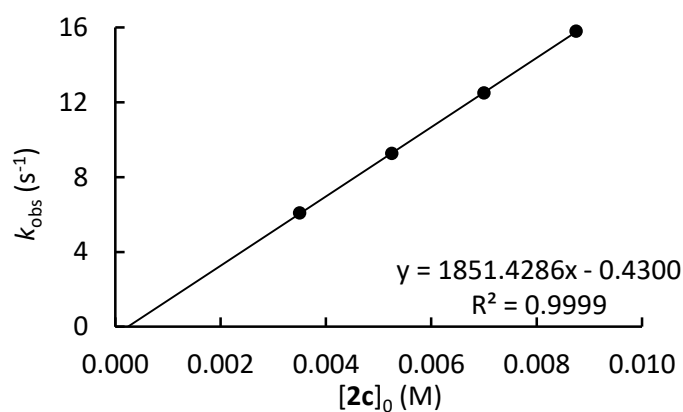
[2b] <sub>0</sub> (M)	[1c] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	3.88
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-3</sup>	8.99
2.00 × 10 <sup>-5</sup>	3.00 × 10 <sup>-3</sup>	1.38 × 10 <sup>1</sup>
2.00 × 10 <sup>-5</sup>	4.00 × 10 <sup>-3</sup>	1.77 × 10 <sup>1</sup>
$k_2 = 4.63 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		



1c + 2c in MeCN (20 °C, stopped flow, increase at 575 nm)

AB-50

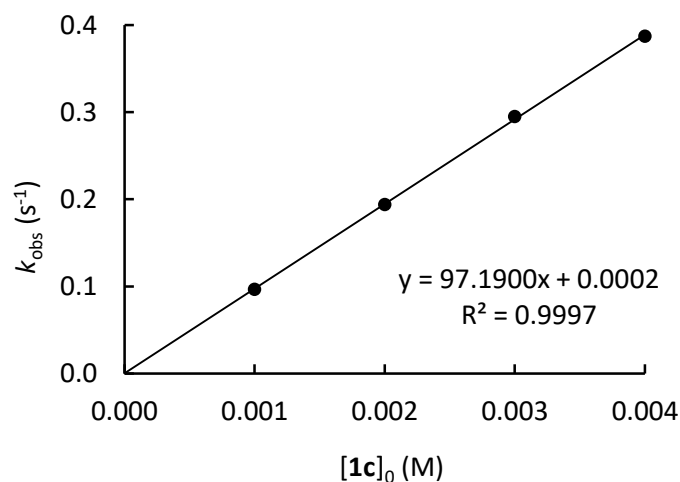
[1c] <sub>0</sub> (M)	[2c] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
3.50 × 10 <sup>-4</sup>	3.50 × 10 <sup>-3</sup>	6.08
3.50 × 10 <sup>-4</sup>	5.25 × 10 <sup>-3</sup>	9.26
3.50 × 10 <sup>-4</sup>	7.00 × 10 <sup>-3</sup>	1.25 × 10 <sup>1</sup>
3.50 × 10 <sup>-4</sup>	8.75 × 10 <sup>-3</sup>	1.58 × 10 <sup>1</sup>
$k_2 = 1.85 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		



1c + 2f in MeCN (20 °C, stopped flow, decrease at 500 nm)

AB-47

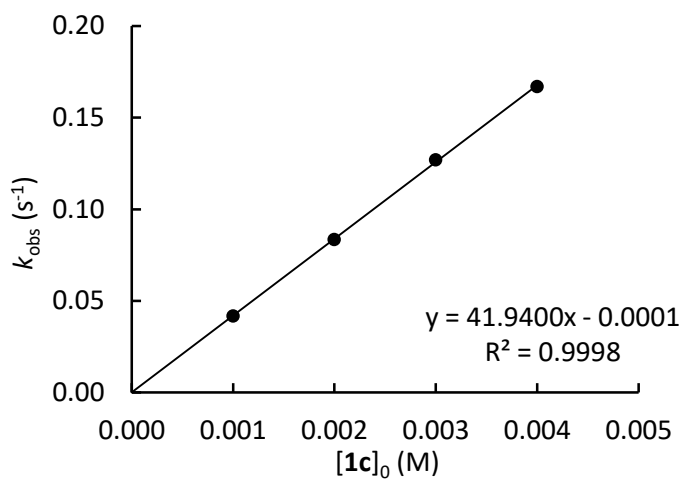
[2f] <sub>0</sub> (M)	[1c] <sub>0</sub> (M)	k <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	9.67 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-3</sup>	1.94 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	3.00 × 10 <sup>-3</sup>	2.95 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	4.00 × 10 <sup>-3</sup>	3.87 × 10 <sup>-1</sup>
$k_2 = 9.72 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$		



**1c + 2g** in MeCN (20 °C, stopped flow, decrease at 500 nm)

AB-48

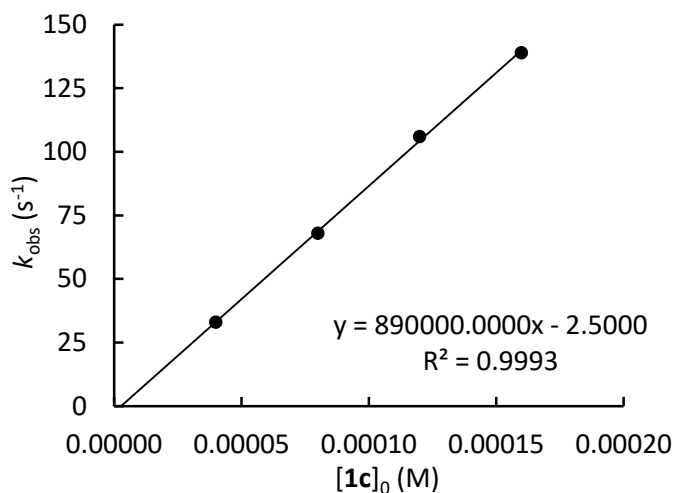
$[2g]_0$ (M)	$[1c]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$2.00 \times 10^{-5}$	$1.00 \times 10^{-3}$	$4.17 \times 10^{-2}$
$2.00 \times 10^{-5}$	$2.00 \times 10^{-3}$	$8.35 \times 10^{-2}$
$2.00 \times 10^{-5}$	$3.00 \times 10^{-3}$	$1.27 \times 10^{-1}$
$2.00 \times 10^{-5}$	$4.00 \times 10^{-3}$	$1.67 \times 10^{-1}$
$k_2 = 4.19 \times 10^1 M^{-1} s^{-1}$		



**1c + 2j** in DMSO (20 °C, stopped flow, decrease at 639 nm)

AB-51

$[2f]_0$ (M)	$[1c]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$5.00 \times 10^{-6}$	$4.00 \times 10^{-5}$	$3.30 \times 10^1$
$5.00 \times 10^{-6}$	$8.00 \times 10^{-5}$	$6.80 \times 10^1$
$5.00 \times 10^{-6}$	$1.20 \times 10^{-4}$	$1.06 \times 10^2$
$5.00 \times 10^{-6}$	$1.60 \times 10^{-4}$	$1.39 \times 10^2$
$k_2 = 8.90 \times 10^5 M^{-1} s^{-1}$		

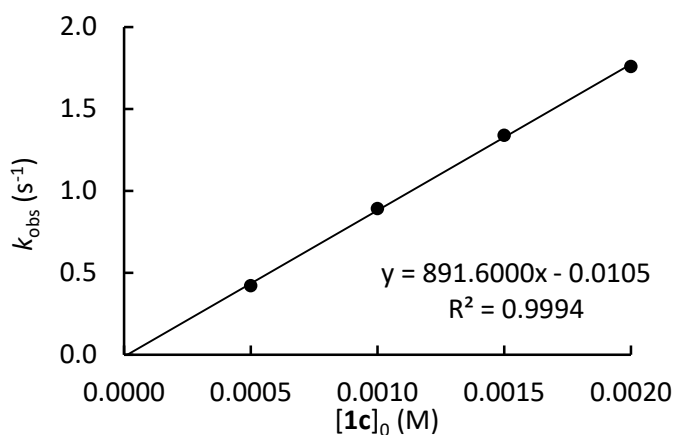


# Kinetics of Reactions of **1c** with Electrophiles **2** in Dichloromethane (DCM)

**1c + 2b** in DCM (20 °C, stopped flow, decrease at 533 nm)

AEM-351

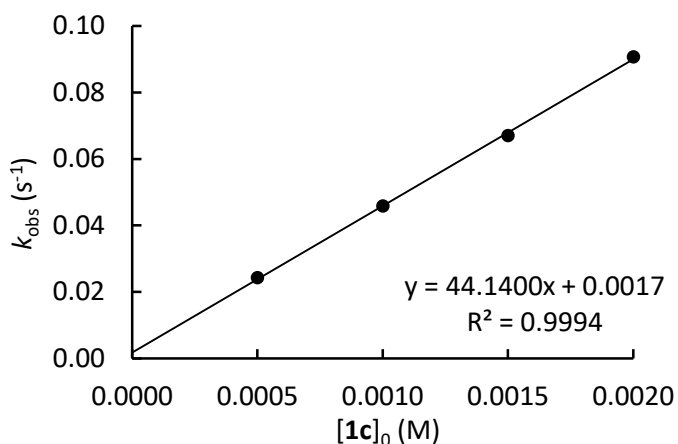
[ <b>2b</b> ] <sub>0</sub> (M)	[ <b>1c</b> ] <sub>0</sub> (M)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )
2.50 × 10 <sup>-5</sup>	5.00 × 10 <sup>-4</sup>	4.23 × 10 <sup>-1</sup>
2.50 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	8.93 × 10 <sup>-1</sup>
2.50 × 10 <sup>-5</sup>	1.50 × 10 <sup>-3</sup>	1.34
2.50 × 10 <sup>-5</sup>	2.00 × 10 <sup>-3</sup>	1.76
<i>k</i> <sub>2</sub> = 8.92 × 10 <sup>2</sup> M <sup>-1</sup> s <sup>-1</sup>		



**1c + 2f** in DCM (20 °C, stopped flow, decrease at 490 nm)

AEM-353

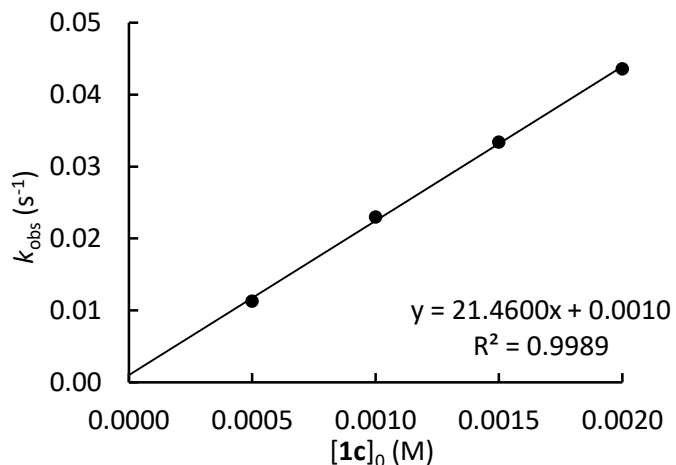
[ <b>2f</b> ] <sub>0</sub> (M)	[ <b>1c</b> ] <sub>0</sub> (M)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	5.00 × 10 <sup>-4</sup>	2.42 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	4.58 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	1.50 × 10 <sup>-3</sup>	6.70 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-3</sup>	9.07 × 10 <sup>-2</sup>
<i>k</i> <sub>2</sub> = 4.41 × 10 <sup>1</sup> M <sup>-1</sup> s <sup>-1</sup>		



**1c + 2g** in DCM (20 °C, stopped flow, decrease at 490 nm)

AEM-352

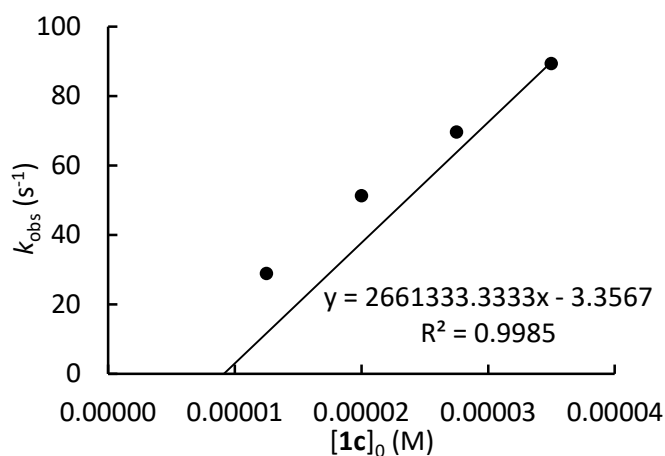
[ <b>2g</b> ] <sub>0</sub> (M)	[ <b>1c</b> ] <sub>0</sub> (M)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	5.00 × 10 <sup>-4</sup>	1.13 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	2.30 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	1.50 × 10 <sup>-3</sup>	3.34 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-3</sup>	4.36 × 10 <sup>-2</sup>
<i>k</i> <sub>2</sub> = 2.15 × 10 <sup>1</sup> M <sup>-1</sup> s <sup>-1</sup>		



**1c + 2h** in DCM (20 °C, stopped flow, decrease at 625 nm)

AEM-358

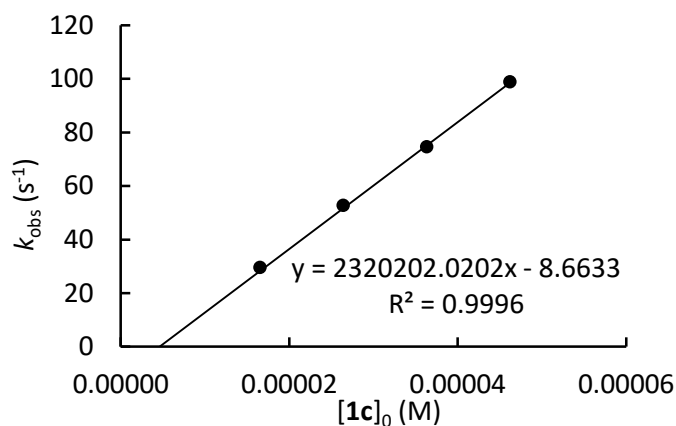
$[2h]_0$ (M)	$[1c]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$2.50 \times 10^{-6}$	$1.25 \times 10^{-5}$	$2.90 \times 10^1$
$2.50 \times 10^{-6}$	$2.00 \times 10^{-5}$	$5.13 \times 10^1$
$2.50 \times 10^{-6}$	$2.75 \times 10^{-5}$	$6.97 \times 10^1$
$2.50 \times 10^{-6}$	$3.50 \times 10^{-5}$	$8.94 \times 10^1$
$k_2 = 2.66 \times 10^6 M^{-1} s^{-1}$		



**1c + 2i** in DCM (20 °C, stopped flow, decrease at 642 nm)

AEM-357

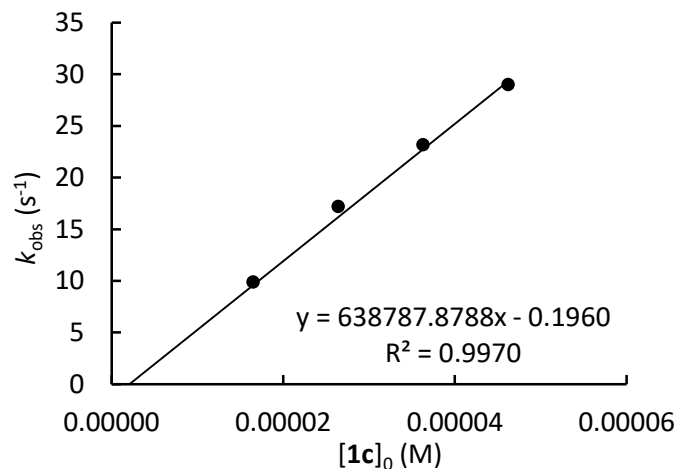
$[2i]_0$ (M)	$[1c]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$3.30 \times 10^{-6}$	$1.65 \times 10^{-5}$	$2.97 \times 10^1$
$3.30 \times 10^{-6}$	$2.64 \times 10^{-5}$	$5.29 \times 10^1$
$3.30 \times 10^{-6}$	$3.63 \times 10^{-5}$	$7.47 \times 10^1$
$3.30 \times 10^{-6}$	$4.62 \times 10^{-5}$	$9.90 \times 10^1$
$k_2 = 2.32 \times 10^6 M^{-1} s^{-1}$		



**1c + 2j** in DCM (20 °C, stopped flow, decrease at 639 nm)

AEM-356

$[2j]_0$ (M)	$[1c]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$3.30 \times 10^{-6}$	$1.65 \times 10^{-5}$	9.92
$3.30 \times 10^{-6}$	$2.64 \times 10^{-5}$	$1.72 \times 10^1$
$3.30 \times 10^{-6}$	$3.63 \times 10^{-5}$	$2.32 \times 10^1$
$3.30 \times 10^{-6}$	$4.62 \times 10^{-5}$	$2.90 \times 10^1$
$k_2 = 6.39 \times 10^5 M^{-1} s^{-1}$		



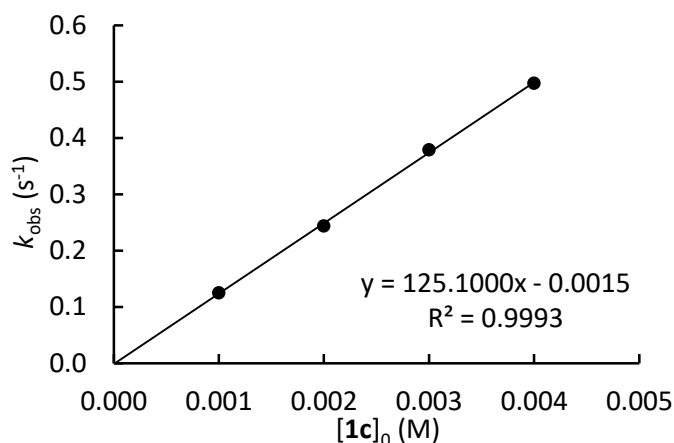


## Kinetics of Reactions of **1c** with Electrophiles **2** in THF

**1c** + **2b** in THF (20 °C, stopped flow, decrease at 533 nm)

AB-11

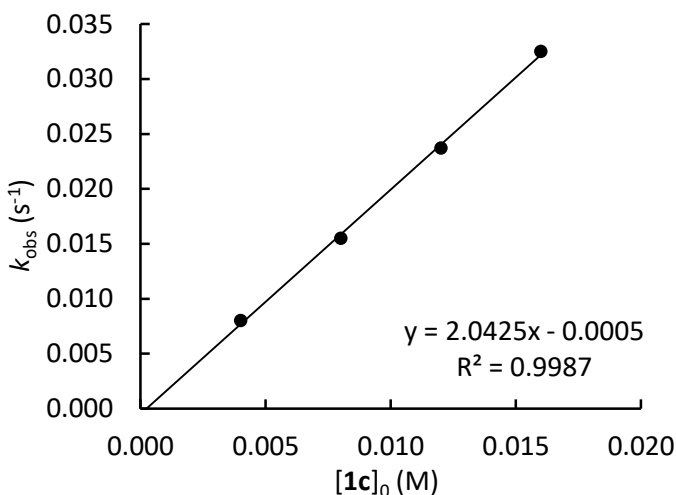
[ <b>2b</b> ] <sub>0</sub> (M)	[ <b>1c</b> ] <sub>0</sub> (M)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	1.25 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	2.00 × 10 <sup>-3</sup>	2.44 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	3.00 × 10 <sup>-3</sup>	3.79 × 10 <sup>-1</sup>
2.00 × 10 <sup>-5</sup>	4.00 × 10 <sup>-3</sup>	4.97 × 10 <sup>-1</sup>
<i>k</i> <sub>2</sub> = 1.25 × 10 <sup>2</sup> M <sup>-1</sup> s <sup>-1</sup>		



**1c** + **2f** in THF (20 °C, stopped flow, decrease at 500 nm)

AB-13

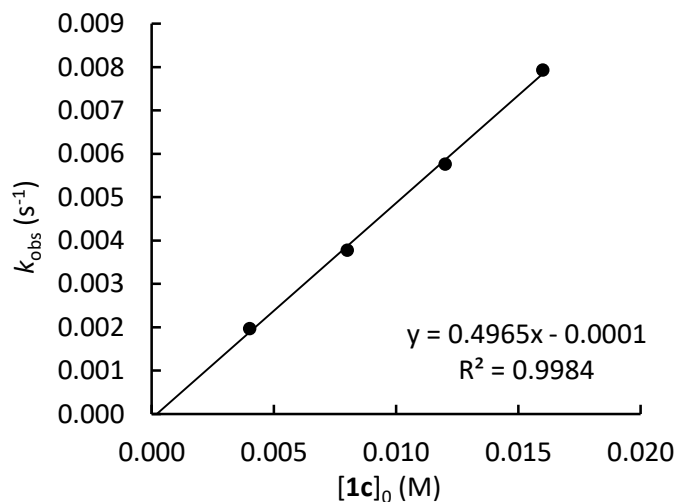
[ <b>2f</b> ] <sub>0</sub> (M)	[ <b>1c</b> ] <sub>0</sub> (M)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	4.00 × 10 <sup>-3</sup>	8.00 × 10 <sup>-3</sup>
2.00 × 10 <sup>-5</sup>	8.00 × 10 <sup>-3</sup>	1.55 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	1.20 × 10 <sup>-2</sup>	2.37 × 10 <sup>-2</sup>
2.00 × 10 <sup>-5</sup>	1.60 × 10 <sup>-2</sup>	3.25 × 10 <sup>-2</sup>
<i>k</i> <sub>2</sub> = 2.04 M <sup>-1</sup> s <sup>-1</sup>		



**1c** + **2g** in THF (20 °C, stopped flow, decrease at 500 nm)

AB-12

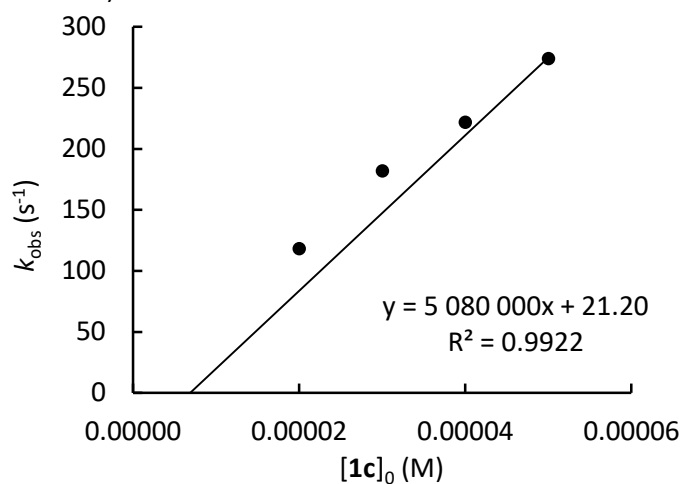
[ <b>2g</b> ] <sub>0</sub> (M)	[ <b>1c</b> ] <sub>0</sub> (M)	<i>k</i> <sub>obs</sub> (s <sup>-1</sup> )
2.00 × 10 <sup>-5</sup>	4.00 × 10 <sup>-3</sup>	1.97 × 10 <sup>-3</sup>
2.00 × 10 <sup>-5</sup>	8.00 × 10 <sup>-3</sup>	3.78 × 10 <sup>-3</sup>
2.00 × 10 <sup>-5</sup>	1.20 × 10 <sup>-2</sup>	5.76 × 10 <sup>-3</sup>
2.00 × 10 <sup>-5</sup>	1.60 × 10 <sup>-2</sup>	7.93 × 10 <sup>-3</sup>
<i>k</i> <sub>2</sub> = 4.97 × 10 <sup>-1</sup> M <sup>-1</sup> s <sup>-1</sup>		



**1c + 2h** in THF (20 °C, stopped flow, decrease at 625 nm)

AB-18

$[2h]_0$ (M)	$[1c]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$5.00 \times 10^{-6}$	$2.00 \times 10^{-5}$	$1.18 \times 10^2$
$5.00 \times 10^{-6}$	$3.00 \times 10^{-5}$	$1.90 \times 10^2$
$5.00 \times 10^{-6}$	$4.00 \times 10^{-5}$	$2.25 \times 10^2$
$5.00 \times 10^{-6}$	$5.00 \times 10^{-5}$	$2.78 \times 10^2$
$k_2 = 5.08 \times 10^6 M^{-1} s^{-1}$		



**1c + 2j** in THF (20 °C, stopped flow, decrease at 639 nm)

AB-16

$[2j]_0$ (M)	$[1c]_0$ (M)	$k_{obs}$ ( $s^{-1}$ )
$5.00 \times 10^{-6}$	$2.00 \times 10^{-5}$	$2.10 \times 10^1$
$5.00 \times 10^{-6}$	$3.00 \times 10^{-5}$	$3.09 \times 10^1$
$5.00 \times 10^{-6}$	$4.00 \times 10^{-5}$	$4.30 \times 10^1$
$5.00 \times 10^{-6}$	$5.00 \times 10^{-5}$	$5.54 \times 10^1$
$k_2 = 1.15 \times 10^6 M^{-1} s^{-1}$		

