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*obs determination [evaluated data]
* pdf files with results of the *k*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 (± 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**]0 (M) | [**1a**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 5.00 × 10-4 | 1.32 × 101 |
| 2.00 × 10-5 | 1.00 × 10-3 | 2.62 × 101 |
| 2.00 × 10-5 | 1.50 × 10-3 | 3.93 × 101 |
| 2.00 × 10-5 | 2.00 × 10-3 | 5.33 × 101 |
| *k*2 = 2.67 × 104 M-1 s-1 | | |

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

*AB-56*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [**2c**]0 (M) | *k*obs (s-1) |
| 1.00 × 10-3 | 5.00 × 10-3 | 8.46 × 101 |
| 1.00 × 10-3 | 8.00 × 10-3 | 1.37 × 102 |
| 1.00 × 10-3 | 1.10 × 10-2 | 1.84 × 102 |
| 1.00 × 10-3 | 1.40 × 10-2 | 2.33 × 102 |
| *k*2 = 1.64 × 104 M-1 s-1 | | |

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

*AB-54*

|  |  |  |
| --- | --- | --- |
| [**2f**]0 (M) | [**1a**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 1.00 × 10-3 | 7.67 × 10-1 |
| 2.00 × 10-5 | 1.50 × 10-3 | 1.20 |
| 2.00 × 10-5 | 2.00 × 10-3 | 1.58 |
| *k*2 = 8.13 × 102 M-1 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 × 10-5 | 5.00 × 10-4 | 1.00 × 10-1 |
| 2.00 × 10-5 | 1.00 × 10-3 | 2.02 × 10-1 |
| 2.00 × 10-5 | 1.50 × 10-3 | 2.96 × 10-1 |
| 2.00 × 10-5 | 2.00 × 10-3 | 4.03 × 10-1 |
| *k*2 = 2.01 × 102 M-1 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 × 10-6 | 2.50 × 10-5 | 1.15 × 102 |
| 5.00 × 10-6 | 4.00 × 10-5 | 1.75 × 102 |
| 5.00 × 10-6 | 5.50 × 10-5 | 2.32 × 102 |
| 5.00 × 10-6 | 7.00 × 10-5 | 3.13 × 102 |
| *k*2 = 4.34 × 106 M-1 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 × 10-5 | 2.00 × 10-4 | 3.86 |
| 2.00 × 10-5 | 4.00 × 10-4 | 8.11 |
| 2.00 × 10-5 | 6.00 × 10-4 | 1.21 × 101 |
| 2.00 × 10-5 | 8.00 × 10-4 | 1.60 × 101 |
| *k*2 = 2.02 × 104 M-1 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 × 10-4 | 4.00 × 10-3 | 3.97 × 101 |
| 8.00 × 10-4 | 6.40 × 10-3 | 6.17 × 101 |
| 8.00 × 10-4 | 8.80 × 10-3 | 8.36 × 101 |
| 8.00 × 10-4 | 1.12 × 10-2 | 1.07 × 102 |
| *k*2 = 9.33 × 103 M-1 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 × 10-5 | 1.20 × 10-4 | 5.42 × 10-2 |
| 2.00 × 10-5 | 2.40 × 10-4 | 1.09 × 10-1 |
| 2.00 × 10-5 | 3.60 × 10-4 | 1.65 × 10-1 |
| 2.00 × 10-5 | 4.80 × 10-4 | 2.19 × 10-1 |
| *k*2 = 4.59 × 102 M-1 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 × 10-5 | 1.20 × 10-4 | 1.45 × 10-2 |
| 2.00 × 10-5 | 2.40 × 10-4 | 2.99 × 10-2 |
| 2.00 × 10-5 | 3.60 × 10-4 | 4.41 × 10-2 |
| 2.00 × 10-5 | 4.80 × 10-4 | 5.61 × 10-2 |
| *k*2 = 1.16 × 102 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 × 10-6 | 2.50 × 10-5 | 4.69 × 101 |
| 5.00 × 10-6 | 4.00 × 10-5 | 8.61 × 101 |
| 5.00 × 10-6 | 5.50 × 10-5 | 1.21 × 102 |
| 5.00 × 10-6 | 7.00 × 10-5 | 1.59 × 102 |
| *k*2 = 2.47 × 106 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**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 5.00 × 10-4 | 5.65 |
| 2.00 × 10-5 | 1.00 × 10-3 | 1.08 × 101 |
| 2.00 × 10-5 | 1.50 × 10-3 | 1.53 × 101 |
| 2.00 × 10-5 | 2.00 × 10-3 | 2.05 × 101 |
| *k*2 = 9.81 × 103 M-1 s-1 | | |

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

*AB-19*

|  |  |  |
| --- | --- | --- |
| [**1c**]0 (M) | [**2c**]0 (M) | *k*obs (s-1) |
| 3.50 × 10-4 | 3.50 × 10-3 | 1.42 × 101 |
| 3.50 × 10-4 | 5.25 × 10-3 | 2.01 × 101 |
| 3.50 × 10-4 | 7.00 × 10-3 | 2.72 × 101 |
| 3.50 × 10-4 | 8.75 × 10-3 | 3.22 × 101 |
| *k*2 = 3.49 × 103 M-1 s-1 | | |

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

*AB-20*

|  |  |  |
| --- | --- | --- |
| [**2f**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 4.00 × 10-3 | 6.36 × 10-1 |
| 2.00 × 10-5 | 8.00 × 10-3 | 1.27 |
| 2.00 × 10-5 | 1.20 × 10-2 | 1.91 |
| 2.00 × 10-5 | 1.60 × 10-2 | 2.57 |
| *k*2 = 1.61 × 102 M-1 s-1 | | |

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

*AB-22*

|  |  |  |
| --- | --- | --- |
| [**2j**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 3.00 × 10-6 | 1.20 × 10-5 | 1.60 × 101 |
| 3.00 × 10-6 | 1.80 × 10-5 | 2.38 × 101 |
| 3.00 × 10-6 | 2.40 × 10-5 | 3.34 × 101 |
| 3.00 × 10-6 | 3.00 × 10-5 | 4.20 × 101 |
| *k*2 = 1.46 × 106 M-1 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**]0 (M) | [**1d**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 2.00 × 10-4 | 4.49 × 10-1 |
| 2.00 × 10-5 | 4.00 × 10-4 | 9.12 × 10-1 |
| 2.00 × 10-5 | 6.00 × 10-4 | 1.44 |
| 2.00 × 10-5 | 8.00 × 10-4 | 1.92 |
| *k*2 = 2.47 × 103 M-1 s-1 | | |

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

*AB-60*

|  |  |  |
| --- | --- | --- |
| [**1d**]0 (M) | [**2c**]0 (M) | *k*obs (s-1) |
| 8.00 × 10-4 | 4.00 × 10-3 | 6.45 |
| 8.00 × 10-4 | 8.00 × 10-3 | 1.20 × 101 |
| 8.00 × 10-4 | 1.20 × 10-2 | 1.71 × 101 |
| 8.00 × 10-4 | 1.60 × 10-2 | 2.23 × 101 |
| *k*2 = 1.32 × 103 M-1 s-1 | | |

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

*AB-58*

|  |  |  |
| --- | --- | --- |
| [**2f**]0 (M) | [**1d**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 2.00 × 10-4 | 1.89 × 10-2 |
| 2.00 × 10-5 | 4.00 × 10-4 | 3.80 × 10-2 |
| 2.00 × 10-5 | 6.00 × 10-4 | 5.81 × 10-2 |
| 2.00 × 10-5 | 8.00 × 10-4 | 7.61 × 10-2 |
| *k*2 = 9.59 × 101 M-1 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 × 10-5 | 2.00 × 10-4 | 5.51 × 10-3 |
| 2.00 × 10-5 | 4.00 × 10-4 | 1.02 × 10-2 |
| 2.00 × 10-5 | 6.00 × 10-4 | 1.57 × 10-2 |
| 2.00 × 10-5 | 8.00 × 10-4 | 2.03 × 10-2 |
| *k*2 = 2.49 × 101 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 × 10-6 | 2.50 × 10-5 | 1.61 × 101 |
| 5.00 × 10-6 | 5.00 × 10-5 | 3.57 × 101 |
| 5.00 × 10-6 | 7.50 × 10-5 | 5.50 × 101 |
| 5.00 × 10-6 | 1.00 × 10-4 | 7.29 × 101 |
| *k*2 = 7.59 × 105 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*

|  |  |  |
| --- | --- | --- |
| [**2a**]0 (M) | [**1e**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 1.00 × 10-4 | 1.15 × 101 |
| 2.00 × 10-5 | 1.60 × 10-4 | 1.81 × 101 |
| 2.00 × 10-5 | 2.20 × 10-4 | 2.44 × 101 |
| 2.00 × 10-5 | 2.80 × 10-4 | 2.98 × 101 |
| *k*2 = 1.02 × 105 M-1 s-1 | | |

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

*AB-28*

|  |  |  |
| --- | --- | --- |
| [**2b**]0 (M) | [**1e**]0 (M) | *k*obs (s-1) |
| 3.00 × 10-5 | 1.50 × 10-4 | 1.48 |
| 3.00 × 10-5 | 3.00 × 10-4 | 2.79 |
| 3.00 × 10-5 | 4.50 × 10-4 | 4.28 |
| 3.00 × 10-5 | 6.00 × 10-4 | 5.82 |
| *k*2 = 9.67 × 103 M-1 s-1 | | |

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

*AB-65*

|  |  |  |
| --- | --- | --- |
| [**2c**]0 (M) | [**1e**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 1.00 × 10-4 | 3.06 × 10-1 |
| 2.00 × 10-5 | 1.60 × 10-4 | 5.00 × 10-1 |
| 2.00 × 10-5 | 2.20 × 10-4 | 6.91 × 10-1 |
| 2.00 × 10-5 | 2.80 × 10-4 | 8.64 × 10-1 |
| *k*2 = 3.11 × 103 M-1 s-1 | | |

**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 × 10-6 | 2.50 × 10-5 | 1.80 × 102 |
| 5.00 × 10-6 | 4.00 × 10-5 | 3.01 × 102 |
| 5.00 × 10-6 | 5.50 × 10-5 | 3.99 × 102 |
| 5.00 × 10-6 | 7.00 × 10-5 | 5.09 × 102 |
| *k*2 = 7.23 × 106 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 × 10-6 | 2.50 × 10-5 | 4.19 × 101 |
| 5.00 × 10-6 | 4.00 × 10-5 | 6.87 × 101 |
| 5.00 × 10-6 | 5.50 × 10-5 | 9.31 × 101 |
| 5.00 × 10-6 | 7.00 × 10-5 | 1.19 × 102 |
| *k*2 = 1.70 × 106 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**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 1.00 × 10-3 | 3.88 |
| 2.00 × 10-5 | 2.00 × 10-3 | 8.99 |
| 2.00 × 10-5 | 3.00 × 10-3 | 1.38 × 101 |
| 2.00 × 10-5 | 4.00 × 10-3 | 1.77 × 101 |
| *k*2 = 4.63 × 103 M-1 s-1 | | |

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

*AB-50*

|  |  |  |
| --- | --- | --- |
| [**1c**]0 (M) | [**2c**]0 (M) | *k*obs (s-1) |
| 3.50 × 10-4 | 3.50 × 10-3 | 6.08 |
| 3.50 × 10-4 | 5.25 × 10-3 | 9.26 |
| 3.50 × 10-4 | 7.00 × 10-3 | 1.25 × 101 |
| 3.50 × 10-4 | 8.75 × 10-3 | 1.58 × 101 |
| *k*2 = 1.85 × 103 M-1 s-1 | | |

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

*AB-47*

|  |  |  |
| --- | --- | --- |
| [**2f**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 1.00 × 10-3 | 9.67 × 10-2 |
| 2.00 × 10-5 | 2.00 × 10-3 | 1.94 × 10-1 |
| 2.00 × 10-5 | 3.00 × 10-3 | 2.95 × 10-1 |
| 2.00 × 10-5 | 4.00 × 10-3 | 3.87 × 10-1 |
| *k*2 = 9.72 × 101 M-1 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 × 10-5 | 1.00 × 10-3 | 4.17 × 10-2 |
| 2.00 × 10-5 | 2.00 × 10-3 | 8.35 × 10-2 |
| 2.00 × 10-5 | 3.00 × 10-3 | 1.27 × 10-1 |
| 2.00 × 10-5 | 4.00 × 10-3 | 1.67 × 10-1 |
| *k*2 = 4.19 × 101 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 × 10-6 | 4.00 × 10-5 | 3.30 × 101 |
| 5.00 × 10-6 | 8.00 × 10-5 | 6.80 × 101 |
| 5.00 × 10-6 | 1.20 × 10-4 | 1.06 × 102 |
| 5.00 × 10-6 | 1.60 × 10-4 | 1.39 × 102 |
| *k*2 = 8.90 × 105 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*

|  |  |  |
| --- | --- | --- |
| [**2b**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.50 × 10-5 | 5.00 × 10-4 | 4.23 × 10-1 |
| 2.50 × 10-5 | 1.00 × 10-3 | 8.93 × 10-1 |
| 2.50 × 10-5 | 1.50 × 10-3 | 1.34 |
| 2.50 × 10-5 | 2.00 × 10-3 | 1.76 |
| *k*2 = 8.92 × 102 M-1 s-1 | | |

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

*AEM-353*

|  |  |  |
| --- | --- | --- |
| [**2f**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 5.00 × 10-4 | 2.42 × 10-2 |
| 2.00 × 10-5 | 1.00 × 10-3 | 4.58 × 10-2 |
| 2.00 × 10-5 | 1.50 × 10-3 | 6.70 × 10-2 |
| 2.00 × 10-5 | 2.00 × 10-3 | 9.07 × 10-2 |
| *k*2 = 4.41 × 101 M-1 s-1 | | |

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

*AEM-352*

|  |  |  |
| --- | --- | --- |
| [**2g**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 5.00 × 10-4 | 1.13 × 10-2 |
| 2.00 × 10-5 | 1.00 × 10-3 | 2.30 × 10-2 |
| 2.00 × 10-5 | 1.50 × 10-3 | 3.34 × 10-2 |
| 2.00 × 10-5 | 2.00 × 10-3 | 4.36 × 10-2 |
| *k*2 = 2.15 × 101 M-1 s-1 | | |

**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 × 10-6 | 1.25 × 10-5 | 2.90 × 101 |
| 2.50 × 10-6 | 2.00 × 10-5 | 5.13 × 101 |
| 2.50 × 10-6 | 2.75 × 10-5 | 6.97 × 101 |
| 2.50 × 10-6 | 3.50 × 10-5 | 8.94 × 101 |
| *k*2 = 2.66 × 106 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 × 10-6 | 1.65 × 10-5 | 2.97 × 101 |
| 3.30 × 10-6 | 2.64 × 10-5 | 5.29 × 101 |
| 3.30 × 10-6 | 3.63 × 10-5 | 7.47 × 101 |
| 3.30 × 10-6 | 4.62 × 10-5 | 9.90 × 101 |
| *k*2 = 2.32 × 106 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 × 10-6 | 1.65 × 10-5 | 9.92 |
| 3.30 × 10-6 | 2.64 × 10-5 | 1.72 × 101 |
| 3.30 × 10-6 | 3.63 × 10-5 | 2.32 × 101 |
| 3.30 × 10-6 | 4.62 × 10-5 | 2.90 × 101 |
| *k*2 = 6.39 × 105 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*

|  |  |  |
| --- | --- | --- |
| [**2b**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 1.00 × 10-3 | 1.25 × 10-1 |
| 2.00 × 10-5 | 2.00 × 10-3 | 2.44 × 10-1 |
| 2.00 × 10-5 | 3.00 × 10-3 | 3.79 × 10-1 |
| 2.00 × 10-5 | 4.00 × 10-3 | 4.97 × 10-1 |
| *k*2 = 1.25 × 102 M-1 s-1 | | |

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

*AB-13*

|  |  |  |
| --- | --- | --- |
| [**2f**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 4.00 × 10-3 | 8.00 × 10-3 |
| 2.00 × 10-5 | 8.00 × 10-3 | 1.55 × 10-2 |
| 2.00 × 10-5 | 1.20 × 10-2 | 2.37 × 10-2 |
| 2.00 × 10-5 | 1.60 × 10-2 | 3.25 × 10-2 |
| *k*2 = 2.04 M-1 s-1 | | |

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

*AB-12*

|  |  |  |
| --- | --- | --- |
| [**2g**]0 (M) | [**1c**]0 (M) | *k*obs (s-1) |
| 2.00 × 10-5 | 4.00 × 10-3 | 1.97 × 10-3 |
| 2.00 × 10-5 | 8.00 × 10-3 | 3.78 × 10-3 |
| 2.00 × 10-5 | 1.20 × 10-2 | 5.76 × 10-3 |
| 2.00 × 10-5 | 1.60 × 10-2 | 7.93 × 10-3 |
| *k*2 = 4.97 × 10-1 M-1 s-1 | | |

**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 × 10-6 | 2.00 × 10-5 | 1.18 × 102 |
| 5.00 × 10-6 | 3.00 × 10-5 | 1.90 × 102 |
| 5.00 × 10-6 | 4.00 × 10-5 | 2.25 × 102 |
| 5.00 × 10-6 | 5.00 × 10-5 | 2.78 × 102 |
| *k*2 = 5.08 × 106 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 × 10-6 | 2.00 × 10-5 | 2.10 × 101 |
| 5.00 × 10-6 | 3.00 × 10-5 | 3.09 × 101 |
| 5.00 × 10-6 | 4.00 × 10-5 | 4.30 × 101 |
| 5.00 × 10-6 | 5.00 × 10-5 | 5.54 × 101 |
| *k*2 = 1.15 × 106 M-1 s-1 | | |