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 (λmax) 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*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°C) = *s*N (*N* + *E*) (1)

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

*AEM-399*

|  |  |  |
| --- | --- | --- |
| [**1a**]0 (M) | [**5b**]0 (M) | *k*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 |
| *k*2 = 2.48 × 101 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) | *k*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 |
| *k*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) | *k*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 |
| *k*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) | *k*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 |
| *k*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) | *k*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 × 101 |
| 2.00 × 10-4 | 4.00 × 10-3 | 1.69 × 101 |
| *k*2 = 3.81 × 103 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) | *k*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 |
| *k*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) | *k*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 × 100 |
| 2.75 × 10-4 | 8.25 × 10-3 | 1.71 × 100 |
| 2.75 × 10-4 | 1.10 × 10-2 | 2.33 × 100 |
| *k*2 = 2.07 × 102 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) | *k*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 |
| *k*2 = 1.19 × 102 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) | *k*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 |
| *k*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) | *k*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 |
| *k*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) | *k*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 |
| *k*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) | *k*obs (s–1) |
| 4.00 × 10-4 | 6.00 × 10-3 | 6.18 × 100 |
| 4.00 × 10-4 | 1.00 × 10-2 | 1.05 × 101 |
| 4.00 × 10-4 | 1.40 × 10-2 | 1.54 × 101 |
| 4.00 × 10-4 | 1.80 × 10-2 | 1.99 × 101 |
| *k*2 = 1.15 × 103 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) | *k*obs (s–1) |
| 4.00 × 10-4 | 1.20 × 10-2 | 8.49 |
| 4.00 × 10-4 | 1.60 × 10-2 | 1.11 × 101 |
| 4.00 × 10-4 | 2.00 × 10-2 | 1.37 × 101 |
| 4.00 × 10-4 | 2.40 × 10-2 | 1.66 × 101 |
| *k*2 = 6.73 × 102 M–1 s–1 | | |

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

*AEM-118*

|  |  |  |
| --- | --- | --- |
| [**1c**]0 (M) | [**5c**]0 (M) | *k*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 |
| *k*2 = 2.36 × 101 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) | *k*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 |
| *k*2 = 1.07 × 101 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) | *k*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 |
| *k*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) | *k*obs (s–1) |
| 5.00 × 10-4 | 5.00 × 10-3 | 2.12 × 101 |
| 5.00 × 10-4 | 1.00 × 10-2 | 3.07 × 101 |
| 5.00 × 10-4 | 1.50 × 10-2 | 4.32 × 101 |
| 5.00 × 10-4 | 2.00 × 10-2 | 5.81 × 101 |
| *k*2 = 2.46 × 103 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) | *k*obs (s–1) |
| 5.00 × 10-4 | 1.00 × 10-2 | 1.37 × 101 |
| 5.00 × 10-4 | 1.50 × 10-2 | 1.80 × 101 |
| 5.00 × 10-4 | 2.00 × 10-2 | 2.36 × 101 |
| 5.00 × 10-4 | 2.50 × 10-2 | 3.08 × 101 |
| *k*2 = 1.14 × 103 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) | *k*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 |
| *k*2 = 2.03 × 101 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) | *k*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 |
| *k*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) | *k*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 |
| *k*2 = 8.11 × 101 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) | *k*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 |
| *k*2 = 4.19 × 101 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) | *k*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 |
| *k*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) | *k*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 |
| *k*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) | *k*obs (s–1) |
| 7.18 × 10-4 | 2.50 × 10-3 | 1.36 × 101 |
| 7.18 × 10-4 | 5.00 × 10-3 | 2.40 × 101 |
| 7.18 × 10-4 | 7.50 × 10-3 | 3.80 × 101 |
| 7.18 × 10-4 | 1.00 × 10-2 | 5.19 × 101 |
| *k*2 = 5.16 × 103 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) | *k*obs (s–1) |
| 7.18 × 10-4 | 5.00 × 10-3 | 1.62 × 101 |
| 7.18 × 10-4 | 1.00 × 10-2 | 2.98 × 101 |
| 7.18 × 10-4 | 1.50 × 10-2 | 4.77 × 101 |
| 7.18 × 10-4 | 2.00 × 10-2 | 6.53 × 101 |
| *k*2 = 3.30 × 103 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) | *k*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 |
| *k*2 = 1.11 × 102 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 × 101 M–1 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 × 101 |
| 2.50 × 10-5 | 3.75 × 10-4 | 2.85 × 101 |
| 2.50 × 10-5 | 5.00 × 10-4 | 4.25 × 101 |
| 2.50 × 10-5 | 6.25 × 10-4 | 5.35 × 101 |
| *k*2 = 1.06 × 105 M–1 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 × 101 |
| 2.50 × 10-5 | 5.00 × 10-4 | 2.13 × 101 |
| 2.50 × 10-5 | 6.25 × 10-4 | 2.91 × 101 |
| 2.50 × 10-5 | 7.50 × 10-4 | 3.50 × 101 |
| *k*2 = 5.21 × 104 M–1 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) | *k*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 |
| *k*2 = 9.39 × 103 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) | *k*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 |
| *k*2 = 4.50 × 103 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) | *k*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 |
| *k*2 = 3.38 × 103 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) | *k*obs (s–1) |
| 8.00 × 10-4 | 4.00 × 10-3 | 1.63 × 102 |
| 8.00 × 10-4 | 6.00 × 10-3 | 2.18 × 102 |
| 8.00 × 10-4 | 8.00 × 10-3 | 2.67 × 102 |
| 8.00 × 10-4 | 1.00 × 10-2 | 3.12 × 102 |
| *k*2 = 2.48 × 104 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) | *k*obs (s–1) |
| 1.00 × 10-3 | 5.00 × 10-3 | 1.55 × 102 |
| 1.00 × 10-3 | 8.00 × 10-3 | 2.10 × 102 |
| 1.00 × 10-3 | 1.10 × 10-2 | 2.72 × 102 |
| 1.00 × 10-3 | 1.40 × 10-2 | 3.31 × 102 |
| *k*2 = 1.97 × 104 M–1 s–1 | | |

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

*AEM-435*

|  |  |  |
| --- | --- | --- |
| [**1h**]0 (M) | [**8**]0 (M) | *k*obs (s–1) |
| 8.00 × 10-4 | 4.00 × 10-3 | 3.55 × 101 |
| 8.00 × 10-4 | 8.00 × 10-3 | 6.48 × 101 |
| 8.00 × 10-4 | 1.20 × 10-2 | 9.09 × 101 |
| 8.00 × 10-4 | 1.60 × 10-2 | 1.17 × 102 |
| *k*2 = 6.77 × 103 M–1 s–1 | | |

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

*AEM-436*

|  |  |  |
| --- | --- | --- |
| [**1h**]0 (M) | [**16**]0 (M) | *k*obs (s–1) |
| 8.00 × 10-4 | 4.00 × 10-3 | 5.86 × 101 |
| 8.00 × 10-4 | 8.00 × 10-3 | 8.95 × 101 |
| 8.00 × 10-4 | 1.20 × 10-2 | 1.32 × 102 |
| 8.00 × 10-4 | 1.60 × 10-2 | 1.62 × 102 |
| *k*2 = 8.82 × 103 M–1 s–1 | | |