Supporting Information

**Kinetic measurements used to determine   
the electrophilicity of *δ*-functionalized *para*-quinone methides (*δ*-FG-*p*QMs)**

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**Data storage system:**

Folder and file names CGxxx 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 of the Reactions of *δ*-FG-*p*QMs with Carbanions**

Kinetic measurements were performed by using UV/Vis photometry on AppliedPhotophysics SX.20 stopped-flow instruments as well as on a conventional J&M TIDAS diode array spectrophotometer, which was controlled by TIDASDAQ3 (v3) software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (light path *d* = 5 mm) via fiber optic cables and standard SMA connectors. The temperature (20.0 ± 0.2 °C) was maintained constant by using circulating bath cryostats.

All solutions were prepared by using dry DMSO (ThermoScientific, DMSO 99.7+%, extra dry, over molecular sieve, AcroSeal) and kept under an atmosphere of dry nitrogen. The kinetic measurements for each *δ*-FG-*p*QM/nucleophile combination **1** + **2** were performed with or without added 18-crown-6 ether (18-c-6) and in some cases with addition of the corresponding CH-acid (**2**-H).



**1a** + **2a** in DMSO (stopped-flow, detection at 310 nm) CG544



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1a**]0 (M) | [**2a**]0 (M) | [**2a**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 2.50 × 10–5 | 1.20 × 10–3 | 1.20 × 10–3 |  | 1.56 × 10–1 |
| 2.50 × 10–5 | 1.80 × 10–3 | 1.80 × 10–3 | 1.98 × 10–3 | 2.26 × 10–1 |
| 2.50 × 10–5 | 2.40 × 10–3 | 2.40 × 10–3 |  | 2.94 × 10–1 |
| 2.50 × 10–5 | 3.00 × 10–3 | 3.00 × 10–3 | 3.30 × 10–3 | 3.69 × 10–1 |
| 2.50 × 10–5 | 3.60 × 10–3 | 3.60 × 10–3 |  | 4.36 × 10–1 |

***k*2 = (1.17 ± 0.01) × 102 M–1 s–1**

**1a** + **2b** in DMSO (stopped-flow, detection at 320 nm) CG708



|  |  |  |  |
| --- | --- | --- | --- |
| [**1a**]0 (M) | [**2b**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 5.50 × 10–5 | 3.00 × 10–4 |  | 5.46 × 10–1 |
| 5.50 × 10–5 | 4.50 × 10–4 | 4.95 × 10–4 | 7.98 × 10–1 |
| 5.50 × 10–5 | 6.00 × 10–4 |  | 1.06 |
| 5.50 × 10–5 | 7.50 × 10–4 | 8.25 × 10–4 | 1.30 |
| 5.50 × 10–5 | 9.00 × 10–4 |  | 1.59 |

***k*2 = (1.73 ± 0.03) × 103 M–1 s–1**

**1a**+ **2c** in DMSO (stopped-flow, detection at 310 nm) CG541



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1a**]0 (M) | [**2c**]0 (M) | [**2c**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 2.18 × 10–5 | 6.00 × 10–4 | 6.00 × 10–4 |  | 5.79 |
| 2.18 × 10–5 | 9.00 × 10–4 | 9.00 × 10–4 | 9.90 × 10–4 | 7.91 |
| 2.18 × 10–5 | 1.20 × 10–3 | 1.20 × 10–3 |  | 9.92 |
| 2.18 × 10–5 | 1.50 × 10–3 | 1.50 × 10–3 | 1.65 × 10–3 | 11.9 |

***k*2 = (6.78 ± 0.08) × 103 M–1 s–1**

**1c** + **2a** in DMSO (stopped-flow, detection at 318 nm) CG081



|  |  |  |  |
| --- | --- | --- | --- |
| [**1c**]0 (M) | [**2a**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.90 × 10–5 | 1.75 × 10–4 |  | 3.32 × 10–3 |
| 1.90 × 10–5 | 2.63 × 10–4 | 2.89 × 10–4 | 5.59 × 10–3 |
| 1.90 × 10–5 | 3.50 × 10–4 |  | 7.39 × 10–3 |
| 1.90 × 10–5 | 4.38 × 10–4 | 4.82 × 10–4 | 9.25 × 10–3 |
| 1.90 × 10–5 | 5.25 × 10–4 |  | 1.15 × 10–2 |

***k*2 = (2.29 ± 0.06) × 101 M–1 s–1**

**1c** + **2c** in DMSO (stopped-flow, detection at 318 nm) CG071



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1c**]0 (M) | [**2c**]0 (M) | [**2c**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.90 × 10–5 | 1.75 × 10–4 | 1.75 × 10–4 |  | 8.97 × 10–1 |
| 1.90 × 10–5 | 2.63 × 10–4 | 2.63 × 10–4 | 2.89 × 10–4 | 1.34 |
| 1.90 × 10–5 | 3.50 × 10–4 | 3.50 × 10–4 |  | 1.76 |
| 1.90 × 10–5 | 4.38 × 10–4 | 4.38 × 10–4 | 4.82 × 10–4 | 2.19 |
| 1.90 × 10–5 | 5.25 × 10–4 | 5.25 × 10–4 |  | 2.65 |

***k*2 = (4.98 ± 0.04) × 103 M–1 s–1**

**1c** + **2d** in DMSO (stopped-flow, detection at 318 nm) CG083



|  |  |  |  |
| --- | --- | --- | --- |
| [**1c**]0 (M) | [**2d**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.13 × 10–5 | 1.13 × 10–4 |  | 2.95 × 10–1 |
| 1.13 × 10–5 | 1.69 × 10–4 | 1.86 × 10–4 | 4.58 × 10–1 |
| 1.13 × 10–5 | 2.25 × 10–4 |  | 5.83 × 10–1 |
| 1.13 × 10–5 | 2.82 × 10–4 | 3.10 × 10–4 | 7.57 × 10–1 |

***k*2 = (2.68 ± 0.11) × 103 M–1 s–1**

**1c** + **2h** in DMSO (stopped-flow, detection at 318 nm) CG074



|  |  |  |  |
| --- | --- | --- | --- |
| [**1c**]0 (M) | [**2h**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.75 × 10–5 | 1.75 × 10–4 |  | 1.62 × 101 |
| 1.75 × 10–5 | 2.63 × 10–4 | 2.89 × 10–4 | 2.37 × 101 |
| 1.75 × 10–5 | 3.50 × 10–4 |  | 3.21 × 101 |
| 1.75 × 10–5 | 4.38 × 10–4 | 4.82 × 10–4 | 3.98 × 101 |
| 1.75 × 10–5 | 5.25 × 10–4 |  | 4.71 × 101 |

***k*2 = (8.90 ± 0.12) × 104 M–1 s–1**

**1c** + **2i** in DMSO (stopped-flow, detection at 318 nm) CG186



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1c**]0 (M) | [**2i**]0 (M) | [**2i**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 2.03 × 10–5 | 1.75 × 10–4 | 1.75 × 10–4 |  | 6.36 × 101 |
| 2.03 × 10–5 | 2.63 × 10–4 | 2.63 × 10–4 | 2.89 × 10–4 | 9.48 × 101 |
| 2.03 × 10–5 | 3.50 × 10–4 | 3.50 × 10–4 |  | 1.31 × 102 |
| 2.03 × 10–5 | 4.38 × 10–4 | 4.38 × 10–4 | 4.82 × 10–4 | 1.60 × 102 |

***k*2 = (3.71 ± 0.11) × 105 M–1 s–1**

**1d** + **2c** in DMSO (stopped-flow, detection at 309 nm) CG534



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1d**]0 (M) | [**2c**]0 (M) | [**2c**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 2.22 × 10–5 | 2.00 × 10–4 | 2.00 × 10–4 |  | 4.95 × 10–1 |
| 2.22 × 10–5 | 3.00 × 10–4 | 3.00 × 10–4 | 3.30 × 10–4 | 7.07 × 10–1 |
| 2.22 × 10–5 | 4.00 × 10–4 | 4.00 × 10–4 |  | 9.39 × 10–1 |
| 2.22 × 10–5 | 5.00 × 10–4 | 5.00 × 10–4 | 5.50 × 10–4 | 1.16 |
| 2.22 × 10–5 | 6.00 × 10–4 | 6.00 × 10–4 |  | 1.38 |

***k*2 = (2.22 ± 0.02) × 103 M–1 s–1**

**1d** + **2e** in DMSO (stopped-flow, detection at 340 nm) CG533



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1d**]0 (M) | [**2e**]0 (M) | [**2e**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 9.78 × 10–5 | 9.50 × 10–4 | 9.50 × 10–4 |  | 9.42 |
| 9.78 × 10–5 | 1.43 × 10–3 | 1.43 × 10–3 | 1.57 × 10–3 | 1.38 × 101 |
| 9.78 × 10–5 | 1.90 × 10–3 | 1.90 × 10–3 |  | 1.83 × 101 |
| 9.78 × 10–5 | 2.38 × 10–3 | 2.38 × 10–3 | 2.61 × 10–3 | 2.34 × 101 |
| 9.78 × 10–5 | 2.85 × 10–3 | 2.85 × 10–3 |  | 2.73 × 101 |

***k*2 = (9.55 ± 0.18) × 103 M–1 s–1**

**1d** + **2g** in DMSO (stopped-flow, detection at 309 nm) CG531



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1d**]0 (M) | [**2g**]0 (M) | [**2g**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.54 × 10–5 | 2.00 × 10–4 | 2.00 × 10–4 |  | 1.56 × 101 |
| 1.54 × 10–5 | 3.00 × 10–4 | 3.00 × 10–4 | 3.30 × 10–4 | 2.34 × 101 |
| 1.54 × 10–5 | 4.00 × 10–4 | 4.00 × 10–4 |  | 3.09 × 101 |
| 1.54 × 10–5 | 5.00 × 10–4 | 5.00 × 10–4 | 5.50 × 10–4 | 3.82 × 101 |
| 1.54 × 10–5 | 6.00 × 10–4 | 6.00 × 10–4 |  | 4.61 × 101 |

***k*2 = (7.58 ± 0.05) × 104 M–1 s–1**

**1d** + **2h** in DMSO (stopped-flow, detection at 309 nm) CG530



|  |  |  |  |
| --- | --- | --- | --- |
| [**1d**]0 (M) | [**2h**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.70 × 10–5 | 1.00 × 10–4 |  | 2.75 |
| 1.70 × 10–5 | 1.50 × 10–4 | 1.65 × 10–4 | 3.83 |
| 1.70 × 10–5 | 2.00 × 10–4 |  | 5.46 |
| 1.70 × 10–5 | 2.50 × 10–4 | 2.75 × 10–4 | 6.53 |
| 1.70 × 10–5 | 3.00 × 10–4 |  | 7.72 |

***k*2 = (2.53 ± 0.10) × 104 M–1 s–1**

**1d** + **2i** in DMSO (stopped-flow, detection at 309 nm) CG532



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1d**]0 (M) | [**2i**]0 (M) | [**2i**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.75 × 10–5 | 1.00 × 10–4 | 1.00 × 10–4 |  | 1.06 × 101 |
| 1.75 × 10–5 | 1.50 × 10–4 | 1.50 × 10–4 | 1.65 × 10–4 | 1.59 × 101 |
| 1.75 × 10–5 | 2.00 × 10–4 | 2.00 × 10–4 |  | 2.13 × 101 |
| 1.75 × 10–5 | 2.50 × 10–4 | 2.50 × 10–4 | 2.75 × 10–4 | 2.60 × 101 |
| 1.75 × 10–5 | 3.00 × 10–4 | 3.00 × 10–4 |  | 3.16 × 101 |

***k*2 = (1.04 ± 0.01) × 105 M–1 s–1**

**1d** + **2j** in DMSO (stopped-flow, detection at 309 nm) CG523\_1



|  |  |  |  |
| --- | --- | --- | --- |
| [**1d**]0 (M) | [**2j**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.38 × 10–5 | 1.00 × 10–4 |  | 6.42 × 101 |
| 1.38 × 10–5 | 1.50 × 10–4 | 1.65 × 10–4 | 9.74 × 101 |
| 1.38 × 10–5 | 2.00 × 10–4 |  | 1.31 × 102 |
| 1.38 × 10–5 | 2.50 × 10–4 | 2.75 × 10–4 | 1.64 × 102 |
| 1.38 × 10–5 | 3.00 × 10–4 |  | 1.98 × 102 |

***k*2 = (6.68 ± 0.02) × 105 M–1 s–1**

**1e**+ **2c** in DMSO (stopped-flow, detection at 310 nm) CG445\_1



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1e**]0 (M) | [**2c**]0 (M) | [**2c**-H]0 (M) | [18-c-6]0  (M) | *k*obs (s–1) |
| 2.18 × 10–5 | 3.00 × 10–4 | 3.00 × 10–4 |  | 9.45 × 10–2 |
| 2.18 × 10–5 | 4.50 × 10–4 | 4.50 × 10–4 | 4.95 × 10–4 | 1.41 × 10–1 |
| 2.18 × 10–5 | 6.00 × 10–4 | 6.00 × 10–4 |  | 1.79 × 10–1 |
| 2.18 × 10–5 | 7.50 × 10–4 | 7.50 × 10–4 | 8.25 × 10–4 | 2.22 × 10–1 |
|  | 9.00 × 10–4 | 9.00 × 10–4 |  | 2.59 × 10–1 |

***k*2 = (2.73 ± 0.06) × 102 M–1 s–1**

**1e** + **2g** in DMSO (stopped-flow, detection at 320 nm) CG444



|  |  |  |  |
| --- | --- | --- | --- |
| [**1e**]0 (M) | [**2g**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.97 × 10–5 | 6.00 × 10–4 |  | 2.07 |
| 1.97 × 10–5 | 9.00 × 10–4 | 9.90 × 10–4 | 3.46 |
| 1.97 × 10–5 | 1.20 × 10–3 |  | 4.38 |
| 1.97 × 10–5 | 1.50 × 10–3 | 1.65 × 10–3 | 5.33 |
| 1.97 × 10–5 | 1.80 × 10–3 |  | 6.41 |

***k*2 = (3.52 ± 0.15) × 103 M–1 s–1**

**1e** + **2h** in DMSO (stopped-flow, detection at 320 nm) CG441



|  |  |  |  |
| --- | --- | --- | --- |
| [**1e**]0 (M) | [**2h**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.97 × 10–5 | 3.00 × 10–4 |  | 1.59 |
| 1.97 × 10–5 | 4.50 × 10–4 | 4.95 × 10–4 | 2.24 |
| 1.97 × 10–5 | 6.00 × 10–4 |  | 3.00 |
| 1.97 × 10–5 | 7.50 × 10–4 | 8.25 × 10–4 | 3.70 |
| 1.97 × 10–5 | 9.00 × 10–4 |  | 4.27 |

***k*2 = (4.55 ± 0.12) × 103 M–1 s–1**

**1e** + **2i** in DMSO (stopped-flow, detection at 320 nm) CG443



|  |  |  |  |
| --- | --- | --- | --- |
| [**1e**]0 (M) | [**2i**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.97 × 10–5 | 3.00 × 10–4 |  | 1.44 |
| 1.97 × 10–5 | 4.50 × 10–4 | 4.95 × 10–4 | 2.29 |
| 1.97 × 10–5 | 6.00 × 10–4 |  | 2.87 |
| 1.97 × 10–5 | 7.50 × 10–4 | 8.25 × 10–4 | 3.83 |
| 1.97 × 10–5 | 9.00 × 10–4 |  | 4.46 |

***k*2 = (5.05 ± 0.20) × 103 M–1 s–1**

**1e** + **2j** in DMSO (stopped-flow, detection at 320 nm) CG442



|  |  |  |  |
| --- | --- | --- | --- |
| [**1e**]0 (M) | [**2j**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.97 × 10–5 | 3.00 × 10–4 |  | 4.28 |
| 1.97 × 10–5 | 4.50 × 10–4 | 4.95 × 10–4 | 6.47 |
| 1.97 × 10–5 | 6.00 × 10–4 |  | 8.75 |
| 1.97 × 10–5 | 7.50 × 10–4 | 8.25 × 10–4 | 1.12 × 101 |
| 1.97 × 10–5 | 9.00 × 10–4 |  | 1.30 × 101 |

***k*2 = (1.48 ± 0.04) × 104 M–1 s–1**

**1f** + **2e** in DMSO (stopped-flow, detection at 345 nm) CG529



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1f**]0 (M) | [**2e**]0 (M) | [**2e**-H]0, (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.80 × 10–5 | 4.40 × 10–4 | 4.40 × 10–4 |  | 2.27 × 10–2 |
| 1.80 × 10–5 | 6.60 × 10–4 | 6.60 × 10–4 | 7.26 × 10–4 | 3.55 × 10–2 |
| 1.80 × 10–5 | 8.80 × 10–4 | 8.80 × 10–4 |  | 4.48 × 10–2 |
| 1.80 × 10–5 | 1.10 × 10–3 | 1.10 × 10–3 | 1.21 × 10–3 | 5.59 × 10–2 |
| 1.80 × 10–5 | 1.32 × 10–3 | 1.32 × 10–3 |  | 6.58 × 10–2 |

***k*2 = (4.85 ± 0.14) × 101 M–1 s–1**

**1f** + **2g** in DMSO (stopped-flow, detection at 345 nm) CG528



|  |  |  |  |
| --- | --- | --- | --- |
| [**1f**]0 (M) | [**2g**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.97 × 10–5 | 2.20 × 10–4 |  | 1.53 × 10–1 |
| 1.97 × 10–5 | 3.30 × 10–4 | 3.63 × 10–4 | 1.99 × 10–1 |
| 1.97 × 10–5 | 4.40 × 10–4 |  | 2.44 × 10–1 |
| 1.97 × 10–5 | 5.50 × 10–4 | 6.05 × 10–4 | 2.85 × 10–1 |
| 1.97 × 10–5 | 6.60 × 10–4 |  | 3.46 × 10–1 |

***k*2 = (4.29 ± 0.17) × 102 M–1 s–1**

**1f** + **2h** in DMSO (stopped-flow, detection at 345 nm) CG527



|  |  |  |  |
| --- | --- | --- | --- |
| [**1f**]0 (M) | [**2h**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 2.04 × 10–5 | 2.20 × 10–4 |  | 2.28 × 10–1 |
| 2.04 × 10–5 | 3.30 × 10–4 | 3.63 × 10–4 | 3.45 × 10–1 |
| 2.04 × 10–5 | 4.40 × 10–4 |  | 4.49 × 10–1 |
| 2.04 × 10–5 | 5.50 × 10–4 | 6.05 × 10–4 | 5.77 × 10–1 |
| 2.04 × 10–5 | 6.60 × 10–4 |  | 6.86 × 10–1 |

***k*2 = (1.04 ± 0.02) × 103 M–1 s–1**

**1f** + **2j** in DMSO (stopped-flow, detection at 345 nm) CG526



|  |  |  |  |
| --- | --- | --- | --- |
| [**1f**]0 (M) | [**2j**]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 2.08 × 10–5 | 2.20 × 10–4 |  | 4.31 × 10–1 |
| 2.08 × 10–5 | 3.30 × 10–4 | 3.63 × 10–4 | 6.72 × 10–1 |
| 2.08 × 10–5 | 4.40 × 10–4 |  | 8.55 × 10–1 |
| 2.08 × 10–5 | 5.50 × 10–4 | 6.05 × 10–4 | 1.09 |
| 2.08 × 10–5 | 6.60 × 10–4 |  | 1.26 |

***k*2 = (1.89 ± 0.06) × 103 M–1 s–1**

**1g** + **2c** in DMSO (conventional photometry, detection at 359 nm) CG116



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1g**]0 (M) | [**2c**]0 (M) | [**2c**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 3.82 × 10–5 | 3.80 × 10–4 | 3.80 × 10–4 |  | 1.15 × 10–3 |
| 3.65 × 10–5 | 5.50 × 10–4 | 5.50 × 10–4 | 6.04 × 10–4 | 1.51 × 10–3 |
| 3.68 × 10–5 | 7.40 × 10–4 | 7.40 × 10–4 |  | 2.06 × 10–3 |
| 3.58 × 10–5 | 9.00 × 10–4 | 9.00 × 10–4 |  | 2.50 × 10–3 |

***k*2 = (2.63 ± 0.12) M–1 s–1**

**1g** + **2e** in DMSO (stopped-flow, detection at 359 nm) CG115



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1g**]0 (M) | [**2e**]0 (M) | [**2e**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 2.20 × 10–5 | 2.25 × 10–4 | 2.25 × 10–4 |  | 6.91 × 10–3 |
| 2.20 × 10–5 | 3.38 × 10–4 | 3.38 × 10–4 | 3.72 × 10–4 | 1.06 × 10–2 |
| 2.20 × 10–5 | 4.50 × 10–4 | 4.50 × 10–4 |  | 1.48 × 10–2 |
| 2.20 × 10–5 | 5.65 × 10–4 | 5.65 × 10–4 | 6.20 × 10–4 | 1.78 × 10–2 |
| 2.20 × 10–5 | 6.75 × 10–4 | 6.75 × 10–4 |  | 2.17 × 10–2 |

***k*2 = (3.26 ± 0.09) × 101 M–1 s–1**

**1g** + **2g** in DMSO (stopped-flow, detection at 359 nm) CG113



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1g**]0 (M) | [**2g**]0 (M) | [**2g**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.54 × 10–5 | 2.25 × 10–4 | 2.25 × 10–4 |  | 4.50 × 10–2 |
| 1.54 × 10–5 | 3.38 × 10–4 | 3.38 × 10–4 | 3.72 × 10–4 | 6.54 × 10–2 |
| 1.54 × 10–5 | 4.50 × 10–4 | 4.50 × 10–4 |  | 8.98 × 10–2 |
| 1.54 × 10–5 | 5.65 × 10–4 | 5.65 × 10–4 | 6.20 × 10–4 | 1.09 × 10–1 |
| 1.54 × 10–5 | 6.75 × 10–4 | 6.75 × 10–4 |  | 1.32 × 10–1 |

***k*2 = (1.93 ± 0.04) × 102 M–1 s–1**

**1g** + **2h** in DMSO (stopped-flow, detection at 359 nm) CG109



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1g**]0 (M) | [**2h**]  (M) | [**2h**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.79 × 10–5 | 2.25 × 10–4 | 2.25 × 10–4 |  | 5.65 × 10–2 |
| 1.79 × 10–5 | 3.38 × 10–4 | 3.38 × 10–4 | 3.72 × 10–4 | 7.99 × 10–2 |
| 1.79 × 10–5 | 4.50 × 10–4 | 4.50 × 10–4 |  | 1.13 × 10–1 |
| 1.79 × 10–5 | 6.75 × 10–4 | 6.75 × 10–4 |  | 1.76 × 10–1 |

***k*2 = (2.70 ± 0.11) × 102 M–1 s–1**

**1g** + **2i** in DMSO (stopped-flow, detection at 359 nm) CG111



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1g**]0 (M) | [**2i**]0 (M) | [**2i**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.82 × 10–5 | 2.25 × 10–4 | 2.25 × 10–4 |  | 1.24 × 10–1 |
| 1.82 × 10–5 | 3.38 × 10–4 | 3.38 × 10–4 | 3.72 × 10–4 | 1.80 × 10–1 |
| 1.82 × 10–5 | 4.50 × 10–4 | 4.50 × 10–4 |  | 2.49 × 10–1 |
| 1.82 × 10–5 | 5.65 × 10–4 | 5.65 × 10–4 | 6.20 × 10–4 | 3.01 × 10–1 |
| 1.82 × 10–5 | 6.75 × 10–4 | 6.75 × 10–4 |  | 3.77 × 10–1 |

***k*2 = (5.56 ± 0.20) × 102 M–1 s–1**

**1g** + **2j** in DMSO (stopped-flow, detection at 359 nm) CG112



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**1g**]0 (M) | [**2j**]0 (M) | [**2j**-H]0 (M) | [18-c-6]0 (M) | *k*obs (s–1) |
| 1.73 × 10–5 | 2.25 × 10–4 | 2.25 × 10–4 |  | 3.51 × 10–1 |
| 1.73 × 10–5 | 3.38 × 10–4 | 3.38 × 10–4 | 3.72 × 10–4 | 4.87 × 10–1 |
| 1.73 × 10–5 | 4.50 × 10–4 | 4.50 × 10–4 |  | 6.62 × 10–1 |
| 1.73 × 10–5 | 5.65 × 10–4 | 5.65 × 10–4 | 6.20 × 10–4 | 8.03 × 10–1 |
| 1.73 × 10–5 | 6.75 × 10–4 | 6.75 × 10–4 |  | 9.67 × 10–1 |

***k*2 = (1.37 ± 0.03) × 103 M–1 s–1**