

– Supporting Information –

Quantification of the Electrophilic Reactivities of Aldehydes, Imines, and Enones

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1. GENERAL

Chemicals. The sulfonium tetrafluoroborates (**4a,b-H**)-BF₄ were prepared by treatment of the corresponding benzylic alcohols with HBF₄/Et₂O and dimethyl sulfide as reported earlier.^[S1] According to literature reports, 2-(methylsulfinyl)acetate (**4e**)-H was prepared by the oxidation of ethyl 2-(methylthio)acetate with NaIO₄,^[S2] *p*-nitrocinnamaldehyde by aldol condensation of *p*-nitrobenzaldehyde with acetaldehyde^[S3] (**1f**), the enone **3b** by aldol condensation of *p*-cyanobenzaldehyde with acetophenone,^[S4] the imines **2a–c,e** by titanium tetrachloride induced reaction of the corresponding benzaldehydes with *p*-methylbenzenesulfonamide or diphenylphosphinic amide,^[S5] imine **2d** by a procedure starting from benzaldehyde, *t*-butyl carbamate, sodium benzene sulfinate, and formic acid.^[S6] The enones **3e,f** were prepared according to analogous aldol condensations as for *p*-nitrocinnamaldehyde (**1f**). The syntheses of the enones **3a,d** were achieved according to the same procedure as for compound **3b**. All other chemicals were purchased from commercial sources and (if necessary) purified by recrystallization or distillation prior to use.

Analytics. ¹H- and ¹³C-NMR spectra were recorded on Varian NMR-systems (300, 400, or 600 MHz) in CDCl₃ or CD₃CN and the chemical shifts in ppm refer to TMS (δ_{H} 0.00, δ_{C} 0.00) or CD₃CN (δ_{H} 1.94, δ_{C} 1.24) as internal standard. The following abbreviations were used for chemical shift multiplicities: brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. For reasons of simplicity, the ¹H-NMR signals of AA'BB'-spin systems of *p*-disubstituted aromatic rings are treated as doublets. NMR signal assignments were based on additional 2D-NMR experiments (e.g., COSY-, NOESY-, HSQC-, and HMBC experiments). Diastereomeric ratios (*dr*) were determined by ¹H-NMR (³¹P-NMR for compounds **6ea** and **6eb**). (HR-)MS was performed on a Finnigan MAT 95 (EI) or a Thermo

^[S1] Appel, R.; Hartmann, N.; Mayr, H. *J. Am. Chem. Soc.* **2010**, *132*, 17894-17900.

^[S2] Preparation of ethyl 2-(methylthio)acetate: Labuschagne, A. J. H.; Malherbe, J. S.; Meyer, C. J.; Schneider, D. F. *J. Chem. Soc., Perkin Trans. 1* **1978**, 955-961. Oxidation with NaIO₄: Coppola, G. M.; Hardtmann, G. E. *J. Heterocycl. Chem.* **1979**, *16*, 1605-1610.

^[S3] Waley, S. G. *J. Chem. Soc.* **1948**, 2008-2011.

^[S4] Reichardt, C.; Harbusch-Görnert, E.; Schäfer, G. *Liebigs Ann. Chem.* **1988**, 839-844.

^[S5] (a) Jennings, W. B.; Lovely, C. J. *Tetrahedron Lett.* **1988**, *29*, 3725-3728. (b) Jennings, W. B.; Lovely, C. J. *Tetrahedron* **1991**, *47*, 5561-5568.

^[S6] Kanazawa, A. M.; Denis, J.-N.; Greene, A. E. *J. Org. Chem.* **1994**, *59*, 1238-1240.

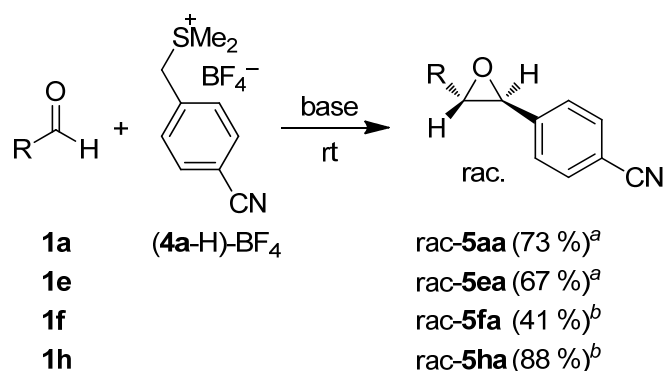
Finnigan LTQ FT (ESI) mass spectrometer. An Elementar Vario Micro Cube or an Elementar vario EL device was used for elemental analysis. Melting points were determined on a Büchi B-540.

Kinetics. The rates of all reactions were determined photometrically. The temperature was kept constant ($20.0 \pm 0.1^\circ\text{C}$) by using a circulating bath thermostat. Stock solutions of the semi-stabilized ylides **4a,b** were prepared by deprotonation of the corresponding CH acids (**4a,b-H**)-BF₄ in dry THF at $\leq -50^\circ\text{C}$ with 1.00-1.05 equiv of KO^{*t*}Bu. Small amounts of these stock solutions were dissolved in DMSO at room temperature directly before each kinetic experiment. The stock solutions of the carbanions **4c-h** were prepared by deprotonation of the corresponding CH-acids (**4c-h**)-H with 1.00-1.05 equiv of KO^{*t*}Bu in DMSO. The kinetic investigations of the reactions of the carbanions **4c-h** with the electrophiles **2a-c** (also prepared as stock solutions in DMSO) were performed with a high excess of the nucleophiles over the electrophiles resulting in first-order kinetics. As the absolute concentrations of the semi-stabilized sulfur ylides **4a,b** cannot be determined precisely (low stability, side reactions during the deprotonation of the CH acids), these compounds have been used as minor components in the reactions with the electrophiles **1-3** also resulting in first-order kinetics. The rates of slow reactions ($\tau_{1/2} > 15\text{-}20\text{ s}$) were determined by using a J&M TIDAS diode array spectrophotometer controlled by Labcontrol Spectacle software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables and standard SMA connectors. For the evaluation of fast kinetics ($\tau_{1/2} < 15\text{-}20\text{ s}$) the stopped-flow spectrophotometer systems Hi-Tech SF-61DX2 or Applied Photophysics SX.18MV-R were used. First-order rate constants k_{obs} (s⁻¹) were obtained by fitting the single exponential $A_t = A_0 \exp(-k_{\text{obs}}t) + C$ (exponential decrease) to the observed time-dependent absorbance (averaged from at least 3 kinetic runs for each nucleophile concentration in case of stopped-flow method). Second-order rate constants k_2 (L mol⁻¹ s⁻¹) were derived from the slopes of the linear correlations of k_{obs} with the concentration of the reaction partner used in excess ([Nu]₀ or [E]₀).

2. PRODUCT ANALYSIS

Although the yields of isolated products are low in some instances, we do not have evidence for significant contributions of side reactions to the rate constants reported in this work. Losses of the products during work up or partial decomposition of the products under the reaction conditions are considered as main reasons for the non-quantitative yields.

2.1 Reactions of the Sulfur Ylide **4a** with the Aldehydes **1a,e,f,h**



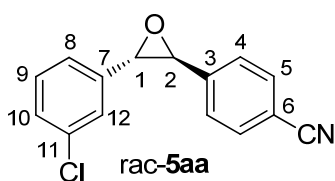
^a KO^tBu, DMSO. ^b K₂CO₃ (aq.), CHCl₃.

Product studies for the reactions of the sulfur ylide **4a** with the aromatic aldehydes **1a,e**

General procedure A. The ylide **4a** was generated by the addition of KO^tBu (dissolved in 2-3 mL DMSO) to a vigorously stirred solution of the sulfonium tetrafluoroborate (**4a-H**)-BF₄ in dry DMSO (2-3 mL) at room temperature. The corresponding aldehyde **1a** or **1e** (dissolved in 2-3 mL DMSO) was then added in one portion. After 10 min of stirring, the reaction was quenched by the addition of water and extracted with CH₂Cl₂. The combined organic layers were washed with water and brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude products were purified by column chromatography on silica gel (*n*-pentane/EtOAc or *i*-hexane/EtOAc) and subsequently characterized by ¹H- and ¹³C-NMR spectroscopy and MS. Signal assignments were based on additional COSY, HSQC and HMBC experiments. Small samples of solid products were recrystallized in appropriate solvent mixtures for the determination of melting points.

4-(3-(3-Chlorophenyl)oxiran-2-yl)benzonitrile (5aa) was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)-BF₄ (300 mg, 1.13 mmol), KO^tBu (127 mg, 1.13 mmol), and *m*-chlorobenzaldehyde (**1a**, 48.0 mg, 341 μmol) as a colorless solid (65 mg, 0.25 mmol, 73 %, only *trans*-isomer).

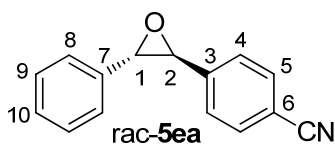
RAP 36.1



R_f (*i*-hexane/EtOAc 12:1, *v/v*): 0.14. Mp. (*n*-pentane/Et₂O): 110-111°C. ¹H-NMR (CDCl₃, 300 MHz): δ = 3.81 (d, 1 H, *J* = 1.8 Hz, 1-H), 3.88 (d, 1 H, *J* = 1.8 Hz, 2-H), 7.21-7.24 (m, 1 H, 12-H), 7.32-7.33 (m, 3 H, 8-H, 9-H, 10-H), 7.44 (d, 2 H, *J* = 8.2 Hz, 4-H), 7.68 (d, 2 H, *J* = 8.4 Hz, 5-H). ¹³C-NMR (CDCl₃, 75.5 MHz): δ = 61.8 (d, C-2), 62.4 (d, C-1), 112.3 (s, C-6), 118.5 (s, CN), 123.8 (d, C-12), 125.5 (d, C-8), 126.2 (d, C-4), 128.9 (d, C-10), 130.0 (d, C-9), 132.5 (d, C-5), 134.9 (s, C-11), 138.3 (s, C-7), 141.9 (s, C-3). MS (EI): *m/e* (%) = 257 (28), 256 (20), 255 (89) [M]⁺, 237 (23), 226 (44), 220 (100), 192 (44), 191 (29), 190 (36), 115 (24), 89 (51). HR-MS (EI): calcd for [C₁₅H₁₀ClNO]⁺: 255.0445, found 255.0447.

4-(3-Phenylloxiran-2-yl)benzonitrile (5ea) was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)-BF₄ (300 mg, 1.13 mmol), KO^tBu (127 mg, 1.13 mmol), and benzaldehyde (**1e**, 31.8 mg, 300 μmol) as a colorless oil (45 mg, 0.20 mmol, 67 %, only *trans*-isomer).

RAP 35.1



R_f (*n*-pentane/EtOAc 8:1, *v/v*): 0.50. ¹H-NMR (CDCl₃, 300 MHz): δ = 3.83 (d, 1 H, *J* = 1.8 Hz, 1-H), 3.92 (d, 1 H, *J* = 1.8 Hz, 2-H), 7.32-7.42 (m, 5 H, 7-H, 8-H, 9-H, 10-H), 7.45 (d, 2 H, *J* = 8.2 Hz, 4-H), 7.67 (d, 2 H, *J* = 8.4 Hz, 5-H). ¹³C-NMR (CDCl₃, 75.5 MHz): δ = 61.8 (d, C-2), 63.2 (d, C-1), 112.1 (s, C-6), 118.6 (s, CN), 125.5 (d, C-8), 126.1 (d, C-4), 128.7 (d, C-9), 128.8 (d, C-10), 132.4 (d, C-5), 136.2 (s, C-7), 142.5 (s, C-3). MS (EI): *m/e* (%) = 221 [M]⁺ (61), 220 (33), 204 (19), 203 (23), 193 (54), 192 (100), 191 (15), 190 (27), 165 (34), 130

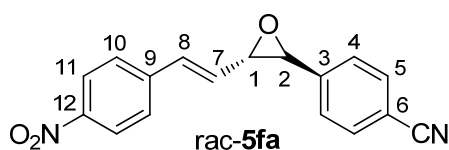
(23), 115 (16), 91 (18), 90 (68), 89 (51), 77 (19), 63 (19). HR-MS (EI): calcd for $[\text{C}_{15}\text{H}_{11}\text{NO}]^+$: 221.0835, found 221.0834.

NMR-signals are in agreement with those reported in the literature.^[S7]

Product studies for the reactions of the sulfur ylide **4a** with the aldehydes **1f,h**

(E)-4-(3-(4-Nitrostyryl)oxiran-2-yl)benzonitrile (5fa). Saturated aqueous K_2CO_3 -solution (5 mL) was added to a vigorously stirred solution of sulfonium tetrafluoroborate (**4a-H**)- BF_4 (150 mg, 566 μmol) and *p*-nitrocinnamaldehyde (**1f**, 100 mg, 564 μmol) in CHCl_3 (15 mL). The resulting biphasic mixture was vigorously stirred for 3 h. During this reaction further portions of (**4a-H**)- BF_4 were added after 1 h (150 mg, 566 μmol) and 2.5 h (75.0 mg, 283 μmol). The reaction was subsequently treated with water, the organic layer was separated and the aqueous phase additionally extracted by CHCl_3 . The combined organic layers were washed with water and brine, dried over Na_2SO_4 , and evaporated under reduced pressure. Purification of the crude product by column chromatography on silica gel (*n*-pentane/EtOAc) furnished **5fa** as a yellow solid (97.0 mg, 0.33 mmol, 59 %, only *trans*-isomer). Recrystallization from *n*-pentane/EtOAc yielded **5fa** as yellow solid (67.0 mg, 0.23 mmol, 41 %, only *trans*-isomer), which was subsequently characterized by ^1H - and ^{13}C -NMR spectroscopy, MS, and elemental analysis. Signal assignments were based on additional COSY, HSQC and HMBC experiments.

RAP 37.3



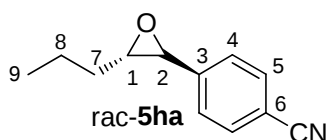
R_f (*n*-pentane/EtOAc 5:1, *v/v*): 0.35. Mp. (*n*-pentane/EtOAc): 175-177°C. ^1H -NMR (CDCl_3 , 400 MHz): δ = 3.51-3.54 (m, 1 H, 1-H), 3.96 (d, 1 H, J = 1.7 Hz, 2-H), 6.26 (dd, 1 H, J = 16.0, 7.3 Hz, 7-H), 6.90 (d, 1 H, J = 16.0 Hz, 8-H), 7.44 (d, 2 H, J = 8.5 Hz, 4-H), 7.54 (d, 2 H, J = 8.9 Hz, 10-H), 7.68 (d, 2 H, J = 8.3 Hz, 5-H), 8.21 (d, 2 H, J = 8.8 Hz, 11-H). ^{13}C -NMR (CDCl_3 , 101 MHz): δ = 60.0 (d, C-2), 62.7 (d, C-1), 112.3 (s, C-6), 118.5 (s, CN),

^[S7] (a) Aggarwal, V. K.; Alonso, E.; Bae, I.; Hynd, G.; Lydon, K. M.; Palmer, M. J.; Patel, M.; Porcelloni, M.; Richardson, J.; Stenson, R. A.; Studley, J. R.; Vasse, J.-L.; Winn, C. L. *J. Am. Chem. Soc.* **2003**, *125*, 10926-10940. (b) Oudeyer, S.; Léonel, E.; Paugam, J. P.; Nédélec, J.-Y. *Synthesis* **2004**, 389-400.

124.2 (d, C-11), 126.1 (d, C-4), 127.1 (d, C-10), 130.1 (d, C-7), 132.5 (d, C-5), 132.6 (d, C-8) 141.9, 142.0 (2s, C-3, C-9) 147.4 (s, C-12). MS (EI): m/e (%) = 292 (7) $[M]^+$, 275 (7), 264 (14), 263 (79), 246 (10), 245 (11), 218 (18), 217 (100), 216 (15), 130 (49), 116 (10), 115 (47), 114 (13), 102 (17), 89 (13), 77 (9), 63 (8). HR-MS (EI) $[M]^+$: calcd for $[C_{17}H_{12}N_2O_3]^+$: 292.0843, found 292.0848. Anal. calcd for $C_{17}H_{12}N_2O_3$ (292.29): C 69.86, H 4.14, N 9.58, found C 69.62, H 3.99, N 9.42.

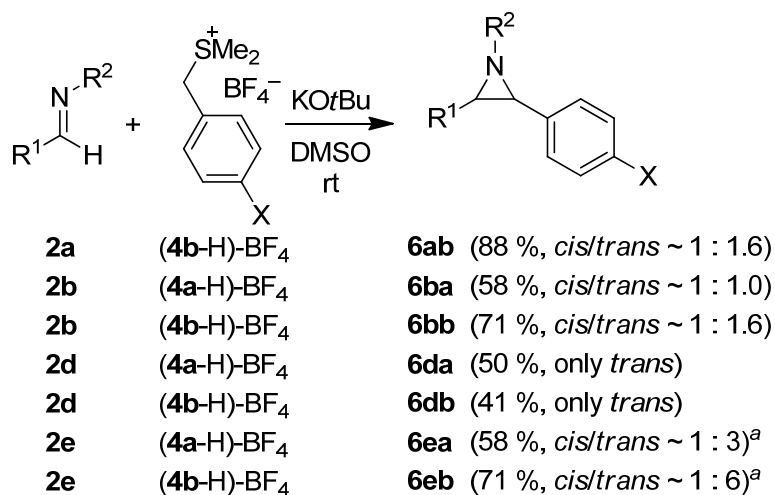
4-(3-Propyloxiran-2-yl)benzonitrile (5ha). Saturated aqueous K_2CO_3 -solution (5 mL) was added to a vigorously stirred solution of the sulfonium tetrafluoroborate (**4a-H**)- BF_4 (300 mg, 1.13 mmol) and butyraldehyde (**1h**, 1.0 mL, 11 mmol) in $CHCl_3$ (5 mL). The resulting biphasic mixture was vigorously stirred for 3 h. The reaction was subsequently treated with water, the organic layer was separated and the aqueous phase additionally extracted by $CHCl_3$. The combined organic layers were washed with water and brine, dried over Na_2SO_4 , and evaporated under reduced pressure. Purification of the crude product by column chromatography on aluminum oxide (*i*-hexane/EtOAc) furnished **5ha** as a colorless oil (187 mg, 999 μ mol, 88 %, only *trans*-isomer), which was subsequently characterized by 1H - and ^{13}C -NMR spectroscopy and MS. Signal assignments were based on additional COSY, HSQC and HMBC experiments.

RAP 46.2



R_f (*i*-hexane/EtOAc 12:1, v/v): 0.42. 1H -NMR ($CDCl_3$, 300 MHz): δ = 1.00 (t, 3 H, J = 7.3 Hz, 9-H), 1.52-1.61 (m, 2 H, 8-H), 1.64-1.73 (m, 2 H, 7-H), 2.90 (td, 1 H, J = 5.5, 2.0 Hz, 1-H), 3.65 (d, 1 H, J = 1.9 Hz, 2-H), 7.37 (d, 2 H, J = 8.4 Hz, 4-H), 7.62 (d, 2 H, J = 8.4 Hz, 5-H). ^{13}C -NMR ($CDCl_3$, 75.5 MHz): δ = 13.9 (q, C-9), 19.2 (t, C-8), 34.2 (t, C-7), 57.6 (d, C-2) 63.7 (d, C-1), 111.7 (s, C-6), 118.7 (s, CN), 126.1 (d, C-4), 132.3 (d, C-5), 143.6 (s, C-3). MS (EI): m/e (%) = 187 $[M]^+$ (79), 186 (36), 158 (89), 145 (25), 144 (24), 132 (81), 130 (100), 117 (30), 116 (67), 115 (79), 114 (25), 104 (47), 102 (20), 56 (47), 41 (37). HR-MS (EI) $[M]^+$: calcd for $[C_{12}H_{13}NO]^+$: 187.0992, found 187.0984.

2.2 Reactions of the Sulfur Ylides **4a,b** with the Imines **2a,b,d,e**



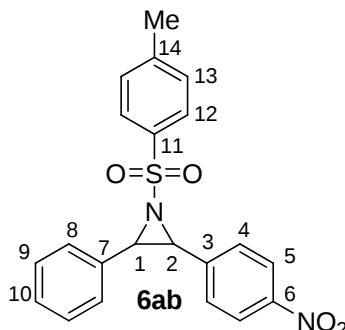
^a Yield isolated refers to *trans*-isomer; *cis/trans*-ratio corresponds to the crude product.

General procedure B. The ylides **4a,b** were generated by the addition of KO^tBu (dissolved in 2-3 mL DMSO) to a vigorously stirred solution of the sulfonium tetrafluoroborates (**4a,b-H**)-BF₄ in dry DMSO (2-3 mL) at room temperature. The electrophiles **2a,b,d,e** (dissolved in 2-3 mL DMSO) were then added in one portion. The resulting mixtures were stirred for 5-15 min at room temperature and subsequently quenched by addition of water followed by extraction with CH₂Cl₂. The combined organic layers were washed with water and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude products were purified by column chromatography on silica gel (*n*-pentane/EtOAc or *i*-hexane/EtOAc) and subsequently characterized by ¹H- and ¹³C-NMR spectroscopy and MS. Signal assignments were based on additional COSY, HSQC and HMBC experiments. If not mentioned otherwise, the diastereomeric ratios of the purified products did not differ significantly from those of the crude mixtures before column chromatography. Additional purifications by recrystallization from appropriate solvent mixtures were sometimes performed and are indicated in the corresponding section.

2-(4-Nitrophenyl)-3-phenyl-1-tosylaziridine (6ab) was obtained from dimethyl(4-nitrobenzyl)sulfonium tetrafluoroborate (**4b-H**)-BF₄ (200 mg, 702 μmol), KO^tBu (78.8 mg,

702 μmol), and imine **2a** (90.0 mg, 347 μmol) as a pale yellow solid (121 mg, 307 μmol , 88 %, *dr* $\sim$ 1 : 1.6 *cis* / *trans*).

RAP 61.1



^1H -NMR (CDCl_3 , 599 MHz): δ = 2.40^{*} (s, 3 H, Ar-Me), 2.46[#] (s, 3 H, Ar-Me), 4.21^{*} (d, 1 H, *J* = 4.5 Hz, 1-H), 4.27[#] (d, 1 H, *J* = 7.3 Hz, 2-H), 4.30[#] (d, 1 H, *J* = 7.3 Hz, 1-H), 4.35^{*} (d, 1 H, *J* = 4.5 Hz, 2-H), 7.00-7.02[#] (m, 2 H, 8-H), 7.12-7.13[#] (m, 3 H, 9-H, 10-H), 7.23-7.24 (m, 4 H, 4-H[#], 13-H^{*}), 7.36-7.42 (m, 7 H, 8-H^{*}, 9-H^{*}, 10-H^{*}, 13-H[#]), 7.61^{*} (d, 2 H, *J* = 8.8 Hz, 4-H), 7.65^{*} (d, 2 H, *J* = 8.4 Hz, 12-H), 7.95-7.98[#] (m, 4 H, 5-H, 12-H), 8.21^{*} (d, 2 H, *J* = 8.8 Hz, 5-H). ^{13}C -NMR (CDCl_3 , 151 MHz): δ = 21.6^{*} (q, Ar-Me), 21.7[#] (q, Ar-Me), 46.2[#] (d, C-2), 47.9[#] (d, C-1), 48.4^{*} (d, C-2), 51.6^{*} (d, C-1), 123.2[#] (d, C-5), 123.7^{*} (d, C-5), 127.5 (2d, C-12^{*}, C-8[#]), 128.1[#] (d, C-12), 128.2[#] (d, C-10), 128.3[#] (d, C-9), 128.4^{*}, 128.59^{*} (2d, C-8, C-9), 128.64[#] (d, C-4), 129.0^{*} (d, C-4), 129.1^{*} (d, C-10), 129.6^{*} (d, C-13), 130.0[#] (d, C-13), 131.1[#] (s, C-7), 131.9^{*} (s, C-7), 134.4[#] (s, C-11), 136.6^{*} (s, C-11), 139.6[#] (s, C-3), 140.9^{*} (s, C-3), 144.5^{*} (s, C-14), 145.3[#] (s, C-14), 147.5[#] (s, C-6), 148.0^{*} (s, C-6). HR-MS (ESI^+) $[\text{M}+\text{H}]^+$: calcd for $[\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_4\text{S}]^+$: 395.1060; found 395.1060.

* signal can be assigned to *trans*-diastereomer

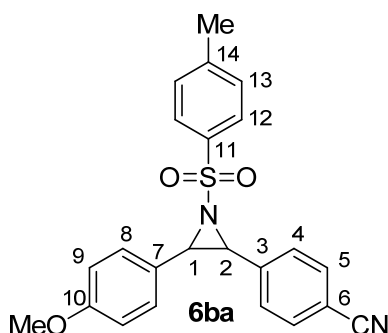
signal can be assigned to *cis*-diastereomer

NMR-signals of the *trans*-isomer are in agreement with those reported in the literature.^[S8]

4-(3-(4-Methoxyphenyl)-1-tosylaziridin-2-yl)benzonitrile (6ba) was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)- BF_4 (265 mg, 1.00 mmol), $\text{KO}t\text{Bu}$ (113 mg, 1.01 mmol), and imine **2b** (100 mg, 346 μmol) as a colorless solid (82 mg, 0.20 mmol, 58 %, *dr* $\sim$ 1 : 1.0 *cis* / *trans*).

^[S8] Gui, Y.; Shen, S.; Wang, H.-Y.; Li, Z.-Y.; Huang, Z.-Z. *Chem. Lett.* **2007**, 36, 1436-1437.

RAP 68.2



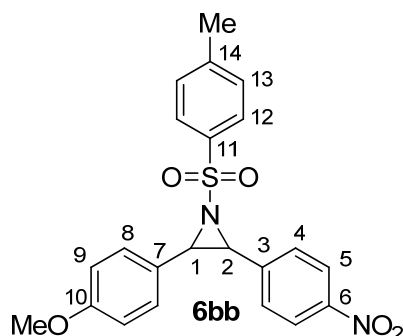
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ = 2.39^{*} (s, 3 H, Ar-Me), 2.44[#] (s, 3 H, Ar-Me), 3.68[#] (s, 3 H, OMe), 3.81^{*} (s, 3 H, OMe), 4.07^{*} (d, 1 H, J = 4.4 Hz, 1-H), 4.18[#] (d, 1 H, J = 7.2 Hz, 2-H), 4.21[#] (d, 1 H, J = 7.3 Hz, 1-H), 4.36^{*} (d, 1 H, J = 4.5 Hz, 2-H), 6.64[#] (d, 2 H, J = 8.3 Hz, 9-H), 6.86-6.90 (m, 4 H, 9-H^{*}, 8-H[#]), 7.17[#] (d, 2 H, J = 8.4 Hz, 4-H), 7.22^{*} (d, 2 H, J = 8.2 Hz, 13-H), 7.32-7.37 (m, 4 H, 8-H^{*}, 13-H[#]), 7.41[#] (d, 2 H, J = 8.1 Hz, 5-H), 7.50^{*} (d, 2 H, J = 8.3 Hz, 4-H), 7.61-7.64 (m, 4 H, 5-H^{*}, 12-H[#]), 7.93[#] (d, 2 H, J = 8.2 Hz, 12-H). $^{13}\text{C-NMR}$ (CDCl_3 , 101 MHz): δ = 21.6^{*} (q, Ar-Me), 21.7[#] (q, Ar-Me), 46.5[#] (d, C-2), 47.6[#] (d, C-1), 47.8^{*} (d, C-2), 52.2^{*} (d, C-1), 55.1[#] (q, OMe), 55.3^{*} (q, OMe), 111.6[#] (s, C-6), 112.3^{*} (s, C-6), 113.7[#] (d, C-9), 113.9^{*} (d, C-9), 118.4, 118.5 (2s, CN^{*}, CN[#]), 123.1[#] (s, C-7), 123.3^{*} (s, C-7), 127.4^{*} (d, C-12), 128.0[#] (d, C-12), 128.4^{*} (d, C-4), 128.5[#] (d, C-4), 128.7[#] (d, C-8), 129.5^{*} (d, C-13), 130.0, 130.1 (2d, C-8^{*}, C-13[#]), 131.8[#] (d, C-5), 132.3^{*} (d, C-5), 134.5[#] (s, C-11), 136.8^{*} (s, C-11), 137.8[#] (s, C-3), 139.5^{*} (s, C-3), 144.3^{*} (s, C-14), 145.1[#] (s, C-14), 159.4[#] (s, C-10), 160.2^{*} (s, C-10). HR-MS (ESI^+) $[\text{M}+\text{H}]^+$: calcd for $[\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_3\text{S}]^+$: 405.1267 ; found 405.1266.

* signal can be assigned to *trans*-diastereomer

[#] signal can be assigned to *cis*-diastereomer

2-(4-Methoxyphenyl)-3-(4-nitrophenyl)-1-tosylaziridine (6bb) was obtained from dimethyl(4-nitrobenzyl)sulfonium tetrafluoroborate (**4b-H**)- BF_4 (200 mg, 702 μmol), $\text{KO}t\text{Bu}$ (78.8 mg, 702 μmol), and imine **2b** (100 mg, 346 μmol) as a yellow solid (105 mg, 247 μmol , 71 %, $dr \sim 1 : 1.6$ *cis* / *trans*).

RAP 62.1



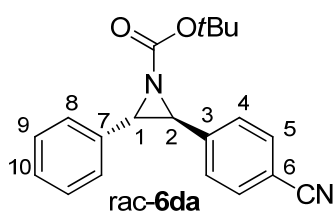
$^1\text{H-NMR}$ (CDCl_3 , 599 MHz): δ = 2.39^{*} (s, 3 H, Ar-Me), 2.45[#] (s, 3 H, Ar-Me), 3.67[#] (s, 3 H, OMe), 3.81^{*} (s, 3 H, OMe), 4.09^{*} (d, 1 H, J = 4.6 Hz, 1-H), 4.22[#] (d, 1 H, J = 7.3 Hz, 2-H), 4.24[#] (d, 1 H, J = 7.3 Hz, 1-H), 4.42^{*} (d, 1 H, J = 4.6 Hz, 2-H), 6.64[#] (d, 2 H, J = 8.7 Hz, 9-H), 6.88^{*} (d, 2 H, J = 8.7 Hz, 9-H), 6.91[#] (d, 2 H, J = 8.8 Hz, 8-H), 7.22-7.24 (m, 4 H, 4-H[#], 13-H^{*}), 7.35-7.38 (m, 4 H, 8-H^{*}, 13-H[#]), 7.56^{*} (d, 2 H, J = 8.8 Hz, 4-H), 7.64^{*} (d, 2 H, J = 8.3 Hz, 12-H), 7.95[#] (d, 2 H, J = 8.3 Hz, 12-H), 7.97[#] (d, 2 H, J = 8.8 Hz, 5-H), 8.18^{*} (d, 2 H, J = 8.8 Hz, 5-H). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz): δ = 21.6^{*} (q, Ar-Me), 21.7[#] (q, Ar-Me), 46.3[#] (d, C-2), 47.5^{*} (d, C-2), 47.6[#] (d, C-1), 52.4^{*} (d, C-1), 55.1[#] (q, OMe), 55.3^{*} (q, OMe), 113.7[#] (d, C-9), 113.9^{*} (d, C-9), 123.0[#] (s, C-7), 123.16^{*} (s, C-7), 123.23[#] (d, C-5), 123.7^{*} (d, C-5), 127.5^{*} (d, C-12), 128.0[#] (d, C-12), 128.6^{*} (d, C-4), 128.69[#], 128.70[#] (2d, C-4, C-8), 129.6^{*} (d, C-13), 130.0[#] (d, C-13), 130.1^{*} (d, C-8), 134.4[#] (s, C-11), 136.7^{*} (s, C-11), 139.8[#] (s, C-3), 141.5^{*} (s, C-3), 144.4^{*} (s, C-14), 145.2[#] (s, C-14), 147.4[#] (s, C-6), 147.9^{*} (s, C-6), 159.4[#] (s, C-10), 160.2^{*} (s, C-10). HR-MS (ESI^+) $[\text{M}+\text{H}]^+$: calcd for $[\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_5\text{S}]^+$: 425.1166; found 425.1165.

* signal can be assigned to *trans*-diastereomer

[#] signal can be assigned to *cis*-diastereomer

***tert*-Butyl 2-(4-cyanophenyl)-3-phenylaziridine-1-carboxylate (6da)** was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)- BF_4 (300 mg, 1.13 mmol), $\text{KO}t\text{Bu}$ (127 mg, 1.13 mmol), and imine **2d** (90.0 mg, 438 μmol) as a colorless oil (72 mg, 0.22 mmol, 50 %, only *trans* diastereomer).

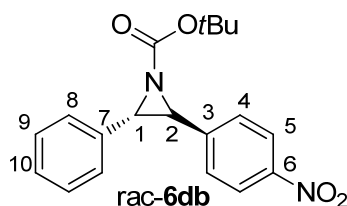
RAP 73.1



R_f (*n*-pentane/EtOAc 9:1, v/v): 0.38. $^1\text{H-NMR}$ (CDCl_3 , 599 MHz): δ = 1.20 (s, 9 H, *Ot*Bu), 3.62 (d, 1 H, J = 3.1 Hz, 1-H), 3.92 (d, 1 H, J = 3.1 Hz, 2-H), 7.31-7.33 (m, 2 H, 8-H), 7.34-7.39 (m, 3 H, 9-H, 10-H), 7.48 (d, 2 H, J = 8.4 Hz, 4-H), 7.65 (d, 2 H, J = 8.5 Hz, 5-H). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz): δ = 27.6 (q, *Ot*Bu), 45.2 (d, C-2), 49.8 (d, C-1), 82.0 (s, *Ot*Bu), 111.7 (s, C-6), 118.6 (s, CN), 127.3 (d, C-8), 127.4 (d, C-4), 128.61 (d, C-10), 128.62 (d, C-9), 132.3 (s, C-5), 134.0 (s, C-7), 141.8 (s, C-3), 158.8 (s, CO). HR-MS (ESI^+) $[\text{M}+\text{H}]^+$: calcd for $[\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_2]^+$: 321.1598; found 321.1599.

***tert*-Butyl 2-(4-nitrophenyl)-3-phenylaziridine-1-carboxylate (6db)** was obtained from dimethyl(4-nitrobenzyl)sulfonium tetrafluoroborate (**4b-H**)- BF_4 (200 mg, 702 μmol), KOtBu (78.8 mg, 702 μmol), and imine **2d** (80.0 mg, 390 μmol) as a pale yellow oil (54 mg, 0.16 mmol, 41 %, only *trans* diastereomer).

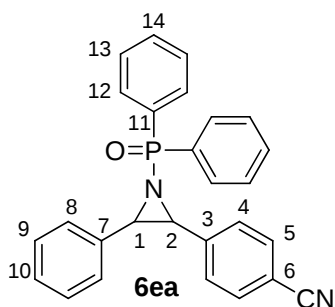
RAP 72.1



R_f (*n*-pentane/EtOAc 9:1, v/v): 0.43. $^1\text{H-NMR}$ (CDCl_3 , 599 MHz): δ = 1.21 (s, 9 H, *Ot*Bu), 3.63 (d, 1 H, J = 3.1 Hz, 1-H), 3.99 (d, 1 H, J = 3.1 Hz, 2-H), 7.32-7.33 (m, 2 H, 8-H), 7.35-7.40 (m, 3 H, 9-H, 10-H), 7.54 (d, 2 H, J = 8.9 Hz, 4-H), 8.22 (d, 2 H, J = 8.9 Hz, 5-H). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz): δ = 27.6 (q, *Ot*Bu), 44.8 (d, C-2), 50.3 (d, C-1), 82.1 (s, *Ot*Bu), 123.8 (d, C-5), 127.3 (d, C-8), 127.4 (d, C-4), 128.65 (d, C-9), 128.70 (d, C-10), 133.8 (s, C-7), 144.0 (s, C-3), 147.6 (s, C-6), 158.7 (s, CO). HR-MS (ESI^+) $[\text{M}+\text{H}]^+$: calcd for $[\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_4]^+$: 341.1496; found 341.1495.

4-(1-(Diphenylphosphoryl)-3-phenylaziridin-2-yl)benzonitrile (6ea) was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)- BF_4 (265 mg, 1.00 mmol), KOtBu (113 mg, 1.01 mmol), and imine **2e** (100 mg, 328 μmol). Based on the $^{31}\text{P-NMR}$ signals, the crude product (before column chromatography) shows a *dr* $\sim$ 1 : 3 (*cis* / *trans*). The two diastereomers were separated by column chromatography. After recrystallization from *n*-pentane/EtOAc, the major (*trans*) diastereomer was isolated as a colorless solid (81 mg, 0.19 mmol, 58 %, only *trans* diastereomer). As the minor (*cis*) diastereomer could not be isolated in pure form, only characteristic NMR-signals are given for this compound.

RAP 70.1



Major (*trans*) diastereomer:

R_f (*n*-pentane/EtOAc 2:3, v/v): 0.35. Mp. (*n*-pentane/EtOAc): 180-182°C. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 4.06-4.14 (m, 2 H, 1-H, 2-H), 7.25-7.44 (m, 11 H, 8-H, 9-H, 10-H, 13-H, 14-H), 7.48 (d, 2 H, J = 8.4 Hz, 4-H), 7.54 (d, 2 H, J = 8.4 Hz, 5-H), 7.60-7.66 (m, 2 H, 12-H), 7.82-7.89 (m, 2 H, 12-H). $^{13}\text{C-NMR}$ (CDCl_3 , 75.5 MHz): δ = 46.5 (d, d, J_{PC} = 6.8 Hz, C-2), 47.5 (d, d, J_{PC} = 6.7 Hz, C-1), 111.7 (s, C-6), 118.6 (s, CN), 127.6 (d, C-8), 128.2 (d, d, J_{PC} = 12.6 Hz, C-13), 128.31 (d, C-10, superimposed by one of the signals of C-13), 128.37 (d, C-9), 128.40 (d, d, J_{PC} = 12.6 Hz, C-13), 128.6 (d, C-4), 131.3 (d, d, J_{PC} = 9.5 Hz, C-12), 131.50 (d, d, J_{PC} = 9.4 Hz, C-12), 131.7 (d, d, J_{PC} = 2.7 Hz, C-14), 131.8 (d, d, J_{PC} = 2.8 Hz, C-14), 132.0 (d, C-5), 132.3 (s, d, J_{PC} = 125 Hz, C-11), 133.8 (s, d, J_{PC} = 134 Hz, C-11), 134.8 (s, d, J_{PC} = 5.1 Hz, C-7, two signals of C-7 and C-11 superimposed), 141.1 (s, d, J_{PC} = 5.4 Hz, C-3). $^{31}\text{P-NMR}$ (CDCl_3 , 81.0 MHz): δ = 28.9. HR-MS (ESI^+) $[\text{M}+\text{H}]^+$: calcd for $[\text{C}_{27}\text{H}_{22}\text{N}_2\text{OP}]^+$: 421.1464; found 421.1462.

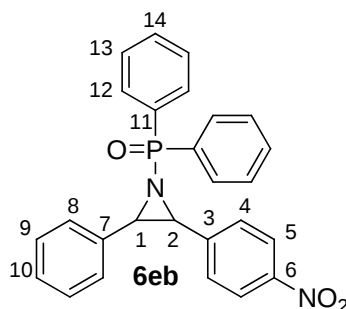
Minor (*cis*) diastereomer (only characteristic signals):

R_f (*n*-pentane/EtOAc 2:3, v/v): 0.20. $^1\text{H-NMR}$ (CDCl_3 , 599 MHz): δ = 4.22 (dd, 1 H, J = 16.0, 6.2 Hz), 4.30 (dd, 1 H, J = 16.2, 6.2 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz): δ = 43.0 (d, d, J_{PC} = 5.6 Hz), 44.1 (d, d, J_{PC} = 5.7 Hz). $^{31}\text{P-NMR}$ (CDCl_3 , 81.0 MHz): δ = 34.7.

(2-(4-Nitrophenyl)-3-phenylaziridin-1-yl)diphenylphosphine oxide (6eb) was obtained from dimethyl(4-nitrobenzyl)sulfonium tetrafluoroborate (**4b-H**)- BF_4 (200 mg, 702 μmol), KOtBu (78.8 mg, 702 μmol), and imine **2e** (100 mg, 328 μmol). Based on the $^{31}\text{P-NMR}$ signals, the crude product (before column chromatography) shows a $dr \sim 1 : 6$ (*cis* / *trans*). The two diastereomers were separated by column chromatography. After recrystallization

from *n*-pentane/EtOAc, the major (*trans*) diastereomer was isolated as a pale yellow solid (102 mg, 232 μ mol, 71 %, only *trans* diastereomer). As the minor (*cis*) diastereomer could not be isolated in pure form, only characteristic NMR-signals are given for this compound.

RAP 71.1



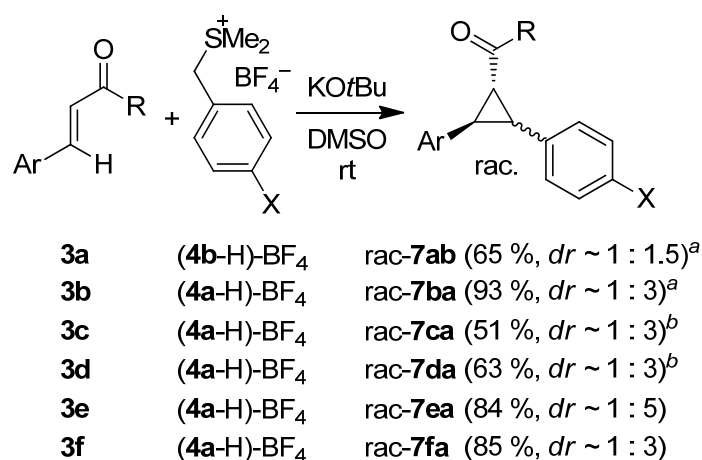
Major (*trans*) diastereomer:

R_f (*n*-pentane/EtOAc 1:1, v/v): 0.38. Mp. (*n*-pentane/EtOAc): 156-157°C. $^1\text{H-NMR}$ (CDCl_3 , 599 MHz): δ = 4.12 (dd, 1 H, J = 14.2, 3.1 Hz, 1-H), 4.17 (dd, 1 H, J = 13.8, 3.1 Hz, 2-H), 7.28-7.32 (m, 5 H, 9-H, 10-H, 13-H), 7.33-7.38 (m, 4 H, 8-H, 13-H), 7.40-7.43 (m, 2 H, 14-H), 7.54 (d, 2 H, J = 8.7 Hz, 4-H), 7.63-7.67 (m, 2 H, 12-H), 7.85-7.89 (m, 2 H, 12-H), 8.11 (d, 2 H, J = 8.8 Hz, 5-H). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz): δ = 46.1 (d, d, J_{PC} = 6.7 Hz, C-2), 47.9 (d, d, J_{PC} = 6.7 Hz, C-1), 123.4 (d, C-5), 127.7 (d, C-8), 128.2 (d, d, J_{PC} = 12.6 Hz, C-13), 128.37 (d, C-10, superimposed by one of the signals of C-13), 128.39 (d, C-9), 128.42 (d, d, J_{PC} = 13.0 Hz, C-13), 128.7 (d, C-4), 131.3 (d, d, J_{PC} = 9.5 Hz, C-12), 131.5 (d, d, J_{PC} = 9.4 Hz, C-12), 131.7 (d, d, J_{PC} = 2.8 Hz, C-14), 131.8 (d, d, J_{PC} = 2.8 Hz, C-14), 132.3 (s, d, J_{PC} = 125 Hz, C-11), 133.7 (s, d, J_{PC} = 134 Hz, C-11), 134.6 (s, d, J_{PC} = 5.1 Hz, C-7), 143.2 (s, d, J_{PC} = 5.3 Hz, C-3), 147.5 (s, C-6). $^{31}\text{P-NMR}$ (CDCl_3 , 81.0 MHz): δ = 29.0. HR-MS (ESI^+) $[\text{M}+\text{H}]^+$: calcd for $[\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_3\text{P}]^+$: 441.1362; found 441.1359.

Minor (*cis*) diastereomer (only characteristic signals):

R_f (*n*-pentane/EtOAc 1:1, v/v): 0.22. $^1\text{H-NMR}$ (CDCl_3 , 599 MHz): δ = 4.26 (dd, 1 H, J = 16.0, 6.3 Hz), 4.32 (dd, 1 H, J = 16.2, 6.3 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz): δ = 42.8 (d, d, J_{PC} = 5.7 Hz), 44.2 (d, d, J_{PC} = 5.9 Hz). $^{31}\text{P-NMR}$ (CDCl_3 , 81.0 MHz): δ = 34.7.

2.3 Reactions of the Sulfur Ylides **4a,b** with the Enones **3a–f**

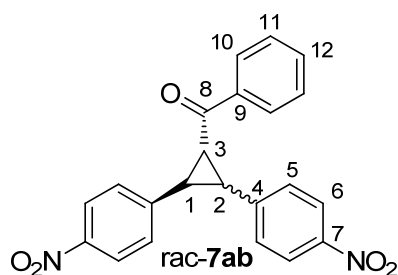


^a Minor diastereomer is a meso compound. ^b Yield isolated refers to major diastereomer; *dr* corresponds to the crude product.

General procedure C. The ylides **4a,b** were generated by the addition of KOtBu (dissolved in 2-3 mL DMSO) to a vigorously stirred solution of the sulfonium tetrafluoroborates (**4a,b-H**)-BF₄ in dry DMSO (2-3 mL) at room temperature. The electrophiles **3a–f** (dissolved in 2-3 mL DMSO) were then added in one portion. The resulting mixtures were stirred for 5-15 min at room temperature and subsequently quenched by the addition of water followed by the extraction with CH₂Cl₂. The combined organic layers were washed with water and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude products were purified by column chromatography on silica gel (*n*-pentane/EtOAc or *i*-hexane/EtOAc) and subsequently characterized by ¹H- and ¹³C-NMR spectroscopy and MS. Signal assignments were based on additional COSY, HSQC and HMBC experiments. If not mentioned otherwise, the diastereomeric ratios of the purified products did not differ significantly from those of the crude mixtures before column chromatography. Additional purifications by recrystallization from appropriate solvent mixtures were sometimes performed and are indicated in the corresponding section.

(2,3-Bis(4-nitrophenyl)cyclopropyl)(phenyl)methanone (7ab) was obtained from dimethyl(4-nitrobenzyl)sulfonium tetrafluoroborate (**4b-H**)-BF₄ (197 mg, 691 μmol), KOtBu (77.5 mg, 691 μmol), and enone **3a** (70.0 mg, 276 μmol) as a yellow solid (70 mg, 0.18 mmol, 65 %, *dr* ~ 1 : 1.5).

RAP 31.1



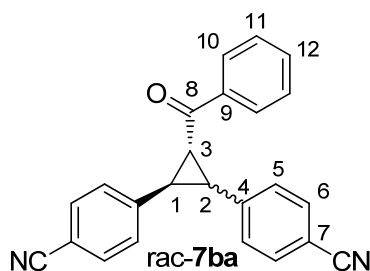
$^1\text{H-NMR}$ (CDCl_3 , 599 MHz): δ = 3.36^{*} (dd, 1 H, J = 9.4 Hz, J = 7.2 Hz, 2-H), 3.45[#] (d, 2 H, J = 5.3 Hz, 1-H, 2-H), 3.59^{*} (dd, 1 H, J = 9.7 Hz, J = 5.3 Hz, 3-H), 3.72-3.74 (m, 2 H, 1-H^{*}, 3-H[#]), 7.19[#] (d, 4 H, J = 8.7 Hz, 5-H), 7.44-7.50^{*} (m, 6 H, 5-H, 11-H), 7.55-7.60 (m, 3 H, 11-H[#], 12-H^{*}), 7.66-7.68[#] (m, 1 H, 12-H), 7.95^{*} (d, 2 H, J = 7.3 Hz, 10-H), 8.05[#] (d, 4 H, J = 8.8 Hz, 6-H), 8.09-8.12 (m, 4 H, 10-H[#], 6-H^{*}), 8.23^{*} (d, 2 H, J = 8.7 Hz, 6-H). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz): δ = 29.9^{*} (d, C-1), 31.7[#] (d, C-3), 35.4[#] (d, C-1, C-2) 37.0^{*} (d, C-3), 37.1^{*} (d, C-2), 123.5^{*} (d, C-6), 123.6[#] (d, C-6), 124.1^{*} (d, C-6), 127.5^{*} (d, C-5), 128.1^{*} (d, C-10), 128.2[#] (d, C-10), 128.8^{*} (d, C-11), 129.0[#] (d, C-11), 129.5[#] (d, C-5), 129.8^{*} (d, C-5), 133.6^{*} (d, C-12) 133.9[#] (d, C-12) 136.9[#] (s, C-9), 137.4^{*} (s, C-9) 142.4^{*} (s, C-4), 142.9[#] (s, C-4), 146.7^{*} (s, C-4), 146.9[#] (s, C-7), 146.96^{*} (s, C-7), 147.01^{*} (s, C-7), 193.5^{*} (s, C-8), 196.5[#] (s, C-8). MS (EI): m/e (%) = 388 (5) $[\text{M}]^+$, 191 (21), 190 (19), 189 (37), 106 (31), 105 (52), 179 (28), 77 (100). HR-MS (EI) $[\text{M}]^+$: calcd for $[\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_5]^+$: 388.1054, found 388.1055.

* signal can be assigned to the major diastereomer (1,2-*trans*)

signal can be assigned to the minor diastereomer (1,2-*cis*, meso compound)

4,4'-(3-Benzoylcyclopropane-1,2-diyl)dibenzonitrile (7ba) was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)- BF_4 (300 mg, 1.13 mmol), $\text{KO}t\text{Bu}$ (127 mg, 1.13 mmol), and enone **3b** (70.0 mg, 300 μmol) as a colorless solid (97 mg, 0.28 mmol, 93 %, $dr \sim 1 : 3$).

RAP 33.2



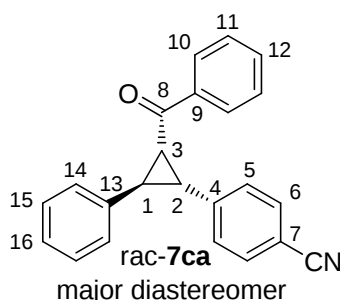
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ = 3.28* (dd, 1 H, J = 9.5 Hz, J = 7.1 Hz, 2-H), 3.38# (d, 2 H, J = 5.3 Hz, 1-H, 2-H), 3.51* (dd, 1 H, J = 9.7 Hz, J = 5.4 Hz, 3-H), 3.62-3.65 (m, 2 H, 1-H*, 3-H#), 7.11# (d, 4 H, J = 8.1 Hz, 5-H), 7.37* (d, 2 H, J = 8.1 Hz, 5-H), 7.41-7.49 (m, 8 H, 5-H*, 6-H#, 11-H*), 7.51-7.59 (m, 5 H, 6-H*, 11-H#, 12-H*), 7.64-7.69 (m, 3 H, 6-H*, 12-H#), 7.93* (d, 2 H, J = 7.5 Hz, 10-H), 8.09# (d, 2 H, J = 7.4 Hz, 10-H). $^{13}\text{C-NMR}$ (CDCl_3 , 101 MHz): δ = 29.9* (d, C-1), 31.52# (d, C-3), 35.54# (d, C-1, C-2) 36.7* (d, C-3), 37.2* (d, C-2), 110.9* (s, C-7), 111.0# (s, C-7), 111.1* (s, C-7), 118.4# (s, CN), 118.59* (s, CN), 118.62* (s, CN), 127.5* (d, C-5), 128.1* (d, C-10), 128.2# (d, C-10), 128.8* (d, C-11), 129.0# (d, C-11), 129.5# (d, C-5), 129.7* (d, C-5), 132.0* (d, C-6), 132.1# (d, C-6), 132.6* (d, C-6), 133.5* (d, C-12), 133.8# (d, C-12), 137.0# (s, C-9), 137.5* (s, C-9), 140.4* (s, C-4), 140.9# (s, C-4), 144.7* (s, C-4), 193.6* (s, C-8), 196.7# (s, C-8). MS (EI): m/e (%) = 348 (1) $[\text{M}]^+$, 217 (5) 106 (6), 105 (100), 77 (18). HR-MS (EI) $[\text{M}]^+$: calcd for $[\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}]^+$: 348.1257, found 348.1249.

* signal can be assigned to the major diastereomer (1,2-*trans*)

signal can be assigned to the minor diastereomer (1,2-*cis*, meso compound)

4-(2-Benzoyl-3-phenylcyclopropyl)benzonitrile (7ca) was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)- BF_4 (300 mg, 1.13 mmol), KO^tBu (127 mg, 1.13 mmol), and enone **3c** (90.0 mg, 432 μmol) as a colorless oil (*dr* ~ 1 : 3) still containing impurities. After recrystallization from *n*-pentane/EtOAc, **7ca** was obtained as a colorless solid (72 mg, 0.22 mmol, 51 %, only major diastereomer).

RAP 99.1

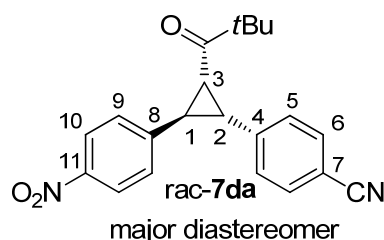


R_f (*i*-hexane/EtOAc 6:1, v/v): 0.29. Mp. (*n*-pentane/EtOAc): 134-135°C. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 3.26 (dd, 1 H, J = 9.5, 7.1 Hz, 2-H), 3.46 (dd, 1 H, J = 9.5, 5.4 Hz, 3-H), 3.60 (dd, 1 H, J = 6.8, 5.6 Hz, 1-H), 7.25-7.58 (m, 12 H, 5-H, 6-H, 11-H, 12-H, 14-H, 15-H, 16-H), 7.91-7.94 (m, 2 H, 10-H). $^{13}\text{C-NMR}$ (CDCl_3 , 75.5 MHz): δ = 30.5 (d, C-1), 36.4 (d, C-3), 37.1 (d, C-2), 110.7 (s, C-7), 118.8 (s, CN), 126.8 (d, C-14), 127.1 (d, C-16), 128.0 (d, C-10),

128.7, 128.8 (2d, C-11, C-15), 129.9 (d, C-5), 131.9 (d, C-6), 133.2 (d, C-12), 137.9 (s, C-9), 139.0 (s, C-13), 141.1 (s, C-4), 194.5 (s, C-8). MS (EI): m/e (%) = 323 (1) $[M]^+$, 217 (7) 106 (8), 105 (100), 77 (22). HR-MS (EI) $[M]^+$: calcd for $[C_{23}H_{17}NO]^+$: 323.1304, found 323.1305.

4-(2-(4-Nitrophenyl)-3-pivaloylcyclopropyl)benzonitrile (7da) was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)-BF₄ (300 mg, 1.13 mmol), KO^tBu (127 mg, 1.13 mmol), and enone **3d** (100 mg, 429 μ mol) as a yellow solid ($dr \sim 1 : 8$, before column chromatography: 1 : 3), still containing impurities. After recrystallization from *n*-pentane/EtOAc, **7da** was obtained as a pale yellow solid (95 mg, 0.27 mmol, 63 %, only major diastereomer).

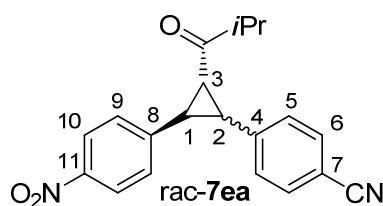
RAP 97.1



R_f (*n*-pentane/EtOAc 5:1, v/v): 0.23. Mp. (*n*-pentane/EtOAc): 209-210°C. ¹H-NMR (CD₃CN, 400 MHz): δ = 1.04 (s, 9 H, *t*Bu), 3.23-3.25 (m, 2 H, 2-H, 3-H), 3.42 (dd, 1 H, J = 6.2, 6.2 Hz, 1-H), 7.46 (d, 2 H, J = 8.2 Hz, 5-H), 7.53 (d, 2 H, J = 8.6 Hz, 9-H), 7.64 (d, 2 H, J = 8.6 Hz, 6-H), 8.18 (d, 2 H, J = 8.9 Hz, 10-H). ¹³C-NMR (CD₃CN, 101 MHz): δ = 25.9 (q, *t*Bu), 30.6 (d, C-1), 36.7 (d, C-3), 38.2 (d, C-2), 44.6 (s, *t*Bu), 111.1 (s, C-7), 119.6 (s, CN), 124.5 (d, C-10), 128.6 (d, C-9), 131.0 (d, C-5), 132.6 (d, C-6), 142.5 (s, C-4), 147.7 (s, C-8), 148.8 (s, C-11), 209.0 (s, CO). MS (EI): m/e (%) = 348 (<1) $[M]^+$, 290 (7), 264 (8), 245 (6), 217 (13), 216 (9), 190 (5), 85 (14), 57 (100). HR-MS (EI) $[M]^+$: calcd for $[C_{21}H_{20}N_2O_3]^+$: 348.1468 found 348.1465.

4-(2-Isobutyryl-3-(4-nitrophenyl)cyclopropyl)benzonitrile (7ea) was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)-BF₄ (300 mg, 1.13 mmol), KO^tBu (127 mg, 1.13 mmol), and enone **3e** (90.0 mg, 411 μ mol) as a colorless solid (115 mg, 344 μ mol, 84 %, $dr \sim 1 : 5$, before column chromatography: 1 : 3).

RAP 96.1



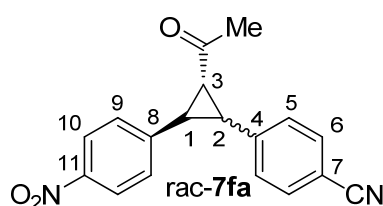
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ = 1.01* (d, 3 H, J = 7.0 Hz, CH_3 from *i*Pr), 1.05* (d, 3 H, J = 6.8 Hz, CH_3 from *i*Pr), 1.278[#] (d, 3 H, J = 6.9 Hz, CH_3 from *i*Pr), 1.281[#] (d, 3 H, J = 6.9 Hz, CH_3 from *i*Pr), 2.71* (sept, 1 H, J = 6.9 Hz, CH from *i*Pr), 2.93-3.04 (m, 3 H, 3-H*, CH from *i*Pr[#], 3-H[#]), 3.11-3.18 (m, 3 H, 2-H*, 1-H[#], 2-H[#]), 3.44* (dd, 1 H, J = 7.0, 5.3 Hz, 1-H), 7.07[#] (d, 2 H, J = 8.4 Hz, 5-H), 7.09[#] (d, 2 H, J = 8.8 Hz, 9-H), 7.40* (d, 4 H, J = 8.7 Hz, 5-H, 9-H, signals identical), 7.46[#] (d, 2 H, J = 8.4 Hz, 6-H), 7.59* (d, 2 H, J = 8.4 Hz, 6-H), 8.02[#] (d, 2 H, J = 8.8 Hz, 10-H), 8.19* (d, 2 H, J = 8.8 Hz, 10-H). $^{13}\text{C-NMR}$ (CDCl_3 , 101 MHz): δ = 17.4* (q, CH_3 from *i*Pr), 17.6* (q, CH_3 from *i*Pr), 17.98[#] (q, CH_3 from *i*Pr), 18.01[#] (q, CH_3 from *i*Pr), 29.8* (d, C-1), 32.9[#] (d, C-3), 34.8[#], 35.2[#] (2d, C-1, C-2), 37.2* (d, C-2), 38.4* (d, C-3), 42.1* (d, CH from *i*Pr), 42.2[#] (d, CH from *i*Pr), 110.9[#] (s, C-7), 111.0* (s, C-7), 118.4[#] (s, CN), 118.7* (s, CN), 123.5[#] (d, C-10), 124.0* (d, C-10), 127.3* (d, C-9), 129.4[#], 129.5[#] (2d, C-5, C-9), 129.7* (d, C-5), 131.9* (d, C-6), 132.1[#] (d, C-6), 140.4* (s, C-4), 140.7[#] (s, C-4), 143.0[#] (s, C-8), 146.8[#] (s, C-11), 146.86*, 146.87* (2s, C-8, C-11), 207.0* (s, CO), 210.4[#] (s, CO). MS (EI): m/e (%) = 334 (1) $[\text{M}]^+$, 217 (34), 216 (25), 214 (10), 190 (15), 71 (100), 43 (72). HR-MS (EI) $[\text{M}]^+$: calcd for $[\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_3]^+$: 334.1312, found 334.1303. MS HR-MS (ESI⁻) $[\text{M-H}]^-$: calcd for $[\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_3]^-$: 333.1245, found 333.1240.

* signal can be assigned to major diastereomer (1,2-*trans*)

[#] signal can be assigned to minor diastereomer (1,2-*cis*)

4-(2-Acetyl-3-(4-nitrophenyl)cyclopropyl)benzonitrile (7fa) was obtained from (4-cyanobenzyl)dimethylsulfonium tetrafluoroborate (**4a-H**)- BF_4 (300 mg, 1.13 mmol), $\text{KO}t\text{Bu}$ (127 mg, 1.13 mmol), and enone **3f** (80.0 mg, 418 μmol) as a pale yellow solid (109 mg, 356 μmol , 85 %, *dr* $\sim$ 1 : 3).

RAP 42.1



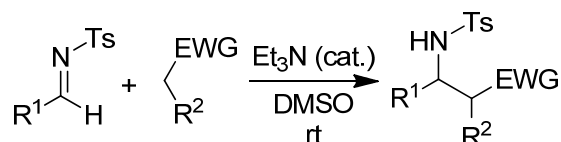
^1H -NMR (CDCl_3 , 599 MHz): δ = 2.22^{*} (s, 3 H, Me), 2.51[#] (s, 3 H, Me), 2.92^{*} (dd, 1 H, J = 9.7, 5.3 Hz, 3-H), 2.99[#] (dd, 1 H, J = 5.3, 5.3 Hz, 3-H), 3.13^{*} (dd, 1 H, J = 9.6, 7.1 Hz, 2-H), 3.19-3.23[#] (m, 2 H, 1-H, 2-H), 3.43^{*} (dd, 1 H, J = 6.9, 5.4 Hz, 1-H), 7.05[#] (d, 2 H, J = 8.3 Hz, 5-H), 7.08[#] (d, 2 H, J = 8.7 Hz, 9-H), 7.37-7.41^{*} (m, 4 H, 5-H, 9-H), 7.46[#] (d, 2 H, J = 8.4 Hz, 6-H), 7.60^{*} (d, 2 H, J = 8.4 Hz, 6-H), 8.02[#] (d, 2 H, J = 8.8 Hz, 10-H), 8.20^{*} (d, 2 H, J = 8.8 Hz, 10-H). ^{13}C -NMR (CDCl_3 , 151 MHz): δ = 29.8^{*} (d, C-1), 31.3[#] (q, Me), 31.9^{*} (q, Me), 34.9[#], 35.0[#], 35.4[#] (3d, C-1, C-2, C-3), 37.0^{*} (d, C-2), 40.1^{*} (d, C-3), 111.0[#] (s, C-7), 111.2^{*} (s, C-7), 118.4[#] (s, CN), 118.6^{*} (s, CN), 123.5[#] (d, C-10), 124.0^{*} (d, C-10), 127.2^{*} (d, C-9), 129.4[#], 129.5[#] (2d, C-5, C-9), 129.7^{*} (d, C-5), 132.0^{*} (d, C-6), 132.1[#] (d, C-6), 140.1^{*} (s, C-4), 140.4[#] (s, C-4), 142.7[#] (s, C-8), 146.6^{*} (s, C-8), 146.8[#] (s, C-11), 146.9^{*} (s, C-11), 201.5^{*} (s, CO), 204.7[#] (s, CO). MS HR-MS (ESI⁻) $[\text{M}-\text{H}]^-$: calcd for $[\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_3]^-$: 305.0932, found 305.0941.

* signal can be assigned to major diastereomer (1,2-*trans*)

signal can be assigned to minor diastereomer (1,2-*cis*)

2.4 Reactions of the Carbanions 4c–h with the Imines 2a–c

Reactions of the carbanions 4c,d,f with the imines 2a–c

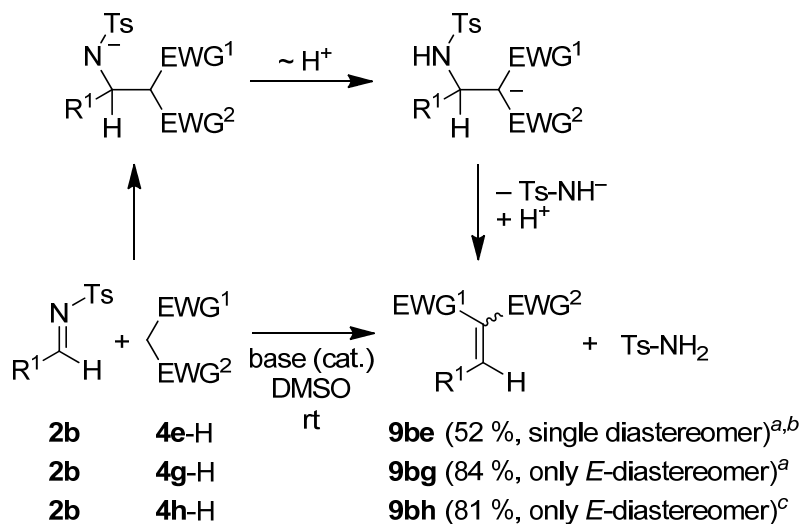


2a	4d-H	8ad (65 %)
2b	4c-H	8bc (52 %) ^a
2b	4d-H	8bd (58 %)
2b	4f-H	8bf (83 %) ^b
2c	4d-H	8cd (18 %)

^a *dr* ~ 1 : 3 for the crude product; only major diastereomer isolated and characterized.

^b Reaction conditions: KO^tBu, THF, –80 to –40°C.

Reactions of the carbanions 4e,g,h with the imine 2b



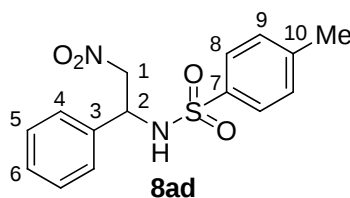
^a KO^tBu (14–18 mol-%), rt. ^b Configuration (*E* or *Z*) was not determined. ^c Et₃N (18 mol-%), rt.

General procedure D. The CH-acids (**4c–h**)-H were dissolved with the corresponding imine **2a–c** in dry DMSO (2–3 mL). After the addition of a catalytic amount of base (Et₃N or KO^tBu) the reaction mixtures were stirred for an appropriate time at rt. The reactions were subsequently quenched by addition of water and brine, followed by extraction with CH₂Cl₂.

The combined organic layers were washed with water and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude products were purified by column chromatography on silica gel (*n*-pentane/EtOAc) and subsequently characterized by ¹H- and ¹³C-NMR (if possible also ³¹P-NMR) spectroscopy and MS. Signal assignments were based on additional COSY, HSQC and HMBC experiments. If not mentioned otherwise, the diastereomeric ratios of the purified products did not differ significantly from those of the crude mixtures before column chromatography. Additional purifications by recrystallization from appropriate solvent mixtures were sometimes performed and are indicated in the corresponding section.

4-Methyl-*N*-(2-nitro-1-phenylethyl)benzenesulfonamide (8ad) was obtained from nitromethane (**4d-H**, 100 mg, 1.64 mmol), the imine **2a** (100 mg, 386 μmol), and Et₃N (7.4 mg, 73 μmol, 19 mol-%) after 1.5 h of reaction time as a colorless solid (91 mg, 0.28 mmol, 73 %). Recrystallization from *n*-pentane/EtOAc yielded **8ad** as colorless needles (79 mg, 0.25 mmol, 65 %).

RAP 63.1



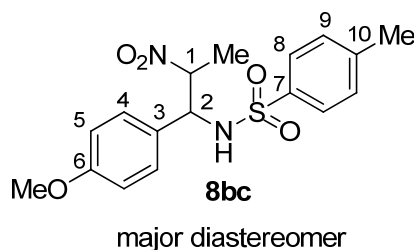
R_f (*n*-pentane/EtOAc 3:1, *v/v*): 0.34. Mp. (*n*-pentane/EtOAc): 154-156°C (Lit.: 155-157°C).^[S9] ¹H-NMR (CDCl₃, 300 MHz): δ = 2.39 (s, 3 H, Ar-Me), 4.65 (dd, 1 H, *J* = 13.0, 6.4 Hz, 1-H), 4.81 (dd, 1 H, *J* = 13.1, 6.8 Hz, 1-H), 4.97-5.04 (m, 1 H, 2-H), 5.60 (d, 1 H, *J* = 7.8 Hz, NH), 7.07-7.10 (m, 2 H, 4-H), 7.20-7.26 (m, 5 H, 5-H, 6-H, 9-H), 7.64 (d, 2 H, *J* = 8.4 Hz, 8-H). ¹³C-NMR (CDCl₃, 75.5 MHz): δ = 21.5 (q, Ar-Me), 55.5 (d, C-2), 79.0 (t, C-1), 126.5 (d, C-4), 127.1 (d, C-8), 129.0 (d, C-6), 129.2 (d, C-5), 129.7 (d, C-9), 135.3 (s, C-3), 136.5 (s, C-7), 144.0 (s, C-10).

¹H-NMR signals are in agreement with those reported in the literature.^[S9]

^[S9] a) Qian, C.; Gao, F.; Chen, R. *Tetrahedron Lett.* **2001**, 42, 4673-4675; b) Gao, F.; Deng, M.; Qian, C. *Tetrahedron* **2005**, 61, 12238-12243.

***N*-(1-(4-Methoxyphenyl)-2-nitropropyl)-4-methylbenzenesulfonamide (8bc)** was obtained from nitroethane (**4c**-H, 60.0 mg, 799 μ mol), the imine **2b** (100 mg, 346 μ mol), and Et₃N (6.0 mg, 59 μ mol, 17 mol-%) after 2 h of reaction time as a colorless solid (*dr* $\sim$ 1 : 3.4) still containing impurities. Twice recrystallization from *n*-pentane/EtOAc yielded **8bc** as colorless solid (65 mg, 0.18 mmol, 52 %, only one diastereomer).

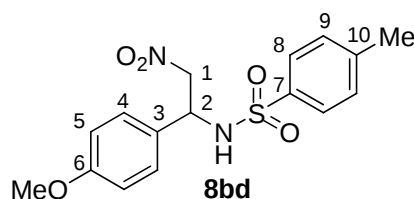
RAP 92.2



R_f (*n*-pentane/EtOAc 2:1, *v/v*): 0.43. Mp. (*n*-pentane/EtOAc): 188-190°C. ¹H-NMR (CDCl₃, 300 MHz): δ = 1.41 (d, 3 H, *J* = 6.6 Hz, Me), 2.34 (s, 3 H, Ar-Me), 3.73 (s, 3 H, OMe), 4.69-4.86 (m, 2 H, 1-H, 2-H), 5.95 (d, 1 H, *J* = 9.2 Hz, NH), 6.68 (d, 2 H, *J* = 8.7 Hz, 5-H), 6.92 (d, 2 H, *J* = 8.7 Hz, 4-H), 7.10 (d, 2 H, *J* = 8.3 Hz, 9-H), 7.52 (d, 2 H, *J* = 8.3 Hz, 8-H). ¹³C-NMR (CDCl₃, 75.5 MHz): δ = 16.8 (q, Me), 21.4 (q, Ar-Me), 55.3 (q, OMe), 60.1 (d, C-2), 86.9 (d, C-1), 114.3 (d, C-5), 127.1 (d, C-8), 127.3 (s, C-3), 128.0 (d, C-4), 129.4 (d, C-9), 137.0 (s, C-7), 143.4 (s, C-10), 159.7 (s, C-6). MS (EI): *m/e* (%) = 364 (1) [M]⁺, 291 (10), 290 (50), 289 (46), 155 (33), 134 (78), 133 (16), 92 (17), 91 (100), 77 (12), 65 (16). HR-MS (EI) [M]⁺: calcd for [C₁₇H₂₀N₂O₅S]⁺: 364.1087, found 364.1087.

***N*-(1-(4-Methoxyphenyl)-2-nitroethyl)-4-methylbenzenesulfonamide (8bd)** was obtained from nitromethane (**4d**-H, 100 mg, 1.64 mmol), the imine **2b** (100 mg, 346 μ mol), and Et₃N (5.3 mg, 52 μ mol, 15 mol-%) after 1.5 h of reaction time as a colorless solid still containing impurities. Recrystallization from *n*-pentane/EtOAc yielded **8bd** as colorless solid (71 mg, 0.20 mmol, 58 %).

RAP 59.1

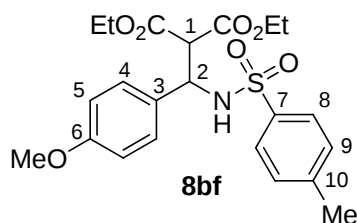


R_f (*n*-pentane/EtOAc 2:1, *v/v*): 0.37. Mp. (*n*-pentane/EtOAc): 174-175°C (Lit.: 142.4°C).^[S9b]
¹H-NMR (CDCl₃, 599 MHz): δ = 2.41 (s, 3 H, Ar-Me), 3.75 (s, 3 H, OMe), 4.63 (dd, 1 H, J = 13.0, 6.7 Hz, 1-H), 4.82 (dd, 1 H, J = 13.0, 6.7 Hz, 1-H), 4.91-4.94 (m, 1 H, 2-H), 5.43 (d, 1 H, J = 7.2 Hz, NH), 6.75 (d, 2 H, J = 8.7 Hz, 5-H), 6.99 (d, 2 H, J = 8.7 Hz, 4-H), 7.24 (d, 2 H, J = 8.0 Hz, 9-H), 7.64 (d, 2 H, J = 8.3 Hz, 8-H). ¹³C-NMR (CDCl₃, 151 MHz): δ = 21.6 (q, Ar-Me), 55.0 (d, C-2), 55.3 (q, OMe), 79.0 (t, C-1), 114.5 (d, C-5), 127.17 (d, C-8), 127.21 (s, C-3), 127.8 (d, C-4), 129.7 (d, C-9), 136.5 (s, C-7), 144.0 (s, C-10), 160.0 (s, C-6).

¹H-NMR signals are in agreement with those reported in the literature.^[S9b]

Diethyl 2-((4-methoxyphenyl)(4-methylphenylsulfonamido)methyl)malonate (8bf) could not be obtained by *General Procedure D* because of the high reversibility of the addition of carbanion **4f** to imine **2b**. Instead, the following procedure was used for the synthesis of **8bf**: Diethyl malonate (**4f**-H, 73.0 mg, 456 μ mol) and KO^tBu (51.0 mg, 455 μ mol) were dissolved in 5 mL of dry THF at rt. The resulting suspension was cooled down to –80°C and the imine **2b** (120 mg, 415 μ mol, dissolved in 5 mL of dry THF) was added dropwise. After 4 h of stirring at a temperature below –40°C, the mixture was again cooled down to –80°C and treated first with concentrated acetic acid (0.1 mL) then with water. The crude mixture was extracted with CH₂Cl₂ and the combined organic layers were washed with water and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by recrystallization from *n*-pentane/Et₂O and yielded **8bf** as a colorless solid (155 mg, 345 μ mol, 83 %), which was subsequently characterized by ¹H- and ¹³C-NMR spectroscopy, MS, and elemental analysis. Signal assignments were based on additional COSY, HSQC and HMBC experiments.

RAP 94.6

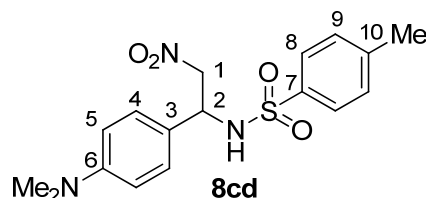


Mp. (*n*-pentane/Et₂O): 107.8-108.4°C. ¹H-NMR (CDCl₃, 300 MHz): δ = 1.13-1.20 (m, 6 H, OCH₂CH₃), 2.33 (s, 3 H, Ar-Me), 3.73-3.74 (m, 4 H, 1-H, OMe), 3.96-4.19 (m, 4 H, OCH₂CH₃), 5.09 (dd, 1 H, J = 9.2, 5.7 Hz, 2-H), 6.27 (d, 1 H, J = 9.3 Hz, NH), 6.65 (d, 2 H, J = 8.6 Hz, 5-H), 7.02 (d, 2 H, J = 8.7 Hz, 4-H), 7.08 (d, 2 H, J = 8.4 Hz, 9-H), 7.50 (d, 2 H, J =

8.2 Hz, 8-H). ^{13}C -NMR (CDCl_3 , 75.5 MHz): δ = 13.86 (q, OCH_2CH_3), 13.90 (q, OCH_2CH_3), 21.4 (q, Ar-Me), 55.2 (q, OMe), 56.6 (d, C-2), 57.9 (d, d, C-1), 61.9 (t, OCH_2CH_3), 62.1 (t, OCH_2CH_3), 113.7 (d, C-5), 127.0 (d, C-8), 128.0 (d, C-4), 129.1 (d, C-9), 129.7 (s, C-3), 138.0 (s, C-7), 142.8 (s, C-10), 159.1 (s, C-6), 166.4 (s, CO), 167.8 (s, CO). MS (EI): m/e (%) = 449 (<1) $[\text{M}]^+$, 302 (11), 301 (55), 155 (28), 134 (77), 133 (18), 92 (16), 91 (100), 77 (10), 65 (13). HR-MS (EI) $[\text{M}]^+$: calcd for $[\text{C}_{22}\text{H}_{27}\text{NO}_7\text{S}]^+$: 449.1502, found 449.1514. HR-MS (ESI^+) $[\text{M}+\text{Na}]^+$: calcd for $[\text{C}_{22}\text{H}_{27}\text{NO}_7\text{SNa}]^+$: 472.1401, found 472.1400. Anal calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_7\text{S}$ (449.52): C 58.78, H 6.05, N 3.12, S 7.31, found C 58.72, H 6.03, N 3.10, S 7.14.

***N*-(1-(4-(Dimethylamino)phenyl)-2-nitroethyl)-4-methylbenzenesulfonamide (8cd)** was obtained from nitromethane (**4d-H**, 100 mg, 1.64 mmol), the imine **2c** (100 mg, 331 μmol), and Et_3N (6.0 mg, 59 μmol , 18 mol-%) after 3.5 h of reaction time as a yellow solid still containing impurities. Recrystallization from *n*-pentane/ CH_2Cl_2 yielded **8cd** as yellow solid (22 mg, 61 μmol , 18 %).

RAP 65.1

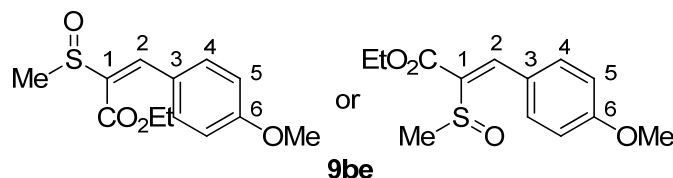


R_f (*n*-pentane/ EtOAc 2:1, v/v): 0.33. Mp. (*n*-pentane/ CH_2Cl_2): 152-153°C. ^1H -NMR (CDCl_3 , 599 MHz): δ = 2.41 (s, 3 H, Ar-Me), 2.90 (s, 6 H, NMe_2), 4.64 (dd, 1 H, J = 15.0, 9.4 Hz, 1-H), 4.83-4.86 (m, 2 H, 1-H, 2-H), 5.29 (d, 1 H, J = 5.6 Hz, NH), 6.54 (d, 2 H, J = 8.3 Hz, 5-H), 6.90 (d, 2 H, J = 8.8 Hz, 4-H), 7.24 (d, 2 H, J = 7.9 Hz, 9-H), 7.66 (d, 2 H, J = 8.3 Hz, 8-H). ^{13}C -NMR (CDCl_3 , 151 MHz): δ = 21.6 (q, Ar-Me), 40.3 (q, NMe_2), 55.2 (d, C-2), 79.0 (t, C-1), 112.5 (d, C-5), 122.3 (s, C-3), 127.2 (d, C-8), 127.4 (d, C-4), 129.7 (d, C-9), 136.5 (s, C-7), 143.8 (s, C-10), 150.7 (s, C-6). HR-MS (ESI^+) $[\text{M}+\text{H}]^+$: calcd for $[\text{C}_{17}\text{H}_{22}\text{N}_3\text{O}_4\text{S}]^+$: 364.1325, found 364.1325.

Ethyl 3-(4-Methoxyphenyl)-2-(methylsulfinyl)acrylate (9be) was obtained from ethyl 2-(methylsulfinyl)acetate (**4e-H**, 75.0 mg, 499 μmol), the imine **2b** (100 mg, 346 μmol), and $\text{KO}t\text{Bu}$ (5.6 mg, 50 μmol , 14 mol-%) after 2.5 h of reaction time as a pale yellow oil (48 mg,

0.18 mmol, 52%). A NOESY experiment did not give conclusive results about the configuration of the olefinic double bond.

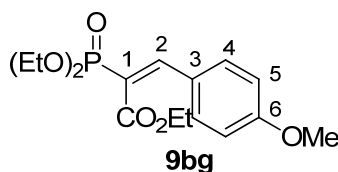
RAP 91.2



R_f (*n*-pentane/EtOAc 2:3, *v/v*): 0.33. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 1.32 (t, 3 H, J = 7.1 Hz, OCH_2CH_3), 2.76 (s, 3 H, SOMe), 3.85 (s, 3 H, OMe), 4.32 (q, 2 H, J = 7.1 Hz, OCH_2CH_3), 6.92 (d, 2 H, J = 8.9 Hz, 5-H), 7.52 (s, 1 H, 2-H), 7.73 (d, 2 H, J = 9.0 Hz, 4-H). $^{13}\text{C-NMR}$ (CDCl_3 , 75.5 MHz): δ = 14.0 (q, OCH_2CH_3), 42.0 (q, SOMe), 55.4 (q, OMe), 61.6 (t, OCH_2CH_3), 113.8 (d, C-5), 125.3 (s, C-3), 133.05 (s, C-1), 133.11 (d, C-4), 140.6 (d, C-2), 161.6 (s, C-6), 163.4 (s, CO). MS (EI): m/e (%) = 268 (3) $[\text{M}]^+$, 206 (11), 205 (100), 177 (25), 159 (20), 132 (47), 89 (10). HR-MS (EI) $[\text{M}]^+$: calcd for $[\text{C}_{13}\text{H}_{16}\text{O}_4\text{S}]^+$: 268.0764, found 268.0774.

(E)-Ethyl 2-(diethoxyphosphoryl)-3-(4-methoxyphenyl)acrylate (9bg) was obtained from ethyl 2-(diethoxyphosphoryl)acetate (**4g-H**, 150 mg, 669 μmol), the imine **2b** (100 mg, 346 μmol), and KO^tBu (7.2 mg, 64 μmol , 18 mol-%) after 1 h of reaction time as a colorless oil (100 mg, 292 μmol , 84%).

RAP 66.2



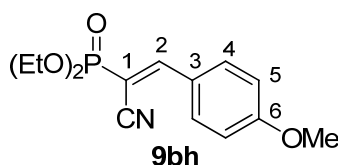
R_f (*n*-pentane/EtOAc 1:2, *v/v*): 0.31. $^1\text{H-NMR}$ (CDCl_3 , 599 MHz): δ = 1.29 (t, 3 H, J = 7.2 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.36 (td, 6 H, J = 7.1, 0.6 Hz, $2 \times \text{POCH}_2\text{CH}_3$), 3.83 (s, 3 H, OMe), 4.13-4.22 (m, 4 H, $2 \times \text{POCH}_2\text{CH}_3$), 4.31 (q, 2 H, J = 7.2 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 6.88 (d, 2 H, J = 8.9 Hz, 5-H), 7.42 (d, 2 H, J = 8.9 Hz, 4-H), 7.58 (d, 1 H, J = 24.4 Hz, 2-H). $^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz): δ = 14.0 (q, $\text{CO}_2\text{CH}_2\text{CH}_3$), 16.2 (q, d, J_{PC} = 6.8 Hz, POCH_2CH_3), 55.4 (q, OMe), 61.6 (t, $\text{CO}_2\text{CH}_2\text{CH}_3$), 62.6 (t, d, J_{PC} = 5.1 Hz, POCH_2CH_3), 114.1 (d, C-5), 121.1 (s, d, J_{PC} = 180 Hz, C-1), 126.1 (s, d, J_{PC} = 20.5 Hz, C-3), 131.5 (d, d, J_{PC} = 1.2 Hz, C-4), 148.0

(d, d, $J_{\text{PC}} = 6.7$ Hz, C-2), 161.5 (s, C-6), 166.8 (s, d, $J_{\text{PC}} = 12.6$ Hz, CO). ^{31}P -NMR (CDCl_3 , 81.0 MHz): $\delta = 16.1$.

^1H -NMR signals are in agreement with those reported in the literature.^[S10]

(E)-Diethyl (1-cyano-2-(4-methoxyphenyl)vinyl)phosphonate (9bh) was obtained from diethyl (cyanomethyl)phosphonate (**4h-H**, 120 mg, 677 μmol), the imine **2b** (100 mg, 346 μmol), and Et_3N (6.5 mg, 64 μmol , 18 mol-%) after 3 h of reaction time as a colorless oil (83 mg, 0.28 mmol, 81%).

RAP 64.1



R_f (*n*-pentane/ EtOAc 1:2, *v/v*): 0.31. ^1H -NMR (CDCl_3 , 599 MHz): $\delta = 1.41$ (td, 6 H, $J = 7.1$, 0.6 Hz, $2 \times \text{OCH}_2\text{CH}_3$), 3.89 (s, 3 H, OMe), 4.17-4.27 (m, 4 H, $2 \times \text{OCH}_2\text{CH}_3$), 6.99 (d, 2 H, $J = 8.9$ Hz, 5-H), 7.93 (d, 1 H, $J = 21.3$ Hz, 2-H), 7.97 (d, 2 H, $J = 8.9$ Hz, 4-H). ^{13}C -NMR (CDCl_3 , 151 MHz): $\delta = 16.3$ (q, d, $J_{\text{PC}} = 6.4$ Hz, OCH_2CH_3), 55.6 (q, OMe), 63.4 (t, d, $J_{\text{PC}} = 5.8$ Hz, OCH_2CH_3), 95.7 (s, d, $J_{\text{PC}} = 200$ Hz, C-1), 114.7 (d, C-5), 116.1 (s, d, $J_{\text{PC}} = 10.4$ Hz, CN), 125.5 (s, d, $J_{\text{PC}} = 18.2$ Hz, C-3), 133.0 (d, d, $J_{\text{PC}} = 1.1$ Hz, C-4), 158.3 (d, d, $J_{\text{PC}} = 7.4$ Hz, C-2), 163.5 (s, C-6). ^{31}P -NMR (CDCl_3 , 81.0 MHz): $\delta = 13.5$.

^1H -NMR signals are in agreement with those reported in the literature.^[S10]

^[S10] Shen, Y.; Jiang, G.-F. *J. Chem. Res.* **2000**, 140-141.

3. KINETICS

3.1 Reactions of the Sulfur Ylide 4a with the Aldehydes 1a–i

Reactions of sulfur ylide 4a with the benzaldehydes 1a–e

Table S1: Kinetics of the reaction of **4a** with **1a** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[1a] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.22-1	$\approx 4 \times 10^{-5}$	3.95×10^{-4}	4.54×10^{-2}
RAK 23.22-2	$\approx 4 \times 10^{-5}$	4.28×10^{-4}	4.83×10^{-2}
RAK 23.22-3	$\approx 5 \times 10^{-5}$	4.73×10^{-4}	5.43×10^{-2}
RAK 23.22-4	$\approx 5 \times 10^{-5}$	5.22×10^{-4}	5.98×10^{-2}
RAK 23.22-5	$\approx 6 \times 10^{-5}$	5.68×10^{-4}	6.53×10^{-2}

$$k_2 = 1.17 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$$

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

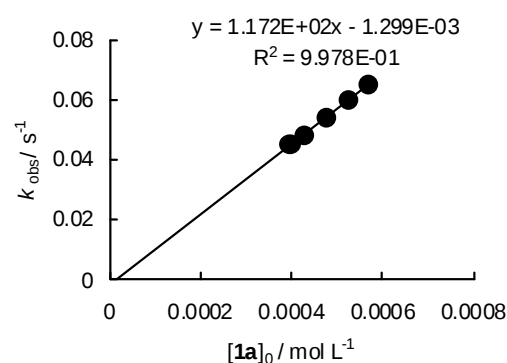


Table S2: Kinetics of the reaction of **4a** with **1b** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[1b] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.27-1	$\approx 4 \times 10^{-5}$	4.12×10^{-4}	3.33×10^{-2}
RAK 23.27-5	$\approx 5 \times 10^{-5}$	4.96×10^{-4}	3.92×10^{-2}
RAK 23.27-2	$\approx 5 \times 10^{-5}$	5.48×10^{-4}	4.25×10^{-2}
RAK 23.27-3	$\approx 5 \times 10^{-5}$	6.81×10^{-4}	5.45×10^{-2}
RAK 23.27-4	$\approx 5 \times 10^{-5}$	8.19×10^{-4}	6.56×10^{-2}

$$k_2 = 8.06 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$$

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

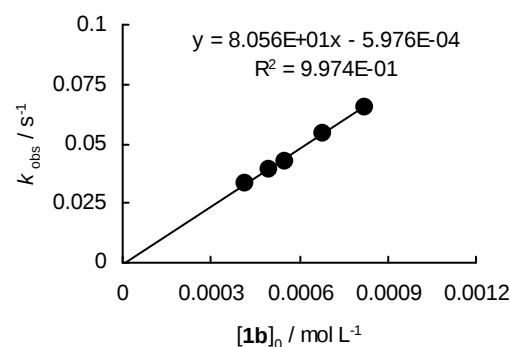
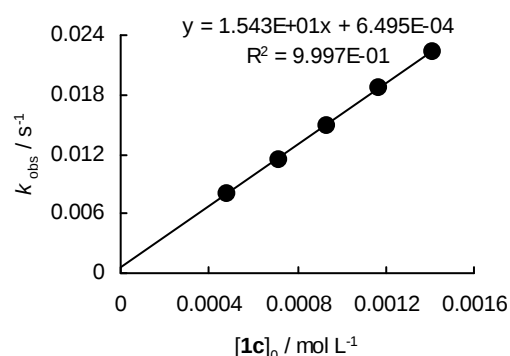


Table S3: Kinetics of the reaction of **4a** with **1c** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[1c] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.29-1	$\approx 5 \times 10^{-5}$	4.78×10^{-4}	8.14×10^{-3}
RAK 23.29-2	$\approx 5 \times 10^{-5}$	7.12×10^{-4}	1.15×10^{-2}
RAK 23.29-3	$\approx 5 \times 10^{-5}$	9.34×10^{-4}	1.50×10^{-2}
RAK 23.29-4	$\approx 5 \times 10^{-5}$	1.17×10^{-3}	1.87×10^{-2}
RAK 23.29-5	$\approx 5 \times 10^{-5}$	1.41×10^{-3}	2.24×10^{-2}

$$k_2 = 1.54 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$$

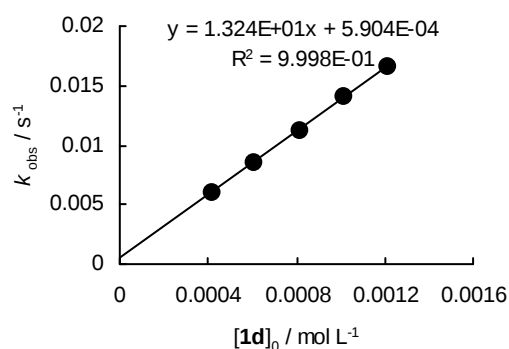
* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

**Table S4:** Kinetics of the reaction of **4a** with **1d** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[1d] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.26-1	$\approx 4 \times 10^{-5}$	4.11×10^{-4}	6.10×10^{-3}
RAK 23.26-2	$\approx 5 \times 10^{-5}$	6.07×10^{-4}	8.54×10^{-3}
RAK 23.26-3	$\approx 5 \times 10^{-5}$	8.11×10^{-4}	1.13×10^{-2}
RAK 23.26-4	$\approx 5 \times 10^{-5}$	1.02×10^{-3}	1.41×10^{-2}
RAK 23.26-5	$\approx 5 \times 10^{-5}$	1.21×10^{-3}	1.66×10^{-2}

$$k_2 = 1.32 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$$

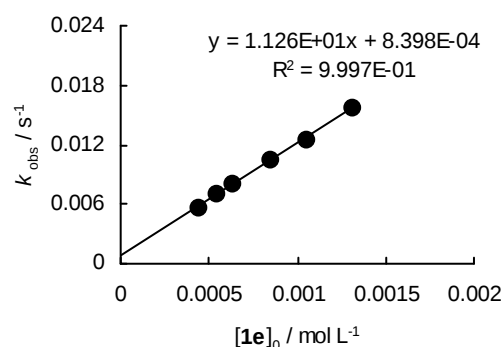
* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

**Table S5:** Kinetics of the reaction of **4a** with **1e** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[1e] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.23-1	$\approx 4 \times 10^{-5}$	4.36×10^{-4}	5.74×10^{-3}
RAK 23.23-6	$\approx 5 \times 10^{-5}$	5.44×10^{-4}	6.97×10^{-3}
RAK 23.23-2	$\approx 5 \times 10^{-5}$	6.35×10^{-4}	8.04×10^{-3}
RAK 23.23-3	$\approx 5 \times 10^{-5}$	8.49×10^{-4}	1.04×10^{-2}
RAK 23.23-4	$\approx 5 \times 10^{-5}$	1.05×10^{-3}	1.26×10^{-2}
RAK 23.26-5	$\approx 5 \times 10^{-5}$	1.31×10^{-3}	1.57×10^{-2}

$$k_2 = 1.13 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$$

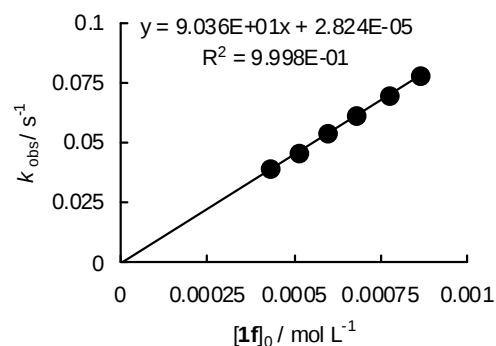
* Only approximate values are given for the initial concentration of the nucleophile (see general comments).



Reactions of sulfur ylide **4a** with the cinnamaldehydes **1f,g****Table S6:** Kinetics of the reaction of **4a** with **1f** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

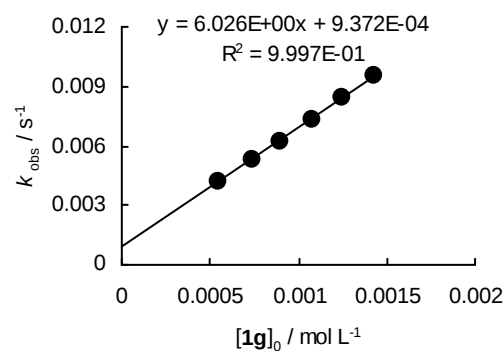
No.	[4a] ₀ / mol L ⁻¹ *	[1f] ₀ / mol L ⁻¹	<i>k</i> _{obs} / s ⁻¹
RAK 23.18-6	$\approx 4 \times 10^{-5}$	4.30×10^{-4}	3.91×10^{-2}
RAK 23.18-1	$\approx 5 \times 10^{-5}$	5.12×10^{-4}	4.59×10^{-2}
RAK 23.18-4	$\approx 5 \times 10^{-5}$	5.95×10^{-4}	5.38×10^{-2}
RAK 23.18-2	$\approx 5 \times 10^{-5}$	6.78×10^{-4}	6.14×10^{-2}
RAK 23.18-5	$\approx 5 \times 10^{-5}$	7.72×10^{-4}	6.99×10^{-2}
RAK 23.18-3	$\approx 6 \times 10^{-5}$	8.63×10^{-4}	7.79×10^{-2}
<i>k</i>₂ = 9.04×10^1 L mol⁻¹ s⁻¹			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

**Table S7:** Kinetics of the reaction of **4a** with **1g** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[1g] ₀ / mol L ⁻¹	<i>k</i> _{obs} / s ⁻¹
RAK 23.24-1	$\approx 5 \times 10^{-5}$	5.45×10^{-4}	4.24×10^{-3}
RAK 23.24-2	$\approx 6 \times 10^{-5}$	7.32×10^{-4}	5.37×10^{-3}
RAK 23.24-3	$\approx 5 \times 10^{-5}$	8.92×10^{-4}	6.29×10^{-3}
RAK 23.24-4	$\approx 6 \times 10^{-5}$	1.08×10^{-3}	7.37×10^{-3}
RAK 23.24-5	$\approx 5 \times 10^{-5}$	1.25×10^{-3}	8.48×10^{-3}
RAK 23.24-6	$\approx 5 \times 10^{-5}$	1.42×10^{-3}	9.54×10^{-3}
<i>k</i>₂ = 6.03 L mol⁻¹ s⁻¹			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).



Reactions of sulfur ylide **4a** with the aliphatic aldehydes **1h,i**

Table S8: Kinetics of the reaction of **4a** with **1h** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[1h] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.20-1	$\approx 6 \times 10^{-5}$	5.69×10^{-4}	2.24×10^{-2}
RAK 23.20-2	$\approx 6 \times 10^{-5}$	7.66×10^{-4}	3.00×10^{-2}
RAK 23.20-3	$\approx 7 \times 10^{-5}$	9.06×10^{-4}	3.52×10^{-2}
RAK 23.20-4	$\approx 7 \times 10^{-5}$	1.14×10^{-3}	4.52×10^{-2}
RAK 23.20-5	$\approx 7 \times 10^{-5}$	1.31×10^{-3}	5.12×10^{-2}
RAK 23.20-6	$\approx 7 \times 10^{-5}$	1.49×10^{-3}	5.90×10^{-2}
$k_2 = 3.98 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

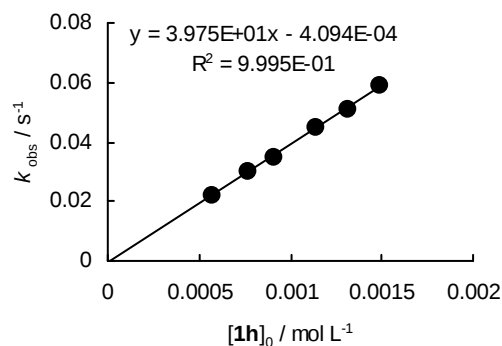


Table S9: Kinetics of the reaction of **4a** with **1i** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[1i] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.28-1	$\approx 5 \times 10^{-5}$	6.16×10^{-4}	2.51×10^{-2}
RAK 23.28-2	$\approx 6 \times 10^{-5}$	8.20×10^{-4}	3.28×10^{-2}
RAK 23.28-3	$\approx 6 \times 10^{-5}$	1.01×10^{-3}	3.96×10^{-2}
RAK 23.28-4	$\approx 6 \times 10^{-5}$	1.22×10^{-3}	4.73×10^{-2}
RAK 23.28-5	$\approx 6 \times 10^{-5}$	1.42×10^{-3}	5.54×10^{-2}
$k_2 = 3.72 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

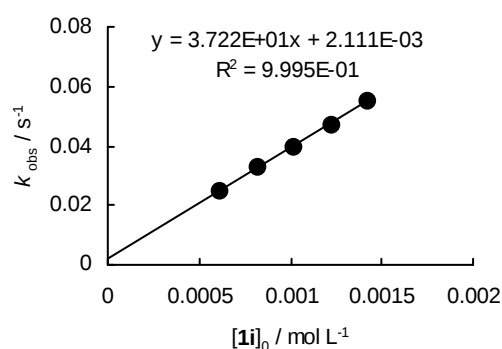
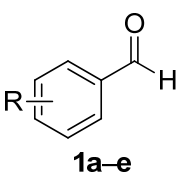
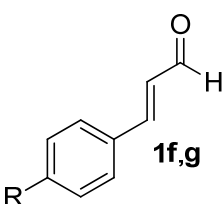
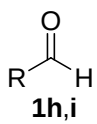


Table S10: Calculation of the electrophilicity parameters E for **1a–i** using the second-order rate constants for their reactions with sulfur ylide **4a** ($N = 21.07$, $s_N = 0.68$) and correlation equation $\log k_2 = s_N(N + E)$.

Electrophile	$k_2 / \text{L mol}^{-1} \text{s}^{-1}$	Electrophilicity E
 1a–e	1a ($R = m\text{-Cl}$)	1.17×10^2 $E(\mathbf{1a}) = -18.03$
	1b ($R = m\text{-F}$)	8.06×10^1 $E(\mathbf{1b}) = -18.27$
	1c ($R = m\text{-OMe}$)	1.54×10^1 $E(\mathbf{1c}) = -19.32$
	1d ($R = p\text{-F}$)	1.32×10^1 $E(\mathbf{1d}) = -19.42$
	1e ($R = \text{H}$)	1.13×10^1 $E(\mathbf{1e}) = -19.52$
 1f,g	1f ($R = \text{NO}_2$)	9.04×10^1 $E(\mathbf{1f}) = -18.19$
	1g ($R = \text{H}$)	6.03 $E(\mathbf{1g}) = -19.92$
 1h,i	1h ($R = n\text{-Pr}$)	3.98×10^1 $E(\mathbf{1h}) = -18.72$
	1i ($R = n\text{-Pent}$)	3.72×10^1 $E(\mathbf{1i}) = -18.76$

3.2 Reactions of the Sulfur Ylides **4a,b** and the Carbanions **4c–h** with the Imines **2a–e**

Reactions of sulfur ylide **4b** and the carbanion **4e** with imine **2a**

Table S11: Kinetics of the reaction of **4b** with **2a** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 530 \text{ nm}$).

No.	$[\mathbf{4b}]_0 / \text{mol L}^{-1} *$	$[\mathbf{2a}]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
RAK 23.33-1	$\approx 4 \times 10^{-5}$	4.55×10^{-4}	1.91×10^1
RAK 23.33-2	$\approx 4 \times 10^{-5}$	6.83×10^{-4}	2.88×10^1
RAK 23.33-3	$\approx 4 \times 10^{-5}$	9.10×10^{-4}	3.79×10^1
RAK 23.33-4	$\approx 4 \times 10^{-5}$	1.14×10^{-3}	4.71×10^1
RAK 23.33-5	$\approx 4 \times 10^{-5}$	1.37×10^{-3}	5.71×10^1
$k_2 = 4.15 \times 10^4 \text{ L mol}^{-1} \text{s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

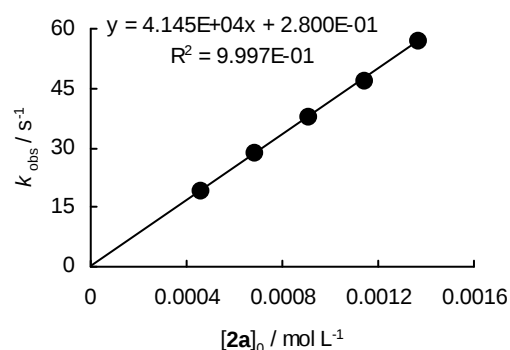
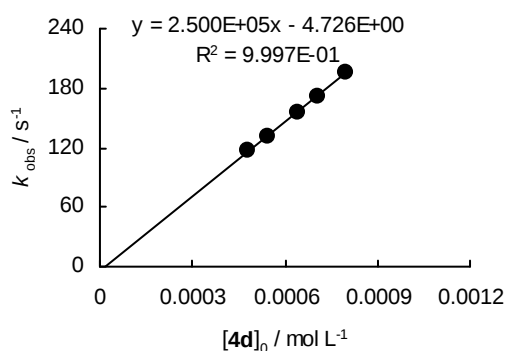


Table S12: Kinetics of the reaction of **4d** with **2a** in DMSO at 20°C (addition of 0-1.8 equiv of 18-crown-6, stopped-flow UV-Vis spectrometer, $\lambda = 300$ nm).

No.	[2a] ₀ / mol L ⁻¹	[4d] ₀ / mol L ⁻¹	[18-crown-6] / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 26.1-1	3.82×10^{-5}	4.80×10^{-4}	-	1.16×10^2
RAK 26.1-4	3.82×10^{-5}	5.44×10^{-4}	-	1.31×10^2
RAK 26.1-2	3.82×10^{-5}	6.41×10^{-4}	-	1.55×10^2
RAK 26.1-5	3.82×10^{-5}	7.05×10^{-4}	-	1.71×10^2
RAK 26.1-3	3.82×10^{-5}	8.01×10^{-4}	1.48×10^{-3}	1.96×10^2
$k_2 = 2.50 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$				



Reactions of the sulfur ylides **4a,b** and the carbanions **4c–h** with imine **2b**

Table S13: Kinetics of the reaction of **4a** with **2b** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[2b] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.36-4	$\approx 4 \times 10^{-5}$	3.32×10^{-4}	1.04×10^2
RAK 23.36-1	$\approx 4 \times 10^{-5}$	4.43×10^{-4}	1.38×10^2
RAK 23.36-2	$\approx 4 \times 10^{-5}$	5.54×10^{-4}	1.75×10^2
RAK 23.36-3	$\approx 4 \times 10^{-5}$	6.65×10^{-4}	2.11×10^2
RAK 23.36-5	$\approx 4 \times 10^{-5}$	7.75×10^{-4}	2.45×10^2
$k_2 = 3.21 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

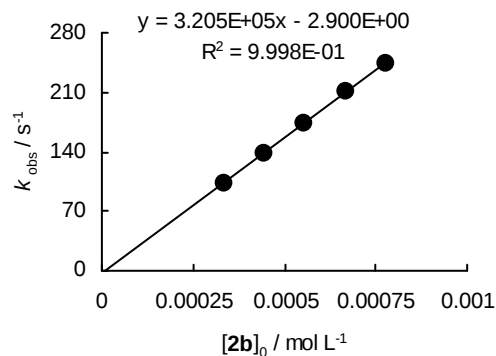
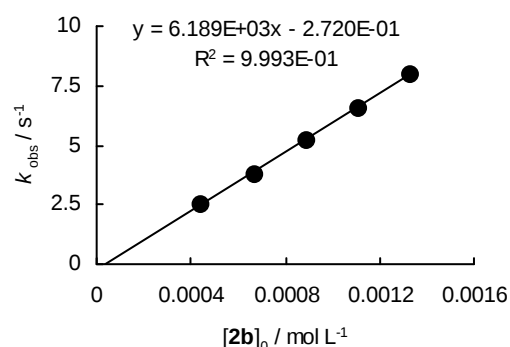


Table S14: Kinetics of the reaction of **4b** with **2b** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 530$ nm).

No.	$[\mathbf{4b}]_0 / \text{mol L}^{-1} *$	$[\mathbf{2b}]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
RAK 23.35-2-1	$\approx 4 \times 10^{-5}$	4.43×10^{-4}	2.53
RAK 23.35-2-2	$\approx 4 \times 10^{-5}$	6.65×10^{-4}	3.78
RAK 23.35-2-3	$\approx 4 \times 10^{-5}$	8.86×10^{-4}	5.21
RAK 23.35-2-4	$\approx 4 \times 10^{-5}$	1.11×10^{-3}	6.53
RAK 23.35-2-5	$\approx 4 \times 10^{-5}$	1.33×10^{-3}	8.01

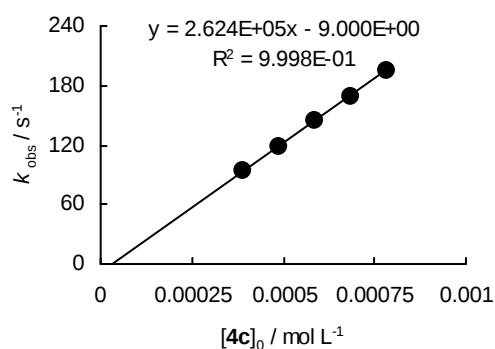
$$k_2 = 6.19 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$$

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

**Table S15:** Kinetics of the reaction of **4c** with **2b** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 330$ nm).

No.	$[\mathbf{2b}]_0 / \text{mol L}^{-1}$	$[\mathbf{4c}]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
RAK 25.3-1	3.89×10^{-5}	3.90×10^{-4}	9.40×10^1
RAK 25.3-2	3.89×10^{-5}	4.88×10^{-4}	1.18×10^2
RAK 25.3-3	3.89×10^{-5}	5.85×10^{-4}	1.45×10^2
RAK 25.3-4	3.89×10^{-5}	6.83×10^{-4}	1.70×10^2
RAK 25.3-5	3.89×10^{-5}	7.81×10^{-4}	1.96×10^2

$$k_2 = 2.62 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$$

**Table S16:** Kinetics of the reaction of **4d** with **2b** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 330$ nm).

No.	$[\mathbf{2b}]_0 / \text{mol L}^{-1}$	$[\mathbf{4d}]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
RAK 25.1-1	3.77×10^{-5}	4.44×10^{-4}	1.95×10^1
RAK 25.1-2	3.77×10^{-5}	6.66×10^{-4}	2.97×10^1
RAK 25.1-3	3.77×10^{-5}	8.88×10^{-4}	3.84×10^1
RAK 25.1-4	3.77×10^{-5}	1.11×10^{-3}	4.82×10^1
RAK 25.1-5	3.77×10^{-5}	1.33×10^{-3}	5.81×10^1

$$k_2 = 4.31 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$$

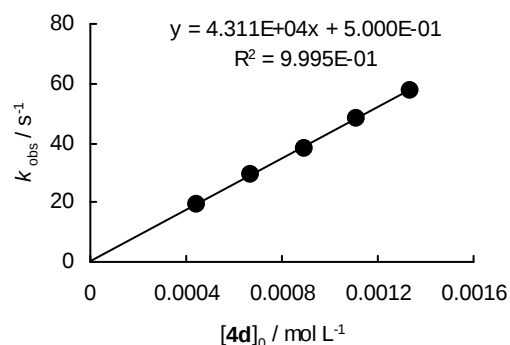
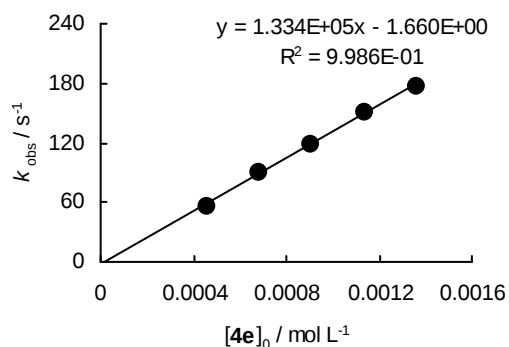
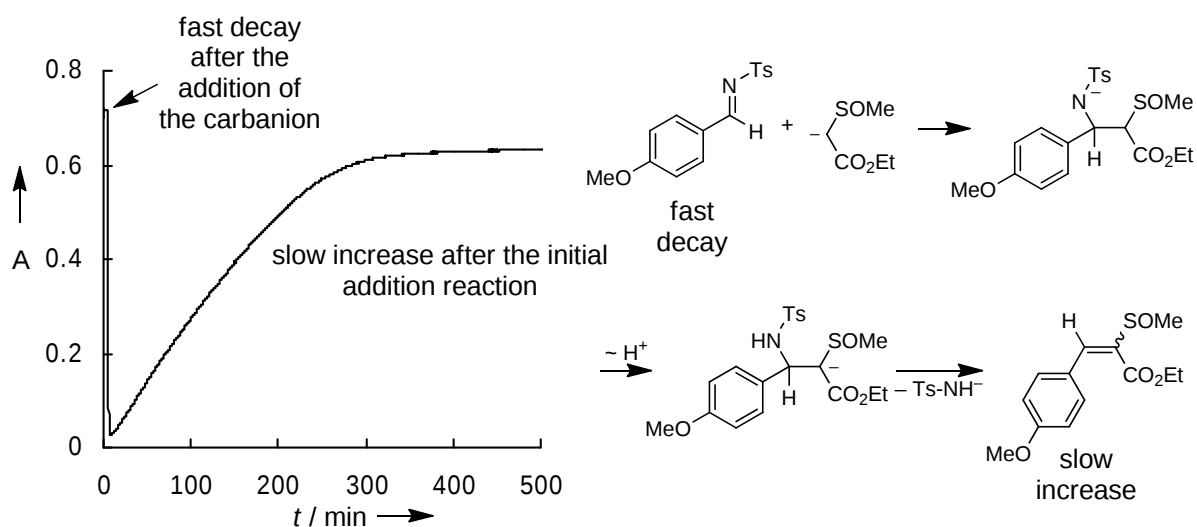


Table S17: Kinetics of the reaction of **4e** with **2b** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 330$ nm).

No.	[2b] ₀ / mol L ⁻¹	[4e] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 25.5-1	3.87×10^{-5}	4.53×10^{-4}	5.68×10^1
RAK 25.5-2	3.87×10^{-5}	6.80×10^{-4}	9.09×10^1
RAK 25.5-3	3.87×10^{-5}	9.07×10^{-4}	1.20×10^2
RAK 25.5-4	3.87×10^{-5}	1.13×10^{-3}	1.51×10^2
RAK 25.5-5	3.87×10^{-5}	1.36×10^{-3}	1.78×10^2
$k_2 = 1.33 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$			

**Table S18:** Mechanistic study for the reaction of **4e** with **2b** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 318$ nm).

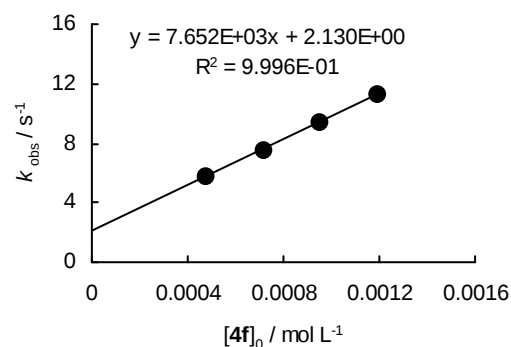
No.	[2b] ₀ / mol L ⁻¹	[4e] ₀ / mol L ⁻¹
RAME4	4.73×10^{-5}	8.03×10^{-5}



The imine **2b** reacts with the carbanion **4e** in a fast addition step (fast decay when carbanion is added, for the second-order rate constant see Table S17). The subsequent slow increase of the absorbance indicates a slow formation of the condensation product.

Table S19: Kinetics of the reaction of **4f** with **2b** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 330$ nm).

No.	[2b] ₀ / mol L ⁻¹	[4f] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 25.2-2-1	3.98×10^{-5}	4.77×10^{-4}	5.81
RAK 25.2-2-2	3.98×10^{-5}	7.15×10^{-4}	7.59
RAK 25.2-2-3	3.98×10^{-5}	9.54×10^{-4}	9.37
RAK 25.2-2-4	3.98×10^{-5}	1.19×10^{-3}	1.13×10^1
$k_2 = 7.65 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$			

**Table S20:** Kinetics of the reaction of **4g** with **2b** in DMSO at 20°C (addition of 0-1.6 equiv of 18-crown-6, stopped-flow UV-Vis spectrometer, $\lambda = 330$ nm).

No.	[2b] ₀ / mol L ⁻¹	[4g] ₀ / mol L ⁻¹	[18-crown-6] / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 25.7-1	3.80×10^{-5}	4.59×10^{-4}	-	1.33
RAK 25.7-2	3.80×10^{-5}	6.89×10^{-4}	-	1.84
RAK 25.7-3	3.80×10^{-5}	9.19×10^{-4}	1.48×10^{-3}	2.49
RAK 25.7-4	3.80×10^{-5}	1.15×10^{-3}	-	2.91
RAK 25.7-5	3.80×10^{-5}	1.38×10^{-3}	-	3.49
$k_2 = 2.35 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$				

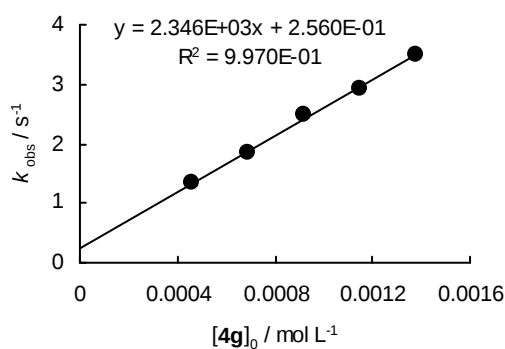
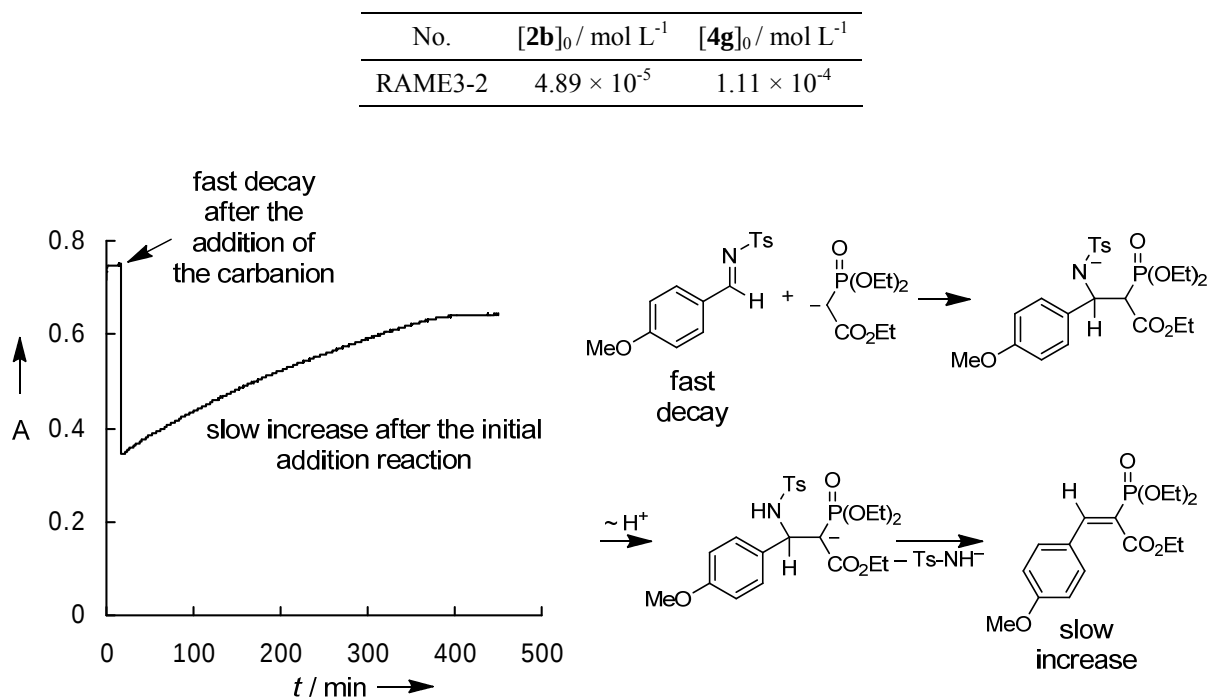


Table S21: Mechanistic study for the reaction of **4g** with **2b** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 318$ nm).

The imine **2b** reacts with the carbanion **4g** in a fast addition step (fast decay when carbanion is added, for the second-order rate constant see Table S20). The subsequent slow increase of the absorbance indicates a slow formation of the condensation product.

Table S22: Kinetics of the reaction of **4h** with **2b** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 330$ nm).

No.	$[2b]_0 / \text{mol L}^{-1}$	$[4h]_0 / \text{mol L}^{-1}$	$k_{\text{obs}} / \text{s}^{-1}$
RAK 25.6-1	3.87×10^{-5}	4.00×10^{-4}	8.82
RAK 25.6-2	3.87×10^{-5}	6.00×10^{-4}	1.22×10^1
RAK 25.6-3	3.87×10^{-5}	7.99×10^{-4}	1.53×10^1
RAK 25.6-4	3.87×10^{-5}	9.99×10^{-4}	1.85×10^1
RAK 25.6-5	3.87×10^{-5}	1.20×10^{-3}	2.20×10^1
$k_2 = 1.63 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$			

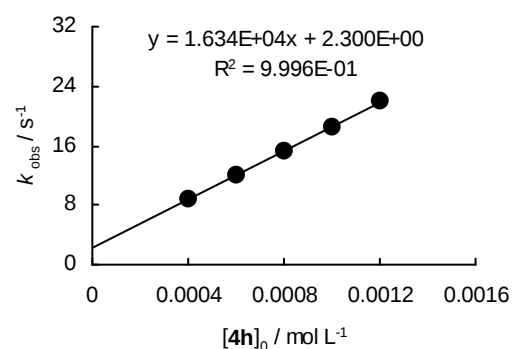
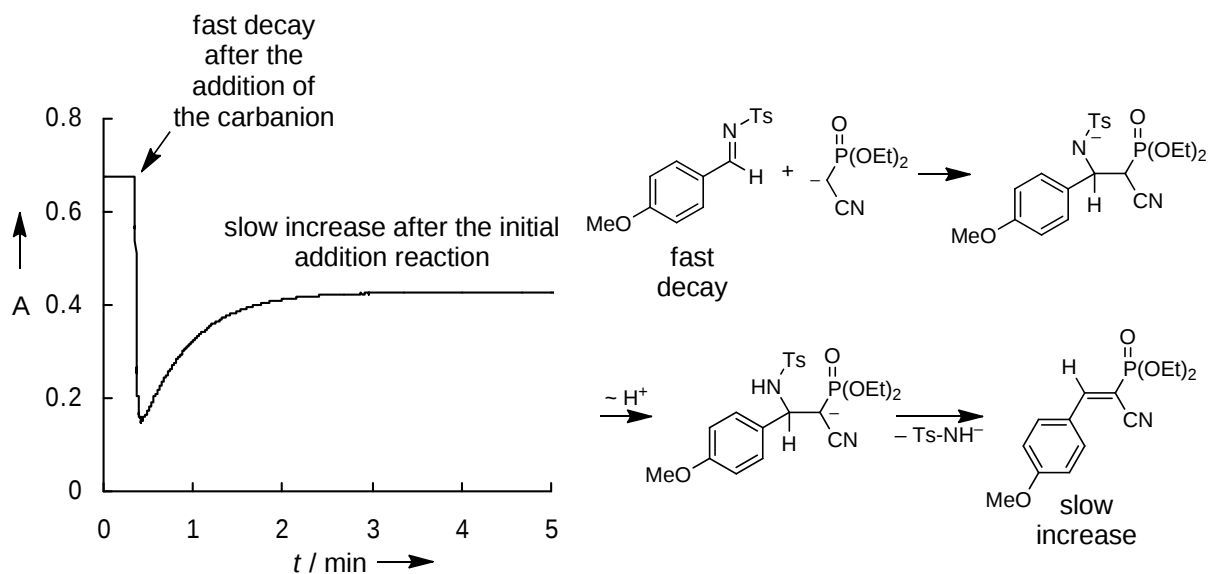


Table S23: Mechanistic study for the reaction of **4h** with **2b** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 318$ nm).

No.	$[\mathbf{2b}]_0 / \text{mol L}^{-1}$	$[\mathbf{4h}]_0 / \text{mol L}^{-1}$
RAME2-1b	4.29×10^{-5}	7.07×10^{-4}



The imine **2b** reacts with the carbanion **4h** in a fast addition step (fast decay when carbanion is added, for the second-order rate constant see Table S22). The subsequent slow increase of the absorbance indicates a slow formation of the condensation product.

Reactions of the carbanions **4c–e** with imine **2c**

Table S24: Kinetics of the reaction of **4c** with **2c** in DMSO at 20°C (addition of 0-1.4 equiv 18-crown-6, stopped-flow UV-Vis spectrometer, $\lambda = 394$ nm).

No.	[2c] ₀ / mol L ⁻¹	[4c] ₀ / mol L ⁻¹	[18-crown-6] / mol L ⁻¹	$k_{\text{obs}} / \text{s}^{-1}$
RAK 27.2-1	3.27×10^{-5}	3.96×10^{-4}	-	4.68
RAK 27.2-2	3.27×10^{-5}	5.93×10^{-4}	-	6.53
RAK 27.2-3	3.27×10^{-5}	7.91×10^{-4}	1.10×10^{-3}	8.76
RAK 27.2-4	3.27×10^{-5}	9.89×10^{-4}	-	1.07×10^1
RAK 27.2-5	3.27×10^{-5}	1.19×10^{-3}	-	1.28×10^1
$k_2 = 1.03 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$				

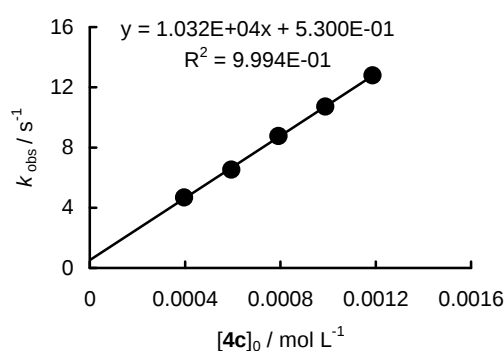


Table S25: Kinetics of the reaction of **4d** with **2c** in DMSO at 20°C (addition of 0-1.3 equiv 18-crown-6, stopped-flow UV-Vis spectrometer, $\lambda = 394$ nm).

No.	[2c] ₀ / mol L ⁻¹	[4d] ₀ / mol L ⁻¹	[18-crown-6] / mol L ⁻¹	$k_{\text{obs}} / \text{s}^{-1}$
RAK 27.1-1	3.70×10^{-5}	4.80×10^{-4}	-	7.88×10^{-1}
RAK 27.1-2	3.70×10^{-5}	8.01×10^{-4}	-	1.28
RAK 27.1-3	3.70×10^{-5}	1.12×10^{-3}	1.48×10^{-3}	1.83
RAK 27.1-4	3.70×10^{-5}	1.44×10^{-3}	-	2.29
RAK 27.1-5	3.70×10^{-5}	1.76×10^{-3}	-	2.82
$k_2 = 1.58 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$				

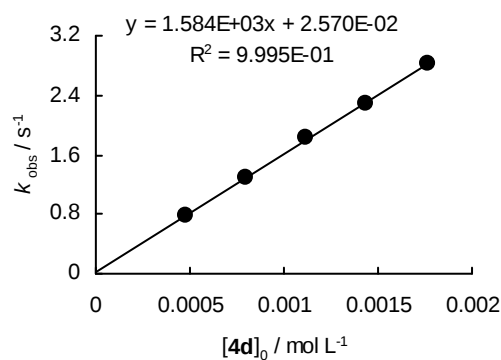
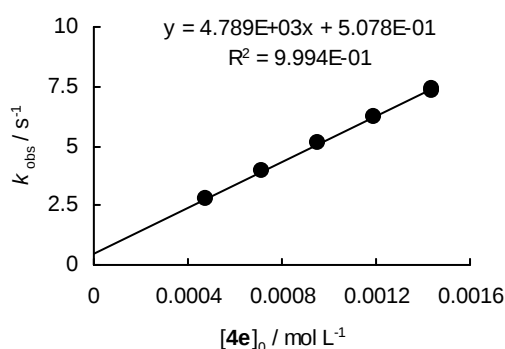
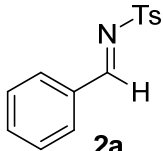
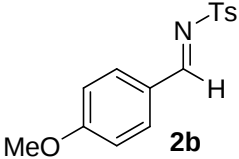
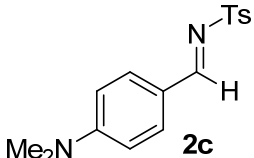


Table S26: Kinetics of the reaction of **4e** with **2c** in DMSO at 20°C (addition of 0-1.5 equiv 18-crown-6, stopped-flow UV-Vis spectrometer, $\lambda = 394$ nm).

No.	[2c] ₀ / mol L ⁻¹	[4e] ₀ / mol L ⁻¹	[18-crown-6] / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 27.3-1	3.27×10^{-5}	4.78×10^{-4}	-	2.79
RAK 27.3-2	3.27×10^{-5}	7.17×10^{-4}	-	3.92
RAK 27.3-3	3.27×10^{-5}	9.56×10^{-4}	1.10×10^{-3}	5.14
RAK 27.3-4	3.27×10^{-5}	1.20×10^{-3}	-	6.22
RAK 27.3-5	3.27×10^{-5}	1.43×10^{-3}	-	7.31
RAK 27.3-5M	3.27×10^{-5}	1.43×10^{-3}	2.21×10^{-3}	7.43
$k_2 = 4.79 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$				

**Table S27:** Determination of the electrophilicity parameters E for **2a–c** (least-squares minimization of $\Delta^2 = \sum(\log k_2 - s_N(N + E))^2$ for the correlation of $\log k_2 / s_N$ of the reactions of **2a–c** with **4a–h** versus the nucleophilicity parameters N for **4a–h**).

Electrophile	Nucleophile (N , s_N)	k_2 / L mol ⁻¹ s ⁻¹	Electrophilicity E
 2a	4b (18.42, 0.65)	4.15×10^4	E (2a) = -11.50
	4d (20.71, 0.60)	2.50×10^5	
 2b	4a (21.07, 0.68)	3.21×10^5	E (2b) = -13.05
	4b (18.42, 0.65)	6.19×10^3	
	4c (21.54, 0.62)	2.62×10^5	
	4d (20.71, 0.60)	4.31×10^4	
	4e (20.61, 0.64)	1.33×10^5	
	4f (20.22, 0.65)	7.65×10^3	
	4g (19.23, 0.65)	2.35×10^3	
 2c	4c (21.54, 0.62)	1.03×10^4	E (2c) = -15.09
	4d (20.71, 0.60)	1.58×10^3	
	4e (20.61, 0.64)	4.79×10^3	

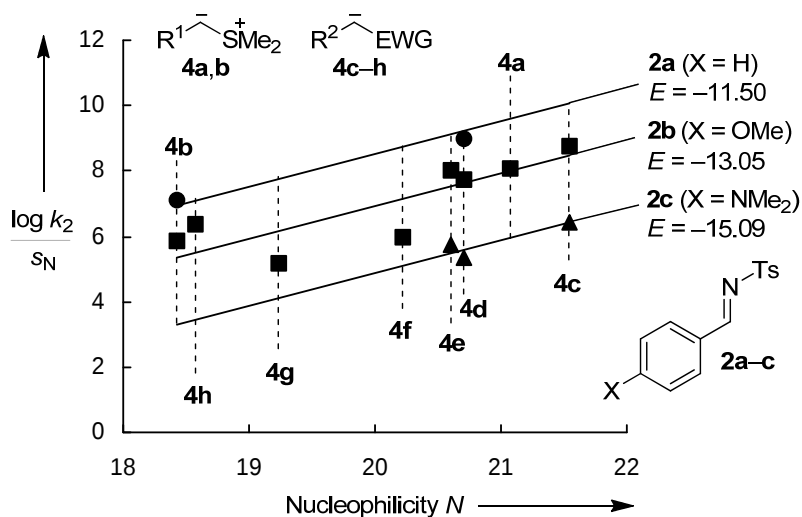
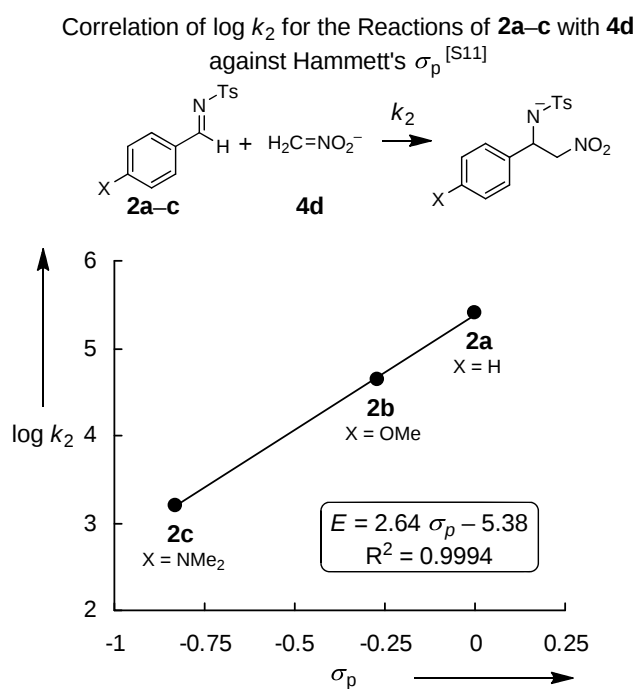


Figure S1: Correlation of the second-order rate constants ($\log k_2 / s_N$) for the reactions of the nucleophiles **4a-h** with the imines **2a-c** versus the nucleophilicity parameters N of **4a-h**. The slopes are fixed to one as required by $\log k_2 = s_N(N + E)$.



^[S11] σ_p -values taken from: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165-195.

Reactions of the sulfur ylides 4a,b with imine 2d

Table S28: Kinetics of the reaction of **4a** with **2d** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[2d] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.48-1	$\approx 6 \times 10^{-5}$	6.88×10^{-4}	2.75×10^1
RAK 23.48-2	$\approx 6 \times 10^{-5}$	8.26×10^{-4}	3.41×10^1
RAK 23.48-3	$\approx 6 \times 10^{-5}$	9.63×10^{-4}	3.86×10^1
RAK 23.48-4	$\approx 6 \times 10^{-5}$	1.10×10^{-3}	4.52×10^1
RAK 23.48-5	$\approx 6 \times 10^{-5}$	1.24×10^{-3}	4.93×10^1
$k_2 = 3.97 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

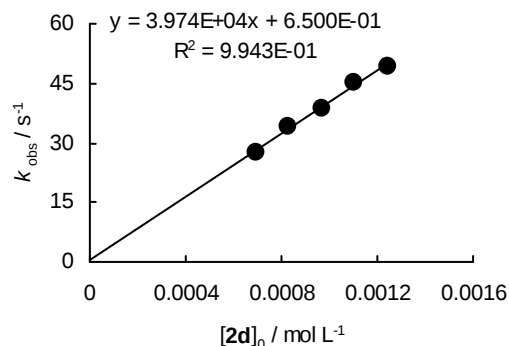
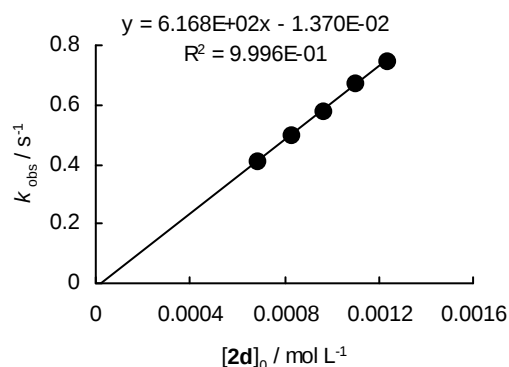


Table S29: Kinetics of the reaction of **4b** with **2d** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 520$ nm).

No.	[4b] ₀ / mol L ⁻¹ *	[2d] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.49-1	$\approx 6 \times 10^{-5}$	6.88×10^{-4}	4.09×10^{-1}
RAK 23.49-2	$\approx 6 \times 10^{-5}$	8.26×10^{-4}	4.98×10^{-1}
RAK 23.49-3	$\approx 6 \times 10^{-5}$	9.63×10^{-4}	5.79×10^{-1}
RAK 23.49-4	$\approx 6 \times 10^{-5}$	1.10×10^{-3}	6.69×10^{-1}
RAK 23.49-5	$\approx 6 \times 10^{-5}$	1.24×10^{-3}	7.48×10^{-1}
$k_2 = 6.17 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).



Reactions of sulfur ylides 4a,b with imine 2e

Table S30: Kinetics of the reaction of **4a** with **2e** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[2e] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.47-1	$\approx 6 \times 10^{-5}$	5.70×10^{-4}	2.40
RAK 23.47-2	$\approx 6 \times 10^{-5}$	8.55×10^{-4}	3.61
RAK 23.47-3	$\approx 6 \times 10^{-5}$	1.14×10^{-3}	4.91
RAK 23.47-4	$\approx 6 \times 10^{-5}$	1.42×10^{-3}	6.17
RAK 23.47-5	$\approx 6 \times 10^{-5}$	1.71×10^{-3}	7.47
$k_2 = 4.46 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

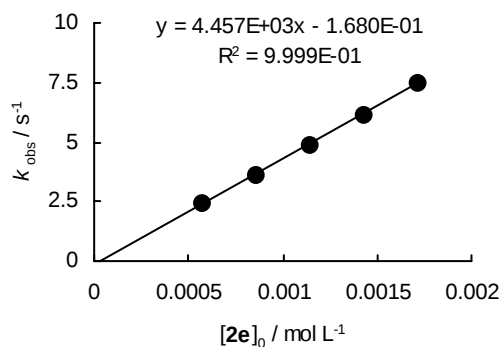
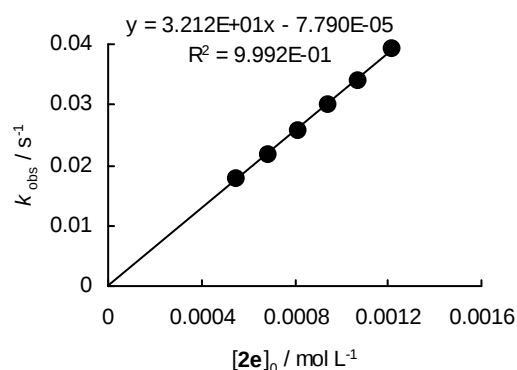


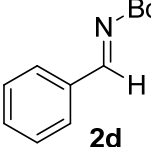
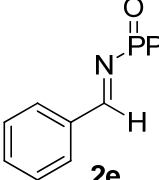
Table S31: Kinetics of the reaction of **4b** with **2e** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 520$ nm).

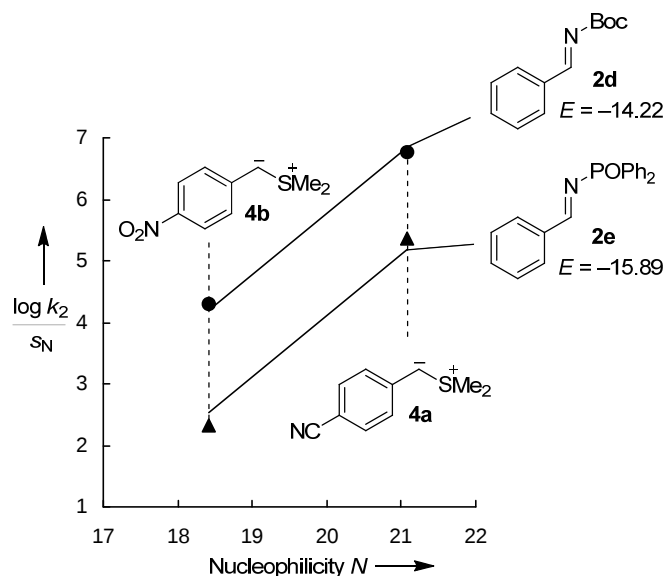
No.	[4b] ₀ / mol L ⁻¹ *	[2e] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.46-1	$\approx 5 \times 10^{-5}$	5.44×10^{-4}	1.77×10^{-2}
RAK 23.46-2	$\approx 6 \times 10^{-5}$	6.82×10^{-4}	2.17×10^{-2}
RAK 23.46-3	$\approx 6 \times 10^{-5}$	8.09×10^{-4}	2.57×10^{-2}
RAK 23.46-4	$\approx 6 \times 10^{-5}$	9.41×10^{-4}	3.00×10^{-2}
RAK 23.46-5	$\approx 6 \times 10^{-5}$	1.07×10^{-3}	3.41×10^{-2}
RAK 23.46-6	$\approx 6 \times 10^{-5}$	1.21×10^{-3}	3.92×10^{-2}

$$k_2 = 3.21 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$$

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

**Table S32:** Determination of the electrophilicity parameters E for **2d,e** (least-squares minimization of $\Delta^2 = \sum(\log k_2 - s_N(N + E))^2$ for the correlation of $\log k_2 / s_N$ of the reactions of **2d,e** with **4a,b** versus the nucleophilicity parameters N for **4a,b**).

Electrophile	Nucleophile (N , s_N)	k_2 / L mol ⁻¹ s ⁻¹	Electrophilicity E
 2d	4a (21.07, 0.68)	3.97×10^4	E (2d) = -14.22
	4b (18.42, 0.65)	6.17×10^2	
 2e	4a (21.07, 0.68)	4.46×10^3	E (2e) = -15.89
	4b (18.42, 0.65)	3.21×10^1	

**Figure S2:** Correlation of the second-order rate constants ($\log k_2 / s_N$) for the reactions of the sulfur ylides **4a,b** with the imines **2d,e** versus the nucleophilicity parameters N of **4a,b**. The slopes are fixed to one as required by $\log k_2 = s_N(N + E)$.

3.3 Reactions of the Sulfur Ylides 4a,b with the Enones 3a–f

Reactions of the sulfur ylides 4a,b with enone 3a

Table S33: Kinetics of the reaction of **4a** with **3a** in DMSO at 20°C (stopped-flow UV-Vis spectrometer, $\lambda = 400$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[3a] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.10-1	$\approx 5 \times 10^{-5}$	5.37×10^{-4}	1.78×10^{-1}
RAK 23.10-2	$\approx 5 \times 10^{-5}$	6.71×10^{-4}	2.22×10^{-1}
RAK 23.10-3	$\approx 5 \times 10^{-5}$	8.06×10^{-4}	2.67×10^{-1}
RAK 23.10-4	$\approx 5 \times 10^{-5}$	9.40×10^{-4}	3.12×10^{-1}
RAK 23.10-5	$\approx 5 \times 10^{-5}$	1.07×10^{-3}	3.56×10^{-1}
$k_2 = 3.32 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$			
RAK 23.10-2-1	$\approx 6 \times 10^{-5}$	6.47×10^{-4}	2.19×10^{-1}
RAK 23.10-2-2	$\approx 6 \times 10^{-5}$	7.76×10^{-4}	2.69×10^{-1}
RAK 23.10-2-3	$\approx 6 \times 10^{-5}$	9.05×10^{-4}	3.16×10^{-1}
RAK 23.10-2-4	$\approx 6 \times 10^{-5}$	1.03×10^{-3}	3.59×10^{-1}
RAK 23.10-2-5	$\approx 6 \times 10^{-5}$	1.16×10^{-3}	4.07×10^{-1}
$k_2 = 3.60 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$			
Average: $k_2 = 3.46 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

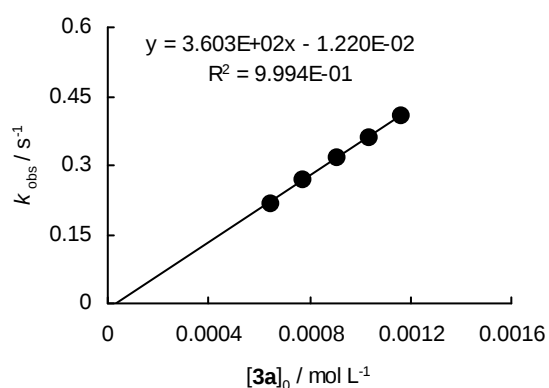
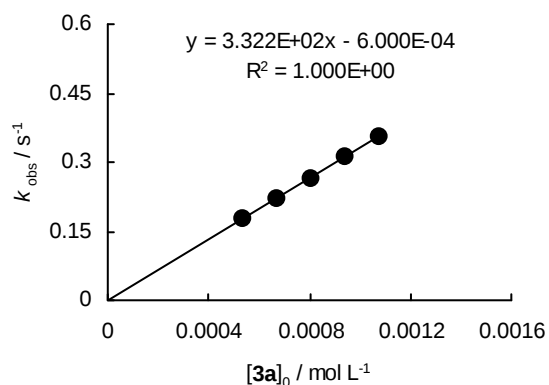
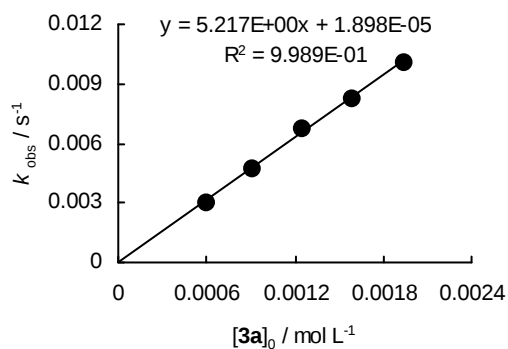


Table S34: Kinetics of the reaction of **4b** with **3a** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 520$ nm).

No.	[4b] ₀ / mol L ⁻¹ *	[3a] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.6-1	$\approx 6 \times 10^{-5}$	5.99×10^{-4}	3.07×10^{-3}
RAK 23.6-2	$\approx 6 \times 10^{-5}$	9.11×10^{-4}	4.77×10^{-3}
RAK 23.6-3	$\approx 6 \times 10^{-5}$	1.25×10^{-3}	6.71×10^{-3}
RAK 23.6-4	$\approx 6 \times 10^{-5}$	1.58×10^{-3}	8.25×10^{-3}
RAK 23.6-5	$\approx 6 \times 10^{-5}$	1.94×10^{-3}	1.01×10^{-2}
$k_2 = 5.22 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).



Reactions of the sulfur ylides **4a,b** with enone **3b**

Table S35: Kinetics of the reaction of **4a** with **3b** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 400$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[3b] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.11-5	$\approx 2 \times 10^{-5}$	2.53×10^{-4}	5.85×10^{-2}
RAK 23.11-2	$\approx 3 \times 10^{-5}$	2.82×10^{-4}	6.55×10^{-2}
RAK 23.11-3	$\approx 3 \times 10^{-5}$	3.23×10^{-4}	7.50×10^{-2}
RAK 23.11-1	$\approx 3 \times 10^{-5}$	3.60×10^{-4}	8.42×10^{-2}
RAK 23.11-4	$\approx 3 \times 10^{-5}$	3.90×10^{-4}	9.16×10^{-2}
$k_2 = 2.41 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

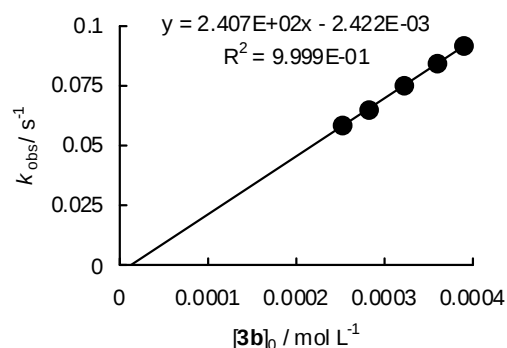
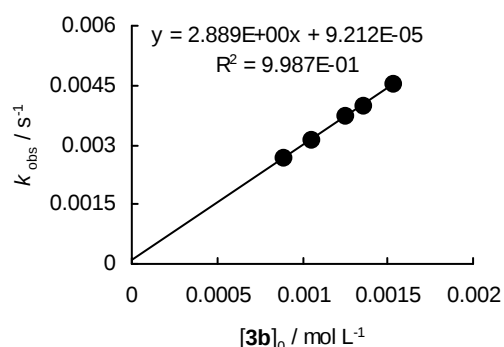


Table S36: Kinetics of the reaction of **4b** with **3b** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 520$ nm).

No.	[4b] ₀ / mol L ⁻¹ *	[3b] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.12-1	$\approx 4 \times 10^{-5}$	8.85×10^{-4}	2.65×10^{-3}
RAK 23.12-5	$\approx 8 \times 10^{-5}$	1.05×10^{-3}	3.12×10^{-3}
RAK 23.12-2	$\approx 5 \times 10^{-5}$	1.25×10^{-3}	3.74×10^{-3}
RAK 23.12-4	$\approx 8 \times 10^{-5}$	1.35×10^{-3}	3.97×10^{-3}
RAK 23.12-3	$\approx 8 \times 10^{-5}$	1.54×10^{-3}	4.53×10^{-3}
$k_2 = 2.89 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).



Reaction of the sulfur ylide **4a** with enone **3c**

Table S37: Kinetics of the reaction of **4a** with **3c** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[3c] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.25-1	$\approx 4 \times 10^{-5}$	5.02×10^{-4}	1.81×10^{-2}
RAK 23.25-2	$\approx 5 \times 10^{-5}$	7.56×10^{-4}	2.60×10^{-2}
RAK 23.25-3	$\approx 5 \times 10^{-5}$	9.93×10^{-4}	3.44×10^{-2}
RAK 23.25-4	$\approx 5 \times 10^{-5}$	1.11×10^{-3}	3.83×10^{-2}
RAK 23.25-5	$\approx 5 \times 10^{-5}$	1.23×10^{-3}	4.28×10^{-2}
$k_2 = 3.41 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

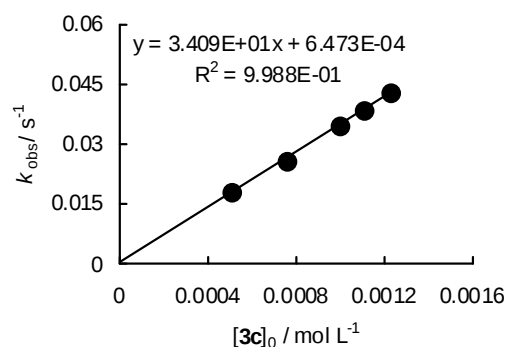
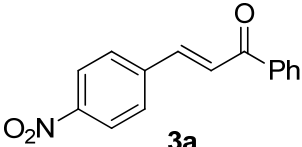
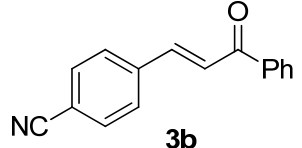
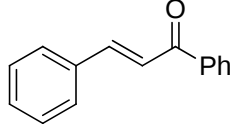


Table S38: Determination of the electrophilicity parameters E for **3a–c** (least-squares minimization of $\Delta^2 = \sum(\log k_2 - s_N(N + E))^2$ for the correlation of $\log k_2 / s_N$ of the reactions of **3a,b** with **4a,b** versus the nucleophilicity parameters N for **4a,b**; Calculation of the electrophilicity parameter E for **3c** using the second-order rate constants for its reaction with sulfur ylide **4a** ($N = 21.07$, $s_N = 0.68$) and correlation equation $\log k_2 = s_N(N + E)$).

Electrophile	Nucleophile (N , s_N)	$k_2 / \text{L mol}^{-1} \text{s}^{-1}$	Electrophilicity E
 3a	4a (21.07, 0.68)	3.46×10^2	$E(\mathbf{3a}) = -17.33$
	4b (18.42, 0.65)	5.22	
 3b	4a (21.07, 0.68)	2.41×10^2	$E(\mathbf{3b}) = -17.64$
	4b (18.42, 0.65)	2.89	
 3c	4a (21.07, 0.68)	3.41×10^1	$E(\mathbf{3c}) = -18.82$

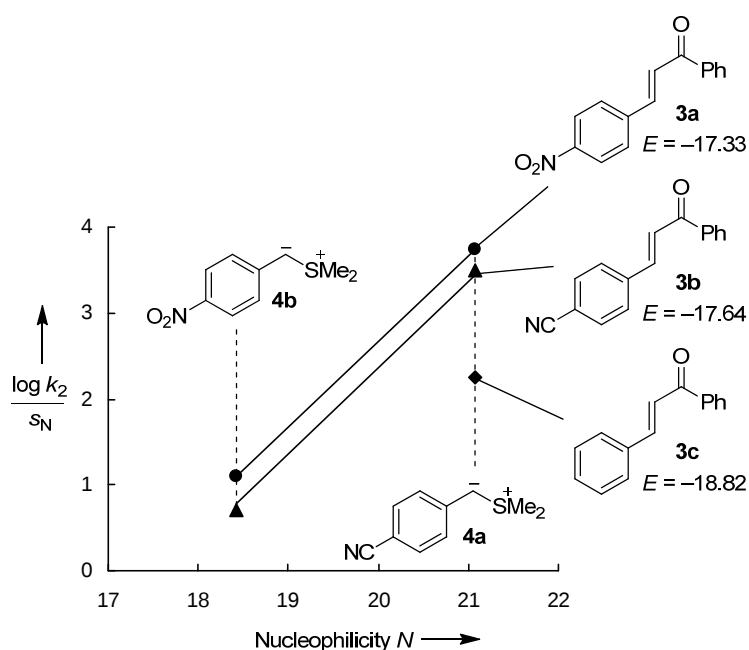
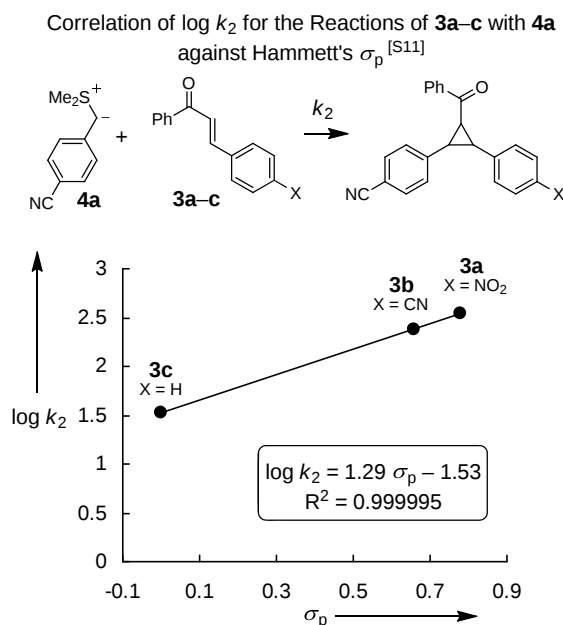


Figure S3: Correlation of the second-order rate constants ($\log k_2 / s_N$) for the reactions of the sulfur ylides **4a,b** with the enones **3a–c** versus the nucleophilicity parameters N of **4a,b**. The slopes are fixed to one as required by $\log k_2 = s_N(N + E)$.



Reactions of the sulfur ylide **4a** with enones **3d–f**

Table S39: Kinetics of the reaction of **4a** with **3d** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[3d] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.54-1	$\approx 6 \times 10^{-5}$	5.69×10^{-4}	1.22×10^{-2}
RAK 23.54-2	$\approx 6 \times 10^{-5}$	7.21×10^{-4}	1.54×10^{-2}
RAK 23.54-3	$\approx 6 \times 10^{-5}$	8.80×10^{-4}	1.85×10^{-2}
RAK 23.54-4	$\approx 6 \times 10^{-5}$	1.03×10^{-3}	2.13×10^{-2}
RAK 23.54-5	$\approx 6 \times 10^{-5}$	1.18×10^{-3}	2.47×10^{-2}
$k_2 = 2.02 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

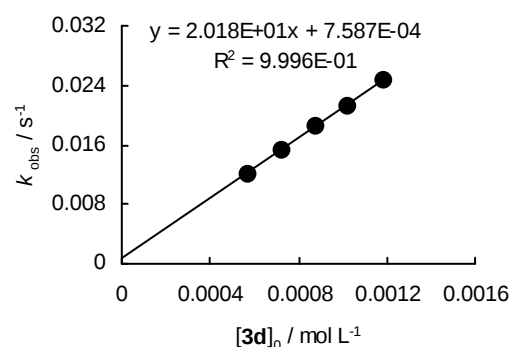


Table S40: Kinetics of the reaction of **4a** with **3e** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[3e] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.53-1	$\approx 5 \times 10^{-5}$	5.96×10^{-4}	1.25×10^{-2}
RAK 23.53-2	$\approx 6 \times 10^{-5}$	7.52×10^{-4}	1.57×10^{-2}
RAK 23.53-3	$\approx 6 \times 10^{-5}$	8.87×10^{-4}	1.84×10^{-2}
RAK 23.53-4	$\approx 6 \times 10^{-5}$	1.03×10^{-3}	2.11×10^{-2}
RAK 23.53-5	$\approx 6 \times 10^{-5}$	1.18×10^{-3}	2.41×10^{-2}
$k_2 = 1.97 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

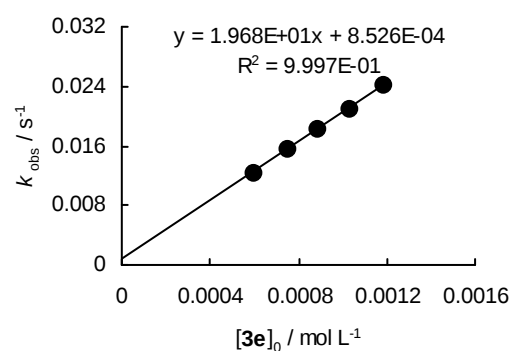
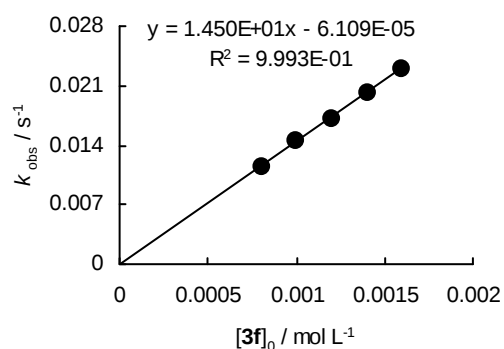
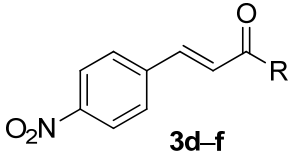


Table S41: Kinetics of the reaction of **4a** with **3f** in DMSO at 20°C (diode array UV-Vis spectrometer, $\lambda = 380$ nm).

No.	[4a] ₀ / mol L ⁻¹ *	[3f] ₀ / mol L ⁻¹	k_{obs} / s ⁻¹
RAK 23.15-2-1	$\approx 4 \times 10^{-5}$	8.01×10^{-4}	1.15×10^{-2}
RAK 23.15-2-2	$\approx 5 \times 10^{-5}$	9.92×10^{-4}	1.45×10^{-2}
RAK 23.15-2-3	$\approx 6 \times 10^{-5}$	1.20×10^{-3}	1.72×10^{-2}
RAK 23.15-2-4	$\approx 6 \times 10^{-5}$	1.40×10^{-3}	2.03×10^{-2}
RAK 23.15-2-5	$\approx 6 \times 10^{-5}$	1.59×10^{-3}	2.31×10^{-2}
$k_2 = 1.45 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$			

* Only approximate values are given for the initial concentration of the nucleophile (see general comments).

**Table S42:** Calculation of the electrophilicity parameters E for **3d–f** using the second-order rate constants for their reactions with sulfur ylide **4a** ($N = 21.07$, $s_N = 0.68$) and correlation equation $\log k_2 = s_N(N + E)$.

Electrophile		k_2 / L mol ⁻¹ s ⁻¹	Electrophilicity E
	3d (R = <i>t</i> Bu)	2.02×10^1	E (3d) = -19.15
	3e (R = <i>i</i> Pr)	1.97×10^1	E (3e) = -19.17
	3f (R = Me)	1.45×10^1	E (3f) = -19.36

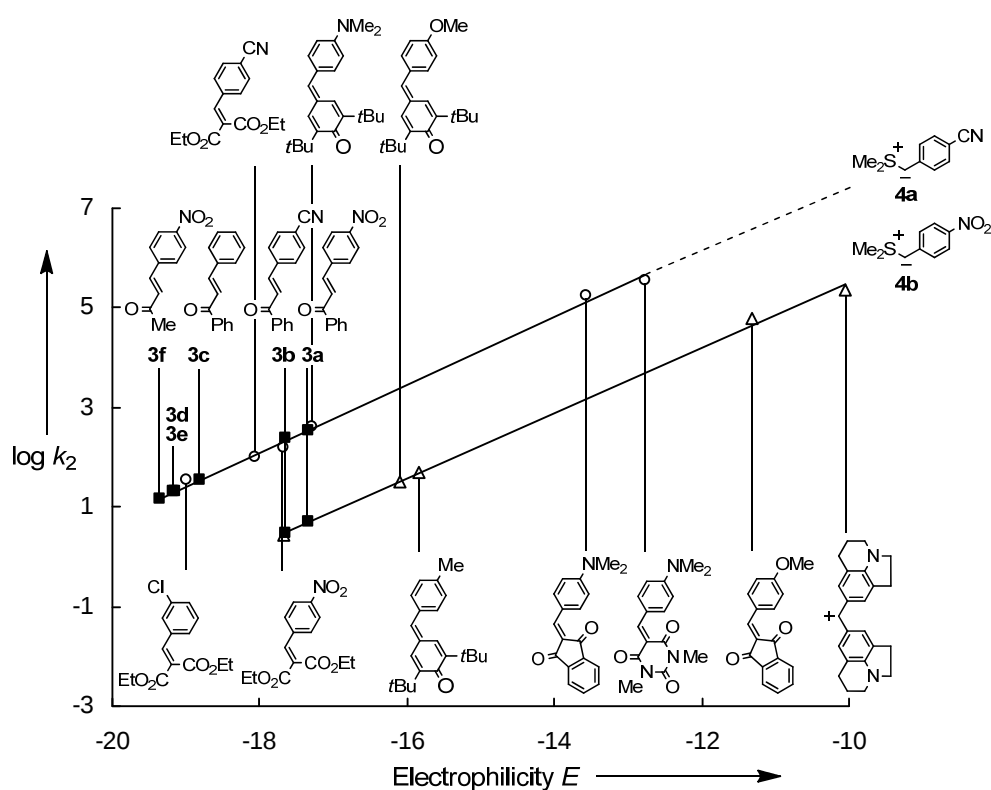


Figure S4: Extended version of Figure 6 of the original manuscript with complete assignment of all data points for the electrophiles. Matching of the rate constants for the reactions of the semistabilized sulfur ylides **4a,b** with the enones **3a-f** to the previously derived correlation lines for the reactions of **4a,b** with reference electrophiles (e.g., benzhydrylium ions, quinone methides, and diethyl benzylidenemalonates) in DMSO at 20°C.^{S1}

