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Supporting Information

for

How Nucleophilic are Diazo Compounds?

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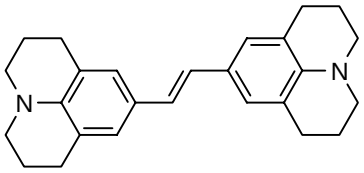
1. General

The reactions of diazo compounds **1** with benzhydryl salts $Ar_2CH^+X^-$ were performed under exclusion of moisture in an atmosphere of dry nitrogen in carefully dried Schlenk glassware. Dichloromethane was freshly distilled from CaH_2 before use.

^1H NMR and ^{13}C NMR spectra were recorded with a Bruker ARX 300 (300 MHz, 75.5 MHz) or Bruker AMX 400 (400 MHz, 100.1 MHz). Chemical shifts are reported on the δ scale relative to tetramethylsilane ($\delta_H = 0.00$), $CDCl_3$ ($\delta_C = 77.00$), or C_6D_6 ($\delta_C = 128.00$) as internal standards. Abbreviations used are s (singlet), d (dublet), t (triplet), q (quartet) and m (multiplet). Infrared spectra were recorded with a Perkin-Elmer FT-IR 1000 spectrophotometer. Mass spectra were measured with a Finnigan MAT 95 Q. Microanalyses were carried out by the Mikroanalytisches Labor des Departments Chemie der LMU München. Melting points were determined on a Büchi B-540 and are uncorrected.

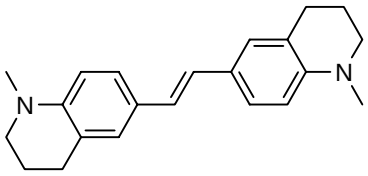
2. Reactions of diazo compounds with benzhydryl salts

***E*-1,2-Bis(julolidin-9-yl)ethene (3-jul)** was obtained from $(jul)_2CH^+PF_6^-$ (502 mg, 1.00 mmol) and benzyltriethylammonium chloride (1.13 g, 5.00 mmol) in 25 mL dichloromethane at room temperature by treating this solution with gaseous diazomethane (**1a**) until the color was faded. After adding 2 M NH_3 (20 mL), the layers were separated and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent evaporated in vacuo. The crude product was dissolved in n-pentane (50 mL). Crystallization from the filtrate gave **3-jul** (95 mg, 26 %) as a pale green powder. M.p. 233–235 °C (Ref.[S1]: M.p. 238 °C, Ref.[S2]: M.p. 221–223 °C); ^{1}H NMR (C_6D_6, 300 MHz): δ = 1.68–1.76 (m, 8 H), 2.62 (t, *J* = 6.5 Hz, 8 H), 2.80 (t, *J* = 5.7 Hz, 8 H), 7.08 (s, 2 H), 7.09 (s, 4 H); ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 22.62 (t), 28.10 (t), 50.22 (t), 121.58 (s), 125.08 (d), 125.61 (d), 127.14 (s), 142.26 (s); IR (KBr): $\tilde{\nu}$ = 2938, 2835, 1607, 1500, 1308, 1161, 952 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 372 (4), 371 (27), 370 (100) [M^+], 185 (11).



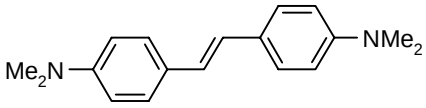
3-jul

***E*-1,2-Bis(1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)ethene (3-thq)** was obtained from $(thq)_2CH^+BF_4^-$ (390 mg, 1.00 mmol) and benzyltriethylammonium chloride (1.10 g, 5.00 mmol) in 1,2-dichloroethane (60 mL) at 0 °C by treating this solution with gaseous diazomethane (**1a**) until the color was faded. After adding 2 M NH_3 (30 mL), the layers were separated and the organic layer was extracted with water (2 × 35 mL). The organic layer was dried over Na_2SO_4, and the solvent evaporated in vacuo. The crude product was stirred with Et_2O (50 mL) for 30 min. Filtration and crystallization from the remaining solution gave **3-thq** (180 mg, 57 %) as yellow crystals. M.p. 154–156 °C (Ref.[S2]: 151–152.5 °C); ^{1}H NMR (C_6D_6, 300 MHz): δ = 1.74–1.82 (m, 4 H), 2.66 (s, 6 H), 2.70 (d, *J* = 6.6 Hz, 4 H), 2.92 (d, *J* = 5.7 Hz, 4 H), 6.66 (d, *J* = 8.4 Hz, 2 H), 7.26 (s, 2 H), 7.36 (br. s, 2 H), 7.50 (dd, *J* = 8.4 Hz, 1.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 22.49 (t), 27.86 (t), 39.12 (q), 51.33 (t), 111.01 (d), 122.83 (s), 124.44 (d), 125.22 (d), 126.37 (d), 126.61 (s), 145.77 (s); IR (KBr): $\tilde{\nu}$ = 3016, 2946, 2812, 1612, 1517, 1316, 1210, 802 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 320 (2), 319 (21), 318 (100) [M^+], 159 (8).



3-thq

***E*-1,2-Bis(4-dimethylaminophenyl)ethene (3-dma)** was obtained from $(dma)_2CH^+BF_4^-$ (340 mg, 1.00 mmol) and benzyltriethylammonium chloride (1.10 g, 5.00 mmol) in 1,2-dichloroethane (80 mL) at room temperature by treating this solution with gaseous diazomethane (**1a**) until the color was faded. After adding 2 M NH_3 (20 mL), the layers were separated and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent evaporated in vacuo. The crude product was stirred 30 min. with acetone (50 mL) and filtrated. The remaining solid gave (85 mg, 32 %) **3-dma** as a yellow powder. M.p. 258–260 °C (Ref.[S2]: M.p. 253–254 °C, Ref.[S3]: M.p. 260 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.97 (s, 12 H), 6.73 (AA'BB' system with J_{AB} = 8.4 Hz, 4 H), 6.86 (s, 2 H), 7.38 (AA'BB' system with J_{AB} = 8.8 Hz, 4 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 40.69 (q), 112.77 (d), 124.82 (d), 127.00 (d), 149.47 (s), missing peak 126.85 (s) not observable (see below in the McMurry reaction); IR (KBr): $\tilde{\nu}$ = 3015, 2905, 2806, 1611, 1523, 1359, 1185, 817 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 268 (2), 267 (19), 266 (100) [M^+], 251 (24), 236 (17), 132 (12).

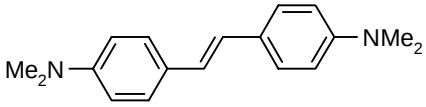


3-dma

3-dma was also obtained from $(dma)_2CH^+OTf^-$ (201 mg, 0.50 mmol) and benzyltriethylammonium chloride (560 mg, 2.50 mmol) dissolved in dichloromethane (50 mL) by adding a 2 M solution of (trimethylsilyl)diazomethane in n-hexane (290 µL, 0.5 mmol) at 0 °C. Isolation of the product was carried out as described above and gave **3-dma** (80 mg, 60 %) as a yellow powder. (Spectral data analogous to that described above).

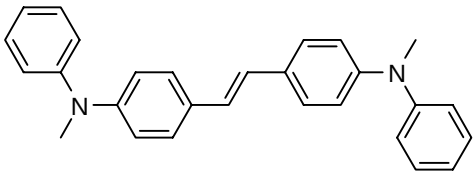
3-dma by McMurry reaction:[S1] To a suspension of Zn (10.0 g, 153 mmol) and 4-(dimethylamino)benzaldehyde (3.50 g, 23.5 mmol) in THF (50 mL) $TiCl_4$ (4.15 mL, 38.2 mmol) was added dropwise during 30 min. After refluxing for 2h the suspension was carefully added to a solution of K_2CO_3 (15.0 g) in icewater (150 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 30 mL). The combined organic

layers were dried over Na_2SO_4, filtrated, and the solvent was removed in vacuo. Recrystallization from acetonitril gave **3-dma** (450 mg, 7 %) as yellow crystals. M.p. 258–260 °C (Ref.[S2]: M.p. 253–254 °C, Ref.[S3]: M.p. 260 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.97 (s, 12 H), 6.74 (AA'BB' system with J_{AB} = 8.1 Hz, 4 H), 6.86 (s, 2 H), 7.38 (AA'BB' system with J_{AB} = 8.7 Hz, 4 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 40.59 (q), 112.67 (d), 124.75 (d), 126.85 (s), 126.97 (d), 149.61 (s); IR (KBr): $\tilde{\nu}$ = 2920, 2801, 1611, 1522, 1360, 1186, 817 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 268 (2), 267 (19), 266 (100) [M^+], 251 (23), 236 (16), 132 (11).



3-dma

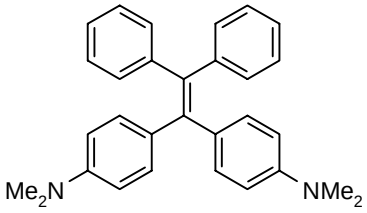
***E*-1,2-Bis(4-(methylphenylamino)phenyl)ethene (3-mpa)**: At 0 °C $(mpa)_2CH^+BF_4^-$ (400 mg, 0.86 mmol) and benzyltriethylammonium chloride (1.00 g, 4.31 mmol) were dissolved in a mixture of dichloromethane (40 mL) and acetonitrile (2 mL). Then a 2 M solution of (trimethylsilyl)diazomethane in n-hexane (380 µL, 0.78 mmol) was added and stirred for 5 min. After adding water (10 mL) and 2 M NH_3 (20 mL), the layers were separated, and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent evaporated in vacuo. The crude product was stirred with n-pentane (50 mL) for 30 min. Filtration and crystallization of the remaining solution gave **3-mpa** (120 mg, 36 %) as a pale yellow powder. ^{1}H NMR (C_6D_6, 300 MHz): δ = 3.13 (s, 6 H), 6.95–7.08 (m, 12 H), 7.22–7.25 (m, 4 H), 7.39–7.42 (m, 4 H); ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 40.08 (q), 119.97 (d), 121.63 (d), 122.10 (d), 126.44 (d), 127.46 (d), 129.50 (d), 130.94 (s), 148.51 (s), 149.22 (s); MS (EI, 70 eV): *m/z* (%): 392 (7), 391 (49), 390 (100) [M^+], 195 (23).



3-mpa

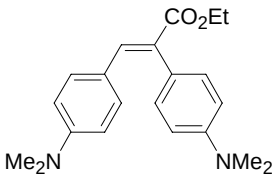
1,1-Bis(4-dimethylaminophenyl)-2,2-diphenylethene (4d-dma) was obtained from $(dma)_2CH^+OTf^-$ (201 mg, 0.50 mmol) dissolved in dichloromethane (25 mL) and diphenyldiazomethane (**1d**) (116 mg, 0.59 mmol) after stirring for 18 h. After adding 2 M NH_3

(20 mL), the layers were separated and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent evaporated in vacuo. The crude product was dissolved in refluxing Et_2O (15 mL) for 20 min, filtrated, and the solvent was evaporated in vacuo. The resulting solid was stirred with n-pentane (15 mL) for 20 min at room temperature and separated by filtration to give **4d-dma** (90 mg, 43 %) as a yellow solid. M.p. 208–211 °C (Ref.[S4]: 212 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.89 (s, 12 H), 6.47 (d, AA'BB' system with J_{AB} = 8.8 Hz, 4 H), 6.90 (d, AA'BB' system with J_{AB} = 8.8 Hz, 4 H), 7.03–7.12 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 40.57 (q), 111.56, 111.82 (2 d), 125.53, 125.76 (2 d), 127.55, 131.52 (2 d), 132.38, 132.54 (2 d), 137.10, 139.15, 141.05 (3 s), 145.17 (s), 148.53 (s); MS (EI, 70 eV): *m/z* (%): 420 (5), 419 (33), 418 (100) [M^+], 209 (6).



4d-dma

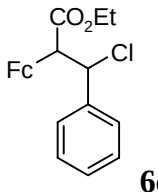
Ethyl *E*-2,3-bis(4-dimethylaminophenyl)acrylate (5e-dma): At room temperature $(dma)_2CH^+OTf^-$ (1.01 g, 2.50 mmol) was dissolved in dichloromethane (20 mL). Then a solution of ethyl diazoacetate (**1e**) (571 mg, 5.00 mmol) in dichlormethane (5 mL) was added. After stirring for 24 h water (20 mL) was added, the layers were separated and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The organic layers were combined, dried over $MgSO_4$, and the solvent evaporated in vacuo. Column chromatography (silica gel, n-hexane:Et_2O (3:1)) gave 310 mg (37 %) of a 9:1 mixture of isomers as yellow crystals (product ratio determined by ^{1}H NMR). According to NMR analysis the signals of the major product were assigned to **5e-dma**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.28 (t, J = 7.1 Hz, 3 H), 2.91 (s, 6 H), 2.98 (s, 6 H), 4.23 (q, J = 7.1 Hz, 2 H), 6.47, 6.74, 7.02, 7.11 (2 AA'BB' systems with J_{AB} = 8.8 and 9.0 Hz, 8 H), 7.70 (s, 1 H, C=CH); ^{1}H{^{1}H} NOE: irradiation at δ = 7.70 (C=CH) caused a signal enhancement at δ = 7.02; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.59 (q), 40.17 (q), 40.69 (q), 60.75 (t), 111.46, 112.74 (2 d), 123.15, 124.89 (2 s), 127.84 (s), 130.87, 132.41 (2 d), 140.05 (d), 149.82, 150.57 (2 s), 169.18 (s); elemental analysis calcd (%) for $C_{21}H_{26}N_2O_2$ (338.45): C 74.53, H 7.74, N 8.28, found C 74.59, H 7.82, N 8.18.



5e-dma **5e-dma**

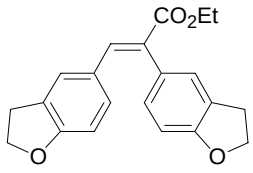
The minor isomer could not be isolated and showed the following resonances: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18 (t, J = 7.1 Hz, 3 H), 2.97 (s, 6 H), 2.98 (s, 6 H), 4.08 (q, J = 7.1 Hz, 2 H), 6.11 (s, 1 H), 6.61, 6.69 (2 AA' from a AA'BB' system with J_{AB} = 8.9, 4 H), 7.22 (BB' from a AA'BB' system with J_{AB} = 8.9, 4 H), second BB' not observable because of the main product.

6e-fc(Ph): At –78 °C 1-Ferrocenyl-1-phenylmethylacetate (334 mg, 1.00 mmol) was dissolved in dichloromethane (20 mL) and a solution of 3.9 M $ZnCl_2 \cdot OEt_2$ in Et_2O (1.00 mL, 3.9 mmol) was added. Then a solution of ethyl diazoacetate (**1d**) (228 mg, 2.00 mmol) in dichloromethane (5 mL) was dropwise added. After 3 h and warming up to room temperature conc. NH_3 (20 mL) was added, the layers were separated and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The organic layers were combined, dried over $MgSO_4$, and the solvent evaporated in vacuo. Column chromatography (silica gel, n-hexane:ethyl acetate (3:1)) gave **6e-fc(Ph)** (300 mg, 76 %) as two diastereomers (1:1) as orange crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.99, 1.47 (2 t, J = 7.1, 7.2 Hz, 2 × 3 H), 3.20–3.21 (m, 1 H), 3.78-4.04 (m, 7 H), 4.06, 4.10 (2 s, 2 × 5 H), 4.21 (t, J = 1.8 Hz, 2 H), 4.32–4.50 (m, 4 H), 4.86 (d, J = 10.6 Hz, 1 H), 4.92 (d, J = 10.6 Hz, 1 H), 7.07–7.12 (m, 2 H), 7.18–7.21 (m, 3 H), 7.30–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.81, 14.32 (2 q), 55.80, 56.40 (2 d), 60.42, 61.01 (2 t), 63.89, 66.31 (2 d), 66.43, 66.66, 67.59, 68.24, 68.57, 68.68, 68.73, 69.70, 71.16 (9 d), 80.90, 82.01 (2 s), 127.55, 127.80, 128.07, 128.31, 128.38, 128.65 (6 d), 138.61, 139.44 (2 s), 169.77, 170.93 (2 s); MS (EI, 70 eV): *m/z* (%): 399 (6), 398 (25), 397 (18), 396 (63) [M^+], 360 (6), 331 (16), 288 (10), 272 (18), 271 (100), 223 (21), 167 (49), 166 (24), 165 (46), 152 (24), 121 (15), 105 (12), 77 (12), 56 (19); elemental analysis calcd (%) for $C_{21}H_{21}ClFeO_2$ (396.72): C 63.58, H 5.34; found: C 63.81, H 5.32.



6e-fc(Ph)

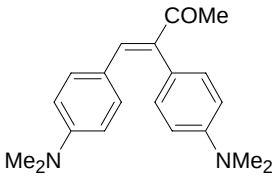
Ethyl *E*-2,3-bis(2,3-dihydrobenzofuran-5-yl)acrylate (5d-fur) was obtained from bis(2,3-dihydro-5-benzofuranyl)(trimethylsiloxy)methane (500 mg, 1.47 mmol) dissolved in dichloromethane (30 mL), trimethylsilyltriflate (290 µL, 1.62 mmol), and dropwise addition of diethyl diazoacetate (**1d**) (180 µL, 1.62 mmol) dissolved in dichloromethane (10 mL) at –40 °C. After 5 min. 2 M NH_3 (20 mL) was added, the layers were separated and the aqueous layer was extracted with dichloromethane (1 × 10 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent evaporated in vacuo. Column chromatography (silica gel, n-hexane:Et_2O (1:1)) gave **5d-fur** (150 mg, 31 %) as a colorless powder. M.p. 119–121 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (t, J = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 3.06, 3.21 (2 t, J = 8.7 Hz, 2 × 2 H, OCH_2CH_2), 4.25 (q, J = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 4.53, 4.60 (2 t, J = 8.7 Hz, 2 × 2 H, OCH_2CH_2), 6.59 (d, J = 8.2 Hz, 1 H), 6.78 (d, J = 8.2 Hz, 1 H), 6.85–6.98 (m, 3 H), 7.00–7.08 (m, 1 H), 7.72 (s, 1 H, C=CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.36 (q, $CO_2CH_2CH_3$), 29.35, 29.70 (2 t, OCH_2CH_2), 60.91 (t, CO_2CH_2), 71.33, 71.60 (2 t, OCH_2CH_2), 109.11, 109.49 (2 d), 126.38 (d), 127.07 (s), 127.34 (s), 127.37 (d), 127.62 (s), 128.35 (s), 129.71 (d), 129.72 (s), 131.77 (d), 139.84 (d, C=CH), 159.62, 160.89 (2 s), 168.50 (s, C=O); signal assignments are based on NOESY, gHSQC and gHMBC experiments; IR (KBr): $\tilde{\nu}$ = 2978, 2900, 1697, 1604, 1493, 1236, 1099, 981, 818 cm^{-1}; MS (EI, 70 eV): *m/z* (%): 338 (3), 337 (20), 336 (100) [M^+], 263 (14), 177 (33), 149 (13); elemental analysis calcd (%) for $C_{21}H_{20}O_4$ (336.38): C 74.98, H 5.99, found C 74.94, H 5.90.



5d-fur

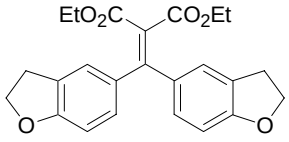
***E*-3,4-Bis(4-dimethylaminophenyl)but-3-en-2-one (5f-dma)** was obtained from diazoacetone (**1f**) (170 mg, 2.02 mmol) dissolved in dichloromethane (20 mL) and $(dma)_2CH^+OTf^-$ (404 mg, 1.00 mmol) dissolved in dichloromethane (20 mL) and stirring for 2 d. After adding 2 M NH_3 (20 mL), the layers were separated and the aqueous layer was extracted with dichloromethane (2 × 15 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent evaporated in vacuo. The crude product was stirred with n-hexane (20 mL) at 40°C for 5 min. Filtration and crystallization from the remaining solution gave **5f-dma** (80 mg, 26 %) as yellow crystals. M.p. 156–158 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.25 (s, 3 H, $COCH_3$), 2.93 (s, 6 H, NMe_2), 3.00 (s, 6 H, NMe_2), 6.48 (d, AA'BB' system with J_{AB} = 9.1 Hz, 2 H), 6.79 (d, AA'BB' system with J_{AB} = 8.7 Hz, 2 H), 7.01 (d, AA'BB' system with J_{AB} = 9.0 Hz, 2 H), 7.05 (d, AA'BB' system with J_{AB} = 8.7 Hz, 2 H), 7.56 (s, 1

H, C=CH); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 27.86 (q, CO*C*H$_3$), 39.98 (q, NMe$_2$), 40.60 (q, NMe$_2$), 111.40, 113.11 (2 d), 122.80 (s), 126.07 (s, CO*C*=CH), 130.49, 132.74 (2 d), 136.40 (s), 139.21 (d, C=*C*H), 149.68, 150.68 (2 s), 200.12 (s, C=O); Signal assignments are based on NOESY, gHSQC and gHMBC experiments; MS (EI, 70 eV): *m/z* (%): 310 (2), 309 (20), 308 (91) [M^+], 266 (20), 265 (100), 221 (21), 132 (20).



5f-dma

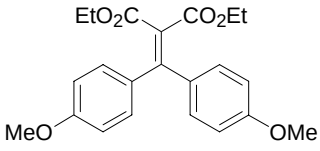
Diethyl (bis-(2,3-dihydro-benzofuran-5-yl)methylene)malonate (4g-fur): At room temperature bis(2,3-dihydro-5-benzofuranyl)(trimethylsiloxy)methane (300 mg, 0.88 mmol) was dissolved in dichloromethane (20 mL) and trimethylsilyltriflat (175 µL, 0.97 mmol) was added. Then diethyl diazomalonate (**1g**) (200 mg, 1.06 mmol) was added and stirred for 2 d. After adding 2 M NH_3 (20 mL), the layers were separated and the aqueous layer was extracted with dichloromethane (1 × 10 mL). The organic layers were combined, dried over Na_2SO_4, and the solvent evaporated in vacuo. Column chromatography (neutral Al_2O_3, n-hexane:Et_2O (1:1)) gave **4g-fur** (110 mg, 31 %) as a colorless powder. M.p. 92–93 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.10 (t, *J* = 7.1 Hz, 6 H), 3.16 (t, *J* = 8.7 Hz, 4 H), 4.10 (q, *J* = 7.0 Hz, 4 H), 4.59 (t, *J* = 8.7 Hz, 4 H), 6.71 (d, *J* = 8.0 Hz, 2 H), 6.93–7.03 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.83 (q), 29.35 (t), 60.95 (t), 71.64 (t), 108.85 (d), 123.55 (s, Ar$_2$C=*C*), 126.52 (d), 126.97 (s), 130.25 (d), 132.91 (s), 156.69 (s, Ar$_2$*C*=C), 161.41 (s), 166.76 (s, C=O); MS (EI, 70 eV): *m/z* (%): 410 (4), 409 (23), 408 (100) [M^+], 363 (29), 264 (15), 262 (14), 249 (10), 147 (38); elemental analysis calcd (%) for $C_{24}H_{24}O_6$ (408.45): C 70.57, H 5.92; found: C 70.77, H 5.97.



4g-fur

Diethyl (bis(4-methoxyphenyl)methylene)malonate (4g-ani) was obtained form bis(4-methoxyphenyl)methylchloride (263 mg, 1.00 mmol) in dichloromethane (20 mL), 3.9 M $ZnCl_2$·OEt_2 in Et_2O (0.20 mL, 0.78 mmol) and diethyl diazomalonate (**1g**) (392 mg, 2.00 mmol) after stirring for 6 h at –78 °C. After adding conc. NH_3 (20 mL), the layers were separated and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The

organic layers were combined, dried over $MgSO_4$, and the solvent evaporated in vacuo. Crystallization of the crude product from n-hexane gave **4g-ani** (110 mg, 29 %) as colorless needles. M.p. 80.5–81 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.08 (t, J = 7.1 Hz, 6 H), 3.81 (s, 6 H), 4.10 (q, J = 7.0 Hz, 4 H), 6.84, 7.12 (AA'BB' system with J_{AB} = 8.8 Hz, 2 × 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.76 (q), 55.23 (q), 61.01 (t), 113.42 (d), 123.89 (s, Ar_2C=*C*), 131.10 (d), 132.63 (s), 155.76 (s, Ar_2*C*=C), 160.58 (s), 166.58 (s, C=O); elemental analysis calcd (%) for $C_{22}H_{24}O_6$ (384.4): C 68.74, H 6.29; found: C 68.38, H 6.21.



4g-ani

3. Concentrations and rate constants of the individual kinetic runs (Tables S1-S31)

Remarks:

- The reactions of diazo compounds **1** with benzhydryl salts $Ar_2CH^+X^-$ were performed under exclusion of moisture in an atmosphere of dry nitrogen in carefully dried Schlenk glassware. Dichloromethane was freshly distilled from CaH_2 before use.
- For the evaluation of the stopped flow kinetics (Stopped-flow spectrophotometer system Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst2 software), rate constants k_{obs} were obtained by fitting the single exponential $A_t = A_0 \exp(-k_{obs}t) + C$ to the observed time-dependent curve of the carbocation absorbance (averaged from at least 4 kinetic runs at each nucleophile concentration). Second-order rate constants k_2(L mol^{-1} s^{-1}) were then calculated from $k_{obs} = k_2[Nuc]_0$.
- For the evaluation of conventional UV-Vis kinetics determined at *J&M* instruments, ln (A_0–A_{end}/A_t–A_{end}) was plotted against t, and the linear part (indicated in the column % conversion) was used to determine k_2. The kinetics at Schölly instruments were also followed photometrically as described in ref. [23]
- Rate constants k_2 that have only been measured at one temperature (20 ± 0.2 °C) were averaged (<k_2>) and given with standard deviations.
- When measurements were made at variable temperatures, k_2 values at 20 ± 0.2 °C were extrapolated from the Eyring parameters.

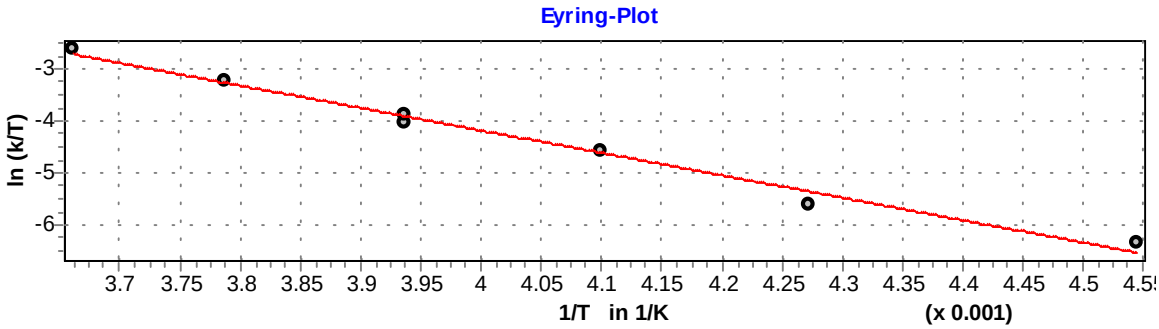
Table S1. Diazomethane (**1a**) and $(jul)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–101–2	20.1	1.36×10^{-5}	7.58×10^{-4}	31	6.42
BUT–K–103–2	20.0	1.16×10^{-5}	9.83×10^{-4}	84	6.71
BUT–K–103–4	20.0	3.66×10^{-5}	1.30×10^{-3}	48	6.59
BUT–K–104–4	20.0	3.02×10^{-5}	1.53×10^{-3}	50	6.60
BUT–K–104–3	20.0	3.41×10^{-5}	1.72×10^{-3}	50	6.77
BUT–K–104–1	20.0	3.70×10^{-5}	1.87×10^{-3}	59	6.76

$<k_2>(20\ °C) = (6.64 \pm 0.12)$ L mol^{-1} s^{-1}

Table S2. Diazomethane (**1a**) and $(thq)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 630 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–102–1	–53.1	1.41×10^{-5}	7.07×10^{-4}	68	3.80×10^{-1}
BUT–K–102–2	–39.1	3.62×10^{-5}	1.81×10^{-3}	80	8.31×10^{-1}
BUT–K–102–3	–29.2	3.67×10^{-5}	1.84×10^{-3}	68	2.48
BUT–K–102–5	–19.1	3.38×10^{-5}	2.70×10^{-3}	64	4.37
BUT–K–102–6	–19.1	2.79×10^{-5}	8.36×10^{-4}	82	5.05
BUT–K–102–7	–9.1	3.94×10^{-5}	1.97×10^{-3}	80	1.03×10^{1}
BUT–K–102–8	0.0	3.82×10^{-5}	1.91×10^{-3}	71	1.97×10^{1}



Eyring parameters:

$\Delta H^{\ddagger}$ = 35.898 ± 1.883 kJ mol^{-1}

$\Delta S^{\ddagger}$ = –88.908 ± 7.614 J mol^{-1} K^{-1}

r^2 = 0.9864

Arrhenius parameters:

E_a = 37.929 ± 1.904 kJ mol^{-1}

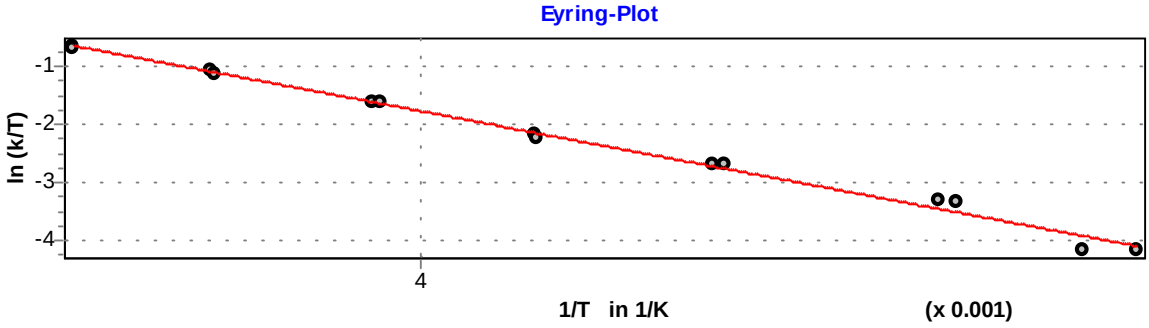
ln A = 19.568 ± 0.926

r^2 = 0.9876

k_2(20 °C) = (5.57 ± 0.79) × 10^1 L mol^{-1} s^{-1}

Table S3. Diazomethane (**1a**) and $(dma)_2CH^+OTf^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
MH–V–111	–60.0	7.60 × 10^{-5}	1.49 × 10^{-3}	75	3.29
MH–V–112	–57.6	7.42 × 10^{-5}	1.46 × 10^{-3}	65	3.27
MH–V–114	–51.8	8.26 × 10^{-5}	9.74 × 10^{-4}	61	7.64
MH–V–113	–50.9	6.30 × 10^{-5}	6.19 × 10^{-4}	84	7.99
MH–V–116	–40.2	7.49 × 10^{-5}	9.11 × 10^{-4}	66	1.55 × 10^1
MH–V–115	–39.6	7.69 × 10^{-5}	5.98 × 10^{-4}	60	1.56 × 10^1
MH–V–117	–29.9	6.75 × 10^{-5}	6.57 × 10^{-4}	68	2.60 × 10^1
MH–V–118	–29.8	6.06 × 10^{-5}	7.37 × 10^{-4}	62	2.73 × 10^1
MH–V–120	–20.7	7.15 × 10^{-5}	4.96 × 10^{-4}	47	4.99 × 10^1
MH–V–119	–20.2	5.93 × 10^{-5}	7.21 × 10^{-4}	49	5.02 × 10^1
MH–V–124	–10.1	6.31 × 10^{-5}	5.55 × 10^{-4}	50	8.26 × 10^1
MH–V–121	–9.8	8.58 × 10^{-5}	3.17 × 10^{-4}	37	9.14 × 10^1
MH–V–122	–0.2	6.31 × 10^{-5}	5.55 × 10^{-4}	62	1.40 × 10^2
MH–V–123	–0.2	7.74 × 10^{-5}	4.08 × 10^{-4}	51	1.38 × 10^2



Eyring parameters:

$\Delta H^{\ddagger} = 28.080 \pm 0.679$ kJ mol^{-1}

$\Delta S^{\ddagger} = -100.079 \pm 2.820$ J mol^{-1} K^{-1}

$r^2 = 0.9930$

Arrhenius parameters:

$E_a = 30.083 \pm 0.673$ kJ mol^{-1}

$\ln A = 18.211 \pm 0.336$

$r^2 = 0.9940$

$k_2(20\ °C) = (3.59 \pm 0.21) \times 10^2$ L mol^{-1} s^{-1}

Table S4. Diazomethane (**1a**) and $(mpa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 620 nm at 20.0 °C (Stopped flow).

No.	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	k_{obs} / s^{-1}	k_2 / L mol^{-1} s^{-1}
BUT–K–105-3	1.25×10^{-5}	5.01×10^{-4}	2.99	5.97×10^3
BUT–K–105-2	1.25×10^{-5}	7.49×10^{-4}	4.36	5.82×10^3
BUT–K–105-1	1.25×10^{-5}	1.00×10^{-3}	5.84	5.84×10^3
BUT–K–105-5	1.25×10^{-5}	1.25×10^{-3}	7.34	5.87×10^3

$\langle k_2 \rangle(20\ °C) = (5.88 \pm 0.06) \times 10^3$ L mol^{-1} s^{-1}

Table S5. Diazomethane (**1a**) and $(dpa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 670 nm at 20.0 °C (Stopped flow).

No.	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	k_{obs} / s^{-1}	k_2 / L mol^{-1} s^{-1}
BUT–K–106-3	1.25×10^{-5}	5.01×10^{-4}	1.26×10^1	2.51×10^4
BUT–K–106-2	1.25×10^{-5}	7.49×10^{-4}	1.82×10^1	2.43×10^4
BUT–K–106-1	1.25×10^{-5}	1.00×10^{-3}	2.36×10^1	2.36×10^4

$\langle k_2 \rangle(20\ °C) = (2.43 \pm 0.06) \times 10^4$ L mol^{-1} s^{-1}

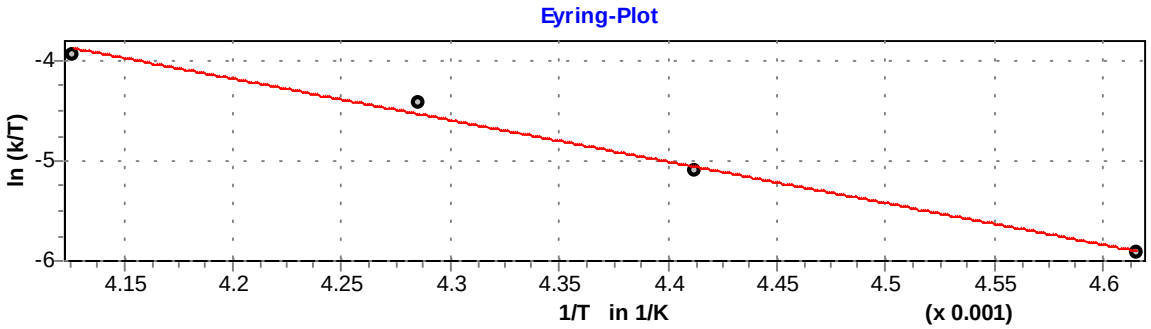
Table S6. Phenyldiazomethane (**1b**) and $(jul)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–112–5	20.0	2.05×10^{-5}	1.02×10^{-3}	26	7.09×10^{-1}
BUT–K–112–2	20.0	4.89×10^{-5}	1.48×10^{-3}	88	7.43×10^{-1}
BUT–K–112–1	20.0	5.42×10^{-5}	2.70×10^{-3}	88	7.61×10^{-1}
BUT–K–112–3	20.0	5.47×10^{-5}	2.72×10^{-3}	74	7.90×10^{-1}
BUT–K–112–4	20.0	4.89×10^{-5}	3.91×10^{-3}	63	7.78×10^{-1}

$<k_2>(20\ °C) = (7.56 \pm 0.28) \times 10^{-1}$ L mol^{-1} s^{-1}

Table S7. Phenyldiazomethane (**1b**) and $(dma)_2CH^+OTf^-$ in CH_2Cl_2 at λ = 630 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
MH–V–105	–56.5	3.55×10^{-5}	4.02×10^{-3}	93	5.78×10^{-1}
MH–V–106	–46.5	3.26×10^{-5}	2.77×10^{-3}	94	1.39
MH–V–107	–39.8	3.65×10^{-5}	2.06×10^{-4}	95	2.78
MH–V–108	–30.8	3.07×10^{-5}	8.70×10^{-4}	85	4.75



Eyring parameters:

$\Delta H^{\ddagger} = 34.593 \pm 2.066$ kJ mol^{-1}

$\Delta S^{\ddagger} = -87.024 \pm 9.016$ J mol^{-1} K^{-1}

$r^2 = 0.9929$

Arrhenius parameters:

$E_a = 36.495 \pm 2.053$ kJ mol^{-1}

$\ln A = 19.727 \pm 1.078$

$r^2 = 0.9937$

$k_2(20\ °C) = (1.19 \pm 0.28) \times 10^2$ L mol^{-1} s^{-1}

Table S8. Phenyldiazomethane (**1b**) and $(mpa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 620 nm 20.0 °C (Stopped flow).

No.	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	k_{obs} / s^{-1}	k_2 / L mol^{-1} s^{-1}
BUT–K–110-3	1.25×10^{-5}	5.03×10^{-4}	2.93×10^{-1}	5.83×10^{2}
BUT–K–110-2	1.25×10^{-5}	7.33×10^{-4}	4.18×10^{-1}	5.70×10^{2}
BUT–K–110-1	1.25×10^{-5}	9.95×10^{-4}	5.83×10^{-1}	5.86×10^{2}

$<k_2>(20\ °C) = (5.80 \pm 0.07) \times 10^2$ L mol^{-1} s^{-1}

Table S9. Phenyldiazomethane (**1b**) and $(dpa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 670 nm 20.0 °C (Stopped flow).

No.	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	k_{obs} / s^{-1}	k_2 / L mol^{-1} s^{-1}
BUT–K–109-3	1.25×10^{-5}	5.03×10^{-4}	3.32	6.60×10^{3}
BUT–K–109-2	1.25×10^{-5}	7.33×10^{-4}	5.03	6.86×10^{3}
BUT–K–109-1	1.25×10^{-5}	9.95×10^{-4}	6.90	6.93×10^{3}
BUT–K–109-4	1.25×10^{-5}	1.26×10^{-3}	8.85	7.02×10^{3}

$<k_2>(20\ °C) = (6.85 \pm 0.16) \times 10^3$ L mol^{-1} s^{-1}

Table S10. Phenyldiazomethane (**1b**) and $(pfa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 603 nm 20.0 °C (Stopped flow).

No.	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	k_{obs} / s^{-1}	k_2 / L mol^{-1} s^{-1}
BUT–K–111-1	1.25×10^{-5}	4.85×10^{-4}	7.11×10^{1}	1.47×10^{5}
BUT–K–111-2	1.25×10^{-5}	7.52×10^{-4}	1.07×10^{2}	1.42×10^{5}
BUT–K–111-3	1.25×10^{-5}	9.22×10^{-4}	1.33×10^{2}	1.44×10^{5}
BUT–K–111-4	1.25×10^{-5}	1.26×10^{-3}	1.86×10^{2}	1.48×10^{5}

$<k_2>(20\ ^oC) = (1.45 \pm 0.02) \times 10^5$ L mol^{-1} s^{-1}

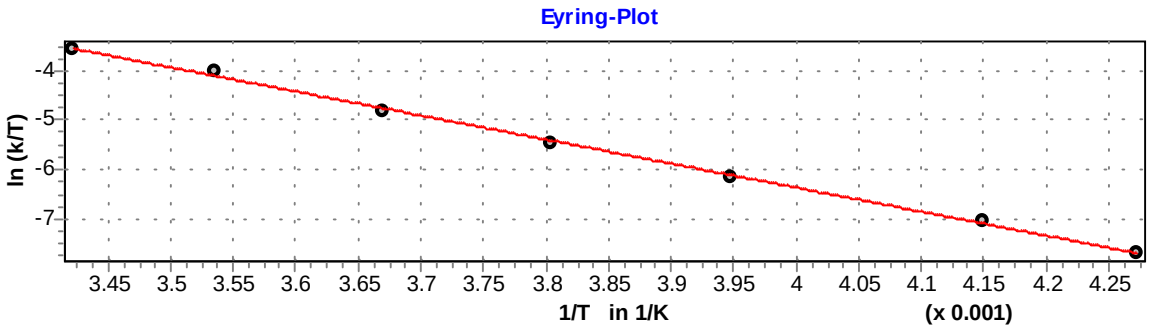
Table S11. (Trimethylsilyl)diazomethane (**1c**) and $(jul)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–121–2	19.9	1.82×10^{-5}	8.48×10^{-4}	72	4.55×10^{-1}
WER–K–13–2	20.0	6.73×10^{-5}	2.02×10^{-3}	90	4.75×10^{-1}
WER–K–13–1	20.0	5.07×10^{-5}	2.53×10^{-3}	94	4.46×10^{-1}
WER–K–12–3	20.0	5.48×10^{-5}	2.74×10^{-3}	68	4.64×10^{-1}
WER–K–12–1	20.0	5.94×10^{-5}	2.96×10^{-3}	88	4.33×10^{-1}
WER–K–12–2	20.0	5.62×10^{-5}	4.49×10^{-3}	62	4.27×10^{-1}

$<k_2>(20\ °C) = (4.50 \pm 0.17) \times 10^{-1}$ L mol^{-1} s^{-1}

Table S12. (Trimethylsilyl)diazomethane (**1c**) and $(pyr)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 600–630 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
MH–V–125	–39.1	5.89×10^{-5}	6.74×10^{-3}	74	1.08×10^{-1}
MH–V–126	–32.2	5.51×10^{-5}	5.04×10^{-3}	88	2.06×10^{-1}
MH–V–127	–19.9	5.60×10^{-5}	3.84×10^{-3}	72	5.34×10^{-1}
MH–V–128	–10.3	5.68×10^{-5}	2.60×10^{-3}	80	1.12
MH–V–129	–0.7	5.86×10^{-5}	1.34×10^{-3}	66	2.21
MH–V–130	9.7	5.45×10^{-5}	6.23×10^{-4}	64	5.04
MH–V–131	19.1	5.49×10^{-5}	1.88×10^{-3}	63	8.11



Eyring parameters:

$\Delta H^{\ddagger}$ = 40.322 ± 0.582 kJ mol^{-1}

$\Delta S^{\ddagger}$ = –89.233 ± 2.234 J mol^{-1} K^{-1}

r^2 = 0.9990

Arrhenius parameters:

E_a = 42.489 ± 0.594 kJ mol^{-1}

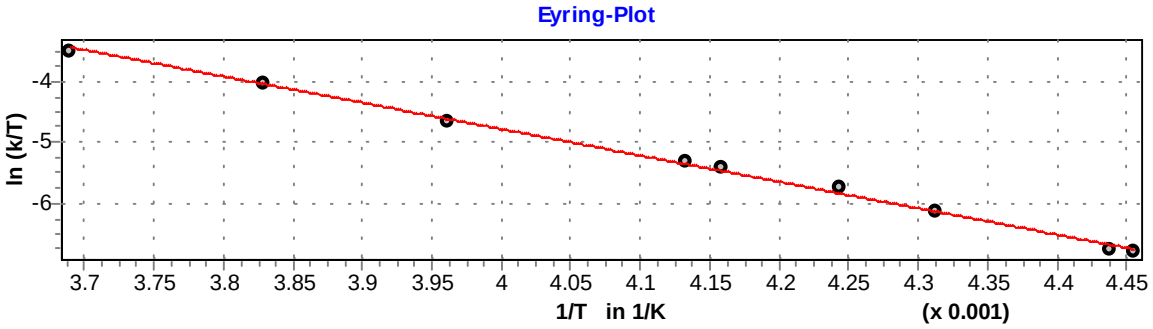
ln A = 19.594 ± 0.275

r^2 = 0.9990

k_2(20 °C) = 8.72 ± 0.25 L mol^{-1} s^{-1}

Table S13. (Trimethylsilyl)diazomethane (**1c**) and (dma)$_2$CH$^+$OTf$^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
MH–V–95	–48.7	8.71 × 10^{-5}	2.45 × 10^{-3}	78	2.57 × 10^{-1}
MH–V–96	–47.8	6.62 × 10^{-5}	2.79 × 10^{-3}	78	2.63 × 10^{-1}
MH–V–41	–41.3	1.53 × 10^{-4}	2.11 × 10^{-3}	70	5.15 × 10^{-1}
MH–V–97	–37.5	6.43 × 10^{-5}	3.38 × 10^{-3}	84	7.69 × 10^{-1}
MH–V–98	–32.7	7.56 × 10^{-5}	2.39 × 10^{-3}	79	1.07
MH–V–42	–31.2	1.18 × 10^{-4}	1.54 × 10^{-3}	81	1.20
MH–V–99	–24.7	6.09 × 10^{-5}	1.28 × 10^{-3}	81	1.97
MH–V–43	–20.7	1.30 × 10^{-4}	1.41 × 10^{-3}	75	2.43
MH–V–44	–12.0	1.17 × 10^{-4}	2.02 × 10^{-3}	87	4.65
MH–V–45	–2.1	1.14 × 10^{-4}	1.48 × 10^{-3}	70	8.06



Eyring parameters:	Arrhenius parameters:
$\Delta H^{‡} = 35.708 \pm 0.710$ kJ mol^{-1}	$E_a = 37.745 \pm 0.693$ kJ mol^{-1}
$\Delta S^{‡} = -94.426 \pm 2.932$ J mol^{-1} K^{-1}	ln $A = 18.906 \pm 0.345$
$r^2 = 0.9969$	$r^2 = 0.9973$

k_2(20 °C) = (3.10 ± 0.19) × 10^1 L mol^{-1} s^{-1}

Table S14. (Trimethylsilyl)diazomethane (**1c**) and $(dpa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 670 nm at 20.0 °C (Stopped flow).

No.	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	k_{obs} / s^{-1}	k_2 / L mol^{-1} s^{-1}
WER–K–14–1	1.25 × 10^{-5}	7.50 × 10^{-4}	1.24	1.65 × 10^3
WER–K–14–2	1.25 × 10^{-5}	1.00 × 10^{-3}	1.61	1.61 × 10^3
WER–K–14–3	1.25 × 10^{-5}	1.25 × 10^{-3}	2.02	1.62 × 10^3
WER–K–14–4	1.25 × 10^{-5}	1.50 × 10^{-3}	2.39	1.59 × 10^3

<k_2>(20 °C) = (1.62 ± 0.02) × 10^3 L mol^{-1} s^{-1}

Table S15. Diphenyldiazomethane (**1d**) and $(dma)_2CH^+OTf^-$ in CH_2Cl_2 at λ = 600–630 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
MH–V–176	20.2	2.55 × 10^{-5}	6.46 × 10^{-4}	54	2.67 × 10^{-2}
MH–V–177	20.0	2.82 × 10^{-5}	8.90 × 10^{-4}	72	2.56 × 10^{-2}
MH–V–178	20.0	2.96 × 10^{-5}	1.87 × 10^{-3}	36	2.90 × 10^{-2}

<k_2>(20 °C) = (2.71 ± 0.17) × 10^{-2} L mol^{-1} s^{-1}

Table S16. Diphenyldiazomethane (**1d**) and $(mpa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 630–640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–119–2	20.0	1.31×10^{-5}	5.37×10^{-4}	22	2.69×10^{-1}
WER–K–2–2	20.0	2.76×10^{-5}	8.36×10^{-4}	51	3.11×10^{-1}
WER–K–3–1	20.0	3.56×10^{-5}	1.79×10^{-3}	85	2.77×10^{-1}
WER–K–1–1	20.0	3.87×10^{-5}	1.93×10^{-3}	48	2.82×10^{-1}
WER–K–3–2	20.0	3.54×10^{-5}	2.84×10^{-3}	64	2.74×10^{-1}
BUT–K–119–1	20.0	7.44×10^{-5}	5.73×10^{-3}	58	3.15×10^{-1}

$<k_2>(20\ °C) = (2.88 \pm 0.18) \times 10^{-1}$ L mol^{-1} s^{-1}

Table S17. Diphenyldiazomethane (**1d**) and $(mpa)_2CH^+OTf^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
WER–K–10–1	20.0	3.69×10^{-5}	1.77×10^{-3}	41	3.27×10^{-1}
WER–K–10–2	20.0	4.46×10^{-5}	2.22×10^{-3}	36	3.07×10^{-1}
WER–K–10–3	20.0	3.26×10^{-5}	2.61×10^{-3}	29	3.13×10^{-1}

$<k_2>(20\ °C) = (3.16 \pm 0.08) \times 10^{-1}$ L mol^{-1} s^{-1}

Table S18. Diphenyldiazomethane (**1d**) and $(dpa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 630–640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–120–2	19.9	1.48×10^{-5}	7.54×10^{-4}	32	2.65
BUT–K–120–6	19.9	3.44×10^{-5}	1.03×10^{-3}	60	2.97
BUT–K–120–9	19.9	2.54×10^{-5}	1.29×10^{-3}	55	2.93
BUT–K–120–8	19.9	2.85×10^{-5}	1.44×10^{-3}	54	3.04
WER–K–8–4	20.0	3.33×10^{-5}	1.66×10^{-3}	35	3.03
WER–K–8–3	20.0	4.21×10^{-5}	2.10×10^{-3}	24	2.99
BUT–K–120–7	19.9	3.09×10^{-5}	2.51×10^{-3}	42	2.93

$\langle k_2 \rangle$(20 °C) = (2.93 ± 0.12) L mol^{-1} s^{-1}

Table S19. Diphenyldiazomethane (**1d**) and (mfa)$_2$CH$^+$BF$_4^-$ in CH_2Cl_2 at λ = 600 nm (Schölly, *J&M*).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–123–3	20.0	4.90×10^{-6}	2.48×10^{-4}	33	2.41×10^{1}
WER–K–11–4	20.0	1.24×10^{-5}	9.93×10^{-4}	40	2.25×10^{1}
BUT–K–122–6	20.0	2.42×10^{-5}	1.20×10^{-3}	72	2.22×10^{1}
BUT–K–122–3	20.0	1.55×10^{-5}	1.24×10^{-3}	35	2.39×10^{1}
BUT–K–123–2	20.0	3.24×10^{-5}	1.64×10^{-3}	48	2.23×10^{1}

$\langle k_2 \rangle$(20 °C) = (2.30 ± 0.08) × 10^1 L mol^{-1} s^{-1}

Table S20. Ethyl diazoacetate (**1e**) and (dma)$_2$CH$^+$BF$_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	T (°C)	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / (%)	k_2 / L mol^{-1} s^{-1}
MH–V–182	20.0	7.63×10^{-5}	1.76×10^{-3}	66	1.37×10^{-2}
MH–V–183	20.0	6.33×10^{-5}	2.92×10^{-3}	69	1.42×10^{-2}

$\langle k_2 \rangle$(20 °C) = (1.40 ± 0.03) × 10^{-2} L mol^{-1} s^{-1}

Table S21. Ethyl diazoacetate (**1e**) and (dpa)$_2$CH$^+$BF$_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–107–7	20.0	3.54×10^{-5}	1.07×10^{-3}	18	8.06×10^{-1}
BUT–K–107–5	20.0	3.67×10^{-5}	1.83×10^{-3}	69	8.63×10^{-1}
BUT–K–107–1	20.0	3.96×10^{-5}	1.96×10^{-3}	28	8.54×10^{-1}
BUT–K–107–4	20.0	3.95×10^{-5}	1.97×10^{-3}	66	8.50×10^{-1}
BUT–K–107–2	20.0	4.04×10^{-5}	2.00×10^{-3}	71	8.46×10^{-1}
BUT–K–107–3	20.0	4.40×10^{-5}	2.20×10^{-3}	53	8.54×10^{-1}

$\langle k_2 \rangle$(20 °C) = (8.46 ± 0.18) × 10^{-1} L mol^{-1} s^{-1}

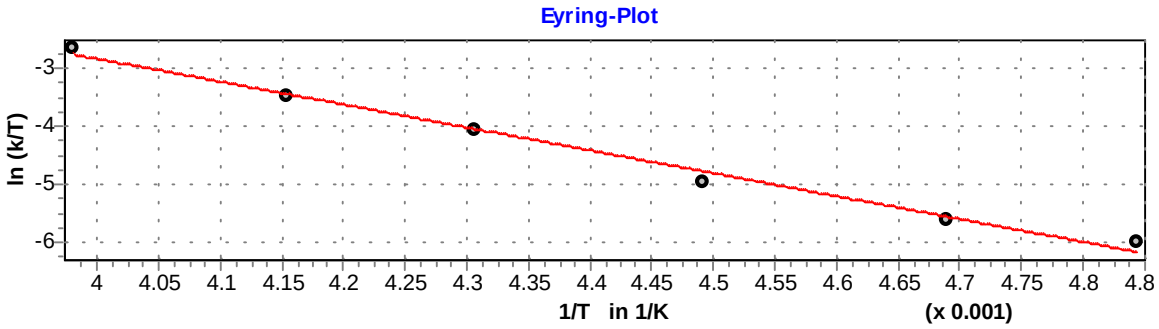
Table S22. Ethyl diazoacetate (**1e**) and $(mfa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 600 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–108–7	20.0	4.07×10^{-5}	1.21×10^{-3}	39	7.87
BUT–K–108–1	20.0	4.94×10^{-5}	2.46×10^{-3}	50	8.60
BUT–K–108–4	20.0	5.08×10^{-5}	2.53×10^{-3}	66	8.80
BUT–K–108–2	20.0	5.19×10^{-5}	2.58×10^{-3}	66	8.65
BUT–K–108–3	20.0	5.20×10^{-5}	2.59×10^{-3}	61	8.81
BUT–K–108–6	20.0	4.76×10^{-5}	3.82×10^{-3}	73	8.63

$<k_2>$(20 °C) = (8.56 ± 0.32) L mol^{-1} s^{-1}

Table S23. Ethyl diazoacetate (**1e**) and fc(Ph)CHOAc in CH_2Cl_2 at λ = 490 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[TMSOTf]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
MH–V–35	–66.7	1.15×10^{-3}	2.74×10^{-3}	7.85×10^{-3}	99	5.06×10^{-1}
MH–V–36	–59.9	1.03×10^{-3}	3.98×10^{-3}	7.05×10^{-3}	71	7.51×10^{-1}
MH–V–31	–50.5	7.97×10^{-4}	5.47×10^{-3}	7.23×10^{-3}	62	1.55
MH–V–32	–40.9	9.59×10^{-4}	4.94×10^{-3}	6.56×10^{-3}	45	4.00
MH–V–33	–32.4	1.07×10^{-3}	4.12×10^{-3}	7.30×10^{-3}	28	7.57
MH–V–34	–21.9	9.16×10^{-4}	2.36×10^{-3}	6.26×10^{-3}	53	1.79×10^{1}



Eyring parameters:

$\Delta H^{\ddagger}$ = 33.089 ± 1.634 kJ mol^{-1}

$\Delta S^{\ddagger}$ = –88.733 ± 7.221 J mol^{-1} K^{-1}

r^2 = 0.9903

Arrhenius parameters:

E_a = 34.978 ± 1.657 kJ mol^{-1}

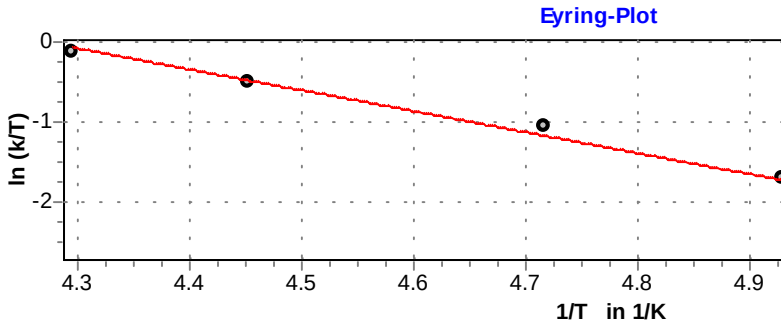
ln A = 19.515 ± 0.881

r^2 = 0.9911

k_2(20 °C) = (1.80 ± 0.36) × 10^2 L mol^{-1} s^{-1}

Table S24. Ethyl diazoacetate (**1e**) and (fur)$_2$CHOMe in CH_2Cl_2 at λ = 490 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[TMSOTf]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
HS220794.5	–82.5	9.47 × 10^{-5}	7.06 × 10^{-3}	2.71 × 10^{-3}	35	1.38 × 10^1
HS140794.0	–70.3	6.60 × 10^{-4}	6.47 × 10^{-3}	1.77 × 10^{-3}	20	3.68 × 10^1
HS210794.1	–61.1	1.14 × 10^{-4}	2.38 × 10^{-3}	3.03 × 10^{-3}	31	7.30 × 10^1
HS210794.2	–48.5	1.27 × 10^{-4}	1.32 × 10^{-3}	9.41 × 10^{-4}	25	1.37 × 10^2
HS210794.3	–40.3	9.66 × 10^{-5}	1.45 × 10^{-3}	1.75 × 10^{-3}	18	2.02 × 10^2



Eyring parameters:

$\Delta H^{\ddagger}$ = 21.704 ± 0.936 kJ mol^{-1}

$\Delta S^{\ddagger}$ = –104.988 ± 4.438 J mol^{-1} K^{-1}

r^2 = 0.9944

Arrhenius parameters:

E_a = 23.453 ± 0.908 kJ mol^{-1}

ln A = 17.484 ± 0.518

r^2 = 0.9955

k_2(20 °C) = (2.72 ± 0.40) × 10^3 L mol^{-1} s^{-1}

Table S25. Diazoacetone (**1f**) and $(mpa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–127–1	20.0	1.99×10^{-5}	1.60×10^{-3}	32	1.25×10^{-2}
BUT–K–127–3	20.0	2.20×10^{-5}	1.12×10^{-3}	26	1.17×10^{-2}

$<k_2>(20\ ^oC) = (1.21 \pm 0.04) \times 10^{-2}$ L mol^{-1} s^{-1}

Table S26. Diazoacetone (**1f**) and $(dpa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

Nr.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–124–5	20.0	2.40×10^{-5}	7.32×10^{-4}	24	3.15×10^{-1}
BUT–K–124–6	20.0	2.92×10^{-5}	1.49×10^{-3}	24	3.15×10^{-1}
BUT–K–124–3	20.0	3.25×10^{-5}	1.65×10^{-3}	18	3.26×10^{-1}
BUT–K–124–7	20.0	5.00×10^{-5}	2.54×10^{-3}	68	3.15×10^{-1}
BUT–K–124–9	20.0	5.16×10^{-5}	2.62×10^{-3}	67	3.38×10^{-1}
BUT–K–124–8	20.0	5.52×10^{-5}	2.81×10^{-3}	70	3.21×10^{-1}
BUT–K–124–4	20.0	6.39×10^{-5}	5.15×10^{-3}	85	3.48×10^{-1}

$<k_2>(20\ °C) = (3.25 \pm 0.12) \times 10^{-1}$ L mol^{-1} s^{-1}

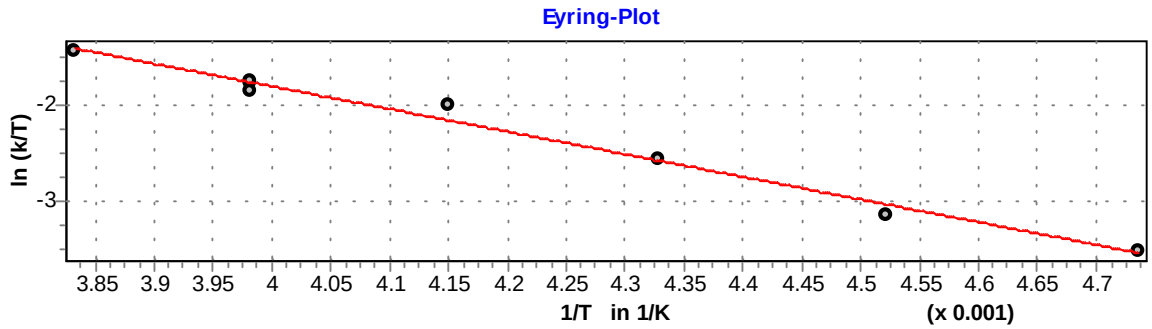
Table S27. Diazoacetone (**1f**) and $(mfa)_2CH^+BF_4^-$ in CH_2Cl_2 at λ = 600 nm (Schölly).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–125–3	20.0	1.63×10^{-5}	4.94×10^{-4}	48	1.27
BUT–K–125–2	19.9	1.88×10^{-5}	9.36×10^{-4}	40	1.28
BUT–K–125–5	19.9	2.84×10^{-5}	1.41×10^{-3}	61	1.34
BUT–K–125–7	19.9	3.33×10^{-5}	1.66×10^{-3}	86	1.27
BUT–K–125–6	19.9	3.43×10^{-5}	1.71×10^{-3}	80	1.29
BUT–K–125–4	19.9	5.34×10^{-5}	4.29×10^{-3}	62	1.32

$<k_2>(20\ °C) = (1.30 \pm 0.03)$ L mol^{-1} s^{-1}

Table S28. Diazoacetone (**1f**) and $(fur)_2CH^+OTf^-$ in CH_2Cl_2 at λ = 530 nm (*J&M*).

Nr.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[TMSOTf]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–126–4	–62.0	1.70×10^{-5}	8.50×10^{-4}	8.36×10^{-5}	51	6.17
BUT–K–126–5	–52.0	1.80×10^{-5}	8.98×10^{-4}	1.61×10^{-4}	42	9.43
BUT–K–126–6	–42.1	1.60×10^{-5}	7.98×10^{-4}	1.78×10^{-4}	60	1.79×10^{1}
BUT–K–126–8	–32.2	1.64×10^{-5}	8.19×10^{-4}	1.83×10^{-4}	50	3.27×10^{1}
BUT–K–126–1	–22.0	1.84×10^{-5}	9.00×10^{-4}	2.28×10^{-4}	54	4.31×10^{1}
BUT–K–126–2	–22.0	8.73×10^{-6}	3.21×10^{-4}	6.13×10^{-5}	45	3.94×10^{1}
BUT–K–126–3	–22.0	1.93×10^{-5}	1.51×10^{-3}	1.45×10^{-4}	80	4.43×10^{1}
BUT–K–126–9	–12.2	1.59×10^{-5}	7.93×10^{-4}	1.77×10^{-4}	50	6.28×10^{1}



Eyring parameters:

$\Delta H^{‡} = 19.851 \pm 0.912$ kJ mol^{-1}

$\Delta S^{‡} = -133.119 \pm 3.828$ J mol^{-1} K^{-1}

$r^2 = 0.9875$

Arrhenius parameters:

$E_a = 21.797 \pm 0.906$ kJ mol^{-1}

$\ln A = 14.208 \pm 0.458$

$r^2 = 0.9897$

$k_2(20\ °C) = (1.98 \pm 0.17) \times 10^2$ L mol^{-1} s^{-1}

Table S29. Diazoacetone (**1f**) and $(ani)_2CHCl$ in CH_2Cl_2 at λ = 510 nm at 20.0 °C (Stopped flow).

No.	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[TMSOTf]_0$ / mol L^{-1}	k_{obs} / s^{-1}	k_2 / L mol^{-1} s^{-1}
BUT–K–128–1	1.24×10^{-5}	5.00×10^{-4}	6.49×10^{-5}	2.13	4.27×10^{3}
BUT–K–128–2	1.24×10^{-5}	7.49×10^{-4}	6.49×10^{-5}	3.03	4.05×10^{3}
BUT–K–128–3	1.24×10^{-5}	9.99×10^{-4}	6.49×10^{-5}	3.96	3.96×10^{3}
BUT–K–128–4	1.24×10^{-5}	1.25×10^{-3}	6.49×10^{-5}	4.93	3.94×10^{3}

$<k_2>(20\ ^{o}C) = (4.06 \pm 0.13) \times 10^{3}$ L mol^{-1} s^{-1}

Table S30. Diethyl diazomalonate (**1g**) and $(fur)_2CH^{+}OTf^{-}$ in CH_2Cl_2 at λ = 540 nm (Schölly).

Nr.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[TMSOTf]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–133-4	19.9	1.25×10^{-5}	7.36×10^{-4}	7.52×10^{-5}	37	2.78×10^{-2}
BUT–K–133-1	19.9	1.62×10^{-5}	8.37×10^{-4}	1.08×10^{-4}	43	2.72×10^{-2}
BUT–K–133-2	19.9	1.97×10^{-5}	1.86×10^{-3}	1.11×10^{-4}	30	2.48×10^{-2}
BUT–K–133-3	19.9	1.96×10^{-5}	2.11×10^{-3}	1.06×10^{-4}	83	2.65×10^{-2}
BUT–K–133-5	19.9	2.73×10^{-5}	3.48×10^{-3}	1.64×10^{-4}	87	2.50×10^{-2}

$<k_2>(20\ °C) = (2.63 \pm 0.12) \times 10^{-2}$ L mol^{-1} s^{-1}

Table S31. Diethyl diazomalonate (**1g**) and $(ani)_2CH^+OTf^-$ in CH_2Cl_2 at λ = 510 nm (Schölly, *J&M*).

No.	T / °C	$[E]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[TMSOTf]_0$ / mol L^{-1}	Conv. / %	k_2 / L mol^{-1} s^{-1}
BUT–K–130-9	19.9	1.29×10^{-5}	8.91×10^{-4}	8.60×10^{-5}	21	4.86×10^{-1}
BUT–K–130-8	19.9	1.65×10^{-5}	9.11×10^{-4}	8.24×10^{-5}	61	5.21×10^{-1}
BUT–K–130-6	19.9	1.88×10^{-5}	1.12×10^{-3}	7.80×10^{-5}	75	4.56×10^{-1}
BUT–K–132-2	19.9	2.65×10^{-5}	1.16×10^{-3}	1.59×10^{-4}	93	4.97×10^{-1}
BUT–K–130-2	19.9	2.06×10^{-5}	1.64×10^{-3}	1.18×10^{-4}	79	4.50×10^{-1}
BUT–K–132-1	19.9	4.75×10^{-5}	3.76×10^{-3}	2.86×10^{-4}	79	4.49×10^{-1}

$\langle k_2 \rangle$(20 °C) = $(4.77 \pm 0.27) \times 10^{-1}$ L mol^{-1} s^{-1}

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