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Supporting Information

for

Structure-Nucleophilicity Relationships for Enamines

Bernhard Kempf, Nathalie Hampel, Armin R. Ofial, and Herbert Mayr*[a]

Department Chemie der Ludwig-Maximilians-Universität München

Butenandtstr. 5–13 (Haus F), D-81377 München, Germany

Fax: (+49) 89-2180-77717, E-mail: Herbert.Mayr@cup.uni-muenchen.de

Content **Page**

A. Products of the reactions of enamines, pyrroles, or indoles with benzhydrylium salts

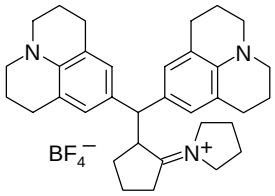
The synthesis of enamines **1a**–**q**, and their reactions with benzhydrylium salts Ar_2CH^+ BF_4^- were performed under exclusion of moisture in an atmosphere of dry nitrogen in carefully dried Schlenk glassware. Dichloromethane was freshly distilled from CaH_2 before use.

Procedure A: A solution of the freshly distilled or recrystallized enamine was added dropwise to a stirred solution of the benzhydrylium salt in CH_2Cl_2 at room temperature. After fading of the color (in cases of reversible reactions after 2 h at the latest) the solvent was evaporated in vacuo to yield the crude product, which was washed with dry Et_2O and dried several hours in vacuo (10^{-2} mbar).

Procedure B: The crude product obtained by Procedure A was dissolved in dilute HCl and stirred for 30 min. The solution was then neutralized by treatment with dilute NaOH. Extraction with CH_2Cl_2 (3 × 30 mL), drying of the combined organic layers with $MgSO_4$, filtration, and evaporation of the solvent in vacuo gave a product which was purified by recrystallization.

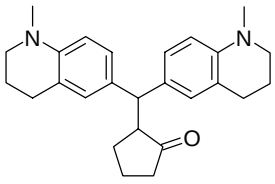
Procedure C: A solution of the benzhydryl salt in dichloromethane (25 mL) was added dropwise to a stirred solution of 10 equiv. of the freshly distilled or recrystallized pyrrole or indole in dichloromethane (25 mL) (An excess of the nucleophile is necessary for trapping the protons which are released during the electrophilic substitution. Reactions with equimolar amounts of the reactants usually do not proceed quantitatively and lead to the formation of side products, e.g., disubstituted arenes). After fading of the color, the solvent was evaporated in vacuo to yield the crude product, which was purified by column chromatography.

***N*-(2-(Bis(julolidin-9-yl)methyl)cyclopentylidene)pyrrolidinium tetrafluoroborate (2a)** was obtained from 1-(*N*-pyrrolidino)cyclopentene (**1a**) (55 mg, 0.40 mmol) and $(jul)_2CH^+$ BF_4^- (0.18 g, 0.40 mmol) as an orange solid (144 mg, 62 %) following Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$): = 1.50–2.25 (m, 16 H), 2.52–3.00 (m, 10 H), 3.01–3.15 (m, 8 H), 3.48–4.05 (m, 6 H), 6.42, 6.64 (2 s, 2 × 2 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 20.2 (t, C-4), 22.0 (t, CH_2), 24.6/24.8 (2 t, CH_2), 27.7 (t, CH_2), 30.0, 34.4 (2 t, C-3 and C-5), 50.5 (t, CH_2), 50.9, 53.7 (2 d, Ar_2CH and C-2), 55.0/55.2 (2 t, CH_2), 121.7 (s, Ar), 126.6/126.9 (2 d, Ar), 128.7 (s, Ar), 141.9/142.1 (2 s, Ar), 197.0 (s, C-1).



2a

2-(Bis(*N*-methyl-1,2,3,4-tetrahydroquinolin-6-yl)methyl)cyclopentanone (3a) was obtained from 1-(*N*-pyrrolidino)cyclopentene (**1a**) (137 mg, 1.00 mmol) and $(thq)_2CH^+$ BF_4^- (392 mg, 1.00 mmol) following Procedure B. Crystallization (EtOH) of the crude product gave a brown solid (207 mg, 39 %). ^{1}H NMR (300 MHz, $CDCl_3$): = 1.65–2.29 (m, 10 H, 5 × CH_2), 2.59–2.86 (m, 11 H, 2 × CH_2, 2 × NMe, 2-H), 3.13–3.18 (m, 4 H, 2 × CH_2), 4.40 (d, ^3J = 4.4 Hz, 1 H, Ar_2CH), 6.42–7.00 (m, 6 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 20.6 (t, C-4), 22.5/22.6 (2 t, CH_2), 27.1 (t, C-3), 27.8/27.9 (2 t, CH_2), 38.6 (t, C-5), 39.1/39.2 (2 q, NMe), 48.2 (d, Ar_2CH), 51.30/51.35 (2 t, CH_2), 53.7 (d, C-2), 110.6/110.8 (2 d, Ar), 122.4/122.7 (2 s, Ar), 126.5/127.7, 129.1/129.6 (2 × 2 d, Ar), 130.9/132.0 (2 s, Ar), 145.0 (s, Ar), 220.4 (s, C-1); MS (70 eV, EI): *m/z* (%): 388 (4) [M^+], 305 (100) [Ar_2CH^+], 269 (52), 207 (12).

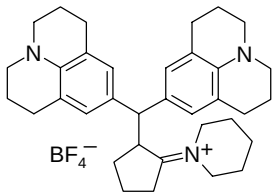


3a

2-(Bis(4-dimethylaminophenyl)methyl)cyclohexanone[17] (**3b**) was obtained from 1-(*N*-pyrrolidino)cyclohexene (**1b**) (151 mg, 0.998 mmol) and $(dma)_2CH^+$ BF_4^- (340 mg, 1.00 mmol) in CH_2Cl_2 (50 mL) following Procedure B. Recrystallization (EtOH) furnished **3b** as a light-brown solid (229 mg, 65 %) which showed identical ^{1}H and ^{13}C NMR spectra as the

corresponding sample that was obtained from 1-(morpholino)cyclohexene and $(dma)_2CH^+$ BF_4^- in ref. 17.

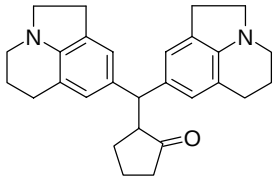
***N*-(2-(Bis(julolidin-9-yl)methyl)cyclopentylidene)piperidinium tetrafluoroborate (2c)** was obtained from 1-(*N*-piperidino)cyclopentene (**1c**) (54 mg, 0.36 mmol) and $(jul)_2CH^+$ BF_4^- (160 mg, 0.360 mmol) as a dark orange solid (190 mg, 89 %) following Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$): = 1.30–2.22 (m, 18 H), 2.45–2.87 (m, 8 H), 2.90–3.11 (m, 10 H), 3.27–3.90 (m, 3 H), 4.22 (d, ^3J = 4.4 Hz, 1 H, Ar_2CH), 6.41, 6.55 (2 s, 2 × 2 H, ArH); MS (FAB): *m/z* (%): 504 (1), 464 (2), 442 (12), 438 (10), 373 (4), 357 (100) [Ar_2CH^+].



2c

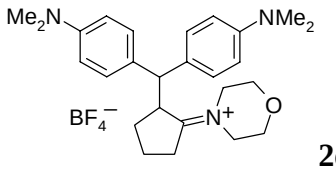
2-(Bis(4-dimethylaminophenyl)methyl)cyclopentanone[43] (**3c**) was obtained from 1-(*N*-piperidino)cyclopentene (**1c**) (153 mg, 1.01 mmol) and $(dma)_2CH^+$ BF_4^- (340 mg, 1.00 mmol) following Procedure B. Crystallization (EtOH) of the crude product gave a light brown solid (166 mg, 49 %) which showed identical ^{1}H and ^{13}C NMR spectra as the corresponding sample that was obtained from 1-(trimethylsiloxy)cyclopentene and $(dma)_2CH^+$ BF_4^- in ref. 43.

2-(Bis(lilolidin-8-yl)methyl)cyclopentanone (3e) was obtained from 1-(*N*-morpholino)-cyclopentene (**1e**) (0.216 mL, 1.35 mmol) and $(lil)_2CH^+$ BF_4^- (510 mg, 1.23 mmol) at –90 °C as described in Procedure B. ^{1}H NMR (300 MHz, $CDCl_3$): = 1.66–1.79 (m, 3 H, 3-H and 4-H_2), 1.99–2.10 (m, 4 H, 2 × CH_2), 2.15–2.27 (m, 3 H, 3-H and 5-H_2), 2.56–2.67 (m, 4 H, 2 × CH_2), 2.72–2.95 (m, 9 H, 2-H and 4 × CH_2), 3.12–3.23 (m, 4 H, 2 × CH_2), 4.42 (d, ^3J = 4.3 Hz, 1 H, Ar_2CH), 6.51, 6.62, 6.73, 6.85 (4 s, 4 × 1 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 20.43 (t, C-4), 23.19/23.25, 23.82, 23.87 (2 × 2 t, CH_2), 27.22 (t, C-3), 28.67/28.76 (2 t, CH_2), 38.37 (t, C-5), 47.48/47.56 (2 t, CH_2), 49.49 (d, Ar_2CH), 53.81 (d, C-2), 55.20/55.29 (2 t, CH_2), 118.65/118.78 (2 s, Ar), 121.96/122.58, 125.82/126.75 (2 × 2 d, Ar), 128.28/128.55, 133.76/134.90 (2 × 2 s, Ar), 148.05 (s, Ar), 220.08 (s, C-1), signal assignments are based on ^{1}H,^{13}C-COSY experiments; MS (EI, 70 eV): *m/z* (%): 412 (14) [M^+], 329 (100), 165 (12).



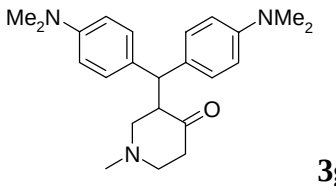
3e

2-(Bis(4-dimethylaminophenyl)methyl)cyclopentenylidene)morpholinium tetrafluoroborate (2e) was obtained from 1-(*N*-morpholino)cyclopentene (**1e**) (0.168 mL, 1.12 mmol) and $(dma)_2CH^+$ BF_4^- (380 mg, 1.12 mmol) following Procedure A: pale green powder (498 mg, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$): = 1.89–2.35 (m, 4 H, 3-H and 4-H), 2.70–2.79 (m, 1 H, ½ × CH_2), 2.86–2.95 (m, partially superimposed, 1 H, ½ × CH_2), 2.86, 2.90 (2 s, 2 × 6 H, NMe_2), 3.00–3.29 (m, 2 H, 5-H_2), 3.60–4.04 (m, 8 H, 2-H, Ar_2CH, 3 × CH_2), 6.59–6.69 (m, 4 H, ArH), 7.02–7.05, 7.15–7.18 (2 m, 2 × 2 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 19.85 (t, C-4), 29.57 (t, C-3), 33.13 (t, C-5), 40.34/40.39 (2 q, NMe_2), 50.74, 51.09 (2 d, Ar_2CH and C-2), 54.23/54.89, 64.69/65.10 (2 × 2 t, CH_2), 112.68/112.77 (2 d, Ar), 127.74/128.69 (2 s, Ar), 128.91/129.40 (2 d, Ar), 149.52/149.88 (2 s, Ar), 200.32 (s, C-1), signal assignments are based on ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY experiments.



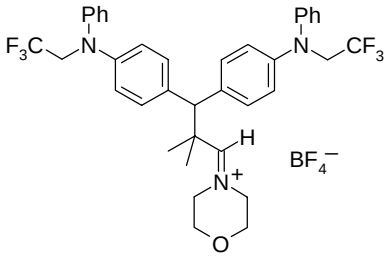
2e

3-(Bis(4-dimethylaminophenyl)methyl)-1-methylpiperidin-4-one (3g) was obtained from 1,2,5,6-tetrahydro-1-methyl-4-(*N*-morpholino)pyridine (**1g**) (150 mg, 0.823 mmol) and $(dma)_2CH^+$ $CF_3SO_3^-$ (231 mg, 0.574 mmol) following Procedure B. Crystallization of the crude product gave **3g** (160 mg, 76 %) as colorless needles. M.p. 162–163 °C (decomp., from ethanol); ^{1}H NMR (300 MHz, $CDCl_3$): = 2.28 (s, 1-Me), 2.32–2.45 (m, 1 H, 5-H), 2.47–2.50 (m, 2 H, 2-H_2), 2.52–2.68 (m, 2 H, 5-H and 6-H), 2.76–2.83 (m, 1 H, 6-H), 2.86, 2.89 (2s, NMe_2), 3.25–3.31 (m, 1 H, 3-H), 4.45 (d, *J* = 11.2 Hz, 1 H, Ar_2CH), 6.60–6.67, 7.10–7.19 (2 m, 2 × 4 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 40.64 (q, NMe_2), 40.83 (t, C-5), 45.29 (q, 1-Me), 48.37 (d, Ar_2CH), 55.33 (d, C-3), 57.15 (t, C-6), 60.09 (t, C-2), 112.74/112.85, 128.40/128.67 (2 × 2 d, Ar), 131.26/131.41, 148.94/149.05 (2 × 2 s, Ar), 211.00 (s, C-4), signal assignments are based on ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY-experiments; MS (EI, 70 eV): *m*/*z* (%): 365 (8) [M^+], 254 (18), 253 (100); elemental analysis calcd (%) for $C_{23}H_{31}N_3O$ (365.52): C 75.58, H 8.55, N 11.50; found: C 75.55, H 8.58, N 11.56.



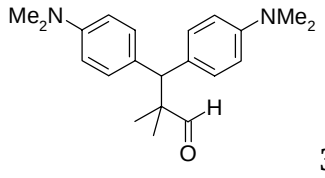
3g

***N*-(3,3-Bis(4-(phenyl(2,2,2-trifluoroethyl)amino)phenyl)-2,2-dimethylpropylidene)morpholinium tetrafluoroborate** (**2j**) was generated by mixing (*N*-morpholino)isobutene (**1j**) (22 mg, 0.16 mmol) and $(pfa)_2CH^+$ BF_4^- (92 mg, 0.15 mmol) in $CDCl_3$ (1 mL). The reaction mixture was transferred into an NMR tube and analyzed without isolation. ^{1}H NMR (200 MHz, $CDCl_3$): = 1.50 (s, 6 H, CH_3), 3.35, 3.67, 3.90, 4.00 (4 m_c, 4 × 2 H, morpholino-CH_2), 4.25 (q, *J*(H,F) = 8.7 Hz, 4 H, NC*H*$_2$CF$_3$), 4.40 (s, 1 H, Ar$_2$C*H*), 6.82–7.35 (m, 18 H, ArH), 8.52 (s, 1 H, N^+=CH).



2j

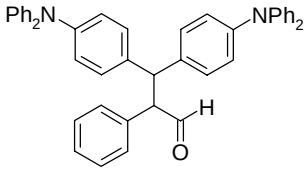
3,3-Bis(4-dimethylaminophenyl)-2,2-dimethylpropanal (**3j**) was obtained from (*N*-morpholino)isobutene (**1j**) (270 mg, 1.91 mmol) and $(dma)_2CH^+$ $CF_3SO_3^-$ (379 mg, 0.942 mmol) following Procedure B. Crystallization from ethanol gave **3j** as beige needles (170 mg, 52 %). M.p. 102 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$): = 1.12 (s, 6 H, 2-CH_3), 2.89 (s, 12 H, NMe_2), 3.99 (s, 1 H, Ar$_2$C*H*), 6.60–6.66, 7.08–7.13 (2 m, 2 × 4 H, ArH), 9.69 (s, 1 H, 1-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 21.5 (q, 2-CH_3), 40.5 (q, NMe_2), 49.8 (s, C-2), 56.9 (d, Ar$_2$*C*H), 112.3 (d, Ar), 129.3 (s, Ar), 130.2 (d, Ar), 149.0 (s, Ar), 207.0 (d, C-1); MS (EI, 70 eV): *m*/*z* (%): 324 (2) [M^+], 254 (34), 253 (100), 237 (14), 126 (20); elemental analysis calcd (%) for $C_{21}H_{28}N_2O$ (324.47): C 77.74, H 8.70, N 8.63; found: C 77.74, H 8.87, N 8.73.



3j

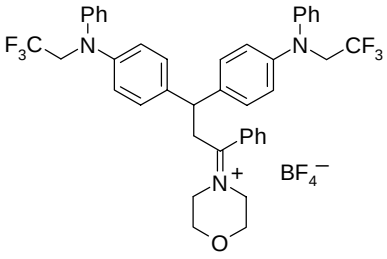
3,3-Bis(4-diphenylaminophenyl)-2-phenylpropanal (**3k**) was obtained from (*E*)- -(*N*-morpholino)styrene (**1k**) (189 mg, 1.00 mmol) and $(dpa)_2CH^+$ BF_4^- (589 mg, 1.00 mmol)

following Procedure B. Crystallization of the crude product gave a pale green solid (432 mg, 70 %). M.p. 130–131 °C (CH_2Cl_2/*n*-pentane); ^{1}H NMR (300 MHz, $CDCl_3$): = 4.30 (dd, ^3J = 11.7 Hz, ^3J = 3.3 Hz, 1 H, 2-H), 4.56 (d, ^3J = 11.7 Hz, 1 H, Ar_2CH), 6.74–7.16 (m, 33 H, ArH), 9.66 (d, ^3J = 3.3 Hz, 1 H, 1-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 51.3 (d, Ar_2CH), 63.9 (d, C-2), 122.6, 122.9, 123.9, 124.0, 124.1, 127.6, 128.9, 129.0, 129.2, 129.2, 129.4, 129.6 (12 d, Ar), 134.9, 136.0, 136.1, 146.0, 146.6, 147.8 (6 s, Ar), 199.3 (d, C-1).



3k

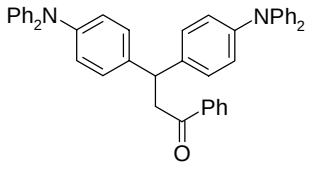
***N*-(3,3-Bis(4-(phenyl(2,2,2-trifluoroethyl)amino)phenyl)-1-phenylpropylidene)morpholinium tetrafluoroborate (2l)** was obtained from -(*N*-morpholino)styrene (**1l**) (51 mg, 0.27 mmol) and $(pfa)_2CH^+$ BF_4^- (163 mg, 0.272 mmol) as a pale violet solid (179 mg, 83 %) following Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$): = 3.55–4.05 (m, 11 H, morpholino-CH_2, 2-H_2, Ar_2CH), 4.17 (q, J(H,F) = 8.7 Hz, 4 H, NCH_2CF_3), 6.73–7.50 (m, 23 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 44.1 (t, C-2), 47.0 (d, Ar_2CH), 54.1 (tq, J(C,F) = 30.2 Hz, NCH_2CF_3), 53.5, 56.1, 65.9, 66.4 (4 t, morpholino-CH_2), 119.7, 123.1, 124.0 (3 d, Ar), 127.0 (s, Ar), 127.4, 128.5, 129.6, 129.7, 132.7 (5 d, Ar), 131.8, 134.6, 146.8 (3 s, Ar), 188.1 (s, C-1), the signal for CF_3 could not be identified.



2l

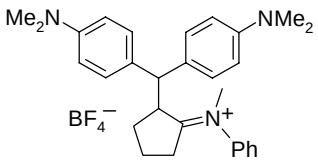
3,3-Bis(4-diphenylaminophenyl)-1-phenylpropan-1-one (3l) was obtained from -(*N*-morpholino)styrene (**1l**) (189 mg, 1.00 mmol) and $(dpa)_2CH^+$ BF_4^- (589 mg, 1.00 mmol) following Procedure B. Crystallization of the crude product gave a pale green solid (284 mg, 46 %). M.p. 96–97 °C (CH_2Cl_2/*n*-pentane); ^{1}H NMR (300 MHz, $CDCl_3$): = 3.67 (d, ^3J = 7.2 Hz, 2 H, 2-H), 4.71 (t, ^3J = 7.3 Hz, 1 H, Ar_2CH), 6.95–7.93 (m, 33 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 45.07 (t, C-2), 45.09 (d, Ar_2CH), 122.6, 124.0, 124.1, 128.1, 128.6, 129.1, 133.0 (7 d, Ar), 137.2, 138.5, 146.0, 147.8 (4 s, Ar), 198.5 (s, C-1); MS (70 eV, EI):

m/z (%): 620 (22) [M^+], 501 (100) [Ar_2CH^+], 251 (10); elemental analysis calcd (%) for $C_{45}H_{36}N_2O$ (620.8): C 87.07, H 5.84, N 4.51; found C 87.26, H 6.00, N 4.42.



3l

***N*-(2-(Bis(4-dimethylaminophenyl)methyl)cyclopentylidene)methylphenylammonium tetrafluoroborate** (**2o**) was obtained from 1-(methylphenylamino)cyclopentene (**1o**) (72 mg, 0.42 mmol) and $(dma)_2CH^+$ BF_4^- (142 mg, 0.417 mmol) as a green solid (197 mg, 92 %) following Procedure A. ^{13}C NMR (75.5 MHz, $CDCl_3$): = 20.4 (t), 29.8 (t), 36.0 (t), 40.4 (q, NMe_2), 40.6 (q, NMe_2), 48.8, 51.3, 52.1 (2 d and 1 q, C-2, Ar_2CH, and N^+CH_3), 112.6, 112.9 (2 d, Ar), 117.4 (s, Ar), 122.9, 123.4, 129.1, 129.4, 130.7 (5 d, Ar), 143.4, 149.6, 150.0 (3 s, Ar), 205.5 (s, C-1); MS (FAB): *m/z* (%): 426 (2) [M^+], 253 (100) [Ar_2CH^+], 237 (11), 174 (13).

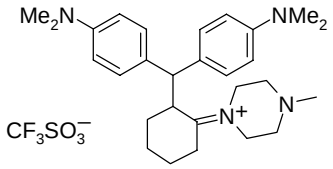


2o

2-(Bis(4-diphenylaminophenyl)methyl)cyclohexanone (**3p**)[17] was obtained from 1-(methylphenylamino)cyclohexene (**1p**) (187 mg, 1.00 mmol) and $(dpa)_2CH^+$ BF_4^- (589 mg, 1.00 mmol) following Procedure B. Crystallization (CH_2Cl_2/*n*-pentane) of the crude product gave **3p** as a pale brown solid (207 mg, 35 %) which showed identical ^1H and ^{13}C NMR spectra as the corresponding sample that was obtained from 1-(trimethylsiloxy)cyclohexene and $(dpa)_2CH^+$ BF_4^- in ref. 17.

1-(2-(Bis(4-dimethylaminophenyl)methyl))cyclohexylidene)-4-methylpiperazinium triflate (2q) was obtained from 1-(1-cyclohexenyl)-4-methylpiperazine (**1q**) (204 mg, 1.13 mmol) and $(dma)_2CH^+$ $CF_3SO_3^-$ (456 mg, 1.13 mmol) as a pale green powder (650 mg, 93 %) following Procedure A. ^1H NMR (300 MHz, $CDCl_3$): = 1.35–1.40 (m, 1 H, 4-H), 1.50–1.56 (m, 1 H, ½ × CH_2), 1.98–2.10 (m, partially superimposed, 2 H, 3-H and ½ × CH_2), 2.03 (s, 3 H, NMe), 2.21–2.26 (m, 1 H, 5-H), 2.42–2.58 (m, 2 H, CH_2), 2.76, 2.81 (2 s, 2 × 6 H, NMe_2), 2.90–2.98, 3.12–3.16 (2 m, 2 × 1 H, 6-H_2), 3.73–4.03 (m, 5 H, 2-H and 2 × CH_2), 4.19 (br d, ^3J = 11.7 Hz, 1 H, Ar_2CH), 6.48–6.59, 6.99–7.23 (2 m, 2 × 4 H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 18.72 (t, C-4), 28.35 (t, C-5), 30.24 (t, C-6), 30.44 (t, C-3), 40.17/40.25 (2 q,

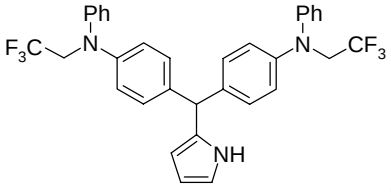
NMe_2), 43.80 (q, NMe), 47.09 (d, C-2), 51.51 (d, Ar_2CH), 52.89/53.00 (2 t, CH_2), 54.05/54.22 (2 t, CH_2), 112.73/112.80 (2 d, Ar), 120.63 (q, J(C,F) = 321 Hz, CF_3SO_3), 127.03/128.55 (2 s, Ar), 127.99/128.71 (2 d, Ar), 149.39/149.56 (2 s, Ar), 194.86 (s, C-1), signal assignments are based on ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY experiments.



2q

2-(Bis(4-dimethylaminophenyl)methyl)cyclohexanone[17] **(3q)** was prepared from the iminium salt **2q** after hydrolysis according to Procedure B as pale beige needles (234 mg, 59 %) which showed identical ^{1}H and ^{13}C NMR spectra as the corresponding sample that was obtained from 1-(morpholino)cyclohexene and $(dma)_2CH^+$ BF_4^- in ref. 17.

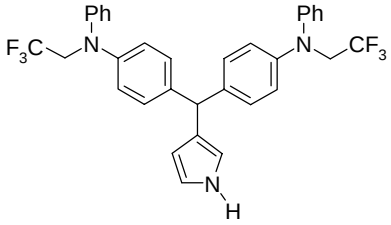
2-(Bis(4-(phenyl(2,2,2-trifluoroethyl)amino)phenyl)methyl)pyrrole (**5a**) was obtained from pyrrole (**4a**) (179 mg, 2.67 mmol) and $(pfa)_2CH^+$ BF_4^- (160 mg, 0.267 mmol) following Procedure C. Column chromatography (silica gel/$CHCl_3$) gave a colorless solid (50 mg, 32 %). ^{1}H NMR (600 MHz, $CDCl_3$): = 4.19 (q, ^3J(H,F) = 8.7 Hz, 4 H, NCH_2CF_3), 5.29 (s, 1 H, Ar_2CH), 5.71–5.75 (m, 1 H, 3-H), 6.07 (dd, J = 6.0 Hz, J = 2.7 Hz, 1 H, 4-H), 6.60–6.64 (m, 1 H, 5-H), 6.80–7.27 (m, 18 H, ArH), 7.73 (br s, 1 H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 49.1 (d, Ar_2CH), 54.0 (tq, J(C,F) = 33 Hz, NCH_2CF_3) 107.8, 108.3, 117.1, 120.8, 121.7, 123.0 (6 d, Ar), 125.2 (sq, J(C,F) = 287 Hz, NCH_2CF_3), 129.5, 129.8 (2 d, Ar), 133.8, 137.2, 146.1, 147.3 (4 s, Ar), signal assignments are based on ^{1}H,^{1}H-COSY experiments.



5a

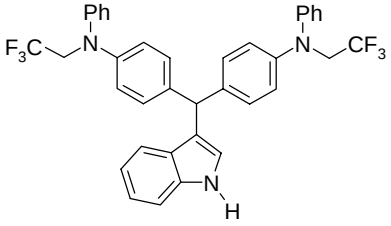
3-(Bis(4-(phenyl(2,2,2-trifluoroethyl)amino)phenyl)methyl)pyrrole (**5c**). A solution of $(pfa)_2CH^+$ BF_4^- (190 mg, 0.317 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of *N*-(triisopropylsilyl)pyrrole (**4c**) (181 mg, 0.814 mmol) in CH_2Cl_2 (30 mL). After 5 min a solution of tetrabutylammonium fluoride in THF (c = 1 M, 1 mL, 1 mmol) was added. The reaction mixture was subsequently washed with 0.2 M hydrochloric acid (50 mL) and water (50 mL). Separation of the organic layer, drying over $CaCl_2$, and evaporation of the

solvent in vacuo gave a brownish oil (134 mg, 73 %). Purification by column chromatography (silica gel/$CHCl_3$) gave **5c** (88 mg, 48 %) and **5a** (17 mg, 9 %). Characterization of **5c**: ^{1}H NMR (300 MHz, $CDCl_3$): = 4.27 (q, *J*(H,F) = 8.8 Hz, 4 H, NCH_2CF_3), 5.31 (s, 1 H, Ar_2CH), 6.05 (br s, 1 H, 5-H), 6.36 (br s, 1 H, 2-H), 6.75 (br s, 1 H, 4-H), 6.91–7.33 (m, 18 H, ArH), 8.02 (br s, 1 H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 48.6 (d, Ar_2CH), 54.1 (tq, *J*(C,F) = 32.7 Hz, NCH_2CF_3), 109.2 (d, C-5), 116.9 (d, C-2), 118.1 (d, C-4), 120.5, 121.7, 122.2, 129.4, 129.5 (5 d, Ar), 125.3 (sq, *J* = 279.4 Hz, NCH_2CF_3), 127.1, 140.2, 145.4, 147.6 (4 s Ar), signal assignments are based on ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY, gHMBC and NOESY experiments.



5c

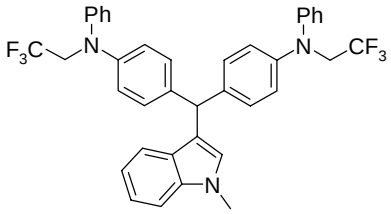
3-(Bis(4-(phenyl(2,2,2-trifluoroethyl)amino)phenyl)methyl)indole (**7a**) was obtained from indole (**6a**) (150 mg, 1.28 mmol) and $(pfa)_2CH^+$ BF_4^- (75 mg, 0.13 mmol) following Procedure C. Column chromatography (silica gel/$CHCl_3$) gave a colorless solid (55 mg, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$): = 4.20 (q, *J*(H,F) = 8.7 Hz, 4 H, NCH_2CF_3), 5.52 (br s, 1 H, Ar_2CH), 6.55 (br s, 1 H, 2-H), 6.83–7.23 (m, 22 H, ArH), 7.86 (br s, 1 H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$): = 47.4 (d, Ar_2CH), 54.0 (tq, *J*(C,F) = 30.2 Hz, NCH_2CF_3), 111.0, 119.4, 119.9 (3d, Ar), 120.1 (s, Ar), 120.9, 121.4, 122.1, 122.4 (4 d, Ar), 123.8 (d, C-2), 125.2 (sq, *J*(C,F) = 283 Hz, NCH_2CF_3), 126.9 (s, Ar), 129.4, 129.9 (2 d, Ar), 136.7, 138.5, 145.6, 147.5 (4 s, Ar), signal assignments are based on ^{1}H,^{1}H and ^{1}H,^{13}C-COSY experiments; MS (70 eV, EI): *m/z* (%): 628 (35) $[M]^+$, 513 (100) $[Ar_2CH]^+$, 379 (18), 264 (75).



7a

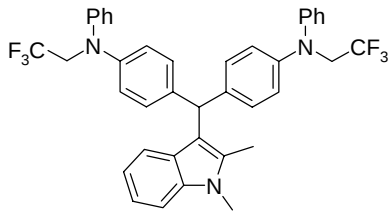
1-Methyl-3-(bis(4-(phenyl(2,2,2-trifluoroethyl)amino)phenyl)methyl)indole (**7b**) was obtained from *N*-methylindole (**6b**) (360 mg, 2.74 mmol) and $(pfa)_2CH^+$ BF_4^- (165 mg, 0.275 mmol) following Procedure C. Column chromatography (silica gel/$CHCl_3$) gave a colorless solid (38 mg, 22 %). ^{1}H NMR (300 MHz, $CDCl_3$): = 3.65 (s, 3 H, NCH_3), 4.21 (q, *J*(H,F) =

8.7 Hz, 4 H, NCH_2CF_3), 5.52 (s, 1 H, Ar_2CH), 6.41 (s, 1 H, 2-H), 6.84–7.24 (m, 22 H, ArH), the presence of additional resonances indicate a contamination of the sample with ca. 15 % of **6b**; ^{13}C NMR (75.5 MHz, $CDCl_3$): = 32.7 (q, NCH_3), 47.4 (d, Ar_2CH), 54.1 (tq, *J*(C,F)= 38 Hz, NCH_2CF_3), 109.1, 118.8, 119.9, 120.9, 121.4, 121.6, 122.4 (7 d, Ar), 128.5 (d, C-2), 129.4, 129.9 (2 d, Ar), 138.7, 145.6, 147.5 (3 s, Ar), because of the low signal-to-noise ratio CF_3 and three aromatic carbons could not be identified in the spectra, signal assignments are based on $^{1}H,^{13}C$-COSY experiments; MS (70 eV, EI): *m/z* (%): 642 (32) $[M]^+$, 513 (57) $[Ar_2CH]^+$, 393 (44), 264 (42).



7b

1,2-Dimethyl-3-(bis(4-(phenyl(2,2,2-trifluoroethyl)amino)phenyl)methyl)indole (**7c**) was obtained from 1,2-dimethylindole (**6c**) (469 mg, 3.23 mmol) and $(pfa)_2CH^+ BF_4^-$ (194 mg, 0.323 mmol) following Procedure C. Column chromatography (silica gel/$CHCl_3$) gave a colorless solid (72 mg, 34 %). ^{1}H NMR (300 MHz, $CDCl_3$): = 2.19 (s, 3 H, 2-CH_3), 3.57 (s, 3 H, NCH_3), 4.18 (q, *J*(H,F) = 8.7 Hz, 4 H, NCH_2CF_3), 5.61 (s, 1 H, Ar_2CH), 6.83–7.19 (m, 22 H, ArH), the presence of additional resonances indicate a contamination of the sample with ca. 15 % of **6c**; ^{13}C NMR (75.5 MHz, $CDCl_3$): = 10.7 (q, 2-CH_3), 29.5 (q, NCH_3), 46.7 (d, Ar_2CH), 54.0 (tq, *J*(C,F) = 30.2 Hz, NCH_2CF_3), 108.6 (d, Ar), 113.5 (s, Ar), 118.7, 119.5, 120.2, 120.3, 122.0 (5 d, Ar), 125.2 (sq, *J*(C,F) = 287 Hz, NCH_2CF_3), 127.3 (s, Ar), 129.3, 130.2 (2 d, Ar), 133.7, 136.7, 139.1, 145.3, 147.7 (5 s, Ar); MS (70 eV, EI): *m/z* (%): 657 (38) $[M^+]$, 513 (100) $[Ar_2CH^+]$, 407 (61), 264 (14).



7c

B. Concentrations and rate constants of the individual kinetic runs (Tables S1-S55)

Table S1. 1-(*N*-Pyrrolidino)cyclopentene (**1a**) and $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
011200-F	8.456×10^{-6}	1.436×10^{-4}	17	20.0	1.251×10^5
011200-B	8.456×10^{-6}	2.871×10^{-4}	34	20.0	1.245×10^5
011200-C	8.456×10^{-6}	4.307×10^{-4}	51	20.0	1.307×10^5
011200-D	8.456×10^{-6}	5.743×10^{-4}	68	20.0	1.203×10^5
011200-E	8.456×10^{-6}	7.178×10^{-4}	85	20.0	1.290×10^5

$<k_2>$(20 °C) = $(1.259 \pm 0.037) \times 10^5$ M^{-1} s^{-1}

Table S2. 1-(*N*-Pyrrolidino)cyclopentene (**1a**) and $(jul)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
011200-M	7.130×10^{-6}	1.425×10^{-4}	20	20.0	3.387×10^5
011200-O	7.130×10^{-6}	2.851×10^{-4}	40	20.0	3.171×10^5
011200-I	7.130×10^{-6}	4.276×10^{-4}	60	20.0	3.182×10^5
011200-J	7.130×10^{-6}	5.702×10^{-4}	80	20.0	3.459×10^5
011200-K	7.130×10^{-6}	7.127×10^{-4}	100	20.0	3.419×10^5

$<k_2>$(20 °C) = $(3.324 \pm 0.122) \times 10^5$ M^{-1} s^{-1}

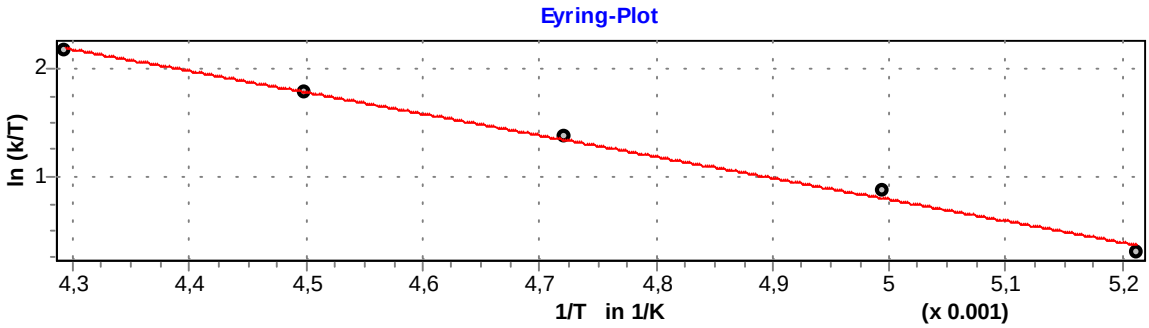
Table S3. 1-(*N*-Pyrrolidino)cyclopentene (**1a**) and $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 628 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
100501-D	5.099×10^{-6}	1.482×10^{-5}	3.4	20.0	4.707×10^6
100501-B	5.099×10^{-6}	2.351×10^{-5}	5.1	20.0	4.112×10^6
100501-E	5.099×10^{-6}	3.220×10^{-5}	6.8	20.0	4.698×10^6
100501-A	5.099×10^{-6}	4.088×10^{-5}	8.5	20.0	4.176×10^6
100501-C	5.099×10^{-6}	4.957×10^{-5}	10	20.0	4.693×10^6

$\langle k_2 \rangle$(20 °C) = (4.477 ± 0.273) × 10^6 M^{-1} s^{-1}

Table S4. 1-(*N*-Pyrrolidino)cyclohexene (**1b**) and $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
241100.PA1	2.407×10^{-5}	1.500×10^{-3}	62	53	–81.3	2.581×10^2
241100.PA2	2.110×10^{-5}	5.258×10^{-4}	25	62	–72.9	4.786×10^2
241100.PA3	3.194×10^{-5}	6.124×10^{-4}	19	55	–61.4	8.234×10^2
241100.PA4	3.355×10^{-5}	3.859×10^{-4}	12	69	–50.9	1.304×10^3
241100.PA5	3.137×10^{-5}	1.804×10^{-4}	6	71	–40.2	2.006×10^3



Eyring parameters:

$\Delta H^{\ddagger}$ = 16.426 ± 0.702 kJ mol^{-1}

$\Delta S^{\ddagger}$ = –108.901 ± 3.341 J mol^{-1} K^{-1}

r^2 = 0.9945

Arrhenius parameters:

E_a = 18.180 ± 0.681 kJ mol^{-1}

ln A = 17.016 ± 0.390

r^2 = 0.9958

k_2(20 °C) = (1.482 ± 0.167) × 10^4 M^{-1} s^{-1}

Table S5. 1-(*N*-Pyrrolidino)cyclohexene (**1b**) and $(jul)_2CH^+$ BF_4^- in CH_2Cl_2 at = 640 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
021200-F	6.698×10^{-6}	1.386×10^{-4}	21	20.0	4.183×10^4
021200-I	6.698×10^{-6}	2.079×10^{-4}	31	20.0	4.722×10^4
021200-B	6.698×10^{-6}	2.772×10^{-4}	41	20.0	4.451×10^4
021200-J	6.698×10^{-6}	3.464×10^{-4}	52	20.0	4.841×10^4
021200-C	6.698×10^{-6}	4.157×10^{-4}	62	20.0	4.732×10^4

$<k_2>(20\ °C) = (4.586 \pm 0.239) \times 10^4\ M^{-1}\ s^{-1}$

Table S6. 1-(*N*-Pyrrolidino)cyclohexene (**1b**) and $(thq)_2CH^+\ BF_4^-$ in CH_2Cl_2 at λ = 628 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / $M^{-1}\ s^{-1}$
030501-C	6.119×10^{-6}	6.565×10^{-5}	11	20.0	7.508×10^5
030501-B	6.119×10^{-6}	1.313×10^{-4}	22	20.0	7.000×10^5
030501-A	6.119×10^{-6}	2.626×10^{-4}	43	20.0	7.377×10^5

$<k_2>(20\ °C) = (7.295 \pm 0.215) \times 10^5\ M^{-1}\ s^{-1}$

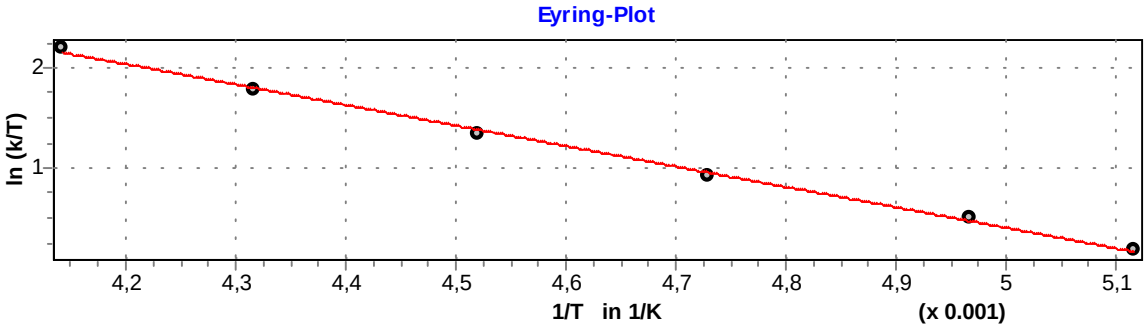
Table S7. 1-(*N*-Pyrrolidino)cyclohexene (**1b**) and $(dma)_2CH^+\ BF_4^-$ in CH_2Cl_2 at λ = 613 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / $M^{-1}\ s^{-1}$
160501-D	5.033×10^{-6}	1.244×10^{-5}	3.0	20.0	4.972×10^6
160501-B	5.033×10^{-6}	2.241×10^{-5}	5.0	20.0	5.438×10^6
160501-C	5.033×10^{-6}	3.238×10^{-5}	6.9	20.0	5.755×10^6
160501-A	5.033×10^{-6}	4.733×10^{-5}	9.9	20.0	5.172×10^6

$<k_2>(20\ °C) = (5.334 \pm 0.294) \times 10^6\ M^{-1}\ s^{-1}$

Table S8. 1-(*N*-Piperidino)cyclopentene (**1c**) and $(lil)_2CH^+\ BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / $M^{-1}\ s^{-1}$
100500.PA1	4.658×10^{-5}	6.218×10^{-4}	13	74	–77.7	2.301×10^2
100500.PA2	5.053×10^{-5}	6.745×10^{-4}	13	60	–71.8	3.297×10^2
100500.PA3	4.417×10^{-5}	5.527×10^{-4}	13	46	–61.7	5.338×10^2
100500.PA5	4.738×10^{-5}	4.744×10^{-4}	10	74	–51.9	8.379×10^2
100500.PA7	5.150×10^{-5}	2.644×10^{-4}	5	61	–41.5	1.383×10^3
100500.PA8	4.031×10^{-5}	2.690×10^{-4}	7	35	–31.7	2.196×10^3



Eyring parameters:

$\Delta H^{\ddagger}$ = 17.128 ± 0.401 kJ mol^{-1}

$\Delta S^{\ddagger}$ = -108.645 ± 1.862 J mol^{-1} K^{-1}

r^2 = 0.9978

Arrhenius parameters:

E_a = 18.928 ± 0.423 kJ mol^{-1}

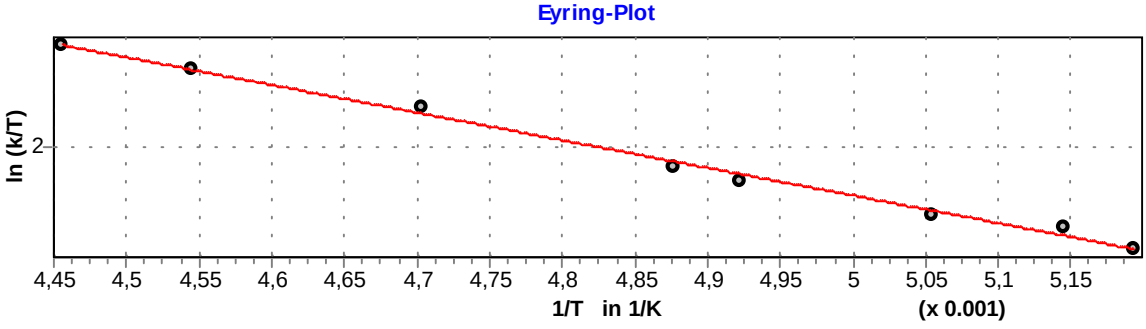
ln A = 17.073 ± 0.236

r^2 = 0.9980

k_2(20 °C) = (1.146 ± 0.067) × 10^4 M^{-1} s^{-1}

Table S9. 1-(*N*-Piperidino)cyclopentene (**1c**) and (jul)$_2$CH$^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
161100.PA0	2.200 × 10^{-5}	1.172 × 10^{-3}	53	65	–80.6	6.366 × 10^2
161100.PA1	1.975 × 10^{-5}	4.209 × 10^{-4}	21	60	–78.8	7.672 × 10^2
161100.PA2	2.636 × 10^{-5}	5.617 × 10^{-4}	21	41	–75.3	8.529 × 10^2
161100.PA3	2.260 × 10^{-5}	3.854 × 10^{-4}	17	33	–70.0	1.141 × 10^3
161100.PA4	4.256 × 10^{-5}	4.883 × 10^{-4}	11	73	–68.1	1.296 × 10^3
161100.PA5	2.835 × 10^{-5}	3.253 × 10^{-4}	11	55	–60.5	2.145 × 10^3
161100.PA6	3.815 × 10^{-5}	3.127 × 10^{-4}	8	48	–53.1	2.964 × 10^3
161100.PA7	3.427 × 10^{-5}	1.685 × 10^{-4}	5	53	–48.7	3.665 × 10^3



Eyring parameters:

Arrhenius parameters:

$\Delta H^{‡}$ = 17.969 ± 0.556 kJ mol^{-1} E_a = 19.695 ± 0.561 kJ mol^{-1}

$\Delta S^{‡}$ = -94.280 ± 2.707 J mol^{-1} K^{-1} ln A = 18.757 ± 0.329

r^2 = 0.9943 r^2 = 0.9952

k_2(20 °C) = (4.565 ± 0.444) × 10^4 M^{-1} s^{-1}

Table S10. 1-(*N*-Piperidino)cyclopentene (**1c**) and $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 624 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
171100-A	1.963 × 10^{-5}	2.034 × 10^{-4}	10	20.0	4.333 × 10^5
171100-B	1.963 × 10^{-5}	4.067 × 10^{-4}	21	20.0	4.429 × 10^5
171100-C	1.963 × 10^{-5}	6.101 × 10^{-4}	31	20.0	4.455 × 10^5
171100-D	1.963 × 10^{-5}	8.135 × 10^{-4}	41	20.0	4.451 × 10^5
171100-E	1.963 × 10^{-5}	1.017 × 10^{-4}	52	20.0	4.538 × 10^5

<k_2>(20 °C) = (4.441 ± 0.066) × 10^5 M^{-1} s^{-1}

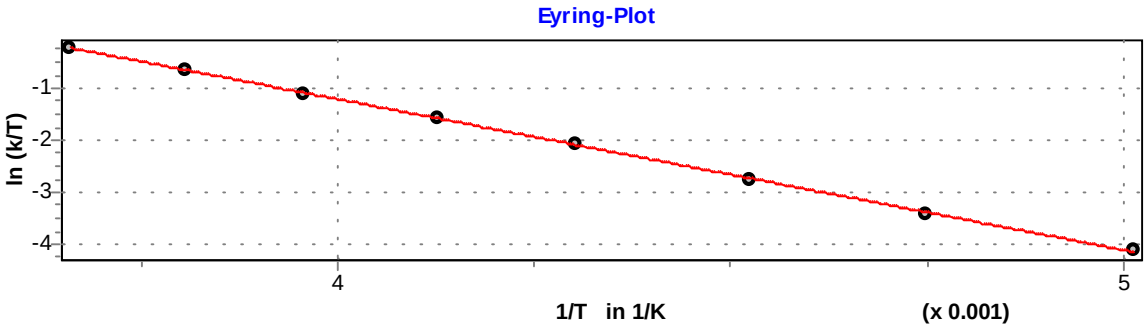
Table S11. 1-(*N*-Piperidino)cyclopentene (**1c**) and $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 613 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
220301-C	3.351 × 10^{-6}	1.845 × 10^{-5}	6	20.0	3.766 × 10^6
220301-B	3.351 × 10^{-6}	3.074 × 10^{-5}	9	20.0	3.605 × 10^6
220301-D	3.351 × 10^{-6}	4.304 × 10^{-5}	13	20.0	3.703 × 10^6
220301-A	3.351 × 10^{-6}	6.149 × 10^{-5}	18	20.0	3.656 × 10^6

<k_2>(20 °C) = (3.683 ± 0.059) × 10^6 M^{-1} s^{-1}

Table S12. 1-(*N*-Morpholino)cyclopentene (**1e**) and $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
040500.PA0	3.707×10^{-5}	1.173×10^{-3}	32	84	–73.7	3.151
040500.PA1	3.123×10^{-5}	7.904×10^{-4}	25	84	–62.6	6.784
040500.PA2	2.802×10^{-5}	4.433×10^{-4}	16	86	–52.1	1.385×10^{1}
040500.PA3	2.455×10^{-5}	7.768×10^{-4}	32	93	–40.8	2.848×10^{1}
040500.PA5	2.623×10^{-5}	6.639×10^{-4}	25	84	–30.8	4.988×10^{1}
040500.PA6	2.382×10^{-5}	4.522×10^{-4}	19	90	–20.4	8.150×10^{1}
040500.PA7	2.468×10^{-5}	3.904×10^{-4}	16	66	–10.5	1.358×10^{2}
040500.PA8	2.743×10^{-5}	6.941×10^{-4}	25	71	0.2	2.135×10^{2}



Eyring parameters:

$\Delta H^{‡} = 24.099 \pm 0.154$ kJ mol^{-1}

$\Delta S^{‡} = -111.413 \pm 0.661$ J mol^{-1} K^{-1}

$r^2 = 0.9998$

Arrhenius parameters:

$E_a = 26.033 \pm 0.164$ kJ mol^{-1}

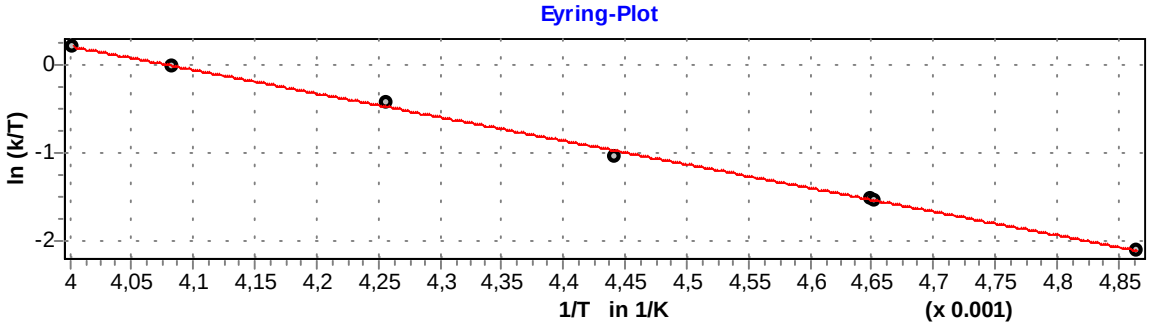
$\ln A = 16.814 \pm 0.085$

$r^2 = 0.9998$

$k_2(20\ °C) = (4.703 \pm 0.075) \times 10^2$ M^{-1} s^{-1}

Table S13. 1-(*N*-Morpholino)cyclopentene (**1e**) and $(jul)_2CH^+ BF_4^-$ in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
KK050520.PA2	2.594×10^{-5}	3.219×10^{-4}	12	34	–67.6	2.523×10^{1}
KK050521.PA2	2.963×10^{-5}	3.677×10^{-4}	12	83	–58.2	4.650×10^{1}
KK050522.PA2	2.429×10^{-5}	3.014×10^{-4}	12	72	–58.1	4.741×10^{1}
KK050523.PA2	1.614×10^{-5}	1.001×10^{-4}	6	79	–48.0	8.000×10^{1}
KK050524.PA2	2.765×10^{-5}	3.431×10^{-4}	12	73	–38.2	1.528×10^{2}
KK050525.PA2	2.551×10^{-5}	2.216×10^{-4}	9	75	–28.3	2.407×10^{2}
KK090523.PA0	1.423×10^{-5}	1.360×10^{-4}	10	64	–23.3	3.084×10^{2}



Eyring parameters:

$\Delta H^{‡} = 22.288 \pm 0.380$ kJ mol^{-1}

$\Delta S^{‡} = -106.620 \pm 1.682$ J mol^{-1} K^{-1}

$r^2 = 0.9986$

Arrhenius parameters:

$E_a = 24.175 \pm 0.385$ kJ mol^{-1}

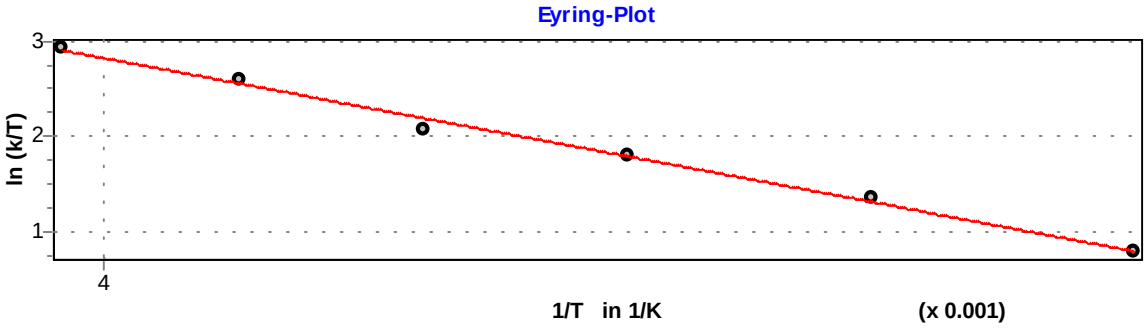
$\ln A = 17.364 \pm 0.205$

$r^2 = 0.9987$

k_2(20 °C) = $(1.760 \pm 0.081) \times 10^3$ M^{-1} s^{-1}

Table S14. 1-(*N*-Morpholino)cyclopentene (**1e**) and $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
080520.PA1	2.363×10^{-5}	2.122×10^{-4}	9	85	–71.7	4.398×10^{2}
080520.PA2	3.623×10^{-5}	4.163×10^{-4}	12	66	–61.2	8.128×10^{2}
080520.PA4	2.476×10^{-5}	1.779×10^{-4}	7	66	–50.5	1.345×10^{3}
080520.PA5	4.099×10^{-5}	2.265×10^{-4}	6	56	–40.6	1.846×10^{3}
080520.PA6	2.423×10^{-5}	1.045×10^{-4}	4	51	–30.9	3.215×10^{3}
080520.PA7	3.374×10^{-5}	1.118×10^{-4}	3	47	–20.7	4.738×10^{3}



Eyring parameters:

$\Delta H^{‡} = 17.550 \pm 0.652$ kJ mol^{-1}

$\Delta S^{‡} = -103.905 \pm 2.896$ J mol^{-1} K^{-1}

$r^2 = 0.9945$

Arrhenius parameters:

$E_a = 19.419 \pm 0.663$ kJ mol^{-1}

ln $A = 17.682 \pm 0.354$

$r^2 = 0.9954$

k_2(20 °C) = $(1.705 \pm 0.136) \times 10^4$ M^{-1} s^{-1}

Table S15. 1-(*N*-Morpholino)cyclopentene (**1e**) and $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 613 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
190401-B	5.080×10^{-6}	8.628×10^{-5}	17	20.0	2.323×10^{5}
190401-A	5.080×10^{-6}	1.726×10^{-4}	34	20.0	2.557×10^{5}
190401-C	5.080×10^{-6}	2.588×10^{-4}	51	20.0	2.421×10^{5}
190401-D	5.080×10^{-6}	3.451×10^{-4}	68	20.0	2.446×10^{5}

$\langle k_2 \rangle$(20 °C) = $(2.437 \pm 0.083) \times 10^5$ M^{-1} s^{-1}

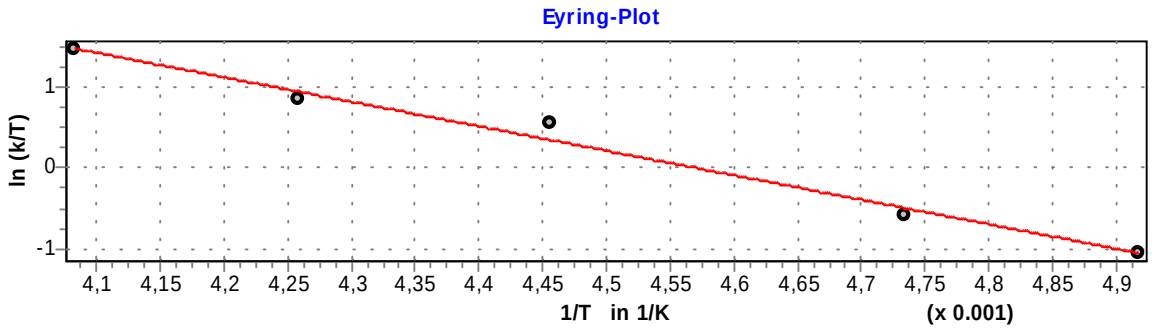
Table S16. 1-(*N*-Morpholino)cyclopentene (**1e**) and $(mpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 622 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
150501-C	4.911×10^{-6}	3.733×10^{-5}	8	20.0	9.585×10^{5}
150501-B	4.911×10^{-6}	7.466×10^{-5}	15	20.0	9.952×10^{5}
150501-E	4.911×10^{-6}	1.120×10^{-4}	23	20.0	9.585×10^{5}
150501-F	4.911×10^{-6}	1.493×10^{-4}	30	20.0	9.669×10^{5}
150501-D	4.911×10^{-6}	1.867×10^{-4}	38	20.0	9.742×10^{5}

$<k_2>(20\ °C) = (9.707 \pm 0.136) \times 10^5\ M^{-1}\ s^{-1}$

Table S17. 1,2,5,6-Tetrahydro-1-methyl-4-(*N*-morpholino)pyridine (**1g**) and $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 600 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
AO-162.2	2.63×10^{-5}	1.78×10^{-4}	6.8	64	–69.8	7.074×10^{1}
AO-162.3	3.02×10^{-5}	2.03×10^{-4}	6.7	72	–61.9	1.166×10^{2}
AO-162.4	2.84×10^{-5}	1.92×10^{-4}	6.8	72	–48.7	3.886×10^{2}
AO-162.5	2.68×10^{-5}	1.81×10^{-4}	6.8	81	–38.3	5.568×10^{2}
AO-162.6	2.60×10^{-5}	1.75×10^{-4}	6.7	87	–28.2	1.068×10^{3}



Eyring parameters:

$\Delta H^{‡} = 25.392 \pm 1.679$ kJ mol^{-1}

$\Delta S^{‡} = -81.151 \pm 7.555$ J mol^{-1} K^{-1}

$r^2 = 0.9871$

Arrhenius parameters:

$E_a = 27.242 \pm 1.670$ kJ mol^{-1}

$\ln A = 17.682 \pm 0.354$

$r^2 = 0.9889$

$k_2(20\ °C) = (1.010 \pm 0.222) \times 10^4\ M^{-1}\ s^{-1}$

Table S18. (*E*)-1-(*N*-Morpholino)propene (**1h**) and $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 672 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
270801-E	4.962×10^{-6}	5.488×10^{-5}	11	20.0	7.722×10^5
270801-D	4.962×10^{-6}	1.098×10^{-4}	22	20.0	7.909×10^5
270801-A	4.962×10^{-6}	1.646×10^{-4}	33	20.0	7.380×10^5
270801-B	4.962×10^{-6}	2.195×10^{-4}	44	20.0	7.250×10^5
270801-C	4.962×10^{-6}	2.744×10^{-4}	55	20.0	6.960×10^5

$\langle k_2 \rangle$(20 °C) = $(7.444 \pm 0.338) \times 10^5$ M^{-1} s^{-1}

Table S19. (*Z*)-1-(*N*-Morpholino)propene[a] (**1i**) and $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 672 nm (Stopped flow).

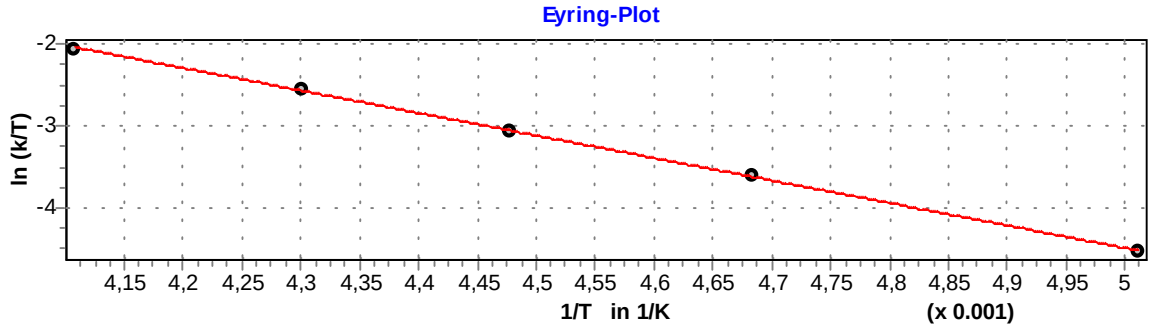
No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
170801-B	4.650×10^{-6}	5.394×10^{-5}	12	20.0	1.148×10^6
170801-C	4.650×10^{-6}	1.079×10^{-4}	23	20.0	1.036×10^6
170801-A	4.650×10^{-6}	1.618×10^{-4}	35	20.0	9.775×10^5
170801-D	4.650×10^{-6}	2.157×10^{-4}	46	20.0	1.141×10^6
170801-E	4.650×10^{-6}	2.697×10^{-4}	58	20.0	1.046×10^6

[a] contaminated by 11 % of (*E*)-1-(*N*-morpholino)propene (**1h**) (^{1}H NMR)

$\langle k_2 \rangle$(20 °C) = $(1.070 \pm 0.065) \times 10^6$ M^{-1} s^{-1}

Table S20. (*N*-Morpholino)isobutylene (**1j**) and $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 600 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
050701.PA1	6.349×10^{-5}	2.314×10^{-3}	37	81	–73.6	2.133
050701.PA2	6.314×10^{-5}	2.301×10^{-3}	37	77	–59.6	5.751
050701.PA3	5.656×10^{-5}	3.298×10^{-3}	58	57	–49.8	1.039×10^1
050701.PA4	5.801×10^{-5}	2.537×10^{-3}	44	61	–40.7	1.801×10^1
050701.PA5	6.162×10^{-5}	1.797×10^{-3}	29	51	–29.7	3.048×10^1



Eyring parameters:

$\Delta H^{‡} = 22.749 \pm 0.282$ kJ mol^{-1}

$\Delta S^{‡} = -121.183 \pm 1.276$ J mol^{-1} K^{-1}

$r^2 = 0.9995$

Arrhenius parameters:

$E_a = 24.575 \pm 0.260$ kJ mol^{-1}

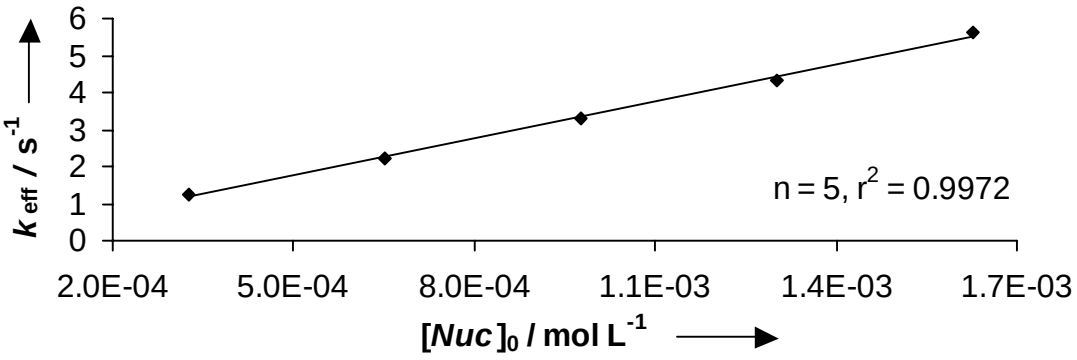
ln $A = 15.580 \pm 0.142$

$r^2 = 0.9997$

k_2(20 °C) = $(2.528 \pm 0.095) \times 10^2$ M^{-1} s^{-1}

Table S21. (*N*-Morpholino)isobutylene (**1j**) and $(mpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 622 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_{eff} / s^{-1}
090701-E	9.735×10^{-6}	3.255×10^{-4}	33	20.0	1.250
090701-D	9.735×10^{-6}	6.509×10^{-4}	67	20.0	2.223
090701-A	9.735×10^{-6}	9.764×10^{-4}	100	20.0	3.274
090701-B	9.735×10^{-6}	1.302×10^{-3}	134	20.0	4.322
090701-C	9.735×10^{-6}	1.627×10^{-3}	167	20.0	5.611



<k_2>(20 °C) = 3.325×10^3 L mol^{-1} s^{-1}

<k_{-2}>(20 °C) = 8.931×10^{-2} s^{-1}

K(20 °C) = 3.723×10^4 L mol^{-1}

Table S22. (*N*-Morpholino)isobutylene (**1j**) and $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 672 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
030701-E	1.041×10^{-5}	7.322×10^{-5}	7	20.0	2.312×10^4
030701-D	1.041×10^{-5}	1.464×10^{-4}	14	20.0	2.368×10^4
030701-A	1.041×10^{-5}	2.197×10^{-4}	21	20.0	2.383×10^4
030701-B	1.041×10^{-5}	2.929×10^{-4}	28	20.0	2.434×10^4
030701-C	1.041×10^{-5}	3.661×10^{-4}	35	20.0	2.557×10^4

$\langle k_2 \rangle$(20 °C) = $(2.411 \pm 0.083) \times 10^4$ M^{-1} s^{-1}

Table S23. (*N*-Morpholino)isobutylene (**1j**) and $(mfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 593 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
030701-J	1.033×10^{-5}	7.365×10^{-5}	7	20.0	1.251×10^5
030701-I	1.033×10^{-5}	1.473×10^{-4}	14	20.0	1.273×10^5
030701-F	1.033×10^{-5}	2.209×10^{-4}	21	20.0	1.283×10^5
030701-G	1.033×10^{-5}	2.946×10^{-4}	29	20.0	1.298×10^5
030701-H	1.033×10^{-5}	3.682×10^{-4}	36	20.0	1.311×10^5

$\langle k_2 \rangle$(20 °C) = $(1.283 \pm 0.021) \times 10^5$ M^{-1} s^{-1}

Table S24. (*N*-Morpholino)isobutylene (**1j**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 601 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
030701-O	6.030×10^{-6}	6.246×10^{-5}	10	20.0	4.087×10^5
030701-N	6.030×10^{-6}	1.249×10^{-4}	21	20.0	4.260×10^5
030701-K	6.030×10^{-6}	1.874×10^{-4}	31	20.0	4.195×10^5
030701-L	6.030×10^{-6}	2.498×10^{-4}	41	20.0	4.420×10^5

$\langle k_2 \rangle$(20 °C) = $(4.240 \pm 0.121) \times 10^5$ M^{-1} s^{-1}

Table S25. (*E*)- -(*N*-Morpholino)styrene (**1k**) and $(mpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 622 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
120701-I	6.099×10^{-6}	5.041×10^{-4}	83	20.0	1.626×10^4
120701-K	6.099×10^{-6}	7.561×10^{-4}	124	20.0	1.476×10^4
120701-J	6.099×10^{-6}	1.008×10^{-3}	165	20.0	1.371×10^4

$<k_2>(20\ °C) = (1.491 \pm 0.105) \times 10^4\ M^{-1}\ s^{-1}$

Table S26. (*E*)- -(*N*-Morpholino)styrene (**1k**) and $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 672 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
120701-E	6.580×10^{-6}	1.008×10^{-4}	15	20.0	2.118×10^5
120701-D	6.580×10^{-6}	2.016×10^{-4}	31	20.0	2.247×10^5
120701-A	6.580×10^{-6}	3.024×10^{-4}	46	20.0	2.218×10^5
120701-B	6.580×10^{-6}	4.033×10^{-4}	61	20.0	2.258×10^5
120701-C	6.580×10^{-6}	5.041×10^{-4}	77	20.0	2.212×10^5

$<k_2>(20\ °C) = (2.210 \pm 0.050) \times 10^5\ M^{-1}\ s^{-1}$

Table S27. (*E*)- -(*N*-Morpholino)styrene (**1k**) and $(mfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 593 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
120701-G	9.005×10^{-6}	5.041×10^{-5}	6	20.0	1.128×10^6
120701-F	9.005×10^{-6}	1.008×10^{-4}	11	20.0	1.075×10^6
120701-H	9.005×10^{-6}	2.016×10^{-4}	22	20.0	9.943×10^5

$<k_2>(20\ °C) = (1.066 \pm 0.055) \times 10^6\ M^{-1}\ s^{-1}$

Table S28. (*E*)- -(*N*-Morpholino)styrene (**1k**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 601 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
120701-M	6.823×10^{-6}	5.041×10^{-5}	7	20.0	3.995×10^{6}
120701-N	6.823×10^{-6}	7.057×10^{-5}	10	20.0	3.675×10^{6}
120701-L	6.823×10^{-6}	1.008×10^{-4}	15	20.0	3.481×10^{6}

$<k_2>(20\ °C) = (3.717 \pm 0.212) \times 10^6\ M^{-1}\ s^{-1}$

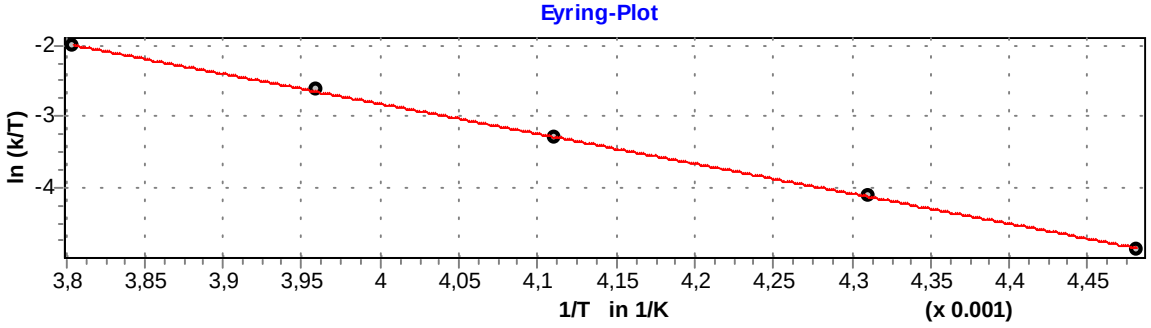
Table S29. -(*N*-Morpholino)styrene (**1l**) and $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
010601.PA2	2.987×10^{-5}	4.332×10^{-4}	15	78	20.0	2.347×10^{1}
010601.PA0	3.442×10^{-5}	9.982×10^{-4}	29	79	20.0	2.330×10^{1}
010601.PA1	2.929×10^{-5}	2.124×10^{-3}	73	70	20.0	2.356×10^{1}

$<k_2>(20\ °C) = (2.344 \pm 0.011) \times 10^1\ M^{-1}\ s^{-1}$

Table S30. -(*N*-Morpholino)styrene (**1l**) and $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 600 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
310501.PA1	3.767×10^{-5}	1.023×10^{-3}	27	68	–50.0	1.692
310501.PA2	4.421×10^{-5}	1.200×10^{-3}	27	79	–41.2	3.809
310501.PA3	3.919×10^{-5}	8.513×10^{-4}	22	80	–29.9	8.979
310501.PA4	3.160×10^{-5}	5.148×10^{-4}	16	76	–20.6	1.818×10^{1}
310501.PA5	3.088×10^{-5}	3.354×10^{-4}	11	81	–10.3	3.519×10^{1}



Eyring parameters:	Arrhenius parameters:
$\Delta H^{‡} = 35.203 \pm 0.413$ kJ mol^{-1}	$E_a = 37.213 \pm 0.396$ kJ mol^{-1}
$\Delta S^{‡} = -80.197 \pm 1.709$ J mol^{-1} K^{-1}	$\ln A = 20.604 \pm 0.197$
$r^2 = 0.9996$	$r^2 = 0.9997$

k_2(20 °C) = (2.111 ± 0.076) × 10^2 M^{-1} s^{-1}

Table S31. -(*N*-Morpholino)styrene (**1l**) and (mpa)$_2$CH$^+$ BF_4^- in CH_2Cl_2 at λ = 622 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
300501-E	1.347 × 10^{-5}	2.220 × 10^{-4}	17	20.0	1.540 × 10^3
300501-D	1.347 × 10^{-5}	4.440 × 10^{-4}	33	20.0	1.552 × 10^3
300501-F	1.347 × 10^{-5}	6.661 × 10^{-4}	49	20.0	1.793 × 10^3
300501-C	1.347 × 10^{-5}	8.881 × 10^{-4}	66	20.0	1.731 × 10^3
300501-B	1.347 × 10^{-5}	1.110 × 10^{-3}	82	20.0	1.776 × 10^3

<k_2>(20 °C) = (1.678 ± 0.110) × 10^3 M^{-1} s^{-1}

Table S32. -(*N*-Morpholino)styrene (**1l**) and (dpa)$_2$CH$^+$ BF_4^- in CH_2Cl_2 at λ = 672 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
290501-E	1.380 × 10^{-5}	1.073 × 10^{-4}	8	20.0	1.327 × 10^4
290501-B	1.380 × 10^{-5}	2.145 × 10^{-4}	16	20.0	1.345 × 10^4
290501-C	1.380 × 10^{-5}	3.218 × 10^{-4}	23	20.0	1.353 × 10^4
290501-D	1.380 × 10^{-5}	4.290 × 10^{-4}	31	20.0	1.377 × 10^4
290501-A	1.380 × 10^{-5}	5.363 × 10^{-4}	39	20.0	1.375 × 10^4

<k_2>(20 °C) = (1.355 ± 0.019) × 10^4 M^{-1} s^{-1}

Table S33. -(*N*-Morpholino)styrene (**1l**) and $(mfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 593 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
290501-J	7.292×10^{-6}	1.073×10^{-4}	15	20.0	6.428×10^4
290501-F	7.292×10^{-6}	2.145×10^{-4}	29	20.0	6.512×10^4
290501-I	7.292×10^{-6}	3.218×10^{-4}	44	20.0	6.737×10^4
290501-H	7.292×10^{-6}	4.290×10^{-4}	59	20.0	6.763×10^4
290501-G	7.292×10^{-6}	5.363×10^{-4}	74	20.0	6.940×10^4

$\langle k_2 \rangle$(20 °C) = $(6.676 \pm 0.184) \times 10^4$ M^{-1} s^{-1}

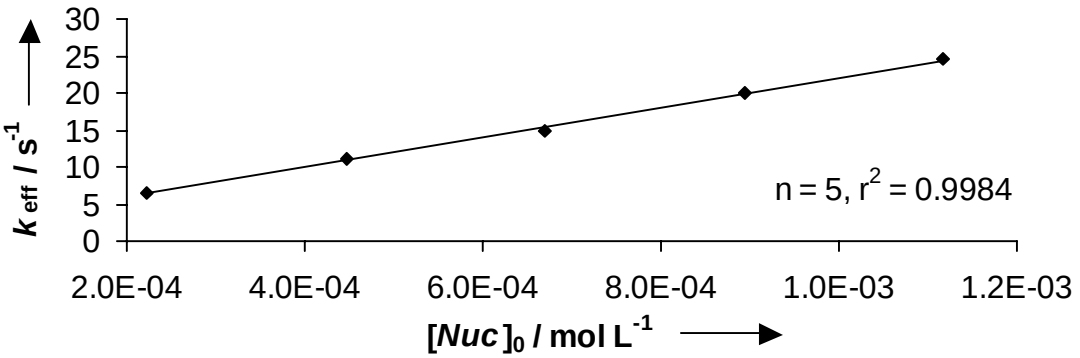
Table S34. -(*N*-Morpholino)styrene (**1l**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 601 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
290501-O	5.251×10^{-6}	1.073×10^{-4}	20	20.0	2.403×10^5
290501-K	5.251×10^{-6}	2.145×10^{-4}	41	20.0	2.352×10^5
290501-N	5.251×10^{-6}	3.218×10^{-4}	61	20.0	2.515×10^5
290501-M	5.251×10^{-6}	4.290×10^{-4}	82	20.0	2.573×10^5
290501-L	5.251×10^{-6}	5.363×10^{-4}	102	20.0	2.611×10^5

$\langle k_2 \rangle$(20 °C) = $(2.491 \pm 0.099) \times 10^5$ M^{-1} s^{-1}

Table S35. Ethyl (*E*)-3-(*N*-morpholino)acrylate (**1m**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 601 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_{eff} / s^{-1}
240701-E	6.397×10^{-6}	2.234×10^{-4}	35	20.0	6.459
240701-D	6.397×10^{-6}	4.468×10^{-4}	70	20.0	1.109×10^1
240701-A	6.397×10^{-6}	6.702×10^{-4}	105	20.0	1.490×10^1
240701-B	6.397×10^{-6}	8.936×10^{-4}	140	20.0	2.008×10^1
240701-C	6.397×10^{-6}	1.117×10^{-3}	175	20.0	2.452×10^1



$\langle k_2 \rangle$(20 °C) = 2.019 × 10^4 M^{-1} s^{-1}

$\langle k_{-2} \rangle$(20 °C) = 1.874 s^{-1}

K(20 °C) = 1.077 × 10^4 M^{-1}

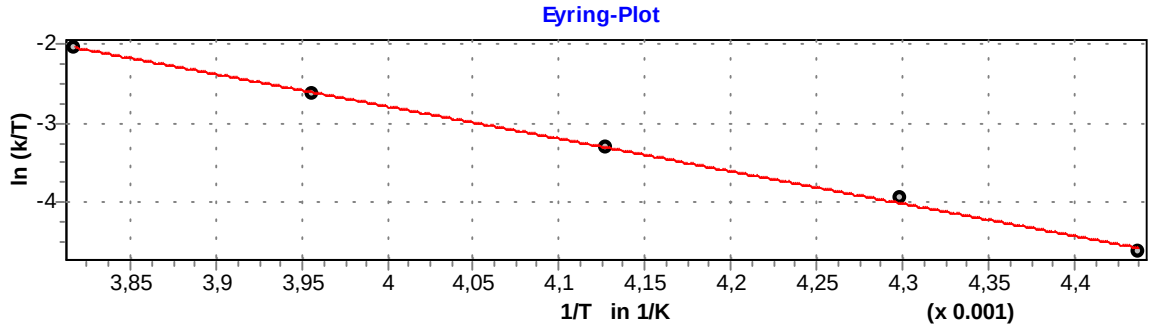
Table S36. Ethyl (*E*)-3-(dimethylamino)acrylate (**1n**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 601 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
240801-B	5.397 × 10^{-6}	1.589 × 10^{-4}	30	20.0	1.128 × 10^5
240801-C	5.397 × 10^{-6}	2.384 × 10^{-4}	44	20.0	1.027 × 10^5
240801-D	5.397 × 10^{-6}	3.179 × 10^{-4}	59	20.0	1.039 × 10^5
240801-E	5.397 × 10^{-6}	3.974 × 10^{-4}	74	20.0	1.064 × 10^5
240801-G	5.397 × 10^{-6}	5.563 × 10^{-4}	103	20.0	1.112 × 10^5

$\langle k_2 \rangle$(20 °C) = (1.074 ± 0.040) × 10^5 M^{-1} s^{-1}

Table S37. 1-(Methylphenylamino)cyclopentene (**1o**) and $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
210601.PA0	3.690 × 10^{-5}	1.106 × 10^{-3}	30	76	–47.8	2.182
210601.PA1	3.383 × 10^{-5}	1.268 × 10^{-3}	38	74	–40.5	4.464
210601.PA2	2.473 × 10^{-5}	8.473 × 10^{-4}	34	70	–30.9	8.740
210601.PA3	3.068 × 10^{-5}	6.898 × 10^{-4}	23	65	–20.4	1.820 × 10^1
210601.PA4	2.584 × 10^{-5}	6.640 × 10^{-4}	26	59	–11.2	3.392 × 10^1



Eyring parameters:

$\Delta H^{\ddagger}$ = 34.168 ± 0.786 kJ mol^{-1}

$\Delta S^{\ddagger}$ = –84.105 ± 3.248 J mol^{-1} K^{-1}

r^2 = 0.9984

Arrhenius parameters:

E_a = 36.186 ± 0.776 kJ mol^{-1}

ln A = 20.138 ± 0.386

r^2 = 0.9986

k_2(20 °C) = (2.017 ± 0.137) × 10^2 M^{-1} s^{-1}

Table S38. 1-(Methylphenylamino)cyclopentene (**1o**) and (jul)$_2$CH$^+$ BF$_4^-$ in CH$_2$Cl$_2$ at λ = 642 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
180601-L	5.131 × 10^{-6}	2.036 × 10^{-4}	40	20.0	4.175 × 10^2
180601-K	5.131 × 10^{-6}	3.394 × 10^{-4}	66	20.0	4.330 × 10^2
180601-M	5.131 × 10^{-6}	6.787 × 10^{-4}	132	20.0	4.435 × 10^2

<k_2>(20 °C) = (4.313 ± 0.107) × 10^2 M^{-1} s^{-1}

Table S39. 1-(Methylphenylamino)cyclopentene (**1o**) and (thq)$_2$CH$^+$ BF$_4^-$ in CH$_2$Cl$_2$ at λ = 628 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
180601-J	6.037 × 10^{-6}	1.357 × 10^{-4}	23	20.0	4.835 × 10^3
180601-G	6.037 × 10^{-6}	2.036 × 10^{-4}	34	20.0	5.101 × 10^3
180601-H	6.037 × 10^{-6}	2.715 × 10^{-4}	45	20.0	5.065 × 10^3
180601-I	6.037 × 10^{-6}	3.394 × 10^{-4}	56	20.0	5.044 × 10^3

<k_2>(20 °C) = (5.011 ± 0.104) × 10^3 M^{-1} s^{-1}

Table S40. 1-(Methylphenylamino)cyclopentene (**1o**) and $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 613 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
180601-F	7.149×10^{-6}	6.014×10^{-5}	8	20.0	4.664×10^4
180601-D	7.149×10^{-6}	1.203×10^{-4}	17	20.0	4.808×10^4
180601-A	7.149×10^{-6}	1.804×10^{-4}	25	20.0	5.082×10^4
180601-B	7.149×10^{-6}	2.406×10^{-4}	34	20.0	5.152×10^4
180601-C	7.149×10^{-6}	3.007×10^{-4}	42	20.0	5.097×10^4

$\langle k_2 \rangle$(20 °C) = $(4.961 \pm 0.190) \times 10^4$ M^{-1} s^{-1}

Table S41. 1-(Methylphenylamino)cyclopentene (**1o**) and $(mpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 622 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
130601-K	4.997×10^{-6}	6.464×10^{-5}	13	20.0	3.334×10^5
130601-G	4.997×10^{-6}	1.293×10^{-4}	26	20.0	3.265×10^5
130601-H	4.997×10^{-6}	1.939×10^{-4}	39	20.0	3.179×10^5
130601-I	4.997×10^{-6}	2.586×10^{-4}	52	20.0	3.141×10^5
130601-J	4.997×10^{-6}	3.232×10^{-4}	65	20.0	3.125×10^5

$\langle k_2 \rangle$(20 °C) = $(3.209 \pm 0.079) \times 10^5$ M^{-1} s^{-1}

Table S42. 1-(Methylphenylamino)cyclopentene (**1o**) and $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 672 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
130601-C	5.791×10^{-6}	3.232×10^{-5}	6	20.0	2.815×10^6
130601-F	5.791×10^{-6}	5.818×10^{-5}	10	20.0	2.738×10^6
130601-B	5.791×10^{-6}	6.464×10^{-5}	11	20.0	2.853×10^6
130601-E	5.791×10^{-6}	1.293×10^{-4}	22	20.0	2.646×10^6

$\langle k_2 \rangle$(20 °C) = $(2.763 \pm 0.079) \times 10^6$ M^{-1} s^{-1}

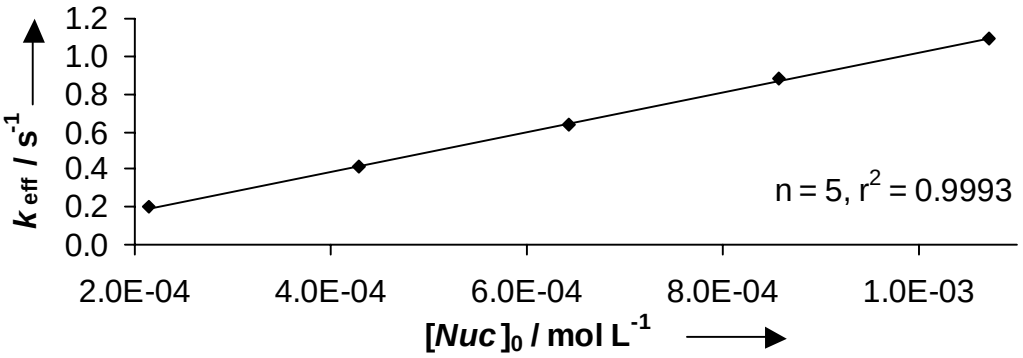
Table S43. 1-(Methylphenylamino)cyclohexene (**1p**) and $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 628 nm (J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
070501-02	1.351×10^{-5}	3.104×10^{-4}	23	86	20.0	1.136×10^{2}
070501-03	1.907×10^{-5}	8.214×10^{-4}	43	95	20.0	1.031×10^{2}
070501-01	1.736×10^{-5}	7.974×10^{-4}	46	95	20.0	1.034×10^{2}
070501-04	2.750×10^{-5}	1.579×10^{-3}	57	93	20.0	9.521×10^{1}

$<k_2>$(20 °C) = $(1.038 \pm 0.065) \times 10^2$ M^{-1} s^{-1}

Table S44. 1-(Methylphenylamino)cyclohexene (**1p**) and $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 613 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_{eff} / s^{-1}
020501-E	8.890×10^{-6}	2.141×10^{-4}	24	20.0	2.023×10^{-1}
020501-B	8.890×10^{-6}	4.282×10^{-4}	48	20.0	4.127×10^{-1}
020501-C	8.890×10^{-6}	6.424×10^{-4}	72	20.0	6.359×10^{-1}
020501-D	8.890×10^{-6}	8.565×10^{-4}	96	20.0	8.813×10^{-1}
020501-A	8.890×10^{-6}	1.071×10^{-3}	120	20.0	1.090



$<k_2>$(20 °C) = 1.048×10^3 M^{-1} s^{-1}

$<k_{-2}>$(20 °C) = 2.860×10^{-2} s^{-1}

K(20 °C) = 3.664×10^4 M^{-1}

Table S45. 1-(Methylphenylamino)cyclohexene (**1p**) and $(mpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 622 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
300401-L	4.256×10^{-6}	2.976×10^{-4}	70	20.0	8.368×10^3
300401-O	4.256×10^{-6}	3.968×10^{-4}	93	20.0	8.503×10^3
300401-K	4.256×10^{-6}	4.960×10^{-4}	117	20.0	8.367×10^3
300401-N	4.256×10^{-6}	6.945×10^{-4}	163	20.0	8.407×10^3
300401-M	4.256×10^{-6}	9.921×10^{-4}	233	20.0	8.492×10^3

$<k_2>(20\ °C) = (8.427 \pm 0.059) \times 10^3\ M^{-1}\ s^{-1}$

Table S46. 1-(Methylphenylamino)cyclohexene (**1p**) and $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 672 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
300401-J	5.975×10^{-6}	9.921×10^{-5}	17	20.0	8.602×10^4
300401-I	5.975×10^{-6}	1.984×10^{-4}	33	20.0	8.720×10^4
300401-H	5.975×10^{-6}	2.976×10^{-4}	50	20.0	8.705×10^4
300401-G	5.975×10^{-6}	3.968×10^{-4}	66	20.0	8.633×10^4
300401-F	5.975×10^{-6}	4.960×10^{-4}	83	20.0	8.519×10^4

$<k_2>(20\ °C) = (8.636 \pm 0.073) \times 10^4\ M^{-1}\ s^{-1}$

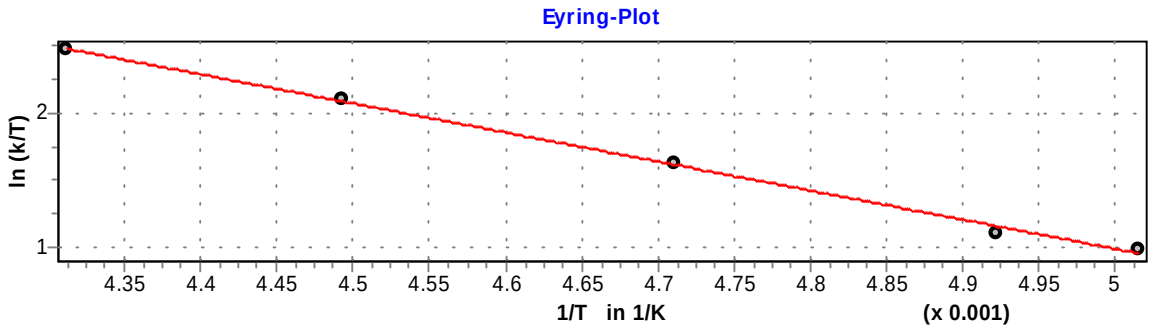
Table S47. 1-(Methylphenylamino)cyclohexene (**1p**) and $(mfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 593 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
300401-B	5.410×10^{-6}	9.921×10^{-5}	18	20.0	3.382×10^5
300401-A	5.410×10^{-6}	1.984×10^{-4}	37	20.0	3.357×10^5
300401-C	5.410×10^{-6}	2.976×10^{-4}	55	20.0	3.376×10^5
300401-D	5.410×10^{-6}	3.968×10^{-4}	73	20.0	3.404×10^5
300401-E	5.410×10^{-6}	4.960×10^{-4}	92	20.0	3.497×10^5

$<k_2>(20\ °C) = (3.403 \pm 0.049) \times 10^5\ M^{-1}\ s^{-1}$

Table S48. 1-(1-Cyclohexenyl)-4-methylpiperazine (**1q**) and $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 640 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
AO-142.1	3.94×10^{-5}	3.76×10^{-4}	9.5	73	–73.8	5.366×10^{2}
AO-139.1	7.90×10^{-5}	9.66×10^{-4}	12	70	–70.0	6.190×10^{2}
AO-142.2	3.86×10^{-5}	2.77×10^{-4}	7.2	58	–60.9	1.075×10^{3}
AO-142.3	2.33×10^{-5}	1.86×10^{-4}	8.0	65	–50.6	1.830×10^{3}
AO-142.4	2.07×10^{-5}	8.26×10^{-5}	4.0	83	–41.2	2.747×10^{3}



Eyring parameters:

$\Delta H^{‡} = 17.973 \pm 0.498$ kJ mol^{-1}

$\Delta S^{‡} = -99.433 \pm 2.339$ J mol^{-1} K^{-1}

$r^2 = 0.9977$

Arrhenius parameters:

$E_a = 19.757 \pm 0.499$ kJ mol^{-1}

ln $A = 18.171 \pm 0.282$

$r^2 = 0.9981$

k_2(20 °C) = $(2.454 \pm 0.188) \times 10^4$ M^{-1} s^{-1}

Table S49. Pyrrole (**4a**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 600 nm (Schölly).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
210801.PA1	2.616×10^{-5}	9.176×10^{-4}	35	55	20.0	3.083×10^{1}
210801.PA2	3.242×10^{-5}	1.624×10^{-3}	50	40	20.0	3.313×10^{1}
210801.PA3	2.839×10^{-5}	3.319×10^{-3}	117	36	20.0	2.973×10^{1}

$\langle k_2 \rangle$(20 °C) = $(3.123 \pm 0.142) \times 10^1$ M^{-1} s^{-1}

Table S50. *N*-(Triisopropylsilyl)pyrrole (**4c**) and $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 674 nm (J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
290801-01	2.596×10^{-5}	1.745×10^{-3}	67	37	20.0	4.367×10^{-2}
290801-02	2.736×10^{-5}	3.218×10^{-3}	118	71	20.0	4.186×10^{-2}
290801-03	2.437×10^{-5}	6.514×10^{-3}	267	93	20.0	4.221×10^{-2}

$<k_2>$(20 °C) = $(4.258 \pm 0.078) \times 10^{-2}$ M^{-1} s^{-1}

Table S51. *N*-(Triisopropylsilyl)pyrrole (**4c**) and $(mfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 593 nm (J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
300801-04	1.545×10^{-5}	2.022×10^{-3}	131	70	20.0	1.170×10^{-1}
300801-03	2.035×10^{-5}	3.873×10^{-3}	190	90	20.0	1.271×10^{-1}
300801-05	1.594×10^{-5}	4.172×10^{-3}	262	87	20.0	1.126×10^{-1}

$<k_2>$(20 °C) = $(1.189 \pm 0.061) \times 10^{-1}$ M^{-1} s^{-1}

Table S52. *N*-(Triisopropylsilyl)pyrrole (**4c**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 601 nm (J&M).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	Conv. / %	T / °C	k_2 / M^{-1} s^{-1}
300801-02	1.550×10^{-5}	7.682×10^{-4}	50	39	20.0	1.114
300801-01	1.369×10^{-5}	1.695×10^{-3}	124	70	20.0	1.448
300801-03	1.449×10^{-5}	2.872×10^{-3}	198	72	20.0	1.416

$<k_2>$(20 °C) = 1.326 ± 0.151 M^{-1} s^{-1}

Table S53. Indole (**6a**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 601 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
230501-D	4.997×10^{-6}	5.250×10^{-4}	105	20.0	1.298×10^{2}
230501-B	4.997×10^{-6}	1.050×10^{-3}	210	20.0	1.367×10^{2}
230501-C	4.997×10^{-6}	1.575×10^{-3}	315	20.0	1.352×10^{2}

$<k_2>$(20 °C) = $(1.339 \pm 0.030) \times 10^{2}$ M^{-1} s^{-1}

Table S54. *N*-Methylindole (**6b**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 601 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
170501-A	5.297×10^{-6}	9.529×10^{-5}	18	20.0	1.089×10^3
170501-E	5.297×10^{-6}	2.382×10^{-4}	45	20.0	1.074×10^3
170501-F	5.297×10^{-6}	4.764×10^{-4}	90	20.0	1.083×10^3
170501-D	5.297×10^{-6}	7.147×10^{-4}	135	20.0	1.068×10^3
170501-C	5.297×10^{-6}	9.529×10^{-4}	180	20.0	1.110×10^3

$<k_2>(20\ °C) = (1.085 \pm 0.015) \times 10^3\ M^{-1}\ s^{-1}$

Table S55. 1,2-Dimethylindole (**6c**) and $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 at λ = 601 nm (Stopped flow).

No.	$[El]_0$ / M	$[Nuc]_0$ / M	$[Nuc]_0/[El]_0$	T / °C	k_2 / M^{-1} s^{-1}
050601-I	4.731×10^{-6}	9.352×10^{-5}	20	20.0	5.666×10^3
050601-C	4.731×10^{-6}	1.434×10^{-4}	30	20.0	5.650×10^3
050601-B	4.731×10^{-6}	2.868×10^{-4}	61	20.0	5.219×10^3
050601-A	4.731×10^{-6}	4.301×10^{-4}	91	20.0	5.335×10^3

$<k_2>(20\ °C) = (5.468 \pm 0.195) \times 10^3\ M^{-1}\ s^{-1}$