



Supporting Information

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Nucleophilicity Parameters for Alkyl and Aryl Isocyanides

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General. All synthetic experiments were carried out under dry nitrogen, using anhydrous solvents purified following the standard methods. TLC analysis was carried out on plates with silica gel (Merck, SiO₂, 60 mesh ASTM). Column chromatography was performed on Merck silica gel (220-240 mesh ASTM).

All kinetic experiments were carried out at 20 °C in dry CH₂Cl₂ in the atmosphere of dry nitrogen. First-order rate constants k_{obs} (s⁻¹) were determined photometrically using a J&M TIDAS diode array spectrometer. As the reactions of the colored Ar₂CH⁺ ions **2** with isocyanides **1** gave rise to colorless products, the reactions could be followed by employing UV-vis spectroscopy. The rates were determined by using a J&M TIDAS diode array spectrophotometer, which was controlled by Labcontrol Spectacle software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (5 mm light path) via fiber optic cables and standard SMA connectors. The temperature of solutions during all kinetic studies was kept constant (usually 20.0 ± 0.2 °C) by using a circulating bath thermostat and monitored with a thermocouple probe that was inserted into the reaction mixture. Isocyanide concentrations at least 10 times higher than the Ar₂CH⁺ ions concentrations were usually employed, resulting in first-order kinetics with an exponential decay of the Ar₂CH⁺ concentration. First-order rate constants k_{obs} (s⁻¹) were obtained by least-squares fitting of the single-exponential $A_t = A_0 \exp(-k_{\text{obs}}t) + C$ to the absorbance data.

Concentrations and rate constants of the individual measurements are given below (Tables S1-S17). In all cases when benzhydrylium cations were generated from corresponding precursors (Tables S10–S11, S13–S17) by treatment with TMSOTf, 2,6-di-tert-butylpyridine (2,6-DTBP) was used as scavenger of triflic acid. The optimal ratio [TMSOTf]/[2,6-DTBP] was determined empirically: a solution of TMSOTf was added gradually to the precursor in the kinetic flask up to the moment of the maximal absorbance value (UV monitoring). Then, a solution of 2,6-DTBP was added gradually until the absorbance value started to decrease. At that point an additional amount of TMSOTf was added to restore the absorbance. The ratio [TMSOTf]/[2,6-DTBP] thus determined was found to be valid for the whole series of kinetic runs for the prepared solutions of the reactants.

Bis(4-methoxyphenyl)acetonitrile (6).^[S1] To a stirred solution of **2a-Cl** (262 mg, 1.00 mmol) in dry CH₂Cl₂ (20 mL) a solution of 0.20 M ZnCl₂/Et₂O (1.0 mL, 0.20 mmol) in CH₂Cl₂ was added at -30 °C. A deep-red precipitate was immediately formed. *tert*-BuNC (**1a**) (118 μL, 1.00 mmol) was added slowly at -30 °C up to the point of an almost complete decoloration. Then the reaction mixture was rapidly warmed up to 20 °C, quenched with 1-methoxy-2-methyl-1-(trimethylsiloxy)-propene (**4**) (300 μL, 1.50 mmol), filtered through silica gel (ether) and evaporated in vacuo to give 190 mg of a pale yellow oil (75 %). Crystallization from benzene afforded **6** (167 mg, 66%) as colorless needles. R_f (petroleum ether : ethyl acetate = 10:1) = 0.16. mp. 148-149 °C. ¹H NMR (250 MHz, CDCl₃): δ 3.80 (s, 3H), 5.06 (s, 1H), 6.89, 7.24 (2d, $J = 8.5$). ¹³C NMR (62.9 MHz, CDCl₃): δ 40.89, 55.17, 114.34, 119.95, 128.14, 128.63, 159.25. MS HR (ESI): m/z (%): 227.106 (100) [M-CN], 228.109 (7). Anal. Calcd. for C₁₆H₁₅NO₂: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.62; H, 6.15; N, 5.30.

4,4-Bis(4-methoxyphenyl)-3-(4-cyanophenylimino)-2,2-dimethylbutanoic acid methyl ester (5e). To a stirred solution of **2a-Cl** (262 mg, 1.00 mmol) in dry CH₂Cl₂ (20 mL) a solution of 0.20 M ZnCl₂/Et₂O (1.0 mL, 0.20 mmol) in CH₂Cl₂ was added at -30 °C. A deep-red precipitate was immediately formed. A solution of 4-cyanophenyl isocyanide (**1e**) (154 mg, 1.20 mmol) in CH₂Cl₂ (2.0 mL) was added slowly at -15 °C up to the point of an almost complete decoloration. After stirring for 5 min the reaction mixture was quenched with 1-methoxy-2-methyl-1-(trimethylsiloxy)-propene (**4**) (300 μL, 1.50 mmol) at -15 °C, kept for an additional 15 min at room temperature, filtered through silica gel (ether) and evaporated in vacuo to give 365 mg of a pale red oil (80%).

[S1] a) K. Saito, S. Kagabu, Y. Horie, K. Takahashi, *Org. Prep. Proc. Int.* **1989**, *21*, 354–355. b) Y. Tamura, H. D. Choi, M. Mizutani, Y. Ueda, H. Ishibashi, *Chem. Pharm. Bull.* **1982**, *30*, 3574–3579. c) D. K. Bates, *J. Org. Chem.* **1977**, *42*, 3452–3454.

Crystallization from benzene afforded **5e** (296 mg, 65%) as colorless needles. R_f (petroleum ether : ethyl acetate = 2:1) = 0.26. mp. 151-152 °C. ^1H NMR (250 MHz, CDCl_3): δ 1.36 (s, 6H), 3.44 (s, 3H), 3.64 (s, 3H), 3.81 (s, 6H), 5.45 (s, 1H), 6.55, 6.57 (2d, J = 8.6, 4H), 6.84, 6.97 (2d, J = 8.5, 4H), 7.10, 7.20 (2d, J = 8.5, 4H). ^{13}C NMR (62.9 MHz, CDCl_3): δ 25.77, 49.45, 51.87, 54.87, 55.04, 99.38, 112.93, 113.23, 113.56, 120.14, 130.24, 131.17, 132.84, 133.01, 134.33, 134.93, 136.95, 148.86, 157.98, 158.83, 176.17. MS HR (ESI): m/z (%): 457.211 (100) [M+H], 458.215 (21), 479.193 (6) [M+Na]. Anal. Calcd. for $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_4$: C, 73.66; H, 6.18; N, 6.14. Found: C, 73.42; H, 6.35; N, 6.26.

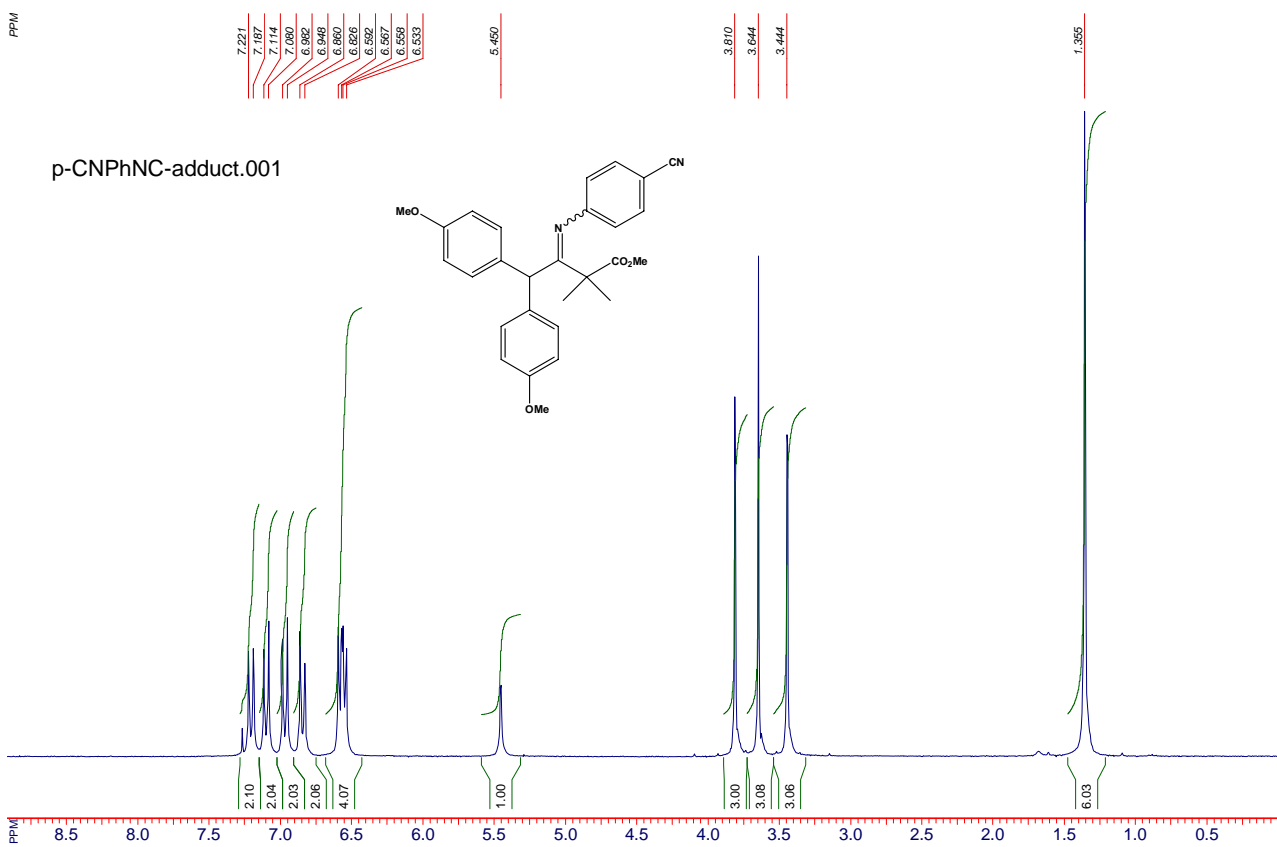
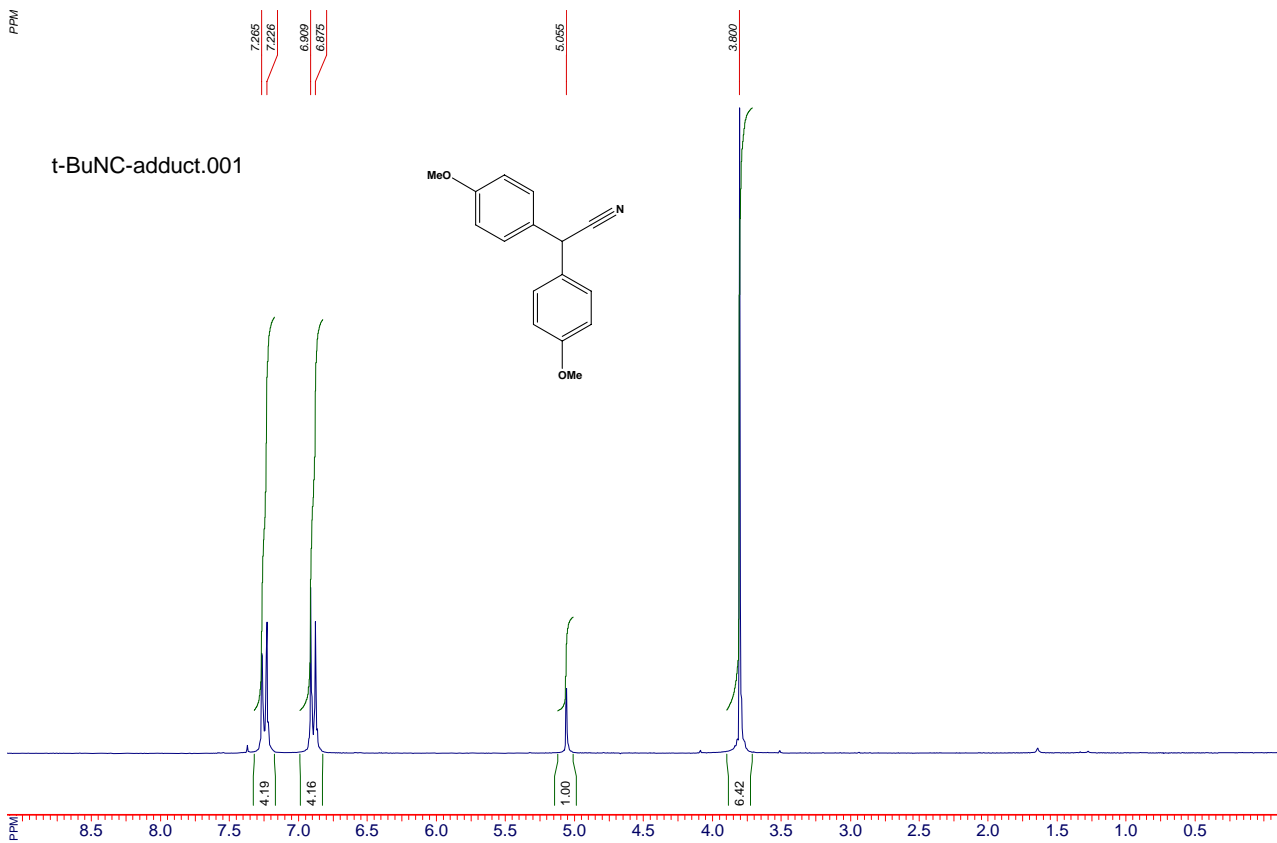
4,4-Bis(4-methoxyphenyl)-3-(tosylmethylimino)-2,2-dimethylbutanoic acid methyl ester (5d).

To a stirred solution of **2a-Cl** (262 mg, 1.00 mmol) in dry CH_2Cl_2 (20 mL) a solution of 0.20 M $\text{ZnCl}_2/\text{Et}_2\text{O}$ (1.0 mL, 0.20 mmol) in CH_2Cl_2 was added at -30 °C. Deep-red precipitate was immediately formed. A solution of p-tosylmethyl isocyanide (**1d**) (195 mg, 1.00 mmol) in CH_2Cl_2 (2.0 ml) was added slowly at -20 °C up to the point of an almost complete decoloration. After stirring for 5 min the reaction mixture was quenched with 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (**4**) (300 μL , 1.50 mmol) at -20 °C, kept for an additional 15 min at room temperature, filtered through silica gel (ether) and evaporated in vacuo to give 434 mg of a pale yellow oil (83%). Crystallization from benzene afforded **5d** (361 mg, 69 %) as a colorless powder. R_f (petroleum ether : ethyl acetate = 2:1) = 0.33. mp. 151-152 °C. ^1H NMR (250 MHz, CDCl_3): δ 1.34 (s, 6H), 2.47 (s, 3H), 3.41 (s, 3H), 3.79 (s, 6H), 4.22 (s, 2H), 5.28 (s, 1H), 6.81 (s, 4H), 7.60, 7.81 (2d, J = 8.5, 4H). ^{13}C NMR (62.9 MHz, CDCl_3): δ 21.49, 24.33, 51.67, 52.62, 54.23, 55.06, 74.25, 114.23, 129.09, 129.44, 129.57, 129.97, 134.65, 144.38, 158.48, 174.93, 175.91. MS HR (ESI): m/z (%): 524.208 (100) [M+H], 525.211 (21), 546.190 (26) [M+Na], 547.193 (7). Anal. Calcd. for $\text{C}_{29}\text{H}_{33}\text{NO}_6\text{S}$: C, 66.52; H, 6.35; N, 2.67. Found: C, 66.71; H, 6.61; N, 2.78.

Reaction of 2a-Cl with 1c in the presence of $\text{ZnCl}_2/\text{Et}_2\text{O}$: 4,4-Bis(4-methoxyphenyl)-3-(2,6-dimethylphenylimino)-2,2-dimethylbutanoic acid methyl ester (5c).

Method A: To a stirred solution of **2a-Cl** (262 mg, 1.00 mmol) in dry CH_2Cl_2 (20 mL) a solution of 0.20 M $\text{ZnCl}_2/\text{Et}_2\text{O}$ (1.0 mL, 0.20 mmol) in CH_2Cl_2 was added at -30 °C. A deep-red precipitate was immediately formed. A solution of 2,6-dimethylphenyl isocyanide (**1c**) (131 mg, 1.00 mmol) in CH_2Cl_2 (5.0 mL) was added slowly at -30 °C up to the point of an almost complete decoloration. The resulting solution was rapidly warmed up to -20 °C and 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (**4**) (300 μL , 1.50 mmol) was added at -20 °C. After stirring for an additional 15 min at room temperature the mixture was poured into $\text{NaHCO}_3/\text{H}_2\text{O}$ (10 mL) and extracted with ether (3 \times 10 mL). After filtration through silica gel (ether) and evaporation in vacuo 450 mg of a dark red oil (~100%) was isolated. The crude product was dissolved in petroleum ether (5 mL) and filtered through silica gel (petroleum ether) to separate upper fraction (red) which contains predominantly isonitrile oligomers. The main fraction was collected using CHCl_3 as the eluent. Removal of the solvent furnished a mixture of the imine **5c** and ester **7** (290 mg, ca. 65%) in a 3/2 ratio (determined from ^1H NMR). R_f (petroleum ether : ethyl acetate = 10:1) = 0.24. ^1H NMR (250 MHz, CDCl_3): **5c**: δ 1.30 (s, 6H), 1.90 (s, 6H), 3.40 (s, 3H), 3.77 (s, 6H), 5.02 (s, 1), 6.71-7.42 (set of multiplets, 11H); **7**: δ 1.27 (s, 6H), 3.54 (s, 3H), 3.77 (s, 6H), 4.32 (s, 1), 6.71-7.42 (set of multiplets, 11H).

Method B: To a stirred solution of **2a-Cl** (262 mg, 1.00 mmol) in dry CH_2Cl_2 (20 mL) a solution of 0.20M $\text{ZnCl}_2/\text{Et}_2\text{O}$ (1.0 mL, 0.20 mmol) in CH_2Cl_2 was added at -30 °C. Deep-red precipitate was immediately formed. A solution of 2,6-dimethylphenyl isocyanide (**1c**) (131 mg, 1.00 mmol) in CH_2Cl_2 (5.0 ml) was added slowly at -30 °C up to the point of an almost complete decoloration. The resulting solution was rapidly warmed up to 0 °C and 1-methoxy-2-methyl-1-(trimethylsiloxy)propene (**4**) (300 μL , 1.50 mmol) was added at 0 °C. After stirring for an additional 15 min at room temperature the mixture was worked up as described above. After purification a mixture of **5c** and **7** (240 mg, ~ 55%) in a ratio 4/1 was obtained.



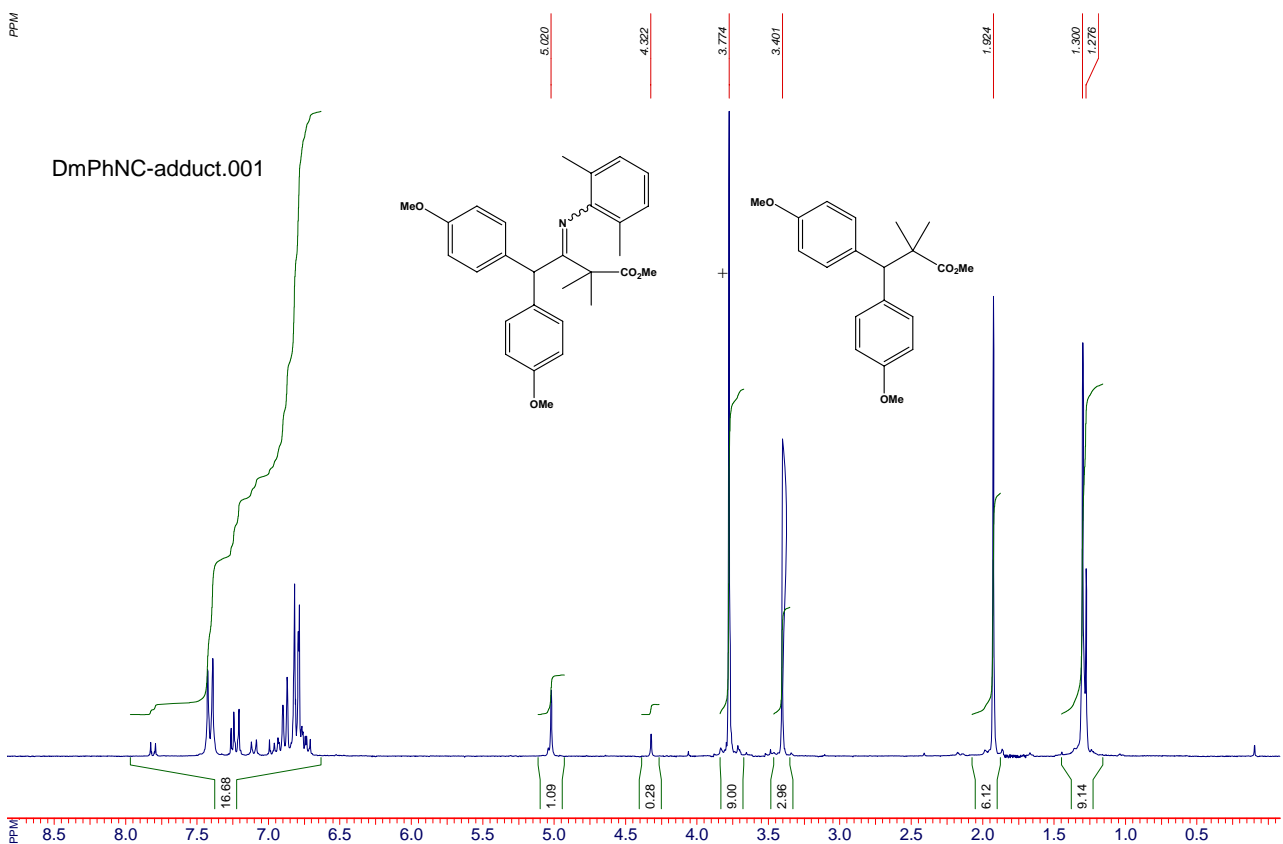
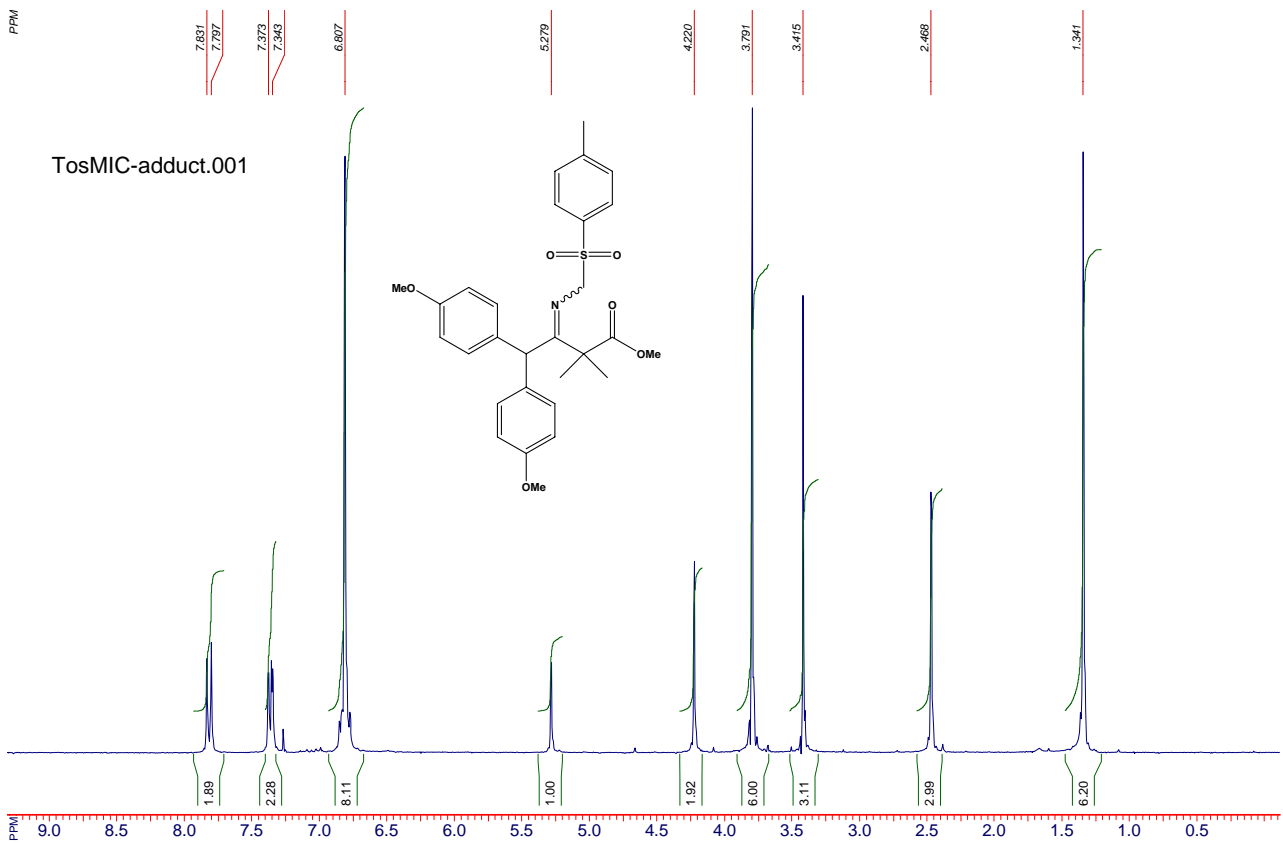
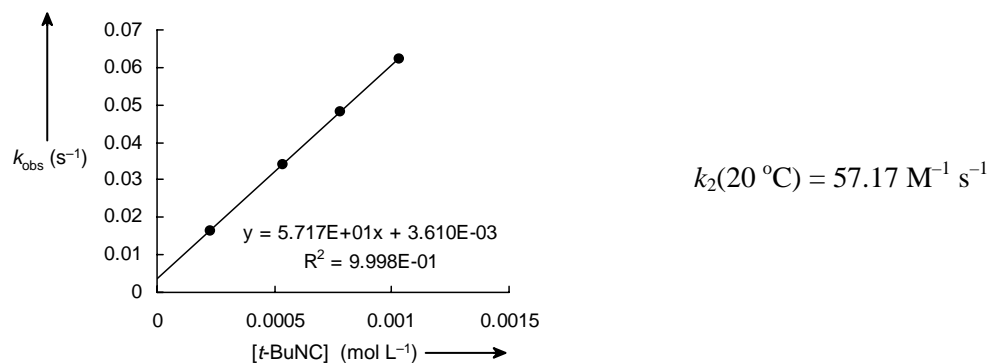
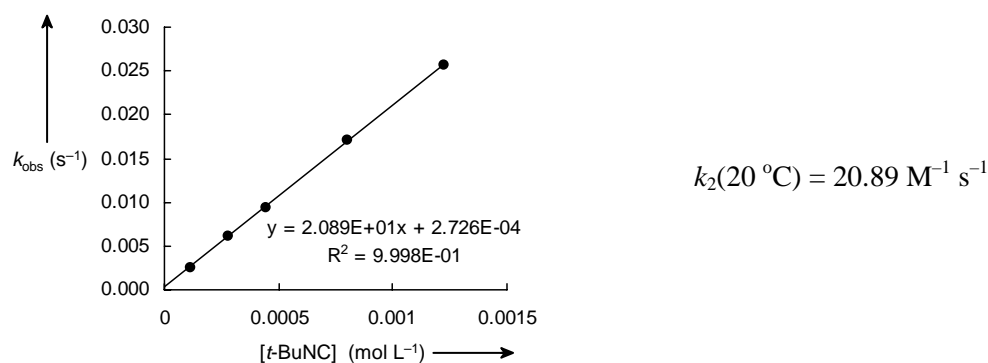


Table S1. Kinetics of the reaction of **2d**-BF₄ with *tert*-BuNC (**1a**) (CH₂Cl₂, 20 °C, λ = 601 nm).

[2d -BF ₄] ₀ , M	[<i>t</i> -BuNC], M	conversion, %	<i>k</i> _{obs} , s ⁻¹
9.09 × 10 ⁻⁶	2.27 × 10 ⁻⁴	67	1.65 × 10 ⁻²
1.49 × 10 ⁻⁵	5.36 × 10 ⁻⁴	36	3.42 × 10 ⁻²
1.36 × 10 ⁻⁵	7.76 × 10 ⁻⁴	36	4.84 × 10 ⁻²
1.28 × 10 ⁻⁵	1.03 × 10 ⁻³	33	6.23 × 10 ⁻²

**Table S2.** Kinetics of the reaction of **2e**-BF₄ with *tert*-BuNC (**1a**) (CH₂Cl₂, 20 °C, λ = 593 nm).

[2e -BF ₄] ₀ , M	[<i>t</i> -BuNC], M	conversion, %	<i>k</i> _{obs} , s ⁻¹
4.31 × 10 ⁻⁶	1.13 × 10 ⁻⁴	65	2.65 × 10 ⁻³
4.27 × 10 ⁻⁶	2.76 × 10 ⁻⁴	84	6.11 × 10 ⁻³
8.91 × 10 ⁻⁶	4.46 × 10 ⁻⁴	51	9.38 × 10 ⁻³
3.82 × 10 ⁻⁶	7.97 × 10 ⁻⁴	90	1.71 × 10 ⁻²
8.11 × 10 ⁻⁶	1.22 × 10 ⁻³	85	2.57 × 10 ⁻²

**Table S3.** Kinetics of the reaction of **2f**-BF₄ with *tert*-BuNC (**1a**) (CH₂Cl₂, 20 °C, λ = 675 nm).

[2f -BF ₄] ₀ , M	[<i>t</i> -BuNC], M	conversion, %	<i>k</i> _{obs} , s ⁻¹
6.70 × 10 ⁻⁶	2.78 × 10 ⁻⁴	80	1.04 × 10 ⁻³
6.84 × 10 ⁻⁶	5.67 × 10 ⁻⁴	77	1.71 × 10 ⁻³
7.10 × 10 ⁻⁶	8.83 × 10 ⁻⁴	88	2.96 × 10 ⁻³
1.24 × 10 ⁻⁵	1.56 × 10 ⁻³	55	5.65 × 10 ⁻³

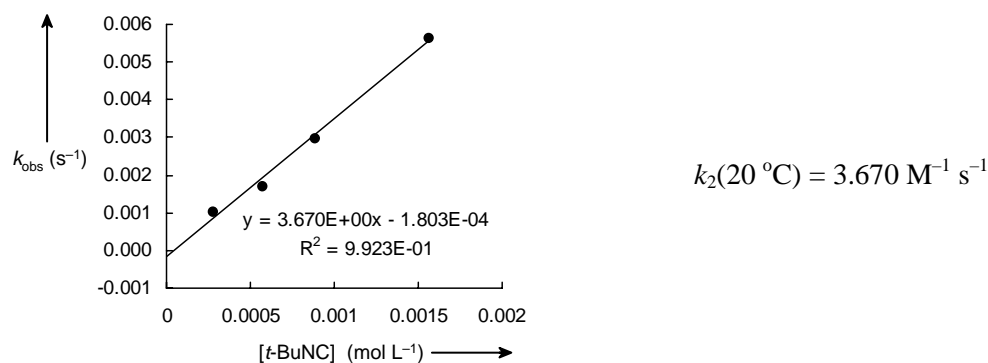
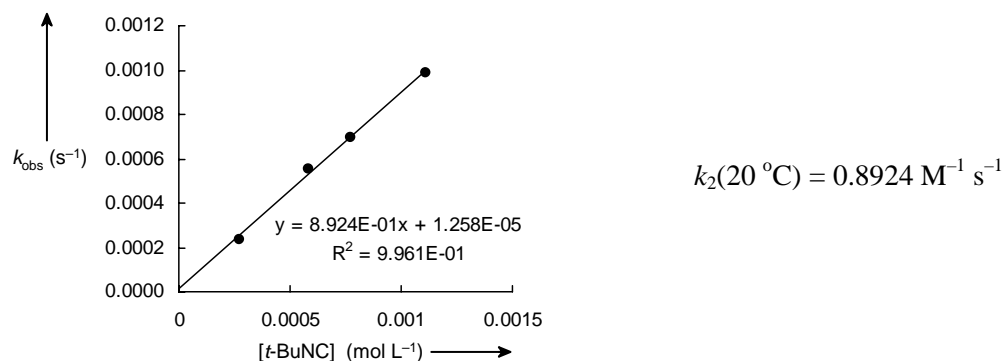
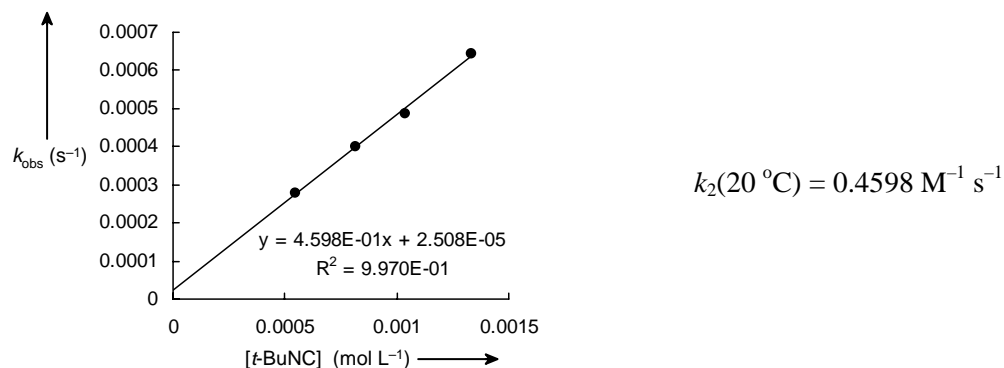


Table S4. Kinetics of the reaction of **2g**-BF₄ with *tert*-BuNC (**1a**) (CH₂Cl₂, 20 °C, λ = 620 nm).

[2g -BF ₄] ₀ , M	[<i>t</i> -BuNC], M	conversion, %	<i>k</i> _{obs} , s ⁻¹
1.26 × 10 ⁻⁵	2.71 × 10 ⁻⁴	80	2.38 × 10 ⁻⁴
1.35 × 10 ⁻⁵	5.80 × 10 ⁻⁴	85	5.58 × 10 ⁻⁴
1.19 × 10 ⁻⁵	7.68 × 10 ⁻⁴	79	6.95 × 10 ⁻⁴
1.29 × 10 ⁻⁵	1.11 × 10 ⁻³	77	9.90 × 10 ⁻⁴

**Table S5.** Kinetics of the reaction of **2h**-BF₄ with *tert*-BuNC (**1a**) (CH₂Cl₂, 20 °C, λ = 620 nm).

[2h -BF ₄] ₀ , M	[<i>t</i> -BuNC], M	conversion, %	<i>k</i> _{obs} , s ⁻¹
9.51 × 10 ⁻⁶	5.45 × 10 ⁻⁴	80	2.78 × 10 ⁻⁴
1.39 × 10 ⁻⁵	8.14 × 10 ⁻⁴	76	4.03 × 10 ⁻⁴
7.23 × 10 ⁻⁶	1.04 × 10 ⁻³	43	4.89 × 10 ⁻⁴
8.07 × 10 ⁻⁶	1.33 × 10 ⁻³	75	6.45 × 10 ⁻⁴

**Table S6.** Kinetics of the reaction of **2d**-BF₄ with PhCH₂NC (**1b**) (CH₂Cl₂, 20 °C, λ = 601 nm).

[2d -BF ₄] ₀ , M	[BnNC], M	conversion, %	<i>k</i> _{obs} , s ⁻¹
9.41 × 10 ⁻⁶	1.69 × 10 ⁻⁴	72	4.20 × 10 ⁻³
8.51 × 10 ⁻⁶	3.39 × 10 ⁻⁴	66	8.20 × 10 ⁻³
9.33 × 10 ⁻⁶	4.18 × 10 ⁻⁴	64	1.01 × 10 ⁻²
8.82 × 10 ⁻⁶	6.66 × 10 ⁻⁴	57	1.51 × 10 ⁻²
8.06 × 10 ⁻⁶	1.02 × 10 ⁻³	68	2.29 × 10 ⁻²

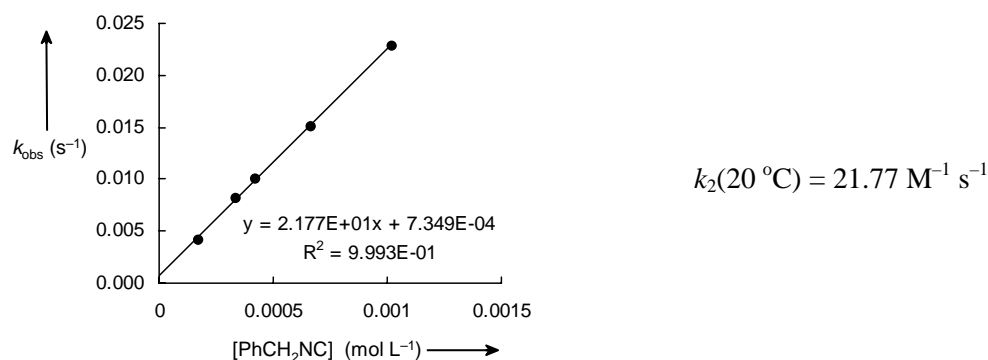
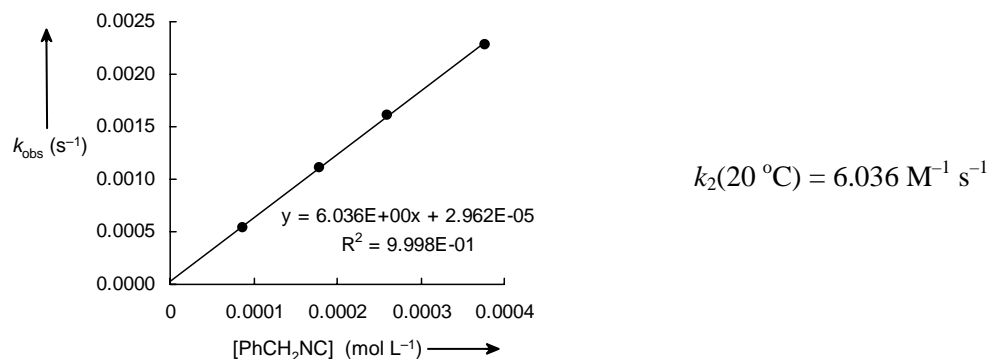
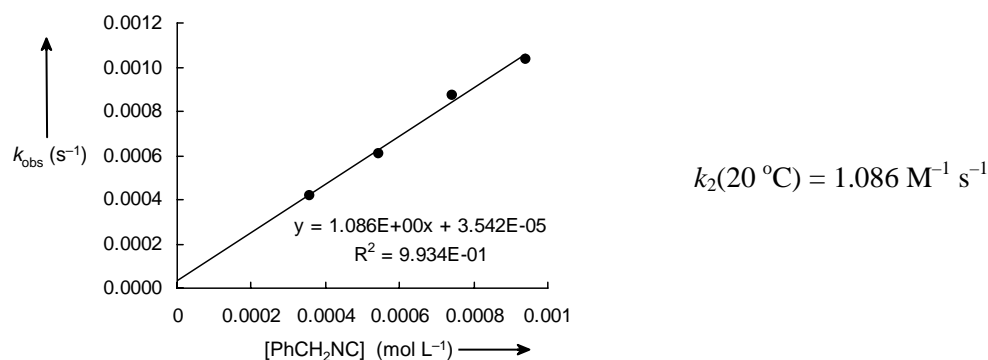


Table S7. Kinetics of the reaction of **2e**-BF₄ with PhCH₂NC (**1b**) (CH₂Cl₂, 20 °C, λ = 593 nm).

[2e -BF ₄] ₀ , M	[BnNC], M	conversion, %	<i>k</i> _{obs} , s ⁻¹
6.09 × 10 ⁻⁶	8.73 × 10 ⁻⁵	78	5.48 × 10 ⁻⁴
3.73 × 10 ⁻⁶	1.78 × 10 ⁻⁴	77	1.11 × 10 ⁻³
4.84 × 10 ⁻⁶	2.60 × 10 ⁻⁴	78	1.61 × 10 ⁻³
4.59 × 10 ⁻⁶	3.76 × 10 ⁻⁴	79	2.29 × 10 ⁻³

**Table S8.** Kinetics of the reaction of **2f**-BF₄ with PhCH₂NC (**1b**) (CH₂Cl₂, 20 °C, λ = 675 nm).

[2f -BF ₄] ₀ , M	[BnNC], M	conversion, %	<i>k</i> _{obs} , s ⁻¹
6.63 × 10 ⁻⁶	3.58 × 10 ⁻⁴	77	4.23 × 10 ⁻⁴
6.68 × 10 ⁻⁶	5.41 × 10 ⁻⁴	71	6.09 × 10 ⁻⁴
6.87 × 10 ⁻⁶	7.41 × 10 ⁻⁴	75	8.72 × 10 ⁻⁴
6.97 × 10 ⁻⁶	9.40 × 10 ⁻⁴	81	1.04 × 10 ⁻³

**Table S9.** Kinetics of the reaction of **2g**-BF₄ with PhCH₂NC (**1b**) (CH₂Cl₂, 20 °C, λ = 620 nm).

[2g -BF ₄] ₀ , M	[BnNC], M	conversion, %	<i>k</i> _{obs} , s ⁻¹
1.74 × 10 ⁻⁵	3.73 × 10 ⁻⁴	72	1.28 × 10 ⁻⁴
1.73 × 10 ⁻⁵	5.57 × 10 ⁻⁴	85	1.95 × 10 ⁻⁴
1.67 × 10 ⁻⁵	7.17 × 10 ⁻⁴	81	2.33 × 10 ⁻⁴
1.62 × 10 ⁻⁵	8.68 × 10 ⁻⁴	74	3.31 × 10 ⁻⁴

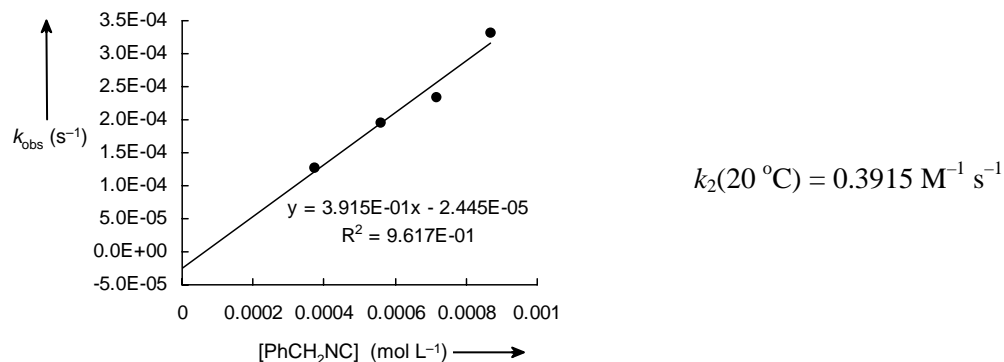
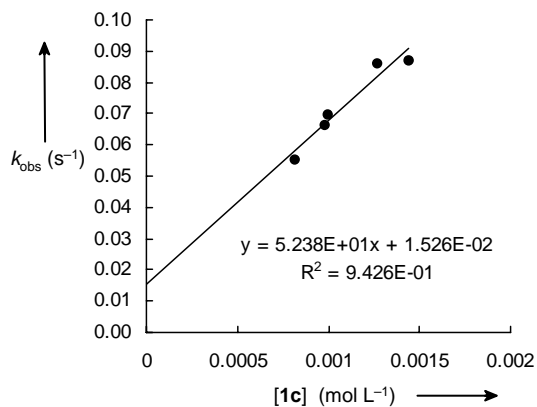


Table S10. Kinetics of the reaction of **2c**-OTf with 2,6-dimethylphenyl isocyanide (**1c**) (CH₂Cl₂, 20 °C, λ = 335 nm).

[2c -OAc] ₀ , M	[1c], M	[TMSOTf] ₀ , M	[2,6-DTBP] ₀ , M ^a	conv., %	k _{obs} , s ⁻¹
5.14 × 10 ⁻⁵	8.11 × 10 ⁻⁴	1.34 × 10 ⁻⁴	2.37 × 10 ⁻⁵	64	5.52 × 10 ⁻²
5.18 × 10 ⁻⁵	9.81 × 10 ⁻⁴	1.35 × 10 ⁻⁴	2.39 × 10 ⁻⁵	49	6.64 × 10 ⁻²
5.25 × 10 ⁻⁵	9.93 × 10 ⁻⁴	1.37 × 10 ⁻⁴	2.42 × 10 ⁻⁵	63	6.95 × 10 ⁻²
5.04 × 10 ⁻⁵	1.27 × 10 ⁻³	1.31 × 10 ⁻⁴	2.33 × 10 ⁻⁵	46	8.60 × 10 ⁻²
5.08 × 10 ⁻⁵	1.44 × 10 ⁻³	1.33 × 10 ⁻⁴	2.34 × 10 ⁻⁵	39	8.71 × 10 ⁻²

^a 2,6-Di-tert-butylpyridine (2,6-DTBP) is used as scavenger of triflic acid (see above).



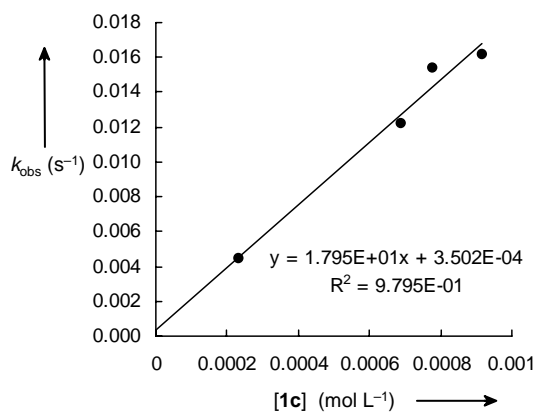
$$k_2(20\text{ }^\circ\text{C}) = 52.38\text{ M}^{-1}\text{ s}^{-1}$$

The kinetic measurements of this series were of relatively poor quality.

Table S11. Kinetics of the reaction of **2d**-OTf with 2,6-dimethylphenyl isocyanide (**1c**) (CH₂Cl₂, 20 °C, λ = 601 nm).

[2d -OH] ₀ , M	[1c], M	[TMSOTf] ₀ , M	[2,6-DTBP] ₀ , M ^a	conv., %	k _{obs} , s ⁻¹
1.22 × 10 ⁻⁵	2.32 × 10 ⁻⁴	8.96 × 10 ⁻⁵	4.07 × 10 ⁻⁵	79	4.44 × 10 ⁻³
1.21 × 10 ⁻⁵	6.87 × 10 ⁻⁴	8.87 × 10 ⁻⁵	4.03 × 10 ⁻⁵	85	1.22 × 10 ⁻²
1.17 × 10 ⁻⁵	7.77 × 10 ⁻⁴	8.55 × 10 ⁻⁵	3.89 × 10 ⁻⁵	71	1.54 × 10 ⁻²
1.21 × 10 ⁻⁵	9.15 × 10 ⁻⁴	8.86 × 10 ⁻⁵	4.03 × 10 ⁻⁵	77	1.62 × 10 ⁻²

^a 2,6-Di-tert-butylpyridine (2,6-DTBP) is used as scavenger of triflic acid (see above).



$$k_2(20\text{ }^\circ\text{C}) = 17.95\text{ M}^{-1}\text{ s}^{-1}$$

Table S12. Kinetics of the reaction of **2e**-BF₄ with 2,6-dimethylphenyl isocyanide (**1c**) (CH₂Cl₂, 20 °C, λ = 593 nm).

[2e -BF ₄] ₀ , M	[1c], M	conversion, %	k _{obs} , s ⁻¹
8.97 × 10 ⁻⁶	3.19 × 10 ⁻⁴	74	1.82 × 10 ⁻³
5.95 × 10 ⁻⁶	4.76 × 10 ⁻⁴	71	2.23 × 10 ⁻³
8.91 × 10 ⁻⁶	6.34 × 10 ⁻⁴	79	3.34 × 10 ⁻³
1.05 × 10 ⁻⁵	7.79 × 10 ⁻⁴	80	3.78 × 10 ⁻³

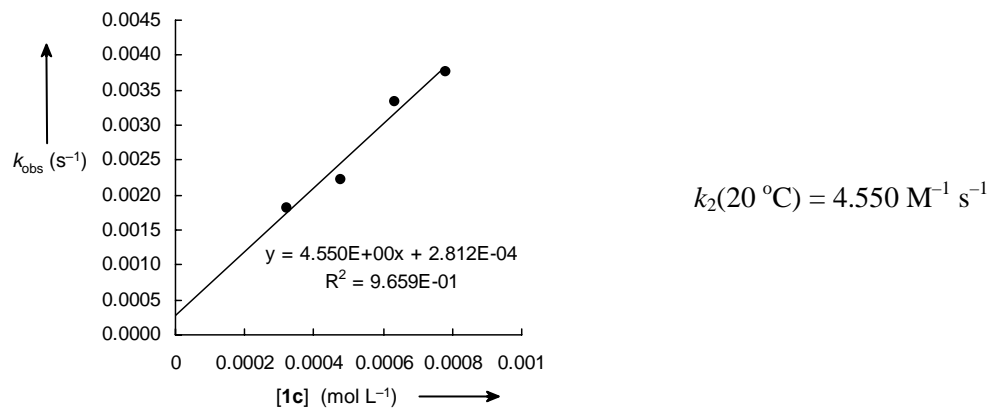


Table S13. Kinetics of the reaction of **2a**-OTf with TosMIC (**1d**) (CH₂Cl₂, 20 °C, λ = 513 nm).

[2a -Cl] ₀ , M	[TosMIC], M	[TMSOTf] ₀ , M	[2,6-DTBP] ₀ , M ^a	conv., %	k _{obs} , s ⁻¹
2.08 × 10 ⁻⁵	2.46 × 10 ⁻⁴	6.66 × 10 ⁻⁵	2.50 × 10 ⁻⁵	77	8.92 × 10 ⁻²
2.03 × 10 ⁻⁵	3.60 × 10 ⁻⁴	6.50 × 10 ⁻⁵	2.44 × 10 ⁻⁵	62	1.41 × 10 ⁻¹
2.05 × 10 ⁻⁵	4.35 × 10 ⁻⁴	6.56 × 10 ⁻⁵	2.46 × 10 ⁻⁵	71	1.77 × 10 ⁻¹
2.03 × 10 ⁻⁵	4.79 × 10 ⁻⁴	6.50 × 10 ⁻⁵	2.44 × 10 ⁻⁵	56	1.95 × 10 ⁻¹
2.00 × 10 ⁻⁵	5.92 × 10 ⁻⁴	6.40 × 10 ⁻⁵	2.40 × 10 ⁻⁵	70	2.33 × 10 ⁻¹

^a 2,6-Di-tert-butylpyridine (2,6-DTBP) is used as scavenger of triflic acid (see above).

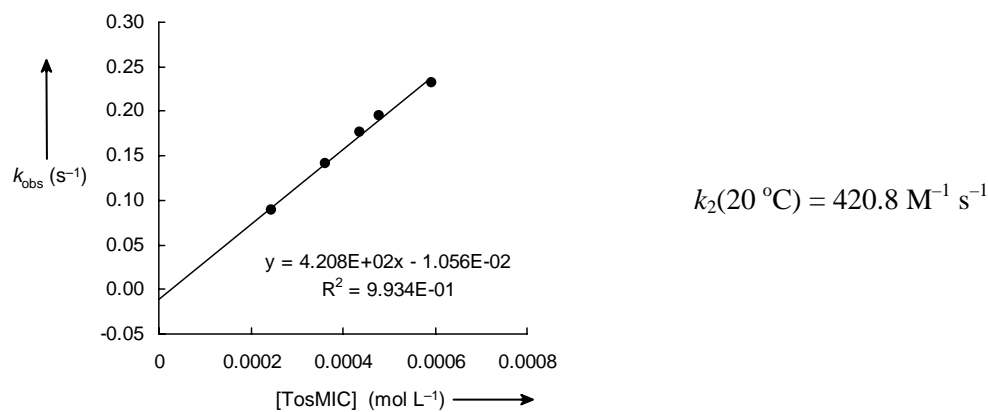
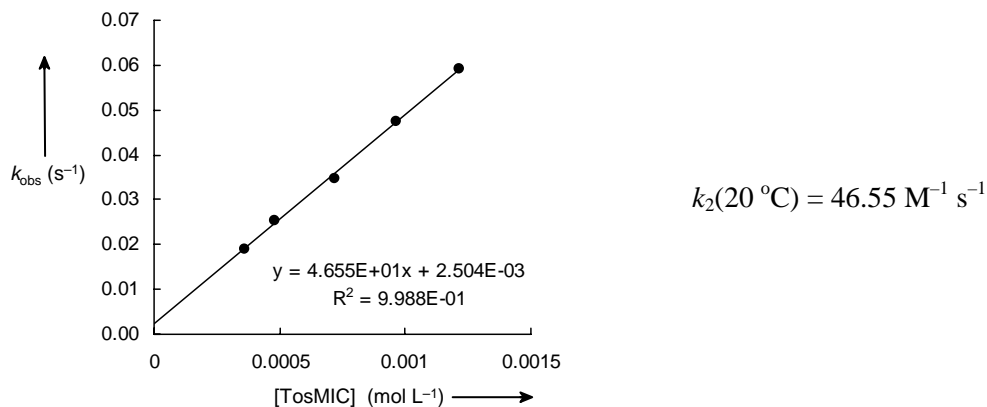


Table S14. Kinetics of the reaction of **2b**-OTf with TosMIC (**1d**) (CH₂Cl₂, 20 °C, λ = 535 nm).

[2b -OH] ₀ , M	[TosMIC], M	[TMSOTf] ₀ , M	[2,6-DTBP] ₀ , M ^a	conv., %	k _{obs} , s ⁻¹
1.17 × 10 ⁻⁵	3.56 × 10 ⁻⁴	5.65 × 10 ⁻⁵	2.42 × 10 ⁻⁵	51	1.91 × 10 ⁻²
1.18 × 10 ⁻⁵	4.80 × 10 ⁻⁴	5.70 × 10 ⁻⁵	2.44 × 10 ⁻⁵	59	2.54 × 10 ⁻²
1.17 × 10 ⁻⁵	7.17 × 10 ⁻⁴	5.65 × 10 ⁻⁵	2.42 × 10 ⁻⁵	74	3.49 × 10 ⁻²
1.18 × 10 ⁻⁵	9.61 × 10 ⁻⁴	5.70 × 10 ⁻⁵	2.44 × 10 ⁻⁵	77	4.74 × 10 ⁻²
1.19 × 10 ⁻⁵	1.21 × 10 ⁻³	5.74 × 10 ⁻⁵	2.46 × 10 ⁻⁵	66	5.92 × 10 ⁻²

^a 2,6-Di-tert-butylpyridine (2,6-DTBP) is used as scavenger of triflic acid (see above).

**Table S15.** Kinetics of the reaction of **2c**-OTf with TosMIC (**1d**) (CH₂Cl₂, 20 °C, λ = 335 nm).

[2c -OAc] ₀ , M	[TosMIC], M	[TMSOTf] ₀ , M	[2,6-DTBP] ₀ , M ^a	conv., %	k _{obs} , s ⁻¹
7.09 × 10 ⁻⁵	8.56 × 10 ⁻⁴	2.42 × 10 ⁻⁴	8.06 × 10 ⁻⁵	47	5.54 × 10 ⁻³
5.39 × 10 ⁻⁵	1.08 × 10 ⁻³	1.87 × 10 ⁻⁴	6.52 × 10 ⁻⁵	46	6.61 × 10 ⁻³
5.34 × 10 ⁻⁵	1.61 × 10 ⁻³	2.59 × 10 ⁻⁴	8.09 × 10 ⁻⁵	47	8.51 × 10 ⁻³
5.11 × 10 ⁻⁵	2.38 × 10 ⁻³	1.70 × 10 ⁻⁴	7.74 × 10 ⁻⁵	57	1.21 × 10 ⁻²

^a 2,6-Di-tert-butylpyridine (2,6-DTBP) is used as scavenger of triflic acid (see above).

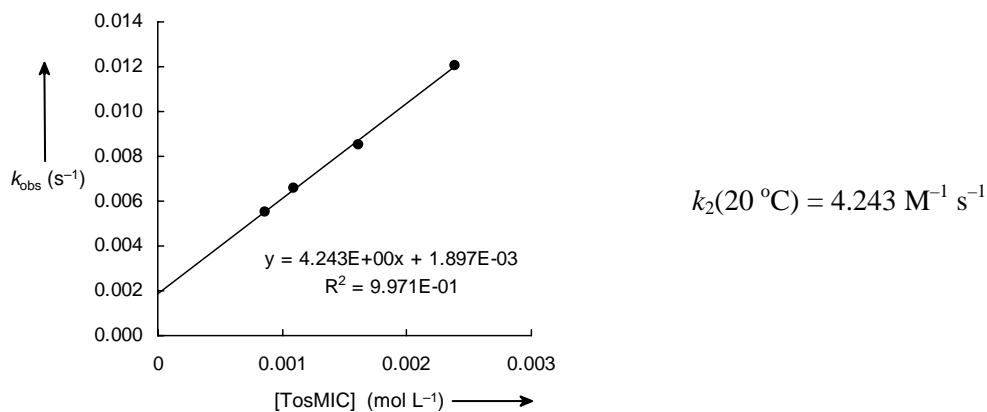
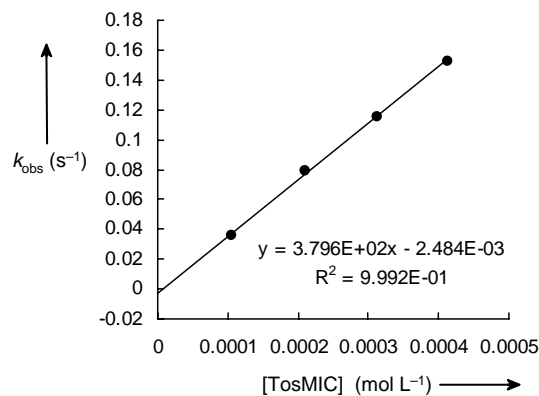


Table S16. Kinetics of the reaction of **2a**-OTf with 4-cyanophenyl isocyanide (**1e**) (CH₂Cl₂, 20 °C, λ = 513 nm).

[2a -Cl] ₀ , M	[1e], M	[TMSOTf] ₀ , M	[2,6-DTBP] ₀ , M ^a	conv., %	k _{obs} , s ⁻¹
7.35 × 10 ⁻⁶	1.05 × 10 ⁻⁴	7.26 × 10 ⁻⁵	1.04 × 10 ⁻⁵	63	3.59 × 10 ⁻²
7.34 × 10 ⁻⁶	2.10 × 10 ⁻⁴	7.26 × 10 ⁻⁵	1.04 × 10 ⁻⁵	60	7.91 × 10 ⁻²
7.28 × 10 ⁻⁶	3.11 × 10 ⁻⁴	7.20 × 10 ⁻⁵	1.03 × 10 ⁻⁵	63	1.16 × 10 ⁻¹
7.24 × 10 ⁻⁶	4.12 × 10 ⁻⁴	7.16 × 10 ⁻⁵	1.02 × 10 ⁻⁵	50	1.53 × 10 ⁻¹

^a 2,6-Di-tert-butylpyridine (2,6-DTBP) is used as scavenger of triflic acid (see above).

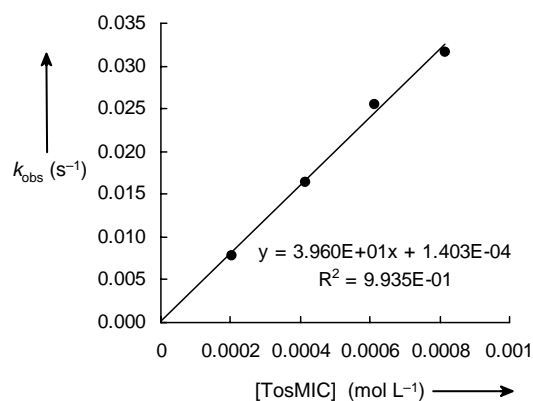


$$k_2(20\text{ }^\circ\text{C}) = 379.6\text{ M}^{-1}\text{ s}^{-1}$$

Table S17. Kinetics of the reaction of **2b**-OTf with 4-cyanophenyl isocyanide (**1e**) (CH₂Cl₂, 20 °C, λ = 535 nm).

[2b -OH] ₀ , M	[1e], M	[TMSOTf] ₀ , M	[2,6-DTBP] ₀ , M ^a	conv., %	k _{obs} , s ⁻¹
1.07 × 10 ⁻⁵	2.03 × 10 ⁻⁴	1.00 × 10 ⁻⁴	2.00 × 10 ⁻⁵	85	7.81 × 10 ⁻³
1.10 × 10 ⁻⁵	4.14 × 10 ⁻⁴	1.03 × 10 ⁻⁴	2.01 × 10 ⁻⁵	75	1.65 × 10 ⁻²
1.08 × 10 ⁻⁵	6.13 × 10 ⁻⁴	1.03 × 10 ⁻⁴	2.01 × 10 ⁻⁵	86	2.56 × 10 ⁻²
1.08 × 10 ⁻⁵	8.17 × 10 ⁻⁴	1.01 × 10 ⁻⁴	2.00 × 10 ⁻⁵	72	3.17 × 10 ⁻²

^a 2,6-Di-tert-butylpyridine (2,6-DTBP) is used as scavenger of triflic acid (see above).



$$k_2(20\text{ }^\circ\text{C}) = 39.60\text{ M}^{-1}\text{ s}^{-1}$$