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Supporting Information

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Ambident Reactivity of the Cyanate Anion

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General

Materials. Commercially available acetonitrile (extra dry, Acros) was used without further purification for all experiments.

The benzhydrylium tetrafluoroborates $\text{Ar}_2\text{CH}^+ \text{BF}_4^-$ and benzhydryl chlorides $\text{Ar}_2\text{CH}-\text{Cl}$ were prepared as described before.^[S1, S2] Tetraethylammonium cyanate was synthesized from $\text{Et}_4\text{N}^+ \text{BF}_4^-$ and KOCN in ethanol according to literature.^[S3]

Spectroscopy. ^1H and ^{13}C NMR chemical shifts are expressed in ppm and refer to CDCl_3 : $d_{\text{H}} = 7.26$, $d_{\text{C}} = 77.2$. An IR-Spectrometer (Spectrum BX from Perkin Elmer) with an ATR unit (attenuated total reflection; Dura Sampler Diamond ATR from Smiths Detection) was used to record the IR spectra.

Kinetics

Determination of the Rates of the Combinations of Benzhydrylium Ions with the Cyanate Anion.

Reactions of cyanate ions with the colored benzhydrylium ions gave colorless products. The reactions of **(1a–l)**- BF_4 with $\text{Et}_4\text{N}^+ \text{OCN}^-$ were followed photometrically at the absorption maxima of Ar_2CH^+ (460–645 nm) by UV-Vis spectroscopy. All experiments were performed under first-order conditions (excess of $\text{Et}_4\text{N}^+ \text{OCN}^-$) at 20 °C in acetonitrile. First-order rate constants k_{obs} were obtained by least-squares fitting of the decay absorbances to the mono-exponential curve $A_t = A_0 \exp(-k_{\text{obs}}t)$.

For electrophiles **1a–f** a stopped-flow instrument (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst3 software) was used in single-mode by mixing equal volumes of a **(1a–f)**- BF_4 and a $\text{Et}_4\text{N}^+ \text{OCN}^-$ solution as reported previously.^[S1]

As described in the main text of this Communication, the less stabilized benzhydrylium ions ($E \geq -6$) were generated from suitable precursors [**1g–i** from **(1g–i)**-NCO, **1j** from **1j**-Cl, **1l** from **1l**-Cl] by laser flash photolysis.^[S4, S5] Initial concentrations of the cation precursors are given in the tables below. The actual carbocation concentrations are much lower than the initial precursor concentrations because each laser pulse converts only 1–4 % of the precursor molecules into the corresponding carbocations. Due to the high molar extinction coefficient of the carbocations and the low one of the precursors, still an excellent detectivity results. Care was taken to exchange the sample between laser shots to avoid accumulative effects. At the same time the sample was kept long enough in the observation region to allow the recording of the full decay curve.

[S1] H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Jancker, B. Kempf, R. Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512.

[S2] B. Denegri, A. Streiter, S. Juric, A. R. Ofial, O. Kronja, H. Mayr, *Chem. Eur. J.* **2006**, *12*, 1648–1656; *Chem. Eur. J.* **2006**, *12*, 5415.

[S3] H. Kobler, R. Munz, G. Al Gasser, G. Simchen, *Liebigs Ann. Chem.* **1978**, 1937–1945.

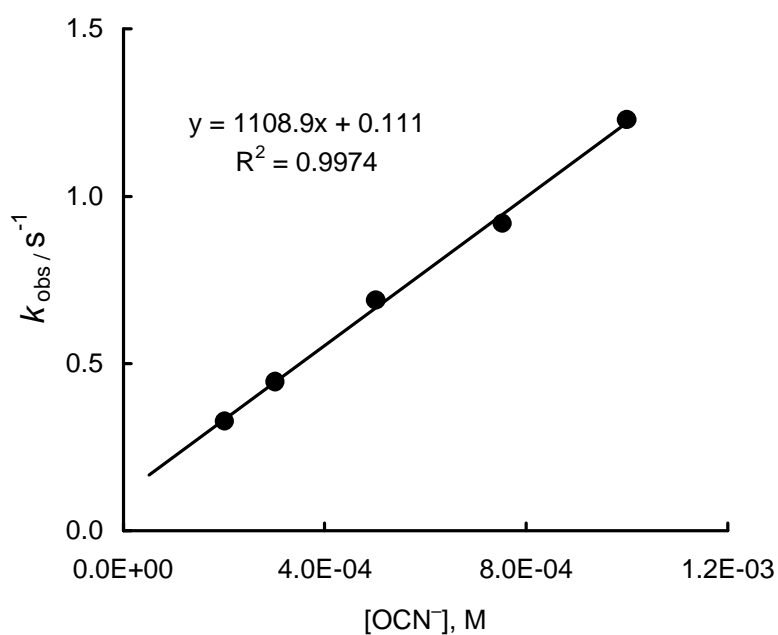
[S4] U. Schmidhammer, S. Roth, E. Riedle, A. A. Tishkov, H. Mayr, *Rev. Sci. Instrum.* **2005**, *76*, 093111.

[S5] A. A. Tishkov, U. Schmidhammer, S. Roth, E. Riedle, H. Mayr, *Angew. Chem.* **2005**, *117*, 4699–4703; *Angew. Chem. Int. Ed.* **2005**, *44*, 4623–4626.

Combination reaction of the cyanate anion with 1a in acetonitrile

(20 °C, stopped-flow technique, monitored at 632 nm)

$[\text{Ar}_2\text{CH}^+]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
9.92×10^{-6}	2.01×10^{-4}	3.28×10^{-1}
9.92×10^{-6}	3.01×10^{-4}	4.45×10^{-1}
9.92×10^{-6}	5.02×10^{-4}	6.90×10^{-1}
9.92×10^{-6}	7.53×10^{-4}	9.19×10^{-1}
9.92×10^{-6}	1.00×10^{-3}	1.23

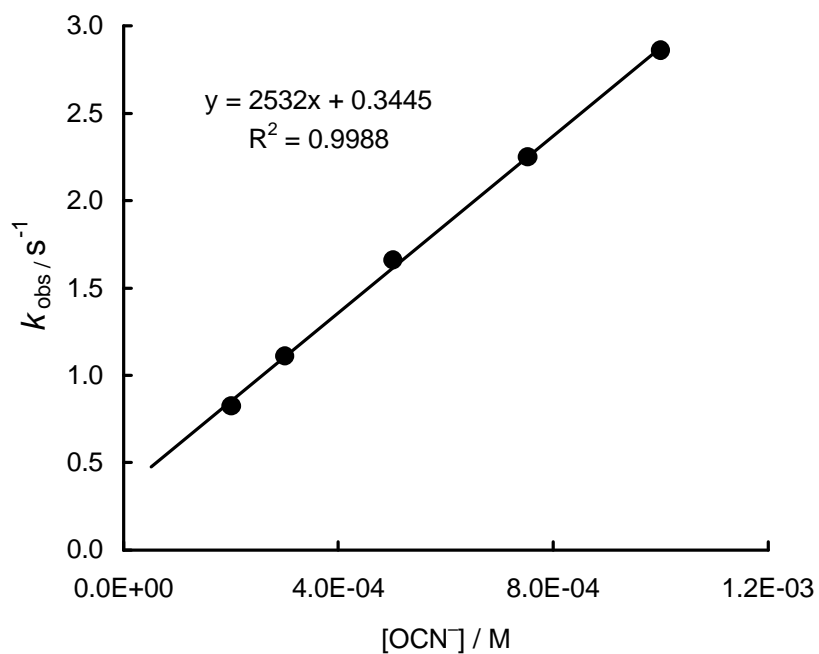


$$k_2 = 1.11 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with 1b in acetonitrile

(20 °C, stopped-flow technique, monitored at 635 nm)

$[\text{Ar}_2\text{CH}^+]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
8.49×10^{-6}	2.01×10^{-4}	8.23×10^{-1}
8.49×10^{-6}	3.01×10^{-4}	1.11
8.49×10^{-6}	5.02×10^{-4}	1.66
8.49×10^{-6}	7.53×10^{-4}	2.25
8.49×10^{-6}	1.00×10^{-3}	2.86

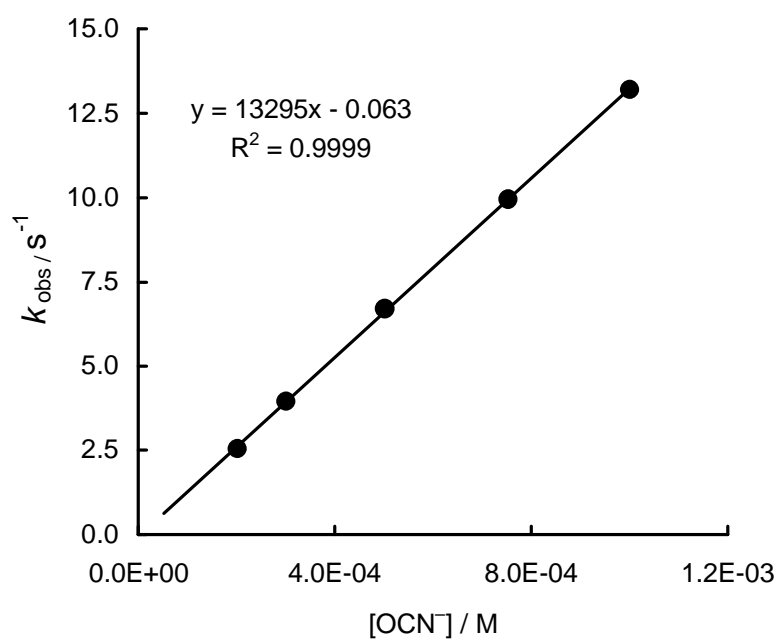


$$k_2 = 2.53 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with 1c in acetonitrile

(20 °C, stopped-flow technique, monitored at 616 nm)

$[\text{Ar}_2\text{CH}^+]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
9.91×10^{-6}	2.01×10^{-4}	2.55
9.91×10^{-6}	3.01×10^{-4}	3.95
9.91×10^{-6}	5.02×10^{-4}	6.69
9.91×10^{-6}	7.53×10^{-4}	9.95
9.91×10^{-6}	1.00×10^{-3}	1.32×10^1

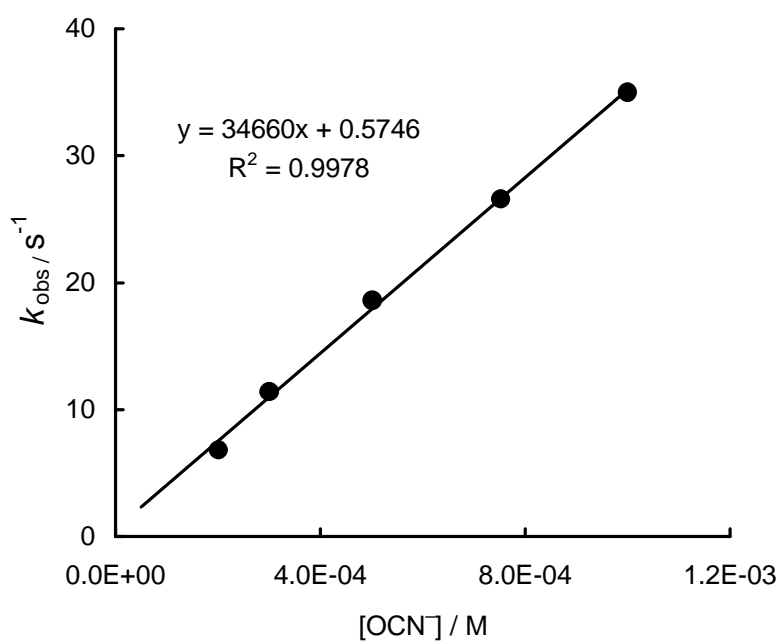


$$k_2 = 1.33 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with 1d in acetonitrile

(20 °C, stopped-flow technique, monitored at 620 nm)

$[\text{Ar}_2\text{CH}^+]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
1.00×10^{-5}	2.01×10^{-4}	6.83
1.00×10^{-5}	3.01×10^{-4}	1.14×10^1
1.00×10^{-5}	5.02×10^{-4}	1.86×10^1
1.00×10^{-5}	7.53×10^{-4}	2.66×10^1
1.00×10^{-5}	1.00×10^{-3}	3.50×10^1

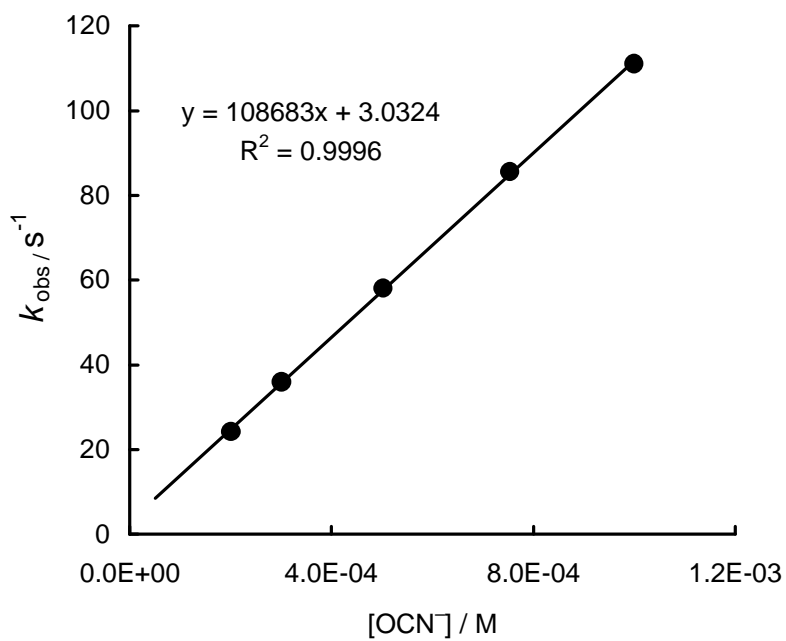


$$k_2 = 3.47 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with 1e in acetonitrile

(20 °C, stopped-flow technique, monitored at 612 nm)

$[\text{Ar}_2\text{CH}^+]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
9.99×10^{-6}	2.01×10^{-4}	2.42×10^1
9.99×10^{-6}	3.01×10^{-4}	3.59×10^1
9.99×10^{-6}	5.02×10^{-4}	5.81×10^1
9.99×10^{-6}	7.53×10^{-4}	8.56×10^1
9.99×10^{-6}	1.00×10^{-3}	1.11×10^2

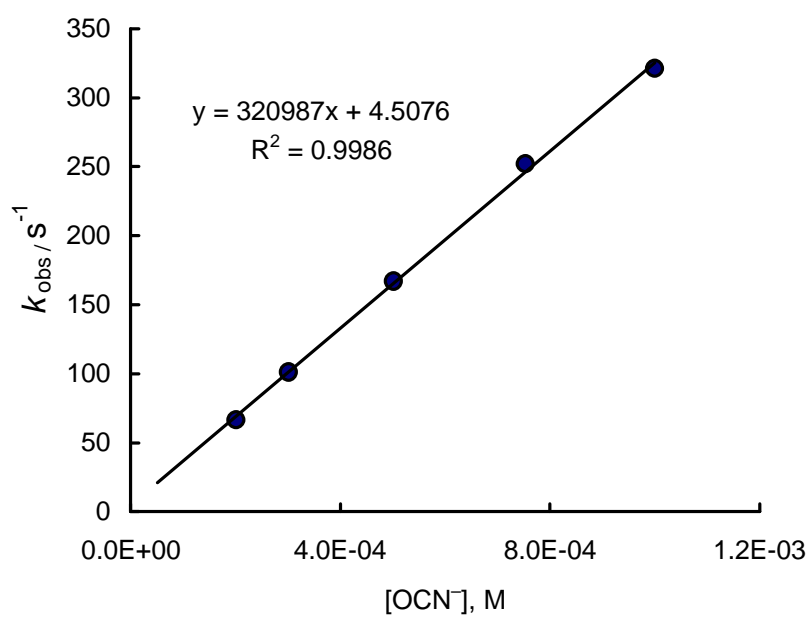


$$k_2 = 1.09 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with 1f in acetonitrile

(20 °C, stopped-flow technique, monitored at 605 nm)

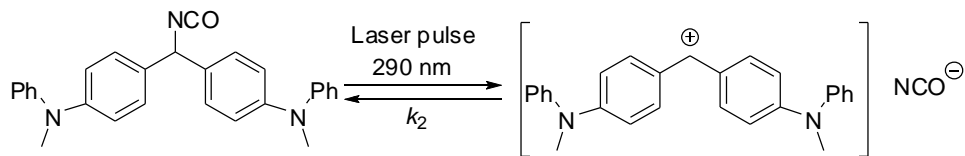
$[\text{Ar}_2\text{CH}^+]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
1.01×10^{-5}	2.01×10^{-4}	6.65×10^1
1.01×10^{-5}	3.01×10^{-4}	1.01×10^2
1.01×10^{-5}	5.02×10^{-4}	1.67×10^2
1.01×10^{-5}	7.53×10^{-4}	2.52×10^2
1.01×10^{-5}	1.00×10^{-3}	3.21×10^2



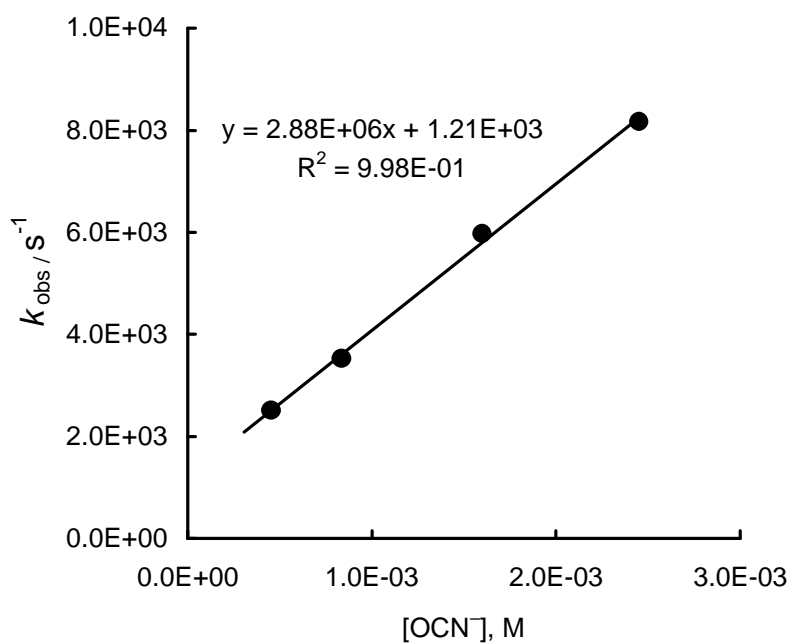
$$k_2 = 3.21 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with 1g in acetonitrile

(20 °C, laser-flash technique, monitored at 613 nm)



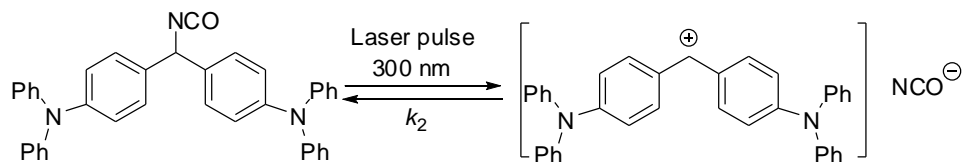
$[\text{Ar}_2\text{CH-NCO}]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
4.01×10^{-4}	4.56×10^{-4}	2.51×10^3
4.01×10^{-4}	8.36×10^{-4}	3.53×10^3
4.01×10^{-4}	1.60×10^{-3}	5.98×10^3
4.01×10^{-4}	2.45×10^{-3}	8.17×10^3



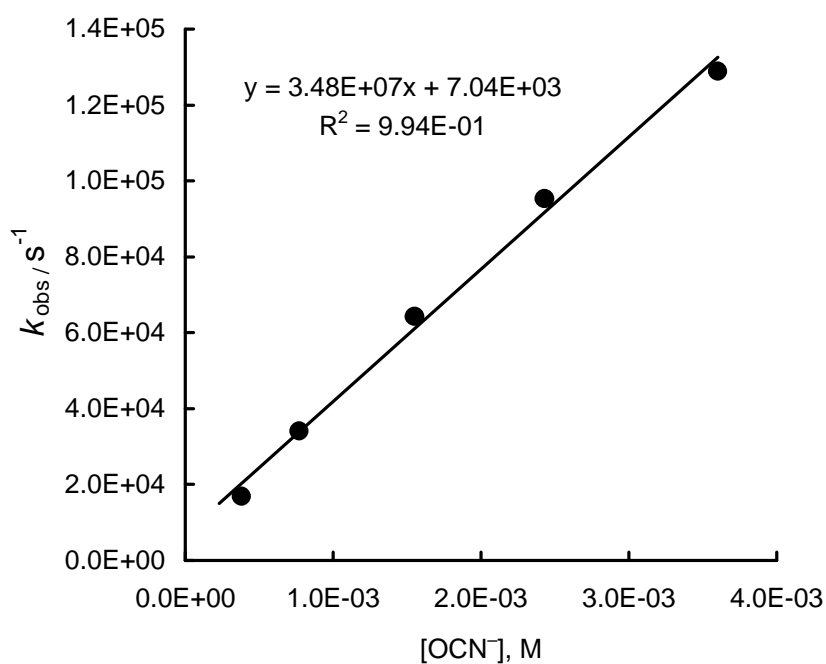
$$k_2 = 2.88 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with 1h in acetonitrile

(20 °C, laser flash technique, monitored at 645 nm)



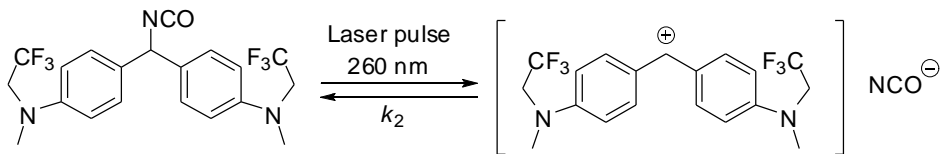
$[\text{Ar}_2\text{CH-NCO}]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
4.00×10^{-4}	5.80×10^{-4}	1.68×10^4
4.00×10^{-4}	9.70×10^{-4}	3.40×10^4
4.00×10^{-4}	1.75×10^{-3}	6.43×10^4
4.00×10^{-4}	2.63×10^{-3}	9.53×10^4
4.00×10^{-4}	3.80×10^{-3}	1.29×10^5



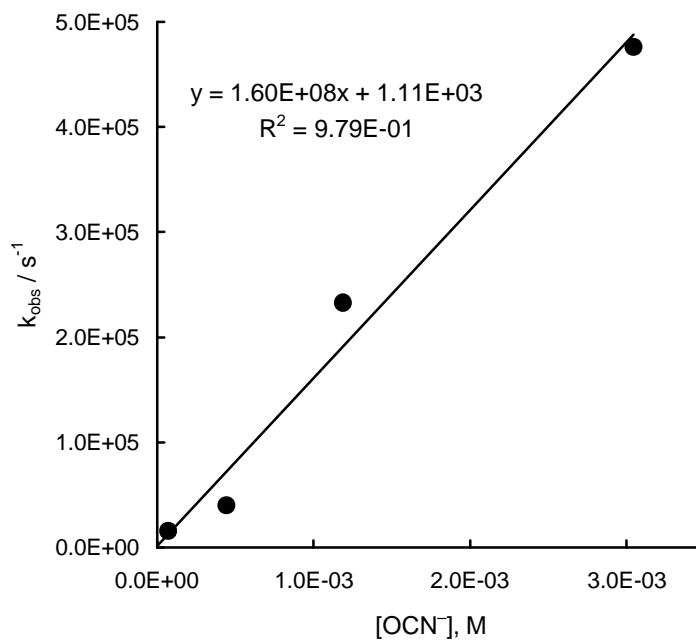
$$k_2 = 3.48 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with **1i** in acetonitrile

(20 °C, laser flash technique, monitored at 585 nm)



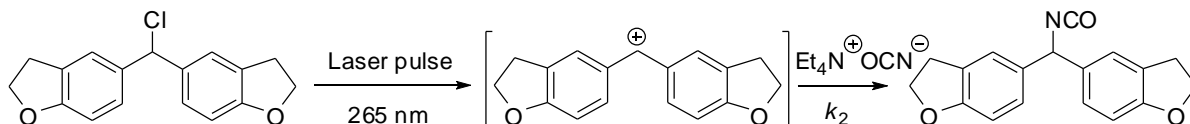
$[\text{Ar}_2\text{CH-NCO}]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
4.00×10^{-4}	7.30×10^{-5}	1.53×10^4
4.00×10^{-4}	4.44×10^{-4}	3.95×10^4
4.00×10^{-4}	1.19×10^{-3}	2.33×10^5
4.00×10^{-4}	3.05×10^{-3}	4.76×10^5



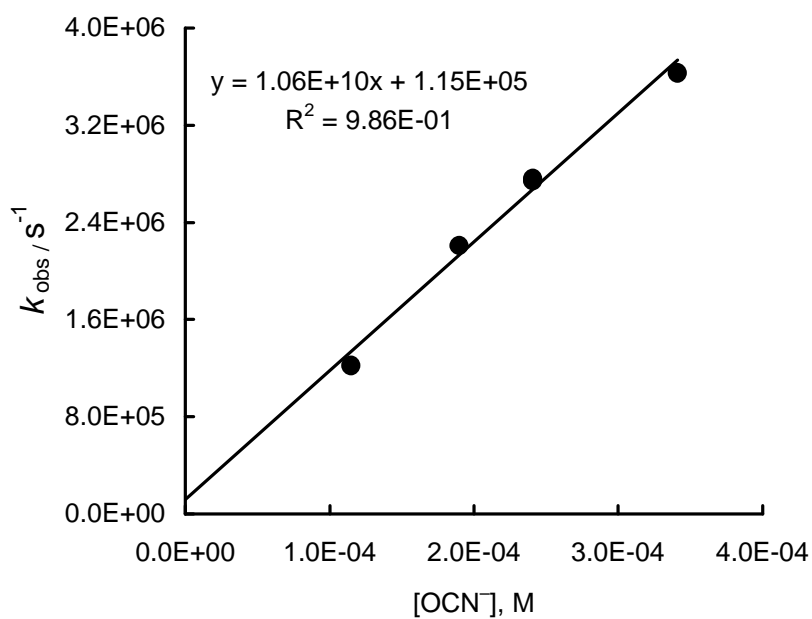
$$k_2 = 1.60 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with 1j in acetonitrile

(20 °C, laser flash technique, monitored at 525 nm)



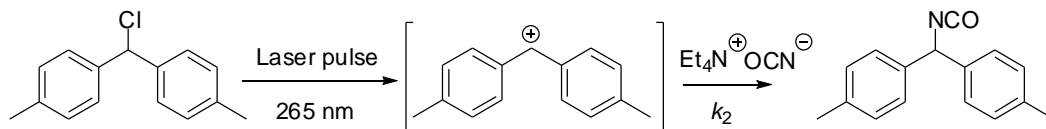
$[\text{Ar}_2\text{CHCl}]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
6.07×10^{-4}	1.15×10^{-4}	1.22×10^6
6.07×10^{-4}	1.90×10^{-4}	2.21×10^6
6.07×10^{-4}	2.41×10^{-4}	2.74×10^6
6.07×10^{-4}	2.41×10^{-4}	2.76×10^6
6.07×10^{-4}	3.41×10^{-4}	3.63×10^6



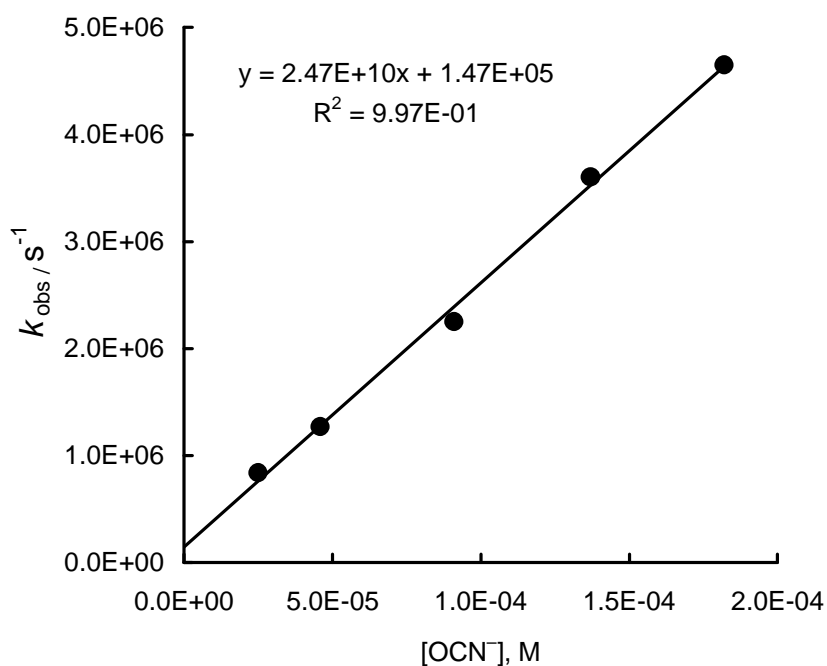
$$k_2 = 1.06 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

Combination reaction of the cyanate anion with 1I in acetonitrile

(20 °C, laser flash technique, monitored at 460 nm)



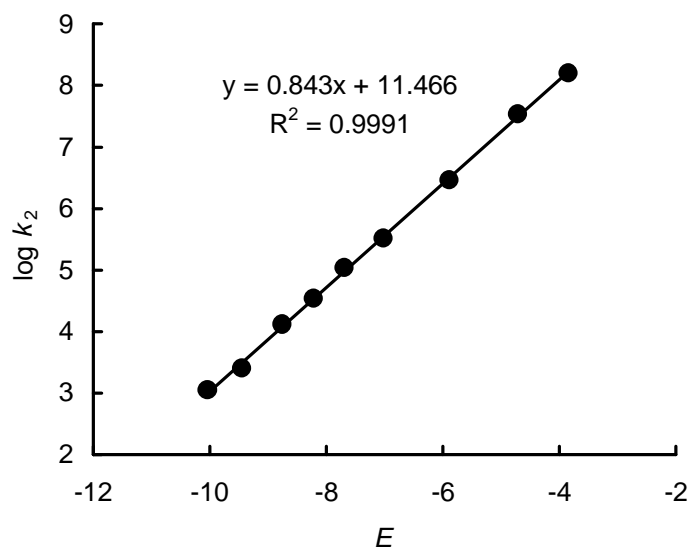
$[\text{Ar}_2\text{CHCl}]_0 / \text{M}$	$[\text{OCN}^-] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
3.76×10^{-3}	2.50×10^{-5}	8.38×10^5
3.76×10^{-3}	4.60×10^{-5}	1.27×10^6
3.76×10^{-3}	9.10×10^{-5}	2.25×10^6
3.76×10^{-3}	1.37×10^{-4}	3.60×10^6
3.76×10^{-3}	1.82×10^{-4}	4.65×10^6



$$k_2 = 2.47 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

**Determination of the nucleophilicity parameters N and s
for the cyanate anion in acetonitrile (at 20 °C)**

Ar_2CH^+	E	$k_2 / \text{M}^{-1} \text{s}^{-1}$	$\log k_2$
1a	-10.04	1.11×10^3	3.05
1b	-9.45	2.53×10^3	3.40
1c	-8.76	1.33×10^4	4.12
1d	-8.22	3.47×10^4	4.54
1e	-7.69	1.09×10^5	5.04
1f	-7.02	3.21×10^5	5.51
1g	-5.89	2.88×10^6	6.46
1h	-4.72	3.48×10^7	7.54
1i	-3.85	1.60×10^8	8.20



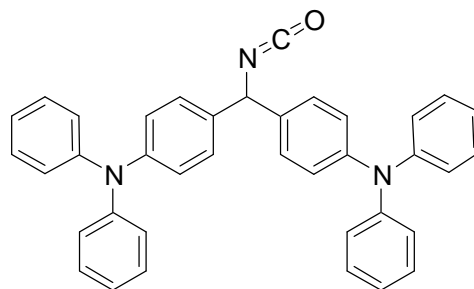
$$N = 13.60$$

$$s = 0.84$$

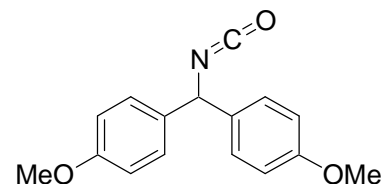
The second-order rate constants $k_2 > 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the reactions of the cyanate anion with electrophiles **1j,1** were excluded because they are affected by the diffusion limit.

Product Characterization

1h-NCO. To a solution of **1h-BF₄** (1.00 mmol, 588 mg) in dry acetonitrile (10 mL) tetraethylammonium cyanate (1.10 mmol, 189 mg) was added under nitrogen atmosphere. Instantly, the deeply green colored solution turned colorless. After evaporation of ca. 8 mL of the acetonitrile, Et₂O (5 mL) was added to the residue. The resulting suspension was treated for 10 min with ultrasound and then filtered through glass wool. The solvents were evaporated under reduced pressure: **1h-NCO** (391 mg, 72 %), slightly yellow solid. ¹H NMR (400 MHz, CDCl₃): *d* = 5.75 (s, 1 H, HCNCO), 7.03–7.29 ppm (m, 28 H, ArH); ¹³C NMR (75.5 MHz, CDCl₃): *d* = 61.5 (d, HCNCO), 123.3, 123.4, 124.7, 124.4, 124.7, 127.5, 129.4, 135.1, 147.7 ppm. MS (EI): *m/z* (%): 543 (13) [M]⁺, 503 (19), 502 (77), 501 (100) [M-NCO]⁺; HR-MS (EI): calcd for C₃₈H₂₉N₃O 543.2311, found 543.2325.



1k-NCO. To a solution of **1k-Cl** (1.00 mmol, 263 mg) in dry acetonitrile (10 mL) tetraethylammonium cyanate (1.10 mmol, 189 mg) was added under nitrogen atmosphere. The solution was stirred at 40 °C for 4 h. After evaporation of ca. 8 mL of the acetonitrile, Et₂O (5 mL) was added to the residue. The resulting suspension was treated for 10 min with ultrasound and then filtered through glass wool. The solvents were evaporated under reduced pressure to give a viscous liquid residue that was purified by column chromatography (silica gel, CH₂Cl₂, R_f = 0.85): **1h-NCO** (166 mg, 62 %), colorless solid. ¹H NMR (600 MHz, CDCl₃): *d* = 3.77 (s, 6 H, OCH₃), 5.75 (s, 1 H, HCNCO) 6.87 (d, *J* = 8.7 Hz, 4 H, ArH), 7.21 ppm (d, *J* = 8.7 Hz, 4 H, ArH); ¹³C NMR (150 MHz, CDCl₃): *d* = 55.4 (q, OMe), 61.3 (d, CHNCO), 114.2 (d, Ar), 127.82 (d, Ar), 128.57 (s, NCO), 134.0 (s, C-CHNCO), 159.3 ppm (C-OMe). MS (EI): *m/z* (%): 269 (21) [M]⁺, 228 (22), 227 (100) [M-NCO]⁺, 212 (7), 197 (7); HR-MS (EI): calcd for C₁₆H₁₅NO₃ 269.1052, found 269.1031.



1m-NCO. A mixture of **1m-Cl** (1.00 mmol, 272 mg) and silver cyanate (1.20 mmol, 180 mg) in diethyl ether (15 mL) was stirred for 1 h at room temperature in the dark. The suspension was filtered, and the solvent was evaporated: **1m-NCO** (264 mg, 95 %), colorless oil.

When **1m-Cl** (1.00 mmol) and silver cyanate (1.20 mmol) reacted in nitromethane (15 mL), 255 mg (92 %) **1m-NCO** was obtained. ¹H NMR (600 MHz, CDCl₃): *d* = 5.80 (s, 1 H, CHNCO), 7.22 (d, *J* = 8.6 Hz, 4 H, Ar-H), 7.33 ppm (d, *J* = 8.6 Hz, 4 H, Ar-H); a crosspeak for ¹H (*d* = 5.80 ppm) and ¹⁵N (*d* = 46.25 ppm) is observed in a gHMBC experiment (400 MHz); ¹³C NMR (150 MHz, CDCl₃): *d* = 60.8 (d, CHNCO), 124.8 (s, NCO), 127.8 (d, Ar), 129.1 (d, Ar), 134.1 (s, C-CHNCO), 139.3 (s, Ar); IR (ATR, cm⁻¹): 2244 (s, -N=C=O), 1498 (m), 1409 (w), 1089 (m), 1013 (m), 814 (m), 785 (m).

