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Supporting Information

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Ambident Reactivity of the Nitrite Ion Revisited

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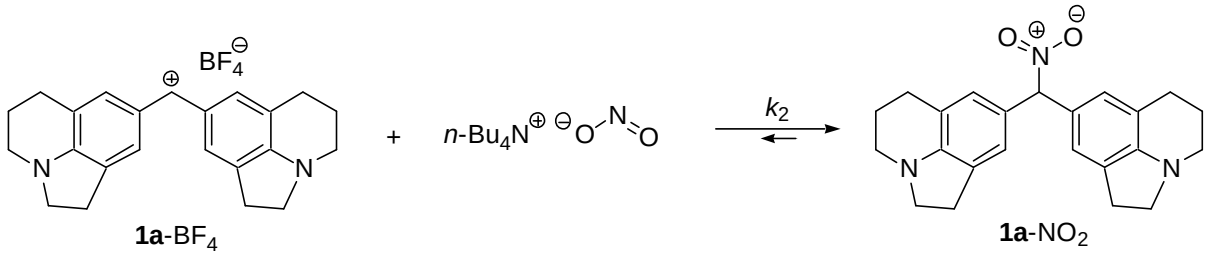
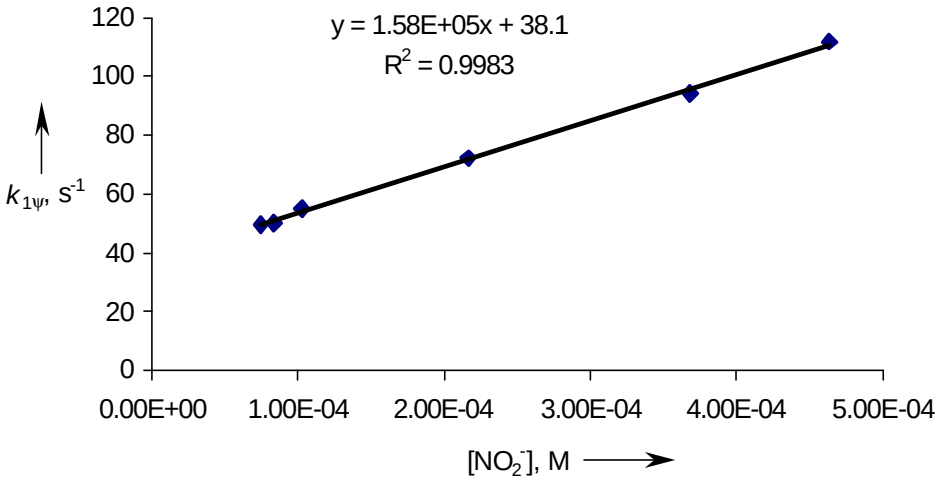
Combination of the nitrite ion with 1a-BF_4 in acetonitrile at 20 °C by stopped flow technique



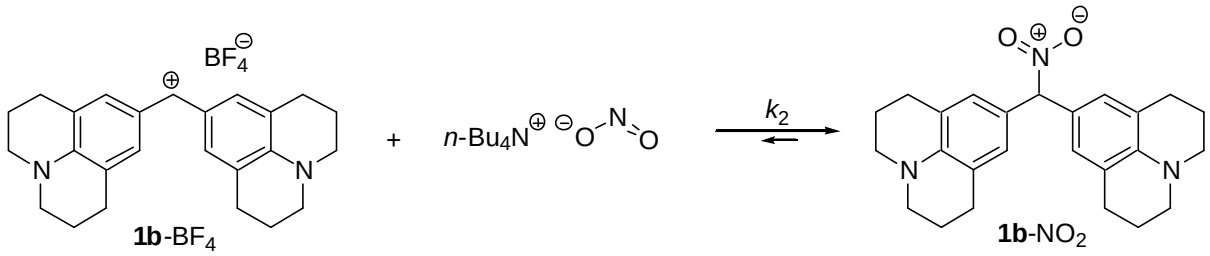
No.	[**1a**-BF_4]$_0$, M [a]	[NO_2^-], M	$k_{1\psi}$ (20 °C), s^{-1}
1	1.12×10^{-5}	7.99×10^{-5}	49.4
2	1.12×10^{-5}	8.94×10^{-5}	50.2
3	1.12×10^{-5}	1.08×10^{-4}	55.0
4	1.12×10^{-5}	2.22×10^{-4}	74.3
5	1.12×10^{-5}	3.74×10^{-4}	94.2
6	1.12×10^{-5}	4.69×10^{-4}	112

[a] Absorption decay was monitored at 631 nm.



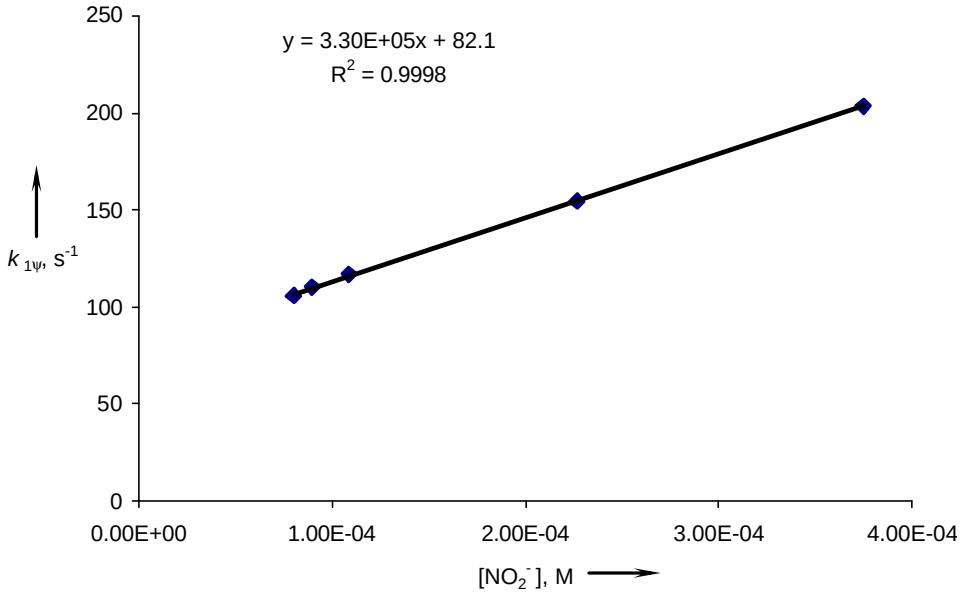
k_2 (20 °C) = (1.57 ± 0.05) × 10^5 M^{-1} s^{-1}

Combination of the nitrite ion with 1b-BF_4 in acetonitrile at 20 °C by stopped flow technique



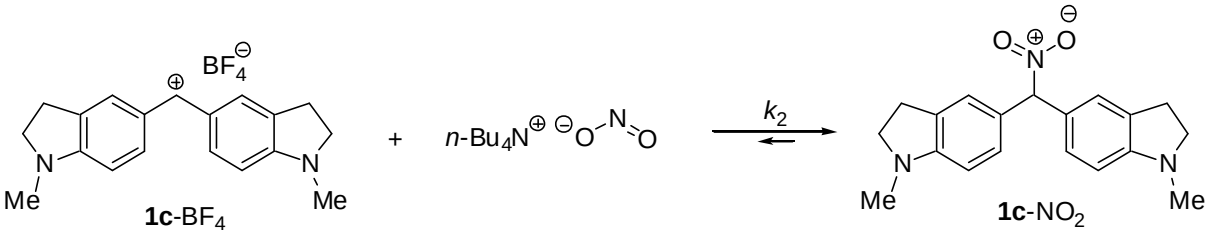
No.	[**1b**-BF_4]$_0$, M [a]	[NO_2^-], M	$k_{1\psi}$(20 °C), s^{-1}
1	1.07×10^{-5}	8.02×10^{-5}	106
2	1.07×10^{-5}	8.96×10^{-5}	110
3	1.07×10^{-5}	1.09×10^{-4}	117
4	1.07×10^{-5}	2.26×10^{-4}	155
5	1.07×10^{-5}	3.75×10^{-4}	204

[a] Absorption decay was monitored at 635 nm.



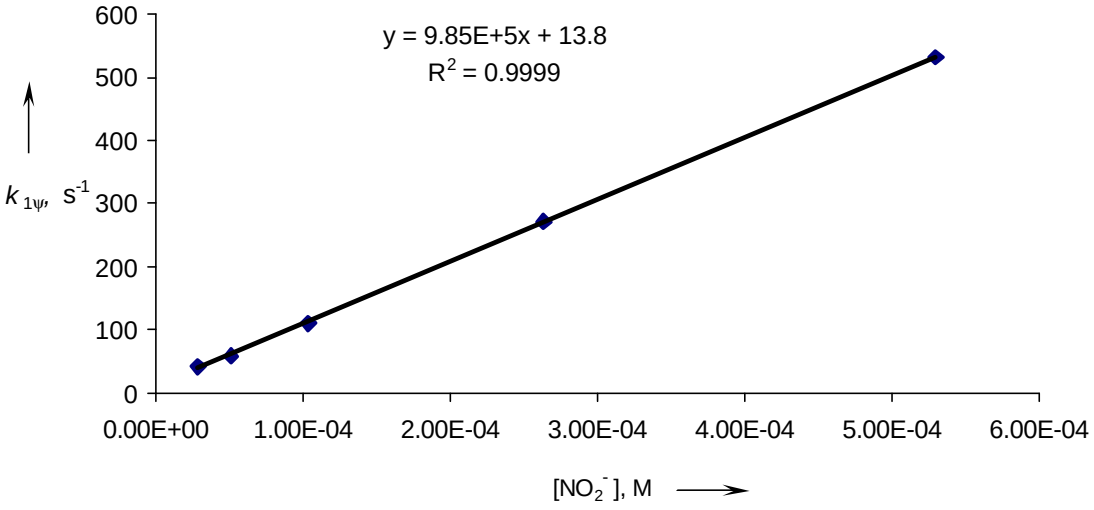
$$k_2\ (20\ ^{\circ}C) = (3.30 \pm 0.02) \times 10^5\ M^{-1}\ s^{-1}$$

Combination of the nitrite ion with 1c-BF_4 in acetonitrile at 20 °C by stopped flow technique



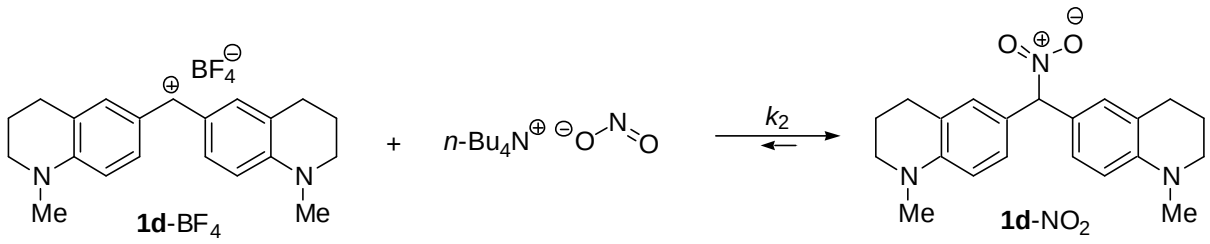
No.	[**1c**-BF_4]$_0$, M [a]	[NO_2^-], M	$k_{1\psi}$(20 °C), s^{-1}
1	5.19×10^{-6}	2.84×10^{-5}	42.2
2	5.19×10^{-6}	5.06×10^{-5}	58.7
3	5.19×10^{-6}	1.03×10^{-4}	111
4	5.19×10^{-6}	2.63×10^{-4}	272
5	5.19×10^{-6}	5.29×10^{-4}	532

[a] Absorption decay was monitored at 616 nm.



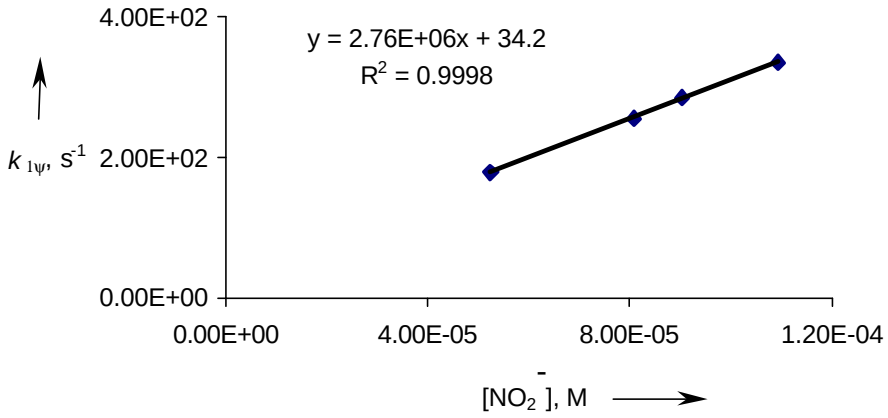
k_2 (20 °C) = (9.85 ± 0.06) × 10^5 M^{-1} s^{-1}

Combination of the nitrite ion with 1d-BF_4 in acetonitrile at 20 °C by stopped flow technique



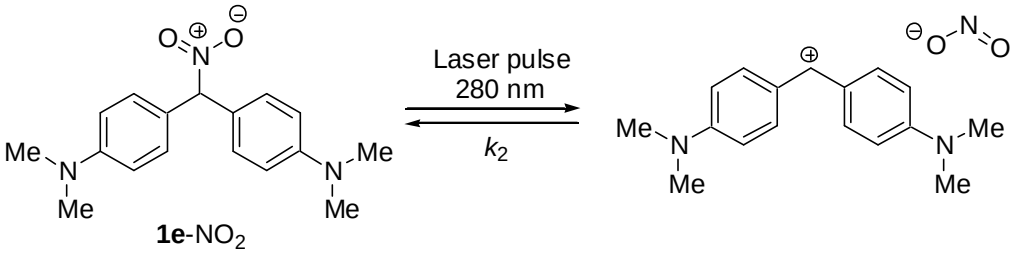
No.	[**1d**-BF_4]$_0$, M [a]	[NO_2^-], M	$k_{1\psi}$ (20 °C), s^{-1}
1	9.38×10^{-6}	5.70×10^{-5}	179
2	9.38×10^{-6}	8.55×10^{-5}	256
3	9.38×10^{-6}	9.50×10^{-5}	285
4	9.38×10^{-6}	1.14×10^{-4}	336

[a] Absorption decay was monitored at 620 nm.



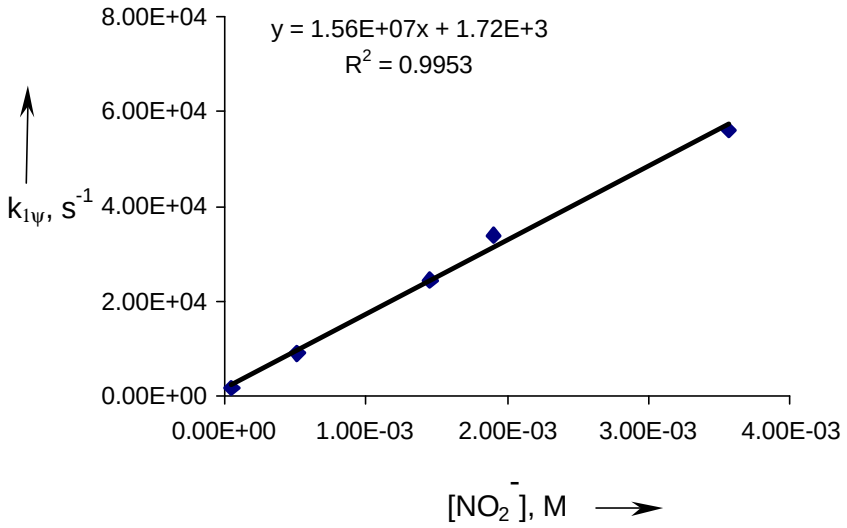
$$k_2(20\ ^{\circ}C) = (2.76 \pm 0.03) \times 10^6\ M^{-1}\ s^{-1}$$

Combination of the nitrite ion with 1e in acetonitrile at 20 °C by laser flash technique



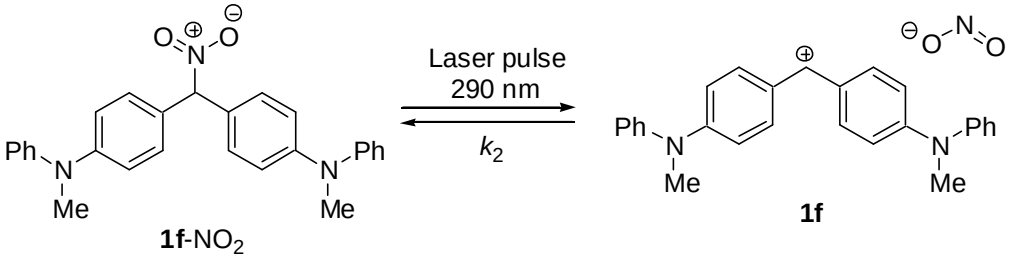
No.	[**1e**-BF_4]$_0$, M [a]	[NO_2^-]$_0$, M	[NO_2^-], M [b]	$k_{1\psi}$ (20 °C), s^{-1}
1	4.12×10^{-4}	4.63×10^{-4}	5.13×10^{-5}	1.78×10^{3}
2	4.12×10^{-4}	9.27×10^{-4}	5.15×10^{-4}	9.18×10^{3}
3	3.28×10^{-4}	1.78×10^{-3}	1.45×10^{-3}	2.45×10^{4}
4	4.12×10^{-4}	2.32×10^{-3}	1.90×10^{-3}	3.39×10^{4}
5	4.12×10^{-4}	3.98×10^{-3}	3.57×10^{-3}	5.61×10^{4}

[a] Absorption decay was monitored at 605 nm. [b] The solution of **1e**-BF_4 was added to a solution of n-$Bu_4N^+NO_2^-$ in a graduated flask and the resulting mixture was diluted to 25 mL. Concentration of the nitrite ion [NO_2^-] = [NO_2^-]$_0$ – [**1e**-BF_4]$_0$.



$$k_2\ (20\ ^{\circ}C) = (1.56 \pm 0.06) \times 10^{7}\ M^{-1}\ s^{-1}$$

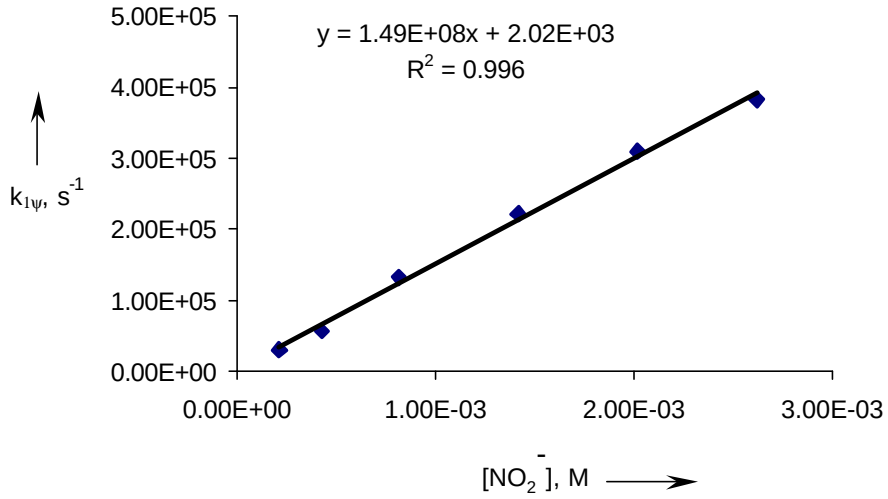
Combination of the nitrite ion with 1f in acetonitrile at 20 °C by laser flash technique



1f-NO_2 **1f**

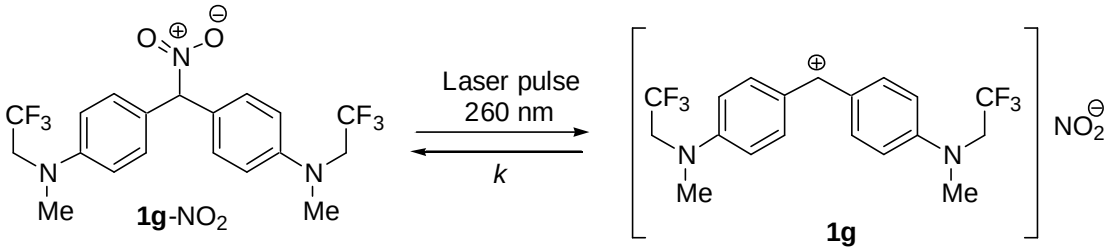
No.	[**1f**-BF_4]$_0$, M [a]	[NO_2^-]$_0$, M	[NO_2^-], M [b]	$k_{1\psi}$ (20 °C), s^{-1}
1	3.88×10^{-4}	6.02×10^{-4}	2.14×10^{-4}	3.04×10^{4}
2	7.75×10^{-4}	1.20×10^{-3}	4.29×10^{-4}	5.64×10^{4}
3	3.88×10^{-4}	1.20×10^{-3}	8.16×10^{-4}	1.32×10^{5}
4	3.88×10^{-4}	1.81×10^{-3}	1.42×10^{-3}	2.22×10^{5}
5	3.88×10^{-4}	2.41×10^{-3}	2.02×10^{-3}	3.09×10^{5}
6	3.88×10^{-4}	3.01×10^{-3}	2.62×10^{-3}	3.82×10^{5}

[a] Absorption decay was monitored at 614 nm. [b] A solution of **1f**-BF_4 was added to a solution of n-$Bu_4N^+NO_2^-$ in a graduated flask and the resulting mixture was diluted to 25 mL. Concentration of the nitrite ion [NO_2^-] = [NO_2^-]$_0$ – [**1f**-BF_4]$_0$.



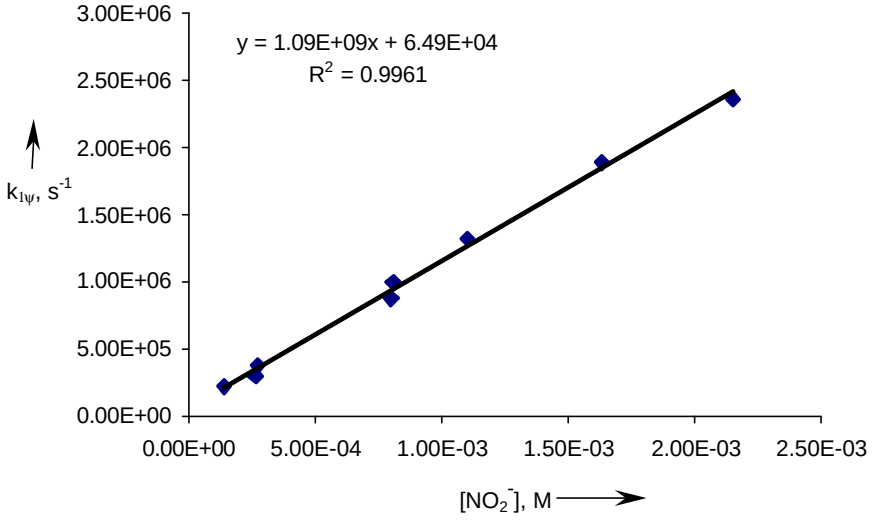
$$k_2\ (20\ ^{\circ}C) = (1.49 \pm 0.05) \times 10^{8}\ M^{-1}\ s^{-1}$$

Combination of the nitrite ion with 1g in acetonitrile at 20 °C by laser flash technique



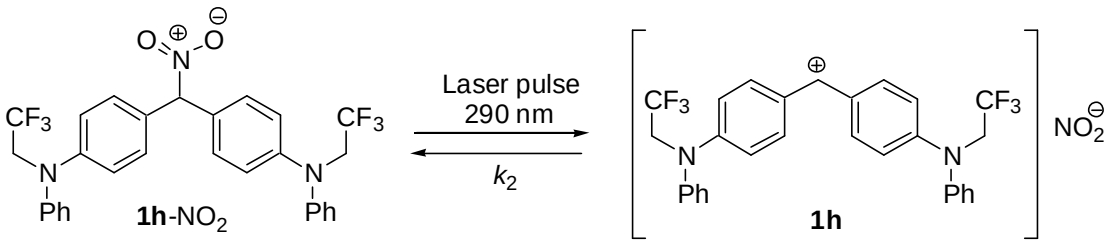
No.	[**1g**-BF_4]$_0$, M [a]	[NO_2^-]$_0$, M	[NO_2^-], M [b]	$k_{1\psi}$ (20 °C), s^{-1}
1	4.12×10^{-4}	1.51×10^{-3}	1.10×10^{-3}	1.32×10^{6}
2	2.49×10^{-4}	1.88×10^{-3}	1.63×10^{-3}	1.89×10^{6}
3	1.99×10^{-4}	2.35×10^{-3}	2.15×10^{-3}	2.36×10^{6}
4	1.65×10^{-4}	3.02×10^{-4}	1.37×10^{-4}	2.19×10^{5}
5	4.92×10^{-4}	7.53×10^{-4}	2.61×10^{-4}	2.98×10^{5}
6	1.99×10^{-4}	4.69×10^{-4}	2.70×10^{-4}	3.75×10^{5}
7	4.12×10^{-4}	1.21×10^{-3}	7.98×10^{-4}	8.76×10^{5}
8	3.93×10^{-4}	1.20×10^{-3}	8.07×10^{-4}	9.92×10^{5}

[a] Absorption decay was monitored at 590 nm. [b] A solution of **1g**-BF_4 was added to a solution of n-$Bu_4N^+NO_2^-$ in a graduated flask and the resulting mixture was diluted to 25 mL. Concentration of the nitrite ion [NO_2^-] = [NO_2^-]$_0$ – [**1g**-BF_4]$_0$.



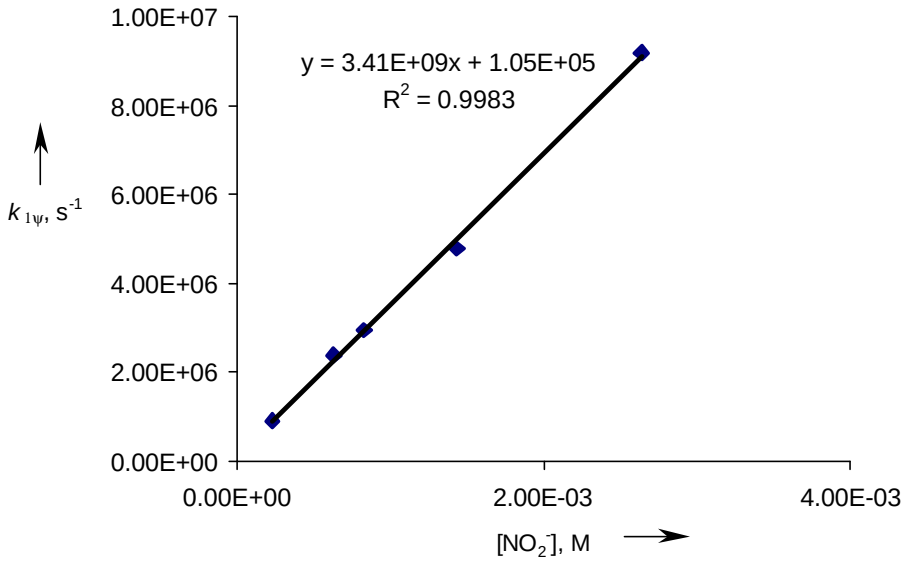
k_2 (20 °C) = (1.09 ± 0.03) × 10^9 M^{-1} s^{-1}

Combination of the nitrite ion with 1h in acetonitrile at 20 °C by laser flash technique



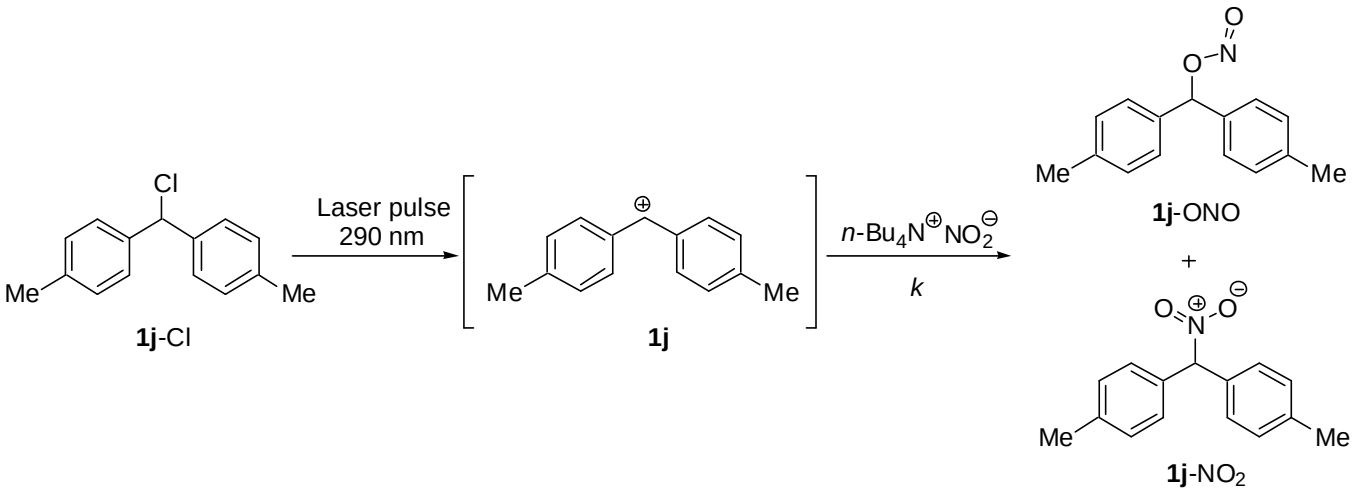
No.	[**1h**-BF_4]$_0$, M [a]	[NO_2^-]$_0$, M	[NO_2^-], M [b]	$k_{1\psi}$ (20 °C), s^{-1}
1	3.70×10^{-4}	6.02×10^{-4}	2.32×10^{-4}	9.00×10^{5}
2	2.75×10^{-4}	9.07×10^{-4}	6.32×10^{-4}	2.38×10^{6}
3	3.70×10^{-4}	1.20×10^{-3}	8.34×10^{-4}	2.95×10^{6}
4	3.70×10^{-4}	1.81×10^{-3}	1.44×10^{-3}	4.79×10^{6}
5	3.70×10^{-4}	3.01×10^{-3}	2.64×10^{-3}	9.20×10^{6}

[a] Absorption decay was monitored at 590 nm. [b] A solution of **1h**-BF_4 was added to a solution of n-$Bu_4N^+NO_2^-$ in a graduated flask and the resulting mixture was diluted to 25 mL. Concentration of the nitrite ion [NO_2^-] = [NO_2^-]$_0$ – [**1h**-BF_4]$_0$.



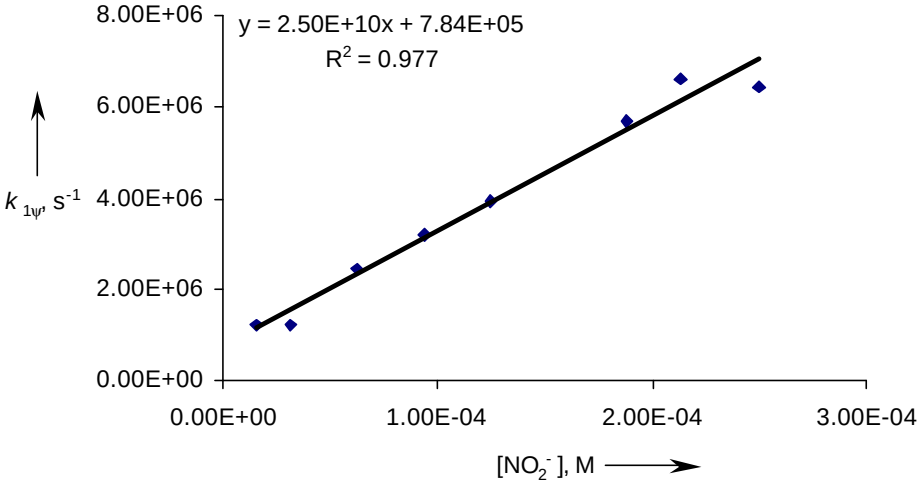
k_2 (20 °C) = $(3.41 \pm 0.08) \times 10^9$ M^{-1} s^{-1}

Combination of the nitrite ion with 1j in acetonitrile at 20 °C by laser flash technique



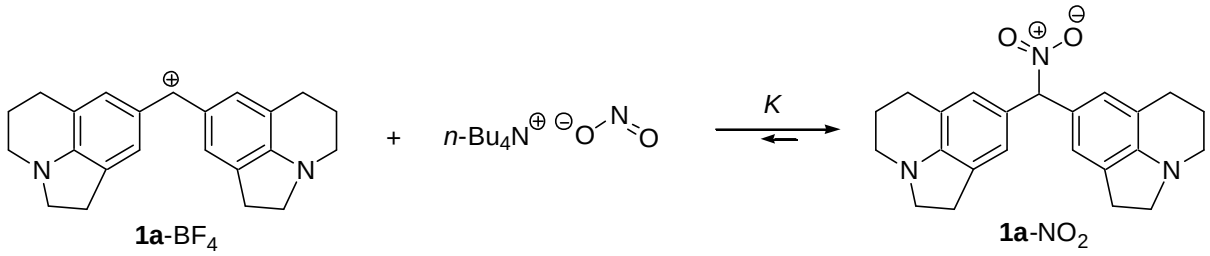
No.	[**1j**–Cl]$_0$, M [a]	[NO_2^-], M [b]	$k_{1\psi}$ (20 °C), s^{-1}
1	3.87×10^{-3}	1.57×10^{-5}	1.22×10^{6}
2	4.76×10^{-3}	3.13×10^{-5}	1.24×10^{6}
3	3.09×10^{-3}	6.26×10^{-5}	2.44×10^{6}
4	3.09×10^{-3}	9.39×10^{-5}	3.21×10^{6}
5	4.19×10^{-3}	1.25×10^{-4}	3.93×10^{6}
6	4.19×10^{-3}	1.88×10^{-4}	5.69×10^{6}
7	3.57×10^{-3}	2.50×10^{-4}	6.44×10^{6}
8	4.93×10^{-3}	2.13×10^{-4}	6.62×10^{6}

[a] Decay of the absorption of **1j** was monitored at 470 nm. [b] A solution of **1j**-Cl was added to a solution of n-$Bu_4N^+NO_2^-$ in a graduated flask and the resulting mixture was diluted to 25 mL. **1j**-Cl reacts with n-$Bu_4N^+NO_2^-$ in MeCN very slow, and initial concentration of the nitrite ion is [NO_2^-].



k_2 (20 °C) = (2.50 ± 0.16) × 10^{10} M^{-1} s^{-1}

Ionisation equilibrium for 1a–NO_2 in acetonitrile at 20 °C by J&M TIDAS spectrometer with Hellma insertion probe



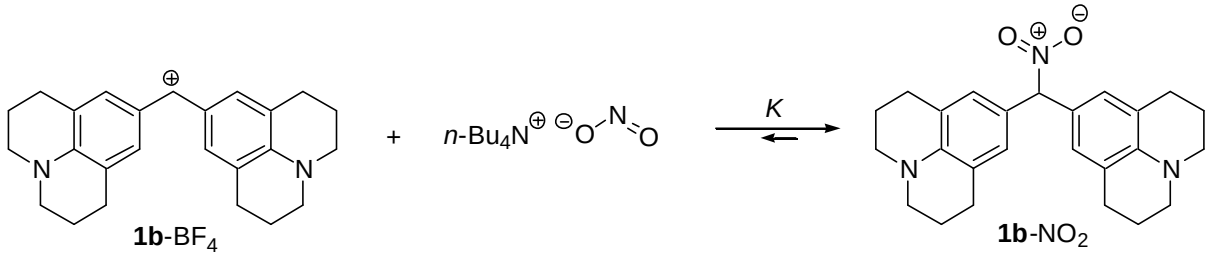
1a-BF_4 **1a**-NO_2

Nr.	[**1a**-BF_4]$_0$ / M	[NO_2^-]$_0$ / M	A_{eq} [a]	[**1a**–BF_4]$_{eq}$ / M [b]	[NO_2^-]$_{eq}$ / M	[**1a**–NO_2]$_{eq}$ / M	K / M^{-1}
1	2.26×10^{-5}	1.30×10^{-4}	0.783	1.32×10^{-5}	1.21×10^{-4}	9.44×10^{-6}	5.95×10^{3}
2	2.17×10^{-5}	2.50×10^{-4}	0.553	9.29×10^{-6}	2.38×10^{-4}	1.24×10^{-5}	5.62×10^{3}
3	2.09×10^{-5}	3.62×10^{-4}	0.427	7.18×10^{-6}	3.48×10^{-4}	1.37×10^{-5}	5.49×10^{3}
4	2.02×10^{-5}	4.65×10^{-4}	0.347	5.83×10^{-6}	4.51×10^{-4}	1.44×10^{-5}	5.47×10^{3}
5	1.24×10^{-5}	7.52×10^{-5}	0.515	8.66×10^{-6}	7.15×10^{-5}	3.74×10^{-6}	6.05×10^{3}
6	1.20×10^{-5}	1.77×10^{-4}	0.353	5.93×10^{-6}	1.71×10^{-4}	6.07×10^{-6}	5.98×10^{3}
7	1.17×10^{-5}	2.72×10^{-4}	0.271	4.55×10^{-6}	2.65×10^{-4}	7.15×10^{-6}	5.92×10^{3}
8	1.13×10^{-5}	3.62×10^{-4}	0.218	3.66×10^{-6}	3.54×10^{-4}	7.64×10^{-6}	5.88×10^{3}

[a] At 631 nm, d = 0.5 cm. [b] For **1a**–BF_4: λ_{max} = 631 nm, e = 1.19×10^5 cm^{-1}?M^{-1}

K (20 °C) = $(5.80 \pm 0.23) \times 10^3$ M^{-1}

Ionisation equilibrium for 1b–NO_2 in acetonitrile at 20 °C



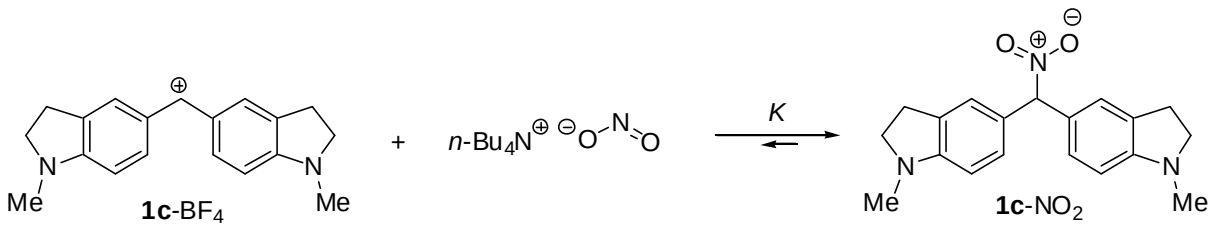
1b-BF_4 **1b**-NO_2

Nr.	[**1b**-BF_4]$_0$ / M	[NO_2^-]$_0$ / M	A_{eq} [a]	[**1b**–BF_4]$_{eq}$ / M [b]	[NO_2^-]$_{eq}$ / M	[**1b**–NO_2]$_{eq}$ / M	K / M^{-1}
1	1.06×10^{-5}	3.54×10^{-5}	0.588	9.33×10^{-6}	3.41×10^{-5}	1.27×10^{-6}	3.98×10^{3}
2	1.04×10^{-5}	1.04×10^{-4}	0.450	7.14×10^{-6}	1.01×10^{-4}	3.26×10^{-6}	4.53×10^{3}
3	1.02×10^{-5}	1.70×10^{-4}	0.370	5.87×10^{-6}	1.66×10^{-4}	4.33×10^{-6}	4.45×10^{3}
4	9.76×10^{-6}	2.94×10^{-4}	0.275	4.37×10^{-6}	2.89×10^{-4}	5.39×10^{-6}	4.28×10^{3}
5	1.99×10^{-5}	1.33×10^{-4}	0.796	1.26×10^{-5}	1.26×10^{-4}	7.27×10^{-6}	4.57×10^{3}
6	1.91×10^{-5}	2.57×10^{-4}	0.560	8.89×10^{-6}	2.47×10^{-4}	1.02×10^{-5}	4.65×10^{3}
7	1.85×10^{-5}	3.71×10^{-4}	0.433	6.87×10^{-6}	3.59×10^{-4}	1.16×10^{-5}	4.71×10^{3}
8	1.50×10^{-5}	1.34×10^{-4}	0.580	9.21×10^{-6}	1.28×10^{-4}	5.79×10^{-6}	4.91×10^{3}
9	1.44×10^{-5}	2.57×10^{-4}	0.410	6.51×10^{-6}	2.49×10^{-4}	7.89×10^{-6}	4.87×10^{3}
10	1.39×10^{-5}	3.72×10^{-4}	0.315	5.00×10^{-6}	3.63×10^{-4}	8.90×10^{-6}	4.90×10^{3}

[a] At 635 nm, d = 0.5 cm. [b] For **1b**-BF_4: λ_{max} = 635 nm, e = 1.26×10^5 cm^{-1}?M^{-1}.

K (20 °C) = $(4.58 \pm 0.30) \times 10^3$ M^{-1}

Ionisation equilibrium for $(ind)_2CH–NO_2$ in acetonitrile at 20 °C

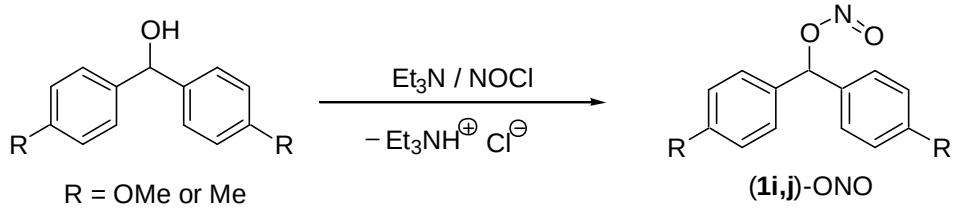


Nr.	[**1c**-BF_4]$_0$ / M	[NO_2^-]$_0$ / M	A_{eq}[a]	[**1c**–BF_4]$_{eq}$ / M[b]	[NO_2^-]$_{eq}$ / M	[**1c**–NO_2]$_{eq}$ / M	K / M^{-1}
1	1.53×10^{-5}	2.88×10^{-5}	0.322	4.67×10^{-6}	1.82×10^{-5}	1.06×10^{-5}	1.25×10^{5}
2	1.51×10^{-5}	8.56×10^{-5}	0.094	1.36×10^{-6}	7.19×10^{-5}	1.37×10^{-5}	1.40×10^{5}
3	1.50×10^{-5}	1.42×10^{-4}	0.052	7.54×10^{-7}	1.28×10^{-4}	1.42×10^{-5}	1.48×10^{5}
4	1.52×10^{-5}	1.43×10^{-5}	0.578	8.38×10^{-6}	7.48×10^{-6}	6.82×10^{-6}	1.09×10^{5}
5	1.51×10^{-5}	4.28×10^{-5}	0.233	3.38×10^{-6}	3.11×10^{-5}	1.17×10^{-5}	1.12×10^{5}
6	1.49×10^{-5}	1.27×10^{-4}	0.079	1.14×10^{-6}	1.13×10^{-4}	1.38×10^{-5}	1.06×10^{5}
7	1.51×10^{-5}	7.11×10^{-6}	0.758	1.10×10^{-5}	3.00×10^{-6}	4.11×10^{-6}	1.25×10^{5}
8	1.50×10^{-5}	3.54×10^{-5}	0.280	4.06×10^{-6}	2.45×10^{-5}	1.09×10^{-5}	1.10×10^{5}
9	1.49×10^{-5}	9.13×10^{-5}	0.105	1.52×10^{-6}	7.79×10^{-5}	1.34×10^{-5}	1.13×10^{5}

[a] Bei 616 nm, d = 0.5 cm. [b] For **1c**-BF_4: λ_{max} = 616 nm, e = 1.38×10^5 cm^{-1}?M^{-1}.

K (20 °C) = $(1.21 \pm 0.14) \times 10^5$ M^{-1}

Synthesis of bis(aryl)methyl nitrites (1i,j)-ONO

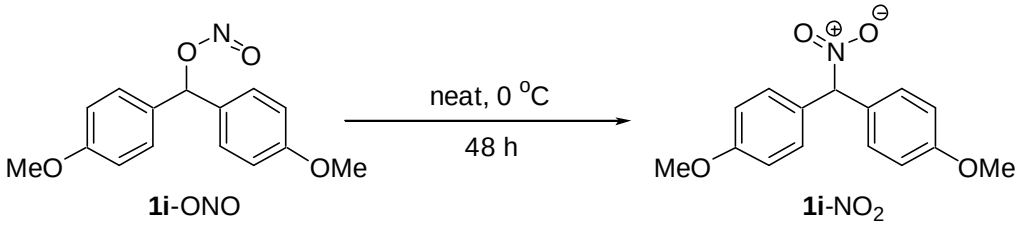


To a stirred solution of bis(aryl)methanol (1.00 mmol) and Et_3N (202 mg, 2.00 mmol) in dry CH_2Cl_2 (5 mL) neat NOCl (ca. 0.2 mL) was added at –78 °C and the resulting mixture was stirred for 20 min at –78 °C and 10 min at –30 °C. The reaction mixture was diluted with heptane (10 mL), and after removal of the cooling bath it was concentrated in vacuum until the excess NOCl is evaporated and colourless suspension of $Et_3NH^+Cl^-$ is left. The residue was filtered through glass-wool and evaporated in vacuum to give product slightly contaminated by unidentified product (^{1}H NMR control) as a yellowish oil [**1i**-ONO: 250 mg (91 %); **1j**-ONO: 219 mg (91 %)].

1i-ONO: ^{1}H NMR (400 MHz, $CDCl_3$): d = 3.80 (s, 6 H), 6.89 (d, 4 H, *J* = 8.8 Hz), 7.22 (d, 4 H, *J* = 8.8 Hz), 7.33 (s, 1 H, Ar_2CH). ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 55.4 (OMe), 81.5 (Ar_2CH), 114.1 (CH), 128.7 (CH), 132.2 (C_q), 159.5 (C_q). ^{15}N NMR (40.5 MHz, gHMBC, $CDCl_3$): d = 176.5 (s, ONO). MS (EI), *m*/*z* (%): 273 (M^+, 0.19), 227 ($M^+ – NO_2$, 100); HRMS (EI) calcd for $C_{15}H_{15}NO_4$: 273.0997; found: 273.0990.

1j-ONO: ^{1}H NMR (300 MHz, $CDCl_3$): d = 2.25 (s, 6 H), 7.06 (d, 4 H, *J* = 8.3 Hz), 7.11 (d, 4 H, *J* = 8.3 Hz), 7.50 (s, 1 H, Ar_2CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): d = 21.3 (Me), 81.8 (Ar_2CH), 127.4 (CH), 129.4 (CH), 137.2 (C_q), 138.1 (C_q). ^{15}N NMR (40.5 MHz, gHMBC, $CDCl_3$): d = 174.6 (s, ONO).

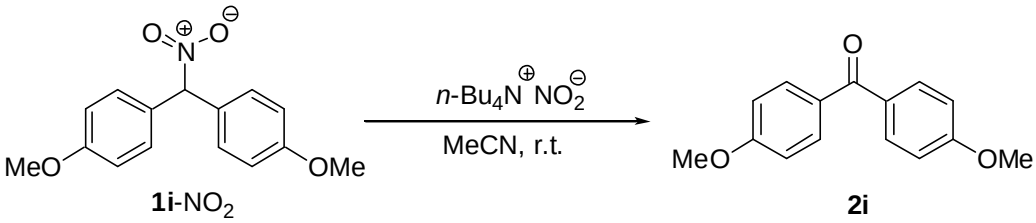
Rearrangement of bis(4-methoxyphenyl)methyl nitrite 1i-ONO into bis(4-methoxyphenyl)nitromethane 1i-NO_2



Neat nitrite **1i**-ONO (90 mg, 0.33 mmol) was maintained at 0 °C for 48 hours and the resulting red solid was subjected to column chromatography (silica gel, CH_2Cl_2) to give **1i**-NO_2 (48 mg, 53 %, slightly contaminated by unidentified product), 4,4'-dimethoxybenzophenone **2i** (12 mg, 15 %) and traces of di[bis(4-methoxyphenyl)methyl] ether.

1i-NO_2: ^{1}H NMR (400 MHz, $CDCl_3$): d = 3.82 (s, 6 H), 6.71 (s, 1 H, Ar_2CH), 6.93 (d, 4 H, *J* = 8.7 Hz), 7.30 (d, 4 H, *J* = 8.7 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): d = 55.5 (OMe), 94.0 (Ar_2CH), 114.3 (CH), 126.8 (C_q), 129.9 (CH), 160.4 (C_q). ^{15}N NMR (40.5 MHz, gHMBC, $CDCl_3$): d = 0.7 (s, NO_2).

Reaction of bis(4-methoxyphenyl)nitromethane 1i-NO_2 with tetra-butylammonium nitrite



1i-NO_2 **2i**

To a stirred solution of *n*-$Bu_4N^+NO_2^-$ (54 mg, 0.19 mmol) in dry MeCN (6 mL) a solution of **1i**-NO_2 (10 mg, 0.037 mmol, slightly contaminated by unidentified product) in benzene (0.2 mL) was added at 20 °C. After 3 h of stirring at 20 °C the solvent was evaporated and the residue was extracted with *n*-heptane (3 × 5 mL). The combined *n*-heptane extracts were filtered through glass-wool and evaporated in vacuum to give **2i** (8 mg, 89 %, slightly contaminated by unidentified product from the starting material).

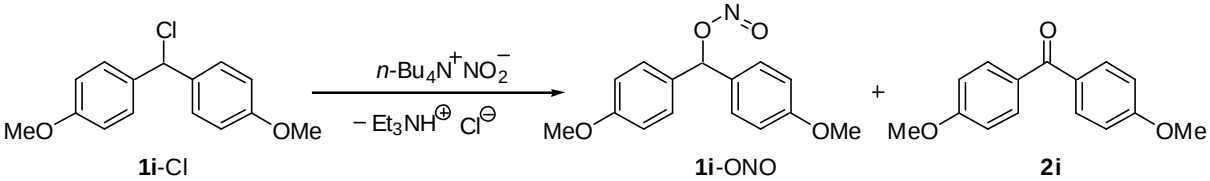
Reaction of bis(4-methoxyphenyl)methyl nitrite 1i-ONO with tetra-butylammonium nitrite

To a stirred solution of *n*-$Bu_4N^+NO_2^-$ (582 mg, 2.02 mmol) in dry MeCN (60 mL) a solution of **1i**-ONO (119 mg, 0.435 mmol) in benzene (1 mL) was added at 20 °C. After 3 h of stirring at 20 °C the reaction mixture was evaporated and the residue was extracted with *n*-hexane (10 × 10 mL). The combined *n*-hexane extracts were filtered through glass-wool and evaporated in vacuum to give **1i**-ONO (109 mg, 92 % recovery, ^{1}H NMR control).

Interaction of bis(4-methylphenyl)methyl nitrite 1j-ONO with tetra-butylammonium nitrite

To a stirred solution of *n*-$Bu_4N^+NO_2^-$ (951 mg, 3.30 mmol) in dry MeCN (100 mL) a solution of **1j**-ONO (155 mg, 0.567 mmol) in MeCN (2 mL) was added at 20 °C. After 25 h of stirring at 20 °C, 15 mL of the reaction mixture was separated. After concentration of the sample, the residue was extracted with *n*-hexane (10 × 10 mL). The combined *n*-hexane extracts were filtered through glass-wool and evaporated in vacuum to give **1j**-ONO (21 mg, corresponds to 92 % recovery, ^{1}H NMR control).

Reaction of bis(4-methoxyphenyl)methylchloride 1i-Cl with tetra-butylammonium nitrite

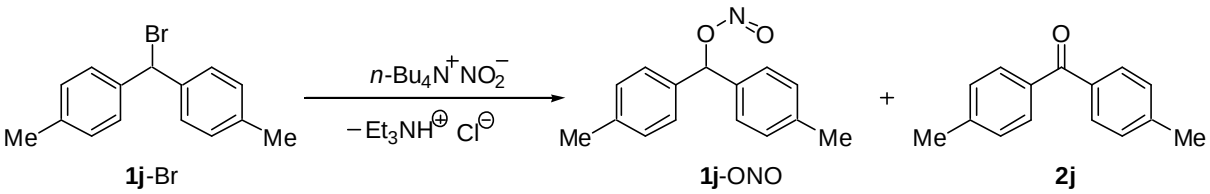


1i-Cl **1i**-ONO **2i**

To a stirred solution of *n*-$Bu_4N^+NO_2^-$ (360 mg, 1.25 mmol) in dry MeCN (35 mL) a solution of **1i**-Cl (72 mg, 0.27 mmol) in MeCN (2 mL) was added at 20 °C. After 3 h of stirring at 20 °C, the reaction mixture was evaporated and the residue was extracted with *n*-hexane (10 × 10 mL). The combined extracts were filtered through glass-wool and evaporated in vacuum to give a mixture of **1i**-ONO (67 %) and **2i** (20 %) [yields determined by ^{1}H NMR with CH_2Cl_2 as an internal standard].

The components of the product mixture were identified by comparison of their ^{1}H, ^{13}C NMR spectra with the spectra of pure **1i**-ONO and **2i**.

Reaction of bis(4-methylphenyl)methyl bromide 1j-Br with tetra-butylammonium nitrite

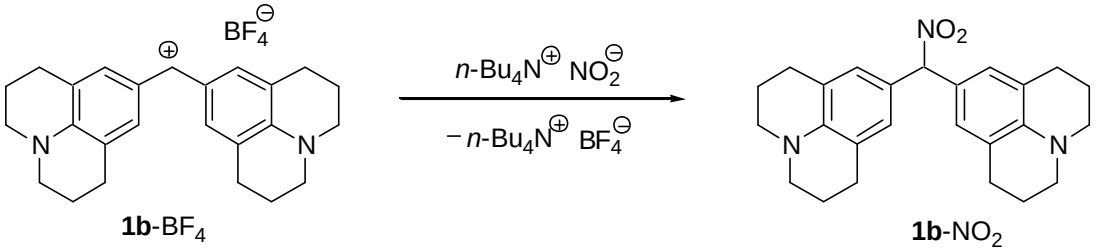


1j-Br **1j**-ONO **2j**

To a stirred solution of *n*-$Bu_4N^+NO_2^-$ (288 mg, 1.00 mmol) in dry MeCN (30 mL) a solution of **1j**-Br[S1] (60 mg, 0.22 mmol) in MeCN (2 mL) was added at 20 °C. After 3 h of stirring at 20 °C, the reaction mixture was evaporated and the residue was extracted with *n*-hexane (10 × 10 mL). The combined *n*-hexane extracts were filtered through glass-wool and evaporated in vacuum to give a mixture of **1j**-ONO (71 %) and **2j** (21 %) [yields determined by ^{1}H NMR with CH_2Cl_2 as an internal standard].

The components of the product mixture were identified by comparison of their ^{1}H and ^{13}C NMR spectra with the spectra of pure **1j**-ONO and **2j**.

Reaction of bis(julolidin-9-yl)methylium tetrafluoroborate 1b-BF_4 with tetra-butylammonium nitrite



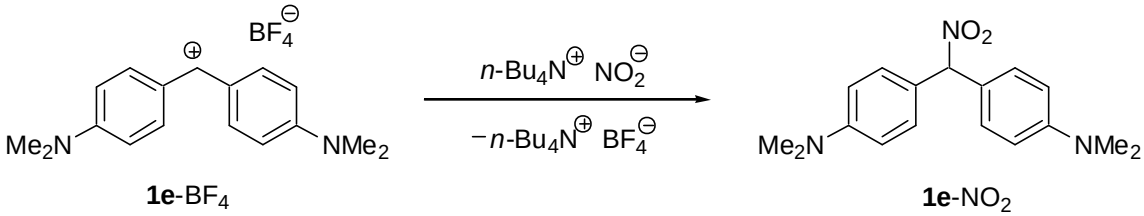
1b-BF_4 **1b**-NO_2

To a solution of **1b**-BF_4 (23 mg, 0.052 mmol) in dry CD_3CN (0.5 mL) quantitative standard (CH_2Cl_2) and a solution of *n*-$Bu_4N^+NO_2^-$ (72 mg, 0.25 mmol) in dry CD_3CN (0.5 mL) were added at 20 °C. The ^{1}H NMR spectrum recorded immediately after the thorough mixing revealed the formation of **1b**-NO_2 with a yield 93 %.

^{1}H NMR (200 MHz, CD_3CN): d = 1.91 (m, 8 H), 2.69 (t, 8 H, *J* = 6.4 Hz), 3.16 (t, 8 H), 6.45 (br.s, 1 H, Ar_2CH), 6.74 (br.s, 4 H).

[S1] W. E. Bachmann, *J. Am. Chem. Soc.* **1933**, *55*, 2135–2139.

Reaction of bis(4-dimethylaminophenyl)methylium tetrafluoroborate 1e-BF_4 with tetrabutylammonium nitrite



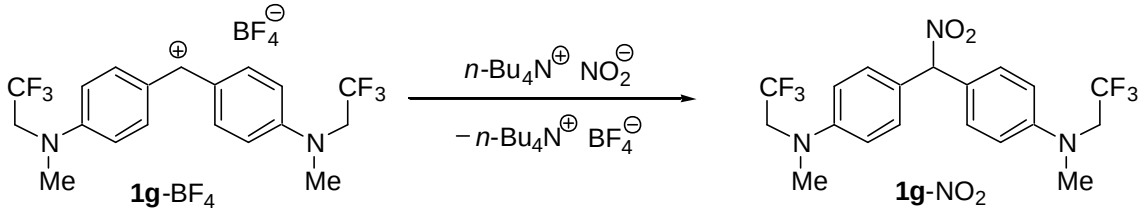
1e-BF_4 **1e**-NO_2

To a solution of **1e**-BF_4 (33 mg, 0.097 mmol) in dry CD_3CN (0.5 mL) quantitative standard (CH_2Cl_2) and a solution of *n*-$Bu_4N^+NO_2^-$ (34 mg, 0.12 mmol) in dry CD_3CN (0.5 mL) were added at 20 °C. After the thorough mixing ^{1}H NMR spectrum was recorded, which revealed the formation of **1e**-NO_2 with a yield 96 % and traces of 4,4'-dimethylaminobenzophenone, which accumulated with time in reaction mixture.

To a solution of **1e**-BF_4 (73 mg, 0.22 mmol) in dry MeCN (20 mL) a solution of *n*-$Bu_4N^+NO_2^-$ (95 mg, 0.33 mmol) in dry MeCN (10 mL) were added at 0 °C. The solvent was evaporated in vacuum and the residue was rapidly extracted with benzene / hexane mixture (1 : 1, 2 × 10 mL). The combined extracts were filtered through glass-wool under inert atmosphere and concentrated in vacuum to give **1e**-NO_2 as an unstable yellow powder (57 mg, 89 %, contains traces of 4,4'-dimethylaminobenzophenone).

^{1}H NMR (200 MHz, CD_3CN): d = 2.95 (s, 12 H), 6.72 (s, 1 H, Ar_2CH), 6.75 (d, 4 H, *J* = 8.8 Hz), 7.23 (d, 4 H, *J* = 8.8 Hz). ^{13}C NMR (100.6 MHz, CD_3CN): d = 40.5 (Me), 95.1 (Ar_2CH), 112.9 (CH), 128.9 (C_q), 130.2 (CH), 152.0 (C_q). ^{15}N NMR (40.5 MHz, gHMBC, C_6D_6 + $CDCl_3$): d = 3.8 (s, NO_2).

Reaction of bis(4-(methyl(2,2,2-trifluoroethyl)amino)phenyl)methylium tetrafluoroborate 1g-BF_4 with tetrabutylammonium nitrite

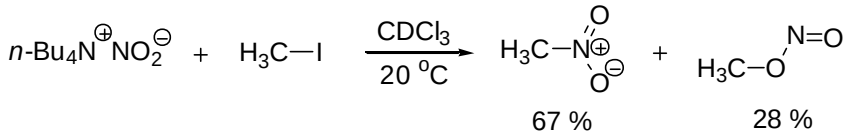


1g-BF_4 **1g**-NO_2

To a solution of **1g**-BF_4 (45 mg, 0.095 mmol) in dry CD_3CN (0.5 mL) quantitative standard (CH_2Cl_2) and a solution of *n*-$Bu_4N^+NO_2^-$ (54 mg, 0.19 mmol) in dry CD_3CN (0.5 mL) were added at 20 °C. After the thorough mixing ^{1}H NMR spectrum was recorded, which revealed the formation of a compound **1g**-NO_2 with a yield 93 % and 5 % of 4,4'-N,N'-(methyl(2,2,2-trifluoroethyl)amino-benzophenone, which accumulated with time in the reaction mixture.

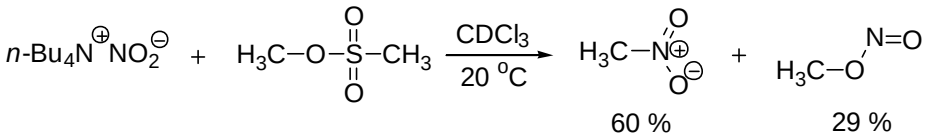
^{1}H NMR (200 MHz, CD_3CN): d = 3.06 (s, 6 H), 4.07 (q, 4 H, *J* = 9.3 Hz) , 6.77 (s, 1 H, Ar_2CH), 6.90 (d, 4 H, *J* = 9.1 Hz), 7.28 (d, 4 H, *J* = 9.1 Hz).

Reaction of methyl iodide with tetra-*n*-butylammonium nitrite



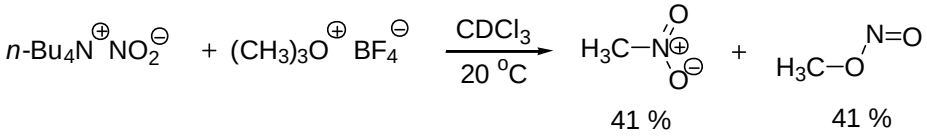
To a solution of *n*-$Bu_4N^+NO_2^-$ (40 mg, 0.14 mmol) in $CDCl_3$ (1 mL) neat MeI (10 mg, 0.070 mmol) and standard (MeOAc) was added. After 35 min ^1H NMR spectrum (200 MHz) was taken, which showed the peaks of $MeNO_2$ (67 %) and MeONO (28 %).[S2]

Reaction of methyl mesylate with tetra-*n*-butylammonium nitrite



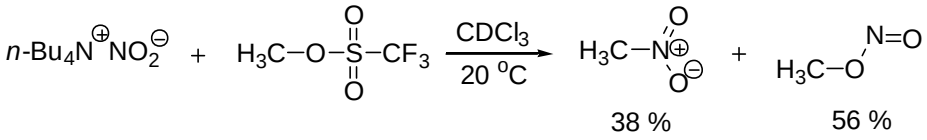
To a solution of *n*-$Bu_4N^+NO_2^-$ (85 mg, 0.30 mmol) in $CDCl_3$ (1 mL) neat MeOMs (21 mg, 0.19 mmol) and standard (MeOAc) was added. After 1 h ^1H NMR spectrum (200 MHz) was taken, which showed the peaks of $MeNO_2$ (60 %) and MeONO (29 %).[S2]

Reaction of trimethyloxonium tetrafluoroborate with tetra-*n*-butylammonium nitrite



To solid $Me_3O^+ BF_4^-$ (18 mg, 0.12 mmol) a solution of *n*-$Bu_4N^+NO_2^-$ (46 mg, 0.16 mmol) in $CDCl_3$ (1 mL) and standard (MeOAc) was added. After the dissolution of $Me_3O^+ BF_4^-$ (ca. 10 min) ^1H NMR spectrum (200 MHz) was recorded, which showed peaks of $MeNO_2$ (41 %), MeONO (41 %) and Me_2O.[S2]

Reaction of methyl triflate with tetra-*n*-butylammonium nitrite



To a solution of *n*-$Bu_4N^+NO_2^-$ (46 mg, 0.16 mmol) in $CDCl_3$ (1 mL) neat MeOTf (13 mg, 0.079 mmol) and standard (MeOAc) was added. After 5 min ^1H NMR spectrum (200 MHz) was taken, which showed the peaks of $MeNO_2$ (38 %) and MeONO (56 %).[S2]

[S2] For MeONO ^1H NMR ($CDCl_3$): d = 4.04 (br.) ppm: K. I. Lasaar, S. H. Bauer, *J. Phys. Chem.* **1984**, *88*, 3052–3059.