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Supporting Information

Nucleophilicities and Carbon Basicities of Pyridines

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Determination of Rate and Equilibrium Constants for Pyridines

Instrumentation. The rates of slow reactions ($\tau_{1/2}$ > 10 s) 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.

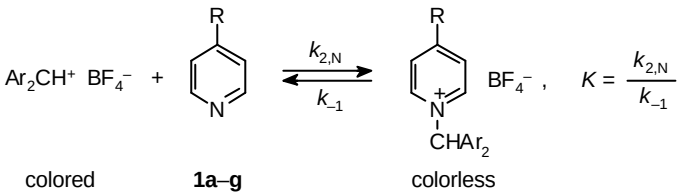
UV-Vis kinetic measurements of rapid reactions ($\tau_{1/2}$ < 10 s) were performed on a Hi-Tech SF-61DX2 stopped-flow spectrophotometer system. The kinetic experiments were initiated by fast mixing equal volumes of solutions of the nucleophile and the diarylcarbenium salt. The pseudo-first-order rate constants k_{obs} for the reactions were obtained from at least five runs at each nucleophile concentration.

The temperature of solutions during all kinetic studies was kept constant (± 0.2 °C) by using a circulating bath thermostat and monitored with a thermocouple probe.

For the evaluation of rate constants, absorption-time curves at wavelenghts in proximity to the absorption maxima of the diarylcarbenium ions Ar_2CH^+ were fitted to the single exponential function $A = A_0 \exp(-k_{obs} t) + C$.

Determination of the equilibrium constants in dichloromethane. For the determination of the equilibrium constants *K*, the pyridine was added to a solution of the benzhydrylium tetrafluoroborate. After reaching the equilibrium (Scheme S1),

Scheme S1



the absorption of the remaining benzhydrylium ions (Ar_2CH^+) was determined photometrically. The corresponding concentration [El] was calculated from a calibration curve. The equilibrium constants were calculated from the Equation (S1), where $[El]_0$ is the initial concentration of the benzhydrylium ions in the solution, [El] is the concentration of the benzhydrylium ions in the equilibrium mixture and $[Nu]_0$ is the initial concentration of the pyridine.

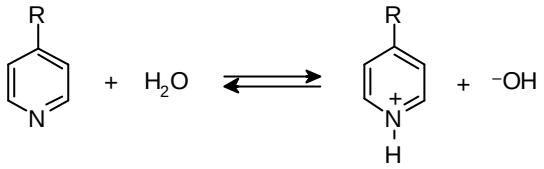
$$K = \frac{[El]_0 - [El]}{[El]([Nu]_0 - [El]_0 + [El])} \quad \text{(S1)}$$

Equilibrium constants *K* that have only been measured at 20 °C have been averaged and are given with standard deviations.

When measurements were made at variable temperatures, the equilibrium constants K(20 °C) have been derived from extrapolations of the linear plots of ln K versus 1/T (van't Hoff plot).

Kinetic measurements in water. If pyridine is dissolved in water, the concentration of hydroxide increases by protolysis (Scheme S2). For that reason we have to calculate the concentration of the free pyridines $[Nu]_{eff}$ and of hydroxide $[OH^-]$ with the pK_B of the pyridines.

Scheme S2.



$$K_B = \frac{[\text{pyridinium}]\ [OH^-]}{[\text{pyridine}]_{eff}} \qquad \text{(S2)}$$

$[\text{pyridine}]_0 = [\text{pyridine}]_{eff} + [\text{pyridinium}] = [\text{pyridine}]_{eff} + [OH^-]$ (S3)

(S3) in (S2)

$$K_B = \frac{[OH^-]^2}{[\text{pyridine}]_0 - [OH^-]} \qquad \text{(S4)}$$

Solving of the quadratic equation (S4) leads to one logic solution for $[OH^-]$, that is Equation S5 (the one with the "+" in the numerator).

$$[OH^-] = -\frac{K_B}{2} + \sqrt{\left(\frac{K_B}{2}\right)^2 + K_B[\text{pyridine}]_0} \qquad \text{(S5)}$$

The rates of the combination reactions were determined by mixing a colored aqueous solution of a benzhydrylium salt with an aqueous solution of a pyridine (>10 equivalents). As the products are colorless, we studied the reactions by UV-Vis spectroscopy and followed the decay of absorption with time [Eq. (S6)].

$$-\frac{d[R^+]}{dt} = k_{obs}[R^+] \qquad \text{(S6)}$$

The consumption of the benzhydrylium cations may be due to the reaction with the pyridines, hydroxide ions and the solvent water [Eq. (S7)].

$k_{obs} = k_{2,N}$ [pyridine]$_{eff} + k_{2,OH}[OH^-] + k_W + k_{-1}$ (S7)

$= k_{1\Psi} + k_{2,OH}[OH^-]$, with $k_{1\Psi} = k_{2,N}$ [pyridine]$_{eff} + k_W + k_{-1}$ and $[OH^-]$ from eq. (5)

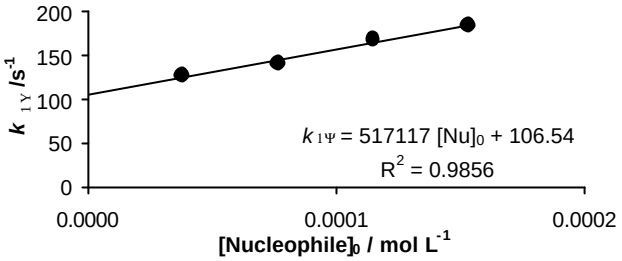
The pyridines are usually used in more than 10-fold excess over the benzhydrylium cations in order to run the reactions under pseudo first-order conditions. The concentrations of the pyridines as well as that of hydroxide remains therefore constant during the reactions. With the already published second-order rate constants $k_{2,OH}$ for the reactions of hydroxide with benzhydrylium ions[S1] and the first-order rate constants k_W for the reactions of water with benzhydrylium ions,[S2] we get the second-order rate constants for the reactions of the pyridines with the benzhydrylium ions $k_{2,N}$ from a plot of $k_{1\Psi}$ versus [pyridine]$_{eff}$.

Determination of the equilibrium constants in water. We were not able to directly measure the equilibrium constants K (Scheme S1) in water. When an aqueous solution of the benzhydrylium salt was combined with the pyridine, the UV/Vis spectrum for the benzhydrylium ion did not show a constant end absorption, because of the slow reactions of the benzhydrylium ions with hydroxide and water in the presence of pyridine. However, the ratio of the second-order rate constants $k_{2,N}$ for the forward reaction and the first order rate constant k_{-1} for the backward reaction, gave equilibrium constants, which are less accurate than the directly measured ones and are written in parentheses.

4-Chloropyridine (**1a**)

Reaction of 4-chloropyridine (**1a**) with $(pfa)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, J&M, detection at 601 nm)

$[(pfa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.80×10^{-6}	3.82×10^{-5}	8	1.28×10^2
4.80×10^{-6}	7.64×10^{-5}	16	1.42×10^2
4.80×10^{-6}	1.15×10^{-4}	24	1.69×10^2
4.80×10^{-6}	1.53×10^{-4}	32	1.85×10^2



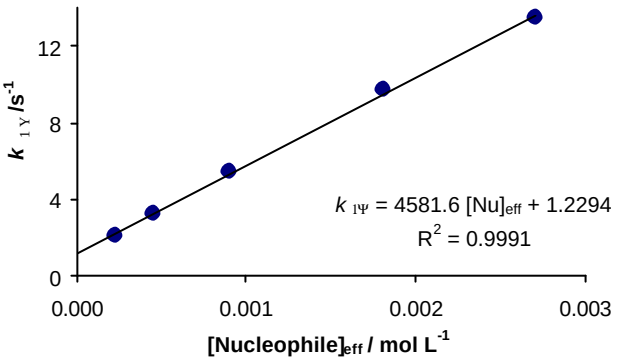
$k_{2,N}$ = 5.17×10^5 $M^{-1}s^{-1}$

k_{-1} = 1.07×10^2 s^{-1}

K = 4.83×10^3 M^{-1}

Reaction of 4-chloropyridine (**1a**) with $(mor)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.57×10^{-5}	2.71×10^{-3}	105	13.5
2.57×10^{-5}	1.81×10^{-3}	70	9.71
2.57×10^{-5}	9.03×10^{-4}	35	5.46
2.57×10^{-5}	4.51×10^{-4}	18	3.27
2.57×10^{-5}	2.26×10^{-4}	9	2.15



$k_{2,N}$ = 4.58×10^3 $M^{-1}s^{-1}$

k_{-1} = 1.23 s^{-1}

K = 3.73×10^3 M^{-1}

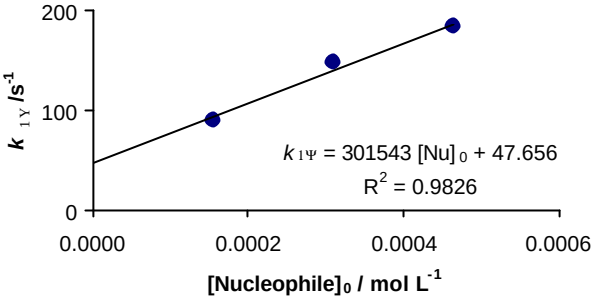
$k_{2,OH}$ = 1.06×10^3 $M^{-1}s^{-1}$

pK_B = 10.17

Pyridine (**1b**)

Reaction of pyridine (**1b**) with $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 674 nm)

$[(dpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.51×10^{-6}	4.64×10^{-4}	62	1.84×10^{2}
7.51×10^{-6}	3.09×10^{-4}	41	1.48×10^{2}
7.51×10^{-6}	1.55×10^{-4}	21	90.8



$k_{2,N}$ = 3.02×10^5 $M^{-1}s^{-1}$

k_{-1} = 47.7 s^{-1}

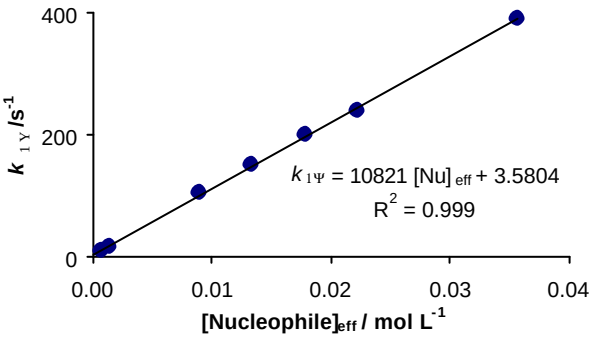
Equilibrium constants for the reaction of pyridine (**1b**) with $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, J&M, detection at 672 nm)

$[(dpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[(dpa)_2CH^+]$ / mol L^{-1}	K / L mol^{-1}
1.08×10^{-5}	1.36×10^{-4}	2.96×10^{-6}	2.07×10^{4}
1.65×10^{-5}	1.03×10^{-4}	5.28×10^{-6}	2.30×10^{4}
1.18×10^{-5}	6.86×10^{-5}	9.47×10^{-6}	2.32×10^{4}

K (20 °C) = $(2.23 \pm 0.11) \times 10^4$ L mol^{-1}

Reaction of pyridine (**1b**) with $(mor)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 607 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.29×10^{-5}	3.57×10^{-2}	1560	3.90×10^{2}
2.29×10^{-5}	2.23×10^{-2}	974	2.39×10^{2}
2.29×10^{-5}	1.79×10^{-2}	781	2.00×10^{2}
2.29×10^{-5}	1.34×10^{-2}	585	1.50×10^{2}
2.29×10^{-5}	8.93×10^{-3}	390	1.07×10^{2}
2.29×10^{-5}	1.43×10^{-3}	62	16.4
2.29×10^{-5}	7.13×10^{-4}	31	8.57



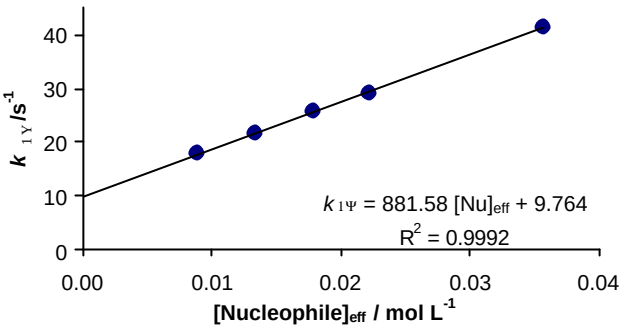
$k_{2,N}$ = 1.08×10^4 $M^{-1}s^{-1}$

$k_{2,OH}$ = 1.06×10^3 $M^{-1}s^{-1}$

pK_B = 8.77

Reaction of pyridine (**1b**) with $(dma)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 607 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.62×10^{-5}	3.57×10^{-2}	468	41.4
7.62×10^{-5}	2.23×10^{-2}	293	29.0
7.62×10^{-5}	1.79×10^{-2}	235	25.7
7.62×10^{-5}	1.34×10^{-2}	176	21.5
7.62×10^{-5}	8.93×10^{-3}	117	17.8



$k_{2,N} = 8.82 \times 10^2$ $M^{-1}s^{-1}$

$k_{-1} = 9.76$ s^{-1}

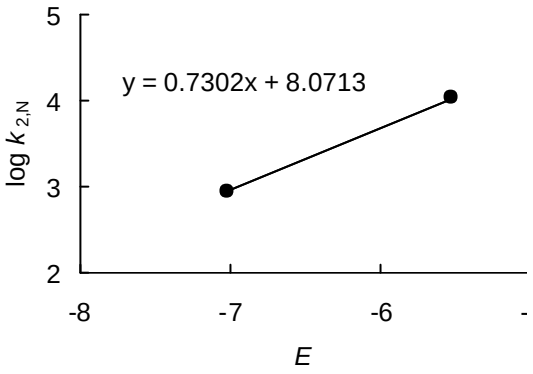
$K = 9.04 \times 10^1$ M^{-1}

$k_{2,OH} = 1.31 \times 10^2$ $M^{-1}s^{-1}$

$pK_B = 8.77$

Reactivity parameters of pyridine (**1b**) in water: $N = 11.05$; $s = 0.730$

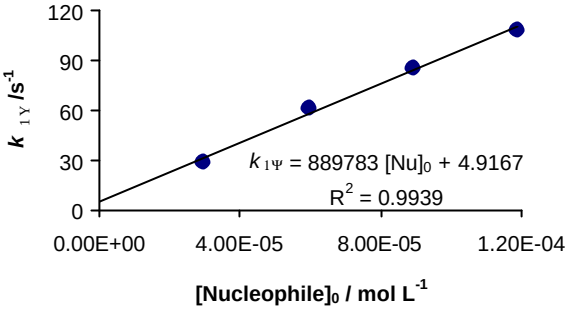
Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	–5.53	1.08×10^4
$(dma)_2CH^+$	–7.02	8.82×10^2



4-Methylpyridine (**1c**)

Reaction of 4-methylpyridine (**1c**) with $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 674 nm)

$[(dpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.30×10^{-6}	1.19×10^{-4}	28	1.09×10^{2}
4.30×10^{-6}	8.96×10^{-5}	21	85.7
4.30×10^{-6}	5.97×10^{-5}	14	61.3
4.30×10^{-6}	2.99×10^{-5}	7	29.0



$k_{2,N}$ = 8.90×10^5 $M^{-1}s^{-1}$

k_{-1} = 4.92 s^{-1}

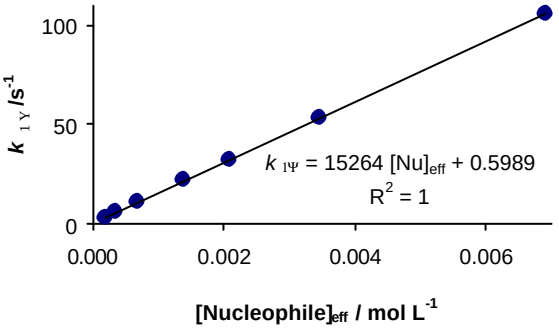
Equilibrium constants for the reaction of 4-methylpyridine (**1c**) with $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, in CH_2Cl_2, J&M, detection at 672 nm)

$[(dpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[(dpa)_2CH^+]$ / mol L^{-1}	K / L mol^{-1}
3.55×10^{-5}	6.49×10^{-5}	2.00×10^{-6}	5.34×10^{5}
3.46×10^{-5}	3.17×10^{-5}	8.63×10^{-6}	5.28×10^{5}
3.29×10^{-5}	1.81×10^{-5}	1.69×10^{-5}	4.60×10^{5}

K (20 °C) = $(5.07 \pm 0.34) \times 10^5$ L mol^{-1}

Reaction of 4-methylpyridine (**1c**) with $(mor)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
1.72×10^{-5}	6.91×10^{-3}	402	1.06×10^{2}
1.72×10^{-5}	3.45×10^{-3}	201	53.5
1.72×10^{-5}	2.08×10^{-3}	121	32.3
1.72×10^{-5}	1.38×10^{-3}	80	21.8
1.72×10^{-5}	6.89×10^{-4}	40	10.9
1.72×10^{-5}	3.44×10^{-4}	20	5.95
1.72×10^{-5}	1.72×10^{-4}	10	3.08



$k_{2,N}$ = 1.53×10^4 $M^{-1}s^{-1}$

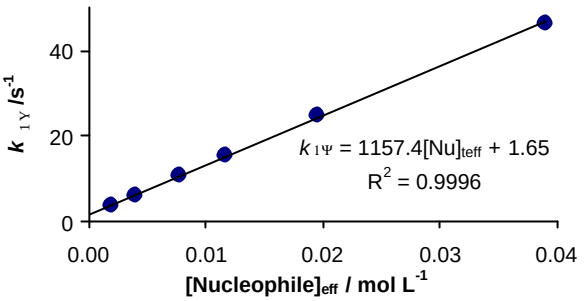
k_W = 0.673 s^{-1} [S2]

k_{2,OH^-} = 1.06×10^3 $M^{-1}s^{-1}$

pK_B = 7.94

Reaction of 4-methylpyridine (**1c**) with $(dma)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.61×10^{-5}	3.91×10^{-2}	848	46.6
4.61×10^{-5}	1.95×10^{-2}	423	24.7
4.61×10^{-5}	1.17×10^{-2}	254	15.4
4.61×10^{-5}	7.81×10^{-3}	169	10.7
4.61×10^{-5}	3.90×10^{-3}	85	5.97
4.61×10^{-5}	1.95×10^{-3}	42	3.66



$k_{2,N} = 1.16 \times 10^3$ $M^{-1}s^{-1}$

$k_{-1} = 1.65$ s^{-1}

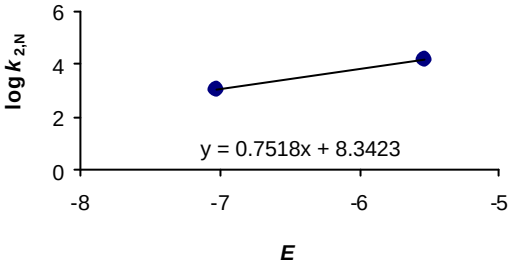
$K = 7.03 \times 10^2$ M^{-1}

$k_{2,OH} = 1.31 \times 10^2$ $M^{-1}s^{-1}$

$pK_B = 7.94$

Reactivity parameters of 4-methylpyridine (**1c**) in water: $N = 11.10$; $s = 0.752$

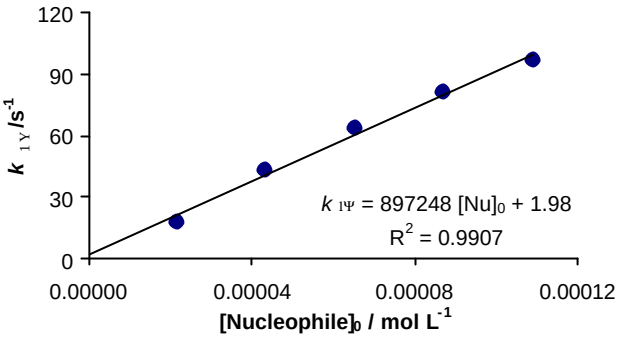
Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.53×10^4
$(dma)_2CH^+$	-7.02	1.16×10^3



4-Methoxypyridine (**1d**)

Reaction of 4-methoxypyridine (**1d**) with $(dpa)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 674 nm)

$[(dpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.30×10^{-6}	1.09×10^{-4}	25	97.0
4.30×10^{-6}	8.72×10^{-5}	20	81.1
4.30×10^{-6}	6.54×10^{-5}	15	63.7
4.30×10^{-6}	4.36×10^{-5}	10	43.5
4.30×10^{-6}	2.18×10^{-5}	5	18.0



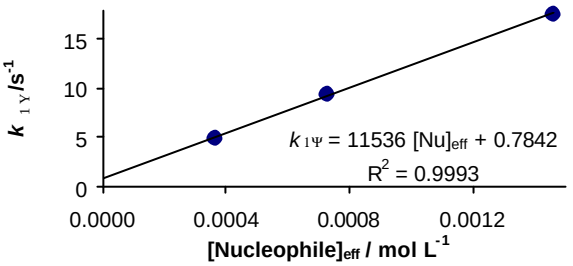
$k_{2,N} = 8.97 \times 10^5$ $M^{-1}s^{-1}$

$k_{-1} = 1.98$ s^{-1}

($K = 4.53 \times 10^5$ M^{-1})

Reaction of 4-methoxypyridine (**1d**) with $(mor)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
1.72×10^{-5}	1.46×10^{-3}	85	17.6
1.72×10^{-5}	7.29×10^{-4}	42	9.39
1.72×10^{-5}	3.63×10^{-4}	21	4.85



$k_{2,N} = 1.15 \times 10^4$ $M^{-1}s^{-1}$

$k_W = 0.673$ s^{-1} [S2]

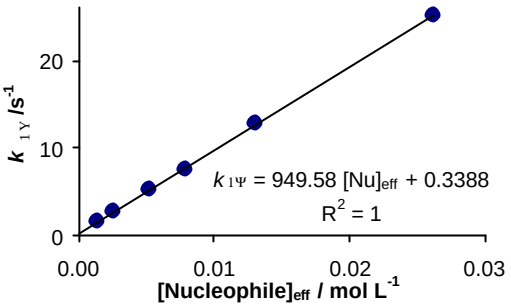
$k_{2,OH} = 1.06 \times 10^3$ $M^{-1}s^{-1}$

pK_B = 7.42

Reaction of 4-methoxypyridine (**1d**) with $(dma)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
4.61×10^{-5}	2.62×10^{-2}	568	25.2
4.61×10^{-5}	1.31×10^{-2}	284	12.8
4.61×10^{-5}	7.83×10^{-3}	170	7.67
4.61×10^{-5}	5.23×10^{-3}	113	5.31
4.61×10^{-5}	2.60×10^{-3}	56	2.82
4.61×10^{-5}	1.30×10^{-3}	28	1.62

$k_{2,N} = 9.50 \times 10^2$ $M^{-1}s^{-1}$



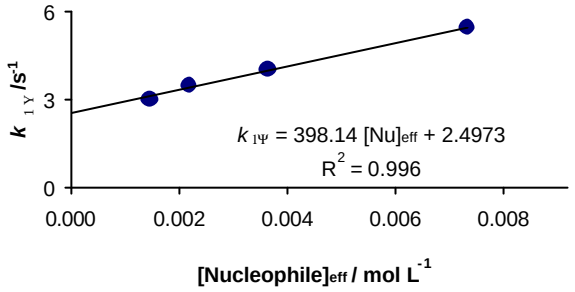
$k_W = 0.0206$ s^{-1} [S2]

$k_{2,OH} = 1.31 \times 10^2$ $M^{-1}s^{-1}$

$pK_B = 7.42$

Reaction of 4-methoxypyridine (**1d**) with $(pyr)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.5 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.54×10^{-5}	7.35×10^{-3}	289	5.41
2.54×10^{-5}	3.66×10^{-3}	144	3.97
2.54×10^{-5}	2.19×10^{-3}	86	3.45
2.54×10^{-5}	1.46×10^{-3}	58	3.01



$k_{2,N} = 3.98 \times 10^2$ $M^{-1}s^{-1}$

$k_{-1} = 2.50$ s^{-1}

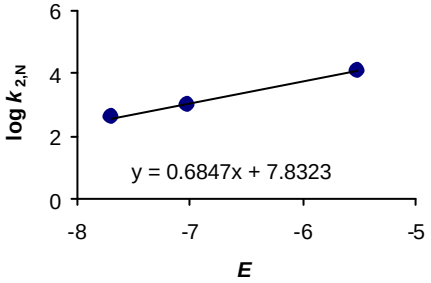
$K = 1.59 \times 10^2$ M^{-1}

$k_{2,OH^-} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 7.42$

Reactivity parameters of 4-methoxypyridine (**1d**) in water: $N = 11.44$; $s = 0.685$

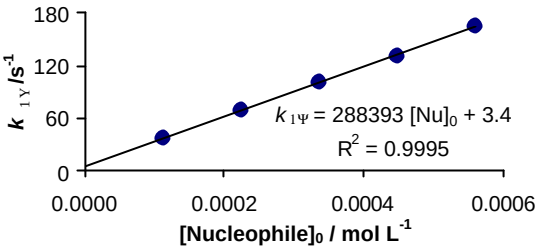
Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	1.15×10^4
$(dma)_2CH^+$	-7.02	9.50×10^2
$(pyr)_2CH^+$	-7.69	3.98×10^2



4-Aminopyridine (**1e**)

Reaction of 4-aminopyridine (**1e**) with $(dma)_2CH^+\ BF_4^-$ in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 612 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.80×10^{-6}	5.60×10^{-4}	72	1.66×10^2
7.80×10^{-6}	4.48×10^{-4}	57	1.31×10^2
7.80×10^{-6}	3.36×10^{-4}	43	1.00×10^2
7.80×10^{-6}	2.24×10^{-4}	29	69.0
7.80×10^{-6}	1.12×10^{-4}	14	35.5



$k_{2,N}$ = 2.88×10^5 $M^{-1}s^{-1}$

k_{-1} = 3.40 s^{-1}

K = 8.48×10^4 M^{-1}

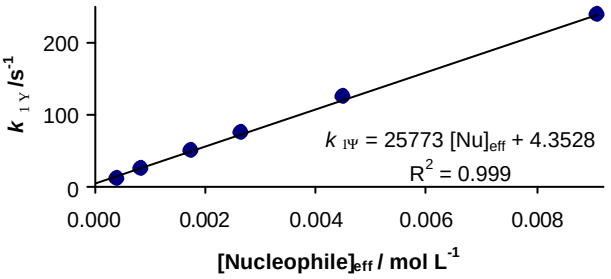
Reaction of 4-aminopyridine (**1e**) with $(mor)_2CH^+\ BF_4^-$ in water (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
3.65×10^{-5}	9.45×10^{-3}	9.10×10^{-3}	3.46×10^{-4}	249	2.37×10^2	3.67×10^{-1}	2.37×10^2
3.65×10^{-5}	4.73×10^{-3}	4.49×10^{-3}	2.43×10^{-4}	123	1.24×10^2	2.58×10^{-1}	1.24×10^2
3.65×10^{-5}	2.84×10^{-3}	2.65×10^{-3}	1.87×10^{-4}	73	74.9	1.98×10^{-1}	74.7
3.65×10^{-5}	1.89×10^{-3}	1.74×10^{-3}	1.51×10^{-4}	48	50.3	1.60×10^{-1}	50.1
3.65×10^{-5}	9.45×10^{-4}	8.40×10^{-4}	1.05×10^{-4}	23	24.6	1.12×10^{-1}	24.5
3.65×10^{-5}	4.73×10^{-4}	4.00×10^{-4}	7.26×10^{-5}	11	11.9	7.70×10^{-2}	11.8

$k_{2,N}$ = 2.58×10^4 $M^{-1}s^{-1}$

$k_{2,OH}$ = 1.06×10^3 $M^{-1}s^{-1}$

pK_B = 4.88



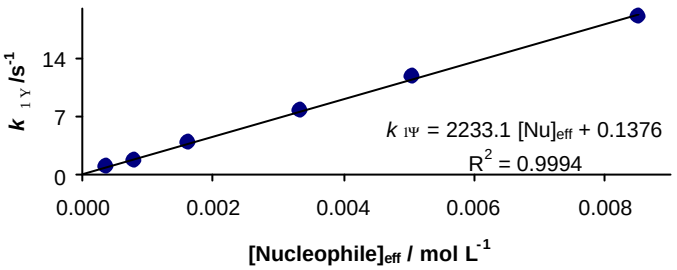
Reaction of 4-aminopyridine (**1e**) with $(dma)_2CH^+\ BF_4^-$ in water (at 20 °C, cosolvent: 0.3 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
5.95×10^{-5}	8.85×10^{-3}	8.51×10^{-3}	3.35×10^{-4}	143	19.0	4.39×10^{-2}	19.0
5.95×10^{-5}	5.31×10^{-3}	5.05×10^{-3}	2.58×10^{-4}	85	11.7	3.38×10^{-2}	11.7
5.95×10^{-5}	3.54×10^{-3}	3.33×10^{-3}	2.10×10^{-4}	56	7.75	2.74×10^{-2}	7.72
5.95×10^{-5}	1.77×10^{-3}	1.62×10^{-3}	1.46×10^{-4}	27	3.82	1.92×10^{-2}	3.80
5.95×10^{-5}	8.85×10^{-4}	7.83×10^{-4}	1.02×10^{-4}	13	1.80	1.33×10^{-2}	1.79
5.95×10^{-5}	4.43×10^{-4}	3.73×10^{-4}	7.01×10^{-5}	6	8.44×10^{-1}	9.18×10^{-3}	8.35×10^{-1}

$k_{2,N} = 2.23 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH} = 1.31 \times 10^2\ M^{-1}s^{-1}$

$pK_B = 4.88$



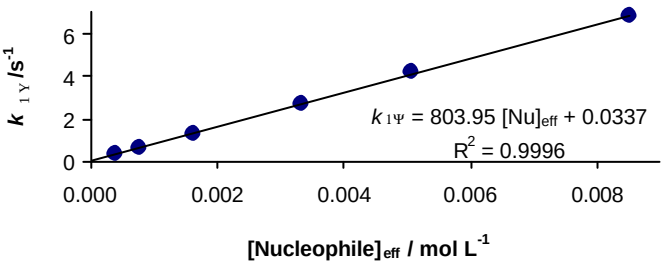
Reaction of 4-aminopyridine (**1e**) with $(pyr)_2CH^+\ BF_4^-$ in water (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 608 nm)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.05×10^{-5}	8.85×10^{-3}	8.51×10^{-3}	3.35×10^{-4}	811	6.84	1.62×10^{-2}	6.82
1.05×10^{-5}	5.31×10^{-3}	5.05×10^{-3}	2.58×10^{-4}	481	4.19	1.25×10^{-2}	4.18
1.05×10^{-5}	3.54×10^{-3}	3.33×10^{-3}	2.10×10^{-4}	317	2.76	1.02×10^{-2}	2.75
1.05×10^{-5}	1.77×10^{-3}	1.62×10^{-3}	1.46×10^{-4}	155	1.31	7.10×10^{-3}	1.30
1.05×10^{-5}	8.85×10^{-4}	7.83×10^{-4}	1.02×10^{-4}	75	6.63×10^{-1}	4.93×10^{-3}	6.58×10^{-1}
1.05×10^{-5}	4.43×10^{-4}	3.73×10^{-4}	7.01×10^{-5}	36	3.13×10^{-1}	3.40×10^{-3}	3.10×10^{-1}

$k_{2,N} = 8.04 \times 10^2\ M^{-1}s^{-1}$

$k_{2,OH} = 48.5\ M^{-1}s^{-1}$

$pK_B = 4.88$



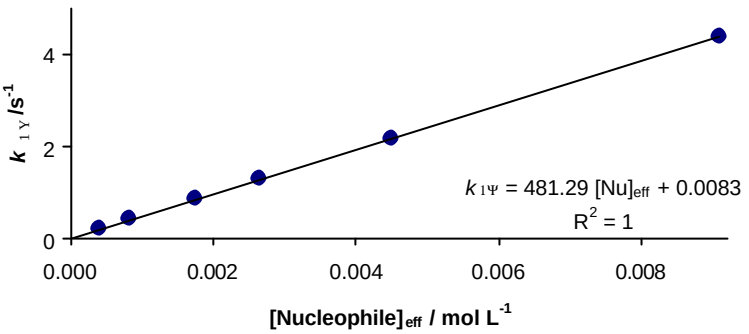
Reaction of 4-aminopyridine (**1e**) with $(thq)_2CH^+ BF_4^-$ in water (at 20 °C, cosolvent: 0.9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
3.01×10^{-5}	9.45×10^{-3}	9.10×10^{-3}	3.46×10^{-4}	302	4.39	8.18×10^{-3}	4.38
3.01×10^{-5}	4.73×10^{-3}	4.49×10^{-3}	2.43×10^{-4}	149	2.19	5.74×10^{-3}	2.18
3.01×10^{-5}	2.84×10^{-3}	2.65×10^{-3}	1.87×10^{-4}	88	1.29	4.41×10^{-3}	1.29
3.01×10^{-5}	1.89×10^{-3}	1.74×10^{-3}	1.51×10^{-4}	58	8.50×10^{-1}	3.57×10^{-3}	8.46×10^{-1}
3.01×10^{-5}	9.45×10^{-4}	8.40×10^{-4}	1.05×10^{-4}	28	4.10×10^{-1}	2.48×10^{-3}	4.08×10^{-1}
3.01×10^{-5}	4.73×10^{-4}	4.00×10^{-4}	7.26×10^{-5}	13	1.97×10^{-1}	1.71×10^{-3}	1.95×10^{-1}

$k_{2,N} = 4.81 \times 10^2\ M^{-1}s^{-1}$

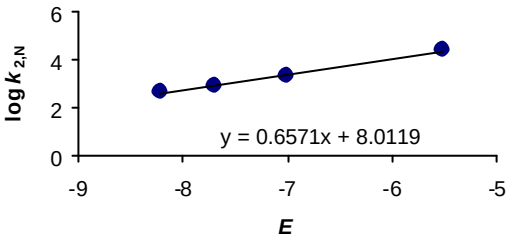
$k_{2,OH} = 23.6\ M^{-1}s^{-1}$ [S3]

$pK_B = 4.88$



Reactivity parameters of 4-aminopyridine (**1e**) in water: $N = 12.19$; $s = 0.657$

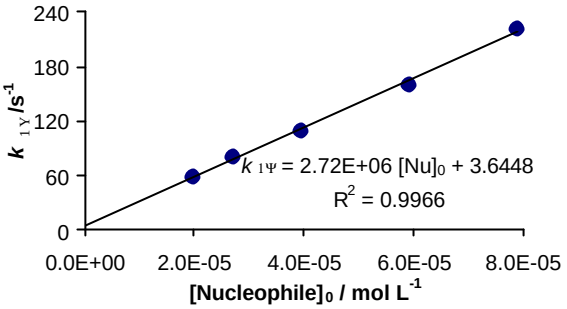
Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	2.58×10^4
$(dma)_2CH^+$	-7.02	2.23×10^3
$(pyr)_2CH^+$	-7.69	8.04×10^2
$(thq)_2CH^+$	-8.22	4.81×10^2



4-(Dimethylamino)pyridine (DMAP, **1f**) in CH_2Cl_2

Reaction of DMAP (**1f**) with $(mpa)_2CH^+ BF_4^-$ in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 622 nm)

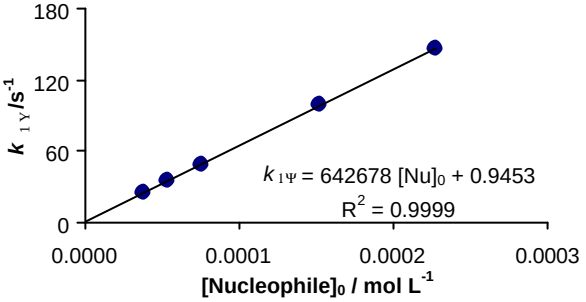
$[(mpa)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.76×10^{-6}	7.89×10^{-5}	29	2.22×10^2
2.76×10^{-6}	5.92×10^{-5}	21	1.59×10^2
2.76×10^{-6}	3.95×10^{-5}	14	1.09×10^2
2.76×10^{-6}	2.70×10^{-5}	10	80.0
2.76×10^{-6}	1.97×10^{-5}	7	57.7



$k_{2,N} = 2.72 \times 10^6\ M^{-1}s^{-1}$

Reaction of DMAP (**1f**) with $(dma)_2CH^+ BF_4^-$ in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 613 nm)

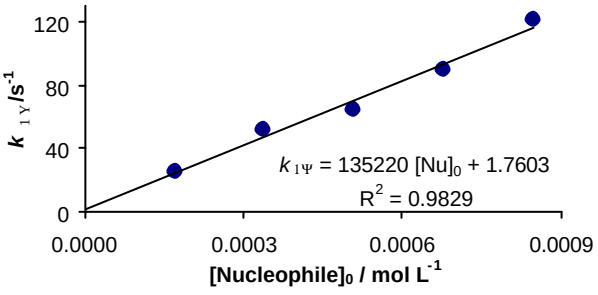
$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.20×10^{-6}	2.28×10^{-4}	32	1.47×10^2
7.20×10^{-6}	1.52×10^{-4}	21	99.5
7.20×10^{-6}	7.60×10^{-5}	11	49.7
7.20×10^{-6}	5.32×10^{-5}	7	34.8
7.20×10^{-6}	3.80×10^{-5}	5	25.4



$k_{2,N} = 6.43 \times 10^5\ M^{-1}s^{-1}$

Reaction of DMAP (**1f**) with $(thq)_2CH^+ BF_4^-$ in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 628 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.59×10^{-6}	8.48×10^{-4}	112	1.21×10^2
7.59×10^{-6}	6.78×10^{-4}	89	89.8
7.59×10^{-6}	5.09×10^{-4}	67	64.6
7.59×10^{-6}	3.39×10^{-4}	45	52.2
7.59×10^{-6}	1.70×10^{-4}	22	25.2



$k_{2,N} = 1.35 \times 10^5\ M^{-1}s^{-1}$

Equilibrium constants for the reaction of DMAP (**1f**) with $(thq)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, J&M, detection at 628 nm)

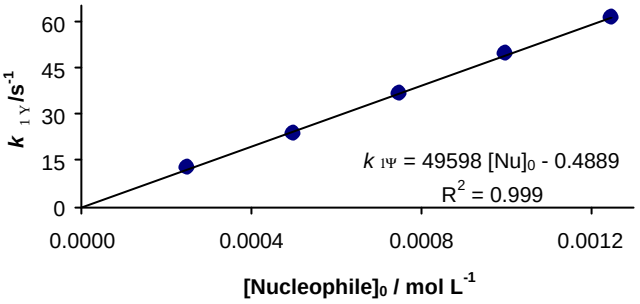
$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[(thq)_2CH^+]$ / mol L^{-1}	K / L mol^{-1}
1.69×10^{-5}	7.04×10^{-5}	1.17×10^{-6}	2.45×10^{5}
2.01×10^{-5}	8.38×10^{-5}	1.68×10^{-6}	1.68×10^{5}
2.65×10^{-5}	7.35×10^{-5}	1.83×10^{-6}	2.76×10^{5}
2.65×10^{-5}	3.68×10^{-5}	4.56×10^{-6}	3.23×10^{5}

K(20 °C) = (2.81 ± 0.32) × 10^5 L mol^{-1}

Reaction of DMAP (**1f**) with $(ind)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 625 nm)

$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.48×10^{-6}	1.25×10^{-3}	167	61.3
7.48×10^{-6}	9.97×10^{-4}	133	49.6
7.48×10^{-6}	7.48×10^{-4}	100	36.5
7.48×10^{-6}	4.99×10^{-4}	67	23.4
7.48×10^{-6}	2.49×10^{-4}	33	12.4

$k_{2,N}$ = 4.96×10^4 $M^{-1}s^{-1}$



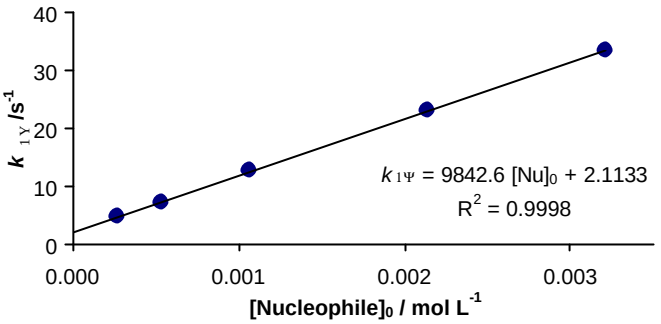
Equilibrium constants for the reaction of DMAP (**1f**) with $(ind)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, J&M, detection at 625 nm)

$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[(ind)_2CH^+]$ / mol L^{-1}	K / L mol^{-1}
2.08×10^{-5}	1.55×10^{-4}	7.27×10^{-7}	2.06×10^{5}
2.08×10^{-5}	7.76×10^{-5}	1.93×10^{-6}	1.67×10^{5}
2.36×10^{-5}	8.78×10^{-5}	1.97×10^{-6}	1.66×10^{5}
2.36×10^{-5}	4.40×10^{-5}	5.01×10^{-6}	1.46×10^{5}

K(20 °C) = (1.71 ± 0.22) × 10^5 L mol^{-1}

Reaction of DMAP (**1f**) with $(jul)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 642 nm)

$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.65×10^{-6}	3.21×10^{-3}	420	33.7
7.65×10^{-6}	2.14×10^{-3}	280	23.1
7.65×10^{-6}	1.07×10^{-3}	140	12.9
7.65×10^{-6}	5.35×10^{-4}	70	7.24
7.65×10^{-6}	2.68×10^{-4}	35	4.72



$k_{2,N} = 9.84 \times 10^3$ $M^{-1}s^{-1}$

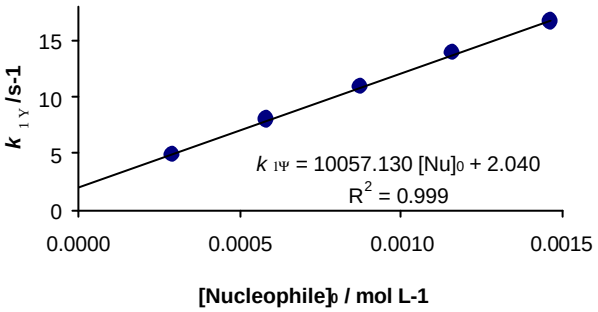
Equilibrium constants for the reaction of DMAP (**1f**) with $(jul)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, J&M, detection at 642 nm)

$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[(jul)_2CH^+]$ / mol L^{-1}	K / L mol^{-1}
2.16×10^{-5}	4.78×10^{-4}	5.82×10^{-6}	5.87×10^3
2.16×10^{-5}	3.20×10^{-4}	7.75×10^{-6}	5.85×10^3
2.16×10^{-5}	1.60×10^{-4}	1.15×10^{-5}	5.83×10^3

K(20 °C) = (5.85 ± 0.02) $\times 10^3$ L mol^{-1}

Reaction of DMAP (**1f**) with $(jul)_2CH^+$ PF_6^- in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 642 nm)

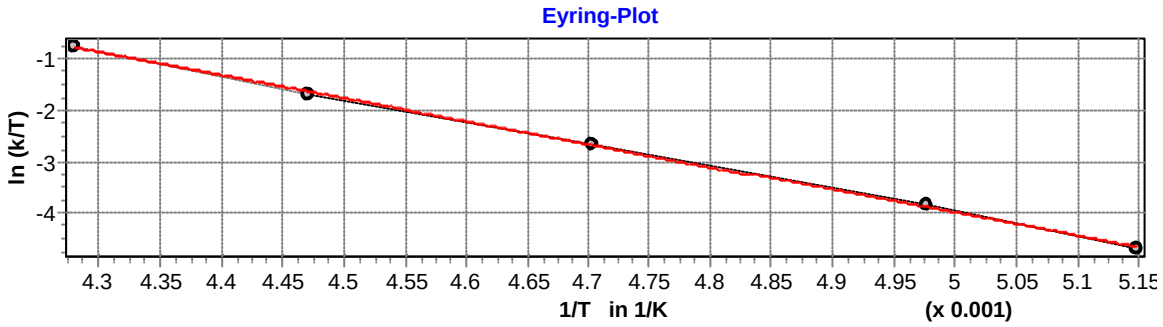
$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
8.40×10^{-6}	1.46×10^{-3}	174	16.6
8.40×10^{-6}	1.16×10^{-3}	138	13.8
8.40×10^{-6}	8.73×10^{-4}	104	10.9
8.40×10^{-6}	5.82×10^{-4}	69	7.95
8.40×10^{-6}	2.91×10^{-4}	38	4.86



$k_{2,N} = 1.01 \times 10^4$ $M^{-1}s^{-1}$

Reaction of DMAP (**1f**) with $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 (CH_2Cl_2, Schölly, detection at 640 nm)

$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	Conv. / %	T / °C	$k_{2,N}$ / L mol^{-1} s^{-1}
3.00×10^{-5}	3.27×10^{-3}	109	84	-78.9	1.77
3.61×10^{-5}	3.04×10^{-3}	84	87	-72.2	4.27
2.69×10^{-5}	2.35×10^{-3}	87	76	-60.5	1.50×10^{1}
3.13×10^{-5}	1.71×10^{-3}	55	73	-49.5	4.13×10^{1}
2.40×10^{-5}	1.05×10^{-3}	44	90	-39.5	1.09×10^{2}



Eyring parameters:

$\Delta H^{\ddagger}$ = 37.1 ± 0.52 kJ mol^{-1}

$\Delta S^{\ddagger}$ = -45.3 ± 2.5 J mol^{-1} K^{-1}

r^2 = 0.9994

$k_{2,N}$ (20 °C) = (6.45 ± 0.53) × 10^3 L mol^{-1} s^{-1}

Arrhenius parameters:

E_a = 38.9 ± 0.52 kJ mol^{-1}

ln A = 24.7 ± 0.30

r^2 = 0.9995

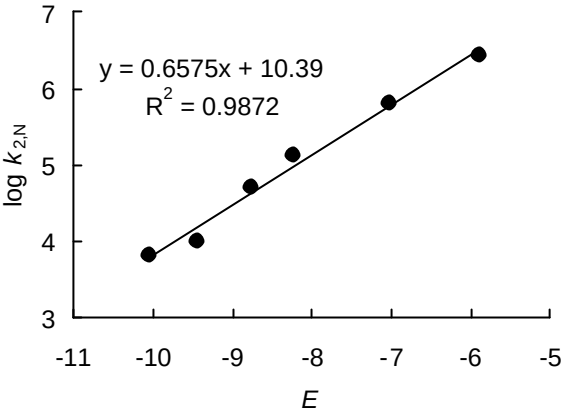
Equilibrium constants for the reaction of DMAP (**1f**) with $(lil)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, J&M, detection at 639 nm)

$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[(lil)_2CH^+]$ / mol L^{-1}	K / L mol^{-1}
1.69×10^{-5}	7.23×10^{-4}	3.33×10^{-6}	5.76×10^{3}
1.69×10^{-5}	4.83×10^{-4}	4.60×10^{-6}	5.70×10^{3}
1.69×10^{-5}	2.42×10^{-4}	7.34×10^{-6}	5.63×10^{3}
1.85×10^{-5}	1.32×10^{-4}	1.08×10^{-5}	5.72×10^{3}

K (20 °C) = (5.70 ± 0.05) × 10^3 L mol^{-1}

Reactivity parameters of DMAP (**1f**) in CH_2Cl_2: N = 15.80; s = 0.658

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mpa)_2CH^+$	-5.89	2.72×10^6
$(dma)_2CH^+$	-7.02	6.43×10^5
$(thq)_2CH^+$	-8.22	1.35×10^5
$(ind)_2CH^+$	-8.76	4.96×10^4
$(jul)_2CH^+$	-9.45	9.84×10^3
$(lil)_2CH^+$	-10.04	6.45×10^3

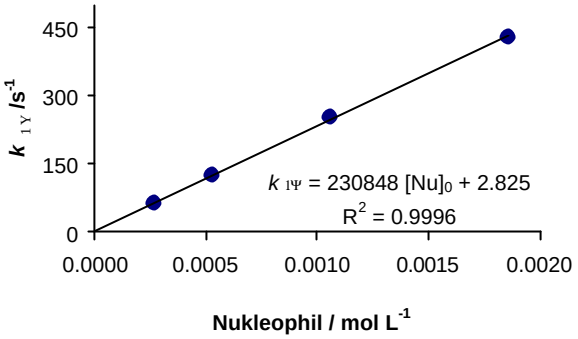


4-(Dimethylamino)pyridine (DMAP, **1f**) in Acetonitrile

Reaction of DMAP (**1f**) with $(dma)_2CH^+\ BF_4^-$ in CH_3CN (at 20 °C, stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
1.14×10^{-5}	1.86×10^{-3}	163	4.30×10^{2}
1.14×10^{-5}	1.06×10^{-3}	93	2.52×10^{2}
1.14×10^{-5}	5.30×10^{-4}	46	1.25×10^{2}
1.14×10^{-5}	2.65×10^{-4}	23	61.9

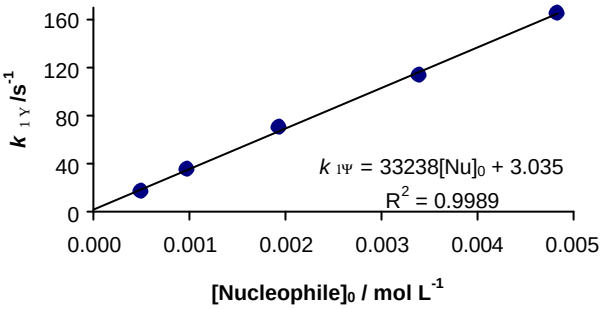
$k_{2,N} = 2.31 \times 10^{5}\ M^{-1}s^{-1}$



Reaction of DMAP (**1f**) with $(thq)_2CH^+\ BF_4^-$ in CH_3CN (at 20 °C, stopped-flow, detection at 622 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
9.64×10^{-6}	4.84×10^{-3}	502	1.64×10^{2}
9.64×10^{-6}	3.39×10^{-3}	352	1.14×10^{2}
9.64×10^{-6}	1.93×10^{-3}	200	70.3
9.64×10^{-6}	9.67×10^{-4}	100	35.3
9.64×10^{-6}	4.84×10^{-4}	50	17.5

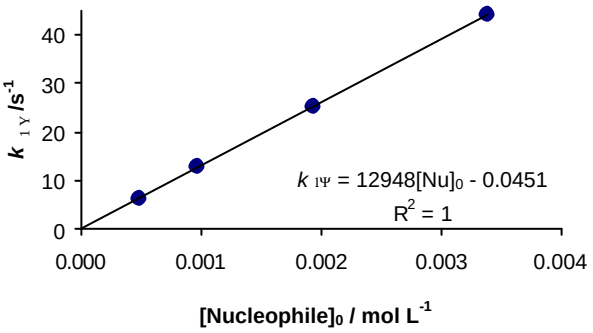
$k_{2,N} = 3.32 \times 10^{4}\ M^{-1}s^{-1}$



Reaction of DMAP (**1f**) with $(ind)_2CH^+\ BF_4^-$ in CH_3CN (at 20 °C, stopped-flow, detection at 630 nm)

$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
7.74×10^{-6}	3.39×10^{-3}	438	43.8
7.74×10^{-6}	1.93×10^{-3}	249	25.0
7.74×10^{-6}	9.67×10^{-4}	125	12.6
7.74×10^{-6}	4.84×10^{-4}	63	6.09

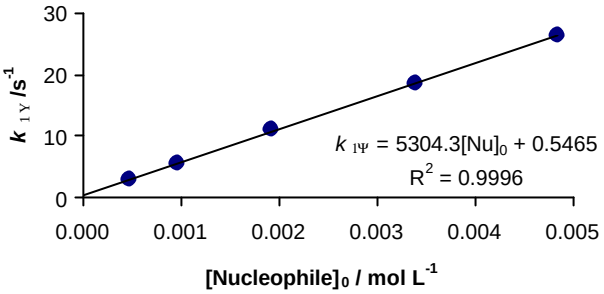
$k_{2,N} = 1.29 \times 10^{4}\ M^{-1}s^{-1}$



Reaction of DMAP (**1f**) with $(jul)_2CH^+ BF_4^-$ in CH_3CN (at 20 °C, stopped-flow, detection at 630 nm)

$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.86×10^{-6}	4.84×10^{-3}	1692	26.2
2.86×10^{-6}	3.39×10^{-3}	1185	18.4
2.86×10^{-6}	1.93×10^{-3}	675	11.1
2.86×10^{-6}	9.67×10^{-4}	338	5.67
2.86×10^{-6}	4.84×10^{-4}	169	2.95

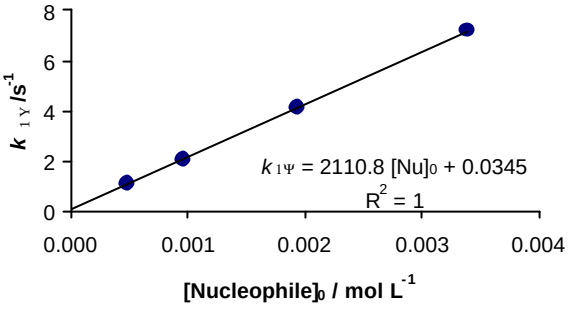
$k_{2,N} = 5.30 \times 10^3$ $M^{-1}s^{-1}$



Reaction of DMAP (**1f**) with $(lil)_2CH^+ BF_4^-$ in CH_3CN (at 20 °C, stopped-flow, detection at 630 nm)

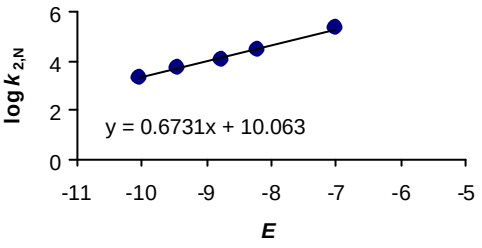
$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
9.18×10^{-6}	3.39×10^{-3}	369	7.20
9.18×10^{-6}	1.93×10^{-3}	210	4.09
9.18×10^{-6}	9.67×10^{-4}	105	2.07
9.18×10^{-6}	4.84×10^{-4}	53	1.07

$k_{2,N} = 2.11 \times 10^3$ $M^{-1}s^{-1}$



Reactivity parameters of DMAP (**1f**) in CH_3CN: $N = 14.95$; $s = 0.673$

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(dma)_2CH^+$	-7.02	2.31×10^5
$(thq)_2CH^+$	-8.22	3.32×10^4
$(ind)_2CH^+$	-8.76	1.29×10^4
$(jul)_2CH^+$	-9.45	5.30×10^3
$(lil)_2CH^+$	-10.04	2.11×10^3



4-(Dimethylamino)pyridine (DMAP, **1f**) in Water

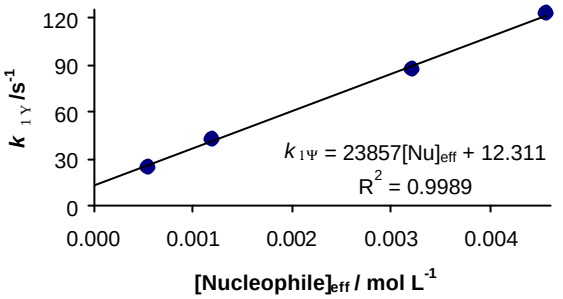
Reaction of DMAP (**1f**) with $(mor)_2CH^+\ BF_4^-$ in water (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 607 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
8.35×10^{-5}	5.06×10^{-3}	4.58×10^{-3}	4.79×10^{-4}	55	1.23×10^{2}	5.08×10^{-1}	1.22×10^{2}
8.35×10^{-5}	3.62×10^{-3}	3.22×10^{-3}	4.02×10^{-4}	39	87.8	4.26×10^{-1}	87.4
8.35×10^{-5}	1.45×10^{-3}	1.20×10^{-3}	2.46×10^{-4}	14	42.8	2.60×10^{-1}	42.5
8.35×10^{-5}	7.24×10^{-4}	5.52×10^{-4}	1.67×10^{-4}	7	25.1	1.77×10^{-1}	24.9

$k_{2,N} = 2.39 \times 10^4\ M^{-1}s^{-1}$

$k_{2,OH} = 1.06 \times 10^3\ M^{-1}s^{-1}$

$pK_B = 4.30$



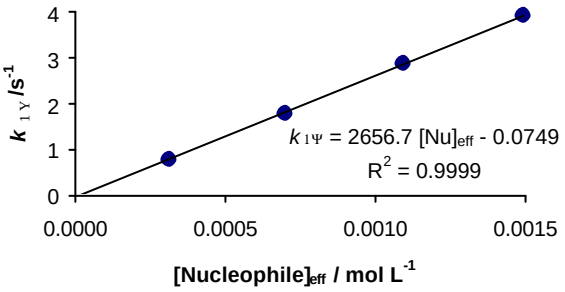
Reaction of DMAP (**1f**) with $(dma)_2CH^+\ BF_4^-$ in water (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 604 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
8.32×10^{-5}	1.78×10^{-3}	1.51×10^{-3}	2.75×10^{-4}	18	3.95	3.60×10^{-2}	3.91
8.32×10^{-5}	1.34×10^{-3}	1.10×10^{-3}	2.35×10^{-4}	13	2.91	3.08×10^{-2}	2.88
8.32×10^{-5}	8.91×10^{-4}	7.03×10^{-4}	1.88×10^{-4}	8	1.81	2.46×10^{-2}	1.79
8.32×10^{-5}	4.45×10^{-4}	3.19×10^{-4}	1.26×10^{-4}	4	$7.87\ 10^{-1}$	1.66×10^{-2}	7.70×10^{-1}

$k_{2,N} = 2.66 \times 10^3\ M^{-1}s^{-1}$

$k_{2,OH} = 1.31 \times 10^2\ M^{-1}s^{-1}$

$pK_B = 4.30$



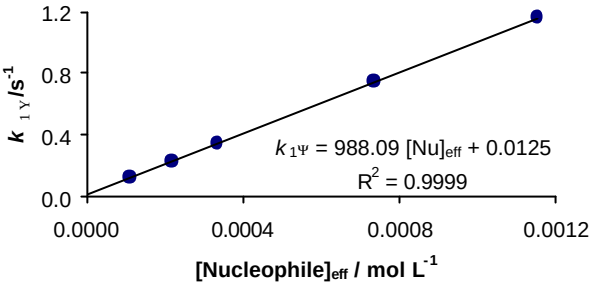
Reaction of DMAP (**1f**) with $(pyr)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 611 nm)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.26×10^{-5}	1.40×10^{-3}	1.16×10^{-3}	2.41×10^{-4}	92	1.17	1.17×10^{-2}	1.16
1.26×10^{-5}	9.35×10^{-4}	7.42×10^{-4}	1.93×10^{-4}	59	7.53×10^{-1}	9.35×10^{-3}	7.44×10^{-1}
1.26×10^{-5}	4.67×10^{-4}	3.37×10^{-4}	1.30×10^{-4}	27	3.53×10^{-1}	6.30×10^{-3}	3.47×10^{-1}
1.26×10^{-5}	3.27×10^{-4}	2.22×10^{-4}	1.05×10^{-4}	18	2.38×10^{-1}	5.11×10^{-3}	2.33×10^{-1}
1.26×10^{-5}	1.87×10^{-4}	1.12×10^{-4}	7.49×10^{-5}	9	1.31×10^{-1}	3.63×10^{-3}	1.27×10^{-1}

$k_{2,N} = 9.88 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH} = 48.5$ $M^{-1}s^{-1}$

pK_B = 4.30



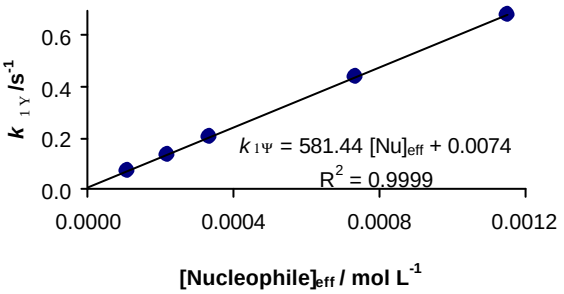
Reaction of DMAP (**1f**) with $(thq)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 611 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.58×10^{-5}	1.40×10^{-3}	1.16×10^{-3}	2.41×10^{-4}	73	6.85×10^{-1}	5.69×10^{-3}	6.79×10^{-1}
1.58×10^{-5}	9.35×10^{-4}	7.42×10^{-4}	1.93×10^{-4}	47	4.45×10^{-1}	4.55×10^{-3}	4.40×10^{-1}
1.58×10^{-5}	4.67×10^{-4}	3.37×10^{-4}	1.30×10^{-4}	21	2.10×10^{-1}	3.07×10^{-3}	2.07×10^{-1}
1.58×10^{-5}	3.27×10^{-4}	2.22×10^{-4}	1.05×10^{-4}	14	1.40×10^{-1}	2.49×10^{-3}	1.38×10^{-1}
1.58×10^{-5}	1.87×10^{-4}	1.12×10^{-4}	7.49×10^{-5}	7	7.40×10^{-2}	1.77×10^{-3}	7.22×10^{-2}

$k_{2,N} = 5.81 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH} = 23.6$ $M^{-1}s^{-1}$ [S3]

pK_B = 4.30



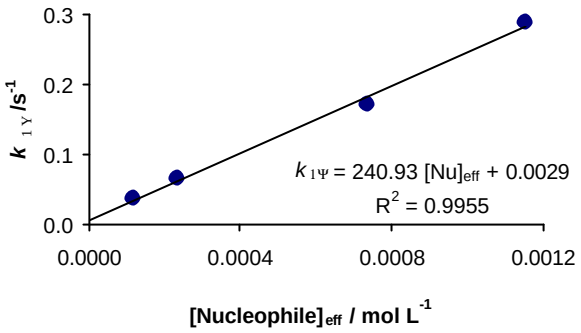
Reaction of DMAP (**1f**) with $(ind)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow and J&M, detection at 614 nm)

$[(ind)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.48×10^{-5}	1.40×10^{-3}	1.16×10^{-3}	2.41×10^{-4}	78	2.91×10^{-1}	2.60×10^{-3}	2.88×10^{-1}
1.48×10^{-5}	9.35×10^{-4}	7.42×10^{-4}	1.93×10^{-4}	50	1.72×10^{-1}	2.08×10^{-3}	1.70×10^{-1}
1.47×10^{-5}	3.43×10^{-4}	2.35×10^{-4}	1.08×10^{-4}	16	6.63×10^{-2}	1.17×10^{-3}	6.51×10^{-2}
1.48×10^{-5}	1.97×10^{-4}	1.20×10^{-4}	7.74×10^{-5}	8	3.60×10^{-2}	8.36×10^{-4}	3.52×10^{-2}

$k_{2,N} = 2.41 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH} = 10.8$ $M^{-1}s^{-1}$

$pK_B = 4.30$



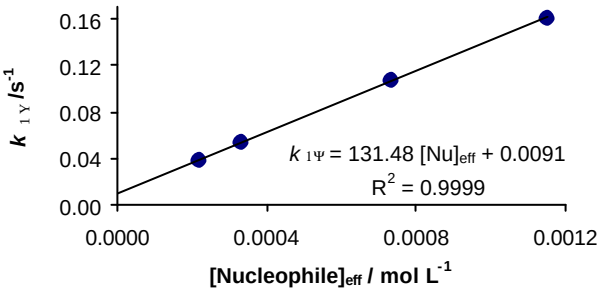
Reaction of DMAP (**1f**) with $(jul)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.2 vol-% CH_3CN, stopped-flow, detection at 630 nm)

$[(jul)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.26×10^{-5}	1.40×10^{-3}	1.16×10^{-3}	2.41×10^{-4}	92	1.62×10^{-1}	8.29×10^{-4}	1.61×10^{-1}
1.26×10^{-5}	9.35×10^{-4}	7.42×10^{-4}	1.93×10^{-4}	59	1.08×10^{-1}	6.63×10^{-4}	1.07×10^{-1}
1.26×10^{-5}	4.67×10^{-4}	3.37×10^{-4}	1.30×10^{-4}	27	5.34×10^{-2}	4.47×10^{-4}	5.30×10^{-2}
1.26×10^{-5}	3.27×10^{-4}	2.22×10^{-4}	1.05×10^{-4}	18	3.87×10^{-2}	3.63×10^{-4}	3.83×10^{-2}

$k_{2,N} = 1.31 \times 10^2$ $M^{-1}s^{-1}$

$k_{2,OH} = 3.44$ $M^{-1}s^{-1}$

$pK_B = 4.30$



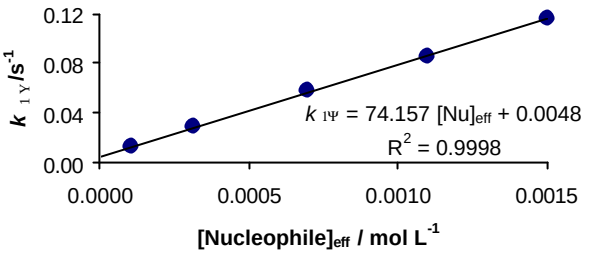
Reaction of DMAP (**1f**) with $(lil)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 630 nm)

$[(lil)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH^-}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.81×10^{-5}	1.78×10^{-3}	1.51×10^{-3}	2.75×10^{-4}	83	1.17×10^{-1}	5.93×10^{-4}	1.16×10^{-1}
1.81×10^{-5}	1.34×10^{-3}	1.10×10^{-3}	2.35×10^{-4}	61	8.66×10^{-2}	5.08×10^{-4}	8.61×10^{-2}
1.81×10^{-5}	8.91×10^{-4}	7.03×10^{-4}	1.88×10^{-4}	39	5.82×10^{-2}	4.06×10^{-4}	5.78×10^{-2}
1.81×10^{-5}	4.45×10^{-4}	3.19×10^{-4}	1.26×10^{-4}	18	2.89×10^{-2}	2.73×10^{-4}	2.86×10^{-2}
1.81×10^{-5}	1.78×10^{-4}	1.05×10^{-4}	7.27×10^{-5}	6	1.22×10^{-2}	1.57×10^{-4}	1.20×10^{-2}

$k_{2,N}$ = 74.2 $M^{-1}s^{-1}$

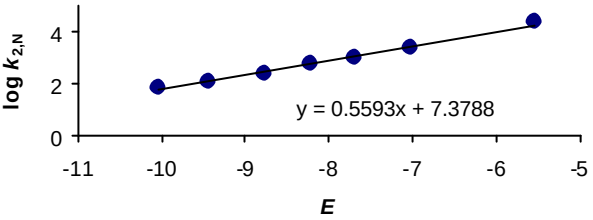
$k_{2,OH}$ = 2.16 $M^{-1}s^{-1}$

pK_B = 4.30



Reactivity parameters of DMAP (**1f**) in water: N = 13.19; s = 0.559

Reference electrophile	E parameter	$k_{2,N}$(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	2.39×10^4
$(dma)_2CH^+$	-7.02	2.66×10^3
$(pyr)_2CH^+$	-7.69	9.88×10^2
$(thq)_2CH^+$	-8.22	5.81×10^2
$(ind)_2CH^+$	-8.76	2.41×10^2
$(jul)_2CH^+$	-9.45	1.31×10^2
$(lil)_2CH^+$	-10.04	7.42×10^1



4-(Dimethylamino)pyridine (DMAP, **1f**) in Methanol

In the reaction of the $(dma)_2CH^+$ BF_4^- with **1f** in methanol, the competing reaction of the carbocation with the solvent methanol has to be considered. The observed pseudo-first-order rate constants k_{obs} reflect the sum of the reactions of the electrophile with **1f** ($k_{1\Psi,N}$), methanol ($k_{1\Psi,MeOH}$) and the reverse reaction (k_{-1}) [Eq. (S9)].

$$k_{obs} = k_{1\Psi,N} + k_{1\Psi,MeOH} + k_{-1} \qquad \text{(S9)}$$

$$k_{1\Psi} = k_{obs} = k_{2,N}[\mathbf{1f}] + k_{1\Psi,MeOH} + k_{-1}$$

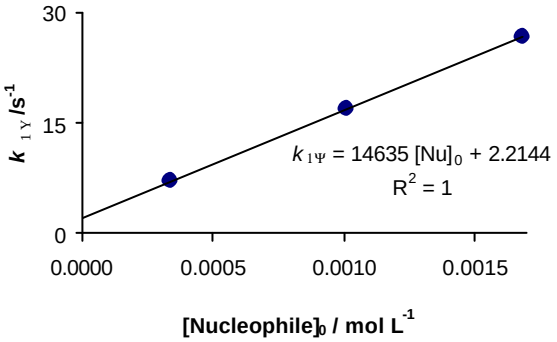
The slopes of the plots $k_{1\Psi}$ versus [**1f**] corresponds to the second-order rate constant $k_{2,N}$. The intercept, which correspond to the reverse reactions and the reactions of $(dma)_2CH^+$ BF_4^- with methanol is negligible. For technical reasons the experiment was performed in a solvent mixture containing 91 vol-% CH_3OH and 9 vol-% CH_3CN (corresponding to a 10/1 mixing ratio in the stopped-flow experiment).

Reaction of DMAP (**1f**) with $(dma)_2CH^+$ BF_4^- in methanol (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
2.02×10^{-5}	1.68×10^{-3}	83	26.8
2.02×10^{-5}	1.01×10^{-3}	50	11.7
2.02×10^{-5}	3.36×10^{-4}	17	7.13

$k_{2,N} = 1.46 \times 10^4$ $M^{-1}s^{-1}$

$k_{1,MeOH}(CH_3OH/CH_3CN$ 91/9 (v/v))$= 2.31$ s^{-1} [S2]

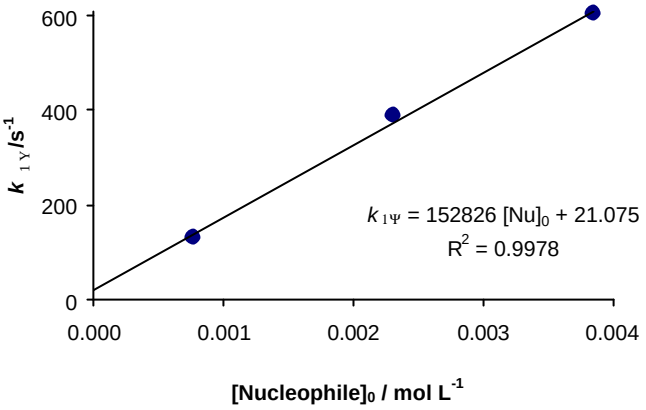


4-(Dimethylamino)pyridine (DMAP, **1f**) in DMSO

Reaction of DMAP (**1f**) with $(dma)_2CH^+ BF_4^-$ in DMSO (at 20 °C, stopped-flow, detection at 616 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
9.27×10^{-6}	3.85×10^{-3}	415	6.03×10^2
9.27×10^{-6}	2.31×10^{-3}	249	3.87×10^2
9.27×10^{-6}	7.68×10^{-4}	83	1.32×10^2

$k_{2,N} = 1.53 \times 10^5$ $M^{-1}s^{-1}$

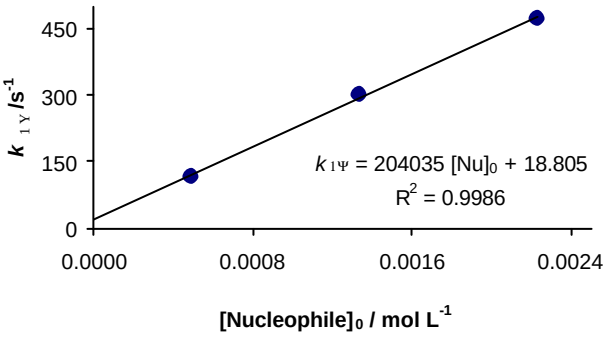


4-(Dimethylamino)pyridine (DMAP, **1f**) in DMF

Reaction of DMAP (**1f**) with $(dma)_2CH^+ BF_4^-$ in DMF (at 20 °C, stopped-flow, detection at 616 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
9.27×10^{-6}	2.23×10^{-3}	241	4.70×10^2
9.27×10^{-6}	1.34×10^{-3}	145	3.00×10^2
9.27×10^{-6}	4.91×10^{-4}	53	1.15×10^2

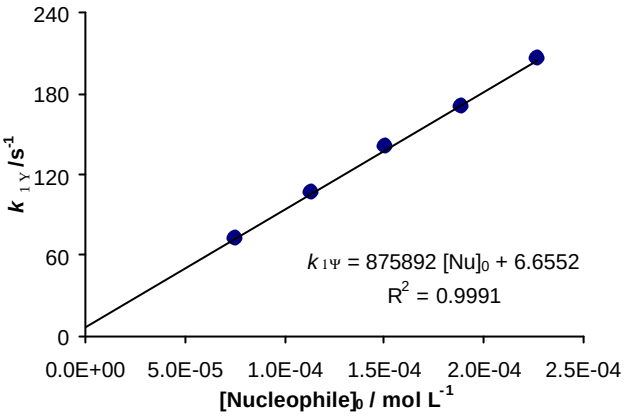
$k_{2,N} = 2.04 \times 10^5$ $M^{-1}s^{-1}$



4-(Pyrrolidino)pyridine (**1g**)

Reaction of 4-pyrrolidinopyridine (**1g**) with $(dma)_2CH^+$ BF_4^- in CH_2Cl_2 (at 20 °C, stopped-flow, detection at 612 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_0/[El]_0$	$k_{1\Psi}$ / s^{-1}
8.61×10^{-6}	2.27×10^{-4}	26	2.06×10^{2}
8.61×10^{-6}	1.89×10^{-4}	22	1.70×10^{2}
8.61×10^{-6}	1.51×10^{-4}	18	1.41×10^{2}
8.61×10^{-6}	1.13×10^{-4}	13	1.06×10^{2}
8.61×10^{-6}	7.56×10^{-5}	9	72.1



$k_{2,N}$ = 8.76×10^{5} $M^{-1}s^{-1}$

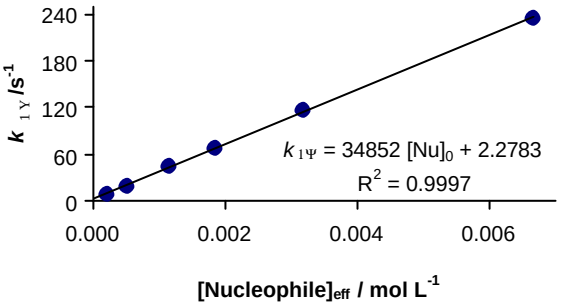
Reaction of 4-pyrrolidinopyridine (**1g**) with $(mor)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(mor)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
3.65×10^{-5}	7.42×10^{-3}	6.69×10^{-3}	7.29×10^{-4}	183	2.35×10^{2}	7.73×10^{-1}	2.34×10^{2}
3.65×10^{-5}	3.71×10^{-3}	3.21×10^{-3}	5.05×10^{-4}	88	1.17×10^{2}	5.35×10^{-1}	1.16×10^{2}
3.65×10^{-5}	2.23×10^{-3}	1.85×10^{-3}	3.83×10^{-4}	51	67.4	4.06×10^{-1}	67.0
3.65×10^{-5}	1.48×10^{-3}	1.17×10^{-3}	3.05×10^{-4}	32	43.9	3.24×10^{-1}	43.6
3.65×10^{-5}	7.42×10^{-4}	5.36×10^{-4}	2.06×10^{-4}	15	20.5	2.19×10^{-1}	20.3
3.65×10^{-5}	3.71×10^{-4}	2.35×10^{-4}	1.36×10^{-4}	6	9.33	1.45×10^{-1}	9.19

$k_{2,N}$ = 3.49×10^{4} $M^{-1}s^{-1}$

$k_{2,OH}$ = 1.06×10^{3} $M^{-1}s^{-1}$

pK_B = 4.1



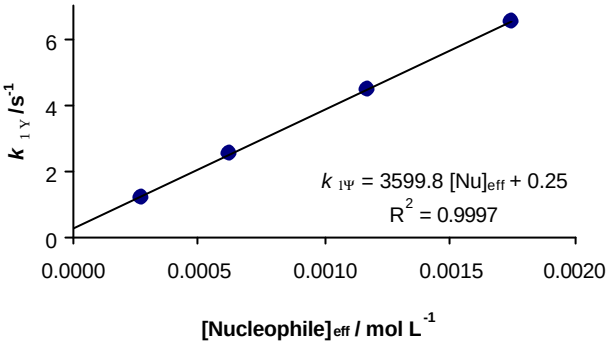
Reaction of 4-pyrrolidinopyridine (**1g**) with $(dma)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.4 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(dma)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
1.22×10^{-5}	2.12×10^{-3}	1.75×10^{-3}	3.73×10^{-4}	143	6.58	4.88×10^{-2}	6.53
1.22×10^{-5}	1.48×10^{-3}	1.17×10^{-3}	3.05×10^{-4}	96	4.51	4.00×10^{-2}	4.47
1.22×10^{-5}	8.48×10^{-4}	6.25×10^{-4}	2.23×10^{-4}	51	2.59	2.92×10^{-2}	2.56
1.22×10^{-5}	4.24×10^{-4}	2.76×10^{-4}	1.48×10^{-4}	23	1.22	1.94×10^{-2}	1.20

$k_{2,N} = 3.60 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH} = 1.31 \times 10^2$ $M^{-1}s^{-1}$

$pK_B = 4.1$



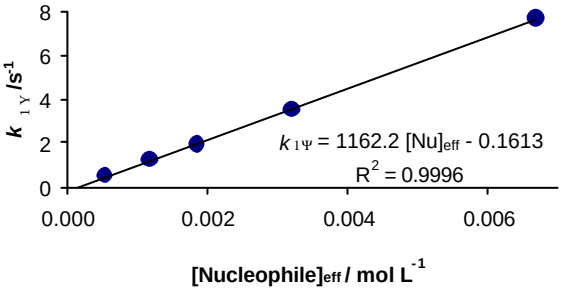
Reaction of 4-pyrrolidinopyridine (**1g**) with $(pyr)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(pyr)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
2.78×10^{-5}	7.42×10^{-3}	6.69×10^{-3}	7.29×10^{-4}	241	7.69	3.54×10^{-2}	7.65
2.78×10^{-5}	3.71×10^{-3}	3.21×10^{-3}	5.05×10^{-4}	115	3.52	2.45×10^{-2}	3.50
2.78×10^{-5}	2.23×10^{-3}	1.85×10^{-3}	3.83×10^{-4}	66	1.95	1.86×10^{-2}	1.93
2.78×10^{-5}	1.48×10^{-3}	1.17×10^{-3}	3.05×10^{-4}	42	1.23	1.48×10^{-2}	1.22
2.78×10^{-5}	7.42×10^{-4}	5.36×10^{-4}	2.06×10^{-4}	19	5.42×10^{-1}	1.00×10^{-2}	5.32×10^{-1}

$k_{2,N} = 1.16 \times 10^3$ $M^{-1}s^{-1}$

$k_{2,OH} = 48.5$ $M^{-1}s^{-1}$

$pK_B = 4.1$



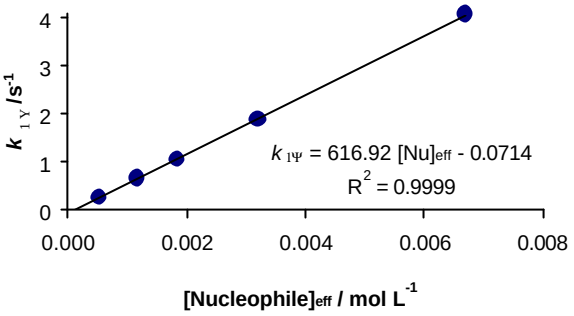
Reaction of 4-pyrrolidinopyridine (**1g**) with $(thq)_2CH^+$ BF_4^- in water (at 20 °C, cosolvent: 0.9 vol-% CH_3CN, stopped-flow, detection at 610 nm)

$[(thq)_2CH^+]_0$ / mol L^{-1}	$[Nu]_0$ / mol L^{-1}	$[Nu]_{eff}$ / mol L^{-1}	$[OH^-]$ / mol L^{-1}	$[Nu]_{eff}/[El]_0$	k_{obs} / s^{-1}	$k_{1\Psi,OH}$ / s^{-1}	$k_{1\Psi}$ / s^{-1}
3.01×10^{-5}	7.42×10^{-3}	6.69×10^{-3}	7.29×10^{-4}	222	4.08	1.72×10^{-2}	4.06
3.01×10^{-5}	3.71×10^{-3}	3.21×10^{-3}	5.05×10^{-4}	106	1.91	1.19×10^{-2}	1.90
3.01×10^{-5}	2.23×10^{-3}	1.85×10^{-3}	3.83×10^{-4}	61	1.06	9.04×10^{-3}	1.05
3.01×10^{-5}	1.48×10^{-3}	1.17×10^{-3}	3.05×10^{-4}	39	6.67×10^{-1}	7.21×10^{-3}	6.60×10^{-1}
3.01×10^{-5}	7.42×10^{-4}	5.36×10^{-4}	2.06×10^{-4}	18	2.76×10^{-1}	4.87×10^{-3}	2.71×10^{-1}

$k_{2,N} = 6.17 \times 10^2$ $M^{-1}s^{-1}$

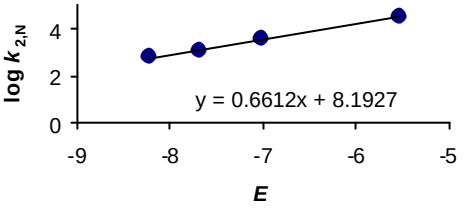
$k_{2,OH} = 23.6$ M^{-1} s^{-1} [S1]

$pK_B = 4.1$



Reactivity parameters of 4-pyrrolidinopyridine (**1g**) in water: $N = 12.39$; $s = 0.661$

Reference electrophile	E parameter	k_2(20°C) / M^{-1} s^{-1}
$(mor)_2CH^+$	-5.53	3.49×10^4
$(dma)_2CH^+$	-7.02	3.60×10^3
$(pyr)_2CH^+$	-7.69	1.16×10^3
$(thq)_2CH^+$	-8.22	6.17×10^2

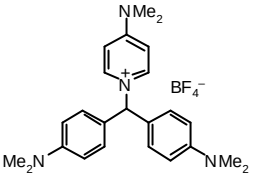


Products from Reactions of DMAP (**1f**) with Benzhydrylium Salts

^{1}H (300 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded with a Bruker ARX 300. Chemical shifts were reported on the δ scale relative to tetramethylsilane (^{1}H) and $CDCl_3$ (^{13}C) as internal standards.

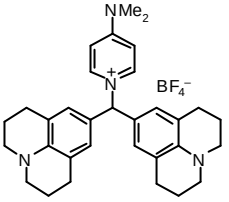
General Procedure. In a carefully dried, nitrogen-flushed Schlenk-flask a solution of 4(dimethylamino)pyridine (DMAP, **1f**) in absolute CH_2Cl_2 (5 mL) was added dropwise to a solution of the benzhydrylium tetrafluoroborate in absolute CH_2Cl_2 (50 mL). After stirring at ambient temperature for 1 h, the solvent was evaporated in the vacuum to yield the crude product, which was washed with absolute Et_2O (20 mL) and dried several hours in the vacuum (10^{-2} mbar).

1-(Bis(4-dimethylaminophenyl)methyl)-4-(dimethylamino)pyridinium tetrafluoroborate (**2a**) was obtained from **1f** (61.8 mg, 0.506 mmol) and bis(4-dimethylaminophenyl)methylium tetrafluoroborat $(dma)_2CH^+$ BF_4^- (172 mg, 0.506 mmol) as a bright blue solid (169 mg, 72 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.88 (s, 12 H), 3.13 (s, 6 H), 6.52 (s, 1 H), 6.59 (d, *J* = 8.8 Hz, 4 H), 6.78 (d, *J* = 7.9 Hz, 2 H), 6.91 (d, *J* = 8.7 Hz, 4 H), 7.83 (d, *J* = 7.9 Hz, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 39.9 (q), 40.0 (q), 73.8 (d), 107.5 (d), 112.2 (d), 123.4 (s), 129.1 (d), 140.7 (d), 150.4 (s), 156.2 (s).



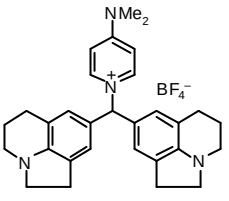
2a

1-(Bis(julolidin-9-yl)methyl)-4-(dimethylamino)pyridinium tetrafluoroborate (**2b**) was obtained from **1f** (20 mg, 0.16 mmol) and bis(julolidin-9-yl)methylium tetrafluoroborat $(jul)_2CH^+$ BF_4^- (73 mg, 0.16 mmol) as a bright blue solid (63 mg, 68 %). ^{1}H NMR (300 MHz, CD_3CN): δ = 1.83–1.89 (m, 8 H), 2.60–2.64 (m, 8 H), 3.13–3.14 (m, 8 H), 3.14 (s, superimposed, 6 H), 6.29 (s, 1 H), 6.50 (s, 4 H), 6.77 (d, *J* = 7.8 Hz, 2 H), 7.85 (d, *J* = 7.9 Hz, 2 H); ^{13}C NMR (75.5 MHz, CD_3CN): δ = 22.5 (t), 28.4 (t), 40.6 (q), 50.4 (t), 75.0 (d), 108.4 (d), 122.6 (d), 127.8 (d), 141.8 (d), 144.1 (s), 148.6 (d), 157.6 (s).



2b

1-(Bis(lilolidin-8-yl)methyl)-4-(dimethylamino)pyridinium tetrafluoroborate (**2c**) was obtained from **1f** (20 mg, 0.16 mmol) and bis(lilolidin-8-yl)methylium tetrafluoroborat $(lil)_2CH^+$ BF_4^- (68 mg, 0.13 mmol) as a bright blue solid (51 mg, 58 %). ^{1}H NMR (300 MHz, CD_3CN): δ = 1.98–2.02 (m, 4 H), 2.55–2.59 (m, 4 H), 2.79–2.85 (m, 4 H), 2.94–2.98 (m, 4 H), 3.15 (s, 6 H), 3.23–3.29 (m, 4 H), 6.45 (s, 1 H), 6.57 (s, 2 H), 6.67 (s, 2 H), 6.78 (d, *J* = 7.9 Hz, 2 H), 7.86 (d, *J* = 7.9 Hz, 2 H); ^{13}C NMR (75.5 MHz, CD_3CN): δ = 23.6 (t), 24.6 (t), 29.1 (t), 40.6 (q), 47.4 (t), 55.6 (t), 75.6 (d), 108.4 (d), 120.2 (s), 123.1 (d), 127.6 (d), 130.4 (s), 141.8 (d), 151.6 (s), 157.6 (s).



2c

Computational Details

General. All calculations were performed with Gaussian 03, Rev. B.01.[18] Structures were optimized at the MP2 (frozen core) level using the 6-31G(d) basis set. The MP2 frequencies (unscaled) were used to calculate the zero-point energies (*ZPE*). For the reaction products of the pyridines **1c**, **1d** and **1g** with the benzhydrylium ion two conformational isomers exist. The corresponding energies are shown in the supplemental material. Values for ΔH_{298} and ΔG_{298} in Table 4 were obtained by conformational averaging for these adducts **3c**, **3d** and **3g**.

Single point energies have subsequently been performed at the MP2(fc)/6-311++G(d,p) level of theory. Combination of the single point energies with thermochemical corrections calculated at the MP2(fc)/6-31G(d) level yields the "E_0", "H_{298}" and "G_{298}" values which can be found in the supplemental material.

Reaction Energies for all Stationary Points as Optimized at the MP2(fc)/6-31G(d) Level of Theory

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
benzhydryl cation	-500.0844505	-499.884452	-499.873233	-499.920254

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	"E_0" / a.u.	"H_{298}" / a.u.	"G_{298}" / a.u.
-500.3260228	-500.126024	-500.114806	-500.161827

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
1a	-706.5146861	-706.434802	-706.428440	-706.463903

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	"E_0" / a.u.	"H_{298}" / a.u.	"G_{298}" / a.u.
-706.6691680	-706.589284	-706.582922	-706.618385

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
1b	-247.4825325	-247.393089	-247.387802	-247.419876

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	$"E_0"$ / a.u.	$"H_{298}"$ / a.u.	$"G_{298}"$ / a.u.
-247.6092285	-247.519785	-247.514498	-247.546573

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
1c	-286.6543269	-286.536514	-286.529459	-286.566813

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	$"E_0"$ / a.u.	$"H_{298}"$ / a.u.	$"G_{298}"$ / a.u.
-286.8107137	-286.692901	-286.685846	-286.723200

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
1d	-361.6730054	-361.549815	-361.542086	-361.580849

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	$"E_0"$ / a.u.	$"H_{298}"$ / a.u.	$"G_{298}"$ / a.u.
-361.8711469	-361.747956	-361.740227	-361.778991

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
1e	-302.6786366	-302.572093	-302.565461	-302.601203

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	$"E_0"$ / a.u.	$"H_{298}"$ / a.u.	$"G_{298}"$ / a.u.
-302.8444452	-302.737901	-302.731269	-302.767011

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
1f	-380.9952652	-380.830420	-380.821016	-380.863686

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	"E_0" / a.u.	"H_{298}" / a.u.	"G_{298}" / a.u.
-381.2156504	-381.050805	-381.041401	-381.084071

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
1g	-458.1656993	-457.963644	-457.953342	-457.999965

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	"E_0" / a.u.	"H_{298}" / a.u.	"G_{298}" / a.u.
-458.4267811	-458.224726	-458.214424	-458.261047

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
3a	-1206.6685233	-1206.384846	-1206.367481	-1206.431088

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	"E_0" / a.u.	"H_{298}" / a.u.	"G_{298}" / a.u.
-1207.0724461	-1206.788769	-1206.771404	-1206.835011

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
3b	-747.6426477	-747.349083	-747.332928	-747.393163

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	"E_0" / a.u.	"H_{298}" / a.u.	"G_{298}" / a.u.
-748.0165883	-747.723023	-747.706868	-747.767104

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
3c conformation 1	-786.8189340	-786.497199	-786.479170	-786.544094
3c conformation 2	-768.8189070	-786.497194	-786.479147	-786.544225

$<H_{298}>$ = -786.479159 a.u., $<G_{298}>$ = -786.544164 a.u.

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	$"E_0"$ / a.u.	$"H_{298}"$ / a.u.	$"G_{298}"$ / a.u.
-787.2226685	-786.900934	-786.882905	-786.947829
-787.2226311	-786.900918	-786.882871	-786.947949

$<"H_{298}">$ = -786.882888 a.u., $<"G_{298}">$ = -786.947893 a.u.

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
3d conformation 1	-861.8410158	-861.513908	-861.495124	-861.561422
3d conformation 2	-861.8407311	-861.513651	-861.494851	-861.561258

$<H_{298}>$ = -861.495007 a.u., $<G_{298}>$ = -861.561347 a.u.

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	$"E_0"$ / a.u.	$"H_{298}"$ / a.u.	$"G_{298}"$ / a.u.
-862.2862137	-861.959106	-861.940322	-862.006620
-862.2862417	-861.959162	-861.940362	-862.006769

$<"H_{298}">$ = -861.940342 a.u., $<"G_{298}">$ = -862.006700 a.u.

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
3e	-802.8531099	-802.543134	-802.525251	-802.589180

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	$"E_0"$ / a.u.	$"H_{298}"$ / a.u.	$"G_{298}"$ / a.u.
-803.2643414	-802.954365	-802.936482	-803.000411

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
3f	-881.1763403	-880.807821	-880.787051	-880.858252

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	$"E_0"$ / a.u.	$"H_{298}"$ / a.u.	$"G_{298}"$ / a.u.
-881.6428677	-881.274348	-881.253579	-881.324780

stationary point	MP2(FC)/6-31G(d)// MP2(FC)/6-31G(d)			
	E_{tot} / a.u.	E_0 / a.u.	H_{298} / a.u.	G_{298} / a.u.
3g conformation 1	-958.3503958	-957.943976	-957.922795	-957.995212
3g conformation 2	-958.3503816	-957.943965	-957.922782	-957.995204

$<H_{298}>$ = -957.922789 a.u., $<G_{298}>$ = -957.995208 a.u.

MP2(FC)/6-311++G(d,p)// MP2(FC)/6-31G(d)			
E_{tot} / a.u.	$"E_0"$ / a.u.	$"H_{298}"$ / a.u.	$"G_{298}"$ / a.u.
-958.8581181	-958.451698	-958.430517	-958.502934
-958.8577907	-958.451375	-958.430192	-958.502614

$<"H_{298}">$ = -958.430382 a.u., $<"G_{298}">$ = -958.502801 a.u.

Structures of all Stationary Points

benzhydryl cation (Ph_2CH^+)

1\1\GINC-LXSRV64\SP\RMP2-FC\6-311++G(d,p)\C13H11(1+)\UI22103\08-Oct-20
03\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ MAXDISK=163
75MB\\SP Benzhydryl-Kation C2-symm.\\1,1\H,0,0.,0.,2.1741320674\C,0,0.
,0.,1.0804800674\C,0,0.,1.273046,0.4681010674\C,0,0.,-1.273046,0.46810
10674\C,0,0.420774,2.37777,1.2610170674\C,0,-0.420774,-2.37777,1.26101
70674\C,0,0.512659,3.640234,0.6963970674\C,0,-0.512659,-3.640234,0.696
3970674\C,0,0.125093,3.835002,-0.6372269326\C,0,-0.125093,-3.835002,-0
.6372269326\C,0,-0.357628,2.767371,-1.4103619326\C,0,0.357628,-2.76737
1,-1.4103619326\C,0,-0.419854,1.490389,-0.8747329326\C,0,0.419854,-1.4
90389,-0.8747329326\H,0,0.712828,2.21301,2.2962920674\H,0,-0.712828,-2
.21301,2.2962920674\H,0,0.861651,4.480154,1.2899140674\H,0,-0.861651,-
4.480154,1.2899140674\H,0,0.171297,4.831711,-1.0694079326\H,0,-0.17129
7,-4.831711,-1.0694079326\H,0,-0.702917,2.947923,-2.4243339326\H,0,0.7
02917,-2.947923,-2.4243339326\H,0,-0.871082,0.680509,-1.4401309326\H,0
,0.871082,-0.680509,-1.4401309326\\Version=x86-Linux-G03RevB.01\State=
1-A\HF=-498.5635824\MP2=-500.3260228\RMSD=3.232e-09\PG=C02 [C2(C1H1),X
(C12H10)]\\@

1a

1\1\GINC-LXSRV107\SP\RMP2-FC\6-311++G(d,p)\C5H4Cl1N1\UI22102\05-Sep-20
05\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ MAXDISK=163
75MB\\SP 4-Chlorpyridin C2V-symm.\\0,1\N,0,0.,0.,-2.2959558103\C,0,0.,
1.143613,-1.5886068103\C,0,0.,1.203155,-0.1945828103\C,0,0.,0.,0.50673
41897\C,0,0.,-1.203155,-0.1945828103\C,0,0.,-1.143613,-1.5886068103\H,
0,0.,2.063062,-2.1709268103\H,0,0.,2.155634,0.3262151897\H,0,0.,-2.155
634,0.3262151897\H,0,0.,-2.063062,-2.1709268103\Cl,0,0.,0.,2.242293189
7\\Version=x86-Linux-G03RevB.01\State=1-A1\HF=-705.6742093\MP2=-706.66
9168\RMSD=6.610e-09\PG=C02V [C2(N1C1Cl1),SGV(C4H4)]\\@

1b

1\1\GINC-LXSRV88\SP\RMP2-FC\6-311++G(d,p)\C5H5N1\UI22103\30-Sep-2003\0
\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Pyridin C2V
-symm.\\0,1\N,0,-1.2354982503,0.,-0.7133152472\C,0,-1.1971091093,0.,0.
6314514583\C,0,-0.01533855,0.,1.3740447612\C,0,1.2019678176,0.,0.69395

64429\C,0,1.1822883939,0.,-0.7003059549\C,0,-0.0517015509,0.,-1.352452
6289\H,0,-2.1641977893,0.,1.1314127745\H,0,-0.0529914578,0.,2.45986912
03\H,0,2.143488262,0.,1.2375435248\H,0,2.1038134189,0.,-1.2758265093\H
,0,-0.1022666904,0.,-2.4399566516\\Version=x86-Linux-G03RevB.01\State=
1-A1\HF=-246.7509496\MP2=-247.6092285\RMSD=2.253e-09\PG=C02V [C2(H1C1N
1),SGV(C4H4)]\\@

1c

1\1\GINC-LXSRV7\SP\RMP2-FC\6-311++G(d,p)\C6H7N1\UI22102\06-Sep-2005\0\
\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ MAXDISK=16375MB\
\SP 4-Methylpyridin CS-symm.\\0,1\N,0,0.00584114,-1.93081684,0.\C,0,0.
00644514,-1.22010084,1.142072\C,0,0.00644514,0.17358816,1.190499\C,0,0
.00882914,0.90684616,0.\C,0,0.00644514,0.17358816,-1.190499\C,0,0.0064
4514,-1.22010084,-1.142072\H,0,0.00893914,-1.80265284,2.062042\H,0,0.0
1176814,0.68145016,2.152762\H,0,0.01176814,0.68145016,-2.152762\H,0,0.
00893914,-1.80265284,-2.062042\C,0,-0.02767786,2.41116316,0.\H,0,0.468
30614,2.81626816,-0.886295\H,0,-1.06050586,2.77568316,0.\H,0,0.4683061
4,2.81626816,0.886295\\Version=x86-Linux-G03RevB.01\State=1-A'\HF=-285
.7990407\MP2=-286.8107137\RMSD=1.945e-09\PG=CS [SG(C2H1N1),X(C4H6)]\\@

1d

1\1\GINC-LXSRV85\SP\RMP2-FC\6-311++G(d,p)\C6H7N1O1\UI22102\05-Sep-2005
\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ MAXDISK=16375
MB\\SP 4-Methoxypyridin CS-symm.\\0,1\N,0,0.9052040345,-2.145158,0.\C,
0,1.7605900345,-1.101883,0.\C,0,1.3677480345,0.229948,0.\C,0,0.0000000
345,0.527541,0.\C,0,-0.9096529655,-0.532688,0.\C,0,-0.3994009655,-1.83
4083,0.\H,0,2.8187920345,-1.356907,0.\H,0,2.0919680345,1.038845,0.\H,0
,-1.9829979655,-0.380473,0.\H,0,-1.0879709655,-2.677838,0.\O,0,-0.3254
049655,1.851253,0.\C,0,-1.7169999655,2.171139,0.\H,0,-2.2123859655,1.7
81694,0.89529\H,0,-1.7619129655,3.259223,0.\H,0,-2.2123859655,1.781694
,-0.89529\\Version=x86-Linux-G03RevB.01\State=1-A'\HF=-360.66555\MP2=-
361.8711469\RMSD=8.811e-09\PG=CS [SG(C6H5N1O1),X(H2)]\\@

1e

1\1\GINC-LXSRV77\SP\RMP2-FC\6-311++G(d,p)\C5H6N2\UI22102\05-Sep-2005\0
\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ MAXDISK=16375MB
\\SP 4-Aminopyridin CS-symm.\\0,1\N,0,-0.00533388,-1.90689116,0.\C,0,-

0.00588788,-1.19079116,1.139214\C,0,-0.00588788,0.19952484,1.19522\C,0
,0.00564112,0.93058884,0.\C,0,-0.00588788,0.19952484,-1.19522\C,0,-0.0
0588788,-1.19079116,-1.139214\H,0,-0.00738088,-1.76889616,2.062096\H,0
,-0.00899588,0.70846384,2.15677\H,0,-0.00899588,0.70846384,-2.15677\H,
0,-0.00738088,-1.76889616,-2.062096\N,0,-0.06216788,2.32261884,0.\H,0,
0.30636412,2.76121684,0.836707\H,0,0.30636412,2.76121684,-0.836707\\Ve
rsion=x86-Linux-G03RevB.01\State=1-A'\HF=-301.8049239\MP2=-302.8444452
\RMSD=8.752e-09\PG=CS [SG(C1N2),X(C4H6)]\\@

1f

1\1\GINC-LXSRV105\SP\RMP2-FC\6-311++G(d,p)\C7H10N2\UI22103\09-Jan-2004
\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Dimethyla
minopyridin CS-symm.\\0,1\N,0,-0.1075100758,-2.6722419091,0.\C,0,-0.05
61730758,-1.9517349091,1.13448\C,0,0.0443269242,-0.5654519091,1.193801
\C,0,0.1028229242,0.1810690909,0.\C,0,0.0443269242,-0.5654519091,-1.19
3801\C,0,-0.0561730758,-1.9517349091,-1.13448\H,0,-0.1028100758,-2.523
2989091,2.060712\H,0,0.0677199242,-0.0887309091,2.166669\H,0,0.0677199
242,-0.0887309091,-2.166669\H,0,-0.1028100758,-2.5232989091,-2.060712\
N,0,0.2506609242,1.5621500909,0.\C,0,-0.0561730758,2.2731450909,-1.232
578\H,0,-1.0969160758,2.1327840909,-1.560631\H,0,0.1202559242,3.337594
0909,-1.071119\H,0,0.6103689242,1.9480160909,-2.034388\C,0,-0.05617307
58,2.2731450909,1.232578\H,0,0.6103689242,1.9480160909,2.034388\H,0,0.
1202559242,3.3375940909,1.071119\H,0,-1.0969160758,2.1327840909,1.5606
31\\Version=x86-Linux-G03RevB.01\State=1-A'\HF=-379.8688486\MP2=-381.2
156504\RMSD=8.072e-09\PG=CS [SG(C1N2),X(C6H10)]\\@

1g

1\1\GINC-LXSRV73\SP\RMP2-FC\6-311++G(d,p)\C9H12N2\UI22102\09-Sep-2005\
0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ MAXDISK=16375M
B\\SP 4-Pyrrolidinopyridin C2-symm.\\0,1\N,0,0.,0.,3.3818480375\C,0,0.
000812,1.13649,2.6604920375\C,0,0.,1.197834,1.2715570375\C,0,0.,0.,0.5
279890375\C,0,0.,-1.197834,1.2715570375\C,0,-0.000812,-1.13649,2.66049
20375\H,0,-0.001239,2.061353,3.2365040375\H,0,-0.016755,2.165513,0.780
4200375\H,0,0.016755,-2.165513,0.7804200375\H,0,0.001239,-2.061353,3.2
365040375\N,0,0.,0.,-0.8411469625\C,0,-0.126017,-1.209471,-1.646836962
5\C,0,0.126017,1.209471,-1.6468369625\C,0,-0.38712,-0.659185,-3.048675
9625\H,0,0.794859,-1.812264,-1.6155699625\C,0,0.38712,0.659185,-3.0486

759625\H,0,-0.794859,1.812264,-1.6155699625\H,0,-0.070316,-1.349161,-3
.8357119625\H,0,0.070316,1.349161,-3.8357119625\H,0,-0.949173,-1.83680
8,-1.2843339625\H,0,0.949173,1.836808,-1.2843339625\H,0,-1.457327,-0.4
6538,-3.1769459625\H,0,1.457327,0.46538,-3.1769459625\\Version=x86-Lin
ux-G03RevB.01\State=1-A\HF=-456.7988852\MP2=-458.4267811\RMSD=4.642e-0
9\PG=C02 [C2(N1C1N1),X(C8H12)]\\@

3a

1\1\GINC-LX64I51\SP\RMP2-FC\6-311++G(d,p)\C18H15Cl1N1(1+)\UI22102\12-S
ep-2005\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Be
nzhydryl-Kation + 4-Chlorpyridin C1-symm.\\1,1\H,0,0.7861159864,0.0012
018844,-1.9384170476\C,0,0.7627219864,0.0022118844,-0.8410270476\N,0,-
0.7248780136,-0.0910031156,-0.5171600476\C,0,1.5000179864,-1.214297115
6,-0.3493870476\C,0,1.2724449864,1.3269588844,-0.3328300476\C,0,1.4813
489864,-2.3734611156,-1.1408500476\C,0,0.8648819864,1.8497438844,0.902
5459524\C,0,2.1235799864,-3.5312921156,-0.7034790476\C,0,1.4061299864,
3.0513988844,1.3621719524\C,0,2.7802399864,-3.5405521156,0.5305799524\
C,0,2.3563669864,3.7317468844,0.5963679524\C,0,2.8033199864,-2.3869101
156,1.3186939524\C,0,2.7629969864,3.2112168844,-0.6346280476\C,0,2.163
4919864,-1.2238601156,0.8858579524\C,0,2.2211779864,2.0129448844,-1.10
10550476\H,0,0.9808579864,-2.3639401156,-2.1087800476\H,0,0.1242099864
,1.3310228844,1.5097909524\H,0,2.1187789864,-4.4217831156,-1.326407047
6\H,0,1.0862809864,3.4559218844,2.3189359524\H,0,3.3286349864,-2.38905
21156,2.2701389524\H,0,3.4976679864,3.7406658844,-1.2352980476\H,0,2.2
115699864,-0.3206691156,1.4883789524\H,0,2.5426579864,1.6072418844,-2.
0591440476\H,0,3.2873999864,-4.4400921156,0.8690589524\H,0,2.775156986
4,4.6674798844,0.9563809524\C,0,-1.2152300136,-1.0071871156,0.34626395
24\C,0,-2.5699010136,-1.0365531156,0.6438949524\C,0,-3.4277350136,-0.1
151661156,0.0395029524\C,0,-2.8970020136,0.8247948844,-0.8521080476\C,
0,-1.5381490136,0.8195528844,-1.1070640476\H,0,-0.4999840136,-1.699555
1156,0.7750879524\H,0,-2.9473820136,-1.7774381156,1.3417739524\H,0,-3.
5337060136,1.5557138844,-1.3407470476\H,0,-1.0585630136,1.5337848844,-
1.7690320476\Cl,0,-5.1017510136,-0.1324251156,0.3816289524\\Version=IA
64-Linux-G03RevB.01\State=1-A\HF=-1204.2740106\MP2=-1207.0724461\RMSD=
6.006e-09\PG=C01 [X(C18H15Cl1N1)]\\@

3b

1\1\GINC-LXSRV166\SP\RMP2-FC\6-311++G(d,p)\C18H16N1(1+)\UI22103\11-Oct
-2003\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Benz
hydryl-Kation + Pyridin C1-symm.\\1,1\H,0,-0.0231710229,0.0065659542,-
1.8946959924\C,0,-0.0293960229,-0.0612670458,-0.7993289924\N,0,0.13349
59771,1.3886649542,-0.3537179924\C,0,-1.3596280229,-0.6171120458,-0.36
63989924\C,0,1.1819369771,-0.8335970458,-0.3414959924\C,0,-2.490974022
9,-0.3288390458,-1.1455679924\C,0,1.7573479771,-0.6252350458,0.9196960
076\C,0,-3.7459800229,-0.7984450458,-0.7600679924\C,0,2.8417999771,-1.
4039090458,1.3269810076\C,0,-3.8794350229,-1.5513760458,0.4101640076\C
,0,3.3516239771,-2.3939000458,0.4831080076\C,0,-2.7542600229,-1.842916
0458,1.1856350076\C,0,2.7783229771,-2.6023670458,-0.7736639924\C,0,-1.
4945890229,-1.3768050458,0.8042940076\C,0,1.6974019771,-1.8231730458,-
1.1875779924\H,0,-2.3866430229,0.2473389542,-2.0645789924\H,0,1.371631
9771,0.1439419542,1.5874410076\H,0,-4.6166410229,-0.5846660458,-1.3743
129924\H,0,3.2879549771,-1.2380580458,2.3041150076\H,0,-2.8554150229,-
2.4427320458,2.0863070076\H,0,3.1758199771,-3.3677040458,-1.4348219924
\H,0,-0.6186680229,-1.6327550458,1.3945190076\H,0,1.2496949771,-1.9902
710458,-2.1660999924\H,0,-4.8559010229,-1.9241890458,0.7076290076\H,0,
4.1964759771,-2.9978320458,0.8026270076\C,0,-0.6809070229,1.9470609542
,0.5678790076\C,0,-0.4721290229,3.2611849542,0.9725770076\C,0,0.572505
9771,4.0003179542,0.4213960076\C,0,1.3977249771,3.3951529542,-0.529273
9924\C,0,1.1640909771,2.0799959542,-0.8988339924\H,0,-1.4789330229,1.3
206419542,0.9486200076\H,0,-1.1361840229,3.6901099542,1.7161530076\H,0
,0.7426639771,5.0291199542,0.7252710076\H,0,2.2230409771,3.9316709542,
-0.9862309924\H,0,1.7770559771,1.5395359542,-1.6130359924\\Version=IA6
4-Linux-G03RevB.01\State=1-A\HF=-745.3572877\MP2=-748.0165883\RMSD=8.4
81e-09\PG=C01 [X(C18H16N1)]\\@

3c conformation 1

1\1\GINC-LX64I52\SP\RMP2-FC\6-311++G(d,p)\C19H18N1(1+)\UI22102\25-Sep-
2005\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Benzh
ydryl-Kation + 4-Methylpyridin C1-symm. Var1\\1,1\H,0,0.4349279928,0.0
022440144,-1.9275719712\C,0,0.4384689928,0.0055840144,-0.8300209712\N,
0,-1.0332080072,-0.1297889856,-0.4676249712\C,0,1.2261829928,-1.187011
9856,-0.3557139712\C,0,0.9279419928,1.3449650144,-0.3391559712\C,0,1.2
141419928,-2.3520029856,-1.1382179712\C,0,0.5275859928,1.8697440144,0.

8973620288\C,0,1.9044449928,-3.4875529856,-0.7160619712\C,0,1.0520149928,3.0851400144,1.3403800288\C,0,2.6037259928,-3.4687369856,0.4942140288\C,0,1.9789529928,3.7772540144,0.5570070288\C,0,2.6201629928,-2.3091689856,1.2735480288\C,0,2.3788349928,3.2545490144,-0.6752959712\C,0,1.9320959928,-1.1684339856,0.8554100288\C,0,1.8539939928,2.0423470144,-1.1245259712\H,0,0.6793759928,-2.3642289856,-2.0875729712\H,0,-0.1957990072,1.3421670144,1.5174530288\H,0,1.9037249928,-4.3825559856,-1.3325599712\H,0,0.7373489928,3.4910780144,2.2983030288\H,0,3.1775369928,-2.2890309856,2.2063920288\H,0,3.0953949928,3.7928070144,-1.2899039712\H,0,1.9731679928,-0.2599169856,1.4504900288\H,0,2.1702309928,1.6349790144,-2.0836589712\H,0,3.1482259928,-4.3507579856,0.8206340288\H,0,2.3846059928,4.7236390144,0.9040570288\C,0,-1.4699700072,-1.0311829856,0.4378070288\C,0,-2.8175040072,-1.0880169856,0.7684850288\C,0,-3.7431870072,-0.2231089856,0.1752390288\C,0,-3.2434370072,0.6956200144,-0.7600709712\C,0,-1.8935010072,0.7334730144,-1.0604889712\H,0,-0.7206650072,-1.6852579856,0.8681430288\H,0,-3.1357870072,-1.8208579856,1.5047400288\H,0,-3.9057790072,1.3983240144,-1.2582569712\H,0,-1.4561890072,1.4416850144,-1.7572169712\C,0,-5.2070850072,-0.2954319856,0.4911450288\H,0,-5.7237090072,-0.9053309856,-0.2578999712\H,0,-5.3777010072,-0.7476939856,1.4703550288\H,0,-5.6596450072,0.6990680144,0.4811820288\\Version=IA64-Linux-G03RevB.01\State=1-A\HF=-784.4111504\MP2=-787.2226685\RMSD=8.372e-09\PG=C01 [X(C19H18N1)]\\@

3c conformation 2

1\1\GINC-LX64I50\SP\RMP2-FC\6-311++G(d,p)\C19H18N1(1+)\UI22102\30-Sep-2005\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Benzhydryl-Kation + 4-Methylpyridin C1-symm. Var2\\1,1\H,0,0.4383180504,0.0039719568,-1.92764\C,0,0.4399020504,0.0074879568,-0.830104\N,0,-1.0314549496,-0.1387960432,-0.469773\C,0,1.2363230504,-1.1787010432,-0.354388\C,0,0.9178460504,1.3507219568,-0.338509\C,0,1.2378950504,-2.3424900432,-1.138795\C,0,0.5135020504,1.8707339568,0.898768\C,0,1.9365210504,-3.4725770432,-0.715634\C,0,1.0271240504,3.0904109568,1.342608\C,0,2.6306240504,-3.4495410432,0.497531\C,0,1.9471330504,3.7917269568,0.559214\C,0,2.6335500504,-2.2911320432,1.278774\C,0,2.3508910504,3.2738809568,-0.673863\C,0,1.9371280504,-1.1558690432,0.859635\C,0,1.8367980504,2.0573649568,-1.12392\H,0,0.7070790504,-2.3579530432,-2.090314\H,0,-0.2044969496,1.3357569568,1.518791\H,0,1.9462720504,-4.3665220432,-1.33358

7\H,0,0.7095260504,3.4925379568,2.301173\H,0,3.1869350504,-2.267557043
2,2.21391\H,0,3.0620500504,3.8192649568,-1.288462\H,0,1.9678840504,-0.
2480130432,1.45632\H,0,2.1560670504,1.6538199568,-2.083663\H,0,3.18159
50504,-4.3272220432,0.82479\H,0,2.3444070504,4.7414259568,0.906902\C,0
,-1.4646709496,-1.0506480432,0.42668\C,0,-2.8131449496,-1.1208340432,0
.751411\C,0,-3.7441589496,-0.2630840432,0.156411\C,0,-3.2474399496,0.6
691609568,-0.767234\C,0,-1.8966619496,0.7205889568,-1.061369\H,0,-0.71
22569496,-1.7031380432,0.853936\H,0,-3.1293929496,-1.8665490432,1.4754
75\H,0,-3.9146639496,1.3644589568,-1.269336\H,0,-1.4627109496,1.435313
9568,-1.753522\C,0,-5.2004639496,-0.3078910432,0.510494\H,0,-5.4318239
496,0.4650679568,1.251354\H,0,-5.8224089496,-0.1229780432,-0.368817\H,
0,-5.4743759496,-1.2759750432,0.934841\\Version=IA64-Linux-G03RevB.01\
State=1-A\HF=-784.4111285\MP2=-787.2226311\RMSD=6.288e-09\PG=C01 [X(C1
9H18N1)]\\@

3d conformation 1

1\1\GINC-LX64I49\SP\RMP2-FC\6-311++G(d,p)\C19H18N1O1(1+)\UI22102\26-Se
p-2005\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Ben
zhydryl-Kation + 4-Methoxypyridin C1-symm. Var1\\1,1\H,0,-0.863671034,
0.0049479252,-1.9515070136\C,0,-0.789837034,0.0128339252,-0.8562550136
\N,0,0.703433966,-0.0390740748,-0.5933630136\C,0,-1.384956034,1.302501
9252,-0.3536550136\C,0,-1.419677034,-1.2437110748,-0.3087150136\C,0,-1
.285966034,2.4464629252,-1.1604210136\C,0,-0.999515034,-1.8138100748,0
.9007379864\C,0,-1.795482034,3.6656049252,-0.7147650136\C,0,-1.6500310
34,-2.9427530748,1.4017819864\C,0,-2.398673034,3.7512719252,0.54332998
64\C,0,-2.722197034,-3.5032700748,0.7032599864\C,0,-2.500859034,2.6133
749252,1.3476979864\C,0,-3.141857034,-2.9355610748,-0.5023290136\C,0,-
1.994229034,1.3895359252,0.9059449864\C,0,-2.492047034,-1.8097010748,-
1.0089860136\H,0,-0.826499034,2.3783509252,-2.1461020136\H,0,-0.163016
034,-1.3891040748,1.4537279864\H,0,-1.729586034,4.5450849252,-1.349868
0136\H,0,-1.319519034,-3.3845080748,2.3383149864\H,0,-2.984778034,2.67
59019252,2.3189179864\H,0,-3.971645034,-3.3722670748,-1.0516150136\H,0
,-2.103451034,0.5011229252,1.5224959864\H,0,-2.823273034,-1.3669180748
,-1.9471640136\H,0,-2.803133034,4.6990829252,0.8884599864\H,0,-3.22557
1034,-4.3830210748,1.0948389864\C,0,1.321006966,0.8149799252,0.2492669
864\C,0,2.679981966,0.7173319252,0.5010409864\C,0,3.428941966,-0.28569
90748,-0.1343340136\C,0,2.758681966,-1.1655630748,-1.0079450136\C,0,1.

406568966,-1.0263430748,-1.2122860136\H,0,0.697156966,1.5741379252,0.7
066489864\H,0,3.125511966,1.4284029252,1.1864739864\H,0,3.315073966,-1
.9495440748,-1.5114520136\H,0,0.836288966,-1.6868000748,-1.8575190136\
C,0,5.479093966,0.3804949252,0.8903769864\H,0,5.425113966,1.4123619252
,0.5357529864\H,0,5.102350966,0.2967729252,1.9123769864\H,0,6.50286396
6,0.0191289252,0.8376709864\O,0,4.736505966,-0.4921880748,0.0088259864
\\Version=IA64-Linux-G03RevB.01\State=1-A\HF=-859.2813681\MP2=-862.286
2137\RMSD=9.251e-09\PG=C01 [X(C19H18N1O1)]\\@

3d conformation 2

1\1\GINC-LX64I48\SP\RMP2-FC\6-311++G(d,p)\C19H18N1O1(1+)\UI22102\28-Se
p-2005\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Ben
zhydryl-Kation + 4-Methoxypyridin C1-symm. Var2\\1,1\H,0,0.7400329796,
0.0169829796,-1.9286399592\C,0,0.7460849796,0.0212709796,-0.8310059592
\N,0,-0.7068970204,-0.2108900204,-0.4583349592\C,0,1.6128489796,-1.118
1440204,-0.3613879592\C,0,1.1572779796,1.3881269796,-0.3432129592\C,0,
1.6687739796,-2.2835770204,-1.1410329592\C,0,0.7201899796,1.8952339796
,0.8881150408\C,0,2.4324259796,-3.3722170204,-0.7215319592\C,0,1.17425
19796,3.1392659796,1.3297220408\C,0,3.1379459796,-3.3062160204,0.48343
30408\C,0,2.0670729796,3.8784089796,0.5498210408\C,0,3.0865489796,-2.1
459370204,1.2600930408\C,0,2.5035449796,3.3735529796,-0.6775489592\C,0
,2.3247779796,-1.0520520204,0.8443890408\C,0,2.0495809796,2.1323409796
,-1.1246529592\H,0,1.1280339796,-2.3322720204,-2.0857849592\H,0,0.0230
229796,1.3305779796,1.5054070408\H,0,2.4832589796,-4.2673310204,-1.335
8069592\H,0,0.8316939796,3.5305869796,2.2842050408\H,0,3.6476959796,-2
.0883480204,2.1891320408\H,0,3.1938699796,3.9478989796,-1.2895789592\H
,0,2.3113989796,-0.1416010204,1.4378520408\H,0,2.3947559796,1.73894097
96,-2.0796739592\H,0,3.7390739796,-4.1514140204,0.8079330408\H,0,2.417
9339796,4.8469019796,0.8956800408\C,0,-1.0818680204,-1.1355720204,0.46
06360408\C,0,-2.4085880204,-1.2827350204,0.8053450408\C,0,-3.389421020
4,-0.4749680204,0.2030550408\C,0,-2.9746880204,0.4777139796,-0.7458969
592\C,0,-1.6303660204,0.5863509796,-1.0445619592\H,0,-0.2901610204,-1.
7380700204,0.8896870408\H,0,-2.7037120204,-2.0235400204,1.5414470408\H
,0,-3.6703930204,1.1360609796,-1.2524539592\H,0,-1.2492120204,1.316976
9796,-1.7513859592\C,0,-5.6959880204,0.1111569796,0.0027550408\H,0,-5.
5428050204,1.1681139796,0.2325400408\H,0,-5.7389510204,-0.0538190204,-
1.0762829592\H,0,-6.6090820204,-0.2454200204,0.4724460408\O,0,-4.64507

70204,-0.6883780204,0.5915540408\\Version=IA64-Linux-G03RevB.01\State=1-A\HF=-859.2810981\MP2=-862.2862417\RMSD=6.643e-09\PG=C01 [X(C19H18N1O1)]\\@

3e

1\1\GINC-LX64I62\SP\RMP2-FC\6-311++G(d,p)\C18H17N2(1+)\UI22102\15-Sep-2005\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Benzhydryl-Kation + 4-Aminopyridin C1-symm.\\1,1\H,0,0.4229091007,0.0042029712,-1.932172\C,0,0.4176391007,0.0077109712,-0.834283\N,0,-1.0439238993,-0.1343090288,-0.472567\C,0,1.2106241007,-1.1830980288,-0.358954\C,0,0.9166371007,1.3444379712,-0.343332\C,0,1.2048651007,-2.3488840288,-1.139725\C,0,0.4908921007,1.8892809712,0.875539\C,0,1.8986111007,-3.4815570288,-0.715144\C,0,1.0244141007,3.0996469712,1.322191\C,0,2.5949981007,-3.4594230288,0.496677\C,0,1.9853841007,3.7676979712,0.559545\C,0,2.6043591007,-2.2993320288,1.275208\C,0,2.4106641007,3.2253519712,-0.655776\C,0,1.9129471007,-1.1616710288,0.853927\C,0,1.8777691007,2.0176799712,-1.107316\H,0,0.6710541007,-2.3638210288,-2.089493\H,0,-0.2599848993,1.3804099712,1.477913\H,0,1.9025551007,-4.3771200288,-1.330933\H,0,0.6899301007,3.5205829712,2.26693\H,0,3.1586921007,-2.2763390288,2.209873\H,0,3.1539091007,3.7447319712,-1.25486\H,0,1.9470041007,-0.2527540288,1.449033\H,0,2.2138801007,1.5948869712,-2.052992\H,0,3.1422361007,-4.3390770288,0.825038\H,0,2.3977331007,4.7103949712,0.908894\C,0,-1.4887988993,-1.0313360288,0.43998\C,0,-2.8219018993,-1.0994190288,0.78038\C,0,-3.7599658993,-0.2312120288,0.17991\C,0,-3.2601308993,0.6956769712,-0.765698\C,0,-1.9185178993,0.7237919712,-1.059891\H,0,-0.7424748993,-1.6857700288,0.874608\H,0,-3.1345458993,-1.8344610288,1.516381\H,0,-3.9226338993,1.3952029712,-1.267209\H,0,-1.4918968993,1.4313109712,-1.763924\N,0,-5.0681448993,-0.2793670288,0.49104\H,0,-5.4276298993,-0.9469930288,1.160662\H,0,-5.7391878993,0.3382829712,0.053512\\Version=IA64-Linux-G03RevB.01\State=1-A\HF=-800.4278436\MP2=-803.2643414\RMSD=3.869e-09\PG=C01 [X(C18H17N2)]\\@

3f

1\1\GINC-IBMSMP\SP\RMP2-FC\6-311++G(d,p)\C20H21N2(1+)\UI22102\02-Sep-2004\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Benzhydryl-Kation + DMAP C1-symm.\\1,1\H,0,1.1293880581,0.0611140065,-1.9543310323\C,0,1.0670570581,0.0305380065,-0.8584460323\N,0,-0.4096529419,-

0.0733769935,-0.5732540323\C,0,1.7976600581,-1.2007349935,-0.3838650323\C,0,1.5891860581,1.3325300065,-0.3009200323\C,0,1.7848020581,-2.3447579935,-1.1957970323\C,0,1.1085890581,1.8664280065,0.9020299677\C,0,2.4205480581,-3.5120899935,-0.7743710323\C,0,1.6629720581,3.0410610065,1.4142609677\C,0,3.0657570581,-3.5465179935,0.4651819677\C,0,2.6992510581,3.6841140065,0.7333209677\C,0,3.0818210581,-2.4083369935,1.2751459677\C,0,3.1794580581,3.1525480065,-0.4662680323\C,0,2.4483050581,-1.2362449935,0.8569839677\C,0,2.6264700581,1.9805590065,-0.9827210323\H,0,1.2904750581,-2.3158619935,-2.1663570323\H,0,0.2984690581,1.3770630065,1.4401879677\H,0,2.4194090581,-4.3909389935,-1.4138640323\H,0,1.2857370581,3.4536550065,2.3465519677\H,0,3.5962320581,-2.4295209935,2.2324479677\H,0,3.9817770581,3.6526420065,-1.0023140323\H,0,2.4869750581,-0.3451109935,1.4782279677\H,0,3.0052960581,1.5658070065,-1.9157530323\H,0,3.5680350581,-4.4533889935,0.7914279677\H,0,3.1276380581,4.5991030065,1.1334449677\C,0,-0.9278939419,-0.9599559935,0.3118449677\C,0,-2.2749589419,-0.9902779935,0.5920769677\C,0,-3.1731819419,-0.0882319935,-0.0404710323\C,0,-2.5866619419,0.8290650065,-0.9583680323\C,0,-1.2336499419,0.8146860065,-1.1897010323\H,0,-0.2245079419,-1.6414839935,0.7757839677\H,0,-2.6190989419,-1.7258879935,1.3084099677\H,0,-3.1813089419,1.5591290065,-1.4933500323\H,0,-0.7555619419,1.5138330065,-1.8689530323\N,0,-4.4950499419,-0.0996649935,0.2094319677\C,0,-5.3811709419,0.8491600065,-0.4678160323\H,0,-5.3494429419,0.7076380065,-1.5523460323\H,0,-6.4001859419,0.6752250065,-0.1283520323\H,0,-5.1077269419,1.8805460065,-0.2255300323\C,0,-5.0533549419,-1.0627789935,1.1603259677\H,0,-4.8632909419,-2.0892429935,0.8323879677\H,0,-4.6317789419,-0.9147069935,2.1591899677\H,0,-6.1296329419,-0.9128839935,1.2152799677\\Version=IBM64-RS6000-G03RevB.01\State=1-A\HF=-878.4978706\MP2=-881.6428677\RMSD=5.115e-09\PG=C01 [X(C20H21N2)]\\@

3g conformation 1

1\1\GINC-LX64I67\SP\RMP2-FC\6-311++G(d,p)\C22H23N2(1+)\UI22102\26-Sep-2005\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Benzhydryl-Kation + 4-Pyrrolidinopyridin C1-symm. Var1\\1,1\H,0,1.7714870651,0.0551239704,-1.953185\C,0,1.6702230651,0.0258919704,-0.860094\N,0,0.1853940651,-0.0676280296,-0.626028\C,0,2.3759060651,-1.2101920296,-0.36005\C,0,2.1845260651,1.3239659704,-0.285894\C,0,2.3777750651,-2.3567750296,-1.168344\C,0,1.6613140651,1.8683279704,0.894249\C,0,2.99085906

51,-3.5279040296,-0.724531\C,0,2.2082710651,3.0383289704,1.424891\C,0,
3.5985770651,-3.5635820296,0.533799\C,0,3.2793830651,3.6663809704,0.78
5209\C,0,3.5998320651,-2.4229220296,1.340354\C,0,3.8021800651,3.124350
9704,-0.391712\C,0,2.9888680651,-1.2470530296,0.899722\C,0,3.256959065
1,1.9569039704,-0.926268\H,0,1.9124350651,-2.3270370296,-2.153091\H,0,
0.8236250651,1.3908609704,1.399786\H,0,3.0012890651,-4.4089070296,-1.3
60996\H,0,1.7978480651,3.4590559704,2.339378\H,0,4.0849830651,-2.44518
70296,2.312803\H,0,4.6318940651,3.6127369704,-0.89594\H,0,3.0156770651
,-0.3542930296,1.51929\H,0,3.6688920651,1.5338999704,-1.841413\H,0,4.0
832270651,-4.4735180296,0.877727\H,0,3.7018570651,4.5778389704,1.19946
8\C,0,-0.3675859349,-0.9409630296,0.253139\C,0,-1.7226549349,-0.960248
0296,0.488316\C,0,-2.5906299349,-0.0564590296,-0.183102\C,0,-1.9704969
349,0.8482419704,-1.091481\C,0,-0.6116969349,0.8201779704,-1.27965\H,0
,0.3169010651,-1.6181950296,0.750456\H,0,-2.1014769349,-1.6726560296,1
.211833\H,0,-2.5513119349,1.5636149704,-1.661976\H,0,-0.1061959349,1.5
037889704,-1.954916\N,0,-3.9135829349,-0.0557450296,0.022689\C,0,-4.84
19079349,0.9167849704,-0.582883\H,0,-4.9682159349,0.7017419704,-1.6518
92\H,0,-4.4536389349,1.9340049704,-0.471899\C,0,-4.6120549349,-1.03055
50296,0.880281\H,0,-4.2720689349,-2.0463800296,0.655702\H,0,-4.4084269
349,-0.8161460296,1.937449\C,0,-6.0804039349,-0.8047670296,0.527199\H,
0,-6.7472479349,-1.0906850296,1.343858\H,0,-6.3475249349,-1.3978630296
,-0.353019\C,0,-6.1333999349,0.6871919704,0.198871\H,0,-6.1225659349,1
.2799519704,1.118893\H,0,-7.0171739349,0.9710949704,-0.377069\\Version
=IA64-Linux-G03RevB.01\State=1-A\HF=-955.4307506\MP2=-958.8581181\RMSD
=9.973e-09\PG=C01 [X(C22H23N2)]\\@

3g conformation 2

1\1\GINC-LX64I67\SP\RMP2-FC\6-311++G(d,p)\C22H23N2(1+)\UI22102\23-Sep-
2005\0\\# MP2(FC)/6-311++G** SCF=TIGHT GEOM=CHECK GUESS=READ\\SP Benzh
ydryl-Kation + 4-Pyrrolidinopyridin C1-symm. Var2\\1,1\H,0,1.769195964
5,0.0615791302,-1.9547600118\C,0,1.6691659645,0.0288511302,-0.86170301
18\N,0,0.1845669645,-0.0648858698,-0.6259580118\C,0,2.3752609645,-1.20
89538698,-0.3665510118\C,0,2.1846039645,1.3248631302,-0.2837740118\C,0
,2.3776289645,-2.3522938698,-1.1794280118\C,0,1.6632999645,1.865318130
2,0.8990129882\C,0,2.9910689645,-3.5249868698,-0.7402380118\C,0,2.2113
429645,3.0333671302,1.4328169882\C,0,3.5986759645,-3.5654728698,0.5179
969882\C,0,3.2816859645,3.6633121302,0.7937049882\C,0,3.5994359645,-2.

4280468698,1.3291159882\C,0,3.8025869645,3.1251771302,-0.3858360118\C,
0,2.9880759645,-1.2506618698,0.8931499882\C,0,3.2562449645,1.9597131302,-0.9235800118\H,0,1.9123259645,-2.3187958698,-2.1640700118\H,0,0.8261969645,1.3863691302,1.4041129882\H,0,3.0018589645,-4.4034328698,-1.3802190118\H,0,1.8023539645,3.4511121302,2.3493109882\H,0,4.0844979645,-2.4540378698,2.3015169882\H,0,4.6316729645,3.6150731302,-0.8896320118\H,0,3.0144999645,-0.3603858698,1.5162939882\H,0,3.6666909645,1.5397401302,-1.8407850118\H,0,4.0836139645,-4.4766068698,0.8583309882\H,0,3.7050049645,4.5732471302,1.2104429882\C,0,-0.3678340355,-0.9419678698,0.2498669882\C,0,-1.7221820355,-0.9592158698,0.4892889882\C,0,-2.5910970355,-0.0549888698,-0.1803660118\C,0,-1.9719750355,0.8514721302,-1.0876560118\C,0,-0.6129560355,0.8261981302,-1.2746180118\H,0,0.3156559645,-1.6283028698,0.7359339882\H,0,-2.1042550355,-1.6954958698,1.1867149882\H,0,-2.5494150355,1.5902681302,-1.6310980118\H,0,-0.1066990355,1.5198601302,-1.9389680118\N,0,-3.9137520355,-0.0544608698,0.0272919882\C,0,-4.8644810355,0.7971361302,-0.7110710118\C,0,-4.5895820355,-0.9108748698,1.0189549882\C,0,-5.9958880355,-0.3188758698,1.0789779882\C,0,-6.2182830355,0.1936971302,-0.3438110118\H,0,-4.7771360355,1.8385541302,-0.3752250118\H,0,-4.6584160355,0.7551291302,-1.7850940118\H,0,-4.0676860355,-0.8647468698,1.9799009882\H,0,-4.5989760355,-1.9524738698,0.6724689882\H,0,-6.0205470355,0.5120061302,1.7909829882\H,0,-6.7381880355,-1.0563848698,1.3927089882\H,0,-7.0266250355,0.9247971302,-0.4175950118\H,0,-6.4501250355,-0.6382398698,-1.0161400118\\Version=IA64-Linux-G03RevB.01\State=1-A\HF=-955.4307029\MP2=-958.8577907\RMSD=3.553e-09\PG=C01 [X(C22H23N2)]\\@

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[S1] S. Minegishi, H. Mayr, *J. Am. Chem. Soc.* **2003**, *125*, 286–295.

[S2] S. Minegishi, S. Kobayashi, H. Mayr, *J. Am. Chem. Soc.* **2004**, *126*, 5174–5181.

[S3] Calculated from the reactivity parameters *E*, *N*, and *s* from ref. [S1].