-Supporting Information-

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Ambident Reactivites of Pyridone Anions

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1 General

Materials

Commercially available DMSO and acetonitrile (both: H_2O content < 50 ppm) were used without further purification. Water was distilled and passed through a Milli-Q water purification system. The reference electrophiles used in this work were synthesized according to literature procedures.[1]

NMR spectroscopy

In the ^{1}H and ^{13}C NMR spectra chemical shifts are given in ppm and refer to tetramethylsilane (δ_H = 0.00, δ_C = 0.0), d^6-DMSO (δ_H = 2.50, δ_C = 39.5), or to $CDCl_3$ (δ_H = 7.26, δ_C = 77.0) as internal standards. The coupling constants are given in Hz. For reasons of simplicity, the ^{1}H-NMR signals of AA'BB'-spin systems of *p*-disubstituted aromatic rings are treated as doublets. Signal assignments are based on additional COSY, gHSQC, and gHMBC experiments.

Kinetics

As the reactions of colored benzhydrylium ions or quinone methides with colorless pyridone anions **1** and **2** result in colorless products, the reactions could be followed by UV-Vis spectroscopy. Slow reactions ($\tau_{1/2}$ > 10 s) were determined by using conventional UV-Vis-spectrophotometers. Stopped-flow techniques were used for the investigation of rapid reactions ($\tau_{1/2}$ < 10 s). The temperature of all solutions was kept constant at 20.0 ± 0.1 °C during all kinetic studies by using a circulating bath thermostat. In all runs the nucleophile concentration was at least 10 times higher than the concentration of the electrophile, resulting in pseudo-first-order kinetics with an exponential decay of the electrophile's concentration. First-order rate constants k_{obs} were obtained by least-squares fitting of the absorbance data to a single-exponential $A_t = A_0 \exp(-k_{obs}t) + C$. The second-order rate constants k_2 were obtained from the slopes of the linear plots of k_{obs} against the nucleophile's concentration.

Determination of rate constants in water:

The combination reactions of **1** and **2** with benzhydrylium ions 3d–h were also studied in water. Due to the low acidities of the pyridones **1-H** (pK_A = 11.74)[2] and **2-H** (pK_A = 11.12),[2] aqueous solutions of the pyridone anions **1** and **2** are partially hydrolyzed and contain hydroxide anions. Therefore, the pyridones **1-H** and **2-H**, which are used in high excess over the electrophiles **3** (pseudo-first-order conditions), were deprotonated with only 0.02 to 0.2 equivalents of KOH.

For these deprotonation reactions [Equation (S1) shows only 2-pyridone **1-H]**, one can calculate the equilibrium constants as shown in equation (S2). Applying the mass balances (S3) and (S4), where the index "0" stands for the initial concentration and "eff" for the equilibrium concentration, equation (S2) can be rewritten as a quadratic equation (S5) with its positive solution (S6).

$$\mathbf{1}\text{–H} + {}^{\ominus}\text{OH} \underset{K_B}{\overset{K}{\rightleftharpoons}} \mathbf{1}^{\ominus} + H_2O \qquad \text{(S1)}$$

$$K = [\mathbf{1}^-]_{\text{eff}} / ([\mathbf{1\text{-}H}]_{\text{eff}}\,[\text{OH}^-]_{\text{eff}}) = 1 / K_B \qquad \text{(S2)}$$

$$[\text{OH}^-]_0 = [\text{OH}^-]_{\text{eff}} + [\mathbf{1}^-]_{\text{eff}} \qquad \text{(S3)}$$

$$[\mathbf{1\text{-}H}]_0 = [\mathbf{1}^-]_{\text{eff}} + [\mathbf{1\text{-}H}]_{\text{eff}} \qquad \text{(S4)}$$

$$[\text{OH}^-]_{\text{eff}}^2 - [\text{OH}^-]_{\text{eff}}\,([\mathbf{1\text{-}H}]_0 - [\text{OH}^-]_0 + K_B) - K_B[\text{OH}^-]_0 = 0 \qquad \text{(S5)}$$

$$[\text{OH}^-]_{\text{eff}} = 0.5\,(-[\mathbf{1\text{-}H}]_0 - [\text{OH}^-]_0 + K_B + (([\mathbf{1\text{-}H}]_0 - [\text{OH}^-]_0 + K_B)^2 + 4K_B[\text{OH}^-]_0)^{1/2} \qquad \text{(S6)}$$

The observed rate constants k_{obs} for the reactions in water reflect the sum of the reaction of the electrophiles with the pyridone anions **1** and **2** (k_2), with hydroxide ($k_{2,\text{OH}}$)[3] and with water (k_w) (eq. S7). Rearrangement of eq. 7, i.e., subtracting the contribution of hydroxide from the observed rate constant k_{obs}, yields equation 8. The second-order rate constants for the reactions of the benzhydrylium ions with **1** and **2** can then be obtained from plots of k_{eff} versus the concentration of the nucleophiles. The intercepts of these plots correspond to the reactions of the electrophiles with water and are generally negligible in agreement with previous work, showing that water (N = 5.20)[4] reacts much slower with benzhydrylium ions than the nucleophiles investigated in this work.

$$k_{\text{obs}} = k_2[\mathbf{1}\text{ or }\mathbf{2}] + k_{2,\text{OH}}[\text{OH}^-] + k_w \qquad \text{(S7)}$$

$$k_{eff} = k_{\text{obs}} - k_{2,\text{OH}}[\text{OH}^-] = k_2[\mathbf{1}\text{ or }\mathbf{2}] + k_w \qquad \text{(S8)}$$

Determination of Equilibrium Constants:

Equilibrium constants were determined by UV/Vis spectroscopy by adding small volumes of stock solutions of the potassium salts of 2- or 4-pyridone (**1-K** and **2-K**) to solutions of the quinone methides in DMSO. The decay of the electrophiles' absorbances was monitored and when the absorbance was constant (typically after less than a minute), another portion of the nucleophile was added. This procedure was repeated several times. In order to determine the equilibrium constants K, the molar absorptivities ε of the electrophiles were determined from the initial absorbance assuming the validity of Lambert-Beer's law. Then, the equilibrium constants for the reaction depicted in Equation (S9) were determined according to equation (10). The equilibrium concentrations of the electrophile $[E]_{eq}$, the nucleophiles $[Nu]_{eq}$, and the product $[P]_{eq}$ were calculated from the initial concentrations $[E]_0$ and $[Nu]_0$ and from the absorptivities of the electrophile.

$$E + Nu \rightarrow P \qquad (S9)$$

$$K = [P]_{eq} / ([E]_{eq} [Nu]_{eq} = ([E]_0 - [E]_{eq}) / (([E]_{eq} ([Nu]_0 - [E]_0 + [E]_{eq})) \qquad (S10)$$

2 Synthesis of Pyridone Salts

2.1 2-Pyridone-Potassium (1-K)

2-Pyridone (1.80 g, 18.9 mmol) was added to a solution of KO*t*Bu (2.00 g, 17.8 mmol) in 25 mL dry ethanol and stirred for 30 min. The solvent was evaporated at low pressure and the solid residue was washed several times with dry diethyl ether to afford 2-pyridone potassium (**1-K,** 2.20 g, 16.5 mmol, 93%) as a colorless solid.

^{1}H-NMR (d_6-DMSO, 400 MHz) δ = 5.81-5.84 (m, 2 H), 6.94-6.98 (m, 1 H), 7.60-7.62 (m, 1 H). ^{13}C-NMR (d_6-DMSO, 101 MHz) δ = 103.9 (d), 113.8 (d), 136.0 (d), 147.7 (d), 173.0 (s).

2.2 2-Pyridone-Tetrabutylammonium (1-NBu$_4$)

2-Pyridone (1.03 g, 10.8 mmol) was added to a solution of 40 wt% aqueous tetrabutylammonium hydroxide (7.00 g, 10.8 mmol) in 10 mL water and stirred for 15 min. The solvent was evaporated at low pressure and the solid residue was dried at 60 °C at 0.01 mbar to afford 2-pyridone tetrabutylammonium (**1-NBu$_4$**, 3.56 g, 10.6 mmol, 98%) as a colorless solid.

^{1}H-NMR (d_6-DMSO, 400 MHz) δ = 0.90-0.93 (m, 12 H), 1.25-1.34 (m, 8 H), 1.52-1.60 (m, 8 H), 3.18-3.22 (m, 8 H), 5.62-5.68 (m, 2 H), 6.80-6.84 (m, 1 H), 7.53-7.55 (m, 1 H). ^{13}C-NMR (d_6-DMSO, 101 MHz) δ = 13.5 (q), 19.2 (t), 23.1 (t), 57.5 (t), 102.6 (d), 113.5 (d), 135.1 (d), 148.3 (d), 172.9. (s).

2.3 4-Pyridone-Potassium (2-K)

4-Pyridone (3.10 g, 32.6 mmol) was added to a solution of KO*t*Bu (3.60 g, 32.1 mmol) in 25 mL dry ethanol and stirred for 30 min. The solvent was evaporated at low pressure and the solid residue was washed several times with dry ether to afford 4-pyridone potassium (**2-K**, 4.05 g, 30.4 mmol, 95%) as a colorless solid.

^{1}H-NMR (d_6-DMSO, 400 MHz) δ = 5.95 (d, ^{3}J = 6.4 Hz, 2 H), 7.60 (d, ^{3}J = 6.4 Hz, 2 H). ^{13}C-NMR (d_6-DMSO, 101 MHz) δ = 116.4 (d), 148.9 (d), 175.3 (s).

2.4 4-Pyridone-Tetrabutylammonium (**2-NBu$_4$**)

4-Pyridone (1.03 g, 10.8 mmol) was added to a solution of 40 wt% aqueous tetrabutylammonium hydroxide (7.00 g, 10.8 mmol) in 10 mL water and stirred for 15 min. The solvent was evaporated at low pressure and the solid residue was dried at 60 °C at 0.01 mbar to afford 4-pyridone tetrabutylammonium (**2-NBu$_4$**, 3.50 g, 10.4 mmol, 96%) as a colorless solid.

^{1}H-NMR (d$_6$-DMSO, 400 MHz) δ = 0.90-0.94 (m, 12 H), 1.25-1.34 (m, 8 H), 1.52-1.59 (m, 8 H), 3.15-3.19 (m, 8 H), 5.78 (d, ^3J = 6.4 Hz, 2 H), 7.49 (d, ^3J = 6.4 Hz, 2 H). ^{13}C-NMR (d$_6$-DMSO, 101 MHz) δ = 13.5 (q), 19.2 (t), 23.1 (t), 57.5 (t), 116.6 (d), 148.7 (d), 175.7. (s).

3 Reaction Products

3.1 Isolated reaction products

General Procedure 1 (GP1):

The pyridone salts were dissolved in dry DMSO or CH_3CN and a solution of the electrophile in the same solvent (with ca. 5–10 % CH_2Cl_2 as cosolvent) was added. The mixture was stirred for 15 min before 0.5 % acetic acid was added. The mixture was extracted with dichloromethane or ethyl acetate, and the combined organic phases were washed with saturated NaCl-solution, dried over Na_2SO_4 and evaporated under reduced pressure. The crude reaction products were purified by column chromatography on silica gel and subsequently characterized by NMR, IR, and MS.

General Procedure 2 (GP2):

The tetrabutylammonium salts **1-NBu$_4$** and **2-NBu$_4$** were dissolved in dry CH_3CN and the benzhydryl bromide was added. After some time the solvent was removed and the crude reaction products were purified by column chromatography on silica gel.

General Procedure 3 (GP3):

In the case of the highly reactive benzhydrylium ion **3b**, a solution of silver triflate in CH_3CN was cooled to –40 °C. Dropwise addition of a solution of the benzhydryl bromide **3b-Br** in dry CH_2Cl_2 to the reaction mixture was accompanied by the appearance of a yellow color. Then, a solution of the potassium salts **1-K** or **2-K** and 18-crown-6 in dry CH_2Cl_2 was added. The mixture was stirred for 15 min before warming to room temperature. The solvent was removed, and the crude reaction products were purified by column chromatography on silica gel.

3.1.1 Products of the Reaction of the 2-Pyridone Anion (**1**)

<u>Reactions with **3l**</u>

<u>MB201:</u>

According to GP1, 2-pyridone-potassium (**1-K**, 63.8 mg, 0.479 mmol) and **3l** (147 mg, 0.477 mmol) furnished 1-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(*p*-tolyl)methyl)pyridin-2(1*H*)-one (**4l-N**, 170 mg, 0.421 mmol, 88%) in DMSO as colorless crystals.

<u>MB204:</u>

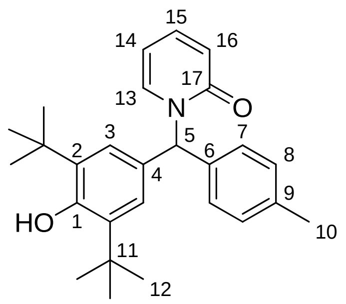
According to GP1, 2-pyridone-potassium (**1-K**, 116 mg 0.871 mmol), 18-crown-6 (230 mg, 0.870 mmol), and **3l** (135 mg, 0.438 mmol) furnished 1-((3,5-di-*tert*-butyl-4-hydroxy-phenyl)(*p*-tolyl)methyl)pyridin-2(1*H*)-one (**4l-N**, 140 mg, 0.347 mmol, 79%) in CH_3CN.

<u>MB218:</u>

According to GP1, 2-pyridone (104 mg, 1.09 mmol), LiOtBu (87.0 mg, 1.09 mmol), and **3l** (120 mg, 0.389 mmol) yielded 1-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(*p*-tolyl)methyl)pyridin-2(1*H*)-one (**4l-N**, 125 mg, 0.310 mmol, 80%) in DMSO.

<u>MB284:</u>

According to GP1, 2-pyridone-NBu_4 (**1-NBu₄**, 275 mg, 0.817 mmol) and **3l** (120 mg, 0.389 mmol) yielded 1-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(*p*-tolyl)methyl)pyridin-2(1*H*)-one (**4l-N**, 140 mg, 0.347 mmol, 89%) in CH_3CN.



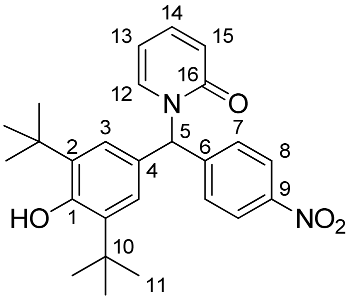
4l-N

Melting point: 164.1-165.1 °C (from $CHCl_3$/pentane). ^{1}H-NMR ($CDCl_3$, 599 MHz) δ = 1.35 (s, 18 H, 12-H), 2.33 (s, 3 H, 10-H), 5.23 (s, OH), 6.10-6.12 (m, 1 H, 14-H), 6.62 (d, ^3J = 9.1 Hz, 1H, 16-H), 6.90 (s, 2 H, 3-H), 7.01 (d, ^3J = 8.0 Hz, 2 H, 7-H), 7.12-7.16 (m, 3 H, 8-H, 13-H), 7.29-7.32 (m, 1 H, 15-H), 7.38 (s, 1H, 5-H). ^{13}C-NMR ($CDCl_3$, 151 MHz) δ = 21.1 (q, C-10), 30.2 (q, C-12), 34.4 (s, C-11), 61.9 (d, C-5), 105.5 (d, C-14), 120.7 (d, C-16), 125.6 (d, C-3), 128.5 (d, C-7), 129.1 (s, C-4), 129.3 (d, C-8), 136.0 (d, C-13), 136.1 (s, C-2), 136.5 (d, C-13), 137.3 (s, C-9), 138.9 (d, C-15), 153.4 (s, C-1), 162.7 (s, C-17). IR (neat, ATR) $\tilde{\nu}$ = 3377 (w), 2959 (m), 2922 (m), 2870 (m), 1658 (vs), 1574 (m), 1538 (m), 1432 (m), 1230 (m), 1222 (m), 1142 (w) 1065 (m), 1020 (w), 892 (w), 874 (w), 796 (w), 760 (m), 732 (w). HR-MS (ESI) $[M-H]^-$: *m*/*z* calcd for $C_{27}H_{32}N_1O_2^-$: 402.2439 found: 402.2447.

Reactions with **3k**

MB209:

According to GP1, 2-pyridone-potassium (**1-K**, 160 mg, 1.20 mmol) and **3k** (200 mg, 0.589 mmol) furnished 1-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-nitrophenyl)methyl)-pyridin-2(1*H*)-one (**4k-N**, 215 mg, 0.495 mmol, 84%) in DMSO.



4k-N

Melting point: 254.1-255.2 °C (from $CHCl_3$/pentane). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 1.36 (s, 18 H, 11-H), 5.37 (s, OH), 6.17-6.22 (m, 1 H, 13-H), 6.65 (d, ^3J = 8.5 Hz, 1 H, 15-H), 6.88 (s, 2 H, 3-H), 7.11 (dd, ^3J = 7.0 Hz, ^4J = 2.0 Hz, 1 H, 12-H), 7.28 (d, ^3J = 7.9 Hz, 2 H, 7-H), 7.35-7.41 (m, 2 H, 5-H, 14-H), 8.21 (d, ^3J = 8.8 Hz, 2 H, 8-H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 30.1 (q, C-11), 34.4 (s, C-10), 62.3 (d, C-5), 106.1 (d, C-13), 121.0 (d, C-15), 123.8 (d, C-8), 126.4 (d, C-3), 127.4 (s, C-4), 128.7 (d, C-7), 135.3 (d, C-12), 136.7 (s, C-2), 139.4 (d, C-14), 147.2 (s, C-6 and C-9 superimposed), 154.2 (s, C-1), 162.5 (s, C-16). IR (neat, ATR) $\tilde{\nu}$ = 3378 (w), 3108 (w), 3081 (w), 3002 (w), 2955 (m), 2925 (m), 2872 (w), 2856 (w), 1657 (vs), 1572 (s), 1541 (m), 1516 (s), 1434 (m), 1346 (vs), 1273 (w), 1232 (w), 1221 (m), 1146 (w), 1108 (w), 1063 (m), 1020 (w), 1009 (w), 896 (w), 868 (w), 844 (w), 764 (m), 746 (w), 736 (w), 709 (w). HR-MS (ESI) $[M-H]^-$: *m*/*z* calcd for $C_{26}H_{29}N_2O_4^-$: 433.2133 found: 433.2137.

Reactions with tol_2CHBr (**3b-Br**) and with tol_2CH^+ (**3b**)

MB287:

According to GP2, 2-pyridone-NBu_4 (**1-NBu$_4$**, 200 mg, 0.594 mmol) and tol_2CHBr (**3b-Br**, 100 mg, 0.363 mmol) yielded 2-(di-*p*-tolylmethoxy)pyridine (**4b-O**, 40 mg, 0.14 mmol, 39%) and 1-(di-*p*-tolylmethyl)-pyridin-2(1*H*)-one (**4b-N**, 52 mg, 0.18 mmol, 50%) in CH_3CN as colorless oils.

MB327:

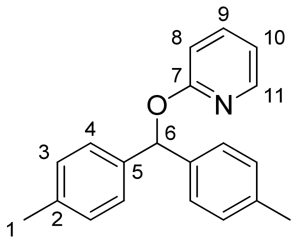
According to GP2, 2-pyridone-NBu_4 (**1-NBu$_4$**, 210 mg, 0.624 mmol) and tol_2CHBr (**3b-Br**, 100 mg, 0.363 mmol) furnished 2-(di-*p*-tolylmethoxy)pyridine (**4b-O**, 43 mg, 0.15 mmol, 41 %) and 1-(di-*p*-tolylmethyl)-pyridin-2(1*H*)-one (**4b-N**, 56 mg, 0.19 mmol, 52%) in 90% aqueous CH_3CN as colorless oils.

MB291:

According to GP2, 2-pyridone-NBu_4 (**1-NBu₄**, 203 mg, 0.603 mmol), $AgNO_3$ (105 mg, 0.618 mmol), and tol_2CHBr (**3b-Br**, 100 mg, 0.363 mmol) yielded 2-(di-*p*-tolylmethoxy)pyridine (**4b-O**, 97.0 mg, 0.34 mmol, 94%) in CH_3CN as colorless oil.

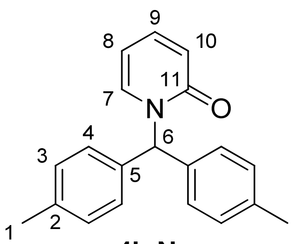
MB344:

According to GP3, 2-pyridone-potassium (**1-K**, 70.0 mg, 0.526 mmol), 18-crown-6 (162 mg, 0.613 mmol), tol_2CHBr (**3b-Br**, 122 mg, 0.443 mmol) and silver triflate (114 mg, 0.444 mmol) furnished 2-(di-*p*-tolylmethoxy)pyridine (**4b-O**, 22.1 mg, 0.0764 mmol, 17%) and 1-(di-*p*-tolyl-methyl)pyridin-2(1*H*)-one (**4b-N**, 62.9 mg, 0.217 mmol, 49 %) and bis(4,4'-dimethyl-benzhydryl)ether (28.3 mg, 0.0696 mmol, 31%) in CH_3CN/CH_2Cl_2 as colorless oils.



4b-O

^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 2.30 (s, 6 H, 1-H), 6.77-6.81 (m, 1 H, 10-H), 6.82-6.85 (m, 1 H, 8-H), 7.11 (d, ^3J = 7.8 Hz, 4 H, 3-H), 7.20 (s, 1 H, 6-H), 7.32 (d, ^3J = 8.0 Hz, 4 H, 4-H), 7.49-7.55 (m, 1 H, 9-H), 8.07-8.10 (m, 1 H, 11-H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 21.1 (q, C-1), 77.3 (d, C-6), 111.6 (d, C-8), 116.8 (d, C-10), 127.1 (d, C-4), 129.0 (d, C-3), 137.0 (s, C-2), 138.6 (d, C-9), 138.8 (s, C-5), 146.9 (d, C-11), 163.1 (s, C-7). HR-MS (EI) $[M]^+$: *m*/*z* calcd for $C_{20}H_{19}NO$: 289.1467 found: 289.1452. MS (EI) *m*/*z* = 289 (16) $[M^+]$, 196 (16), 195 (100) $[M-C_5H_4NO^+]$, 180 (17), 179 (18), 178 (12), 165 (20).



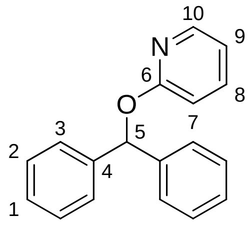
4b-N

^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 2.33 (s, 6 H, 1-H), 6.06-6.11 (m, 1 H, 8-H), 6.58-6.62 (m, 1 H, 10-H), 7.02 (d, ^3J = 8.1 Hz, 4 H, 4-H), 7.13-7.16 (m, 5 H, 3-H 7-H), 7.25-7.32 (m, 1 H, 9-H), 7.42 (s, 1 H, 6-H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 21.1 (q, C-1), 61.5 (d, C-6), 105.5 (d, C-8), 120.8 (d, C-10), 128.7 (d, C-4), 129.4 (d, C-3), 135.9 (s, C-5), 136.0 (d, C-7), 137.7 (s, C-2), 138.9 (d, C-9), 162.5 (s, C-11). IR (neat, ATR) $\tilde{\nu}$ = 3284 (w), 3130 (w), 3052 (w), 3024 (m), 2922 (m), 2860 (m), 2364 (w), 1906 (vw), 1654 (vs), 1610 (s), 1592 (s), 1568 (m), 1542 (m), 1512 (m), 1468 (vs), 1428 (vs), 1378 (w), 1308 (m), 1284 (s), 1246 (s), 1174 (m), 1112 (w), 1036 (m), 988 (s), 940 (w), 894 (m), 848 (m), 806 (s), 766 (s), 722 (m), 614 (w). HR-MS (EI) $[M]^+$: *m*/*z* calcd for $C_{20}H_{19}NO$: 289.1467 found: 289.1459. MS (EI) *m*/*z* = 289 (30) $[M^+]$, 196 (15), 195 (100) $[M-C_5H_4NO^+]$, 180 (17), 179 (18), 178 (13), 165 (19).

Reactions with Ph_2CHBr (**3a-Br**)

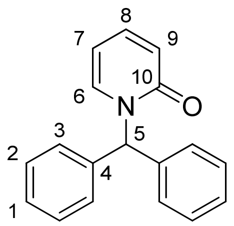
MB292:

According to GP2, 2-pyridone-NBu_4 (**1-NBu$_4$**, 298 mg, 0.885 mmol) and Ph_2CHBr (**3a-Br**, 100 mg, 0.405 mmol) furnished 2-(benzhydryloxy)pyridine (**4a-O**, 40 mg, 0.15 mmol, 37%) and 1-benzhydrylpyridin-2(1*H*)-one (**4a-N**, 63 mg, 0.24 mmol, 59%) in CH_3CN as colorless oils.



4a-O

^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 6.78-6.82 (m, 1 H, 9-H), 6.84-6.87 (m, 1 H, 7-H), 7.20-7.34 (m, 7 H, 1-H, 2-H, 5-H), 7.42-7.45 (m, 4 H, 3-H), 7.51-7.57 (m, 1 H, 8-H), 8.07-8.10 (m, 1 H, 10-H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 77.5 (d, C-5), 111.6 (d, C-7), 117.0 (d, C-9), 127.2 (d, C-3), 127.4 (d, C-1), 128.3 (d, C-2), 138.6 (d, C-8), 141.6 (s, C-4), 146.9 (d, C-10), 162.9 (s, C-6). IR (neat, ATR) $\tilde{\nu}$ = 3088 (w), 3062 (w), 3030 (w), 2958 (w), 2918 (m), 2850 (m), 2362 (vw), 1738 (w), 1596 (s), 1570 (m), 1494 (w), 1468 (s), 1430 (vs), 1308 (m), 1284 (m), 1262 (s), 1248 (s), 1186 (w), 1142 (w), 1080 (w), 1040 (m), 988 (m), 918 (w), 886 (w), 800 (w), 778 (m), 740 (m), 696 (s), 664 (w).



4a-N

^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 6.08-6.13 (m, 1 H, 7-H), 6.60-6.64 (m, 1 H, 9-H), 7.12-7.15 (m, 5 H, 3-H, 6-H), 7.27-7.37 (m, 7 H, 1-H, 2-H, 8-H), 7.52 (s, 1 H, 5-H).^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 61.8 (d, C-5), 105.7 (d, C-7), 120.9 (d, C-9), 128.0 (d, C-1), 128.8 (2 d, C-2, C-3), 135.9 (d, C-6), 138.8 (s, C-4), 139.0 (d, C-8), 162.5 (s, C-10). IR (neat, ATR) $\tilde{\nu}$ = 3082 (w), 3064 (w), 3028 (w), 3010 (w), 2940 (w), 2360 (w), 2332 (w), 1810 (vw), 1652 (vs), 1572 (vs), 1528 (s), 1496 (m), 1450 (m), 1400 (w), 1336 (w), 1238 (w), 1148 (m), 888 (w), 778 (m), 756 (w), 730 (m), 696 (m). HR-MS (ESI) $[M-H]^-$: $[M+Na]^+$: *m*/*z* calcd for $C_{18}H_{15}NONa$: 284.1051 found: 284.1045.

3.1.2 Products of the Reaction of the 4-Pyridone Anion (**2**)

Reactions with tol_2CHBr (**3b-Br**) and tol_2CH^+ (**3b**)

MB299:

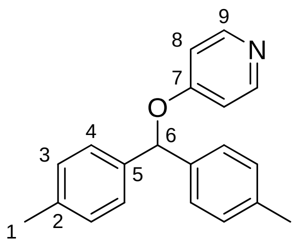
According to GP2, 4-pyridone-NBu_4 (**2-NBu$_4$**, 266 mg, 0.790 mmol) and tol_2CHBr (**3b-Br**, 103 mg, 0.374 mmol) yielded 4-(di-*p*-tolylmethoxy)pyridine (**5b-O**, 77.0 mg, 0.266 mmol, 71%) in CH_3CN as colorless oil.

MB300:

According to GP2, 4-pyridone-NBu4 (**2-NBu₄**, 199 mg, 0.591 mmol), $AgNO_3$ (107 mg, 0.630 mmol), and tol_2CHBr (**3-Br**, 92.0 mg, 0.334 mmol) furnished 4-(di-*p*-tolylmethoxy)pyridine (**5b-O**, 70.0 mg, 0.242 mmol, 72%) in CH_3CN as colorless oil.

MB340:

According to GP3, 4-pyridone-potassium (**2-K**, 118 mg, 0.886 mmol), 18-crown-6 (240 mg, 0.908 mmol), silver triflate (149 mg, 0.580 mmol), and tol_2CHBr (**3b-Br**, 160 mg, 0.581 mmol) yielded 4-(di-*p*-tolylmethoxy)pyridine (**5b-O**, 124 mg, 0.429 mmol, 74%) and bis(4,4'-dimethyl-benzhydryl)ether (29 mg, 0.071 mmol, 24%) in CH_3CN/CH_2Cl_2 as colorless oils.



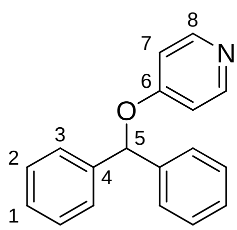
5b-O

^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 2.31 (s, 6 H, 1-H), 6.22 (s, 1 H, 6-H), 6.83 (d, ^3J = 6.4 Hz, 2 H, 8-H), 7.14 (d, ^3J = 7.9 Hz, 4 H, 3-H), 7.26 (d, ^3J = 8.1 Hz, 4 H, 4-H), 8.34 (d, ^3J = 6.0 Hz, 2 H, 9-H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 21.1 (q, C-1), 81.4 (d, C-6), 111.6 (d, C-8), 126.7 (d, C-4), 129.4 (d, C-3), 137.2 (s, C-5), 137.9 (s, C-2), 151.0 (d, C-9), 164.1 (s, C-7). HR-MS (EI) $[M]^+$: *m*/*z* calcd for $C_{20}H_{19}NO$: 289.1467 found: 289.1445. MS (EI) *m*/*z* = 289 (26) $[M^+]$, 196 (14), 195 (100) $[M-C_5H_4NO^+]$, 180 (14), 179 (10), 165 (15).

Reactions with Ph_2CHBr (**3a-Br**)

MB298:

According to GP2, 4-pyridone-NBu4 (**2-NBu₄**, 306 mg, 0.909 mmol) and Ph_2CHBr (**3a-Br**, 102 mg, 0.413 mmol) furnished 4-(benzhydryloxy)pyridine (**5a-O**, 83.1 mg, 0.318 mmol, 77%) in CH_3CN as colorless oil.



5a-O

^{1}H-NMR ($CDCl_3$, 300 MHz) δ = 6.27 (s, 1 H, 5-H), 6.84 (d, ^3J = 6.4 Hz, 2 H, 7-H), 7.24-7.41 (m, 10 H, 1-H, 2-H, and 3-H), 8.36 (d, ^3J = 6.4 Hz, 2 H, 8-H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ = 81.5 (d, C-5), 111.6 (d, C-7), 126.8 (d, C-3), 128.1 (d, C-1), 128.8 (d, C-2), 140.0 (s, C-4), 151.0 (d, C-8), 164.0 (s, C-6). IR (neat, ATR) $\tilde{\nu}$ = 3384 (vw), 3088 (w), 3064 (w), 3030 (w), 2922 (w), 2367 (vw), 1590 (vs), 1568 (s), 1496 (s), 1454 (m), 1418 (w), 1266 (s), 1210 (s), 1184 (w), 1082 (w), 1002 (s), 910 (w), 884 (m), 830 (m), 812 (m), 740 (m), 696 (s), 650 (w), 630 (w). HR-MS (EI) $[M]^+$: *m*/*z* calcd for $C_{18}H_{15}NO$: 261.1154 found: 261.1153. MS (EI) *m*/*z* = 261 (1) $[M^+]$, 168 (13), 167 (100) $[M-C_5H_4NO^+]$, 165 (25), 152 (12).

3.2 NMR reaction products

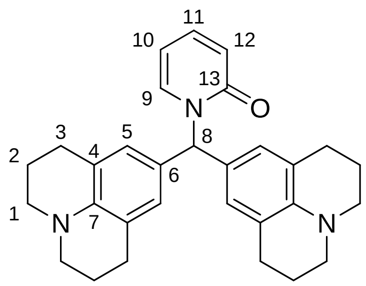
3.2.1 General Procedure:

In an NMR tube equimolar amounts (approx. 10–30 mg) of the pyridone-salt and the electrophile were mixed in 1 mL d_6-DMSO. NMR spectra were recorded shortly after the mixing.

3.2.2 Products of the Reaction of the 2-Pyridone Anion (**1**)

MB229

2-pyridone-potassium (**1-K**, 10.9 mg, 81.8 µmol) and $jul_2CH^+BF_4^-$ (**3g**, 35.7 mg, 80.3 µmol) were mixed in 1 mL d_6-DMSO.

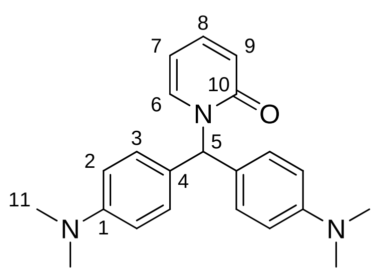


4g-N

^{1}H-NMR (d_6-DMSO, 400 MHz) δ =1.79-1.85 (m, 8 H, 2-H), 2.57-2.60 (m, 8 H, 3-H), 3.06-3.08 (m, 8 H, 1-H), 6.16-6.20 (m, 1 H, 10-H), 6.35-6.38 (m, 1 H, 12-H), 6.41 (s, 4 H, 5-H), 6.85 (s, 1 H, 8-H), 7.31-7.39 (m, 2 H, 9-H, 11-H). ^{13}C-NMR (d_6-DMSO, 101 MHz) δ = 21.5 (t, C-2), 27.2 (t, C-3), 49.2 (t, C-1), 60.7 (d, C-8), 105.1 (d, C-10), 119.4 (d, C-12), 120.8 (s, C-4), 125.8 (s, C-6), 126.7 (d, C-5), 136.6 (d, C-9), 139.3 (d, C-11), 142.0 (s, C-7), 161.2 (s, C-13).

MB230

2-pyridone-potassium (**1-K**, 15.3 mg, 0.115 mmol) and $dma_2CH^+BF_4^-$ (**3c**, 38.6 mg, 0.113 mmol) were mixed in 1 mL d_6-DMSO.

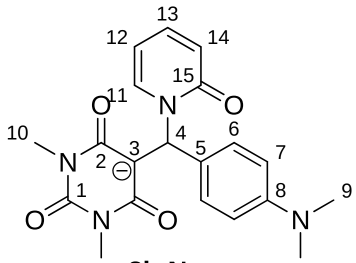


4c-N

^{1}H-NMR (d_6-DMSO, 400 MHz) δ = 2.87 (s, 12 H, 11-H), 6.17-6.20 (m, 1 H, 7-H), 6.40-6.43 (m, 1 H, 9-H), 6.70 (d, ^3J = 8.9 Hz, 4 H, 2-H), 6.89 (d, ^3J = 8.4 Hz, 4 H, 3-H), 7.09 (s, 1 H, 5-H), 7.26-7.28 (m, 1 H, 6-H), 7.37-7.41 (m, 1 H, 8-H). ^{13}C-NMR (d_6-DMSO, 101 MHz) δ = 40.1 (q, C-11), 60.4 (d, 5-H), 105.2 (d, C-7), 112.3 (d, C-2), 119.5 (d, C-9), 126.5 (s, C-4), 129.1 (d, C-3), 136.4 (d, C-6), 139.4 (d, C-8), 149.7 (s, C-1), 161.3 (s, C-10).

MB206

2-pyridone-potassium (**1-K**, 17.1 mg, 0.128 mmol) and **6b** (36.8 mg, 0.128 mmol) were mixed in 1 mL d_6-DMSO.

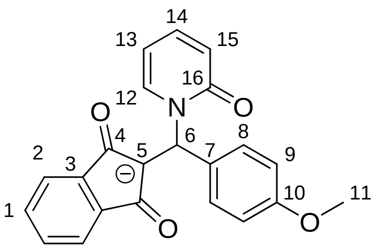


8b-N

^{1}H-NMR (d_6-DMSO, 400 MHz) δ = 2.82 (s, 6 H, 9-H), 3.06 (s, 6 H, 10-H), 6.07-6.11 (m, 1 H, 12-H), 6.26-6.29 (m, 1 H, 14-H), 6.57 (d, ^3J = 8.9 Hz, 2 H, 7-H), 6.74-6.77 (m, 2 H, 6-H), 7.25 (s, 1 H, 4-H), 7.30-7.34 (m, 1 H, 13-H), 8.19-8.22 (m, 1 H, 11-H). ^{13}C-NMR (d_6-DMSO, 101 MHz) δ = 27.0 (q, C-10), 40.5 (q, C-9), 55.8 (d, C-4), 85.3 (s, C-3), 103.7 (d, C-12), 112.0 (d, C-7), 118.4 (d, C-14), 127.3 (d, C-6), 130.5 (s, C-5), 138.8 (d, C-13), 140.0 (d, C-11), 148.5 (s, C-8), 152.9 (s, C-1), 161.6 (s, C-15), 162.8 (s, C-2).

MB210

2-pyridone-potassium (**1-K**, 20.6 mg, 0.155 mmol) and 7**c** (41.0 mg, 0.155 mmol) were mixed in 1 mL d_6-DMSO.



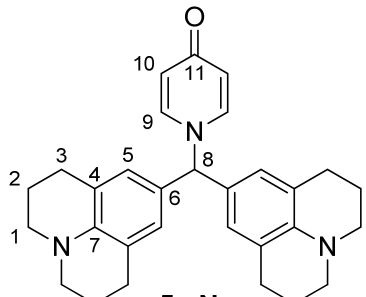
8c-N

^{1}H-NMR (d_6-DMSO, 400 MHz) δ = 3.69 (s, 3 H, 11-H), 6.13-6.16 (m, 1 H, 13-H), 6.31-6.34 (m, 1 H, 15-H), 6.76-6.78 (m, 2 H, 9-H), 7.00 (s, 1 H, 6-H), 7.04-7.06 (m, 2 H, 8-H), 7.10-7.12 (m, 2 H, 2-H), 7.24-7.26 (m, 2 H, 1-H), 7.31-7.35 (m, 1 H, 14-H), 8.50-8.53 (m, 1 H, 12 H). ^{13}C-NMR (d_6-DMSO, 101 MHz) δ= 52.9 (d, C-6), 55.0 (q, C-11), 103.1 (s, C-5), 104.6 (d, C-13), 113.0 (d, C-9), 117.0 (d, C-2), 118.7 (d, C-15), 128.1 (d, C-8), 129.3 (d, C-1), 134.6 (s, C-7), 139.0 (d, C-14), 139.9 (s + d, C-3 and C-12 superimposed), 157.3 (s, C-10), 161.4 (s, C-16), 189.0 (s, C-4).

3.2.3 Products of the Reaction of the 4-Pyridone Anion (**2**)

MB223

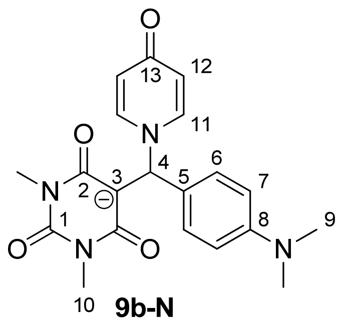
4-pyridone-potassium (**2-K**, 13 mg, 0.10 mmol) and $jul_2CH^+BF_4^-$ (**3g**, 44 mg, 0.10 mmol) were mixed in 1 mL d_6-DMSO.



^{1}H-NMR (d_6-DMSO, 400 MHz) δ = 1.81-1.84 (m, 8 H, 2-H), 2.58-2.61 (m, 8 H, 3-H), 3.07-3.10 (m, 8 H, 1-H), 6.08 (d, ^3J = 7.7 Hz, 2 H, 10-H), 6.16 (s, 1 H, 8-H), 6.46 (s, 4 H, 5-H), 7.52 (d, ^3J = 7.7 Hz, 2 H, 9-H).^{13}C-NMR (d_6-DMSO, 101 MHz) δ = 21.4 (t, C-2), 27.2 (t, C-3), 49.2 (t, C-1), 71.0 (d, C-8), 117.3 (d, C-10), 120.9 (s, C-4), 125.0 (s, C-6), 126.4 (d, C-5), 140.0 (d, C-9), 142.4 (s, C-7), 177.4 (s, C-11).

MB213

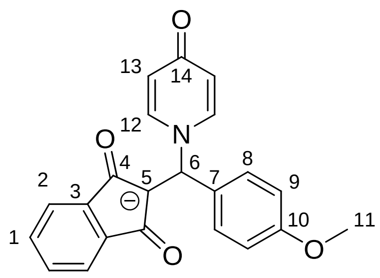
4-pyridone-potassium (**2-K**, 28.7 mg, 0.215 mmol) and **6b** (61.5 mg, 0.214 mmol) were mixed in 1 mL d_6-DMSO.



^{1}H-NMR (d_6-DMSO, 400 MHz) δ = 2.84 (s, 6 H, 9-H), 3.07 (s, 6 H, 10-H), 6.01 (d, ^3J = 7.7 Hz, 2 H, 12-H), 6.40 (s, 1 H, 4-H), 6.61 (d, ^3J = 8.9 Hz, 2 H, 7-H), 6.87 (d, ^3J = 8.3 Hz, 2 H, 6-H), 7.80 (d, ^3J = 7.8 Hz, 2 H, 11-H). ^{13}C-NMR (d_6-DMSO, 101 MHz) δ = 27.0 (q, C-10), 40.3 (q, C-9), 66.1 (d, C-4), 84.8 (s, C-3), 112.0 (d, C-7), 116.4 (d, C-12), 127.6 (d, C-6), 128.8 (s, C-5), 141.3 (d, C-11), 149.0 (s, C-8), 152.9 (s, C-1), 162.4 (s, C-2), 177.5 (s, C-13).

MB212

4-pyridone-potassium (**2-K**, 28.7 mg, 0.215 mmol) and **7c** (56.9 mg, 0.215 mmol) were mixed in 1 mL d_6-DMSO.



^{1}H-NMR (d_6-DMSO, 400 MHz) δ = 3.71 (s, 3 H, 11-H), 6.04 (s, 1 H, 6-H), 6.06 (d, ^3J = 7.7 Hz, 2 H, 13-H), 6.84 (d, ^3J = 8.8 Hz, 2 H, 9-H), 7.14-7.18 (m, 4 H, 2-H and 8-H), 7.26-7.28 (m, 2 H, 1-H), 8.03 (d, ^3J = 7.7 Hz, 2 H, 12-H). ^{13}C-NMR (d_6-DMSO, 101 MHz) δ = 55.0 (q, C-11), 63.8 (d, C-6), 102.0 (s, C-5), 113.4 (d, C-9), 116.8 (d, C-13), 117.3 (d, C-2), 128.3 (d, C-8), 129.5 (d, C-1), 133.7 (s, C-7), 139.8 (s, C-3), 141.1 (d, C-12), 158.0 (s, C-10), 177.3 (s, C-14), 188.5 (s, C-4).

4 Determination of the Nucleophilicity of Pyridone Anions

4.1 Reactions of the Potassium Salt of 2-Pyridone (1-K) in DMSO

Table 1: Kinetics of the reaction of **1-K** with **3o** (20 °C, stopped-flow, at 521 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.98×10^{-5}	7.95×10^{-4}		26.7	0.151
2.98×10^{-5}	1.59×10^{-3}	2.14×10^{-3}	53.4	0.163
2.98×10^{-5}	2.39×10^{-3}		80.1	0.175
2.98×10^{-5}	3.18×10^{-3}	4.28×10^{-3}	107	0.187
2.98×10^{-5}	3.98×10^{-3}		134	0.199

$k_2 = 1.51 \times 10^1$ L mol^{-1} s^{-1}

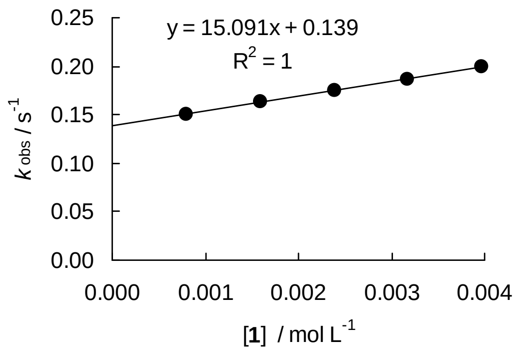


Table 2: Kinetics of the reaction of **1-K** with **3n** (20 °C, stopped-flow, at 533 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / molL^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.61×10^{-5}	5.56×10^{-4}		21.3	0.123
2.61×10^{-5}	1.11×10^{-3}	1.34×10^{-3}	42.7	0.144
2.61×10^{-5}	1.67×10^{-3}		64.0	0.164
2.61×10^{-5}	2.23×10^{-3}	2.68×10^{-3}	85.3	0.181
2.61×10^{-5}	2.78×10^{-3}		107	0.207

$k_2 = 3.68 \times 10^1$ L mol^{-1} s^{-1}

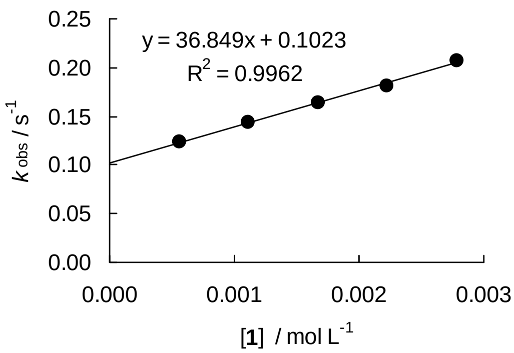


Table 3: Kinetics of the reaction of **1-K** with 3**m** (20 °C, stopped-flow, at 393 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.86×10^{-5}	5.02×10^{-4}		17.5	0.128
2.86×10^{-5}	1.00×10^{-3}	1.26×10^{-3}	35.1	0.221
2.86×10^{-5}	1.51×10^{-3}		52.6	0.328
2.86×10^{-5}	2.01×10^{-3}	2.53×10^{-3}	70.1	0.414
2.86×10^{-5}	2.51×10^{-3}		87.7	0.517

$k_2 = 1.94 \times 10^2$ L mol^{-1} s^{-1}

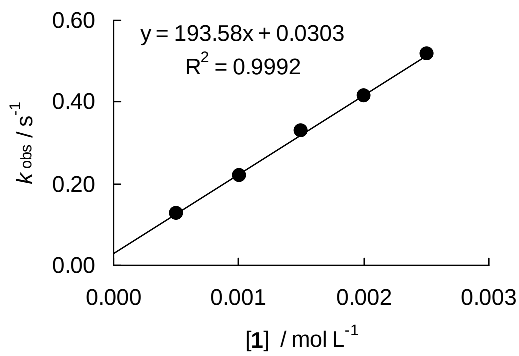


Table 4: Kinetics of the reaction of **1-K** with **3l** (20 °C, stopped-flow, at 371 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.32×10^{-5}	5.02×10^{-4}		15.1	0.153
3.32×10^{-5}	1.00×10^{-3}	1.26×10^{-3}	30.2	0.280
3.32×10^{-5}	1.51×10^{-3}		45.3	0.421
3.32×10^{-5}	2.01×10^{-3}	2.53×10^{-3}	60.4	0.538
3.32×10^{-5}	2.51×10^{-3}		75.5	0.635

$k_2 = 2.44 \times 10^2$ L mol^{-1} s^{-1}

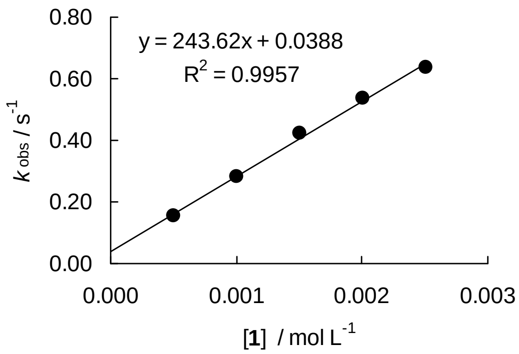


Table 5: Kinetics of the reaction of **1-K** with **3k** (20 °C, stopped-flow, at 374 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.96×10^{-5}	5.03×10^{-4}		12.7	1.52
3.96×10^{-5}	1.01×10^{-3}	1.35×10^{-3}	25.4	2.97
3.96×10^{-5}	1.51×10^{-3}		38.1	4.69
3.96×10^{-5}	2.01×10^{-3}	2.71×10^{-3}	50.8	6.14
3.96×10^{-5}	2.52×10^{-3}		63.5	7.62

$k_2 = 3.06 \times 10^3$ L mol-1 s^{-1}

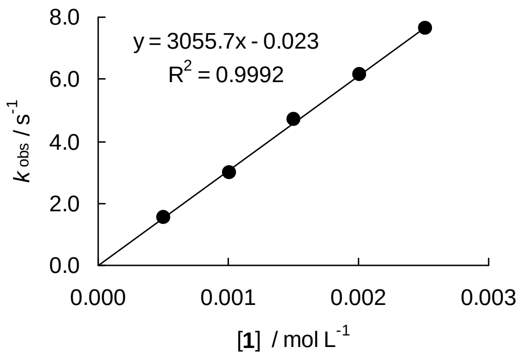


Table 6: Kinetics of the reaction of **1-K** with **3j** (20 °C, stopped-flow, at 533 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.67×10^{-5}	3.45×10^{-4}		12.9	2.04
2.67×10^{-5}	6.89×10^{-4}	1.07×10^{-3}	25.8	4.02
2.67×10^{-5}	1.03×10^{-3}		38.7	6.49
2.67×10^{-5}	1.38×10^{-3}	2.14×10^{-3}	51.6	8.47
2.67×10^{-5}	1.72×10^{-3}		64.5	11.0

$k_2 = 6.49 \times 10^3$ L mol^{-1} s^{-1}

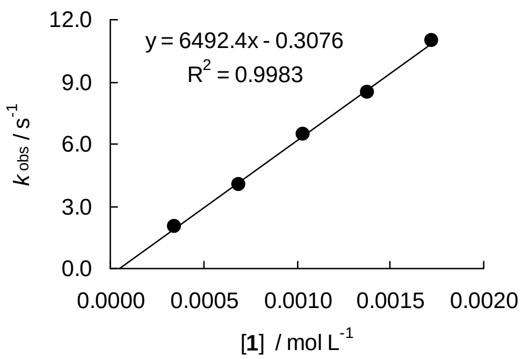


Table 7: Kinetics of the reaction of **1-K** with **3i** (20 °C stopped-flow, at 422 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.85×10^{-5}	3.45×10^{-4}		12.1	13.3
2.85×10^{-5}	6.89×10^{-4}	1.07×10^{-3}	24.1	26.7
2.85×10^{-5}	1.03×10^{-3}		36.2	42.0
2.85×10^{-5}	1.38×10^{-3}	2.14×10^{-3}	48.3	54.3
2.85×10^{-5}	1.72×10^{-3}		60.4	69.3

$k_2 = 4.05 \times 10^4$ L mol^{-1} s^{-1}

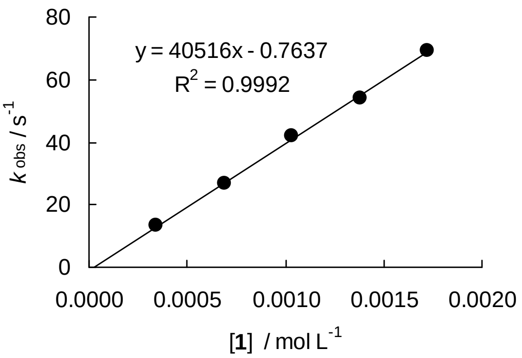


Table 8: Kinetics of the reaction of **1-K** with **3h** (20 °C, stopped-flow, at 630 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
1.37×10^{-5}	1.50×10^{-4}		11.0	110
1.37×10^{-5}	1.88×10^{-4}	2.15×10^{-4}	13.7	141
1.37×10^{-5}	2.25×10^{-4}		16.4	182
1.37×10^{-5}	2.63×10^{-4}	3.23×10^{-4}	19.2	205
1.37×10^{-5}	3.00×10^{-4}		21.9	241

$k_2 = 8.69 \times 10^5$ L mol^{-1} s^{-1}

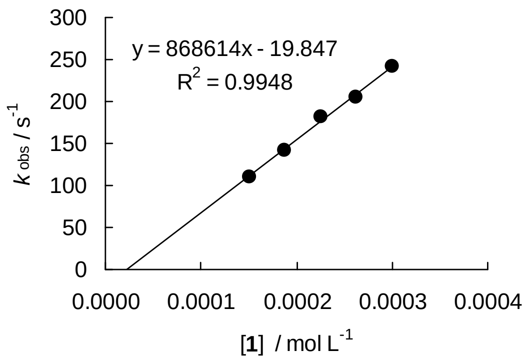


Table 9: Kinetics of the reaction of **1-K** with **3g** (20 °C, stopped-flow, at 635 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
1.22×10^{-5}	1.50×10^{-4}		12.4	204
1.22×10^{-5}	1.88×10^{-4}	2.15×10^{-4}	15.4	258
1.22×10^{-5}	2.25×10^{-4}		18.5	335
1.22×10^{-5}	2.63×10^{-4}	3.23×10^{-4}	21.6	378
1.22×10^{-5}	3.00×10^{-4}		24.7	454

$k_2 = 1.65 \times 10^6$ L mol^{-1} s^{-1}

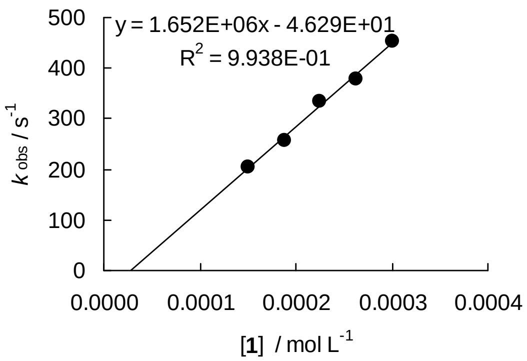


Table 10: Kinetics of the reaction of **1-K** with **6a** (20 °C, stopped-flow, at 487 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
4.13×10^{-5}	7.06×10^{-4}		17.1	0.869
4.13×10^{-5}	1.41×10^{-3}	1.83×10^{-3}	34.2	1.59
4.13×10^{-5}	2.12×10^{-3}		51.4	2.65
4.13×10^{-5}	2.82×10^{-3}	3.79×10^{-3}	68.4	3.45
4.13×10^{-5}	3.53×10^{-3}		85.6	4.42

$k_2 = 1.27 \times 10^3$ L mol^{-1} s^{-1}

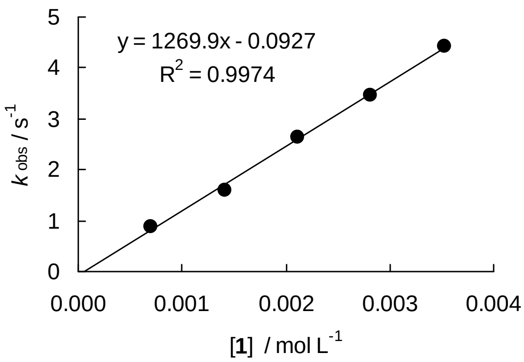


Table 11: Kinetics of the reaction of **1-K** with **6b** (20 °C, stopped-flow, at 487 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
4.87×10^{-5}	7.06×10^{-4}		14.5	5.01
4.87×10^{-5}	1.41×10^{-3}	1.83×10^{-3}	28.9	9.74
4.87×10^{-5}	2.12×10^{-3}		43.5	15.5
4.87×10^{-5}	2.82×10^{-3}	3.79×10^{-3}	57.9	20.8
4.87×10^{-5}	3.53×10^{-3}		72.4	26.1

$k_2 = 7.54 \times 10^3$ L mol^{-1} s^{-1}

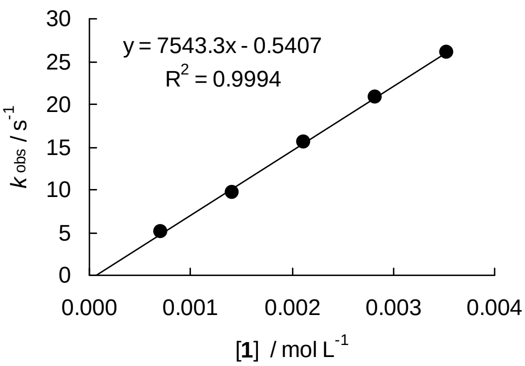


Table 12: Kinetics of the reaction of **1-K** with **7a** (20 °C, stopped-flow, at 490 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.91×10^{-5}	5.03×10^{-4}		17.3	0.406
2.91×10^{-5}	1.01×10^{-3}	1.35×10^{-3}	34.7	0.776
2.91×10^{-5}	1.51×10^{-3}		51.8	1.23
2.91×10^{-5}	2.01×10^{-3}	2.71×10^{-3}	69.0	1.61
2.91×10^{-5}	2.52×10^{-3}		86.5	2.01

$k_2 = 8.03 \times 10^2$ L mol^{-1} s^{-1}

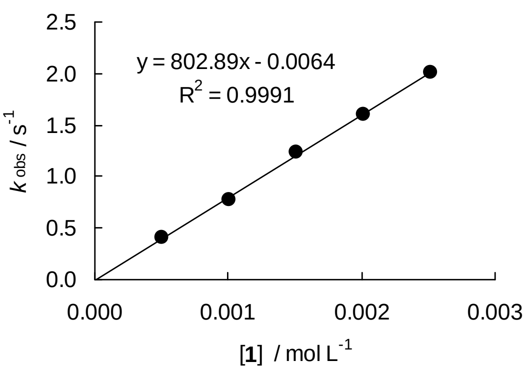
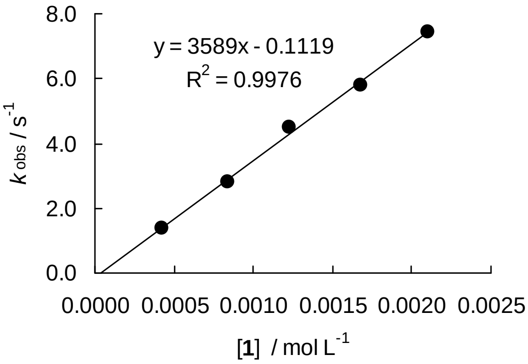


Table 13: Kinetics of the reaction of **1-K** with **7b** (20 °C, stopped-flow, at 490 nm)

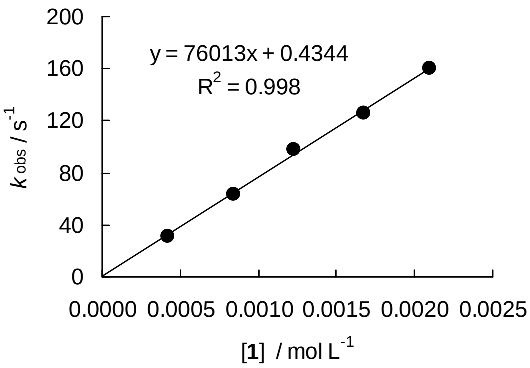
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.55×10^{-5}	4.20×10^{-4}		16.5	1.40
2.55×10^{-5}	8.39×10^{-4}	1.08×10^{-3}	32.9	2.81
2.55×10^{-5}	1.23×10^{-3}		48.2	4.48
2.55×10^{-5}	1.68×10^{-3}	2.16×10^{-3}	65.8	5.80
2.55×10^{-5}	2.10×10^{-3}		82.3	7.45



$k_2 = 3.59 \times 10^3$ L mol^{-1} s^{-1}

Table 14: Kinetics of the reaction of **1-K** with **7c** (20 °C, stopped-flow, at 390 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.31×10^{-5}	4.20×10^{-4}		12.7	31.4
3.31×10^{-5}	8.39×10^{-4}	1.08×10^{-3}	25.3	63.6
3.31×10^{-5}	1.23×10^{-3}		37.2	97.7
3.31×10^{-5}	1.68×10^{-3}	2.16×10^{-3}	50.8	126
3.31×10^{-5}	2.10×10^{-3}		63.4	160



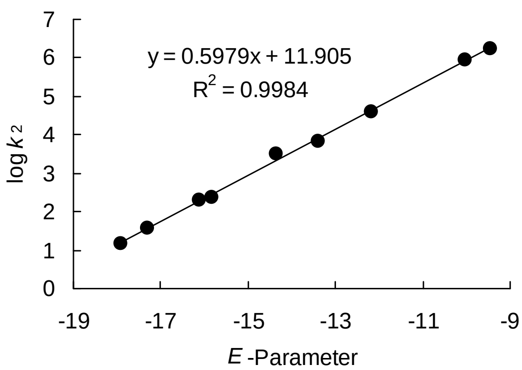
$k_2 = 7.60 \times 10^4$ L mol^{-1} s^{-1}

Determination of Reactivity Parameters *N* and *s* for the anion of 2-pyridone (1) in DMSO

Table 15: Rate Constants for the reactions of **1-K** with different electrophiles (20 °C)

Electrophile	E	k_2 / L mol^{-1} s^{-1}	log k_2
jul-tBu (**3o**)	-17.90	1.51×10^1	1.18
dma-tBu (**3n**)	-17.29	3.68×10^1	1.57
OMe-tBu (**3m**)	-16.11	1.94×10^2	2.29
Me-tBu (**3l**)	-15.83	2.44×10^2	2.39
NO_3-tBu (**3k**)	-14.36	3.06×10^3	3.49
dma-Ph (**3j**)	-13.39	6.49×10^3	3.81
OMe-Ph (**3i**)	-12.18	4.05×10^4	4.61
$(lil)_3CH^+$ (**3h**)	-10.04	8.69×10^5	5.94
$(jul)_3CH^+$ (**3g**)	-9.45	1.65×10^6	6.22

$N = 19.91$, $s = 0.60$



4.2 Reactions of the Lithium Salt of 2-Pyridone (1-Li) in DMSO

Table 16: Kinetics of the reaction of **1-Li** with **3l** (20 °C, stopped-flow, at 371 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[LiO*t*Bu] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.32×10^{-5}	3.42×10^{-4}	3.59×10^{-4}	10.3	0.117
3.32×10^{-5}	6.83×10^{-4}	7.17×10^{-4}	20.6	0.177
3.32×10^{-5}	1.02×10^{-3}	1.08×10^{-3}	30.8	0.236
3.32×10^{-5}	1.37×10^{-3}	1.43×10^{-3}	41.1	0.293
3.32×10^{-5}	1.72×10^{-3}	1.79×10^{-3}	51.4	0.342

$k_2 = 1.66 \times 10^2$ L mol^{-1} s^{-1}

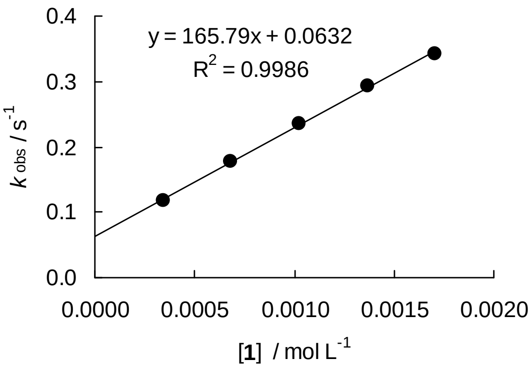
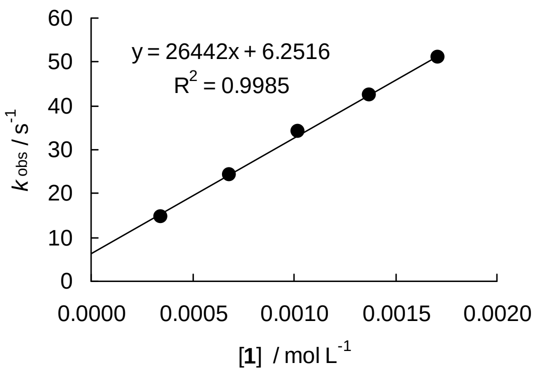


Table 17: Kinetics of the reaction of **1-Li** with **3i** (20 °C, stopped-flow, at 422 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[LiO*t*Bu] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.47×10^{-5}	3.42×10^{-4}	3.59×10^{-4}	13.9	14.8
2.47×10^{-5}	6.83×10^{-3}	7.17×10^{-4}	27.7	24.4
2.47×10^{-5}	1.02×10^{-3}	1.08×10^{-3}	41.3	34.1
2.47×10^{-5}	1.37×10^{-3}	1.43×10^{-3}	55.5	42.5
2.47×10^{-5}	1.72×10^{-3}	1.79×10^{-3}	69.3	51.0

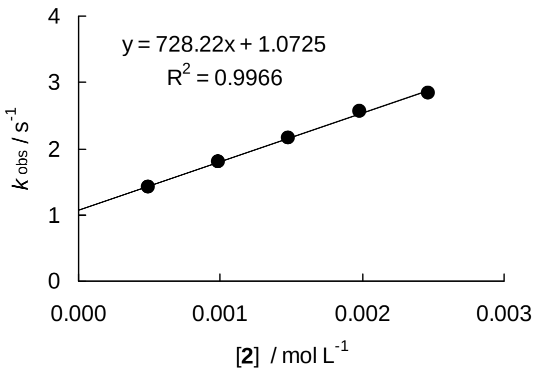
$k_2 = 2.64 \times 10^4$ L mol^{-1} s^{-1}



4.3 Reactions of the Potassium Salt of 4-Pyridone (2-K) in DMSO

Table 18: Kinetics of the reaction of **2-K** with **3k** (20 °C, stopped-flow, at 374 nm)

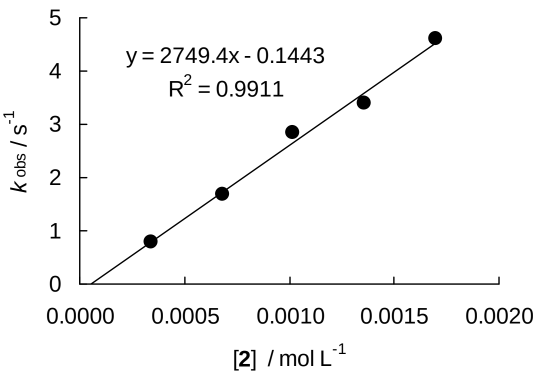
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
5.09×10^{-5}	4.94×10^{-4}		9.7	1.41
5.09×10^{-5}	9.88×10^{-4}	1.35×10^{-3}	19.4	1.80
5.09×10^{-5}	1.48×10^{-3}		29.1	2.16
5.09×10^{-5}	1.98×10^{-3}	2.71×10^{-3}	38.9	2.56
5.09×10^{-5}	2.47×10^{-3}		48.5	2.83



$k_2 = 7.28 \times 10^2$ L mol^{-1} s^{-1}

Table 19: Kinetics of the reaction of **2-K** with **3j** (20 °C, stopped-flow, at 533 nm)

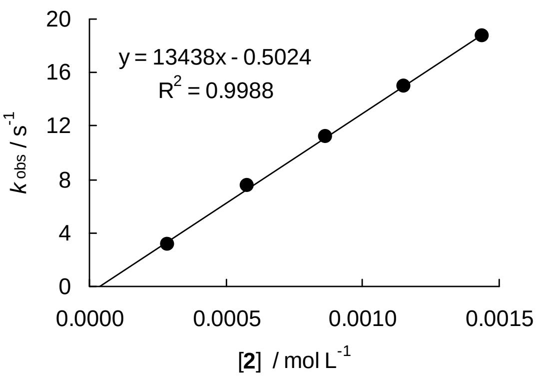
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.12×10^{-5}	3.40×10^{-4}		16.1	0.784
2.12×10^{-5}	6.80×10^{-4}	8.13×10^{-3}	32.1	1.69
2.12×10^{-5}	1.02×10^{-3}		48.1	2.83
2.12×10^{-5}	1.36×10^{-3}	1.63×10^{-3}	64.2	3.39
2.12×10^{-5}	1.70×10^{-3}		80.3	4.61



$k_2 = 2.75 \times 10^3$ L mol^{-1} s^{-1}

Table 20: Kinetics of the reaction of **2-K** with **3i** (20 °C stopped-flow, at 422 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.61×10^{-5}	2.88×10^{-4}		11.0	3.10
2.61×10^{-5}	5.77×10^{-4}	7.53×10^{-4}	22.1	7.54
2.61×10^{-5}	8.65×10^{-4}		33.1	11.2
2.61×10^{-5}	1.15×10^{-3}	1.51×10^{-3}	44.1	15.0
2.61×10^{-5}	1.44×10^{-3}		55.2	18.7



$k_2 = 1.34 \times 10^4$ L mol^{-1} s^{-1}

Table 21: Kinetics of the reaction of **2-K** with **3h** (20 °C, stopped-flow, at 630 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
1.44×10^{-5}	1.29×10^{-4}		9.0	37.8
1.44×10^{-5}	1.94×10^{-4}	2.33×10^{-4}	13.5	59.6
1.44×10^{-5}	2.59×10^{-4}		18.0	82.2
1.44×10^{-5}	3.24×10^{-4}	4.19×10^{-4}	22.5	102
1.44×10^{-5}	3.88×10^{-4}		26.9	122

$k_2 = 3.26 \times 10^5$ L mol^{-1} s^{-1}

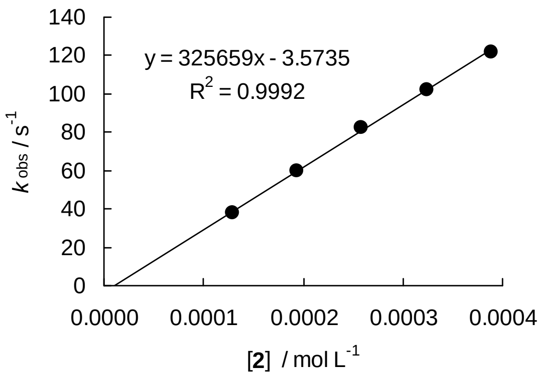


Table 22: Kinetics of the reaction of **2-K** with **3g** (20 °C, stopped-flow, at 635 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
1.30×10^{-5}	1.29×10^{-4}		10.0	97.5
1.30×10^{-5}	1.94×10^{-4}	2.33×10^{-4}	15.0	146
1.30×10^{-5}	2.59×10^{-4}		20.0	198
1.30×10^{-5}	3.24×10^{-4}	4.19×10^{-4}	25.0	241
1.30×10^{-5}	3.88×10^{-4}		30.0	291

$k_2 = 7.45 \times 10^5$ L mol^{-1} s^{-1}

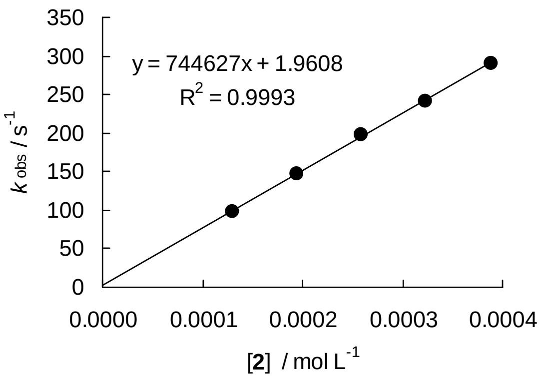


Table 23: Kinetics of the reaction of **2-K** with **6a** (20 °C, stopped-flow, at 487 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
4.30×10^{-5}	7.96×10^{-4}		18.5	4.95
4.30×10^{-5}	1.59×10^{-3}	1.88×10^{-3}	37.0	10.8
4.30×10^{-5}	2.39×10^{-3}		55.6	15.9
4.30×10^{-5}	3.18×10^{-3}	3.75×10^{-3}	74.0	21.3
4.30×10^{-5}	3.95×10^{-3}		91.9	25.4

$k_2 = 6.51 \times 10^3$ L mol^{-1} s^{-1}

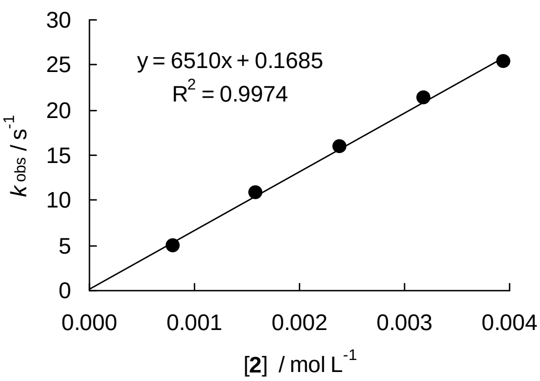


Table 24: Kinetics of the reaction of **2-K** with **6b** (20 °C, stopped-flow, at 487 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.95×10^{-5}	5.74×10^{-4}		14.5	15.9
3.95×10^{-5}	1.15×10^{-3}	1.35×10^{-3}	29.1	33.1
3.95×10^{-5}	1.72×10^{-3}		43.5	52.0
3.95×10^{-5}	2.30×10^{-3}	2.71×10^{-3}	58.2	66.7
3.95×10^{-5}	2.87×10^{-3}		72.7	85.9

$k_2 = 3.02 \times 10^4$ L mol^{-1} s^{-1}

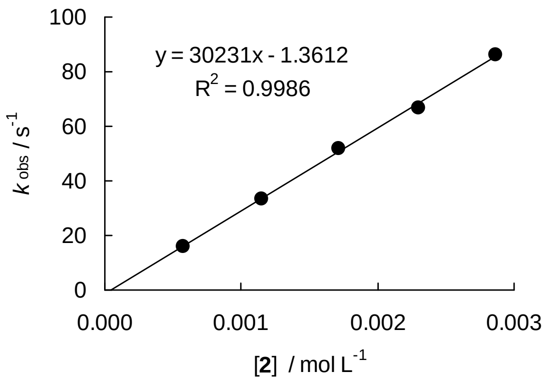


Table 25: Kinetics of the reaction of **2-K** with **7a** (20 °C, stopped-flow, at 490 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.52×10^{-5}	4.94×10^{-4}		14.0	2.49
3.52×10^{-5}	9.88×10^{-4}	1.35×10^{-3}	28.1	3.69
3.52×10^{-5}	1.48×10^{-3}		42.0	4.98
3.52×10^{-5}	1.98×10^{-3}	2.71×10^{-3}	56.3	6.21
3.52×10^{-5}	2.47×10^{-3}		70.2	7.29

$k_2 = 2.45 \times 10^3$ L mol^{-1} s^{-1}

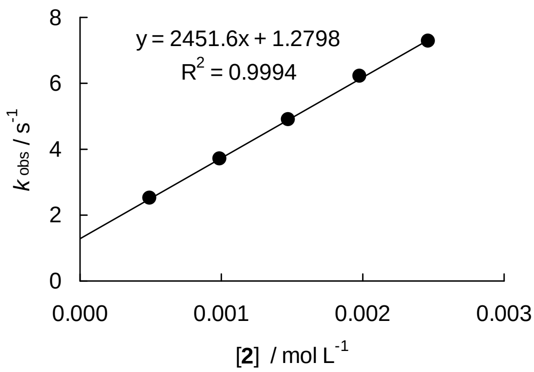


Table 26: Kinetics of the reaction of **2-K** with **7b** (20 °C, stopped-flow, at 490 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.88×10^{-5}	7.96×10^{-4}		27.6	7.24
2.88×10^{-5}	1.59×10^{-3}	1.88×10^{-3}	55.2	14.6
2.88×10^{-5}	2.39×10^{-3}		83.0	21.0
2.88×10^{-5}	3.18×10^{-3}	3.75×10^{-3}	110	27.7
2.88×10^{-5}	3.98×10^{-3}		138	32.6

$k_2 = 8.02 \times 10^3$ L mol^{-1} s^{-1}

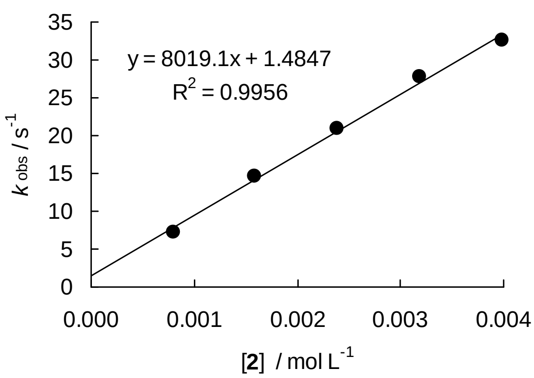
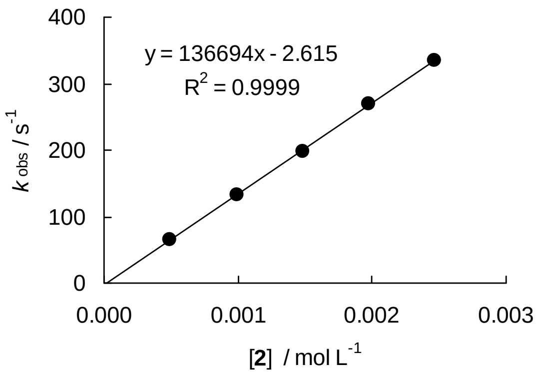


Table 27: Kinetics of the reaction of **2-K** with **7c** (20 °C, stopped-flow, at 390 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
4.63×10^{-5}	4.94×10^{-4}		10.7	65.1
4.63×10^{-5}	9.88×10^{-4}	1.35×10^{-3}	21.3	133
4.63×10^{-5}	1.48×10^{-3}		32.0	198
4.63×10^{-5}	1.98×10^{-3}	2.71×10^{-3}	42.8	269
4.63×10^{-5}	2.47×10^{-3}		53.3	335

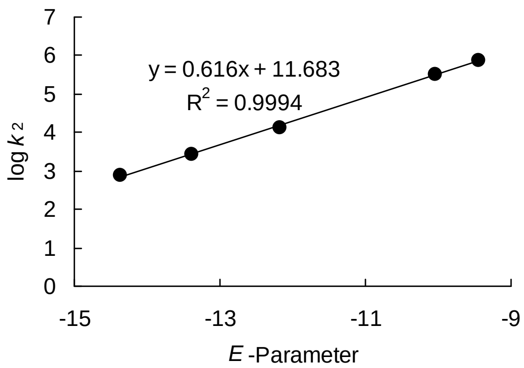


$k_2 = 1.37 \times 10^5$ L mol^{-1} s^{-1}

Determination of Reactivity Parameters *N* and *s* for the anion of 4-pyridone (**2**) in DMSO

Table 28: Rate Constants for the reactions of **2-K** with different electrophiles (20 °C)

Electrophile	*E*	k_2 / L mol^{-1} s^{-1}	log k_2
NO_2-tBu (**3k**)	-14.36	7.28×10^2	2.86
dma-Ph (**3j**)	-13.39	2.75×10^3	3.44
OMe-Ph (**3i**)	-12.18	1.34×10^4	4.13
$(lil)_2CH^+$ (**3h**)	-10.04	3.26×10^5	5.51
$(jul)_2CH^+$ (**3g**)	-9.45	7.45×10^5	5.87

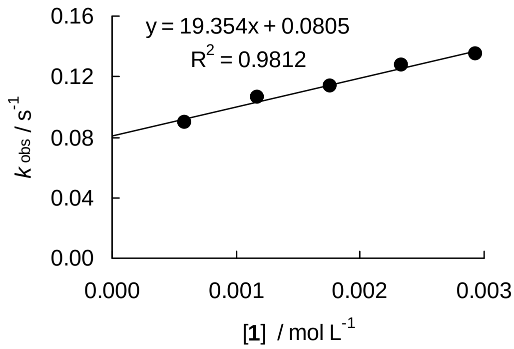


$N = 18.97$, $s = 0.62$

4.4 Reactions of the Potassium Salt of 2-Pyridone (1-K) in CH_3CN

Table 29: Kinetics of the reaction of **1-K** with **3o** (20 °C, stopped-flow, at 521 nm)

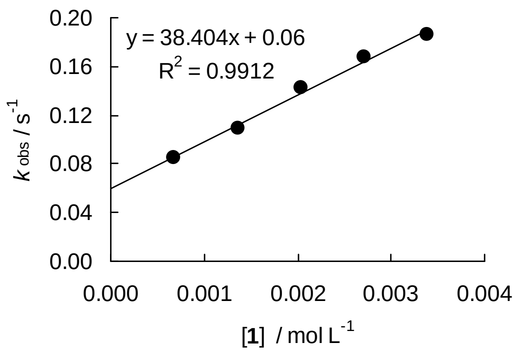
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.79×10^{-5}	5.86×10^{-4}	7.44×10^{-4}	21.0	0.0893
2.79×10^{-5}	1.17×10^{-3}	1.49×10^{-3}	41.9	0.106
2.79×10^{-5}	1.76×10^{-3}	2.24×10^{-3}	63.1	0.114
2.79×10^{-5}	2.34×10^{-3}	2.97×10^{-3}	83.9	0.128
2.79×10^{-5}	2.93×10^{-3}	3.72×10^{-3}	105	0.135



$k_2 = 1.94 \times 10^1$ L mol^{-1} s^{-1}

Table 30: Kinetics of the reaction of **1-K** with **3n** (20 °C, stopped-flow, at 533 nm)

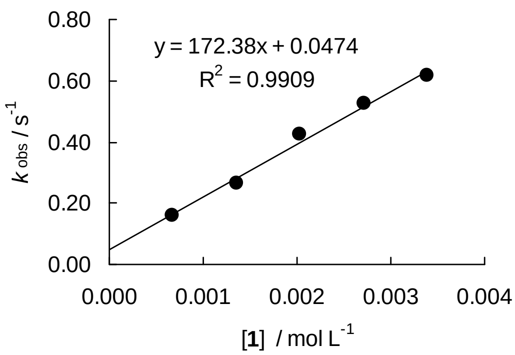
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.83×10^{-5}	6.78×10^{-4}	8.41×10^{-4}	17.7	0.0854
3.83×10^{-5}	1.36×10^{-3}	1.69×10^{-3}	35.5	0.109
3.83×10^{-5}	2.03×10^{-3}	2.52×10^{-3}	53.0	0.142
3.83×10^{-5}	2.71×10^{-3}	3.36×10^{-3}	70.8	0.168
3.83×10^{-5}	3.39×10^{-3}	4.20×10^{-3}	88.5	0.186



$k_2 = 3.84 \times 10^1$ L mol^{-1} s^{-1}

Table 31: Kinetics of the reaction of **1-K** with **3m** (20 °C, stopped-flow, at 393 nm)

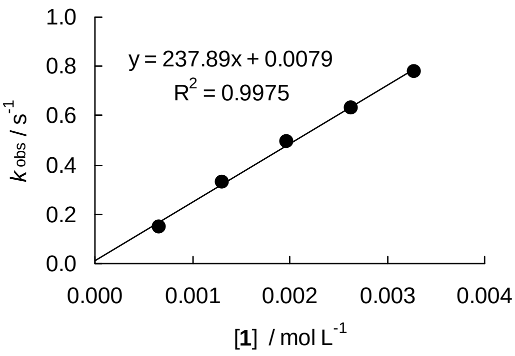
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.95×10^{-5}	6.78×10^{-4}	8.41×10^{-4}	17.2	0.161
3.95×10^{-5}	1.36×10^{-3}	1.69×10^{-3}	34.5	0.266
3.95×10^{-5}	2.03×10^{-3}	2.52×10^{-3}	51.5	0.423
3.95×10^{-5}	2.71×10^{-3}	3.36×10^{-3}	68.7	0.524
3.95×10^{-5}	3.39×10^{-3}	4.20×10^{-3}	85.9	0.616



$k_2 = 1.72 \times 10^2$ L mol^{-1} s^{-1}

Table 32: Kinetics of the reaction of **1-K** with **3l** (20 °C, stopped-flow, at 371 nm)

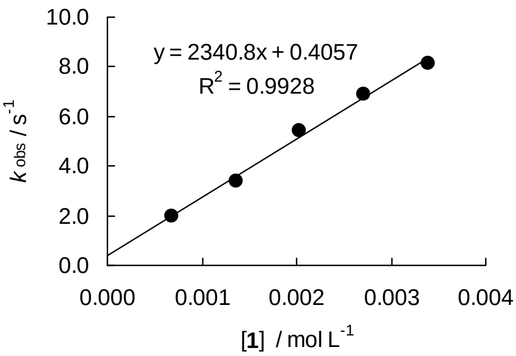
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.03×10^{-5}	6.57×10^{-4}	8.34×10^{-4}	21.7	0.150
3.03×10^{-5}	1.31×10^{-3}	1.66×10^{-3}	43.2	0.329
3.03×10^{-5}	1.97×10^{-3}	2.50×10^{-3}	64.9	0.492
3.03×10^{-5}	2.63×10^{-3}	3.34×10^{-3}	86.7	0.631
3.03×10^{-5}	3.28×10^{-3}	4.17×10^{-3}	108	0.780



$k_2 = 2.38 \times 10^2$ L mol^{-1} s^{-1}

Table 33: Kinetics of the reaction of **1-K** with **3k** (20 °C, stopped-flow, at 374 nm)

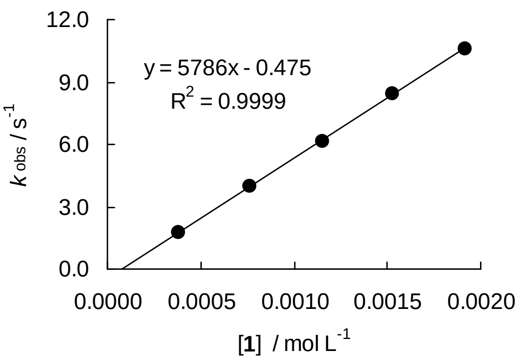
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
5.60×10^{-5}	6.78×10^{-4}	8.41×10^{-4}	12.1	1.97
5.60×10^{-5}	1.36×10^{-3}	1.69×10^{-3}	24.3	3.38
5.60×10^{-5}	2.03×10^{-3}	2.52×10^{-3}	36.3	5.45
5.60×10^{-5}	2.71×10^{-3}	3.36×10^{-3}	48.4	6.88
5.60×10^{-5}	3.39×10^{-3}	4.20×10^{-3}	60.6	8.15



$k_2 = 2.34 \times 10^3$ L mol^{-1} s^{-1}

Table 34: Kinetics of the reaction of **1-K** with **3j** (20 °C, stopped-flow, at 533 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.96×10^{-5}	3.84×10^{-4}	6.11×10^{-4}	13.0	1.73
2.96×10^{-5}	7.67×10^{-4}	1.22×10^{-3}	25.9	3.98
2.96×10^{-5}	1.15×10^{-3}	1.83×10^{-3}	38.8	6.16
2.96×10^{-5}	1.53×10^{-3}	2.43×10^{-3}	51.6	8.43
2.96×10^{-5}	1.92×10^{-3}	3.05×10^{-3}	64.8	10.6



$k_2 = 5.79 \times 10^3$ L mol^{-1} s^{-1}

Table 35: Kinetics of the reaction of **1-K** with **3i** (20 °C, stopped-flow, at 422 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.80×10^{-5}	3.84×10^{-4}	6.11×10^{-4}	13.7	9.56
2.80×10^{-5}	7.67×10^{-4}	1.22×10^{-3}	27.4	22.8
2.80×10^{-5}	1.15×10^{-3}	1.83×10^{-3}	41.1	34.3
2.80×10^{-5}	1.53×10^{-3}	2.43×10^{-3}	54.7	45.8
2.80×10^{-5}	1.92×10^{-3}	3.05×10^{-3}	68.6	57.9

$k_2 = 3.12 \times 10^4$ L mol^{-1} s^{-1}

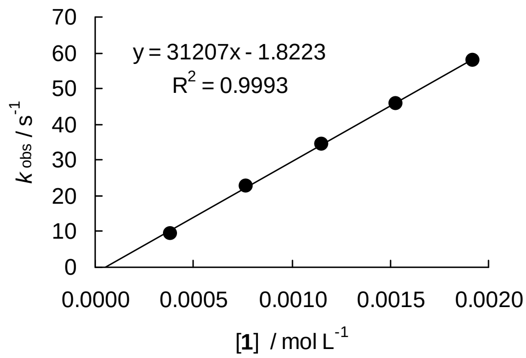


Table 36: Kinetics of the reaction of **1-K** with **6a** (20 °C, stopped-flow, at 487 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.37×10^{-5}	4.15×10^{-4}	5.27×10^{-4}	17.5	0.425
2.37×10^{-5}	8.30×10^{-4}	1.05×10^{-3}	35.0	1.00
2.37×10^{-5}	1.23×10^{-3}	1.56×10^{-3}	51.9	1.58
2.37×10^{-5}	1.66×10^{-3}	2.11×10^{-3}	70.0	2.13
2.37×10^{-5}	2.08×10^{-3}	2.64×10^{-3}	87.8	2.66

$k_2 = 1.35 \times 10^3$ L mol^{-1} s^{-1}

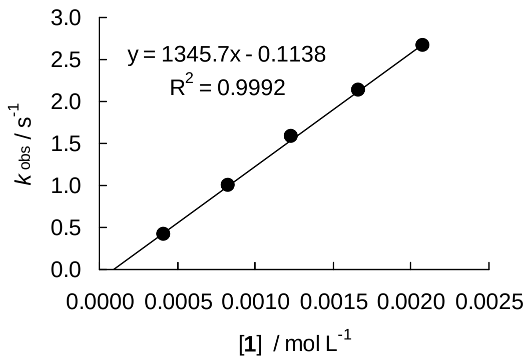


Table 37: Kinetics of the reaction of **1-K** with **6b** (20 °C, stopped-flow, at 487 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.48×10^{-5}	4.15×10^{-4}	5.27×10^{-4}	16.7	3.20
2.48×10^{-5}	8.30×10^{-4}	1.05×10^{-3}	33.5	7.05
2.48×10^{-5}	1.23×10^{-3}	1.56×10^{-3}	49.6	10.7
2.48×10^{-5}	1.66×10^{-3}	2.11×10^{-3}	66.9	14.6
2.48×10^{-5}	2.08×10^{-3}	2.64×10^{-3}	83.9	18.1

$k_2 = 8.98 \times 10^3$ L mol^{-1} s^{-1}

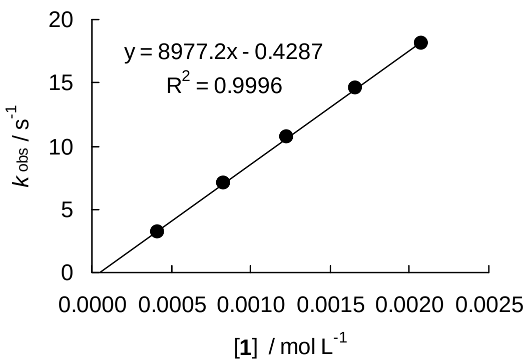
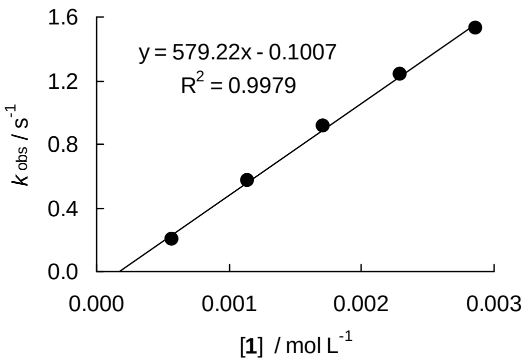


Table 38: Kinetics of the reaction of **1-K** with **7a** (20 °C, stopped-flow, at 490 nm)

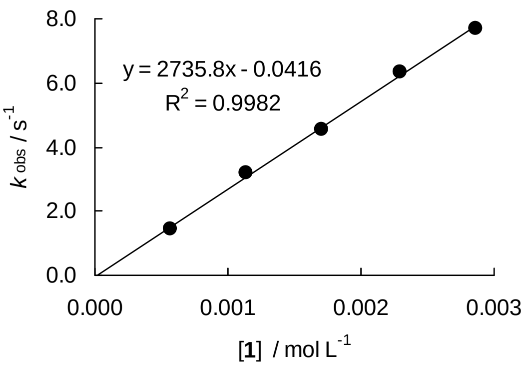
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.37×10^{-5}	5.71×10^{-4}	6.57×10^{-4}	24.1	0.204
2.37×10^{-5}	1.14×10^{-3}	1.31×10^{-3}	48.1	0.574
2.37×10^{-5}	1.71×10^{-3}	1.97×10^{-3}	72.2	0.913
2.37×10^{-5}	2.29×10^{-3}	2.63×10^{-3}	96.6	1.24
2.37×10^{-5}	2.86×10^{-3}	3.29×10^{-3}	121	1.53



$k_2 = 5.79 \times 10^2$ L mol^{-1} s^{-1}

Table 39: Kinetics of the reaction of **1-K** with **7b** (20 °C, stopped-flow, at 490 nm)

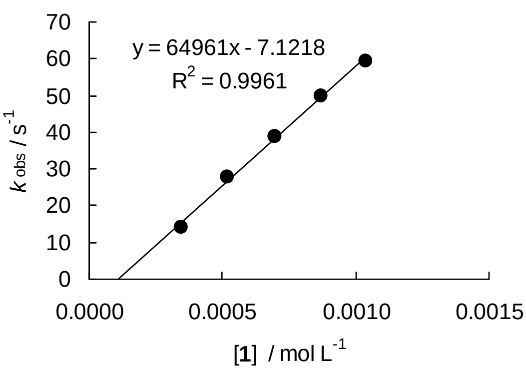
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
1.50×10^{-5}	5.71×10^{-4}	6.57×10^{-4}	38.1	1.44
1.50×10^{-5}	1.14×10^{-3}	1.31×10^{-3}	76.0	3.20
1.50×10^{-5}	1.71×10^{-3}	1.97×10^{-3}	114	4.56
1.50×10^{-5}	2.29×10^{-3}	2.63×10^{-3}	153	6.33
1.50×10^{-5}	2.86×10^{-3}	3.29×10^{-3}	191	7.71



$k_2 = 2.74 \times 10^3$ L mol^{-1} s^{-1}

Table 40: Kinetics of the reaction of **1-K** with **7c** (20 °C, stopped-flow, at 390 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.56×10^{-5}	3.48×10^{-4}	4.84×10^{-4}	9.8	14.2
3.56×10^{-5}	5.21×10^{-4}	7.24×10^{-4}	14.6	27.7
3.56×10^{-5}	6.95×10^{-4}	9.66×10^{-4}	19.5	38.8
3.56×10^{-5}	8.69×10^{-4}	1.21×10^{-3}	24.4	50.0
3.56×10^{-5}	1.04×10^{-3}	1.45×10^{-3}	29.2	59.3



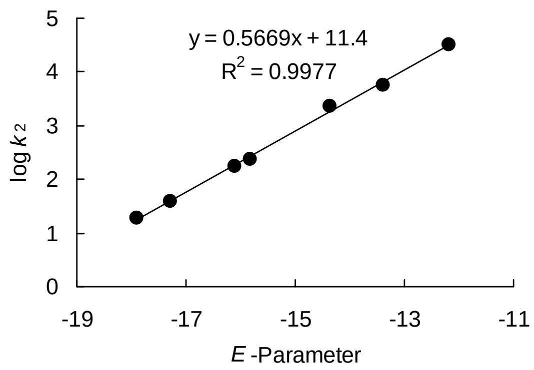
$k_2 = 6.50 \times 10^4$ L mol^{-1} s^{-1}

Determination of Reactivity Parameters *N* and *s* for the anion of 2-pyridone (**1**) in CH_3CN

Table 41: Rate Constants for the reactions of **1-K** with different electrophiles (20 °C)

Electrophile	*E*	k_2 / L mol^{-1} s^{-1}	log k_2
jul-tBu (**3o**)	-17.90	1.94×10^1	1.29
dma-tBu (**3n**)	-17.29	3.84×10^1	1.58
OMe-tBu (**3m**)	-16.11	1.72×10^2	2.24
Me-tBu (**3l**)	-15.83	2.38×10^2	2.38
NO_3-tBu (**3k**)	-14.36	2.34×10^3	3.37
dma-Ph (**3j**)	-13.39	5.79×10^3	3.76
OMe-Ph (**3i**)	-12.18	3.12×10^4	4.49

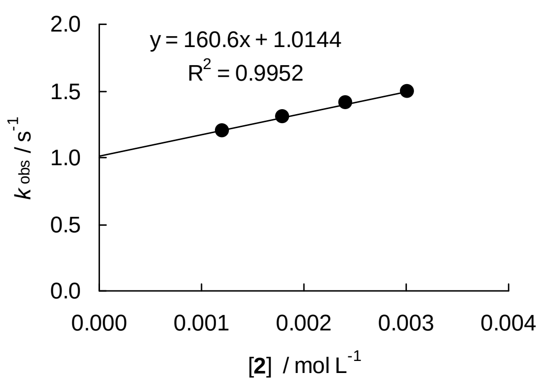
$N = 20.11$, $s = 0.57$



4.5 Reactions of the Potassium Salt of 4-Pyridone (2-K) in CH_3CN

Table 42: Kinetics of the reaction of **2-K** with **3l** (20 °C, stopped-flow, at 371 nm)

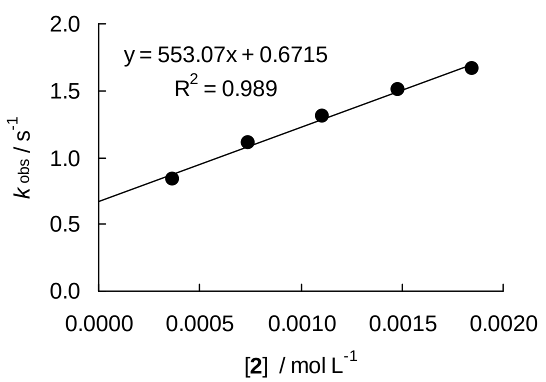
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
4.95×10^{-5}	1.20×10^{-3}	1.61×10^{-3}	24.2	1.20
4.95×10^{-5}	1.80×10^{-3}	2.41×10^{-3}	36.4	1.31
4.95×10^{-5}	2.41×10^{-3}	3.23×10^{-3}	48.7	1.41
4.95×10^{-5}	3.01×10^{-3}	4.03×10^{-3}	60.8	1.49



$k_2 = 1.61 \times 10^2$ L mol^{-1} s^{-1}

Table 43: Kinetics of the reaction of **2-K** with **3k** (20 °C, stopped-flow, at 374 nm)

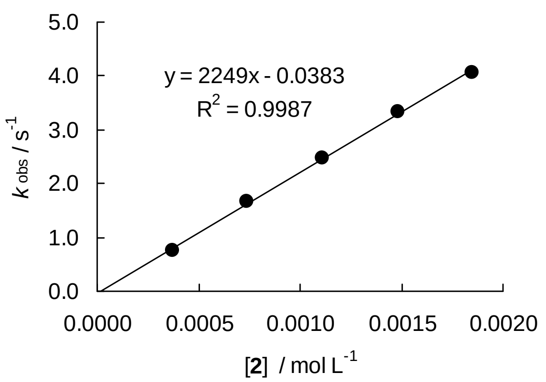
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
4.60×10^{-5}	3.69×10^{-4}	6.16×10^{-4}	8.0	0.836
4.60×10^{-5}	7.39×10^{-4}	1.23×10^{-3}	16.1	1.11
4.60×10^{-5}	1.11×10^{-3}	1.85×10^{-3}	24.1	1.31
4.60×10^{-5}	1.48×10^{-3}	2.47×10^{-3}	32.2	1.51
4.60×10^{-5}	1.85×10^{-3}	3.09×10^{-3}	40.2	1.66



$k_2 = 5.53 \times 10^2$ L mol^{-1} s^{-1}

Table 44: Kinetics of the reaction of **2-K** with **3j** (20 °C, stopped-flow, at 533 nm)

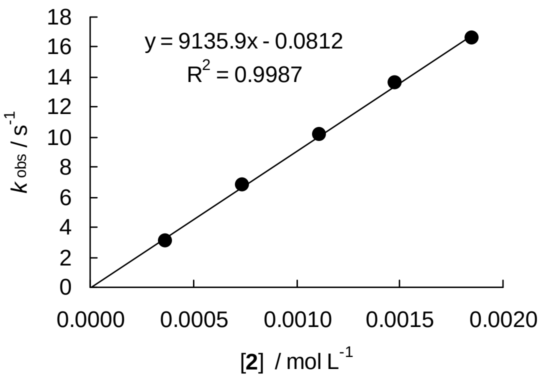
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
4.28×10^{-5}	3.69×10^{-4}	6.16×10^{-4}	8.6	0.746
4.28×10^{-5}	7.39×10^{-4}	1.23×10^{-3}	17.3	1.66
4.28×10^{-5}	1.11×10^{-3}	1.85×10^{-3}	25.9	2.47
4.28×10^{-5}	1.48×10^{-3}	2.47×10^{-3}	34.6	3.34
4.28×10^{-5}	1.85×10^{-3}	3.09×10^{-3}	43.2	4.07



$k_2 = 2.25 \times 10^3$ L mol^{-1} s^{-1}

Table 45: Kinetics of the reaction of **2-K** with **3i** (20 °C, stopped-flow, at 422 nm)

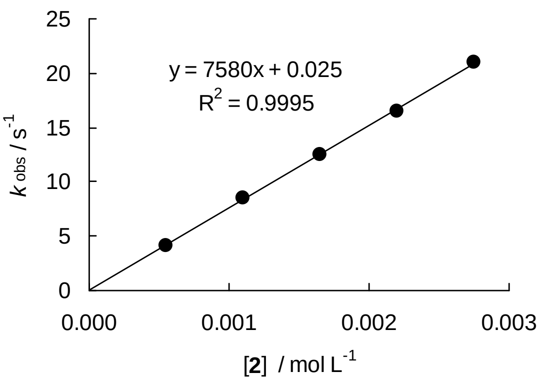
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
4.12×10^{-5}	3.69×10^{-4}	6.16×10^{-4}	9.0	3.09
4.12×10^{-5}	7.39×10^{-4}	1.23×10^{-3}	17.9	6.79
4.12×10^{-5}	1.11×10^{-3}	1.85×10^{-3}	26.9	10.2
4.12×10^{-5}	1.48×10^{-3}	2.47×10^{-3}	35.9	13.6
4.12×10^{-5}	1.85×10^{-3}	3.09×10^{-3}	44.9	16.6



$k_2 = 9.14 \times 10^3$ L mol^{-1} s^{-1}

Table 46: Kinetics of the reaction of **2-K** with **6a** (20 °C, stopped-flow, at 487 nm)

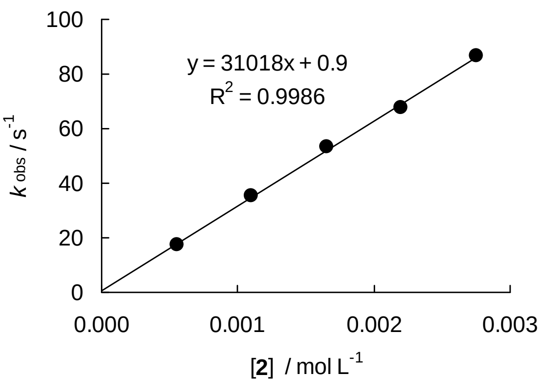
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
2.25×10^{-5}	5.50×10^{-4}	7.32×10^{-4}	24.4	4.15
2.25×10^{-5}	1.10×10^{-3}	1.46×10^{-3}	48.9	8.51
2.25×10^{-5}	1.65×10^{-3}	2.19×10^{-3}	73.3	12.5
2.25×10^{-5}	2.20×10^{-3}	2.93×10^{-3}	97.8	16.5
2.25×10^{-5}	2.75×10^{-3}	3.66×10^{-3}	122	21.0



$k_2 = 7.58 \times 10^3$ L mol^{-1} s^{-1}

Table 47: Kinetics of the reaction of **2-K** with **6b** (20 °C, stopped-flow, at 487 nm)

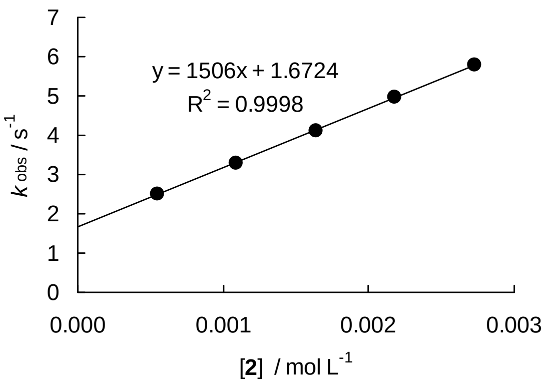
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.20×10^{-5}	5.50×10^{-4}	7.32×10^{-4}	17.2	17.5
3.20×10^{-5}	1.10×10^{-3}	1.46×10^{-3}	34.4	35.3
3.20×10^{-5}	1.65×10^{-3}	2.19×10^{-3}	51.6	53.3
3.20×10^{-5}	2.20×10^{-3}	2.93×10^{-3}	68.8	67.7
3.20×10^{-5}	2.75×10^{-3}	3.66×10^{-3}	85.9	86.6



$k_2 = 3.10 \times 10^4$ L mol^{-1} s^{-1}

Table 48: Kinetics of the reaction of **2-K** with **7a** (20 °C, stopped-flow, at 490 nm)

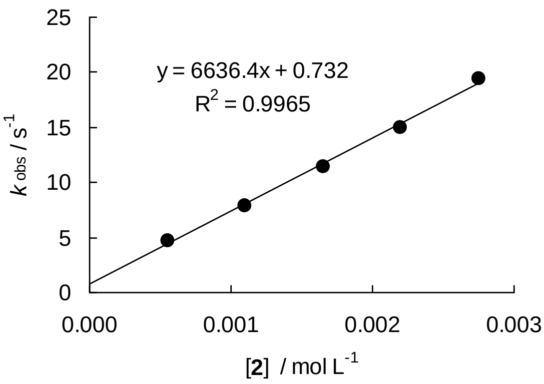
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.40×10^{-5}	5.46×10^{-4}	6.99×10^{-4}	16.1	2.51
3.40×10^{-5}	1.09×10^{-3}	1.40×10^{-3}	32.1	3.30
3.40×10^{-5}	1.64×10^{-3}	2.10×10^{-3}	48.2	4.12
3.40×10^{-5}	2.18×10^{-3}	2.79×10^{-3}	64.1	4.98
3.40×10^{-5}	2.73×10^{-3}	3.49×10^{-3}	80.3	5.78



$k_2 = 1.51 \times 10^3$ L mol^{-1} s^{-1}

Table 49: Kinetics of the reaction of **2-K** with **7b** (20 °C, stopped-flow, at 490 nm)

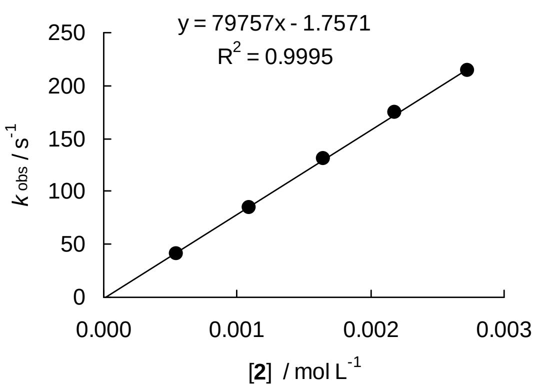
[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
1.44×10^{-5}	5.50×10^{-4}	7.26×10^{-4}	38.2	4.69
1.44×10^{-5}	1.10×10^{-3}	1.45×10^{-3}	76.4	7.92
1.44×10^{-5}	1.65×10^{-3}	2.18×10^{-3}	115	11.4
1.44×10^{-5}	2.20×10^{-3}	2.90×10^{-3}	153	15.0
1.44×10^{-5}	2.75×10^{-3}	3.63×10^{-3}	191	19.4



$k_2 = 6.64 \times 10^3$ L mol^{-1} s^{-1}

Table 50: Kinetics of the reaction of **2-K** with **7c** (20 °C, stopped-flow, at 390 nm)

[E] / mol L^{-1}	[Nu] / mol L^{-1}	[18-crown-6] / mol L^{-1}	[Nu]/[E]	k_{obs} / s^{-1}
3.56×10^{-5}	5.46×10^{-4}	6.99×10^{-4}	15.3	40.8
3.56×10^{-5}	1.09×10^{-3}	1.40×10^{-3}	30.6	85.1
3.56×10^{-5}	1.64×10^{-3}	2.10×10^{-3}	46.3	131
3.56×10^{-5}	2.18×10^{-3}	2.79×10^{-3}	61.2	174
3.56×10^{-5}	2.73×10^{-3}	3.49×10^{-3}	76.7	214

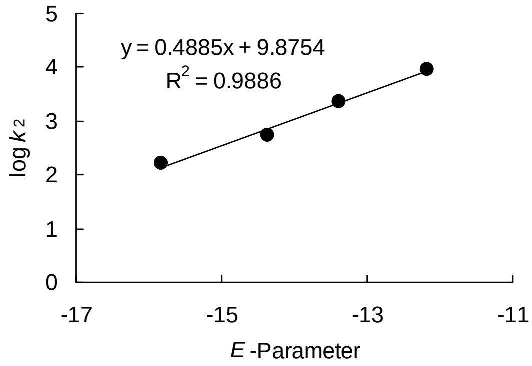


$k_2 = 7.98 \times 10^4$ L mol^{-1} s^{-1}

Determination of Reactivity Parameters *N* and *s* for the anion of 4-pyridone (**2**) in CH_3CN

Table 51: Rate Constants for the reactions of **2-K** with different electrophiles (20 °C)

Electrophile	*E*	k_2 / L mol^{-1} s^{-1}	log k_2
Me-tBu (**3l**)	-15.83	1.61×10^2	2.21
NO_2-tBu (**3k**)	-14.36	5.53×10^2	2.74
dma-Ph (**3j**)	-13.39	2.25×10^3	3.35
OMe-Ph (**3i**)	-12.18	9.14×10^3	3.96

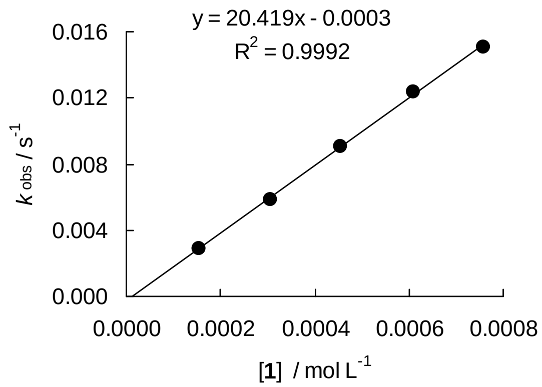


$N = 20.22$, $s = 0.49$

4.6 Reactions of the Potassium Salt of 2-Pyridone (1-K) in Water

Table 52: Kinetics of the reaction of **1-K** with **3h** (20 °C, Conventional UV/Vis, at 630 nm)

[E] / $molL^{-1}$	[**1-H**]$_0$ / $molL^{-1}$	$[KOH]_0$ / $molL^{-1}$	[**1-K**]$_{eff}$ / $molL^{-1}$	$[KOH]_{eff}$ / $molL^{-1}$	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
1.87×10^{-5}	1.18×10^{-2}	2.27×10^{-4}	1.54×10^{-4}	7.30×10^{-5}	8.2	3.05×10^{-3}	1.58×10^{-4}	2.89×10^{-3}
1.87×10^{-5}	1.18×10^{-2}	4.55×10^{-4}	3.07×10^{-4}	1.48×10^{-4}	16.4	6.15×10^{-3}	3.20×10^{-4}	5.83×10^{-3}
1.87×10^{-5}	1.18×10^{-2}	6.38×10^{-4}	4.56×10^{-4}	1.82×10^{-4}	24.4	9.46×10^{-3}	3.93×10^{-4}	9.07×10^{-3}
1.87×10^{-5}	1.18×10^{-2}	9.09×10^{-4}	6.10×10^{-4}	2.99×10^{-4}	32.6	1.30×10^{-2}	6.46×10^{-4}	1.24×10^{-2}
1.87×10^{-5}	1.18×10^{-2}	1.14×10^{-3}	7.59×10^{-4}	3.81×10^{-4}	40.6	1.59×10^{-2}	8.23×10^{-4}	1.51×10^{-2}



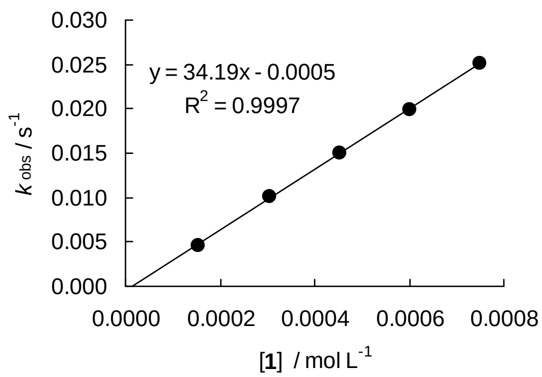
$k_2(OH^-)^5 = 2.16$ L mol^{-1} s^{-1}

pK_A (**1-H**) = 11.74[2]

$k_2 = 2.04 \times 10^1$ L mol^{-1} s^{-1}

Table 53: Kinetics of the reaction of **1-K** with **3g** (20 °C, Conventional UV/Vis, at 635 nm)

[E] / $molL^{-1}$	[**1-H**]$_0$ / $molL^{-1}$	$[KOH]_0$ / $molL^{-1}$	[**1-K**]$_{eff}$ / $molL^{-1}$	$[KOH]_{eff}$ / $molL^{-1}$	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
1.44×10^{-5}	1.14×10^{-2}	2.27×10^{-4}	1.53×10^{-4}	7.40×10^{-5}	10.6	4.87×10^{-3}	2.55×10^{-4}	4.62×10^{-3}
1.44×10^{-5}	1.14×10^{-2}	4.55×10^{-4}	3.04×10^{-4}	1.51×10^{-4}	21.1	1.06×10^{-2}	5.19×10^{-4}	1.01×10^{-2}
1.44×10^{-5}	1.14×10^{-2}	6.38×10^{-4}	4.53×10^{-4}	1.85×10^{-4}	31.5	1.57×10^{-2}	6.36×10^{-4}	1.51×10^{-2}
1.44×10^{-5}	1.14×10^{-2}	9.09×10^{-4}	6.02×10^{-4}	3.07×10^{-4}	41.8	2.10×10^{-2}	1.06×10^{-3}	1.99×10^{-2}
1.44×10^{-5}	1.14×10^{-2}	1.14×10^{-3}	7.49×10^{-4}	3.91×10^{-4}	52.0	2.65×10^{-2}	1.35×10^{-3}	2.52×10^{-2}



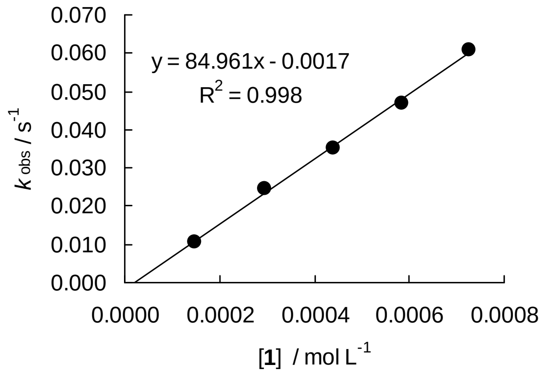
$k_2(OH^-)^5 = 3.44$ L mol^{-1} s^{-1}

pK_A (**1-H**) = 11.74[2]

$k_2 = 3.42 \times 10^1$ L mol^{-1} s^{-1}

Table 54: Kinetics of the reaction of **1-K** with **3f** (20 °C, Conventional UV/Vis, at 627 nm)

[E] / molL^{-1}	[**1-H**]$_0$ / molL^{-1}	[KOH]$_0$ / molL^{-1}	[**1-K**]$_{eff}$ / molL^{-1}	[KOH]$_{eff}$ / molL^{-1}	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
1.25×10^{-5}	1.05×10^{-2}	2.27×10^{-4}	1.48×10^{-4}	7.90×10^{-5}	11.8	1.16×10^{-2}	8.55×10^{-4}	1.07×10^{-2}
1.25×10^{-5}	1.05×10^{-2}	4.55×10^{-4}	2.95×10^{-4}	1.60×10^{-4}	23.6	2.61×10^{-2}	1.73×10^{-3}	2.44×10^{-2}
1.25×10^{-5}	1.05×10^{-2}	6.38×10^{-4}	4.40×10^{-4}	1.98×10^{-4}	35.2	3.72×10^{-2}	2.14×10^{-3}	3.51×10^{-2}
1.25×10^{-5}	1.05×10^{-2}	9.09×10^{-4}	5.84×10^{-4}	3.25×10^{-4}	46.7	5.05×10^{-2}	3.51×10^{-3}	4.70×10^{-2}
1.25×10^{-5}	1.05×10^{-2}	1.14×10^{-3}	7.26×10^{-4}	4.14×10^{-4}	58.1	6.53×10^{-2}	4.47×10^{-3}	6.08×10^{-2}



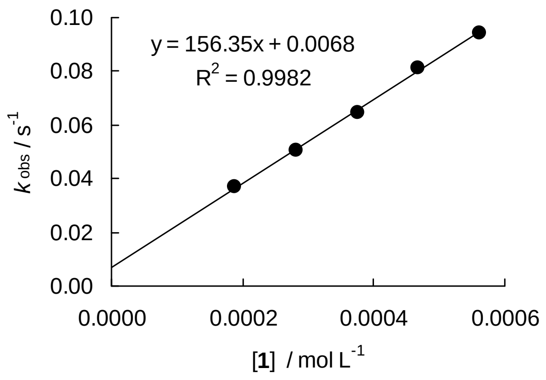
$k_2(OH^-)^5 = 10.8$ L mol^{-1} s^{-1}

pK_A (**1-H**) = 11.74[2]

$k_2 = 8.50 \times 10^1$ L mol^{-1} s^{-1}

Table 55: Kinetics of the reaction of **1-K** with **3e** (20 °C, Stopped-flow, at 618 nm)

[E] / molL^{-1}	[**1-H**]$_0$ / molL^{-1}	[KOH]$_0$ / molL^{-1}	[**1-K**]$_{eff}$ / molL^{-1}	[KOH]$_{eff}$ / molL^{-1}	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
1.12×10^{-5}	1.69×10^{-2}	2.50×10^{-4}	1.88×10^{-4}	6.20×10^{-5}	16.8	3.84×10^{-2}	1.46×10^{-3}	3.68×10^{-2}
1.12×10^{-5}	1.69×10^{-2}	3.75×10^{-4}	2.82×10^{-4}	9.30×10^{-5}	25.2	5.25×10^{-2}	2.19×10^{-3}	5.03×10^{-2}
1.12×10^{-5}	1.69×10^{-2}	5.00×10^{-4}	3.75×10^{-4}	1.25×10^{-4}	33.5	6.74×10^{-2}	2.94×10^{-3}	6.45×10^{-2}
1.12×10^{-5}	1.69×10^{-2}	6.25×10^{-4}	4.68×10^{-4}	1.57×10^{-4}	41.8	8.51×10^{-2}	3.69×10^{-3}	8.14×10^{-2}
1.12×10^{-5}	1.69×10^{-2}	7.50×10^{-e}	5.61×10^{-4}	1.89×10^{-4}	50.1	9.86×10^{-2}	4.44×10^{-3}	9.42×10^{-2}



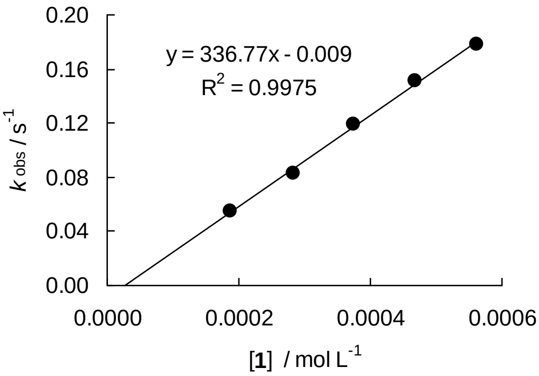
$k_2(OH^-)^5 = 23.5$ L mol^{-1} s^{-1}

pK_A (**1-H**) = 11.74[2]

$k_2 = 1.56 \times 10^2$ L mol^{-1} s^{-1}

Table 56: Kinetics of the reaction of **1-K** with **3d** (20 °C, Stopped-flow, at 620 nm)

[E] / $molL^{-1}$	[**1-H**]$_0$ / $molL^{-1}$	[KOH]$_0$ / $molL^{-1}$	[**1-K**]$_{eff}$ / $molL^{-1}$	[KOH]$_{eff}$ / $molL^{-1}$	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
1.08×10^{-5}	1.69×10^{-2}	2.50×10^{-4}	1.88×10^{-4}	6.20×10^{-5}	17.4	5.81×10^{-2}	3.01×10^{-3}	5.51×10^{-2}
1.08×10^{-5}	1.69×10^{-2}	3.75×10^{-4}	2.82×10^{-4}	9.30×10^{-5}	26.1	8.75×10^{-2}	4.51×10^{-3}	8.30×10^{-2}
1.08×10^{-5}	1.69×10^{-2}	5.00×10^{-4}	3.75×10^{-4}	1.25×10^{-4}	34.7	1.25×10^{-1}	6.06×10^{-3}	1.19×10^{-1}
1.08×10^{-5}	1.69×10^{-2}	6.25×10^{-4}	4.68×10^{-4}	1.57×10^{-4}	43.3	1.59×10^{-1}	7.61×10^{-3}	1.51×10^{-1}
1.08×10^{-5}	1.69×10^{-2}	7.50×10^{-e}	5.61×10^{-4}	1.89×10^{-4}	51.9	1.87×10^{-1}	9.17×10^{-3}	1.78×10^{-1}



$k_2(OH^-)$[5] $= 48.5$ L mol^{-1} s^{-1}

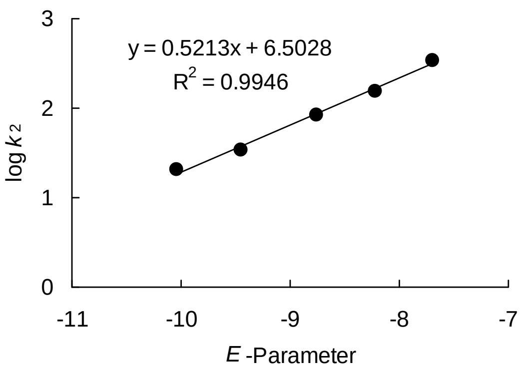
pK_A (**1-H**) = 11.74[2]

$k_2 = 3.37 \times 10^2$ L mol^{-1} s^{-1}

Determination of Reactivity Parameters *N* and *s* for the anion of 2-pyridone (**1**) in Water

Table 57: Rate Constants for the reactions of **1-K** with different electrophiles (20 °C)

Electrophile	*E*	k_2 / L mol^{-1} s^{-1}	log k_2
lil$_2$CH$^+$ (**3h**)	-10.04	2.04×10^1	1.31
jul$_2$CH$^+$ (**3g**)	-9.45	3.42×10^1	1.53
ind$_2$CH$^+$ (**3f**)	-8.76	8.50×10^1	1.93
thq$_2$CH$^+$ (**3e**)	-8.22	1.56×10^2	2.19
pyr$_2$CH$^+$ (**3d**)	-7.69	3.37×10^2	2.53

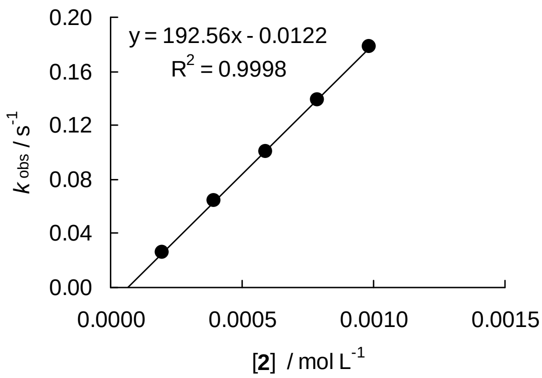


$N = 12.47$, $s = 0.52$

4.7 Reactions of the Potassium Salt of 4-Pyridone (2-K) in Water

Table 58: Kinetics of the reaction of **2-K** with **3h** (20 °C, Conventional UV/Vis, at 630 nm)

[E] / $molL^{-1}$	[**2-H**]$_0$ / $molL^{-1}$	[KOH]$_0$ / $molL^{-1}$	[**2-K**]$_{eff}$ / $molL^{-1}$	[KOH]$_{eff}$ / $molL^{-1}$	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
1.84×10^{-5}	1.10×10^{-2}	2.22×10^{-4}	1.98×10^{-4}	2.40×10^{-5}	10.8	2.63×10^{-2}	5.18×10^{-5}	2.62×10^{-2}
1.84×10^{-5}	1.10×10^{-2}	4.44×10^{-4}	3.95×10^{-4}	4.90×10^{-5}	21.5	6.44×10^{-2}	1.06×10^{-4}	6.43×10^{-2}
1.84×10^{-5}	1.10×10^{-2}	6.67×10^{-4}	5.92×10^{-4}	7.50×10^{-5}	32.2	1.01×10^{-1}	1.62×10^{-4}	1.01×10^{-1}
1.84×10^{-5}	1.10×10^{-2}	8.89×10^{-4}	7.87×10^{-4}	1.02×10^{-4}	42.8	1.39×10^{-1}	2.20×10^{-4}	1.39×10^{-1}
1.84×10^{-5}	1.10×10^{-2}	1.11×10^{-3}	9.82×10^{-4}	1.28×10^{-4}	53.4	1.78×10^{-1}	2.76×10^{-4}	1.78×10^{-1}



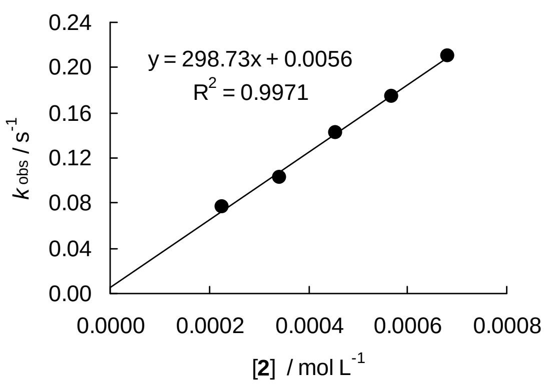
$k_2(OH^-)^5 = 2.16$ L mol^{-1} s^{-1}

pK_A (**2-H**) = 11.12[2]

$k_2 = 1.93 \times 10^2$ L mol^{-1} s^{-1}

Table 59: Kinetics of the reaction of **2-K** with **3g** (20 °C, Stopped-Flow, at 635 nm)

[E] / $molL^{-1}$	[**2-H**]$_0$ / $molL^{-1}$	[KOH]$_0$ / $molL^{-1}$	[**2-K**]$_{eff}$ / $molL^{-1}$	[KOH]$_{eff}$ / $molL^{-1}$	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
1.17×10^{-5}	1.35×10^{-2}	2.50×10^{-4}	2.27×10^{-4}	2.30×10^{-5}	19.4	7.67×10^{-2}	7.91×10^{-5}	7.66×10^{-2}
1.17×10^{-5}	1.35×10^{-2}	3.75×10^{-4}	3.41×10^{-4}	3.40×10^{-5}	29.1	1.03×10^{-1}	1.17×10^{-4}	1.03×10^{-1}
1.17×10^{-5}	1.35×10^{-2}	5.00×10^{-4}	4.54×10^{-4}	4.60×10^{-5}	38.8	1.42×10^{-1}	1.58×10^{-4}	1.42×10^{-1}
1.17×10^{-5}	1.35×10^{-2}	6.25×10^{-4}	5.67×10^{-4}	5.80×10^{-5}	48.5	1.75×10^{-1}	2.00×10^{-4}	1.75×10^{-1}
1.17×10^{-5}	1.35×10^{-2}	7.50×10^{-3}	6.80×10^{-4}	7.00×10^{-5}	58.1	2.10×10^{-1}	2.41×10^{-4}	2.10×10^{-1}



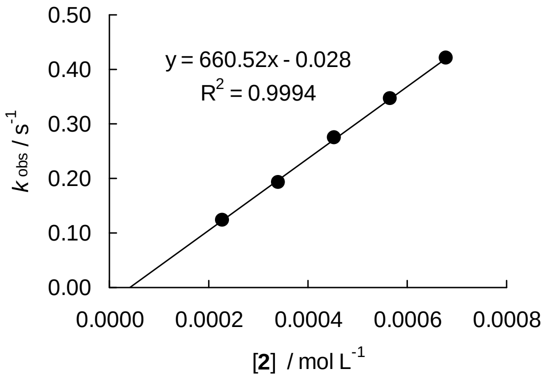
$k_2(OH^-)^5 = 3.44$ L mol^{-1} s^{-1}

pK_A (**2-H**) = 11.12[2]

$k_2 = 2.99 \times 10^2$ L mol^{-1} s^{-1}

Table 60: Kinetics of the reaction of **2-K** with **3f** (20 °C, Stopped-Flow, at 627 nm)

[E] / molL^{-1}	[**2-H**]$_0$ / molL^{-1}	[KOH]$_0$ / molL^{-1}	[**2-K**]$_{eff}$ / molL^{-1}	[KOH]$_{eff}$ / molL^{-1}	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
9.34×10^{-6}	1.35×10^{-2}	2.50×10^{-4}	2.27×10^{-4}	2.30×10^{-5}	24.3	1.24×10^{-1}	2.48×10^{-4}	1.24×10^{-1}
9.34×10^{-6}	1.35×10^{-2}	3.75×10^{-4}	3.41×10^{-4}	3.40×10^{-5}	36.5	1.93×10^{-1}	3.67×10^{-4}	1.93×10^{-1}
9.34×10^{-6}	1.35×10^{-2}	5.00×10^{-4}	4.54×10^{-4}	4.60×10^{-5}	48.6	2.75×10^{-1}	4.97×10^{-4}	2.75×10^{-1}
9.34×10^{-6}	1.35×10^{-2}	6.25×10^{-4}	5.67×10^{-4}	5.80×10^{-5}	60.7	3.48×10^{-1}	6.26×10^{-4}	3.47×10^{-1}
9.34×10^{-6}	1.35×10^{-2}	7.50×10^{-3}	6.80×10^{-4}	7.00×10^{-5}	72.8	4.21×10^{-1}	7.56×10^{-4}	4.20×10^{-1}



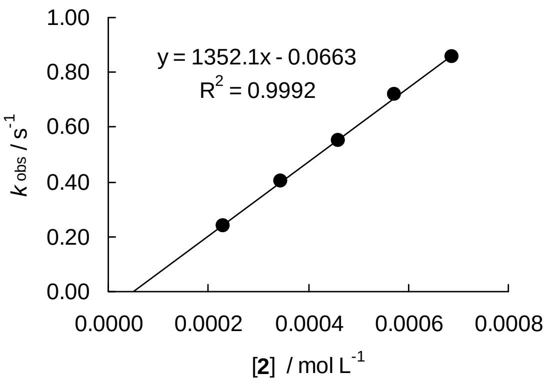
$k_2(OH^-)^5 = 10.8$ L mol^{-1} s^{-1}

pK_A (**2-H**) = 11.12[2]

$k_2 = 6.61 \times 10^2$ L mol^{-1} s^{-1}

Table 61: Kinetics of the reaction of **2-K** with **3e** (20 °C, Stopped-flow, at 618 nm)

[E] / molL^{-1}	[**2-H**]$_0$ / molL^{-1}	[KOH]$_0$ / molL^{-1}	[**2-K**]$_{eff}$ / molL^{-1}	[KOH]$_{eff}$ / molL^{-1}	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
1.12×10^{-5}	1.51×10^{-2}	2.50×10^{-4}	2.30×10^{-4}	2.00×10^{-5}	20.5	2.40×10^{-1}	4.70×10^{-4}	2.40×10^{-1}
1.12×10^{-5}	1.51×10^{-2}	3.75×10^{-4}	3.44×10^{-4}	3.10×10^{-5}	30.7	4.05×10^{-1}	7.29×10^{-4}	4.04×10^{-1}
1.12×10^{-5}	1.51×10^{-2}	5.00×10^{-4}	4.59×10^{-4}	4.10×10^{-5}	41.0	5.53×10^{-1}	9.64×10^{-4}	5.52×10^{-1}
1.12×10^{-5}	1.51×10^{-2}	6.25×10^{-4}	5.73×10^{-4}	5.20×10^{-5}	51.2	7.19×10^{-1}	1.22×10^{-3}	7.18×10^{-1}
1.12×10^{-5}	1.51×10^{-2}	7.50×10^{-4}	6.87×10^{-4}	6.30×10^{-5}	61.3	8.57×10^{-1}	1.48×10^{-3}	8.56×10^{-1}



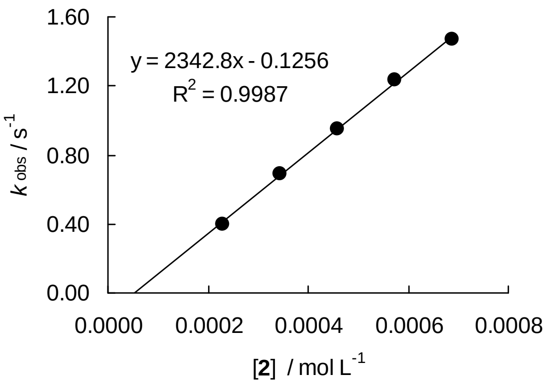
$k_2(OH^-)^5 = 23.5$ L mol^{-1} s^{-1}

pK_A (**2-H**) = 11.12[2]

$k_2 = 1.35 \times 10^3$ L mol^{-1} s^{-1}

Table 62: Kinetics of the reaction of **2-K** with **3d** (20 °C, Stopped-Flow, at 620 nm)

[E] / $molL^{-1}$	[**2-H**]$_0$ / $molL^{-1}$	[KOH]$_0$ / $molL^{-1}$	[**2-K**]$_{eff}$ / $molL^{-1}$	[KOH]$_{eff}$ / $molL^{-1}$	[Nu]/[E]	k_{obs} / s^{-1}	k_{OH-} / s^{-1}	k_{eff} / s^{-1}
1.08×10^{-5}	1.51×10^{-2}	2.50×10^{-4}	2.30×10^{-4}	2.00×10^{-5}	21.3	4.03×10^{-1}	9.70×10^{-4}	4.02×10^{-1}
1.08×10^{-5}	1.51×10^{-2}	3.75×10^{-4}	3.44×10^{-4}	3.10×10^{-5}	31.9	6.91×10^{-1}	1.50×10^{-3}	6.89×10^{-1}
1.08×10^{-5}	1.51×10^{-2}	5.00×10^{-4}	4.59×10^{-4}	4.10×10^{-5}	42.5	9.50×10^{-1}	1.99×10^{-3}	9.48×10^{-1}
1.08×10^{-5}	1.51×10^{-2}	6.25×10^{-4}	5.73×10^{-4}	5.20×10^{-5}	53.1	1.24×10^{0}	2.52×10^{-3}	1.24×10^{0}
1.08×10^{-5}	1.51×10^{-2}	7.50×10^{-e}	6.87×10^{-4}	6.30×10^{-5}	63.6	1.47×10^{0}	3.06×10^{-3}	1.47×10^{0}



$k_2(OH^-)^5 = 48.5$ L mol^{-1} s^{-1}

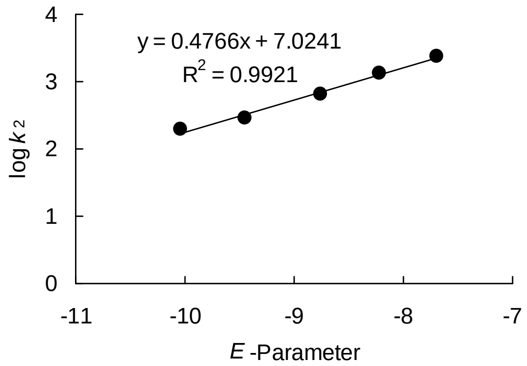
pK_A (**2-H**) = 11.12[2]

$k_2 = 2.34 \times 10^3$ L mol^{-1} s^{-1}

Determination of Reactivity Parameters *N* and *s* for the anion of 4-pyridone (**2**) in Water

Table 63: Rate Constants for the reactions of **2-K** with different electrophiles (20 °C)

Electrophile	*E*	k_2 / L mol^{-1} s^{-1}	log k_2
lil$_2$CH$^+$ (**3h**)	-10.04	1.93×10^2	2.29
jul$_2$CH$^+$ (**3g**)	-9.45	2.99×10^2	2.47
ind$_2$CH$^+$ (**3f**)	-8.76	6.61×10^2	2.82
thq$_2$CH$^+$ (**3e**)	-8.22	1.35×10^3	3.13
pyr$_2$CH$^+$ (**3d**)	-7.69	2.34×10^3	3.37



$N = 14.76$, $s = 0.48$

5 Determination of Equilibrium Constants in DMSO

5.1 Equilibrium Constants for Reactions of the Potassium Salt of 2-Pyridone (1-K)

Table 64: Equilibrium constant for the reaction of **1-K** with **3o** (20 °C, at 521 nm)

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	K
0	3.65×10^{-5}	-	0.724	-	3.65×10^{-5}	-	-	-
1	3.61×10^{-5}	5.00×10^{-4}	0.716	0.685	3.45×10^{-5}	4.99×10^{-4}	1.54×10^{-6}	8.94×10^{1}
2	3.58×10^{-5}	8.27×10^{-4}	0.710	0.656	3.31×10^{-5}	8.24×10^{-4}	2.72×10^{-6}	9.98×10^{1}
3	3.55×10^{-5}	1.15×10^{-3}	0.705	0.629	3.17×10^{-5}	1.15×10^{-3}	3.81×10^{-6}	1.05×10^{2}
4	3.52×10^{-5}	1.47×10^{-3}	0.699	0.605	3.05×10^{-5}	1.46×10^{-3}	4.74×10^{-6}	1.07×10^{2}
5	3.50×10^{-5}	1.78×10^{-3}	0.694	0.582	2.93×10^{-5}	1.77×10^{-3}	5.64×10^{-6}	1.08×10^{2}
6	3.47×10^{-5}	2.09×10^{-3}	0.689	0.560	2.82×10^{-5}	2.08×10^{-3}	6.48×10^{-6}	1.11×10^{2}
7	3.44×10^{-5}	2.39×10^{-3}	0.684	0.543	2.74×10^{-5}	2.38×10^{-3}	7.08×10^{-6}	1.09×10^{2}
0	4.19×10^{-5}	-	0.824	-	4.19×10^{-5}	-	-	-
1	4.10×10^{-5}	9.47×10^{-4}	0.806	0.757	3.85×10^{-5}	9.45×10^{-4}	2.48×10^{-6}	(6.81×10^{1})
2	4.01×10^{-5}	1.85×10^{-3}	0.788	0.675	3.43×10^{-5}	1.84×10^{-3}	5.76×10^{-6}	9.08×10^{1}
3	3.92×10^{-5}	2.72×10^{-3}	0.772	0.612	3.11×10^{-5}	2.71×10^{-3}	8.11×10^{-6}	9.61×10^{1}
4	3.84×10^{-5}	3.55×10^{-3}	0.755	0.561	2.85×10^{-5}	3.54×10^{-3}	9.89×10^{-6}	9.79×10^{1}
5	3.76×10^{-5}	4.35×10^{-3}	0.740	0.520	2.64×10^{-5}	4.34×10^{-3}	1.12×10^{-5}	9.75×10^{1}
6	3.69×10^{-5}	5.12×10^{-3}	0.725	0.485	2.47×10^{-5}	5.10×10^{-3}	1.22×10^{-5}	9.71×10^{1}
7	3.62×10^{-5}	5.85×10^{-3}	0.711	0.455	2.31×10^{-5}	5.84×10^{-3}	1.30×10^{-5}	9.64×10^{1}
8	3.55×10^{-5}	6.56×10^{-3}	0.697	0.430	2.19×10^{-5}	6.55×10^{-3}	1.36×10^{-5}	9.50×10^{1}
9	3.48×10^{-5}	7.24×10^{-3}	0.684	0.407	2.07×10^{-5}	7.23×10^{-3}	1.41×10^{-5}	9.43×10^{1}
10	3.42×10^{-5}	7.90×10^{-3}	0.672	0.387	1.97×10^{-5}	7.88×10^{-3}	1.45×10^{-5}	9.33×10^{1}

Data in parenthesis were not used for the calculation of equilibrium constants.

$K = (9.91 \pm 0.66) \times 10^{1}$ L mol^{-1}

Table 65: Equilibrium constant for the reaction of **1-K** with **3n** (20 °C, at 533 nm)

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	*K*
0	4.47×10^{-5}	-	0.748	-	4.47×10^{-5}	-	-	-
1	4.39×10^{-5}	1.05×10^{-3}	0.734	0.515	3.08×10^{-5}	1.04×10^{-3}	1.31×10^{-5}	4.08×10^{2}
2	4.31×10^{-5}	2.07×10^{-3}	0.720	0.399	2.39×10^{-5}	2.05×10^{-3}	1.92×10^{-5}	3.93×10^{2}
3	4.23×10^{-5}	3.05×10^{-3}	0.707	0.330	1.97×10^{-5}	3.02×10^{-3}	2.25×10^{-5}	3.78×10^{2}
4	4.15×10^{-5}	3.99×10^{-3}	0.694	0.284	1.70×10^{-5}	3.96×10^{-3}	2.45×10^{-5}	3.64×10^{2}
5	4.08×10^{-5}	4.90×10^{-3}	0.682	0.251	1.50×10^{-5}	4.87×10^{-3}	2.58×10^{-5}	3.52×10^{2}
6	4.01×10^{-5}	5.78×10^{-3}	0.670	0.226	1.35×10^{-5}	5.75×10^{-3}	2.66×10^{-5}	3.42×10^{2}
7	3.94×10^{-5}	6.62×10^{-3}	0.659	0.206	1.23×10^{-5}	6.60×10^{-3}	2.71×10^{-5}	3.33×10^{2}
8	3.87×10^{-5}	7.44×10^{-3}	0.648	0.190	1.14×10^{-5}	7.41×10^{-3}	2.74×10^{-5}	3.25×10^{2}
9	3.81×10^{-5}	8.23×10^{-3}	0.637	0.177	1.06×10^{-5}	8.21×10^{-3}	2.75×10^{-5}	3.17×10^{2}
0	4.47×10^{-5}	-	0.756		4.47×10^{-5}	-	-	-
1	4.39×10^{-5}	1.54×10^{-3}	0.736	0.459	2.72×10^{-5}	1.53×10^{-3}	1.67×10^{-5}	4.03×10^{2}
2	4.31×10^{-5}	3.03×10^{-3}	0.716	0.339	2.01×10^{-5}	3.01×10^{-3}	2.30×10^{-5}	3.81×10^{2}
3	4.23×10^{-5}	4.46×10^{-3}	0.698	0.273	1.62×10^{-5}	4.44×10^{-3}	2.61×10^{-5}	3.64×10^{2}
4	4.15×10^{-5}	5.85×10^{-3}	0.680	0.231	1.37×10^{-5}	5.82×10^{-3}	2.78×10^{-5}	3.50×10^{2}
5	4.08×10^{-5}	7.18×10^{-3}	0.664	0.202	1.20×10^{-5}	7.15×10^{-3}	2.88×10^{-5}	3.37×10^{2}
6	4.01×10^{-5}	8.46×10^{-3}	0.648	0.181	1.07×10^{-5}	8.43×10^{-3}	2.94×10^{-5}	3.25×10^{2}
7	3.94×10^{-5}	9.71×10^{-3}	0.633	0.164	9.70×10^{-6}	9.68×10^{-3}	2.97×10^{-5}	3.16×10^{2}

$K = (3.56 \pm 0.30) \times 10^{2}$ L mol^{-1}

Table 66: Equilibrium constant for the reaction of **1-K** with **3m** (20 °C, at 393 nm)

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	*K*
0	4.19×10^{-5}	-	0.844	-	4.19×10^{-5}	-	-	-
1	4.17×10^{-5}	1.11×10^{-4}	0.840	0.527	2.62×10^{-5}	9.55×10^{-4}	1.55×10^{-5}	6.22×10^{3}
2	4.15×10^{-5}	2.21×10^{-4}	0.836	0.370	1.84×10^{-5}	1.98×10^{-4}	2.21×10^{-5}	6.36×10^{3}
3	4.13×10^{-5}	3.30×10^{-4}	0.832	0.285	1.42×10^{-5}	3.03×10^{-4}	2.72×10^{-5}	6.34×10^{3}
4	4.11×10^{-5}	4.38×10^{-4}	0.828	0.232	1.15×10^{-5}	4.08×10^{-4}	2.96×10^{-5}	6.29×10^{3}
5	4.09×10^{-5}	5.45×10^{-4}	0.824	0.197	9.78×10^{-6}	5.13×10^{-4}	3.11×10^{-5}	6.20×10^{3}
6	4.07×10^{-5}	6.50×10^{-4}	0.820	0.173	8.59×10^{-6}	6.18×10^{-4}	3.21×10^{-5}	6.05×10^{3}
7	4.05×10^{-5}	7.55×10^{-4}	0.816	0.156	7.75×10^{-6}	7.22×10^{-4}	3.28×10^{-5}	5.86×10^{3}
8	4.03×10^{-5}	8.59×10^{-4}	0.812	0.143	7.10×10^{-6}	8.26×10^{-4}	3.32×10^{-5}	5.67×10^{3}

Table 66: Continued

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	*K*
0	4.60×10^{-5}	-	0.849	-	4.60×10^{-5}	-	-	-
1	4.56×10^{-5}	1.18×10^{-4}	0.842	0.517	2.80×10^{-5}	1.00×10^{-4}	1.76×10^{-5}	6.27×10^{3}
2	4.52×10^{-5}	2.33×10^{-4}	0.834	0.358	1.94×10^{-5}	2.07×10^{-4}	2.58×10^{-5}	6.41×10^{3}
3	4.48×10^{-5}	3.47×10^{-4}	0.827	0.274	1.48×10^{-5}	3.17×10^{-4}	3.00×10^{-5}	6.37×10^{3}
4	4.44×10^{-5}	4.59×10^{-4}	0.820	0.222	1.20×10^{-5}	4.26×10^{-4}	3.24×10^{-5}	6.32×10^{3}
5	4.39×10^{-5}	6.22×10^{-4}	0.809	0.173	9.37×10^{-6}	5.88×10^{-4}	3.45×10^{-5}	6.26×10^{3}
6	4.33×10^{-5}	7.82×10^{-4}	0.799	0.144	7.80×10^{-6}	7.47×10^{-4}	3.55×10^{-5}	6.09×10^{3}
7	4.28×10^{-5}	9.38×10^{-4}	0.789	0.125	6.77×10^{-6}	9.02×10^{-4}	3.60×10^{-5}	5.89×10^{3}
8	4.23×10^{-5}	1.09×10^{-3}	0.780	0.111	6.01×10^{-6}	1.05×10^{-3}	3.62×10^{-5}	5.72×10^{3}

$K = (6.15 \pm 0.24) \times 10^{3}$ L mol^{-1}

Table 67: Equilibrium constant for the reaction of **1-K** with **3l** (20 °C, at 371 nm)

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	*K*
0	3.89×10^{-5}	-	0.725	-	3.89×10^{-5}	-	-	-
1	3.87×10^{-5}	1.02×10^{-4}	0.722	0.329	1.76×10^{-5}	8.05×10^{-5}	2.11×10^{-5}	1.48×10^{4}
2	3.85×10^{-5}	2.02×10^{-4}	0.719	0.199	1.07×10^{-5}	1.74×10^{-4}	2.79×10^{-5}	1.50×10^{4}
3	3.84×10^{-5}	3.02×10^{-4}	0.715	0.146	7.83×10^{-6}	2.72×10^{-4}	3.05×10^{-5}	1.44×10^{4}
4	3.82×10^{-5}	4.01×10^{-4}	0.712	0.116	6.22×10^{-6}	3.69×10^{-4}	3.20×10^{-5}	1.39×10^{4}
5	3.80×10^{-5}	4.99×10^{-4}	0.709	0.098	5.26×10^{-6}	4.66×10^{-4}	3.28×10^{-5}	1.34×10^{4}
6	3.79×10^{-5}	5.96×10^{-4}	0.706	0.086	4.61×10^{-6}	5.63×10^{-4}	3.33×10^{-5}	1.28×10^{4}
0	3.89×10^{-5}	-	0.680	-	3.89×10^{-5}	-	-	-
1	3.85×10^{-5}	1.18×10^{-4}	0.674	0.278	1.59×10^{-5}	9.50×10^{-5}	2.26×10^{-5}	1.50×10^{4}
2	3.82×10^{-5}	2.33×10^{-4}	0.668	0.166	9.49×10^{-6}	2.05×10^{-4}	2.87×10^{-5}	1.48×10^{4}
3	3.79×10^{-5}	3.47×10^{-4}	0.662	0.122	6.98×10^{-6}	3.16×10^{-4}	3.09×10^{-5}	1.40×10^{4}
4	3.76×10^{-5}	4.59×10^{-4}	0.657	0.098	5.60×10^{-6}	4.27×10^{-4}	3.20×10^{-5}	1.34×10^{4}
5	3.71×10^{-5}	6.22×10^{-4}	0.648	0.078	4.46×10^{-6}	5.90×10^{-4}	3.26×10^{-5}	1.24×10^{4}

$K = (1.40 \pm 0.09) \times 10^{4}$ L mol^{-1}

5.2 Equilibrium Constants for Reactions of the Potassium Salt of 4-Pyridone (2-K)

Table 68: Equilibrium constant for the reaction of **2-K** with **3k** (20 °C, at 374 nm)

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	K
0	3.86×10^{-5}	-	0.667	-	3.86×10^{-5}	-	-	-
1	3.84×10^{-5}	2.55×10^{-4}	0.664	0.501	2.90×10^{-5}	2.45×10^{-4}	9.43×10^{-6}	1.33×10^{3}
2	3.82×10^{-5}	5.07×10^{-4}	0.661	0.402	2.32×10^{-5}	4.92×10^{-4}	1.50×10^{-5}	1.31×10^{3}
3	3.81×10^{-5}	7.57×10^{-4}	0.658	0.341	1.97×10^{-5}	7.39×10^{-4}	1.83×10^{-5}	1.26×10^{3}
4	3.79×10^{-5}	1.01×10^{-3}	0.655	0.301	1.74×10^{-5}	9.85×10^{-4}	2.05×10^{-5}	1.20×10^{3}

$$\underline{K = (1.27 \pm 0.06) \times 10^{3}\ \mathrm{L\ mol^{-1}}}$$

Table 69: Equilibrium constant for the reaction of **2-K** with **3l** (20 °C, at 371 nm)

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	K
0	3.51×10^{-5}	-	0.662	-	3.51×10^{-5}	-	-	-
1	3.47×10^{-5}	1.42×10^{-3}	0.654	0.580	3.07×10^{-5}	1.41×10^{-3}	3.91×10^{-6}	9.01×10^{1}
2	3.42×10^{-5}	2.80×10^{-3}	0.646	0.521	2.76×10^{-5}	2.79×10^{-3}	6.61×10^{-6}	8.58×10^{1}
3	3.38×10^{-5}	4.15×10^{-3}	0.638	0.473	2.51×10^{-5}	4.14×10^{-3}	8.74×10^{-6}	8.43×10^{1}
4	3.34×10^{-5}	5.46×10^{-3}	0.630	0.432	2.29×10^{-5}	5.45×10^{-3}	1.05×10^{-5}	8.42×10^{1}
5	3.29×10^{-5}	7.17×10^{-3}	0.620	0.391	2.07×10^{-5}	7.15×10^{-3}	1.22×10^{-5}	8.20×10^{1}
6	3.24×10^{-5}	8.82×10^{-3}	0.611	0.356	1.89×10^{-5}	8.81×10^{-3}	1.35×10^{-5}	8.13×10^{1}
7	3.19×10^{-5}	1.04×10^{-2}	0.601	0.332	1.76×10^{-5}	1.04×10^{-2}	1.43×10^{-5}	7.80×10^{1}
8	3.14×10^{-5}	$1.20 \times 10^{-}$	0.592	0.308	1.63×10^{-5}	1.20×10^{-2}	1.51×10^{-5}	7.72×10^{1}
No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	K
0	3.37×10^{-5}	-	0.629	-	3.37×10^{-5}	-	-	-
1	3.31×10^{-5}	2.38×10^{-3}	0.619	0.512	2.74×10^{-5}	2.73×10^{-3}	5.73×10^{-6}	8.83×10^{1}
2	3.26×10^{-5}	4.68×10^{-3}	0.610	0.434	2.32×10^{-5}	4.67×10^{-3}	9.40×10^{-6}	8.66×10^{1}
3	3.21×10^{-5}	6.91×10^{-3}	0.600	0.380	2.03×10^{-5}	6.90×10^{-3}	1.18×10^{-5}	8.40×10^{1}
4	3.17×10^{-5}	9.07×10^{-3}	0.591	0.340	1.82×10^{-5}	9.06×10^{-3}	1.35×10^{-5}	8.16×10^{1}
5	3.11×10^{-5}	1.17×10^{-2}	0.580	0.301	1.61×10^{-5}	1.17×10^{-2}	1.50×10^{-5}	7.95×10^{1}
6	3.05×10^{-5}	1.42×10^{-2}	0.570	0.271	1.45×10^{-5}	1.42×10^{-2}	1.60×10^{-5}	7.77×10^{1}
7	3.00×10^{-5}	1.66×10^{-2}	0.560	0.249	1.33×10^{-5}	1.66×10^{-2}	1.66×10^{-5}	7.51×10^{1}
8	2.94×10^{-5}	1.90×10^{-2}	0.550	0.231	1.24×10^{-5}	1.90×10^{-2}	1.71×10^{-5}	7.28×10^{1}

$$\underline{K = (8.18 \pm 0.49) \times 10^{1}\ \mathrm{L\ mol^{-1}}}$$

Table 70: Equilibrium constant for the reaction of **2-K** with **3m** (20 °C, at 393 nm)

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	*K*
0	2.99×10^{-5}	-	0.549	-	2.99×10^{-5}	-	-	-
1	2.94×10^{-5}	1.83×10^{-3}	0.540	0.501	2.73×10^{-5}	1.83×10^{-3}	2.13×10^{-6}	4.27×10^{1}
2	2.90×10^{-5}	3.61×10^{-3}	0.532	0.460	2.51×10^{-5}	3.60×10^{-3}	3.90×10^{-6}	4.32×10^{1}
3	2.85×10^{-5}	5.33×10^{-3}	0.523	0.427	2.33×10^{-5}	5.32×10^{-3}	5.25×10^{-6}	4.24×10^{1}
4	2.81×10^{-5}	6.99×10^{-3}	0.515	0.400	2.18×10^{-5}	6.99×10^{-3}	6.28×10^{-6}	4.13×10^{1}
5	2.75×10^{-5}	9.01×10^{-3}	0.506	0.369	2.01×10^{-5}	9.00×10^{-3}	7.44×10^{-6}	4.11×10^{1}
6	2.70×10^{-5}	1.09×10^{-2}	0.496	0.344	1.87×10^{-5}	1.09×10^{-2}	8.29×10^{-6}	4.05×10^{1}
7	2.65×10^{-5}	1.28×10^{-2}	0.487	0.322	1.75×10^{-5}	1.28×10^{-2}	9.00×10^{-6}	4.01×10^{1}
8	2.61×10^{-5}	1.46×10^{-2}	0.479	0.302	1.64×10^{-5}	1.46×10^{-2}	9.62×10^{-6}	4.00×10^{1}
0	3.97×10^{-5}	-	0.692	-	3.97×10^{-5}	-	-	-
1	3.89×10^{-5}	3.01×10^{-3}	0.678	0.592	3.40×10^{-5}	3.01×10^{-3}	4.95×10^{-6}	4.85×10^{1}
2	3.82×10^{-5}	5.90×10^{-3}	0.665	0.523	3.00×10^{-5}	5.89×10^{-3}	8.14×10^{-6}	4.60×10^{1}
3	3.74×10^{-5}	8.68×10^{-3}	0.652	0.471	2.70×10^{-5}	8.67×10^{-3}	1.04×10^{-5}	4.44×10^{1}
4	3.67×10^{-5}	1.14×10^{-2}	0.640	0.426	2.44×10^{-5}	1.13×10^{-3}	1.23×10^{-5}	4.42×10^{1}
5	3.60×10^{-5}	1.39×10^{-2}	0.628	0.391	2.24×10^{-5}	1.39×10^{-3}	1.36×10^{-5}	4.35×10^{1}
6	3.54×10^{-5}	1.64×10^{-2}	0.617	0.365	2.09×10^{-5}	1.64×10^{-2}	1.44×10^{-5}	4.20×10^{1}
7	3.48×10^{-5}	1.88×10^{-2}	0.606	0.340	1.95×10^{-5}	1.88×10^{-2}	1.52×10^{-5}	4.16×10^{1}
8	3.41×10^{-5}	2.11×10^{-2}	0.595	0.319	1.83×10^{-5}	2.11×10^{-2}	1.58×10^{-5}	4.10×10^{1}

$K = (4.27 \pm 0.23) \times 10^{1}$ L mol^{-1}

Table 71: Equilibrium constant for the reaction of **2-K** with **7a** (20 °C, at 525 nm)

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	*K*
0	2.68×10^{-5}	-	1.204	-	2.68×10^{-5}	-	-	-
1	2.66×10^{-5}	3.61×10^{-4}	1.198	0.732	1.63×10^{-5}	3.51×10^{-4}	1.04×10^{-5}	1.82×10^{3}
2	2.65×10^{-5}	7.18×10^{-4}	1.192	0.516	1.15×10^{-5}	7.03×10^{-4}	1.50×10^{-5}	1.86×10^{3}
3	2.64×10^{-5}	1.07×10^{-3}	1.187	0.401	8.92×10^{-6}	1.05×10^{-3}	1.75×10^{-5}	1.86×10^{3}
4	2.63×10^{-5}	1.42×10^{-3}	1.181	0.323	7.18×10^{-6}	1.40×10^{-3}	1.91×10^{-5}	1.89×10^{3}
5	2.61×10^{-5}	1.77×10^{-3}	1.175	0.277	6.16×10^{-6}	1.75×10^{-3}	2.00×10^{-5}	1.85×10^{3}
6	2.60×10^{-5}	2.11×10^{-3}	1.170	0.239	5.32×10^{-6}	2.09×10^{-3}	2.07×10^{-5}	1.86×10^{3}
7	2.59×10^{-5}	2.45×10^{-3}	1.164	0.209	4.65×10^{-6}	2.43×10^{-3}	2.12×10^{-5}	1.88×10^{3}
8	2.58×10^{-5}	2.79×10^{-3}	1.159	0.188	4.18×10^{-6}	2.77×10^{-3}	2.16×10^{-5}	1.86×10^{3}

Table 71: Continued

No.	$[E]_0$ / molL^{-1}	$[Nu]_0$ / molL^{-1}	A_0	A_{eq}	$[E]_{eq}$ / molL^{-1}	$[Nu]_{eq}$ / molL^{-1}	$[E\text{-}Nu]_{eq}$ / molL^{-1}	K
0	2.65×10^{-5}	-	1.198	-	2.65×10^{-5}	-	-	-
1	2.64×10^{-5}	5.35×10^{-4}	1.189	0.606	1.34×10^{-5}	5.22×10^{-4}	1.29×10^{-5}	1.84×10^{3}
2	2.62×10^{-5}	1.06×10^{-3}	1.181	0.404	8.95×10^{-6}	1.05×10^{-3}	1.72×10^{-5}	1.84×10^{3}
3	2.60×10^{-5}	1.58×10^{-3}	1.172	0.306	6.78×10^{-6}	1.56×10^{-3}	1.92×10^{-5}	1.81×10^{3}
4	2.58×10^{-5}	2.10×10^{-3}	1.164	0.246	5.45×10^{-6}	2.08×10^{-3}	2.03×10^{-5}	1.80×10^{3}
5	2.56×10^{-5}	2.60×10^{-3}	1.156	0.207	4.59×10^{-6}	2.58×10^{-3}	2.10×10^{-5}	1.78×10^{3}
6	2.54×10^{-5}	3.10×10^{-3}	1.148	0.179	3.97×10^{-6}	3.08×10^{-3}	2.15×10^{-5}	1.76×10^{3}
7	2.53×10^{-5}	3.59×10^{-3}	1.140	0.157	3.48×10^{-6}	3.57×10^{-3}	2.18×10^{-5}	1.75×10^{3}
8	2.51×10^{-5}	4.08×10^{-3}	1.132	0.141	3.12×10^{-6}	4.05×10^{-3}	2.20×10^{-5}	1.73×10^{3}
9	2.49×10^{-5}	4.56×10^{-3}	1.124	0.128	2.84×10^{-6}	4.53×10^{-3}	2.21×10^{-5}	1.72×10^{3}

$K = (1.82 \pm 0.05) \times 10^3$ L mol^{-1}

6 Quantum Chemical Calculations

6.1 General

Free energies G_{298} were calculated at MP2/6-311+G(2d,p) or B3LYP/6-31+G(d,p) level of theory. Thermal corrections to 298.15 K have been calculated using unscaled harmonic vibrational frequencies. All calculations were performed with Gaussian 03.[6]

6.2 Archive Entries for Geometry Optimization at MP2/6-311+G(2d,p)

2-Pyridone-Anion

```
1\1\GINC-NODE24\FOpt\RMP2-FC\6-311+G(2d,p)\C5H4N1O1(1-)\MAY04\19-Mar-2
010\0\\#p opt freq mp2/6-311+g(2d,p)\\Pyridon-Anion\\-1,1\C,-0.5078159
22,0.3174712691,-0.00033035\C,0.5557416285,1.3019612731,0.0000758494\C
,1.8879337699,0.9384730937,0.0003572117\C,2.2306011548,-0.4240841715,0
.0002423715\C,1.1721886819,-1.3323685826,-0.0001599317\H,0.2611295773,
2.3488173802,0.0001506027\H,2.6622721506,1.7058380009,0.000664958\H,3.
2614385647,-0.765713842,0.0004488693\H,1.3968516613,-2.4029447266,-0.0
002590387\N,-0.1308382566,-1.0235221694,-0.0004400782\O,-1.7220580103,
0.653721475,-0.000637464\\Version=AM64L-G03RevD.01\State=1-A\HF=-321.0
809963\MP2=-322.2072908\RMSD=7.440e-09\RMSF=9.657e-06\Thermal=0.\Dipol
e=2.1998222,0.2395337,0.0006167\PG=C01 [X(C5H4N1O1)]\\@
```

N-Methyl-2-Pyridone

```
1\1\GINC-NODE25\FOpt\RMP2-FC\6-311+G(2d,p)\C6H7N1O1\MAY04\20-Mar-2010\
0\\#p MP2/6-311+g(2d,p) Opt Freq\\N-Methylpyridon\\0,1\C,0.4057042647,
0.8927231118,-0.0097223337\C,-0.9900639327,1.2563002782,-0.0274225168\
C,-1.9878478387,0.3184624305,-0.014843361\C,-1.6747527429,-1.061987863
7,0.0164352824\C,-0.3571664832,-1.4274481577,0.0335783167\H,-1.2053292
752,2.3184265347,-0.0513445123\H,-3.0257327306,0.6376768849,-0.0290276
898\H,-2.4412077624,-1.8257230348,0.0269661245\H,-0.0369310245,-2.4630
679501,0.0575976998\N,0.6380935621,-0.4978044423,0.0211569405\O,1.3641
266144,1.6723740322,-0.0192033424\C,2.0420860226,-0.897869622,0.039681
1555\H,2.5442466637,-0.5103071861,-0.8465886383\H,2.5314640794,-0.4736
439197,0.916257822\H,2.0970315835,-1.9847230959,0.0626750529\\Version=
AM64L-G03RevD.01\State=1-A\HF=-360.6950389\MP2=-361.9672936\RMSD=5.332
e-09\RMSF=3.466e-06\Thermal=0.\Dipole=-0.5957751,-1.4773101,0.0267229\
PG=C01 [X(C6H7N1O1)]\\@
```

N-Ethyl-2-Pyridone

```
1\1\GINC-NODE13\FOpt\RMP2-FC\6-311+G(2d,p)\C7H9N1O1\MAY04\08-Sep-2010\
0\\#p opt freq mp2/6-311+g(2d,p)\\N-Ethyl-2-pyridon\\0,1\C,-0.77066456
12,-1.092548964,0.1624416081\C,-2.2061822191,-0.9519756332,0.139354929
4\C,-2.8206634165,0.2625871743,-0.0122704131\C,-2.0511077713,1.4433528
```

949,-0.1442513239\C,-0.6883892546,1.3330613316,-0.1136135013\H,-2.7745
978039,-1.8692995531,0.2426788149\H,-3.9051097122,0.3180506544,-0.0292
722322\H,-2.507201174,2.417736145,-0.2609788287\H,-0.0290499565,2.1898
509719,-0.2035088584\N,-0.0723428211,0.1278353743,0.0386185201\O,-0.14
86943521,-2.1546920751,0.2771612234\C,1.3912166557,0.0454089997,0.0306
257602\C,1.9136238081,-0.3525144101,-1.3417499248\H,3.0037741829,-0.41
64174468,-1.3234462775\H,1.5134386964,-1.3269810495,-1.6218337985\H,1.
6227187453,0.3837382222,-2.0942192441\H,1.6746822448,-0.6967604225,0.7
772081603\H,1.7729917193,1.0211795161,0.3369039061\\Version=AM64L-G03R
evD.01\State=1-A\HF=-399.7425449\MP2=-401.1740124\RMSD=3.199e-09\RMSF=
1.340e-05\Thermal=0.\Dipole=-0.0106398,1.5237767,-0.2324537\PG=C01 [X(
C7H9N1O1)]\\@

N-iso-Propyl-2-Pyridone

1\1\GINC-NODE20\FOpt\RMP2-FC\6-311+G(2d,p)\C8H11N1O1\MAY04\08-Sep-2010
\0\\#p MP2/6-311+G(2d,p) opt freq\\N-iso-Propyl-2-pyridon\\0,1\C,-0.70
64654594,-1.0170065077,0.2679255994\C,-2.1444943698,-0.9239353899,0.31
85232149\C,-2.8151457833,0.2354438611,0.0340494306\C,-2.0984952845,1.4
052699806,-0.3095218782\C,-0.7315963018,1.3468479594,-0.3342611252\H,-
2.6680363165,-1.836659348,0.5796534286\H,-3.9003137435,0.2538009506,0.
0727254421\H,-2.5962659785,2.3370110126,-0.5450876311\H,-0.1264534868,
2.2089281253,-0.5832844468\N,-0.0559284657,0.2017622933,-0.0393368294\
O,-0.0483292669,-2.0448993026,0.4669460571\C,1.4186504317,0.1405235534
,-0.1146498151\C,1.8322544693,-0.3070009587,-1.511177378\H,2.917976988
7,-0.4178316367,-1.564826364\H,1.3735646101,-1.2669096239,-1.751863712
4\H,1.5232877862,0.434299967,-2.2539001081\C,2.0768465361,1.4484987573
,0.2973496157\H,1.9631358105,2.230239793,-0.4572514152\H,1.6809230314,
1.8130031974,1.2476555342\H,3.1472284595,1.2710670708,0.4197173815\H,1
.6888013732,-0.6407011543,0.5977011693\\Version=AM64L-G03RevD.01\State
=1-A\HF=-438.785751\MP2=-440.3797554\RMSD=6.687e-09\RMSF=2.027e-05\The
rmal=0.\Dipole=0.0247395,1.4954189,-0.3629996\PG=C01 [X(C8H11N1O1)]\\@

N-tert-Butyl-2-Pyridone

1\1\GINC-NODE9\FOpt\RMP2-FC\6-311+G(2d,p)\C9H13N1O1\MAY04\24-Jul-2010\
0\\#p MP2/6-311+g(2d,p) opt freq\\N-Tert-butyl-2-pyridon\\0,1\C,0.4445
232792,0.9250113362,-0.0021139613\C,-0.9210343962,1.3911232793,-0.0026
021764\C,-1.9969214628,0.5480397551,-0.002574695\C,-1.7820074969,-0.84
72741564,-0.0017057753\C,-0.4958559327,-1.313813622,-0.0005979611\H,-1
.0376604666,2.4690575806,-0.0033120205\H,-3.0054101953,0.9507793063,-0
.0031836423\H,-2.5984758582,-1.5580160798,-0.0018215299\H,-0.298488853
2,-2.3740479203,0.0002658805\N,0.5947006387,-0.4883232924,-0.000376271
6\O,1.4222255313,1.6828901049,-0.0029896347\C,1.9892017157,-1.05264330
33,0.000995329\C,2.7072885555,-0.5887189913,1.2709792598\H,3.709748163
5,-1.0241945722,1.2895640698\H,2.7911453367,0.4948100359,1.3069636996\
H,2.1661954802,-0.9383356389,2.1546972279\C,2.7082682663,-0.5927320927
,-1.2698734005\H,2.7922745592,0.4906792833,-1.3090827086\H,3.710645789

3,-1.0284700578,-1.2864771508\H,2.1676961865,-0.9448843522,-2.15291974
05\C,1.9683424822,-2.5802478203,0.003506451\H,1.4900422285,-2.99057358
04,0.8959254389\H,1.4916012798,-2.9935963933,-0.8883496653\H,3.0077118
493,-2.9139807083,0.0049529811\\Version=AM64L-G03RevD.01\State=1-A\HF=
-477.8210652\MP2=-479.5818994\RMSD=8.455e-09\RMSF=5.176e-06\Thermal=0.
\Dipole=-0.485659,-1.4006597,0.0016584\PG=C01 [X(C9H13N1O1)]\\@

N-Acetyl-2-Pyridone

1\1\GINC-NODE25\FOpt\RMP2-FC\6-311+G(2d,p)\C7H7N1O2\MAY04\24-Jun-2010\
0\\#p MP2/6-311+g(2d,p) opt=tight freq\\N-Acetyl-2-pyridon - Geometrie
1-\\0,1\C,-0.5133914903,0.7639683195,-0.57851882\C,-1.9536163318,0.62
77209746,-0.4828828209\C,-2.5561682521,-0.4705644437,0.0498525861\C,-1
.7661750927,-1.5568448486,0.5219099657\C,-0.415527078,-1.4847849845,0.
4118014894\H,-2.5204865813,1.4795204457,-0.8407148439\H,-3.6390160368,
-0.5153896597,0.1159723187\H,-2.2141389522,-2.4416054983,0.9553841585\
H,0.2565777393,-2.2666346128,0.7384382023\N,0.2133957181,-0.3869142946
,-0.1487116656\O,0.0476763611,1.7820360246,-0.9760680277\C,1.663489559
1,-0.4789903309,-0.2407946429\O,2.2268088617,-1.3533517719,0.381197459
6\C,2.3894501968,0.4724643798,-1.1421060036\H,1.870459085,0.6028885759
,-2.0904278156\H,2.4479343845,1.4571225893,-0.679049751\H,3.3876530596
,0.0625188157,-1.2883171789\\Version=AM64L-G03RevD.01\State=1-A\HF=-47
3.4690243\MP2=-475.082377\RMSD=8.174e-09\RMSF=8.470e-08\Thermal=0.\Dip
ole=-0.8273705,-0.5630999,-0.0310119\PG=C01 [X(C7H7N1O2)]\\@

Transition State: Methyl-Transfer *N*-Methyl-2-Pyridone to 2-Pyridone (*N*-attack)

1\1\GINC-NODE10\FTS\RMP2-FC\6-311+G(2d,p)\C11H11N2O2(1-)\MAY04\30-Mar-
2010\0\\#P GEOM=ALLCHECK GUESS=READ SCRF=CHECK MP2/6-311+G(2d,p) opt=(
readfc,ts,noeigentest) freq\\Methyl Transfer N->N\\-1,1\C,2.6701033499
,-1.0402261676,0.0774184025\C,4.1075133446,-0.8891697153,0.0767767274\
C,4.7068714587,0.3509494463,0.0345365808\C,3.9158128714,1.515710358,-0
.0095339829\C,2.5423769284,1.3441997586,-0.0078740231\H,4.6980963664,-
1.8002895588,0.1111997258\H,5.7927192489,0.4262071165,0.0354038208\H,4
.3489672073,2.509130552,-0.0434760867\H,1.8697589412,2.2025298228,-0.0
40586723\N,1.9443025248,0.1446209976,0.0328429029\O,2.0835392227,-2.14
80406587,0.1149091673\C,-0.0066647318,0.0232704345,0.0310589668\H,0.03
65231346,-0.5553812433,-0.8755339064\H,0.0320518344,-0.5029516124,0.96
92452191\H,-0.0903122061,1.098080399,-0.0001819256\N,-1.9465779877,-0.
0924663577,0.0296055125\C,-2.4986187633,-1.3145867048,0.0692869483\C,-
2.7145985774,1.0655331644,-0.0115923211\C,-3.8641223816,-1.537054536,0
.0729690928\H,-1.7907765587,-2.1442519085,0.0992363315\C,-4.1452514205
,0.8591325437,-0.0085430279\C,-4.6980471464,-0.4022156778,0.0324163663
\H,-4.2599334656,-2.545908326,0.1058868378\H,-4.7693481113,1.747690114
,-0.040187401\H,-5.7803314846,-0.5174533951,0.0333121724\O,-2.17456559
81,2.1970061548,-0.0483143773\\Version=AM64L-G03RevD.01\State=1-A\HF=-
681.7293888\MP2=-684.1487151\RMSD=8.258e-09\RMSF=2.229e-06\Thermal=0.\
Dipole=-0.0044181,-0.0463367,-0.0011731\PG=C01 [X(C11H11N2O2)]\\@

<u>*O*-Methyl-2-Pyridone</u>

1\1\GINC-NODE25\FOpt\RMP2-FC\6-311+G(2d,p)\C6H7N1O1\MAY04\19-Mar-2010\
0\\#p MP2/6-311+g(2d,p) Opt Freq\\2-Methoxypyridin - Geometrie 1\\0,1\
C,-0.4275608987,0.2982722807,0.0001742738\C,0.5419376236,1.3130012732,
0.0000958739\C,1.8742254402,0.9369074348,0.0000689395\C,2.1973489502,-
0.4254778067,0.0001375677\C,1.1600840073,-1.3460311302,0.0002286999\H,
0.2306355748,2.3514355012,0.0000634895\H,2.6535570014,1.6923098682,0.0
000129719\H,3.227867371,-0.7617818472,0.0001182275\H,1.3621990817,-2.4
135007477,0.0002943575\N,-0.1436057782,-0.9988134401,0.0002408514\O,-1
.7218766096,0.6986134149,0.0001507805\C,-2.6976406062,-0.3510944388,0.
0005784017\H,-3.6591905904,0.1569021786,0.0008486734\H,-2.594610704,-0
.9765714367,-0.8866673556\H,-2.594013863,-0.9764101042,0.8878662475\\V
ersion=AM64L-G03RevD.01\State=1-A\HF=-360.6887837\MP2=-361.954828\RMSD
=5.305e-09\RMSF=5.931e-05\Thermal=0.\Dipole=0.3068339,0.0859297,0.0001
569\PG=C01 [X(C6H7N1O1)]\\@

<u>*O*-Ethyl-2-Pyridone</u>

1\1\GINC-NODE9\FOpt\RMP2-FC\6-311+G(2d,p)\C7H9N1O1\MAY04\08-Sep-2010\0
\\#p opt freq mp2/6-311+g(2d,p)\\O-Ethyl-2-pyridon\\0,1\C,-0.564329492
8,0.3962877981,-0.005722908\C,-1.5762592955,1.3649083647,-0.0954721112
\C,-2.8926004951,0.9387446198,-0.0440159004\C,-3.1606814889,-0.4282914
678,0.0934152637\C,-2.0861312492,-1.3018698636,0.1717315062\H,-1.30743
05756,2.4100744397,-0.1988842792\H,-3.701441109,1.6595654727,-0.109321
286\H,-4.1764360541,-0.8043976893,0.1366815855\H,-2.2447529149,-2.3716
221252,0.277051229\N,-0.7977107913,-0.9057752728,0.121640453\O,0.71018
53211,0.8560922104,-0.0427997899\C,1.7601327029,-0.1314669649,-0.00450
19506\C,1.9759041339,-0.765541837,-1.3634733894\H,2.8273751667,-1.4495
58446,-1.3194878851\H,1.0950729639,-1.3300377877,-1.6681683165\H,2.186
8386498,0.001322022,-2.110867759\H,1.5249390415,-0.8819034994,0.751390
9214\H,2.6378302865,0.4340005163,0.3091864266\\Version=AM64L-G03RevD.0
1\State=1-A\HF=-399.7368783\MP2=-401.1614286\RMSD=9.361e-09\RMSF=1.310
e-05\Thermal=0.\Dipole=-0.2770722,0.0398121,-0.0642896\PG=C01 [X(C7H9N
1O1)]\\@

<u>*O*-*iso*-Propyl-2-Pyridone</u>

1\1\GINC-NODE15\FOpt\RMP2-FC\6-311+G(2d,p)\C8H11N1O1\MAY04\08-Sep-2010
\0\\#p MP2/6-311+G(2d,p) opt freq\\O-iso-Propyl-2-pyridon\\0,1\C,-0.56
73827751,0.4449765878,-0.0853266435\C,-1.617923514,1.3683602427,-0.207
5053011\C,-2.9148356064,0.9040979917,-0.0680362966\C,-3.127035726,-0.4
559900994,0.186009687\C,-2.0186441326,-1.2838783042,0.2865248188\H,-1.
3919103988,2.4104751752,-0.4033966081\H,-3.7514146831,1.5901410946,-0.
1553709696\H,-4.1257983232,-0.8614765681,0.3008438707\H,-2.1337759799,
-2.3467304412,0.4810184372\N,-0.7483004821,-0.8506534661,0.1525562719\
O,0.6856220852,0.9462223549,-0.2085682945\C,1.7899846747,0.0091594444,
-0.1510093261\C,1.9281002437,-0.7067191287,-1.4814306853\H,2.774170959
6,-1.3978536995,-1.4463582323\H,1.0275244448,-1.2765738792,-1.70995955

86\H,2.105371463,0.0203055594,-2.2778626293\C,3.0031752142,0.848144209
,0.1904604953\H,3.8883229246,0.2120850117,0.2600084781\H,3.1743221626,
1.598319433,-0.5848306175\H,2.8632807074,1.3583620806,1.1444864898\H,1
.5829808814,-0.7119091486,0.6429654137\\Version=AM64L-G03RevD.01\State
=1-A\HF=-438.7865398\MP2=-440.370898\RMSD=5.268e-09\RMSF=3.285e-06\The
rmal=0.\Dipole=-0.2422936,0.0518936,-0.0286164\PG=C01 [X(C8H11N1O1)]\\
@

O-tert-Butyl-2-Pyridone

1\1\GINC-NODE26\FOpt\RMP2-FC\6-311+G(2d,p)\C9H13N1O1\MAY04\24-Jul-2010
\0\\#p MP2/6-311+g(2d,p) opt freq\\O-Tert-butyl-2-pyridon\\0,1\C,0.339
7866894,-0.1847144374,0.0000038959\C,-0.5782525486,-1.2494489021,-0.00
07218817\C,-1.9303774846,-0.9530381245,-0.0016057475\C,-2.3319491556,0
.38763019,-0.0017836896\C,-1.3466210816,1.3635059847,-0.001088221\H,-0
.2087457685,-2.2687018307,-0.0005754492\H,-2.6635442382,-1.7534795675,
-0.0021642713\H,-3.3796108626,0.666139115,-0.00245185\H,-1.6094911785,
2.4180629093,-0.0012239491\N,-0.0244146832,1.0946873203,-0.0001983235\
O,1.6429855206,-0.5515144335,0.0008801002\C,2.7298947301,0.4265223181,
0.0011443448\C,2.6987471719,1.2722792021,1.2676491321\H,3.6211196286,1
.8564715116,1.3281203161\H,1.8495680386,1.9528182784,1.2726850319\H,2.
6452858526,0.624887617,2.1466011564\C,2.7000723211,1.2712637925,-1.266
0664812\H,3.622406944,1.8555613273,-1.3260063818\H,2.6476554667,0.6231
703106,-2.1445647654\H,1.8508187453,1.9517115132,-1.2725479086\C,3.958
0904239,-0.4718399054,0.0022258344\H,4.8650360313,0.1366028407,0.00260
17139\H,3.9608982487,-1.10856897,0.8892285136\H,3.9619920087,-1.109103
1298,-0.8843859494\\Version=AM64L-G03RevD.01\State=1-A\HF=-477.8275661
\MP2=-479.5763112\RMSD=9.082e-09\RMSF=6.639e-06\Thermal=0.\Dipole=-0.1
946945,-0.0903042,-0.0003887\PG=C01 [X(C9H13N1O1)]\\@

O-Acetyl-2-Pyridone

1\1\GINC-NODE24\FOpt\RMP2-FC\6-311+G(2d,p)\C7H7N1O2\MAY04\18-Jun-2010\
0\\#p MP2/6-311+g(2d,p) opt freq\\O-Acetyl-2-pyridon - Geometrie 1-\\0
,1\C,1.647985794,-1.2669664601,-1.3127617101\C,0.3537751168,-1.7693772
196,-1.2362986901\C,-0.2461576145,-2.181427283,-2.4220140688\C,0.47336
97601,-2.0674758579,-3.6113104561\C,1.7652834569,-1.5495649026,-3.5627
171031\H,-0.1518212316,-1.8274276683,-0.2793822871\H,-1.2555862411,-2.
5793181621,-2.4170365028\H,0.0451895211,-2.3741074884,-4.5591347729\H,
2.3587154459,-1.4469636157,-4.4664975822\N,2.3580461287,-1.1516307451,
-2.4235326032\O,2.2917139243,-0.900913669,-0.1316612601\C,2.3048002412
,0.4543059287,0.1179331216\O,1.7023434613,1.2536650822,-0.5532847804\C
,3.1568375585,0.7447868675,1.3171692116\H,2.8699090489,0.0987072543,2.
1471275756\H,4.1982566921,0.5306306924,1.0706236323\H,3.0493402174,1.7
910479766,1.5923838359\\Version=AM64L-G03RevD.01\State=1-A\HF=-473.475
4351\MP2=-475.0856131\RMSD=4.448e-09\RMSF=1.725e-05\Thermal=0.\Dipole=
-0.4933718,-0.706197,0.2268334\PG=C01 [X(C7H7N1O2)]\\@

Transition State: Methyl-Transfer *O*-Methyl-2-Pyridone to 2-Pyridone (*O*-attack)

1\1\GINC-NODE13\FTS\RMP2-FC\6-311+G(2d,p)\C11H11N2O2(1-)\MAY04\02-Apr-
2010\0\\#P GEOM=ALLCHECK GUESS=READ SCRF=CHECK MP2/6-311+G(2d,p) opt=(
readfc,ts,noeigentest) freq\\Methyl Transfer O->O\\-1,1\C,0.0360817534
,-0.6878947508,-0.3715986698\C,-1.1058387781,-1.5482604313,-0.38556646
91\C,-2.3030985411,-1.1317518768,0.1643492325\C,-2.3856988274,0.146180
3082,0.7371913115\C,-1.2362722681,0.92731036,0.7151459874\H,-0.9979905
06,-2.5295331715,-0.8378047888\H,-3.1679959772,-1.7918905168,0.1508679
799\H,-3.3020926573,0.5196367144,1.1825368506\H,-1.2536543791,1.927354
7803,1.1495382981\N,-0.0589533929,0.551302666,0.1884733868\O,1.1475460
945,-1.0940859063,-0.892735817\C,2.6412641901,0.1086748432,-0.83657011
99\H,3.1914069302,-0.6581332693,-1.3485968688\H,2.0940415927,0.8570106
467,-1.3782013542\H,2.6383301889,0.1275221707,0.2368774627\O,4.1354050
205,1.3088139509,-0.9267136206\C,5.2440889729,0.9210622026,-0.38596419
68\C,6.3861773995,1.7804880011,-0.4239034502\C,7.580504173,1.383427263
7,0.1463870214\H,6.2807990009,2.7454384313,-0.9105382608\C,6.510568126
1,-0.6552855209,0.7629242675\C,7.6599621909,0.1261935158,0.7637553343\
H,8.4455445772,2.0427431446,0.1144493687\H,6.5255582253,-1.6396079186,
1.2319361003\H,8.5739805424,-0.2314965028,1.2265821107\N,5.3360483888,
-0.2978892943,0.2173692138\\Version=AM64L-G03RevD.01\State=1-A\HF=-681
.7317594\MP2=-684.1399159\RMSD=3.422e-09\RMSF=2.499e-06\Thermal=0.\Dip
ole=-0.0010445,0.0073131,0.4202548\PG=C01 [X(C11H11N2O2)]\\@

4-Pyridone-Anion

1\1\GINC-NODE10\FOpt\RMP2-FC\6-311+G(2d,p)\C5H4N1O1(1-)\MAY04\21-Mar-2
010\0\\#p opt freq mp2/6-311+g(2d,p)\\4-Pyridon-Anion\\-1,1\C,0.008894
5736,0.0174432153,0.0000285182\C,1.3955278289,0.0090319809,-0.00014185
56\C,2.1600894272,1.2296653974,-0.0008636546\C,1.3086297644,2.39134998
99,-0.0004708493\C,-0.0737069639,2.2819328864,-0.0002744718\N,-0.77201
04936,1.122710646,-0.0001640815\H,-0.5277291084,-0.9333671668,0.000295
3427\H,1.9325521743,-0.9377558724,0.0001833321\H,1.7752409857,3.374750
538,-0.0004184283\H,-0.6781756463,3.191121406,-0.000275753\O,3.4288604
681,1.2759433892,-0.0003729288\\Version=AM64L-G03RevD.01\State=1-A\HF=
-321.0857162\MP2=-322.211157\RMSD=3.336e-09\RMSF=4.134e-05\Thermal=0.\
Dipole=-0.8817997,-0.0321658,0.0000995\PG=C01 [X(C5H4N1O1)]\\@

N-Methyl-2-Pyridone

1\1\GINC-NODE24\FOpt\RMP2-FC\6-311+G(2d,p)\C6H7N1O1\MAY04\21-Mar-2010\
0\\#p opt freq mp2/6-311+g(2d,p)\\N-Methyl-4-pyridon\\0,1\C,0.01852227
72,-0.0265303101,-0.0296568324\C,1.3811774245,-0.0139008173,0.00092464
94\C,2.1392181771,1.2288908081,0.0211153327\C,1.2926411258,2.413132408
7,0.0000542256\C,-0.0673115942,2.3264213478,-0.0305006948\N,-0.7192806
076,1.1245876721,-0.0549924357\H,-0.5538542071,-0.9481131114,-0.042473
6614\H,1.9212262214,-0.9540430415,0.0066652042\H,1.7627541983,3.390128
4307,0.0051072191\H,-0.7053143072,3.2038410199,-0.043962732\O,3.379585
4726,1.2741481539,0.0481598621\C,-2.17420616,1.0715404447,0.021239364\

H,-2.5295319421,0.1730802053,-0.4822873737\H,-2.5117441137,1.059599914
5,1.0602069901\H,-2.5940375187,1.9413621494,-0.4829215273\\Version=AM6
4L-G03RevD.01\State=1-A\HF=-360.6787482\MP2=-361.9488497\RMSD=9.022e-0
9\RMSF=2.653e-05\Thermal=0.\Dipole=-2.9584176,-0.1079333,-0.0349639\PG
=C01 [X(C6H7N1O1)]\\@

N-Acetyl-4-Pyridone

1\1\GINC-NODE22\FOpt\RMP2-FC\6-311+G(2d,p)\C7H7N1O2\MAY04\19-Jun-2010\
0\\#p MP2/6-311+g(2d,p) opt freq\\N-Acetyl-4-pyridon - Geometrie 1-\\0
,1\C,-0.6035425574,-1.1624685443,0.0051332053\C,0.7488931045,-1.219909
8737,-0.0291232643\C,1.5767688725,-0.0167252452,-0.0295366668\C,0.8037
561747,1.2217508854,0.0097184818\C,-0.5512302051,1.2206883744,0.043098
1289\N,-1.2822127999,0.0458843177,0.0417876\H,-1.2441158616,-2.0344851
658,0.006456392\H,1.2396269524,-2.1862601937,-0.057158275\H,1.33547936
15,2.1665457402,0.0121374658\H,-1.1201571129,2.1388730108,0.0722877635
\O,2.8124778296,-0.0415603908,-0.0602526025\C,-2.7071252254,0.02018777
66,0.0763633421\O,-3.2967896299,-1.0403013182,0.0733465941\C,-3.413679
4839,1.3506949695,0.1157282969\H,-4.4810904882,1.1443721181,0.13857536
82\H,-3.1372569203,1.9203358932,1.0048828268\H,-3.1808766007,1.9496599
56,-0.7666127869\\Version=AM64L-G03RevD.01\State=1-A\HF=-473.4609962\M
P2=-475.0733717\RMSD=4.510e-09\RMSF=1.127e-05\Thermal=0.\Dipole=-1.743
2342,1.0320723,0.059811\PG=C01 [X(C7H7N1O2)]\\@

Transition State: Methyl-Transfer *N*-Methyl-4-Pyridone 4-Pyridone (*N*-attack)

1\1\GINC-NODE25\FTS\RMP2-FC\6-311+G(2d,p)\C11H11N2O2(1-)\MAY04\06-Apr-
2010\0\\#P GEOM=ALLCHECK GUESS=READ SCRF=CHECK MP2/6-311+G(2d,p) opt=(
readfc,ts,noeigentest) freq\\4-Pyridon-Anion: Methyl Transfer N->N\\-1
,1\C,-0.9650618931,0.5038648693,-1.0368346282\C,0.4105287443,0.4935045
632,-1.1124869238\C,1.2261542096,-0.0167884541,-0.0312835854\C,0.43452
66802,-0.4915957252,1.0832608262\C,-0.9421922017,-0.4402786904,1.06531
5553\N,-1.6584142721,0.0513048587,0.0307627986\H,-1.5674424623,0.89026
90522,-1.859673823\H,0.907121334,0.8766194574,-1.9996266545\H,0.950205
1025,-0.8963288345,1.9496648113\H,-1.525998582,-0.8045012475,1.9113333
662\O,2.4831882921,-0.0441157413,-0.0573758474\C,-3.582793628,0.001379
7588,0.0233479302\H,-3.6013950614,0.9082583119,-0.5584706456\H,-3.5642
767107,-0.9557039286,-0.4715621524\H,-3.5827099037,0.0516532263,1.1014
79162\N,-5.5071712564,-0.0477007562,0.0356575958\C,-6.2233009575,0.538
4237381,1.0198065488\C,-6.2006336573,-0.5984179569,-0.9846977675\C,-7.
6000270932,0.5908889364,1.0331801963\H,-5.6394079545,0.9803926763,1.82
7869651\C,-7.576244338,-0.5954941163,-1.0606752786\H,-5.5983309145,-1.
0600492087,-1.7678730834\C,-8.3917706105,0.0136254756,-0.0318258895\H,
-8.1156260946,1.0748561768,1.8579969202\H,-8.0729252039,-1.0601164798,
-1.9079250243\O,-9.6488165873,0.0381127285,-0.060073316\\Version=AM64L
-G03RevD.01\State=1-A\HF=-681.717635\MP2=-684.1385766\RMSD=9.466e-09\R
MSF=5.508e-07\Thermal=0.\Dipole=0.0000329,0.0036456,0.0673108\PG=C01 [
X(C11H11N2O2)]\\@

O-Methyl-2-Pyridone

```
1\1\GINC-NODE10\FOpt\RMP2-FC\6-311+G(2d,p)\C6H7N1O1\MAY04\21-Mar-2010\
0\\#p opt freq mp2/6-311+g(2d,p)\\O-Methyl-4-pyridon\\0,1\C,-0.0933741
011,0.0293953075,-0.0007357738\C,1.3013950102,-0.0533111809,0.00859659
46\C,2.0318321042,1.1357102058,0.0101159073\C,1.3274926233,2.342486847
6,0.0022263485\C,-0.0599120183,2.3077397572,-0.0067887499\N,-0.7869089
668,1.1741413976,-0.0084190914\H,-0.6802537351,-0.885663756,-0.0020229
674\H,1.775535815,-1.0266307466,0.0142797926\H,1.8696404018,3.28203676
54,0.0032711176\H,-0.6239818692,3.2363773688,-0.0130066465\O,3.3876539
643,1.2223749368,0.0188220029\C,4.1041967,-0.0101251925,0.0275342111\H
,3.8824387415,-0.5990018338,-0.8663613487\H,5.1569376242,0.2607615583,
0.0343341949\H,3.8695643862,-0.5938209553,0.9215329181\\Version=AM64L-
G03RevD.01\State=1-A\HF=-360.6782949\MP2=-361.944965\RMSD=4.128e-09\RM
SF=3.106e-05\Thermal=0.\Dipole=1.189993,-0.550956,0.0096189\PG=C01 [X(
C6H7N1O1)]\\@
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O-Acetyl-4-Pyridone

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1\1\GINC-NODE13\FOpt\RMP2-FC\6-311+G(2d,p)\C7H7N1O2\MAY04\23-Jun-2010\
0\\#p MP2/6-311+g(2d,p) opt=readfc freq geom=Check Guess=Read SCRF=Che
ck\\O-Acetyl-4-pyridon - Geometrie 1-\\0,1\C,2.0450385794,1.1628633579
,0.9038691411\C,0.6734519395,0.9197171283,0.9624083915\C,0.2308400529,
-0.3518523871,0.6214786807\C,1.1480230491,-1.322176263,0.244445854\C,2
.4976876165,-0.9735488068,0.2252658278\N,2.9580888668,0.246042912,0.54
48036146\H,2.4301104955,2.1459911534,1.1595823088\H,-0.0192228857,1.69
7636516,1.2596076882\H,0.8154128765,-2.3198924451,-0.0200518299\H,3.24
4845637,-1.7083973986,-0.0611955836\O,-1.1061654938,-0.7263581816,0.71
90620758\C,-2.0276363933,0.0155400183,0.0071825787\O,-1.7329964688,0.9
440024152,-0.7010844068\C,-3.4037142838,-0.5278494053,0.2535744052\H,-
3.4485644097,-1.5692387958,-0.0680802248\H,-3.6241354347,-0.4995036115
,1.3214960342\H,-4.1287644033,0.0657879535,-0.2973925354\\Version=AM64
L-G03RevD.01\State=1-A\HF=-473.4689483\MP2=-475.0797218\RMSD=5.436e-09
\RMSF=3.443e-06\Thermal=0.\Dipole=-1.1275639,-0.6300417,0.3811495\PG=C
01 [X(C7H7N1O2)]\\@
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Transition State: Methyl-Transfer O-Methyl-4-Pyridone 4-Pyridone (O-attack)

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1\1\GINC-NODE13\FTS\RMP2-FC\6-311+G(2d,p)\C11H11N2O2(1-)\MAY04\24-Apr-
2010\0\\#P GEOM=ALLCHECK GUESS=READ SCRF=CHECK MP2/6-311+G(2d,p) opt=(
readfc,ts,noeigentest) freq\\4-Pyridon-Anion: Methyl Transfer O->O\\-1
,1\C,5.0452093062,-0.5686764755,-0.2125048035\C,3.9175009914,-1.127072
1445,0.3692375396\C,2.6721896882,-0.4455109158,0.3438776782\C,2.710166
2629,0.8124446171,-0.3145814098\C,3.9010936251,1.2778590157,-0.8646377
356\N,5.0787934885,0.6279518892,-0.8368444671\H,5.9893575021,-1.111177
3247,-0.1797411945\H,3.9694179579,-2.0974816026,0.8551139523\H,1.82102
6932,1.4271536391,-0.3992784102\H,3.9082080475,2.2454344381,-1.3652539
906\O,1.6162768578,-0.9766298118,0.895427877\C,-0.0000277877,-0.000571
5721,0.8447982118\H,-0.4338300834,-0.8230307842,1.3848171141\H,0.43377
```

52603,0.8212159045,1.3858373828\H,-0.0000247618,0.0000987828,-0.231258
5202\O,-1.6163348315,0.9754175752,0.896650133\C,-2.6722139557,0.445040
6547,0.3443215819\C,-3.9175152983,1.1265898181,0.3704769644\C,-2.71016
04407,-0.8120501603,-0.3157882751\C,-5.0451874552,0.5689768442,-0.2120
856257\H,-3.9694536727,2.0963624399,0.8576209473\C,-3.9010523844,-1.27
67222647,-0.8665483039\H,-1.8210254186,-1.4266639391,-0.4012185941\N,-
5.0787430873,-0.6268314271,-0.8379961496\H,-5.9893288281,1.1114507337,
-0.1786852845\H,-3.9081442697,-2.2436406867,-1.3684326742\\Version=AM6
4L-G03RevD.01\State=1-A\HF=-681.727558\MP2=-684.13997\RMSD=8.493e-09\R
MSF=2.468e-06\Thermal=0.\Dipole=-0.0000132,-0.0001495,0.2197337\PG=C01
X(C11H11N2O2)]\\@

N,*N*-Dimethylacetamide

1\1\GINC-NODE22\FOpt\RMP2-FC\6-311+G(2d,p)\C4H9N1O1\MAY04\30-Jul-2010\
0\\#P MP2/6-311+G(2d,p) opt=(calcfc,tight) freq\\N,N-Dimethylacetamide
\\0,1\C,0.721847793,-0.2915530156,0.0242399327\O,1.0624934946,-1.47073
30505,0.1072826699\N,-0.5906222902,0.0779214696,-0.1078906492\C,1.7547
383346,0.8188346118,0.0447611632\H,1.7184137358,1.4210395956,-0.865412
8897\H,1.6115305709,1.4831059963,0.8997972954\H,2.7314515527,0.3470928
421,0.1208334668\C,-1.6200748473,-0.9444474772,-0.0435792625\H,-2.1246
265798,-0.9298271558,0.9287208843\H,-2.362876731,-0.765322721,-0.82461
7924\H,-1.1577932544,-1.9172861803,-0.1894495653\C,-1.0659619281,1.445
1287937,-0.0331223466\H,-1.4651502327,1.6747239906,0.9620556139\H,-0.2
713198023,2.1496585158,-0.2614727629\H,-1.8675508157,1.589408785,-0.76
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14479,-0.0485465\PG=C01 [X(C4H9N1O1)]\\@

(*E*)-Methyl *N*-Methylacetimidate

1\1\GINC-NODE28\FOpt\RMP2-FC\6-311+G(2d,p)\C4H9N1O1\MAY04\31-Jul-2010\
0\\#p MP2/6-311+G(2d,p) opt=(calcfc) freq\\(E)-methyl N-methylacetimid
ate\\0,1\C,0.025242,0.324903,-0.002182\O,-1.31683,0.524673,-0.003458\N
,0.508092,-0.854207,-0.000636\C,0.773709,1.626335,0.000915\H,1.351711,
1.724995,0.923018\H,1.477766,1.659113,-0.833344\H,0.082162,2.46285,-0.
076853\C,1.962585,-0.969761,0.00075\H,2.231094,-2.021352,0.090808\H,2.
398147,-0.588978,-0.929704\H,2.422482,-0.42874,0.835258\C,-2.105374,-0
.67286,0.002417\H,-3.139017,-0.334896,0.002771\H,-1.893129,-1.274707,-
0.881527\H,-1.890192,-1.267927,0.890286\\Version=AM64L-G03RevD.01\Stat
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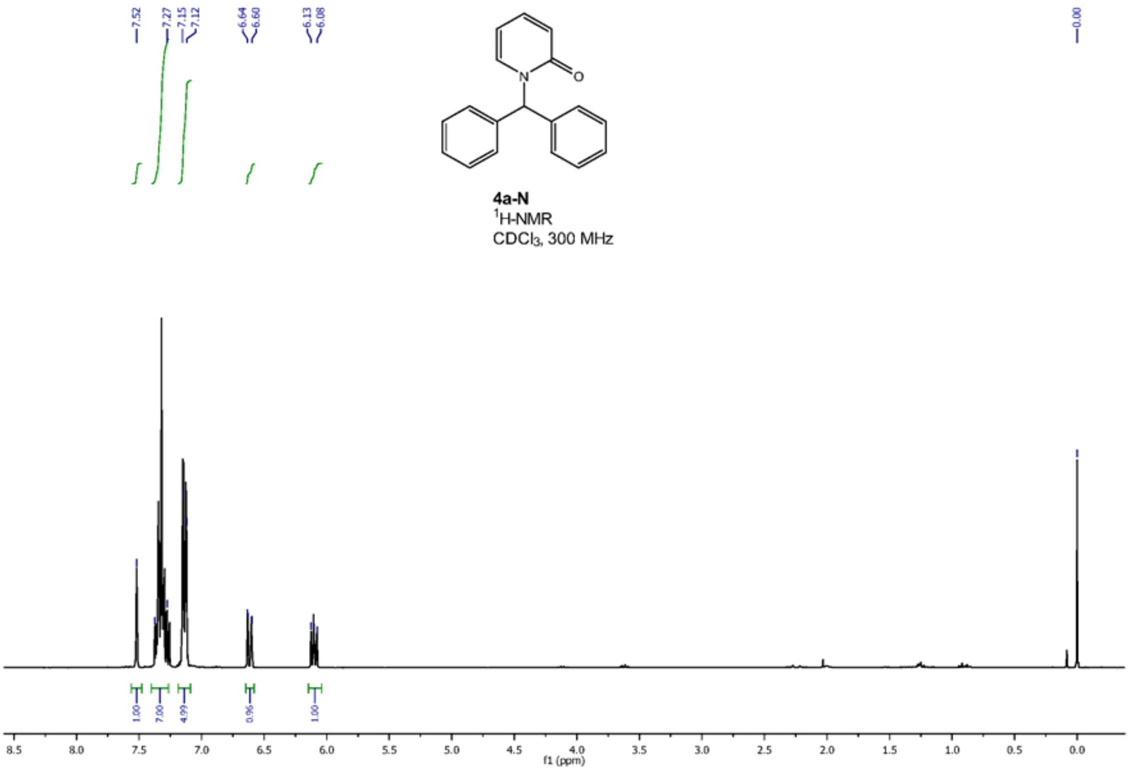
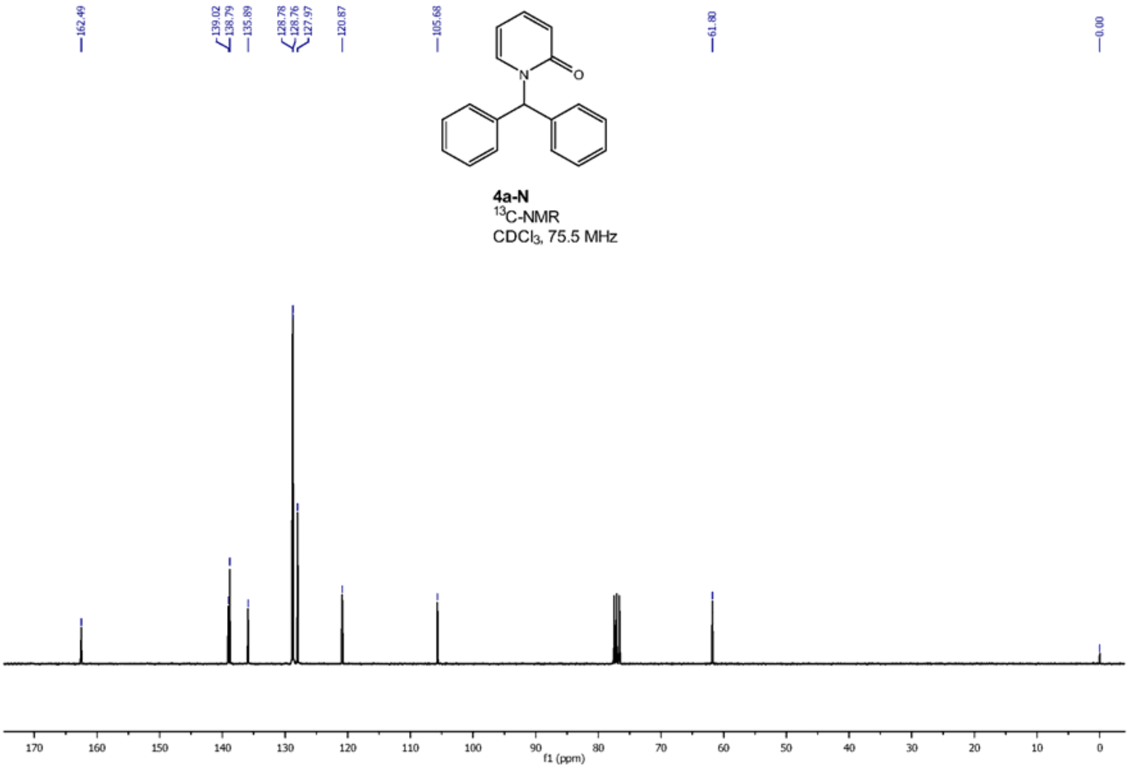
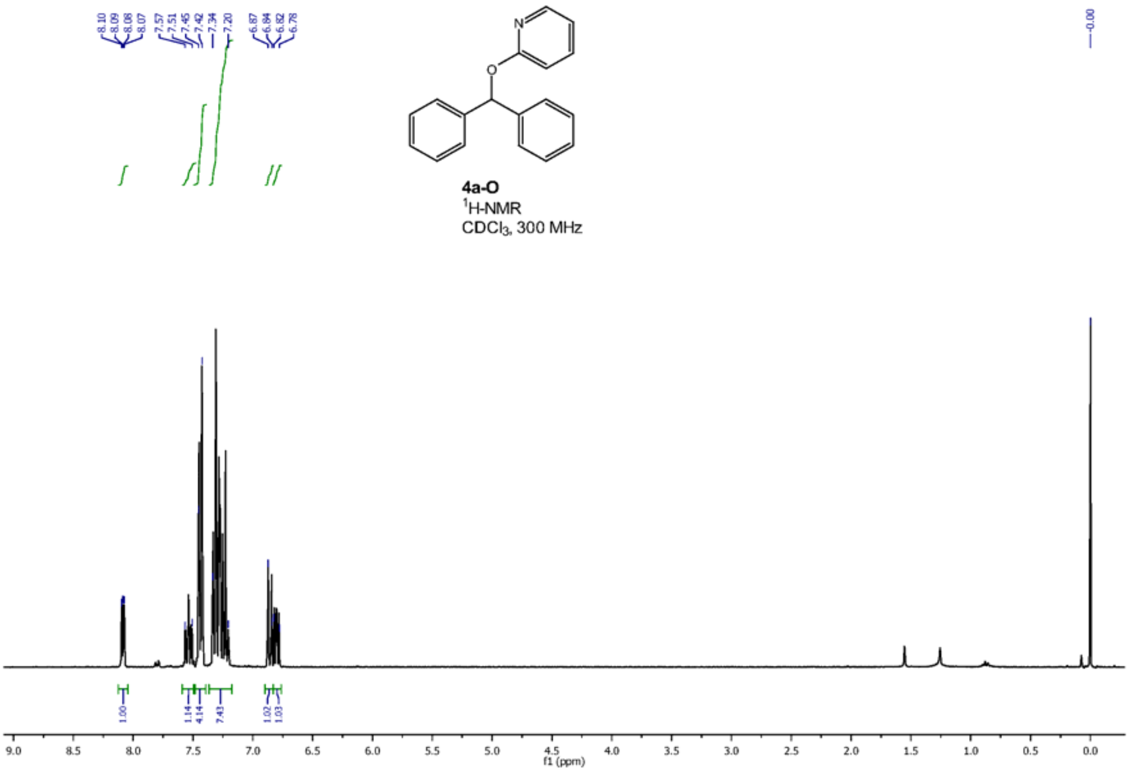
8826,63.1233237,-0.0405999,0.1000207,47.0289656\PG=C01 [X(C4H9N1O1)]\\

7 ^{1}H and ^{13}C NMR Spectra of the Isolated Reaction Products



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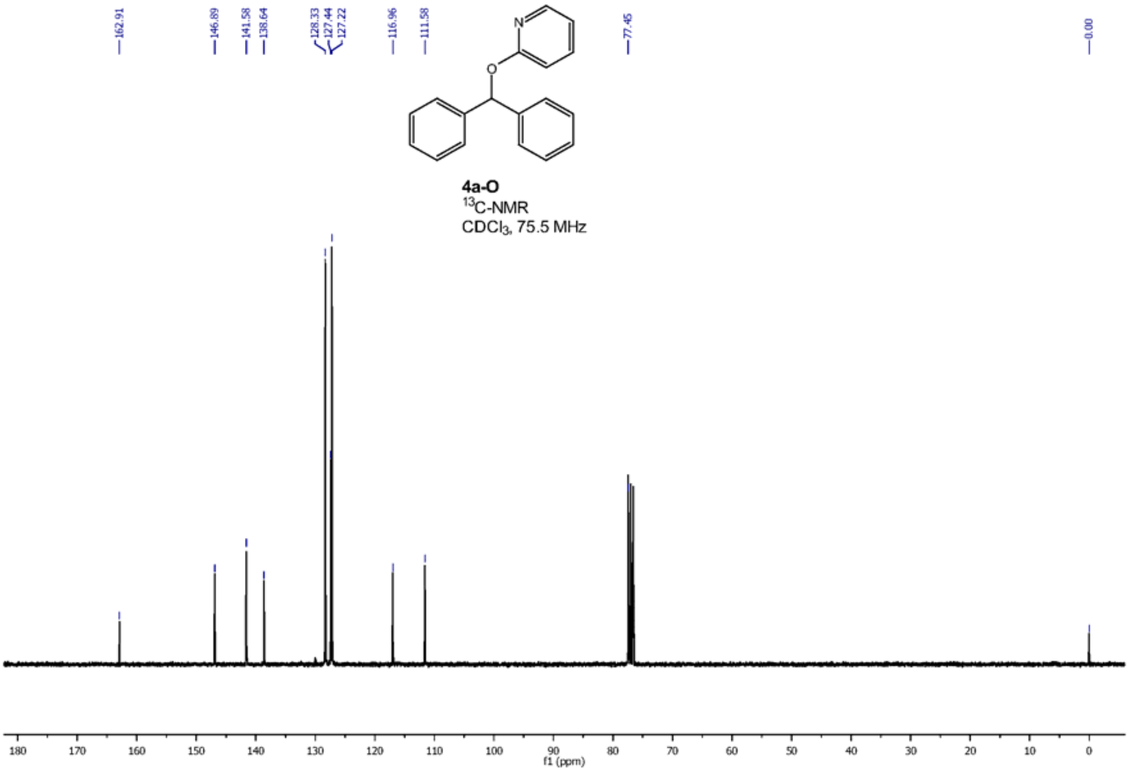
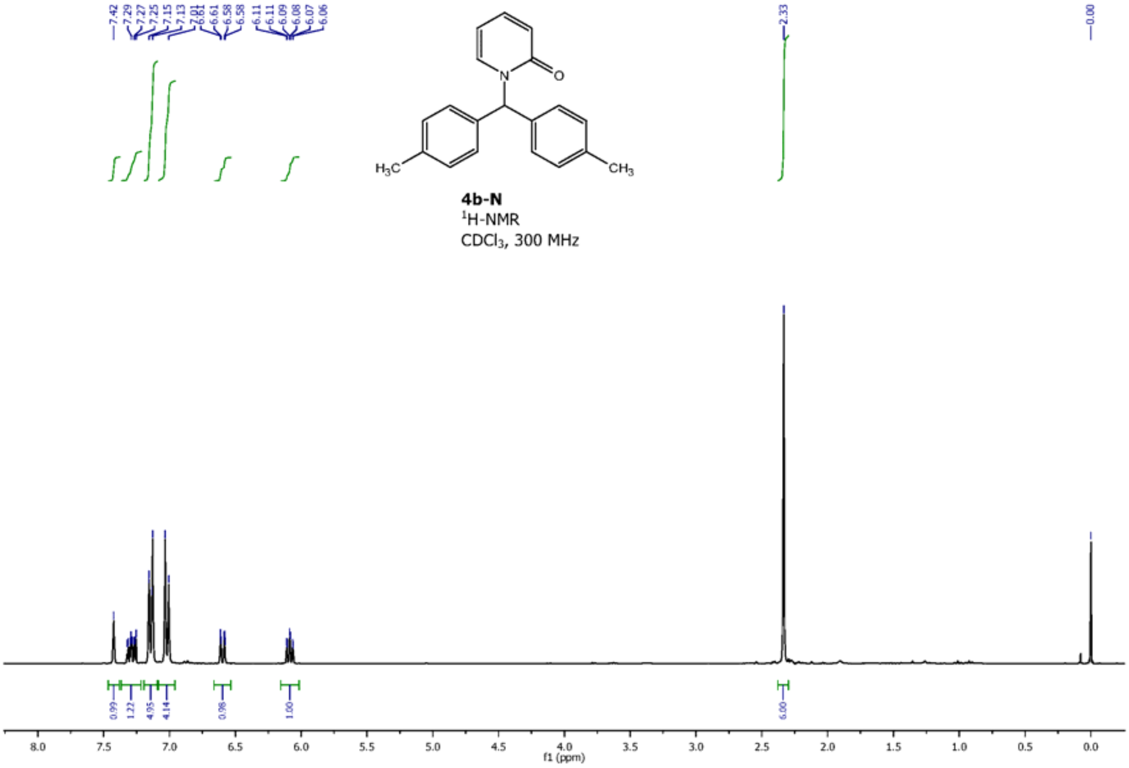
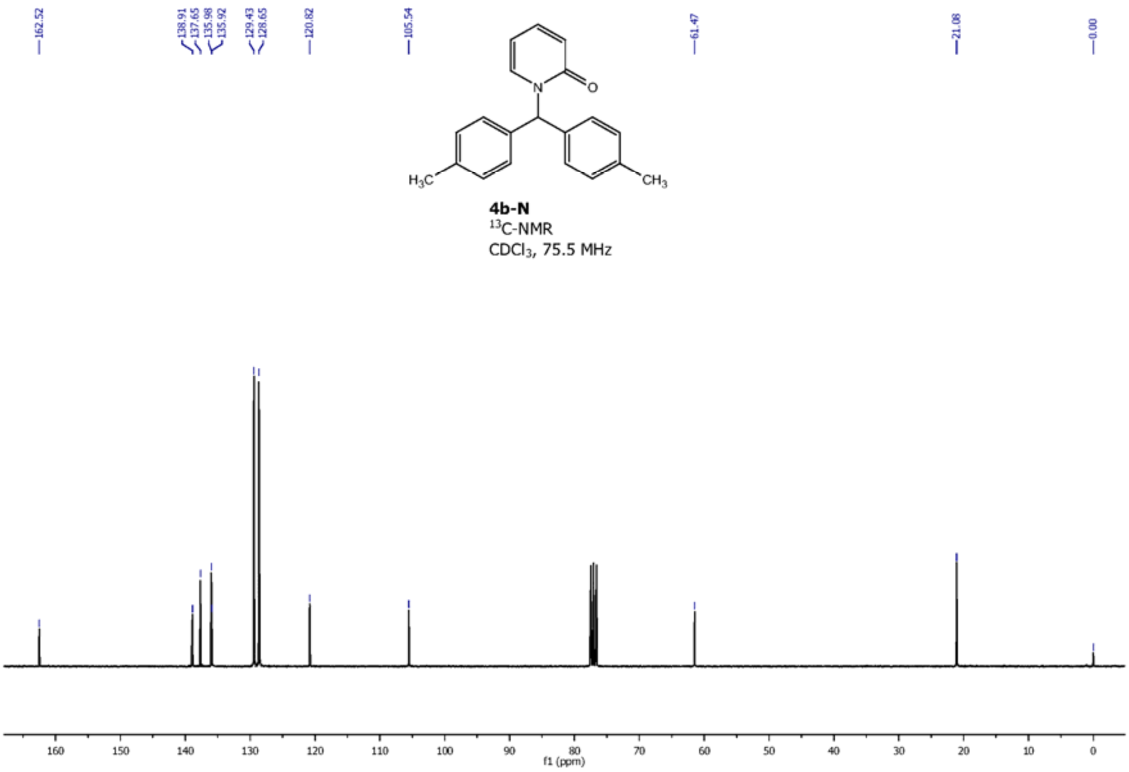
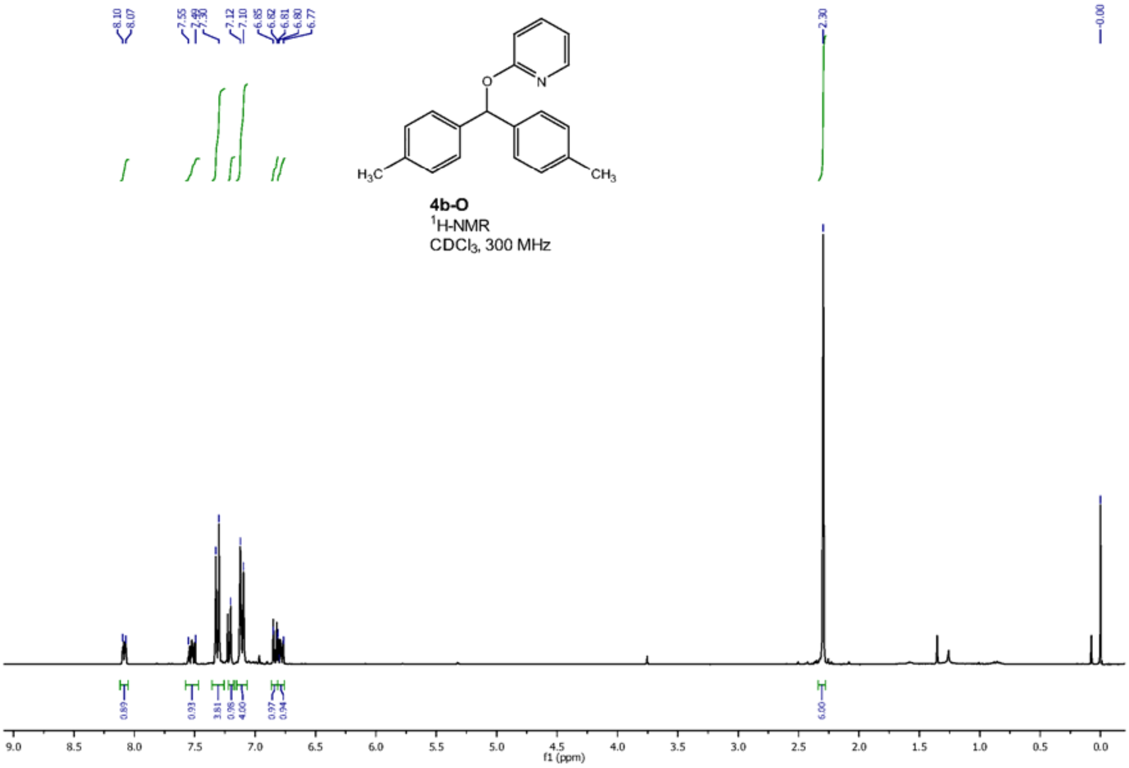
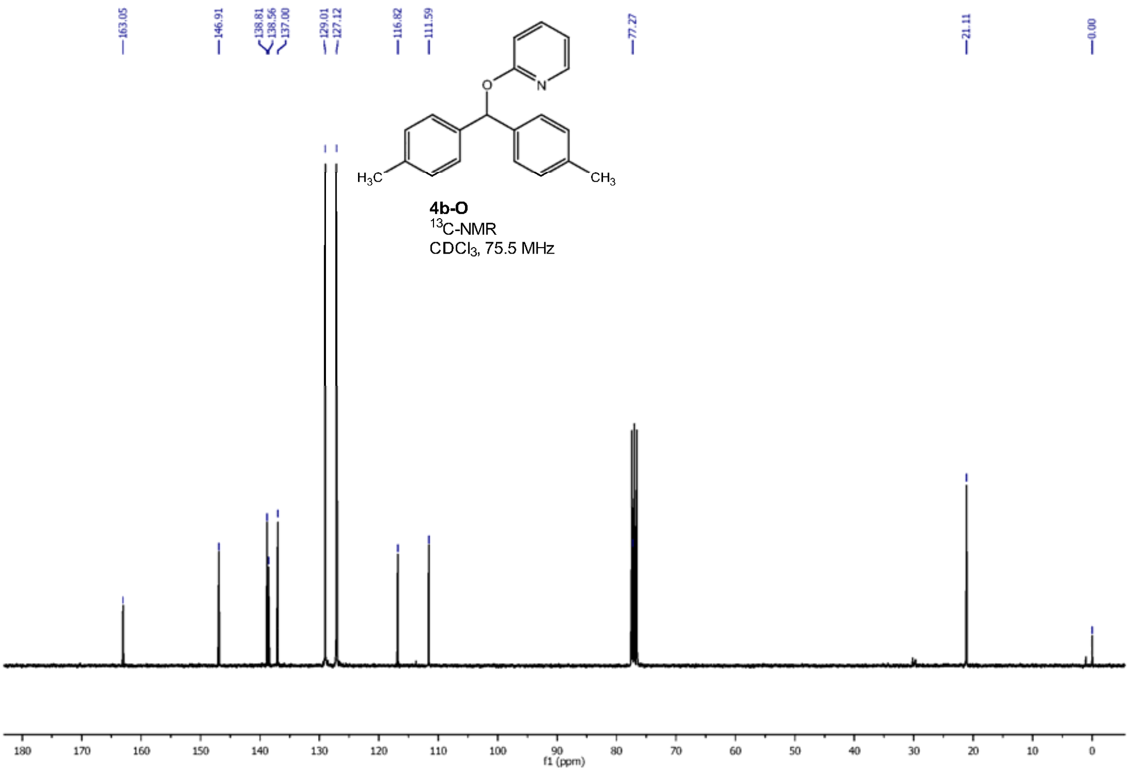
8.09
8.08
8.07
7.57
7.51
7.45
7.42
7.34
7.20
6.87
6.84
6.82
6.78
0.00
N
O
4a-O
^{1}H-NMR
$CDCl_3$, 300 MHz
1.00
1.14
4.14
7.43
1.02
1.03
f1 (ppm)

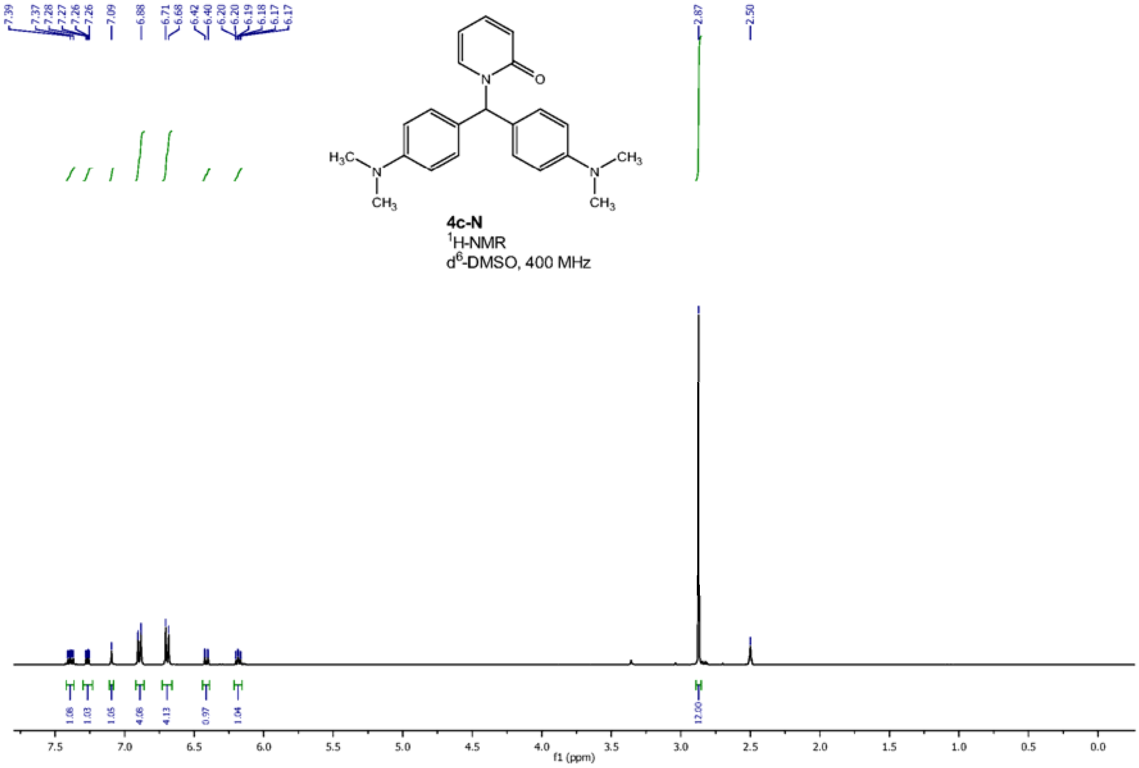

162.91
146.89
141.58
138.64
128.33
127.44
127.22
116.96
111.58
77.45
0.00
N
O
4a-O
^{13}C-NMR
$CDCl_3$, 75.5 MHz
f1 (ppm)

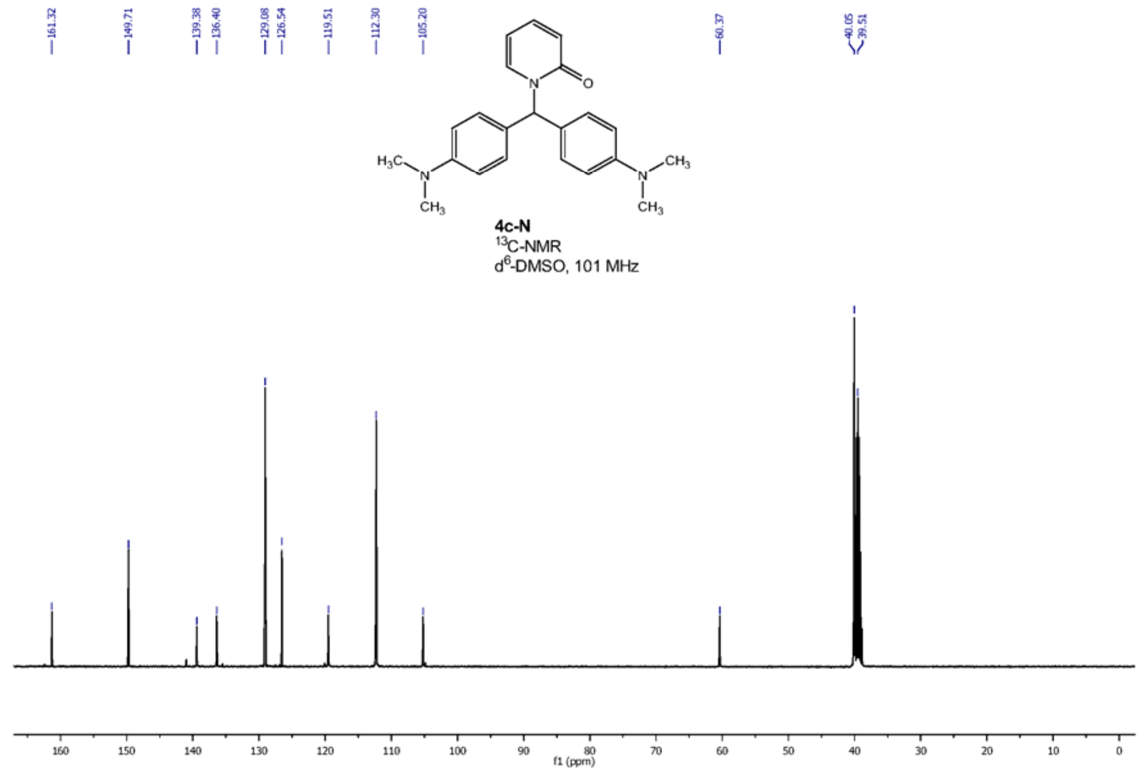

4b-N
¹H-NMR
CDCl₃, 300 MHz
f1 (ppm)

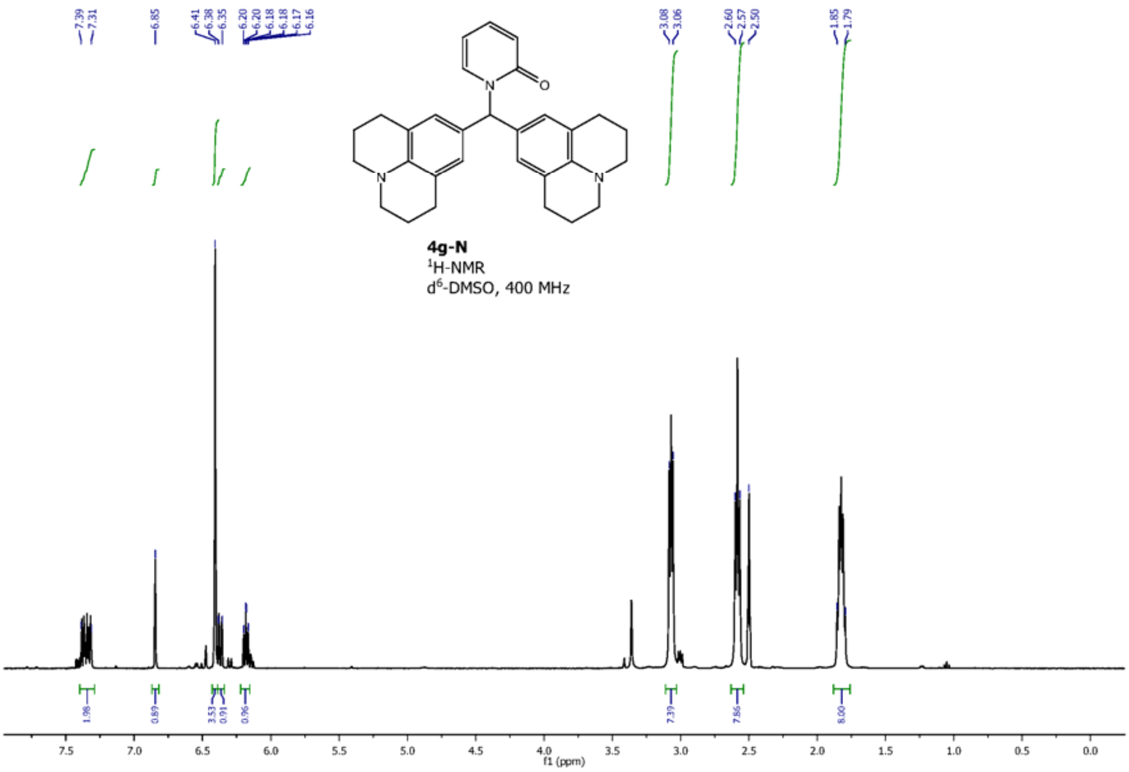

4b-N
¹³C-NMR
CDCl₃, 75.5 MHz
f1 (ppm)

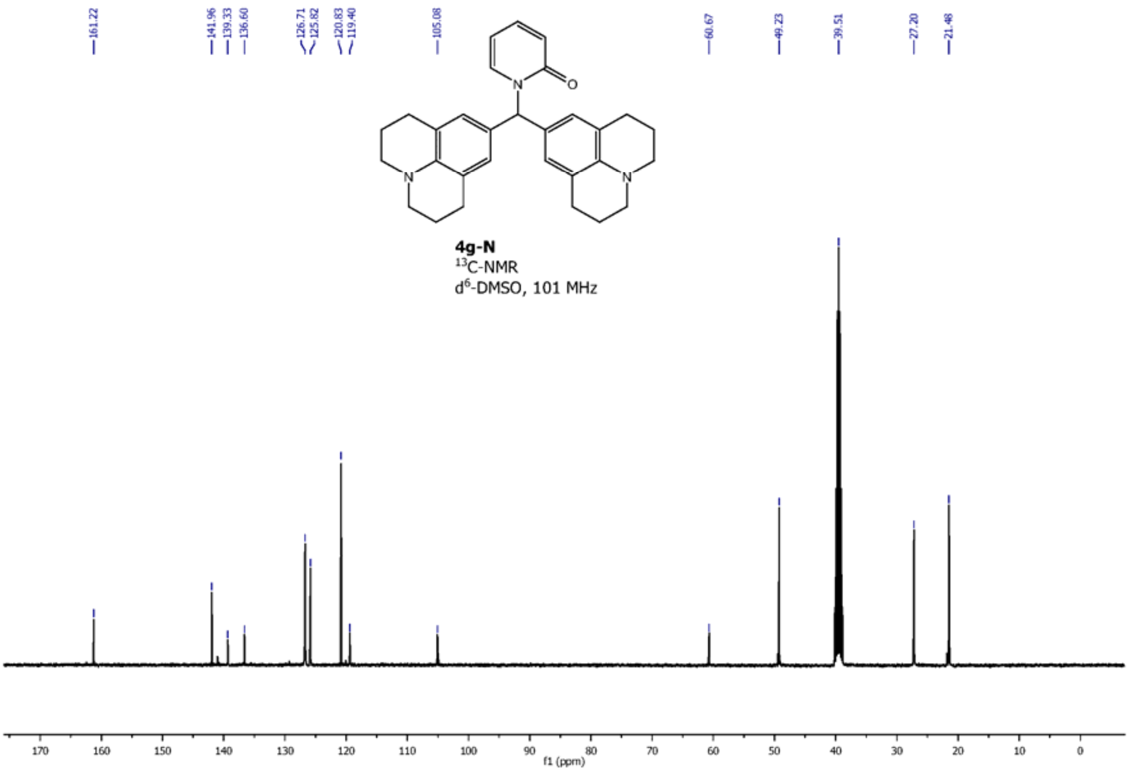

4b-O
¹H-NMR
CDCl3, 300 MHz
f1 (ppm)

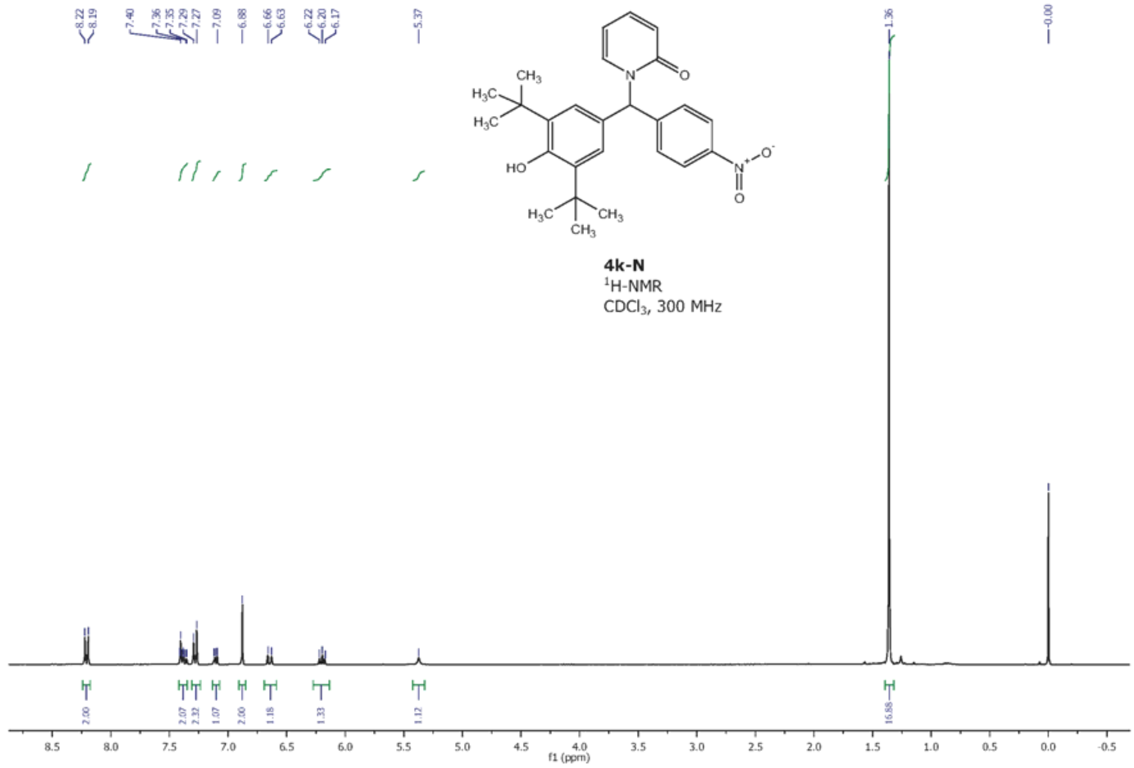

4b-O
¹³C-NMR
CDCl3, 75.5 MHz
f1 (ppm)


4c-N
1H-NMR
d6-DMSO, 400 MHz
f1 (ppm)

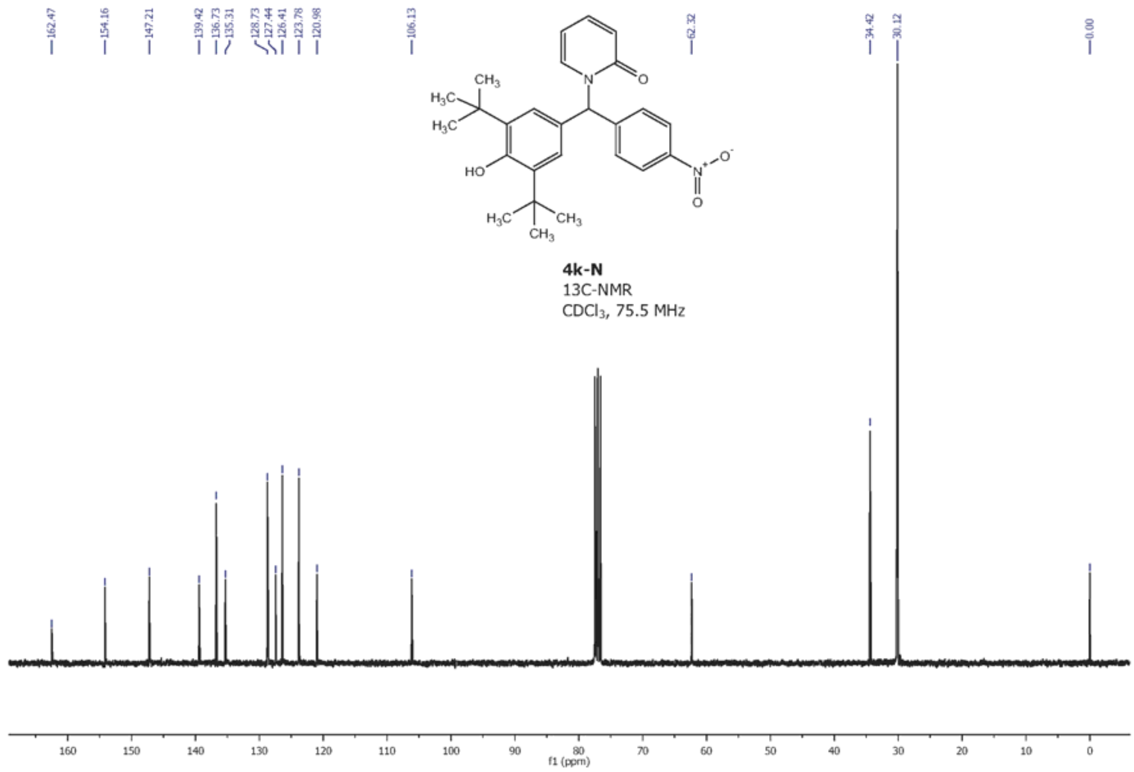

4c-N
13C-NMR
d6-DMSO, 101 MHz
f1 (ppm)


7.39
7.31
6.85
6.41
6.38
6.35
6.20
6.20
6.18
6.18
6.17
6.16
3.08
3.06
2.60
2.57
2.50
1.85
1.79
N
O
N
N
4g-N
1H-NMR
d6-DMSO, 400 MHz
1.98
0.89
3.53
0.91
0.96
7.39
7.86
8.00
f1 (ppm)

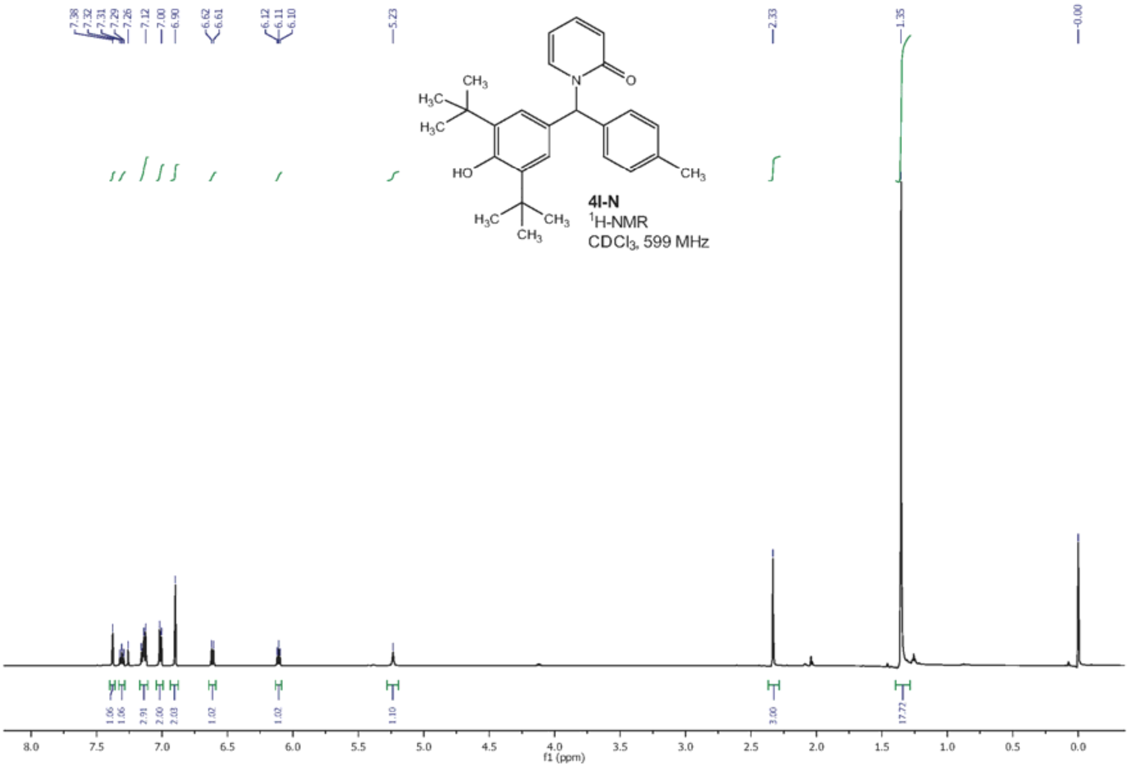

161.22
141.96
139.33
136.60
126.71
125.82
120.83
119.40
105.08
60.67
49.23
39.51
27.20
21.48
N
O
N
N
4g-N
13C-NMR
d6-DMSO, 101 MHz
f1 (ppm)

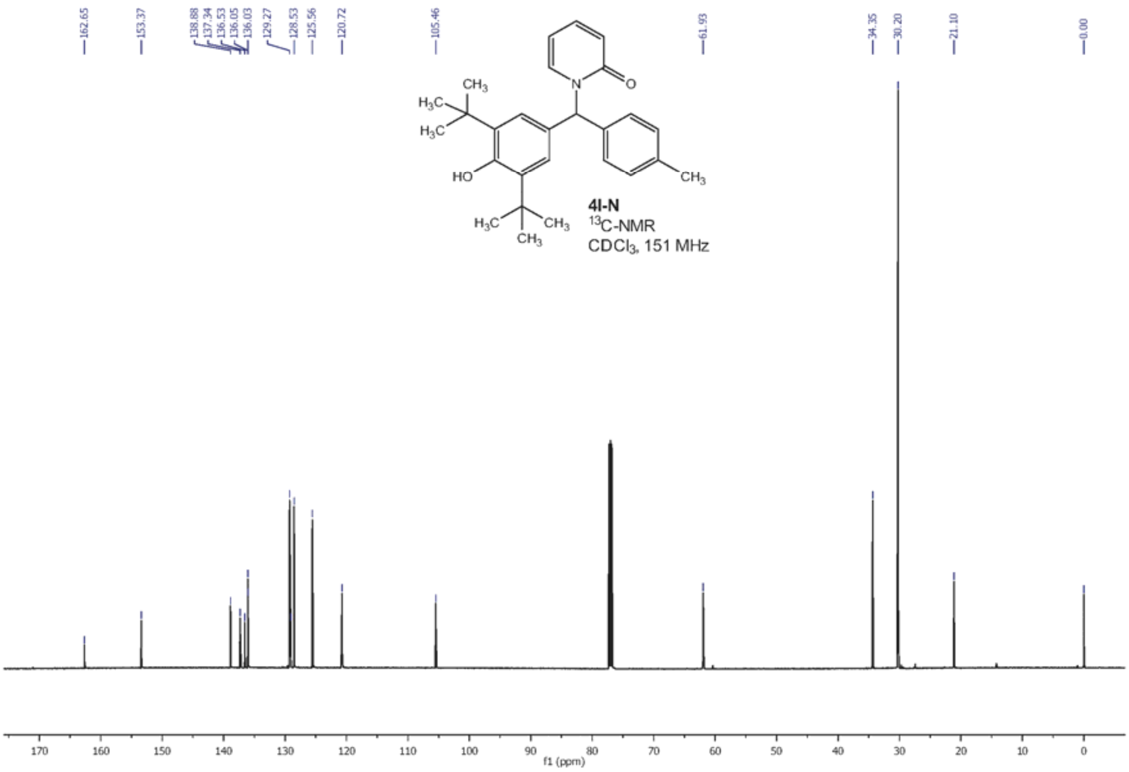


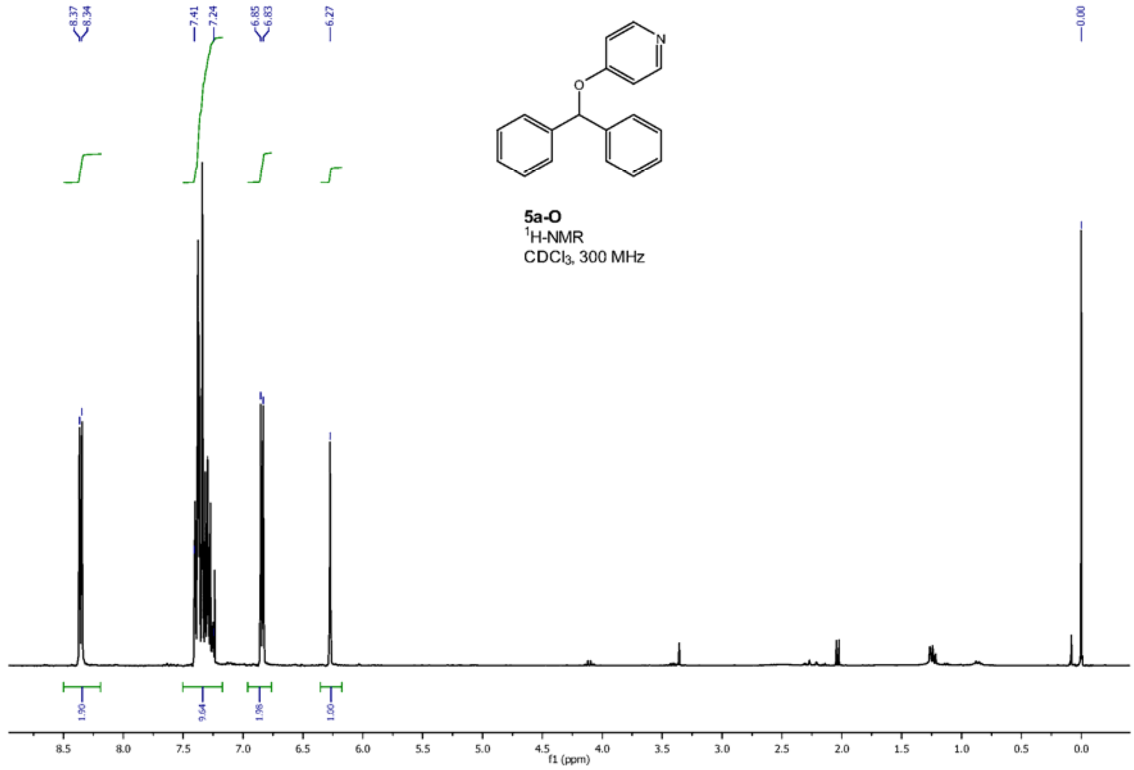
4k-N
^{1}H-NMR
CDCl$_3$, 300 MHz
f1 (ppm)

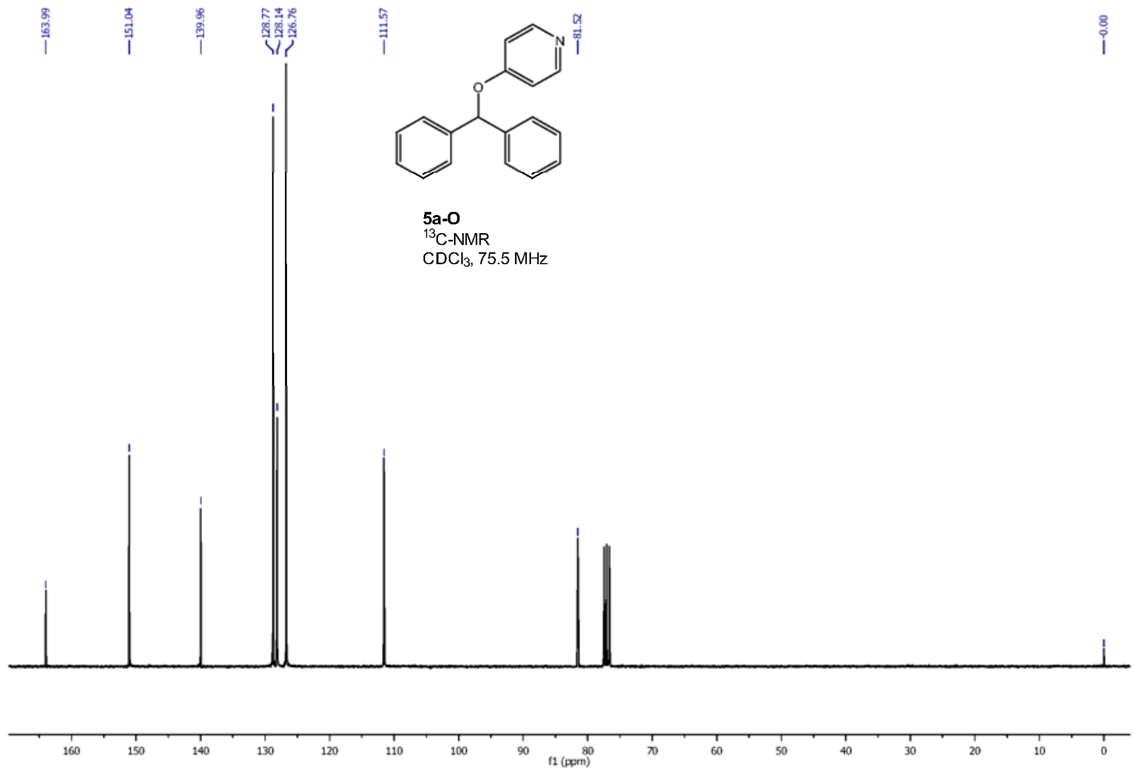


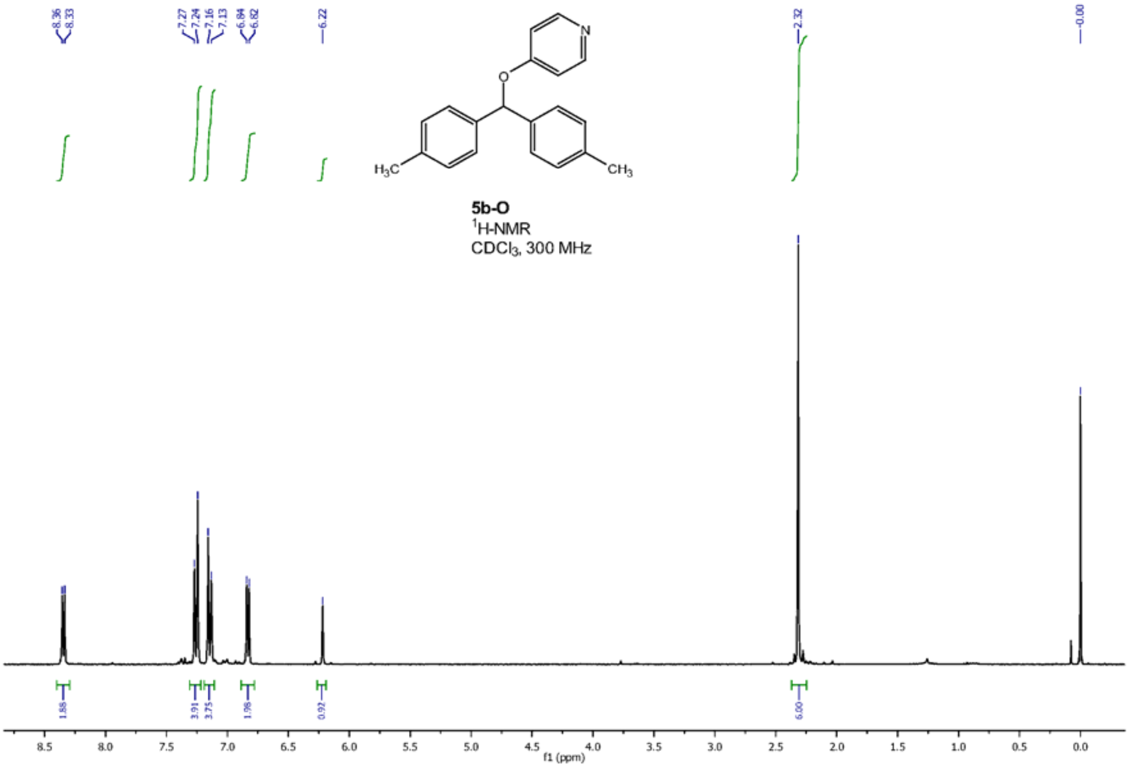
4k-N
13C-NMR
CDCl$_3$, 75.5 MHz
f1 (ppm)

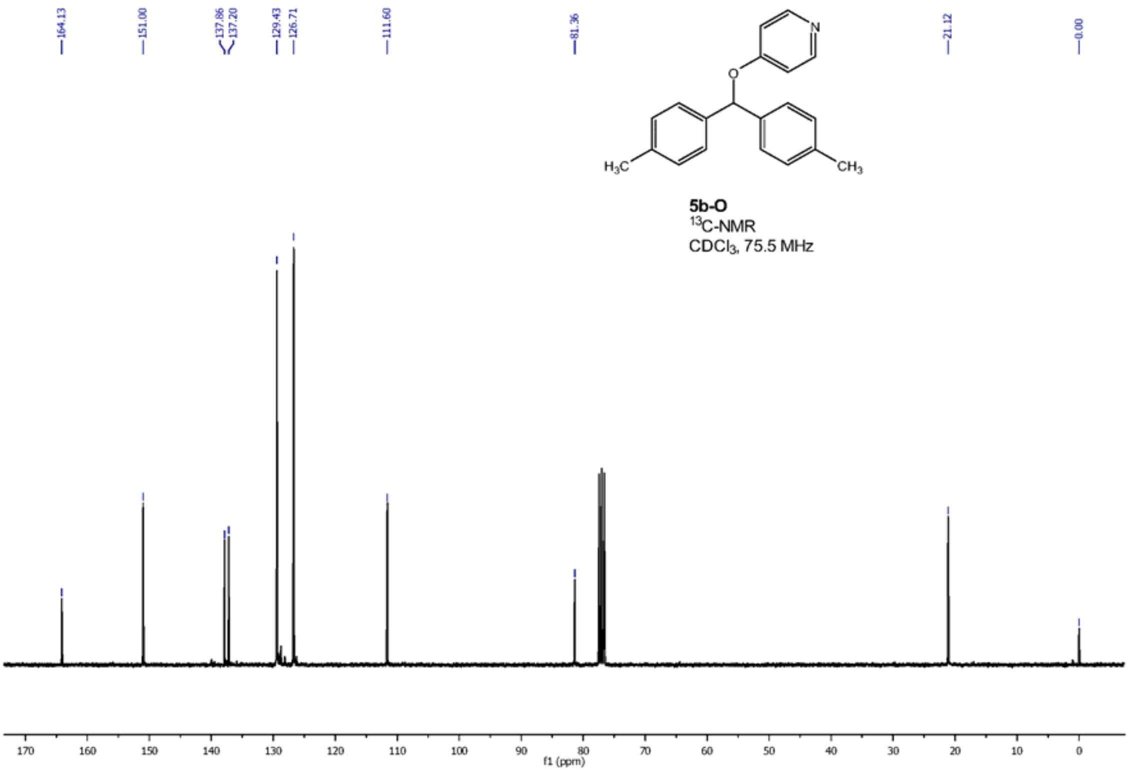

4l-N
1H-NMR
CDCl3, 599 MHz
f1 (ppm)

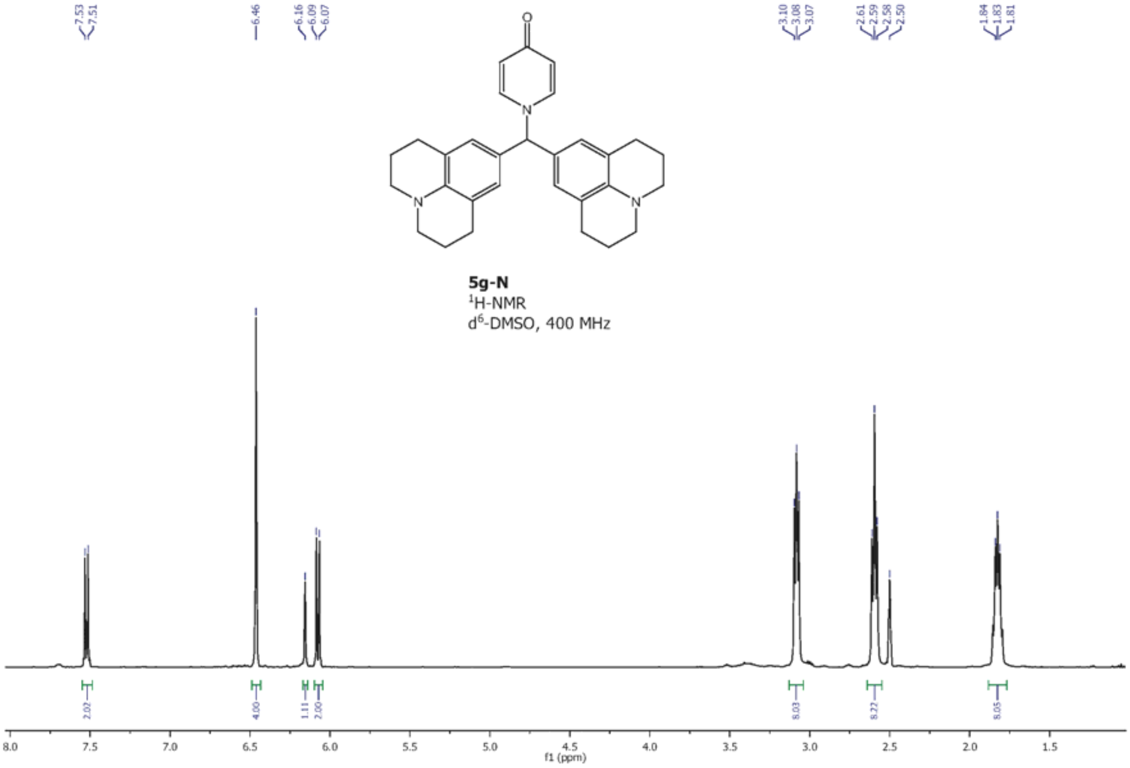

4l-N
13C-NMR
CDCl3, 151 MHz
f1 (ppm)

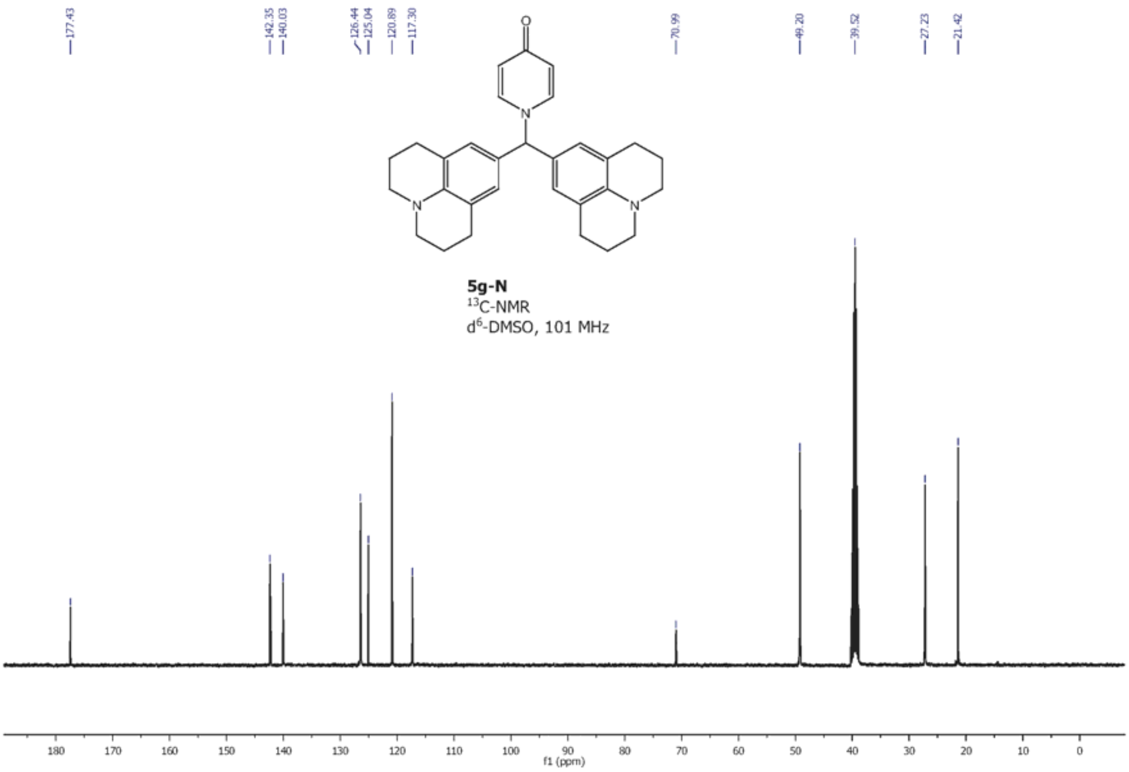

8.37
8.34
7.41
7.24
6.85
6.83
6.27
0.00
5a-O
^{1}H-NMR
CDCl$_3$, 300 MHz
1.90
9.64
1.98
1.00
f1 (ppm)

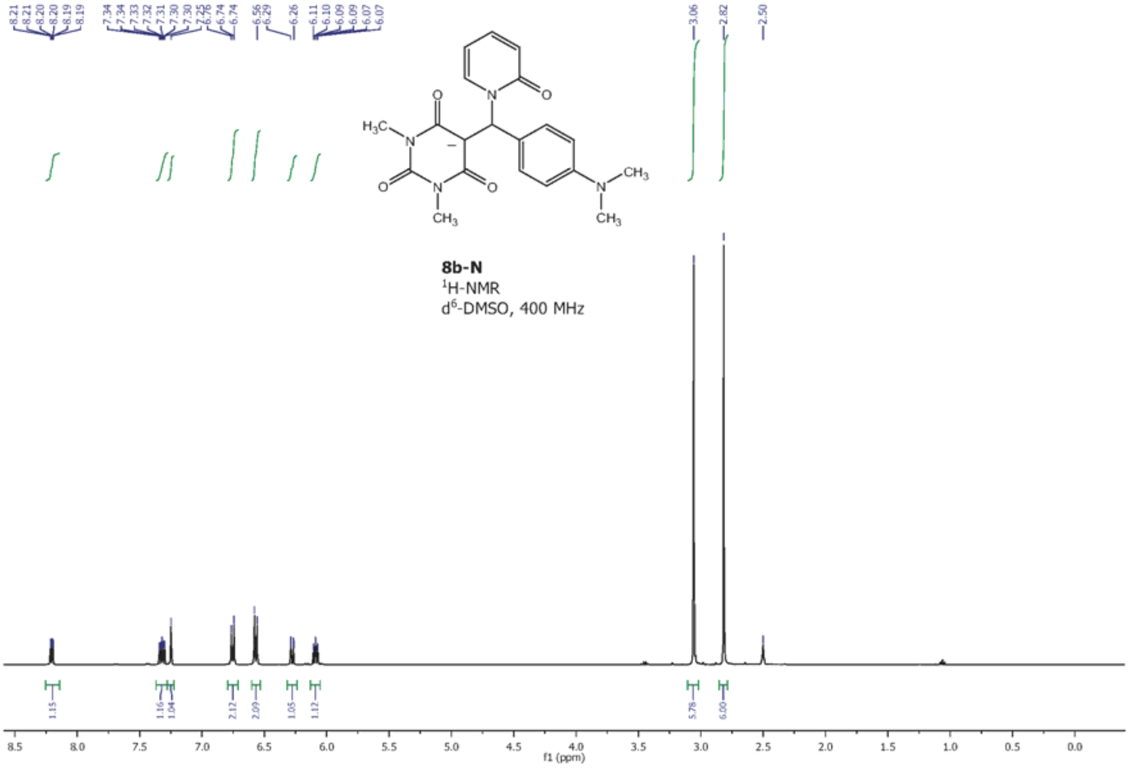

163.99
151.04
139.96
128.77
128.14
126.76
111.57
81.52
0.00
5a-O
^{13}C-NMR
CDCl$_3$, 75.5 MHz
f1 (ppm)

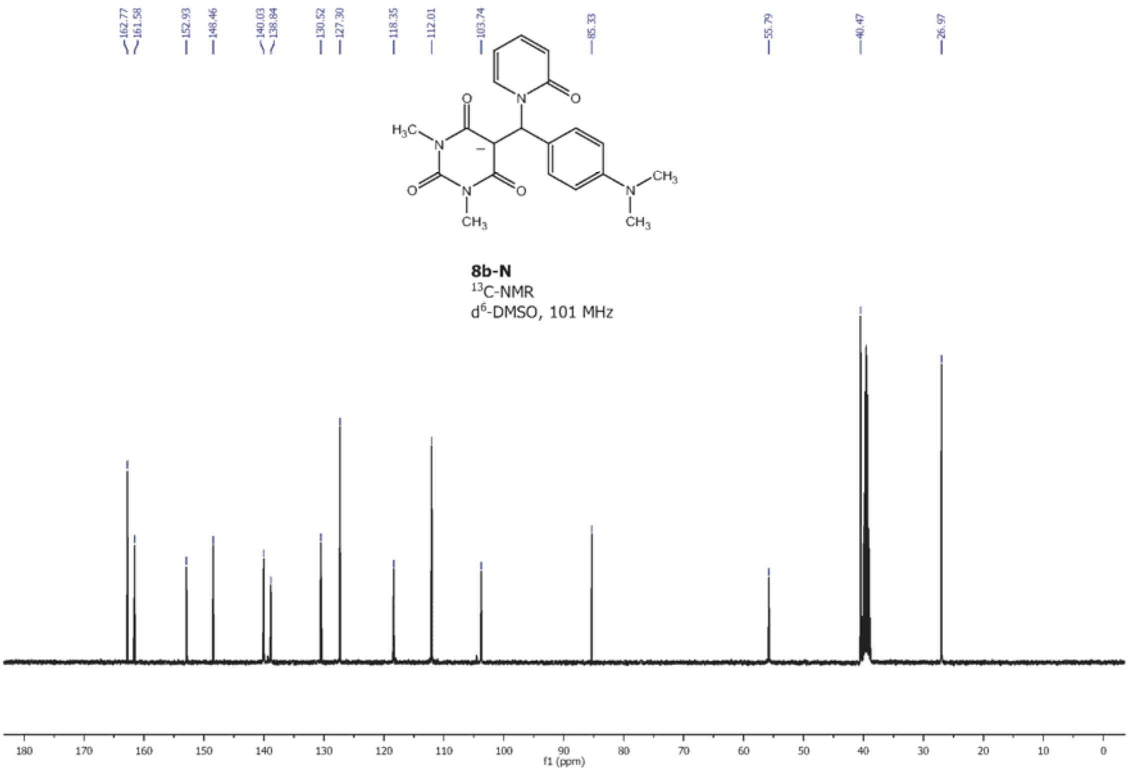

5b-O
1H-NMR
CDCl3, 300 MHz

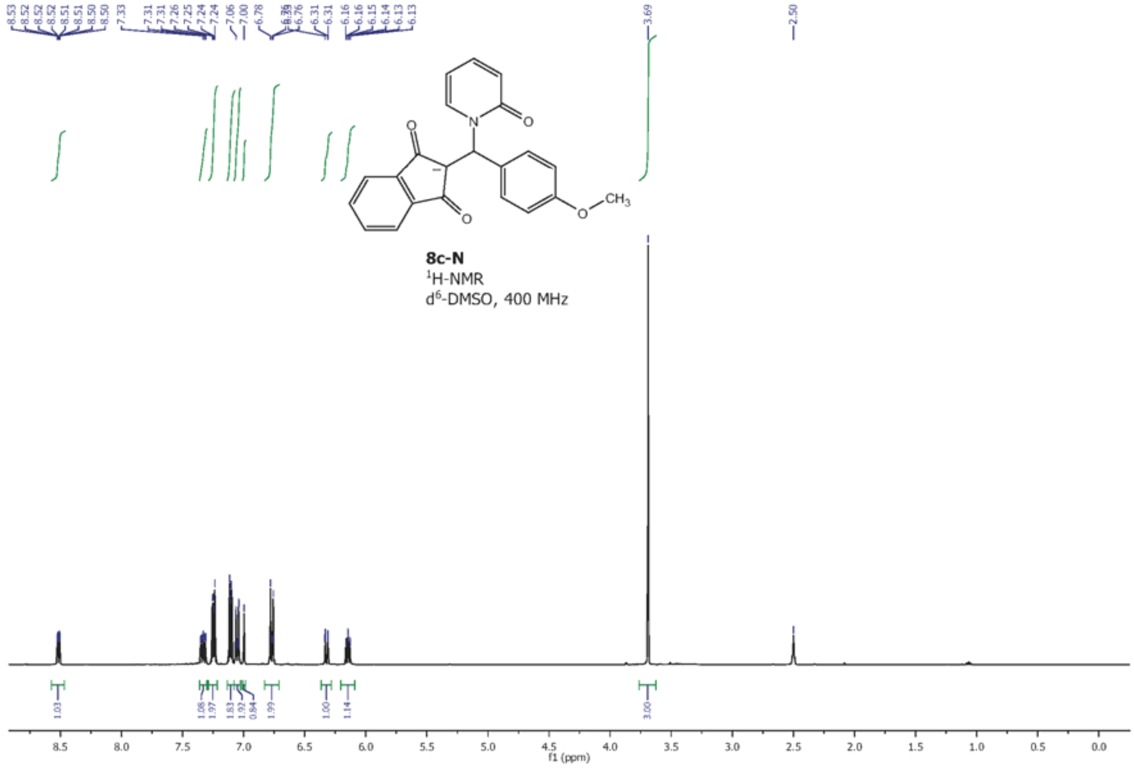

5b-O
13C-NMR
CDCl3, 75.5 MHz

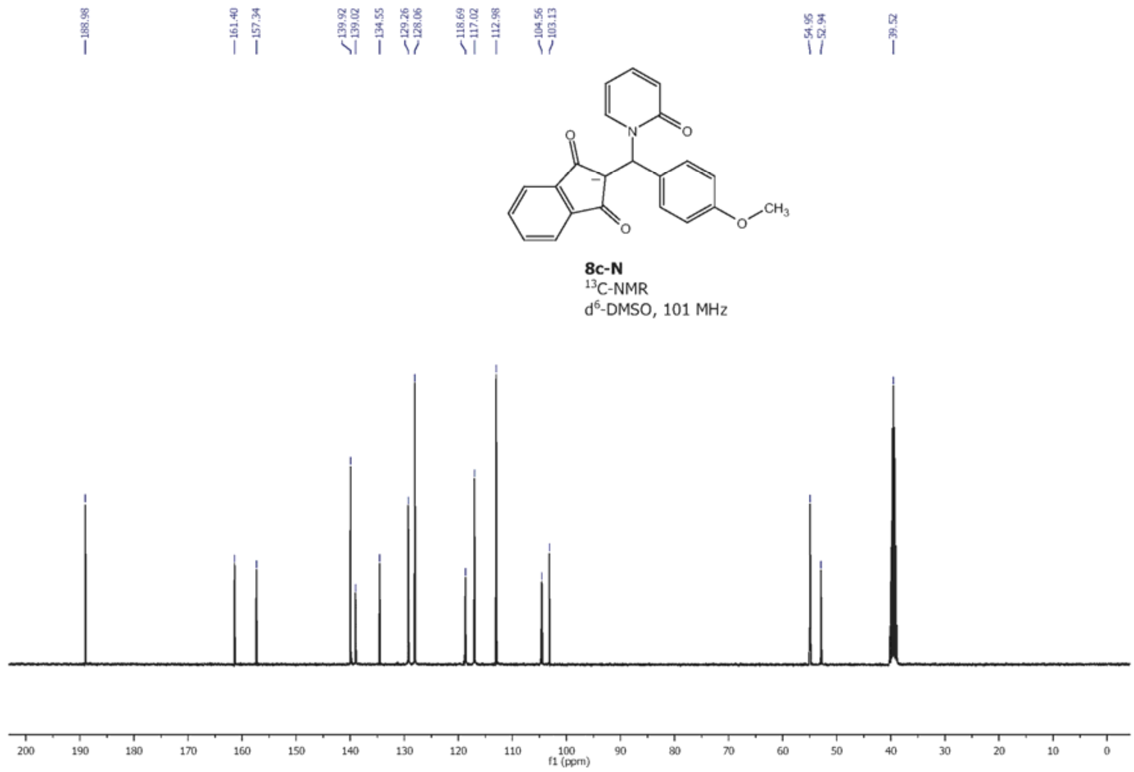

7.53
7.51
6.46
6.16
6.09
6.07
3.10
3.08
3.07
2.61
2.59
2.58
2.50
1.84
1.83
1.81
O
N
5g-N
1H-NMR
d6-DMSO, 400 MHz
2.02
4.00
1.11
2.00
8.03
8.27
8.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

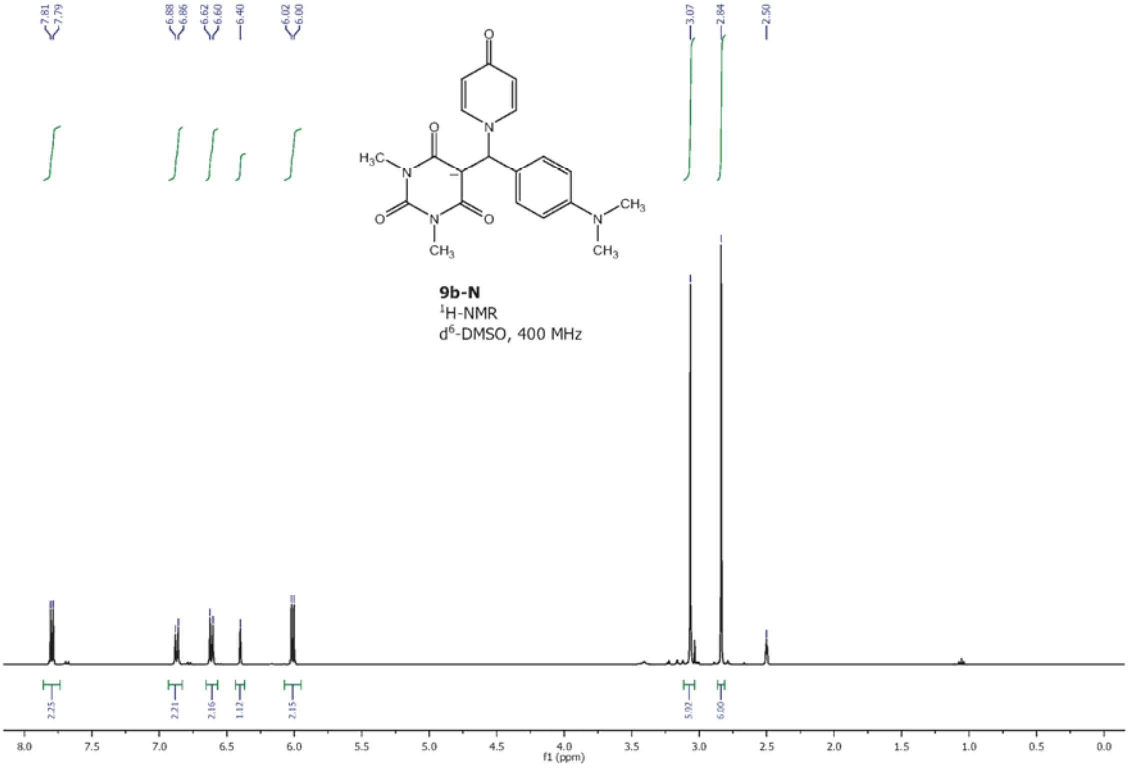

177.43
142.35
140.03
126.44
125.04
120.89
117.30
70.99
49.20
39.52
27.23
21.42
O
N
5g-N
13C-NMR
d6-DMSO, 101 MHz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

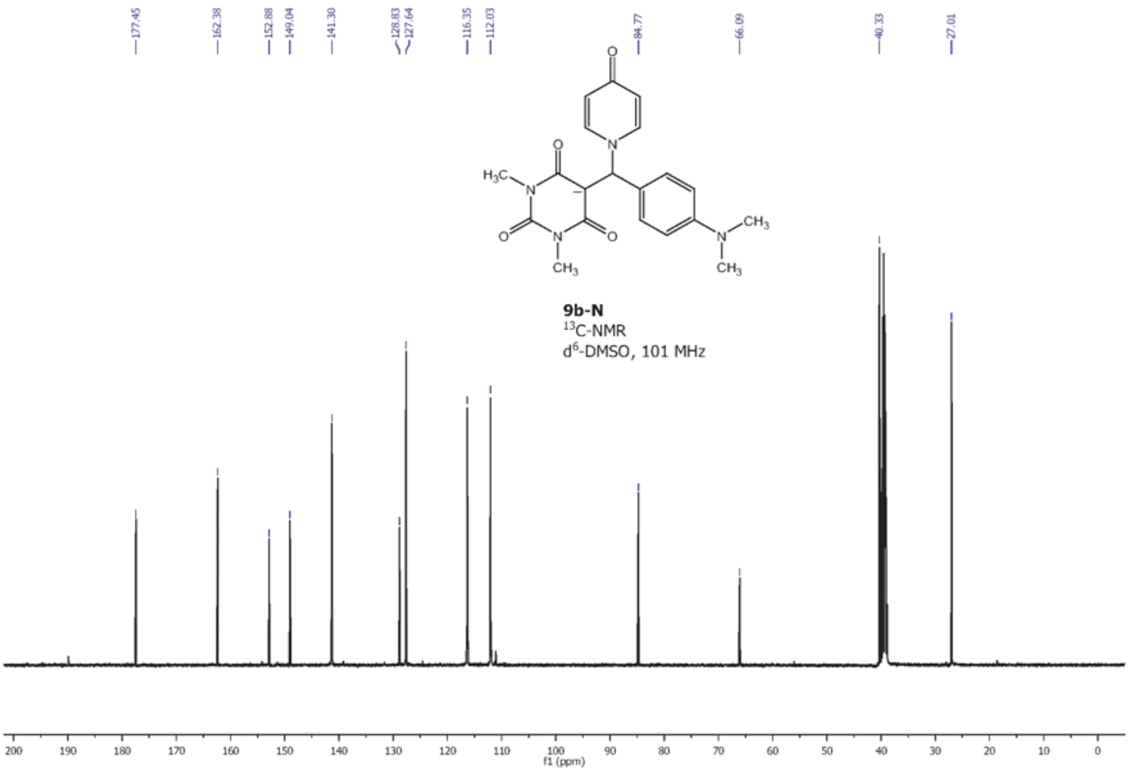

8b-N
¹H-NMR
d⁶-DMSO, 400 MHz
f1 (ppm)

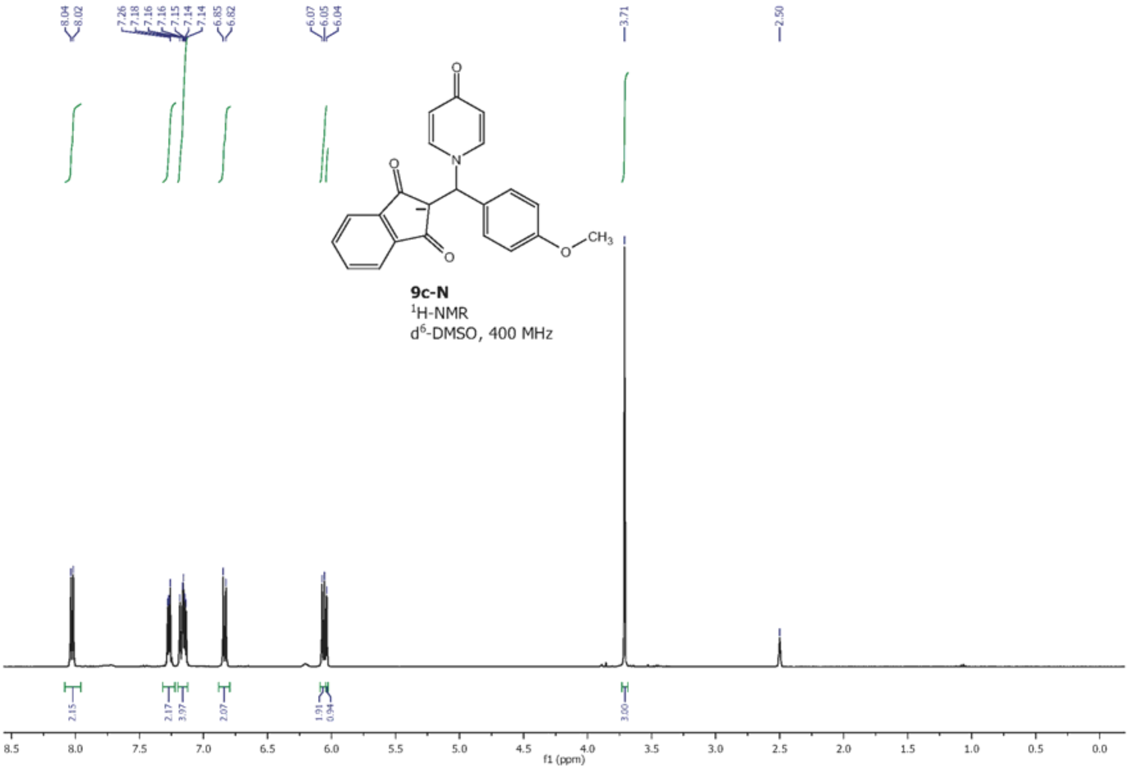

8b-N
¹³C-NMR
d⁶-DMSO, 101 MHz
f1 (ppm)

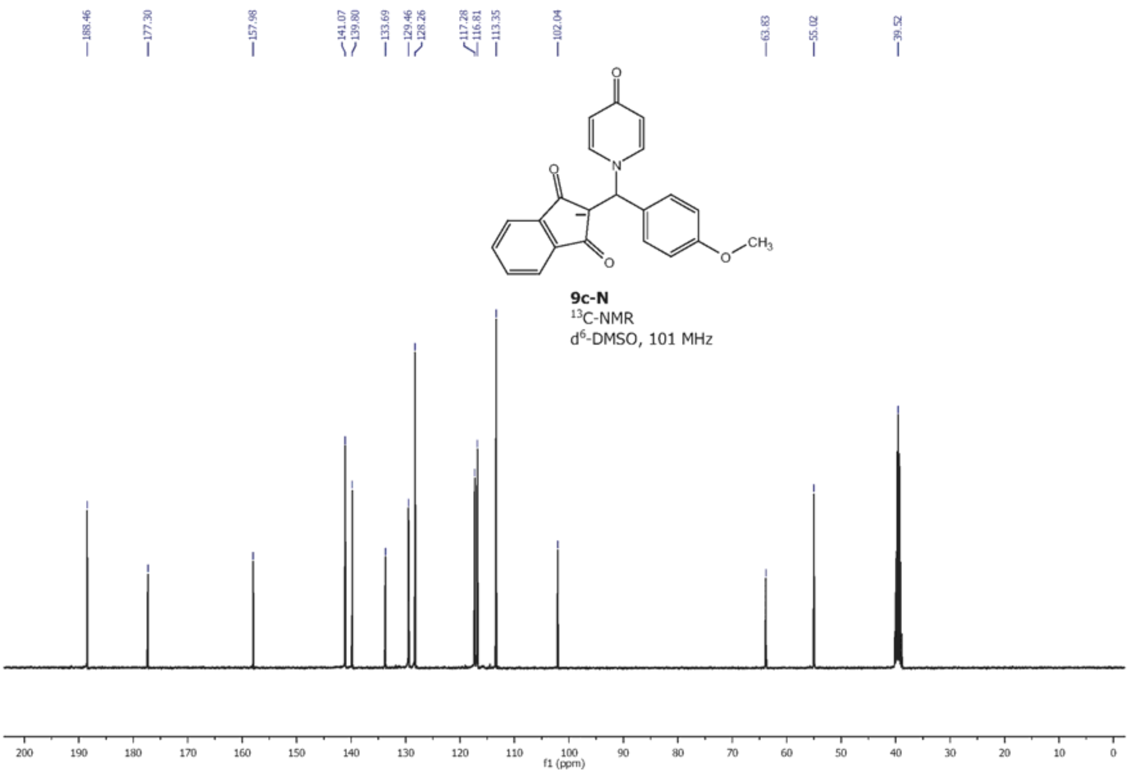

8c-N
^{1}H-NMR
d^{6}-DMSO, 400 MHz
f1 (ppm)


8c-N
^{13}C-NMR
d^{6}-DMSO, 101 MHz
f1 (ppm)


9b-N
^{1}H-NMR
d^6-DMSO, 400 MHz
f1 (ppm)


9b-N
^{13}C-NMR
d^6-DMSO, 101 MHz
f1 (ppm)


8.04
8.02
7.26
7.18
7.16
7.16
7.15
7.14
7.14
6.85
6.82
6.07
6.05
6.04
3.71
2.50
9c-N
1H-NMR
d6-DMSO, 400 MHz
2.15
2.17
3.97
2.07
1.91
0.94
3.00
f1 (ppm)


188.46
177.30
157.98
141.07
139.80
133.69
129.46
128.26
117.28
116.81
113.35
102.04
63.83
55.02
39.52
9c-N
13C-NMR
d6-DMSO, 101 MHz
f1 (ppm)

8 References

(1) (a) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500-9512; (b) Lucius, R.; Loos, R.; Mayr, H. *Angew. Chem. Int. Ed.* **2002**, *41*, 91-95; (c) Richter, D.; Hampel, N.; Singer, T.; Ofial, A. R.; Mayr, H. *Eur. J. Org. Chem.* **2009**, *2009*, 3203-3211.

(2) (a) Bunting, J. W.; Toth, A.; Heo, C. K. M.; Moors, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 8878-8885; (b) Heo, C. K. M.; Bunting, J. W. *J. Org. Chem.* **1992**, *57*, 3570-3578.

(3) Minegishi, S.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 286-295.

(4) Minegishi, S.; Kobayashi, S.; Mayr, H. *J. Am. Chem. Soc.* **2004**, *126*, 5174-5181.

(5) Minegishi, S.; Mayr, H. *J. Am. Chem. Soc.* **2003**, *125*, 286-295; The rate constants for the reaction of hydroxide with the benzhydrylium ion **2e** were calculated from the *N*- / *s*-parameters from ref. 5 and the electrophilicity parameters *E* from ref 1a.

(6) Corresponds to reference 34 of the manuscirpt; Gaussian 03, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Wallingford, CT, **2004**.