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SUPPORTING INFORMATION

Highly Efficient Synthesis of O-(2,4-dinitrophenyl)hydroxylamine. Application to the Synthesis of Substituted N-benzoyliminopyridinium Ylides.

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General information. All non-aqueous reactions were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.¹ All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by filtration through drying columns (THF, ether, CH₂Cl₂, benzene, DMF, CH₃CN, toluene, hexane, methanol) on a GlassContour system (Irvine, CA), by distillation over calcium hydride (Et₃N, ClCH₂CH₂Cl, pyridine, diisopropylamine, isopropanol) or by distillation over sodium/benzophenone (DME). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel (Merck 60 F₂₅₄). Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, iodine, or aqueous potassium permanganate. Flash column chromatography was performed using 230-400 mesh silica of the indicated solvent system according to standard technique.² Melting points were obtained on a melting point apparatus and are uncorrected. Infrared spectra were taken on a FTIR and are reported in reciprocal centimeters (cm⁻¹). Nuclear magnetic resonance spectra (¹H, ¹³C, DEPT 135, COSY, HMQC, NOESY) were recorded either on a 300 or 400 MHz spectrometer. Chemical shifts for ¹H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sext = sextuplet m = multiplet and br = broad), coupling constant in Hz, integration. Chemical shifts for ¹³C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuteriochloroform (77.23 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, NOESY, HMQC and DEPT experiments.

N-aminopyridinium 2,4-(dinitro)phenolate (13a). Pyridine (50 μ L, 0.62 mmol) and **5** (135 mg, 0.67 mmol) were mixed in MeCN (400 μ L). The reaction vessel was sealed and the reaction was stirred at 40 °C for 24 h. The reaction was concentrated and the resulting residue was triturated in three times with Et₂O (5 mL). The resulting solid was filtered and dried under vacuum affording **13a** (168 mg, 98 % yield) as a bright orange solid: mp 156 °C; ¹H NMR (300 MHz, *d*₆-DMSO) δ 8.81 (d, *J* = 6.1 Hz, 1H), 8.66-8.60 (m, 3H), 8.25 (t, *J* = 7.7 Hz, 1H), 8.01 (t, *J* = 6.9 Hz, 1H), 7.80 (dd, *J* = 9.8, 3.1 Hz, 1H), 6.37 (d, *J* = 9.7 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO) δ 170.2, 139.5, 138.2, 136.0, 128.2, 127.8, 127.7, 126.7, 125.1; IR (neat) 3277, 3057, 3014, 1595, 1549, 1531, 1306, 1246 cm⁻¹; LRMS (ES, Pos) calcd for C₅H₇N₂ [M]⁺ : 95.1 *m/z*, observed: 95.1 *m/z*.

N-amino-2,6-dimethylpyridinium 2,4-(dinitro)phenolate (13b). The title compound was obtained as a bright orange solid (96%) according to the general procedure described for **13a**: mp 148 °C; ¹H NMR (400 MHz, *d*₆-DMSO) δ 8.58 (s, 1H), 8.14 (t, *J* = 7.8 Hz, 1H), 7.85-7.75 (m, 3H), 7.33 (s, 2H), 6.33 (d, *J* = 9.6 Hz, 1H), 2.78 (s, 6H); ¹³C NMR (100 MHz, *d*₆-DMSO) δ 170.2, 153.3, 140.8, 136.0, 127.7, 127.6, 126.7, 126.5, 125.0, 19.7; IR (neat) 3301, 3113, 1595, 1533, 1476, 1316, 1250, 1124, 808 cm⁻¹; LRMS (ES, Pos) calcd for C₇H₁₁N₂ [M]⁺ : 123.1 *m/z*, observed: 123.1 *m/z*.

m/z.

N-isoquinolinium 2,4-(dinitro)phenolate (13c). The title compound was obtained as a bright orange solid (99%) according to the general procedure described for **13a**: mp 148 °C; ¹H NMR (300 MHz, *d*₆-DMSO) δ 8.81 (d, *J* = 6.1 Hz, 1H), 8.66-8.60 (m, 3H), 8.25 (t, *J* = 7.7 Hz, 1H), 8.01 (t, *J* = 6.9 Hz, 1H), 7.80 (dd, *J* = 9.8, 3.1 Hz, 1H), 6.37 (d, *J* = 9.7 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO) δ 170.2, 139.5, 138.2, 136.0, 128.2, 127.8, 127.7, 126.7, 125.1; IR (neat) 3331, 3081, 1606, 1566, 1323, 1248, 1129, 821 cm⁻¹; LRMS (ES, Pos) calcd for C₉H₉N₂ [M]⁺ : 145.1 *m/z*, observed: 145.1

N-quinolinium 2,4-(dinitro)phenolate (13d). Quinoline (50 μ L, 0.42 mmol) and **5** (86 mg, 0.43 mmol) were dissolved in THF (1 mL). The reaction was then concentrated under reduced pressure and the residue was let at room temperature for 20 h. It was then dried completely under vacuum and the resulting residue was triturated three times with Et₂O (5 mL). The solid was filtered and dried under vacuum affording **13d** (128 mg, 95 % yield) as a bright orange solid: mp 131 °C; ¹H NMR (300 MHz, *d*₆-DMSO) δ 9.35 (d, *J* = 6.0 Hz, 1H), 9.01 (d, *J* = 8.4 Hz, 1H), 8.59-8.55 (m, 3H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.23 (t, *J* = 7.2 Hz, 1H), 8.09-7.97 (m, 2H), 7.77 (dd, *J* = 9.7, 3.2 Hz, 1H), 6.32 (d, *J* = 9.8 Hz, 1H); ¹³C NMR (75 MHz, *d*₆-DMSO) δ 170.3, 142.7, 142.4, 136.3, 136.0, 134.7, 130.1, 129.8, 129.7, 127.6, 127.5, 126.5, 125.0, 122.0, 118.2; IR (neat) 3212, 3078, 1596, 1555, 1525, 1471, 1322, 1258, 1242, 819, 766 cm⁻¹; LRMS (ES, Pos) calcd for C₉H₉N₂ [M]⁺ : 145.1 *m/z*, observed: 145.1 *m/z*.

3-Pyrrolidinopyridine (14g). 3-Iodopyridine (205 mg, 1 mmol), CuI (8mg, 0.05 mmol) and K₃PO₄ (425 mg, 2 mmol) were put in a flame dried seal tube under argon. To the tube was added *i*PrOH (1 mL), ethylene glycol (110 μ L, 2 mmol) and pyrrolidine (100 μ L, 1.2 mmol). The tube was sealed and the reaction was stirred vigorously at 80 °C for 14 hrs. The reaction mixture was cooled to room temperature, diluted with H₂O (5 mL) and extracted four times with Et₂O (5 mL). The combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (30->50% EtOAc/Hexanes) affording 3-pyrrolidinopyridine (114 mg, 77%) as a pale yellow solid: *R*_f 0.13 (30% EtOAc/Hexanes) mp 30 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 2.7 Hz, 1H), 7.85 (d, *J* = 4.0 Hz, 1H), 7.01 (dd, *J* = 8.3, 4.6 Hz, 1H), 6.70 (dd, *J* = 8.3, 1.6 Hz, 1H), 3.21-3.17 (m, 4H), 1.95-1.91 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 143.6, 136.8, 134.3, 123.4, 117.6, 47.2, 25.3; IR (neat) 3034, 2967, 2838, 1583, 1486, 1371, 710 cm⁻¹; LRMS (APCI, Pos) calcd for C₉H₁₂N₂ [M+H]⁺ : 149.1 *m/z*, observed: 149.1 *m/z*.

2-Isopropoxy pyridine (14h). NaH (1.1 g, 60% in oil, 27 mmol) was put in a flame dried round bottom flask under argon containing 100 mL of THF. *i*PrOH (2mL, 27 mmol) was added and the reaction was stirred at room temperature for 30 min. 2-Chloropyridine (1 mL, 13.5 mmol) was added, the reaction flask fitted with a condenser and stirred at reflux for 48 h. The reaction was cooled, diluted with 50 mL of water and extracted twice with 100 mL Et₂O. The combined organic phases were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude oil was purified by flash chromatography on silica gel (100% pentane -> 20% Et₂O/pentane) affording **14h** (1.29 g, 62%) as a colorless liquid: *R*_f 0.62 (50% Et₂O/Hexane); ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 4.1 Hz, 1H), 7.50 (t, *J* = 6.5 Hz, 1H), 6.78 (t, *J* = 6.1 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 5.29 (sept, *J* = 6.1 Hz, 1H), 1.32 (d, *J* = 6.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 147.0, 138.6, 116.3, 111.8, 67.9, 22.2; IR (neat) 2936, 2977, 1594, 1568, 1471, 1431, 1285, 1271, 1115, 952, 778 cm⁻¹; LRMS (APCI, Pos) calcd for C₈H₁₁NO [M+H]⁺ : 138.1 *m/z*, observed: 138.1 *m/z*.

3-Methyl-N-benzoyliminopyridinium ylide (15b). The title compound was obtained as a white solid (99%) according to the general procedure: mp 142 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.64 (s, 1H), 8.58 (d, *J* = 6.2 Hz, 1H), 8.17-8.13 (m, 2H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 6.5 Hz, 1H), 7.43-7.37 (m, 4H), 2.47 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 143.5, 140.8, 138.0, 137.4, 137.2, 130.3, 128.1, 128.0, 125.6, 18.7; IR (neat) 3055, 1592, 1548, 1334, 705 cm⁻¹; Anal. calcd for C₁₃H₁₂N₂O: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.49; H, 5.92; N, 13.02.

2-Methyl-N-benzoyliminopyridinium ylide (15c). The title compound was obtained as a white solid (98%) according to the general procedure: mp 111 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.58 (d, J = 6.2 Hz, 1H), 8.19-8.15 (m, 2H), 7.80 (dt, J = 7.7, 1.3 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.43-7.38 (m, 3H), 2.69 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.3, 154.3, 145.4, 137.8, 137.6, 130.5, 128.5, 128.4, 128.2, 128.1, 124.0, 19.9; IR (neat) 3054, 1593, 1553, 1491, 1330, 773, 707 cm^{-1} ; Anal. calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.41; H, 6.09; N, 13.08.

2,4-dimethyl-N-benzoyliminopyridinium ylide (15d). The title compound was obtained as a white solid on a (93%) according to the general procedure: mp 135 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, J = 6.5 Hz, 1H), 8.16 (d, J = 6.8 Hz, 2H), 7.41-7.35 (m, 4H), 7.30-7.26 (m, 1H), 2.63 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 153.1, 150.5, 144.2, 137.4, 130.1, 128.2, 128.1, 127.9, 124.6, 21.3, 19.3; IR (neat) 3060, 1593, 1547, 1338, 715 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 227.1 m/z , observed: 227.1 m/z .

2,6-dimethyl-N-benzoyliminopyridinium ylide (15e). The title compound was obtained as a white solid (95%) according to the general procedure: mp 127 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.16-8.10 (m, 2H), 7.65 (t, J = 7.8 Hz, 1H), 7.39-7.32 (m, 5H), 2.67 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 169.0, 154.9, 137.5, 137.3, 130.1, 128.2, 128.0, 125.5, 20.1; IR (neat) 1596, 1556, 1334, 781, 717 cm^{-1} ; Anal. calcd for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.40; H, 6.60; N, 12.36.

3-Methoxy-N-benzoyliminopyridinium ylide (15f). The title compound was obtained as an off white solid (96%) according to the general procedure: mp 129 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.65 (s(br), 1H), 8.44 (d, J = 6.1 Hz, 1H), 8.19-8.12 (m, 2H), 7.54 (dd, J = 8.7, 6.2 Hz, 1H), 7.48-7.37 (m, 4H), 3.95 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.5, 157.4, 137.3, 135.6, 130.9, 130.0, 127.8 (2), 125.7, 123.1, 56.5; IR (neat) 3086, 1576, 1550, 1331, 905, 715 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 229.1 m/z , observed: 229.1 m/z .

3-Pyrrolidino-N-benzoyliminopyridinium ylide (15g). The title compound was obtained as a beige solid (91%) according to the general procedure: mp 119 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.12-8.05 (m, 2H), 7.91-7.87 (m, 1H), 7.81 (d, J = 6.0 Hz, 1H), 7.35-7.23 (m, 4H), 6.86 (dd, J = 8.6, 2.3 Hz, 1H), 3.24-3.14 (m, 4H), 1.99-1.86 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.6, 145.3, 137.6, 129.8, 127.8, 127.7, 125.5, 119.1, 47.6, 25.2; IR (neat) 3107, 3055, 2844, 1606, 1644, 1327, 710 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 268.1 m/z , observed: 268.1 m/z .

2-Isopropoxy-N-benzoyliminopyridinium ylide (15h). The title compound was obtained as a beige solid (54%) according to the general procedure but using a saturated aqueous NaHCO_3 solution instead of the aqueous NaOH solution: mp 112 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (dd, J = 6.4, 1.6 Hz, 1H), 8.16-8.12 (m, 2H), 7.93 (ddd, J = 8.6, 7.1, 1.7 Hz, 1H), 7.43-7.38 (m, 3H), 7.22-7.14 (m, 2H), 4.88 (sept, J = 6.1 Hz, 1H), 1.46 (d, J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 158.4, 144.8, 140.4, 137.7, 129.9, 128.2, 127.9, 117.2, 111.7, 76.4, 21.9; IR (neat) 3064, 2984, 2935, 1621, 1593, 1551, 1497, 1338, 1314, 1099, 716 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 257.1 m/z , observed: 257.1 m/z .

N-Benzoyliminopyrazinium ylide (15i). The title compound was obtained as a beige solid (43%) according to the general procedure: mp 121 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.30 (dd, J = 3.5, 1.4 Hz, 2H), 8.88 (dd, J = 3.5, 1.4 Hz, 2H), 8.19 (dd, J = 8.0, 1.3 Hz, 2H), 7.50-7.43 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 148.6, 136.6, 133.3, 131.4, 128.5, 128.3; IR (neat) 3060, 1607, 1590, 1557, 1424, 1315, 1283, 1184, 709 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{11}\text{H}_9\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 200.1 m/z , observed: 200.1 m/z .

N-Benzoyliminoquinolinium ylide (15j). The title compound was obtained as a beige solid (93%) according to the general procedure but adding benzoyl chloride first and letting it react for 30 min before adding the aqueous NaOH solution: ^1H NMR (400 MHz, CDCl_3) δ 9.25(d, J = 5.9 Hz, 1H), 8.85 (d, J = 8.9 Hz, 1H), 8.45 (d, J = 8.4 Hz, 1H), 8.35-8.30 (m, 2H), 8.05 (d, J = 8.2 Hz, 1H), 7.94 (t, J = 7.3 Hz, 1H), 7.81 (t, J = 7.4 Hz, 1H), 7.73 (dd, J = 8.3, 5.9 Hz, 1H), 7.50-7.47 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 145.5, 139.5, 138.3, 137.5, 133.2, 130.1, 129.9, 129.2, 128.5, 128.1, 127.9, 120.3, 120.1; IR (neat) 3063, 1598, 1551, 1515, 1325, 1296, 801, 714 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 249.1 m/z , observed: 249.1 m/z .

N-Benzoyliminoisoquinolinium ylide (15k). The title compound was obtained as a beige solid (93%) according to the general procedure but adding benzoyl chloride first and letting it react for 30 min before adding the aqueous NaOH solution: mp 174 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.89(s, 1H), 8.43 (d, J = 6.9 Hz, 1H), 8.23-8.20 (m, 2H), 8.08 (t, J = 8.3 Hz, 1H), 7.98 (t, J = 6.6 Hz, 1H), 7.91 (t, J = 7.3 Hz, 1H), 7.83 (t, J = 7.6 Hz, 1H), 7.46-7.42 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 145.2, 137.6, 136.5, 134.1, 133.5, 130.3, 130.1, 128.5, 128.1, 128.0, 126.9, 124.1; IR (neat) 3053, 1590, 1546, 1336, 1298, 908, 707 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 249.1 m/z , observed: 249.1 m/z .

2-(dimethylamino)-N-aminopyridinium 2,4-(dinitro)phenolate (17). The title compound was obtained as a bright orange solid (92%) according to the general procedure described for **13a**: mp 83 $^{\circ}\text{C}$; ^1H NMR (300 MHz, d_6 -DMSO) δ 8.66 (d, J = 4.7 Hz, 1H), 8.61 (d, J = 3.2 Hz, 1H), 8.25 (dt, J = 8.5, 1.8 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.80 (dd, J = 9.8, 3.2 Hz, 1H), 7.73 (dd, J = 7.2, 5.3 Hz, 1H), 6.78 (s(br), 2H), 6.34 (d, J = 9.8 Hz, 1H), 3.68 (s, 6H); ^{13}C NMR (100 MHz, d_6 -DMSO) δ 170.1, 158.5, 148.3, 141.1, 136.1, 127.5, 126.5, 125.0, 115.0, 57.4; IR (neat) 3275, 3105, 3045, 1590, 1548, 1530, 1464, 1314, 1269, 833 cm^{-1} ; LRMS (ES, Pos) calcd for $\text{C}_7\text{H}_{12}\text{N}_3$ $[\text{M}]^+$: 138.1 m/z , observed: 138.2 m/z .

3-Chloro-N-benzoyliminopyridinium ylide (19d). The title compound was obtained as a beige solid (94%) according to the general procedure: mp 129 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.10 (s(br), 1H), 8.76 (d, J = 6.2 Hz, 1H), 8.13 (d, J = 6.4 Hz, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.51 (t, J = 6.6 Hz, 1H), 7.49-7.35 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 142.4, 141.0, 137.0, 136.3, 133.7, 130.5, 128.1, 128.0, 126.0; IR (neat) 3096, 1591, 1547, 1324, 711 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{12}\text{H}_9\text{ClN}_2\text{O}$ $[\text{M}+\text{H}]^+$: 233.0 m/z , observed: 233.0 m/z .

3-Benzoyl-N-benzoyliminopyridinium ylide (19f). The title compound was obtained as a beige solid (49%) according to the general procedure but using a saturated aqueous NaHCO_3 solution instead of the aqueous NaOH solution: mp 143 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 9.19 (s, 1H), 9.04 (d, J = 6.3 Hz, 1H), 8.31 (dt, J = 6.8, 1.2 Hz, 2H), 8.29-8.13 (m, 2H), 7.89-7.84 (m, 2H), 7.80 (dd, J = 7.8, 6.4 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 8.0 Hz, 2H), 7.45-7.36 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 190.8, 171.0, 145.6, 144.5, 137.3, 136.9, 136.2, 134.5, 130.6, 130.2, 129.4, 128.2, 128.1, 126.0; IR (neat) 3062, 1668, 1593, 1551, 1322, 1284, 712 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 303.1 m/z , observed: 303.1 m/z .

3-Methoxycarbonyl-N-benzoyliminopyridinium ylide (19g). The title compound was obtained as a beige solid (67%) according to the general procedure but using a saturated aqueous NaHCO_3 solution instead of the aqueous NaOH solution: mp 132 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 9.43 (s, 1H), 9.04 (d, J = 5.8 Hz, 1H), 8.46 (d, J = 7.3 Hz, 1H), 8.16 (d, J = 7.7 Hz, 2H), 7.74 (t, J = 6.6 Hz, 1H), 7.46-7.39 (m, 3H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 162.6, 146.3, 144.5, 137.2, 136.9, 130.6, 129.6, 128.2, 128.1, 125.9, 53.6; IR (neat) 3063, 2954, 1730, 1592, 1551, 1437, 1323, 1286, 1128, 714 cm^{-1} ; LRMS (APCI, Pos) calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 257.1 m/z , observed: 257.1 m/z .

4-Cyano-*N*-benzoyliminopyridinium ylide (19h). The title compound was obtained as a beige solid (42%) according to the general procedure but using a saturated aqueous NaHCO₃ solution instead of the aqueous NaOH solution: mp 184 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.34 (d, *J* = 6.4 Hz, 2H), 8.15 (d, *J* = 7.3 Hz, 2H), 7.79 (d, *J* = 6.1 Hz, 2H), 7.49-7.40 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.9, 142.4, 136.7, 131.3, 128.5 (2), 128.3, 117.2, 115.0; IR (neat) 3097, 3048, 2237, 1587, 1557, 1543, 1436, 1319, 1291, 1164, 704 cm⁻¹; LRMS (APCI, Pos) calcd for C₁₃H₉N₃O [M+H]⁺ : 224.1 *m/z*, observed: 224.1 *m/z*.

4-Benzoyl-*N*-benzoyliminopyridinium ylide (19i). The title compound was obtained as a beige solid (75%) according to the general procedure but using a saturated aqueous NaHCO₃ solution instead of the aqueous NaOH solution: mp 179 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.13 (d, *J* = 7.1 Hz, 2H), 8.18 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.92 (d, *J* = 7.1 Hz, 2H), 7.84-7.79 (m, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.47-7.39 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 191.8, 170.8, 142.9, 137.0, 135.2, 134.4, 132.9, 130.8, 130.2, 129.2, 128.3, 128.2, 126.0; IR (neat) 3106, 3080, 3049, 1669, 1589, 1557, 1543, 1437, 1332, 1282, 1171, 713, 696 cm⁻¹; LRMS (APCI, Pos) calcd for C₁₉H₁₄N₂O₂ [M+H]⁺ : 303.1 *m/z*, observed: 303.1 *m/z*.

4-Methoxycarbonyl-*N*-benzoyliminopyridinium ylide (19j). The title compound was obtained as a beige solid (82%) according to the general procedure but using a saturated aqueous NaHCO₃ solution instead of the aqueous NaOH solution: mp 189 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.12 (d, *J* = 7.2 Hz, 2H), 8.18-8.13 (m, 4H), 7.47-7.38 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 163.0, 142.9, 137.1, 135.9, 130.8, 128.3, 128.1, 125.9, 53.6; IR (neat) 3103, 3071, 3032, 1721, 1548, 1437, 1324, 1287, 1240, 1179, 711, 702, 678 cm⁻¹; LRMS (APCI, Pos) calcd for C₁₄H₁₂N₂O₃ [M+H]⁺ : 257.1 *m/z*, observed: 257.1 *m/z*.

References

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^1H and ^{13}C spectra of selected compounds