Supporting Information

Facile metal-assisted hydrolysis of a urethane.

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2-Acetoxy-6-(bromomethyl)pyridine 11: 2-Acetoxy-6-methylpyridine (**10**, prepared following literature procedures[1]) (200 mg, 1.32 mmol), 2,2'-azobisisobutyronitrile (AIBN, 11 mg, 5 mol %) and CCl_4 (50 mL) were introduced into a 100 mL two-necked round-bottomed flask fitted with a reflux condenser and nitrogen inlet. The mixture was heated at reflux, and N-bromosuccinimide (NBS, 236 mg, 1.32 mmol) was added in 20 mg portions over a period of 2 hours. The resulting mixture was refluxed overnight. Two thirds of the solvent was evaporated under house vacuum and the mixture was allowed to cool down to room temperature and filtered. The filtrate was concentrated to give a yellow residue. This was chromatographed on silica gel (30 cm x 1.5 cm), eluting with EtOAc/hexane (1:4) to afford 160 mg (52 %) of the title compound as a colorless crystalline solid. **mp**: 55-56 ^{o}C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.80 (app.t, *J*=7.8 Hz, 1H), 7.38 (d, *J*=7.2 Hz, 1H), 7.04 (d, *J*=8.4 Hz, 1H), 4.50 (s, 2H), 2.35 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 168.8, 157.1, 156.1, 140.5, 121.7, 115.9, 32.9, 21.6. **HRMS** (ES): calculated for C_6H_7NBrO (M – CH_2=C=O +1) 187.9711. Found: 187.9718.

Pyridone 13: To a solution of methyl(pyridin-2-ylmethyl)amine (**12**, 200 mg, 1.64 mmol, prepared following literature procedures[2]) and triethylamine (600 µL, 6 equiv.) in CH_2Cl_2 (5 mL) was added a solution of 2-acetoxy-6-(bromomethyl)pyridine (**11**, 170 mg, 0.74 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred at room temperature for two hours. The reaction mixture was washed with water (4 mL x 2) and the aqueous layer was extracted with more CH_2Cl_2 (8 mL x 2). The combined organic layers were washed with brine (4 mL x 2), dried over Na_2SO_4, and the solvent evaporated to give a yellow-brown oil. This was chromatographed on silica gel (30 cm x 1.5 cm), eluting with EtOAc/MeOH (8:1) to afford 83 mg (49 %) of the title compound as a colourless viscous oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 10.59 (bs, 1H), 8.60 (d, *J*=5.2 Hz, 1H), 7.70 (dt, *J*=7.6, 2.0 Hz, 1H), 7.40 (d, *J*=7.6 Hz, 1H), 7.32 (dd, *J*= 9.2, 6.4 Hz, 1H), 7.21 (app.dd, *J*=7.2, 5.2 Hz, 1H), 6.45 (d, *J*=9.2 Hz, 1H), 6.05 (d, *J*=6.8 Hz, 1H), 3.78 (s, 2H), 3.50 (s, 2H), 2.31 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 163.8, 157.8, 149.2, 145.2, 140.9, 136.9, 123.4, 122.6, 119.5, 104.6, 63.1, 57.7, 42.9. **HRMS** (ES): calculated for $C_{13}H_{16}N_3O$ (M+1) 230.1293. Found: 230.1298. **UV** λ_{max} (water:MeCN 9:1 + TFA, c=2x10^{-4} M) 260, 285, 300 (ε= 3,300; 3,000; 3,700).

Carbamate 9: To a solution of pyridone **13** (83 mg, 0.36 mmol and *N*-methyl-*N*-phenylcarbamoyl chloride (**15**, from Aldrich, 183 mg, 3 equiv.) in anhydrous acetonitrile (15 mL) was added triethylamine (350 µL). The resulting mixture was heated at reflux overnight. The mixture was evaporated to dryness affording a yellow-brown oil. This was chromatographed on silica gel (30 cm x 1.5 cm), eluting with EtOAc/MeOH (4:1) to afford 110 mg (87 %) of the title compound as a colorless viscous oil. **^{1}H NMR** (CD_3COCD_3, 400 MHz): δ 8.49 (m, 1H), 7.84 (t, *J*=7.6 Hz, 1H), 7.74 (dt, *J*=7.2, 1.6 Hz, 1H), 7.58 (d, *J*=7.6 Hz, 1H), 7.51-7.46 (m, 3H), 7.43-7.39 (m, 2H), 7.27 (t, *J*=7.2Hz, 1H), 7.23-

1. Takashi, K.; Yasumasa, H.; Takasi, B.; Ichiro, T.; Hidehiko, K. *Chem. Lett*. **1991**, 1989.
2. Holzgrabe , U. *Arch. Pharm*. **1987**, *320*, 647.

7.19 (m, 1H), 7.01 (d, *J*= 7.6 Hz, 1H), 3.74 (s, 2H), 3.69 (s, 2H), 3.40 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (CD_3COCD_3, 100 MHz): δ 160.2, 159.6, 158.7, 153.5, 149.5, 143.9, 140.4, 136.9, 129.6, 127.1, 126.8, 123.4, 122.6, 120.9, 114.9, 64.2, 63.5, 42.9, 38.4. **HRMS** (ES): calculated for $C_{21}H_{23}N_4O_2$ (M+1) 363.1821. Found: 363.1809. **UV** λ_{max} (MeCN+TFA, c=2x10^{-4} M) 260, 285 (ε=13,700; 800); λ_{max} (MeCN/H_2O 1:1 + TFA) 260, 285 (ε=8,800; 900).

***N*-Methylaniline: UV** λ_{max} (water:MeCN 9:1 + TFA, c= 2x10^{-4} M) 254, 260, 276, 280, 285 (ε= 300, 250, 90, 90, 90).

Kinetic studies, general procedures.

Ionic strength was maintained with $NaClO_4$. pHs reported are those of the buffer solution prior to dilution with the organic solvent.[3] The buffers used were of the aminosulfonate type since these are known[4] to be poor ligands to divalent metals. Buffers used: 2-(*N*-morpholino)ethanesulfonic acid hydrate (MES, pK_a=6.1), 2-{[tris(hydroxymethyl)methyl]amino}-1-ethanesulfonic acid (TES, pK_a=7.5), *N*-[tris(hydroxymethyl)methyl]-3-aminopropane-1-sulfonic acid (TAPS, pK_a=8.4), 2-(cyclohexylamino)ethanesulfonic acid (CHES, pK_a=9.3), 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS, pK_a=10.4). Reactions were followed by reverse-phase HPLC (C18) by monitoring the changes in the areas of the *N*-methylaniline and carbamate **9** peaks at 254 nm (carbamate elutes at 4.75 min and aniline at 2.01 min in 65:35 water/acetonitrile containing 0.1 % v/v trifluoroacetic acid) and the area of the pyridone **13** peak at 300 nm (2.01 minutes). From the areas, concentrations were calculated using an external calibration method. Areas *vs* concentration plots were linear between 0-10 mM for aniline, 0-8 mM for carbamate and 0-5 mM for pyridone. Two mM solutions of the complex were used for kinetic studies. The majority of reactions were followed to at least 95 % completion and all of them (except when the contrary has been stated in the discussion) obeyed first-order reaction kinetics. Values of k_{obs} were calculated from the plots of ln[carbamate] *vs* time, using computer-assisted least-squares regression analysis (Excel 2000). Correlation coefficients were generally > 0.99 and never < 0.985.

3. Quoted pHs correspond to the buffers before mixing with the organic solvent. This may have an effect on the absolute rates of reaction but it should not significantly affect the relative rates.

4. Groves, J. T.; Baron, L. A. *J. Am. Chem. Soc*. **1989**, *111*, 5442.