Supporting Information

An efficient Mo(VI)-catalyzed hydration of nitrile with acetaldoxime

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General Methods.

Melting points were determined on a Thomas Hoover capillary apparatus and were uncorrected. ¹H NMR spectra were recorded on Bruker DPX-400 or DPX-500 spectrometer. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Yields refer to the isolated yields of the products after purification by silica-gel column chromatography (300 mesh). All starting chemicals are commercially available. All the amide products are known compounds and they were characterised by melting point and ¹H NMR spectra.

Experimental Procedures for Hydration of Various Nitriles

To a 25 mL round-bottom flask equipped with magnetic stirrer were added nitrile (2 mmol), acetaldoxime (6 mmol), sodium molybdate(VI) dihydrate (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 5-16 h. After cooling to room temperature, the solution was directly evaporated to dryness and the residue was purified by column chromatography on silica gel (ethyl acetate/n-hexane) to give the corresponding amide.

Benzamide (Table 1, entry 8). To a 25 mL round-bottom flask equipped with magnetic stirrer were added benzonitrile 206 mg (2 mmol), acetaldoxime 354 mg (6 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 12 h. After cooling to room temperature, the solution was directly evaporated to dryness and the residue was purified by column chromatography on silica gel (ethyl acetate/n-hexane = 1:1) to give benzamide as a white solid (218 mg, 90%). m.p. 127–128 °C (lit.^[1] m.p. 126–127 °C). ¹H NMR (500 MHz, DMSO-d₆): δ 7.98 (br. s, 1H), 7.87 (m, 2H), 7.53 (m, 1H), 7.45 (m, 2H), 7.40 (br. s, 1H). Data are in good agreement with the literature.^[2]

4-Methoxybenzamide (Table 2, entry 1). To a 25 mL round-bottom flask equipped with magnetic stirrer were added 4-methoxybenzonitrile 266 mg (2 mmol), acetaldoxime 472 mg (8 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 16 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:2) to give 4-methoxybenzamide as a white solid (220 mg, 73%). m.p. 166–167 °C (lit.^[3] m.p. 166 °C). ¹H NMR (400 MHz, DMSO-d₆): δ 7.87-7.85 (m, 3H), 7.19 (br. s, 1H), 6.98 (d, 2H, *J* = 8.2 Hz), 3.81 (s, 3H). Data are in good agreement with the literature.^[2]

3-Methylbenzamide (Table 2, entry 2). To a 25 mL round-bottom flask equipped with magnetic stirrer were added 3-methylbenzonitrile 234 mg (2 mmol), acetaldoxime 472 mg (8 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 16 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:1) to give 3-methylbenzamide as a white solid (224 mg, 83%). m.p. 93–94 °C

(lit.^[4] m.p. 92–93 °C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.92 (br. s, 1H), 7.70 (s, 1H), 7.66 (m, 1H), 7.34–7.31 (m, 3H), 2.36 (s, 3H). Data are in good agreement with the literature.^[2]

4-Chlorobenzamide (Table 2, entry 3). To a 25 mL round-bottom flask equipped with magnetic stirrer were added 4-chlorobenzonitrile 275 mg (2 mmol), acetaldoxime 354 mg (6 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 12 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:1) to give 4-chlorobenzamide as a white solid (283 mg, 91%). m.p. 178–179 °C (lit.^[5] m.p. 178–180 °C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.05 (br. s, 1H), 7.88 (d, 2H, *J* = 8.4 Hz), 7.52 (d, 2H, *J* = 8.4 Hz), 7.47 (br. s, 1H). Data are in good agreement with the literature.^[2]

4-Nitrobenzamide (Table 2, entry 4). To a 25 mL round-bottom flask equipped with magnetic stirrer were added 4-nitrobenzonitrile 296 mg (2 mmol), acetaldoxime 354 mg (6 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 12 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 2:1) to give 4-nitrobenzamide as a white solid (305 mg, 92%). m.p. 199–201 °C (lit.^[6] m.p. 200–202 °C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.33–8.30 (m, 3H), 8.11 (d, 2H, *J* = 8.4 Hz), 7.74 (br. s, 1H). Data are in good agreement with the literature.^[2]

Picolinamide (Table 2, entry 5). To a 25 mL round-bottom flask equipped with magnetic stirrer were added picolinonitrile 208 mg (2 mmol), acetaldoxime 236 mg (4 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 5 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 3:1) to give picolinamide as a white solid (212 mg, 87%). m.p. 104–106 °C (lit.^[5] m.p. 105–106 °C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.63 (d, 1H, *J* = 4.8 Hz), 8.13 (br. s, 1H), 8.04 (d, 1H, *J* = 7.6), 7.99 (m, 1H), 7.66 (br. s, 1H), 7.59 (m, 1H). Data are in good agreement with the literature.^[2]

Nicotinamide (Table 2, entry 6). To a 25 mL round-bottom flask equipped with magnetic stirrer were added nicotinonitrile 208 mg (2 mmol), acetaldoxime 236 mg (4 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 5 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:3) to give nicotinamide as a white solid (232 mg, 95%). m.p. 128–129 °C (lit.^[1] m.p. 128–129 °C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.03 (s, 1H), 8.70 (d, 1H, *J* = 4.4 Hz), 8.22–8.17 (m, 2H), 7.62 (br. s, 1H), 7.51 (m, 1H). Data are in good agreement with the literature.^[2]

Isonicotinamide (Table 2, entry 7). To a 25 mL round-bottom flask equipped with magnetic stirrer were added isonicotinonitrile 208 mg (2 mmol), acetaldoxime 236 mg (4 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 5 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:3) to give isonicotinamide as a white solid (232 mg, 95%). m.p. 157–158 °C (lit.^[7] m.p. 158 °C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.72 (d, 2H, *J* = 6.0 Hz), 8.25 (br. s, 1H), 7.76 (d, 2H, *J* = 6.0 Hz), 7.74 (br. s, 1H). Data are in good agreement with the literature.^[2]

3-Methylpicolinamide (Table 2, entry 8). To a 25 mL round-bottom flask equipped with magnetic stirrer were added 3-methylpicolinonitrile 236 mg (2 mmol), acetaldoxime 472 mg (8 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 16 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:2) to give 3-methylpicolinamide as a white solid (209 mg, 77%). m.p. 138–140 °C (lit.^[8] m.p. 140–141 °C). ¹H NMR (DMSO-*d*₆) δ 8.42 (1H, t), 7.98 (1H, br), 7.72 (1H, d, *J* = 7.6 Hz), 7.49 (1H, br), 7.43 (1H, m), 2.53 (3H, s). Data are in good agreement with the literature.^[8]

2-Furoamide (Table 2, entry 9). To a 25 mL round-bottom flask equipped with magnetic stirrer were added 2-Furonitrile 186 mg (2 mmol), acetaldoxime 236 mg (4 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 5 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:2) to give 2-furoamide as a white solid (191 mg, 86%). m.p. 139–141 °C (lit.^[9] m.p. 140–142 °C). ¹H NMR (400 MHz, DMSO-d₆): δ 7.81 (d, 1H, *J* = 0.8 Hz), 7.79 (br. s, 1H), 7.40 (br. s, 1H), 7.10 (d, 1H, *J* = 3.2 Hz), 6.61 (m, 1H). Data are in good agreement with the literature.^[2]

2-Phenylacetamide (Table 2, entry 10). To a 25 mL round-bottom flask equipped with magnetic stirrer were added 2-phenylacetonitrile 234 mg (2 mmol), acetaldoxime 354 mg (6 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 12 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:2) to give 2-phenylacetamide as a white solid (240 mg, 89%). m.p. 157–158 °C (lit.^[1] m.p. 158–159 °C) ¹H NMR (500 MHz, DMSO-d₆): δ 7.49 (br. s, 1H), 7.20–7.31 (m, 5H), 6.91 (br. s, 1H), 3.36 (s, 2H). Data are in good agreement with the literature.^[10]

Dodecanamide (Table 2, entry 11). To a 25 mL round-bottom flask equipped with magnetic stirrer were added dodecanenitrile 362 mg (2 mmol), acetaldoxime 354 mg (6 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 12 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:2) to give dodecanamide as a white solid (350 mg, 88%). m.p. 101–102 °C (lit.^[11] m.p. 101–102 °C) ¹H NMR (400 MHz, DMSO-d₆): δ 7.22 (br. s, 1H), 6.68 (br. s, 1H), 2.02 (t, 2H, *J* = 7.2 Hz), 1.46 (m, 2H), 1.29–1.25 (m, 16H), 0.87 (t, 3H, *J* = 6.0 Hz). Data are in good agreement with the literature.^[12]

Dodecanamide (Table 2, entry 12). To a 25 mL round-bottom flask equipped with magnetic stirrer were added octanenitrile 250 mg (2 mmol), acetaldoxime 354 mg (6 mmol), sodium molybdate(VI) dihydrate 48 mg (0.2 mmol) and H₂O (10 mL). The mixture was heated to reflux for 12 h. After removal of the solvent (H₂O) the residue was purified by column chromatography (hexanes/EtOAc = 1:3) to give octanamide as a white solid (249 mg, 87%). m.p. 105–106 °C (lit.^[13] m.p. 106–107 °C) ¹H NMR (500 MHz, DMSO-d₆): δ 7.18 (br. s, 1H), 6.63 (br. s, 1H), 1.99 (t, 2H, *J* = 7.4 Hz), 1.45 (m, 2H), 1.27–1.22 (m, 8H), 0.84 (t, 3H, *J* = 6.4 Hz). Data are in good agreement with the literature.^[12]

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