One-pot synthesis of amines from biomass resources catalyzed by $HReO_4$

João A. T. Caetano and Ana C. Fernandes*

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

anacristinafernandes@tecnico.ulisboa.pt

1.General information

All the reactions were carried out under air atmosphere and without any dry solvent. Carbohydrates, anilines, silanes and the catalyst $HReO_4$ (75-80% aqueous solution) were obtained from commercial suppliers and were used without further purification. Flash chromatography was performed on MN Kieselgel 60M 230-400 mesh. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were measured on a Bruker Avance II^{+} 400 MHz and 300 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard. The furfural yields were determined by ^{1}H NMR spectroscopy using mesitylene as internal standard, the pulse sequence zg30, D1 = 1.0 s and position of O1 = 2470.97 Hz.

2.General procedure for the conversion of xylose into furfural catalyzed by $HReO_4$

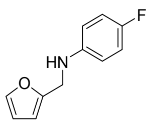
To a Schlenk flask equipped with a J. Young tap containing a solution of xylose (1.0 mmol) in 1,4-dioxane (10 mL) was added $HReO_4$ (5 mol%). The reaction mixture was stirred in a closed Schlenk at 140 °C during 2 h. The yield of furfural was determined by spectroscopy ^{1}H NMR using mesitylene as internal standard.

3.General procedure for the one-pot synthesis of furfurylamines

To a Schlenk flask equipped with a J. Young tap containing a solution of carbohydrate (1.0 mmol of pentose) in 1,4-dioxane (10 mL) was added $HReO_4$ (5 mol%). The reaction mixture was stirred in a closed Schlenk at 140 °C during 2 h. Then, the reaction mixture was cooled at room temperature and aniline (1.0 mmol) and dimethylphenylsilane (1.2 mmol) was added. After 1h at 140ºC, the reaction mixture was evaporated and the residue was purified by flash chromatography with appropriate mixtures of *n*-hexane:ethyl acetate, affording the furfurylamines.

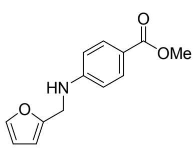
4. Characterization of the products

Table 3, entry 2



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (s, 1H), 6.95 (t, J = 8.70, 8.73 Hz, 2H), 6.64-6.60 (m, 2H), 6.35 (d, J = 3.06 Hz, 1H), 6.25 (d, J = 3.06 Hz, 1H), 4.29 (s, 2H), 3.89 (brs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2 (d, J_{CF} = 241.5Hz), 152.7, 144.0 (d, J_{CF} = 1.93 Hz), 142.1, 115.7 (d, J_{CF} = 22.2 Hz), 114.2 (d, J_{CF} = 7.4 Hz), 110.4, 107.2, 42.1 ppm. Anal. Calcd. for $C_{11}H_{10}FNO$: C, 69.10; H, 5.27; N, 7.33. Found: C, 69.33; H, 5.48; N, 7.59.

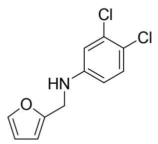
Table 3, entry 3



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, J = 8.67 Hz, 2H), 7.36 (s, 1H), 6.61 (d, J = 8.67 Hz, 2H), 6.31 (d, J = 0.69 Hz, 1H), 6.22 (d, J = 3.0 Hz, 1H), 4.68 (brs, 1H), 4.33 (d,

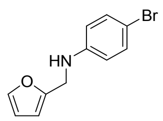
J = 2.91Hz, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.4, 151.8, 151.5, 142.2, 131.5, 118.8, 111.8, 110.5, 107.4, 51.6, 40.7 ppm. Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.83; H, 5.90; N, 6.27.

Table 3, entry 4



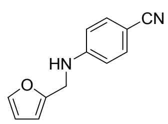
^1H NMR (300 MHz, $CDCl_3$): δ 7.38 (t, J = 0.81, 0.9 Hz,1H), 7.19 (d, J = 8.73 Hz, 1H), 6.73 (d, J = 2.58 Hz, 1H), 6.48 (dd, J = 2.64, 6.09 Hz, 1H), 6.34-6.33 (m, 1H), 6.24 (d, J = 3.12 Hz, 1H), 4.27 (s, 2H), 4.13 (brs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.7, 147.1, 142.3, 132.8, 130.7, 120.4, 114.2, 112.9, 110.5, 107.5, 41.3 ppm. Anal. Calcd. for $C_{11}H_9Cl_2NO$: C, 54.57; H, 3.75; N, 5.79. Found: C, 54.70; H, 3.93; N, 5.96.

Table 3, entry 5



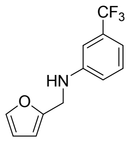
^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.26 (d, J = 8.73 Hz, 2H), 6.55 (d, J = 8.73 Hz, 2H), 6.32 (d, J = 1.68 Hz, 1H), 6.23 (d, J = 2.82 Hz, 1H), 4.29 (s, 2H), 4.05 (brs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 146.7, 142.2, 132.1, 114.8, 110.5, 109.8, 107.3, 41.5 ppm. Anal. Calcd. for $C_{11}H_{10}BrNO$: C, 52.41; H, 4.00; N, 5.56. Found: C, 52.58; H, 3.98; N, 5.69.

Table 3, entry 6



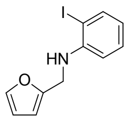
^1H NMR (300 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.38 (d, J = 3.18 Hz, 2H), 6.64 (d, J = 8.58 Hz, 2H),6.34 (s, 1H), 6.26 (d, J = 2.82 Hz, 1H), 4.87 (brs, 1H), 4.35 (d, J = 5.25 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.2, 150.8, 142.2, 133.5, 120.4, 112.4, 110.4, 107.5, 98.8, 40.3 ppm. Anal. Calcd. for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.97; H, 5.28; N, 14.29.

Table 3, entry 7



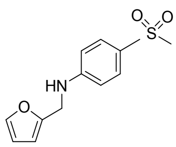
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (s, 1H), 7.24 (s, 1H), 6.95 (d, *J* = 6.27 Hz, 1H), 6.85 (s, 1H), 6.77 (d, *J* = 7.65 Hz, 1H), 6.31 (s, 1H), 6.23 (s, 1H), 4.31 (s, 2H), 4.21 (brs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.0, 147.8, 142.3, 131.65 (q, J_{CF} = 31.56 Hz), 129.8, 124.4 (d, J_{CF} = 270.6 Hz), 116.1, 114.5 (d, J_{CF} = 3.68 Hz), 110.5, 109.40 (d, J_{CF} = 3.62 Hz), 107.5, 41.2 ppm. Anal. Calcd. for $C_{12}H_{10}F_3NO$: C, 59.75; H, 4.18; N, 5.81. Fou31.56Hz), nd: C, 59.91; H, 4.33; N, 5.99.

Table 3, entry 8



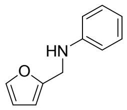
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.32 Hz, 1H), 7.40 (s, 1H), 7.22 (t, *J* = 7.48, 7.24 Hz, 1H), 6.67 (d, *J* = 7.92 Hz, 1H), 6.49 (t, *J* = 7.16, 6.88 Hz, 1H), 6.35 (s, 1H), 6.27 (s, 1H), 4.59 (brs, 1H), 4.37 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1, 146.8, 142.1, 139.2, 129.5, 119.3, 111.0, 110.5, 107.2,85.7,41.7 ppm. Anal. Calcd. for $C_{11}H_{10}INO$: C, 44.17; H, 3.37; N, 4.68. Found: C, 44.30; H, 3.51; N, 4.82.

Table 3, entry 9



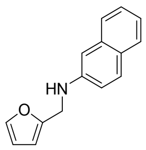
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.79 Hz, 2H), 7.33 (d, *J* = 0.96 Hz, 1H), 6.66 (d, *J* = 8.79Hz, 2H), 6.29 (d, *J* = 1.2Hz, 1H), 6.22 (s, 1H), 4.99 (brs, 1H), 4.32 (d, *J* = 4.95Hz, 2H), 2.95 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.8, 151.3, 142.2, 129.2, 127.4, 112.1, 110.4, 107.5, 45.0, 40.4 ppm. Anal. Calcd. for $C_{13}H_{16}NO_3S$: C, 58.62; H, 6.06; N, 5.26. Found: C, 58.79; H, 6.20; N, 5.38.

Table 3, entry 10



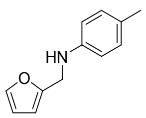
[1]H NMR (300 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.20 (t, *J* = 7.50, 8.22 Hz, 2H), 6.75 (t, *J* = 7.29, 7.35 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 2H), 6.33 (dd, *J* = 2.04, 0.96 Hz, 1H), 6.24 (d, *J* = 3.06 Hz), 4.33 (s, 2H), 4.02 (brs, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.9, 147.8, 142.1, 129.4, 118.2, 113.3, 110.5, 107.1, 41.6 ppm. Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.40; H, 6.59; N, 8.30.

Table 3, entry 11



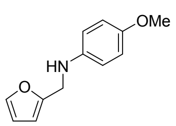
[1]H NMR (300 MHz, $CDCl_3$): δ 7.70-7.62 (m, 3H), 7.40-7.35 (m, 2H), 7.25-7.20 (m, 1H), 6.94-6.91 (m, 2H), 6.34 (d, *J* = 4.92 Hz, 1H), 6.29 (d, *J* = 3.15 Hz, 1H), 4.43 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5, 145.3, 142.1, 135.1, 129.1, 127.9, 127.7, 126.5, 126.2, 122.4, 118.1, 110.5, 107.3, 105.3, 41.6 ppm. Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.81; H, 6.05; N, 6.33.

Table 3, entry 12



[1]H NMR (300 MHz, $CDCl_3$): δ 7.38 (s, 1H), 7.01 (d, *J* = 8.1Hz, 2H), 6.62 (d, *J* = 8.25 Hz, 2H), 6.33 (s, 1H), 6.24 (d, *J* = 2.79 Hz, 1H), 4.31 (s, 2H), 2,26 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.1, 145.5, 142.0, 129.8, 127.4, 113.5, 110.4, 107.0, 41.9, 20.5 ppm. Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 77.12; H, 7.15; N, 7.63.

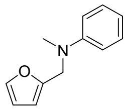
Table 3, entry 13



[1]H NMR (300 MHz, $CDCl_3$): δ 7.42 (s, 1H), 6.85 (d, *J* = 5.04 Hz, 2H), 6.68 (d, *J* = 7.26 Hz, 2H), 6.37 (s, 1H), 6.27 (s, 1H), 4.30 (s, 2H), 3.78 (s, 4H) ppm. ^{13}C NMR (101 MHz,

$CDCl_3$): δ 153.0, 152.4, 141.8, 141.7, 114.7, 114.5, 110.3, 106.8, 55.5, 42.2 ppm. Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.10; H, 6.59; N, 7.01.

Table 3, entry 14



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (s, 1H), 7.29-7.23 (m, 2H), 6.85 (d, *J* = 8.22 Hz, 2H), 6.76 (t, *J* = 7.26 Hz, 1H), 6.31 (s, 1H), 6.15 (d, *J* = 2.76 Hz, 1H), 4.48 (s, 2H), 3.01 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 149.4, 141.8, 129.1, 117.1, 113.0, 110.2, 107.2, 49.9, 38.3 ppm. Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 77.11; H, 7.16; N, 7.59.