One-pot synthesis of amines from biomass resources catalyzed by HReO₄

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1. General information

All the reactions were carried out under air atmosphere and without any dry solvent. Carbohydrates, anilines, silanes and the catalyst HReO₄ (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. ¹H NMR, ¹³C NMR and ³¹P 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 ¹H NMR spectroscopy using mesitylene as internal standard, the pulse sequence zg30, D1 = 1.0 s and position of O1 = 2470.97 Hz.

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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 140°C, 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

1H 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, $J_{CF} = 241.5$Hz), 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

1H 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$_3$): $\delta$ 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

![Chemical structure image]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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$_9$Cl$_2$NO: C, 54.57; H, 3.75; N, 5.79. Found: C, 54.70; H, 3.93; N, 5.96.

Table 3, entry 5

![Chemical structure image]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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

![Chemical structure image]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 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$_3$): $\delta$ 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$_{16}$N$_2$O: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.97; H, 5.28; N, 14.29.
Table 3, entry 7

\[ \text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): } \delta 7.35 (s, 1H), 7.24 (s, 1H), 6.95 (d, } J = 6.27 \text{ Hz, 1H), } \]
\[ 6.85 (s, 1H), 6.77 (d, } J = 7.65 \text{ Hz, 1H), 6.31 (s, 1H), 6.23 (s, 1H), 4.31 (s, 2H), 4.21 (brs, 1H) ppm. } \]
\[ \text{\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): } \delta 152.0, 147.8, 142.3, 131.65 (q, } J_{CF} = 31.56 \text{ Hz), 129.8, 124.4 (d, } J_{CF} = 270.6 \text{ Hz), 116.1, 114.5 (d, } J_{CF} = 3.68 \text{ Hz), 110.5, 109.40 (d, } J_{CF} = 3.62 \text{ Hz), 107.5, 41.2 ppm. Anal. Calcd. for C\textsubscript{12}H\textsubscript{10}F\textsubscript{3}NO: C, 59.75; H, 4.18; N, 5.81. Fou31.56Hz), nd: C, 59.91; H, 4.33; N, 5.99. } \]

Table 3, entry 8

\[ \text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): } \delta 7.70 (d, } J = 7.32 \text{ Hz, 1H), 7.40 (s, 1H), 7.22 (t, } J = 7.48, 7.24 \text{ Hz, 1H), 6.67 (d, } J = 7.92 \text{ Hz, 1H), 6.49 (t, } J = 7.16, 6.88 \text{ Hz, 1H), 6.35 (s, 1H), 6.27 (s, 1H), 4.59 (brs, 1H), 4.37 (s, 2H) ppm. } \]
\[ \text{\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): } \delta 152.1, 146.8, 142.1, 139.2, 129.5, 119.3, 111.0, 110.5, 107.2, 85.7, 41.7 \text{ ppm. Anal. Calcd. for C\textsubscript{11}H\textsubscript{10}INO: C, 44.17; H, 3.37; N, 4.68. Found: C, 44.30; H, 3.51; N, 4.82. } \]

Table 3, entry 9

\[ \text{\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): } \delta 7.63 (d, } J = 8.79 \text{ Hz, 2H), 7.33 (d, } J = 0.96 \text{ Hz, 1H), 6.66 (d, } J = 8.79Hz, 2H), 6.29 (d, } J = 1.2Hz, 1H), 6.22 (s, 1H), 4.99 (brs, 1H), 4.32 (d, } J = 4.95Hz, 2H), 2.95 (s, 3H) ppm. } \]
\[ \text{\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): } \delta 151.8, 151.3, 142.2, 129.2, 127.4, 112.1, 110.4, 107.5, 45.0, 40.4 \text{ ppm. Anal. Calcd. for C\textsubscript{13}H\textsubscript{16}NO\textsubscript{3}S: C, 58.62; H, 6.06; N, 5.26. Found: C, 58.79; H, 6.20; N, 5.38. } \]
Table 3, entry 10

\[
\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta 7.37 (s, 1H), 7.20 (t, J = 7.50, 8.22 \text{ Hz, } 2H), 6.75 (t, J = 7.29, 7.35 \text{ Hz, } 1H), 6.69 (d, J = 8.4 \text{ Hz, } 2H), 6.33 (dd, J = 2.04, 0.96 \text{ Hz, } 1H), 6.24 (d, J = 3.06 \text{ Hz}), 4.33 (s, 2H), 4.02 (brs, 1H) \text{ ppm.} \\
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta 152.9, 147.8, 142.1, 129.4, 118.2, 113.3, 110.5, 107.1, 41.6 \text{ ppm. Anal. Calcd. for C}\text{H}_{11}\text{NO: } C, 76.28; H, 6.40; N, 8.09. \text{ Found: C, 76.40; H, 6.59; N, 8.30.}
\end{align*}
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Table 3, entry 11

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\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta 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 \text{ Hz, } 1H), 6.29 (d, J = 3.15 \text{ Hz, } 1H), 4.43 (s, 2H) \text{ ppm.} \\
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta 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 \text{ ppm. Anal. Calcd. for C}\text{H}_{13}\text{NO: } C, 80.69; H, 5.87; N, 6.27. \text{ Found: C, 80.81; H, 6.05; N, 6.33.}
\end{align*}
\]

Table 3, entry 12

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\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta 7.38 (s, 1H), 7.01 (d, J = 8.1Hz, 2H), 6.62 (d, J = 8.25 \text{ Hz, 2H}), 6.33 (s, 1H), 6.24 (d, J = 2.79 \text{ Hz, 1H}), 4.31 (s, 2H), 2.26 (s, 3H) \text{ ppm.} \\
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta 153.1, 145.5, 142.0, 129.8, 127.4, 113.5, 110.4, 107.0, 41.9, 20.5 \text{ ppm. Anal. Calcd. for C}\text{H}_{13}\text{NO: } C, 76.98; H, 7.00; N, 7.48. \text{ Found: C, 77.12; H, 7.15; N, 7.63.}
\end{align*}
\]

Table 3, entry 13

\[
\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta 7.42 (s, 1H), 6.85 (d, J = 5.04 \text{ Hz, 2H}), 6.68 (d, J = 7.26 \text{ Hz, 2H}), 6.37 (s, 1H), 6.27 (s, 1H), 4.30 (s, 2H), 3.78 (s, 4H) \text{ ppm.} \\
\text{C NMR (101 MHz, } \text{CDCl}_3\text{): } & \delta 155.0, 145.0, 142.0, 129.8, 127.4, 113.5, 110.4, 107.0, 41.9, 20.5 \text{ ppm. Anal. Calcd. for C}\text{H}_{13}\text{NO: } C, 76.98; H, 7.00; N, 7.48. \text{ Found: C, 77.12; H, 7.15; N, 7.63.}
\end{align*}
\]
CDCl₃): 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 C₁₂H₁₃NO₂: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.10; H, 6.59; N, 7.01.

Table 3, entry 14

\[
\text{\( ^1H \) NMR (300 MHz, CDCl₃): \( \delta \) 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.} \\
\text{\( ^{13}C \) NMR (75 MHz, CDCl₃): \( \delta \) 152.3, 149.4, 141.8, 129.1, 117.1, 113.0, 110.2, 107.2, 49.9, 38.3 ppm. Anal. Calcd. for C₁₂H₁₃NO: C, 76.98; H, 7.00; N, 7.48. Found: C, 77.11; H, 7.16; N, 7.59.}
\]