Conversion of furfural to tetrahydrofuran-derived secondary amines under mild conditions

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Experimental Section

Chemicals

Furfural (99%), 1-butylamine (99.5%), 1-octylamine (99%), 1-dodecylamine (98%), cyclohexylamine (99%), ethanolamine (99%, Sigma-Aldrich), 3-amino-1-propanol (99%), amino-2-propanol (93%), 3-amino-1,2-propanediol (97%), aniline (99%), benzylamine (99%), p-toluidine (99%, Sigma-Aldrich), p-anisidine (99%), ethylenediamine (99%), 3,4-dimethoxyphenethylamine (97%), N,N-dimethylethlenediamine (95%), 3-(dimethylamino)-1-propylamine (99%), 3-(diethylamino)propylamine (99%) and acetonitrile (99.8%), all supplied by Sigma-Aldrich, were used as reagents. Ethanol (99.8%), tetrahydrofuran (99.9%) and toluene (99.8%), all supplied by Sigma-Aldrich, were used as solvents for the catalytic tests. Chloroform-d (99.8 atom% D) and dimethyl sulfoxide-D6 (99.8 atom% D), also supplied by Sigma-Aldrich, were used as deuterated solvents for NMR analysis. Finally, Pt(5%)/C, Pt(5%)/Al₂O₃, Pd(5%)/C, Pd(5%)/Al₂O₃, all provided by Johnson Matthey, were used as catalysts.

General procedure for synthesis of secondary amines

The reactions were carried in a 20-mL round bottom flask equipped with a H₂ balloon. In a typical experiment, the reactor was charged with 1 mmol of furfural, 1 mmol of the given amine, 5 g of ethanol and 9.6 mg of the catalyst. The reactor was sealed and flushed with H₂ three times. Then a H₂ balloon (0.1 MPa H₂) was introduced into the reactor and the reaction was started. After the reaction, the products were analyzed and quantified on a BRUKER SCION 455-GC equipped with a HP-5MS capillary column with 5 wt% phenyl groups, a FID detector, and a split/splitless injection. N-dodecane was used as internal standard. ¹H and ¹³C NMR and HRMS analyses were also performed.
**Fig. S1** TG profiles of Pd/Al₂O₃ under air: (a) fresh and (b) spent catalyst.

**Fig. S2** Effect of reaction temperature; Reaction conditions: FF (1 mmol), BuNH₂ (1 mmol), EtOH (5 g), Pd/Al₂O₃ (10 mg), H₂ (1 MPa).
Characterization of products

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\begin{align*}
\mathrm{H} \text{ NMR} \ (400 \text{ MHz, CDCl}_3): & \ \delta \ 8.06 \ (s, \ 1\text{H}), \ 7.49 \ (d, \ J = 1.7 \text{Hz, 1H}), \ 6.70 \ (d, \ J = 3.4 \text{Hz, 1H}), \ 6.45 \ (dd, \ J = 3.4, 1.8 \text{Hz, 1H}), \ 3.56 \ (td, \ J = 7.0, 1.3 \text{Hz, 2H}), \ 1.76 \ – \ 1.60 \ (m, \ 2\text{H}), \ 1.44 \ – \ 1.26 \ (m, \ 2\text{H}), \ 0.92 \ (t, \ J = 7.4 \text{Hz, 3H}). \\
\mathrm{C} \text{ NMR} \ (101 \text{ MHz, CDCl}_3): & \ \delta \ 151.61, \ 149.35, \ 144.52, \ 113.55, \ 111.49, \ 61.59, \ 32.90, \ 20.42, \ 13.87.
\end{align*}
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\begin{align*}
\mathrm{H} \text{ NMR} \ (400 \text{ MHz, CDCl}_3): & \ \delta \ 7.35 \ (dd, \ J = 1.8, 0.8 \text{Hz, 1H}), \ 6.30 \ (dd, \ J = 3.1, 1.9 \text{Hz, 1H}), \ 6.16 \ (d, \ J = 3.1 \text{Hz, 1H}), \ 3.77 \ (s, \ 2\text{H}), \ 2.66 \ – \ 2.51 \ (m, \ 2\text{H}), \ 1.66 \ – \ 1.41 \ (m, \ 3\text{H}), \ 1.38 \ – \ 1.29 \ (m, \ 2\text{H}), \ 0.89 \ (d, \ J = 7.3 \text{Hz, 3H}). \\
\mathrm{C} \text{ NMR} \ (101 \text{ MHz, CDCl}_3): & \ \delta \ 154.07, \ 141.70, \ 110.05, \ 106.73, \ 48.88, \ 46.29, \ 32.11, \ 20.45, \ 14.00.
\end{align*}
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\begin{align*}
\mathrm{H} \text{ NMR} \ (400 \text{ MHz, CDCl}_3): & \ \delta \ 3.98 \ (qd, \ J = 7.4, 4.0 \text{Hz, 1H}), \ 3.82 \ (dt, \ J = 8.2, \ 6.7 \text{Hz, 1H}), \ 3.77 \ – \ 3.67 \ (m, \ 1\text{H}), \ 2.69 \ – \ 2.53 \ (m, \ 4\text{H}), \ 2.00 \ – \ 1.90 \ (m, \ 1\text{H}), \ 1.90 \ – \ 1.77 \ (m, \ 2\text{H}), \ 1.57 \ – \ 1.40 \ (m, \ 4\text{H}), \ 1.38 \ – \ 1.25 \ (m, \ 2\text{H}), \ 0.89 \ (t, \ J = 7.3 \text{Hz, 3H}). \\
\mathrm{C} \text{ NMR} \ (101 \text{ MHz, CDCl}_3): & \ \delta \ 78.36, \ 67.88, \ 54.63, \ 49.93, \ 32.27, \ 29.35, \ 25.77, \ 20.50, \ 14.05.
\end{align*}
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HRMS (ESI-TOF, m/z): Calcd for C_{13}H_{20}NO [M+H]+ 158.1539; found 158.1540

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\begin{align*}
\mathrm{H} \text{ NMR} \ (400 \text{ MHz, CDCl}_3): & \ \delta \ 3.99 \ (qd, \ J = 7.4, 4.1 \text{Hz, 1H}), \ 3.83 \ (dt, \ J = 8.2, \ 6.7 \text{Hz, 1H}), \ 3.78 \ – \ 3.68 \ (m, \ 1\text{H}), \ 2.74 \ – \ 2.51 \ (m, \ 4\text{H}), \ 2.05 \ – \ 1.77 \ (m, \ 3\text{H}), \ 1.61 \ – \ 1.38 \ (m, \ 4\text{H}), \ 1.36 \ – \ 1.16 \ (d, \ J = 6.2 \text{Hz, 10H}), \ 0.96 \ – \ 0.75 \ (m, \ 3\text{H}). \\
\mathrm{C} \text{ NMR} \ (101 \text{ MHz, CDCl}_3): & \ \delta \ 78.37, \ 67.87, \ 54.62, \ 50.27, \ 31.83, \ 30.15, \ 29.55, \ 29.36, \ 29.26, \ 27.38, \ 25.77, \ 22.66, \ 14.09.
\end{align*}
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HRMS (ESI-TOF, m/z): Calcd for C_{13}H_{28}NO [M+H]+ 214.2165; found 214.2169
\[ \text{NMR (400 MHz, CDCl}_3\text{): } \delta 4.00 \text{ (qd, } J = 7.4, 4.1 \text{ Hz, 1H), 3.84 \text{ (dt, } J = 8.3, 6.7 \text{ Hz, 1H), 3.78} \text{ – } 3.69 \text{ (m, 1H), 2.75} \text{ – } 2.53 \text{ (m, 4H), 2.02 – } 1.92 \text{ (m, 1H), 1.92 – } 1.80 \text{ (m, 2H), 1.64 \text{ (bvs, 1H), 1.58} \text{ – } 1.41 \text{ (m, 3H), } 1.35 \text{ – } 1.17 \text{ (m, 1H), 0.93 – } 0.80 \text{ (m, 3H).} \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{): } \delta 78.32, 67.89, 54.58, 50.25, 31.92, 30.11, 29.67, 29.64, 29.62, 29.61, 29.59, 29.37, 29.35, 29.37, 25.77, 22.69, 14.12. \]

HRMS (ESI-TOF, m/z): Calcd for C\textsubscript{17}H\textsubscript{35}NO \([\text{M+H}]^+\) 270.2791; found 270.2805

\[ \text{NMR (400 MHz, CDCl}_3\text{): } \delta 3.99 \text{ (qd, } J = 7.3, 3.8 \text{ Hz, 1H), 3.84 \text{ (dt, } J = 8.2, 6.6 \text{ Hz, 1H), 3.78} \text{ – } 3.70 \text{ (m, 1H), 3.62 \text{ (t, } J = 5.2 \text{ Hz, 2H), 2.79 \text{ (td, } J = 4.9, 1.5 \text{ Hz, 2H), 2.75} \text{ – } 2.59 \text{ (m, 2H), 2.39 \text{ (bvs, 2H), 2.02} – \text{ 1.81 \text{ (m, 3H), 1.62 – } 1.45 \text{ (m, 1H).} \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{): } \delta 78.30, 67.96, 60.82, 53.76, 51.14, 29.22, 25.80. \]

HRMS (ESI-TOF, m/z): Calcd for C\textsubscript{17}H\textsubscript{35}NO \([\text{M+H}]^+\) 270.2791; found 270.2805

\[ \text{NMR (400 MHz, CDCl}_3\text{): } \delta 3.98 \text{ (qd, } J = 7.2, 3.7 \text{ Hz, 1H), 3.88} \text{ – } 3.77 \text{ (m, 3H), 3.72 \text{ (dt, } J = 8.2, 6.7 \text{ Hz, 1H), 3.14 \text{ (bvs, 2H), 2.89 \text{ (t, } J = 5.6 \text{ Hz, 2H), 2.74 \text{ (dd, } J = 12.0, 3.7 \text{ Hz, 1H), 2.61 \text{ (dd, } J = 12.0, 7.3 \text{ Hz, 1H), 2.01} – \text{ 1.80 \text{ (m, 3H), 1.75 – } 1.61 \text{ (m, 2H), 1.61 – } 1.47 \text{ (m, 1H).} \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{): } \delta 77.90, 68.01, 64.34, 53.97, 49.97, 30.55, 29.14, 25.87. \]

HRMS (ESI-TOF, m/z): Calcd for C\textsubscript{17}H\textsubscript{35}NO \([\text{M+H}]^+\) 270.2791; found 270.2805
\( ^{13} \text{C NMR (101 MHz, CDCl}_3 \): \delta 78.31, 78.30, 68.03, 67.97, 65.52, 65.34, 56.88, 56.87, 53.95, 53.87, 29.18, 29.14, 25.86, 25.83, 20.35, 20.31.} \\
HRMS (ESI-TOF, m/z): Calcd for C\(_8\)H\(_{18}\)NO\(_2\) \([\text{M+H}]^+\) 160.1332; found 160.1337

\( ^{1} \text{H NMR (400 MHz, CDCl}_3 \): \delta 4.00 (qt, J = 7.1, 3.4 Hz, 1H), 3.89 – 3.80 (m, 1H), 3.80 – 3.64 (m, 3H), 3.58 (ddd, J = 11.3, 7.8, 5.0 Hz, 1H), 3.01 (brs, 3H), 2.86 – 2.57 (m, 4H), 2.03 – 1.80 (m, 3H), 1.60 – 1.45 (m, 1H).} \\

\( ^{13} \text{C NMR (101 MHz, CDCl}_3 \): \delta 78.15, 78.10, 69.76, 69.74, 68.01, 68.00, 65.65, 65.58, 54.22, 52.45, 52.30, 29.23, 29.21, 25.80.} \\
HRMS (ESI-TOF, m/z): Calcd for C\(_8\)H\(_{18}\)NO\(_3\) \([\text{M+H}]^+\) 176.1281; found 176.1287

\( ^{1} \text{H NMR (400 MHz, CDCl}_3 \): \delta 4.02 – 3.92 (m, 1H), 3.84 (dt, J = 8.2, 6.7 Hz, 1H), 3.78 – 3.68 (m, 1H), 2.72 (dd, J = 11.8, 3.8 Hz, 1H), 2.62 (dd, J = 11.8, 8.1 Hz, 1H), 2.41 (tt, J = 10.5, 3.8 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.92 – 1.80 (m, 4H), 1.76 – 1.66 (m, 2H), 1.65 – 1.45 (m, 3H), 1.31 – 0.98 (m, 5H).} \\

\( ^{13} \text{C NMR (101 MHz, CDCl}_3 \): \delta 78.61, 67.84, 56.96, 51.65, 33.55, 33.47, 29.43, 26.18, 25.73, 25.07, 25.05.} \\
HRMS (ESI-TOF, m/z): Calcd for C\(_{11}\)H\(_{22}\)NO \([\text{M+H}]^+\) 184.1696; found 184.1704

\( ^{1} \text{H NMR (400 MHz, CDCl}_3 \): \delta 3.99 (qd, J = 7.4, 4.1 Hz, 1H), 3.90 – 3.79 (m, 1H), 3.79 – 3.68 (m, 1H), 2.78 – 2.51 (m, 4H), 2.04 – 1.78 (m, 3H), 1.73 – 1.58 (m, 5H), 1.57 – 1.42 (m, 2H), 1.37 (dt, J = 8.5, 6.2 Hz, 2H), 1.33 – 1.06 (m, 4H), 0.96 – 0.81 (m, 2H).} \\

\( ^{13} \text{C NMR (101 MHz, CDCl}_3 \): \delta 78.38, 67.89, 54.72, 47.91, 37.85, 35.78, 33.49, 33.43, 29.37, 26.62, 26.33, 25.78.}
HRMS (ESI-TOF, m/z): Calcd for C_{13}H_{26}NO [M+H]^+ 212.2009; found 212.2007

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\text{O} \quad \text{N} \quad \text{H} \quad \text{C} \quad \text{N}
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$^1$H NMR (400 MHz, CDCl$_3$): δ 7.23 – 7.11 (m, 2H), 6.74 – 6.67 (m, 1H), 6.67 – 6.59 (m, 2H), 4.14 (qd, J = 7.1, 3.8 Hz, 1H), 4.00 (brs, 1H), 3.89 (dt, J = 8.4, 6.6 Hz, 1H), 3.79 (dt, J = 8.3, 6.8 Hz, 1H), 3.26 (dd, J = 12.3, 3.8 Hz, 1H), 3.08 (dd, J = 12.3, 7.5 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.97 – 1.86 (m, 2H), 1.72 – 1.60 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 148.40, 129.21, 117.48, 113.04, 77.58, 68.06, 48.19, 29.12, 25.82.

HRMS (ESI-TOF, m/z): Calcd for C_{11}H_{16}NO [M+H]^+ 178.1226; found 178.1228

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\text{O} \quad \text{N} \quad \text{H} \quad \text{C} \quad \text{N}
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$^1$H NMR (400 MHz, CDCl$_3$): δ 7.39 – 7.28 (m, 4H), 7.27 – 7.21 (m, 1H), 4.04 (qd, J = 7.3, 3.8 Hz, 1H), 3.89 – 3.79 (m, 3H), 3.74 (dt, J = 8.2, 6.7 Hz, 1H), 2.77 – 2.57 (m, 2H), 2.01 – 1.92 (m, 2H), 1.91 – 1.80 (m, 2H), 1.64 – 1.47 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 140.18, 128.36, 128.15, 126.90, 78.30, 67.95, 53.95, 53.64, 29.28, 25.80.

HRMS (ESI-TOF, m/z): Calcd for C_{12}H_{18}NO [M+H]^+ 192.1383; found 192.1384

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\text{O} \quad \text{N} \quad \text{H} \quad \text{C} \quad \text{N}
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$^1$H NMR (400 MHz, CDCl$_3$): δ 7.33 – 7.26 (m, 2H), 7.24 – 7.15 (m, 3H), 3.99 (qd, J = 7.3, 4.1 Hz, 1H), 3.83 (dt, J = 8.3, 6.7 Hz, 1H), 3.73 (dt, J = 8.3, 6.7 Hz, 1H), 2.95 – 2.87 (m, 2H), 2.85 – 2.77 (m, 2H), 2.75 – 2.61 (m, 2H), 2.01 – 1.80 (m, 3H), 1.63 (brs, 1H), 1.57 – 1.44 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 140.11, 128.71, 128.42, 126.08, 78.33, 67.93, 54.41, 51.60, 36.53, 29.37, 25.78.

HRMS (ESI-TOF, m/z): Calcd for C_{13}H_{20}NO [M+H]^+ 206.1539; found 206.1549
**1H NMR (400 MHz, CDCl$_3$): $\delta$ 7.06 – 6.92 (m, 2H), 6.63 – 6.50 (m, 2H), 4.13 (qd, $J$ = 7.1, 3.8 Hz, 1H), 3.90 (b, 1H), 3.89 (dt, $J$ = 8.3, 6.7 Hz, 1H), 3.79 (dt, $J$ = 8.2, 6.8 Hz, 1H), 3.24 (dd, $J$ = 12.3, 3.8 Hz, 1H), 3.06 (dd, $J$ = 12.3, 7.5 Hz, 1H), 2.24 (s, 3H), 2.10 – 1.98 (m, 1H), 1.98 – 1.85 (m, 2H), 1.71 – 1.58 (m, 1H).**

**13C NMR (101 MHz, CDCl$_3$): $\delta$ 146.16, 129.70, 126.70, 113.25, 77.63, 68.04, 48.63, 29.13, 25.83, 20.41.**

HRMS (ESI-TOF, m/z): Calcd for C$_{12}$H$_{18}$NO [M+H]+ 192.1383; found 192.1388

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**1H NMR (400 MHz, CDCl$_3$): $\delta$ 6.87 – 6.70 (m, 2H), 6.69 – 6.52 (m, 2H), 4.12 (qd, $J$ = 7.2, 3.7 Hz, 1H), 4.01 – 3.59 (m, 6H), 3.21 (dd, $J$ = 12.1, 3.7 Hz, 1H), 3.03 (dd, $J$ = 12.1, 7.7 Hz, 1H), 2.08 – 1.98 (m, 1H), 1.96 – 1.86 (m, 2H), 1.71 – 1.59 (m, 1H).**

**13C NMR (101 MHz, CDCl$_3$): $\delta$ 152.19, 142.66, 114.84, 114.40, 77.63, 68.04, 55.81, 49.33, 29.14, 25.83.**

HRMS (ESI-TOF, m/z): Calcd for C$_{13}$H$_{18}$NO$_2$ [M+H]+ 208.1332; found 208.1337

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**1H NMR (400 MHz, CDCl$_3$): $\delta$ 6.86 – 6.61 (m, 3H), 3.98 (qd, $J$ = 7.3, 4.0 Hz, 1H), 3.90 – 3.77 (m, 7H), 3.72 (dt, $J$ = 8.2, 6.7 Hz, 1H), 2.95 – 2.81 (m, 2H), 2.80 – 2.60 (m, 4H), 2.00 – 1.90 (m, 1H), 1.90 – 1.81 (m, 2H), 1.75 (b, 1H), 1.58 – 1.44 (m, 1H).**

**13C NMR (101 MHz, CDCl$_3$): $\delta$ 148.82, 147.34, 132.65, 120.53, 111.95, 111.24, 78.26, 67.93, 55.90, 55.80, 54.40, 51.67, 35.99, 29.37, 25.76.**

HRMS (ESI-TOF, m/z): Calcd for C$_{15}$H$_{24}$NO$_3$ [M+H]+ 266.1751; found 266.1753
1H NMR (400 MHz, CDCl₃): δ 3.99 (qd, J = 7.1, 4.6 Hz, 1H), 3.84 (dt, J = 8.3, 6.7 Hz, 1H), 3.77 – 3.67 (m, 1H), 2.77 – 2.61 (m, 4H), 2.45 – 2.36 (m, 2H), 2.21 (s, 6H), 2.03 – 1.76 (m, 4H), 1.61 – 1.44 (m, 1H).

13C NMR (101 MHz, CDCl₃): δ 78.37, 67.88, 59.22, 54.63, 47.68, 45.64, 29.42, 25.72.

HRMS (ESI-TOF, m/z): Calcd for C₉H₂₁N₂O [M+H]+ 173.1648; found 173.1653

1H NMR (400 MHz, CDCl₃): δ 4.00 (qd, J = 7.3, 4.0 Hz, 1H), 3.83 (dt, J = 8.3, 6.7 Hz, 1H), 3.78 – 3.69 (m, 1H), 2.76 – 2.56 (m, 4H), 2.34 – 2.26 (m, 2H), 2.20 (s, 6H), 2.09 – 1.73 (m, 4H), 1.71 – 1.61 (m, 2H), 1.58 – 1.46 (m, 1H).

13C NMR (101 MHz, CDCl₃): δ 78.24, 67.91, 58.01, 54.56, 48.55, 45.55, 29.34, 28.08, 25.78.

HRMS (ESI-TOF, m/z): Calcd for C₁₀H₂₃N₂O [M+H]+ 187.1805; found 187.1809

1H NMR (400 MHz, CDCl₃): δ 4.00 (qd, J = 7.3, 4.0 Hz, 1H), 3.83 (dt, J = 8.3, 6.7 Hz, 1H), 3.78 – 3.69 (m, 1H), 2.73 – 2.58 (m, 4H), 2.55 – 2.43 (m, 6H), 2.14 – 1.78 (m, 4H), 1.72 – 1.59 (m, 2H), 1.58 – 1.46 (m, 1H), 1.00 (t, J = 7.1 Hz, 6H).

13C NMR (101 MHz, CDCl₃): δ 78.26, 67.89, 54.57, 51.11, 48.92, 46.85, 29.36, 27.23, 25.79, 11.66.

HRMS (ESI-TOF, m/z): Calcd for C₁₂H₂₇N₂O [M+H]+ 215.2118; found 215.2127

1H NMR (400 MHz, CDCl₃): δ 3.99 – 3.90 (m, 1H), 3.90 – 3.80 (m, 1H), 3.75 – 3.67 (m, 1H), 2.63 – 2.40 (m, 6H), 2.01 – 1.90 (m, 1H), 1.90 – 1.76 (m, 2H), 1.57 – 1.47 (m, 1H), 1.47 – 1.36 (m, 2H), 1.34 – 1.22 (m, 2H), 1.00 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H).

13C NMR (101 MHz, CDCl₃): δ 77.66, 67.90, 58.27, 53.90, 48.18, 30.29, 29.07, 25.42, 20.73, 14.12, 11.59.

HRMS (ESI-TOF, m/z): Calcd for C₁₁H₂₄NO [M+H]+ 186.1852; found 186.1860