Conversion of primary amines into secondary amines on a metal-organic framework using a tandem post-synthetic modification

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Supplementary information

General experimental details

Zn(NO$_3$)$_2$·6H$_2$O, 2-aminobenzene-1,4-dicarboxylic acid (H$_2$bdc-NH$_2$), anhydrous DMF, NaBH$_3$CN, ethanal, propanal, butanal and octanal were purchased from Sigma-Aldrich and used without further purification. Anhydrous THF was taken from an in-house solvent purification system and kept under an inert atmosphere of nitrogen. Methanol (Fisher) was laboratory reagent grade and kept over 4 Å molecular sieves. Reactions were carried out in glass 10 cm$^3$ vials (Biotage) in a Sanyo drying oven. [Zn$_4$O(bdc-NH$_2$)$_3$] (IRMOF-3) was prepared following the previously reported method.$^1$

Powder X-ray diffraction (PXRD) was carried out on a Bruker axs D8 Advance diffractometer with a Super Speed detector, using copper K$_\alpha$ radiation, with wavelength, $\lambda = 1.5406$ Å, at 298 K and with a beam slit set to 1 mm, detector slit set to 0.2 mm and anti-scattering slit set to 1 mm. Samples were ground in THF, then packed into 0.5 mm diameter capillary tubes. The scan speed was 1 s per step with a step size ($\theta$) of 0.02.

Samples for NMR studies were dried in an oven for 1 h at 100 °C, then digested in 0.4 cm$^3$ DMSO-$d_6$ and 0.2 cm$^3$ stock DCl solution (0.1 cm$^3$ 35% DCl/D$_2$O, in 3 cm$^3$ DMSO-$d_6$). Spectra were recorded at 298 K on a Bruker Advance 300 MHz Ultrashield NMR spectrometer. $^1$H NMR spectra were referenced to the residual protio peaks at $\delta$ 2.50 ppm for DMSO-$d_6$. 

Electronic Supplementary Material (ESI) for CrystEngComm

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Synthesis of 2-(ethylamino)benzene-1,4-dicarboxylic acid, H$_2$bdc-NHEt

2-Aminobenzene-1,4-dicarboxylic acid (H$_2$bdc-NH$_2$) (0.200 g, 1.104 mmol) was dissolved in N,N’-dimethylformamide (DMF) (10 cm$^3$), then ethanal (0.124 cm$^3$, 2.208 mmol) was added at 10 °C and the solution stirred at this temperature for 1 h. The solution was then cooled in an ice bath and NaBH$_3$CN (0.139 g, 2.204 mmol) was added. The resulting reaction mixture was stirred at room temperature for 24 h. The mixture was acidified with 1 M HCl, and water was added until a yellow solid precipitated. Yield: 0.146 g (63 %). $^1$H NMR (300MHz, DMSO-$d_6$) δ/ppm: 7.79 (d, 1H, $J = 7.8$ Hz), 7.05 (s (br), 1H), 6.97 (dd, 1H, $J = 7.8$ Hz, 1.5 Hz), 3.11 (q, 2H, $J = 7.0$ Hz), 1.21 (t, 3H, $J = 7.0$ Hz). $^{13}$C NMR (300MHz, DMSO-$d_6$) δ/ppm: 169.9, 167.5, 150.7, 136.1, 132.3, 114.7, 113.3, 112.1, 37.05, 14.6. m/z (ESI) 208.0598 ([M − H]$^-$; [C$_{10}$H$_{10}$O$_4$N]$^-$ requires 208.0610). Found C: 57.15, H: 5.41, N: 7.01 %. C$_{10}$H$_{11}$O$_4$N requires C: 57.41, H: 5.30, N: 6.70 %.

![Fig. S1. Infrared spectrum for H$_2$bdc-NHHe](image1)

![Fig. S2. $^1$H NMR spectrum for H$_2$bdc-NHHe in DMSO-$d_6$.](image2)
Synthesis of 2-(propylamino)benzene-1,4-dicarboxylic acid, H$_2$bdc-NHPr

2-Aminobenzene-1,4-dicarboxylic acid (H$_2$bdc-NH$_2$) (0.200 g, 1.104 mmol) was dissolved in N,N'-dimethylformamide (DMF) (10 cm$^3$), then propanol (0.161 cm$^3$, 2.208 mmol) was added and the solution stirred for 1 h. The solution was then cooled in an ice bath and NaBH$_3$CN (0.139 g, 2.044 mmol) added. The resulting reaction mixture was stirred at room temperature for 24 h. The mixture was acidified with 1 M HCl, and water was added until a yellow solid precipitated. Yield: 0.227 g (92 %). $^1$H NMR (300MHz, DMSO-d$_6$) δ/ppm: 7.85 (d, 1H, $J = 8.0$ Hz), 7.22 (d, 1H, $J = 1.6$ Hz), 7.05 (dd, 1H, $J = 8.0$ Hz, 1.4 Hz), 3.15 (t, 2H, $J = 7.2$ Hz), 1.61 (sextet, 2H, $J = 7.2$ Hz), 0.95 (t, 3H, $J = 7.2$ Hz). $^{13}$C NMR (300MHz, DMSO-d$_6$) δ/ppm: 169.9, 167.5, 150.9, 136.1, 132.3, 114.6, 113.3, 112.1, 44.2, 22.1, 11.8. m/z (ESI) 222.0807 ([M – H]–. [C$_{11}$H$_{13}$O$_4$N]– requires 222.0766). Found C: 59.00, H: 5.95, N: 6.50 %. C$_{11}$H$_{13}$O$_4$N requires C: 59.45, H: 5.44, N: 6.30 %.

Fig. S3. Infrared spectrum for H$_2$bdc-NHPr

Fig. S4. $^1$H NMR spectrum for H$_2$bdc-NHPr in DMSO-d$_6$. 
Synthesis of 2-(butylamino)benzene-1,4-dicarboxylic acid, H$_2$bdc-NHBu

2-Aminobenzene-1,4-dicarboxylic acid (H$_2$bdc-NH$_2$) (0.200 g, 1.104 mmol) was dissolved in N,N’-dimethylformamide (DMF) (10 cm$^3$), then butanal (0.195 cm$^3$, 2.208 mmol) was added and the solution stirred for 1 h. The solution was then cooled in an ice bath and NaBH$_3$CN (0.139 g, 2.204 mmol) was added. The resulting reaction mixture was stirred at room temperature for 24 h. The mixture was acidified with 1 M HCl, and water was added until a yellow solid precipitated. Yield: 0.117 g (45 %). $^1$H NMR (300MHz, DMSO-$d_6$) δ/ppm: 7.84 (d, 1H, $J$ = 8.2 Hz), 7.22 (d, 1H, $J$ = 1.5 Hz), 7.05 (dd, 1H, $J$ = 7.8 Hz, 1.5 Hz), 3.18 (t, 2H, $J$ = 7.5 Hz), 1.58 (quintet, 2H, $J$ = 6.7 Hz), 1.38 (sextet, 2H, $J$ = 7.5 Hz), 0.91 (t, 3H, $J$ = 6.7 Hz). $^{13}$C NMR (300MHz, DMSO-$d_6$) δ/ppm: 169.9, 167.5, 150.9, 136.1, 132.3, 114.6, 113.3, 112.1, 42.1, 30.9, 20.1, 14.0. m/z (ESI) 236.0948 ([M – H]$^-$). [C$_{12}$H$_{14}$O$_4$N]$^-$ requires 236.0923). Found C: 60.80, H: 6.49, N: 6.06 %. C$_{12}$H$_{15}$O$_4$N requires C: 60.75, H: 6.37, N: 5.90 %.

Fig. S5. Infrared spectrum for H$_2$bdc-NHBu

Fig. S6. $^1$H NMR spectrum for H$_2$bdc-NHBu in DMSO-$d_6$. 
Synthesis of 2-(octylamino)benzene-1,4-dicarboxylic acid, H$_2$bdc-NHC$_8$H$_{17}$

2-Aminobenzene-1,4-dicarboxylic acid (H$_2$bdc-NH$_2$) (0.200 g, 1.104 mmol) was dissolved in N,N’-dimethylformamide (DMF) (10 cm$^3$), then octanal (0.345 cm$^3$, 2.208 mmol) was added and the solution stirred for 1 h. The solution was then cooled in an ice bath and NaBH$_3$CN (0.139 g, 2.204 mmol) added. The resulting reaction mixture was stirred at room temperature for 24 h. The mixture was acidified with 1 M HCl, and water was added until a yellow solid precipitated. Yield: 0.313 g (97 %). $^1$H NMR (300MHz, DMSO-d$_6$) δ/ppm: 7.84 (d, 1H, $J$ = 8.2 Hz), 7.21 (d, 1H, $J$ = 1.4 Hz), 7.05 (dd, 1H, $J$ = 8.2 Hz, 1.4 Hz), 3.17 (t, 2H, $J$ = 7.0 Hz), 1.58 (quintet, 2H, $J$ = 6.3 Hz), 1.40-1.15 (m, 10H), 0.83 (t, 3H, $J$ = 6.9 Hz). $^{13}$C NMR (300MHz, DMSO-d$_6$) δ/ppm: 169.9, 167.6, 150.9, 136.1, 132.3, 114.6, 113.3, 112.1, 42.4, 31.5, 29.01, 28.98, 28.8, 26.8, 22.4, 14.3. $m/z$ (ESI) 292.1574 ([M – H]$^-$). [C$_{16}$H$_{32}$O$_4$N]$^-$ requires 292.1549). Found C: 66.20, H: 8.75, N: 4.26 %. C$_{16}$H$_{32}$O$_4$N requires C: 65.51, H: 7.90, N: 4.77 %.

Fig. S7. Infrared spectrum for H$_2$bdc-NHC$_8$H$_{17}$.

Fig. S8. $^1$H NMR spectrum for H$_2$bdc-NHC$_8$H$_{17}$ in DMSO-d$_6$. 

Electronic Supplementary Material (ESI) for CrystEngComm

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General procedure for post-synthetic modification reactions

Crystals of IRMOF-3 (0.100 g, 0.23 mmol eq. NH$_2$) were soaked in anhydrous THF for 3 days, replacing with fresh anhydrous THF every 24 h. 4 equivalents of the aldehyde (0.92 mmol) were added and the reaction mixture was left for 24 h at 293 K. 4 equivalents of NaBH$_3$CN (0.058 g, 0.92 mmol) were then added to the reaction mixture, which was left for a further 48 h. The product was then washed by decantation, with fresh anhydrous THF every 24 h for 3 days. The resulting solid was stored under anhydrous THF until needed for analysis.

Reactions in THF-MeOH (15:1) were carried out in a similar way, differing only in the solvent used. These reactions were carried out at 293 K and 323 K.

Fig. S9. Powder X-ray diffraction patterns for IRMOF-3 (red) and the product from the reaction between IRMOF-3, MeCHO and NaBH$_3$CN in THF (in black).
**Fig. S10.** $^1$H NMR spectrum for the digested product from the reaction between IRMOF-3, MeCHO and NaBH$_3$CN in THF, showing (a) the aromatic region, (b) the aliphatic region.
**Fig. S11.** Powder X-ray diffraction pattern for the product from the reaction between IRMOF-3, EtCHO and NaBH₃CN in THF, after 1 day (red), 3 days (black) and 6 days (blue).

**Fig. S12.** $^1$H NMR spectrum for the digested product from the reaction between IRMOF-3, EtCHO and NaBH₃CN in THF, showing the aromatic region.
**Fig. S13.** Powder X-ray diffraction pattern for IRMOF-3 (red) and the product from the reaction between IRMOF-3, PrCHO and NaBH₃CN in THF (black).

**Fig. S14.** ¹H NMR spectrum for the digested product from the reaction between IRMOF-3, PrCHO and NaBH₃CN in THF, showing the aromatic region.
**Fig. S15.** Powder X-ray diffraction pattern for IRMOF-3 (red) and the product from the reaction between IRMOF-3, C$_7$H$_{15}$CHO and NaBH$_3$CN in THF (black).

**Fig. S16.** $^1$H NMR spectrum for the digested product from the reaction between IRMOF-3, C$_7$H$_{15}$CHO and NaBH$_3$CN in THF, showing the aromatic region.
**Fig. S17.** Powder X-ray diffraction pattern for IRMOF-3 (red) and the product from the reaction between IRMOF-3, EtCHO and NaBH₃CN in THF-MeOH (15:1) (black).

(a)

(b)

**Fig. S18.** ¹H NMR spectrum for the digested product from the reaction between IRMOF-3, EtCHO and NaBH₃CN in THF-MeOH (15:1), showing (a) the aromatic region, (b) the aliphatic region.
Fig. S19. Powder X-ray diffraction patterns for IRMOF-3 (black) and the products from the reactions between IRMOF-3, RCHO (R = Me, Et, Pr, C$_7$H$_{15}$) and NaBH$_3$CN in THF-MeOH (15:1).
Fig. S20. $^1$H NMR spectrum for the digested product from the reaction between IRMOF-3, MeCHO and NaBH$_3$CN in THF-MeOH (15:1), showing (a) the aromatic region, (b) the aliphatic region.
Fig. S21. $^1$H NMR spectrum for the digested product from the reaction between IRMOF-3, PrCHO and NaBH$_3$CN in THF-MeOH (15:1), showing (a) the aromatic region, (b) the aliphatic region.
Fig. S22. $^1$H NMR spectrum for the digested product from the reaction between IRMOF-3, C$_7$H$_{15}$CHO and NaNH$_3$CN in THF-MeOH (15:1), showing (a) the aromatic region, (b) the aliphatic region.
Fig. S23. $^1$H NMR spectrum for the digested product from the reaction between IRMOF-3, EtCHO and NaBH$_3$CN in THF-MeOH (15:1) at 50 °C, showing (a) the aromatic region, (b) the aliphatic region.
Fig. S24. $^1$H NMR spectrum for the digested product from the reaction between IRMOF-3, PrCHO and NaBH$_3$CN in THF-MeOH (15:1) at 50 °C, showing (a) the aromatic region, (b) the aliphatic region.
Fig. S25. $^1$H NMR spectrum for the digested product from the reaction between IRMOF-3, C$_7$H$_{15}$CHO and NaBH$_3$CN in THF-MeOH (15:1) at 50 °C, showing (a) the aromatic region, (b) the aliphatic region.
Fig. S26. $^{11}$B NMR spectrum for the digested product from the reaction between IRMOF-3, EtCHO and NaBH$_3$CN in THF, showing the presence of a boron-containing by-product. (a) original spectrum, and (b) reprocessed spectrum.

Reference