Supporting Information for

Coordination Polymers with free Brønsted acid Sites for Selective Catalysis

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Materials and instrumentation: All reagents were commercially available and were used as received without further purification. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Flash 2000 organic elemental analyzer. The infrared spectra ($4000 \sim 600 \text{ cm}^{-1}$) were recorded on a NICOLET 6700 FT-IR spectrometer. Thermalgravimetric analyses were performed on a SII EXStar6000 TG/DTA6300 analyzer heated from 30 to 900 °C under nitrogen. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8-ADVANCE X-ray diffractometer with Cu *K* α radiation.

X-ray diffraction analysis. Suitable single crystals of **1-2** were carefully selected under an optical microscope and glued to thin glass fibers. Whereafter, single-crystal X-ray diffraction analyses were performed on a computer-controlled X-ray diffractometer with graphite monochromated Mo K α radiation ($\lambda_{Mo-K\alpha}$ =0.71073 Å) at T = 293 K. The structures were solved using the direct method and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package.



Figure S1. Picture showing the product yields of recycle use of catalyst 1.



Figure S2. XRD patterns of **1** and **2**: (a) the simulated XRD pattern, (b) dehydrated solid obtained on heating at 140 °C for 4 h under vacuum, (c) after the first recycling, (d) after the second recycling, (e) after the third recycling and (f) after the fourth recycling.



Figure S3. Picture showing the variation of intensity of recycle use of catalyst 1.

1)



2-phenyl-2-(phenylamino)ethanol: ¹H NMR (400 MHz, CDCl₃) δ: 7.35–7.24 (m, 5H), 7.09 (t, *J* = 8.0 Hz, 2H), 6.67 (t, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 2H), 4.49 (br s, 1H), 3.91–3.94 (m, 1H), 3.72-3.76 (dd, *J* = 4.0 Hz, 1H) 1.84 (br s, 1H). ¹³C NMR (CDCl₃, 400 MHz) δ: 60.00, 67.45, 113.99, 118.02, 126.86, 127.72, 128.94, 129.28, 140.28, 147.38. 2)



2-(o-chlorophenylamino)-2-phenylethanol: ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.28 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 5.15 (br s, 1H), 5.54 (d, *J* = 4.0 Hz, 1H), 3.97 (t, *J* = 4.0 Hz, 1H), 3.82 (s, 1H) 1.82 (br s, 1H). ¹³C NMR (CDCl₃, 400 MHz) δ: 59.81, 67.47, 112.99, 117.97, 119.89, 126.78, 127.77, 127.91, 129.04, 129.24, 139.67, 143.19.

3)



2-(o-methylphenylamino)-2-phenylethanol: ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.25 (m, 5H), 7.05 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 8.0 Hz, 1H), 6.63 (t, J = 4.0 Hz, 1H), 6.37 (d, J = 8.0 Hz, 1H), 4.54 (t, J = 4.0 Hz, 1H), 3.97 (dd, J = 4.0 Hz, 1H), 3.79 (dd, J = 4.0, 8.0 Hz, 1H), 2.27 (s, 3H), 1.75 (br s, 1H). ¹³C

NMR (CDCl₃, 400 MHz) δ: 17.37, 59.94, 67.64, 111.64, 117.66, 122.70, 126.80, 127.11, 127.74, 128.97, 130.23, 140.36, 145.26.

4)



trans-(2-(phenylamino)cyclohexanol: ¹H NMR (400 MHz, CDCl₃) δ7.23–7.15 (m, 2H), 6.75–6.69 (m, 3H), 3.35–3.31 (m, 1H), 3.14–3.09 (m, 1H), 3.02 (br s, 1H), 2.21–2.08 (m, 2H), 1.77–1.69 (m, 2H), 1.42–1.03 (m, 6H). ¹³C NMR (CDCl₃, 400 MHz) δ: 24.36, 25.08, 60.19, 74.56, 114.44, 118.38, 129.41, 147.94.

5)



tran-2-(o-chlorophenylamino)cyclohexanol: ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 4.0 Hz, 1H), 7.12 (t, *J* = 4.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.65 (t, *J* = 4.0 Hz, 1H), 4.06 (br s, 1H), 3.46 (t, J = 8.0 Hz, 1H), 3.20 (s, 1H), 2.59 (s, 1H), 2.15–2.07 (m, 2H), 1.78–1.74 (m, 2H), 1.44–1.12 (m, 6H). ¹³C NMR (CDCl₃, 400 MHz) δ : 24.33, 25.10, 31.84, 33.29, 60.00, 74.71, 113.02, 118.20, 120.43, 127.96, 129.47, 143.97.

6)



trans-2-(o-methylphenylamino)cyclohexanol: ¹H NMR (400 MHz, CDCl₃) δ 7.13–7.06 (m, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.69 (t, *J* = 8.0 Hz, 1H), 3.42 (dd, J = 8.0 Hz, 1H), 3.21 (dd, J = 8.0 Hz, 1H), 2.73 (br s, 1H), 2.16 (s, 3H), 2.13 (s, 2H), 1.79–1.74 (m, 2H), 1.43–1.11 (m, 6H). ¹³C NMR (CDCl₃, 400 MHz) δ: 17.81, 24.44, 25.18, 32.03, 33.38, 60.03, 74.79, 111.74, 118.02, 123.24, 127.30, 130.56, 145.87.

trans-2-(phenylamino)cyclopentanol: ¹H NMR (400 MHz, CDCl₃) δ7.20–7.16 (m, 2H), 6.73–6.66 (m, 3H), 4.07 (t, *J* = 4.0 Hz, 1H), 3.62 (t, *J* = 4.0 Hz, 1H), 2.31 (s, 1H), 2.02–1.37 (m, 6H). ¹³C NMR (CDCl₃, 400 MHz) δ: 21.19, 31.36, 33.09, 62.25, 78.45, 113.45, 117.67, 129.45, 147.89. 8)



trans-2-(o-chlorophenylamino)cyclopentanol: ¹H NMR (400 MHz, CDCl₃) δ7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.63 (t, *J* = 8.0 Hz, 1H), 4.20 (br s, 1H), 4.11 (s, 1H), 3.66 (s, 1H), 2.59 (s, 1H), 2.36–2.27 (m, 1H), 2.07–2.00 (m, 1H), 1.98–1.47 (m, 6H). ¹³C NMR (CDCl₃, 400 MHz) δ: 21.33, 31.47, 33.30, 61.96, 78.40, 112.26, 117.47, 119.31, 127.97, 129.28, 143.70. 9)



trans-2-(o-methylphenylamino)cyclopentanol: ¹H NMR (400 MHz, CDCl₃) δ 7.15–7.11 (m, 1H), 7.06– 7.04 (m, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.10 (dd, J = 4.0, 8.0 Hz, 1H), 3.67 (dd, J = 4.0, 8.0 Hz, 1H), 2.35–2.30 (m, 1s), 2.28 (s, 3H), 2.05–2.01 (m, 1H), 1.98–1.38 (m, 5H). ¹³C NMR (CDCl₃, 400 MHz) δ: 17.63, 21.25, 31.62, 33.11, 62.07, 78.42, 110.77, 117.20, 122.20, 127.26, 130.26, 145.75.

NMR Spectra

1. 2-phenyl-2-(phenylamino)ethanol



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2. 2-(o-chlorophenylamino)-2-phenylethanol



3. 2-(o-methylphenylamino)-2-phenylethanol



4. trans-(2-(phenylamino)cyclohexanol



5. tran-2-(o-chlorophenylamino)cyclohexanol



6. trans-2-(o-methylphenylamino)cyclohexanol



7. trans-2-(phenylamino)cyclopentanol



8. trans-2-(o-chlorophenylamino)cyclopentanol



9. trans-2-(o-methylphenylamino)cyclopentanol

