Selective and Recyclable Rhodium Nanocatalysts for the Reductive N-Alkylation of Nitrobenzenes and Amines with Aldehydes

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Supporting Information

Reagents

All reagents were purchased Aladdin Reagent Company and Alfa-Aesar Company without further purification.

Analytical Methods

Gas chromatography analysis was performed on a Hewlett Packard 5890 instrument with a FID detector and Hewlett Packard 24 m x 0.2 mm i.d. HP-5 capillary column. The ICP-OES (inductively coupled plasma optical emission spectroscopy) analysis was performed with a Perkin Elmer OPTIMA 2000DV. TEM (Transmission electron microscopy) images were obtained on a transmission electron microscope (Tecnai 12) with an accelerating voltage of 120 kV. ^{1}H-NMR spectra were recorded on a Bruker 400 MHz instrument with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane. The specific surface areas and the average pore sizes of the materials were measured on a Belsorp II physical adsorption apparatus by BET and BJH methods. X-ray diffraction (XRD) patterns were collected on a Bruker Advanced X-Ray Diffractometer (40 kV, 30 mA) with Cu-Ka radiation (l=1.5406 Å). Thermogravimetric (TG) analysis was carried out using a Perkin-Elmer TG/DTA-6300 instrument. XPS measurements were performed with a XSAM 800 spectrometer using Al Kα radiation (E=1486.6 eV).

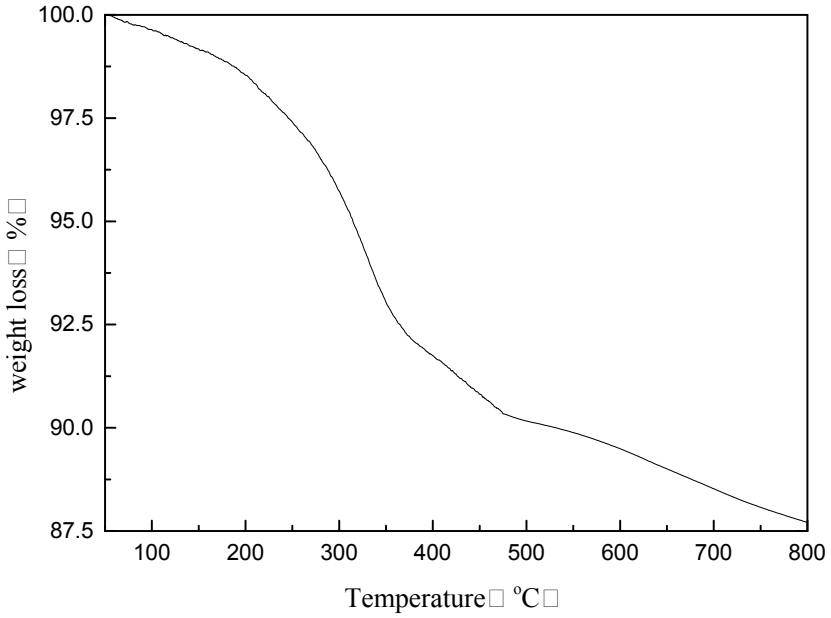


Figure S1. The TG analysis of the precursor of Rh@CN

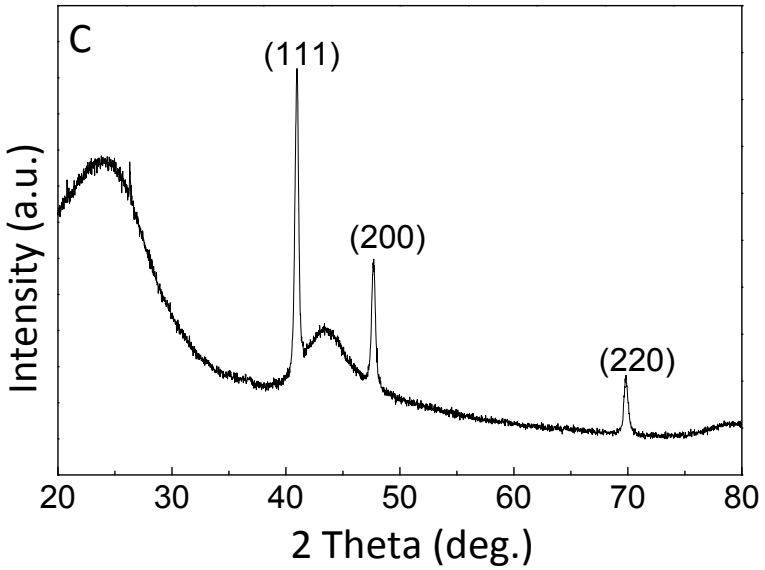


Figure S2 XRD patterns of Rh@CN

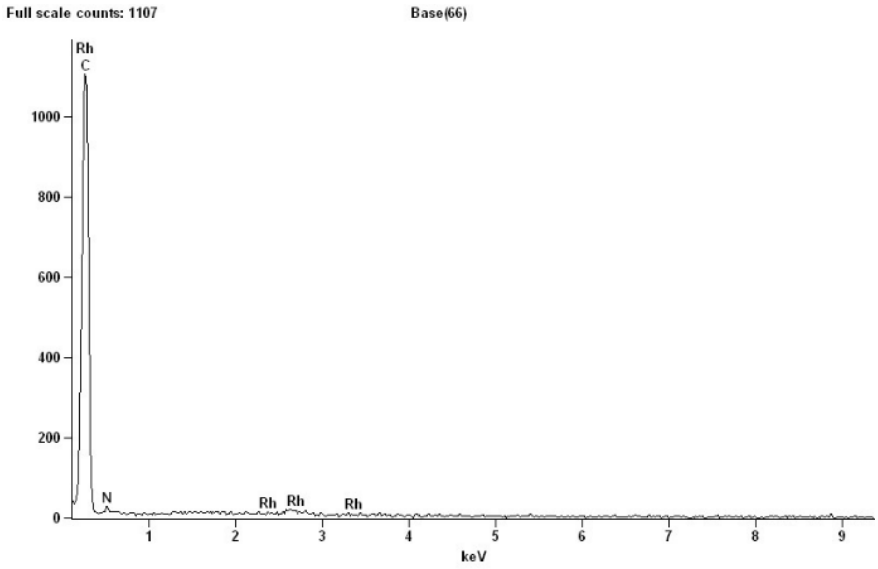


Figure S3. EDX patterns of Rh@CN

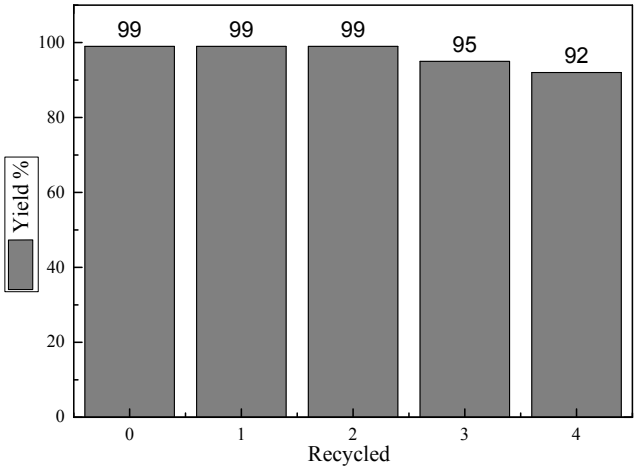
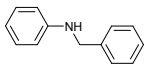
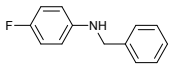


Figure S4. Recycling experiments of the benchmark reaction in the presence of the Rh@CN nanocatalyst.

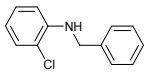
^{1}H-NMR data for the produced amines.



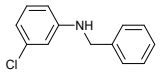
N-benzylaniline, (Table 2 Entry 1) ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 4.38 (s, 2H), 6.68 (d, 2H, *J*=7.8 Hz), 6.76 (t, 1H, *J*=7.2Hz), 7.21 (d, 2H, *J*=7.5 Hz), 7.28-7.44 (m, 5H).



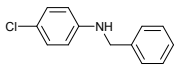
N-benzyl-4-fluoroaniline, (Table 2 Entry 2) ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 4.32 (s, 2H), 6.59 (dd, 2H, *J*=4.39 and 8.78 Hz), 6.90 (t, 2H, *J*=8.78 Hz), 7.28-7.39 (m, 5H).



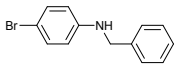
N-benzyl-2-chloroaniline, (Table 2 Entry 3) ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 4.43 (s, 2H), 6.60-6.65 (m, 2H), 7.08-7.12 (m, 1H), 7.27-7.38 (m, 6H).



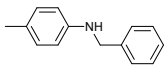
N-benzyl-3-chloroaniline, (Table 2 Entry 4) ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 4.05 (s, 1H), 4.27 (s, 2H), 6.47 (dd, 1H, *J*=6.4 and 10.4Hz), 6.60 (d, 1H, *J*= 1.6 Hz), 6.68 (d, 1H, *J*= 8.8 Hz), 7.07 (t, 1H, *J*= 8.4 Hz), 7.27-7.38 (m, 4H).



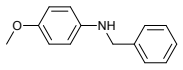
N-benzyl-4-chloroaniline, (Table 2 Entry 5) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.33 (s, 2H), 6.60 (d, 2H, *J*=8.8Hz), 7.13 (d, 2H, *J*=8.8 Hz), 7.28-7.38 (m, 5H).



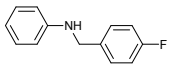
N-benzyl-4-bromoaniline, (Table 2 Entry 6) ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 4.33 (s, 2H), 6.53-6.56 (m, 2H), 7.26-7.30 (m, 2H), 7.31-7.38 (m, 5H).



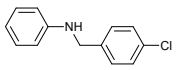
N-benzyl-4-methylaniline, (Table 2 Entry 7) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.27 (s, 3H), 4.34 (s, 2H), 6.62 (d, 2H, *J*=8.5 Hz), 7.01 (d, 2H, *J*=8.5 Hz), 7.28 – 7.41 (m, 5H).



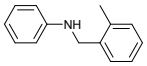
N-benzyl-4-methoxyaniline, (Table 2 Entry 8) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.76 (s, 3H), 4.31 (s, 2H), 6.63 (d, 2H, *J*=9.0 Hz), 6.79 (d, 2H, *J*=9.0 Hz), 7.29-7.41 (m, 5H).



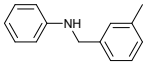
N-(4-fluorobenzyl)aniline, (Table 2 Entry 9) ^{1}H-NMR (400 MHz d-DMSO) δ: 4.23 (s, 2H), 6.22 (t, 1H), 6.49 (d, 2H, *J*=7.8 Hz), 6.55 (t, 1H, *J*=7.3 Hz), 7.02 (t, 2H, *J*=8.6 Hz), 7.11 (t, 2H, *J*=7.5), 7.38-7.43 (m, 2H).



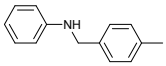
N-(4-chlorobenzyl)aniline, (Table 2 Entry 10) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.26 (s, 2H), 6.64 (d, 2H, *J*=8.7 Hz), 6.73 (t, 1H, *J*=7.3 Hz), 7.19-7.20 (m, 2H), 7.31 (s, 4H).



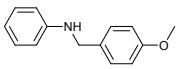
N-(2-methylbenzyl)aniline, (Table 2 Entry 11) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 4.26 (s, 2H), 6.62-6.65 (m, 2H), 6.72 (tt, 1H, J = 7.4, 1.1 Hz), 7.16-7.23 (m, 5H), 7.33 (d, 1H, J = 6.9 Hz).



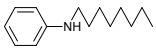
N-(3-methylbenzyl)aniline, (Table 2 Entry 12) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.34 (s, 3H), 4.28 (s, 2H), 6.61-6.73 (m, 3H), 7.07–7.27 (m, 6H).



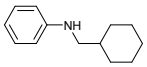
N-(4-methylbenzyl)aniline, (Table 2 Entry 13) ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.37 (s, 3H), 4.31 (s, 2H), 6.68 (d, 2H, *J*=7.6 Hz), 6.75 (t, 1H, *J*=7.4 Hz), 7.10 – 7.22 (m, 4H), 7.29 (d, 2H, *J*=7.9 Hz).



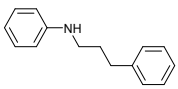
N-(4-methoxybenzyl)aniline, (Table 2 Entry 14)^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.82 (s, 3H), 4.28 (s, 2H), 6.71 (d, 2H, *J*=7.6 Hz), 6.77 (t, 1H, *J*=7.4 Hz), 6.90 (d, 2H, *J*=8.5 Hz), 7.19 (t, 2H, *J*=7.4 Hz), 7.31 (d, 2H, *J*=8.7 Hz).



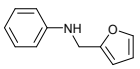
N-octylaniline, (Table 2 Entry 15)^{1}H-NMR (400 MHz, d-DMSO) δ: 0.85(t, 3H, *J*=6.9Hz), 1.26-1.35(m,10H), 1.49 (m, 2H, *J*=7.4Hz), 2.94 (t, 2H, *J*=7.2Hz), 5.46 (s, 1H), 6.47-6.54 (m, 3H), 7.02 (t, 2H, *J*=7.9Hz).



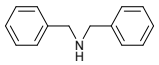
N-(cyclohexylmethyl)aniline, (Table 2 Entry 16) ^{1}HNMR (400 MHz, $CDCl_3$) δ: 0.984(m,2H), 1.21-1.28 (m,4H), 1.59-1.86 (m, 6H), 2.97 (d, 2H, J=6.6 Hz), 6.65 (d, 2H, J=7.8 Hz), 6.71 (t, 1H, J=7.4 Hz), 7.18 (td, 2H, J=7.5, 1.7 Hz).



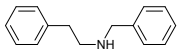
N-(3-phenylpropyl)aniline, (Table 2 Entry 17) ^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.96 (q, J=7.3 Hz, 2H), 2.75 (t, J=7.5 Hz, 2H), 3.17 (t, J=7.1 Hz, 2H), 6.63 (dd, J=8.4, 1.1 Hz, 2H), 6.73 (t, J=7.4 Hz, 1H), 7.15-7.35 (m, 7H).



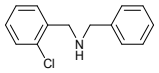
N-phenyl furfurylamine, (Table 2 Entry 18) ^{1}HNMR (400 MHz, $CDCl_3$) δ: 4.35 (s, 2H), 6.27 (m, 1H), 6.35 (m, 1H), 6.69 (d, 2H,*J*=7.63 Hz), 6.76 (t, 1H, *J*=7.33 Hz), 7.18 (t, 2H, *J*=7.94 Hz), 7.40 (d, 1H, *J*=0.92 Hz).



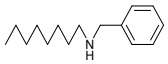
Dibenzylamine, (Table 3 Entry 3) ^{1}H-NMR (400 MHz, d-DMSO) δ: 2.50 (bs, 1H), 3.67 (s, 4H), 7.20 (m, 2H),7.29-7.35 (m,8H).



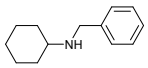
N-benzyl-2-phenylethanamine, (Table 3 Entry 4) ^{1}H-NMR (400 MHz, d-DMSO) δ: 2.73 (s, 4H), 3.62 (s, 2H), 7.10-7.31 (m, 11H).



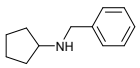
N-benzyl-1-(2-chlorophenyl)methanamine, (Table 3 Entry 5) ^{1}H-NMR (400 MHz, d-DMSO) δ: 2.65 (s, 1H), 3.73 (t, 4H), 7.22-7.42 (m, 8H),7.57 (d 1H).



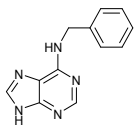
N-benzyloctan-1-amine, (Table 3 Entry 6) ^{1}H-NMR (400 MHz, d-DMSO) δ: 0.84 (d, 3H, *J*=7.0 Hz), 1.24 (s, 10H), 1.39–1.40 (d, 2H),2.07 (bs 1H), 2.43 (t, 2H, *J*=7.6 Hz), 3.66 (s, 2H), 7.18-7.30 (m, 5H)



N-benzylcyclohexanamine, (Table 3 Entry 7) ^{1}H-NMR (400 MHz, d-DMSO) δ: 1.04-1.23 (m, 3H), 1.24-1.41 (m, 2H), 1.53-1.64 (m, 1H), 1.64-1.77 (m, 2H), 1.86-1.96 (m, 2H), 3.15 (s, 1H), 5.25 (d, 1H), 6.45 (t, 1H), 6.50 (d, 2H), 6.90 (t, 2H).



N-benzylcyclopentanamine, (Table 3 Entry 8) ^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.18–1.26 (m, 8H), 3.58–3.62 (m, 1H), 6.57 (d, 2H), 6.64–6.68 (m, 1H), 7.13–7.17 (m, 2H).



6-benzylaminopurine, ^{1}H-NMR (400 MHz, d-DMSO) δ: 4.70 (s 2H), 7.19-7.35 (m, 5H), 8.11 (s, 1H), 8.35 (s, 1H), 12.79 (s, 1H).