SUPPLEMENTARY INFORMATIONS

N-alkylation of amines through hydrogen borrowing over a heterogeneous Cu catalyst

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Materials:

All the substrates and amines were supplied by Sigma Aldrich and used without any further manipulation. Toluene and xylene were supplied by Sigma Aldrich. Toluene was used without any pretreatment, xylene was dehydrated on molecular sieves before use. The features of the supports and the copper catalysts used are reported in Table S1.

Support	Supplier	Co-oxide loading (wt%)	Cu loading (wt%)	BET (m ² /g)	PV (mL/g)
SiO ₂	Aldrich	-		480	0.75
Cu/ SiO ₂		-	8.50	363	0.68
AI_2O_3	Sasol	-		210	0.50
Cu/Al_2O_3		-	7.50		

Table S1. Textural properties of supports and copper catalysts.

Catalysts preparation and activation:

Copper catalysts, all with a metal loading of 8-9 wt%, were prepared by chemisorption-hydrolysis method. The support was added to a $[Cu(NH_3)_4]^{2+}$ solution prepared by adding NH₄OH to a Cu(NO₃)₂·3H₂O solution until pH=9. After 20 min under stirring, the slurry, held in an ice bath at 0°C, was slowly diluted in order to allow hydrolysis of the copper complex and deposition of the finely dispersed product to occur. The solid was separated by filtration, washed with water, dried overnight at 120°C, and calcined in air at 350°C for 4 h. The copper loading of the catalyst was determined by ICP analysis (ICAP 6200 Upgrade Thermo Scientific) after microwave HNO₃ digestion. The catalyst was activated into a glass reaction vessel before use by treatment at 270°C in air for 20 min, under reduced pressure at the same temperature for 20 min and then under H₂ at the same temperature by removing the water formed by the reduction under reduced pressure.

Experimental procedure for the Amination reactions of alcohols by borrowing hydrogen:

in a typical reaction a solution of alcohol/amine 1/1 molar ratio were dissolved in the solvent (8 mL), and the solution transferred under N_2 into a glass reaction vessel in which the catalyst (100 mg) had been previously activated. Reactions were carried out under atmospheric pressure of N_2 and constant magnetic stirring (1000 rpm) using Teflon-coated magnetic stir bar at 130°C (bath oil temperature) Reaction mixtures were analysed by GC-MS (5%-phenyl-methyl polysiloxane capillary column length 30 m, injection T=60°C) with n-dodecane as internal standard, and by ¹HNMR and ¹³CNMR spectroscopy .

Experimental procedure for the Hot filtration test:

for the leaching test, after 10 min the reaction solution was separated from the catalyst by hot filtration and transferred in a new reaction vessel. The solution was stirred (1000 rpm) under N_2 at 130°C for a 12 h.



Figure S1. Hot filtration test carried out in the reductive amination of p-methoxy benzyl alcohol with aniline.

Experimental procedure for the Recycling tests:

recycling tests were performed starting from 0.3 g of substrate. The reaction solution was separated from the catalyst after each run by filtration; the recovered catalyst was washed with xylene at RT for 30 min, dried overnight at 100°C and reactivated by hydrogenation following the above procedure. After activation a fresh reaction mixture was charged in the reactor.

Spectral data:

N-(4-tert-butylcyclohexyl)aniline (Table 1, entry 4)¹

White solid, recrystallized from methanol; MP: 107.4°C

¹H NMR (300 MHz, CDCl₃, δ ppm): 7.18 (t, *J* = 7.8 Hz, 2H), 6.75 – 6.54 (m, 3H), 3.51 (s, 1H), 3.19 (s, 1H), 2.21 (d, *J* = 9.4 Hz, 2H), 1.86 (d, *J* = 8.7 Hz, 2H), 1.23 – 1.00 (m, 5H), 0.90 (s, 9H). ¹³C {H} APT NMR (75 MHz, CDCl₃, δ ppm): 147.78, 129.65, 117.38, 113.69, 52.92, 48.10, 34.39, 32.79, 28.02, 26.73. [M]⁺: m/z calcd: 231.4; found: 231.2, 132.1, 118.1, 93.1,77.1.

N-(adamantyl)aniline (Table 1, entry 5)



Tab 1-5

White solid, recrystallized from methanol; MP: 56.3°C

¹H NMR (400 MHz, CDCl₃, δ ppm): 1.69-2.06 (m, 14H), 3.57 (s, 1H), 4.24 (brs, 1H), 6.68 (m, 3H), 7.22 (m, 2H). ¹³C{H} APT NMR (75.5 MHz, CDCl₃, δ ppm): 129.67, 117.34, 113.66, 57.23, 38.12, 37.82, 31.99, 27.87, 27.73; [M]⁺: m/z calcd: 227.34; found: 227.2, 135.1, 106.1, 93.1, 77.1.

N-[1-(4-Methoxyphenyl)ethyl]aniline (Table 1, entry 10)⁵



Tab 1-10

¹H NMR (300 MHz, CDCl₃, δ ppm): 7.40 – 7.29 (m, 2H), 7.21 – 7.09 (m, 2H), 7.04 – 6.87 (m, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.59 (dd, J = 8.6, 1.0 Hz, 2H), 4.51 (q, J = 6.6 Hz, 1H), 3.83 (s, 3H), 1.54 (d, J = 6.6 Hz, 3H). ¹³C{H} APT NMR (75 MHz, CDCl₃, δ ppm): 158.95, 147.77, 137.68, 129.53, 127.35, 117.66, 114.46, 113.82, 55.66, 53.30, 25.37. [M]⁺: m/z calcd: 227.13; found: 227.2, 212.1, 135.1, 120.1, 105.1, 91.1, 77.1.

N-(octan-3-yl)aniline (Table 1, entry 11)



Tab 1-11

¹H NMR (300 MHz, CDCl₃, δ ppm) δ 7.25 – 7.18 (m, 2H), 6.77 – 6.54 (m, 3H), 3.48 (brs, 1H), 3.40 – 3.31 (m, 1H), 1.75 – 1.30 (m, 10H), 0.98 (dt, *J* = 10.4, 7.1 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃, δ ppm) 148.65, 129.68, 116.94, 113.36, 54.55, 34.83, 32.46, 27.69, 26.11, 23.09, 14.49, 10.48. [M]⁺: m/z calcd: 205.34; found: 205.2, 176.2, 134.1, 120.1, 106.1, 93.1, 77.1.

N-benzylaniline (Table 2 entry 1)^{3, 4, 5, 8}



¹H NMR (CDCl₃, 300 MHz, δ ppm): 4.05 (brs, 1H), 4,37 (s, 2H), 6.70 (m, 3H), 7.21-7.41 (m, 7 H). ¹³C{H} APT NMR (75 MHz, CDCl₃, δ ppm): 148.58, 139.86, 129.67, 129.04, 127.92, 127.64, 117.98, 113.26, 48.75. [M]+: m/z calcd: 183.25; found: 183.1, 106.1, 91.1, 77.1.

N-(4-methylbenzyl)aniline (Table 2 entry 4)^{4,5}



Tab 2-4

White solid, recrystallized from methanol; MP: 44.6°C

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.30 (t, J = 6.4 Hz, 2H), 7.26 – 7.15 (m, 4H), 6.76 (t, J = 7.3 Hz, 1H), 6.71 – 6.64 (m, 2H), 4.32 (s, 2H), 4.01 (brs, 1H), 2.39 (s, 3H). ¹³C {H} APT NMR (75 MHz, CDCl₃, δ ppm):148.49, 137.30, 136.67, 129.71, 129.66, 127.96, 118.03, 113.37, 48.59, 21.49. [M]⁺: m/z calcd: 197.28 ; found: 197.2, 105.1, 91.1, 77.1

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N-(4-fluorobenzyl)aniline (Table 2, entry 7)



¹H NMR (300 MHz, CDCl₃, δ ppm) : 7.41 – 7.33 (m, 2H), 7.25 – 7.18 (m, 2H), 7.12 – 7.01 (m, 2H), 6.81 – 6.62 (m, 3H), 4.33 (s, 2H), 4.03 (brs, 1H). ¹³C NMR (75 MHz, CDCl₃, δ ppm) 160.93, 148.37, 135.51, 129.70, 129.35, 121.24, 115.70, 113.29, 48.03. $[M]^+$: m/z calcd: 201.2; found: 201.1, 109.1, 83.1, 65.1.

N-(4-chlorobenzyl)aniline (Table 2, entry 9)^{2, 3, 5}





¹H NMR (300 MHz, CDCl₃, δ ppm) 7.36 (m, 4H), 7.23 (m, 2H), 6.79 (m, 1H), 6.66 (m, 2H), 4.35 (s, 2H), 3.99 (brs, 1H). ¹³C NMR (75 MHz, CDCl₃, δ ppm) 148.27, 138.46, 133.30, 129.74, 129.18, 129.14, 118.27, 113.37, 48.05. [M]⁺: m/z calcd: 217.7 ; found: 217.1, 182.1, 125.0, 106.1, 89.1.

N-(4-methoxybenzyl)aniline (Table 2 entry 2, table 3 entry 1)^{2, 3, 4, 5}



Tab 3-1

¹H NMR (CDCl₃, 300 MHz, δ ppm): 3.70 (brs, 1H), 3.86 (s, 3H), 4.31 (s, 2H), 6.70 (m, 2H), 6.80 (m, 1H), 6.95 (m, 2H), 7.25 (m, 2H), 7.34 (m, 2H); ¹³C{¹H} APT NMR (75 MHz, CDCl₃, δ ppm): 48.25, 55.74, 113.3, 114.5, 117.9, 129.3, 129.7, 131.9, 148.7, 159.3. [M]⁺: m/z calcd: 213.28 ; found: 213.1, 121.1, 106.3, 91.1, 77.1

4-methoxy-N-(4-methoxybenzyl)aniline (Table 3, entry 3)^{6,8}



White solid, recrystallized from methanol; MP: 96.6°C. ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.32 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 4.24 (s, 2H), 3.84 (s, 3H), 3.78 (s,

3H). ¹³C NMR (101 MHz, CDCl₃, δ ppm): 158.85, 152.22, 142.54, 131.70, 128.84, 114.94, 114.16, 114.01, 55.83, 55.29, 48.76. [M]⁺: m/z calcd: 243.30 ; found: 243.1, 121.1, 107.0, 91.1, 77.1

4-fluoro-N-(4-methoxybenzyl)aniline (Table 3 entry 4)⁷



Tab 3-4

White solid, recrystallized from methanol; MP: 72.3°C.

¹H NMR (CDCl₃, 300 MHz, δ ppm): 3.83 (s, 3H), 4.24 (s, 2H), 6.60 (m, 2 H), δ 7.35 – 7.25 (m, 2H), 6.90 (m, 4H). ¹³C {H} APT NMR (75 MHz, CDCl₃, δ ppm): 159.36, 157.93, 154.81, 144.76, 131.49, 129.22, 116.19, 115.90, 114.47, 55.69, 48.93. [M]⁺: m/z calcd: 231.27 ; found: 231.1, 121.1.

N-(4-fluorobenzyl)-4-methoxyaniline (Table 3, entry 6)⁸



Tab 3-6

¹H{¹⁹F} NMR (300 MHz, CDCl₃, δ ppm): 7.36 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.87 – 6.77 (m, 2H), 6.70 – 6.57 (m, 2H), 4.28 (s, 2H), 3.78 (s, 3H), 3.60 (s, 1H). ¹³C {H} APT NMR (75 MHz, CDCl₃, δ ppm): 164.07, 152.77, 142.60, 135.80, 129.51, 115.94, 115.36, 114.62, 56.20, 48.97. [M]⁺: m/z calcd: 231.27 ; found: 231.1, 214.1, 122.1, 109.1, 96.1, 83.1.

4-fluoro-N-(4-fluorobenzyl)aniline (Table 3, entry 7)



Tab 3-7

¹H NMR (300 MHz, CDCl₃, δ ppm): 7.41 – 7.30 (m, 2H), 7.13 – 7.00 (m, 2H), 6.99 – 6.83 (m, 2H), 6.64 – 6.52 (m, 2H), 4.29 (s, 2H), 3.90 (s, 1H). ¹³C {H} APT NMR (75 MHz, CDCl₃, δ ppm): 164.14, 157.96, 144.69, 135.33, 129.36, 116.26, 115.96, 114.19, 48.64. [M]+: m/z calcd: 219.23 ; found: 219.1, 109.1, 96.1, 83.1.

N-benzylethanamine (Table 3, entry 8)⁹

Tab 3-8

¹H NMR (300 MHz, CDCl_{3,} δ ppm): 7.36 (m, 5H), 3.82 (s, 2H), 2.71 (q, *J* = 7.0 Hz, 2H), 1.77 (brs, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl_{3,} δ ppm) δ 140.83, 128.79, 128.55, 127.30, 54.28, 43.98, 15.60. [M-1]+: m/z calcd: 134.21; found: 134.1, 120.1, 106.1, 91.1, 78.1, 65.1, 51.1.



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