Electronic Supplementary Information for

Heterogeneously catalyzed self-condensation of primary amines to secondary amines by supported copper catalysts

Insu Kim, Shintaro Itagaki, Xiongjie Jin, Kazuya Yamaguchi and Noritaka Mizuno*

Compound data

Dibenzylamine (**2a**, CAS registry number: 103-49-1): 81 % isolated yield (Table 2, entry 1, 24 h). ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 1.70 (brs, 1H), 3.78 (s, 4H), 7.21-7.34 (m, 10H). ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ 53.07, 126.85, 128.06, 128.30, 140.23. MS (EI): *m*/*z* (%): 197 (11) [M^+], 196 (11), 120 (8), 118 (5), 107 (6), 106 (68), 91 (100), 79 (5), 77 (5), 65 (16).

Bis(4-methoxybenzyl)amine (**2b**, CAS registry number: 17061-62-0): 93 % isolated yield (Table 2, entry 6, 26 h). δ 2.15 (brs, 1H), 3.63 (s, 4H), 3.69 (s, 6H), 6.77 (d, J = 8.64 Hz, 4H), 7.15 (d, J = 8.64 Hz, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ 55.25, 55.14, 113.67, 129.27, 132.21, 158.54. MS (EI): *m*/*z* (%): 257 (9) [M^+], 149 (11), 148 (10), 136 (40), 122 (22), 121 (100), 91 (7), 78 (8), 77 (11).

Bis(3-methoxybenzyl)amine (**2c**, CAS registry number: 148234-82-6): 257 (1) [M^+], 137 (9), 136 (95), 123 (9), 122 (100), 121 (66), 107 (10), 92 (9), 91 (26), 78 (12), 77 (14), 65 (9).

Bis(2-methoxybenzyl)amine (**2d**, CAS registry number: 178903-65-6): 93 % isolated yield (Table 2, entry 6, 48 h). ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 2.21 (brs, 1H), 3.72 (brs, 10H), 6.76 (d, J = 8.08 Hz, 2H), 6.83 (t, J = 7.24 Hz, 2H), 7.14 (t, J = 8.08 Hz, 2H), 7.20 (d, J = 7.24 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ 55.09 (overlapped), 110.03, 120.30, 128.06, 128.07, 129.76, 157.55. MS (EI): *m*/*z* (%): 257 (8) [M^+], 256 (13), 138 (22), 137 (7), 136 (79), 122 (18), 121 (100), 120 (6), 118 (6), 107 (12), 93 (12), 92 (7), 91 (71), 78 (7), 77 (9), 65 (16).

Bis(4-methylbenzyl)amine (**2e**, CAS registry number: 98180-43-9): 94 % isolated yield (Table 2, entry 12, 48 h). ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 1.53 (brs, 1H), 2.26 (s, 6H), 3.68 (s, 4H), 7.05 (d, J = 7.83 Hz, 4H), 7.15 (d, J = 7.83 Hz, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ 21.07, 52.79, 128.08, 129.02, 136.42, 137.32. MS (EI): *m*/*z* (%): 225 (10) [M^+], 224 (7), 132(5), 121(7), 120 (73), 118 (5), 106 (22), 105 (100), 104 (6), 93 (6), 91 (19), 79 (13), 77 (16).

Bis[4-(trifluoromethyl)benzyl]amine (**2f**, CAS registry number: 145126-91-6): MS (EI): *m*/*z* (%): 333 (10) [M^+], 332 (9), 188 (14), 186 (10), 175 (5), 174 (59), 160 (21), 159 (100), 140 (7), 119 (7), 109 (26), 91 (17).

4,4'-Dipicolylamine (**2g**, CAS registry number: 1539-39-5): 57 % isolated yield (Table 2, entry 16, 60 h). ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 2.24 (brs, 1H), 3.76 (s, 4H), 7.11-7.31 (m, 4H), 8.34-8.59 (m, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ 51.76, 122.84, 148.86, 149.74. MS (EI): *m*/*z* (%): 199 (11) [M^+], 198 (6), 121 (45), 119 (6), 107 (20), 94 (11), 93 (100), 92 (79), 80 (16), 79 (13), 66 (6), 65 (34), 52 (8), 51 (11).

3,3'-Dipicolylamine (**2h**, CAS registry number: 1656-94-6): 199 (11) [M^+], 198 (14), 196 (8), 170 (6), 121 (26), 119 (17), 107 (22), 93 (33), 92 (100), 80 (27), 79 (7), 65 (36), 63 (5), 52 (5), 51 (6).

2,2'-Dipicolylamine (**2i**, CAS registry number: 1539-42-0): ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 2.64 (brs, 1H), 3.98 (s, 4H), 7.13-7.18 (m, 2H), 7.36 (d, J = 7.74 Hz, 2H), 7.60-7.67 (m, 2H),

8.55-8.57 (m, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ 54.66, 121.78, 122.12, 136.29, 149.18, 159.61. MS (EI): *m*/*z* (%): 199 (0.1) [M^+], 198 (0.2), 121 (6), 107 (45), 94 (8), 93 (100), 92 (19), 80 (5), 66 (6), 65 (13).

Dioctylamine (**2j**, CAS registry number: 1120-48-5): 93 % isolated yield (Table 2, entry 22, 36 h). ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 0.88 (t, J = 6.75 Hz, 6H), 1.24-1.32 (m, 20H), 1.33 (brs, 1H) 1.48 (quin, J = 6.75 Hz, 4H), 2.58 (t, J = 7.24 Hz, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ 14.03, 22.61, 27.39, 29.23, 29.51, 30.19, 31.80, 50.15. MS (EI): *m*/*z* (%): 241 (4) [M^+], 240 (1), 212 (1), 198 (1), 186 (1), 156 (1), 143 (10), 142 (100), 140 (6), 128 (3), 112 (1), 98 (2), 84 (2), 72 (1), 71 (3), 70 (4), 69 (4), 58 (1), 57 (7), 56 (4), 55 (5).

Didodecylamine (**2k**, CAS registry number: 3007-31-6): 95 % isolated yield (Table 2, entry 24, 36 h). ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 0.81 (t, J = 6.91 Hz, 6H), 1.13-1.24 (m, 37H), 1.40 (quin, J = 6.91 Hz, 4H), 2.51 (t, J = 7.24 Hz, 4H). ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ 14.07, 22.66, 27.41, 29.33, 29.58, 29.59, 29.60, 29.62, 29.65, 30.17, 31.90, 50.13. MS (EI): *m*/*z* (%): 353 (2) [M^+], 352 (2), 254 (1), 240 (1), 212 (2), 200 (1), 199 (16), 198 (100), 197 (1), 196 (4), 186 (1), 185 (1), 184 (4), 126 (2), 112 (2), 98 (2), 97 (1), 86 (1), 85 (1), 84 (2), 83 (2), 81 (1), 72 (1), 71 (2), 70 (4), 69 (3), 58 (1), 57 (8), 56 (3), 55 (7).

***N*-Octylcyclooctanamine** (**2l**, CAS registry number: 1040017-43-3): MS (EI): *m*/*z* (%): 239 (9) [M^+], 196 (17), 194 (7), 182 (14), 169 (12), 168 (100), 152 (5), 141 (10), 140 (95), 138 (8), 128 (6), 126 (13), 112 (17), 111 (8), 110 (6), 98 (15), 96 (5), 84 (12), 82 (7), 71 (9), 70 (17), 69 (24), 68 (6), 67 (8), 57 (16), 56 (23), 55 (20).

***N*-Octylbenzylamine** (**2m**, CAS registry number: 1667-16-9): MS (EI): *m*/*z* (%): 219 (1) [M^+], 160 (2), 134 (2), 128 (6), 121 (8), 120 (85), 118 (3), 107 (4), 106 (11), 92 (8), 91 (100), 65 (6).

***N*-Phenylbenzylamine** (**2n**, CAS registry number: 103-32-2): ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ 4.00 (brs, 1H), 4.31 (s, 2H), 6.59-6.64 (m, 2H), 6.68-6.74 (m, 1H), 7.13-7.20 (m, 2H), 7.24-7.38 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS): δ 48.25, 112.79, 117.51, 127.18, 127.46, 128.59, 129.22, 139.39, 148.11. MS (EI): *m*/*z* (%): 184 (9), 183 (63) [M^+], 182 (22), 180 (3), 106 (19), 104 (9), 92 (9), 91 (100), 77 (17), 65 (16), 51 (7).

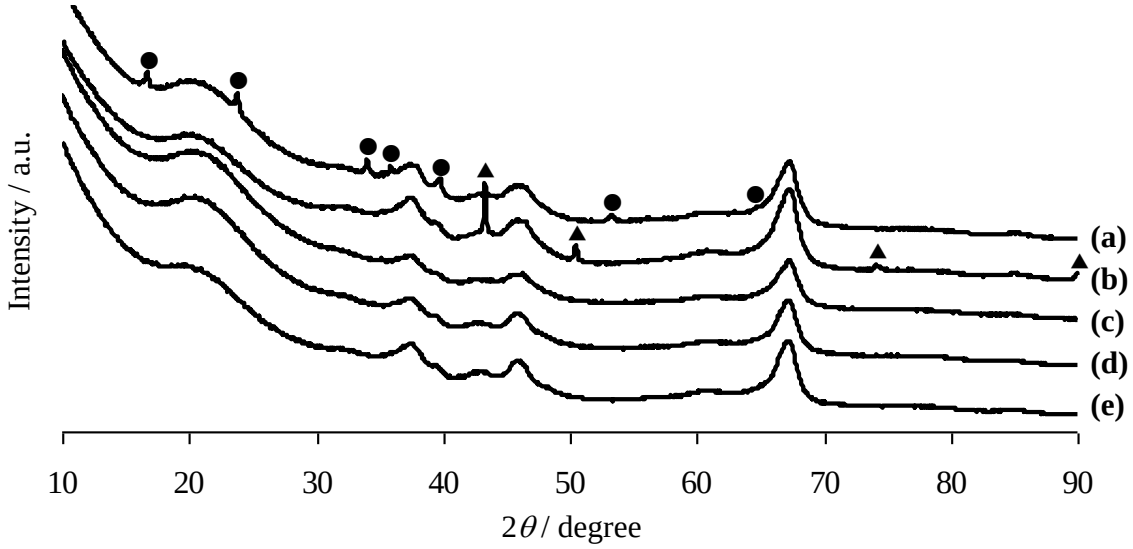

Fig. S1 XRD patterns of (a) a mixture of $Cu(OH)_2$ (Cu: 1 wt%) and Al_2O_3, (b) a mixture of Cu metal (Cu: 1 wt%) and Al_2O_3, (c) Al_2O_3, (d) $Cu(OH)_x/Al_2O_3$, and (e) Cu/Al_2O_3. The circles and triangles indicate the diffractions of $Cu(OH)_2$ and Cu, respectively.

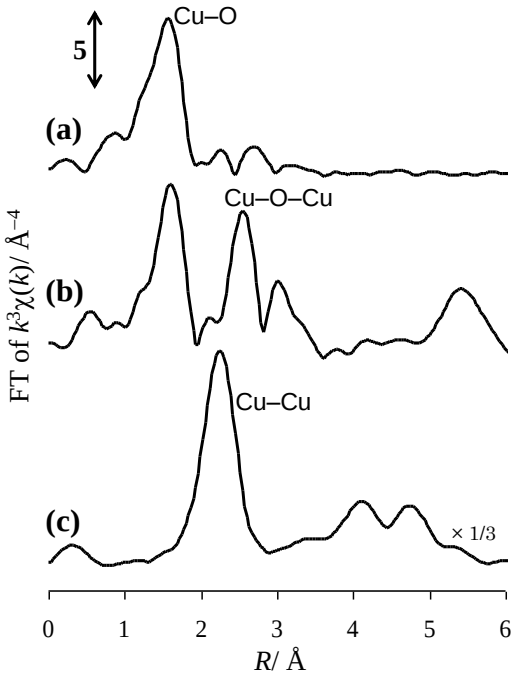

Fig. S2 Radial distribution functions from the Fourier transform of the k^3-weighed EXAFS for (a) $Cu(OH)_x/Al_2O_3$, (b) CuO, and (c) Cu foil. The phase shift was not corrected.