Supporting information

Size- and support-dependent selective amine cross-coupling with platinum nanocluster catalysts

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1. TEM

Transmission electron microscopy (TEM) measurement was carried out using a JEOL JEM-2100F TEM operated at 200 kV. The average Pt particle size from TEM (2.43 ± 0.65 nm) was consistent with that from CO adsorption (2.5 nm) within the experimental error. Based on the result, we adopted Pt particle sizes from CO adsorption (Table 1) in this study.

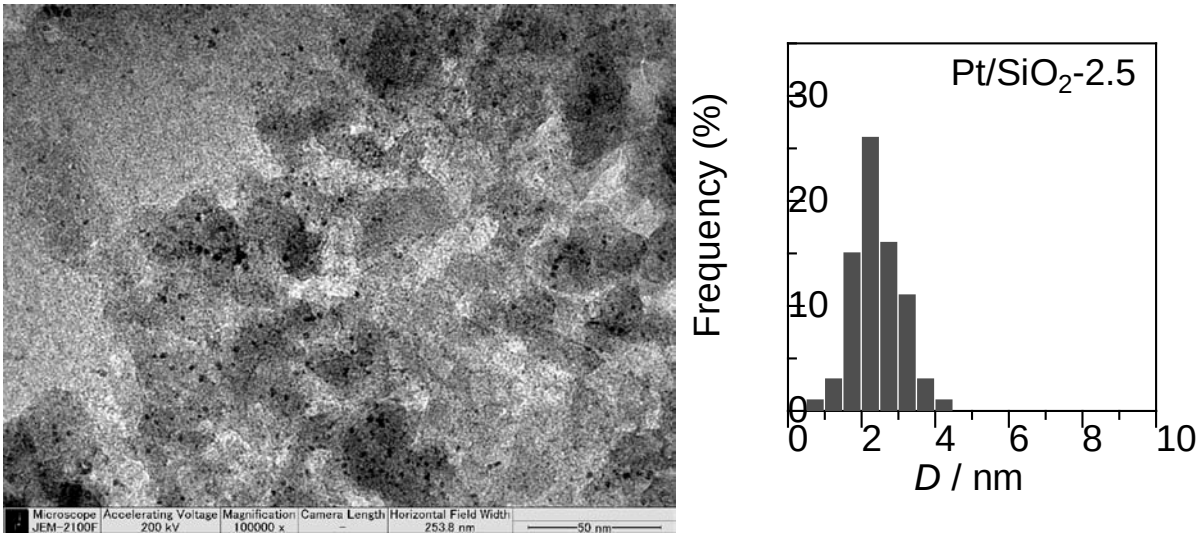


Fig. S1. TEM image and particle size distribution of Pt/SiO_2-2.5.

2. EXAFS curve-fitting

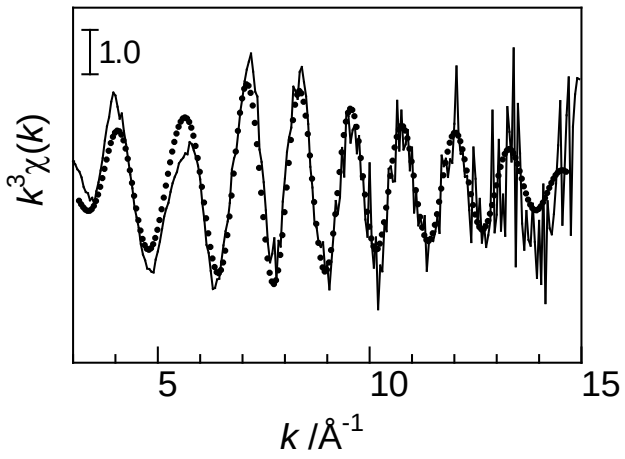
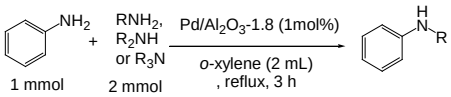
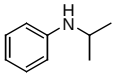
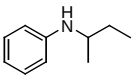
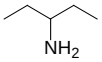
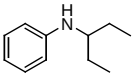
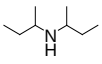
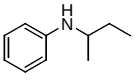
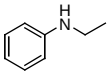


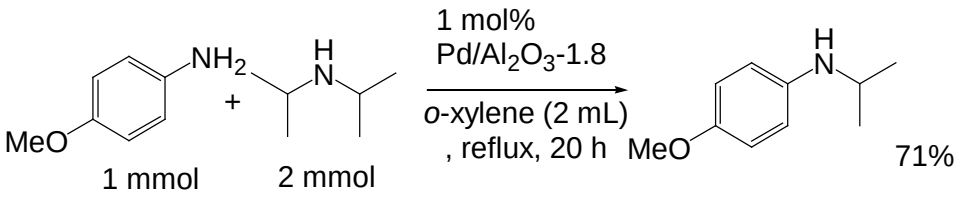
Fig. S2. The inverse Fourier transform of k^3-weighted Pt L3-edge EXAFS spectrum of (solid line) Pt/Al_2O_3-0.8 and (•) its best fit derived from curve-fitting analysis.

Table S1. N-alkylation of aniline with various amines by Pd/Al_2O_3-1.8.[a]

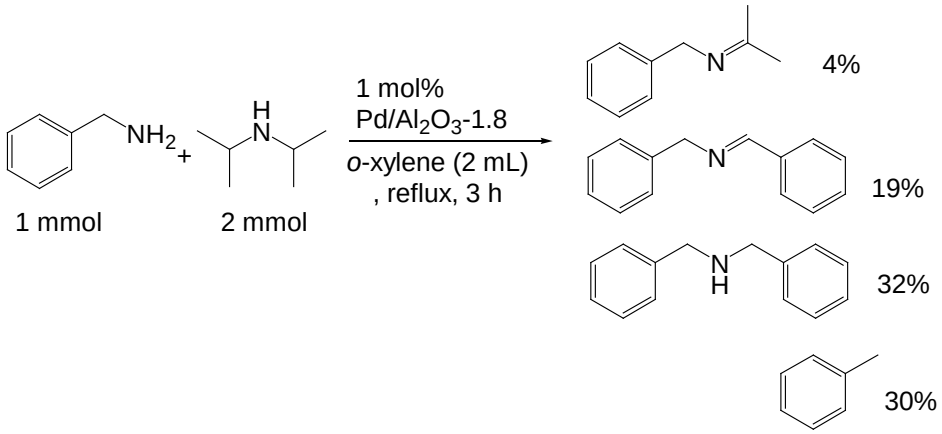


Entry	Amine donor	Product	Conversion/ %	Yield / %
1	 **2**	 **3**	0	0
2		**3**	0	0
3			0	0
4			0	0
5			0	0
6	Et_3N		93	79

[a] Yields of product determined by GC are based on aniline. Conditions are shown in Table 4.



Scheme S1. N-alkylation of *p*-methoxyaniline with *i*Pr_2NH by Pd/Al_2O_3-1.8.



Scheme S2. N-alkylation of benzylamine with *i*Pr_2NH by Pd/Al_2O_3-1.8.

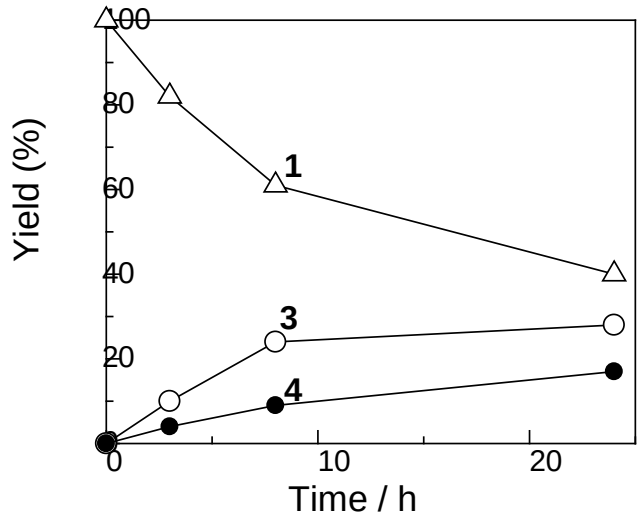
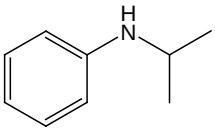


Fig. S3. Yields of (△) unreacted aniline **1,** (○) *N*-isopropylaniline **3** and (●) isopropylidene-phenylamine **4** for the reaction of aniline with *i*Pr_2NH by Pt/CeO_2-1.8 *vs.* reaction time. Reaction conditions are shown in Table 3.

3. ^{1}H-NMR and GC/MS Analysis

^{1}H-NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard at ambient temperature on a Varian INOVA-500 operating at 500 MHz. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

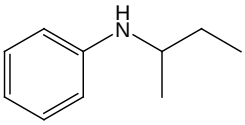
***N*-Isopropylaniline**: (Table 2, Entry 1)



^{1}H NMR ($CDCl_3$): δ 7.37-7.31 (m, 2H), 6.88-6.82 (m, 1H), 6.76-6.73 (m, 2H), 3.82-3.75 (m, 1H), 3.55 (br, s, 1H), 1.36 (d, J = 6.3 Hz, 6H).

MS: *m/z* (relative intensity) 135 (M^+,27), 120 (100).

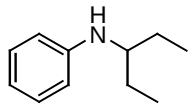
***N*-sec-Butylaniline**: (Table 2, Entries 7)



^{1}H NMR ($CDCl_3$): δ 7.33-7.40 (m, 2H), 6.74-6.90 (m, 3H), 3.71 (m, 1H), 3.39 (br, s, 1H), δ 1.62 (m, 2H), δ 1.23 (d, J = 7.1 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H).

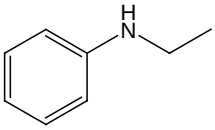
MS: *m/z* (relative intensity) 149 (M^+,28), 120 (100).

N-(pentan-3-yl)aniline: (Table 2, Entry 8)



MS: *m/z* (relative intensity) 163 (M^+,16), 134 (100).

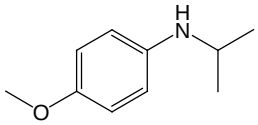
***N*-Ethylaniline**: (Table 2, Entry 10)



^{1}H NMR ($CDCl_3$): δ 6.79(m, 2H), 6.57 (m, 3H), 3.27 (br, s, 1H), 3.09 (q, J = 7.2 Hz, 2H), 1.23(t, J = 7.2 Hz, 3H).

MS: *m/z* (relative intensity) 121 (M^+,36), 106 (100).

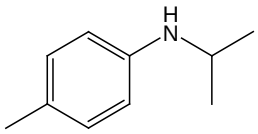
_N_-Isopropyl-4-methoxyaniline: (Table 3, Entry 1)



^{1}H NMR ($CDCl_3$): δ 6.81 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 3.77 (s, 3H), 3.57 (heptet, *J* = 6.3 Hz, 1H), 3.16 (br, s, 1H), 1.22 (d, *J* = 6.3 Hz, 6H).

MS: *m/z* (relative intensity) 165 (M^+,33), 150 (100).

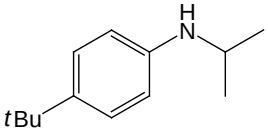
_N_-Isopropyl-4-methylaniline: (Table 3, Entry 2)



^{1}H NMR ($CDCl_3$): δ 7.06 (d, *J* = 8.1 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 3.67 (heptet, *J* = 6.3 Hz, 1H), 3.32 (br, 1H), 2.32 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 6H).

MS: *m/z* (relative intensity) 149 (M^+,31), 134 (100).

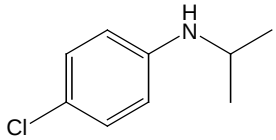
4-*t*-Butyl-*N*-isopropylaniline: (Table 3, Entry 3)



^{1}H NMR ($CDCl_3$): δ7.39 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 3.79 (heptet, *J* = 6.3 Hz, 1H), 3.50 (br, s, 1H), 1.49 (s, 9H), 1.38 (d, *J* = 6.3 Hz, 6H).

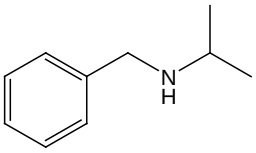
MS: *m/z* (relative intensity) 191 (M^+,31), 176 (100).

4-Chloro-N-isopropylaniline: (Table 3, Entry 4)



MS: *m/z* (relative intensity) 169 (M^+,25), 154 (100).

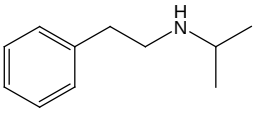
***N*-Benzylpropan-2-amine**: (Table 3, Entry 5)



^{1}H NMR ($CDCl_3$): δ 7.28-7.15 (m, 5H), 3.73 (s, 2H), 2.80 (heptet, *J* = 6.3 Hz, 1H), 1.39 (br, s, 1H), 1.04 (d, *J* = 6.3 Hz, 6H).

MS: *m/z* (relative intensity) 149 (M^+,8), 91 (100).

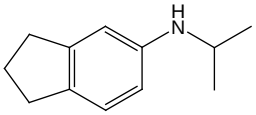
***N*-Phenethylpropan-2-amine**: (Table 3, Entry 6)



^{1}H NMR ($CDCl_3$): δ 7.35-7.18 (m, 5H), 2.91-2.83 (m, 5H), 1.08 (d, *J* = 6.0 Hz, 6H).

MS: *m/z* (relative intensity) 162 (M^+,1), 72 (100).

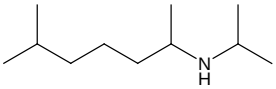
***N*-Isopropyl-2,3-dihydro-1H-inden-5-amine**: (Table 3, Entry 8)



^{1}H NMR ($CDCl_3$): δ 7.08 (d, *J* = 8.1 Hz, 2H), 6.57 (s, 1H), 6.47 (d, *J* = 8.1 Hz, 2H), 3.66 (heptet, *J* = 6.3 Hz, 1H), 3.29 (br, s, 1H), 2.88 (q, *J* = 7.8 Hz, 2H), 2.11 (sextet, *J* = 7.5 Hz, 2H), 1.26 (d, *J* = 6.3 Hz, 6H).

MS: *m/z* (relative intensity) 175 (M^+,24), 86(100).

***N*-Isopropyl-6-methylheptan-2-amine**: (Table 3, Entry 8)



^{1}H NMR ($CDCl_3$): δ 2.81 (heptet, *J* = 6.3 Hz, 1H), 2.60-2.40 (m, 1H), 1.45 (heptet, *J* = 6.6 Hz, 1H), 1.32-1.00 (m, 6H), 0.97-0.90 (m, 9H), 0.78 (d, *J* = 6.6 Hz, 6H), 0.63 (br, s, 1H).

MS: *m/z* (relative intensity) 171 (M^+,1), 86 (100).