Supporting Information

Heterogeneous Ni Catalysts for N-Alkylation of Amines with Alcohols

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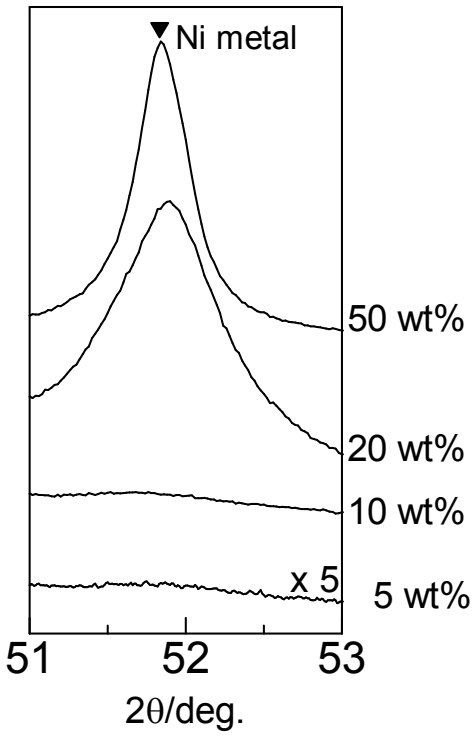


Figure S1 XRD patterns of Ni/Al_2O_3 catalysts with different Ni loadings pre-reduced at 500°C.

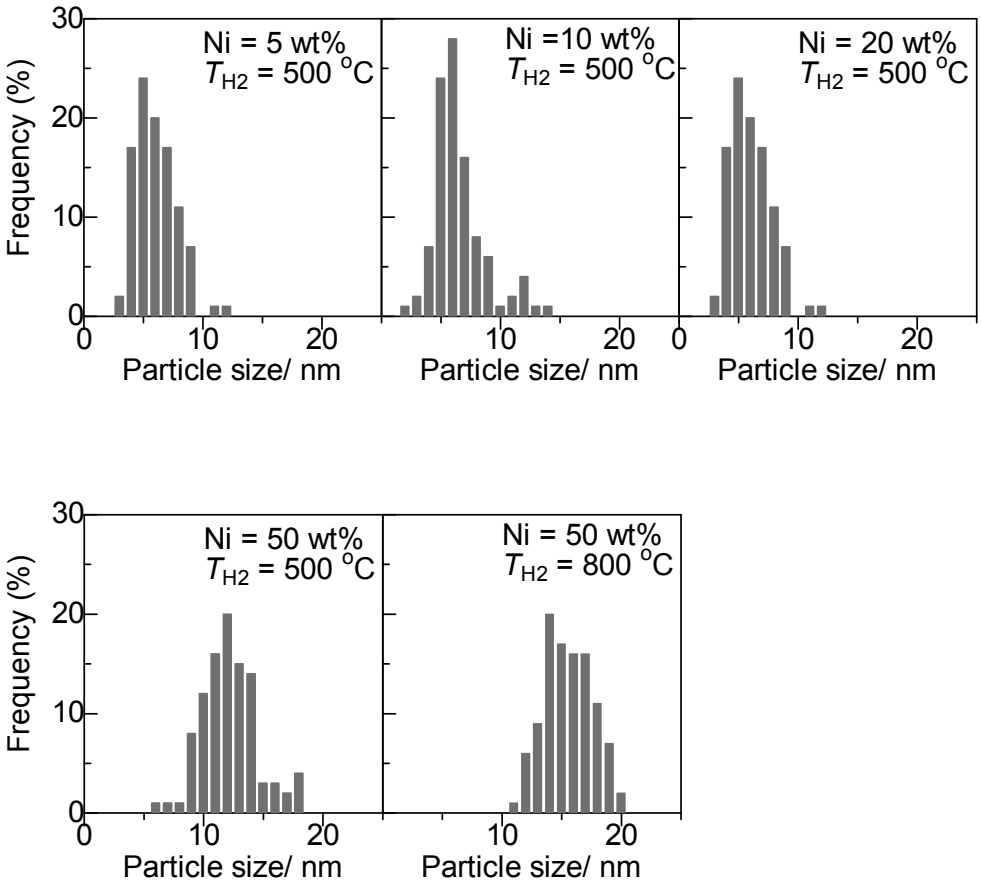


Figure S2. Particle size distribution of from TEM analysis. Particle size analysis was conducted on 103-108 particles.

Table S1. Catalysts for N-alkylation of aniline with 1-octanol.

catalyst	cat. /mol%	*T* /°C	*t* /h	yield (%)	TOF /h^{-1}	TON	remarks (additives)	ref.
Ni/θ-Al_2O_3	1	144	3	99	33	99 (800) [a]	-	this study
Ni-Cu/γ-Al_2O_3 [b]	38	160	12	86	0.2	2.2	25 mol% NaOH 12.5 mol% $CaCl_2$	37
Au/TiO_2	1	120	48	96	2	96	5 atm N_2	23
Cu-Ag/γ-Al_2O_3	1	144	24	86	3.6	86	-	22
Ru/Al_2O_3	5	132	24	89	0.7	18	-	17
Pd/Fe_2O_3	0.43	150	24	86	8.6	207	-	16
Pt-Sn/γ-Al_2O_3	0.25	145	24	93	15	356	-	24
Cp* Ir complex	2	110	17	97	2.9	49	2 mol% $NaHCO_3$	10
$FeBr_3$/amino acid	3	200	36	85	0.8	33	-	26

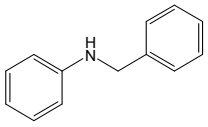
[a] cat. = 0.1 mol%, t = 120 h

[b] 1-dodecanol

^{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.

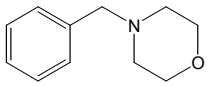
N-Benzylaniline[1]



^{1}H NMR($CDCl_3$): δ 7.40 - 7.17 (7H, m, aromatic) , δ 6.74 - 6.71 (1H, m, aromatic) , δ 6.66 - 6.64 (2H, m, aromatic) , δ 4.34 (2H, s, CH_2) , δ 4.08 (1H, br, NH).

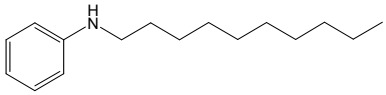
MS: m/z(relative intensity) 183 (M^+, 41), 91 (100).

N-benzylmorpholine[1]



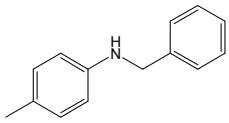
^{1}H NMR($CDCl_3$): δ 7.26 - 7.19 (5H, m, aromatic) , δ 3.64 (4H, t, J=4.5Hz, CH_2) , δ 3.43 (2H, s, CH_2) , δ 2.38 (4H, t, J=8.5Hz, CH_2).

N-Decylaniline[2]



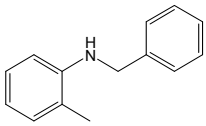
^{1}H NMR($CDCl_3$): δ 7.15 - 7.19 (2H, m, aromatic) , δ 6.67 - 6.71 (1H, m, aromatic) , δ 6.60 - 6.62 (2H, m, aromatic) , δ 3.71(1H, br, , NH), δ 3.12 - 3.09 (2H, t, J=7.5Hz, CH_2) , δ 1.59 - 1.65 (2H, m, CH_2) , δ 1.27 - 1.41 (14H, m, CH_2) , δ 0.89(3H, t, J=7.0Hz , CH_3).
MS: m/z(relative intensity) 233 (M^+,7), 106 (100).

Benzyl-p-tolyl-amine[3]



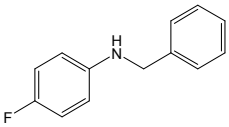
^{1}H NMR($CDCl_3$): δ 7.39 - 7.26 (5H, m, aromatic) , δ 7.01 - 6.98 (2H, m, aromatic) , δ 6.59 - 6.56 (2H, m, aromatic) , δ 4.31 (2H, s, CH_2) , δ 3.92 (1H, br, NH), δ 2.25 (3H, s, CH_3).

Benzyl-o-tolyl-amine[3]



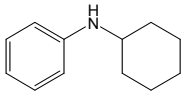
^{1}H NMR($CDCl_3$): δ 7.41 - 7.29 (5H, m, aromatic) , δ 7.12 - 7.08 (2H, m, aromatic) , δ 6.70 - 6.67 (1H, m, aromatic) , δ 6.62 (1H, d, J=8.0Hz, aromatic) , δ 4.38 (2H, s, CH_2) , δ 3.88 (1H, br, NH), δ 2.17 (3H, s, CH_3).
MS: m/z(relative intensity) 197 (M^+,18), 91 (100)

N-Benzyl-4-fluoroaniline[3]



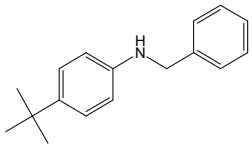
^{1}H NMR($CDCl_3$): δ 7.38 - 7.26 (5H, m, aromatic) , δ 7.91 - 6.88 (2H, m, aromatic) , δ 6.59 - 6.56 (2H, m, aromatic), δ 4.30 (2H, s, CH_2) , δ 3.93 (1H, br, NH).

N-cyclohexyl-N-phenylamine[4]



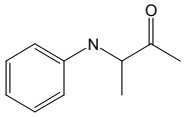
^{1}H NMR($CDCl_3$): δ 7.17 - 7.13 (2H, m, aromatic) , δ 6.67 - 6.63 (1H, m, aromatic) , δ 6.60 - 6.56 (2H, m, aromatic) , δ 3.53 (1H, br, NH) , δ 3.27 - 3.22 (1H, m, CH) , δ 2.05 - 2.03 (1H, m) , δ 1.77 - 1.62 (4H, m) , δ 1.41 - 1.31 (2H, m), δ 1.27 - 1.09 (3H, m).
MS: m/z(relative intensity) 175 (M^+,36), 132 (100).

N-(4-tert-butylphenyl)benzylamine



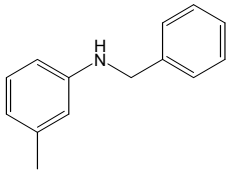
^{1}H NMR($CDCl_3$): δ 7.43 - 7.32 (4H, m, aromatic) , δ 7.26 - 7.17 (3H, m, aromatic) , δ 6.62 - 6.58 (2H, m, aromatic) , δ 4.30 (2H, s, CH_2) , δ 3.93 (1H, br, NH), δ 1.27 (9H, s, CH_3).
MS: m/z(relative intensity) 239 (M^+,31), 91 (100)

N-(1-metyl-2-propanone)aniline[5]



^{1}H NMR($CDCl_3$): δ 7.19 - 7.15 (2H, m, aromatic) , δ 6.74 - 6.69 (1H, m, aromatic) , δ 6.57 - 6.54 (2H, m, aromatic) , δ 4.38 (1H, br, NH) , δ 4.09 - 4.04 (1H, m, CH), δ 2.20 (3H, s, CH_3), δ 1.41 (3H, d, J=6.8Hz, CH_3).
MS: m/z(relative intensity) 163 (M^+, 6), 120 (100).

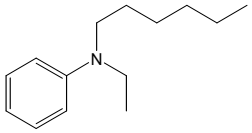
Benzyl-m-tolyl-amine[3]



^{1}H NMR($CDCl_3$): δ 7.38 - 7.32 (4H, m, aromatic) , δ 7.29 - 7.24 (1H, m, aromatic) , δ 7.06

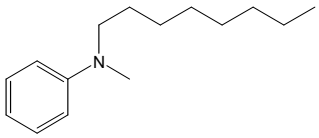
(1H, t, J=7.8Hz, aromatic) , δ 6.54 (1H, d, J=7.4Hz, aromatic) , δ 6.47 - 6.43 (2H, m, aromatic), δ 4.31 (2H, s, CH_2), δ 3.96 (1H, br, NH), δ 2.27 (3H, s, CH_3).
MS: m/z(relative intensity) 197 (M^+, 30), 91 (100).

N-hexyl-N-ethylaniline[6]



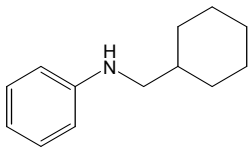
^{1}H NMR($CDCl_3$): δ 7.22 - 7.15 (2H, m, aromatic) , δ 6.67 - 6.59 (3H, m, aromatic) , δ 3.38 - 3.32 (2H, q, J=6.9Hz, CH_2) , δ 3.23 (2H, t, J=7.8Hz, CH_2) , δ 1.60 - 1.54 (2H, m, CH_2), δ 1.32 - 1.27 (6H, m, CH_2), δ 1.42 (3H, t, J=7.3Hz, CH_3), δ 0.90 (3H, t, J=6.8Hz, CH_3).
MS: m/z(relative intensity) 205 (M^+, 14), 134 (100).

N-octyl-N-methylaniline[1]



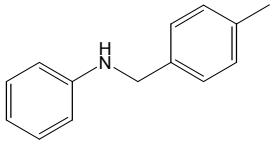
^{1}H NMR($CDCl_3$): δ 7.25 - 7.20 (2H, m, aromatic) , δ 6.70 - 6.64 (3H, m, aromatic) , δ 3.29 (2H, t, J=7.5Hz, CH_2) , δ 2.92 (3H, s, CH_3) , δ 1.58 - 1.54 (2H, m, CH_2), δ 1.30 - 1.27 (10H, m, CH_2), δ 0.90 - 0.86 (3H, m, CH_3).
MS: m/z(relative intensity) 219 (M^+, 6), 120 (100).

N-(cyclohexylmethyl)aniline[4]



^{1}H NMR($CDCl_3$): δ 7.18 - 7.13 (2H, m, aromatic) , δ 6.66 (1H, t, J=7.3Hz, aromatic) , δ 6.58 (2H, d, J=7.8Hz, aromatic) , δ 3.69 (1H, br, NH) , δ 2.94 (2H, d, J=6.4Hz, CH_2) , δ 1.83 - 1.67 (5H, m) , δ 1.62 - 1.52 (1H, m) , δ 1.30 - 1.14 (3H, m), δ 1.02 - 0.93 (2H, m).
MS: m/z(relative intensity) 189 (M^+, 13), 106 (100).

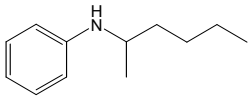
N-(cyclohexylmethyl)aniline[3]



^{1}H NMR($CDCl_3$): δ 7.29 - 7.24 (2H, m, aromatic) , δ 7.19 - 7.14 (4H, m, aromatic) , δ 6.71 (1H, t, J=7.3Hz, aromatic) , δ 6.63 (2H, d, J=7.8Hz, aromatic) , δ 4.28 (2H, s, CH_2) , δ 3.97 (1H, br, NH), δ 2.34 (3H, s, CH_3).

MS: m/z(relative intensity) 197 (M^+, 37), 105 (100).

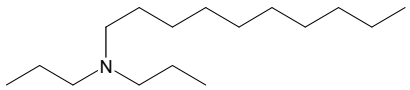
N-(cyclohexylmethyl)aniline[7]



^{1}H NMR($CDCl_3$): δ 7.17 - 7.13 (2H, m, aromatic) , δ 6.67 - 6.63 (1H, m, aromatic) , δ 6.60 - 6.56 (2H, m, aromatic) , δ 3.48 - 3.41 (2H, m) , δ 1.61 - 1.52 (1H, m) , δ 1.44 - 1.30 (5H, m) , δ 1.17 (3H, d, J=6.0Hz, CH_3) , δ 0.90 (3H, t, J=7.3Hz, CH_3).

MS: m/z(relative intensity) 177 (M^+, 10), 120 (100).

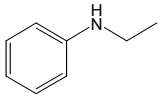
N,N-dipropyl-1-decanamine



^{1}H NMR($CDCl_3$): δ 2.58 - 2.36 (6H, m, CH_2) , δ 1.50 - 1.26 (20H, m, CH_2) , δ 0.89 - 0.85 (9H, m, CH_3).

MS: m/z(relative intensity) 241 (M^+,4), 114 (100).

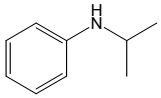
N-ethylaniline[8]



^{1}H NMR($CDCl_3$): δ 7.19 - 7.15 (2H, m, aromatic) , δ 6.71 - 6.67 (1H, m, aromatic) , δ 6.62 - 6.59 (2H, m, aromatic) , δ 3.53 (1H, br, NH) , δ 3.16 (3H, q, J=7.3Hz, CH_2) , δ 1.25 (3H, t, J=7.3Hz, CH_3).

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

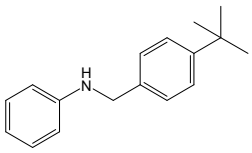
N-isopropylaniline[9]



^{1}H NMR($CDCl_3$): δ 7.18 - 7.11 (2H, m, aromatic) , δ 6.68 - 6.65 (1H, m, aromatic) , δ 6.60 - 6.57 (2H, m, aromatic) , δ 3.66 - 3.60 (1H, m, CH) , δ 3.44 (1H, br, NH) , δ 1.21 (6H, d, J=6.4Hz, CH_3).

MS: m/z(relative intensity) 135 (M^+, 25), 120 (100).

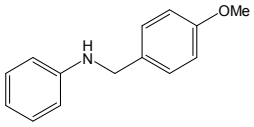
N-(4-tert-butylbenzyl)aniline



^{1}H NMR($CDCl_3$): δ 7.39 - 7.36 (2H, m, aromatic) , δ 7.32 - 7.30 (2H, m, aromatic) , δ 7.20 - 7.16 (2H, m, aromatic) , δ 6.73 - 6.70 (1H, m, aromatic) , δ 6.66 - 6.64 (2H, m, aromatic), δ 4.29 (2H, s, CH_2) , δ 3.98 (1H, br, NH) , δ 1.32 (9H, s, CH_3).

MS: m/z(relative intensity) 239 (M^+, 17), 147 (100).

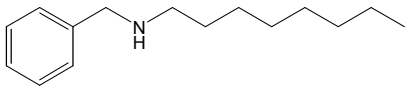
N-(4-methoxybenzyl)aniline[3]



^{1}H NMR($CDCl_3$): δ 7.30 - 7.25 (2H, m, aromatic) , δ 7.20 - 7.17 (2H, m, aromatic) , δ 6.89 - 6.86 (2H, m, aromatic) , δ 6.72 - 6.69 (1H, m, aromatic) , δ 6.65 - 6.62 (2H, m, aromatic) , δ 4.25 (2H, s, CH_2), δ 3.93 (1H, br, NH), δ 3.80 (3H, s, CH_3).

MS: m/z(relative intensity) 213 (M^+, 21), 121 (100).

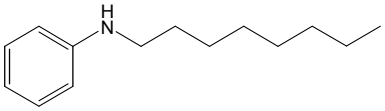
N-octylbenzylaniline[10]



^{1}H NMR($CDCl_3$): δ 7.38 - 7.21 (5H, m, aromatic) , δ 3.79 (2H, s) , δ 2.64 - 2.58 (2H, m) , δ 1.53 - 1.43 (2H, m) , δ 1.36 - 1.20 (11H, m) , δ 0.88 (2H, t, J=7.3Hz, CH_3).

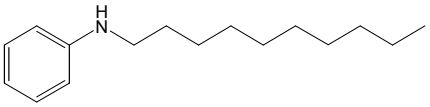
MS: m/z(relative intensity) 219 (M^+, 2), 91 (100).

N-octylaniline[4]



^{1}H NMR($CDCl_3$): δ 7.19 - 7.14 (2H, m, aromatic) , δ 6.70 - 6.66 (1H, m, aromatic) , δ 6.61 - 6.59 (2H, m, aromatic) , δ 3.58 (1H, br, , NH), δ 3.12 - 3.08 (2H, t, J=7.3Hz, CH_2) , δ 1.65 - 1.54 (2H, m, CH_2) , δ 1.41 - 1.23 (10H, m, CH_2) , δ 0.88 (3H, t, J=7.1Hz , CH_3).
MS: m/z(relative intensity) 205 (M^+, 10), 106 (100).

N-octylaniline



^{1}H NMR($CDCl_3$): δ 2.612 - 2.56 (2H, m, CH_2) , δ 2.41 - 2.33 (1H, m, CH) , δ 1.91 - 1.02 (26H, m, CH_2) , δ 0.88 (3H, t, J=7.3Hz, CH_3).
MS: m/z(relative intensity) 239 (M^+, 2), 112 (100).

References

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