Secondary amines from catalytic amination of bio-derived phenolics over Pd/C and Rh/C: Effect of operation parameters.

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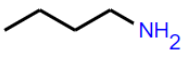
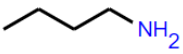
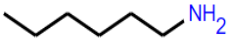
Table S1. Binding energy (BE, eV), kinetic energy (KE, eV) and modified Auger parameter (α'=BE+KE, eV) values of Pd $3d_{5/2}$ and Rh $3d_{5/2}$ on catalysts before reduction the H_2 and after reduction conditions (400°C and H_2)

Catalysts	Condition	Chemical state	Pd $3d_{5/2}$			
			BE (eV)	**KE (eV)**	**α' (eV)**	**Pd, at. %**
Pd/C	Before Reduction	Pd^0	335.1	327.5	662.6	46.38
		Pd^{2+}	335.9	322.6	658.5	52.61
	After reduction	Pd^0	336.2	327.2	663.1	61.46
		Pd^{2+}	335.3	321.9	667,2	38.54
	Condition	**Chemical state**	**Rh $3d_{5/2}$**			
			BE (eV)	**KE (eV)**	**α' (eV)**	**Rh, at. %**
Rh/C	Before Reduction	Rh^0	314.0	294.6	608.6	40.21
		Rh^{2+}	312.1	295.4	607.5	59.79
	After reduction	Rh^0	308.8	299.6	608.4	60.45
		Rh^{2+}	307.4	299.9	607.3	39.55

Table S2. Amination the phenol of different amines catalyst Pd/C and Rh/C in presence of H_2 (1.5 bar). Reactions were carried in 10 mL glass autoclaves, 0.2 mol/L of phenol, using tert- amyl alcohol as a solvent.

Catalyst	Amine	Conditions reactions	Conversion (%)	Yield (%)
Pd/C		120°C, 1.4 eq amine, 6h	24.5	36
		160°C, 1.4 eq amine, 8h	31	42
		160°C, 2 eq amine, 6h	27.3	25
		120°C, 1.4 eq amine, 6h	0	-
		160°C, 1.4 eq amine, 8h	1	-
		160°C, 2 eq amine, 6h	1	-
Rh/C		120°C, 1.4 eq amine, 6h	15.4	19
		160°C, 1.4 eq amine, 8h	22.6	18
		160°C, 2 eq amine, 6h	17.1	11
		160°C, 1.4 eq amine, 6h	0	-
		160°C, 1.4 eq amine, 8h	0.1	-
		160°C, 2 eq amine, 6h	0	-

$X_i = 100\times\left({}^{(n_{i,o}-n_{i,t})}/_{n_{i,o}}\right)$, i = reactants, t = reaction time.

$S_i = 100\times\left({}^{n_{i,t}}/_{\sum_{i=1}^{n} n_{i,t}}\right)$, i = reactants, n = products, t = reaction time.

*Quantities results were determined by GC-FID analysis (Agilent Technologies 7890A), and an HP-5 MS capillary column (30 m x 250 µm x 0.25 µm), nonone as internal standard.

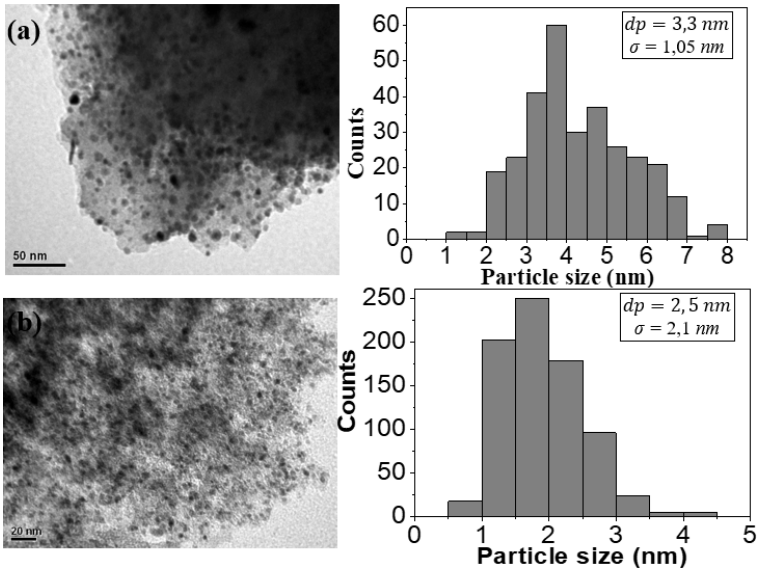


Figure S1. Transmission electron microscopy images and mean particle size (dp) of a) Pd/C, (b) Rh/C after reduction..

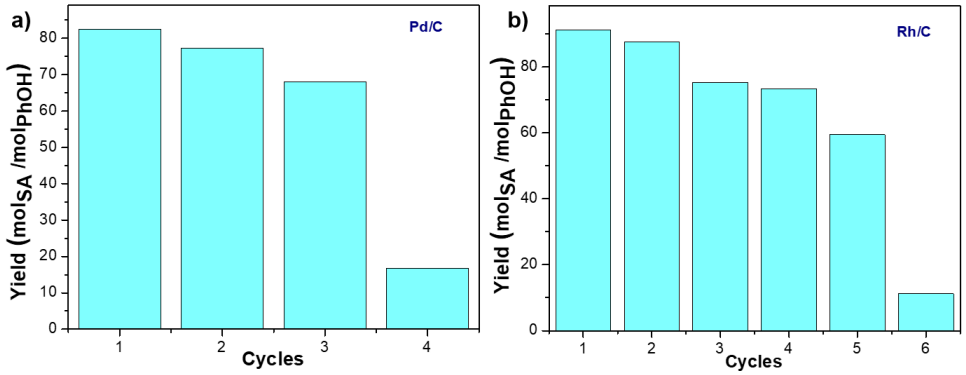


Figure S2. Stability catalytic assays a) Pd/C and b) Rh/C. T = 120 ºC, P_{H2}= 1.5 bar, C^0_{PhOH} = 0.2 mol/L, C^0_{Amine} = 1.4 Eqv., t = 6 h, V_R = 4 mL.

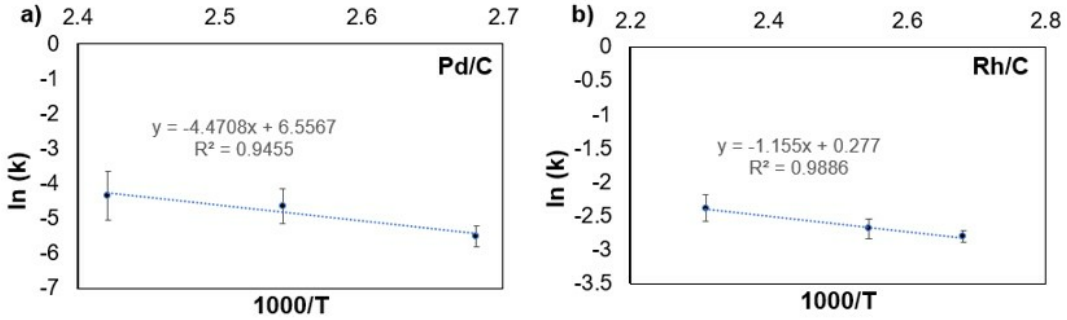


Figure S3. Arrhenius plots for reductive phenol amination with cyclohexylamine (a) reaction performed on Pd/C, (b) reaction performed on Rh/C.

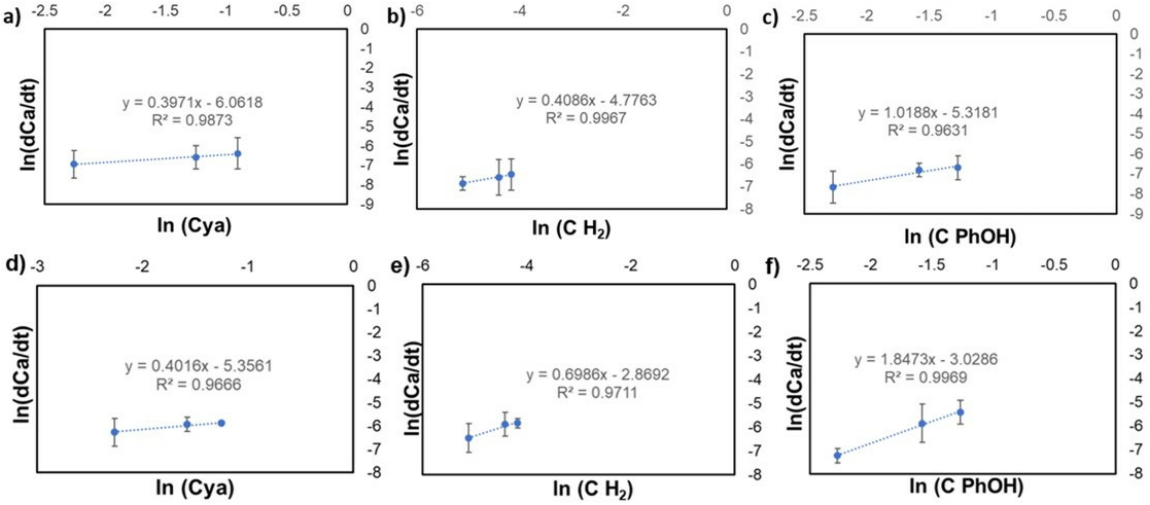


Figure S4. Fitting plots of power law kinetic model data fit to determine reaction orders of (a), (d) cyclohexylamine (CyA); (b), (e), Hydrogen (H_2) and (c), (f) phenol (PhOH) of Pd/C and Rh/C, respectively.