Supporting Information

Direct amination of poly(p-phenylene oxide) to substituted anilines over bimetallic Pd-Ru catalysts

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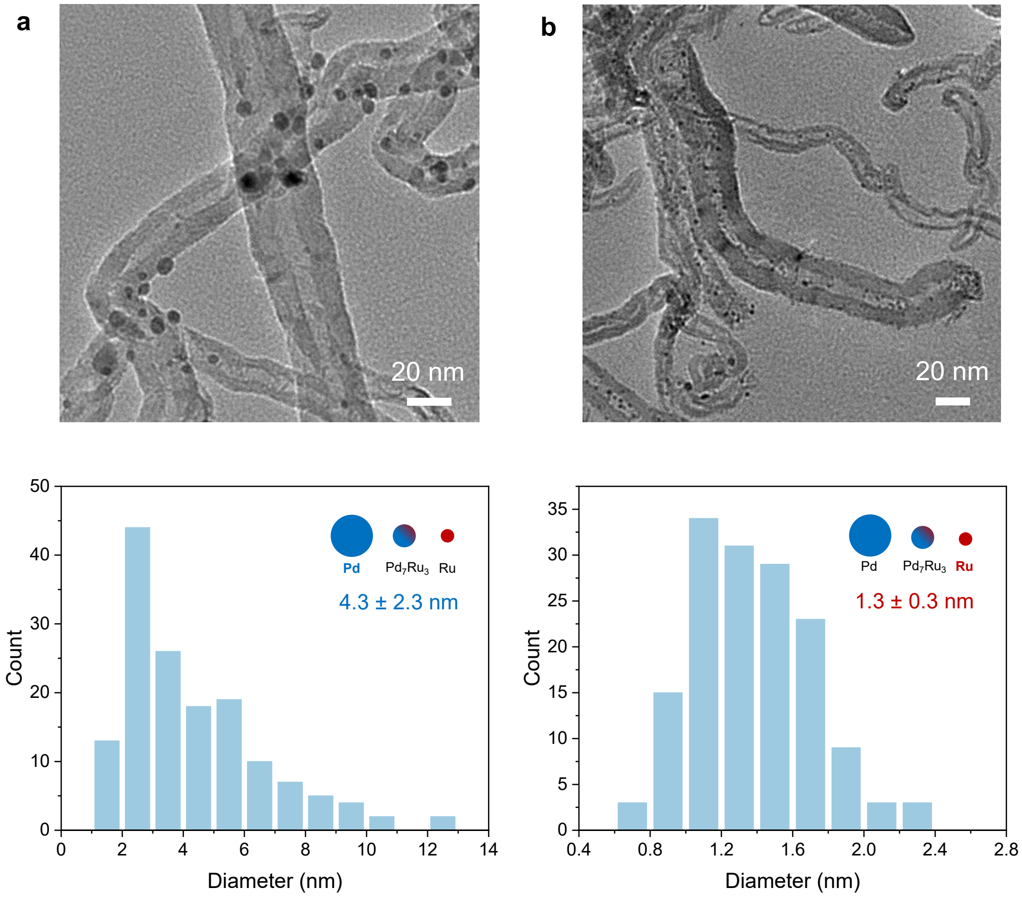
Number of pages: 13
Number of figures: 11
Number of tables: 1



2% Pd/CNT

2% Ru/CNT

Fig. S1. TEM images and particle size distribution of (a) Pd/CNT and (b) Ru/CNT at 2% loading. The circle illustrates the relative particle size of Pd/CNT, Pd$_7$Ru$_3$/CNT and Ru/CNT.

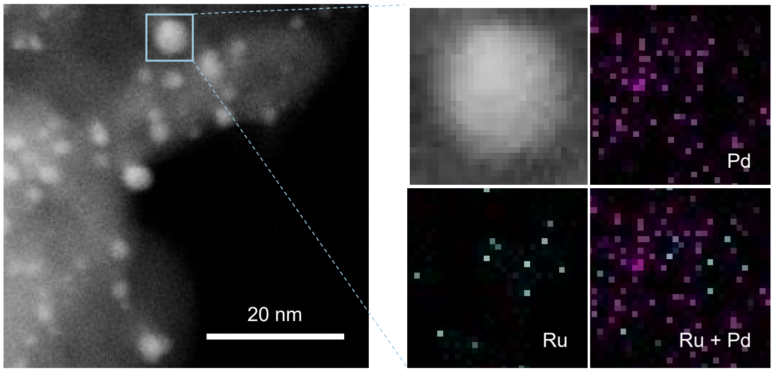


Fig. S2. (a) STEM of 2% Pd_7Ru_3/CNT and elemental maps of (b-d) Pd and Ru of a nanoparticle.

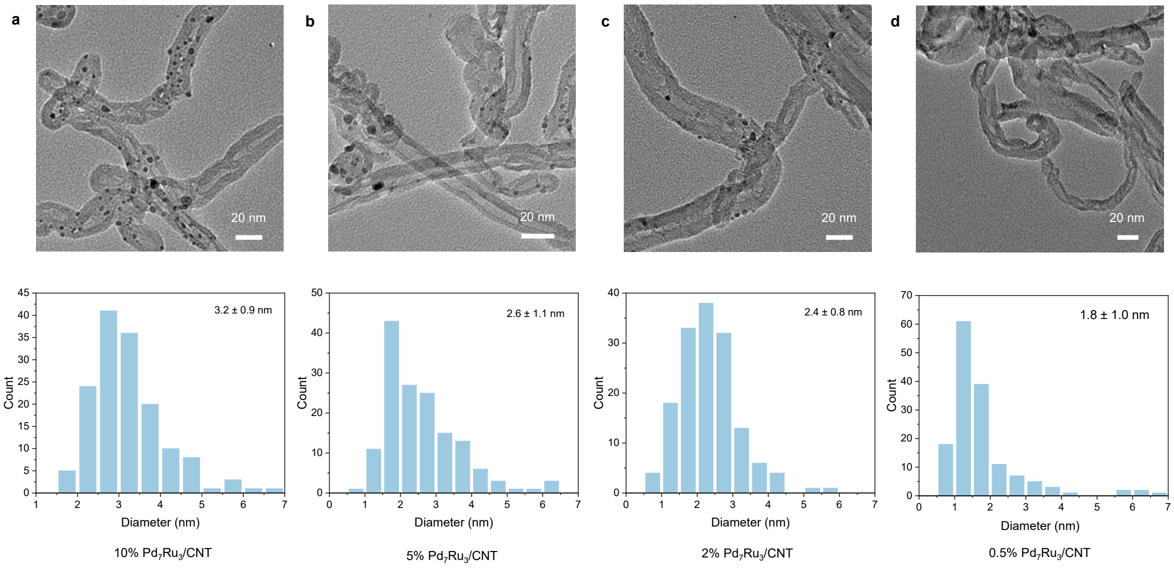


Fig. S3. TEM images and particle size distribution of the bimetallic Pd_7Ru_3/CNT at (a) 10%, (b) 5%, (c) 2%, and (d) 0.5% metal loading. The scale bars on the TEM images are 20 nm.

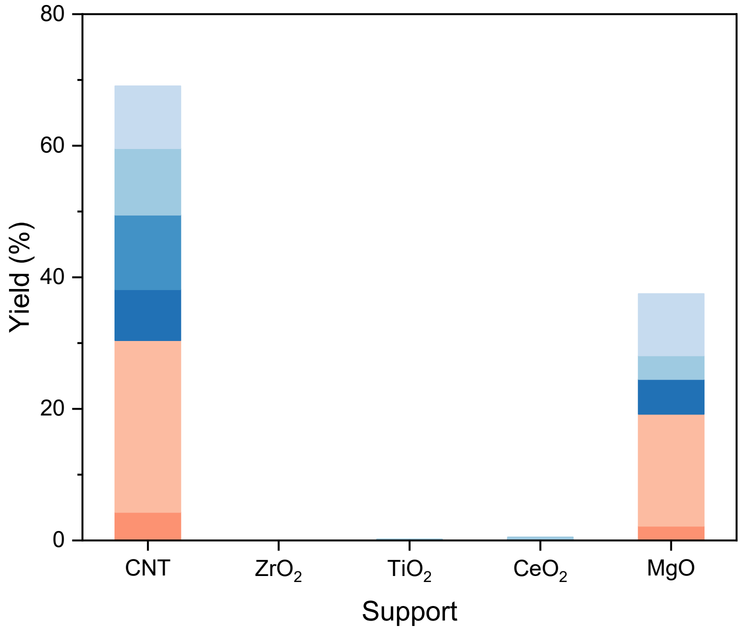


Fig. S4. Effect of various catalyst supports for the conversion of PPO into dimethylanilines. Reaction condition: 50 mg PPO, 50 mg 2% Pd_7Ru_3/support, 4 mL octane, 1 mL 25% aqueous NH_3 solution, 5 bar H_2, 280 °C, 4 h.

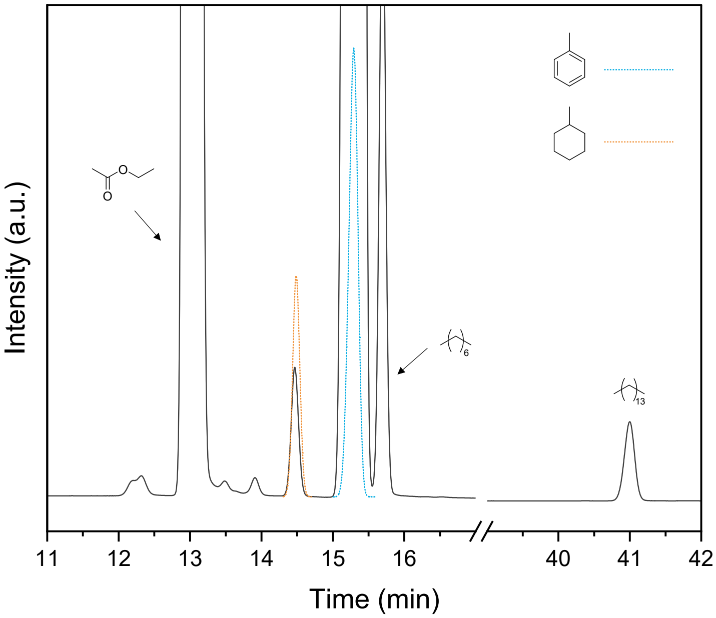


Fig. S5. Generation of methylcyclohexane from toluene over 2% Pd_7Ru_3/CNT (without PPO). Reaction condition: 50 mg Pd_7Ru_3/CNT (2 wt% metal loading), 4 mL toluene, 1 mL 25% aqueous NH_3 solution, 5 bar H_2, 280 °C, 4 h. Ethyl acetate was used as extraction solvent, and pentadecane in octane (100 mg/mL) was used as internal standard. The hydrogenation of toluene, which occupied the catalytic sites and consumed hydrogen, could explain its poor performance when being employed as the solvent.

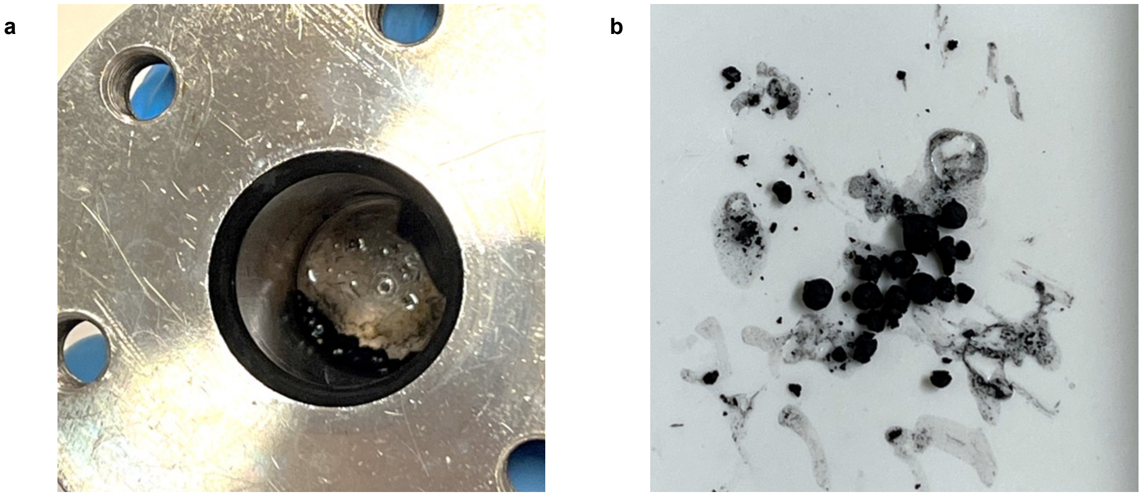


Fig. S6. Formation of black particles after the reaction through the aggregation of PPO and the catalyst when the volume ratio of octane to NH3 solution is 3.5:1.5: (a) observed at the bottom of the reactor, (b) displayed in a white container after extraction. Reaction condition: 50 mg PPO, 50 mg Pd_7Ru_3/CNT (2 wt% metal loading), 3.5 mL octane, 1.5 mL 25% aqueous NH_3 solution, 5 bar H_2, 280 °C, 4 h.

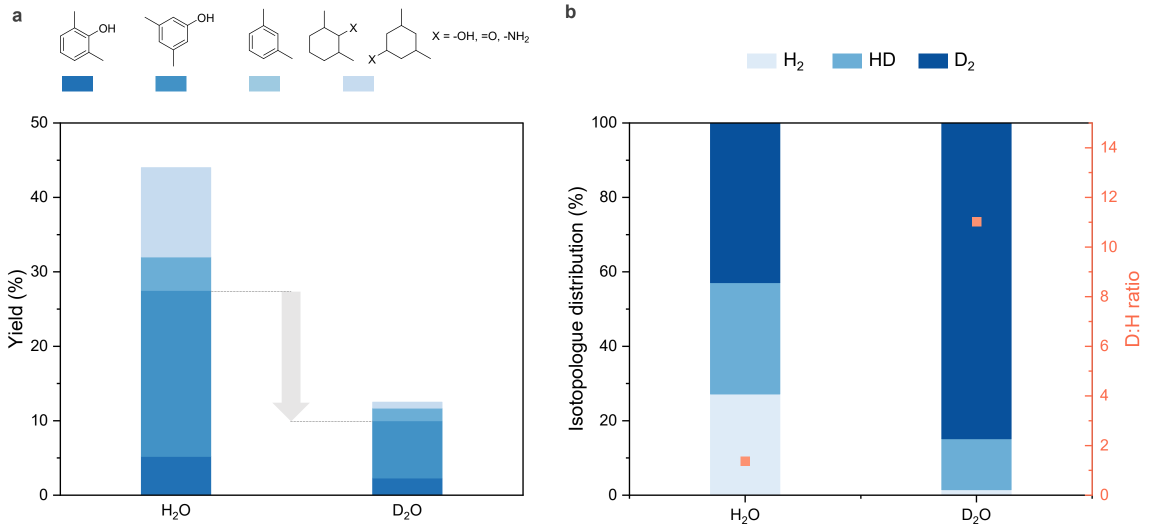


Fig. S7. Step 1 carried under deuterium with H_2O or D_2O as solvent: (a) product yield and (b) gas phase analysis by GC-MS. Reaction condition: 50 mg 2,6-DMP, 50 mg Pd_7Ru_3/CNT (2 wt% metal loading), 4 mL octane, 1 mL solvent, 5 bar D_2, 280 °C, 4 h.

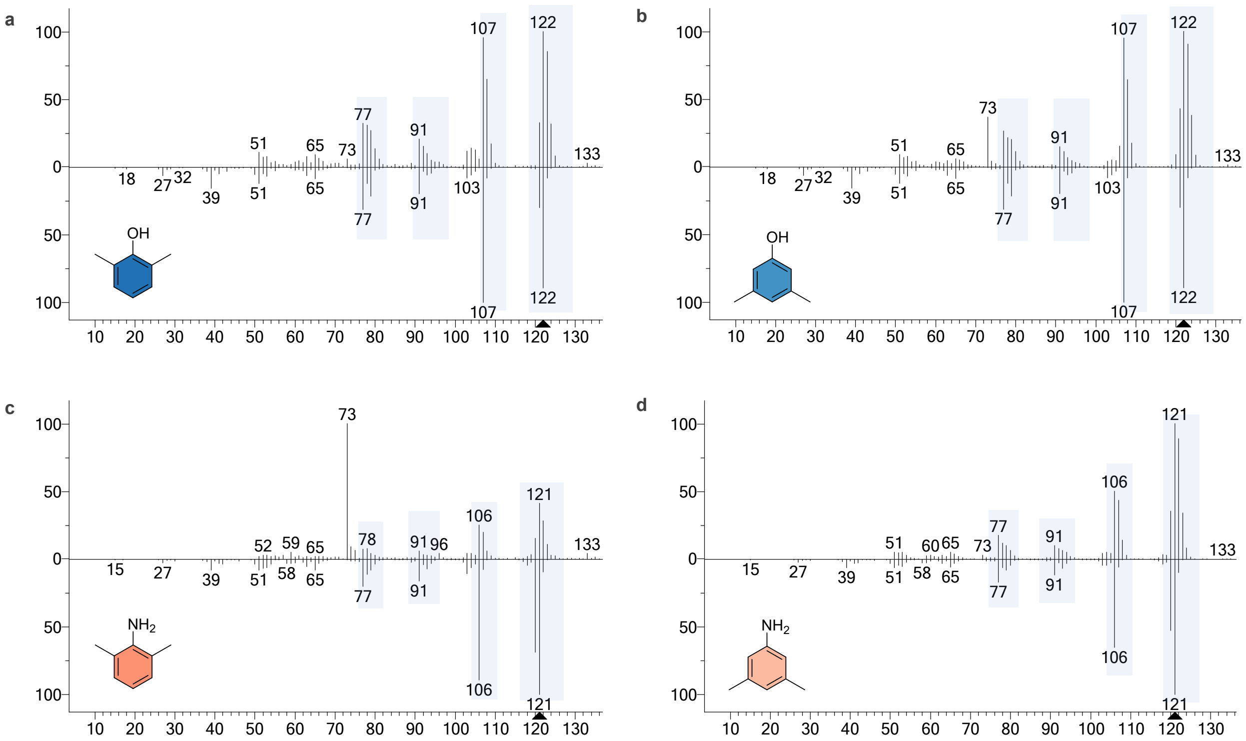


Fig. S8. MS spectra of products in the one-pot reaction carried under deuterium (top) compared to the reference library (bottom): (a) 2,6-DMP, (b) 3,5-DMP, (c) 2,6-DMA, (d) 3,5-DMA. Reaction conditions: 50 mg PPO, 50 mg Pd_7Ru_3/CNT (2 wt% metal loading), 4 mL octane, 1 mL NH_3 aqueous solution 25%, 5 bar D_2, 280 °C, 4 h.

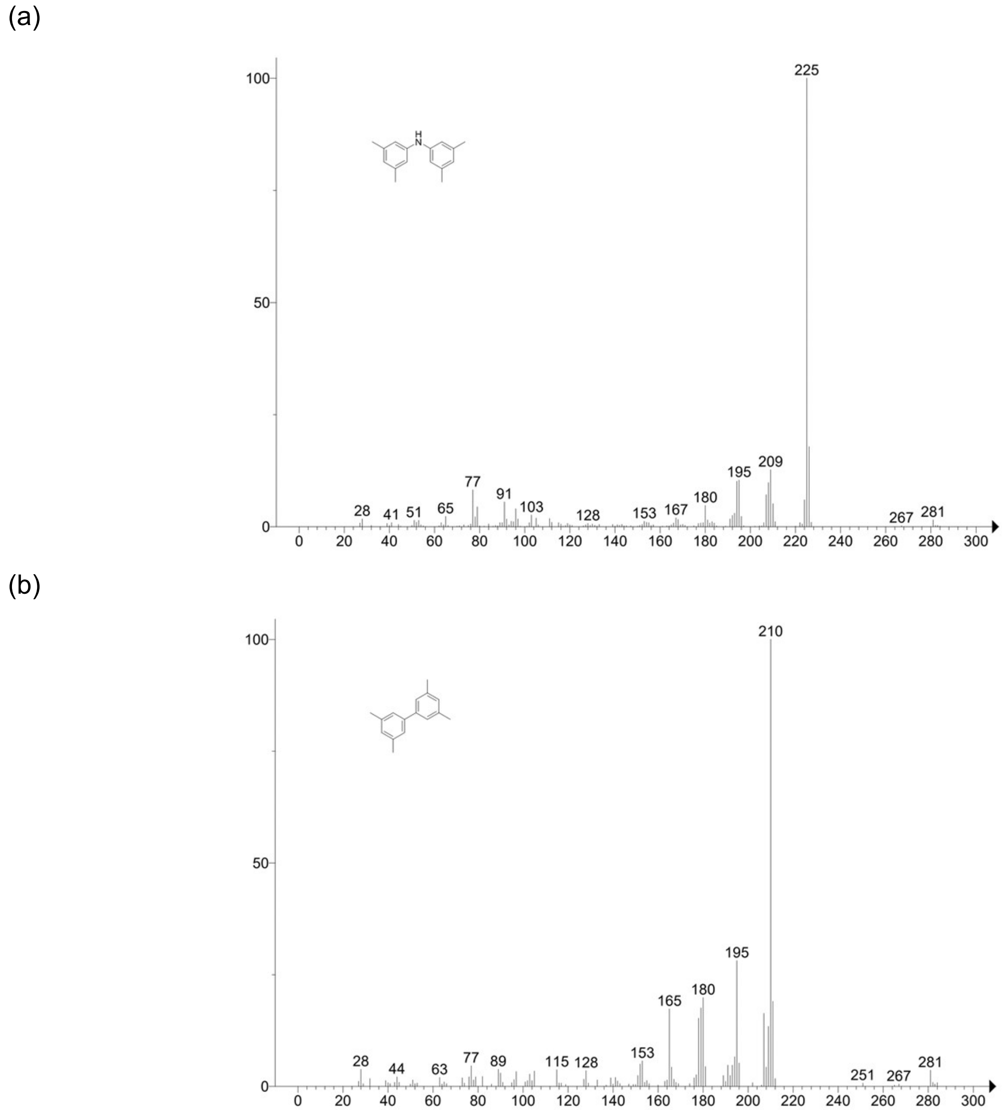
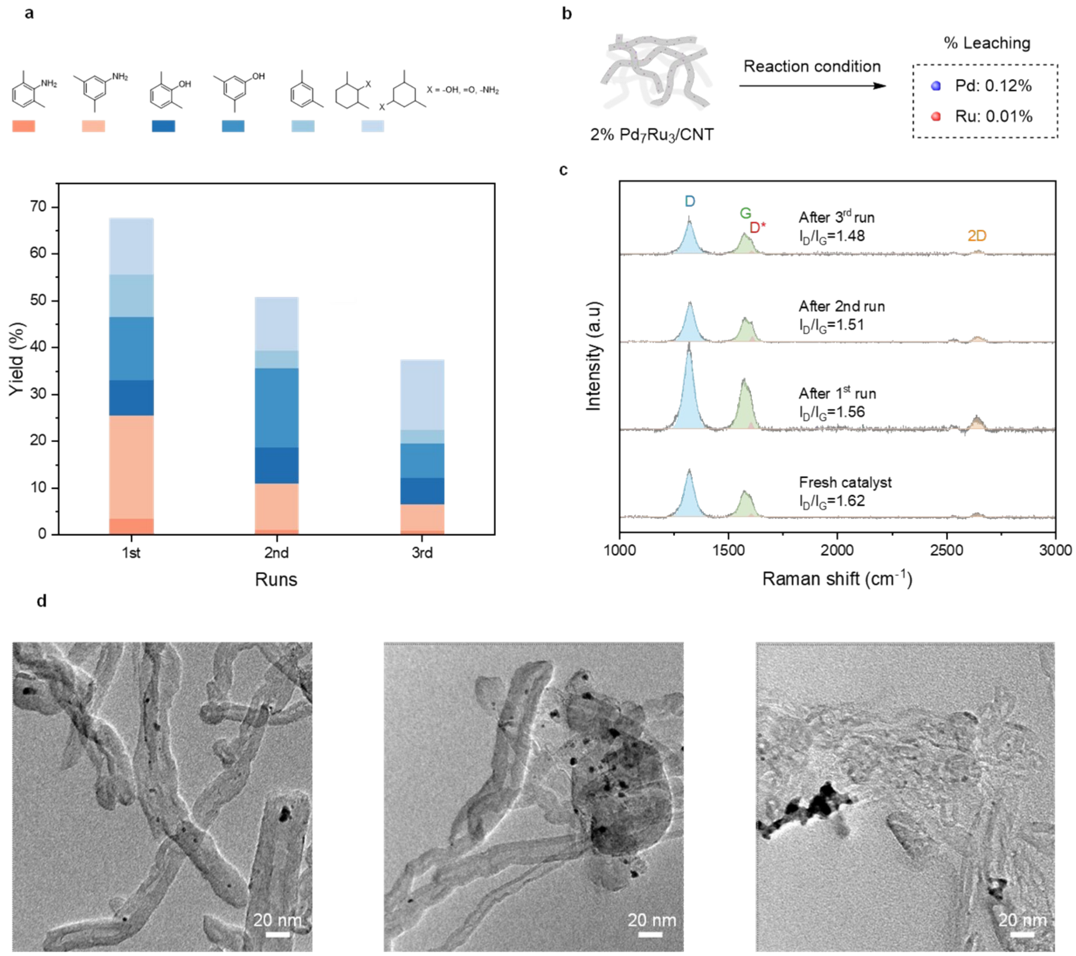


Fig. S9. MS spectra of by-products: (a) bis(3,5-dimethylphenyl)amine and (b) 3,3',5,5'-tetramethyl-1,1'-biphenyl



After 1st run
After 2nd run
After 3rd run

Fig. S10. (a) Recycling test over 2% Pd$_7$Ru$_3$/CNT catalyst; (b) metal leaching percentage from the catalyst after the first run; (c) Raman spectra and (d) TEM images of the catalysts after each run. Reaction conditions: 50 mg PPO, 50 mg Pd$_7$Ru$_3$/CNT (2 wt% metal loading), 4 mL octane, 1 mL NH$_3$ aqueous solution 25%, 5 bar H$_2$, 280 °C, 4 h.

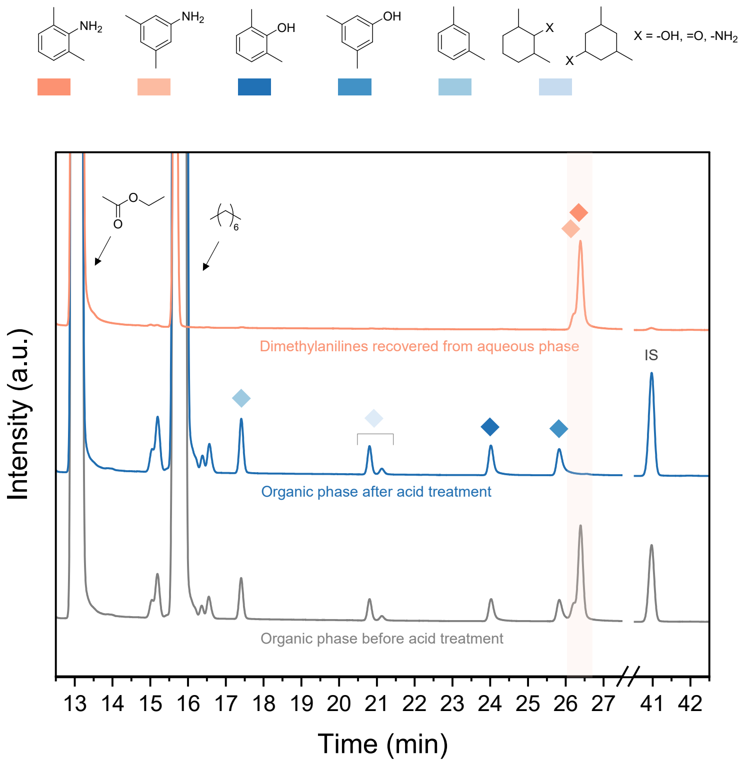


Fig. S11. The GC spectra illustrate the isolation of dimethylanilines from the product mixture. The product mixture in ethyl acetate (~20 mL) was treated with 15 mL of 1M HCl. The aqueous phase was collected and treated with 20 mL of 2M NaOH. Dimethylanilines were recovered from the aqueous phase by extraction with 15 mL of ethyl acetate. The clear isolation of dimethylanilines from the product mixture illustrates that separation can be achieved by simple acid and base treatment without the need for column chromatography or distillation.

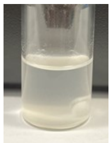
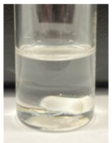
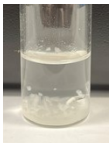
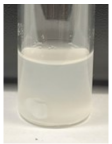
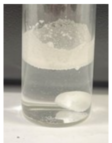
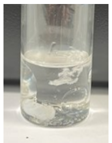
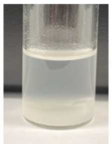
Solvent	Octane	Toluene	2-MeTHF	TAA	NH_3 solution	Toluene + NH_3 solution (4:1)
Before stirring						
After stirring						

Table S1. Dispersion of PPO in different solvents before and after stirring for 15 minutes. 2-MeTHF: 2-methyltetrahydrofuran, TAA: tert-amyl alcohol. It is evident that PPO is not mixable with NH_3 solution 25%, necessitating the use of a co-solvent. PPO could be well dispersed in octane, TAA and toluene, but aggregated in 2Me-THF.