

Supporting Information

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

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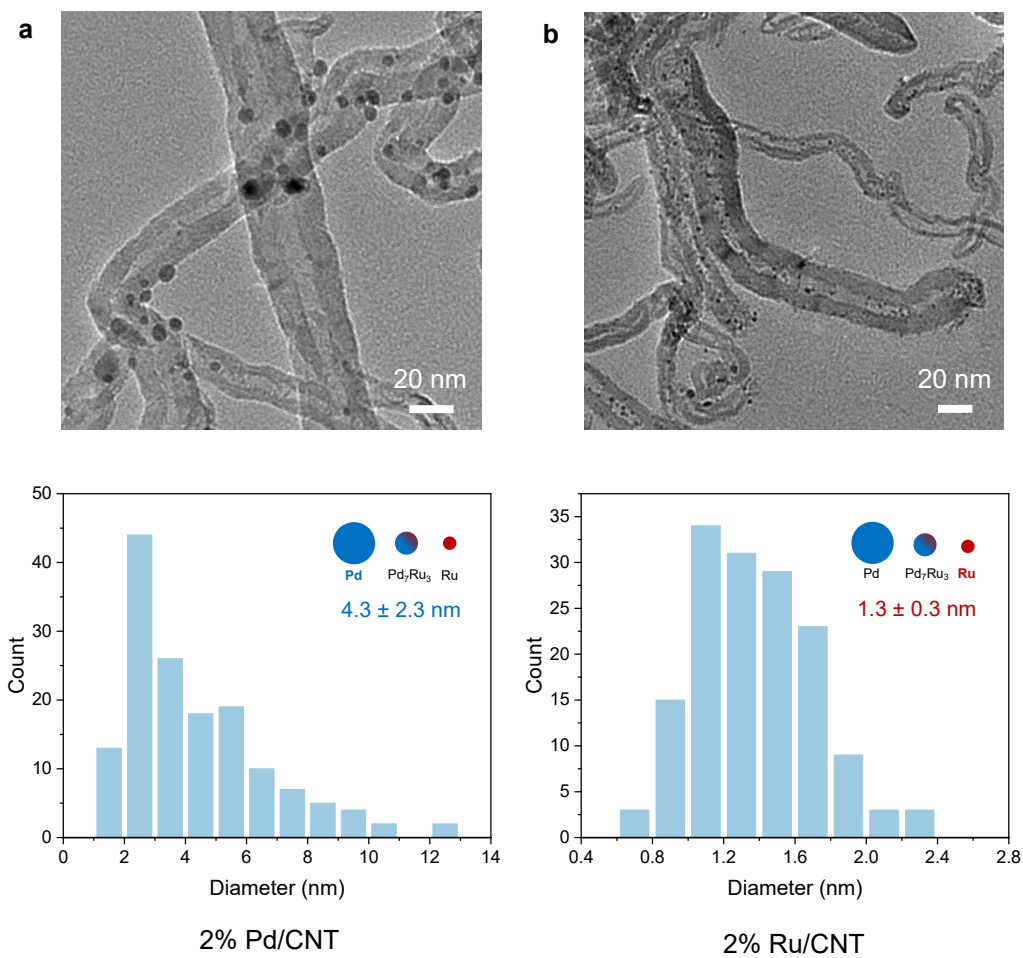


Fig. S1. TEM images and particle size distribution of (a) Pd/CNT and (b) Ru/CNT at 2% loading. The circle illustrates the relative particle size of Pd/CNT, Pd₇Ru₃/CNT and Ru/CNT.

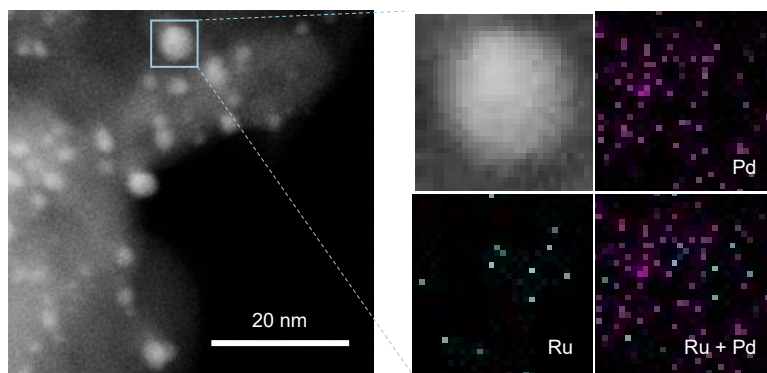


Fig. S2. (a) STEM of 2% Pd₇Ru₃/CNT and elemental maps of (b-d) Pd and Ru of a nanoparticle.

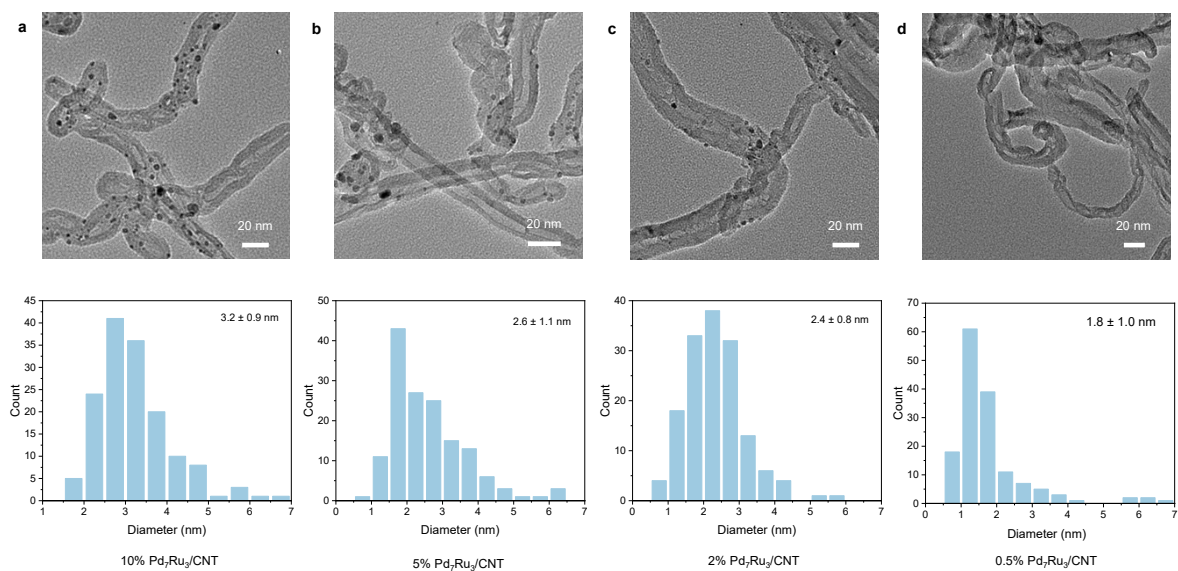


Fig. S3. TEM images and particle size distribution of the bimetallic Pd₇Ru₃/CNT at (a) 10%, (b) 5%, (c) 2%, and (d) 0.5% metal loading. The scale bars on the TEM images are 20 nm.

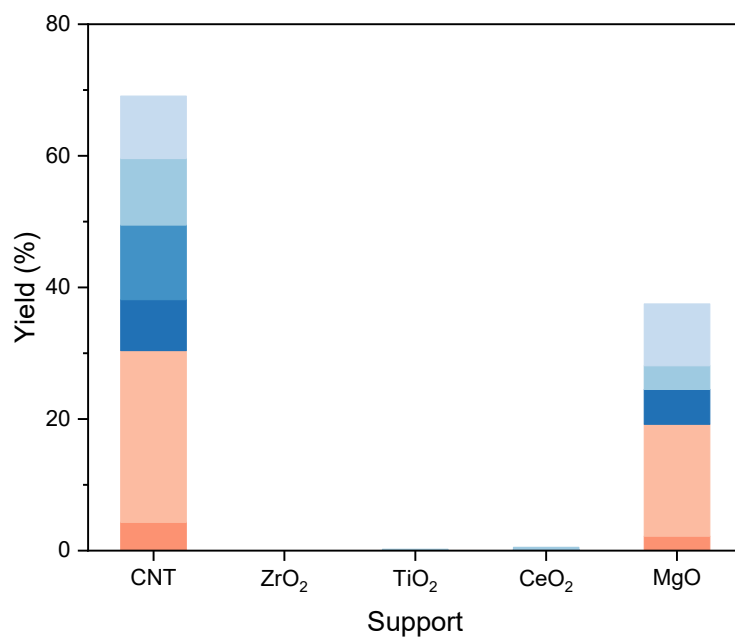


Fig. S4. Effect of various catalyst supports for the conversion of PPO into dimethylanilines. Reaction condition: 50 mg PPO, 50 mg 2% Pd₇Ru₃/support, 4 mL octane, 1 mL 25% aqueous NH₃ solution, 5 bar H₂, 280 °C, 4 h.

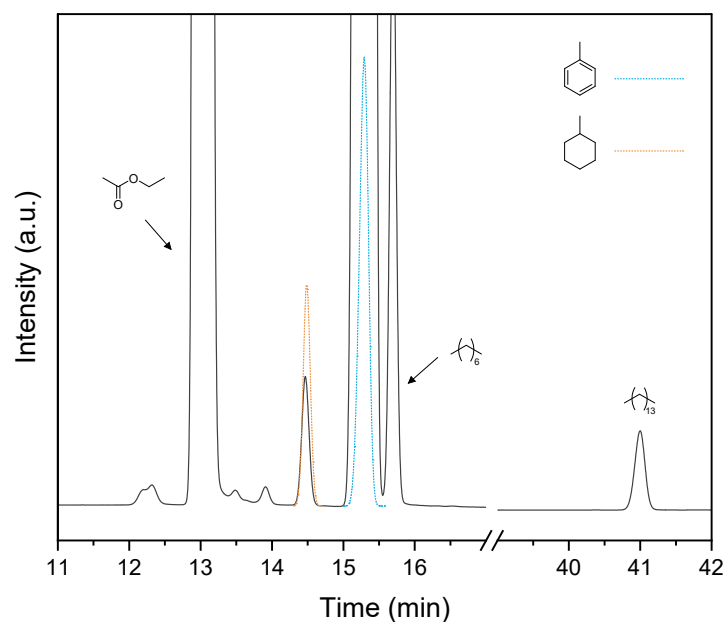


Fig. S5. Generation of methylcyclohexane from toluene over 2% Pd₇Ru₃/CNT (without PPO). Reaction condition: 50 mg Pd₇Ru₃/CNT (2 wt% metal loading), 4 mL toluene, 1 mL 25% aqueous NH₃ solution, 5 bar H₂, 280 °C, 4 h. Ethyl acetate was used as extraction solvent, and pentadecane in octane (100 mg/mL) was 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.

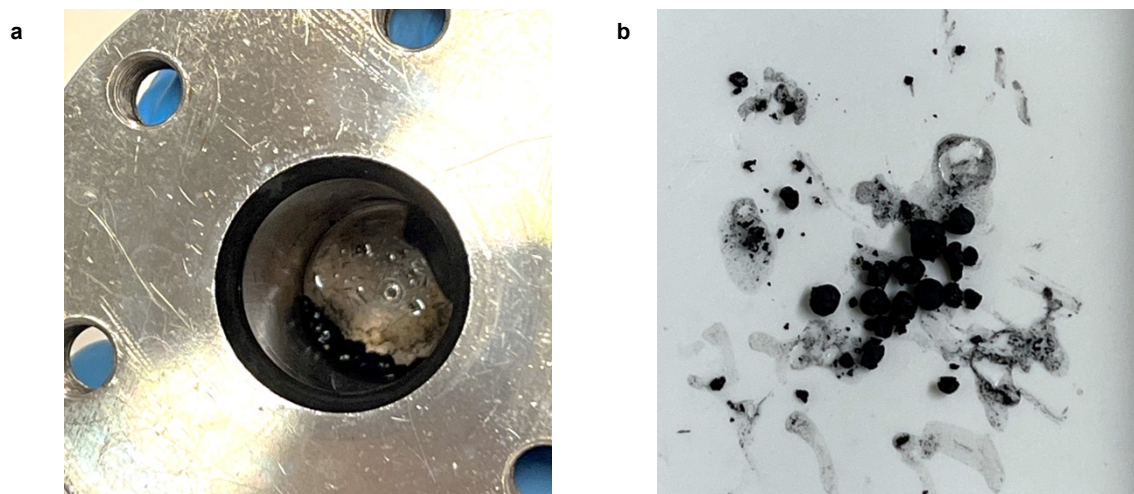


Fig. S6. Formation of black particles after the reaction through the aggregation of PPO and the catalyst when the volume ratio of octane to NH_3 solution is 3.5:1.5: (a) observed at the bottom of the reactor, (b) displayed in a white container after extraction. Reaction condition: 50 mg PPO, 50 mg $\text{Pd}_7\text{Ru}_3/\text{CNT}$ (2 wt% metal loading), 3.5 mL octane, 1.5 mL 25% aqueous NH_3 solution, 5 bar H_2 , 280 °C, 4 h.

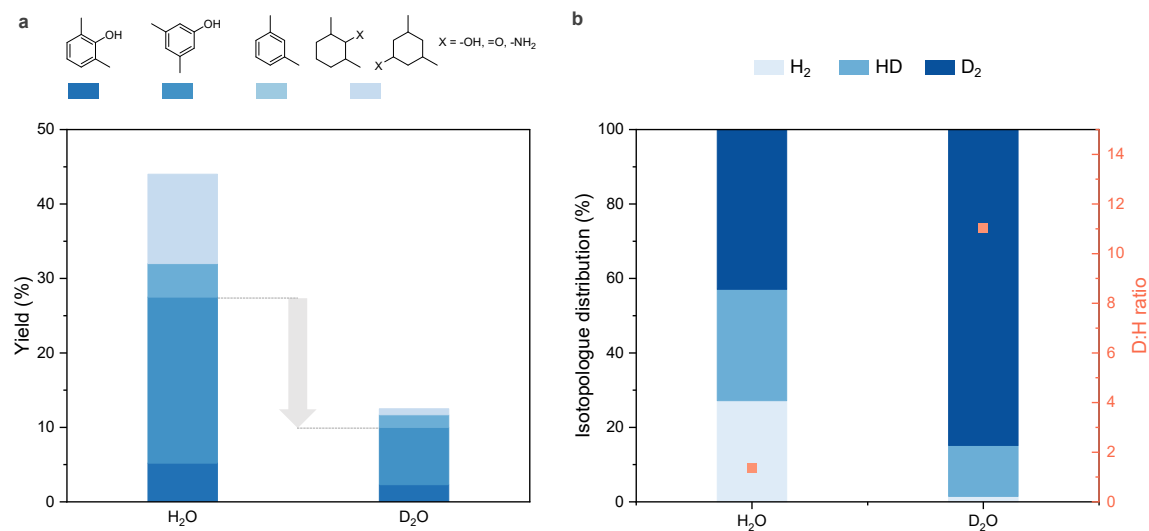


Fig. S7. Step 1 carried under deuterium with H₂O or D₂O as solvent: (a) product yield and (b) gas phase analysis by GC-MS. Reaction condition: 50 mg 2,6-DMP, 50 mg Pd₇Ru₃/CNT (2 wt% metal loading), 4 mL octane, 1 mL solvent, 5 bar D₂, 280 °C, 4 h.

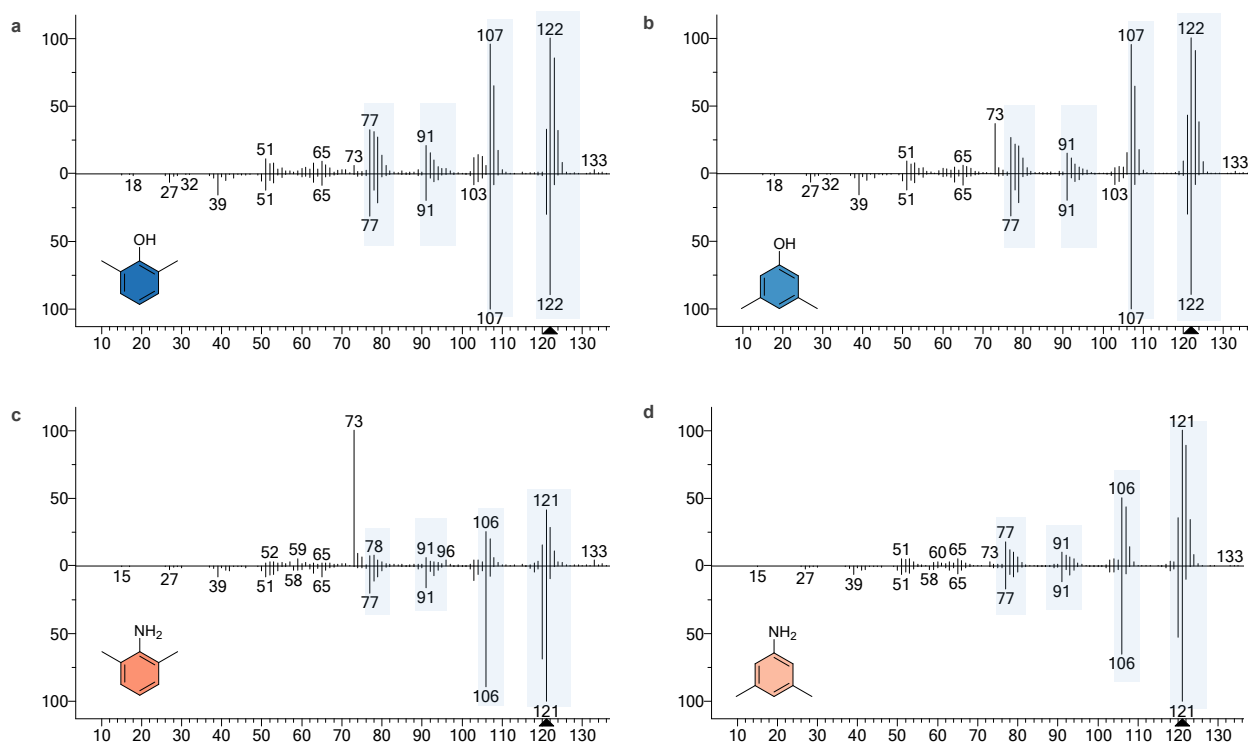
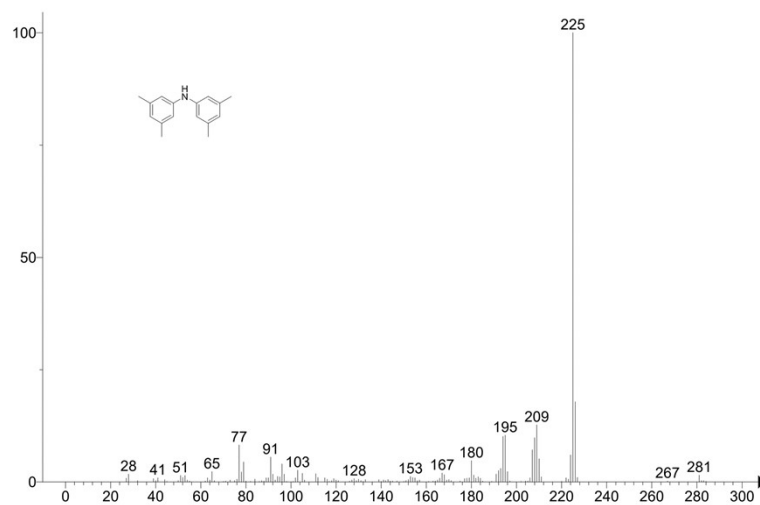


Fig. S8. MS spectra of products in the one-pot reaction carried under deuterium (top) compared to the reference library (bottom): (a) 2,6-DMP, (b) 3,5-DMP, (c) 2,6-DMA, (d) 3,5-DMA. Reaction conditions: 50 mg PPO, 50 mg Pd₇Ru₃/CNT (2 wt% metal loading), 4 mL octane, 1 mL NH₃ aqueous solution 25%, 5 bar D₂, 280 °C, 4 h.

(a)



(b)

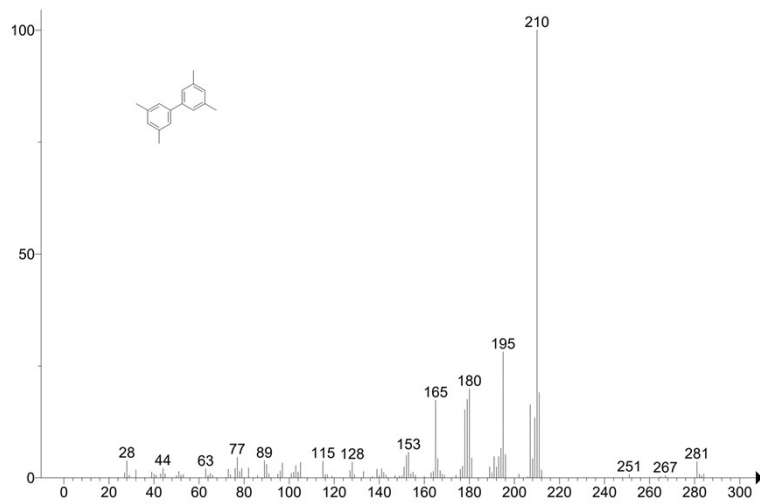


Fig. S9. MS spectra of by-products: (a) bis(3,5-dimethylphenyl)amine and (b) 3,3',5,5'-tetramethyl-1,1'-biphenyl

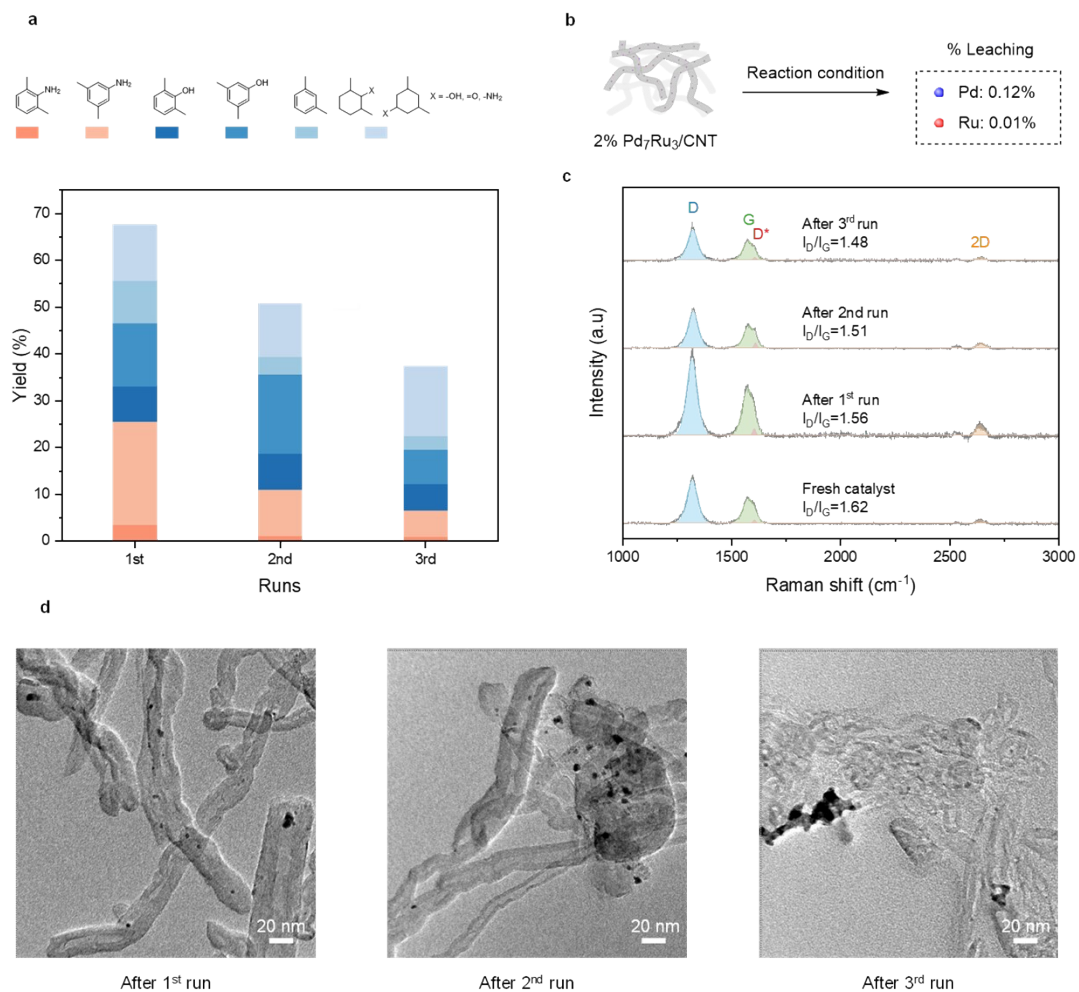


Fig. S10. (a) Recycling test over 2% Pd₇Ru₃/CNT catalyst; (b) metal leaching percentage from the catalyst after the first run; (c) Raman spectra and (d) TEM images of the catalysts after each run. Reaction conditions: 50 mg PPO, 50 mg Pd₇Ru₃/CNT (2 wt% metal loading), 4 mL octane, 1 mL NH₃ aqueous solution 25%, 5 bar H₂, 280 °C, 4 h.

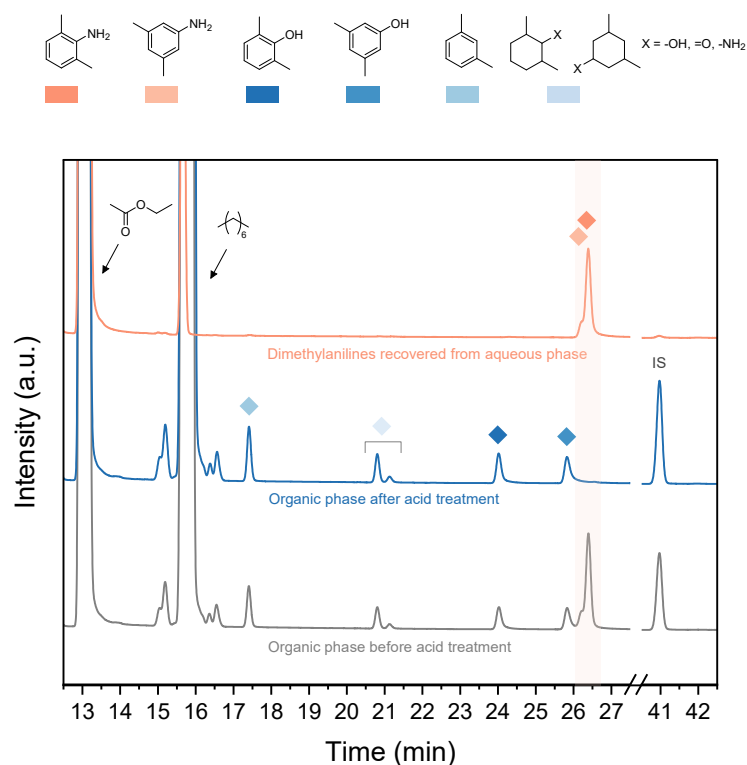


Fig. S11. The GC spectra illustrate the isolation of dimethylanilines from the product mixture. The product mixture in ethyl acetate (~20 mL) was treated with 15 mL of 1M HCl. The aqueous phase was collected and treated with 20 mL of 2M NaOH. Dimethylanilines were recovered from the aqueous phase by 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.

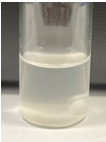
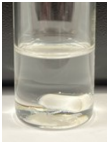
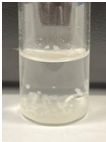
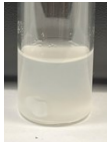
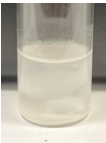
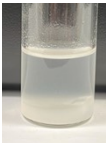
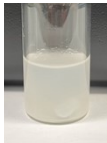
Solvent	Octane	Toluene	2-MeTHF	TAA	NH ₃ solution	Toluene + NH ₃ solution (4:1)
Before stirring						
After stirring						

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 NH₃ solution 25%, necessitating the use of a co-solvent. PPO could be well dispersed in octane, TAA and toluene, but aggregated in 2Me-THF.