

Supporting Information

Multifunctional PdAg@MIL-101 for One-Pot Cascade Reactions: Combination of Host-Guest Cooperation and Bimetallic Synergy in Catalysis

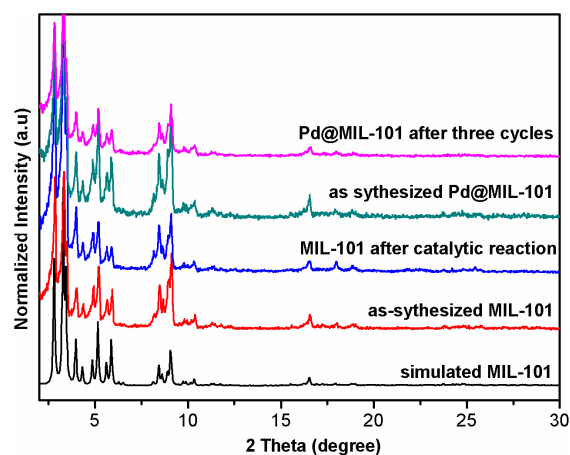
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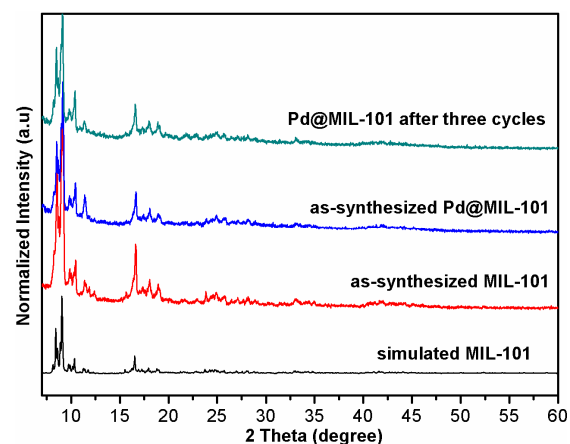
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(a)



(b)

Figure S1. (a) Powder XRD patterns in the range of small angles for simulated MIL-101, as-synthesized MIL-101 (before and after catalytic reaction) and Pd@MIL-101 (before and after three catalytic cycles), demonstrating the well retained crystallinity and framework of MIL-101 during the catalyst preparation and catalytic process. (b) Powder XRD patterns of Pd@MIL-101 (before and after catalytic three cycles) in a wide angle range. The undetectable diffraction at $\theta = 40.02^\circ$ for Pd NPs implies that the Pd NPs could be very small and not aggregated in all samples.

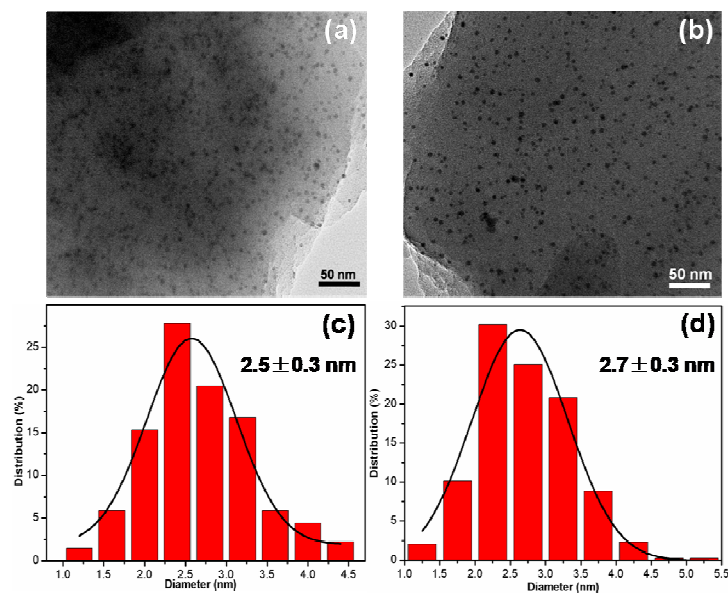
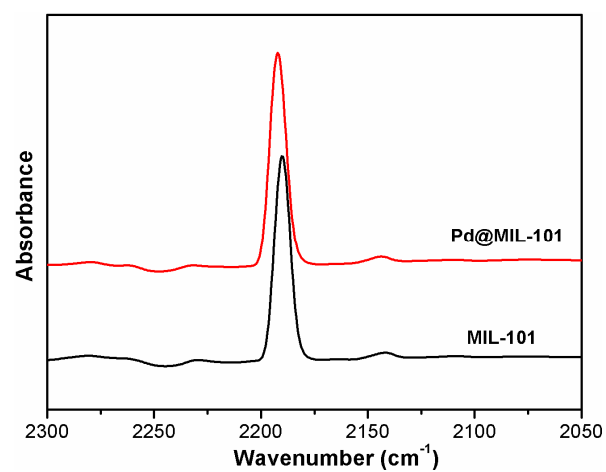
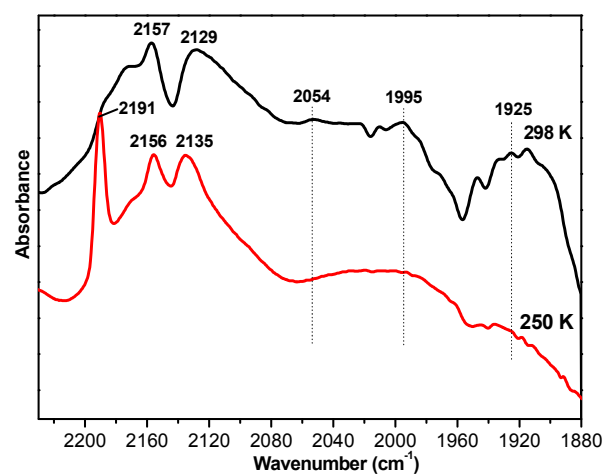


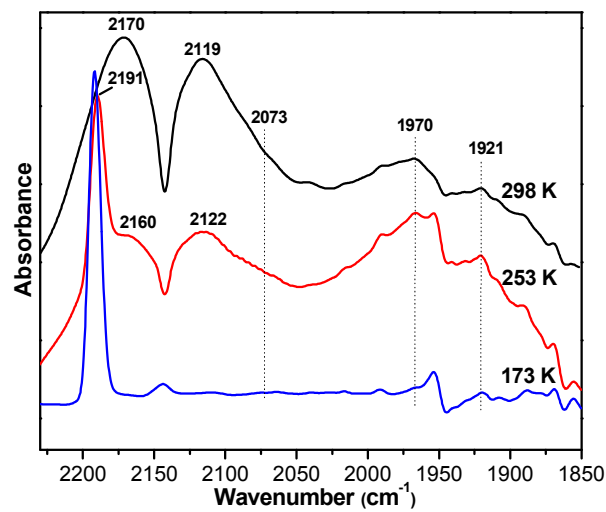
Figure S2. TEM images of Pd@MIL-101 catalyst (a) before catalytic reaction and (b) after three catalytic cycles as well as corresponding size distributions of Pd NPs (c) before reaction and (d) after three catalytic cycles.



(a)



(b)



(c)

Figure S3. In situ DRIFT-IR spectra of CO adsorption on (a) MIL-101 and Pd@MIL-101 at 158 K, (b) Pd@MIL-101 at 250 K and 298 K, and (c) Pd₂Ag₁@MIL-101 at different temperatures.

When room-temperature CO was introduced into the DRIFT reflectance cell at 173 K, the sample temperature gradually increased due to its large BET surface area; thus the spectra at 173 K could only be collected in a very short time. During such short time, only a small amount of CO molecules flew through the sample and would dominantly adsorb onto exposed Cr(III) centers in the outer shell of MIL-101, but much less on the Pd or PdAg NP surface, since the metal NPs were majorly confined in the pores of MIL-101 (evidenced by the TEM rotation results). As continuously introducing CO, CO molecules started diffusing into the inner surface of MIL-101 and reached the metal NP surface, thus CO adsorption at metal NPs became pronounced in the DRIFT spectra, even though the sample temperature was higher than the initial temperature (Figure S3b,c). The bands for Pd@MIL-101 at ~ 2054 , ~ 1995 and ~ 1925 cm^{-1} could be assigned to linear CO and two-fold bridged CO on the steps and edges, and two-fold bridged CO on (111) facets of Pd NPs, respectively (Figure S3b), according to the previous reports (see SI: ref. S1). Similarly, the bands at ~ 2073 (shoulder peak of the peak at ~ 2120 cm^{-1}), ~ 1970 , and ~ 1921 cm^{-1} are assignable to chemisorbed CO on PdAg nanoparticles in Pd₂Ag₁@MIL-101 (Figure S3c).

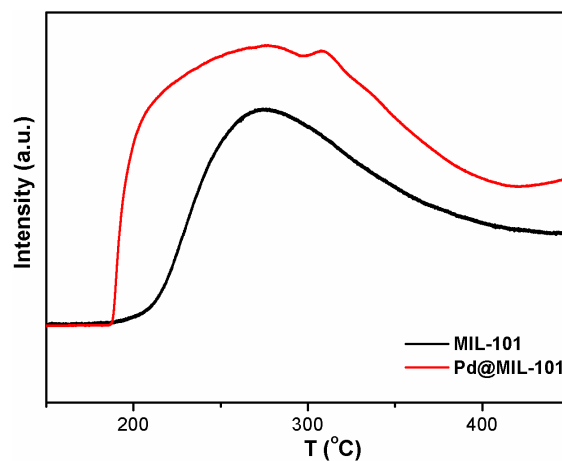
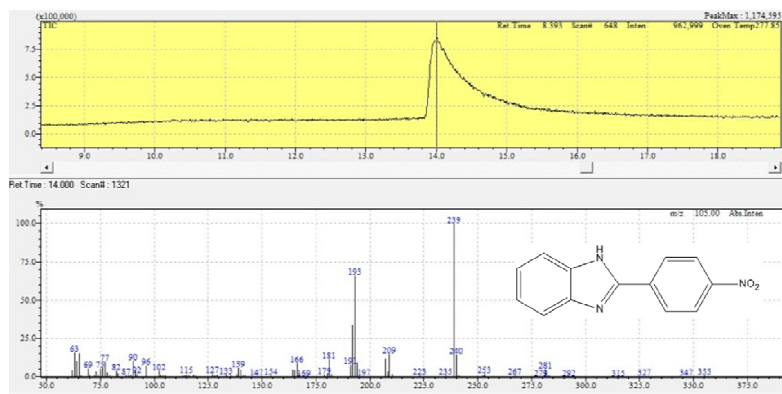
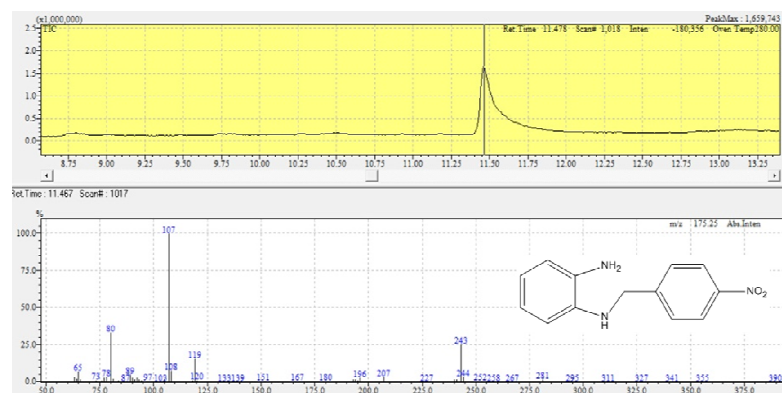


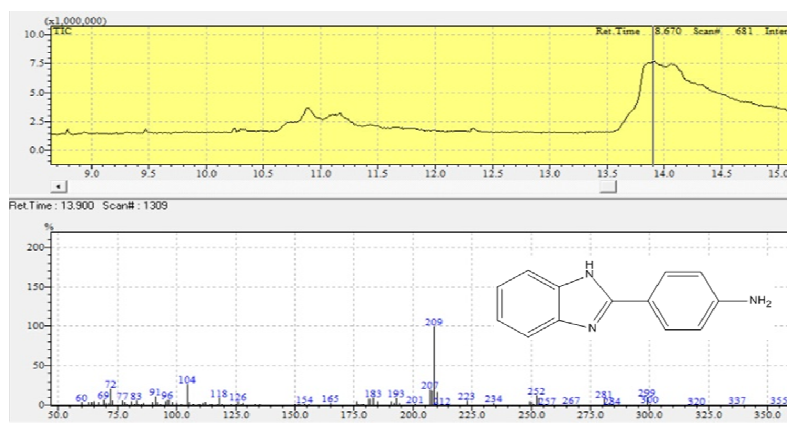
Figure S4. NH_3 -TPD profiles of MIL-101 and Pd@MIL-101-DSA. Experimental conditions: the sample was pre-treated in N_2 atmosphere at 150 °C for 4 h, and then allowed NH_3 adsorption at 50 °C for 0.5 h. Then, the sample was heated from 50 to 600 °C at a rate of 10 °C/min. The broad peak in the range of 190-420 °C could be assigned to NH_3 adsorption on the open Cr^{3+} Lewis acid sites at <300 °C and partial decomposition of MIL-101 at higher temperature.^{S2}



(a)

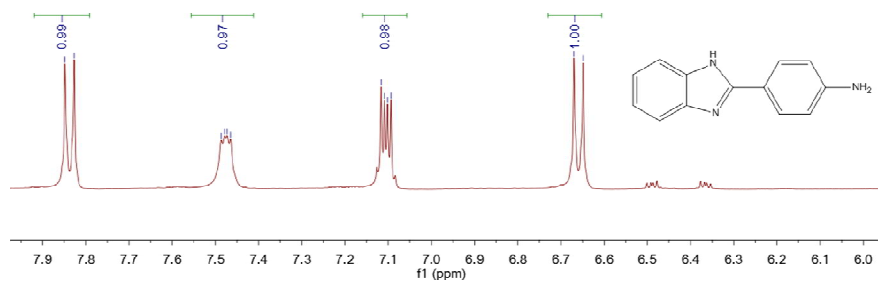


(b)

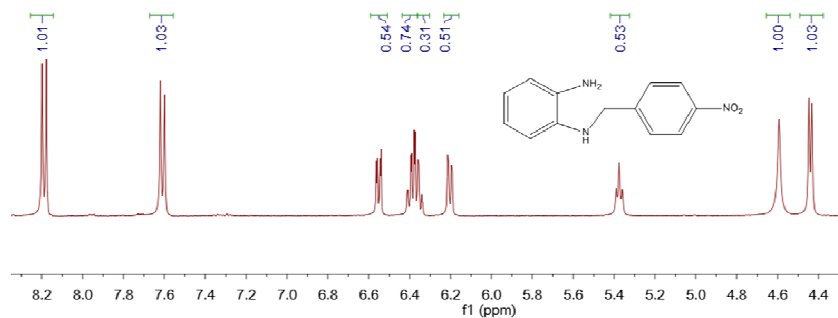


(c)

Figure S5. GC-MS spectra identification for (a) intermediate **B**, (b) byproduct **C** and (c) product **D** for the tandem synthesis of 2-(4-aminophenyl)-1H-benzimidazole.

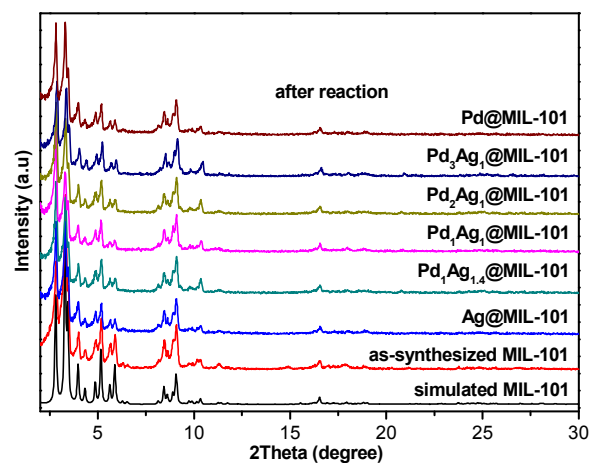


(a)

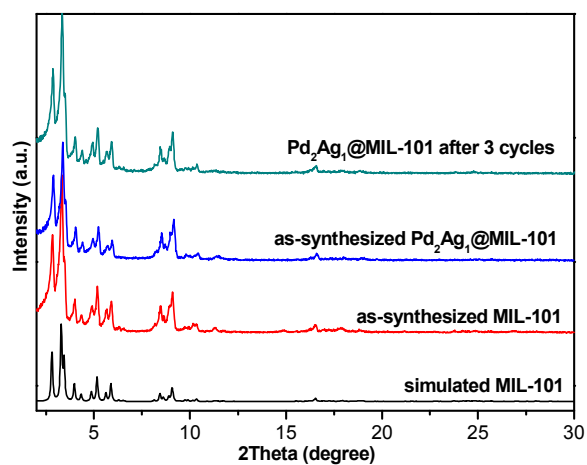


(b)

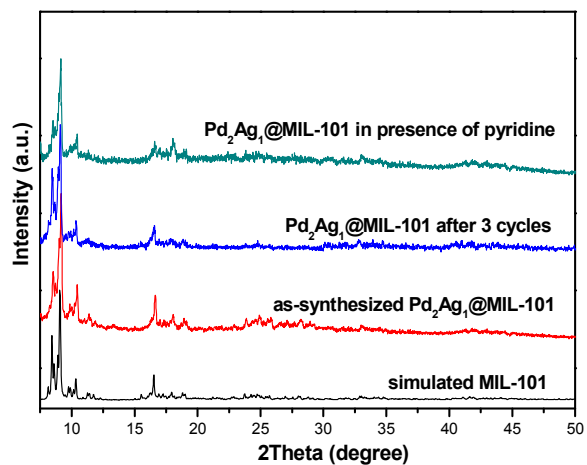
Figure S6. ^1H NMR spectra (400 MHz, DMSO, r.t.) of (a) the final product **D** (^1H NMR: δ 7.85, 7.83, 7.49, 7.48, 7.47, 7.46, 7.12, 7.11, 7.10, 7.09, 6.67, 6.65, 5.60, 3.36) and (b) the byproduct **C** for the two-step tandem synthesis of 2-(4-aminophenyl)-1H-benzimidazole (^1H NMR: δ 8.20, 8.18, 7.62, 7.60, 6.56, 6.56, 6.55, 6.54, 6.41, 6.41, 6.39, 6.39, 6.38, 6.37, 6.36, 6.36, 6.34, 6.34, 6.21, 6.21, 6.20, 6.19, 5.39, 5.37, 5.36, 4.59, 4.45, 4.43).



(a)



(b)



(c)

Figure S7. Powder XRD profiles of (a) MIL-101, Pd@MIL-101, Ag@MIL-101 and PdAg@MIL-101 after catalytic reaction (run 1), indicating the framework of

MIL-101 remains well after loading Pd/Ag NPs. (b) Powder XRD profile comparison of Pd₂Ag₁@MIL-101 before and after 3 catalytic cycles as well as MIL-101 in the range of 2-30 degree only for clarity. (c) Powder XRD patterns in a wide angle range for Pd₂Ag₁@MIL-101 before and after 3 catalytic cycles and after introducing pyridine. The relatively weak intensity is due to the fact that MOFs usually present weak peaks at higher angles.

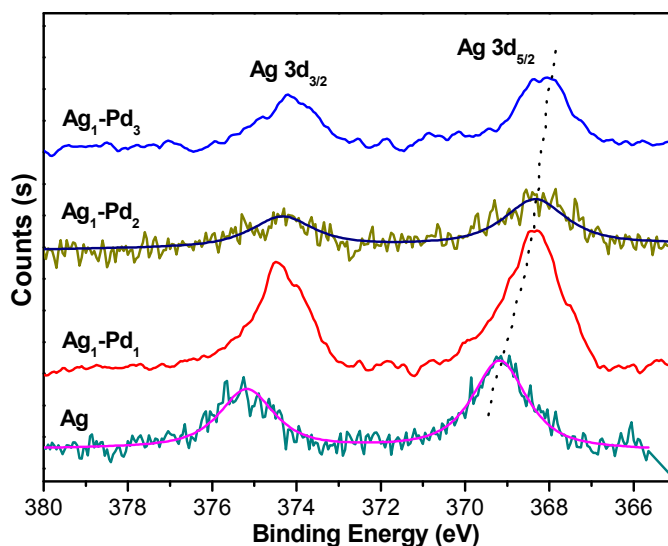


Figure S8. XPS spectra of Ag 3d for Pd₃Ag₁@MIL-101, Pd₂Ag₁@MIL-101, Pd₁Ag₁@MIL-101 and Ag@MIL-101, showing that the 3d peaks for Ag(0) in PdAg@MIL-101 shift gradually to lower binding energies with decreasing contents of Ag in PdAg bimetallic NPs. The different peak intensities of Pd₂Ag₁@MIL-101 from the other samples could be caused by different instrument settings (measured at different time).

Table S1. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis results for PdAg@MIL-101 catalysts. The results have confirmed that the actual contents of Pd and Ag are close to the nominal values and the Pd/Ag ratios match the predesigned trend.

Nanoparticles	(Pd+Ag) content (%)	$n_{\text{Pd}} / n_{\text{Ag}}$ (mol / mol)
Pd	0.9	-
Pd ₃ Ag ₁	0.97	3.1
Pd ₂ Ag ₁	0.88	2.3
Pd ₁ Ag ₁	0.89	0.93
Pd ₁ Ag _{1.4}	1.1	0.52
Ag	0.6	-

Table S2. Peak positions of the XPS binding energy of Pd 3d_{5/2} and Ag 3d_{5/2} in different nanocomposite catalysts with monometallic and alloy NPs. Results reveal the formation of PdAg alloy NPs, which can also be explained that the two soluble metal salts have close reduction potentials ($E^{\circ}_{\text{Pd}^{2+}/\text{Pd}} = +0.915 \text{ eV vs SHE}$; $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ eV vs SHE}$). Upon heating in H₂/Ar flow, both Pd²⁺ and Ag⁺ would be simultaneously reduced to afford PdAg alloys.

Sample	Pd 3d _{5/2} (eV)	Ag 3d _{5/2} (eV)
Pd@MIL-101	336.1	-
Pd ₃ Ag ₁ @MIL-101	336.0	368.10
Pd ₂ Ag ₁ @MIL-101	335.9	368.3
Pd ₁ Ag ₁ @MIL-101	335.7	368.38
Ag@MIL-101	-	369.1
Ag ⁺ @MIL-101	-	368.85

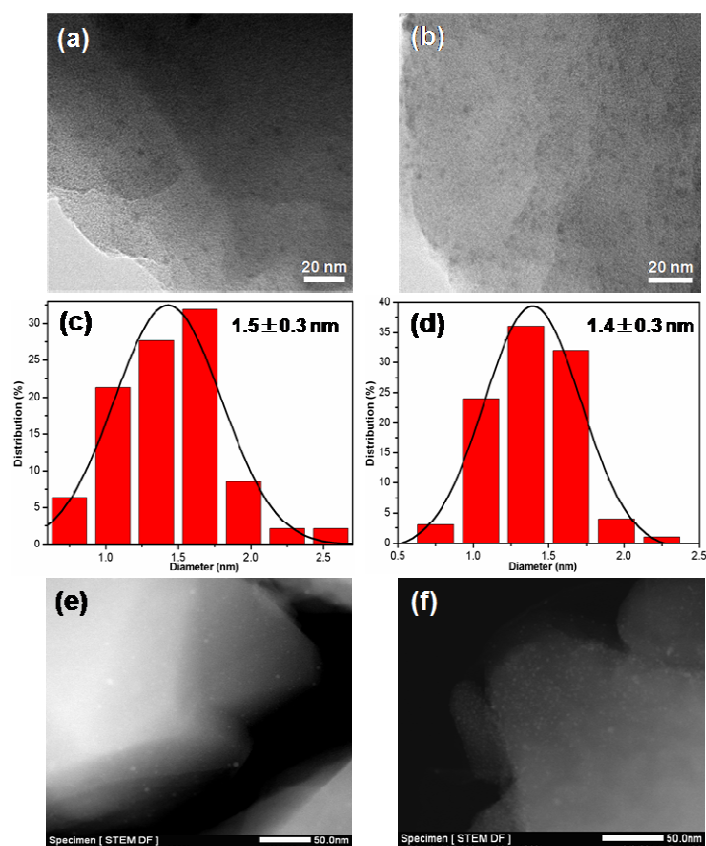


Figure S9. TEM images of Pd₂Ag₁@MIL-101 catalyst (a) before reaction and (b) after three catalytic cycles as well as corresponding size distributions of PdAg NPs (c) before reaction and (d) after three cycles. The HAADF-STEM images of Pd₂Ag₁@MIL-101 catalyst (e) before reaction and (f) after three cycles.

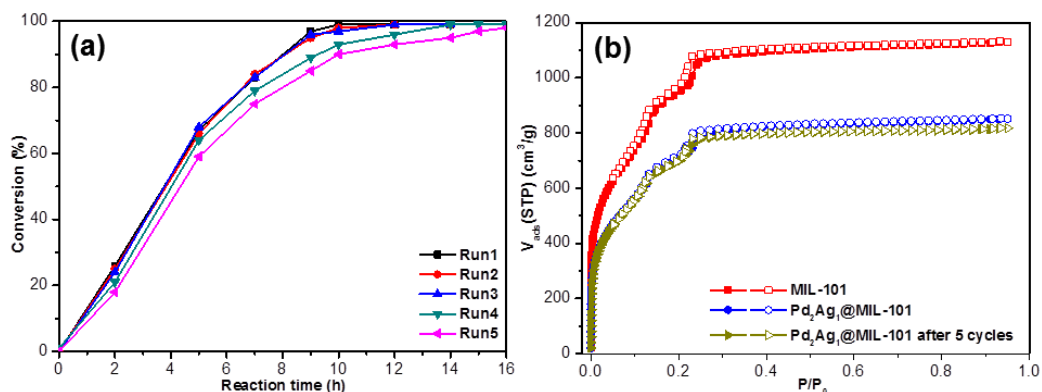


Figure S10. (a) Recycling performance for the synthesis of secondary arylamines through hydrogenation of nitrobenzene and reductive amination of benzaldehyde over Pd₂Ag₁@MIL-101. (b) N₂ sorption isotherms for MIL-101, PdAg@MIL-101 before reaction and after 5 catalytic cycles at 77 K. Filled and open symbols represent adsorption and desorption branches, respectively.

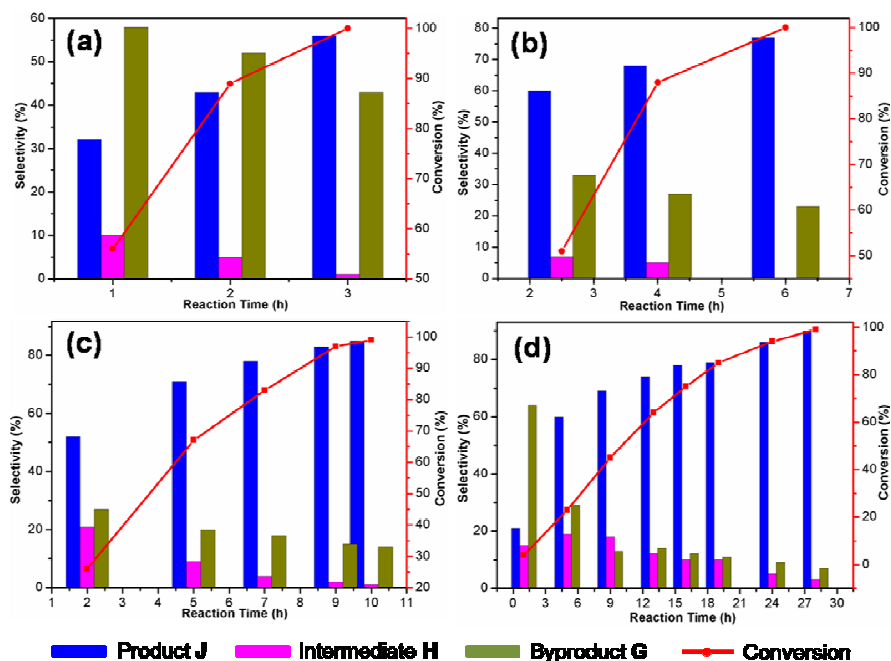


Figure S11. The conversion of benzaldehyde and selectivity of the products over different catalysts: (a) Pd@MIL-101, (b) Pd₃Ag₁@MIL-101, (c) Pd₂Ag₁@MIL-101, and (d) Pd₁Ag₁@MIL-101 for the catalytic synthesis of secondary arylamines through hydrogenation of nitrobenzene and reductive amination of benzaldehyde.

Table S3. Synthesis of secondary arylamines through hydrogenation of nitrobenzene and reductive amination of benzaldehyde.^a

Entry	Catalyst	Time (h)	Conversion (%)	Selectivity ^b (%)		
				J	I	G
1	Pd@MIL-101	4	100	70	1	29
2	Pd ₃ Ag ₁ @MIL-101	11	100	85	9	6
3	Pd ₂ Ag ₁ @MIL-101	10	99	80	3	17
4	Ag@MIL-101	-	-	-	-	-
5	MIL-101	-	-	-	-	-
6	Pd/C	3	99	53	5	42
7	no	-	-	-	-	-

^aReaction conditions: substrate **E** (1.0 mmol), **F** (1.0 mmol), 0.17 mol% catalyst (based on n(Pd+Ag)) in 4 mL toluene at room temperature, 0.2 MPa H₂. ^bConversion of **E** and selectivity were analyzed by GC and n-dodecane was used as the internal standard.

References

- (S1) (a) Lear, T.; Marshall, R.; Lopez-Sanchez, J. A.; Jackson, S. D.; Klapotke, T. M.; Baumer, M.; Rupprechter, G.; Freund, H. J.; Lennon, D. *J. Chem. Phys.* **2005**, *123*, 174706. (b) Feng, H.; Lu, J.; Stair, P. C.; Elam, J. W. *Catal. Lett.* **2011**, *141*, 512-517. (c) Hugon, A.; Delannoy, L.; Krafft, J.-M.; Louis, C. *J. Phys. Chem. C* **2010**, *114*, 10823-10835. (d) Chen, Y.; Wang, H.; Liu, C.-J.; Zeng, Z.; Zhang, H.; Zhou, C.; Jia, X.; Yang Y. *J. Catal.* **2012**, *289*, 105-117. (e) Zhang, L.; Wang, A.; Miller, J. T.; Liu, X.; Yang, X.; Wang, W.; Li, L.; Huang, Y.; Mou, C.-Y.; Zhang, T. *ACS Catal.* **2014**, *4*, 1546-1553. (f) Wang, H.; Wang, C.; Yan, H.; Yi, H.; Lu, J. *J. Catal.* **2015**, DOI: 10.1016/j.jcat.2015.01.019.
- (S2) Pan, Y.; Yuan, B.; Li, Y.; He, D. *Chem. Commun.* **2010**, *46*, 2280-2282.