Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Highly efficient $Mo^{IV}_3\cdots Sb^{III}$ cluster FLP hydrogenation

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1. Experimental Section

1.1 Methods and Materials

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses (C, H and N) were performed using a vario MICRO elemental analyzer. ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) analyses (Sb, Mo) were carried on Ultima 2. ^1H NMR spectra were recorded on a Bruker-BioSpin AVANCE III instrument at a constant temperature of 300 K. IR spectra were recorded with a Magna 750 FTIR spectrometer photometer as KBr pellets in the 4000–400 cm^{-1} region. Thermogravimetric analyses (TGA) were performed on a Netzsch STA449C apparatus. Selectivity and conversion of catalysis reactions were measured with a Shimadzu GC 2014 plus chromatograph. The intensity data were collected on a Bruker D8-venture diffractometer with graphite-monochromated MoKα radiation (λ= 0.71073 Å). All absorption corrections were performed using multiscan. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELXTL-2016 program package.

1.2 Synthesis

$[Mo^{IV}{}_3O_2(O_2CCH_3)_6(H_2O)_3]ZnCl_4\cdot 8H_2O$ was prepared according to the published procedure.[13-15]

$[Sb^{III}{}_3Mo^{IV}{}_3Mo^{VI}{}_{15}O_{55}(OH)_2py_3]\bullet NH_2(CH_3)_2\bullet 4NH(CH_3)_2\bullet 2H_2O$(**1**). $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]ZnCl_4\cdot 8H_2O$ (0.1 g, 0.1 mmol), Sb_2O_3 (0.01g, 0.03 mmol) was added into a mixture of H_2O (2 mL), DMF (2 mL), pyridine (8 mL) and $PyCO_2H$ (0.01 g). The resulting mixture was sealed in a 20 mL pressure bottle and heated at 120℃ for two days. The reactor was cooled to room temperature at a rate of 1K/h to produce black crystals of **1** (>60% yield based on Mo). Anal. calcd. For $C_{25}H_{57}Mo_{18}N_8O_{59}Sb_3$ (Mr. = 3505.95): C, 8.56; H, 1.63; N, 3.1; Sb, 10.41; Mo, 49.26%. Found: C, 9.70; H, 1,69; N, 3.29; Sb, 10.11; Mo, 50.67%. IR (KBr): 1605m (py),1446m (py), 974m (Mo^{VI}=O), 864s (Mo^{VI}–O–Mo), 744s($[Mo^{IV}{}_3O_4]$). Pnma, a = 17.6129(6), b = 20.4536(5), c = 20.3947(7) Å, V = 7347.1(4) $Å^3$, Z = 4, R1/wR2 =4.41/8.88% for the observed data (I≥2σ(I)), R1/wR2 = 7.12/9.86% for all data; CCDC-1949159.

1.3 Catalytic activity tests

The hydrogenation reduction of nitroarenes to anilines with hydrazine hydrate in the presence of $\{Sb^{III}{}_3Mo^{IV}{}_3Mo^{VI}{}_{15}\}$-**1** was investigated as a benchmark system for the optimization of the conditions. The effects of cycle number, reaction time and temperature were evaluated (see also the Supporting Information).

General procedure for the reduction of nitroarenes: Nitroarenes (10 μL, 0.097 mmol), EtOH (2 mL) and **1** (3.5 mg, 1 mol %, 0.0029 mmol) were added into a 25 mL round bottomed flask with magnetic stirring. Then, $N_2H_4\bullet H_2O$ (85%) (20 μL, 0.3 mmol) were added into the reactor and heated to reflux with stirring at 60°C for 0.5 hours. The reaction was complete (incomplete or messy) detected by TLC (n-hexane/ethyl acetate = 5:1). The samples were obtained by centrifugation and filtration and analyzed by Shimadzu GC-2014. Recycled catalyst analyzed by IR spectrum after centrifugal separation was used in the same manner as with fresh catalyst to determine the reusability of the catalyst as a hydrogenation agent (Figure **S10**). Recycle experiments were conducted under similar conditions.

The reduction of nitroarenes to anilines in this catalytic system based on {γ-$Mo^{IV}_6Mo^{VI}_7$}-**4** has been conducted for performance comparisons and mechanism study. Reaction conditions: catalyst (3 mol %), $PhNO_2$ (10 µL, 0.097 mmol), $N_2H_4 \cdot H_2O$ (20 µL, 0.3 mmol), EtOH(2 mL), 80 °C, 2 h. no: only EtOH.

To determine the yield of isolated products for different functionalized anilines, the general procedure was scaled up by the factor of three. After full conversion was achieved, the resultant suspension was centrifugated and filtered through filter paper and the solvent of the filtrate was removed by rotary evaporator and dissolved in deuterated solvents ($CDCl_3$) for NMR analysis. In a general protocol, the reaction time is usually limited to 0.5-2 hours, detected by TLC (n-hexane/ethyl acetate = 5:1→2:1) to ensure complete reaction conversion.

2. Tables

Table **S1** Bond valance sum (BVS) calculation of $H[Sb^{III}_3Mo^{IV}_3Mo^{VI}_{15}O_{55}(OH)_2py_3]$. [a]

Sb1 2.962	Sb2 3.080	Sb3 3.126	Mo1 4.519	Mo2 4.501	Mo3 6.004
Mo4 5.901	Mo5 5.914	Mo6 5.696	Mo7 5.617	Mo8 5.856	Mo9 5.913
Mo10 5.950	O1 1.931	O2 2.069	O3 2.050	O4 2.155	O5 1.879
O6 1.920	O7 1.738	O8 2.015	O9 1.970	O10 1.912	O11 2.042
O12 1.759	O13 1.988	O14 1.819	O15 2.007	O16 1.940	O17 1.880
O18 2.089	O19 1.961	O20 1.842	O21 1.983	O22 2.109	O23 2.240
O24 1.887	O25 1.169	O26 2.102	O27 1.827	O28 1.754	O29 1.754
O30 1.696	O31 1.898	O32 1.837	O33 1.857		

[a] Oxygen atoms with the BVS values below 1.2 are assigned as OH^- (capping O25, marked in red).

3. Figures

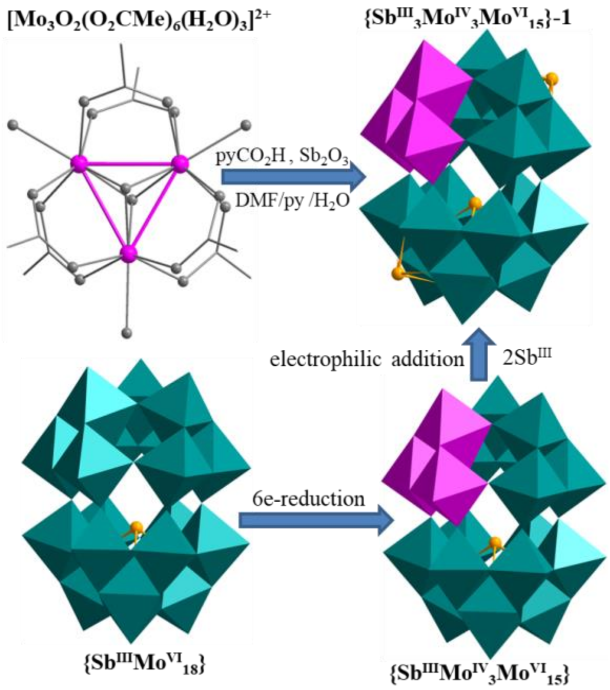


Figure S1. Solvothermal synthesis of $\{Sb^{III}_3Mo^{IV}_3Mo^{VI}_{15}\}$-**1** through organic acid-assisted oxidative aggregation of $[Mo^{IV}_3O_2(O_2CMe)_6(H_2O)_3]^{2+}$ and Sb_2O_3. It is related to the non-tetrahedral Dawson variant $\{Sb^{III}Mo^{VI}_{18}\}$ subject to 6e-reduction at one (marked in purple) of the six $[Mo^{VI}_3O_4]$ incomplete cuboidal units followed by electrophilic addition of two Sb^{III} (Sb^{III}, light orange; Mo^{IV} octahedron, purple; Mo^{VI} octahedron, teal).

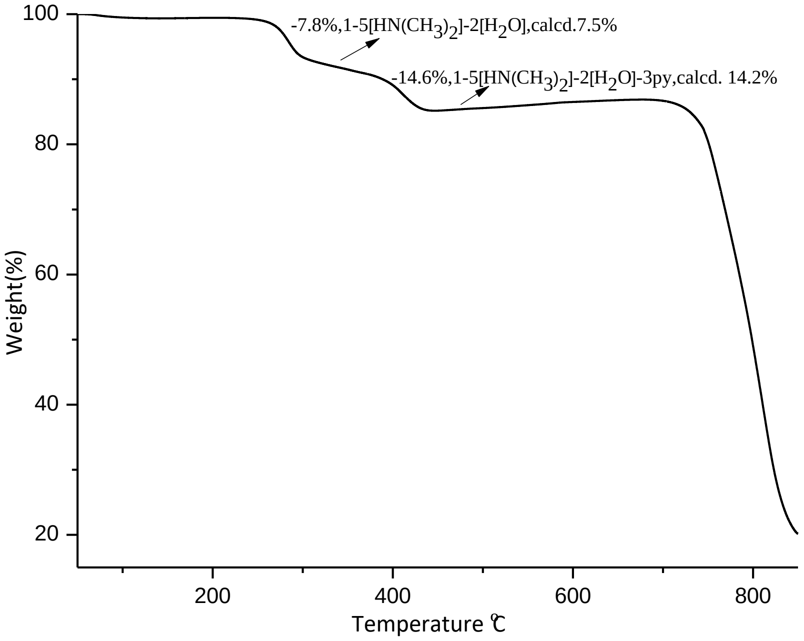


Figure S2. Thermogravimetric analysis of **1** under nitrogen.

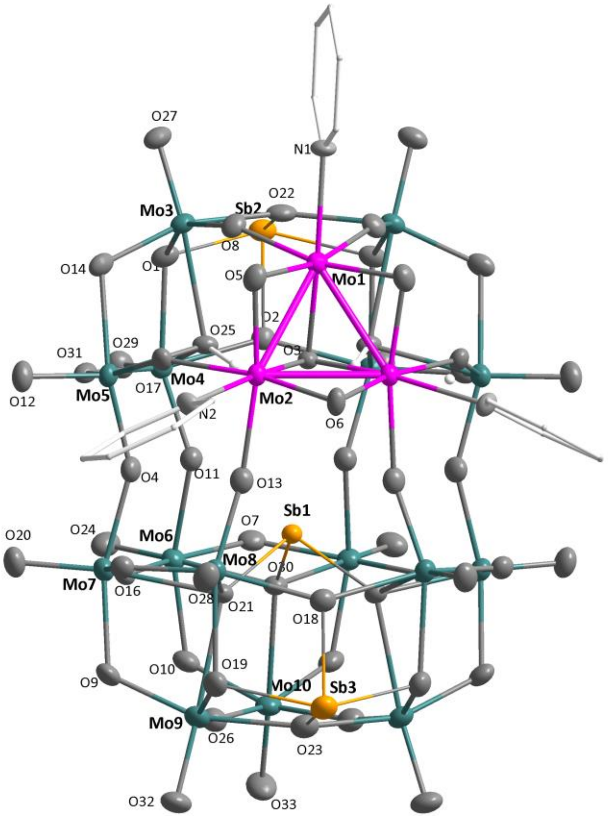


Figure S3. Structure of $[Sb^{III}{}_3Mo^{IV}{}_3Mo^{VI}{}_{15}O_{55}(OH)_2py_3]^-$ (Sb^{III}, light orange; Mo^{IV}, purple; Mo^{VI}, teal.) with 50% probability thermal ellipsoids for non-carbon atoms.

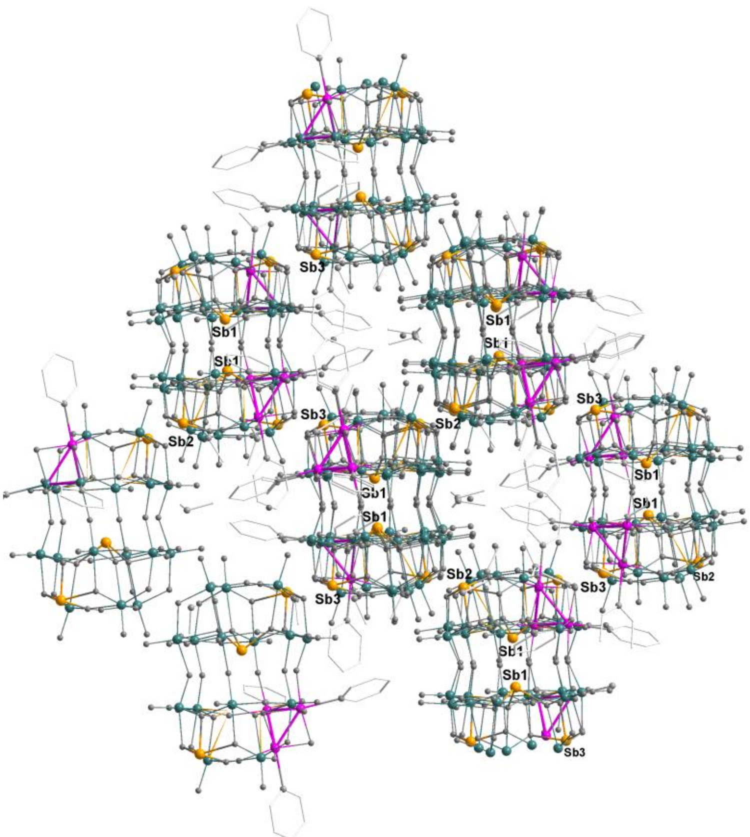
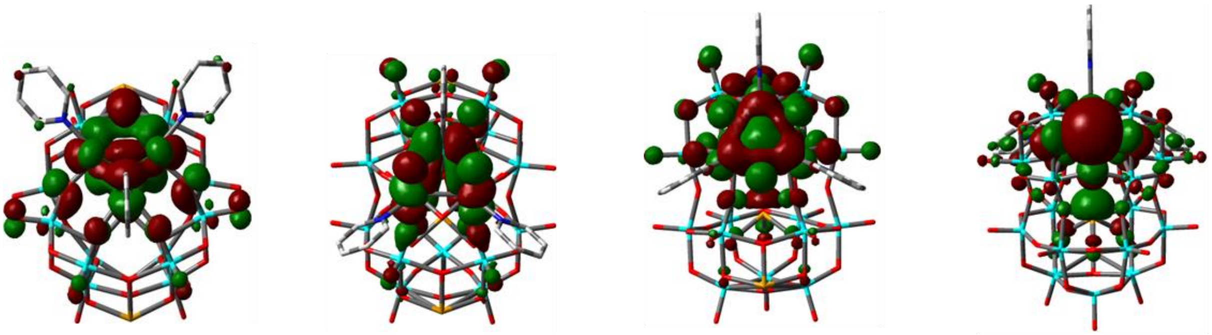
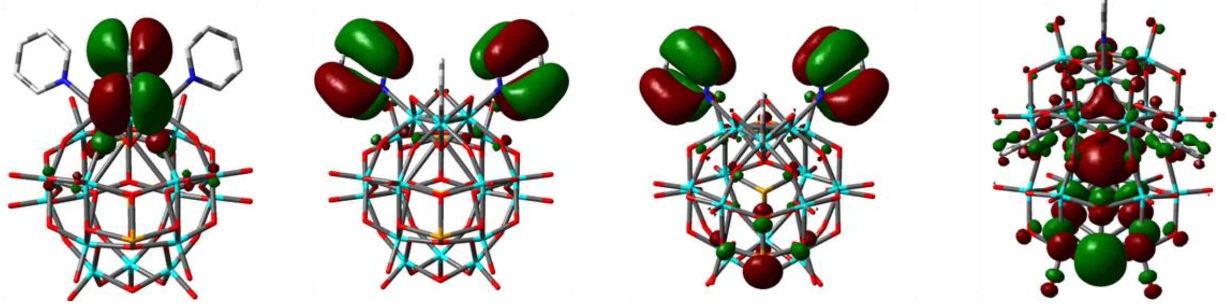


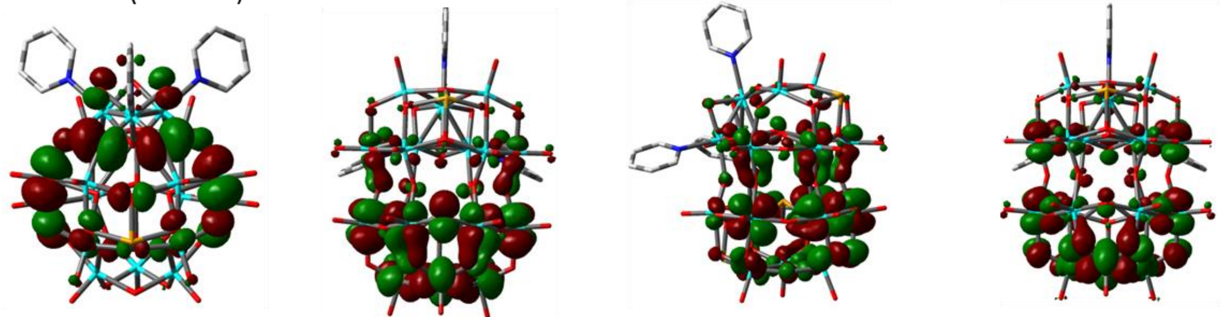
Figure S4. Crystal packing of $[Sb^{III}{}_3Mo^{IV}{}_3Mo^{VI}{}_{15}O_{55}(OH)_2py_3]\cdot NH_2(CH_3)_2\cdot 4NH(CH_3)_2\cdot 2H_2O$ showing the capping arrangement between Sb3 (light orange) and $Mo^{VI}{}_3$ triangles (purple).



HOMO(-6.76eV) HOMO-1(-6.82eV) HOMO-2(-7.42eV) HOMO-3(-7.67eV)



HOMO-4(-7.70eV) HOMO-5(-7.73eV) HOMO-6(-7.74eV) HOMO-7(-7.85eV)



HOMO-8(-8.02eV) LUMO(-5.99eV) LUMO+1(-5.84eV) LUMO+2(-4.83eV)

Figure S5. Diagrams of frontier molecular orbitals of **1**.

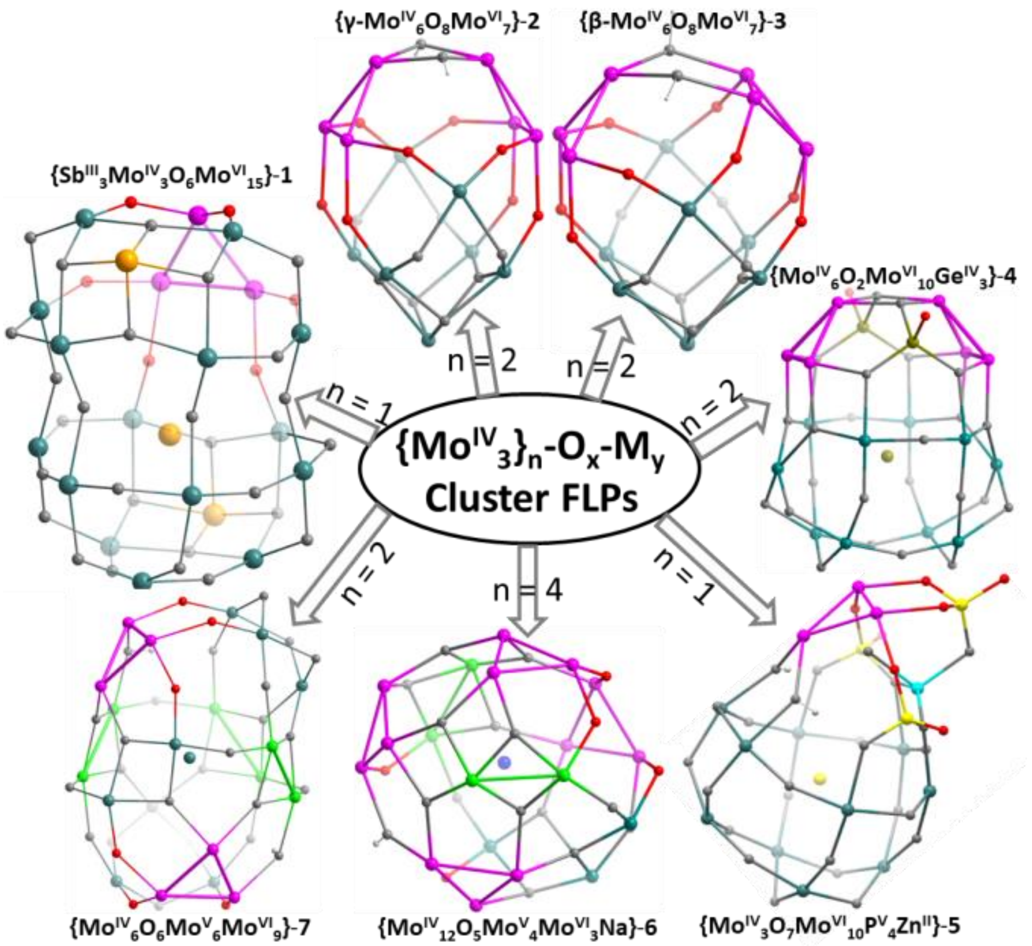


Figure 6. POM-FLPs nanocages of the CFLP hybrid clusters **1-7** built of multiple Mo^{IV}-μ$_2$-O-M Lewis pairs wherein the most negative μ$_2$-O bonded to Mo^{IV} are marked in red (Mo^{IV}, purple; Mo^{V}, green; Mo^{VI}, teal; Sb^{III}, light orange; P^{V}, yellow; Ge^{4+}, dark yellow; Zn^{II}, turquoise; Na^{+}, blue).

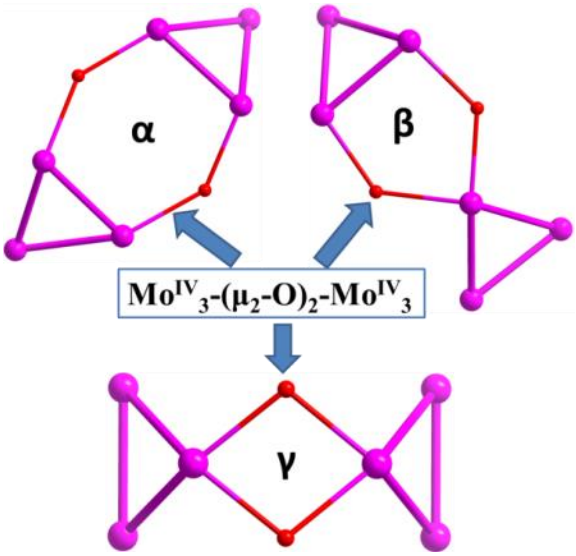


Figure S7. Three types of linkage between two neighbouring triangular Mo$^{IV}_3$ units bridged by oxygen atoms.

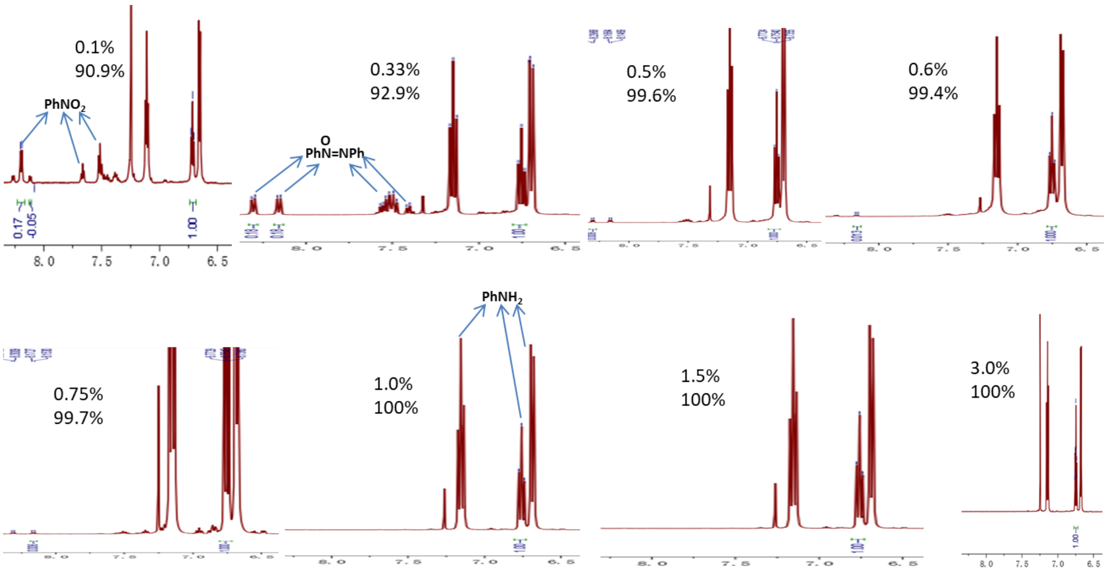


Figure S8. ^{1}H NMR spectra for hydrazine hydrogenation of nitrobenzene to aniline catalyzed by different amount of **1**. reaction conditions: (PhNO$_2$, 10 μL, 0.097 mmol, $N_2H_4 \cdot H_2O$, 20 μL, 0.3 mmol, EtOH, 2 mL, 2h, 60°C).

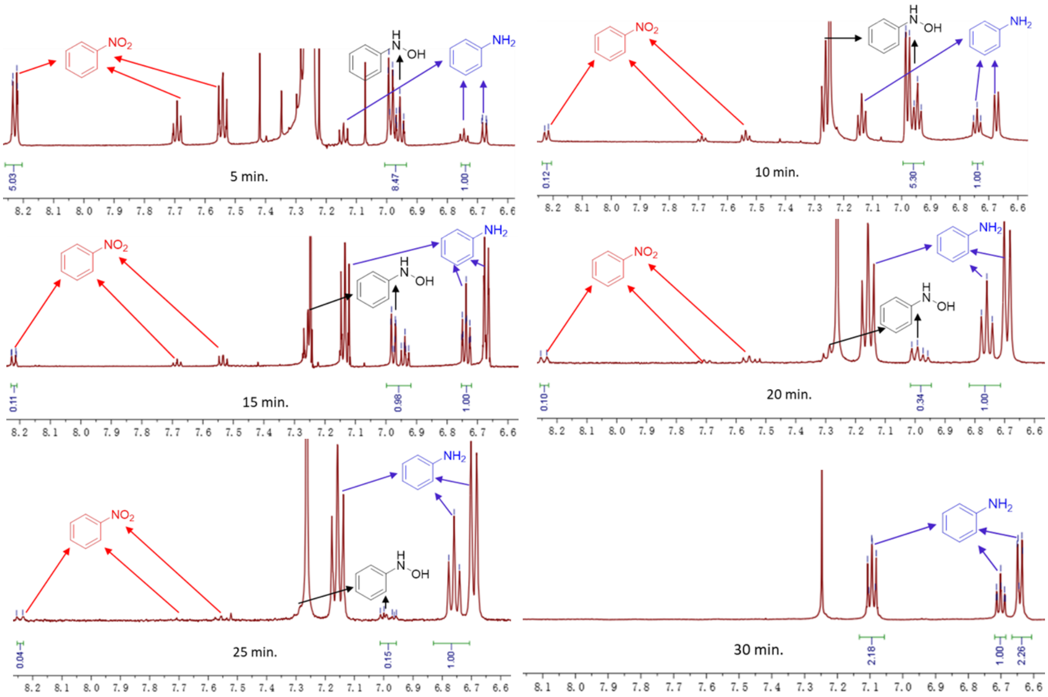
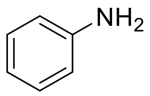
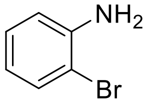


Figure S9. ^{1}H NMR spectra for hydrazine reduction of nitrobenzene to aniline catalysed by **1** at different reaction time. reaction conditions: **1**, 3 mol%, PhNO$_2$, 10 μL, 0.097 mmol, $N_2H_4 \cdot H_2O$, 20 μL, 0.3 mmol, EtOH, 2 mL, 80°C.

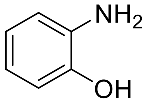
4. Characterization data of the isolated products.



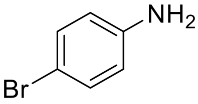
Aniline: isolated yield: 100%. ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.35 – 7.13 (m, 2H), 6.90 – 6.77 (m, 1H), 6.74 – 6.63 (m, 1H), 3.66 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$), δ 146.59, 129.45, 118.67, 115.28.



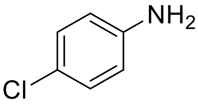
2-bromoaniline: isolated yield: 99.9%. ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.40 – 7.41 (m, 1.4 Hz, 1H), 7.11 – 7.09 (m, 1H), 6.76 – 6.75 (m, 1H), 6.63 – 6.60 (m, 1H), 4.07 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$), δ 144.17, 132.68, 128.45, 119.52, 115.87, 109.43.



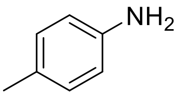
2-aminophenol: isolated yield: 99.8%. ^{1}H NMR (600 MHz, DMSO – D_6), δ 8.89 (s, 1H), 6.59 – 6.68 (m, 1.2 Hz, 1H), 6.54 – 6.52 (m, 1.6 Hz, 1H), 6.50 – 6.47 (m, 1.3 Hz, 1H), 6.36 – 6.34 (m, 1.6 Hz, 1H), 4.42 (s, 1H). ^{13}C NMR (151 MHz, DMSO – D_6), δ 144.48, 137.05, 120.01, 116.92, 114.93, 114.86.



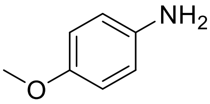
4-bromoaniline: isolated yield: 99.9%. ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 3.65 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$), δ 145.50, 132.09, 116.80, 110.28.



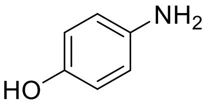
4-chloroaniline: isolated yield: 99.9%. ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.20 – 6.98 (m, 2H), 6.76 – 6.39 (m, 2H), 3.64 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$), δ 145.04, 129.20, 123.22, 116.32.



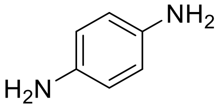
p-toluidine: isolated yield: 99.8%. ^{1}H NMR (600 MHz, $CDCl_3$), δ 6.97 – 6.95 (m, 2H), 6.61 – 6.60 (m, 2H), 3.52 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$), δ 143.88, 129.84, 127.90, 115.36, 20.55.



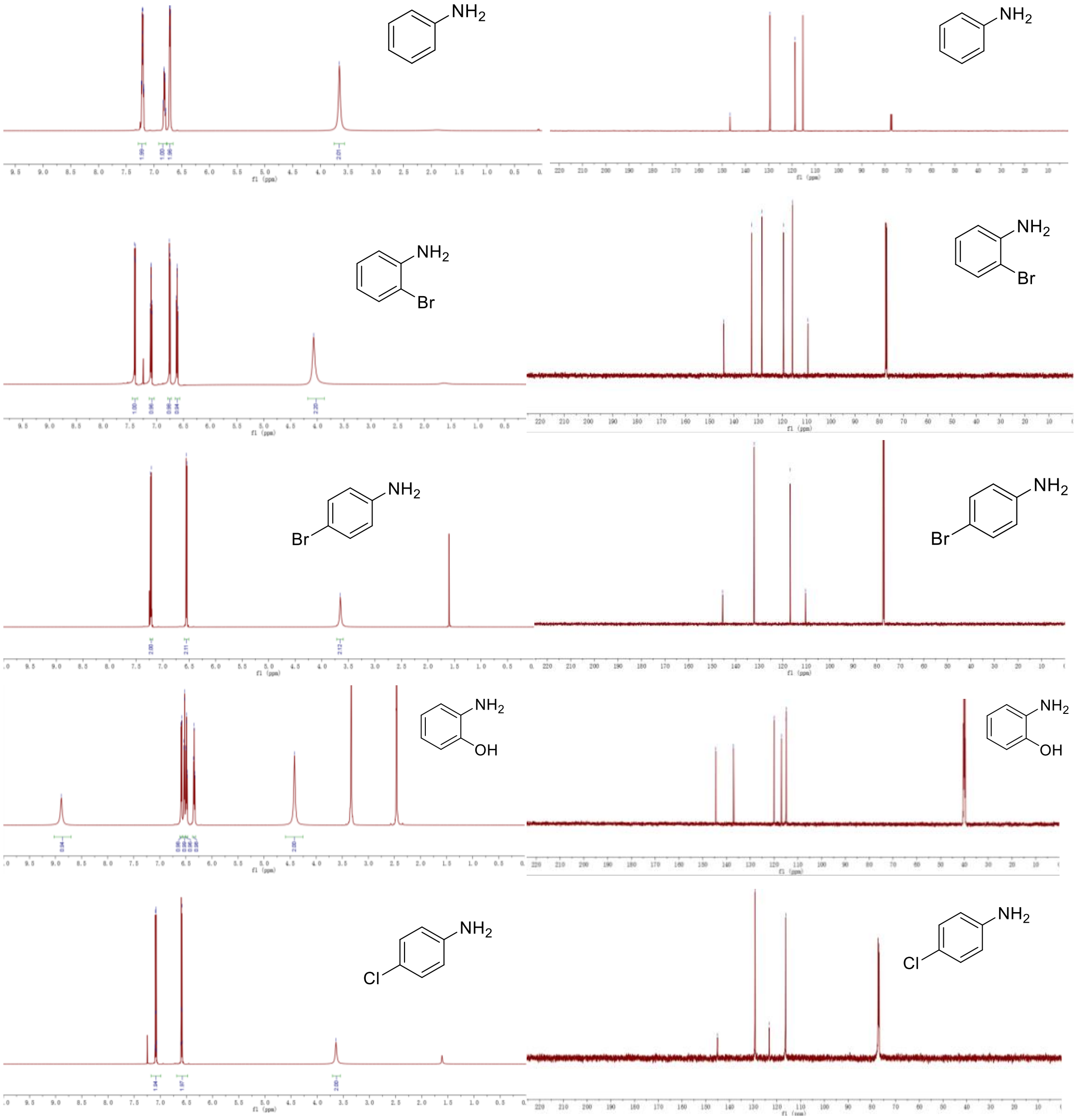
4-methoxyaniline: isolated yield: 81.2%. ^{1}H NMR (600 MHz, $CDCl_3$), δ 6.74 – 6.72 (m, 2H), 6.65 – 6.53 (m, 2H), 3.73 (s, 3H), 3.41 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$), δ 152.88, 140.02, 116.52, 114.89, 55.83.



4-aminophenol: isolated yield: 61.2%. ^{1}H NMR (600 MHz, DMSO – D_6), δ 8.32 (s, 1H), 6.54 – 6.40 (m, 2H), 6.40 – 6.18 (m, 2H), 4.33 (s, 2H). ^{13}C NMR (151 MHz, DMSO – D_6), δ 148.73, 141.17, 116.06, 115.77.



benzene-1,4-diamine: isolated yield: 39.2%. ^{1}H NMR (600 MHz, $CDCl_3$), δ 6.56 (s, 4H), 3.32 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$), δ 138.67, 116.82.



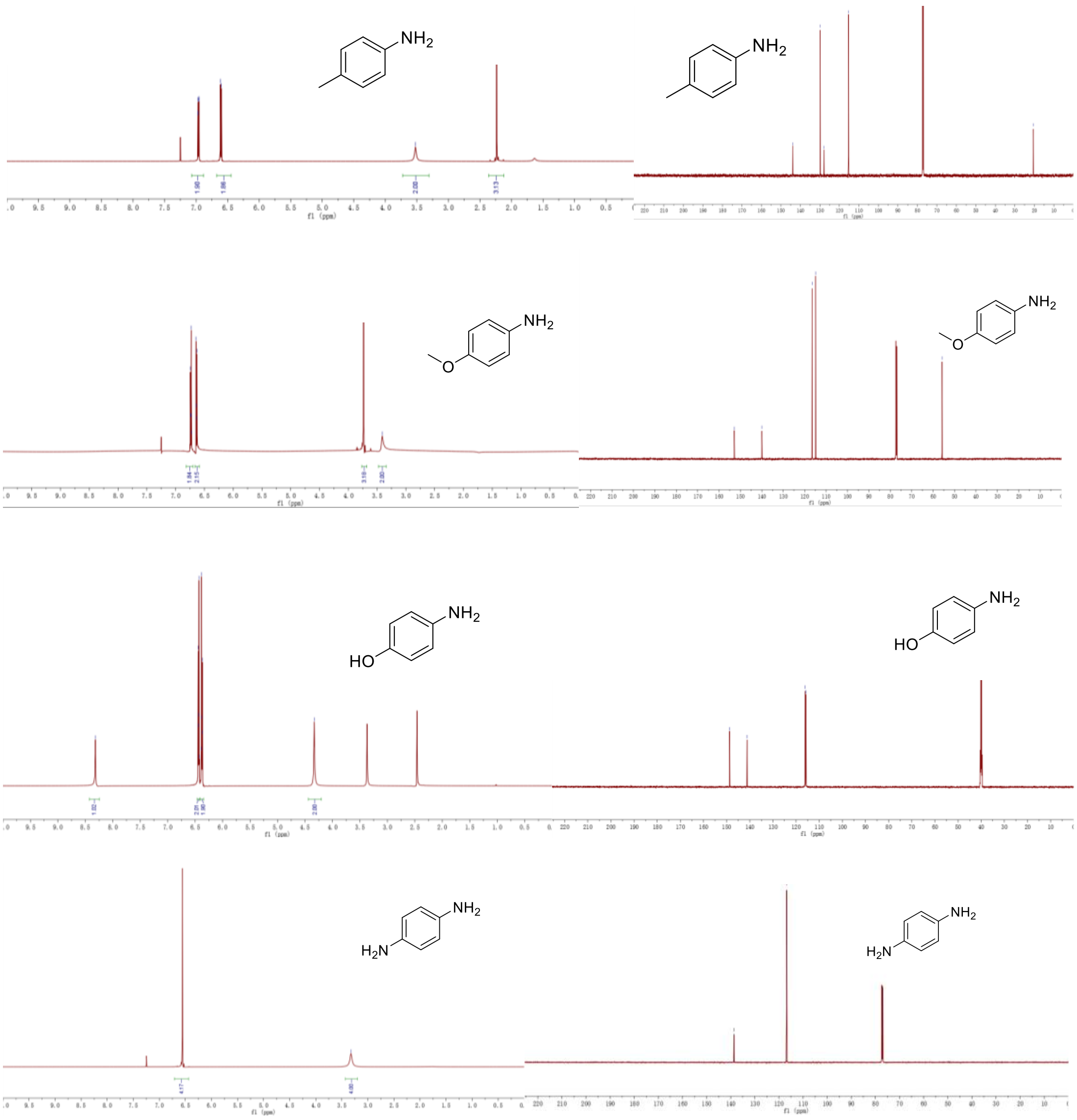


Figure S10. ^{1}H NMR and ^{13}C NMR spectra of the isolated products.

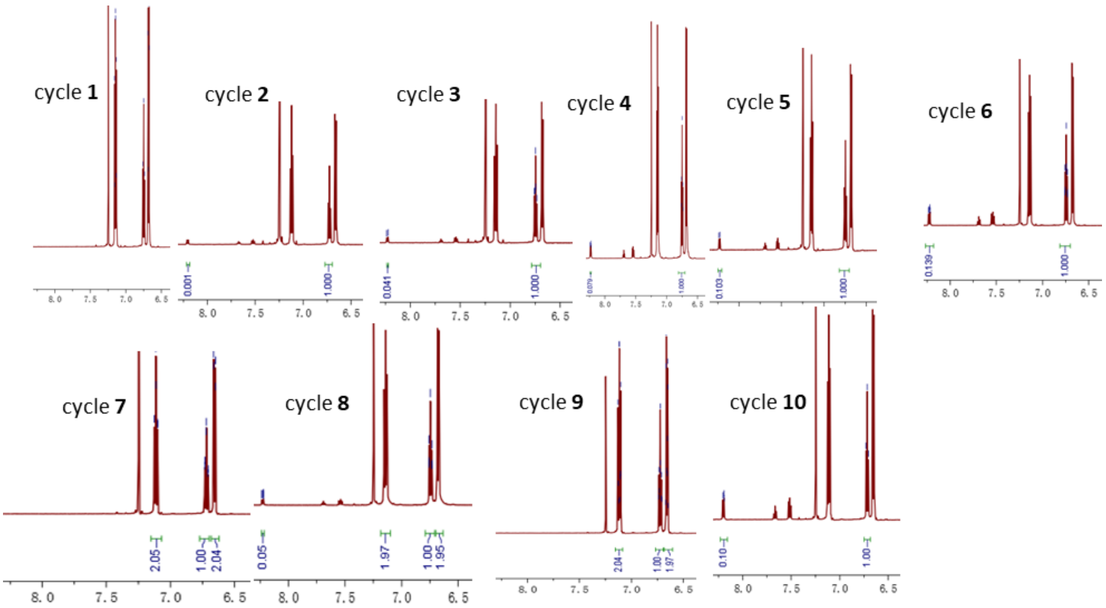


Figure S11. ^{1}H NMR spectra of cycle 1-10 hydrazine reduction of nitrobenzene to aniline. catalysis conditions: 1, 3 mol%, $PhNO_2$, 10 μL, 0.097 mmol, $N_2H_4{\cdot}H_2O$, 20 μL, 0.3 mmol, EtOH, 2 mL, 80°C, fresh and cycle 1, 0.5 h, cycle 2, 1h, cycles 3-10, 2h.

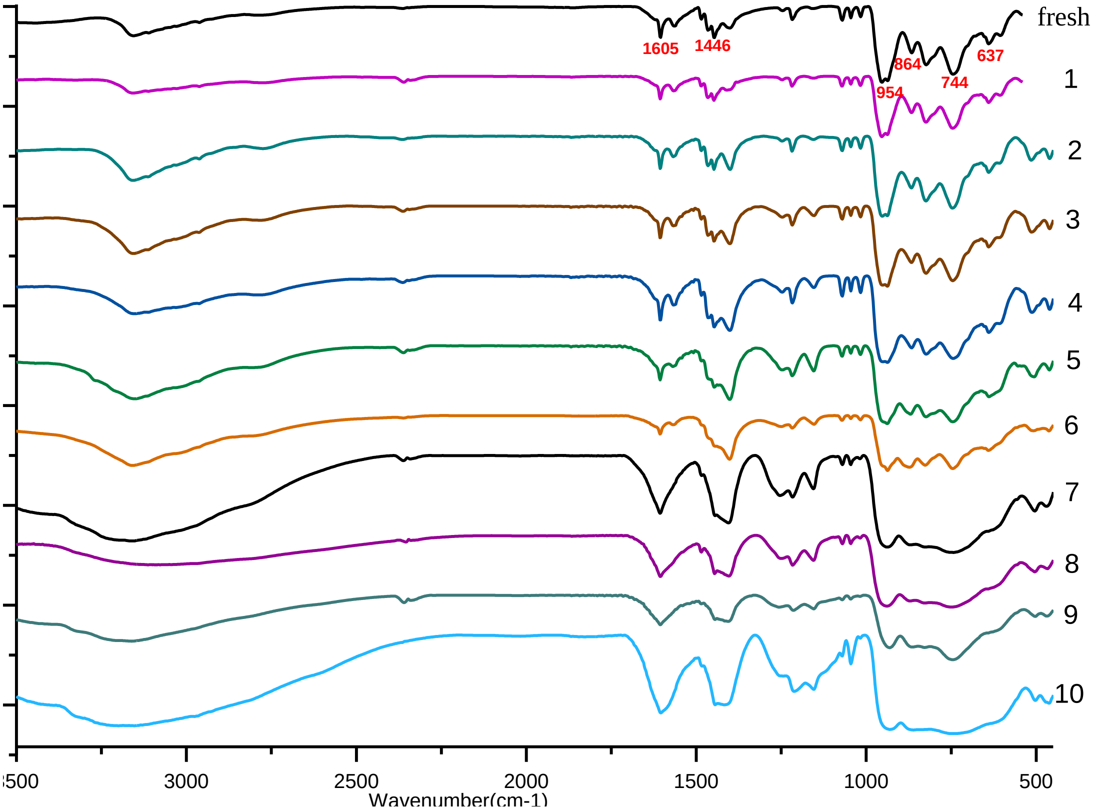
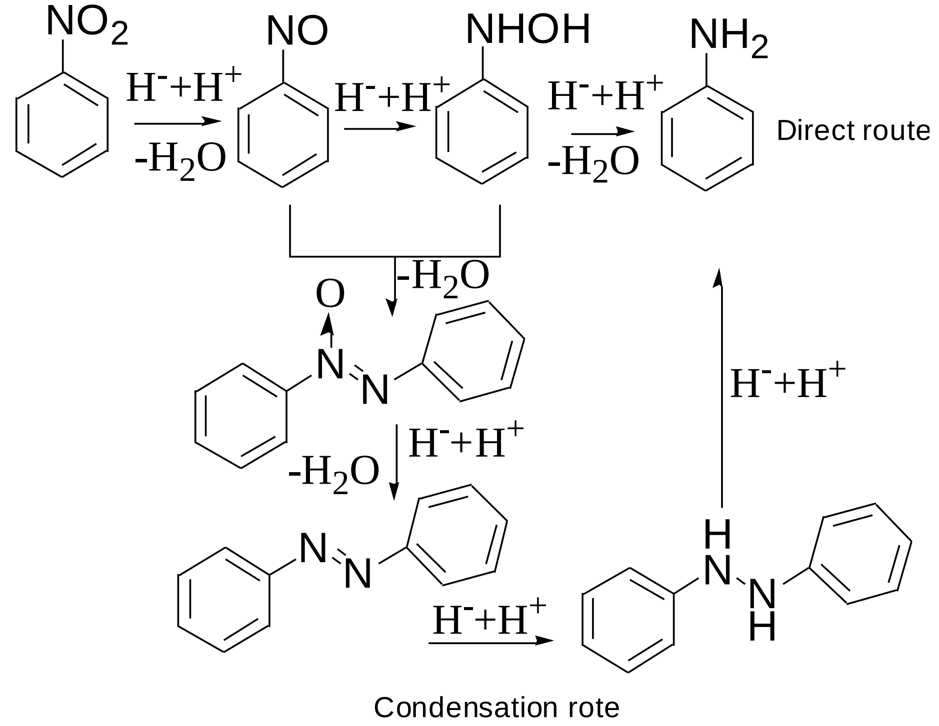


Figure S12. IR spectra of the heterogeneous catalyst **1** in fresh and cycles **1**-**10**.



Scheme S1. Direct and condensation route of the nitrobenzene reduction to aniline.