

# Supporting Information

for

## **1T-MoS<sub>2</sub> catalysed reduction of nitroarenes and one-pot synthesis of imines**

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Dedicated to *Prof. Sasidharan Manickam* (1969-2021)

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## 1. Experimental section

### General Information

All of the nitroarenes, polyethylene glycol-block-polypropylene glycol-polyethylene glycol (PEG-block-PPG-block-PEG) (P123), sodium molybdate ( $\text{Na}_2\text{MoO}_4$ ) and ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) were purchased from Sigma-Aldrich. HF, HCl and ethanol were purchased from Merck and used as received. Thiourea is procured from Alfa aesar and used as received. DI water is used in the entire synthetic process. Ethyl acetate and hexane was purchased from chempure (India). All chemicals were of analytical grade and used directly without further purification.

### Catalyst Characterization

The as-prepared 1T- $\text{MoS}_2$  material was characterized by X-ray diffraction (XRD) analysis in the  $2\theta$  range of  $10 - 90^\circ$  with a scan rate of  $5^\circ$  per minute using a Bruker X-ray powder diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm). Raman spectroscopy was performed by using HORIBA, LabRAM HR Evolution with 532 nm laser excitation. The morphology of  $\text{MoS}_2$  materials was analysed by the FESEM (SUPRA 55VP Carl zeiss) and HR-TEM (Tecnai G2 TF20) instruments. The X-ray photoelectron spectroscopy (XPS) analysis was performed using a Theta Probe AR-XPS system (Thermo Fisher Scientific, UK). Specific surface area of synthesized 1T- $\text{MoS}_2$  materials was analysed using the Quantachrome instrument. Hydrogenation of nitroarene and imine conversion and selectivity were analysed by Gas chromatography Agilent Technologies 7890B GC system.

### General procedure for the synthesis of 1T- $\text{MoS}_2$

For the formation of 1T- $\text{MoS}_2$ , we adopted a mesoporous silica template-assisted technique. The employed mesoporous silica template is SBA-15 with a uniform pore size of 10-15 nm, which is capable to behave as a nanoreactor by providing confined space to do highly sensitive reactions within it. The SBA-15 was prepared using the procedure which was stated in the previous report and was stored in a container which was moisture-free for the synthesis of 1T- $\text{MoS}_2$ .<sup>59</sup> At first, 10 mM of  $\text{Na}_2\text{MoO}_4$  was taken in a beaker and 5 mL of DI water was added and stirred for 10 minutes and to it 1 g of the prepared SBA-15 was also added and continued stirring for 24 h to impregnate  $\text{MoO}_4^{2-}$  ions into the channels of SBA-15. The ions adsorbed on the exterior of the template were removed by washing with ethanol. In another beaker, 30 mM of thiourea was taken and it was dissolved with 10 mL of DI water. The prepared  $\text{MoO}_4^{2-}$  ion

impregnated SBA-15 was then added to this and stirred for 24 h. Consequently, the whole precursor mixture was transferred to a 50 mL autoclave and heated in a hot air oven at 200 °C for 24 h. Once the reaction was completed, the residual 1T-MoS<sub>2</sub>-SBA-15 was collected using centrifugation and washed several times with DI water and with ethanol. Then the SBA-15 silica template of 1T-MoS<sub>2</sub>-SBA-15 was carved out by stirring it with 0.5 % of HF. At the end, the black powder of 1T-MoS<sub>2</sub> was obtained and dried overnight at 40 °C and was labelled as 1T-MoS<sub>2</sub>.

### **Catalyst performance Test**

#### **General procedure for reduction of nitroaromatic compounds**

In a 15 mL glass tube, nitroaromatic compound (1.0 mmol), hydrazine (4.0 mmol), catalyst (3.12 mol %), water (3.0 mL) or toluene (1.0 mL) was taken. The reactant mixture in the glass tube was stirred and heated at 100 °C for 15 min. for case of water solvent and 3 h for toluene solvent. Then the reaction vessel was cooled down to room temperature and diluted with ethyl acetate (5.0 mL), filtered through celite, and washed two times with 10 mL of ethyl acetate. Subsequently, the reaction mixture was analysed using TLC and Gas chromatography for reaction conversion and selectivity. At the end, the reaction mixture was analysed using TLC and purified the product through column chromatography using 5% of Ethylacetate/Hexane.

#### **General procedure for one-pot synthesis of imines**

In a 15 mL glass tube, nitroaromatic compound (1 mmol), hydrazine (4 mmol), catalyst (6.25 mol %), toluene (1 mL) was taken in inert atmosphere (argon gas). Then it was stirred and heated at 100 °C for 3 hours. The reaction progress was monitored using TLC after the complete conversion of nitrobenzene into corresponding amine, aromatic aldehyde (1.2 mmol) was added and then the reaction mixture was stirred continuously for 19 hours at 100 °C. Next, the reaction mixture was cooled down to room temperature and diluted with ethyl acetate 5 mL, filtered through celite and washed two times with 10 mL of ethyl acetate. Then the reaction mixture was analysed using TLC and Gas chromatography to know the reaction conversion and selectivity.

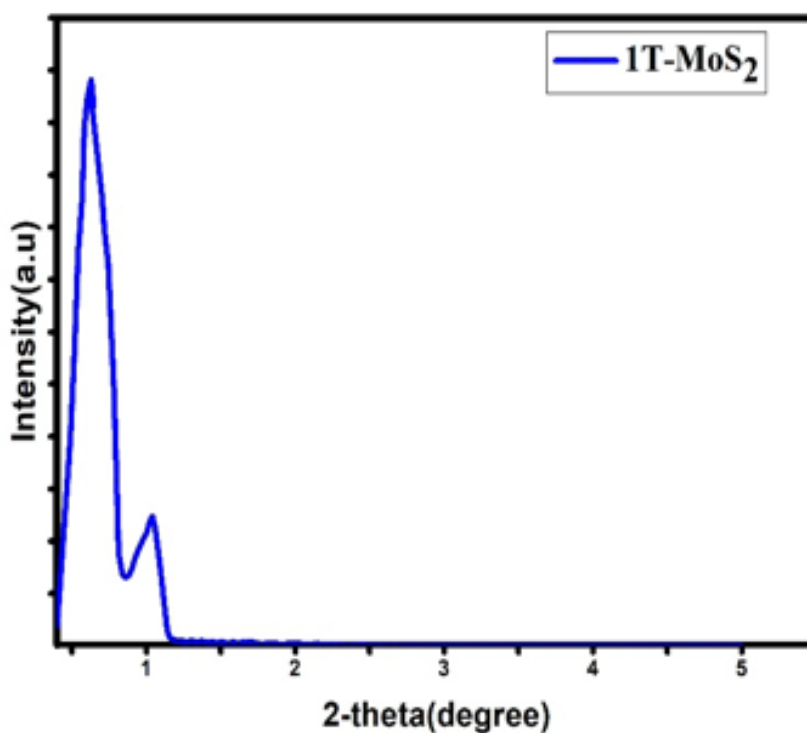
#### **Leaching and recyclability test**

To study if any Mo is leached into the solution, a hot filtration experiment was done. The reduction of nitrobenzene was considered as a test reaction for the hot-filtration studies. Initially, the reaction was carried out for 1.5 h at a 79% conversion level and then, the catalyst

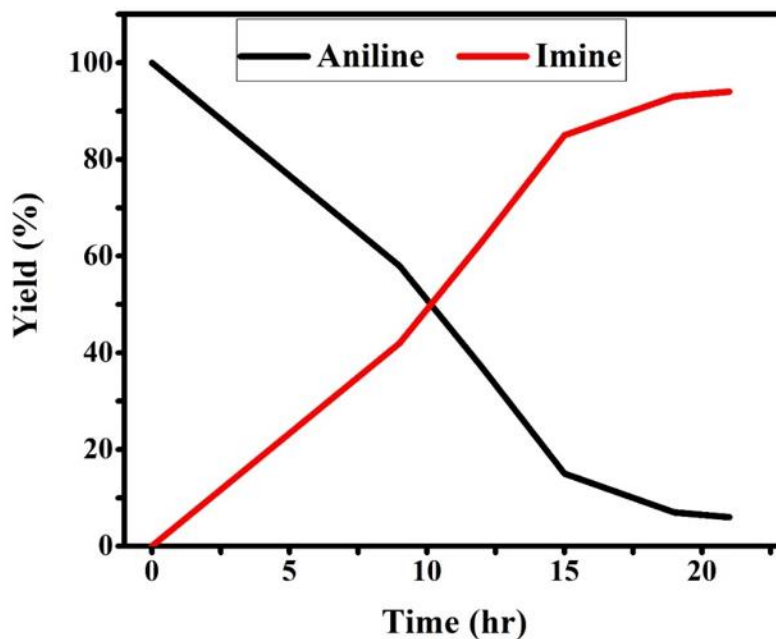
was removed by hot filtration technique. Using the filtrate collected from above, the reaction was further continued for another 1.5 h under the ideal reaction conditions. After completion of 3 h, GC analysis of the filtrate was performed and it showed no progress in the reaction which in fact confirmed the true heterogeneous nature of the 1T-MoS<sub>2</sub> catalyst.

For the catalyst recyclability test, the catalyst recovered from the first reaction was separated using centrifugation, washed well with ethanol and water and dried overnight in a hot air oven at 100 °C to remove the organics present on the catalyst surface. The catalyst was further recycled for another 6 cycles under the ideal reaction conditions by following the above-described procedures.

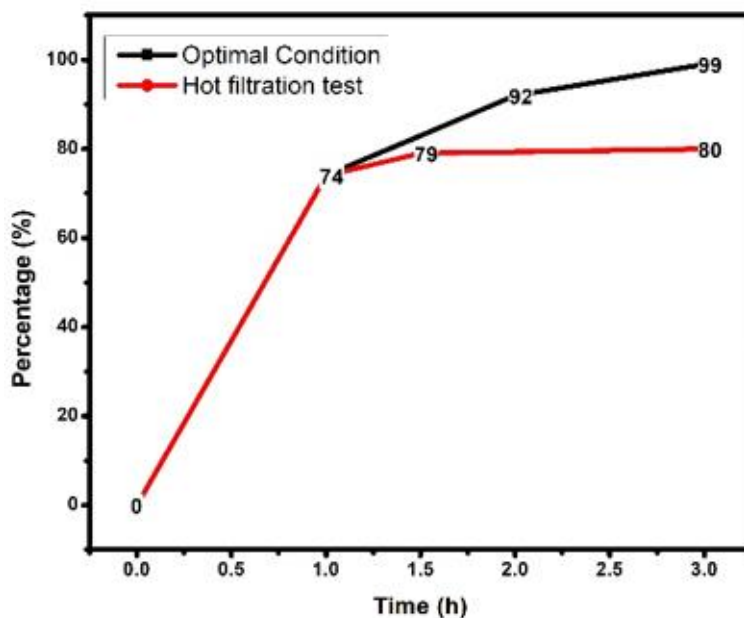
## 2. Figures



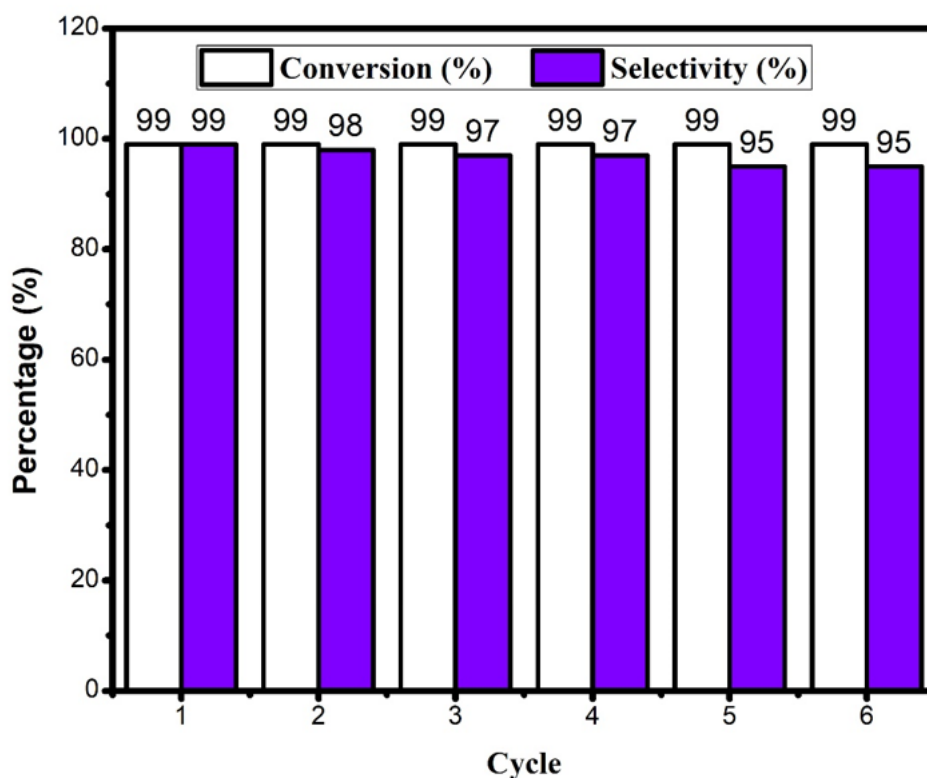
**Figure S1.** Low angle XRD patterns of 1T-MoS<sub>2</sub>



**Figure S2.** Optimization of imine. <sup>a</sup> **Reaction conditions:** Nitrobenzene (1.0 mmol), toluene (1.0 mL) and 1T-MoS<sub>2</sub> (6.25 mol%) were added and stirred for 3 h at 100 °C. After the completion of the reaction (monitored by TLC) benzaldehyde (1.2 mmol) was added and stirred at the specified temperature.



**Figure S3.** Hot filtration test for 1T MoS<sub>2</sub>. **Reaction conditions:** Nitrobenzene (1.0 mmol), hydrazine (4.0 mmol), catalyst (3.12 mol %) and toluene (1.0 mL) were stirred at 100 °C for 1.5 h. Next, the catalyst was removed using filtration process and continued remaining hours.



**Figure S4.** Recycling studies of 1T-MoS<sub>2</sub>. **Reaction conditions:** Nitrobenzene (10.0 mmol), hydrazine hydrate (40.0 mmol), 1T-MoS<sub>2</sub> (3.12 mol %) and toluene (10.0 mL) were stirred at 100 °C for 1.5 h. Then the catalyst was removed using filtration process and continued the reaction for successive cycles.

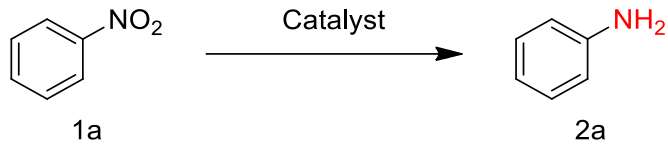
### 3. Tables

**Table S1.** Optimization of Hydrazine hydrate for nitrobenzene reduction using 1T-MoS<sub>2</sub>

Entries	Reagent (mmol)	T (°C)	Solvents	t (h)	Conversion % of 1a	Selectivity % of 2a
1	-	100	Toluene	3	-	-
2	0.002	100	Toluene	3	05	91
3	0.003	100	Toluene	3	48	93
4	0.004	100	Toluene	3	>99	>99

<sup>a</sup> Reaction conditions: Nitrobenzene (1.0 mmol), and solvent (1.0 mL). <sup>b</sup> Selectivity is based on GC analysis using mesitylene as internal standard.

**Table S2.** Optimization of Temperature for nitrobenzene reduction using 1T-MoS<sub>2</sub>

						
Entries	Reagent (mmol)	T (°C)	Solvents	t (h)	Conversion % of 1a	Selectivity % of 2a
1	0.0312	120	Toluene	3	>99	>99
2	0.0312	100	Toluene	3	>99	>99
3	0.0312	80	Toluene	3	88	43

<sup>a</sup> Reaction conditions: Nitrobenzene (1.0 mmol), hydrazine hydrate (4.0 mmol), and solvent (1.0 mL). <sup>b</sup> Selectivity is based on GC analysis using mesitylene as internal standard.

**Table S3.** The hydrogenation of nitroarene using efficient 1T-MoS<sub>2</sub> with comparison of reported literature using hydrazine hydrate as hydrogen source.

S. No	Catalyst	Time	Temp.	H-Source	Yield	No. of reuse	Ref.
1	Pd@SBA15	120 min	RT	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	99	4	2
2	Fe@N	80min	80	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	97	10	3
3	Fe <sub>3</sub> C	120min	60	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	99	5	4
4	Co@C	30h	80	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	99	5	5
5	C@Ni	12h	RT	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	99	4	6
6	Co@SiO <sub>2</sub>	70 min	70	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	99	5	7
7	C-N90	24 h	Light	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	99	4	8
8	Mo	2h	80	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	99	5	9
9	Mo@Sb	30min	60	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	99	5	10
10	Mo@C	5h	80	N <sub>2</sub> H <sub>4</sub> .H <sub>2</sub> O	99	7	11
<b>11</b>	<b>1T-MoS<sub>2</sub></b>	<b>0.1h</b>	<b>100</b>	<b>N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O</b>	<b>99</b>	<b>6</b>	<b>This work</b>



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