Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

## Radical-Friedel-Crafts Benzylation of Arenes with Benzyl Ethers over the 2H-$MoS_2$: Ether Cleavage into Carbon- and Oxygen-Centered Radicals

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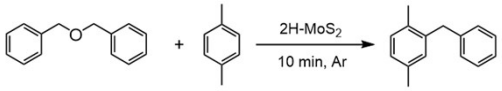
## 1.1 Optimization of Reaction Conditions

1) The effect of reaction temperature




1a 2a 3a

| Entry | Temperature (℃) | 1a Conv. (%) | 3a Yield (%) |
|---|---|---|---|
| 1 | 110 | 7.8 | 3.6 |
| 2 | 120 | 16.4 | 13.1 |
| 3 | 130 | 34.8 | 30.9 |
| 4 | 140 | 59.6 | 57.1 |

Reaction conditions: 2H-$MoS_2$ 100 mg, dibenzyl ether 0.25 mmol, PX 2.0 mL, Ar 1 atm, 10min.

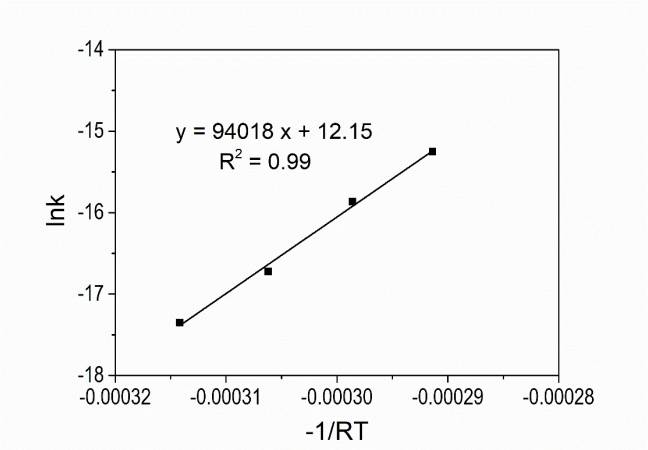



**Figure S1. Apparent activation energy.**

To calculate the apparent activation energy, the initial rate of the reaction was measured as a function of temperature (110, 120, 130 and 140℃). In a typical reaction, in the glove box under the Ar atmosphere, dibenzyl ether (0.25 mmol) and 2H-$MoS_2$ (100 mg) were added in p-xylene (2 mL) in a 15 mL tube equipped with a Teflon stopcock. The reaction was stirred in an oil bath preset at a preset temperature for 10 min. Then, the tube was taken out of the oil bath and immediately cooled in an ice-water bath. After the tube was open to the air, the dodecane (36.9 mg) as the standard substance was added to the reaction mixture. After the filtration with a Teflon filter membrane, the organic products are analyzed by GC-FID. The slope was used to calculate the apparent activation energy $E_a$=94.0 kJ/mol according the Arrhenius Equation:

$$lnk = E_a \times \left(\frac{-1}{RT}\right) + lnA$$

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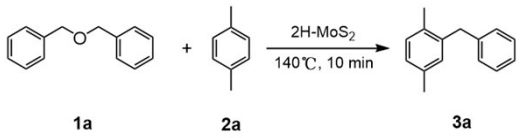
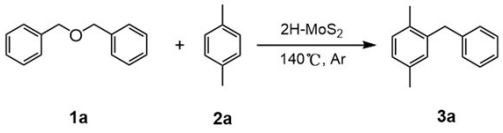
2) The effect of atmosphere




| Entry | Atmosphere | 1a Conv. (%) | 3a Yield (%) |
|---|---|---|---|
| 1 | Ar | 59.6 | 57.1 |
| 2 | Air | 63.9 | 57.7 |
| 3 | $O_2$ | 64.8 | 51.6 |

Reaction conditions: 2H-$MoS_2$ 100 mg, dibenzyl ether 0.25 mmol, PX 2.0 mL, 140 °C, 10min.

3) The effect of reaction time



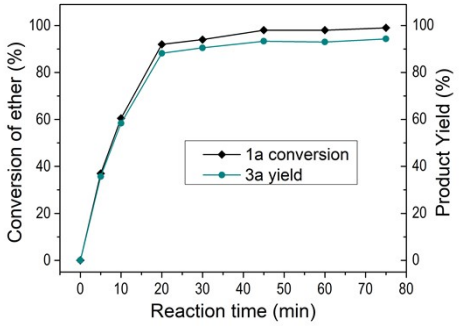




**Figure S2.** The effect of reaction time on **1a** conversion and **3a** yield. Reaction conditions: 2H-$MoS_2$ 100 mg, dibenzyl ether 0.25 mmol, PX 2.0 mL, 140 °C, Ar 1 atm.

### 1.2 Reuse test of 2H-$MoS_2$

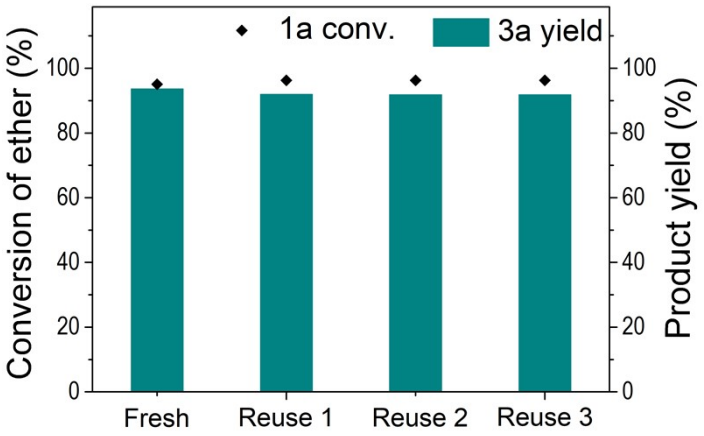
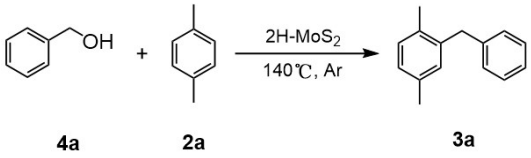



**Figure S3.** Reuse test of 2H-$MoS_2$. Reaction conditions: 2H-$MoS_2$ 100 mg, dibenzyl ether 0.25 mmol, PX 2.0 mL, 140 °C, Ar 1 atm, 30 min. The recycled catalyst was used without further pretreatment after separation from the reaction mixture in the previous test.

### 1.3 Benzylation of the PX with Benzyl Alcohol on 2H-$MoS_2$




**4a** **2a** **3a**

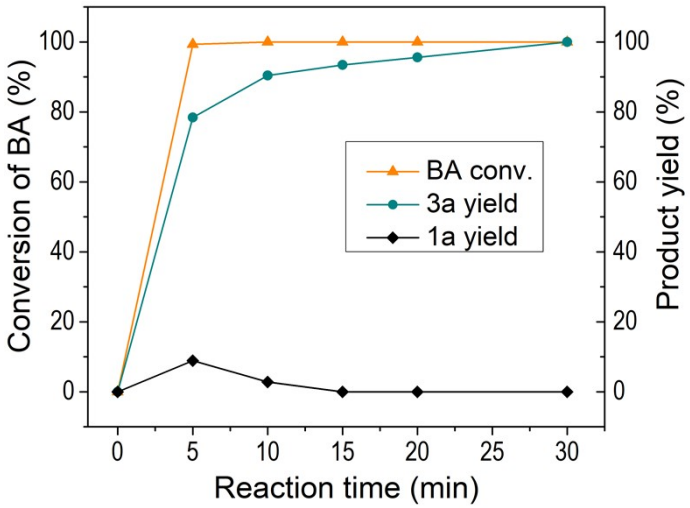
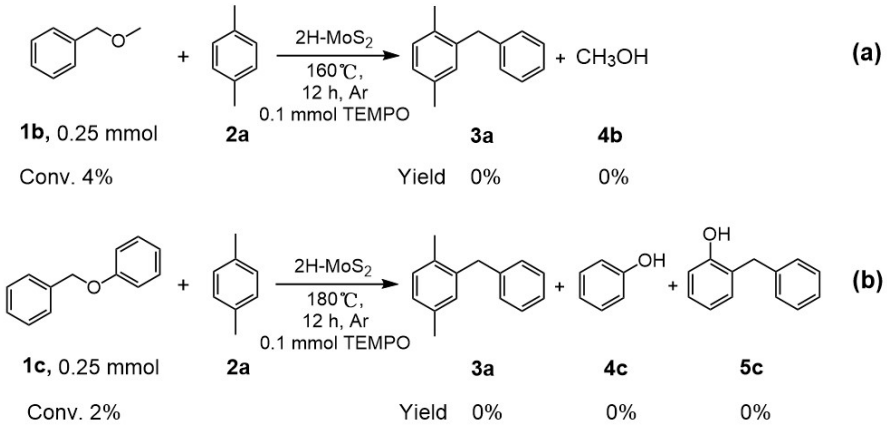



**Figure S4.** Time profile of benzylation of the PX with benzyl alcohol on 2H-$MoS_2$. Reaction conditions: 2H-MoS2 100 mg, benzyl alcohol 0.5 mmol, PX 2.0 mL, 140 °C, Ar 1 atm.

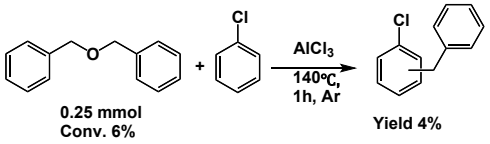
## 1.4 Benzylation of PX with Benzyl Ethers in the Presence of TEMPO




**Scheme S1. Benzylation of PX with Benzyl Ethers in the Presence of TEMPO.**

The benzylation of PX with of benzyl methyl ether (**1b**) and benzyl phenyl ether (**1c**) could significantly be restrained by TEMPO, which was consistent with the reaction using DBE as substrate. The result indicates that radicals still play a crucial role in the benzylation process with these benzyl ethers as the benzylation reagents.

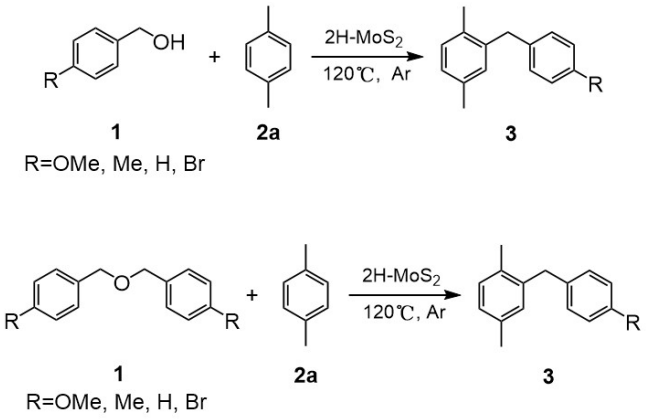
## 1.5 Benzylation Reactions Catalyzed by $AlCl_3$




**Scheme S2. Benzylation of Chlorobenzene Catalyzed by $AlCl_3$**

The benzylation of chlorobenzene catalyzed by $AlCl_3$ only gave a 4% yield. Chlorobenzene was not a good substrate in classical FC-mechanism because of the electron withdrawing effect of chlorine.

## 2.1 General procedure of Hammett Study




**Scheme S2.** Hammett study.

In a glove box under the Ar atmosphere, para-substituted benzyl alcohols (1 mmol) or para-substituted dibenzyl ether (0.25 mmol), and 2H-$MoS_2$ (100 mg) were added in p-xylene (2 mL) in a 15 mL tube equipped with a Teflon stopcock. The reaction was stirred in an oil bath preset at 120°C for 3 min (8 min for para-substituted dibenzyl ether). Then, the tube was taken out of the oil bath and immediately cooled in an ice-water bath. After the tube was open to air, the 1,3,5-Trimethylbenzene (57.1 mg) as the standard substance was added into the reaction mixture. After the filtration with a Teflon filter membrane, the organic products are analyzed by NMR. The conversion was determined by NMR by measuring the appearance of the product.

## 2.2 Hammett profiles of benzylation reactions catalyzed by $AlCl_3$

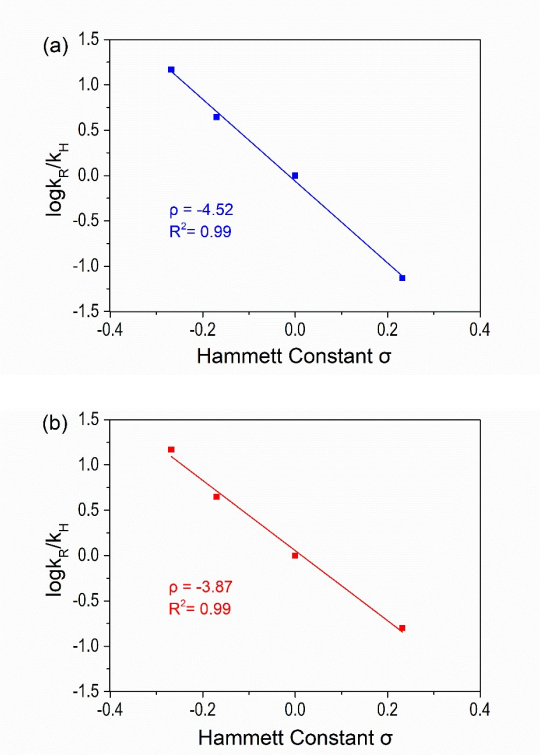
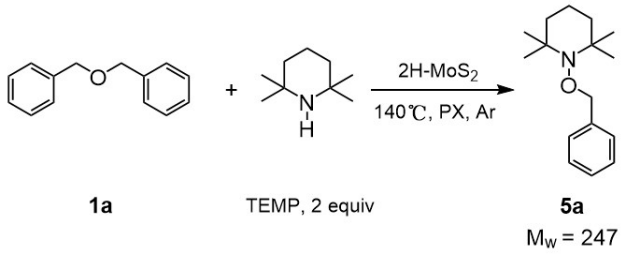



**Fig. S5** Hammett plots (log $k_R/k_H$ versus Hammett constant σ) of the benzylation reactions catalyzed by $AlCl_3$: (a) substituted benzyl alcohols with PX at 120 °C; (b) substituted dibenzyl ethers with PX at 120 °C.

### 3.1 Radical Trap Experiment with TEMP




**Scheme S3.** Radical trap experiment with TEMP.

In a glove box under the Ar atmosphere, dibenzyl ether (0.5 mmol), and 2H-$MoS_2$ (200 mg) were added in p-xylene (2 mL) in a 15 mL tube equipped with a Teflon stopcock. The reaction was stirred in an oil bath preset at 140°C for 2 min. Then, 2,2,6,6-tetramethylpiperidine (TEMP, 1mmol) was added under Argon atmosphere and the reaction was cooled down. After the filtration with a Teflon filter membrane, the organic products are analyzed by GC-MS (GC: Agilent 7890A, MS: Agilent 5975C). The mass spectrum of **5a** is shown in Figure S4 with an m/z = 247.

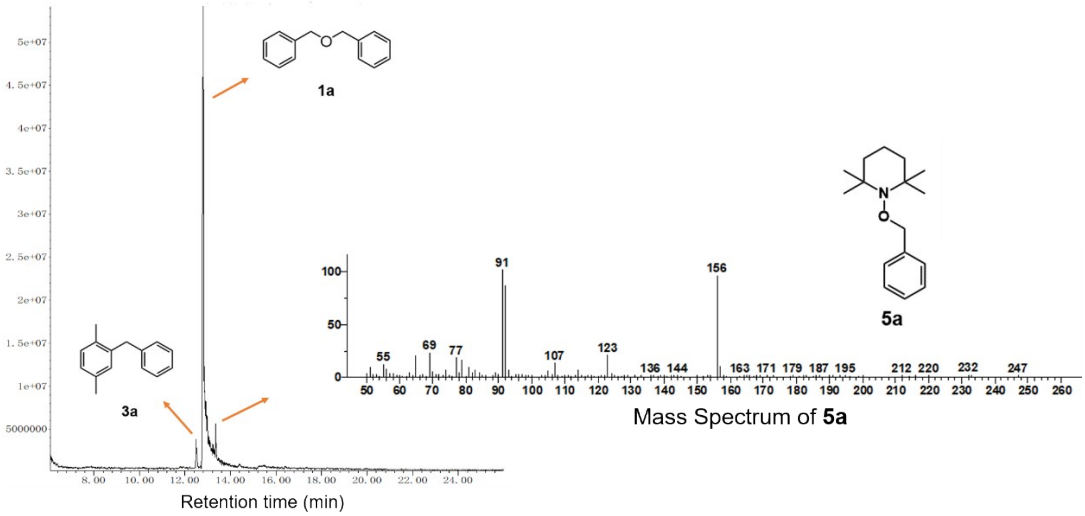
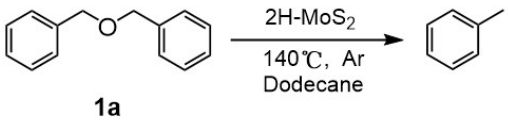



**Figure S6.** The GC-MS pattern of radical trap experiment with TEMP.

### 3.2. Self-decomposition of DBE in the Dodecane




1a

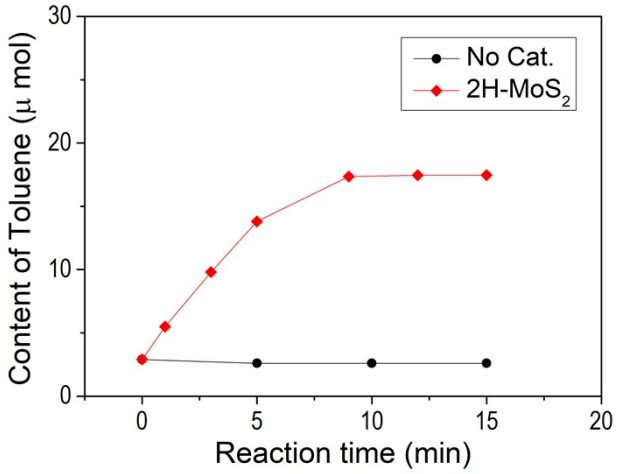



**Figure S7.** Content of toluene versus reaction time of self-decomposition of DBE in the absence or presence of 2H-$MoS_2$. Reaction conditions: 2H-$MoS_2$ 100 mg, dibenzyl ether 0.25 mmol, dodecane 2.0 mL, 140 °C, Ar 1 atm.

The general procedure was similar to the previous experiments. Trace amount of toluene was detected from the DBE even after vacuum distillation. Thus, control experiment with no catalyst was performed as a control group. The significantly increased content of toluene in the presence of 2H-$MoS_2$ suggests that the generation of toluene was from self-decomposition of DBE in dodecane.

**4.1 The Molecular Adsorption States of Benzyl Alcohol and Two Radical Fragments over the 2H-$MoS_2$ (100) Surface**

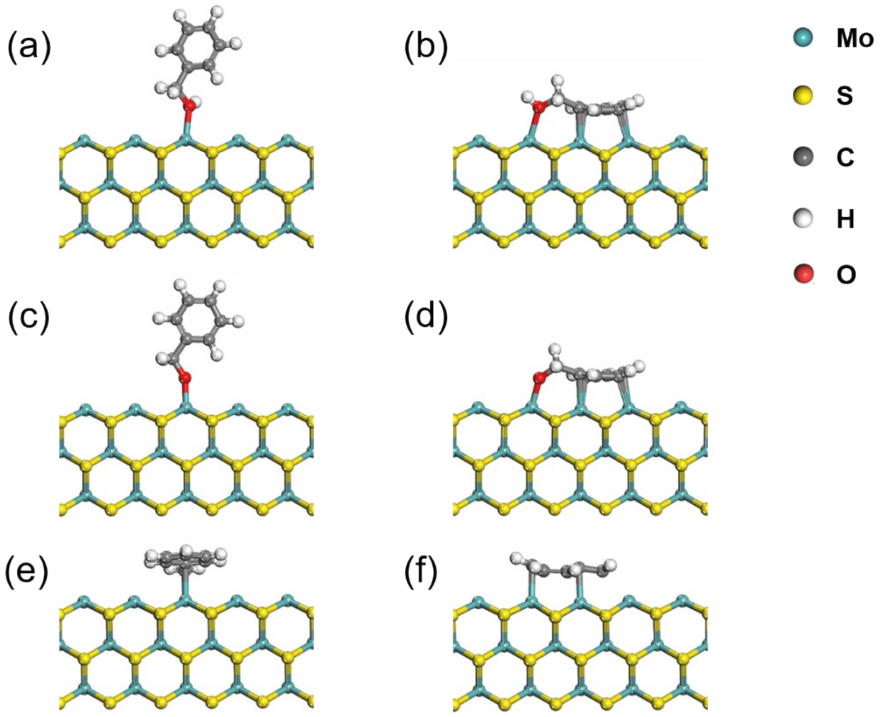



**Figure S8.** The Molecular Adsorption States of : benzyl alcohol (a, O end; b, ring end), BnO• radical (c, O end; d, ring end) and Bn• radical (e, C end; f, ring end).

## 4.2 Adsorption Energy of DBE and Two Radical Fragments

**Table S1.** The Adsorption Energy of DBE, Benzyl Alcohol and Two Radical Fragments over the 2H-$MoS_2$ (100) Surface

| **Molecule or Adsorbate** | **$E_{tot}$ (eV)** | **$E_{ads}$ (eV)** |
|---|---|---|
| Ph-$CH_2OCH_2$-Ph(g) | -184.268 | - |
| Ph-$CH_2OH$(g) | -99.101 | - |
| * | -248.437 | - |
| Ph-$CH_2OCH_2$-Ph* | -436.339 | -3.63 |
| Ph-$CH_2OH$*, O end | -348.466 | -0.93 |
| Ph-$CH_2OH$*, ring end | -350.947 | -3.41 |
| Ph-$CH_2O$*, O end | -346.023 | - |
| Ph-$CH_2O$*, ring end | -348.451 | - |
| Ph-$CH_2$*, C end | -338.826 | - |
| Ph-$CH_2$*, ring end | -340.443 | - |