Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

# Efficient and Controlled $H_2$ Release from Sodium Formate

Fuhua Xu,[a] Wenkai Huang,[a] Yanlan Wang[b], Didier Astruc,[c]* and Xiang Liu[a,d]*

[a]Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, College of Materials and Chemical Engineering, China Three Gorges University, Yichang, Hubei 443002, China. E-mail: xiang.liu@ctgu.edu.cn

[b]Department of chemistry and chemical engineering, Liaocheng University, 252059 Liaocheng, China

[c]ISM, UMR CNRS N°5255, Université de Bordeaux, 351 Cours de la Libération, 33405 Talence Cedex, France. E-mail: didier.astruc@u-bordeaux.fr

[d]Hubei Three Gorges Laboratory, Yichang, Hubei 443007, China.

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## 1. Chemicals and reagents

All chemicals and solvents were used without further purification. The deionized water was prepared in the laboratory. Cupric chloride dihydrate ($CuCl_2 \cdot 2H_2O$), deuterium oxide ($D_2O$), iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), phosphoric acid ($H_3PO_4$) and sodium formate (HCOONa) were purchased from Shanghai Macklin Biochemical Co., Ltd. Palladium on activated charcoal (Pd/C, 5 wt%) was purchased from Shanghai Bide Pharmaceutical Technology Co., Ltd. Silver nitrate ($AgNO_3$) was obtained from Shangdong Xiya Chemical Co., Ltd. Butyric acid ($C_4H_8O_2$), Propionic acid ($C_3H_6O_2$) , valeric acid ($C_5H_{10}O_2$), acetic acid-d ($CH_3COOD$) and nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) were purchased from Aladdin Reagent Co., Ltd. Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), 1,1-diphenylethylene (stabilized with HQ) ($(C_6H_6)_2C{=}CH_2$) were obtained from Shanghai Jiuding Chemical Technology Co., Ltd. Sodium hydroxide (NaOH) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Sulfuric acid ($H_2SO_4$), nitric acid ($HNO_3$), hydrochloric acid (HCl) were obtained from Chengdu Chron Chemicals Co., Ltd. Acetic acid glacial was purchased from Sahn Chemical Technology (Shanghai) Co., Ltd. Sodium borohydride ($NaBH_4$) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Methanol ($CH_3OH$) was purchased from Tian in Fuyu Fine Chemical Co., Ltd.

## 2. Characterization

Morphology analysis by transmission electron microscopy (TEM) measurements wase performed on a TECNAI F-20 electron microscope (JEOL 2100F, Netherlands) at an accelerating voltage of 200 kV. Surface analysis by XPS was performed with a Thermo SCIENTIFIC ESCALAB 250Xi (ThermoFischer, USA) system spectrometer in an ultra-high vacuum (UHV) chamber. The distribution of element was recorded by Energy-dispersive X-ray Spectroscopy (EDS) on a JEM-ARM200F (URP) ED. EDX compositional mapping were performed with a TECNAI F-20 microscope (JEOL 2100F) operated at 200 kV. Detailed analyses for $CO_2$, $H_2$, $N_2$ and CO were performed on GC-6890 with thermal conductivity detector (TCD) and flame ionization detector (FID)-Methanator (detection limit for CO: ~ 2 ppm).

## 3. Synthesis of $Ag_{16}Pd_1$/C

First, 0.02 mmol of dried Pd/C (42.6 mg), 8 mL of deionized water and 1 mL $AgNO_3$ solution (including 0.32 mmol of $AgNO_3$) were added into the round-bottom flask, and this reaction mixture was stirred for 5 minutes at 30 °C. Then, 1 mL solution of $NaBH_4$ (3.2 mmol) was injected into the above mixture solution and stirring was continued for 40 minutes. Finally, the resulting precipitate was centrifuged and washed with deionized water for three times to obtain $Ag_{16}Pd_1$/C. Other composites $M_{16}Pd_1$/C were synthesized under the same conditions.

## 4. Decomposition of SF

Generally, the decomposition of SF was carried out at 60 ℃. 0.02 mmol of $Ag_{16}Pd_1$/C and 4 mL of deionized water were added into a 10 mL round-bottom flask. Under the stirring condition, 1 mL solution of SF/$H_3PO_4$ (1 mmol of SF and 1 mmol of $H_3PO_4$) was added into the flask. The volume of produced $H_2$ was determined by measuring the displacement of water in the burette. Cycle experiment: the $Ag_{16}Pd_1$/C was collected by filtered and washed with deionized water for two times, and used for next cycle. Reaction conditions: 1 mmol of SF, 1 mmol of $H_3PO_4$, 0.02 mmol of $Ag_{16}Pd_1$/C and 5 mL of deionized water at 60 $^{o}$C.

All the data above are presented as a mean value with an error bar, while each experiment was run three times in parallel.

The error bar is the standard error of the mean (SEM), which is the standard deviation of the sample-mean's estimate of a population mean. (It can also be viewed as the standard deviation of the error in the sample mean with respect to the true mean, since the sample mean is an unbiased estimator.) SEM is usually estimated by the sample estimate of the population standard deviation (sample standard deviation) divided by the square root of the sample size (assuming statistical independence of the values in the sample): $\mathrm{SE}_{\bar{x}} = \frac{s}{\sqrt{n}} \mathrm{SE}_{\bar{x}} = \frac{s}{\sqrt{n}}$

Where：**s** is the sample standard deviation (i.e., the sample-based estimate of the standard deviation of the population), and **n** is the size (number of observations) of the sample.

## 5. “On-off” switch

0.02 mmol of $Ag_{16}Pd_1/C$ and 2 mL of deionized water were added into a 10 mL round-bottom flask. Under the stirring conditions, 1 mL solution of SF/$CH_3COOH$ (1 mmol of SF and 1 mmol of $CH_3COOH$)) was added into the flask. The “on−off” control of $H_2$ generation was achieved by addition of an equimolar amount of NaOH and $H_2SO_4$ aqueous solution into the reaction media. After reaction for 30 s, 0.4 mL NaOH (2 M) solution was slowly added into the flask and the SF decomposition was stopped. After 2 min, 0.2 mL $H_2SO_4$ (2 M) solution was added into the flask and the SF dehydrogenation was switched on again.

## 6. Physical characterization of the nanocatalysts (Fig S1-S15)

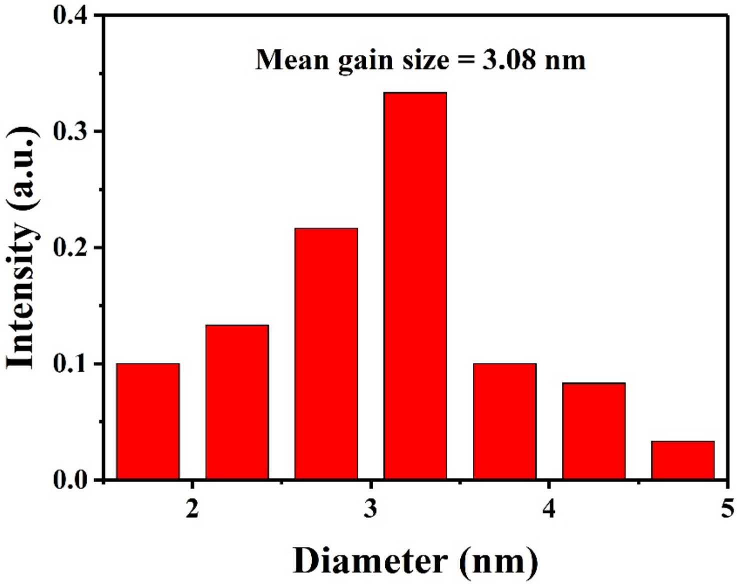

**Figure S1**. Distribution diagram of Pd/C.

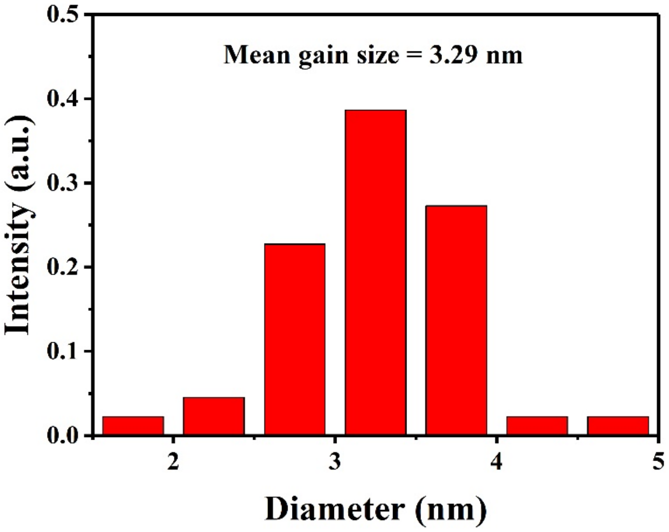

**Figure S2**. Distribution diagram of $Ni_{16}Pd_1/C$.

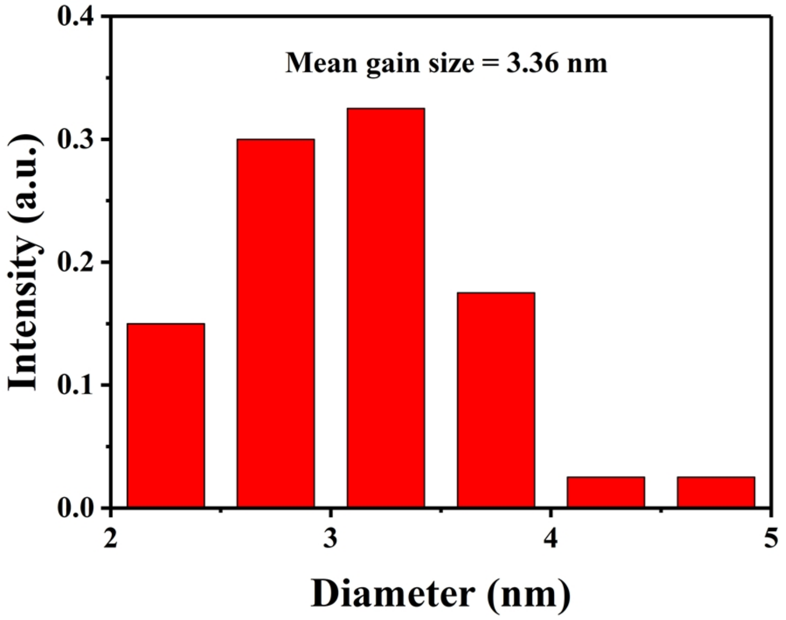

**Figure S3**. Distribution diagram of $Ag_{16}Pd_1/C$.

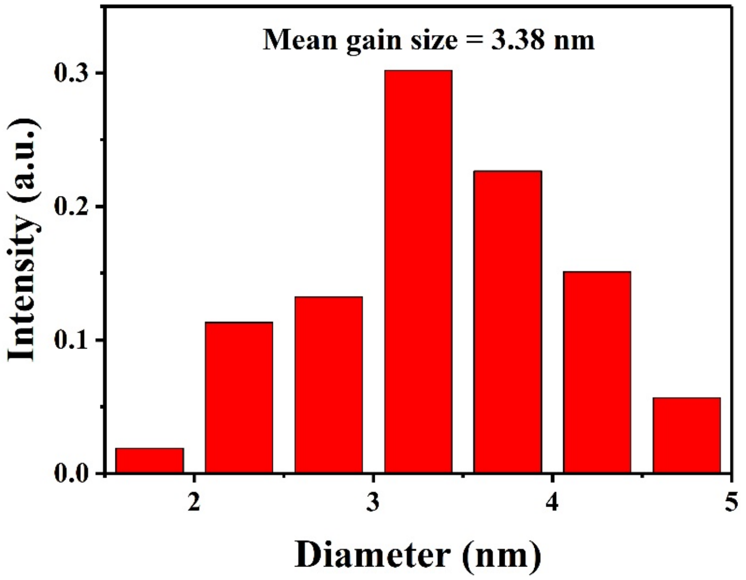

**Figure S4**. Distribution diagram of $Fe_{16}Pd_1/C$.

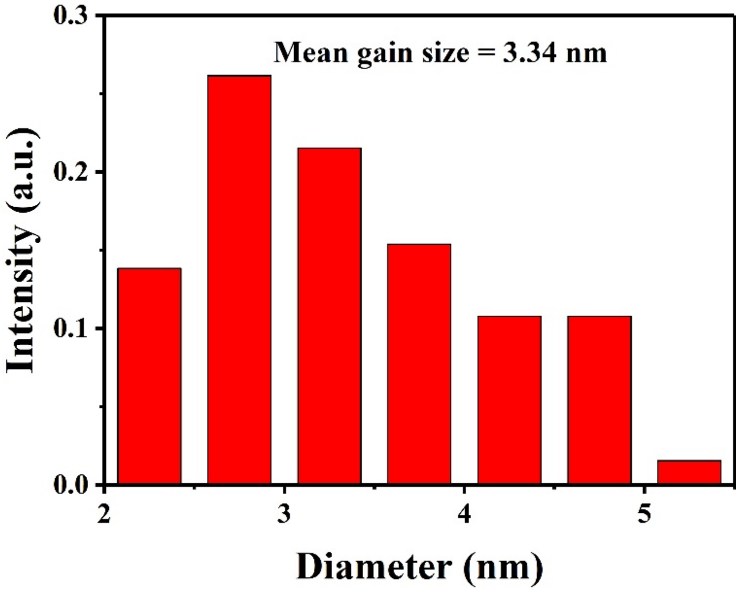

**Figure S5**. Distribution diagram of $Co_{16}Pd_1/C$.

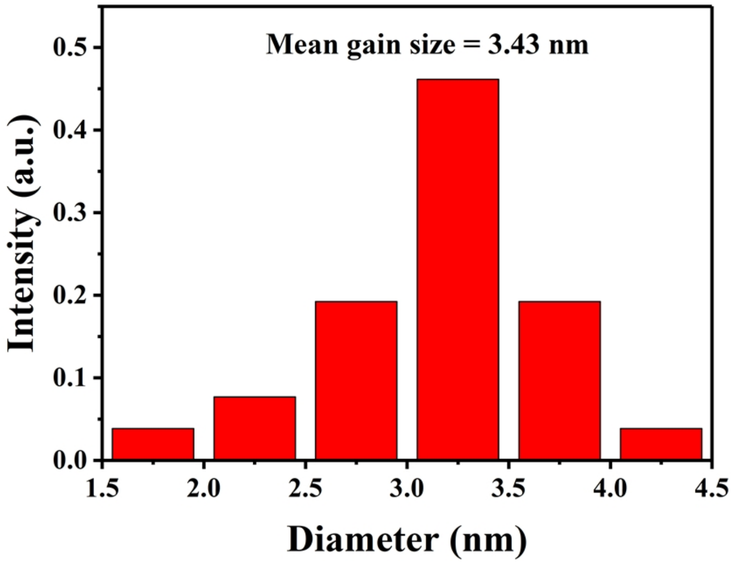

**Figure S6**. Distribution diagram of $Cu_{16}Pd_1/C$.

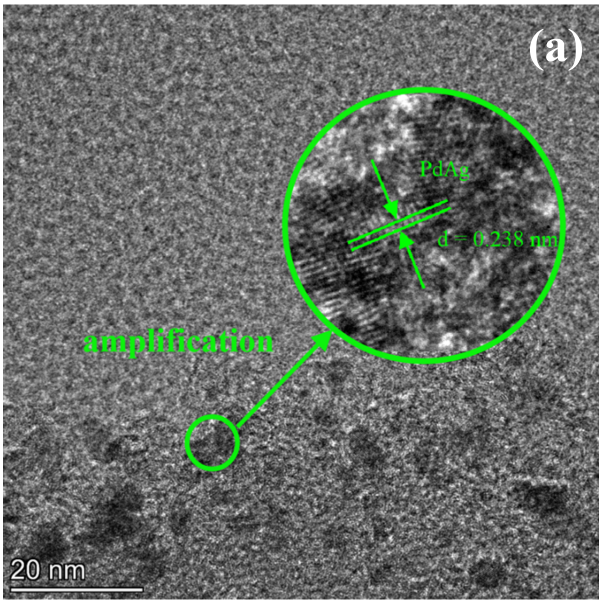

**Figure S7.** HRTEM image of $Ag_{16}Pd_1/C$

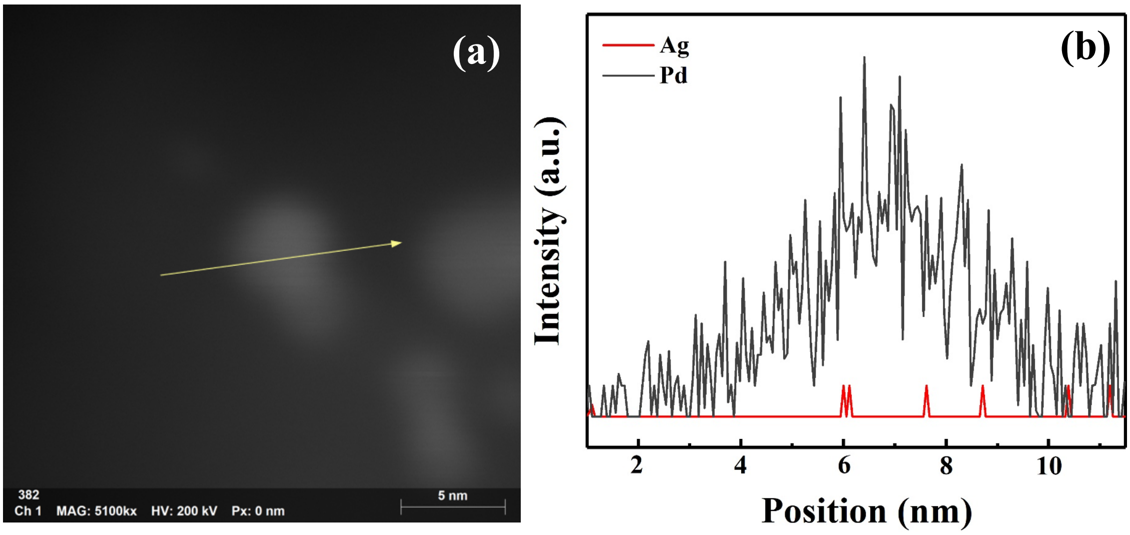

**Figure S8.** (a) STEM image of $Ag_{16}Pd_1/C$, (b) EDX spectrum of $Ag_{16}Pd_1/C$, distributions of Pd and Ag along line scan outline;

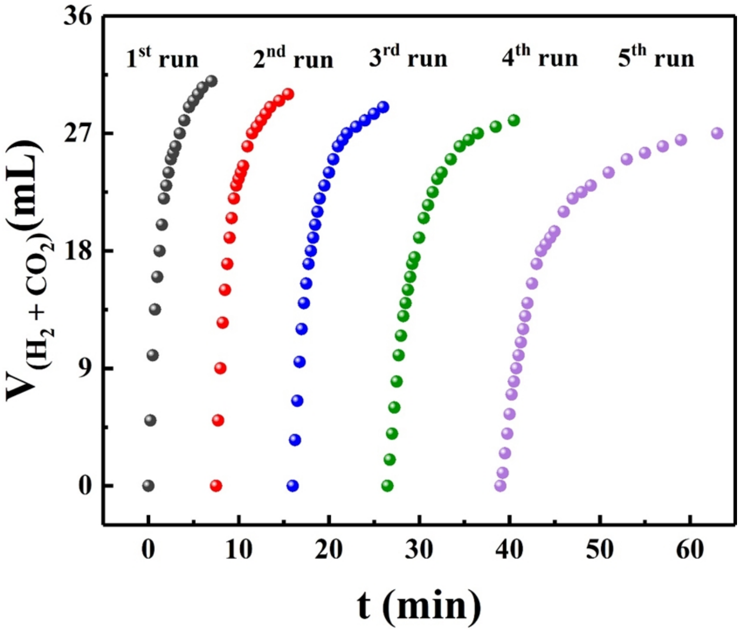

**Figure S9.** Stability test on the $Ag_{16}Pd_1/C$ catalyst upon decomposition of SF. Reaction conditionS: 1 mmol of $CH_3COOH$, 1 mmol of HCOONa, 0.02 mmol of $Ag_{16}Pd_1/C$ and 5 mL of deionized water at 60 °C

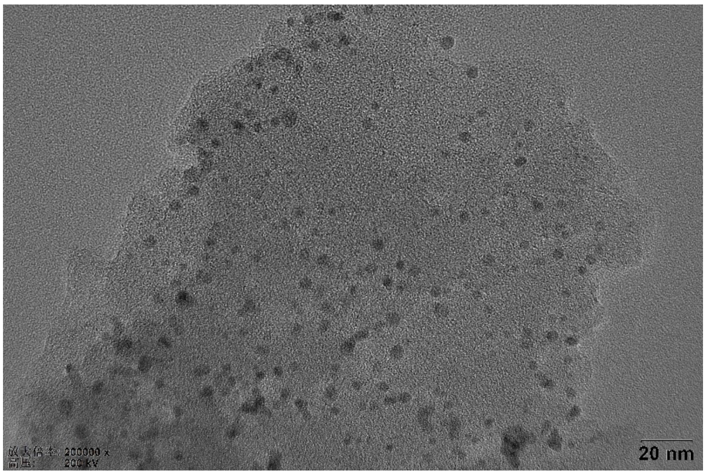

**Figure S10.** The TEM image of 5th reused $Ag_{16}Pd_1/C$ catalyst

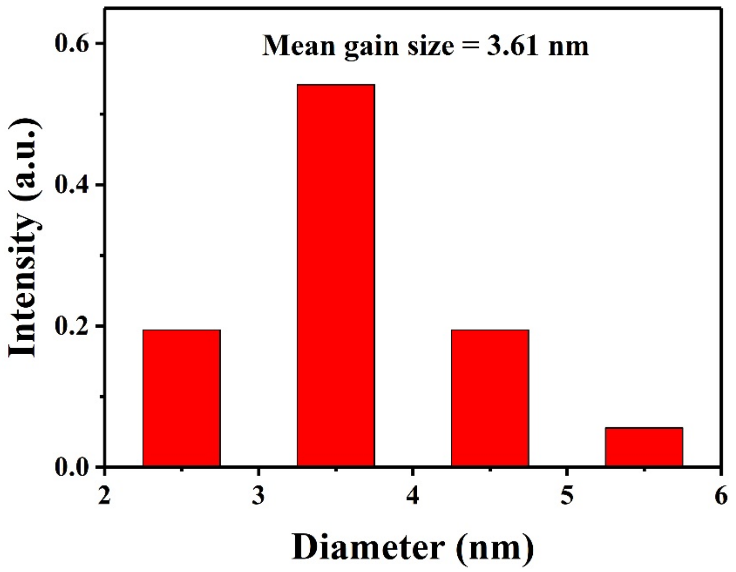

**Figure S11**. Distribution diagram of $Ag_{16}Pd_1/C$.

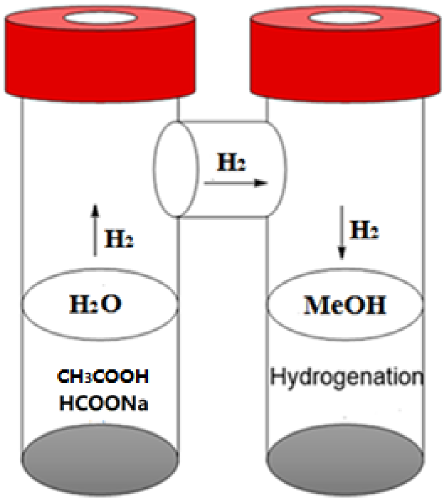

**Figure S12**. Dehydrogenation-hydrogenation tandem reactions. Hydrogenation of 1,1-diphenylethlene: 0.02 mmol of $Ag_{16}Pd_1/C$ and 4 mmol of $H_3PO_4$ was added into the left tube. Meanwhile, 10.6 mg (5 mmol % per 1,1-diphenylethlene) $Ag_{16}Pd_1/C$ catalyst was added to the right tube. Air was removed *in vacuo*, and 1.5 mL methanol included 17.6 uL (0.1 mmol) 1,1-diphenylethlene was injected into the right tube. Then, 4 mmol of HCOONa dissolved in 5 mL water was injected into the left tube. After 5 min, reaction was conducted at 30 °C for 12 h. The combined organic phases were washed with brine (2 × 5mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to flash column chromatography with hexanes/EtOAc (10:1) as eluent yielding 1,1-diphenylethane as a light-yellow liquid.

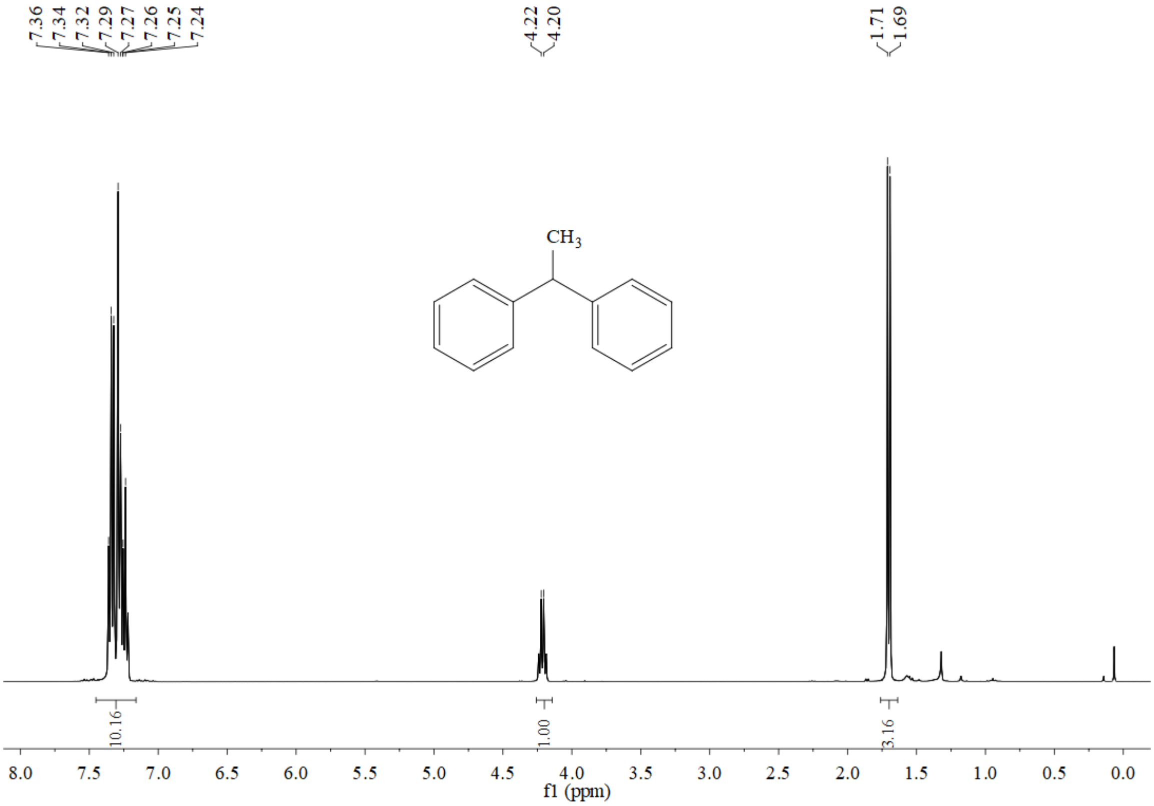

**Figure S13**. $^1$H NMR of 1,1-diphenylethane. $^1$H NMR (600 MHz, $CDCl_3$) δ7.08-7.22 (m, 10H), 4.06-4.08 (q, 1H), 1.55-1.57 (d, 3H).