

## Supporting Information

Coupling Photocatalytic Overall Water Splitting with Hydrogenation of Organic Molecules: a Strategy for Using Water as a Hydrogen Source and an Electron Donor to Enable the Hydrogenation

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## 1 General

### 1.1 Reaction chemicals

The quality and suppliers of the reagents are listed in Table S1. All the chemicals were obtained from commercial vendors and used without further purification.

**Table S1** Quality and suppliers of chemicals

Entry	Compound	Purity	Supplier
1	K <sub>2</sub> PdCl <sub>6</sub>	98%	Bide Pharmatech Ltd
2	Melamine	99.9%	Bide Pharmatech Ltd.
3	1,3,5-triazinane-2,4,6-trione	98%	Bide Pharmatech Ltd.
4	FeCl <sub>3</sub>	99%	Aladdin Chemistry Co., Ltd.
5	1,4-dioxane	99.5%	J&K Scientific Ltd.
6	H <sub>2</sub> <sup>18</sup> O	95%	Aladdin Chemistry Co., Ltd.
7	D <sub>2</sub> O (96% D)	96%	Aladdin Chemistry Co., Ltd.
8	2,6-Ditbutyl-4-methylphenol	99%	J&K Scientific Ltd
9	2,2,6,6-Tetramethyl-1-piperidinyloxy	98%	J&K Scientific Ltd
10	3,4-Dimethoxybromobenzene	98%	Bide Pharmatech Ltd
11	4-Bromocatatechol	98%	Bide Pharmatech Ltd
12	4-Bromothioanisole	99%	Bide Pharmatech Ltd
13	2-Bromothioanisole	99%	Bide Pharmatech Ltd
14	4-Bromophthalonitrile	98%	Bide Pharmatech Ltd.
15	3-Bromophthalonitrile	95%	Bide Pharmatech Ltd.
16	4-Bromoacetophenone	98%	J&K Scientific Ltd.
17	4-Bromo-2,6-dichlorobenzaldehyde	98%	Bide Pharmatech Ltd.
18	2-Bromobenzofuran	95%	Bide Pharmatech Ltd.
19	5-Bromothiophene-2-carboxylic acid	98%	Bide Pharmatech Ltd.
20	3,7-Dibromodibenzothiophene	95%	Bide Pharmatech Ltd
21	5-Bromophthalide	98%	Bide Pharmatech Ltd
22	2-Bromo-9-fluorenone	97%	Bide Pharmatech Ltd.
23	3,4,5-Dimethoxybromobenzene	98%	Bide Pharmatech Ltd.
24	4-Benzyloxybromobenzen	98%	Bide Pharmatech Ltd.
25	4'4-Oxybis(bromobenzene)	95%	Bide Pharmatech Ltd
26	4-Bromobiphenyl	99.9%	Bide Pharmatech Ltd
27	4-Hydroxy-4'-bromobiphenyl	97%	Bide Pharmatech Ltd
28	2-Bromobiphenyl	99.7%	Bide Pharmatech Ltd
29	1-Bromonaphthalene	98%	Bide Pharmatech Ltd
30	2-Bromonaphthalene	98%	Bide Pharmatech Ltd
31	2-Bromo-6-methoxynaphthalene	99.9%	Bide Pharmatech Ltd
32	2,7-Dibromonaphthalene	98%	Bide Pharmatech Ltd
33	2-Bromofluorene	95%	J&K Scientific Ltd.
34	9-Bromophenanthrene	98.7%	Bide Pharmatech Ltd
35	1-Bromopyrene	99.9%	Bide Pharmatech Ltd
36	2-Bromotriphenylene	95%	Bide Pharmatech Ltd

## 1.2 Instrumentents

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker 500 MHz instrument with chemical shifts reported in ppm relative to the internal standard tetramethylsilane. GC-MS spectra was recorded on an Agilent 6890/5973N gas chromatography-mass spectrometry instrument. Gas chromatography analyses were performed on a Varian CP-3800 instrument with a FID detector and a CP-WAX 57CB FS capillary chromatographic column (25 m  $\times$  0.32 mm). The morphology of Pd/g- $\text{C}_3\text{N}_4$  was investigated by a FEI talos F200S transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) analysis was performed on a ESCALAB 250Xi. The UV-Vis absorption spectra were obtained on a JASCO model V-670 spectrometer equipped with an integrating sphere. Cyclic voltammetry curves were conducted on CHI760E Electrochemical Workstation (Shanghai Chen Hua Electrochemical Instrument) by using a three-electrode (a glassy-carbon or ITO working electrode, a saturated calomel reference electrode and a Ag/AgCl wire counter electrode) electrochemical cell.

## 2. Experimental procedure for preparation of catalysts

**2.1 Procedure for preparation of g- $\text{C}_3\text{N}_4$ :** polymeric carbon nitride (g- $\text{C}_3\text{N}_4$ ) was prepared based on previous procedures in literatures<sup>[1,2]</sup>. After 774.42 mg of cyanuric acid and 756.72 mg of melamine were added to a flask equipped with 45 mL of water, the system was shaken for 24 h to give a milky suspension. Subsequently, the obtained suspension was centrifuged, and then dried at 60  $^\circ\text{C}$  under vacuum. Then the obtained powder was annealed in a crucible at 550  $^\circ\text{C}$  for 4 h under Ar atmosphere, and then cooled to room temperature to provide yellow g- $\text{C}_3\text{N}_4$  powder.

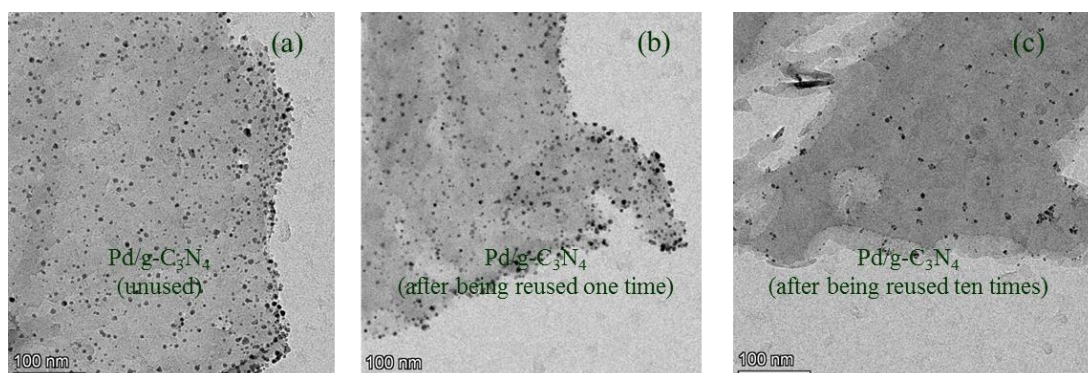
**2.2 Procedure for preparation of Pd/g- $\text{C}_3\text{N}_4$  (x wt% Pd):** Pd/g- $\text{C}_3\text{N}_4$  was prepared based on previous procedures in literatures.<sup>[1,2]</sup> After 150 mg g- $\text{C}_3\text{N}_4$  was added to a 250 mL flask equipped with 150 mL ethanol, the system was sonicated for 3 h to make g- $\text{C}_3\text{N}_4$  to be dispersed in ethanol. Then y mL ( $y = 7.0, 4.2, 1.5, 0.7, 0.3$  and  $0.15$ , respectively for 4.5 wt%, 2.8 wt%, 1.0 wt%, 0.5 wt%, 0.2 wt% and 0.1 wt% Pd-loaded on g- $\text{C}_3\text{N}_4$ ) solution of  $\text{K}_2\text{PdCl}_6$  in ethanol (0.01 mol/L) was added and the mixture was stirred for 10 min. Subsequently, 10 mL of water was added and the

mixture was refluxed at 90 °C for 1 h. Finally, the reaction mixture was cooled to room temperature. The precipitation was collected, washed with ethanol, dried at 60 °C under reduced pressure to give Pd/g-C<sub>3</sub>N<sub>4</sub> (4.5 wt%, 2.8 wt%, 1.0 wt%, 0.5 wt%, 0.2 wt% or 0.1 wt% Pd). The Pd loading amount was determined by the inductively coupled plasma–mass spectrometry.

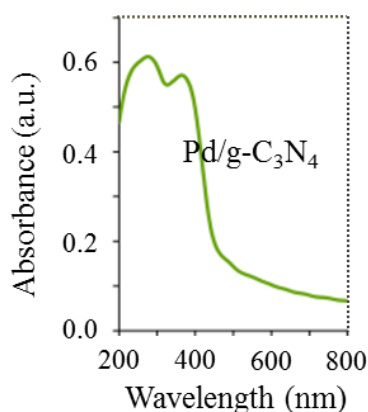
**2.3 Procedure for preparation of Fe/g-C<sub>3</sub>N<sub>4</sub> (9.9 wt% Fe), Pt/g-C<sub>3</sub>N<sub>4</sub> (2.8 wt% Pt), Ni/g-C<sub>3</sub>N<sub>4</sub> (2.6 wt% Ni) and Cu/g-C<sub>3</sub>N<sub>4</sub> (2.7 wt% Cu):** M/g-C<sub>3</sub>N<sub>4</sub> was prepared based on previous procedures in literatures.<sup>[1,2]</sup> After 150 mg g-C<sub>3</sub>N<sub>4</sub> was added to a 250 mL flask equipped with 150 mL ethanol, the system was sonicated for 3 h to make g-C<sub>3</sub>N<sub>4</sub> to be dispersed in ethanol. Then x mL solution of metal salt (54 mL solution of FeCl<sub>3</sub>, 2.3 mL solution of PtCl<sub>4</sub>, 7.6 mL solution of NiCl<sub>2</sub> 6H<sub>2</sub>O and 7.0 mL solution of Cu(OAc)<sub>2</sub> H<sub>2</sub>O, respectively for Fe/g-C<sub>3</sub>N<sub>4</sub>, Pt/g-C<sub>3</sub>N<sub>4</sub>, Ni/g-C<sub>3</sub>N<sub>4</sub> and Cu/g-C<sub>3</sub>N<sub>4</sub>) in ethanol (0.01mol/L) was added and the mixture was stirred for 10 min. Subsequently, 10 mL of water was added and the mixture was refluxed at 90 °C for 1 h. Finally, the reaction mixture was cooled to room temperature. The precipitation was collected, washed with ethanol, dried at 60 °C under reduced pressure to give Fe/g-C<sub>3</sub>N<sub>4</sub> (9.9 wt% Fe), Pt/g-C<sub>3</sub>N<sub>4</sub> (2.8 wt% Pt), Ni/g-C<sub>3</sub>N<sub>4</sub> (2.6 wt% Ni) and Cu/g-C<sub>3</sub>N<sub>4</sub> (2.7 wt% Cu), respectively. The transition metal loading amount was determined by the inductively coupled plasma-mass spectrometry.

**2.4 Procedure for preparation of FePd/g-C<sub>3</sub>N<sub>4</sub> (0.9 wt% Pd, 6.9 wt% Fe):** FePd/g-C<sub>3</sub>N<sub>4</sub> was prepared based on previous procedures in literatures.<sup>[1,2]</sup> After 150 mg g-C<sub>3</sub>N<sub>4</sub> was added to a 250 mL flask equipped with 150 mL ethanol, the system was sonicated for 3 h to make g-C<sub>3</sub>N<sub>4</sub> to be dispersed in ethanol. Then 7.0 mL solution of K<sub>2</sub>PdCl<sub>6</sub> and 54 mL solution of FeCl<sub>3</sub> 6H<sub>2</sub>O in ethanol (0.01mol/L) was successively added, and the mixture was stirred for 10 min. Subsequently, 10 mL of water was added and the mixture was refluxed at 90 °C for 1 h. Finally, the reaction mixture was cooled to room temperature. The precipitation was collected, washed with ethanol, dried at 60 °C under reduced pressure to give FePd/g-C<sub>3</sub>N<sub>4</sub> (0.9 wt% Pd, 6.9 wt% Fe). The transition metal loading amount was determined by the inductively coupled plasma–mass spectrometry.

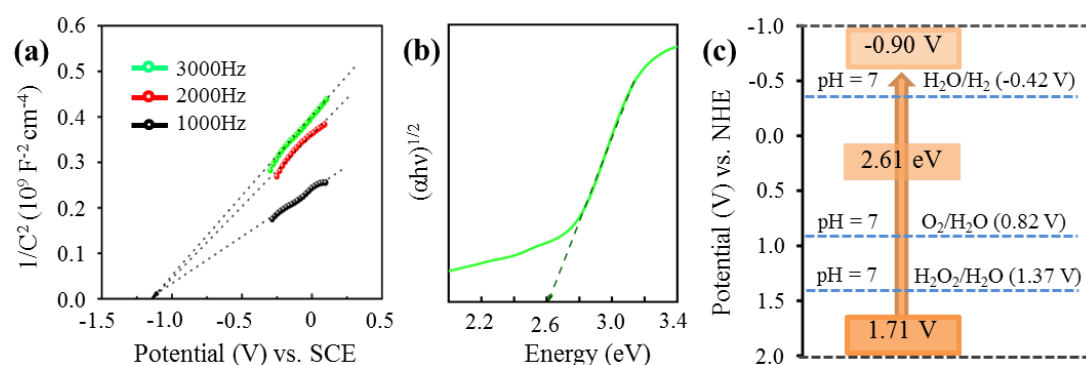
### 3. Characterization of Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd)



**Figure S1.** TEM images of (a) the unused Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt%), (b) Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt%) after being reused one time and (c) Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt%) after being reused ten times.



**Figure S2.** UV-visible diffuse reflection spectra of 1.0 wt% Pd/g-C<sub>3</sub>N<sub>4</sub>.

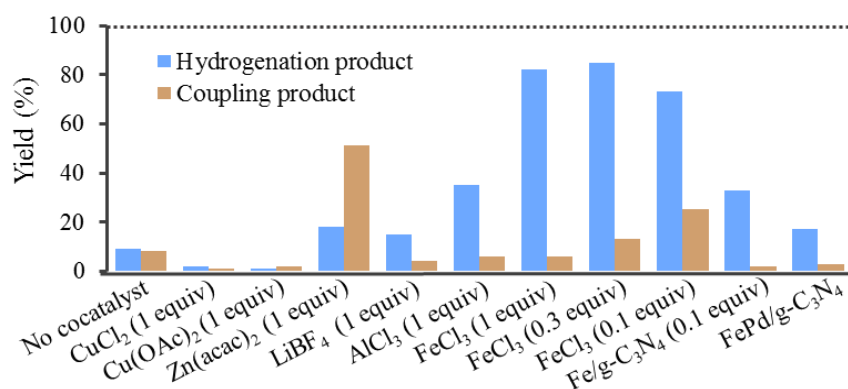


**Figure S3.** (a) Electrochemical Mott-Schottky plots of Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) in 0.5 mol/L aqueous solution of Na<sub>2</sub>SO<sub>4</sub>. (b) Tauc plots of Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd). (c) Energy-band positions. Note: Standard electrode potentials ( $E^{\theta}$ ) of H<sub>2</sub>O/H<sub>2</sub>, O<sub>2</sub>/H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O are 0.00, 1.23 and 1.78 V vs. NHE, respectively (see Ref. 3). Thus their redox potentials at pH = 7 are calculated to be -0.42, 0.82 V and 1.37 V vs. NHE, respectively, based on Nernst equation.

### 4. Experimental procedures and results related to the hydrogenation under different conditions

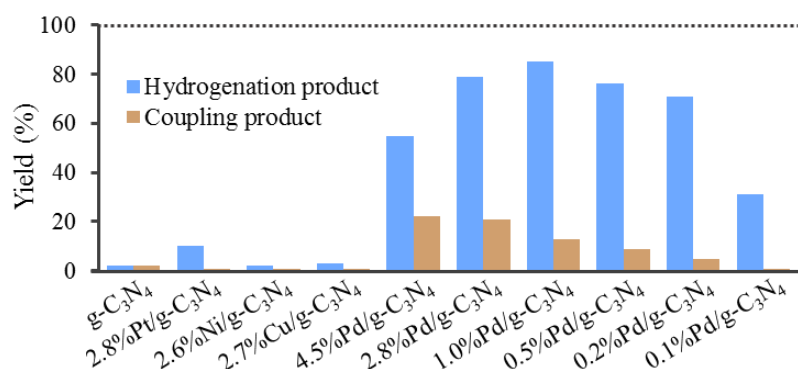
#### 4.1 Hydrogenation using various cocatalysts

0.5 mmol 3,4-dimethoxybromobenzene, 15.00 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and cocatalyst (for the cocatalyst loading, see Figure S4) were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O, 3 mL 1,4-dioxane and a magnetic stirrer. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 20 h with magnetic stirring under the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>) and argon atmosphere. Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the product with 1,2,3,4-tetramethylbenzene as an internal standard.



**Figure S4.** Pd/g-C<sub>3</sub>N<sub>4</sub>-catalyzed hydrogenation of 3,4-dimethoxybromobenzene in the presence of various cocatalysts. under the conditions: 0.5 mmol 3,4-dimethoxybromobenzene, 15 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd), cocatalyst, 5 mL H<sub>2</sub>O, 3 mL 1,4-dioxane, Ar atmosphere, light (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Note: the loading of Fe in Fe/g-C<sub>3</sub>N<sub>4</sub> is 9.9 wt% (15 mg Fe/g-C<sub>3</sub>N<sub>4</sub> was used). No Pd/g-C<sub>3</sub>N<sub>4</sub> was added in the case of FePd/g-C<sub>3</sub>N<sub>4</sub> (15 mg, 0.9 wt% Pd, 6.9 wt% Fe). CuCl<sub>2</sub>, Cu(OAc)<sub>2</sub> and Zn(acac)<sub>2</sub> represent CuCl<sub>2</sub> · 2H<sub>2</sub>O, Cu(OAc)<sub>2</sub> · H<sub>2</sub>O and Zn(acac)<sub>2</sub> · H<sub>2</sub>O, respectively.

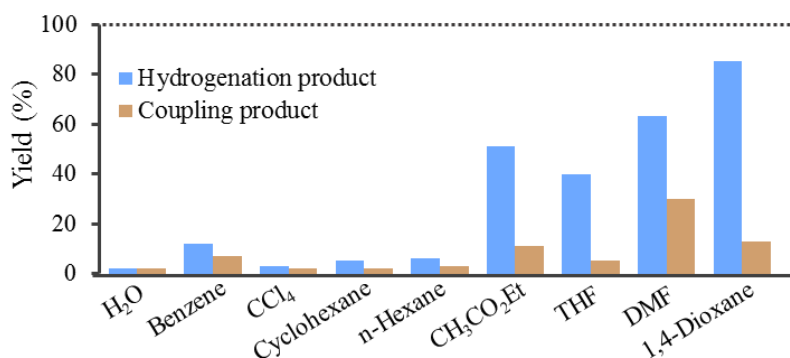
#### 4.2 Hydrogenation using various catalysts



**Figure S5.** Hydrogenation of 3,4-dimethoxybromobenzene with various catalysts under the conditions: 0.5 mmol 3,4-dimethoxybromobenzene, 15 mg M/g-C<sub>3</sub>N<sub>4</sub>, 0.15 mmol FeCl<sub>3</sub>, 5 mL H<sub>2</sub>O, 3 mL 1,4-dioxane, Ar atmosphere, light (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Note: x%Pd/g-C<sub>3</sub>N<sub>4</sub> means that the amounts of Pd on g-C<sub>3</sub>N<sub>4</sub> is x wt%.

0.5 mmol 3,4-dimethoxybromobenzene, 15.00 mg M/g-C<sub>3</sub>N<sub>4</sub> (or g-C<sub>3</sub>N<sub>4</sub>) and 0.3 equiv FeCl<sub>3</sub> were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O and 3 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 20 h with magnetic stirring under the light irradiation and argon atmosphere (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the product with 1,2,3,4-tetramethylbenzene as an internal standard.

### 4.3 Hydrogenation using various solvents



**Figure S6.** Hydrogenation of 3,4-dimethoxybromobenzene with various solvents under the conditions: 0.5 mmol 3,4-dimethoxybromobenzene, 15 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd), 0.15 mmol FeCl<sub>3</sub>, 5 mL H<sub>2</sub>O, 3 mL solvent, Ar atmosphere, light (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>).

0.5 mmol 3,4-dimethoxybromobenzene, 15.00 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 0.3 equiv FeCl<sub>3</sub> were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O and 3 mL solvent. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 20 h with magnetic stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the product with 1,2,3,4-tetramethylbenzene as an internal standard.

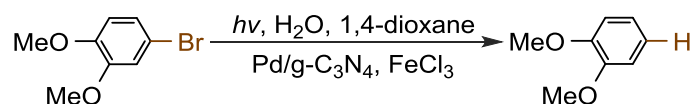
### 4.4 Hydrogenation under different wavelengths of light

0.5 mmol 3,4-dimethoxybromobenzene, 15.00 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 0.3 equiv FeCl<sub>3</sub> were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O and 3 mL solvent. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 20 h with magnetic stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm,



actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction time was reached, GC analysis of the mixture provided the conversion of the substrate and the GC yields of the product with 1,2,3,4-tetramethylbenzene as an internal standard.

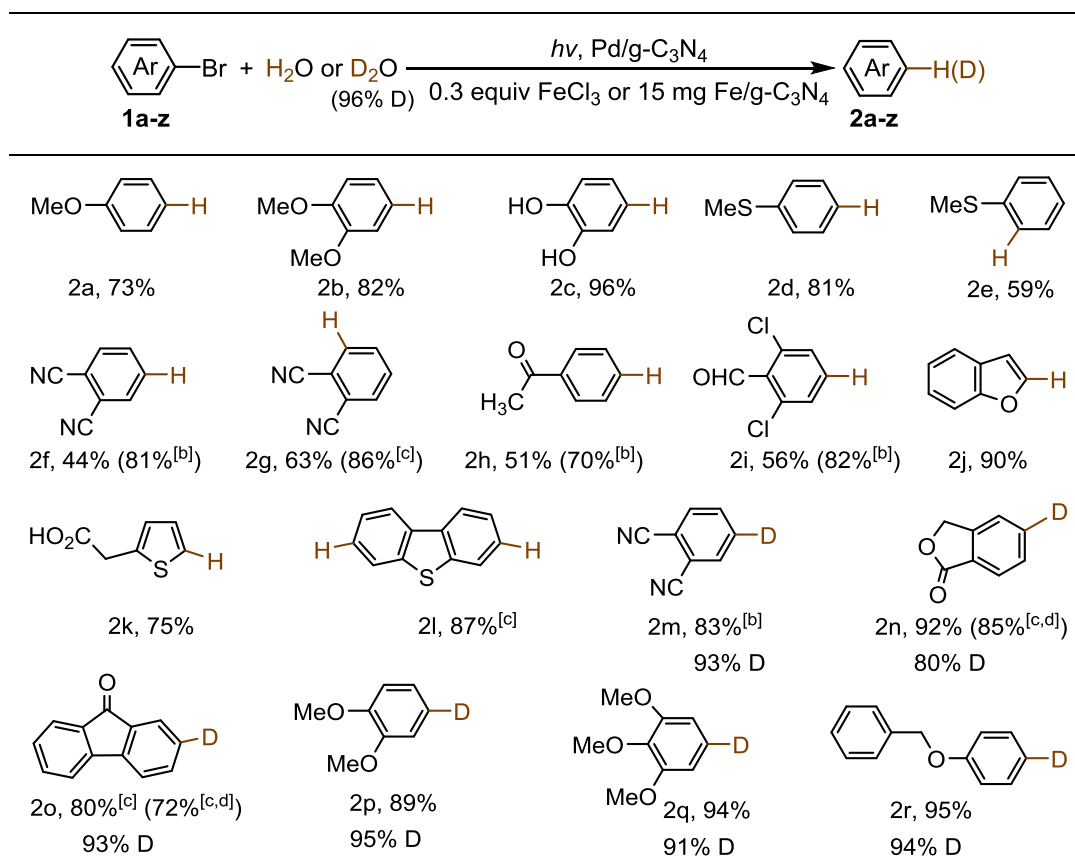
**Table S2** Effect of different wavelength on the reaction

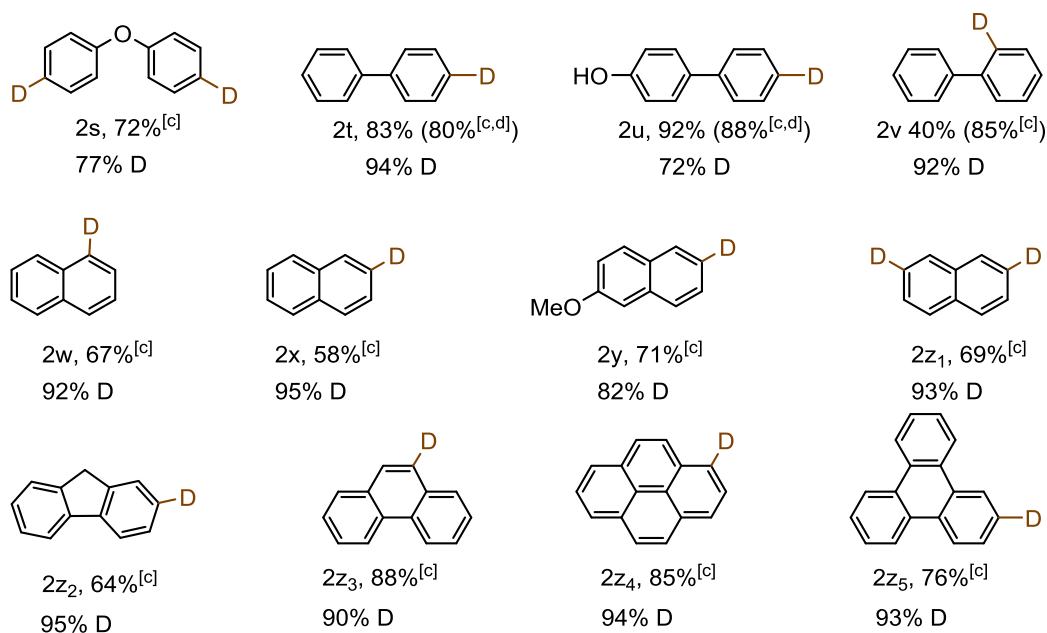


Wavelength/nm	Conversion/%	Yield of 3,4-dimethoxybenzene/%
254	> 99	88
320	> 99	80
365	> 99	85
500	trace	trace
560	trace	trace

#### 4.5 Hydrogenation of various aryl bromides

**Table S3** Photocatalytic hydrogenation/deuterization of aryl bromides<sup>[a]</sup>

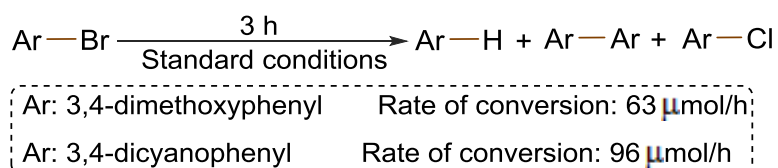




[a] Standard condition: 0.5 mmol aryl bromide, 15 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd), 0.15 mmol FeCl<sub>3</sub>, 5 mL H<sub>2</sub>O or D<sub>2</sub>O (96% D), 3 mL 1,4-dioxane, Ar atmosphere, 20 h, light (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). The yields of 2a-h were from GC analysis, while all the other yields were the isolated yields. [b] 2 mmol FeCl<sub>3</sub> was used. [c] 15 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (2.8 wt% Pd) was used. [d] FeCl<sub>3</sub> was replaced by 15 mg Fe/g-C<sub>3</sub>N<sub>4</sub> (the loading of Fe in Fe/g-C<sub>3</sub>N<sub>4</sub> is 9.9 wt%).

0.5 mmol aryl bromide, 15.00 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 0.3 equiv FeCl<sub>3</sub> were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O or D<sub>2</sub>O and 3 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 20 h with magnetic stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the product. Then the crude product from another parallel experiment was purified by silica gel chromatography to give the desired product.

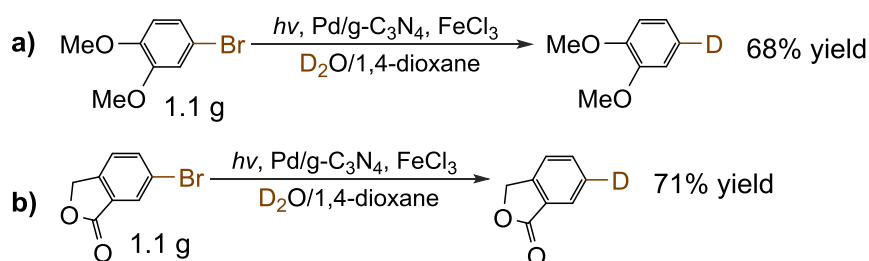
## 5. Procedure for investigation on average conversion rate of two aryl bromides



**Figure S7.** Average conversion rate of two aryl bromides.

0.5 mmol aryl bromide, 15.00 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 0.3 equiv FeCl<sub>3</sub> were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O and 3 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 3 h with magnetic stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction time was reached, GC analysis of the mixture provided the residual amount of the substrate with 1,2,3,4-tetramethylbenzene as an internal standard. The average rate of the substrate conversion was calculated based on the residual amount of the substrate and the reaction time.

## 6. Procedure for gram-scale deuterization of aryl bromides

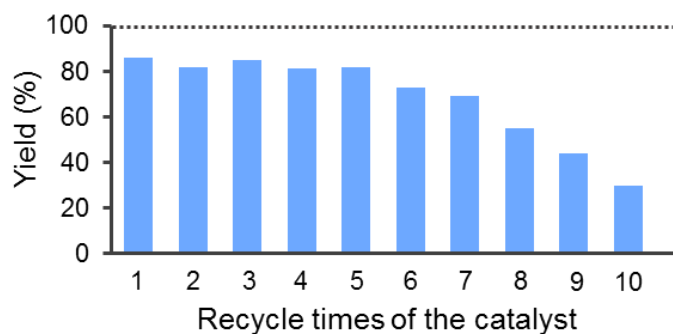


**Figure S8.** Gram-scale deuterization of aryl bromides.

**Procedure for Figure S8a:** 1.1 g 3,4,5-trimethoxybromobenzene, 135 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 0.3 equiv FeCl<sub>3</sub> were added to a 100 mL quartz glass tube equipped with 40 mL D<sub>2</sub>O and 25 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 60 h with stirring under the light irradiation (light source: LED, wavelength: 365 nm, incident light intensity: 0.35 W/cm<sup>2</sup>) and argon atmosphere. Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the product.

**Procedure for Figure S8b:** 1.1 g 5-bromophthalide (5.2 mmol), 156 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 0.3 equiv FeCl<sub>3</sub> were added to a 100 mL quartz glass tube equipped with 46 mL D<sub>2</sub>O and 30 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 60 h with stirring under the light irradiation (light source: LED, wavelength: 365 nm, incident light intensity: 0.35 W/cm<sup>2</sup>) and argon atmosphere. Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the product.

## 7. Procedure for catalytic recycling test of Pd/g-C<sub>3</sub>N<sub>4</sub> and Fe/g-C<sub>3</sub>N<sub>4</sub>



**Figure S9.** Catalytic recycling test of Pd/g-C<sub>3</sub>N<sub>4</sub> and Fe/g-C<sub>3</sub>N<sub>4</sub> in hydrogenation of 5-bromophthalide.

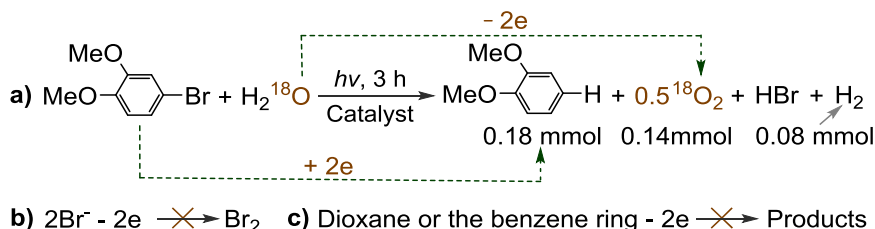
0.5 mmol 5-bromophthalide, 15.00 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 15 mg Fe/g-C<sub>3</sub>N<sub>4</sub> (9.9 wt%) were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O and 3 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 20 h with magnetic stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the product with 1,2,3,4-tetramethylbenzene as an internal standard. After reaction, the mixture was filtered to get solid catalyst. The obtained catalyst was washed with a small amount of water and anhydrous ethanol, dried at 55 °C in a vacuum oven, then used as the catalyst for next cycle.

As shown in Figure S9, the catalyst could be recycled for five times with a very slight change in the catalytic activity, but the yield of the targeted product dropped significantly after six cycling runs. According to our observation, the loss of the catalyst during recovering the catalyst is one of the main reasons for the decrease in the catalytic efficiency. Other possible reason is the leaching of Pd nanoparticle from the catalyst surface during the reaction (see N. Wang, L. X. Ma, J. Wang, Y. P. Zhang, R. B. Jiang, *ChemPlusChem* **2019**, *84*, 1164–1168; B. W. Crabbe, O. P. Kuehm, J. C. Bennett, G. L. Hallett-Tapley, *Catal. Sci. Technol.* **2018**, *8*, 4907–4915). For example, when the catalyst was reused for ten times, the Pd loading decreased from 2.8 to 1.2 wt% based on the inductively coupled plasma-mass spectrometry.

## 8. Procedure for investigation on who is the electron donor

0.5 mmol 3,4-dimethoxybromobenzene, 15.00 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 0.3 equiv FeCl<sub>3</sub> were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub><sup>18</sup>O and 3 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 3 h with magnetic

stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the hydrogenation product. H<sub>2</sub> and <sup>18</sup>O<sub>2</sub> was detected by another Gas chromatography. Formation of <sup>18</sup>O<sub>2</sub> was confirmed by GC-MS.



**Figure S10.** Investigation on who is the electron donor.

## 9. Comparison of our catalyst system against other catalyst systems

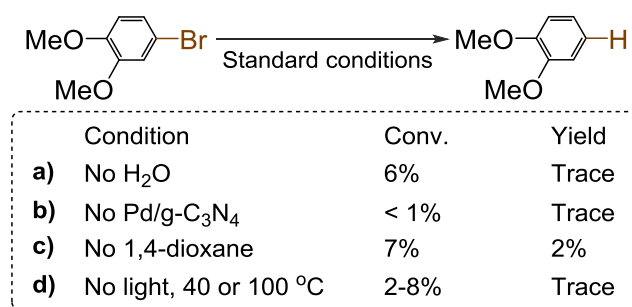
**Table S4** Comparison of photocatalytic performance for overall water splitting over the reported g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts.

Entry	Ref.	Rate (μM/h)	AQE (%)	Catalyst	Condition
1	This work	87.00	1.00	15 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 24 mg FeCl <sub>3</sub>	365nm, LED lamp Light intensity: 175 mW/cm <sup>2</sup> Irradiation area: 9.15 cm <sup>2</sup>
2	This work	0	0	24 mg FeCl <sub>3</sub>	365nm, LED lamp Light intensity: 175 mW/cm <sup>2</sup> Irradiation area: 9.15 cm <sup>2</sup>
3	This work	1.30	0.02	15 mg Pd/g-C <sub>3</sub> N <sub>4</sub>	365nm, LED lamp Light intensity: 175 mW/cm <sup>2</sup> Irradiation area: 9.15 cm <sup>2</sup>
4	Ref. 4a	10.81	11.80	100 mg Boron-doped N-deficient g-C <sub>3</sub> N <sub>4</sub>	420nm, 300W Xe lamp Light power: 14.50 mW
5	This work	4.40	4.80	100 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 160 mg FeCl <sub>3</sub>	
6	Ref. 4b	12.26	16.00	80 mg CDots-C <sub>3</sub> N <sub>4</sub>	420nm, 300W Xe lamp Light intensity: 2.84 mW/cm <sup>2</sup>
7	This work	2.73	3.57	80 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 128 mg FeCl <sub>3</sub>	Irradiation area: 4.27 cm <sup>2</sup>
8	Ref. 4c	3.16	4.94	25mg g-C <sub>3</sub> N <sub>4</sub> /rGO/PDIP	420nm, 300W Xe lamp Light intensity: 10.13 mW/cm <sup>2</sup>
9	This work	0.80	1.24	25 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 40 mg FeCl <sub>3</sub>	Irradiation area: 1 cm <sup>2</sup>
10	Ref. 4d	648.60	6.20	100mg WO <sub>3</sub> -H <sub>2</sub> O/g-C <sub>3</sub> N <sub>4</sub>	420nm, 300W Xe lamp Light intensity: 180 mW/cm <sup>2</sup>
11	This work	491.14	4.70	100 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 160 mg FeCl <sub>3</sub>	Irradiation area: 9.2 cm <sup>2</sup>

12	Ref. 4e	325.40	7.29	30mg NiFe-LDH/NrGO/ g-C <sub>3</sub> N <sub>4</sub>	420 nm, 125W Hg lamp Light intensity: 100 mW/cm <sup>2</sup> Irradiation area: 7.065 cm <sup>2</sup>
13	This work	66.69	1.48	30 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 48 mg FeCl <sub>3</sub>	
14	Ref. 4f	1.46	1.91	50 mg CoO/g-C <sub>3</sub> N <sub>4</sub>	420nm, 300W Xe lamp Light intensity: 2.84mW/cm <sup>2</sup> Irradiation area: 4.27cm <sup>2</sup>
15	This work	1.72	2.25	50 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 80 mg FeCl <sub>3</sub>	
16	Ref. 4g	13.78	1.45	100mg Pt/Na-CN	420nm, 300W Xe lamp Light intensity: 5.9 mW/cm <sup>2</sup> Irradiation area: 25.5 cm <sup>2</sup>
17	This work	45.62	4.81	100 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 160 mg FeCl <sub>3</sub>	
18	Ref. 4h	3.10	3.82	100mg MnO <sub>2</sub> /C <sub>3</sub> N <sub>4</sub>	420nm, 300W Xe lamp Light intensity: 2.84 mW/cm <sup>2</sup> Irradiation area: 4.52 cm <sup>2</sup>
19	This work	3.88	4.79	100 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 160 mg FeCl <sub>3</sub>	
20	Ref. 4i	2.74	1.32	50mg Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	420nm, 300W Xe lamp Light intensity: 10.97 mW/cm <sup>2</sup> Irradiation area: 3 cm <sup>2</sup>
21	This work	4.95	2.38	50 mg Pd/g-C <sub>3</sub> N <sub>4</sub> + 80 mg FeCl <sub>3</sub>	

Note: AQY represents the apparent quantum yield.

## 10. Procedure for investigation on necessity for using Pd/g-C<sub>3</sub>N<sub>4</sub>, water, 1,4-dioxane and light

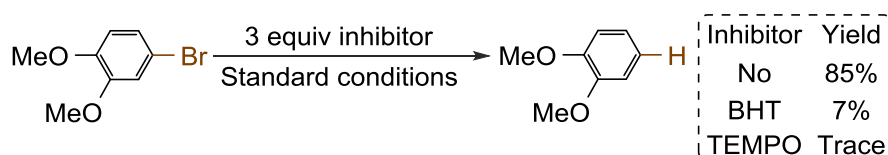


**Figure S11.** Several control experiments for hydrogenation of 3,4-dimethoxybromobenzene.

0.5 mmol 3,4-dimethoxybromobenzene, 15.00 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 0.3 equiv FeCl<sub>3</sub> were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O and 3 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 3 h with magnetic stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction

time was reached, GC analysis of the mixture provided the GC yields of the hydrogenation product. Note: (a) “No H<sub>2</sub>O”: H<sub>2</sub>O was not added. (b) “No Pd/g-C<sub>3</sub>N<sub>4</sub>\*”: Pd/g-C<sub>3</sub>N<sub>4</sub>\* was not added. (c) “No 1,4-dioxane”: 1,4-dioxane was not added. (d) “No light, 40 or 100 °C”: the reaction was performed under irradiation-free condition and the reaction temperature was 40 or 100 °C.

## 11. Procedure for investigation on effect of radical inhibitors on the reaction



**Figure S12.** Effect of radical inhibitors on the reaction.

0.5 mmol 3,4-dimethoxybromobenzene, 1.5 mmol radical inhibitor, 15.00 mg Pd/g-C<sub>3</sub>N<sub>4</sub> (1.0 wt% Pd) and 0.3 equiv FeCl<sub>3</sub> were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O and 3 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 3 h with magnetic stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the hydrogenation product.

## 12. Procedure for rotating disk-ring electrode (RRDE) experiments

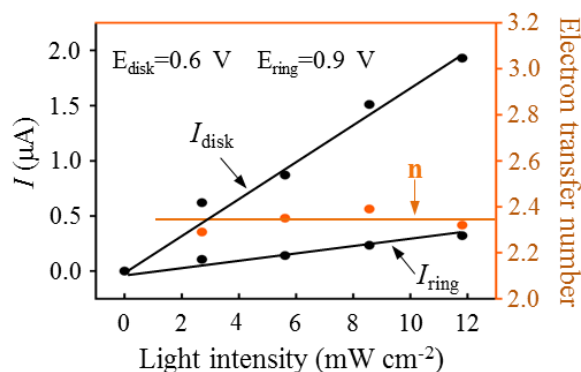
**Table S5** Results from RRDE experiments

Light intensity (mW cm <sup>-2</sup> )	I <sub>disk</sub> (μA)	I <sub>ring</sub> (μA)	n <sup>[a]</sup>
0	0	0	0
2.71	0.62	0.106	2.29
5.62	0.87	0.141	2.35
8.57	1.51	0.234	2.39
11.82	1.93	0.321	2.32

<sup>[a]</sup>The electron transfer numbers (n) were calculated from equation:  $n = 4I_{\text{disk}} / (I_{\text{disk}} + I_{\text{Ring}}/N)$  where N is the RRDE collection efficiency, measured to be 0.23.

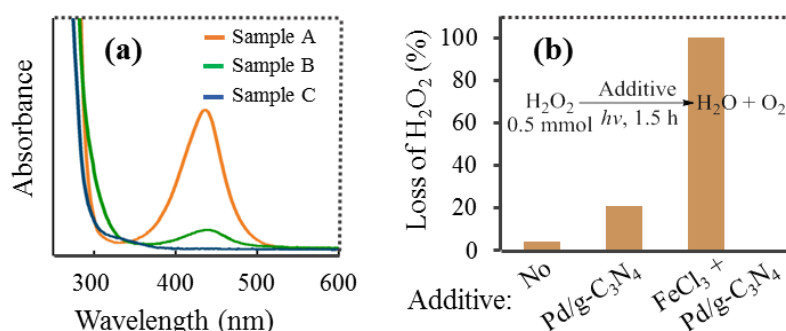
According to previous literature,<sup>[3]</sup> The electron transfer number was studied by rotating disk-ring electrodes (RRDE). The Pd/g-C<sub>3</sub>N<sub>4</sub> modified bare glassy carbon electrodes at a rotating speed of 1600 rpm in N<sub>2</sub>-saturated solution of FeCl<sub>3</sub> in water/1,4-dioxane (V/V = 5:3). The disk potential was set at 0.6 V (vs. SCE) under

different light intensity irradiation ( $\lambda = 365$  nm). The ring potential was set at 0.9 V (vs. SCE). The results from RRDE experiments are shown in Table S5 and Fig. S11.

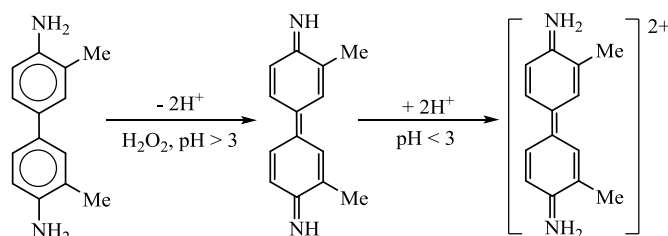


**Figure S13.** Results from rotating disk-ring electrode (RRDE) experiments

### 13. Experimental procedure for determination of H<sub>2</sub>O<sub>2</sub>



**Figure S14.** (a) UV-Vis spectroscopy related to the produced H<sub>2</sub>O<sub>2</sub> in hydrogenation of 3,4-dimethoxybromobenzene. **Sample A:** 0.4 mmol/L aqueous solution of H<sub>2</sub>O<sub>2</sub>; **Sample B:** the produced H<sub>2</sub>O<sub>2</sub> under standard conditions (no FeCl<sub>3</sub> and 3 h of reaction time) in Table S3; **Sample C:** the produced H<sub>2</sub>O<sub>2</sub> under standard conditions in Table S3 (3 h of reaction time). (b) The H<sub>2</sub>O<sub>2</sub> decomposition in the presence of additives. Reaction condition: 0.5 mmol H<sub>2</sub>O<sub>2</sub>, 2 mL H<sub>2</sub>O, 1.5 h, additive, light (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>).



**Figure S15.** Formation of protonated monomer with absorbance at 436-438 nm.<sup>[5]</sup>

**Experimental procedure for Figure 14a (measurement of H<sub>2</sub>O<sub>2</sub>):** According to previous literature,<sup>[5]</sup> 0.5 mL volume of 1% o-tolidine in 0.1 mol/L HCl and 2 mL volume of 0.8mg/mL suspension of Pt/g-C<sub>3</sub>N<sub>4</sub> in water were added into the sample. After being shaken for 5 min, this mixture turned blue due to the oxidation of



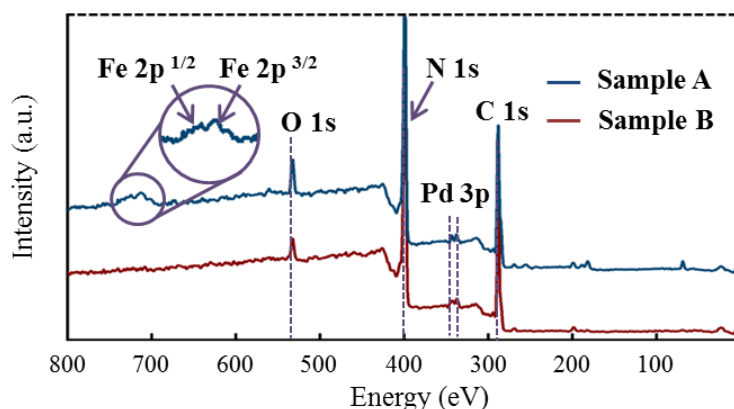
*o*-tolidine. Then this mixture was acidified with 1 mol/L HCl (2 mL), and was set for 10 h to give yellow dispersion (for the reaction formulation of the yellow species formation, see Figure S15 and Reference 5). The yellow dispersion was quickly filtered through a 0.22  $\mu\text{m}$  membrane filter and the absorption spectrum of the filtrate was immediately recorded with a UV-Vis spectrophotometer. **Note: Sample A:** 0.4 mmol/L aqueous solution of  $\text{H}_2\text{O}_2$ . **Sample B:** the produced  $\text{H}_2\text{O}_2$  in hydrogenation of 3,4-dimethoxybromobenzene under the following conditions: 0.5 mmol 3,4-dimethoxybromobenzene, 15 mg Pd/g- $\text{C}_3\text{N}_4$  (1.0 wt% Pd), 5 mL  $\text{H}_2\text{O}$ , 3 mL 1,4-dioxane, Ar atmosphere, 3 h, light (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175  $\text{W}/\text{cm}^2$ ). **Sample C:** the produced  $\text{H}_2\text{O}_2$  in hydrogenation of 3,4-dimethoxybromobenzene under the following conditions: 0.5 mmol 3,4-dimethoxybromobenzene, 15 mg Pd/g- $\text{C}_3\text{N}_4$  (1.0 wt% Pd), 0.15 mmol  $\text{FeCl}_3$ , 5 mL  $\text{H}_2\text{O}$ , 3 mL 1,4-dioxane, Ar atmosphere, 3 h, light (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175  $\text{W}/\text{cm}^2$ ).

**Experimental procedure for Figure 14b:** The additive (Pd/g- $\text{C}_3\text{N}_4$  or  $\text{FeCl}_3$  + Pd/g- $\text{C}_3\text{N}_4$  or no additive) were added to a 20 mL quartz glass tube equipped with 5 mL of  $\text{H}_2\text{O}$ , 3 mL 1,4-dioxane and 0.5 mmol of  $\text{H}_2\text{O}_2$ . Then the reaction tube was stirred magnetically to perform the  $\text{H}_2\text{O}_2$  decomposition for 1.5 h with stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175  $\text{W}/\text{cm}^2$ ). Once the reaction time was reached, UV-Vis spectroscopy analysis of the remaining  $\text{H}_2\text{O}_2$  was performed based on the procedure for Figure S14a. The concentration of the remaining  $\text{H}_2\text{O}_2$  in the reaction system was determined by the calibrated curve and fitting by the calibrated curve and fitting equation (the calibrated curve and fitting equation was made using  $\text{H}_2\text{O}_2$  with different concentration as external standard materials).

#### 14. XPS spectra of the recovered Pd/g- $\text{C}_3\text{N}_4$ after reaction

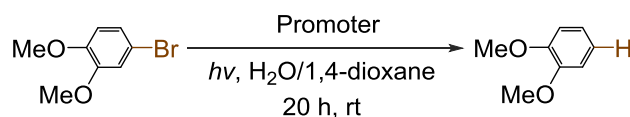
**Procedure for preparation of Sample A and B in Figure S16:** 0.5 mmol 3,4-dimethoxybromobenzene, 15.00 mg Pd/g- $\text{C}_3\text{N}_4$  (1.0 wt% Pd) and 0.15 mmol  $\text{FeCl}_3$  were added to a 10 mL quartz glass tube equipped with 5 mL  $\text{H}_2\text{O}$  and 3 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25  $^\circ\text{C}$ ) to perform the reaction for 20 h with magnetic stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175  $\text{W}/\text{cm}^2$ ). After reaction, the mixture was filtered to give the solid catalyst. The recovered Pd/g- $\text{C}_3\text{N}_4$  was washed with 0.5 mL water and 1 mL ethanol for one time to give Sample A. The recovered Pd/g- $\text{C}_3\text{N}_4$  was

washed with 1 mL water and 2 mL ethanol for five times to give Sample B.



**Figure S16.** XPS spectra of the recovered Pd/g-C<sub>3</sub>N<sub>4</sub> after reaction. Note: shoulder peaks in this figure were assigned based on reference 6 and 7. **Sample A:** the mixture after reaction was filtered to give the recovered catalyst, then the obtained Pd/g-C<sub>3</sub>N<sub>4</sub> was washed with 0.5 mL water and 1 mL ethanol for one time to give Sample A. **Sample B:** the mixture after reaction was filtered to give the recovered catalyst, then the obtained Pd/g-C<sub>3</sub>N<sub>4</sub> was washed with 1 mL water and 2 mL ethanol for five times to give Sample B.

### 15. Procedure for investigation on the role of Fe species



Promoter	Conversion	Yield
<b>a)</b> 0.008 equiv [Pd] (15 mg Pd/g-C <sub>3</sub> N <sub>4</sub> , Purity of Pd: 99.99% metals basis)	19	10
<b>b)</b> 0.008 equiv [Pd] (15 mg Pd/g-C <sub>3</sub> N <sub>4</sub> , Purity of Pd: 99.99% metals basis)	62 <sup>[a]</sup>	36 <sup>[a]</sup>
<b>c)</b> 0.3 equiv [Fe] (0.15 mmol FeCl <sub>3</sub> , Purity of Fe: 99.99% metals basis)	trace	trace
<b>d)</b> 1 equiv [Fe] (0.5 mmol FeCl <sub>3</sub> , Purity of Fe: 99.99% metals basis)	trace	trace
<b>e)</b> 0.3 equiv [Fe] (85 mg Fe/g-C <sub>3</sub> N <sub>4</sub> , Purity of Fe: 99.99% metals basis)	trace	trace
<b>f)</b> 1 equiv [Fe] (282 mg Fe/g-C <sub>3</sub> N <sub>4</sub> , Purity of Fe: 99.99% metals basis)	trace	trace

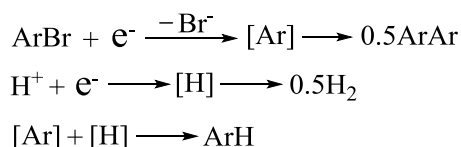
**Figure S17.** Control experiments for the hydrodehalogenation. Note: [Pd]: Pd species, [Fe]: Fe species, x equiv: molar ratio of the catalytic species to the substrate. Pd/g-C<sub>3</sub>N<sub>4</sub>: the loading of Pd on g-C<sub>3</sub>N<sub>4</sub> is 2.8 wt%. Fe/g-C<sub>3</sub>N<sub>4</sub>: the loading of Fe on g-C<sub>3</sub>N<sub>4</sub> is 9.9 wt%.

0.5 mmol 3,4-dimethoxybromobenzene and promoter (for the promoter, see Figure S17) were added to a 10 mL quartz glass tube equipped with 5 mL H<sub>2</sub>O and 3 mL 1,4-dioxane. Then the reaction tube was sealed and placed in a constant-temperature bath (25 °C) to perform the reaction for 3 h with magnetic stirring under argon atmosphere and the light irradiation (light source: 75 W LED, wavelength: 365 nm, actual incident light intensity: 0.175 W/cm<sup>2</sup>). Once the reaction time was reached, GC analysis of the mixture provided the GC yields of the hydrogenation product.



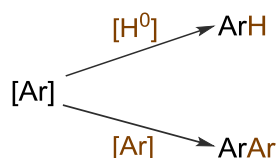
$$\begin{array}{l}
 \text{a) } \bar{V}_{[H]} = 2\bar{V}_{H_2} + \bar{V}_{ArH} \\
 \text{b) } \bar{V}_{[Ar]} = 2\bar{V}_{ArAr} + \bar{V}_{ArH} \\
 \text{c) } \frac{\bar{V}_{[H]}}{\bar{V}_{[Ar]}} = \frac{2\bar{V}_{H_2} + \bar{V}_{ArH}}{2\bar{V}_{ArAr} + \bar{V}_{ArH}}
 \end{array}$$

**Figure S19.** Equation that is used to calculate  $\bar{V}_{[H]}$  and  $\bar{V}_{[Ar]}$  ( $\bar{V}_{[H]}$ : the average rate of the [H] production in 5 h,  $\bar{V}_{[Ar]}$ : the average rate of the [Ar] production in 5 h,  $\bar{V}_{ArAr}$ : the average rate of the 4,4'-dimethoxybiphenyl production in 5 h,  $\bar{V}_{ArH}$ : the average rate of the anisole production in 5 h,  $\bar{V}_{H_2}$ : the average rate of the  $H_2$  production in 5 h).



**Figure S20.** The resulting products from reductive half reactions under our conditions

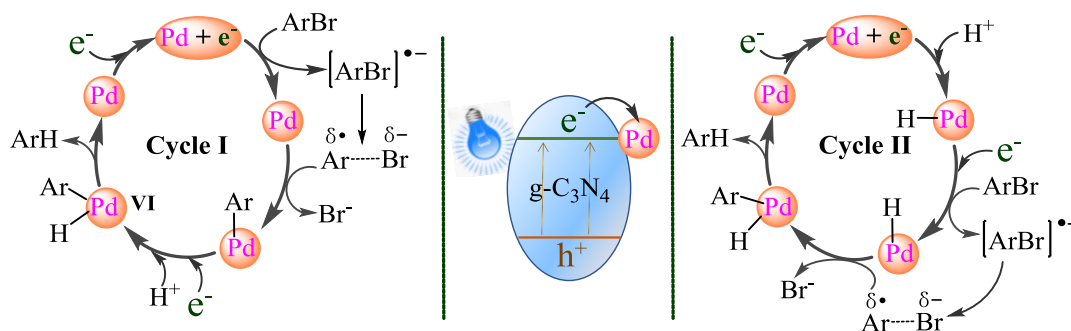
### 17. Reasons why Fe species can improve the hydrogenation selectivity.



**Figure S21.** Diagrammatic sketch regarding the competition between the hydrogenation and the coupling

As seen from Figure S18, an addition of Fe species into the reaction system can increase the ratio of the  $[H^0]$  production rate to the [Ar] production rate. As shown in Figure S21, [Ar] reacts with  $[H^0]$  to give the hydrogenation product, while [Ar] reacts with [Ar] to provide the coupling product. Thus it is obvious that an increase in the ratio of the  $[H^0]$  production rate to the [Ar] production rate would result in increasing the probability that [Ar] reacts with  $[H^0]$  to form the hydrogenation product, which would obviously suppress the coupling, and improve the hydrogenation selectivity.

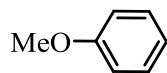
### 18. Detailed mechanism for the hydrogenation half-reaction proposed by us



**Figure S22.** Proposed mechanism for hydrogenation half-reactions of aryl bromide (Note: these mechanisms are proposed based on the experimental evidences in this paper and previous literatures<sup>[8,9]</sup>)

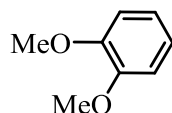
## 19. The spectroscopic and physical data of the isolated products

### Methoxybenzene<sup>[10]</sup>



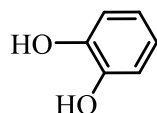
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.35–7.25 (m, 2H), 7.00–6.86 (m, 3H), 3.79 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 159.6, 129.5, 120.7, 113.9, 55.2.

### 1,2-Dimethoxybenzene<sup>[11]</sup>



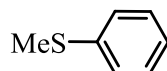
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 6.98–6.78 (m, 4H), 3.87 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 149.0, 120.9, 111.4, 55.8.

### 1,2-Dihydroxybenzene<sup>[12]</sup>



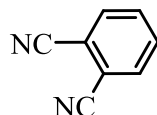
<sup>1</sup>H NMR (400 MHz, DMSO): δ (ppm) = 8.80 (s, 2H), 6.79–6.67 (m, 2H), 6.64–6.57 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO): δ (ppm) = 145.7, 119.8, 116.2.

### Methylthiobenzene<sup>[13]</sup>



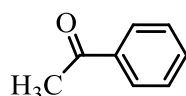
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.41–6.92 (m, 5H), 2.45 (d, *J* = 1.5 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 138.5, 128.9, 126.7, 125.1, 15.9.

### 1,2-Dicyanobenzene<sup>[14]</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.86 (dd, *J*<sub>1</sub> = 5.7, *J*<sub>2</sub> = 3.4 Hz, 2H), 7.80 (dd, *J*<sub>1</sub> = 5.9, *J*<sub>2</sub> = 3.3 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 133.6, 133.3, 115.9, 115.4.

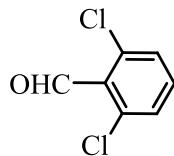
### Acetophenone<sup>[10]</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.99–7.90 (m, 2H), 7.56 (tt, *J*<sub>1</sub> = 7.6 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.60 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ

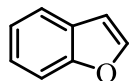
(ppm) = 198.2, 137.1, 133.1, 128.5, 26.6.

### 2,6-Dichlorobenzaldehyde<sup>[15]</sup>



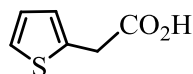
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 10.49 (s, 1H), 7.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 188.8, 136.9, 133.6, 130.4, 129.8.

### Benzofuran<sup>[16]</sup>



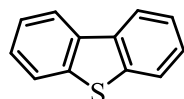
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.59 (dd, *J*<sub>1</sub> = 7.7, *J*<sub>2</sub> = 1.3 Hz, 2H), 7.50 (dd, *J*<sub>1</sub> = 8.1, *J*<sub>2</sub> = 0.6 Hz, 1H), 7.25 (dt, *J*<sub>1</sub> = 22.5, *J*<sub>2</sub> = 7.0 Hz, 2H), 6.75 (dd, *J*<sub>1</sub> = 2.1, *J*<sub>2</sub> = 0.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 155.0, 144.9, 127.5, 124.3, 122.8, 121.2, 111.5, 106.6.

### 2-Thiopheneacetic acid<sup>[17]</sup>



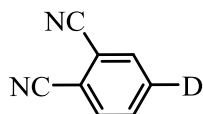
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 9.91 (s, 1H), 7.37–7.10 (m, 1H), 7.03–6.81 (m, 2H), 3.87 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 176.9, 134.1, 127.3, 127.0, 125.4, 35.1.

### Dibenzothiophene<sup>[18]</sup>



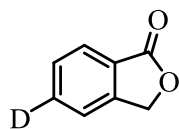
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.18–8.10 (m, 2H), 7.88–7.80 (m, 2H), 7.49–7.40 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 139.5, 135.6, 126.7, 124.4, 122.8, 121.6.

### 1,2-Dicyanobenzene-4-*d*<sup>[14]</sup>



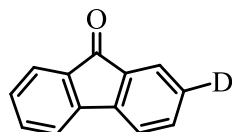
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.84 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 6.7 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 133.6, 133.1, 116.1, 115.3.

**Phthalide-5-*d*** <sup>[19]</sup>



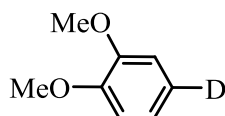
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.93 (d, *J* = 7.7 Hz, 1H), 7.57–7.49 (m, 2H), 5.34 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 171.2, 146.6, 134.1, 129.0, 125.8, 122.1, 69.7.

**Fluoren-9-one-2-*d*** <sup>[20]</sup>



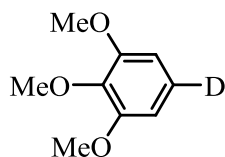
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.65 (d, *J* = 4.0 Hz, 2H), 7.55–7.44 (m, 4H), 7.28 (t, *J* = 7.4 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 194.0, 144.5, 134.7, 134.2, 129.1, 124.3, 120.3.

**1,2-Dimethoxybenzene-4-*d*** <sup>[11]</sup>



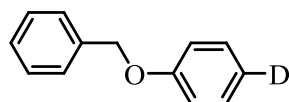
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 6.90 (s, 3H), 3.89 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 149.0, 120.7, 111.3, 55.8.

**1,2,3-Trimethoxybenzene-5-*d*** <sup>[21]</sup>



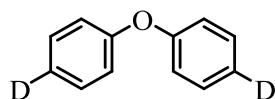
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 6.50 (s, 2H), 3.77 (d, *J* = 1.8 Hz, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 152.5, 137.1, 122.2, 104.1, 59.8, 55.0.

**1-(Benzyloxy)benzene-4-*d*** <sup>[22]</sup>



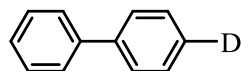
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.43–7.16 (m, 7H), 6.99–6.97 (m, 2H), 5.06 (d, *J* = 3.2 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 158.8, 137.1, 129.4, 128.6, 128.0, 127.52, 121.0, 114.9, 69.9.

**1,1'-oxybis(benzene)-4,4'-d<sub>2</sub>** <sup>[23]</sup>



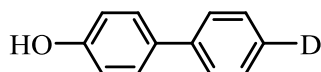
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.33 (d, *J* = 8.2 Hz, 4H), 7.01 (d, *J* = 8.5 Hz, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 157.27, 129.63, 123.22, 118.90.

**Biphenyl-4-d** <sup>[22]</sup>



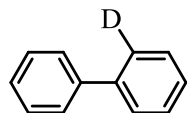
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.60 (d, *J* = 7.3 Hz, 4H), 7.44 (d, *J* = 7.4 Hz, 4H), 7.35 (t, *J* = 7.3 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 141.3, 128.8, 128.7, 127.3, 127.2, 127.0.

**4-Biphenylol -4'-d** <sup>[24]</sup>



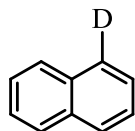
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.54 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.45–7.36 (m, 2H), 6.90 (d, *J* = 7.3 Hz, 2H), 4.96 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 155.1, 140.8, 134.1, 128.7, 128.4, 126.8, 115.7.

**1,1'-Biphenyl-2-d** <sup>[22]</sup>



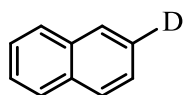
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.61–7.58 (m, 3H), 7.44 (t, *J* = 7.3 Hz, 4H), 7.34 (t, *J* = 7.3 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 141.3, 141.24, 141.19, 128.8, 128.7, 127.3, 127.2.

**Naphthalene-1-d** <sup>[22]</sup>

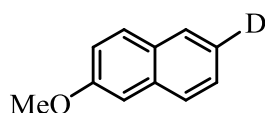


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.86–7.82 (m, 3H), 7.50–7.45 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 133.5, 128.0, 127.8, 125.9, 125.8.

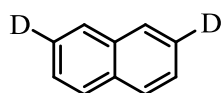


**Naphthalene-2-*d*** <sup>[22]</sup>

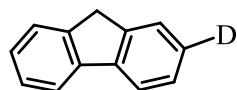
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.83 (dt, *J*<sub>1</sub> = 6.3, *J*<sub>2</sub> = 3.2 Hz, 4H), 7.47 (dd, *J*<sub>1</sub> = 6.3, *J*<sub>2</sub> = 3.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 133.5, 127.9, 127.8, 125.9, 125.77, 125.75.

**2-Methoxynaphthalene-6-*d*** <sup>[22]</sup>

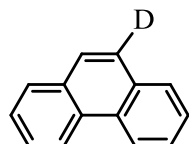
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.77–7.71 (m, 3H), 7.46–7.40 (m, 1H), 7.18–7.11 (m, 2H), 3.91 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 157.6, 134.6, 129.4, 129.0, 127.6, 126.8, 126.3, 123.4 (t, *J* = 24.2 Hz), 118.8, 105.8, 55.3.

**Naphthalene-2,7-*d*** <sup>[22]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.82 (s, 4H), 7.51–7.40 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 133.5, 128.0, 127.9, 125.9, 125.8.

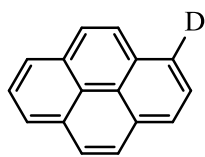
**Fluorene-2-*d*** <sup>[25]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.78 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 4.2 Hz, 2H), 7.37 (t, *J* = 6.0 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 3.89 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 143.2, 141.7, 126.7, 125.0, 119.9, 37.0.

**Phenanthrene-9-*d*** <sup>[26]</sup>

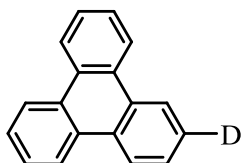
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.70 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.74 (s, 1H), 7.69–7.64 (m, 2H), 7.63–7.57 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ (ppm) = 132.1, 132.0, 130.3, 128.6, 128.6, 127.0, 126.8, 126.8, 126.6, 126.6, 122.7.

### Pyrene-1-*d* [27]



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.16 (d,  $J$  = 7.7 Hz, 3H), 8.05 (s, 4H), 8.01–7.95 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 131.2, 127.4, 125.9, 125.0, 124.7.

### Triphenylene-2-*d* [28]



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.84–8.47 (m, 6H), 7.75–7.50 (m, 5H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 129.8, 127.2, 127.1, 123.3, 123.2.

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## 21. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR for the products

