

## Electronic Supporting Information

### **Parts per million level, green, and magnetically-recoverable triazole ligand-stabilized Au and Pd nanoparticle catalysts**

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## General information

All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. Yields refer to chromatographically purified products, unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC) carried out on Merck KGaA TLC silica gel 60 F<sub>254</sub> (aluminium sheets) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. Tsingdao Hailang silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography.

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. NMR spectra were recorded on either a Brüker Advance 400 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz). Brüker Advance 600 (<sup>1</sup>H: 600 MHz, <sup>13</sup>C: 150 MHz). Mass spectrometric data were obtained using Bruker Apex IV RTMS. UV-vis. absorption spectra were measured with a UV-1800, SHIMADZU spectrometer, STEM images were obtained by a FEI, TECNAI G2 STEM spectrometer.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

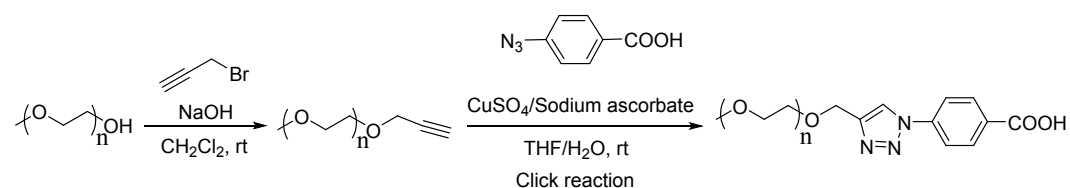
## Experimental

### 1 Synthesis of the Fe<sub>3</sub>O<sub>4</sub> NP1

Sodium oleate (4.57 g, 15.0 mmol), FeCl<sub>3</sub>·6H<sub>2</sub>O (1.35 g, 5.0 mmol), deioned water (7.5 ml), hexane (17.5 mL) and ethanol (10.0 mL) were added to a three-necked flask, equipped with a stir bar. The solution was heated up to 70°C for 4 h under nitrogen atmosphere and stirring. After the reaction was deemed complete and cooled to r.t., the red organic phases were washed three times with deioned water. The combined organic phase was dried at r.t. Then the solvent was removed *in vacuo*. The obtained black oils are iron-oleate.

Fe<sub>3</sub>O<sub>4</sub> NP 1 was prepared according to Sun Shouheng's method<sup>1</sup>. 2.0 mmol of iron-oleate was dissolved in a mixture of oleylamine (6.0 mL) and oleic acid (2.0 mL) at 120°C for 1 h. Then the dark solution was heated up to 200°C for 2 h. During the heating, nitrogen gas was gently blown through the reaction system to remove the trace hydrate vapor. After that, the solution was further heated up to 300°C and kept at this temperature for 2 h. The Fe<sub>3</sub>O<sub>4</sub> NPs 1 were precipitated by adding ethanol into the solution and washed several times with CH<sub>2</sub>Cl<sub>2</sub> and ethanol. The as-prepared Fe<sub>3</sub>O<sub>4</sub> NPs 1 were dispersed in CH<sub>2</sub>Cl<sub>2</sub>.

### 2 Synthesis of the heterobifunctional triazole ligand 2



**Scheme S1.** Synthetic route of ligand 2

In a typical procedure, polyethylene oxide (PEO, 3.50 g, 10.0 mmol) was dissolved in 40.0 mL CH<sub>2</sub>Cl<sub>2</sub> at r.t. NaOH (1.0 g, 25.0 mmol) was then added under stirring, followed by 10.0 mL CH<sub>2</sub>Cl<sub>2</sub> containing 1.62 g 3-bromo-1-propyne (80 wt%, 14.0 mmol). After the reaction was deemed complete (59 h, TLC), the yellow reaction mixture was diluted with deioned water (30.0 mL), and introduced into a separatory funnel. The aqueous phases was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10.0 mL), the combined

organic phase was dried over MgSO<sub>4</sub>, and the solvent was removed *in vacuo*. The obtained yellow liquids are 3-PEO-propyne.

The ligand **2** was prepared according to the “click” chemistry. 3-PEO-propyne (0.78 g, 2.0 mmol) and 4-azidobenzoic acid (0.33 g, 2.0 mmol) were added to a three-necked flask at r.t., equipped with a stir bar, under nitrogen atmosphere and stirring, followed by 10mL THF, 5mL of an aqueous solution of CuSO<sub>4</sub> (0.32 g, 2.0 mmol) and sodium ascorbate (0.79 g, 4.0 mmol), respectively. After the reaction was deemed complete according to TLC (24 h), THF was removed *in vacuo*. Ethylene diamine tetraacetic acid (EDTA, 80 mg) was then added under stirring. After 10 min, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and introduced into a separation funnel, and the organic phases were washed with deionized water (3 x 10.0 mL). Then the combined organic phase was dried over MgSO<sub>4</sub>, and the as-prepared ligand **2** was dispersed in CH<sub>2</sub>Cl<sub>2</sub> for further uses. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.26-8.16 (m, 3H), 7.89-7.81 (m, 2H), 4.78 (s, 2H), 3.78-3.50 (m, 28H), 3.36 (s, 3H).

### 3 Synthesis of the Fe<sub>3</sub>O<sub>4</sub> NPs **3**

Fe<sub>3</sub>O<sub>4</sub> NP **3** was prepared according to the ligand exchange reaction. 0.10 g Fe<sub>3</sub>O<sub>4</sub> NP1 (2 ml, 0.4 mmol) and 0.28 g ligand **2** were added to a round bottom flask. Under nitrogen protection and stirring for 12 h. Then the solvent was removed under vacuum. The tan solid was washed with hexane and ether for several times. Finally, the tan solid was dissolved in 10ml deionized water and dialysis for 8 h to remove the excess ligands and salts. The as-prepared Fe<sub>3</sub>O<sub>4</sub> NP **3** were dispersed in water for further uses.

### 4 Syntheses of the catalysts **4** (Au: 0.7wt%) and **5** (Pd: 1.4wt%)

The amount of Au and Pd load on the surface of Fe<sub>3</sub>O<sub>4</sub> NP **3** can be calculated with equation I, II, III, IV.

$$\text{Au(wt\%)} = \frac{m(\text{HAu}^{\text{III}}\text{Cl}_4) \times \omega_1\%}{m(\text{HAu}^{\text{III}}\text{Cl}_4) + m(\text{Fe}_3\text{O}_4\text{NP3})} \quad (\text{I})$$

$$\omega_1\% = \frac{M(\text{Au})}{M(\text{HAu}^{\text{III}}\text{Cl}_4)} \times 100\% \quad (\text{II})$$

$$\text{Pd}(\text{wt}\%) = \frac{m(\text{Na}_2\text{Pd}^{\text{II}}\text{Cl}_4) \times \omega_2\%}{m(\text{Na}_2\text{Pd}^{\text{II}}\text{Cl}_4) + m(\text{Fe}_3\text{O}_4\text{NP3})} \quad (\text{III})$$

$$\omega_2\% = \frac{M(\text{Pd})}{M(\text{Na}_2\text{Pd}^{\text{II}}\text{Cl}_4)} \times 100\% \quad (\text{IV})$$

Thus, 1.0 mL Fe<sub>3</sub>O<sub>4</sub> NP **3** (10.44 mg/ml) and 0.16 mg HAu<sup>III</sup>Cl<sub>4</sub> (0.44 mg, Na<sub>2</sub>Pd<sup>II</sup>Cl<sub>4</sub>) were added in a sample bottle. The obtained solution was stirred for 10 min. Then, the fresh-prepared sodium borohydride aqueous solution 0.1mL (0.6 mg/mL, 1.6 mg/mL) was added dropwise to the reaction mixture under vigorous stirring for 5 min. The catalysts **4** and **5** were kept in aqueous solution at 25°C.

Besides, in order to demonstrated that the AuNPs and PdNPs are all attached on the surface of Fe<sub>3</sub>O<sub>4</sub> NP **3**. The aqueous solution which was separated by an external magnetic field was used to catalyze the reduction of 4-NP and Suzuki-Miyaura C-C coupling reaction. We found that the aqueous solution did not show any catalytic activity towards these reactions.

### **5 The calculation of catalyst 4 and catalyst 5 for the reduction of 4-NP and Suzuki-Miyaura C-C coupling reaction.**

The amount of catalyst 4 (0.16mg/ml) and catalyst5 (0.44mg/ml) that added in the reaction could be calculated with equation V, VI. (The substrate refers to 4-NP or aryl halide. The  $\omega$  is the molar ratio of catalyst to the substrate. ) Thus, we could take amount precisely *via* adding the volume ( $V_1$ ,  $V_2$ ) of aqueous solution of catalyst 4 or 5 into the reactions.

$$V_1(\text{catalyst4}) = \frac{\omega \times n(\text{substrate}) \times M(\text{HAu}^{\text{III}}\text{Cl}_4)}{0.16} \quad (\text{V})$$

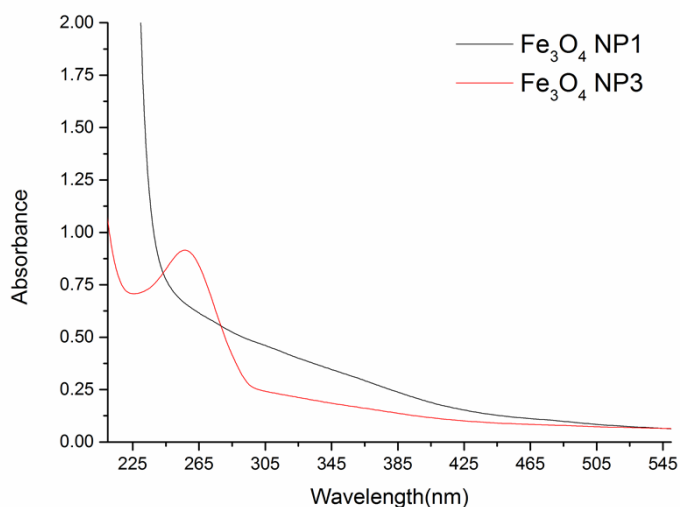
$$V_2(\text{catalyst5}) = \frac{\omega \times n(\text{substrate}) \times M(\text{Na}_2\text{Pd}^{\text{II}}\text{Cl}_4)}{0.44} \quad (\text{VI})$$

## 6 General procedure for the Suzuki coupling of aryl halide and arylboronic acid

A mixture of aryl halide (0.5 mmol), phenylboronic acid (0.65 mmol),  $K_2CO_3$  (1.0 mmol), THF/ $H_2O^a$  (2 mL, volume ratio = 1:1), EtOH/ $H_2O^{b,c}$  (2 mL, volume ratio = 1:1) and the catalyst **4** or **5** ( $V_1$  or  $V_2$ ) was charged in a 10 mL test tube and stirred at  $66^\circ C^a$ ,  $25^\circ C^b$ , and  $70^\circ C^c$ . The end of the reaction was tracked by TLC. After the reaction, the mixture was extracted three times with  $Et_2O$ , and the organic phase was dried over  $MgSO_4$ . These crude products were further purified by flash chromatography column that was conducted with silica gel as stationary phase and petroleum ether/ethyl acetate (volume ratio = 50:1) as mobile phase. The catalyst **4** or **5** was separated with a magnet and washed with diethyl ether (2 x 1mL), deionized water (2 x 1mL), and then dried *in vacuo* for the next run. (The recycle method of this catalyst in the reduction of 4-NP is same as this way)  $^1H$  NMR (400 MHz,  $CDCl_3$ ) of entry **4**:  $\delta$  7.55 (m, 2H), 7.49 (m, 2H), 7.29 – 7.25 (m, 2H), 7.01 (d, 2H), 3.88 (s, 3H), 2.42 (s, 3H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  158.9, 138.0, 136.4, 133.7, 129.4, 128.0, 126.6, 114.1, 55.4, 21.1.

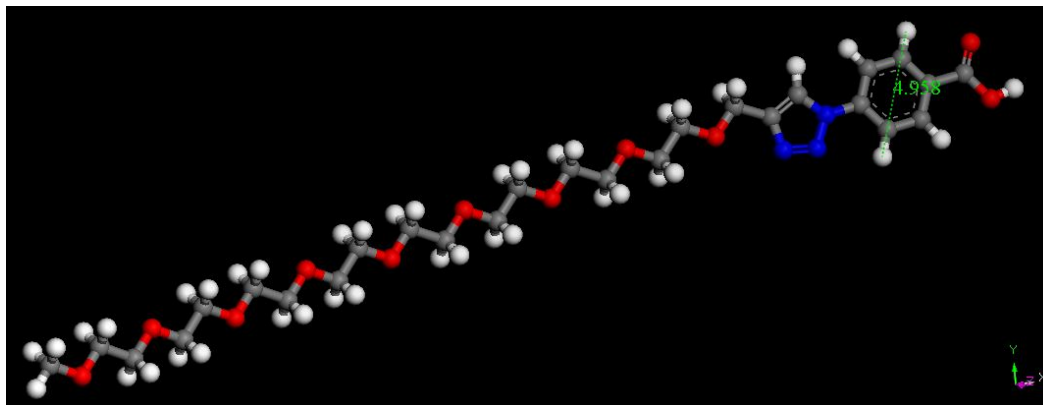
$^1H$  NMR (400 MHz,  $CDCl_3$ ) of entry **10**:  $\delta$  7.64 – 7.53 (m, 4H), 7.46 (m, 2H), 7.39 – 7.32 (m, 1H), 7.05 – 6.98 (m, 2H), 3.89 (s, 3H).

## 7 The UV-Vis spectra of $Fe_3O_4$ NP 1 and $Fe_3O_4$ NP 3

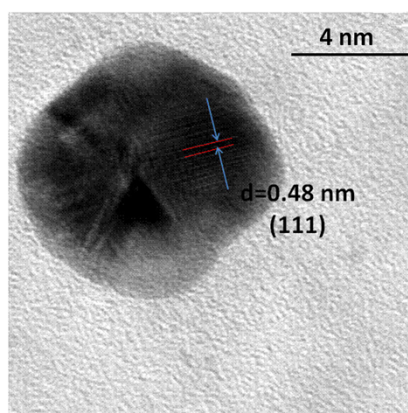


**Figure S1** The UV-Vis spectra of  $Fe_3O_4$  NP 1 and  $Fe_3O_4$  NP 3

## 8 The simulation on the footprint of ligand 2



**Figure S2** the 3D structure model of ligand 2



**Figure S3** TEM images of a  $\text{Fe}_3\text{O}_4$  NP **3** ( $R = 3.3\text{nm}$ )

Energy-minimized structures of ligand **2** are determined using Materials Studio 6.0 (Forcite modle). The carboxylic acid in the ligand **2** was strongly coordinated to the  $\text{Fe}_3\text{O}_4$  surface, and the footprint of ligand **2** could be estimated by equation (1)

$$S = \pi r^2 \quad (1)$$

$$S = \pi \times (4.959/2)^2 \text{ \AA}^2 = 0.193 \text{ nm}^2 \quad r: \text{radius of aromatic ring as Figure S1}$$

The number of ligands **2** on the  $\text{Fe}_3\text{O}_4$ NP **3** surface was estimated by equation (2)

$$N = \frac{A}{S} = \frac{4\pi R^2}{S} \quad (2)$$

N: The number of ligands **2** on the  $\text{Fe}_3\text{O}_4$ NP **3** surface

A: Surface area of  $\text{Fe}_3\text{O}_4$  NP **3**

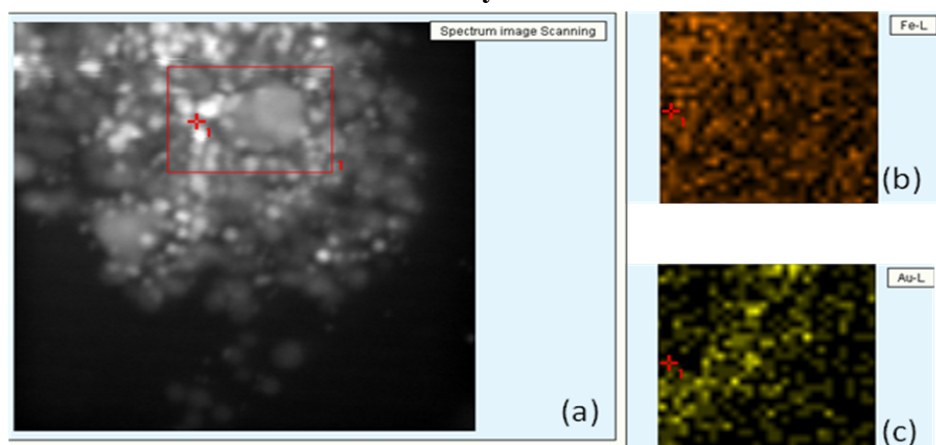
R: radius of  $\text{Fe}_3\text{O}_4$  NP **3**

S: footprint of ligand **2**

Thus, the number of ligands **2** on the  $\text{Fe}_3\text{O}_4$ NP **3** surface was 797.

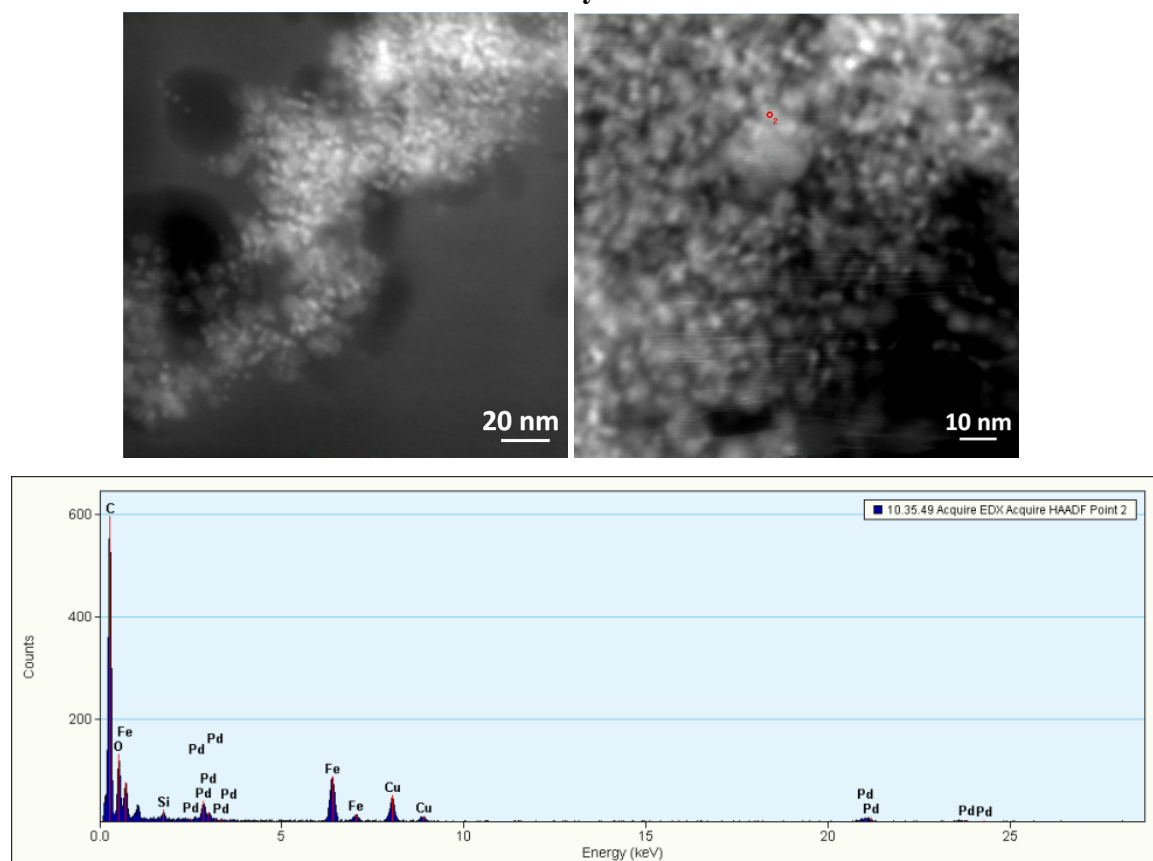


## 9 The characterization of trz-AuNP catalyst 4

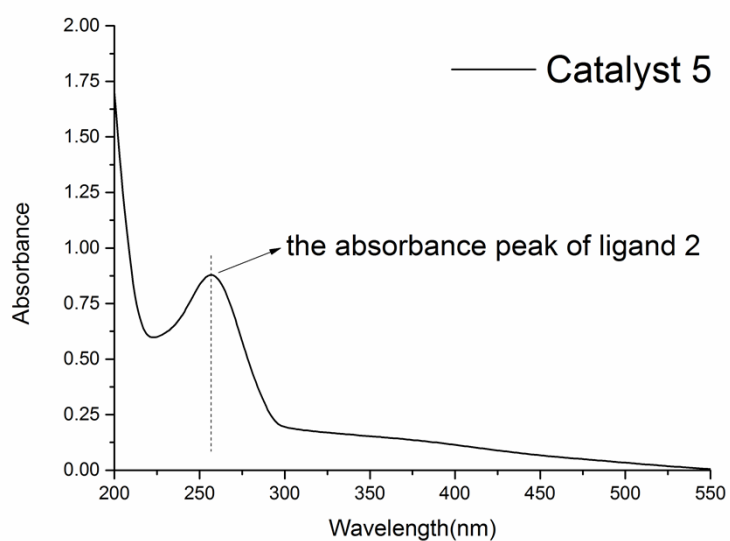


**Figure S4** STEM dark-field image (a) and elemental maps of catalyst **4** for Fe (b), AND Au (c) obtained by EDX.

## 10 The characterization of trz-PdNP catalyst 5

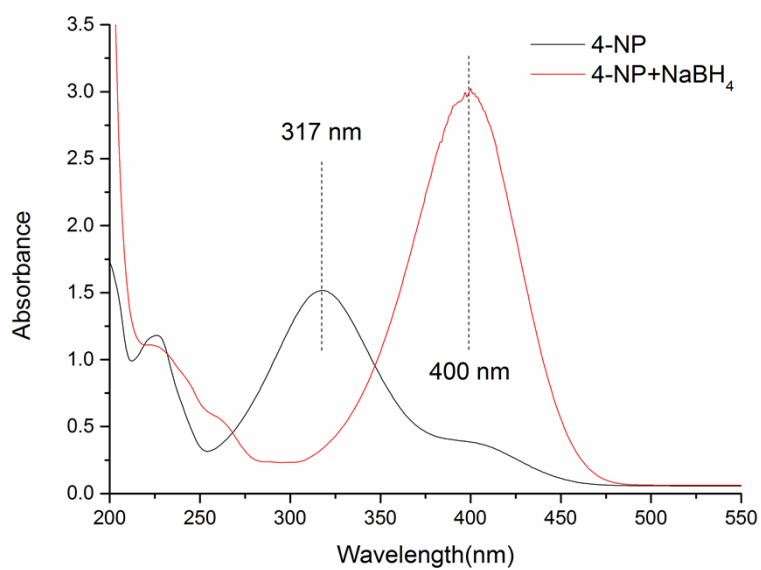


**Figure S5** The TEM images of catalyst **5** and EDX analysis of catalyst **5**

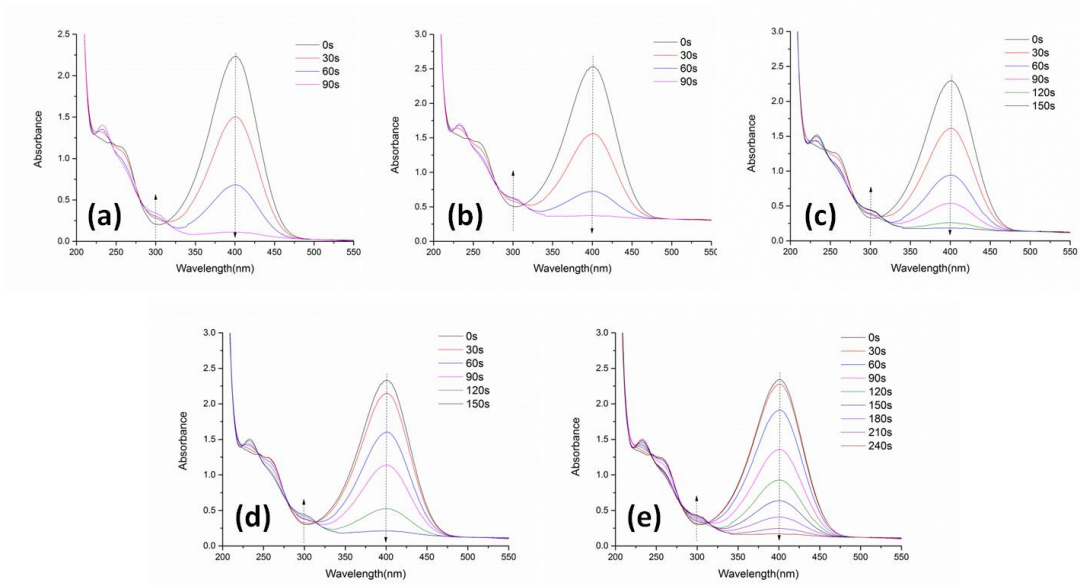


**Figure S6** UV-vis spectra of catalyst 5

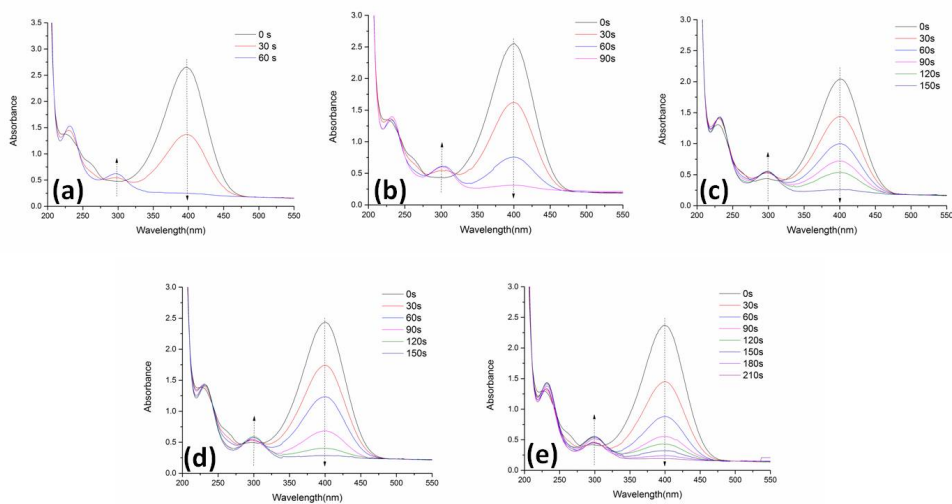
### 11 The UV-vis spectra of 4-nitrophenolate during the reduction process



**Figure S7** UV-vis spectra of 4-NP before and after adding NaBH<sub>4</sub> solution.



**Figure S8** UV-vis. spectroscopy during the reduction of 4-nitrophenol catalyzed by catalyst **4**, the amount of catalyst is (a) 30%,(b) 25%, (c) 20%, (d) 15%, (e) 10%.

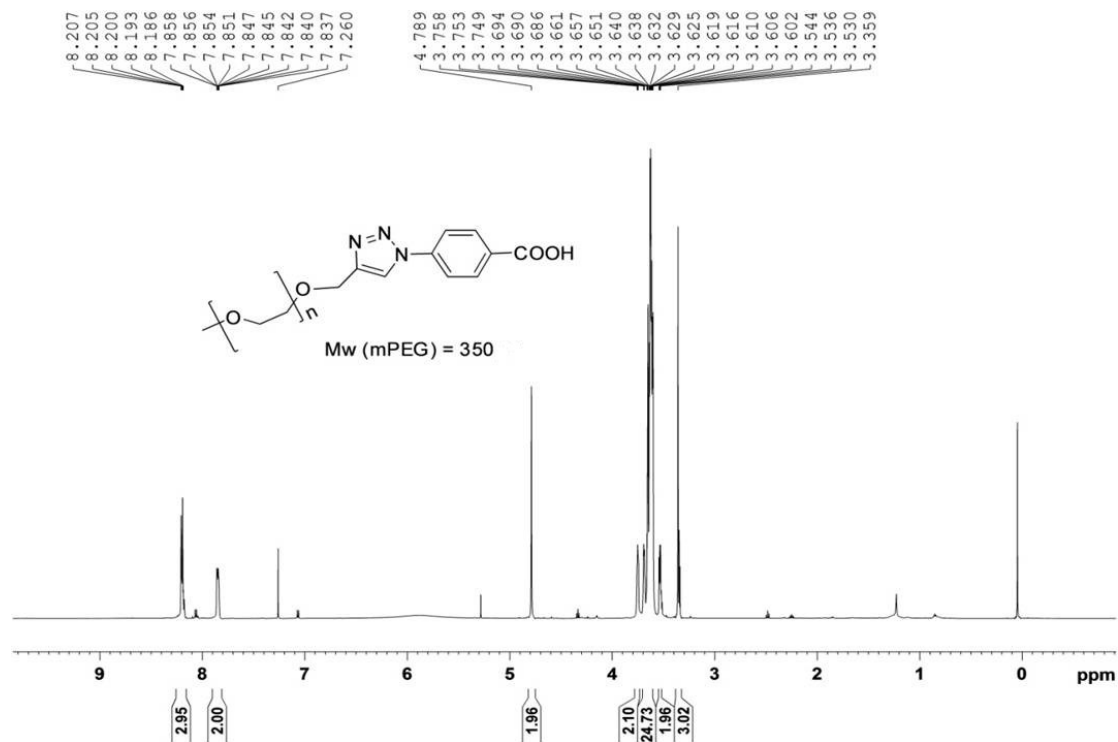


**Figure S9** UV-vis. spectroscopy during the reduction of 4-nitrophenol catalyzed by catalyst **5**, the amount of catalyst is (a) 30%, (b) 20%, (c) 10%, (d) 5%, (e) 3%.

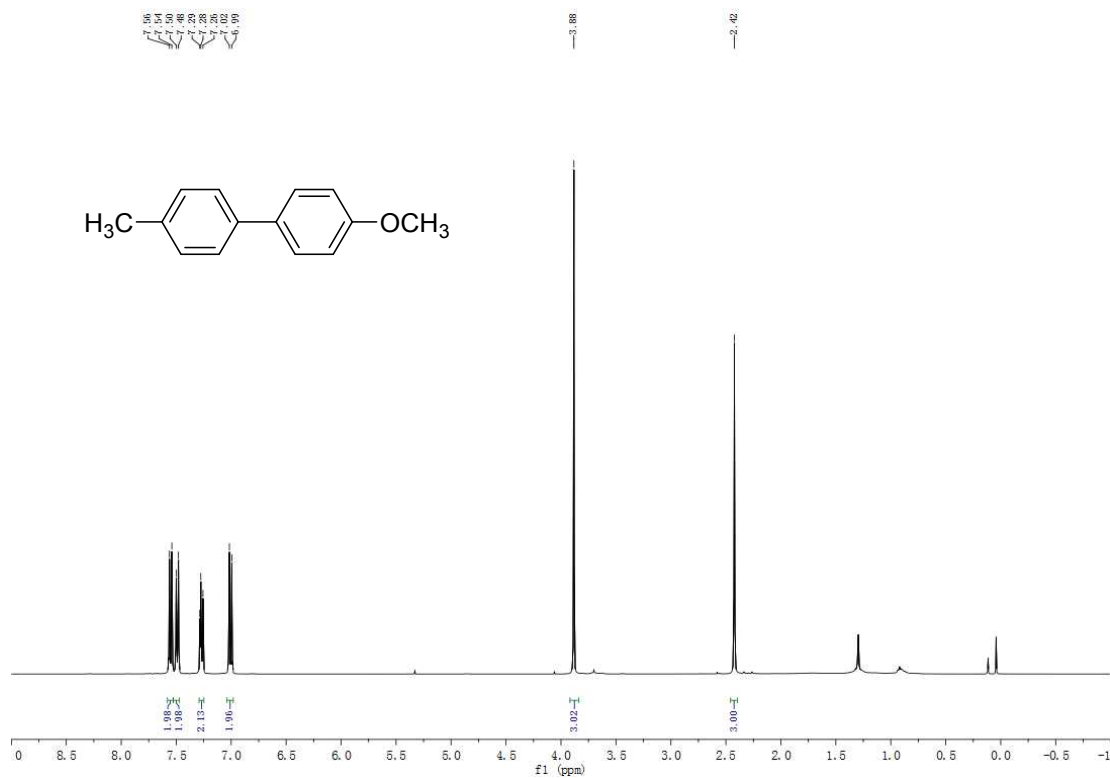
## Spectra for the synthesized compounds

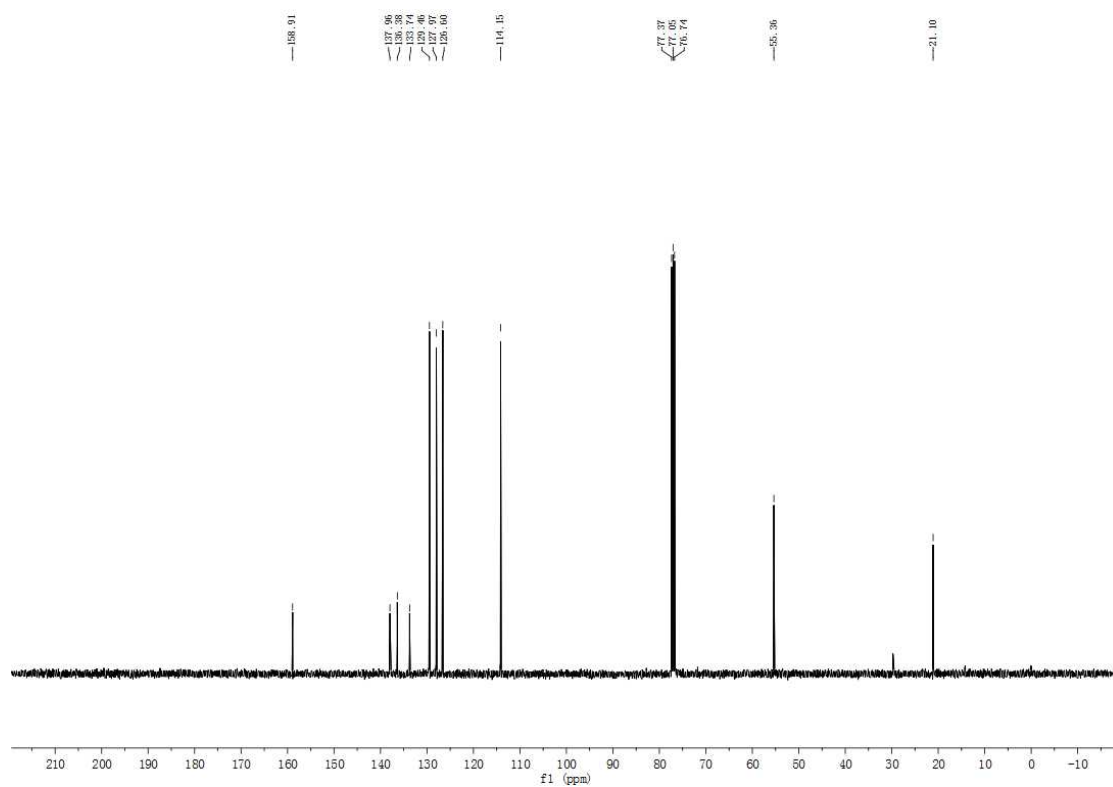
### NMR spectra of ligand 2, entry 4, 10

ligand 2:



Entry 4:





Entry 10:

