

Supplementary

# Mesoporous Palladium *N,N'*-Bis(3-Allylsalicylidene)*o*-Phenylenediamine-Methyl Acrylate Resins as Heterogeneous Catalysts for the Heck Coupling Reaction

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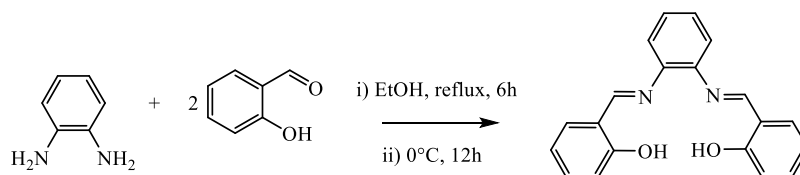
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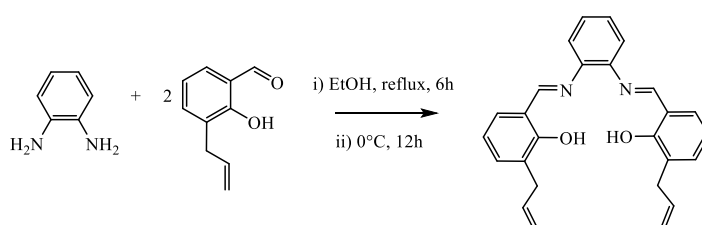
## 1. Ligands and Pd-Complexes Synthesis

### 1.1. Synthesis of SALOPHEN Ligand



The ligand *N,N'*-bis(salicylidene)*o*-phenylenediamine (SALOPHEN) was synthesized according to a reported procedure [1]. A 250-mL round-bottomed flask was charged with salicylaldehyde (40.0 mmol) in EtOH, and a solution with *o*-phenylenediamine (20.0 mmol) in 50 mL of EtOH was added to it dropwise. The reaction mixture was then refluxed for 2 h with magnetic stirring. After the reaction, the mixture was cooled at 0 °C for 12 h to obtain a precipitate, which was recrystallized repeatedly from EtOH until the purified ligand AS was obtained as an orange well-defined solid with 78% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 13.04 (s, 2H, –OH); 8.65 (s, 2H, –N=C–H); 7.38 (m, 6H, H-Ar); 7.36–7.24 (m, 4H, H-Ar); 7.06 (d, 2H, H-Ar); and 6.93 (t, 2H, H-Ar). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 164.90 (Ar-OH); 150.60 (Ar-C=N); 142.05; 135.98; 134.71; 126.95; 120.08; 119.60; 116.91; 114.95 (Aromatic carbons).

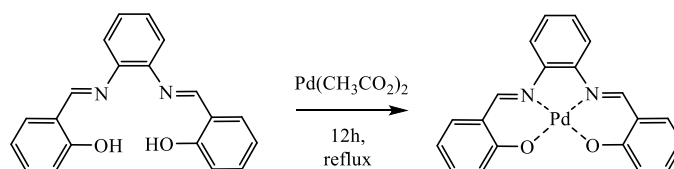
### 1.2. Synthesis of AS ligand



The ligand *N,N'*-bis(3-allylsalicylidene)*o*-phenylenediamine (AS) was synthesized follow the same procedure as a SALOPHEN ligand using 3-allylsalicylaldehyde instead of 3-salicylaldehyde. After the reaction, the mixture was cooled at 0 °C for 12 h to obtain a precipitate, which was recrystallized repeatedly from EtOH until the purified ligand AS was obtained as an orange well-defined solid with 81% yield. <sup>1</sup>H NMR (400 MHz, DMSO *d*<sub>6</sub>): δ 13.51 (s, 2H, –OH); 8.94 (s, 2H, –N=C–H); 7.50 (m, 4H, H-

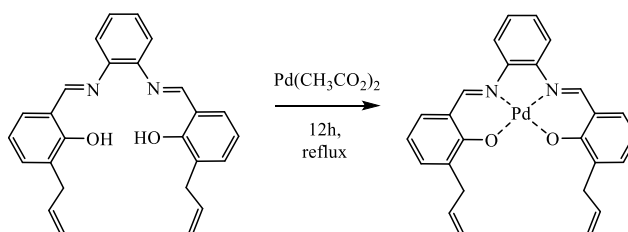
Ar); 7.43 (m, 2H, H-Ar); 7.29 (d, 2H, H-Ar); 6.93 (2H, H-Ar); 6.02 (m, 2H,  $-\text{HC}=\text{C}-$ ); 5.08 (dd, 2H,  $\text{HC}=\text{C}-$ ); 5.0 (dd, 2H,  $-\text{HC}=\text{C}-$ ), and 3.49 (d, 4H,  $\text{Ar}-\text{H}_2\text{C}-\text{C}=\text{C}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  165.90 (Ar-O); 152.49 (Ar-C=N); 143.64; 135.30; 133.60; 132.72; 127.65; 120.01; 115.86; 115.60;  $\gamma$  115.48 (Aromatic carbons); 137.30 ( $\text{C}=\text{CH}-$ ), ( $\text{H}_2\text{C}=\text{C}-$ ), 35.90 ( $-\text{CH}_2-$ ) corresponding to allyl group.

### 1.3. Synthesis of Pd-SALOPHEN Complex



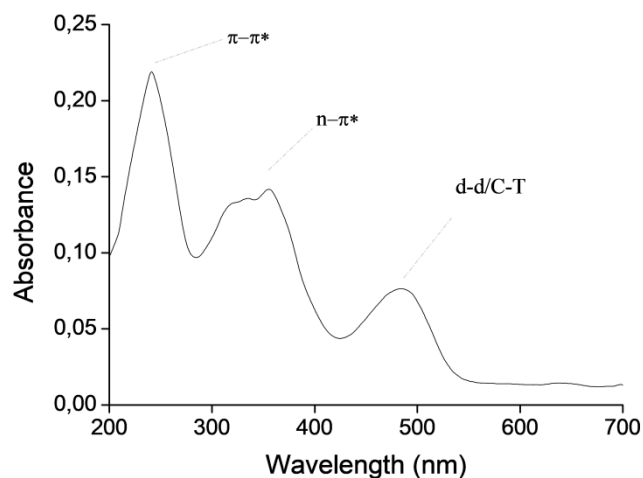
The SALOPHEN ligand (15 mmol) was added to 150 mL of DCM and stirred at room temperature, followed by adding  $\text{Pd}(\text{CH}_3\text{COO})_2$  (15.5 mmol) to the mixture and refluxing for 12 h [2,3]. A brown precipitate was separated by filtration and washed using MeOH and DCM ( $4 \times 5$  mL).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  9.19 (s, 2H,  $-\text{N}=\text{C}-\text{H}$ ); 8.34 (m, 2H, H-Ar); 7.74 (d, 2, H-Ar); 7.45 (m, 4, H-Ar); 7.03 (d, 2H, H-Ar); 6.72 (t, 2H, H-Ar).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  165.80 (Ar-O); 153.61 (Ar-C=N); 142.85; 136.35; 135.80; 127.90; 120.73; 120.40; 117.15; 115.51 (Aromatic carbons).

### 1.4. Synthesis of Pd-AS Complex



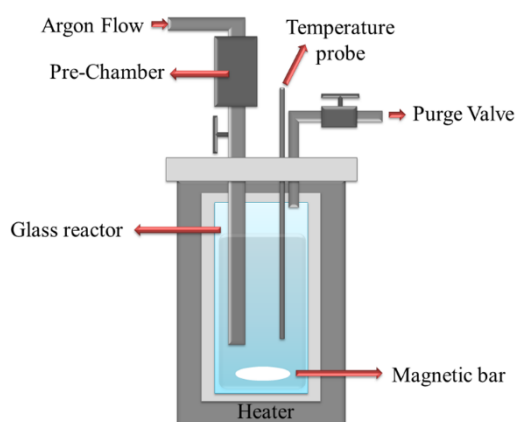
The homogeneous catalysts PdAS was synthesized in the same way as Pd-SALOPHEN was prepared, producing a brown solid with 80% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  8.41 (s, 2H,  $-\text{N}=\text{C}-\text{H}$ ); 7.78 (dq, 2H, H-Ar); 7.30–7.25 (m, 4H, H-Ar); 6.62 (dd, 2H, H-Ar); 6.15 (m, 2H,  $-\text{HC}=\text{C}-$ ); 5.28 (dd, 2H,  $\text{HC}=\text{C}-$ ); 5.25 (dd, 2H,  $-\text{HC}=\text{C}-$ ); and 3.59 ppm (d, 4H,  $\text{Ar}-\text{H}_2\text{C}-\text{C}=\text{C}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  165.90 (Ar-O); 152.49 (Ar-C=N); 143.64; 135.30; 133.60; 132.72; 127.65; 120.01; 115.86; 115.60;  $\gamma$  115.48 (Aromatic carbons); 137.30 ( $\text{C}=\text{CH}-$ ), ( $\text{H}_2\text{C}=\text{C}-$ ), 35.90 ( $-\text{CH}_2-$ ) corresponding to allyl group.

## 2. UV-Vis of PdAS Complex Characterization



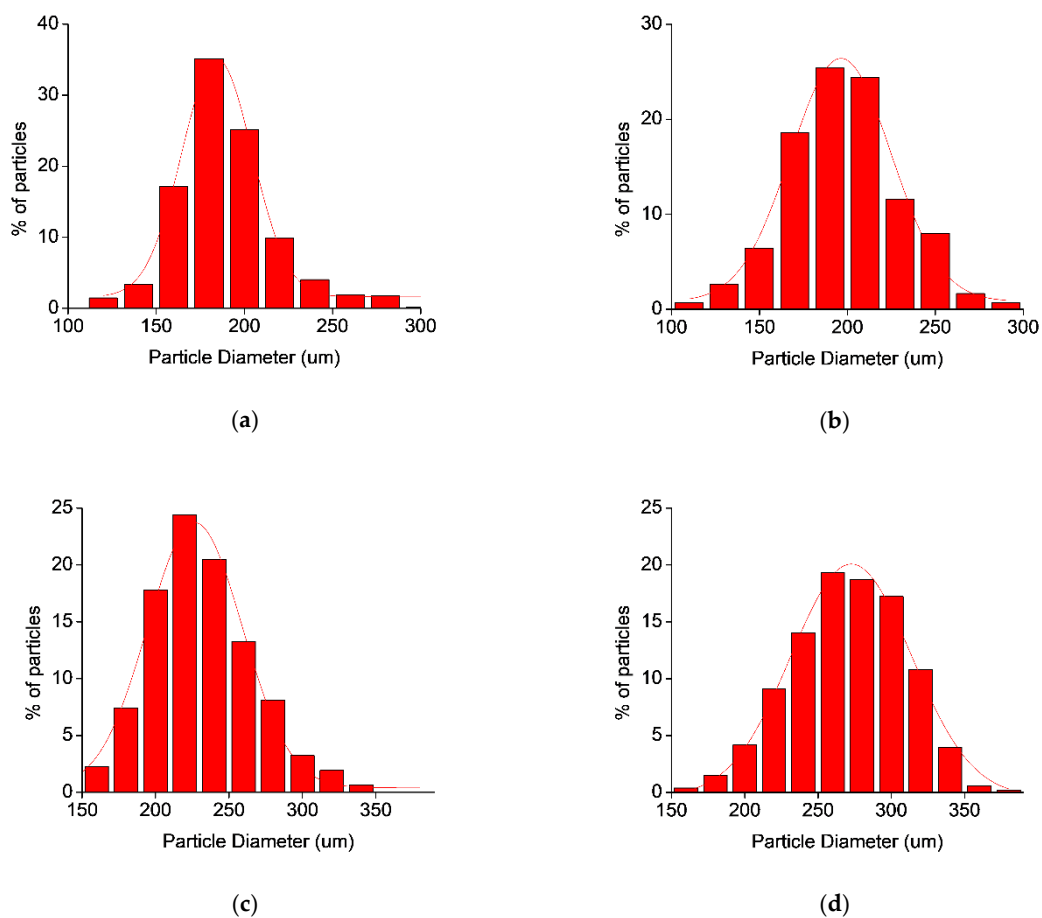
The UV-visible spectra in liquid phase showed the transition bands  $\pi \rightarrow \pi^*$  at 241 nm,  $n \rightarrow \pi^*$  between 336 and 355 nm and charge-transfer (C-T) transition at 481 nm, in agreement with results reported by Choudhary et al. [4].

## 3. Schemes

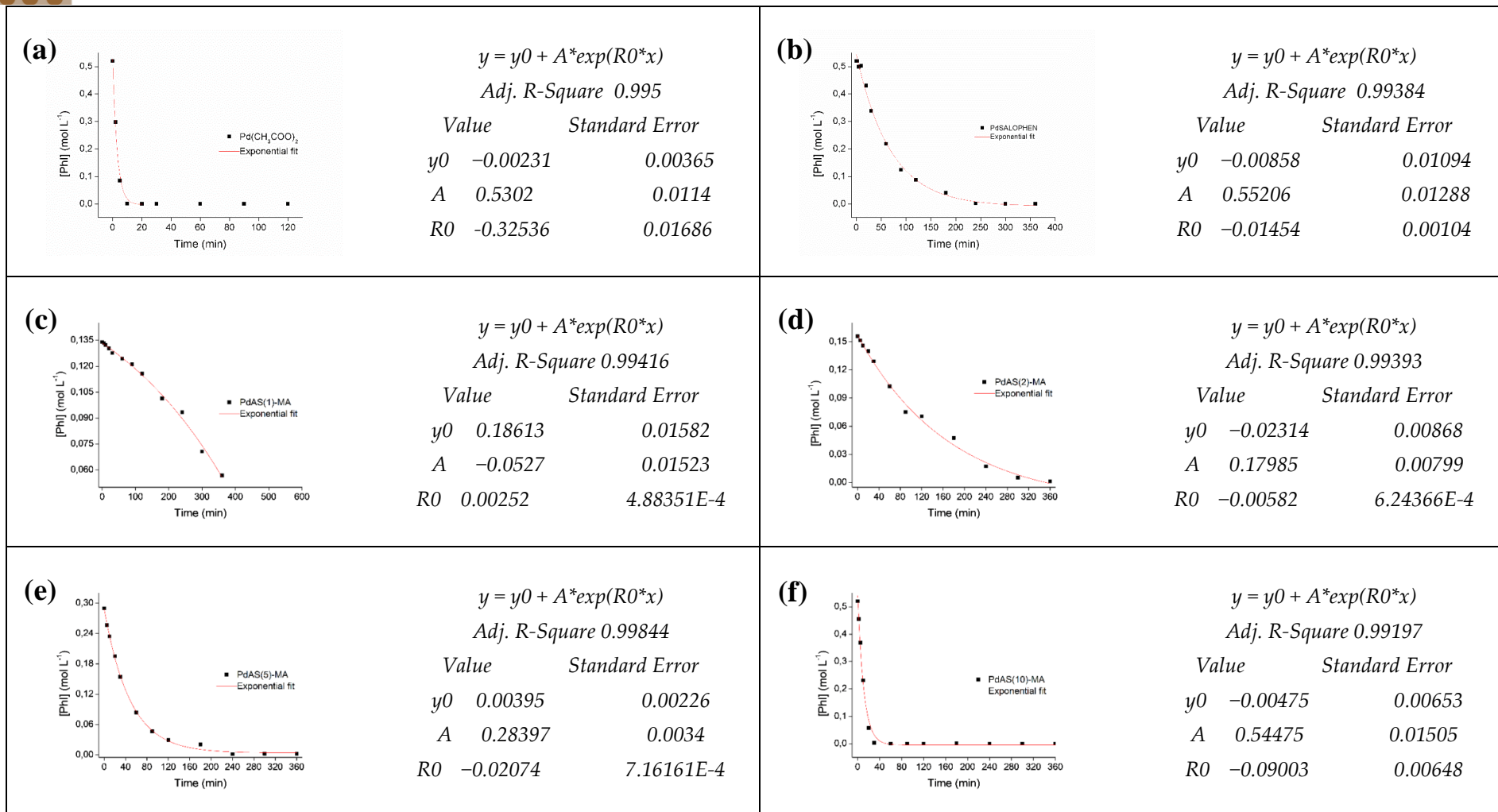


**Scheme S1.** Semi-Batch reactor used for the catalytic measurements.

#### 4. Complementary PdAS(x)-MA Catalysts Characterization



**Figure S1.** Microsphere diameter distribution of PdAS(x)-MA catalysts. (a) PdAS(1)-MA, (b) PdAS(2)-MA, (c) PdAS(5)-MA, and (d) PdAS(10)-MA.



**Figure S2.** Exponential fitting decrease curves of concentration of I-Ph on time for Pd-based catalysts. (a) Pd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, (b) Pd-SALOPHEN, (c) PdAS(1)-MA, (d) PdAS(2)-MA, (e) PdAS(5)-MA, and (f) PdAS(10)-MA.

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