## SUPPORTING INFORMATION

# Nanocrystalline magnesium oxide-stabilized palladium(0): the Heck reaction of heteroaryl bromides in the absence of additional ligands and base

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#### **General Information:**

NAP-MgO (commercial name: NanoActive<sup>TM</sup> Magnesium Oxide Plus, Specific surface area = 590 m<sup>2</sup>/g) was purchased from NanoScaleMaterials, Inc. (Manhattan, USA). All chemicals were purchased commercially and were used as received. All solvents used for experiments were dried using standard procedures and distilled prior to use. The X-ray diffraction (XRD) patterns of the fresh and used samples were obtained on a Rigaku Miniflex X-ray diffractometer using Ni filtered Cu K<sub>a</sub> radiation ( $\lambda = 0.15406$ nm), at a scan rate of  $2^{\circ}$  min<sup>-1</sup>, with the beam voltage and beam current of 30 kV and 15 mA respectively. The X-ray photoelectron spectroscopic (XPS) analysis of the fresh and used Pd-NAP-MgO sample was recorded using a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer equipped with Mg anode and a multichannel detector. Charge referencing was done against adventitious carbon (C 1s, 284.8 eV). Shirley-type background was subtracted from the signals. The recorded spectra were always fitted using Gauss-Lorentz curves to determine the binding energies of the different elements. For the transmission electron microscope (TEM) analysis samples were dispersed in methanol solution and dropped on a 200-mesh Cu grid, and images were taken using JEOL JEM 2100F high-resolution transmission electron microscope at an acceleration voltage of 200 kV. The <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Inova 500 and Avance 300 (300 MHz<sup>1</sup>H and <sup>13</sup>C) spectrometer in CDCl<sub>3</sub> using TMS as internal standard. ACME silica gel (60-120 mesh) was used for column chromatography purposes and thin layer chromatography was performed on Merck pre coated silica gel 60-F254 plates. Pd-C was purchased from commercial sources and has 10%Pd on carbon.

#### **Preparation of the catalyst:**

Preparation of Nanocrystalline MgO stabilized Palladium Catalyst:

NAP-Mg-PdCl<sub>4</sub>: NAP-MgO was calcined in air at 450 °C for four hours (1.0g) and treated with Na<sub>2</sub>PdCl<sub>4</sub> (0.294g, 1 mmol) dissolved in 100 mL decarbonated water with vigorous stirring for 12 h at room temperature under nitrogen atmosphere to afford the brown colored NAP-Mg-PdCl<sub>4</sub>. Then the catalyst was filtered and washed with deionized water and acetone and dried under vacuum.

NAP-Mg-Pd(0): NAP-Mg-PdCl<sub>4</sub> (1.0g) was reduced with hydrazine hydrate (5 mL) in 20 mL of dry ethanol with vigorous stirring for 3 h at under a nitrogen atmosphere at room temperature. Then the reduced catalyst was filtered through a G-3 sintered glass funnel and washed with deionized water and acetone and dried under vacuum to get the black-colored, air stable NAP-Mg-Pd(0). The Pd/C was purchased from commercial sources and has 10% Pd on carbon.

#### **Catalyst Characterization:**

#### **SEM-EDX analysis:**

The scanning electron microscopy-energy dispersive X-ray analysis of fresh and used NAP-Mg-Pd(0) catalysts showed 0.90 and 0.889 mmolg<sup>-1</sup> of Pd respectively.

#### **XRD** analysis:

XRD patterns of the fresh and used Pd supported on NAP-MgO catalysts are reported in **Figure S1**. The fresh and used catalysts displayed diffraction lines due to metallic Pd phase (PCPDF # 88-2335) appeared at  $2\theta = 40.0$ ,  $46.5^{\circ}$  and their corresponding 'd' values are 0.225, 0.195 nm. Both fresh and used catalysts exhibited metallic Pd phase only. Absence of peaks due to Pd-halides either may be due to lower amounts or below the X-ray detection limit.



Figure S1: XRD patterns of the fresh and used NAP-Mg-Pd(0) catalysts

#### **XPS** analysis :

**Figure. S2** represents the X-ray photoelectron spectra of NAP-Mg-Pd(0) fresh and used catalysts. The binding energy (B.E) values of Pd  $3d_{5/2}$  in the NAP-Mg-Pd(0) fresh and used catalysts are 335.2 and 335.3 eV respectively. These values clearly indicate the existence of Pd in metallic form. The B.E values of Pd  $3d_{5/2}$  show that Pd is stabilized to large extent in the form of Pd(0) on NAP-MgO support with traces of Pd<sup>2+</sup> species. Shen *et al* have reported the shift in the B.E of Pd  $3d_{5/2}$  from 335.1 to 336.2 eV in the Pd/MgO catalysts with Pd from PdCl<sub>2</sub> precursor to the intimate contact of Pd and Mg that lead to an electron transfer from Pd to Mg as also evidenced by the presence of Pd<sup>n+</sup> ions in used catalysts. The appearance of traces of Pd(II) in both fresh and used catalysts are explained based on Shen et al observations . We anticipate that such a phenomenon seems to exist in NAP-Mg-Pd(0) catalyst.



Fig S2: XPS analysis of the fresh and used NAP-Mg-Pd(0) catalysts

#### Particle size distribution:

The Pd particle size distribution of 3 samples namely fresh, used (recovered after 1<sup>st</sup> cycle) and the sample recovered after 5th cycle were represented in the histograms and reported Figure S3. It shows that the avearge Pd particle size is not much varied in the fresh and used form of catalysts.



Figure S3: The histograms of Pd particle size measured from the TEM analysis of (a) fresh, (b) used (recovered after 1<sup>st</sup> cycle) and (c) sample recovered after 5<sup>th</sup> cycle.

#### Typical Procedure for the Heck reaction of heteroaryl halides:

The reaction vessel was charged with aryl halide (1 mmol), alkene (2 mmol), and the catalyst NAP-Mg-Pd(0) (0.020g ) in *N*,*N*-dimethylformamide (2.5 mL). The reaction mixture was heated at 130 °C for the desired time and the progress of the reaction was monitored by TLC. At the end of the reaction, the reaction mixture was filtered to separate the catalyst. The solid residue was first washed with water and then with diethyl ether to remove any excess base and any organic material. It was then dried at room temperature and used as it is for further reactions. The reaction mixture was diluted with water (20 mL) and then extracted with EtOAc (20 mL). The combined organic layer was washed with brine solution (10 mL) and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the crude product was purified by flash chromatography over silica gel (60-120 mesh) column using hexane/ethyl acetate as an eluent to afford the pure product.

#### **Spectroscopic Data:**

#### 2-Styryl- pyridine (Table 2, entry 1)<sup>1</sup>:

White solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.60(d, 1H, J = 3.77H_Z)$ , 7.69-7.57(m, 4H), 7.38 (t, 3H,  $J = 7.55H_Z$ ) 7.32-7.27 (m, 1H,), 7.20-713 (m, 2H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 155.5$ , 149.6, 136.5, 132.6, 128.6, 128.2, 127.8, 127.0, 122.0.

#### **3-Styryl-pyridine** (Table 2, entry 2)<sup>1</sup>:

White solid; <sup>1</sup>H-NMR (300 MHz,CDCl<sub>3</sub>):  $\delta = 8.69(s, 1H)$ ,  $8.45(d, 1H, J = 3.77 H_z)$ , 7.78(d, 1H, J = 7.74Hz), 7.47(d, 2H, J = 7.36 Hz),  $7.34(t, 2H, J = 7.43H_z)$ , 7.27-7.22(m, 2H), 7.14(d, 1H, J = 16.43 Hz), 7.04(d, 1H, J = 16.43 Hz); <sup>13</sup>C NMR (75 MH<sub>z</sub>, CDCl<sub>3</sub>):  $\delta = 148.4$ , 136.5 132.6, 130.7, 128.7, 128.1, 126.6, 124.7, 123.4.

## **3-Styryl-thiophene** (Table 2, entry 3)<sup>1</sup>:

White solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47(d, 2H, *J* = 7.55 Hz), 7.36-7.29 (m, 4H), 7.26-7.21(m, 2H, ), 7.12(d, 1H, *J* = 16.43 Hz), 6.94(d, 1H, *J* = 16.61 Hz); <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.0, 137.3, 128.6, 127.4, 126.2, 126.1, 124.8, 122.8, 122.3.

## 2-Styryl-thiophene (Table 2, entry 4)<sup>1</sup>:

White solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.46(d, 2H, *J* = 7.55 Hz), 7.33 (t, 2H *J* = 7.17 Hz), 7.24-7.17(m, 3H,), 7.00-6.98(m, 1H,), 6.96(m 1H), 6.92(d, 1H *J* = 16.61 Hz); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.8, 136.9, 128.6, 128.2, 127.5, 126.2, 126.0, 124.2, 121.7.

## **3-Styryl-quinoline** (Table 2, entry 5)<sup>1</sup>:

White solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 9.09(s, 1H)$ , 8.14(s, 1H), 8.07(d, 1H, J = 8.30 Hz), 7.79(d, 1H, J = 7.93 Hz), 7.66(t, 1H, J = 8.12 Hz), 7.57-7.52(m, 3H), 7.37(t, 2H, J = 7.17 Hz), 7.29-7.18(m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 149.4$ , 136.6, 132.2, 130.8, 129.2, 129.1, 128.7, 128.2, 127.7, 126.9, 126.6, 125.1.

#### 4-Styryl-isoquinoline (Table 2, entry 6):

Semi solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 9.09(s, 1H)$ , 8.68(s, 1H), 8.10(d, 1H, J = 8.30 Hz), 7.91(d, 1H, J = 7.55 Hz), 7.70-7.52 (m, 5H), 7.34(t, 2H, J = 7.55 Hz), 7.28-7.23(m, 1H), 7.13(d, 1H, J = 15.86 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 151.5$ , 140.0, 136.9, 133.6, 133.1, 130.3, 128.6, 128.5, 128.1, 128.0, 127.1, 126.7, 122.7, 122.4.

## **3-Styryl-furan** (Table 2, entry 7)<sup>2</sup>:

White solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.48(s, 1H)$ , 7.40-7.38(m, 3H), 7.28(t, 2H,  $J = 7.17 \text{ H}_Z$ ), 7.18(t, 1H, J = 7.27 Hz), 6.93(d, 1H, J = 16.24 Hz), 6.75(d, 1H, J = 16.24 Hz), 6.61(s, 1H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 143.6$ , 140.9, 128.6, 128.3, 127.3, 126.0, 118.3, 107.3.

## 3-Methoxy-5-styryl pyridine (Table 2, entry 8):

Brown solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.34(s, 1H)$ , 8.20(s, 1H), 7.52(d, 2H, J = 7.32 Hz), 7.38(t, 2H, J = 7.55 Hz ), 7.34-7.29(m, 2H) 7.16(d, 1H, J = 16.47 Hz), 7.06(d,1H, J = 16.47 Hz), 3.91(s, 3H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 155.9$ , 141.0, 136.5, 131.0, 128.7, 128.1, 126.2, 124.6, 116.7, 55.5; ESI MS (m/z): 212 (M + H)<sup>+</sup>; HRMS (m/z): calcd for C<sub>14</sub>H<sub>14</sub>NO: 212.1026, Found: 212.1029.

## 2-Nitro-5-styryl pyridine (Table 2, entry 9):

Yellow solid; <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>):  $\delta = 8.71(s, 1H)$ , 8.26(d, 1H, J = 8.30 Hz), 8.12(dd 1H, J = 9.06, 2.26 Hz), 7.57(d, 2H, J = 6.79 Hz), 7.45-7.37(m, 3H), 7.28(d, 1H, J = 18.12 Hz), 7.15(d, 1H, J = 16.61 Hz); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 155.2$ , 146.9, 138.9, 135.6, 135.2, 129.3, 128.9, 127.1, 122.3, 118.2; ESI MS (m/z): 227 (M + H)<sup>+</sup>; HRMS (m/z): calcd for C<sub>13</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> :227.0274, Found: 227.0276.

## 2-metyl 6-styrylpyridine (Table 2, entry 10):

yellow solid; <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.59-7.47(m, 4H)$ , 7.32(t, 2H *J* = 7.55 H<sub>Z</sub>), 7.26-7.21(m, 1H), 7.15(d, 1H, *J* = 7.55H<sub>Z</sub>), 7.09(d, 1H, *J* = 15.84 H<sub>Z</sub>), 6.96(d, 1H, J = 7.55 H<sub>Z</sub>), 2.57(s, 3H); <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 158.2$ , 155.0, 136.5, 132.3, 128.6, 128.3, 128.1, 127.0, 121.6, 118.7, 24.6; ESI MS (m/z): 196 (M + H)<sup>+</sup>. HRMS (ESI) (m/z): calcd for C<sub>14</sub>H<sub>1 4</sub>N :196.1123, Found:196.1120.

## 3-(4-Metylstyryl)pyridine (Table 3, entry 1):

White solid; <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.71(s, 1H)$ , 8.46(dd, 1H,  $J = 4.32, 1.56 H_Z$ ), 7.82(d, 1H,  $J = 7.93 H_Z$ ), 7.41(d, 2H, J = 8.08 Hz), 7.28-7.27(m, 1H), 7.18-(d, 2H,  $J = 7.93 H_Z$ ), 7.13(d, 1H, J = 16.32, H<sub>Z</sub>), 7.01(d, 1H, J = 16.32Hz), 2.37(s, 3H); <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 148.4$ , 148.3, 138.2, 133.8, 133.1, 132.4, 130.7, 129.4, 126.5, 123.8, 123.4, 21.2; ESI MS (m/z): 196 (M + H)<sup>+</sup>. HRMS (m/z): calcd for C<sub>14</sub>H<sub>14</sub>N :196.1123, Found:196.1126.

## 3-(4-Chlorostyryl)pyridine (Table 3, entry 2):

White solid; <sup>1</sup>H-NMR (300MHz, CDCl3):  $\delta = 8.72(s, 1H)$ , 8.49(d, 1H,  $J = 6.04 \text{ H}_Z$ ), 7.81(d, 2H,  $J = 8.30 \text{ H}_Z$ ), 7.45(d, 2H,  $J = 9.06 \text{ H}_Z$ ), 7.36-7.26(m, 3H), 7.11(d,1H,  $J = 16,61 \text{ H}_Z$ ), 7.03(d, 1H,  $J = 16.61 \text{ H}_Z$ ); NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 148.7$ , 148.5, 135.1, 133.8, 132.6, 129.4, 128.9, 127.7, 125.4, 123.5; ESI MS (m/z): 216 (M + H)<sup>+</sup>. HRMS (m/z): calcd for C<sub>13</sub>H<sub>11</sub>NCl: 216.0583, Found: 216.0580.

**3-(2-(Napthalen-2-yl)vinyl)pyridine (Table 3, entry 3):**White solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.77(s, 1H)$ , 8.48(d, 1H, J = 4.72 Hz), 7.87-7.81(m, 5H), 7.74(dd, 1H, J = 8.68, 1.56 Hz), 7.51-7.45(m, 2H), 7.34-7.29(m, 2H), 7.18(d, 1H, J = 16.47 Hz),; <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 148.5$ , 134.0, 133.5, 133.1, 132.9, 132.5, 130.7, 128.4, 128.0, 127.6, 127.1, 126.4, 126.1, 125.1, 123.5, 123.2; ESI MS (m/z): 232 (M + H)<sup>+</sup>. HRMS (m/z): calcd for C<sub>17</sub>H<sub>14</sub>N :232.1129 , Found: 232.1123.

#### (E)-Butyl 3-(pyridine-3-yl)acrylate (Table 3, entry 4)<sup>3</sup>:

Yellow oil; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.74(s, 1H)$ , 8.58(s, 1H), 7.82(d,1H, J = 8.30 Hz), 7.63(d, 1H, J = 16.61 Hz), 7.32-7.27(m, 1H), 6.58(d, 1H, J = 16.61 Hz), 4.19(t, 2H, J = 7.55 Hz), 1.77-1.64(m, 3H), 1.48-1.40(m, 2H), 0.92-0.92(m, 3H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 166.3$ , 150.7, 149.5, 140.6, 134.2, 123.7, 120.5, 64.6, 30.6, 19.1, 13.6.

#### (E)-phenyl 3-(pyridin-3-yl)acrylate (Table 3, entry 5) :

δ = 8.81(s, 1H), 8.65(d, 1H, J = 4.15 Hz), 7.90 (d, 1H J = 7.93 Hz), 7.86(d, 1H, J = 16.17 Hz) 7.43-7.35(m, 3H), Hz), 7.26(t, 1H J = 7.43 Hz), 7.17(d, 2H, J = 7.47 Hz), 6.71(d, 1H, J = 16.02 Hz); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): <math>δ = 164.5, 151.0, 150.4, 149.5, 142.5, 134.4, 129.8, 129.3, 128.8, 123.7, 121.3, 119.4; ESI MS (m/z): 226 (M + H)<sup>+</sup>. HRMS (m/z): calcd for C<sub>14</sub>H<sub>11</sub>NO<sub>2</sub>:226.0790, Found: 226.0793.

#### 3-(4-Metylstyryl)thiophene (Table 3, entry 5):

Light yellow solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.35(d, 2H, J = 8.08 \text{ Hz})$ , 7.34-7.33(m, 1H),7.31-7.30(m, 1H), 7.15(d, 2H, J = 7.78 Hz), 7.07(d, 1H, J = 16.23 Hz), 6.92(d, 1H, J = 16.17 Hz), 2.35(s, 3H); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 140.2$ , 137.3, 134.5, 129.3, 128.5, 126.1, 126.0, 124.8, 121.9, 21.2; ESI MS (m/z): 201 (M + H)<sup>+</sup>. HRMS (m/z): calcd for C<sub>13</sub>H<sub>13</sub>S: 201.0653, Found: 201.0658.

## 3-(4-Chlorostyryl)thiophene (Table 3, entry 6):

Light yellow solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): $\delta$  = 7.36(d, 2H, *J* = 9.06 H<sub>z</sub>), 7.28-7.26(m, 4H), 7.22-7.21(m, 1H), 7.04(d, 1H, *J* = 16.61 Hz), 6.84(d, 1H, *J* = 16.61 Hz); <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 139.7, 135.8, 132.9, 128.7, 127.3, 127.2, 126.3, 124.7, 123.4, 122.7; ESI MS (m/z): 221 (M + H)<sup>+</sup>. HRMS (m/z): calcd for C<sub>12</sub>H<sub>10</sub>ClS :221.0123, Found: 221.0127.

## **3-(2-(Napthalen-2-yl)vinyl)quinoline (Table 3, entry 7)<sup>1</sup>:**

Yellow solid; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 9.17(s, 1H)$ , 8.10(d, 2H, J = 8.93 Hz ), 7.91-7.67(m, 7H), 7.61- 7.46(m, 5H), 7.35(d, 1H, J = 16.43 Hz); <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 149.4$ , 132.2, 130.9, 129.2, 128.4, 128.1, 127.8, 127.7, 127.2, 127.0, 126.4, 126.2, 125.4, 123.2; ESI MS (m/z): 282 (M + H)<sup>+</sup>. HRMS (m/z): calcd for C<sub>21</sub>H<sub>16</sub>N: 282.1282 Found: 282.1283.

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# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of Heck products:







# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-styryl-pyridine



# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-styryl-thiophene



# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 2-styryl-thiophene



# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-styryl-quinoline





# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 4-styryl-isoquinoline





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# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-styryl-furan







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<sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 2-nitro-5-stryl-pyridine



# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 2-metyl 6-yrylpyridine













8.0 7.5 6.5 5.5 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 6.0 5.0 0.0 7.0



# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(4-chloroystyryl)pyridine





# <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(4-chloroystyryl)thiophene

























# Dimethyl amine was detcted in reaction solution by using GC-MS Headphase anylysis.

