Supporting Information

Biopolymer-metal complex wool-Pd as a highly active catalyst for suzuki reaction in water

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General Information

All NMR spectra are recorded on MERCURY (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) spectrometers; chemical shifts are expressed in ppm (δunits) relative to TMS signal as internal reference in $CDCl_3$. Gas chromatography (GC) analysis was performed on a Shimadezu GC-2010 equipped with a 15 m × 0.53 mm × 1.5 μm RTX-1 capillary column and a oxyhydrogen flame detector. X-ray photoelectron spectroscopy analysis (XPS) measurement was recorded on PHI5702 photoelectron spectrometer. Scanning electron microscopy (SEM) was performed with field emission scanning electron microscopy (FESEM, JSM-6701F, Japan) at an accelerating voltage of 5.0 kV. X-ray diffraction (XRD) of samples was performed on a diffractometer (D/Max-2400, Rigaku) advance instrument using Cu Kα radiation (k =1.5418 Å) at 40 kV, 100mA.

Synthesis and Characterization of the catalysts

Common commercial white wool was washed with distilled water and ethanol, and then cut to pieces. Subsequently, the wool pieces were treated by the mixture of $KMnO_4$ (3g/L) and NaCl (25 g/L), and the pH was adjusted to 2.0, the mixture was stirred at 45 ^{o}C about 45 minutes, and then wool was turned to black-brown. Whereafter, the black-brown wool was dipped in the solution of Na_2SO_3 (20g/L) and HAc (10 mol/L), stirred at 50 ^{o}C for 10minutes, after the wool was returned to white, washed with water several times, and then dried at 80 ^{o}C. 1.0 g oftreated-wool pieces, 2.25 mmol $PdCl_2$ were dissolved in 30 mL of de-ionized water, the mixturewas stirred at r.t. for 8 h to cause white wool pieces to become brown and the solution to become colorless and transparent. Then, the product was filtered, and washed with de-ionized water(3 × 20 mL) and acetone (3 × 20 mL), dried in a vacuum oven at 60 ^{o}C for 4 h to obtain wool supported palladium complex（Pd 11.74%）.

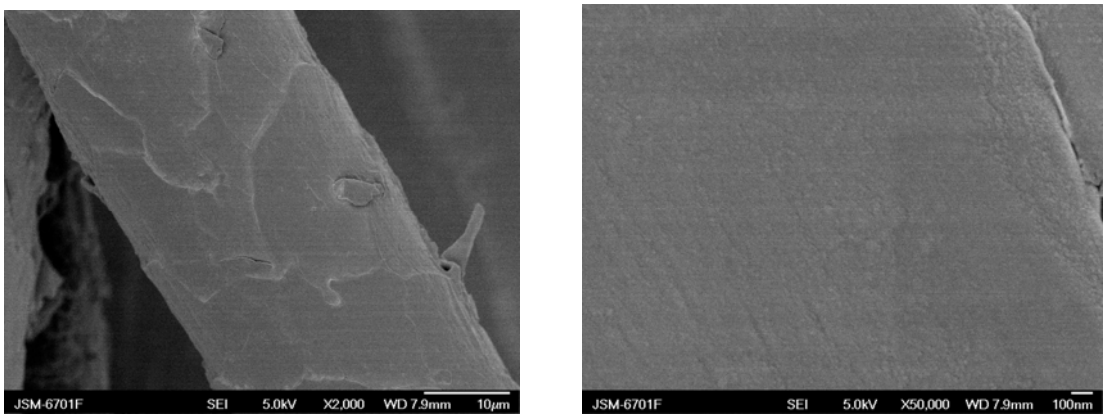


Figure 1. SEM of the wool

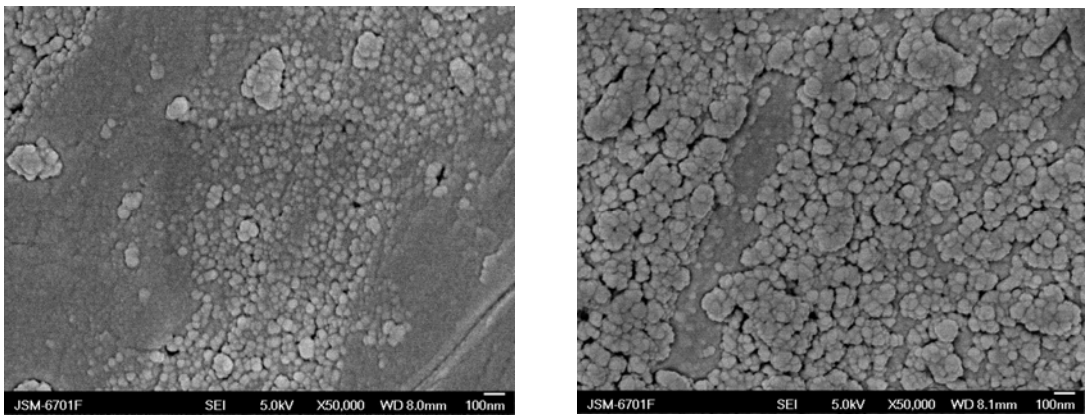


Figure 2. SEM of the wool-Pd complex after reduction

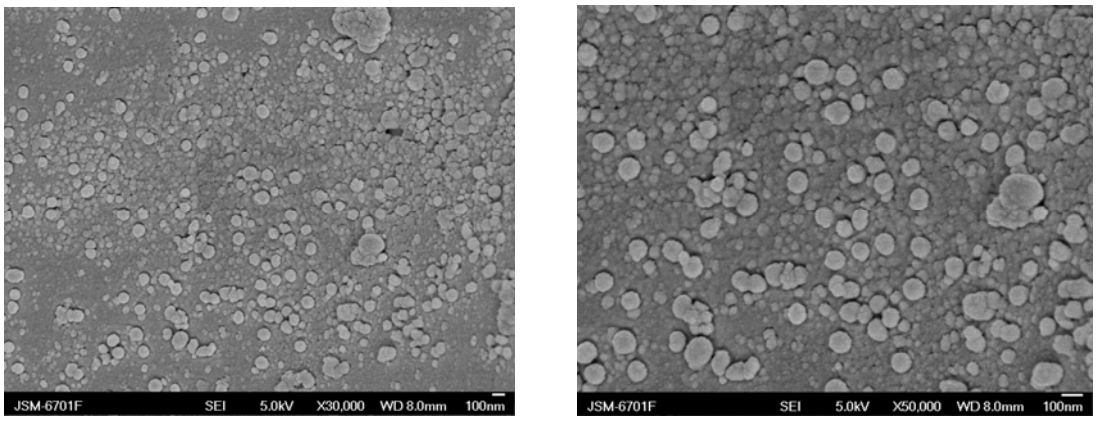


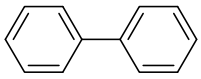
Figure 3. SEM of the wool-Pd complex after reaction

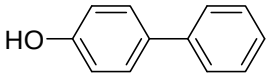
Through the observation of figure(1-3), Pd was loaded on the wool, and the average diameter of the Pd particle was about 60 nm.

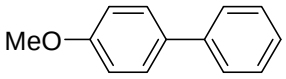
General experimental procedure for the Suzuki Reaction

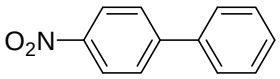
In air, arylhalide (0.2 mmol), arylboronic acid (0.22 mmol), K_2CO_3 (0.3mmol), 5mL of distilled water, and 2 mg of wool–Pd complex catalyst (Pd 0.0022 mmol) were combined in a 10 mL round-bottomed flask. The reaction mixture was magnetically stirred and the temperature was maintained at 75^{o}C with an oil bath. Reaction progress was monitored by TLC. After reaction was completed, the reaction mixture was cooled to room temperature and fitrated. The solid was washed by water(3 × 5 mL) , then by EtAc (3 × 5 mL), and the organic phase was combined. The catalyst was separated by filtration, washed with water, and dried in vacuum. The combined organic layer was dried with anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to give the product.

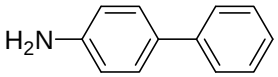
The Data for the Products 1c ~27c

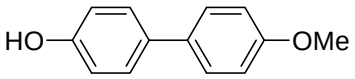
 **Biphenyl (1c)**.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.48 (m, 4H), 7.32 (m, 4H); m.p. 70~72 °C.

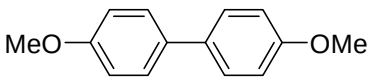
 **biphenyl-4-ol (2c)**.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.54 (m, 2H), 7.48 (m, 2H), 7.41 (m, 2H), 7.29 (m, 1H), 6.91 (m, 2H), 4.82 (m, 1H); m.p. 164~165 °C.

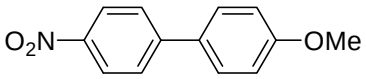
 **4-methoxybiphenyl (3c)**.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.54 (m, 4H), 7.41 (m, 2H), 7.27 (m, 1H), 6.97 (m, 2H), 3.85 (m, 3H); m.p. 88~90 °C.

 **4-nitrobiphenyl (4c)**.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.25 (m, 2H), 7.74 (m, 2H), 7.48 (m, 2H), 7.32 (m, 3H); m.p. 118~120 °C.

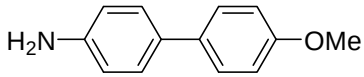
 **biphenyl-4-amine (5c)**.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.53 (m, 2H), 7.40 (m, 4H), 7.26 (m, 1H), 6.74 (m, 2H), 3.67 (m, 2H); m.p. 53~55 °C.

 **4'-methoxybiphenyl-4-ol (6c)**.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 4H), 6.96 (m, 2H), 6.89 (m, 2H), 4.73 (m, 1H), 3.84 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 158.6, 138.6, 133.4, 127.7, 124.8, 114.1, 102.6, 55.3; m.p. 180~183 °C.

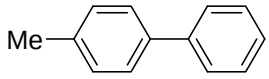
 **4,4'-dimethoxybiphenyl (7c)**.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.48 (m, 4H), 6.96 (m, 4H), 3.84 (m, 6H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 127.8, 115.6, 114.1, 55.3; m.p. 168~170 °C.

 **4-methoxy-4'-nitrobiphenyl (8c)**.[7] ^{1}H NMR (400 MHz,

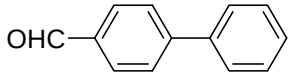
$CDCl_3$): δ =7.93 (m, 4H), 7.48 (m, 2H), 6.97 (m, 2H), 3.85 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 158.6, 133.4, 127.7, 114.1, 55.3; m.p. 110~113 °C.



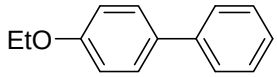
4'-methoxybiphenyl-4-amine (9c).[8] ^1H NMR (400 MHz, $CDCl_3$): δ =7.46 (m, 2H), 7.36 (m, 2H), 6.96 (m, 2H), 6.74 (m, 2H), 3.84 (m, 3H), 3.66 (m, 2H); m.p. 153~155 °C.



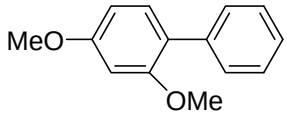
4-methylbiphenyl (10c).[9] ^1H NMR (400 MHz, $CDCl_3$): δ =7.58 (m, 3H), 7.50 (m, 2H), 7.44 (m, 3H), 7.26 (m, 1H), 3.84 (m, 3H); m.p. 60~62 °C.



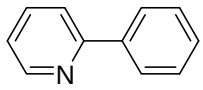
biphenyl-4-carbaldehyde (11c).[7] ^1H NMR (400 MHz, $CDCl_3$): δ =9.87 (m, 1H), 7.87 (m, 2H), 7.67 (m, 2H), 7.48 (m, 2H), 7.32 (m, 2H); m.p. 62~65 °C.



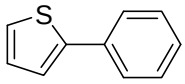
4-ethoxybipheny (12c).[10] ^1H NMR (400 MHz, $CDCl_3$): δ =7.53 (m, 4H), 7.41 (m, 2H), 7.26 (m, 2H), 6.96 (m, 1H), 4.08 (m, 2H), 1.44 (m, 3H).



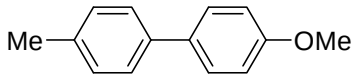
2,4-dimethoxybiphenyl (13c).[11] ^1H NMR (400 MHz, $CDCl_3$): δ =7.48 (m, 2H), 7.38 (m, 4H), 6.51 (m, 2H), 3.84 (m, 6H).



2-phenylpyridine (14c).[12] ^1H NMR (400 MHz, $CDCl_3$): δ =8.70 (m, 1H), 7.98 (m, 2H), 7.75 (m, 2H), 7.48 (m, 3H), 7.43 (m, 1H).

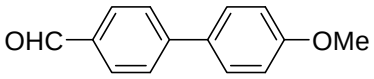


2-phenylthiophene (15c).[13] ^1H NMR (400 MHz, $CDCl_3$): δ =7.61 (m, 2H), 7.37 (m, 2H), 7.28 (m, 3H), 7.08 (m, 1H).

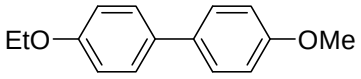


4-methoxy-4'-methylbiphenyl (16c).[14] ^1H NMR (400 MHz, $CDCl_3$): δ =7.48 (m, 4H), 7.24 (m, 2H), 6.96 (m, 2H), 3.85 (m, 3H), 2.38 (m,

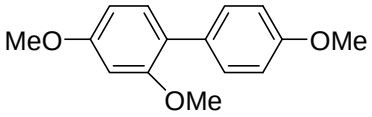
3H).



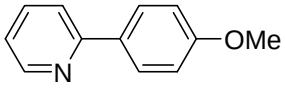
4'-methoxybiphenyl-4-carbaldehyde (17c). ^{1}H NMR (400 MHz, $CDCl_3$): δ =10.04 (m, 1H), 7.92 (m, 2H), 7.73 (m, 2H), 7.60 (m, 2H), 7.03 (m, 2H), 3.87 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 191.9, 160.1, 146.8, 134.6, 132.0, 130.2, 128.5, 127.0, 114.2, 55.4; m.p. 105~108 ^{o}C.



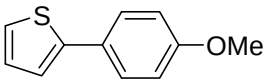
4-ethoxy-4'-methoxybiphenyl (18c).[15] ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.47 (m, 4H), 6.96 (m, 4H), 4.07 (m, 3H), 3.85 (m, 3H), 1.43 (m, 3H).



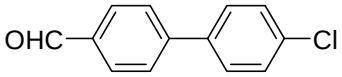
2,4,4'-trimethoxybiphenyl (19c). ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.42 (m, 2H), 7.21 (m, 1H), 6.94 (m, 2H), 6.55 (m, 2H), 3.83 (m, 9H).



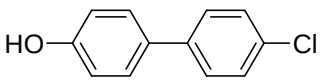
2-(4-methoxyphenyl)pyridine (20c). ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.66 (m, 1H), 7.95 (m, 2H), 7.70 (m, 2H), 7.18 (m, 1H), 7.00 (m, 2H), 3.85 (m, 3H).



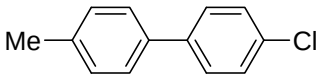
2-(4-methoxyphenyl)thiophene (21c). ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.37 (m, 2H), 7.20 (m, 1H), 6.99 (m, 2H), 6.83 (m, 2H), 3.73 (m, 3H).



4'-chlorobiphenyl-4-carbaldehyde (22c). ^{1}H NMR (400 MHz, $CDCl_3$): δ =10.06 (m, 1H), 7.96 (m, 2H), 7.73 (m, 2H), 7.54 (m, 2H), 7.26 (m, 2H).

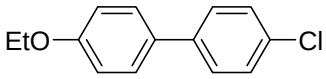


4'-chlorobiphenyl-4-ol (23c).[16] ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.45 (m, 4H), 7.37 (m, 2H), 6.90 (m, 2H), 4.88 (m, 1H).

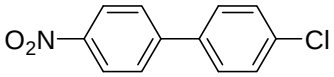


4-chloro-4'-methylbiphenyl (24c). ^{1}H NMR (400 MHz,

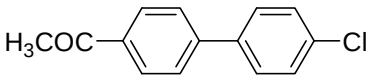
$CDCl_3$): δ =7.43 (m, 6H), 7.26 (m, 2H), 2.39 (m, 3H).



4-chloro-4'-ethoxybiphenyl (25c). ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.46 (m, 6H), 6.96 (m, 2H), 4.08 (m, 2H), 1.43 (m, 3H).



4-chloro-4'-nitrobiphenyl (26c). ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.11 (m, 2H), 7.70 (m, 2H), 7.26 (m, 4H).



1-(4'-chlorobiphenyl-4-yl)ethanone (27c). ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.03 (m, 2H), 7.65 (m, 2H), 7.56 (m, 2H), 7.44 (m, 2H), 2.65 (m, 3H).

References

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