Supporting Information
for DOI: 10.1055/s-0035-1561113
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Supporting Information

Palladium–Polypyrrole Nanocomposites Pd@PPy for Direct C–H Functionalization of Pyrroles and Imidazoles with Bromoarenes

Pierre Bizouarda
Christelle Testa¹
Veronika A. Zinovyevab
Julien Rogera
Jean-Cyrille Hiersoa,c

¹ Institut de Chimie Moléculaire de l’Université de Bourgogne, ICMUB-UMR CNRS 6302, Univ. de Bourgogne Franche-Comté, 9 Avenue Alain Savary, 21078 Dijon Cedex, France.

b Institut de Physique Nucléaire, CNRS-IN2P3, Univ. Paris-Sud, Université Paris-Saclay, 91406 Orsay Cedex, France.

c Institut Universitaire de France (IUF), 103 Boulevard Saint Michel, 75005 Paris Cedex, France.
**Synthesis of Pd@PPy Nanocomposites:**
In typical synthesis, equal volumes (250 ml) of initial aqueous solutions containing 0.6587 g (2.5 mmol) of Pd(NH$_3$)$_4$Cl$_2$ monohydrate and 10.065 g (150 mmol) of pyrrole monomer were mixed. The color of the mixture changed from pale yellow to light brown due to colloid formation in the first 15 min after starting the reaction. Progressive darkening of the solution occurred. The reaction mixture was stirred in an ultrasonic bath ($T = 40–50 \degree C$) for 5 hours per day during 5 days, until colloid sedimentation occurred. For all investigated systems supernatant was decanted after completion of the precipitation process. The colloid sedimentation could eventually be effected by addition of a sufficient amount of (NH$_4$)$_2$CO$_3$ (2.5 g). The obtained dark precipitate was rinsed several times with water until the effluent became colourless and pH-neutral, and was then dried under vacuum at 60 °C for 4 hours. Pd@PPy composite was used without further operation for characterization and catalytic tests.

**Characterization of coupling products**

5-(4-Acetylphenyl)-1-methyl-2-formylpyrrole (3a):
The reaction of 4-bromoacetophenone (0.200 g, 1 mmol), 1-methyl-2-formylpyrrole (0.200 ml, 2 mmol) and KOAc (0.196 g, 2 mmol) with the Pd@pPy (0.006 g, 2 mol%) affords the corresponding product 3a in 58% isolated yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 9.60 (s, 1H), 8.05 (d, $J = 8.2$ Hz, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.00 (d, $J = 4.0$ Hz, 1H), 6.38 (d, $J = 4.0$ Hz, 1H), 3.95 (s, 3H), 2.65 (s, 3H).

4-(5-Formyl-1-methylpyrrol-2-yl)-benzonitrile (3b):
The reaction of 4-bromobenzonitrile (0.091 g, 1 mmol), 1-methyl-2-formylpyrrole (0.100 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product 3b in 41% isolated yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 9.61 (s, 1H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.00 (d, $J = 4.1$ Hz, 1H), 6.37 (d, $J = 4.1$ Hz, 1H), 3.95 (s, 3H).

1-methyl-5-(4-(trifluoromethyl)phenyl)-1H-pyrrole-2-carbaldehyde (3c):
The reaction of 4-trifluoromethylbromobenzene (0.070 ml, 1 mmol), 1-methyl-2-formylpyrrole (0.100 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product 3c in 42% isolated yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 9.64 (s, 1H), 7.75 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.02 (d, $J = 4.1$ Hz, 1H), 6.38 (d, $J = 4.1$ Hz, 1H), 3.96 (s, 3H).
5-(4-Methoxyphenyl)-1-methyl-2-formylpyrrole (3d):
The reaction of 4-bromoanisole (0.063 ml, 1 mmol), 1-methyl-2-formylpyrrole (0.100 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product 3d in 35% isolated yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta = 9.56$ (s, 1H), 7.36 ($J = 8.3$ Hz, 2H), 7.01 ($J = 8.3$ Hz, 2H), 6.99 ($J = 4.1$ Hz, 1H), 6.27 ($J = 4.1$ Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H).

5-(4-Methylphenyl)-1-methyl-2-formylpyrrole (3e):
The reaction of 4-bromotoluene (0.062 ml, 1 mmol), 1-methyl-2-formylpyrrole (0.100 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product 3e in 68% isolated yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta = 9.59$ (s, 1H), 7.34 ($J = 8.5$ Hz, 2H), 7.28 ($J = 8.5$ Hz, 2H), 7.00 ($J = 4.1$ Hz, 1H), 6.30 ($J = 4.1$ Hz, 1H), 3.94 (s, 3H), 2.44 (s, 3H).

1-(4-(5-acetyl-1-methyl-1H-pyrrol-2-yl)phenyl)ethanone (6a):
The reaction of 4-bromoacetophenone (0.100 g, 1 mmol), 1-methyl-2-acetylpyrrole (0.120 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2% mol) affords the corresponding product 6a in 28% isolated yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta = 8.02$ ($J = 8.4$ Hz, 2H), 7.51 ($J = 8.4$ Hz, 2H), 7.03 ($J = 4.0$ Hz, 1H), 6.29 ($J = 4.0$ Hz, 1H), 3.91 (s, 3H), 2.64 (s, 3H), 2.48 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 197.4$, 188.7, 141.4, 136.4, 136.3, 132.7, 129.3, 128.6, 119.7, 110.1, 35.4, 27.5, 26.7.

Elemental analysis: Calcld (%) for C$_{15}$H$_{15}$NO$_2$: C 74.67, H 6.27, N 5.81. Found: C 73.92, H 6.33, N 5.40

HRMS + p ESI (m/z) [M+H$^+$] Calcld for C$_{15}$H$_{15}$NO$_2$: 242.118. Found: m/z = 242.172.

2-(5-Formyl-1-methylpyrrol-2-yl)benzonitrile (7a):
The reaction of 2-bromobenzonitrile (0.091 g, 1 mmol), 1-methyl-2-formylpyrrole (0.100 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product 7a in 57% isolated yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta = 9.65$ (s, 1H), 7.82 ($J = 8.0$ Hz, 1H), 7.69 ($J = 8.0$ Hz, 1H), 7.56 ($J = 7.5$ Hz, 1H), 7.50 ($J = 7.5$ Hz, 1H), 7.03 ($J = 4.1$ Hz, 1H), 6.46 ($J = 4.1$ Hz, 1H), 3.87 (s, 3H).

5-(2-fluorophenyl)-1-methyl-1H-pyrrole-2-carbaldehyde (7b):
The reaction of 2-bromofluorobenzene (0.055 ml, 1 mmol), 1-methyl-2-formylpyrrole (0.100 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product 7b in 26% isolated yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta = 9.62$ (s, 1H), 7.80-7.05 (m, 4H), 7.02 ($J = 4.1$ Hz, 1H), 6.33 ($J = 4.1$ Hz, 1H), 3.86 (s, 3H).
**1-methyl-5-(o-tolyl)-1H-pyrrole-2-carbaldehyde (7c):**
The reaction of 2-bromotoluene (0.060 ml, 1 mmol), 1-methyl-2-formylpyrrole (0.100 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product **7c** in 35% isolated yield.
$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 9.55$ (s, 1H), 7.32–7.18 (m, 5H), 6.98 (d, $J = 3.9$ Hz, 1H), 6.16 (d, $J = 3.9$ Hz, 1H), 3.67 (s, 3H), 2.14 (s, 3H).

**1-methyl-5-(m-tolyl)-1H-pyrrole-2-carbaldehyde (7d):**
The reaction of 3-bromotoluene (0.060 ml, 1 mmol), 1-methyl-2-formylpyrrole (0.100 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product **7d** in 41% isolated yield.
$^1$H NMR (300 MHz, CDCl$_3$): 9.57 (s, 1H), 7.37–7.32 (m, 1H), 7.26–7.20 (m, 3H), 6.96 (dd, $J = 4.1$ Hz, 1H), 6.29 (d, $J = 4.1$ Hz, 1H), 3.93 (s, 3H), 2.41 (s, 3H).

**1-(2-(5-acetyl-1-methyl-1H-pyrrol-2-yl)phenyl)ethan-1-one (8a):**
The reaction of 2-bromoacetophenone (0.067 ml, 1 mmol), 1-methyl-2-acetylpyrrole (0.100 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product **8a** in 14% ($^1$H NMR yield).

**5-(2-Tolyl)-1-methyl-2-acetylpyrrole (8b):**
The reaction of 2-bromotoluene (0.060 ml, 1 mmol), 1-methyl-2-acetylpyrrole (0.120 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product **8b** in 23% isolated yield.
$^1$H NMR (200 MHz, CDCl$_3$): $\delta = 7.50$–7.20 (m, 4H), 7.06 (d, $J = 4.1$ Hz, 1H), 6.12 (d, $J =$4.1 Hz, 1H), 3.67 (s, 3H), 2.50 (s, 3H), 2.17 (s, 3H).

**1-(4-(1-methyl-1H-imidazol-5-yl)phenyl)ethanone (10a):**
The reaction of 4-bromoacetophenone (0.100 g, 1 mmol), 1-methylimidazole (0.080 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product **10a** in 62% ($^1$H NMR yield).
$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.50$ (s, 1H), 7.31 (m, 2H), 7.04 (m, 2H), 3.84 (s, 3H), 3.63 (s, 3H) ppm.

**1-(4-(1-methyl-1H-imidazol-5-yl)phenyl)ethanone (10b):**
The reaction of 4-bromoacetophenone (0.187 g, 1 mmol), 1-methylimidazole (0.159 ml, 2 mmol), CuI (0.190 mg, 1 mmol) and Cs$_2$CO$_3$ (0.651 g, 2 mmol) with the Pd@pPy (0.006 g, 2 mol%) affords the corresponding product **10b** in 77% ($^1$H NMR yield).
5-(4-Methoxyphenyl)-1-methylimidazole (11a):
The reaction of 4-bromoanisole (0.100 g, 1 mmol), 1-methylimidazole (0.080 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product 11a in 92% (1H NMR yield).

$^{1}$H NMR (200 MHz, CDCl$_3$) $\delta$ = 7.53 (s, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.05 (s, 1H), 6.99 (d, $J = 8.0$ Hz, 2H), 3.87 (s, 3H), 3.65 (s, 3H).

5-(4-Tolyl)-1-methylimidazole (12a):
The reaction of 2-bromotoluene (0.060 ml, 1 mmol), 1-methylimidazole (0.080 ml, 2 mmol) and KOAc (0.098 g, 2 mmol) with the Pd@pPy (0.003 g, 2 mol%) affords the corresponding product 12a in 76% (1H NMR yield).

$^{1}$H NMR (200 MHz, CDCl$_3$) $\delta$ = 7.51 (s, 1H), 7.29 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.2$ Hz, 2H), 7.08 (s, 1H), 3.65 (s, 3H), 2.40 (s, 3H).