Supporting Information

Efficient, recyclable and phosphine-free carbonylative Suzuki coupling reaction using immobilized palladium ion-containing ionic liquid: Synthesis of aryl ketones and heteroaryl ketones

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1 General information

1.1 Materials and Methods:

N-Methylimidazole (99+%) and 3-trimethoxysilylpropyl chloride (97+%) were purchased from Aldrich. $PdCl_2$ was purchased from WAKO, Japan. Anhydrous redistilled 1-methylimidazole (99+%) was purchased from Aldrich. All the dehydrated solvents were obtained from WAKO. Aerosil 300 (300 m^2/g) was obtained from Japan Aerosil Co. and calcined at 573K for 1.5 h in air and 30 min in vacuum before use as a support. The procedures for the catalyst preparation were based on our previous publication with some modifications.[1-3] Prepared catalyst was characterized by using IR, elemental analysis, and loading of the catalyst was calculated by XRF measurements (SEA-2010, Seiko Electronic Industrial Co.). The XPS of ImmPd-IL was measured using a PHI5000 Versa Probe with a monochromatic focused (100 x 100 μm) Al Kα X-ray radiation (15kV, 30 mA) and dual beam neutralization using a combination of Argon ion gun and electron irradiation.

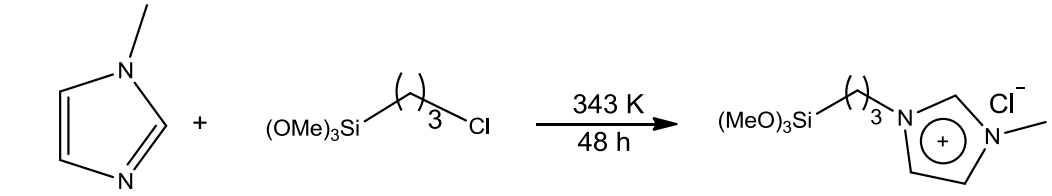
The products are well known in the literature and were confirmed by GC, GC-MS, ^1H NMR spectroscopic techniques. Progress of the reaction was monitored with gas chromatography. The product was purified by column chromatography on silica gel (100-200 mesh). Gas chromatography analysis was carried out on Perkin Elmer Clarus 400 GC equipped with a capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID). GC-MS-QP 2010 instrument (Rtx-17, 30 m, 25 mm ID, film thickness 0.25 mm df) (column flow 2 mLmin1, 80 °C to 240 °C at 10 °/min rise.). The ^1H NMR spectra were recorded with Varian-400 MHz FT-NMR spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as internal standard. *J* (coupling constant) values were reported in Hz. Splitting patterns of proton are described as s (singlet), d (doublet), t (triplet), and m (multiplet).

1.2 Preparation of ImmPd-IL

Immobilized metal ion-containing ionic liquid catalysts were prepared as shown below.[1-3]

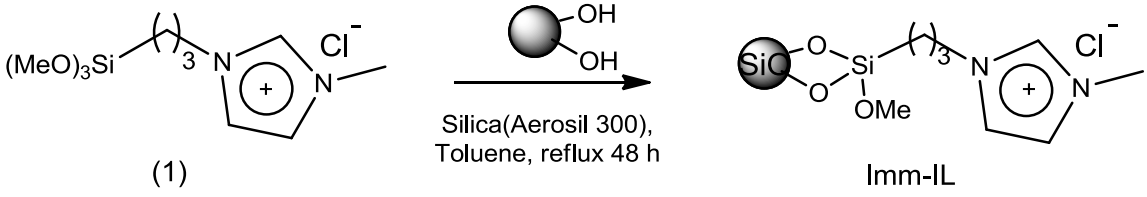
Step 1.2.1:

1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride was synthesized by mixing *N*-methylimidazole (0.690 mol) and 3-trimethoxysilylpropyl chloride (0.690 mol) in a dry 300 ml flask under a nitrogen atmosphere and refluxed for 48 h. After cooling to room temperature, the resultant liquid was washed with dehydrated ethyl acetate five times and dried at room temperature under reduced pressure for 48 h.



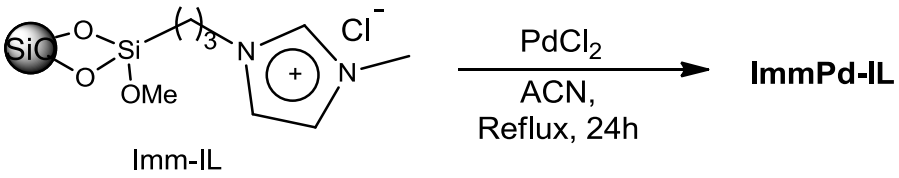
Step 1.2.2:

The obtained compound was stored at 253 K under dry nitrogen. Silica (Aerosil 300, surface area 300 m^2/g, calcined at 573 K for 1.5 h in air) and 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride (weight ratio 1:1) were dispersed in dehydrated toluene and the mixture was refluxed for 48 h under nitrogen. After the reflux, toluene was removed by filtration using glass filter and the excess ionic liquid was removed by washing with dichloromethane several times. The resultant solid is denoted as Imm-IL.



Step 1.2.3

In the next step, Imm-IL was added to an acetonitrile solution of $PdCl_2$ and refluxed for 24 h. Acetonitrile and excess of metal chloride was removed by washing acetone using glass filter several times.



1.3 Characterization of ImmPd-IL

The metal loading of ImmPd-IL was 3.4 wt% as determined by XRF measurements (SEA-2010, Seiko Electronic Industrial Co.). Figure 1 shows the IR spectrum taken for the ImmPd-IL (3 mg in KBr 200 mg disc). Absorption peaks appear at 1427, 1458, 1570, 1624, 1863, 2949, 3108 and 3151 cm^{-1}, which are commonly observed for alkylimidazolium salts, indicating that alkylimidazolium groups are retained in ImmPd-IL.

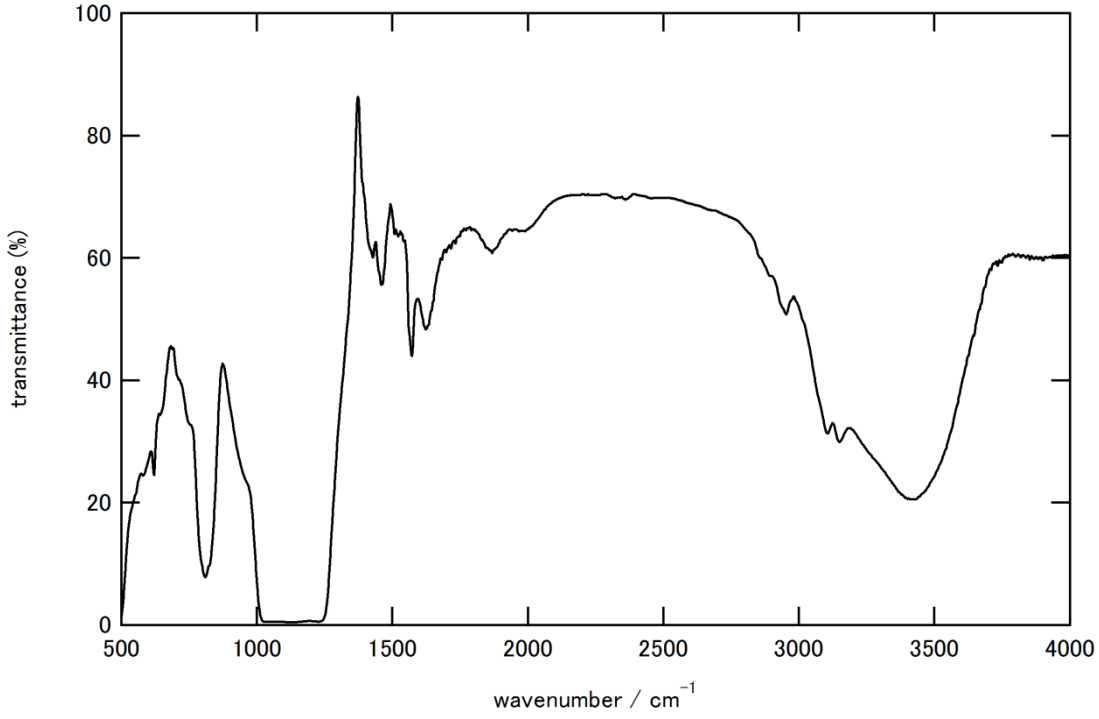


Figure 1: IR spectrums taken for the fresh ImmPd-IL catalyst with KBr disc.

1.4 General experimental procedure for the carbonylative Suzuki reaction of aryl iodide

To a 100 ml autoclave aryl iodide (1.0 mmol), aryl boronic acid (1.2 mmol), ImmPd-IL (2 mol%), toluene (10 mL) and K_2CO_3 (3 mmol) was added. The mixture was first stirred for 10 min and then flushed with CO three times, then 1 Mpa of CO was taken and the reaction mixture was heated at 100 °C for 8 h. After completion of reaction, the reaction mixture was cooled to room temperature and remaining CO gas was carefully vented and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate (2 x 10 mL) to remove any traces of product and catalyst if present. The catalyst was filtered and residue obtained was purified by column chromatography (silica gel, 100-200 mesh; petroleum ether/ethyl acetate) to afford the desired carbonylated product. The products were confirmed by GC, GC-MS, ^{1}H NMR spectroscopic techniques. The purity of compounds was determined by GC-MS analysis.

1.5 General experimental procedure for the carbonylative Suzuki reaction of heteroaryl iodide

To a 100 ml autoclave heteroaryl iodide (1.0 mmol), aryl boronic acid (1.2 mmol), ImmPd-IL (2.5 mol%), toluene (10 mL) and K_2CO_3 (3 mmol) was added. The mixture was first stirred for 10 min and then flushed with CO three times, then 1 Mpa of CO was taken and the reaction mixture was heated at 100 °C for 10 h. After completion of reaction, the reaction mixture was cooled to room temperature and remaining CO gas was carefully vented and the reactor was opened. The reactor vessel was thoroughly washed with ethyl acetate (2 x 10 mL) to remove any traces of product and catalyst if present. The catalyst was filtered and residue obtained was purified by column chromatography (silica gel, 100-200 mesh; petroleum ether/ethyl acetate) to afford the desired carbonylated product. The products were confirmed by GC, GC-MS, ^{1}H NMR spectroscopic techniques. The purity of compounds was determined by GC-MS analysis.

1.5 Procedure for catalyst recycling

The catalyst obtained after filtration was washed with distilled water (5 mL × 3) and then with methanol (5 mL × 3) to remove any organic material present. The resulting catalyst was dried under reduced pressure and used for the next cycle.

2 Spectral Data of the products

Benzophenone [4]

(160 mg, 88%), GC-MS (EI, 70 eV): *m/z* (%) = 182 [M^+] (55), 105 (100), 77 (70).

4-methylbenzophenone[4]

(172 mg, 88%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.77-7.75 (d, 2H, *J* = 7.0 Hz), 7.71-7.69 (d, 2H, *J* = 8.2 Hz), 7.54-7.42 (m, 3H), 7.26-7.24 (d, 2H, *J* = 7.9 Hz), 2.4 (s, 3H); GC-MS (EI, 70 eV): *m/z* (%) = 196 [M^+] (72), 119 (100), 105 (35), 91 (39), 77 (28).

4-Acetylbenzophenone[5]

(170 mg, 76%), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07-8.04 (d, *J* = 8.8 Hz, 2 H), 7.88-7.87 (d, *J* = 8.4 Hz, 2 H), 7.82-7.79 (d, *J* = 8.4 Hz, 2 H), 7.65-7.59 (t, *J* = 8.8 Hz, 2 H), 7.52-7.47 (t, *J* = 7.5 Hz, 1 H), 2.66 (s, 3 H); GCMS (EI, 70 eV): *m/z* (%) = 224 [M^+] (50), 209 (100), 181 (20), 147 (30), 105 (75), 77 (79), 43 (30).

4-Nitrobenzophenone[5]

(204 mg, 90%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.35-8.34 (d, 2H, *J* = 8.8 Hz), 7.95-7.93 (d, 2H, *J* = 8.4 Hz), 7.81-7.79 (d, 2H, *J* = 6.8 Hz), 7.65-7.49 (m, 3H); GC-MS (EI, 70 eV): *m/z* (%) = 227 [M^+] (45), 105 (100), 77 (55).

4-Methoxybenzophenone[5]

(170 mg, 80%), GC-MS (EI, 70 eV): *m/z* (%) = 212 [M^+] (50), 135 (100), 105 (25), 77 (35).

4-Bromobenzophenone[5]

(206 mg, 79%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.78-7.76 (d, 2H, *J* = 7.3 Hz), 7.69-7.67 (d, 2H, *J* = 8.2 Hz), 7.63-7.61(d, 2H, *J* = 8.2 Hz), 7.60-7.47 (m, 3H); GC-MS (EI, 70 eV): *m/z* (%) = 260 [M^+] (45), 181 (40), 105 (100), 77 (55).

3-Benzoylpyridine[6]

(162mg, 89%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.03-9.01 (d, *J* = 1.2 Hz, 1H), 8.86-8.85 (dd, *J* = 4.8 and 1.8 Hz, 1H), 8.18-8.16 (dd, *J* = 7.9 and 1.8 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.79-7.39 (m, 4H); GC-MS (EI, 70 eV): *m/z* (%) = 183 [M^+] (100), 105 (90) 77 (85), 51 (40).

Pyridin-3-yl-*p*-tolyl-methanone[6]

(160 mg, 81%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.90 (s, 1H), 8.74-8.72 (d, *J* = 4.4 Hz, 1H), 8.09-8.06 (d, *J* = 1.4 Hz, 1H), 7.72-7.70 (d, *J* = 7.8 Hz, 2H), 7.43-7.46 (dd, *J* = 4.87 & 4.87 Hz, 1H), 7.29-7.25 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H); GC-MS (EI, 70 eV): *m/z* (%) = 197 [M^+] (51), 182 (50), 119 (100), 91 (39), 77 (40).

(4-Methoxy-phenyl)-pyridin-3-yl-methanone[7]

(171 mg, 80%), GC-MS (EI, 70 eV): *m/z* (%) = 213 [M^+] (60), 198 (20), 135 (100).

2-Benzoylthiophene[8]

(151 mg, 80%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.88-7.85 (d, *J* = 7.6 Hz, 2H), 7.73-7.71 (m, 5H), 7.15-7.17 (m, 1H); GC-MS (EI, 70 eV): *m/z* (%) = 188 [M^+] (70), 111 (100), 77 (31).

Thiophen-2-yl-*p*-tolyl-methanone[7]

(159 mg, 79%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.75-7.70 (d, *J* = 8.5 Hz, 2H), 7.65-7.73 (m, 1H), 7.60-7.58 (m, 1H), 7.29-7.28 (d, *J* = 7.6 Hz, 2H), 7.14-7.11 (m, 1H), 2.45 (s, 3H); GC-MS (EI, 70 eV): *m/z* (%) = 202 [M^+] (100), 187 (55), 119 (80), 111 (71), 77 (35).

(4-methoxyphenyl)(thiophen-2-yl)methanone[7]

(168 mg, 77%), ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.91-7.89 (d, J = 8.5 Hz, 2H), 7.69-7.67 (m, 2H), 7.17-7.15 (m, 1H), 6.95-6.98 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H); GC-MS (EI, 70 eV): *m/z* (%) = 218 [M^+] (75), 187 (35), 135 (100), 77 (39).

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