Experimental section:

Reagents: All reagents were purchased from Aladdin Reagent Company and Alfa-Aesar Company without further purification.

Analytical Methods: ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 500 MHz instrument with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane. Gas chromatography analyses were performed on a Hewlett Packard 5890 instrument with a FID detector and Hewlett Packard 24 m x 0.2 mm i.d. HP-5 capillary column. Yield refers to isolated yields of compounds greater than 95% purity as determined by capillary gas chromatography (GC) and proton Nuclear Magnetic Resonance spectroscopy (¹H-NMR) analysis.

The ICP-OES (inductively coupled plasma optical emission spectroscopy) analysis was performed with Perkin Elmer OPTIMA 2000DV. Element analysis was carried out on the Elementar Vario EL III instrument. TEM (Transmission electron microscopy) images were obtained on a transmission electron microscope (Tecnai 12) with an accelerating voltage of 120 kV and SEM images were taken using a scanning electron microscope (HITACHI S4800) operated at an accelerating voltage of 10–20 kV.

Preparation of IL monomer VIA-HBr:

Bromoacetic acid (27.79 g, 0.2 mol) was dissolved in toluene (300 mL) in ice-bath condition, and 1-vinylimidazole (18.82 g, 0.2 mol) was added drop slowly to the solution. The mixture was refluxed for 24 h under a nitrogen atmosphere after stirring half an hour at rt. Then, the reaction mixture was cooled down, and the liquid was poured out and the solid was washed by anhydrous acetonitrile (200 mL) three times to remove the unreacted starting materials. After dried by vacuum for 24 h, a light yellow solid was obtained as the IL monomer VIA-HBr (42 g, 90% yield). ¹H NMR (500 MHz, DMSO): δ 5.19 (s, 2H), 5.46-5.48 (m, 1H), 5.98-6.02 (m, 1H), 7.38-7.43 (m, 1H), 7.88-7.89(m, 1H), 8.23-8.24 (m, 1H), 9.47-9.48 (m, 1H), 13.81 (s, 1H). ¹³C NMR (300 MHz): δ 49.99, 109.12., 118.52, 124.65, 128.78, 136.50, 167.84. Calcd for C₇H₉BrN₂O₂: C, 36.7%; H, 3.89%; N, 12.0%; Br, 34.3%. Found: C, 34.23%; H, 4.92%; N, 11.48%; Br, 34.4%.

Preparation of PIC:

IL monomer VIA-HBr (39 g, 0.167 mol), divinylbenzene (21 g, 0.16 mol) and AIBN (azobisisobutyronitrile) (2.4 g, 14.6 mmol) was dissolved in anhydrous ethanol (250 mL) under argon. After stirring at 70 °C for 4 h, the mixture was heated to 80 °C for another 24 h without stirring and then a white solid formed in the mixture. The solid was filtrated and washed with THF and ethanol 3 times respectively after the reaction mixture cooled, and then solid was treated with excess of Na₂CO₃ solution of to remove HBr on the copolymer. After washed completely with water, the solid was dried under vacuum at 100 °C for 12 h, and then PIC (42 g) was obtained in 70% yield. The composition of PIC was examined by elemental analysis, and the result indicated that the content of IL VIA was 22.3 wt% (25.1 mol%). Element analysis: C, 68.89%; H, 7.47%; N, 4.61%.

Preparation of Pd(OAc)₂/PIC:

The $Pd(OAc)_2$ (0.422 g, 1.88 mmol) was dissolved in 20 mL acetone. The material PIC (10.0 g) was added to it with vigorous stirring. The mixture was further stirred for 3 h, and then acetone was removed to give $Pd(OAc)_2/PIC$ (10.4 g, Pd wt 2%).



Fig. S1 TG analysis of the PIC.



Fig. S2 SEM image of the PIC (High-resolution image of fig. 1).



Fig. S3 Nitrogen adsorption-desorption isotherms of PIC.



Fig. S4 the Pd nanoparticles on the PIC (collected after the 1^{st} time reaction). (High-resolution image of fig. 2 left).



Fig. S5 the Pd nanoparticles on the PIC (collected after the 5th time reaction) (High-resolution image of fig. 2 right).



Fig. S6 Reusability of the Pd nanocatalyst (1% Pd) for the coupling of 4-bromoanisole with phenylboronic acid.

Recycling Procedure: When the reaction completed and the reaction mixture was cooled, the catalyst (Pd/PIC (Pd, 1 mol%)) was collected by filtration and dried by vacuum pump at the 50 °C for 12 h. The catalyst was added to a pressure tube with 4-bromoanisole (0.187 g, 1.0 mmol), phenylboronic acid (0.1463 g, 1.2 mmol, 1.2 eqv.), TBAB (0.3224 g, 1.0 mmol, 1 eqv.), Na₂CO₃ (0.212 g, 2.0 mmol, 2 eqv.) and water (2 mL) under air for the next reaction cycle. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and 100 μ L C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 15 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield (Fig. S6).



Fig.S7 Reusability of the Pd nanocatalyst (0.1% Pd) for the coupling of 4-bromoanisole with phenylboronic acid.

Recycling Procedure: The catalyst (Pd(OAc)₂/PIC (0.0267 g, 5.0×10^{-6} mol Pd, 0.1 mol%) was added to a pressure tube with 4-bromoanisole (0.9352 g, 5.0 mmol), phenylboronic acid (0.7316 g, 6.0 mmol, 1.2 eqv.), TBAB (1.6119 g, 5.0 mmol, 1 eqv.), Na₂CO₃ (1.060 g, 10.0 mmol, 2 eqv.) and water (10 mL) under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and 100 μ L C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 15 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield.

When the reaction completed and the reaction mixture was cooled, the catalyst Pd/PIC was collected by filtration and dried by vacuum pump at the 50 $^{\circ}$ C for 12 h. And then the Pd/PIC was added to a pressure tube with 4-bromoanisole (0.9352 g, 5.0 mmol), phenylboronic acid (0.7316 g, 6.0 mmol, 1.2 eqv.), TBAB (1.6119 g, 5.0 mmol, 1 eqv.), Na₂CO₃ (1.060 g, 10.0 mmol, 2 eqv.) and water (10 mL) under air for the next reaction cycle. The yields of 5 reaction runs were shown in Fig. S7.



Fig.S8 Reusability of the Pd nanocatalyst (1% Pd) for the coupling of 4-chloroacetophenone with phenylboronic acid.

Recycling Procedure: When the reaction $[Pd(OAc)_2/PIC (0.0532 \text{ g}, 1.0 \times 10^{-5} \text{ mol Pd}, 1 \text{ mol}\%$, the same reaction condition as Table 3, entry 7)] completed and the reaction mixture was cooled, the catalyst (Pd/PIC) was collected by filtration and dried by vacuum pump at the 50 °C for 12 h. The catalyst was added to a pressure tube with 4-chloroacetophenone (0.1546 g, 1.0 mmol), phenylboronic acid (0.1463 g, 1.2 mmol, 1.2 eqv.), TBAB (0.3224 g, 1.0 mmol, 1 eqv.), NaOH (0.080 g, 2.0 mmol, 2 eqv.) and water (2 mL) under air for the next reaction cycle. The pressure tube was placed in an oil bath for 10 h at 120 °C. The reaction mixture was cooled to room temperature and 100 μ L C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 15 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield. The yields of 5 reaction runs were shown in Fig. S8.

Typical Procedure for Pd catalytic Suzuki reactions of Aryl halides with Phenylboronic acid: A pressure tube was charged with aryl halide, phenylboronic acid, Pd(OAc)₂/PIC (Pd 0.001

mol%-3.0 mol%), TBAB, Na₂CO₃, H₂O. The reaction mixture was heated (to desired temperature) and stirred for 2-10 hours under air. The mixture was cooled to room temperature, then extracted with ethyl acetate (15 mL×3). The organic extracts were dried over anhydrous Mg₂SO₄. And then the products were isolated by column with silica gel.

Suzuki coupling of aryl bromides and phenylboronic acid (Table 2):

4-bromoanisole (0.468 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 30:1). **4-Methoxy-biphenyl** was collected as a white solid (0.455 g, 99% yield).^[1] ¹H-NMR (500 MHz, CDCl₃): δ 3.82 (s, 3H), 6.96 (d, *J* = 8.5 Hz, 2H), 7.27-7.30 (m, 1H), 7.39 (t, *J* = 6.3 Hz, 2H), 7.50-7.54 (m, 4H).

2-bromoanisole (0.468 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 30:1). **2-Methoxy-biphenyl** was collected as colorless oil (0.45 g, 98% yield).^[2] ¹H-NMR (300 MHz, CDCl₃): δ 3.90 (s, 3H), 7.03 (d, *J* = 9.0 Hz, 2H), 7.32-7.36 (m, 3H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 2H).

4-tert-butylbromobenzene (0.533 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane). **4-tert-Butylbiphenyl** was collected as a white solid (0.51 g, 97% yield).^{[2] 1}H-NMR (300 MHz, CDCl₃): δ 1.34 (s, 9H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.38-7.47 (m, 4H), 7.52-7.59 (m, 4H).

4-bromobenzaldehyde (0.463 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 30:1). **4-Phenylbenzaldehyde** was collected as a light yellow solid (0.441 g, 97% yield).^[1] 1H NMR (500 MHz, CDCl₃): δ 7.37-7.40 (m, 1H), 7.42-7.46 (m, 2H), 7.58-7.60 (m, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 10.01 (s, 1H).

4-bromoacetophenone (0.498 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 30:1). **4–Acetylbiphenyl** was collected as a white solid (0.485 g, 99% yield).^[1] ¹H-NMR (500 MHz, CDCl₃): δ 2.58 (s, 3H), 7.36-7.38 (m, 1H), 7.41-7.45 (m, 2H), 7.51-7.59 (m, 2H), 7.62-7.65 (m, 2H), 7.99 (d, *J* = 5.1 Hz, 2H).

4-bromobenzonitrile (0.455 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 30:1). **4-Phenylbenzonitrile** was collected as a pale yellow solid (0.438 g, 98% yield).^[1] ¹H-NMR (300 MHz, CDCl₃): δ 7.39-7.50 (m, 3H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.54-7.61 (m, 4H).

4-bromotoluene (0.428 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane). **4-Methyl-biphenyl** was collected as a white solid (0.405 g, 97% yield).^[1] ¹H-NMR (500 MHz, CDCl₃): δ 2.57 (s, 3H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.48-7.51 (m, 1H), 7.58-7.61 (m, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.76-7.78 (m, 2H).

1-bromo-4-nitrobenzene (0.505 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 100:1). **4-Nitro-biphenyl** was collected as a pale yellow solid (0.482 g, 97% yield).^[1] ¹H-NMR (300 MHz, CDCl₃): δ 7.42-7.52 (m, 3H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 8.30 (d, *J* = 8.7 Hz, 2H).

1-bromonaphthalene (0.518 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane). **1-Phenyl-naphthalene** was collected as a white solid (0.484 g, 95% yield).^[3] ¹H-NMR (300 MHz, CDCl₃): δ 7.39-7.46 (m, 3H), 7.46-7.55 (m, 6H), 7.84 (d, *J* = 7.5Hz, 1H), 7.885 (d, *J* = 6.9 Hz, 2H).

2-bromonaphthalene (0.518 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane). **2-Phenyl-naphthalene** was collected as a white solid (0.494 g, 97% yield).^[3] ¹H-NMR (500 MHz, CDCl₃): δ 7.37 (t, *J* = 7.4 Hz, 1H), 7.46-7.52 (m, 4H), 7.74-7.77 (m, 3H), 7.85-7.93 (m, 3H), 8.04 (s, 1H).

3-bromotoluene (0.428 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane). **3-Methyl-biphenyl** was collected as a colorless oil (0.406 g, 97% yield).^[3] ¹H-NMR (300 MHz, CDCl₃): δ 2.41 (s, 3H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.29-7.34 (m, 2H), 7.38-7.44 (m, 4H), 7.58 (d, *J* = 8.1 Hz, 2H).

2-bromobenzonitrile (0.455 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 5:1). **Biphenyl-2-carbonitrile** was collected as a colorless oil (0.43 g, 96% yield).^[4] ¹H-NMR (500 MHz, CDCl₃): δ 7.41-7.45 (m, 2H), 7.47-7.51 (m, 3H), 7.54-7.56 (m, 2H), 7.61-7.64 (m, 1H), 7.74-7.76 (m, 1H).

2-bromobenzaldehyde (0.463 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 30:1). **Biphenyl-2-carbaldehyde** was collected as a colorless oil (0.441 g, 97% yield).^{[5] 1}H-NMR (300 MHz, CDCl₃): δ 7.37-7.41 (m, 2H), 7.43-7.50 (m, 5H), 7.60-7.64 (m, 1H), 8.02 (d, *J* = 5.0 Hz, 1H), 9.98 (s, 1H).

2-bromo-4-nitrotoluene (0.216 g, 1.0 mmol), phenylboronic acid (0.146 g, 1.2 mmol, 1.2 eqv.), TBAB(0.3224 g, 1.0 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0053 g, 1.0×10^{-6} mol Pd, 0.1 mol%), Na₂CO₃ (0.212 g, 2 mol, 2 eqv.), and water (2 ml) were added to a pressure tube under air. The pressure tube was placed in an oil for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 20:1). **2-Methyl-5-nitro-biphenyl** was collected as a pale yellow solid (0.2 g, 94% yield).^[6] ¹H-NMR (500 MHz, CDCl3): δ 2.36 (s, 3H), 7.30-7.32

(m, 2H), 7.41-7.42 (m, 2H), 7.44-7.48 (m, 2H), 8.09-8.11 (m, 2H).

2-bromo-5-nitrobenzene (0.54 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), Na₂CO₃ (0.53 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 2 h at 100 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 30:1). **2-Methyl-4-nitro-biphenyl** was collected as a pale yellow solid (0.527 g, 99% yield).^[7] ¹H-NMR (300 MHz, CDCl3): δ 2.467 (s, 3H), 7.40-7.43 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.52-7.60 (m, 3H), 8.16-8.19 (m, 1H), 8.242 (s, 1H).

Suzuki coupling of aryl chlorides and phenylboronic acid (Table 3):

4-chlorobenzaldehyde (0.0703 g, 0.5 mmol), phenylboronic acid (0.0732 g, 0.6 mmol, 1.2 eqv.), TBAB (0.1612 g, 0.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0266 g, 5.0×10^{-6} mol Pd, 1 mol%), NaOH (0.04 g, 1.0 mmol, 2 eqv.) and water (1 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 10 h at 120 °C. The reaction mixture was cooled to room temperature and 100 μ L C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 15 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield (95%).

4-chlorobenzonitrile (0.0688 g, 0.5 mmol), phenylboronic acid (0.0732 g, 0.6 mmol, 1.2 eqv.), TBAB (0.1612 g, 0.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0266 g, 5.0×10^{-6} mol Pd, 1 mol%), Na₂CO₃ (0.106 g, 1.0 mmol, 2 eqv.) and water (1 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 10 h at 120 °C. The reaction mixture was cooled to room temperature and 100 μ L C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 10 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield (97%).

4-chloronitrobenzene (0.394 g, 2.5 mmol), phenylboronic acid (0.366 g, 3.0 mmol, 1.2 eqv.), TBAB (0.806 g, 2.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0013 g, 2.5×10^{-7} mol Pd, 0.01 mol%), NaOH (0.2 g, 5.0 mmol, 2 eqv.) and water (5 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 10 h at 120 °C. The reaction mixture was cooled to room temperature and 100 µL C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 15 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield (99%).

4-chloroanisole (0.0713 g, 0.5 mmol), phenylboronic acid (0.0732 g, 0.6 mmol, 1.2 eqv.), TBAB (0.1612 g, 0.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0798 g, 1.5×10^{-5} mol Pd, 3 mol%), KOH (0.0561 g, 1.0 mmol, 2 eqv.) and water (1 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 10 h at 120 °C. The reaction mixture was cooled to room temperature and 100 µL C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 10 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield (87%).

2-chlorobenzonitrile (0.0688 g, 0.5 mmol), phenylboronic acid (0.0732 g, 0.6 mmol, 1.2 eqv.), TBAB (0.1612 g, 0.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0266 g, 5.0×10^{-6} mol Pd, 1 mol%), Na₂CO₃ (0.106 g, 1.0 mmol, 2 eqv.) and water (1 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 10 h at 120 °C. The reaction mixture was cooled to room temperature and 100 μ L C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 10 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield (95%).

2-chlorobenzaldehyde (0.0703 g, 0.5 mmol), phenylboronic acid (0.0732 g, 0.6 mmol, 1.2 eqv.), TBAB (0.1612 g, 0.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0266 g, 5.0×10^{-6} mol Pd, 1 mol%), NaOH (0.04 g, 1.0 mmol, 2 eqv.) and water (1 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 10 h at 120 °C. The reaction mixture was cooled to room temperature and 100 μ L C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 10 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield (93%).

4-chloroacetophenone (0.0773 g, 0.5 mmol), phenylboronic acid (0.0732 g, 0.6 mmol, 1.2 eqv.), TBAB (0.1612 g, 0.5 mmol, 1 eqv.), Pd(OAc)₂/PIC (0.0266 g, 5.0×10^{-6} mol Pd, 1 mol%), NaOH (0.04 g, 1.0 mmol, 2 eqv.) and water (1 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 10 h at 120 °C. The reaction mixture was cooled to room temperature and 100 μ L C₁₆H₃₄ was added as internal standard. The mixture was extracted with ethyl acetate (3 × 10 mL). The organic extract was dried with anhydrous MgSO₄ and analyzed by GC to determine the yield (96%).

methyl 4-chlorobenzoate (0.1706 g, 1.0 mmol), phenylboronic acid (0.1463 g, 1.2 mmol, 1.2 eqv.), Pd(OAc)₂/PIC (0.0532 g, 1.0×10^{-6} mol Pd, 0.1 mol%), TBAB (0.3224 g, 0.5 mmol, 1 eqv.), Na₂CO₃ (0.212 g, 2.0 mol, 2 eqv.), and water (2 mL) were added to a pressure tube under air. The pressure tube was placed in an oil bath for 10 h at 120 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). And then the products were isolated by column with silica gel (hexane/ethyl acetate = 10:1). **Methyl biphenyl-4-carboxylate** was collected as a white solid (0.204 g, 96% yield).^{[5] 1}H-NMR (300 MHz, CDCl₃): δ 3.95 (s, 3H), 7.40-7.50 (m, 3H), 7.66 (t, *J* = 9.0 Hz 4H), 8.12 (d, *J* = 8.4 Hz, 2H).

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¹H-NMR and ¹³C-NMR Spectra for the IL monomer:





¹H-NMR Spectra of Coupled Products:

















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