### Supporting Information for the manuscript entitled

# Bipyridinium Ionic Liquid Promoted Cross-Coupling Reactions Between Perfluoroalkyl or Pentafluorophenyl Halides with Aryl Iodides

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**S5. References** 

All reagents were purchased from commercial sources and used without further purification. Copper was freshly activated by treatment with iodine and then washed with HCl in acetone, followed by acetone alone, ether, and dried in vacuo.<sup>1</sup> TLC analysis was performed with Al backed plates precoated with silica gel and examined under UV (254 nm). Flash column chromatography was executed on silica gel (60-200 µm, 60 A). <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> and CD<sub>3</sub>COCD<sub>3</sub> on an instrument operating at 300 MHz. Chemical shifts are reported in parts per million relative to the appropriate standard: CFCl<sub>3</sub> for <sup>19</sup>F and TMS for <sup>1</sup>H and <sup>13</sup>C NMR spectra. IR spectra were recorded using KBr plates for neat liquid. Mass spectra for ionic compounds were determined by insertion using a solid probe.  $M^+$  is the mass of the cation. Differential scanning calorimetry (DSC) measurements were performed using a calorimeter equipped with an auto-cool accessory and calibrated using indium. The following procedure was used: cooling from 40 °C to -80 °C and heating to 400 °C at 10 °C/min. The transition temperature, T<sub>m</sub>, was taken as peak maximum. Onset of decomposition was taken as when the abnormal section of the plot began. Thermo-gravimetric analysis (TGA) measurements were carried out by heating the sample at 10  $^{\circ}$ C/min from room temperature to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min). Elemental analysis was carried out commercially.

#### 1. Synthesis of 1-butyl-2,2'-bipyridinium bis(trifluoromethanesulfonyl)amide, 1

2,2'-Bipyridine (1 mmol, 0.156 g) and  $CH_3CH_2CH_2CH_2I$  (1.5 mmol, 0.276 g) were mixed at room temperature in a 6 mL Schlenk tube. After the tube was cooled to -195 °C, it was evacuated and closed. The reaction mixture was heated at 100 ~ 110 °C for 24 h. The brown residue was dissolved in a mixture of water and acetone (1 : 1) and

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treated with an aqueous solution of LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (1.5 mmol, 0.431 g). After 6 h, acetone was removed at reduced pressure. The water layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, 3 × 15 mL. The combined organic layer was washed with water (3 × 15 mL), dried by MgSO<sub>4</sub>, and evaporated in vacuo . Removing traces of 2,2'-bipyridine by sublimation gave **1** as a pale yellow liquid (0.445 g, 90 %). <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>): 9.29 (d, J = 5.9 Hz, 1 H), 8.81-8.92 (m, 2H), 8.32-8.37 (m, 2H), 8.20 (td, J = 7.8, 1.7 Hz, 1 H), 8.02 (dt, J = 7.9, 1.0 Hz, 1 H), 7.73-7.78 (m, 1 H), 4.88 (t, J = 7.9 Hz, 2 H), 1.93-1.99 (m, 2 H), 1.28-1.36 (m, 2 H), 0.82 (t, J = 7.4 Hz, 3 H). <sup>19</sup>F NMR (CD<sub>3</sub>COCD<sub>3</sub>): -79.85 (s, 6 F). <sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>): 154.0, 151.3, 150.9, 147.5, 147.2, 139.3, 131.6, 129.0, 127.1, 127.0, 121.1 (q, J = 319.5 Hz), 59.9, 33.8, 20.0, 13.5. MS (solid probe) (EI) m/z (%): 213 (M<sup>+</sup>, 100). IR (KBr) v 3107, 2967, 2940, 2877, 1624, 1579, 1514, 1464, 1439, 1352, 1193, 1138, 1057, 996, 780, 746, 653, 615, 511. Anal. Calcd for C<sub>16</sub>H<sub>17</sub>F<sub>6</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>: C, 38.94; H, 3.47; N, 8.52. Found: C, 38.82; H, 3.55; N, 8.68. T<sub>g</sub>: -58.79 °C. T<sub>d</sub>: 308.14 °C.

## 2. Experimental details for the reaction of perfluoroalkyl or perfluoroaryl halides with aromatic compounds

**General Procedure**: To the ionic liquid **1** (6 mmol, 3 g) was added copper (1 mmol), perfluoroalkyl or perfluoroaryl halide (1 equiv) and aryl iodide (1 equiv) under dinitrogen atmosphere. The resulting mixture was heated at 75 °C for 20 h. The product was extracted from the mixture by addition of ethyl ether (10 mL), followed by decanting the ethyl ether solution of the product. This was repeated three times. The combined organic layer was concentrated by rotary evaporation. The residue was subjected to short-path column chromatography over silica gel with hexane as the eluent to give the desired product **3a-j**.

Nonafluorobutylbenzene, **3a**:<sup>2</sup> colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.54-7.59 (m, 3 H), 7.46-7.51 (m, 2 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -81.02 (tt, J = 9.9, 3.1 Hz, 3 F), -110.97 (t, J = 11.3 Hz, 2 F), -122.72 (m, 2 F), -125.54 (m, 2 F). GC-MS (EI) m/z (%): 296 (M<sup>+</sup>, 7). **1-Methyl-4-(nonafluorobutyl)benzene, 3b**:<sup>3</sup> colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.47 (d, J = 8.1 Hz, 2 H), 7.29 (d, J = 8.1 Hz, 2 H), 2.41 (s, 3 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -81.21 (tt, J = 9.6, 3.1 Hz, 3 F), -110.68 (t, J = 11.3 Hz, 2 F), -122.88 (m, 2 F), -125.65 (m, 2 F). GC-MS (EI) m/z (%): 310 (M<sup>+</sup>, 20).

**1-Nitro-4-(nonafluorobutyl)benzene, 3c**:<sup>2</sup> white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.36 (d, J = 9.0 Hz, 2 H), 7.80 (d, J = 9.0 Hz, 2 H) <sup>19</sup>F NMR (CDCl<sub>3</sub>): -80.94 (tt, J = 9.6, 3.1 Hz, 3 F), -111.29 (t, J = 14.1 Hz, 2 F), -122.43 (m, 2 F), -125.38 (m, 2 F). GC-MS (EI) m/z (%): 341 (M<sup>+</sup>, 9).

(**Tridecafluorohexyl)benzene**, **3d**:<sup>4</sup> pale yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.54-7.59 (m, 3 H), 7.46-7.51 (m, 2 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -80.77 (tt, J = 10.1, 2.8 Hz, 3 F), -110.71 (t, J = 14.1 Hz, 2 F), -121.35 (m, 2 F), -121.84 (m, 2 F), -122.71 (m, 2 F), -126.03 (m, 2 F). GC-MS (EI) m/z (%): 396 (M<sup>+</sup>, 4).

**1-Methyl-4-(tridecafluorohexyl)benzene, 3e**:<sup>4</sup> colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.46 (d, J = 8.1 Hz, 2 H), 7.28 (d, J = 8.1 Hz, 2 H), 2.41 (s, 3 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -80.84 (tt, J = 9.9, 2.5 Hz, 3 F), -110.35 (t, J = 14.1 Hz, 2 F), -121.42 (m, 2 F), -121.90 (m, 2 F), -

122.75 (m, 2 F), -126.08 (m, 2 F). GC-MS (EI) m/z (%): 410 ( $M^+$ , 11).

**2,3,4,5,6-Pentafluoro-1,1'-biphenyl, 3f**:<sup>5</sup> white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.44-7.48 (m, 3 H), 7.38-7.42 (m, 2 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -143.20 (dd, J = 22.6, 8.5 Hz, 2 F), -155.67 (t, J = 22.6 Hz, 1 F), -162.30 (td, J = 22.6, 8.5 Hz, 2 F). GC-MS (EI) m/z (%): 244 (M<sup>+</sup>, 100).

**4'-Methyl-2,3,4,5,6-pentafluorobiphenyl, 3g**:<sup>6</sup> white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.29 (s, 4 H), 2.40 (s, 3 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -143.33 (dd, J = 22.6, 8.5 Hz, 2 F), -156.18 (t, J = 22.6 Hz, 1 F), -162.50 (td, J = 22.6, 8.5 Hz, 2 F). GC-MS (EI) m/z (%): 258 (M<sup>+</sup>, 100). **4'-Nitro-2,3,4,5,6-pentafluorobiphenyl, 3h**:<sup>7</sup> pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.35 (d, J = 8.4 Hz, 2 H), 7.62 (d, J = 8.4 Hz, 2 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -142.46 (dd, J = 22.6, 8.5 Hz, 2 F), -152.47 (t, J = 22.6 Hz, 1 F), -160.77 (td, J = 22.6, 8.5 Hz, 2 F). GC-MS (EI) m/z (%): 289 (M<sup>+</sup>, 100).

**1,4-Bis(tridecafluorohexyl)-benzene, 3i**:<sup>8</sup> pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.75 (s, 4 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -80.75 (tt, J = 9.9, 2.5 Hz, 6 F), -111.15 (t, J = 14.1 Hz, 4 F), -121.30 (m, 4 F), -121.64 (m, 4 F), -122.68 (m, 4 F), -126.03 (m, 4 F). GC-MS (EI) m/z (%): 714 (M<sup>+</sup>, 1).

**2,2'',3,3'',4,4'',5,5'',6,6''-Decafluoro-1,1':4',1''-terphenyl, 3j**:<sup>9</sup> white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.55 (s, 4 H). <sup>19</sup>F NMR (CDCl<sub>3</sub>): -142.91 (dd, J = 22.6, 8.5 Hz, 4 F), -154.48 (t, J = 22.6 Hz, 2 F), -161.70 (td, J = 22.6, 8.5 Hz, 4 F). GC-MS (EI) m/z (%): 410 (M<sup>+</sup>, 100).

### **3. Procedure for the recycling of ionic liquid, 1**

After the product was extracted from the reaction mixture with ethyl ether, methylene chloride (15 mL) was added to the residue and stirred for 10 min. The insoluble material was filtered, and washed with  $CH_2Cl_2$  (3 × 10 mL). The filtrate was washed with pyridine solution (10 wt %, 2 × 15 mL), H<sub>2</sub>O (2 × 15 mL). Then the  $CH_2Cl_2$ layer was concentrated under reduced pressure. The resulting liquid was dried in vacuo while heating at 80 °C for 4 h before next cycle.

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