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# Synthesis of 2,2′-Biimidazolium-Based Ionic Liquids: Use as a New Reaction Medium and Ligand for Palladium-Catalyzed Suzuki Cross-Coupling Reactions

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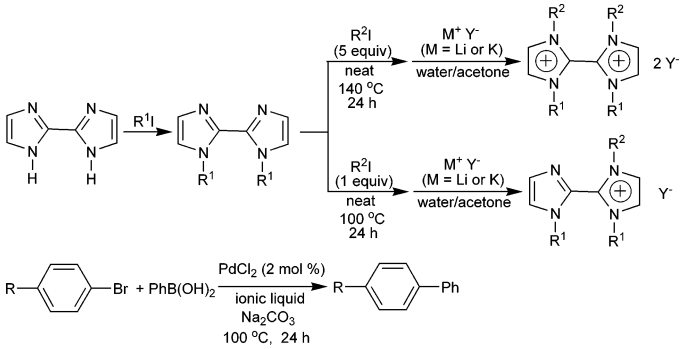


Neat reactions of 2,2′-biimidazole with an excess of alkyl or polyfluoroalkyl iodides at 140 °C, followed by anion exchange with $LiN(SO_2CF_3)_2$ or $KPF_6$, gave the diquaternary salts **3a**−**k** in >80% yields. However, by controlling the reaction stoichiometry, 2,2′-biimidazole can also be monoquaternized with the same electrophiles at 100 °C under similar conditions. Subsequent metathesis reactions with $LiN(SO_2CF_3)_2$ or $KPF_6$ resulted in the ionic liquids **4a**−**m** in high yields. Thermal properties were determined with a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA). Most of the monoquaternary salts are room-temperature ionic liquids. 1,3,1′-Tributyl-2,2′-biimidazolium hexafluorophosphate was demonstrated to be an excellent solvent and ligand for palladium-catalyzed Suzuki cross-coupling reactions. The catalytic ionic liquid system may be recycled at least 14 times without a significant decrease in catalytic performance.

## Introduction

Ionic liquids are low-melting salts that are nonvolatile, thermally stable, recyclable, and easy to handle. These unique physical properties make them attractive replacements for conventional organic solvents in green chemistry.[1] The predominant research into ionic liquids as reaction media has been focused extensively on homogeneous catalysis since ionic liquids have been shown to be ideal immobilizing agents for various "classical" transition-metal catalysts.[2] However, just as with conventional organic solvents, not all ionic liquids are appropriate for a particular reaction, and a single ionic liquid will not always be the best for every reaction.[3] It continues to be worthwhile to synthesize new ionic liquids for particular chemical processes even though a large number of these novel compounds are already known.

As the name implies, ionic liquids are comprised primarily of cations and anions, and although the mechanism is not clear, both play an important role in the reaction media.[4] Most of the cations being used are monoquaternized imidazolium species with only one quaternization center. However, we were interested in

(1) For recent review, see, for example: (a) *Ionic Liquids as Green Solvents*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 856; American Chemical Society: Washington, DC, 2003. (b) *Ionic Liquids in Synthesis;* Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, 2003. (c) Forsyth, S. A.; Pringle, J. M.; MacFarlane, D. R. *Aust. J. Chem.* **2004**, *57*, 113−119. (d) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667−3692. (e) Rogers, S. *Chem. Commun.* **2001**, 2399−2407. (f) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789.

(2) For example, see: (a) Dyson, P. J.; Ellis, D. J.; Welton, T. *Can. J. Chem.* **2001**, *79*, 705−708. (b) Dyson, P. J.; Ellis, D. J.; Parker, D. G.; Welton, T. *Chem. Commun.* **1999**, 25−26. (c) Müller, L. A.; Dupont, J.; de Souza, R. F. *Macromol. Rapid Commun.* **1998**, *19*, 409−411. (d) Stenzel, O.; Raubenheimer, H. G.; Esterhuysen, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1132−1138. (e) Handy, S. T.; Zhang, X. *Org. Lett.* **2001**, *3*, 233−236.

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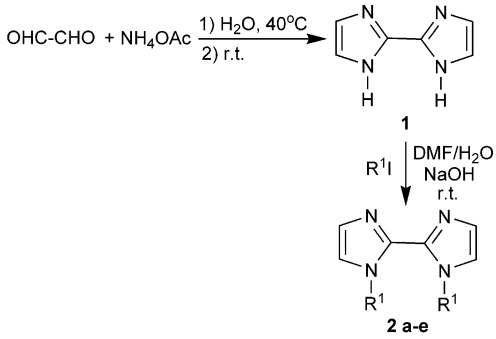
**SCHEME 1**




**a:** $R^1 = CH_3$, **b:** $R^1 = CH_2CH_3$, **c:** $R^1 = CH_2CH_2CH_3$, **d:** $R^1 = CH_2CH_2CH_2CH_3$, **e:** $R^1 = CH_2CH_2CH_2CF_3$.

continuing our study of such compounds with multiple quaternary centers. In our previous work, it was found that 4,4′-bipyridine could be mono- or diquaternized to form low-melting ionic liquids.[5] Therefore, we now have extended our research to 2,2′-biimidazole. A series of bis-annulated 2,2′-biimidazolium salts and their redox behavior and spectroscopic properties have been described.[6] Recently, we have reported a monoquaternary 2,2′-biimidazolium-based ionic liquid and found it to be extremely effective in catalytic reactions.[7] Now, in this paper, we describe fully the syntheses and characterization of mono- and diquaternized 2,2′-biimidazoles and their highly successful application in playing a catalytic role in Suzuki reactions.

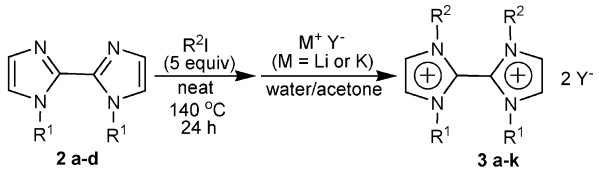
## Results and Discussion

2,2′-Biimidazole is an intriguing biaryl molecule which is prepared from glyoxal and ammonium acetate (Scheme 1).[8] Alkylation of 2,2′-biimidazole occurred at N-1 and N-1′ to form 1,1′-dialkyl-2,2′-biimidazoles in high yields.[6] The alkylation reactions occurred under mild conditions by addition of the appropriate iodoalkane in DMF in the presence of aqueous base.

In compounds **2a**−**e**, there are two basic nitrogen atoms available to participate in quaternization reactions. These reactions were carried out by heating the biimidazole with five equivalents of alkyl iodide at 140 °C for 24 h under neat reaction conditions (Scheme 2). Subsequent metathetical reactions with metal salts, such as lithium bis(trifluoromethanesulfonyl)amide ($LiNTf_2$) or potassium hexafluorophosphate ($KPF_6$), led to the formation of the dicationic ionic salts **3a**−**k** in excellent yields.

All of these diquaternary ionic salts are hydrolytically and air stable. Their solubilities are related to the length of the alkyl chain on the cationic ring, e.g., **3a** and **3g** are soluble in water and partially soluble in ethyl acetate and acetone; **3b** and **3h** are partially soluble in water, but soluble in ethyl acetate and acetone. Therefore, not surprisingly, as the alkyl group on the cation is lengthened, the solubility of the ionic compound in organic solvents increases while concomitantly decreasing in $H_2O$.

**SCHEME 2**[a]




| compd | $R^1$ | $R^2$ | Y | $T_m$ (°C) [a] | $T_d$ (°C) [b] |
|---|---|---|---|---|---|
| **3a** | $CH_3$ | $CH_3$ | $NTf_2$ | 93 | 395 |
| **3b** | $CH_2CH_3$ | $CH_2CH_3$ | $NTf_2$ | 189 | 345 |
| **3c** | $(CH_2)_2CH_3$ | $(CH_2)_2CH_3$ | $NTf_2$ | 157 | 327 |
| **3d** | $(CH_2)_3CH_3$ | $(CH_2)_3CH_3$ | $NTf_2$ | 95 | 338 |
| **3e** | $(CH_2)_3CH_3$ | $(CH_2)_3CF_3$ | $NTf_2$ | 119 | 331 |
| **3f** | $(CH_2)_3CH_3$ | $CH_3$ | $NTf_2$ | -55 ($T_g$) [c] | 348 |
| **3g** | $CH_3$ | $CH_3$ | $PF_6$ | 117 | 363 |
| **3h** | $CH_2CH_3$ | $CH_2CH_3$ | $PF_6$ | 256 | 379 |
| **3i** | $(CH_2)_2CH_3$ | $(CH_2)_2CH_3$ | $PF_6$ | 252 | 320 |
| **3j** | $(CH_2)_3CH_3$ | $(CH_2)_3CH_3$ | $PF_6$ | 163 | 319 |
| **3k** | $(CH_2)_3CH_3$ | $CH_3$ | $PF_6$ | 75 | 328 |

[a] Key: (a) melting point; (b) thermal degradation; (c) glass transition temperature.

Melting points or glass transition temperatures determined by differential scanning calorimeter (DSC) are given in Scheme 2. The relationship between the structure and melting point of these diquaternary salts is clearly observed. On one hand, the anion exhibits a major influence on the melting point. With constant substituents on the dication, changing the anion $PF_6^-$ in **3g**−**k** to $-NTf_2$ in **3a**−**d** and **3f** lowers the respective melting points greatly. On the other hand, comparison of the melting points of biimidazolium salts containing differently substituted cations with a constant anion clearly illustrates the influence of the cation. For example, with bis(trifluoromethanesulfonyl)amide ($NTf_2$) as the anion, variation of the alkyl groups from ethyl (**3b**) to butyl (**3d**), the melting points decreased from 189 °C (**3b**) to 95 °C (**3d**). A similar tendency can also be observed from **3h** to **3j** with $PF_6^-$ as the anion. The relatively low melting points of **3a** and **3g** are somewhat surprising. Changing the nonfluorinated butyl chain in **3d** to fluorinated trifluorobutyl in **3e** resulted in an increase in the melting point, but the $T_d$ was essentially not impacted. Furthermore, as can be seen in **3k** and **3f**, substitution of the amide ion by $PF_6^-$, moving from an anion where the negative charge is spread over essentially all of the elements to one where the charge is nearly a point charge results in stronger cation/anion interaction and thus a higher melting point. All of these diquaternary salts are remarkably thermally stable to 300 °C as determined by thermogravimetric analysis (TGA).

In the course of preparing the above diquaternary ionic salts, we observed the formation of monoquaternary products when the reaction was carried out at 120 °C.

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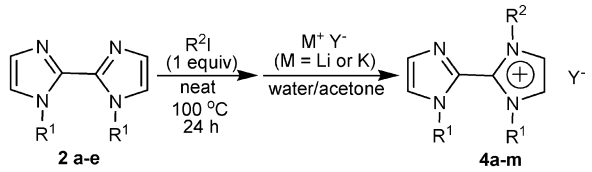
**SCHEME 3**[a]




| compd | $R^1$ | $R^2$ | Y | Tg or Tm (°C)[a] | $T_d$ (°C)[b] |
|---|---|---|---|---|---|
| **4a** | $CH_3$ | $CH_3$ | $NTf_2$ | -46 | 423 |
| **4b** | $CH_2CH_3$ | $CH_2CH_3$ | $NTf_2$ | -51 | 326 |
| **4c** | $(CH_2)_2CH_3$ | $(CH_2)_2CH_3$ | $NTf_2$ | -55 | 344 |
| **4d** | $(CH_2)_3CH_3$ | $(CH_2)_3CH_3$ | $NTf_2$ | -56 | 332 |
| **4e** | $(CH_2)_3CH_3$ | $(CH_2)_3CF_3$ | $NTf_2$ | -21 | 322 |
| **4f** | $CH_3$ | $(CH_2)_2CF_3$ | $NTf_2$ | -28 | 333 |
| **4g** | $CH_3$ | $CH_3$ | $PF_6$ | 110 | 342 |
| **4h** | $CH_2CH_3$ | $CH_2CH_3$ | $PF_6$ | 70 | 326 |
| **4i** | $(CH_2)_2CH_3$ | $(CH_2)_2CH_3$ | $PF_6$ | -2 | 302 |
| **4j** | $(CH_2)_3CH_3$ | $(CH_2)_3CH_3$ | $PF_6$ | -43 | 299 |
| **4k** | $(CH_2)_3CH_3$ | $(CH_2)_3CF_3$ | $PF_6$ | -13 | 313 |
| **4l** | $(CH_2)_3CF_3$ | $(CH_2)_3CF_3$ | $PF_6$ | -6 | 357 |
| **4m** | $CH_3$ | $(CH_2)_2CF_3$ | $PF_6$ | 70 | 317 |

[a] Key: (a) glass transition temperature or melting point; (b) thermal degradation.

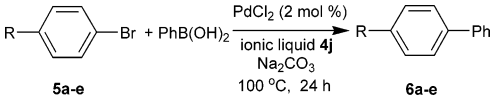
This prompted us to investigate the synthesis of monoquaternary 2,2′-biimidazolium-based ionic liquids.

1,1′-Dialkyl-2,2′-biimidazoles **2a**−**e** were monoquaternized at N-3 by reaction with stoichiometric quantities of alkyl iodide under neat reaction conditions at 100 °C for 24 h (Scheme 3). Subsequent metathesis with $LiNTf_2$ or $KPF_6$ resulted in the formation of monoquaternary ionic liquids **4a**−**m** in high yields.

Thermal properties determined by DSC and TGA are given in Scheme 3. Generally, the phase-transition temperatures (midpoints of glass transitions and/or melting points) of these monoquaternary ionic liquids **4a**−**m** are lower than those for the corresponding diquaternary compounds **3a**−**k**. Most of these monoquaternary salts fall into the ionic liquid class of compounds because of their lower melting points. This is predictable because the monoquaternary products **4a**−**m** are of lower symmetry and would be expected to be more poorly packed in their crystalline lattices compared with the respective diquaternary compounds **3a**−**k**. The variation of the melting point or glass transition temperatures showed a similar trend to those diquaternary ionic compounds **3a**−**k**. For example, with $PF_6^-$ as the anion, changing the alkyl group from methyl (**4g**) to butyl (**4j**), the phase transition temperature decreased from +110 to −43 °C. These monoquaternary ionic liquids are also thermally and hydrolytically stable.

The application of ionic liquids in organic reactions focuses on homogeneous catalysis since ionic liquids have been demonstrated to be ideal immobilizing agents for various organometallic catalysts.[2] However, in certain cases the catalysts are often removed from the catalyst/ionic liquid solution by polar products, thus leading to lower recyclability of the catalysts.[2d,9] This is partially because of the poor coordination abilities of the ordinary ionic liquids. As a result, some ionic liquids which can serve as both immobilization solvent and ligand to the catalyst have been synthesized by introducing functional groups into the ionic liquid.[10] In the monoquaternary 2,2′-biimidazolium-based ionic liquids **4a**−**m**, the nonquaternized N-4 is a potent coordination center. This is actually the case, and we have already reported previously a palladium complex with monoquaternary ionic liquid **4j**, which showed highly successful utility in Heck reactions.

**TABLE 1. Recyclable Suzuki Coupling Reaction in Ionic Liquid 4j**




**a**: R = H, **b**: R = F, **c**: R = $CF_3$, **d**: R = $NO_2$, **e**: R = $CH_3$.

| entry | product | (cycle) yield[a] (%) | | |
|---|---|---|---|---|
| 1 | **6a** | (1) 83 | (2) 84 | (3) 80 |
| 2 | **6b** | (4) 86 | (5) 86 | (6) 85 |
| 3 | **6c** | (7) 85 | (8) 90 | (9) 88 |
| 4 | **6d** | (10) 86 | (11) 86 | (12) 90 |
| 5 | **6e** | (13) 85 | (14) 80 | (15) 82 |

[a] Isolated yields.

As with Heck reactions, the Suzuki reaction is a powerful and general synthetic method for the formation of C−C bonds.[11] Because of the excellent results of this catalytic ionic liquid system in the Heck reaction, we were encouraged to investigate further its application to the Suzuki coupling.

Therefore, we employed the monoquaternary ionic liquid **4j** as both the solvent and ligand. Sodium carbonate, phenylboronic acid and bromobenzene were added directly to a preformed solution of 2 mol % $PdCl_2$ in **4j** (Table 1). Complete formation of the coupled product was obtained after heating at 100 °C for 24 h. The crude product was easily separated from the reaction mixture by simple extraction and decantation with ethyl ether. Purification of the crude mixture by column chromatography on silica gel using hexane as the eluent was performed to give the desired product, diphenyl **6a**, in 83% yield. Then we examined the scope of this reaction by coupling the phenylboronic acid with the nonactive chlorobenzene under the same reaction condition. However, only 15% yield of **6a** could be detected from GC−MS.

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This catalyst−ionic liquid solution was recovered and reused with the same substrate. A similarly high yield was still obtained after two cycles. Then we extended the reaction to other aryl bromides bearing a range of electron-donating and -withdrawing substituents (Table 1). In all cases, similar results were obtained for each substrate. It was gratifying to observe that this catalyst−ionic liquid solution showed very good recyclability. As can be seen from Table 1, this catalytic ionic liquid system still remained active even after being recycled for 14 runs. This likely arises because the catalyst is tightly complexed with the ionic liquid and therefore not easily lost during extraction of the product.[7]

## Conclusions

A number of di- and monoquaternized 2,2′-biimidazolium-based ionic liquids, including polyfluoroalkylated, have been prepared and characterized. Their physical and thermal stabilities are reported. The majority of the monoquaternary products are room-temperature ionic liquids. 1,3,1′-Tributyl-2,2′-biimidazolium hexafluorophosphate, a monoquaternary room temperature ionic liquid, was demonstrated to be a very efficient and recyclable solvent for palladium-catalyzed Suzuki cross-coupling reactions. Derived from its coordination ability, the monoquaternary ionic liquid markedly avoids palladium leaching in recycling experiments.

## Experimental Section

All the reagents used were purchased from commercial sources and used without further purification. 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 $\mu$m, 60 A). $^1$H, $^{19}$F, and $^{13}$C NMR spectra were recorded in $CDCl_3$, DMSO-$d_6$, and $CD_3COCD_3$ operating at 300 MHz. Chemical shifts are reported in parts per million relative to the appropriate standard: $CFCl_3$ for $^{19}$F and TMS for $^1$H and $^{13}$C NMR spectra. Mass spectra for ionic compounds were determined by insertion using the solid probe. $M^+$ is the mass of the cation. IR spectra were recorded using KBr plates for neat liquids and KBr pellets for solids. 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 in experiments for each sample: cooling from 40 °C to −80 °C and heating to 400 or 500 °C at 10 °C/min. The transition temperature, $T_m$, was taken as peak maximum. Onset of decomposition was taken as when the abnormal section of the plot began. Thermogravimetric analysis (TGA) measurements were carried out by heating samples at 10 °C/min from room temperature to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min). Elemental analyses were carried out commercially.

**Synthesis of 2,2′-Biimidazole, 1.** This synthesis is a slightly modified literature procedure.[8] To a mixture of ammonium acetate (0.46 mol, 35.4 g) and $H_2O$ (6.5 mL) glyoxal (0.173 mol, 10.0 g) solution (20%) was added dropwise with vigorous stirring at 40 °C over a period of 3 h. The mixture was allowed to stir for an additional 5h at room temperature. The reaction mixture was filtered, and the precipitate was then washed with $H_2O$ (3 × 20 mL) and acetone (3 × 20 mL) to give a crude product. This material was dissolved in 130 mL of hot ethylene glycol and treated with decolorizing carbon. After hot filtration, the product precipitated instantly to provide 3.2 g (42%) of white crystalline **1**. $^1$H NMR (DMSO-$d_6$) $\delta$: 7.06 (s).

**General Procedure for Preparation of 1,1′-Dialkyl-2,2′-biimidazoles, 2a−e.** In a 50 mL flask, 2,2′-biimidazole **1** (7.2 mmol, 0.965 g), 12 mL of DMF and 1.5 mL of 35% aqueous NaOH were stirred for 1 h. The mixture turned green and then black after which the appropriate alkyl iodide (21.6 mmol) was added slowly. The mixture was stirred overnight at room temperature. The reaction crude was poured into $H_2O$ (30 mL) and extracted with chloroform (3 × 20 mL). The combined organic layers were washed with $H_2O$ (3 × 20 mL) and dried over $Na_2SO_4$. After evaporating the solvent, the residue was chromatographed on silica gel. Elution with $CH_2Cl_2/C_2H_5OH$ (95: 5) afforded the pure product **2a**−**e**.

**1,1′-Dimethyl-2,2′-biimidazole, 2a.**[12] Off-white solid, yield 80%. $^1$H NMR ($CDCl_3$) $\delta$: 4.00 (s, 6 H), 6.92 (d, $J$ = 1.1 Hz, 2 H), 7.08 (d, $J$ = 1.1 Hz, 2 H). $^{13}$C NMR ($CDCl_3$) $\delta$: 35.3, 122.6, 127.8, 138.6. GC−MS (EI): *m/z* 162 ($M^+$, 100).

**1,1′-Diethyl-2,2′-biimidazole, 2b.** Off-white solid, yield 85%. $^1$H NMR ($CDCl_3$) $\delta$: 1.31 (t, $J$ = 7.2 Hz, 6 H), 4.41 (q, $J$ = 7.2 Hz, 4 H), 6.94 (s, 2 H), 7.04 (s, 2 H). $^{13}$C NMR ($CDCl_3$) $\delta$: 16.3, 42.3, 120.3, 127.9, 137.7. GC−MS (EI): *m/z* 190 ($M^+$, 100). Anal. Calcd for $C_{10}H_{14}N_4$: C, 63.13; H, 7.42; N, 29.45. Found: C, 63.39; H, 7.33; N, 29.62.

**1,1′-Dipropyl-2,2′-biimidazole, 2c.** Off-white solid, yield 84%. $^1$H NMR ($CDCl_3$) $\delta$: 0.85 (t, $J$ = 7.4 Hz, 6 H), 1.68−1.80 (m, 4 H), 4.38 (t, $J$ = 7.2 Hz, 4 H), 6.96 (d, $J$ = 1.1 Hz, 2 H), 7.08 (d, $J$ = 1.1 Hz, 2 H). $^{13}$C NMR ($CDCl_3$) $\delta$: 11.0, 24.3, 48.9, 121.3, 127.9, 138.0. GC−MS (EI): *m/z* 218 ($M^+$, 100). Anal. Calcd for $C_{12}H_{18}N_4$: C, 66.02; H, 8.31; N, 25.67. Found: C, 65.81; H, 8.38; N, 25.75.

**1,1′-Dibutyl-2,2′-biimidazole, 2d.** Viscous liquid, yield 88%. $^1$H NMR ($CDCl_3$) $\delta$: 0.81 (t, $J$ = 7.3 Hz, 6 H), 1.20−1.27 (m, 4 H), 1.60−1.69 (m, 4 H), 4.38 (t, $J$ = 7.2 Hz, 4 H), 6.93 (s, 2 H), 7.04 (s, 2 H). $^{13}$C NMR ($CDCl_3$) $\delta$: 13.6, 19.6, 33.1, 47.0, 121.0, 127.9, 138.1. GC−MS (EI): *m/z* 246 ($M^+$, 100). Anal. Calcd for $C_{14}H_{22}N_4$: C, 68.26; H, 9.00; N, 22.74. Found: C, 68.43; H, 8.87; N, 22.92.

**1,1′-Di(4,4,4-trifluorobutyl)-2,2′-biimidazole, 2e.** Viscous liquid, yield 87%. $^1$H NMR ($CDCl_3$) $\delta$: 2.04−2.13 (m, 8 H), 4.58 (t, $J$ = 6.6 Hz, 4 H), 6.95 (s, 2 H), 7.08 (s, 2 H). $^{13}$C NMR ($CDCl_3$) $\delta$: 23.7 (q, $J$ = 2.9 Hz), 30.8 (q, $J$ = 29.1 Hz), 46.1, 121.2, 127.0 (q, $J$ = 273.8 Hz), 128.3, 137.9. Anal. Calcd for $C_{14}H_{16}F_6N_4$: C, 47.46; H, 4.55; N, 15.81. Found: C, 47.68; H, 4.52; N, 16.04.

**General Procedure for the Synthesis of 3a−k.** 1,1′-Dialkyl-2,2′-biimidazole **2** (1 mmol) and $R^2I$ (5 mmol) were mixed at room temperature in a 6 mL Schlenk tube. After the sample was cooled to −195 °C, the tube was evacuated and closed. The reaction mixture was heated at 140 °C for 24 h. The brown residue was dissolved in a mixture of water and acetone (1:1, 10 mL) and treated with an aqueous solution of $LiN(SO_2CF_3)_2$ (3 mmol) or $KPF_6$ (3 mmol). After 6 h, acetone was removed at reduced pressure. The water layer was extracted with EtOAc, 3 × 15 mL. The combined organic layer was washed with water (3 × 15 mL), dried over $MgSO_4$, and evaporated in vacuo to give **3b**−**f** and **3h**−**k**. Compounds **3a** and **3g** are water soluble. Purification was achieved by recrystallization from water/acetone after metathesis.

**1,3,1′,3′-Tetramethyl-2,2′-biimidazolium Di[bis(trifluoromethanesulfonyl)amide], 3a.** White solid, yield 90%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 4.23 (s, 12 H), 8.37 (s, 4 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$ −79.9 (s, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 37.6, 120.9 (q, $J$ = 319.3 Hz), 123.1, 129.5. MS (solid probe) (EI): *m/z* 177 ($M^+ - CH_3$, 65). IR (KBr) $\nu$: 4149, 3145, 3035, 2384, 2181, 2014, 1936, 1847, 1791, 1571, 1361, 1042, 792, 679, 568, 510 cm$^{-1}$. Anal. Calcd for $C_{14}H_{16}F_{12}N_6O_8S_4$: C, 22.34; H, 2.14; N, 11.17. Found: C, 22.53; H, 2.20; N, 11.31.

**1,3,1′,3′-Tetraethyl-2,2′-biimidazolium Di[bis(trifluoromethanesulfonyl)amide], 3b.** White solid, yield 92%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 1.63 (t, $J$ = 7.3 Hz, 12 H), 4.52 (q, $J$ = 7.3 Hz, 8 H), 8.55 (s, 4 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$ −79.9 (s,

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12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 15.3, 46.6, 121.8 (q, $J$ = 319.4 Hz), 124.8, 128.2. MS (solid probe) (EI): *m/z* 219 ($M^+ - CH_2CH_3$, 6). IR (KBr) $\nu$: 3447, 3140, 2998, 2589, 2473, 1938, 1561, 1510, 1449, 1352, 1203, 1045, 793, 729, 615, 568 cm$^{-1}$. Anal. Calcd for $C_{18}H_{24}F_{12}N_6O_8S_4$: C, 26.73; H, 2.99; N, 10.39. Found: C, 26.57; H, 3.01; N, 10.42.

**1,3,1′,3′-Tetrapropyl-2,2′-biimidazolium Di[bis(trifluoromethanesulfonyl)amide], 3c.** White solid, yield 95%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 0.98 (t, $J$ = 7.4 Hz, 12 H), 2.02−2.09 (m, 8 H), 4.43 (t, $J$ = 7.6 Hz, 8 H), 8.54 (s, 4 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −79.9 (s, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 10.7, 23.8, 52.3, 121.0 (q, $J$ = 319.3 Hz), 125.0, 128.4. MS (solid probe) (EI): *m/z* 218 ($M^+ - 2\ C_3H_7$, 100). IR (KBr) $\nu$: 3437, 3144, 2983, 2889, 1562, 1514, 1447, 1350, 1202, 1140, 905, 792, 742, 616, 569, 511 cm$^{-1}$. Anal. Calcd for $C_{22}H_{32}F_{12}N_6O_8S_4$: C, 30.56; H, 3.73; N, 9.72. Found: C, 30.31; H, 3.52; N, 9.79.

**1,3,1′,3′-Tetrabutyl-2,2′-biimidazolium Di[bis(trifluoromethanesulfonyl)amide], 3d.** Pale yellow solid, yield 95%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 0.90 (t, $J$ = 7.5 Hz, 12 H), 1.39 (q, $J$ = 7.5 Hz, 8 H), 1.99−2.06 (m, 8 H), 4.44 (t, $J$ = 7.8 Hz, 8 H), 8.51 (s, 4 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −79.9 (s, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 13.7, 20.1, 32.4, 51.0, 121.0 (q, $J$ = 319.4 Hz), 125.0, 128.4. MS (solid probe) (EI): *m/z* 303 ($M^+ - C_4H_9$, 100). IR (KBr) $\nu$: 3142, 2980, 2884, 1563, 1515, 1462, 1347, 1200, 1138, 1060, 795, 738, 617, 570, 511 cm$^{-1}$. Anal. Calcd for $C_{26}H_{40}F_{12}N_6O_8S_4$: C, 33.91; H, 4.38; N, 9.13. Found: C, 34.15; H, 4.39; N, 9.31.

**1,1′-Dibutyl-3,3′-di-(4,4,4-trifluorobutyl)-2,2′-biimidazolium Di[bis(trifluoromethanesulfonyl)amide], 3e.** Brown solid, yield 96%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 0.91 (t, $J$ = 7.4 Hz, 6H), 1.37−1.45 (m, 4 H), 2.37−2.41 (m, 12 H), 4.48 (t, $J$ = 7.8 Hz, 4 H), 4.64 (t, $J$ = 6.8 Hz, 4 H), 8.57 (d, $J$ = 1.8 Hz, 2 H), 8.63 (d, $J$ = 1.8 Hz, 2 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −67.0 (t, $J$ = 10.2 Hz, 6 F), −79.9 (s, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 13.6, 20.0, 23.7, 32.5, 49.5, 51.0, 60.5, 120.9 (q, $J$ = 319.1 Hz), 124.8, 127.7 (q, $J$ = 273.7 Hz), 128.8, 129.5. MS (solid probe) (EI): *m/z* 411 ($M^+ - C_4H_9$, 100). IR (KBr) $\nu$: 3553, 3143, 2971, 2884, 1663, 1559, 1465, 1347, 1209, 1059, 791, 741, 654, 615, 514 cm$^{-1}$. Anal. Calcd for $C_{26}H_{34}F_{18}N_6O_8S_4$: C, 30.35; H, 3.33; N, 8.17. Found: C, 30.68; H, 3.37; N, 8.40.

**1,1′-Dibutyl-3,3′-dimethyl-2,2′-biimidazolium Di[bis(trifluoromethanesulfonyl)amide], 3f.** Pale yellow liquid, yield 93%. $^1$H NMR ($CD_3COCD_3$) $\delta$ 0.90 (t, $J$ = 7.4 Hz, 6 H), 1.34−1.42 (m, 4 H), 1.94−2.03 (m, 4 H), 4.20 (s, 6 H), 4.46 (t, $J$ = 7.7 Hz, 4 H), 8.36 (d, $J$ = 1.7 Hz, 2 H), 8.44 (d, $J$ = 1.7 Hz, 2 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$ −79.9 (s, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 13.5, 19.9, 32.4, 37.5, 51.0, 120.8 (q, $J$ = 319.1 Hz), 125.5, 127.7, 130.0. MS (solid probe) (EI) *m/z* 261 ($M^+ - 15$, 100). IR (KBr) $\nu$: 3551, 3146, 2970, 2882, 1632, 1563, 1512, 1465, 1330, 1192, 1057, 790, 740, 616, 514 cm$^{-1}$. Anal. Calcd for $C_{20}H_{28}F_{12}N_6O_8S_4$: C, 28.71; H, 3.37; N, 10.04. Found: C, 28.89; H, 3.39; N, 10.27.

**1,3,1′,3′-Tetramethyl-2,2′-biimidazolium Bis(hexafluorophosphate), 3g.** White solid, yield 80%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 4.19 (s, 12 H), 8.31 (s, 4 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$ −71.2 to −73.7 (d, $J$ = 707.0 Hz, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 37.6, 125.9, 129.4. $^{31}$P NMR ($CD_3COCD_3$) $\delta$: −144.25 (sept, $J$ = 705.4 Hz, 2 P). MS (solid probe) (EI): *m/z* 177 ($M^+ - CH_3$, 37). IR (KBr) $\nu$: 3161, 3059, 1512, 1442, 1386, 1340, 1241, 873, 750, 685, 556 cm$^{-1}$. Anal. Calcd for $C_{10}H_{16}F_{12}N_4P_2$: C, 24.91; H, 3.34; N, 11.62. Found: C, 24.78; H, 3.19; N, 11.95.

**1,3,1′,3′-Tetraethyl-2,2′-biimidazolium Bis(hexafluorophosphate), 3h.** White solid, yield 83%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 1.62 (t, $J$ = 7.2 Hz, 12 H), 4.50 (q, $J$ = 7.2 Hz, 8 H), 8.51 (s, 4H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −71.3 to −73.8 (d, $J$ = 707.0 Hz, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 15.3, 46.5, 124.5, 128.1. $^{31}$P NMR ($CD_3COCD_3$) $\delta$: −144.24 (sept, $J$ = 705.4 Hz, 2 P). MS (solid probe) (EI): *m/z* 190 ($M^+ - 2C_2H_5$, 34). IR (KBr) $\nu$: 3147, 2997, 2950, 1668, 1564, 1513, 1470, 1392, 1355, 1287, 1224, 1089, 839, 727, 555 cm$^{-1}$. Anal. Calcd for $C_{14}H_{24}F_{12}N_4P_2$: C, 31.24; H, 4.49; N, 10.41. Found: C, 31.59; H, 4.53; N, 10.23.

**1,3,1′,3′-Tetrapropyl-2,2′-biimidazolium bis(hexafluorophosphate), 3i.** White solid, yield 83%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 0.99 (t, $J$ = 7.4 Hz, 12 H), 2.01−2.05 (m, 8 H), 4.43 (t, $J$ = 7.8 Hz, 8 H), 8.53 (s, 4 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −71.3 to −73.8 (d, $J$ = 706.7 Hz, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 10.7, 23.8, 52.3, 125.0, 128.4. $^{31}$P NMR ($CD_3COCD_3$) $\delta$: −144.20 (sept, $J$ = 705.4 Hz, 2 P). MS (solid probe) (EI): *m/z* 261 ($M^+ - C_3H_7$, 13). IR (KBr) $\nu$: 3154, 2981, 2890, 1563, 1504, 1468, 1392, 1265, 1217, 1126, 1020, 833, 773, 557, cm$^{-1}$. Anal. Calcd for $C_{18}H_{32}F_{12}N_4P_2$: C, 36.37; H, 5.43; N, 9.43. Found: C, 36.48; H, 5.44; N, 9.52.

**1,3,1′,3′-Tetrabutyl-2,2′-biimidazolium Bis(hexafluorophosphate), 3j.** White solid, yield 87%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 0.91 (t, $J$ = 7.4 Hz, 12 H), 1.34−1.46 (m, 8 H), 1.95−2.06 (m, 8 H), 4.41 (t, $J$ = 7.7 Hz, 8 H), 8.44 (s, 4 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −71.2 to −73.7 (d, $J$ = 709.5 Hz, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 13.7, 20.0, 32.4, 50.8, 124.9, 128.3. MS (solid probe) (EI): *m/z* 303 ($M^+ - C_4H_9$, 44). IR (KBr) $\nu$: 3644, 3585, 3147, 2966, 2878, 1651, 1561, 1514, 1461, 1382, 1300, 1248, 1207, 1038, 835, 557 cm$^{-1}$. Anal. Calcd for $C_{22}H_{40}F_{12}N_4P_2$: C, 40.62; H, 6.20; N, 8.61. Found: C, 40.88; H, 6.12; N, 8.77.

**1,1′-Dibutyl-3,3′-dimethylbiimidzaolium Bis(hexafluorophosphate), 3k.** White solid, yield 84%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 0.89 (t, $J$ = 7.4 Hz, 6 H), 1.35−1.42 (m, 4 H), 1.94−2.04 (m, 4 H), 4.16 (s, 6 H), 4.42 (t, $J$ = 7.7 Hz, 4 H), 8.28 (d, $J$ = 2.0 Hz, 2 H), 8.37 (d, $J$ = 2.0 Hz, 2 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −71.1 to −73.6 (d, $J$ = 707.2 Hz, 12 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 13.6, 19.9, 32.4, 37.4, 50.9, 124.2, 127.6, 130.1. MS (solid probe) (EI): *m/z* 261 ($M^+ - CH_3$, 100). IR (KBr) $\nu$: 3158, 2968, 2880, 1564, 1512, 1466, 1245, 837, 759, 558 cm$^{-1}$. Anal. Calcd for $C_{16}H_{28}F_{12}N_4P_2$: C, 33.93; H, 4.98; N, 9.89. Found: C, 33.72; H, 5.12; N, 9.93.

**General Procedure for the Preparation of 4a−m.** This synthesis was similar to that for **3a−k** except for the ratio of the reactants and the reaction temperature. A mixture of **2** (1 mmol) with $R^2I$ (1 mmol) was heated under neat reaction conditions at 100 °C for 24 h. The brown residue was dissolved in a mixture of water and acetone (1:1, 10 mL) and treated with an aqueous solution of $LiN(SO_2CF_3)_2$ (1.5 mmol) or $KPF_6$ (1.5 mmol). After 6 h, acetone was removed at reduced pressure. The water layer was extracted with $CH_2Cl_2$, 3 × 15 mL. The combined organic layer was washed with water (3 × 15 mL), dried by $MgSO_4$, and evaporated in vacuo to give **4a−m**.

**1,3,1′-Trimethyl-2,2′-biimidazolium Bis(trifluoromethanesulfonyl)amide, 4a.** Pale yellow oil, yield 81%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 3.87 (s, 3 H), 3.95 (s, 6 H), 7.36 (s, 1 H), 7.61 (s, 1 H), 7.95 (s, 2 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −79.9 (s, 6 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 34.3, 36.6, 121.0 (q, $J$ = 319.4 Hz), 125.6, 126.9, 129.6, 132.2, 137.0. MS (solid probe) (EI): *m/z* 177 ($M^+$, 100). IR (KBr) $\nu$: 3584, 3385, 3152, 2972, 1937, 1637, 1611, 1531, 1474, 1418, 1350, 1198, 1141, 1057, 934, 789, 727, 655, 614 cm$^{-1}$. Anal. Calcd for $C_{11}H_{13}F_6N_5O_4S_2$: C, 28.89; H, 2.86; N, 15.31. Found: C, 29.13; H, 2.84; N, 15.58.

**1,3,1′-Triethyl-2,2′-biimidazolium Bis(trifluoromethanesulfonyl)amide, 4b.** Pale yellow oil, yield 85%. $^1$H NMR ($CDCl_3$) $\delta$: 1.40−1.47 (m, 9 H), 3.85−3.94 (m, 2 H), 3.96−4.03 (m, 2 H), 4.16−4.23 (m, 2 H), 7.36 (s, 1 H), 7.38 (s, 1 H), 7.60 (s, 2 H). $^{19}$F NMR ($CDCl_3$) $\delta$: −78.8 (s, 6 F). $^{13}$C NMR ($CDCl_3$) $\delta$: 14.9, 16.1, 42.4, 44.9, 119.8 (q, $J$ = 319.3 Hz), 123.1, 123.2, 127.2, 132.4, 134.4. MS (solid probe) (EI): *m/z* 219 ($M^+$, 100). IR (KBr) $\nu$: 3619, 3420, 3146, 2990, 1602, 1512, 1443, 1387, 1352, 1273, 1194, 1140, 1058, 957, 920, 786, 728, 654, 615, 571, 511 cm$^{-1}$. Anal. Calcd for $C_{14}H_{19}F_6N_5O_4S_2$: C, 33.67; H, 3.83; N, 14.02. Found: C, 33.82; H, 3.83; N, 13.95.

**1,3,1′-Tripropyl-2,2′-biimidazolium Bis(trifluoromethanesulfonyl)amide, 4c.** Pale yellow oil, yield 91%. $^1$H NMR ($CDCl_3$) $\delta$: 0.84−0.89 (m, 9 H), 1.72−1.87 (m, 6 H), 3.70−3.77 (m, 2 H), 3.83−3.88 (m, 2 H), 4.09−4.18 (m, 2 H), 7.34 (d, $J$ = 1.1 Hz, 1 H), 7.37 (d, $J$ = 1.1 Hz, 1 H), 7.62 (s, 2 H). $^{19}$F NMR ($CDCl_3$) $\delta$: −78.9 (s, 6 F). $^{13}$C NMR ($CDCl_3$) $\delta$: 10.5, 10.6, 23.1,

24.0, 48.7, 51.1, 119.8 (q, $J$ = 319.4 Hz), 123.4, 123.5, 127.6, 132.3, 134.8. MS (solid probe) (EI): *m/z* 218 ($M^+ - C_3H_7$, 5). IR (KBr) $\nu$: 3616, 3145, 2973, 2943, 2895, 1600, 1510, 1467, 1440, 1352, 1194, 1140, 1058, 910, 788, 740, 616, 571, 513 $cm^{-1}$. Anal. Calcd for $C_{17}H_{25}F_6N_5O_4S_2$: C, 37.70; H, 4.65; N, 12.93. Found: C, 37.84; H, 4.77; N, 13.15.

**1,3,1′-Tributyl-2,2′-biimidazolium Bis(trifluoromethanesulfonyl)amide, 4d.** Pale yellow oil, yield 86%. $^1$H NMR ($CDCl_3$) $\delta$: 0.81−0.93 (m, 9 H), 1.20−1.30 (m, 6 H), 1.67−1.80 (m, 6 H), 3.75−3.80 (m, 2 H), 3.85−3.90 (m, 2 H), 4.14−4.18 (m, 2 H), 7.34 (d, $J$ = 1.0 Hz, 1 H), 7.37 (d, $J$ = 1.0 Hz, 1 H), 7.62 (s, 2 H). $^{19}$F NMR ($CDCl_3$) $\delta$: −78.9 (s, 6 F). $^{13}$C NMR ($CDCl_3$) $\delta$: 13.1, 13.4, 19.3, 19.4, 31.6, 32.7, 47.2, 49.4, 119.8 (q, $J$ = 319.1 Hz), 123.4, 123.6, 127.6, 132.3, 134.7. MS (solid probe) (EI): *m/z* 303 ($M^+$, 100). IR (KBr) $\nu$: 3613, 3316, 3145, 2965, 2938, 2876, 1600, 1510, 1464, 1352, 1194, 1138, 1058, 919, 740, 654, 571, 511 $cm^{-1}$. Anal. Calcd for $C_{20}H_{31}F_6N_5O_4S_2$: C, 41.16; H, 5.35; N, 12.00. Found: C, 40.98; H, 5.32; N, 11.89.

**1,1′-Dibutyl-3-(4,4,4-trifluorobutyl)-2,2′-biimidazolium Bis(trifluoromethanesulfonyl)amide, 4e.** Yellow oil, yield 81%. $^1$H NMR ($CDCl_3$) $\delta$: 0.83−0.92 (m, 6 H), 1.23−1.30 (m, 4 H), 1.71−1.83 (m, 4 H), 2.08−2.15 (m, 4 H), 3.72−3.86 (m, 2 H), 3.90−3.95 (m, 2 H), 4.33−4.38 (m, 2 H), 7.34 (d, $J$ = 1.1 Hz, 1 H), 7.39 (d, $J$ = 1.1 Hz, 1 H), 7.61 (d, $J$ = 2.1 Hz, 1 H), 7.71 (d, $J$ = 2.1 Hz, 1 H). $^{19}$F NMR ($CDCl_3$) $\delta$: −66.1 (t, $J$ = 9.9 Hz, 3 F), −78.9 (s, 6F). $^{13}$C NMR ($CDCl_3$) $\delta$: 13.1, 13.4, 19.4, 22.7, 30.2, 30.6, 31.5, 32.8, 47.2, 48.2, 49.5, 119.7 (q, $J$ = 318.8 Hz), 123.4, 123.7, 123.8, 127.3, 132.5, 134.7. MS (solid probe) (EI): *m/z* 357 ($M^+$, 100). IR (KBr) $\nu$: 3314, 3145, 2967, 2878, 1510, 1464, 1352, 1254, 1194, 1141, 1058, 785, 740, 654, 615, 571, 511 $cm^{-1}$. Anal. Calcd for $C_{20}H_{28}F_9N_5O_4S_2$: C, 37.68; H, 4.43; N, 10.98. Found: C, 37.75; H, 4.45; N, 10.81.

**1,1′-Dimethyl-3-(3,3,3-trifluoropropyl)-2,2′-biimidazolium Bis(trifluoromethanesulfonyl)amide, 4f.** Yellow oil, yield 82%. $^1$H NMR ($CDCl_3$) $\delta$: 2.95−3.08 (m, 2 H), 3.88 (s, 3 H), 4.01 (s, 3 H), 4.59 (t, $J$ = 7.1 Hz, 2 H), 7.39 (d, $J$ = 1.0 Hz, 1 H), 7.65 (d, $J$ = 1.0 Hz, 1 H), 8.02 (d, $J$ = 2.0 Hz, 1 H), 8.14 (d, $J$ = 2.0 Hz, 1H). $^{19}$F NMR ($CDCl_3$) $\delta$: −65.9 (t, $J$ = 10.7 Hz, 3 F), −79.9 (s, 6F). $^{13}$C NMR ($CDCl_3$) $\delta$: 34.5 (q, $J$ = 29.1 Hz), 34.6, 36.9, 43.8 (q, $J$ = 3.9 Hz), 121.0 (q, $J$ = 319.4 Hz), 125.0, 125.9, 127.4, 127.6 (q, $J$ = 143.0 Hz), 128.4, 132.2, 135.4. MS (solid probe) (EI): *m/z* 259 ($M^+$, 100). IR (KBr) $\nu$: 3576, 3148, 1607, 1522, 1466, 1353, 1198, 1142, 1059, 996, 919, 770, 735, 616, 513 $cm^{-1}$. Anal. Calcd for $C_{13}H_{14}F_9N_5O_4S_2$: C, 28.95; H, 2.62; N, 12.98. Found: C, 29.07, H, 2.51; N, 13.13.

**1,3,1′-Trimethyl-2,2′-biimidazolium Hexafluorophosphate, 4g.** White solid, yield 80%. $^1$H NMR ($CD_3COCD_3$) $\delta$:3.81 (s, 3 H), 3.96 (s, 6 H), 7.30 (s, 1 H), 7.44 (s, 1 H), 7.61 (s, 2 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −71.3 to −73.8 (d, $J$ = 707.0 Hz, 6 F). $^{13}$C NMR ($CD_3COCD_3$) $\delta$: 34.6, 36.6, 125.7, 127.2, 128.9, 131.5, 135.3. $^{31}$P NMR ($CD_3COCD_3$) $\delta$: −144.99 (sept, $J$ = 704.7 Hz, 1 P). MS (solid probe) (EI): *m/z* 177 ($M^+$, 19). IR (KBr) $\nu$: 3173, 2963, 2363, 1609, 1262, 1096, 1022, 799, 725, 557 $cm^{-1}$. Anal. Calcd for $C_9H_{13}F_6N_4P$: C, 33.55; H, 4.07; N, 17.39. Found: C, 33.81; H, 3.99; N, 17.52.

**1,3,1′-Triethyl-2,2′-biimidazolium Hexafluorophosphate, 4h.** White solid, yield 83%. $^1$H NMR ($CDCl_3$) $\delta$: 1.44−1.48 (m, 9 H), 3.88−3.92 (m, 2 H), 3.99−4.06 (m, 2 H), 4.16−4.23 (m, 2 H), 7.35 (s, 1 H), 7.39 (s, 1 H), 7.53 (s, 2 H). $^{19}$F NMR ($CDCl_3$) $\delta$: −72.4 to −74.9 (d, $J$ = 722.2 Hz, 6 F). $^{13}$C NMR ($CDCl_3$) $\delta$: 14.9, 16.1, 42.4, 44.9, 121.9, 123.0, 123.1, 127.3, 132.5. $^{31}$P NMR ($CDCl_3$) $\delta$: −144.24 (sept, $J$ = 705.4 Hz, 1 P). MS (solid probe) (EI): *m/z* 219 ($M^+$, 18). IR (KBr) $\nu$: 3100, 1606, 1514, 1444, 1392, 1270, 1225, 1092, 1041, 866, 839, 778, 731, 558, $cm^{-1}$. Anal. Calcd for $C_{12}H_{19}F_6N_4P$: C, 39.57; H, 5.26; N, 15.38. Found: C, 39.79; H, 5.24; N, 15.45.

**1,3,1′-Tripropyl-2,2′-biimidazolium Hexafluorophosphate, 4i.** Pale yellow viscous liquid, yield 85%. $^1$H NMR ($CDCl_3$) $\delta$: 0.81−0.87 (m, 9 H), 1.70−1.84 (m, 6 H), 3.71−3.85 (m, 4 H), 4.09−4.13 (m, 2 H), 7.33 (s, 1 H), 7.35 (s, 1 H), 7.60 (s, 2 H). $^{19}$F NMR ($CDCl_3$) $\delta$: −71.4 to −73.9 (d, $J$ = 711.5 Hz, 6 F). $^{13}$C NMR ($CDCl_3$) $\delta$: 10.4, 10.5, 23.2, 23.9, 48.6, 51.0, 123.3, 123.5, 127.5, 132.1, 134.7. $^{31}$P NMR ($CDCl_3$) $\delta$: −144.35 (sept, $J$ = 709.1 Hz, 1 P). MS (solid probe) (EI): *m/z* 175 ($M^+ - 2C_3H_7$, 31). IR (KBr) $\nu$: 3156, 2970, 2941, 2882, 1600, 1510, 1466, 1262, 1207, 1102, 1022, 840, 773, 558 $cm^{-1}$. Anal. Calcd for $C_{15}H_{25}F_6N_4P$: C, 44.34; H, 6.20; N, 13.79. Found: C, 44.51; H, 6.34; N, 13.60.

**1,3,1′-Tributyl-2,2′-biimidazolium Hexafluorophosphate, 4j.** Pale yellow oil, yield 95%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 0.77−0.87 (m, 9H), 1.19−1.27 (m, 6 H), 1.74−1.84 (m, 6 H), 3.99−4.10 (m, 4 H), 4.26−4.35 (m, 2 H), 7.37 (d, $J$ = 1.1 Hz, 1 H), 7.69 (d, $J$ = 1.1 Hz, 1 H), 8.03 (s, 2 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −71.5 to −74.0 (d, $J$ = 707.9 Hz, 6 F). $^{19}$C NMR ($CD_3COCD_3$) $\delta$: 13.2, 13.4, 19.3, 19.4, 31.7, 32.7, 47.1, 49.3, 123.4, 123.6, 127.6, 132.1, 134.5. MS (solid probe) (EI): *m/z* 303 ($M^+$, 72). IR (KBr) $\nu$: 3648, 3378, 3154, 2963, 2937, 2874, 1600, 1510, 1464, 1381, 1264, 1133, 840, 762, 558 $cm^{-1}$. Anal. Calcd for $C_{18}H_{31}F_6N_4P$: C, 48.21; H, 6.97; N, 12.49. Found: C, 47.94; H, 7.00; N, 12.64.

**1,1′-Dibutyl-3-(4,4,4-trifluorobutyl)-2,2′-biimidazolium Hexafluorophosphate, 4k.** Pale yellow oil, yield 81%. $^1$H NMR ($CDCl_3$) $\delta$: 0.82−1.93 (m, 6 H), 1.21−1.32 (m, 4 H), 1.71−1.78 (m, 4 H), 2.09−2.15 (m, 4 H), 3.80−3.94 (m, 2 H), 4.14−4.21 (m, 2 H), 4.25−4.33 (m, 2 H), 7.35 (s, 1 H), 7.38 (s, 1 H), 7.63 (s, 1 H), 7.73 (s, 1 H). $^{19}$F NMR ($CDCl_3$) $\delta$: −66.0 (t, $J$ = 10.2 Hz, 3 F), −71.2 to −73.7 (d, $J$ = 711.2 Hz, 6 F). $^{13}$C NMR ($CDCl_3$) $\delta$: 13.2, 13.5, 19.4, 19.5, 22.9, 30.3 (q, $J$ = 29.5 Hz), 31.6, 32.8, 47.4, 48.3, 49.6, 121.1 (q, $J$ = 318.2 Hz), 123.5, 123.8, 123.9, 127.3, 132.4, 134.9. $^{31}$P NMR ($CDCl_3$) $\delta$: −144.39 (sept, $J$ = 709.1 Hz, 1 P). MS (solid probe) (EI): *m/z* 357 ($M^+$, 100). IR (KBr) $\nu$: 3161, 2963, 2875, 2363, 1510, 1465, 1257, 1143, 1022, 841, 764, 558 $cm^{-1}$. Anal. Calcd for $C_{18}H_{28}F_9N_4P$: C, 43.03; H, 5.62; N, 11.15. Found: C, 43.21; H, 5.49; N, 11.38.

**1,3,1′-Tri-(4,4,4-trifluorobutyl)-2,2′-biimidazolium Hexafluorophosphate, 4l,** Pale yellow viscous liquid, yield 90%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 2.17−2.33 (m, 12 H), 4.23−4.33 (m, 4 H), 4.50−4.55 (m, 2 H), 7.46 (d, $J$ = 1.2 Hz, 1 H), 7.84 (d, $J$ = 1.2 Hz, 1 H), 8.19 (s, 2 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −66.9 (m, 9 F), −71.3 to −73.8 (d, $J$ = 706.7 Hz, 6 F). $^{31}$P NMR ($CD_3COCD_3$) $\delta$: −144.16 (sept, $J$ = 704.2 Hz, 1 P). MS (solid probe) (EI): *m/z* 465 ($M^+$, 100). Anal. Calcd for $C_{18}H_{22}F_{15}N_4P$: C, 35.42; H, 3.63; N, 9.18. Found: C, 35.27; H, 3.59; N, 9.33.

**1,1′-Dimethyl-3-(3,3,3-trifluoropropyl)-2,2′-biimidazolium Hexafluorophosphate, 4m.** White solid, yield 83%. $^1$H NMR ($CD_3COCD_3$) $\delta$: 3.01−3.05 (m, 2 H), 3.87 (s, 3 H), 3.99 (s, 3 H), 4.54−4.59 (m, 2 H), 7.38 (s, 1 H), 7.64 (s, 1 H), 7.97 (s, 1 H), 8.09 (s, 1 H). $^{19}$F NMR ($CD_3COCD_3$) $\delta$: −65.9 (t, $J$ = 10.7 Hz, 3 F), −71.2 to −73.7 (d, $J$ = 707.0 Hz, 6 F). $^{19}$C NMR ($CD_3COCD_3$) $\delta$: 34.3, 34.4 (q, $J$ = 29.0 Hz), 36.8, 43.7 (q, $J$ = 3.9 Hz), 124.8, 126.0, 127.3, 127.5 (q, $J$ = 143.2 Hz), 128.4, 132.3, 137.1. MS (solid probe) (EI): *m/z* 259 ($M^+$, 100). IR (KBr) $\nu$: 3649, 3414, 3165, 2971, 1708, 1608, 1523, 1466, 1414, 1257, 1155, 995, 847, 776, 617, 559 $cm^{-1}$. Anal. Calcd for $C_{11}H_{14}F_9N_4P$: C, 32.69; H, 3.49; N, 13.86. Found: C, 32.84; H, 3.55; N, 14.01.

**General Procedure for the Cross-Coupling Reactions of Phenylboronic Acid with Aryl Bromides in Ionic Liquid 4j.** To a solution of **4j** (4.5 mmol, 2 g) in methanol (8 mL) was added $PdCl_2$ (0.04 mmol, 7.1 mg). After 6 h of stirring at room temperature, removing the methanol in vacuo gave the catalyst ionic liquid solution. $Na_2CO_3$ (3 mmol, 0.318 g), aryl bromide **5a**−**e** (2 mmol), and phenylboronic acid (2.5 mmol) were added to the catalyst ionic liquid solution. The resulting mixture was stirred for 24 h at 100 °C. The product was extracted from the reaction 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 purified by short-path silica gel column chromatography to give the desired product. The identity of the products was confirmed by comparison with literature spectroscopic data.

**Biphenyl, 6a.**[13] White solid. $^1$H NMR ($CDCl_3$) $\delta$: 7.33−7.38 (m, 2 H), 7.42−7.47 (m, 4 H), 7.59−7.62 (m, 4 H). GC−MS (EI): *m/z* 154 ($M^+$, 100).

**4-Fluorobiphenyl, 6b.**[14] White solid. $^1$H NMR ($CDCl_3$) $\delta$: 7.08−7.13 (m, 2 H), 7.30−7.35 (m, 1 H), 7.39−7.45 (m, 2 H), 7.50−7.59 (m, 4 H). $^{19}$F NMR ($CDCl_3$) $\delta$: −115.9 (m, 1 F). GC−MS (EI): *m/z* 172 ($M^+$, 100).

**4-Trifluoromethylbiphenyl, 6c.**[14] White solid. $^1$H NMR ($CDCl_3$) $\delta$: 7.36−7.41 (m, 1 H), 7.43−7.48 (m, 2 H), 7.57−7.59 (m, 2 H), 7.68 (d, $J$ = 0.6 Hz, 4 H). $^{19}$F NMR ($CDCl_3$) $\delta$: −62.4 (d, $J$ = 0.6 Hz, 3 F). GC−MS (EI): *m/z* 222 ($M^+$, 100).

**4-Nitrobiphenyl, 6d.**[14] Pale yellow solid. $^1$H NMR ($CDCl_3$) $\delta$: 7.42−7.51 (m, 3 H), 7.59−7.63 (m, 2 H), 7.70−7.75 (m, 2 H), 8.26−8.31 (m, 2 H). GC−MS (EI): *m/z* 199 ($M^+$, 85).

**4-Methylbiphenyl, 6e.**[15] White solid. $^1$H NMR ($CDCl_3$) $\delta$: 2.38 (s, 3 H), 7.20−7.24 (m, 2 H), 7.29−7.32 (m, 1 H), 7.38−7.49 (m, 4 H), 7.55−7.58 (m, 2 H). GC−MS (EI): *m/z* 168 ($M^+$, 100).

**Procedure for the Recycling of Catalyst−Ionic Liquid Solution** After the product was extracted from the reaction mixture with ethyl ether (3 × 10 mL), the sodium salts were removed by extraction with $H_2O$ (3 × 8 mL). The water layer was decanted, and the ionic liquid layer was concentrated under reduced pressure to remove traces of ethyl ether and water. The resulting liquid was dried in vacuo before the next cycle.

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