Ring-closure reaction of 2-benzoylbenzenediazonium salts in 1-butyl-3-methylimidazolium ionic liquids

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Dedicated to Professor Kenneth K. Laali on the occasion of his 65th birthday

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Abstract

A ring-closure reaction by thermal dediazoniation of 2-substituted benzenediazonium tetrafluoroborates in imidazolium-based ionic liquids was investigated. Dediazoniation of 2-(4-R-benzoyl)benzenediazonium tetrafluoroborates (R = H, Me, OMe, Cl) in ionic liquid [BMIM][TfO] gave 3-R-9-fluorenones as ring-closure products and 2-(4-R-benzoyl)phenyl trifluoromethanesulfonates as substitution products. Dediazoniation in [BMIM][Tf2N] afforded 3-R-9-fluorenones and R-C6H4-CO-C6H4-OSO(CF3)(NSO2CF3). Yields of the ring-closure products were higher in [BMIM][Tf2N] than in [BMIM][TfO]. 2-Benzylbenzenediazonium and 2-phenoxybenzenediazonium tetrafluoroborates exclusively produced substitution products in both ionic liquids. DFT calculations suggest that electron transfer from the anion to render homolytic process should be induced more readily in [BMIM][Tf2N] than in [BMIM][TfO]. This ability may be responsible for the higher yields of the ring-closure products via homolytic pathway and the smaller yields of the substitution products via heterolytic pathway in [BMIM][Tf2N].

Keywords: Ionic liquids, diazonium ions, dediazoniation, arylation, Pschorr reaction, fluorenone

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Introduction

Ionic liquids have recently attracted much attention because of their great potential as novel solvents for organic reactions. They usually consist of organic cations and anions, and have melting points of 100 °C or below. Their properties as reaction media have been exploited in organic syntheses. Reaction products in ionic liquids can be separated by simple liquid-liquid extraction with organic solvents, since ionic liquids are immiscible in many organic solvents. In an imidazolium-based ionic liquid with tetafluoroborate ([BMIM][BF₄], Figure 1), dediazoniation of arenediazonium tetrafluoroborates (ArN₂BF₄) was reported to afford Schiemann reaction products (Ar-F) as shown in Figure 2.² Dediazoniation in an imidazolium-based ionic liquid with bis(trifluoromethylsulfonyl)imide ([BMIM][Tf₂N]) produced ArOSO(CF₃)(NSO₂CF₃) with a small amount of ArNTf₂ due to the ambident nucleophilic character of Tf₂N⁻.³ These successes suggest that the scope of their application could be expanded to the dediazoniative arylation of arenediazonium ions in ionic liquids.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Abbreviation for an imidazolium-based cation and anions of ionic liquids.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Products of the dediazoniation of arenediazonium ions in ionic liquids.

The dediazoniative arylation of arenediazonium salts has been examined in common solvents as a method for the synthesis of polycyclic aromatic compounds.⁴⁻⁹ Dediazoniation of arenediazonium ion ArN₂⁺ potentially gives aryl cation Ar⁺ via a heterolytic pathway (Figure 3). The aryl cation Ar⁺ reacts with a nucleophile (X⁻) to produce a substitution product ArX. Alternatively, reduction of ArN₂⁺ via one-electron transfer from a nucleophile (X⁻) affords an intermediate Ar-N₂⁺, which, with a loss of a molecular of nitrogen, produces an aryl radical Ar⁺ (a homolytic pathway). The radical Ar⁺ abstracts a hydrogen atom from solvent to give ArH. When arene molecules are present, the radical intermediate Ar⁺ can react with arenes to form arylated compounds by homolytic aromatic substitution. This arylation is known as the Gomberg-Bachmann reaction, and its intramolecular analogue is referred to as the Pschorr reaction. Dediazoniative intramolecular cyclization of 2-benzoylbenzenediazonium gave 9-fluorenone (2a in Figure 4) as a ring-closure product with/without Cu catalyst.⁴ In addition, 2-benzylbenzenediazonium and 2-phenoxybenzenediazonium afforded fluorene (2e) and dibenzofuran (2f), respectively, in aqueous acids.⁵⁻⁷ Dediazoniation of 2-benzoylbenzenediazonium tetrafluoroborate (1a) in the presence of KOAc in Freon-113 (CCl₃FCCl₂F) was reported to give 2a in 73% yield.⁸ Dediazoniation of 1a in the presence of Cu₂O catalyst in aqueous sulfuric acid produced 2a in 93% yield.⁹ The ring-closure products in the presence of the catalyst are believed to be produced predominantly via homolytic dediazoniation process.
Figure 3. Heterolytic and homolytic dediazoniation mechanisms of arenediazonium ions: (1) Heterolytic dissociation of the C-N bond, (2) electron-transfer process, and (3) homolytic dissociation of the C-N bond.

Figure 4. Structures of diazonium salts and dediazoniation products. Tf denotes a CF$_3$SO$_2$ group.

Hoping to expand the scope of the application of ionic liquids to dediazoniation, we explored the ring-closure reactions by the dediazoniation of arenediazonium salts 1a-1f in ionic liquids, [BMIM][TfO] and [BMIM][Tf$_2$N] (Figure 4). The effect of substituents on the yield of ring-closure products was also examined. In addition, the efficiency of electron transfer from the ionic liquids was investigated by the DFT (density functional theory) calculations to examine selectivity in the heterolytic and homolytic processes of the dediazoniation.
Results and Discussion

The ionic liquids, [BMIM][Tf_2N] and [BMIM][Tfo], were prepared by methods similar to those described in the literature.\textsuperscript{10-12} A reaction of 1-methylimidazole with 1-chlorobutane in acetonitrile gave [BMIM][Cl],\textsuperscript{10} the anion of which could be exchanged with either LiOTf or LiNTf\textsubscript{2} to afford [BMIM][TfO]\textsuperscript{11} or [BMIM][Tf_2N],\textsuperscript{12} respectively.

Solutions of 1a-1f in the ionic liquids were heated, and then the extracted products were analyzed by NMR measurements. The product distributions are summarized in Table 1. Dediazoniation of 1a afforded a mixture of ring-closure product 2a and substitution product 3a in [BMIM][TfO]. Their yield ratio was 66:34. In [BMIM][NTf_2], 2a, 4a, and 5a were formed at a ratio of 85:15:<1. It is noteworthy that the ring-closure product was produced more selectively in [BMIM][Tf_2N] than in [BMIM][TfO]. The preferential formation of 4a over 5a is attributed to the preference for O-attack over N-attack, which is consistent with that reported in the earlier studies.\textsuperscript{3}

To investigate the effect of substituents on benzoyl group, product distributions of dediazoniation of the diazonium ions with Me, OMe, and Cl groups (1b-d) were examined. The yields of ring-closure products 2b-d were found to be higher in [BMIM][Tf_2N] than in [BMIM][TfO], and substitution products 3b-d and 4b-d were formed in considerable yields. The substituent groups had only a small effect on the product distributions. It is likely that the substituents have little influence on the product-forming step.

To further explore the effect of the ionic liquids, we examined the dediazoniation of diazonium salts 1e-1f, which have a more strongly electron-donating substituent on the benzenediazonium ring. Dediazoniation of 1e significantly decreased the yield of the ring-closure product, and predominantly gave 3e and 4e. 1f reacted slowly even at 100 °C—although most of 1f remained intact after 24 h, substitution products 3f, 4f, and 5f were detected by NMR. However no ring closure product 2f could be found. These results suggest that 1e-1f predominantly reacted via a heterolytic mechanism in the ionic liquids.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ionic liquid</th>
<th>Temp, Time</th>
<th>Product (yield ratio)\textsuperscript{a}</th>
<th>Total yield of 2-5, % \textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>[BMIM][TfO]</td>
<td>50 °C, 6 h</td>
<td>2a, 3a (66:34)</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>[BMIM][Tf_2N]</td>
<td>50 °C, 6 h</td>
<td>2a, 4a, 5a (85:15:&lt;1)</td>
<td>91</td>
</tr>
<tr>
<td>1b</td>
<td>[BMIM][TfO]</td>
<td>80 °C, 1.5 h</td>
<td>2b, 3b (58:42)</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>[BMIM][Tf_2N]</td>
<td>80 °C, 1.5 h</td>
<td>2b, 4b, 5b (75:24:1)</td>
<td>94</td>
</tr>
<tr>
<td>1c</td>
<td>[BMIM][TfO]</td>
<td>80 °C, 2 h</td>
<td>2c, 3c (53:47)</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>[BMIM][Tf_2N]</td>
<td>80 °C, 2 h</td>
<td>2c, 4c, 5c (72:27:1)</td>
<td>84</td>
</tr>
<tr>
<td>1d</td>
<td>[BMIM][TfO]</td>
<td>80 °C, 1 h</td>
<td>2d, 3d (42:58)</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>[BMIM][Tf_2N]</td>
<td>80 °C, 1 h</td>
<td>2d, 4d, 5d (78:22:&lt;1)</td>
<td>72</td>
</tr>
<tr>
<td>1e</td>
<td>[BMIM][TfO]</td>
<td>80 °C, 6 h</td>
<td>2e, 3e (11:89)</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>[BMIM][Tf_2N]</td>
<td>80 °C, 6 h</td>
<td>2e, 4e, 5e (9:86:5)</td>
<td>85</td>
</tr>
<tr>
<td>1f</td>
<td>[BMIM][TfO]</td>
<td>100 °C, 24 h</td>
<td>3f</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>[BMIM][Tf_2N]</td>
<td>100 °C, 24 h</td>
<td>4f, 5f (84:9)</td>
<td>14</td>
</tr>
</tbody>
</table>

\textsuperscript{a} After extraction with hexane. The yield ratio was determined by \textsuperscript{1}H and \textsuperscript{19}F NMR.

DFT calculations\textsuperscript{13} were employed to estimate reaction energies for understanding the effect of the ionic liquids on the dediazoniation of the arenediazonium ions. The first chemical process of the heterolytic
mechanism in dediazoniation is heterolytic cleavage of the C-N bond to give aryl cations Ar⁺ (equation 1 in Figure 3). The reactions between aryl cations and X⁻ (CF₃SO₃⁻ or Tf₂N⁻) give the substitution products (3-5). In the homolytic process, the reduction of the diazoniums by one electron transfer from X⁻ gives radicals (equation 2) and the subsequent homolytic dissociation of the C-N bond generates aryl radicals Ar• (equation 3).

To take the solvent effect into account, the widely used PCM (Polarizable Continuum Model)¹⁴ method was employed, with ethanol chosen as a model solvent for ionic liquids.¹⁵ Calculated Gibbs free energies of reactions were summarized in Table 2.

### Table 2. Gibbs Free Energy of Reaction (ΔG) for the Dediazoiation by the DFT Calculations

<table>
<thead>
<tr>
<th>ArN₂⁺</th>
<th>ΔG (EtOH), kcal/mol⁰</th>
<th>eq. 1⁰</th>
<th>eq. 2 (X = TfO)</th>
<th>eq. 2 (X = Tf₂N)</th>
<th>eq. 3</th>
<th>eq. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>13.2</td>
<td>57.8</td>
<td>54.7</td>
<td>-19.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>12.7</td>
<td>57.8</td>
<td>54.7</td>
<td>-19.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>– c</td>
<td>57.5</td>
<td>54.5</td>
<td>-19.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>13.6</td>
<td>57.2</td>
<td>54.1</td>
<td>-19.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td>12.2</td>
<td>60.8</td>
<td>57.7</td>
<td>-15.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1f</td>
<td>24.5</td>
<td>62.4</td>
<td>59.3</td>
<td>-14.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹⁰ PCM(EtOH)-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). Structures and energies of the diazonium ions were computed without counter anion (BF₄⁻).

¹⁵ The reactions of eqs. 1-3 were shown in Figure 3.

¹ The aryl cation could not be obtained due to isomerization into the ring-closure product during the structural optimization.

The Gibbs free energies of reactions for heterolytic dediazoniation (eq. 1) were calculated to be 13.2 kcal/mol for 1a, 12.2 kcal/mol for 1e, and 24.5 kcal/mol for 1f by PCM(EtOH)-B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). The reaction energies of equation 2 for 1e-f were higher than that for 1a. These energies can be interpreted as reflecting relative stabilities of diazonium ions.

The energies of the electron transfer from the anions to diazonium ions 1a (eq. 2) were estimated to be 57.8 kcal/mol for X = CF₃SO₃ and 54.7 kcal/mol for X = Tf₂N. These energies were significantly higher than that of the heterolytic dediazoniation (eq. 1). Since a large amount of ring-closure product via the homolytic process was experimentally formed, the high Gibbs free energy of reaction might be attributed to the overestimation of the solvation energies for ionic species ArN₂⁺ and X⁻. Comparison of the energies of the electron transfer suggests that the ability of the electron-transfer from TfO⁻ to the diazonium is higher than that from Tf₂N⁻. The arenediazonium ions could be reduced to the radical more rapidly in [BMIM][Tf₂N] than in [BMIM][TfO]. Consequently, the ring-closure products from the aryl radical by intramolecular C-C bond formation could become more dominant in [BMIM][Tf₂N]. This result could rationalize the experimental trend.

The formations of the aryl radicals (eq. 3) for 1a-1f were found to be exergonic. It is likely that the ArN₂⁺ radicals immediately decompose to aryl radicals and nitrogen. Moreover, the energies (eqs. 1-3) for 1b-d were similar to that for 1a. This is consistent with the experimentally found small substituent effect on the product distribution. A change in ΔG from 1f to 1a (= ΔG(1f) - ΔG(1a)) for eq. 1 was larger than those for eq. 2, suggesting that 1f should react via the heterolytic process more dominantly than 1a. However, experimentally
the ring-closure product from 1a via the homolytic process was formed more significantly. The reason for this discrepancy remains unclear.

Conclusions

The product distributions of deazionization of diazonium salts 1a-f in ionic liquids were examined. 1a-d afforded both ring-closure products and substituted compounds, while 1e-f predominantly reacted via the heterolytic process to give the substituted products. The yields of the ring-closure products in [BMIM][NTf2] were higher than those in [BMIM][TfO]. This was attributed to the higher ability of the electron-transfer from Tf2N−, indicating that [BMIM][Tf2N] was an adequate solvent for the formation of the ring-closure products.

The effect of substituents on the benzoyl group on the product distribution was not significant.

Experimental Section

General. NMR spectra were recorded on a 300 MHz spectrometer at room temperature. IR data were collected using an FT-IR instrument. High-resolution mass spectral data were recorded with electron impact ionization at 70 eV. Diazonium tetrafluoroborates 1a, 1b, 1c, 1d, 1e, and 1f were synthesized by the reaction of their corresponding anilines with sodium nitrite in aqueous HBF4 solution. Ionic liquids [BMIM][Cl], [BMIM][TfO], and [BMIM][Tf2N] were prepared using methods similar to those reported in the literature. The other reagents were commercially available and were used as received.

General procedure for product analysis of the deazionization of diazonium salts in ionic liquid

The diazonium tetrafluoroborates (10–20 mg) were dissolved in ionic liquids (0.4 mL). The solution was heated using the conditions shown in Table 1. The ionic liquids were extracted with hexane. After removal of the solvent, the residues were analyzed by NMR, and the product distributions are summarized in Table 1.

Compounds 2a, 2b, 2c, 2d, 2e, 3a, 3b, 3c, 3d, 3e, and 3f were identified by comparing their NMR spectra with those reported in the literature. The isomers ArOSO(CF3)(NTf) (4a-4f) and ArNTf2 (5a-5f) were attempted to be purified with SiO2 column chromatography using hexane–CH2Cl2 or hexane–ether as an eluent. However, they could not be separated by chromatography.

4a: pale yellow oil (mixture of 4a and 5a, 10:1); 1H NMR (300 MHz, CDCl3) δ 7.80 (d, 2H, J 7.2 Hz), 7.70–7.40 (m, 7H); 13C NMR (75 MHz, CDCl3) δ 191.4 (CO), 144.9 (C), 135.9 (C), 134.0 (CH), 132.9 (CH), 132.4 (C), 131.8 (CH), 130.1 (2CH), 129.2 (CH), 128.6 (2CH), 122.9 (CH), 118.4 (CF3, q, J 320 Hz), 118.1 (CF3, q, J 320 Hz); 19F NMR (282 MHz, CDCl3) δ -73.5 (s, 3F), -78.3 (s, 3F).

5a: 19F NMR (282 MHz, CDCl3) δ -70.9 (s, 6F).

3b: pale yellow oil; IR (KRS-6) 2923, 2849, 1668, 1212, 1141 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 7.71 (d, 2H, J 8.1 Hz, 2H), 7.62 (td, J 7.2, 2.0 Hz, 1H), 7.57 (dd, J 7.7, 2.0 Hz, 1H), 7.49 (t, J 7.1 Hz, 1H), 7.42 (d, J 8.1 Hz, 1H), 7.28 (d, J 6.9 Hz, 2H), 2.44 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 192.2 (C=O), 146.7 (C), 144.9 (C), 133.9 (C), 132.7 (C), 132.4 (CH), 131.1 (CH), 130.4 (2CH), 129.3 (2CH), 128.0 (CH), 122.4 (CH), 21.8 (CH3); HRMS (EI, 70 eV) Calc’d for C15H11F3O3S 344.0323, Found 344.0330.

3b: pale yellow crystals (mixture of 4b and 5b, 20:1); IR (KRS-6) 3021, 2921, 2851, 1668, 1396, 1219 cm⁻¹; 1H NMR (300 MHz, CDCl3) δ 7.70 (d, J 8.1 Hz, 2H), 7.70–7.66 (m, 1H), 7.63–7.59 (m, 1H), 7.56 (d, J 7.8 Hz, 1H), 7.53 (d, J 8.1 Hz, 1H), 7.29 (d, J 8.1 Hz, 1H), 2.45 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 192.0 (C=O), 145.3 (C), 145.1 (C), 144.9 (C), 133.9 (C), 132.7 (C), 132.4 (CH), 131.1 (CH), 130.4 (2CH), 129.3 (2CH), 128.0 (CH), 122.4 (CH), 21.8 (CH3); HRMS (EI, 70 eV) Calc’d for C15H11F3O3S 344.0323, Found 344.0330.
133.5 (C), 132.9 (C), 132.7 (CH), 131.7 (CH), 130.4 (2CH), 129.4 (2CH), 129.2 (CH), 123.0 (CH), 21.8 (CH);

$^{19}$F NMR (CDCl$_3$, 282 MHz) $\delta$ -73.5 (s, 3F, CF$_3$), -78.3 (s, 3F, CF$_3$); HRMS (EI, 70 eV) Calc'd for C$_{16}$H$_{11}$F$_6$NO$_5$S$_2$ 474.9982, Found 474.9982.

5b: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -70.8 (s, 6F).

3c: pale yellow oil; IR (KRS-6) 2918, 2848, 1662, 1211, 1139, 1027 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.80 (dd, $J$ 6.9, 2.1 Hz, 2H), 7.61 (td, $J$ 7.7, 2.0 Hz, 1H), 7.56 (td, $J$ 7.7, 2.0 Hz, 1H), 7.48 (t, $J$ 7.5 Hz, 1H), 7.41 (d, $J$ 8.1 Hz, 1H), 6.95 (d, $J$ 8.7 Hz, 2H), 3.89 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 139.8 (C=O), 164.2 (C), 146.6 (CH), 132.9 (C), 132.6 (2CH), 132.2 (CH), 130.9 (CH), 129.3 (C), 128.0 (CH), 122.4 (C), 113.9 (2CH), 55.6 (CH$_3$); HRMS (EI, 70 eV) Calc'd for C$_{18}$H$_{13}$F$_3$O$_5$S 360.0279; Found 360.0272.

4c: colorless oil (mixture of 4c and 5c, 10:1); IR (KRS-6) 3019, 2923, 2849, 1662, 1394, 1211 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.79 (dd, $J$ 6.9, 2.1 Hz, 2H), 7.68 (td, $J$ 7.4, 2.1 Hz, 1H), 7.60 (td, $J$ 7.8, 2.4 Hz, 1H), 7.58 (d, $J$ 7.8 Hz, 1H), 7.53 (d, $J$ 8.1 Hz, 1H), 6.96 (dd, $J$ 6.3, 2.0 Hz, 2H), 3.89 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 190.0 (C=O), 164.4 (C), 133.1 (C), 132.7 (2CH), 132.5 (CH), 131.5 (C), 131.4 (CH), 129.2 (CH), 128.9 (C), 123.0 (CH), 114.0 (2CH), 55.6 (CH$_3$); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -73.6 (s, 3F), -78.3 (s, 3F); HRMS (EI, 70 eV) Calc'd for C$_{18}$H$_{11}$F$_6$NO$_5$S$_2$ 490.9931, Found 490.9934.

5c: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -70.9 (s, 6F).

3d: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J$ 8.1 Hz, 2H), 7.65 (td, $J$ 7.7, 2.0 Hz, 1H), 7.55 (td, $J$ 7.2, 2.1 Hz, 1H), 7.52 (d, $J$ 7.2 Hz, 1H), 7.47 (dd, $J$ 6.7, 1.9 Hz, 2H), 7.43 (d, $J$ 8.6 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 191.5 (C=O), 146.5 (C), 140.4 (C), 134.8 (C), 132.9 (C), 132.0 (CH), 131.5 (2CH), 131.1 (CH), 129.0 (2CH), 128.2 (CH), 122.6 (CH); HRMS (EI, 70 eV) Calc'd for C$_{18}$H$_{13}$F$_3$O$_5$S 363.9784; Found 363.9788.

4d: pale yellow crystals (mixture of 4d and 5d, 40:1); mp 56.7–57.1 °C; IR (KBr) 1671, 1394, 1211, 1134, 1091 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ 8.1 Hz, 2H), 7.61 (td, $J$ 7.7, 2.0 Hz, 1H), 7.55 (td, $J$ 7.2, 2.1 Hz, 1H), 7.52 (d, $J$ 7.2 Hz, 1H), 7.47 (dd, $J$ 6.7, 1.9 Hz, 2H), 7.43 (d, $J$ 8.6 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 190.3 (C=O), 144.9 (C), 140.8 (C), 134.3 (C), 133.3 (CH), 132.2 (C), 131.6 (CH), 131.5 (2CH), 129.4 (CH), 129.1 (2CH), 123.0 (CH), 118.6 (CF$_3$, q, $J$ 320 Hz), 118.5 (CF$_3$, q, $J$ 320 Hz); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -73.5 (s, 3F), -78.3 (s, 3F); HRMS (EI, 70 eV) Calc'd for C$_{18}$H$_{13}$F$_6$NO$_5$S$_2$ 494.9436; Found 494.9436.

5d: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -70.8 (s, 6F).

4e: pale yellow oil (mixture of 4e and 5e, 20:1); IR (KRS-6) 3031, 2924, 1232, 1135, 1141 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.40–7.36 (m, 3H), 7.32 (t, $J$ 7.1 Hz, 1H), 7.30 (t, $J$ 6.9 Hz, 2H), 7.26–7.22 (m, 1H), 7.20 (d, $J$ 6.6 Hz, 2H), 4.07 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 146.5 (C), 137.8 (C), 134.2 (C), 132.5 (CH), 129.7 (CH), 129.0 (2CH), 128.8 (2CH), 128.6 (CH), 121.8 (CH), 35.5 (CH$_2$); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -73.8 (s, 3F), -78.4 (s, 3F); HRMS (EI, 70eV) Calc'd for C$_{18}$H$_{13}$F$_6$NO$_5$S$_2$ 474.0033, Found 474.0035.

5e: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -70.5 (s, 6F).

4f: pale yellow crystals (mixture of 2f, 4f, and 5f, trace:10:1); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.41 (t, $J$ 8.0 Hz, 3H), 7.34 (t, $J$ 7.8 Hz, 1H), 7.23 (t, $J$ 8.7 Hz, 1H), 7.17 (d, $J$ 8.1 Hz, 1H), 7.09 (d, $J$ 7.5 Hz, 2H), 6.96 (d, $J$ 8.4 Hz, 1H); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -73.3 (s, 3F), -78.5 (s, 3F).

5f: $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -71.7 (s, 6F).

**DFT calculations**

Structures were optimized using a C$_1$ molecular point group by the density function theory (DFT) method$^{13}$ at B3LYP/6-31G(d) level using the Gaussian 03 package.$^{28}$ All computed geometries were verified by frequency calculations to have no imaginary frequencies. The solvent effects were calculated using the Polarizable
Continuum Model (PCM)\textsuperscript{14} for the optimized structures with ethanol (relative static permittivity, ε = 24.852) at the B3LYP/6-311+G(2d,p) level.

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Supplementary Material

Energies of the Optimized Structures by the DFT Calculations.

References and Notes


2. Laali, K. K.; Gettwert, V. J. Fluorine Chem. 2001, 107, 31–34. [https://doi.org/10.1016/S0022-1139(00)00337-7](https://doi.org/10.1016/S0022-1139(00)00337-7)


15. Empirical solvent polarity scale $E_I^{30}$, which is defined by using the solvatochromic shifts of Reichardt's dye, was reported to be 52.3 for [BMIM][TfO] and 51.5 for [BMIM][Tf$_2$N].$^{16}$ These values are comparable to that of ethanol (51.9). In addition, solvolytic studies suggested that the solvent effect of ionic liquids is similar to that of alcohols.$^{12,17}$


