



Novel biphasic reaction system of ferric chloride dissolved imidazolium hexafluorophosphate and benzotrifluoride: application to electron transfer reaction of cyclopropyl silyl ethers

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ABSTRACT

Ferric chloride (FeCl_3) promoted electron transfer oxidation of bicyclic cyclopropyl silyl ethers was performed in biphasic solution system of 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆) and benzotrifluoride (BTF). The resulting chloro-substituted ring-expanded cycloalkanones were treated with an appropriate base to produce substituted cyclic enones. These two-step reactions were successfully devised to proceed in a simpler manner in which the ordinary work-up operations for the former oxidation step, such as water-quench, extraction, and evaporation, were omitted; imidazole was found to be the most suitable base for the latter elimination step.

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1. Introduction

Development of practically convenient as well as environmentally benign procedures to promote the transformation of organic molecules should be appreciated not only for organic synthesis but also for green sustainable chemistry.¹ Among the efforts to achieve this objective is the use of environmentally benign reagents and solvents. Iron salts are recognized as one of the least expensive and toxic reagents, and thus the use of iron salt reagents is beneficial.² Some imidazolium salts, known as room temperature ionic liquids and environmentally benign solvents, have been frequently used for organic synthesis.³ As suggested by Ogawa and Curran, benzotrifluoride (PhCF_3 , BTF) is also known to be an environmentally benign solvent, and thus BTF could replace benzene and methylene chloride in several cases.⁴ On the other hand, a procedure to promote the sequential chemical processes with less experimental operations is also compatible with green sustainable chemistry. For example, one-pot reaction that promotes sequential processes in a single flask is one of the representative examples.⁵

Electron transfer (ET) is a fundamental chemical process that is operating in chemical as well as biological reduction and oxidation reactions, and various ET based synthetic procedures have been developed.^{6,7} Several years ago, we planned to develop synthetically useful procedures that could promote the desired ET reactions in a green sustainable manner, and have reported

several successful examples.⁸ In the course of these efforts, we encountered an intriguing observation in which addition of 1-butyl-3-methylimidazolium hexafluorophosphate (BmimPF₆) to ferric chloride (FeCl_3) in BTF significantly accelerated the ring-expansion reaction of a bicyclic cyclopropyl silyl ether.^{8c} Upon addition of BmimPF₆, solid FeCl_3 dissolved in this ionic liquid and the reaction proceeded under the liquid–liquid biphasic condition.

In this paper, we would like to report the characteristic feature of this novel biphasic reaction system of FeCl_3 dissolved in BmimPF₆, which could be recognized as FeCl_3 –BmimPF₆ hybrid reagent, and BTF to promote electron transfer reaction of the title substrates. Substrates and products together with representative reagents and solvents investigated are shown in Chart 1.

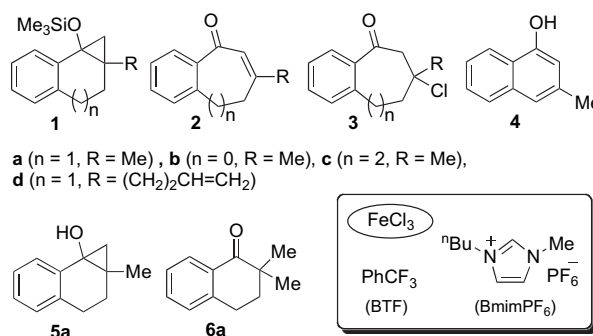
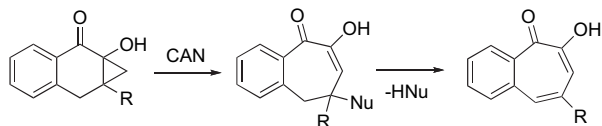


Chart 1.

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2. Results and discussion

In our earlier effort, we have found that ceric ammonium nitrate, $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ (CAN), was effective for oxidative ring-opening reaction of certain bicyclic cyclopropanol derivatives as shown below.⁹



Thus, silyl ether **1a** was subjected to the reaction with CAN in CH_3CN , and desired ring-expanded enone **2a** was obtained in moderate yield as shown in Table 1 (entry 1).^{8e} Then, we replaced CH_3CN by BTF, and found the reaction did not go to completion, and only a trace amount of **2a** was formed; deprotected cyclopropanol **5a** was the major isolable product (entry 2). FeCl_3 with pyridine in DMF was also effective to obtain **2a** in good yield after the treatment of β -chlorobenzosuberone **3a** with a methanolic NaOAc solution at reflux (entry 3).^{8e} We were rather surprised to find that toluene could be used for the reaction giving **2a** in moderate yield although FeCl_3 appears to be insoluble in toluene (entry 4). On the other hand, BTF was not as effective as above two solvents (entry 5).^{8c} However, addition of BmimPF₆ to this reaction mixture completely consumed **1a** and gave **2a** in the comparable yield to the reaction conducted in DMF (entries 3 and 6).^{8c,e}

Table 1
Reaction of **1a** with oxidizing reagents (Ox)^a

Entry	Ox	Additive (equiv vs 1a)	Solvent	Recovery of 1a (%)	Yield of 2a (%)
1	CAN ^c	None	CH_3CN	0	53
2	CAN ^c	None	BTF	50	Trace ^d
3 ^b	FeCl_3	Pyridine (1.0)	DMF	0	72
4 ^b	FeCl_3	Pyridine (1.0)	PhCH_3	0	59
5 ^b	FeCl_3	Pyridine (1.0)	BTF	67	15
6 ^b	FeCl_3	Pyridine (1.0) BmimPF ₆ (2.2)	BTF	0	68 ^e

^a Substrate **1a** (0.50 mmol), Ox (2.2 equiv), solvent (5.0–10.0 mL), at room temperature for 1 h.

^b Crude product mixture was heated with NaOAc (5.0 equiv) in MeOH (2.0–5.0 mL) at 85 °C for 2 h.

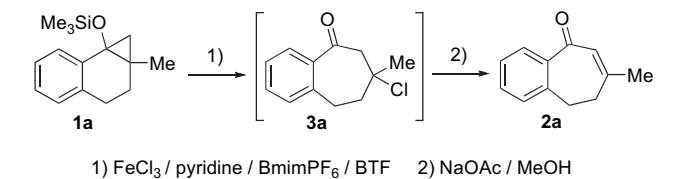
^c $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$.

^d Compound **5a** was obtained (22%).

^e Compound **6a** was obtained (12%).

These preliminary observations prompted us to further explore the characteristics of this new reagent system of FeCl_3 with BmimPF₆ in BTF. Our working hypothesis for the observation was that the liquid–liquid biphasic system of FeCl_3 dissolved in BmimPF₆ and BTF might provide better condition for an effective contact between **1a** and Fe(III) ion compared to the solid–liquid biphasic system of FeCl_3 and BTF. If so, the quantity of BmimPF₆ might influence the reaction, which was examined at first. In these experiments, instead of water-quench and Et_2O extraction used for the experiments in Table 1, separation of BTF layer followed by the rinse of BmimPF₆ layer with Et_2O was performed (see Experimental section).¹⁰ The results are summarized in Table 2. In all entries, NaOAc treatment of crude **3a** afforded **2a** in various yields depending on the quantity of BmimPF₆ while trace amount of **6a** was also detected in certain case. Addition of some quantities of BmimPF₆ increased both the conversion of **1a** and the yields of **2a** (entries 1–3), however further addition significantly decreased them (entries 4 and 5).

Table 2
BmimPF₆ quantity effect on the oxidation of **1a** with FeCl_3 and pyridine in BTF^a



Entry	BmimPF ₆ (mL) (equiv vs 1a)	Recovery of 1a (%)	Yield of 2a (%)
1 ^b	0.00 (0.0)	67	15
2	0.10 (1.0)	0	50
3	0.23 (2.2)	0	62
4	0.50 (4.8)	31	29
5	1.00 (9.6)	44	23

^a Substrate **1a** (0.50 mmol), FeCl_3 (2.2 equiv), pyridine (1.0 equiv), BTF (5.0 mL), at room temperature for 1 h. Crude product mixture was heated with NaOAc (5.0 equiv) in MeOH (5.0 mL) at 85 °C for 2 h.

^b Same as the entry 5 of Table 1.

The solubility of solid FeCl_3 in BTF appears to be minimal since BTF became only pale yellow upon addition of FeCl_3 . The oxidation reaction of **1** in BTF was indeed inefficient without BmimPF₆ (entry 5 in Table 1). On the other hand, addition of BmimPF₆ to FeCl_3 resulted in the formation of liquid phase containing FeCl_3 . Notably, this brown colored liquid appears to be in part dissolved in BTF because BTF phase clearly colored yellow by mixing these two phases. Increasing the quantity of BmimPF₆ decreased the concentration of FeCl_3 , and therefore the reaction was gradually decelerated by adding more quantity of BmimPF₆ (entries 4 and 5 in Table 2).

We next attempted to devise the simpler experimental operations, which are illustrated in Figure 1. If upper BTF layer of the reaction mixture is transferred to another flask and subsequently treated with appropriate base, requisite two-step transformations

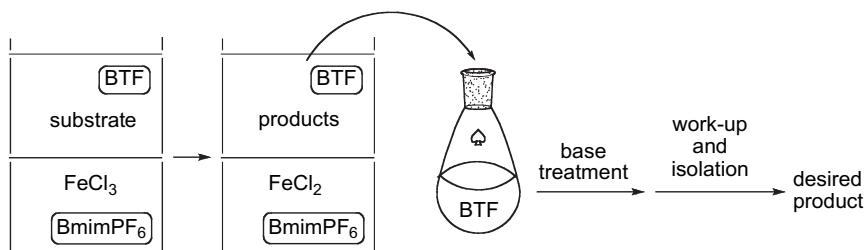
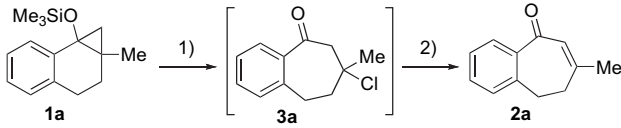


Figure 1.

could be achieved in simpler manner. For this purpose, we needed to search for the base compatible with BTF. As shown in Table 3, NaOAc, which is insoluble in BTF was not efficient (entry 1). Thus, we examined BTF soluble amine bases. While pyridine was not effective at all (entry 2), more basic Et₃N promoted the reaction (entry 5). Raising the reaction temperature and extending the reaction time increased the yield of **2a** (entry 6). Notably, imidazole was effective to give **2a** in the best yields (entries 3 and 4). On the other hand, an attempt to optimize the reaction conditions using strong base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was less successful (entries 7 and 8). Consequently, imidazole was chosen for the further experiments.

Table 3
Base effect on the elimination of **3a** derived from **1a** in BTF^a



1) FeCl₃ / pyridine / BmimPF₆ / BTF 2) base / BTF

Entry	Base	pKa (conjugate acid)	Temp (°C)	Time (h)	Yield of 2a (%)
1	NaOAc	4.75 ^c	85	2	35
2	Pyridine	5.2 ^c	85	2	0 ^b
3	Imidazole	6.95 ^d	85	21	61
4	Imidazole		120	21	57
5	Et ₃ N	10.65 ^e	85	2	41 ^b
6	Et ₃ N		120	21	56
7	DBU	14.3 ^f	85	2	22
8	DBU		rt	2	0 ^b

^a Substrate **1a** (0.50 mmol), FeCl₃ (2.2 equiv), pyridine (1.0 equiv), BmimPF₆ (2.2 equiv), BTF (5.0 mL), at room temperature for 1 h. BTF layer containing crude product mixture was treated with base (5.0 equiv) after additional BTF (2.0 mL) was combined.

^b Unreacted **3a** was detected by ¹H NMR.

^c Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

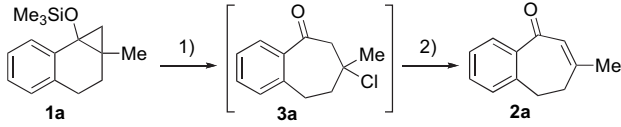
^d Hall, H. K, Jr. *J. Am. Chem. Soc.* **1957**, *79*, 5441–5444.

^e Bruice, T. C.; Schmir, G. L. *J. Am. Chem. Soc.* **1958**, *80*, 148–156.

^f Leffek, K. T.; Pruszyński, P.; Thanapaalasingham, K. *Can. J. Chem.* **1989**, *67*, 590–595.

In order to determine the utility of BTF, screening of other solvents was also performed. We chose toluene and cyclohexane, which dissolve compounds such as **1a**, **2a** and **3a**, and are insoluble in BmimPF₆. As shown in Table 4, less quantity of BTF (1.0 mL) did

Table 4
Solvent effect on the oxidation of **1a** and the subsequent elimination of **3a**^a



1) FeCl₃ / pyridine / BmimPF₆ / solvent 2) imidazole / solvent

Entry	Solvent (mL)	Yield of 2a (%)
1 ^b	BTF (5.0)	61
2	BTF (1.0)	60
3	No ^c	0 ^d
4	PhCH ₃ (5.0)	14
5	c-C ₆ H ₁₂ (5.0)	Trace

^a Substrate **1a** (0.50 mmol), FeCl₃ (2.2 equiv), pyridine (1.0 equiv), BmimPF₆ (2.2 equiv), at room temperature for 1 h. Organic layer containing crude product mixture was heated at 85 °C with imidazole (5.0 equiv) for 18–21 h after addition of same solvent (2.0 mL).

^b Same as the entry 3 of Table 3.

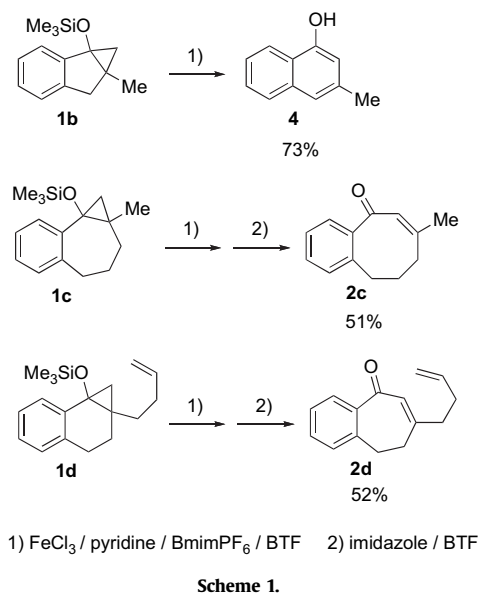
^c BTF (2.0 mL) was used for the reaction with imidazole.

^d Compound **5a** was obtained (7%).

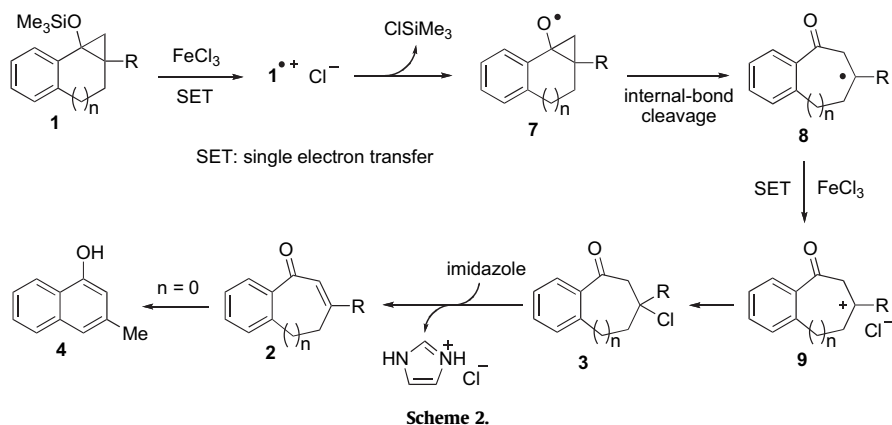
not significantly change the yield of **2a** (compare entry 2 to 1). However, the reaction in neat ionic liquid without BTF, resulted in no formation of **2a** (entry 3). Then, BTF was replaced with toluene and cyclohexane. Mixing each solvent with BmimPF₆ resulted in the formation of biphasic solutions. When the reaction of **1a** was conducted under the formed biphasic conditions, the yields of **2a** were quite low in both cases (entries 4 and 5).¹¹ These observations clearly suggest that the use of proper quantity of BTF is essential and BTF is certainly superior to toluene and cyclohexane for the FeCl₃ promoted biphasic reaction with BmimPF₆.

We also examined the following experiments to further devise the reaction procedure.¹² First, the elimination reaction of **3a** with imidazole was conducted in biphasic solutions without a prior separation of a BTF layer from a BmimPF₆ layer. However, this one-pot procedure resulted in the less formation of **2a** (34%) than that for the above described two-step procedure (see entry 3 in Table 3). Secondly, we attempted to reuse the recovered BmimPF₆ layer from the biphasic solutions after the reaction of **1a**, and found that **3a** was indeed obtained, however, its yield was low (33%).

As described above, the new procedure in which FeCl₃ promoted oxidation in the biphasic solvent system of BmimPF₆ and BTF followed by imidazole treatment in BTF was found to be effective for the transformation of **1a** to **2a**. Then, this procedure was applied to other substrates such as **1b**, **1c**, and **1d** (Scheme 1). In the reactions of **1c** and **1d**, the corresponding ring-expanded enones **2c** and **2d** were obtained in moderate yields. On the other hand, the imidazole treatment was not necessary for the reaction of **1b** to obtain naphthol **4** in good yield.



On the basis of the related investigations,^{8a,c,e,f,13} plausible reaction pathways are shown in Scheme 2. Single electron transfer (SET) from the substrate **1** to FeCl₃ to give the pair of radical cation of **1** and chloride ion. Desilylation within the formed ion pair follows. Cyclopropoxy radical **7**, that is a hypothetical intermediate,¹⁴ undergoes regioselective ring-opening to produce tertiary alkyl radical **8** that is subsequently oxidized by another equivalent of FeCl₃ to give thermodynamically stable tertiary carbocation **9**. Addition of the simultaneously generated chloride ion to **9** gives the chlorine adduct **3**. Heating **3** with imidazole leads the elimination of HCl giving enones **2**. In the case of **1b**, aromatization of the expected enone **2b** spontaneously occurred without imidazole to give naphthol **4**.



3. Conclusion

We have developed a novel liquid–liquid biphasic reaction system utilizing a combination of FeCl_3 and BmimPF_6 in BTF, which could promote electron transfer reaction of bicyclic cyclopropyl silyl ethers to give chloro-substituted ring-expanded cycloalkanones. Following treatment of these compounds with an appropriate base finally produced substituted cyclic enones. Also noteworthy is that these two-step reactions were successfully performed in BTF, which allowed us to skip the ordinary work-up operations for the former oxidation step, such as water-quench, extraction, and evaporation, and find imidazole as the best suitable base for the latter elimination step. FeCl_3 is among the most convenient and least expensive iron reagents, and can be used not only as oxidizing reagent¹⁵ but also as Lewis acid.^{2,16} Therefore, our newly developed procedure must be also applicable to other reactions in which both FeCl_3 and imidazolium salts are used.¹⁷ Currently, related investigation is undergoing in our group.

4. Experimental section

4.1. General

NMR spectra were recorded in CDCl_3 with Me_4Si as an internal standard at 200 MHz and 270 MHz for ^1H NMR, and 50 MHz and 68 MHz for ^{13}C NMR. Column chromatography was performed with silica gel (Wakogel C-200). Preparative TLC was performed on 20 cm \times 20 cm plates coated with silica gel (Wakogel B-5F). FeCl_3 and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ were purchased and used for the reactions. BTF, anhydrous DMF, and BmimPF_6 were purchased and used without distillation. MeCN was distilled over P_2O_5 and subsequently distilled with K_2CO_3 . Substrates **1a–d**^{8c,13} were synthesized according to literature procedures. Substrates and products (**2a**,¹³ **2c**,¹³ **2d**,¹³ **3a**,¹³ **4**,^{8c} **5a**,^{8f} and **6a**¹³) are known compounds.

4.2. Reaction with oxidizing reagents

4.2.1. FeCl_3 or $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ promoted reaction of **1a in DMF or MeCN.** FeCl_3 promoted reaction of **1a** in DMF was previously reported.^{8e} A MeCN solution (6 mL) of **1a** (123.2 mg, 0.50 mmol) was added to $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ (603.0 mg, 1.10 mmol) in MeCN (4 mL) under N_2 . The resulting mixture was stirred under N_2 at room temperature for 1 h. Then, it was extracted with Et_2O (30 mL \times 3) after addition of water. The extract was treated with water, satd aqueous $\text{Na}_2\text{S}_2\text{O}_3$, satd aqueous NaHCO_3 , satd aqueous NaCl , and dried over anhydrous MgSO_4 . The residue obtained after concentration was subjected to TLC ($\text{CH}_2\text{Cl}_2/n\text{-C}_6\text{H}_{14}=1/1$, three times) to give **2a** (45.6 mg, 0.265 mmol, 53%).

4.2.2. FeCl_3 promoted reaction of **1a in the presence or absence of BmimPF_6 in BTF.** A BTF solution (3 mL) of **1a** (123.2 mg, 0.50 mmol)

was added to FeCl_3 (178.4 mg, 1.10 mmol) and pyridine (0.040 mL, 0.50 mmol) in the presence or absence of BmimPF_6 (0.23 mL, 1.10 mmol) in BTF (2 mL) under N_2 . The resulting mixture was stirred under N_2 at room temperature for 1 h. Then, it was extracted with Et_2O (30 mL \times 3) after addition of water. The extract was treated with water, satd aqueous $\text{Na}_2\text{S}_2\text{O}_3$, satd aqueous NaHCO_3 , satd aqueous NaCl , and dried over anhydrous MgSO_4 . The residue obtained after concentration was subjected to TLC ($\text{CH}_2\text{Cl}_2/n\text{-C}_6\text{H}_{14}=1/1$) to give **3a**. In the absence of BmimPF_6 , 82.7 mg of **1a** (0.34 mmol, 67%) was also recovered. Then, NaOAc (5.0 equiv vs converted **1a**) and MeOH (2–5 mL) were added to **3a**. The mixture was refluxed at 85 °C for 2 h. After cooling, the mixture was concentrated, then water (30 mL) was added. The mixture was extracted with Et_2O (30 mL \times 3). The extract was treated with water, satd aqueous $\text{Na}_2\text{S}_2\text{O}_3$, satd aqueous NaHCO_3 , satd aqueous NaCl , and dried over anhydrous MgSO_4 . The residue obtained after concentration was subjected to TLC ($\text{CH}_2\text{Cl}_2/n\text{-C}_6\text{H}_{14}=1/1$) to give **2a**, 12.7 mg (0.074 mmol, 15%) or 58.5 mg (0.34 mmol, 68%) in the absence or presence of BmimPF_6 , respectively.

4.2.3. BmimPF_6 quantity effect on FeCl_3 promoted reaction of **1a in BTF.** A BTF solution (3 mL) of **1a** (123.2 mg, 0.50 mmol) was added to FeCl_3 (178.4 mg, 1.10 mmol), pyridine (0.040 mL, 0.50 mmol), and BmimPF_6 (0.10–1.00 mL, 0.96–9.6 mmol) in BTF (2 mL) under N_2 . The resulting mixture was stirred under N_2 at room temperature for 1 h. Then, a BmimPF_6 layer was rinsed with Et_2O (2 mL) after separation from a BTF layer. The residue obtained after concentration of BTF and Et_2O was subjected to TLC ($\text{CH}_2\text{Cl}_2/n\text{-C}_6\text{H}_{14}=1/1$) to give **1a** and **3a**. Then, **3a** was subjected to NaOAc treatment described above to give **2a**.

4.2.4. Base effect on the elimination of **3a derived from **1a** in BTF.** A BTF solution (3 mL) of **1a** (123.2 mg, 0.50 mmol) was added to FeCl_3 (178.4 mg, 1.10 mmol), pyridine (0.040 mL, 0.50 mmol), and BmimPF_6 (0.23 mL, 1.1 mmol) in BTF (2 mL) under N_2 . The resulting mixture was stirred under N_2 at room temperature for 1 h. Then, a BmimPF_6 layer was rinsed with BTF (2 mL) after separation from BTF layer. A base (2.5 mmol) was added to BTF solution, and the mixture was stirred at room temperature ~ 120 °C for 2–21 h. After cooling, the mixture was filtrated and concentrated. The residue was subjected to TLC ($\text{CH}_2\text{Cl}_2/n\text{-C}_6\text{H}_{14}=1/1$) to give **2a**.

4.2.5. Solvent effect on the oxidation of **1a and the subsequent elimination of **3a**.** An appropriate solution (0.75 or 3.0 mL) of **1a** (123.2 mg, 0.50 mmol) was added to FeCl_3 (178.4 mg, 1.10 mmol), pyridine (0.040 mL, 0.50 mmol), and BmimPF_6 (0.23 mL, 1.1 mmol) in the same solvent (0.25 or 2.0 mL) under N_2 . In the case of neat reaction (entry 3 in Table 4), **1a** was dissolved in pyridine and then the solution was added to FeCl_3 and BmimPF_6 . The resulting mixture was stirred under N_2 at room temperature for 1 h. Then,

a BmimPF₆ layer was rinsed with same solvent (2 mL) after separation from the solvent layer. Imidazole (170.2 mg, 2.5 mmol) was added to this solution, and the mixture was heated at 85 °C for 18–21 h. After cooling, the mixture was filtrated and concentrated. The residue was subjected to TLC to give **2a**.

4.2.6. General procedure of FeCl₃ promoted reaction of 1 and sequential elimination of 3 in BTF. A BTF solution (3 mL) of **1a** (123.2 mg, 0.50 mmol) was added to FeCl₃ (178.4 mg, 1.10 mmol), pyridine (0.040 mL, 0.50 mmol), and BmimPF₆ (0.23 mL, 1.1 mmol) in BTF (2 mL) under N₂. The resulting mixture was stirred under N₂ at room temperature for 1 h. Then, a BmimPF₆ layer was rinsed with BTF (2 mL) after separation from BTF layer. Imidazole (170.2 mg, 2.5 mmol) was added to BTF solution, and the mixture was heated at 85 °C for 21 h. After cooling, the mixture was filtrated and concentrated. The residue was subjected to TLC to give **2a**. Same treatment of **1c** and **1d** gave **2c** (0.253 mmol, 51%) or **2d** (0.258 mmol, 52%), respectively. In the case of **1b**, **4** (57.6 mg, 0.364 mmol, 73%) was obtained without NaOAc treatment.

4.2.7. FeCl₃ promoted reaction of 1a and sequential elimination of 3a in biphasic solutions without separation of a BTF layer from a BmimPF₆ layer. A BTF solution (3 mL) of **1a** (123.2 mg, 0.50 mmol) was added to FeCl₃ (178.4 mg, 1.10 mmol), pyridine (0.040 mL, 0.50 mmol), and BmimPF₆ (0.23 mL, 1.1 mmol) in BTF (2 mL) under N₂. The resulting mixture was stirred under N₂ at room temperature for 1 h. Imidazole (170.2 mg, 2.5 mmol) was added, and the biphasic solution mixture was heated at 85 °C for 21 h. After cooling, the mixture was filtrated by Celite and concentrated. The residue was subjected to TLC (CH₂Cl₂/n-C₆H₁₄=1/1, three times) to give **2a** (29.5 mg, 0.171 mmol, 34%).

4.2.8. The reaction of 1a with the recovered BmimPF₆ after the reaction of 1a. A BTF solution (5 mL) of **1a** (123.2 mg, 0.50 mmol) was added to the BmimPF₆ layer that was separated from the BTF layer after the reaction of **1a** with FeCl₃ (2.2 equiv). The resulting mixture was stirred under N₂ at room temperature for 1 h. Then, BmimPF₆ layer was rinsed with BTF (2 mL) after separation from BTF layer. Imidazole (170.2 mg, 2.5 mmol) was added to BTF solution, and the mixture was heated at 85 °C for 21 h. After cooling, the mixture was filtrated and concentrated. The residue was subjected to TLC (CH₂Cl₂/n-C₆H₁₄=1/1, twice) to give **2a** (28.2 mg, 0.164 mmol, 33%).

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- Same experiments using toluene were conducted (comparable to entries 3, 4, and 5 in Table 2). However, the reactions were not completed (contrastive to entry 4 in Table 1). Results are as follows. The quantity of BmimPF₆ (equiv): 2.2, 4.8, 9.6; the recovery of **1a** (%): 68, 39, 52; the yield of **2a** (%): 16, 26, 23, respectively.
- The difference of the yield of **2a** between the result reported in the note 10 and that of entry 4 in Table 4 could be due to the difference of the solvent to rinse BmimPF₆ phase. While Et₂O was used in the former experiment, toluene was used in the latter. These observations also suggest that toluene would not be an effective extraction solvent toward BmimPF₆.
- Although these devised procedures, that are more compatible with green chemistry, do not reach the satisfactory level at this moment, the improvement of them would be certainly the future subject to investigate. We thank two reviewers who independently suggested us to conduct these experiments.
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