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Tris(trimethylsilyl)silane promoted radical reaction and electron-transfer reaction in benzotrifluoride

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ABSTRACT

Tris(trimethylsilyl)silane (TTMSS) promoted free radical reaction in benzotrifluoride (BTF) was investigated. Compared to same reaction using environmentally less desirable tri-*n*-butyltin hydride (TBTH) in benzene, less quantity of BTF than that of benzene can be used because of slower hydrogen atom transfer from TTMSS than that from TBTH toward primary alkyl radicals. Also, electron-transfer reactions promoted by tris(*p*-bromophenyl)aminium hexachloroantimonate (TBPA) and $FeCl_3$ were conducted in BTF. Then, TBPA was found to be effective in BTF comparably to that in methylene chloride. In addition, an interesting observation that $FeCl_3$ promoted reaction was accelerated by the addition of imidazolium salt was made. All the results suggest that BTF is a tolerable solvent for free radical reaction with TTMSS and electron-transfer reactions using TBPA as well as $FeCl_3$.

1. Introduction

Because of neutral and mild condition, free radical reactions have been extensively utilized for various organic transformations that often play key roles for total synthesis of natural products.[1,2] Among the methods to promote free radical reactions, tri-*n*-butyltin hydride (TBTH) in benzene has been most widely employed.[1–3] However, the use of TBTH and benzene is considered to be environmentally less desirable. About 10 years ago, Ogawa and Curran suggested that benzotrifluoride (BTF) is an environmentally more benign solvent than benzene and methylene chloride, both of which are commonly used for organic reactions, and these solvents could be substituted by BTF.[4,5] Also, about two decades ago, tris(trimethylsilyl)silane (TTMSS) was proposed as a less toxic radical reagent than organotin hydride.[6] Then, we noticed that the combination of TTMSS and BTF has not been previously applied to free radical reactions although several examples using TBTH and other organotin hydrides in BTF were already reported.[5,7] Therefore, a tolerance of BTF for TTMSS promoted free radical reaction is not clear at present.

Electron-transfer (ET) is another way to generate radical species.[8,9] Thus, single electron-transfer (SET) of neutral organic molecules generates radical ions that often undergo fragmentation to give free radicals and ions. Triarylamine radical cation salts, aminium salts, are well-known SET oxidants that promote oxidative transformation of various organic compounds.[10] In these reactions, methylene chloride has been frequently used as a suitable solvent. Therefore, we were interested in determining if methylene chloride could be substituted by BTF in aminium salt promoted ET reactions. Also, to the best of our knowledge, BTF has not been previously applied to ET reactions of organic compounds.

In this paper, we would like to report results and discussion obtained from the study of TTMSS promoted free radical reactions as well as aminium salt promoted ET reactions in BTF. Also, we studied $FeCl_3$ promoted ET reaction in BTF.

2. Results and discussion

2.1. Free radical reaction in BTF

At first, in order to determine if TTMSS is effective in BTF, we examined Et_3B initiated free radical reaction[11] of 2-bromomethyl-2-(3′-butenyl)-1-benzocycloalkanones **1**, which we previously developed as effective radical probe substrates,[12] with TTMSS in BTF and benzene (Table 1).

The reaction is expected to proceed involving initial bromine atom abstraction by TTMSS derived silyl radical, and to be followed by fast 5-*exo* cyclization (Scheme 1).[12,13] In both cases of **1a** and **1b**, reactions in BTF were clean and yields of spiro-cyclization products **2a** and **2b** were greater in BTF than those in benzene. These results clearly indicate that BTF is tolerable for the free radical reaction using TTMSS.

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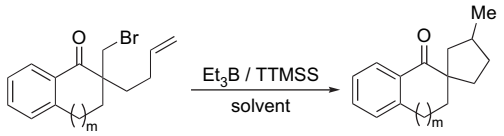
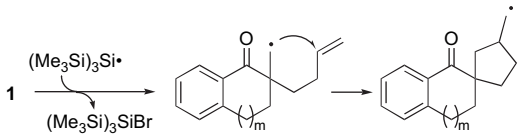
Table 1
Radical cyclization reaction of **1** with TTMSS[a]



1a (m = 1) **1b** (m = 0) **2a** (m = 1) **2b** (m = 0)

Entry	1	Solvent	Conversion (%)	Yield of **2** (%)
1	**1a**	Benzene	100	90
2	**1a**	BTF	100	96
3	**1b**	Benzene	100	78
4	**1b**	BTF	100	~100

[a] Compound **1** (0.50 mmol), TTMSS (1.0 equiv vs **1**), Et_3B (0.20 equiv vs **1**), solvent (10 mL), rt, 6 h.



Scheme 1.

Next, we applied the above method to the reaction of 2-bromomethylated benzocyclic β-keto esters **3**.[14,15] Substrates **3** and the products **4** and **5** are shown in Chart 1, and the results are summarized in Table 2.

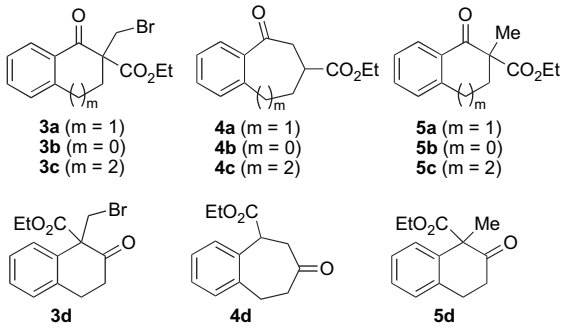
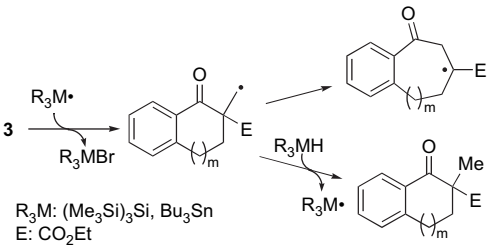


Chart 1.

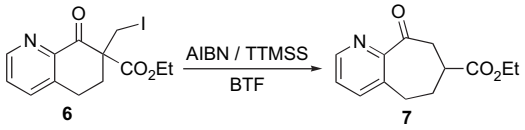
In this case, cyclization and ring-expansion rearrangement of initially generated primary alkyl radical occur while competitive hydrogen atom abstraction of the same primary alkyl radical is also expected because of relatively slow radical rearrangement (Scheme 2).[16]



Scheme 2.

Indeed, Et_3B promoted reactions of **3a** at room temperature produced a simply reduced product **5a** as a major product along with minor formation of the desired ring-expansion product **4a** in benzene and BTF (entries 1 and 2, Table 2). Also, the ratio of **4a** to **5a** and the total yield of **4a** and **5a** in BTF were similar to those in benzene. Under the refluxing conditions using AIBN as a radical initiator, BTF was again an effective solvent comparably to benzene, and the ratio of **4a** to **5a** became reversed to that under the room temperature conditions (entries 3 and 4). Expectedly, decreasing the volume of BTF increased the ratio of **5a** to **4a** (entry 5). Reactions of **3a** with TBTH in benzene were also performed (entries 6 and 7). In the case of TBTH, the use of 10 times volume of benzene compared to BTF was required to obtain **4a** in a comparable yield to that in BTF (entries 4 and 7). This observation is consistent with the difference in rate constant of hydrogen atom abstraction by primary alkyl radical toward TTMSS and TBTH.[17] Similar tendencies in the product ratio of **4** to **5** were also observed in the reactions of other substrates **3** (compare entries 8 and 9; 10 and 11; 12 and 13).

A recent report suggests that above type of radical cyclization and ring-expansion protocol has been successfully applied to the synthesis of potential precursors for antagonists of several G-protein coupled receptors found in the central nervous system.[18] For example, refluxing of toluene solution of the iodide **6** with AIBN and TBTH was reported to produce **7** in 75% under the high dilution condition using syringe-pump method. Notably, it was also reported that the reaction did not proceed when TBTH was replaced by TTMSS. However, our findings described above prompted us to apply our method using TTMSS in BTF to the transformation of **6** to **7**. Then, we were fortunate to discover that **7** was obtained in 54% when a BTF (10 mL) solution of **6** was refluxed with TTMSS (1.0 equiv) and AIBN (0.10 equiv) for 6 h (Eq. 1).



(1)

Table 2
Cyclization and ring-expansion reaction of **3** with TTMSS or TBTH[a]

Entry	3	Solvent (mL)	H-donor, initiator	Temperature	Conversion (%)	**4** (%)	**5** (%)
1	**3a**	Benzene (10)	TTMSS, Et_3B	rt	100	29	66
2	**3a**	BTF (10)	TTMSS, Et_3B	rt	100	24	74
3	**3a**	Benzene (10)	TTMSS, AIBN	Reflux	100	76	18
4	**3a**	BTF (10)	TTMSS, AIBN	Reflux	100	76	22
5	**3a**	BTF (2)	TTMSS, AIBN	Reflux	100	31	64
6	**3a**	Benzene (10)	TBTH, AIBN	Reflux	96	36	47
7	**3a**	Benzene (100)	TBTH, AIBN	Reflux	95	72	11
8	**3b**	BTF (10)	TTMSS, AIBN	Reflux	100	78	22
9	**3b**	Benzene (100)	TBTH, AIBN	Reflux	85	74	10
10	**3c**	BTF (10)	TTMSS, AIBN	Reflux	95	28	14
11	**3c**	Benzene (100)	TBTH, AIBN	Reflux	82	23	33
12	**3d**	BTF (10)	TTMSS, AIBN	Reflux	96	68	4
13	**3d**	Benzene (100)	TBTH, AIBN	Reflux	100	72	10

[a] Compound **1** (0.50 mmol), H-donor (1.0 equiv vs **1**), Et_3B (0.20 equiv vs **1**), AIBN (0.10 equiv vs **1**), 6 h.

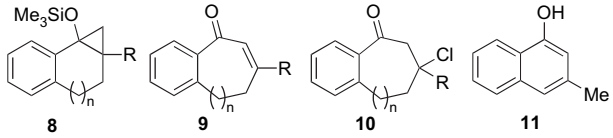
2.2. Electron-transfer reaction in BTF

In ET reactions in solution, solvent polarity is among key factors to govern reaction pathways.[8,9] Therefore, we decided to estimate the polarity of BTF and other solvents used for our experiments by measuring the absorption spectra of pyridinium *N*-phenolate betaine dye (Table 3).[19] Estimated polarity of BTF is slightly lesser than methylene chloride.

Table 3
Solvent E_T values of BTF and other solvents

Solvent	THF	BTF	CH_2Cl_2	DMF	MeCN
E_T^{30} (kcal/mol)	37.4	39.3	41.0	43.3	45.7
E_T^N	0.207	0.265	0.318	0.389	0.463

In order to investigate the compatibility of BTF with ET reactions, we chose oxidative ring-opening reaction of bicyclic cyclopropyl silyl ethers that was recently developed by us.[20] Substrates **8** and products **9**–**11** are shown in Chart 2.

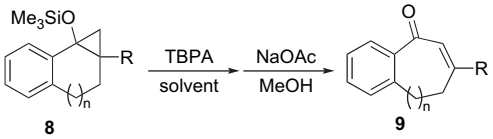


a (n = 1, R = Me) , **b** (n = 0, R = Me), **c** (n = 2, R = Me),
d (n = 1, R = $(CH_2)_2CH=CH_2$), **e** (n = 1, R = $(CH_2)_3CH=CH_2$)

Chart 2.

Reaction of **8** with tris(*p*-bromophenyl)aminium hexachloroantimonate (TBPA) at room temperature resulted in the product mixture of ring-expanded enones **9** and chlorine adducts **10**. Then, the crude reaction mixture was subjected to refluxing methanolic NaOAc to achieve complete conversion of **10** to **9**. In this sequence, no **8** were recovered in all cases presented in Table 4.

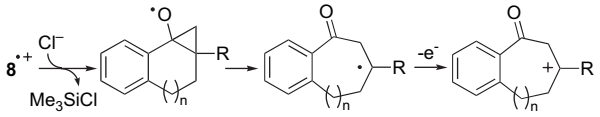
Table 4
TBPA promoted ring-opening reaction of **8**[a] and subsequent treatment with NaOAc[b]



Entry	**8**	Solvent	TBPA (equiv vs **8**)	Yield of **9** (%)
1	**8a**	CH_2Cl_2	2.0	79
2	**8a**	MeCN	2.0	43
3	**8a**	BTF	2.0	67
4	**8a**	BTF	1.0	89
5	**8c**	BTF	1.0	68
6	**8d**	BTF	1.0	74
7	**8e**	BTF	1.0	47

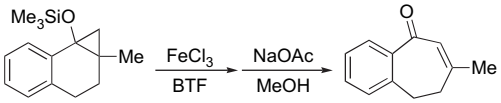
[a] Compound **8** (0.40 mmol), solvent (8 mL), rt, 30 min.
[b] NaOAc (5.0 equiv vs **8**), MeOH (8.0 mL), 85 °C, 2 h.

Key process for this ET reaction is shown in Scheme 3. Initial SET produces radical cation of **8**, which then undergoes desilylation to give cyclopropoxy radical. Regioselective ring-opening of cyclopropane gives tertiary alkyl radical. Then, the formation of tertiary carbocation through further SET by TBPA is expected.[20] As seen the fact that the yield of **9a** for BTF was less than that for methylene chloride and greater than that for acetonitrile (entries 1–3, Table 4), BTF is compatible with the TBPA promoted reaction. Attempt to optimize reaction condition let us to find that a use of 1 equiv of TBPA produced **9a** in good yield (entry 4). Applying this condition to other substrates, corresponding enones **9** were obtained from modest to good yields (entries 5–7). In the case of **8b**, reaction with TBPA produced hydroxy naphthalene **11** (28%) without NaOAc treatment. This low yield is perhaps due to the further oxidation of **11** since it was found to react with TBPA.



Scheme 3.

Next, we briefly conducted the transformation of **8a** to **9a** by using $FeCl_3$ in BTF (Eq. 2).[21](2).



(2)

As previously reported, $FeCl_3$ (2.2 equiv vs **8a**) promoted the reaction of **8a** giving **9a** in good yield (72%) in DMF.[20a] Then, we switched the solvent from DMF to BTF to find that the reaction was not completed and the yield of **9a** was low (45% based on 33% conversion of **8a**). This inefficiency could be due to the low solubility of $FeCl_3$ in BTF. Then, after several attempts, we unexpectedly discovered that addition of 1-butyl-3-methylimidazolium hexafluorophosphate ($Bmim^+PF_6^-$, 1.0 equiv vs $FeCl_3$) to the reaction mixture completed the reaction and yielded **9a** in 68%.[22]

3. Conclusion

As described above, BTF is a tolerable solvent both for free radical reaction with TTMSS and for ET reaction with TBPA. In the former case, compared with TBTH in benzene, less quantity of BTF than that of benzene can be used because of slower hydrogen atom transfer from TTMSS than that from TBTH toward primary alkyl radicals. In the latter, the corresponding amine was recovered after the reaction, which then could be used to prepare TBPA again. An observation that imidazolium salt accelerated the $FeCl_3$ promoted reaction should also be notable. All these results clearly suggest that further investigation to determine how BTF is generally useful for other free radical as well as ET reaction systems will be worth conducting.

4. Experimental section

4.1. General

^1H NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal standard at 200, 270 and 500 MHz. Column chromatography was performed with silica gel (Wakogel C-200). Preparative TLC was performed on 20 cm×20 cm plates coated with silica gel (Wakogel B-5F). BTF and anhydrous DMF were purchased and used without distillation. Benzene and CH_2Cl_2 were treated with H_2SO_4, water, 5% NaOH, water, $CaCl_2$, and then distilled with CaH_2. MeCN was distilled over P_2O_5 and subsequently distilled with K_2CO_3. THF was distilled over sodium-benzophenone under N_2. TTMSS, TBTH and $FeCl_3$ were purchased and used for the reactions. Pyridinium *N*-phenolate betaine dye was purchased and its absorption spectra in several solvents were measured. TBPA was prepared according to the literature procedure.[23] Other reagents and solvents were purchased and used without further purification. Substrates (**1a**,[12,24] **3a**–**d**,[14c,25] **6**,[18] **8a**–**e**[20]) and products (**2a**,[12,24] **4a**–**d**,[14c,25] **5a**,**c**,[14c,25]

7,[18] **9a–d**,[20b]) are known compounds. Spectral data of **1b–3b**, **5b**,**d**, **8b**, **9e** and **11** are presented below. While **10a** was previously characterized,[20b] crude **10** were usually treated with NaOAc in MeOH.

4.2. Free radical reactions with TTMSS and TBTH

4.2.1. Et_3B initiated reaction with TTMSS in BTF or benzene

Typical procedure is represented by **3a**. TTMSS (0.15 mL, 0.49 mmol) and Et_3B (1.0 M in THF, 0.10 mL, 0.10 mmol) were added to a N_2 prepurged BTF solution (10 mL) of **3a** (155.6 mg, 0.50 mmol). Then, air was introduced by syringe (2 mL). The resulting solution was stirred at room temperature for 6 h. The residue obtained by concentration was subjected to column chromatography using EtOAc/*n*-C_6H_{14} (1/5). Then, **4a** (27.7 mg, 0.12 mmol, 24%) and **5a** (86.0 mg, 0.37 mmol, 74%) were separated. Reactions of **3a** in benzene, other **3** in BTF, and **1a**,**b** were similarly performed. When column separation could not remove organosilicone compounds, further TLC separation was necessary. If these separations were not satisfactory, ^{1}H NMR analysis was performed using an internal standard (triphenyl methane).

4.2.2. AIBN initiated reaction with TTMSS or TBTH in BTF or benzene

TTMSS (0.15 mL, 0.49 mmol) was added to a N_2 prepurged BTF solution (10 mL) of **3a** (155.6 mg, 0.50 mmol) and AIBN (8.3 mg, 0.051 mmol). The resulting solution was refluxed for 6 h. The residue obtained by concentration was subjected to same column chromatography separation as described above to give **4a** (87.7 mg, 0.38 mmol, 76%) and **5a** (26.0 mg, 0.11 mmol, 22%). Reactions of **3a** with TBTH in benzene, other **3** with TTMSS in BTF and with TBTH in benzene, were similarly performed. In the case of TBTH reactions, reaction solutions were subjected to DBU workup procedure to remove organotin compounds.[26]

*4.2.2.1. Compound **1b**.* Pale yellow oil; IR (Neat) 1710 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.72–2.10 (m, 4H), 3.09 (d, J=18.9 Hz, 1H), 3.37 (d, J=18.9 Hz, 1H), 3.56 (d, J=10.0 Hz, 1H), 3.65 (d, J=10.0 Hz, 1H), 4.89–4.96 (m, 2H), 5.62–5.77 (m, 1H), 7.36–7.50 (m, 2H), 7.63 (m, 1H), 7.76 (m, 1H); ^{13}C NMR (50 MHz) δ 28.6, 36.2, 37.4, 38.8, 53.2, 115.2, 124.2, 126.4, 127.7, 135.4, 136.4, 137.3, 152.7, 206.9. LRMS (EI) m/z (relative intensity) 278 (M^+, 0.4), 280 (M^++2, 0.4), 129 (100).

*4.2.2.2. Compound **2b** (mixture of two diastereomers).* Pale yellow oil; IR (Neat) 1700 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.07 (d, J=6.5 Hz, 3H, major isomer), 1.10 (d, J=7.6 Hz, 3H, minor isomer), 1.22–1.46 (m, 2H), 1.61–1.70 (m, 1H), 1.96–2.08 (m, 2H), 2.24–2.45 (m, 2H), 3.11 (d, J=16.2 Hz, 1H), 3.16 (d, J=16.2 Hz, 1H), 7.33–7.42 (m, 2H), 7.57 (m, 1H), 7.75 (m, 1H); ^{13}C NMR (50 MHz) δ 20.1, 21.0, 34.8, 35.6, 39.3, 44.7, 46.1, 56.8, 124.0, 126.2, 127.2, 134.5, 136.1, 152.8, 211.4. LRMS (EI) m/z (relative intensity) 200 (M^+, 11.5), 145 (100). HRMS (EI) calcd for $C_{14}H_{16}O$ 200.1201, found 200.1204.

*4.2.2.3. Compound **3b**.* Colorless oil; IR (Neat) 1736, 1712 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.23 (t, J=7.0 Hz, 3H), 3.39 (d, J=18.0 Hz, 1H), 3.79 (d, J=18.0 Hz, 1H), 3.80 (d, J=10.4 Hz, 1H), 4.01 (d, J=10.4 Hz, 1H), 4.19 (qd, J=7.0, 1.1 Hz, 2H), 7.42–7.67 (m, 3H), 7.79 (m, 1H); ^{13}C NMR (50 MHz) δ 14.0, 34.4, 36.7, 61.4, 62.3, 125.0, 126.4, 127.9, 134.8, 135.8, 153.2, 168.5, 199.0. LRMS (EI) m/z (relative intensity) 296 (M^+, 2.8), 298 (M^++2, 2.8), 218 (100).

*4.2.2.4. Compound **5b**.* Pale yellow oil; IR (Neat) 1684 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.19 (t, J=7.1 Hz, 3H), 1.52 (s, 3H), 3.00 (d, J=17.5 Hz, 1H), 3.71 (d, J=17.5 Hz, 1H), 4.15 (q, J=7.1 Hz, 2H), 7.37–7.50 (m, 2H), 7.60–7.68 (m, 1H), 7.80 (m, 1H); ^{13}C NMR (50 MHz) δ 14.0, 21.0, 40.0, 56.0, 61.5, 124.9, 126.4, 127.8, 134.7, 135.3, 152.6, 172.0, 203.5. LRMS (EI) m/z (relative intensity) 218 (M^+, 66.4), 145 (100). HRMS (EI) calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0943.

*4.2.2.5. Compound **5d**.* Colorless oil; IR (Neat) 1742, 1716 cm^{-1}; ^{1}H NMR (200 MHz) δ 1.15 (t, J=7.1 Hz, 3H), 1.68 (s, 3H), 2.58–3.27 (m, 4H), 4.12 (qd, J=7.1, 1.4 Hz, 2H), 7.20–7.28 (m, 4H); ^{13}C NMR (50 MHz) δ 13.9, 22.2, 28.0, 37.5, 59.2, 61.7, 126.7, 127.3, 127.5, 128.3, 135.8, 137.6, 171.4, 208.5. LRMS (EI) m/z (relative intensity) 232 (M^+, 29.2), 159 (100). HRMS (EI) calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1093.

4.3. Electron-transfer reaction with TBPA and $FeCl_3$

4.3.1. TBPA promoted reaction in BTF

TBPA (332.7 mg, 0.41 mmol) was added to a solution of **8a** (98.7 mg, 0.40 mmol) in BTF (8 mL) under N_2. The resulting mixture was stirred for 30 min. Then, it was filtered and washed with Et_2O to remove unreacted TBPA. The filtrate was concentrated and subjected to column chromatography using CH_2Cl_2/*n*-C_6H_{14} (1/1) to give the mixture of **9a** and **10a** together with tris(*p*-bromophenyl)amine. Subsequently, this product mixture was refluxed with NaOAc (2.06 mmol) for 2 h in MeOH (8 mL). Then, extraction with Et_2O was performed, and the extract was treated with water, satd aqueous $NaHCO_3$, satd aqueous NaCl, and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to TLC (CH_2Cl_2/*n*-C_6H_{14}=1/1) and **9a** was obtained. Reactions of **8a** in other solvents and other **8** in BTF were similarly performed. However, in the case of **8b**, TLC separation of the crude reaction mixture obtained from the reaction with TBPA produced **11**.

4.3.2. $FeCl_3$ promoted reaction on BTF

A BTF solution (3 mL) of **8a** (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 $Bmim^+PF_6^-$ (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 after addition of water. The extract was treated with water, satd aqueous $Na_2S_2O_3$, satd aqueous $NaHCO_3$, satd aqueous NaCl, and dried over anhydrous $MgSO_4$. The residue obtained after concentration was subjected to TLC (CH_2Cl_2/*n*-C_6H_{14}=1/1) to give **10a**. In the absence of $Bmim^+PF_6^-$, 82.7 mg of **8a** (0.34 mmol, 67%) was also recovered. Then, **10a** was subjected to NaOAc treatment described above to give **9a**, 12.7 mg (0.074 mmol, 15%) or 58.5 mg (0.34 mmol, 68%), in the absence or presence of $Bmim^+PF_6^-$, respectively.

*4.3.2.1. Compound **8b**.* Pale yellow oil; IR (Neat) 1322, 1250, 1186, 1144, 872, 840 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.22 (s, 9H), 0.53 (d, J=4.9 Hz, 1H), 1.13 (d, J=4.9 Hz, 1H), 1.44 (s, 3H), 2.84 (d, J=16.7 Hz, 1H), 2.98 (d, J=16.7 Hz, 1H), 7.11–7.23 (m, 3H), 7.35–7.38 (m, 1H); ^{13}C NMR (68 MHz) δ 1.4, 17.6, 27.6, 28.6, 41.2, 71.0, 121.9, 125.0, 125.8, 126.0, 138.6, 147.3. LRMS (EI) m/z (relative intensity) 232 (M^+, 0.8), 73 (100).

*4.3.2.2. Compound **9e**.* Pale yellow oil; IR (Neat) 1638, 1302 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.56–1.67 (m, 2H), 2.04–2.10 (m, 2H), 2.22–2.28 (m, 2H), 2.52–2.56 (m, 2H), 3.01–3.05 (m, 2H), 4.97–5.05 (m, 2H), 5.71–5.86 (m, 1H), 6.22 (s, 1H), 7.15–7.18 (m, 1H), 7.27–7.42 (m, 2H), 7.77–7.80 (m, 1H); ^{13}C NMR (68 MHz) δ 27.0, 33.2, 33.6, 34.2, 40.1, 115.1, 126.6, 128.4, 129.1, 129.5, 131.8, 137.7, 139.1, 139.8, 162.1, 193.2. LRMS (EI) m/z (relative intensity) 226 (M^+, 21.7), 129 (100). HRMS (EI) calcd for $C_{16}H_{18}O$ 226.1358, found 226.1359.

*4.3.2.3. Compound **11**.* Orange oil; IR (KBr) 3308 cm^{-1}; ^{1}H NMR (200 MHz) δ 2.44 (s, 3H), 6.65 (s, 1H), 7.21 (s, 1H), 7.35–7.49 (m, 2H), 7.67–7.74 (m, 1H); 8.05–8.12 (m, 1H); ^{13}C NMR (50 MHz) δ 21.8, 110.8, 119.7, 121.3, 122.6, 124.3, 126.5, 127.0, 134.8, 135.8, 151.0. LRMS

(EI) *m*/*z* (relative intensity) 158 (M^+, 100). HRMS (EI) calcd for $C_{11}H_{10}O$ 158.0732, found 158.0729.

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15. According to the literature,[14c] toluene refluxing of **3a** with TBTH and AIBN also produced **4a**, but typically in low yields (10–39%).
16. The rate constant of rearrangement (k_r) was estimated by the equation, $k_r=k_H\times$[TTMSS or TBTH]$_{eff}\times$(**4a**/**5a**) in which k_H is the rate constant of hydrogen atom abstraction,[15] [TTMSS or TBTH]$_{eff}$ means 0.5[TTMSS or TBTH]$_{initial}$. Then, 1.5×10^4, 1.2×10^5 and 1.4×10^5 s^{-1} were obtained at 25, 80 and 102 °C, respectively.
17. (a) Rate constants of hydrogen atom abstraction by primary alkyl radical from TTMSS and TBTH were estimated.[17b] Those are 3.9×10^5 and 2.4×10^6 M^{-1} s^{-1} at 25 °C, 1.2×10^6 and 6.4×10^6 M^{-1} s^{-1} at 80 °C, 1.9×10^6 and 8.7×10^6 M^{-1} s^{-1} at 102 °C for TTMSS and TBTH, respectively. (b) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151–1176.
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21. Ceric ammonium nitrate (CAN) was not effective in BTF while CAN promoted the reaction of **8a** to give **9a** in MeCN.
22. At the moment, it seems difficult to rationalize this interesting observation. On addition of $Bmim^+PF_6^-$, solid $FeCl_3$ was dissolved in this ionic liquid and the reaction proceeded under the liquid–liquid biphase condition. This BTF–imidazolium (liquid–liquid) biphase system might provide better condition for an efficient contact between **8** and Fe(III) ion compared to BTF–$FeCl_3$ (liquid–solid) biphase system.
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