First application of ionic liquids in electrophilic fluorination of arenes; Selectfluor™ (F-TEDA-BF_4) for "green" fluorination

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The NF fluorinating agent F-TEDA-BF_4 dication salt (Selectfluor™) **1** dissolves in imidazolium-based ionic liquids [emim][OTf] **7**, [emim][BF_4] **8**, [bmim][PF_6] **9** and [bmim][BF_4] **10** (assisted by sonication), providing a convenient medium for fluorination of arenes under essentially acid-free conditions in a simple set-up (no volatile solvent; simple extraction of the aromatics without aqueous work-up), from which the ionic liquid can be easily recycled and reused. Comparative studies in [emim][OTf] **7** with anisole as substrate show that **1** is superior to NFTh-BF_4 (Accufluor®) **2** and that the *N*-fluoropyridinium salt NFPy-B_2F_7 **4** is least effective. The scope of the reaction has been surveyed. Substrate selectivity ($k_{mesitylene} : k_{durene} = 10$) measured in competitive experiments in **7** is clearly indicative of a conventional polar mechanism. Substrate selectivity measured without the ionic liquid in MeCN solvent is also indicative of a polar mechanism but exhibits lower magnitude ($k_{mesitylene} : k_{durene} = 6$).

Addition of dicyclohexano-24-crown-8 to the fluorination reaction mixture (**1** and anisole) in **7** reduced the conversion but did not change the isomer distribution. AM1 minimization was used to model the complexation of **1** with this crown.

With reactive aromatics optimal fluorination yields in ionic liquids (using 1 equivalent of the NF reagent) are around 50% (higher for naphthalene). A key control experiment suggests that the free base (produced upon transfer-fluorination) could complex to unreacted **1** (generating a bulky dimer complex which may be ineffective for fluorine transfer) in competition to *N*-protonation.

Introduction

Rapidly growing interest in fluorinated organic compounds, dictated by an ever-increasing demand for fluorinated pharmaceuticals, agrochemicals, dyestuffs, liquid crystals, materials and polymers,[1,2] has placed paramount importance on the development of selective fluorination methods and reagents that can deliver electrophilic (F^+)[1,3–6] or nucleophilic fluorine (F^-)[1,7] to target molecules under mild, nondestructive, and very desirably "eco-friendly" conditions.

Among the "F^+" reagents (Fig. 1), the NF fluorinating agents

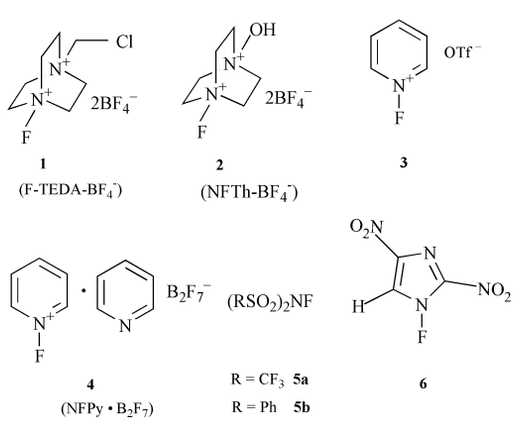

Fig. 1

F-TEDA-BF_4 (Selectfluor™)[3–6] **1** and NFTh (Accufluor®)[3–5] **2**, *N*-fluoropyridinium salts[3–5] (such as **3** and **4**) and sulfonimides[3–5,8] of type **5** (Fig. 1; all commercially available except **5a**) have shown promise in selective fluorination of various functional groups. However, direct fluorination of aromatics with NF reagents represents a continuing challenge. By and large, transfer-fluorination to aromatics with the NF reagents is only possible with activated arenes and yields are variable depending on the reagents, the arene substrates and the solvent system.[3–6,8] The use of excess fluorinating agent is necessary in the case of **1** to increase conversion. Reactions are typically performed in MeCN (usually under reflux), MeOH or TFA.[3–6] Intervention by a radical cation mechanism has been inferred in some cases.[3]

An interesting recent study employed TfOH as solvent which substantially increased the yields.[9] The observed $k_{toluene}/k_{benzene} = 13.8$ clearly supports an electrophilic reaction with a reactive electrophile proposed to be the *O*-protonated CF_3SO_2OF formed *in situ*.[9]

With **5a**, several examples of arene fluorination under mild conditions have been reported,[10–12] whereas with **3**, fluorination of anisole required high temperatures and prolonged reaction times.[12] Reagent **6** exhibited some success in PAH fluorination, which is especially difficult.[13]

There is tremendous current interest in the utility and application of room temperature ionic liquids as designer solvents (and catalysts) for organic[14–19] and organometallic transformations.[20] The increasingly popular imidazolium-based ionic liquids [emim][X] (emim = 1-ethyl-3-methylimidazolium) and [bmim][X] (bmim = 1-butyl-3-ethylimidazolium), especially those with less nucleophilic counterions (Fig. 2), promise to be

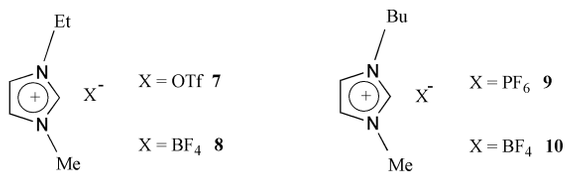

Fig. 2

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Table 1 Electrophilic fluorination of anisole with the NF reagents in ionic liquid solvents

Ionic liquid	ArH : NF ratio (molar ratio)	Yield (%)[a]		Isomer distribution (%) NMR[b]		GC	
		NMR	GC	*ortho*	*para*	*ortho*	*para*
F-TEDA-BF_4 (1)							
[emim][CF_3SO_3]	9 : 1	53	56	47	53	[d]	[d]
Recycled once	10 : 1	41	36	48	52	[d]	[d]
Recycled twice	11 : 1	45	46	47	53	[d]	[d]
Recycled 3rd time	11 : 1	42	40	46	54	[d]	[d]
[emim][BF_4]	10 : 1	37	42	43	57	[d]	[d]
[bmim][PF_6]	12 : 1	43	39	48	52	[d]	[d]
[emim][CF_3SO_3] + dicyclohexano-24-crown-8	9 : 1	13	11	47	53	[d]	[d]
NFTh-BF_4 (2)							
[emim][CF_3SO_3]	10 : 1	28	30	56	44	[d]	[d]
NFPy-B_2F_7 (4)							
[emim][CF_3SO_3]	10 : 1	11	[d]	54[c]	46[c]	[d]	[d]

[a] Yields for fluorinated products were determined from ^{1}H NMR and GC using mesitylene as internal standard. [b] Determined from ^{1}H NMR spectra. [c] Determined from ^{19}F NMR spectra. [d] Incomplete GC peak separation for anisole and 4-fluoroanisole.

ideal media for performing ionic reactions involving electron-deficient intermediates (carbocations and onium ions) under "green" chemistry.

Recent examples of electrophilic reactions include Friedel–Crafts acylation of arenes,[15] alkylation of aromatics with alkenes,[16] halogenation of alkenes and alkynes,[17] nitration of aromatics,[18] and fluorodediazoniation of arenediazonium salts.[19] The present study was undertaken to determine the efficacy of transfer-fluorination of arenes with NF salts in ionic liquids, a process that could take "tamed" fluorination into the realm of "green" chemistry.

Results and discussion

Dication salt **1** slowly dissolves in excess ionic liquids [emim][OTf] **7**, [emim][BF_4] **8**, [bmim][PF_6] **9** and [bmim][BF_4] **10** at room temperature. In the case of ionic liquids **7** and **9** dissolution of **1** is accompanied by counterion exchange,‡ but this does not create any limitation relative to fluorination. In all cases, sonication at rt increases solubility, leading to homogeneous (or nearly homogeneous) liquids, which eventually become clear solutions upon warming to 80 °C (reaction temperature for fluorination). Anisole was used as model substrate to compare different ionic liquids and to determine the efficiency of recycling. The results are summarized in Table 1. Yields were determined both by NMR and by GC. The isomer distribution for fluoroanisoles (47% *ortho*, 53% *para*) closely resembles that reported for fluorination of anisole with **1** in TfOH (45% *ortho*, 55% *para*)[9] but differs from the data reported in refluxing MeCN and TFA solvents.[21] The ionic liquid was recycled and reused three times for the same reaction. This led to about 10% decrease in conversion (see Table 1). Comparative fluorination of anisole with **2** and **4** by using **7** resulted in decreased conversions, with **4** showing the lowest yield (Table 1). Isomer distribution observed in the case of **2** is closely analogous to that reported in MeCN under reflux.[21]

In an effort to use complexation as a means to create a more sterically crowded electrophile, which might lead to increased *para* selectivity, fluorination of anisole with **1** in **7** as solvent was re-examined in the presence of dicyclohexano-24-crown-8. This led to decreased yield (consistent with lowered reactivity of the electrophile) but did not influence the isomer distribution (Table 1). AM1 minimizations on the F-TEDA dication and dicyclohexano-24-crown-8 showed that both N–F and N–CH_2-Cl could complex, with the energy difference between the free and bound forms being 48.2 and 47.0 kcal mol^{-1} respectively. It is, therefore, conceivable that the two host–guest forms rapidly interconvert in solution resulting in rate retardation but no noticeable overall change in regioselectivity. Attempts to detect a host–guest cation–molecule cluster (either intact $\mathbf{1}^{2+}$·crown or intact $\mathbf{1}^{+}$·crown) by electrospray mass spectrometry were unsuccessful due to rapid defluorination of $\mathbf{1}^{2+}$ forming abundant monocation (*m*/*z* 161), with intact $\mathbf{1}^{+}$ (*m*/*z* 180) being observed in very low abundance.

Table 2 summarizes the results of the reactivity survey for simple aromatics using only one equivalent of the NF reagent. The reported yields may be increased by addition of an extra equivalent of the NF reagent to the reaction mixture after the completion of the first fluorination cycle, as exemplified for *p*-xylene (Table 2). With *p*-chloroanisole there was no drop in yield relative to parent anisole or *p*-methylanisole, but *p*-fluoroanisole gave lower conversions. With the more deactivated aromatics such as nitrotoluene, no fluorination took place, as was found previously with nitrobenzene in TfOH solvent.[9]

Table 3 summarizes examples of bicyclic and polycyclic arenes and the resulting isomer distributions and conversions. The ionic liquids used in this study were all used samples which had been recovered. Fluorination of naphthalene with **1** in MeCN was reported to give a 30% conversion, but in hot TFA the yield increased to 75%.[22] The isomer distribution was reported as 1-F : 2-F = 3 : 1. The latter is at variance with the regioselectivity observed in ionic liquids in the present study (13 : 1). Fluorination of 1-methylnaphthalene with the F-TEDA-BF_4 reagent had not been studied before. For dibenzofuran, the conversion observed in **7** is superior to those previously reported in MeCN, TFA and MeCN + TFA as solvent.[21] Chart 1 is a cumulative summary of the ^{19}F data for the products obtained in this survey.

A noteworthy feature is that optimal fluorination yields (using 1 equivalent of the NF reagent) in ionic liquids are around 50% (except for naphthalene which was higher). In a control experiment (Scheme 1), the ^{19}F resonance of F-TEDA-BF_4 shifted downfield by over 2 ppm upon addition of authentic 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (*ca.* 1 equiv.).§

‡ For examples of counterion exchange (metathesis) observed in electrophilic nitration of aromatics in [emim][X] solvents see ref. 18.

§ The positive charge on fluorine is larger in the complex (0.086) than in free F-TEDA (0.065) (AM1 calculations).

Table 2 Electrophilic fluorination of ArH with F-TEDA-BF_4

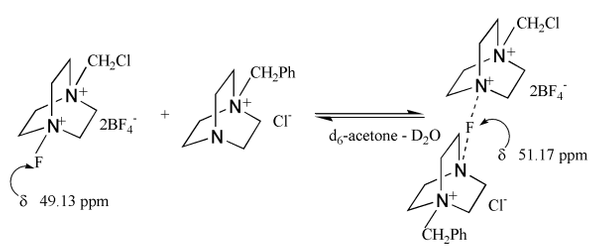
ArH	Ionic liquid	ArH : NF (molar ratio)	Yield (%)[a] NMR	Yield (%)[a] GC	Composition of reaction mixture (%)
p-Methylanisole	[emim][CF_3SO_3]	4 : 1	56	46[b]	2-Fluoro-4-methylanisole (93), 3-fluoro-4-methylanisole (6),[c] 2,6-difluoro-4-methylanisole (1)[c]
p-Chloroanisole	[emim][CF_3SO_3]	5 : 1	50	50[b]	2-Fluoro-4-chloroanisole (95), 2,6-difluoro-4-chloroanisole (5)[c]
p-Fluoroanisole	[emim][CF_3SO_3]	4 : 1	24	22	2,4-Difluoroanisole (~100)
p-Xylene	[emim][BF_4]	10 : 1	24	21[b c]	2-Fluoro-1,4-dimethylbenzene (~100)
p-Xylene	[emim][CF_3SO_3]	10 : 1	51[d]	46[b d]	2-Fluoro-1,4-dimethylbenzene (~100)
Mesitylene	[bmim][PF_6]	4 : 1	52[e]	50[b e]	2-Fluoromesitylene (~100)
p-Nitrotoluene	[bmim][BF_4]	4 : 1	<1	0	
p-Nitrotoluene	[bmim][CF_3SO_3]	4 : 1	<1	0	

[a] Yields of fluorinated products were calculated from ^{1}H NMR and GC using mesitylene as internal standard. [b] No authentic fluorinated sample was available as GC standard. [c] Specific assignment tentative. [d] Yield of 2-fluoro-1,4-dimethylbenzene after repeating the fluorination reaction in the same reaction vessel by adding a second equivalent of F-TEDA-BF_4. [e] Yield of 2-fluoromesitylene was calculated from ^{1}H NMR and GC using anisole as internal standard.

Table 3 Electrophilic fluorination of bicyclic and polycyclic aromatic hydrocarbons with F-TEDA-BF_4

ArH	Ionic liquid	ArH : NF (molar ratio)	Yield (%)[a] NMR	Yield (%)[a] GC	Composition of reaction mixture (%)[b]
Naphthalene	[emim][CF_3SO_3] (recycled once)	4 : 1	88	[f]	1-Fluoronaphthalene (91), 2-fluoronaphthalene (7), 1,8-difluoronaphthalene[c] (2)
1-Methylnaphthalene	[bmim][PF_6] (recycled twice)	2 : 1	23	[f]	1-Fluoro-4-methylnaphthalene (53), 2-fluoro-1-methylnaphthalene (21), 5-fluoro-1-methylnaphthalene[c] (11), 1-fluoro-8-methylnaphthalene[c] (15)
Dibenzofuran	[emim][CF_3SO_3] (recycled 3-times)	4 : 1	49[d]	38[d e]	1-Fluorodibenzofuran (20, NMR; 18, GC), 2-fluorodibenzofuran (41, NMR; 42, GC), 3-fluorodibenzofuran (39, NMR; 40, GC)

[a] Yields of fluorinated products were calculated from ^{1}H NMR and GC using mesitylene as internal reference. [b] Determined from ^{19}F NMR spectra. [c] Specific assignment tentative. [d] Yields of fluorinated products were calculated from ^{1}H NMR and GC using 4-fluoroanisole as internal reference. [e] No authentic fluorinated dibenzofuran isomers were available as GC standard. [f] No isomer separation.

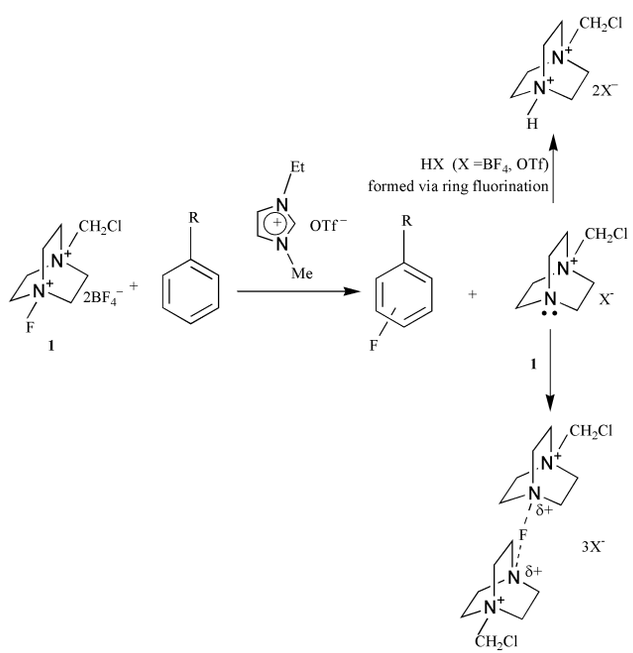


Scheme 1

On the basis of this observation it is suggested that the free base (produced as transfer-fluorination progresses) could complex to unreacted **1** (generating a bulky dimer complex which may be ineffective for fluorine transfer) in competition with *N*-protonation (Scheme 2).

For competitive reactions, a 1 : 1 mixture of mesitylene and durene was allowed to react with **1** in ionic liquid **7**. The k_{MES} : k_{DUR} values determined by ^{19}F NMR and by GC were 9 and 12, respectively. An identical experiment performed in MeCN solvent gave the k_{MES} : k_{DUR} ratio as 5 (by NMR) and 7 (by GC) respectively. The observed substrate selectivities in both media are consistent with a polar mechanism (σ-complex) involving a reactive electrophile, with slightly greater degree of polar character developing in the ionic liquid solvent. As a comparison, the k_{MES} : k_{DUR} ratio recently measured for iodination with ICl in MeCN solvent is 46.[23] Therefore, **1** is a more reactive (less selective) electrophile which nevertheless relies heavily on the nucleophilicity of the arene nucleophile (consistent with lack of reaction with deactivated arenes).

In summary, the feasibility of aromatic fluorination with NF reagent **1** in ionic liquid solvents has been tested. The yields are



Scheme 2

comparable and in some cases exceed those reported in MeCN and TFA but are lower that those found in TfOH solvent. However, the present process, which uses only one equivalent of the NF reagent, avoids the use of strong acids and involves no aqueous work up. The ionic liquid solvent can be recycled and reused. The yields can be increased by repeating the fluorination cycle as was demonstrated for *p*-xylene.

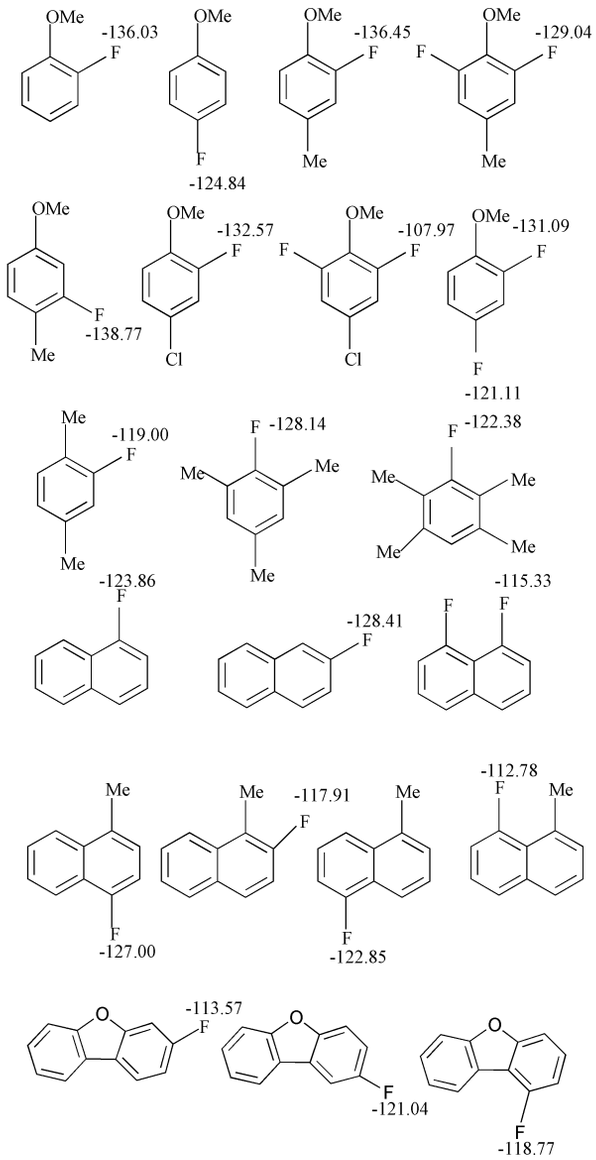


Chart 1

Experimental

The [emim][X] ionic liquids (X = BF_4, OTf) were purchased from Aldrich, whereas [bmim][BF_4] and [bmim][PF_6] were synthesized from [bmim][Cl] by metathesis with $NaBF_4$ and HPF_6 respectively as previously reported.[18] The Selectfluor™ reagent (F-TEDA-BF_4) was a sample from Aldrich. Accufluor® (NFTh-BF_4/alumina blend) was a gift sample from Allied Signal from which the alumina was removed by extracting the Accufluor® with CH_2Cl_2 under argon and removal of solvent under high vacuum. The *N*-fluoropyridinium pyridine heptafluoroborate (NRPy-B_2F_7) was a gift from Allied Signal. Dicyclohexano-24-crown-8 and the aromatics were all high purity commercial samples purchased from Aldrich or Acros. The 1-benzyl-4-aza-1-azonia-bicyclo[2.2.2]octane chloride was prepared as previously described.[24] Liquid arenes were dried over molecular sieves. Ether was dried over sodium. Fluorination reactions in ionic liquids were carried out in Schlenk tubes under an argon atmosphere.

NMR spectra, GC analysis and electrospray MS

^{1}H and ^{19}F NMR spectra were recorded in acetone-d_6 and chloroform-d_3 at room temperature on a Varian INOVA 500 MHz instrument using a 5 mm broad-band probe. GC analyses were performed with an HP-5890 capillary GC instrument utilizing a 25 m OV101 capillary column. ES-MS analysis was performed on a Bruker Esquire LCQ-MS instrument in infusion mode.

Typical fluorination procedure

The [emim][BF_4] ionic liquid (1.55 g, 7.8 mmol) was transferred to a Schlenk tube and F-TEDA-BF_4 (110 mg, 0.31 mmol) was added (under argon atmosphere). The closed Schlenk tube was placed inside an ultrasonic bath (frequency 40 kHz; Branson 1510R-MTH) at room temperature for 2 h (to increase solubility). After addition of anisole (337 mg, 3.12 mmol) at rt the mixture was stirred at 80 °C for 15 h. The organics were extracted with ether (5 mL × 4), washed with H_2O (5 mL × 2), dried ($CaSO_4$) and filtered. The organic extract was concentrated by slowly bubbling a slow stream of nitrogen through the reaction mixture. The residue was directly analyzed by GC and NMR (^{1}H and ^{19}F) using internal standards (see footnotes in Tables 1–3). The procedure was similar for fluorinations with [emim][OTf] and [bmim][PF_6] (in these cases counterion exchange takes place but does not interfere with the subsequent step).

Competitive experiments

a) In [emim][OTf]. The ionic liquid (1.15 g, 4.43 mmol) was transferred to a Schlenk tube. A homogeneous solution of durene (44 mg, 0.33 mmol) and mesitylene (39 mg, 0.33 mmol) in CH_2Cl_2 (1.3 g) was added to the ionic liquid under argon. The CH_2Cl_2 solvent was then removed under vacuum and F-TEDA-BF_4 (58 mg, 0.16 mmol) was added. The reaction mixture was stirred at 80 °C for 16 h, following which the aromatics were extracted as described above and analyzed by NMR and GC. The product ratio (1-fluoro-2,4,6-trimethylbenzene : 1-fluoro-2,3,5,6-tetramethylbenzene) was 9 (based on ^{19}F NMR) and 12 (based on GC).

b) In CH_3CN. F-TEDA-BF_4 (131 mg, 0.37 mmol), durene (98 mg, 0.73 mmol) and mesitylene (88 mg, 0.73 mmol) were transferred to a Schlenk tube and dry MeCN (5 mL) was added under argon. The solution was stirred at 80 °C for 16 h and was analyzed directly by ^{19}F NMR (product ratio: 1-fluoro-2,4,6-trimethylbenzene : 1-fluoro-2,3,5,6-tetramethylbenzene = 5). A portion of the solution was then passed through a short silica-gel column (ether eluent) to remove the TEDA-derived mono and dication salts by-products (see Scheme 2) (these remained on the column). The eluent was analyzed directly by GC (product ratio: 1-fluoro-2,4,6-trimethylbenzene : 1-fluoro-2,3,5,6-tetramethylbenzene = 7).

Complexation of F-TEDA-BF_4 to 1-benzyl-4-aza-1-azoniabicyclo-[2.2.2]octane chloride

The ^{19}F NMR spectrum of F-TEDA-BF_4 (25.4 mg, 0.072 mmol) in acetone-d_6 + D_2O (92 : 8) solvent gives a singlet at δ 49.13. Addition of 1-benzyl-4-aza-1-azonia-bicyclo[2.2.2]-octane chloride (18.3 mg, 0.077 mmol) to the NMR tube caused the fluorine resonance to shift to δ 51.17($\Delta\delta_F$ = 2.04 ppm).

Effect of crown ether

[emim][OTf] (1.13 g, 4.35 mmol) was transferred into a Schlenk tube and F-TEDA-BF_4 (73 mg, 0.20 mmol) was added under argon. After sonication, dicyclohexano-24-crown-8 (78 mg, 0.17 mmol) and anisole (192 mg, 1.77 mmol) were added and the mixture was stirred at 80 °C for 15 h (for subsequent steps see general procedure).

Recycling of ionic liquid [emim][BF_4] and [bmim][BF_4]

This was accomplished by extraction with dry CH_2Cl_2. The dichloromethane layer was separated by filtration and the

solvent was removed reduced pressure to afford the pure ionic liquid (assayed by ^{1}H NMR).

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