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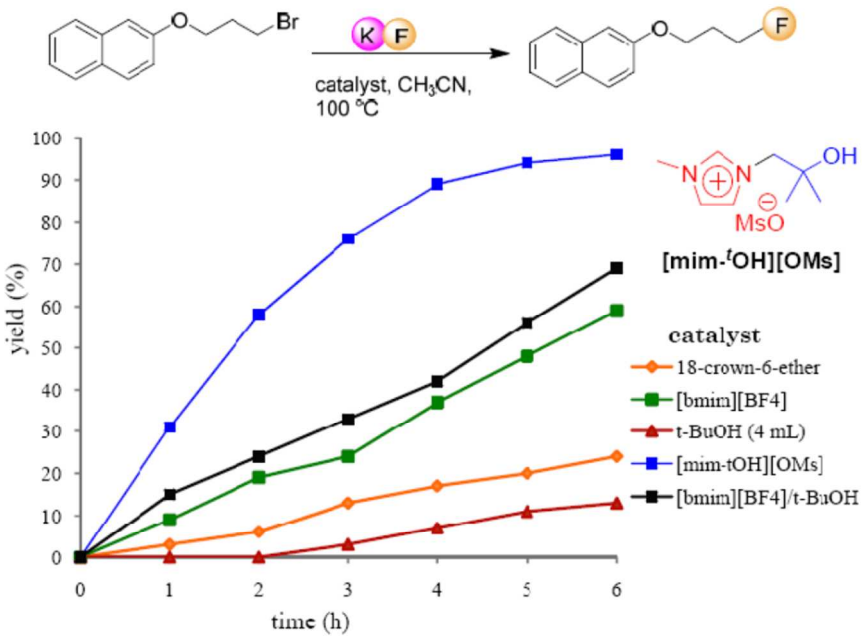
Nucleophilic Fluorination using Imidazolium based Ionic liquid bearing *tert*-Alcohol moiety

Sandip S. Shinde,* Sunil N. Patil, Amruta Ghatge, and Pradeep Kumar



The ionic liquid bearing *tert*-butanol moiety ([mim-^{t}OH][OMs]) was employed as catalyst in nucleophilic fluorination of 2-(3-bropropyloxy)-naphthalene using alkali metal fluorides.

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ARTICLE TYPE

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The ionic liquid bearing *tert*-butanol moiety ([mim-^{t}OH][OMs]) was employed as an organocatalyst in nucleophilic fluorination of a variety of substrates containing halogen / sulfonate as a leaving group. The low reactive metal fluorides including KF were used as a fluoride source in the reaction. Ionic liquid [mim-tOH][OMs] has shown excellent selectivity in nucleophilic fluorination of 2-(3-bromopropyloxy)naphthalene with KF or CsF affording 2-(3-fluoropropyloxy)-naphthalene in high yield. Among the various solvents screened, activity of alkali metal fluoride was found to be better due to the improved solubility of both metal fluoride and [mim-tOH][OMs] in acetonitrile media.

Introduction

Among the halides, fluorine has attracted much interest due to its intriguing physicochemical properties, it is found to increase metabolic stability, liphophilicity and/or receptor-binding properties of bioactive compounds.[1] Fluorine-18 is being widely used in the area of radiopharmaceutical to develop imaging probes by positron emission tomography (PET).[2] Substitution of fluorine atom into the organic compound employing metal fluoride is one of the classical method and widely applied in academic and industrial research. Alkali metal fluorides are generally economical and potent source of fluoride occupying a privileged position in such reactions.[3] However, due to its restricted solubility and low nucleophilicity, they were used in combination of phase-transfer catalyst (PTC). In particular, reagent potassium fluoride with 18-crown-6-ether,[4] immobilized on calcium salt[5] or polymer,[6] and anhydrous KF,[7] etc are being developed to facilitate the substitution reactions.

Ionic liquids have attracted considerable attention as environmentally benign reaction media, PTC for numerous organic transformations.[8] Over the last decade, there has been increasing application of task-specific imidazolium-based ionic liquids for specific reactions[9] such as click reaction,[10] nucleophilic substitution,[11] fluorination,[12] and fluorohydrin etc.[13] Recently, we reported that the imidazolium salt bearing *tert*-butanol moiety ([mim-^{t}OH][OMs]) remarkably improves the reactivity and selectivity in nucleophilic fluorination using CsF.[14] The combined synergistic effect of the ionic liquid and *tert*-OH group of [mim-^{t}OH][OMs] facilitates the interaction between substrate and fluoride and therefore accelerates the rate of reaction.[15]

To expand the scope of [mim-^{t}OH][OMs], herein we report the dual advantages of [mim-^{t}OH][OMs] in fluorination using tight-ion pair alkali metal fluorides from the third to sixth period of the periodic table. Comparative study of its synergism, solubility and solvent effect in nucleophilic fluorination suggested that the high selectivity and yield were obtained by using this unique bifunctional molecule than the other catalyst reported previously for this reaction.

Results and discussion

1. Reactivity of alkali metal fluorides in presence of [mim-^{t}OH][OMs].

To investigate the reactivity of other alkali metal fluorides, we carried out nucleophilic fluorination of 2-(3-methylsulfoxypropyloxy)-naphthalene (**1**) using various fluoride sources such as sodium fluoride, potassium fluoride, rubidium fluoride, and caesium fluoride in the presence of [mim-^{t}OH][OMs] (2 equiv) in CH_3CN for 6h, results are summarized in Figure 1A.

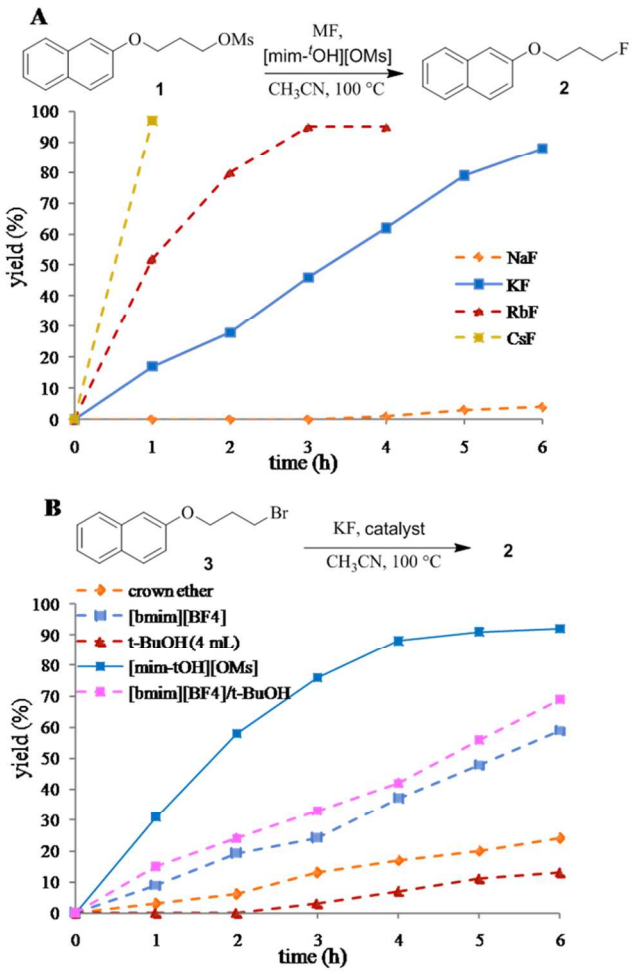


Figure1. Nucleophilic fluorination A) Reactivity of 1 with MF in presence of [mim-^{t}OH][OMs]. B) Reactivity of 3 with KF using [mim-^{t}OH][OMs] or other catalyst. Progress of reaction was determined by 1H NMR.

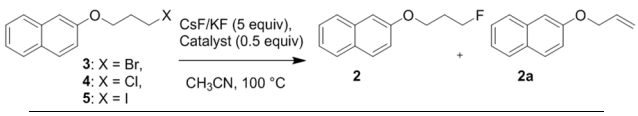
The fluorination of **1** with NaF in the presence of [mim-^{t}OH][OMs] did not proceed at all. Same reaction using KF, RbF and CsF as fluoride source was completed in 6h affording 2-(3-fluoropropyloxy)-naphthalene (**2**) (95-98%). However, the fluorination using CsF was most effective in combination with [mim-^{t}OH][OMs] in this method among the other alkali metal fluorides, but the high yield (95%) of the desired product from the reaction using KF clearly suggests that the reactivity of [mim-^{t}OH][OMs] was not limited to low-tighten ion paired CsF or RbF salts. It is noteworthy that comparatively the price of KF is almost 51 time cheaper than CsF (KF = $3.56/mol vs CsF = $181/mol, commercial sources from Sigma Aldrich in >95% purity.)[16]

Figure 1B illustrates the comparative study of [mim-^{t}OH][OMs] with other catalyst protocols in nucleophilic fluorination of 2-(3-bromopropyloxy)-naphthalene (**3**), the fluorination using KF in the presence of 18-crown-6-ether proceeded very slowly. The same fluorination in combination of KF and [mim-^{t}OH][OMs] proceeded much faster, affording the desired product **2** in high yield with good selectivity. In contrast to these result the same reaction in *t*-BuOH media[17] or using conventional IL ([bmim][BF$_4$])[11f] as catalyst in CH_3CN media was ineffective and reaction was found to be very slow and incomplete even after 6h long run. These results are analogous to those reported previously in protic media such as *t*-BuOH using CsF.[17] Comparative study showed that the same reaction in the presence of catalytic amount of both [bmim][BF$_4$] and *t*-BuOH instead of [mim-^{t}OH][OMs], was very sluggish, affording fluorinated product only in 19% yield. Moreover, these results suggest that the use of [mim-^{t}OH][OMs] in nucleophilic fluorination of both the substrates **1** & **3**, under the reaction conditions, allowed the isolation of **2** in excellent yield. Such superior reactivity and selectivity was obviously due to the dual functional effect of *tert*-butanol moiety and imidazolium mesylate. These results again suggest that the controlled hydrogen-bonding of the *tert*-OH group of [mim-^{t}OH][OMs] with the fluorine of KF might be a contributing factor for increase in the nucleophilicity by a flexible-fluoride effect.[15, 18] Moreover, acceleration of the reactivity of KF in combination of [mim-^{t}OH][OMs] can be considered as an economically and commercially viable method to this reaction.

2. Synergistic effect of *t*-BuOH and imidazolium moiety of [mim-^{t}OH][OMs] in fluorination of halogenated substrates:

To demonstrate the detailed synergistic effect of [mim-^{t}OH][OMs] in fluorination reaction, we carried out few fluorination with chloro, bromo and iodo-haloalkane substrates in the presence [mim-^{t}OH][OMs], or non-functional IL ([bmim][BF$_4$]) and *t*-BuOH in CH_3CN as shown in Table 1.

Table 1. Synergistic effect of [mim-^{t}OH][OMs] in nucleophilic fluorination of various haloalkanes using different conditions.[a]



entry	X	Method	Time (h)	Yield of product (%)[b] SM	2	2a
1	Cl	A	18		79	14
2		B	24	trace	67	21, 3% alcohol[c]
3		C	24	87	11	
4	Br	A	1		87	11[c]
5		B	9		68	29
6		C	24	46	34	7[c], 6% ether[c]
7	I	A	30min		84	14
8		B	6		38	56
9		C	24	25	47	23, trace ether[c]
10	Cl	D	24	12	72	9[c]
11	Br	D	7		91	8[c]
12	I	D	3		83	12

[a]All reactions were carried out on a 1.0 mmol scale of substrate with 5.0 equiv of CsF in the presence of 0.5 equiv of catalyst in CH_3CN at 100 °C. Method A: 0.5 equiv of [mim-^{t}OH][OMs]. Method B: 0.5 equiv of [bmim][BF$_4$]. Method C: 0.5 equiv of *t*-BuOH. Method D: KF instead of CsF in 0.5 equiv of [mim-^{t}OH][OMs]. [b]Isolated yield. [c]determined by ^{1}H NMR.

Entries 1, 4, and 7 represent the fluorination of chloroalkane **4** bromoalkane **3,** and iodoalkane **5** using CsF in the presence of [mim-^{t}OH][OMs], furnishing **2** in 79%, 87%, and 84% yield respectively (Method A). Replacement of [mim-^{t}OH][OMs] with [bmim][BF$_4$], gave low selectivity with significant amount of alkene as byproduct (Method B, entries 2, 5, and 8). Due to the

absence of hydroxyl group in [bmim][BF_4], the synergetic effect of catalyst and fluoride could not be observed, and therefore the formation of byproduct alkene was predominant and only low yield of the desired product was obtained. However when the reactions were carried out in presence of *t*-BuOH to generate hydrogen-bonding, it was found to be incomplete with all tested haloalkane substrates (Method C, entries 3, 6, and 9).

As a comparison of nucleophilic fluorination in Method A and D conditions, the rate of consumption of all halo-substrates in presence KF was very sluggish than that of CsF. The iodoalkane **5** was consumed faster than among other substrates, the high selectivity for fluoroalkane 91% was achieved from bromoalkane **3** (Method D, entry 11). It should be noted, that the fluorination using CsF provided slightly more amount of alkene byproduct in comparison to KF reactions with all the halogenated substrates, this might be due to fast generating fluoride anion from CsF which acts as base instead of nucleophile.[19] These results are in good agreement with our earlier report of synergistic effect of imidazolium and *t*-BuOH moiety as a key factor for facilitating high reactivity of fluoride nucleophile.[14] The ionic liquid [mim-^{t}OH][OMs] plays as an ambiphilic "electro-nucleophiles" dual activation function (i.e., the counteranion of the ionic liquid acts as a Lewis base toward alkali metal, drastically reducing its electrostatic effects and thereby facilitates the interaction of fluoride and the *tert*-OH proton and thus contributes to the significant increase in the reaction rate and selectivity mainly for the fluorination.[15]

3. Effect of Alkyl chain length of *tert*-alcohol functionalized ILs in CH_3CN and *t*-BuOH at 100°C in fluorination:

We have investigated the influence of various alkyl chain substituted at N^3-position of *t*-BuOH functionalized imidazole.[14] The chain length of *t*-BuOH moiety remain same in all the tested ILs. Table 2 summarizes the results of *t*-BuOH functionalized ILs such as *n*-hexyl of [him-^{t}OH][OMs], *n*-butyl of [bim-^{t}OH][OMs], *iso*-propyl of [ipim-^{t}OH] [OMs] and methyl of [mim-^{t}OH] [OMs] nucleophilic fluorination of **3** under protic and aprotic media. The reaction in the presence of [ipim-^{t}OH][OMs] showed excellent activity compared to longer chain length in CH_3CN (entries 1-3). The same reactions in protic media such as *t*-BuOH, was ineffective with reactions proceeding at slow rate (entires 4-6). Moreover, polar aprotic solvent such as CH_3CN was found to be much better for these *t*-BuOH-functionalized-IL compared to *t*-BuOH. Moreover, the less alkyl chain length-IL particularly [mim-^{t}OH][OMs], which has methyl group provides flexible interaction between a *tert*-OH group and fluoride of KF by sufficient hydrogen-bonding to generate fluoride with less basicity to obtain selective fluorinated product. This could be due to length of alkyl chain affect on nucleophilic fluorine and *tert*-alcohol restricted hydrogen fluorine bond according to Newman effect (Newman Rule of Six).[20] Therefore the butyl and hexyl chain ionic have shown low reactivity compared to methyl side chain IL.

Table 2. Nucleophilic fluorination of **3** with KF and [mim-^{t}OH][OMs] in CH_3CN and *t*-BuOH.[a]

entry	[imidazolium][OMs]	Co-solvent	Yield (%)[b]	
			2	**2a**
1	[ipim-^{t}OH]	CH_3CN	90	trace[c]
2	[bim-^{t}OH]	CH_3CN	58	3
3	[him-^{t}OH]	CH_3CN	40	trace[c]
4	[ipim-^{t}OH]	*t*-BuOH	16	-
5	[bim-^{t}OH]	*t*-BuOH	12	-
6	[him-^{t}OH]	*t*-BuOH	trace[c]	-

[a]Unless otherwise indicated, all reactions were carried out under same condition of entry 5 of Table 1. [b]Isolated yield. [c]determined by ^{1}H NMR.

4. Solubility of [mim-^{t}OH][OMs] in various solvents:

We examined the solubility of [mim-^{t}OH][OMs] in various polar, aprotic and non-polar solvents. The mix of [mim-^{t}OH][OMs] in solvents (CH_3CN, $CHCl_3$, DCM, dioxane, EtOH, *t*-BuOH, toluene, THF and DMF) in (1/5; w/v) was prepared. The solubility results suggested that the [mim-^{t}OH][OMs] had good solubility in polar solvents such as DMF, *t*-BuOH, and CH_3CN. Interestingly it was found to be fairly soluble in non-polar toluene as well as, immiscible in dioxane, THF, $CHCl_3$, and DCM but partial soluble in diethylether (see supporting information).

5. Solvent influence on activity of [mim-^{t}OH][OMs] in nucleophilic fluorination:

To determine the influences of [mim-^{t}OH][OMs] in various reaction media such as DMF, CH_3CN, dioxane, and toluene, which are generally used for nucleophilic substitution reactions, we carried out fluorination of **3** using 5 equiv of KF and 0.5 equiv of [mim-^{t}OH][OMs] in various solvent media. The results are graphically depicted in Figure 2.

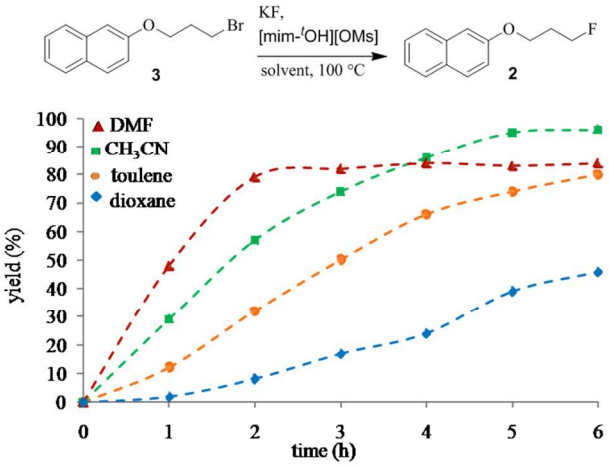


Figure 2. Solvent dependence activity of [mim-^{t}OH][OMs] in nucleophilic fluorination

Reactions in CH_3CN and DMF significantly enhance the reactivity of KF. However, significant amount of by-product alkene formation was observed in ^{1}H NMR in DMF because of the enhancement in solvation of metal cation, and thus generating the fluoride anion, as a base instead of nucleophile.[18] Comparatively, the same fluorination reaction in toluene was very sluggish, even though catalyst has good solubility in this media. Reactions poorly performed in toluene and dioxane at 100

^{o}C, were incomplete after 6h. The remarkably increased reactivity of KF in presence of [mim-^{t}OH][OMs] could be due to improved solubility of both KF and catalyst [mim-^{t}OH][OMs] in CH_3CN, which allows adequate hydrogen-bonding with fluorine anion in reaction media.

6. Reactivity of variety of substrates in nucleophilic fluorination using KF and CsF:

To expand scope of [mim-^{t}OH][OMs] with variety of substrates, we performed nucleophilic fluorination of substrate containing variety of leaving groups including halides and alkyl sulfonate using KF and CsF in the presence of [mim-^{t}OH][OMs] under various conditions, the results are summarized in Table 3. Entries 1-6 show the nucleophilic fluorination of base-sensitive estrogens analogues containing halide as leaving group such as 3-(3-chloropropyloxy)-estrone, 3-(3-bromopropyloxy)-estrone and 3-(3-iodopropyloxy)-estrone in presence of [mim-^{t}OH][OMs], affording the desired 3-(3-fluoropropyloxy)estrone in 13%, 90% and 86% respectively(entries 1, 3 and 5). In these results, we found the high synergistic effect when the bifunctional [mim-^{t}OH][OMs] molecule was used in reactions. It should be noted that the same fluorination is inefficient in *t*-BuOH mediated protocol.[17] Fluorination of these halogenated-substrates using CsF as fluoride source produces by product alkene in significant amount as compared to KF reactions (entries 2, 4, and 6).

As depicted in table 3(Entries 7-9), the substitution reactions of primary alkyl sulfonate precursors such as mesylate and nosylate of naphthalene and triflate of sugar substrates afforded the corresponding fluorinated products in very high yield within short time. Interestingly, the fluorination of 2-bromoacetophenone proceeded much faster and gave 2-fluoroacetophenone in excellent yield (entry 10). Entries 11-13 represent the highly base sensitive secondary mesylate and tosylate alkyl substrate, affording corresponding fluorinated products in reasonably good yields.

Table 3. Nucleophilic fluorination of various substrates using [mim-^{t}OH][OMs] as catalyst.[a]

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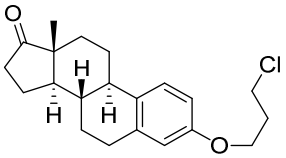
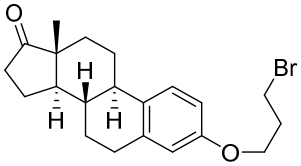
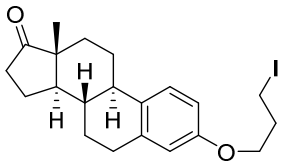
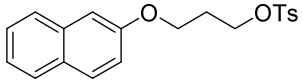
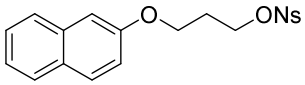
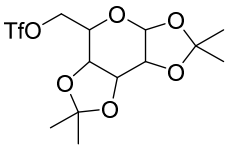
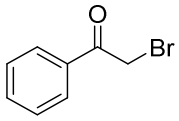
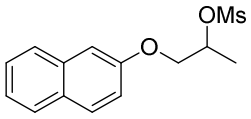
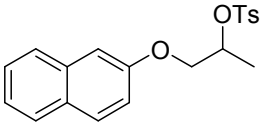
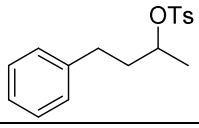
Entry	SM	MF	Time (h)	Yield (%)[b] Fluorinated product	comment
1		KF	12	13	trace alkene,[c] 54% SM
2		CsF	12	83	11% alkene[c]
3		KF	4	90	trace[c]
4		CsF	1	85	9 % alkene[c]
5		KF	3	86	6% alkene[c]
6		CsF	6	79	18% alkene
7		KF	5	93	trace alkene[c]
8		KF	5	97	
9		KF	6	73	
10[d]		KF	50 min	82	
11		KF	12	84	13% alkene
12		KF	8	76	19% alkene
13[d]		KF	10	65 (79)c	15% alkene

[a] Unless otherwise indicated, all reactions were carried out on a 1.0 mmol scale of **SM** with 5 equiv of KF/CsF at 100 °C.[b]Isolated yield. [c]Determined by ^{1}H NMR. [d]Reaction carried out at 50 °C.

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Conclusions

The [mim-^{t}OH][OMs] serves as a highly efficient organocatalyst for the nucleophilic fluorination of variety of aliphatic substrates containing halide or sulfonate as a leaving group by fluorine nucleophile using alkali metal fluorides including KF. In this method, synergistic effect of ionic liquid and *tert*-alcohol moiety not only enhances solubility and reactivity of potassium fluoride, but also significantly accelerates the nucleophilicity of fluorine in the reaction. Furthermore, this protocol is attractive in terms of inexpensive alkali metal fluorides and an easy access to the task specific ionic liquid.

Experimental

Materials and General Method

All chemicals were obtained from commercial suppliers and were used without further purification unless otherwise stated. Flash chromatography was carried out using Merck silica gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was performed with Merck Silica gel-60, F-254 aluminium -backed plates. Visualization on TLC was monitored by UV light. ^{1}H and ^{13}C NMR spectra were recorded using Varian (200 MHz) and calibrated using residual undeuterated solvent or tetramethylsilane as an internal reference. High-resolution mass spectra were recorded using Jeol-JMS 700 and low-resolution mass spectra were obtained using VK Quattro II GC-MS/MS spectrometer (ESI or EI).

1-(2-Hydroxy-2-methylpropyl) methylimadazolium mesylate [mim-^{t}OH][OMs]. [14]

Thick oil: ^{1}H NMR (400 MHz, $CDCl_3$) 1.21 (s, 6H), 2.76 (s, 3H) 3.97 (s, 3H), 4.26 (s, 2H) 7.24 (s, 1H) 7.33 (s, 1H) 9.69 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) 26.4, 36.4, 39.6, 59.7, 68.5, 121.8, 123.7, 139.1.

General procedure for fluorination

To the mixture of 2-(3-bromopropoxy)-naphthalene (**3**, 265 mg, 1.0 mmol) and [mim-^{t}OH][OMs] (125 mg, 0.5 mmol) in CH_3CN (4 mL) was added KF (290 mg, 5 mmol). The mixture was stirred at 100 °C and reaction progress monitored by TLC. Then the reaction mixture was diluted with water and extracted with diethyl ether (10 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography (5% EtOAc/Hx) affording 196 mg (95%) of 2-(3-fluoropropyloxy)-naphthalene (**2**)[14] as colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$) 2.16-2.35 (dm, J = 26.0 Hz, 2H), 4.23 (t, J = 6.2 Hz, 2H), 4.70 (dt, J = 46.8, 5.8 Hz, 2H), 7.13-7.17 (m, 2H), 7.34 -7.44 (t, J = 7.6 Hz, 2H), 7.71-7.77 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 30.4 (d, J = 19.7 Hz), 63.5 (d, J = 5.3 Hz), 80.8 (d, J = 163.0 Hz), 106.7, 118.8, 123.7, 126.4, 126.7, 127.6, 129.0, 129.4, 134.5, 156.7; HRMS (EI) calcd for $C_{13}H_{13}FO$ (M^+) 204.0950, found 204.0947.

Procedures for Table 1.

To a mixture of 2-(3-bromopropyloxy)-naphthalene (265 mg, 1.0 mmol) and [mim-^{t}OH][OMs] (125 mg, 0.5 mmol) [(or [*t*-BuOH (48 µL, 0.5 mmol) or [bmim][OMs] (67 mg, 0.5 mmol) or [bmim][BF_4] (113 mg, 0.5 mmol)] in CH_3CN (4 mL) was added KF (290 mg, 5 mmol) or [CsF (5 mmol). The reaction was stirred at 100 °C. Then the reaction mixture was extracted with diethylether (10 mL × 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by flash column chromatography (20% EtOAc/hexane) to obtain 2-(3-fluoropropyloxy)naphthalene.

General Procedures of Figure 2

To a mixture of 2-(3-bromopropoxy)naphthalene (265 mg, 1.0 mmol) and [mim-^{t}OH][OMs] (125 mg, 0.5 mmol in CH_3CN (4 mL) [dioxane or DMF or toluene] was added KF (290 mg, 5 mmol). The reaction was stirred at 100 °C. Reaction progress was monitored by ^{1}H NMR analysis. Then the reaction mixture was extracted with diethylether (10 mL × 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by flash column chromatography (20% EtOAc/hexane) to obtain 2-(3-fluoropropyloxy)naphthalene.

Procedures of Table 2

3-(3-Fluoropropoxy)estrone.[12a]
White solid: m.p. 78.3-80.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 0.90 (s, 3H), 1.43-1.62 (m, 6H), 1.96-2.19 (m, 7H), 2.38 (b 1H), 2.47 (d, J = 8.4 Hz, 1H), 2.88 (q, J = 3.6 Hz, 2H), 4.07 (t, J = 6.0 Hz, 2H), 4.63 (dt, J = 46.8, 6.0 Hz, 2H), 6.65 (d, J = 2.4 Hz, 1H), 6.71 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 13.8, 21.5, 25.9, 26.5, 29.6, 30.4 (d, J = 20.0 Hz), 31.5, 35.8, 38.3, 43.9, 47.9, 50.4, 63.4 (d, J = 4.8 Hz), 80.7 (d, J = 163.0 Hz), 112.1, 114.5, 126.3, 132.2, 137.7, 156.7, 220.9. HRMS (EI) calcd for $C_{21}H_{27}FO_2$ (M+) 330.1995, found 330.1998.

1,2:3,4-Di-O-isopropylidene-6-fluoro-6-deoxy-α-D-galactopyranose.[21]
As a colorless oil; ^{1}H NMR (400MHz, $CDCl_3$) 1.32 (s, 6H), 1.43 (s, 3H), 1.53 (s, 3H), 4.02-4.09 (m, 1H), 4.24-4.26 (m, 1H), 4.32-4.34 (m, 1H), 4.43-4.52 (m, 1H), 4.55-4.64 (m, 2H), 5.53 (d, J = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 24.3, 24.8, 25.8, 25.9, 66.5 (d, J = 22.8 Hz), 70.3, 70.4 (d, J = 6.1 Hz), 70.4, 82.0 (d, J = 167.6 Hz), 96.1, 108.7, 109.5; registery No. 2021-97-8.

2-Fluoro-acetophenone.[22]

Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) 5.58 (d, J = 47.0 Hz, 2H), 7.44-7.50 (m, 2H), 7.58-7.66(m, 1H) 7.84-7.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 83.49 (d, J = 182.2 Hz), 127.81, 128.84, 133.81, 134.01, 193.38 (d, J = 15.7 Hz); HRMS (EI) calcd for $C_8H_7FO[M]^+$ 138.0481, found 138.0462; Registery No. 445-27-2.[11g]

2-(2-Fluoropropyloxy)-naphthalene.[14]

Colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) 1.50 (dd, J = 23.6, 6.4 Hz, 3H), 4.09-4.24 (m, 2H), 5.00-5.16 (m, 1H), 7.13-7.46 (m, 4H), 7.71-7.78 (m, 3H); ^{13}C (100 MHz, $CDCl_3$) 17.5 (d, J = 22 Hz) 70.7 (d, J = 23.5 Hz) 88.3 (d, J = 167.5 Hz) 106.7, 118.7, 123.7, 126.3, 126.6, 127.5, 129.0, 129.4, 134.3, 156.3; HRMS (EI) calcd for $C_{13}H_{13}FO$ (M^+) 204.0950, found 204.0953 registery No.398-53-8.

3-Fluorobutyl benzene.[23]

Yellow oil, (volatile at room temp) ^{1}H NMR (400 MHz, $CDCl_3$) 1.39 (dd, J = 23.6, 6.4 Hz, 3H), 1.81-2.07 (m, 2H), 2.69-2.88 (m, 2H), 4.62- 4.78 (m, 1H), 7.18-7.35 (m, 5H); ^{13}C (100 MHz, $CDCl_3$) 20.97 (d, J = 22.2 Hz), 31.34 (d, J = 5.3 Hz), 38.64 (d, 21.2 Hz), 90.02 (d, J = 163.7 Hz), 125.92, 128.41, 141.47; HRMS (EI) calcd for $C_{10}H_{13}F$ $[M]^+$ 152.1001, found 152.1031; registery No. 20651-66-5.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [1H and 13C NMR of compounds and image of solublity new IL]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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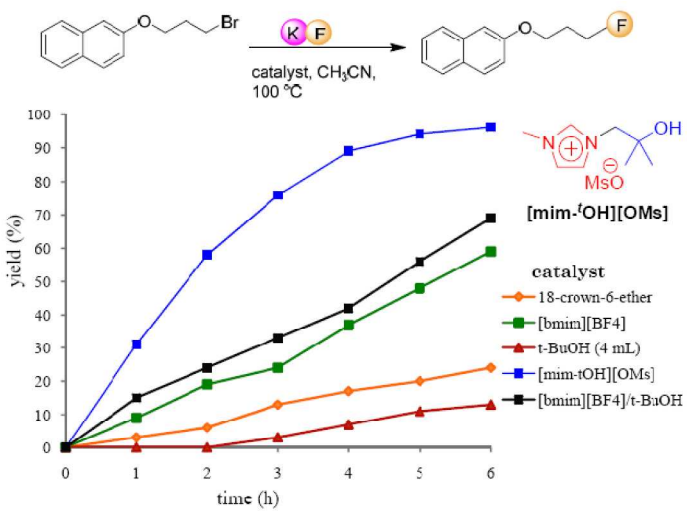

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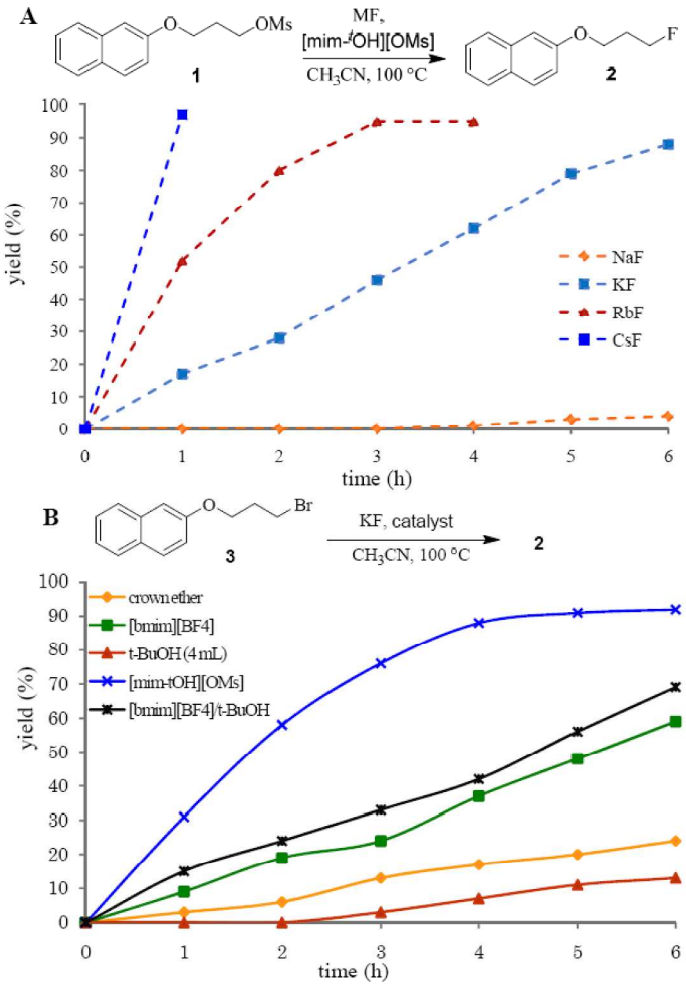

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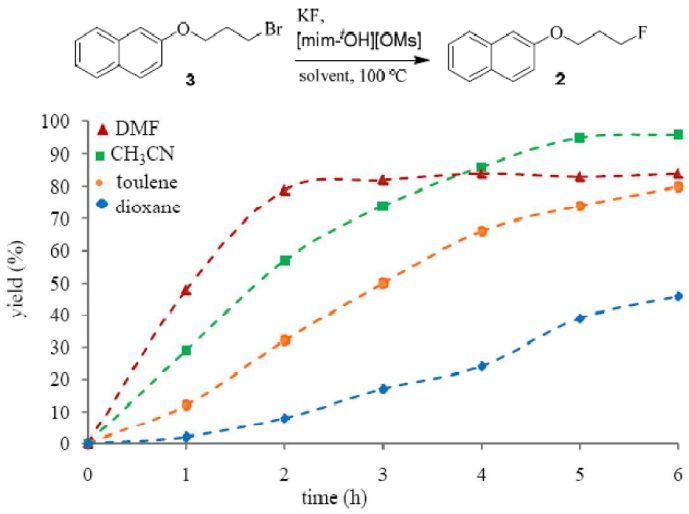

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