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Crown ether metal complex fluoride salt as a facile and low hygroscopic fluoride source for nucleophilic fluorination

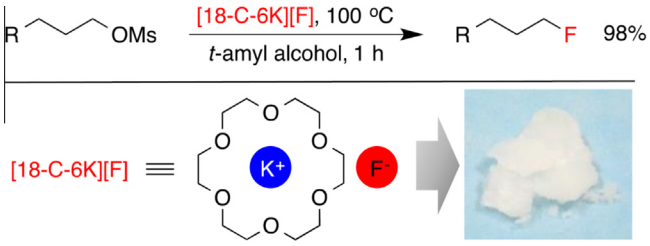
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HIGHLIGHTS

- We prepared crown ether metal complex fluorides (CEMCFs) in water.
- CEMCFs were used as fluoride source for nucleophilic fluorination reaction.
- CEMCF/*t*-alcohol system showed excellent chemo-selectivity in the fluorination.
- Phenolic TBDMS ether was cleaved selectively using CEMCF/methanol.

GRAPHICAL ABSTRACT



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ABSTRACT

A variety of crown ether metal complex fluorides (CEMCFs), such as [18-C-6K][F], [18-C-6Cs][F], [18-C-6Rb][F], and [18-C-6Na][F] ([18-C-6K] = 18-crown-6 potassium cation complex; [18-C-6Cs] = 18-crown-6 cesium cation; [18-C-6Rb] = 18-crown-6 rubidium cation; [18-C-6Na] = 18-crown-6 sodium cation; [F] = fluoride), were prepared in quantitative yields by simply treating the correct molar ratio of 18-crown-6 with the corresponding alkali metal fluorides at 25 °C for 24 h in water after evaporation and vacuum drying. In particular, [18-C-6K][F] exhibited relatively low hygroscopic properties compared with the conventional tetrabutylammonium fluoride (TBAF). The efficiency of these CEMCFs as a fluoride source was examined in various nucleophilic fluorination reactions. The results showed that these CEMCFs had good reactivity except for [18-C-6Na][F]. Furthermore, *tert*-alcohol media enhanced the reactivity and chemo-selectivity of [18-C-6K][F] significantly in the nucleophilic fluorination of base-sensitive substrates. In addition, [18-C-6K][F] showed good performance in the selective phenolic desilylation of bis-TBDMS ether in methanol.

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1. Introduction

Often, the installation of a fluorine atom on pharmaceuticals or agrochemicals causes dramatic improvement in their metabolic stability, lipophilicity, bioavailability, and biological activity compared to the original molecules [1,2]. Fluorination chemistry is also becoming important in positron emission tomography (PET) using radiopharmaceuticals, which necessitates the radiolabeling of molecules with a single [^{18}F]fluorine atom [3–5]. The nucleophilic fluorination of organic compounds is one of the most widely used methodologies in fluorine chemistry. Alkali metal fluorides (MFs), particularly potassium fluoride (KF), have traditionally occupied a privileged position in nucleophilic fluorination because of their easy availability and thermal stability [6,7]. On the other hand, the low solubility and nucleophilicity of MFs in organic solvents restrict their wider applications in nucleophilic fluorination [6,7]. To overcome these problems, a range of phase transfer catalyst (PTC) methods have been discovered, such as bulky tetraalkylammonium fluorides and crown ether/MF complexes [8,9]. In particular, tetrabutylammonium fluoride (TBAF) has been used widely as a fluoride source for nucleophilic fluorination. High hygroscopic and basic properties of TBAF make handling difficult and provide low chemo-selectivity and chemical yield frequently

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[10]. Crown ethers, which are heterocyclic oligomers of dioxane, can also act as excellent PTCs [11,12], and have attracted significant attention in a range of fields because they are popular host compounds in host–guest chemistry in a selective manner [13–19]. By forming complexes of alkali metal cations in the cavity of crown ethers *in situ* during the reaction process, crown ethers can help dissolve alkali metal salts (MXs) in organic solvents and reduce the electrostatic interactions between M^+ and X^-, as well as enhance the reactivity of X^- as nucleophiles [11,12]. For example, the 18-crown-6/KF system is considered one of the most efficient and economical protocols for nucleophilic fluorination [20]. In addition, ionic liquids can enhance significantly the reactivity of MXs in nucleophilic displacement reactions using the corresponding MX including nucleophilic fluorination [21,22].

Recently, Jing et al. [23,24] developed crown ether complex cation ionic liquids (CECILs), as novel types of ionic liquids, by simply mixing crown ether with the relevant MXs in water. These isolated CECILs showed good performance in a range of organic reactions, as well as a clear solvent effect as with traditional ionic liquids. In this regard, isolated crown ether metal complex fluorides (CEMCFs) were designed and synthesized using 18-crown-6 and various alkali metal fluorides, such as KF, CsF, RbF, and NaF, and their efficiency as a fluoride source in the nucleophilic fluorination reactions was investigated.

2. Experimental

2.1. Material

18-Crown-6, NaF, KF, RbF, and CsF were purchased from Sigma Aldrich. Unless otherwise noted all reagent and solvents were commercially available and purchased from Sigma Aldrich. Reaction progress was followed by TLC on 0.25 mm silica gel glass plates containing F-254 indicator. Visualization on TLC was monitored by UV light. Flash chromatography was performed with 230–400 mesh silica gel. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 or 600 MHz spectrometer, and chemical shifts were reported in δ units (ppm) relative to tetramethylsilane. Low- and high-resolution electron impact (EI, 70 eV) spectra were obtained.

2.2. Procedure of crown ether metal complex fluorides [CEMCFs]

2.2.1. Preparation of [18-C-6Na][F]

The inorganic sodium fluoride salt (420 mg, 10 mmol) was mixed with 18-crown-6 (2.7 g, 10 mmol) in water (15 mL). After stirring at RT for 24 h, the excess water was evaporated under reduced pressure. The residue was vacuum dried to generate 3.10 g (9.93 mmol, 99.3%) of 18-crown-6 ether sodium complex fluoride [18-C-6Na][F]. To obtain the pure [18-C-6Na][F], the substrates must be weighed accurately. Nature: white solid; mp: 41 °C; ^{1}H NMR (600 MHz, D_2O) δ 3.55 (s, 24H); ^{13}C NMR (150 MHz, D_2O) δ 69.49; ^{19}F NMR (600 MHz, D_2O) δ −121.07; MS (FAB) *m/z* 287.1 (M^+−X); HRMS (FAB TOF) *m/z* calcd for $C_{12}H_{24}O_6$-Na (M^+−X) 287.1469, found 287.1471; (X = [F]).

2.2.2. Preparation of [18-C-6K][F]

Prepared according to the procedure of [18-C-6Na][F] except using potassium fluoride salt (582 mg, 10 mmol), instead of using sodium fluoride salt (420 mg, 10 mmol), this reaction provided 3.26 g (9.91 mmol, 99.1%) of [18-C-6K][F]. Nature: white solid; mp: 56 °C; ^{1}H NMR (600 MHz, D_2O) δ 3.56 (s, 24H); ^{13}C NMR (150 MHz, D_2O) δ 69.74; ^{19}F NMR (600 MHz, D_2O) δ −122.13; MS (FAB) *m/z* 303.1 (M^+−X, 100); HRMS (FAB TOF) *m/z* calcd for $C_{12}H_{24}O_6K$ (M^+−X) 303.1210, found 303.1212; (X = [F]).

2.2.3. Preparation of [18-C-6Rb][F]

Prepared according to the procedure of [18-C-6Na][F] except using rubidium fluoride salt (1.05 g, 10 mmol), instead of using sodium fluoride salt (420 mg, 10 mmol), this reaction provided 3.74 g (9.94 mmol, 99.5%) of [18-C-6Rb][F]. Nature: white solid; mp: 54 °C; ^{1}H NMR (600 MHz, D_2O) δ 3.56 (s, 24H); ^{13}C NMR (150 MHz, D_2O) δ 69.57; ^{19}F NMR (600 MHz, D_2O) δ −121.15; MS (FAB) *m/z* 349.1 (M^+−X, 100); HRMS (FAB TOF) *m/z* calcd for $C_{12}H_{24}O_6Rb$ (M^+−X) 349.0693, found 349.0691; (X = [F]).

2.2.4. Preparation of [18-C-6Cs][F]

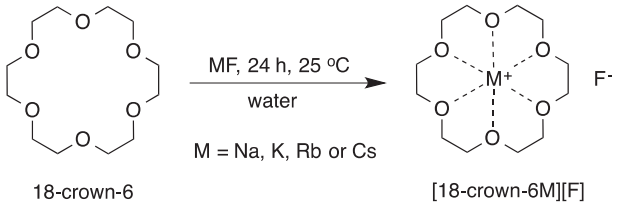
Prepared according to the procedure of [18-C-6Na][F] except using cesium fluoride salt (1.52 g, 10 mmol), instead of using potassium fluoride salt (420 mg, 10 mmol), this reaction provided 4.22 g (9.93 mmol, 99.3%) of [18-C-6Cs][F]. Nature: white solid; hygroscopic; ^{1}H NMR (600 MHz, D_2O) δ 3.56 (s, 24H); ^{13}C NMR (150 MHz, D_2O) δ 69.50; ^{19}F NMR (600 MHz, D_2O) δ −120.81; MS (FAB) *m/z* 397.1 (M^+−X, 100); HRMS (FAB TOF) *m/z* calcd for $C_{12}H_{24}O_6Cs$ (M^+−X) 397.0627, found 397.0629; (X = [F]).

2.3. Typical procedure of fluorination in Table 1, entry 4

[18-C-6K][F] (645 mg, 2 mmol) was added to the solution of mesylate **1** (281 mg, 1.0 mmol) in *tert*-amylalcohol (4 mL). The reaction mixture was stirred over 1 h at 100 °C. We determined the reaction time by checking TLC. The reaction mixture was filtered and washed with diethyl ether. The filtrate was evaporated under reduced pressure. Flash column chromatography (10% EtOAc/hexanes) of the filtrate afforded 200 mg (0.98 mmol, 98%) of 2-(3-fluoropropoxy)naphthalene (**2a**) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14–2.39 (m, 2H), 4.24 (t, *J* = 6.2 Hz, 2H), 4.72 (dt, *J* = 46.8, 5.8 Hz, 2H), 7.16–7.22 (m, 2H), 7.34–7.53 (m, 2H), 7.76–7.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4 (d, *J* = 20.1 Hz), 63.6 (d, *J* = 25.3 Hz), 80.8 (d, *J* = 163.9 Hz), 106.8, 118.8, 123.6, 126.4, 126.7, 127.6, 129.1, 129.4, 134.6, 156.7; ^{19}F NMR (400 MHz, $CDCl_3$) δ −24.80; MS (EI) *m/z* 204 (M^+, 100); HRMS (EI TOF) *m/z* calcd for $C_{13}H_{13}FO$ (M^+) 204.0950, found 204.0932. Registry No. provided by the author: 398-53-8.

2.4. Procedure of selective deprotection of phenolic TBDMS-ether (scheme-2)

[18-C-6K][F] (161 mg, 0.5 mmol) was added to the solution of *tert*-butyl(3-(4′-(*tert*- butyldimethylsilyloxy)biphenyl-4-yloxy)propoxy)dimethylsilane **3** (473 mg, 1.0 mmol) in methanol (4 mL). The reaction mixture was stirred over 30 min at room temperature. We determined the reaction time by checking TLC. The reaction mixture was filtered and washed with diethyl ether. The filtrate was evaporated under reduced pressure. Flash column chromatography (5% EtOAc/hexane) of the filtrate afforded 348 mg (0.98 mmol, 98%) of 4′-(3-*tert*- butyldimethylsilyloxy)propoxy)biphenyl-4-ol (**4**); ^{1}H NMR (600 MHz, $CDCl_3$ + $MeOD_4$) δ 0.00 (s, 6H), 0.84 (s, 9H), 1.95–1.98 (m, 2H), 3.76 (t, *J* = 6.2 Hz, 2H), 4.04 (t, *J* = 6.2 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 7.35–7.40 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$)



Scheme 1. Preparation of the crown ether metal complex fluorides (CEMCFs).

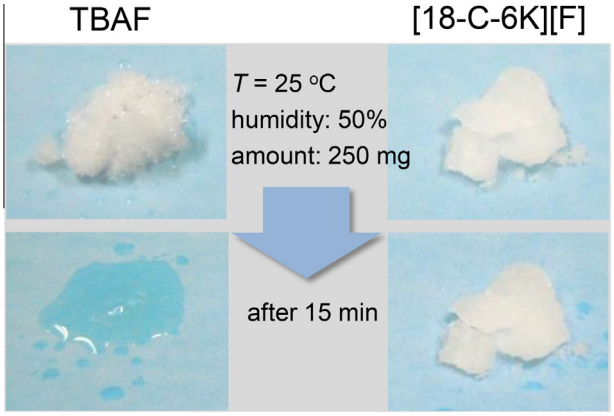


Fig. 1. Hygroscopicity of [18-C-6K][F] and commercially available TBAF.

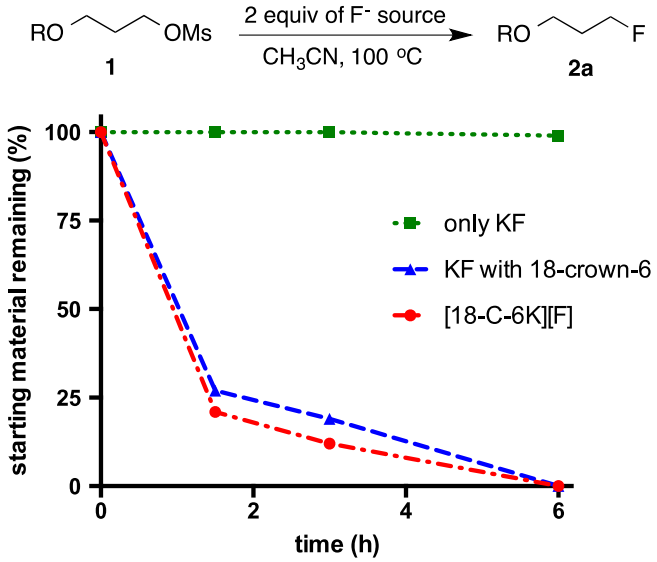


Fig. 2. Reactivity of [18-C-6K][F], conventional KF/18-crown-6, and only KF. The quantity of product was determined by ^{1}H NMR. R = 2-naphthyl.

δ −5.25, 18.42, 25.73, 26.03, 32.53, 59.66, 64.68, 114.84, 115.66, 127.74, 128.00, 133.32, 133.81, 154.72, 158.28; MS (FAB) *m/z* 358.20 (M^+, 100); HRMS (FAB TOF) *m/z* calcd for $C_{21}H_{30}O_3Si$ (M^+) 358.2014, found 358.2011.

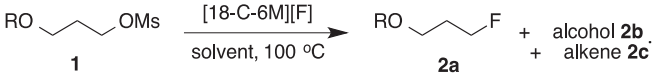
3. Results and discussions

CEMCFs, such as [18-C-6K][F], [18-C-6Cs][F], [18-C-6Rb][F], and [18-C-6Na][F] ([18-C-6K] = 18-crown-6 potassium cation complex; [18-C-6Cs] = 18-crown-6 cesium cation complex; [18-C-6Rb] = 18-crown-6 rubidium cation complex; [18-C-6Na] = 18-crown-6 sodium cation complex; [F] = fluoride), were prepared simply using the procedure shown in Scheme 1. The treatment of the correct molar ratio of 18-crown-6 with the corresponding MF (such as KF, CsF, RbF, and NaF) at 25 °C for 24 h in water afforded the desired CEMCFs (i.e., [18-C-6K][F], [18-C-6Cs][F], [18-C-6Rb][F] and [18-C-6Na][F] respectively) in quantitative yield after evaporation and vacuum drying. Of these, [18-C-6K][F] exhibited very low hygroscopic properties compared to commercially available TBAF (Fig. 1). This favorable property might assist in its easy handling and help maintain anhydrous conditions during the reaction process.

To determine the envisaged protocol, the reactivity of [18-C-6K][F] as a fluoride source in the nucleophilic fluorination of 2-(3-methanesulfonyloxypropyl)naphthalene (**1**) as a model compound at 100 °C in CH_3CN was initially investigated (Fig. 2). This isolated CEMCF [18-C-6K][F] could provide a slightly faster reaction rate than that using the conventional PTC method (18-crown-6/KF). In the absence of any PTC, the same fluorination reaction proceeded very slowly. This suggests that [18-C-6K][F] can be a good alternative fluoride source for nucleophilic fluorination.

Table 1 lists the results of nucleophilic fluorination with various CEMCFs, such as [18-C-6K][F], [18-C-6Cs][F], [18-C-6Rb][F], and [18-C-6Na][F] in different reaction media. First, we performed the fluorination of **1** in various solvents to investigate the solvent effect on [18-C-6K][F]. The fluorination reaction using [18-C-6K][F] in benzene or 1, 4-dioxane produced the fluoro-product **2a** only in 13% or 12% yields even after 12 h (entries 1 and 2, respectively). In contrast, the same fluorination in a polar aprotic solvent, DMF, gave **2a** in 85% yield with 15% of alkene **2c** within 3 h (entry 3). In polar protic solvent such as *tert*-amyl alcohol, the fluorination was completed within 1 h affording product **2a** in quantitatively yield without forming a by-product (entry 4). This result clearly suggests that a *tert*-alcohol media could also increase the reactivity and chemo-selectivity of [18-C-6K][F] significantly in nucleophilic fluorination [25–27]. Both [18-C-6Cs][F] and [18-C-6Rb][F] exhibited good reactivity. However, the reaction using them formed 8–9% of an alkene compound **2c** by a side-reaction, such as the elimination in polar aprotic CH_3CN (entries 5 and 6). [18-C-6Na][F] was totally inactive for this fluorination even after 12 h (entry 7) because of the small size and strong Coulombic influence of Na^+. In this regard, the reactivity of [18-C-6M][F] is

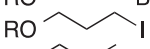
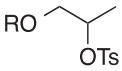
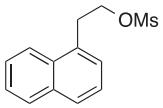
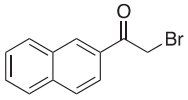
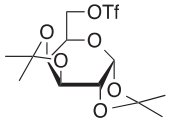
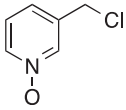
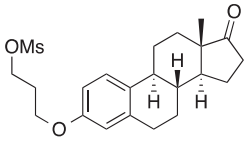
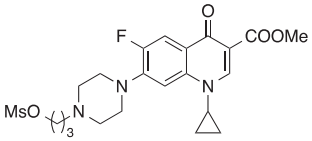
Table 1
Fluorination of mesylate **1** with [18-C-6M][F] under a range of reaction conditions.[a]



Entry	[18-C-6M][F]	Solvent	Time (h)	Yield of product (%)[b]			
				1	**2a**	**2b**	**2c**
1	[18-C-6K][F]	Benzene	12	87	13	–	–
2	[18-C-6K][F]	1,4-dioxane	12	66	12	22	–
3	[18-C-6K][F]	DMF	3	–	85	–	15
4	[18-C-6K][F]	*t*-amyl alcohol	1	–	98	–	–
5	[18-C-6Cs][F]	CH_3CN	3	–	90	trace	9
6	[18-C-6Rb][F]	CH_3CN	4		89	trace	8
7	[18-C-6Na][F]	CH_3CN	12	100	–	–	–

[a] All reactions were carried out on a 1.0 mmol scale of **1** with 2.0 equiv of [18-C-6][F] in 4 mL of solvent at 100 °C.
[b] Yields determined by ^{1}H NMR spectroscopy. R = 2-naphthyl.

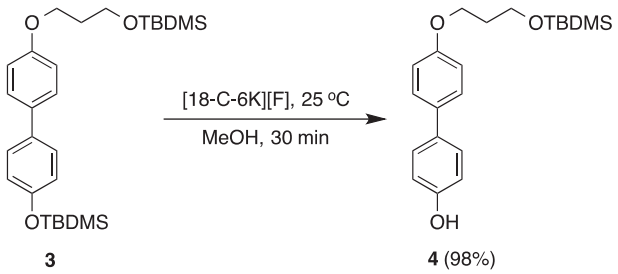
Table 2
Nucleophilic fluorinations of various substrates using [18-C-6K][F] in *tert*-amyl alcohol.[a]

Entry	Substrates	Time (h)	Temp (°C)	Yield (%)[b]	
				Product	Alkene
1		4	100	93	6
2		3	100	86	12
3		4	100	91	8
4		2	100	88	10
5		1	100	86	–
6		1	90	95	–
7		3	90	87[c]	–
8		4	100	97	–
9		4	100	96	–

[a] Unless stated otherwise, all reactions were carried out on a 1.0 mmol scale of substrate with 2.0 equiv of [18-C-6K][F] in 4.0 mL of *tert*-amyl alcohol.
[b] Isolated yields.
[c] With 11% alcohol as by-product. R = naphthyl.

dependent on the Coulombic influence of its alkali metal cation on fluoride.

To extend the scope of the application of the CEMCF, we performed the nucleophilic fluorinations of various substrates including base sensitive compounds using 2 equiv of [18-C-6K][F] in *tert*-amyl alcohol, thereby showing that [18-C-6K][F] is generally applicable to other substrates. Entries 1–4 in Table 2 showed that *tert*-alcohol media fluorinations of base sensitive substrates (primary alkyl bromide as well as iodide, *sec*-alkyl tosylate, and 2-mesyloxyethylnaphthalene) with [18-C-6K][F] proceeded highly chemo-selectively and afforded the corresponding fluoro-products in high yields (86–93%) with minimal alkene by-products. A α-fluoroacetophenone compound was produced successfully from an α-bromoacetophenone compound in a good yield via this fluorination process using [18-C-6K][F] (entry 5). A primary triflate of α-*D*-galactopyranose was converted to fluorosugar in an excellent yield (95%, entry 6). The nucleophilic displacement reaction of 3-chloro-picoline-*N*-oxide proceeded smoothly to afford 3-fluoro-picoline-*N*-oxide in 87% yield along with 11% alcohol as a byproduct (entry 7). In the final examples, two bioactive molecules, such as fluoropropyl estrone and fluoropropyl ciprofloxacin [28], were synthesized from the fluorination reactions of the corresponding mesylate precursors in high yields (97 and 96%, entries 8 and 9, respectively).



Scheme 2. Selective phenolic deprotection of bis-TBDMS ether **3** using [18-C-6K][F].

To further extend the scope of the application of CEMCFs, [18-C-6K][F] was used as a fluoride source for the selective deprotection of phenolic *tert*-butyldimethylsilyl (TBDMS) ether [29]. The selective phenolic desilylation of bis-TBDMS ether **3** containing both phenolic and aliphatic TBDMS ether with [18-C-6K][F] in methanol proceeded quantitatively, affording the monosilylated product **4** in 98% yield (Scheme 2).

4. Conclusions

In summary, we have described the preparation of various isolated crown ether metal complex fluorides (CEMCFs), such as

[18-C-6K][F], [18-C-6Cs][F], [18-C-6Rb][F] and [18-C-6Na][F], using 18-crown-6 with relevant alkali metal fluorides in water. These complexes could act as highly efficient fluoride sources for nucleophilic fluorination reactions except for [18-C-6Na][F]. Moreover, CEMCF [18-C-6K][F] exhibited relatively low hygroscopic properties compared with commercially available TBAF. In particular, the synergistic combination of [18-C-6K][F] with *tert*-alcohol media showed significant efficacy in the chemo-selective nucleophilic fluorinations of base sensitive substrates. In addition, [18-C-6K][F] was useful for the selective phenolic deprotection of bis-TBDMS ether containing both phenolic and aliphatic TBDMS ether in methanol. Considering the ease preparation and favorable properties of these CEMCFs, they also are expected to be useful for industrial field. Further studies of the development of more efficient CEMCFs are currently underway.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2015.01.087.

References

[1] Special Issue: Fluorine in the life Sciences. ChemBioChem, 2004, 5, 557-726.
[2] D.A. Watson, M. Sue, G. Teverovskiy, Y. Zhang, J. Garcia-Fortanet, T. Kinzel, S.L. Buchwald, Formation of ArF from LPdAr(F): catalytic conversion of aryl triflates to arly fluorides, Science 325 (2009) 1661–1664.
[3] M.E. Phelps, Positron emission tomography provides molecular imaging of biological processes, Proc. Natl. Acad. Sci. U.S.A. 97 (2000) 9226–9233.
[4] S.M. Ametamey, M. Honer, P.A. Schubiger, Molecular imaging with PET, Chem. Rev. 108 (2008) 1501–1516.
[5] M.C. Koag, H.-K. Kim, A.S. Kim, Efficient microscale synthesis of [^{18}F]-2-fluoro-2-deoxy-D-glucose, Chem. Eng. J. 258 (2014) 62–68.
[6] M.R.C. Gerstenberger, A. Haas, Methods of fluorination in organic chemistry, Angew. Chem. Int. Ed. 20 (1981) 647–667.
[7] O.A. Mascaretti, Modern methods for the monofluorination of aliphatic organic compounds, Aldrichimica. Acta 26 (1993) 47–58.
[8] E.V. Dehmlow, S.S. Dehmlow, Phase Transfer Catalysis, 3rd ed., VCH Ltd., New York, 1993.
[9] H. Sun, S.G. DiMango, Anhydrous tetrabutylammonium fluoride, J. Am. Chem. Soc. 127 (2005) 2050–2051.
[10] A.S. Pilcher, H.L. Ammon, P. DeShong, Utilization of tetrabutylammonium triphenylsilylfluoride as a fluoride source for nucleophilic fluorination, J. Am. Chem. Soc. 117 (1995) 5166–5167.
[11] C.J. Pedersen, Cyclic polyethers and their complexes with metal salts, J. Am. Chem. Soc. 89 (1977) 7017–7036.
[12] G.W. Gokel, In Crown Ethers and Cryptands, Royal Society of Chemistry, Cambridge, 1991.
[13] D.J. Cram, J.M. Cram, Design of complexes between synthetic hosts and organic guests, Acc. Chem. Res. 11 (1978) 8–14.
[14] C.J.J. Pedersen, New macrocyclic polyethers, J. Am. Chem. Soc. 92 (1970) 391–394.
[15] D.E. Fenton, Across the living barrier, Chem. Soc. Rev. 6 (1977) 325–343.
[16] C. Sun, G. Zhang, R. Qu, Y. Yu, Removal of transition metal ions from aqueous solution by crosslinked polystyrene-supported bis-8-oxyquinoline-terminated open-chain crown ethers, Chem. Eng. J. 170 (2011) 250–257.
[17] T. Lee, J.W. Chen, H.L. Lee, T.Y. Lin, Y.C. Tsai, S.-L. Cheng, S.-W. Lee, J.-C. Hu, L.-T. Chen, Stabilization and spheroidization of ammonium nitrate: co-crystallization with crown ethers and spherical crystallization by solvent screening, Chem. Eng. J. 225 (2013) 809–817.
[18] R.E.C. Torrejos, G.M. Nisola, M.J. Park, H.K. Shon, J.G. Seo, S. Koo, W.-J. Chung, Synthesis and characterization of multi-walled carbon nanotubes-supported dibenzo-14-crown-4 ether with proton ionizable carboxyl sidearm as Li^+ adsorbents, Chem. Eng. J. 264 (2015) 89–98.
[19] W. Qin, S. Xu, G. Xu, Q. Xie, C. Wang, Z. Xu, Preparation of silica gel bound crown ether and its extraction performance towards zirconium and hafnium, Chem. Eng. J. 225 (2013) 528–534.
[20] C.L. Liotta, H.P. Harris, The chemistry of naked anions. I Reactions of the 18-crown-6 complex of potassium fluoride with organic substrates in aprotic solvents, J. Am. Chem. Soc. 96 (1974) 2250–2252.
[21] D.W. Kim, C.E. Song, D.Y. Chi, New method of fluorination using potassium fluoride in ionic liquid: significantly enhanced reactivity of fluoride and improved selectivity, J. Am. Chem. Soc. 124 (2002) 10278–10279.
[22] D.W. Kim, C.E. Song, D.Y. Chi, Significantly enhanced reactivities of the nucleophilic substitution reactions in ionic liquid, J. Org. Chem. 68 (2003) 4281–4285.
[23] Y. Song, H. Jing, B. Li, D. Bai, Crown ether complex cation ionic liquid: preparation and applications in organic reactions, Chem. Eur. J. 17 (2011) 8731–8738.
[24] H. Jing, Z. Hou, S. Chen, Z. Li, D. Li, Synthesis, characterization of 4-[2-(3-nitro-4-methoxyphenyl)vinyl]-1-methylpyridinium penta- and hexa-nitrato rare earth(III) complexes, Acta. Chim. Sin. 52 (1994) 1058–1063.
[25] D.W. Kim, D.-S. Ahn, Y.-H. Oh, S. Lee, S.J. Oh, S.J. Lee, J.S. Kim, J.-S. Ryu, D.H. Moon, D.Y. Chi, A new class of S_N2 reactions catalyzed by protic solvents; facile fluorination for isotopic labeling of diagnostic molecules, J. Am. Chem. Soc. 128 (2006) 16394–16397.
[26] D.W. Kim, H.-J. Jeong, S.T. Lim, M.H. Sohn, J.A. Katzenellenbogen, D.Y. Chi, Facile nucleophilic fluorination reactions using *tert*-alcohols as a reaction medium: significantly enhanced reactivity of alkali metal fluorides and improved selectivity, J. Org. Chem. 73 (2008) 957–962.
[27] D.W. Kim, H.-J. Jeong, S.T. Lim, M.H. Sohn, Tetrabutylammonium tetra(*tert*-butyl alcohol)-coordinated fluoride as a facile fluoride source, Angew. Chem. Int. Ed. 47 (2008) 8404–8406.
[28] S. Kalme, E.-M. Kim, S.-J. Cheong, H.-J. Jeong, S.T. Lim, M.H. Sohn, D.W. Kim, Synthesis of N-4′-[F-18]fluoroalkylated ciprofloxacin as a potential bacterial infection imaging agnet for PET study, Bioconjugate Chem. 21 (2010) 2282–2288.
[29] V.H. Jadhav, S.B. Lee, H.-J. Jeong, S.T. Lim, M.H. Sohn, D.W. Kim, An efficient and chemoselective deprotection of tert-butyldimethylsilyl (TBDMS) ethers using tailor-made ionic liquid, Tetrahedron Lett. 53 (2012) 2051–2053.