Supporting Information

Synergistic Effect of Two-Solvents-in-One-Molecule in Nucleophilic Fluorination: Two Solvents are \textit{tert}-Alcohol and Ionic Liquid

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1. Materials & 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 F-254 glass-backed plates. Visualization on TLC was monitored by UV light or phosphomolybdc acid indicator. $^1$H and $^{13}$C NMR spectra were recorded using both Varian Gemini-2000 (200 MHz) and Varian UNITY-INNOVA 400 (400 MHz) and calibrated using residual undeuterated solvent or tetramethylsilane as an internal reference.

2. Preparation and Characterization of 1 and Ionic Liquids (2a-2d).

2.1. 1-(2-Hydroxy-2-methyl-3-propyl)imidazole (1). Imidazole (2.00 g, 29.37 mmol) and isobutylene oxide (2.90 mL, 32.31 mmol) was stirred at 55 °C in reaction vial for 12 h. The resulting thick liquid was dried under high vacuum at room temperature to afford 4.07 g (99%) of 1 as a colorless liquid: $^1$H NMR (400 MHz, CDCl$_3$) δ 1.22 (s, 6H), 3.87 (s, 2H), 4.21 (br, 1H), 6.93-6.98 (m, 2H), 7.48 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 27.0, 58.0, 69.7, 120.5, 127.9, 138.0; MS (EI) 140 (M$^+$), 82 (100), 59. HRMS (EI) calcd for C$_7$H$_{12}$N$_2$O (M$^+$) 140.0950, found 140.0949. Copies of $^1$H and $^{13}$C NMR spectra are in this SI. Known compound. See Arnold, P. L.; Rodden, M.; Davis, K. M.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. Chem. Commun. 2004, 1612-1613.

2.2. 1-(2-Hydroxy-2-methyl-3-propyl)-3-methylimidazolium Mesylate [mim-OH][OMs] (2a). Methyl methanesulfonate (0.72 mL, 8.57 mmol) was added drop-wise to the solution of 1 (1.00 g, 7.14 mmol) in CH$_3$CN (15 mL). The reaction mixture was stirred at 90 °C for 24 h and evaporated under reduced pressure to remove CH$_3$CN. The residue was repeatedly washed with diethyl ether (5 mL × 7) and dried under high vacuum for 12 h at room
temperature to afford 1.62 g (91%) of 2a as a colorless thick liquid: $^1$H NMR (400 MHz, CDCl$_3$) δ 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 NMR (100 MHz, CDCl$_3$) δ 26.4, 36.4, 39.6, 59.7, 68.5, 121.8, 123.7, 139.1. Anal. Calcd for C$_9$H$_{18}$N$_2$O$_4$S: C, 43.18; H, 7.25; N, 11.19. Found: C, 42.93; H, 7.09; N, 11.14. Copies of $^1$H and $^{13}$C NMR spectra are in this SI.

2.3. 1-(2-Hydroxy-2-methyl-\(n\)-propyl)-3-isopropylimidazolium Mesylate [ipim-\(\text{OH}\)][OMs] (2b). This compound was prepared by a procedure similar to that for the preparation of 2a: Colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.20 (s, 6H) 1.57 (d, $J = 6.8$ Hz, 6H) 2.75 (s, 3H), 4.28 (s, 2H), 4.57-4.69 (m, 1H), 7.30 (s, 1H), 7.43 (s, 1H), 9.65 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 22.8, 26.3, 39.6, 52.8, 59.2, 68.5, 118.7, 124.2, 136.4. Anal Calcd for C$_{11}$H$_{22}$N$_2$O$_4$S: C, 47.46; H, 7.97; N, 10.06. Found: C, 47.55; H, 8.34; N, 10.19. Copies of $^1$H and $^{13}$C NMR spectra are in this SI.

2.4. 1-(2-Hydroxy-2-methyl-\(n\)-propyl)-3-\(n\)-butylimidazolium Mesylate [bim-\(\text{OH}\)][OMs] (2c). This compound was prepared by a procedure similar to that for the preparation of 2a: Colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.94 (t, $J = 7.2$ Hz, 3H), 1.20 (s, 6H), 1.32-1.36 (m, 2H), 1.86 (q, $J = 7.6$ Hz, 2H ), 2.74 (s, 3H), 4.22 (t, $J = 7.2$ Hz, 2H), 4.27 (s, 2H), 7.38 (s, 1H), 7.60 (s, 1H), 9.46 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.2, 19.2, 26.2, 31.7, 39.5, 49.4, 59.3, 68.6, 120.7, 124.2, 137.4. Anal Calcd for C$_{12}$H$_{24}$N$_2$O$_4$S: C, 49.29; H, 8.27; N, 9.58. Found: C, 49.05; H, 8.26; N, 9.47. Copies of $^1$H and $^{13}$C NMR spectra are in this SI.

2.5. 1-(2-Hydroxy-2-methyl-\(n\)-propyl)-3-\(n\)-hexylimidazolium Mesylate [him-\(\text{OH}\)][OMs] (2d). This compound was prepared by a procedure similar to that for the preparation of 2a: Pale yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) δ 0.86 (t, $J = 6.4$ Hz, 3H), 1.22 (s, 6H), 1.26-1.39 (m, 6H), 1.88 (q, $J = 6.8$ Hz, 2H), 2.78 (s, 3H), 4.19 (t, $J = 7.2$ Hz, 2H), 4.33 (s, 2H), 7.21 (s, 1H), 7.40 (s, 1H), 9.77 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.8, 22.3, 25.8, 26.5, 30.0, 31.0, 39.6, 50.1, 59.6, 68.6, 120.2, 123.8, 138.3. Anal. Calcd for C$_{14}$H$_{28}$N$_2$O$_4$S: C, 52.47; H, 8.81; N, 8.74. Found: C, 52.63; H, 8.73; N, 8.88. Copies of $^1$H and $^{13}$C NMR spectra are in
3. Procedure for Fluorination in Table 1.

3.1. Typical Fluorination Procedure (entry 4). CsF (755 mg, 5.0 mmol) was added to the mixture of 2-(3-methanesulfonyloxypropoxy)naphthalene 3 (280 mg, 1.0 mmol) and [mim-\(\text{OH}\)][OMs] 2a (125 mg, 0.5 mmol) in 3 mL CH\(_3\)CN. The mixture was stirred for 50 min at 100 °C. The reaction mixture was extracted with diethyl ether (10 mL \(\times\) 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The conversion was determined by \(^1\)H NMR and the crude product was purified by flash column chromatography (5% EtOAc/hexane) to obtain 2-(3-fluoro-\(n\)-propoxy)naphthalene 4a (198 mg, 97%) as a colorless oil: \(^1\)H NMR (200 MHz, CDCl\(_3\)) 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 (50 MHz, CDCl\(_3\)) \(\delta\) 30.4 (d, \(J = 20.1\) Hz), 63.6 (d, \(J = 5.3\) Hz), 80.8 (d, \(J = 163.9\) Hz), 106.8, 118.8, 123.7, 126.4, 126.7, 127.6, 129.1, 129.4, 134.6, 156.7. Copies of \(^1\)H NMR and \(^{13}\)C NMR spectra are in this SI; Known compound. See Kim, D. W.; Song, C. E.; Chi, D. Y. *J. Am. Chem. Soc.* 2002, 124, 10278-10279.

3.2. Procedure of Entries 8 and 9. CsF (755 mg, 5.0 mmol) was added to the mixture of 2-(3-methanesulfonyloxypropoxy)naphthalene 3 (280 mg, 1.0 mmol) and [mim-\(\text{OH}\)][OMs] 2a (750 mg, 3 mmol or 3 mL) in 3 mL CH\(_3\)CN or without CH\(_3\)CN. The mixture was stirred for 40 min at 100 °C. The reaction mixture was extracted with diethyl ether (15 mL \(\times\) 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was checked by \(^1\)H NMR.

3.3. Procedure of Entry 10. CsF (755 mg, 5.0 mmol) was added to the mixture of 2-(3-methanesulfonyloxypropoxy)naphthalene 3 (280 mg, 1.0 mmol), t-BuOH (37 mg, 0.5 mmol) in CH\(_3\)CN (2.5 mL). The mixture was stirred for 50 min at 100 °C. The reaction mixture was extracted with diethyl ether (10 mL \(\times\) 3). The organic layer was dried over anhydrous sodium
sulfate and evaporated under reduced pressure. The crude product was checked by $^1$H NMR.

3.4. Procedure of Entry 11. CsF (755 mg, 5.0 mmol) was added to the mixture of 2-(3-methanesulfonyloxypropoxy)naphthalene 3 (280 mg, 1.0 mmol), [bmim][OMs] (67 mg, 0.5 mmol) and $t$-BuOH (37 mg, 0.5 mmol) in CH$_3$CN (2.5 mL). The mixture was stirred for 50 min at 100 °C. The reaction mixture was extracted with diethyl ether (10 mL × 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was checked by $^1$H NMR.

3.5. Procedure of Entry 12. CsF (755 mg, 5.0 mmol) was added to the mixture of 2-(3-methanesulfonyloxypropoxy)naphthalene 3 (280 mg, 1.0 mmol), [mim-$t$OH][OMs] 2a (125 mg, 0.5 mmol) and H$_2$O (100 μL, 5.5 mmol) in 3 mL CH$_3$CN. The mixture was stirred for 50 min at 100 °C. The reaction mixture was extracted with diethyl ether (10 mL × 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was checked by $^1$H NMR to found 2-(3-fluoro-$n$-propoxy)naphthalene (4a) and 2-(3-hydroxyl-$n$-propoxy)naphthalene (4c).

3. Procedure for Fluorination in Table 2.

4.1. Typical Procedure of $t$-BuOH Solvent Mediated Reaction: 1,2:3,4-Di-$O$-isopropylidene-6-fluoro-6-deoxy-$\alpha$-$d$-galactopyranose (entry 1). A mixture of 1,2:3,4-di-$O$-isopropylidene-6-trifluoromethanesulfonyloxy-$\alpha$-$d$-galactopyranose (392 mg, 1.0 mmol), CsF (456 mg, 3.0 mmol) in $t$-BuOH (4 mL) was stirred at 100 °C. After 5 h solvent evaporated, the mixture was extracted with ethyl ether (10 mL × 3). The organic layer dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by flash chromatography (50 % EtOAc/hexanes) to obtain 246 mg (94%) of 1,2:3,4-di-$O$-isopropylidene-6-fluoro-6-deoxy-$\alpha$-$d$-galactopyranose as a colorless oil: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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, CDCl₃) δ 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; known compound. See Pilcher, A. S.; Ammon, H. L.; DeShong, P. J. Am. Chem. Soc. 1995, 117, 5166-5167.

4.2. Typical Procedure of [bmim][BF₄] Solvent Mediated Reactions. CsF (456 mg, 3.0 mmol) was added to the mixture of di-O-isopropylidene-6-trifluoromethanesulfonyloxy-α-D-galactopyranose (392 mg, 1.0 mmol), and [bmim][BF₄] (1.6 mL) in CH₃CN (2 mL). The mixture was stirred for 1 h at 100 °C. The reaction mixture was extracted from ionic liquid phase with ethyl ether (10 mL × 3). The organic layer was purified by flash column chromatography (50% EOAc/hexane) to afford 238 mg (91%) of 1,2:3,4-di-O-isopropylidene-6-fluoro-6-deoxy-α-D-galactopyranose.

4.3. Typical Procedure by Using [mim-铑[OMs] Reactions. CsF (456 mg, 3.0 mmol) was added to the mixture of di-O-isopropylidene-6-trifluoromethanesulfonyloxy-α-D-galactopyranose (392 mg, 1.0 mmol) and [mim-铑[OMs] (126 mg, 0.5 mmol) in 4 mL CH₃CN. The mixture was stirred for 50 min at 100 °C. The reaction mixture was extracted with diethyl ether (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 (50% EtOAc/hexane) to afford 253 mg (97%) of 1,2:3,4-di-O-isopropylidene-6-fluoro-6-deoxy-α-D-galactopyranose.

4.4. 2-(2-Fluoro-ν-propoxy)naphthalene (entry 4). Colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (100 MHz, CDCl₃) δ 17.5 (d, J = 22.0 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; MS (EI) 204 (M⁺), 144 (100), 115. HRMS (EI) calcd for C₁₃H₁₃FO (M⁺) 204.0950, found 204.0947. Copies of ¹H NMR and ¹³C NMR spectra are in this SI.

4.5. 3-(3-Fluoro-ν-propoxy)estrone. White solid, mp 78.3-80.4 °C; ¹H NMR (400 MHz, CDCl₃) δ0.90 (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, S6
1H), 2.88 (q, J = 3.6 Hz, 2H), 4.07 (t, J = 6.0 Hz, 2H), 4.63 (dt, J = 46.8, 5.6 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); 13C (100 MHz, 
CDCl3) δ 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 = 163.1 Hz), 112.1, 114.5, 126.3, 132.2, 137.7, 156.7, 220.9; 
MS (El) 330 (M+, 100), 245, 206. HRMS (El) calcd for C21H27FO2 (M+) 330.1995, found 
330.1993. Copies of 1H and 13C NMR spectra are in this SI.
4. Characterization of Fluorinated Products in Table 2. 1-(2-Methyl-2-hydroxy-n-propyl)imidazole (1) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
1-(2-Hydroxy-2-methyl-n-propyl)-3-methylimidazolium Mesylate [mim-\textsuperscript{\textit{\textit{\textit{\textit{\textit{\textit{\textit{-OH}}}}}}}}][\textit{OMs}] (2a)

\textit{\textit{\textit{\textit{\textit{\textit{\textit{1H NMR (400 MHz, CDCl\textsubscript{3})}}}}}}}}

\textit{\textit{\textit{\textit{\textit{\textit{\textit{13C NMR (100 MHz, CDCl\textsubscript{3})}}}}}}}}
1-(2-Hydroxy-2-methyl-\textit{n}-propyl)-3-isopropylimidazolium Mesylate \textit{[ipim-\textasciitilde OH][OMs]} (2b)

$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
1-(2-Hydroxy-2-methyl-\(n\)-propyl)-3-\(n\)-butylimidazolium Mesylate [bim-\(^\text{1}^\text{OH}\)\([\text{OMs}]\) (2c)

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\))

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\))
1-(2-Hydroxy-2-methyl-\(n\)-propyl)-3-\(n\)-hexylimidazolium Mesylate [him-'OH][OMs] (2d) \(^1\)H NMR (400 MHz, CDCl\(_3\))

\[ \text{13C NMR (100 MHz, CDCl}_3\) \]
5.6. 2-(3-Fluoro-n-propoxy)naphthalene (4a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
2-(2-Fluoro-\textit{n}-propoxy)naphthalene $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
3-O-(3-Fluoro-n-propyl)estrone $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)