Supporting Information
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Supporting Information

A Highly Efficient Conversion of Primary or Secondary Alcohols into Their Fluorides with \( n \)-Perfluorobutanesulfonyl Fluoride-Tetrabutylammonium Triphenyldifluorosilicate

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1. Experimental Section

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<tr>
<th>Entry</th>
<th>Alcohol</th>
<th>Product</th>
<th>Reaction time (h)</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhCO(CH₂)₉OH</td>
<td>PhCO(CH₂)₉F</td>
<td>24</td>
<td>94</td>
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<tr>
<td>2</td>
<td>O</td>
<td>O</td>
<td>24</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>MeO</td>
<td>MeO</td>
<td>24</td>
<td>91</td>
</tr>
<tr>
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<td>24</td>
<td>79</td>
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<tr>
<td>5</td>
<td>O</td>
<td>O</td>
<td>24</td>
<td>86</td>
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<tr>
<td>6</td>
<td>O</td>
<td>O</td>
<td>24</td>
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</tr>
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<td>7</td>
<td>O</td>
<td>O</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>8</td>
<td>Ph-CH₂CO₂Ph</td>
<td>Ph-CH₂CO₂Ph</td>
<td>24</td>
<td>88</td>
</tr>
<tr>
<td>9</td>
<td>Ph-CH₂CO₂Ph</td>
<td>Ph-CH₂CO₂Ph</td>
<td>24</td>
<td>91</td>
</tr>
</tbody>
</table>

**General procedure for Table 2:** To a mixture of alcohol 1 (1 equiv) and TBAT (0.8 equiv), iPr₂EtN (2.5 equiv) and toluene (8 ml per mmol of alcohol) were added in turns at room temperature. The resulting mixture was stirred and then PBSF (2.2 equiv) was introduced. The stirring was continued until TLC revealed complete conversion. The reaction mixture was concentrated under reduced pressure. The residual was mixed with a little bit of silica gel, dried in ventilation, and finally purified by flash chromatography (silica gel, 300-400 mesh; eluent: from petroleum ether to petroleum ether/acetone) to give desired product, whose structure was determined by IR, NMR and HRMS.

9-Fluorononyl benzoate (3b)

Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 1.27–1.48 (m, 10 H), 1.63–1.81 (m, 4 H), 4.32 (t, J = 5.3 Hz, 2H), 4.44 (dt, J = 39.5, 5.0 Hz, 2 H), 7.34–7.58 (m, 3H), 7.65 (d, J = 6.0 Hz, 1 H), 8.05 (d, J = 6.0 Hz, 1 H); IR (NaCl): ~ν 3071, 2932, 2857, 1720, 1275, 1123, 714 cm⁻¹; HRMS (C₁₆H₂₃FO₂): [M+Na]⁺, calculated: 289.1579; measured: 289.1583.

2-Methoxy-1-(3-fluoropropoxy) benzene (3c)

Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 2.10–2.19 (m, 2 H), 3.77 (s, 3 H), 4.05 (t, J = 6.0 Hz, 2 H), 4.64 (td, J = 5.7, 47.2 Hz, 2 H), 6.81–7.58 (m, 3H); IR (NaCl): ~ν 3065, 2967, 2840, 1594, 1506, 1254, 1227, 1125, 743 cm⁻¹; HRMS (C₁₀H₅FO₂): [M+Na]⁺, calculated: 207.0797; measured: 207.0802.
4-Methoxy-1-(3-fluoropropoxy) benzene (3d)
Colorless oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 2.18~2.27 (m, 2 H), 3.87 (s, 3 H), 4.16 (t, $J = 6.2$ Hz, 2 H), 4.67 (td, $J = 5.7$, 47.1, 2 H), 6.88~6.96 (m, 4 H); IR (NaCl): $\tilde{\nu}$ 3043, 2966, 2833, 1509, 1233, 1054, 826 cm$^{-1}$.

1-Fluoro-(4-triphenylmethoxy) butane (3e)
Colorless oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.69~1.87 (m, 4 H), 3.11 (t, $J = 5.8$ Hz, 2 H), 4.43 (td, $J = 5.3$, 47.2 Hz, 2 H), 7.21~7.33 (m, 9 H), 7.44 (d, $J = 7.7$ Hz, 6 H); IR (NaCl): $\tilde{\nu}$ 3086, 3059, 2962, 2873, 1597, 1490, 1449, 1075, 1047, 764, 746, 705 cm$^{-1}$; HRMS (C$_{23}$H$_{23}$F): calculated: 357.1630; measured: 357.1638.

4-Fuoro-1,1-bis(3-methyl-2-thienyl)-1-butene (3f)
Gray oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 2.03 (s, 3 H), 2.05 (s, 3 H), 2.55 (qd, $J = 6.8$, 24.1 Hz, 2 H), 4.50 (td, $J = 6.3$, 47.2 Hz, 2 H), 6.10 (t, $J = 7.2$ Hz, 1 H), 6.77 (d, $J = 5.1$ Hz, 1 H), 6.86 (d, $J = 5.1$ Hz, 1 H), 7.07 (d, $J = 5.1$ Hz, 1 H), 7.23 (d, $J = 5.1$ Hz, 1 H); IR (NaCl): $\tilde{\nu}$ 3104, 3070, 2964, 2863, 1430, 1382, 1123, 1008, 716 cm$^{-1}$; HRMS (C$_{14}$H$_{15}$FS): calculated: 289.0496; measured: 289.0492.

$^{2S,4S}$-Methyl 1-[4,4-bis(3-methyl-2-thienyl)-3-buten-1-yl]-4-fluoropyrrolidine-2-carboxylate (3g)
Yellow oil; $^1$HNMR (600 MHz, CDCl$_3$) $\delta$ 2.00 (s, 3 H), 2.03 (s, 3 H), 2.19~2.58 (m, 6 H), 2.93 (b. s, 1 H), 3.20 (b. s, 1 H), 3.33~3.42 (m, 1 H), 3.73 (s, 3 H), 5.13 (d, $J = 59.8$ Hz, 1 H), 6.04 (t, $J = 6.6$ Hz, 1 H), 6.76 (d, $J = 3.8$ Hz, 1 H), 6.84 (d, $J = 3.8$ Hz, 1 H), 7.05 (d, $J = 3.8$ Hz, 1 H), 7.21 (d, $J = 3.8$ Hz, 1 H); $^{13}$C NMR (600 MHz, CDCl$_3$) $\delta$ 14.8, 28.7, 37.0, 37.1, 52.0, 53.6, 59.3, 59.4, 64.6, 91.0, 92.2, 122.7, 124.3, 128.7, 129.6, 131.2, 135.4, 139.5, 173.3; IR (KBr): $\tilde{\nu}$ 3104, 3060, 2952, 2843, 1748, 1733, 1435, 1200, 1174, 715 cm$^{-1}$; HRMS (C$_{20}$H$_{24}$FNO$_2$S$_2$): [M+1]$^+$ calculated: 394.1310; measured: 394.1316.

$^{2S,4S}$-Methyl 4-fluoro-1-(triphenylmethyl) pyrrolidine-2-carboxylate (3h)
White crystals; Mp: 142-148 °C; $^1$HNMR (600 MHz, CDCl$_3$) $\delta$ 0.73~0.90 (m, 1 H), 1.85 (dd, $J = 14.0$, 25.0 Hz, 1 H), 3.33 (ddd, $J = 5.8$, 14.0, 25.0 Hz, 1 H), 3.64 (dd, $J = 14.0$, 29.0 Hz, 1 H), 3.76 (s, 3 H), 3.97 (d, $J = 9.5$ Hz, 1 H), 7.18 (t, $J = 7.2$ Hz, 3 H), 7.26 (t, $J = 7.2$ Hz, 6 H), 7.59 (d, $J = 7.2$ Hz, 6 H); IR (KBr) $\tilde{\nu}$ 3063, 2954, 1743, 1448, 1205, 714 cm$^{-1}$; HRMS (C$_{20}$H$_{23}$FNO$_2$S$_2$): [M+Na]$^+$ calculated: 412.1688; measured: 412.1704.

$^{\alpha}$-Fluorobenzyl phenyl ketone (3i)
Colorless oil; $^1$HNMR (600 MHz, CDCl$_3$) $\delta$ 6.51 (d, $J = 40.5$ Hz, 1H), 7.34~7.65 (m, 8 H), 7.91~7.96 (m, 2 H); IR (NaCl) $\tilde{\nu}$ 3031, 3065, 2962, 1963, 1596, 1058, 972, 759, 699 cm$^{-1}$.

Benzyl 2-fluoro-2-phenylacetate (3j)

Colorless oil; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 5.21 (dd, $J = 42.5$, 10 Hz, 2 H), 5.82 (d, $J = 39.5$ Hz, 1 H), 7.17-7.51 (m, 10 H); IR (NaCl) $\tilde{\nu}$ 3067, 3036, 2961, 1760, 1683, 1266, 1057, 735, 696 cm$^{-1}$
2. Copies of Spectra for IR, $^1$H NMR, $^{13}$CNMR, and MS