Brønsted acid-catalyzed 1,2-fluorine migration with fluoroepoxides

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1. General Information

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. The THF was distilled over sodium. The dichloromethane and CH₃CN were distilled over CaH₂. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a 400 MHz or 300 MHz NMR spectrometer. ¹H NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.0 or to the signal of a residual protonated solvent: CDCl₃ δ 7.26. ¹³C NMR chemical shifts were determined relative to internal TMS at δ 0.0. ¹⁹F NMR chemical shifts were determined relative to CFCl₃ (external standard) at δ 0.0. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode. Melting points are reported without correction. The ee values determination was carried out using chiral high performance liquid chromatography (HPLC) with Phenomenex Lux Cellulose column or Daicel Chiralpak AD-H column on Dionex Utimate 3000.

2. Typical Procedures for the Synthesis of Sulfoximines 6¹

![Chemical Structure](image)

Under N₂ atmosphere, to a solution of compound (s-1) (500 mg, 1.53 mmol) in THF (10 mL), was added n-BuLi (1.6 M in THF, 1 mL, 1.6 mmol) slowly at −78 °C. After 45 min, MeI (0.24 mL, 3.8 mmol) was added. After one hour, the solution was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding water (20 mL), followed by extraction with ethyl ether (30 mL*3). The organic phase was washed with brine and then dried over anhydrous MgSO₄. After the solution was filtered and the solvent was evaporated under vacuum, the residue was recrystallized in EtOH to give product sulfoximine 6a (400 mg, 76 % yield).
**Sulfoximine 6a:** White solid. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.99 (d, $J = 7.8$ Hz, 2H), 7.86 (d, $J = 8.1$ Hz, 2H), 7.78–7.74 (m, 1H), 7.65–7.60 (m, 2H), 7.27–7.26 (m, 2H), 5.98 (dq, $J = 46.8$ Hz, $J = 5.9$ Hz, 1H), 2.40 (s, 3H), 1.63 (dd, $J = 22.8$ Hz, $J = 6$ Hz, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –169.4 (m, 1F). MS (ESI) $m/z$ 364.0 (M+Na$^+$). HRMS (ESI): Calcd. for C$_{15}$H$_{16}$NO$_3$FS$_2$Na: 364.0448; Found: 364.0448.

**Sulfoximine 6b:** White solid. Mp: 129–130 °C. IR (film): 2954, 2926, 2856, 1450, 1320, 1306, 1252, 1236, 1150, 1093, 1062, 770, 747, 686, 654, 618, 568, 545 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.98 (d, $J = 7.8$ Hz, 2H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.77–7.72 (m, 1H), 7.64–7.59 (m, 2H), 7.28–7.25 (m, 2H), 5.89–5.69 (m, 1H), 2.40 (s, 3H), 2.21–1.98 (m, 1H), 1.67–1.45 (m, 3H), 1.24 (s, 8H), 0.88–0.84 (m, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –175.8 (m, 1F). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 143.0, 140.6, 135.0, 132.3, 129.8, 129.5, 129.3, 126.7, 103.8 (d, $J = 224.8$ Hz), 31.5, 28.86, 28.82, 28.2 (d, $J = 18.9$ Hz), 24.5, 22.5, 21.5, 14.0. MS (ESI): $m/z$ 448.1 (M+Na$^+$). HRMS (ESI): Calcd. for C$_{21}$H$_{28}$NO$_3$FS$_2$Na: 448.1387; Found: 448.1392.

**Sulfoximine 6c:** White solid. Mp: 135-136 °C. IR (film): 2969, 1448, 1327, 1246, 1223, 1153, 1088, 1059, 815, 764, 732, 653, 623, 577, 556, 545, 508 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.03 (d, $J = 7.5$ Hz, 2H), 7.88 (d, $J = 8.1$ Hz, 2H), 7.79–7.74 (m, 1H), 7.66–7.61 (m, 2H), 7.29–7.17 (m, 7H), 5.99–5.79 (m, 1H), 3.57–3.39 (m, 1H), 2.96–2.82 (m, 1H), 2.41 (s, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –176.3 (m, 1F). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 143.2, 140.5, 135.2, 132.4, 129.8, 129.7, 129.5, 129.4, 128.9, 127.8, 126.7, 103.5 (d, $J = 229.7$ Hz), 34.5 (d, $J = 19$ Hz), 21.6. MS (ESI): $m/z$ 440.0 (M+Na$^+$). HRMS (ESI): Calcd. for C$_{21}$H$_{20}$NO$_3$FS$_2$Na: 440.0761; Found: 440.0759.
3. Typical Procedures for Synthesis of Fluoroepoxides 4

Under N\textsubscript{2} atmosphere, to a solution of sulfoximine 6 (R\textsubscript{3} = Me) (512 mg, 1.5 mmol, 1.5 equiv.) in 10 mL THF, was added n-BuLi (2.5 M in THF, 0.6 mL, 1.5 mmol, 1.5 equiv.) slowly at \(-78\) °C. After 30 min, a solution of (4-fluorophenyl)(phenyl)methanone 7 (R\textsubscript{1} = 4-F, R\textsubscript{2} = Ph) (200 mg, 1.0 mmol, 1.0 equiv.) in THF (1 mL) was added into the reaction system. After 45 min, the reaction system was allowed to warm to room temperature and stirred for another 5 h. The reaction was quenched by adding water (20 mL), followed by extraction with ethyl ether (30 mL*3). The organic phase was washed with brine and then dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to TLC preparative plate (pre-treated with triethylamine in PE, 2% v/v) by using PE : EA = 40 : 1 (PE: petroleum ether; EA: ethyl acetate) as eluent to get fluoroepoxides 4b (195 mg, 79% yield).

\textbf{(NOTE): The relative configuration of the isolated fluoroepoxides 4o-s were determined by comparing the 1\textsuperscript{H} NMR signals of the methyl groups with those of the known fluoroepoxides.\textsuperscript{2}}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fluoroepoxide.png}
\caption{Fluoroepoxide 4b}
\end{figure}

\textbf{2-fluoro-2-methyl-3,3-diphenyloxirane (4a):} 72% yield. Colorless oil. IR (film): 3063, 3032, 2939, 1603, 1496, 1449, 1417, 1377, 1196, 1178, 1109, 1078, 888, 670 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \(\delta\) 7.48–7.33 (m, 10H), 1.64 (d, \(J = 16.2\) Hz, 3H). \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz): \(\delta\) –121.8 (q, \(J = 15.5\) Hz, 1F). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta\) 137.0, 136.4 (d, \(J = 3.2\) Hz), 128.5, 128.2, 128.1, 127.9, 127.1, 127.0, 99.5 (d, \(J = 264.6\) Hz), 70.4 (d, \(J = 18.9\) Hz), 17.1 (d, \(J = 32.6\) Hz). MS (EI, \textit{m/z}, %): 228 (M\textsuperscript{+}, 0.12), 166 ([M-MeCOF\textsuperscript{+}], 70.53), 165 (100). HRMS (EI): Calcd. for C\textsubscript{13}H\textsubscript{10} (M-MeCOF): 166.0783; Found: 166.0780.
**(cis)**&**(trans)**-2-fluoro-3-(4-fluorophenyl)-2-methyl-3-phenyloxirane (4b): 79% yield. Colorless oil. IR (film): 3064, 1608, 1510, 1225, 1176, 1159, 907, 892, 835, 698, 575 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.44–7.41 (m, 2H), 7.37–7.32 (m, 5H), 7.07–7.00 (m, 2H), 1.66–1.61 (m, 3H). \(^1^9\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –113.4 (m), –113.8 (m), –121.2 (q, \(J = 16.5\) Hz), –121.8 (q, \(J = 15.3\) Hz). \(^1^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 162.6 (d, \(J = 247.4\) Hz), 162.5 (d, \(J = 247.3\) Hz), 136.8 (d, \(J = 3.3\) Hz), 136.2 (d, \(J = 4.7\) Hz), 132.9 (t, \(J = 3\) Hz), 132.3 (t, \(J = 4\) Hz), 129.9 (dd, \(J_1 = 1.6\) Hz, \(J_2 = 8.3\) Hz), 129.0 (dd, \(J_1 = 1.5\) Hz, \(J_2 = 8.4\) Hz), 128.6, 128.33, 128.31, 128.29, 127.9, 127.0 (d, \(J = 1.5\) Hz), 115.5 (d, \(J = 38.2\) Hz), 115.2 (d, \(J = 39\) Hz), 99.5 (d, \(J = 267.4\) Hz), 99.4 (d, \(J = 267.3\) Hz), 69.86 (d, \(J = 20.0\) Hz), 69.85 (d, \(J = 20.0\) Hz), 17.1 (d, \(J = 32.9\) Hz), 17.0 (d, \(J = 32.7\) Hz). MS (EI, \(m/z\), %): 184 ([M-MeCOF]\(^+\), 55.22). HRMS (EI): Calcd. for C\(_{13}\)H\(_9\)F (M-MeCOF): 184.0688; Found: 184.0686.

**(cis)**&**(trans)**-2-((4-chlorophenyl)-3-fluoro-3-methyl-2-phenyloxirane (4c): 80% yield. Colorless oil. IR (film): 3063, 1597, 1496, 1463, 1376, 1172, 1111, 1011, 922, 908, 827, 774, 727, 718, 695, 609 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.44–7.30 (m, 9H), 1.66–1.61 (m, 3H). \(^1^9\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –120.9 (q, \(J = 15.4\) Hz), –121.9 (q, \(J = 16.4\) Hz). \(^1^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 137.4 (d, \(J = 3.0\) Hz), 135.8 (d, \(J = 3.9\) Hz), 135.5 (d, \(J = 3.0\) Hz), 134.9 (d, \(J = 3.8\) Hz), 134.2, 129.4 (d, \(J = 1.3\) Hz), 128.8, 128.63, 128.62, 128.5 (d, \(J = 1.6\) Hz), 128.41, 128.40, 128.3, 127.85, 127.84, 127.0 (d, \(J = 1.6\) Hz), 99.4 (d, \(J = 267.1\) Hz), 99.3 (d, \(J = 267.1\) Hz), 69.80 (d, \(J = 19.7\) Hz), 69.78 (d, \(J = 20.0\) Hz), 17.1 (d, \(J = 32.3\) Hz), 16.9 (d, \(J = 32.7\) Hz). MS (EI, \(m/z\), %): 262 (M\(^+\), 0.07), 200 ([M-MeCOF]\(^+\), 35.30). HRMS (EI): Calcd. for C\(_{13}\)H\(_{12}\)OFCl: 262.0561; Found: 262.0564.
(cis)&(trans)-2-(4-bromophenyl)-3-fluoro-2-methyl-2-phenyloxirane (4d): 81% yield. Colorless oil. IR (film): 3062, 3031, 2986, 2939, 1592, 1488, 1395, 1195, 1173, 1112, 1071, 1033, 918, 891, 820, 762, 698, 610 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.31–7.24 (m, 9H), 1.66–1.61 (m, 3H).

\(^1\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –121.3 (m), –122.3 (m). \(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 136.4 (d, \(J = 2.8\) Hz), 136.1 (d, \(J = 2.8\) Hz), 135.8 (d, \(J = 4.2\) Hz), 135.4 (d, \(J = 4.2\) Hz), 131.7, 131.3, 129.6, 128.76, 128.6, 128.4, 128.3, 127.8, 127.8, 127.04, 127.02, 122.44, 122.37, 99.3 (d, \(J = 265.8\) Hz), 99.2 (d, \(J = 266.0\) Hz), 99.84 (d, \(J = 19.4\) Hz), 99.81 (d, \(J = 20.0\) Hz), 17.1 (d, \(J = 33.1\) Hz), 16.9 (d, \(J = 32.1\) Hz). MS (EI, \(m/z\), %): 306 (M\(^{+}\), 0.06), 244 ([M-MeCOF]\(^{+}\), 24.46). HRMS (EI): Calcd. for C\(_{15}\)H\(_{12}\)OFBr: 306.0056; Found: 306.0053.

(cis)&(trans)-2-fluoro-2-methyl-3-phenyl-3-(4-(trifluoromethyl)phenyl)oxirane (4e): 76% yield. Colorless oil. IR (film): 3065, 3033, 2942, 1621, 1497, 1448, 1408, 1378, 1327, 1170, 1128, 1105, 1068, 921, 895, 837, 698 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.62–7.58 (m, 3H), 7.52–7.45 (m, 2H), 7.37–7.31 (m, 4H), 1.66–1.56 (m, 3H). \(^1\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –62.28 (s), –62.31 (s), –120.0 (q, \(J = 15.7\) Hz), –121.5 (q, \(J = 16.3\) Hz). \(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 141.1, 140.5 (d, \(J = 4.2\) Hz), 136.1 (d, \(J = 3.0\) Hz), 135.6 (d, \(J = 4.9\) Hz), 130.5 (q, \(J = 33.0\) Hz), 130.4 (q, \(J = 32.5\) Hz), 128.8, 128.63, 128.60, 128.5, 128.4, 128.0, 127.5, 127.1, 125.6 (q, \(J = 38.3\) Hz), 125.2 (q, \(J = 39.7\) Hz), 124.2 (q, \(J = 270.3\) Hz), 124.0 (q, \(J = 270.6\) Hz), 99.4 (d, \(J = 265.5\) Hz), 99.2 (d, \(J = 265.9\) Hz), 99.87 (d, \(J = 19.4\) Hz), 69.86 (d, \(J = 19.4\) Hz), 17.1 (d, \(J = 32.1\) Hz), 16.8 (d, \(J = 33\) Hz). MS (EI, \(m/z\), %): 234 ([M-MeCOF]\(^{+}\), 24.46). HRMS (EI): Calcd. for C\(_{14}\)H\(_{9}\)F\(_3\) (M-MeCOF): 234.0656; Found: 234.0654.
(cis)&(trans)-2-(biphenyl-4-yl)-3-fluoro-3-methyl-2-phenyloxirane (4f): 70% yield. Colorless oil. IR (film): 3060, 3030, 2992, 1598, 1496, 1488, 1462, 1416, 1378, 1172, 1106, 1076, 1007, 934, 912, 891, 833, 762, 724, 609 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.60–7.34 (m, 14H), 1.72–1.64 (m, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ -121.3 (q, $J = 16.4$ Hz), -122.1 (q, $J = 15.5$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 141.1, 140.7, 140.4, 136.9 (d, $J = 3.3$ Hz), 136.4 (d, $J = 4.8$ Hz), 136.0 (d, $J = 2.9$ Hz), 135.3 (d, $J = 4.5$ Hz), 128.9, 128.8, 128.5, 128.3, 128.24, 128.22, 127.9, 127.6, 127.5, 127.4, 127.3, 127.20, 127.17, 127.1, 127.0, 99.6 (d, $J = 264.3$ Hz), 99.5 (d, $J = 265.1$ Hz), 70.31 (d, $J = 19.4$ Hz), 70.30 (d, $J = 19.4$ Hz), 17.2 (d, $J = 33.0$ Hz), 17.1 (d, $J = 32.3$ Hz). MS (EI, $m/z$, %): 304 (M$^+$, 0.63), 242 ([M-MeCOF]$^+$, 100.00). HRMS (EI): Calcd. for C$_{19}$H$_{14}$ (M-MeCOF): 242.1096; Found: 242.1100.

(cis)&(trans)-2-(3-chlorophenyl)-3-fluoro-3-methyl-2-phenyloxirane (4g): 81% yield. Colorless oil. IR (film): 3064, 3031, 2938, 2856, 1598, 1572, 1497, 1474, 1448, 1415, 1377, 1180, 1112, 1079, 931, 897, 879, 789, 734, 700 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.46–7.26 (m, 9H), 1.66–1.61 (m, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ -120.4 (q, $J = 16.0$ Hz), -121.4 (q, $J = 16.1$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 139.0 (d, $J = 3.2$ Hz), 138.4 (d, $J = 4.6$ Hz), 136.3 (d, $J = 2.8$ Hz), 135.7 (d, $J = 4.0$ Hz), 134.6, 134.2, 129.9, 129.5, 128.7, 128.5, 128.41, 128.38, 128.1, 127.9, 127.22, 127.20, 127.05, 127.04, 126.1, 125.2, 99.3 (d, $J = 266.0$ Hz), 99.2 (d, $J = 265.9$ Hz), 69.72 (d, $J = 19.3$ Hz), 69.68 (d, $J = 20.6$ Hz), 17.1 (d, $J = 32.8$ Hz), 17.0 (d, $J = 32.5$ Hz). MS (EI, $m/z$, %): 262 (M$^+$, 0.1), 200 ([M-MeCOF]$^+$, 32.51). HRMS (EI): Calcd. for C$_{13}$H$_9$Cl (M-MeCOF): 200.0393; Found: 200.0391.
(cis)&(trans)-2-(2-chlorophenyl)-3-fluoro-3-methyl-2-phenyloxirane (4h): 76% yield. Colorless oil. IR (film): 3063, 3030, 2990, 2930, 1596, 1572, 1497, 1478, 1447, 1438, 1416, 1377, 1182, 1062, 987, 921, 909, 893, 697, 670, 612 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.57–7.27 (m, 9H), 1.74–1.67 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 135.9, 135.7, 134.7, 133.1, 130.5, 129.83, 129.78, 129.67, 128.4, 128.3, 128.0, 127.1, 126.9, 99.30 (d, J = 266.6 Hz), 99.29 (d, J = 266.6 Hz), 68.91 (d, J = 19.4 Hz), 68.90 (d, J = 19.4 Hz), 15.59 (d, J = 31.7 Hz), 15.58 (d, J = 31.7 Hz). MS (EI, m/z %): 200 ([M-MeCOF]⁺, 22.14). HRMS (EI): Calcd. for C₁₃H₉Cl (M-MeCOF): 200.0393; Found: 200.0391.

2-fluoro-3,3-bis(4-fluorophenyl)-2-methylloxirane (4i): 76% yield. Colorless oil. IR (film): 3078, 2942, 1607, 1510, 1234, 1177, 1159, 933, 917, 896, 837, 562 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.41–7.27 (m, 8H), 1.63 (d, J = 16.0 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 162.6 (d, J = 245.1 Hz), 162.5 (d, J = 246.7 Hz), 132.7, 132.0, 129.8 (d, J = 8.3 Hz), 128.9 (d, J = 7.8 Hz), 115.6 (d, J = 20.9 Hz), 115.2 (d, J = 21.4 Hz), 99.3 (d, J = 265.2 Hz), 89.3 (d, J = 19.9 Hz), 17.0 (d, J = 32.8 Hz). MS (EI, m/z %): 264 (M⁺, 0.33), 202 ([M-MeCOF]⁺, 64.83). HRMS (EI): Calcd. for C₁₅H₁₁OF₃: 264.0762; Found: 264.0763.

2,2-bis(4-chlorophenyl)-3-fluoro-3-methylloxirane (4j): 71% yield. Colorless oil. IR (film): 2940, 1598, 1492, 1418, 1402, 1376, 1196, 1182, 1092, 1016, 934, 917, 895, 826, 615 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.37–7.27 (m, 8H), 1.63 (d, J = 16.2 Hz, 3H). ¹³C NMR (CDCl₃, 282 MHz): δ −121.8 (q, J = 15.6 Hz).
\[ m/z, \%): 234 ([M-MeCOF]^+, 38.10). \] HRMS (EI): Calcd. for C\(_{13}\)H\(_8\)Cl\(_2\) (M-MeCOF): 234.0003; Found: 234.0001.

**2,2-bis(4-bromophenyl)-3-fluoro-3-methyloxirane (4k):** 71% yield. Colorless oil. IR (film): 2938, 1593, 1489, 1418, 1396, 1195, 1099, 1072, 912, 916, 895, 821, 613, 550 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta 7.52-7.47 \) (m, 4H), \( 7.30-7.21 \) (m, 4H), 1.62 (d, \( J = 16.1 \) Hz, 3H). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \( \delta -121.3 \) (q, \( J = 16.5 \) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta 135.4 \) (d, \( J = 3.1 \) Hz), 134.9 (d, \( J = 3.8 \) Hz), 131.9, 131.5, 129.7, 128.8, 122.8, 122.7, 99.1 (d, \( J = 266.2 \) Hz), 69.3 (d, \( J = 19.7 \) Hz), 17.0 (d, \( J = 32.1 \) Hz). MS (EI, \( m/z, \%): 322 ([M-MeCOF]^+, 48). HRMS (EI): Calcd. for C\(_{13}\)H\(_{18}\)Br\(_2\) (M-MeCOF): 321.8993; Found: 321.8989.

\[ \text{(cis)} \&(\text{trans)}-2-(4-chlorophenyl)-3-fluoro-3-methyl-2-p-tolyloxirane (4l): 77% yield. Colorless oil. IR (film): 3029, 2924, 2867, 1598, 1514, 1491, 1196, 1173, 1093, 1012, 934, 917, 893, 814 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta 7.39-7.14 \) (m, 8H), 2.34–2.33 (m, 3H), 1.66–1.59 (m, 3H). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \( \delta -121.3 \) (q, \( J = 16.2 \) Hz), -122.3 (q, \( J = 16.1 \) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta 138.3, 135.8, 135.2, 134.1, 133.5, 132.9, 129.34, 129.27, 129.2, 129.0, 128.7, 128.4, 128.3, 127.8, 127.0, 99.5 \) (d, \( J = 264.6 \) Hz), 99.3 (d, \( J = 265.2 \) Hz), 69.8 (d, \( J = 23.3 \) Hz), 69.7 (d, \( J = 22.3 \) Hz), 21.2, 17.1 (d, \( J = 33.2 \) Hz), 17.0 (d, \( J = 33.0 \) Hz). MS (EI, \( m/z, \%): 276 (M^+, 0.12), 214 ([M-MeCOF]^+, 43.26). HRMS (EI): Calcd. for C\(_{14}\)H\(_{11}\)Cl (M-MeCOF): 214.0549; Found: 214.0550.
(cis)&(trans)-2-(4-chlorophenyl)-3-fluoro-3-heptyl-2-phenyloxirane (4m): 64% yield. Colorless oil. IR (film): 2957, 2929, 2857, 1492, 1448, 1195, 1092, 1016, 976, 932, 824, 760, 699, 650 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.45–7.32 (m, 9H), 1.83–1.73 (m, 2H), 1.63–1.54 (m, 2H), 1.26–1.22 (m, 8H), 0.89–0.84 (M, 3H). ¹⁹F NMR (CDCl₃, 282 MHz): δ –128.7 (t, J = 19 Hz), –129.8 (t, J = 19 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 136.4 (d, J = 2.9 Hz), 136.1 (d, J = 3.8 Hz), 135.5 (d, J = 3.8 Hz), 135.1 (d, J = 4.7 Hz), 134.1, 134.0, 129.4 (d, J = 1.4 Hz), 128.6, 128.5, 128.4, 128.33, 128.31, 128.29, 128.23, 127.9, 126.8 (d, J = 1.4 Hz), 101.3 (d, J = 271 Hz), 101.2 (d, J = 271.9 Hz), 69.87 (d, J = 19.8 Hz), 69.86 (d, J = 19.8 Hz), 31.6, 30.3, 30.1, 30.0, 29.8, 29.1, 28.92, 28.90, 23.32, 23.27, 22.6, 14.0. MS (EI, m/z, %): 346 (M⁺, 0.14), 200 ([M-C₇H₁₅COF]⁺, 100). HRMS (EI): Calcd. for C₂₁H₂₄OFCl: 346.1500; Found: 346.1499.

(cis)&(trans)-2-benzyl-3-(4-bromophenyl)-2-fluoro-3-phenyloxirane (4n): 60% yield. Colorless oil. IR (film): 3088, 3063, 3031, 2928, 1604, 1591, 1496, 1456, 1448, 1432, 1394, 1220, 1188, 1124, 1072, 1012, 941, 906, 887, 820, 759, 726, 699, 593 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.52–7.44 (m, 2H), 7.37–7.25 (m, 10H), 7.16–7.14 (m, 2H), 3.23–3.01 (m, 2H). ¹⁹F NMR (CDCl₃, 282 MHz): δ –126.4 (t, J = 20.2 Hz), –127.5 (t, J = 19.9 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 136.1 (d, J = 3.1 Hz), 135.8 (d, J = 2.8 Hz), 135.7 (d, J = 3.7 Hz), 135.3 (d, J = 3.4 Hz), 133.8, 133.7, 131.7, 131.4, 129.8, 129.6, 129.5, 128.8, 128.6, 128.49, 128.4, 127.9, 127.23, 127.20, 127.1, 122.54, 122.50, 100.8 (d, J = 270.6 Hz), 100.7 (d, J = 271.2 Hz), 70.31 (d, J = 19.5 Hz), 70.30 (d, J = 19.5 Hz), 36.7 (d, J = 29.5 Hz), 36.6 (d, J = 28.9 Hz). MS (EI, m/z, %): 244 ([M-BnCOF]⁺, 26.61). HRMS (EI): Calcd. for C₁₅H₉Br (M-BnCOF): 243.9888; Found: 243.9886.
(cis)-2-fluoro-2,3-dimethyl-3-(naphthalen-2-yl)oxirane (cis-4o): The less polar component, 33% yield. Colorless oil. IR (film): 3508, 3010, 2938, 1603, 1507, 1467, 1376, 1186, 1110, 967, 887, 798, 749, 479 cm\(^{-1}\).\(^{1}\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.86–7.83 (m, 3H), 7.76 (s, 1H), 7.52–7.48 (m, 2H), 7.43–7.40 (m, 1H), 1.87 (s, 3 H), 1.46 (d, \(J = 16.2\) Hz, 3H). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –125.0 (q, \(J = 16.1\) Hz, 1F). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 135.7, 133.0, 132.8, 128.3, 128.0, 127.7, 126.5, 126.3, 124.7 (d, \(J = 1.4\) Hz), 123.4, 100.0 (d, \(J = 264.1\) Hz), 64.4 (d, \(J = 20.2\) Hz), 19.1, 16.0 (d, \(J = 33.2\) Hz). MS (EI, \(m/z\), %): 216 (M\(^+\), 8.47). HRMS (EI): Calcd. for C\(_{14}\)H\(_{13}\)OF: 216.0950; Found: 216.0947.

(trans)-2-fluoro-2,3-dimethyl-3-(naphthalen-2-yl)oxirane (trans-4o): The more polar component, 37% yield. Colorless oil. The isolated compound is not stable enough for further characterization.

(cis)-2-(4-chlorophenyl)-3-fluoro-2,3-dimethyloxirane (cis-4p): The less polar component, 21% yield. Colorless oil. IR (film): 3011, 2974, 2938, 1908, 1601, 1494, 1475, 1377, 1286, 1189, 1115, 1093, 1074, 1015, 961, 895, 855, 831, 570, 531 cm\(^{-1}\).\(^{1}\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.34 (d, \(J = 8.7\) Hz, 2H), 7.23 (d, \(J = 8.7\) Hz, 2H), 1.76 (s, 3H), 1.42 (d, \(J = 16.2\) Hz, 3H). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –124.2 (q, \(J = 16.2\) Hz, 1F). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 136.0 (d, \(J = 2.8\) Hz), 133.8, 128.3, 127.9, 98.8 (d, \(J = 259.1\) Hz), 66.1 (d, \(J = 20.1\) Hz), 19.8 (d, \(J = 2.4\) Hz), 16.3 (d, \(J = 34.2\) Hz). MS (EI, \(m/z\), %): 200 (M\(^+\), 2.86). HRMS (EI): Calcd. for C\(_{10}\)H\(_{10}\)OFCl: 200.0404; Found: 200.0403.

(trans)-2-(4-chlorophenyl)-3-fluoro-2,3-dimethyloxirane (trans-4p): The more polar component, 38% yield. Colorless oil. IR (film): 2997, 2939, 1600, 1495, 1386, 1187, 1116, 1092, 1046, 963, 893, 847, 832, 733, 579, 547 cm\(^{-1}\).\(^{1}\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.33 (s, 4H), 1.81 (d, \(J = 16.2\) Hz, 3H), 1.64 (s, 3H). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –124.6 (q, \(J = 16.2\) Hz, 1F). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 136.8, 133.8, 128.7, 127.1 (d, \(J = 1.7\) Hz), 99.6 (d, \(J = 264.4\) Hz), 66.6 (d, \(J = 20\) Hz), 18.9 (d, \(J = 0.9\) Hz), 15.9 (d, \(J = 34.1\) Hz). MS (EI, \(m/z\), %): 200 (M\(^+\), 2.79). HRMS (EI): Calcd. for C\(_{10}\)H\(_{10}\)OFCl: 200.0404; Found: 200.0402.
\[(\text{cis})-2-(4\text{-bromophenyl})-3\text{-fluoro}-2,3\text{-dimethyloxirane} \ (\text{cis}-4q)\]: The less polar component, 16% yield. Colorless oil. IR (film): 3010, 2932, 2855, 1594, 1490, 1396, 1189, 1115, 1078, 1011, 960, 895, 853, 825, 530 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.49 (d, \(J = 8.7\) Hz, 2H), 7.18 (d, \(J = 8.4\) Hz, 2H), 1.75 (d, \(J = 0.9\) Hz, 3H), 1.42 (d, \(J = 16.2\) Hz, 3H). \(^19\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –122.5 (q, \(J = 16.2\) Hz, 1F). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 137.3 (d, \(J = 2.8\) Hz), 131.6, 127.5 (d, \(J = 1.4\) Hz), 121.9, 99.5 (d, \(J = 264.1\) Hz), 66.6 (d, \(J = 19.3\) Hz), 18.8 (d, \(J = 1.3\) Hz), 15.9 (d, \(J = 33.4\) Hz). MS (EI, \(m/\zeta\), %): 244 ([\(^{78}\)Br]M\(^+\), 2.32), 246 ([\(^{80}\)Br]M\(^+\), 2.04). HRMS (EI): Calcd. for \(\text{C}_{10}\text{H}_{10}\text{OFBr}\): 243.9899; Found: 243.9902.

\[(\text{trans})-2-(4\text{-bromophenyl})-3\text{-fluoro}-2,3\text{-dimethyloxirane} \ (\text{trans}-4q)\]: The more polar component, 30% yield. Colorless oil. IR (film): 2996, 2938, 1593, 1490, 1386, 1186, 1118, 1098, 1011, 962, 894, 846, 827, 721, 593, 570, 547 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.48 (d, \(J = 8.4\) Hz, 2H), 7.27 (d, \(J = 8.4\) Hz, 2H), 1.81 (d, \(J = 16.5\) Hz, 3H), 1.63 (d, \(J = 1.8\) Hz, 3H). \(^19\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –125.2 (q, \(J = 16.8\) Hz, 1F). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 136.6 (d, \(J = 3.0\) Hz), 131.3, 128.3, 122.0, 98.7 (d, \(J = 259.9\) Hz), 66.2, 19.8 (d, \(J = 2.4\) Hz), 16.3 (d, \(J = 34.7\) Hz). MS (EI, \(m/\zeta\), %): 246 ([\(^{80}\)Br]M\(^+\), 2.17), 244 ([\(^{78}\)Br]M\(^+\), 3.61). HRMS (EI): Calcd. for \(\text{C}_{10}\text{H}_{10}\text{OFBr}\): 243.9899; Found: 243.9904.

\[(\text{cis})-2\text{-fluoro}-3\text{-}(4\text{-iodophenyl})-2,3\text{-dimethyloxirane} \ (\text{cis}-4r)\]: The less polar component, 30% yield. Colorless oil. IR (film): 3009, 2973, 2937, 1908, 1652, 1590, 1488, 1389, 1189, 1114, 1076, 1040, 1007, 960, 894, 851, 821, 529 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.69 (d, \(J = 7.5\) Hz, 2H), 7.04 (d, \(J = 7.2\) Hz, 2H), 1.75 (s, 3H), 1.42 (d, \(J = 16.2\) Hz, 3H). \(^19\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –125.0 (q, \(J = 16.1\) Hz, 1F). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 138.0, 137.6, 127.7, 99.5 (d, \(J = 265.1\) Hz), 93.5, 66.7 (d, \(J = 19.2\) Hz), 18.8 (d, \(J = 1.9\) Hz), 15.9 (d, \(J = 33.3\) Hz). MS (EI, \(m/\zeta\), %): 292 (M\(^+\), 5.93). HRMS (EI): Calcd. for \(\text{C}_{10}\text{H}_{10}\text{OFI}\): 291.9760; Found: 291.9764.
(trans)-2-fluoro-3-(4-iodophenyl)-2,3-dimethyloxirane (trans-4r): The more polar component, 38% yield. Colorless oil. The isolated compound is not stable enough for further characterization.

(cis)-2-(3,4-dichlorophenyl)-3-fluoro-2,3-dimethyloxirane (cis-4s): The less polar component, 24% yield. Colorless oil. IR (film): 3010, 2938, 1558, 1472, 1388, 1190, 1114, 1082, 1031, 964, 895, 835, 771 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.46–7.39 (m, 2H), 7.16–7.13 (m, 1H), 1.75 (s, 3H), 1.44 (d, $J = 15.9$ Hz, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ −124.7 (q, $J = 15.2$ Hz, 1F). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 138.5 (d, $J = 2.7$ Hz), 132.9, 132.2, 130.6, 127.9 (d, $J = 1.0$ Hz), 125.1, 99.3 (d, $J = 265.5$ Hz), 65.9 (d, $J = 19.7$ Hz), 18.7 (d, $J = 1.6$ Hz), 15.8 (d, $J = 32.6$ Hz). MS (EI, $m/z$, %): 234 (M$^+$, 2.57). HRMS (EI): Calcd. for C$_{10}$H$_9$OFCl$_2$: 234.0014; Found: 234.0015.

(trans)-2-(3,4-dichlorophenyl)-3-fluoro-2,3-dimethyloxirane (trans-4s): The more polar component, 29% yield. Colorless oil. IR (film): 3074, 2998, 2940, 1560, 1473, 1388, 1286, 1187, 1121, 1107, 1031, 967, 892, 878, 773, 673, 617 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.50–7.49 (m, 1H), 7.44–7.42 (m, 1H), 7.25–7.22 (m, 1H), 1.82 (d, $J = 16.5$ Hz, 3H), 1.64–1.63 (m, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ −125.3 (q, $J = 15.9$ Hz, 1F). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 137.8 (d, $J = 3.8$ Hz), 132.4, 132.1, 130.1, 128.7, 125.9, 98.7 (d, $J = 260.6$ Hz), 65.5 (d, $J = 20.4$ Hz), 19.6 (d, $J = 2.4$ Hz), 16.3 (d, $J = 33.4$ Hz). MS (EI, $m/z$, %): 234 (M$^+$, 3.78). HRMS (EI): Calcd. for C$_{10}$H$_9$OFCl$_2$: 234.0014; Found: 234.0020.
4. Initial Optimization Studies Using *Crude* Fluoroepoxide 4o as Model Substrate

![Chemical Structure](image)

Summary of results:

From data of the table we found that: 1) The 1,2-fluorine migration reaction did not occur in the presence of different kinds of additives (entries 1-3, 5-11). 2) An efficient 1,2-fluorine migration reaction could be obtained by adding a large amount of external fluorination reagents (entries 4, 12-16).

*Note: Possible impurities in crude fluoroepoxide 4o*

<table>
<thead>
<tr>
<th>entry</th>
<th>additives (mol%)</th>
<th>solvent (3 mL)</th>
<th>temp. (°C)</th>
<th>time (h)</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^a)</td>
<td>Null (0)</td>
<td>DCM</td>
<td>60</td>
<td>10</td>
<td>N.R.</td>
</tr>
<tr>
<td>2(^a)</td>
<td>AgF (20)</td>
<td>dioxane</td>
<td>60</td>
<td>40</td>
<td>N.R.</td>
</tr>
<tr>
<td>3(^a)</td>
<td>FeF(_3) (20)</td>
<td>dioxane</td>
<td>60</td>
<td>24</td>
<td>N.R.</td>
</tr>
<tr>
<td>4(^a)</td>
<td>AgSbF(_6) (20)</td>
<td>dioxane</td>
<td>60</td>
<td>24</td>
<td>mess</td>
</tr>
<tr>
<td>5(^a)</td>
<td>MgSO(_4) (60)</td>
<td>dioxane</td>
<td>60</td>
<td>24</td>
<td>N.R.</td>
</tr>
<tr>
<td>6(^a)</td>
<td>Al(_2)O(_3) (50)</td>
<td>DCM</td>
<td>60</td>
<td>16</td>
<td>N.R.</td>
</tr>
<tr>
<td>7(^a)</td>
<td>Ti(O-iPr)(_4) (20)</td>
<td>DCM</td>
<td>60</td>
<td>8</td>
<td>N.R.</td>
</tr>
<tr>
<td>8(^a)</td>
<td>P(n-Bu)(_4) (20)</td>
<td>t-BuOH</td>
<td>80</td>
<td>22</td>
<td>N.R.</td>
</tr>
<tr>
<td>9(^a)</td>
<td>NEt(_3) (20)</td>
<td>t-BuOH</td>
<td>80</td>
<td>22</td>
<td>N.R.</td>
</tr>
<tr>
<td>10(^a)</td>
<td>NEt(_3) (100)</td>
<td>dioxane</td>
<td>60</td>
<td>24</td>
<td>N.R.</td>
</tr>
<tr>
<td>11(^a)</td>
<td>CH(_3)COOH (100)</td>
<td>DCM</td>
<td>60</td>
<td>5</td>
<td>N.R.</td>
</tr>
<tr>
<td>12(^a)</td>
<td>H(_2)O (20)</td>
<td>neat</td>
<td>50</td>
<td>6</td>
<td>21(^b)</td>
</tr>
<tr>
<td>13(^c)</td>
<td>TiF(_4) (10)</td>
<td>THF</td>
<td>60</td>
<td>48</td>
<td>33</td>
</tr>
<tr>
<td>14(^c)</td>
<td>TiF(_4) (20)</td>
<td>THF</td>
<td>60</td>
<td>18</td>
<td>67</td>
</tr>
<tr>
<td>15(^c)</td>
<td>TiF(_4) (30)</td>
<td>THF</td>
<td>60</td>
<td>18</td>
<td>77</td>
</tr>
<tr>
<td>16(^c)</td>
<td>TiF(_4) (40)</td>
<td>THF</td>
<td>60</td>
<td>24</td>
<td>90</td>
</tr>
</tbody>
</table>

\(^a\)General conditions: Crude fluoroepoxides (0.2 mmol) were dissolved in solvent (3 mL) and stirred with additives in sealed tube. The yield was detected by \(^{19}\)F-NMR using PhCF\(_3\) as internal standard. N.R. = No Reaction.  
\(^b\)The fluoroepoxides were completely consumed. \(^c\)The data were from our previous work.

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 ketone  
fluorosulfoximines  
sulfamidine

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These possible impurities can influence the 1,2-fluorine migration reaction in two ways: 1) forming complexes with the acid catalyst, thus inhibiting the to activation of fluoroepoxides; 2) competing with fluoride to capture the reactive intermediate.

5. Typical Procedures for 1,2-Fluorine Migration Reactions

**Method A:** Under N₂ atmosphere, the fluoroepoxide 4b (74 mg, 0.3 mmol) were dissolved in dichloromethane (3 mL) and stirred with p-TsOH (1.0 mg, 2 mol%) in sealed tube at room temperature. The reaction progress was detected by ¹⁹F-NMR. When the reaction was finished (generally, the color of the reaction system turned to be light yellow from colorless), after removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 50 : 1 as eluent to obtain α-fluoroketone 5b (65 mg, 88% yield).

**Method B:** Under N₂ atmosphere, the fluoroepoxide 4b (100 mg, 0.4 mmol) were dissolved in dichloromethane (3 mL) and stirred with Nafion-212 (1.1 mg, 0.001 mmol H⁺, 0.25 mol%) in sealed tube at room temperature. The reaction progress was detected by ¹⁹F-NMR. When the reaction was finished (generally, the color of the reaction system turned to be light yellow from colorless), after filtering and removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 50 : 1 as eluent to obtain 1,2-F migration product 5b (88 mg, 88% yield).

Fluoro-1,1-diphenylpropan-2-one (5a): Colorless oil. IR (film): 3427, 3060, 3008, 2920, 1724, 1494, 1448, 1414, 1353, 1219, 1279, 1016, 894, 761, 703, 593 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.37 (s, 10H), 2.42 (d, J = 6 Hz, 3H). ¹⁹F NMR (CDCl₃, 282 MHz): δ −142.9 (q, J = 6 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz): δ 206.5 (d, J = 31.8 Hz), 138.2 (d, J = 23.1 Hz), 128.8 (d, J = 1.8 Hz), 128.4, 126.7 (d, J = 6.5
Hz), 102.2 (d, J = 184.5 Hz), 26.7. MS (EI, m/z, %): 228 (M⁺, 0.33), 185 ([M-MeCO]⁺, 100.00). HRMS (EI): Calcd. for C₁₅H₁₃OF: 228.0950; Found: 228.0951.

1-fluoro-1-(4-fluorophenyl)-1-phenylpropan-2-one (5b): IR (film): 3064, 2926, 2854, 1727, 1603, 1508, 1356, 1236, 1178, 1163, 1023, 896, 832, 812, 755, 699, 592 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.36–7.33 (m, 7H), 7.03 (t, J = 8.6 Hz, 2H), 2.40 (d, J = 5.7 Hz, 3H). ¹⁹F NMR (CDCl₃, 282 MHz): δ -112.5 (m, 1F), -141.7 (m, 1F). ¹³C NMR (CDCl₃, 100 MHz): δ 206.4 (d, J = 32.7 Hz), 163.0 (dd, J = 246.8 Hz, J = 2.1 Hz), 137.9 (d, J = 21.7 Hz), 134.2 (dd, J = 22.7 Hz, J = 3.1 Hz), 128.9 (d, J = 18.6 Hz), 128.9 (d, J = 9.5 Hz), 128.5, 126.5 (d, J = 7.3 Hz), 115.4 (d, J = 21.1 Hz), 101.8 (d, J = 184.5 Hz), 26.2. MS (EI, m/z, %): 246 (M⁺, 0.29), 203 ([M-MeCO]⁺, 100.00). HRMS (EI): Calcd. for C₁₅H₁₂OF: 246.0856; Found: 246.0859.

1-(4-chlorophenyl)-1-fluoro-1-phenylpropan-2-one (5c): IR (film): 3063, 3037, 2925, 2853, 1728, 1491, 1449, 1356, 1179, 1094, 1014, 925, 894, 821, 758, 698, 592 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.37–7.33 (m, 9H), 2.41 (d, J = 5.7 Hz, 3H). ¹⁹F NMR (CDCl₃, 282 MHz): δ -143.2 (q, J = 5.7 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz): δ 206.1 (d, J = 32.3 Hz), 137.7 (d, J = 22.6 Hz), 136.8 (d, J = 23.4 Hz), 135.0 (d, J = 2.4 Hz), 129.1 (d, J = 1.8 Hz), 128.60, 128.59, 128.2 (d, J = 6.7 Hz), 126.5 (d, J = 7.2 Hz), 101.7 (d, J = 185.6 Hz), 26.7. MS (EI, m/z, %): 262 (M⁺, 0.59), 219 ([M-MeCO]⁺, 100.00). HRMS (EI): Calcd. for C₁₅H₁₂OFCl: 262.0561; Found: 262.0564.
1-(4-bromophenyl)-1-fluoro-1-phenylpropan-2-one (5d): IR (film): 3062, 3032, 2924, 2852, 1728, 1590, 1288, 1449, 1355, 1178, 1010, 893, 817, 757, 698, 592 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.52–7.27 (m, 9H), 2.42 (d, \(J = 6\) Hz, 3H). \(^1\)F NMR (CDCl\(_3\), 282 MHz): \(\delta -143.8\) (q, \(J = 5.9\) Hz, 1F). \(^1\)\(^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 206.0 (d, \(J = 32.4\) Hz), 137.6 (d, \(J = 22.6\) Hz), 137.3 (d, \(J = 22.6\) Hz), 131.6, 129.1 (d, \(J = 1.4\) Hz), 128.6, 128.5 (d, \(J = 8.5\) Hz), 126.5 (d, \(J = 6.6\) Hz), 123.3 (d, \(J = 2.4\) Hz), 101.8 (d, \(J = 185.8\) Hz), 26.7. MS (EI, \(m/z\), %): 263 ([M–MeCO]+, 100). HRMS (EI): Calcd. for C\(_{13}\)H\(_9\)FBr (M–MeCO): 262.9872; Found: 262.9871.

![Fluoro-1-phenyl-1-(4-(trifluoromethyl)phenyl)propan-2-one (5e)](image_url)

Fluoro-1-phenyl-1-(4-(trifluoromethyl)phenyl)propan-2-one (5e): Colorless oil. IR (film): 3065, 3033, 2928, 2856, 1728, 1619, 1495, 1449, 1412, 1357, 1328, 1170, 1129, 1070, 896, 834, 755, 697, 611, 593 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.62 (d, \(J = 8.4\) Hz, 2H), 7.55 (d, \(J = 8.4\) Hz, 2H), 7.38 (s, 5H), 2.42 (d, \(J = 6\) Hz, 3H). \(^1\)\(^9\)F NMR (CDCl\(_3\), 282 MHz): \(\delta -62.5\) (s, 3F), –145.2 (q, \(J = 5.4\) Hz, 1F). \(^1\)\(^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 205.7 (d, \(J = 31.4\) Hz), 142.0 (d, \(J = 23.4\) Hz), 137.5 (d, \(J = 21.2\) Hz), 130.9 (q, \(J = 33.4\) Hz), 129.2, 128.7, 127.0 (d, \(J = 7.8\) Hz), 126.4 (d, \(J = 6.6\) Hz), 125.3 (q, \(J = 3.1\) Hz), 123.9 (q, \(J = 270.6\) Hz), 101.6 (d, \(J = 185.6\) Hz), 26.6. MS (EI, \(m/z\), %): 296 (M\(^+\), 1.16), 253 ([M-MeCO]+, 100.00). HRMS (EI): Calcd. for C\(_{16}\)H\(_{12}\)OF\(_4\): 296.0824; Found: 296.0827.

![1-(biphenyl-4-yl)-1-fluoro-1-phenylpropan-2-one (5f)](image_url)

1-(biphenyl-4-yl)-1-fluoro-1-phenylpropan-2-one (5f): Colorless oil. IR (film): 3060, 3031, 2924, 2852, 1725, 1600, 1488, 1448, 1355, 1178, 1008, 896, 835, 763, 746, 730, 698, 596 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.60–7.55 (m, 4H), 7.46–7.31 (m, 10H), 2.43 (d, \(J = 5.7\) Hz, 3H). \(^1\)\(^9\)F NMR (CDCl\(_3\), 282 MHz): \(\delta -143.3\) (q, \(J = 5.1\) Hz, 1F). \(^1\)\(^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 206.5 (d, \(J = 31.7\) Hz), 141.8 (d, \(J = 1.5\) Hz), 140.4, 138.1 (d, \(J = 22.5\) Hz), 137.2 (d, \(J = 22.2\) Hz), 128.9, 128.5, 127.7, 127.3, 127.2, 127.1, 126.73, 126.66, 102.2 (d, \(J = 184.8\) Hz), 26.7. MS (EI, \(m/z\), %): 304 (M\(^+\), 0.86), 261 ([M–MeCO]+, 100.00). HRMS (EI): Calcd. for C\(_{19}\)H\(_{14}\)F (M–MeCO): 261.1080; Found: 261.1079.
1-(3-chlorophenyl)-1-fluoro-1-phenylpropan-2-one (5g): Colorless oil. IR (film): 3065, 3030, 2925, 1728, 1574, 1421, 1212, 1186, 1103, 1026, 877, 786, 765, 738, 696, 599 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.41–7.28 (m, 9H), 2.42 (d, J = 6 Hz, 3H). ¹⁹F NMR (CDCl₃, 282 MHz): δ −144.0 (q, J = 5.8 Hz, 1F). ¹³C NMR (CDCl₃, 100 MHz): δ 205.8 (d, J = 31.7 Hz), 140.1 (d, J = 23.4 Hz), 137.5 (d, J = 22.6 Hz), 134.5, 129.6, 129.1 (d, J = 1.6 Hz), 129.0 (d, J = 2.0 Hz), 128.6, 126.8 (d, J = 8.6 Hz), 126.4 (d, J = 7.2 Hz), 124.9 (d, J = 7.8 Hz), 101.5 (d, J = 187.3 Hz), 25.8. MS (EI, m/z, %): 262 (M⁺, 1.16), 219 ([M-MeCO]⁺, 100.00). HRMS (EI): Calcd. for C₁₅H₁₉OFCl: 262.0561; Found: 262.0560.

1-(2-chlorophenyl)-1-fluoro-1-phenylpropan-2-one (5h): Colorless oil. IR (film): 3080, 3011, 2927, 1728, 1603, 1508, 1412, 1356, 1238, 1177, 1162, 1027, 1016, 900, 835, 591, 565 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.49–7.44 (m, 6H), 7.30 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 7.5 Hz, 1H), 2.44 (d, J = 4.8 Hz, 3H). ¹⁹F NMR (CDCl₃, 282 MHz): δ −145.9 (s, 1F). ¹³C NMR (CDCl₃, 100 MHz): δ 205.7 (d, J = 31.7 Hz), 137.6 (d, J = 20.9 Hz), 134.7 (d, J = 23.6 Hz), 134.5, 131.7 (d, J = 3.5 Hz), 130.8 (d, J = 2.1 Hz), 129.1, 128.8, 126.6, 126.5, 126.3, 101.9 (d, J = 188.2 Hz), 25.8. MS (EI, m/z, %): 262 (M⁺, 0.43), 219 ([M-MeCO]⁺, 100.00). HRMS (EI): Calcd. for C₁₅H₁₉OFCl: 262.0561; Found: 262.0557.

1-fluoro-1,1-bis(4-fluorophenyl)propan-2-one (5i): Colorless oil. IR (film): 3080, 3011, 2927, 1728, 1603, 1508, 1412, 1356, 1238, 1177, 1162, 1027, 1016, 900, 835, 591, 565 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.34 (t, J = 6.6 Hz, 4H), 7.05 (t, J = 8.7 Hz, 4H), 2.41 (d, J = 6.3 Hz, 3H). ¹⁹F NMR (CDCl₃, 282 MHz): δ −112.4 (m, 1F), −140.8 (s, 1F). ¹³C NMR (CDCl₃, 100 MHz): δ 206.3 (d, J = 32.4 Hz), 163.0 (dd,
$J = 248$ Hz, $J = 1.7$ Hz), 133.9 (dd, $J = 22.6$ Hz, $J = 3.3$ Hz), 128.7 (t, $J = 8.1$ Hz), 115.5 (d, $J = 21.7$ Hz), 101.4 (d, $J = 185.2$ Hz), 26.5. MS (EI, $m/z$, %): 264 (M', 0.24), 221 ([M-MeCO]'), 100.00). HRMS (EI): Calcd. for C_{15}H_{11}OF_3: 264.0762; Found: 264.0766.

1,1-bis(4-chlorophenyl)-1-fluoropropan-2-one (5j): Colorless oil. IR (film): 3073, 2925, 2853, 1731, 1594, 1491, 1417, 1402, 1356, 1210, 1178, 1095, 1031, 914, 895, 818, 593 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.35 (d, $J = 9$ Hz, 4H), 7.30 (d, $J = 8.7$ Hz, 4H), 7.21 (d, $J = 8.7$ Hz, 4H), 2.41 (d, $J = 6.3$ Hz, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –143.4 (q, $J = 6.2$ Hz, 1F). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 205.8 (d, $J = 32.7$ Hz), 136.3 (d, $J = 22.8$ Hz), 135.2 (d, $J = 2.4$ Hz), 128.8, 128.0 (d, $J = 6.5$ Hz), 101.2 (d, $J = 186.3$ Hz), 26.6. MS (EI, $m/z$, %): 296 (M', 0.51), 253 ([M-MeCO]'), 100.00). HRMS (EI): Calcd. for C$_{15}$H$_{11}$OFCl$_2$: 296.0171; Found: 296.0168.

1,1-bis(4-bromophenyl)-1-fluoropropan-2-one (5k): Colorless oil. IR (film): 3070, 2924, 1728, 1559, 1485, 1416, 1397, 1355, 1212, 1177, 1074, 1030, 910, 894, 812, 591, 488 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.52–7.47 (m, 4H), 7.24–7.22 (m, 4H), 2.42–2.37 (m, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –144.4 (m, $J = 6.2$ Hz, 1F). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 205.6 (d, $J = 32.3$ Hz), 136.7 (d, $J = 22.9$ Hz), 131.7, 128.2 (d, $J = 8.2$ Hz), 123.5 (d, $J = 2.4$ Hz), 101.3 (d, $J = 187.1$ Hz), 26.6. MS (EI, $m/z$, %): 341 ([M–MeCO]$^+$, 43.86). HRMS (EI): Calcd. for C$_{13}$H$_9$FBr$_2$: 340.8977; Found: 340.8980.

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1-(4-chlorophenyl)-1-fluoro-1-p-tolylpropan-2-one (5l): Colorless oil. IR (film): 3031, 2923, 1728, 1511, 1490, 1418, 1355, 1215, 1175, 1094, 1031, 1014, 897, 811, 591 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.32 (s, 4H), 7.20 (q, $J = 8.2$ Hz, 4H), 2.40 (d, $J = 5.7$ Hz, 3H), 2.35 (s, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –143.1 (q, $J = 5.6$ Hz, 1F). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 206.2 (d, $J = 32.6$ Hz), 139.0 (d, $J = 1.5$ Hz), 136.9 (d, $J = 23.6$ Hz), 134.9 (d, $J = 2.5$ Hz), 134.8 (d, $J = 23.0$ Hz), 129.2, 128.5, 128.2 (d, $J = 6.5$ Hz), 126.5 (d, $J = 7.0$ Hz), 101.8 (d, $J = 184.7$ Hz), 26.6, 21.1. MS (EI, m/z, %): 276 (M$^+$, 0.31), 233 ([M-MeCO]$^+$, 100.00). HRMS (EI): Calcd. for C$_{16}$H$_{14}$OFCl: 276.0717; Found: 276.0714.

1-(4-chlorophenyl)-1-fluoro-phenylnonan-2-one (5m): Colorless oil. IR (film): 2928, 2856, 1727, 1491, 1449, 1400, 1093, 1015, 821, 755, 699 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.36 (s, 5H), 7.32 (s, 4H), 2.81–2.75 (m, 2H), 1.60–1.55 (m, 2H), 1.24 (s, 8H), 0.86 (t, $J = 6.4$ Hz, 3H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –146.4 (s, 1F). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 208.2 (d, $J = 30.9$ Hz), 138.0 (d, $J = 22.0$ Hz), 137.1 (d, $J = 23.3$ Hz), 134.9 (d, $J = 2.3$ Hz), 128.9 (d, $J = 2.0$ Hz), 128.51, 128.50, 128.1 (d, $J = 8.3$ Hz), 126.4 (d, $J = 7.9$ Hz), 101.8 (d, $J = 184.5$ Hz), 38.6, 31.6, 29.0, 23.05, 23.03, 22.6, 14.0. MS (EI, m/z, %): 346 (M$^+$, 0.89), 219 ([M–C$_7$H$_{15}$CO]$^+$, 78.75). HRMS (EI): Calcd. for C$_{13}$H$_9$FCl (M–C$_7$H$_{15}$CO): 219.0377; Found: 219.0376.

1-(4-bromophenyl)-1-fluoro-1,3-diphenylpropan-2-one (5n): Colorless oil. IR (film): 3088, 3062, 3030, 2925, 1732, 1588, 1488, 1449, 1396, 1318, 1185, 1122, 1073, 1028, 1010, 896, 819, 752, 724, 697, 588 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.47 (d, $J = 8.4$ Hz, 2H), 7.49–7.46 (m, 10H), 7.15–7.11 (m, 2H), 4.08 (d, $J = 3.3$ Hz, 2H). $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ –146.6 (s, 1F). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 205.0 (d, $J = 31.7$ Hz), 137.6 (d, $J = 22.2$ Hz), 137.3 (d, $J = 23.0$ Hz), 132.8, 131.5, 129.9, 129.0, 128.6, 128.5, 128.4 (d, $J = 8.1$ Hz), 127.1, 126.5 (d, $J = 7.6$ Hz), 123.2 (d, $J = 3.3$ Hz), 102.2 (d, $J = 186.7$ Hz), 276.0717; Found: 276.0714.
3-fluoro-3-(naphthalen-2-yl)butan-2-one (5o): Colorless oil. IR (film): 3060, 2988, 2936, 1725, 1600, 1507, 1373, 1355, 1126, 1108, 907, 858, 820, 747 cm\(^{-1}\). \(^{1}\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.93–7.82 (m, 4H), 7.53–7.48 (m, 3H), 2.26 (d, \(J = 5.1\) Hz, 3H), 1.87 (d, \(J = 23.1\) Hz, 3H). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –154.7 (qq, \(J = 22.8\) Hz, \(J = 4.9\) Hz, 1F). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 207.1 (d, \(J = 30.8\) Hz), 136.3 (d, \(J = 21.8\) Hz), 133.0 (d, \(J = 2.4\) Hz), 128.6, 128.6, 128.3, 127.7, 126.6, 126.6, 126.3 (d, \(J = 9.9\) Hz), 121.9 (d, \(J = 7.6\) Hz), 100.7 (d, \(J = 182.7\) Hz), 24.6, 24.2 (d, \(J = 23.6\) Hz). MS (EI, \(m/z\), %): 216 (M\(^+\), 10.44), 173 ([M–MeCO]\(^+\), 100.00). HRMS (EI): Calcd. for C\(_{13}\)H\(_9\)FBr (M–BnCO): 262.9872; Found: 262.9868.

3-(4-chlorophenyl)-3-fluorobutan-2-one (5p): Colorless oil. IR (film): 2989, 2928, 2855, 1729, 1598, 1491, 11356, 1246, 1096, 1014, 904, 842, 819, 582 cm\(^{-1}\). \(^{1}\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.36 (s, 4H), 2.22 (d, \(J = 5.1\) Hz, 3H), 1.76 (d, \(J = 23.1\) Hz, 3H). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –154.4 (qq, \(J = 22.3\) Hz, \(J = 4.9\) Hz, 1F). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 206.9 (d, \(J = 30.1\) Hz), 137.3 (d, \(J = 22.5\) Hz), 134.5, 128.8 (d, \(J = 1.4\) Hz), 125.7 (d, \(J = 9.4\) Hz), 100.2 (d, \(J = 184.5\) Hz), 24.5, 24.2 (d, \(J = 23.7\) Hz). MS (EI, \(m/z\), %): 200 (M\(^+\), 5.94), 157 ([M–MeCO]\(^+\), 100.00). HRMS (EI): Calcd. for C\(_{10}\)H\(_{10}\)OFCl: 200.0404; Found: 200.0400.

3-(4-bromophenyl)-3-fluorobutan-2-one (5q): Colorless oil. IR (film): 2989, 2936, 2854, 1728, 1592, 1488, 1396, 1356, 1235, 1010, 904, 840, 814, 580 cm\(^{-1}\). \(^{1}\)H NMR (CDCl\(_3\), 300 MHz): \(\delta\) 7.51 (d, \(J = 8.4\) Hz, 2H), 7.30 (d, \(J = 8.4\) Hz, 2H), 2.22 (d, \(J = 5.1\) Hz, 3H), 1.75 (d, \(J = 22.5\) Hz, 3H). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz): \(\delta\) –154.9 (qq, \(J = 22.8\) Hz, \(J = 5.4\) Hz, 1F). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 206.8 (d, \(J = 31.0\) Hz), 138.8 (d, \(J = 22.7\) Hz), 131.8, 126.0 (d, \(J = 9.6\) Hz), 122.7, 100.2 (d, \(J = 183.8\) Hz), 22.5, 24.2 (d, \(J =
23.8 Hz). MS (EI, m/z, %): 246 ([\textsuperscript{80}Br]M\textsuperscript{+}, 2.55), 244 ([\textsuperscript{48}Br]M\textsuperscript{+}, 2.64), 201([M-MeCO]\textsuperscript{+}, 100). HRMS (EI): Calcd. for C\textsubscript{10}H\textsubscript{10}OFBr: 243.9899; Found: 243.9896.

3-fluoro-3-(4-iodophenyl)butan-2-one (5r): Colorless oil. IR (film): 2988, 2936, 2853, 1728, 1587, 1484, 1392, 1355, 1232, 1109, 1006, 904, 838, 809, 580 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): δ 7.72 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 2.22 (d, J = 5.1 Hz, 3H), 1.74 (d, J = 22.8 Hz, 3H). \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz): δ –155.0 (qq, J = 22.3 Hz, J = 5.6 Hz, 1F). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): δ 206.8 (d, J = 31.1 Hz), 138.7 (d, J = 22.7 Hz), 137.8, 126.2 (d, J = 9.5 Hz), 100.2 (d, J = 184.4 Hz), 94.4, 24.5, 24.1 (d, J = 23.0 Hz). MS (EI, m/z, %): 292 (M\textsuperscript{+}, 9.18), 249 ([M-MeCO]\textsuperscript{+}, 100.00). HRMS (EI): Calcd. for C\textsubscript{10}H\textsubscript{10}OFI: 291.9760; Found: 291.9762.

3-(3,4-dichlorophenyl)-3-fluorobutan-2-one (5s): Colorless oil. IR (film): 3096, 2991, 2939, 1728, 1472, 1382, 1356, 1238, 1140, 1126, 1031, 912, 832, 678, 606 cm\textsuperscript{-1}. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): δ 7.55 (m, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.28–7.25 (m, 1H), 2.25 (d, J = 5.1 Hz, 3H), 1.75 (d, J = 23.1 Hz, 3H). \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz): δ –155.3 (qq, J = 23.1 Hz, J = 4.5 Hz, 1F). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): δ 206.5 (d, J = 30.6 Hz), 139.1 (d, J = 22.9 Hz), 133.0 (d, J = 1.4 Hz), 132.8, 130.6 (d, J = 1.5 Hz), 126.4 (d, J = 9.9 Hz), 123.7 (d, J = 9.9 Hz), 99.6 (d, J = 185.7 Hz), 24.6, 24.2 (d, J = 23.1 Hz). MS (EI, m/z, %): 234 (M\textsuperscript{+}, 11.00), 191 ([M-MeCO]\textsuperscript{+}, 100.00). HRMS (EI): Calcd. for C\textsubscript{10}H\textsubscript{9}OFCl\textsubscript{2}: 234.0014; Found: 234.0013.
6. The Reuse of Nafion-212 as Catalyst

\[
\begin{align*}
\text{Ph} \quad \text{O} & \quad \text{F} \\
\text{Br} & \\
4d \ (0.4 \text{ mmol}) \end{align*}
\]

\[
\begin{align*}
&+ \quad \text{Nafion-212} \\
\text{CH}_2\text{Cl}_2 \ (3 \text{ mL}) & \\
\text{r.t.} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} \quad \text{O} & \quad \text{F} \\
\text{Br} & \\
5d \end{align*}
\]

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</table>

$^a$ Conditions: fluoroepoxide 4d (0.4 mmol) was dissolved in CH$_2$Cl$_2$ (3 mL) and stirred with Nafion-212 (1.1 mg, 0.001 mmol H$^+$, 0.25 mol%) in sealed tube. The reaction progress was determined by $^{19}$F NMR. $^b$ Yields given refer to the isolated yields of analytically pure products 5d.

Under N$_2$ atmosphere, fluoroepoxide 4d (123 mg, 0.4 mmol) was dissolved in dichloromethane (3 mL), and stirred with recovered Nafion-212 (1.1 mg, 0.001 mmol H$^+$, 0.25 mol%) in sealed tube at room temperature. The reaction progress was detected by $^{19}$F NMR. After filtering to recover the Nafion-212 and removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 50 : 1 as eluent to get the product 5d. The recycled Nafion-212 could be reused after soaking in HCl (1 M, aq.) for 6 hours and drying under an infrared lamp.

7. Mechanism Studies

7.1 CsF-Promoted Rearrangement of Fluoroepoxide 1c

\[
\begin{align*}
\text{Ph} \quad \text{O} & \quad \text{Me} \\
\text{Cl} & \\
4c \\
\text{Me} \quad \text{F} \\
\text{Cl} \end{align*}
\]

\[
\begin{align*}
&+ \quad \text{CsF (10 mol\%)} \\
\text{CH}_2\text{Cl}_2, \text{rt, 20 h} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} \quad \text{O} & \quad \text{F} \\
\text{Cl} & \\
5c \end{align*}
\]

(eq 1)

Under N$_2$ atmosphere, fluoroepoxide 4c (52 mg, 0.2 mmol) was dissolved in dichloromethane (2 mL), and stirred with CsF (3 mg, 10 mol%) in sealed tube at room temperature for 20 h. The reaction system
was detected by $^{19}$F NMR. From the spectra we can see there are only the signals of unreacted fluoroepoxide 4c.

The $^{19}$F NMR spectra of the reaction system:

7.2 The Rearrangement of Enantiomerically Enriched Fluoroepoxide 4s

Under N$_2$ atmosphere, fluoroepoxide $cis$-4s (24 mg, 0.1 mmol, $ee = 82\%$) was dissolved in dichloromethane (1 mL), and stirred with Nafion-212 (1.1 mg, 0.001 mmol H$^+$, 1 mol%) in sealed tube at room temperature for 1 day. After filtering and removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 50 : 1 as eluent to get the product 5s (16 mg, 65%, $ee = 53\%$).

The Enantiomerically enriched fluoroepoxide $cis$-4s ($ee = 82\%$) was prepared from optically pure sulfoximine 6a. For $cis$-4s, the enantiomeric excess was determined by Lux 5u Cellulose-2 (4.6 mm × 250 mm), Hexane / IPA= 98 / 2, 0.7 mL/min, $\lambda = 214$ nm, $t_R$ (minor) = 6.23 min, $t_R$ (major) = 6.62 min on DIOMEX Ultimate 3000; 82% $ee$.

HPLC chart of $cis$-4s
<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.30</td>
<td>n.a.</td>
<td>1479443</td>
<td>220.252</td>
<td>49.99</td>
<td>n.a.</td>
<td>BM</td>
</tr>
<tr>
<td>2</td>
<td>6.71</td>
<td>n.a.</td>
<td>1510955</td>
<td>220.326</td>
<td>50.01</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>2990.378</td>
<td>440.578</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.23</td>
<td>n.a.</td>
<td>372643</td>
<td>54.892</td>
<td>8.81</td>
<td>n.a.</td>
<td>BM*</td>
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<tr>
<td>2</td>
<td>6.62</td>
<td>n.a.</td>
<td>4855686</td>
<td>567.980</td>
<td>91.19</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>5229309</td>
<td>622852</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>
For 1,2-fluorine migration products 5s, the enantionmetric excess was determined by CHIRAPAK AD-H (4.6 mm x 250 mm, 5 µm), Hexane / IPA= 98 / 2, 0.5 mL/min, λ = 214 nm, tR (minor) = 7.84 min, tR (major) = 8.21 min on DIOMEX Ultimate 3000s; 53% ee.

HPLC chart of 5s

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time min</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>n.a.</td>
<td>431.232</td>
<td>75.781</td>
<td>49.17</td>
<td>n.a.</td>
<td>BM</td>
</tr>
<tr>
<td>2</td>
<td>7.97</td>
<td>n.a.</td>
<td>409.645</td>
<td>78.353</td>
<td>50.83</td>
<td>n.a.</td>
<td>MB</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>840.877</td>
<td>154.134</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>
7.3 The Reaction of Fluorooepoxide 4a with N-methyl Indole 10

Under N₂ atmosphere, monofluorinated epoxide 4a (46 mg, 0.2 mmol) and N-methyl indole 10 (26 mg, 0.2 mmol, 1.0 equiv.) were dissolved in dichloromethane (2 mL), and stirred with p-TsOH (3.6 mg, 10 mol%) in sealed tube at room temperature for 20 h. The reaction system was detected by ¹⁹F-NMR using PhCF₃ as internal standard. After removing the solvent under vacuum, the residue was subjected to silica gel column chromatography using PE : EA = 30 : 1 as eluent to get the major product 11 (41 mg, 60%).

The ¹⁹F NMR spectra of the reaction system
1-(1-methyl-1H-indol-3-yl)-1,1-diphenylpropan-2-one (11): Brown solid. Mp: 183-185 °C. IR (film): 3055, 2926, 1708, 1532, 1485, 1446, 1350, 1154, 771, 746, 696, 579 cm⁻¹. ¹H NMR (CDCl₃, 300 MHz): δ 7.32–7.17 (m, 12H), 6.94–6.93 (m, 3H), 3.78 (s, 3H), 2.12 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 206.8, 142.6, 137.5, 130.1, 129.7, 127.9, 127.2, 126.6, 121.9, 121.8, 119.4, 115.2, 109.3, 67.6, 32.9, 29.5. MS (EI, m/z, %): 339 (M⁺, 0.35), 296 ([M–MeCO⁺, 100.00). HRMS (EI): Calcd. for C₂₄H₂₁NO: 339.1623; Found: 339.1628.

8. References

9. NMR Spectra of Isolated Products

- NTs
- SO
- F
- Me
- 6a $^1$H NMR
- (CDCl$_3$, 300 MHz)

- NTs
- SO
- F
- Me
- 6a $^{19}$F NMR
- (CDCl$_3$, 282 MHz)
trans-4q \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz)

trans-4q \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz)
trans-4s $^{19}$F NMR (CDCl$_3$, 282 MHz)

trans-4s $^{13}$C NMR (CDCl$_3$, 100 MHz)
$5c$ $^{13}$C NMR
(CDCl$_3$, 100 MHz)

$5d$ $^1$H NMR
(CDCl$_3$, 300 MHz)
$\textbf{Chloroformate Derivatives}$

**5k** $^{13}\text{C}$ NMR (CDCl$_3$, 100 MHz)

**5l** $^1\text{H}$ NMR (CDCl$_3$, 300 MHz)
$5p^{19}F$ NMR
(CDCl$_3$, 282 MHz)

$5p^{13}C$ NMR
(CDCl$_3$, 100 MHz)
$^{13}$C NMR (CDCl$_3$, 100 MHz)