Supporting Information

Silver-Catalyzed Decarboxylative Alkylfluorination of Alkenes
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1. General Information

Materials

All reagents were used as received from commercial sources unless specified otherwise, or prepared as described in the literature. CH₃CN, CH₂Cl₂, DCM, DMF, THF, DMSO, 1,4-Dioxane and MeOH were purchased from Sigma-Aldrich and used without any purification.

Analytic Methods

¹H NMR, ¹³C NMR, ¹⁹F NMR spectra were recorded on a Bruker Advance 600 spectrometer at the ambient temperature in CDCl₃, d₆-DMSO or D₂O. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ¹³C NMR are reported in terms of chemical shift (δ ppm). Data for ¹⁹F NMR are reported in terms of chemical shift (δ ppm). Gas Chromatography-Mass Spectrometer (GC-MS) analyses were performed on a Thermo Trace 1300 ISQ Series GC-MS System. GC-MS method: initial temp.: 50 °C (hold for 1 min), rate: 40 °C/min, final temp.: 250 °C (hold for 12 min). Room-temperature Electron Spin Resonance (ESR) spectra were obtained using a JEOL JES-FA200 ESR spectrometer (300 K, 9.063 GHz, X-band). Microwave power employed was 5 mW; sweep width ranged from 2000 to 4000 G. Modulation frequency and modulation amplitude were 100 kHz and 3.5 G, respectively. Column chromatography was performed using 50-500 mesh silica gel. High-resolution mass spectra (HRMS) were recorded on an ACQUITY UPLC LCT Premier XE spectrometer with ESI mode. Organic solutions were concentrated under reduced pressure on a BUCHI rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. General Procedure

AgNO₃ (20 mol%, 0.04 mmol, 6.8 mg), potassium carboxylate (3 equiv, 0.6 mmol) were placed in a Schlenk tube equipped with a stirring bar. The solvent 1,4-dioxane/H₂O (v/v = 1:1, 2 mL) and alkene (0.2 mmol) were added under Ar atmosphere. The reaction mixture was stirred at room temperature for 12 h. Then, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo, purified by flash column chromatography with a mixture of ethyl acetate/petroleum ether as eluent on silica gel to afford alkylfluorination product.

3. Preparation of Potassium Carboxylate

\[ \text{Me} \begin{array}{c} \text{CO}_2H \\ \text{EtOH, RT} \end{array} \xrightarrow{\text{KHCO}_3 (1.05 \text{ equiv})} \text{Me} \begin{array}{c} \text{CO}_2K \\ \text{EtOH, RT} \end{array} \]

To a solution of n-hexanoic acid (1.16 g, 10 mmol) in EtOH (5 mL) was added dropwise KHCO₃ (1.05 g, 10.5 mmol, dissolved in 5 mL of EtOH). The reaction mixture was stirred at room temperature for 3 h. Then, the reaction solution was dried over with anhydrous MgSO₄. After filtration, anhydrous Et₂O was added dropwise, and dropping was stopped when a small amount of crystals precipitated, followed by cooled the solution at a 0 °C. Filtration and collected the white crystals, dried in vacuum to obtain potassium hexanoate (92% yield, 1.41 g).
4. Optimization of Reaction Conditions

Table S1. Optimization Experiments for the Catalysts.

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<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)</th>
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<td>1</td>
<td>AgNO₃</td>
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</tr>
<tr>
<td>2</td>
<td>Ag₂CO₃</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>AgOTF</td>
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</tr>
<tr>
<td>4</td>
<td>Ag₂SO₄</td>
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<td>5</td>
<td>AgSbF₆</td>
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<td>6</td>
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*Reaction conditions: 1b (0.2 mmol), 2b (0.6 mmol), Selectfluor (0.6 mmol), AgNO₃ (0.04 mmol), KHCO₃ (0.5 mmol), MeCN/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolated yield.

Table S2. Optimization Experiments for Other Conditions.

<table>
<thead>
<tr>
<th>Entry</th>
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<td>KOAc (3 equiv)</td>
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<tr>
<td>2</td>
<td>NaOAc (3 equiv)</td>
<td>RT</td>
<td>12</td>
<td>56</td>
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<tr>
<td>3</td>
<td>KOAc (4 equiv)</td>
<td>RT</td>
<td>12</td>
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<td>4</td>
<td>KOAc (2 equiv)</td>
<td>RT</td>
<td>12</td>
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<td>5</td>
<td>KOAc (3 equiv)</td>
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<td>RT</td>
<td>8</td>
<td>64</td>
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*Reaction conditions: 1b (0.2 mmol), Me–CO₂X (0.6 mmol), Selectfluor (0.6 mmol), AgNO₃ (0.04 mmol), KHCO₃, 1,4-dioxane/H₂O (v/v = 1/1, 2 mL). Isolated yield.
5. Radical Trapping Experiment

When one equivalent of TEMPO (2,2,6,6-tetramethyl-1-oxypiperidine), the radical trapper, was added in the reaction, the desired alkylfluorination product was reduced in a trace yield, with the adduct of alkyl radical with TEMPO be detected by GC-MS.

[Diagram showing the reaction between 1a and TEMPO (2,2,6,6-tetramethyl-1-oxypiperidine) with the formation of the desired alkylfluorination product and the detection of the adduct by GC-MS.]
Fig S1. GC-MS Analysis of the Radical Trapping Reaction Mixture
6. Reaction of Tertiary Aliphatic Carboxylic Acid

![Reaction Scheme]

The reaction with tertiary aliphatic carboxylic acid, such as 1-adamantane carboxylic acid, delivered the desired alkylfluorination product in trace amount. The competitive undesired decarboxylative fluorination of tertiary aliphatic carboxylic acid occurred, affording the fluorination byproduct in moderate yield.

7. Gram-Scale Synthesis

![Gram-Scale Scheme]

Potassium hexanoate 2c (45 mmol, 6.93 g), Selectfluor (45 mmol, 15.93 g), AgNO₃ (3.0 mmol, 510 mg) were placed in a 250 mL flask equipped with a stirring bar. The solvent 1,4-dioxane/H₂O (v/v = 1:1, 150 mL) and 4-fluoro-styrene 1d (15 mmol, 1.83 g) were added under Ar atmosphere. The reaction mixture was stirred at room temperature for 12 h. Then, the mixture was quenched with water and extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and concentrated under vacuo, purified by flash column chromatography with ethyl acetate/petroleum ether (v/v =1:100) as eluent on silica gel to afford 1.72 g (54%) of 3dc as a colorless oil.
8. Characterization of product

(1-Fluoropentane-1,5-diyl)dibenzene (3aa). The representative procedure was followed using styrene 1a (21 mg, 0.2 mmol), potassium 4-phenylbutanoate 2a (122 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/ EtOAc: 100/1) yielded 36.8 mg (76%) of 3aa as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.31 (m, 3H), 7.30 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 5.44 (ddd, J = 47.9, 7.9, 4.9 Hz, 1H), 2.66 – 2.62 (m, 2H), 2.03 – 1.96 (m, 1H), 1.94 – 1.80 (m, 1H), 1.76 – 1.64 (m, 2H), 1.62 – 1.51 (m, 1H), 1.48 – 1.45 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 142.36, 140.48 (d, J = 19.9 Hz), 128.39, 128.35, 128.27, 128.15 (d, J = 1.8 Hz), 126.69, 125.49 (d, J = 6.8 Hz), 94.55 (d, J = 170.4 Hz), 37.09 (d, J = 23.6 Hz), 35.77, 31.22, 24.82 (d, J = 4.2 Hz). ¹⁹F NMR (564 MHz, CDCl₃) δ -174.32 – -174.55 (m). HRMS (EI⁺) calcld for [C₁₃H₁₃F⁺]⁺ ([M⁺]): 242.1471, found: 242.1468. The spectrum data matches previously reported values.

1-Chloro-4-(1-fluoropropyl)benzene (3bb). The representative procedure was followed using 1-chloro-4-vinylbenzene 1b (28 mg, 0.2 mmol), potassium acetate 2b (59 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/ EtOAc: 100/1) yielded 26.1 mg (76%) of 3bb as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.34 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 5.34 (ddd, J = 47.5, 7.4, 5.3 Hz, 1H), 2.04 – 1.73 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 138.90 (d, J = 20.4 Hz), 134.00 (d, J = 2.6 Hz), 128.66, 127.04 (d, J = 7.1 Hz), 95.08 (d, J = 171.5 Hz), 30.20 (d, J = 24.1 Hz), 9.30 (d, J = 5.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -175.83 – -175.99 (m). HRMS (EI⁺) calcld for [C₆H₅ClF⁺]⁺ ([M⁺]): 172.0455, found: 172.0450.

(1-Fluorobutyl) benzene (3ac). The representative procedure was followed using styrene 1a (21 mg, 0.2 mmol), potassium hexanoate 2c (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/ EtOAc: 100/1) yielded 31.0 mg (80%) of 3ac as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.39 (d, J = 7.5 Hz, 2H), 7.37 – 7.33 (m, 3H), 5.44 (ddd, J = 47.9, 7.8, 5.1 Hz, 1H), 2.05 – 1.92 (m, 1H), 1.90 – 1.74 (m, 1H), 1.43 – 1.24 (m, 8H), 0.91 (t, J = 6.7 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 140.65 (d, J = 19.8 Hz), 128.36, 128.10 (d, J = 2.0 Hz), 125.53 (d, J = 6.8 Hz), 94.68 (d, J = 170.1 Hz), 37.24 (d, J = 24.0 Hz), 31.68, 29.03, 25.08.
22.56, 14.04. ^19^F NMR (564 MHz, CDCl$_3$) δ -174.12 – -174.33 (m). HRMS (EI+) calef for [C$_{13}$H$_{19}$F]$^+$ ([M$^+$]): 194.1471, found: 194.1465. The spectrum data matches previously reported values.$^1$

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1-Chloro-4-(1-fluoroheptyl)benzene (3bc). The representative procedure was followed using 1-chloro-4-vinylbenzene 1b (28 mg, 0.2 mmol), potassium hexanoate 2c (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO$_3$ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H$_2$O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/ EtOAc: 100/1) yielded 29.6 mg (65%) of 3bc as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.43 – 7.30 (m, 4H), 5.45 (ddd, J = 47.9, 8.0, 5.0 Hz, 1H), 2.05 – 1.78 (m, 2H), 1.56 – 1.24 (m, 8H), 0.92 (t, J = 7.0 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 140.65 (d, J = 19.9 Hz), 128.35, 128.09 (d, J = 2.0 Hz), 125.52 (d, J = 6.9 Hz), 94.67 (d, J = 170.1 Hz), 37.24 (d, J = 23.5 Hz), 31.68, 29.03, 25.06 (d, J = 4.4 Hz), 22.56, 14.03. $^{19}$F NMR (564 MHz, CDCl$_3$) δ -174.48 – -174.71 (m). HRMS (EI+) calef for [C$_{13}$H$_{19}$ClF]$^+$ ([M$^+$]): 228.1081, found: 228.1089.

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(1-Fluoropropane-1,3-diyl)dibenzene (3ad). The representative procedure was followed using styrene 1a (21 mg, 0.2 mmol), potassium 2-phenylacetate 2d (105 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO$_3$ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H$_2$O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/ EtOAc: 100/1) yielded 25.7 mg (60%) of 3ad as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.40 – 7.34 (m, 2H), 7.34 – 7.26 (m, 5H), 7.22 – 7.17 (m, 3H), 5.43 (ddd, J = 47.8, 8.5, 4.3 Hz, 1H), 2.86 – 2.68 (m, 2H), 2.37 – 2.23 (m, 1H), 2.18 – 2.00 (m, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 141.10, 140.20, 140.08, 140.07, 128.45, 128.44, 128.28, 128.27, 93.64 (d, J = 171.0 Hz), 38.81 (d, J = 22.5 Hz), 31.31 (d, J = 4.3 Hz). $^{19}$F NMR (564 MHz, CDCl$_3$) δ -175.55 – -176.19 (m). HRMS (EI+) calef for [C$_{13}$H$_{19}$F]$^+$ ([M$^+$]): 214.1158, found: 214.1152.

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Ethyl 3-fluoro-3-phenylpropanoate (3ae). The representative procedure was followed using styrene 1a (21 mg, 0.2 mmol), potassium 2-ethoxy-2-oxoacetate 2e (94 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO$_3$ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H$_2$O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/ EtOAc: 100/1) yielded 20.0 mg (51%) of 3ae as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.48 – 7.29 (m, 5H), 5.98 – 5.86 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.05 – 3.00 (m, 1H), 2.83 – 2.74 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 172.29 (d, J = 5.1 Hz), 141.34 (d, J = 19.6 Hz), 131.46 (d, J = 1.9 Hz), 131.29, 128.26 (d, J = 6.5 Hz), 93.30 (d, J = 171.0 Hz), 63.62, 45.16 (d, J = 27.0 Hz), 16.78. $^{19}$F NMR (564 MHz, CDCl$_3$) δ -172.50 – -172.84 (m). HRMS (EI+) calef for [C$_{11}$H$_{13}$FO$_2$]$^+$ ([M$^+$]): 196.0900,

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(2-Cyclopentyl-1-fluoroethyl)benzene (3af). The representative procedure was followed using styrene 1a (21 mg, 0.2 mmol), potassium cyclopentanecarboxylate 2f (92 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in CH₂CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 21.9 mg (57%) of 3af as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.40 – 7.30 (m, 5H), 5.45 (ddd, J = 48.0, 8.5, 4.9 Hz, 1H), 2.06 (dd, J = 14.1, 6.7 Hz, 1H), 1.97 – 1.87 (m, 1H), 1.87 – 1.72 (m, 3H), 1.63 (d, J = 6.9 Hz, 2H), 1.53 (dd, J = 7.4, 4.0 Hz, 2H), 1.23 – 1.11 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 143.41 (d, J = 19.8 Hz), 131.06, 130.83 (d, J = 6.6 Hz), 97.08 (d, J = 169.6 Hz), 46.20 (d, J = 23.0 Hz), 39.03 (d, J = 3.8 Hz), 35.59, 35.22, 27.74, 27.58. ¹⁹F NMR (564 MHz, CDCl₃) δ -173.06 – -173.50 (m). HRMS (EI⁺) calcld for [C₁₁H₁₁F⁺][M⁺]: 192.1314, found: 192.1306.

(2-Cyclohexyl-1-fluoroethyl)benzene (3ag). The representative procedure was followed using styrene 1a (21 mg, 0.2 mmol), cyclohexanecarboxylic acid 2g (77 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), KHCO₃ (50 mg, 0.5 mmol), in CH₂CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 26.8 mg (65%) of 3ag as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.18 (m, 5H), 5.54 (ddd, J = 12.5, 9.4, 3.8 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.69 – 1.49 (m, 5H), 1.22 – 1.00 (m, 4H), 0.97 – 0.85 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 128.44, 128.17, 125.59, 125.53, 92.80 (d, J = 182.0 Hz), 45.24, 33.87, 32.81, 26.49, 26.25, 26.10. ¹⁹F NMR (376 MHz, CDCl₃) δ -173.78 (s). HRMS (EI⁺) calcld for [C₁₄H₁₃F⁺][M⁺]: 206.1471, found: 206.1465.

(3-Ethyl-1-fluoroheptyl)benzene (3ah). The representative procedure was followed using styrene 1a (21 mg, 0.2 mmol), 2-ethylhexanoic acid 2h (87 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), KHCO₃ (50 mg, 0.5 mmol), in CH₂CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 22.6 mg (51%) of 3ah as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 5.51 (ddd, J = 48.3, 9.2, 4.0 Hz, 1H), 1.99 – 1.95 (m, 1H), 1.69 – 1.63 (m, 1H), 1.53 – 1.23 (m, 9H), 0.94 – 0.85 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 141.03 (d, J = 19.8 Hz), 128.40, 128.11, 125.52 (d, J = 6.5 Hz), 93.29 (d, J = 169.7 Hz), 41.41 (d, J = 23.2 Hz), 35.23 (d, J = 26.6 Hz), 32.72 (d, J = 77.5 Hz), 28.61 (d, J = 14.6 Hz), 25.84 (d, J = 114.0 Hz), 23.03 (d, J = 5.6 Hz), 14.11, 10.51 (d, J = 29.5 Hz). ¹⁹F NMR (564 MHz, CDCl₃) δ -172.97 – -175.35 (m). HRMS (EI⁺) calcld for [C₁₃H₂₃F⁺][M⁺]: 222.1784, found: 222.1778.
1-Bromo-4-(1-fluoroheptyl)benzene (3cc). The representative procedure was followed using 1-bromo-4-vinylbenzene 1c (37 mg, 0.2 mmol), potassium hexanoate 2c (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 37.0 mg (68%) of 3cc as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.50 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.45 – 5.31 (m, 1H), 1.99 – 1.71 (m, 2H), 1.51 – 1.41 (m, 1H), 1.40 – 1.21 (m, 7H), 0.88 (t, J = 6.6 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 139.61 (d, J = 20.3 Hz), 131.50, 127.20 (d, J = 6.9 Hz), 121.97 (d, J = 2.4 Hz), 93.94 (d, J = 171.2 Hz), 37.13 (d, J = 23.3 Hz), 31.64, 28.97, 24.88 (d, J = 4.3 Hz), 22.53, 14.04. ¹⁹F NMR (564 MHz, CDCl₃) δ -175.02 – -175.26 (m). HRMS (EI+) calcd for [C₁₃H₁₈¹⁹BrF⁺] ([M⁺]): 272.0576, found: 272.0570.

1-Fluoro-4-(1-fluoroheptyl)benzene (3dc). The representative procedure was followed using 1-fluoro-4-vinylbenzene 1d (25 mg, 0.2 mmol), potassium hexanoate 2c (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 25.0 mg (59%) of 3dc as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.30 (m, 4H), 5.45 (ddd, J = 47.9, 8.0, 5.0 Hz, 1H), 2.05 – 1.78 (m, 2H), 1.56 – 1.24 (m, 8H), 0.92 (t, J = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 140.65 (d, J = 19.9 Hz), 128.35, 128.09 (d, J = 2.0 Hz), 125.52 (d, J = 6.9 Hz), 94.67 (d, J = 170.1 Hz), 37.24 (d, J = 23.5 Hz), 31.68, 29.03, 25.06 (d, J = 4.4 Hz), 22.56, 14.03. ¹⁹F NMR (564 MHz, CDCl₃) δ -174.48 – -174.71 (m). HRMS (EI+) calcd for [C₁₃H₁₉Fl⁺] ([M⁺]): 212.1377, found: 212.1371.

1-(tert-butyl)-4-(1-fluoroheptyl) benzene (3ec). The representative procedure was followed using 1-tert-butyl-4-vinylbenzene 1e (32 mg, 0.2 mmol), potassium hexanoate 2c (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in CH₂CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 40.0 mg (80%) of 3ec as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.40 (d, J = 8.0 Hz, 2H), 7.30 – 7.24 (m, 2H), 5.40 (ddd, J = 48.0, 8.1, 4.9 Hz, 1H), 2.03 – 1.75 (m, 2H), 1.54 – 1.44 (m, 1H), 1.40 – 1.25 (m, 15H), 0.89 (t, J = 6.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 151.17, 137.55 (d, J = 19.9 Hz), 125.41 (d, J = 6.4 Hz), 125.29, 94.70 (d, J = 169.0 Hz), 37.06 (d, J = 23.7 Hz), 34.57, 31.69, 31.32, 29.05, 25.18 (d, J = 4.1 Hz), 22.57, 14.06. ¹⁹F NMR (564 MHz, CDCl₃) δ -172.13 – -172.38 (m). HRMS (EI+) calcd for [C₁₃H₂₃F⁺] ([M⁺]): 250.2097, found: 250.2091.
4-(1-Fluoroheptyl)-1,1'-biphenyl (3fc). The representative procedure was followed using 4-vinylbiphenyl 1f (36 mg, 0.2 mmol), potassium hexanoate 2e (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 43.7 mg (81%) of 3fc as a colorless oil. H NMR (600 MHz, CDCl₃) δ 7.63 – 7.61 (m, 4H), 7.48 – 7.36 (m, 5H), 5.49 (ddd, J = 47.9, 7.8, 5.1 Hz, 1H), 2.12 – 1.77 (m, 2H), 1.58 – 1.49 (m, 1H), 1.46 – 1.27 (m, 7H), 0.91 (t, J = 6.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 144.93, 143.64, 142.87, 131.42, 130.20, 129.72, 129.66, 80.70 (d, J = 171.0 Hz), 41.23, 34.46, 31.88, 28.55, 25.32, 16.79. ¹⁹F NMR (564 MHz, CDCl₃) δ -173.62 – -173.87 (m). HRMS (EI+) cld for [C₁₉H₂₃F⁺][M⁺]: 270.1784, found: 270.1778.

4-(1-Fluoroheptyl)benzonitrile (3gc). The representative procedure was followed using 4-vinylbenzonitrile 1g (26 mg, 0.2 mmol), potassium hexanoate 2e (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 18.8 mg (43%) of 3gc as a colorless oil. H NMR (600 MHz, acetone-d₆) δ 7.58 – 7.19 (m, 4H), 5.40 (ddd, J = 47.9, 8.0, 5.0 Hz, 1H), 2.21 – 1.87 (m, 1H), 1.84 – 1.73 (m, 1H), 1.58 – 1.38 (m, 1H), 1.39 – 1.16 (m, 7H), 0.87 (t, J = 7.0 Hz, 3H). ¹³C NMR (151 MHz, acetone-d₆) δ 148.80 (d, J = 20.2 Hz), 134.92, 128.93 (d, J = 7.5 Hz), 120.89, 114.40, 96.05 (d, J = 171.5 Hz), 39.51 (d, J = 22.8 Hz), 34.14, 31.40, 27.32 (d, J = 4.0 Hz), 24.95, 16.04. ¹⁹F NMR (564 MHz, acetone-d₆) δ -180.14 – 180.31 (m). HRMS (EI+) cld for [C₁₄H₁₃FN⁺][M⁺]: 219.1423, found: 219.1418.

1-Chloro-3-(1-fluoroheptyl)benzene (3hc). The representative procedure was followed using 1-chloro-3-vinylbenzene 1h (28 mg, 0.2 mmol), potassium hexanoate 2e (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 32.4 mg (71%) of 3hc as a colorless oil. H NMR (600 MHz, CDCl₃) δ 7.32 (s, 1H), 7.30 – 7.29 (m, 2H), 7.21 – 7.17 (m, 1H), 5.39 (ddd, J = 47.7, 8.0, 4.8 Hz, 1H), 1.98 – 1.88 (m, 1H), 1.84 – 1.73 (m, 1H), 1.50 – 1.41 (m, 1H), 1.36 – 1.25 (m, 7H), 0.88 (t, J = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 142.68 (d, J = 20.4 Hz), 134.34, 129.69, 128.18 (d, J = 1.5 Hz), 125.63 (d, J = 7.5 Hz), 123.56 (d, J = 7.0 Hz), 93.80 (d, J = 172.0 Hz), 37.18 (d, J = 23.2 Hz), 31.63, 28.97, 24.89 (d, J = 4.1 Hz), 22.54, 14.04. ¹⁹F NMR (564 MHz, CDCl₃) δ -176.12 – -176.35 (m). HRMS (EI+) cld for [C₁₃H₁₄ClF⁺][M⁺]: 228.1081, found: 228.1076.
**1-Bromo-2-(1-fluoroheptyl)benzene (3ic).** The representative procedure was followed using 1-bromo-2-vinylbenzene 1i (37 mg, 0.2 mmol), potassium hexanoate 2c (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 33.2 mg (61%) of 3ic as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.35 (dd, J = 8.0, 1.1 Hz, 1H), 7.49 (dd, J = 7.8, 1.7 Hz, 1H), 7.36 (dd, J = 7.6, 1.1 Hz, 1H), 7.18 – 7.14 (m, 1H), 5.75 (ddd, J = 47.3, 8.4, 3.6 Hz, 1H), 2.01 – 1.69 (m, 2H), 1.57 – 1.44 (m, 2H), 1.41 – 1.24 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 140.35 (d, J = 21.6 Hz), 132.66, 129.37 (d, J = 2.1 Hz), 127.70, 126.91 (d, J = 10.1 Hz), 120.81 (d, J = 6.3 Hz), 93.47 (d, J = 172.0 Hz), 36.33 (d, J = 23.7 Hz), 31.77, 28.98, 25.15 (d, J = 3.1 Hz), 22.66. ¹⁹F NMR (564 MHz, CDCl₃) δ -181.53 – -181.70 (m). HRMS (El⁺) calcd for [C₁₃H₁₈F⁷Br]⁺ ([M]+): 272.0576, found: 272.0570.

**1-(1-Fluoroheptyl)-2-methylbenzene (3jc).** The representative procedure was followed using 1-methyl-2-vinylbenzene 1j (24 mg, 0.2 mmol), potassium hexanoate 2c (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 31.2 mg (75%) of 3jc as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.42 (m, 1H), 7.26 – 7.17 (m, 3H), 5.67 (ddd, J = 47.5, 8.6, 4.1 Hz, 1H), 2.35 (s, 3H), 1.98 – 1.77 (m, 2H), 1.59 – 1.56 (m, 1H), 1.34 – 1.12 (m, 7H), 0.92 (t, J = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 138.83 (d, J = 18.9 Hz), 134.18 (d, J = 5.2 Hz), 130.34, 127.84 (d, J = 1.9 Hz), 126.07, 125.17 (d, J = 8.6 Hz), 91.91 (d, J = 168.8 Hz), 36.34 (d, J = 24.0 Hz), 31.71, 29.04, 25.37 (d, J = 3.4 Hz), 22.58, 18.92, 14.07. ¹⁹F NMR (564 MHz, CDCl₃) δ -177.27 – -177.73 (m). HRMS (El⁺) calcd for [C₁₄H₂₁F⁺ ([M]+): 208.1627, found: 208.1622.

**2-(1-Fluoroheptylnaphthalene (3kc).** The representative procedure was followed using 2-vinylnaphthalene 1k (31 mg, 0.2 mmol), potassium hexanoate 2c (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 27.3 mg (56%) of 3kc as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.87 – 7.79 (m, 3H), 7.78 (s, 1H), 7.52 – 7.47 (m, 2H), 7.46 (d, J = 8.3 Hz, 1H), 5.59 (ddd, J = 47.7, 7.8, 5.2 Hz, 1H), 2.12 – 2.00 (m, 1H), 1.95 – 1.84 (m, 1H), 1.54 – 1.43 (m, 1H), 1.41 – 1.23 (m, 7H), 0.88 (t, J = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 137.94 (d, J = 19.7 Hz), 133.15, 133.03, 128.26, 128.04, 127.69, 126.25, 126.12, 124.68 (d, J = 8.1 Hz), 123.31 (d, J = 5.7 Hz), 94.88 (d, J = 170.3 Hz), 37.16 (d, J = 23.5 Hz), 31.68, 29.05, 25.07 (d, J = 4.3 Hz), 22.56. ¹⁹F NMR (564 MHz, CDCl₃) δ -173.76 – -173.98 (m). HRMS
(1-Fluoropropane-1,1-diyl)dibenzene (3lb). The representative procedure was followed using ethene-1,1-diylidibenzene 11 (36 mg, 0.2 mmol), potassium acetate 2b (59 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 18.4 mg (43%) of 3lb as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.46 – 7.40 (m, 4H), 7.38 – 7.31 (m, 4H), 7.24 – 7.22 (m, 2H), 2.33 (q, J = 7.3 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 149.54, 130.78, 129.42, 128.76, 81.12, 37.09, 10.84. ¹⁹F NMR (564 MHz, CDCl₃) δ -152.29 (t, J = 24.5 Hz). HRMS (EI⁺) calcd for [C₁₇H₂₁F⁺]⁺ ([M⁺]): 244.1627, found: 244.1622.

1-Bromo-4-(2-fluorobutoxy)benzene (3mb). The representative procedure was followed using 1-(allyloxy)-4-bromobenzene 1m (43 mg, 0.2 mmol), potassium acetate 2b (59 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), KHCO₃ (20 mg, 0.2 mmol), in CH₂CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 20.7 mg (42%) of 3mb as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H), 4.84 – 4.66 (m, 1H), 4.10 – 3.98 (m, 2H), 1.84 – 1.74 (m, 2H), 1.05 (t, J = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.70, 132.33, 116.46, 113.40, 92.91 (d, J = 17.25 Hz), 69.69 (d, J = 23.6 Hz), 24.68 (d, J = 21.1 Hz), 9.21 (d, J = 5.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -187.41 – -187.85 (m). HRMS (EI⁺) calcd for [C₁₀H₁₂F⁺][BrFO]⁺ ([M⁺]): 246.0056, found: 246.0050.

(2-Fluoroctyl)benzene (3nc). The representative procedure was followed using allylbenzene 1n (23 mg, 0.2 mmol), potassium hexanoate 2c (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), KHCO₃ (20 mg, 0.2 mmol), in CH₂CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 19.6 mg (47%) of 3nc as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.32 – 7.30 (m, 2H), 7.25 – 7.22 (m, 3H), 4.74 – 4.58 (m, 1H), 3.04 – 2.78 (m, 2H), 1.69 – 1.47 (m, 4H), 1.33 – 1.23 (m, 6H), 0.88 (t, J = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 137.49 (d, J = 4.5 Hz), 129.35, 128.37, 126.46, 94.62 (d, J = 170.7 Hz), 41.66 (d, J = 21.7 Hz), 34.63, 31.71, 29.08, 25.06 (d, J = 4.3 Hz), 22.55, 14.04. ¹⁹F NMR (564 MHz, CDCl₃) δ -167.58 – -179.99 (m). HRMS (EI⁺) calcd for [C₁₄H₂₁F⁺]⁺ ([M⁺]): 208.1627, found: 208.1622.
9. Reference

10. Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra
$^{1}H$ NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (600 MHz, CDCl$_3$)
\[3\text{ac}\]

$^1\text{H}$ NMR (564 MHz, CDCl$_3$)

\[3\text{bc}\]

$^1\text{H}$ NMR (600 MHz, CDCl$_3$)
$^{1}H$ NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)

S24
$3cc$

$^{13}C$ NMR (151 MHz, CDCl$_3$)

$^{19}F$ NMR (564 MHz, CDCl$_3$)
$^{1}H$ NMR (600 MHz, CDCl$_3$)

$^{13}C$ NMR (151 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

3mb

Br

$^{13}$C NMR (101 MHz, CDCl$_3$)

3mb

Br