Supporting Information

For

Cyanofluorination of vinyl ethers enabled by electron
donor-acceptor complexes

Jia-Li Liu,* Ze-Fan Zhu* and Feng Liu* a,b

aJiangsu Key Laboratory of Neuropsychiatric Diseases and Department of Medicinal Chemistry, College of Pharmaceutical Sciences, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People’s Republic of China.
E-mail: flu2@suda.edu.cn

bKey Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People’s Republic of China.

Table of Contents

1. General remarks S2
2. Synthesis of vinyl ethers S2
3. Typical experimental procedures S3
4. References for known products S5
5. Characterization of the substrates and products S5
6. NMR Spectra for the substrates and products S16
1. General remarks

$^1$H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for $^{13}$C NMR, 564 MHz for $^{19}$F NMR) agilent NMR spectrometer with CDCl$_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the CDCl$_3$ at 7.26 ppm (for $^1$H NMR) or 77.16 ppm (for $^{13}$C NMR). $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ at δ 0.00 ppm. HRMS was recorded on a GCT Premier$^\text{TM}$ (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, $\nu_{\text{max}}$ in cm$^{-1}$. Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates were readily prepared according to known methods. (Angew. Chem., Int. Ed. 2011, 50, 12605; Org. Process. Res. Dev. 2016, 20, 1203; J. Org. Chem. 1995, 60, 1880.)

2. Synthesis of vinyl ethers

Synthetic Scheme:

Typical synthetic procedures:

1: Ketone (0.98 g, 5 mmol), (MeO)$_3$CH (0.8 g, 7.5 mmol), and H$_2$SO$_4$ (40 μL, 3.44 mmol) in MeOH (1 mL) were stirred at 40 °C for 2 h. Et$_3$N (9 mL) was added, and the solution was poured into Et$_2$O (10 mL), washed with saturated NaHCO$_3$ solution (40 mL × 2), and dried over MgSO$_4$. After evaporation of the solvent, the resulting crude material (1.09 g) was used for the next step without further purification.

Acetal (1.09 g, 4.5 mmol), pyridine (2 mL), TMSCl (3.59 g, 33 mmol), and PhCO$_2$H (50 mg, 0.4 mmol) were heated at 65 °C for 2 h. After cooling to the room temperature, 15% NaOH solution (2 mL) was added and the mixture was extracted with Et$_2$O (10 mL × 3). The combined organic phases were washed with saturated NaHCO$_3$ solution (10 mL × 2), dried over MgSO$_4$, and evaporated under reduced pressure. The residue was purified by flash column chromatography with petroleum ether on Al$_2$O$_3$ to afford 0.66 g (3.2 mmol, 70%) of 1a as a colorless oil. (Angew. Chem. Int. Ed. 2011, 50, 12605; J. Org. Chem. 1995, 60, 1880.)
2: A solution of 4-bromobenzonitrile (0.91 g, 5 mmol), DIPEA (2 mL, 15 mmol), Pd(OAc)$_2$ (25 mg, 2 mol%), DPEDhos (65 mg, 2.4 mol%) and $n$-Butyl vinyl ether in $n$-BuOH was stirred at 95 °C for 1 h. The solution was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 200:1 to 100:1) to afford 0.54 g (2.7 mmol, 54%) of 1u as a colorless oil. (Org. Process. Res. Dev. 2016, 20, 1203.)

3. Typical experimental procedures

To a mixture of vinyl ether 1a (42 mg, 0.2 mmol) and TMS-CN (0.5 ml, 4.0 mmol) was stirred for 10 minutes and then added Selectfluor (106.3 mg, 0.3 mmol) at rt under argon atmosphere. The resulting mixture was stirred for 1.5 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 75:1) to give 2a as a white solid (92% yield, 47 mg).

Procedures for control experiment: (1) To a mixture of vinyl ether 1a (42 mg, 0.2 mmol) and TMS-CN (0.5 mL, 4.0 mmol) was added Selectfluor (106.3 mg, 0.3 mmol) and TEMPO (62.5 mg, 0.4 mmol) at rt under argon atmosphere. The resulting mixture was stirred for 8 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 150:1 to 75:1) to give 2a (32% yield, 16 mg) and 4 as a white solid (46% yield, 36 mg).
Procedures for synthesis of dimerized products: To a solution of vinyl ether 1 (0.2 mmol) and TMS-CN (53 μl, 0.4 mmol) in CH₃CN (2 mL) was added Selectfluor (43 mg, 0.12 mmol) at rt under argon atmosphere. The resulting mixture was stirred for 3 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 50:1) to give 3a/b/c as a white solid (the major isomer, ca. 50% yield). However, we can’t isolate the other isomer from the resulting messy mixture.

2,4-Di([1,1′-biphenyl]-4-yl)-5-fluoro-2,4-dimethoxypentanenitrile (3a): One isomer; White solid; m.p. 54-56 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.63 – 7.55 (m, 8H), 7.51 (d, J = 8.3 Hz, 2H), 7.47 – 7.41 (m, 6H), 7.40 – 7.34 (m, 2H), 4.99 (dd, J = 46.2, 10.2 Hz), 4.86 (dd, J = 48.0, 10.3 Hz), 3.24 (s, 3H), 3.16 (s, 3H), 2.83 (d, J = 15.1 Hz), 2.56 (d, J = 15.2 Hz), 1H; ¹³C NMR (150 MHz, CDCl₃) δ 142.2, 141.1, 140.1, 137.4 (d, J_C-F = 3.4 Hz), 136.6, 129.0, 128.9, 127.9, 127.54, 127.52, 127.25, 127.24, 127.20, 126.7, 117.1, 84.0 (d, J_C-F = 178.0 Hz), 79.0, 78.98 (d, J_C-F = 16.8 Hz), 53.5, 51.4, 49.5 (d, J_C-F = 4.2 Hz); ¹⁹F NMR (564 MHz, CDCl₃) δ -226.67 (t, J = 47.1 Hz); FT-IR (thin film, KBr): ν (cm⁻¹) 3028, 2935, 2831, 1481, 732; HRMS (CI) calcd C₃₁H₂₉FNO₂ [M + H]⁺: 466.2182, found: 466.2180.

5-Fluoro-2,4-bis(4-iodophenyl)-2,4-dimethoxypentanenitrile (3b): One isomer; White solid; m.p. 69-71 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.66 (m, 4H), 7.10 (d, J = 8.3 Hz), 4.92 – 4.62 (m, 2H), 3.17 (s, 3H), 3.08 (s, 3H), 2.61 (d, J = 15.1 Hz), 2.39 (d, J = 15.1 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 138.2 (d, J_C-F = 3.6 Hz), 138.1, 137.7, 137.5, 129.0, 128.0, 116.5, 95.3, 94.3, 83.9 (d, J_C-F = 179.4 Hz), 78.8 (d, J_C-F = 17.1 Hz), 87.8, 53.6, 51.4 (d, J_C-F = 2.6 Hz), 49.0 (d, J_C-F = 4.4 Hz); ¹⁹F NMR (564 MHz, CDCl₃) δ -226.38 (t, J = 47.1 Hz); FT-IR (thin film, KBr); ν (cm⁻¹) 2929, 2831, 1483, 995, 814; HRMS (CI) calcd C₁₉H₁₉FI₂NO₂ [M + H]⁺: 565.9489, found: 565.9476.

5-Fluoro-2,4-dimethoxy-2,4-bis(4-(phenylethynyl)phenyl)pentanenitrile (3c): One isomer; White solid; m.p. 124-126 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.59 – 7.51 (m, 8H), 7.45 (d, J = 8.4 Hz), 7.39 (d, J = 8.3 Hz), 7.37 – 7.33 (m, 6H), 4.89 (dd, J = 46.3, 10.3 Hz), 4.76 (dd, J = 47.7, 10.3 Hz), 3.20 (s, 3H), 3.12 (s, 3H), 2.70 (d, J = 15.2 Hz), 2.47 (d, J = 15.2 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 138.7 (d, J_C-F = 3.5 Hz), 137.7, 132.1, 131.81, 131.78, 128.7, 128.54, 128.48, 128.46, 127.2, 126.3, 124.6, 123.4, 123.3, 123.0, 116.7, 90.8, 90.1, 89.2, 88.5, 84.1 (d, J_C-F = 3.5 Hz).
178.9 Hz), 79.0 (d, $J_{C,F} = 17.0$ Hz), 78.9, 53.6, 51.4 (d, $J_{C,F} = 2.4$ Hz), 49.1 (d, $J = 4.2$ Hz); $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -226.38 (t, $J = 47.0$ Hz, 1F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2956, 2828, 1504, 751, 683; HRMS (CI) calcd C$_{35}$H$_{29}$FNO$_2$ [M + H]$^+$: 514.2182, found: 514.2183.

4. References for known products

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reference</th>
<th>Compound</th>
</tr>
</thead>
</table>

5. Characterization of the substrates and products

4-(1-Methoxyvinyl)-1,1'-biphenyl (1a): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 8.0$ Hz, 2H), 7.67 – 7.57 (m, 4H), 7.46 (t, $J = 7.4$ Hz, 2H), 7.37 (t, $J = 7.2$ Hz, 1H), 4.74 (d, $J = 1.6$ Hz, 1H), 4.28 (s, 1H), 3.79 (s, 3H).

(1-Methoxyvinyl)benzene (1b): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 (d, $J = 6.7$ Hz, 2H), 7.37 – 7.29 (m, 3H), 4.66 (d, $J = 2.4$ Hz, 1H), 4.22 (d, $J = 2.3$ Hz, 1H), 3.75 (s, 3H).

1-Fluoro-4-(1-methoxyvinyl)benzene (1c): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 4.64 (d, $J = 2.6$ Hz, 1H), 4.23 (d, $J = 2.6$ Hz, 1H), 3.74 (s, 3H).

1-Bromo-4-(1-methoxyvinyl)benzene (1d): $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.47 – 7.42 (m, 4H), 4.63 (d, $J = 3.0$ Hz, 1H), 4.21 (d, $J = 3.0$ Hz, 1H), 3.70 (s, 3H).
1-Iodo-4-(1-methoxyvinyl)benzene (1e): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.3$ Hz, 2H), 4.66 (d, $J = 2.7$ Hz, 1H), 4.23 (d, $J = 2.6$ Hz, 1H), 3.73 (s, 3H).

1-(1-Methoxyvinyl)-4-methylbenzene (1f): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 7.9$ Hz, 2H), 4.66 (d, $J = 2.2$ Hz, 1H), 4.21 (d, $J = 2.1$ Hz, 1H), 3.77 (s, 3H), 2.39 (s, 3H).

1-Methoxy-4-(1-methoxyvinyl)benzene (1g): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 4.55 (d, $J = 2.4$ Hz, 1H), 4.14 (d, $J = 2.3$ Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H).

1-(1-Methoxyvinyl)-4-(trifluoromethyl)benzene (1h): $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 8.3$ Hz, 2H), 7.60 (d, $J = 8.3$ Hz, 2H), 4.76 (d, $J = 3.1$ Hz, 1H), 4.34 (d, $J = 3.1$ Hz, 1H), 3.77 (s, 3H).

1-(1-Methoxyvinyl)-4-nitrobenzene (1i): $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J = 8.8$ Hz, 2H), 7.76 (d, $J = 8.8$ Hz, 2H), 4.83 (d, $J = 3.4$ Hz, 1H), 4.42 (d, $J = 3.4$ Hz, 1H), 3.77 (s, 3H).

S6
1-Chloro-3-(1-methoxyvinyl)benzene (1j): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (s, 1H), 7.49 (d, $J = 6.8$ Hz, 1H), 7.31 – 7.22 (m, 2H), 4.67 (d, $J = 2.7$ Hz, 1H), 4.25 (d, $J = 2.7$ Hz, 1H), 3.73 (s, 3H).

1-(1-Methoxyvinyl)-3-methylbenzene (1k): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 – 7.34 (m, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.11 (d, $J = 6.7$ Hz, 1H), 4.63 (s, 1H), 4.19 (s, 1H), 3.73 (s, 3H), 2.35 (s, 3H).

1-Bromo-2-(1-methoxyvinyl)benzene (1l): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 7.9$ Hz, 1H), 7.39 (d, $J = 7.4$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.18 (t, $J = 7.2$ Hz, 1H), 4.41 (s, 1H), 4.31 (s, 1H), 3.73 (s, 3H).

1-Methoxy-2-(1-methoxyvinyl)benzene (1m): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 7.5$ Hz, 1H), 7.30 (t, $J = 11.4$, 4.2 Hz, 1H), 7.05 – 6.87 (m, 2H), 4.66 (d, $J = 1.6$ Hz, 1H), 4.46 (d, $J = 1.4$ Hz, 1H), 3.87 (s, 3H), 3.74 (s, 3H).

1-(1-Methoxyvinyl)-2-(trifluoromethyl)benzene (1n): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J = 7.7$ Hz, 1H), 7.54 – 7.40 (m, 3H), 4.36 (s, 1H), 4.28 (d, $J = 1.9$ Hz, 1H), 3.72 (s, 3H).

2-(1-Methoxyvinyl)naphthalene (1o): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (s, 1H), 7.93 – 7.87 (m, 1H), 7.86 – 7.80 (m, 2H), 7.76 (d, $J = 8.6$ Hz, 1H), 7.54 – 7.42 (m, 2H), 4.86 (d, $J = 2.1$ Hz, 1H), 4.37 (d, $J = 2.1$ Hz, 1H), 3.84 (s, 3H).
1-(1-Methoxyvinyl)-4-(phenylethynyl)benzene (1p): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 (d, $J = 8.2$ Hz, 2H), 7.60 – 7.48 (m, 4H), 7.43 – 7.30 (m, 3H), 4.73 (d, $J = 2.6$ Hz, 1H), 4.29 (d, $J = 2.5$ Hz, 1H), 3.77 (s, 3H).

2-(1-Methoxyvinyl)thiophene (1q): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 – 7.17 (m, 2H), 6.99 – 6.93 (m, 1H), 4.63 (d, $J = 2.8$ Hz, 1H), 4.16 (d, $J = 2.8$ Hz, 1H), 3.71 (s, 3H).

4-Methoxy-1,2-dihyronaphthalene (1r): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, $J = 7.1$ Hz, 1H), 7.25 – 7.11 (m, 3H), 5.01 (t, $J = 4.4$ Hz, 1H), 3.73 (s, 3H), 2.78 (t, $J = 7.8$ Hz, 2H), 2.40 – 2.32 (m, 2H).

1-(1-Methoxyprop-1-en-1-yl)-4-methylbenzene (1s): Two isomers (1:1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.19 (m, 4H), 5.37 (q, $J = 6.8$ Hz, 1H)/4.82 (q, $J = 7.0$ Hz, 1H), 3.66 (s, 3H)/3.58 (s, 3H), 2.40 (s, 3H)/2.39 (s, 3H), 1.83 (d, $J = 6.9$ Hz, 3H)/1.74 (d, $J = 7.0$ Hz, 3H).

1-(1-Ethoxyvinyl)-4-nitrobenzene (1t): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.17 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 4.81 (s, 1H), 4.39 (s, 1H), 3.94 (q, $J = 6.8$ Hz, 2H), 1.44 (t, $J = 6.8$ Hz, 3H).
4-(1-Butoxyvinyl)benzonitrile (1u): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 8.3$ Hz, 2H), 7.61 (d, $J = 8.3$ Hz, 2H), 4.75 (d, $J = 2.8$ Hz, 1H), 4.35 (d, $J = 2.8$ Hz, 1H), 3.86 (t, $J = 6.3$ Hz, 2H), 1.89 – 1.68 (m, 2H), 1.55 – 1.45 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H).

\[
\text{\begin{tikzpicture}
\draw[black, very thick] (0,0) -- (0.5,0);
\draw[black, very thick] (0,0) -- (0,0.5);
\draw[black, very thick] (0.5,0) -- (0.5,0.5);
\draw[black, very thick] (0.5,0.5) -- (0,0.5);
\end{tikzpicture}}
\]

(1-Methoxy-2-methylprop-1-en-1-yl)benzene (1v): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.14 (m, 5H), 3.23 (s, 3H), 1.77 (s, 3H), 1.59 (s, 3H).

2-([1,1’-Biphenyl]-4-yl)-3-fluoro-2-methoxypropanenitrile (2a): White solid; m.p. 55-57 °C; 92% yield (47 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 (d, $J = 8.1$ Hz, 2H), 7.67 – 7.57 (m, 4H), 7.48 (t, $J = 7.4$ Hz, 2H), 7.41 (t, $J = 7.2$ Hz, 1H), 4.65 (dd, $J = 47.2$, 9.6 Hz, 1H), 4.50 (dd, $J = 46.6$, 9.6 Hz, 1H), 3.45 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 143.4, 139.9, 131.1 (d, $J_{C-F} = 2.4$ Hz), 129.1, 128.1, 128.0, 127.3, 127.1, 116.1 (d, $J_{C-F} = 2.2$ Hz), 86.2 (d, $J_{C-F} = 190.8$ Hz), 80.90 (d, $J_{C-F} = 18.8$ Hz), 54.6; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -217.58 (t, $J = 46.8$ Hz, 1F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2959, 2834, 1480, 1049, 763; HRMS (CI) calcd C$_{18}$H$_{15}$FNO [M + H]$^+$: 256.1138, found: 256.1135.

\[
\text{\begin{tikzpicture}
\draw[black, very thick] (0,0) -- (0.5,0);
\draw[black, very thick] (0,0) -- (0,0.5);
\draw[black, very thick] (0.5,0) -- (0.5,0.5);
\draw[black, very thick] (0.5,0.5) -- (0,0.5);
\end{tikzpicture}}
\]

3-Fluoro-2-methoxy-2-phenylpropanenitrile (2b): Colorless oil; 70% yield (25 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 – 7.53 (m, 2H), 7.50 – 7.46 (m, 3H), 4.59 (dd, $J = 47.2$, 9.6 Hz, 1H), 4.44 (dd, $J = 46.5$, 9.6 Hz, 1H), 3.40 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 132.3, 130.4, 129.4, 126.6, 116.1 (d, $J_{C-F} = 2.1$ Hz), 86.2 (d, $J_{C-F} = 190.8$ Hz), 81.1 (d, $J_{C-F} = 18.8$ Hz), 54.6; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -217.58 (t, $J = 46.8$ Hz, 1F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2962, 2837, 1447, 1049, 695; HRMS (CI) calcd C$_{10}$H$_{10}$FNO [M]$: 179.0746, found: 179.0743.

\[
\text{\begin{tikzpicture}
\draw[black, very thick] (0,0) -- (0.5,0);
\draw[black, very thick] (0,0) -- (0,0.5);
\draw[black, very thick] (0.5,0) -- (0.5,0.5);
\draw[black, very thick] (0.5,0.5) -- (0,0.5);
\end{tikzpicture}}
\]

3-Fluoro-2-(4-fluorophenyl)-2-methoxypropanenitrile (2c): Colorless oil; 82% yield (32 mg); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.56 – 7.51 (m, 2H), 7.19 – 7.14 (m, 2H), 4.58 (dd, $J = 47.1$, 9.6 Hz, 1H), 4.43 (dd, $J = 46.5$, 9.6 Hz, 1H), 3.40 (s, 3H); $^{13}$C
NMR (150 MHz, CDCl3) δ 163.8 (d, JCF = 250.4 Hz), 128.7 (d, JCF = 8.6 Hz), 128.3 (t, JCF = 2.7 Hz), 116.5 (d, JCF = 22.1 Hz), 116.0 (d, JCF = 2.2 Hz), 86.1 (d, JCF = 190.7 Hz), 80.5 (d, JCF = 19.2 Hz), 54.5; 19F NMR (564 MHz, CDCl3) δ -110.46 – -110.53 (m, 1F), -218.11 (t, J = 46.7 Hz, 1F); FT-IR (thin film, KBr): ν (cm⁻¹) 2923, 2852, 1301, 1141, 1034; HRMS (CI) calcd C₁₀H₁₀F₂NO [M + H]⁺: 198.0730, found: 198.0731.

2-(4-Bromophenyl)-3-fluoro-2-methoxypropanenitrile (2d): Colorless oil; 93% yield (48 mg); 1H NMR (600 MHz, CDCl3) δ 7.61 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 4.57 (dd, J = 47.0, 9.6 Hz, 1H), 4.42 (dd, J = 46.4, 9.6 Hz, 1H), 3.40 (s, 3H); 13C NMR (150 MHz, CDCl3) δ 132.6, 131.6 (d, JCF = 2.1 Hz), 128.3, 124.8, 115.7 (d, JCF = 2.4 Hz), 85.9 (d, JCF = 190.8 Hz), 80.5 (d, JCF = 19.4 Hz), 54.6; 19F NMR (564 MHz, CDCl3) δ -218.48 (t, J = 46.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm⁻¹) 2959, 2837, 1486, 1049, 820; HRMS (CI) calcd C₁₀H₁₀BrFNO [M + H]⁺: 257.9930, found: 257.9927.

3-Fluoro-2-(4-iodophenyl)-2-methoxypropanenitrile (2e): Colorless oil; 85% yield (52 mg); 1H NMR (600 MHz, CDCl3) δ 7.82 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 4.57 (dd, J = 47.0, 9.6 Hz, 1H), 4.42 (dd, J = 46.4, 9.6 Hz, 1H), 3.40 (s, 3H); 13C NMR (150 MHz, CDCl3) δ 138.5, 132.3 (d, JCF = 2.4 Hz), 128.4, 115.7 (d, JCF = 2.5 Hz), 96.6, 85.8 (d, JCF = 190.8 Hz), 80.6 (d, JCF = 19.4 Hz), 54.6; 19F NMR (564 MHz, CDCl3) δ -218.44 (t, J = 46.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm⁻¹) 2960, 2834, 1391, 1052, 813; HRMS (CI) calcd C₁₀H₁₀INO [M + H]⁺: 305.9791, found: 305.9792.

3-Fluoro-2-methoxy-2-(p-tolyl)propanenitrile (2f): Colorless oil; 87% yield (34 mg); 1H NMR (400 MHz, CDCl3) δ 7.42 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 4.57 (dd, J = 47.3, 9.7 Hz, 1H), 4.41 (dd, J = 46.6, 9.6 Hz, 1H), 3.37 (s, 3H), 2.39 (s, 3H); 13C NMR (150 MHz, CDCl3) δ 140.5, 130.0, 129.2 (d, JCF = 2.8 Hz), 126.5, 116.2 (d, JCF = 2.1 Hz), 86.2 (d, JCF = 190.6 Hz), 80.9 (d, JCF = 18.6 Hz), 54.3, 21.2; 19F NMR (564 MHz, CDCl3) δ -217.25 (t, J = 46.9 Hz, 1F); FT-IR (thin film, KBr): ν (cm⁻¹) 2974, 2902, 1046, 639, 617; HRMS (CI) calcd C₁₁H₁₃FNO [M + H]⁺: 194.0981,
3-Fluoro-2-methoxy-2-(4-methoxyphenyl)propanenitrile (2g): Colorless oil; 91% yield (38 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, \(J = 8.6\) Hz, 2H), 6.98 (d, \(J = 8.6\) Hz, 2H), 4.57 (dd, \(J = 47.3, 9.6\) Hz, 1H), 4.40 (dd, \(J = 46.6, 9.6\) Hz, 1H), 3.83 (s, 3H), 3.36 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.1, 128.0, 123.9 (d, \(J_{C-F} = 3.1\) Hz), 116.3 (d, \(J_{C-F} = 2.3\) Hz), 114.7, 86.2 (d, \(J_{C-F} = 190.7\) Hz), 80.7 (d, \(J_{C-F} = 18.7\) Hz), 55.5, 54.2; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -216.99 (t, \(J = 47.0\) Hz, 1F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2962, 2840, 1513, 1251, 837; HRMS (CI) calcd C\(_{11}\)H\(_{13}\)FNO\(_2\) [M + H]\(^+\): 210.0930, found: 210.0934.

3-Fluoro-2-methoxy-2-(4-(trifluoromethyl)phenyl)propanenitrile (2h): Colorless oil; 70% yield (35 mg); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J = 8.3\) Hz, 2H), 7.70 (d, \(J = 8.2\) Hz, 2H), 4.62 (dd, \(J = 46.9, 9.5\) Hz, 1H), 4.47 (dd, \(J = 46.3, 9.5\) Hz, 1H), 3.43 (s, 3H); \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 136.7, 132.7 (q, \(J_{C-F} = 32.9\) Hz), 127.2, 126.4 (dd, \(J_{C-F} = 7.2, 3.5\) Hz), 123.7 (q, \(J_{C-F} = 269.2\) Hz), 115.6 (d, \(J_{C-F} = 2.6\) Hz), 85.9 (d, \(J_{C-F} = 190.8\) Hz), 80.5 (d, \(J_{C-F} = 19.7\) Hz), 54.9; \(^19\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -63.02 (s, 3F), -219.29 (t, \(J = 46.6\) Hz, 1F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2941, 2837, 1319, 1123, 840; HRMS (CI) calcd C\(_{11}\)H\(_9\)F\(_4\)NO \([M]\)^+: 247.0620, found: 247.0627.

3-Fluoro-2-methoxy-2-(4-nitrophenyl)propanenitrile (2i): Colorless oil; 90% yield (40 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.34 (d, \(J = 8.5\) Hz, 2H), 7.77 (d, \(J = 8.5\) Hz, 2H), 4.64 (dd, \(J = 46.7, 9.5\) Hz, 1H), 4.49 (dd, \(J = 46.3, 9.5\) Hz, 1H), 3.46 (s, 3H); \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 149.2, 139.6 (d, \(J_{C-F} = 1.4\) Hz), 127.9, 124.5, 115.3 (d, \(J_{C-F} = 2.8\) Hz), 85.6 (d, \(J_{C-F} = 190.7\) Hz), 80.2 (d, \(J_{C-F} = 20.3\) Hz), 55.0; \(^19\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -220.20 (t, \(J = 46.4\) Hz, 1F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2923, 2849, 1519, 1034, 855; HRMS (CI) calcd C\(_{10}\)H\(_{10}\)FN\(_2\)O\(_3\) [M + H]\(^+\): 225.0675, found: 225.0672.
2-(3-Chlorophenyl)-3-fluoro-2-methoxypropanenitrile (2j): Colorless oil; 86% yield (37 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 (s, 1H), 7.47 – 7.36 (m, 3H), 4.59 (dd, $J = 47.0$, 9.6 Hz, 1H), 4.44 (dd, $J = 46.4$, 9.6 Hz, 1H), 3.42 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 135.6, 134.6, 130.7, 130.6, 126.7, 124.9, 115.6 (d, $J_{C-F} = 2.4$ Hz), 85.9 (d, $J_{C-F} = 190.8$ Hz), 80.4 (d, $J_{C-F} = 19.4$ Hz), 54.7; $^{19}$F NMR (564 MHz, CDCl$_3$) δ -218.54 (t, $J = 46.7$ Hz, 1F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2962, 2837, 1058, 790, 698; HRMS (CI) calcd C$_{10}$H$_{10}$F$_3$ClNO [M + H]$^+$: 214.0435, found: 214.0439.

3-Fluoro-2-methoxy-2-(m-tolyl)propanenitrile (2k): Colorless oil; 90% yield (35 mg); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.41 – 7.30 (m, 3H), 7.27 (d, $J = 7.7$ Hz, 1H), 4.58 (dd, $J = 47.3$, 9.6 Hz, 1H), 4.42 (dd, $J = 46.5$, 9.6 Hz, 1H), 3.39 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 139.3, 132.1 (d, $J_{C-F} = 2.4$ Hz), 131.1, 129.2, 127.1, 123.6, 116.2 (d, $J_{C-F} = 2.1$ Hz), 86.3 (d, $J_{C-F} = 190.7$ Hz), 81.1 (d, $J_{C-F} = 18.6$ Hz), 54.5, 21.6; $^{19}$F NMR (564 MHz, CDCl$_3$) δ -217.33 (t, $J = 46.9$ Hz, 1F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2959, 2831, 1049, 784, 698; HRMS (CI) calcd C$_{11}$H$_{12}$FNO [M]$^+$: 193.0903, found: 193.0906.

2-(2-Bromophenyl)-3-fluoro-2-methoxypropanenitrile (2l): Colorless oil; 89% yield (46 mg); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, $J = 7.8$ Hz, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.31 (t, $J = 7.5$ Hz, 1H), 4.85 (dd, $J = 46.3$, 9.5 Hz, 1H), 4.79 (dd, $J = 46.7$, 9.5 Hz, 1H), 3.49 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.0, 131.7, 130.8 (d, $J_{C-F} = 0.6$ Hz), 130.0 (d, $J_{C-F} = 3.0$ Hz), 128.2, 120.6, 115.1 (d, $J_{C-F} = 3.0$ Hz), 83.5 (d, $J_{C-F} = 188.7$ Hz), 81.6 (d, $J_{C-F} = 19.7$ Hz), 54.6; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -220.57 (t, $J = 46.5$ Hz, 1F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2965, 2843, 1257, 1084, 614; HRMS (CI) calcd C$_{10}$H$_{9}$BrFNO [M]$^+$: 256.9852, found: 256.9859.

3-Fluoro-2-methoxy-2-(2-methoxyphenyl)propanenitrile (2m): Colorless oil; 80%
yield (33 mg); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J$ = 7.6 Hz, 1H), 7.41 (t, $J$ = 7.7 Hz, 1H), 7.05 (t, $J$ = 7.5 Hz, 1H), 6.99 (d, $J$ = 8.2 Hz, 1H), 4.76 (dd, $J$ = 46.9, 9.5 Hz, 1H), 4.55 (dd, $J$ = 47.3, 9.5 Hz, 1H), 3.92 (s, 3H), 3.56 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 157.0, 131.5, 128.1, 121.2, 119.7 (d, $J_{C-F}$=3.4 Hz), 115.6 (d, $J_{C-F}$ = 3.3 Hz), 112.3, 84.3 (d, $J_{C-F}$ = 188.6 Hz), 78.3 (d, $J_{C-F}$ = 18.8 Hz), 55.9, 54.9; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -219.28 (t, $J$ = 47.1 Hz, 1F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2974, 2849, 1031, 1016, 766; HRMS (CI) calcd C$_{11}$H$_{12}$FNO$_2$ [M]$^+$: 209.0852, found: 209.0861.

3-Fluoro-2-methoxy-2-(2-(trifluoromethyl)phenyl)propanenitrile (2n): Colorless oil; 67% yield (33 mg); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J$ = 7.9 Hz, 1H), 7.88 (d, $J$ = 7.9 Hz, 1H), 7.68 (t, $J$ = 7.7 Hz, 1H), 7.60 (t, $J$ = 7.7 Hz, 1H), 4.79 (dd, $J$ = 46.7, 9.6 Hz, 1H), 4.62 (dd, $J$ = 46.2, 9.6 Hz, 1H), 3.50 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 132.6, 131.2, 130.9, 130.6, 129.2 (q, $J_{C-F}$ = 6.7 Hz), 128.3 (q, $J_{C-F}$ = 3.2 Hz), 123.7 (q, $J_{C-F}$ = 273.4 Hz), 115.8 (d, $J_{C-F}$ = 1.8 Hz), 85.2 (dq, $J_{C-F}$ = 187.7, 4.0 Hz), 82.4 (d, $J_{C-F}$ = 19.6 Hz), 55.7; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -56.05 (s, 3F), -217.96 (t, $J$ = 46.5 Hz, 1F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2971, 2843, 1129, 1037, 769; HRMS (CI) calcd C$_{11}$H$_{9}$F$_4$NO $[M]^+$: 247.0620, found: 247.0628.

3-Fluoro-2-methoxy-2-(naphthalen-2-yl)propanenitrile (2o): Colorless oil; 88% yield (40 mg); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.12 (s, 1H), 7.96 (d, $J$ = 8.6 Hz, 1H), 7.95 – 7.92 (m, 1H), 7.92 – 7.88 (m, 1H), 7.61 – 7.57 (m, 2H), 7.57 – 7.54 (m, 1H), 4.71 (dd, $J$ = 47.1, 9.7 Hz, 1H), 4.54 (dd, $J$ = 46.4, 9.7 Hz, 1H), 3.44 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 134.0, 133.0, 129.6, 128.5, 127.9, 127.7, 127.4, 127.3, 122.5, 116.2 (d, $J_{C-F}$ = 2.2 Hz), 86.1 (d, $J_{C-F}$ = 190.6 Hz), 81.3 (d, $J_{C-F}$ = 18.9 Hz), 54.6; $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ -217.89 (t, $J$ = 46.5 Hz, 1F); FT-IR (thin film, KBr): $\nu$ (cm$^{-1}$) 2959, 2938, 1046, 817, 748; HRMS (CI) calcd C$_{14}$H$_{12}$FNO $[M]^+$: 229.0903, found: 229.0914.

3-Fluoro-2-methoxy-2-(4-(phenylethynyl)phenyl)propanenitrile (2p): White solid;
m.p. 73-75 °C; 88% yield (49 mg); 1H NMR (600 MHz, CDCl3) δ 7.65 – 7.62 (m, 2H), 7.58 – 7.52 (m, 4H), 7.40 – 7.35 (m, 3H), 4.60 (dd, J = 47.1, 9.6 Hz, 1H), 4.45 (dd, J = 46.4, 9.6 Hz, 1H), 3.42 (s, 3H); 13C NMR (150 MHz, CDCl3) δ 132.4, 132.1 (d, JC-F = 2.3 Hz), 131.8, 128.8, 128.5, 126.6, 125.7, 122.8, 115.9 (d, JC-F = 2.3 Hz), 91.4, 88.2, 86.0 (d, JC-F = 191.0 Hz), 80.8 (d, JC-F = 19.1 Hz), 54.6; 19F NMR (564 MHz, CDCl3) δ -218.07 (t, J = 46.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm⁻¹) 2923, 2858, 1049, 840, 760; HRMS (CI) calcld C18H15FNO [M + H]⁺: 280.1138, found: 280.1142.

3-Fluoro-2-methoxy-2-(thiophen-2-yl)propanenitrile (2q): Colorless oil; 80% yield (30 mg); 1H NMR (600 MHz, CDCl3) δ 7.47 (d, J = 5.1 Hz, 1H), 7.38 (d, J = 3.5 Hz, 1H), 7.08 (t, J = 4.3 Hz, 1H), 4.70 (dd, J = 46.9, 9.5 Hz, 1H), 4.55 (dd, J = 46.3, 9.5 Hz, 1H), 3.42 (s, 3H); 13C NMR (150 MHz, CDCl3) δ 135.7 (d, JC-F = 2.4 Hz), 129.3, 128.6, 127.3, 115.6 (d, JC-F = 2.0 Hz), 86.1 (d, JC-F = 191.3 Hz), 77.5, 54.5; 19F NMR (564 MHz, CDCl3) δ -216.94 (t, J = 46.6 Hz, 1F); FT-IR (thin film, KBr): ν (cm⁻¹) 2920, 2855, 1266, 1025, 801; HRMS (CI) calcld C8H9FNOS [M + H]⁺: 186.0389, found: 186.0390.

2-Fluoro-1-methoxy-1,2,3,4-tetrahydronaphthalene-1-carbonitrile (2r): Colorless oil; 85% yield (35 mg); Two isomers (1:1.1); 1H NMR (600 MHz, CDCl3) δ 7.66 (d, J = 7.6 Hz, 1H), 7.40 – 7.27 (m, 2H), 7.20 (d, J = 7.4 Hz, 1H), 5.20 – 4.98 (m, 1H), 3.51 (s, 1.4H)/3.49 (s, 1.6H), 3.18 – 2.77 (m, 2H), 2.54 – 2.10 (m, 2H); 13C NMR (150 MHz, CDCl3) δ 135.8, 135.4, 130.4, 130.2, 129.8, 129.6 (d, JC-F = 2.1 Hz), 129.42, 129.38, 129.3, 129.1, 126.6, 117.12, 117.08 (d, JC-F = 3.6 Hz), 90.6 (d, JC-F = 192.1 Hz), 90.3 (d, JC-F = 183.1 Hz), 76.7 (d, JC-F = 22.6 Hz), 76.5 (d, JC-F = 18.4 Hz), 54.2 (d, JC-F = 1.5 Hz), 54.1, 26.0 (d, JC-F = 10.5 Hz), 24.3 (d, JC-F = 6.5 Hz), 23.9 (d, JC-F = 19.7 Hz), 22.9 (d, JC-F = 19.5 Hz); 19F NMR (564 MHz, CDCl3) δ -186.06 – -186.39 (m), -188.80 – -189.13 (m); FT-IR (thin film, KBr): ν (cm⁻¹) 2962, 2840, 1450, 1063, 760; HRMS (CI) calcld C12H12FNO [M + H]⁺: 205.0903, found: 205.0913.

3-Fluoro-2-methoxy-2-(p-tolyl)butanenitrile (2s): Colorless oil; 92% yield (38 mg); Two isomers (1:1.2); 1H NMR (600 MHz, CDCl3) δ 7.41 (d, J = 8.1 Hz, 1H)/7.38 (d, J
= 8.1 Hz, 1H), 7.26 (d, J = 7.3 Hz, 2H), 4.80 (dq, J = 47.3, 6.4 Hz, 0.45H)/4.69 (dq, J = 45.9, 6.2 Hz, 0.55H), 3.34 (s, 1.4H)/3.33 (s, 1.6H), 2.39 (s, 3H), 1.53 (dd, J = 24.1, 6.2 Hz, 1.6H)/1.20 (dd, J = 23.6, 6.4 Hz, 1.4H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 140.3, 140.0, 130.6, 129.9, 129.73 (d, \(J_{CF} = 2.3\) Hz), 129.69, 126.9, 126.8, 116.3, 116.0 (d, \(J_{CF} = 2.1\) Hz), 92.6 (d, \(J_{CF} = 187.9\) Hz), 92.4 (d, \(J_{CF} = 182.2\) Hz), 85.1 (d, \(J_{CF} = 18.5\) Hz), 84.2 (d, \(J_{CF} = 24.1\) Hz), 54.4, 54.2, 21.2, 16.2 (d, \(J_{CF} = 22.2\) Hz), 16.0 (d, \(J_{CF} = 22.5\) Hz); \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -177.51 – -177.78 (m), -179.96 – -180.25 (m); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2926, 2858, 1084, 817, 608; HRMS (CI) calcd C\(_{12}\)H\(_{14}\)FNO [M]+: 207.1059, found: 207.1065.

2-Ethoxy-3-fluoro-2-(4-nitrophenyl)propanenitrile (2t): White solid; m.p. 84-86 °C; 98% yield (47 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.32 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 4.64 (dd, J = 46.7, 9.3 Hz, 1H), 4.48 (dd, J = 46.2, 9.3 Hz, 1H), 3.79 (p, J = 7.0 Hz, 1H), 3.44 (p, J = 7.0 Hz, 1H), 1.31 (t, J = 6.8 Hz, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 149.1, 140.4 (d, \(J_{CF} = 1.3\) Hz), 127.8, 124.4, 115.7 (d, \(J_{CF} = 2.7\) Hz), 85.7 (d, \(J_{CF} = 190.5\) Hz), 79.3 (d, \(J_{CF} = 20.4\) Hz), 63.7, 15.0; \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -220.10 (t, J = 46.5 Hz, 1F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2920, 2855, 1513, 1049, 855; HRMS (CI) calcd C\(_{11}\)H\(_{12}\)FN\(_2\)O\(_3\) [M + H]+: 239.0832, found: 239.0841.

4-(1-Butoxy-1-cyano-2-fluoroethyl)benzonitrile (2u): Colorless oil; 80% yield (39 mg); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 4.61 (dd, J = 46.8, 9.4 Hz, 1H), 4.45 (dd, J = 46.3, 9.4 Hz, 1H), 3.69 (d, J = 14.7, 6.6 Hz, 1H), 3.35 (dd, J = 14.8, 6.6 Hz, 1H), 1.71 – 1.58 (m, 2H), 1.46 – 1.32 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 138.6, 133.0, 127.4, 117.9, 115.7 (d, \(J_{CF} = 2.6\) Hz), 114.3, 85.7 (d, \(J_{CF} = 190.4\) Hz), 79.4 (d, \(J_{CF} = 20.2\) Hz), 67.6, 31.4, 19.2, 13.8; \(^{19}\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -218.48 – -220.93 (m, 1F); FT-IR (thin film, KBr): \(\nu\) (cm\(^{-1}\)) 2965, 2878, 2227, 1049, 840; HRMS (CI) calcd C\(_{14}\)H\(_{16}\)FN\(_2\)O [M + H]+: 247.1247, found: 247.1248.

3-Fluoro-2-methoxy-3-methyl-2-phenylbutanenitrile (2v): Colorless oil; 81% yield
(33.6 mg); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.54 – 7.50 (m, 2H), 7.46 – 7.42 (m, 3H), 3.43 (s, 3H), 1.52 (d, $J = 21.6$ Hz, 3H), 1.36 (d, $J = 21.7$ Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 132.7, 129.7, 128.5, 127.9 (d, $J_{CF} = 1.0$ Hz), 117.4 (d, $J_{CF} = 3.2$ Hz), 96.6 (d, $J_{CF} = 183.4$ Hz), 86.7 (d, $J_{CF} = 24.7$ Hz), 55.1, 23.2 (d, $J_{CF} = 23.4$ Hz), 22.5 (d, $J_{CF} = 23.4$ Hz); $^{19}$F NMR (564 MHz, CDCl$_3$) δ -147.03 – -147.31 (m, 1F); FT-IR (thin film, KBr): ν (cm$^{-1}$) 2988, 2943, 1102, 751, 700; HRMS (ESI) calcd C$_{12}$H$_{14}$FNNaO [M + Na]$^+$: 230.0952, found: 230.0946.

5. NMR Spectra for the substrates and products

$^1$H NMR of 1a
$^1$H NMR of 1b

$^1$H NMR of 1c
$^1$H NMR of 1d

$^1$H NMR of 1e
$^1$H NMR of 1f

$^1$H NMR of 1g
$^1$H NMR of 1h

$^1$H NMR of 1i
$^1$H NMR of 1j

$^1$H NMR of 1k
$^1$H NMR of 1l

$^1$H NMR of 1m
$^1$H NMR of 1n

$^1$H NMR of 1o
$^1$H NMR of 1p

$^1$H NMR of 1q
$^1$H NMR of 1r

[Diagram of 1r NMR spectrum]

$^1$H NMR of 1s

[Diagram of 1s NMR spectrum]
$^1$H NMR of 1t

$^1$H NMR of 1u
$^1$H NMR of 1v

$^1$H NMR of 2a

S27
$^{13}$C NMR of 2a

$^{19}$F NMR of 2a
$^1$H NMR of 2b

$^{13}$C NMR of 2b
$^{19}$F NMR of 2b

$^1$H NMR of 2c
$^{13}$C NMR of 2c

$^{19}$F NMR of 2c
$^1$H NMR of 2d

$^{13}$C NMR of 2d
$^{19}$F NMR of 2d

$^1$H NMR of 2e

S33
$^{13}\text{C} \text{ NMR of } 2e$

$^{19}\text{F} \text{ NMR of } 2e$
$^{1}$H NMR of 2f

$^{13}$C NMR of 2f
$^{19}\text{F NMR of } 2f$

$^{1}\text{H NMR of } 2g$
$^{13}$C NMR of 2g

$^{19}$F NMR of 2g
$^1$H NMR of 2h

$^{13}$C NMR of 2h
$^{19}$F NMR of 2h

$^{1}$H NMR of 2i
$^{13}$C NMR of 2i

$^{19}$F NMR of 2i
$^1$H NMR of 2j

$^{13}$C NMR of 2j
$^{19}$F NMR of 2j

$^1$H NMR of 2k
$^{13}$C NMR of 2k

$^{19}$F NMR of 2k
$^1$H NMR of 2l

$^{13}$C NMR of 2l
$^{19}$F NMR of 2l

$^1$H NMR of 2m
$^{13}$C NMR of $2m$

$^{19}$F NMR of $2m$
$^1$H NMR of 2n

$^{13}$C NMR of 2n
$^{19}$F NMR of 2n

$^{1}$H NMR of 2o
$^{13}$C NMR of 2o

$^{19}$F NMR of 2o
$^1$H NMR of 2p

$^{13}$C NMR of 2p
$^{19}$F NMR of 2p

$^1$H NMR of 2q
$^{13}$C NMR of 2q

$^{19}$F NMR of 2q
$^1$H NMR of 2r

$^{13}$C NMR of 2r
$^{19}$F NMR of 2r

$^1$H NMR of 2s
$^{13}$C NMR of 2s

$^{19}$F NMR of 2s
$^1$H NMR of 2t

$^{13}$C NMR of 2t
$^{19}$F NMR of 2t

\[ \text{Structure of 2t} \]

$^1$H NMR of 2u

\[ \text{Structure of 2u} \]
$^{13}$C NMR of 2u

$^{19}$F NMR of 2u
$^{1}H$ NMR of 2v

$^{13}C$ NMR of 2v
$^{19}$F NMR of 2v

$^1$H NMR of 3a
$^{13}$C NMR of 3a

$^{19}$F NMR of 3a
$^1$H NMR of 3b

$^{13}$C NMR of 3b
$^{19}$F NMR of 3b

$^1$H NMR of 3c
$^{13}$C NMR of 3c

$^{19}$F NMR of 3c