Supporting Information

Nickel-Catalyzed Monofluoromethylation of (Hetero)aryl Bromides via Reductive Cross-coupling

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General Information

NMR spectra were recorded on Bruker-400 (400 MHz for $^1$H, 101 MHz for $^{13}$C and 376 MHz for $^{19}$F { $^1$H, $^{13}$C decoupled}) instruments internally referenced to SiMe$_4$ signal. High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight) or Micromass GCT using EI (electron impact). Anhydrous DMAC was obtained from Infsci. BrCH$_2$F was obtained from ShangFluoro. NiI$_2$ was obtained from Strem. Substrates 1a and 1c were obtained from Adamas-beta. DMAP and substrate 1e were obtained from SCR. Substrates 1d, 1h and 1m were obtained from Accela. Substrates 1b, 1f, 1g, 1u and 1ac were obtained from Energy. Substrates 1l, 1k, 1l, 1p, 1q, 1s, 1t, 1v, 1x and 1aa were obtained from Bidepharm. Substrates 1r and 1z were obtained from Leyan. Dtbpy and substrate 1n were obtained from J&K. Substrate 1o was obtained from Macklin. Mn powder and substrate 1ad were obtained from Aladdin. Substrate 1y was obtained from AikonChem. All reagents were used as received without further purification.
Tables of the Optimization of Reaction Conditions

Table S1. Ligands Screening<sup>a</sup>

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<th>Entry</th>
<th>Ligand (x mol%)</th>
<th>Yield(%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Entry</th>
<th>Ligands (x mol%)</th>
<th>Yield(%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>dmbpy(12)/PPh&lt;sub&gt;3&lt;/sub&gt;(24)</td>
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<sup>a</sup> Reaction conditions (unless otherwise specified): 1a (0.2 mmol, 1.0 equiv), 2 (2.5 equiv), NiL<sub>2</sub> (10 mol%), ligands, Mn (200 mesh, 3.0 equiv), DMac (1 mL), 40 °C, under N<sub>2</sub> atmosphere, 24 h. <sup>b</sup> Yields determined by 19F NMR using PhCF<sub>3</sub> as an internal standard. <sup>c</sup> Isolated yield.
**Table S2. Nickel Sources Screening**

\[
\begin{align*}
&\text{Entry} & \text{[Ni]} & \text{Yield\%}^b & \text{Entry} & \text{[Ni]} & \text{Yield\%}^b \\
&1 & \text{None} & 0 & 5 & \text{Ni(\text{OAc})}_2 & 19 \\
&2 & \text{NiCl}_2 & 39 & 6 & \text{Ni(NO}_3)_2\cdot6\text{H}_2\text{O} & 0 \\
&3 & \text{NiBr}_2 & <5 & 7 & \text{Ni(\text{acac})}_2 & 68 \\
&4 & \text{NiI}_2 & 86^c & 8 & \text{Ni(\text{OTf})}_2 & 0 \\
\end{align*}
\]

*a Reaction conditions (unless otherwise specified): 1 (0.2 mmol, 1.0 equiv), 2 (2.5 equiv), [Ni] (10 mol%), dbpy (12 mol%), DMAP (24 mol%), Mn (3 equiv), N\textsubscript{2}, DMAc, 40 °C, 24 h.  
*b Yields determined by \textsuperscript{19}F NMR using PhCF\textsubscript{3} as an internal standard.  
*c Isolated yield.

**Table S3. Optimization of Other Conditions**

\[
\begin{align*}
&\text{Entry} & \text{x} & \text{y} & \text{z} & \text{solvent} & \text{Yield\%}^b \\
&1 & 10 & 20 & 3.0 & \text{DMAc} & 80 \\
&2 & 12 & 24 & 3.0 & \text{DMF} & 0 \\
&3 & 12 & 24 & 3.0 & \text{MeCN} & 41 \\
&4 & 12 & 24 & 3.0 & \text{DMSO} & 0 \\
&5 & 12 & 24 & 3.0 & \text{DMAc} & 79 \\
&6^c & 12 & 24 & 3.0 & \text{DMAc} & 81 \\
&7^d & 12 & 24 & 3.0 & \text{DMAc} & 76 \\
\end{align*}
\]

*a Standard reaction conditions (unless otherwise specified): 1a (0.2 mmol, 1.0 equiv), 2 (2.5 equiv), NiI\textsubscript{2} (10 mol%), dbpy (12 mol%), DMAP (24 mol%), Mn (200 mesh, 3.0 equiv), DMAc (1 mL), 40 °C, under N\textsubscript{2} atmosphere, 24 h.  
*b Yields determined by \textsuperscript{19}F NMR using PhCF\textsubscript{3} as an internal standard.  
*c \text{H}_2\text{O} (3 equiv) was added.  
*d 60 °C.
Preparation of Substrates

Substrates 1j, 1w and 1ab were prepared in accordance with methods described in the references.

Synthesis of Fenofibrate bromide (1ae):

Fenofibrate boronic acid (2 mmol, 0.74 g), 1,3-dibromo-5,5-dimethylhydantoin (2.2 mmol, 0.63 mg) and NaOMe (0.1 mmol, 5.4 mg) were added to a 50 mL Schlenk tube equipped with a magnetic stirring bar. The vessel was evacuated and backfilled with N₂ (repeated for 3 times). Acetonitrile (10 mL) were added to the tube at room temperature under a stream of nitrogen, and the tube was sealed and put into a pre-heated oil bath at 40 °C for 4 h under nitrogen atmosphere. After the resulting solution was cooled to room temperature, Na₂SO₃ (10% aq, ~20 mL) was added, and the aqueous layer was extracted with MTBE (3 × 15 mL). The combined organic phase was washed with NaOH (10% aq) and dried over anhydrous Na₂SO₄, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography (PE/EA = 5:1) to give the product as a white solid (> 80%). ¹H NMR (400 MHz, Chloroform-d) δ 7.76–7.70 (m, 2H), 7.61 (s, 4H), 6.89–6.82 (m, 2H), 5.08 (hept, J = 6.3 Hz, 1H), 1.66 (s, 6H), 1.20 (d, J = 6.3 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ 194.51, 173.21, 159.88, 136.98, 132.09, 131.63, 131.41, 130.25, 127.03, 117.33, 79.53, 69.48, 25.49, 21.66. HRMS ESI (m/z): [M+H]⁺ calcd. For C₂₀H₂₂BrO₄: 405.0701 found: 405.0685.

Preparation of BrCH₂F Stock Solution

Dry DMAc (~23 mL) was added to a Schlenk graduated cylinder under nitrogen. The vessel and solvent were weighed. Next, BrCH₂F (~2mL) was added and the total volume of the solution reached approximately 25 mL. The vessel was sealed and weighed again. The concentration of the BrCH₂F stock solution was calculated based on the mass of BrCH₂F added and the total volume of the solution (~0.2 mol/L).
General Procedure for Nickel-Catalyzed Cross-Coupling between (Hetero)aryl Bromides and Bromofluoromethane

To a 5 mL of sealing tube were added NiI₂ (10 mol%), dtbpy (4,4’-Di-tert-butyl-2,2’-bipyridine, 12 mol%), DMAP (4-Dimethylaminopyridine, 24 mol%) and manganese powder (200 mesh, 3.0 equiv). The vessel was evacuated and backfilled with N₂ (repeated for 3 times), after that, aryl bromine 1 (0.2 mmol, 1.0 equiv) and dry DMAc (1 mL) were added. The solution then premix for 10 s before BrCH₂F₂ (solution in DMAc, 2.5 equiv) was added. The tube was sealed with a Teflon lined cap and heated in a preheated oil bath at 40°C for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (~20 mL) and filtered through a pad of celite. The filtrate was added brine (30 mL) and extracted with EtOAc (2×15 mL), the combined organic layer was dried over Na₂SO₄, filtrated and concentrated under vacuum. The residue was then purified by flash column chromatography to give 3 as a colorless solid or oil.

4-(fluoromethyl)-1,1'-biphenyl (3a) was purified with silica gel chromatography (PE) as a white solid (86% yield). The compound is known⁵. ¹H NMR (400 MHz, Chloroform-d) δ 7.66 (t, J = 8.5 Hz, 4H), 7.53-7.47 (m, 4H), 7.41 (t, J = 7.3 Hz, 1H), 5.46 (d, J = 47.9 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 141.83 (d, J = 3.3 Hz), 140.69 (d, J = 1.1 Hz), 135.23 (d, J = 17.0 Hz), 128.95, 128.19 (d, J = 5.7 Hz), 127.66, 127.47 (d, J = 1.4 Hz), 127.27, 84.51 (d, J = 166.0 Hz). ¹⁹F NMR (376 MHz, Chloroform-d) δ -206.03 (t, J = 47.8 Hz).

3-(fluoromethyl)-1,1'-biphenyl (3b) was purified with silica gel chromatography (PE) as a colorless liquid (89% yield). The compound is known⁶. ¹H NMR (400 MHz, Chloroform-d) δ 7.67-7.60 (m, 4H), 7.53-7.45 (m, 3H), 7.43-7.36 (m, 2H), 5.48 (d, J = 47.8 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-d) δ 141.79 (d, J = 1.0 Hz), 140.80, 136.85 (d, J = 17.1 Hz), 129.19, 128.95, 127.67, 127.65, 127.30, 126.43 (d, J = 2.0 Hz), 126.37 (d, J = 2.1 Hz), 84.72 (d, J = 166.6 Hz). ¹⁹F NMR (376 MHz, Chloroform-d) δ -207.15 (t, J = 47.8 Hz).
1-(fluoromethyl)-2-methylbenzene (3c) due to the low boiling point of the product, the yield (74%) was determined by $^{19}$F NMR using PhCF$_3$ as an internal standard. This compound is known$^7$. The product was characterized by $^{19}$F NMR and GC-MS analysis.

(Fluoromethyl)benzene (3e) due to the low boiling point of the product, the yield (83%) was determined by $^{19}$F NMR using PhCF$_3$ as an internal standard. This compound is known$^6$. The product was characterized by $^{19}$F NMR and GC-MS analysis.

1-(fluoromethyl)-3-methoxybenzene (3f) due to the low boiling point of the product, the yield (77%) was determined by $^{19}$F NMR using PhCF$_3$ as an internal standard. This compound is known$^6$. The product was characterized by $^{19}$F NMR and GC-MS analysis.

1-(fluoromethyl)-3,5-dimethoxybenzene (3h) was purified with silica gel chromatography (PE/EA = 20:1) as a colorless liquid (84% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 6.52 (t, $J = 1.7$ Hz, 2H), 6.45 (q, $J = 2.1$ Hz, 1H), 5.32 (d, $J = 47.6$ Hz, 2H), 3.80 (s, 6H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 161.13, 138.62 (d, $J = 17.3$ Hz), 105.03 (d, $J = 6.5$ Hz), 100.77 (d, $J = 2.6$ Hz), 84.60 (d, $J = 167.5$ Hz), 55.53. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -208.96 (t, $J = 47.7$ Hz). HRMS EI (m/z): [M]$^+$ calcd. For C$_9$H$_{11}$F$_2$O$_2$: 170.0743 found: 170.0739.

1-(benzyloxy)-3-(fluoromethyl)benzene (3i) was purified with silica gel chromatography (PE/EA = 20:1) as a white solid (94% yield). The compound is known$^8$. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.53–7.39 (m, 4H), 7.39–7.29 (m, 2H), 7.04 (s,
1H), 6.99 (d, J = 7.7 Hz, 2H), 5.38 (d, J = 47.7 Hz, 2H), 5.10 (s, 2H). 13C NMR (101 MHz, Chloroform-d) δ 159.11, 137.90 (d, J = 17.1 Hz), 136.91, 129.85, 128.73, 128.15, 127.61, 119.90 (d, J = 6.1 Hz), 115.30 (d, J = 2.8 Hz), 113.77 (d, J = 6.3 Hz), 84.54 (d, J = 166.9 Hz), 70.12. 19F NMR (376 MHz, Chloroform-d) δ -207.84 (t, J = 47.7 Hz).

4-(fluoromethyl)phenyl-4-methylbenzoate (3j) was purified with silica gel chromatography (PE/EA = 20:1) as a white solid (77% yield). 1H NMR (400 MHz, Chloroform-d) δ 8.11 (d, J = 8.0 Hz, 2H), 7.45 (dd, J = 8.5, 1.9 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 5.40 (d, J = 47.8 Hz, 2H), 2.46 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 165.23 (d, J = 0.4 Hz), 151.42 (d, J = 3.3 Hz), 144.68, 133.87 (d, J = 17.5 Hz), 130.35, 129.44, 128.92 (d, J = 5.8 Hz), 126.73, 122.13 (d, J = 1.1 Hz), 84.13 (d, J = 166.6 Hz), 21.89. 19F NMR (376 MHz, Chloroform-d) δ -206.06 (t, J = 47.8 Hz). HRMS ESI (m/z): [M+Na]+ calcd. For C15H13FO2Na: 267.0797 found: 267.0792.

(4-(fluoromethyl)phenyl)(phenyl)methanone (3k) was purified with silica gel chromatography (PE/EA = 15:1) as a pale yellow oil (95% yield). The compound is known. 1H NMR (400 MHz, Chloroform-d) δ 7.85-7.71 (m, 4H), 7.63–7.56 (m, 1H), 7.51-7.46 (m, 4H), 5.47 (d, J = 47.2 Hz, 2H). 13C NMR (101 MHz, Chloroform-d) δ 196.28, 140.72 (d, J = 17.2 Hz), 137.80 (d, J = 2.5 Hz), 137.51, 132.66, 130.41, 130.11, 128.44, 128.70 (d, J = 6.5 Hz), 83.83 (d, J = 168.4 Hz). 19F NMR (376 MHz, Chloroform-d) δ -212.32 (t, J = 47.2 Hz).

(3-(fluoromethyl)phenyl)(phenyl)methanone (3l) was purified with silica gel chromatography (PE/EA = 15:1) as a colorless liquid (83% yield). 1H NMR (400 MHz, Chloroform-d) δ 7.95–7.74 (m, 4H), 7.60 (t, J = 7.5 Hz, 2H), 7.57–7.44 (m, 3H), 5.44 (d, J = 47.5 Hz, 2H). 13C NMR (101 MHz, Chloroform-d) δ 196.38, 138.08, 137.41, 136.67 (d, J = 17.5 Hz), 132.74, 131.27 (d, J = 5.8 Hz), 130.44 (d, J = 2.6 Hz), 130.14, 128.81 (d, J = 6.2 Hz), 128.74, 128.49, 84.06 (d, J = 167.7 Hz). 19F NMR (376 MHz, Chloroform-d) δ -208.92 (t, J = 47.7 Hz). HRMS ESI (m/z): [M+H]+ calcd. For C14H12FO: 215.0872 found: 215.0869.

(3-(fluoromethyl)phenyl)(thiophen-2-yl)methanone (3m) was purified with silica gel chromatography (PE/EA = 5:1) as a colorless liquid (68% yield). 1H NMR (400 MHz,
Chloroform-d) δ 7.91–7.81 (m, 2H), 7.74 (dd, J = 5.0, 1.1 Hz, 1H), 7.64 (dd, J = 3.8, 1.1 Hz, 1H), 7.62–7.59 (m, 1H), 7.58–7.48 (m, 1H), 7.17 (dd, J = 4.9, 3.8 Hz, 1H), 5.46 (d, J = 47.5 Hz, 2H). 13C NMR (101 MHz, Chloroform-d) δ 187.85, 143.49, 138.62, 136.84 (d, J = 17.6 Hz), 135.08, 134.60, 131.04 (d, J = 5.9 Hz), 129.50 (d, J = 2.6 Hz), 128.88, 128.19, 127.95 (d, J = 6.3 Hz), 84.03 (d, J = 167.8 Hz). 19F NMR (376 MHz, Chloroform-d) δ -209.28 (t, J = 47.5 Hz).

1H NMR (400 MHz, Chloroform-d) δ 8.74 (dd, J = 7.3, 2.2 Hz, 1H), 8.69 (d, J = 8.3 Hz, 1H), 8.11 (dt, J = 6.6, 1.8 Hz, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 3.1 Hz, 1H), 7.70 (ddt, J = 10.8, 7.0, 3.4 Hz, 3H), 7.65–7.59 (m, 1H), 5.89 (d, J = 47.8 Hz, 2H). 13C NMR (101 MHz, Chloroform-d) δ 131.13 (d, J = 1.3 Hz), 131.03 (d, J = 1.8 Hz), 130.74, 130.36 (d, J = 15.2 Hz), 130.04 (d, J = 1.1 Hz), 129.08 (d, J = 1.4 Hz), 128.03 (d, J = 9.5 Hz), 127.51 (d, J = 1.1 Hz), 127.16, 127.01 (d, J = 0.6 Hz), 126.92, 124.37 (d, J = 1.3 Hz), 123.29, 122.70 (d, J = 1.0 Hz), 83.87 (d, J = 166.4 Hz). 19F NMR (376 MHz, Chloroform-d) δ -207.89 (t, J = 47.5 Hz). HRMS ESI (m/z): [M+H]+ calcd. For C_{15}H_{15}F_{3}: 210.0845 found: 210.0835.

9-(4-(fluoromethyl)phenyl)-9H-carbazole (3p) was purified with silica gel chromatography (PE/EA = 20:1) as a white solid (77% yield). 1H NMR (400 MHz, Chloroform-d) δ 8.18 (dt, J = 7.7, 1.0 Hz, 2H), 7.63 (s, 4H), 7.47–7.40 (m, 4H), 7.36–7.28 (m, 2H), 5.52 (d, J = 47.7 Hz, 2H). 13C NMR (101 MHz, Chloroform-d) δ 140.84, 138.25 (d, J = 3.1 Hz), 135.43 (d, J = 17.4 Hz), 129.17 (d, J = 5.8 Hz), 127.33 (d, J = 0.9 Hz), 126.14, 123.57, 120.48, 120.22, 109.81, 84.21 (d, J = 167.0 Hz). 19F NMR (376 MHz, Chloroform-d) δ -207.06 (t, J = 47.7 Hz). HRMS ESI (m/z): [M+H]+ calcd. For C_{19}H_{15}FN: 276.1189 found: 276.1180.
9-(3-(fluoromethyl)phenyl)-9H-carbazole (3q) was purified with silica gel chromatography (PE/EA = 20:1) as a colorless liquid (93% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.20 (dt, $J = 7.8, 1.0$ Hz, 2H), 7.70–7.58 (m, 3H), 7.54–7.42 (m, 5H), 7.39–7.31 (m, 2H), 5.52 (d, $J = 47.5$ Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 140.85, 138.42 (d, $J = 17.5$ Hz), 138.18, 130.29, 127.38 (d, $J = 2.5$ Hz), 126.25 (d, $J = 6.0$ Hz), 126.12, 125.89 (d, $J = 6.3$ Hz), 123.54, 120.46, 120.20, 109.78, 84.02 (d, $J = 167.9$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -208.81 (t, $J = 47.4$ Hz). HRMS ESI (m/z): [M+H]$^+$ calcd. For C$_{19}$H$_{15}$FN: 276.1189 found: 276.1177.

4-(3-(fluoromethyl)phenyl)morpholine (3r) was purified with silica gel chromatography (PE/EA = 5:1) as a colorless liquid (93% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.30 (t, $J = 7.8$ Hz, 1H), 6.97–6.84 (m, 3H), 5.35 (d, $J = 47.8$ Hz, 2H), 3.91–3.81 (m, 4H), 3.24–3.13 (m, 4H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 151.66, 137.35 (d, $J = 16.9$ Hz), 129.56 (d, $J = 0.8$ Hz), 118.95 (d, $J = 5.9$ Hz), 116.02 (d, $J = 2.9$ Hz), 114.57 (d, $J = 6.3$ Hz), 84.97 (d, $J = 166.5$ Hz), 66.99, 49.31. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -207.25 (t, $J = 47.8$ Hz). HRMS EI (m/z): [M]$^+$ calcd. For C$_{11}$H$_{14}$FNO: 195.1059 found: 195.1050.

2-(4-(fluoromethyl)phenyl)pyridine (3s) was purified with silica gel chromatography (PE/EA = 5:1) as a colorless liquid (80% yield). The compound is known.$^{10}$ $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.74–8.67 (m, 1H), 8.03 (dd, $J = 8.4, 1.3$ Hz, 2H), 7.81–7.70 (m, 2H), 7.56–7.44 (m, 2H), 7.23 (ddd, $J = 6.0, 4.8, 2.5$ Hz, 1H), 5.43 (d, $J = 47.7$ Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 156.90 (d, $J = 1.4$ Hz), 149.83, 139.87 (d, $J = 3.0$ Hz), 136.96 (d, $J = 17.3$ Hz), 136.89, 127.86 (d, $J = 5.9$ Hz), 127.20 (d, $J = 1.3$ Hz), 122.43, 120.66, 84.36 (d, $J = 166.6$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -208.00 (t, $J = 47.7$ Hz).

2-(4-(fluoromethyl)phenyl)thiophene (3t) was purified with silica gel chromatography (PE) as a white solid (75% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.71–7.60 (m, 2H), 7.40 (ddd, $J = 6.5, 2.8, 1.1$ Hz, 2H), 7.35 (dd, $J = 3.6, 0.8$ Hz, 1H), 7.31 (dd, $J = 5.1, 1.1$ Hz, 1H), 7.10 (dd, $J = 5.1, 3.6$ Hz, 1H), 5.40 (d, $J = 47.8$ Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 143.85 (d, $J = 1.5$ Hz), 135.38 (d, $J = 17.0$ Hz), 135.00 (d,
$J = 3.3 \text{ Hz}$), 128.31 (d, $J = 5.8 \text{ Hz}$), 128.22, 126.19 (d, $J = 1.3 \text{ Hz}$), 125.31, 123.60 (d, $J = 0.5 \text{ Hz}$), 84.40 (d, $J = 166.2 \text{ Hz}$). $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -206.37 (t, $J = 47.8 \text{ Hz}$). HRMS EI (m/z): [M$^+$] calcd. For C$_{11}$H$_9$FS: 192.0409 found: 192.0398.

6-(fluoromethyl)-2-methylquinoline (3u) was purified with silica gel chromatography (PE/EA = 4:1) as a white solid (72% yield). The compound is known.$^{11}$ $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.02 (d, $J = 8.4 \text{ Hz}$, 2H), 7.75 (s, 1H), 7.65 (d, $J = 8.6 \text{ Hz}$, 1H), 7.29 (d, $J = 8.4 \text{ Hz}$, 1H), 5.52 (d, $J = 4.8 \text{ Hz}$, 2H), 2.74 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 159.77 (d, $J = 1.1 \text{ Hz}$), 147.93 (d, $J = 2.1 \text{ Hz}$), 136.34 (d, $J = 0.9 \text{ Hz}$), 133.64 (d, $J = 17.1 \text{ Hz}$), 129.27, 128.52 (d, $J = 4.8 \text{ Hz}$), 126.25 (d, $J = 7.4 \text{ Hz}$), 126.24 (d, $J = 1.0 \text{ Hz}$), 122.59, 84.38 (d, $J = 167.2 \text{ Hz}$), 25.52. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -207.64 (t, $J = 47.6 \text{ Hz}$).

7-(fluoromethyl)-2-methylquinoline (3v) was purified with silica gel chromatography (PE/EA = 4:1) as a white solid (79% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.01 (d, $J = 8.4 \text{ Hz}$, 1H), 7.97 (s, 1H), 7.77 (d, $J = 8.3 \text{ Hz}$, 1H), 7.47 (d, $J = 8.8 \text{ Hz}$, 1H), 7.27 (d, $J = 8.8 \text{ Hz}$, 1H), 5.55 (d, $J = 47.4 \text{ Hz}$, 2H), 2.73 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 159.68, 147.73, 137.58 (d, $J = 17.1 \text{ Hz}$), 136.01, 128.11, 127.10 (d, $J = 7.3 \text{ Hz}$), 126.42 (d, $J = 1.9 \text{ Hz}$), 124.54 (d, $J = 5.3 \text{ Hz}$), 122.55, 84.43 (d, $J = 167.6 \text{ Hz}$), 25.47. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -209.44 (t, $J = 47.5 \text{ Hz}$). HRMS ESI (m/z): [M+H$^+$] calcd. For C$_{11}$H$_{11}$FN: 176.0876 found: 176.0873.

5-(fluoromethyl)-1-tosyl-1H-indole (3w) was purified with silica gel chromatography (PE/EA = 5:1) as a colorless liquid (87% yield). The compound is known.$^5$ $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.02 (d, $J = 8.5 \text{ Hz}$, 1H), 7.76 (d, $J = 8.4 \text{ Hz}$, 2H), 7.60 (d, $J = 3.7 \text{ Hz}$, 1H), 7.55 (t, $J = 2.0 \text{ Hz}$, 1H), 7.34 (dt, $J = 8.5, 1.7 \text{ Hz}$, 1H), 7.21 (d, $J = 8.1 \text{ Hz}$, 2H), 6.66 (d, $J = 3.6 \text{ Hz}$, 1H), 5.42 (d, $J = 48.2 \text{ Hz}$, 2H), 2.33 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 145.23, 135.22, 135.04 (d, $J = 2.7 \text{ Hz}$), 131.36 (d, $J = 17.2 \text{ Hz}$), 130.99 (d, $J = 1.3 \text{ Hz}$), 130.03, 127.21, 126.89, 124.63 (d, $J = 4.9 \text{ Hz}$), 121.21 (d, $J = 6.1 \text{ Hz}$), 113.80 (d, $J = 1.1 \text{ Hz}$), 109.10, 84.94 (d, $J = 165.8 \text{ Hz}$), 21.65. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -201.63 (t, $J = 48.2 \text{ Hz}$).

3-(fluoromethyl)dibenzo[b,d]furan (3x) was purified with silica gel chromatography (PE) as a white solid (93% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.03–7.92 (m, 2H), 7.62–
7.56 (m, 2H), 7.49 (ddd, J = 8.4, 7.4, 1.3 Hz, 1H), 7.40–7.34 (m, 2H), 5.54 (d, J = 47.8 Hz, 2H). 13C NMR (101 MHz, Chloroform-d) δ 156.73, 156.29 (d, J = 0.6 Hz), 135.59 (d, J = 17.1 Hz), 127.59, 124.78 (d, J = 2.7 Hz), 123.90 (d, J = 1.0 Hz), 122.99, 122.24 (d, J = 5.8 Hz), 120.91, 120.85 (d, J = 0.9 Hz), 111.89, 110.99 (d, J = 6.6 Hz), 84.76 (d, J = 167.3 Hz). 19F NMR (376 MHz, Chloroform-d) δ -204.77 (t, J = 47.8 Hz). HRMS EI (m/z): [M]+ calcd. For C13H9FO: 200.0637 found: 200.0630.

3-(fluoromethyl)dibenzo[b,d]thiophene (3y) was purified with silica gel chromatography (PE) as a white solid (77% yield). 1H NMR (400 MHz, Chloroform-d) δ 8.21–8.09 (m, 2H), 7.87 (dtd, J = 6.6, 3.1, 1.7 Hz, 2H), 7.56–7.38 (m, 3H), 5.52 (d, J = 47.8 Hz, 2H). 13C NMR (101 MHz, Chloroform-d) δ 139.90, 139.77 (d, J = 1.0 Hz), 135.96 (d, J = 2.7 Hz), 135.16 (d, J = 1.1 Hz), 134.90 (d, J = 17.1 Hz), 127.09, 124.60, 123.95 (d, J = 5.4 Hz), 122.97, 121.99 (d, J = 6.7 Hz), 121.86, 121.78 (d, J = 0.6 Hz), 84.67 (d, J = 167.2 Hz). 19F NMR (376 MHz, Chloroform-d) δ -205.39 (t, J = 47.8 Hz). HRMS EI (m/z): [M]+ calcd. For C13H9F: 216.0409 found: 216.0400.

5-(fluoromethyl)-2-methylbenzo[d]oxazole (3z) was purified with silica gel chromatography (PE/EA = 5:1) as a white solid (89% yield). 1H NMR (400 MHz, Chloroform-d) δ 7.66 (s, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 5.45 (d, J = 48.1 Hz, 2H), 2.64 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 164.79, 151.29 (d, J = 2.9 Hz), 141.90 (d, J = 1.0 Hz), 132.48 (d, J = 17.4 Hz), 124.62 (d, J = 5.4 Hz), 119.20 (d, J = 5.8 Hz), 110.41, 84.76 (d, J = 166.6 Hz), 14.69. 19F NMR (376 MHz, Chloroform-d) δ -201.70 (t, J = 48.1 Hz). HRMS ESI (m/z): [M+H]+ calcd. For C9H9FNO: 166.0668 found: 166.0664.

5-(fluoromethyl)-2-methylbenzo[d]thiazole (3aa) was purified with silica gel chromatography (PE/EA = 5:1) as a white solid (81% yield). 1H NMR (400 MHz, Chloroform-d) δ 7.93 (s, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 5.49 (d, J = 47.9 Hz, 2H), 2.84 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 168.02, 153.62, 136.20 (d, J = 2.8 Hz), 134.41 (d, J = 17.3 Hz), 124.28 (d, J = 5.3 Hz), 121.73 (d, J = 0.8 Hz), 121.62 (d, J = 6.4 Hz), 84.60 (d, J = 167.0 Hz), 20.32. 19F NMR (376 MHz, Chloroform-d) δ -204.70 (t, J = 47.8 Hz). HRMS ESI (m/z): [M+H]+ calcd. For C9H9FNS: 182.0440 found: 182.0435.
3-(fluoromethyl)-1-tosyl-1H-indole (3ab) was purified with silica gel chromatography (PE/EA = 5:1) as a white solid (65% yield). The compound is known\(^{12}\). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.00 (d, \(J = 8.3\) Hz, 1H), 7.79 (d, \(J = 8.4\) Hz, 2H), 7.66 (d, \(J = 4.7\) Hz, 1H), 7.62 (d, \(J = 7.8\) Hz, 1H), 7.40–7.33 (m, 1H), 7.32–7.26 (m, 1H), 7.23 (d, \(J = 8.3\) Hz, 2H), 5.52 (d, \(J = 48.4\) Hz, 2H), 2.34 (s, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 145.38, 135.32, 135.18, 130.12, 129.36 (d, \(J = 0.9\) Hz), 127.02, 125.97 (d, \(J = 9.3\) Hz), 125.34, 123.71, 119.87, 117.78 (d, \(J = 19.7\) Hz), 113.77, 76.52 (d, \(J = 162.9\) Hz), 21.69. \(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) -207.22 (td, \(J = 48.4, 4.8\) Hz).

3-(fluoromethyl)quinoline (3ac) was purified with silica gel chromatography (PE/EA = 4:1) as a white solid (81% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.93 (s, 1H), 8.22–8.07 (m, 2H), 7.83 (d, \(J = 8.2\) Hz, 1H), 7.75 (t, \(J = 7.6\) Hz, 1H), 7.57 (t, \(J = 4.7\) Hz), 5.58 (d, \(J = 47.6\) Hz, 2H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 149.94 (d, \(J = 4.7\) Hz), 148.31 (d, \(J = 2.2\) Hz), 135.15 (d, \(J = 6.5\) Hz), 130.19 (d, \(J = 1.0\) Hz), 129.51 (d, \(J = 1.0\) Hz), 128.91 (d, \(J = 17.3\) Hz), 128.08 (d, \(J = 1.2\) Hz), 127.62 (d, \(J = 0.9\) Hz), 127.25 (d, \(J = 0.4\) Hz), 82.55 (d, \(J = 167.7\) Hz). \(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) -208.67 (t, \(J = 47.6\) Hz). HRMS ESI (m/z): [M+H]\(^+\) calcd. For C\(_{10}\)H\(_{19}\)FN: 162.0719 found: 162.0716.

5-(fluoromethyl)-2-phenylpyridine (3ad) was purified with silica gel chromatography (PE/EA = 10:1) as a white solid (77% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.70 (s, 1H), 8.09–7.95 (m, 2H), 7.86–7.73 (m, 2H), 7.57–7.39 (m, 3H), 5.44 (d, \(J = 47.7\) Hz, 2H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 158.14 (d, \(J = 3.2\) Hz), 149.09 (d, \(J = 6.0\) Hz), 138.91, 136.49 (d, \(J = 4.8\) Hz), 129.95 (d, \(J = 17.5\) Hz), 129.39, 128.93, 127.10, 120.43, 82.25 (d, \(J = 167.0\) Hz). \(^{19}\)F NMR (376 MHz, Chloroform-\(d\)) \(\delta\) -208.42 (t, \(J = 47.8\) Hz). HRMS ESI (m/z): [M+H]\(^+\) calcd. For C\(_{12}\)H\(_{11}\)FN: 188.0876 found: 188.0872.

Isopropyl 2-(4-(4-(fluoromethyl)benzoyl)phenoxy)-2-methylpropanoate (3ae) was purified with silica gel chromatography (PE/EA = 5:1) as a white solid (81% yield). The compound is known\(^5\). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.80–7.71 (m, 4H), 7.50–7.43 (m, 2H), 6.90–6.82 (m, 2H), 5.46 (d, \(J = 47.3\) Hz, 2H), 5.08 (hept, \(J = 6.3\) Hz, 1H), 2.32 (s, 3H), 1.23 (d, \(J = 6.3\) Hz, 6H).
1.66 (s, 6H), 1.20 (d, J = 6.3 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 195.06, 173.19, 159.76, 140.20 (d, J = 17.2 Hz), 138.37 (d, J = 2.4 Hz), 132.11, 130.48, 130.07, 126.69 (d, J = 6.4 Hz), 117.28, 83.86 (d, J = 168.2 Hz), 79.47, 69.40, 25.44, 21.59. $^{19}$F NMR (376 MHz, Chloroform-d) δ -211.76 (t, J = 47.6 Hz).

Mechanistic Studies

1. Radical Inhibition Experiment

To a 5 mL of sealing tube were added aryl bromine 1 (0.2 mmol, 1.0 equiv), NiI$_2$ (10 mol%), dtbpy (12 mol%), DMAP (24 mol%) and Mn powder (200 mesh, 3.0 equiv). The mixture was added DMAc (1 mL), TEMPO (1 equiv) and 2 (2.5 equiv) under N$_2$ atmosphere. The tube was sealed with a Teflon lined cap and heated up into a preheated oil bath (40 °C) for 48 h. Then the mixture was cooled to room temperature and diluted with ethyl acetate (2 mL) and filtered through a pad of silica gel. The mixture was detected by crude $^{19}$F NMR and GC-MS. No product 3a was found.

2. Radical Clock Experiment

To a 5 mL of sealing tube were added aryl bromine 1 (0.2 mmol, 1.0 equiv), NiI$_2$ (10 mol%), dtbpy (12 mol%), DMAP (24 mol%) and Mn powder (200 mesh, 2.0 equiv). The mixture was added DMAc (1 mL), 4 (2 equiv) and 2 (2.5 equiv) under N$_2$ atmosphere. The tube was sealed with a Teflon lined cap and heated up into a preheated oil bath (40 °C) for 24 h. Then the mixture was cooled to room temperature and diluted with ethyl acetate (2 mL) and filtered through a pad of silica gel. The mixture was then concentrated under vacuum and purified with silica gel chromatography to give product
3a in 85% yield and product 5 was yield by crude $^{19}$F NMR and identified by GC-MS. HRMS EI (m/z): [M]+ calcd. For C$_{11}$H$_{17}$F: 168.1314 found: 168.1303.

3. Direct Insertion of Bromofluoromethane (2) with Mn$^0$

To a 5 mL of sealing tube was added Mn powder (3.0 equiv, 0.6 mmol) in air. The mixture was then added DMAc (1 mL) and 2 (2.5 equiv) under N$_2$ atmosphere. The tube was sealed with a Teflon lined cap and heated up into a preheated oil bath (40 °C) for 24 h. After the mixture was cooled to room temperature, 2 M HCl (1 mL) was added via syringe and the reaction was stirred at room temperature for 30 min. No product 2' was detected by crude $^{19}$F NMR.
4. Direct Insertion of Bromofluoromethane (2) with Mn\(^0\) at Standard Condition

To a 5 mL of sealing tube was added dtbpy (12 mol%, 0.024 mmol), DMAP (24 mol%), Mn powder (3.0 equiv) and Nil\(_2\) (10 mol%). The mixture was then added DMAc (1 mL) and 2 (2.5 equiv) under N\(_2\) atmosphere. The tube was sealed with a Teflon lined cap and heated up into a preheated oil bath (40 ℃) for 24 h. After the mixture was cooled to room temperature, 2 M HCl (1 mL) was added via syringe and the reaction was stirred at room temperature for 30 min. No product 2\(^*\) was detected by crude \(^{19}\)F NMR.

5. Proposed mechanism: a) Radical-cage-rebound process; b) A radical chain process
References

$^{1}H$, $^{19}F$, and $^{13}C$ NMR Spectra
$3r$