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Short Communication

2-Position-selective C—H fluoromethylation of six-membered heteroaryl *N*-oxides with (fluoromethyl)triphenylphosphonium iodide

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ABSTRACT

A mild and efficient method for the regioselective C—H fluoromethylation of heteroaryl *N*-oxides with (fluoromethyl)triphenylphosphonium iodide is presented. With LiO*t*-Bu as the base and DMSO as the solvent, this reaction delivers a series of C2-fluoromethylated pyridine and quinoline derivatives in moderate to good yields. This protocol also extends the synthetic applications of (fluoromethyl)triphenylphosphonium iodide.

1. Introduction

Fluoromethyl (CH_2F) is a unique fluorine-containing group, which acts as a metabolically stable bioisostere for methyl group and is also considered as a CH_2OH group mimic [1]. Compounds with CH_2F moiety have a broad spectrum of applications in the agrochemicals, pharmaceuticals, and materials [2]. Consequently, numerous methods have been reported for the preparation of CH_2F-substituted compounds [3]. Traditional protocols mainly include C—H fluorination of CH_3-containing compounds [4], fluorination of functionalized substrates [5], and transformation of CHFR-containing building blocks [6]. However, these methods suffer from limited substrate scope, low regioselectivity, and/or prior installation of a functional group.

Recently, the emergence of new fluoromethylating reagents has stimulated the development of direct fluoromethylation reactions. In this context, the electrophilic fluoromethylation of heteroatom (*N*-, *P*-, *O*-, *S*-, *Se*-) and carbon (*C*-) nucleophiles [7] as well as nucleophilic fluoromethylation of carbonyls, imines, and Weinreb amides [8] have been reported. Furthermore, the radical fluoromethylation of activated alkenes have been achieved by the groups of Dolbier, Hu, and Koike-&Akita for the preparation of linear fluoromethylated alkanes [9]. Very recently, our group developed a copper-catalyzed boryl-fluoromethylation of alkenes to afforded branched fluoromethylated products [10].

On the other hand, particular attention has been paid to direct fluoromethylation of (hetero)aromatic compounds, since fluoromethylated (hetero)arenes have become increasingly prevalent in numerous fields. In 2012, Baran and co-workers reported a direct C—H fluoromethylation of heteroarenes with $Zn(SO_2CH_2F)_2$ through a radical pathway (Scheme 1a) [11]. In 2015, Zhang [12a] and Hu [12b] respectively developed nickel- and palladium-catalyzed fluoromethylations of aryl boron compounds with fluoromethyl halides (Scheme 1b). Recently, Baran disclosed a nickel-catalyzed radical cross-coupling of aryl zinc reagents and fluoromethyl phenyl-tetrazole sulfone (Scheme 1c) [13]. Very recently, the nickel-catalyzed reductive crossing-coupling of aryl halides and bromofluoromethane was realized by Wang (Scheme 1d) [14]. Despite these elegant achievements, the development of other methods for fluoromethylation of (hetero)aromatic compounds is still in a high demand.

Heteroaryl *N*-oxides are important and readily available synthetic intermediates, which react with nucleophiles for the preparation of various *N*-heterocycles bearing substituents in the C2 position. Recently, the C—H trifluoromethylation [15], polyfluoroalkylation [16], trifluoromethoxylation [17], and trifluoromethylthiolation [18] of heteroaryl *N*-oxides have been reported for the regioselective incorporation of fluorine-containing groups into heteroarenes. Inspired by these works, we became interested in exploring the C—H fluoromethylation of heteroaryl *N*-oxides. However, this reaction is more challenging, since the lack of efficient nucleophilic fluoromethylating reagents [8]. In 2018, Han and Kim reported a C—H alkylation of pyridine and quinoline *N*-oxides with alkylphosphonium salts as alkylating reagents to furnish C2-alkylated pyridines and quinolines [19]. We envisioned that the

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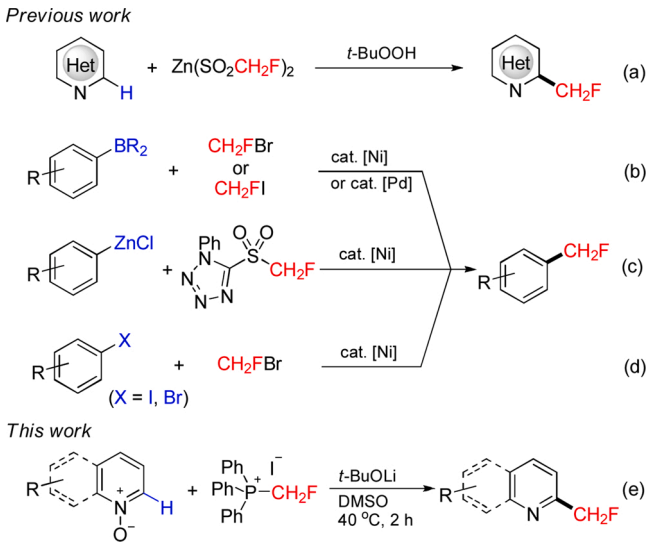


Scheme 1. Fluoromethylation of (hetero)aromatic compounds.

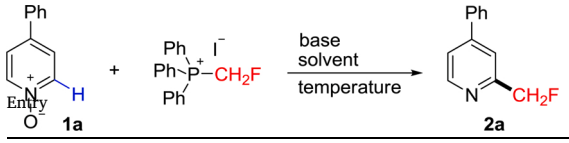
analogous C—H fluoromethylation of heteroaryl *N*-oxides with (fluoromethyl)triphenylphosphonium salt should be feasible. In continuation of our research interest in direct fluoroalkylation of heteroarenes [18b, 20], herein we disclose a regioselective C—H fluoromethylation of heteroaryl *N*-oxides with (fluoromethyl)triphenylphosphonium iodide (Scheme 1e).

2. Results and discussion

Normally, (fluoromethyl)triphenylphosphonium iodide is prepared from the reaction of stoichiometric amounts of Ph_3P and CH_2FI (Scheme 2a) [21]. However, CH_2FI is very expensive. Thus, we modified the synthetic route using cheaper CH_2FBr as the CH_2F source. The reaction of Ph_3P and CH_2FBr in the presence of NaI in THF at reflux could afford (fluoromethyl)triphenylphosphonium iodide in 69 % yield (Scheme 2b). This phosphonium salt is a white solid, which can be stored under ambient conditions for months without noticeable decomposition. Its structure was determined by X-ray crystallographic analysis.

(Fluoromethyl)triphenylphosphonium iodide has been widely used as the precursor of fluoromethylene phosphonium ylide, which then reacted with aldehydes or ketones for the preparation of corresponding terminal vinyl fluorides [21a,22]. To extend its synthetic applications, we initiated our exploration by investigating the fluoromethylation of 4-phenylpyridine 1-oxide (**1a**) with (fluoromethyl)triphenylphosphonium iodide (Table 1). The reaction in the presence of *t*-BuOLi in different solvents at 80 °C for 12 h afforded fluoromethylated product **2a** in low yields (entries 1–4). DMSO was found to be the optimal solvent (entry 4). Switching the base from *t*-BuOLi to *t*-BuOK or *t*-BuONa gave

Table 1
Optimization of reaction conditions.[a].

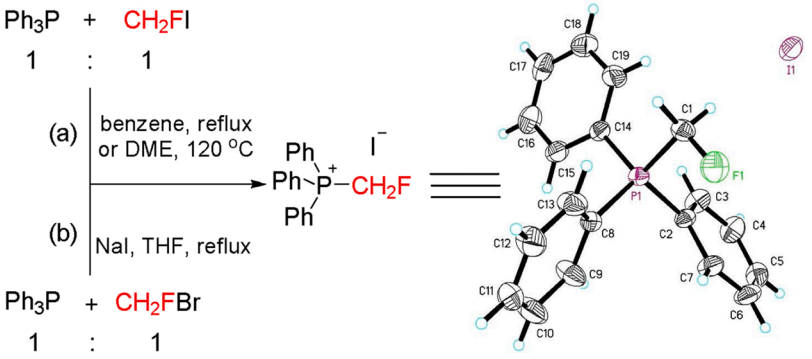


	Base	Solvent	Temperature	Yield (%)[b]
1	*t*-BuOLi	toluene	80 °C	trace
2	*t*-BuOLi	THF	80 °C	6
3	*t*-BuOLi	MeCN	80 °C	trace
4	*t*-BuOLi	DMSO	80 °C	29
5	*t*-BuONa	DMSO	80 °C	25
6	*t*-BuOK	DMSO	80 °C	10
7[c]	*t*-BuOLi	DMSO	80 °C	54
8[c]	*t*-BuOLi	DMSO	100 °C	48
9[c]	*t*-BuOLi	DMSO	60 °C	78
10[c]	*t*-BuOLi	DMSO	40 °C	81
11[c]	*t*-BuOLi	DMSO	rt	76
12[c,d]	*t*-BuOLi	DMSO	40 °C	80

[a] Reaction conditions: **1a** (0.2 mmol), (fluoromethyl)triphenylphosphonium iodide (0.3 mmol), base (0.4 mmol), solvent (2.0 mL), temperature, under N_2, 12 h.
[b] Yields were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard.
[c] (Fluoromethyl)triphenylphosphonium iodide (0.4 mmol), *t*-BuOLi (0.6 mmol).
[d] 2 h.

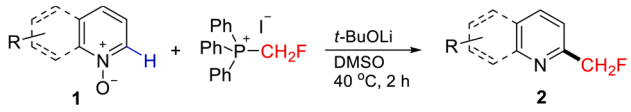
inferior results (entries 5 and 6). Higher yield of **2a** was observed by increasing the amounts of (fluoromethyl)triphenylphosphonium iodide and *t*-BuOLi (entry 7). To further improve the yield, the reaction temperature was investigated (entries 8–11). Pleasingly, the reaction proceeded smoothly at 40 °C to produce **2a** in 81 % yield (entry 10). Finally, reducing the reaction time from 12 h to 2 h still furnished **2a** in comparable yield (entry 12).

With the optimized reaction conditions in hand (Table 1, entry 12), the substrate scope of this regioselective deoxygenative fluoromethylation reaction was explored (Table 2). Pyridine *N*-oxides (**1a-e**) containing electron-donating or electron-withdrawing groups at different positions of the pyridine ring all underwent this transformation smoothly, affording the desired products (**2a-g**) in moderate to high yields. This protocol was successfully applied to fluoromethylation of 2,2′-bipyridine *N*-oxide (**1 h**). Quinoline *N*-oxides (**1i-p**) were also suitable substrates, giving the fluoromethylated products (**2i-p**) in good yields. However, 2,6-disubstituted pyridine *N*-oxides and 2-substituted quinoline *N*-oxides were not converted under the standard conditions. Remarkably, synthetically useful functional groups including vinyl, alkynyl, bromo, and iodo were well tolerated under the reaction conditions. Heteroaromatic *N*-oxide derived from phenanthridine (**1q**) was converted to the fluoromethylated product (**2q**) in moderate yield. The

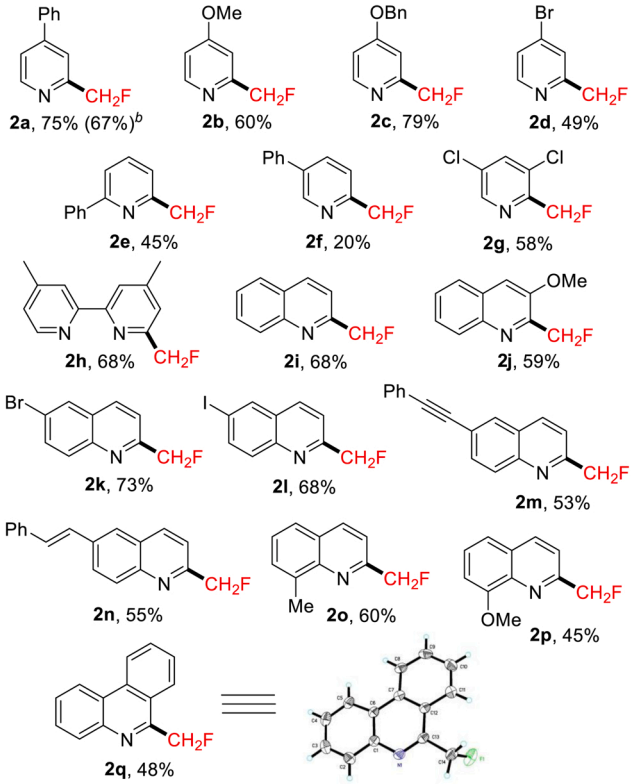


Scheme 2. Preparation of (fluoromethyl)triphenylphosphonium iodide.

Table 2
Scope of heteroaryl *N*-oxides.[a]



1 2

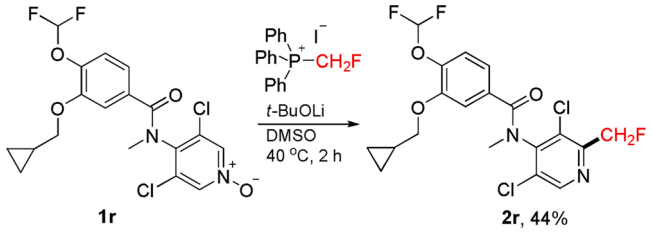


[a]Reaction conditions: **1** (0.4 mmol), (fluoromethyl)triphenylphosphonium iodide (0.8 mmol), *t*-BuOLi (1.2 mmol), DMSO (4.0 mL), 40 °C, under N_2, 2 h, isolated yields.
[b]Reaction was performed on a 6.0 mmol scale.

structure of **2q** was confirmed by the X-ray crystallographic analysis. In none of the cases were any other regioisomers observed. In addition, the reaction of **1a** could be easily scaled up to 6.0 mmol, affording **2a** in 67 % yield.

To demonstrate further the synthetic application of this protocol, the late-stage fluoromethylation of pharmaceutically relevant compounds was attempted. As shown in Scheme 3, substrate **1 r** derived from roflumilast, a drug used to treat chronic obstructive pulmonary disease, was subjected to the standard reaction conditions, furnishing fluoromethylated roflumilast analogous **2 r** in moderate yield.

On the basis of previous report [19,22], a plausible reaction mechanism was proposed in Scheme 4. Initially, treatment of (fluoromethyl) triphenylphosphonium iodide with *t*-BuOLi affords fluoromethylene phosphonium ylide. Subsequently, an intermolecular [3 + 2] annulation reaction of heteroaryl *N*-oxides **1** and fluoromethylene phosphonium ylide forms intermediate **A**. Finally, aromatization of intermediate **A** by an external base delivers the fluoromethylated products **2**.



1r 2r, 44%

Scheme 3. Fluoromethylation of roflumilast derivative (**1r**).

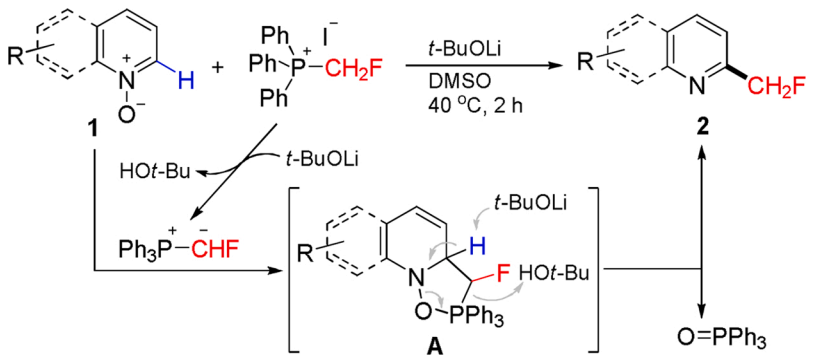
3. Conclusion

In conclusion, we have reported a new method for the direct incorporation of CH_2F group into heteroarenes. The reaction of heteroaryl *N*-oxides and (fluoromethyl)triphenylphosphonium iodide proceeded under mild conditions, affording the fluoromethylated heteroarenes in moderate to good yields with excellent regioselectivities. Further extending the applications of (fluoromethyl)triphenylphosphonium iodide in fluoromethylation of other substrates is currently in progress.

4. Experimental section

4.1. General information

^{1}H NMR (TMS as the internal standard), ^{19}F NMR spectra ($CFCl_3$ as the outside standard and low field is positive), and ^{31}P NMR (85 % H_3PO_4 as the external standard) spectra were recorded on a 400 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM400 spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. MS experiments were performed on a



Scheme 4. Proposed reaction mechanism.

Waters Premier GC-TOF MS for HRMS-EI and a Thermo Scientific Q Exactive HF Oribitrap-FTMS instrument for HRMS-ESI. All reagents were used as received from commercial sources without further purification or prepared as described in references. Substrates **1a-d** and **1g-i** were purchased and used directly from commercial sources. Substrates **1e** [23], **1f** [23], **1 j** [24], **1k** [24], **1 m** [15a], **1n** [15a], **1o** [15a], **1p** [17], and **1q** [15a] were prepared in accordance with methods described in the references.

4.2. General procedure for the synthesis of heteroaryl N-oxides

To a solution of heteroaromatic compound (1.25 mmol) in CH_2Cl_2 (6.0 mL) was added *m*-CPBA (253.8 mg, 85 %, 1.25 mmol) at 0 °C. The reaction mixture was then stirred at room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 (10.0 mL). Powdered potassium carbonate (172.7 mg, 1.25 mmol) was added to the reaction mixture, and the mixture was stirred for 1 h. The resulting mixture was filtered through a pad of Celite. After removal of the volatiles under reduced pressure, the residue was purified by column chromatography to give the product.

4.2.1. 6-Iodoquinoline 1-oxide (*1l*)

After purification by silica gel column chromatography (EtOAc/MeOH = 10:1), compound 1 L was obtained as a yellow solid (256.8 mg, 76 %), M.P. 139–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J =6.1 Hz, 1 H), 8.35 (d, J =9.2 Hz, 1 H), 8.16 (s, 1 H), 7.89 (dd, J = 9.1, 1.9 Hz, 1 H), 7.52 (d, J =8.5 Hz, 1 H), 7.23 (dd, J = 8.5, 6.0 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 139.0, 136.7, 135.9, 131.9, 124.4, 122.0, 121.5, 95.2. IR (thin film) ν 3086, 3063, 1558, 1498, 1419, 1354, 1225, 1174, 1094, 817, 787, 732, 518 cm^{-1}; MS (ESI): *m/z* 272.0 $[M+H]^+$; HRMS (ESI) *m/z*: $[M+H]^+$ Calculated for C_9H_7INO: 271.9567; Found: 271.9566.

4.2.2. 3,5-Dichloro-4-(3-(cyclopropylmethoxy)-4-(difluoromethoxy)-N-methylbenzamido)pyridine 1-oxide (*1r*)

After purification by silica gel column chromatography (hexane/EtOAc = 1:1), compound **1 r** was obtained as a white solid (447.1 mg, 83 %). The compound exists as an 11:1 ratio of amide diastereomers on the NMR time scale. Spectral data for major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2 H), 7.10 (d, J =2.0 Hz, 1 H), 6.99 (d, J =8.3 Hz, 1 H), 6.86 (dd, J = 8.3, 2.0 Hz, 1 H), 6.61 (t, J =74.7 Hz, 1 H), 3.80 (d, J =6.8 Hz, 2 H), 3.29 (s, 3 H), 1.23 (dt, J = 14.2, 7.0 Hz, 1 H), 0.67–0.62 (m, 2 H), 0.35–0.32 (m, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.83 (d, J =74.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 150.2, 142.6, 139.0, 132.9, 132.8, 121.7, 119.9, 115.8 (t, J =260.5 Hz), 113.9, 74.1, 35.5, 10.1, 3.4. IR (thin film) ν 3079, 3009, 1667, 1594, 1506, 1429, 1310, 1271, 1123, 1025, 833, 756 cm^{-1}; MS (ESI): *m/z* 433.1 $[M+H]^+$; HRMS (ESI) *m/z*: $[M+H]^+$ Calculated for $C_{18}H_{17}Cl_2F_2N_2O_4$: 433.0528; Found: 433.0528.

4.3. Synthesis of (fluoromethyl)triphenylphosphonium iodide

A mixture of triphenylphosphine (30.2 g, 115 mmol) and NaI (17.2 g, 115 mmol) was added in a 250 mL round-bottom flask, and then THF (150 mL) was added. CH_2FBr (7.4 mL, 115 mmol) was added to the mixture and then the resulting mixture was stirred at 80 °C for 48 h. After cooling to room temperature, the resulting mixture was filtered and washed with THF. Then the residue was added to DCM (600 mL), and the mixture was shaken for several minutes. The organic layer was filtered, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to give (fluoromethyl)triphenylphosphonium iodide as a white solid (33.5 g, 69 %). M.P. 169–171 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.94–7.88 (m, 3 H), 7.86–7.79 (m, 6 H), 7.78–7.71 (m, 6 H), 6.75 (d, J =44.9 Hz, 2 H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -243.27 (dt, J = 57.2, 45.0 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 136.4 (d, J =3.0 Hz), 134.6 (dd, J = 10.4, 1.3 Hz), 131.0 (d, J =13.1 Hz), 114.7 (d, J =86.7 Hz), 78.4 (dd, J = 196.6, 64.1 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 17.75 (d, J =57.3 Hz). IR (thin film) ν 3444, 3053, 2915, 2826, 1586, 1438, 1317, 1114, 722, 687, 532 cm^{-1}; MS (ESI): *m/z* 295.1 $[M-I]^+$; HRMS (ESI) *m/z*: $[M-I]^+$ Calculated for $C_{19}H_{17}FP$: 295.1046; Found: 295.1045.

4.4. General procedure for C—H fluoromethylation of heteroaryl N-oxides

A mixture of heteroaryl *N*-oxide (0.4 mmol), $[Ph_3PCFH_2]I$ (337.6 mg, 0.8 mmol), *t*-BuOLi (96.0 mg, 1.2 mmol) was added in a 10 mL Schlenk tube under N_2 atmosphere, and then DMSO (4.0 mL) was added. The mixture was stirred at 40 °C for 2 h. After the reaction was complete, water was added. The resulting mixture was extracted with DCM for four times. The organic layer was washed with brine, dried over Na_2SO_4, filtered and removed under reduced pressure. The residue was purified by silica gel column chromatography to give the desired product **(2a-2p)**.

4.4.1. 2-(Fluoromethyl)-4-phenylpyridine (*2a*)

After purification by silica gel column chromatography (hexane/EtOAc = 10:1), compound **2a** was obtained as a yellow oil (56.1 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J =5.2 Hz, 1 H), 7.71–7.60 (m, 3 H), 7.57–7.41 (m, 4 H), 5.55 (d, J =46.9 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.30 (t, J =46.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (d, J =21.0 Hz), 149.8 (d, J =2.2 Hz), 149.6, 138.1, 129.4, 129.3, 127.2, 121.1, 118.5 (d, J =5.9 Hz), 84.6 (d, J =170.0 Hz). IR (thin film) ν 3060, 3031, 2947, 1606, 1550, 1503, 1475, 1027, 846, 762, 696 cm^{-1}; MS (EI): *m/z* 187.0 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_{12}H_{10}FN$: 187.0792; Found: 187.0788.

4.4.2. 2-(Fluoromethyl)-4-methoxypyridine (*2b*)

After purification by silica gel column chromatography (hexane/EtOAc = 4:1), compound **2b** was obtained as a yellow oil (33.8 mg, 60

%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J =5.7 Hz, 1 H), 6.91 (d, J =2.5 Hz, 1 H), 6.69 (dd, J = 5.7, 2.6 Hz, 1 H), 5.38 (d, J =46.9 Hz, 2 H), 3.80 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.89 (t, J =46.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 158.2 (d, J =21.0 Hz), 150.4 (d, J =2.3 Hz), 109.3, 106.2 (d, J =6.5 Hz), 84.2 (d, J =170.4 Hz), 55.2. IR (thin film) ν 3403, 2948, 2840, 1602, 1571, 1488, 1460, 1374, 1306, 836, 759 cm^{-1}; MS (EI): *m/z* 141 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for C_7H_8FNO: 141.0584; Found: 141.0587.

4.4.3. 4-Benzyloxy-2-(fluoromethyl)pyridine (2c)

After purification by silica gel column chromatography (hexane/EtOAc = 5:1), compound **2c** was obtained as a yellow oil (68.6 mg, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J =5.7 Hz, 1 H), 7.50−7.30 (m, 5 H), 7.06 (s, 1 H), 6.81 (d, J =3.3 Hz, 1 H), 5.44 (d, J =46.9 Hz, 2 H), 5.13 (s, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.95 (t, J =46.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 158.4 (d, J =21.2 Hz), 150.6 (d, J =2.2 Hz), 135.6, 128.9, 128.5, 127.7, 110.0, 107.1 (d, J =6.5 Hz), 84.3 (d, J =170.4 Hz), 70.0. IR (thin film) ν 3030, 2852, 1598, 1569, 1483, 1310, 1177, 1026, 741, 697 cm^{-1}; MS (EI): *m/z* 217 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_{13}H_{12}FNO$: 217.0897; Found: 217.0900.

4.4.4. 4-Bromo-2-(fluoromethyl)pyridine (2d)

After purification by silica gel column chromatography (hexane/EtOAc = 10:1), compound **2d** was obtained as a yellow oil (37.2 mg, 49 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J =5.3 Hz, 1 H), 7.64 (s, 1 H), 7.41 (dd, J = 5.3, 1.9 Hz, 1 H), 5.46 (d, J =46.7 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -223.06 (t, J =46.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (d, J =21.9 Hz), 149.9 (d, J =2.2 Hz), 134.1, 126.5, 123.9 (d, J =6.6 Hz), 83.6 (d, J =171.6 Hz). IR (thin film) ν 3056, 2922, 1574, 1469, 1454, 1372, 1229, 1029, 825, 682 cm^{-1}; MS (EI): *m/z* 188.9 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for C_6H_5BrFN: 188.9584; Found: 188.9585.

4.4.5. 2-(Fluoromethyl)-6-phenylpyridine (2e)

After purification by silica gel column chromatography (hexane/EtOAc = 15:1), compound **2e** was obtained as a yellow oil (33.7 mg, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.97 (m, 2 H), 7.82 (t, J =7.8 Hz, 1 H), 7.68 (d, J =7.9 Hz, 1 H), 7.53−7.37 (m, 4 H), 5.58 (d, J =47.0 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.22 (t, J =47.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (d, J =2.1 Hz), 156.6 (d, J =22.0 Hz), 139.1, 137.7, 129.3, 128.9, 127.1, 119.9, 118.8 (d, J =5.9 Hz), 84.8 (d, J =169.7 Hz). IR (thin film) ν 3063, 2954, 1592, 1578, 1460, 1449, 1358, 1032, 809, 760, 694, 624 cm^{-1}; MS (EI): *m/z* 187.0 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_{12}H_{10}FN$: 187.0792; Found: 187.0797.

4.4.6. 2-(Fluoromethyl)-5-phenylpyridine (2f)

After purification by silica gel column chromatography (hexane/EtOAc = 15:1), compound **2f** was obtained as a yellow oil (15.1 mg, 20 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J =2.2 Hz, 1 H), 7.96 (dd, J = 8.1, 2.3 Hz, 1 H), 7.64−7.38 (m, 6 H), 5.55 (d, J =46.9 Hz, 2 H). ^{19}F NMR (376 MHz,$CDCl_3$) δ -220.26 (t, J =46.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1 (d, J =21.5 Hz), 147.7, 137.5, 136.4, 135.6, 129.3, 128.5, 127.3, 120.9 (d, J =5.5 Hz), 84.4 (d, J =169.7 Hz). IR (thin film) ν 3060, 3031, 2953, 1597, 1480, 1449, 1376, 1031, 1006, 838, 760, 697 cm^{-1}; MS (EI): *m/z* 187.0 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_{12}H_{10}FN$: 187.0792; Found: 187.0795.

4.4.7. 3,5-Dichloro-2-(fluoromethyl)pyridine (2g)

After purification by silica gel column chromatography (hexane/EtOAc = 10:1), compound **2 g** was obtained as a yellow oil (41.5 mg, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1 H), 7.76 (s, 1 H), 5.55 (d, J =47.0 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -217.90 (t, J =47.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4 (d, J =16.0 Hz), 146.7, 137.0 (d, J =1.6 Hz), 132.7 (d, J =3.4 Hz), 131.8 (d, J =2.3 Hz), 82.0 (d, J =171.2 Hz). IR (thin film) ν 3065, 2965, 1566, 1443, 1377, 1118, 1061, 1002, 874, 710, 655 cm^{-1}; MS (EI): *m/z* 178.9 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_6H_4Cl_2FN$: 178.9699; Found: 178.9697.

4.4.8. 6-(Fluoromethyl)-4,4′-dimethyl-2,2′-bipyridine (2h)

After purification by silica gel column chromatography (hexane/EtOAc = 10:1), compound **2 h** was obtained as a yellow solid (58.8 mg, 68 %). M.P. 46−48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J =5.0 Hz, 1 H), 8.19 (s, 1 H), 8.15 (s, 1 H), 7.29 (s, 1 H), 7.12 (d, J =5.1 Hz, 1 H), 5.53 (d, J =47.1 Hz, 2 H), 2.45 (s, 3 H), 2.42 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -220.26 (t, J =47.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 155.8 (d, J =2.8 Hz), 155.7, 149.2, 149.0, 148.4, 124.9, 122.3, 121.53 (d, J =5.5 Hz), 121.46, 84.8 (d, J =169.3 Hz), 21.4, 21.3. IR (thin film) ν 2952, 1598, 1562, 1434, 1361, 1034, 830, 530 cm^{-1}; MS (EI): *m/z* 216.0 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_{13}H_{13}FN_2$: 216.1057; Found: 216.1054.

4.4.9. 2-(Fluoromethyl)quinoline (2i)

After purification by silica gel column chromatography (hexane/EtOAc = 10:1), compound **2i** was obtained as a yellow oil (43.8 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J =8.5 Hz, 1 H), 8.02 (d, J =8.2 Hz, 1 H), 7.73 (d, J =8.2 Hz, 1 H), 7.66 (dd, J = 8.5, 6.9 Hz, 1 H), 7.51−7.45 (m, 2 H), 5.61 (d, J =47.0 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.20 (t, J =47.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7 (d, J =21.7 Hz), 147.3 (d, J =1.8 Hz), 137.0, 130.0, 129.0, 127.7, 127.6, 126.6, 118.1 (d, J =5.1 Hz), 85.0 (d, J =170.3 Hz). IR (thin film) ν 3056, 2952, 1601, 1507, 1429, 1376, 1038, 825, 753 cm^{-1}; MS (EI): *m/z* 161.0 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_{10}H_8FN$: 161.0635; Found: 161.0632.

4.4.10. 2-(Fluoromethyl)-3-methoxyquinoline (2j)

After purification by silica gel column chromatography (hexane/EtOAc = 10:1), compound **2 j** was obtained as a yellow oil (45.1 mg, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J =8.7 Hz, 1 H), 7.69 (d, J =8.0 Hz, 1 H), 7.60−7.41 (m, 2 H), 7.36 (s, 1 H), 5.68 (d, J =47.1 Hz, 2 H), 3.92 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.44 (t, J =47.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 148.4 (d, J =14.7 Hz), 142.6, 129.4, 127.5, 127.1, 126.5, 112.4, 81.7 (d, J =169.3 Hz), 55.6. IR (thin film) ν 3100, 2970, 1606, 1500, 1455, 1421, 1357, 1326, 1198, 1166, 1024, 750 cm^{-1}; MS (EI): *m/z* 191.0 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_{11}H_{10}FNO$: 191.0741; Found: 191.0735.

4.4.11. 6-Bromo-2-(fluoromethyl)quinoline (2k)

After purification by silica gel column chromatography (hexane/EtOAc = 10:1), compound **2k** was obtained as a yellow solid (69.8 mg, 73 %). M.P. 97−99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J =8.5 Hz, 1 H), 7.95 (d, J =2.2 Hz, 1 H), 7.88 (d, J =9.0 Hz, 1 H), 7.75 (dd, J = 9.0, 2.2 Hz, 1 H), 7.58 (d, J =8.5 Hz, 1 H), 5.61 (d, J =46.9 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.96 (t, J =46.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4 (d, J =21.9 Hz), 146.0, 136.2, 133.5, 130.8, 129.8, 128.8, 120.7, 119.1 (d, J =5.2 Hz), 84.8 (d, J =170.7 Hz). IR (thin film) ν 3030, 2939, 1596, 1493, 1036, 886, 829, 636 cm^{-1}; MS (EI): *m/z* 238.9 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_{10}H_7BrFN$: 238.9740; Found: 238.9737.

4.4.12. 2-(Fluoromethyl)-6-iodoquinoline (2l)

After purification by silica gel column chromatography (hexane/EtOAc = 15:1), compound 2 L was obtained as a yellow solid (78.2 mg, 68 %). M.P. 111−113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1 H), 8.08 (d, J =8.5 Hz, 1 H), 7.93 (dd, J = 8.9, 2.0 Hz, 1 H), 7.75 (d, J =8.9 Hz, 1 H), 7.58 (d, J =8.5 Hz, 1 H), 5.61 (d, J =46.9 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -222.08 (t, J =46.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (d, J =21.9 Hz), 146.4 (d, J =1.9 Hz), 138.8, 136.6, 136.0, 130.8, 129.4, 118.9 (d, J =5.4 Hz), 92.4, 84.9 (d, J =170.9 Hz). IR (thin film) ν 2950, 1590, 1487, 1386, 1267, 1034, 895, 829, 737, 630 cm^{-1}; MS (EI): *m/z* 286.9 $[M]^+$; HRMS (EI) *m/z*: $[M]^+$ Calculated for $C_{10}H_7FIN$: 286.9602; Found: 286.9601.

4.4.13. 2-(Fluoromethyl)-6-(phenylethynyl)quinoline (**2m**)

After purification by silica gel column chromatography (hexane/EtOAc = 15:1), compound **2 m** was obtained as a yellow solid (55.3 mg, 53 %). M.P. 107−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J =8.5 Hz, 1 H), 8.01 (dd, J = 5.4, 3.4 Hz, 2 H), 7.82 (dd, J = 8.8, 1.8 Hz, 1 H), 7.65−7.53 (m, 3 H), 7.42−7.32 (m, 3 H), 5.66 (d, J =46.9 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.85 (t, J =46.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (d, J =21.9 Hz), 146.9 (d, J =1.8 Hz), 136.9, 132.8, 131.8, 131.1, 129.2, 128.7, 128.6, 127.5, 123.0, 121.9, 119.0 (d, J =5.3 Hz), 91.0, 89.0, 84.9 (d, J =170.7 Hz). IR (thin film) ν 3065, 2931, 1598, 1497, 1442, 1041, 842, 759, 691 cm^{-1}; MS (EI): m/z 261.0 $[M]^+$; HRMS (EI) m/z: $[M]^+$ Calculated for $C_{18}H_{12}FN$: 261.0948; Found: 261.0953.

4.4.14. (E)-2-(fluoromethyl)-6-styrylquinoline (**2n**)

After purification by silica gel column chromatography (hexane/EtOAc = 15:1), compound **2n** was obtained as a yellow solid (58.1 mg, 55 %). M.P. 132−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J =8.5 Hz, 1 H), 8.06−7.91 (m, 2 H), 7.79 (s, 1 H), 7.60−7.50 (m, 3 H), 7.39 (t, J =7.6 Hz, 2 H), 7.29 (d, J =7.3 Hz, 1 H), 7.24 (s, 2 H), 5.65 (d, J =47.0 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.00 (t, J =47.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (d, J =21.7 Hz), 147.2, 137.1, 137.0, 135.9, 130.4, 129.4, 128.9, 128.2, 128.1, 127.83, 127.76, 126.8, 125.9, 118.8 (d, J =5.2 Hz), 85.0 (d, J =170.2 Hz). IR (thin film) ν 1696, 1592, 1560, 1445, 964, 833, 746, 691 cm^{-1}; MS (EI): m/z 263.0 $[M]^+$; HRMS (EI) m/z: $[M]^+$ Calculated for $C_{18}H_{14}FN$: 263.1105; Found: 263.1099.

4.4.15. 2-(Fluoromethyl)-8-methylquinoline (**2o**)

After purification by silica gel column chromatography (hexane/EtOAc = 15:1), compound **2o** was obtained as a yellow oil (42.0 mg, 60 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.19 (d, J =8.4 Hz, 1 H), 7.68 (d, J =8.2 Hz, 1 H), 7.58 (d, J =8.7 Hz, 2 H), 7.45 (t, J =7.6 Hz, 1 H), 5.67 (d, J =47.2 Hz, 2 H), 2.79 (s, 3 H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -219.76 (t, J =47.2 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 155.9 (d, J =21.3 Hz), 146.9, 137.5, 130.3, 128.0, 126.8, 126.1, 118.51, 118.46, 86.0 (d, J =168.7 Hz), 17.9. IR (thin film) ν 3056, 2952, 2922, 1602, 1505, 1366, 1324, 1036, 835, 763 cm^{-1}; MS (EI): m/z 175.0 $[M]^+$; HRMS (EI) m/z: $[M]^+$ Calculated for $C_{11}H_{10}FN$: 175.0792; Found: 175.0795.

4.4.16. 2-(Fluoromethyl)-8-methoxyquinoline (**2p**)

After purification by silica gel column chromatography (hexane/EtOAc = 10:1), compound **2p** was obtained as a white solid (35.0 mg, 45 %). M.P. 62−64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J =8.5 Hz, 1 H), 7.62 (d, J =8.5 Hz, 1 H), 7.50−7.33 (m, 2 H), 7.05 (d, J =7.6 Hz, 1 H), 5.71 (d, J =46.9 Hz, 2 H), 4.06 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -221.24 (t, J =47.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0 (d, J =22.6 Hz), 155.1, 139.3 (d, J =2.2 Hz), 137.2, 128.9, 126.9, 119.7, 118.9 (d, J =5.5 Hz), 108.2, 85.3 (d, J =169.5 Hz), 56.2. IR (thin film) ν 1640, 1275, 1261, 1112, 834, 750, 720 cm^{-1}; MS (EI): m/z 191.0 $[M]^+$; HRMS (EI) m/z: $[M]^+$ Calculated for $C_{11}H_{10}FNO$: 191.0741; Found: 191.0737.

4.4.17. 2-Fluoromethylphenanthridine (**2q**)

After purification by silica gel column chromatography (hexane/EtOAc = 15:1), compound **2q** was obtained as a white solid (40.3 mg, 48 %). M.P. 121−123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J =8.5 Hz, 1 H), 8.55 (d, J =8.1 Hz, 1 H), 8.32 (d, J =8.0 Hz, 1 H), 8.19 (d, J =8.1 Hz, 1 H), 7.86 (dd, J = 8.3, 7.0 Hz, 1 H), 7.80−7.63 (m, 3 H), 6.01 (d, J =47.3 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -212.89 (t, J =47.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (d, J =16.8 Hz), 143.2, 133.3, 131.0, 130.4, 129.0, 127.9, 127.8, 126.3 (d, J =4.2 Hz), 124.8, 124.7, 122.5, 122.2, 85.6 (d, J =169.5 Hz). IR (thin film) ν 3078, 1578, 1445, 1039, 1014, 1013, 971, 763, 725 cm^{-1}; MS (EI): m/z 211.0 $[M]^+$; HRMS (EI) m/z: $[M]^+$ Calculated for $C_{14}H_{10}FN$: 211.0792; Found: 211.0791.

4.4.18. 3-(Cyclopropylmethoxy)-N-(3,5-dichloro-2-(fluoromethyl)pyridin-4-yl)-4-(difluoromethoxy)-N-methylbenzamide (**2r**)

After purification by silica gel column chromatography (hexane/EtOAc = 5:1), compound **2 r** was obtained as a yellow oil (79.1 mg, 44 %). The compound exists as an 11:1 ratio of amide diastereomers on the NMR time scale. Spectral data for major diastereomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1 H), 7.00 (s, 1 H), 6.90 (d, J =3.3 Hz, 2 H), 6.54 (t, J =74.9 Hz, 1 H), 5.46 (dd, J = 46.8, 2.1 Hz, 2 H), 3.75−3.61 (m, 2 H), 3.27 (d, J =0.9 Hz, 3 H), 1.24−1.09 (m, 1 H), 0.63−0.51 (m, 2 H), 0.33−0.20 (m, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.88 (d, J =74.9 Hz, 2 F), -217.57 (t, J =46.8 Hz, 1 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 152.9 (d, J =16.2 Hz), 149.9, 148.3, 147.9, 142.5 (t, J =3.2 Hz), 132.7, 121.6, 120.4, 115.8 (t, J =260.5 Hz), 113.8, 82.2 (d, J =172.5 Hz), 74.0, 35.0, 10.0, 3.3, 3.2. IR (thin film) ν 3084, 2917, 1667, 1510, 1334, 1266, 1122, 1050, 1006, 913, 747 cm^{-1}; MS (ESI): m/z 449.1 $[M+H]^+$; HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{19}H_{18}Cl_2F_3N_2O_3$: 449.0641; Found: 449.0640.

4.5. Procedure for gram-scale reaction

A mixture of 4-phenylpyridine-*N*-oxide **1a** (1.03 g, 6.0 mmol), $[Ph_3PCFH_2]I$ (5.12 g, 12.0 mmol) and *t*-BuOLi (1.44 g, 18.0 mmol) was added in a 250 mL round-bottom flask under N_2, and then DMSO (60.0 mL) was added. The mixture was stirred at 40 °C for 2 h. After the reaction was complete, water was added. The resulting mixture was extracted with DCM for four times. The organic layer was washed with brine, dried over Na_2SO_4, filtered and removed under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to give product **2a** as a yellow oil (750.3 mg, 67 %).

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfluchem.2020.109695.

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