Supporting Information

For

Copper-Catalyzed Fluorination of 2-Pyridyl Aryl Bromides

Xin Mu, Hao Zhang, Pinhong Chen and Guosheng Liu*

State Key Laboratory of Organometallics Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,

345 Lingling Road, Shanghai, China, 200032.

Email: *gliu@mail.sioc.ac.cn*

General Procedures and New Compounds Characterization

Content:

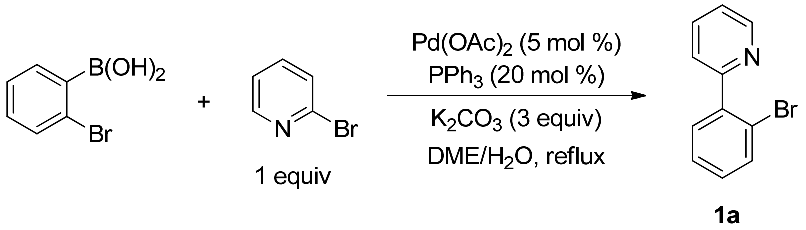
1. General Considerations.

All commercially available compounds were purchased from Sigma-Aldrich or Alfa Aesar. NMR spectra were recorded on a Varian Inova 400 or Agilent 400 (400 MHz for ^1H; 376 MHz for ^{19}F; 100 MHz for ^{13}C) spectrometer. The chemical shifts (δ) are given in parts per million relative to internal standard TMS (0 ppm for ^1H) and $CDCl_3$ (77.0 ppm for ^{13}C). Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. Acetonitrile was dried by refluxing over CaH_2 and distillated before used.

Note: This fluorination reactions are relatively sensitive toward the stirring speed and position due to heterogeneous reaction condition, thus stirring speed was maintained at 600 rpm and positioned at center of the stirrer during the fluorination reaction.

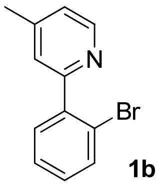
2. Typical Procedures for the Synthesis of Substrates 1.

*2.1 The synthesis of Substrates **1a-1d***



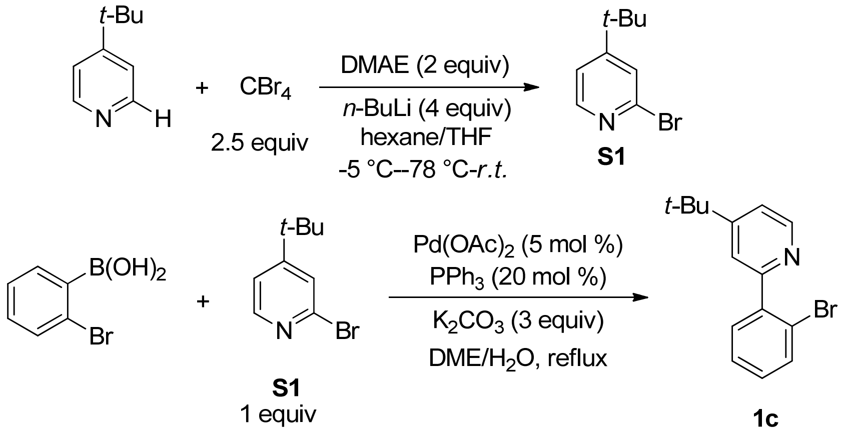
Scheme S1

To 250 mL three-necked bottle, 2-bromo phenyl boronic acid (4.02 g, 20 mmol), 2-bromo pyridine (3.16 g, 20 mmol), triphenylphospine (1.02 g, 4 mmol) were dissolved in DME (28 mL) under N_2 atmosphere. After stirring for 3 min, aqueous potassium carbonate K_2CO_3 (8.29 g in 30 mL deionized water) and $Pd(OAc)_2$ (0.22 g, 1 mmol) was added, and the reaction mixture was refluxed for 6h. The reaction was monitored by TLC. After reaction completed, the reaction mixture was allowed to cool to room temperature. The mixture was extracted by ethyl acetate (20 mL×3). The organic phase was combined, dried over anhydrous $MgSO_4$, vacuum evaporation. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1) to provide colorless oil as cross-coupling product **1a** (2.3712 g, 51%), R_f= 0.5 (petroleum ether/ethyl acetate = 5:1).



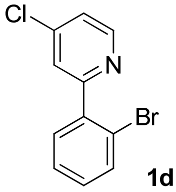
1b

The same procedure (Scheme S1) for the synthesis of **1b**, flash chromatography (petroleum ether/ethyl acetate = 15:1) provide **1b** in 68% yield (1.68 g), R_f = 0.6 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.66 (dd, J = 8, 0.8 Hz, 1H), 7.50 (dd, J = 7.6, 1.6 Hz, 1H), 7.39 (m, 2H), 7.24 (ddd, *J* = 8.0, 8.0, 2 Hz, 1H), 7.12 (d, *J* = 5.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 149.1, 146.9, 141.3, 133.2, 131.3, 129.5, 127.4, 125.5, 123.4, 121.7, 21.1. HRMS: m/z (EI) calculated $[M]^+$: 246.9997, measured: 246.9995.



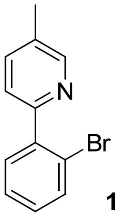
Scheme S2

To a 250 mL three-necked bottle, the mixture of DMAE (2.7580 g, 32 mmol) and anhydrous hexane (40 mL) were cooled to -5 °C, *n*-BuLi (25.6 mL, 2.5 M) was added slowly via dropping funnel. The resultant orange solution was maintained -5 °C for 15min， then 4-*tert* pyridine (2.1663 g, 16 mmol) was added and the mixture was continued to stir for 1h. The red mixture was coolded again to -78 °C, and the solution of CBr_4 (13.25 g, 40 mmol) in THF was added. The mixture was maintained at -78 °C for 1h. The dark brown mixture was allowed to warm to room tempereture and continued stirring for addtional 1h. The mixture was quenched at 0 °C by adding 40 mL H_2O. The mixture was extacted by ethyl acetate. The combination organic phase was dried over anhydrous $MgSO_4$, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 12:1) to provided 2-bromo-4-*t*-butyl pyridine **S1** (0.88 g, 25% yield), R_f = 0.6 (petroleum ether/ethyl acetate = 4:1). The second step was followed the same procedure of **1a** (Scheme S1), flash chromatography (petroleum ether/ethyl acetate = 16:1) provide the yellow oil **1c** (0.47 g, 41%), R_f = 0.4 (petroleum ether/ethyl acetate = 6:1). Compound **1c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.2 Hz, 1H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61 (m, 1H), 7.57 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.39 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.27 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.23 (ddd, *J* = 7.6, 7.6, 2.0 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 157.9, 149.2, 141.6, 133.2, 131.4, 129.5, 127.4, 122.1, 121.8, 119.4, 34.8, 30.4. HRMS: m/z (EI) calculated $[M]^+$: 289.0466, measured: 289.0473.



1d

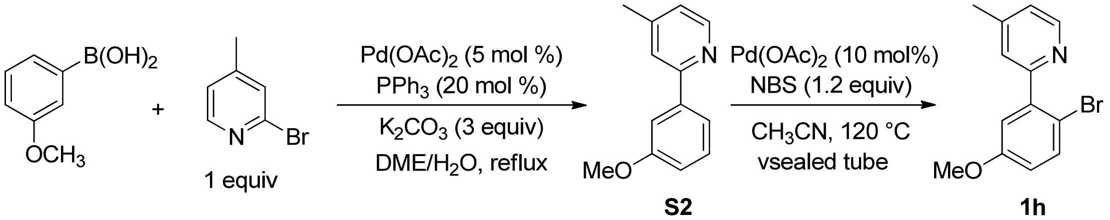
The same procedure (Scheme S1) for the synthesis of **1d**, flash chromatography (petroleum ether/ethyl acetate = 20:1) provide the **1d** in 84% yield (2.26 g), R_f = 0.3 (petroleum ether/ethyl acetate = 12:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.2 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.63(m, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.30(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 150.2, 143.8, 140.0, 133.4, 131.3, 130.2, 127.6, 125.0, 122.7, 121.6. HRMS: m/z (EI) calculated $[M]^+$: 266.9450, measured: 266.9454.



1e

The same procedure (Scheme S1) for the synthesis of **1e**, flash chromatography (petroleum ether/ethyl acetate = 12:1) provide the **1d** in 84% yield (2.26 g), R_f = 0.5 (petroleum ether/ethyl acetate = 6:1). in 68% yield (1.67 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 0.8 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.51 (m, 2H), 7.39 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.23 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 149.8, 141.1, 136.3, 133.2, 131.9, 131.4, 129.5, 127.5, 124.1, 121.8, 18.2. HRMS: m/z (EI) calculated $[M]^+$: 246.9997, measured: 247.0001.

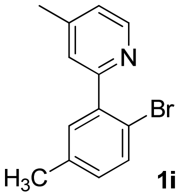
2.2 The typical procedure for the synthesis of **1h-1w**



Scheme S3

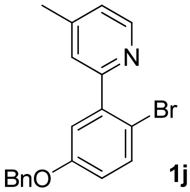
The synthesis of the **S2** was followed the same procedure in Scheme **S1**in 54% yield (1.07 g). Then **S2** (1.07 g, 5.3 mmol), NBS (1.15 g, 6.44 mmol) and $Pd(OAc)_2$ (0.12 g, 0.54 mmol) were dissolved in CH_3CN (40 mL). The reaction tube was sealed and heated to 120 °C. The reaction was monitored by TLC. After reaction completed, organic solvent was removed under vacuum and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 20:1) to provide **1h** as colorless oil (0.84 g, 56%), R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.56 (d, *J* = 5.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.12 (d, *J* = 5.6 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 9.6, 2.8 Hz, 1H), 3.81(s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 158.0, 148.9, 146.9, 142.0, 133.8, 125.4, 123.5, 116.2, 112.1, 55.5, 21.1. HRMS: m/z (EI) calculated $[M-1]^+$: 276.0024, measured: 276.0021.



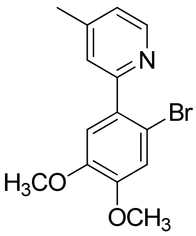
1i

The same procedure (Scheme S3) for the synthesis of **1i**, flash chromatography (petroleum ether/ethyl acetate = 12:1) provide in 62% yield (0.78 g), R_f = 0.4 ((petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.8 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.10 (d, *J* = 5.2 Hz, 1H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 149.1, 146.8, 140.9, 137.4, 132.9, 132.0, 130.4, 125.5, 123.3, 118.3, 21.1, 20.8. HRMS: m/z (EI) calculated $[M]^+$: 261.0157, measured: 261.0153.



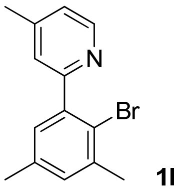
1j

The same procedure (Scheme S3) for the synthesis of **1j**, flash chromatography (petroleum ether/ethyl acetate = 12:1) provide **1j** in 41% yield (0.56 g), R_f = 0.5 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.2 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.35 (m, 6H), 7.16 (d, *J* = 3.2 Hz, 1H), 7.08 (d, *J* = 4.8 Hz, 1H), 6.85 (dd, *J* = 8.8, 3.2 Hz, 1H), 5.04 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 157.89, 148.9, 146.9, 142.0, 136.4, 133.8, 128.5, 127.9, 127.4, 125.4, 123.4, 117.3, 116.7, 112.3, 70.1, 21.0. HRMS: m/z (EI) calculated $[M]^+$: 353.0420, measured: 353.0415.



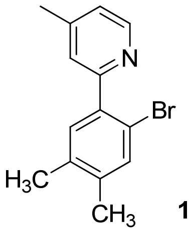
1k

The same procedure (Scheme S3) for the synthesis of **1k,** flash chromatography (petroleum ether/ethyl acetate = 10:1) provide **1k** in 45% yield (0.51 g), R_f = 0.4 (petroleum ether/ethyl acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.2 Hz, 1H), 7.44 (s, 1H), 7.10 (s, 1H), 7.09 (s, 1H), 7.07 (d, *J* = 5.2 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 149.2, 148.8, 148.2, 146.6, 133.3, 125.5, 122.9, 115.5, 113.6, 111.6, 55.9, 55.8, 20.9. HRMS: m/z (EI) calculated $[M]^+$: 307.0208, measured: 307.0213.



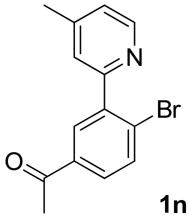
1l

The same procedure (Scheme S3) for the synthesis of **1l**, flash chromatography (petroleum ether/ethyl acetate = 15:1) provide **1l** in 62% yield (0.83 g), R_f = 0.7 (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.2 Hz, 1H), 7.33 (s, 1H), 7.09 (m, 3H), 2.44 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 148.8, 146.9, 141.6, 138.4, 136.6, 131.4, 129.3, 125.6, 123.2, 120.9, 23.8, 21.1, 20.6. HRMS: m/z (EI) calculated $[M]^+$: 275.0312, measured: 275.0310.



1m

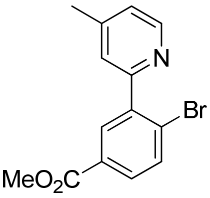
The same procedure (Scheme S3) for the synthesis of **1m**, flash chromatography (petroleum ether/ethyl acetate = 12:1) provide **1m** in 47% yield (0.65 g), R_f = 0.6 (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.2 Hz, 1H), 7.43 (s, 1H), 7.40 (s, 1H), 7.26 (s, 1H), 7.07 (dd, *J* = 4.0, 0.8 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 149.0, 146.7, 138.5, 138.48，136.1，133.8， 132.3, 125.6, 123.1, 118.2, 21.1, 19.2, 19.1. HRMS: m/z (EI) calculated $[M]^+$: 274.0231, measured: 274.0234.



1n

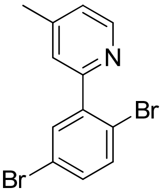
The same procedure (Scheme S3) for the synthesis of **1n**, flash chromatography (petroleum ether/ethyl acetate = 5:1) provide the **1n** in 52% yield (0.76 g), R_f = 0.5 (petroleum ether/ethyl acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.2 Hz, 1H), 8.06 (d, *J* = 2.0 Hz, 1H), 7.83 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.41 (s, 1H), 7.16 (d, *J* = 4.8 Hz, 1H), 2.61 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 157.3, 149.3, 147.3, 141.7, 136.2, 133.7, 131.3, 128.8, 127.4, 125.5, 123.8, 26.6, 21.1. HRMS: m/z (EI) calculated $[M]^+$: 289.0102, measured:

289.0103.



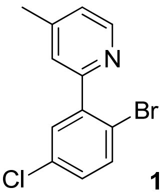
1o

The same procedure (Scheme S3) for the synthesis of **1o**, flash chromatography (petroleum ether/ethyl acetate = 10:1) provide **1o** in 31% yield (0.28 g), R$_f$ = 0.5 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.57 (d, *J* = 5.2 Hz, 1H), 8.16 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.39 (s, 1H), 7.15 (dd, *J* = 4.0, 0.8 Hz, 1H), 3.91 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.1, 157.4, 149.2, 147.2, 141.6, 133.5, 132.3, 130.2, 129.5, 127.2, 125.3, 123.7, 52.2, 21.1. HRMS: m/z (EI) calculated [M]$^+$: 305.0051, measured: 305.0056.



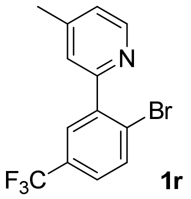
1p

The same procedure (Scheme S3) for the synthesis of **1p**, flash chromatography (petroleum ether/ethyl acetate = 12:1) provide **1p** in 54% yield (0.72 g), R$_f$ = 0.4 (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 (d, *J* = 5.2 Hz, 1H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.36 (m, 2H), 7.14 (dd, *J* = 5.2, 0.8 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.8, 149.3, 147.3, 143.0, 134.6, 134.2, 132.5, 125.4, 123.8, 121.4, 120.4, 21.1. HRMS: m/z (EI) calculated [M]$^+$: 324.9102, measured: 324.9100.



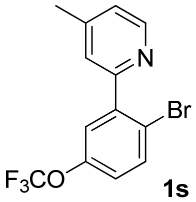
1q

The same procedure (Scheme S3) for the synthesis of **1q**, flash chromatography (petroleum ether/ethyl acetate = 12:1) provide **1q** in 52% yield (0.72 g), R$_f$ = 0.7 (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 2.8 Hz, 1H), 7.39 (s, 1H), 7.21 (dd, *J* = 8.4, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.9, 149.2, 147.2, 142.6, 134.3, 133.5, 131.3, 129.5, 125.4, 123.8, 119.6, 21.1. HRMS: m/z (EI) calculated [M]$^+$: 280.9607, measured: 280.9610.



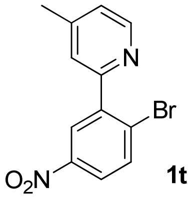
1r

The same procedure (Scheme S3) for the synthesis of **1r**, flash chromatography (petroleum ether/ethyl acetate = 8:1) provide **1r** in 55% yield (0.69 g), R_f = 0.5 (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 7.79 (m, 2H), 7.49 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.42 (s, 1H), 7.16 (dd, *J* = 5.2, 0.8 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.9, 149.4, 147.4, 142.1, 133.9, 130.0 (q, *J* = 30 Hz), 128.2 (d, *J* = 3.4 Hz), 126.0 (d, *J* = 3.4 Hz), 125.7, 125.4, 123.9, 123.7 (q, *J* = 270.9 Hz), 21.1. ^{19}F NMR (376 MHz, CDCl$_3$) δ -62.7(s). HRMS: m/z (EI) calculated [M]$^+$: 314.9870, measured: 314.9873.



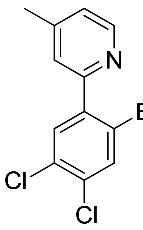
1s

The same procedure (Scheme S3) for the synthesis of **1s**, flash chromatography (petroleum ether/ethyl acetate = 15:1) provide **1s** in 54% yield (0.72 g), R_f = 0.7 (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.57 (d, *J* = 5.2 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.41 (m, 2H), 7.13 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.8, 149.3, 148.4, 148.38, 147.3, 142.9, 134.5, 125.4, 123.9 (d, *J* = 1.9 Hz), 121.99, 120.2 (q, *J* = 256.2 Hz), 119.5, 21.1. ^{19}F NMR (376 MHz, CDCl$_3$) δ -59.8 (s). HRMS: m/z (EI) calculated [M]$^+$: 330.9820, measured: 330.9821.



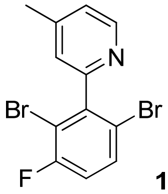
1t

The same procedure (Scheme S3) for the synthesis of **1u**, flash chromatography provide **1u** in 43% yield, R_f = 0.4 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.60 (d, *J* = 5.2 Hz, 1H), 8.38 (d, *J* = 2.8 Hz, 1H), 8.09 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.44 (s, 1H), 7.20 (d, *J* =8.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 156.0, 149.5, 147.7, 147.2, 142.7, 134.4, 129.2, 126.2, 125.3, 124.3, 123.9, 21.2. HRMS: m/z (ESI) calculated [M+H]$^+$: 292.9926, measured: 292.9914.



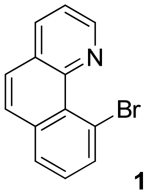
1u

The same procedure (Scheme S3) for the synthesis of **1u**, flash chromatography provide **1u** in 50% yield, $R_f = 0.4$ (petroleum ether/ethyl acetate = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.8 Hz, 1H), 7.77 (s, 1H), 7.64 (s, 1H), 7.40 (s, 1H), 7.15 (dd, *J* = 4.8, 0.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 149.4, 147.4, 141.0, 134.3, 133.0, 132.6, 132.0, 125.4, 124.0, 119.7, 21.1. HRMS: m/z (EI) calculated $[M]^+$: 314.9217, measured: 314.9215.



1v

The same procedure (Scheme S3) for the synthesis of **1v**, flash chromatography (petroleum ether/ethyl acetate = 5:1) provide **1v** in 57% yield (0.98 g), $R_f = 0.5$ (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.2 Hz, 1H), 7.60 (m, 1H), 7.18 (m, 1H), 7.08 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 (d, *J* = 158.6 Hz), 157.6 (d, *J* = 1.9 Hz), 149.3, 147.8, 143.5, 132.4 (d, *J* = 7.7 Hz), 125.2, 124.2, 117.8 (d, *J* =3.9 Hz), 117.0 (d, *J* = 23.1 Hz), 111.6 (d, *J* = 19.7 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.2(dd, *J* = 7.9, 4.8 Hz). HRMS: m/z (EI) calculated $[M]^+$: 342.9007, measured: 342.9010.



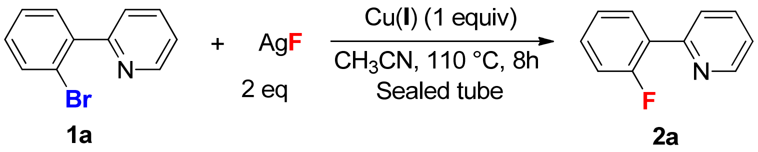
1w

The same procedure (Scheme S3) for the synthesis of **1m**, flash chromatography (petroleum ether/ethyl acetate = 10:1) provide **1w** in 65% yield (0.84 g), $R_f = 0.7$ (petroleum ether/ethyl acetate = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (dd, *J* = 4.0, 2.0 Hz, 1H), 8.17 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.10 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.56 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.46 (dd, *J* = 8.0, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 145.9, 136.2, 135.6, 135.5, 128.4, 128.3, 128.1, 127.9, 127.3, 126.5, 121.9, 119.4.

3. Screening of Reaction Conditions.

3.1 Stiochiometric Reactions

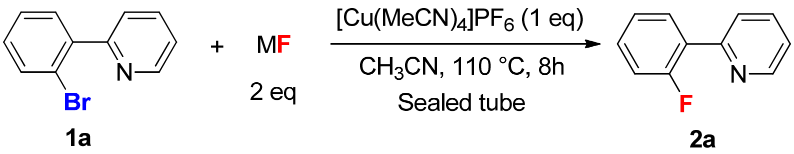
Table S1. Screening of Copper Reagents [a]



entry	copper salt	yield (%)
1	CuBr	--
2	CuCl	--
3	CuI	--
4	CuTC	--
5	$[Cu(OTf)]_2C_6H_6$	--
6	$[Cu(MeCN)_4]PF_6$	55
7	$[Cu(MeCN)_4]BF_4$	37
8	CuOAc	--
9	$CuBr{\cdot}Me_2S$	--
10	--	--

[a]: substrate 0.1 mmol, CH_3CN(1 mL), ^{19}F-NMR yield

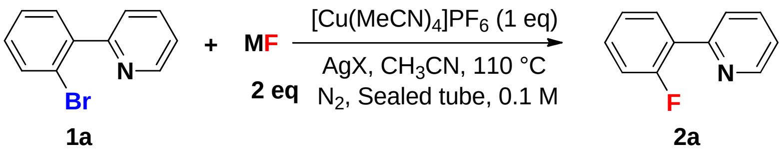
Table S2. Screening of Fluoride Source[a]



entry	fluorine source	yield (%)
1	AgF	55
2	CsF	0
3	KF	0
4	$Et_3N{\cdot}3HF$	0
5	TMAF	trace
6	NaF	0
7	MnF_3	0

[a]: Substrate 0.1 mmol in CH_3CN(1 mL), ^{19}F-NMR yield

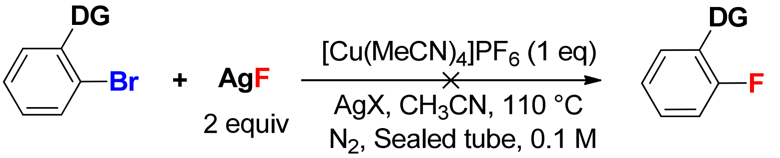
Table S3. *In situ* generation of AgF Source

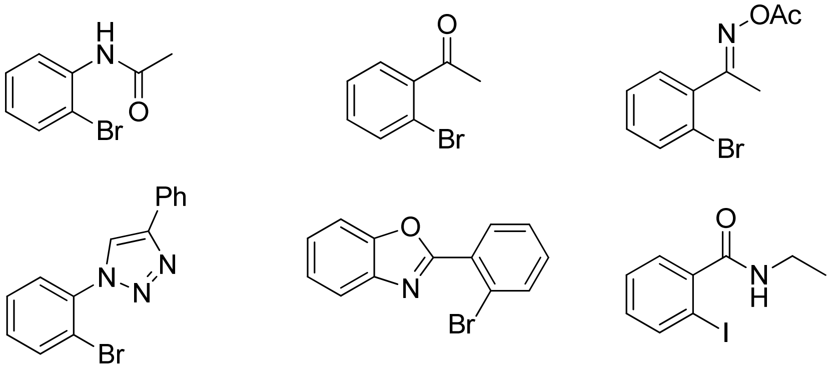


entry	AgX+"F"="AgF"	yield (%)
1	$AgHF_2$	12
2	$AgBF_4$ + TMAF	24
3	AgOTf + TMAF	21
4	AgF	63[b]
5	CuF_2	--[b,c]
6	AgOTf + CsF	44[b]
7	AgOTf + KF	11[b]
8	AgOAc + CsF	--[b,c]
9	AgOAc + KF	--[b,c]
10	$AgSbF_6$ + CsF	54[b]
11	$AgBF_4$ + CsF	57[b]

[a]: ^{19}F-NMR yield. [b]: reactions were carried at 120 °C. [c] no product

Table S4. Screening of other Directing Group.

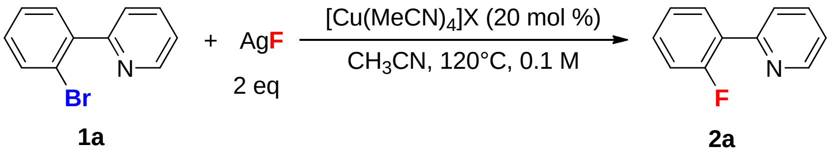




Under above reaction condition, these substrates bearing different types of coordination groups could not be transformed to corresponding fluorination products.

3.2 Catalytic Reactions

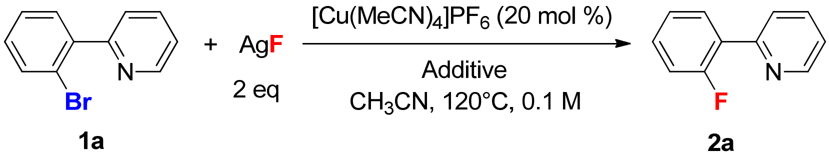
Table S5. Screening of Cationic Copper Catalysts



entry	copper	yield (%)[a]
1	$[Cu(MeCN)_4]PF_6$	38
2	$Cu(MeCN)_4]BF_4$	29
3	$Cu(MeCN)_4]OTf$	31

[a]: ^{19}F-NMR yield.

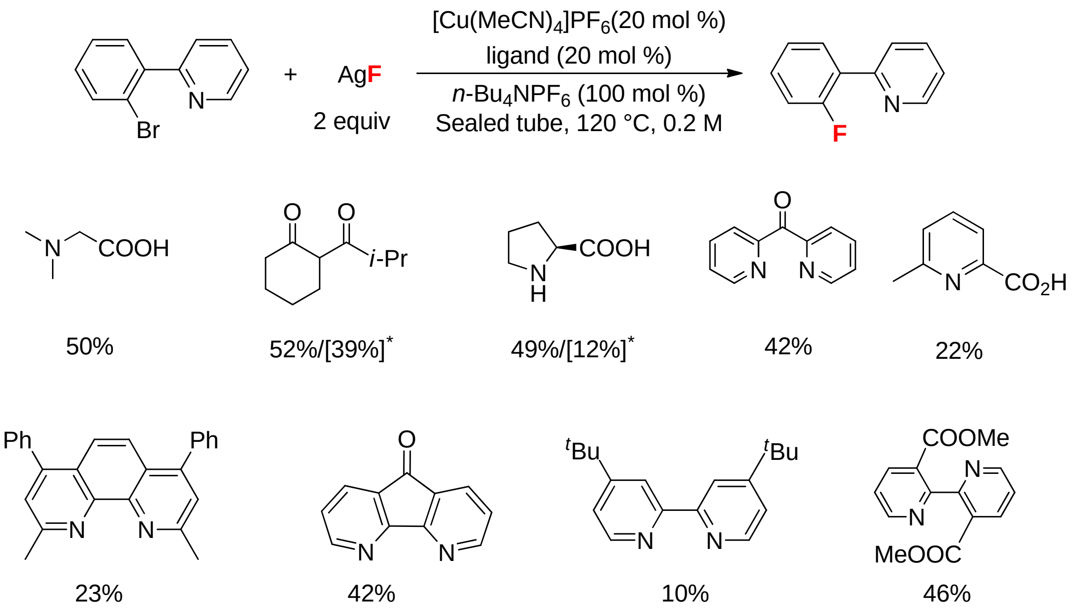
Table S6. Screening of Additives under Catalytic Reactions



entry	additive	yield (%)[a]
1	--	38
2	*n*-Bu_4NPF_6 (50%)	45
3	*n*-Bu_4NPF_6 (80%)	47
4	*n*-Bu_4NPF_6 (100%)	53
5	Me_4NPF_6 (20%)	32
6	Me_4NPF_6 (100%)	38
7	Et_4NPF_6 (20%)	31
8	Et_4NPF_6 (100%)	36

[a]: ^{19}F-NMR yield.

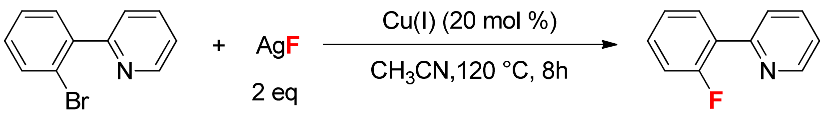
Table S7. Effects of Exogenous Ligands to the Reaction Condition



* [Ligand (1 equiv) was added]

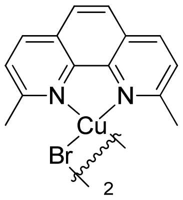
Catalytic amount of additional Ligands did not improve the reaction yield, however, when one equivalent of additional ligands are added, the yields were decreased, which indicated that the competing coordination of the additional ligands with pyridyl group impede the fluorination reactions.

Table S8. Screening of Copper Complexes.

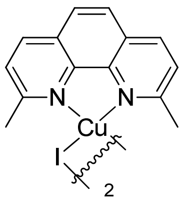


1a **2a**

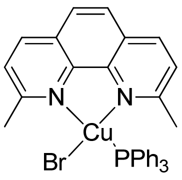
entry	Cu(**I**)	yield (%)
1	CuBr (1 equiv)	0
2	CuBr/**phen**(20%, 1:1)	27
3	Cu complex **A**	63
4	Cu complex **B**	42
5	Cu complex **C**	39



Cu complex **A**

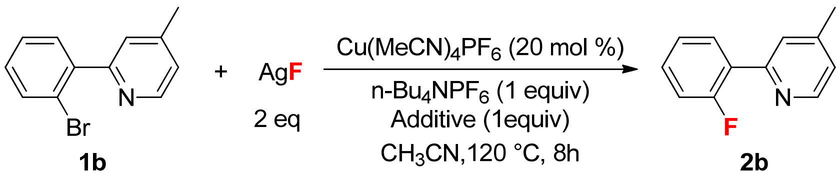


Cu complex **B**



Cu complex **C**

Table S9. SET and Radical Scavenger Tests

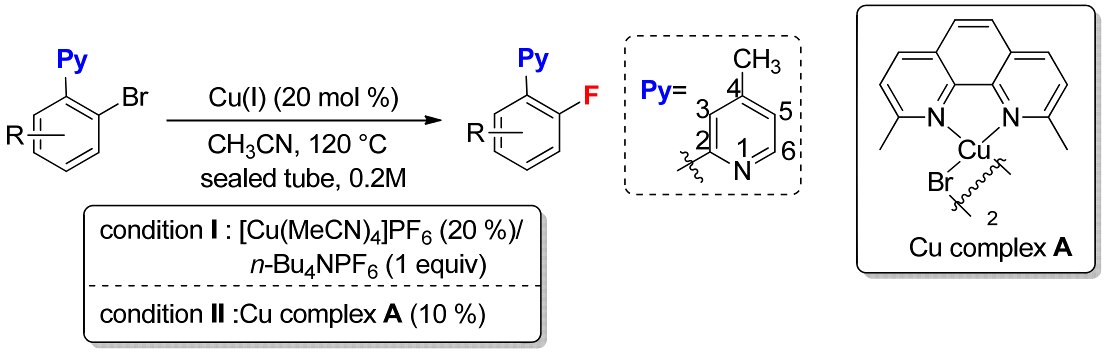


1b **2b**

entry	Additive	yield (%)
1	--	75
2	TEMPO	52
3	*p*-dinitrobenzene	66
4	BQ	72

4. Typical procedure for the fluorination of aryl bromides.

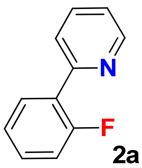
4.1 Procedures for the Synthesis of Aryl Fluorides via Two Conditions.



Scheme S4

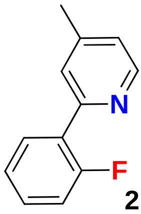
Condition I: To a 10 mL tube, $Cu(MeCN)_4PF_6$ (14.4 mg, 0.04 mmol), AgF (50.8 mg, 0.4 mmol), *n*-Bu_4NPF_6 (77.4 mg, 0.2 mmol), and substrate **1** (0.2 mmol) was dissolved in dry MeCN (1 mL) under N_2 atmosphere. The tube was sealed and the mixture was heated to 120 ^{o}C for 8h. After reaction completed, the organic solvent was removed under vacuum and the residue was subjected to flash column chromatography to provide the fluorination product **2**.

Condition II: To a 10 mL tube, Cu complex **A** (15.2 mg, 0.02 mmol), AgF (50.8 mg, 0.4 mmol), and substrate **1** (0.2 mmol) was dissolved in dry MeCN (1 mL) under N_2 atmosphere. The tube was sealed and the mixture was heated to 120 ^{o}C for 8h. After reaction completed, the organic solvent was removed under vacuum and the residue was subjected to flash column chromatography to provide the fluorination product **2**.



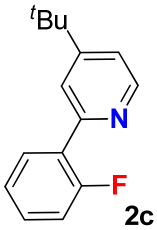
2a

Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 15/1 to 10/1) gave the product **2a**. R_f = 0.5 (Petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.8 Hz, 1H), 7.97 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.73 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 7.36 (m, 1H), 7.24 (m, 2H), 7.15 (ddd, *J* = 11.6, 8.4, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160. 4 (d, *J* = 248.2 Hz), 153.3 (d, *J* = 2.3 Hz), 149.7, 136.3, 130.9 (d, *J* = 3.0 Hz), 130.3 (d, *J* = 8.4 Hz), 127.4 (d, *J* = 11.4 Hz), 124.5 (d, *J* = 4.2 Hz), 124.4, 122.3, 116.1 (d, *J* = 22.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.5 (m).



2b

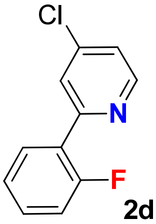
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 15/1 to 10/1) gave the product **2b**. R_f = 0.5 (Petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.93 (ddd, *J* = 8.0, 8.0, 2Hz, 1H), 7.58 (s, 1H), 7.33 (m, 1H), 7.23 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.13 (ddd, *J* = 11.6, 8.4, 1.2 Hz, 1H), 7.04 (dd, *J* = 4.8, 0.8 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (d, *J* = 248.2 Hz), 153.2 (d, *J* = 2.3 Hz), 149.4, 147.3, 130.9(d, *J* = 3.0 Hz), 130.1 (d, *J* = 8.4 Hz), 127.5 (d, *J* = 11.8 Hz), 125.3 (d, *J* = 8.8 Hz), 124.3 (d, *J* = 3.4 Hz), 123.3, 116.0 (d, *J* = 22.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.4 (dddd, *J* = 11.3, 4.9, 2.9, 1.5 Hz). HRMS: m/z (EI) calculated $[M]^+$: 187.0797, measured: 187.0796.



2c

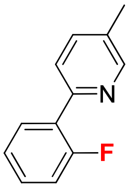
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 15/1 to 12/1) gave the product **2c**. R_f = 0.7 (Petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.2 Hz, 1H), 7.93 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 7.76 (m, 1H), 7.36 (m, 1H), 7.26 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.25 (ddd, *J* = 7.6, 7.2, 1.2 Hz, 1H), 7.15 (ddd, *J* = 10.4, 8.0, 1.2 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.29 (d, *J* = 248.0 Hz), 160.28, 153.3(d, *J* = 2.2 Hz), 149.5, 131.1 (d, *J* = 2.9 Hz), 130.1 (d, *J* = 8.5 Hz), 128.0 (d, *J* = 11.6 Hz), 124.4 (d, *J* = 3.4 Hz), 121.7 (d, *J* = 8.2

Hz), 119.5, 116.1(d, *J* = 22.7 Hz), 34.7, 30.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.5 (dddd, *J* = 10.9, 4.9, 1.9, 0.8 Hz). HRMS: m/z (EI) calculated $[M]^+$: 229.1267, measured: 229.1271.



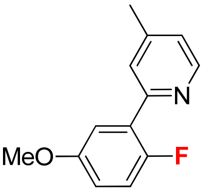
2d

Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to 8/1) gave the product **2d**. R_f = 0.4 (Petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.2 Hz, 1H), 7.98 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 7.82 (s, 1H), 7.40 (m, 1H), 7.27 (m, 2H), 7.17 (ddd, *J* = 11.6, 8.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (d, *J* = 249.3 Hz), 154.7, 150.4, 144.3, 131.0 (d, *J* = 8.7 Hz), 130.9 (d, *J* = 2.7 Hz), 126.2 (d, *J* = 11.3 Hz), 124.7 (d, *J* = 10.3 Hz), 124.6 (d, *J* = 3.8 Hz), 122.7, 116.3 (d, *J* = 22.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.9 (m). HRMS: m/z (EI) calculated $[M]^+$: 207.0251, measured: 207.0249.



2e

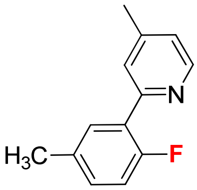
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 15/1 to 8/1) gave the product **2e**. R_f = 0.5 (Petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.94 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 7.68 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.56 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.34 (m, 1H), 7.24 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.14 (ddd, *J* = 11.6, 8.8, 1.2 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (d, *J* = 248.2 Hz), 150.6, 150.2, 136.8, 131.9, 130.8 (d, *J* = 3.0 Hz), 130.0 (d, *J* = 8.7 Hz), 127.5 (d, *J* = 11.8 Hz), 124.4 (d, *J* = 3.4 Hz), 123.9 (d, *J* = 8.7 Hz), 116.1 (d, *J* = 23.2 Hz), 18.2. HRMS: m/z (EI) calculated $[M]^+$: 187.0797, measured: 187.0799.



2h

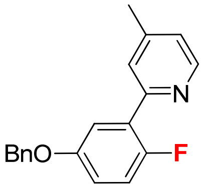
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to 6/1) gave the product **2h**. R_f = 0.5 (Petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.60 (s, 1H), 7.48 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.06 (m, 2H), 6.87 (ddd, *J* = 9.2, 3.6, 3.6 Hz, 1H), 3.84 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8 (d, *J* = 1.9 Hz), 154.7 (d, *J* = 240.7 Hz), 153.0 (d, *J*

= 2.7 Hz), 149.3，147.4，127.7 (d, *J* = 13.2 Hz), 125.3 (d, *J* = 9.1 Hz), 123.4, 116.7 (d, *J* = 26.5 Hz), 116.3 (d, *J* = 8.4 Hz), 114.3 (d, *J* = 2.7 Hz), 55.7 (d, *J* = 2.3 Hz), 21.0 (d, *J* = 1.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.8(m). HRMS: m/z (EI) calculated $[M]^+$: 216.0825, measured: 216.0829.



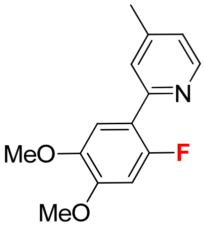
2i

Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to 6/1) gave the product **2i**. R_f = 0.7 (Petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.73 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.58 (s, 1H), 7.13 (ddd, *J* = 8.0, 4.8, 2.4 Hz, 1H), 7.05 (d, *J* = 5.6 Hz, 1H), 7.02 (dd, *J* = 11.2, 8.0 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5 (d, *J* = 245.2 Hz), 153.3 (d, *J* = 2.3 Hz), 149.3, 147.3, 133.8 (d, *J* = 3.8 Hz), 131.1 (d, *J* = 2.3 Hz), 130.6 (d, *J* = 7.9 Hz), 126.9 (d, *J* = 11.8 Hz), 125.4 (d, *J* = 8.0 Hz), 123.2, 115.7 (d, *J* = 23.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.7(m). HRMS: m/z (EI) calculated $[M]^+$: 201.0954, measured: 201.0952.



2j

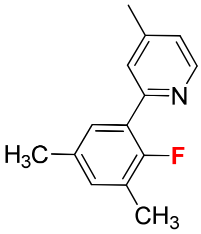
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 15/1 to 6/1) gave the product **2j**. R_f = 0.5 (Petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8 Hz, 1H), 7.60 (m, 2H), 7.43 (m, 2H), 7.37 (m, 2H), 7.31 (m, 1H), 7.06 (m, 2H), 6.95 (m, 1H), 5.09 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1 (d, *J* = 2.2 Hz), 154.9 (d, *J* = 240.4 Hz), 153.0 (d, *J* = 2.6 Hz), 149.4, 147.4, 136.8, 128.5, 127.9 (d, *J* = 3.0 Hz), 127.5, 125.4 (d, *J* = 9.3 Hz), 123.5, 117.1, 117.0 (d, *J* = 3.7 Hz), 116.7, 115.6 (d, *J* = 3.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.2 (m). HRMS: m/z (EI) calculated $[M]^+$: 293.1216, measured: 293.1212.



2k

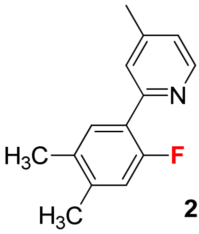
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 10/1 to 4/1) gave the product **2k**. R_f = 0.4 (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.2 Hz, 1H), 7.62 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 4.8 Hz, 1H), 6.70 (d, *J* = 12.4 Hz, 1H), 3.95 (s, 3H), 3.91 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8 (d, *J* = 242.2 Hz), 152.9 (d, *J* = 3.0 Hz), 150.2 (d, *J* = 10.3 Hz), 149.2, 147.3, 145.5(d, *J* = 2.3 Hz), 125.0 (d, *J* = 10.6 Hz), 122.8, 118.3 (d, *J* = 12.1 Hz), 111.9 (d, *J* = 4.6 Hz), 100.2 (d, *J* = 29.2 Hz), 56.3, 56.1, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.4 (ddd, *J* = 12.4, 7.9, 2.3 Hz). HRMS: m/z (EI) calculated $[M]^+$: 247.1009, measured: 247.1005.



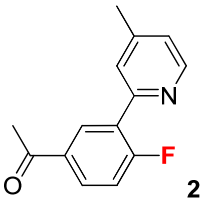
2l

Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 15/1 to 8/1) gave the product **2l**. R_f = 0.5 (Petroleum ether/EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.2 Hz, 1H), 7.56 (m, 1H), 7.50 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.06 (m, 1H), 7.01 (m, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 2.30 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (d, *J* = 244.4 Hz), 153.8 (d, *J* = 1.9 Hz), 149.3, 147.2, 133.1 (d, *J* = 4.1 Hz), 132.3 (d, *J* = 4.9 Hz), 128.6 (d, *J* = 3.1 Hz), 126.8 (d, *J* = 12.5 Hz), 125.4 (d, *J* = 8.4 Hz), 124.9 (d, *J* = 18.2 Hz), 123.2, 21.1, 20.6, 14.6 (d, *J* = 5.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.2 (m). HRMS: m/z (EI) calculated $[M]^+$: 215.1110, measured: 215.1107.



2m

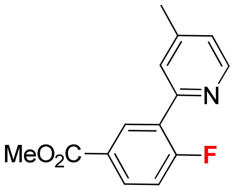
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 15/1 to 8/1) gave the product **2m**. R_f = 0.6 (Petroleum ether/EtOAc = 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.02 (d, *J* = 5.2 Hz, 1H), 6.92 (d, *J* = 12 Hz, 1H), 2.38 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4 (d, *J* = 245.1 Hz), 153.4 (d, *J* = 2.3 Hz), 149.2, 147.2, 139.2 (d, *J* = 8.0 Hz), 132.5 (d, *J* = 3.4 Hz), 131.3 (d, *J* = 3.0 Hz), 125.2 (d, *J* = 8.7 Hz), 124.3 (d, *J* = 11.4 Hz), 123.0, 116.9 (d, *J* = 22.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.7 (dd, *J* = 9.4, 9.4 Hz). HRMS: m/z (EI) calculated $[M]^+$: 215.1110, measured: 215.1108.



2n

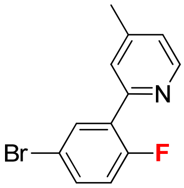
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to

4/1) gave the product **2n**. R_f = 0.4 (Petroleum ether/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (m, 2H), 8.02 (m, 1H), 7.61 (s, 1H), 7.24 (m, 1H), 7.13 (d, *J* = 4.8 Hz, 1H), 2.65 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 163.1 (d, *J* = 256.6 Hz), 152.0 (d, *J* = 2.2 Hz), 149.5, 147.7, 133.8 (d, *J* = 3.0 Hz), 132.2 (d, *J* = 4.9 Hz), 130.3 (d, *J* = 9.9 Hz), 127.6 (d, *J* = 12.9 Hz), 125.3 (d, *J* = 8.4 Hz), 123.8, 116.6 (d, *J* = 23.9 Hz), 26.6, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.8 (ddd, *J* = 7.1, 4.9, 2.6 Hz). HRMS: m/z (EI) calculated $[M]^+$: 229.0903, measured: 229.0907.



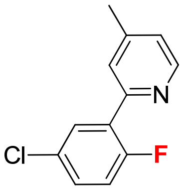
2o

Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to 8/1) gave the product **2o**. R_f = 0.6 (Petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.60 (d, *J* = 4.8 Hz, 1H), 8.06 (ddd, *J* = 8.8, 4.8, 2.4 Hz, 1H), 7.59 (s, 1H), 7.21 (dd, *J* = 10.4, 8.8 Hz, 1H), 7.10 (dd, *J* = 5.2, 0.8 Hz, 1H), 3.90 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.1 (d, *J* = 255.4 Hz), 152.1 (d, *J* = 2.3 Hz), 149.5, 147.6, 133.0 (d, *J* = 4.6 Hz), 131.8 (d, *J* = 9.9 Hz), 127.7 (d, *J* = 12.5 Hz), 126.7 (d, *J* = 4.6 Hz), 125.2 (d, *J* = 7.9 Hz), 123.7, 116.4 (d, *J* = 23.9 Hz), 52.1, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.3 (ddd, *J* = 10.2, 4.9, 2.3 Hz). HRMS: m/z (EI) calculated $[M]^+$: 245.0852, measured: 245.0850.



2p

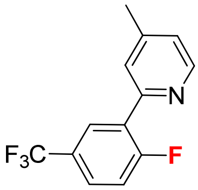
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to 8/1) gave the product **2p**. R_f = 0.6 (Petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8 Hz, 1H), 8.12 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.59 (s, 1H), 7.46 (m,1H), 7.11 (d, *J* = 4.8 Hz, 1H), 7.04 (dd, *J* = 10.8, 8.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, *J* = 248.6 Hz), 151.7 (d, *J* = 2.7 Hz), 149.5, 147.7, 133.7 (d, *J* = 3.4 Hz), 132.9 (d, *J* = 8.8 Hz), 129.4 (d, *J* = 13.2 Hz), 125.4 (d, *J* = 9.1 Hz), 123.9, 117.9 (d, *J* = 24.7 Hz), 117.2 (d, *J* = 3.1 Hz), 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.7 (m). HRMS: m/z (EI) calculated $[M]^+$: 264.9902, measured: 264.9904.



2q

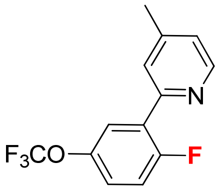
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to

6/1) gave the product **2q**. R_f = 0.6 (Petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.2 Hz, 1H), 7.97 (dd, *J* = 6.8, 2.8 Hz, 1H), 7.59 (s, 1H), 7.30 (ddd, *J* = 8.8, 4.0, 2.8 Hz, 1H), 7.09 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J* = 247.9 Hz), 151.8(d, *J* = 2.2 Hz), 149.5, 147.6, 130.7(d, *J* = 3.5 Hz), 129.9 (d, *J* = 8.7 Hz), 129.7 (d, *J* = 3.0 Hz), 128.9 (d, *J* = 13.3 Hz), 125.3 (d, *J* = 9.1 Hz), 123.9, 117.5 (d, *J* = 25.1 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.9 (m). HRMS: m/z (EI) calculated $[M]^+$: 221.0408, measured: 221.0411.



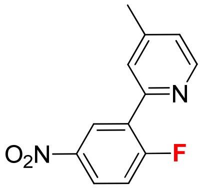
2r

Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to 8/1) gave the product **2r**. R_f = 0.7 (Petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.2 Hz, 1H), 8.31 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.63 (m, 2H), 7.27 (m, 1H), 7.13 (ddd, *J* = 5.2, 1.6, 0.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 255.0 Hz), 151.6 (d, *J* = 2.3 Hz), 149.7, 147.8, 128.8 (dd, *J* = 7.5, 4.2 Hz), 128.3 (d, *J* = 12.9 Hz), 127.2 (dd, *J* = 10.0, 3.8 Hz), 125.4 (d, *J* = 7.7 Hz), 124.1, 123.8 (q, *J* = 270.6 Hz), 117.0 (d, *J* = 24.2 Hz), 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.0 (m), -62.1 (s). HRMS: m/z (EI) calculated $[M]^+$: 255.0671, measured: 255.0668.



2s

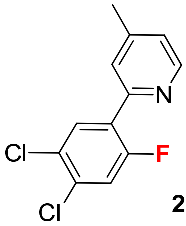
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 15/1 to 6/1) gave the product **2s**. R_f = 0.7 (Petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 7.90 (dd, *J* = 6.4, 2.8 Hz, 1H), 7.62 (m, 1H), 7.21 (m, 1H), 7.18 (dd, *J* = 18.8, 9.2 Hz, 1H), 7.11 (ddd, *J* = 5.2, 1.6, 0.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4 (d, *J* = 248.2 Hz), 151.6 (d, *J* = 3.0 Hz), 149.6, 147.7, 145.3 (d, *J* = 2.7 Hz), 128.9 (d, *J* = 13.7 Hz), 125.3 (d, *J* = 9.5 Hz), 124.0, 123.7 (d, *J* = 3.0 Hz), 122.7 (d, *J* = 8.3 Hz), 120.4 (q, 255.4 Hz), 117.4 (d, *J* = 25.8 Hz), 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.2 (s), -118.9 (ddd, *J* = 6.7, 4.5, 2.3 Hz). HRMS: m/z (EI) calculated $[M]^+$: 271.0620, measured: 271.0622.



2t

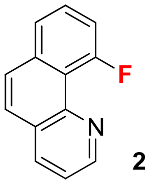
Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to

6/1) gave the product **2t**. R_f = 0.7 (Petroleum ether/EtOAc = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 6.8, 6.8 Hz, 1H), 8.62 (d, *J* = 5.2 Hz, 1H), 8.26 (ddd, *J* = 8.8, 4.0, 3.2 Hz, 1H), 7.65 (s, 1H), 7.31 (dd, *J* = 9.6, 8.8 Hz, 1H), 7.17 (ddd, *J* = 4.8, 1.2, 0.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, *J* = 258.8 Hz), 150.7 (d, *J* = 2.9 Hz), 149.8, 148.0, 144.7, 128.9 (d, *J* = 13.7 Hz), 127.3 (d, *J* = 5.5 Hz), 125.5 (d, *J* = 9.4 Hz), 125.3 (d, *J* = 9.3 Hz), 124.5, 117.4 (d, *J* = 26.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.5 (m). HRMS: m/z (EI) calculated $[M]^+$: 232.0648, measured: 232.0651.



2u

Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 15/1 to 6/1) gave the product **2u**. R_f = 0.8 (Petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.2 Hz, 1H), 8.14, (d, *J* = 7.6 Hz, 1H), 7.59 (s, 1H), 7.28 (d, *J* = 10.4 Hz, 1H), 7.11 (d, *J* = 4.4 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2 (d, *J* = 251.6 Hz), 150.9 (d, *J* = 3.0 Hz), 149.6, 147.8, 133.1 (d, *J* = 11.0 Hz), 131.9 (d, *J* = 3.8 Hz), 128.5 (d, *J* = 3.7 Hz), 127.4 (d, *J* = 12.9 Hz), 125.2 (d, *J* = 10.0 Hz), 124.1, 118.4 (d, *J* = 28 Hz), 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.0 (ddd, *J* = 9.8, 7.5, 2.3 Hz). HRMS: m/z (EI) calculated $[M]^+$: 255.0018, measured: 255.0015.

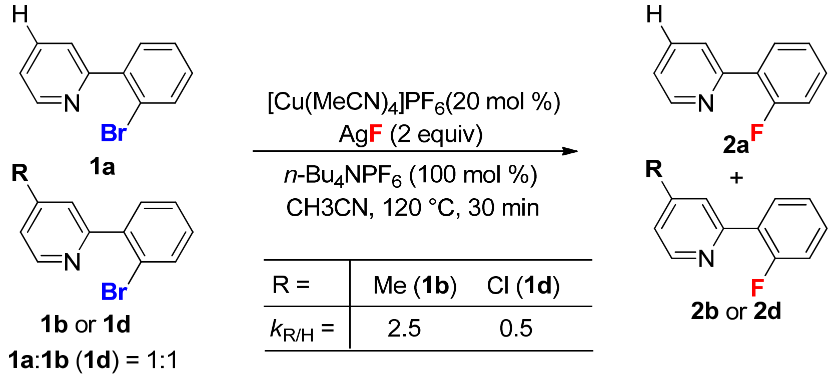


2w

Follow the standard procedure, flash chromatography (Petroleum ether/EtOAc 12/1 to 6/1) gave the product **2w**. R_f = 0.6 (Petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (ddd, *J* = 4.0, 4.0, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.74 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.58 (ddd, *J* = 8.0, 8.0, 4.8 Hz, 1H), 7.51 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.43 (ddd, *J* = 12.8, 8.0, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, *J* = 258.8 Hz), 149.0 (d, *J* = 1.2 Hz), 145.8 (d, *J* = 7.6 Hz), 136.1 (d, *J* = 2.6 Hz), 135.6, 128.2 (d, *J* = 9.5 Hz), 127.4 (d, *J* = 3.0 Hz), 127.0, 126.5 (d, *J* = 1.5 Hz), 124.0 (d, *J* = 4.1 Hz), 121.5 (d, *J* = 1.9 Hz), 120.1 (d, *J* = 6.4 Hz), 114.4 (d, *J* = 23.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.0 (m). HRMS: m/z (EI) calculated $[M]^+$: 197.0641, measured: 197.0642.

5. Preliminary Mechanistic Studies.

5.1 Competition Experiments of the para-Substituted Pyridyl Substrates.

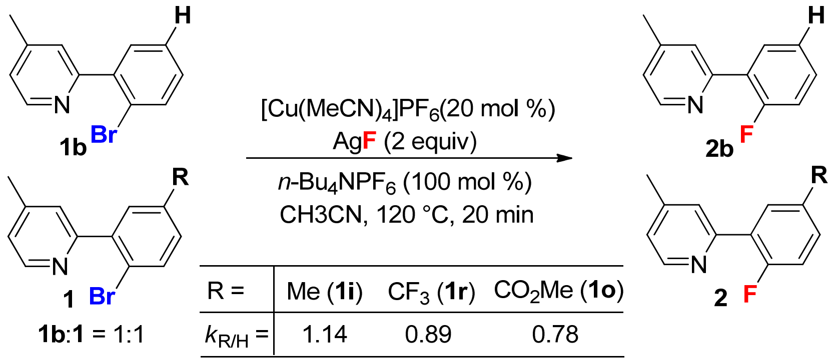


R =	Me (**1b**)	Cl (**1d**)
$k_{R/H}$ =	2.5	0.5

Scheme S5

To a 10 mL tube, AgF (25.4 mg, 0.2 mmol), $Cu(MeCN)_4PF_6$ (7.4 mg, 0.02 mmol), *n*-Bu_4NPF_6 (38.8 mg, 0.1 mmol) were added in the glove box, then the solution of substrates **1a** (0.1 mmol) and **1b** (or **1d**) (0.1 mmol) in anhydrous MeCN (1 mL) was added under nitrogen. The tube was sealed and the mixture was heated to 120 ^{o}C for 30 min within low conversion of substrates (less than 20%). After workup procedure, the ratio of the yields could be determined by ^{19}F-NMR spectrum.

5.2 Competition Experiments of the para-Substituted Aryl Bromides.

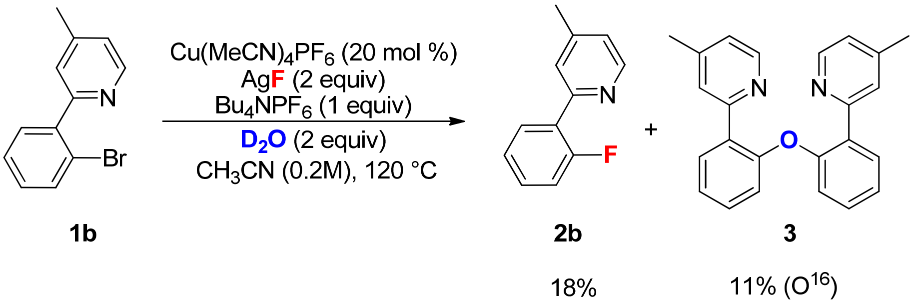


R =	Me (**1i**)	CF_3 (**1r**)	CO_2Me (**1o**)
$k_{R/H}$ =	1.14	0.89	0.78

Scheme S6

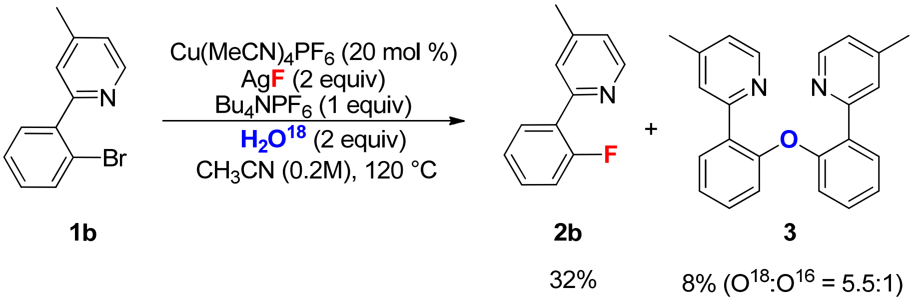
To a 10 mL tube, AgF (26 mg, 0.2 mmol), $Cu(MeCN)_4PF_6$ (7.8 mg, 0.02 mmol), *n*-Bu_4NPF_6 (38.8 mg, 0.1 mmol) were added in the glove box, then the solution of substrates **1b** (0.1 mmol) and **1i** (**1r** or **1o**) (0.1 mmol) in anhydrous MeCN (1 mL) was added under nitrogen. The tube was sealed and the mixture was heated to 120 ^{o}C for 20 min within low conversion of substrates (less than 20%). After workup procedure, the ratio of the yields could be determined by ^{19}F-NMR spectrum.
The results suggested the electron-donating groups at *para*-position of the bromide react faster than electron-withdrawing groups.

5.3 Experiments on the Addition of D_2O and $H_2{}^{18}O$.



Scheme S7

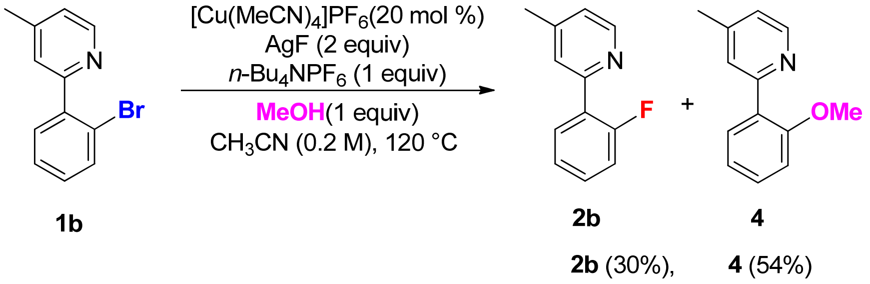
To a 10 mL tube, AgF (25.4 mg, 0.2 mmol), $Cu(MeCN)_4PF_6$ (7.4 mg, 0.02 mmol), *n*-Bu_4NPF_6 (38.8 mg, 0.1 mmol) were added in the glove box, then the solution of substrates **1b** (49.6 mg, 0.2 mmol) and D_2O (8.2 mg, 0.4 mmol) in anhydrous MeCN (1 mL) was added under nitrogen. The tube was sealed and the mixture was heated to 120 ^{o}C for 8 hour. After above workup procedure, the reaction provided **2b** (6.7 mg, 18%), and **3** (3.9 mg, 11%). Compound **3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.2 Hz, 2H), 7.83 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.55 (s, 2H), 7.29 (m, 2H), 7.19 (m, 2H), 6.99 (d, 2H), 6.94 (d, *J* = 8.0, 0.8 Hz, 2H), 2.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 153.9, 149.2, 146.7, 131.5, 131.4, 129.8, 125.6, 123.7, 123.0, 118.8, 21.1. HRMS: m/z (EI) calculated $[M]^+$: 352.1576, measured: 352.1573.



Scheme S8

With the above procedure replacing D_2O by $H_2{}^{18}O$. the reaction provided **2b** (11.9 mg, 32%), and **3** (2.9 mg, 8%). Compound 3 was analyzed by high resolution MS, and the ratio of the abundance for $[C_{24}H_{21}N_2{}^{18}O+H^+]$: 355.1683 and $[C_{24}H_{21}N_2{}^{16}O+H^+]$: 353.1639 is 5.5, indicating the incorporation of $H_2{}^{18}O$ into the product **3**.

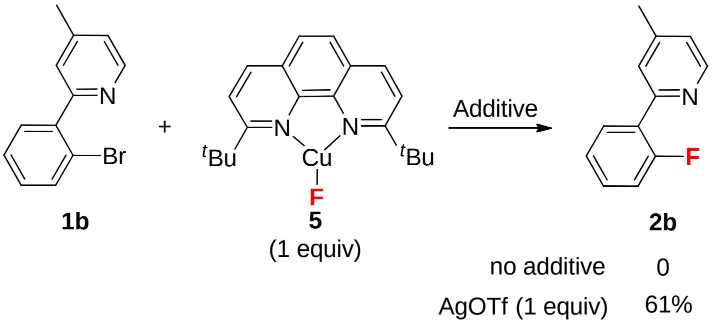
5.4 Copper-Catalyzed Fluorination of Aryl Bromides in the Presence of MeOH Nucleophile.



Scheme S9

With the same procedure in 5.3 replacing H2O by MeOH (1 equiv): To a 10 mL tube, AgF (25.4 mg, 0.2 mmol), $Cu(MeCN)_4PF_6$ (7.4 mg, 0.02 mmol), n-Bu_4NPF_6 (38.8 mg, 0.1 mmol) were added in the glove box, then the solution of substrates **1b** (49.6 mg, 0.2 mmol) and anhydrous MeOH (6.4 mg, 0.2 mmol) in anhydrous MeCN (1 mL) was added under nitrogen. The tube was sealed and the mixture was heated to 120 °C for 8 hour. After above workup procedure, the reaction provided **2b** (11.8 mg, 30%) and **4** (21.2 mg, 54%). Spectrum data for **4**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 5.2 Hz, 1H), 7.70 (dd, J = 7.6, 1.6 Hz, 1H), 7.58 (d, J = 0.8 Hz, 1H), 7.35 (ddd, J = 8.4, 7.6, 1.6 Hz, 1H), 7.06 (ddd, J = 8.0, 8.0, 0.8 Hz, 1H), 7.03 (dd, J = 5.2, 0.8 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 3.84 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 156.0, 149.1, 146.5, 131.1, 129.7, 129.3, 125.8, 122.7, 120.9, 111.2, 55.5, 21.2.

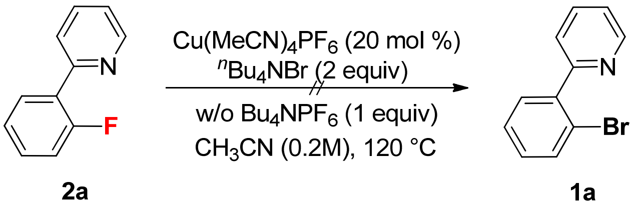
5.5 Stoichiometric Reactions with Copper-Fluoride complex 5



Scheme S10

To a 10 mL sealed tube, copper fluoride complex **5** (18.8 mg, 0.05 mmol), substrate **1b** (12.6 mg, 0.05 mmol), and AgOTf (12.7 mg, 0.05 mmol) were dissolved in anhydrous MeCN (1 mL). The sealed tube was heated to 120 °C for 8h. After same workup, the reaction provided **2b** (5.7 mg, 61%). In the absence of AgOTf, no **2b** was observed.

5.6 Reversibility of the Copper-Catalyzed Fluorination of Aryl Bromides



Scheme S11

To a 10 mL tube, compound **2a** (34.8 mg, 0.2 mmol), $Cu(MeCN)_4PF_6$ (14.5 mg, 0.04 mmol), *n*-Bu_4NBr (65.1 mg, 0.2 mmol) and *n*-Bu_4NPF_6 (73.8 mg, 0.2 mmol) were dissolved in anhydrous MeCN (1 mL). The sealed tube was heated to 120 ^oC for 8h. After faster flash column chromatography and removal solvent, the residue was analyzed by ^1H-NMR and ^{19}F-NMR. In the presence or absence of *n*-Bu_4NPF_6, no reaction occurred, and 2a was recovered quantitively.

5.7 XANES/XAFS Experiments.

The XANES/XAFS Experiments were conducted at Shanghai Synchrotron Radiation Facility. The experiments were conducted at Beamline BL14W1:

X-ray Source	38 pole Wiggler
Electron Energy	3.5 GeV
Magnetic Field	1.2 T
Electron Beam Current	300 mA
Photon Energy Range	3.5-22.5 keV, focused
Energy Resolution(Δ E/E)	2×10^{-4} Si(111)@10keV
Focal Spot Size	$\leqslant 0.5\times0.5$ mm2 (H×V)
Harmonic Content	$<10^{-4}$ HRM
Detection Limit	~ 1ppm

The standard sample Ag and Cu was provided by Shanghai Synchrotron Radiation Facility. AgF, $CuBr_2$ and $Cu(MeCN)_4PF_6$ were used as purchased from Sigma-Aldrich and stored at glove box under N_2 atmosphere.

The preparation of the residue was carried out following *condition I.*

In the case of PhI: To a 10 mL tube, PhI (40.9 mg, 0.2 mmol), $Cu(MeCN)_4PF_6$ (14.5 mg, 0.04 mmol) and AgF (51.4 mg, 0.2 mmol) were dissolved in MeCN (1 mL). The sealed tube was heated to 120 ^oC for 8hrs. After that, the mixture was cooled to room temperature, and the solvent was evaporated under vacuum. The tube was transferred into the glove box to give gray powder. Two reactions were conducted at the same time, and the combined gray powder were used to prepare sample for further XAFS/XANES analysis.

In the case of substrate **1b:** the procedure is the same as above by using substrate **1b** stead of PhI.

XAFS/XANES Experiments to Analyze the Oxidation State of Cu.

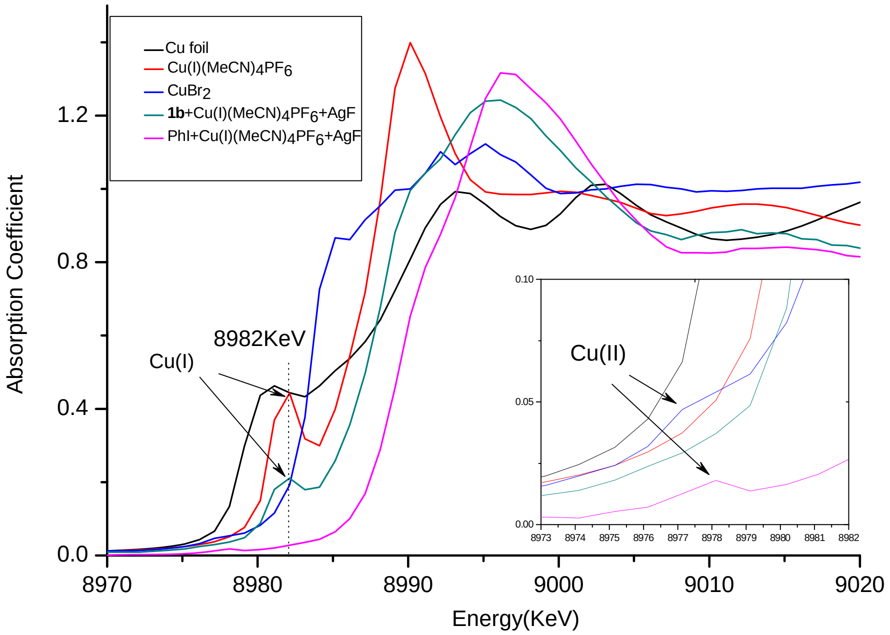


Figure S2 The XANES/XAFS Spectrum of Cu In Reaction Residue.

The green curve represented the oxidation state of Cu in the presence of substrate **1b**. the edge absorption peak is 8982KeV, which presented identical value to the standard sample of Cu(MeCN)$_4$PF$_6$ indicating the Cu(I) species remained during the catalytic process. However, in the presence of PhI, edge absorption for Cu(I) is not observed and typical edge absorption energy for Cu(II) was identified at 8978 KeV, standard Cu(II) signal was at 8977 KeV.