Visible-light-mediated radical arylthiodifluoromethylation of isocyanides with fluorinated 2-pyridyl sulfones

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## Supporting Information

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1. General information

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Reactions were monitored by thin layer chromatography purchased from commercial suppliers. Subsequent to elution, spots were visualized using UV radiation (254 nm). Flash chromatography was performed using 200-300 mesh silica gel. \(^1\)H, \(^{13}\)C and \(^{19}\)F NMR spectra were recorded on Bruker Avance III 500 MHz. \(^1\)H NMR and \(^{13}\)C NMR chemical shifts were determined relative to internal (CH\(_3\))\(_4\)Si (TMS) at \(\delta 0.0\). High resolution MS (HRMS) were performed on an Agilent 6224 TOF LC/MS spectrometer.

\([\text{Ru(bpy)}\text{Cl}_2]\cdot6\text{H}_2\text{O, t-BuONa, Na}_2\text{CO}_3, \text{DMF, DMSO, 6W LED bulb were commercial available. The substituted 1,2-diphenyldisulfane derivatives and the Isocyanides (2a-2m, 5a-5c) were prepared according to the literature.}^1\)\cite{2]}

2. Variation of reaction parameters

\[
\begin{array}{cccccc}
\text{Entry} & \text{Base} & \text{Solvent} & \text{Time} & \text{Yield(\%)}^b \\
1 & \text{t-BuONa} & \text{DMF} & 10 \text{ min} & \text{A} = 6, \text{ B} = 65 \\
2 & \text{LiHMDS} & \text{THF} & 10 \text{ min} & \text{A} = 7, \text{ B} = 82.3 \\
3 & \text{KHMDS} & \text{THF} & 10 \text{ min} & \text{A} = \text{Trace}, \text{ B} = 32 \\
4 & \text{NaHMDS} & \text{THF} & 10 \text{ min} & \text{A} = \text{Trace}, \text{ B} = 34 \\
5 & \text{LiHMDS} & \text{THF} & 1 \text{ second} & \text{A} = 12, \text{ B} = 62 \\
6 & \text{LiHMDS} & \text{THF:HMPA=10:1} & 1 \text{ second} & \text{A} = 26, \text{ B} = 56 \\
7 & \text{LiHMDS} & \text{THF:HMPA=5:1} & 1 \text{ second} & \text{A} = 9, \text{ B} = 45 \\
8 & \text{LiHMDS} & \text{THF:HMPA=2:1} & 1 \text{ second} & \text{A} = 7, \text{ B} = 34 \\
\end{array}
\]

\(^a\) Reaction condition: 2-BTSO\(_2\)CF\(_2\)H (1.0 equiv.), PhSSPh (1.5 equiv.). \(^b\) \(\text{A}: \text{Yields were determined by }^{19}\text{F NMR using PhCF}_3\text{ as an internal standard. B: Isolated yield of B.}\)

2-(phenylthio)benzo[d]thiazole

\[
\begin{array}{c}
\text{S} \quad \text{N} \quad \text{SO}_2\text{CF}_2\text{H} \quad + \quad \text{S} \quad \text{S} \quad \text{Ph} \\
\end{array}
\]

\(1^1\)H NMR (400MHz, CDCl\(_3\) \(\delta 7.86 \text{ (d, } J = 8.0 \text{ Hz, 1H)}, 7.73 \text{ – } 7.71 \text{ (m, 2H), 7.63 (d, } J = 8.0 \text{ Hz, 1H), 7.50 – 7.43 (m, 3H), 7.40-7.36 (m, 1H), 7.24 – 7.22 (m, 1H). MS (EI, m/z, %): 243 (M\(^+\)).}

3. Typical procedure for the synthesis of 1a-1l
Supporting Figure 1 Left: 1,2-diphenyldisulfane and 2-(Difluoromethylsulfonyl)pyridine were dissolved in DMF; Right: slightly shook after the addition of t-BuONa (about 5 seconds)

t-BuONa (2.5 equiv.) was added to a solution of 1,2-diphenyldisulfane (1.2 mmol, 1.2 equiv.) and 2-(difluoromethylsulfonyl)-pyridine (1.0 mmol, 1.0 equiv.) in 10 mL DMF at room temperature. The mixture was slightly shook and the reaction completed within few seconds. Then mixture was poured into ice water and a white precipitate of compound 1a appeared, which was filtered and dried in vacuum for direct use without further purification.

4. Characterization data of 1a-1l

2-((difluoro(phenythio)methyl)sulfonyl)pyridine (1a)

White solid. 87% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.84 (dd, $J$ = 1.0 Hz, 4.5 Hz, 1H), 8.15 (d, $J$ = 8.0 Hz, 1H), 8.02 (td, $J$ = 2.0 Hz, 8.0 Hz, 1H), 7.71 (d, $J$ = 7.0 Hz, 2H), 7.66-7.63 (m, 1H), 7.49-7.45 (m, 1H), 7.40-7.37 (m, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –77.0. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 152.3, 151.0, 138.3, 137.3, 131.3 (t, $J$ = 325.0 Hz), 131.0, 129.4, 128.7, 126.5, 123.2 (t, $J$ = 2.5 Hz). HRMS (ESI): m/z calcd. for C$_{12}$H$_9$F$_2$NO$_2$S$_2$ [M+H]$^+$ 302.0115, found 302.0114.

2-((difluoro(p-tolythio)methyl)sulfonyl)pyridine (1b)

White solid, 92% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.77-8.60 (m, 1H), 8.08 (d, $J$ = 8.0 Hz, 1H), 7.95 (td, $J$ = 1.5 Hz, 8.0 Hz, 1H), 7.59-7.56 (m, 1H), 7.51 (d, $J$ = 8.0 Hz, 2H), 7.13 (d, $J$ = 8.0 Hz, 2H), 2.29 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –77.4. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 152.4,
151.0, 141.7, 138.3, 137.3, 131.3 (t,  $J = 323.7$ Hz), 130.2, 128.7, 126.5, 119.6 (t,  $J = 2.6$ Hz), 21.4. HRMS (ESI): m/z calcd. for C$_{13}$H$_{11}$F$_{2}$NO$_{3}$S$_{2}$ [M+H]$^+$ 316.0272, found 316.0271.

2-((difluoro((4-methoxyphenyl)thio)methyl)sulfonyl)pyridine (1c)

White solid, 83% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.84 (d,  $J = 4.5$ Hz, 1H), 8.14 (d,  $J = 8.0$ Hz, 1H), 8.02 (td,  $J = 1.5$, 7.5 Hz, 1H), 7.66 – 7.61 (m, 3H), 6.91-6.89 (m, 2H), 3.81 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –78.1. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.0, 152.5, 151.0, 139.2, 138.3, 131.1 (t,  $J = 325.0$ Hz), 128.7, 126.5, 114.9, 113.4 (t,  $J = 3.3$ Hz), 55.4. HRMS (ESI): m/z calcd. for C$_{13}$H$_{11}$F$_{2}$NO$_{3}$S$_{2}$ [M+H]$^+$ 332.0221, found 332.0222.

2-((difluoro((2-methoxyphenyl)thio)methyl)sulfonyl)pyridine (1d)

White solid, 71% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.85 (dd,  $J = 0.5$, 4.5 Hz, 1H), 8.17 (d,  $J = 8.0$ Hz, 1H), 8.02 (td,  $J = 1.5$, 7.5 Hz, 1H), 7.68-7.63 (m, 2H), 7.47 (td,  $J = 2.0$, 8.0 Hz, 1H), 6.98-6.94 (m, 2H), 3.87 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –77.3. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.4, 152.6, 150.9, 139.6, 138.2, 133.4, 131.3 (t,  $J = 326.2$ Hz), 128.6, 126.5, 121.1, 111.7, 111.2 (t,  $J = 2.6$ Hz), 56.1. HRMS (ESI): m/z calcd. for C$_{13}$H$_{11}$F$_{2}$NO$_{3}$S$_{2}$ [M+H]$^+$ 332.0221, found 332.0222.

2-((difluoro((3-methoxyphenyl)thio)methyl)sulfonyl)pyridine (1e)

White solid, 78% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.87 (d,  $J = 4.5$ Hz, 1H), 8.19 (d,  $J = 7.5$ Hz, 2H), 8.06-8.02 (m, 1H), 7.69-7.67 (m, 1H), 7.34-7.29 (m, 2H), 7.26 (m, 1H), 7.04-7.02 (m, 1H), 3.84 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –76.8. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 159.8, 152.3, 151.0, 138.3, 131.4 (t,  $J = 325.0$ Hz), 130.0, 129.5, 126.5, 123.9 (t,  $J = 2.8$ Hz), 122.0, 127.4, 117.4, 55.5. HRMS (ESI): m/z calcd. for C$_{13}$H$_{11}$F$_{2}$NO$_{3}$S$_{2}$ [M+H]$^+$ 332.0221, found 332.0220.

2-((difluoro((4-fluorophenyl)thio)methyl)sulfonyl)pyridine (1f)

White solid, 82% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.85 – 8.84 (m, 1H), 8.15 (d,  $J = 8.0$ Hz, 1H), 8.03 (td,  $J = 1.5$Hz, 7.5 Hz, 1H), 7.73-7.70 (m, 2H), 7.67-7.65 (m, 1H), 7.14-7.05 (m, 2H).
$^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –77.8, –108.2. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 164.7 (d, $J = 252.5$ Hz), 152.2, 151.1, 139.7 (d, $J = 8.7$ Hz), 138.3, 131.0 (t, $J = 325.0$ Hz), 128.8, 126.5, 118.5 (d, $J = 3.4$ Hz), 116.7 (d, $J = 22.2$ Hz). HRMS (ESI): m/z calcd. for C$_{12}$H$_8$F$_3$NO$_2$S$_2$ [M+H]$^+$ 320.0021, found 320.0020.

2-(((4-bromophenyl)thio)difluoromethyl)sulfonyl)pyridine (1g)

White solid, 85% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.85–8.84 (m, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.03 (td, $J = 1.5$ Hz, 8.0 Hz, 1H), 7.68–7.65 (m, 1H), 7.59–7.52 (m, 4H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –77.4. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 152.2, 151.1, 138.8, 138.3, 132.7, 130.9 (t, $J = 325.0$ Hz), 128.8, 126.5, 126.3, 122.3 (t, $J = 3.3$ Hz). HRMS (ESI): m/z calcd. for C$_{12}$H$_8$BrF$_2$NO$_2$S$_2$ [M+H]$^+$ 379.9221, found 379.9220.

2-(((4-chlorophenyl)thio)difluoromethyl)sulfonyl)pyridine (1h)

White solid, 82% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.86 (d, $J = 4.5$ Hz, 1H), 8.16 (d, $J = 8.0$ Hz, 1H), 8.04 (td, $J = 1.5$ Hz, 7.5 Hz, 1H), 7.68–7.65 (m, 3H), 7.39 (d, $J = 8.5$ Hz, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –77.5. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 152.2, 151.1, 138.6, 138.3, 138.0, 131.0 (t, $J = 325.0$ Hz), 129.7, 128.8, 126.5, 121.7 (t, $J = 4.4$ Hz). HRMS (ESI): m/z calcd. for C$_{12}$H$_8$ClF$_2$NO$_2$S$_2$ [M+H]$^+$ 335.9726, found 335.9725.

2-(((2-chlorophenyl)thio)difluoromethyl)sulfonyl)pyridine (1i)

White solid. 79% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.86 (d, $J = 4.5$ Hz, 1H), 8.19 (d, $J = 8.0$ Hz, 1H), 8.04 (td, $J = 1.5$, 7.5 Hz, 1H), 7.86 (d, $J = 7.5$ Hz, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.43 (td, $J = 1.0$, 7.5 Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –76.8. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 152.2, 151.0, 141.1, 139.8, 138.3, 132.6, 131.2 (t, $J = 326.2$ Hz), 130.6, 128.8, 127.5, 126.6, 122.9. HRMS (ESI): m/z calcd. for C$_{12}$H$_8$ClF$_2$NO$_2$S$_2$ [M+H]$^+$ 335.9726, found 335.9724.

2-(((3-chlorophenyl)thio)difluoromethyl)sulfonyl)pyridine (1j)

White solid. 79% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.85 (s, 1H), 8.16 (d, $J = 7.5$ Hz, 1H), 8.04 (t,
$J = 7.5 \text{ Hz, 1H}$, 7.69-7.66 (m, 2H), 7.62 (d, $J = 7.5 \text{ Hz, 1H}$), 7.46 (d, $J = 7.0 \text{ Hz, 1H}$), 7.36 (t, $J = 7.5 \text{ Hz, 1H}$). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -77.0. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 152.2, 151.1, 138.4, 136.8, 135.4, 134.9, 131.4, 131.1 (t, $J = 325.0 \text{ Hz}$), 130.4, 128.9, 126.6, 124.9 (t, $J = 2.8 \text{ Hz}$).

HRMS (ESI): m/z calcd. for C$_{13}$H$_8$ClF$_2$NO$_2$S$_2$ [M+H]$^+$ 335.9726, found 335.9725.

2-((difluoro(naphthalen-2-ylthio)methyl)sulfonyl)pyridine (1k)

White solid. 90% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.82-8.81 (m, 1H), 8.25 (s, 1H), 8.15 (d, $J = 8.0 \text{ Hz, 1H}$), 7.99 (tt, $J = 2.0 \text{ Hz, 8.0 \text{ Hz, 1H}$), 7.86-7.83 (m, 3H), 7.71 (d, $J = 8.5 \text{ Hz, 1H}$), 7.63-7.60 (m, 1H), 7.58-7.52 (m, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -76.9. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 152.4, 151.0, 138.3, 138.2, 134.0, 133.3, 132.6, 131.5 (t, $J = 325.0 \text{ Hz}$), 129.1, 128.8, 128.3, 128.0, 127.8, 126.9, 126.5, 120.3 (t, $J = 2.8 \text{ Hz}$). HRMS (ESI): m/z calcd. for C$_{15}$H$_{11}$F$_2$NO$_2$S$_2$ [M+H]$^+$ 352.0272, found 352.0274.

2-((difluoro(methylthio)methyl)sulfonyl)pyridine (1l)

White solid. 61% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.86(d, $J = 4.5 \text{ Hz, 1H}$), 8.17 (d, $J = 7.5 \text{ Hz, 1H}$), 8.04 (t, $J = 8.0 \text{ Hz, 1H}$), 7.76-7.66 (m, 1H), 2.56 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -81.5. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.3, 150.0, 137.3, 131.3 (t, $J = 321.2 \text{ Hz}$), 127.8, 125.5, 12.2 (t, $J = 5.0 \text{ Hz}$). HRMS (ESI): m/z calcd. for C$_{7}$H$_7$F$_2$NO$_2$S$_2$ [M+H]$^+$ 239.9959, found 239.9960.

5. Cyclic voltammetry study

The cyclic voltammetry measurements were performed on an EG & G-Princeton Applied Research PARSTAT 2273 electrochemical workstation, using a standard three-electrode setup with two platinum wire electrode (a working electrode and a counter electrode) and a Ag/AgCl (3 M KCl) system in anhydrous CH$_2$Cl$_2$ as the reference electrode. All solutions of the compounds under the study were in the supporting electrolyte n-Bu$_4$NPF$_6$ 0.1 M with the voltage scan rate of 0.05 V s$^{-1}$. Solutions (5 mL) were thoroughly bubbled with dry nitrogen for 15 min to remove oxygen before any experiment and kept under positive pressure of nitrogen. Under these experimental conditions, the [FeCp$_2$]/[FeCp$_2$]$^+$ couple was located at $E_{1/2}$ = +0.49 V in CH$_2$Cl$_2$.

The first reduction potentials of fluoroalkyl sulfones: cathodic peak potential quoted vs. SCE (the saturated calomel electrode). E (V vs. SCE) = E (V vs. Ag/AgCl) - 0.03 V (Potential for reference electrode: Ag/AgCl (3 M KCl): +0.21 V, SCE: +0.24 V).
Supporting Figure 2: The cyclic voltammetry of four heteroaryl sulfone reagents.

Supporting Figure 3. Oxidative and Reductive Quenching Cycle of Ru(bpy)$_3$$_{2+}$ [3]
6. General procedure for the synthesis of 3a-3m, 4b-4k, 6a-6c

A mixture of 1 (1.2 mmol, 1.2 equiv.), 2 or 5 (1.0 mmol, 1.0 equiv.), photocatalyst (2.0 mol%) and Na₂CO₃ (3.0 equiv.), DMSO (5 mL) were added in a Schlenk tube. The tube was evacuated and backfilled with pure N₂ for 3 times. The mixture was irradiated by a 6 W blue LED for 8 h. After the reaction was complete, H₂O (20 mL) and saturated NH₄Cl solution were added. The aqueous layer was extracted with EtOAc (10 mL × 3) and the organic phase was combinated and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography to provide products 3a-3m, 4b-4k and 6a-6c.

7. Light on/off experiment

A mixture of 1a (1.2 mmol, 1.2 equiv.), 2a (1.0 mmol, 1.0 equiv.), photocatalyst (2 mol%), Na₂CO₃ (3.0 mmol, 3.0 equiv.) were added to a dry Schlenk tube. The flask was evacuated and backfilled with pure N₂ for 3 times. Then 5 mL DMSO and 110 mg PhCF₃ (internal standards) were added with syringe under N₂ atmosphere. The mixture was irradiated by a 6 W blue LED at room temperature. The blue LED was turned on (for 2 h)-off (for 2 h)-on (for 2 h)-off (for 2 h)-on (for 2 h)-on (for 2 h)-on (for 2 h)-off (for 2 h)-on (for 2 h)-off (for 2 h)-on (for 2 h). The reaction was monitored by ¹⁹F NMR.
8. Luminescence Quenching Experiments \[4\]

8.1 Absorbance of Catalyst:

Absorbance of a $5.0 \times 10^{-4}$ M solution of $\text{Ru(bpy)}_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ in DMSO

8.2 Luminescence Quenching Experiments

**Instrument**

Model: Agilent Cary Eclipse FL Spectrophotometer

**Instrument parameters**

Measurement type: Wavelength scan

Scan mode: Emission

Data mode: Fluorescence

EX WL: 455.0 nm

EM Start WL: 500.0 nm

EM End WL: 750.0 nm

$I_0$ is the luminescence intensity without the quencher, $I$ is the intensity with the quencher.
**Supporting Figure 3.** Relationship between concentration of Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O and fluorescence intensity

First, we tested the fluorescence value of catalyst with different concentration, and found that when the concentration exceeds $1.0 \times 10^{-4}$ mol/L, the fluorescence is significantly weakened. So we deduced maybe the catalyst exist aggregation-caused quenching (ACQ) effect, which has greatly influence of the result of the fluorescence quenching experiment. With the result in hand, so we choose $5.0 \times 10^{-5}$ mol/L catalyst to perform all the fluorescence quenching experiment.

Fluorescence-emission of a $5.0 \times 10^{-5}$ M solution of Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O(without the quencher) in DMSO, $I_0 = 141.1$
Fluorescence-emission of a solution of Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O ($5.0 \times 10^{-5}$ M) with 1a ($1.3 \times 10^{-2}$ M) in DMSO, $I = 132.7$

Fluorescence-emission of a solution of Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O ($5.0 \times 10^{-5}$ M) with isocyanide 2a ($1.1 \times 10^{-2}$ M) in DMSO, $I = 131.8$

Fluorescence-emission of a solution of Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O ($5.0 \times 10^{-5}$ M) with Na$_2$CO$_3$
(3.2 \times 10^{-2} \text{ M}) in DMSO, I = 111.5 (Samples with Na$_2$CO$_3$ was stirred for 10 min and filtrated with a syringe filter before the luminescence measurement.)

Fluorescence-emission of a solution of Ru(bpy)$_3$Cl$_2\cdot$6H$_2$O (5.0 \times 10^{-5} \text{ M}) with H$_2$O

(1.6 \times 10^{-2} \text{ M}) in DMSO, I = 142.7

Fluorescence-emission of a solution of Ru(bpy)$_3$Cl$_2\cdot$6H$_2$O (5.0 \times 10^{-5} \text{ M}) with H$_2$O

(3.2 \times 10^{-2} \text{ M}) in DMSO, I = 144.7
Fluorescence-emission of a solution of Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O ($5.0 \times 10^{-5}$ M) with Na$_2$CO$_3$ ($3.2 \times 10^{-2}$ M) in DMSO, $I = 80.9$ (A stock solution of Na$_2$CO$_3$ (0.5 mmol) in 1 ml of H$_2$O was used).

Fluorescence-emission of a solution of Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O ($5.0 \times 10^{-5}$ M) with NaHCO$_3$ ($3.2 \times 10^{-2}$ M) in DMSO, $I = 112.3$ (A stock solution of NaHCO$_3$ (0.5 mmol) in 1 ml of H$_2$O was used).
Fluorescence-emission of a solution of Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O (5.0$\times$10$^{-5}$ M) with TMEDA 

(3.2$\times$10$^{-2}$ M) in DMSO, $I_0$ = 131.3

Fluorescence-emission of a solution of Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O (5.0$\times$10$^{-5}$ M) with 2,6-Lutidine

(3.2$\times$10$^{-2}$ M) in DMSO, $I_0$ = 132.5

Supporting Table 1. Luminescence Quenching Experiment Results-1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Relative luminescence intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru(bpy)$_3$Cl$_2$$\cdot$6H$_2$O (5$\times$10$^{-5}$ M)</td>
<td>$I_0$ = 1</td>
</tr>
<tr>
<td>2</td>
<td>[Ru] (5$\times$10$^{-5}$ M) + 1a (1.3$\times$10$^{-2}$ M)</td>
<td>$I_0/I_0$ = 1.06</td>
</tr>
<tr>
<td>3</td>
<td>[Ru] (5$\times$10$^{-5}$ M) + isocyanide 2a (1.1$\times$10$^{-2}$ M)</td>
<td>$I_0/I_0$ = 1.07</td>
</tr>
<tr>
<td>4</td>
<td>[Ru] (5$\times$10$^{-5}$ M) + Na$_2$CO$_3$ (3.2$\times$10$^{-2}$ M)</td>
<td>$I_0/I_0$ = 1.26</td>
</tr>
<tr>
<td>5</td>
<td>[Ru] (5$\times$10$^{-5}$ M) + H$_2$O (1.6$\times$10$^{-2}$ M)</td>
<td>$I_0/I_0$ $\approx$ 1</td>
</tr>
<tr>
<td>6</td>
<td>[Ru] (5$\times$10$^{-5}$ M) + H$_2$O (3.2$\times$10$^{-2}$ M)</td>
<td>$I_0/I_0$ $\approx$ 1</td>
</tr>
<tr>
<td>7&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁵ M) + Na₂CO₃ (3.2 × 10⁻² M)</td>
<td>I₀/I = 1.74</td>
</tr>
<tr>
<td>8&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁵ M) + NaHCO₃ (3.2 × 10⁻² M)</td>
<td>I₀/I = 1.25</td>
</tr>
<tr>
<td>9</td>
<td>[Ru] (5 × 10⁻⁵ M) + TMEDA (3.2 × 10⁻² M)</td>
<td>I₀/I = 1.07</td>
</tr>
<tr>
<td>10&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁵ M) + 2,6-Lutidine (3.2 × 10⁻² M)</td>
<td>I₀/I = 1.06</td>
</tr>
<tr>
<td>11&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁵ M) + Na₂CO₃ (5 × 10⁻⁴ M)</td>
<td>I₀/I ≈ 1</td>
</tr>
<tr>
<td>12&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁵ M) + Na₂CO₃ (1 × 10⁻³ M)</td>
<td>I₀/I = 1.03</td>
</tr>
<tr>
<td>13&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁵ M) + Na₂CO₃ (2 × 10⁻³ M)</td>
<td>I₀/I = 1.01</td>
</tr>
<tr>
<td>14&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁵ M) + Na₂CO₃ (4 × 10⁻³ M)</td>
<td>I₀/I = 1.10</td>
</tr>
<tr>
<td>15&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁵ M) + Na₂CO₃ (8 × 10⁻³ M)</td>
<td>I₀/I = 1.17</td>
</tr>
<tr>
<td>16&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁶ M) + Na₂CO₃ (16 × 10⁻³ M)</td>
<td>I₀/I = 1.35</td>
</tr>
<tr>
<td>17&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁶ M) + Na₂CO₃ (32 × 10⁻³ M)</td>
<td>I₀/I = 1.55</td>
</tr>
<tr>
<td>18&lt;sup&gt;b&lt;/sup&gt;</td>
<td>[Ru] (5 × 10⁻⁶ M) + Na₂CO₃ (64 × 10⁻³ M)</td>
<td>I₀/I = 2.21</td>
</tr>
</tbody>
</table>
Samples with Na₂CO₃ was stirred for 10 min and filtrated with a syringe filter before the luminescence measurement. A stock solution of the Na₂CO₃ (0.5 mmol) in 1 ml of H₂O was used.

Results and Discussion.

In the luminescence quenching experiments, there was no obvious change in luminescence intensity when isocyanide 2a or sulfone 1a was used as a quencher to [Ru]* (entries 2 and 3). NaHCO₃ seemed to be a weak quencher to [Ru]*, while TMEDA and 2,6-Lutidine did not demonstrated effective quenching effect to [Ru]* (entries 8, 9 and 10). Na₂CO₃ was a weak quencher to [Ru]* due to the poor solubility in DMSO (entry 4). In order to improve the solubility, the stock solution of the Na₂CO₃ (0.5 mmol) in 1 ml of H₂O was used. While excluding the effects of water (entry 5 and 6), a significant decrease of
Ru(bpy)$_3$Cl$_2$·6H$_2$O luminescence was observed (entry 7), and the quenching effect of Na$_2$CO$_3$ increased with its concentration (Supporting Figure 4).

9. Characterization data of 3a-3m, 4b-4k, 6a-6c.

6-(difluoro(phenylthio)methyl)phenanthridine (3a)

White solid, 93% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 8.0$ Hz, 1H), 8.62-8.59 (m, 2H), 8.30-8.29 (m, 1H), 7.92-7.89 (m, 1H), 7.82-7.76 (m, 4H), 7.74 (td, $J = 1.5$ Hz, 7.0 Hz, 1H), 7.49-7.43 (m, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -66.0. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.3 (t, $J = 28.0$ Hz), 141.7, 137.2, 135.0, 134.1, 131.7 (d, $J = 277.5$ Hz), 131.1, 130.9, 129.9, 129.1, 129.0, 128.8, 128.6, 127.6, 127.0 (t, $J = 5.4$ Hz), 125.0, 122.3, 122.0. HRMS (Cl): m/z calcd. for C$_{20}$H$_{13}$F$_2$NS [M+H]$^+$ 338.0809, found 337.0802.

6-(difluoro(phenylthio)methyl)-8-fluorophenanthridine (3b)

White solid. 75% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.67-8.64 (m, 1H), 8.52 (d, $J = 8.0$ Hz, 1H), 8.29-8.27 (m, 1H), 8.22 (dd, $J = 6.5$ Hz, $J = 10.0$ Hz, 1H), 7.81-7.75 (m, 4H), 7.65-7.61 (m, 1H), 7.51-7.44 (m, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -66.7, -110.5. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 164.1 (d, $J = 250.0$ Hz), 150.6 (td, $J = 3.7$, 28.7 Hz), 140.6, 138.3 (d, $J = 8.7$ Hz), 138.2, 133.0, 130.7 (t, $J = 277.5$ Hz), 130.1, 129.8, 128.1, 127.8, 126.7, 126.0 (t, $J = 5.4$ Hz), 124.0, 121.6, 121.4, 121.0, 120.8, 115.2 (d, $J = 22.5$ Hz). HRMS (Cl): m/z calcd. for C$_{20}$H$_{12}$F$_3$NS [M+H]$^+$ 356.0715, found 356.0714.

8-bromo-6-(difluoro(phenylthio)methyl)phenanthridine (3c)

White solid. 78% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.69 (s, 1H), 8.52-8.50 (m, 2H), 8.28 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.5$ Hz, 1H), 7.81-7.75 (m, 4H), 7.52-7.44 (m, 3H). $^{19}$F NMR (470 MHz,
CDCl$_3$ $\delta$ –65.8. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 150.2 (t, $J$ = 28.7 Hz), 141.6, 137.3, 134.4, 132.7, 131.6 (t, $J$ = 282.5 Hz), 131.0, 130.0, 129.5, 129.4, 129.3, 129.0, 127.0, 124.5, 124.2, 123.0, 122.0, 121.9. HRMS (CI): m/z calcd. for C$_{20}$H$_{12}$BrF$_2$NS [M+H]$^+$ 415.9915, found 415.9913.

**6-(difluoro(phenylthio)methyl)-8-phenylphenanthridine (3d)**

White solid. 86% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.79 (s, 1H), 8.75 (d, $J$ = 8.5 Hz, 1H), 8.61 (d, $J$ = 7.0 Hz, 1H), 8.31 (d, $J$ = 7.0 Hz, 1H), 8.15 (d, $J$ = 8.5 Hz, 1H), 7.84-7.72 (m, 6H), 7.52-7.42 (m, 6H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.7. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.2 (t, $J$ = 27.5 Hz), 141.7, 140.4, 140.0, 137.3, 133.1, 132.0 (t, $J$ = 277.5 Hz), 131.0, 130.4, 130.0, 129.1, 129.0, 128.9, 128.8, 128.0, 127.5, 127.4, 127.1, 123.0 (t, $J$ = 5.0 Hz), 123.0, 122.3, 122.1. HRMS (CI): m/z calcd. for C$_{26}$H$_{17}$F$_2$NS [M+H]$^+$ 414.1122, found 414.1122.

**6-(difluoro(phenylthio)methyl)-8-methoxyphenanthridine (3e)**

White solid. 87% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.58 (d, $J$ = 9.0 Hz, 1H), 8.50-8.48 (m, 1H), 8.27-8.25 (m, 1H), 7.89 (d, $J$ = 1.5 Hz, 1H), 7.83 (d, $J$ = 7.0 Hz, 2H), 7.74-7.71 (m, 2H), 7.52-7.44 (m, 4H), 3.94 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –66.7. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 158.7, 150.3 (t, $J$ = 28.2 Hz), 140.9, 137.3, 132.2 (t, $J$ = 277.5 Hz), 130.8, 129.9, 129.0, 128.9, 128.6, 128.1, 127.5, 125.2, 124.0, 123.2, 122.4, 121.5, 106.4 (t, $J$ = 5.5 Hz), 55.5. HRMS (CI): m/z calcd. for C$_{21}$H$_{15}$F$_2$NOS [M+H]$^+$ 368.0915, found 368.0914.

**6-(difluoro(phenylthio)methyl)-8-(trifluoromethyl)phenanthridine (3f)**

White solid. 65% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.86 (s, 1H), 8.81 (d, $J$ = 8.5 Hz, 1H), 8.63 (d, $J$ = 8.0 Hz, 1H), 8.34 (d, $J$ = 8.0 Hz, 1H), 8.09 (d, $J$ = 9.0 Hz, 1H), 7.89-7.80 (m, 4H), 7.53-7.45 (m, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –62.4, –65.7. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.1 (t, $J$ = 28.7 Hz), 142.3, 137.3, 136.1, 131.5 (t, $J$ = 277.5 Hz), 131.1, 130.3, 130.1, 129.6, 129.5, 129.4, 129.3, 129.1, 127.0 (m), 126.8, 124.9 (q, $J$ = 162.5 Hz), 124.6 (m), 124.1, 122.7. HRMS (CI): m/z calcd. for C$_{21}$H$_{15}$F$_3$NS [M+H]$^+$ 406.0683, found 406.0682.
6-(difluoro(phenylthio)methyl)-10-methoxyphenanthridine (3g)

White solid. 73% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.56 (dd, $J = 1.0$ Hz, $J = 8.0$ Hz, 1H), 8.30 (dd, $J = 1.5$ Hz, $J = 8.0$ Hz, 1H), 8.24-8.22 (m, 1H), 7.82-7.74 (m, 4H), 7.67 (t, $J = 8.5$ Hz, 1H), 7.49-7.43 (m, 3H), 7.37 (d, $J = 8.0$ Hz, 1H), 4.16 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.9. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 158.2, 150.9 (t, $J = 27.8$ Hz), 142.2, 137.2, 132.1 (t, $J = 277.5$ Hz), 130.7, 129.8, 128.9, 128.7, 128.4, 128.0, 127.8, 127.7, 124.9, 124.7, 123.9, 119.0 (t, $J = 5.9$ Hz), 112.0, 55.9. HRMS (CI): m/z calcd. for C$_{21}$H$_{15}$F$_2$NOS [M+H]$^+$ 368.0915, found 368.0914.

6-(difluoro(phenylthio)methyl)-9-methoxyphenanthridine (3h)

White solid. 30% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.51 (d, $J = 8.5$ Hz, 2H), 8.26 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 2.0$ Hz, 1H), 7.82 (m, 4H), 7.50 (m, 3H), 7.31 (dd, $J = 2.5$, 9.5 Hz, 1H), 4.05 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.9. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.5, 150.7 (t, $J = 27.5$ Hz), 142.0, 137.2, 136.5, 131.8 (t, $J = 277.5$ Hz) 130.9, 129.9, 129.2, 129.0, 128.9 (t, $J = 5.0$ Hz), 128.2, 127.4, 124.8, 122.0, 118.0, 116.8, 103.1, 55.6. HRMS (CI): m/z calcd. for C$_{21}$H$_{15}$F$_2$NOS [M+H]$^+$ 368.0915, found 368.0914.

6-(difluoro(phenylthio)methyl)-7-methoxyphenanthridine (3h)

White solid. 42% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.54 (d, $J = 8.0$ Hz, 1H), 8.26 (t, $J = 7.5$ Hz, 2H), 7.81 – 7.71 (m, 5H), 7.48 -7.41(m, 3H), 7.15 (d, $J = 8.0$ Hz, 1H), 3.97 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –68.5. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 157.3, 150.1 (t, $J = 30.0$ Hz), 141.2, 137.2, 136.4, 131.9, 131.8 (t, $J = 272.5$ Hz), 130.5, 129.7, 129.4, 129.2, 128.7, 127.3, 124.6, 122.5, 114.5, 114.4, 109.4, 56.2. HRMS (CI): m/z calcd. for C$_{21}$H$_{15}$F$_2$NOS [M+H]$^+$ 368.0915, found 368.0916.

5-(difluoro(phenylthio)methyl)benzo[c][2,7]naphthyridine (3i)
White solid, 45% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.94 (s, 1H), 8.99 (d, $J$ = 5.5 Hz, 1H), 8.59 (d, $J$ = 8.0 Hz, 1H), 8.45 (d, $J$ = 5.5Hz, 1H), 8.33 (d, $J$ = 8.0 Hz, 1H), 7.92 (t, $J$ = 7.5 Hz, 1H), 7.85 (t, $J$ = 7.5 Hz, 1H), 7.80 (d, $J$ = 7.0 Hz, 2H), 7.49 – 7.43 (m, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.9. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.3 (t, $J$ = 28.7 Hz), 150.8 (t, $J$ = 7.5 Hz), 148.6, 143.0, 138.8, 137.2, 131.4, 131.2, 130.8 (t, $J$ = 276.2), 130.2, 129.5, 129.1, 126.5, 122.9, 122.6, 117.3, 115.6. HRMS (Cl): m/z calcd. for C$_{19}$H$_{12}$F$_2$N$_2$S [M+H]$^+$ 339.0762, found 339.0761.

**6-(difluoro(phenylthio)methyl)-3-fluorophenanthridine (3j)**

White solid. 78% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.51-8.44 (m, 3H), 7.85 (dd, $J$ = 2.0 Hz, $J$ = 9.5 Hz, 1H), 7.81 (t, $J$ = 8.0 Hz, 1H), 7.71 (d, $J$ = 7.0 Hz, 2H), 7.62 (t, $J$ = 7.5 Hz, 1H), 7.44-7.33 (m, 4H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –66.2, –111.1. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.7 (d, $J$ = 248.0 Hz), 151.6 (t, $J$ = 27.5 Hz), 141.9, 141.8, 136.1, 132.8, 130.4, 128.9, 128.2 (t, $J$ = 261.2Hz), 127.9, 126.4, 126.1 – 126.0, 123.0 (d, $J$ = 8.7 Hz), 121.1, 120.7, 120.4, 117.0 (d, $J$ = 23.7 Hz), 114.3 (d, $J$ = 20.8Hz). HRMS (Cl): m/z calcd. for C$_{20}$H$_{12}$F$_2$S [M+H]$^+$ 356.0715, found 356.0714.

**3-chloro-6-(difluoro(phenylthio)methyl)phenanthridine (3k)**

White solid, 87% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.58-8.57 (m, 2H), 8.53 (d, $J$ = 1.5 Hz, 1H), 8.21 (d, $J$ = 9.0 Hz, 1H), 7.91 (t, $J$ = 7.0 Hz, 1H), 7.80 (d, $J$ = 7.0 Hz, 2H), 7.76-7.72 (m, 2H), 7.50-7.43 (m, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.3. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.6 (t, $J$ = 25.5 Hz), 140.1, 137.2, 135.0, 133.0, 132.3, 131.5 (t, $J$ = 276.2 Hz), 131.4, 130.0, 129.7, 129.0, 128.3, 127.1 (m), 126.1, 122.4, 122.1, 121.8. HRMS (Cl): m/z calcd. for C$_{20}$H$_{12}$ClF$_2$NS [M+H]$^+$ 372.0420, found 372.0418.

**6-(difluoro(phenylthio)methyl)-3-methylphenanthridine (3l)**

White solid. 87% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.58-8.57 (m, 2H), 8.53 (d, $J$ = 1.5 Hz, 1H), 8.21 (d, $J$ = 9.0 Hz, 1H), 7.91 (t, $J$ = 7.0 Hz, 1H), 7.80 (d, $J$ = 7.0 Hz, 2H), 7.76-7.72 (m, 2H), 7.50-7.43 (m, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.3. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.6 (t, $J$ = 25.5 Hz), 140.1, 137.2, 135.0, 133.0, 132.3, 131.5 (t, $J$ = 276.2 Hz), 131.4, 130.0, 129.7, 129.0, 128.3, 127.1 (m), 126.1, 122.4, 122.1, 121.8. HRMS (Cl): m/z calcd. for C$_{20}$H$_{12}$ClF$_2$NS [M+H]$^+$ 372.0420, found 372.0418.
White solid. 89% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.63 (d, $J = 8.5$ Hz, 1H), 8.57 (d, $J = 8.0$ Hz, 1H), 8.46 (d, $J = 8.5$ Hz, 1H), 8.09 (s, 1H), 7.86-7.81 (m, 3H), 7.68 (t, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.49-7.43 (m, 3H), 2.61 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.9. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.0 (t, $J = 28.5$ Hz), 141.8, 139.4, 137.2, 134.1, 131.9 (t, $J = 276.6$ Hz), 131.0, 130.6, 130.4, 129.9, 129.0, 127.5, 127.2, 126.9 (t, $J = 4.8$ Hz), 122.7, 122.2, 121.8, 21.4. HRMS (Cl): m/z calcd. for C$_{21}$H$_{15}$F$_2$NS [M+H]$^+$ 352.0966, found 352.0965.

6-(difluoro(phenylthio)methyl)-2-(trifluoromethyl)phenanthridine (3m)

White solid, 74% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.86 (s, 1H), 8.71 (d, $J = 8.5$ Hz, 1H), 8.64 (d, $J = 8.5$ Hz, 1H), 8.64 (d, $J = 8.5$ Hz, 1H), 8.39 (d, $J = 8.5$ Hz, 1H), 8.00-7.94 (m, 2H), 7.80-7.77 (m, 3H), 7.51-7.43 (m, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –62.0, –66.5. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 153.5 (t, $J = 27.5$ Hz), 143.1, 137.2, 133.8, 131.8, 131.3 (t, $J = 277.5$ Hz), 130.8 (q, $J = 32.5$ Hz), 130.1, 129.0, 128.6, 127.4 (t, $J = 5.0$ Hz), 126.9, 125.2, 125.1 (q, $J = 2.0$ Hz), 124.7, 123.0, 122.4, 122.2, 119.9 (q, $J = 3.75$Hz). HRMS (Cl): m/z calcd. for C$_{21}$H$_{12}$F$_5$NS [M+H]$^+$ 406.0683, found 406.0681.

6-(difluoro(p-tolylthio)methyl)phenanthridine (4b)

White solid. 85% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.69 (d, $J = 8.5$ Hz, 1H), 8.61-8.59 (m, 2H), 8.31 (dd, $J = 1.0$ Hz, $J = 9.5$ Hz, 1H), 7.90 (t, $J = 8.0$ Hz, 1H), 7.81-7.75 (m, 2H), 7.73-7.69 (m, 3H), 7.27 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –66.5. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 150.4 (t, $J = 27.9$ Hz), 140.7, 139.2, 136.1, 133.0, 130.5 (t, $J = 276.2$ Hz), 130.0, 129.9, 128.8, 128.0, 127.7, 127.5, 126.6, 126.0 (t, $J = 5.3$ Hz), 124.0, 122.6, 121.3, 120.9, 20.3. HRMS (Cl): m/z calcd. for C$_{21}$H$_{13}$F$_3$NS [M+H]$^+$ 352.0966, found 352.0965.

6-(difluoro((4-methoxyphenyl)thio)methyl)phenanthridine (4c)

White solid. 92% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.70 (d, $J = 8.5$ Hz, 1H), 8.61 (d, $J = 8.5$ Hz, 2H), 8.30 (d, $J = 7.5$ Hz, 1H), 7.90 (t, $J = 8.0$ Hz, 1H), 7.81-7.70 (m, 5H), 6.98 (d, $J = 8.5$ Hz, 2H), 3.85 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –67.1. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 160.2, 150.4 (t, $J = 27.9$ Hz), 140.7, 137.8, 133.0, 130.3 (t, $J = 282.0$ Hz), 130.0, 129.9, 128.0, 127.7, 126.6,
126.0 (t, J = 3.4 Hz), 123.9, 121.4, 121.0, 116.7, 113.5, 54.3. HRMS (Cl): m/z calcd. for C_{21}H_{15}F_{2}NOS [M+H]^+ 368.0915, found 368.0913.

6-((difluoro((2-methoxyphenyl)thio)methyl)phenanthridine (4d)

White solid. 74% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.69 (d, J = 8.0 Hz, 1H), 8.66 (d, J = 8.0 Hz, 1H), 8.60-8.58 (m, 1H), 7.96 (t, J = 7.5 Hz, 1H), 7.62-7.70 (m, 4H), 7.47-7.43 (m, 1H), 7.04 (t, J = 7.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H). ¹⁹F NMR (470 MHz, CDCl₃) δ –67.3. ¹³C NMR (125 MHz, CDCl₃) δ 160.3, 150.5 (t, J = 278 Hz), 130.0, 129.9, 128.0, 127.6, 126.5, 126.1 (t, J = 5.0 Hz), 123.9, 121.3, 121.1, 120.9, 119.9, 114.1, 110.4, 54.9. HRMS (Cl): m/z calcd. for C_{21}H_{15}F_{2}NOS [M+H]^+ 368.0915, found 368.0913.

6-((difluoro((3-methoxyphenyl)thio)methyl)phenanthridine (4e)

White solid. 83% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.69 (d, J = 8.0 Hz, 1H), 8.61-8.58 (m, 2H), 8.30 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.96 (t, J = 7.5 Hz, 1H), 7.81-7.76 (m, 4H), 7.73 (t, J = 7.5 Hz, 1H), 7.16 (t, J = 8.5 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃) δ –66.0. ¹³C NMR (125 MHz, CDCl₃) δ 158.6, 150.0 (t, J = 279 Hz), 140.6, 133.0, 130.7 (t, J = 279 Hz), 130.1, 129.8, 128.6, 128.3, 128.0, 127.8, 127.3, 126.6, 125.9 (t, J = 5.2 Hz), 124.0, 121.4, 121.0, 120.9, 115.1, 54.4. HRMS (Cl): m/z calcd. for C_{21}H_{15}F_{2}NOS [M+H]^+ 368.0915, found 368.0916.

6-((difluoro((4-fluorophenyl)thio)methyl)phenanthridine (4f)

White solid. 83% yield. ¹H NMR (500 MHz, CDCl₃): δ 8.70 (d, J = 10.0 Hz, 1H), 8.61 (d, J = 7.5 Hz, 1H), 8.57 (d, J = 8.5 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.91 (t, J = 7.5 Hz, 1H), 7.81-7.76 (m, 4H), 7.73 (t, J = 7.5 Hz, 1H), 7.16 (t, J = 8.5 Hz, 2H). ¹⁹F NMR (470 MHz, CDCl₃) δ –66.0, –110.8. ¹³C NMR (125 MHz, CDCl₃) δ 164.1 (d, J = 250 Hz), 150.1 (t, J = 29.3 Hz), 140.6, 138.3 (d, J = 8.7 Hz), 133.0, 130.7 (t, J = 278 Hz), 130.1, 129.8, 128.1, 127.8, 126.7, 126.0 (t, J = 5.4 Hz), 124.0, 121.6, 121.4, 121.0, 120.8, 115.2 (d, J = 22.5Hz). HRMS (Cl): m/z calcd. for C_{20}H_{13}F_{3}NS [M+H]^+ 356.0715, found 356.0716.
6-(((4-bromophenyl)thio)difluoromethyl)phenanthridine (4g)

White solid. 85% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.70 (d, $J = 8.5$ Hz, 1H), 8.61 (dd, $J = 1.5$ Hz, $J = 7.5$ Hz, 1H), 8.54 (d, $J = 8.5$ Hz, 1H), 8.28 (dd, $J = 1.5$ Hz, $J = 8.0$ Hz, 1H), 7.91 (td, $J = 1.0$ Hz, $J = 7.0$ Hz, 1H), 7.80-7.75 (m, 2H), 7.73-7.70 (m, 1H), 7.67-7.65 (m, 2H), 7.58-7.56 (m, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.6. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.0 (t, $J = 28.3$ Hz), 141.6, 138.6, 134.1, 132.2, 131.8 (t, $J = 278$ Hz), 131.2, 130.9, 129.2, 128.9, 127.7, 126.8 (t, $J = 5.4$ Hz), 126.6, 125.1, 124.9, 122.5, 122.1, 121.8. HRMS (CI): m/z calcd. for C$_{20}$H$_{12}$BrF$_2$NS [M+H]$^+$ 415.9915, found 415.9914.

6-(((4-chlorophenyl)thio)difluoromethyl)phenanthridine (4h)

White solid. 85% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.70 (d, $J = 8.5$ Hz, 1H), 8.55 (dd, $J = 1.5$ Hz, $J = 7.5$ Hz, 1H), 8.29 (dd, $J = 1.5$ Hz, $J = 8.5$ Hz, 1H), 7.91-7.88 (m, 1H), 7.82-7.71 (m, 5H), 7.43-7.41 (m, 2H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.7. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 150.8 (t, $J = 28.1$ Hz), 141.6, 138.4, 136.6, 134.1, 131.9 (t, $J = 278$ Hz), 131.2, 130.9, 129.2, 128.9, 127.7, 126.8 (t, $J = 5.4$ Hz), 126.0, 125.1, 122.5, 122.1, 121.8. HRMS (CI): m/z calcd. for C$_{20}$H$_{12}$ClF$_2$NS [M+H]$^+$ 372.0420, found 372.0421.

6-(((2-chlorophenyl)thio)difluoromethyl)phenanthridine (4i)

White solid. 75% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.68 (d, $J = 8.0$ Hz, 1H), 8.59 (t, $J = 5.5$ Hz, 2H), 8.30 (dd, $J = 1.5$ Hz, $J = 8.5$ Hz, 1H), 7.97-7.95 (m, 1H), 7.89 (t, $J = 8.0$ Hz, 1H), 7.80-7.74 (m, 2H), 7.72 (t, $J = 8.0$ Hz, 1H), 7.58 (dd, $J = 1.5$ Hz, $J = 8.0$ Hz, 1H), 7.44 (td, $J = 1.5$ Hz, $J = 7.5$ Hz, 1H), 7.37 (td, $J = 1.5$ Hz, $J = 7.5$ Hz, 1H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –65.8. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.0 (t, $J = 278$ Hz), 141.6, 140.8, 139.7, 134.0, 132.1 (t, $J = 797$ Hz), 131.4, 131.1, 130.9, 130.3, 129.1, 128.9, 127.7, 127.1, 127.0, 126.8 (t, $J = 5.3$ Hz), 125.1, 122.4, 122.0, 121.8. HRMS (CI): m/z calcd. for C$_{20}$H$_{12}$ClF$_2$NS [M+H]$^+$ 372.0420, found 372.0418.

6-(((3-chlorophenyl)thio)difluoromethyl)phenanthridine (4j)
White solid. 67% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.70 (d, \(J = 8.0\) Hz, 1H), 8.60 (d, \(J = 7.5\) Hz, 1H), 8.56 (d, \(J = 8.0\) Hz, 1H), 8.29 (d, \(J = 7.0\) Hz, 1H), 7.91 (t, \(J = 7.5\) Hz, 1H), 7.82-7.76 (m, 3H), 7.74-7.69 (m, 2H), 7.47 (d, \(J = 7.5\) Hz, 1H), 7.39 (t, \(J = 8.0\) Hz, 1H). \(^{19}\)F NMR (470 MHz, CDCl\(_3\)) \(\delta\) –65.3. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 151.0 (t, \(J = 28.3\) Hz), 141.6, 136.6, 135.1, 134.5, 134.1, 132.0 (t, \(J = 279\) Hz), 131.2, 130.9, 130.1, 129.4, 129.2, 128.9, 127.8, 126.8 (t, \(J = 5.3\) Hz), 125.1, 122.5, 122.1, 121.8. HRMS (Cl): m/z calcd. for C\(_{20}\)H\(_{12}\)ClF\(_2\)NS [M+H]\(^+\) 372.0420, found 372.0419.

6-(difluoro(naphthalen-2-ylthio)methyl)phenanthridine (4k)

White solid. 86% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.68 (d, \(J = 8.5\) Hz, 1H), 8.59-8.57 (m, 2H), 8.34 (s, 1H), 8.30 (d, \(J = 7.5\) Hz, 1H), 7.88-7.84 (m, 5H), 7.80-7.73 (m, 2H), 7.71 (t, \(J = 8.0\) Hz, 1H), 7.56-7.51 (m, 2H). \(^{19}\)F NMR (470 MHz, CDCl\(_3\)) \(\delta\) –65.8. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 151.1 (t, \(J = 27.9\) Hz), 141.7, 137.4, 134.1, 133.7, 133.5, 133.2, 132.0 (t, \(J = 278\) Hz), 131.1, 130.9, 129.1, 128.8, 128.5, 128.2, 127.8, 127.7, 127.3, 127.0 (t, \(J = 5.3\) Hz), 126.6, 125.1, 124.7, 122.4, 122.1, 121.9. HRMS (Cl): m/z calcd. for C\(_{24}\)H\(_{15}\)ClF\(_2\)NS [M+H]\(^+\) 388.0966, found 388.0965.

methyl 1-(difluoro(phenylthio)methyl)-4-phenylisoquinoline-3-carboxylate (6a)

White solid. 85% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.62 (d, \(J = 8.5\) Hz, 1H), 7.81 (d, \(J = 7.0\) Hz, 2H), 7.76-7.70 (m, 3H), 7.54-7.51 (m, 3H), 7.50-7.48 (m, 1H), 7.46-7.43 (m, 2H), 7.35-7.33 (m, 2H), 3.75 (s, 3H). \(^{19}\)F NMR (470 MHz, CDCl\(_3\)) \(\delta\) –65.8. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 165.3, 149.5 (t, \(J = 28.7\) Hz), 138.3, 136.2, 136.1, 136.1, 134.3, 130.3 (t, \(J = 276.2\) Hz), 130.1, 128.9, 128.4, 128.3, 127.9, 127.3, 127.3, 126.3, 126.0, 124.7 (t, \(J = 5.0\) Hz), 123.8, 51.5. HRMS (Cl): m/z calcd. for C\(_{26}\)H\(_{17}\)F\(_2\)NO\(_2\)S [M+H]\(^+\) 422.1021, found 422.1018.

Methyl 1-(difluoro(phenylthio)methyl)-7-fluoro-4-(4-fluorophenyl)isoquinoline-3-
carboxylate (6b)

White solid. 83% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.22 (dd, $J = 2.0$ Hz, $J = 10.0$ Hz, 1H), 7.79 (d, $J = 7.0$ Hz, 2H), 7.72-7.69 (m, 1H), 7.52-7.48 (m, 2H), 7.46-7.43 (m, 2H), 7.31-7.29 (m, 2H), 7.25-7.22 (m, 2H), 3.78 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –66.7, –105.9, –112.6. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.0, 163.9 (d, $J = 246.2$ Hz), 163.0 (d, $J = 252.0$ Hz), 150.3 (td, $J = 6.2$, 28.75 Hz), 139.1, 137.2, 136.2, 134.5, 131.3 (d, $J = 8.7$ Hz), 131.0 (t, $J = 277.5$ Hz), 130.9 (d, $J = 3.7$ Hz), 130.2 (t, $J = 5.0$ Hz), 129.0, 128.7, 126.7, 126.1 (d, $J = 10.0$ Hz), 122.0 (d, $J = 25.0$ Hz), 115.8 (d, $J = 21.2$ Hz), 110.2 (td, $J = 5.0$, 23.7 Hz), 52.7. HRMS (CI): m/z calcd. for C$_{24}$H$_{15}$F$_4$NO$_2$S [M+H]$^+$ 458.0832, found 458.0832.

Methyl 7-chloro-4-(4-chlorophenyl)-1-(difluoro(phenylthio)methyl)isoquinoline- 3-carboxylate (6c)

White solid. 67% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.57 (s, 1H), 7.79 (d, $J = 7.5$ Hz, 2H), 7.66-7.59 (m, 2H), 7.52-7.44 (m, 6H), 7.26-7.24 (m, 1H), 3.79 (s, 3H). $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ –66.0. $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.8, 150.1 (t, $J = 28.7$ Hz), 139.4, 137.2, 136.2, 136.1, 135.6, 134.9, 133.3, 132.5, 131.1 (t, $J = 277.5$ Hz), 130.8, 130.2, 129.1, 128.8, 128.7, 126.5, 125.4, 125.0 (t, $J = 5.0$ Hz), 52.8. HRMS (CI): m/z calcd. for C$_{24}$H$_{15}$Cl$_2$F$_2$NO$_2$S [M+H]$^+$ 490.0241, found 490.0239.
6. Copies of NMR Spectra