

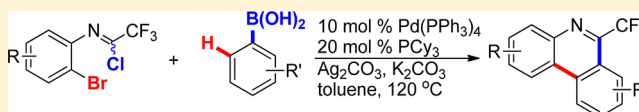
# Synthesis of 6-(Trifluoromethyl)phenanthridines via Palladium-Catalyzed Tandem Suzuki/C–H Arylation Reactions

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**S** Supporting Information

**ABSTRACT:** A palladium-catalyzed tandem Suzuki/C–H arylation reaction of *N*-aryltrifluoroacetimidoyl chlorides with arylboronic acids has been developed. A variety of 6-(trifluoromethyl)phenanthridines were prepared in moderate to excellent yields from *N*-(2-bromophenyl)-trifluoroacetimidoyl chlorides which can be conveniently prepared from 2-bromoaniline derivatives.

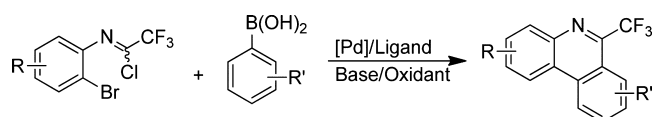


## INTRODUCTION

Phenanthridines are important heteroaromatic compounds and commonly encountered in biologically active molecules,<sup>1</sup> natural products,<sup>2</sup> and optoelectronic materials.<sup>3</sup> As a consequence, a number of useful synthetic procedures have been developed to prepare phenanthridines and their derivatives.<sup>4</sup> However, simple, mild, and versatile preparations of phenanthridines with specific substitution patterns are still highly desirable. For example, efficient synthetic methods for trifluoromethylated phenanthridines are scarcely reported although the incorporation of a CF<sub>3</sub> group into aromatics often enhances their biological activity and has become a powerful and widely used strategy in the process of drug design.<sup>5,6</sup>

Recently, transition-metal-catalyzed arene C–H bond functionalization reactions have emerged as versatile tools for the atom- and step-economical assembly of aromatic compounds.<sup>7,8</sup> For example, Yoshikai and co-workers reported a cobalt-catalyzed *ortho*-arylation of aromatic imines with aryl chlorides.<sup>8</sup> As part of our ongoing studies toward the synthesis of trifluoromethylated heterocyclic compounds,<sup>9</sup> we have been investigating the preparation of CF<sub>3</sub>-containing phenanthridines from our previously reported building blocks which can be conveniently prepared from 2-bromoaniline derivative and trifluoroacetic acid.<sup>10</sup> Herein, we report a simple and efficient protocol for the synthesis of 6-trifluoromethylphenanthridines by the palladium-catalyzed tandem Suzuki coupling reaction and subsequent intramolecular C–H arylation of *N*-aryltrifluoroacetimidoyl chlorides with arylboronic acids in one pot (Scheme 1).

### Scheme 1



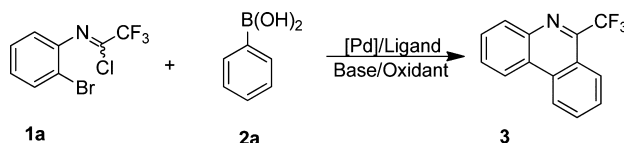
## RESULTS AND DISCUSSION

The reaction of *N*-(2-bromophenyl)-2,2,2-trifluoroacetimidoyl chloride **1a** with phenylboronic acid **2a** was used as a model reaction to screen the optimal reaction conditions, and the results are summarized in Table 1. Initially, treatment of substrate **1a** with phenylboronic acid, Pd(OAc)<sub>2</sub> (10 mol %), K<sub>2</sub>CO<sub>3</sub> (2 equiv), PPh<sub>3</sub>, and Ag<sub>2</sub>CO<sub>3</sub> in toluene at 120 °C afforded the desired product **3** in 49% yield (entry 1). Further investigation into catalysts demonstrated that Pd(0) was more effective than Pd(II) species, and the reaction yield increased to 73% using Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst (entries 1–4). Some bulky phosphine ligands such as XPhos, SPhos, and RuPhos were examined with the aim of increasing the reaction yield, but all were less effective than PPh<sub>3</sub> (entries 5–7). To our surprise, a 94% yield was obtained when PCy<sub>3</sub> (tricyclohexylphosphine) was used as ligand (entry 8). Subsequently, some other oxidants and bases were also evaluated, but lower yields were observed (entries 9–13). It is noteworthy that only 18% yield was obtained in the absence of oxidant (entry 14). Polar solvents such as DMF, DMSO and MeCN were unfavorable for this transformation (entries 15–17). Lower yields were observed when the reaction was conducted at 100 °C or when the loading of catalyst reduced to 5 mol % (entries 18 and 19).

With these optimized conditions in hand, we surveyed the substrate scope of *N*-aryltrifluoroacetimidoyl chlorides and arylboronic acids (Table 2). Initially, a variety of arylboronic acids were investigated by reacting with substrate **1a** under standard conditions. The results demonstrated that both electron-rich and electron-poor phenylboronic acids were suitable coupling partners, and the reactions afforded the corresponding products in moderate to excellent yields (4–14). *o*- or *p*-methyl-substituted phenylboronic acid gave the product in 72% and 86% yield, respectively (**4** and **5**). Similar results were obtained for MeO-substituted phenylboronic acid (**6** and **7**). The reactions of biphenyl-4-boronic acid also

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Table 1. Screening Conditions<sup>a</sup>

entry	[Pd]	base	ligand	oxidant	solvent	yield <sup>b</sup> (%)
1	Pd(OAc) <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	PPh <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	toluene	49
2	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	PPh <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	toluene	53
3	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	PPh <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	toluene	5
4	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PPh <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	toluene	73
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	XPhos	Ag <sub>2</sub> CO <sub>3</sub>	toluene	47
6	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	SPhos	Ag <sub>2</sub> CO <sub>3</sub>	toluene	51
7	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	RuPhos	Ag <sub>2</sub> CO <sub>3</sub>	toluene	45
8	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	toluene	94
9	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	Ag <sub>2</sub> O	toluene	59
10	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	AgOTf	toluene	31
11	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	toluene	68
12	Pd(PPh <sub>3</sub> ) <sub>4</sub>	Cs <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	toluene	88
13	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<i>t</i> -BuONa	PCy <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	toluene	5
14	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>		toluene	18
15	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	DMF	11
16	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	DMSO	trace
17	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	NR
18 <sup>c</sup>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	toluene	81
19 <sup>d</sup>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	PCy <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>	toluene	65

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), [Pd] (10 mol %), ligand (20 mol %), oxidant (2 equiv), and base (2 equiv) in solvent (2 mL) at 120 °C under N<sub>2</sub> atmosphere for 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>At 100 °C. <sup>d</sup>(PPh<sub>3</sub>)<sub>4</sub> (5 mol %).

afforded the desired product in 81% yield (**8**). 4-Fluoro- and 4-chlorophenylboronic acid provided 67% and 82% yields, respectively (**9** and **10**). 2-Position C–H-arylated product was exclusively obtained in 86% yield using 3-nitrophenylboronic acid as substrate (**11**). Other cyclizations of phenylboronic acids bearing strongly electron-withdrawing groups (such as cyano, acetyl, and trifluoromethyl) proceeded smoothly to give their corresponding products in 66–87% yields (**12**–**14**). Interestingly, naphthalen-1-ylboronic acid underwent the tandem reactions to afford  $\beta$ -position C–H arylation product in a 51% yield (**15**). Subsequently, various substituents on the 3- or 4-position of *N*-(2-bromophenyl)trifluoroacetimidoyl chlorides were tested. The reaction between 4-methyl-substituted phenylimine and various arylboronic acids gave excellent yields (**16**–**18**). 4-Chloro- and 4-fluorophenylimine also provided the corresponding product in 72–93% yields (**19**–**21**). The cyclization of 3-trifluoromethylphenylimine proceeded smoothly to give the corresponding product in 82% yield (**22**), whereas 3-nitrophenylimine afforded a lower yield (42%, **23**).

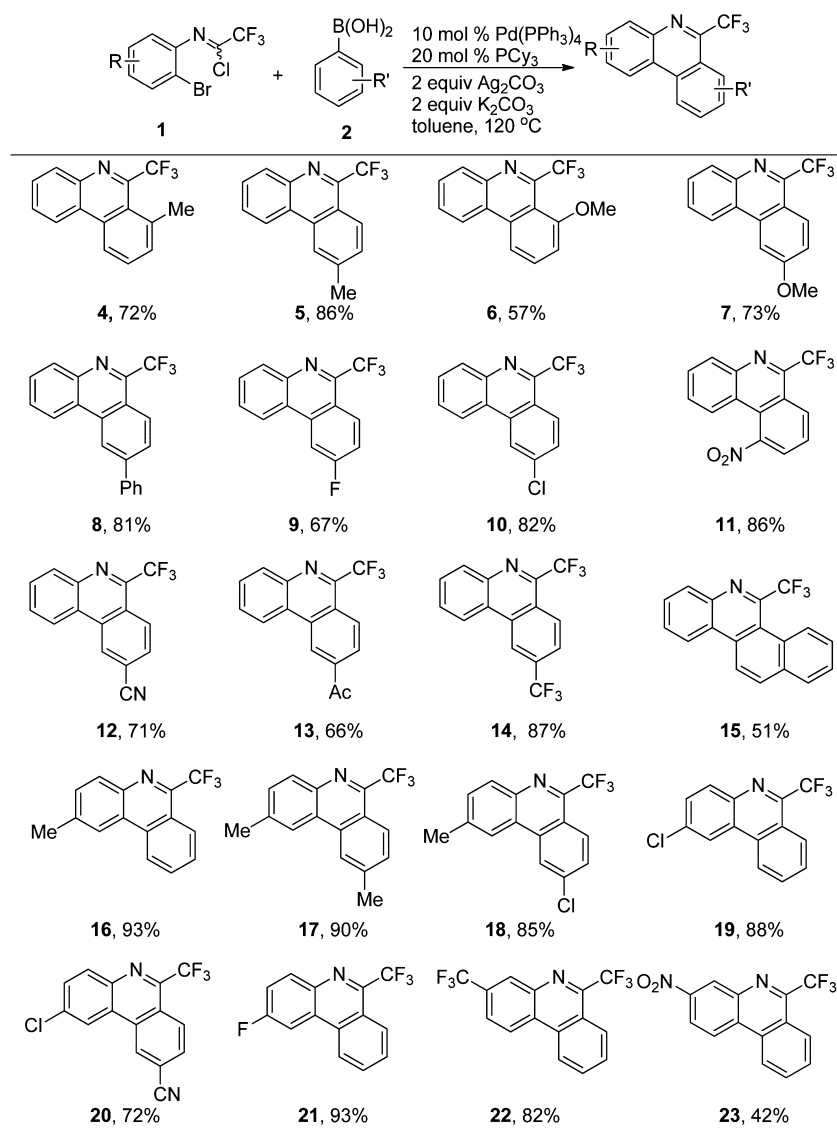
To elucidate the mechanism of the transformation, some control experiments were carried out as shown in Scheme 2. First, treatment of substrate **1a** with phenylboronic acid **2a** in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, PCy<sub>3</sub>, Ag<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub> at 60 °C for 5 h afforded the 2-bromo-*N*-(2,2,2-trifluoro-1-phenylethylidene)aniline **24** in 90% yield, and no product **3** was detected (Scheme 2, eq 1). These results indicated that the Suzuki coupling reaction occurred preferentially under the standard conditions. As expected, compound **24** could be converted into the desired product **3** in a 93% yield under standard conditions for 12 h (eq 2). It is noteworthy that no cyclization product was detected using *o*-bromostyrene derivative **25** as substrate under the standard conditions (eq

**3**), which suggested that the directing group of imine probably played a key role during C–H arylation reaction.

On the basis of the observed results and the reported mechanism,<sup>11</sup> a possible mechanism was proposed as outlined in Scheme 3. The reaction afforded product **3** in poor yield in the absence of oxidant, which suggested that the C–H arylation possibly proceeded through a Pd(II)/Pd(IV) pathway although a Pd(0)/Pd(II) pathway could not be ruled out. The Suzuki coupling reaction between substrate **1a** and **2a** occurred preferentially at low temperature to provide compound **24**. In path a, the oxidative addition of aryl bromide **24** to Pd(0) species afforded intermediate **A**. The elimination of HBr might yield palladacycle **B**, and the following reductive elimination furnished product **3**. In path b, imine-directing C–H activation produced palladium(II) complex **C**. Intramolecular oxidative addition with phenyl bromide moiety provided seven-membered palladacycle **D**,<sup>12</sup> and the subsequent reductive elimination afforded the desired product **3** and regenerated Pd(II) species. Study of the detailed mechanism is in progress.

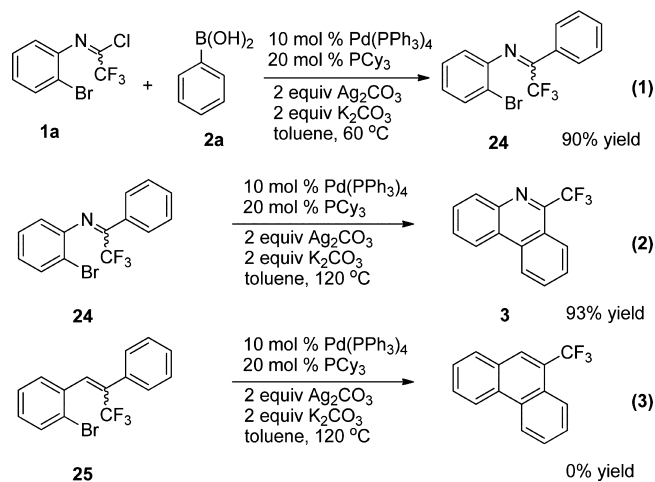
## CONCLUSION

In summary, we have developed an efficient method for the synthesis of trifluoromethylated phenanthridines. In the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, PCy<sub>3</sub>, Ag<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>, a variety of *N*-aryltrifluoroacetimidoyl chlorides underwent the tandem Suzuki/C–H arylation reactions with arylboronic acids to afford the corresponding phenanthridines in moderate to excellent yields. The present process could be used for the synthesis of trifluoromethyl-containing building blocks from simple starting materials, and it also provided a new optional route for constructing phenanthridine rings.

Table 2. Palladium-Catalyzed Tandem Suzuki/C–H Arylation Reactions<sup>a</sup>

<sup>a</sup>Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol %), PCy<sub>3</sub> (20 mol %), Ag<sub>2</sub>CO<sub>3</sub> (2 equiv) and K<sub>2</sub>CO<sub>3</sub> (2 equiv) in toluene (2 mL) at 120 °C under N<sub>2</sub> atmosphere for 24 h.

## Scheme 2. Control Experiments

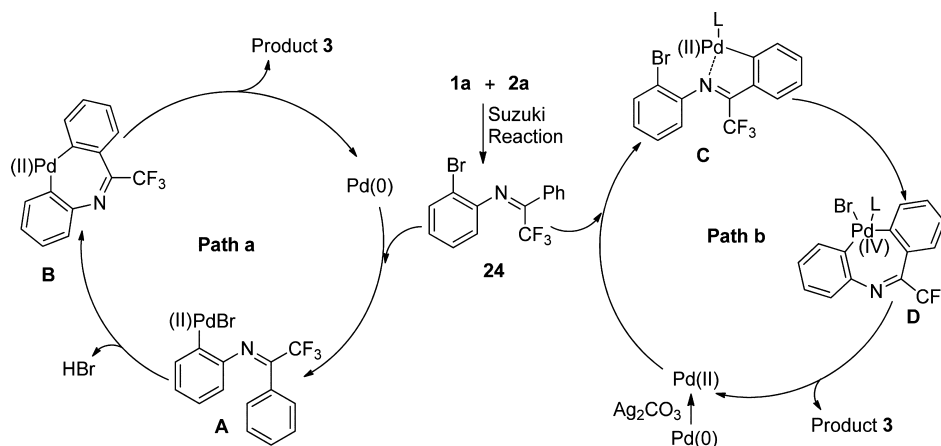


## EXPERIMENTAL SECTION

**General Information.** Chemicals were either purchased or purified by standard techniques. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a 500 MHz spectrometer (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 125 MHz), using CDCl<sub>3</sub> as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in Hz. <sup>19</sup>F NMR spectra were recorded on a 500 MHz spectrometer (<sup>19</sup>F: 470 MHz) and are reported relative to the CFCl<sub>3</sub> as the internal standard. High-resolution mass spectra were recorded on ESI-Q-TOF mass spectrometry. All reactions under nitrogen atmosphere were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300–400 mesh).

**Typical Experimental Procedure for Synthesis of 6-(Trifluoromethyl)phenanthridine.** A mixture of *N*-(2-bromophenyl)-2,2,2-trifluoroacetimidoyl chloride (57.2 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (23.1 mg, 10 mol %), PCy<sub>3</sub> (11.2 mg, 20 mol %), Ag<sub>2</sub>CO<sub>3</sub> (110.4 mg, 2 equiv), K<sub>2</sub>CO<sub>3</sub> (55.2 mg, 2 equiv), and phenylboronic acid (29.3 mg, 1.2 equiv) in toluene (2 mL) was evacuated and backfilled with nitrogen (3 cycles) and then stirred at 120 °C until complete consumption of starting material as detected by TLC or

Scheme 3. Possible Mechanism



GC-MS analysis. After the reaction was finished, the mixture was poured into ethyl acetate, evaporated under vacuum. The residue was purified by flash column chromatography (hexane/ethyl acetate) to afford the desired product 3.

**6-(Trifluoromethyl)phenanthridine (3):**<sup>5</sup> pale yellow solid (46.4 mg, 94% yield); mp 71.2–73.1 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.70 (d, *J* = 8.5 Hz, 1H), 8.62–8.60 (m, 1H), 8.39–8.37 (m, 1H), 8.30–8.28 (m, 1H), 7.94–7.91 (m, 1H), 7.83–7.76 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 146.5 (q, *J*<sub>C-F</sub> = 32.8 Hz), 141.7, 133.9, 131.4, 131.1, 129.3, 129.2, 128.0, 125.9 (q, *J*<sub>C-F</sub> = 3.3 Hz), 125.1, 122.5, 122.1, 121.9 (q, *J*<sub>C-F</sub> = 275.5 Hz), 121.7; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.5 (s, 3F); IR (neat, cm<sup>-1</sup>): 1620, 1382, 1179, 972, 757, 611; LRMS (EI, 70 eV) *m/z* 247 (M<sup>+</sup>, 100), 178 (60), 151 (30), 124 (9), 75 (8); HRMS (ESI) calcd for C<sub>14</sub>H<sub>9</sub>F<sub>3</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 248.0682, found 248.0680.

**7-Methyl-6-(trifluoromethyl)phenanthridine (4):** pale yellow solid (37.6 mg, 72% yield); mp 46.8–48.5 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.56–8.51 (m, 2H), 8.22–8.20 (m, 1H), 7.78–7.70 (m, 3H), 7.56 (d, *J* = 7.0 Hz, 1H), 2.81 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.0 (q, *J*<sub>C-F</sub> = 33.5 Hz), 140.6, 135.8, 135.5, 132.6, 130.6, 130.4, 129.2, 129.1, 125.3, 122.3, 122.2, 122.0 (q, *J*<sub>C-F</sub> = 273.8 Hz), 120.7, 23.4; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -59.7 (s, 3F); IR (neat, cm<sup>-1</sup>) 1600, 1346, 1168, 1121, 963, 758, 716; LRMS (EI, 70 eV) *m/z* 261 (M<sup>+</sup>, 100), 241 (15), 192 (41), 165 (43), 82 (11); HRMS (ESI) calcd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 262.0838, found 262.0840.

**9-Methyl-6-(trifluoromethyl)phenanthridine (5):** pale yellow solid (44.9 mg, 86% yield); mp 51.4–53.2 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.55 (d, *J* = 7.5 Hz, 1H), 8.42 (s, 1H), 8.26–8.23 (m, 2H), 7.79–7.73 (m, 2H), 7.55 (d, *J* = 8.5 Hz, 1H), 2.64 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 146.4 (q, *J*<sub>C-F</sub> = 32.8 Hz), 142.0, 141.9, 134.1, 131.0, 129.8, 129.1, 128.9, 125.7 (q, *J*<sub>C-F</sub> = 3.3 Hz), 124.9, 122.1, 122.0, 121.9 (q, *J*<sub>C-F</sub> = 275.5 Hz), 119.8, 22.3; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.5 (s, 3F); IR (neat, cm<sup>-1</sup>) 1626, 1251, 970, 744, 623, 556; LRMS (EI, 70 eV) *m/z* 261 (M<sup>+</sup>, 100), 241 (15), 165 (43), 192 (41), 82 (11); HRMS (ESI) calcd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 262.0838, found 262.0847.

**7-Methoxy-6-(trifluoromethyl)phenanthridine (6):** pale yellow solid (31.6 mg, 57% yield); mp 92.1–94.0 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.54–8.52 (m, 1H), 8.24 (d, *J* = 8.0 Hz, 2H), 7.82–7.72 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 156.8, 144.6 (q, *J*<sub>C-F</sub> = 34.8 Hz), 141.5, 136.2, 132.0, 130.9, 129.3, 129.0, 124.6, 122.4, 122.0 (q, *J*<sub>C-F</sub> = 273.4 Hz), 114.5, 114.3, 109.2, 56.1; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.7 (s, 3F); IR (neat, cm<sup>-1</sup>) 1609, 1462, 1275, 1142, 963, 739, 682; LRMS (EI, 70 eV) *m/z* 277 (M<sup>+</sup>, 100), 234 (53), 208 (14), 178 (12), 164 (10), 135 (8); HRMS (ESI) calcd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>NO<sup>+</sup> ([M + H]<sup>+</sup>) 278.0787, found 278.0789.

**9-Methoxy-6-(trifluoromethyl)phenanthridine (7):** pale yellow solid (40.4 mg, 73% yield); mp 150.4–152.3 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.49 (d, *J* = 8.0 Hz, 1H), 8.29–8.23 (m, 2H), 7.94 (s,

1H), 7.80–7.72 (m, 2H), 7.34–7.32 (m, 1H), 4.05 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 161.7, 146.1 (q, *J*<sub>C-F</sub> = 32.6 Hz), 142.1, 136.4, 131.1, 129.4, 128.6, 127.8 (q, *J*<sub>C-F</sub> = 3.4 Hz), 124.8, 122.0, 122.0 (q, *J*<sub>C-F</sub> = 275.5 Hz), 118.4, 116.6, 103.1, 55.6; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.3 (s, 3F); IR (neat, cm<sup>-1</sup>) 1616, 1393, 1177, 1113, 971, 839, 735; LRMS (EI, 70 eV) *m/z* 277 (M<sup>+</sup>, 100), 278 (17), 234 (38), 178 (12), 164 (9); HRMS (ESI) calcd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>NO<sup>+</sup> ([M + H]<sup>+</sup>) 278.0787, found 278.0799.

**9-Phenyl-6-(trifluoromethyl)phenanthridine (8):** pale yellow solid (52.3 mg, 81% yield); mp 85.9–87.8 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.85 (s, 1H), 8.68–8.66 (m, 1H), 8.45–8.43 (m, 1H), 8.30–8.29 (m, 1H), 8.00–7.98 (m, 1H), 7.81–7.77 (m, 4H), 7.57–7.54 (m, 2H), 7.49–7.46 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 146.4 (q, *J*<sub>C-F</sub> = 33.0 Hz), 144.1, 142.1, 140.0, 134.4, 131.2, 129.4, 129.2, 129.1, 128.6, 127.7, 127.5, 126.4 (q, *J*<sub>C-F</sub> = 3.4 Hz), 125.2, 122.1, 122.0 (q, *J*<sub>C-F</sub> = 275.4 Hz), 120.8, 120.6; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.4 (s, 3F); IR (neat, cm<sup>-1</sup>) 1616, 1252, 1117, 973, 832, 762, 610; LRMS (EI, 70 eV) *m/z* 323 (M<sup>+</sup>, 100), 254 (36), 226 (12), 127 (11), 113 (14); HRMS (ESI) calcd for C<sub>20</sub>H<sub>13</sub>F<sub>3</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 324.0995, found 324.1005.

**9-Fluoro-6-(trifluoromethyl)phenanthridine (9):** pale yellow solid (35.5 mg, 67% yield); mp 52.4–54.3 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.50–8.48 (m, 1H), 8.43–8.40 (m, 1H), 8.31–8.28 (m, 2H), 7.87–7.79 (m, 2H), 7.53–7.49 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 164.1 (d, *J*<sub>C-F</sub> = 252.9 Hz), 146.0 (q, *J*<sub>C-F</sub> = 32.0 Hz), 142.0, 136.6 (d, *J*<sub>C-F</sub> = 9.5 Hz), 131.2, 130.1, 129.3, 129.1 (q, *J*<sub>C-F</sub> = 9.6 Hz), 124.6 (d, *J*<sub>C-F</sub> = 4.3 Hz), 122.3, 121.8 (q, *J*<sub>C-F</sub> = 275.3 Hz), 118.8, 117.5 (d, *J*<sub>C-F</sub> = 23.9 Hz), 107.8 (d, *J*<sub>C-F</sub> = 19.9 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.4 (s, 3F), -104.4 (s, 1F); IR (neat, cm<sup>-1</sup>) 1625, 1256, 1116, 972, 837, 705, 557; LRMS (EI, 70 eV) *m/z* 262 (M<sup>+</sup>, 100), 196 (63), 170 (5), 169 (18), 133 (6); HRMS (ESI) calcd for C<sub>14</sub>H<sub>8</sub>F<sub>4</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 266.0588, found 266.0579.

**9-Chloro-6-(trifluoromethyl)phenanthridine (10):** pale yellow solid (46.1 mg, 82% yield); mp 94.5–96.3 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.64 (s, 1H), 8.52–8.50 (m, 1H), 8.32–8.28 (m, 2H), 7.86–7.79 (m, 2H), 7.72–7.70 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 146.1 (q, *J*<sub>C-F</sub> = 33.3 Hz), 142.1, 138.1, 135.3, 131.2, 130.0, 129.5, 128.8, 128.2, 127.5 (q, *J*<sub>C-F</sub> = 3.3 Hz), 122.3, 122.1, 121.7 (q, *J*<sub>C-F</sub> = 275.4 Hz), 120.0; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.5 (s, 3F); IR (neat, cm<sup>-1</sup>) 1607, 1383, 1249, 1113, 971, 825, 767; LRMS (EI, 70 eV) *m/z* 281 (M<sup>+</sup>, 100, <sup>35</sup>Cl), 283 (33, <sup>37</sup>Cl), 177 (63), 212 (43), 150 (16), 75 (12); HRMS (ESI) calcd for C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>NCl<sup>+</sup> ([M + H]<sup>+</sup>) 282.0292, found 282.0296.

**10-Nitro-6-(trifluoromethyl)phenanthridine (11):** pale yellow solid (50.2 mg, 86% yield); mp 129.7–131.5 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.58–8.56 (m, 1H), 8.35–8.33 (m, 1H), 8.12–8.10 (m, 1H), 8.04–8.03 (m, 1H), 7.91–7.85 (m, 2H), 7.77–7.73 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 148.2, 145.6 (q, *J*<sub>C-F</sub> = 33.4 Hz), 142.7, 131.8, 130.9, 130.0, 129.2 (q, *J*<sub>C-F</sub> = 3.6 Hz), 127.5, 126.5, 125.1, 124.0, 123.1, 121.5 (q, *J*<sub>C-F</sub> = 275.5 Hz), 120.5; <sup>19</sup>F NMR (470 MHz,



CDCl<sub>3</sub>) δ -63.1 (s, 3F); IR (neat, cm<sup>-1</sup>) 1521, 1172, 1028, 823, 764, 657; LRMS (EI, 70 eV) *m/z* 262 (M<sup>+</sup>, 100), 260 (80), 242 (77), 191 (32), 292 (31), 234 (25), 139 (23); HRMS (ESI) calcd for C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> ([M + H]<sup>+</sup>) 293.0533, found 293.0538.

**6-(Trifluoromethyl)phenanthridine-9-carbonitrile (12):** pale yellow solid (38.6 mg, 71% yield); mp 192.4–194.2 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.03 (s, 1H), 8.59–8.57 (m, 1H), 8.48–8.46 (m, 1H), 8.35–8.33 (m, 1H), 7.97–7.95 (m, 1H), 7.92–7.88 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.9 (q, *J*<sub>C-F</sub> = 33.6 Hz), 142.1, 133.7, 131.5, 130.7, 130.4, 129.3, 127.9, 127.1 (q, *J*<sub>C-F</sub> = 3.4 Hz), 123.7, 123.1, 122.0, 121.5 (q, *J*<sub>C-F</sub> = 275.4 Hz), 117.9, 115.0; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.5 (s, 3F); IR (neat, cm<sup>-1</sup>) 1374, 1174, 972, 772, 569, 549; LRMS (EI, 70 eV) *m/z* 272 (M<sup>+</sup>, 100), 203 (52), 176 (26), 149 (7), 136 (5); HRMS (ESI) calcd for C<sub>15</sub>H<sub>8</sub>F<sub>3</sub>N<sub>2</sub><sup>+</sup> ([M + H]<sup>+</sup>) 273.0634, found 273.0634.

**1-(6-(Trifluoromethyl)phenanthridin-9-yl)ethanone (13):** pale yellow solid (38.1 mg, 66% yield); mp 154.0–156.0 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.26 (s, 1H), 8.70–8.68 (m, 1H), 8.45 (d, *J* = 8.5 Hz, 1H), 8.32–8.30 (m, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.87–7.85 (m, 2H), 2.83 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 197.3, 146.1 (q, *J*<sub>C-F</sub> = 33.3 Hz), 142.0, 138.3, 133.8, 131.4, 130.0, 129.9, 126.7, 126.5 (q, *J*<sub>C-F</sub> = 3.4 Hz), 125.2, 123.7, 123.0, 122.1, 121.7 (q, *J*<sub>C-F</sub> = 275.4 Hz), 27.0; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.6 (s, 3F); IR (neat, cm<sup>-1</sup>) 1686, 1244, 1117, 972, 768, 548; LRMS (EI, 70 eV) *m/z* 274 (M<sup>+</sup>, 100), 289 (62), 246 (45), 226 (27), 151 (13), 247 (8); HRMS (ESI) calcd for C<sub>16</sub>H<sub>11</sub>F<sub>3</sub>NO<sup>+</sup> ([M + H]<sup>+</sup>) 290.0787, found 290.0793.

**6, 9-Bis(trifluoromethyl)phenanthridine (14):** pale yellow solid (54.8 mg, 87% yield); mp 87.2–89.1 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.96 (s, 1H), 8.64–8.62 (m, 1H), 8.51 (d, *J* = 9.0 Hz, 1H), 8.34–8.32 (m, 1H), 7.98–7.96 (m, 1H), 7.90–7.85 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.8 (q, *J*<sub>C-F</sub> = 27.3 Hz), 142.1, 133.8, 132.9 (q, *J*<sub>C-F</sub> = 32.8 Hz), 131.5, 130.3, 130.0, 127.1 (q, *J*<sub>C-F</sub> = 3.4 Hz), 124.6, 124.1 (q, *J*<sub>C-F</sub> = 2.9 Hz), 123.6 (q, *J*<sub>C-F</sub> = 271.3 Hz), 123.2, 122.1, 121.6 (q, *J*<sub>C-F</sub> = 275.4 Hz), 120.1 (q, *J*<sub>C-F</sub> = 4.4 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.5 (s, 3F), -62.9 (s, 3F); IR (neat, cm<sup>-1</sup>) 1576, 1321, 1077, 974, 829, 740, 684; LRMS (EI, 70 eV) *m/z* 315 (M<sup>+</sup>, 100), 296 (9), 246 (58), 226 (29), 177 (15); HRMS (ESI) calcd for C<sub>15</sub>H<sub>8</sub>F<sub>6</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 316.0556, found 316.0561.

**5-(Trifluoromethyl)benzo[*i*]phenanthridine (15):** pale yellow solid (30.3 mg, 51% yield); mp 138.7–140.5 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.74 (d, *J* = 8.5 Hz, 1H), 8.53–8.47 (m, 2H), 8.25–8.23 (m, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.91–7.89 (m, 1H), 7.77–7.69 (m, 2H), 7.66–7.59 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 144.4 (q, *J*<sub>C-F</sub> = 33.4 Hz), 142.4, 135.1, 133.1, 132.9, 130.4, 129.6, 129.0, 128.4, 128.3, 127.7 (q, *J*<sub>C-F</sub> = 7.9 Hz), 127.4, 127.2, 124.8, 122.6 (q, *J*<sub>C-F</sub> = 274.6 Hz), 122.6, 119.9, 119.6; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -60.1 (s, 3F); IR (neat, cm<sup>-1</sup>) 1322, 1125, 945, 736, 594, 535; LRMS (EI, 70 eV) *m/z* 297 (M<sup>+</sup>, 100), 228 (78), 200 (22), 138 (14), 100 (30); HRMS (ESI) calcd for C<sub>18</sub>H<sub>11</sub>F<sub>3</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 298.0838, found 298.0842.

**2-Methyl-6-(trifluoromethyl)phenanthridine (16):** pale yellow solid (48.5 mg, 93% yield); mp 100.7–102.5 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.66 (d, *J* = 8.5 Hz, 1H), 8.36–8.34 (m, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.90–7.87 (m, 1H), 7.75–7.72 (m, 1H), 7.63–7.61 (m, 1H), 2.65 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.5 (q, *J*<sub>C-F</sub> = 32.6 Hz), 140.1, 139.5, 133.6, 131.1 (2C), 130.8, 127.9, 125.8 (q, *J*<sub>C-F</sub> = 3.3 Hz), 125.0, 122.5, 122.0 (q, *J*<sub>C-F</sub> = 275.3 Hz), 121.8, 121.6, 22.1; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.3 (s, 3F); IR (neat, cm<sup>-1</sup>) 1613, 1257, 1109, 971, 825, 768; LRMS (EI, 70 eV) *m/z* 261 (M<sup>+</sup>, 100), 241 (35), 190 (18), 165 (16), 121 (7), 82 (7); HRMS (ESI) calcd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 262.0838, found 262.0842.

**2,9-Dimethyl-6-(trifluoromethyl)phenanthridine (17):** pale yellow solid (49.5 mg, 90% yield); mp 99.3–101.2 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.40 (s, 1H), 8.32 (s, 1H), 8.23–8.21 (m, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.60–7.58 (m, 1H), 7.54–7.52 (m, 1H), 2.64 (s, 3H), 2.63 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.4 (q, *J*<sub>C-F</sub> = 32.6 Hz), 141.7, 140.2, 139.2, 133.8, 130.9, 130.7, 129.6, 125.6 (q, *J*<sub>C-F</sub> = 3.3 Hz), 124.8, 122.1 (q, *J*<sub>C-F</sub> = 275.4 Hz), 122.0, 121.6, 119.9, 22.3, 22.1; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.4 (s, 3F); IR (neat, cm<sup>-1</sup>)

1621, 1256, 1105, 812, 710, 535; LRMS (EI, 70 eV) *m/z* 275 (M<sup>+</sup>, 100), 255 (35), 240 (12), 206 (14), 190 (17), 102 (9); HRMS (ESI) calcd for C<sub>16</sub>H<sub>13</sub>F<sub>3</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 276.0995, found 276.0997.

**9-Chloro-2-methyl-6-(trifluoromethyl)phenanthridine (18):** pale yellow solid (50.2 mg, 85% yield); mp 96.5–98.1 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.56 (s, 1H), 8.26–8.24 (m, 1H), 8.22 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.67–7.62 (m, 2H), 2.64 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.1 (q, *J*<sub>C-F</sub> = 33.0 Hz), 140.4, 139.9, 137.8, 134.9, 131.8, 130.9, 128.5, 127.4 (q, *J*<sub>C-F</sub> = 3.3 Hz), 123.8, 122.2, 121.8 (q, *J*<sub>C-F</sub> = 275.1 Hz), 121.6, 120.0, 22.1; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.4 (s, 3F); IR (neat, cm<sup>-1</sup>) 1607, 1383, 1114, 971, 814, 708; LRMS (EI, 70 eV) *m/z* 295 (M<sup>+</sup>, 100, <sup>35</sup>Cl), 297 (34, <sup>37</sup>Cl), 275 (42), 190 (40), 163 (20), 82 (20); HRMS (ESI) calcd for C<sub>15</sub>H<sub>10</sub>F<sub>3</sub>NCl<sup>+</sup> ([M + H]<sup>+</sup>) 296.0449, found 296.0455.

**2-Chloro-6-(trifluoromethyl)phenanthridine (19):** pale yellow solid (49.5 mg, 88% yield); mp 101.3–103.1 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.53 (d, *J* = 8.5 Hz, 1H), 8.47 (s, 1H), 8.3 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.91–7.88 (m, 1H), 7.79–7.76 (m, 1H), 7.72–7.70 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 146.7 (q, *J*<sub>C-F</sub> = 33.1 Hz), 140.1, 135.4, 132.8, 132.5, 131.6, 129.9, 128.7, 126.1, 126.0 (q, *J*<sub>C-F</sub> = 3.3 Hz), 122.5, 121.9, 121.8 (q, *J*<sub>C-F</sub> = 275.5 Hz), 121.7; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.5 (s, 3F); IR (neat, cm<sup>-1</sup>) 1601, 1387, 1178, 973, 829, 767, 681; LRMS (EI, 70 eV) *m/z* 281 (M<sup>+</sup>, 100, <sup>35</sup>Cl), 283 (33, <sup>37</sup>Cl), 212 (41), 177 (73), 150 (14), 123 (7); HRMS (ESI) calcd for C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>NCl<sup>+</sup> ([M + H]<sup>+</sup>) 282.0292, found 282.0299.

**2-Chloro-6-(trifluoromethyl)phenanthridine-9-carbonitrile (20):** pale yellow solid (44.1 mg, 72% yield); mp 177.5–179.4 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.96 (s, 1H), 8.56 (s, 1H), 8.51–8.49 (m, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.02–8.00 (m, 1H), 7.88–7.85 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 146.1 (q, *J*<sub>C-F</sub> = 33.9 Hz), 140.6, 136.9, 132.9, 132.8, 131.4, 130.1, 127.8, 127.3 (q, *J*<sub>C-F</sub> = 3.4 Hz), 124.8, 123.3, 121.8, 121.4 (q, *J*<sub>C-F</sub> = 275.6 Hz), 117.6, 115.4; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.5 (s, 3F); IR (neat, cm<sup>-1</sup>) 1507, 1254, 1133, 975, 826, 743, 680; LRMS (EI, 70 eV) *m/z* 306 (M<sup>+</sup>, 100, <sup>35</sup>Cl), 308 (34, <sup>37</sup>Cl), 237 (36), 202 (52), 175 (15), 153 (6); HRMS (ESI) calcd for C<sub>13</sub>H<sub>7</sub>F<sub>3</sub>N<sub>2</sub>Cl<sup>+</sup> ([M + H]<sup>+</sup>) 307.0245, found 307.0247.

**2-Fluoro-6-(trifluoromethyl)phenanthridine (21):** pale yellow solid (49.3 mg, 93% yield); mp 104.3–106.2 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.51 (d, *J* = 8.5 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.27–8.24 (m, 1H), 8.15–8.13 (m, 1H), 7.92–7.89 (m, 1H), 7.80–7.77 (m, 1H), 7.54–7.50 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 162.6 (d, *J*<sub>C-F</sub> = 249.1 Hz), 145.8 (q, *J*<sub>C-F</sub> = 32.9 Hz), 138.5, 133.5 (d, *J*<sub>C-F</sub> = 9.5 Hz), 133.3, 131.4, 128.7, 126.7, 126.0, 122.7, 121.9 (q, *J*<sub>C-F</sub> = 275.3 Hz), 121.8, 118.4 (d, *J*<sub>C-F</sub> = 24.4 Hz), 107.1 (d, *J*<sub>C-F</sub> = 23.5 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.5 (s, 3F), -108.8 (s, 1F); IR (neat, cm<sup>-1</sup>) 1619, 1453, 1128, 971, 863, 767, 557; LRMS (EI, 70 eV) *m/z* 265 (M<sup>+</sup>, 100), 215 (5), 196 (71), 169 (21), 132 (7); HRMS (ESI) calcd for C<sub>14</sub>H<sub>8</sub>F<sub>4</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 266.0588, found 266.0582.

**3, 6-Bis(trifluoromethyl)phenanthridine (22):** pale yellow solid (51.7 mg, 82% yield), mp 104.7–106.5 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.68–8.65 (m, 2H), 8.56 (s, 1H), 8.40 (d, *J* = 8.5 Hz, 1H), 7.99–7.94 (m, 2H), 7.86–7.83 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 148.0 (q, *J*<sub>C-F</sub> = 33.1 Hz), 141.0, 133.2, 132.0, 131.2 (q, *J*<sub>C-F</sub> = 33.0 Hz), 129.3, 128.6 (q, *J*<sub>C-F</sub> = 4.1 Hz), 127.3, 126.2 (q, *J*<sub>C-F</sub> = 3.3 Hz), 125.0 (q, *J*<sub>C-F</sub> = 3.4 Hz), 123.7 (q, *J*<sub>C-F</sub> = 270.9 Hz), 123.2, 122.9, 122.3, 121.6 (q, *J*<sub>C-F</sub> = 275.8 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.7 (s, 3F), -62.5 (s, 3F); IR (neat, cm<sup>-1</sup>) 1610, 1332, 1116, 971, 834, 775, 686; LRMS (EI, 70 eV) *m/z* 315 (M<sup>+</sup>, 100), 296 (10), 246 (66), 226 (38), 177 (22); HRMS (ESI) calcd for C<sub>15</sub>H<sub>8</sub>F<sub>6</sub>N<sup>+</sup> ([M + H]<sup>+</sup>) 316.0556, found 316.0559.

**3-Nitro-6-(trifluoromethyl)phenanthridine (23):** pale yellow solid (24.5 mg, 42% yield); mp 168.7–170.2 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.15 (s, 1H), 8.77–8.74 (m, 2H), 8.58–8.56 (m, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.08–8.05 (m, 1H), 7.95–7.92 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.0 (q, *J*<sub>C-F</sub> = 33.5 Hz), 147.8, 141.2, 132.9, 132.4, 130.1, 129.5, 126.8, 126.4 (q, *J*<sub>C-F</sub> = 3.4 Hz), 123.7, 123.4, 122.8, 122.7, 121.4 (q, *J*<sub>C-F</sub> = 275.9 Hz); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -63.8 (s, 3F); IR (neat, cm<sup>-1</sup>) 1610, 1539, 1345, 1121, 974, 734; LRMS (EI, 70 eV) *m/z* 292 (M<sup>+</sup>, 100), 262 (73), 234 (44), 226

(54), 177 (20), 149 (12); HRMS (ESI) calcd for  $C_{14}H_8F_3N_2O_2^+$  ( $[M + H]^+$ ) 293.0533, found 293.0536.

**2-Bromo-N-(2,2,2-trifluoro-1-phenylethylidene)aniline (24):** pale yellow liquid (58.9 mg, 90% yield);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.53–7.51 (m, 1H), 7.37–7.32 (m, 1H), 7.31–7.25 (m, 4H), 7.08–7.05 (m, 1H), 6.91–6.88 (m, 1H), 6.50–6.48 (m, 1H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  158.6 (q,  $J_{C-F} = 34.0$  Hz), 146.5, 133.7 (q,  $J_{C-F} = 19.4$  Hz), 132.8, 130.7, 128.5, 128.1, 127.8, 126.1, 119.9, 119.6 (q,  $J_{C-F} = 277.8$  Hz), 114.3;  $^{19}F$  NMR (470 MHz,  $CDCl_3$ )  $\delta$  –69.8 (s, 3F); IR (neat,  $cm^{-1}$ ) 1673, 1466, 1231, 1134, 970, 760, 697; LRMS (EI, 70 eV)  $m/z$  258 (100), 260 (91), 327 ( $M^{+}$ , 32,  $^{79}Br$ ), 329 (32,  $^{81}Br$ ), 76 (24), 155 (20); HRMS (ESI) calcd for  $C_{14}H_{10}BrF_3N^+$  ( $[M + H]^+$ ) 327.9949, found 327.9943.

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1H$  and  $^{13}C$  NMR spectra of compounds 3–24. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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