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An efficient synthesis of 2-trifluoromethyl quinolines via gold-catalyzed cyclization of trifluoromethylated propargylamines

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ABSTRACT

A highly efficient cyclization reaction of trifluoromethylated propargylamines leading to 2-trifluoromethyl-4-aryl quinolines was developed by using gold(I) as a catalyst under extremely mild conditions.

1. Introduction

Quinolines are important chemicals that exhibit a wide range of biological activities. The quinolines are found as key structural elements in various natural products, especially in alkaloids, and used for the construction of many synthetic compounds with diverse pharmacological properties [1–3]. In particular, fluorine-containing quinolines are of significant interest because fluorine atoms enhance biological and therapeutic activities of organic compounds, and they provide a further avenue for structural elaboration [4–12]. Examples include antimalarial agents [13], PDE4 inhibitors [14,15], antituberculosis agents [16,17], DPP-IV inhibitors [18], and leishmanicidal agents [19]. As a consequence, much attention has been paid to the synthesis of fluorinated quinoline derivatives. The traditional methods for the introduction of a CF_3 group into aromatic systems have been fluorination of a suitable functional group (e.g., halogen exchange of $-CCl_3$, $-CBr_3$ [20] and fluorination of $-CO_2H$ [21]) or by Ullmann-type reaction of perfluoroalkyl iodides and aryl halides using copper powder [22]. Recently, transition-metal-catalyzed heteroannulation reactions have been developed with remarkable improvements in terms of efficiency and wide scope of application. Uneyama developed an efficient Rh(I)-catalyzed 2-trifluoromethylated quinolines formation by tandem coupling-cyclization reaction of trifluoroacetimidoyl chlorides with alkynes [23]. Wu and co-workers reported that coupling-cyclization *N*-aryl-fluorinated imidoyl iodides with terminal alkynes proceeded successfully to give 2-trifluoromethylated quinolines in the presence of copper(I) iodide catalyst [24]. Nevertheless, it is still of interest to develop efficient methods for the synthesis of trifluoromethylated functionalized quinoline derivatives.

The previous investigations have shown that Au(III) salts and Au(I) complex display considerable catalytic activity under moderate conditions [25–38]. The activation of alkynes or allenes with carbophilic, Lewis-acidic gold salts is the most widespread application of homogeneous gold catalysis, and it is also utilized for the construction of carbocyclic or heterocyclic compounds [39–49]. Recently, the design of gold-catalyzed hydroarylation of alkynes has attracted attention because of the application to efficient construction of molecular structures [50–52]. As a continuation of our interest in the design and discovery of new reactions for the synthesis of heterocycles [53–55], we envisioned that trifluoromethyl propargylamines **1** might cyclize via hydroarylation of alkynes to afford 2-trifluoromethyl quinolines (Scheme 1). In this paper, we wish to describe our results on the synthesis of 2- trifluoromethyl quinolines starting from propargyl amines **1** catalyzed by gold(I) under mild conditions.

2. Results and discussion

Our initial investigation focused on the reaction of 1-trifluoromethyl-substituted propargylamine **1a** as an example for the optimization of the reaction conditions. We found that treatment **1a** with $AuCl_3$ (5 mol%) in 1,2-dichloroethane at 80 °C

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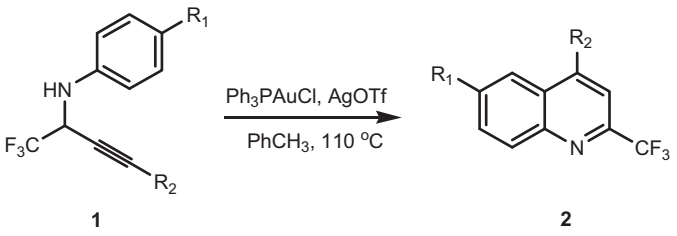
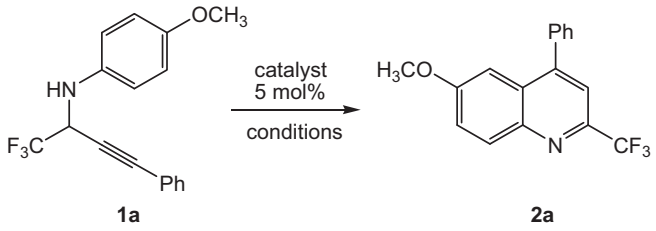


Scheme 1. Gold(I)-catalyzed cyclization of propargyl amines.

afforded the desired product **2a** in 55% yield after 24 h (Table 1, entry 1). With this encouraging result, we first examined the influence of the gold source on the reaction. AuCl and $Ph_3PAuOTf$ worked well to give **2a** in 63% and 77% yield, respectively (Table 1, entries 2–3). Reaction with $Ph_3PAuOTf$ as catalyst gave better results. Significantly, we found that using toluene as the solvent at higher reaction temperature could shorten the reaction time and the yield showed moderate improvement (Table 1, entry 5). Subsequently, other catalysts were further scanned. It was found that $Cu(OTf)_2$ and $InCl_3$ were active, but low yields were obtained after long reaction times (Table 1, entries 6–7). In contrast, employment of CuI as the catalyst, product **2a** was formed in trace amount. It was worthwhile to note that protonic acids were turned out to be totally disfavored (Table 1, entries 9–10). Finally, the annulation was failed when heating propargylamine **1a** in toluene at 80 °C for 24 h in the absence of any catalysts (Table 1, entry 11).

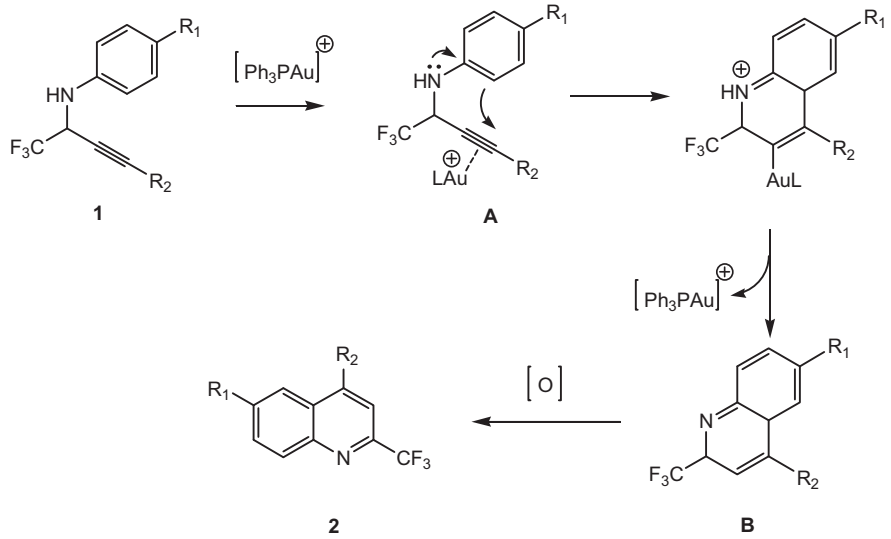
After having established the optimized conditions for the present reaction, various trifluoromethylpropargylamine derivatives **1a–m** were subjected to the above conditions, and the results are summarized in Table 2. As indicated, the cyclization reaction of 1-trifluoromethylpropargylamine derivatives **1a–m** proceeded smoothly to provide the corresponding products **2a–m** in moderate to good yields. The reaction could tolerate various

Table 1
Optimization of the reaction conditions [a]



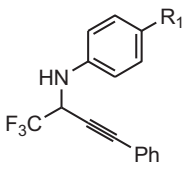
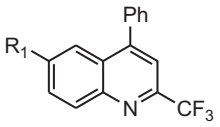
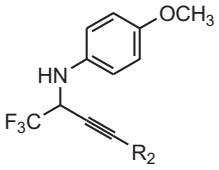
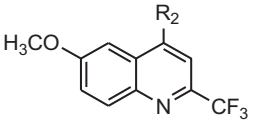
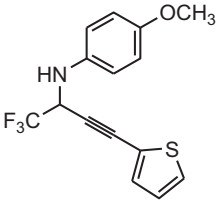
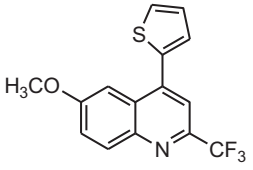
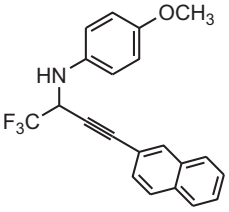
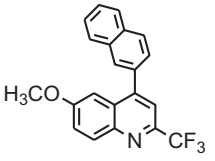
Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	$AuCl_3$	DCE	80	24	55
2	AuCl	DCE	80	24	63
3	$Ph_3PAuOTf$	DCE	80	24	77
4	$Ph_3PAuOTf$	Toluene	80	24	76
5	$Ph_3PAuOTf$	Toluene	110	18	90
6	$Cu(OTf)_2$	Toluene	110	36	65
7	$InCl_3$	Toluene	110	36	70
8	CuI	Toluene	110	36	Trace
9[c]	TfOH	Toluene	110	10	NR
10	TsOH	Toluene	110	24	NR
11	No catalyst	Toluene	110	24	NR

[a] Reaction conditions: **1a** (0.5 mmol), catalyst (5 mol%), solvent (5.0 mL) and the reactions were carried out at various temperatures.
[b] Isolated yield.
[c] A complex mixture was obtained.



Scheme 2. Possible mechanisms of the Au-catalyzed transformation.

Table 2
Synthesis of 2-trifluoromethyl quinolines.[a]

Entry	Propargyl amines	Product	Yield (%)[b]
			
1	$R_1 = OCH_3$	$R_1 = OCH_3$	**2a,** 90
2	$R_1 = CH_3$	$R_1 = CH_3$	**2b,** 91
3	$R_1 = H$	$R_1 = H$	**2c,** 88
4	$R_1 = Cl$	$R_1 = Cl$	**2d,** 82
5	$R_1 = F$	$R_1 = F$	**2e,** 74
6	$R_1 = CF_3$	$R_1 = CF_3$	**2f,** 69
			
7	$R_2 = 4\text{-}CH_3OC_6H_4$	$R_2 = 4\text{-}CH_3OC_6H_4$	**2g,** 88
8	$R_2 = 4\text{-}CH_3C_6H_4$	$R_2 = 4\text{-}CH_3C_6H_4$	**2h,** 92
9	$R_2 = 4\text{-}ClC_6H_4$	$R_2 = 4\text{-}ClC_6H_4$	**2i,** 81
10	$R_2 = 4\text{-}FC_6H_4$	$R_2 = 4\text{-}FC_6H_4$	**2j,** 75
11	$R_2 = 3\text{-}CH_3OC_6H_4$	$R_2 = 3\text{-}CH_3OC_6H_4$	**2k,** 90
12			**2l,** 89
			
13			**2m**, 83
			

[a] Reaction conditions: **1** (0.5 mmol), $Ph_3PAuCl/AgOTf$ (5 mol%), toluene (5.0 mL), at 110 °C.
[b] Isolated yield.

substituents on the aromatic groups. Generally, electron-donating substituent on the benzene ring such as methoxy (Table 2, entry 1) and methyl (Table 2, entry 2) proceeded well. On the other hand, electron-withdrawing aryl groups including chloro, fluoro and trifluoromethyl (Table 2, entries 4–6) would reduce the yield. Subsequently, the scope of alkynes in this reaction was further investigated, and it was found that substituted phenylacetylenes with electron-donating or electron-withdrawing groups were perfectly suitable substrates for this transformation, and the expected products were obtained in moderate to excellent yields (Table 2, entries 7–11). Interestingly, substrates like **1l–m** with heteroaromatic alkyne or bulky naphthylacetylene also gave the corresponding cyclization compounds **2l–m** in good yields.

Based on the experimental results above and together with our previous work [54], a mechanism for the formation of the quinoline derivatives is proposed in Scheme 2. Initially, a cationic Au(I) species first coordinates to the triple bond to generate an intermediate **A**, which then undergoes an intramolecular nucleophilic attack by the *N*-substituted aromatic ring to give dihydroquinoline intermediate **B** and regenerates the Au(I) catalyst. Subsequent oxidation of the dihydroquinoline intermediate **B** by air O_2 produces the corresponding quinoline.

3. Conclusion

In conclusion, we have developed a gold-catalyzed cyclization reaction of trifluoromethylated propargylamines that provides an efficient route to 2-trifluoromethyl-4-aryl quinolines under mild conditions. The substrates can be readily prepared from the corresponding imidoyl iodide and alkynes [56]. Further studies, including the reaction mechanism and synthetic application of this methodology, are in progress.

4. Experimental

4.1. General

Chemicals used were obtained from commercial suppliers and used without further purifications. Trifluoromethylated propargylamines **1a–n** were prepared as described previously [57]. ^{1}H NMR spectra and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) with TMS as an internal standard. EIMS were determined with a HP5989B mass spectrometer. Elemental analyses were performed on an EA-1110 instrument. Melting points were measured on a Melt-Temp apparatus and uncorrected.

4.2. Typical procedure for synthesis of 2-trifluoromethyl-4-aryl quinolines

A solution of trifluoromethylated propargylamine **1** (0.5 mmol) in dry toluene was added to a solution of Ph_3AuOTf (generated by mixing equal equivalents of Ph_3PAuCl and AgOTf, 5 mol% in toluene). The mixture was then stirred at 110 °C until the substrate had been consumed completely, cooled to room temperature and filtered through a short silica gel column using CH_2Cl_2 as eluent. After evaporation of the solvent, the residue was purified by SiO_2 gel column chromatography to give the corresponding product **2**.

4.2.1. 2-(trifluoromethyl)-6-methoxy-4-phenylquinoline (2a)

White solid, mp 68–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 9.2 Hz, 1H), 7.61 (s, 1H), 7.50–7.56 (m, 5H), 7.45 (dd, J = 9.2, 2.8 Hz, 1H), 7.21 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 148.8, 145.0 (q, J = 35.7 Hz), 143.6, 137.5, 131.9, 129.3, 128.9, 128.8, 128.6, 123.4, 121.7 (q, J = 276 Hz), 117.4, 103.4, 55.4; MS (EI) m/z 303 (M^+); Anal. Calcd for $C_{17}H_{12}F_3NO$: (%) C, 67.32; H,3.99; N, 4.62. Found: C, 67.48; H, 3.82; N, 4.68.

4.2.2. 2-(trifluoromethyl)-6-methyl-4-phenylquinoline (2b)

White solid, mp 37–39 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.8 Hz, 1H), 7.69 (s, 1H), 7.75–7.62 (m, 2H), 7.58–7.51 (m, 5H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 146.5 (q, J = 35.1 Hz), 146.3, 139.1, 137.0, 132.8, 130.1, 129.4, 128.9, 128.8, 127.6, 124.1, 121.8 (q, J = 275.4 Hz), 117.2, 21.9; MS (EI) m/z 287 (M^+); Anal. Calcd. For $C_{17}H_{12}F_3N$: (%) C, 71.07; H, 4.21; N, 4.88. Found: C, 71.20; H, 4.50; N, 4.81.

4.2.3. 2-(trifluoromethyl)-4-phenylquinoline (2c)

White solid, mp 60–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.71 (s, 1H), 7.69–7.60 (m, 1H), 7.58–7.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 148.1, 147.5 (q, J = 34.8 Hz), 137.7, 131.2, 130.8, 129.9, 129.5, 129.2, 129.1, 127.8, 126.4, 122.0 (q, J = 275.5 Hz), 117.3; MS (EI) m/z 273 (M^+); Anal. Calcd for $C_{16}H_{10}F_3N$: (%) C, 70.33; H, 3.69; N, 5.13. Found: C, 70.21; H, 3.87; N, 4.93.

4.2.4. 6-chloro-2-(trifluoromethyl)-4-phenylquinoline (2d)

White solid, mp 85–87 °C; ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 9.2 Hz, 1H), 7.90 (d, J = 2.1 Hz, 1H), 7.77–7.71 (m, 2H), 7.59–7.54 (m, 3H), 7.52–7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 147.5 (q, J = 34.7 Hz), 146.0, 136.4, 135.1, 132.3, 131.5, 129.4, 129.3, 128.9, 128.1, 124.7, 121.5 (q, J = 275.5 Hz), 117.5; MS (EI) m/z 307 (M^+); Anal. Calcd. For $C_{16}H_9ClF_3N$: (%) C, 62.45; H, 2.95; N, 4.55. Found: C, 62.27; H, 3.16; N, 4.59.

4.2.5. 6-fluoro-2-(trifluoromethyl)-4-phenylquinoline (2e)

White solid, mp 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27–8.23 (m, 1H), 7.71 (s, 1H), 7.59–7.45 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, J = 250.9 Hz), 150.4 (d, J = 6.0 Hz), 147.6 (qd, J = 35.2 Hz, J = 3.0 Hz), 144.6, 135.9, 133.0 (d, J = 9.8 Hz), 129.5, 129.3, 128.5 (d, J = 10.1 Hz), 121.6 (q, J = 275.8 Hz), 120.0 (d, J = 25.7 Hz), 117.3, 109.5 (d, J = 23.5 Hz); MS (EI) m/z 291 (M^+); Anal. Calcd. For $C_{16}H_9F_4N$: (%) C, 65.98; H, 3.11; N, 4.81. Found: C, 65.18; H, 3.26; N, 4.81.

4.2.6. 2,6-bis(trifluoromethyl)-4-phenylquinoline (2f)

White solid, mp 94–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.8 Hz, 1H), 8.32 (s, 1H), 8.05 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H), 7.78 (s, 1H), 7.60–7.51 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 149.7 (q, J = 35.5 Hz), 148.6, 136.0, 131.9, 130.2 (q, J = 33.2 Hz), 129.5, 129.4, 129.2, 126.5, 126.2 (d, J = 3.0 Hz), 123.8 (q, J = 4.7 Hz), 123.5 (d, J = 274.5 Hz), 121.5 (q, J = 276.0 Hz), 117.9; MS (EI) m/z 341 (M^+); Anal. Calcd. For $C_{17}H_9F_6N$: (%) C, 59.83; H, 2.66; N, 4.10. Found: C, 59.80; H, 2.41; N, 4.25.

4.2.7. 2-(trifluoromethyl)-6-methoxy-4-(4-methoxyphenyl)quinoline(2g)

White solid, mp 60–62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 9.2 Hz, 1H), 7.60 (s, 1H), 7.46–7.42 (m, 2H), 7.41 (dd, J = 9.2, J = 2.8 Hz, 1H), 7.24 (d, J = 2.8 Hz, 1H), 7.06–7.00 (m, 2H), 3.86 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 159.3, 148.7, 144.8 (q, J = 35.2 Hz), 143.7, 131.8, 130.3, 129.4, 128.8, 123.2, 121.8 (q, J = 275.0 Hz), 117.1, 114.3, 103.3, 55.4, 55.3; MS (EI) m/z 333 (M^+); Anal. Calcd. For $C_{18}H_{14}F_3NO_2$: (%) C, 64.86; H, 4.23; N, 4.20. Found: C, 64.95; H, 4.48; N, 4.06.

4.2.8. 2-(trifluoromethyl)-6-methoxy-4-p-tolylquinoline (2h)

White solid, mp 138–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 9.2 Hz, 1H), 7.61 (s, 1H), 7.45–7.32 (m, 5H), 7.25 (d, J = 2.8 Hz, 1H), 3.82 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 149.1, 145.0 (q, J = 35.0 Hz), 138.8, 134.5, 131.8, 129.6, 129.1, 128.8, 125.9, 123.3, 121.8 (q, J = 275.2 Hz), 117.2, 103.3, 55.3, 21.5; MS (EI) m/z: 317 (M^+); Anal. Calcd. For $C_{18}H_{14}F_3NO$: (%) C, 68.13; H, 4.45; N, 4.41. Found: C, 68.25; H, 4.28; N, 4.53.

4.2.9. 4-(4-chlorophenyl)-2-(trifluoromethyl)-6-methoxyquinoline (2i)

White solid, mp 100–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 9.2 Hz, 1H), 7.59 (s, 1H), 7.57–7.47 (m, 5H), 7.16 (d, J = 2.8 Hz, 1H), 3.83(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 147.7, 145.1 (q, J = 34.2 Hz), 143.8, 135.7, 135.1, 131.8, 130.2, 129.0, 128.4, 123.5, 121.7 (q, J = 275.5 Hz), 117.2, 103.0, 55.5; MS (EI) m/z 337 (M^+); Anal. Calcd. For $C_{17}H_{11}ClF_3NO$: (%) C, 60.46; H, 3.28; N, 4.15. Found: C, 60.58; H, 3.12; N, 4.07.

4.2.10. 2-(trifluoromethyl)-4-(4-fluorophenyl)-6-methoxyquinoline (2j)

White solid, mp 100–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 9.2 Hz, 1H), 7.59 (s, 1H), 7.55–7.48 (m, 2H), 7.42 (dd, J = 9.2, 2.8 Hz, 1H), 7.15 (d, J = 2.8 Hz, 1H), 7.28–7.21 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (d, J = 250.1 Hz), 159.3, 147.8, 144.9 (q, J = 35.0 Hz), 144.0, 133.2 (d, J = 3.2 Hz), 132.1, 130.9 (d, J = 8.6 Hz), 128.8, 123.3, 121.7 (q, J = 274.9 Hz), 117.3, 115.9 (d, J = 21.9 Hz), 103.3, 55.5; MS (EI) m/z 321 (M^+); Anal. Calcd. For $C_{17}H_{11}F_4NO$: (%) C, 63.55; H, 3.45; N, 4.36. Found: C, 63.32; H, 3.57; N, 4.28.

4.2.11. 2-(trifluoromethyl)-6-methoxy-4-(3-methoxyphenyl)quinoline (2k)

White solid, mp 58–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 9.2 Hz, 1H), 7.62 (s, 1H), 7.51–7.44 (m, 2H), 7.27–7.25 (m, 1H), 7.10–7.00 (m, 3H), 3.88 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (d, J = 249.8 Hz), 159.8, 159.8, 148.5, 145.0 (q, J = 35.0 Hz), 138.8, 131.6, 129.5, 128.6, 123.4, 121.7 (q, J = 275.0 Hz), 121.4, 117.3, 114.8, 114.4, 103.2, 55.5, 55.3; MS

(EI) *m/z* 333 (M^+); Anal. Calcd. For $C_{18}H_{14}F_3NO_2$: (%) C, 64.86; H, 4.23; N, 4.20. Found: C, 64.57; H, 4.39; N, 4.28.

4.2.12. 2-(trifluoromethyl)-6-methoxy-4-(thiophen-2-yl)quinoline (2l)

White solid, mp 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 9.2 Hz, 1H), 7.71 (s, 1H), 7.57 (d, J = 2.8 Hz, 1H), 7.54 (d, J = 5.2 Hz, 1H), 7.42–7.35 (m, 2H), 7.25–7.20 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 145.0 (q, J = 34.7 Hz), 144.0, 141.1, 138.3, 131.7, 128.7, 128.4, 128.2, 127.9, 123.4, 121.8 (q, J = 275.5 Hz), 117.6, 103.2, 55.4; MS (EI) *m/z* 309 (M^+); Anal. Calcd. For $C_{15}H_{10}F_3NOS$: (%) C, 58.25; H, 3.26; N, 4.53. Found: C, 58.47; H, 3.58; N, 4.42.

4.2.13. 2-(trifluoromethyl)-6-methoxy-4-(naphthalen-6-yl)quinoline (2m)

White solid, mp 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 9.2 Hz, 1H), 8.03–7.89 (m, 4H),7.69 (s, 1H), 7.65–7.55 (m, 3H), 7.47 (dd, J = 9.2 Hz, 2.8 Hz, 1H), 7.25 (d, J = 2.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 149.0, 145.3 (q, J = 34.2 Hz), 143.8, 135.1, 133.3, 133.2, 131.9, 128.7, 128.5, 128.4, 128.1, 127.8, 126.9, 126.7, 126.6, 123.4, 121.7 (q, J = 274.8 Hz), 117.5, 103.3, 55.5; MS (EI) *m/z* 309 (M^+); Anal. Calcd. For $C_{21}H_{14}F_3NO$: (%) C, 71.38; H, 3.99; N, 3.96. Found: C, 71.20; H, 4.18; N, 3.85.

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