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A dual removable activating group enabled the Povarov reaction of *N*-arylalanine esters: synthesis of quinoline-4-carboxylate esters†

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A dual removable activating group enabled Povarov reaction of *N*-arylalanine esters was reported. *N*-Arylalanine ester was utilized as the sole carbon source to generate *N*-arylimine and its tautomer, enamine, *in situ* by aerobic oxidation of sp^3 C–H bonds, and then the consecutive reaction delivered the desired quinoline-4-carboxylate esters in high yields.

Introduction

The [4 + 2] cycloaddition of a diene and alkene to form a six-membered ring, named the Diels–Alder reaction, is one of the most widely used powerful tools to construct polycarbocycles and polyheterocycles.[1–3] It is well-known that the reaction between inactivated dienes and dienophiles does not proceed readily due to the high activation energy and low reaction rate. Consequently, activating groups on dienes and dienophiles are essential to achieve efficient transformations, and generally two kinds of Diels–Alder cycloadditions attracted extensive investigations, which are *normal* and *inverse electron demand Diels–Alder reactions* (Fig. 1, eqn (1)). To reinforce the interaction between the HOMO and LUMO of a diene and dienophile, if the diene component is electron rich, the dienophile is usually electron poor, or *vice versa*. However, it is still a big challenge for synthetic chemists to realize the [4 + 2] cycloaddition between a diene and a dienophile with the same type substituents (EWG for example) (Fig. 1, eqn (2)) To steer away these big barriers, we hypothesized that when the electron-poor diene and dienophile were used, we could install a removable EDG (REDG) on the dienophile and a removable EWG (REWG) on the diene to enhance the interaction between the HOMO of the dienophile and the LUMO of the diene (Fig. 1, eqn (2)). If this hypothesis is feasible, we could realize the electronic property-forbidden [4 + 2] cycloaddition by a roundabout way.

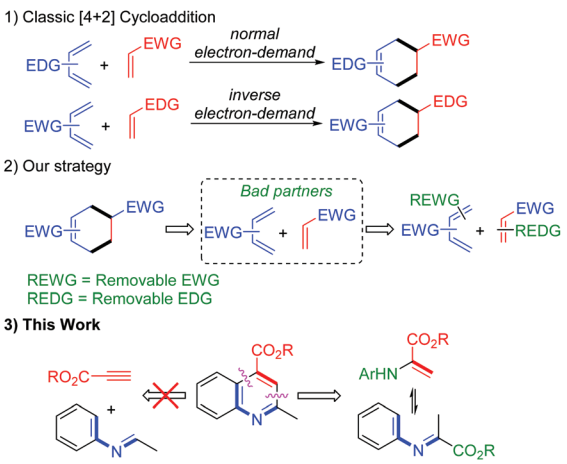

Fig. 1 [4 + 2] cycloaddition and our design.

Quinoline derivatives are widespread in natural products and drugs, and have been widely recognized as important structural motifs of synthetic drug candidates due to their significant pharmacological properties, such as antimalarial,[4] anti-inflammatory,[5] antibacterial[6] and others.[7] Among the various quinoline derivatives, quinoline carboxylate esters are of great interest as pharmaceutical and synthetic molecules, because the carboxyl groups play a crucial role in endowing the quinoline pharmacophore with unique bioactivities,[8] and such functional groups also provide an important possibility for further structural modifications.

Generally, a variety of methods have been developed for the synthesis of a quinoline skeleton, such as Conrad–Limpach–Knorr synthesis,[9] Skraup–Doebner–Von Miller synthesis,[10] Friedländer synthesis,[11] and other methods,[12] in which the Povarov reaction of *N*-arylaldimines with dienophiles might be

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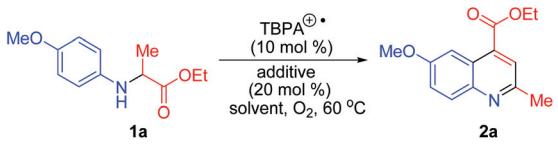
one of the most accessible approaches to construct the quinoline skeleton due to its high efficiency and the ready availability of starting materials.[13] However, construction of quinoline-4-carboxylate esters is still a great problem, and only limited examples have been reported.[14] It is well-known that *N*-arylaldimines can act as a kind of good 2-azadiene, participating in the Povarov reaction. Due to their electron-deficient nature, only electron-rich dienophiles can react with them (*inverse electron demand Diels–Alder reaction*). Nevertheless, the synthesis of quinoline-4-carboxylates using the Povarov reaction means that an electron-deficient azadiene should react with a dienophile with the same electronic properties (ester group substituted). It is electronic property-forbidden (Fig. 1, eqn (3)).

As part of our ongoing research program on the construction of heterocycles, the synthesis of quinolines using a radical cation salt as an inductor is focused for years.[15] Among these reactions, arylimines or their equivalents were employed as the 2-azadienes to react with electron-rich alkenes, providing 1,2,3,4-tetrahydroquinolines and quinolines in high yields. Recently, an efficient construction of 1,2-dihydroquinolines was achieved by the sp^3 C–H oxidation of *N*-arylalanine esters,[15e] in which the aniline group in the α-anilinoacrylic ester intermediate (Fig. 1, eqn (3)) as a REDG was eventually eliminated to form the C=C double bond. It was also found that aromatization is a powerful driving force to achieve an efficient transformation. So we questioned whether the ester group in the imine intermediate could also be removed to accomplish the electronic property-forbidden Povarov reaction, facilitated by the terminal aromatization (Fig. 1, eqn (3)). Herein, we report this dual removable activating group enabled Povarov reaction, providing a series of quinoline-4-carboxylate derivatives in high yields.

Results and discussion

Since the construction of the corresponding 1,2-dihydroquinolines has been established,[15e] we focused on the removal of the ester group to realize the synthesis of quinoline-4-carboxylate esters. The reaction of **1a** was chosen as a model reaction to screen the best reaction conditions (Table 1). In the presence of 10 mol% $TBPA^{+\bullet}$ (tris(4-bromophenyl)aminium hexachloroantimonate), only a trace amount of the desired ethyl quinoline-4-carboxylate was detected, and the corresponding 1,2-dihydroquinoline was isolated in 72% yield (not shown in the table). When the reaction time was prolonged to 48 hours, the desired decarboxylation product was detected in 36% yield (Table 1, entry 1). This promising result encouraged us to further optimize the reaction conditions, and then different additives were tested (entries 2–6). Addition of Brønsted and Lewis acids was tried to increase the yield, and $BF_3{\cdot}Et_2O$ gave the best result, providing the desired product in 90% yield (entry 6). Further screening of the solvents did not give positive effects on the reaction (entries 7–10), and DCE was still the best solvent. At lower temperatures, the yields were decreased

Table 1 Optimization of the reaction conditions[a]



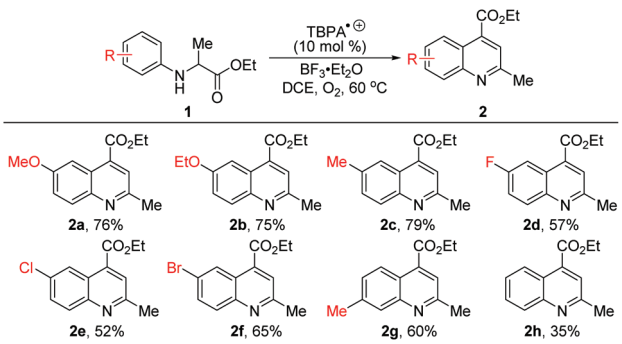
1a 2a

Entry	Additive	Solvent	Time (h)	Yield[b] (%)
1	No	DCE	48	36
2	TsOH	DCE	46	41
3	$InCl_3$	DCE	46	71
4	CuCl	DCE	46	28
5	$AlCl_3$	DCE	46	57
6	$BF_3{\cdot}Et_2O$	DCE	43	90 (76)[c]
7	$BF_3{\cdot}Et_2O$	DCM	43	Trace
8	$BF_3{\cdot}Et_2O$	THF	43	Trace
9	$BF_3{\cdot}Et_2O$	$CHCl_3$	43	47
10	$BF_3{\cdot}Et_2O$	MeCN	43	80
11[d]	$BF_3{\cdot}Et_2O$	DCE	50	Trace
12[e]	$BF_3{\cdot}Et_2O$	DCE	46	52
13[f]	$BF_3{\cdot}Et_2O$	DCE	43	89
14[g]	$BF_3{\cdot}Et_2O$	DCE	46	58
15[h]	$BF_3{\cdot}Et_2O$	DCE	46	88

[a] Unless otherwise specified, the reaction was carried out with **1a** (0.1 mmol) in the presence of $TBPA^{+\bullet}$ and anhydrous solvent (1.0 mL) at 60 °C. [b] Yield of crude product ^1H NMR using 1,3,5-trimethoxylbenzene as the internal standard, and the yields were calculated based on 0.05 mmol of **1a**. [c] Yield in the parenthesis is the isolated yield. [d] The reaction was performed at room temperature. [e] The reaction was performed at 40 °C. [f] The reaction was performed at 80 °C. [g] The catalyst loading is 5 mol%. [h] The catalyst loading is 15 mol%.

(entries 11 and 12), while a comparable yield was obtained at an elevated temperature (entry 13). Screening of the catalyst loading revealed that the highest yield was obtained in the presence of 10 mol% DCE (entries 6, 14 and 15).

With the best conditions in hand, the scope and limitations of this synthesis of quinoline-4-carboxylate esters were then investigated. Firstly, the substituents on anilines were varied to evaluate their effects on the reaction efficiency, and the results are compiled in Scheme 1. Electron-donating groups, such as methoxyl (**2a**), ethoxyl (**2b**) and methyl (**2c**) groups, gave higher yields of the desired product, while the substrates with elec-



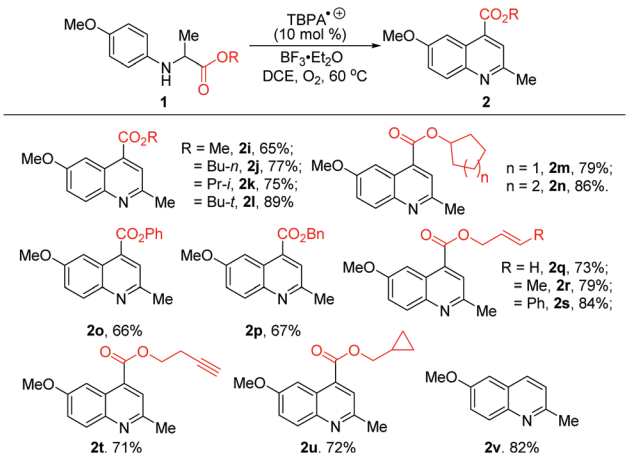
Scheme 1 Scope of aniline derivatives. Reaction conditions: **1** (1 mmol), $TBPA^{+\bullet}$ (10 mol%), $BF_3{\cdot}(OEt)_2$ (20 mol%), DCE (5 mL), 60 °C under O_2, isolated yield.

tron-withdrawing groups decreased the yields, and the quinoline-4-carboxylate esters were isolated in moderate yields (**2d** to **2f**). However, when NO_2 was introduced, the reaction was thoroughly blocked, and the corresponding starting material remained unchanged and was recovered in 94% yield (not shown in Scheme 1). The reason was attributed to the poor conjugation between the lone pair electrons of nitrogen and the generated radical, which made the adjacent sp^3 C–H bonds too inert to be oxidized. When *m*-methylaniline was used, the cyclization occurred regioselectively on the *para*-position of the methyl group, affording the expected quinoline in 60% yield (**2g**). The substrates bearing *ortho*-substituents (2-Me, 2-F) were also employed (not shown in Scheme 1), however, the decarboxylation process was inhibited and only the corresponding dihydroquinolines were isolated, which was probably due to the higher steric hindrance blocking the coordination of BF_3 (see the mechanism for details). In the absence of a substituent, the reaction efficiency was reduced, and the desired product was obtained in 35% yield.[15,16]

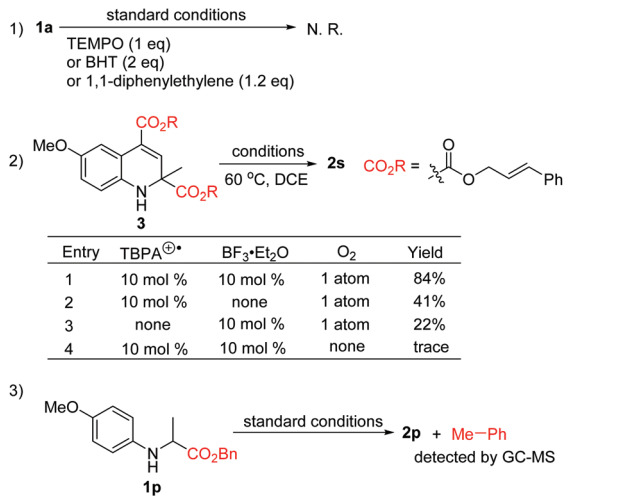
Next, different functionalized esters were varied to evaluate the tolerance of functional groups (Scheme 2). Various alkyl groups including bulk ones, such as i-propyl and *t*-butyl groups, could also be tolerated, providing the quinoline derivatives in good yields (**2i** to **2l**). Cyclopentyl and cyclohexyl esters did not exert negative effects on the Povarov reaction, giving **2m** and **2n** in 79% and 86% isolated yields, respectively. When phenyl ester was employed, this dual removable activating group enabled reaction occurred smoothly, and the desired product **2o** was isolated in 66% yield. The benzyl group with another active sp^3 C–H bond did not disturb the reaction process obviously, generating the expected **2p** in 67% yield. The existence of double and triple bonds, even a fragile cyclopropyl ring could also be well tolerated under these mild oxidative conditions, which enables further functionalization in the synthesis of complicated compounds (**2q** to **2u**). Interestingly, when furfuryl ester was used, a 4-unsubstituted quinoline **2v** was isolated in 82% yield, which resulted from a double decarboxylation process.[17]

To elucidate the reaction mechanism, several control experiments were conducted (Scheme 3). In the presence of a radical scavenger, TEMPO (1 eq.), BHT (2 eq.) or 1,1-diphenylethylene (1.2 eq.), the reaction was totally inhibited, and the starting material was recovered in 96% yield, which implies that a radical intermediate was involved in this transformation. When the reaction of the corresponding 1,2-dihydroquinoline **3** was tried under the standard conditions, the desired product **2s** was obtained in 84% yield (eqn (2), entry 1). This result suggested that the 1,2-dihydroquinoline might be a key intermediate, which underwent a decarboxylation to afford the quinoline product. Then, the mechanism of decarboxylation was investigated. A moderate yield of the desired product was obtained in the absence of $BF_3{\cdot}OEt_2$, suggesting that the decarboxylation/aromatization process is accelerated by $BF_3{\cdot}OEt_2$, albeit the exact reason remains unknown (entry 2). In the absence of $TBPA^{+\bullet}$ and dioxygen, the decarboxylation product was isolated in only 22% yield (entry 3) and a trace amount (entry 4), respectively, which means that the oxidant is crucial to the terminal decarboxylation and aromatization. To reveal the fate of the ester group in the decarboxylation process, the reaction of **1p** was performed under the standard reaction conditions (eqn (3)). Besides the generation of **2p**, the released toluene was detected by GC-MS. These results implied that after decarboxylation, a benzyl radical was generated and further abstracted a hydrogen from the solvent or substrate **1p**. This radical mediated mechanism was also supported by the easy formation of **2o** (Scheme 2).

Based on the above results and our previous research,[15e] a radical mediated reaction process is proposed to rationalize the formation of products (Scheme 4). Under the aerobic atmosphere, an *N*-arylalaninate was oxidized, yielding a radical intermediate **A** (for the mechanistic details of interactions

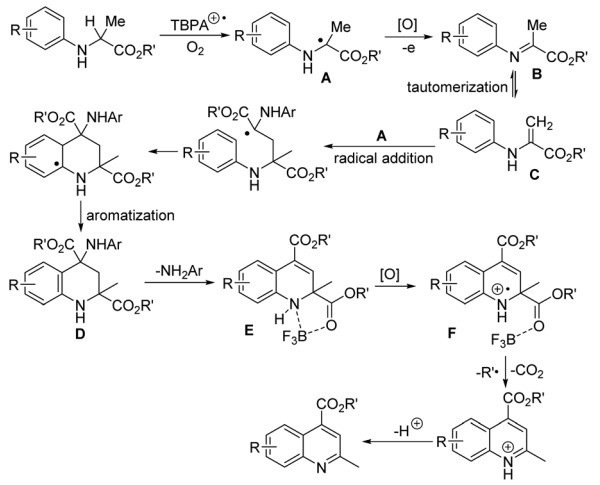


Scheme 2 Scope of esters. Reaction conditions: **1** (1 mmol), $TBPA^{+\bullet}$ (10 mol%), $BF_3{\cdot}(OEt)_2$ (20 mol%), DCE (5 mL), 60 °C under O_2, isolated yield.



Entry	$TBPA^{+\bullet}$	$BF_3{\cdot}Et_2O$	O_2	Yield
1	10 mol %	10 mol %	1 atom	84%
2	10 mol %	none	1 atom	41%
3	none	10 mol %	1 atom	22%
4	10 mol %	10 mol %	none	trace

Scheme 3 Control experiments.



Scheme 4 Proposed mechanism.

between $TBPA^{+\bullet}$ and dioxygen, see ref. 15*a*). After intermolecular radical addition between intermediates **A** and **C**, and further aromatization, a 1,2,3,4-tetrahydroquinoline **D** is afforded. The following elimination of aniline gave a 1,2-dihyroquinoline intermediate **E**, which coordinates to BF_3. Then, the 1,2-dihydroquinoline continues to be oxidized to its radical cation, which undergoes further decarboxylation, yielding a quinolinium salt.[18,19] We think that the coordination of BF_3 enhances the electron-deficient nature of intermediate **F** (Scheme 4) and accelerate the decarboxylation process, although the exact role of $BF_3{\cdot}OEt_2$ remains unknown. Due to the fact that the phenyl cation is unstable, and it is hard to generate, the good result obtained in the case of phenyl ester (**2o**) highly supported that the decarboxylation proceeded in a radical mediated process, which also ruled out the participation of a cationic intermediate in the decarboxylation process.[20] Finally, the terminal deprotonation leads to a quinolin-4-carboxylate derivative. In this reaction, the removable aniline group, which increases the reactivity of the enamine tautomer **C** as an EDG, and the electron-withdrawing ester group, which reinforces the electron-deficient nature of intermediate **B**, were also removed by the oxidative decarboxylation/aromatization.

Conclusions

In summary, induced by an aerobic oxidation of *N*-arylalaninate, an efficient synthesis of quinolin-4-carboxylate derivatives was achieved, in which the reaction between the mismatching 2-azadiene and dienophile was enabled by the dual removable activating groups (REWG and REDG). The scope examination shows extensive substrate generality and good functional group tolerance. This reaction provides a conceptually new way to overcome the electronic property limitations in the Povarov reaction, and will be beneficial to new reaction design. Further applications of this reaction and the strategy of the removable activating group are still under investigation in our laboratory.

Experimental

General information

All solvents are anhydrous. $TBPA^{+\bullet}$ was purchased from a commercial source and used without further purification. Flash chromatography was carried out with silica gel (200–300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^1H NMR and ^{13}C NMR (400 MHz, 600 MHz and 100 MHz, 150 MHz respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as an internal standard and spin–spin coupling constants (J) are given in Hz. EI-MS spectra were measured by direct inlet at 70 eV. The high resolution mass spectra (HRMS) were measured on electrospray ionization (ESI) apparatus using time of flight (TOF) mass spectrometry.

General experimental procedure

A solution of **1** (1 mmol) and $BF_3{\cdot}(OEt)_2$ (20 mol%) in DCE (5 ml) was mixed fully and flushed with O_2, then $TBPA^{+\bullet}$ (10 mol%) was added dropwise under an oxygen atmosphere. The reaction solution was stirred at 60 °C. After completion monitored by TLC (by UV visualization), the reaction was quenched by the addition of saturated Na_2CO_3 in MeOH (10 mL) solution. The mixture was poured into a separator funnel with the addition of excess DCM (10 mL), and then the crude organic solution was extracted three times with water to remove inorganic salts. The organic phase was then dried over anhydrous magnesium sulfate, filtered, and the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/acetone (v/v 25 : 1) to afford the products.

Ethyl 6-methoxy-2-methylquinoline-4-carboxylate (2a). ^1H NMR (600 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.91 (d, J = 9.1 Hz, 1H), 7.76 (s, 1H), 7.33 (d, J = 9.1 Hz, 1H), 4.45 (m, 2H), 3.90 (s, 3H), 2.70 (s, 3H), 1.43 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 158.3, 155.3, 145.1, 133.1, 130.51, 124.6, 123.4, 122.2, 103.2, 61.5, 55.4, 24.8, 14.2; EI-MS m/z (relative intensity, %): 245 (100%), 146 (11.6%), 217 (38.8%), 200, (16.6%), 173 (53.6%); HRMS (ESI): Calc'd for $C_{14}H_{15}NO_3 + H^+$, 246.1130; found, 246.1138.

Ethyl 6-ethoxy-2-methylquinoline-4-carboxylate (2b). ^1H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.91 (d, J = 9.1 Hz, 1H), 7.75 (s, 1H), 7.33 (d, J = 7.7 Hz, 1H), 4.44 (q, J = 7.0 Hz, 2H), 4.14 (q, J = 7.7 Hz, 2H), 2.70 (s, 3H), 1.44 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 157.7, 155.3, 145.1, 133.2, 130.5, 124.7, 123.4, 122.6, 104.0, 63.7, 61.5, 24.8, 14.6, 14.3; EI-MS m/z (relative intensity, %): 259 (100%), 231 (55.2%), 203 (53.4%), 186 (27.8%), 159 (69.7%), 103 (7.9%); HRMS (ESI): Calc'd for $C_{15}H_{17}NO_3 + H^+$, 260.1287; found, 260.1296.

Ethyl 2,6-dimethylquinoline-4-carboxylate (2c). ^1H NMR (600 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.71 (s, 1H), 7.52 (d, J = 8.4 Hz, 1H), 4.47 (q, J = 6.4 Hz, 2H), 2.74 (s, 3H), 2.52 (s, 3H), 1.44 (t, J = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 157.3, 147.4, 137.1, 134.6, 131.8, 128.8, 124.2, 123.3, 122.9, 61.6, 25.1, 21.9, 14.3; EI-MS m/z (relative intensity,

%): 229 (100%), 201 (27.2%), 184 (32.3%), 156 (59.1%), 115 (12.8%); HRMS (ESI): Calc'd for $C_{14}H_{15}NO_2 + H^+$, 230.1181; found, 230.1189.

Ethyl 6-fluoro-2-methylquinoline-4-carboxylate (2d). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (dd, J = 10.8, 2.7 Hz, 1H), 8.04 (dd, J = 9.1, 5.6 Hz, 1H), 7.84 (s, 1H), 7.50–7.43 (m, 1H), 4.48 (q, J = 7.1 Hz, 2H), 2.76 (s, 3H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 161.8, 160.1, 157.7 (d, J_{CF} = 2.8 Hz), 146.1, 134.4 (d, J_{CF} = 5.7 Hz) 131.5 (d, J_{CF} = 9.3 Hz), 124.02, 119.8 (d, J_{CF} = 25.9 Hz), 109.4 (d, J_{CF} = 24.9 Hz), 61.85, 25.02, 14.23; EI-MS m/z (relative intensity, %): 233 (100%), 205 (47.6%), 188 (54.3%), 160 (73.3%), 134 (16.1%), 99 (17.2%); HRMS (ESI): Calc'd for $C_{13}H_{12}FNO_2 + H^+$, 234.0930; found, 234.0940.

Ethyl 6-chloro-2-methylquinoline-4-carboxylate (2e). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.95 (s, 1H), 7.79 (s, 1H), 7.62 (s, 1H), 4.47 (q, J = 7.1 Hz, 2H), 2.75 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 158.7, 147.2, 134.1, 133.19, 130.6, 130.5, 124.5, 123.9, 123.96, 61.9, 25.1, 14.2; EI-MS m/z (relative intensity, %): 251 (30.9%), 249 (100%), 223 (13.9%), 221 (40.1%), 206 (15.2%), 204 (47.8%), 176 (54.3%), 141 (18.6%), 99 (21.1%); HRMS (ESI): Calc'd for $C_{13}H_{12}ClNO_2 + H^+$, 250.0635; found, 250.0642.

Ethyl 6-bromo-2-methylquinoline-4-carboxylate (2f). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (d, J = 2.1 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.76 (dd, J = 8.9, 2.1 Hz, 1H), 4.48 (q, J = 7.1 Hz, 3H), 2.75 (s, 3H), 1.46 (t, J = 7.2 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 158.9, 147.4, 134.1, 133.1, 130.8, 127.8, 124.4, 124.0, 121.5, 62.0, 25.2, 14.3; EI-MS m/z (relative intensity, %): 295 (98.1%), 293 (100%), 267 (32.3%), 265 (33.2%), 250 (32.8%), 248 (35.0%), 222 (40.2%), 220 (42.2%), 170 (30.5%), 141 (30.4%); HRMS (ESI): Calc'd for $C_{13}H_{12}BrNO_3 + H^+$, 294.0130; found, 294.0141.

Ethyl 2,7-dimethylquinoline-4-carboxylate (2g). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, J = 8.7 Hz, 1H), 7.82 (s, 1H), 7.68 (s, 1H), 7.37 (d, J = 8.7 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 2.73 (s, 3H), 2.51 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 158.3, 149.1, 139.9, 135.1, 129.3, 128.2, 125.0, 122.2, 121.3, 61.6, 25.2, 21.6, 14.2; EI-MS m/z (relative intensity, %): 229 (100%), 201 (37.2%), 184 (42.7%), 156 (60.0%), 115 (15.5%); HRMS (ESI): Calc'd for $C_{14}H_{15}NO_2 + H^+$, 230.1181; found, 230.1184.

Ethyl 2-methylquinoline-4-carboxylate (2h). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.77(s, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.7 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 2.78 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 158.4, 148.8, 135.4, 129.6, 129.2, 127.1, 125.4, 123.3, 123.0, 61.7, 25.24, 14.3; EI-MS m/z (relative intensity, %): 215 (100%), 187 (42.3%), 170 (51.3%), 142 (72.3%), 115 (18.9%), 75 (14.1%); HRMS (ESI): Calc'd for $C_{13}H_{13}NO_2 + H^+$, 216.1025; found, 216.1029.

Methyl 6-methoxy-2-methylquinoline-4-carboxylate (2i). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.92 (d, J = 9.1 Hz, 1H), 7.76 (s, 1H), 7.34 (d, J = 9.1 Hz, 1H), 3.98 (s, 3H), 3.91 (s, 3H), 2.70 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.80, 158.42, 155.37, 145.14, 132.71, 130.47, 124.67, 123.59, 122.35, 103.24, 55.44, 52.42, 24.76; EI-MS m/z (relative intensity, %): 231 (100%), 216 (10.0%), 200 (20.6%), 172 (31.0%), 130 (16.8%); HRMS (ESI): Calc'd for $C_{13}H_{13}NO_3 + H^+$, 232.0974; found, 232.0985.

Butyl 6-methoxy-2-methylquinoline-4-carboxylate (2j). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.77 (s, 1H), 7.35 (d, J = 8.6 Hz, 1H), 4.41 (t, J = 5.7 Hz, 2H), 3.92 (s, 3H), 2.73 (s, 3H), 1.85–1.75 (m, 2H), 1.51 (m, 2H), 0.99 (t, J = 5.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 158.4, 155.4, 145.2, 133.3, 130.5, 124.7, 123.5, 122.4, 103.3, 65.4, 55.4, 30.7, 24.8, 19.3, 13.7; EI-MS m/z (relative intensity, %): 273 (85.0%), 217 (100%), 173 (29.5%), 150 (21.0%); HRMS (ESI): Calc'd for $C_{16}H_{19}NO_3 + H^+$, 274.1443; found, 274.1446.

Isopropyl 6-methoxy-2-methylquinoline-4-carboxylate (2k). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.75 (s, 1H), 7.34 (d, J = 9.1 Hz, 1H), 5.39–5.27 (m, 1H), 3.91 (s, 3H), 2.72 (s, 3H), 1.43 (d, J = 6.0, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 158.3, 155.4, 145.2, 133.8, 130.5, 124.6, 123.4, 122.3, 103.3, 69.2, 55.4, 24.8, 21.9; EI-MS m/z (relative intensity, %): 259 (63.7%), 217 (100%), 202 (17.3%), 174 (25.1%), 146 (11.0%); HRMS (ESI): Calc'd for $C_{15}H_{17}NO_3 + H^+$, 260.1287; found, 260.1294.

***tert*-Butyl 6-methoxy-2-methylquinoline-4-carboxylate (2l).** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.92 (d, J = 9.2 Hz, 1H), 7.69 (s, 1H), 7.33 (dd, J = 9.0, 1.6 Hz, 1H), 3.91 (s, 3H), 2.71 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 158.1, 155.4, 145.2, 135.1, 130.5, 124.6, 123.3, 122.1, 103.4, 82.5, 55.4, 28.2, 24.8; EI-MS m/z (relative intensity, %): 273 (22.2%), 217 (100%), 202 (12.5%), 174 (17.1%), 146 (6.7%); HRMS (ESI): Calc'd for $C_{16}H_{19}NO_3 + H^+$, 274.1443; found, 274.1450.

Cyclopentyl 6-methoxy-2-methylquinoline-4-carboxylate (2m). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.72 (s, 1H), 7.33 (d, J = 9.1 Hz, 1H), 5.50 (m, 1H), 3.91 (s, 3H), 2.71 (s, 3H), 2.07–1.96 (m, 2H), 1.96–1.86 (m, 2H), 1.82 (td, J = 3.7 Hz, 2H), 1.68 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 158.3, 155.4, 145.2, 133.7, 130.5, 124.6, 123.4, 122.3, 103.2, 78.6, 55.4, 32.8, 24.9, 23.8; EI-MS m/z (relative intensity, %): 285 (45.0%), 217 (100%), 200 (17.3%), 172 (17.0%); HRMS (ESI): Calc'd for $C_{17}H_{19}NO_3 + H^+$, 286.1443; found, 286.1451.

Cyclohexyl 6-methoxy-2-methylquinoline-4-carboxylate (2n). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.92 (d, J = 9.1 Hz, 1H), 7.75 (s, 1H), 7.33 (d, J = 9.0 Hz, 1H), 5.11 (m, 1H), 3.90 (s, 3H), 2.72 (s, 3H), 2.02 (m, 2H), 1.81 (m, 2H), 1.66–1.56 (m, 3H), 1.50–1.40 (m, 2H), 1.32 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 158.3, 155.4, 145.2, 133.9, 130.5, 124.6, 123.4, 122.3, 103.3, 74.1, 55.4, 31.7, 25.3, 24.8, 23.8; EI-MS m/z (relative intensity, %): 299 (42.9%), 217 (100%), 202 (10.7%), 174 (15%), 146 (6.1%); HRMS (ESI): Calc'd for $C_{18}H_{21}NO_3 + H^+$, 300.1600; found, 300.1604.

Phenyl 6-methoxy-2-methylquinoline-4-carboxylate (2o). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (d, J = 2.5 Hz, 1H), 8.08 (s, 1H), 7.99 (d, J = 9.2 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.40 (dd, J = 9.2, 2.4 Hz, 1H), 7.35–7.30 (m, 1H), 7.28 (dd, J = 8.4, 7.9 Hz, 2H), 3.91 (s, 3H), 2.80 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9,

158.8, 155.5, 150.6, 145.4, 131.6, 130.7, 129.7, 126.3, 125.0, 124.2, 122.7, 121.7, 103.1, 55.5, 24.9; EI-MS *m*/*z* (relative intensity, %): 293 (23.4%), 217 (34.6%), 200 (100%), 172 (70.8%), 150 (19.4%); HRMS (ESI): Calc'd for $C_{18}H_{13}NO_2 + H^+$, 294.1130; found, 294.1142.

Benzyl 6-methoxy-2-methylquinoline-4-carboxylate (2p). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.93 (d, J = 9.2 Hz, 1H), 7.80 (s, 1H), 7.49 (d, J = 6.9 Hz, 2H), 7.44–7.38 (m, 2H), 7.38–7.29 (m, 2H), 5.44 (s, 2H), 3.81 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.29, 158.41, 155.41, 145.22, 135.44, 132.88, 130.57, 128.74, 128.58, 128.54, 124.64, 123.67, 122.45, 103.21, 67.34, 55.35, 24.82; EI-MS *m*/*z* (relative intensity, %): 307 (83.8%), 173 (100%), 91 (90.8%), 65 (8.9%); HRMS (ESI): Calc'd for $C_{17}H_{19}NO_3 + H^+$, 308.1287; found, 308.1280.

Allyl 6-methoxy-2-methylquinoline-4-carboxylate (2q). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.92 (d, J = 9.2 Hz, 1H), 7.79 (s, 1H), 7.34 (d, J = 9.2 Hz, 1H), 6.11–6.04 (m, 1H), 5.45 (d, J = 17.1 Hz, 1H), 5.36–5.29 (m, 1H), 4.89 (m, 2H), 3.90 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 158.4, 155.4, 145.2, 132.8, 131.7, 130.6, 124.7, 123.6, 122.4, 119.1, 103.2, 66.1, 55.4, 24.8; EI-MS *m*/*z* (relative intensity, %): 257 (88.9%), 200 (16.6%), 173 (100%), 158 (20.6%), 116 (10.8%); HRMS (ESI): Calc'd for $C_{15}H_{15}NO_3 + H^+$, 258.1130; found, 258.1139.

But-2-en-1-yl 6-methoxy-2-methylquinoline-4-carboxylate (2r). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.92 (d, J = 9.1 Hz, 1H), 7.79 (s, 1H), 7.34 (d, J = 9.1 Hz, 1H), 5.93 (m, 1H), 5.79–5.70 (m, 1H), 4.82 (d, J = 5.9 Hz, 2H), 3.91 (s, 3H), 2.72 (s, 3H), 1.76 (d, J = 5.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 158.4, 155.4, 145.2, 133.1, 132.4, 130.5, 124.7, 124.6, 123.5, 122.4, 103.3, 66.2, 55.4, 24.8, 17.8; EI-MS *m*/*z* (relative intensity, %): 271 (73.4%), 217 (100%), 202 (17.3%), 173 (45.1%), 55 (15.8%); HRMS (ESI): Calc'd for $C_{16}H_{17}NO_3 + H^+$, 272.1287; found, 272.1292.

3-Phenylallyl 6-methoxy-2-methylquinoline-4-carboxylate (2s). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.96 (d, J = 9.2 Hz, 1H), 7.84 (s, 1H), 7.43 (s, 1H), 7.42 (s, 1H), 7.37 (d, J = 9.1 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.6 Hz, 1H), 6.79 (d, J = 15.9 Hz, 1H), 6.48–6.41 (m, 1H), 5.06 (d, J = 6.5 Hz, 2H), 3.90 (s, 3H), 2.74 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 158.5, 155.4, 145.2, 136.0, 135.3, 133.0, 130.5, 128.7, 128.3, 126.7, 124.7, 123.7, 122.5, 122.5, 103.3, 66.1, 55.5, 24.8; EI-MS *m*/*z* (relative intensity, %): 333 (42.4%), 200 (27.7%), 173 (56.6%), 117 (100%), 115 (38.0%), 91 (15.0%); HRMS (ESI): Calc'd for $C_{21}H_{19}NO_3 + H^+$, 334.1443; found, 334.1453.

But-3-yn-1-yl 6-methoxy-2-methylquinoline-4-carboxylate (2t). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.92 (d, J = 9.2 Hz, 1H), 7.79 (s, 1H), 7.33 (dd, J = 9.2, 2.8 Hz, 1H), 4.53–4.46 (m, 2H), 3.91 (s, 3H), 2.71 (m, 5H), 2.06 (t, J = 2.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 158.5, 155.4, 145.2, 132.6, 130.6, 124.6, 123.7, 122.4, 103.3, 79.8, 70.4, 63.1, 55.5, 24.8, 19.1; EI-MS *m*/*z* (relative intensity, %): 269 (100%), 217 (63.4%), 200 (28.3%), 172 (42.9), 150 (25.5%); HRMS (ESI): Calc'd for $C_{16}H_{15}NO_3 + H^+$, 270.1130; found, 270.1142.

Cyclopropylmethyl 6-methoxy-2-methylquinoline-4-carboxylate (2u). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.95 (d, J = 9.2 Hz, 1H), 7.83 (s, 1H), 7.37 (d, J = 9.2 Hz, 1H), 4.26 (d, J = 7.4 Hz, 2H), 3.94 (s, 3H), 2.75 (s, 3H), 1.40–1.27 (m, 1H), 0.68 (td, J = 6.0, 4.7 Hz, 2H), 0.47–0.39 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 158.3, 155.4, 145.2, 133.4, 130.5, 124.6, 123.6, 122.3, 103.3, 70.4, 55.4, 24.8, 9.8, 3.5; EI-MS *m*/*z* (relative intensity, %): 271 (72.4%), 217 (100%), 200 (41.4%), 172 (34.1%), 55 (18.5%); HRMS (ESI): Calc'd for $C_{18}H_{21}NO_3 + H^+$, 272.1287; found, 272.1294.

6-Methoxy-2-methylquinoline (2v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.33 (d, J = 9.1 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.04 (s, 1H), 3.91 (s, 3H), 2.70 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 156.3, 143.9, 135.0, 130.0, 127.28, 122.2, 121.8, 105.2, 55.5, 25.0; EI-MS *m*/*z* (relative intensity, %): 173 (100%), 158 (43.8), 130 (46.0%), 103 (12.4%); HRMS (ESI): Calc'd for $C_{11}H_{11}NO + H^+$, 174.0919; found, 174.0918.

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