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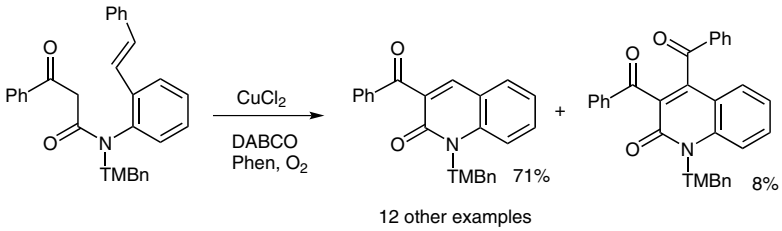
Copper-Catalyzed Aerobic Oxidative Carbocyclization Reactions of *N*-[(*E*)-Stilben-2-yl]amine Derivatives

Cheng-Yen Lu
Che-Ping Chuang*

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 70101, Taiwan
cpchuang@mail.ncku.edu.tw



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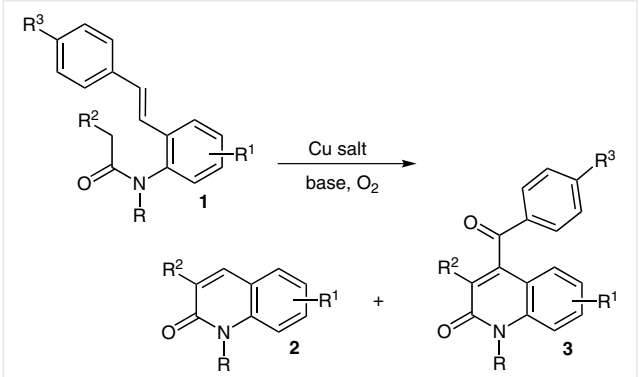
Abstract A synthetic method for highly functionalized 2-quinolinones and quinolines has been developed. The copper(II)-catalyzed aerobic oxidative carbocyclization reactions of α-substituted *N*-[(*E*)-stilben-2-yl]acetamides, via the intramolecular carbocupration onto the alkenyl moiety, produced 3-substituted 2-quinolinones. Several useful functional groups including benzoyl, acetyl, cyano, and ethoxycarbonyl groups are compatible with the reaction conditions. This strategy was further applied to *N*-[(*E*)-stilben-2-yl]enamines to prepare 2,3-disubstituted quinolines in good yields.

Key words copper salts, oxidative, cyclization, *N*-[(*E*)-stilben-2-yl]amines, quinolines

2-Quinolinones have long been targeted in synthetic investigations for their known biological activities and pharmacological properties, which include antiviral (HIV) activities,[1a–c] inotropic,[1d] $5HT_3$ receptor antagonists,[1e] farnesyl transferase inhibitors,[1f] and maxi-K channel opening agents.[1g] The development of new and efficient method for their synthesis represents a challenge in organic and medical chemistry. Besides classic base-catalyzed Friedländer reaction and acid-catalyzed Knorr reaction,[2] several alternative methods have been employed in the synthesis of 2-quinolinones including free radical cyclization of anilides,[3] cyclization of Baylis–Hillman adducts,[4] transition-metal-catalyzed cyclization of anilines,[5] and Pd-catalyzed amidation of 3-arylacrylamides.[6] Since the substituents on the 2-quinolinone rings have a great influence on the properties of these compounds, effective methods for the preparation of highly functionalized 2-quinolinones are highly desirable.

In the past decades, transition-metal-catalyzed functionalization of the C–H bond has emerged as an attractive strategy in organic synthesis.[7] The use of molecular oxygen as oxidant coupled with catalytic metal system provides an attractive greener approach owing to its economic, high abundance, and environmentally friendly features. The copper-catalyzed oxidative reactions through direct C–H functionalization have received considerable attention because of their efficiencies and low costs, and have become a powerful tool for the construction of synthetically useful heterocycles, such as pyrroles,[8] indoles,[9] oxazoles,[10] oxindoles,[11] pyrazoles,[12] and quinolines.[13]

Although a number of synthetic methods for 2-quinolinones are available, the search for mild and simple methods is continuously being pursued. As part of our studies on the development of new methods for the synthesis of heterocyclic compounds,[14–17] we now report an effective route for the synthesis of various functionalized 2-quinolinone derivatives via the carbocyclization of copper-enolate onto the alkenyl moiety in which the molecular oxygen was employed as the oxidant (Scheme 1).



Scheme 1

Our studies were initiated with the readily available 2-benzoyl-*N*-[(*E*)-stilben-2-yl]acetamide **1a** (R^1 = H, R^2 = COPh, R^3 = H, R = TMBn), which was prepared by the DCC-mediat-

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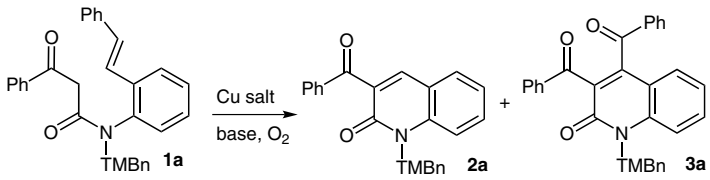
ed condensation reaction between 2-benzoylacetic acid and (*E*)-stilben-2-ylamine (see the Supporting Information). With this acetamide **1a** in hand, its reaction was examined under various conditions (Table 1). The reaction of **1a** with $CuCl_2$ (10 mol%), 1,10-phenanthroline (20 mol%), and DABCO (2 equiv) was carried out in DMF at 100 °C under an oxygen atmosphere until **1a** was completely consumed (7 h). To our surprise, the expected 4-benzoyl-substituted product **3a**, derived from the elimination[18] of [Cu(II)OH] from peroxy intermediate **7a** followed by oxidation (Scheme 1, path B), was obtained in only 8% yield and the unexpected fragmentation (path A) product **2a** was produced in 71% yield (Table 1, entry 1). Identical results were achieved at a loading of 20 mol% of $CuCl_2$ (entry 2). In the absence of 1,10-phenanthroline as a ligand, the reaction became sluggish and the yield of **2a** dropped (entry 3). Screening of various solvents, such as DMF, DMAc, and DMSO, showed that DMF and DMAc were suitable for this reaction (entries 1, 4, and 5). Experiments suggest that the choice of base also plays an important role in this reaction: Li_2CO_3 and NMP were found to be inferior to DABCO (entries 6 and 7). Other copper salts were also evaluated with the result that $CuCl_2$ and CuCl displayed a higher catalytic activity than other copper salts, such as CuBr, CuI, and $Cu(OAc)_2$ (entries 1 and 8–11).

To probe into the possible reaction mechanism, the reaction of **1a** was carried out under the optimized conditions in the presence of TEMPO (1 equiv), an effective radical scavenger, and products **2a** and **3a** were obtained in comparable yields (Table 1, entries 1 and 12). Thus, a radical intermediate might not be involved in the reaction. Based on this observation and the previous literature reports,[19–21] a plausible reaction mechanism for the formation of 2-quinolinones **2a** and **3a** is formulated (Scheme 2). The reaction of **1a** with copper(II) chloride under basic conditions leads to the formation of copper(II) enolate **4a**. Subsequently, copper-catalyzed 6-*exo*-trig cyclization of **4a** onto the alkenyl moiety gives copper(II) intermediate **5a**, which is then oxidized by oxygen to generate the copper peroxy intermediate **6a**. Finally, peroxy intermediate **7a**, formed by the isomerization of **6a**, undergoes either fragmentation[20c,21] to give 2-quinolinone **2a** and benzaldehyde[22a] (path A) or elimination[18] of [Cu(II)OH] followed by oxidation to produce 4-benzoyl-2-quinolinone **3a** (path B).

Under the optimal $CuCl_2$/DABCO/Phen conditions (Table 1, entry 1, Method A), the scope and limitations of this copper-catalyzed oxidative cyclization reactions were investigated (Table 2, entries 1–6). *N*-[(*E*)-Stilben-2-yl]acetamides **1a**–**e** underwent efficient intramolecular ring closure to provide the expected 2-quinolinones **2a**–**e** in moderate

Table 1 Optimization of Reaction Conditions with 2-Benzoyl-*N*-[(*E*)-stilben-2-yl]acetamide **1a**[a]



Entry	Cu salt	Base[b]	Solvent[c]	Time (h)	**2a**, Yield (%)[d]	**3a**, Yield (%)[d]
1	$CuCl_2$	DABCO/Phen	DMF	7	71	8
2[e]	$CuCl_2$	DABCO/Phen	DMF	7	72	7
3	$CuCl_2$	DABCO	DMF	12	58	7
4	$CuCl_2$	DABCO/Phen	DMAc	7	70	6
5	$CuCl_2$	DABCO/Phen	DMSO	9	11	7
6	$CuCl_2$	Li_2CO_3/Phen	DMF	12	58	6
7	$CuCl_2$	NMP/Phen	DMF	7	55	7
8	CuCl	DABCO/Phen	DMF	7	71	8
9	CuBr	DABCO/Phen	DMF	9	58	6
10	CuI	DABCO/Phen	DMF	12	43	5
11	$Cu(OAc)_2$	DABCO/Phen	DMF	12	43	5
12[f]	$CuCl_2$	DABCO/Phen	DMF	7	70	8

[a] TMBn: 2,4,6-trimethylbenzyl.
[b] DABCO: 1,4-diazobicyclo[2,2,2]octane; Phen: 1,10-phenanthroline; NMP: *N*-methylpiperidine.
[c] DMAc: *N*,*N*-dimethylacetamide.
[d] Yield of isolated product.
[e] With 20 mol% of $CuCl_2$.
[f] TEMPO (1 equiv) was added. TEMPO: 2,2,6,6-Tetramethyl-piperidinyloxy.

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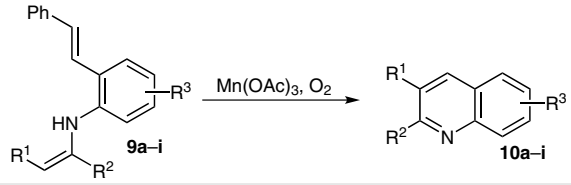
yields. A variety of electron-withdrawing or -donating groups (R^1) on the aniline moiety, including 4-chloro, 4-fluoro, 4-methyl, and 4,5-dimethyl, survived well in this transformation (entries 2–5). However, with **1f** (R^1 = 4,6-Me_2) bearing a methyl group at the 6-position of aniline fragment, it proceeded much slower (24 h) and a much poor result was obtained (entry 6). This is presumably due to the steric effect between 6-Me and *N*-TMBn groups. Indeed, by decreasing the size of R group, the reaction yield for **2g** (R = Bn) was improved to 57% and the reaction time was shortened to 15 hours (entry 7). Other acetamides **1h**–**m**, bearing different functional groups (R^2) such as acetyl, cyano, and ethoxycarbonyl groups at the α-position also worked well, and 3-substituted 2-quinolinones **2h**–**m** were obtained in reasonable yields (entries 8–13). 4-Benzoyl-2-quinolinones **3** were also obtained in 0–31% yields. The chemoselectivities for the formation of **2k**–**m** (R^2 = CN and CO_2Et) are much lower than that of **2a**–**j** (R^2 = COPh and COMe). It can be ascribed to the weaker acidity of H_A in **7k**–**m** and the rate of fragmentation (path A) was diminished. This copper(II) chloride-catalyzed oxidative carbocyclization of *N*-[(*E*)-stilben-2-yl]acetamides **1** provides an efficient and low cost method for the synthesis of 3-substituted 2-quinolinones **2**.

3-Enaminones are useful synthetic precursors and their utilization in organic synthesis is a subject of great current interest. The transition-metal-catalyzed annulations of 3-enaminones provided efficient methods for the synthesis of pyrroles,[8,23] indoles,[9,24] pyridine,[25] pyrazoles,[12] and quinolines.[13,26]

Quinolines also represent an important class of heterocycles and are known to possess a wide range of biological activities[27] and a large number of methods for the syntheses of functionalized quinolines have been developed.[28] Nevertheless, most of these methods suffer from harsh reaction conditions, low yields, and low stability of carbonyl reagents.

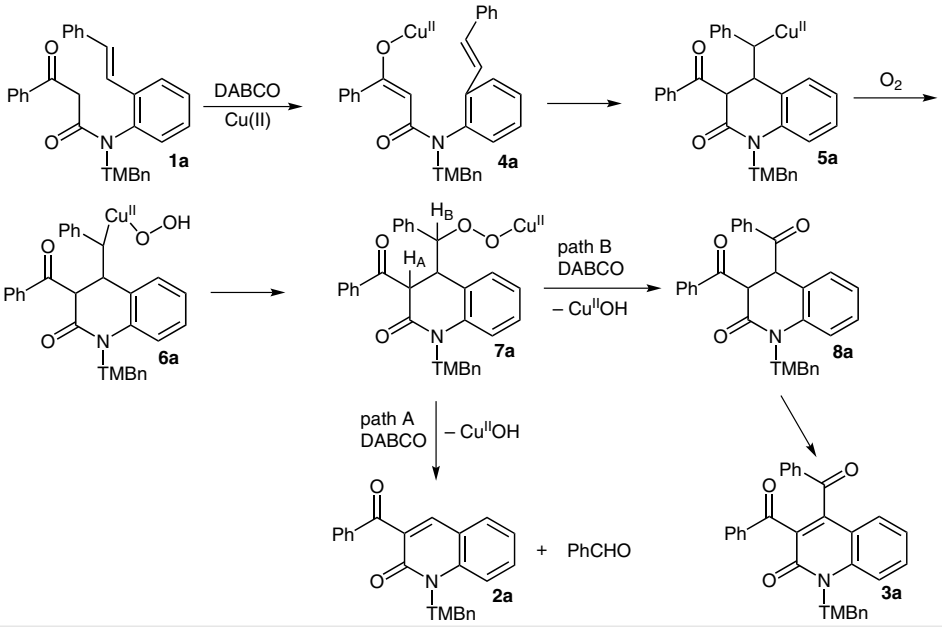
Recently, we reported that the manganese(III) acetate mediated oxidative free radical cyclizations of *N*-[(*E*)-stilben-2-yl]enamines **9a**–**i** (Scheme 3).[16c] This transformation provided a synthetically useful method for the synthesis of 2,3-disubstituted quinolines **10a**–**i**, however, a stoichiometric amount of manganese(III) acetate was required.



Scheme 3

In view of the good results shown above, we reasoned that it might be possible to produce these 2,3-disubstituted quinolines **10** by the copper(II)-catalyzed oxidative carbocyclization reactions of *N*-[(*E*)-stilben-2-yl]enamines **9** via a similar reaction route shown in Scheme 2.

N-[(*E*)-Stilben-2-yl]enaminone **9a** (R^1 = H, R^2 = Ph, R^3 = COPh), prepared readily by the condensation of dibenzoylmethane with (*E*)-stilben-2-ylamine (see the Support-



Scheme 2

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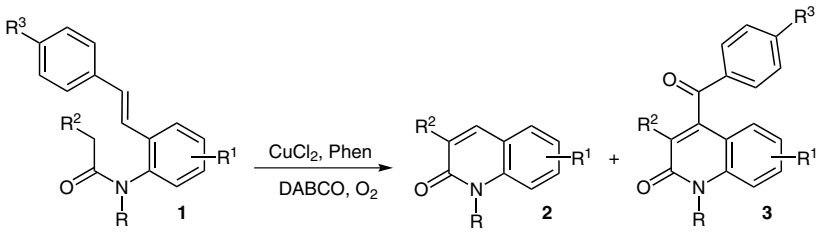
Table 2 Oxidative Carbocyclic Reactions of *N*-[(*E*)-Stilben-2-yl]acetamides **1**[a]



Entry	R^1	R^2	R^3	R	Time (h)	**2**, Yield (%)[b]	**3**, Yield (%)[b]
1	H	COPh	H	TMBn	7	**2a** (71)	**3a** (8)
2	6-Cl	COPh	H	TMBn	11	**2b** (73)	**3b** (6)
3	6-F	COPh	H	TMBn	9	**2c** (73)	**3c** (6)
4	6-Me	COPh	H	TMBn	11	**2d** (73)	**3d** (6)
5	6,7-Me_2	COPh	H	TMBn	9	**2e** (74)	**3e** (7)
6	6,8-Me_2	COPh	H	TMBn	24	**2f** (35)	**3f** (4)
7	6,8-Me_2	COPh	H	Bn	15	**2g** (57)	**3g** (7)
8	H	COMe	H	TMBn	2	**2h** (59)	**3h** (0)
9	6-Me	COMe	H	TMBn	2	**2i** (62)	**3i** (0)
10	6-Cl	COMe	H	TMBn	2	**2j** (65)	**3j** (0)
11[22b]	H	CN	4-MeO	TMBn	1	**2k** (62)	**3k** (30)
12[22b]	6-Me	CN	4-MeO	TMBn	1	**2l** (61)	**3l** (31)
13[22b]	H	CO_2Et	4-MeO	TMBn	24	**2m** (49)	**3m** (21)

[a] Method A: 1 (0.21 mmol), $CuCl_2$ (10 mol%), Phen (20 mol%), DABCO (2.0 equiv), O_2 (1 atm) in DMF (2.5 mL) at 100 °C. TMBn: 2,4,6-trimethylbenzyl.
[b] Yield of isolated product.

ing Information), was chosen as the model substrate to probe the feasibility of the proposed conversion. We were pleased to find that the reaction of **9a** with $CuCl_2$ (10 mol%), 1,10-phenanthroline (20 mol%), and DABCO (2 equiv) in DMF at 100 °C under an oxygen atmosphere for six hours (Method A), successfully afforded quinolines **10a** and **11a** in 84% and 9% yield, respectively (Table 3, entry 1). The generalities of this reaction were examined with other enaminones **9b**–**f** (R^3 = COPh), and the results are summarized in Table 3. Substrates **9b** and **9c**, bearing 4-methyl and 4-chloro groups (R^1) on the aniline moiety, were tolerated in the developed reaction conditions and **10b**,**c** were obtained in good yields (Table 3, entries 2 and 3). When R^2 was a methyl substituent, the desired oxidative cyclization products **10d**–**f** were also obtained in acceptable yields (entries 4–6). 2-[(*E*)-Stilben-2-yl]aminoacrylonitriles **9g**–**i** (R^3 = CN) also showed good reactivity, producing the corresponding quinolines **10g**–**i** in 79–84% yields (entries 7–9). In most cases, small amounts of 4-benzoylquinolines **11a**–**i** were also obtained as the minor products.

Due to the structural analogy of 2-[(*E*)-stilben-2-yl]aminofumarates with *N*-[(*E*)-stilben-2-yl]enaminones, the copper(II)-catalyzed oxidative carbocyclization of 2-[(*E*)-stilben-2-yl]aminofumarates **9j**–**n** could be envisioned to occur. These 2-aminofumarates **9j**–**n** were readily available from the addition of (*E*)-stilben-2-ylamines to dimethyl acetylenedicarboxylate (see the Supporting Information). Indeed, when the reaction of 2-[(*E*)-stilben-2-yl]aminofumarate **9j** (R^1 = H, R^2 = R^3 = CO_2Me) was carried out under $CuCl_2$/DABCO/Phen conditions (method A) for one hour, the target cyclization product **10j** was obtained in 67% yield (Table 3, entry 10). It is noteworthy that the yield can be improved to 86% using CuCl/NMP conditions (method B) and the reaction time was shortened to 30 minutes (entry 13, see also Table 2 in the Supporting Information). As shown in Table 3 (entries 13–17), a variety of 2-aminofumarates **9j**–**n** were converted to the corresponding quinolines effectively. Regardless of R^1 on the aniline moiety, electron-donating or -withdrawing substituents, the oxidative cyclization products **10j**–**n** were achieved in good to moderate yields. These copper-catalyzed oxidative carbocyclization reactions of *N*-[(*E*)-stilben-2-yl]enamines **9** provide a mild and straightforward method for the synthesis of 2,3-disubstituted quinolines **10** in high yields.

In conclusion, the syntheses of highly functionalized 2-quinolinones and 2,3-disubstituted quinolines are described. Copper(II) enolate **4**, produced by the reaction of *N*-[(*E*)-stilben-2-yl]acetamide **1** with copper(II) chloride and

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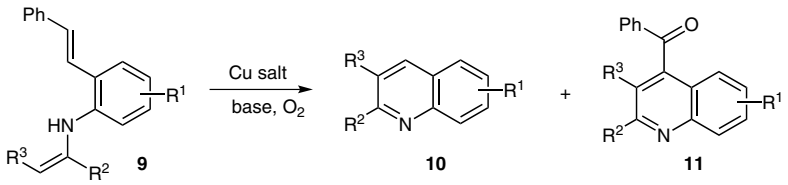
Table 3 Oxidative Carbocyclic Reactions of *N*-[(*E*)-Stilben-2-yl]enamines **9a–i** and 2-[(*E*)-Stilben-2-yl]aminofumarates **9j–n**



Entry	R^1	R^2	R^3	Time (h)	**10**, Yield (%)[a]	**11**, Yield (%)[a]
1[b]	H	Ph	COPh	6	**10a** (84)	**11a** (9)
2[b]	6-Me	Ph	COPh	6	**10b** (82)	**11b** (7)
3[b]	6-Cl	Ph	COPh	6	**10c** (81)	**11c** (10)
4[b]	H	Me	COPh	6	**10d** (43)	**11d** (19)
5[b]	6-Me	Me	COPh	6	**10e** (50)	**11e** (17)
6[b]	6-Cl	Me	COPh	6	**10f** (51)	**11f** (18)
7[b]	H	Ph	CN	1	**10g** (80)	**11g** (0)
8[b]	6-Me	Ph	CN	1	**10h** (79)	**11h** (7)
9[b]	6-Cl	Ph	CN	1	**10i** (84)	**11i** (6)
10[b]	H	CO_2Me	CO_2Me	1	**10j** (67)	**11j** (9)
11[b]	6-Me	CO_2Me	CO_2Me	1	**10k** (61)	**11k** (8)
12[b]	6-Cl	CO_2Me	CO_2Me	1	**10l** (61)	**11l** (10)
13[c]	H	CO_2Me	CO_2Me	0.5	**10j** (86)	**11j** (8)
14[c]	6-Me	CO_2Me	CO_2Me	0.5	**10k** (79)	**11k** (13)
15[c]	6-Cl	CO_2Me	CO_2Me	0.5	**10l** (87)	**11l** (11)
16[c]	6,7-Me_2	CO_2Me	CO_2Me	0.5	**10m** (76)	**11m** (11)
17[c]	6,8-Me_2	CO_2Me	CO_2Me	0.5	**10n** (73)	**11n** (10)

[a] Yield of isolated product. For abbreviations, see Table 1.
[b] Method A: **9** (0.25 mmol), $CuCl_2$ (10 mol%), Phen (20 mol%), DABCO (2.0 equiv), O_2 (1 atm) in DMF (2.5 mL) at 100 °C.
[c] Method B: **9** (0.31 mmol), CuCl (10 mol%), NMP (2.0 equiv), O_2 (1 atm) in DMAc (2.5 mL) at 100 °C.

DABCO, undergoes an intramolecular carbocupration onto the alkenyl moiety efficiently. This reaction provides an efficient and low costs method for the synthesis of 3-substituted 2-quinolinones. A variety of functional groups including benzoyl, acetyl, cyano, and ethoxycarbonyl groups are compatible with the reaction conditions. This strategy was further applied to *N*-[(*E*)-stilben-2-yl]enamines derivatives affording 2,3-disubstituted quinolines in good yields.

Melting points are uncorrected. IR spectra were taken with a Hitachi 260-30 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. The multiplicity of the ^{13}C NMR signals was determined by means of DEPT 135 experiments. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. Mass spectra were recorded on a Jeol JMS-SX 102A mass spectrometer. Analytical TLC was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized by UV. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70–230 mesh).

Copper(II)-Catalyzed Cyclization Reactions of *N*-[(*E*)-Stilben-2-yl]acetamides 1; 3-Benzoyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2a) and 3,4-Dibenzoyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3a); Typical Procedure (Method A)

A mixture of 2-benzoyl-*N*-[(*E*)-stilben-2-yl]acetamide **1a** (101 mg, 0.21 mmol), $CuCl_2$ (4 mg, 0.02 mmol), 1,10-phenanthroline (7 mg, 0.04 mmol), and DABCO (47 mg, 0.42 mmol) in DMF (2.5 mL) was stirred at 100 °C for 7 h under an O_2 atmosphere (1 atm). The reaction mixture was then diluted with EtOAc (50 mL), and the organic layer was washed with H_2O (3 × 50 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20 g, eluent: 1:8 EtOAc–hexane) followed by crystallization (EtOAc–hexane) to give **2a** (57 mg, 71%) and **3a** (8 mg, 8%).

3-Benzoyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2a)

Yield: 57 mg (71%); light yellow needles; mp 201–202 °C (EtOAc–hexane).

IR (KBr): 1660, 1645, 1565, 1455, 1215 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 9 H, 3 × CH_3), 5.65 (s, 2 H, NCH_2), 6.81 (s, 2 H, ArH), 7.06 (d, *J* = 7.9 Hz, 1 H, ArH), 7.19 (t, *J* = 7.9 Hz, 1 H, ArH), 7.40 (t, *J* = 7.9 Hz, 1 H, ArH), 7.46 (t, *J* = 7.7 Hz, 2 H, ArH),

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7.59 (t, J = 7.7 Hz, 1 H, ArH), 7.62 (d, J = 7.9 Hz, 1 H, ArH), 7.88 (d, J = 7.7 Hz, 2 H, ArH), 8.01 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3 (2 q), 20.7 (q), 42.3 (t), 115.3 (d), 119.8 (s), 122.6 (d), 128.4 (2 d), 129.4 (2 d), 130.0 (d), 130.22 (s), 130.26 (2 d), 131.4 (s), 131.9 (d), 133.3 (d), 135.9 (2 s), 136.7 (s), 137.2 (s), 140.2 (s), 140.6 (d), 160.7 (s), 194.3 (s).

Anal. Calcd for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; N, 3.67. Found: C, 81.97; H, 6.08; N, 3.63.

3-Benzoyl-6-chloro-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2b)

Yield: 61 mg (73%); white needles; mp 253–254 °C (EtOAc–hexane).

IR (KBr): 1675, 1645, 1485, 1285, 1215 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 6 H, 2 × CH_3), 2.26 (s, 3 H, CH_3), 5.65 (s, 2 H, NCH_2), 6.84 (s, 2 H, ArH), 7.02 (d, J = 9.1 Hz, 1 H, ArH), 7.36 (dd, J = 9.1, 2.3 Hz, 1 H, ArH), 7.49 (t, J = 7.5 Hz, 2 H, ArH), 7.60 (d, J = 2.3 Hz, 1 H, ArH), 7.62 (t, J = 7.5 Hz, 1 H, ArH), 7.89 (d, J = 7.5 Hz, 2 H, ArH), 7.92 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3 (2 q), 20.7 (q), 42.4 (t), 116.7 (d), 120.8 (s), 128.1 (s), 128.5 (2 d), 128.8 (d), 129.4 (2 d), 129.9 (s), 130.4 (2 d), 131.8 (d), 132.6 (s), 133.5 (d), 135.9 (2 s), 136.8 (s), 137.0 (s), 138.6 (s), 139.1 (d), 160.3 (s), 193.8 (s).

Anal. Calcd for $C_{26}H_{22}ClNO_2$: C, 75.08; H, 5.33; N, 3.37. Found: C, 75.04; H, 5.42; N, 3.37.

3-Benzoyl-6-fluoro-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2c)

Yield: 60 mg (73%); white needles; mp 212–213 °C (EtOAc–hexane).

IR (KBr): 1670, 1645, 1575, 1440, 1235 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 6 H, 2 × CH_3), 2.24 (s, 3 H, CH_3), 5.64 (s, 2 H, NCH_2), 6.82 (s, 2 H, ArH), 7.03 (dd, J = 9.4, 4.3 Hz, 1 H, ArH), 7.13 (ddd, J = 9.4, 8.0, 2.9 Hz, 1 H, ArH), 7.28 (dd, J = 8.0, 2.9 Hz, 1 H, ArH), 7.46 (t, J = 7.6 Hz, 2 H, ArH), 7.59 (t, J = 7.6 Hz, 1 H, ArH), 7.87 (d, J = 7.6 Hz, 2 H, ArH), 7.91 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3 (2 q), 20.7 (q), 42.5 (t), 114.5 (dd, $J_{C,F}$ = 22.1 Hz), 117.0 (dd, $J_{C,F}$ = 8.0 Hz), 119.8 (dd, $J_{C,F}$ = 24.1 Hz), 120.6 (d, $J_{C,F}$ = 8.0 Hz), 128.5 (2 d), 129.4 (2 d), 130.0 (s), 130.3 (2 d), 132.8 (s), 133.5 (d), 135.9 (2 s), 136.7 (s), 136.8 (s), 136.9 (s), 139.2 (dd, $J_{C,F}$ = 3.0 Hz), 157.7 (d, $J_{C,F}$ = 244.5 Hz), 160.3 (s), 193.9 (s).

Anal. Calcd for $C_{26}H_{22}FNO_2$: C, 78.18; H, 5.55; N, 3.51. Found: C, 78.06; H, 5.59; N, 3.48.

3-Benzoyl-6-methyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2d)

Yield: 60 mg (73%); white needles; mp 231–232 °C (EtOAc–hexane).

IR (KBr): 1675, 1645, 1570, 1445, 1235 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 9 H, 3 × CH_3), 2.35 (s, 3 H, CH_3), 5.63 (s, 2 H, NCH_2), 6.81 (s, 2 H, ArH), 6.96 (d, J = 8.7 Hz, 1 H, ArH), 7.22 (dd, J = 8.7, 1.9 Hz, 1 H, ArH), 7.39 (s, 1 H, ArH), 7.45 (t, J = 7.6 Hz, 2 H, ArH), 7.58 (t, J = 7.6 Hz, 1 H, ArH), 7.87 (d, J = 7.6 Hz, 2 H, ArH), 7.95 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3 (2 q), 20.4 (q), 20.7 (q), 42.3 (t), 115.1 (d), 119.8 (s), 128.4 (2 d), 129.4 (2 d), 129.6 (d), 130.2 (2 d), 130.4 (s), 131.3 (s), 132.2 (s), 133.2 (d), 133.3 (d), 135.9 (2 s), 136.6 (s), 137.3 (s), 138.3 (s), 140.5 (d), 160.6 (s), 194.5 (s).

Anal. Calcd for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54. Found: C, 81.87; H, 6.36; N, 3.50.

3-Benzoyl-6,7-dimethyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2e)

Yield: 63 mg (74%); white needles; mp 249–250 °C (EtOAc–hexane).

IR (KBr): 1640, 1595, 1555, 1455, 1240 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.26 (s, 6 H, 2 × CH_3), 5.61 (s, 2 H, NCH_2), 6.81 (s, 2 H, ArH), 6.89 (s, 1 H, ArH), 7.33 (s, 1 H, ArH), 7.44 (t, J = 7.6 Hz, 2 H, ArH), 7.56 (t, J = 7.6 Hz, 1 H, ArH), 7.86 (d, J = 7.6 Hz, 2 H, ArH), 7.95 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.9 (q), 20.3 (2 q), 20.7 (q), 20.9 (q), 42.1 (t), 116.2 (d), 118.0 (s), 128.3 (2 d), 129.4 (2 d), 130.0 (d), 130.08 (s), 130.13 (2 d), 130.5 (s), 131.6 (s), 133.1 (d), 136.0 (2 s), 136.6 (s), 137.5 (s), 138.7 (s), 140.6 (d), 142.0 (s), 160.6 (s), 194.7 (s).

Anal. Calcd for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65; N, 3.42. Found: C, 82.05; H, 6.64; N, 3.41.

3-Benzoyl-6,8-dimethyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2f)

Yield: 43 mg (35%); yellow crystals; mp 208–209 °C (EtOAc–hexane).

IR (KBr): 1655, 1565, 1445, 1275, 1235 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 6 H, 2 × CH_3), 2.26 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.68 (s, 3 H, CH_3), 5.36 (s, 2 H, NCH_2), 6.77 (s, 2 H, ArH), 7.21 (t, J = 7.8 Hz, 2 H, ArH), 7.26 (s, 1 H, ArH), 7.28 (s, 1 H, ArH), 7.44 (t, J = 7.8 Hz, 1 H, ArH), 7.49 (d, J = 7.8 Hz, 2 H, ArH), 7.83 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.29 (q), 20.32 (2 q), 20.8 (q), 23.2 (q), 49.9 (t), 121.6 (s), 124.7 (s), 128.0 (2 d), 128.2 (d), 129.4 (2 d), 129.6 (2 d), 131.0 (s), 131.7 (s), 132.3 (s), 132.9 (d), 136.37 (s), 136.43 (s), 136.9 (2 s), 137.9 (d), 141.1 (d), 141.6 (s), 162.1 (s), 194.0 (s).

Anal. Calcd for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65; N, 3.42. Found: C, 82.00; H, 6.68; N, 3.35.

3-Benzoyl-1-benzyl-6,8-dimethylquinolin-2(1*H*)-one (2g)

Yield: 49 mg (57%); yellow needles; mp 132–133 °C (EtOAc–hexane).

IR (KBr): 1595, 1455, 1280, 1240, 1020 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 5.71 (s, 2 H, CH_2), 7.05 (d, J = 7.2 Hz, 2 H, ArH), 7.21 (s, 1 H, ArH), 7.19 (t, J = 7.2 Hz, 1 H, ArH), 7.29 (t, J = 7.2 Hz, 2 H, ArH), 7.31 (s, 1 H, ArH), 7.42 (t, J = 7.5 Hz, 2 H, ArH), 7.54 (t, J = 7.5 Hz, 1 H, ArH), 7.85 (d, J = 7.5 Hz, 2 H, ArH), 8.00 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.1 (q), 23.9 (q), 49.4 (t), 121.6 (s), 124.6 (s), 125.5 (2 d), 126.8 (d), 128.3 (2 d), 128.7 (2 d), 129.1 (d), 129.4 (2 d), 130.6 (s), 132.6 (s), 133.1 (d), 137.2 (s), 138.0 (s), 138.9 (d), 139.5 (s), 142.1 (d), 161.8 (s), 194.0 (s).

Anal. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.73; H, 5.78; N, 3.78.

3-Acetyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2h)

Yield: 47 mg (59%); light yellow needles; mp 196–197 °C (EtOAc–hexane).

IR (KBr): 1675, 1645, 1560, 1445, 1215 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 6 H, 2 × CH_3), 2.23 (s, 3 H, CH_3), 2.80 (s, 3 H, CH_3), 5.67 (s, 2 H, NCH_2), 6.80 (s, 2 H, ArH), 7.01 (d, J = 8.6 Hz, 1 H, ArH), 7.17 (t, J = 7.5 Hz, 1 H, ArH), 7.40 (ddd, J = 8.6, 7.5, 1.5 Hz, 1 H, ArH), 7.66 (dd, J = 7.5, 1.5 Hz, 1 H, ArH), 8.40 (s, 1 H, CH).

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^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.2 (2 q), 20.7 (q), 31.0 (q), 42.3 (t), 115.1 (d), 119.5 (s), 122.6 (d), 128.9 (s), 130.1 (s), 130.3 (2 d), 131.1 (d), 132.8 (d), 135.8 (2 s), 136.6 (s), 140.9 (s), 142.9 (d), 161.4 (s), 198.6 (s).

Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 78.91; H, 6.66; N, 4.35.

3-Acetyl-6-methyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2i)

Yield: 49 mg (62%); yellow crystals; mp 206–207 °C (EtOAc–hexane).

IR (KBr): 1675, 1645, 1565, 1350, 1225 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 6 H, 2 × CH_3), 2.23 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.79 (s, 3 H, CH_3), 5.65 (s, 2 H, NCH_2), 6.79 (s, 2 H, ArH), 6.91 (d, *J* = 8.7 Hz, 1 H, ArH), 7.22 (dd, *J* = 8.7, 1.6 Hz, 1 H, ArH), 7.43 (s, 1 H, ArH), 8.34 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.2 (2 q), 20.4 (q), 20.7 (q), 31.1 (q), 42.3 (t), 115.0 (d), 119.5 (s), 128.9 (s), 130.27 (2 d), 130.28 (s), 130.6 (d), 132.2 (s), 134.3 (d), 135.8 (2 s), 136.6 (s), 139.0 (s), 142.7 (d), 161.3 (s), 198.8 (s).

Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.24; H, 6.96; N, 4.20.

3-Acetyl-6-chloro-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2j)

Yield: 53 mg (65%); light yellow needles; mp 204–205 °C (EtOAc–hexane).

IR (KBr): 1680, 1655, 1560, 1485, 1210 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 6 H, 2 × CH_3), 2.23 (s, 3 H, CH_3), 2.78 (s, 3 H, CH_3), 5.65 (s, 2 H, NCH_2), 6.81 (s, 2 H, ArH), 6.94 (d, *J* = 9.1 Hz, 1 H, ArH), 7.33 (dd, *J* = 9.1, 2.4 Hz, 1 H, ArH), 7.62 (d, *J* = 2.4 Hz, 1 H, ArH), 8.28 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.2 (2 q), 20.7 (q), 31.0 (q), 42.4 (t), 116.6 (d), 120.5 (s), 128.1 (s), 129.7 (d), 129.8 (s), 130.0 (s), 130.4 (2 d), 132.7 (d), 135.8 (2 s), 136.9 (s), 139.3 (s), 141.4 (d), 161.0 (s), 198.2 (s).

Anal. Calcd for $C_{21}H_{20}ClNO_2$: C, 71.28; H, 5.70; N, 3.96. Found: C, 71.21; H, 5.73; N, 3.90.

3-Cyano-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2k)

Yield: 47 mg (62%); light yellow crystals; mp 232–233 °C (EtOAc–hexane).

IR (KBr): 2230, 1645, 1590, 1565, 1455 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19 (s, 6 H, 2 × CH_3), 2.23 (s, 3 H, CH_3), 5.65 (s, 2 H, NCH_2), 6.81 (s, 2 H, ArH), 7.07 (d, *J* = 8.6 Hz, 1 H, ArH), 7.23 (t, *J* = 7.5 Hz, 1 H, ArH), 7.47 (ddd, *J* = 8.6, 7.5, 1.4 Hz, 1 H, ArH), 7.60 (dd, *J* = 7.5, 1.4 Hz, 1 H, ArH), 8.23 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3 (2 q), 20.7 (q), 43.1 (t), 106.9 (s), 115.3 (s), 115.6 (d), 118.9 (s), 123.2 (d), 129.4 (s), 130.2 (d), 130.4 (2 d), 133.9 (d), 135.9 (2 s), 137.0 (s), 140.6 (s), 147.6 (d), 159.4 (s).

Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.33; H, 6.01; N, 9.29.

3-Cyano-6-methyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2l)

Yield: 44mg (61%); light yellow needles; mp 215–216 °C (EtOAc–hexane).

IR (KBr): 2230, 1655, 1570, 1500, 1230 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 6 H, 2 × CH_3), 2.23 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 5.63 (s, 2 H, NCH_2), 6.80 (s, 2 H, ArH), 6.96 (d, *J* = 8.8 Hz, 1 H, ArH), 7.29 (dd, *J* = 8.8, 1.9 Hz, 1 H, ArH), 7.37 (s, 1 H, ArH), 8.16 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3 (2 q), 20.4 (q), 20.7 (q), 43.0 (t), 106.7 (s), 115.47 (s), 115.51 (d), 118.9 (s), 129.6 (s), 129.7 (d), 130.3 (2 d), 133.0 (s), 135.3 (d), 135.9 (2 s), 137.0 (s), 138.7 (s), 147.4 (d), 159.4 (s).

Anal. Calcd for $C_{21}H_{20}N_2O$: C, 79.92; H, 6.37; N, 8.85. Found: C, 79.65; H, 6.37; N, 8.81.

3-Ethoxycarbonyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (2m)

Yield: 37 mg (49%); light yellow crystals; mp 127–128 °C (EtOAc–hexane).

IR (KBr): 1745, 1650, 1565, 1450, 1210 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.18 (s, 6 H, 2 × CH_3), 2.22 (s, 3 H, CH_3), 4.44 (q, *J* = 7.1 Hz, 2 H, OCH_2), 5.67 (s, 2 H, NCH_2), 6.79 (s, 2 H, ArH), 7.00 (d, *J* = 8.7 Hz, 1 H, ArH), 7.16 (t, *J* = 7.5 Hz, 1 H, ArH), 7.39 (ddd, *J* = 8.7, 7.5, 1.4 Hz, 1 H, ArH), 7.61 (dd, *J* = 7.5, 1.4 Hz, 1 H, ArH), 8.40 (s, 1 H, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.3 (q), 20.3 (2 q), 20.7 (q), 42.5 (t), 61.6 (t), 115.1 (d), 119.1 (s), 122.4 (d), 122.5 (s), 130.2 (2 d), 130.3 (d), 132.6 (d), 135.9 (2 s), 136.6 (s), 140.7 (s), 143.8 (d), 159.7 (s), 165.0 (s).

Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N 4.01. Found: C, 75.59; H, 6.66; N, 4.01.

3,4-Dibenzoyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3a)

Yield: 8 mg (8%); white crystals; mp 206–207 °C (EtOAc–hexane).

IR (KBr): 1670, 1635, 1610, 1455, 1235 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 2.31 (s, 6 H, 2 × CH_3), 5.70 (s, 2 H, NCH_2), 6.85 (s, 2 H, ArH), 7.06 (t, *J* = 7.8 Hz, 1 H, ArH), 7.14 (d, *J* = 7.8 Hz, 1 H, ArH), 7.30 (d, *J* = 7.8 Hz, 1 H, ArH), 7.39 (t, *J* = 7.8 Hz, 1 H, ArH), 7.41 (t, *J* = 7.6 Hz, 2 H, ArH), 7.43 (t, *J* = 7.7 Hz, 2 H, ArH), 7.54 (t, *J* = 7.6 Hz, 1 H, ArH), 7.58 (t, *J* = 7.7 Hz, 1 H, ArH), 7.81 (d, *J* = 7.6 Hz, 2 H, ArH), 7.86 (d, *J* = 7.7 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.4 (2 q), 20.7 (q), 42.4 (t), 115.7 (d), 118.0 (s), 122.9 (d), 127.9 (d), 128.4 (2 d), 128.8 (2 d), 129.26 (2 d), 129.28 (s), 129.9 (2 d), 130.0 (s), 130.4 (2 d), 131.9 (d), 133.5 (d), 134.5 (d), 135.9 (2 s), 136.1 (s), 136.89 (s), 136.94 (s), 139.6 (s), 148.5 (s), 160.3 (s), 193.7 (s), 194.7 (s).

Anal. Calcd for $C_{33}H_{27}NO_3$: C, 81.63; H, 5.60; N, 2.88. Found: C, 81.38; H, 5.63; N, 2.81.

3,4-Dibenzoyl-6-chloro-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3b)

Yield: 6 mg (6%); white needles; mp 217–218 °C (EtOAc–hexane).

IR (KBr): 1665, 1640, 1560, 1420, 1315, 1230 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, CH_3), 2.29 (s, 6 H, 2 × CH_3), 5.67 (s, 2 H, NCH_2), 6.85 (s, 2 H, ArH), 7.08 (d, *J* = 9.2 Hz, 1 H, ArH), 7.25 (d, *J* = 2.4 Hz, 1 H, ArH), 7.34 (dd, *J* = 9.2, 2.4 Hz, 1 H, ArH), 7.41 (t, *J* = 7.5 Hz, 2 H, ArH), 7.44 (t, *J* = 7.5 Hz, 2 H, ArH), 7.55 (t, *J* = 7.5 Hz, 1 H, ArH), 7.61 (t, *J* = 7.5 Hz, 1 H, ArH), 7.78 (d, *J* = 7.5 Hz, 2 H, ArH), 7.84 (d, *J* = 7.5 Hz, 2 H, ArH).

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^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.4 (2 q), 20.8 (q), 42.5 (t), 117.1 (d), 119.0 (s), 126.8 (d), 128.5 (2 d), 128.6 (s), 129.0 (2 d), 129.3 (2 d), 129.6 (s), 129.9 (2 d), 130.2 (s), 130.5 (2 d), 132.0 (d), 133.8 (d), 134.9 (d), 135.7 (s), 135.9 (2 s), 136.6 (s), 137.2 (s), 138.1 (s), 147.1 (s), 159.9 (s), 193.1 (s), 194.0 (s).

Anal. Calcd for $C_{33}H_{26}ClNO_3$: C, 76.22; H, 5.04; N, 2.69. Found: C, 76.06; H, 5.06; N, 2.63.

3,4-Dibenzoyl-6-fluoro-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3c)

Yield: 6 mg (6%); yellow needles; mp 220–220 °C (EtOAc–hexane).

IR (KBr): 1670, 1645, 1600, 1440, 1235 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, CH_3), 2.29 (s, 6 H, CH_3), 5.69 (s, 2 H, NCH_2), 6.85 (s, 1 H, ArH), 6.96 (d, *J* = 9.1 Hz, 1 H, ArH), 7.09–7.14 (m, 2 H, ArH), 7.40 (t, *J* = 7.7 Hz, 2 H, ArH), 7.44 (t, *J* = 7.7 Hz, 2 H, ArH), 7.54 (t, *J* = 7.7 Hz, 1 H, ArH), 7.60 (t, *J* = 7.7 Hz, 1 H, ArH), 7.79 (dd, *J* = 7.7, 1.0 Hz, 2 H, ArH), 7.84 (dd, *J* = 7.7, 1.1 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.4 (2 q), 20.8 (q), 42.6 (t), 112.9 (dd, $J_{C,F}$ = 24.1 Hz), 117.4 (dd, $J_{C,F}$ = 8.0 Hz), 118.8 (d, $J_{C,F}$ = 9.1 Hz), 119.9 (dd, $J_{C,F}$ = 24.1 Hz), 128.5 (2 d), 129.0 (2 d), 129.3 (2 d), 129.8 (s), 129.9 (2 d), 130.5 (2 d), 133.7 (d), 134.8 (d), 135.7 (s), 135.9 (2 s), 136.2 (s), 136.7 (s), 137.2 (s), 147.3 (s), 157.7 (d, $J_{C,F}$ = 244.5 Hz), 158.9 (s), 160.0 (s), 193.3 (s), 194.1 (s).

Anal. Calcd for $C_{33}H_{26}FNO_3$: C, 78.71; H, 5.20; N, 2.78. Found: C, 78.28; H, 5.22; N, 2.76.

3,4-Dibenzoyl-6-methyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3d)

Yield: 6 mg (6%); white crystals; mp 243–244 °C (EtOAc–hexane).

IR (KBr): 1645, 1445, 1240, 1210 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.30 (s, 6 H, 2 × CH_3), 5.68 (s, 2 H, NCH_2), 6.84 (s, 2 H, ArH), 7.04 (d, *J* = 8.8 Hz, 1 H, ArH), 7.07 (s, 1 H, ArH), 7.21 (dd, *J* = 8.8, 1.8 Hz, 1 H, ArH), 7.39 (t, *J* = 7.4 Hz, 2 H, ArH), 7.43 (t, *J* = 7.5 Hz, 2 H, ArH), 7.53 (t, *J* = 7.4 Hz, 1 H, ArH), 7.58 (t, *J* = 7.5 Hz, 1 H, ArH), 7.80 (d, *J* = 7.4 Hz, 2 H, ArH), 7.86 (d, *J* = 7.5 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.4 (2 q), 20.6 (q), 20.8 (q), 42.4 (t), 115.6 (d), 118.0 (s), 127.4 (d), 128.4 (2 d), 128.8 (2 d), 129.0 (s), 129.3 (2 d), 129.9 (2 d), 130.2 (s), 130.3 (2 d), 132.6 (s), 133.4 (d), 133.5 (d), 134.5 (d), 135.9 (2 s), 136.1 (s), 136.8 (s), 137.0 (s), 137.7 (s), 148.2 (s), 160.1 (s), 193.8 (s), 194.9 (s).

Anal. Calcd for $C_{34}H_{29}NO_3$: C, 81.74; H, 5.85; N, 2.80. Found: C, 81.39; H, 5.89; N, 2.74.

3,4-Dibenzoyl-6,7-dimethyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3e)

Yield: 7 mg (7%); yellow crystals; mp 219–220 °C (EtOAc–hexane).

IR (KBr): 1685, 1635, 1450, 1230, 1020 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.32 (s, 6 H, 2 × CH_3), 5.66 (s, 2 H, NCH_2), 6.85 (s, 2 H, ArH), 6.98 (s, 1 H, ArH), 7.01 (s, 1 H, ArH), 7.39 (t, *J* = 7.6 Hz, 2 H, ArH), 7.42 (t, *J* = 7.6 Hz, 2 H, ArH), 7.52 (t, *J* = 7.6 Hz, 1 H, ArH), 7.57 (t, *J* = 7.6 Hz, 1 H, ArH), 7.79 (d, *J* = 7.6 Hz, 2 H, ArH), 7.85 (d, *J* = 7.6 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.0 (q), 20.4 (2 q), 20.7 (q), 20.9 (q), 42.2 (t), 116.1 (s), 116.6 (d), 127.6 (d), 127.8 (s), 128.3 (2 d), 128.8 (2 d), 129.2 (2 d), 129.8 (2 d), 130.2 (2 d), 130.3 (s), 132.0 (s), 133.3 (d), 134.4 (d), 136.0 (2 s), 136.2 (s), 136.8 (s), 137.2 (s), 138.1 (s), 142.2 (s), 148.5 (s), 160.2 (s), 194.0 (s), 195.1 (s).

Anal. Calcd for $C_{35}H_{31}NO_3$: C, 81.84; H, 6.08; N, 2.73. Found: C, 81.69; H, 6.10; N, 2.71.

3,4-Dibenzoyl-6,8-dimethyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3f)

Yield: 6 mg (4%), yellow crystals; mp 246–247 °C (EtOAc–hexane).

IR (KBr): 1650, 1555, 1450, 1260 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 6 H, 2 × CH_3), 2.24 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.71 (s, 3 H, CH_3), 5.37 (s, 2 H, NCH_2), 6.79 (s, 2 H, ArH), 6.95 (s, 1 H, ArH), 7.12 (t, *J* = 7.7 Hz, 2 H, ArH), 7.28 (s, 1 H, ArH), 7.39 (t, *J* = 7.7 Hz, 1 H, ArH), 7.39 (t, *J* = 7.4 Hz, 2 H, ArH), 7.40 (d, *J* = 7.7 Hz, 2 H, ArH), 7.55 (t, *J* = 7.4 Hz, 1 H, ArH), 7.81 (d, *J* = 7.4 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.40 (2 q), 20.43 (q), 20.8 (q), 23.2 (q), 50.5 (t), 119.8 (s), 125.2 (s), 125.7 (d), 128.0 (2 d), 128.7 (2 d), 129.37 (2 d), 129.44 (2 d), 129.7 (2 d), 130.5 (s), 132.6 (s), 133.1 (d), 134.3 (d), 136.24 (s), 136.26 (s), 136.7 (s), 136.9 (2 s), 137.7 (d), 141.3 (s), 148.4 (s), 161.6 (s), 193.3 (s), 195.2 (s).

Anal. Calcd for $C_{35}H_{31}NO_3$: C, 81.84; H, 6.08; N, 2.73. Found: C, 81.54; H, 6.13; N, 2.67.

3,4-Dibenzoyl-1-benzyl-6,8-dimethylquinolin-2(1*H*)-one (3g)

Yield: 8 mg (7%); yellow crystals; mp 187–188 °C (EtOAc–hexane).

IR (KBr): 1650, 1555, 1450, 1255, 1215 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 5.71 (s, 2 H, NCH_2), 7.01 (s, 1 H, ArH), 7.12 (d, *J* = 7.2 Hz, 2 H, ArH), 7.20 (s, 1 H, ArH), 7.23 (t, *J* = 7.2 Hz, 1 H, ArH), 7.31 (t, *J* = 7.2 Hz, 2 H, ArH), 7.35 (t, *J* = 7.4 Hz, 2 H, ArH), 7.43 (t, *J* = 7.5 Hz, 2 H, ArH), 7.48 (t, *J* = 7.4 Hz, 1 H, ArH), 7.58 (t, *J* = 7.5 Hz, 1 H, ArH), 7.76 (d, *J* = 7.4 Hz, 2 H, ArH), 7.90 (d, *J* = 7.5 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3 (q), 23.9 (q), 50.2 (t), 119.9 (s), 125.3 (s), 125.6 (2 d), 126.3 (d), 126.9 (d), 128.3 (2 d), 128.4 (s), 128.7 (2 d), 128.8 (2 d), 129.1 (2 d), 129.8 (2 d), 132.9 (s), 133.3 (d), 134.4 (d), 136.1 (s), 136.9 (s), 137.6 (s), 138.8 (d), 139.3 (s), 149.3 (s), 161.5 (s), 193.3 (s), 195.2 (s).

Anal. Calcd for $C_{32}H_{25}NO_3$: C, 81.51; H, 5.34; N, 2.97. Found: C, 81.44; H, 5.38; N, 2.95.

3-Cyano-4-(4-methoxybenzoyl)-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3k)

Yield: 33 mg (30%); yellow needles; mp 206–207 °C (EtOAc–hexane).

IR (KBr): 2230, 1650, 1600, 1555, 1455, 1255 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 2.26 (s, 6 H, 2 × CH_3), 3.90 (s, 3 H, CH_3), 5.71 (s, 2 H, NCH_2), 6.84 (s, 2 H, ArH), 6.99 (d, *J* = 8.5 Hz, 2 H, ArH), 7.13 (t, *J* = 7.9 Hz, 1 H, ArH), 7.14 (d, *J* = 7.9 Hz, 1 H, ArH), 7.38 (d, *J* = 7.9 Hz, 1 H, ArH), 7.47 (t, *J* = 7.9 Hz, 1 H, ArH), 7.86 (d, *J* = 8.5 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.4 (2 q), 20.7 (q), 43.3 (t), 55.7 (q), 103.5 (s), 113.4 (s), 114.7 (2 d), 116.0 (d), 117.1 (s), 123.5 (d), 127.6 (s), 128.5 (d), 129.3 (s), 130.5 (2 d), 132.5 (2 d), 134.2 (d), 135.9 (2 s), 137.2 (s), 140.5 (s), 157.2 (s), 158.9 (s), 165.5 (s), 189.9 (s).

Anal. Calcd for $C_{28}H_{24}N_2O_3$: C, 77.04; H, 5.54; N, 6.42. Found: C, 77.07; H, 5.55; N, 6.43.

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3-Cyano-4-(4-methoxybenzoyl)-6-methyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3l)

Yield: 32 mg (31%); yellow crystals; mp 212–213 °C (EtOAc–hexane).

IR (KBr): 2230, 1645, 1595, 1560, 1510, 1250, 1165 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3 H, CH_3), 2.25 (s, 9 H, 3 × CH_3), 3.90 (s, 3 H, CH_3), 5.69 (s, 2 H, NCH_2), 6.83 (s, 2 H, ArH), 6.99 (d, *J* = 8.5 Hz, 2 H, ArH), 7.03 (d, *J* = 8.6 Hz, 1 H, ArH), 7.13 (s, 1 H, ArH), 7.29 (dd, *J* = 8.6, 1.8 Hz, 1 H, ArH), 7.87 (d, *J* = 8.5 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.39 (2 q), 20.44 (q), 20.7 (q), 43.2 (t), 55.7 (q), 103.3 (s), 113.5 (s), 114.7 (2 d), 115.9 (d), 117.1 (s), 127.6 (s), 127.8 (d), 129.5 (s), 130.4 (2 d), 132.5 (2 d), 133.4 (s), 135.7 (d), 135.9 (2 s), 137.1 (s), 138.6 (s), 156.9 (s), 158.8 (s), 165.5 (s), 190.1 (s).

Anal. Calcd for $C_{29}H_{26}N_2O_3$: C, 77.31; H, 5.82; N, 6.22. Found: C, 77.38; H, 5.86; N, 6.17.

3-Ethoxycarbonyl-4-(4-methoxybenzoyl)-1-(2,4,6-trimethylbenzyl)quinolin-2(1*H*)-one (3m)

Yield: 21 mg (21%); white crystals; mp 181–182 °C (EtOAc–hexane).

IR (KBr): 1745, 1645, 1600, 1560, 1455, 1260, 1165 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.07 (t, *J* = 6.8 Hz, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.26 (s, 6 H, 2 × CH_3), 3.87 (s, 3 H, CH_3), 4.12 (q, *J* = 6.8 Hz, 2 H, OCH_2), 5.71 (s, 2 H, NCH_2), 6.83 (s, 2 H, ArH), 6.94 (d, *J* = 8.3 Hz, 2 H, ArH), 7.04 (t, *J* = 7.9 Hz, 1 H, ArH), 7.08 (d, *J* = 7.9 Hz, 1 H, ArH), 7.34 (d, *J* = 7.9 Hz, 1 H, ArH), 7.37 (t, *J* = 7.9 Hz, 1 H, ArH), 7.85 (d, *J* = 8.3 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.6 (q), 20.4 (2 q), 20.7 (q), 42.7 (t), 55.6 (q), 61.8 (t), 114.2 (2 d), 115.5 (d), 117.4 (s), 121.8 (s), 122.8 (d), 128.2 (d), 129.0 (s), 130.0 (s), 130.3 (3 d), 131.9 (d), 132.3 (d), 135.9 (2 s), 136.8 (s), 139.9 (s), 149.2 (s), 159.2 (s), 164.1 (s), 164.6 (s), 192.1 (s).

Anal. Calcd for $C_{30}H_{29}NO_5$: C, 74.52; H, 6.04; N, 2.90. Found: C, 74.63; H, 6.07; N, 2.88.

Copper(II)-Catalyzed Cyclization Reactions of *N*-[(*E*)-Stilben-2-yl]enamines 9a–i; 3-Benzoyl-2-phenylquinoline (10a) and 3,4-Benzoyl-2-phenylquinoline (11a); Typical Procedure (Method A)

A mixture of *N*-[(*E*)-stilben-2-yl]enaminone **9a** (101 mg, 0.25 mmol), $CuCl_2$ (3 mg, 0.03 mmol), 1,10-phenanthroline (9 mg, 0.05 mmol), and DABCO (59 mg, 0.53 mmol) in DMF (2.5 mL) was stirred at 100 °C for 6 h under an O_2 atmosphere (1 atm). The reaction mixture was then diluted with EtOAc (50 mL), washed with H_2O (3 × 50 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20 g, eluent: 1:8 EtOAc–hexane) followed by crystallization (EtOAc–hexane) to give **10a** (65 mg, 84%) and **11a** (9 mg, 9%).

3-Benzoyl-2-phenylquinoline (10a)[16c]

Yield: 65 mg (84%); white needles; mp 133–134 °C (EtOAc–hexane).

IR (KBr): 1655, 1595, 1270, 775, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.31 (m, 3 H, ArH), 7.33 (t, *J* = 7.6 Hz, 2 H, ArH), 7.48 (t, *J* = 7.8 Hz, 1 H, ArH), 7.60–7.66 (m, 3 H, ArH), 7.72 (d, *J* = 7.6 Hz, 2 H, ArH), 7.84 (t, *J* = 7.8 Hz, 1 H, ArH), 7.92 (d, *J* = 7.8 Hz, 1 H, ArH), 8.25 (d, *J* = 7.8 Hz, 1 H, ArH), 8.35 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 125.8 (s), 127.3 (d), 128.1 (d), 128.4 (4 d), 128.8 (d), 129.3 (2 d), 129.7 (d), 130.0 (2 d), 131.2 (d), 132.8 (s), 133.3 (d), 137.0 (s), 137.6 (d), 139.7 (s), 148.3 (s), 157.5 (s), 196.9 (s).

Anal. Calcd for $C_{22}H_{15}NO$: C, 85.41; H, 4.89; N, 4.53. Found: C, 85.21; H, 5.01; N, 4.60.

3-Benzoyl-6-methyl-2-phenylquinoline (10b)[16c]

Yield: 96 mg (82%); white needles; mp 148–149 °C (EtOAc–hexane).

IR (KBr): 1660, 1445, 1270, 890, 735 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.58 (s, 3 H, CH_3), 7.22–7.30 (m, 3 H, ArH), 7.32 (t, *J* = 7.6 Hz, 2 H, ArH), 7.47 (t, *J* = 7.6 Hz, 1 H, ArH), 7.58–7.63 (m, 2 H, ArH), 7.65–7.69 (m, 2 H, ArH), 7.71 (d, *J* = 8.2 Hz, 2 H, ArH), 8.14 (d, *J* = 9.2 Hz, 1 H, ArH), 8.25 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.6 (q), 125.8 (s), 126.8 (d), 128.3 (4 d), 128.6 (d), 129.2 (2 d), 129.3 (d), 129.9 (2 d), 132.7 (s), 133.2 (d), 133.5 (d), 136.9 (d), 137.1 (s), 137.3 (s), 139.8 (s), 147.0 (s), 156.5 (s), 197.1 (s).

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.27; H, 5.33; N, 4.29.

3-Benzoyl-6-chloro-2-phenylquinoline (10c)[16c]

Yield: 96 mg (81%); white needles; mp 161–162 °C (EtOAc–hexane).

IR (KBr): 1665, 1475, 1270, 885, 720 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.31 (m, 3 H, ArH), 7.34 (t, *J* = 7.5 Hz, 2 H, ArH), 7.49 (t, *J* = 7.5 Hz, 1 H, ArH), 7.58–7.64 (m, 2 H, ArH), 7.70 (d, *J* = 7.5 Hz, 2 H, ArH), 7.76 (dd, *J* = 9.0, 2.3 Hz, 1 H, ArH), 7.89 (d, *J* = 2.3 Hz, 1 H, ArH), 8.18 (d, *J* = 9.0 Hz, 1 H, ArH), 8.24 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 126.4 (s), 126.6 (d), 128.4 (4 d), 129.0 (d), 129.2 (2 d), 129.9 (2 d), 131.2 (d), 132.1 (d), 133.0 (s), 133.5 (d), 133.6 (s), 136.5 (d), 136.7 (s), 139.3 (s), 146.7 (s), 157.6 (s), 196.5 (s).

Anal. Calcd for $C_{22}H_{14}ClNO$: C, 76.86; H, 4.10; N, 4.07. Found: C, 76.77; H, 4.15; N, 4.03.

3-Benzoyl-2-methylquinoline (10d)[16c]

Yield: 32 mg (43%); pale yellow oil.

IR (film): 1660, 1595, 1240, 880, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.75 (s, 3 H, CH_3), 7.51 (t, *J* = 7.6 Hz, 2 H, ArH), 7.56 (t, *J* = 7.8 Hz, 1 H, ArH), 7.65 (t, *J* = 7.6 Hz, 1 H, ArH), 7.76–7.83 (m, 1 H, ArH), 7.80 (d, *J* = 7.8 Hz, 1 H, ArH), 7.85 (d, *J* = 7.6 Hz, 2 H, ArH), 8.09 (d, *J* = 7.8 Hz, 1 H, ArH), 8.13 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.2 (q), 125.3 (s), 126.6 (d), 128.1 (d), 128.7 (3 d), 130.1 (2 d), 131.0 (d), 132.2 (s), 133.7 (d), 136.7 (d), 137.3 (s), 148.0 (s), 156.6 (s), 196.7 (s).

HMRS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{13}NO$: 247.0997; found: 247.0992.

3-Benzoyl-2,6-Dimethylquinoline (10e)[16c]

Yield: 37 mg (50%); colorless needles; mp 68–69 °C (EtOAc–hexane).

IR (KBr): 1660, 1595, 1245, 830, 730 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.54 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 7.50 (t, *J* = 7.7 Hz, 2 H, ArH), 7.56 (s, 1 H, ArH), 7.62 (dd, *J* = 8.7, 1.9 Hz, 1 H, ArH), 7.64 (t, *J* = 7.7 Hz, 1 H, ArH), 7.84 (d, *J* = 7.7 Hz, 2 H, ArH), 7.98 (d, *J* = 8.7 Hz, 1 H, ArH), 8.04 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.5 (q), 24.1 (q), 125.3 (s), 126.9 (d), 128.3 (d), 128.7 (2 d), 130.1 (2 d), 132.1 (s), 133.3 (d), 133.6 (d), 136.2 (d), 136.6 (s), 137.4 (s), 146.7 (s), 155.6 (s), 196.9 (s).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.59; H, 5.79; N, 5.32.

3-Benzoyl-6-chloro-2-methylquinoline (10f)[16c]

Yield: 39 mg (51%); colorless needles; mp 121–122 °C (EtOAc–hexane).

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IR (KBr): 1660, 1595, 1275, 835, 725 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.72 (s, 3 H, CH_3), 7.51 (t, *J* = 7.7 Hz, 2 H, ArH), 7.65 (t, *J* = 7.7 Hz, 1 H, ArH), 7.71 (dd, *J* = 8.9, 2.3 Hz, 1 H, ArH), 7.78 (d, *J* = 2.3 Hz, 1 H, ArH), 7.83 (d, *J* = 7.7 Hz, 2 H, ArH), 8.02 (d, *J* = 8.9 Hz, 1 H, ArH), 8.02 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.2 (q), 125.9 (s), 126.6 (d), 128.8 (2 d), 130.1 (2 d), 130.3 (d), 131.8 (d), 132.3 (s), 133.1 (s), 133.9 (d), 135.4 (d), 136.9 (s), 146.4 (s), 156.9 (s), 196.3 (s).

Anal. Calcd for $C_{17}H_{12}ClNO$: C, 72.47; H, 4.29; N, 4.97. Found: C, 72.34; H, 4.35; N, 4.95.

3-Cyano-2-phenylquinoline (10g)[16c]

Yield: 58 mg (80%); white needles; mp 195–196 °C (EtOAc–hexane).

IR (KBr): 2220, 1555, 1375, 755, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.61 (m, 3 H, ArH), 7.67 (t, *J* = 7.9 Hz, 1 H, ArH), 7.90 (t, *J* = 7.9 Hz, 1 H, ArH), 7.91 (d, *J* = 7.9 Hz, 1 H, ArH), 7.97–8.04 (m, 2 H, ArH), 8.21 (d, *J* = 7.9 Hz, 1 H, ArH), 8.67 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 105.6 (s), 117.9 (s), 125.0 (s), 127.7 (d), 128.1 (d), 128.7 (2 d), 129.1 (2 d), 129.9 (d), 130.1 (d), 133.0 (d), 137.6 (s), 144.2 (d), 148.7 (s), 158.0 (s).

Anal. Calcd for $C_{16}H_{10}N_2$: C, 83.46; H, 4.38; N, 12.17. Found: C, 83.38; H, 4.38; N, 12.16.

3-Cyano-6-methyl-2-phenylquinoline (10h)[16c]

Yield: 88 mg (79%); colorless needles; mp 172–173 °C (EtOAc–hexane).

IR (KBr): 2220, 1590, 1380, 830, 695 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.59 (s, 3 H, CH_3), 7.50–7.62 (m, 3 H, ArH), 7.66 (s, 1 H, ArH), 7.72 (dd, *J* = 8.6, 1.9 Hz, 1 H, ArH), 7.96–8.03 (m, 2 H, ArH), 8.10 (d, *J* = 8.6 Hz, 1 H, ArH), 8.57 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.6 (q), 105.4 (s), 118.1 (s), 125.0 (s), 126.4 (d), 128.6 (2 d), 129.0 (2 d), 129.5 (d), 129.9 (d), 135.3 (d), 137.7 (s), 138.3 (s), 143.4 (d), 147.3 (s), 157.1 (s).

Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.58; H, 4.97; N, 11.47.

6-Chloro-3-cyano-2-phenylquinoline (10i)[16c]

Yield: 96 mg (84%); white needles; mp 197–198 °C (EtOAc–hexane).

IR (KBr): 2220, 1550, 1475, 925, 695 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.61 (m, 3 H, ArH), 7.82 (dd, *J* = 9.0, 2.2 Hz, 1 H, ArH), 7.90 (d, *J* = 2.2 Hz, 1 H, ArH), 7.96–8.03 (m, 2 H, ArH), 8.15 (d, *J* = 9.0 Hz, 1 H, ArH), 8.58 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 106.6 (s), 117.5 (s), 125.5 (s), 126.2 (d), 128.8 (2 d), 129.1 (2 d), 130.3 (d), 131.5 (d), 133.9 (d), 134.1 (s), 137.3 (s), 143.1 (d), 147.1 (s), 158.2 (s).

Anal. Calcd for $C_{16}H_9ClN_2$: C, 72.60; H, 3.43; N, 10.58. Found: C, 72.36; H, 3.46; N, 10.53.

3,4-Benzoyl-2-phenylquinoline (11a)

Yield: 9 mg (9%), white crystals; mp 192–193 °C (EtOAc–hexane).

IR (KBr): 1655, 1595, 1550, 1450, 1235 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 7.4 Hz, 2 H, ArH), 7.19–7.28 (m, 3 H, ArH), 7.33 (t, *J* = 7.4 Hz, 1 H, ArH), 7.41 (t, *J* = 7.4 Hz, 2 H, ArH), 7.47 (d, *J* = 7.4 Hz, 2 H, ArH), 7.52 (t, *J* = 7.8 Hz, 1 H, ArH), 7.58 (t, *J* = 7.9 Hz, 1 H, ArH), 7.59–7.67 (m, 3 H, ArH), 7.81 (d, *J* = 7.4 Hz, 2 H, ArH), 7.84 (t, *J* = 7.8 Hz, 1 H, ArH), 8.32 (d, *J* = 7.8 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 123.3 (s), 125.8 (d), 127.8 (d), 128.0 (2 d), 128.4 (2 d), 128.7 (2 d), 129.0 (d), 129.3 (2 d), 129.6 (2 d), 130.0 (2 d), 130.1 (d), 130.4 (s), 131.2 (d), 133.2 (d), 134.3 (d), 136.9 (s), 137.2 (s), 139.5 (s), 147.0 (s), 148.0 (s), 156.9 (s), 196.4 (s), 196.7 (s).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{29}H_{19}NO_2$: 413.1416; found: 413.1414.

3,4-Benzoyl-6-methyl-2-phenylquinoline (11b)

Yield: 11 mg (7%), white crystals; mp 182–183 °C (EtOAc–hexane).

IR (KBr): 1660, 1550, 1450, 1345, 1230 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 7.14 (t, *J* = 7.5 Hz, 2 H, ArH), 7.17–7.27 (m, 3 H, ArH), 7.31 (t, *J* = 7.5 Hz, 1 H, ArH), 7.40 (t, *J* = 7.6 Hz, 2 H, ArH), 7.40 (s, 1 H, ArH), 7.45 (d, *J* = 7.5 Hz, 2 H, ArH), 7.56 (t, *J* = 7.6 Hz, 1 H, ArH), 7.58–7.63 (m, 2 H, ArH), 7.67 (dd, *J* = 8.7, 1.7 Hz, 1 H, ArH), 7.80 (d, *J* = 7.6 Hz, 2 H, ArH), 8.20 (d, *J* = 8.7 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.8 (q), 123.3 (s), 124.4 (d), 128.0 (2 d), 128.3 (2 d), 128.7 (2 d), 128.8 (d), 129.3 (2 d), 129.5 (2 d), 129.7 (d), 130.0 (2 d), 130.1 (s), 133.2 (d), 133.6 (d), 134.2 (d), 136.9 (s), 137.2 (s), 138.1 (s), 139.6 (s), 146.1 (s), 146.8 (s), 155.9 (s), 196.6 (s), 196.8 (s).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{30}H_{21}NO_2$: 427.1572; found: 427.1577.

3,4-Benzoyl-6-chloro-2-phenylquinoline (11c)

Yield: 16 mg (10%); white crystals; mp 172–173 °C (EtOAc–hexane).

IR (KBr): 1660, 1595, 1450, 1310, 1225 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (t, *J* = 7.4 Hz, 2 H, ArH), 7.20–7.29 (m, 3 H, ArH), 7.34 (t, *J* = 7.4 Hz, 1 H, ArH), 7.41 (t, *J* = 7.8 Hz, 2 H, ArH), 7.45 (d, *J* = 7.4 Hz, 2 H, ArH), 7.55–7.64 (m, 4 H, ArH), 7.77 (d, *J* = 9.0, 2.1 Hz, 1 H, ArH), 7.78 (d, *J* = 7.8 Hz, 2 H, ArH), 8.25 (d, *J* = 9.0 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 123.9 (s), 124.4 (d), 128.1 (2 d), 128.4 (2 d), 128.8 (2 d), 129.23 (d), 129.27 (2 d), 129.6 (2 d), 130.0 (2 d), 131.1 (s), 131.6 (d), 132.3 (d), 133.5 (d), 133.9 (s), 134.6 (d), 136.5 (s), 136.9 (s), 139.2 (s), 145.9 (s), 146.4 (s), 157.1 (s), 195.6 (s), 196.3 (s).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{29}H_{18}ClNO_2$ 447.1026; found: 447.1017.

3,4-Benzoyl-2-methylquinoline (11d)

Yield: 20 mg (19%); yellow crystals; mp 175–176 °C (EtOAc–hexane).

IR (KBr): 1660, 1595, 1320, 1290 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3 H, CH_3), 7.38 (t, *J* = 7.4 Hz, 2 H, ArH), 7.40 (t, *J* = 7.4 Hz, 2 H, ArH), 7.45 (t, *J* = 7.3 Hz, 1 H, ArH), 7.53–7.59 (m, 3 H, ArH), 7.69 (d, *J* = 7.4 Hz, 2 H, ArH), 7.71 (d, *J* = 7.4 Hz, 2 H, ArH), 7.78 (t, *J* = 7.3 Hz, 1 H, ArH), 8.16 (d, *J* = 7.3 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.4 (q), 122.9 (s), 125.7 (d), 127.2 (d), 128.66 (2 d), 128.69 (2 d), 129.2 (d), 129.8 (2 d), 130.0 (2 d), 130.8 (d), 130.9 (s), 134.1 (d), 134.4 (d), 136.7 (s), 136.9 (s), 144.4 (s), 147.7 (s), 155.1 (s), 196.0 (s), 196.7 (s).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{17}NO_2$: 351.1259; found: 351.1250.

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3,4-Benzoyl-2,6-dimethylquinoline (11e)

Yield: 18 mg (17%); yellow solid; mp 177–178 °C (EtOAc–hexane).

IR (KBr): 1670, 1595, 1450, 1380, 1290 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 2.58 (s, 3 H, CH_3), 7.31 (s, 1 H, ArH), 7.38 (t, *J* = 7.6 Hz, 4 H, ArH), 7.56 (t, *J* = 7.6 Hz, 2 H, ArH), 7.61 (d, *J* = 8.5 Hz, 1 H, ArH), 7.68 (d, *J* = 7.6 Hz, 2 H, ArH), 7.69 (d, *J* = 7.6 Hz, 2 H, ArH), 8.04 (d, *J* = 8.5 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.7 (q), 24.2 (q), 122.9 (s), 124.3 (d), 128.65 (2 d), 128.67 (2 d), 128.8 (d), 129.9 (2 d), 130.1 (2 d), 130.6 (s), 133.2 (d), 134.1 (d), 134.4 (d), 136.7 (s), 136.9 (s), 137.5 (s), 143.7 (s), 146.5 (s), 154.0 (s), 196.3 (s), 196.8 (s).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{25}H_{19}NO_2$: 365.1416; found: 365.1417.

3,4-Benzoyl-6-chloro-2-methylquinoline (11f)

Yield: 19 (18%); light yellow crystals; mp 213–214 °C (EtOAc–hexane).

IR (KBr): 1670, 1595, 1450, 1380, 1240 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3 H, CH_3), 7.40 (t, *J* = 7.7 Hz, 4 H, ArH), 7.54 (d, *J* = 2.0 Hz, 1 H, ArH), 7.55–7.62 (m, 2 H, ArH), 7.66 (d, *J* = 7.7 Hz, 4 H, ArH), 7.72 (dd, *J* = 9.0, 2.0 Hz, 1 H, ArH), 8.09 (d, *J* = 9.0 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.3 (q), 123.5 (s), 124.4 (d), 128.75 (2 d), 128.77 (2 d), 129.8 (2 d), 130.1 (2 d), 130.8 (d), 131.5 (s), 131.8 (d), 133.3 (s), 134.3 (d), 134.7 (d), 136.3 (s), 136.6 (s), 143.3 (s), 146.2 (s), 155.5 (s), 195.3 (s), 196.2 (s).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{16}ClNO_2$: 385.0870; found: 385.0862.

4-Benzoyl-3-cyano-6-methyl-2-phenylquinoline (11h)

Yield: 11 mg (7%); white crystals; mp 145–146 °C (EtOAc–hexane).

IR (KBr): 1670, 1545, 1450, 1345, 1230 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 7.41 (s, 1 H, ArH), 7.49–7.59 (m, 5 H, ArH), 7.70 (t, *J* = 7.8 Hz, 1 H, ArH), 7.74 (d, *J* = 8.5 Hz, 1 H, ArH), 7.88 (d, *J* = 7.8 Hz, 2 H, ArH), 8.00 (m, 2 H, ArH), 8.17 (d, *J* = 8.5 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.8 (q), 102.2 (s), 115.8 (s), 122.4 (s), 124.1 (s), 128.7 (2 d), 129.20 (2 d), 129.26 (2 d), 130.0 (d), 130.1 (3 d), 135.26 (s), 135.27 (d), 135.7 (d), 137.4 (s), 139.3 (s), 147.3 (s), 152.9 (s), 157.1 (s), 193.9 (s).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{16}N_2O$: 348.1263; found: 348.1269.

4-Benzoyl-6-chloro-3-cyano-2-phenylquinoline (11i)

Yield: 9 mg (6%); white needles; mp 211–212 °C (EtOAc–hexane).

IR (KBr): 1665, 1595, 1550, 1450, 1365, 1225 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (t, *J* = 7.4 Hz, 2 H, ArH), 7.51–7.61 (m, 3 H, ArH), 7.64 (d, *J* = 2.3 Hz, 1 H, ArH), 7.72 (t, *J* = 7.4 Hz, 1 H, ArH), 7.83 (dd, *J* = 9.1, 2.3 Hz, 1 H, ArH), 7.87 (d, *J* = 7.4 Hz, 2 H, ArH), 7.97–8.04 (m, 2 H, ArH), 8.22 (d, *J* = 9.1 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 103.3 (s), 115.4 (s), 122.9 (s), 124.2 (d), 128.8 (2 d), 129.2 (2 d), 129.4 (2 d), 130.2 (2 d), 130.5 (d), 131.9 (d), 134.3 (d), 134.9 (s), 135.0 (s), 135.6 (d), 136.9 (s), 147.0 (s), 152.7 (s), 158.1 (s), 192.9 (s).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_3ClN_2O$: 368.0716; found: 368.0725.

Copper(I)-Catalyzed Cyclization Reactions of 2-[(*E*)-Stilben-2-yl]aminofumarates 9j–n; Dimethyl Quinoline-2,3-dicarboxylate (10j) and Dimethyl 4-Benzoylquinoline-2,3-dicarboxylate (11j); Typical Procedure (Method B)

A mixture of 2-[(*E*)-stilben-2-yl]aminofumarate (**9j**; 104 mg, 0.31 mmol), CuCl (3 mg, 0.03 mmol), and NMP (66 mg, 0.67 mmol) in DMAc (2.5 mL) was stirred at 100 °C for 30 min under an O_2 atmosphere (1 atm). The reaction mixture was then diluted with EtOAc (50 mL), and the organic layer was washed with H_2O (3 × 50 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20 g, eluent: 1:8 EtOAc–hexane) followed by crystallization (EtOAc–hexane) to give **10j** (65 mg, 86%) and **11j** (9 mg, 8%).

Dimethyl Quinoline-2,3-dicarboxylate (10j)

Yield: 65 mg (86%); white crystals; mp 106–107 °C (EtOAc–hexane).

IR (KBr): 1730, 1445, 1270, 1200, 1135 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 3 H, OCH_3), 4.07 (s, 3 H, OCH_3), 7.69 (t, *J* = 7.9 Hz, 1 H, ArH), 7.88 (t, *J* = 7.9 Hz, 1 H, ArH), 7.95 (d, *J* = 7.9 Hz, 1 H, ArH), 8.22 (d, *J* = 7.9 Hz, 1 H, ArH), 8.78 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 52.9 (q), 53.2 (q), 122.3 (s), 127.0 (s), 128.6 (d), 128.7 (d), 129.9 (d), 132.5 (d), 139.6 (d), 148.1 (s), 150.5 (s), 165.6 (s), 167.1 (s).

Anal. Calcd for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.63; H, 4.55; N, 5.73.

Dimethyl 6-Methylquinoline-2,3-dicarboxylate (10k)

Yield: 59 mg (79%); white crystals; mp 109–110 °C (EtOAc–hexane).

IR (KBr): 1735, 1565, 1230, 1200, 1130 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.57 (s, 3 H, CH_3), 3.97 (s, 3 H, OCH_3), 4.05 (s, 3 H, OCH_3), 7.68 (s, 1 H, ArH), 7.69 (d, *J* = 9.0 Hz, 1 H, ArH), 8.10 (d, *J* = 9.0 Hz, 1 H, ArH), 8.65 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.7 (q), 52.9 (q), 53.2 (q), 122.5 (s), 127.2 (s), 127.3 (d), 129.5 (d), 134.8 (d), 138.7 (d), 139.1 (s), 146.7 (s), 149.5 (s), 165.8 (s), 167.2 (s).

Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.88; H, 5.07; N, 5.36.

Dimethyl 6-Chloroquinoline-2,3-dicarboxylate (10l)

Yield: 67 mg (87%); white crystals; mp 157–158 °C (EtOAc–hexane).

IR (KBr): 1730, 1450, 1275, 1140 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.98 (s, 3 H, OCH_3), 4.05 (s, 3 H, OCH_3), 7.79 (dd, *J* = 9.0, 2.3 Hz, 1 H, ArH), 7.91 (d, *J* = 2.3 Hz, 1 H, ArH), 8.14 (d, *J* = 9.0 Hz, 1 H, ArH), 8.66 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 53.0 (q), 53.3 (q), 123.4 (s), 127.1 (d), 127.7 (s), 131.4 (d), 133.4 (d), 134.8 (s), 138.4 (d), 146.4 (s), 150.6 (s), 165.2 (s), 166.8 (s).

Anal. Calcd for $C_{13}H_{10}ClNO_4$: C, 55.83; H, 3.60; N, 5.01. Found: C, 55.80; H, 3.63; N, 5.00.

Dimethyl 6,7-Dimethylquinoline-2,3-dicarboxylate (10m)

Yield: 85 mg (76%), white crystals; mp 121–122 °C (EtOAc–hexane).

IR (KBr): 1755, 1720, 1560, 1280, 1215, 1065 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 3.96 (s, 3 H, OCH_3), 4.04 (s, 3 H, OCH_3), 7.65 (s, 1 H, ArH), 7.96 (s, 1 H, ArH), 8.63 (s, 1 H, ArH).

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^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.1 (q), 20.7 (q), 52.8 (q), 53.1 (q), 121.5 (s), 125.7 (s), 127.7 (d), 129.1 (d), 138.3 (d), 139.2 (s), 143.5 (s), 147.2 (s), 149.6 (s), 165.9 (s), 167.4 (s).

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.89; H, 5.53; N, 5.08.

Dimethyl 6,8-Dimethylquinoline-2,3-dicarboxylate (10n)

Yield: 55 mg (73%), white crystals; mp 128–129 °C (EtOAc–hexane).

IR (KBr): 1725, 1570, 1360, 1095, 970 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.52 (s, 3 H, CH_3), 2.78 (s, 3 H, CH_3), 3.97 (s, 3 H, OCH_3), 4.04 (s, 3 H, OCH_3), 7.51 (s, 1 H, ArH), 7.54 (s, 1 H, ArH), 8.64 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.7 (q), 21.6 (q), 52.7 (q), 52.9 (q), 121.5 (s), 125.3 (d), 127.2 (s), 134.9 (d), 137.7 (s), 138.5 (s), 138.9 (d), 145.9 (s), 148.7 (s), 165.8 (s), 167.8 (s).

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.92; H, 5.56; N, 5.09.

Dimethyl 4-Benzoylquinoline-2,3-dicarboxylate (11j)

Yield: 9 mg (8%); white needles; mp 115–116 °C (EtOAc–hexane).

IR (KBr): 1725, 1670, 1435, 1235, 1125 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3 H, OCH_3), 4.07 (s, 3 H, OCH_3), 7.47 (t, *J* = 7.6 Hz, 2 H, ArH), 7.61 (t, *J* = 7.9 Hz, 1 H, ArH), 7.63 (t, *J* = 7.6 Hz, 1 H, ArH), 7.67 (d, *J* = 7.9 Hz, 1 H, ArH), 7.78 (d, *J* = 7.6 Hz, 2 H, ArH), 7.88 (t, *J* = 7.9 Hz, 1 H, ArH), 8.31 (d, *J* = 7.9 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 52.9 (q), 53.4 (q), 121.2 (s), 124.6 (s), 126.1 (d), 129.0 (2 d), 129.4 (2 d), 129.6 (d), 130.5 (d), 132.4 (d), 134.4 (d), 136.3 (s), 147.6 (s), 148.2 (s), 149.3 (s), 165.2 (s), 166.3 (s), 194.6 (s).

Anal. Calcd for $C_{20}H_{15}NO_5$: C, 68.76; H, 4.33; N, 4.01. Found: C, 68.70; H, 4.31; N, 4.02.

Dimethyl 4-Benzoyl-6-methylquinoline-2,3-dicarboxylate (11k)

Yield: 14 mg (13%); white solid; mp 148–149 °C (EtOAc–hexane).

IR (KBr): 1730, 1565, 1440, 1310, 1260 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 3.64 (s, 3 H, OCH_3), 4.05 (s, 3 H, OCH_3), 7.42 (s, 1 H, ArH), 7.48 (t, *J* = 7.5 Hz, 2 H, ArH), 7.63 (t, *J* = 7.5 Hz, 1 H, ArH), 7.71 (dd, *J* = 8.7, 1.8 Hz, 1 H, ArH), 7.78 (d, *J* = 7.5 Hz, 2 H, ArH), 8.20 (d, *J* = 8.7 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.9 (q), 52.8 (q), 53.4 (q), 121.3 (s), 124.7 (d), 129.0 (2 d), 129.4 (2 d), 130.2 (d), 134.4 (d), 134.8 (d), 136.3 (s), 140.4 (2 s), 146.3 (s), 147.1 (s), 148.1 (s), 165.3 (s), 166.4 (s), 194.8 (s).

Anal. Calcd for $C_{21}H_{17}NO_5$: C, 69.41; H, 4.72; N, 3.85. Found: C, 69.29; H, 4.74; N, 3.80.

Dimethyl 4-Benzoyl-6-chloroquinoline-2,3-dicarboxylate (11l)

Yield: 11 mg (11%); white solid; mp 143–144 °C (EtOAc–hexane).

IR (KBr): 1730, 1670, 1580, 1305, 1255, 1130 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 3 H, OCH_3), 4.06 (s, 3 H, OCH_3), 7.49 (t, *J* = 7.6 Hz, 2 H, ArH), 7.65 (t, *J* = 7.6 Hz, 1 H, ArH), 7.65 (d, *J* = 2.2 Hz, 1 H, ArH), 7.77 (d, *J* = 7.6 Hz, 2 H, ArH), 7.82 (dd, *J* = 9.1, 2.2 Hz, 1 H, ArH), 8.25 (d, *J* = 9.1 Hz, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 53.0 (q), 53.5 (q), 122.3 (s), 124.8 (d), 125.3 (s), 129.1 (2 d), 129.4 (2 d), 132.0 (d), 133.5 (d), 134.7 (d), 136.0 (s), 136.1 (s), 146.0 (s), 147.0 (s), 149.2 (s), 164.9 (s), 166.0 (s), 193.8 (s).

Anal. Calcd for $C_{20}H_{14}ClNO_5$: C, 62.59; H, 3.68; N, 3.65. Found: C, 62.56; H, 3.74; N, 3.68.

Dimethyl 4-Benzoyl-6,7-dimethylquinoline-2,3-dicarboxylate (11m)

Yield: 17 mg (11%); white needles; mp 146–147 °C (EtOAc–hexane).

IR (KBr): 1670, 1590, 1435, 1210 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 3.62 (s, 3 H, OCH_3), 4.05 (s, 3 H, OCH_3), 7.38 (s, 1 H, ArH), 7.46 (t, *J* = 7.6 Hz, 2 H, ArH), 7.62 (t, *J* = 7.6 Hz, 1 H, ArH), 7.77 (d, *J* = 7.6 Hz, 2 H, ArH), 8.06 (s, 1 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.4 (q), 20.6 (q), 52.7 (q), 53.3 (q), 120.3 (s), 123.2 (s), 125.0 (d), 128.9 (2 d), 129.3 (2 d), 129.7 (d), 134.3 (d), 136.4 (s), 140.4 (s), 143.6 (s), 146.88 (s), 146.94 (s), 148.3 (s), 165.4 (s), 166.6 (s), 194.9 (s).

Anal. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71. Found: C, 69.97; H, 5.08; N, 3.69.

Dimethyl 4-Benzoyl-6,8-dimethylquinoline-2,3-dicarboxylate (11n)

Yield: 15 mg (10%); white crystals; mp 121–122 °C (EtOAc–hexane).

IR (KBr): 1725, 1670, 1445, 1235, 1165 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 2.83 (s, 3 H, CH_3), 3.63 (s, 3 H, OCH_3), 4.03 (s, 3 H, OCH_3), 7.24 (s, 1 H, ArH), 7.46 (t, *J* = 7.5 Hz, 2 H, ArH), 7.55 (s, 1 H, ArH), 7.61 (t, *J* = 7.5 Hz, 1 H, ArH), 7.76 (d, *J* = 7.5 Hz, 2 H, ArH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.9 (q), 21.9 (q), 52.7 (q), 53.1 (q), 120.2 (s), 122.6 (d), 124.7 (s), 128.9 (2 d), 129.3 (2 d), 134.2 (d), 135.0 (d), 136.5 (s), 138.4 (s), 139.8 (s), 145.6 (s), 147.42 (s), 147.46 (s), 165.3 (s), 167.0 (s), 195.2 (s).

Anal. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71. Found: C, 70.02; H, 5.08; N, 3.67.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1378870.

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