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Manganese(III) acetate mediated oxidative radical cyclizations of α-substituted *N*-[(*E*)-stilben-2-yl]acetamides

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ABSTRACT

A synthetic method of 3-substituted 2-quinolinones from readily available α-substituted *N*-[(*E*)-stilben-2-yl]acetamides have been developed. α-Carbonylalkyl radical, produced by the manganese(III) acetate oxidation of *N*-[(*E*)-stilben-2-yl]acetamides, undergoes an intramolecular *6-exo-dig* cyclization onto the C=C bond efficiently and 2-quinolinones was produced. A variety of functional groups, including benzoyl, acetyl, cyano, and ethoxycarbonyl groups, are compatible with the reaction conditions. Under Mn(II)/Co(II)/O_2 conditions, these *N*-[(*E*)-stilben-2-yl]acetamides were also converted into the corresponding 2-quinolinones effectively and a catalytic amount of manganese(II) acetate was used.

1. Introduction

The addition of carbon-centered radicals to alkenes is an effective tool for the formation of carbon–carbon bonds, and many new methods proceeding through radical reactions have been developed for the synthesis of useful and structure diverse organic molecules.[1,2] Metal salts [Mn(III), Ce(IV), and Ag(I)] can readily undergo a ligand-exchange reaction with α-dicarbonyl compound to produce metal-enolate complex, which then undergoes one-electron oxidation to produce *a*-dicarbonylalkyl radical. This α-dicarbonylalkyl radical can undergo efficient oxidative addition to the C=C bond. The metal salts mediated oxidative radical reactions have been explored extensively, and they have become valuable methods for the formation of highly functionalized compounds.[2–5] Among them, the oxidative intramolecular cyclization reaction is one of the efficient methods for the synthesis of cyclic compounds.

Quinolinones have attracted considerable attention for their known biological activities and pharmacological properties, which include antiviral (HIV) activities,[6a–c] inotropic,[6d] $5HT_3$ receptor antagonists,[6e] farnesyl transferase inhibitors,[6f] and maxi-K channel opening agents.[6g] Thus, considerable efforts have been made toward the development of efficient methods for their syntheses. In addition to classic base-catalyzed Friedländer reaction and acid-catalyzed Knorr reaction,[7] several alternative methods have been employed in the synthesis of 2-quinolinones including radical cyclization of anilides,[8] cyclization of Baylis-Hillman adducts,[9] Pd-catalyzed cyclocarbonylation of 2-alkenylanilines,[10] Pd-catalyzed amidation of 3-arylacrylamides,[11] Ru-catalyzed oxidative cyclization of 2-(3-hydroxypropyl)aniline,[12] and Ru-mediated addition-cyclization between aminophenylboronates and enones.[13] Although a number of methods are available as cited above, the search for newer methods for 2-quinolinone synthesis is continuously being pursued. As part of our study on the development of new routes to heterocyclic systems,[14–17] we now report a manganese(III) mediated synthesis of 3-substituted 2-quinolinones from α-substituted *N*-[(*E*)-stilben-2-yl]acetamides.

2. Results and discussion

Our studies commenced with the readily available 2-ethoxycarbonyl-*N*-[(*E*)-stilben-2-yl]acetamide **1aa** (R^1=CO_2Et, R^2=H, R^3=H, R^4=TMBn), which was prepared by the acylation of (*E*)-stilben-2-ylamine with ethyl malonyl chloride (see Supplementary data). With this acetamide **1aa** in hand, we first examined the radical reaction of **1aa** with manganese(III) acetate under various reaction conditions (Table 1). The reaction of **1aa** and manganese(III) acetate (4 equiv) was carried out in DCE at 70 °C under a nitrogen atmosphere until **1aa** was completely consumed (7 h). The cyclization product **2a** was produced exclusively in 61% yield and the expected 4-benzyl substituted 2-quinolinone **3aa**, derived from the Mn(III) mediated oxidative elimination of radical intermediate **7aa** followed by double bond migration, was not

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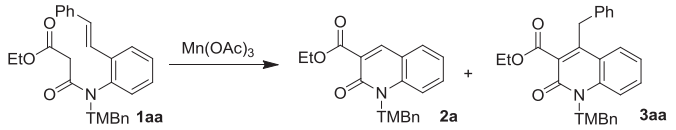
Table 1
Optimization of reaction conditions with 2-ethoxycarbonyl-*N*-[(*E*)-stilben-2-yl] acetamide **1aa**[18a]



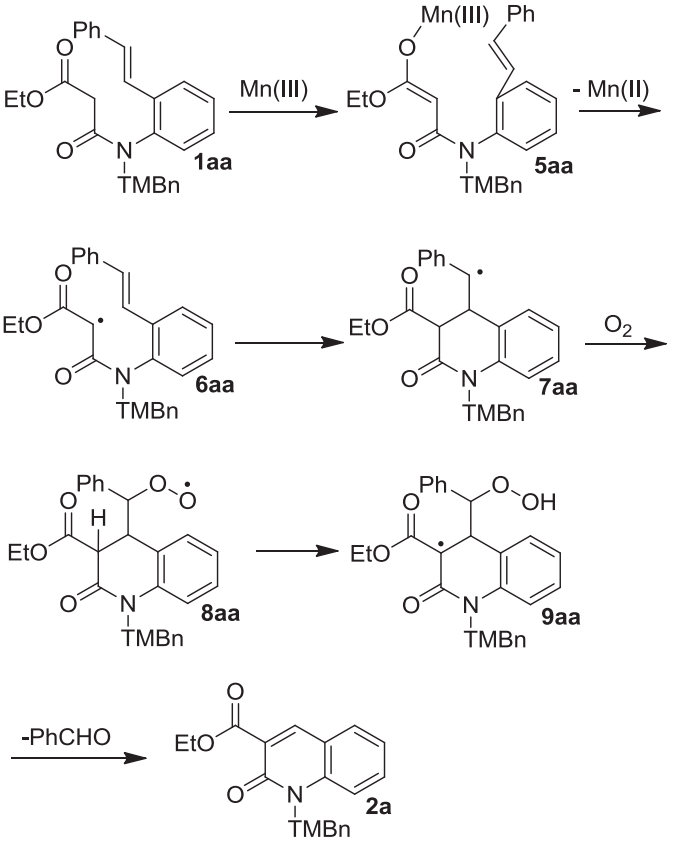
	Solvent		Temp	t (h)	Product (Yield (%))[a]
1	DCE	N_2	70 °C	7	**2a** (61)
2	DCE	Air	70 °C	7	**2a** (84)
3	DCE	O_2	70 °C	7	**2a** (86)
4	HOAc	O_2	70 °C	1	**2a** (74)
5	CH_3CN	O_2	70 °C	7	**2a** (77)
6	C_6H_6	O_2	70 °C	7	**2a** (79)
7	DME	O_2	70 °C	24	**2a** (76)
8	1,4-dioxane	O_2	70 °C	24	**2a** (67)[b]
9[c]	DCE	Air	70 °C	7	**2a** (nd)

[a] Yield of isolated product.
[b] Based on 85% conversion of starting **1aa**.
[c] TEMPO (2 equiv) was added. DCE=1,2-dichloroethane. DME=1,2-dimeth oxyethane. TEMPO=2,2,6,6-tetramethylpiperidinyloxy.

observed (Table 1, entry 1). It is noteworthy that the yield can be improved to 84% under air instead of a nitrogen atmosphere (entry 2). Under an oxygen atmosphere, 2-quinolinone **2a** was formed in a slightly higher yield (entry 3). In attempt to investigate the range of solvents compatible with this reaction, reaction between **1aa** and manganese(III) acetate was next performed in other solvents. In acetic acid, it proceeded much faster (1 h), however, a lower yield (74%) of **2a** was obtained (entry 4). In acetonitrile and benzene, it required 7 h at 70 °C to go to completion and **2a** was produced in 77% and 79% yields, respectively (entries 5 and 6). In DME and 1,4-dioxane, the desired product **2a** was produced in lower yields (entries 7 and 8).

To gain insight into the possible reaction mechanism, the reaction of **1aa** with manganese(III) acetate was then carried out in the presence of TEMPO (2 equiv), an effective radical scavenger (entry 9). No trace of **2a** was detected, indicating that this reaction presumably involves a radical process. Since dioxygen plays an important role in this reaction, a possible mechanism for the formation of 2-quinolinone **2a** is outlined in Scheme 1. Initiation occurs with the chelation of manganese(III) acetate by the enolate oxygen of **1aa** to produce Mn(III)-complex **5aa**. Subsequently, homolytic cleavage of Mn(III)-complex **5aa** takes place to generate radical **6aa** and manganese(II) acetate. This resulting radical intermediate **6aa** undergoes a 6-*exo*-*trig* cyclization to give radical **7aa**, which is then trapped by O_2 to give peroxy radical intermediate **8aa**. Finally, hydroperoxide **9aa**, formed by the intramolecular hydrogen atom abstraction of **8aa**, undergoes fragmentation to produce 2-quinolinone **2a** and benzaldehyde.[18a]

With these optimized reaction conditions in hand (Table 1, entry 2, Method A), we next explored the scope and limitations of this process, and the results are summarized in Table 2. In all cases, *N*-[(*E*)-stilben-2-yl]acetamides **1** were converted to the corresponding 2-quinolinones **2** effectively. By varying substituents R^1 of acetamides **1**, it was shown that several useful functional groups, including ethoxycarbonyl, acetyl, cyano, and benzoyl groups, were tolerated toward the reaction conditions. Substrates bearing different functional groups (R^2) on the aniline moiety, including 4-chloro, 4-fluoro, 4-methoxylcarbonyl, 4-methyl, and 4,5-dimethyl, regardless if they were electronic-withdrawing or -donating, all worked well in moderate to good yields (entries 1–6). However, with **1ga** (R^2=4,6-dimethyl) bearing a methyl group on the 6-position of aniline fragment, it proceeded much slower (24 h) and **2g** was obtained in slightly lower yield (entry 7). This is presumably due to the steric effect between 6-Me and *N*-TMBn groups.



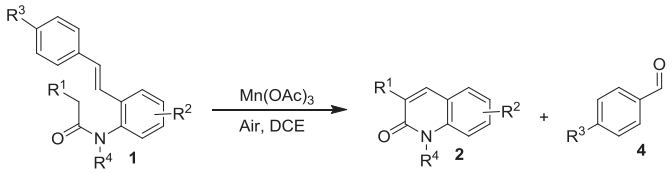
Scheme 1.

Indeed, by decreasing the size of R^4 group, the reaction time for **1ha** (R^4=Bn) was shorten to 5 h and **2h** was afforded in 76% yield (entry 8). With unprotected amides **1ia**–**ka** (R^4=H), the desired oxidative cyclization products **2i**–**k** were also obtained in acceptable yields (entries 9–11). A variety of aryl substituents (R^3) at the terminal of C=C, such as methyl, methoxy, chloro, and cyano groups, was well tolerated under the reaction conditions and **2a** was obtained in comparable yields (entries 12–15). This manganese(III) acetate mediated oxidative radical reaction of *N*-[(*E*)-stilben-2-yl]acetamides **1** provides a straightforward method for the synthesis of 3-substituted 2-quinolinones **2**. The traditional harshly basic and acidic conditions can be avoided.

A α-carbonylalkyl radical, produced by the Mn(II)/Co(II)/O_2 conditions, undergoes efficient addition to the C=C bond.[19] In this reaction, Mn(III) can be regenerated from Mn(II) by the oxidation of Co(III)-dioxygen complex and a catalytic amount of Mn(II) is used. Due to the much lower cost of manganese(II) acetate and cobalt(II) acetate, we next examined the radical cyclization reaction of *N*-[(*E*)-stilben-2-yl]acetamides **1** under the Mn(II)/Co(II)/O_2 conditions to develop greener reaction conditions.

When *N*-[(*E*)-stilben-2-yl]acetamide **1aa** was reacted with manganese(II) acetate (0.3 equiv) and cobalt(II) acetate (2 equiv) in acetic acid at 80 °C under an oxygen atmosphere, the target cyclization product **2a** was obtained in 68% yield (Table 3, entry 1). The cobalt(II) acetate loading can be decreased to 0.5 equiv without lowering the product yield (entry 2). Under air atmosphere, it proceeded much slower (1.5 h) and 2-quinolinone **2a** was formed in 61% yield (entry 3). Other acetamides **1** were also employed to examine the scope of this oxidative radical reaction using the Mn(II)/Co(II)/O_2 conditions (Table 3, Method B). In all cases, *N*-[(*E*)-stilben-2-yl]acetamides **1** were successfully converted to the corresponding 2-quinolinones **2**.

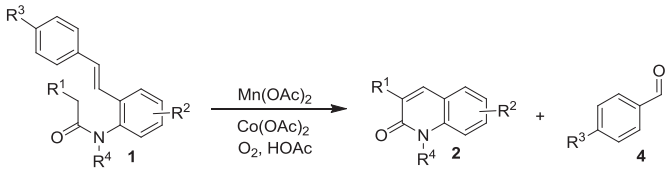
Table 2
Reactions of *N*-[(*E*)-stilben-2-yl]acetamides **1** under Mn(III)/DCE conditions (Method A)[a]



		R^1	R^2	R^3	R^4	t (h)	Product (Yield (%)[b]
1	**1aa**	CO_2Et	H	H	TMBn	7	**2a** (84)[18a]
2	**1ba**	CO_2Et	4-Cl	H	TMBn	10	**2b** (79)[18a]
3	**1ca**	CO_2Et	4- F	H	TMBn	16	**2c** (77)[18a]
4	**1da**	CO_2Et	4- CO_2Me	H	TMBn	16	**2d** (84)[18a]
5	**1ea**	CO_2Et	4-Me	H	TMBn	7	**2e** (88)[18a]
6	**1fa**	CO_2Et	4,5-diMe	H	TMBn	9	**2f** (82)[18a]
7	**1ga**	CO_2Et	4,6-diMe	H	TMBn	24	**2g** (78)[18a]
8	**1ha**	CO_2Et	4.6-diMe	H	Bn	5	**2h** (76)[18a]
9	**1ia**	CO_2Et	4-Cl	H	H	9	**2i** (61)[18a]
10	**1ja**	CO_2Et	4-Me	H	H	7	**2j** (68)[18a]
11	**1ka**	CO_2Et	4,5-diMe	H	H	7	**2k** (65)[18a]
12	**1ab**	CO_2Et	H	Me	TMBn	5	**2a** (87)[18a]
13	**1ac**	CO_2Et	H	OMe	TMBn	9	**2a** (87)[18b]
14	**1ad**	CO_2Et	H	Cl	TMBn	5	**2a** (89)[18a]
15	**1ae**	CO_2Et	H	CN	TMBn	7	**2a** (89)[18c]
16	**1la**	COMe	H	H	TMBn	1	**2l** (61)[18a]
17	**1ma**	COMe	4-Me	H	TMBn	1.5	**2m** (64)[18a]
18	**1na**	COMe	4-Cl	H	TMBn	1.5	**2n** (66)[18a]
19	**1oa**	CN	H	H	TMBn	13	**2o** (73)[18a]
20	**1pa**	CN	4-Me	H	TMBn	13	**2p** (76)[18a]
21	**1qa**	CN	4-Cl	H	TMBn	16	**2q** (75)[18a]
22	**1ra**	COPh	H	H	TMBn	6	**2r** (74)[18a]
23	**1sa**	COPh	4-Cl	H	TMBn	7	**2s** (70)[18a]
24	**1ta**	COPh	4- F	H	TMBn	9	**2t** (73)[18a]
25	**1ua**	COPh	4-Me	H	TMBn	4	**2u** (78)[18a]
26	**1va**	COPh	4,5-diMe	H	TMBn	3	**2v** (72)[18a]
27	**1wa**	COPh	4,6-diMe	H	TMBn	8	**2w** (53)[18a]

[a] The reaction was carried out using 0.34 mmol of **1** with 1.36 mmol of $Mn(OAc)_3$ in 5 mL of DCE at 70 °C under air atmosphere.
[b] Yield of isolated product. DCE=1,2-dichloroethane. TMBn=2,4,6-trimethyl benzyl.

Table 3
Reactions of *N*-[(*E*)-stilben-2-yl]acetamides **1** under Mn(II)/Co(II) conditions (Method B)[a,18a]



		R^1	R^2	R^3	R^4	t (h)	Product (Yield (%)[b]
1	**1aa**	CO_2Et	H	H	TMBn	0.5	**2a** (68)[c]
2	**1aa**	CO_2Et	H	H	TMBn	0.5	**2a** (69)
3	**1aa**	CO_2Et	H	H	TMBn	1.5	**2a** (61)[d]
4	**1ba**	CO_2Et	4-Cl	H	TMBn	0.5	**2b** (67)
5	**1ca**	CO_2Et	4- F	H	TMBn	0.5	**2c** (66)
6	**1ea**	CO_2Et	4-Me	H	TMBn	0.5	**2e** (65)
7	**1fa**	CO_2Et	4,5-diMe	H	TMBn	0.5	**2f** (67)
8	**1ga**	CO_2Et	4,6-diMe	H	TMBn	0.5	**2g** (53)
9	**1oa**	CN	H	H	TMBn	9	**2o** (65)
10	**1pa**	CN	4-Me	H	TMBn	11	**2p** (65)
11	**1qa**	CN	4-Cl	H	TMBn	9	**2q** (66)
12	**1ra**	COPh	H	H	TMBn	0.5	**2r** (73)
13	**1sa**	COPh	4-Cl	H	TMBn	0.5	**2s** (74)
14	**1ta**	COPh	4- F	H	TMBn	0.5	**2t** (73)
15	**1ua**	COPh	4-Me	H	TMBn	0.5	**2u** (75)
16	**1va**	COPh	4,5-diMe	H	TMBn	0.5	**2v** (72)
17	**1wa**	COPh	4,6-diMe	H	TMBn	0.5	**2w** (70)

[a] The reaction was carried out using 0.34 mmol of **1** with 0.10 mmol of $Mn(OAc)_2$ and 0.17 mmol of $Co(OAc)_2$ in 5 mL of acetic acid at 80 °C under O_2 atmosphere.
[b] Yield of isolated product.
[c] $Co(OAc)_2$ (2 equiv) was used.
[d] The reaction was performed under air atmosphere. TMBn=2,4,6-trimethyl benzyl.

3. Conclusion

The syntheses of 3-substituted 2-quinolinones from α-substituted *N*-[(*E*)-stilben-2-yl]acetamides are described. α-Carbonylalkyl radical can be produced by the manganese(III) acetate oxidation of *N*-[(*E*)-stilben-2-yl]acetamides, and, which undergo an intramolecular *6-exo-dig* cyclization onto the C=C bond efficiently. This reaction provides a synthetically useful method for the synthesis of 3-substituted 2-quinolinones. Compared to the traditional methods, this process has the advantages such as mild reaction conditions, high reaction yields and tolerance of a broad range of functional groups, including ethoxycarbonyl, acetyl, benzoyl, and cyano groups. Under Mn(II)/Co(II)/O_2 conditions, these *N*-[(*E*)-stilben-2-yl]acetamides were also converted into the corresponding 2-quinolinones effectively. In these conditions, a catalytic amount of manganese(II) acetate was used.

4. Experimental section

4.1. General

Melting points are uncorrected. Infrared 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 thin-layer chromatography 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).

4.1.1. Typical experimental procedure for the manganese(III) mediated radical cyclization reactions (Method A). A mixture of 2-ethoxycarbonyl-*N*-[(*E*)-stilben-2-yl]acetamides (**1aa**; 150 mg, 0.34 mmol) and manganese(III) acetate (366 mg, 1.36 mmol) in 1,2-dichloroethane (5 mL) was stirred at 70 °C for 7 h under an atmosphere of air. The reaction mixture was then diluted with ethyl acetate (50 mL), washed with saturated aqueous sodium bisulfite (3×50 mL), and water (3×50 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20 g) (eluted with 1:8 ethyl acetate–hexane) followed by crystallization (ethyl acetate–hexane) to give **2a** (100 mg, 84%).

4.1.2. Typical experimental procedure for the Mn(II)/Co(II) catalyzed radical cyclization reactions (Method B). A mixture of 2-ethoxycarbonyl-*N*-[(*E*)-stilben-2-yl]acetamide (**1aa**; 150 mg, 0.34 mmol), manganese(II) acetate (27 mg, 0.10 mmol), and cobalt(II) acetate (42 mg, 0.17 mmol) in acetic acid (5 mL) was stirred at 80 °C for 0.5 h under an oxygen atmosphere (1 atm). The reaction mixture was then diluted with ethyl acetate (50 mL), washed with saturated aqueous sodium bisulfite (1×50 mL), and water (3×50 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20 g) (eluted with 1:8 ethyl acetate–hexane) followed by crystallization (ethyl acetate–hexane) to give **2a** (82 mg, 69%).

4.1.3. 3-Ethoxycarbonyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2a***. Light yellow crystals; mp 127–128 °C (ethyl

acetate–hexane); IR (KBr) 1745, 1650, 1565, 1450, 1210 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, J=7.1 Hz, 3H, CH_3), 2.18 (s, 6H, 2× CH_3), 2.22 (s, 3H, CH_3), 4.44 (q, J=7.1 Hz, 2H, OCH_2), 5.67 (s, 2H, NCH_2), 6.79 (s, 2H, ArH), 7.00 (d, J=8.7 Hz, 1H, ArH), 7.16 (t, J=7.5 Hz, 1H, ArH), 7.39 (ddd, J=8.7, 7.5, 1.4 Hz, 1H, ArH), 7.61 (dd, J=7.5, 1.4 Hz, 1H, ArH), 8.40 (s, 1H, 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.

4.1.4. 6-Chloro-3-ethoxycarbonyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2b***. Light yellow needles; mp 171–172 °C (ethyl acetate–hexane); IR (KBr) 1705, 1660, 1485, 1290, 1255 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, J=7.1 Hz, 3H, CH_3), 2.17 (s, 6H, 2× CH_3), 2.23 (s, 3H, CH_3), 4.44 (q, J=7.1 Hz, 2H, OCH_2), 5.64 (s, 2H, NCH_2), 6.79 (s, 2H, ArH), 6.94 (d, J=9.1 Hz, 1H, ArH), 7.33 (dd, J=9.1, 2.5 Hz, 1H, ArH), 7.58 (d, J=2.5 Hz, 1H, ArH), 8.29 (s, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3 (q), 20.3 (2× q), 20.7 (q), 42.5 (t), 61.8 (t), 116.6 (d), 120.0 (s), 123.8 (s), 127.9 (s), 129.0 (d), 129.9 (s), 130.3 (2× d), 132.5 (d), 135.9 (2× s), 136.9 (s), 139.0 (s), 142.3 (d), 159.3 (s), 164.6 (s); Anal. Calcd for $C_{22}H_{22}ClNO_3$: C, 68.83; H 5.78; N, 3.65. Found: C, 68.90; H, 5.83; N, 3.64.

4.1.5. 3-Ethoxycarbonyl-6-fluoro-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2c***. Light yellow needles; mp 136–137 °C (ethyl acetate–hexane); IR (KBr) 1700, 1655, 1570, 1255, 1235 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, J=7.1 Hz, 3H, CH_3), 2.17 (s, 6H, 2× CH_3), 2.23 (s, 3H, CH_3), 4.44 (q, J=7.1 Hz, 2H, OCH_2), 5.66 (s, 2H, NCH_2), 6.80 (s, 2H, ArH), 6.97 (dd, J=9.4, 4.3 Hz, 1H, ArH), 7.13 (ddd, J=9.4, 8.0, 2.9 Hz, 1H, ArH), 7.28 (dd, J=8.0, 2.9 Hz, 1H, ArH), 8.30 (s, 1H, CH). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3 (q), 20.3 (2× q), 20.7 (q), 42.6 (t), 61.7 (t), 114.7 (dd, J_{C-F}=22.1 Hz), 116.9 (dd, J_{C-F}=8.0 Hz), 119.8 (d, J_{C-F}=9.1 Hz), 120.5 (dd, J_{C-F}=23.1 Hz), 124.0 (s), 130.0 (s), 130.3 (2× d), 135.9 (2× s), 136.8 (s), 137.2 (s), 142.4 (dd, J_{C-F}=2.0 Hz), 157.6 (d, J_{C-F}=243.5 Hz), 159.3 (s), 164.7 (s). Anal. Calcd for $C_{22}H_{22}FNO_3$: C, 71.92; H, 6.04; N, 3.81. Found: C, 71.92; H, 6.16; N, 3.78.

4.1.6. 3-Ethoxycarbonyl-6-methoxycarbonyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2d***. White crystals; mp 209–210 °C (ethyl acetate–hexane); IR (KBr) 1715, 1670, 1625, 1300, 1210 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (t, J=7.2 Hz, 3H, CH_3), 2.18 (s, 6H, 2× CH_3), 2.22 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 4.44 (q, J=7.2 Hz, 2H, OCH_2), 5.67 (s, 2H, NCH_2), 6.79 (s, 2H, ArH), 7.04 (d, J=9.0 Hz, 1H, ArH), 8.02 (dd, J=9.0, 1.8 Hz, 1H, ArH), 8.32 (d, J=1.8 Hz, 1H, ArH), 8.44 (s, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3 (q), 20.3 (2× q), 20.7 (q), 42.6 (t), 52.3 (q), 61.7 (t), 115.2 (d), 118.5 (s), 123.3 (s), 124.3 (s), 129.8 (s), 130.3 (2× d), 132.3 (d), 133.0 (d), 135.8 (2× s), 136.9 (s), 143.3 (s), 143.7 (d), 159.6 (s), 164.4 (s), 165.7 (s) ppm; Anal. Calcd for $C_{24}H_{25}NO_5$: C, 70.74; H, 6.18; N, 3.44. Found: C, 70.77; H, 6.21; N, 3.40.

4.1.7. 3-Ethoxycarbonyl-6-methyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2e***. Light yellow needles; mp 114–115 °C (ethyl acetate–hexane); IR (KBr) 1700, 1655, 1570, 1300, 1225 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, J=7.1 Hz, 3H, CH_3), 2.17 (s, 6H, 2×CH_3), 2.22 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.43 (q, J=7.1 Hz, 2H, OCH_2), 5.65 (s, 2H, NCH_2), 6.78 (s, 2H, ArH), 6.90 (d, J=8.7 Hz, 1H, ArH), 7.21 (dd, J=8.7, 2.1 Hz, 1H, ArH), 7.39 (s, 1H, ArH), 8.34 (s, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3 (q), 20.3 (2× q), 20.4 (q), 20.7 (q), 42.4 (t), 61.5 (t), 115.0 (d), 119.1 (s), 122.4 (s), 129.9 (d), 130.2 (2× d), 130.4 (s), 132.0 (s), 134.0 (d), 135.9 (2× s), 136.5 (s), 138.7 (s), 143.6 (d), 159.6 (s), 165.1 (s); Anal. Calcd for $C_{23}H_{25}NO_3$: C, 76.01; H, 6.93; N, 3.85. Found: C, 76.02; H, 6.93; N, 3.85.

4.1.8. 3-Ethoxycarbonyl-6,7-dimethyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2f***. White needles; mp 141–142 °C (ethyl acetate–hexane); IR (KBr) 1695, 1660, 1560, 1460, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.42 (t, J=7.1 Hz, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.21 (s, 6H, 2× CH_3), 2.22 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 4.42 (q, J=7.1 Hz, 2H, OCH_2), 5.63 (s, 2H, NCH_2), 6.79 (s, 2H, ArH), 6.83 (s, 1H, ArH), 7.33 (s, 1H, ArH), 8.34 (s, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3 (q), 18.9 (q), 20.3 (2× q), 20.7 (q), 21.0 (q), 42.2 (t), 61.4 (t), 116.1 (d), 117.3 (s), 121.1 (s), 130.1 (2× d), 130.2 (d), 130.6 (s), 131.4 (s), 136.0 (2× s), 136.5 (s), 139.2 (s), 142.8 (s), 143.6 (d), 159.7 (s), 165.3 (s); Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; N, 3.70. Found: C, 76.33; H, 7.18; N, 3.68.

4.1.9. 3-Ethoxycarbonyl-6,8-dimethyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2g***. Yellow oils; IR (Neat) 1740, 1660, 1570, 1280, 1235 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2) δ 1.32 (t, J=7.1 Hz, 3H, CH_3), 2.03 (s, 6H, 2× CH_3), 2.21 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 4.26 (q, J=7.1 Hz, 2H, OCH_2), 5.30 (s, 2H, NCH_2), 6.75 (s, 2H, ArH), 7.29 (s, 1H, ArH), 7.30 (s, 1H, ArH), 8.21 (s, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.2 (q), 20.2 (q), 20.3 (2× q), 20.7 (q), 23.2 (q), 49.8 (t), 61.3 (t), 121.1 (s), 122.5 (s), 124.7 (s), 128.6 (d), 129.7 (2× d), 130.9 (s), 132.2 (s), 136.2 (s), 136.3 (2× s), 138.7 (d), 141.9 (s), 143.9 (d), 160.6 (s), 164.7 (s); HMRS (EI): calcd for $C_{24}H_{27}NO_3$ 377.1991; found 377.1984.

4.1.10. 1-Benzyl-3-ethoxycarbonyl-6,8-dimethylquinolin-2(1H)-one ***2h***. Light yellow needles; mp 101–102 °C (ethyl acetate–hexane); IR (KBr) 1695, 1660, 1565, 1450, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.40 (t, J=7.1 Hz, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 4.41 (q, J=7.1 Hz, 2H, OCH_2), 5.71 (brs, 2H, NCH_2), 7.05 (d, J=7.3 Hz, 2H, ArH), 7.16–7.23 (m, 2H, ArH), 7.24–7.30 (m, 2H, ArH), 7.31 (s, 1H, ArH), 8.39 (s, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3 (q), 20.1 (q), 23.8 (q), 49.7 (t), 61.5 (t), 121.0 (s), 121.9 (s), 124.4 (s), 125.5 (2× d), 126.7 (d), 128.7 (2× d), 129.4 (d), 132.4 (s), 138.2 (s), 139.7 (d), 140.1 (s), 145.1 (d), 160.6 (s), 165.1 (s); Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.26; H, 6.33; N, 4.15.

4.1.11. 6-Chloro-3-ethoxycarbonylquinolin-2(1H)-one ***2i***. White needles; mp 276–277 °C (ethyl acetate–hexane); IR (KBr) 1685, 1555, 1480, 1290, 1195 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.29 (t, J=7.1 Hz, 3H, CH_3), 4.27 (q, J=7.1 Hz, 2H, OCH_2), 7.33 (d, J=8.8 Hz, 1H, ArH), 7.64 (dd, J=8.8, 2.4 Hz, 1H, ArH), 7.95 (d, J=2.4 Hz, 1H, ArH), 8.45 (s, 1H, CH), 12.17 (brs, 1H, NH); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 14.1 (q), 60.9 (t), 117.0 (d), 118.8 (s), 124.7 (s), 126.0 (s), 128.2 (d), 132.4 (d), 138.7 (s), 142.3 (d), 158.2 (s), 164.2 (s); Anal. Calcd for $C_{12}H_{10}ClNO_3$: C, 57.27; H, 4.01; N, 5.57. Found: C, 56.98; H, 4.08; N, 5.57.

4.1.12. 3-Ethoxycarbonyl-6-methylquinolin-2(1H)-one ***2j***. Light yellow needles; mp 183–184 °C (ethyl acetate–hexane); IR (KBr) 3150, 1695, 1650, 1290, 1260 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 (t, J=7.1 Hz, 3H, CH_3), 2.43 (s, 3H, CH_3), 4.45 (q, J=7.1 Hz, 2H, OCH_2), 7.38 (d, J=8.9 Hz, 1H, ArH), 7.41–7.45 (m, 2H, ArH), 8.51 (s, 1H, CH), 12.20 (brs, 1H, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.2 (q), 20.7 (q), 61.2 (t), 116.2 (d), 118.4 (s), 121.7 (s), 128.3 (d), 132.5 (s), 134.5 (d), 138.1 (s), 145.3 (d), 161.4 (s), 164.5 (s); Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.43; H, 5.71; N, 6.04.

4.1.13. 3-Ethoxycarbonyl-6,7-dimethylquinolin-2(1H)-one ***2k***. White needles; mp 241–242 °C (ethyl acetate–hexane); IR (KBr) 1730, 1645, 1480, 1220, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.46 (t, J=7.1 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 4.45 (q, J=7.1 Hz, 2H, OCH_2), 7.23 (s, 1H, ArH), 7.39 (s, 1H, ArH), 8.51 (s, 1H, CH), 11.91 (brs, 1H, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3 (q), 19.3 (q), 20.5 (q), 61.3 (t), 116.4 (d), 116.9 (s), 120.7 (s), 128.9 (d), 132.3 (s), 138.7 (s), 143.9 (s), 145.5 (d), 161.2 (s), 164.8 (s); Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.40; H, 6.18; N, 5.70.

4.1.14. 3-Acetyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2l***. Light yellow needles; mp 196–197 °C (ethyl acetate–hexane);

IR (KBr) 1675, 1645, 1560, 1445, 1215 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 6H, 2× CH_3), 2.23 (s, 3H, CH_3), 2.80 (s, 3H, CH_3), 5.67 (s, 2H, NCH_2), 6.80 (s, 2H, ArH), 7.01 (d, J=8.6 Hz, 1H, ArH), 7.17 (t, J=7.5 Hz, 1H, ArH), 7.40 (ddd, J=8.6, 7.5, 1.5 Hz, 1H, ArH), 7.66 (dd, J=7.5, 1.5 Hz, 1H, ArH), 8.40 (s, 1H, CH); ^{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.

4.1.15. 3-Acetyl-6-methyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2m***. Yellow crystals; mp 206–207 °C (ethyl acetate–hexane); IR (KBr) 1675, 1645, 1565, 1350, 1225 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 6H, 2× CH_3), 2.23 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 5.65 (s, 2H, NCH_2), 6.79 (s, 2H, ArH), 6.91 (d, J=8.7 Hz, 1H, ArH), 7.22 (dd, J=8.7, 1.6 Hz, 1H, ArH), 7.43 (s, 1H, ArH), 8.34 (s, 1H, 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.

4.1.16. 3-Acetyl-6-chloro-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2n***. Light yellow needles; mp 204–205 °C (ethyl acetate–hexane); IR (KBr) 1680, 1655, 1560, 1485, 1210 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 6H, 2× CH_3), 2.23 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 5.65 (s, 2H, NCH_2), 6.81 (s, 2H, ArH), 6.94 (d, J=9.1 Hz, 1H, ArH), 7.33 (dd, J=9.1, 2.4 Hz, 1H, ArH), 7.62 (d, J=2.4 Hz, 1H, ArH), 8.28 (s, 1H, 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.

4.1.17. 3-Cyano-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2o***. Light yellow crystals; mp 232–233 °C (ethyl acetate–hexane); IR (KBr) 2230, 1645, 1590, 1565, 1455 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 6H, 2×CH_3), 2.23 (s, 3H, CH_3), 5.65 (s, 2H, NCH_2), 6.81 (s, 2H, ArH), 7.07 (d, J=8.6 Hz, 1H, ArH), 7.23 (t, J=7.5 Hz, 1H, ArH), 7.47 (ddd, J=8.6, 7.5, 1.4 Hz, 1H, ArH), 7.60 (dd, J=7.5, 1.4 Hz, 1H, ArH), 8.23 (s, 1H, 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.

4.1.18. 3-Cyano-6-methyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2p***. Light yellow needles; mp 215–216 °C (ethyl acetate–hexane); IR (KBr) 2230, 1655, 1570, 1500, 1230 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 6H, 2× CH_3), 2.23 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 5.63 (s, 2H, NCH_2), 6.80 (s, 2H, ArH), 6.96 (d, J=8.8 Hz, 1H, ArH), 7.29 (dd, J=8.8, 1.9 Hz, 1H, ArH), 7.37 (s, 1H, ArH), 8.16 (s, 1H, 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.

4.1.19. 6-Chloro-3-cyano-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2q***. Light yellow needles (ethyl acetate–hexane); mp 221–222 °C; IR (KBr) 2230, 1655, 1560, 1420, 1210 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 6H, 2× CH_3), 2.23 (s, 3H, CH_3), 5.62 (s, 2H, NCH_2), 6.81 (s, 2H, ArH), 7.00 (d, J=9.1 Hz, 1H, ArH), 7.40 (dd, J=9.1, 2.2 Hz, 1H, ArH), 7.57 (d, J=2.2 Hz, 1H, ArH), 8.14 (s, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.3 (2× q), 20.7 (q), 43.2 (t), 108.2 (s), 114.8 (s), 117.2 (d), 119.7 (s), 128.86 (s), 128.89 (d), 129.1 (s), 130.5 (2× d), 133.8 (d), 135.8 (2× s), 137.4 (s), 138.9 (s), 146.3 (d), 159.0 (s); Anal. Calcd for $C_{20}H_{17}ClN_2O$: C, 71.32; H, 5.09; N, 8.32. Found: C, 71.34; H, 5.15; N, 8.26.

4.1.20. 3-Benzoyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2r***. Light yellow needles; mp 201–202 °C (ethyl acetate–hexane); IR (KBr) 1660, 1645, 1565, 1455, 1215 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 9H, 3× CH_3), 5.65 (s, 2H, NCH_2), 6.81 (s, 2H, ArH), 7.06 (d, J=7.9 Hz, 1H, ArH), 7.19 (t, J=7.9 Hz, 1H, ArH), 7.40 (t, J=7.9 Hz, 1H, ArH), 7.46 (t, J=7.7 Hz, 2H, ArH), 7.59 (t, J=7.7 Hz, 1H, ArH), 7.62 (d, J=7.9 Hz, 1H, ArH), 7.88 (d, J=7.7 Hz, 2H, ArH), 8.01 (s, 1H, 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.

4.1.21. 3-Benzoyl-6-chloro-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2s***. White needles; mp 253–254 °C (ethyl acetate–hexane); IR (KBr) 1675, 1645, 1485, 1285, 1215 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 6H, 2× CH_3), 2.26 (s, 3H, CH_3), 5.65 (s, 2H, NCH_2), 6.84 (s, 2H, ArH), 7.02 (d, J=9.1 Hz, 1H, ArH), 7.36 (dd, J=9.1, 2.3 Hz, 1H, ArH), 7.49 (t, J=7.5 Hz, 2H, ArH), 7.60 (d, J=2.3 Hz, 1H, ArH), 7.62 (t, J=7.5 Hz, 1H, ArH), 7.89 (d, J=7.5 Hz, 2H, ArH), 7.92 (s, 1H, 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.

4.1.22. 3-Benzoyl-6-fluoro-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2t***. White needles; mp 212–213 °C (ethyl acetate–hexane); IR (KBr) 1670, 1645, 1575, 1440, 1235 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 6H, 2× CH_3), 2.24 (s, 3H, CH_3), 5.64 (s, 2H, NCH_2), 6.82 (s, 2H, ArH), 7.03 (dd, J=9.4, 4.3 Hz, 1H, ArH), 7.13 (ddd, J=9.4, 8.0, 2.9 Hz, 1H, ArH), 7.28 (dd, J=8.0, 2.9 Hz, 1H, ArH), 7.46 (t, J=7.6 Hz, 2H, ArH), 7.59 (t, J=7.6 Hz, 1H, ArH), 7.87 (d, J=7.6 Hz, 2H, ArH), 7.91 (s, 1H, 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.

4.1.23. 3-Benzoyl-6-methyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2u***. White needles; mp 231–232 °C (ethyl acetate–hexane); IR (KBr) 1675, 1645, 1570, 1445, 1235 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 9H, 3× CH_3), 2.35 (s, 3H, CH_3), 5.63 (s, 2H, NCH_2), 6.81 (s, 2H, ArH), 6.96 (d, J=8.7 Hz, 1H, ArH), 7.22 (dd, J=8.7, 1.9 Hz, 1H, ArH), 7.39 (s, 1H, ArH), 7.45 (t, J=7.6 Hz, 2H, ArH), 7.58 (t, J=7.6 Hz, 1H, ArH), 7.87 (d, J=7.6 Hz, 2H, ArH), 7.95 (s, 1H, 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.

4.1.24. 3-Benzoyl-6,7-dimethyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2v***. White needles; mp 249–250 °C (ethyl acetate–hexane); IR (KBr) 1640, 1595, 1555, 1455, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.20 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.25 (s, 3H,

CH_3), 2.26 (s, 6H, 2× CH_3), 5.61 (s, 2H, NCH_2), 6.81 (s, 2H, ArH), 6.89 (s, 1H, ArH), 7.33 (s, 1H, ArH), 7.44 (t, *J*=7.6 Hz, 2H, ArH), 7.56 (t, *J*=7.6 Hz, 1H, ArH), 7.86 (d, *J*=7.6 Hz, 2H, ArH), 7.95 (s, 1H, 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.

4.1.25. 3-Benzoyl-6,8-dimethyl-1-(2,4,6-trimethylbenzyl)quinolin-2(1H)-one ***2w***. Yellow crystals; mp 208–209 °C (ethyl acetate–hexane); IR (KBr) 1655, 1565, 1445, 1275, 1235 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 6H, 2× CH_3), 2.26 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 5.36 (s, 2H, NCH_2), 6.77 (s, 2H, ArH), 7.21 (t, *J*=7.8 Hz, 2H, ArH), 7.26 (s, 1H, ArH), 7.28 (s, 1H, ArH), 7.44 (t, *J*=7.8 Hz, 1H, ArH), 7.49 (d, *J*=7.8 Hz, 2H, ArH), 7.83 (s, 1H, 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.

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Supplementary data

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