Iron/Palladium-Catalyzed Intramolecular Hydroamination: An Expedient Synthesis of Pyrrole-Annulated Coumarin and Quinolone Derivatives

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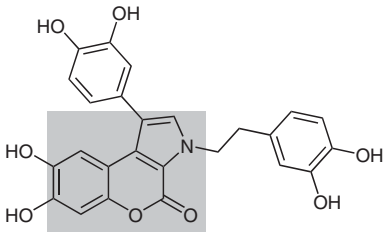
Abstract: A highly efficient intramolecular hydroamination reaction of heterocycle-centered aminoalkynes using both substituted and free amines catalyzed by $PdCl_2/FeCl_3$ catalytic system to form the biologically important pyrrolocoumarin and pyrroloquinolone derivatives is reported. The use of both aliphatic and aromatic substituted alkynes with different heterocyclic skleton in this strategy demonstrated the diversity of this method.

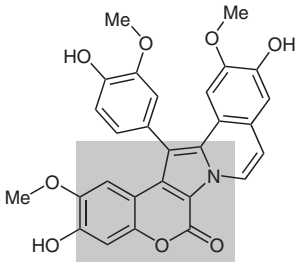
Key words: hydroamination, pyrrolocoumarin, pyrroloquinolone, $FeCl_3$, aminoalkynes

The synthesis of nitrogen containing heterocycles such as substituted indole derivatives have attracted considerable attention since this basic motif is present in various natural products and biologically active substances.[1] After extensive research over the hundred years of the Fisher indole synthesis, a variety of other well-documented methods for their synthesis are now available. Among the various routes employed, the metal-catalyzed intramolecular hydroamination reaction of aminoalkynes[2] are the mostly popular one as it is highly atom economic and can tolerate a wide range of functionality.

On the other hand coumarins and quinolones are the important subunits present in a number of natural products showing broad spectrum biological activity such as antibacterial, antifungal, antiviral, antimicrobial, and sedative properties.[3,4] In particular, the pyrrolocoumarin derivatives exhibit photobiological activity[5a] and antiproliferative effect,[5b] DNA-binding properties,[6] photophysical properties,[7] anti-inflamatory, and antioxidant activities.[8] These also act as ideal dyes for various modern fluorescent imaging technologies such as FRET.[9] Pyrrolocoumarin derivatives are the important precursors for the construction of the scaffold of two biologically active marine alkaloids, namely, ningalin B and lamellarin D[10] (Figure 1). Both the alkaloids possess potential bioactivity such as cytotoxicity, HIV-1 integrase inhibition, immunomodulatory activity, multidrug resistance (MDR) reversal activity, etc.[11] The pyrroloquinolone derivatives are also important as these can act as phosphodiesterase 5 inhibitors,[12a] show analgesic activity,[12b] and are important precursors for the antibiotic martinelline.[13] Our continuous efforts in synthesizing important heterocycles in a simplified manner[14] motivated us to prepare such type of molecules as these analogues may be interesting and useful to the medicinal chemists or pharmacologists for further study.



ningalin B



lamellarin D

Figure 1 Natural products containing pyrrolocoumarin nucleus

In general, the intramolecular cyclization reactions involving a heteroatom-centered nucleophile and the carbon–carbon unsaturated bonds are the most important in synthetic heterocyclic chemistry. Among the several metals used for such cyclizations, palladium is the most widely used and accepted one.[1b,15] Recently, a number of methods using gold,[16a] indium,[2c] mercury,[16b] copper,[16c] zinc,[16d] iridium,[2e] rhodium,[16e] or platinum[16f] salts proved efficient for intramolecular alkyne hydroamination reactions. Among them, there are only few methods that describe the cyclization of unprotected amines.[16a,17] Moreover, these cases also necessitate the use of expensive catalytic system. Only Prim et al. have reported[18] such type of cyclization using $FeCl_3$ in association with $PdCl_2$. Therefore, in order to explore further scope of this methodology we have undertaken a study to synthesize both protected and unprotected pyrrole-annulated coumarins and quinolones using $FeCl_3/PdCl_2$ catalytic system.

The requisite precursors **3a–i** were prepared in good yields by the Sonogashira coupling of the corresponding

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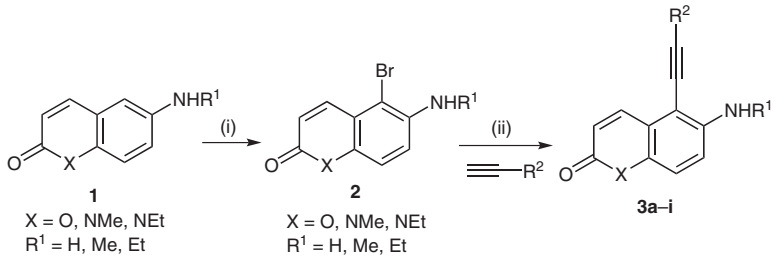


Scheme 1 *Reagents and conditions*: (i) NBS (1.2 equiv), MeCN, r.t., 1 h; (ii) $Pd(PPh_3)_2Cl_2$ (0.05 equiv), CuI (0.05 equiv) DMF, Et_3N, 80 °C, 1.5–3 h.

bromo compounds **2**, which in turn were prepared by NBS bromination of the corresponding 6-aminocoumarin and 6-aminoquinolone moiety using MeCN as solvent at room temperature (Scheme 1).

We selected compound **3a** as a model substrate to study the cyclization reaction under a variety of reaction conditions like varying the catalyst composition, the solvent system etc. The results of the investigation are summarized in Table 1. The results show that both $PdCl_2$ and $FeCl_3$ are required for this hydroamination reaction irrespective of the solvent used. First, 10 mol% $PdCl_2$ with 10 mol% $FeCl_3$ catalyst composition (entry 1) in 1,2-dicholoroethane (DCE) as solvent was used. At refluxing condition (85 °C) the cyclized product **4a** was obtained in 88% yield and the reaction was completed just in 3 hours (monitored by TLC).

Similar result was also obtained when the catalyst composition was varied by reducing $PdCl_2$ (1 mol%) and $FeCl_3$ (5 mol%) and the reaction time to 2.5 hours (entry 6). Among various solvents used, DCE was found to be the suitable one. We also used other Pd(II) sources like $Pd(PPh_3)_2Cl_2$, $Pd(OAc)_2$, but these were found to be ineffective. To investigate the role of $FeCl_3$ from the mechanistic viewpoint other oxidants such as benzoquinone and IBX were used in stoichiometric ratio in combination with $PdCl_2$. In these cases (entries 11, 12), the cyclized product was obtained, but in much lower yields. From this result it is evident that an oxidant is necessary for this hydroamination reaction to occur and that may facilitate the in situ reoxidation of Pd(0) to Pd(II) in the catalytic cycle.

All the other precursors **3b–i** were then subjected to the optimized reaction conditions to give the corresponding cyclized products **4b–i** in 87–98% yields. The results are summarized in Table 2.

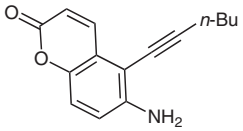
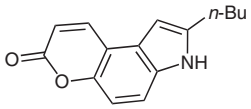
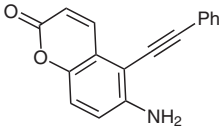
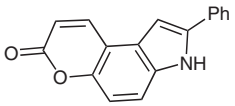
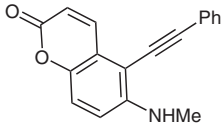
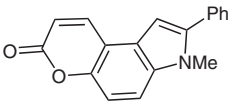
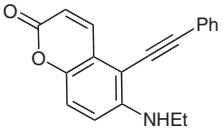
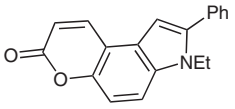
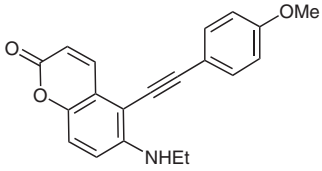
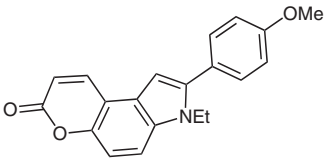
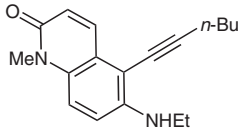
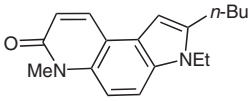
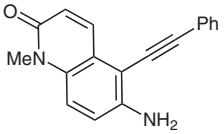
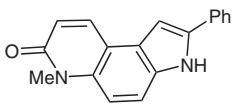
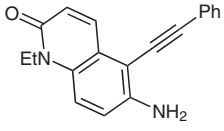
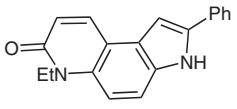
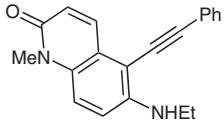
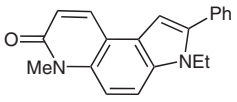
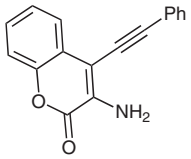
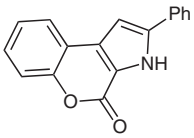
It is important to note that an electron-withdrawing substituent is usually required for the cyclization of acetylenic amines to increase the nucleophilicity of the amine nitrogen. Moreover, there are few methods that describe the cyclizaion of unprotected acetylenic amines using expensive catalysts or high catalyst loading. Here, we have achieved hydroamination of the unprotected, unactivated amines or the acetylenic amines with an electron-donating group in excellent yields to form the pyrrolocoumarin and pyrroloquinolone derivatives.

Table 1 Optimization of the Reaction Conditions[a]

Entry	Catalyst (mol%)	Oxidant (mol%)	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	$PdCl_2$ (10)	$FeCl_3$ (10)	DCE	85	3	88
2	$PdCl_2$ (5)	$FeCl_3$ (5)	DCE	85	2.5	90
3	$PdCl_2$ (10)	–	DCE	85	9	trace
4	–	$FeCl_3$ (10)	DCE	85	9	nr
5	$PdCl_2$ (1)	$FeCl_3$ (2)	DCE	85	8	76
6	$PdCl_2$ (1)	$FeCl_3$ (5)	DCE	85	2.5	93
7	$PdCl_2$ (1)	$FeCl_3$ (5)	EtOH	85	6	25
8	$PdCl_2$ (1)	$FeCl_3$ (5)	MeCN	85	6	17
9	$Pd(PPh_3)_2Cl_2$ (5)	$FeCl_3$ (5)	DCE	85	8	trace
10	$Pd(OAc)_2$ (5)	$FeCl_3$ (5)	DCE	85	3	crm
11	$PdCl_2$ (5)	BQ (1 equiv)	DCE	85	4	44
12	$PdCl_2$ (5)	IBX (1 equiv)	DCE	85	6	33

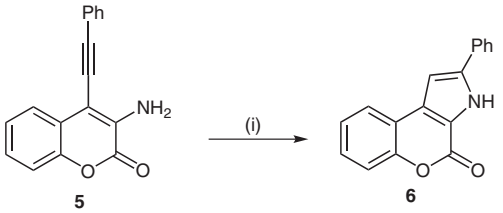
[a] Optimization was done using **3a** as the model substrate.
[b] Isolated yield, nr = no reaction, crm = nonisolatable complicated reaction mixture; BQ = benzoquinone.

Table 2 Summarized Results of the Hydroamination Reaction under Optimized Conditions

Entry	Substrate	Product	Time (h)	Yield (%)
1	**3a** 	**4a** 	2.5	93
2	**3b** 	**4b** 	2.5	87
3	**3c** 	**4c** 	2	98
4	**3d** 	**4d** 	2	96
5	**3e** 	**4e** 	2	96
6	**3f** 	**4f** 	3	93
7	**3g** 	**4g** 	4	89
8	**3h** 	**4h** 	2	91
9	**3i** 	**4i** 	2.5	96
10	**5** 	**6** 	2	95

The scope of the reaction was further examined by changing the substituents in the terminal alkynes. It was observed that both aromatic and aliphatic substituents are equally effective. The generalization of this method was then verified using another coumarin derivative **5**. In this case the product is pyrrolocoumarin derivative **6** obtained in 95% yield (Scheme 2), which is the precursor for the synthesis of two naturally occurring potential marine alkaloid analogues, namely ningalin B and lamellarin D.

The mechanistic aspect of this hydroamination is outlined in Scheme 3. It is assumed that initially the Pd(II) species coordinates with the alkyne thus activating the C≡C bond.[19] The cyclization occurs by the nucleophilic attack of the amine nitrogen atom[20] to the resulting electron de-



Scheme 2 *Reagents and conditions*: (i) $PdCl_2$ (1 mol%), $FeCl_3$ (5 mol%), DCE, 85 °C, 2 h, 95%.

ficient triple bond forming the organopalladium[15c] species **II**. It may be assumed that a 5-*endo*-dig cyclization pathway is maintained during cyclization as 4-*exo*-dig pathway is energetically unfavorable.[21] The reductive elimination afforded the cyclized products **4a–i** and **6**. The active Pd(II) species is regenerated by the oxidation of Pd(0) by $FeCl_3$.[18] The reaction was performed in open air flask. It may be concluded that the reoxidation of Fe(II) to Fe(III) may occur by aerial oxidation, which may account for the use of catalytic amount of $FeCl_3$.

In conclusion, we have demonstrated the development of intramolecular hydroamination strategy in synthesizing the biologically active pyrrolocoumarin and pyrroloquinolone derivatives. The methodology is straightforward and mild using less expensive catalytic system in low catalyst-loading resulting in high yield of the products in the cyclization of both substituted and unprotected amines.

All the chemicals were procured from either Sigma Aldrich Chemicals Pvt. Ltd. or Spectrochem, India. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a PerkinElmer L 120-000A spectrometer (cm^{-1}) on KBr disks. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-300, Bruker DPX-400, Bruker DPX-500 spectrometers in $CDCl_3$/DMSO (chemical shift in δ) with TMS as internal standard. CHN was recorded on 2400 series II CHN analyzer PerkinElmer. Silica gel [(60–120 mesh) was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for TLC. Petroleum ether (PE) refers to the fraction boiling between 60–80 °C.

Compounds **3b–d**, **3g**, **4b–d**, **4g** were reported earlier,[14c] compounds **5** and **6** were also reported in the literature,[10] and their spectroscopic data are in accordance with the reported values.

6-Amino-5-hex-1-ynyl-2*H*-chromen-2-one (3a); Typical Procedure

A mixture of 6-amino-5-bromocoumarin (**2**; R^1 = H, X = O; 300 mg, 1.25 mmol) and hex-1-yne (0.18 mL, 1.50 mmol) in DMF–Et_3N (3:2, 5 mL) was degassed with N_2. $[Pd(PPh_3)_2Cl_2]$ (42.2 mg, 0.06 mmol) and CuI (11.4 mg, 0.06 mmol) were then added to the well-stirred solution. The mixture was heated with stirring at 100 °C for 3 h. The reaction mixture was allowed to cool and $CHCl_3$ (20 mL) was added. After filtration of the mixture over Celite, the filtrate was washed with H_2O (10 mL) followed by brine (10 mL) and dried (Na_2SO_4). The solvent was removed to give a crude mass, which was purified by column chromatography over silica gel using EtOAc–PE (15:85) to afford compound **3a** as a yellow solid; yield: 215 mg (72%); mp 126–128 °C.

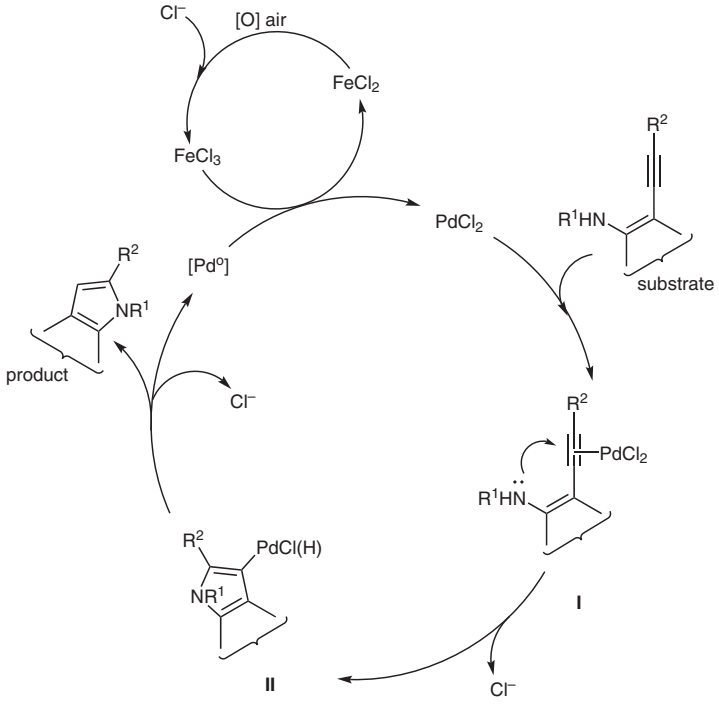
IR (KBr): 1705, 3353, 3466 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.53 (m, 2 H, CH_2), 1.50 (t, *J* = 7.2 Hz, 2 H, CH_2), 2.57 (t, *J* = 7.2 Hz, 2 H, CH_2), 4.23 (s, 2 H, NH_2), 6.42 (d, *J* = 9.6 Hz, 1 H, C_3-H of coumarin), 6.87 (d, *J* = 8.8 Hz, 1 H, ArH), 7.10 (d, *J* = 8.8 Hz, 1 H, ArH), 8.04 (d, *J* = 9.6 Hz, 1 H, C_4-H of coumarin).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 19.5, 22.2, 30.9, 73.4,102.4, 105.1, 116.7, 116.9, 118.3, 119.7, 142.1, 144.8, 147.0, 161.1.

MS (EI): *m/z* = 241 $[M]^+$.

Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.49; H, 6.43; N, 5.97.



Scheme 3 Probabale mechanistic pathway for the hydroamination reaction

3e
Yield: 70%; yellow solid; mp 107–109 °C.

IR (KBr): 1713, 2187, 3407 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.2 Hz, 3 H, CH_3), 3.29 (q, *J* = 7.2 Hz, 2 H, CH_2), 3.86 (s, 3 H, OCH_3), 4.58 (s, 1 H, NH), 6.44 (d, *J* = 9.6 Hz, 1 H, C_3-H of coumarin), 6.82 (d, *J* = 9.2 Hz, 1 H, ArH), 6.93 (d, *J* = 8.8 Hz, 2 H, ArH), 7.19 (d, *J* = 9.2 Hz, 1 H, ArH), 7.50 (d, *J* = 8.8 Hz, 2 H, ArH), 8.12 (d, *J* = 9.6 Hz, 1 H, C_4-H of coumarin).

Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.41; H, 5.20; N, 4.49.

3f
Yield 68%; yellow solid; mp 106–108 °C.

IR (KBr): 1646, 3401 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.32 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.52 (m, 2 H, CH_2), 1.68 (m, 2 H, CH_2), 2.60 (t, *J* = 7.6 Hz, 2 H, CH_2), 3.26 (q, *J* = 7.2 Hz, 2 H, NCH_2), 3.68 (s, 3 H, NCH_3), 4.48 (s, 1 H, NH), 6.71 (d, *J* = 9.6 Hz, 1 H, C_3-H of quinolone), 6.90 (d, *J* = 9.2 Hz, 1 H, ArH), 7.21 (d, *J* = 9.2 Hz, 1 H, ArH), 8.07 (d, *J* = 9.6 Hz, 1 H, C_4-H of quinolone).

Anal. Calcd for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.71; H, 8.01; N, 9.67.

3h
Yield: 65%; yellow solid; mp 121–123 °C.

IR (KBr): 1719, 3337, 3438 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7.2 Hz, 3 H, CH_3), 3.32 (q, *J* = 7.2 Hz, 2 H, NCH_2), 4.60 (s, 2 H, NH), 6.76 (d, *J* = 9.6 Hz, 1 H, C_3-H of quinolone), 6.96 (d, *J* = 9.2 Hz, 1 H, ArH), 7.28 (m, 1 H, ArH), 7.41 (m, 3 H, ArH), 7.59 (m, 2 H, ArH), 8.16 (d, *J* = 9.6 Hz, 1 H, C_4-H of quinolone).

Anal. Calcd for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.72. Found: C, 78.97; H, 5.43; N, 9.81.

3i
Yield: 64%; yellow solid; mp 192–193 °C.

IR (KBr): 1682, 3381 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.01 (s, 3 H, NCH_3), 3.69 (q, *J* = 7.1 Hz, 2 H, NCH_2), 4.69 (s, 1 H, NH), 6.76 (d, *J* = 9.5 Hz, 1 H, C_3-H of quinolone), 6.91 (d, *J* = 8.9 Hz, 1 H, ArH), 7.31 (d, *J* = 8.6 Hz, 1 H, ArH), 7.38–7.40 (m, 3 H, ArH), 7.58–7.59 (m, 2 H, ArH), 8.14 (d, *J* = 9.5 Hz, 1 H, C_4-H of quinolone).

Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.13; H, 5.98; N, 9.49.

Compounds 4a–i and 6; 2-Butylpyrano[3,2-*e*]indol-7(3*H*)-one (4a); Typical Procedure
Compound **3a** (200 mg, 0.828 mmol) was dissolved in 1,2-dichloroethane (6 mL) in a 10 mL round-bottomed flask fitted with a reflux condenser. $PdCl_2$ (1.5 mg, 0.0084 mmol) and $FeCl_3$ (11 mg, 0.0406 mmol) were added to the flask, and then the reaction mixture was heated with stirring at 85 °C for 3 h. The mixture was cooled to r.t., and $CHCl_3$ (10 mL) and H_2O (10 mL) were added. The organic layer was collected, washed with H_2O (10 mL) and brine (10 mL), and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to furnish a crude mass, which was purified by column chromatography over silica gel using EtOAc–PE (20:80) as eluent to give compound **4a** as yellow solid; yield: 186 mg (93%); mp 157–159 °C.

IR (KBr): 1694, 3234 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.6 Hz, 3 H, CH_3), 1.43 (m, 2 H, CH_2), 1.75 (m, 2 H, CH_2), 2.83 (t, *J* = 7.6 Hz, 2 H, CH_2), 6.44 (d, *J* = 9.6 Hz, 1 H, C_3-H of coumarin), 6.49 (s, 1 H, CH) 7.10 (d, *J* = 8.8 Hz, 1 H, ArH), 7.44 (d, *J* = 8.8 Hz, 1 H, ArH), 8.09 (d, *J* = 9.6 Hz, 1 H, C_4-H of coumarin), 8.25 (s, 1 H, NH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.4, 28.1, 31.3, 97.6, 110.0, 110.2, 114.4, 114.5, 125.3, 131.8, 141.2, 142.9, 149.9, 162.2.

HRMS (TOF, ES^+): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{15}NO_2$ + Na: 264.1000; found: 264.1000.

4e
Yield: 96%; off-white solid; mp 120–122 °C.

IR (KBr): 1709 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.2 Hz, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 4.22 (q, *J* = 7.2 Hz, 2 H, CH_2), 6.45 (d, *J* = 9.6 Hz, 1 H, C_3-H of coumarin), 6.69 (s, 1 H), 7.03 (d, *J* = 8.8 Hz, 2 H, ArH), 7.20 (d, *J* = 8.8 Hz, 1 H, ArH), 7.43 (d, *J* = 8.8 Hz, 2 H, ArH), 7.52 (d, *J* = 8.8 Hz, 1 H, ArH), 8.13 (d, *J* = 9.6 Hz, 1 H, C_4-H of coumarin).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6, 39.1, 55.4, 99.3, 110.5, 113.8, 114.2, 114.5, 114.7, 124.6, 130.6, 131.8, 133.0, 140.9, 143.3, 150.0, 159.9, 162.0.

MS (EI): *m*/*z* = 319 $[M]^+$.

Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.33; H, 5.17; N, 4.45.

4f
Yield: 93%; yellow solid; mp 99–101 °C.

IR (KBr): 1643 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.0 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.38 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.50 (m, 2 H, CH_2), 1.74–1.82 (m, 2 H, CH_2), 2.78 (t, *J* = 7.6 Hz, 2 H, CH_2), 3.81 (s, 3 H, NCH_3), 4.19 (q, *J* = 7.2 Hz, 2 H, NCH_2), 6.56 (s, 1 H, CH), 6.76 (d, *J* = 9.6 Hz, 1 H, C_3-H of quinolone), 7.17 (d, *J* = 9.2 Hz, 1 H, ArH), 7.49 (d, *J* = 9.2 Hz, 1 H, ArH), 8.10 (d, *J* = 9.6 Hz, 1 H, C_4-H of quinolone).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 15.6, 22.6, 26.5, 30.1, 30.8, 37.9, 96.7, 107.5, 112.5, 119.8, 125.3, 131.2, 134.9, 135.4, 142.5, 162.5.

MS (EI): *m*/*z* = 282 $[M]^+$.

Anal. Calcd for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.67; H, 8.02; N, 9.71.

4h
Yield: 91%; yellow solid; mp 261–263 °C.

IR (KBr): 1639, 3222 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.42 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.48 (q, *J* = 7.2 Hz, 2 H, NCH_2), 6.81 (d, *J* = 9.6 Hz, 1 H, C_3-H of quinolone), 7.13 (s, 1 H, CH), 7.28 (d, *J* = 8.8 Hz, 1 H, ArH), 7.37 (t, *J* = 7.2 Hz, 1 H, ArH), 7.48 (t, *J* = 8.0 Hz, 2 H, ArH), 7.62 (d, *J* = 8.8 Hz, 1 H, ArH), 7.72 (d, *J* = 7.6 Hz, 2 H, ArH), 8.17 (d, *J* = 9.6 Hz, 1 H, C_4-H of quinolone), 8.76 (s, 1 H, NH).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 12.9, 36.8, 97.1, 109.0, 112.0, 115.3, 119.3, 124.9, 125.8, 127.6, 128.9, 131.8, 131.9, 133.7, 135.6, 130.8, 160.5.

MS (EI): *m*/*z* = 288 $[M]^+$.

Anal. Calcd for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.72. Found: C, 78.95; H, 5.71; N, 9.79.

4i
Yield: 96%; yellow solid; mp 243–245 °C.

IR (KBr): 1681 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 6.9 Hz, 3 H, CH_3), 3.79 (s, 3 H, NCH_3), 3.83 (q, *J* = 6.9 Hz, 2 H, NCH_2), 6.81 (d, *J* = 9.5 Hz, 1 H, C_3-H of quinolone), 6.84 (s, 1 H, =CH), 7.27 (d, *J* = 9.0 Hz, 1 H, ArH), 7.45 (d, *J* = 7.2 Hz, 1 H, ArH), 7.48–7.58 (m, 5 H, ArH), 8.15 (d, *J* = 9.5 Hz, 1 H, C_4-H of quinolone).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.7, 30.1, 39.1, 99.9, 108.8, 112.9, 113.5, 120.2, 125.4, 128.4, 128.7, 129.3, 132.2, 132.5, 135.3, 142.6, 162.6, 162.5.

MS (EI): *m*/*z* = 302 $[M]^+$.

Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.59; H, 6.19; N, 9.09.

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