An Efficient and Highly Selective Method for the Synthesis of 3-Arylbenzoquinoline Derivatives Catalyzed by Iodine via Three-Component Reactions

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Abstract: A mild, efficient and highly selective method for the synthesis of benzo[*f*]quinoline derivatives via three-component reactions of arylaldehydes, naphthalen-2-amine and ketones or β-keto esters using iodine as catalyst is described. It should be noted that only one product was obtained, with high selectivity, when ketones or β-keto esters with two different α-hydrogen atoms were chosen as reactants.

Key words: benzo[*f*]quinoline, iodine, ketone, β-keto ester, synthesis

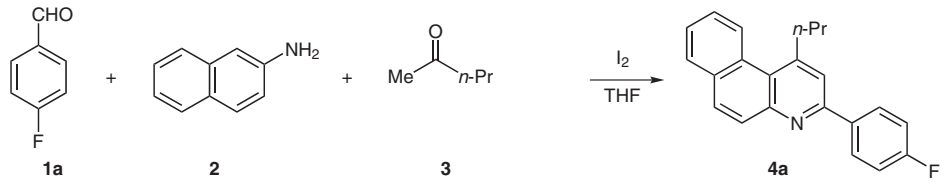
Multi-component reactions (MCRs), often involving three or more reactants combined in a one-pot procedure, generate complex organic molecules and have become increasingly popular during the last decade.[1] They are considered as a new type of green chemistry in economical reaction steps, because ordinary multi-step syntheses produce considerable amounts of waste, mainly due to complex isolation procedures often involving expensive, toxic, and hazardous solvents after each step. Thus MCRs offer a convenient strategy for the rapid and convergent construction of complex organic molecules without the need for isolating and purifying the intermediates – this results in substantial minimization of waste, labor, time and cost. They provide a powerful tool for the one-pot synthesis of diverse and complex compounds as well as small and drug-like heterocycles. Benzo[*f*]quinoline and its derivatives are very useful compounds in various fields of chemistry, biology and pharmacology. Some of these compounds exhibit antibacterial,[2] UGT,[3] inhibitory,[4] antimicrobial,[5] antimalarial,[6] agonistic,[7] antipsychotic,[8] and antagonist activity.[9]

In view of the importance of benzoquinoline and its derivatives, several methods for the synthesis of benzo[*f*]quinolines were developed by Kozlov[10] and other groups.[11] However, many of these reported methods suffer from drawbacks such as harsh reaction conditions, unsatisfactory yields, prolonged reaction times and cumbersome product isolation procedures. Furthermore, in the original reaction of Schiff base with ketones reported by Kozlov et al., almost all the ketones were limited to acetone or acetophenone. Thus, the development of efficient, mild, especially highly selective processes for the preparation of biologically active 3-arylquinoline derivatives appeared interesting.

Wang et al.[12] recently reported that Schiff bases could react with aliphatic aldehydes, under the influence of iodine, to give 3-aryl-2-substituted quinolines, demonstrating that iodine was an efficient catalyst for this reaction. However, no ketones were explored in this iodine-catalyzed reaction, in particular, no attempt was made to investigate ketones with α-hydrogen atoms in two different environments in order to study selectivity. In connection with our previous research on multi-component reactions,[13] the procedure reported herein successfully realized a three-component reaction of arylaldehyde, naphthalen-2-amine and either ketones or β-keto esters, catalyzed by iodine, without isolating or purifying the intermediates, to afford benzo[*f*]quinolines in good to high yields. Importantly, only one 3-aryl-1-substituted benzo[*f*] quinoline product was isolated, with high selectivity, when ketones or β-keto esters with α-hydrogen atoms in different environments were chosen as starting materials.

Treatment of 4-fluorobenzaldehyde (**1a**), naphthalen-2-amine (**2**) and 2-pentanone (**3**) in tetrahydrofuran, in the presence of 5 mol% iodine at reflux, selectively afforded the corresponding 3-(4-fluorophenyl)-1-(*n*-propyl)benzo[*f*]quinoline (**4a**) in 89% yield (Scheme 1).

Initially, the above reaction was used as a model with which to optimize the conditions. When the reaction was



1a 2 3 4a

Scheme 1

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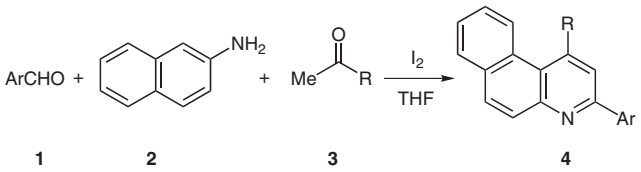
carried out in tetrahydrofuran in the absence of iodine, no reaction occurred at either room temperature or under reflux (Table 1, entries 1 and 2). We also evaluated the amount of catalyst required for this transformation. It was found that 5 mol% iodine in tetrahydrofuran at reflux was sufficient to push the reaction forward. Larger amounts of catalyst did not improve yields. To find the optimum reaction temperature, the reaction was carried out with 5 mol% iodine at room temperature, 50 °C and at reflux; these conditions resulted in the isolation of **4a** in trace amounts, 72% and 89% yields, respectively (Table 1, entries 3, 4 and 5). Thus, 5 mol% iodine in refluxing THF were optimal conditions. The effect of solvent under reflux conditions was also investigated for this reaction. As shown in Table 1, THF gave the most satisfactory result in comparison with other solvents (Table 1, entries 8–11).

Table 1 Synthesis of **4a** under Different Reaction Conditions[a]

Entry	Temp	I_2 (mol%)	Solvent	Yield (%)[b]
1	r.t.	0	THF	0
2	reflux	0	THF	0
3	r.t.	5	THF	trace
4	50 °C	5	THF	72
5	**reflux**	**5**	**THF**	**89**
6	reflux	10	THF	88
7	reflux	20	THF	89
8	reflux	5	MeCN	54
9	reflux	5	benzene	72
10	80 °C	5	DMF	76
11	reflux	5	DCE	78

[a] Reagents and conditions: **1a** (2 mmol), **2** (2 mmol), **3** (2.5 mmol), solvent (10 mL), 10 h.
[b] Isolated yield.



Scheme 2

Similarly, various benzaldehydes reacted with naphthalen-2-amine (**2**) and straight chain ketones, such as pentan-2-one and hexan-2-one, giving 3-arylbenzo[*f*]quinoline derivatives, in good to high yields and high selectivity (Scheme 2). The results, summarized in Table 2, show that the process tolerates both electron-donating and electron-withdrawing substituents in the benzaldehydes. In all cases, the reactions proceeded efficiently at reflux under mild conditions to afford the corresponding benzo[*f*]quinolines (Table 2, entries 1–22). However, we failed to get the expected products when aliphatic aldehydes were used. We also tested the sterically hindered 3-methylbutan-2-one, 4,4-dimethylpentan-2-one, 3,3-dimethylbutan-2-one and acetophenone. The desired products were obtained, though in poor yields, if 3-methylbutan-2-one was used instead of pentan-2-one or hexan-2-one (Table 2, entries 23 and 24). Perhaps the 3-methylbutan-2-one, because of its steric hindrance, was not easy to convert into the enol form in the presence of

Table 2 Iodine-Catalyzed Reaction of Benzaldehydes, Naphthalen-2-amine and Ketones in THF[a]

Entry	Ar	R	Product	Time (h)	Yield (%)[b]
1	4-FC_6H_4	*n*-Pr	**4a**	10	89
2	4-ClC_6H_4	*n*-Pr	**4b**	12	84
3	4-BrC_6H_4	*n*-Pr	**4c**	12	84
4	3-BrC_6H_4	*n*-Pr	**4d**	14	80
5	3-ClC_6H_4	*n*-Pr	**4e**	12	84
6	2,4-$(Cl)_2C_6H_3$	*n*-Pr	**4f**	12	83
7	2-thienyl	*n*-Pr	**4g**	15	78
8	3,4-$(MeO)_2C_6H_3$	*n*-Pr	**4h**	14	81
9	4-MeC_6H_4	*n*-Pr	**4i**	14	82
10	4-$MeOC_6H_4$	*n*-Pr	**4j**	16	79
11	4-$O_2NC_6H_4$	*n*-Pr	**4k**	10	80
12	2,4-$(Cl)_2C_6H_3$	*n*-Bu	**4l**	12	84
13	4-ClC_6H_4	*n*-Bu	**4m**	12	86
14	2-thioenyl	*n*-Bu	**4n**	14	80
15	3-BrC_6H_4	*n*-Bu	**4o**	12	84
16	4-FC_6H_4	*n*-Bu	**4p**	10	88
17	3-$O_2NC_6H_4$	*n*-Bu	**4q**	14	83
18	4-$O_2NC_6H_4$	*n*-Bu	**4r**	12	89
19	4-MeC_6H_4	*n*-Bu	**4s**	14	84
20	4-$MeOC_6H_4$	*n*-Bu	**4t**	14	80
21	4-BrC_6H_4	*n*-Bu	**4u**	12	84
22	3-ClC_6H_4	*n*-Bu	**4v**	12	84
23	3-ClC_6H_4	*i*-Pr	**4w**	48	13[c]
24	4-FC_6H_4	*i*-Pr	**4x**	48	18[c]
25	3-BrC_6H_4	Ph	**4y**	12	90
26	4-$O_2NC_6H_4$	Ph	**4z**	12	88

[a] Reagents and conditions: **1** (2 mmol), **2** (2 mmol), **3** (2.5 mmol), I_2 (5 mol%), THF (10 mL).
[b] Isolated yield.
[c] Separated by silica gel column chromatography.

iodine. In our continued tests, we failed to get the corresponding benzo[*f*]quinolines using 4,4-dimethylpentan-2-one or 3,3-dimethylbutan-2-one as reactants. To our delight, acetophenone, which lacks an α-methylene moiety, successfully gave satisfactory yields (Table 2, entries 25 and 26). In order to show the general scope of this reaction, we also performed the reaction with a substituted aniline such as *p*-toluidine, instead of naphthalene-2-amine. However, we could not get the expected benza[*f*]quinoline derivatives, possibly because the activity of *p*-toluidine is less than that of 2-aminonaphthalene. All the products were characterized by ^{1}H NMR, IR and elemental analyses. The product **4c** was further confirmed by X-ray diffraction analysis,[14] and the crystal structure is shown in Figure 1.

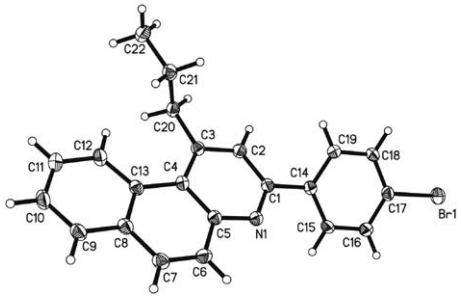
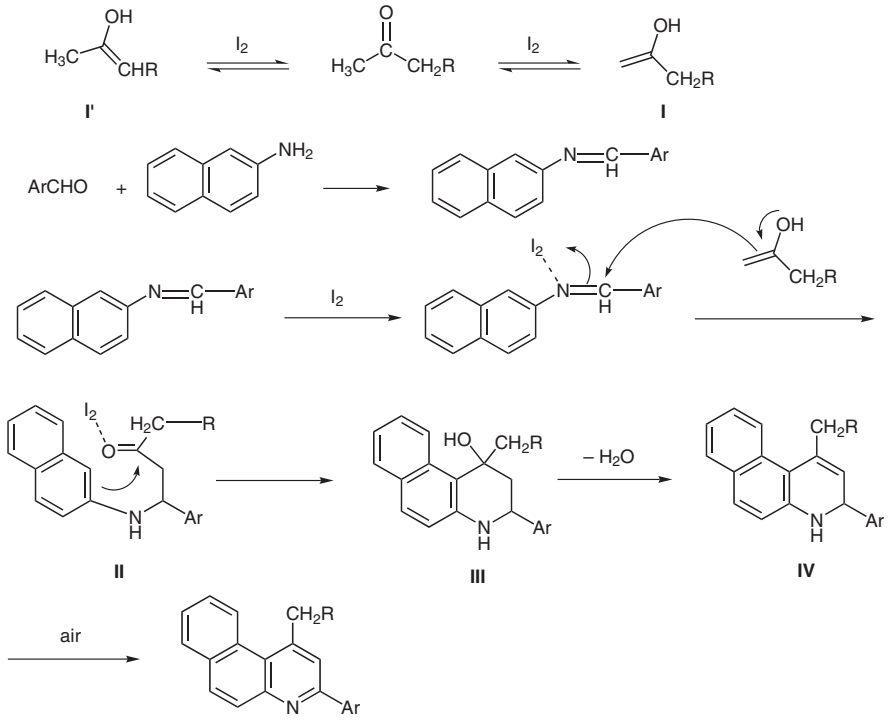


Figure 1 ORTEP diagram of **4c**

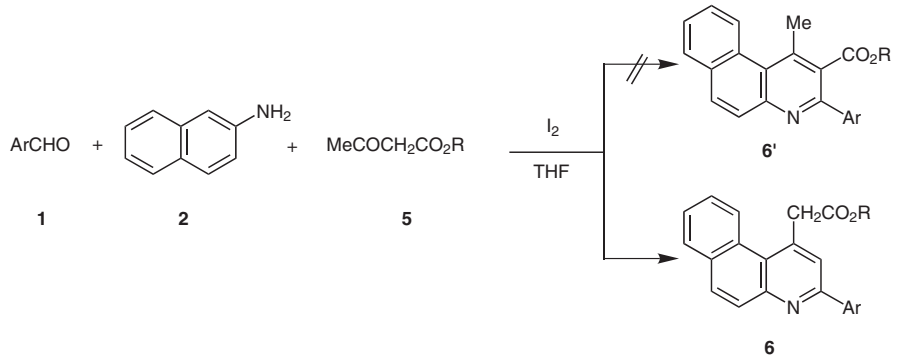
According to the literature,[15] we think that iodine catalyzes the reaction as a mild Lewis acid. The proposed mechanism is shown in Scheme 3. In the presence of iodine, the ketone is in equilibrium with the enol form **I** or **I′**. However, the enol **I**, not **I′** due its steric hindrance, immediately reacts with the iodine-activated Schiff base to form intermediate **II**, followed by an intramolecular Friedel–Crafts cyclization to give **III**. Subsequent dehydration of **III** results in dihydroquinoline **IV**, which is further oxidized by air to give an aromatized benzo[*f*]quinoline **4**.

Wang et al.[12] demonstrated by ^{1}H NMR that an aliphatic aldehyde could convert into the enol in the presence of iodine, thus we selected the β-keto esters as reactants due to their higher enol content. In order to obtain the desired 3-aryl-1-methylbenzo[*f*]quinoline-2-carbonylate, we carried out the above reaction under the same reaction conditions (Scheme 4, Table 3). Interestingly, it was the 2-{3-(4-chlorophenyl)benzo[*f*]quinolin-1-yl}acetate (**6a**; Ar = 4-ClC_6H_4) which formed. The structure of this compound was supported by ^{1}H NMR since a singlet was observed at δ = 4.63 ppm due to a methylene rather than methyl group. In total, eleven further ^{1}H NMR signals arising from aromatic protons were detected, which further established the structure of the product as **6** rather than **6′**. These results conformed to those obtained by Kozlov et al., reported in 2000,[16] which showed that the reaction was catalyzed by HCl in propan-2-ol with poor yields (15–55%).

In conclusion, we have found an efficient method for the synthesis of 3-aryl-1-substituted benzo[*f*]quinoline derivatives via three-component reactions of arylaldehydes, naphthalen-2-amine and either ketones or β-keto esters, using 5 mol% iodine as catalyst. It should be noted that only one product was obtained, with high selectivity, when ketones or β-keto esters with two α-hydrogen atoms in different environments were chosen as reactants. The features of this procedure are mild reaction conditions, operational simplicity and high selectivity.



Scheme 3



Scheme 4

Table 3 Iodine-Catalyzed Reactions of Benzaldehydes, Naphthalen-2-amine and β-Keto Esters in THF[a]

Entry	Ar	R	Product	Time (h)	Yield (%)[b]
1	4-ClC_6H_4	Me	**6a**	8	92
2	2,4-$Cl_2C_6H_3$	Me	**6b**	6	90
3	2,3-$Cl_2C_6H_3$	Me	**6c**	8	93
4	4-$NO_2C_6H_4$	Me	**6d**	6	94
5	4-BrC_6H_4	Me	**6e**	8	90
6	4-CH_3 °C_6H_4	Me	**6f**	8	93
7	2,3-$(CH_3O)_2C_6H_3$	Me	**6g**	8	89
8	3-$NO_2C_6H_4$	Me	**6h**	6	90
9	2,4-$Cl_2C_6H_3$	Et	**6i**	8	82
10	4-BrC_6H_4	Et	**6j**	8	83
11	3-BrC_6H_4	Et	**6k**	8	80
12	4-ClC_6H_4	Et	**6l**	8	84

[a] Reagents and conditions: **1** (2 mmol), **2** (2 mmol), **5** (2.5 mmol), I_2 (5 mol%), THF (10 mL).
[b] Isolated yields.

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr pellets. ^{1}H NMR spectra were obtained from solution in DMSO-d_6 or $CDCl_3$ with TMS as internal standard using an Inova-400 spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 II analyzer.

Syntheses of 3-Arylbenzo[*f*]quinoline Derivatives 4; General Procedure

A dry 50 mL flask was charged with arylaldehyde (2.0 mmol), naphthalen-2-amine (2.0 mmol, 0.286 g), ketone (2.5 mmol), I_2 (0.1 mmol, 0.025 g) and THF (10 mL). The reaction mixture was stirred at reflux for 10–16 h (48 h for **4w** and **4x**). After completion of the reaction as indicated by TLC, the mixture was cooled to r.t. and the generated crystals were collected by filtration to give **4a–v**, **4y** and **4z**. The products **4w** and **4x** were purified by silica gel (200–300 μm) column chromatography (acetone–PE, 1:3).

3-(4-Fluorophenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4a)

Mp 123–124 °C.

IR (KBr): 3041, 2987, 2956, 2931, 2873, 1599, 1580, 1549, 1525, 1482, 1458, 1435, 1376, 1350, 1295, 1224, 1157, 1097, 989, 910, 863, 831, 747 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 1.10 (t, *J* = 7.6 Hz, 3 H, CH_3), 1.86–1.93 (m, 2 H, CH_2), 3.48 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.39 (d, *J* = 8.8 Hz, 2 H, ArH), 7.69–7.78 (m, 2 H, ArH), 7.96 (d, *J* = 8.8 Hz, 1 H, ArH), 8.07–8.12 (m, 3 H, ArH), 8.39 (dd, *J* = 8.4, 1.6 Hz, 2 H, ArH), 8.69 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{22}H_{18}FN$: C, 83.78; H, 5.75; N, 4.44. Found: C, 83.66; H, 5.90; N, 4.31.

3-(4-Chlorophenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4b)

Mp 116–117 °C.

IR (KBr): 3047, 2963, 2932, 2873, 1592, 1579, 1548, 1528, 1482, 1447, 1403, 1377, 1346, 1330, 1167, 1099, 1087, 1014, 989, 861, 837, 822, 745, 723 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 1.06 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.83–1.90 (m, 2 H, CH_2), 3.45 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.58 (d, *J* = 8.4 Hz, 2 H, ArH), 7.65–7.75 (m, 2 H, ArH), 7.93 (d, *J* = 9.2 Hz, 1 H, ArH), 8.01–8.08 (m, 2 H, ArH), 8.12 (s, 1 H, ArH), 8.32 (d, *J* = 8.4 Hz, 2 H, ArH), 8.66 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{22}H_{18}ClN$: C, 79.63; H, 5.47; N, 4.22. Found: C, 79.75; H, 5.40; N, 4.45.

3-(4-Bromophenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4c)

Mp 109–111 °C.

IR (KBr): 3047, 2960, 2871, 1578, 1547, 1482, 1440, 1401, 1376, 1359, 1272, 1165, 1102, 1068, 1010, 989, 941, 900, 861, 834, 821, 797, 745, 719 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 1.04 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.78–1.86 (m, 2 H, CH_2), 3.40 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.65–7.71 (m, 4 H, ArH), 7.90 (d, *J* = 8.8 Hz, 1 H, ArH), 8.01–8.06 (m, 3 H, ArH), 8.22 (d, *J* = 8.4 Hz, 2 H, ArH), 8.62 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{22}H_{18}BrN$: C, 70.22; H, 4.82; N, 3.72. Found: C, 70.26; H, 4.66; N, 3.88.

3-(3-Bromophenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4d)

Mp 140–142 °C.

IR (KBr): 3051, 2953, 2866, 1583, 1548, 1523, 1478, 1452, 1436, 1338, 1245, 1070, 1011, 898, 850, 831, 797, 776, 738, 709, 681 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 1.11 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.87–1.95 (m, 2 H, CH_2), 3.49 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.51–7.55 (m, 1 H, ArH), 7.69–7.80 (m, 3 H, ArH), 7.98 (d, *J* = 9.2 Hz, 1 H, ArH),

8.08–8.12 (m, 2 H, ArH), 8.18 (s, 1 H, ArH), 8.34 (d, *J* = 8.0 Hz, 1 H, ArH), 8.53 (s, 1 H, ArH), 8.70 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{22}H_{18}BrN$: C, 70.22; H, 4.82; N, 3.72. Found: C, 70.34; H, 4.70; N, 3.89.

3-(3-Chlorophenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4e)
Mp 117–118 °C.

IR (KBr): 3054, 2954, 2926, 2867, 1584, 1550, 1527, 1483, 1452, 1438, 1421, 1379, 1339, 1259, 1245, 1079, 992, 899, 850, 831, 778, 740, 682 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.11 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.87–1.95 (m, 2 H, CH_2), 3.49 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.55–7.62 (m, 2 H, ArH), 7.70–7.80 (m, 2 H, ArH), 7.99 (d, *J* = 8.8 Hz, 1 H, ArH), 8.09–8.12 (m, 2 H, ArH), 8.19 (s, 1 H, ArH), 8.30 (d, *J* = 7.6 Hz, 1 H, ArH), 8.39 (d, *J* = 1.6 Hz, 1 H, ArH), 8.70 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{22}H_{18}ClN$: C, 79.63; H, 5.47; N, 4.22. Found: C, 79.73; H, 5.33; N, 4.34.

3-(2,4-Dichlorophenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4f)
Mp 131–133 °C.

IR (KBr): 3064, 2958, 2932, 2873, 1590, 1556, 1527, 1477, 1454, 1439, 1379, 1348, 1251, 1145, 1100, 1044, 989, 910, 891, 855, 833, 823, 794, 740, 731 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.10 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.87–1.94 (m, 2 H, CH_2), 3.50 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.63 (dd, *J* = 8.4, 2.0 Hz, 1 H, ArH), 7.74–7.84 (m, 5 H, ArH), 7.95 (d, *J* = 9.2 Hz, 1 H, ArH), 8.12–8.15 (m, 2 H, ArH), 8.77 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{22}H_{17}Cl_2N$: C, 72.14; H, 4.68; N, 3.82. Found: C, 72.30; H, 4.42; N, 3.78.

1-(*n*-Propyl)-3-(2-thienyl)benzo[*f*]quinoline (4g)
Mp 117–118 °C.

IR (KBr): 3072, 2957, 2928, 2868, 1581, 1548, 1522, 1480, 1454, 1439, 1421, 1378, 1349, 1250, 1226, 1067, 1035, 989, 866, 833, 751, 732 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.11 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.86–1.93 (m, 2 H, CH_2), 3.47 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.24–7.26 (m, 1 H, ArH), 7.68–7.79 (m, 3 H, ArH), 7.87 (d, *J* = 8.8 Hz, 1 H, ArH), 8.02–8.10 (m, 4 H, ArH), 8.68 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{20}H_{17}NS$: C, 79.17; H, 5.65; N, 4.62. Found: C, 79.28; H, 5.49; N, 4.75.

3-(3,4-Dimethoxyphenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4h)
Mp 135–136 °C.

IR (KBr): 3057, 2988, 2957, 2866, 2834, 1601, 1581, 1547, 1511, 1482, 1457, 1416, 1337, 1317, 1252, 1227, 1172, 1148, 1107, 1029, 851, 849, 833, 811, 761 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.12 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.88–1.94 (m, 2 H, CH_2), 3.50 (t, *J* = 7.6 Hz, 2 H, CH_2), 3.86 (s, 3 H, CH_3O), 3.93 (s, 3 H, CH_3O), 7.13 (d, *J* = 8.4 Hz, 1 H, ArH), 7.68–7.71 (m, 1 H, ArH), 7.75–7.79 (m, 1 H, ArH), 7.90 (dd, *J* = 8.4, 2.0 Hz, 1 H, ArH), 7.95–7.98 (m, 2 H, ArH), 8.03–8.11 (m, 3 H, ArH), 8.70 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.55; H, 6.30; N, 4.05.

3-(4-Methylphenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4i)
Mp 101–102 °C.

IR (KBr): 3057, 2958, 2868, 1604, 1581, 1546, 1525, 1479, 1454, 1434, 1374, 1348, 1259, 1180, 1113, 1017, 988, 833, 821, 745 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.11 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.88–1.94 (m, 2 H, CH_2), 2.41 (s, 3 H, CH_3), 3.49 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.39 (d, *J* = 8.0 Hz, 2 H, ArH), 7.68–7.72 (m, 1 H, ArH), 7.75–7.79 (m, 1 H, ArH), 7.97 (d, *J* = 9.2 Hz, 1 H, ArH), 8.08–8.10 (m, 3 H, ArH), 8.24 (d, *J* = 8.0 Hz, 2 H, ArH), 8.70 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50. Found: C, 88.89; H, 6.71; N, 4.55.

3-(4-Methoxyphenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4j)
Mp 103–104 °C.

IR (KBr): 3056, 2964, 2934, 2872, 2842, 1605, 1583, 1547, 1510, 1480, 1457, 1435, 1353, 1294, 1254, 1173, 1113, 1026, 831, 793, 742 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.10 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.88–1.93 (m, 2 H, CH_2), 3.48 (t, *J* = 7.6 Hz, 2 H, CH_2), 3.86 (s, 3 H, CH_3O), 7.12 (d, *J* = 8.4 Hz, 2 H, ArH), 7.67–7.71 (m, 1 H, ArH), 7.75–7.78 (m, 1 H, ArH), 7.95 (d, *J* = 8.8 Hz, 1 H, ArH), 8.07–8.09 (m, 3 H, ArH), 8.30 (d, *J* = 8.8 Hz, 2 H, ArH), 8.69 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.50; H, 6.37; N, 4.33.

3-(4-Nitrophenyl)-1-(*n*-propyl)benzo[*f*]quinoline (4k)
Mp 146–147 °C.

IR (KBr): 2955, 2886, 2864, 1597, 1581, 1552, 1511, 1481, 1450, 1339, 1196, 1164, 1108, 1090, 869, 848, 834, 801, 747 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.12 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.90–1.96 (m, 2 H, CH_2), 3.52 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.73–7.82 (m, 2 H, ArH), 8.00 (d, *J* = 9.2 Hz, 1 H, ArH), 8.10–8.15 (m, 2 H, ArH), 8.29 (s, 1 H, ArH), 8.40 (d, *J* = 8.8 Hz, 2 H, ArH), 8.60 (d, *J* = 8.8 Hz, 2 H, ArH), 8.73 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.29; H, 5.16; N, 8.26.

1-(*n*-Butyl)-3-(2,4-dichlorophenyl)benzo[*f*]quinoline (4l)
Mp 84–85 °C.

IR (KBr): 3055, 2960, 2927, 2860, 1590, 1556, 1525, 1509, 1476, 1459, 1450, 1438, 1380, 1348, 1249, 1186, 1145, 1099, 1043, 893, 857, 834, 815, 794, 740 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 0.98 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.49–1.57 (m, 2 H, CH_2), 1.83–1.89 (m, 2 H, CH_2), 3.52 (t, *J* = 7.0 Hz, 2 H, CH_2), 7.63 (dd, *J* = 8.4, 2.0 Hz, 1 H, ArH), 7.75–7.83 (m, 5 H, ArH), 7.95 (d, *J* = 8.8 Hz, 1 H, ArH), 8.12–8.15 (m, 2 H, ArH), 8.78 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{19}Cl_2N$: C, 72.64; H, 5.04; N, 3.68. Found: C, 72.77; H, 5.18; N, 3.57.

1-(*n*-Butyl)-3-(4-chlorophenyl)benzo[*f*]quinoline (4m)
Mp 99–100 °C.

IR (KBr): 3057, 2940, 2868, 1579, 1547, 1527, 1479, 1452, 1429, 1407, 1388, 1347, 1275, 1175, 1090, 1011, 992, 970, 942, 887, 871, 835, 812, 756, 740, 712 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 0.97 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.48–1.55 (m, 2 H, CH_2), 1.79–1.87 (m, 2 H, CH_2), 3.47 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.60 (d, *J* = 8.4 Hz, 2 H, ArH), 7.68–7.77 (m, 2 H, ArH), 7.95 (d, *J* = 8.8 Hz, 1 H, ArH), 8.06–8.11 (m, 3 H, ArH), 8.34 (d, *J* = 8.4 Hz, 2 H, ArH), 8.69 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{20}ClN$: C, 79.87; H, 5.83; N, 4.05. Found: C, 79.72; H, 5.65; N, 4.11.

1-(*n*-Butyl)-3-(2-thienyl)benzo[*f*]quinoline (4n)
Mp 86–87 °C.

IR (KBr): 3063, 2949, 2923, 2867, 1579, 1549, 1523, 1481, 1455, 1430, 1349, 1248, 1225, 868, 833, 754, 724 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.08 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.61–1.68 (m, 2 H, CH_2), 1.92–2.00 (m, 2 H, CH_2), 3.49 (t, *J* = 8.0 Hz, 2 H, CH_2), 7.19–7.21 (m, 1 H, ArH), 7.48–7.50 (m, 1 H, ArH), 7.62–7.71 (m, 2 H, ArH), 7.78–7.80 (m, 2 H, ArH), 7.94–7.97 (m, 2 H, ArH), 8.02 (d, *J* = 9.2 Hz, 1 H, ArH), 8.69 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{21}H_{19}NS$: C, 79.45; H, 6.03; N, 4.41. Found: C, 79.52; H, 5.92; N, 4.54.

3-(3-Bromophenyl)-1-(*n*-butyl)benzo[*f*]quinoline (4o)
Mp 106–107 °C.

IR (KBr): 3054, 2959, 2930, 2872, 2858, 1584, 1568, 1549, 1487, 1478, 1456, 1436, 1419, 1340, 1260, 1242, 1091, 1070, 903, 866, 833, 816, 773, 742, 710, 682 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.06 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.59–1.65 (m, 2 H, CH_2), 1.91–1.99 (m, 2 H, CH_2), 3.50 (t, *J* = 8.0 Hz, 2 H, CH_2), 7.40 (t, *J* = 8.0 Hz, 1 H, ArH), 7.57 (dd, *J* = 2.0, 1.2 Hz, 1 H, ArH), 7.59–7.70 (m, 2 H, ArH), 7.79 (s, 1 H, ArH), 7.96 (d, *J* = 8.4 Hz, 2 H, ArH), 8.05 (d, *J* = 9.2 Hz, 1 H, ArH), 8.12–8.14 (m, 1 H, ArH), 8.38–8.39 (m, 1 H, ArH), 8.69 (d, *J* = 8.0 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{20}BrN$: C, 70.78; H, 5.16; N, 3.59. Found: C, 70.67; H, 5.22; N, 3.50.

1-(*n*-Butyl)-3-(4-fluorophenyl)benzo[*f*]quinoline (4p)
Mp 95–96 °C.

IR (KBr): 3055, 2950, 2925, 2865, 1600, 1580, 1549, 1528, 1481, 1450, 1388, 1353, 1330, 1295, 1219, 1156, 1100, 1012, 865, 851, 838, 809, 753, 735, 717 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.06 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.59–1.65 (m, 2 H, CH_2), 1.91–1.99 (m, 2 H, CH_2), 3.50 (t, *J* = 8.0 Hz, 2 H, CH_2), 7.20–7.24 (m, 2 H, ArH), 7.62–7.69 (m, 2 H, ArH), 7.79 (s, 1 H, ArH), 7.94–7.97 (m, 2 H, ArH), 8.05 (d, *J* = 9.2 Hz, 1 H, ArH), 8.19–8.22 (m, 2 H, ArH), 8.69 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{20}FN$: C, 83.86; H, 6.12; N, 4.25. Found: C, 83.98; H, 6.03; N, 4.37.

1-(*n*-Butyl)-3-(3-nitrophenyl)benzo[*f*]quinoline (4q)
Mp 128–129 °C.

IR (KBr): 3084, 3052, 2959, 2931, 2862, 1583, 1534, 1486, 1456, 1435, 1343, 1308, 1259, 1244, 1165, 1074, 926, 872, 857, 850, 834, 815, 799 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.07 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.59–1.68 (m, 2 H, CH_2), 1.93–2.00 (m, 2 H, CH_2), 3.51 (t, *J* = 8.0 Hz, 2 H, CH_2), 7.64–7.72 (m, 3 H, ArH), 7.87 (s, 1 H, ArH), 7.96–7.99 (m, 2 H, ArH), 8.06 (d, *J* = 7.2 Hz, 1 H, ArH), 8.28–8.31 (m, 1 H, ArH), 8.59 (d, *J* = 7.6 Hz, 1 H, ArH), 8.69 (d, *J* = 8.0 Hz, 1 H, ArH), 9.06 (s, 1 H, ArH).

Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.64; H, 5.52; N, 7.95.

1-(*n*-Butyl)-3-(4-nitrophenyl)benzo[*f*]quinoline (4r)
Mp 150–151 °C.

IR (KBr): 3056, 2952, 2929, 2882, 2868, 1597, 1580, 1551, 1531, 1508, 1481, 1453, 1430, 1337, 1258, 1163, 1108, 857, 850, 835, 799, 746 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.07 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.59–1.67 (m, 2 H, CH_2), 1.94–2.01 (m, 2 H, CH_2), 3.53 (t, *J* = 8.0 Hz, 2 H, CH_2), 7.66–7.73 (m, 2 H, ArH), 7.89 (s, 1 H, ArH), 7.97–8.01 (m, 2 H, ArH), 8.07 (d, *J* = 8.8 Hz, 1 H, ArH), 8.37–8.42 (m, 4 H, ArH), 8.71 (d, *J* = 8.0 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.43; H, 5.55; N, 7.80.

1-(*n*-Butyl)-3-(4-methylphenyl)benzo[*f*]quinoline (4s)
Mp 124–125 °C.

IR (KBr): 3055, 3030, 2960, 2947, 2923, 2867, 1579, 1547, 1525, 1509, 1479, 1464, 1429, 1392, 1350, 1255, 1180, 1018, 872, 835, 821, 811, 751, 733, 714 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.05 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.56–1.67 (m, 2 H, CH_2), 1.91–1.99 (m, 2 H, CH_2), 2.44 (s, 3 H, CH_3), 3.49 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.34 (d, *J* = 8.0 Hz, 2 H, ArH), 7.60–7.68 (m, 2 H, ArH), 7.81 (s, 1 H, ArH), 7.93–7.95 (m, 2 H, ArH), 8.06 (d, *J* = 8.8 Hz, 1 H, ArH), 8.11 (d, *J* = 8.0 Hz, 2 H, ArH), 8.69 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30. Found: C, 88.66; H, 7.18; N, 4.17.

1-(*n*-Butyl)-3-(4-methoxyphenyl)benzo[*f*]quinoline (4t)
Mp 117–118 °C.

IR (KBr): 3055, 2951, 2935, 2868, 2840, 1609, 1581, 1548, 1510, 1479, 1465, 1452, 1355, 1293, 1253, 1169, 1029, 872, 836, 811, 754 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.05 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.58–1.66 (m, 2 H, CH_2), 1.91–1.98 (m, 2 H, CH_2), 3.48 (t, *J* = 8.0 Hz, 2 H, CH_2), 3.89 (s, 3 H, CH_3O), 7.04–7.08 (m, 2 H, ArH), 7.59–7.68 (m, 2 H, ArH), 7.78 (s, 1 H, ArH), 7.92–7.95 (m, 2 H, ArH), 8.05 (d, *J* = 9.2 Hz, 1 H, ArH), 8.16–8.20 (m, 2 H, ArH), 8.68 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.56; H, 6.70; N, 4.22.

3-(4-Bromophenyl)-1-(*n*-butyl)benzo[*f*]quinoline (4u)
Mp 113–114 °C.

IR (KBr): 3055, 2947, 2924, 2867, 2851, 1579, 1546, 1478, 1450, 1429, 1386, 1346, 1276, 1176, 1101, 1009, 993, 942, 886, 872, 829, 753, 712 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.00 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.52–1.58 (m, 2 H, CH_2), 1.83–1.90 (m, 2 H, CH_2), 3.52 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.70–7.79 (m, 4 H, ArH), 7.97 (d, *J* = 9.2 Hz, 1 H, ArH), 8.08–8.12 (m, 2 H, ArH), 8.31 (s, 1 H, ArH), 8.30 (d, *J* = 8.0 Hz, 2 H, ArH), 8.72 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{20}BrN$: C, 70.78; H, 5.16; N, 3.59. Found: C, 70.66; H, 5.30; N, 3.55.

1-(*n*-Butyl)-3-(3-chlorophenyl)benzo[*f*]quinoline (4v)
Mp 96–97 °C.

IR (KBr): 3055, 2960, 2932, 2859, 1585, 1550, 1525, 1484, 1456, 1436, 1420, 1340, 1260, 1241, 1166, 1094, 1076, 902, 868, 833, 815, 774, 742, 730 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.00 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.52–1.58 (m, 2 H, CH_2), 1.83–1.89 (m, 2 H, CH_2), 3.52 (t, *J* = 7.6 Hz, 2 H, CH_2), 7.56–7.63 (m, 2 H, ArH), 7.70–7.80 (m, 2 H, ArH), 7.99 (d, *J* = 9.2 Hz, 1 H, ArH), 8.09–8.12 (m, 2 H, ArH), 8.20 (s, 1 H, ArH), 8.29–8.32 (m, 1 H, ArH), 8.39–8.40 (m, 1 H, ArH), 8.73 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{20}ClN$: C, 79.87; H, 5.83; N, 4.05. Found: C, 79.76; H, 5.93; N, 4.05.

3-(3-Chlorophenyl)-1-(isopropyl)benzo[*f*]quinoline (4w)
Mp 150–151 °C.

IR (KBr): 3050, 2962, 2928, 2869, 1597, 1581, 1547, 1480, 1451, 1420, 1394, 1333, 1294, 1249, 1162, 1078, 1068, 876, 829, 791, 755, 736, 698 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.57 (d, J = 6.8 Hz, 6 H, 2 × CH_3), 4.22–4.28 (m, 1 H, CH), 7.58–7.63 (m, 2 H, ArH), 7.72–7.76 (m, 2 H, ArH), 7.95 (d, J = 8.8 Hz, 1 H, ArH), 8.10 (d, J = 8.8 Hz, 2 H, ArH), 8.31 (s, 1 H, ArH), 8.35 (d, J = 9.2 Hz, 1 H, ArH), 8.43 (s, 1 H, ArH), 8.60 (d, J = 8.0 Hz, 1 H, ArH).

Anal. Calcd for $C_{22}H_{18}ClN$: C, 79.63; H, 5.47; N, 4.22. Found: C, 79.85; H, 5.40; N, 4.10.

3-(4-Fluorophenyl)-1-(isopropyl)benzo[*f*]quinoline (4x)
Mp 162–163 °C.

IR (KBr): 3053, 2977, 2962, 2928, 2870, 1599, 1581, 1547, 1527, 1508, 1480, 1452, 1392, 1366, 1343, 1233, 1214, 1158, 844, 831, 801, 753, 719 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.56 (d, J = 6.8 Hz, 6 H, 2 × CH_3), 4.21–4.28 (m, 1 H, CH), 7.38–7.42 (m, 2 H, ArH), 7.69–7.77 (m, 2 H, ArH), 7.93 (d, J = 8.8 Hz, 1 H, ArH), 8.07–8.10 (m, 2 H, ArH), 8.24 (s, 1 H, ArH), 8.40–8.46 (m, 2 H, ArH), 8.60 (d, J = 8.0 Hz, 1 H, ArH).

Anal. Calcd for $C_{22}H_{18}FN$: C, 83.78; H, 5.75; N, 4.44. Found: C, 83.70; H, 5.57; N, 4.52.

3-(3-Bromophenyl)-1-phenylbenzo[*f*]quinoline (4y)
Mp 208–210 °C.

IR (KBr): 3054, 1601, 1576, 1543, 1477, 1419, 1389, 1345, 1328, 1275, 1252, 1231, 1150, 1083, 1069, 996, 943, 870, 838, 781, 756, 702, 689 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.19–7.23 (m, 1 H, ArH), 7.50–7.62 (m, 8 H, ArH), 7.70–7.72 (m, 1 H, ArH), 8.03–8.09 (m, 3 H, ArH), 8.18 (d, J = 8.8 Hz, 1 H, ArH), 8.37 (d, J = 7.6 Hz, 1 H, ArH), 8.58–8.59 (m, 1 H, ArH).

Anal. Calcd for $C_{25}H_{16}BrN$: C, 73.18; H, 3.93; N, 3.41. Found: C, 73.03; H, 3.94; N, 3.55.

3-(4-Nitrophenyl)-1-phenylbenzo[*f*]quinoline (4z)
Mp 255–257 °C.

IR (KBr): 3053, 1599, 1578, 1547, 1509, 1475, 1397, 1340, 1259, 1153, 1106, 1078, 1008, 860, 849, 832, 801, 774, 755, 699 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 7.21–7.25 (m, 1 H, ArH), 7.55–7.62 (m, 7 H, ArH), 8.09–8.12 (m, 2 H, ArH), 8.17 (s, 1 H, ArH), 8.22 (d, J = 8.8 Hz, 1 H, ArH), 8.40 (d, J = 8.8 Hz, 2 H, ArH), 8.67 (d, J = 8.8 Hz, 2 H, ArH).

Anal. Calcd for $C_{25}H_{16}N_2O_2$: C, 79.77; H, 4.28; N, 7.44. Found: C, 79.89; H, 4.10; N, 7.50.

Syntheses of 2-(3-Arylbenzo[*f*]quinolin-1-yl)acetate Derivatives 6; General Procedure
A dry 50 mL flask was charged with arylaldehyde (2.0 mmol), naphthalen-2-amine (2.0 mmol, 0.286 g), β-keto ester (2.5 mmol), I_2 (0.1 mmol, 0.025 g) and THF (10 mL). The reaction mixture was stirred at reflux for 6–8 h. After completion of the reaction as indicated by TLC, a little DMF was added to the mixture until all the yellow solid was dissolved. After the mixture was cooled to r.t., the generated crystals were collected by filtration to give **6**.

Methyl 2-{3-(4-Chlorophenyl)benzo[*f*]quinolin-1-yl}acetate (6a)
Mp 138–139 °C.

IR (KBr): 3024, 2994, 2944, 2841, 1743, 1582, 1551, 1528, 1479, 1454, 1433, 1424, 1368, 1326, 1300, 1271, 1215, 1198, 1154, 1106, 1090, 1012, 991, 945, 898, 890, 875, 833, 803, 753, 742, 732 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.77 (s, 3 H, CH_3O), 4.49 (s, 2 H, CH_2), 7.50 (d, J = 8.4 Hz, 2 H, ArH), 7.64–7.67 (m, 2 H, ArH), 7.82 (s, 1 H, ArH), 7.82–7.98 (m, 2 H, ArH), 8.05 (d, J = 8.8 Hz, 1 H, ArH), 8.16 (d, J = 8.4 Hz, 2 H, ArH), 8.48–8.51 (m, 1 H, ArH).

Anal. Calcd for $C_{22}H_{16}ClNO_2$: C, 73.03; H, 4.46; N, 3.87. Found: C, 72.89; H, 4.57; N, 3.80.

Methyl 2-{3-(2,4-Dichlorophenyl)benzo[*f*]quinolin-1-yl}acetate (6b)
Mp 155–156 °C.

IR (KBr): 3058, 2955, 2843, 1732, 1591, 1557, 1477, 1448, 1434, 1382, 1356, 1337, 1222, 1200, 1158, 1098, 1046, 984, 899, 853, 833, 826, 796, 744 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.65 (s, 3 H, CH_3O), 4.72 (s, 2 H, CH_2), 7.64 (dd, J = 8.4, 2.0 Hz, 1 H, ArH), 7.74–7.76 (m, 2 H, ArH), 7.81–7.84 (m, 2 H, ArH), 7.92 (s, 1 H, ArH), 7.98 (d, J = 8.8 Hz, 1 H, ArH), 8.13–8.15 (m, 1 H, ArH), 8.17 (d, J = 9.2 Hz, 1 H, ArH), 8.55–8.58 (m, 1 H, ArH).

Anal. Calcd for $C_{22}H_{15}Cl_2NO_2$: C, 66.68; H, 3.82; N, 3.53. Found: C, 66.70; H, 3.77; N, 3.67.

Methyl 2-{3-(2,3-Dichlorophenyl)benzo[*f*]quinolin-1-yl}acetate (6c)
Mp 158–159 °C.

IR (KBr): 3053, 2955, 1733, 1591, 1579, 1551, 1485, 1447, 1435, 1413, 1389, 1360, 1334, 1229, 1194, 1156, 1046, 988, 924, 905, 833, 802, 791, 746, 733, 708 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.65 (s, 3 H, CH_3O), 4.73 (s, 2 H, CH_2), 7.54–7.58 (m, 1 H, ArH), 7.71 (dd, J = 7.6, 1.2 Hz, 1 H, ArH), 7.75–7.79 (m, 2 H, ArH), 7.82 (dd, J = 8.0, 1.6 Hz, 1 H, ArH), 7.90 (s, 1 H, ArH), 7.98 (d, J = 9.2 Hz, 1 H, ArH), 8.13–8.15 (m, 1 H, ArH), 8.18 (d, J = 9.2 Hz, 1 H, ArH), 8.56–8.58 (m, 1 H, ArH).

Anal. Calcd for $C_{22}H_{15}Cl_2NO_2$: C, 66.68; H, 3.82; N, 3.53. Found: C, 66.51; H, 3.67; N, 3.70.

Methyl 2-{3-(4-Nitrophenyl)benzo[*f*]quinolin-1-yl}acetate (6d)
Mp 185–186 °C.

IR (KBr): 3054, 3008, 2954, 2844, 1732, 1595, 1583, 1553, 1516, 1483, 1454, 1438, 1364, 1333, 1259, 1216, 1201, 1163, 1108, 1088, 1023, 1011, 987, 950, 899, 871, 857, 849, 834, 802, 758, 744, 717, 690 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.67 (s, 3 H, CH_3O), 4.75 (s, 2 H, CH_2), 7.73–7.75 (m, 2 H, ArH), 8.03 (d, J = 9.2 Hz, 1 H, ArH), 8.11–8.13 (m, 1 H, ArH), 8.17 (d, J = 8.8 Hz, 1 H, ArH), 8.40 (s, 1 H, ArH), 8.42 (d, J = 8.8 Hz, 2 H, ArH), 8.51–8.53 (m, 1 H, ArH), 8.56 (d, J = 8.8 Hz, 2 H, ArH).

Anal. Calcd for $C_{22}H_{16}N_2O_4$: C, 70.96; H, 4.33; N, 7.52. Found: C, 70.85; H, 4.21; N, 7.68.

Methyl 2-{3-(4-Bromophenyl)benzo[*f*]quinolin-1-yl}acetate (6e)
Mp 143–144 °C.

IR (KBr): 3019, 2992, 2943, 1742, 1582, 1550, 1525, 1478, 1454, 1431, 1423, 1366, 1326, 1301, 1271, 1215, 1198, 1154, 1084, 1071, 1007, 991, 875, 830, 753, 742, 730 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.78 (s, 3 H, CH_3O), 4.49 (s, 2 H, CH_2), 7.63–7.69 (m, 4 H, ArH), 7.82 (s, 1 H, ArH), 7.95–7.99 (m, 2 H, ArH), 8.05 (d, J = 9.2 Hz, 1 H, ArH), 8.10 (d, J = 8.4 Hz, 2 H, ArH), 8.48–8.51 (m, 1 H, ArH).

Anal. Calcd for $C_{22}H_{16}BrNO_2$: C, 65.04; H, 3.97; N, 3.45. Found: C, 64.90; H, 4.10; N, 3.55.

Methyl 2-{3-(4-Methoxyphenyl)benzo[*f*]quinolin-1-yl}acetate (6f)
Mp 168–169 °C.

IR (KBr): 3001, 2957, 2935, 2836, 1737, 1605, 1580, 1549, 1531, 1509, 1481, 1454, 1436, 1393, 1355, 1336, 1308, 1292, 1202, 1182, 1113, 1029, 981, 936, 903, 866, 844, 816, 799, 747 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.66 (s, 3 H, CH_3O), 3.86 (s, 3 H, CH_3O), 4.70 (s, 2 H, CH_2), 7.14 (d, *J* = 8.8 Hz, 2 H, ArH), 7.69–7.71 (m, 2 H, ArH), 7.99 (d, *J* = 9.2 Hz, 1 H, ArH), 8.08–8.12 (m, 2 H, ArH), 8.19 (s, 1 H, ArH), 8.29 (d, *J* = 8.8 Hz, 2 H, ArH), 8.48–8.50 (m, 1 H, ArH).

Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.18; H, 5.50; N, 3.89.

Methyl 2-{3-(2,3-Dimethoxyphenyl)benzo[*f*]quinolin-1-yl}acetate (6g)
Mp 180–182 °C.

IR (KBr): 3041, 3009, 2938, 2837, 1732, 1622, 1580, 1497, 1468, 1436, 1405, 1358, 1330, 1272, 1194, 1156, 1093, 1055, 1022, 998, 957, 904, 833, 765, 747 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.68 (s, 3 H, CH_3O), 3.75 (s, 3 H, CH_3O), 3.92 (s, 3 H, CH_3O), 4.81 (s, 2 H, CH_2), 7.30–7.32 (m, 2 H, ArH), 7.44–7.46 (m, 1 H, ArH), 7.80–7.82 (m, 2 H, ArH), 8.08 (d, *J* = 9.2 Hz, 1 H, ArH), 8.13 (s, 1 H, ArH), 8.18–8.21 (m, 1 H, ArH), 8.29 (d, *J* = 8.8 Hz, 1 H, ArH), 8.59–8.62 (m, 1 H, ArH).

Anal. Calcd for $C_{24}H_{21}NO_4$: C, 74.40; H, 5.46; N, 3.62. Found: C, 74.55; H, 5.37; N, 3.80.

Methyl 2-{3-(3-Nitrophenyl)benzo[*f*]quinolin-1-yl}acetate (6h)
Mp 183–185 °C.

IR (KBr): 3092, 3075, 3053, 3007, 2958, 1733, 1587, 1553, 1520, 1491, 1446, 1436, 1346, 1276, 1261, 1200, 1156, 1109, 1065, 1017, 986, 943, 905, 853, 833, 809, 800, 745, 712, 681 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.80 (s, 3 H, CH_3O), 4.52 (s, 2 H, CH_2), 7.67–7.72 (m, 3 H, ArH), 7.91 (s, 1 H, ArH), 7.96–8.01 (m, 2 H, ArH), 8.07 (d, *J* = 8.8 Hz, 1 H, ArH), 8.29–8.32 (m, 1 H, ArH), 8.49–8.52 (m, 1 H, ArH), 8.59 (d, *J* = 7.6 Hz, 1 H, ArH), 9.06–9.07 (m, 1 H, ArH).

Anal. Calcd for $C_{22}H_{16}N_2O_4$: C, 70.96; H, 4.33; N, 7.52. Found: C, 70.89; H, 4.28; N, 7.69.

Ethyl 2-{3-(2,4-Dichlorophenyl)benzo[*f*]quinolin-1-yl}acetate (6i)
Mp 126–128 °C.

IR (KBr): 3057, 3030, 2973, 2930, 1731, 1590, 1556, 1529, 1476, 1450, 1383, 1368, 1353, 1332, 1229, 1201, 1156, 1099, 1045, 1029, 884, 858, 833, 825, 796, 741 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.24 (t, *J* = 6.8 Hz, 3 H, CH_3), 4.24 (q, *J* = 6.8 Hz, 2 H, CH_2), 4.48 (s, 2 H, CH_2), 7.42 (d, *J* = 8.0 Hz, 1 H, ArH), 7.55 (s, 1 H, ArH), 7.67–7.69 (m, 2 H, ArH), 7.77–7.80 (m, 2 H, ArH), 7.97–8.05 (m, 3 H, ArH), 8.58 (d, *J* = 8.4 Hz, 1 H, ArH).

Anal. Calcd for $C_{23}H_{17}Cl_2NO_2$: C, 67.33; H, 4.18; N, 3.41. Found: C, 67.50; H, 4.09; N, 3.53.

Ethyl 2-{3-(4-Bromophenyl)benzo[*f*]quinolin-1-yl}acetate (6j)
Mp 143–144 °C (Lit.[16] 143–144 °C).

IR (KBr): 3051, 2981, 2935, 1729, 1589, 1551, 1531, 1481, 1445, 1371, 1328, 1275, 1213, 1201, 1159, 1089, 1073, 1029, 1008, 947, 863, 834, 823, 744, 729 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.23 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.24 (q, *J* = 7.2 Hz, 2 H, CH_2), 4.46 (s, 2 H, CH_2), 7.62–7.67 (m, 4 H, ArH), 7.81 (s, 1 H, ArH), 7.93–7.97 (m, 2 H, ArH), 8.04 (d, *J* = 8.8 Hz, 1 H, ArH), 8.09 (d, *J* = 8.4 Hz, 2 H, ArH), 8.50–8.82 (m, 1 H, ArH).

Ethyl 2-{3-(3-Bromophenyl)benzo[*f*]quinolin-1-yl}acetate (6k)
Mp 125–126 °C.

IR (KBr): 3061, 2975, 2936, 2901, 1733, 1588, 1551, 1479, 1455, 1444, 1428, 1373, 1326, 1268, 1214, 1199, 1172, 1158, 1067, 1032, 995, 946, 903, 881, 837, 783, 751, 708, 683 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.24 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.25 (q, *J* = 7.2 Hz, 2 H, CH_2), 4.49 (s, 2 H, CH_2), 7.38–7.42 (m, 1 H, ArH), 7.58–7.60 (m, 1 H, ArH), 7.65–7.68 (m, 2 H, ArH), 7.83 (s, 1 H, ArH), 7.95–7.99 (m, 2 H, ArH), 8.06 (d, *J* = 8.4 Hz, 1 H, ArH), 8.13 (d, *J* = 8.0 Hz, 1 H, ArH), 8.40–8.41 (m, 1 H, ArH), 8.52–8.54 (m, 1 H, ArH).

Anal. Calcd for $C_{23}H_{18}BrNO_2$: C, 65.73; H, 4.32; N, 3.33. Found: C, 65.87; H, 4.15; N, 3.38.

Ethyl 2-{3-(4-Chlorophenyl)benzo[*f*]quinolin-1-yl}acetate (6l)
Mp 140–141 °C.

IR (KBr): 3052, 2982, 2728, 1590, 1552, 1531, 1482, 1446, 1390, 1371, 1329, 1295, 1214, 1201, 1158, 1093, 1030, 1012, 862, 835, 824, 744 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 1.14 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.13 (q, *J* = 7.2 Hz, 2 H, CH_2), 4.72 (s, 2 H, CH_2), 7.67 (d, *J* = 8.8 Hz, 2 H, ArH), 7.71–7.74 (m, 2 H, ArH), 8.02 (d, *J* = 8.8 Hz, 1 H, ArH), 8.10–8.13 (m, 1 H, ArH), 8.15 (d, *J* = 8.8 Hz, 1 H, ArH), 8.29 (s, 1 H, ArH), 8.36 (d, *J* = 8.4 Hz, 2 H, ArH), 8.53–8.55 (m, 1 H, ArH).

Anal. Calcd for $C_{23}H_{18}ClNO_2$: C, 73.50; H, 4.83; N, 3.73. Found: C, 73.65; H, 4.90; N, 3.67.

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(14) X-ray crystal data for **4c**. Empirical formula: $C_{22}H_{18}BrN$; Formula weight: 376.28; Colorless block crystals; Crystal size: 0.46 × 0.45 × 0.17 mm; Crystal system: triclinic; Space group: $P\bar{1}$; Unit cell dimensions: a = 9.203 (2) Å, b = 10.173 (2) Å, c = 10.582 (2) Å, α = 97.868 (3)°, β = 107.038 (3)°, γ = 112.235 (3)°; V = 841.7 (3) Å^3; Z = 2; D(calcd) = 1.485 g/cm^3; F(000) = 384, μ(MoKα) = 2.444 mm^{-1}. Intensity data were collected on a Rigaku Mercury diffractometer with graphite monochromated MoKα radiation (λ = 0.71070 Å) using ω scan mode with 3.09° < θ < 25.35°. Unique reflections collected 3062; 2625 reflections with I > 2σ (I) were used in the refinement. The structure was solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique gave R = 0.0374 and wR = 0.0877.
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