An Efficient Synthesis of 1,3-Diarylbenzo[*f*]quinolines from 2-Halogenated Acetophenone, Aromatic Aldehyde, and Naphthalen-2-Amine Catalyzed by Iodine

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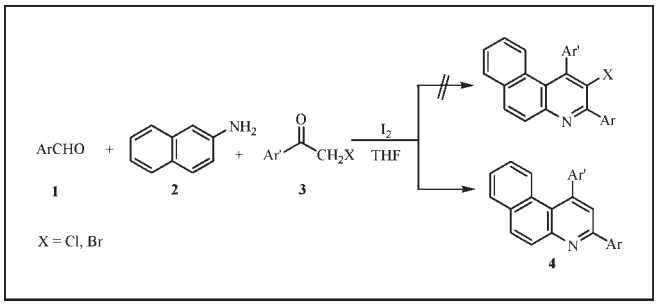

The three-component reaction of aromatic aldehyde, naphthalen-2-amine and 2-halogenated acetophenone in THF catalyzed by 5 mol % iodine at reflux unexpectedly gave 1,3-diarylbenzo[*f*]quinolines, with halogen losing in the formation of the products. The formation of unexpected 1,3-diarylbenzo[*f*]-quinolines was tentatively explained by Cram's rule to one of the steps in the mechanism.

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INTRODUCTION

There has been tremendous interest in developing highly efficient transformations for the preparation of organic compounds, as well as, biologically active materials. There is also a need for synthetic chemists to find new, efficient, and strategically important processes, which are environmentally benign and lead to greater structural variation in short period of times with high yields and simple work-up procedures. Multicomponent reactions are useful and efficient methods in organic synthesis. The major advantages of these reactions are a single purification step, higher yields than stepwise assembly, the use of simple and diverse precursors to construct complex molecules, and the use of only a single promoter or catalyst. Thus, the development of new multicomponent reactions is a popular area of research in current organic chemistry and is also acceptable from a ''Green Chemistry" point of view [1]. They provide a powerful tool toward the one-pot synthesis of diverse and complex compounds as well as small and drug-like heterocycles [2]. Such as benzo[*f*]quinoline and its derivatives, are very useful compounds in the various fields of chemistry including biological and pharmacological viewpoints. Some of which exhibit antibacterial activity [3], UDP (Uridine diphosphate)-glucuronosyl transferase activity [4], antimicrobial activity [5], antimalarial activity [6], agonistic activity [7], and antipsychotic activity [8].

In view of the importance of the benzoquinoline and its derivatives, several methods for the synthesis of benzo[*f*]quinoline and its derivatives were developed by Kozlov [9] and other groups [10]. However, many of these reported methods suffer from drawbacks such as harsh reaction conditions, unsatisfactory yields, prolonged reaction time or cumbersome product isolation procedure. In our previous paper, we have reported the 1,3-substituented benzoquinolines *via* three component reaction of aromatic aldehyde, naphthalen-2-amine and ketones [11]. Our interest in synthesis of heterocyclic compounds [12] by multicomponent reaction stimulates us to find some new and more substituented benzoquinolines, such as 1,3-diaryl-2-halogenated benzoquinoline derivatives, so we perform the 2-halogenated acetophenone in the aforementioned reaction instead of acetophenone. To our surprised, the desired products 1,3-diaryl-2-halogenated benzoquinolines were not observed, with 1,3-diarylbenzoquinoline derivatives being obtained. It should be noted that the halogen lose in these I_2-catalyzed three-component reactions.

RESULTS AND DISCUSSION

Initially, the reaction of 4-chlorobenzaldehyde **1a**, naphthalen-2-amine **2** and 2-bromo-1-(4-nitrophenyl) ethanone **3a** was used as a model reaction to optimize the

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Table 1

Synthesis of **4a** under different reaction conditions.[a]

Entry	Temperature(°C)	I_2 (mol %)	Solvent	Yields[b](%)
1	RT	0	THF	0
2	Reflux	0	THF	0
3	RT	5	THF	Trace
4	50	5	THF	76
5	Reflux	5	THF	90
6	Reflux	10	THF	86
7	Reflux	20	THF	89
8	Reflux	5	CH_3CN	82
9	Reflux	5	Benzene	78
10	80	5	DMF	84
11	Reflux	5	$ClCH_2CH_2Cl$	79

[a] Reagents and conditions: **1a** (2 mmol, 0.281 g), **2** (2 mmol, 0.286 g), **3a** (2 mmol, 0.488 g), solvent (10 mL), 12 h.
[b] Isolated yields.

conditions. The reaction was first carried out in THF in the absence of I_2. No reaction occurred at room temperature and reflux condition (Table 1, entries 1 and 2). We also evaluated the amount of catalyst required for this transformation. It was found that 5 mol % of I_2 at reflux in THF was sufficient to push the reaction forward. More amounts of the catalyst did not improve yields. To find the optimum reaction temperature, the reaction was carried out with 5 mol % of I_2 at room temperature, 50 and refluxing temperature, resulting in the isolation of **4a** in trace amount, 76% and 90% yields (Table 1, entries 3, 4, and 5), respectively. Thus, 5 mol % of I_2 and a reaction temperature at reflux were optimal conditions. In addition, we also looked into the solvent effect at reflux condition for this reaction. As showed in Table 1, THF gave the most satisfactory result in comparison with other solvents. (Table 1, entries 8–11).

In our initial study, we think it was an unexpected product. Subsequently, we repeated the reactions under the same reaction conditions with various kinds of benzaldehydes bearing either electron-withdrawing groups (such as halide, nitro) or electron-donating groups (such as alkyl group, or alkoxyl group) or α-halogenated acetophenones (Scheme 1). However, the designed reactions all gave the products of 1,3-diarylbenzoquinoline derivatives rather than 1,3-diaryl-2-halogenated benzoquinolines in good to high yields (Table 2). Furthermore, in order to confirm the structure of product, the X-ray diffraction of **4a** was carried out [13]. The crystal structure of **4a** was shown in Figure 1, which made further confirmation of structure **4**. This raises an interesting question: why do the halogens lose in the formation of the benzoquinolines?

According to the literatures [14], in these I_2-catalyzed reactions, the subsequent reactions including condensation, addition, Friedel–Crafts, dehydration and aromatization were proposed to form the quinoline or benzoquinoline derivatives (Scheme 2). However, no stereoselectivity was put forward in the Friedel–Crafts cyclization of the addition product. It is a Friedel–Crafts cyclization as well as an intra-molecular nucleophilic addition reaction with benzene as nucleophilic reagent attacking carboxyl group, with a chiral centre being connected with this carboxyl group. The stereochemistry of the Friedel–Crafts cyclization should be in agreement with Cram's rule, so the hydroxyl group and the hydrogen atom lie on syn periplanar geometry with halogen on the anti periplanar geometry. Subsequent elimination reaction of HX for their anti periplanar rather than H_2O results in oxirenoquinoline. The oxirane ring is opened to give 2-hydroxybenzoquinoline induced by iodine, which is further dehydrated to afford final 1,3-diaryl benzoquinoline (Scheme 2). The reason why the halogens lose is perhaps best explained by Cram's rule in the formation of the benzoquinolines.

In conclusion, we found an efficient method for the synthesis of benzo[*f*]quinoline derivatives via three-component reaction of aromatic aldehyde, naphthalen-2-amine and 2-halogenated acetophenone using 5 mol % of iodine as catalyst, with halogen losing in the formation of the products. A Cram's rule in the I_2-catalyzed Friedel–Crafts reaction was proposed to occur in the formation of the products.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr pellet. ^{1}H NMR spectra were obtained from solution in DMSO-d_6 with Me_4Si as internal standard using a Bruker-400 spectrometer. HRMS analyses were carried out using a Bruker-micro-TOF-Q-MS analyzer.

Typical procedure for 1,3-diarylbenzo[f]quinoline derivatives 4. A dry 50 mL flask was charged with aromatic aldehyde (2.0 mmol), naphthalen-2-amine (2.0 mmol, 0.286 g), 2-halogenated acetophenone (2.0 mmol), I_2 (0.1 mmol, 0.026 g) and THF (10 mL). The reaction mixture was stirred at reflux for 11–15 h. After completion of the reaction as indicated by TLC, a little DMF was added to the mixture until the all yellow solid was dissolved. The generated crystals were collected by filtration to give 4 when the mixture was cooled to room temperature.

Scheme 1

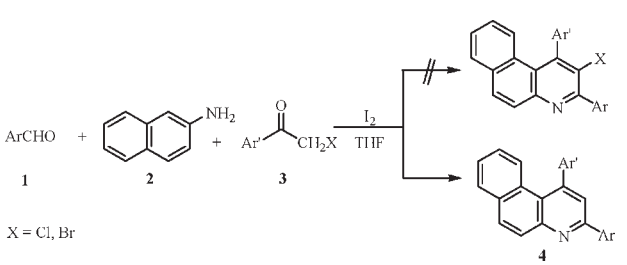


Table 2

I_2-catalyzed reactions of benzaldehyde, naphthalen-2-amine, and α-halogenated acetophenones in THF.[a]

Entry	Ar	Ar′	X	Products	Time (h)	Yields[b] (%)
1	4-ClC_6H_4	4-$NO_2C_6H_4$	Br	**4a**	12	90
2	2,3-$(CH_3O)_2C_6H_3$	4-$NO_2C_6H_4$	Br	**4b**	14	86
3	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	Br	**4c**	11	91
4	2,3-$Cl_2C_6H_3$	4-$NO_2C_6H_4$	Br	**4d**	12	82
5	2,4-$Cl_2C_6H_3$	4-$NO_2C_6H_4$	Br	**4e**	13	81
6	3,4-$(CH_3)_2C_6H_3$	4-$NO_2C_6H_4$	Br	**4f**	14	84
7	2,4-$Cl_2C_6H_3$	4-FC_6H_4	Br	**4g**	15	88
8	3-BrC_6H_4	4-FC_6H_4	Br	**4h**	12	79
9	4-ClC_6H_4	4-FC_6H_4	Br	**4i**	13	80
10	3,5-$(CH_3O)_2C_6H_3$	4-FC_6H_4	Br	**4j**	15	82
11	4-BrC_6H_4	4-FC_6H_4	Br	**4k**	13	89
12	3-$NO_2C_6H_4$	4-FC_6H_4	Br	**4l**	13	84
13	3-BrC_6H_4	4-ClC_6H_4	Br	**4m**	15	78
14	2,4-$Cl_2C_6H_3$	4-ClC_6H_4	Br	**4n**	12	83
15	2-Thiophenyl	3-ClC_6H_4	Br	**4o**	13	82
16	3-BrC_6H_4	3-ClC_6H_4	Br	**4p**	15	78
17	4-BrC_6H_4	3-ClC_6H_4	Br	**4q**	14	80
18	3-$NO_2C_6H_4$	3-ClC_6H_4	Br	**4r**	15	81
19	3,4-$(CH_3)_2C_6H_3$	3-ClC_6H_4	Br	**4s**	15	86
20	4-$NO_2C_6H_4$	C_6H_5	Cl	**4t**	12	82
21	4-ClC_6H_4	C_6H_5	Cl	**4u**	12	79
22	4-BrC_6H_4	C_6H_5	Cl	**4v**	14	87
23	3-BrC_6H_4	C_6H_5	Cl	**4w**	15	84
24	2-Thiophenyl	3-$NO_2C_6H_4$	Br	**4x**	15	89
25	4-ClC_6H_4	3-$NO_2C_6H_4$	Br	**4y**	13	86
26	4-BrC_6H_4	3-$NO_2C_6H_4$	Br	**4z**	15	86

[a] Reagents and conditions: **1** (2 mmol), **2** (2 mmol, 0.286g), **3** (2 mmol), I_2 (0.1 mmol, 0.026 g), and THF (10 mL).
[b] Isolated yields.

3-(4-Chlorophenyl)-1-(4-nitrophenyl)benzo[*f*] quinoline (4a). This compound was obtained as pale yellow crystals, mp 286–288°C; ir (KBr): ν_{max} 3101, 3074, 3048, 1596, 1580, 1544, 1514, 1493, 1476, 1449, 1408, 1388, 1344, 1305, 1282, 1177, 1152, 1107, 1091, 1010, 851, 832, 797, 758, 744, 717, 704, 692; ^{1}H NMR (DMSO-d_6): δ 7.28–7.32 (m, 1H, ArH), 7.48–7.50 (m, 1H, ArH), 7.57–7.64 (m, 3H, ArH), 7.85 (d, J = 8.4 Hz, 2H, ArH), 8.08 (d, J = 8.4 Hz, 2H, ArH), 8.09 (s, 1H, ArH), 8.21–8.23 (m, 1H, ArH), 8.41–8.47 (m, 4H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{16}N_2O_2$ ($M+H^+$) 411.0900, found 411.0915.

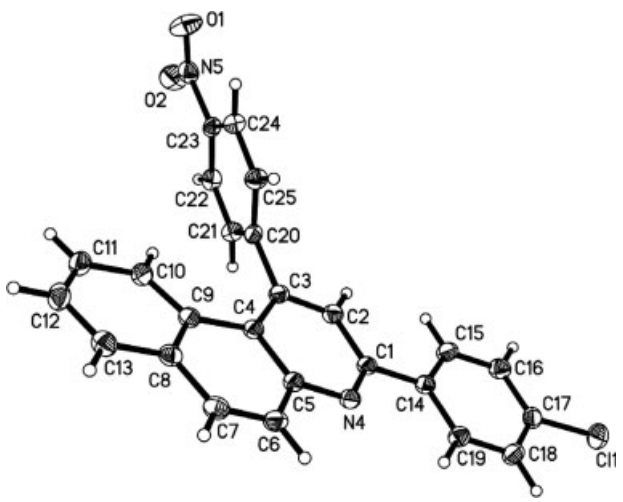


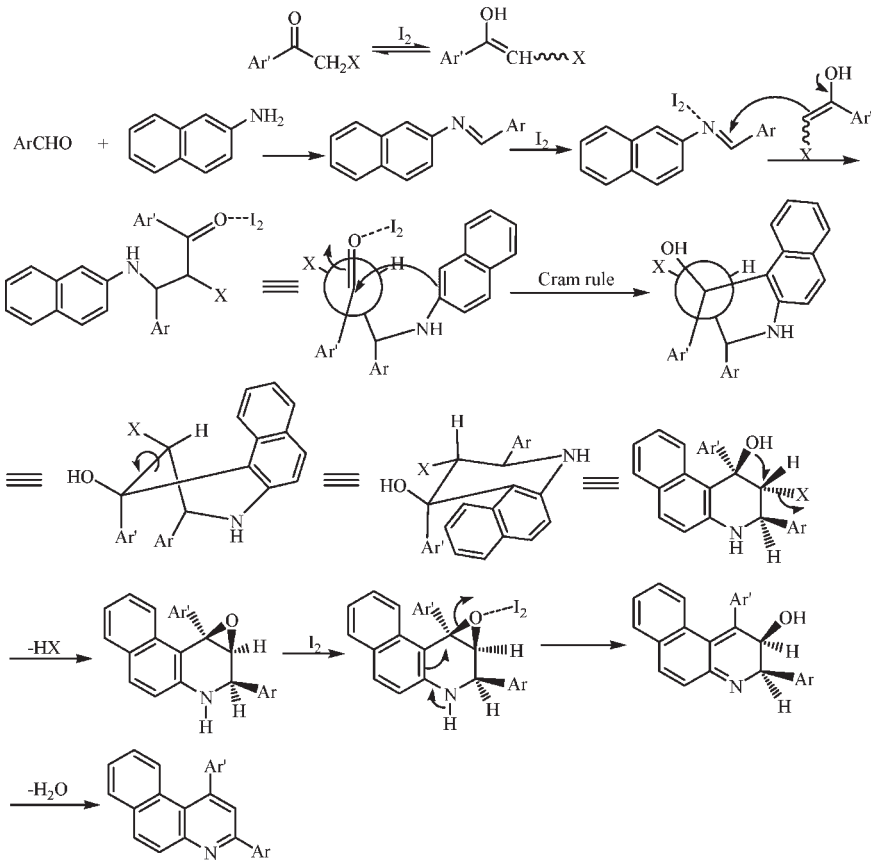
Figure 1. The crystal structure of product **4a.**

3-(2,3-Dimethoxyphenyl)-1-(4-nitrophenyl)benzo[*f*] quinoline (4b). This compound was obtained as pale yellow crystals, mp 140–141°C; ir (KBr): ν_{max} 3073, 3006, 2970, 2937, 2838, 1598, 1578, 1519, 1465, 1430, 1302, 1263, 1227, 1167, 1179, 1167, 1107, 1085, 1040, 1001, 856, 837, 805, 781, 746, 703; ^{1}H NMR (DMSO-d_6): δ 3.75 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 7.05 (dd, J = 8.0 Hz, J' = 1.2 Hz, 1H, ArH), 7.19–7.26 (m, 2H, ArH), 7.51–7.61 (m, 3H, ArH), 7.68 (d, J = 8.8 Hz, 2H, ArH), 7.91–7.93 (m, 2H, ArH), 8.03 (d, J = 8.8 Hz, 1H, ArH), 8.14 (d, J = 8.8 Hz, 1H, ArH), 8.39 (d, J = 8.8 Hz, 2H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{27}H_{21}N_2O_4$ ($M+H^+$) 437.1501, found 437.1498.

3-(4-Nitrophenyl)-1-(4-nitrophenyl)benzo[*f*]quinoline (4c). This compound was obtained as pale yellow crystals, mp 235–237°C, Lit.[15] 231–232 °C; ir (KBr): ν_{max} 3083, 1598, 1578, 1545, 1514, 1450, 1343, 1257, 1163, 1106, 1084, 1041, 1015, 993, 850, 816, 750, 694; ^{1}H NMR (DMSO-d_6): δ 7.22–7.24 (m, 1H, ArH), 7.54–7.59 (m, 2H, ArH), 7.70 (d, J = 8.4 Hz, 2H, ArH), 7.82 (s, 1H, ArH), 7.95 (d, J = 7.6 Hz, 1H, ArH), 8.09 (d, J = 9.2 Hz, 1H, ArH), 8.15 (d, J = 8.8 Hz, 1H, ArH), 8.38–8.46 (m, 6H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{16}N_3O_4$ ($M+H^+$) 422.1141, found 422.1145.

3-(2,3-Dichlorophenyl)-1-(4-nitrophenyl)benzo[*f*]quinoline (4d). This compound was obtained as pale yellow crystals, mp 196–197°C; ir (KBr): ν_{max} 3099, 3056, 1597, 1575, 1545,

Scheme 2



1515, 1478, 1446, 1412, 1341, 1286, 1251, 1192, 1156, 1124, 1104, 1049, 875, 859, 844, 789, 767, 723, 705; ^{1}H NMR (DMSO-d_6): δ 7.21–7.25 (m, 1H, ArH), 7.36–7.40 (m, 1H, ArH), 7.53–7.59 (m, 3H, ArH), 7.65–7.71 (m, 4H, ArH), 7.94 (d, J = 7.6 Hz, 1H, ArH), 8.06 (d, J = 9.2 Hz, 1H, ArH), 8.11 (d, J = 9.2 Hz, 1H, ArH), 8.40 (d, J = 8.8 Hz, 2H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{15}N_2Cl_2O_2$ (M+H$^+$) 445.0511, found 445.0508.

3-(2,4-Dichlorophenyl)-1-(4-nitrophenyl)benzo[*f*]quinoline (4e). This compound was obtained as pale yellow crystals, mp 202–203°C. ir (KBr): ν_{max} 3104, 3077, 1589, 1579, 1556, 1545, 1516, 1473, 1448, 1381, 1348, 1249, 1162, 1142, 1102, 1048, 1038, 991, 860, 838, 824, 803, 789, 758, 707; ^{1}H NMR (DMSO-d_6): δ 7.30–7.34 (m, 1H, ArH), 7.54 (d, J = 8.4 Hz, 1H, ArH), 7.60–7.66 (m, 2H, ArH), 7.78 (s, 1H, ArH), 7.82–7.89 (m, 4H, ArH), 8.06 (d, J = 8.8 Hz, 1H, ArH), 8.11 (d, J = 8.0 Hz, 1H, ArH), 8.25 (d, J = 9.2 Hz, 1H, ArH), 8.44 (d, J = 8.8 Hz, 2H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{15}N_2Cl_2O_2$ (M+H$^+$) 445.0511, found 445.0493.

3-(3,4-Dimethylphenyl)-1-(4-nitrophenyl)benzo[*f*]quinoline (4f). This compound was obtained as pale yellow crystals, mp 234–236°C; ir (KBr): ν_{max} 3068, 2974, 2917, 2858, 1595, 1579, 1544, 1452, 1477, 1451, 1339, 1283, 1260, 1126, 1103, 1015, 1005, 885, 860, 851, 831, 802, 759, 742, 714, 705; ^{1}H NMR (DMSO-d_6): δ 2.31 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 7.29–7.34 (m, 2H, ArH), 7.48 (d, J = 8.8 Hz, 1H, ArH), 7.55–7.59 (m, 1H, ArH), 7.85 (d, J = 8.4 Hz, 2H, ArH), 8.02 (s, 1H, ArH), 8.06–8.12 (m, 3H, ArH), 8.17–8.21 (m, 2H, ArH), 8.45 (d, J = 8.4 Hz, 2H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{27}H_{21}N_2O_2$ (M+H$^+$) 405.1603, found 405.1593.

3-(2,4-Dichlorophenyl)-1-(4-fluorophenyl)benzo[*f*]quinoline (4g). This compound was obtained as pale yellow crystals, mp 172–174°C; ir (KBr): ν_{max} 3069, 1601, 1586, 1555, 1507, 1475, 1448, 1378, 1347, 1332, 1246, 1217, 1158, 1139, 1100, 1048, 1038, 1016, 952, 896, 873, 859, 849, 825, 805, 775, 752; ^{1}H NMR (DMSO-d_6): δ 7.28–7.30 (m, 1H, ArH), 7.32–7.45 (m, 2H, ArH), 7.53–7.63 (m, 5H, ArH), 7.71 (s, 1H, ArH), 7.81 (d, J = 2.0 Hz, 1H, ArH), 7.85 (d, J = 8.4 Hz, 1H, ArH), 8.02 (d, J = 8.8 Hz, 1H, ArH), 8.07 (d, J = 7.6 Hz, 1H, ArH), 8.20 (d, J = 8.8 Hz, 1H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{15}Cl_2NF$ (M+H$^+$) 418.0566, found 418.0550.

3-(3-Bromophenyl)-1-(4-fluorophenyl)benzo[*f*]quinoline (4h). This compound was obtained as pale yellow crystals, mp 221–222°C; ir (KBr): ν_{max} 3058, 1601, 157 2, 1542, 1506, 1477, 1446, 1386, 1344, 1328, 1252, 1230, 1154, 1088, 1069, 994, 873, 834, 796, 782, 756, 709, 689; ^{1}H NMR (DMSO-d_6): δ 7.26–7.30 (m, 1H, ArH), 7.42–7.46 (m, 2H, ArH), 7.50–7.59 (m, 5H, ArH), 7.69–7.72 (m, 1H, ArH), 8.03–8.07 (m, 3H, ArH, 8.17 (d, J = 9.2 Hz, 1H, ArH), 8.36 (d, J = 8.0 Hz, 1H, ArH), 8.56–8.57 (m, 1H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{16}BrFN$ (M+H$^+$) 428.0450, found 428.0468.

3-(4-Chlorophenyl)-1-(4-fluorophenyl)benzo[*f*]quinoline (4i). This compound was obtained as pale yellow crystals, mp 173–174°C; ir (KBr): ν_{max} 3054, 1602, 1579, 1544, 1505, 1 478, 1449, 1406, 1385, 1356, 1330, 1215, 1155, 1090, 1010, 866, 830, 799, 745, 714; ^{1}H NMR (DMSO-d_6): δ 7.25–7.30

(m, 1H, ArH), 7.42–7.46 (m, 2H, ArH), 7.54–7.63 (m, 6H, ArH), 8.01 (s, 1H, ArH), 8.04 (d, J = 8.8 Hz, 2H, ArH), 8.16 (d, J = 9.2 Hz, 1H, ArH), 8.36 (d, J = 8.4 Hz, 1H, ArH), 8.39 (d, J = 8.8 Hz, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{16}ClFN$ ($M+H^+$) 384.0955, found 384.0966.

3-(3,5-Dimethoxyphenyl)-1-(4-fluorophenyl)benzo[*f*]quinoline (4j). This compound was obtained as pale yellow crystals, mp 119–120°C; ir (KBr): ν_{max} 3051, 2984, 2952, 2935, 2830, 1592, 1549, 1528, 1508, 1488, 1451, 1357, 1301, 1216, 1201, 1157, 1061, 1047, 941, 862, 833, 807, 752, 698; ^{1}H NMR (DMSO-d_6): δ 3.87 (s, 6H, $2CH_3O$), 6.64–6.66 (m, 1H, ArH), 7.27–7.29 (m, 1H, ArH), 7.42–7.46 (m, 2H, ArH), 7.50 (d, J = 2.4 Hz, 2H, ArH), 7.54–7.59 (m, 4H, ArH), 8.01–8.05 (m, 3H, ArH), 8.16 (d, J = 9.2 Hz, 1H, ArH). HRMS (ESI, m/z): calcd. for $C_{27}H_{21}FNO_2$ ($M+H^+$) 410.1556, found 410.1558.

3-(4-Bromophenyl)-1-(4-fluorophenyl)benzo[*f*]quinoline (4k). This compound was obtained as white powder, mp 167–169°C, ir (KBr): ν_{max} 3050, 1603, 1579, 1544, 1505, 1475, 1448, 1354, 1227, 1153, 1089, 1073, 1007, 865, 830, 756; ^{1}H NMR (DMSO-d_6): δ 7.26–7.30 (m, 1H, ArH), 7.42–7.47 (m, 2H, ArH), 7.55–7.59 (m, 4H, ArH), 7.25 (d, J = 8.8 Hz, 2H, ArH), 8.02 (s, 1H, ArH), 8.04 (d, J = 8.8 Hz, 2H, ArH), 8.17 (d, J = 8.8 Hz, 1H, ArH), 8.33 (d, J = 8.4 Hz, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{16}FBrN$ ($M+H^+$) 428.0450, found 428.0435.

1-(4-Fluorophenyl)-3-(3-nitrophenyl)benzo[*f*]quinoline (4l). This compound was obtained as pale yellow crystals, mp 222–224°C; ir (KBr): ν_{max} 3055, 1605, 1580, 1527, 1481, 1450, 1434, 1345, 1256, 1225, 1163, 1109, 1072, 896, 873, 849, 834, 801, 791, 746, 712; ^{1}H NMR (DMSO-d_6): δ 7.21–7.29 (m, 3H, ArH), 7.45–7.55 (m, 3H, ArH), 7.67–7.73 (m, 2H, ArH), 7.82 (s, 1H, ArH), 7.91 (d, J = 7.6 Hz, 1H, ArH), 8.04 (d, J = 8.8 Hz, 2H, ArH), 8.13 (d, J = 8.8 Hz, 1H, ArH), 8.30–8.33 (m, 1H, ArH), 8.61–8.63 (m, 1H, ArH), 9.08–9.09 (m, 1H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{16}FN_2O_2$ ($M+H^+$) 395.1196, found 395.1196.

3-(3-Bromophenyl)-1-(4-chlorophenyl)benzo[*f*]quinoline (4m). This compound was obtained as white powder, mp 218–220°C; ir (KBr): ν_{max} 3049, 1595, 1577, 1564, 1547, 1524, 1491, 1477, 1449, 1394, 1350, 1330, 1255, 1236, 1084, 1067, 1015, 993, 890, 870, 837, 804, 755, 710, 699; ^{1}H NMR (DMSO-d_6): δ 7.29–7.32 (m, 1H, ArH), 7.50–7.72 (m, 8H, ArH), 8.04–8.08 (m, 3H, ArH), 8.18 (d, J = 9.2 Hz, 1H, ArH), 8.37 (d, J = 8.0 Hz, 1H, ArH), 8.51–8.58 (m, 1H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{16}BrClN$ ($M+H^+$) 444.0155, found 444.0155.

3-(2,4-Dichlorophenyl)-1-(4-chlorophenyl)benzo[*f*]quinoline (4n). This compound was obtained as pale yellow crystals, mp 172–174°C; ir (KBr): ν_{max} 3086, 3049, 1585, 1552, 1524, 1490, 1474, 1448, 1392, 1378, 1347, 1332, 1247, 1138, 1100, 1090, 1047, 1037, 1013, 952, 871, 861, 834, 822, 802, 791, 751, 716; ^{1}H NMR (DMSO-d_6): δ 7.30–7.35 (m, 1H, ArH), 7.54 (d, J = 8.4 Hz, 1H, ArH), 7.59–7.66 (m, 5H, ArH), 7.71 (m, 1H, ArH), 7.82 (d, J = 2.4 Hz, 1H, ArH), 7.86 (d, J = 8.4 Hz, 1H, ArH), 8.03 (d, J = 9.2 Hz, 1H, ArH), 8.08 (d, J = 7.6 Hz, 1H, ArH), 8.21 (d, J = 9.2 Hz, 1H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{15}Cl_3N$ ($M+H^+$) 434.0270, found 434.0264.

1-(3-Chlorophenyl)-3-(2-thiophenyl)benzo[*f*]quinoline (4o). This compound was obtained as pale yellow crystals, mp 211–213°C; ir (KBr): ν_{max} 3097, 3067, 1580, 1562, 1469, 1453, 1421, 1352, 1321, 1255, 1242, 1166, 1154, 1098, 1068, 1027, 860, 851, 829, 794, 779, 744, 716; ^{1}H NMR (DMSO-d_6): δ 7.21–7.23 (m, 1H, ArH), 7.24–7.28 (m, 1H, ArH), 7.43–7.67 (m, 6H, ArH), 7.76 (dd, J = 8.0 Hz, J' = 1.2 Hz, 1H, ArH), 7.95 (d, J = 8.8 Hz, 1H, ArH), 8.02 (s, 1H, ArH), 8.03 (d, J = 8.8 Hz, 1H, ArH), 8.09 (dd, J = 8.0 Hz, J' = 1.2 Hz, 1H, ArH), 8.15 (d, J = 8.8 Hz, 1H, ArH). HRMS (ESI, m/z): calcd. for $C_{23}H_{15}ClNS$ ($M+H^+$) 372.0614, found 372.0625.

3-(3-Bromophenyl)-1-(3-chlorophenyl)benzo[*f*]quinoline (4p). This compound was obtained as pale yellow crystals, mp 195–196°C; ir (KBr): ν_{max} 3052, 1592, 1578, 1544, 1529, 1467, 1451, 1407, 1382, 1358, 1327, 1262, 1239, 1161, 1098, 1078, 1066, 951, 881, 872, 834, 793, 770, 745, 718, 702, 692; ^{1}H NMR (DMSO-d_6): δ 7.27–7.32 (m, 1H, ArH), 7.46 (dd, J = 7.6 Hz, J' = 1.2 Hz, 1H, ArH), 7.51–7.73 (m, 7H, ArH), 8.05–8.11 (m, 3H, ArH), 8.20 (d, J = 8.8 Hz, 1H, ArH), 8.39 (d, J = 8.0 Hz, 1H, ArH), 8.59–8.60 (m, 1H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{16}BrClN$($M+H^+$) 444.0155, found 444.0163.

3-(4-Bromophenyl)-1-(3-chlorophenyl)benzo[*f*]quinoline (4q). This compound was obtained as pale yellow crystals, mp 216–218°C; ir (KBr): ν_{max} 3047, 1578, 1562, 1543, 1527, 1472, 1451, 1417, 1384, 1355, 1329, 1101, 1074, 1008, 871, 862, 834, 825, 806, 784, 745, 718, 706; ^{1}H NMR (DMSO-d_6): δ 7.28–7.32 (m, 1H, ArH), 7.47 (d, J = 7.2 Hz, 1H, ArH), 7.56–7.69 (m, 5H, ArH), 7.76 (d, J = 8.4 Hz, 2H, ArH), 8.05–8.08 (m, 3H, ArH), 8.19 (d, J = 9.2 Hz, 1H, ArH), 8.35 (d, J = 8.4 Hz, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{16}BrClN$ ($M+H^+$) 444.0155, found 444.0157.

1-(3-Chlorophenyl)-3-(3-nitrophenyl)benzo[*f*]quinoline (4r). This compound was obtained as pale yellow crystals, mp 221–222°C; ir (KBr): ν_{max} 3052, 1580, 1563, 1531, 1484, 1472, 1450, 1408, 1347, 1297, 1278, 1256, 1237, 1164, 1113, 1098, 1074, 909, 871, 833, 801, 745, 717, 704; ^{1}H NMR (DMSO-d_6): δ 7.28–7.32 (m, 1H, ArH), 7.47 (d, J = 7.2 Hz, 1H, ArH), 7.56–7.70 (m, 5H, ArH), 7.82–7.86 (m, 1H, ArH), 8.06–8.11 (m, 2H, ArH), 8.20– 8.22 (m, 2H, ArH), 8.35 (d, J = 7.6 Hz, 1H, ArH), 8.81 (d, J = 7.6 Hz, 1H, ArH), 9.17 (s, 1H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{16}N_2O_2$ ($M+H^+$) 411.0900, found 411.0899.

1-(3-Chlorophenyl)-3-(3,4-dimethylphenyl)benzo[*f*]quinoline (4s). This compound was obtained as yellow crystals, mp 182–184°C; ir (KBr): ν_{max} 3053, 2963, 2939, 2916, 1580, 1561, 1544, 1505, 1471, 1451, 1416, 1390, 1345, 1327, 1258, 1246, 1163, 1133, 1097, 1073, 998, 890, 873, 832, 812, 790, 745, 716, 705; ^{1}H NMR (DMSO-d_6): δ 2.31 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 7.25–7.32 (m, 2H, ArH), 7.44–7.47 (m, 1H, ArH), 7.53–7.67 (m, 5H, ArH), 7.98 (s, 1H, ArH), 8.03–8.10 (m, 3H, ArH), 8.15– 8.17 (m, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{27}H_{21}NCl$ ($M+H^+$) 394.1363, found 394.1366.

3-(4-Nitrophenyl)-1-phenylbenzo[*f*]quinoline (4t). This compound was obtained as yellow crystals, mp 200-201 °C, Lit.[15] 192 °C; ir (KBr): ν_{max} 3053, 1599, 1578, 1547, 1509, 1475, 1397, 1340, 1259, 1153, 1106, 1078, 1008, 860, 849, 832, 774, 755, 699; ^{1}H NMR (DMSO-d_6): δ 7.22–7.25 (m, 1H, ArH), 7.55–7.63 (m, 7H, ArH), 8.07 (d, J = 7.0 Hz, 1H, ArH), 8.11 (d, J = 9.2 Hz, 1H, ArH), 8.17 (s, 1H, ArH), 8.22 (d, J = 8.8 Hz, 1H, ArH), 8.40 (d, J = 8.8 Hz, 2H, ArH), 8.67 (d, J = 8.8 Hz, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{17}N_2O_2$ ($M+H^+$) 377.1290, found 377.1274.

3-(4-Chlorophenyl)-1-phenylbenzo[*f*]quinoline (4u). This compound was obtained as yellow crystals, mp 164–165°C; ir (KBr): ν_{max} 3051, 1576, 1545, 1527, 1491, 1474, 1449, 1354, 1279, 1255.1167, 1088, 1009, 834, 722, 753, 700; ^{1}H NMR (DMSO-d_6): δ 7.19–7.23 (m, 1H, ArH), 7.51–7.62 (m, 9H,

ArH), 8.01–8.07 (m, 3H, ArH), 8.17 (d, J = 8.8 Hz, 1H, ArH), 8.41 (d, J = 8.4 Hz, 2H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{17}ClN$ ($M+H^{+}$) 366.1050, found 366.1057.

3-(4-Bromophenyl)-1-phenylbenzo[*f*]quinoline (4v). This compound was obtained as yellow crystals, mp 171–172°C; ir (KBr): ν_{max} 3051, 3028, 1575, 1544, 1527, 1474, 1448, 1353, 1329, 1278, 1256, 1073, 1006, 833, 814, 771, 753, 700; ^{1}H NMR (DMSO-d_6): δ 7.19–7.23 (m, 1H, ArH), 7.51–7.61 (m, 7H, ArH), 7.75 (d, J = 8.4 Hz, 2H, ArH). 8.01–8.07 (m, 3H, ArH), 8.17 (d, J = 8.8 Hz, 1H, ArH), 8.33 (d, J = 8.4 Hz, 2H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{17}BrN$ ($M+H^{+}$) 410.0544, found 410.0544.

3-(3-Bromophenyl)-1-phenylbenzo[*f*]quinoline (4w). This compound was obtained as yellow crystals, mp 207–209°C; ir (KBr): ν_{max} 3054, 1576, 1542, 1522, 1476, 1447, 1388, 1345, 1328, 1252, 1231, 1083, 1069, 995, 943, 869, 838, 781, 756, 702, 689; ^{1}H NMR (DMSO-d_6): δ 7.15–7.19 (m, 1H, ArH), 7.37–7.41 (m, 1H, ArH), 7.47–7.59 (m, 7H, ArH), 7.67 (d, J = 8.4 Hz, 1H, ArH), 7.77 (s, 1H, ArH), 7.89 (d, J = 8.0 Hz, 1H, ArH), 8.02 (d, J = 9.2 Hz, 1H, ArH), 8.10–8.16 (m, 2H, ArH), 8.41 (s, 1H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{17}BrN$ ($M+H^{+}$) 410.0544, found 410.0556.

1-(3-Nitrophenyl)-3-(2-thiophenyl) benzo[*f*]quinoline (4x). This compound was obtained as yellow crystals, mp 278–280°C; ir (KBr): ν_{max} 3050, 1584, 1845, 1525, 1484, 1454, 1420, 1347, 1259, 1042, 1092, 1083, 883, 870, 835, 799, 753, 743, 696; ^{1}H NMR (DMSO-d_6): δ 7.23–7.27 (m, 2H, ArH), 7.46 (d, J = 8.4 Hz, 1H, ArH), 7.54–7.58(m, 1H, ArH), 7.78 (dd, J = 5.2 Hz;J' = 1.2 Hz, 1H, ArH), 7.85–7.90 (m, 1H, ArH), 7.94–7.97 (m, 2H, ArH), 8.05 (d, J = 8.8 Hz, 1H, ArH), 8.09–8.10 (m, 2H, ArH), 8.18 (d, J = 8. 8 Hz, 1H, ArH), 8.45–8.47 (m, 2H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{23}H_{15}N_2O_2S$ ($M+H^{+}$) 383.0854, found 383.0841.

3-(4-Chlorophenyl)-1-(3-nitrophenyl)benzo[*f*] quinoline (4y). This compound was obtained as yellow crystals, mp 258–259°C; ir (KBr): ν_{max} 3083, 3058, 1582, 1527, 1489, 1451, 1407, 1351, 1303, 1258, 1209, 1164, 1092, 1047, 1009, 892, 862, 832, 813, 745, 715; ^{1}H NMR (DMSO-d_6): δ 7.24–7.28 (m, 1H, ArH), 7.51 (d, J = 8.4 Hz, 1H, ArH), 7.56–7.60 (m, 1H, ArH), 7.62 (d, J = 8.4 Hz, 2H, ArH), 7.85–7.88 (m, 1H, ArH), 7.95 (d, J = 7.6 Hz, 1H, ArH), 8.06–8.08 (m, 2H, ArH), 8.13 (s, 1H, ArH), 8.20 (d, J = 9.2 Hz, 1H, ArH), 8.42 (d, J = 8.4 Hz, 2H, ArH), 8.45–8.47 (m, 2H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{16}ClN_2O_2$ ($M+H^{+}$) 411.0900, found 411.0894.

3-(4-Bromophenyl)-1-(3-nitrophenyl)benzo[*f*] quinoline (4z). This compound was obtained as yellow crystals, mp 263–264°C; ir (KBr): ν_{max} 3056, 1581, 1527, 1486, 1451, 1384, 1351, 1304, 1258, 1210, 1179, 1163, 1075, 1006, 891, 861, 831, 814, 744, 705; ^{1}H NMR (DMSO-d_6): δ 7.25–7.29 (m, 1H, ArH), 7.52 (d, J = 8.4 Hz, 1H, ArH), 7.57–7.61(m, 1H, ArH), 7.77 (d, J = 8.4 Hz, 2H, ArH), 7.88 (d, J = 8.0 Hz, 1H, ArH), 7.95–7.97 (m, 1H, ArH), 8.04–8.10 (m, 2H, ArH), 8.15 (m, 1H, ArH), 8.27 (d, J = 9.2 Hz, 1H, ArH), 8.37 (d, J = 8.4 Hz, 2H, ArH), 8.45–8.48 (m, 2H, ArH). HRMS (ESI, *m*/*z*): calcd. for $C_{25}H_{16}BrN_2O_2$ ($M+H^{+}$) 455.0395, found 455.0399.

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[13] Crystal data for **4a**: $C_{25}H_{15}ClN_2O_2$; M = 410.84, colorless block crystals, 0.34 × 0.32 × 0.22 mm^3, Triclinic, space group P-1, a = 9.1390 (12), b = 9.5350 (11), c = 11.9668 (17) Å, α = 108.182 (4), β = 105.366 (4), γ = 92.739 (3)°, V = 945.6 (2) ^{3}, Z = 2, D_c = 1.443 g cm^{-3}. $F(000)$ = 424, μ(Mo$K\alpha$) = 0.228 mm^{-1}. Intensity data were collected on Rigaku Mercury diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ = 0.71070 Å) using ω scan mode with 2.27 ° < θ < 27.87 °. 4467

unique reflections were measured and 3779 reflections with $I > 2\sigma$ (I) were used in the refinement. Structure solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique to $R = 0.0493$ and $wR = 0.1209$.

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