

SUPPORTING INFORMATION

Title: An Efficient Method for the Synthesis of Benzo[*f*]quinoline and Benzo[*a*]phenanthridine Derivatives Catalyzed by Iodine by a Three-Component Reaction of Arenecarbaldehyde, Naphthalen-2-amine, and Cyclic Ketone

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4.1. General procedure for the syntheses of benzo[*f*]quinolines **4**, **6**, **7**, **8** and benza[*a*]phenanthridines **5**

A dry 50 mL flask was charged with arylaldehyde (2.0 mmol), naphthalen-2-amine (2.0 mmol, 0.286 g), cycloketone (2.0 mmol), I₂ (0.1 mmol, 0.026 g) and THF (10 mL). The reaction mixture was stirred at reflux for 6–20 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**, **5**, **6**, **7** or **8**, when the mixture was cooled to room temperature.

4.1.11. 4-(2,4-Dichlorophenyl)-2,3-dihydro-1H-benzo[*f*]cyclophenta[*c*]quinoline (**4c**).

Pale yellow crystals (0.640 g, 88 %), mp 170–171 °C.

IR (KBr): 3050, 2958, 2846, 1588, 1562, 1487, 1474, 1448, 1342, 1381, 1366, 1313, 1297, 1260, 1244, 1139, 1099, 1087, 1052, 1038, 926, 863, 829, 801, 751 cm⁻¹.

¹H NMR (DMSO-*d*₆, 400 MHz): δ 2.22–2.27 (m, 2H, CH₂), 2.91 (t, *J* = 7.2 Hz, 2H, CH₂), 3.83 (t, *J* = 7.6 Hz, 2H, CH₂), 7.59–7.62 (m, 2H, ArH), 7.24–7.82 (m, 3H, ArH), 7.95 (d, *J* = 8.8 Hz, 1H, ArH), 8.09–8.12 (m, 2H, ArH), 8.78 (d, *J* = 8.4 Hz, 1H, ArH).

¹³C NMR (CDCl₃, 100 MHz): δ 25.2, 31.1, 37.5, 123.9, 126.6, 126.77, 126.80, 127.4, 128.8, 129.0, 129.5, 130.4, 130.5, 131.7, 132.7, 133.7, 134.8, 138.1, 138.2, 147.8, 150.4, 152.6.

Anal. calcd for C₂₂H₁₅Cl₂N (364.27): C 72.54, H 4.15, N 3.85; found C 72.50, H 4.30, N 3.79.

4.1.12. 6-(3-Chlorophenyl)-2,3-dihydro-1H-benzo[*f*]cyclophenta[*c*]quinoline (**4d**).

Pale yellow crystals (0.576 g, 87 %), mp 146–147 °C.

IR (KBr): 3054, 2958, 2929, 2851, 1594, 1555, 1489, 1474, 1448, 1434, 1372, 1329, 1264, 1126, 1099, 1077, 985, 935, 887, 833, 797, 754, 711, 696 cm⁻¹.

¹H NMR (DMSO-*d*₆, 400 MHz): δ 2.19–2.26 (m, 2H, CH₂), 3.26 (t, *J* = 7.2 Hz, 2H, CH₂), 3.77 (t, *J* = 7.2 Hz, 2H, CH₂), 7.57–7.60 (m, 2H, ArH), 7.73–7.79 (m, 2H,

ArH), 7.89 (d, $J = 6.8$ Hz, 1H, ArH), 7.98 (s, 1H, ArH), 7.99 (d, $J = 8.8$ Hz, 1H, ArH), 8.07–8.10 (m, 2H, ArH), 8.74 (d, $J = 8.0$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 26.1, 32.8, 37.3, 12.4, 126.5, 126.7, 126.8, 127.0, 128.6, 128.8, 129.0, 129.2, 129.6, 130.3, 130.5, 132.7, 134.4, 136.6, 142.2, 147.9, 151.2, 152.8.

Anal. calcd for $\text{C}_{22}\text{H}_{16}\text{ClN}$ (329.82): C 80.11, H 4.89, N 4.25; found C 80.22, H 4.80, N 4.33.

4.1.13. 4-(4-Bromophenyl)-2,3-dihydro-1H-benzo[*ff*]cyclophenta[*c*]quinoline (**4e**).

Pale yellow crystals (0.657 g, 88 %), mp 185–186 °C.

IR (KBr): 3049, 2959, 2919, 2847, 1587, 1560, 1551, 1480, 1445, 1433, 1399, 1367, 1326, 1257, 1167, 1120, 1101, 1070, 1010, 985, 871, 828, 752, 740 cm^{-1} .

^1H NMR ($\text{DMSO}-d_6$, 400 MHz): δ 2.20–2.26 (m, 2H, CH_2), 3.27 (t, $J = 7.2$ Hz, 2H, CH_2), 3.79 (t, $J = 7.2$ Hz, 2H, CH_2), 7.73–7.79 (m, 4H, ArH), 7.92 (d, $J = 8.4$ Hz, 2H, ArH), 7.99 (d, $J = 8.8$ Hz, 1H, ArH), 8.08–8.11 (m, 2H, ArH), 8.75 (d, $J = 8.0$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 26.1, 32.9, 37.3, 122.9, 123.3, 126.5, 126.6, 126.7, 128.8, 129.2, 130.3, 130.5, 131.6, 132.7, 136.5, 139.3, 148.0, 151.2, 153.1.

Anal. calcd for $\text{C}_{22}\text{H}_{16}\text{BrN}$ (374.27): C 70.60, H 4.31, N 3.74; found C 70.48, H 4.55, N 3.70.

4.1.14. 2,3-Dihydro-4-(4-fluorophenyl)-1H-benzo[*ff*]cyclophenta[*c*]quinoline (**4f**).

Pale yellow crystals (0.603 g, 96 %), mp 149–151 °C.

IR (KBr): 3050, 2975, 2955, 1597, 1557, 1505, 1481, 1446, 1432, 1410, 1381, 1308, 1327, 1294, 1262, 1218, 1154, 1122, 1097, 1011, 946, 845, 832, 809, 751 cm^{-1} .

^1H NMR ($\text{DMSO}-d_6$, 400 MHz): δ 2.18–2.24 (m, 2H, CH_2), 3.24 (t, $J = 7.2$ Hz, 2H, CH_2), 3.26 (t, $J = 7.2$ Hz, 2H, CH_2), 7.38 (t, $J = 8.8$ Hz, 2H, ArH), 7.71–7.76 (m, 2H, ArH), 7.96–8.01 (m, 3H, ArH), 8.05–8.09 (m, 2H, ArH), 8.72 (d, $J = 8.0$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 26.0, 32.9, 37.3, 115.2, 115.4, 123.1, 126.4, 126.5, 126.7, 126.8, 129.2, 130.2, 130.5, 130.65, 130.74, 132.6, 136.4, 136.50, 136.53, 147.9, 151.1, 153.3, 161.8, 164.3.

Anal.calcd for C₂₂H₁₆FN (313.37): C 84.32, H 5.15, N 4.47; found C 84.35, H 4.99, N 4.59.

4.1.15. 4-(3-Bromophenyl)-2,3-dihydro-1H-benzo[*ff*]cyclophenta[*c*]quinoline (**4g**).

Pale yellow crystals (0.653g, 87 %), mp 160–162 °C.

IR (KBr): 3051, 2957, 2928, 2850, 1590, 1501, 1488, 1472, 1433, 1413, 1371, 1329, 1263, 1169, 1125, 1069, 995, 984, 930, 886, 834, 796, 770, 754, 738, 693 cm⁻¹.

¹H NMR (DMSO-*d*₆, 400 MHz): δ 2.20–2.26 (m, 2H, CH₂), 3.27 (t, *J* = 7.6 Hz, 2H, CH₂), 3.78 (t, *J* = 7.6 Hz, 2H, CH₂), 7.51–7.55 (m, 1H, ArH), 7.70–7.78 (m, 3H, ArH), 7.93 (d, *J* = 8.0 Hz, 1H, ArH), 7.99 (d, *J* = 9.2 Hz, 1H, ArH), 8.08–8.13 (m, 3H, ArH), 8.74 (d, *J* = 8.4 Hz, 1H, ArH).

¹³C NMR (CDCl₃, 100 MHz): δ 26.0, 32.8, 37.3, 122.7, 123.4, 126.5, 126.7, 126.8, 127.4, 128.8, 129.2, 129.9, 130.4, 130.5, 131.5, 131.9, 132.7, 136.6, 142.5, 147.9, 151.2, 152.7.

Anal.calcd for C₂₂H₁₆BrN (374.27): C 70.60, H 4.31, N 3.74; found C 70.54, H 4.58, N 3.65.

4.1.16. 4-(4-Chlorophenyl)-2,3-dihydro-1H-benzo[*ff*]cyclophenta[*c*]quinoline (**4h**).

Pale yellow crystals (0.586 g, 89 %), mp 180–182 °C.

IR (KBr): 3050, 2977, 2957, 2937, 1593, 1551, 1480, 1435, 1404, 1367, 1327, 1273, 1261, 1234, 1121, 1106, 1088, 1011, 985, 868, 830, 752, 742, 708, 672 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ 2.23–2.30 (m, 2H, CH₂), 3.24 (t, *J* = 7.6 Hz, 2H, CH₂), 3.78 (t, *J* = 7.6 Hz, 2H, CH₂), 7.49 (d, *J* = 8.4 Hz, 2H, ArH), 7.62–7.69 (m, 2H, ArH), 7.85 (d, *J* = 8.4 Hz, 2H, ArH), 7.91–7.96 (m, 2H, ArH), 8.06 (d, *J* = 8.8 Hz, 1H, ArH), 8.68 (d, *J* = 8.0 Hz, 1H, ArH).

¹³C NMR (CDCl₃, 100 MHz): δ 26.0, 32.9, 37.3, 123.2, 126.5, 126.6, 126.7, 128.6, 128.8, 129.2, 130.2, 130.3, 130.5, 132.7, 134.6, 136.5, 138.8, 147.9, 151.2, 153.1.

Anal.calcd for C₂₂H₁₆ClN (329.82): C 80.11, H 4.89, N 4.25; found C 80.18, H 4.88, N 4.38.

4.1.17. 2,3-Dihydro-4-(2-nitrophenyl)-1H-benzo[*ff*]cyclophenta[*c*]quinoline (**4i**). Pale yellow crystals (0.612 g, 90 %), mp 206–207 °C.

IR (KBr): 3053, 2980, 2948, 2916, 2849, 1606, 1574, 1557, 1522, 1461, 1450, 1437, 1352, 1325, 1295, 1255, 1162, 1036, 982, 864, 852, 826, 789, 758, 730, 708, 690 cm^{-1} .

^1H NMR (CDCl_3 , 400 MHz): δ 2.25–2.33 (m, 2H, CH_2), 2.93 (d, $J = 7.6$ Hz, 2H, CH_2), 3.82 (d, $J = 7.6$ Hz, 2H, CH_2), 7.58–7.76 (m, 5H, ArH), 7.92–8.01 (m, 3H, ArH), 8.13 (dd, $J = 8.0$ Hz, $J' = 0.8$ Hz, 1H, ArH), 8.72 (d, $J = 8.0$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 25.2, 31.1, 37.4, 123.8, 124.7, 126.6, 126.7, 126.8, 128.8, 128.9, 129.2, 130.4, 130.5, 131.7, 132.8, 133.3, 135.9, 137.1, 147.8, 148.5, 150.5, 152.2.

Anal. calcd for $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2$ (340.37): C 77.63, H 4.74, N 8.23; found C 77.80, H 4.76, N 4.70.

*4.1.18. 2,3-Dihydro-4-(2,3-dimethoxyphenyl)-1H-benzo[*ff*]cyclophenta[*c*]quinoline 4j.*

Pale yellow crystals (0.611 g, 86 %), mp 194–196 °C.

IR (KBr): 3062, 2999, 2966, 2834, 1581, 1565, 1470, 1425, 1375, 1294, 1264, 1169, 1126, 1081, 1063, 1008, 955, 867, 839, 794, 748, 682 cm^{-1} .

^1H NMR (CDCl_3 , 100 MHz): δ 2.21–2.29 (m, 2H, CH_2), 3.06 (t, $J = 7.6$ Hz, 2H, CH_2), 3.58 (s, 3H, CH_3O), 3.82 (t, $J = 7.6$ Hz, 2H, CH_2), 3.94 (s, 3H, CH_3O), 7.02 (dd, $J = 8.0$ Hz, $J' = 1.6$ Hz, 1H, ArH), 7.12 (dd, $J = 8.0$ Hz, $J' = 1.6$ Hz, 1H, ArH), 7.20 (t, $J = 8.0$ Hz, 1H, ArH), 7.62–7.70 (m, 2H, ArH), 7.92–7.97 (m, 2H, ArH), 8.09 (d, $J = 9.2$ Hz, 1H, ArH), 8.25 (d, $J = 8.0$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 25.2, 31.5, 37.5, 56.0, 61.6, 112.5, 122.6, 123.4, 124.4, 126.39, 126.44, 126.8, 128.7, 129.3, 129.8, 130.7, 132.6, 135.3, 139.0, 147.0, 147.6, 149.7, 152.8, 153.4.

Anal. calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_2$ (355.43): C 81.10, H 5.96, N 3.94; found C 81.00, H 6.03, N 3.80.

*4.1.19. 2,3-Dihydro-4-(4-methylphenyl)-1H-benzo[*ff*]cyclophenta[*c*]quinoline (4k).*

Pale yellow crystals (0.522 g, 84 %), mp 190–193 °C.

IR (KBr): 3045, 2920, 1602, 1561, 1510, 1481, 1434, 1368, 1327, 1256, 1181, 1113, 1079, 1044, 1018, 984, 961, 871, 828, 783, 750, 680 cm^{-1} .

^1H NMR (CDCl_3 , 400 MHz): δ 2.20–2.28 (m, 2H, CH_2), 3.25 (t, $J = 7.2$ Hz, 2H, CH_2), 3.76 (t, $J = 7.2$ Hz, 2H, CH_2), 7.32 (dd, $J = 8.0$ Hz, 2H, ArH), 7.59–7.67 (m, 2H, ArH), 7.80 (d, $J = 8.0$ Hz, 2H, ArH), 7.90–7.94 (m, 2H, ArH), 8.08 (d, $J = 9.2$ Hz, 1H, ArH), 8.68 (d, $J = 8.4$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 21.4, 26.0, 33.0, 37.3, 123.0, 126.3, 126.4, 126.7, 128.7, 128.8, 129.1, 129.4, 130.0, 130.6, 132.6, 136.6, 137.6, 138.4, 147.9, 150.8, 154.5.

Anal. calcd for $\text{C}_{23}\text{H}_{19}\text{N}$ (309.40): C 89.28, H 6.19, N 4.53; found C 89.10, H 6.22, N 4.60.

4.1.20. *5-(4-Bromophenyl)-1,2,3,4-tetrahydrobenza[a]phenanthridine (5b)*. Pale yellow crystals (0.690 g, 89 %), mp 218–219 °C (Lit. ^[22] 220 °C).

IR (KBr): 3050, 2937, 1589, 1561, 1510, 1475, 1445, 1432, 1368, 1351, 1317, 1258, 1120, 1100, 1067, 1008, 978, 945, 845, 822, 763, 747 cm^{-1} .

^1H NMR ($\text{DMSO}-d_6$, 400 MHz): δ 1.79–1.85 (m, 4H, 2CH_2), 2.82 (t, $J = 5.2$ Hz, 2H, CH_2), 3.60 (t, $J = 5.2$ Hz, 2H, CH_2), 7.53 (d, $J = 8.4$ Hz, 2H, ArH), 7.70–7.73 (m, 4H, ArH), 7.83 (d, $J = 8.8$ Hz, 1H, ArH), 8.04 (d, $J = 8.8$ Hz, 1H, ArH), 8.08–8.10 (m, 1H, ArH), 8.84 (d, $J = 8.4$ Hz, 1H, ArH).

4.1.21. *5-(3-Bromophenyl)-1,2,3,4-tetrahydrobenza[a]phenanthridine (5c)*. Pale yellow crystals (0.715 g, 92 %), mp 245–247 °C (Lit. ^[22] 248–250 °C).

IR (KBr): 3054, 2937, 2858, 1593, 1561, 1474, 1445, 1433, 1408, 1368, 1341, 1318, 1255, 1135, 1069, 995, 884, 830, 797, 766, 748, 699 cm^{-1} .

^1H NMR ($\text{DMSO}-d_6$, 400 MHz): δ 1.78–1.84 (m, 4H, 2CH_2), 2.80–2.83 (m, 2H, CH_2), 3.57–3.60 (m, 2H, CH_2), 7.45–7.49 (m, 1H, ArH), 7.57 (d, $J = 7.6$ Hz, 1H, ArH), 7.67–7.75 (m, 4H, ArH), 7.83 (d, $J = 8.8$ Hz, 1H, ArH), 8.06 (d, $J = 9.2$ Hz, 1H, ArH), 8.08–8.10 (m, 1H, ArH), 8.82–8.84 (m, 1H, ArH).

4.1.22. *5-(4-Fulorophenyl)-1,2,3,4-tetrahydrobenza[a]phenanthridine (5d)*. Pale yellow crystals (0.587 g, 90 %), mp 255–256 °C (Lit. ^[22] 258–260 °C).

IR (KBr): 3056, 2962, 2937, 2860, 1604, 1554, 1509, 1475, 1446, 1434, 1382, 1369, 1317, 1257, 1219, 1159, 1119, 1095, 1015, 969, 872, 828, 808, 753 cm^{-1} .

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.79–1.85 (m, 4H, 2CH₂), 2.82 (t, J = 6.0 Hz, 2H, CH₂), 3.58–3.60 (m, 2H, CH₂), 7.33 (t, J = 8.8 Hz, 2H, ArH), 7.09–7.63 (m, 2H, ArH), 7.70–7.74 (m, 2H, ArH), 7.83 (d, J = 8.8 Hz, 1H, ArH), 8.03 (d, J = 8.8 Hz, 1H, ArH), 8.07–8.09 (m, 1H, ArH), 8.83 (d, J = 8.8 Hz, 1H, ArH).

4.1.23. 5-(2-Thiophenyl)-1,2,3,4-tetrahydrobenza[*a*]phenanthridine (**5f**). Pale yellow crystals (0.548 g, 87 %), mp 147–149 °C.

IR (KBr): 3046, 2925, 2849, 1601, 1544, 1473, 1435, 1365, 1350, 1321, 1263, 1225, 1132, 1088, 1070, 1005, 966, 873, 852, 826, 813, 753, 694 cm⁻¹.

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.79–1.83 (m, 2H, CH₂), 1.96–1.99 (m, 2H, CH₂), 3.18–3.21 (m, 2H, CH₂), 3.57–3.60 (m, 2H, CH₂), 7.22–7.24 (m, 1H, ArH), 7.69–7.74 (m, 4H, ArH), 7.80 (d, J = 8.8 Hz, 1H, ArH), 8.02 (d, J = 8.8 Hz, 1H, ArH), 8.06–8.08 (m, 1H, ArH), 8.81 (d, J = 8.8 Hz, 1H, ArH).

^{13}C NMR (CDCl₃, 100 MHz): δ 22.4, 23.0, 28.7, 33.7, 124.7, 125.7, 126.2, 127.4, 127.7, 127.9, 128.4, 128.5, 129.0, 129.1, 130.1, 130.2, 133.5, 144.7, 145.6, 146.5, 151.4.

Anal. calcd for C₂₁H₁₇NS (315.43): C 79.96, H 5.43, N 4.44; found C 80.11, H 5.35, N 4.57.

4.1.24. 5-(2,3-Dichlorophenyl)-1,2,3,4-tetrahydrobenza[*a*]phenanthridine (**5g**). Pale yellow crystals (0.681 g, 90 %), mp 174–175 °C.

IR (KBr): 3049, 3020, 2947, 2856, 1557, 1516, 1477, 1450, 1407, 1354, 1339, 1320, 1259, 1198, 1181, 1126, 1046, 1005, 848, 829, 775, 757, 738, 719, 677 cm⁻¹.

^1H NMR (CDCl₃, 400 MHz): δ 1.78–1.96 (m, 4H, 2CH₂), 2.59–2.82 (m, 2H, CH₂), 3.63–3.66 (m, 2H, CH₂), 7.28–7.40 (m, 2H, ArH), 7.58 (dd, J = 8.4 Hz, J' = 2.0 Hz, 1H, ArH), 7.66–7.70 (m, 2H, ArH), 7.93–8.00 (m, 3H, ArH), 8.81–8.84 (m, 1H, ArH).

^{13}C NMR (CDCl₃, 100 MHz): δ 22.1, 23.3, 27.5, 33.5, 125.6, 125.8, 126.5, 127.9, 128.4, 128.5, 128.96, 128.99, 129.0, 129.3, 130.2, 130.4, 131.3, 133.49, 133.53, 142.2, 145.4, 146.6, 156.7.

Anal. calcd for C₂₃H₁₇Cl₂N (378.29): C 73.02, H 4.53, N 3.70; found C 72.90, H 4.66, N 3.59.

4.1.25. 5-(4-Chlorophenyl)-1,2,3,4-tetrahydrobenza[*a*]phenanthridine (**5h**). Pale yellow crystals (0.580 g, 84 %), mp 196–197 °C (Lit. ^[22] 200–202 °C).

IR (KBr): 3064, 2938, 2861, 1595, 1561, 1511, 1490, 1475, 1445, 1432, 1395, 1369, 1318, 1258, 1230, 1177, 1120, 1100, 1085, 1013, 968, 945, 823, 765, 746, 680 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz): δ 1.82–1.92 (m, 4H, 2CH₂), 2.83–2.86 (m, 2H, CH₂), 3.61–3.64 (m, 2H, CH₂), 7.46–7.51 (m, 4H, ArH), 7.62–7.67 (m, 2H, ArH), 7.91 (d, *J* = 8.8 Hz, 1H, ArH), 7.96–7.97 (m, 2H, ArH), 8.76–8.79 (m, 1H, ArH).

4.1.26. 5-(4-Nitrophenyl)-1,2,3,4-tetrahydrobenza[*a*]phenanthridine (**5i**). Pale yellow crystals (0.611 g, 86 %), mp 230–232 °C (Lit. ^[22] 240–242 °C).

IR (KBr): 3049, 2933, 2863, 1601, 1558, 1519, 1476, 1434, 1350, 1319, 1288, 1256, 1104, 1047, 1014, 969, 945, 860, 833, 740, 698 cm⁻¹.

¹H NMR (DMSO-*d*₆, 400 MHz): δ 1.77–1.83 (m, 4H, 2CH₂), 2.86–2.90 (m, 2H, CH₂), 3.60–3.64 (m, 2H, CH₂), 7.69–7.75 (m, 2H, ArH), 7.83 (d, *J* = 8.4 Hz, 3H, ArH), 8.03–8.09 (m, 2H, ArH), 8.35 (d, *J* = 8.8 Hz, 2H, ArH), 8.82–8.84 (m, 1H, ArH).

Anal. calcd for C₂₃H₁₈N₂O₂ (354.40): C 77.95, H 5.12, N 7.90; found C 77.99, H 5.02, N 7.77.

4.1.27. 5-(4-Methoxyphenyl)-1,2,3,4-tetrahydrobenza[*a*]phenanthridine (**5j**). Pale yellow crystals (0.571 g, 84 %), mp 184–185 °C (Lit. ^[22] 182–183 °C).

IR (KBr): 3052, 2991, 2934, 2857, 1608, 1560, 1513, 1473, 1433, 1369, 1345, 1317, 1290, 1244, 1179, 1135, 1108, 1036, 1005, 963, 941, 908, 871, 832, 793, 743 cm⁻¹.

¹H NMR (DMSO-*d*₆, 400 MHz): δ 1.74–1.81 (m, 4H, 2CH₂), 2.81–2.84 (m, 2H, CH₂), 3.55–3.59 (m, 2H, CH₂), 3.82 (s, 3H, CH₃O), 7.05 (d, *J* = 8.8 Hz, 2H, ArH), 7.48 (d, *J* = 8.4 Hz, 2H, ArH), 7.68–7.72 (m, 2H, ArH), 7.81 (d, *J* = 9.2 Hz, 1H, ArH), 8.00 (d, *J* = 8.8 Hz, 1H, ArH), 8.04–8.07 (m, 1H, ArH), 8.80 (d, *J* = 8.4 Hz, 1H, ArH).

4.1.28. 5-(3-Hydroxyphenyl)-1,2,3,4-tetrahydrobenza[*a*]phenanthridine (**5k**). Pale yellow crystals (0.507 g, 78 %), mp 268–269 °C (Lit. ^[22] 268 °C).

IR (KBr): 2923, 1608, 1576, 1548, 1484, 1446, 1417, 1385, 1358, 1344, 1320, 1271, 1224, 1157, 1117, 1076, 1010, 892, 866, 831, 797, 758, 699, 684 cm⁻¹.

¹H NMR (DMSO-*d*₆, 400 MHz): δ 1.73–1.79 (m, 4H, 2CH₂), 2.76–2.79 (m, 2H, CH₂), 3.51–3.54 (m, 2H, CH₂), 6.84–6.90 (m, 3H, ArH), 7.27–7.31 (m, 1H, ArH),

7.67–7.69 (m, 2H, ArH), 7.80 (d, $J = 8.8$ Hz, 1H, ArH), 7.99 (d, $J = 8.8$ Hz, 1H, ArH), 8.03–8.05 (m, 1H, ArH), 8.77 (d, $J = 8.8$ Hz, 1H, ArH), 9.74 (s, 1H, OH).

4.1.29. *8-(3-Bromophenyl)-10,11,12,13-tetrahydro-9H-benzo[*ff*]cyclohepta[*c*]quinoline (6c)*. Pale yellow crystals (0.694 g, 86 %), mp 102–103 °C.

IR (KBr): 3057, 2922, 2854, 1592, 1556, 1481, 1440, 1413, 1383, 1368, 1337, 1270, 1233, 1215, 1164, 1068, 968, 891, 865, 832, 802, 783, 749, 701 cm^{-1} .

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.75 (b, 2H, CH_2), 1.96 (b, 2H, CH_2), 2.04–2.05 (m, 2H, CH_2), 2.91–2.94 (m, 2H, CH_2), 3.42–3.44 (m, 2H, CH_2), 7.41–7.49 (m, 2H, ArH), 7.62–7.67 (m, 3H, ArH), 7.71–7.74 (m, 2H, ArH), 7.95 (d, $J = 9.2$ Hz, 1H, ArH), 8.00–8.02 (m, 1H, ArH), 8.37–8.39 (m, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 25.9, 27.4, 30.6, 31.7, 32.8, 113.4, 122.6, 124.7, 125.7, 126.6, 127.9, 128.6, 128.7, 129.8, 130.3, 131.0, 132.3, 133.2, 135.2, 143.6, 146.7, 150.4, 156.1.

Anal. calcd for $\text{C}_{24}\text{H}_{20}\text{BrN}$ (402.33): C 71.65, H 5.01, N 3.48; found C 71.54, H 5.20, N 3.59.

4.1.30. *8-(4-Chlorophenyl)-10,11,12,13-tetrahydro-9H-benzo[*ff*]cyclohepta[*c*]quinoline (6d)*. Pale yellow crystals (0.609 g, 85 %), mp 145–146 °C (Lit. ^[23] 145–146 °C).

IR (KBr): 3050, 2979, 2929, 2915, 2849, 1593, 1558, 1545, 1481, 1439, 1371, 1347, 1273, 1235, 1214, 1164, 1089, 1014, 988, 950, 900, 823, 751, 722, 701 cm^{-1} .

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.81 (b, 2H, CH_2), 2.01 (b, 2H, CH_2), 2.11 (b, 2H, CH_2), 2.97–2.99 (m, 2H, CH_2), 3.48–3.49 (m, 2H, CH_2), 7.59 (s, 4H, ArH), 7.69–7.71 (m, 2H, ArH), 7.77 (d, $J = 8.8$ Hz, 1H, ArH), 8.00 (d, $J = 8.8$ Hz, 1H, ArH), 8.05–8.07 (m, 1H, ArH), 8.43 (d, $J = 8.0$ Hz, 1H, ArH).

4.1.31. *8-(4-Bromophenyl)-10,11,12,13-tetrahydro-9H-benzo[*ff*]cyclohepta[*c*]quinoline (6e)*. Pale yellow crystals (0.690 g, 86 %), mp 149–150 °C (Lit. ^[23] 152–153 °C).

IR (KBr): 3055, 2973, 2933, 2898, 2849, 1591, 1560, 1478, 1444, 1374, 1356, 1319, 1236, 1099, 1075, 1009, 970, 953, 900, 835, 823, 804, 751, 686 cm^{-1} .

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.81 (b, 2H, CH₂), 2.01 (b, 2H, CH₂), 2.96–2.98 (m, 2H, CH₂), 3.47–3.49 (m, 2H, CH₂), 7.52 (dd, $J = 8.4$ Hz, $J' = 1.2$ Hz, 2H, ArH), 7.69–7.78 (m, 4H, ArH), 7.77 (dd, $J = 8.8$ Hz, $J' = 1.2$ Hz, 1H, ArH), 8.00 (d, $J = 9.2$ Hz, 1H, ArH), 8.05–8.07 (m, 1H, ArH), 8.43 (d, $J = 8.0$ Hz, 1H, ArH).

4.1.32. *8-(4-Fulorophenyl)-10,11,12,13-tetrahydro-9H-benzo[*ff*]cyclohepta[*c*]quinoline (6f)*. Pale yellow crystals (0.585 g, 86 %), mp 131–132 °C.

IR (KBr): 3054, 2982, 2929, 2906, 2852, 1598, 1560, 1550, 1507, 1476, 1465, 1447, 1375, 1353, 1296, 1222, 1153, 1092, 1034, 1013, 955, 880, 831, 812, 751, 688 cm⁻¹.

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.81 (b, 2H, CH₂), 2.01 (b, 2H, CH₂), 3.10 (b, 2H, CH₂), 2.97–2.99 (m, 2H, CH₂), 3.47–3.49 (m, 2H, CH₂), 7.33–7.37 (m, 2H, ArH), 7.58–7.62 (m, 2H, ArH), 7.69–7.72 (m, 2H, ArH), 7.77 (d, $J = 8.8$ Hz, 1H, ArH), 7.99 (d, $J = 8.8$ Hz, 1H, ArH), 8.04–8.07 (m, 1H, ArH), 8.42–8.44 (m, 1H, ArH).

^{13}C NMR (CDCl₃, 100 MHz): δ 25.9, 27.4, 30.6, 31.7, 32.8, 115.2, 115.4, 124.5, 125.7, 126.5, 127.8, 128.6, 128.7, 129.3, 130.2, 130.96, 131.05, 133.1, 135.3, 137.58, 137.61, 146.6, 150.3, 156.7, 161.5, 163.9.

Anal. calcd for C₂₄H₂₀FN (341.42): C 84.43, H 5.90, N 4.10; found C 84.65, H 5.79, N 4.03.

4.1.33. *8-(4-Methoxyphenyl)-10,11,12,13-tetrahydro-9H-benzo[*ff*]cyclohepta[*c*]quinoline (6g)*. Pale yellow crystals (0.623 g, 88 %), mp 174–176 °C (Lit. [23] 170–171 °C).

IR (KBr): 3015, 2931, 2905, 2852, 1608, 1574, 1560, 1548, 1516, 1476, 1440, 1374, 1354, 1334, 1288, 1248, 1218, 1172, 1135, 1102, 1025, 970, 955, 833, 801, 752, 690 cm⁻¹.

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.81 (b, 2H, CH₂), 2.01 (b, 2H, CH₂), 2.09 (b, 2H, CH₂), 2.99–3.01 (m, 2H, CH₂), 3.49 (b, 2H, CH₂), 3.83 (s, 3H, CH₃O), 7.07 (d, $J = 8.4$ Hz, 2H, ArH), 7.50 (d, $J = 8.4$ Hz, 2H, ArH), 7.67–7.69 (m, 2H, ArH), 7.75 (d, $J = 8.8$ Hz, 1H, ArH), 7.97 (d, $J = 9.2$ Hz, 1H, ArH), 8.03–8.05 (m, 1H, ArH), 8.40–8.42 (m, 1H, ArH).

4.1.34. *8-(3,5-Dimethoxyphenyl)-10,11,12,13-tetrahydro-9H-benzo[*ff*]cyclohepta[*c*]quinoline (6h)*. Pale yellow crystals (0.629 g, 82 %), mp 152–153 °C.

IR (KBr): 3004, 2918, 2849, 1592, 1530, 1483, 1452, 1374, 1354, 1312, 1287, 1261, 1234, 1204, 1155, 1064, 991, 965, 925, 871, 862, 833, 808, 776, 756, 744, 699, 686 cm^{-1} .

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.79 (b, 2H, CH_2), 1.99 (b, 2H, CH_2), 2.08 (b, 2H, CH_2), 2.96–2.98 (m, 2H, CH_2), 3.44–3.46 (m, 2H, CH_2), 3.80 (s, 6H, 2 CH_3O), 6.59–6.60 (m, 1H, ArH), 6.66 (d, $J = 8.8$ Hz, 2H, ArH), 7.67–7.69 (m, 2H, ArH), 7.76 (d, $J = 8.8$ Hz, 1H, ArH), 7.98 (d, $J = 8.8$ Hz, 1H, ArH), 8.03–8.05 (m, 1H, ArH), 8.39–8.42 (m, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 25.9, 27.5, 30.6, 31.7, 32.8, 55.5, 100.4, 107.2, 124.6, 125.6, 126.5, 127.8, 128.6, 128.8, 129.9, 130.0, 133.1, 135.3, 143.5, 146.5, 150.2, 157.6, 160.7.

Anal. calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_2$ (383.48): C 81.43, H 6.57, N 3.65; found C 81.65, H 6.49, N 3.72.

4.1.35. *8-(2,3-Dimethoxyphenyl)-10,11,12,13-tetrahydro-9H-benzo[*f*]cyclohepta[*c*]quinoline (6i)*. Pale yellow crystals (0.608 g, 79 %), mp 126–128°C.

IR (KBr): 3007, 2986, 2965, 2923, 2855, 2834, 1579, 1561, 1552, 1472, 1424, 1374, 1345, 1299, 1265, 1218, 1168, 1128, 1099, 1085, 1058, 1035, 1006, 973, 962, 838, 793, 751, 689 cm^{-1} .

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.66 (b, 2H, CH_2), 1.94–1.98 (m, 2H, CH_2), 2.05 (b, 2H, CH_2), 2.79–2.84 (m, 2H, CH_2), 3.42–3.46 (m, 2H, CH_2), 3.50 (s, 3H, CH_3O), 3.87 (s, 3H, CH_3O), 6.86 (dd, $J = 6.8$ Hz, $J' = 2.4$ Hz, 1H, ArH), 7.13–7.19 (m, 2H, ArH), 7.66–7.71 (m, 2H, ArH), 7.75 (d, $J = 8.8$ Hz, 1H, ArH), 7.97 (d, $J = 8.8$ Hz, 1H, ArH), 8.04–8.06 (m, 1H, ArH), 8.44–8.46 (m, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 26.0, 27.4, 31.1, 31.9, 33.0, 56.0, 61.1, 112.2, 122.5, 124.4, 124.9, 125.6, 126.4, 127.9, 128.6, 128.9, 129.8, 129.9, 133.1, 136.3, 137.1, 146.6, 146.7, 149.5, 152.7, 155.3.

Anal. calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_2$ (383.48): C 81.43, H 6.57, N 3.65; found C 81.54, H 6.64, N 3.55.

4.1.36. *8-(4-Nitrophenyl)-10,11,12,13-tetrahydro-9H-benzo[*f*]cyclohepta[*c*]quinoline (6j)*. Pale yellow crystals (0.625 g, 85 %), mp 168–170°C (Lit. $^{[23]}$ 165–166 °C).

IR (KBr): 3048, 2850, 1602, 1545, 1524, 1479, 1441, 1406, 1372, 1346, 1260, 1168, 1124, 1105, 1031, 1010, 987, 860, 849, 832, 805, 756, 744, 702 cm^{-1} .

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.87 (b, 2H, CH_2), 2.06 (b, 2H, CH_2), 2.15–2.16 (m, 2H, CH_2), 2.99–3.02 (m, 2H, CH_2), 2.53–3.55 (m, 2H, CH_2), 7.75–7.77 (m, 2H, ArH), 7.83 (d, $J = 8.8$ Hz, 1H, ArH), 7.88 (d, $J = 8.8$ Hz, 2H, ArH), 8.07 (d, $J = 8.8$ Hz, 1H, ArH), 8.11–8.13 (m, 1H, ArH), 8.42 (d, $J = 8.8$ Hz, 2H, ArH), 8.48–8.50 (m, 1H, ArH).

Anal. calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2$ (368.43): C 78.24, H 5.47, N 7.60; found C 78.30, H 5.46, N 7.68.

4.1.37. *8-(2-Nitrophenyl)-10,11,12,13-tetrahydro-9H-benzo[*ff*]cyclohepta[*c*]quinoline (6k)*. Pale yellow crystals (0.580 g, 79 %), mp 140–141°C.

IR (KBr): 3089, 3053, 2929, 2854, 1613, 1574, 1557, 1525, 1478, 1441, 1371, 1345, 1250, 1232, 1165, 1147, 1128, 1060, 989, 955, 854, 833, 806, 790, 778, 750, 741, 702, 682 cm^{-1} .

^1H NMR (DMSO- d_6 , 400 MHz): δ 1.67 (b, 2H, CH_2), 1.96 (b, 2H, CH_2), 2.06 (b, 2H, CH_2), 3.49–3.50 (m, 2H, CH_2), 7.60 (d, $J = 7.6$ Hz, 1H, ArH), 7.68–7.77 (m, 4H, ArH), 7.85–7.89 (m, 1H, ArH), 7.99 (d, $J = 9.2$ Hz, 1H, ArH), 8.05–8.07 (m, 1H, ArH), 8.19 (d, $J = 8.0$ Hz, 1H, ArH), 8.45–8.47 (m, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 25.8, 27.0, 31.0, 31.8, 33.0, 124.6, 125.2, 125.8, 126.7, 127.9, 128.5, 128.7, 129.0, 129.8, 130.3, 131.8, 133.2, 133.4, 135.5, 137.1, 146.8, 148.3, 150.1, 154.6.

Anal. calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2$ (368.43): C 78.24, H 5.47, N 7.60; found C 78.43, H 5.41, N 7.53.

4.1.38.

*8-(4-Chlorophenyl)-9,10,11,12,13,14-hexahydrobenzo[*ff*]cycloocta[*c*]quinoline (7c)*. Pale yellow crystals (0.594 g, 80 %), mp 230–232°C.

IR (KBr): 3055, 2923, 2850, 1593, 1557, 1543, 1490, 1477, 1449, 1436, 1396, 1362, 1252, 1175, 1102, 1087, 1007, 944, 862, 835, 805, 768, 744, 704, 683 cm^{-1} .

^1H NMR (CDCl_3 , 400 MHz): δ 1.53–1.55 (m, 2H, CH_2), 1.63–1.74 (m, 4H, 2 CH_2), 2.23–2.29 (m, 2H, CH_2), 2.93–2.96 (m, 2H, CH_2), 3.61 (s, 2H, CH_2), 7.43–7.48 (m,

4H, ArH), 7.63–7.70 (m, 2H, ArH), 7.89–7.97 (m, 3H, ArH), 8.82 (d, $J = 8.0$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 25.8, 27.3, 28.0, 30.7, 31.0, 31.1, 113.4, 124.8, 126.2, 126.4, 127.7, 128.4, 129.3, 129.5, 130.1, 130.6, 133.0, 133.5, 133.9, 140.7, 147.4, 148.7, 158.3.

Anal. calcd for $\text{C}_{25}\text{H}_{22}\text{ClN}$ (371.90): C 80.74, H 5.96, N 3.77; found C 80.65, H 5.88, N 3.89

4.1.39. *8-(3-Chlorophenyl)-9,10,11,12,13,14-hexahydrobenzo[*f*]cycloocta[*c*]quinoline (7d)*. Pale yellow crystals (0.529 g, 71 %), mp 147–149 °C.

IR (KBr): 3064, 2927, 2855, 1598, 1566, 1557, 1546, 1494, 1475, 1436, 1410, 1348, 1254, 1232, 1181, 1079, 1011, 889, 868, 849, 836, 806, 774, 754, 724, 701, 683 cm^{-1} .

^1H NMR (CDCl_3 , 400 MHz): δ 1.54–1.57 (m, 2H, CH_2), 1.68–1.75 (m, 4H, 2 CH_2), 2.29–2.30 (m, 2H, CH_2), 2.96–2.99 (m, 2H, CH_2), 3.64 (s, 2H, CH_2), 7.41–7.45 (m, 3H, ArH), 7.54 (s, 1H, ArH), 7.66–7.72 (m, 2H, ArH), 7.92–7.99 (m, 3H, ArH), 8.85 (d, $J = 8.4$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 25.8, 27.3, 28.0, 30.7, 31.0, 31.1, 124.9, 126.3, 126.5, 126.9, 127.8, 128.0, 128.9, 129.3, 129.5, 130.1, 130.7, 132.9, 133.5, 134.1, 143.9, 147.3, 148.8, 158.0.

Anal. calcd for $\text{C}_{25}\text{H}_{22}\text{ClN}$ (371.90): C 80.74, H 5.96, N 3.77; found C 80.70, H 6.07, N 3.70

4.2. General procedure for the syntheses of benzo[*f*]quinolines **9**

A dry 50 mL flask was charged with arylaldehyde (2.0 mmol), naphthalen-2-amine (2.0 mmol, 0.286 g), acetone or propionaldehyde (2.5 mmol), I_2 (0.1 mmol, 0.026 g) and THF (10 mL). The reaction mixture was stirred at 50 °C for 6–8 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 **9**, when the mixture was cooled to room temperature.

4.2.3. 3-(2-Fluorophenyl)-1-methylbenzo[*f*]quinoline (**9b**). Pale yellow crystals (0.519 g, 90 %), mp 117–118 °C.

IR (KBr): 3054, 2990, 1613, 1604, 1579, 1549, 1457, 1376, 1349, 1225, 1111, 1077, 1031, 875, 835, 809, 756 cm^{-1} .

^1H NMR (CDCl_3 , 400 MHz): δ 3.18 (s, 3H, CH_3), 7.18–7.25 (m, 1H, ArH), 7.30–7.34 (m, 1H, ArH), 7.39–7.41 (m, 1H, ArH), 7.62–7.69 (m, 2H, ArH), 7.88 (d, $J = 2.4$ Hz, 1H, ArH), 7.96 (d, $J = 8.4$ Hz, 2H, ArH), 8.06 (d, $J = 9.2$ Hz, 1H, ArH), 8.17–8.21 (m, 1H, ArH), 8.32 (d, $J = 8.4$ Hz, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 26.9, 116.1, 116.4, 124.66, 124.70, 124.9, 126.2, 126.3, 126.4, 126.5, 127.6, 129.1, 129.5, 130.6, 130.7, 130.8, 131.1, 131.4, 131.5, 133.0, 145.1, 149.7, 151.9, 159.6, 162.1

Anal. calcd for $\text{C}_{20}\text{H}_{14}\text{FN}$ (287.33): C 83.60, H 4.91, N 4.87; found C 83.62, H 4.99, N 4.70.

4.2.4. 3-(4-Methoxyphenyl)-2-methylbenzo[*f*]quinoline (**9d**). Pale yellow crystals (0.515 g, 86 %), mp 167–169 °C.

IR (KBr): 3059, 2998, 2964, 2834, 1602, 1507, 1480, 1452, 1401, 1381, 1288, 1248, 1175, 1031, 1003, 833, 758 cm^{-1} .

^1H NMR (CDCl_3 , 400 MHz): δ 2.60 (s, 3H, CH_3), 3.88 (s, 3H, CH_3O), 7.03 (d, $J = 8.8$ Hz, 2H, ArH), 7.60–7.70 (m, 4H, ArH), 7.91 (d, $J = 8.8$ Hz, 2H, ArH), 8.01 (d, $J = 8.8$ Hz, 1H, ArH), 8.62 (d, $J = 8.0$ Hz, 1H, ArH), 8.77 (s, 1H, ArH).

^{13}C NMR (CDCl_3 , 100 MHz): δ 21.1, 55.4, 113.8, 122.6, 124.1, 126.9, 127.0, 128.2, 128.7, 129.2, 129.3, 130.0, 130.5, 131.8, 132.3, 133.3, 146.3, 159.0, 159.7.

Anal. calcd for $\text{C}_{21}\text{H}_{17}\text{NO}$ (299.37): C 84.25, H 5.72, N 4.68; found C 84.50, H 5.66, N 4.60.