

Supporting Information

Diversity Oriented Synthesis of Benzoxanthene and Benzochromene Libraries via One-Pot, Three-Component Reactions and Their Anti-proliferative Activity

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General Information: Unless otherwise specified all the reagents and catalysts were purchased from Sigma-Aldrich and were used without further any purification. The common organic solvents were purchased from Ranbaxy. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using flash chromatography on 230-400 mesh silica gel. Reactions were monitored by thin-layer chromatography (TLC) on 0.25mm silica gel plates visualized under UV light, iodine or KMnO_4 staining. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX -200 & 300 Mhz Spectrometer. Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (J) in Hz. IR spectra were recorded on a FT IR spectrophotometer Shimadzu 8201 PC and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra (ESI MS) were obtained by Micromass Quattro II instrument.

General Procedures:

General procedure for the synthesis of 12-substituted-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-ones (4a-o): A mixture of 2-naphthol (1 mmol), diketone (1 mmol), aldehyde(1 mmol), and CAN (5 mol %) was stirred in a round bottom flask at 120 °C for 30 minutes under solvent free conditions. After completion, ethyl acetate was added to the reaction mixture and was shaken well to dissolve all organic compounds. Then it was filtered to remove CAN. The filtrate was concentrated and the crude obtained was purified by silica-gel column chromatography to yield pure compounds.

General procedure for the synthesis of 14-substituted-14H-dibenzo[a, j]xanthenes (5a-n):

In a 25 ml round bottom flask, aldehyde (1 mmol), 2-naphthol (2 mmol), and CAN (5 mol %) were taken. The reaction mixture was stirred at 120 °C under solvent-free conditions for 30 minutes. After completion, the reaction mixture was cooled to room temperature and ethyl acetate was added and shaken well to dissolve all organic components then filtered to remove CAN. The filtrate was concentrated to yield crude which was purified by silica gel column chromatography.

General procedure for the synthesis of 3-amino-1-substituted-1H-benzo[f]chromenes (7a-k): In a 25 ml round bottom flask, aldehyde (1 mmol), 2-naphthol (1 mmol), malononitrile/ethyl cyanoacetate (1 mmol), and CAN (5 mol %) were taken. The reaction mixture was stirred at 120 °C under solvent-free conditions for 30 minutes. After completion, the reaction mixture was cooled to room temperature and ethyl acetate was added and shaken well to dissolve all organic components then filtered to remove CAN. The filtrate was concentrated to yield crude which was purified by silica gel column chromatography.

Characterization data for synthesized compounds:

9,9-dimethyl-12-phenyl-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (4a).

Mp 154-155 °C; ESI MS (m/z) = 355 [M+H]. IR (KBr, cm⁻¹): 3125, 2954, 1651, 1595, 1398, 1375, 1228, 1176, 1025, 808, 743, 699, 510. ¹H NMR (CDCl₃, 300 MHz) δ = 0.96 (s, 3H), 1.11 (s, 3H), 2.27 (dd, *J* = 7.0 & 16.0 Hz, 2H), 2.57 (s, 2H), 5.71 (s, 1H), 7.03-7.06 (m, 1H), 7.15-7.18 (m, 2H), 7.31-7.44 (m, 5H), 7.75-7.78 (m, 2H), 7.99 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ = 27.2, 29.3, 32.3, 34.7, 41.4, 50.9, 114.3, 117.0, 117.7, 123.7147.8, 124.9, 126.3, 127.0, 128.3, 128.4, 128.5, 128.9, 131.4, 131.5, 144.7, 163.9, 196.9. Elemental Analysis Calculated for C₂₅H₂₂O₂: C, 84.72; H, 6.26. Found: C, 84.75; H, 6.28.

12-(4-Methoxyphenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11-one (4b).

Mp 205-206 °C; ESI MS (m/z) = 385 [M+H]. IR (KBr, cm⁻¹): 3121, 2958, 1652, 1607, 1507, 1462, 1382, 1218, 1143, 1028, 834, 747, 661, 539. ¹H NMR (CDCl₃, 300 MHz) δ = 0.97 (s, 3H), 1.11 (s, 3H), 2.27 (dd, *J* = 6.0 & 16.0 Hz, 2H), 2.56 (s, 2H), 3.68 (s, 3H), 5.65 (s, 1H), 6.69-6.71 (m, 2H), 7.24-7.45 (m, 5H), 7.74-7.78 (m, 2H), 7.98 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ = 27.2, 29.3, 32.3, 33.9, 41.4, 50.9, 55.1, 113.6, 114.4, 117.1, 117.9, 123.7, 124.9, 127.0, 128.4, 128.7, 129.4, 131.4, 131.5, 137.2, 147.7,

157.8, 163.7, 197.0. Elemental Analysis Calculated for C₂₆H₂₄O₃: C, 81.22; H, 6.29. Found: C, 81.15; H, 6.20.

12-(4-Chlorophenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11-one (4c).

Mp 181-182 °C; ESI MS (m/z) = 389 [M+H]. IR (KBr, cm⁻¹): 3133, 2958, 1648, 1596, 1483, 1400, 1375, 1224, 1139, 1009, 841, 747, 535. ¹H NMR (CDCl₃, 300 MHz) δ = 0.96 (s, 3H), 1.12 (s, 3H), 2.28 (dd, *J* = 8.5 & 16.0 Hz, 2H), 2.56 (s, 2H), 5.68 (s, 1H), 7.12-7.14 (m, 2H), 7.25-7.45 (m, 5H), 7.76-7.79 (m, 2H), 7.90 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ = 27.1, 29.3, 32.3, 34.2, 41.4, 50.9, 113.9, 117.1, 123.5, 125.0, 127.2, 128.4, 128.5, 129.1, 129.8, 131.2, 131.5, 131.9, 143.3, 147.7, 164.1, 196.9. Elemental Analysis Calculated for C₂₅H₂₁ClO₂: C, 77.21; H, 5.44. Found: C, 77.12; H, 5.33.

12-(3,4-Dimethylphenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11-one (4d).

Mp 181-182 °C; ESI MS (m/z) = 383 [M+H]. IR (KBr, cm⁻¹): 3125, 2958, 1650, 1593, 1398, 1371, 1237, 1226, 1172, 819, 747, 478. ¹H NMR (CDCl₃, 300 MHz) δ = 0.99 (s, 3H), 1.11 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 2.27 (dd, *J* = 4.0 & 16.0 Hz, 2H), 2.56 (dd, *J* = 2.5 & 17.5 Hz, 2H), 5.63 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 7.03-7.10 (m, 2H), 7.25-7.43 (m, 3H), 7.72-7.77 (m, 2H), 8.04 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ = 19.4, 20.0, 27.4, 29.2, 32.4, 34.3, 41.4, 51.0, 114.5, 117.1, 118.1, 123.8, 124.9, 125.9, 127.0, 128.4, 128.7, 129.5, 129.7, 131.5, 134.4, 136.2, 142.3, 147.7, 163.8, 196.2. Elemental Analysis Calculated for C₂₇H₂₆O₂: C, 84.78; H, 6.85. Found: C, 84.71; H, 6.80.

9,9-Dimethyl-12-(3-nitrophenyl)-9,10-dihydro-8H-benzo[a]xanthen-11-one (4e).

Mp 169-170 °C; ESI MS (m/z) = 400 [M+H]. IR (KBr cm⁻¹): 3125, 2954, 2864, 1649, 1596, 1529, 1375, 1344, 1225, 1025, 812, 748, 683, 510. ¹H NMR (CDCl₃, 300 MHz) δ = 0.95 (s, 3H), 1.13 (s, 3H), 2.29 (dd, *J*₁ = 13.0 & 16.0 Hz, 2H), 2.61 (s, 2H), 5.82 (s, 1H), 7.35-7.47 (m, 4H), 7.79-8.12 (m, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ = 27.1, 29.3, 32.3, 34.8, 41.4, 50.8, 113.1, 116.0, 117.3, 121.6, 123.1, 123.3, 125.2, 127.4, 128.7, 129.1, 129.7, 131.0, 131.6, 134.9, 146.8, 147.8, 148.4, 164.6, 196.8. Elemental Analysis Calculated for C₂₅H₂₁NO₄: C, 75.17; H, 5.30; N, 3.51. Found: C, 75.08; H, 5.20; N, 3.38.

9,9-Dimethyl-12-(thiophen-2-yl)-9,10-dihydro-8H-benzo[a]xanthen-11-one (4f).

Mp 180-181 °C; ESI MS (m/z) = 361 [M+H]. IR (KBr, cm^{-1}): 3105, 2958, 1651, 1593, 1376, 1224, 1177, 1147, 1009, 813, 746, 700, 661, 507. ^1H NMR (CDCl_3 , 300 MHz) δ = 1.05 (s, 3H), 1.14 (s, 3H), 2.35 (s, 2H), 2.57 (s, 2H), 6.04 (s, 1H), 6.74-6.77 (m, 2H), 7.00-7.01 (m, 1H), 7.30-7.51 (m, 3H), 7.78-7.82 (m, 2H), 8.04 (d, J = 8.5 Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 27.2, 29.3, 29.4, 32.3, 41.4, 50.9, 113.8, 117.1, 117.2, 123.5, 124.0, 125.0, 125.1, 126.3, 127.2, 128.4, 129.1, 131.4, 147.8, 148.6, 164.6, 196.8. Elemental Analysis Calculated for $\text{C}_{23}\text{H}_{20}\text{O}_2\text{S}$: C, 76.64; H, 5.59. Found: C, 76.55; H, 5.50.

12-Tert-butyl-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11-one (4g).

Mp 110-111 °C; ESI MS (m/z) = 335 [M+H]. IR (KBr, cm^{-1}): 3125, 2962, 1642, 1592, 1394, 1220, 1176, 1005, 812, 750, 616, 490. ^1H NMR (CDCl_3 , 300 MHz) δ = 0.78 (s, 9H), 1.14 (s, 3H), 1.27 (s, 3H), 2.28 (d, J = 16.5 Hz, 1H), 2.42 (d, J = 16.5 Hz, 1H), 2.52 (d, J = 18.0 Hz, 1H), 2.65 (d, J = 18.0 Hz, 1H), 4.62 (s, 1H), 7.28 (d, J = 9.0 Hz, 1H), 7.40-7.43 (m, 1H), 7.49-7.52 (m, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 9.0 Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 27.4, 27.8, 30.1, 31.7, 35.9, 40.0, 41.6, 51.0, 113.9, 116.8, 118.4, 124.6, 126.0, 127.8, 128.2, 131.3, 132.7, 150.6, 167.6, 197.2. Elemental Analysis Calculated for $\text{C}_{23}\text{H}_{26}\text{O}_2$: C, 82.60; H, 7.84. Found: C, 82.51; H, 7.71.

12-Ethyl-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11-one (4h).

Yellow oil; ESI MS (m/z) = 307 [M+H]. IR (Neat, cm^{-1}): 3130, 2960, 1651, 1595, 1394, 1225, 1177, 1145, 813, 748, 649, 480. ^1H NMR (CDCl_3 , 300 MHz) δ = 0.61 (t, J = 7.5 Hz, 3H), 1.16 (s, 3H), 1.20 (s, 3H), 1.83-1.86 (m, 2H), 2.37 (d, J = 4.5 Hz, 2H), 2.55 (d, J = 3.5 Hz, 2H), 4.74 (t, J = 4.0 Hz, 1H), 7.20 (d, J = 8.5 Hz, 1H), 7.42-7.45 (m, 1H), 7.56-7.53 (m, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 9.0, 27.3, 27.4, 28.7, 29.7, 32.2, 41.4, 51.1, 112.1, 116.8, 117.7, 123.3, 124.8, 126.7, 128.0, 128.6, 131.2, 131.5, 148.7, 166.3, 197.6. Elemental Analysis Calculated for $\text{C}_{21}\text{H}_{22}\text{O}_2$: C, 82.32; H, 7.24. Found: C, 82.22; H, 7.30.

12-(4-Hydroxyphenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11-one (4i)

Mp 210 °C. ESI MS (m/z) = 371 (M+H). IR (KBr, cm^{-1}): 3223, 3071, 2957, 2870, 1631, 1590, 1511, 1449, 1380. ^1H NMR (CDCl_3 , 300 MHz) δ = 0.97 (s, 3H), 1.11 (s, 3H), 2.18-

2.36 (m, 2H), 2.57 (s, 2H), 5.65 (s, 1H), 6.61 (d, $J = 8.5$ Hz, 2H), 6.98 (s, 1H), 7.17 (d, $J = 9.0$ Hz, 2H), 7.31-7.44 (m, 3H), 7.75-7.80 (m, 2H), 7.99 (d, $J = 8.3$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) $\delta = 27.1, 29.2, 32.3, 33.9, 41.4, 50.8, 114.5, 115.4, 116.9, 117.9, 123.8, 124.9, 126.9, 128.3, 128.7, 129.5, 131.4, 131.5, 136.4, 147.5, 154.5, 164.5, 198.2$. Elemental Analysis calculated for $\text{C}_{25}\text{H}_{22}\text{O}_3$: C, 81.06; H, 5.99. Found C, 80.96; H, 5.90.

12-Phenyl-9,10-dihydro-8H-benzo[a]xanthen-11-one (4j).

Mp 202-203 $^{\circ}\text{C}$; ESI MS (m/z) = 327 (M+H). IR (KBr, cm^{-1}): 3129, 3052, 2954, 1645, 1594, 1453, 1373, 1229, 1189, 999, 955, 816, 758, 701, 531. ^1H NMR (CDCl_3 , 300 MHz) $\delta = 1.96$ -2.06 (m, 2H), 2.34-2.47 (m, 2H), 2.66-2.75 (m, 2H), 5.74 (s, 1H), 7.04-7.08 (m, 1H), 7.15-7.18 (m, 2H), 7.32-7.43 (m, 5H), 7.75-7.78 (m, 2H), 7.96 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) $\delta = 20.3, 27.8, 34.7, 37.1, 115.6, 117.0, 117.7, 123.7, 124.9, 126.3, 127.0, 128.3, 128.4, 128.5, 128.9, 131.4, 131.5, 145.1, 147.8, 165.6, 197.1$. Elemental Analysis Calculated for $\text{C}_{23}\text{H}_{18}\text{O}_2$: C, 84.64; H, 5.56. Found: C, 84.50; H, 5.48.

12-(4-Chlorophenyl)-9,10-dihydro-8H-benzo[a]xanthen-11-one (4k).

Mp 208-209 $^{\circ}\text{C}$; ESI MS (m/z) = 313 (M+H). IR (KBr, cm^{-1}): 3130, 3052, 2962, 1647, 1593, 1488, 1368, 1228, 1189, 1139, 1089, 1000, 954, 818, 753, 530. ^1H NMR (CDCl_3 , 300 MHz) $\delta = 1.93$ -2.08 (m, 2H), 2.35-2.48 (m, 2H), 2.63-2.76 (m, 2H), 5.72 (s, 1H), 7.12-7.16 (m, 2H), 7.25-7.44 (m, 5H), 7.76-7.79 (m, 2H), 7.88 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) $\delta = 20.3, 27.8, 34.2, 37.0, 115.1, 117.0, 117.1, 123.5, 125.1, 127.1, 128.5, 129.1, 129.9, 131.2, 131.5, 132.0, 143.6, 147.8, 165.8, 197.1$. Elemental Analysis Calculated for $\text{C}_{23}\text{H}_{17}\text{ClO}_2$: C, 76.56; H, 4.75. Found: C, 76.42; H, 4.68.

12-(3,4-Dimethylphenyl)-9,10-dihydro-8H-benzo[a]xanthen-11-one (4l).

Mp 174-175 $^{\circ}\text{C}$; ESI MS (m/z) = 355 [M+H]. IR (KBr, cm^{-1}): 3121, 2962, 2933, 1651, 1594, 1373, 1225, 1190, 1140, 997, 955, 821, 747, 617, 495, 459. ^1H NMR (CDCl_3 , 300 MHz) $\delta = 1.97$ -2.07 (m, 2H), 2.11 (s, 3H), 2.14 (s, 3H), 2.34-2.48 (m, 2H), 2.62-2.77 (m, 2H), 5.67 (s, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 7.03-7.09 (m, 2H), 7.32-7.44 (m, 3H), 7.74-7.78 (m, 2H), 7.99 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) $\delta = 19.3, 19.9, 20.3, 27.8, 34.2, 37.1, 115.9, 117.0, 118.1, 123.8, 124.8, 125.9, 127.0, 128.3, 128.6, 129.5, 129.7, 131.4, 131.5, 134.4, 136.3, 142.6, 147.8, 165.5, 197.0$. Elemental Analysis Calculated for $\text{C}_{25}\text{H}_{22}\text{O}_2$: C, 84.72; H, 6.26. Found: C, 84.60; H, 6.15.

11-Phenyl-8,11-dihydro-benzo[f]cyclopenta[b]chromen-10(9H)-one (4m).

Mp 237-238 °C; ESI MS (m/z) = 313 (M+H). IR (KBr, cm^{-1}): 3391, 3125, 1705, 1667, 1596, 1377, 1232, 1101, 1011, 942, 811, 747, 696, 528, 509. ^1H NMR (CDCl_3 , 300 MHz) δ = 2.45-2.55 (m, 2H), 2.73-2.84 (m, 2H), 5.58 (s, 1H), 7.09-7.12 (m, 1H), 7.18-7.21 (m, 2H), 7.26-7.28 (m, 2H), 7.38-7.40 (m, 3H), 7.77-7.84 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 25.4, 33.8, 36.0, 116.1, 117.4, 118.9, 124.2, 125.2, 126.6, 127.2, 128.2, 128.4, 128.5, 129.6, 131.7, 131.8, 143.6, 149.2, 177.1, 202.5. Elemental Analysis Calculated for $\text{C}_{22}\text{H}_{16}\text{O}_2$: C, 84.59; H, 5.16. Found: C, 84.48; H, 5.09.

11-(4-Chlorophenyl)-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11H)-one (4n).

Mp 233-234 °C; ESI MS (m/z) = 347 (M+H). IR (KBr, cm^{-1}): 3426, 3131, 1699, 1658, 1396, 1233, 1088, 1013, 9445, 819, 744, 527. ^1H NMR (CDCl_3 , 300 MHz) δ = 2.45-2.56 (m, 2H), 2.75-2.84 (m, 2H), 5.55 (s, 7.82-7.85 (m, 2H),, 1H), 7.15-7.21 (m, 4H), 7.38-7.41 (m, 3H), 7.69-7.71 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ = 25.4, 33.8, 35.5, 115.5, 117.4, 118.3, 124.0, 125.3, 127.3, 128.6, 128.7, 129.5, 129.9, 131.6, 131.8, 132.4, 142.0, 149.2, 177.2, 202.4. Elemental Analysis Calculated for $\text{C}_{22}\text{H}_{15}\text{ClO}_2$: C, 76.19; H, 4.36. Found: C, 76.07; H, 4.28.

11-(3,4-Dimethylphenyl)-8,9-dihydrobenzo[f]cyclopenta[b]chromen-10(11H)-one (4o).

Mp 223-224 °C; ESI MS (m/z) = 313 (M+H). IR (KBr, cm^{-1}): 3407, 3131, 1709, 1670, 1591, 1396, 1237, 943, 825, 746, 498. ^1H NMR (CDCl_3 , 300 MHz) δ = 2.12 (s, 3H), 2.13 (s, 3H), 2.47-2.50 (m, 2H), 2.75-2.79 (m, 2H), 5.50 (s, 1H), 6.93-7.03 (m, 3H), 7.36-7.40 (m, 3H), 7.79-7.83 (m, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 19.4, 19.9, 25.3, 33.8, 35.5, 116.5, 117.4, 119.2, 124.2, 125.1, 125.5, 127.1, 128.4, 129.3, 129.4, 129.7, 131.8, 131.9, 134.8, 136.6, 141.2, 149.2, 177.1, 202.5. Elemental Analysis Calculated for $\text{C}_{24}\text{H}_{20}\text{O}_2$: C, 84.68; H, 5.92. Found: C, 84.56; H, 5.85.

14-Phenyl-14H-dibenzo[a,j]xanthene (5a)

Mp 181 °C; ESI MS (m/z) = 359 (M+H). IR (KBr, cm^{-1}): 3024, 1590, 1410, 1245. ^1H NMR (CDCl_3 , 300 MHz) δ = 6.49 (s, 1H), 6.98 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 8.40 (d, J = 8.4 Hz, 2H). Elemental Analysis Calculated for $\text{C}_{27}\text{H}_{18}\text{O}$: C, 90.47; H, 5.06. Found: C, 90.35; H, 4.94.

14-(3-Hydroxyphenyl)-14H-dibenzo[a,j]xanthene (5b)

Mp 261-263 °C; ESI MS (m/z) = 375 (M+H). IR (KBr, cm^{-1}): 3446, 1620, 1588, 1247, 961, 816, 745, 694. ^1H NMR (DMSO- d_6 , 200 MHz) δ = 6.41 (s, 1H), 6.79-7.11 (m, 3H), 7.35-7.86 (m, 12H), 8.44 (d, J = 9.6 Hz, 2H), 8.84 (bs, 1H). ^{13}C NMR (DMSO- d_6 , 75 MHz) δ = 36.40, 113.32, 114.89, 117.53, 117.60, 118.90, 123.36, 124.36, 126.73, 128.43, 128.77, 129.00, 130.86, 131.12, 146.70, 147.88, 157.31. Elemental Analysis Calculated for $\text{C}_{27}\text{H}_{18}\text{O}_2$: C, 86.61; H, 4.85. Found: C, 86.55; H, 4.88.

14-(4-Methoxyphenyl)-14H-dibenzo[a,j]xanthene (5c)

Mp 213-215 °C; ESI MS (m/z) = 389 (M+H). IR (KBr, cm^{-1}): 2999, 2833, 1734, 1591, 1508, 1457, 1430, 1399, 1247, 1027, 958, 829, 807, 740. ^1H NMR (CDCl_3 , 200 MHz) δ = 3.58 (s, 3H), 6.40 (s, 1H), 6.65 (d, J = 9.7 Hz, 2H), 7.32-7.85 (m, 12H), 8.35 (d, J = 9.6 Hz, 2H). ^{13}C NMR (CDCl_3 , 50 MHz) δ = 36.9, 53.2, 114.3, 117.2, 118.3, 123.5, 124.1, 127.4, , 129.1, 129.4, 131.4, 133.7, 137.2, 149.3, 158.2. Elemental Analysis Calculated for $\text{C}_{28}\text{H}_{20}\text{O}_2$: C, 86.57; H, 5.19. Found: C, 86.41; H, 5.20.

14-(4-Methylphenyl)-14H-dibenzo[a,j]xanthene (5d)

Mp 238-240 °C; ESI MS (m/z) = 373 (M+H). IR (KBr, cm^{-1}): 3020, 2908, 1620, 1591, 1509, 1457, 1430, 1247, 959, 837, 810, 739. ^1H NMR (CDCl_3 , 200 MHz) δ = 2.18 (s, 3H), 6.39 (s, 1H), 6.90 (d, J = 9.6 Hz, 2H), 7.32-7.80 (m, 12H), 8.36 (d, J = 9.4 Hz, 2H). ^{13}C NMR (CDCl_3 , 50 MHz) δ = 19.1, 35.4, 115.7, 116.2, 121.3, 122.7, 125.2, 126.4, 127.4, 129.2, 129.5, 134.0, 140.8, 146.6. Elemental Analysis Calculated for $\text{C}_{28}\text{H}_{20}\text{O}$: C, 90.29; H, 5.41. Found: C, 90.32; H, 5.44.

14-(2-chlorophenyl)-14H-dibenzo[a,j]xanthene (5e)

Mp 213–215 °C; ESI MS (m/z) = 393 (M+H). IR (KBr, cm^{-1}): 3059, 1625, 1594, 1516, 1462, 1404, 1248. ^1H NMR (CDCl_3 , 300 MHz): d 6.82 (s, 1H), 6.92 (m, 2H), 7.25-7.27 (m, 1H), 7.37–7.65 (m, 8H), 7.79-7.84 (m, 4H), 8.75 (d, J = 8.5 Hz, 1H). Elemental Analysis Calculated for $\text{C}_{27}\text{H}_{17}\text{ClO}$: C, 82.54; H, 4.36. Found: C, 82.44; H, 4.25.

14-(4-(3-Chloropropoxy)phenyl)-14H-dibenzo[a,j]xanthene (5f)

Mp 158 °C; ESI MS (m/z) = 451 (M+H). IR (KBr, cm^{-1}): 3065, 2912, 2846, 1590, 1509, 1399, 1378, 1250, 1182. ^1H NMR (CDCl_3 , 300 MHz) δ = 1.98-2.17 (m, 2H), 3.42 (t, J = 6.4 Hz, 1H), 3.57 (t, J = 6.4 Hz, 1H), 3.79-3.87 (m, 2H), 6.46 (s, 1H), 6.64 (d, J = 8.7 Hz, 2H), 7.41-7.59 (m, 8H), 7.62-7.83 (m, 4H), 8.39 (d, J = 8.5 Hz, 2H). ^{13}C NMR (CDCl_3 ,

75 MHz) δ = 32.6, 37.5, 41.9, 64.4, 114.8, 117.9, 118.4, 123.1, 124.6, 127.2, 129.2, 129.2, 129.6, 131.5, 131.8, 138.0, 149.1, 157.4. Elemental Analysis Calculated for $C_{30}H_{23}ClO_2$: C, 79.90; H, 5.14. Found: C, 79.82; H, 5.05.

14-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthene (5g)

Mp 286-288 °C; ESI MS (m/z) = 393 (M+H). IR (KBr, cm^{-1}): 3026, 2914, 1621, 1590, 1241. 1H NMR ($CDCl_3$, 300 MHz) δ = 6.42 (s, 1H), 7.10 (d, J = 9.6 Hz, 2H), 7.62–7.30 (m, 12H), 8.30 (d, J = 9.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 35.4, 116.5, 117.2, 122.8, 124.1, 126.6, 127.9, 128.2, 128.8, 129.2, 130.2, 147.5. Elemental Analysis Calculated for $C_{27}H_{17}ClO$: C, 82.54; H, 4.36. Found: C, 82.44; H, 4.25.

14-(2,4-Dichlorophenyl)-14H-dibenzo[a,j]xanthene (5h)

Mp 252 °C; ESI MS (m/z) = 427 (M+H). IR (KBr, cm^{-1}): 3066, 2933, 1619, 1592, 1248. 1H NMR ($CDCl_3$, 300 MHz) δ = 6.71 (s, 1H), 6.90 (d, J = 9.5 Hz, 1H), 7.23-7.82 (m, 12H), 8.60 (d, J = 9.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 42.8, 125.8, 126.8, 131.6, 132.9, 133.3, 135.4, 135.8, 137.0, 137.6, 138.9, 139.6, 140.1, 141.4, 150, 157.5. Elemental Analysis Calculated for $C_{27}H_{16}Cl_2O$: C, 75.89; H, 3.77. Found: C, 75.78; H, 3.68.

14-(3-Fluorophenyl)-14H-dibenzo[a,j]xanthene (5i)

Mp 259 °C; ESI MS (m/z) = 377 (M+H). IR (KBr, cm^{-1}): 3154, 1594, 1403, 1240, 1207, 1069, 817, 747; 1H NMR ($CDCl_3$, 300 MHz) δ = 6.51 (s, 1H) 6.72–8.38 (m, 16H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 38.1, 113.8 and 114.0 (J_{C-F} 21.5 Hz), 115.6 and 115.9 (J_{C-F} 21.5 Hz), 117.1, 118.2, 122.9, 124.31 and 124.34 (J_{C-F} 2.8 Hz), 124.8, 127.4, 129.3, 129.5, 130.1 and 130.2 (J_{C-F} 8.3 Hz), 131.5, 131.7 (J_{C-F} 19.4 Hz), 147.8, 147.9 (J_{C-F} 6.2 Hz), 149.2, 161.7, 165.0; Elemental Analysis Calculated for $C_{27}H_{17}FO$: C, 86.15; H, 4.55; F, 5.05. Found: C, 86.11; H, 4.54, F, 5.07.

14-(2-Nitrophenyl)-14H-dibenzo[a,j]xanthene (5j)

Mp 293 °C; ESI MS (m/z) = 404 (M+H). IR (KBr, cm^{-1}): 3400, 3058, 1593, 1523, 1350, 1240, 1142, 810, 748; 1H NMR ($CDCl_3$, 300 MHz) δ = 7.52 (s, 1H) 7.10-8.56 (m, 16H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 32.9, 118.0, 118.4, 123.0, 124.6, 125.0, 125.3, 127.8, 128.0, 129.4, 129.5, 129.9, 130.8, 132.1, 132.6, 134.5, 141.3, 147.5, 149.8; Elemental Analysis Calculated for $C_{27}H_{17}NO_3$: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.25; H, 4.24, N, 3.57.

14-(3-Trifluoromethylphenyl)-14-H-3,11-dibromodibenzo[a,j]xanthene (5k)

Mp 202-204 °C; ESI MS (*m/z*) = 582 (M+H). ¹H NMR (CDCl₃, 300 MHz) δ = 6.41 (s, 1H), 7.25-7.30 (m, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.61-7.73 (m, 6H), 7.99 (d, 2H, *J* = 1.8 Hz), 8.14 (d, *J* = 8.8 Hz, 2H). ¹³C NMR (CDCl₃, 75MHz) δ = 37.9, 116.4, 118.5, 119.2, 123.8, 123.9, 124.4, 124.5, 125.2, 128.6, 129.3, 129.7, 130.3, 130.8, 131.0, 131.1, 131.4, 132.3, 145.3, 148.8. Elemental Analysis Calculated for C₂₈H₁₅Br₂F₃O: C, 57.56; H; 2.59. Found: C, 57.47; H; 2.65.

14-Isopropyl-14H-dibenzo[a,j]xanthene (5l)

Mp 155 °C; ESI MS (*m/z*) = 325 (M+H). IR (KBr, cm⁻¹): 1622, 1591, 1515, 1457, 1240. ¹H NMR (CDCl₃, 200 MHz) δ = 8.26 (d, *J* = 8.0 Hz, 2H), 7.90-7.72 (m, 4H), 7.61-7.49 (m, 2H), 7.43-7.32 (m, 4H), 5.42 (d, *J* = 7.0 Hz, 1H), 2.28 (m, 1H), 0.81 (d, *J* = 7.0 Hz, 6H). Elemental Analysis Calculated for C₂₄H₂₀O: C, 88.85; H 6.21. Found: C, 88.78; H, 6.15.

14-Benzyl-14H-dibenzo[a,j]xanthene (5m)

Mp 178 °C; ESI MS (*m/z*) = 373 (M+H). IR (KBr, cm⁻¹): 3061, 3019, 1617, 1587, 1511, 1488, 1451, 1397, 1241. ¹H NMR (CDCl₃, 300 MHz) δ = 3.27 (d, *J* = 4.7 Hz, 2H), 5.80 (t, *J* = 4.7 Hz, 1H), 6.12 (d, *J* = 9.0 Hz, 2H), 6.84-7.20 (m, 5H), 7.45-7.91 (m, 8H), 8.25 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ = 33.0, 41.33, 115.27, 117.39, 122.18, 124.10, 126.10, 126.68, 127.18, 128.35, 128.88, 129.76, 130.84, 131.30, 137.55, 150.11; Elemental Analysis Calculated for C₂₈H₂₀O: C, 90.33; H, 5.37; found: C, 90.27; H, 5.37

14-Propyl-14H-dibenzo[a,j]xanthene (5n)

Mp 152 °C; ESI MS (*m/z*) = 325 (M+H). IR (KBr): 3066, 2961, 2874, 1623, 1591, 1518, 1488, 1461, 1434, 1400, 1245 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ = 0.62 (t, *J* = 7.2 Hz, 3H), 1.04 (m, 2H), 2.03 (m, 2H), 5.58 (t, *J* = 4.6 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.45-7.66 (m, 4H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 7.7 Hz, 2H), 8.27 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ = 14.8, 20.20, 42.0, 43.10, 115.40, 118.60, 122.48, 123.40, 126.24, 128.3, 128.48, 128.80, 133.60, 150.3; Elemental Analysis Calculated for C₂₄H₂₀O: C, 88.85; H, 6.21; found: C, 88.90; H, 6.12.

.3-Amino-1-(4-nitrophenyl)-1H-benzo[f]chromene-2-carbonitrile (7a)

Mp 190 °C; ESI MS (*m/z*) = 344 (M+H). IR (KBr, cm⁻¹): 3429, 3331, 2190. ¹H NMR (DMSO-d₆, 300 MHz) δ = 5.56 (s, 1H), 7.16 (bs, 2H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.40-7.50

(m, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.71-8.00 (m, 2H), 7.98 (d, $J = 9.0$ Hz, 1H), 8.15 (d, $J = 8.5$ Hz, 2H); Elemental Analysis Calculated for $C_{28}H_{20}O$: C, 69.96; H, 3.82; N, 12.24. Found: C, 69.89; H, 3.71; N, 12.10.

3-Amino-1-(1H-indol-3-yl)-1H-benzo[f]chromene-2-carbonitrile (7b)

Mp 220 °C; ESI MS (m/z) = 336 (M+H). IR (KBr, cm^{-1}): 3420, 3215, 2155, 1648, 1538. 1H NMR ($CDCl_3$, 200 MHz) $\delta = 3.82$ (s, 1H), 7.01 (bs, 2H), 7.40-7.81 (m, 11H), 10.30 (s, 1H). Elemental Analysis Calculated for $C_{27}H_{17}NO_3$: C, 78.32; H, 4.48; N, 12.46. Found: C, 78.25; H, 4.34, N, 12.59.

3-Amino-1-(4-fluorophenyl)-9-methoxy-1H-benzo[f]-chromene-2-carbonitrile (7c)

Mp 238–239 °C; ESI MS (m/z) = 347 (M+H). IR (KBr, cm^{-1}): 3465, 3359, 2183, 1662, 1654, 1592, 1509, 1408, 1239, 1218, 827. 1H NMR ($CDCl_3$, 300 MHz) $\delta = 3.69$ (s, 3H), 4.52 (s, 2H), 5.12 (s, 1H), 6.85 (s, 1H), 6.96 (t, $J = 8.2$ Hz, 2H), 7.02-7.19 (m, 4H), 7.70 (t, $J = 8.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 37.8, 55.5, 58.3, 103.6, 114.5, 115.1, 115.7, 116.0, 117.3, 121.0, 126.5, 129.5, 129.6, 130.5, 132.1, 142.5, 147.7, 158.5, 159.6, 160.1, 162.9$. Elemental Analysis Calculated for $C_{21}H_{15}FN_2O_2$: C, 72.82; H, 4.37; N, 8.09. Found: C, 72.70; H, 4.40; N, 8.10;

3-Amino-1-(4-fluorophenyl)-1H-benzo[f]chromene-2- carbonitrile (7d)

Mp 237–238 °C; ESI MS (m/z) = 317 (M+H). 1H NMR ($CDCl_3$, 300 MHz) $\delta = 4.62$ (s, 2H), 5.24 (s, 1H), 6.94 (t, $J = 8.6$ Hz, 2H), 7.12-7.17 (m, 2H), 7.25 (d, $J = 6.8$ Hz, 1H), 7.40 (dd, $J = 2.8$ Hz, 2H), 7.63-7.65 (m, 1H), 7.80-7.83 (m, 2H). Elemental Analysis Calculated for $C_{20}H_{13}FN_2O$: C, 75.94; H, 4.14; N, 8.86. Found: C, 76.00; H, 4.02; N, 8.72.

3-Amino-1-(furan-2-yl)-1H-benzo[f]chromene-2-carbonitrile (7e)

Mp 225–226 °C; ESI MS (m/z) = 289 (M+H). 1H NMR ($CDCl_3$, 300 MHz) $\delta = 5.48$ (s, 1H), 6.22-6.30 (m, 2H), 7.08 (s, 2H), 7.27 (d, $J = 9.2$ Hz, 1H), 7.42-7.54 (m, 3H), 7.91 (d, $J = 8.9$ Hz, 2H), 8.03 (d, $J = 8.5$ Hz, 1H). Elemental Analysis Calculated for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72. Found: C, 75.05; H, 4.12; N, 9.60.

3-Amino-1-pentyl-1H-benzo[f]chromene-2-carbonitrile (7f)

Colourless oil. ESI MS (m/z) = 293 (M+H). 1H NMR ($CDCl_3$, 300 MHz) $\delta = 0.79$ -0.83 (t, $J = 6.1$ Hz, 3H), 1.21-1.46 (m, 6H), 7.44-7.59 (m, 2H), 1.79-1.82 (m, 2H), 4.25 (t, $J = 8.7$ Hz, 1H), 4.68 (s, 2H), 7.14 (d, $J = 9.2$ Hz, 1H), 7.71 (d, $J = 8.6$ Hz, 1H), 7.81-7.91

(m, 2H). Elemental Analysis Calculated for C₁₉H₂₀N₂O: C, 78.05; H, 6.89; N, 9.58. Found: C, 77.92; H, 6.82; N, 9.45.

3-Amino-1-phenyl-1H-benzo[f]chromene-2-carbonitrile (7g)

Mp 278–279 °C; ESI MS (m/z) = 299 (M+H). IR (KBr, cm⁻¹): 3435, 3208, 2185, 1669, 1560. ¹H NMR (DMSO-d₆, 300 MHz) δ = 5.30 (s, 1H), 7.00 (s, 1H), 7.13-7.47 (m, 8H), 7.85 (d, *J* = 4.5 Hz, 1H), 7.90-7.96 (m, 2H). Elemental Analysis Calculated for C₂₀H₁₄N₂O: C, 80.52; H, 4.73; N, 9.39. Found: C, 80.40; H, 4.60; N, 9.25.

3-Amino-1-(2-chlorophenyl)-1H-benzo[f]chromene-2-carbonitrile (7h)

Mp 265-267 °C; ESI MS (m/z) = 333 (M+H). ¹H NMR (CDCl₃, 300 MHz) δ = 4.54 (s, 2H), 5.89 (s, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 7.02-7.12 (m, 2H), 7.24-7.26 (m, 1H), 7.37-7.45 (m, 3H), 7.67 (d, *J* = 7.7 Hz, 1H); 7.78-7.82 (m, 2H). Elemental Analysis Calculated for C₂₀H₁₃ClN₂O: C, 72.18; H, 3.94; N, 8.42. Found: C, 72.10; H, 4.00; N, 8.30.

3-Amino-1-(4-methoxyphenyl)-1H-benzo[f]chromene-2-carbonitrile (7i)

Mp 194 °C; ESI MS (m/z) = 329 (M+H). ¹H NMR (CDCl₃, 300 MHz) δ = 3.72 (s, 3H), 4.60 (s, 2H), 5.19 (s, 1H), 6.78 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 10 Hz, 1H), 7.39-7.36 (m, 2H), 7.69-7.66 (m, 1H), 7.78 (d, *J* = 8.6 Hz, 2H). Elemental Analysis Calculated for C₂₁H₁₆N₂O₂: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.86; H, 4.98; N, 8.65.

3-Amino-1-p-tolyl-1H-benzo[f]chromene-2-carbonitrile (7j)

Mp 253-254 °C; ESI MS (m/z) = 313 (M+H). ¹H NMR (CDCl₃, 300 MHz) δ = 4.57 (s, 2H), 5.21 (s, 1H), 7.02-7.12 (m, 4H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.37-7.40 (m, 2H), 7.68-7.71 (m, 1H), 7.78-7.81 (m, 2H). Elemental Analysis Calculated for C₂₁H₁₆N₂O: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.84; H, 5.05; N, 9.15.

Ethyl 3-amino-1-(4-chlorophenyl)-1H-benzo[f]chromene-2-carboxylate (7k)

Mp 190–191 °C; ESI MS (m/z) = 380 (M+H). ¹H NMR (CDCl₃, 300 MHz) δ = 1.36 (t, *J* = 5.9 Hz, 3H), 4.21(q, *J* = 5.1 Hz, 2H), 6.31 (s, 2H), 5.56 (s, 1H), 7.13 (d, *J* = 7.1 Hz, 2H), 7.25-7.27 (m, 3H), 7.35-7.47 (m, 2H), 7.76 (t, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.7 Hz, 1H). Elemental Analysis Calculated for C₂₂H₁₈ClNO₃: C, 69.57; H, 4.78; N, 3.69. Found: C, 69.45; H, 4.80; N, 3.58.