Synthesis of Novel Functional Polycyclic Chromones through Michael Addition and Double Cyclizations

Yang Liu, Liping Huang, Fuchun Xie, Xuxing Chen and Youhong Hu*.

State Key Laboratory of Drug Research, Shanghi Institute of Materia Medica, Chinese Academy of Sciences, 555 Zu Chong Zhi Road, Shanghai, 201203, China

yhhu@mail.shcnc.ac.cn

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1. Experiment procedures

All reactions were performed under nitrogen atmosphere. Dry solvents were distilled prior to use: DMF was dried over microwave-dried molecular sieve; Petroleum ether refers to the fraction with boiling point in the range 60-90 °C. All $^1$H NMR and $^{13}$C NMR spectra were measured in CDCl$_3$ or $d_6$-DMSO with TMS as the internal standard. Chemical shifts are expressed in ppm and $J$ values are given in Hz. High resolution mass spectra were recorded on a Finnigan MAT 95 mass spectrometer (EI). Column chromatography was performed with 200-300 mesh silica gel using flash column techniques. Melting points was uncorrected.

General Procedure:
1.1 Tandem reaction of 3-(1-Alkynyl)chromones and 2-(2-bromophenyl)acetonitrile compounds to novel functional polycyclic chromenones 3

A typical procedure for the preparation of 3aa: To a solution of 2-(2-bromophenyl)acetonitrile 2aa (40 mg, 0.2 mmol) in dry DMF (1 mL) was added $t$-BuOK (24 mg, 0.2 mmol) at room temperature under nitrogen atmosphere. After stirring for 5 min, compound 1a (50 mg, 0.2 mmol) was added and the resulting dark red solution was irradiated for 10 min at 130 °C (monitored by TLC). The mixture was extracted with ethyl acetate (10 mL×3). The combined organic layers were washed with brine( 10 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated to give the crude product, which was further purified by column chromatography (petroleum ether/ethyl acetate 6:1) to afford compound 3aa as a white solid.

1.2 Tandem reaction of 1a with 2g to Xanthone 4b

To a solution of 1-(2-bromophenyl)propan-2-one 2g (44 mg, 0.2 mmol) in dry DMF (1 mL) was added $t$-BuOK (24 mg, 0.2 mmol) at room temperature under nitrogen atmosphere. After stirring for 5 min, compound 1a (50 mg, 0.2 mmol) was added and the resulting dark red solution was irradiated for 10 min at 130 °C (monitored by TLC). The mixture was extracted with ethyl acetate (10 mL×3). The combined
organic layers were washed with brine (10 mL), dried over anhydrous Na$_2$SO$_4$, filtered and concentrated to give the crude product, which was further purified by column chromatography (petroleum ether/ethyl acetate 10:1) to afford compound 4b as a white solid.

2. Characterization Data:

2.1 3aa-3ma

13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3aa)

As a white solid: m.p. 235-236 °C; IR (KBr) $\nu$$_{max}$ 3429, 3053, 2212, 1651, 1620, 1570, 1464, 1400, 1365, 1217, 1167, 764, 710 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 8.27 (dd, $J$ = 1.8, 7.9 Hz, 1H), 7.91 (dd, $J$ = 1.4, 7.4 Hz, 1H), 7.70-7.79 (m, 2H), 7.44-7.67 (m, 5H), 7.12-7.21 (m, 3H), 6.70-6.77 (m, 2H), 5.51 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 175.8, 166.0, 155.9, 136.2, 135.8, 134.3, 133.9, 131.2, 131.1, 128.9, 128.6, 128.3, 127.6, 126.4, 126.3, 126.1, 122.6, 118.8, 118.1, 116.1, 114.9, 55.0. HRMS [M$^+$] Calculated for C$_{25}$H$_{15}$NO$_2$ 361.1103, found 361.1106.

13-oxo-6-(4-(trifluoromethyl)phenyl)-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3ba)

As a white solid: m.p. 225-226 °C; IR (KBr) $\nu$$_{max}$ 3425, 3041, 2216, 1657, 1620, 1570, 1466, 1400, 1327, 1217, 1180, 1130, 1016, 941, 845, 766, 492 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 8.27 (dd, $J$ = 1.8, 7.8 Hz, 1H), 7.94 (dd, $J$ = 1.5, 7.7 Hz, 1H), 7.74-7.80 (m, 2H), 7.67 (td, $J$ = 1.5, 7.4 Hz, 1H), 7.53-7.62 (m, 3H), 7.51 (t, $J$ = 7.4 Hz, 1H), 7.44 (d, $J$ = 8.3 Hz, 2H), 6.88 (d, $J$ = 8.3 Hz, 2H), 5.52 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 175.6, 164.8, 155.8, 140.0, 135.4, 134.5, 133.9, 131.5, 131.1, 131.0, 130.1, 129.8, 129.1, 129.0, 126.7, 126.5, 126.3, 125.3, 125.1, 122.5, 122.4, 118.5, 118.1, 116.2, 115.0, 54.7. HRMS [M$^+$] Calculated for C$_{26}$H$_{14}$F$_3$NO$_2$ 429.0977, found 429.0973.
6-(4-methoxyphenyl)-13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3ca)

As a white solid: m.p. 244-245 °C; IR (KBr) \( \nu_{\text{max}} \) 3432, 3037, 2926, 2829, 2218, 1645, 1566, 1510, 1464, 1400, 1254, 1178, 1038, 939, 835, 768, 669, 517 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 8.26 (d, \( J = 8.0 \) Hz, 1H), 7.91 (d, \( J = 7.7 \) Hz, 1H), 7.72-7.78 (m, 2H), 7.45-7.64 (m, 5H), 7.63-7.73 (m, 4H), 5.45 (s, 1H), 3.74 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 175.8, 166.3, 158.8, 155.8, 136.5, 134.3, 133.9, 131.2, 131.0, 130.9, 128.8, 128.5, 127.6, 126.4, 126.1, 122.5, 118.9, 118.1, 115.9, 114.9, 113.6, 55.1, 54.3. HRMS [M]\(^+\) Calculated for C\(_{26}\)H\(_{17}\)NO\(_3\) 391.1208, found 391.1204.

13-oxo-6-(pyridin-2-yl)-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3da)

As a light brown solid: m.p. 215-216 °C; IR (KBr) \( \nu_{\text{max}} \) 3425, 3036, 2924, 2218, 1720, 1651, 1568, 1466, 1400, 1223, 1175, 995, 908, 770, 673 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 8.38 (d, \( J = 4.1 \) Hz, 1H), 8.25 (dd, \( J = 1.7, 8.0 \) Hz, 1H), 7.91 (d, \( J = 7.4 \) Hz, 1H), 7.66-7.77 (m, 2H), 7.34-7.56 (m, 4H), 7.43-7.52 (m, 2H), 7.11 (dd, \( J = 4.7, 7.4 \) Hz, 1H), 6.56 (d, \( J = 8.0 \) Hz, 1H), 5.59 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 176.0, 165.9, 156.1, 156.0, 149.0, 136.3, 135.4, 134.6, 134.1, 131.2, 131.1, 128.7, 126.2, 125.9, 122.6, 122.4, 121.1, 118.7, 118.2, 115.9, 114.1, 57.5. HRMS [M]\(^+\) Calculated for C\(_{24}\)H\(_{14}\)N\(_2\)O\(_2\) 362.1055, found 362.1057.

13-oxo-6-(pyrimidin-2-yl)-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3ea)

As a light yellow solid: m.p. 221-222 °C; IR (KBr) \( \nu_{\text{max}} \) 3431, 3037, 2222, 1641, 1562, 1464, 1402, 1213, 889, 770, 635 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 9.06 (s, 1H), 8.19-8.29 (m, 3H), 7.94 (dd, \( J = 1.0, 7.7 \) Hz, 1H), 7.73-7.82 (m, 2H), 7.67 (td, \( J = 1.4, 7.4 \) Hz, 1H), 7.56-7.63 (m, 3H), 7.50 (td, \( J = 1.0, 7.4 \) Hz, 1H), 5.49 (s, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 175.2, 162.6, 158.1, 155.8, 154.8, 134.7, 133.9, 133.6, 131.9, 130.8, 129.7, 129.5, 129.4, 126.6, 126.5, 122.5, 118.0, 116.4, 115.3, 51.0. HRMS [M]\(^+\) Calculated for C\(_{23}\)H\(_{13}\)N\(_3\)O\(_2\) 363.1008, found 363.1003.
13-oxo-6-(thiophen-2-yl)-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3fa)
As a white solid: m.p. 208-209 °C; IR (KBr) ν_{max} 3425, 3041, 2922, 2216, 1649, 1620, 1562, 1485, 1402, 1223, 1020, 847, 764, 717 cm^{-1}; ^1H NMR (300 MHz, CDCl₃) δ: 8.26 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 7.4 Hz, 1H), 7.85 (s, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.42-7.65 (m, 5H), 7.12 (d, J = 5.2 Hz, 1H), 6.83 (t, J = 4.3 Hz, 1H), 6.50 (s, 1H), 5.60 (s, 1H). ^13C NMR (100 MHz, CDCl₃) δ: 175.6, 155.8, 136.4, 134.4, 133.8, 131.3, 131.0, 129.0, 128.9, 126.5, 126.4, 126.1, 124.9, 122.6, 118.8, 118.1, 116.1, 115.2, 51.5. HRMS [M]^+ Calculated for C_{23}H_{13}NO_{2}S 367.0667, found 367.0662.

2-nitro-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3ga)
As a light yellow solid: m.p. 277-278 °C; IR (KBr) ν_{max} 3431, 3088, 2220, 1655, 1529, 1452, 1344, 1254, 1221, 1161, 908, 839, 746, 677 cm^{-1}; ^1H NMR (300 MHz, CDCl₃) δ: 9.13 (d, J = 2.8 Hz, 1H), 8.58 (dd, J = 2.9, 9.2 Hz, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 9.3 Hz, 1H), 7.63-7.70 (m, 2H), 7.56-7.62 (m, 1H), 7.54 (dd, J = 1.4, 7.4 Hz, 1H), 7.14-7.23 (m, 3H), 6.71-6.76 (m, 2H), 5.54 (s, 1H). ^13C NMR (100 MHz, CDCl₃) δ: 174.4, 166.0, 158.6, 145.4, 136.1, 135.2, 132.5, 131.7, 131.1, 131.0, 129.2, 128.9, 128.6, 128.5, 127.9, 126.4, 126.3, 123.1, 122.8, 120.0, 118.3, 116.5, 54.8. HRMS [M]^+ Calculated for C_{25}H_{14}N_{2}O_{4} 406.0954, found 406.0953.

2-methoxy-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3ha)
As a white solid: m.p. 267-268 °C; IR (KBr) ν_{max} 3425, 2935, 2220, 1649, 1485, 1394, 1296, 1207, 1032, 895, 825, 764, 708 cm^{-1}; ^1H NMR (300 MHz, CDCl₃) δ: 7.91 (dd, J = 1.1, 7.7 Hz, 1H), 7.74 (s, 1H), 7.59-7.65 (m, 2H), 7.56 (dd, J = 1.7, 7.3 Hz, 1H), 7.32 (dd, J = 2.9, 8.9 Hz, 1H), 7.13-7.20 (m, 3H), 6.69-6.75 (m, 2H), 5.49 (s, 1H), 3.91 (s, 3H). ^13C NMR (100 MHz, CDCl₃) δ: 175.6, 165.7, 157.5, 150.5, 136.1, 135.9, 134.1, 131.1, 131.0, 128.8, 128.5, 128.2, 127.5, 126.3, 124.2, 123.2, 119.5, 118.8, 115.3, 114.6, 56.0, 54.9. HRMS [M]^+ Calculated for C_{26}H_{17}NO_{3} 391.1208, found 391.1201.
12-methyl-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3ia)
As a white solid: m.p. 244-245 °C; IR (KBr) \( \nu_{\text{max}} \) 3431, 3057, 2929, 2214, 1647, 1556, 1466, 1389, 1338, 1223, 1138, 1065, 764, 710, 658 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 8.21 (dd, \( J = 1.4, 8.0 \) Hz, 1H), 7.67-7.77 (m, 2H), 7.48-7.57 (m, 4H), 7.44 (dd, \( J = 1.4, 7.4 \) Hz, 1H), 7.18-7.24 (m, 3H), 6.80-6.87 (m, 2H), 5.41 (s, 1H), 2.34 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 176.0, 166.9, 155.3, 148.1, 139.2, 136.4, 134.0, 131.4, 130.0, 129.5, 128.5, 128.4, 127.5, 126.3, 125.8, 123.3, 117.8, 117.6, 117.2, 114.5, 55.0, 21.8. HRMS \([M]^+\) Calculated for C\(_{26}\)H\(_{17}\)NO\(_2\) 375.1259, found 375.1254.

13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3ja)
As a light yellow solid: m.p. 173-174 °C; IR (KBr) \( \nu_{\text{max}} \) 3425, 3039, 2214, 1734, 1643, 1556, 1460, 1402, 1360, 1217, 1155, 1020, 766, 683, 635 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \): 8.22 (dd, \( J = 1.7, 8.0 \) Hz, 1H), 8.07 (s, 1H), 7.80 (d, \( J = 7.7 \) Hz, 1H), 7.69 (td, \( J = 1.7, 7.2 \) Hz, 1H), 7.38-7.54 (m, 5H), 3.79 (s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 174.9, 162.2, 155.7, 135.9, 134.1, 133.2, 131.6, 131.1, 128.9, 128.0, 127.5, 126.3, 125.9, 122.6, 119.0, 117.9, 116.2, 115.1, 38.9. HRMS \([M]^+\) Calculated for C\(_{19}\)H\(_{11}\)NO\(_2\) 285.0790, found 285.0789.

6-butyl-13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3ka)
As a white solid: m.p. 161-162 °C; IR (KBr) \( \nu_{\text{max}} \) 3431, 3049, 2955, 2862, 2216, 1637, 1616, 1554, 1466, 1400, 1227, 770 cm\(^{-1}\); \(^1\)H NMR (300 MHz, \( d_6\)-DMSO, TEMP=70 °C) \( \delta \): 8.06 (dd, \( J = 1.3, 7.8 \) Hz, 1H), 7.86 (s, 1H), 7.81 (td, \( J = 1.6, 7.8 \) Hz, 1H), 7.72 (d, \( J = 7.9 \) Hz, 1H), 7.66 (d, \( J = 8.3 \) Hz, 1H), 7.58 (t, \( J = 7.0 \) Hz, 1H), 7.46-7.54 (m, 3H), 4.20 (s, 1H), 1.51-1.79 (m, 2H), 0.98-1.35 (m, 4H), 0.75 (s, 3H). \(^{13}\)C NMR (100 MHz, \( d_6\)-DMSO) \( \delta \): 174.6, 167.3, 155.3, 137.1, 134.9, 133.9, 131.5, 131.1, 129.2, 128.2, 128.0, 126.3, 125.5, 121.6, 119.1, 118.4, 114.7, 113.3, 50.6, 28.7, 27.7, 21.5, 13.6. HRMS \([M]^+\) Calculated for C\(_{23}\)H\(_{19}\)NO\(_2\) 341.1416, found 341.1414.

6-benzyl-13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3la)
As a white solid: m.p. 179-180 °C; IR (KBr) ν\text{max} 3429, 3030, 2858, 2218, 1641, 1564, 1464, 1406, 1346, 1225, 1180, 1022, 920, 760, 702, 503 cm\(^{-1}\); \(^1\)H NMR (300 MHz, d\(_6\)-DMSO, TEMP=70 °C) δ: 8.05 (d, J = 7.8 Hz, 1H), 7.98 (s, 1H), 7.74-7.84 (m, 2H), 7.37-7.60 (m, 5H), 6.97-7.24 (m, 5H), 4.55 (s, 1H), 2.81-3.09 (m, 2H). \(^13\)C NMR (100 MHz, d\(_6\)-DMSO) δ: 174.6, 166.2, 155.2, 137.2, 136.4, 134.9, 133.9, 131.4, 131.3, 131.2, 129.5, 129.0, 128.8, 128.3, 128.1, 128.0, 126.5, 126.2, 125.4, 121.4, 119.2, 118.1, 115.3, 113.5, 52.5, 33.6. HRMS [M]\(^{+}\) Calculated for C\(_{26}\)H\(_{17}\)NO\(_2\) 375.1259, found 375.1264.

6-(tert-butyl)-13-oxo-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile(3ma)

As a white solid: m.p. 194-195 °C; IR (KBr) ν\text{max} 3431, 2964, 2868, 2210, 1649, 1620, 1564, 1465, 1402, 1221, 1157, 906, 770 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ: 8.24 (dd, J = 1.6, 8.0 Hz, 1H), 7.95 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 7.3 Hz, 1H), 7.39-7.55 (m, 4H), 7.23 (d, J = 7.8 Hz, 1H), 0.91 (s, 9H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ: 175.6, 164.9, 155.7, 134.4, 134.3, 133.8, 133.4, 131.0, 130.9, 128.8, 128.1, 126.3, 125.8, 122.1, 119.5, 118.0, 117.3, 115.7, 63.1, 40.2, 28.4. HRMS [M]\(^{+}\) Calculated for C\(_{23}\)H\(_{19}\)NO\(_2\) 341.1416, found 341.1421.

2.2 3ab-3af

As a white solid: m.p. 212-213 °C; IR (KBr) ν\text{max} 3429, 3049, 2222, 1653, 1618, 1564, 1462, 1392, 1319, 1126, 764, 710 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ: 8.27 (dd, J = 1.4, 8.0 Hz, 1H), 8.15 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H), 7.77 (td, J = 1.7, 7.2 Hz, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.18-7.24 (m, 3H), 6.70-6.76 (m, 2H), 5.59 (s, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ: 175.5, 165.6, 155.9, 135.9, 135.6, 134.8, 134.6, 131.8, 131.4, 131.1, 128.6, 128.0, 127.7, 126.6, 126.4, 126.3, 125.8, 122.6, 118.1, 116.3, 113.9, 54.8. HRMS [M]\(^{+}\) Calculated for C\(_{26}\)H\(_{14}\)F\(_3\)NO\(_2\) 429.0977, found 429.0975.
8-methoxy-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carbonitrile (3ac)

As a white solid: m.p. 229-230 °C; IR (KBr) ν\textsubscript{max} 3431, 3054, 2937, 2837, 2224, 1726, 1651, 1610, 1572, 1498, 1464, 1265, 1217, 1034, 858, 762 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ: 8.26 (dd, J = 1.7, 8.0 Hz, 1H), 7.70-7.79 (m, 2H), 7.58 (d, J = 8.5 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 2.8 Hz, 1H), 7.15-7.20 (m, 4H), 6.73-6.79 (m, 2H), 5.45 (s, 1H), 3.90 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 175.8, 166.6, 159.6, 155.9, 136.3, 134.3, 134.2, 132.3, 128.7, 128.3, 127.5, 126.5, 126.3, 126.1, 122.6, 118.8, 118.1, 117.9, 115.9, 114.8, 112.9, 55.6, 54.2. HRMS [M]\textsuperscript{+} Calculated for C\textsubscript{26}H\textsubscript{17}NO\textsubscript{3} 391.1208, found 391.1207.

Ethyl 13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carboxylate (3ad)

As a white solid: m.p. 172-173 °C; IR (KBr) ν\textsubscript{max} 3431, 2991, 2220, 1709, 1657, 1464, 1402, 1246, 1113, 1028, 905, 760, 704, 611 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ: 8.25 (dd, J = 1.7, 7.9 Hz, 1H), 7.94 (s, 1H), 7.64-7.75 (m, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.39-7.53 (m, 4H), 7.08-7.17 (m, 3H), 6.79-6.92 (m, 2H), 5.47 (s, 1H), 4.24 (q, J = 7.0 Hz, 2H), 1.26 (t, J = 7.0 Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 176.7, 166.5, 166.4, 155.9, 137.8, 136.2, 133.9, 133.3, 132.6, 130.8, 129.9, 129.5, 128.5, 127.9, 127.3, 127.0, 126.5, 126.2, 125.6, 122.8, 118.0, 116.1, 61.0, 55.2, 14.2. HRMS [M]\textsuperscript{+} Calculated for C\textsubscript{27}H\textsubscript{20}NaO\textsubscript{4} 431.1259, found 431.1265.

N-methyl-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carboxamide (3ae)

As a light yellow solid: m.p. 183-184 °C; IR (KBr) ν\textsubscript{max} 3433, 3248, 3057, 2931, 1651, 1543, 1466, 1400, 1300, 1219, 1157, 764, 702, 611 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ: 8.23 (dd, J = 1.7, 8.0 Hz, 1H), 7.66-7.74 (m, 2H), 7.55 (d, J = 8.3 Hz, 1H), 7.47-7.53 (m, 2H), 7.39-7.46 (m, 2H), 7.33 (s, 1H), 7.12-7.19 (m, 2H), 6.85-6.95 (m, 2H), 5.65 (br. s., 1H), 5.45 (s, 1H), 2.82 (d, J = 5.0 Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 176.9, 169.3, 164.5, 156.0, 138.5, 138.0, 136.7, 133.8, 132.8, 130.3, 129.9, 129.7, 128.0, 127.8, 127.2, 126.6, 126.2, 125.6, 122.8, 122.4, 118.0, 116.1, 55.1, 26.6. HRMS [M]\textsuperscript{+} Calculated for C\textsubscript{26}H\textsubscript{19}NO\textsubscript{3} 393.1365, found 393.1361.
N,N-diethyl-13-oxo-6-phenyl-6,13-dihydrobenzo[5,6]cyclohepta[1,2-b]chromene-11-carboxamide (3af)

As a white solid: m.p. 197-198 °C; IR (KBr) $\nu_{\text{max}}$ 3442, 2972, 1637, 1466, 1402, 1277, 1221, 1165, 762, 706, 600 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 8.27 (dd, $J = 1.5$, 8.0 Hz, 1H), 7.68 (td, $J = 1.7$, 7.1 Hz, 1H), 7.49-7.62 (m, 4H), 7.38-7.46 (m, 2H), 7.13-7.20 (m, 4H), 6.89-6.98 (m, 2H), 5.50 (s, 1H), 3.43 (q, $J = 7.0$ Hz, 2H), 2.51 (s, 2H), 1.17 (t, $J = 7.0$ Hz, 3H), 0.66 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 176.5, 169.8, 156.0, 138.3, 136.8, 136.2, 133.7, 132.6, 131.4, 130.0, 128.5, 128.2, 128.1, 127.2, 126.7, 126.3, 125.4, 122.7, 119.7, 118.0, 117.2, 55.5, 42.2, 38.7, 13.8, 12.6. HRMS [M]$^+$ Calculated for C$_{29}$H$_{25}$NO$_3$ 435.1834, found 435.1835.

2.3 4b

2-(2-bromophenyl)-3-methyl-4-phenyl-9H-xanthen-9-one (4b)

As a white solid: m.p. 185-186 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 8.33 (dd, $J = 1.7$, 7.9 Hz, 1H), 8.15 (s, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.63 (td, $J = 1.6$, 7.7 Hz, 1H), 7.26-7.58 (m, 9H), 7.23 (d, $J = 8.8$ Hz, 1H), 2.01 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 177.3, 156.1, 153.0, 143.0, 141.5, 137.9, 135.5, 134.5, 132.6, 131.3, 131.1, 130.3, 129.2, 128.4, 128.3, 127.6, 127.4, 126.4, 126.0, 124.0, 123.8, 121.5, 119.5, 118.2, 18.9. HRMS [M]$^+$ Calculated for C$_{26}$H$_{17}$BrO$_2$Na 463.0310, found 463.0298.

3. $^1$H NMR and $^{13}$C NMR spectra
3ba
Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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3ea
3ia

![NMR spectrum of compound 3ia](image)

[Molecular structure of compound 3ia](image)

![Integration table for compound 3ia](image)
TEMP = 70 °C

TEMP = 20 °C
3ab
4. X-ray crystal structure of 3aa and 3ka

ORTEP plot of 3aa shown with ellipsoids at the 50%

ORTEP plot of 3ka shown with ellipsoids at the 50%