# MODIFIED COUMARINS. 15. CONDENSED PSORALEN DERIVATIVES BASED ON SUBSTITUTED DIBENZO[*b,d*]PYRAN-6-ONES

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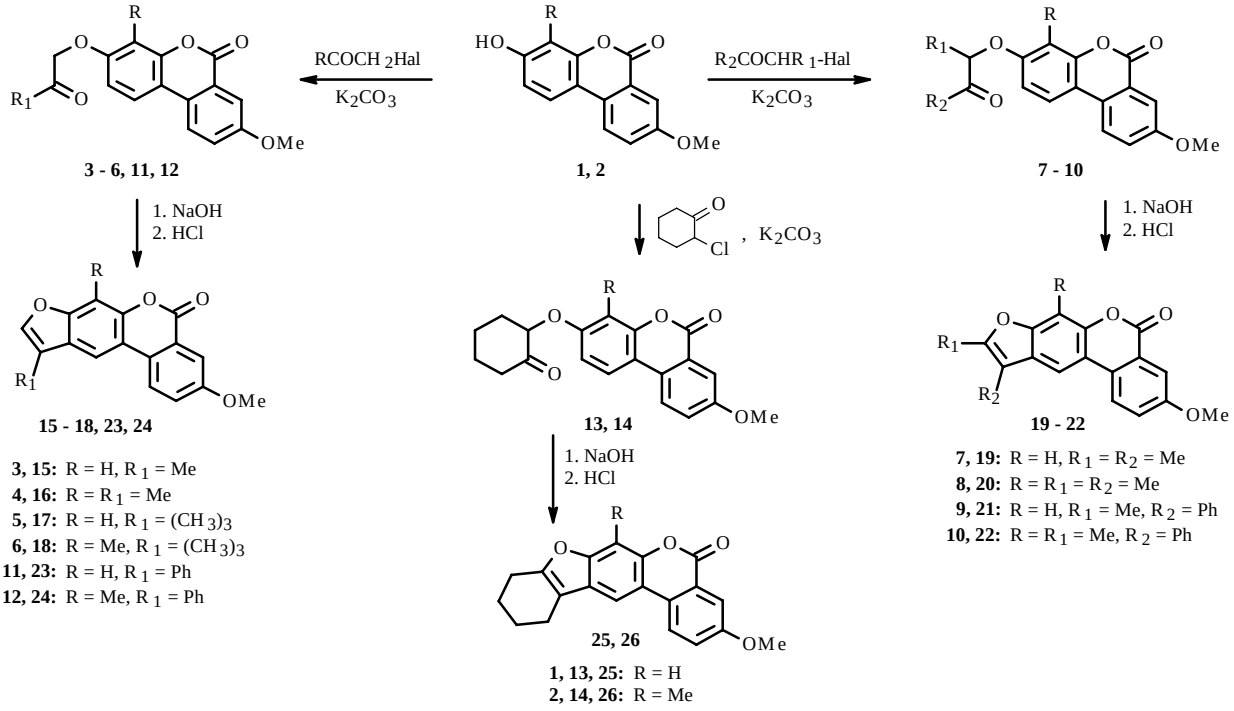
*Benzo[c]furo[3,2-g]chromen-5-ones, modified psoralen analogs containing a substituted benzene ring annelated at the 5,6-position of the furo[3,2-g]chromen-7-one system, were prepared by the MacLeod method.*

**Key words:** coumarins, furocoumarins, psoralen, dibenzo[*b,d*]puran-6-one.

Natural and synthetic dibenzo[*b,d*]pyran-6-ones are known to possess a wide spectrum of biological activity, in particular, insecticidal [1], antimicrobial [2], antiviral [3], and anti-hepatitic [4], and to act as inhibitors of aldosereductase [5], tyrosinekinase [6], and 3-phosphoglyceratekinase [7].

In continuation of the synthesis and investigation of the properties of condensed furocoumarins [8-10], we prepared new tetracyclic psoralen analogs based on 3-methoxybenzo[*c*]furo[3,2-*g*]chromen-5-one. Modification of the dibenzo[*b,d*]pyran-6-one system by adding a furan ring was expected to produce new biologically active compounds based on natural bioregulators.

Of the numerous possibilities for constructing the furocoumarins [11-14], we selected the MacLeod method for forming the psoralen system that is based on cyclization in alkaline medium of 7-(2-oxoethyl)coumarin derivatives. In most instances this led exclusively to linear furocoumarins (psoralen-type furocoumarins) since the 6-position of the coumarin ring is more strongly activated than the 8-position [15, 16].

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The starting materials for further conversions were 3-hydroxy-8-methoxybenzo[*c*]chromen-6-one (**1**) and 3-hydroxy-8-methoxy-4-methylbenzo[*c*]chromen-6-one (**2**), which were prepared by Hartley condensation [17] of 5-methoxy-2-bromobenzoic acid and resorcinol and 2-methylresorcinol, respectively, in NaOH solution using a catalyst of copper sulfate (10% solution).

The Williamson reaction of the 3-hydroxydibenzo-$\alpha$-pyrones (**1** and **2**) with $\alpha$-haloketones gave in high yields (62-88%) the corresponding substituted 8-methoxy-3-(2-oxopropoxy)benzo[*c*]chromen-6-ones **3-14**. The alkalyating agents in this synthesis were chloroacetone (**3**, **4**), 1-chloropinacolone (**5**, **6**), 3-chlorobutan-2-one (**7**, **8**), 2-bromopropiophenone (**9**, **10**), phenacylbromide (**11**, **12**), and 2-chlorocyclohexanone (**13**, **14**).

The PMR spectra of **3-14** contain signals characteristic of the corresponding alkyl substituents and benzo[*c*]chromen-6-one system. The IR spectra of ketones **3-14** have two absorption bands near 1692-1746 $cm^{-1}$ that are due to stretching vibrations of the coumarin C=O bond and the carbonyl in the alkoxyl substituent.

Heating alcoholic solutions of oxoketones **3-14** with NaOH solution (1 N) with subsequent acidolysis of the reaction mixture after the reaction was complete formed the corresponding benzo[*c*]furo[3,2-*g*]chromen-5-ones **15-26**, tetracyclic analogs of psoralen-type furocoumarins that contain an annelated benzene ring. The structures of the furocoumarins were proved using PMR spectroscopy. The PMR spectra of **15-26** exhibit a simplified splitting pattern for the aromatic protons compared with the starting ketones owing to the lack of coupling for the H-2 proton of the benzo[*c*]chromen-6-one ring. For the 7-methylbenzo[*c*]furo[3,2-*g*]chromen-5-ones, the H-11 proton is observed as a singlet near 7.92-8.46 ppm. Protons H-7 and H-11 resonate in the spectra of furocoumarins without a substituent in the 7-position as singlets at 7.39-7.74 and 8.17-8.51 pm, respectively. Furthermore, furocoumarins **15-18**, **23**, and **24**, which have no substituent at the 9-position, show a 1H singlet for H-9. This is also typical of an annelated furocoumarin ring.

## EXPERIMENTAL

The course of reactions and purity of products were monitored by TLC on Merck 60 F254 plates using $CHCl_3$:$CH_3OH$ (9:1) as eluent. Melting points were determined on a Kofler block. IR and UV spectra were measured on a Nicolet FTIR Nexus 475 spectrometer and a Specord M40 spectrophotometer, respectively. PMR spectra were recorded on a Varian Mercury 400 spectrometer at 400 MHz relative to TMS (internal standard). Elemental analyses of all compounds agreed with those calculated.

**3-Hydroxy-8-methoxybenzo[*c*]chromen-6-one (1).** A solution of 5-methoxy-2-bromobenzoic acid (11.55 g, 0.05 mol), resorcinol (11.00 g, 0.1 mol), and NaOH (4.00 g, 0.1 mol) in $H_2O$ (50 mL) was heated to 60°C and treated with copper sulfate solution (10%, 5 mL). The reaction mixture was held at 80-90°C, stirred vigorously until it thickened, and left at room temperature overnight. The resulting solid was filtered off, thoroughly washed with water, dried, and crystallized from glacial acetic acid. Yield 7.51 g (62%), mp 242°C (lit. 271-280°C [18]), $C_{14}H_{10}O_4$.

IR spectrum (KBr, $cm^{-1}$): 3345, 1694, 1633, 1620, 1495, 1460, 1321, 1295, 1278, 1173, 1034, 810. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 215 (4.43), 221 (4.46), 235 (4.39), 272 (4.11), 282 (4.21), 296 (4.07), 311 (4.03), 349 (3.75).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 3.89 (3H, s, OMe-8), 6.75 (1H, d, J = 2.0, H-4), 6.83 (1H, dd, J = 1.2, J = 8.8, H-2), 7.49 (1H, dd, J = 2.8, J = 8.8, H-9), 7.60 (1H, d, J = 2.8, H-7), 8.09 (1H, d, J = 8.8, H-1), 8.21 (1H, d, J = 8.8, H-10), 10.25 (1H, s, OH-3).

**3-Hydroxy-8-methoxy-4-methylbenzo[*c*]chromen-6-one (2)** was prepared analogously to **1** from 5-methoxy-2-bromobenzoic acid (11.55 g, 0.05 mol) and 2-methylresorcinol (12.41 g, 0.1 mol). Yield 9.35 g (73%), mp 265°C, $C_{15}H_{12}O_4$.

IR spectrum (KBr, $cm^{-1}$): 3273, 1699, 1612, 1484, 1354, 1321, 1302, 1278, 1138, 1111, 1079, 1027, 815, 778. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 225 (4.68), 235 (4.57), 278 (4.32), 284 (4.38), 298 (4.21), 310 (4.21), 349 (3.96), 364 (3.86).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.19 (3H, s, Me-4), 3.88 (3H, s, OMe-8), 6.87 (1H, d, J = 8.8, H-2), 7.45 (1H, dd, J = 2.8, J = 8.8, H-9), 7.57 (1H, d, J = 2.8, H-7), 7.89 (1H, d, J = 8.8, H-1), 8.15 (1H, d, J = 8.8, H-10), 10.07 (1H, s, OH-3).

**8-Methoxy-3-(2-oxopropoxy)benzo[*c*]chromen-6-ones (3-14).** A hot solution of hydroxycoumarin **1** or **2** (4 mmol) in absolute acetone (30 mL) was treated with freshly calcined potash (1.38 g, 10 mmol), stirred vigorously, heated (50-55°C), and treated with the appropriate α-haloketone (4.2 mmol). The reaction mixture was held for 1-3 h with heating and vigorous stirring. The course of the reaction was monitored by TLC. The reaction mixture was poured into $H_2SO_4$ solution (100 mL, 1 N). The resulting precipitate was filtered off and crystallized from propan-2-ol.

**8-Methoxy-3-(2-oxopropoxy)benzo[*c*]chromen-6-one (3).** Yield 75%, $C_{17}H_{14}O_5$, mp 174°C.

IR spectrum (KBr, $cm^{-1}$): 1724, 1699, 1624, 1612, 1489, 1353, 1319, 1298, 1275, 1164, 1150, 1059, 1035. UV spectrum ($CH_3CN$, $\lambda_{max}$, nm, log ε): 202 (4.62), 221 (4.68), 234 (4.61), 274 (4.36), 282 (4.47), 298 (4.26), 308 (4.29), 346 (3.98).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.18 (3H, s, $CH_3$-3′), 3.89 (3H, s, OMe-8), 4.96 (2H, s, $CH_2$-1′), 6.96 (1H, d, J = 2.8, H-4), 6.98 (1H, dd, J = 2.8, J = 9.2, H-2), 7.50 (1H, dd, J = 2.8, J = 8.8, H-9), 7.60 (1H, d, J = 2.8, H-7), 8.17 (1H, d, J = 9.2, H-1), 8.26 (1H, d, J = 8.8, H-10).

**8-Methoxy-4-methyl-3-(2-oxopropoxy)benzo[*c*]chromen-6-one (4).** Yield 81%, $C_{18}H_{16}O_5$, mp 158°C.

IR spectrum (KBr, $cm^{-1}$): 1718, 1700, 1614, 1484, 1350, 1313, 1288, 1222, 1125, 1063, 1026, 773. UV spectrum ($CH_3CN$, $\lambda_{max}$, nm, log ε): 202 (4.60), 226 (4.74), 234 (4.61), 277 (4.36), 284 (4.44), 297 (4.26), 308 (4.24), 348 (3.97).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.20 (3H, s, $CH_3$-3′), 2.28 (3H, s, Me-4), 3.89 (3H, s, OMe-8), 4.95 (2H, s, $CH_2$-1′), 6.91 (1H, d, J = 9.2, H-2), 7.48 (1H, dd, J = 2.8, J = 8.8, H-9), 7.60 (1H, d, J = 2.8, H-7), 8.03 (1H, d, J = 9.2, H-1), 8.26 (1H, d, J = 8.8, H-10).

**3-(3,3-Dimethyl-2-oxobutoxy)-8-methoxybenzo[*c*]chromen-6-one (5).** Yield 84%, $C_{20}H_{20}O_5$, mp 179-180°C.

IR spectrum (KBr, $cm^{-1}$): 1720, 1621, 1489, 1435, 1349, 1277, 1180, 1105, 1053, 1040, 808, 774. UV spectrum (EtOH, $\lambda_{max}$, nm, log ε): 202 (4.53), 221 (4.60), 234 (4.56), 272 (4.30), 282 (4.42), 298 (4.22), 308 (4.25), 350 (3.96).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.20 [9H, s, $(CH_3)_3$], 3.89 (3H, s, OMe-8), 5.31 (2H, s, $CH_2$-1′), 6.96 (1H, d, J = 2.8, H-4), 6.98 (1H, dd, J = 2.8, J = 9.2, H-2), 7.50 (1H, dd, J = 2.8, J = 8.8, H-9), 7.60 (1H, d, J = 2.8, H-7), 8.17 (1H, d, J = 9.2, H-1), 8.26 (1H, d, J = 8.8, H-10).

**3-(3,3-Dimethyl-2-oxobutoxy)-8-methoxy-4-methylbenzo[*c*]chromen-6-one (6).** Yield 81%, $C_{20}H_{20}O_5$, mp 194-195°C.

IR spectrum (KBr, $cm^{-1}$): 1715, 1615, 1487, 1315, 1290, 1152, 1140, 1085, 1038, 997, 808, 776. UV spectrum (EtOH, $\lambda_{max}$, nm, log ε): 228 (4.71), 277 (4.30), 285 (4.39), 298 (4.22), 310 (4.23), 346 (3.93).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.20 [9H, s, $(CH_3)_3$], 2.30 (3H, s, Me-4), 3.91 (3H, s, OMe-8), 5.31 (2H, s, $CH_2$-1′), 6.90 (1H, d, J = 9.2, H-2), 7.50 (1H, dd, J = 2.8, J = 8.8, H-9), 7.63 (1H, d, J = 2.8, H-7), 8.06 (1H, d, J = 9.2, H-1), 8.28 (1H, d, J = 8.8, H-10).

**8-Methoxy-3-(1-methyl-2-oxopropoxy)benzo[*c*]chromen-6-one (7).** Yield 73%, $C_{18}H_{16}O_5$, mp 147°C.

IR spectrum (KBr, $cm^{-1}$): 1726, 1698, 1618, 1489, 1434, 1349, 1265, 1180, 1120, 1096, 1042. UV spectrum ($CH_3CN$, $\lambda_{max}$, nm, log ε): 202 (4.62), 221 (4.69), 234 (4.62), 273 (4.36), 282 (4.48), 298 (4.26), 308 (4.30), 346 (3.99).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.47 (3H, d, J = 6.8, $CH_3$-1′), 2.21 (3H, s, $CH_3$-3′), 3.88 (3H, s, OMe-8), 5.12 (1H, q, J = 6.8, H-1′), 6.91 (1H, d, J = 2.8, H-4), 6.94 (1H, dd, J = 2.8, J = 8.8, H-2), 7.49 (1H, dd, J = 2.8, J = 8.8, H-9), 7.59 (1H, d, J = 2.8, H-7), 8.16 (1H, d, J = 8.8, H-1), 8.24 (1H, d, J = 8.8, H-10).

**8-Methoxy-4-methyl-3-(1-methyl-2-oxopropoxy)benzo[*c*]chromen-6-one (8).** Yield 79%, $C_{19}H_{18}O_5$, mp 130°C.

IR spectrum (KBr, $cm^{-1}$): 1716, 1699, 1613, 1482, 1311, 1287, 1153, 1134, 1117, 1098, 1026, 804, 774. UV spectrum ($CH_3CN$, $\lambda_{max}$, nm, log ε): 202 (4.53), 225 (4.64), 233 (4.48), 272 (4.19), 286 (4.31), 296 (4.18), 308 (4.16), 344 (3.95).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.48 (3H, d, J = 7.2, $CH_3$-1′), 2.21 (3H, s, $CH_3$-3′), 2.26 (3H, s, Me-4), 3.88 (3H, s, OMe-8), 5.07 (1H, q, J = 7.2, H-1′), 6.84 (1H, d, J = 8.4, H-2), 7.45 (1H, dd, J = 2.8, J = 8.8, H-9), 7.56 (1H, d, J = 2.8, H-7), 7.98 (1H, d, J = 8.4, H-1), 8.19 (1H, d, J = 8.8, H-10).

**8-Methoxy-3-(1-methyl-2-oxo-2-phenylethoxy)benzo[*c*]chromen-6-one (9).** Yield 85%, $C_{23}H_{18}O_5$, mp 117°C.

IR spectrum (KBr, $cm^{-1}$): 1729, 1700, 1619, 1597, 1485, 1346, 1266, 1229, 1177, 1142, 1119, 1036, 823. UV spectrum ($CH_3CN$, $\lambda_{max}$, nm, log ε): 201 (4.76), 222 (4.60), 238 (4.64), 274 (4.32), 282 (4.41), 298 (4.21), 308 (4.21), 348 (3.91).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.57 (3H, d, J = 6.8, $CH_3$-2′), 3.88 (3H, s, OMe-8), 6.21 (1H, q, J = 6.8, H-2′), 6.92 (1H, d, J = 2.8, H-4), 6.95 (1H, dd, J = 2.8, J = 8.8, H-2), 7.49 (1H, dd, J = 2.8, J = 8.8, H-9), 7.60 (3H, m, H-7, H-3″, H-5″), 7.72 (1H, m, H-4″), 8.11 (2H, d, J = 7.2, H-2″, H-6″), 8.17 (1H, d, J = 8.8, H-1), 8.23 (1H, d, J = 8.8, H-10).

**8-Methoxy-4-methyl-3-(1-methyl-2-oxo-2-phenylethoxy)benzo[*c*]chromen-6-one (10).** Yield 88%, $C_{24}H_{20}O_5$, mp 143°C.

IR spectrum (KBr, $cm^{-1}$): 1735, 1692, 1614, 1597, 1480, 1350, 1324, 1278, 1217, 1138, 1114, 1095, 1027. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 215 (4.61), 226 (4.70), 234 (4.66), 277 (4.34), 285 (4.41), 295 (4.26), 308 (4.20), 346 (3.95).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.61 (3H, d, J = 6.4, $CH_3$-2′), 2.28 (3H, s, Me-4), 3.88 (3H, s, OMe-8), 6.17 (1H, q, J = 6.4, H-2′), 6.85 (1H, d, J = 8.4, H-2), 7.45 (1H, dd, J = 2.8, J = 8.8, H-9), 7.59 (3H, m, H-7, H-3″, H-5″), 7.70 (1H, m, H-4″), 7.97 (1H, d, J = 8.4, H-1), 8.09 (2H, d, J = 7.2, H-2″, H-6″), 8.19 (1H, d, J = 8.8, H-10).

**8-Methoxy-3-(2-oxo-2-phenylethoxy)benzo[*c*]chromen-6-one (11).** Yield 76%, $C_{22}H_{16}O_5$, mp 191-192°C.

IR spectrum (KBr, $cm^{-1}$): 1718, 1702, 1618, 1486, 1439, 1287, 1235, 1175, 1120, 1065, 1037, 968, 833. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 215 (4.71), 221 (4.73), 236 (4.75), 272 (4.41), 282 (4.50), 298 (4.29), 309 (4.32), 346 (4.02).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 3.89 (3H, s, OMe-8), 5.73 (2H, s, $CH_2$-2′), 7.05 (1H, dd, J = 2.4, J = 8.8, H-2), 7.09 (1H, d, J = 2.4, H-4), 7.50 (1H, dd, J = 2.8, J = 8.8, H-9), 7.60 (3H, m, H-7, H-3″, H-5″), 7.71 (1H, m, H-4″), 8.05 (2H, d, J = 7.2, H-2″, H-6″), 8.19 (1H, d, J = 8.8, H-1), 8.27 (1H, d, J = 8.8, H-10).

**8-Methoxy-4-methyl-3-(2-oxo-2-phenylethoxy)benzo[*c*]chromen-6-one (12).** Yield 82%, $C_{23}H_{18}O_5$, mp 184-185°C.

IR spectrum (KBr, $cm^{-1}$): 1712, 1699, 1616, 1485, 1434, 1358, 1314, 1280, 1224, 1133, 1070, 763. UV spectrum ($CH_3CN$, $\lambda_{max}$, nm, log ε): 202 (4.86), 226 (4.82), 235 (4.77), 278 (4.48), 284 (4.55), 298 (4.31), 307 (4.21), 348 (3.95).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.32 (3H, s, Me-4), 3.89 (3H, s, OMe-8), 5.75 (2H, s, $CH_2$-2′), 7.02 (1H, d, J = 8.4, H-2), 7.48 (1H, dd, J = 2.8, J = 8.8, H-9), 7.60 (3H, m, H-7, H-3″, H-5″), 7.71 (1H, m, H-4″), 8.04 (3H, m, H-1, H-2″, H-6″), 8.26 (1H, m, J = 8.8, H-10).

**8-Methoxy-3-(2-oxocyclohexyloxy)benzo[*c*]chromen-6-one (13).** Yield 62%, $C_{20}H_{18}O_5$, mp 183-185°C.

IR spectrum (KBr, $cm^{-1}$): 1746, 1728, 1719, 1621, 1599, 1486, 1470, 1433, 1343, 1316, 1267, 1181, 1110, 1064, 1034, 807. UV spectrum (EtOH, $\lambda_{max}$, nm, log ε): 204 (4.25), 221 (4.32), 235 (4.24), 272 (4.00), 282 (4.10), 299 (3.94), 308 (3.96), 352 (3.66).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.68-2.65 (8H, m, $CH_2$-3′, $CH_2$-4′, $CH_2$-5′, $CH_2$-6′), 3.88 (3H, s, OMe-8), 5.10 (1H, m, H-2′), 6.91 (1H, d, J = 2.8, H-4), 6.94 (1H, dd, J = 2.8, J = 8.8, H-2), 7.49 (1H, dd, J = 2.8, J = 8.8, H-9), 7.59 (1H, d, J = 2.8, H-7), 8.16 (1H, d, J = 8.8, H-1), 8.24 (1H, d, J = 8.8, H-10).

**8-Methoxy-4-methyl-3-(2-oxocyclohexyloxy)benzo[*c*]chromen-6-one (14).** Yield 79%, $C_{21}H_{20}O_5$, mp 184-185°C.

IR spectrum (KBr, $cm^{-1}$): 1733, 1712, 1614, 1483, 1312, 1281, 1146, 1131, 1111, 1028, 798. UV spectrum (EtOH, $\lambda_{max}$, nm, log ε): 204 (4.37), 226 (4.53), 286 (4.30), 298 (4.17), 307 (4.12), 352 (3.83).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.68-2.65 (8H, m, $CH_2$-3′, $CH_2$-4′, $CH_2$-5′, $CH_2$-6′), 2.29 (3H, s, Me-4), 3.90 (3H, s, OMe-8), 5.10 (1H, m, H-2′), 6.82 (1H, d, J = 9.2, H-2), 7.42 (1H, dd, J = 2.8, J = 8.8, H-9), 7.59 (1H, d, J = 2.8, H-7), 7.88 (1H, d, J = 9.2, H-1), 8.16 (1H, d, J = 8.8, H-10).

**3-Methoxybenzo[*c*]furo[3,2-*g*]chromen-5-ones (15-26).** A solution or suspension of ketone **3-14** (2 mmol) in propan-2-ol (10 mL) was treated with NaOH solution (10 mL, 1 N). The reaction mixture was heated for 3-4 h until the starting ketone had completely dissolved (course of reaction monitored by TLC) and then poured into HCl (50 mL, 1 N). The resulting precipitate was filtered off and crystallized from propan-2-ol.

**3-Methoxy-10-methylbenzo[*c*]furo[3,2-*g*]chromen-5-one (15).** Yield 79%, $C_{17}H_{12}O_4$, mp 221-222°C.

IR spectrum (KBr, $cm^{-1}$): 1722, 1700, 1615, 1517, 1460, 1354, 1344, 1298, 1269, 1141, 1047, 1033, 827. UV spectrum ($CH_3CN$, $\lambda_{max}$, nm, log ε): 205 (4.38), 235 (4.96), 246 (4.69), 253 (4.61), 286 (4.19), 313 (4.08), 326 (4.13), 340 (4.10), 350 (4.04).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.25 (3H, s, Me-10), 3.88 (3H, s, OMe-3), 7.45 (1H, dd, J = 2.4, J = 9.2, H-2), 7.48 (1H, s, H-7), 7.52 (1H, d, J = 2.4, H-4), 7.78 (1H, s, H-9), 8.33 (1H, s, H-11), 8.35 (1H, d, J = 9.2, H-1).

**3-Methoxy-7,10-dimethylbenzo[*c*]furo[3,2-*g*]chromen-5-one (16).** Yield 73%, $C_{18}H_{14}O_4$, mp 246-247°C.

IR spectrum (KBr, $cm^{-1}$): 1716, 1614, 1515, 1455, 1438, 1345, 1291, 1137, 1094, 1036, 834. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 215 (4.49), 237 (4.84), 250 (4.80), 255 (4.75), 278 (4.31), 289 (4.26), 314 (4.14), 326 (4.20), 340 (4.17), 353 (4.08).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.29 (3H, s, Me-10), 2.49 (3H, s, Me-7), 3.92 (3H, s, OMe-3), 7.53 (1H, dd, J = 2.4, J = 8.8, H-2), 7.64 (1H, d, J = 2.4, H-4), 7.84 (1H, s, H-9), 8.35 (1H, s, H-11), 8.48 (1H, d, J = 8.8, H-1).

**10-(*t*-Butyl)-3-methoxybenzo[*c*]furo[3,2-*g*]chromen-5-one (17).** Yield 79%, $C_{20}H_{18}O_4$, mp 205-206°C.

IR spectrum (KBr, $cm^{-1}$): 1720, 1615, 1512, 1479, 1464, 1350, 1270, 1251, 1134, 1078, 1014, 840. UV spectrum ($CH_3CN$, $\lambda_{max}$, nm, log ε): 204 (4.27), 236 (4.65), 248 (4.55), 255 (4.45), 288 (3.98), 313 (3.94), 326 (4.02), 338 (3.97), 356 (3.84).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.48 [9H, s, $(CH_3)_3$], 3.93 (3H, s, OMe-3), 7.48 (1H, dd, J = 2.4, J = 9.2, H-2), 7.55 (1H, s, H-7), 7.64 (1H, d, J = 2.4, H-4), 7.67 (1H, s, H-9), 8.51 (1H, s, H-11), 8.59 (1H, d, J = 9.2, H-1).

**10-(*t*-Butyl)-3-methoxy-7-methylbenzo[*c*]furo[3,2-*g*]chromen-5-one (18).** Yield 81%, $C_{21}H_{20}O_4$, mp 206-207°C.

IR spectrum (KBr, $cm^{-1}$): 1721, 1615, 1513, 1461, 1439, 1365, 1343, 1277, 1256, 1137, 1087, 1031, 827. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 212 (4.33), 237 (4.67), 250 (4.57), 256 (4.47), 288 (4.00), 326 (4.08), 340 (4.01).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.47 [9H, s, $(CH_3)_3$], 2.49 (3H, s, Me-7), 3.92 (3H, s, OMe-3), 7.52 (1H, dd, J = 2.4, J = 8.8, H-2), 7.64 (1H, d, J = 2.4, H-4), 7.79 (1H, s, H-9), 8.43 (1H, s, H-11), 8.66 (1H, d, J = 8.8, H-1).

**3-Methoxy-9,10-dimethylbenzo[*c*]furo[3,2-*g*]chromen-5-one (19).** Yield 76%, $C_{18}H_{14}O_4$, mp 214-215°C.

IR spectrum (KBr, $cm^{-1}$): 1717, 1615, 1513, 1458, 1428, 1345, 1300, 1265, 1151, 1045, 841. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 215 (4.53), 237 (4.80), 255 (4.80), 278 (4.27), 287 (4.25), 317 (4.20), 329 (4.27), 340 (4.23), 359 (4.06).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.19 (3H, s, Me-10), 2.37 (3H, s, Me-9), 3.90 (3H, s, OMe-3), 7.47 (1H, s, H-7), 7.51 (1H, dd, J = 3.2, J = 8.4, H-2), 7.59 (1H, d, J = 3.2, H-4), 8.28 (1H, s, H-11), 8.41 (1H, d, J = 8.4, H-1).

**3-Methoxy-7,9,10-trimethylbenzo[*c*]furo[3,2-*g*]chromen-5-one (20).** Yield 82%, $C_{19}H_{16}O_4$, mp 239°C.

IR spectrum (KBr, $cm^{-1}$): 1713, 1613, 1514, 1463, 1438, 1301, 1285, 1182, 1146, 1089, 1036, 833. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 215 (4.72), 237 (4.86), 256 (4.84), 279 (4.40), 288 (4.36), 313 (4.24), 327 (4.27), 339 (4.23), 356 (4.04).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.12 (3H, s, Me-10), 2.34 (3H, s, Me-7), 2.36 (3H, s, Me-9), 3.88 (3H, s, OMe-3), 7.47 (1H, dd, J = 2.8, J = 8.8, H-2), 7.64 (1H, d, J = 2.8, H-4), 8.06 (1H, s, H-11), 8.34 (1H, d, J = 8.8, H-1).

**3-Methoxy-9-methyl-10-phenylbenzo[*c*]furo[3,2-*g*]chromen-5-one (21).** Yield 81%, $C_{23}H_{16}O_4$, mp 233-235°C.

IR spectrum (KBr, $cm^{-1}$): 1717, 1616, 1518, 1456, 1431, 1360, 1346, 1301, 1268, 1148, 1064, 1037, 834. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 215 (4.55), 237 (4.76), 255 (4.75), 287 (4.21), 316 (4.12), 329 (4.21), 340 (4.18), 353 (4.06).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.55 (3H, s, Me-9), 3.90 (3H, s, OMe-3), 7.45 (1H, m, H-4′), 7.47 (1H, dd, J = 2.4, J = 8.8, H-2), 7.59 (3H, m, H-4, H-3′, H-5′), 7.63 (2H, m, H-2′, H-6′), 7.67 (1H, s, H-7), 8.29 (1H, s, H-11), 8.42 (1H, d, J = 8.8, H-1).

**3-Methoxy-7,9-dimethyl-10-phenylbenzo[*c*]furo[3,2-*g*]chromen-5-one (22).** Yield 74%, $C_{24}H_{18}O_4$, mp 209-210°C.

IR spectrum (KBr, $cm^{-1}$): 1728, 1614, 1510, 1453, 1345, 1304, 1274, 1174, 1136, 1093, 1024, 821. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 215 (4.63), 237 (4.76), 256 (4.79), 291 (4.29), 329 (4.21), 340 (4.19), 353 (4.11).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.39 (3H, s, Me-7), 2.47 (3H, s, Me-9), 3.84 (3H, s, OMe-3), 7.36 (1H, dd, J = 2.8, J = 8.8, H-2), 7.46 (2H, m, H-4, H-4′), 7.56 (4H, m, H-2′, H-3′, H-5′, H-6′), 7.92 (1H, s, H-11), 8.18 (1H, d, J = 8.8, H-1).

**3-Methoxy-10-phenylbenzo[*c*]furo[3,2-*g*]chromen-5-one (23).** Yield 88%, $C_{22}H_{14}O_4$, mp 195°C.

IR spectrum (KBr, $cm^{-1}$): 1740, 1618, 1517, 1454, 1294, 1156, 1115, 1056, 1032, 820. UV spectrum ($CH_3CN$, $\lambda_{max}$, nm, log ε): 236 (4.69), 248 (4.57), 279 (4.15), 333 (4.03), 340 (4.04), 352 (3.95).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 3.90 (3H, s, OMe-3), 7.44 (1H, m, H-4′), 7.50 (1H, dd, J = 2.4, J = 8.8, H-2), 7.55 (2H, m, H-3′, H-5′), 7.62 (1H, d, J = 2.4, H-4), 7.74 (1H, s, H-7), 7.85 (2H, m, H-2′, H-6′), 8.45 (1H, s, H-11), 8.54 (1H, d, J = 8.8, H-1), 8.62 (1H, s, H-9).

**3-Methoxy-7-methyl-10-phenylbenzo[*c*]furo[3,2-*g*]chromen-5-one (24).** Yield 91%, $C_{23}H_{16}O_4$, mp 215-217°C.

IR spectrum (KBr, $cm^{-1}$): 1723, 1610, 1514, 1453, 1346, 1294, 1251, 1134, 1115, 1081, 1029, 820. UV spectrum (dioxane, $\lambda_{max}$, nm, log ε): 237 (4.61), 253 (4.50), 292 (4.03), 327 (4.05), 340 (4.00).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 2.53 (3H, s, Me-7), 3.91 (3H, s, OMe-3), 7.44 (1H, m, H-4′), 7.47 (1H, dd, J = 2.4, J = 8.8, H-2), 7.56 (2H, m, H-3′, H-5′), 7.60 (1H, d, J = 2.4, H-4), 7.85 (2H, m, H-2′, H-6′), 8.45 (1H, s, H-11), 8.46 (1H, s, H-9), 8.52 (1H, d, J = 8.8, H-1).

**3-Methoxy-9,10,11,12-tetrahydrobenzo[*c*]benzo[4,5]furo[3,2-*g*]chromen-5-one (25).** Yield 82%, $C_{20}H_{16}O_4$, mp 209-211°C.

IR spectrum (KBr, $cm^{-1}$): 2930, 1722, 1619, 1512, 1454, 1438, 1346, 1311, 1287, 1265, 1143, 1042, 834. UV spectrum (EtOH, $\lambda_{max}$, nm, log ε): 205 (4.29), 238 (4.52), 256 (4.53), 290 (3.95), 351 (3.89).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.85 (2H, m, $CH_2$-11), 1.94 (2H, m, $CH_2$-10), 2.65 (2H, m, $CH_2$-12), 2.73 (2H, m, $CH_2$-9), 3.90 (3H, s, OMe-3), 7.39 (1H, s, H-7), 7.45 (1H, dd, J = 3.2, J = 8.4, H-2), 7.61 (1H, d, J = 3.2, H-4), 8.17 (1H, d, H-13), 8.31 (1H, d, J = 8.4, H-1).

**3-Methoxy-7-methyl-9,10,11,12-tetrahydrobenzo[*c*]benzo[4,5]furo[3,2-*g*]chromen-5-one (26).** Yield 87%, $C_{21}H_{18}O_4$, mp 292-293°C.

IR spectrum (KBr, $cm^{-1}$): 2938, 1714, 1610, 1513, 1439, 1320, 1290, 1276, 1147, 1098, 1033, 835. UV spectrum (EtOH, $\lambda_{max}$, nm, log ε): 203 (4.37), 238 (4.48), 256 (4.51), 280 (4.02), 350 (3.84).

PMR spectrum (400 MHz, DMSO-$d_6$, δ, ppm, J/Hz): 1.80 (2H, m, $CH_2$-11), 1.94 (2H, m, $CH_2$-10), 2.50 (3H, s, Me-11), 2.62 (2H, m, $CH_2$-12), 2.75 (2H, m, $CH_2$-9), 3.92 (3H, s, OMe-3), 7.46 (1H, dd, J = 2.8, J = 8.8, H-2), 7.64 (1H, d, J = 2.8, H-4), 8.00 (1H, s, H-11), 8.31 (1H, d, J = 8.8, H-1).

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