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MODIFIED COUMARINS. 6. SYNTHESIS OF SUBSTITUTED 5,6-BENZOPSORALENS

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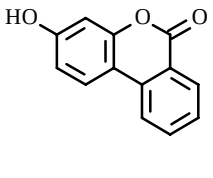
Substituted 5H-benzo[c]furo[3,2-g]chromen-5-ones, modified analogs of psoralen that contain a benzene ring annelated at the 5,6-position of a furo[3,2-g]chromen-7-one system, were synthesized from 3-hydroxy-6H-benzo[c]chromen-6-ones.

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

6H-Dibenzo[*b*,*d*]pyran-6-ones are a unique group of coumarins that have been isolated from plant and animal sources and are metabolic products of microorganisms. At present about 30 compounds have been isolated from natural sources. These are based on the 6H-benzo[*c*]chromen-6-one skeleton. Urolitin B (**1**) was isolated from latex of *Euphorbia royleana* [1] and metabolic products of the bird *Trogopterus xanthipes* [2]. Dibenzo[*b*,*d*]pyran-6-one (**2**) is one of the yellow pigments isolated from the beaver scent gland [3]. The mycotoxins alternariol **3** and its monomethyl ether **4** were obtained from the dry mycelium of the fungi *Alternaria tenuis* [4], *A. dauci* [5], and *A. cucumerina* [6]. 3,4,8,9,10-Pentahydroxydibenzo[*b*,*d*]pyran-6-one (**5**) was isolated from flowers of *Tamarix nilotica* [7], leaves of *Punica granatum* [8], and fruit of *Terminalia arborea* [9]. The 2,2-dimethylpyranocoumarin sarolactone **6** is produced by *Hypericum japonicum* [10]. Dibenzo-α-pyrones of more complicated structure **7** and **8** that contain the dihydrobenzofuran fragment were isolated from wood of *Umtiza listerana* [11]. It is assumed that 3,4-benzocoumarins are metabolites of ellagic acid (**9**), which is widely distributed in nature.



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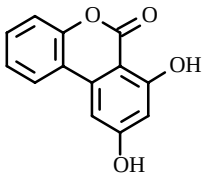

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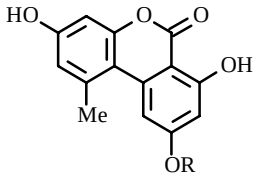
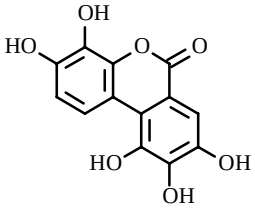


3: R = H; **4:** R = Me



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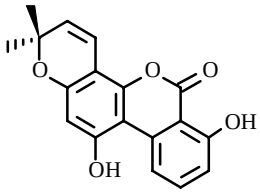

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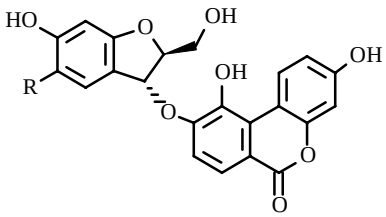
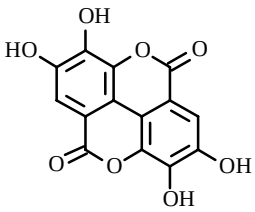


7: R = H, **8:** R = OH



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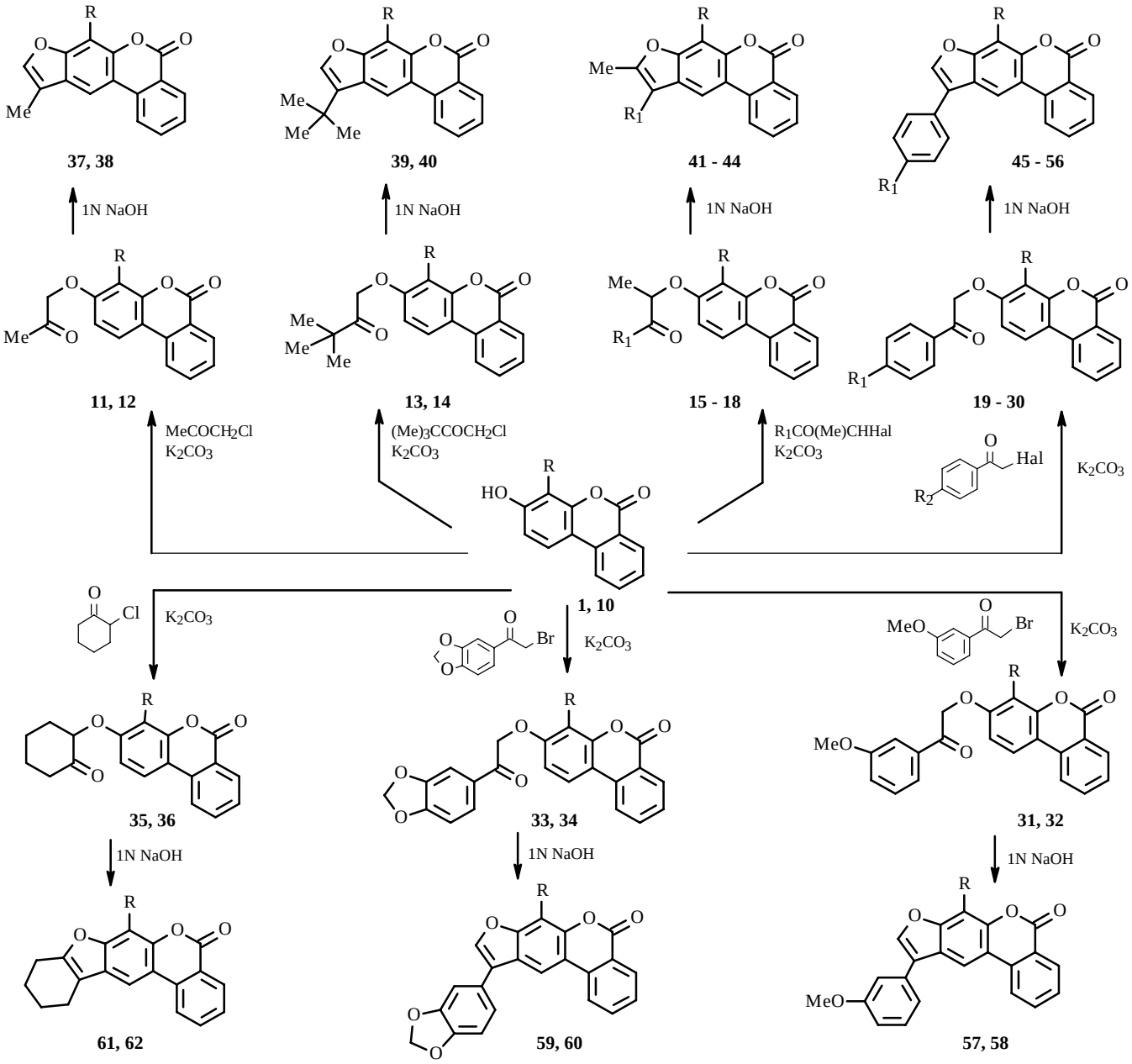

1, 11, 13, 31, 33, 35, 37, 39, 57, 59, 61: R = H; **10, 12, 14, 32, 34, 36, 38, 40, 58, 60, 62:** R = Me;
15, 41: R = H, R_1 = Me; **16, 42:** R = R_1 = Me; **17, 43:** R = H, R_1 = Ph; **18, 44:** R = Me, R_1 = Ph;
19, 45: R = R_1 = H; **20, 46:** R = Me, R_1 = H; **21, 47:** R = H, R_1 = Me; **22, 48:** R = R_1 = Me;
23, 49: R = H, R_1 = F; **24, 50:** R = Me, R_1 = F; **25, 51:** R = H, R_1 = Cl; **26, 52:** R = Me, R_1 = Cl;
27, 53: R = H, R_1 = Br; **28, 54:** R = Me, R_1 = Br; **29, 55:** R = H, R_1 = OMe; **30, 56:** R = Me, R_1 = OMe

Compounds based on the 6H-benzo[*c*]chromen-6-one skeleton are insecticidal [12], antimicrobial [13], antiviral [14], and antihepatitis agents [15]. They inhibit aldosereductase [16], tyrosinekinase [17], and 3-phosphoglyceratekinase [18]. It is also known that natural furocoumarins and their synthetic analogs exhibit various pharmacologic properties. In particular, they possess photosensitizing action [19] and can be used as antitumor agents because they inhibit pathological tissue growth [20]. Spasmolytic and coronary vasodilating [21], antibacterial [22], antihepatitis [23], anti-infection [24], and anti-HIV [25, 26] properties are also characteristic of furocoumarins.

Our goal was to modify the structures of substituted dibenzo-α-pyrones by fusing a furan ring at the 2,3-positions of the 6H-benzo[*c*]chromen-6-one system. This could possibly produce compounds with useful biological properties.

The dibenzo[*b*,*d*]pyrones that were necessary for further transformations were prepared by the Hartley method via

condensation of 2-bromobenzoic acid with polyphenols in NaOH solution using copper sulfate solution (10%) as a catalyst [27]. If resorcinol and 2-methylresorcinol were used as starting materials, the corresponding 3-hydroxy-6H-benzo[*c*]chromen-6-one (**1**) and 3-hydroxy-4-methyl-6H-benzo[*c*]chromen-6-one (**10**) were obtained. The furan ring was fused to the 6*H*-benzo[*c*]chromen-6-one ring using the MacLeod method based on cyclization in alkaline medium of 7-(2-hydroxyethyl)coumarin derivatives [28]. In this instance cyclization leads exclusively to the linear furocoumarins (psoralen-type furocoumarins) because the 6-position of the coumarin ring is more strongly activated compared with the 8-position [29].

The Williamson reaction of 3-hydroxydibenzo-α-pyrones **1** and **10** with α-haloketones in the presence of potash formed in high yields (68-95%) the corresponding substituted oxoethers **11**-**36**. Chloroacetone (**11**, **12**), 1-chloropinacolone (**13**, **14**), 3-chloro-2-butanone (**15**, **16**), 2-bromopropiophenone (**17**, **18**), phenacylbromide (**19**, **20**), 2-bromo-4′-methylacetophenone (**21**, **22**), 2-chloro-4′-fluoroacetophenone (**23**, **24**), 2,4′-dichloroacetophenone (**25**, **26**), 4-bromophenacylbromide (**27**, **28**), 4-methoxyphenacylbromide (**29**, **30**), 2-bromo-3′-methoxyacetophenone (**31**, **32**), α-bromo-3,4-methylenedioxyacetophenone (**33**, **34**), and 2-chlorocyclohexanone (**35**, **36**) were used as the alkylating agents in this reaction. The PMR spectra of the synthesized 3-(2-oxoethyl)dibenzo-α-pyrones **11**-**36** exhibit signals typical of the alkyl substituents and the 6H-benzo[*c*]chromen-6-one system.

Ketones **11**-**36** were heated with NaOH (1 N) to cyclize smoothly in high yields (76-93%) into the corresponding 5H-benzo[*c*]furo[*3,2-g*]chromen-5-ones **37**-**62**. These are synthetic analogs of psoralen-type furocoumarins that contain an annelated benzene ring. Fusion of the furan ring at the 2,3-position of the 6H-benzo[*c*]chromen-6-one was confirmed by PMR spectroscopy. The PMR spectra of **37**-**62** give a simplified splitting pattern for the aromatic protons compared with the starting ketones owing to a lack of coupling of ring proton 2 of the 6H-benzo[*c*]chromen-6-one. For 7-methyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-ones, proton H-11 is observed as a singlet at 8.10-8.46 ppm. Protons H-7 and H-11 in spectra of furocoumarins that lack a methyl group in the 7-position resonate as singlets at 7.46-7.82 and 8.20-8.59 ppm, respectively. Furthermore, for furocoumarins **37**-**40** and **45**-**60**, which are unsubstituted at the 9-position, a 1H singlet for H-9 appears. This is also a characteristic sign of the formation of the furocoumarin ring. If alkyl substituents are present in the 10-position of benzo[*c*]furo[*3,2-g*]chromen-5-ones (**37**-**40**), the singlet for H-9 is located at 7.67-7.85 ppm. The presence of aryl substituents in the 10-position (**45**-**60**) shifts the signal for H-9 to weaker field (8.39-8.76 ppm).

EXPERIMENTAL

The course of reactions and purity of compounds were monitored by TLC on Merck 60 F254 plates using $CHCl_3$—CH_3OH (9:1 and 95:5). IR and UV spectra were measured on a Nicolet FTIR Nexus 475 spectrometer and a Specord M40 spectrophotometer, respectively. PMR spectra were measured on a Varian Mercury-400 spectrometer relative to TMS internal standard. Elemental analyses of all compounds agree with those calculated.

3-Hydroxy-6H-benzo[*c*]chromen-6-one (1). A solution of 2-bromobenzoic acid (20.10 g, 0.1 mole), resorcinol (22.02 g, 0.2 mole), and NaOH (8.00 g, 0.2 mole) in H_2O (50 mL) was heated to 60°C, treated with copper sulfate solution (10 mL, 10%), held at 80-90°C until completely thickened, and left overnight at room temperature. The resulting precipitate was filtered off, washed with H_2O, dried, and crystallized from glacial acetic acid. Yield 11.24 g (53%), mp 255-256°C (lit. 230-234°C [30], 231-232°C [1], 234-236°C [31]), $C_{13}H_8O_3$. IR spectrum (KBr, cm^{-1}): 3388, 3296, 1703, 1628, 1610, 1461, 1329, 1318, 1278, 1228, 1171, 836, 758. UV spectrum (EtOH, λ_{max}, nm, log ε): 206 (4.83), 237 (4.19), 305 (3.95). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.67 (1H, d, J = 2.4, H-4), 6.85 (1H, dd, J = 2.4, J = 8.4, H-2), 7.57 (1H, t, J = 8.0, H-8), 7.89 (1H, t, J = 8.0, H-9), 8.18 (1H, d, J = 8.4, H-1), 8.19 (1H, d, J = 8.0, H-10), 8.27 (1H, d, J = 8.0, H-7), 10.38 (1H, s, OH-3).

3-Hydroxy-4-methyl-6H-benzo[*c*]chromen-6-one (10). This was prepared analogously to **2** from 2-methylresorcinol (24.83 g, 0.2 mole). Yield 14.50 g (64%), mp 268-269°C (lit. 258-260°C [30]), $C_{14}H_{10}O_3$. IR spectrum (KBr, cm^{-1}): 3274, 1694, 1616, 1573, 1480, 1469, 1406, 1339, 1318, 1127, 1108, 766. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.62), 222 (4.69), 248 (4.25), 282 (4.33), 304 (4.14), 331 (4.02). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.21 (3H, s, Me-4), 6.90 (1H, d, J = 8.4, H-2), 7.55 (1H, t, J = 8.0, H-8), 7.87 (1H, t, J = 8.0, H-9), 8.00 (1H, d, J = 8.4, H-1), 8.19 (1H, d, J = 8.0, H-10), 8.24 (1H, d, J = 8.0, H-7), 10.23 (1H, s, OH-3).

3-(2-Oxoethyl)-6H-benzo[*c*]chromen-6-ones 11-34. A hot solution of **1** or **10** (4 mmole) in absolute acetone (30 mL) was treated with freshly calcined potash (1.38 g, 10 mmole), stirred vigorously and heated (50-56°C), and treated with the

appropriate α-haloketone (4.2 mmole). The reaction mixture was held for 1-3 h with heating and vigorous stirring (course of the reaction was monitored by TLC) and poured into H_2SO_4 solution (100 mL, 1 N). The resulting precipitate was filtered off and crystallized from propan-2-ol.

3-(2-Oxopropoxy)-6H-benzo[*c*]chromen-6-one (11). Yield 78%, mp 145-146°C, $C_{16}H_{12}O_4$. IR spectrum (KBr, cm^{-1}): 1732, 1701, 1624, 1608, 1480, 1461, 1303, 1267, 1167, 1153, 1101, 764. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 209 (4.54), 216 (4.53), 227 (4.46), 234 (4.43), 266 (4.11), 277 (4.24), 304 (4.09), 326 (3.95). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.19 (3H, s, Me-3′), 4.93 (2H, s, CH_2-1′), 6.99 (1H, d, J = 2.4, H-4), 7.01 (1H, dd, J = 2.4, J = 8.8, H-2), 7.61 (1H, t, J = 8.0, H-8), 7.92 (1H, t, J = 8.0, H-9), 8.21 (1H, d, J = 8.0, H-10), 8.26 (1H, d, J = 8.8, H-1), 8.33 (1H, d, J = 8.0, H-7).

4-Methyl-3-(2-oxopropoxy)-6H-benzo[*c*]chromen-6-one (12). Yield 82%, mp 160-162°C, $C_{17}H_{14}O_4$. IR spectrum (KBr, cm^{-1}): 1720, 1699, 1625, 1607, 1469, 1427, 1408, 1351, 1313, 1289, 1239, 1166, 1133, 772. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.47), 218 (4.55), 223 (4.58), 249 (4.15), 271 (4.17), 282 (4.24), 302 (4.04), 328 (3.96). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.21 (3H, s, Me-3′), 2.29 (3H, s, Me-4), 4.98 (2H, s, CH_2-1′), 6.94 (1H, d, J = 8.4, H-2), 7.60 (1H, t, J = 8.0, H-8), 7.90 (1H, t, J = 8.0, H-9), 8.12 (1H, d, J = 8.4, H-1), 8.21 (1H, d, J = 8.0, H-10), 8.33 (1H, d, J = 8.0, H-7).

3-(3,3-Dimethyl-2-oxobutoxy)-6H-benzo[*c*]chromen-6-one (13). Yield 83%, mp 163-164°C, $C_{19}H_{18}O_4$. IR spectrum (KBr, cm^{-1}): 1723, 1623, 1481, 1458, 1360, 1281, 1179, 1101, 1054, 762. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.47), 217 (4.48), 225 (4.42), 233 (4.40), 268 (4.08), 278 (4.20), 304 (4.05), 328 (3.88). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.19 [9H, s, $(CH_3)_3$], 5.23 (2H, s, CH_2-1′), 6.98 (1H, d, J = 2.4, H-4), 7.01 (1H, dd, J = 2.4, J = 8.8, H-2), 7.61 (1H, t, J = 8.0, H-8), 7.92 (1H, t, J = 8.0, H-9), 8.21 (1H, d, J = 8.0, H-10), 8.26 (1H, d, J = 8.8, H-1), 8.33 (1H, d, J = 8.0, H-7).

3-(3,3-Dimethyl-2-oxobutoxy)-4-methyl-6H-benzo[*c*]chromen-6-one (14). Yield 79%, mp 187-188°C, $C_{20}H_{20}O_4$. IR spectrum (KBr, cm^{-1}): 1713, 1618, 1478, 1423, 1316, 1292, 1164, 1141, 1099, 1081, 995, 763. UV spectrum (EtOH, λ_{max}, nm, log ε): 210 (4.65), 221 (4.74), 251 (4.31), 282 (4.38), 305 (4.13), 331 (4.08). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.20 [9H, s, $(CH_3)_3$], 2.28 (3H, s, Me-4), 5.24 (2H, s, CH_2-1′), 6.95 (1H, d, J = 8.4, H-2), 7.61 (1H, t, J = 8.0, H-8), 7.89 (1H, t, J = 8.0, H-9), 8.12 (1H, d, J = 8.4, H-1), 8.21 (1H, d, J = 8.0, H-10), 8.33 (1H, d, J = 8.0, H-7).

3-(1-Methyl-2-oxopropoxy)-6H-benzo[*c*]chromen-6-one (15). Yield 74%, mp 117-118°C, $C_{17}H_{14}O_4$. IR spectrum (KBr, cm^{-1}): 1738, 1700, 1622, 1605, 1478, 1457, 1347, 1278, 1265, 1181, 1137, 1103, 1037, 768. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 212 (4.49), 218 (4.51), 225 (4.45), 234 (4.41), 269 (4.10), 278 (4.22), 304 (4.04), 326 (3.87). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.49 (3H, d, J = 6.8, Me-1′), 2.22 (3H, s, Me-3′), 5.16 (1H, q, H-1′), 6.95 (1H, d, J = 2.4, H-4), 6.99 (1H, dd, J = 2.4, J = 8.8, H-2), 7.61 (1H, t, J = 8.0, H-8), 7.92 (1H, t, J = 8.0, H-9), 8.21 (1H, d, J = 8.0, H-10), 8.28 (1H, d, J = 8.8, H-1), 8.34 (1H, d, J = 8.0, H-7).

4-Methyl-3-(1-methyl-2-oxopropoxy)-6H-benzo[*c*]chromen-6-one (16). Yield 79%, mp 143-144°C, $C_{18}H_{16}O_4$. IR spectrum (KBr, cm^{-1}): 1722, 1701, 1615, 1469, 1309, 1295, 1284, 1234, 1119, 771. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.56), 218 (4.63), 224 (4.65), 271 (4.20), 282 (4.27), 305 (4.02), 328 (3.96). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.50 (3H, d, J = 6.8, Me-1′), 2.22 (3H, s, Me-3′), 2.30 (3H, s, Me-4), 5.12 (1H, q, H-1′), 6.90 (1H, d, J = 8.4, H-2), 7.60 (1H, t, J = 8.0, H-8), 7.90 (1H, t, J = 8.0, H-9), 8.12 (1H, d, J = 8.4, H-1), 8.21 (1H, d, J = 8.0, H-10), 8.32 (1H, d, J = 8.0, H-7).

3-(1-Methyl-2-oxo-2-phenylethoxy)-6H-benzo[*c*]chromen-6-one (17). Yield 81%, mp 158-159°C, $C_{22}H_{16}O_4$. IR spectrum (KBr, cm^{-1}): 1738, 1702, 1670, 1619, 1605, 1594, 1480, 1459, 1344, 1309, 1271, 1176, 1102, 1064, 1035, 768. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 202 (4.58), 225 (4.37), 233 (4.38), 248 (4.22), 278 (4.12), 304 (3.95), 326 (3.81). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.59 (3H, d, J = 7.2, Me-2′), 6.24 (1H, q, H-2′), 6.94 (1H, d, J = 2.4, H-4), 6.99 (1H, dd, J = 2.4, J = 8.8, H-2), 7.60 (3H, m, H-8, H-3″, H-5″), 7.73 (1H, m, H-4″), 7.90 (1H, t, J = 8.0, H-9), 8.12 (2H, d, J = 7.2, H-2″, H-6″), 8.20 (1H, d, J = 8.0, H-10), 8.25 (1H, d, J = 8.8, H-1), 8.30 (1H, d, J = 8.0, H-7).

4-Methyl-3-(1-methyl-2-oxo-2-phenylethoxy)-6H-benzo[*c*]chromen-6-one (18). Yield 79%, mp 156-157°C, $C_{23}H_{18}O_4$. IR spectrum (KBr, cm^{-1}): 1726, 1701, 1688, 1611, 1466, 1314, 1278, 1228, 1138, 1111, 770. UV spectrum (EtOH, λ_{max}, nm, log ε): 204 (4.74), 227 (4.70), 250 (4.54), 283 (4.38), 305 (4.09), 336 (4.03). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.62 (3H, d, J = 7.2, Me-2′), 2.30 (3H, s, Me-4), 6.23 (1H, q, H-2′), 6.90 (1H, d, J = 8.4, H-2), 7.59 (3H, m, H-8, H-3″, H-5″), 7.71 (1H, m, H-4″), 7.88 (1H, t, J = 8.0, H-9), 8.12 (3H, m, H-1, H-2″, H-6″), 8.21 (1H, d, J = 8.0, H-10), 8.32 (1H, d, J = 8.0, H-7).

3-(2-Oxo-2-phenylethoxy)-6H-benzo[*c*]chromen-6-one (19). Yield 91%, mp 188-189°C, $C_{21}H_{14}O_4$. IR spectrum (KBr, cm^{-1}): 1720, 1701, 1620, 1608, 1480, 1458, 1435, 1316, 1299, 1269, 1233, 1177, 1104, 1036, 763. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.62), 234 (4.50), 247 (4.35), 268 (4.13), 278 (4.23), 304 (4.05), 326 (3.87). PMR spectrum

(400 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.76 (2H, s, CH_2-2′), 7.08 (1H, dd, J = 2.4, J = 8.8, H-2), 7.12 (1H, d, J = 2.4, H-4), 7.60 (3H, m, H-8, H-3″, H-5″), 7.72 (1H, m, H-4″), 7.92 (1H, t, J = 8.0, H-9), 8.06 (2H, d, J = 7.2, H-2″, H-6″), 8.21 (1H, d, J = 8.0, H-10), 8.28 (1H, d, J = 8.8, H-1), 8.34 (1H, d, J = 8.0, H-7),

4-Methyl-3-(2-oxo-2-phenylethoxy)-6H-benzo[*c*]chromen-6-one (20). Yield 89%, mp 192-193°C, $C_{22}H_{16}O_4$. IR spectrum (KBr, cm^{-1}): 1725, 1709, 1607, 1471, 1316, 1284, 1226, 1168, 1137, 1110, 1091, 764. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 202 (4.81), 226 (4.74), 248 (4.55), 280 (4.44), 304 (4.26), 326 (4.13). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.34 (3H, s, Me-4), 5.79 (2H, s, CH_2-2′), 7.06 (1H, d, J = 8.4, H-2), 7.60 (3H, m, H-8, H-3″, H-5″), 7.72 (1H, m, H-4″), 7.90 (1H, t, J = 8.0, H-9), 8.05 (2H, d, J = 7.2, H-2″, H-6″), 8.14 (1H, d, J = 8.4, H-1), 8.23 (1H, d, J = 8.0, H-10), 8.34 (1H, d, J = 8.0, H-7).

3-[2-(4-Methylphenyl)-2-oxoethoxy)-6H-benzo[*c*]chromen-6-one (21). Yield 87%, mp 191-192°C, $C_{22}H_{16}O_4$. IR spectrum (KBr, cm^{-1}): 1723, 1705, 1620, 1607, 1476, 1461, 1313, 1292, 1271, 1234, 1172, 1148, 1112, 1101, 1034, 762. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.74), 233 (4.52), 248 (4.42), 266 (4.37), 278 (4.38), 316 (3.95), 326 (3.98). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.41 (3H, s, Me-4″), 5.70 (2H, s, CH_2-2′), 7.07 (1H, dd, J = 2.4, J = 8.8, H-2), 7.01 (1H, d, J = 2.4, H-4), 7.40 (2H, d, J = 8.0, H-3″, H-5″), 7.61 (1H, t, J = 8.0, H-8), 7.92 (1H, t, J = 8.0, H-9), 7.96 (2H, d, J = 8.0, H-2″, H-6″), 8.21 (1H, d, J = 8.0, H-10), 8.28 (1H, d, J = 8.8, H-1), 8.34 (1H, d, J = 8.0, H-7).

4-Methyl-3-[2-(4-methylphenyl)-2-oxoethoxy]-6H-benzo[*c*]chromen-6-one (22). Yield 91%, mp 196-197°C, $C_{23}H_{18}O_4$. IR spectrum (KBr, cm^{-1}): 1725, 1704, 1607, 1470, 1434, 1316, 1285, 1233, 1166, 1138, 1091, 768. UV spectrum (dioxane, λ_{max}, nm, log ε): 213 (4.55), 250 (4.33), 283 (4.21), 305 (3.98), 327 (3.84). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.33 (3H, s, Me-4), 2.41 (3H, s, Me-4″), 5.73 (2H, s, CH_2-2′), 7.03 (1H, d, J = 8.4, H-2), 7.39 (2H, d, J = 8.0, H-3″, H-5″), 7.60 (1H, t, J = 8.0, H-8), 7.90 (1H, t, J = 8.0, H-9), 7.95 (2H, d, J = 8.0, H-2″, H-6″), 8.13 (1H, d, J = 8.8, H-1), 8.22 (1H, d, J = 8.0, H-10), 8.33 (1H, d, J = 8.0, H-7).

3-[2-(4-Fluorophenyl)-2-oxoethoxy)-6H-benzo[*c*]chromen-6-one (23). Yield 85%, mp 180-181°C, $C_{21}H_{13}FO_4$. IR spectrum (KBr, cm^{-1}): 1720, 1703, 1622, 1600, 1509, 1480, 1317, 1298, 1233, 1177, 1159, 1104, 834, 760. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 203 (4.73), 234 (4.60), 245 (4.48), 269 (4.26), 277 (4.34), 304 (4.15), 326 (3.98). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.74 (2H, s, CH_2-2′), 7.08 (1H, dd, J = 2.4, J = 8.8, H-2), 7.13 (1H, d, J = 2.4, H-4), 7.44 (2H, t, J = 8.8, H-3″, H-5″), 7.61 (1H, t, J = 8.0, H-8), 7.92 (1H, t, J = 8.0, H-9), 8.13 and 8.15 (2H, two d, J = 8.8, H-2″, H-6″), 8.21 (1H, d, J = 8.0, H-10), 8.28 (1H, d, J = 8.8, H-1), 8.34 (1H, d, J = 8.0, H-7).

3-[2-(4-Fluorophenyl)-2-oxoethoxy]-4-methyl-6H-benzo[*c*]chromen-6-one (24). Yield 89%, mp 182-183°C, $C_{22}H_{15}FO_4$. IR spectrum (KBr, cm^{-1}): 1733, 1698, 1601, 1510, 1470, 1439, 1316, 1293, 1234, 1162, 1141, 1128, 1089, 838, 770. UV spectrum (CH_3CH, λ_{max}, nm, log ε): 202 (4.68), 235 (4.55), 245 (4.44), 271 (4.16), 278 (4.31), 304 (4.13), 326 (4.01). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.32 (3H, s, Me-4), 5.75 (2H, s, CH_2-2′), 7.06 (1H, d, J = 8.4, H-2), 7.43 (2H, t, J = 8.8, H-3″, H-5″), 7.60 (1H, t, J = 8.0, H-8), 7.90 (1H, t, J = 8.0, H-9), 8.14 (3H, m, H-1, H-2″, H-6″), 8.22 (1H, d, J = 8.0, H-10), 8.33 (1H, d, J = 8.0, H-7).

3-[2-(4-Chlorophenyl)-2-oxoethoxy]-6H-benzo[*c*]chromen-6-one (25). Yield 90%, mp 186-187°C, $C_{21}H_{13}ClO_4$. IR spectrum (KBr, cm^{-1}): 1137, 1697, 1626, 1611, 1589, 1479, 1461, 1309, 1270, 1175, 1152, 1103, 1091, 1032, 983, 759. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 209 (4.61), 234 (4.47), 248 (4.40), 277 (4.31), 304 (4.08), 326 (3.90). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.74 (2H, s, CH_2-2′), 7.09 (1H, dd, J = 2.4, J = 8.8, H-2), 7.14 (1H, d, J = 2.4, H-4), 7.61 (1H, t, J = 8.0, H-8), 7.68 (2H, d, J = 8.4, H-3″, H-5″), 7.92 (1H, t, J = 8.0, H-9), 8.07 (2H, d, J = 8.4, H-2″, H-6″), 8.22 (1H, d, J = 8.0, H-10), 8.29 (1H, d, J = 8.8, H-1), 8.35 (1H, d, J = 8.0, H-7).

3-[2-(4-Chlorophenyl)-2-oxoethoxy]-4-methyl-6H-benzo[*c*]chromen-6-one (26). Yield 86%, mp 179-180°C, $C_{22}H_{15}ClO_4$. IR spectrum (KBr, cm^{-1}): 1725, 1699, 1605, 1589, 1469, 1433, 1400, 1315, 1287, 1225, 1166, 1139, 1091, 988, 768. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.73), 226 (4.65), 280 (4.37), 304 (4.15), 326 (4.08). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.32 (3H, s, Me-4), 5.76 (2H, s, CH_2-2′), 7.07 (1H, d, J = 8.4, H-2), 7.60 (1H, t, J = 8.0, H-8), 7.67 (2H, d, J = 8.4, H-3″, H-5″), 7.90 (1H, t, J = 8.0, H-9), 8.06 (2H, d, J = 8.4, H-2″, H-6″), 8.14 (1H, d, J = 8.8, H-1), 8.22 (1H, d, J = 8.0, H-10), 8.34 (1H, d, J = 8.0, H-7).

3-[2-(4-Bromophenyl)-2-oxoethoxy]-6H-benzo[*c*]chromen-6-one (27). Yield 89%, mp 190-192°C, $C_{21}H_{13}BrO_4$. IR spectrum (KBr, cm^{-1}): 1735, 1697, 1626, 1611, 1584, 1479, 1461, 1310, 1270, 1174, 1152, 1103, 1069, 981, 759. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.67), 234 (4.53), 266 (4.47), 277 (4.44), 304 (4.18), 326 (4.02). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.73 (2H, s, CH_2-2′), 7.09 (1H, dd, J = 2.4, J = 8.8, H-2), 7.14 (1H, d, J = 2.4, H-4), 7.61 (1H, t, J = 8.0, H-8), 7.82 (2H, d, J = 8.8, H-3″, H-5″), 7.92 (1H, t, J = 8.0, H-9), 7.99 (2H, d, J = 8.8, H-2″, H-6″), 8.22 (1H, d,

J = 8.0, H-10), 8.29 (1H, d, J = 8.8, H-1), 8.35 (1H, d, J = 8.0, H-7).

3-[2-(4-Bromophenyl)-2-oxoethoxy]-4-methyl-6H-benzo[*c*]chromen-6-one (28). Yield 95%, mp 195-196°C, $C_{22}H_{15}BrO_4$. IR spectrum (KBr, cm^{-1}): 1725, 1712, 1606, 1585, 1469, 1433, 1314, 1287, 1224, 1165, 1139, 1128, 1091, 1070, 987, 768. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.67), 226 (4.62), 250 (4.48), 262 (4.46), 280 (4.39), 304 (4.06), 328 (3.69). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.33 (3H, s, Me-4), 5.76 (2H, s, CH_2-2′), 7.07 (1H, d, J = 8.4, H-2), 7.60 (1H, t, J = 8.0, H-8), 7.82 (2H, d, J = 8.8, H-3″, H-5″), 7.90 (1H, t, J = 8.0, H-9), 7.98 (2H, d, J = 8.8, H-2″, H-6″), 8.14 (1H, d, J = 8.8, H-1), 8.22 (1H, d, J = 8.0, H-10), 8.34 (1H, d, J = 8.0, H-7).

3-[2-(4-Methoxyphenyl)-2-oxoethoxy]-6H-benzo[*c*]chromen-6-one (29). Yield 88%, mp 171-172°C, $C_{22}H_{16}O_5$. IR spectrum (KBr, cm^{-1}): 1726, 1699, 1674, 1618, 1606, 1458, 1288, 1279, 1247, 1173, 1101, 759. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 205 (4.58), 218 (4.65), 233 (4.47), 279 (4.56), 304 (4.25), 326 (4.01). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.87 (3H, s, OMe-4″), 5.67 (2H, s, CH_2-2′), 7.06 (1H, dd, J = 2.4, J = 8.8, H-2), 7.09 (1H, d, J = 2.4, H-4), 7.11 (2H, d, J = 8.8, H-3″, H-5″), 7.60 (1H, t, J = 8.0, H-8), 7.92 (1H, t, J = 8.0, H-9), 8.04 (2H, d, J = 8.0, H-2″, H-6″), 8.21 (1H, d, J = 8.0, H-10), 8.27 (1H, d, J = 8.8, H-1), 8.33 (1H, d, J = 8.0, H-7).

3-[2-(4-Methoxyphenyl)-2-oxoethoxy]-4-methyl-6H-benzo[*c*]chromen-6-one (30). Yield 92%, mp 189-190°C, $C_{23}H_{18}O_5$. IR spectrum (KBr, cm^{-1}): 1727, 1691, 1601, 1575, 1470, 1315, 1292, 1267, 1239, 1170, 1140, 1128, 1033, 767. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 222 (4.62), 250 (4.15), 282 (4.49), 304 (4.10), 326 (3.90). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.33 (3H, s, Me-4), 3.87 (3H, s, OMe-4″), 5.70 (2H, s, CH_2-2′), 7.02 (1H, d, J = 8.4, H-2), 7.11 (2H, d, J = 8.8, H-3″, H-5″), 7.60 (1H, t, J = 8.0, H-8), 7.90 (1H, t, J = 8.0, H-9), 8.03 (2H, d, J = 8.0, H-2″, H-6″), 8.13 (1H, d, J = 8.8, H-1), 8.22 (1H, d, J = 8.0, H-10), 8.33 (1H, d, J = 8.0, H-7).

3-[2-(3-Methoxyphenyl)-2-oxoethoxy]-6H-benzo[*c*]chromen-6-one (31). Yield 84%, mp 183-184°C, $C_{22}H_{16}O_5$. IR spectrum (KBr, cm^{-1}): 1736, 1700, 1619, 1597, 1480, 1458, 1431, 1350, 1263, 1173, 1101, 1034, 771. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.62), 234 (4.49), 249 (4.28), 267 (4.21), 278 (4.28), 304 (4.18), 322 (4.03). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.85 (3H, s, OMe-3″), 5.74 (2H, s, CH_2-2′), 7.08 (1H, dd, J = 2.4, J = 8.8, H-2), 7.12 (1H, d, J = 2.4, H-4), 7.29 (1H, dd, J = 2.4, J = 8.4, H-4″), 7.51 (1H, t, J = 8.0, H-5″), 7.55 (1H, dd, J = 2.4, J = 2.4, H-2″), 7.61 (1H, t, J = 8.0, H-8), 7.65 (1H, t, J = 8.0, H-6″), 7.92 (1H, t, J = 8.0, H-9), 8.21 (1H, d, J = 8.0, H-10), 8.27 (1H, d, J = 8.8, H-1), 8.33 (1H, d, J = 8.0, H-7).

3-[2-(3-Methoxyphenyl)-2-oxoethoxy]-4-methyl-6H-benzo[*c*]chromen-6-one (32). Yield 91%, mp 186-187°C, $C_{23}H_{18}O_5$. IR spectrum (KBr, cm^{-1}): 1735, 1707, 1610, 1467, 1426, 1316, 1292, 1268, 1168, 1127, 1037, 764. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 222 (4.77), 248 (4.33), 282 (4.26), 304 (4.11), 321 (4.00). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.33 (3H, s, Me-4), 3.85 (3H, s, OMe-3″), 5.77 (2H, s, CH_2-2′), 7.05 (1H, d, J = 8.4, H-2), 7.29 (1H, dd, J = 2.4, J = 8.4, H-4″), 7.51 (1H, t, J = 8.0, H-5″), 7.54 (1H, dd, J = 2.4, J = 2.4, H-2″), 7.60 (1H, t, J = 8.0, H-8), 7.64 (1H, t, J = 8.0, H-6″), 7.90 (1H, t, J = 8.0, H-9), 8.13 (1H, d, J = 8.8, H-1), 8.22 (1H, d, J = 8.0, H-10), 8.33 (1H, d, J = 8.0, H-7).

3-[2-(1,3-Benzodioxol-5-yl)-2-oxoethoxy]-6H-benzo[*c*]chromen-6-one (33). Yield 91%, mp 214-215°C, $C_{22}H_{14}O_6$. IR spectrum (KBr, cm^{-1}): 1716, 1689, 1623, 1606, 1504, 1480, 1457, 1431, 1300, 1269, 1174, 1111, 1033, 761. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 207 (4.70), 226 (4.71), 267 (4.32), 278 (4.46), 305 (4.40), 322 (4.29). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.65 (2H, s, CH_2-2′), 6.17 (2H, s, CH_2-2″), 7.06 (1H, dd, J = 2.4, J = 8.8, H-2), 7.10 (1H, d, J = 2.4, H-4), 7.11 (1H, d, J = 8.4, H-7″), 7.55 (1H, d, J = 2.0, H-4″), 7.61 (1H, t, J = 8.0, H-8), 7.70 (1H, dd, J = 2.0, J = 8.4, H-6″), 7.92 (1H, t, J = 8.0, H-9), 8.21 (1H, d, J = 8.0, H-10), 8.27 (1H, d, J = 8.8, H-1), 8.33 (1H, d, J = 8.0, H-7).

3-[2-(1,3-Benzodioxol-5-yl)-2-oxoethoxy]-4-methyl-6H-benzo[*c*]chromen-6-one (34). Yield 84%, mp 204-205°C, $C_{23}H_{16}O_6$. IR spectrum (KBr, cm^{-1}): 1728, 1690, 1605, 1506, 1471, 1440, 1315, 1290, 1256, 1141, 1111, 1041, 768. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 206 (4.43), 227 (4.49), 272 (4.04), 305 (3.99), 326 (3.89). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.32 (3H, s, Me-4), 5.67 (2H, s, CH_2-2′), 6.17 (2H, s, CH_2-2″), 7.03 (1H, d, J = 8.4, H-2), 7.11 (1H, d, J = 8.4, h-7″), 7.53 (1H, d, J = 2.0, H-4″), 7.60 (1H, t, J = 8.0, H-8), 7.70 (1H, dd, J = 2.0, J = 8.4, H-6″), 7.90 (1H, t, J = 8.0, H-9), 8.13 (1H, d, J = 8.8, H-1), 8.22 (1H, d, J = 8.0, H-10), 8.33 (1H, d, J = 8.0, H-7).

3-(2-Oxocyclohexyloxy)-6H-benzo[*c*]chromen-6-one (35). A solution of **1** (1.27 g, 6 mmole) in absolute DMF (20 mL) was treated with freshly calcined potash (2.07 g, 15 mmole) and 2-chlorocyclohexanone (1.14 mL, 10 mmole). The reaction mixture was vigorously stirred and heated (75-80°C) for 24 h and treated with H_2SO_4 (100 mL, 1 N). The resulting precipitate was filtered off and crystallized from propan-2-ol. Yield 68%, mp 213-214°C, $C_{19}H_{16}O_4$. IR spectrum (KBr, cm^{-1}): 1723, 1700, 1619, 1476, 1456, 1342, 1313, 1282, 1267, 1181, 1105, 1074, 770. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 212 (4.29), 217 (4.30), 226 (4.22), 234 (4.19), 246 (3.84), 269 (3.86), 278 (4.01), 294 (3.77), 304 (3.86), 328 (3.64). PMR spectrum

(400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.63-2.71 (8H, m, CH_2-3′, CH_2-4′, CH_2-5′, CH_2-6′), 5.22 (1H, m, H-2′), 6.95 (2H, m, H-2, H-4), 7.59 (1H, t, J = 8.0, H-8), 7.90 (1H, t, J = 8.0, H-9), 8.19 (1H, d, J = 8.4, H-1), 8.21 (1H, d, J = 8.0, H-10), 8.31 (1H, d, J = 8.0, H-7).

4-Methyl-3-(2-oxocyclohexyloxy)-6H-benzo[*c*]chromen-6-one (36). This was prepared analogously to **35** from **10** (1.36 g, 6 mmole) and 2-chlorocyclohexanone (1.14 mL, 10 mmole). Yield 71%, mp 198-200°C, $C_{20}H_{18}O_4$. IR spectrum (KBr, cm^{-1}): 1728, 1699, 1612, 1468, 1316, 1282, 1265, 1159, 1119, 772. UV spectrum (EtOH, λ_{max}, nm, log ε): 211 (4.41), 228 (4.49), 248 (4.60), 254 (4.58), 268 (4.25), 284 (4.13), 305 (3.91), 332 (3.99). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.63-2.71 (8H, m, CH_2-3′, CH_2-4′, CH_2-5′, CH_2-6′), 2.25 (3H, s, Me-4), 5.21 (1H, m, H-2′), 6.91 (1H, d, J = 8.4, H-2), 7.62 (1H, t, J = 8.0, H-8), 7.92 (1H, t, J = 8.0, H-9), 8.08 (1H, d, J = 8.8, H-1), 8.21 (1H, d, J = 8.0, H-10), 8.30 (1H, d, J = 8.0, H-7).

5H-Benzo[*c*]furo[*3,2-g*]chromen-5-ones 37-62. A solution or suspension of ketone **11-36** (2 mmole) in propan-2-ol (10 mL) was treated with NaOH (10 ml, 1 N). The reaction mixture was heated for 3-4 h until the starting ketone dissolved completely (course of the reaction was monitored by TLC) and poured into H_2SO_4 (50 mL, 1 N). The precipitate was filtered off and crystallized from propan-2-ol.

10-Methyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (37). Yield 81%, mp 188-189°C, $C_{16}H_{10}O_3$. IR spectrum (KBr, cm^{-1}): 1743, 1723, 1633, 1610, 1572, 1445, 1330, 1299, 1264, 1142, 1110, 1076, 768. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 232 (4.59), 241 (4.65), 283 (3.85), 326 (3.94). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.30 (3H, s, Me-10), 7.62 (1H, s, H-7), 7.64 (1H, t, J = 8.0, H-3), 7.85 (1H, s, H-9), 7.95 (1H, t, J = 8.0, H-2), 8.22 (1H, d, J = 8.0, H-1), 8.54 (1H, d, J = 8.0, H-4), 8.57 (1H, s, H-11).

7,10-Dimethyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (38). Yield 88%, mp 226-227°C, $C_{17}H_{12}O_3$. IR spectrum (KBr, cm^{-1}): 1740, 1722, 1609, 1577, 1442, 1300, 1284, 1269, 1147, 1119, 1076, 765. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 207 (4.24), 245 (4.71), 284 (3.97), 328 (3.96). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.28 (3H, s, Me-10), 2.48 (3H, s, Me-7), 7.62 (1H, t, J = 8.0, H-3), 7.84 (1H, s, H-9), 7.93 (1H, t, J = 8.0, H-2), 8.22 (1H, d, J = 8.0, H-1), 8.38 (1H, s, H-11), 8.51 (1H, d, J = 8.0, H-4).

10-(*t*-Butyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (39). Yield 86%, mp 193-194°C, $C_{19}H_{16}O_3$. IR spectrum (KBr, cm^{-1}): 1736, 1721, 1608, 1570, 1441, 1298, 1280, 1150, 1080, 769. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 233 (4.76), 241 (4.81), 283 (4.06), 326 (4.14), 342 (3.98). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.48 [9H, s, $(CH_3)_3$], 7.55 (1H, s, H-7), 7.62 (1H, t, J = 8.0, H-3), 7.67 (1H, s, H-9), 7.92 (1H, t, J = 8.0, H-2), 8.23 (1H, d, J = 8.0, H-1), 8.59 (1H, s, H-11), 8.62 (1H, d, J = 8.0, H-4).

10-(*t*-Butyl)-7-methyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (40). Yield 83%, mp 215-216°C, $C_{20}H_{18}O_3$. IR spectrum (KBr, cm^{-1}): 1734, 1608, 1460, 1419, 1345, 1297, 1272, 1258, 1117, 1077, 766. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 249 (4.74), 284 (4.02), 328 (4.02). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.47 [9H, s, $(CH_3)_3$], 2.53 (3H, s, Me-7), 7.61 (1H, t, J = 8.0, H-3), 7.69 (1H, s, H-9), 7.91 (1H, t, J = 8.0, H-2), 8.23 (1H, d, J = 8.0, H-1), 8.43 (1H, s, H-11), 8.61 (1H, d, J = 8.0, H-4).

9,10-Dimethyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (41). Yield 76%, mp 196-198°C, $C_{17}H_{12}O_3$. IR spectrum (KBr, cm^{-1}): 1740, 1721, 1639, 1608, 1572, 1449, 1296, 1260, 1153, 1109, 1082, 770. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 207 (4.21), 235 (4.58), 244 (4.71), 252 (4.63), 284 (3.87), 329 (3.95). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.23 (3H, s, Me-10), 2.40 (3H, s, Me-9), 7.56 (1H, s, H-7), 7.64 (1H, t, J = 8.0, H-3), 7.95 (1H, t, J = 8.0, H-2), 8.22 (1H, d, J = 8.0, H-1), 8.46 (1H, s, H-11), 8.55 (1H, d, J = 8.0, H-4).

7,9,10-Trimethyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (42). Yield 83%, mp 211-212°C, $C_{18}H_{14}O_3$. IR spectrum (KBr, cm^{-1}): 1746, 1720, 1639, 1609, 1577, 1502, 1438, 1299, 1273, 1165, 1124, 766. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 204 (4.46), 246 (4.63), 252 (4.60), 283 (3.99), 329 (3.92). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.14 (3H, s, me-10), 2.35 (3H, s, Me-9), 2.40 (3H, s, Me-7), 7.58 (1H, t, J = 8.0, H-3), 7.88 (1H, t, J = 8.0, H-2), 8.10 (1H, s, H-11), 8.16 (1H, d, J = 8.0, H-1), 8.40 (1H, d, J = 8.0, H-4).

9-Methyl-10-phenyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (43). Yield 86%, mp 188-189°C, $C_{22}H_{14}O_3$. IR spectrum (KBr, cm^{-1}): 1748, 1726, 1635, 1607, 1446, 1301, 1261, 1148, 1109, 1033, 766. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 231 (4.46), 244 (4.50), 254 (4.49), 284 (3.92), 328 (3.94). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.55 (3H, s, Me-9), 7.47 (1H, m, H-4′), 7.58 (2H, t, J = 8.0, H-3′, H-5′), 7.64 (3H, m, H-3, H-2′, H-6′), 7.69 (1H, s, H-7), 7.90 (1H, t, J = 8.0, H-2), 8.23 (1H, d, J = 8.0, H-1), 8.37 (1H, s, H-11), 8.48 (1H, d, J = 8.0, H-4).

7,9-Dimethyl-10-phenyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (44). Yield 88%, mp 230-231°C, $C_{23}H_{16}O_3$. IR

spectrum (KBr, cm^{-1}): 1721, 1650, 1607, 1576, 1503, 1418, 1303, 1274, 1162, 1119, 1101, 769. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 232 (4.57), 248 (4.64), 255 (4.63), 287 (4.06), 328 (4.00). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.51 (3H, m, Me-7), 2.55 (3H, s, Me-9), 7.46 (1H, m, H-4′), 7.58 (2H, t, J = 8.0, H-3′, H-5′), 7.62 (3H, m, H-3, H-2′, H-6′), 7.88 (1H, t, J = 8.0, H-2), 8.19 (1H, s, H-11), 8.22 (1H, d, J = 8.0, H-1), 8.43 (1H, d, J = 8.0, H-4).

10-Phenyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (45). Yield 90%, mp 177-178°C, $C_{21}H_{12}O_3$. IR spectrum (KBr, cm^{-1}): 1737, 1607, 1444, 1293, 1262, 1164, 1155, 1108, 1088, 1033, 763. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 231 (4.68), 244 (4.68), 286 (4.08), 326 (4.10). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.47 (1H, t, J = 8.0, H-4′), 7.56 (2H, t, J = 8.0, H-3′, H-5′), 7.68 (1H, t, J = 8.0, H-3), 7.81 (1H, s, H-7), 7.88 (2H, d, J = 7.2, H-2′, H-6′), 7.96 (1H, t, J = 8.0, H-2), 8.26 (1H, d, J = 8.0, H-1), 8.49 (1H, s, H-11), 8.67 (1H, d, J = 8.0, H-4), 8.76 (1H, s, H-9).

7-Methyl-10-phenyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (46). Yield 91%, mp 241-242°C, $C_{22}H_{14}O_3$. IR spectrum (KBr, cm^{-1}): 1723, 1607, 1577, 1450, 1316, 1294, 1277, 1252, 1119, 1082, 767. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 231 (4.66), 246 (4.71), 252 (4.67), 279 (4.21), 287 (4.16), 324 (4.10), 338 (4.00). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.48 (3H, s, Me-7), 7.44 (1H, t, J = 8.0, H-4′), 7.55 (2H, t, J = 8.0, H-3′, H-5′), 7.61 (1H, t, J = 8.0, H-3), 7.83 (2H, d, J = 7.2, H-2′, H-6′), 7.88 (1H, t, J = 8.0, H-2), 8.18 (1H, d, J = 8.0, H-1), 8.43 (1H, s, H-11), 8.46 (1H, s, H-9), 8.51 (1H, d, J = 8.0, H-4).

10-(4-Methylphenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (47). Yield 81%, mp 209-210°C, $C_{22}H_{14}O_3$. IR spectrum (KBr, cm^{-1}): 1736, 1631, 1608, 1444, 1293, 1262, 1153, 1109, 1077, 1033, 865, 808, 764. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 231 (4.66), 244 (4.62), 324 (4.01). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.40 (3H, s, Me-4′), 7.36 (2H, d, J = 8.0, H-3′, H-5′), 7.66 (1H, t, J = 8.0, H-3), 7.75 (2H, d, J = 8.0, H-2′, H-6′), 7.78 (1H, s, H-7), 7.95 (1H, t, J = 8.0, H-2), 8.25 (1H, d, J = 8.0, H-1), 8.42 (1H, s, H-11), 8.63 (1H, d, J = 8.0, H-4), 8.71 (1H, s, H-9).

7-Methyl-10-(4-methylphenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (48). Yield 84%, mp 236-237°C, $C_{23}H_{16}O_3$. IR spectrum (KBr, cm^{-1}): 1724, 1606, 1576, 1313, 1294, 1275, 1251, 1117, 1080, 1041, 770. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 232 (4.68), 247 (4.70), 290 (4.12), 324 (4.06). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.40 (3H, s, Me-4′), 2.50 (3H, s, Me-7), 7.35 (2H, d, J = 8.0, H-3′, H-5′), 7.61 (1H, t, J = 8.0, H-3), 7.71 (2H, d, J = 8.0, H-2′, H-6′), 7.89 (1H, t, J = 8.0, H-2), 8.19 (1H, d, J = 8.0, H-1), 8.38 (1H, s, H-11), 8.46 (1H, s, H-9), 8.52 (1H, d, J = 8.0, H-4).

10-(4-Fluorophenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (49). Yield 92%, mp 248-249°C, $C_{21}H_{11}FO_3$. IR spectrum (KBr, cm^{-1}): 1734, 1608, 1573, 1509, 1446, 1305, 1292, 1264, 1227, 1159, 1117, 1090, 764. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 232 (4.73), 244 (4.74), 277 (4.22), 326 (4.19), 340 (4.09). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.37 (2H, m, H-3′, H-5′), 7.65 (1H, t, J = 8.0, H-3), 7.75 (1H, s, H-7), 7.89 (2H, m, H-2′, H-6′), 7.94 (1H, t, J = 8.0, H-2), 8.23 (1H, d, J = 8.0, H-1), 8.44 (1H, s, H-11), 8.61 (1H, d, J = 8.0, H-4), 8.68 (1H, s, H-9).

7-Methyl-10-(4-fluorophenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (50). Yield 87%, mp 237-238°C, $C_{22}H_{13}FO_3$. IR spectrum (KBr, cm^{-1}): 1735, 1608, 1574, 1508, 1305, 1292, 1276, 1253, 1219, 1124, 1112, 1041, 764. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 232 (4.56), 246 (4.61), 278 (4.06), 326 (3.93). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.45 (3H, s, Me-7), 7.35 (2H, m, H-3′, H-5′), 7.58 (1H, t, J = 8.0, H-3), 7.71 (2H, d, J = 8.0, H-2′, H-6′), 7.89 (3H, m, H-2, H-2′, H-6′), 8.14 (1H, d, J = 8.0, H-1), 8.38 (1H, s, H-11), 8.39 (1H, s, H-9), 8.47 (1H, d, J = 8.0, H-4).

10-(4-Chlorophenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (51). Yield 86%, mp 303-304°C, $C_{21}H_{11}ClO_3$). IR spectrum (KBr, cm^{-1}): 1735, 1632, 1608, 1445, 1303, 1291, 1267, 1156, 1109, 1094, 867, 815, 764. UV spectrum (dioxane, λ_{max}, nm, log ε): 215 (4.42), 233 (4.58), 245 (4.63), 251 (4.60), 289 (4.08), 326 (4.04). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.59 (2H, d, J = 8.4, H-3′, H-5′), 7.67 (1H, t, J = 8.0, H-3), 7.78 (1H, s, H-7), 7.90 (2H, d, J = 8.4, H-2′, H-6′), 7.96 (1H, t, J = 8.0, H-2), 8.25 (1H, d, J = 8.0, H-1), 8.49 (1H, s, H-11), 8.64 (1H, d, J = 8.0, H-4), 8.72 (1H, s, H-9).

7-Methyl-10-(4-chlorophenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (52). Yield 89%, mp 249-250°C, $C_{22}H_{13}ClO_3$. IR spectrum (KBr, cm^{-1}): 1725, 1606, 1577, 1488, 1306, 1288, 1273, 1252, 1115, 1094, 1080, 1039, 811, 771. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 210 (4.32), 231 (4.34), 247 (4.36), 278 (4.04), 321 (3.94). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.42 (3H, s, Me-7), 7.54 (2H, d, J = 8.4, H-3′, H-5′), 7.56 (1H, t, J = 8.0, H-3), 7.79 (2H, d, J = 8.4, H-2′, H-6′), 7.83 (1H, t, J = 8.0, H-2), 8.12 (1H, d, J = 8.0, H-1), 8.35 (1H, s, H-11), 8.42 (1H, s, H-9), 8.44 (1H, d, J = 8.0, H-4).

10-(4-Bromophenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (53). Yield 87%, mp 299-300°C, $C_{21}H_{11}BrO_3$. IR spectrum (KBr, cm^{-1}): 1735, 1631, 1607, 1575, 1444, 1303, 1290, 1266, 1155, 1110, 1088, 1033, 867, 812, 764. UV spectrum (dioxane, λ_{max}, nm, log ε): 215 (4.48), 231 (4.61), 245 (4.66), 252 (4.63), 288 (4.17), 326 (4.09). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.67 (1H, t, J = 8.0, H-3), 7.73 (2H, d, J = 8.8, H-3′, H-5′), 7.79 (1H, s, H-7), 7.83 (2H, d, J = 8.8, H-2′, H-6′), 7.96 (1H, t, J = 8.0, H-2), 8.25 (1H, d, J = 8.0, H-1), 8.52 (1H, s, H-11), 8.65 (1H, d, J = 8.0, H-4), 8.72 (1H, s, H-9).

7-Methyl-10-(4-bromophenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (54). Yield 93%, mp 280-282°C, $C_{22}H_{13}BrO_3$. IR spectrum (KBr, cm^{-1}): 1723, 1606, 1576, 1305, 1288, 1273, 1251, 1115, 1076, 1038, 811, 771. UV spectrum (dioxane, λ_{max}, nm, log ε): 215 (4.30), 245 (4.52), 254 (4.50), 290 (4.01), 321 (3.86). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.46 (3H, s, Me-7), 7.59 (1H, t, J = 8.0, H-3), 7.69 (2H, d, J = 8.8, H-3′, H-5′), 7.76 (2H, d, J = 8.8, H-2′, H-6′), 7.86 (1H, t, J = 8.0, H-2), 8.15 (1H, d, J = 8.0, H-1), 8.41 (1H, s, H-11), 8.45 (1H, s, H-9), 8.49 (1H, d, J = 8.0, H-4).

10-(4-Methoxyphenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (55). Yield 88%, mp 175-176°C, $C_{22}H_{14}O_4$. IR spectrum (KBr, cm^{-1}): 1722, 1631, 1608, 1582, 1508, 1443, 1297, 1251, 1177, 1158, 1118, 1095, 1035, 865, 834, 767. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 207 (4.52), 238 (4.64), 250 (4.62), 292 (4.07), 323 (4.07). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.85 (3H, s, OMe-4′), 7.12 (2H, d, J = 8.8, H-3′, H-5′), 7.67 (1H, t, J = 8.0, H-3), 7.79 (1H, s, H-7), 7.80 (2H, d, J = 8.8, H-2′, H-6′), 7.96 (1H, t, J = 8.0, H-2), 8.26 (1H, d, J = 8.0, H-1), 8.39 (1H, s, H-11), 8.64 (1H, d, J = 8.0, H-4), 8.72 (1H, s, H-9).

7-Methyl-10-(4-methoxyphenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (56). Yield 85%, mp 222-223°C, $C_{23}H_{16}O_4$. IR spectrum (KBr, cm^{-1}): 1733, 1608, 1567, 1510, 1444, 1312, 1297, 1278, 1250, 1181, 1127, 1026, 805, 769. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 232 (4.66), 245 (4.66), 291 (4.12), 322 (4.03). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.45 (3H, s, Me-7), 3.84 (3H, s, OMe-4′), 7.08 (2H, d, J = 8.8, H-3′, H-5′), 7.60 (1H, t, J = 8.0, H-3), 7.72 (2H, d, J = 8.8, H-2′, H-6′), 7.86 (1H, t, J = 8.0, H-2), 8.16 (1H, d, J = 8.0, H-1), 8.30 (1H, s, H-11), 8.37 (1H, s, H-9), 8.45 (1H, d, J = 8.0, H-4).

10-(3-Methoxyphenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (57). Yield 83%, mp 181-182°C, $C_{22}H_{14}O_4$. IR spectrum (KBr, cm^{-1}): 1733, 1610, 1588, 1446, 1342, 1302, 1266, 1227, 1152, 1114, 1080, 1033, 839, 764. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 217 (4.48), 231 (4.52), 242 (4.49), 288 (3.94), 324 (3.92). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.88 (3H, s, OMe-3′), 7.03 (1H, dd, J = 2.4, J = 6.8, H-4′), 7.35 (1H, dd, J = 2.4, J = 2.4, H-2′), 7.48 (2H, m, H-5′, H-6′), 7.68 (1H, t, J = 8.0, H-3), 7.82 (1H, s, H-7), 7.96 (1H, t, J = 8.0, H-2), 8.26 (1H, d, J = 8.0, H-1), 8.50 (1H, s, H-11), 8.65 (1H, d, J = 8.0, H-4), 8.75 (1H, s, H-9).

7-Methyl-10-(3-methoxyphenyl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (58). Yield 89%, mp 211-212°C, $C_{23}H_{16}O_4$. IR spectrum (KBr, cm^{-1}): 1727, 1609, 1589, 1578, 1446, 1303, 1278, 1238, 1209, 1122, 1023, 836, 767. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 218 (4.53), 231 (4.57), 244 (4.58), 288 (4.07), 322 (3.98). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.52 (3H, s, Me-7), 3.88 (3H, s, OMe-3′), 7.02 (1H, dd, J = 2.4, J = 6.8, H-4′), 7.31 (1H, dd, J = 2.4, J = 2.4, H-2′), 7.42 (1H, dd, J = 8.0, J = 2.4, H-6′), 7.47 (1H, t, J = 8.0, H-5′), 7.63 (1H, t, J = 8.0, H-3), 7.91 (1H, t, J = 8.0, H-2), 8.21 (1H, d, J = 8.0, H-1), 8.46 (1H, s, H-11), 8.51 (1H, s, H-9), 8.55 (1H, d, J = 8.0, H-4).

10-(1,3-Benzodioxol-5-yl)-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (59). Yield 92%, mp 215-216°C, $C_{22}H_{12}O_5$. IR spectrum (KBr, cm^{-1}): 1734, 1606, 1503, 1485, 1443, 1294, 1264, 1229, 1168, 1142, 1110, 1096, 1035, 862, 770. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 223 (4.59), 231 (4.60), 240 (4.58), 257 (4.46), 311 (4.12), 328 (4.07). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 6.09 (2H, s, CH_2-2′), 7.08 (1H, d, J = 7.2, H-7′), 7.37 (1H, dd, J = 2.0, J = 7.2, H-6′), 7.40 (1H, d, J = 2.0, H-′4′), 7.66 (1H, t, J = 8.0, H-3), 7.77 (1H, s, H-7), 7.95 (1H, t, J = 8.0, H-2), 8.25 (1H, d, J = 8.0, H-1), 8.38 (1H, s, H-11), 8.65 (1H, d, J = 8.0, H-4), 8.69 (1H, s, H-9).

10-(1,3-Benzodioxol-5-yl)-7-methyl-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (60). Yield 87%, mp 223-224°C, $C_{23}H_{14}O_5$. IR spectrum (KBr, cm^{-1}): 1726, 1607, 1504, 1487, 1454, 1288, 1270, 1237, 1123, 1100, 1035, 929, 770. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 225 (4.55), 233 (4.56), 243 (4.57), 257 (4.48), 326 (4.02). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.54 (3H, s, Me-7), 6.11 (2H, s, CH_2-2′), 7.08 (1H, d, J = 7.2, H-7′), 7.35 (1H, dd, J = 2.0, J = 7.2, H-6′), 7.39 (1H, d, J = 2.0, H-4′), 7.64 (1H, t, J = 8.0, H-3), 7.93 (1H, t, J = 8.0, H-2), 8.24 (1H, d, J = 8.0, H-1), 8.38 (1H, s, H-11), 8.51 (1H, s, H-9), 8.60 (1H, d, J = 8.0, H-4).

9,10,11,12-Tetrahydro-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (61). Yield 81%, mp 204-205°C, $C_{19}H_{14}O_3$. IR spectrum (KBr, cm^{-1}): 2929, 1725, 1609, 1445, 1311, 1284, 1265, 1142, 1115, 1033, 766. UV spectrum (EtOH, λ_{max}, nm, log ε): 209 (4.47), 246 (4.85), 253 (4.83), 285 (4.15), 331 (4.18). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.79 (2H, m, CH_2-11), 1.87 (2H, m, CH_2-10), 2.61 (2H, m, CH_2-12), 2.68 (2H, m, CH_2-9), 7.46 (1H, s, H-7), 7.60 (1H, t, J = 8.0, H-3), 7.90 (1H, t, J = 8.0, H-2), 8.18 (1H, d, J = 8.0, H-1), 8.29 (1H, s, H-11), 8.41 (1H, d, J = 8.0, H-4).

7-Methyl-9,10,11,12-tetrahydro-5H-benzo[*c*]furo[*3,2-g*]chromen-5-one (62). Yield 86%, mp 229-230°C, $C_{20}H_{16}O_3$. IR spectrum (KBr, cm^{-1}): 2932, 1727, 1612, 1503, 1455, 1438, 1318, 1284, 1269, 1159, 1117, 1101, 773. UV spectrum (CH_3CN, λ_{max}, nm, log ε): 209 (4.49), 227 (4.59), 246 (4.76), 254 (4.75), 267 (4.40), 283 (4.21), 329 (4.16). PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.81 (2H, m, CH_2-11), 1.89 (2H, m, CH_2-10), 2.43 (3H, s, Me-7), 2.62 (2H, m, CH_2-12), 2.71 (2H, m, CH_2-9), 7.59 (1H, t, J = 8.0, H-3), 7.88 (1H, t, J = 8.0, H-2), 8.15 (1H, s, H-11), 8.20 (1H, d, J = 8.0, H-1), 8.41 (1H, d, J = 8.0, H-4).

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