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MODIFIED COUMARINS.
3. PSORALEN AND ALLOPSORALEN ANALOGS

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1,2,3,4-Tetrahydro-5H-benzo[c]furo[3,2-g]chromen-5-ones and 8,9,10,11-tetrahydro-7H-benzo[c]furo[2,3-f]chromen-7-ones, analogs of psoralen and allopsoralen, were synthesized from 1-hydroxy- and 3-hydroxy-7,8,9,10-tetrahydro-6H-benzo[c]chromen-6-ones.

Key words: coumarins, furocoumarins, psoralen, allopsoralen, 7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one.

Furocoumarins are an important class of natural compounds and are mainly derivatives of the linear furocoumarin psoralen (7H-furo[3,2-*g*]chromen-7-one) or its angular isomer angelicin (2H-furo[2,3-*h*]chromen-2-one). Derivatives of the angular furocoumarin allopsoralen (7H-furo[2,3-*f*]chromen-7-one) are rarer in nature. Allopsoralen was isolated from seeds of *Psoralea corylifolia* [1] and the aerial parts of *Psoralea plicata* [2].

Natural furocoumarins and their synthetic analogs exhibit a variety of pharmacologic properties. In particular, they increase the sensitivity of the organism to sunlight, i.e., they possess photosensitizing activity. Furocoumarins are used to treat vitiligo (leucodermia), alopecia areata, and other skin diseases [3]. 8-Substituted furocoumarins are used as antitumor agents because they inhibit pathological tissue growth [4]. Derivatives of psoralen and angelicin typically have spasmolytic and coronary vasodilating properties. They have a papaverine-like mechanism of action on smooth muscle of internal organs and cardiovascular tissues [5].

Compounds based on the 7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one skeleton are known to act as insecticides [6, 7], antireserpine agents, CNS depressants, anticonvulsants, analgetics, antipyretics, and anti-inflammatory agents [8, 9].

Thus, the goal of our research is to modify the structure of 7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one by fusing a furan ring to it. The starting 3-hydroxy- (**1**), 3-hydroxy-4-methyl- (**2**), and 1-hydroxy-3-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (**3**) were prepared by Pechmann condensation of 2-carbethoxycyclohexanone with resorcinol, 2-methylresorcinol, and orcinol, respectively, in the presence of conc. H_2SO_4 at 0°C [10].

The furan ring was fused to the 7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one system using the method of MacLeod that is based on cyclization in alkaline medium of 7-(2-oxopropoxy)coumarin derivatives [11].

The Williamson reaction of **1**-**3** with α-halogenketones forms the corresponding substituted oxoethers **4**-**39**. The reactions included α-bromoacetone (**4**, **5**, and **28**), 3-chloro-2-butanone (**6**, **7**, and **29**), α-bromopropiophenone (**8**, **9**, and **30**), α-bromoacetophenone (**10**, **11**, and **31**), α-chloro-4-fluoroacetophenone (**12**, **13**, and **32**), α-bromo-4-chloroacetophenone (**14**, **15**, and **33**), 4-bromophenacylbromide (**16**, **17**, and **34**), 4-methylphenacylbromide (**18**, **19**, and **35**), 4-methoxyphenacylbromide (**20**, **21**, and **36**), 3-methoxyphenacylbromide (**22**, **23**, and **37**), α-bromo-3,4-methylenedioxyacetophenone (**24**, **25**, and **38**), and 2-chlorocyclohexanone (**26**, **27**, and **39**).

The resulting ketones cyclized readily on heating in 1 N NaOH to the corresponding 1,2,3,4-tetrahydro-5H-benzo [*c*]furo[3,2-*g*]chromen-5-ones **24**-**37** (psoralen-type furocoumarins) and 8,9,10,11-tetrahydro-7H-benzo[*c*]furo [2,3-*f*] chromen-7-ones **38**-**43** (allopsoralen-type furocoumarins).

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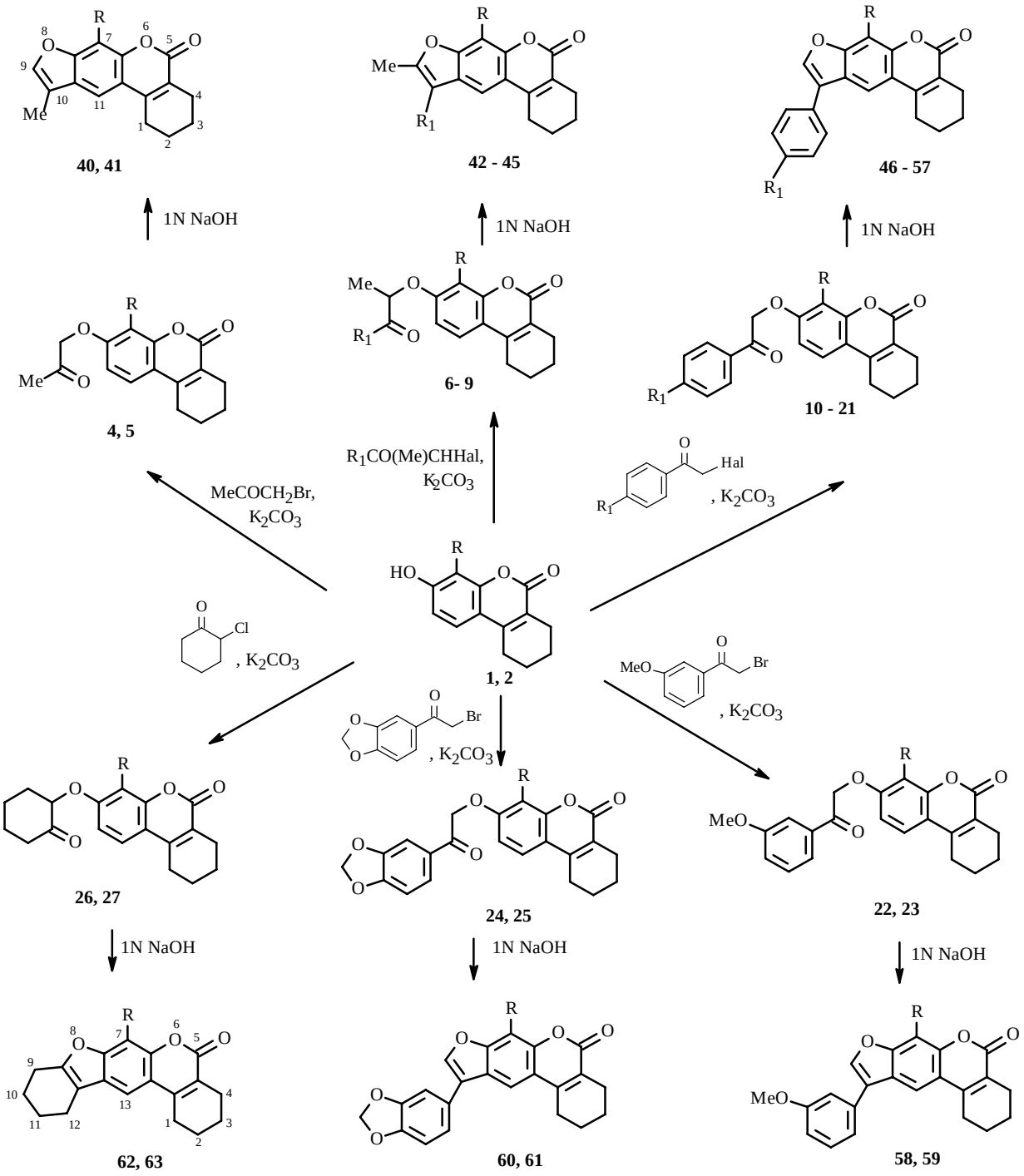
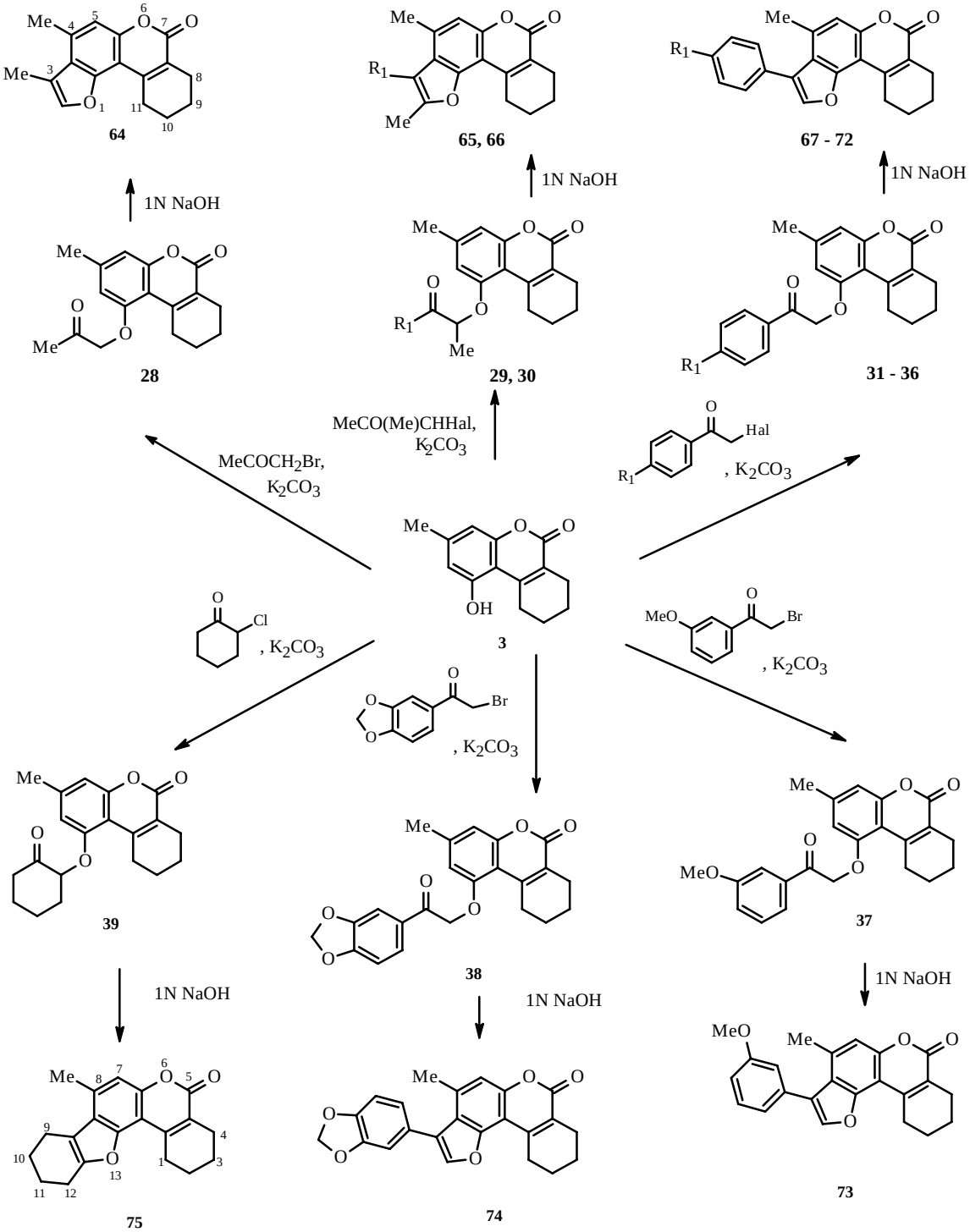


1: R = H; **2:** R = Me; **4:** R = H; **5:** R = Me; **6:** R = H, R_1 = Me; **7:** R = R_1 = Me; **8:** R = H, R_1 = Ph; **9:** R = Me, R_1 = Ph; **10:** R = R_1 = H; **11:** R = Me, R_1 = H; **12:** R = H, R_1 = F; **13:** R = Me, R_1 = F; **14:** R = H, R_1 = Cl; **15:** R = Me, R_1 = Cl; **16:** R = H, R_1 = Br; **17:** R = Me, R_1 = Br; **18:** R = H, R_1 = Me; **19:** R = R_1 = Me; **20:** R = H, R_1 = OMe; **21:** R = Me, R_1 = OMe; **22:** R = H; **23:** R = H; **24:** R = H; **25:** R = Me; **26:** R = H; **27:** R= Me; **40:** R = H; **41:** R = Me; **42:** R = H, R_1 = Me; **43:** R = R_1 =Me; **44:** R = H, R_1 = Ph; **45:** R = Me, R_1 = Ph; **46:** R = R_1 = H; **47:** R = Me, R_1 = H; **48:** R = H, R_1 = F; **49:** R = Me, R_1 = F; **50:** R = H, R_1 = Cl; **51:** R = Me, R_1 = Cl; **52:** R = H, R_1 = Br; **53:** R = Me, R_1 = Br; **54:** R = H, R_1 = Me; **55:** R = R_1 = Me; **56:** R = H, R_1 = OMe; **57:** R = Me, R_1 = OMe; **58:** R = H; **59:** R = Me; **60:** R = H; **61:** R = Me; **62:** R= H; **63:** R = Me

Many routes to furocoumarins are known. In particular, psoralen and its isomers are prepared by the Späth method [11] and those based on Dickman condensation[12], Perkin reaction [13], and Claisen rearrangement [14]. The above methods

involve several steps, give low yields, and have limited capability to modify the coumarin and furan moieties. A different method for forming psoralen and its angular isomers is known. This is the MacLeod method based on cyclization in alkaline medium of 7-(2-oxopropoxy)coumarin derivatives [15].



29: R_1 = Me; **30:** R_1 = Ph; **31:** R_1 = H; **32:** R_1 = F; **33:** R_1 = Cl; **34:** R_1 = Br; **35:** R_1 = Me; **36:** R_1 = OMe;
65: R_1 = Me; **66:** R_1 = Ph; **67:** R_1 = H; **68:** R_1 = F; **69:** R_1 = Cl; **70:** R_1 = Br; **71:** R_1 = Me; **72:** R_1 = OMe

In our opinion, this method is most acceptable because the target furocoumarins can be modified without limitation in high yields.

We confirmed the fusion of the furan ring to the 2,3-position of 7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (for

40-63) or the 1,2-position of this same system (for **64-75**) using PMR spectroscopy. The aromatic protons in the PMR spectra of **40-63** are simply split due to the lack of coupling to H-2 of the 7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one. As a result, aromatic H-11 of the furocoumarin appears as a singlet. The situation is analogous for **64-75**, where H-5 of the furocoumarin gives a singlet owing to a lack of coupling with H-2 of the starting coumarin. Furthermore, a 1H singlet is observed at 7.8-8.5 ppm for **40**, **41**, and **46-61**, which are unsubstituted in the 9-position, and for **64** and **67-74**, which are unsubstituted in the 2-position. This is also a characteristic feature of furocoumarin ring formation.

Thus, we prepared new synthetic analogs of psoralen and allopsoralen based on 1-hydroxy- and 3-hydroxy-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-ones.

EXPERIMENTAL

The course of the reactions and the purity of the products were monitored by TLC on Silufol UV-254 plates in $CHCl_3$—CH_3OH (9:1 and 95:5). PMR spectra were measured on a Varian VXR-300 instrument in DMSO-d_6 and deuteroacetone relative to TMS (internal standard). Elemental analyses of all compounds corresponded with those calculated.

Hydroxycoumarins **1**, **2**, and **3** were prepared by the literature method [10].

3-(2-Oxopropoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (4). A hot solution of **1** (2.16 g, 10 mmole) in absolute acetone (50 mL) was treated with freshly calcined potash (2.76 g, 20 mmole), vigorously stirred and heated (50-56°C), and treated with α-bromoacetone (1.5 g, 11 mmole). The reaction mixture was held for 1 h with heating and vigorous stirring (the completion of the reaction was determined by TLC) and transferred into H_2SO_4 solution (1 N, 200 mL) The resulting precipitate was filtered off and crystallized from propan-2-ol (70%). Yield 74%, mp 131°C, $C_{16}H_{16}O_4$.

PMR spectrum (300 MHz, deuteroacetone, δ, ppm, J/Hz): 1.82 (4H, m, CH_2-8 and CH_2-9), 2.25 (3H, s, CH_3CO), 2.46 (2H, m, CH_2-10), 2.77 (2H, m, CH_2-7), 4.89 (2H, s, $COCH_2O$), 6.84 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 6.98 (1H, d, J = 2, H-4), 7.61 (1H, d, J = 8, H-1).

4-Methyl-3-(2-oxopropoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (5) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and α-bromoacetone (1.5 g, 11 mmole). Yield 79%, mp 157°C (70% propan-2-ol), $C_{17}H_{18}O_4$.

PMR spectrum (300 MHz, deuteroacetone, δ, ppm, J/Hz): 1.81 (4H, m, CH_2-8 and CH_2-9), 2.25 (3H, s, CH_3CO), 2.32 (3H, s, CH_3-4), 2.47 (2H, m, CH_2-10), 2.76 (2H, m, CH_2-7), 4.86 (2H, s, $COCH_2O$), 6.87 (1H, d, J = 8, H-2), 7.48 (1H, d, J = 8, H-1).

3-(1-Methyl-2-oxopropoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (6) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and 3-chloro-2-butanone (1.11 mL, 11 mmole). The reaction mixture was heated for 3 h. Yield 65%, mp 87°C (60% propan-2-ol), $C_{17}H_{18}O_4$.

PMR spectrum (300 MHz, deuteroacetone, δ, ppm, J/Hz): 1.53 (3H, d, α-CH_3), 1.82 (4H, m, CH_2-8 and CH_2-9), 2.21 (3H, s, CH_3CO), 2.44 (2H, m, CH_2-10), 2.79 (2H, m, CH_2-7), 4.98 (1H, q, COCHO), 6.82 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 6.96 (1H, d, J = 2, H-4), 7.64 (1H, d, J = 8, H-1).

4-Methyl-3-(1-methyl-2-oxopropoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (7) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and 3-chloro-2-butanone (1.11 mL, 11 mmole). The reaction mixture was heated for 3 h. Yield 76%, mp 93°C (60% propan-2-ol), $C_{18}H_{20}O_4$.

PMR spectrum (300 MHz, deuteroacetone, δ, ppm, J/Hz): 1.55 (3H, d, α-CH_3), 1.81 (4H, m, CH_2-8 and CH_2-9), 2.21 (3H, s, CH_3CO), 2.32 (3H, s, CH_3-4), 2.45 (2H, m, CH_2-10), 2.76 (2H, m, CH_2-7), 4.95 (1H, q, COCHO), 6.79 (1H, d, J = 8, H-2), 7.46 (1H, d, J = 8, H-1).

3-(1-Methyl-2-oxo-2-phenylethoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (8) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and 2-bromopropiophenone (1.64 mL, 11 mmole). The reaction mixture was heated for 2 h. Yield 86%, mp 121°C (propan-2-ol), $C_{22}H_{20}O_4$.

PMR spectrum (300 MHz, deuteroacetone, δ, ppm, J/Hz): 1.67 (3H, d, α-CH_3), 1.78 (4H, m, CH_2-8 and CH_2-9), 2.43 (2H, m, CH_2-10), 2.76 (2H, m, CH_2-7), 6.00 (1H, q, COCHO), 6.81 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 6.94 (1H, d, J = 2, H-4), 7.62 (1H, d, J = 8, H-1), 7.64 (3H, m, H-3′, H-4′, H-5′ PhCO), 8.14 (2H, m, H-2′, H-6′ PhCO).

4-Methyl-3-(1-methyl-2-oxo-2-phenylethoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (9) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and 2-bromopropiophenone (1.64 mL, 11 mmole). The reaction mixture was heated for 2 h. Yield 88%, mp 155°C (propan-2-ol), $C_{23}H_{22}O_4$.

PMR spectrum (300 MHz, deuteroacetone, δ, ppm, J/Hz): 1.71 (3H, d, α-CH_3), 1.78 (4H, m, CH_2-8 and CH_2-9), 2.30 (3H, s, CH_3-4), 2.45 (2H, m, CH_2-10), 2.71 (2H, m, CH_2-7), 5.96 (1H, q, COCHO), 6.82 (1H, d, J = 8, H-2), 7.41 (1H, d, J = 8, H-1), 7.60 (3H, m, H-3′, H-4′, H-5′ PhCO), 8.12 (2H, m, H-2′, H-6′ PhCO).

3-(2-Oxo-2-phenylethoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (10) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and α-bromoacetophenone (2.19 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 95%, mp 169°C (propan-2-ol), $C_{21}H_{18}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.41 (2H, m, CH_2-10), 2.75 (2H, m, CH_2-7), 5.68 (2H, s, $COCH_2O$), 6.88 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 7.02 (1H, d, J = 2, H-4), 7.59 (1H, d, J = 8, H-1), 7.65 (3H, m, H-3′, H-4′, H-5′ PhCO), 8.04 (2H, m, H-2′, H-6′ PhCO).

4-Methyl-3-(2-oxo-2-phenylethoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (11) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and **3.** α-bromoacetophenone (2.19 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 96%, mp 199°C (propan-2-ol), $C_{22}H_{20}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.28 (3H, s, CH_3-4), 2.41 (2H, m, CH_2-10), 2.74 (2H, m, CH_2-7), 5.71 (2H, s, $COCH_2O$), 6.98 (1H, d, J = 8, H-2), 7.45 (1H, d, J = 8, H-1), 7.55-7.70 (3H, m, H-3′, H-4′, H-5′ PhCO), 8.01 (2H, m, H-2′, H-6′ PhCO).

3[2-(4-Fluorophenyl)-2-oxoethoxy]-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (12) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and α-chloro-4-fluoroacetophenone (1.90 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 91%, mp 147°C (propan-2-ol), $C_{21}H_{17}FO_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.40 (2H, m, CH_2-10), 2.76 (2H, m, CH_2-7), 5.70 (2H, s, $COCH_2O$), 7.02 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 7.05 (1H, d, J = 2, H-4), 7.42 (2H, m, H-3′, H-5′ ArCO), 7.60 (1H, d, J = 8, H-1), 8.13 (2H, m, H-2′, H-6′ ArCO).

3-[2-(4-Fluorophenyl)-2-oxoethoxy]-4-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (13) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and α-chloro-4-fluoroacetophenone (1.90 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 94%, mp 197°C (propan-2-ol), $C_{22}H_{19}FO_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.28 (3H, s, CH_3-4), 2.41 (2H, m, CH_2-10), 2.75 (2H, m, CH_2-7), 5.72 (2H, s, $COCH_2O$), 7.00 (1H, d, J = 8, H-2), 7.42 (1H, d, J = 8, H-1), 7.47 (2H, m, H-3′, H-5′ ArCO), 8.11 (2H, m, H-2′, H-6′ ArCO).

3-[2-(4-Chlorophenyl)-2-oxoethoxy]-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (14) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and α-bromo-4-chloroacetophenone (2.57 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 88%, mp 178°C (propan-2-ol), $C_{21}H_{17}ClO_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.39 (2H, m, CH_2-10), 2.75 (2H, m, CH_2-7), 5.67 (2H, s, $COCH_2O$), 6.98 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 7.05 (1H, d, J = 2, H-4), 7.62 (1H, d, J = 8, H-1), 7.64 (2H, d, J = 8, H-3′, H-5′ ArCO), 8.05 (2H, d, J = 8, H-2′, H-6′ ArCO).

3-[2-(4-Chlorophenyl)-2-oxoethoxy]-4-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (15) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and α-bromo-4-chloroacetophenone (2.57 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 90%, mp 182°C (propan-2-ol), $C_{22}H_{19}ClO_4$.

PMR spectrum (300 MHz, DMSO-d_6, , δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.27 (3H, s, CH_3-4), 2.41 (2H, m, CH_2-10), 2.74 (2H, m, CH_2-7), 5.68 (2H, s, $COCH_2O$), 6.99 (1H, d, J = 8, H-2), 7.44 (1H, d, J = 8, H-1), 7.65 (2H, d, J = 8, H-3′, H-5′ ArCO), 8.01 (2H, d, J = 8, H-2′, H-6′ ArCO).

3-[2-(4-Bromophenyl)-2-oxoethoxy]-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (16) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and 4-bromophenacylbromide (3.06 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 91%, mp 194°C (propan-2-ol), $C_{21}H_{17}BrO_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.40 (2H, m, CH_2-10), 2.76 (2H, m, CH_2-7), 5.69 (2H, s, $COCH_2O$), 6.98 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 7.05 (1H, d, J = 2, H-4), 7.60 (1H, d, J = 8, H-1), 7.82 (2H, d, J = 8, H-3′, H-5′ ArCO), 7.95 (2H, d, J = 8, H-2′, H-6′ ArCO).

3-[2-(4-Bromophenyl)-2-oxoethoxy]-4-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (17) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and 4-bromophenacylbromide (3.06 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 93%, mp 207°C (propan-2-ol), $C_{22}H_{19}BrO_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.27 (3H, s, CH_3-4), 2.41 (2H, m, CH_2-10), 2.75 (2H, m, CH_2-7), 5.69 (2H, s, $COCH_2O$), 6.99 (1H, d, J = 8, H-2), 7.45 (1H, d, J = 8, H-1), 7.80 (2H, d,

J = 8, H-3′, H-5′ ArCO), 7.94 (2H, d, J = 8, H-2′, H-6′ ArCO).

3-[2-(4-Methylphenyl)-2-oxoethoxy]-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (18) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and 4-methylphenacylbromide (2.34 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 81%, mp 169°C (propan-2-ol), $C_{22}H_{20}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.74 (4H, m, CH_2-8 and CH_2-9), 2.40 (3H, s, CH_3-4′ ArCO), 2.41 (2H, m, CH_2-10), 2.75 (2H, m, CH_2-7), 5.66 (2H, s, $COCH_2O$), 6.98 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 7.02 (1H, d, J = 2, H-4), 7.40 (2H, d, J = 8, H-3′, H-5′ ArCO), 7.59 (1H, d, J = 8, H-1), 7.93 (2H, d, J = 8, H-2′ H-6′ ArCO).

3-[2-(4-Methylphenyl)-2-oxoethoxy]-4-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (19) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and 4-methylphenacylbromide (2.34 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 82%, mp 197°C (propan-2-ol), $C_{23}H_{22}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.28 (3H, s, CH_3-4), 2.40 (3H, s, CH_3-4′ ArCO), 2.41 (2H, m, CH_2-10), 2.74 (2H, m, CH_2-7), 5.68 (2H, s, $COCH_2O$), 6.96 (1H, d, J = 8, H-2), 7.39 (2H, d, J = 8, H-3′, H-5′ ArCO), 7.45 (1H, d, J = 8, H-1), 7.91 (2H, d, J = 8, H-2′, H-6′ ArCO).

3-[2-(4-Methoxyphenyl)-2-oxoethoxy]-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (20) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and 4-methoxyphenacylbromide (2.52 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 90%, mp 168°C (propan-2-ol), $C_{22}H_{20}O_5$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.74 (4H, m, CH_2-8 and CH_2-9), 2.39 (2H, m, CH_2-10), 2.74 (2H, m, CH_2-7), 3.87 (3H, s, CH_3O-4′ ArCO), 5.64 (2H, s, $COCH_2O$), 6.97 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 7.01 (1H, d, J = 2, H-4), 7.11 (2H, d, J = 8, H-3′, H-5′ ArCO), 7.58 (1H, d, J = 8, H-1), 8.01 (2H, d, J = 8, H-2′, H-6′ ArCO).

3-[2-(4-Methoxyphenyl)-2-oxoethoxy]-4-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (21) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and 4-methoxyphenacylbromide (2.52 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 89%, mp 200°C (propan-2-ol), $C_{23}H_{22}O_5$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.74 (4H, m, CH_2-8 and CH_2-9), 2.28 (3H, s, CH_3-4), 2.41 (2H, m, CH_2-10), 2.75 (2H, m, CH_2-7), 3.86 (3H, s, CH_3O-4′ ArCO), 5.66 (2H, s, $COCH_2O$), 6.96 (1H, d, J = 8, H-2), 7.11 (2H, d, J = 8, H-3′, H-5′ ArCO), 7.46 (1H, d, J = 8, H-1), 7.99 (2H, d, J = 8, H-2′, H-6′ ArCO).

3-[2-(3-Methoxyphenyl)-2-oxoethoxy]-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (22) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and 3-methoxyphenacylbromide (2.52 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 92%, mp 161°C (propan-2-ol), $C_{22}H_{20}O_5$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.40 (2H, m, CH_2-10), 2.76 (2H, m, CH_2-7), 3.85 (3H, s, CH_3O-3′ ArCO), 5.69 (2H, s, $COCH_2O$), 7.00 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 7.03 (1H, d, J = 2, H-4), 7.28 (1H, dd, $J_{5',6'}$ = 2, $J_{5',4'}$ = 2, H-5′ ArCO), 7.48 (1H, d, J = 8, H-1), 7.52 (1H, m, H-4′ ArCO), 7.62 (2H, m, H-2′, H-6′ ArCO).

3-[2-(3-Methoxyphenyl)-2-oxoethoxy]-4-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (23) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and 3-methoxyphenacylbromide (2.52 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 95%, mp 167°C (propan-2-ol), $C_{23}H_{22}O_5$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.73 (4H, m, CH_2-8 and CH_2-9), 2.28 (3H, s, CH_3-4), 2.40 (2H, m, CH_2-10), 2.75 (2H, m, CH_2-7), 3.84 (3H, s, CH_3O-3′ ArCO), 5.74 (2H, s, $COCH_2O$), 6.96 (1H, d, J = 8, H-2), 7.29 (1H, dd, $J_{5',6'}$ = 2, $J_{5',4'}$ = 2, H-5′ ArCO), 7.46 (1H, d, J = 8, H-1), 7.50 (1H, m, H-4′ ArCO), 7.60 (2H, m, H-2′, H-6′ ArCO).

3-[2-(1,3-Benzodioxol-5-yl)-2-oxoethoxy]-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (24) was prepared analogously to **4** from **1** (2.16 g, 10 mmole) and α-bromo-3,4-methylenedioxyacetophenone (2.67 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 88%, mp 174°C (propan-2-ol), $C_{22}H_{18}O_6$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.74 (4H, m, CH_2-8 and CH_2-9), 2.39 (2H, m, CH_2-10), 2.74 (2H, m, CH_2-7), 5.64 (2H, s, $COCH_2O$), 6.13 (2H, s, OCH_2O), 6.97 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 7.01 (1H, d, J = 2, H-4), 7.08 (1H, d, J = 8.5, H-7′ ArCO), 7.48 (1H, d, J = 2.0, H-4′ ArCO), 7.58 (1H, d, J = 8, H-1), 7.69 (1H, dd, $J_{6,4}$ = 2.0, $J_{6,7}$ = 8.5, H-6′ ArCO).

3-[2-(1,3-Benzodioxol-5-yl)-2-oxoethoxy]-4-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (25) was prepared analogously to **4** from **2** (2.30 g, 10 mmole) and α-bromo-3,4-methylenedioxyacetophenone (2.67 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 91%, mp 208°C (propan-2-ol), $C_{23}H_{20}O_6$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.28 (3H, s, CH_3-4), 2.41 (2H, m, CH_2-10), 2.75 (2H, m, CH_2-7), 5.64 (2H, s, $COCH_2O$), 6.16 (2H, s, OCH_2O), 6.94 (1H, d, J = 8, H-2), 7.09 (1H, d, J = 8.5,

H-7′ ArCO), 7.47 (1H, d, J = 8, H-1), 7.51 (1H, d, J = 2.0, H-4′ ArCO), 7.67 (1H, dd, $J_{6,4}$ = 2.0, $J_{6,7}$ = 8.5, H-6′ ArCO).

3-(2-Oxocyclohexyloxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (26). A solution of **1** (3.24 g, 15 mmole) in dry DMF (50 mL) was treated with freshly calcined potash (6.2 g, 45 mmole) and 2-chlorocyclohexanone (3.43 mL, 30 mmole). The reaction mixture was vigorously stirred and heated (75-80ºC) for 24 h and treated with H_2SO_4 solution (1 N, 200 mL). The resulting precipitate was filtered off and crystallized from propan-2-ol. Yield 62%, mp 163ºC (propan-2-ol), $C_{19}H_{20}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.70-2.80 [16H, m, CH_2-7, CH_2-8, CH_2-9, CH_2-10 and $(CH_2)_4$ of cyclohexanone], 5.18 (1H, m, α-CH), 6.82 (1H, dd, $J_{2,4}$ = 2, $J_{2,1}$ = 8, H-2), 6.89 (1H, d, J = 2, H-4), 7.55 (1H, d, J = 8, H-1).

4-Methyl-3-(2-oxocyclohexyloxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (27) was prepared analogously to **26** from **2** (3.45 g, 15 mmole) and 2-chlorocyclohexanone (3.43 mL, 30 mmole). Yield 68%, mp 184ºC (propan-2-ol), $C_{20}H_{22}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.70-2.80 [16H, m, CH_2-7, CH_2-8, CH_2-9, CH_2-10 and $(CH_2)_4$ of cyclohexanone], 2.22 (3H, s, CH_3-4), 5.15 (1H, m, α-CH), 6.85 (1H, d, J = 8, H-2), 7.40 (1H, d, J = 8, H-1).

3-Methyl-1-(2-oxopropoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (28) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and α-bromoacetone (1.5 g, 11 mmole). Yield 78%, mp 176ºC (70% propan-2-ol), $C_{17}H_{18}O_4$.

PMR spectrum (300 MHz, deuteroacetone, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-8 and CH_2-9), 2.25 (3H, s, CH_3CO), 2.35 (3H, s, CH_3-3), 2.47 (2H, m, CH_2-10), 3.21 (2H, m, CH_2-7), 4.93 (2H, s, $COCH_2O$), 6.65 (1H, d, J = 2, H-2), 6.71 (1H, d, J = 2, H-4).

3-Methyl-1-(1-methyl-2-oxopropoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (29) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and 3-chloro-2-butanone (1.11 mL, 11 mmole). The reaction mixture was heated for 3 h. Yield 71%, mp 159ºC (60% propan-2-ol), $C_{18}H_{20}O_4$.

PMR spectrum (300 MHz, deuteroacetone, δ, ppm, J/Hz): 1.58 (3H, d, α-CH_3), 1.76 (4H, m, CH_2-8 and CH_2-9), 2.22 (3H, s, CH_3CO), 2.33 (3H, s, CH_3-3), 2.46 (2H, m, CH_2-10), 3.23 (2H, m, CH_2-7), 5.06 (1H, q, COCHO), 6.54 (1H, d, J = 2, H-2), 6.72 (1H, d, J = 2, H-4).

3-Methyl-1-(1-methyl-2-oxo-2-phenylethoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (30) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and 2-bromopropiophenone (1.64 mL, 11 mmole). The reaction mixture was heated for 2 h. Yield 85%, mp 157ºC (propan-2-ol), $C_{23}H_{22}O_4$.

PMR spectrum (300 MHz, deuteroacetone, δ, ppm, J/Hz): 1.71 (3H, d, α-CH_3), 1.78 (4H, m, CH_2-8 and CH_2-9), 2.26 (3H, s, CH_3-3), 2.48 (2H, m, CH_2-10), 3.21 (2H, m, CH_2-7), 6.16 (1H, q, COCHO), 6.64 (1H, d, J = 2, H-2), 6.70 (1H, d, J = 2, H-4), 7.62 (3H, m, H-3′, H-4′, H-5′ PhCO), 8.10 (2H, m, H-2′, H-6′ PhCO).

3-Methyl-1-(2-oxo-2-phenylethoxy)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (31) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and α-bromoacetophenone (2.19 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 88%, mp 161ºC (propan-2-ol), $C_{22}H_{20}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.68 (4H, m, CH_2-8 and CH_2-9), 2.28 (3H, s, CH_3-3), 2.42 (2H, m, CH_2-10), 3.19 (2H, m, CH_2-7), 5.69 (2H, s, $COCH_2O$), 6.77 (1H, d, J = 2, H-2), 6.87 (1H, d, J = 2, H-4), 7.58 (2H, m, H-3', H-5′ PhCO), 7.71 (1H, m, H-4′ PhCO), 8.05 (2H, m, H-2′, H-6′ PhCO).

1-[2-(4-Fluorophenyl)-2-oxoethoxy]-3-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (32) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and α-chloro-4-fluoroacetophenone (1.90 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 94%, mp 197ºC (propan-2-ol), $C_{22}H_{19}FO_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.68 (4H, m, CH_2-8 and CH_2-9), 2.33 (3H, s, CH_3-3), 2.42 (2H, m, CH_2-10), 3.19 (2H, m, CH_2-7), 5.69 (2H, s, $COCH_2O$), 6.79 (1H, d, J = 2, H-2), 6.88 (1H, d, J = 2, H-4), 7.42 (2H, m, H-3′, H-5′ ArCO), 8.14 (2H, m, H-2′, H-6′ ArCO).

1-[2-(4-Chlorophenyl)-2-oxoethoxy]-3-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (33) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and α-bromo-4-chloroacetophenone (2.57 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 93%, mp 185ºC (propan-2-ol), $C_{22}H_{19}ClO_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.68 (4H, m, CH_2-8 and CH_2-9), 2.33 (3H, s, CH_3-3), 2.41 (2H, m, CH_2-10), 3.16 (2H, m, CH_2-7), 5.67 (2H, s, $COCH_2O$), 6.78 (1H, d, J = 2, H-2), 6.86 (1H, d, J = 8, H-4), 7.65 (2H, d, J = 8, H-3′, H-5′ ArCO), 8.05 (2H, d, J = 8, H-2′, H-6′ ArCO).

1-[2-(4-Bromophenyl)-2-oxoethoxy]-3-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (34) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and 4-bromophenacylbromide (3.06 g, 11 mmole). The reaction mixture was heated

for 1 h. Yield 91%, mp 203ºC (propan-2-ol), $C_{22}H_{19}BrO_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.68 (4H, m, CH_2-8 and CH_2-9), 2.33 (3H, s, CH_3-3), 2.42 (2H, m, CH_2-10), 3.19 (2H, m, CH_2-7), 5.69 (2H, s, $COCH_2O$), 6.80 (1H, d, J = 2, H-2), 6.87 (1H, d, J = 2, H-4), 7.82 (2H, d, J = 8, H-3′, H-5′ ArCO), 7.97 (2H, d, J = 8, H-2′, H-6′ ArCO).

1-[2-(4-Methylphenyl)-2-oxoethoxy]-3-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (35) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and 4-methylphenacylbromide (2.34 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 88%, mp 167ºC (propan-2-ol), $C_{23}H_{22}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.68 (4H, m, CH_2-8 and CH_2-9), 2.30 (3H, s, CH_3-3), 2.40 (3H, s, CH_3-4′ ArCO), 2.41 (2H, m, CH_2-10), 3.16 (2H, m, CH_2-7), 5.59 (2H, s, $COCH_2O$), 6.73 (1H, d, J = 2, H-2), 6.83 (1H, d, J = 2, H-4), 7.39 (2H, d, J = 8, H-3′, H-5′ ArCO), 7.92 (2H, d, J = 8, H-2′, H-6′ ArCO).

1-[2-(4-Methoxyphenyl)-2-oxoethoxy]-3-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (36) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and 4-methoxyphenacylbromide (2.52 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 93%, mp 183ºC (propan-2-ol), $C_{23}H_{22}O_5$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.68 (4H, m, CH_2-8 and CH_2-9), 2.32 (3H, s, CH_3-3), 2.43 (2H, m, CH_2-10), 3.19 (2H, m, CH_2-7), 3.87 (3H, s, CH_3O-4′ ArCO), 5.62 (2H, s, $COCH_2O$), 6.77 (1H, d, J = 2, H-2), 6.86 (1H, d, J = 2, H-4), 7.11 (2H, d, J = 8, H-3′, H-5′ ArCO), 8.01 (2H, d, J = 8, H-2′, H-6′ ArCO).

1-[2-(3-Methoxyphenyl)-2-oxoethoxy]-3-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (37) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and 3-methoxyphenacylbromide (2.52 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 92%, mp 169ºC (propan-2-ol), $C_{23}H_{22}O_5$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.68 (4H, m, CH_2-8 and CH_2-9), 2.32 (3H, s, CH_3-3), 2.42 (2H, m, CH_2-10), 3.19 (2H, m, CH_2-7), 3.85 (3H, s, CH_3O-3′ ArCO), 5.67 (2H, s, $COCH_2O$), 6.77 (1H, d, J = 2, H-2), 6.86 (1H, d, J = 2, H-4), 7.28 (1H, dd, $J_{5',6'}$ = 2, $J_{5',4'}$ = 2, H-5′ ArCO), 7.50 (1H, m, H-4′ ArCO), 7.62 (2H, m, H-2′, H-6′ ArCO).

1-[2-(1,3-Benzodioxol-5-yl)-2-oxoethoxy]-3-methyl-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (38) was prepared analogously to **4** from **3** (2.30 g, 10 mmole) and α-bromo-3,4-methylenedioxyacetophenone (2.67 g, 11 mmole). The reaction mixture was heated for 1 h. Yield 85%, mp 178ºC (propan-2-ol), $C_{23}H_{20}O_6$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.69 (4H, m, CH_2-8 and CH_2-9), 2.30 (3H, s, CH_3-4), 2.42 (2H, m, CH_2-10), 3.18 (2H, m, CH_2-7), 5.64 (2H, s, $COCH_2O$), 6.16 (2H, s, OCH_2O), 6.73 (1H, d, J = 2, H-2), 6.84 (1H, d, J = 2, H-4), 7.09 (1H, d, J = 8.5, H-7′ ArCO), 7.51 (1H, d, J = 2.0, H-4′ ArCO), 7.67 (1H, dd, $J_{6,4}$ = 2.0, $J_{6,7}$ = 8.5, H-6′ ArCO).

3-Methyl-1-(2-oxocyclohexyl)-7,8,9,10-tetrahydro-6H-benzo[*c*]chromen-6-one (39) was prepared analogously to **26** from **3** (3.45 g, 15 mmole) and 2-chlorocyclohexanone (3.43 mL, 30 mmole). Yield 53%, mp 149ºC (propan-2-ol), $C_{20}H_{22}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.70-2.50 [14H, m, CH_2-8, CH_2-9, CH_2-10, and $(CH_2)_4$ of cyclohexanone], 2.30 (3H, s, CH_3-3), 3.10 (2H, m, CH_2-7), 5.24 (1H, m, α-CH), 6.63 (1H, d, J = 2, H-2), 6.74 (1H, d, J = 2, H-4).

1,2,3,4-Tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-ones (40-63) and 8,9,10,11-tetrahydro-7H-benzo[*c*]furo [2,3-*f*]chromen-7-ones (64-75). A solution or suspension of ketone **4-39** (6 mmole) in propan-2-ol (50 mL) was diluted with NaOH solution (1 N, 50 mL). The reaction mixture was heated for 3-4 h until the starting ketone completely dissolved (course of reaction monitored by TLC) and transferred into H_2SO_4 solution (1 N, 300 mL). The resulting precipitate was filtered off and crystallized from propan-2-ol.

10-Methyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (40). Yield 81%, mp 198ºC, $C_{16}H_{14}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.78 (4H, m, CH_2-2 and CH_2-3), 2.25 (3H, s, CH_3-10), 2.43 (2H, m, CH_2-1), 2.71 (2H, m, CH_2-4), 7.58 (1H, s, H-11), 7.84 (1H, s, H-9), 7.86 (1H, s, H-7).

7,10-Dimethyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (41). Yield 84%, mp 199ºC, $C_{17}H_{16}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.78 (4H, m, CH_2-2 and CH_2-3), 2.24 (3H, s, CH_3-10), 2.45 (3H, s, CH_3-7), 2.43 (2H, m, CH_2-1), 2.86 (2H, m, CH_2-4), 7.66 (1H, s, H-11), 7.78 (1H, s, H-9).

9,10-Dimethyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (42). Yield 87%, mp 214ºC, $C_{17}H_{16}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.76 (4H, m, CH_2-2 and CH_2-3), 2.16 (3H, s, CH_3-10), 2.38 (3H, s, CH_3-9), 2.49 (2H, m, CH_2-1), 2.86 (2H, m, CH_2-4), 7.40 (1H, s, H-11), 7.67 (1H, s, H-7).

7,9,10-Trimethyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (43). Yield 83%, mp 195ºC,$C_{18}H_{18}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-2 and CH_2-3), 2.15 (3H, s, CH_3-10), 2.39 (3H,

s, CH_3-9), 2.42 (3H, s, CH_3-7), 2.49 (2H, m, CH_2-1), 2.84 (2H, m, CH_2-4), 7.51 (1H, s, H-11).

9-Methyl-10-phenyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (44). Yield 89%, mp 176ºC, $C_{22}H_{18}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-2 and CH_2-3), 2.43 (2H, m, CH_2-1), 2.54 (3H, s, CH_3-9), 2.83 (2H, m, CH_2-4), 7.42-7.60 (5H, m, Ph-10), 7.62 (1H, s, H-11), 7.71 (1H, s, H-7).

7,9-Dimethyl-10-phenyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (45). Yield 91%, mp 249ºC, $C_{23}H_{20}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.74 (4H, m, CH_2-2 and CH_2-3), 2.43 (2H, m, CH_2-1), 2.47 (3H, s, CH_3-7), 2.54 (3H, s, CH_3-9), 2.77 (2H, m, CH_2-4), 7.43-7.53 (5H, m, Ph-10), 7.55 (1H, s, H-11).

10-Phenyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (46). Yield 88%, mp 192ºC, $C_{21}H_{16}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.79 (4H, m, CH_2-2 and CH_2-3), 2.44 (2H, m, CH_2-1), 2.93 (2H, m, CH_2-4), 7.43 (1H, m, H-4′ Ph-10), 7.54 (2H, m, H-3′ and H-5′ Ph-10), 7.73 (1H, s, H-11), 7.79 (2H, m, H-2′ and H-6′ Ph-10), 8.05 (1H, s, H-7), 8.44 (1H, s, H-9).

7-Methyl-10-phenyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (47). Yield 89%, mp 200ºC, $C_{22}H_{18}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-2 and CH_2-3), 2.45 (2H, m, CH_2-1), 2.50 (3H, s, CH_3-7), 2.89 (2H, m, CH_2-4), 7.42 (1H, m, H-4′ Ph-10), 7.53 (2H, m, H-3′ and H-5′ Ph-10), 7.76 (2H, m, H-2′ and H-6′ Ph-10), 7.87 (1H, s, H-11), 8.41 (1H, s, H-9).

10-(4-Fluorophenyl)-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (48). Yield 89%, mp 199ºC, $C_{21}H_{15}FO_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.78 (4H, m, CH_2-2 and CH_2-3), 2.45 (2H, m, CH_2-1), 2.93 (2H, m, CH_2-4), 7.37 (2H, m, H-3′ and H-5′ Ar-10), 7.72 (1H, s, H-11), 7.83 (2H, m, H-2′ and H-6′ Ar-10), 8.03 (1H, s, H-7), 8.42 (1H, s, H-9).

10-(4-Fluorophenyl)-7-methyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (49). Yield 86%, mp 201ºC, $C_{22}H_{17}FO_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.72 (4H, m, CH_2-2 and CH_2-3), 2.40 (2H, m, CH_2-1), 2.42 (3H, s, CH_3-7), 2.80 (2H, m, CH_2-4), 7.34 (2H, m, H-3′ and H-5′ Ar-10), 7.73 (1H, s, H-11), 7.77 (2H, m, H-2′ and H-6′ Ar-10), 8.39 (1H, s, H-9).

10-(4-Chlorophenyl)-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (50). Yield 88%, mp 234ºC, $C_{21}H_{15}ClO_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.74 (4H, m, CH_2-2 and CH_2-3), 2.44 (2H, m, CH_2-1), 2.91 (2H, m, CH_2-4), 7.57 (2H, d, J = 8, H-3′ and H-5′ Ar-10), 7.71 (1H, s, H-11), 7.81 (2H, d, J = 8, H-2′ and H-6′ Ar-10), 8.01 (1H, s, H-7), 8.47 (1H, s, H-9).

10-(4-Chlorophenyl)-7-methyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (51). Yield 91%, mp 205ºC, $C_{22}H_{17}ClO_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.76 (4H, m, CH_2-2 and CH_2-3), 2.42 (2H, m, CH_2-1), 2.44 (3H, s, CH_3-7), 2.82 (2H, m, CH_2-4), 7.53 (2H, d, J = 8, H-3′ and H-5′ Ar-10), 7.72 (2H, d, J = 8, H-2′ and H-6′ Ar-10), 7.76 (1H, s, H-11), 8.42 (1H, s, H-9).

10-(4-Bromophenyl)-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (52). Yield 90%, mp 248ºC, $C_{21}H_{15}BrO_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.79 (4H, m, CH_2-2 and CH_2-3), 2.45 (2H, m, CH_2-1), 2.91 (2H, m, CH_2-4), 7.68 (1H, s, H-11), 7.70 (2H, d, J = 8, H-3′ and H-5′ Ar-10), 7.76 (2H, d, J = 8, H-2′ and H-6′ Ar-10), 8.01 (1H, s, H-7), 8.44 (1H, s, H-9).

10-(4-Bromophenyl)-7-methyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (53). Yield 88%, mp 191ºC, $C_{22}H_{17}BrO_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.79 (4H, m, CH_2-2 and CH_2-3), 2.45 (2H, m, CH_2-1), 2.49 (3H, s, CH_3-7), 2.89 (2H, m, CH_2-4), 7.68 (2H, d, J = 8, H-3′ and H-5′ Ar-10), 7.74 (2H, d, J = 8, H-2′ and H-6′ Ar-10), 7.86 (1H, s, H-11), 8.48 (1H, s, H-9).

10-(4-Methylphenyl)-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (54). Yield 82%, mp 193ºC, $C_{22}H_{18}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.78 (4H, m, CH_2-2 and CH_2-3), 2.38 (3H, s, CH_3-4′ Ar-10), 2.43 (2H, m, CH_2-1), 2.89 (2H, m, CH_2-4), 7.35 (2H, d, J = 8, H-3′ and H-5′ Ar-10), 7.63 (2H, d, J = 8, H-2′ and H-6′ Ar-10), 7.68 (1H, s, H-11), 7.99 (1H, s, H-7), 8.36 (1H, s, H-9).

7-Methyl-10-(4-methylphenyl)-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (55). Yield 88%, mp 202°C, $C_{23}H_{20}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.74 (4H, m, CH_2-2 and CH_2-3), 2.38 (3H, s, CH_3-4′ Ar-10), 2.43 (2H, m, CH_2-1), 2.46 (3H, s, CH_3-7), 2.84 (2H, m, CH_2-4), 7.34 (2H, d, J = 8, H-3′ and H-5′ Ar-10), 7.62 (2H, d, J = 8, H-2′ and H-6′ Ar-10), 7.80 (1H, s, H-11), 8.37 (1H, s, H-9).

10-(4-Methoxyphenyl)-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (56). Yield 81%, mp 201°C, $C_{22}H_{18}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.79 (4H, m, CH_2-2 and CH_2-3), 2.43 (2H, m, CH_2-1), 2.90 (2H, m, CH_2-4), 3.83 (3H, s, CH_3O-4′ Ar-10), 7.08 (2H, d, J = 8, H-3′ and H-5′ Ar-10), 7.68 (1H, s, H-11), 7.75 (2H, d, J = 8, H-2′ and H-6′ Ar-10), 7.98 (1H, s, H-7), 8.33 (1H, s, H-9).

10-(4-Methoxyphenyl)-7-methyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (57). Yield 86%, mp 203°C, $C_{23}H_{20}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-2 and CH_2-3), 2.41 (2H, m, CH_2-1), 2.44 (3H, s, CH_3-7), 2.82 (2H, m, CH_2-4), 3.83 (3H, s, CH_3O-4′ Ar-10), 7.07 (2H, d, J = 8, H-3′ and H-5′ Ar-10), 7.66 (2H, d, J = 8, H-2′ and H-6′ Ar-10), 7.76 (1H, s, H-11), 8.32 (1H, s, H-9).

10-(3-Methoxyphenyl)-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (58). Yield 86%, mp 182°C, $C_{22}H_{18}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.79 (4H, m, CH_2-2 and CH_2-3), 2.44 (2H, m, CH_2-1), 2.90 (2H, m, CH_2-4), 3.86 (3H, s, CH_3O-3′ Ar-10), 7.00 (1H, dd, $J_{5',6'}$ = 2, $J_{5',4'}$ = 2, H-5′ Ar-10), 7.27 (1H, m, H-4′ Ar-10), 7.35 (1H, m, H-6′ Ar-10), 7.45 (1H, dd, $J_{2',6'}$ = 2, $J_{2',4'}$ = 2, H-2′ Ar-10), 7.66 (1H, s, H-11), 8.00 (1H, s, H-7), 8.39 (1H, s, H-9).

10-(3-Methoxyphenyl)-7-methyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (59). Yield 88%, mp 224°C, $C_{23}H_{20}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.78 (4H, m, CH_2-2 and CH_2-3), 2.44 (2H, m, CH_2-1), 2.48 (3H, s, CH_3-7), 2.88 (2H, m, CH_2-4), 3.85 (3H, s, CH_3O-3′ Ar-10), 7.01 (1H, dd, $J_{5',6'}$ = 2, $J_{5',4'}$ = 2, H-5′ Ar-10), 7.27 (1H, m, H-4′ Ar-10), 7.36 (1H, m, H-6′ Ar-10), 7.45 (1H, dd, $J_{2',6'}$ = 2, $J_{2',4'}$ = 2, H-2′ Ar-10), 7.83 (1H, s, H-11), 8.43 (1H, s, H-9).

10-(1,3-Benzodioxol-5-yl)-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (60). Yield 80%, mp 189°C, $C_{22}H_{16}O_5$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-2 and CH_2-3), 2.44 (2H, m, CH_2-1), 2.90 (2H, m, CH_2-4), 6.09 (2H, s, OCH_2O Ar-10), 7.04 (1H, d, J = 8.5, H-7′ Ar-10), 7.25 (1H, dd, $J_{6,4}$ = 2.0, $J_{6,7}$ = 8.5, H-6′ Ar-10), 7.30 (1H, d, J = 2, H-4′ Ar-10), 7.63 (1H, s, H-11), 7.96 (1H, s, H-7), 8.30 (1H, s, H-9).

10-(1,3-Benzodioxol-5-yl)-7-methyl-1,2,3,4-tetrahydro-5H-benzo[*c*]furo[3,2-*g*]chromen-5-one (61). Yield 89%, mp 198°C, $C_{23}H_{18}O_5$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.76 (4H, m, CH_2-2 and CH_2-3), 2.42 (2H, m, CH_2-1), 2.44 (3H, s, CH_3-7), 2.83 (2H, m, CH_2-4), 6.08 (2H, s, OCH_2O Ar-10), 7.03 (1H, d, J = 8.5, H-7′ Ar-10), 7.21 (1H, dd, $J_{6,4}$ = 2.0, $J_{6,7}$ = 8.5, H-6′ Ar-10), 7.25 (1H, d, J = 2, H-4′ Ar-10), 7.74 (1H, s, H-11), 8.26 (1H, s, H-9).

1,2,3,4,9,10,11,12-Octahydro-5H-benzo[*c*]benzo[4,5]furo[3,2-*g*]chromen-5-one (62). Yield 78%, mp 187°C, $C_{19}H_{18}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75-1.90 (8H, m, CH_2-2, CH_2-3, CH_2-10, CH_2-11), 2.44 (2H, m, CH_2-1), 2.62 (2H, m, CH_2-12), 2.73 (2H, m, CH_2-9), 2.86 (2H, m, CH_2-4), 7.48 (1H, s, H-11), 7.71 (1H, s, H-7).

7-Methyl-1,2,3,4,9,10,11,12-octahydro-2H-benzo[*c*]benzo[4,5]furo[3,2-*g*]chromen-5-one (63). Yield 86%, mp 242°C, $C_{20}H_{20}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.80-1.90 (8H, m, CH_2-2, CH_2-3, CH_2-10, CH_2-11), 2.42 (2H, m, CH_2-1), 2.44 (3H, s, CH_3-7), 2.60 (2H, m, CH_2-12), 2.74 (2H, m, CH_2-9), 2.83 (2H, m, CH_2-4), 7.52 (1H, s, H-11).

3,4-Dimethyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (64). Yield 79%, mp 176°C, $C_{17}H_{16}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.77 (4H, m, CH_2-9 and CH_2-10), 2.36 (3H, s, CH_3-4), 2.44 (2H, m, CH_2-11), 2.64 (3H, s, CH_3-3), 3.13 (2H, m, CH_2-8), 6.97 (1H, s, H-5), 7.77 (1H, s, H-2).

2,3,4-Trimethyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (65). Yield 82%, mp 189°C, $C_{18}H_{18}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.75 (4H, m, CH_2-9 and CH_2-10), 2.27 (3H, s, CH_3-4), 2.36 (3H, s, CH_3-3), 2.41 (2H, m, CH_2-11), 2.50 (3H, s, CH_3-2), 3.06 (2H, m, CH_2-8), 6.88 (1H, s, H-5).

2,4-Dimethyl-3-phenyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (66). Yield 79%, mp 154°C, $C_{23}H_{20}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.76 (4H, m, CH_2-9 and CH_2-10), 2.06 (3H, s, CH_3-4), 2.32 (3H, s, CH_3-2), 2.42 (2H, m, CH_2-11), 3.14 (2H, m, CH_2-8), 6.95 (1H, s, H-5), 7.38-7.52 (5H, m, Ph-3).

4-Methyl-3-phenyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (67). Yield 83%, mp 179°C, $C_{22}H_{18}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.78 (4H, m, CH_2-9 and CH_2-10), 2.21 (3H, s, CH_3-4), 2.45 (2H, m, CH_2-11), 3.18 (2H, m, CH_2-8), 7.07 (1H, s, H-5), 7.40-7.50 (5H, m, Ph-3), 8.12 (1H, s, H-2).

3-(4-Fluorophenyl)-4-methyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (68). Yield 84%, mp 207°C, $C_{22}H_{17}FO_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.76 (4H, m, CH_2-9 and CH_2-10), 2.18 (3H, s, CH_3-4), 2.40 (2H, m, CH_2-11), 3.09 (2H, m, CH_2-8), 6.98 (1H, s, H-5), 7.30 (2H, m, H-3′ and H-5′ Ar-3), 7.50 (2H, m, H-2′ and H-6′ Ar-3), 8.09 (1H, s, H-2).

3-(4-Chlorophenyl)-4-methyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (69). Yield 89%, mp 224°C, $C_{22}H_{17}ClO_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.79 (4H, m, CH_2-9 and CH_2-10), 2.23 (3H, s, CH_3-4), 2.47 (2H, m, CH_2-11), 3.21 (2H, m, CH_2-8), 7.10 (1H, s, H-5), 7.50 (4H, m, Ar-3), 8.14 (1H, s, H-2).

3-(4-Bromophenyl)-4-methyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (70). Yield 82%, mp 238°C, $C_{22}H_{17}BrO_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.80 (4H, m, CH_2-9 and CH_2-10), 2.22 (3H, s, CH_3-4), 2.45 (2H, m, CH_2-11), 3.18 (2H, m, CH_2-8), 7.08 (1H, s, H-5), 7.46 (2H, d, J = 8, H-3′ and H-5′ Ar-3), 7.66 (2H, d, J = 8, H-2′ and H-6′ Ar-3), 8.13 (1H, s, H-2).

4-Methyl-3-(4-methylphenyl)-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (71). Yield 81%, mp 195°C, $C_{23}H_{20}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.76 (4H, m, CH_2-9 and CH_2-10), 2.18 (3H, s, CH_3-4), 2.38 (3H, s, CH_3-4′ Ar-3), 2.40 (2H, m, CH_2-11), 3.12 (2H, m, CH_2-8), 6.99 (1H, s, H-5), 7.25 (2H, d, J = 8, H-3′ and H-5′ Ar-3), 7.33 (2H, d, J = 8, H-2′ and H-6′ Ar-3), 8.04 (1H, s, H-2).

3-(4-Methoxyphenyl)-4-methyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (72). Yield 89%, mp 200°C, $C_{23}H_{20}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.81 (4H, m, CH_2-9 and CH_2-10), 2.22 (3H, s, CH_3-4), 2.44 (2H, m, CH_2-11), 3.17 (2H, m, CH_2-8), 3.82 (3H, s, CH_3O-4′ Ar-3), 7.02 (2H, d, J = 8, H-3′ and H-5′ Ar-3), 7.05 (1H, s, H-5), 7.38 (2H, d, J = 8, H-2′ and H-6′ Ar-3), 8.06 (1H, s, H-2).

3-(3-Methoxyphenyl)-4-methyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (73). Yield 83%, mp 210°C, $C_{23}H_{20}O_4$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.81 (4H, m, CH_2-9 and CH_2-10), 2.24 (3H, s, CH_3-4), 2.44 (2H, m, CH_2-11), 3.19 (2H, m, CH_2-8), 3.81 (3H, s, CH_3O-3′ Ar-3), 7.03 (1H, s, H-5), 7.05 (3H, m, H-4′, H-5′, H-6′ Ar-3), 7.39 (1H, m, H-2′ Ar-3), 8.08 (1H, s, H-2).

3-(1,3-Benzodioxol-5-yl)-4-methyl-8,9,10,11-tetrahydro-7H-benzo[*c*]furo[2,3-*f*]chromen-7-one (74). Yield 82%, mp 181°C, $C_{23}H_{18}O_5$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.79 (4H, m, CH_2-9 and CH_2-10), 2.25 (3H, s, CH_3-4), 2.40 (2H, m, CH_2-11), 3.15 (2H, m, CH_2-8), 6.05 (2H, s, OCH_2O Ar-10), 7.01 (1H, s, H-5), 7.05 (1H, d, J = 8.5, H-7′ Ar-10), 7.18 (1H, dd, $J_{6,4}$ = 2.0, $J_{6,7}$ = 8.5, H-6′ Ar-10), 7.25 (1H, d, J = 2, H-4′ Ar-10), 8.07 (1H, s, H-2).

8-Methyl-1,3,4,5,9,10,11,12-octahydro-2H-benzo[*c*]benzo[4,5]furo[2,3-*f*]chromen-5-one (75). Yield 65%, mp 172°C, $C_{20}H_{20}O_3$.

PMR spectrum (300 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.70-1.90 (8H, m, CH_2-2, CH_2-3, CH_2-10, CH_2-11), 2.41 (2H, m, CH_2-9), 2.57 (3H, s, CH_3-8), 2.78 (4H, m, CH_2-1, CH_2-12), 3.14 (2H, m, CH_2-4), 6.93 (1H, s, H-7).

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