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Reductive rearrangement of 2-aroyl-2,3-dihydrobenzofurans into 2-hydroxydihydrochalcones and flav-2-enes

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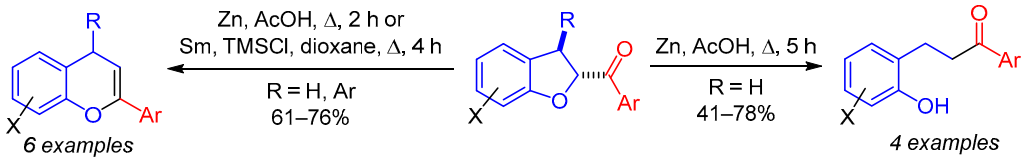


X = H, Cl, *t*-Bu, Me, adamantan-1-yl; Ar = Ph, 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 3,4,5-(MeO)$_3$C$_6$H$_2$

A two-step procedure was proposed for the synthesis of 2-aryl- and 2,4-diaryl-substituted 4*H*-chromenes by the formal [4+1] cycloaddition reaction of *o*-quinone methides and pyridinium ylides followed by reductive rearrangement of 2-aroyl-2,3-dihydrobenzofurans by the action of zinc in acetic acid or samarium and trimethylchlorosilane in 1,4-dioxane. The reduction of 3-unsubstituted 2-aroyl-2,3-dihydrobenzofurans by the action of zinc in acetic acid leads mainly to 2-hydroxydihydrochalcones.

Keywords: 2-aroyl-2,3-dihydrobenzofurans, 4*H*-chromenes, flav-2-enes, 2-hydroxydihydrochalcones, *o*-quinone methides, samarium, zinc, reductive rearrangement.

The 4*H*-chromene fragment is a key structural feature of many biologically active compounds. Among them, promising drugs with anticancer and antibacterial effects were found.[1] At the same time, 2-aryl-4*H*-chromenes (flav-2-enes) are rarely encountered in the structure of natural compounds, which may be explained by their high chemical activity due to which they themselves can potentially be synthetic precursors to many other natural flavonoids and their derivatives.[2] Flavonoids **A**–**E** can be given as examples of 2-aryl-4*H*-chromenes of plant origin (Fig. 1).[3]

Currently, the principal methods for the preparation of 2-substituted and 2,4-disubstituted 4*H*-chromenes are the addition of nucleophiles to benzopyrylium salts, reduction of flavones, cyclization reactions with the participation of α,β-enones, isomerization of 2*H*-chromenes, and [4+2] cycloaddition involving *o*-quinone methides.[4]

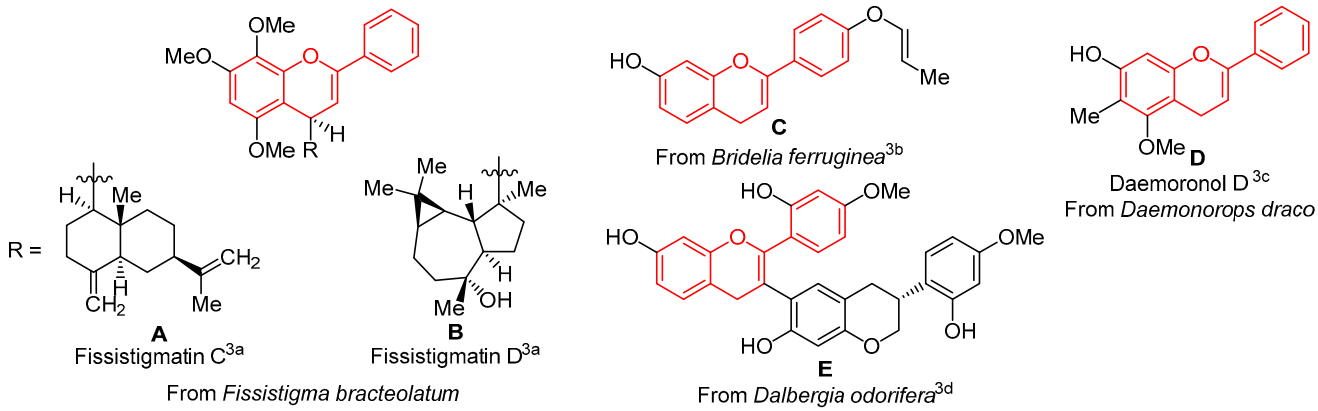
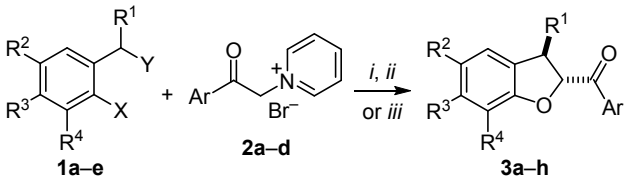


Figure 1. Natural 2-aryl-4*H*-chromenes.

As enol esters, flav-2-enes easily enter into addition reactions with electrophilic reagents, are sensitive to oxidants, including atmospheric oxygen, readily hydrolyze to form 2-hydroxydihydrochalcones, and can also undergo disproportionation to chromanes and benzopyrylium salts and isomerize to 2*H*-chromenes.[5] However, the study of the chemical properties and biological activity of flav-2-enes is constrained by their low content in natural sources, low availability of biological material, laborious methods of isolation and purification, as well as a relatively small number of methods for their synthesis. In this regard, the development of novel methods for the preparation of 2-aryl-4*H*-chromenes is of practical interest.

We have previously developed an efficient approach to the synthesis of 2-acyl-2,3-dihydrobenzofurans and 2-acyl-1,2-dihydronaphtho[2,1-*b*]furans based on the precursors of *o*-quinone methides[6] and pyridinium ylides as synthetic equivalents of acylcarbenes.[7] Using the proposed method, a series of 2-aroyl-2,3-dihydrobenzofurans, both new and previously described in the literature but synthesized by other methods, were obtained (Scheme 1). Diacetates of salicylic alcohols and products of *o*-aminomethylation and quaternization of phenols **1a**–**e** were used as precursors of benzene *o*-quinone methides. The reactions were carried out under an inert atmosphere to prevent possible oxidation to benzofurans by heating under reflux in MeCN or in DMF in the case of the less active precursor of *o*-quinone methide, the phenol Mannich base (X = OH, Y = NMe_2). DBU or DIPEA were used as bases to generate pyridinium ylides from *N*-phenacylpyridinium salts **2a**–**d**. In the case of 2,3-disubstituted dihydrobenzofurans **3f**–**h**, the reaction proceeds diastereoselectively and leads to the *trans*-isomers, as evidenced by ^{1}H NMR spectroscopy data. The methine protons of the dihydrofuran ring appear as doublets in the ranges of 4.87–5.00 (3-CH) and 5.77–5.84 (2-CH) ppm with ^3J = 6.4–6.7 Hz, which is typical for *trans*-isomers.

Scheme 1

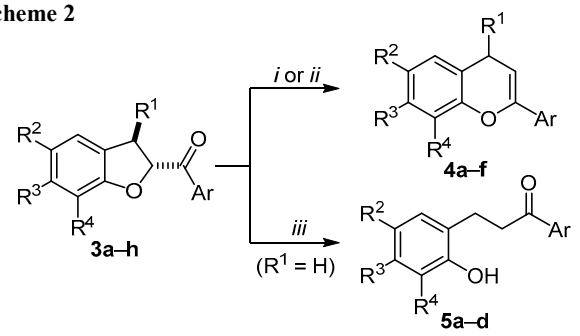


3a R^1 = R^3 = R^4 = H, R^2 = Cl, Ar = Ph (52%)
b R^1 = R^3 = R^4 = H, R^2 = *t*-Bu, Ar = Ph (54%)
c R^1 = R^4 = H, R^2 = R^3 = Me, Ar = Ph (57%)
d R^1 = R^3 = H, R^2 = *t*-Bu, R^4 = adamantan-1-yl, Ar = Ph (60%)
e R^1 = R^3 = R^4 = H, R^2 = Cl, Ar = 4-MeC_6H_4 (73%)
f R^1 = Ph, R^2 = R^3 = R^4 = H, Ar = 4-MeC_6H_4 (61%)
g R^1 = Ph, R^2 = R^3 = R^4 = H, Ar = 4-$MeOC_6H_4$ (67%)
h R^1 = Ph, R^2 = R^3 = R^4 = H, Ar = 3,4,5-$(MeO)_3C_6H_2$ (66%)

For **3a**,**e**–**h** X = Y = OAc
i: DBU (2 equiv), argon, MeCN, Δ, 8 h
For **3b**,**c** X = OH, Y = $N^+Me_3I^-$
ii: DBU (1 equiv), argon, MeCN, Δ, 12 h
For **3d** X = OH, Y = NMe_2
iii: DIPEA (1.2 equiv), argon, DMF, Δ, 12 h

Upon the action of zinc on 2-aroyl-2,3-dihydrobenzofurans **3a**–**h** in AcOH, it turned out that 3-phenyl-substituted derivatives **3f**–**h**, as well as compound **3d**, rearranged into 2-aryl-4*H*-chromenes **4a**–**d** in 62–76% yields; however, in the case of substrates **3a**–**c**,**e** unsubstituted at the C-3 position, the main products were 3-(2-hydroxyaryl)propan-1-ones **5a**–**d** (Scheme 2).

Scheme 2



4a R^1 = Ph, R^2 = R^3 = R^4 = H, Ar = 4-MeC_6H_4 (76%)
b R^1 = Ph, R^2 = R^3 = R^4 = H, Ar = 4-$MeOC_6H_4$ (72%)
c R^1 = Ph, R^2 = R^3 = R^4 = H, Ar = 3,4,5-$(MeO)_3C_6H_2$ (69%)
d R^1 = R^3 = H, R^2 = *t*-Bu, R^4 = adamantan-1-yl, Ar = Ph (62%)
e R^1 = R^3 = R^4 = H, R^2 = *t*-Bu, Ar = Ph (72%)
f R^1 = R^4 = H, R^2 = R^3 = Me, Ar = Ph (61%)
5a R^2 = Cl, R^3 = R^4 = H, Ar = Ph (59%)
b R^2 = *t*-Bu, R^3 = R^4 = H, Ar = Ph (41%)
c R^2 = R^3 = Me, R^4 = H, Ar = Ph (63%)
d R^2 = Cl, R^3 = R^4 = H, Ar = 4-$MeOC_6H_4$ (78%)

For **4a**–**d** *i*: Zn (5 equiv), argon, AcOH, Δ, 2 h
For **4e**,**f** *ii*: Sm (4 equiv), TMSCl (4 equiv), argon, dioxane, Δ, 4 h
For **5a**–**d** *iii*: Zn (5 equiv), argon, AcOH, Δ, 5 h

The reactions were carried out by heating under reflux in AcOH with vigorous stirring for 2–5 h using excess zinc dust. Increasing the stirring speed and the amount of Zn up to 5 equiv shortens the reaction time and increases the product yield. The use of stoichiometric amounts of metal does not lead to complete conversion of dihydrobenzofurans **3a**–**h** even during prolonged heating under reflux of the reaction mixture, which is apparently due to the accompanying reaction of Zn and AcOH with the formation of $Zn(OAc)_2$ and H_2. The tendency of 2-aryl-4*H*-chromenes to oxidize makes it necessary to use an inert atmosphere to achieve acceptable yields. The obtained 3-(2-hydroxyaryl)propan-1-ones **5a**–**d** may also be of some interest due to the wide spectrum of biological activity of dihydrochalcones, of which they are representatives.[8]

The successful synthesis of 2-phenyl-4*H*-chromenes **4e**,**f** from the corresponding 3-unsubstituted 2-benzoyl-2,3-dihydrobenzofurans **3b**,**c** was carried out by replacing the Zn–AcOH reducing system with a combination of Sm with TMSCl in 1,4-dioxane, which made it possible to avoid the formation of 2-hydroxydihydrochalcones **5b**,**c** (Scheme 2). Chromenes **4e**,**f** were obtained in 72 and 61% yields by heating with an excess of finely dispersed Sm and TMSCl in 1,4-dioxane under reflux. It should be noted that although metallic Sm is less active in reduction processes than the widely used SmI_2, its use offers a number of advantages. It is much less sensitive to atmospheric oxygen, stable during storage, convenient to use, and is a cheaper reducing agent, and the Sm activity can be easily

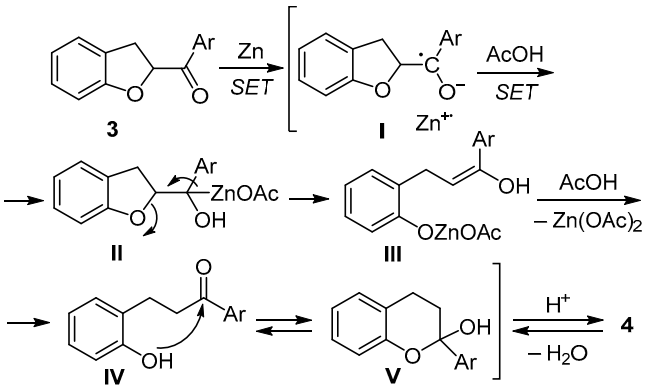
modified by adding halogen-containing reagents (I_2, TMSCl, RHal, HCl, etc.). These factors are responsible for the increasing popularity of the use of metallic Sm in organic synthesis.[9]

In the ^{1}H NMR spectra of 2,4-diaryl-substituted 4*H*-chromenes **4a**–**c**, the pyran ring protons appear as doublets at 4.83–4.85 (4-CH) and 5.48–5.56 (3-CH) ppm with ^3J = 4.0–4.1 Hz, and the carbon atoms bound to them in the ^{13}C NMR spectra are found in the ranges 41.2–41.3 (C-4) and 99.3–100.8 (C-3) ppm. In the ^{1}H NMR spectra of chromenes **4d**–**f** unsubstituted at position 4, protons at positions 4 and 3 appear, respectively, as a doublet (at 3.51–3.61 ppm) and a triplet (at 5.48–5.56 ppm) with ^3J = 3.9 Hz, whereas the carbon atoms bound to them in the ^{13}C NMR spectra resonate in the ranges of 24.2–25.6 (C-4) and 96.4–97.0 (C-3) ppm.

In the ^{1}H NMR spectra of dihydrochalcones **5a**–**d**, the protons of the methylene groups appear as multiplets at 2.95–3.05 and 3.37–3.46 ppm. The carbonyl carbon atom in the ^{13}C NMR spectra corresponds to the signal at 200.5–202.1 ppm.

The mechanism of the rearrangement of 2-aroyl-2,3-dihydrobenzofurans **3** by the action of Zn in AcOH, apparently, involves a double one-electron reduction of the carbonyl group *via* ketyl radical **I** with the formation of organozinc intermediate **II**. Opening of the dihydrofuran ring in it gives phenolate **III**, the protonation of which followed by ketalization of 2-hydroxydihydrochalcone **IV** and dehydration of chromanol **V** leads to chromene **4** (Scheme 3).

Scheme 3



No dihydrochalcones formed upon the reduction with metallic Sm, which can be explained by a change in the reaction mechanism which apparently involves carbenoid-type intermediates, as was previously described for the reductive rearrangement of annulated dihydrofurans.[10]

To conclude, we proposed two reduction systems (Zn in AcOH and Sm + TMSCl in 1,4-dioxane) for the transformation of 2-aroyl-2,3-dihydrobenzofurans into 2-aryl-4*H*-chromenes.

Experimental

IR spectra were registered on a Shimadzu IRAffinity-1 spectrometer equipped with a Specac Diamond ATR GS 10800-B attachment. A JEOL JNM-ECX400 spectrometer was used to record ^{1}H and ^{13}C NMR spectra (400 and 100 MHz, respectively) as well as perform DEPT-135 experiments. NMR spectra were recorded in $CDCl_3$ using residual solvent signals as internal standard (7.26 ppm for ^{1}H nuclei, 77.2 ppm for ^{13}C nuclei). Elemental analysis was performed on a Euro Vector EA-3000 CHNS-analyzer. Melting points were determined by the capillary method on an SRS OptiMelt MPA100 apparatus. Monitoring of the reaction progress and assessment of the purity of synthesized compounds were done by TLC on Merck Silica gel 60 F_{254} plates, visualization with UV light or by iodine stain. Merck Silica gel 60, 0.04–0.063 mm fraction was used for column chromatography.

Synthesis of 2-aroyl-2,3-dihydrobenzofurans 3a,e–h (General method). DBU (0.9 ml, 0.91 g, 6 mmol) was added to a mixture of 2-acetoxy-5-chlorobenzyl acetate (0.73 g, 3 mmol) or 2-[acetoxy(phenyl)methyl]phenyl acetate (0.85 g, 3 mmol), pyridinium salt (3 mmol) in MeCN (20 ml), and the resulting solution was heated under reflux under an argon atmosphere for 8 h. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent CCl_4–$CHCl_3$, 1:1) followed by recrystallization from EtOH.

Synthesis of 2-aroyl-2,3-dihydrobenzofurans 3b,c (General method). DBU (0.45 ml, 0.46 g, 3 mmol) was added to a mixture of 1-(5-*tert*-butyl-2-hydroxyphenyl)-*N*,*N*,*N*-trimethylmethane ammonium iodide (1.05 g, 3 mmol) or 1-(2-hydroxy-4,5-dimethylphenyl)-*N*,*N*,*N*-trimethylmethane ammonium iodide (0.96 g, 3 mmol), 2-oxo-2-phenylethylpyridinium bromide (0.83 g, 3 mmol) in MeCN (20 ml), and the resulting solution was heated under reflux under an argon atmosphere for 12 h. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent $CHCl_3$) followed by recrystallization from EtOH.

5-Chloro-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (3a). Yield 405 mg (52%), colorless crystals, mp 140–141°C. IR spectrum, ν, cm^{-1}: 3063, 1697 (C=O), 1595, 1476, 1447, 1379, 1298, 1279, 1240, 1227, 1173, 1115, 1003, 993, 918, 885, 825, 694, 677. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.51 (1H, dd, *J* = 16.0, *J* = 10.3, 3-CH$_2$); 3.58 (1H, dd, *J* = 16.0, *J* = 7.3, 3-CH$_2$); 5.96 (1H, dd, *J* = 10.3, *J* = 7.3, 2-CH); 6.77 (1H, d, *J* = 8.5, H-7); 7.08 (1H, dd, *J* = 8.5, *J* = 2.3, H-6); 7.13 (1H, d, *J* = 2.3, H-4); 7.48–7.52 (2H, m, H-3',5'); 7.62 (1H, t, *J* = 7.6, H-4'); 8.02 (2H, d, *J* = 7.8, H-2',6'). ^{13}C NMR spectrum, δ, ppm: 32.4 (CH$_2$); 83.1 (2-CH); 110.8 (CH); 125.1 (CH); 126.0; 127.3; 128.3 (CH); 128.9 (2CH Ph); 129.2 (2CH Ph); 134.0 (CH); 134.3; 157.8 (C-7a); 195.0 (C=O). Found, %: C 69.72; H 4.34. $C_{15}H_{11}ClO_2$. Calculated, %: C 69.64; H 4.29.

[5-(*tert*-Butyl)-2,3-dihydrobenzofuran-2-yl](phenyl)methanone (3b). Yield 455 mg (54%), colorless crystals, mp 102–104°C. IR spectrum, ν, cm^{-1}: 2951, 2907, 1692 (C=O), 1595, 1582, 1493, 1449, 1364, 1312, 1233, 1179, 1167, 1123, 1057, 1018, 993, 918, 905, 880, 818, 770, 700, 669. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.29 (9H, s, C(CH$_3$)$_3$); 3.54 (1H, dd, *J* = 15.6, *J* = 10.3, 3-CH$_2$); 3.60 (1H, dd, *J* = 15.6, *J* = 7.6, 3-CH$_2$); 5.92 (1H, dd, *J* = 10.3, *J* = 7.6, 2-CH); 6.80 (1H, d, *J* = 8.5, H-7); 7.16 (1H, dd, *J* = 8.5,

J = 2.3, H-6); 7.22 (1H, br. s, H-4); 7.48–7.52 (2H, m, H-3',5'); 7.61 (1H, tt, *J* = 7.6, *J* = 1.4, H-4'); 8.03–8.06 (2H, m, H-2',6'). ^{13}C NMR spectrum, δ, ppm: 31.8 (C($\underline{C}$H$_3$)$_3$); 32.9 (CH$_2$); 34.4 ($\underline{C}$(CH$_3$)$_3$); 82.9 (2-CH); 109.0 (CH); 121.9 (CH); 124.8; 125.2 (CH); 128.8 (2CH Ph); 129.2 (2CH Ph); 133.7 (CH); 134.7; 144.3; 156.9 (C-7a); 195.8 (C=O). Found, %: C 81.32; H 7.13. $C_{19}H_{20}O_2$. Calculated, %: C 81.40; H 7.19.

(5,6-Dimethyl-2,3-dihydrobenzofuran-2-yl)(phenyl)-methanone (3c). Yield 430 mg (57%), colorless crystals, mp 97–99°C. IR spectrum, ν, cm^{-1}: 2899, 2845, 1674 (C=O), 1597, 1539, 1493, 1447, 1339, 1317, 1256, 1219, 1157, 1126, 1090, 1061, 914, 860, 806, 773, 692, 658. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.18 (3H, s, CH$_3$); 2.21 (3H, s, CH$_3$); 3.49–3.51 (2H, m, 3-CH$_2$); 5.89 (1H, dd, *J* = 9.4, *J* = 8.0, 2-CH); 6.70 (1H, s, H-7); 6.94 (1H, s, H-4); 7.47–7.52 (2H, m, H-3',5'); 7.60 (1H, tt, *J* = 7.4, *J* = 1.4, H-4'); 8.01–8.04 (2H, m, H-2',6'). ^{13}C NMR spectrum, δ, ppm: 19.4 (CH$_3$); 20.2 (CH$_3$); 32.8 (CH$_2$); 82.9 (2-CH); 111.0 (CH); 122.2; 125.8 (CH); 128.8 (2CH Ph); 129.1; 129.2 (2CH Ph); 133.7 (CH); 134.6; 136.7; 157.5 (C-7a); 196.0 (C=O). Found, %: C 80.85; H 6.33. $C_{17}H_{16}O_2$. Calculated, %: C 80.93; H 6.39.

[7-(Adamantan-1-yl)-5-(*tert*-butyl)-2,3-dihydrobenzo-furan-2-yl](phenyl)methanone (3d). A mixture of 6-(adamantan-1-yl)-4-(*tert*-butyl)-2-[(dimethylamino)methyl]-phenol (1.02 g, 3 mmol), 1-(2-oxo-2-phenylethyl)pyridinium bromide (0.83 g, 3 mmol), and Hünig's base (DIPEA) (0.6 ml, 0.45 g, 3.5 mmol) in DMF (10 ml) was heated under reflux under an argon atmosphere for 12 h. The solution was cooled to room temperature and poured into H$_2$O (50 ml). The product was extracted with EtOAc (2×25 ml), the extract was washed with H$_2$O, saturated aqueous NaCl and dried over anhydrous Na$_2$SO$_4$. The solvent was distilled off under reduced pressure, the residue was purified by column chromatography on silica gel (eluent CHCl$_3$) followed by recrystallization from EtOH. Yield 475 mg (60%), colorless crystals, mp 152–154°C. IR spectrum, ν, cm^{-1}: 2965, 2903, 2847, 1694 (C=O), 1599, 1479, 1450, 1362, 1300, 1221, 1177, 1099, 1015, 978, 924, 872, 826, 748, 692. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 (9H, s, C(CH$_3$)$_3$); 1.73 (6H, br. s, 3CH$_2$ Ad); 1.97–2.01 (9H, m, 3CH Ad, 3CH$_2$ Ad); 3.47 (1H, dd, *J* = 15.6, *J* = 10.6, 3-CH$_2$); 3.67 (1H, dd, *J* = 15.6, *J* = 6.6, 3-CH$_2$); 5.87 (1H, dd, *J* = 10.6, *J* = 6.6, 2-CH); 7.06 (1H, d, *J* = 1.8, H-4(6)); 7.10 (1H, d, *J* = 1.8, H-6(4)); 7.49 (2H, dd, *J* = 7.8, *J* = 7.3, H-3',5'); 7.59 (1H, t, *J* = 7.3, H-4'); 8.11 (2H, d, *J* = 7.8, H-2',6'). ^{13}C NMR spectrum, δ, ppm: 29.0 (3CH Ad); 31.8 (3-CH$_2$); 31.9 (C($\underline{C}$H$_3$)$_3$); 34.6 ($\underline{C}$(CH$_3$)$_3$); 36.2 (C Ad); 37.1 (3CH$_2$ Ad); 40.5 (3CH$_2$ Ad); 83.0 (2-CH); 119.3 (CH); 121.8 (CH); 125.3; 128.6 (2CH Ph); 129.5 (2CH Ph); 132.7; 133.5 (CH); 135.0; 144.0; 154.5 (C-7a); 196.7 (C=O). Found, %: C 83.94; H 8.32. $C_{29}H_{34}O_2$. Calculated, %: C 84.02; H 8.27.

(5-Chloro-2,3-dihydrobenzofuran-2-yl)(4-methoxy-phenyl)methanone (3e). Yield 632 mg (73%), colorless crystals, mp 123–124°C. IR spectrum, ν, cm^{-1}: 2943, 1670 (C=O), 1605, 1574, 1512, 1481, 1447, 1423, 1323, 1273, 1250, 1169, 1115, 1065, 1022, 988, 907, 853, 810, 679. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.48 (1H, dd, *J* = 16.0, *J* = 10.3, 3-CH$_2$); 3.59 (1H, dd, *J* = 16.0, *J* = 7.3, 3-CH$_2$); 3.88 (3H, s, CH$_3$O); 5.91 (1H, dd, *J* = 10.3, *J* = 7.3, 2-CH); 6.77 (1H, d, *J* = 8.5, H-7); 6.97 (2H, d, *J* = 8.9, H-3',5'); 7.08 (1H, dd, *J* = 8.5, *J* = 2.3, H-6); 7.14 (1H, br. s, H-4); 8.01 (2H, d, *J* = 8.9, H-2',6'). ^{13}C NMR spectrum, δ, ppm: 32.4 (CH$_2$); 55.7 (CH$_3$O); 83.0 (2-CH); 110.7 (CH); 114.1 (2CH Ph); 125.1 (CH); 125.9; 127.3; 127.5; 128.2 (CH); 131.6 (2CH Ph); 157.8 (C-7a); 164.2 ($\underline{C}$OCH$_3$); 193.4 (C=O). Found, %: C 66.47; H 4.48. $C_{16}H_{13}ClO_3$. Calculated, %: C 66.56; H 4.54.

((2*R,3*R**)-3-Phenyl-2,3-dihydrobenzofuran-2-yl)-(*p*-tolyl)methanone (3f)**. Yield 575 mg (61%), colorless crystals, mp 100–101°C. IR spectrum, ν, cm^{-1}: 3028, 2951, 1694 (C=O), 1601, 1477, 1462, 1408, 1234, 1207, 1184, 1099, 1053, 1011, 984, 968, 953, 891, 814, 756, 702. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.42 (3H, s, CH$_3$); 4.98 (1H, d, *J* = 6.4, 3-CH); 5.80 (1H, d, *J* = 6.4, 2-CH); 6.89 (1H, td, *J* = 7.6, *J* = 0.9, H Ar); 6.97–7.01 (2H, m, H Ar); 7.19–7.36 (8H, m, H Ar); 7.86 (2H, d, *J* = 8.3, H Ar). ^{13}C NMR spectrum, δ, ppm: 21.9 (CH$_3$); 51.0 (3-CH); 90.6 (2-CH); 110.1 (CH); 121.7 (CH); 125.4 (CH); 127.5 (CH); 128.3 (2CH); 129.0 (CH); 129.1 (2CH); 129.4; 129.5 (4CH); 132.0; 142.5; 144.9; 159.2 (C-7a); 194.4 (C=O). Found, %: C 83.95; H 5.86. $C_{22}H_{18}O_2$. Calculated, %: C 84.05; H 5.77.

(4-Methoxyphenyl)((2*R,3*R**)-3-phenyl-2,3-dihydro-benzofuran-2-yl)methanone (3g)**. Yield 665 mg (67%), colorless crystals, mp 151–152°C. IR spectrum, ν, cm^{-1}: 1684 (C=O), 1597, 1574, 1477, 1462, 1423, 1256, 1231, 1213, 1180, 1049, 1015, 961, 837, 810, 756, 698. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.87 (3H, s, CH$_3$O); 5.00 (1H, d, *J* = 6.6, 3-CH); 5.77 (1H, d, *J* = 6.6, 2-CH); 6.87–6.93 (3H, m, H Ar); 6.97 (1H, d, *J* = 8.0, H Ar); 7.00 (1H, d, *J* = 7.6, H Ar); 7.18–7.30 (4H, m, H Ar); 7.31–7.36 (2H, m, H Ar); 7.94 (2H, d, *J* = 8.9, H Ar). ^{13}C NMR spectrum, δ, ppm: 51.0 (3-CH); 55.6 (CH$_3$O); 90.6 (2-CH); 110.0 (CH); 114.0 (2CH); 121.6 (CH); 125.4 (CH); 127.5 (CH); 127.6; 128.3 (2CH); 128.9 (CH); 129.1 (2CH); 129.5; 131.8 (2CH); 142.5; 159.2 (C-7a); 164.1 ($\underline{C}$OCH$_3$); 193.2 (C=O). Found, %: C 79.92; H 5.43. $C_{22}H_{18}O_3$. Calculated, %: C 79.98; H 5.49.

((2*R,3*R**)-3-Phenyl-2,3-dihydrobenzofuran-2-yl)-(3,4,5-trimethoxyphenyl)methanone (3h)**. Yield 773 mg (66%), colorless crystals, mp 122–124°C. IR spectrum, ν, cm^{-1}: 1688 (C=O), 1584, 1506, 1481, 1456, 1418, 1323, 1248, 1161, 1125, 1036, 989, 860, 822, 762, 698, 625. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.72 (6H, s, 2CH$_3$O); 3.91 (3H, s, CH$_3$O); 4.87 (1H, d, *J* = 6.7, 3-CH); 5.84 (1H, d, *J* = 6.7, 2-CH); 6.88 (1H, t, *J* = 7.5, H Ar); 6.97 (1H, d, *J* = 7.6, H Ar); 7.00 (1H, d, *J* = 8.0, H Ar); 7.12 (2H, s, H-2',6'); 7.19–7.36 (6H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 52.0 (3-CH); 56.1 (2CH$_3$O); 61.1 (CH$_3$O); 90.7 (2-CH); 106.6 (2CH); 110.1 (CH); 121.7 (CH); 125.4 (CH); 127.7 (CH); 128.3 (2CH Ph); 129.1 (CH); 129.2 (CH, 2CH Ph); 129.2; 129.3; 142.4; 143.1; 153.2 (2$\underline{C}$OCH$_3$); 159.2 (C-7a); 193.7 (C=O). Found, %: C 73.78; H 5.60. $C_{24}H_{22}O_5$. Calculated, %: C 73.83; H 5.68.

Synthesis of 2-aryl-4*H*-chromenes 4a–d and 2-hydroxy-dihydrochalcones 5a–d (General method). A mixture of 2-aroyl-2,3-dihydrobenzofuran **3a–c**,**e** (1 mmol) and zinc

dust (0.33 g, 5 mmol) in AcOH (10 ml) was heated under reflux with vigorous stirring for 2 h (for products **4a**–**d**) or 5 h (for products **5a**–**d**) under an argon atmosphere (TLC control, eluent $CHCl_3$–CCl_4, 1:1). After completion of the reaction, the mixture was cooled, poured into H_2O (50 ml), and the product was extracted with EtOAc (2×20 ml). The organic phase was washed with H_2O, aqueous $NaHCO_3$, saturated aqueous NaCl and dried over anhydrous Na_2SO_4. The solvent was distilled off under reduced pressure, the residue was purified by column chromatography on silica gel (eluent $CHCl_3$–CCl_4, 1:1), followed by recrystallization from a suitable solvent.

Synthesis of 2-aryl-4*H*-chromenes 4e,f (General method). TMSCl (0.5 ml, 0.43 g, 4 mmol) was added to a mixture of 2-aroyl-2,3-dihydrobenzofuran **3b**,**c** (1 mmol) and finely dispersed samarium (0.6 g, 4 mmol) in 1,4-dioxane (15 ml). The reaction mixture was heated under reflux with vigorous stirring under an argon atmosphere for 4 h (TLC control, eluent $CHCl_3$–CCl_4, 1:1), cooled, and poured into H_2O (50 ml). The product was extracted with EtOAc (2×20 ml). The organic phase was washed with H_2O, saturated aqueous NaCl and dried over anhydrous Na_2SO_4. The solvent was distilled off under reduced pressure, the residue was purified by column chromatography on silica gel (eluent CCl_4) followed by recrystallization from MeOH.

4-Phenyl-2-(*p*-tolyl)-4*H*-chromene (4a). Yield 227 mg (76%), colorless crystals, mp 137–138°C (EtOH) (mp 137°C[11]). IR spectrum, ν, cm^{-1}: 3028, 1667 (C=C pyran), 1585, 1512, 1489, 1454, 1323, 1277, 1234, 1115, 1061, 1037, 999, 822, 795, 756, 698. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.39 (3H, s, CH_3); 4.85 (1H, d, *J* = 4.1, 4-CH); 5.56 (1H, d, *J* = 4.1, 3-CH); 6.94–6.99 (2H, m, H Ar); 7.14 (1H, d, *J* = 7.8, H Ar); 7.17–7.25 (4H, m, H Ar); 7.30–7.35 (4H, m, H Ar); 7.64 (2H, d, *J* = 8.2, H Ar). ^{13}C NMR spectrum, δ, ppm: 21.4 (CH_3); 41.2 (4-CH); 100.2 (3-CH); 116.8 (CH); 123.4; 123.5 (CH); 124.8 (2CH); 126.8 (CH); 127.8 (CH); 128.5 (2CH); 128.8 (2CH); 129.1 (2CH); 129.8 (CH); 131.5; 138.5; 146.9; 147.9; 151.1. Found, %: C 88.47; H 6.03. $C_{22}H_{18}O$. Calculated, %: C 88.56; H 6.08.

2-(4-Methoxyphenyl)-4-phenyl-4*H*-chromene (4b). Yield 225 mg (72%), colorless crystals, mp 116–118°C (EtOH) (mp 118–119°C[12]). IR spectrum, ν, cm^{-1}: 1665 (C=C pyran), 1609, 1582, 1512, 1485, 1454, 1290, 1252, 1231, 1175, 1111, 1028, 997, 831, 785, 760, 750, 692. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.84 (3H, s, CH_3O); 4.83 (1H, d, *J* = 4.0, 4-CH); 5.48 (1H, d, *J* = 4.0, 3-CH); 6.92 (2H, d, *J* = 8.9, H Ar); 6.95–6.99 (2H, m, H Ar); 7.12 (1H, d, *J* = 7.8, H Ar); 7.16–7.25 (2H, m, H Ar); 7.29–7.34 (4H, m, H Ar); 7.67 (2H, d, *J* = 8.9, H Ar). ^{13}C NMR spectrum, δ, ppm: 41.2 (4-CH); 55.4 (CH_3O); 99.3 (3-CH); 113.8 (2CH); 116.8 (CH); 123.5 (2CH); 126.2 (2CH); 126.7 (CH); 127.0; 127.7 (CH); 128.5 (2CH); 128.8 (2CH); 129.8 (CH); 147.0; 147.7; 151.1; 160.0 ($\underline{C}OCH_3$). Found, %: C 84.12; H 5.71. $C_{22}H_{18}O_2$. Calculated, %: C 84.05; H 5.77.

4-Phenyl-2-(3,4,5-trimethoxyphenyl)-4*H*-chromene (4c). Yield 258 mg (69%), colorless crystals, mp 167–168°C (EtOH). IR spectrum, ν, cm^{-1}: 2938, 1663 (C=C pyran), 1582, 1506, 1485, 1455, 1414, 1341, 1225, 1126, 993, 932, 841, 792, 756, 696. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.87 (3H, s, CH_3O); 3.90 (6H, s, $2CH_3O$); 4.84 (1H, d, *J* = 4.1, 4-CH); 5.51 (1H, d, *J* = 4.1, 3-CH); 6.94 (2H, s, H-2',6'); 6.96 (2H, d, *J* = 3.9, H Ar); 7.12 (1H, d, *J* = 8.0, H Ar); 7.16–7.25 (2H, m, H Ar); 7.29–7.35 (4H, m, H Ar). ^{13}C NMR spectrum, δ, ppm: 41.3 (4-CH); 56.3 ($2CH_3O$); 61.0 (CH_3O); 100.8 (3-CH); 102.3 (2CH); 116.7 (CH); 123.3; 123.7 (CH); 126.9 (CH); 127.8 (CH); 128.5 (2CH Ph); 128.8 (2CH Ph); 129.8 (CH); 130.0; 138.7; 146.7; 147.7; 150.9; 153.2 ($2\underline{C}OCH_3$). Found, %: C 76.90; H 5.96. $C_{24}H_{22}O_4$. Calculated, %: C 76.99; H 5.92.

8-(Adamantan-1-yl)-6-(*tert*-butyl)-2-phenyl-4*H*-chromene (4d). Yield 247 mg (62%), colorless crystals, mp 147–149°C (*i*-PrOH). IR spectrum, ν, cm^{-1}: 2959, 2905, 2851, 1674 (C=C pyran), 1597, 1497, 1470, 1450, 1362, 1342, 1323, 1285, 1196, 1126, 1045, 999, 872, 756, 737, 687. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.33 (9H, s, $C(CH_3)_3$); 1.80–1.88 (6H, m, $3CH_2$ Ad); 2.13 (3H, br. s, 3CH Ad); 2.23 (6H, br. s, $3CH_2$ Ad); 3.61 (2H, d, *J* = 3.9, 4-CH); 5.56 (1H, t, *J* = 3.9, 3-CH); 6.95 (1H, d, *J* = 2.3, H-5(7)); 7.19 (1H, d, *J* = 2.3, H-7(5)); 7.31–7.43 (3H, m, H Ph); 7.79–7.82 (2H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 25.6 (CH_2); 29.2 (3CH Ad); 31.6 ($C(\underline{C}H_3)_3$); 34.5 ($\underline{C}(CH_3)_3$); 37.2 ($3CH_2$ Ad); 37.4 (C Ad); 40.9 ($3CH_2$ Ad); 97.0 (3-CH); 118.9 (C); 122.3 (CH); 123.7 (CH); 124.9 (2CH); 128.1 (CH); 128.3 (2CH); 135.1; 137.1; 145.2; 148.7; 149.3. Found, %: C 87.25; H 8.59. $C_{29}H_{34}O$. Calculated, %: C 87.39; H 8.60.

6-(*tert*-Butyl)-2-phenyl-4*H*-chromene (4e). Yield 190 mg (72%), colorless crystals, mp 71–72°C. IR spectrum, ν, cm^{-1}: 2955, 2924, 1670 (C=C pyran), 1503, 1449, 1364, 1267, 1236, 1182, 1130, 1043, 1001, 880, 826, 754, 689. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.31 (9H, s, $C(CH_3)_3$); 3.58 (2H, d, *J* = 3.9, 4-CH); 5.50 (1H, t, *J* = 3.9, 3-CH); 6.96 (1H, d, *J* = 8.5, H-8); 7.08 (1H, d, *J* = 2.3, H-5); 7.19 (1H, dd, *J* = 8.5, *J* = 2.3, H-7); 7.31–7.39 (3H, m, H Ph); 7.66–7.68 (2H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 24.9 (CH_2); 31.6 ($C(\underline{C}H_3)_3$); 34.3 ($\underline{C}(CH_3)_3$); 96.4 (3-CH); 116.2 (CH); 118.9; 124.6 (CH, 2CH Ph); 125.7 (CH); 128.26 (CH); 128.34 (2CH Ph); 134.8; 146.2; 149.2; 149.8. Found, %: C 86.40; H 7.58. $C_{19}H_{20}O$. Calculated, %: C 86.32; H 7.63.

6,7-Dimethyl-2-phenyl-4*H*-chromene (4f). Yield 145 mg (61%), colorless crystals, mp 81–83°C. IR spectrum, ν, cm^{-1}: 2922, 2855, 1667 (C=C pyran), 1624, 1580, 1503, 1447, 1317, 1306, 1261, 1202, 1179, 1099, 1001, 868, 754, 689, 625. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.20 (3H, s, CH_3); 2.23 (3H, s, CH_3); 3.51 (2H, d, *J* = 3.9, 4-CH); 5.48 (1H, t, *J* = 3.9, 3-CH); 6.83 (2H, s, H-5,8); 7.29–7.40 (3H, m, H Ph); 7.66–7.68 (2H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 19.0 (CH_3); 19.6 (CH_3); 24.2 (CH_2); 96.4 (3-CH); 116.6; 117.5 (CH); 124.6 (2CH Ph); 128.2 (CH); 128.3 (2CH Ph); 129.7 (CH); 131.4; 134.9; 135.8; 149.1; 149.9. Found, %: C 86.48; H 6.86. $C_{17}H_{16}O$. Calculated, %: C 86.40; H 6.82.

3-(5-Chloro-2-hydroxyphenyl)-1-phenylpropan-1-one (5a). Yield 155 mg (59%), slowly crystallizing light-yellow oil, mp 48–50°C. IR spectrum, ν, cm^{-1}: 3322 (OH), 2832, 1663 (C=O), 1597, 1501, 1450, 1420, 1292, 1269, 1169, 1115, 994, 814, 663. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.97–3.00 (2H, m, CH_2); 3.43–3.46 (2H, m, CH_2); 6.85

(1H, d, *J* = 8.5, H-3); 7.05 (1H, dd, *J* = 8.5, *J* = 2.3, H-4); 7.09 (1H, d, *J* = 2.3, H-6); 7.43–7.47 (2H, m, H-3',5'); 7.56–7.60 (1H, m, H-4'); 7.95–7.98 (2H, m, H-2',6'); 8.19 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 23.3 (CH_2); 40.3 (CH_2); 119.1 (CH); 125.2; 127.9 (CH); 128.5 (2CH); 128.8 (2CH); 129.6; 130.2 (CH); 134.1 (CH); 135.9; 153.4 (C–OH); 202.1 (C=O). Found, %: C 69.17; H 5.08. $C_{15}H_{13}ClO_2$. Calculated, %: C 69.10; H 5.03.

3-[5-(*tert*-Butyl)-2-hydroxyphenyl]-1-phenylpropan-1-one (5b). Yield 115 mg (41%), light-yellow oil. IR spectrum, ν, cm^{-1}: 3354 (OH), 2959, 1663 (C=O), 1597, 1580, 1504, 1449, 1364, 1271, 1236, 1206, 1182, 1155, 1125, 1098, 976, 826, 741, 687. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 (9H, s, $C(CH_3)_3$); 3.02–3.05 (2H, m, CH_2); 3.43–3.46 (2H, m, CH_2); 6.84 (1H, d, *J* = 8.2, H-3); 7.11–7.14 (2H, m, H-4,6); 7.42–7.47 (2H, m, H-3',5'); 7.54–7.59 (1H, m, H-4'); 7.97–8.00 (2H, m, H-2',6'). The position of the signal of the proton of the OH group cannot be reliably identified due to its strong broadening. ^{13}C NMR spectrum, δ, ppm: 23.9 (CH_2); 31.7 ($C(\underline{C}H_3)_3$); 34.1 ($\underline{C}(CH_3)_3$); 40.6 (CH_2); 116.9 (CH); 125.0 (CH); 127.0; 127.4 (CH); 128.4 (2CH); 128.7 (2CH); 133.8 (CH); 136.3; 143.5; 152.2 (C–OH); 202.1 (C=O). Found, %: C 80.75; H 7.80. $C_{19}H_{22}O_2$. Calculated, %: C 80.82; H 7.85.

3-(2-Hydroxy-4,5-dimethylphenyl)-1-phenylpropan-1-one (5c). Yield 160 mg (63%), light-yellow oil. IR spectrum, ν, cm^{-1}: 3454 (OH), 1670 (C=O), 1597, 1580, 1518, 1450, 1412, 1368, 1290, 1204, 1179, 1084, 999, 972, 905, 847, 739, 685, 642, 592. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.16 (3H, s, CH_3); 2.17 (3H, s, CH_3); 2.96–2.99 (2H, m, CH_2); 3.39–3.42 (2H, m, CH_2); 6.72 (1H, s, H-3); 6.87 (1H, s, H-6); 7.42–7.46 (2H, m, H-3',5'); 7.54–7.58 (1H, m, H-4'); 7.95–7.98 (2H, m, H-2',6'). The position of the signal of the proton of the OH group cannot be reliably identified due to its strong broadening. ^{13}C NMR spectrum, δ, ppm: 18.8 (CH_3); 19.4 (CH_3); 23.1 (CH_2); 40.7 (CH_2); 118.7 (CH); 124.9; 128.4 (2CH); 128.5; 128.7 (2CH); 131.6 (CH); 133.7 (CH); 136.2; 136.4; 152.3 (C–OH); 202.0 (C=O). Found, %: C 80.21; H 7.09. $C_{17}H_{18}O_2$. Calculated, %: C 80.28; H 7.13.

3-(5-Chloro-2-hydroxyphenyl)-1-(4-methoxyphenyl)-propan-1-one (5d). Yield 227 mg (78%), slowly crystallizing light-yellow oil, mp 65–67°C. IR spectrum, ν, cm^{-1}: 3307 (OH), 3193, 1663 (C=O), 1593, 1512, 1427, 1327, 1300, 1261, 1177, 1119, 1028, 829. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.95–2.98 (2H, m, CH_2); 3.37–3.40 (2H, m, CH_2); 3.85 (3H, s, CH_3O); 6.84 (1H, d, *J* = 8.5, H-3); 6.90 (2H, d, *J* = 8.9, H-3',5'); 7.04 (1H, dd, *J* = 8.5, *J* = 2.5, H-4); 7.07 (1H, d, *J* = 2.5, H-6); 7.93 (2H, d, *J* = 8.9, H-2',6'); 8.54 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 23.4 (CH_2); 40.0 (CH_2); 55.7 (CH_3O); 114.0 (2CH); 119.1 (CH); 125.1; 127.9 (CH); 128.9; 129.9; 130.2 (CH); 130.9 (2CH); 153.5 (COH); 164.3 ($\underline{C}OCH_3$); 200.5 (C=O). Found, %: C 66.03; H 5.26. $C_{16}H_{15}ClO_3$. Calculated, %: C 66.10; H 5.20.

Supplementary information file containing ^{1}H and ^{13}C NMR spectra of all synthesized compounds is available at the journal website http://link.springer.com/journal/10593.

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