ISSN 1070-4280, Russian Journal of Organic Chemistry, 2013, Vol. 49, No. 1, pp. 99–107. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.B. Lipeeva, E.E. Shul'ts, M.M. Shakirov, G.A. Tolstikov, 2013, published in Zhurnal Organicheskoi Khimii, 2013, Vol. 49, No. 1, pp. 105–112.

Plant Coumarins: XI.* Cross Coupling Reactions with 2-(Tosyl)oreoselone

A. B. Lipeeva, E. E. Shul'ts, M. M. Shakirov, and G. A. Tolstikov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: schultz@nioch.nsc.ru

Received July 26, 2012

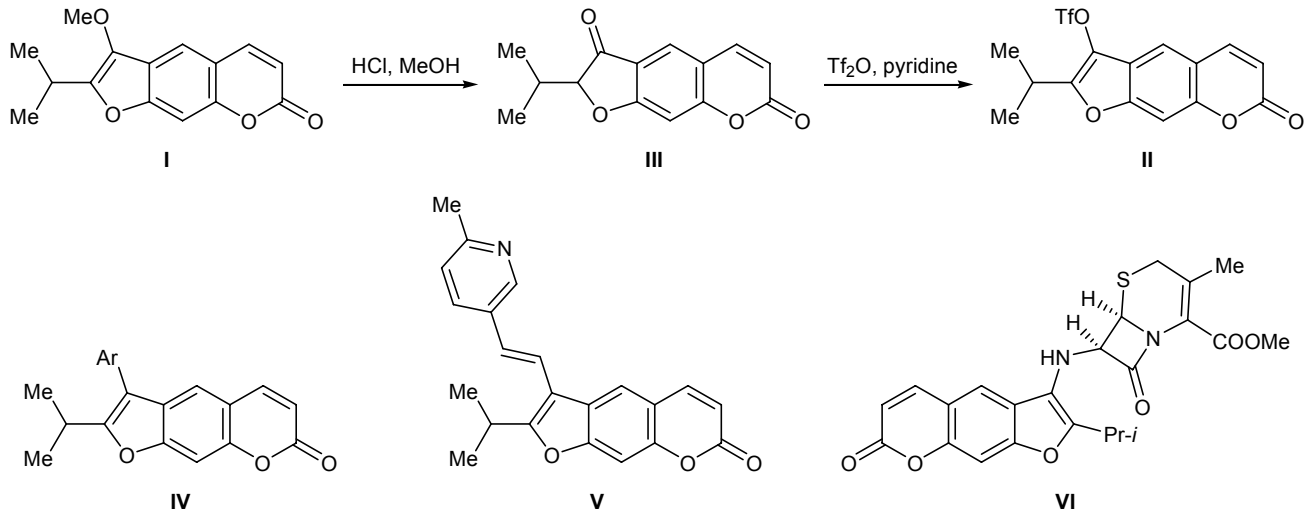
Abstract—The reaction of a linearly fused furocoumarin, oreoselone, with *p*-toluenesulfonyl chloride gave 2-tosyloreoselone which showed a high reactivity in palladium-catalyzed cross-coupling reactions with formation of a new carbon–carbon bond. 2-Tosyloreoselone reacted with terminal alkynes in the presence of $Pd(PPh_3)_2Cl_2$ to give the corresponding 2-alkynylfuro[3,2-*g*]chromen-3-ones. 2-Aryl(hetaryl)alkynyloreoselones were obtained in high yield directly by palladium-catalyzed reaction of oreoselone with tosyl chloride and aryl(hetaryl)acetylenes. The reaction of 2-tosyloreoselone with aryl(hetaryl)boronic acids in the presence of palladium complexes with uni- and bidentate ligands, tetrabutylammonium bromide, and a base afforded 2-aryl(hetaryl)-substituted oreoselones. 2-Vinyloreoselone was synthesized from 2-tosyloreoselone and potassium trifluoro(vinyl)borate.

DOI: 10.1134/S107042801301017X

While studying transformations of peucedanin (**I**, 2-isopropyl-3-methoxy-7*H*-furo[3,2-*g*]chromen-7-one) in the presence of metal complex catalysts, we found that oreoselone trifluoromethanesulfonate **II** prepared from peucedanin (**I**) through intermediate oreoselone (**III**) can be involved in the Heck, Suzuki, and amination reactions. We succeeded in synthesizing compounds **IV**–**VI** by palladium-catalyzed reactions [2–4] (Scheme 1).

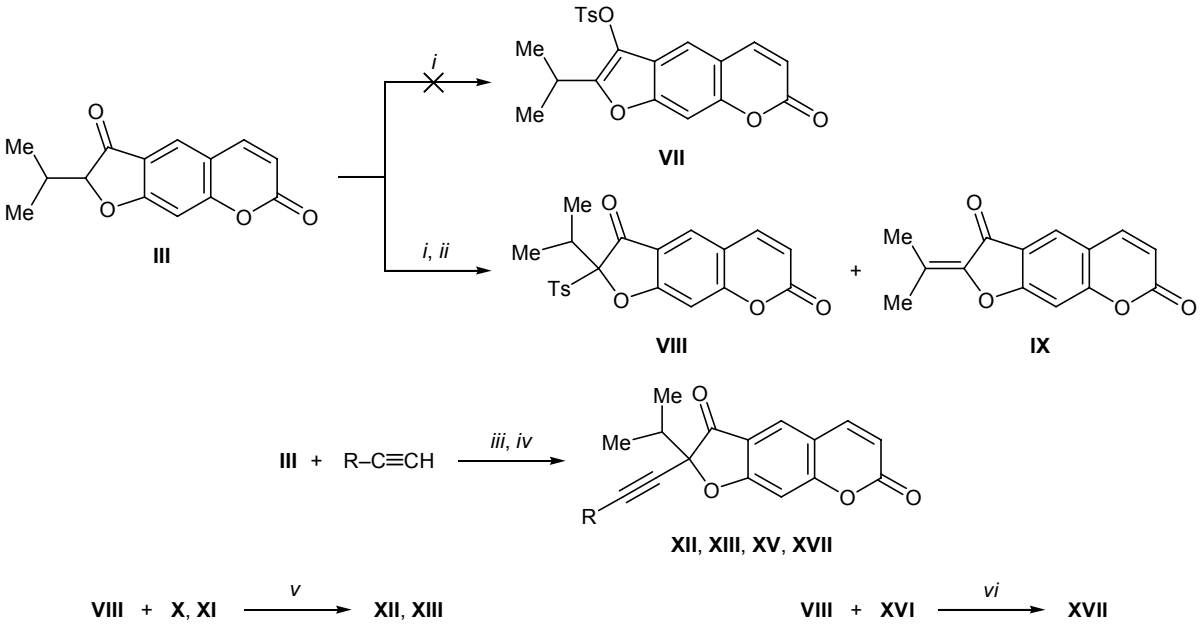
By reaction of oreoselone (**III**) with *p*-toluenesulfonyl chloride we obtained 2-tosyloreoselone (**VIII**) instead of expected 3-tosyloxy derivative **VII**. The highest yield of **VIII** (87%) was attained when a mixture of **III**, TsCl (1.2 equiv), and Et_3N (1.3 equiv) was

Scheme 1.



* For communication X, see [1].

Scheme 2.



X, **XII**, R = Ph; **XI**, **XIII**, R = pyridin-2-yl; **XIV**, **XV**, R = 4-$MeOC_6H_4$; **XVI**, **XVII**, R = Me_3Si. *i*: TsCl, Et_3N, THF, 60°C, 4 h; *ii*: TsCl, $Pd(PPh_3)_2Cl_2$, THF, 60°C, 5 h; *iii*: (1) TsCl, $Pd(PPh_3)_2Cl_2$, THF, 60°C, 5 h; (2) Et_3N, **X** or **XI**, THF, 60ºC, 5–7 h; *iv*: TsCl, $Pd(PPh_3)_2Cl_2$, $(i\text{-}Pr)_2NEt$, THF, 60ºC, 5 h; *v*: $Pd(PPh_3)_2Cl_2$, Et_3N, THF, 60ºC, 7 h; *vi*: $Pd(PPh_3)_2Cl_2$, CuI, THF, 60ºC, 7 h.

heated in boiling THF. In addition, we isolated previously described 2-(propan-2-ylidene)-7*H*-furo[3,2-*g*]-chromene-3,7(2*H*)-dione (**IX**) [5–7]; presumably, the latter was formed as a result of elimination of *p*-toluenesulfonic acid molecule from compound **VIII** (Scheme 2).

2-Tosyloreoselone (**VIII**) turned out to be a reactive substrate in C–C bond formation processes. It reacted with phenylacetylene (**X**) and (pyridin-2-yl)acetylene (**XI**) in THF in the presence of $Pd(PPh_3)_2Cl_2$ (5 mol %) and Et_3N (1.3 equiv) to produce [2-2-phenyl(pyridin-2-yl)ethynyl]furocoumarins **XII** and **XIII** (yield 62–70%) and compound **IX** as by-product. It was interesting to perform direct Pd-catalyzed cross coupling of oreoselone (**III**) with terminal acetylenes using tosyl chloride as activator. In fact, by reactions of oreoselone (**III**) with tosyl chloride (1.2 equiv) and aryl(hetaryl)-alkynes **X**, **XI**, and **XIV** in the presence of $Pd(PPh_3)_2Cl_2$ (5 mol %) and Et_3N (1.3 equiv) in THF we obtained alkynyl-substituted dioxofurocoumarins **XII**, **XIII**, and **XV** in 72–88% yield.

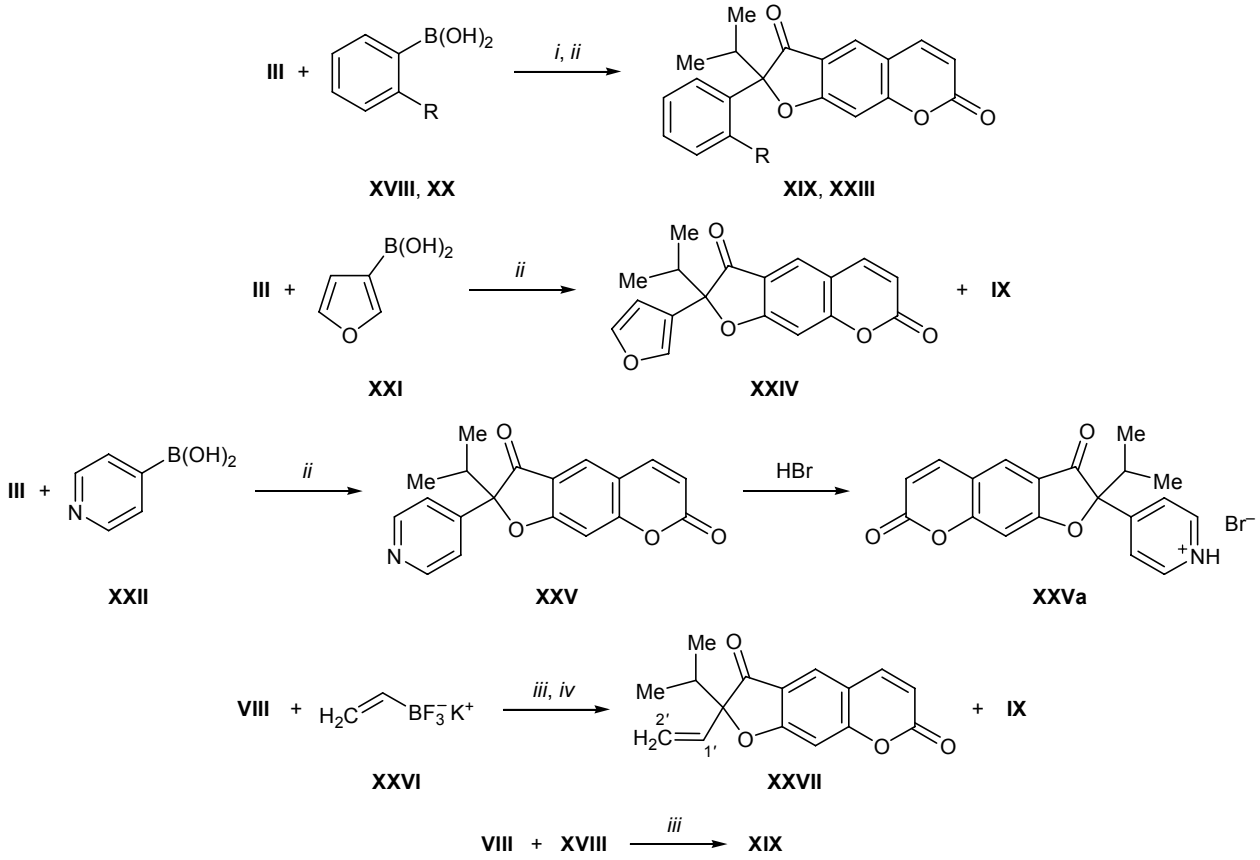
The use of ethyl(diisopropyl)amine (Hunig's base) in the reaction of **III** with TsCl and 4-methoxyphenylacetylene (**XIV**) afforded compound **XV** in up to 75% yield. Thus, the direct cross coupling of oreoselone (**III**) with aryl(hetaryl)acetylenes and tosyl chloride occurs under mild conditions, and it may be regarded as a convenient method for the preparation of 2-arylethynylfurocoumarines **XII**, **XIII**, and **XV**. Cross coupling of alkynes with 2-tosyloreoselone (**VIII**) requires no copper(I) iodide which is commonly used in the Sonogashira reactions. A successful example of direct cross coupling of alkynes with 4-hydroxycoumarins in the presence of TsCl but without copper iodide was described in [8].

In the reaction of **III** with trimethylsilylacetylene (**XVI**) in the presence of TsCl, the corresponding ethynyl derivative **XVII** was isolated in a poor yield (22%), whereas the major product was 2-tosyloreoselone (**VIII**). The reaction of **VIII** with alkyne **XVI** in the presence of CuI gave 52% of **XVII**.

Thus we have proposed a procedure for the direct ethynylation of oreoselone at C^2. Taking into account synthetic potential of β-oxo acetylene derivatives, the obtained products may be promising as precursors of various heteropolycyclic structures [9].

It should be noted that cross coupling reactions of compounds activated by sulfonylation have attracted considerable attention in recent time. Successful migration of endocyclic double bond to exo position in palladium-catalyzed desulfonation of allyl sulfones was reported in [10], facile aminospirocyclization of tertiary allyl sulfones in the presence of palladium(0) compounds was described in [11], and a procedure for

Scheme 3.



i: TsCl, $Pd(PPh_3)_4$, K_2CO_3, $Bu_4N^+ Br^-$, THF, 60°C; *ii*: TsCl, $PdCl_2$(dppf), K_2CO_3, $Bu_4N^+ Br^-$, MeCN, 80°C; *iii*: $PdCl_2$(dppf), K_2CO_3, $Bu_4N^+ Br^-$, MeCN, 80°C; *iv*: $Pd(OAc)_2$, dioxane, 100°C.

cross coupling of Grignard reagents with sulfonyl-activated sp^3-carbon–nitrogen bonds in the presence of copper salts was proposed [12].

We were interested in performing cross coupling of oreoselone (**III**) with aryl(hetaryl)boronic acids in the presence of tosyl chloride as activator. Direct reactions of phenols and heteroaromatic compounds with arylboronic acids via activation of the C–OH bond by various compounds, including tosyl chloride, were described in some publications [13]. The reaction of **III** with TsCl and phenylboronic acid (**XVIII**) in THF in the presence of $Pd(PPh_3)_4$ (which is widely used in the Suzuki cross couplings), K_2CO_3 (3 equiv), and $Bu_4N^+ Br^-$ (10 mol %) at 60°C led to the formation of 45% of 2-isopropyl-2-phenylfurocoumarin (**XIX**) (Scheme 3). When the reaction was carried out in acetonitrile using $PdCl_2$(dppf) as catalyst (80°C), the yield of **XIX** increased to 78%. Compound **XIX** was also formed in 76% yield in the reaction of **VIII** with phenylboronic acid (**XVIII**) in acetonitrile in the presence of $PdCl_2$(dppf), K_2CO_3, and $(Bu)_4N^+ Br^-$. The reactions of **III** with 2-methylphenylboronic acid (**XX**), furan-3-ylboronic acid (**XXI**), and pyridin-4-ylboronic acid (**XXII**) in acetonitrile in the presence of tosyl chloride, $PdCl_2$(dppf), K_2CO_3, and $(Bu)_4N^+ Br^-$ afforded the corresponding 2-substituted furocoumarins **XXIII**–**XXV** (yield 80, 57, and 46%, respectively) through intermediate formation of sulfonyl ketone **VIII**. Compound **XXV** was isolated as hydrobromide **XXVa**. In addition, 2-isopropylidene derivative **IX** was isolated in 28 and 38% yield, respectively, in the reactions of **III** with hetarylboronic acids **XXI** and **XXII**.

With a view to introduce a vinyl substituent into the 2-position of furocoumarins we examined the reaction of **VIII** with potassium trifluoro(vinyl)borate (**XXVI**) which showed high reactivity in cross couplings with aryl halides and trifluoromethanesulfonates [14, 15]. 2-Vinyl derivative **XXVII** was isolated in 19% yield in the $Pd(OAc)_2$-catalyzed reaction of **VIII** with potassium salt **XXVI** in dioxane, whereas the cross-coupling in the presence of $PdCl_2$(dppf) [15] quantitatively produced compound **IX** (Scheme 3).

The structure of the isolated compounds was determined on the basis of their spectral parameters. Their ^{1}H and ^{13}C NMR spectra contained only one set of signals typical of the furocoumarin skeleton and the corresponding substituent. Compound **VIII** displayed in the ^{13}C NMR spectrum a signal at δ_C 190.39 ppm due to C^3 carbonyl carbon atom. In the mass spectrum of **VIII** we observed the molecular ion peak, ion peak with *m*/*z* 243 [*M* – 4-Me$C_6H_4SO_2$], and fragment ion peaks with *m*/*z* 229, 202, 189, and 188, the latter being characteristic of oreoselone fragmentation [16]. The formation of alkynylfurocoumarins **XII**, **XIII**, **XV**, and **XVII** was also confirmed by the IR spectra which contained strong absorption bands at 2216–2251 and 2068–2195 cm^{-1}.

In the ^{1}H NMR spectrum of **XXVII**, protons in the vinyl group resonated at δ 4.97 (2H, CH_2=) and 5.39 ppm (1H, CH=). Signals from the corresponding carbon atoms were located in the JMOD ^{13}C NMR spectrum at δ_C 120.95 (t, $C^{2'}$) and 139.72 ppm (d, $C^{1'}$).

Thus modification of oreoselone via palladium-catalyzed cross coupling of its 2-tosyl derivative gives rise to various 2-substituted furocoumarins which attract interest as potentially pharmacologically active compounds.

EXPERIMENTAL**

The NMR spectra were recorded from solutions in $CDCl_3$ on Bruker AV-300 (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C), AV-400 (400.13 MHz for ^{1}H and 100.78 MHz for ^{13}C), and AV-600 spectrometers (600.30 MHz for ^{1}H and 150.96 MHz for ^{13}C). The chemical shifts were measured relative to the residual proton signal and carbon signal of the solvent (δ 7.24, δ_C 76.90 ppm). Signal multiplicity in the ^{13}C NMR spectra was determined by recording the *J* modulation spectra. The IR spectra were obtained on a Bruker Vector-22 instrument from samples prepared as KBr pellets. The UV spectra were measured on an HP 8453 UV Vis spectrophotometer. The melting points were determined using a Stuart SMF-38 melting point apparatus. The optical rotations $[\alpha]_D^{20}$ were measured from solutions in chloroform on a PolAAr3005 polarimeter.

The mass spectra were recorded on a DFS Thermo Scientific high-resolution mass-spectrometer (vaporizer temperature 240°C), and the molecular weights and elemental compositions were determined from the high-resolution mass spectra.

Elemental analyses were obtained on a Carlo Erba 1106 CHN analyzer. The molecular weight of **XXVa** was determined with the aid of a Knauer vapor pressure osmometer. The products were isolated by column chromatography on silica gel (Acros, 0.035–0.070 mm) using chloroform and chloroform–ethanol (50:2) as eluents. The progress of reactions was monitored by TLC on Silufol UV-254 plates (chloroform–ethanol, 50:2; detection under UV light or by treatment with iodine vapor).

2-Ethynylpyridine (**XI**), 4-ethynyl-1-methoxybenzene (**XIV**), trimethylsilylacetylene (**XVI**), aryl(hetaryl)boronic acids **XVIII** and **XX**–**XXII**, and $PdCl_2$(dppf) were commercial products (Alfa Aesar); $Pd(PPh_3)_4$ was synthesized as described in [17]. The solvents (acetonitrile and tetrahydrofuran) and triethylamine were purified according to standard procedures and were distilled in a stream of argon just before use. Oreoselone (**III**) was synthesized from peucedanin (**I**) as reported in [6].

2-Isopropyl-2-(4-methylphenylsulfonyl)-2*H*-furo[3,2-*g*]chromene-3,7-dione (VIII). *a*. *p*-Toluenesulfonyl chloride, 0.456 g (2.4 mmol), and triethylamine, 0.26 g (2.6 mmol), were added at 20°C under argon to a solution of 0.5 g (2 mmol) of oreoselone (**III**) in 3 ml of THF. The mixture was heated for 4 h under reflux (TLC) and cooled, 5 ml of water was added, the mixture was extracted with methylene chloride (4×5 ml), the extract was dried over $MgSO_4$ and evaporated, and the residue was recrystallized from ethanol to isolate 0.69 g (87%) of **VIII** and traces of **IX**.

b. *p*-Toluenesulfonyl chloride, 0.47 g (2.5 mmol), and $Pd(PPh_3)Cl_2$, 0.07 g (0.1 mmol), were added to a solution of 0.5 g (2 mmol) of **III** in 3 ml of anhydrous THF. The mixture was heated for 5 h under reflux and cooled, 5 ml of water was added, and the mixture was treated as described above in *a* to isolate 0.35 g (44%) of **VIII** and 0.058 g (12%) of **IX**.

Compound **VIII**. $[\alpha]_D^{20}$ = –8.8° (*c* = 0.5, $CHCl_3$), mp 91–92°C (from EtOH). IR spectrum, ν, cm^{-1}: 3119, 3047, 2974, 2935, 2854, 1736, 1702, 1628, 1585, 1473, 1390, 1356, 1286, 1195, 1121, 1100, 1034, 1011, 972, 912, 866, 827, 756, 741, 698, 681. UV spectrum (EtOH), λ_{max}, nm (log ε): 200 (4.38), 220 (4.23), 258 (4.38), 305 (3.88), 347 (3.86). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.81 d and 0.95 d [3H each, (C**H**$_3$)$_2$CH, *J* = 7], 2.26 s (3H, CH_3), 2.92 m [1H, $(CH_3)_2$C**H**],

** Analytical and spectral studies were performed at the Shared Chemical Service Center, Siberian Division, Russian Academy of Sciences.

6.33 d (1H, 6-H, J = 9.4), 7.08 d (2H, 3′-H, 5′-H), 7.39 s (1H, 9-H), 7.63 d (2H, 2′-H, 6′-H), 7.80 d (1H, 5-H, J = 9.4), 7.96 s (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 14.51 q and 16.12 q [(**C**H$_3$)$_2$CH], 21.26 d [(CH$_3$)$_2$**C**H], 36.83 q (CH$_3$), 100.30 s (C^2), 102.78 d (C^9), 114.84 s (C^{4a}), 115.79 d (C^6), 117.03 s (C^{3a}), 124.42 s (C$^{1'}$), 125.86 d (C$^{2'}$, C$^{6'}$), 126.58 d (C^4), 128.58 d (C$^{3'}$, C$^{5'}$), 139.24 s (C$^{4'}$), 143.43 d (C^5), 158.31 s (C^{9a}), 161.84 s (C^{8a}), 170.89 s (C^7), 190.39 s (C^3). Mass spectrum, m/z (I_{rel}, %): 398 (2), 359 (5), 344 (15), 316 (22), 290 (17), 244 (12), 243 (55), 242 (11), 229 (28), 202 (21), 189 (30), 188 (64), 160 (19), 144 (34), 116 (86), 102 (100), 85 (35), 83 (54), 76 (22). Found: m/z 398.0820 $[M]^+$. $C_{21}H_{18}O_6S$. Calculated: M 398.0814.

2-Isopropyl-2-(phenylethynyl)-2*H*-furo[3,2-*g*]-chromene-3,7-dione (XII). *a*. A mixture of 0.6 g of compound **VIII**, 0.4 g of phenylacetylene (**X**), 0.42 g of triethylamine, and 0.07 g of Pd(PPh$_3$)Cl$_2$ in 5 ml of anhydrous THF was heated for 7 h under reflux in a stream of argon. The mixture was evaporated, the residue was treated with 10 ml of water and extracted with methylene chloride (4×5 ml), the combined extracts were dried over MgSO$_4$ and evaporated, and the residue was subjected to column chromatography on silica gel to isolate 0.32 g (62%) of **XII** and 0.09 g (26%) of **IX**.

b. A solution of 0.5 g (2 mmol) of oreoselone (**III**), 0.47 g (2.5 mmol) of tosyl chloride, and 0.07 g (0.1 mmol) of Pd(PPh$_3$)Cl$_2$ in 5 ml of anhydrous THF was heated for 5 h at 60°C under argon, 0.40 g (2 equiv) of phenylacetylene (**X**), 0.42 g (3 equiv) of triethylamine, and 0.07 g of Pd(PPh$_3$)Cl$_2$ in 5 ml of THF were added, and the mixture was heated for 7 h more at 60°C until the initial compound disappeared (TLC). The mixture was treated with 10 ml of water and extracted with methylene chloride (4×5 ml), the combined extracts were dried over MgSO$_4$ and evaporated, and the residue was subjected to column chromatography on silica gel. The solvent was distilled off from the eluate, and the residue was recrystallized from ethanol. Yield 0.49 g (72%).

c. A solution of 0.5 g (2 mmol) of oreoselone (**III**), 0.47 g (2.5 mmol) of tosyl chloride, and 0.07 g (0.1 mmol) of Pd(PPh$_3$)Cl$_2$ in 5 ml of anhydrous THF was heated for 5 h at 60°C under argon, 2 equiv of phenylacetylene (**X**) and 0.62 g (3 equiv) of ethyl(diisopropyl)amine were added, and the mixture was heated for 5 h until the initial compound disappeared (TLC) and treated as described above in *b*.

Compound **XII**. $[\alpha]_D^{20}$ = +6° (c = 0.5, CHCl$_3$), mp 95–96°C (from EtOH). IR spectrum, ν, cm^{-1}: 3078, 3061, 3050, 2962, 2926, 2874, 2854, 2216, 2195, 1742, 1726, 1713, 1626, 1597, 1576, 1485, 1441, 1392, 1355, 1317, 1302, 1178, 1141, 1121, 1105, 1090, 1070, 1045, 1026, 935, 914, 881, 826, 814, 756, 723, 688. UV spectrum (EtOH), λ_{max}, nm (log ε): 251 (4.39), 291 (4.20), 309 (4.28), 330 (4.22), 354 (3.72). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.82 d and 1.12 d [3H each, (C**H**$_3$)$_2$CH, J = 7], 2.29 m [1H, (CH$_3$)$_2$C**H**], 6.24 d (1H, 6-H, J = 9.4), 6.92 s (1H, 9-H), 7.33 m (3H, 2′-H, 4′-H, 6′-H), 7.43 m (2H, 3′-H, 5′-H), 7.61 d (1H, 5-H, J = 9.4), 7.71 s (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 15.83 q and 19.01 q [(**C**H$_3$)$_2$CH], 31.25 d [(CH$_3$)$_2$**C**H], 74.02 s (C^{1a}), 81.39 s (C^{1b}), 91.13 s (C^2), 101.06 d (C^9), 114.29 d (C$^{2'}$, C$^{6'}$), 114.78 d (C^6), 115.61 s (C^{4a}), 117.87 s (C^{3a}), 119.36 d (C$^{4'}$), 124.50 d (C^4), 130.49 d (C$^{1'}$), 134.19 d (C$^{3'}$, C$^{5'}$), 143.89 d (C^5), 159.61 s (C^{9a}), 161.14 s (C^{8a}), 172.56 s (C^7), 199.66 s (C^3). Mass spectrum, m/z (I_{rel}, %): 345 (2), 344 (15), 278 (4), 277 (5), 263 (18), 262 (100), 247 (67), 243 (28), 229 (36), 202 (95), 189 (27), 188 (21), 174 (8), 160 (11), 155 (18), 91 (32), 88 (10). Found, %: C 76.39; N 4.38. m/z 344.1000 $[M]^+$. $C_{22}H_{16}O_4$. Calculated, %: C 76.73; H 4.68. M 344.1020.

2-Isopropyl-2-(pyridin-2-ylethynyl)-2*H*-furo-[3,2-*g*]chromene-3,7-dione (XIII). *a*. The reaction of 0.5 g of oreoselone (**III**) with 0.47 g of tosyl chloride and 0.42 g of 2-ethynylpyridine (**XI**) in the presence of 0.42 g of triethylamine and 0.07 g of Pd(PPh$_3$)Cl$_2$ (60°C, 5 h) gave 0.48 g (70%) of **XIII**.

b. A mixture of 0.6 g (1.5 mmol) of 2-tosyloreoselone (**VIII**), 0.3 g (2.9 mmol) of 2-ethynylpyridine (**XI**), 0.42 g of triethylamine, and 0.07 g of Pd(PPh$_3$)Cl$_2$ in THF was heated for 7 h under reflux in a stream of argon. The mixture was evaporated and treated with 10 ml of water, and the subsequent extraction followed by column chromatography on silica gel gave 0.49 g (72%) of **XIII**. mp 105–106°C (from EtOH). IR spectrum, ν, cm^{-1}: 3433, 3064, 3041, 2964, 2931, 2989, 2875, 2185, 1739, 1726, 1710, 1629, 1575, 1485, 1469, 1394, 1355, 1334, 1303, 1247, 1155, 1143, 1105, 1045, 975, 935, 881, 844, 831, 813, 744. UV spectrum (EtOH), λ_{max}, nm (log ε): 193 (3.98), 209 (4.24), 221 (4.28), 251 (4.54), 295 (4.07), 306 (4.05), 343 (4.19), 351 (4.21). ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.82 d and 1.09 d [3H each, (C**H**$_3$)$_2$CH, J = 7], 2.31 m [1H, (CH$_3$)$_2$C**H**], 6.26 d (1H, 6-H, J = 9.4), 6.94 s (1H, 9-H), 7.20 m (1H, 4′-H), 7.42 d (1H, 2′-H), 7.59 m (1H, 3′-H), 7.68 d (1H, 5-H, J = 9.4),

7.74 s (1H, 4-H), 8.52 d (1H, 5′-H). ^{13}C NMR spectrum, δ_C, ppm: 15.38 q and 18.32 q [(**C**H$_3$)$_2$CH], 30.76 d [(CH$_3$)$_2$**C**H], 76.43 s (C^{1a}), 82.26 s (C^{1b}), 90.64 s (C^2), 100.53 d (C^9), 114.12 d (C^6), 118.92 s (C^{4a}), 119.53 s (C^{3a}), 123.15 d (C$^{4'}$), 124.07 d (C^4), 127.19 d (C$^{2'}$), 135.94 d (C$^{3'}$), 141.99 s (C$^{1'}$), 143.29 d (C^5), 149.67 d (C$^{5'}$), 159.18 s (C^{8a}), 160.67 s (C^{9a}), 173.55 s (C^7), 199.11 s (C^3). Found, %: C 73.53; H 4.28; N 4.00. $C_{21}H_{15}NO_4$. Calculated, %: C 73.03; H 4.38; N 4.06.

2-Isopropyl-2-[(4-methoxyphenyl)ethynyl]-2*H*-furo[3,2-*g*]chromene-3,7-dione (XV). *a*. As described above for compound **XII** (method *a*), the reaction with 0.5 g of **III** afforded 0.66 g (88%) of **XV**.

b. The reaction of 0.5 g of **III** with 0.47 g of tosyl chloride and 0.40 g of 4-methoxyphenylacetylene (**XII**) in the presence of 0.07 g of Pd(PPh$_3$)Cl$_2$ and 0.62 g of ethyl(diisopropyl)amine in 5 ml of THF (5 h, 60°C) gave 0.56 g (75%) of **XV**. $[\alpha]_D^{20}$ = +5.2° (*c* = 0.5, CHCl$_3$), mp 103–104°C (from EtOH). IR spectrum, ν, cm^{-1}: 3035, 2999, 2956, 2931, 2835, 2251, 2190, 1742, 1717, 1626, 1605, 1576, 1508, 1462, 1441, 1290, 1247, 1174, 1137, 1107, 1085, 1030, 908, 829, 729. UV spectrum (EtOH), λ_{max}, nm (logε): 232 (4.11), 253 (4.29), 269 (4.23), 281 (4.20), 299 (4.15), 320 (4.09), 343 (4.06), 355 (3.92). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.87 d and 1.15 d [3H each, (C**H**$_3$)$_2$CH, *J* = 7], 3.46 m [1H, (CH$_3$)$_2$C**H**], 3.80 s (3H, OMe), 6.32 d (1H, 6-H, *J* = 9.4), 6.83 d.d (2H, 2′-H, 6′-H), 7.00 s (1H, 9-H), 7.43 d.d (2H, 3′-H, 5′-H), 7.68 d (1H, 5-H, *J* = 9.4), 7.77 s (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 15.61 q and 18.62 q [(**C**H$_3$)$_2$CH], 31.03 d [(CH$_3$)$_2$**C**H], 55.28 q (CH$_3$), 72.89 s (C^{1a}), 81.18 s (C^{1b}), 90.91 s (C^2), 100.82 d (C^9), 114.07 d (C$^{3'}$, C$^{5'}$), 114.53 d (C^6), 117.18 s (C^{3a}), 119.13 s (C^{4a}), 124.27 d (C^4), 131.40 s (C$^{1'}$), 133.96 d (C$^{2'}$, C$^{6'}$), 143.48 d (C^5), 159.45 s (C^{8a}), 160.16 d (C$^{4'}$), 160.90 s (C^{9a}), 173.81 s (C=O), 199.39 s (C=O). Found, %: C 73.46; H 5.05. $C_{23}H_{18}O_5$. Calculated, %: C 73.79; H 4.85.

2-Isopropyl-2-[(trimethylsilyl)ethynyl]-2*H*-furo-[3,2-*g*]chromene-3,7-dione (XVII). *a*. The reaction of 0.5 g of **III** with 0.47 g of TsCl and 0.47 g of trimethylsilylacetylene (**XVI**) in the presence of 0.07 g of Pd(PPh$_3$)Cl$_2$ and 0.42 g of triethylamine in 5 ml of THF gave 0.16 g (22%) of **XVII**.

b. A solution of 0.5 g (1.26 mmol) of 2-tosyloreoselone (**VIII**), 0.23 g (2.4 mmol) of trimethylsilylacetylene (**XVI**), 0.12 g (1.6 mmol) of triethylamine, 0.042 g (0.06 mmol) of Pd(PPh$_3$)Cl$_2$, and 0.011 g (0.06 mmol) of CuI in 5 ml of anhydrous THF was heated for 7 h at 60°C (TLC), and the mixture was treated as described above for compound **XII** (method *a*). Yield 0.39 g (52%), $[\alpha]_D^{20}$ = +4° (*c* = 0.5, CHCl$_3$), mp 98–99°C (from EtOH). IR spectrum, ν, cm^{-1}: 3062, 3044, 2966, 2930, 2876, 2854, 2210, 2068, 1738, 1726, 1711, 1628, 1600, 1578, 1485, 1468, 1387, 1354, 1335, 1285, 1250, 1190, 1180, 1155, 1138, 1105, 1045, 976, 953, 934, 901, 843, 826, 814, 760, 744, 706, 683, 671. UV spectrum (CHCl$_3$), λ_{max}, nm (logε): 253 (4.44), 296 (4.00), 308 (3.98), 342 (4.00), 354 (4.01). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.10 s [9H, (CH$_3$)$_3$Si], 0.81 d and 1.08 d [3H each, (C**H**$_3$)$_2$CH, *J* = 7], 1.57 m [1H, (CH$_3$)$_2$C**H**], 6.25 d (1H, 6-H, *J* = 9.4), 6.91 s (1H, 9-H), 7.50 d (1H, 5-H, *J* = 9.4), 7.74 s (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 2.39 q [(CH$_3$)$_3$Si], 17.71 q and 18.37 q [(**C**H$_3$)$_2$CH], 31.03 d [(CH$_3$)$_2$**C**H], 98.59 s (C^2), 100.93 d (C^9), 113.82 d (C^6), 114.07 s (C^{3a}), 114.55 s (C^{4a}), 124.28 d (C^4), 143.47 d (C^5), 158.71 s (C^{8a}), 159.41 s (C^{9a}), 173.83 s (C=O), 199.38 s (C=O). Found, %: C 66.13; H 5.12; Si 8.07. $C_{19}H_{20}O_4Si$. Calculated, %: C 67.03; H 5.92; Si 8.25.

2-Isopropyl-2-phenyl-2*H*-furo[3,2-*g*]chromene-3,7-dione (XIX). *a*. Tosyl chloride, 0.456 g (2.4 mmol), and Pd(PPh$_3$)$_4$, 17 mg (5 mol %), were added under stirring in a stream of argon to a solution of 0.5 g (2 mmol) of oreoselone (**III**) in 5 ml of THF, and the mixture was heated for 4 h under reflux until the initial compound disappeared (TLC). Phenylboronic acid (**XVIII**), 0.49 g (4 mmol), tetrabutylammonium bromide, 0.05 g (10 mol %), and potassium carbonate, 1.27 g (6 mmol), were then added, and the mixture was heated for 4 h under reflux (TLC). The mixture was cooled, 10 ml of water was added, the mixture was extracted with methylene chloride (4×5 ml), the combined extracts were dried over MgSO$_4$ and evaporated, and the residue was subjected to column chromatography on silica gel, followed by recrystallization from ethanol. Yield 0.288 g (45%).

b. Tosyl chloride, 0.47 g (2.5 mmol), and Pd(dppf)Cl$_2$, 0.011 g (5 mol %), were added to a solution of 0.5 g (2 mmol) of oreoselone (**III**) in 5 ml of anhydrous acetonitrile. The mixture was heated for 4 h under reflux, 0.49 g (4 mmol) of phenylboronic acid (**XVIII**), 0.05 g (10 mol %) of Bu$_4$NBr, and 1.27 g (6 mmol) of K$_2$CO$_3$ were added, and the mixture was heated for 4 h under reflux (TLC). The mixture was cooled, diluted with 10 ml of water, and extracted with methylene chloride (4×5 ml), the combined extracts were dried over MgSO$_4$, and evaporated, and the residue was subjected to column chromatography on

silica gel, followed by recrystallization from ethanol. Yield 0.5 g (78%).

c. Compound **VIII**, 0.5 g (1.2 mmol), and phenylboronic acid (**XVIII**), 0.3 g (2.4 mmol), were dissolved in 4 ml of acetonitrile, 0.042 g (5 mol %) of $PdCl_2$(dppf), 0.028 g (10 mol %) of Bu_4NBr, and 0.76 g (3.6 mmol) of K_2CO_3 were added, and the mixture was heated for 5 h under reflux until the initial compound disappeared (TLC). The mixture was cooled, treated with 10 ml of water, and extracted with methylene chloride (4×5 ml), the extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography on silica gel, followed by recrystallization from ethanol. Yield 0.28 g (74%), mp 98–99°C. IR spectrum, ν, cm^{-1}: 3078, 3047, 3026, 2979, 2945, 1741, 1724, 1629, 1581, 1481, 1467, 1442, 1390, 1352, 1307, 1284, 1145, 1101, 1018, 933, 837, 702, 626. UV spectrum (EtOH), λ_{max}, nm (logε): 348 (3.70), 308 (3.74), 260 (4.25), 221 (4.17), 200 (4.24), 193 (3.95). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 d and 1.30 d [3H each, (C**H**$_3$)$_2$CH, *J* = 7], 2.48 m [1H, (CH$_3$)$_2$C**H**], 6.34 d (1H, 6-H, *J* = 9.7), 6.99 s (1H, 9-H), 7.25–7.32 m (5H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 7.72 d (1H, 5-H, *J* = 9.7), 7.90 s (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 16.60 q and 17.43 q [(**C**H$_3$)$_2$CH], 36.50 d [(CH$_3$)$_2$**C**H], 98.81 s (C^2), 101.84 d (C^9), 115.23 d (C^6), 115.66 s (C^{3a}), 115.74 s (C^{4a}), 122.48 s ($C^{3'}$, $C^{5'}$), 126.03 d (C^4), 126.87 s ($C^{1'}$), 127.53 d ($C^{2'}$, $C^{6'}$), 133.30 d ($C^{1'}$), 143.25 d (C^5), 159.15 s (C^{9a}), 161.06 s (C^{8a}), 169.60 s (C^7), 192.93 s (C^3). Found, %: C 74.05; H 4.95. $C_{20}H_{16}O_4$. Calculated, %: C 74.99; H 5.03.

2-Isopropyl-2-(2-methylphenyl)-2*H*-furo[3,2-*g*]-chromene-3,7-dione (XXIII) was synthesized from 0.5 g (2 mmol) of compound **III** and 0.54 g (4 mmol) of 2-methylphenylboronic acid (**XX**) using 0.47 g (2.5 mmol) of tosyl chloride, 0.011 g (5 mol %) of Pd(dppf)Cl_2, 0.05 g (10 mol %) of Bu_4NBr, and 1.27 g (6 mmol) of K_2CO_3. Yield 0.53 g (80%), mp 96–97°C (from Et_2O). IR spectrum, ν, cm^{-1}: 3080, 3064, 2979, 2925, 2854, 1741, 1726, 1629, 1598, 1581, 1483, 1440, 1392, 1353, 1299, 1282, 1253, 1145, 1116, 1101, 1076, 1018, 933, 918, 837, 734, 723, 686, 626. UV spectrum (EtOH), λ_{max}, nm (logε): 227 (4.17), 236 (4.23), 255 (4.34), 296 (3.96), 310 (3.90), 344 (3.80), 354 (3.80). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.95 d and 1.37 d [3H each, (C**H**$_3$)$_2$CH, *J* = 7], 2.54 m [1H, (CH$_3$)$_2$C**H**], 2.78 s (CH$_3$), 6.37 d (1H, 6-H, *J* = 9.4), 7.03 s (1H, 9-H), 7.23 m (2H, 4′-H, 5′-H), 7.42 d (1H, 5-H, *J* = 9.4), 7.72 d (1H, 6′-H), 7.92 s (1H, 4-H), 8.17 d (1H, 3′-H). ^{13}C NMR spectrum, δ_C, ppm: 16.70 q and 17.55 q [(**C**H$_3$)$_2$CH], 23.05 d [(CH$_3$)$_2$**C**H], 36.49 q (CH$_3$), 98.90 s (C^2), 101.63 d (C^9), 115.40 d (C^6), 115.69 s (C^{3a}), 115.73 s (C^{4a}), 125.08 d (C^4), 125.95 s ($C^{6'}$), 130.47 d ($C^{5'}$), 131.32 s ($C^{1'}$), 132.08 d ($C^{3'}$), 132.98 d ($C^{4'}$), 137.13 d ($C^{2'}$), 143.07 d (C^5), 158.88 s (C^{9a}), 161.15 s (C^{8a}), 169.61 s (C^7), 192.69 s (C^3). Found, %: C 74.94; H 5.41. $C_{21}H_{18}O_4$. Calculated, %: C 75.43; H 5.43.

2-(Furan-3-yl)-2-isopropyl-2*H*-furo[3,2-*g*]chromene-3,7-dione (XXIV) was synthesized from 0.5 g (2 mmol) of **III** and 0.45 g (4 mmol) of furan-3-ylboronic acid (**XXI**) using 0.47 g (2.5 mmol) of tosyl chloride, 0.011 g (5 mol %) of Pd(dppf)Cl_2, 0.05 g (10 mol %) of Bu_4NBr, and 1.27 g (6 mmol) of K_2CO_3. When the reaction was complete (TLC), the mixture was treated with 10 ml of water and extracted with methylene chloride (4×5 ml), the extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography on silica gel, followed by recrystallization from ethanol and diethyl ether. Yield of **XXIV** 0.35 g (57%). Recrystallization from acetone gave 28% of **IX**.

Compound **XXIV**. mp 100–101°C, $[\alpha]_D^{20}$ = +3.2° (*c* = 0.5, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3082, 3066, 2974, 2934, 2876, 1732, 1630, 1584, 1564, 1502, 1467, 1430, 1398, 1387, 1369, 1356, 1335, 1283, 1227, 1157, 1126, 1100, 1072, 1055, 1013, 997, 934, 902, 878, 824, 814, 743, 725, 689, 617, 601. UV spectrum (EtOH), λ_{max}, nm (logε): 204 (4.22), 249 (4.03), 253 (4.03), 270 (3.88), 290 (3.84), 299 (3.83), 349 (3.65). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.88 d and 1.26 d [3H each, (C**H**$_3$)$_2$CH, *J* = 7], 2.44 m [1H, (CH$_3$)$_2$C**H**], 6.32 d (1H, 6-H, *J* = 9.4), 6.46 s (2H, 4′-H), 6.96 s (1H, 9-H), 7.32 s (2H, 3′-H), 7.60 s (2H, 2′-H), 7.69 d (1H, 5-H, *J* = 9.4), 7.88 s (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 16.53 q and 17.24 q [(**C**H$_3$)$_2$CH], 36.34 d [(CH$_3$)$_2$**C**H], 98.69 s (C^2), 101.77 d (C^9), 114.65 d (C^6), 115.07 d ($C^{5'}$), 115.53 s (C^{3a}), 115.73 s (C^{4a}), 124.04 d (C^4), 126.04 s ($C^{1'}$), 135.01 d ($C^{2'}$), 142.53 d (C^5), 143.34 d ($C^{4'}$), 159.24 s (C^{9a}), 160.99 s (C^{8a}), 169.54 s (C^7), 192.95 s (C^3). Found, %: C 69.51; H 4.32. $C_{18}H_{14}O_5$. Calculated, %: C 69.67; N 4.55.

2-Isopropyl-2-(pyridin-4-yl)-2*H*-furo[3,2-*g*]chromene-3,7-dione (XXV) was synthesized from 0.5 g (2 mmol) of oreoselone (**III**) and 0.5 g (4 mmol) of pyridin-4-ylboronic acid (**XXII**) using 0.47 g (2.5 mmol) of tosyl chloride, 0.011 g (5 mol %) of Pd(dppf)Cl_2, 0.05 g (10 mol %) of Bu_4NBr, and 1.27 g

(6 mmol) of K_2CO_3. A fraction isolated by column chromatography on silica gel was recrystallized from acetone to isolate compound **IX** (yield 38%). The residue, 0.3 g contained compound **XXV** (46%), which was identified by ^{1}H NMR spectrum. It was dried and dissolved in 4 ml of water, a solution of 0.05 ml (0.0009 mol) of HBr in 4 ml of water was added, and the mixture was stirred overnight. The yellow precipitate was filtered off, washed with diethyl ether, and dried. We thus isolated 0.23 g (66%) of hydrobromide **XXVa**. mp 232–233°C (from EtOH). IR spectrum, ν, cm^{-1}: 3398, 3130, 3105, 3066, 2927, 2854, 1732, 1627, 1535, 1483, 1473, 1390, 1352, 1288, 1226, 1153, 1132, 1122, 1014, 912, 867, 829, 742, 675, 513. UV spectrum (EtOH), λ_{max}, nm (log ε): 348 (3.70), 306 (3.65), 257 (4.21), 224 (3.79), 201 (4.35). ^{1}H NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm (*J*, Hz): 0.86 d and 0.95 d [3H each, (C**H**$_3$)$_2$CH, *J* = 7], 3.29 m [1H, (CH$_3$)$_2$C**H**], 6.15 d (1H, 6-H, *J* = 9.4), 6.78 s (1H, 9-H), 7.62 s (1H, 4-H), 7.73 d (1H, 5-H, *J* = 9.4), 7.90 d (2H, 2′-H, 6′-H), 8.44 d (2H, 3′-H, 5′-H). ^{13}C NMR spectrum ($CDCl_3$–CD_3OD), δ_C, ppm: 14.72 q and 16.11 q [(**C**H$_3$)$_2$CH], 37.17 d [(CH$_3$)$_2$**C**H], 100.65 s (C^2), 102.54 d (C^9), 115.22 s (C^{3a}), 116.59 d (C^6), 117.69 s (C^{4a}), 124.93 s (C$^{1'}$), 126.42 d (C^4), 129.56 d (C$^{2'}$, C$^{6'}$), 143.54 d (C^5), 147.14 d (C$^{3'}$, C$^{5'}$), 159.04 s (C^{9a}), 162.56 s (C^{8a}), 170.96 s (C=O), 190.35 s (C=O). Found, %: C 56.18; H 3.97; Br 19.88, N 3.35. *m*/*z* 399 [*M*]$^+$. $C_{19}H_{15}BrNO_4$. Calculated, %: C 56.88; H 3.77; Br 19.91; N 3.49. *M* 401.

2-Isopropyl-2-vinyl-2*H*-furo[3,2-*g*]chromene-3,7-dione (XXVII). *a*. Compound **VIII**, 0.25 g (0.6 mmol), and potassium trifluoro(vinyl)borate (**XXVI**), 0.16 g (1.2 mmol), were dissolved in 4 ml of acetonitrile, 0.021 g (5 mol %) of $PdCl_2$(dppf), 0.014 g (10 mol %) of Bu_4NBr, and 0.38 g (3.6 mmol) of K_2CO_3 were added, and the mixture was heated for 5 h under reflux (TLC). The mixture was cooled, 10 ml of water was added, and the mixture was extracted with methylene chloride (4×5 ml). The extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography on silica gel, followed by recrystallization from acetone, to isolate 0.13 g (93%) of compound **IX** and traces of **XXVII**.

b. Compound **VIII**, 0.25 g (0.6 mmol), and potassium trifluoro(vinyl)borate (**XXVI**), 0.1 g (0.75 mmol), were dissolved in 4 ml of dioxane, 0.007 g (5 mol %) of $Pd(OAc)_2$ was added, and the mixture was heated for 7 h under reflux. The mixture was cooled, 10 ml of water was added, and the mixture was extracted with methylene chloride (4×5 ml). The extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography on silica gel to isolate 30 mg (19%) of **XXVII** and 110 mg (76%) of **IX**.

Compound **XXVII**. mp 93–94°C (from Et_2O). IR spectrum, ν, cm^{-1}: 3398, 3066, 2927, 2854, 1732, 1627, 1573, 1535, 1483, 1473, 1390, 1352, 1288, 1226, 1193, 1132, 1122, 1014, 912, 867, 829, 742, 675, 609. UV spectrum (EtOH), λ_{max}, nm (log ε): 343 (3.76), 310 (3.89), 277 (4.04), 255 (4.24), 236 (4.12), 225 (4.00), 190 (3.97). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.93 d and 1.33 d [3H each, (C**H**$_3$)$_2$CH, *J* = 7], 2.51 m [1H, (CH$_3$)$_2$C**H**], 4.97 d (2H, 2′-H), 5.39 d (1H, 1′-H), 6.36 d (1H, 6-H, *J* = 9.4), 7.02 s (1H, 9-H), 7.71 d (1H, 5-H, *J* = 9.4), 7.92 s (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 16.79 q and 17.64 q [(**C**H$_3$)$_2$CH], 36.65 d [(CH$_3$)$_2$**C**H], 99.99 s (C^2), 101.79 d (C^9), 115.45 d (C^6), 115.85 s (C^{3a}), 115.96 s (C^{4a}), 120.95 t (C$^{2'}$), 127.75 d (C^4), 139.72 d (C$^{1'}$), 143.47 d (C^5), 159.37 s (C^{9a}), 161.28 s (C^{8a}), 169.82 s (C=O), 193.15 s (C=O). Found, %: C 70.92; H 5.26. $C_{16}H_{14}O_4$. Calculated, %: C 71.10; H 5.22.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 12-03-92200) and by the Program for Support of Leading Scientific Schools (project no. NSh-3986.2012.3).

REFERENCES

1. Makhneva, E.A., Lipeeva, A.V., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2012, vol. 48, p. 1094.
2. Lipeeva, A.V., Shul'ts, E.E., Bagryanskaya, I.Yu., Shakirov, M.M., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2011, vol. 47, p. 1083.
3. Lipeeva, A.V., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2011, vol. 47, p. 1390.
4. Lipeeva, A.V., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2011, vol. 47, p. 1404.
5. Bruchhausen, F. and Hoffman, H., *Chem. Ber*., 1941, vol. 74, p. 1584.
6. Osadchii, S.A., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Izv. Akad. Nauk, Ser. Khim*., 2006, p. 362.
7. Lipeeva, A.V., Shul'ts, E.E., Shakirov, M.M., and Tolstikov, G.A., *Russ. J. Org. Chem*., 2010, vol. 46, p. 1858.
8. Luo, Y. and Wu, J., *Tetrahedron*, 2009, vol. 65, p. 6810.
9. Saito, S. and Yamamoto, Y., *Chem. Rev*., 2000, vol. 100, p. 2901.
10. Mandai, T., Matsumoto, T., and Tsuji, J., *Synlett*, 1993, no. 2, p. 113.

11. Jin, Z. and Fuchs, P.L., *Tetrahedron Lett*., 1996, vol. 37, p. 5253.
12. Li, M.-B., Tang, X.L., and Tian, S.-K., *Adv. Synth. Catal*., 2011, vol. 353, p. 1980.
13. Ackermann, L. and Mulzer, M., *Org. Lett*., 2008, vol. 10, p. 5043; Kang, F.-A., Sui, Z., and Murray, W.V., *J. Am. Chem. Soc*., 2008, vol. 130, p. 11300; Luo, Y. and Wu, J., *Tetrahedron Lett*., 2009, vol. 50, p. 2103.
14. Molander, G.A. and Rivero, M.R., *Org. Lett*., 2002, vol. 4, p. 107.
15. Darses, S., Michaud, G., and Genêt, J.-P., *Eur. J. Org. Chem*., 1999, no. 8, p. 1875.
16. Shul'ts, E.E., Petrova, T.N., Shakirov, M.M., Chernyak, E.I., Pokrovskii, L.M., Nekhoroshev, S.A., and Tolstikov, G.A., *Khim. Inter. Ustoich. Razv*., 2003, vol. 11, p. 683.
17. Dzhemilev, U.M., Popod'ko, N.R., and Kozlova, E.V., *Metallokompleksnyi kataliz v organicheskom sinteze* (Metal Complex Catalysis in Organic Synthesis), Moscow: Khimiya, 1999, p. 109.