ISSN 1070-4280, Russian Journal of Organic Chemistry, 2012, Vol. 48, No. 8, pp. 1094–1102. © Pleiades Publishing, Ltd., 2012.
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Study of Plant Coumarins: X*. Peurutenicin Triflate in Cross-Coupling Reactions

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Received January 31, 2012

Abstract—By Suzuki cross-coupling reaction of peurutenicin triflate with arylboric, furanylboric, pyridinylboric, and indolylboric acids the corresponding 7-aryl(hetaryl)coumarins were synthesized. The high activity of hetaryl-substituted boric acids in the Suzuki reaction was observed. Heck reaction of 7-*O*-trifluoromethylsulfonylpeur utenicin with terminal olefins (styrene, vinylpyridines, vinylpyrazine, vinyltriazole) was used to prepare (*E*)-7-[aryl(hetaryl)vinyl]coumarins. The dependence of reaction products yield on the nature of the catalytic system was found.

DOI: 10.1134/S1070428012080106

Peurutenicin [7-hydroxy-6-(methoxycarbonyl) coumarin] (**I**) is produced by various plant species of genus *Peucedanum* (hog's fennel) [2]. Its structure was unambiguously established from the product of its alkaline hydrolysis (umbelliferone-6-carboxylic acid), and also by an independent synthesis [3]. We described in [4] an efficient procedure of the preparation of peurutenicin (**I**) from peucedanine (**II**), a metabolite of *Peucedanum morisonii*. The availability of compound **I**, and also the known pharmacological activity of the functionally substituted coumarins arouse our interest in the investigation of its transformations, in particular, in the preparation of 7-substituted derivatives.

Coumarins with diverse substituents in the position C^7 are extensively studied because of their antibacterial and fungicidal action [5], their effect on aromatase [6] and monoamine oxides A and B [7], providing the potential of these compounds in the treatment of neurodegenerative diseases. 7-Aryl-substituted coumarins are regarded as a new group of selective nonsteroid inhibitors of hydroxysteroid 17-β- dehydrogenase of the first type [8].

Styrylcoumarins were obtained by Wittig reaction of the appropriate 7-formyl derivatives [9] or by the conversion of 3-styrylphenols [7]. In the synthesis of 7-(indol-3-yl)coumarins a Pd-catalyzed reaction of umbelliferone triflate with *o*-alkynyl-trifluoroacetanilides was used [10]. Suzuki–Miyaura reactions were described involving 4-trifluoromethylsulfonyloxycoumarins affording 4-aryl(hetaryl)coumarins [11], and also 7-trifluoromethylsulfonyloxycoumarins providing 7-arylcoumarins [8]. 7-Trifluoromethylsulfonyloxycoumarins were not brought into Heck reaction.

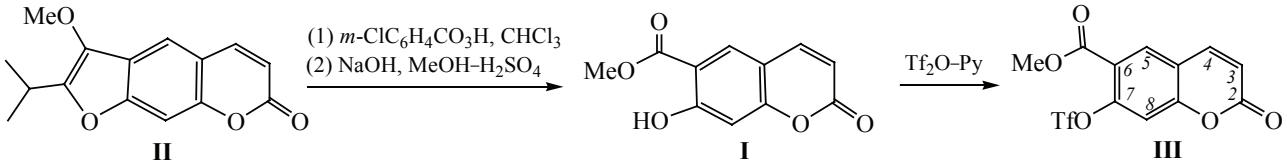
The aim of this study was the synthesis of peurutenicin derivatives with aromatic, heterocyclic, or styryl and hetarylvinyl substituents in the position C^7 using Pd-catalyzed cross-coupling of peurutenicin triflate (III) with boric acids (Suzuki– Miyaura reaction) or with terminal olefins (Heck reaction).

7-*O*-Trifluoromethylsulfonylpeurutenicin (**III**) formed in the reaction of peurutenicin (**I**) with trifluoromethanesulfonic anhydride in pyridine (yield 77%) (Scheme 1).

The reaction of triflate **III** with arylboric acids **IV, V** in dioxane in the presence of the complex $Pd(PPh_3)_4$ widely used in the Suzuki coupling and 3 equiv of K_2CO_3, and also of 10 mol% of $Bu_4N^+Br^-$ led to the formation of the

* For Communication IX, see [1]

Scheme 1.

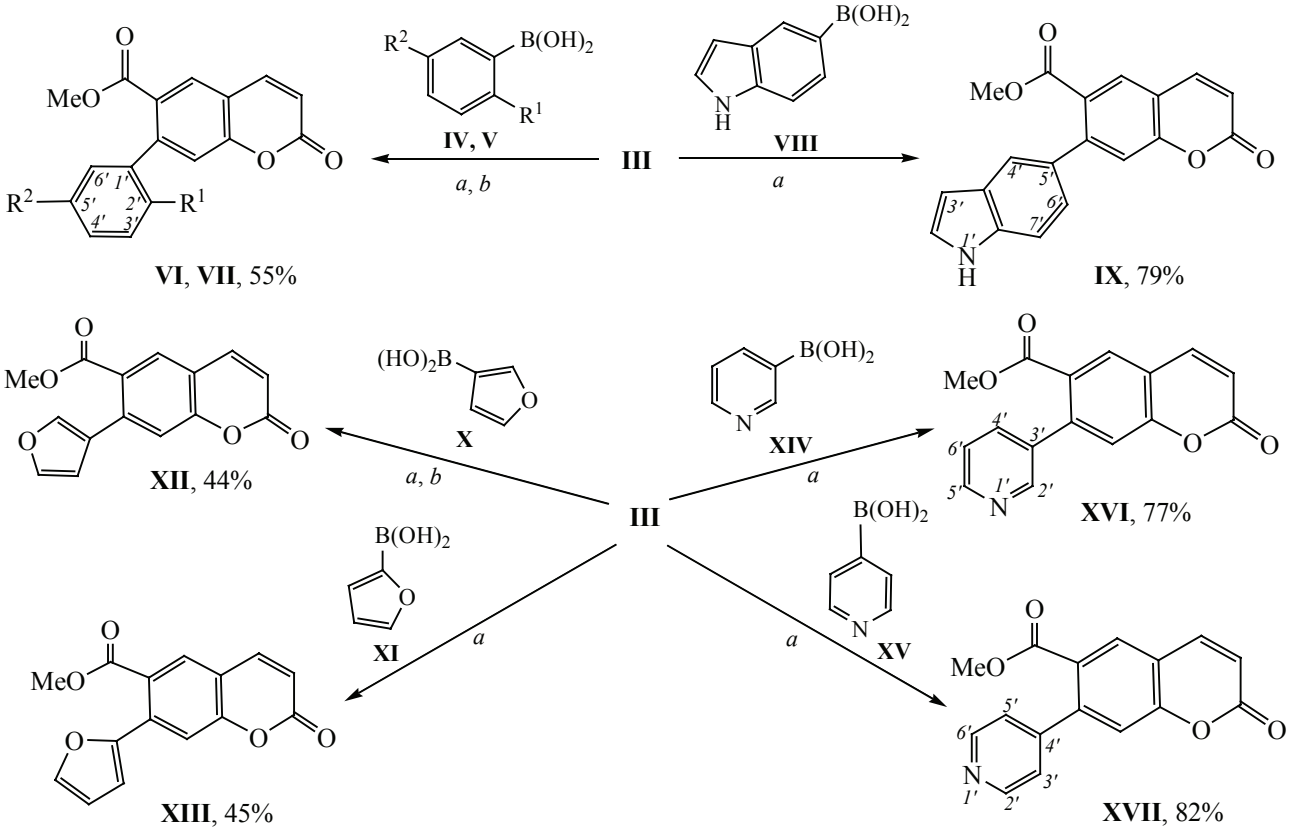


products of coumarin arylation **VI, VII** (Scheme 2). The attempt to react triflate **III** with 2-aminophenylboric acid (**V**) in acetonitrile using as a catalyst complex $PdCl_2$(dppf) [dppf is a bidentate ligand 1,1'-bis(diphenylphosphino) ferrocene) under the conditions utilized in [12] has not increased the yield of the reaction product. The cross-coupling of triflate **III** with indole-5-boric acid (**VIII**) in the presence of $Pd(PPh_3)_4$ made it possible to synthesize coumarin derivative **IX** with an indole fragment in the position C^7. The reaction of peurutenicin triflate (**III**) with 3-furanboric acid (**X**) or 2-furanboric acid (**XI**) furnished the corresponding 6-methoxycarbonyl-7-(furan-2-yl)- (**XII**) or 6-methoxycarbonyl-3-(furan-3-yl)coumarins (**XIII**). The reactions of triflate **III** with pyridineboric acids **XIV, XV** gave 7-(pyridin-4-yl)coumarins **XVI**, **XVII** in a high yield.

Thus by the Suzuki reaction of peurutenicin triflate (**III**) with aryl(hetaryl)boric acids we synthesized versatile compounds, among them combining in the structure the fragments of coumarin and the other heterocyclic compounds (indole, furan, or pyridine).

We investigated the possibility to use Heck reaction of triflate **III** with vinylpyridines **XVIII, XIX** for the synthesis of 7-(pyridin-4-ylvinyl)-substituted peurutenicin (**I**) derivatives. The reaction conditions were chosen by an example of triflate **III** interaction with 2-vinylpyridine (**XVIII**). The reaction was first carried out in DMF using a catalyst system $Pd(OAc)_2$–(o-tol)$_3$P (2/8 mol%) in the

Scheme 2.



R^1 = Cl, R^2 = CF_3 (**IV, VI**); R^1 = NH_2, R^2 = H (**V, VII**). (*a*) $Pd(PPh_3)_4$, K_2CO_3, Bu_4NBr, dioxane, 100°C; (*b*) $PdCl_2$(dppf), K_2CO_3, Bu_4NBr, MeCN, 80°C.

presence of triethylamine (115°C, 7 h), under the conditions of reaction of vinylpyridine **XVIII** with furocoumarin oreoselone triflate [13], but the process required more stringent conditions (135–140°C, 10–16 h). The conversion of triflate **III** and the reaction product yield grew with increased charge of the palladium source, 4/8 mol% of $Pd(OAc)_2$–$(o\text{-tol})_3P$. The reaction of triflate **III** with 2-vinylpyridine (**XVIII**) was carried out over 16 h in the presence of the catalytic system $Pd(OAc)_2$–$(o\text{-tol})_3P$ (4/8 mol%), the conversion of triflate **III** reached 66%. The complete conversion of initial compound **III** was obtained at the use BINAP as the ligand; the yield of (*E*)-[7-(pyridin-2-yl)vinyl]coumarin (**XX**) was 75% (Scheme 3). By the reaction of triflate **III** with 5-vinyl-2-methylpyridine (**XIX**) (*E*)-[7-(pyridin-2-yl)vinyl] coumarin (**XXI**) was obtained. The reaction of triflate **III** with 2-vinylpyrazine (**XXII**) or 1-vinyl-1*H*-1,2,4-triazole (**XXIII**) resulted in individual (*E*)-7-pyrazinylvinyl- or (*E*)-7-triazolylvinyl-6-methoxycarbonyl-2*H*-chromen-2-ones (**XXIV, XXV**). In the reaction of peurutenicin triflate (**III**) with styrene (**XXVI**) in the presence of the catalytic system $Pd(OAc)_2$–BINAP (4/8 mol%) we isolated only 7-styrylcoumarin (**XXVII**).

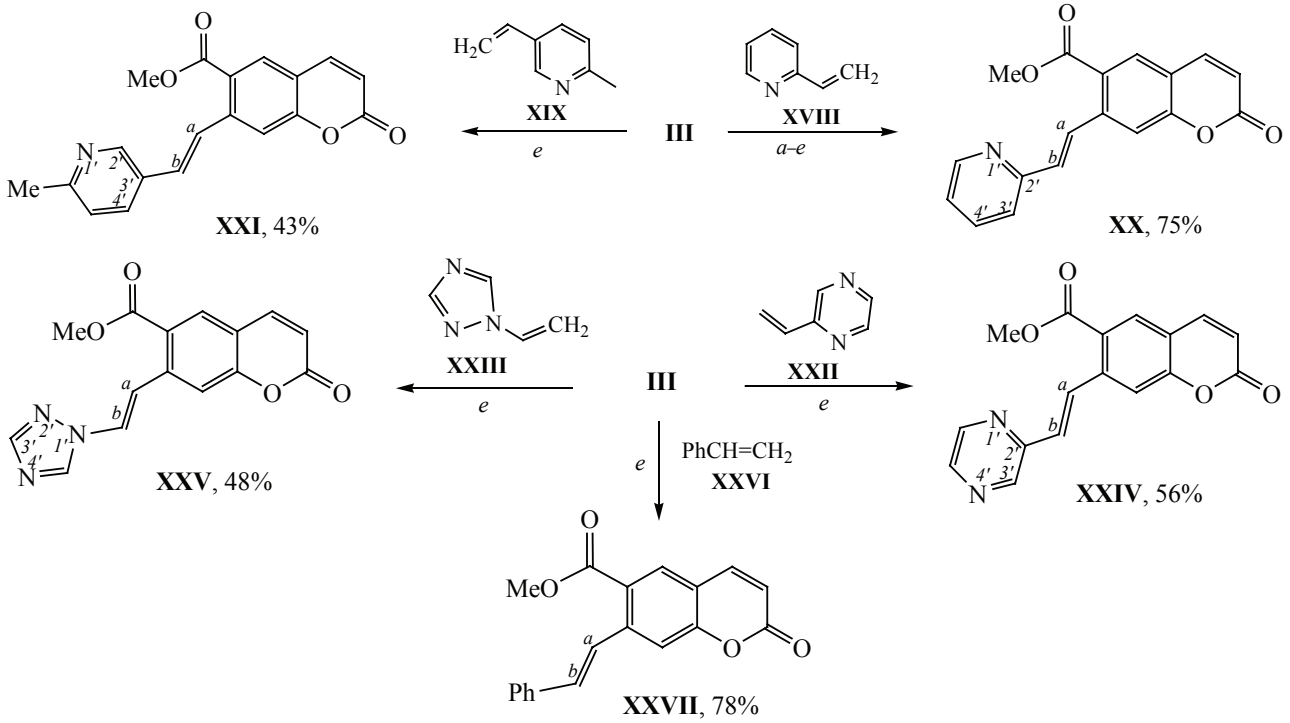
The structure and composition of compounds synthesized was established from the spectral data and elemental analyses. ^1H and ^{13}C NMR spectra of compounds obtained contain one set of characteristic signals of the coumarin framework and of the corresponding substituent. The protons of the double bond $H^{a,b}$ in the ^1H NMR spectra of compounds **XX, XXI, XXIV, XXV, XXVII** give rise to doublets in the region 8.42–8.05, 6.88 or 7.50–7.04, 6.74 ppm. The spin-spin coupling constant between the protons $H^{a,b}$ in the ^1H NMR spectra of compounds **XX**, **XXI**, **XXIV**, **XXV** (*J* 15.8–16.6 Hz) and **(XXVII)** (*J* 14.8 Hz) indicates their *trans*-position.

Therefore the Pd-catalyzed reactions of peurutenicin triflate with aryl(hetaryl)boric acids or with terminal alkenes provide new opportunities of peurutenicin modification and permit syntheses of versatile coumarins substituted at the C^7 atom that may possess valuable pharmacological properties.

EXPERIMENTAL

NMR spectra from solutions of compounds in $CDCl_3$ or in a mixture $CDCl_3$ + CD_3OD (**XII, XVII,**

Scheme 3.



Reagents and conditions: (*a*) $Pd(OAc)_2$, $(o\text{-tol})_3P$, Et_3N, DMF, 115°C, 7 h; (*b*) $Pd(OAc)_2$, $(o\text{-tol})_3P$, Et_3N, DMF, 135–140°C, 10 h; (*c*) $Pd(OAc)_2$, $(o\text{-tol})_3P$, Et_3N, DMF, 135–140°C, 10 h; (*d*) $Pd(OAc)_2$, $(o\text{-tol})_3P$, Et_3N, DMF, 135–140°C, 16 h; (*e*) $Pd(OAc)_2$, BINAP, Et_3N, DMF, 135–140°C, 16 h.

XXV) were registered on spectrometers Bruker AV-300 [300.13 (^{1}H) and 75.47 MHz (^{13}C)], AV-400 [400.13 (^{1}H) and 100.78 MHz (^{13}C)], and AV-600 [600.30 (^{1}H) and 150.96 MHz (^{13}C)]. Chemical shifts in the ^{1}H and ^{13}C NMR spectra were measured with respect to the residual signals of the solvent $CHCl_3$ (δ_H 7.24, δ_C 76.90 ppm). Chemical shifts in the ^{19}F NMR spectra were measured with respect to the internal reference C_6F_6. The multiplicity of signal in the ^{13}C NMR spectra were determined at recording the spectra in the *J* modulation mode. IR spectra were taken on a spectrophotometer Vector-22 from pellets with KBr. UV absorption spectra were recorded on a spectrometer HP 8453 UV Vis. The melting points were measured on a heating block Stuart SMF-38. Elemental analysis was carried out on a CHN-analyzer Carlo Erba 1106. The reaction products were isolated by column chromatography on silica gel Acros (0.035–0.070 mm), eluents chloroform, chloroform–ethanol, 50:2. The reaction progress was monitored by TLC on Silufol UV-254 plates, eluent chloroform–ethanol, 50:2. The spots were visualized in the iodine chamber or under UV irradiation.

In the study was used $PdCl_2$(dppf) from Alfa Aesar. $Pd(PPh_3)_4$ was synthesized by procedure [14]. Arylboric acids **IV, V**, hetepoarylboric acids **VIII, X, XI, XIV, XV**, and vinylarenes **XVIII, XIX, XXII** were bought from Alfa Aesar.

The solvents (acetonitrile, dioxane, DMF), and also Et_3N were purified by standard procedures and distilled in an argon flow just before reactions. Peurutenicin [7-hydroxy-6-(methoxycarbonyl)coumarin] (**I**) was obtained from peucedanine (**II**) as described in [4].

6-(Methoxycarbonyl)-7-(trifluoromethylsulfonyloxy)-2*H*-chromen-2-one (III). A solution of 500 mg (2.27 mmol) of peurutenicin (**I**) in 5 ml of pyridine was cooled to 0°C and at stirring under an argon atmosphere 1.15 ml (6.81 mmol) of trifluoromethanesulfonic anhydride was added within 30 min, the reaction mixture was warmed to the room temperature and was left standing for 48 h with intermittent stirring. On the completion of the reaction (TLC monitoring by the disappearance of the spot of compound **I**) the reaction mixture was quenched with 10 ml of water, the reaction product was extracted into ether (4 × 5 ml), the combined organic solvents were dried with magnesium sulfate. The solvent was distilled off in a vacuum, the traces of pyridine were removed by azeotropic distillation with benzene, the residue was crystallized from ethanol. Yield 585 mg (77%), mp 106–108°C (from ethanol). IR spectrum, cm^{-1}: 3127, 3087, 3059, 2960, 1744, 1725, 1630, 1431, 1226, 1135, 960, 870, 750, 658, 601. UV spectrum (EtOH), λ_{max}, nm (log ε): 206 (3.99), 231 (4.11), 320 (4.06). ^{1}H NMR spectrum, δ, ppm: 3.99 s (3H, OCH_3), 6.29 d (1H, H^3, *J* 9.5 Hz), 6.87 s (1H, H^8), 7.62 d (1H, H^4, *J* 9.5 Hz), 8.01 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 51.55 (OCH_3), 104.09 s (C^6), 108.10 d (C^8), 113.52 d (C^3), 113.88 s (C^{4a}), 119.02, 120.23, 122.87, 125.32 s (CF_3, *J* 266.6 Hz), 133.38 d (C^5), 144.35 d (C^4), 152.18 s (C^7), 158.41 s (C^{8a}), 160.68 s (C^2), 167.04 s (C=O). ^{19}F NMR spectrum, δ, ppm: 88.70 (CF_3). Found, %: F 16.12; S 9.05. $C_{12}H_7F_3O_7S$. Calculated, %: F 16.18; S 9.10.

6-(Methoxycarbonyl)-7-[2-chloro-5-(trifluoromethyl)phenyl]-2*H*-chromen-2-one (VI). To a solution of 100 mg (0.3 mmol) of peurutenicin triflate (**III**) in 3 ml of dioxane under an argon atmosphere was added at stirring in succession 90 mg (0.39 mmol) of 5-(trifluoromethyl)-2-chlorophenylboric acid (**IV**), 17 mg (5 mol%) of $Pd(PPh_3)_4$, 7 mg (10 mol%) of Bu_4NBr, and 123 mg (0.9 mmol) of K_2CO_3. The mixture was stirred over 8 h at 100°C. On the completion of the reaction (TLC monitoring) the reaction mixture was evaporated to 1 ml, the residue was diluted with 5 ml of water, the reaction product was extracted into dichloromethane (4 × 5 ml), the combined extracts were dried with $MgSO_4$. The solvent was distilled off, the residue was chromatographed on silica gel, the fraction containing the reaction product was treated with ether. Yield 60 mg (52%), mp 144–145°C (from ether). IR spectrum, cm^{-1}: 3450, 3380, 3118, 2953, 1740, 1729, 1644, 1608, 1473, 1416, 1198, 1220, 1137, 1105, 1040, 872, 743, 623. UV spectrum (EtOH), λ_{max}, nm (log ε): 208 (4.42), 241 (4.20), 276 (3.63), 286 (3.66), 311 (3.66). ^{1}H NMR spectrum, δ, ppm: 3.69 s (3H, OCH_3), 6.52 d (1H, H^3, *J* 9.6 Hz), 7.48 d (1H, H$^{3'}$, *J* 8.8 Hz), 7.56 d.d (1H, H$^{4'}$, *J* 8.8, 1.9 Hz), 7.61 s (1H, H^8), 7.66 d (1H, H$^{6'}$, *J* 1.9 Hz), 7.81 d (1H, H^4, *J* 9.6 Hz), 8.29 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 51.80 q (OCH_3), 109.47 d (C^8), 112.92 d (C^3), 114.41 s (C^{4a}), 121.33 s (C$^{5'}$), 123.04 d (C$^{4'}$), 125.83 q (CF_3, *J* 285.4 Hz), 126.09 s (C^6), 129.90 d (C^5), 130.08 d (C$^{6'}$), 131.70 d (C$^{3'}$), 138.67 s (C^7), 141.84 s (C$^{2'}$), 142.95 s (C$^{1'}$), 144.74 d (C^4), 161.30 s (C^2), 164.89 s (C^{8a}), 166.40 s (C=O). Found, %: C 57.02; H 2.73; Cl 916; F 14.70. $C_{18}H_{10}ClF_3O_4$. Calculated, %: C 56.49; H 2.63; Cl 9.26; F 14.89.

7-(2-Aminophenyl)-6-(methoxycarbonyl)-2*H*-chromen-2-one (VII). *a*. To a solution of 100 mg (0.3 mmol) of peurutenicin triflate (**III**) in 3 ml of dioxane under an argon atmosphere was added at stirring in suc-

cession 53 mg (0.39 mmol) of 2-aminophenylboric acid (**V**), 17 mg (5 mol%) of $Pd(PPh_3)_4$, 7 mg (10 mol%) of Bu_4NBr, 123 mg (0.9 mmol) of K_2CO_3. The reaction mixture was stirred over 8 h at 100°C, was evaporated to 1 ml, the residue was diluted with 5 ml of water, the reaction product was extracted into dichloromethane (4 × 5 ml), the combined extracts were dried with $MgSO_4$. The drying agent was filtered off, the solvent was evaporated in a vacuum, the residue was subjected to chromatography on silica gel, the fraction containing the reaction product was treated with ether. Yield 50 mg (55%), mp 139–140°C (from ether). IR spectrum, cm^{-1}: 3448, 3395, 3320, 3233, 3128, 3061, 2857, 1744, 1727, 1677, 1630, 1612, 1584, 1504, 1430, 1331, 1297, 1223, 1137, 1102, 1060, 1033, 991, 961, 904. 884, 871, 843, 753, 655, 602. UV spectrum (EtOH), λ_{max}, nm (log ε): 208 (4.42), 241 (4.20), 276 (3.63), 286 (3.66), 311 (3.66). ^{1}H NMR spectrum, δ, ppm: 3.73 s (2H, NH_2), 3.93 s (3H, OCH_3), 6.15 d (1H, H^3, *J* 9.6 Hz), 6.46 d.d (1H, H$^{3'}$, *J* 7.8, 1.2 Hz), 6.90 d.d.d (1H, H$^{5'}$, *J* 8.1, 7.6, 1.2 Hz), 6.95 d.d.d (1H, H$^{4'}$, *J* 8.1, 7.8, 1.5 Hz), 7.46 d.d (1H, H$^{6'}$, *J* 7.6, 1.5 Hz), 7.52 s (1H, H^8), 7.72 d (1H, H^4, *J* 9.6 Hz), 7.92 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 51.82 q (OCH_3), 101.65 d (C^8), 112.45 d (C^3), 113.42 s (C^{4a}), 117.02 s (C$^{1'}$), 117.71 d (C$^{5'}$), 119.93 d (C$^{6'}$), 125.75 s (C^6), 128.51 d (C^5), 130.45 d (C$^{6'}$), 139.59 s (C^7), 143.33 s (C$^{2'}$), 144.30 d (C^4), 146.24 d (C$^{4'}$), 160.22 s (C^2), 164.79 s (C^{8a}), 167.43 s (C=O). Found, %: C 69.09; H 4.24; N 4.80. $C_{17}H_{13}NO_4$. Calculated, %: C 69.15; H 4.44; N 4.74.

b. To a solution of 100 mg (0.3 mmol)of peurutenicin triflate (**III**) in 3 ml of acetonitrile under an argon atmosphere was added 53 mg (0.39 mmol) of 2-aminophenylboric acid (**V**), 11 mg (5 mol%) of $PdCl_2$(dppf), 7 mg (10 mol%) of Bu_4NBr, 123 mg (0.9 mmol) of K_2CO_3. The reaction mixture was stirred for 12 h at 80°C, it was evaporated to 1 ml and diluted with 5 ml of water. The reaction product was extracted into dichloromethane (4 × 5 ml). The residue was chromatographed on silica gel, trace amount of the reaction product was isolated insufficient for further analysis, and 85 mg of the initial triflate.

7-(1*H*-Indol-5-yl)-6-(methoxycarbonyl)-2*H*-chromen-2-one (IX). To a solution of 50 mg (0.15 mmol) of peurutenicin triflate (**III**) in 3 ml of acetonitrile under an argon atmosphere was added at stirring in succession 32 mg (0.2 mmol) of 5-indolylboric acid (**VIII**), 8.5 mg (5 mol%) of $Pd(PPh_3)_4$, 3.5 mg (10 mol%) of Bu_4NBr, and 62 mg (0.45 mmol) of K_2CO_3. The reaction mixture was stirred for 12 h at 80°C (TLC monitoring), it was evaporated to 1 ml and diluted with 5 ml of water. The reaction product was extracted into dichloromethane (4 × 5 ml), the combined extracts were dried with $MgSO_4$. The residue was subjected to chromatography on silica gel, the fraction containing the reaction product was treated with ether. Yield 38 mg (79%), mp 133–135°C (from ether). IR spectrum, cm^{-1}: 3393, 3222, 3080, 3061, 2964, 2925, 2852, 2702, 1735, 1676, 1626, 1600, 1579, 1510, 1491, 1446, 1430, 1342, 1299, 1234, 1214, 1145, 1109, 1076, 1064, 948, 915, 903, 826, 797, 735, 687. UV spectrum (EtOH), λ_{max}, nm (log ε): 202 (4.41), 226 (4.46), 245 (4.12), 288 (3.79), 300 (3.60), 325 (3.86). ^{1}H NMR spectrum, δ, ppm: 3.90 s (3H, OCH_3), 6.20 d (1H, H^3, *J* 9.7 Hz), 6.59 d (1H, H$^{3'}$, *J* 3.0 Hz), 7.15 d (1H, H$^{2'}$, *J* 3.0 Hz), 7.22 d (1H, H$^{7'}$, *J* 8.4 Hz), 7.36 d (1H, H$^{6'}$, *J* 8.4 Hz), 7.50 s (1H, H^8), 7.68 s (1H, H$^{4'}$), 7.78 d (1H, H^4, *J* 9.7 Hz), 7.94 s (1H, H^4), 9.82 s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 51.72 q (OCH_3), 105.11 d (C$^{3'}$), 108.75 d (C$^{7'}$), 109.54 d (C^8), 112.72 d (C^3), 113.40 d (C$^{6'}$), 122.61 d (C$^{4'}$), 123.75 s (C$^{4a'}$), 125.90 s (C^6), 126.70 d (C^5), 134.31 d (C^2), 136.47 s (C$^{3a'}$), 138.29 s (C^7), 144.19 d (C^4), 145.22 s (C$^{7a'}$), 146.93 s (C$^{5'}$), 161.24 s (C^2), 162.72s (C^{8a}), 165.67 s (C=O). Found, %: C 71.93; H 3.99; N 4.27. $C_{19}H_{13}NO_4$. Calculated, %: C 71.47; H 4.10; N 4.39.

6-(Methoxycarbonyl)-7-(furan-3-yl)-2*H*-chromen-2-one (XII). *a*. To a solution of 85 mg (0.26 mmol) of peurutenicin triflate (**III**) in 3 ml of dioxane under an argon atmosphere was added at stirring in succession 37 mg (0.33 mmol) of 3-furanboric acid (**X**), 15 mg (5 mol%) of $Pd(PPh_3)_4$, 6 mg (10 mol%) of Bu_4NBr, 104 mg (0.78 mmol) of K_2CO_3. The reaction mixture was stirred for 8 h at 100°C, cooled, it was evaporated in a vacuum to 1 ml and diluted with 5 ml of water. The reaction product was extracted into dichloromethane (4 × 5 ml), the combined extracts were dried with $MgSO_4$. The residue was subjected to chromatography on silica gel. Yield 36 mg (44%), mp 123–125°C (from ether). IR spectrum, cm^{-1}: 3316, 2945, 2857, 2797, 1744, 1727, 1678, 1630, 1607, 1565, 1503, 1431, 1378, 1329, 1300, 1225, 1205, 1140, 1099, 1064, 1019, 960, 933, 904, 878, 840, 827, 773, 750, 685, 657, 602. UV spectrum (EtOH), λ_{max}, nm (log ε): 203 (4.15), 240 (3.85), 275 (3.38), 285 (3.35), 312 (3.24). ^{1}H NMR spectrum, δ, ppm: 3.93 s (3H, OCH_3), 6.48 d (1H, H^3, *J* 9.6 Hz), 6.51 d.d (1H, H$^{4'}$, *J* 3.6, 1.6 Hz), 7.25 s (1H, H^8), 7.48 d.d (1H, H$^{5'}$, *J* 3.6, 1.8 Hz), 7.65 d (1H, H$^{2'}$, *J* 1.6 Hz), 7.75 d (1H, H^4, *J* 9.6 Hz),

8.24 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 52.93 q (OCH_3), 111.80 d (C^8), 113.19 d (C^3), 118.33 d ($C^{4'}$), 118.46 s (C^{4a}), 120.67 s (C^6), 128.17 s ($C^{3'}$), 132.64 d (C^5), 137.87 s (C^7), 139.65 d ($C^{5'}$), 141.91 d (C^4), 142.52 d ($C^{2'}$), 156.60 s (C^{8a}), 158.64 s (C^2), 162.98 s (C=O). Found, %: C 67.93; H 3.99. $C_{15}H_{10}O_5$. Calculated, %: C 67.67; H 3.83.

b. To a solution of 100 mg (0.3 mmol) of peurutenicin triflate (**III**) in 3 ml of acetonitrile under an argon atmosphere was added at stirring in succession 43 mg (0.39 mmol) of 3-furanboric acid (**X**), 11 mg (5 mol%) of $PdCl_2$(dppf), 7 mg (10 mol%) of Bu_4NBr, and 123 mg (0.9 mmol) of K_2CO_3. The reaction mixture was stirred for 12 h at 80°C, it was evaporated to 1 ml and diluted with 5 ml of water. The reaction product was extracted into dichloromethane (4 × 5 ml), the combined extracts were dried with $MgSO_4$. The residue was chromatographed on silica gel. Yield 15 mg (18%).

6-(Methoxycarbonyl)-7-(furan-2-yl)-2*H*-chromen-2-one (XIII). To a solution of 85 mg (0.26 mmol) of peurutenicin triflate (**III**) in 3 ml of dioxane under an argon atmosphere was added at stirring in succession 37 mg (0.33 mmol) of 2-furanboric acid (**XI**), 15 mg (5 mol%) of $Pd(PPh_3)_4$, 6 mg (10 mol%) of Bu_4NBr, and 104 mg (0.78 mmol) of K_2CO_3. The reaction mixture was stirred for 8 h at 100°C. On the completion of the reaction (TLC monitoring) the reaction mixture was evaporated, the residue was diluted with 5 ml of water. The reaction product was extracted into dichloromethane (4 × 5 ml), the combined extracts were dried with $MgSO_4$. The residue was chromatographed on silica gel. Yield 36 mg (44%), mp 130–132°C (from ether). IR spectrum, cm^{-1}: 2944, 2858, 1745, 1727, 1677, 1630, 1607, 1432, 1332, 1297, 1224, 1202, 1182, 1136, 1101, 1060, 1040, 960, 934, 904, 871, 835, 828, 794, 750, 683, 656, 630, 601. UV spectrum (EtOH), λ_{max}, nm (log ε): 200 (4.00), 237 (4.01), 275 (3.39), 285 (3.36), 311 (3.24). ^1H NMR spectrum, δ, ppm: 3.94 s (3H, OCH_3), 6.37 br.s (1H, $H^{4'}$), 6.50 d (1H, H^3, *J* 9.6 Hz), 6.94 br.s (1H, $H^{3'}$), 7.22 s (1H, H^8), 7.56 br.s (1H, $H^{5'}$), 7.75 d (1H, H^4, *J* 9.6 Hz), 8.24 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 51.71 q (OCH_3), 104.99 d (C^8), 107.26 d ($C^{3'}$), 107.46 s (C^{4a}), 108.97 d ($C^{4'}$), 112.52 d (C^3), 113.80 s (C^6), 123.32 d (C^5), 138.38 s (C^7), 140.79 d (C^4), 144.20 s ($C^{2'}$), 152.87 d ($C^{5'}$), 158.41 s (C^2), 161.68 s (C^{8a}), 160.64 s (C=O). Found, %: C 66.46; H 4.00. $C_{15}H_{10}O_5$. Calculated, %: C 66.67; H 3.73.

6-(Methoxycarbonyl)-7-(pyridine-3-yl)-2*H*-chromen-2-one (XVI). To a solution of 85 mg (0.26 mmol) of peurutenicin triflate (**III**) in 3 ml of dioxane under an argon atmosphere was added at stirring in succession 40 mg (0.33 mmol) of 3-pyridineboric acid (**XIV**), 15 mg (5 mol%) of $Pd(PPh_3)_4$, 6 mg (10 mol%) of Bu_4NBr, and 104 mg (0.78 mmol) of K_2CO_3. The reaction mixture was stirred for 8 h at 100°C, cooled, evaporated in a vacuum, the residue was diluted with 5 ml of water. The reaction product was extracted into dichloromethane (4 × 5 ml), the combined extracts were dried with $MgSO_4$. The residue was chromatographed on silica gel. Yield 60 mg (82%), mp 123–124°C (from ether). IR spectrum, cm^{-1}: 3060, 2956, 2924, 2854, 1728, 1674, 1627, 1600, 1582, 1491, 1452, 1431, 1394, 1375, 1346, 1299, 1278, 1236, 1224, 1180, 1140, 1101, 1074, 1061, 1010, 1001, 960, 943, 903, 870, 827, 796, 752, 721, 651, 599. UV spectrum (EtOH), λ_{max}, nm (log ε): 202 (4.19), 225 (4.14), 242 (4.19), 275 (3.66), 287 (3.70), 306 (3.72), 322 (3.73). ^1H NMR spectrum, δ, ppm: 3.99 s (3H, OCH_3), 6.27 d (1H, H^3, *J* 9.8 Hz), 6.87 s (1H, H^8), 7.46 m (1H, $H^{5'}$), 7.50 d.d (1H, $H^{4'}$, *J* 7.7, 1.8 Hz), 7.53 d.d (1H, $H^{6'}$, *J* 7.5, 1.8 Hz), 7.75 d (1H, H^4, *J* 9.8 Hz), 8.01 s (1H, H^5), 8.28 br.s (1H, $H^{2'}$). ^{13}C NMR spectrum, δ, ppm: 52.51 q (OCH_3), 104.85 d (C^8), 114.14 d (C^3), 119.26 s (C^{4a}), 120.76 s (C^6), 124.17 d ($C^{5'}$), 130.64 d (C^5), 132.00 s ($C^{1'}$), 135.85 s (C^7), 137.60 d ($C^{6'}$), 142.94 d ($C^{2'}$), 144.20 d (C^4), 149.50 d ($C^{4'}$), 160.04 s (C^2), 164.26 s (C^{8a}), 169.32 s (C=O). Found, %: C 68.04; H 3.78; N 4.88. $C_{16}H_{11}NO_4$. Calculated, %: C 68.32; H 3.94; N 4.98.

6-(Methoxycarbonyl)-7-(pyridine-4-yl)-2*H*-chromen-2-one (XVII). To a solution of 85 mg (0.26 mmol) of peurutenicin triflate (**III**) in 3 ml of dioxane under an argon atmosphere was added at stirring in succession 40 mg (0.33 mmol) of 4-pyridineboric acid (**XV**), 15 mg (5 mol%) of $Pd(PPh_3)_4$, 6 mg (10 mol%) of Bu_4NBr, and 104 mg (0.78 mmol) of K_2CO_3. The reaction mixture was stirred for 8 h at 100°C, cooled, evaporated in a vacuum, the residue was diluted with 5 ml of water. The reaction product was extracted into dichloromethane (4 × 5 ml), the combined extracts were dried with $MgSO_4$. The residue was chromatographed on silica gel. Yield 56 mg (77%), mp 143–144°C (from ether). IR spectrum, cm^{-1}: 3431, 3060, 2960, 1728, 1674, 1627, 1579, 1490, 1431, 1377, 1296, 1222, 1180, 1137, 1101, 1060, 960, 902, 871, 842, 750, 655, 599. UV spectrum (EtOH), λ_{max}, nm (log ε): 213 (3.91), 219 (4.11), 222 (4.13), 225 (4.14), 244 (4.38), 276 (3.85), 287 (3.87), 323 (3.87), 338 (3.74). ^1H NMR spectrum, δ, ppm: 3.99 s (3H, OCH_3), 6.30 d (1H, H^3, *J* 9.6 Hz), 6.61 d (1H, $H^{3',5'}$, *J* 7.5 Hz), 6.75 s (1H, H^8), 7.75 d (1H, H^4, *J* 9.6 Hz), 7.81 d (1H, $H^{2',6'}$,

J 7.5 Hz), 8.08 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 52.32 q (OCH_3), 104.05 d (C^8), 113.16 d (C^3), 117.88 d ($C^{3',5'}$), 118.37 s (C^{4a}), 120.31 s (C^6), 130.69 d (C^5), 132.47 s (C^7), 142.05 d (C^4), 143.44 d (C^2), 146.53 d ($C^{6'}$), 156.36 s ($C^{1'}$), 161.75 s (C^2), 163.50 s (C^{8a}), 168.94 s (C=O). Found, %: C 67.94; H 4.08; N 4.86. $C_{16}H_{11}NO_4$. Calculated, %: C 68.32; H 3.94; N 4.98.

(*E*)-6-(Methoxycarbonyl)-7-[2-(pyridine-2-yl) vinyl]-2*H*-chromen-2-one (XX). *a*. To solution of 300 mg (0.93 mmol) of peurutenicin triflate (**III**) in 5 ml of DMF under an argon atmosphere was added at stirring 194.4 mg (1.86 mmol) of 2-vinylpyridine (**XVIII**), 4 mg (2 mol%) of $Pd(OAc)_2$, 23 mg (8 mol%) of $(o\text{-tol})_3P$, and 0.128 ml (0.93 mmol) of triethylamine. The reaction mixture was stirred for 7 h at 115°C and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform), trace amount of the reaction product was isolated insufficient for further analysis, and 268 mg of the initial compound.

b. To a solution of 150 mg (0.46 mmol) of peurutenicin triflate (**III**) in 3 ml of DMF under an argon atmosphere was added at stirring in succession 97.2 mg (0.93 mmol) of 2-vinylpyridine (**XVIII**), 2 mg (2 mol%) of $Pd(OAc)_2$, 11 mg (8 mol%) of $(o\text{-tol})_3P$, and 0.064 ml (0.46 mmol) of NEt_3. The reaction mixture was stirred for 8 h at 135–140°C and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform). Yield 10 mg (9%) of the reaction product and 100 mg of the initial compound.

c. To a solution of 150 mg (0.46 mmol) of peurutenicin triflate (**III**) in 3 ml of DMF under an argon atmosphere was added at stirring 97.2 mg (0.93 mmol) of 2-vinylpyridine (**XVIII**), 2 mg (2 mol%) of $Pd(OAc)_2$, 11 mg (8 mol%) of $(o\text{-tol})_3P$, and 0.064 ml (0.46 mmol) of triethylamine. The reaction mixture was stirred for 10 h at 135–140°C and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform) the fraction with the reaction product was collected, and after the recrystallization from ether we isolated 30 mg (47%) of compound **XX**, conversion of triflate **III** 80%.

d. To a solution of 150 mg (0.46 mmol) of peurutenicin triflate (**III**) in 3 ml of DMF under an argon atmosphere was added at stirring in succession 97.2 mg (0.93 mmol) of 2-vinylpyridine (**XVIII**), 4 mg (4 mol%) of $Pd(OAc)_2$, 11 mg (8 mol%) of $(o\text{-tol})_3P$, and 0.064 ml (0.46 mmol) of NEt_3. The reaction mixture was stirred for 10 h at 135–140°C and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform) to isolate 50 mg (75%) of the reaction product, conversion of triflate 47%.

e. To a solution of 150 mg (0.46 mmol) of peurutenicin triflate (**III**) in 3 ml of DMF under an argon atmosphere was added at stirring in succession 97.2 mg (0.93 mmol) of 2-vinylpyridine (**XVIII**), 4 mg (4 mol%) of $Pd(OAc)_2$, 11 mg (8 mol%) of $(o\text{-tol})_3P$, and 0.064 ml (0.46 mmol) of NEt_3. The reaction mixture was stirred for 16 h at 135–140°C and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform) to isolate 56 mg (60%) of compound **XX**, conversion of triflate 66%.

f. To a solution of 150 mg (0.46 mmol) of peurutenicin triflate (**III**) in 3 ml of DMF under an argon atmosphere was added at stirring in succession 97.2 mg (0.93 mmol) of 2-vinylpyridine (**XVIII**), 4 mg (4 mol%) of $Pd(OAc)_2$, 22 mg (8 mol%) of BINAP, and 0.064 ml (0.46 mmol) of NEt_3. The reaction mixture was stirred for 16 h at 135–140°C (TLC monitoring) and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform), and after the recrystallization from ether we obtained 106 mg (75%) of compound **XX**, conversion of triflate 100%, mp 202–204°C (from ethanol). IR spectrum, cm^{-1}: 3050, 3018, 2852, 1718, 1612, 1585, 1564, 1547, 1500, 1468, 1430, 1380, 1286, 1213, 1182, 1147, 1111, 1072, 991, 966, 910, 845, 825, 789, 762, 740, 700. UV spectrum (EtOH), λ_{max}, nm (log ε): 200 (4.31), 219 (4.09), 246 (4.21), 333 (4.16). ^1H NMR spectrum, δ, ppm: 3.95 s (3H, OCH_3), 6.43 d (1H, H^3, *J* 9.6 Hz), 7.18 d (1H, H^b, *J* 15.8 Hz), 7.21 s (1H, H^8), 7.28 m (1H, $H^{4'}$), 7.47 d.d (1H, $H^{6'}$, *J* 7.2, 1.6 Hz), 7.69 m (1H, $H^{5'}$), 7.72 d (1H, H^4, *J* 9.6 Hz), 8.12 s (1H, H^5), 8.42 d (1H, H^a, *J* 15.8 Hz), 8.64 d (1H, $H^{3'}$). ^{13}C NMR spectrum, δ, ppm: 52.06 q (OCH_3), 108.07 d (C^8), 112.02 d (C^3), 113.34 s (C^{4a}), 119.26 d ($C^{4'}$), 121.11 d ($C^{6'}$), 123.08 s (C^6), 127.03 d (C^5), 129.27 d (C^b), 136.30 d ($C^{5'}$), 137.21 d (C^a), 138.09 s (C^7), 144.15 d (C^4), 149.16 d ($C^{3'}$), 155.86 s ($C^{1'}$), 161.52 s (C^2), 163.37 s (C^{8a}), 165.87 s (C=O). Found, %: C 67.76; H 4.59; N 4.78. $C_{18}H_{13}NO_4$ + 1/3DMF. Calculated, %: C 70.35; H 4.26; N 4.56 (without DMF); C 67.05; H 4.40; N 5.14 (with DMF).

(*E*)-6-(Methoxycarbonyl)-7-[2-(6-methylpyridin-3-yl)vinyl]-2*H*-chromen-2-one (XXI). To a solution of 150 mg (0.46 mmol) of peurutenicin triflate (**III**) in

3 ml of DMF under an argon atmosphere was added at stirring in succession 110 mg (0.93 mmol) of 5-vinyl-2-methylpyridine (**XIX**), 4 mg (4 mol%) of $Pd(OAc)_2$, 22 mg (8 mol%) of BINAP, and 0.064 ml (0.46 mmol) of triethylamine. The reaction mixture was stirred for 16 h at 135–140°C (TLC monitoring) and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform), and after the recrystallization from ether we obtained 64 mg (43%) of compound **XXI**, triflate conversion 100%, mp 231–232°C (from ether). IR spectrum, cm^{-1}: 3086, 3008, 2924, 2850, 2717, 1755, 1714, 1616, 1600, 1551, 1491, 1441, 1423, 1383, 1292, 1217, 1178, 1147, 1109, 1070, 1030, 955, 912, 837, 785, 769, 729, 629. UV spectrum (EtOH), λ_{max}, nm (log ε): 201 (4.30), 246 (4.28), 337 (4.23). ^1H NMR spectrum, δ, ppm: 2.58 s (3H, CH_3 at C$^{3'}$), 3.95 s (3H, OCH_3), 6.44 d (1H, H^3, *J* 9.6 Hz), 7.04 d (1H, H^b, *J* 16.6 Hz), 7.18 d (1H, H$^{5'}$, *J* 7.6 Hz), 7.61 s (1H, H^8), 7.70 d (1H, H^4, *J* 9.6 Hz), 7.81 d.d (1H, H$^{4'}$, *J* 7.6, 1.8 Hz), 8.08 d (1H, H^a, *J* 16.6 Hz), 8.14 s (1H, H^5), 8.63 d (1H, H$^{2'}$, *J* 1.8 Hz). ^{13}C NMR spectrum, δ, ppm: 23.55 q (OCH_3), 52.18 q (OCH_3), 108.56 d (C^8), 112.54 d (C^3), 113.39 s (C^{4a}), 119.93 d (C$^{5'}$), 122.21 s (C^6), 123.91 d (C^b), 125.34 d (C^5), 130.44 d (C$^{1'}$), 130.82 d (C$^{4'}$), 131.87 d (C^a), 137.56 s (C^7), 142.96 d (C$^{2'}$), 144.15 d (C^4), 157.18 s (C$^{6'}$), 160.59 s (C^2), 163.15 s (C^{8a}), 167.13 s (C=O). Found, %: C 70.67; H 4.84; N 4.64. $C_{19}H_{15}NO_4$. Calculated, %: C 71.02; H 4.71; N 4.36.

(*E*)-6-(Methoxycarbonyl)-7-[2-(pyrazin-2-yl)-vinyl]-2*H*-chromen-2-one (XXIV). To a solution of 100 mg (0.3 mmol) of peurutenicin triflate (**III**) in 3 ml of DMF under an argon atmosphere was added at stirring in succession 63 mg (0.6 mmol) of 2-vinylpyrazine (**XXII**), 2.7 mg (4 mol%) of $Pd(OAc)_2$, 15 mg (8 mol%) of BINAP, and 0.042 ml (0.3 mmol) of NEt_3. The reaction mixture was stirred for 16 h at 135–140°C (TLC monitoring) and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform), and after the recrystallization from ether we obtained 51 mg (56%) of compound XXIV, mp 200–201°C (from ether). IR spectrum, cm^{-1}: 3058, 2955, 2922, 2851, 1718, 1680, 1620, 1548, 1500, 1488, 1405, 1379, 1285, 1212, 1184, 1149, 1106, 1070, 1031, 1017, 962, 913, 866, 826, 805, 785, 751, 720, 699. UV spectrum (EtOH), λ_{max}, nm (log ε): 201 (4.29), 230 (4.16), 247 (4.33), 335 (4.23). ^1H NMR spectrum, δ, ppm: 3.89 s (3H, OCH_3), 6.42 d (1H, H^3, *J* 9.6 Hz), 7.08 d (1H, H^b, *J* 15.9 Hz), 7.59 s (1H, H^8), 7.69 d (1H, H^4, *J* 9.6 Hz), 8.05 d (1H, H^a, *J* 15.9 Hz), 8.11 s (1H, H^5), 8.25 d (1H, H$^{5'}$, *J* 7.5 Hz), 8.37 d (1H, H$^{6'}$, *J* 7.5 Hz), 8.68 s (1H, H$^{3'}$). ^{13}C NMR spectrum, δ, ppm: 52.16 q (OCH_3), 109.38 d (C^8), 112.15 d (C^3), 113.04 s (C^{4a}), 124.37 s (C^6), 126.14 d (C^b), 130.45 d (C^5), 136.35 d (C^a), 137.60 s (C^7), 139.24 d (C$^{5'}$), 140.75 d (C$^{3'}$), 141.76 d (C$^{6'}$), 144.25 d (C^4), 150.46 s (C$^{2'}$), 161.29 s (C^2), 163.68 s (C^{8a}), 167.21 s (C=O). Found, %: C 66.15; H 4.05; N 9.03. $C_{17}H_{12}N_2O_4$. Calculated, %: C 66.23; H 3.92; N 9.09.

(*E*)-6-(Methoxycarbonyl)-7-[2-(1*H*-1,2,4-triazol-1-yl)vinyl]-2*H*-chromen-2-one (XXV). To a solution of 100 mg (0.3 mmol) of peurutenicin triflate (**III**) in 3 ml of DMF under an argon atmosphere was added at stirring in succession 60 mg (0.6 mmol) of 1-vinyl-1*H*-1,2,4-triazole (**XXIII**), 2.7 mg (4 mol%) of $Pd(OAc)_2$, 15 mg (8 mol%) of BINAP, and 0.042 ml (0.3 mmol) of triethylamine. The reaction mixture was stirred for 16 h at 135–140°C (TLC monitoring) and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform), and after the recrystallization from ether we obtained 40 mg (45%) of compound **XXV**, mp 239–240°C (from ether). IR spectrum, cm^{-1}: 2922, 2852, 1721, 1680, 1660, 1624, 1600, 1558, 1507, 1500, 1438, 1283, 1214, 1149, 1111, 1048, 1000, 961, 908, 828, 750, 674. UV spectrum (EtOH), λ_{max}, nm (log ε): 200 (4.72), 242 (4.30), 273 (3.84), 295 (3.92), 319 (4.00). ^1H NMR spectrum, δ, ppm: 3.87 s (3H, OCH_3), 6.40 d (1H, H^3, *J* 9.8 Hz), 7.50 d (1H, H^b, *J* 15.8 Hz), 7.46 s (1H, H^8), 7.70 d (1H, H^4, *J* 9.8Hz), 8.08 d (1H, H^a, *J* 15.8 Hz), 7.98 s (1H, H$^{5'}$), 8.09 s (1H, H^5), 8.43 br.s (1H, H$^{3'}$). ^{13}C NMR spectrum, δ, ppm: 52.19 q (OCH_3), 107.40 d (C^8), 110.56 s (C^{4a}), 113.36 d (C^3), 118.27 d (C^b), 121.07 d (C^5), 122.36 d (C^a), 128.21 s (C^6), 137.11 s (C^7), 144.46 d (C^4), 145.63 d (C$^{5'}$), 154.28 s (C$^{3'}$), 161.06 s (C^2), 166.22 s (C^{8a}), 167.26 s (C=O). Found, %: C 60.88; H 3.52; N 14.05. $C_{15}H_{11}N_3O_4$. Calculated, %: C 60.61; H 3.73; N 14.14.

(*E*)-6-(Methoxycarbonyl)-7-styryl-2*H*-chromen-2-one (XXVII). To a solution of 150 mg (0.46 mmol) of peurutenicin triflate (**III**) in 3 ml of DMF under an argon atmosphere was added at stirring in succession 97 mg (0.93 mmol) of styrene (**XXVI**), 4 mg (4 mol%) of $Pd(OAc)_2$, 22 mg (8 mol%) of BINAP, and 0.064 ml (0.46 mmol) of triethylamine. The reaction mixture was stirred for 16 h at 135–140°C (TLC monitoring) and poured in a Petri dish. On evaporation of the solvent the residue was subjected to column chromatography on silica gel (eluent chloroform), and after the recrystalliza-

tion from ether we obtained 112 mg (79%) of compound **XXVII**, mp 240–242°C (from ether). IR spectrum, cm^{-1}: 3059, 3026, 2966, 2927, 2856, 1734, 1678, 1624, 1600, 1580, 1487, 1450, 1389, 1354, 1281,1203, 1165, 1140, 1060, 1036, 900, 820, 806, 756, 717, 696. UV spectrum (EtOH), λ_{max}, nm (log ε): 203 (4.50), 230 (4.08), 250 (3.71), 271 (3.52), 279 (3.48), 335 (3.54). ^{1}H NMR spectrum, δ, ppm: 3.80 s (3H, OCH_3), 6.19 d (1H, H^3, *J* 9.6 Hz), 6.74 d (1H, H^b, *J* 14.8 Hz), 6.88 d (1H, H^a, *J* 14.8 Hz), 7.16 m (2H, H$^{2',6'}$), 7.23 m (3H, H$^{3',4',5'}$), 7.41 s (1H, H^8), 7.77 d (1H, H^4, *J* 9.6 Hz), 8.36 s (1H, H^5). ^{13}C NMR spectrum, δ, ppm: 52.33 q (OCH_3), 106.02 d (C^8), 112.96 d (C^3), 113.08 s (C^{4a}), 124.31 d (C^b), 125.34 d (C$^{2',6'}$), 125.80 s (C^6), 125.66 d (C$^{4'}$), 128.58 d (C$^{3',5'}$), 129.34 d (C^5), 130.14 d (C^a), 137.10 d (C$^{1'}$), 137.41 s (C^7), 144.45 d (C^4), 159.70 s (C^2), 163.80 s (C^{8a}), 168.05 s (C=O). Found, %: C 74.61; H 4.82. $C_{19}H_{14}O_4 \cdot H_2O$. Calculated, %: C 74.50; H 4.61.

ACKNOWLEDGMENTS

The study was carried out under the financial support of the Russian Foundation for Basic Research (grant no. 11-03-00242-a) and of the Program of the President of the Russian Federation for the support of the leading scientific schools (grant NSh-3986.2012.3).

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