DOI 10.1007/s10593-016-1971-y

Chemistry of Heterocyclic Compounds **2016**, *52*(10), 814–822

3-Nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromenes: synthesis and reactions with nucleophiles

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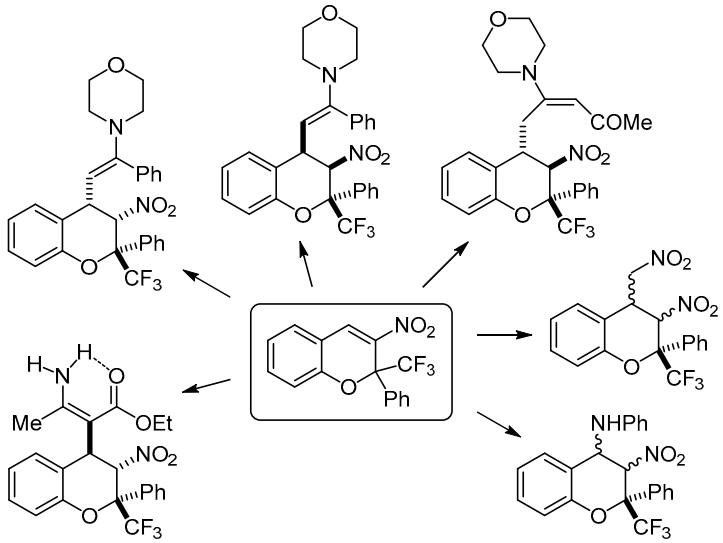
Translated from Khimiya Geterotsiklicheskikh Soedinenii, 2016, *52*(10), 814–822

Submitted August 26, 2016
Accepted September 20, 2016



A method is proposed for the synthesis of 3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromenes by tandem condensation of salicylic aldehydes with (*E*)-3,3,3-trifluoro-1-nitro-2-phenylprop-1-ene in the presence of triethylamine. The example of 3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromene was used to demonstrate conjugated addition reactions with enamines, nitromethane, and aniline, which are characteristic for this class of compounds. The structure of the obtained products was confirmed by X-ray structural analysis.

Keywords: 3,3,3-trifluoro-1-nitro-2-phenylprop-1-ene, 3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromenes, salicylic aldehydes, 2,2,3,4-tetrasubstituted chromanes, diastereoselectivity, nucleophilic addition.

3-Nitro-2*H*-chromenes represent an important class of organic compounds, the properties of which have been intensively studied in recent years.[1] The interest toward these heterocycles as starting substrates for the preparation of more complex bioactive molecules is linked to their availability and high reactivity, as well as the common occurrence of many derivatives of chromene and chromane (3,4-dihydro-2*H*-1-benzopyran) in plants. Such compounds show promise as pesticides and potential drug molecules.[2]

The reactivity of 3-nitro-2*H*-chromenes is mostly determined by the nitroalkene moiety, although the substituent at position 2 can also substantially affect the rate and direction of some reactions, even though it is bonded to sp^3-hybridized carbon atom. For example, we recently studied 3-nitro-2-(trifluoromethyl)-2*H*-chromenes **1** (Fig. 1), the reactivity of which toward nucleophiles significantly exceeded[1] the previously known 3-nitro-2-phenyl-2*H*-chromenes **2**, due to the presence of a CF_3 group providing an additional strong negative inductive effect, thus activating the double bond in pyran ring. Besides that, the addition reactions involving 2-(trifluoromethyl)chromenes **1** were found to be more stereoselective, compared to the analogous reactions of 2-phenylchromenes **2**, allowing us to obtain a wide range of new 2,3,4-trisubstituted chromanes as individual diastereomers, the structures of which were reliably established by X-ray structural analysis.[3]

The introduction of a bulky phenyl substituent along with the CF_3 group at position 2 of chromenes **1** was clearly of interest, as it allowed to obtain 3-nitro-2-phenyl-

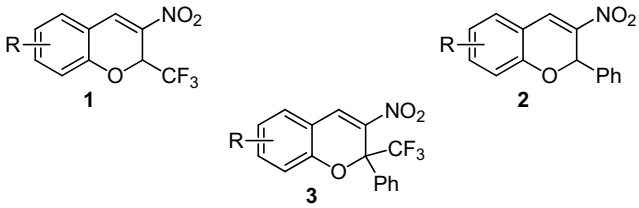


Figure 1. 2-Substituted 3-nitro-2*H*-chromenes **1**–**3**.

2-(trifluoromethyl)-2*H*-chromenes **3** that represented a combination of chromenes **1** and **2** (Fig. 1). The structural features of compounds **3** can not only increase the stereoselectivity of addition reactions involving these compounds and to expand the range of stereochemically different 2,2,3,4-tetrasubstituted chromanes, but also lead to the emergence of new, useful properties of chromenes themselves, as well as in products obtained from them.

The most common method that has been used for obtaining 3-nitro-2*H*-chromenes is based on the reaction of salicylic aldehydes with conjugated nitroalkenes in the presence of bases, due to the wide availability of these starting materials.[1] The process represented a nucleophilic addition of the respective phenolate anion to nitroalkene molecule, followed by intramolecular Henry reaction and led to the formation of 4-hydroxy-3-nitrochromane, dehydration of which provided the desired product (Scheme 1). This approach can be used for the synthesis of a wide range of nitrochromenes containing various substituents both at position 2 of the pyran system and in the aromatic ring.

In a continuation of our efforts directed toward the synthesis[4] and understanding of the chemical properties[5] of 3-nitro-2-(trifluoromethyl)-2*H*-chromenes **1**, in the current work we propose a method for the preparation of previously unknown 3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromenes **3** and describe representative reactions of N- and C-nucleophiles with a compound of this class, which lacks substituents in the benzene ring.

Nitrochromenes **3a**–**g** were synthesized from the corresponding salicylic aldehydes and (*E*)-3,3,3-trifluoro-1-nitro-2-phenylprop-1-ene, obtained by Henry reaction from trifluoroacetophenone and nitromethane, followed by dehydration of the formed nitro alcohol with thionyl chloride in the presence of pyridine.[6] The synthesis of chromenes **3a**,**d**–**g** was performed in dichloromethane at room temperature for 3 h, using triethylamine as base. The formation of 4-hydroxy-3-nitrochromane intermediate was not observed, and the yields of chromenes **3a**,**d**–**g** reached 80–96% (Scheme 1, Table 1). Additional refluxing for 3 min was required for obtaining chromenes **3b**,**c** from 5-chloro- and 5-bromosalicylic aldehydes, while their yields were lower (64–69%).

Chromenes **3a**–**g** were isolated as yellow fine crystalline powders. ^{1}H NMR spectra of these compounds contained a characteristic singlet of 4-CH proton in the range of 8.07–8.24 ppm. The diastereotopic methylene protons in 8-ethoxychromene **3g** were observed as two double quartets at 4.07 and 4.11 ppm, pointing to the presence of asymmetric carbon atom in the molecule. The trifluoromethyl group bonded to sp^3 carbon atom was observed in ^{19}F NMR spectra of chromenes **3a**–**g** as a singlet at 88.8–89.5 ppm, which was shifted downfield compared to chromenes **1** (83.9–84.3 ppm),[3a–c,4a,5b] due to the deshielding effect of 2-phenyl substituent. ^{13}C NMR spectra of compounds **3a**–**g** featured quartets of the CF_3 group and the C-2 atom in the ranges of 123.2−123.7 and 82.4−83.7 ppm, respectively, with the spin-spin coupling constants of $^1J_{CF}$ = 289.4−290.6 and $^2J_{CF}$ = 30.8−31.3 Hz, as well as a quartet or broadened singlet of the C_{ipso} atom in the phenyl substituent at 127.2−127.4 ppm ($^3J_{CF}$ = 1.0−1.5 Hz). IR spectra of the obtained compounds contained absorption bands due to the stretching vibrations of double bond at 1631−1641 cm^{-1} and the olefinic nitro group at 1519−1528 and 1289−1342 cm^{-1}. The structure of nitrochromene **3a** was confirmed by X-ray structural analysis (Fig. 2).

Scheme 1

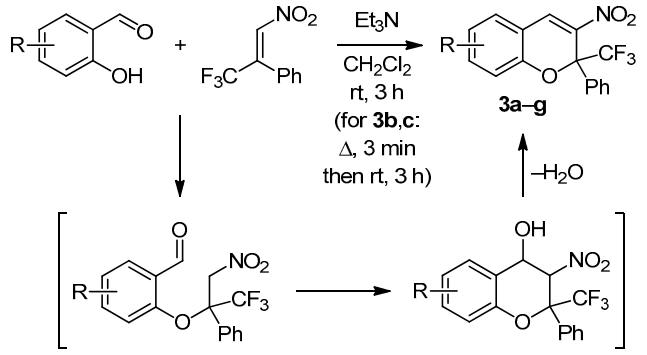


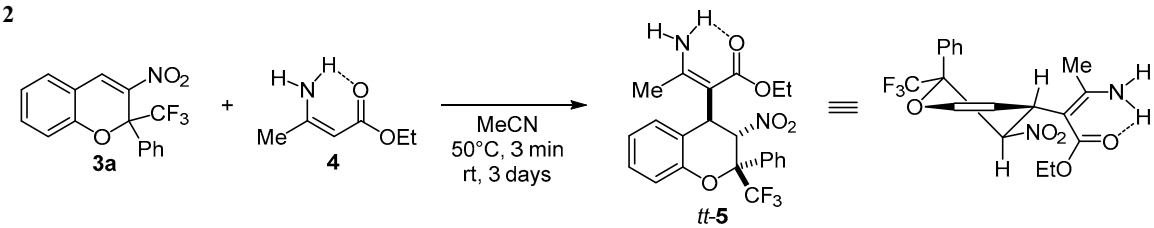
Table 1. Yields of nitrochromenes **3a**–**g**

Chromene	R	Yield, %
3a	H	96
3b	6-Cl	64
3c	6-Br	69
3d	6,8-Br_2	95
3e	6-Me	80
3f	6-OMe	95
3g	8-OEt	89

We further studied the interaction of 3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromene (**3a**) with primary and tertiary push-pull enamines, which were synthesized from acetoacetic ester and acetylacetone. It was found that ethyl (*Z*)-3-aminocrotonate (**4**), similarly as in the case of 3-nitro-2-(trifluoromethyl)-2*H*-chromenes **1**,[7] added with its most nucleophilic α-carbon atom at position 4 of chromene **3a** that was activated by nitro group, forming 2,2,3,4-tetrasubstituted chromane **5** in 74% yield as an individual *trans*,*trans*-diastereomer *tt*-**5** with (*Z*)-configuration of the enaminoester moiety, stabilized by intramolecular hydrogen bond. The reaction was performed by brief heating in anhydrous acetonitrile, followed by maintaining at room temperature for 3 days (Scheme 2).

The *trans*-diequatorial configuration of nitro group and enaminoester moiety was identified from the large value of

Scheme 2



spin-spin coupling constant between 3-CH and 4-CH protons ($J_{3,4}$ = 11.7 Hz), observed in ^{1}H NMR spectrum of compound **5** in $CDCl_3$ solution. The presence of intramolecular hydrogen bond both in solution and solid state, associated with the (*Z*)-configuration of double bond, was evident from the broadened singlet of NH proton in the downfield region (8.94 ppm) and from the presence of ν(NH) absorption band at 3490 cm^{-1} in the IR spectrum of chromane **5**. The CF_3 group was observed as a singlet in ^{19}F NMR spectrum of this compound at 85.6 ppm.

The validity of conclusions about the structure of compound **5** that were reached from the examination of spectral data, as well as the relative configuration of substituents at the C-2 atom were confirmed by monocrystal X-ray structural analysis of this chromane, proving its *trans*,*trans* configuration at C-2, C-3, and C-4 atoms (*tt*-isomer). As shown in Figure 3, all three bulky substituents in the heterocycle (CF_3, NO_2, and the enaminoester group) occupied equatorial positions, while the planar phenyl substituent at the C-2 carbon atom and the 3,4-CH hydrogen atoms were axially oriented. The unfavorable steric interactions between the bulky substituents caused the pyran ring to assume a twisted half-chair conformation. The planarity of enaminoester moiety was caused by the presence of an intramolecular hydrogen bond between the hydrogen atom of amino group and the carbonyl oxygen atom, with the interatomic distances N(2)–H(2A) 0.90(2), H(2A)···O(5) 1.96(2), N(2)···O(5) 2.660(3) Å, and the angle N(2)–H(2A)···O(5) 133(2)°. The plane of enaminoester moiety was nearly orthogonal to the aromatic ring plane (the dihedral angle between these planes was equal to 85.8(2)°).

It should be noted that chromane *tt*-**5** both in crystalline state (Fig. 3) and in solution phase (as indicated by the presence of one set of signals in ^{1}H and ^{19}F NMR spectra) existed in the form of the energetically favored atropoisomer with *anti* configuration of the 4-CH atom and the CO_2Et group, due to the hindered rotation around the C(4)–C(2') bond (Scheme 2).[7]

In contrast to the primary (*Z*)-enaminoester **4**, the interaction of chromene **3a** with tertiary (*E*)-enamino ketone **6** under analogous conditions occurred with the participation of vinylogous β-methyl group and led to the formation of *cis*,*trans*-chromane **7** in 49% yield. The reaction time could be shortened to 5 h, if the process was performed at 60°C (Scheme 3). Chromenes **1** reacted with enamino ketone **6** in analogous way.[3c]

^{1}H NMR spectrum of compound **7** contained two double doublets of diastereotopic methylene protons at 3.19 and 3.71 ppm, with spin-spin coupling constants of ^2J = 13.1 Hz; ^3J = 3.0 and 2.5 Hz, respectively, a singlet of the =CH proton

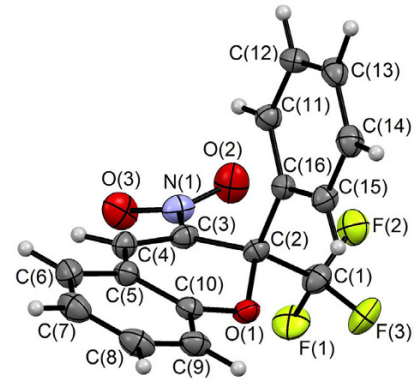


Figure 2. The molecular structure of compound **3a** with atoms represented by thermal vibration ellipsoids of 30% probability.

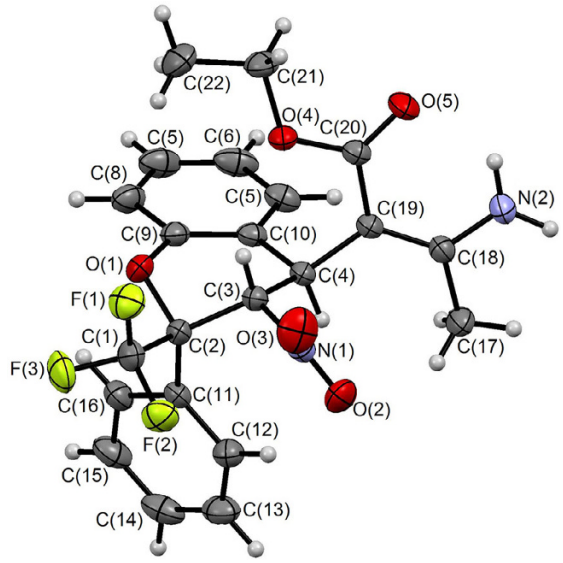
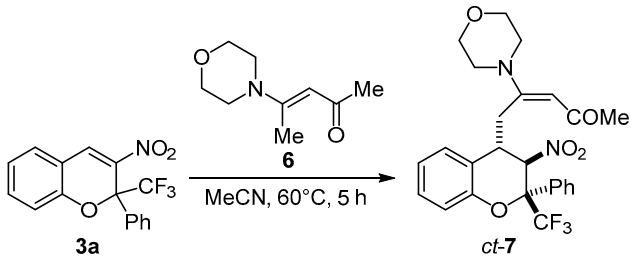


Figure 3. The molecular structure of compound *tt*-**5** with atoms represented by thermal vibration ellipsoids of 30% probability.

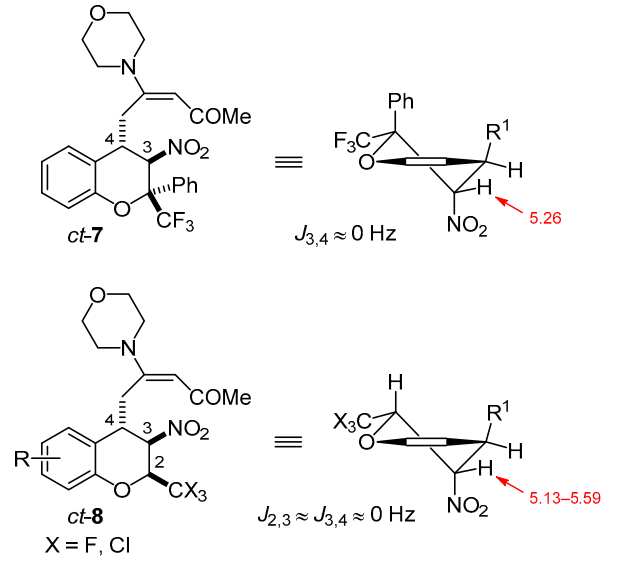
(6.00 ppm) and a broadened singlet of the 3-CH proton (5.26 ppm); the signal of the 4-CH proton overlapped with the signals of morpholine CH_2OCH_2 protons. The similar chemical shifts of 3-CH proton and spin-spin coupling constant $J_{3,4}$ ≈ 0 Hz were earlier observed in the case of *cis*,*trans*-2,3,4-trisubstituted 2-CX_3-chromanes **8** (X = F, Cl), the structure of which has been definitely proved by X-ray structural analysis.[3c] Based on this, we can propose that the same *cis*,*trans* configuration and preferred conformation with *cis* configuration of equatorial CF_3 group and *trans* configuration of pseudoaxial aminoenone moiety relative to

Scheme 3



the axial nitro group also existed in the molecule of chromane *ct*-**7**, with the only difference that the axial position was occupied by phenyl substituent instead of the 2-CH proton (Scheme 4). The CF_3 group in the ^{19}F NMR spectrum of compound *ct*-**7** was manifested as a singlet at 85.1 ppm.

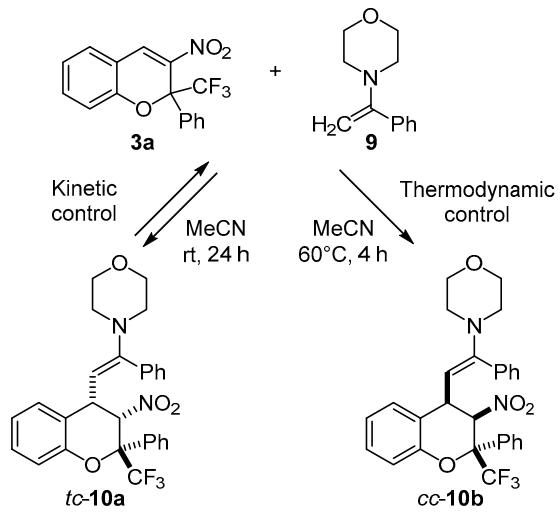
Scheme 4



Chromene **3a** readily reacted with α-morpholinostyrene (**9**) in acetonitrile solution, giving a good yield of the respective 2,2,3,4-tetrasubstituted chromane **10**. It is interesting to note that the spatial structure of this product substantially depended on the temperature regime. For example, when the reaction was performed at room temperature for 1 day, a 3:1 mixture of stereoisomeric chromanes **10a** and **10b** was formed in 96% yield, from which the major isomer **10a** could be isolated as pure sample by simple recrystallization from a mixture of dichloromethane–hexane (2:1). At the same time, the chromane **10b** was formed in 71% yield by heating a mixture of chromene **3a** and enamine **9** for 4 h in acetonitrile at 60°C (Scheme 5). It is logical to assume that the isomer **10a** resulted from kinetic control, and was transformed upon heating *via* a retro-Michael reaction to the thermodynamically more stable isomer **10b**. We have previously identified and studied a similar transformation in the series of 3-nitro-2-(trihalomethyl)-2*H*-chromenes.[3e]

The spatial structure of compounds **10a**,**b** was established by X-ray structural analysis. The structure of

Scheme 5



diastereomer *tc*-**10a** is presented in Figure 4, and it is obvious that the bulkiest enamine moiety of the molecule occupies an equatorial position, while the CF_3 and NO_2 groups are arranged in a *trans*-diaxial configuration (*trans*,*cis*-isomer). The pyran ring, similarly as in chromane *tt*-**5**, exists in a twisted half-chair conformation. A similar conformation of heterocycles was identified also in chromane *cc*-**10b**, and in that case both of the bulky substituents (CF_3 and enamine group) occupied equatorial positions (*cis*,*cis*-isomer) (Fig. 5). The phenyl substituent in enamine group deviated by 80.7(3)° from the plane of double bond in isomer *tc*-**10a** and by −67.7(3)° in the isomer *cc*-**10b**, while the nitrogen atom of morpholine ring in both molecules only slightly deviated from this plane, as indicated by the 3(1)° value of the torsion angle N(2)–C(18)–C(17)–H(17) in chromane **10a** and −7(2)° value of the torsion angle N(1)–C(18)–C(17)–H(18) in chromane **10b**. The planes of chromane system benzene ring and the enamine moiety in compounds **10a**,**b** were rotated one relative to the other by −74.3(3) and 78.5(3)°, respectively.

The diastereomers *tc*-**10a** and *cc*-**10b** were characterized by similar chemical shift values of the 3-CH proton (5.40 and 5.32 ppm, respectively) and the spin-spin coupling constant $J_{3,4}$ (5.6 and 5.4 Hz, respectively), while the signal of the 4-CH proton in the spectrum of chromane *tc*-**10a** was observed at lower field (4.07 ppm), compared to the spectrum of chromane *cc*-**10b** (3.39 ppm). This fact can be explained by the preferred existence of compound *tc*-**10a** as conformer with axial CF_3 group both in solid state (Fig. 4) and in solution phase, while the same group preferred an equatorial position in isomer *cc*-**10b** both in crystal structure (Fig. 5) and in solution. For this reason, the pseudoaxial 4-CH proton in the isomer *cc*-**10b** was located in the region shielded by axial phenyl substituent, resulting in an upfield shift of its ^1H NMR signal. ^{19}F NMR signals of CF_3 group in the stereoisomeric products *tc*-**10a** and *cc*-**10b** were observed as singlets at 87.2 and 84.2 ppm, respectively (Scheme 6, Table 2).

In contract to the diastereoselective reactions of enamines described above, the interaction of nitrochromene **3a** with

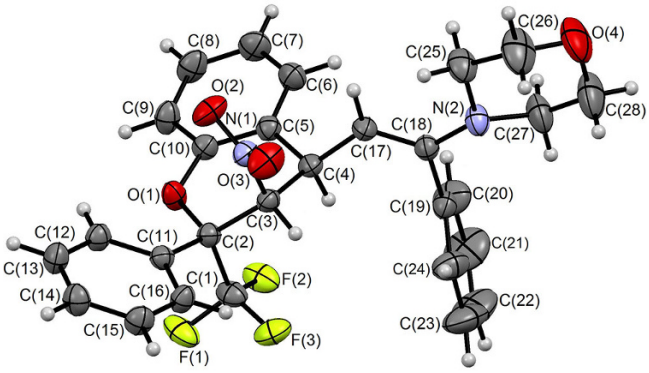


Figure 4. The molecular structure of compound *tc*-**10a** with atoms represented by thermal vibration ellipsoids of 30% probability.

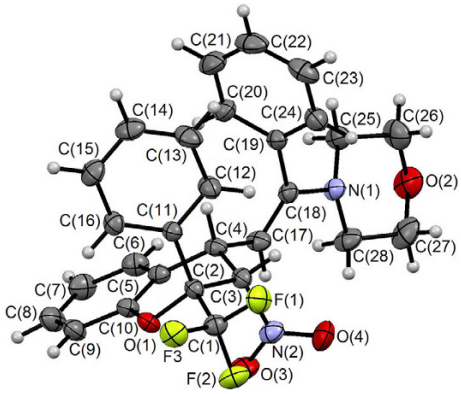
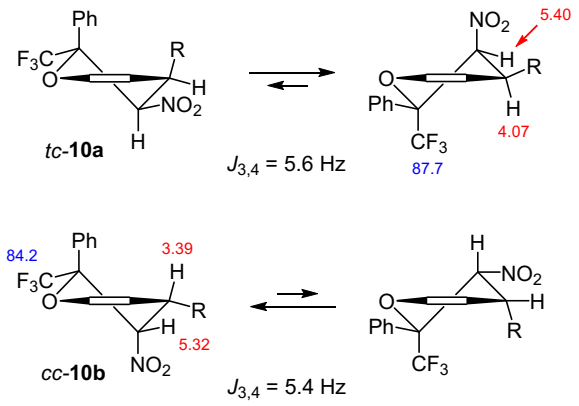


Figure 5. The molecular structure of compound *cc*-**10b** with atoms represented by thermal vibration ellipsoids of 30% probability.

Scheme 6



nitromethane in the presence of K_2CO_3 at room temperature without solvent after 2 days led to the formation of a mixture of three out of the four possible stereoisomers of 3-nitro-4-(nitromethyl)-2-phenyl-2-(trifluoromethyl)chromane (**11**) in the ratio of *ct*-**11a** : *cc*-**11b** : *tc*-**11c** = 44:38:18, and 77% yield. Analogous diastereomers of 2,2,3,4-tetrasubstituted chromanes were obtained in a total yield of 37% by reacting chromene **3a** with aniline at 100°C for 2 h, albeit at a different isomer ratio of *ct*-**12a** : *cc*-**12b** : *tc*-**12c** = 9:36:55 (Scheme 7).

The relative molecular configurations of products **11a**–**c** and **12a**–**c** were successfully established by NMR spectroscopy, based on the results obtained for the individual stereoisomers *ct*-**7**, *tc*-**10a**, and *cc*-**10b**. For example, ^{1}H NMR spectra of *ct*-isomers **11a** and **12a** contained the signal of 3-CH proton as only slightly broadened singlet (5.94 ppm, $J_{3,4} \approx 0$). The pairs of compounds *tc*-**11c**, *tc*-**12c** and *cc*-**11b**, *cc*-**12b** showed close values of spin-spin coupling constants ($J_{3,4}$ = 4.9–5.6 Hz), but different ^{19}F NMR chemical shifts of CF_3 group (87.8–88.0 ppm in *tc*-isomers and 84.2–84.6 ppm in *cc*-isomers) (Table 2).

It should be noted that the chemical shifts of 3,4-CH protons and CF_3 group along with the vicinal spin-spin coupling constant $J_{3,4}$ had a diagnostic value and could be useful for establishing the relative configurations of stereoisomeric chromanes *via* NMR spectroscopy. The 4-CH proton in *cc*-isomers of chromanes **11** and **12** was shielded by the phenyl substituent and its signal was shifted upfield relative to the analogous signal of *tc*-isomer (Δδ = 0.73–0.77 ppm). As expected, the largest spin-spin coupling constant $J_{3,4}$ = 11.7 Hz was observed for chromane *tt*-**5** with *trans*-diaxially oriented 3-CH and 4-CH protons. The moderate values of $J_{3,4}$ = 4.9–5.6 Hz were characteristic for the *tc*- and *cc*-isomers with axially-equatorial hydrogen atoms, while $J_{3,4} \approx 0$ Hz in *ct*-isomers, where the 3-CH and 4-CH protons were oriented *trans*-diequatorially. The axial CF_3 group in *tc*-isomer was deshieded by the phenyl ring, resulting in a downfield shift of its ^{19}F NMR signal by 2.8–3.8 ppm, compared to the other isomers. This feature enabled rapid detection of *tc*-isomer in the reaction mixture by ^{19}F NMR spectroscopy. The situation changed to the opposite in *cc*-isomers, where the equatorial CF_3 group was shielded by the phenyl substituent. In that case, its signal was slightly (by 0.4 ppm) shifted upfield relative to the signal of *ct*-isomer (Table 2).

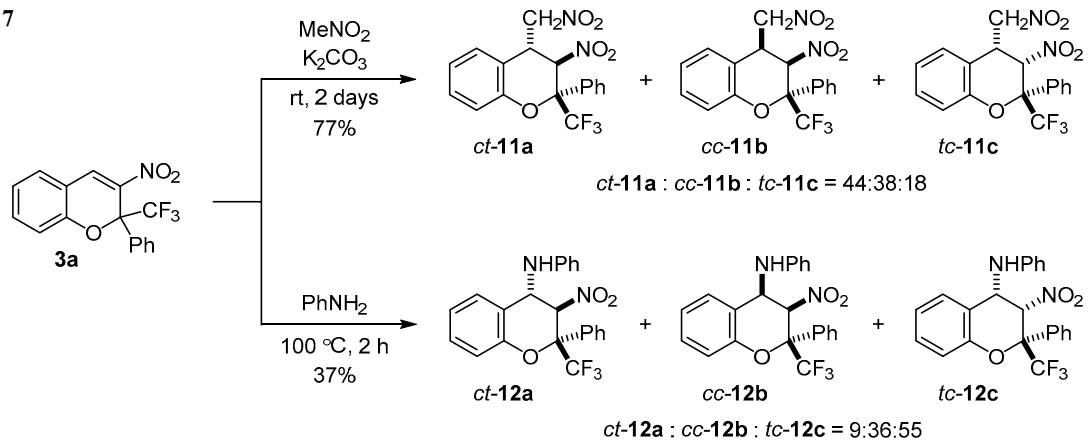
Thus, 3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromenes served as readily available and highly reactive substrates in a series of reactions with C- and N-nucleophiles, which

Table 2. The characteristic signals in ^{1}H and ^{19}F NMR spectra of compounds **5**, **7**, **10a**,**b**, **11a**–**c**, **12a**–**c**

Chromane	^{1}H NMR spectrum, δ, ppm			^{19}F NMR spectrum, δ, ppm
	3-CH	4-CH	$J_{3,4}$, Hz	CF_3
tt-**5**	6.18	4.12	11.7	85.6
ct-**7**	5.26	–*	≈ 0	85.1
tc-**10a**	5.40	4.07	5.6	87.2
cc-**10b**	5.32	3.39	5.4	84.2
ct-**11a**	5.94	4.12	≈ 0	85.0
cc-**11b**	6.06	3.85	4.9	84.6
tc-**11c**	6.04	4.58	5.1	88.0
ct-**12a**	5.94	4.69	≈ 0	84.6
cc-**12b**	6.08	4.72	5.2	84.2
tc-**12c**	6.12	5.49	5.6	87.8

* Signal was not detected due to overlapping.

Scheme 7



allowed us to demonstrate the utility of such substrates for diastereoselective synthesis of new 2,2,3,4-tetrasubstituted chromanes.

Experimental

IR spectra were recorded on a Bruker Alpha spectrometer with ATR accessory (ZnSe crystal). ^{1}H and ^{19}F NMR spectra were acquired on a Bruker DRX-400 spectrometer (400 and 376 MHz, respectively) in $CDCl_3$, using TMS and C_6F_6 as internal standards. ^{13}C NMR spectra were acquired on a Bruker Avance 500 spectrometer (126 MHz) in $CDCl_3$ with TMS as internal standard. Elemental analysis was performed on a PE 2400 automatic analyzer. Melting points were determined on an SMP40 apparatus.

The starting (*E*)-3,3,3-trifluoro-1-nitro-2-phenylprop-1-ene was synthesized according to a published procedure.[6]

Synthesis of nitrochromenes 3a–g (General method). Anhydrous Et_3N (0.014 ml, 0.1 mmol) was added to a solution of the appropriate salicylic aldehyde (1.0 mmol) and (*E*)-3,3,3-trifluoro-1-nitro-2-phenylprop-1-ene (0.24 g, 1.1 mmol) in anhydrous CH_2Cl_2 (3 ml), and the mixture was maintained at room temperature for 3 h. In the case of 5-chloro- and 5-bromosalicylic aldehydes, the mixture after addition of Et_3N was at first refluxed for 3 min, then left for 3 h at room temperature. After the reaction was complete, the solvent was removed at reduced pressure, the residue was recrystallized from MeOH (compound **3d**) or from ethanol (the rest of the compounds), and the target compounds were isolated as yellow powders.

3-Nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromene (3a). Yield 0.31 g (96%), mp 141–142°C. IR spectrum, ν, cm^{-1}: 1640, 1608, 1570, 1519, 1483, 1455, 1330, 1314. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.99 (1H, br. d, *J* = 8.2, H-8); 7.09 (1H, td, *J* = 7.5, *J* = 1.0, H-6); 7.37 (1H, dd, *J* = 7.6, *J* = 1.6, H-5); 7.40–7.43 (3H, m, H-3,4,5 Ph); 7.44 (1H, ddd, *J* = 8.2, *J* = 7.4, *J* = 1.6, H-7); 7.60–7.67 (2H, m, H-2,6 Ph); 8.24 (1H, s, 4-CH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 82.4 (q, *J* = 30.9, C-2); 116.2; 116.3; 123.4; 123.7 (q, *J* = 290.6, CF_3); 127.2 (q, *J* = 1.4); 128.5; 129.6; 130.5; 133.7; 135.2; 135.3; 138.8; 152.6. ^{19}F NMR spectrum, δ, ppm: 88.8 (s, CF_3). Found, %: C 59.80; H 3.12; N 4.30. $C_{16}H_{10}F_3NO_3$. Calculated, %: C 59.82; H 3.14; N 4.36.

6-Chloro-3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromene (3b). Yield 0.23 g (64%), mp 77–78°C. IR spectrum, ν, cm^{-1}: 1634, 1566, 1525, 1474, 1451, 1420, 1332. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.95 (1H, d, *J* = 8.3, H-8); 7.35 (1H, d, *J* = 2.3, H-5); 7.38 (1H, dd, *J* = 8.3, *J* = 2.3, H-7); 7.40–7.46 (3H, m, H Ph); 7.57–7.64 (2H, m, H Ph); 8.14 (1H, s, 4-CH). ^{19}F NMR spectrum, δ, ppm: 89.0 (s, CF_3). Found, %: C 54.08; H 2.37; N 3.96. $C_{16}H_9ClF_3NO_3$. Calculated, %: C 54.03; H 2.55; N 3.94.

6-Bromo-3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromene (3c). Yield 0.28 g (69%), mp 74–75°C. IR spectrum, ν, cm^{-1}: 1632, 1560, 1525, 1472, 1415, 1331. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.90 (1H, d, *J* = 8.6, H-8); 7.38–7.46 (3H, m, H Ph); 7.49 (1H, d, *J* = 2.4, H-5); 7.52 (1H, dd, *J* = 8.6, *J* = 2.4, H-7); 7.56–7.65 (2H, m, H Ph); 8.14 (1H, s, 4-CH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 82.6 (q, *J* = 30.8, C-2); 115.4; 118.0; 118.2; 123.5 (q, *J* = 290.2, CF_3); 127.2 (q, *J* = 1.5); 128.6; 129.9; 132.1; 132.4; 134.6; 137.6; 139.8; 151.5. ^{19}F NMR spectrum, δ, ppm: 89.0 (s, CF_3). Found, %: C 48.09; H 2.14; N 3.48. $C_{16}H_9BrF_3NO_3$. Calculated, %: C 48.03; H 2.27; N 3.50.

6,8-Dibromo-3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromene (3d). Yield 0.46 g (95%), mp 151–152°C. IR spectrum, ν, cm^{-1}: 1635, 1550, 1527, 1407, 1289. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.26 (1H, d, *J* = 2.1, H-5(7)); 7.36–7.48 (3H, m, H Ph); 7.57–7.66 (2H, m, H Ph); 7.76 (1H, d, *J* = 2.1, H-7(5)); 8.07 (1H, s, 4-CH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 83.7 (q, *J* = 31.3, C-2); 111.6; 115.6; 119.4; 123.2 (q, *J* = 289.4, CF_3); 127.3 (br. s); 128.6; 130.2; 131.3; 131.4; 133.6; 139.9; 141.1; 148.4. ^{19}F NMR spectrum, δ, ppm: 89.5 (s, CF_3). Found, %: C 40.20; H 1.64; N 2.89. $C_{16}H_8Br_2F_3NO_3$. Calculated, %: C 40.12; H 1.68; N 2.92.

6-Methyl-3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromene (3e). Yield 0.27 g (80%), mp 96–97°C. IR spectrum, ν, cm^{-1}: 1634, 1575, 1522, 1487, 1422, 1332. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.32 (3H, s, CH_3); 6.88 (1H, d, *J* = 8.3, H-8); 7.14 (1H, br. d, *J* = 1.6, H-5); 7.23 (1H, dd, *J* = 8.3, *J* = 1.6, H-7); 7.34–7.46 (3H, m, H Ph); 7.55–7.69 (2H, m, H Ph); 8.19 (1H, s, 4-CH). ^{19}F NMR spectrum, δ, ppm: 88.9 (s, CF_3). Found, %: C 61.23; H 3.55; N 4.18. $C_{17}H_{12}F_3NO_3$. Calculated, %: C 60.90; H 3.61; N 4.18.

6-Methoxy-3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromene (3f). Yield 0.33 g (95%), mp 101–102°C. IR spectrum, ν, cm^{-1}: 1641, 1576, 1525, 1487, 1454, 1429, 1332, 1308. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.81 (3H, s, OCH_3); 6.84 (1H, d, *J* = 2.9, H-5); 6.93 (1H, d, *J* = 8.9, H-8); 6.99 (1H, dd, *J* = 8.9, *J* = 2.9, H-5); 7.37–7.45 (3H, m, H-3,4,5 Ph); 7.58–7.66 (2H, m, H-2,6 Ph); 8.18 (1H, s, 4-CH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 55.8; 82.4 (q, *J* = 30.9, C-2); 113.7; 116.8; 117.1; 121.4; 123.7 (q, *J* = 290.6, CF_3); 127.2 (br. s); 128.4; 129.6; 133.7; 135.1; 139.6; 146.6; 155.3. ^{19}F NMR spectrum, δ, ppm: 89.1 (s, CF_3). Found, %: C 57.91; H 3.59; N 3.93. $C_{17}H_{12}F_3NO_4$. Calculated, %: C 58.13; H 3.44; N 3.99.

8-Ethoxy-3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromene (3g). Yield 0.33 g (89%), mp 90–91°C. IR spectrum, ν, cm^{-1}: 1631, 1606, 1574, 1528, 1473, 1396, 1342, 1323. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.38 (3H, t, *J* = 7.0, $OCH_2C\underline{H}_3$); 4.07 (1H, dq, *J* = 9.8, *J* = 7.0) and 4.11 (1H, dq, *J* = 9.8, *J* = 7.0, $OC\underline{H}_2CH_3$); 6.94 (1H, dd, *J* = 7.5, *J* = 1.6, H-7); 6.99 (1H, t, *J* = 7.8, H-6); 7.05 (1H, dd, *J* = 8.0, *J* = 1.6, H-7); 7.36–7.44 (3H, m, H-3,4,5 Ph); 7.61–7.69 (2H, m, H-2,6 Ph); 8.17 (1H, s, 4-CH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 14.7; 65.5; 82.7 (q, *J* = 31.0, C-2); 117.7; 120.4; 122.2; 123.4; 123.6 (q, *J* = 289.7, CF_3); 127.4 (q, *J* = 1.0); 128.4; 129.6; 133.7; 134.8; 139.7; 142.3; 147.3. ^{19}F NMR spectrum, δ, ppm: 89.2 (s, CF_3). Found, %: C 59.34; H 3.86; N 3.87. $C_{18}H_{14}F_3NO_4$. Calculated, %: C 59.18; H 3.86; N 3.83.

Ethyl (*Z*)-3-amino-2-[(2*S,3*S**,4*S**)-3-nitro-2-phenyl-2-(trifluoromethyl)chroman-4-yl]but-2-enoate (*tt*-5)**. A mixture of chromene **3a** (0.32 g, 1.0 mmol) and ethyl (*Z*)-3-aminocrotonate (**4**) (0.13 g, 1.0 mmol) in anhydrous MeCN (1 ml) was heated until dissolution at 50°C (3 min) and then maintained at room temperature for 3 days. The obtained solid product was filtered off and recrystallized from a system of CH_2Cl_2–hexane, 1:2. Yield 0.33 g (74%), white powder, mp 165–166°C. IR spectrum, ν, cm^{-1}: 3490, 3319, 1659, 1613, 1585, 1556, 1512, 1485, 1454, 1369. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.88 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 1.91 (3H, s, CH_3); 3.85 (1H, dq, *J* = 10.7, *J* = 7.1) and 3.96 (1H, dq, *J* = 10.7, *J* = 7.1, $OC\underline{H}_2CH_3$); 4.12 (1H, d, *J* = 11.7, 4-CH); 4.78 (1H, br. s, NH); 6.18 (1H, d, *J* = 11.7, 3-CH); 6.91–6.98 (2H, m, H-6,8); 7.11 (1H, d, *J* = 8.1, H-5); 7.21–7.23 (1H, m, H-7); 7.34 (2H, t, *J* = 7.6, H-3,5 Ph); 7.40 (1H, tt, *J* = 7.3, *J* = 1.2, H-4 Ph); 7.50 (2H, d, *J* = 7.9, H-2,6 Ph); 8.94 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 13.7; 21.3; 37.6; 59.0; 81.4 (q, *J* = 29.7, C-2); 85.5; 87.7; 116.2; 122.6; 123.5 (q, *J* = 286.1, CF_3); 124.2; 127.0; 127.7 (q, *J* = 1.6); 128.3; 129.8; 130.9; 151.0; 162.1; 168.7 (one carbon atom was not observed). ^{19}F NMR spectrum, δ, ppm: 85.6 (s, CF_3). Found, %: C 58.66; H 4.60; N 6.21. $C_{22}H_{21}F_3N_2O_5$. Calculated, %: C 58.67; H 4.70; N 6.22.

(*E*)-4-Morpholino-5-[(2*S,3*R**,4*S**)-3-nitro-2-phenyl-2-(trifluoromethyl)chroman-4-yl]pent-3-en-2-one (*ct*-7)**. A mixture of chromene **3a** (0.32 g, 1.0 mmol) and (*E*)-4-morpholinopent-3-en-2-one (**6**) (0.17 g, 1.0 mmol) in anhydrous MeCN (0.5 ml) was maintained for 5 h at 60°C. The mixture was then cooled to room temperature, the solvent was removed at reduced pressure, the residue was treated with anhydrous Et_2O (5 ml). The precipitate formed was filtered off and washed with hexane (3×0.5 ml). Yield 0.24 g (49%), white powder, mp 202–203°C (decomp.). IR spectrum, ν, cm^{-1}: 1658, 1636, 1563, 1535, 1490, 1446, 1367, 1321. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.10 (3H, s, CH_3); 2.62 (4H, br. s, CH_2NCH_2); 3.19 (1H, dd, *J* = 13.1, *J* = 3.0) and 3.71 (1H, dd, *J* = 13.1, *J* = 2.5, $C\underline{H}_2CH$); 3.23–3.40 (5H, m, 4-CH, CH_2OCH_2); 5.26 (1H, br. s, 3-CH); 6.00 (1H, s, =C$\underline{H}$–COMe); 6.89 (1H, d, *J* = 7.7, H-8); 6.94 (1H, t, *J* = 7.7, H-6); 7.25 (1H, d, *J* = 7.9, H-5); 7.32 (1H, t, *J* = 7.6, H-7); 7.37–7.45 (3H, m, H-3,4,5 Ph); 7.61 (2H, d, *J* = 7.6, H-2,6 Ph). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 31.8; 35.0; 38.2; 46.5; 65.6; 79.6 (q, *J* = 30.7, C-2); 84.2; 96.5; 117.2; 119.9; 122.1; 122.7 (q, *J* = 286.0, CF_3); 127.4; 129.1; 129.2; 129.6; 130.2; 132.7; 150.3; 161.8; 194.7. ^{19}F NMR spectrum, δ, ppm: 85.1 (s, CF_3). Found, %: C 61.06; H 5.27; N 5.63. $C_{25}H_{25}F_3N_2O_5$. Calculated, %: C 61.22; H 5.14; N 5.71.

4-{(*E*)-2-(2*S,3*S**,4*S**)-[3-Nitro-2-phenyl-2-(trifluoromethyl)chroman-4-yl]-1-phenylvinyl}morpholine (*tc*-10a)**. A mixture of chromene **3a** (0.32 g, 1.0 mmol) and α-morpholinostyrene (**9**) (0.19 g, 1.0 mmol) was dissolved in anhydrous MeCN (0.5 ml) and maintained at room temperature for 1 day. The obtained solid product was filtered off and washed with hexane, providing chromane *tc*-**10a** as a 3:1 mixture with isomer *cc*-**10b**. Yield of the isomer mixture was 0.47 g (96%), beige powder, mp 202–203°C (decomp.). Recrystallization from a system of CH_2Cl_2–hexane, 2:1, gave the individual isomer *tc*-**10a**. Yield 0.33 g (67%), light-yellow powder, mp 204–205°C. IR spectrum, ν, cm^{-1}: 1616, 1584, 1485, 1453, 1382, 1360. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.77–2.90 (4H, m, CH_2NCH_2); 3.66–3.75 (4H, m, CH_2OCH_2); 4.07 (1H, dd, *J* = 9.4, *J* = 5.6, 4-CH); 4.20 (1H, d, *J* = 9.4, =C$\underline{H}$–CPh); 5.40 (1H, d, *J* = 5.6, 3-CH); 7.06 (1H, td, *J* = 7.5, *J* = 1.1, H-6); 7.14 (1H, dd, *J* = 8.2, *J* = 1.1, H-8); 7.28 (1H, dddd, *J* = 8.2, *J* = 7.8, *J* = 1.5, *J* = 1.0, H-7); 7.31–8.01 (11H, m, H-5, H Ph). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 35.6 (q, *J* = 1.7); 49.0; 66.7; 78.7 (q, *J* = 28.8, C-2); 85.8; 96.9; 116.0; 120.5; 122.2; 123.4 (q, *J* = 290.1, CF_3); 127.7; 128.5; 128.7; 128.8; 128.9; 129.7; 132.4; 136.1; 152.0; 156.2 (two carbon atoms were not observed). ^{19}F NMR spectrum, δ, ppm: 87.2 (s, CF_3). Found, %: C 65.97; H 4.89; N 5.45. $C_{28}H_{25}F_3N_2O_4$. Calculated, %: C 65.88; H 4.94; N 5.49.

4-{(*E*)-2-(2*S,3*R**,4*R**)-[3-Nitro-2-phenyl-2-(trifluoromethyl)chroman-4-yl]-1-phenylvinyl}morpholine (*cc*-10b)**. A mixture of chromene **3a** (0.32 g, 1.0 mmol) and α-morpholinostyrene (**9**) (0.19 g, 1.0 mmol) in anhydrous MeCN (1.0 ml) was maintained for 4 h at 60°C. The obtained solid product was filtered off and recrystallized from a system of CH_2Cl_2–hexane, 1:3. Yield 0.36 g (71%), white powder, mp 265–266°C (decomp.). IR spectrum, ν, cm^{-1}: 1616, 1587, 1486, 1455, 1361. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.69–2.87 (4H, m, CH_2NCH_2); 3.39 (1H, dd, *J* = 8.9, *J* = 5.4, 4-CH); 3.63–3.73 (4H, m, CH_2OCH_2); 4.27 (1H, d, *J* = 8.9, =C$\underline{H}$–CPh); 5.32 (1H, d, *J* = 5.4, 3-CH); 7.00 (1H, td, *J* = 7.7, *J* = 1.0, H-6); 7.01–7.44 (13H,

m, H-5,7,8, H Ph). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 35.5; 48.8; 66.7; 80.0 (q, *J* = 30.8, C-2); 83.5; 96.8; 116.6; 122.1; 122.4 (q, *J* = 285.3, CF_3); 122.6; 128.0; 128.5; 128.6; 128.8; 128.9; 129.0; 129.4; 132.5; 136.3; 151.0; 156.3 (one carbon atom was not observed). ^{19}F NMR spectrum, δ, ppm: 84.2 (s, CF_3). Found, %: C 65.72; H 4.80; N 5.56. $C_{28}H_{25}F_3N_2O_4$. Calculated, %: C 65.88; H 4.94; N 5.49.

3-Nitro-4-nitromethyl-2-phenyl-2-(trifluoromethyl)chromane (11). A solution of chromene **3a** (0.32 g, 1.0 mmol) in CH_3NO_2 (1 ml) in the presence of K_2CO_3 (15 mg, 0.1 mmol) was stirred for 2 days at room temperature, then treated with 10% HCl (5 ml), extracted with CH_2Cl_2 (2×1 ml), and the organic phase was dried over Na_2SO_4. The solvent was removed and the residue was recrystallized from a system of CH_2Cl_2–hexane, 1:3, giving a mixture of isomers *ct*-**11a**, *cc*-**11b**, and *tc*-**11c** in 44:38:18 ratio. Yield 0.29 g (77%), white powder, mp 125–126°C. IR spectrum, ν, cm^{-1}: 1557, 1493, 1453, 1373. **Isomer *ct*-11a**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.16 (1H, dd, *J* = 14.7, *J* = 10.8) and 4.08 (1H, dd, *J* = 14.7, *J* = 4.8, CH_2); 4.12 (1H, dd, *J* = 10.8, *J* = 4.8, 4-CH); 5.94 (1H, s, 3-CH); 7.05 (1H, br. d, *J* = 8.1, H-8); 7.11 (1H, td, *J* = 7.9, *J* = 1.1, H-6); 7.33 (1H, dd, *J* = 8.3, *J* = 0.7, H-5); 7.38 (1H, br. t, *J* = 7.9, H-7); 7.41–7.52 (5H, m, H Ph). ^{19}F NMR spectrum, δ, ppm: 85.0 (s, CF_3). **Isomer *cc*-11b**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.85 (1H, dt, *J* = 9.7, *J* = 4.7, 4-CH); 4.42 (1H, dd, *J* = 15.4, *J* = 9.7) and 4.99 (1H, dd, *J* = 15.4, *J* = 4.5, CH_2); 6.06 (1H, d, *J* = 4.9, 3-CH); 6.92 (1H, br. d, *J* = 8.0, H-8); 7.04 (1H, td, *J* = 7.9, *J* = 1.1, H-6); 7.30 (1H, dd, *J* = 8.2, *J* = 1.0, H-5); 7.41–7.52 (5H, m, H Ph); the signal of H-7 proton overlapped with the corresponding signal of the major isomer. ^{19}F NMR spectrum, δ, ppm: 84.6 (s, CF_3). **Isomer *tc*-11c**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.48 (1H, dd, *J* = 15.4, *J* = 9.0) and 5.14 (1H, dd, *J* = 15.4, *J* = 5.0, CH_2); 4.58 (1H, dt, *J* = 9.0, *J* = 5.1, 4-CH); 6.04 (1H, d, *J* = 5.1, 3-CH); 7.07 (1H, br. d, *J* = 7.9, H-8); 7.10 (1H, br. t, *J* = 7.9, H-6); 7.29 (1H, dd, *J* = 8.2, *J* = 1.0, H-5); 7.41–7.52 (5H, m, H Ph); the signal of H-7 proton overlapped with the corresponding signal of the major isomer. ^{19}F NMR spectrum, δ, ppm: 88.0 (s, CF_3). Found, %: C 53.39; H 3.52; N 7.30. $C_{17}H_{13}F_3N_2O_5$. Calculated, %: C 53.41; H 3.43; N 7.33.

(2*S,3*R**,4*R**)-3-Nitro-*N*,2-diphenyl-2-(trifluoromethyl)chroman-4-amine (12)**. A mixture of chromene **3a** (0.32 g, 1.0 mmol) and aniline (0.47 g, 5.0 mmol) was maintained for 2 h at 100°C, then cooled to room temperature. The excess of aniline was removed at reduced pressure, the residue was washed with water (2×5 ml) and dried. Recrystallization from a system of CH_2Cl_2–hexane, 1:3, provided a mixture of isomers *ct*-**12a**, *cc*-**12b**, and *tc*-**12c** in 9:36:55 ratio. Yield 0.15 g (37%), white powder, mp 129–130°C. IR spectrum, ν, cm^{-1}: 3388, 1604, 1591, 1562, 1513, 1491, 1453, 1364, 1330. **Isomer *ct*-12a**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.69 (1H, d, *J* = 10.4, 4-CH); 4.95 (1H, d, *J* = 10.4, NH); 5.94 (1H, s, 3-CH); 6.31 (2H, d, *J* = 8.0, H-2,6 Ph aniline); the aromatic proton signals overlapped with the corresponding signals of the major isomer. ^{19}F NMR spectrum, δ, ppm: 84.6 (s, CF_3). **Isomer *cc*-12b**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.82 (1H, d, *J* = 9.9, NH); 4.72 (1H, dd, *J* = 9.9, *J* = 5.2, 4-CH); 6.08 (1H, d, *J* = 5.2, 3-CH); 6.54 (2H, d, *J* = 8.0, H-2,6 Ph aniline); 6.85 (1H, t, *J* = 7.4, H-6); 7.04 (1H, t, *J* = 7.4, H-7); 7.20–7.27 (3H, m, H-5,8, H-4 Ph aniline); 7.36 (2H, d, *J* = 7.6, H-2,6 Ph); 7.45–7.60 (5H, m, H-3,4,5 Ph, H-3,5 Ph aniline). ^{19}F NMR spectrum, δ, ppm: 84.2 (s, CF_3). **Isomer *tc*-12c**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.83 (1H, d, *J* = 9.9, NH); 5.49 (1H, dd, *J* = 9.9, *J* = 5.6, 4-CH); 6.12 (1H, d, *J* = 5.6, 3-CH); 6.78 (2H, d, *J* = 7.9, H-2,6 Ph aniline); 6.91 (1H, t, *J* = 7.4, H-6); 7.11 (1H, t, *J* = 7.4, H-7); 7.24–7.34 (3H, m, H-5,8, H-4 aniline); 7.38 (2H, d, *J* = 7.6, H-2,6 Ph); 7.39–7.90 (5H, m, H-3,4,5 Ph, H-3,5 Ph aniline). ^{19}F NMR spectrum, δ, ppm: 87.8 (s, CF_3). Found, %: C 63.56; H 3.98; N 6.88. $C_{22}H_{17}F_3N_2O_3$. Calculated, %: C 63.77; H 4.14; N 6.76.

X-ray structural study of compounds 3a, 5, and 10a,b. Crystals suitable for X-ray structural analysis were obtained by slow evaporation of MeCN solutions of compounds **3a**, **5**, and **10a,b**. The X-ray structural analysis was performed on an Xcalibur Eos diffractometer with CCD-detector according to the standard procedure (MoKα radiation, graphite monochromator, ω-scanning, $2\theta_{max}$ 56.44°) at 22°C. The structures were solved by direct method using the SHELX97 software suite.[8] The positions of non-hydrogen atoms were independently refined in anisotropic approximation, while hydrogen atoms were placed in geometrically calculated positions and included in the refinement according to "rider" model with dependent thermal parameters. The complete X-ray structural data set for compounds **3a**, **5**, and **10a,b** was deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1499968, CCDC 1499970, CCDC 1499971, and CCDC 1499969, respectively).

The work was financially supported by the government of the Russian Federation (program 211, contract No. 02.A03.21.0006).

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