

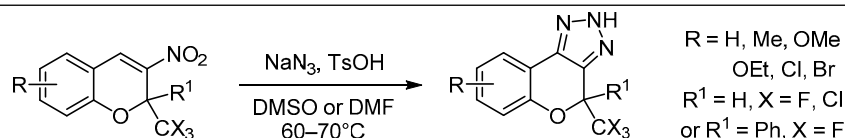
3-Nitro-2-(trihalomethyl)-2*H*-chromenes in reactions with sodium azide: synthesis of 4-(trihalomethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazoles

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A method was developed for the synthesis of 4-(trihalomethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazoles, based on the reaction of 3-nitro-2-(trifluoro(trichloro)methyl)- and 3-nitro-2-(trifluoromethyl)-2-phenyl-2*H*-chromenes with sodium azide in DMSO or DMF in the presence of *p*-toluenesulfonic acid.

Keywords: 3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromenes, 3-nitro-2-(trihalomethyl)-2*H*-chromenes, sodium azide, 4-(trihalomethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazoles, 1,3-dipolar cycloaddition.

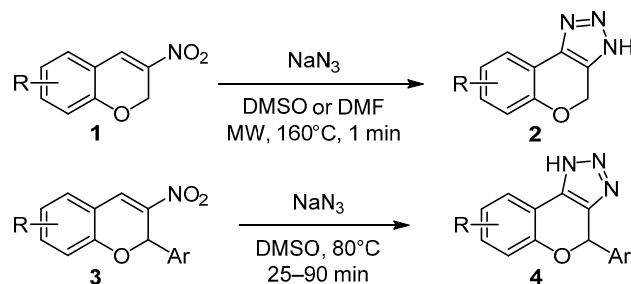
1,2,3-Triazoles represent an important class of heterocyclic compounds with a broad spectrum of biological effects, including anti-inflammatory, antimicrobial, tuberculostatic, antiplatelet, and antiviral activity.¹ Reports have been published in recent years on the use of 1,2,3-triazoles in the design of liquid crystals,^{2a} metallo-supramolecular gels for the restoration of metallic coatings,^{2b} and thermally stable materials for organic light-emitting devices.^{2c}

One of the most effective methods for the preparation of 1,2,3-triazoles is based on 1,3-dipolar cycloaddition of sodium azide at the activated double bond of conjugated nitroalkenes with elimination of the nitro group.³ The availability and diversity of the starting nitroalkenes, as well as the simplicity of isolation and high yields of the target products correspond to the basic principles of the modern concept of click chemistry.⁴ The reaction is usually performed by moderate heating in DMSO or DMF, using an excess of the reagent (1.5–2.0 equiv). At the same time, the interaction of β -nitrostyrenes with NaN_3 is often accompanied by dimerization or trimerization of the nitroalkene in the presence of azide anion, leading to the formation of 4-aryl-5-(1-aryl-2-nitroethyl)-1*H*-1,2,3-triazoles and 1,3,5-triarylbenzenes as by-products.^{3c,d} The addition of small amounts of *p*-toluenesulfonic acid (0.1–0.5 equiv) to the reaction mixture allowed to completely suppress these side reactions.^{3c}

It has been recently shown^{5a} that 2-unsubstituted 3-nitro-2*H*-chromenes **1** containing β -nitrostyrene moiety in their molecules interacted with sodium azide in DMSO or DMF at 160°C under the conditions of microwave heating, forming chromeno[3,4-*d*]triazoles **2** in 63–89% yields. An analogous reaction involving 2-aryl-3-nitro-2*H*-chromenes **3** (DMSO, 80°C, 25–90 min) gave 61–82% yields of 4-aryl-substituted chromenotriazoles **4** (Scheme 1).^{5b} The sterically hindered 2,2-dimethyl-3-nitro-2*H*-chromene was found to be less active and reacted with sodium azide under the same conditions over 3 h, forming the respective triazole in 58% yield, while 3-nitro-2,2-diphenyl-2*H*-chromene did not participate in a cycloaddition reaction at all.^{5b}

It should be noted that products **2** and **4** represent chromene derivatives annulated with triazole ring, while chromene also forms the structural framework of many

Scheme 1



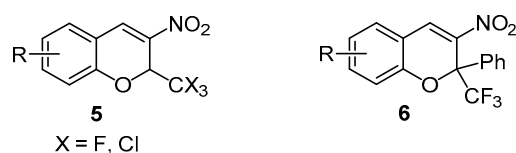


Figure 1. 2-(Trihalomethyl)-substituted 3-nitro-2*H*-chromenes **5** and **6**.

natural and synthetic compounds with valuable biological and pharmacological properties.⁶

In a continuation of our studies aimed at the development of methods for Δ^3 -annulation of 3-nitro-2-(trifluoro(trichloro)methyl)-2*H*-chromenes **5** with a carbo- or heterocycle,⁷ in the current work we investigated the reaction of chromenes **5** and 3-nitro-2-phenyl-2-(trifluoromethyl)-2*H*-chromenes **6**, representing hybrid structures of chromenes **3** and **5** (Fig. 1), with sodium azide under various conditions. This method may be useful for the preparation of chromeno[3,4-*d*]triazoles containing a trihalomethyl group at position 4.

For the purpose of optimizing the reaction conditions, in the first step we studied the reaction with 2- CF_3 -nitrochromene **5a** lacking any substituents at the benzene ring, which led to the formation of 4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (**7a**). The highest yields of compound **7a** were observed when performing the process in DMSO or DMF at 60°C for 10 min (control by TLC) in the presence of 0.5 equiv of *p*-toluenesulfonic acid (TsOH) (Scheme 2, Table 1). The role of TsOH in this reaction was not entirely clear, but was probably linked to the additional activation of double bond in the starting chromene *via* protonation of oxygen atom in the nitro group.

The optimized reaction conditions allowed to obtain high yields of 4- CF_3 -chromenotriazoles **7b–h** containing electron-donating or electron-withdrawing substituents in the aromatic ring (Scheme 3, Table 2). In the case of the more active 6-mono- and 6,8-dihalo-substituted chromenes **5e–h**, the reactions both in DMSO and in DMF were complete after 5 min. It should be noted that chromeno-

Scheme 2

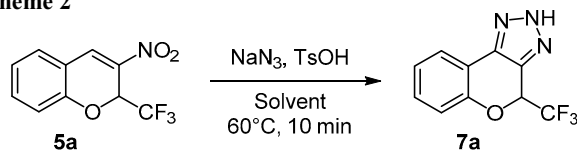


Table 1. Optimization of conditions for the reaction of chromene **5a** with NaN_3

Solvent	NaN_3 , equiv	TsOH, equiv	Yield of 7a , %	
			in DMSO	in DMF
DMSO	2.0	–	60*	
DMSO	1.5	0.5	86	
DMSO	2.0	0.25	81	
DMSO	2.0	0.5	89	
DMF	2.0	–	47**	
DMF	1.5	0.5	71	
DMF	2.0	0.5	86	

* At 80°C.

** For 30 min.

Scheme 3

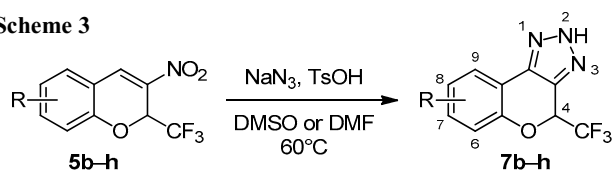


Table 2. Reaction conditions and yields of 4- CF_3 -chromenotriazoles **7b–h**

Triazole	R	Time, min	Yield, %	
			in DMSO	in DMF
7b	8-Me	10	90	84
7c	8-OMe	10	93	85
7d	6-OEt	10	87	86
7e	8-Cl	5	88	90
7f	8-Br	5	86	84
7g	6,8- Cl_2	5	96	85
7h	6,8- Br_2	5	87	88

triazoles **7a–h** were isolated from the reaction mixture by simple filtration as pure samples that were suitable for analysis, and did not require additional purification by recrystallization or column chromatography. As shown in Table 2, the yields of products **7a–h** practically did not depend on the electron-donating or electron-withdrawing properties of the substituent R in the aromatic ring.

2-(Trichloromethyl)-substituted nitrochromenes **5i–p** under analogous conditions formed the respective triazoles **7i–p** in 37–64% yields. The more active chromenes **5m–p** reacted with sodium azide over 10–25 min, while the reactions with chromene **5i** lacking substituents in the benzene ring and chromenes **5j–l** containing electron-donating substituents in the aromatic ring were complete in only 1–1.5 h and were accompanied by noticeable resinification (Scheme 4, Table 3). Similarly to the case of 4-(trifluoromethyl)-substituted triazoles **7a–h**, the target products **7i–p** were isolated from reaction mixtures by filtration and the impurities were removed by washing with a small amount of hexane- CH_2Cl_2 mixture.

Scheme 4

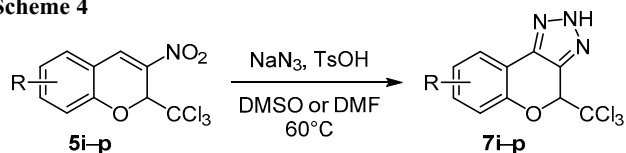
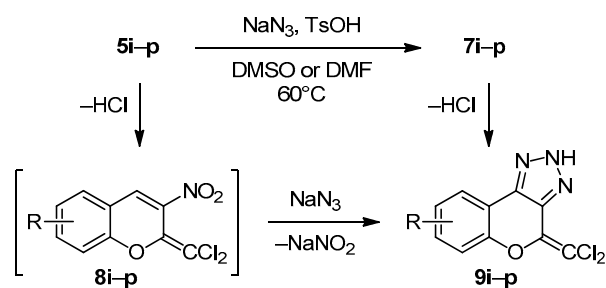


Table 3. Reaction conditions and yields of 4-(trichloromethyl)-substituted chromenotriazoles **7i–p**

Triazole	R	Time, min	Yield, %	
			in DMSO	in DMF
7i	H	60	50	49
7j	8-Me	75	49	45
7k	8-OMe	90	47	41
7l	6-OEt	75	43	37
7m	8-Cl	25	51	50
7n	8-Br	25	59	58
7o	6,8- Cl_2	10	56	56
7p	6,8- Br_2	10	63	64

The lower yields of chromenotriazoles **7i–p** compared to 4-trifluoromethyl analogs **7a–h** were caused by the formation of 4-(dichloromethylidene)chromeno[3,4-*d*]triazoles **9i–p** as by-products upon elimination of HCl molecule from triazoles **7i–p** in the presence of basic azide and nitrite anions. We can not exclude the possibility that compounds **9i–p** were formed as a result of HCl elimination from 2-(trichloromethyl)nitrochromenes **5i–p**, followed by addition of sodium azide to the intermediates, 4-(dichloromethylidene)chromenes **8i–p**. This process can be accompanied by partial resinification of the unstable nitrochromenes **8i–p** (Scheme 5).

Scheme 5



Indeed, the reaction of 6,8-dibromo-3-nitro-2-(trichloromethyl)-2*H*-chromene (**5p**) with NaN_3 in DMSO allowed to isolate a mixture of products **7p** and **9p** in 4:1 ratio. Despite the fact that triazole **9p** could not be isolated as analytically pure sample, its structure was proved with ^1H NMR spectroscopy by analysis using chromatography coupled to high-resolution mass spectrometry. Mixtures with similar composition were formed also in reactions involving 2-(trichloromethyl)chromenes **5i–o**. Elimination of HCl by the action of nitrite anion in DMSO or DMF has been previously observed in the series of 2,2-diaryl-1,1,1-trichloroethanes.⁸

IR spectra of chromenotriazoles **7a–p** showed a strong absorption band due to $\nu(\text{NH})$ stretching vibrations in the range of $3278\text{--}2469\text{ cm}^{-1}$. ^1H NMR spectra recorded in $\text{DMSO-}d_6$ solution contained a characteristic quartet (compounds **7a–h**) or singlet (compounds **7i–p**) of the 4-CH proton in the narrow range of 6.49–6.94 ppm and the triazole NH proton signal as a broadened singlet at 15.51–15.95 ppm. The signal of trifluoromethyl group linked to sp^3 -hybridized carbon atom was manifested in ^{19}F NMR spectra of 2-(trifluoromethyl)chromenotriazoles **7a–h** at 84.5–84.9 ppm as a broadened singlet or doublet with $^3J_{\text{FH}} = 6.5\text{--}6.8\text{ Hz}$. ^{13}C NMR spectra of compounds **7a–e,g** featured quartets of the CF_3 group and the C-4 carbon atom in the range of 122.4–122.9 and 70.4–71.4 ppm, respectively, with spin-spin coupling constants $^1J_{\text{CF}} = 284.2\text{--}284.8$ and $^2J_{\text{CF}} = 33.6\text{--}34.4\text{ Hz}$.

The structure of chromenotriazole **7d** was proved by X-ray structural analysis (Fig. 2). As shown in Figure 2, the hydrogen atom of triazole ring in this crystal structure was located at the N(2) nitrogen atom.

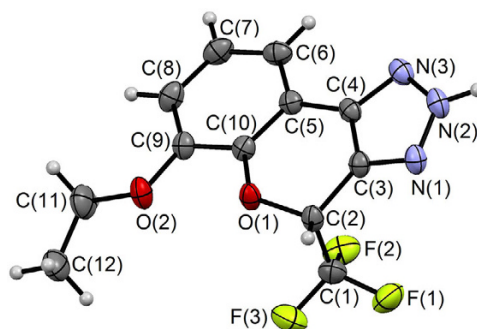


Figure 2. The molecular structure of compound **7d** with atoms represented by thermal vibration ellipsoids of 50% probability.

The sterically hindered 2,2-disubstituted nitrochromenes **6a–f** were found to be less active than the respective 2-(trifluoromethyl)nitrochromenes **5a–h** and reacted with sodium azide at 70°C over 10–90 min, forming 4-phenyl-4-(trifluoromethyl)chromeno[3,4-*d*]triazoles **10a–f** in 60–78% yields (Scheme 6, Table 4). Products **10a–f** were isolated from reaction mixture by filtration and impurities were removed by recrystallization from CH_2Cl_2 –hexane system. It should be emphasized that the presence of an electron-withdrawing trifluoromethyl group was the reason for the considerably higher reactivity of compounds **6a–f** compared to 3-nitro-2,2-diphenyl-2*H*-chromene, which did not react with sodium azide under these conditions.^{5b}

IR spectra of chromenotriazoles **10a–f** showed a $\nu(\text{NH})$ vibration band in the range of $3290\text{--}3114\text{ cm}^{-1}$. The broadened singlet of triazole NH proton appeared at 11.92–12.12 ppm in ^1H NMR spectra acquired in CDCl_3 solution (compounds **10a,d–f**) or at ~ 15.8 ppm in $\text{DMSO-}d_6$ solution (compounds **10b,c**). ^{19}F NMR spectra of compounds **10a–f** featured a singlet of trifluoromethyl group at 83.5–83.9 ppm in CDCl_3 solution or at 85.6–85.7 ppm in $\text{DMSO-}d_6$ solution. ^{13}C NMR spectra of triazoles **10a,b,e,f** contained characteristic quartets of the CF_3 group and the C-4 carbon atom with spin-spin coupling constants $^1J_{\text{CF}} = 284.7\text{--}285.5$ and $^2J_{\text{CF}} = 30.8\text{--}32.7\text{ Hz}$.

Scheme 6

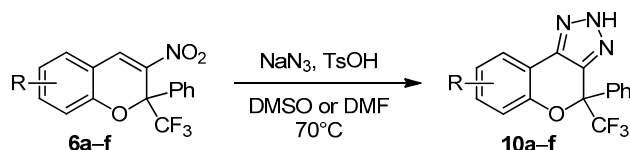


Table 4. Reaction conditions and yields of 4- CF_3 -4-Ph-chromenotriazoles **10a–f**

Triazole	R	Time, min	Yield, %	
			in DMSO	in DMF
10a	H	60	73	76
10b	8-Me	60	63	60
10c	8-OMe	90	78	75
10d	6-OEt	60	74	76
10e	8-Br	25	74	71
10f	6,8-Br ₂	10	77	74

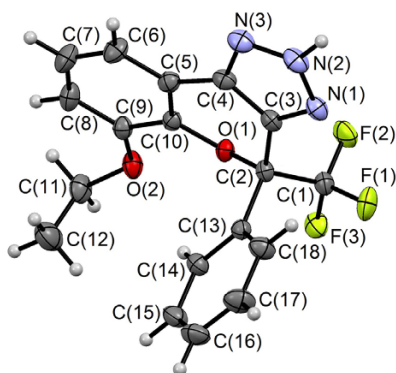


Figure 3. The molecular structure of compound **10d** with atoms represented by thermal vibration ellipsoids of 50% probability.

The structure of chromenotriazole **10d** was confirmed by X-ray structural analysis (Fig. 3). Similarly to triazole **7d**, the triazole ring hydrogen atom in the molecule of compound **10d** in crystal structure was located at the N(2) nitrogen atom.

Thus, 3-nitro-2-(trifluoromethyl)-2H-chromenes were significantly more reactive toward sodium azide compared to 2-aryl-3-nitro-2H-chromenes, while 3-nitro-2-phenyl-2-(trifluoromethyl)-2H-chromenes were found to be more reactive than their 2,2-dimethyl- and 2,2-diphenyl-substituted analogs. In the case of 2-(trichloromethyl)nitrochromenes, the cycloaddition was accompanied by partial elimination of HCl. Our developed method for the preparation of 4-(trihalomethyl)-substituted chromeno[3,4-*d*]triazoles was sufficiently simple, and the synthesized products clearly are of interest for researchers in the fields of medicinal chemistry and materials science.

Experimental

IR spectra were recorded on a Bruker Alpha spectrometer with ZnSe ATR accessory. ^1H and ^{19}F NMR spectra were acquired on Bruker DRX-400 (400 and 376 MHz, respectively, compounds **5g,o**, **7a–f,h,k,o**, **10e,f**) and Bruker Avance 500 (500 and 471 MHz, respectively, the rest of the compounds) spectrometers. The solvents were CDCl_3 (compounds **5g,o**, **10a,d–f**) or $\text{DMSO-}d_6$ (the rest of the compounds). The internal standards were TMS (for ^1H nuclei) and C_6F_6 (for ^{19}F nuclei). ^{13}C NMR spectra were acquired on a Bruker Avance-500 spectrometer (126 MHz) in CDCl_3 solution (compounds **5g,o**, **10a,e,f**) or $\text{DMSO-}d_6$ solution (the rest of the compounds), with solvent signals as internal standard (77.0 ppm for CDCl_3 , 39.5 ppm for $\text{DMSO-}d_6$). High-resolution mass spectra (electrospray ionization) were obtained on a Waters Xevo QToF instrument. Elemental analysis was performed on a PerkinElmer 2400 automatic analyzer. Melting points were determined on a Stuart SMP40 apparatus. The reaction progress and purity of the obtained compounds were controlled by TLC on Sorbfil PTSKh-AF-A-UF plates. The starting nitrochromenes **5a–p** and **6a–f** were obtained according to published procedures.^{9,10}

6,8-Dichloro-3-nitro-2-(trifluoromethyl)-2H-chromene (5g). Yield 65%, yellow powder, mp 111–112°C (EtOH). IR spectrum, ν , cm^{-1} : 1650, 1561, 1524, 1451, 1435, 1361,

1330. ^1H NMR spectrum, δ , ppm (J , Hz): 6.19 (1H, q, $J = 6.1$, 2-CH); 7.29 (1H, d, $J = 2.2$, H-5(7)); 7.50 (1H, d, $J = 2.2$, H-7(5)); 8.03 (1H, s, 4-CH). ^{13}C NMR spectrum, δ , ppm (J , Hz): 70.1 (q, $J = 34.9$, C-2); 118.8; 122.3 (q, $J = 287.9$, CF_3); 123.2; 128.5; 128.7; 130.8; 134.5; 135.3; 147.5. ^{19}F NMR spectrum, δ , ppm (J , Hz): 83.9 (d, $J = 6.1$, CF_3). Found, %: C 38.22; H 1.26; N 4.46. $\text{C}_{10}\text{H}_4\text{Cl}_2\text{F}_3\text{NO}_3$. Calculated, %: C 38.25; H 1.28; N 4.46.

6,8-Dichloro-3-nitro-2-(trichloromethyl)-2H-chromene (5o). Yield 54%, yellow powder, mp 146–147°C (EtOH). IR spectrum, ν , cm^{-1} : 1642, 1558, 1552, 1447, 1434, 1418, 1327. ^1H NMR spectrum, δ , ppm (J , Hz): 6.40 (1H, s, 2-CH); 7.27 (1H, d, $J = 2.4$, H-5(7)); 7.50 (1H, d, $J = 2.4$, H-7(5)); 8.02 (1H, s, 4-CH). ^{13}C NMR spectrum, δ , ppm: 80.2; 98.2; 119.5; 123.0; 127.9; 128.3; 130.8; 134.3; 138.0; 148.0. Found, %: C 33.24; H 0.97; N 3.85. $\text{C}_{10}\text{H}_4\text{Cl}_3\text{NO}_3$. Calculated, %: C 33.05; H 1.11; N 3.85.

Synthesis of chromeno[3,4-*d*]triazoles 7a–p (General method). A solution of nitrochromene **5a–p** (1.0 mmol), NaN_3 (130 mg, 2.0 mmol), and TsOH (86 mg, 0.5 mmol) in DMSO or DMF (3 ml) was stirred at 60°C for the duration indicated in Tables 1–3. The reaction mixture was then cooled to room temperature and poured into H_2O (20 ml). In order to completely precipitate 4-(trichloromethyl)triazoles **7i–p**, saturated aqueous NaCl solution (1.0 ml) was added to the reaction mixture. The precipitate that formed was filtered off, washed with water (3×10 ml), and dried at 60°C. In the case of 4-(trichloromethyl)chromenotriazoles **7i–p**, the product was dried and washed with a small amount of 1:2 CH_2Cl_2 –hexane mixture (3×0.5 ml) for the purpose of removing impurities.

4-(Trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]-triazole (7a). Yield 89% (DMSO), 86% (DMF), white powder, mp 193–194°C. IR spectrum, ν , cm^{-1} : 2469, 1645, 1493, 1452, 1423, 1353, 1302. ^1H NMR spectrum, δ , ppm (J , Hz): 6.68 (1H, q, $J = 6.8$, 4-CH); 7.12–7.19 (2H, m, H-6,8); 7.38 (1H, td, $J = 7.9$, $J = 1.3$, H-7); 7.71 (1H, d, 7.2, H 9); 15.61 (1H, br. s, NH). ^{13}C NMR spectrum, δ , ppm (J , Hz): 70.7 (q, $J = 33.9$, C-4); 114.1 (br. s); 116.8; 122.8; 122.9 (q, $J = 284.3$, CF_3); 123.2; 130.6; 132.4 (br. s); 136.7 (br. s); 151.4. ^{19}F NMR spectrum, δ , ppm: 84.8 (br. s, CF_3). Found, m/z : 242.0535 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_7\text{F}_3\text{N}_3\text{O}$. Calculated, m/z : 242.0536.

8-Methyl-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7b). Yield 90% (DMSO), 84% (DMF), light-yellow powder, mp 171–172°C. IR spectrum, ν , cm^{-1} : 3146, 1630, 1542, 1505, 1470, 1353, 1316. ^1H NMR spectrum, δ , ppm (J , Hz): 2.31 (3H, s, CH_3); 6.62 (1H, q, $J = 6.8$, 4-CH); 7.03 (1H, d, $J = 8.3$, H-6); 7.15 (1H, dd, $J = 8.3$, $J = 1.4$, H-7); 7.52 (1H, br. s, H-9); 15.54 (1H, br. s, NH). ^{13}C NMR spectrum, δ , ppm (J , Hz): 20.1; 70.6 (q, $J = 33.7$, C-4); 113.8 (br. s); 116.6; 122.9 (q, $J = 284.7$, CF_3); 123.0; 131.1; 132.2; 132.6 (br. s); 137.2 (br. s); 149.3. ^{19}F NMR spectrum, δ , ppm: 84.9 (br. s, CF_3). Found, m/z : 256.0697 $[\text{M}+\text{H}]^+$. $\text{C}_{11}\text{H}_9\text{F}_3\text{N}_3\text{O}$. Calculated, m/z : 256.0692.

8-Methoxy-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7c). Yield 93% (DMSO), 85% (DMF), mp 200–201°C. IR spectrum, ν , cm^{-1} : 3150, 1603, 1515, 1505, 1476, 1441, 1350. ^1H NMR spectrum, δ , ppm

(*J*, Hz): 3.79 (3H, s, OCH₃); 6.59 (1H, q, *J* = 6.9, 4-CH); 6.92 (1H, dd, *J* = 9.0, *J* = 3.0, H-7); 7.09 (1H, d, *J* = 9.0, H-6); 7.23 (1H, d, *J* = 3.0, H-9); 15.65 (1H, br. s, NH). ¹³C NMR spectrum, δ, ppm (*J*, Hz): 55.5; 70.4 (q, *J* = 33.6, C-4); 107.0; 114.6 (br. s); 116.4; 117.9; 122.9 (q, *J* = 284.8, CF₃); 132.9 (br. s); 137.0 (br. s); 145.2; 154.8. ¹⁹F NMR spectrum, δ, ppm: 84.9 (br. s, CF₃). Found, *m/z*: 272.0643 [M+H]⁺. C₁₁H₉F₃N₃O₂. Calculated, *m/z*: 272.0641.

6-Ethoxy-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7d). Yield 87% (DMSO), 86% (DMF), mp 159–160°C. IR spectrum, ν, cm⁻¹: 3278, 1591, 1548, 1461, 1391, 1356, 1301. ¹H NMR spectrum, δ, ppm (*J*, Hz): 1.34 (3H, t, *J* = 7.0, OCH₂CH₃); 4.08 (1H, dq, *J* = 9.7, *J* = 7.0) and 4.11 (1H, dq, *J* = 9.7, *J* = 7.0, OCH₂CH₃); 6.69 (1H, q, *J* = 6.8, 4-CH); 7.03–7.13 (2H, m, H-7,9); 7.22–7.35 (1H, m, H-8); 15.54 (1H, br. s, NH). ¹³C NMR spectrum, δ, ppm (*J*, Hz): 14.6; 64.4; 70.4 (q, *J* = 33.9, C-4); 114.5; 115.0 (br. s); 115.4; 122.8 (q, *J* = 284.6, CF₃); 123.0; 132.6 (br. s); 137.8 (br. s); 140.8; 147.5. ¹⁹F NMR spectrum, δ, ppm: 84.8 (br. s, CF₃). Found, *m/z*: 286.0801 [M+H]⁺. C₁₂H₁₁F₃N₃O₂. Calculated, *m/z*: 286.0798.

8-Chloro-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7e). Yield 88% (DMSO), 90% (DMF), white powder, mp 180–181°C. IR spectrum, ν, cm⁻¹: 3213, 1480, 1459, 1443, 1399, 1362, 1325. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.74 (1H, q, *J* = 6.8, 4-CH); 7.20 (1H, d, *J* = 8.8, H-6); 7.40 (1H, dd, *J* = 8.8, *J* = 2.6, H-7); 7.72 (1H, d, *J* = 2.6, H-9); 15.73 (1H, br. s, NH). ¹³C NMR spectrum, δ, ppm (*J*, Hz): 70.9 (q, *J* = 34.0, C-4); 115.8 (br. s); 118.8; 122.1; 122.7 (q, *J* = 284.3, CF₃); 127.0; 130.1; 132.6 (br. s); 135.9 (br. s); 150.0. ¹⁹F NMR spectrum, δ, ppm: 84.8 (br. s, CF₃). Found, *m/z*: 297.9964 [M+Na]⁺. C₁₀H₅ClF₃N₃NaO. Calculated, *m/z*: 297.9965.

8-Bromo-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7f). Yield 86% (DMSO), 84% (DMF), white powder, mp 183–184°C. IR spectrum, ν, cm⁻¹: 3206, 1482, 1460, 1437, 1396, 1358, 1316. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.75 (1H, q, *J* = 6.8, 4-CH); 7.15 (1H, d, *J* = 8.8, H-6); 7.53 (1H, dd, *J* = 8.8, *J* = 2.4, H-7); 7.84 (1H, d, *J* = 2.4, H-9); 15.82 (1H, br. s, NH). ¹⁹F NMR spectrum, δ, ppm (*J*, Hz): 84.8 (d, *J* = 6.8, CF₃). Found, *m/z*: 341.9458 [M+Na]⁺. C₁₀H₅BrF₃N₃NaO. Calculated, *m/z*: 341.9460.

6,8-Dichloro-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7g). Yield 96% (DMSO), 85% (DMF), white powder, mp 149–150°C. IR spectrum, ν, cm⁻¹: 3148, 1494, 1442, 1428, 1396, 1376, 1352, 1309. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.94 (1H, q, *J* = 6.7, 4-CH); 7.71 (1H, d, *J* = 2.5, H-7(9)); 7.73 (1H, d, *J* = 2.5, H-9(7)); 15.95 (1H, br. s, NH). ¹³C NMR spectrum, δ, ppm (*J*, Hz): 71.4 (q, *J* = 34.4, C-4); 117.2 (br. s); 121.1; 122.3; 122.4 (q, *J* = 284.2, CF₃); 127.2; 129.9; 132.7 (br. s); 135.6 (br. s); 145.9. ¹⁹F NMR spectrum, δ, ppm (*J*, Hz): 84.8 (d, *J* = 6.7, CF₃). Found, *m/z*: 309.9752 [M+H]⁺. C₁₀H₅Cl₂F₃N₃O. Calculated, *m/z*: 309.9756.

6,8-Dibromo-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7h). Yield 87% (DMSO), 88% (DMF), white powder, mp 186–187°C. IR spectrum, ν, cm⁻¹: 3150, 1490, 1435, 1408, 1350, 1305. ¹H NMR spectrum,

δ, ppm (*J*, Hz): 6.93 (1H, q, *J* = 6.5, 4-CH); 7.87 (1H, d, *J* = 2.1, H-7(9)); 7.90 (1H, d, *J* = 2.1, H-9(7)); 15.94 (1H, br. s, NH). ¹⁹F NMR spectrum, δ, ppm (*J*, Hz): 84.5 (d, *J* = 6.5, CF₃). Found, *m/z*: 399.8725 [M+H]⁺. C₁₀H₅Br₂F₃N₃O. Calculated, *m/z*: 399.8726.

4-(Trichloromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7i). Yield 50% (DMSO), 49% (DMF), light-yellow powder, mp 212–213°C (decomp.). IR spectrum, ν, cm⁻¹: 3185, 1624, 1590, 1479, 1446, 1332. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.58 (1H, s, 4-CH); 7.09–7.17 (2H, m, H-6,8); 7.34 (1H, td, *J* = 7.9, *J* = 1.3, H-7); 7.72 (1H, d, *J* = 7.1, H-9); 15.54 (1H, br. s, NH). ¹³C NMR spectrum, δ, ppm: 81.5; 99.8; 114.6 (br. s); 116.6; 122.6; 122.7; 130.4; 134.7 (br. s); 138.6 (br. s); 152.1. Found, *m/z*: 311.9468 [M+Na]⁺. C₁₀H₆Cl₃N₃NaO. Calculated, *m/z*: 311.9469.

8-Methyl-4-(trichloromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7j). Yield 49% (DMSO), 45% (DMF), light-yellow powder, mp 195–196°C (decomp.). IR spectrum, ν, cm⁻¹: 3135, 1644, 1523, 1470, 1321. ¹H NMR spectrum, δ, ppm (*J*, Hz): 2.30 (3H, s, CH₃); 6.52 (1H, s, 4-CH); 7.03 (1H, d, *J* = 8.3, H-6); 7.15 (1H, br. d, *J* = 8.3, H-7); 7.53 (1H, br. s, H-9); 15.51 (1H, br. s, NH). ¹³C NMR spectrum, δ, ppm: 20.2; 81.4; 99.9; 114.1 (br. s); 116.4; 122.7; 131.0; 131.7; 134.4 (br. s); 138.2 (br. s); 149.9. Found, *m/z*: 303.9805 [M+H]⁺. C₁₁H₉Cl₃N₃O. Calculated, *m/z*: 303.9806.

8-Methoxy-4-(trichloromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7k). Yield 47% (DMSO), 41% (DMF), beige powder, mp 145–146°C (decomp.). IR spectrum, ν, cm⁻¹: 3156, 1530, 1494, 1464, 1439, 1414. ¹H NMR spectrum, δ, ppm (*J*, Hz): 3.78 (3H, s, OCH₃); 6.49 (1H, s, 4-CH); 6.92 (1H, br. d, *J* = 8.0, H-7); 7.07 (1H, d, *J* = 8.0, H-6); 7.23 (1H, br. s, H-9); 15.55 (1H, br. s, NH). Found, *m/z*: 319.9757 [M+H]⁺. C₁₁H₉Cl₃N₃O₂. Calculated, *m/z*: 319.9755.

8-Ethoxy-4-(trichloromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7l). Yield 43% (DMSO), 37% (DMF), beige powder, mp 133–134°C (decomp.). IR spectrum, ν, cm⁻¹: 3202, 1592, 1528, 1454, 1433, 1389. ¹H NMR spectrum, δ, ppm (*J*, Hz): 3.30 (3H, t, *J* = 6.9, OCH₂CH₃); 4.11 (2H, br. q, *J* = 6.9, OCH₂CH₃); 6.59 (1H, s, 4-CH); 6.99–7.36 (3H, m, H Ar); 15.51 (1H, br. s, NH). Found, *m/z*: 333.9913 [M+H]⁺. C₁₂H₁₁Cl₃N₃O₂. Calculated, *m/z*: 333.9911.

8-Chloro-4-(trichloromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7m). Yield 51% (DMSO), 50% (DMF), light-yellow powder, mp 204–205°C (decomp.). IR spectrum, ν, cm⁻¹: 3219, 1476, 1453, 1434, 1396. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.65 (1H, s, 4-CH); 7.19 (1H, d, *J* = 8.8, H-6); 7.40 (1H, dd, *J* = 8.8, *J* = 2.6, H-7); 7.72 (1H, d, *J* = 2.6, H-9); 15.72 (1H, br. s, NH). ¹³C NMR spectrum, δ, ppm: 81.5; 99.4; 116.0 (br. s); 118.5; 121.9; 126.5; 130.1; 134.5 (br. s); 137.5 (br. s); 150.7. Found, *m/z*: 347.9047 [M+Na]⁺. C₁₀H₅Cl₄N₃NaO. Calculated, *m/z*: 347.9049.

8-Bromo-4-(trichloromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7n). Yield 59% (DMSO), 58% (DMF), light-yellow powder, mp 219–220°C (decomp.). IR spectrum, ν, cm⁻¹: 3114, 2876, 1493, 1462, 1454, 1430,

1398, 1380, 1349, 1326. ^1H NMR spectrum, δ , ppm (J , Hz): 6.65 (1H, s, 4-CH); 7.13 (1H, d, $J = 8.7$, H-6); 7.52 (1H, br. d, $J = 8.7$, H-7); 7.84 (1H, br. s, H-9); 15.76 (1H, br. s, NH). Found, m/z : 369.8733 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_6\text{BrCl}_3\text{N}_3\text{O}$. Calculated, m/z : 369.8734.

6,8-Dichloro-4-(trichloromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7o). Yield 56% (DMSO), 56% (DMF), light-yellow powder, mp 114–115°C (decomp.). IR spectrum, ν , cm^{-1} : 3152, 1524, 1487, 1440, 1426, 1394. ^1H NMR spectrum, δ , ppm (J , Hz): 6.82 (1H, s, 4-CH); 7.68 (1H, d, $J = 2.1$, H-7(9)); 7.74 (1H, d, $J = 2.1$, H-9(7)); 15.93 (1H, br. s, NH). Found, m/z : 357.8865 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_5\text{Cl}_5\text{N}_3\text{O}$. Calculated, m/z : 357.8870.

6,8-Dibromo-4-(trichloromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (7p). Yield 63% (DMSO), 64% (DMF), pink powder, mp 124–125°C (decomp.). IR spectrum, ν , cm^{-1} : 3149, 1519, 1486, 1432, 1388, 1369. ^1H NMR spectrum, δ , ppm (J , Hz): 6.83 (1H, s, 4-CH); 7.87 (1H, d, $J = 2.3$, H-7(9)); 7.90 (1H, d, $J = 2.3$, H-9(7)); 15.92 (1H, br. s, NH). ^{13}C NMR spectrum, δ , ppm: 82.0; 99.0; 111.4; 114.6; 117.7 (br. s); 124.1 (2C); 135.2; 148.1 (One C signal was not observed). Found, m/z : 445.7861 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_5\text{Br}_2\text{Cl}_3\text{N}_3\text{O}$. Calculated, m/z : 445.7859.

6,8-Dibromo-4-(dichloromethylidene)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (9p) was obtained as a mixture with triazole **7p**. ^1H NMR spectrum, δ , ppm (J , Hz): 7.92 (1H, d, $J = 2.2$, H-7(9)); 7.98 (1H, br. d, $J = 2.2$, H-9(7)); 16.05 (1H, br. s, NH). Found, m/z : 409.8093 $[\text{M}+\text{H}]^+$. $\text{C}_{10}\text{H}_4\text{Br}_2\text{Cl}_2\text{N}_3\text{O}$. Calculated, m/z : 409.8093.

Synthesis of chromeno[3,4-*d*]triazoles 10a–f (General method). A solution of the appropriate nitrochromene **6a–f** (1.0 mmol), NaN_3 (0.13 g, 2.0 mmol), and TsOH (86 mg, 0.5 mmol) in DMSO or DMF (3 ml) was stirred at 70°C for the duration indicated in Table 4. The reaction mixture was then cooled to room temperature and poured into H_2O (20 ml). The precipitate that formed was filtered off and recrystallized from a 1:2 mixture of CH_2Cl_2 –hexane. Compounds **10a,e** were extracted with EtOAc (3×10 ml), the solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography, using CHCl_3 as eluent. Triazoles **10a–f** were obtained as white powders.

4-Phenyl-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (10a). Yield 73% (DMSO), 76% (DMF), mp 146–147°C. IR spectrum, ν , cm^{-1} : 3289, 1622, 1472, 1450, 1426, 1312. ^1H NMR spectrum, δ , ppm (J , Hz): 7.10 (1H, td, $J = 7.5$, $J = 1.1$, H-7); 7.28 (1H, dd, $J = 8.3$, $J = 0.8$, H-6); 7.33–7.41 (4H, m, H-8, H-3,4,5 Ph); 7.73–7.78 (3H, m, H-9, H-2,6 Ph); 12.12 (1H, br. s, NH). ^{13}C NMR spectrum, δ , ppm (J , Hz): 81.2 (q, $J = 32.1$, C-4); 114.6; 117.9; 123.1 (q, $J = 285.5$, CF_3); 123.3; 123.4; 127.2; 128.4; 129.5; 131.0; 134.1; 138.3; 139.3 (br. s); 151.6. ^{19}F NMR spectrum, δ , ppm: 83.7 (s, CF_3). Found, m/z : 318.0851 $[\text{M}+\text{H}]^+$. $\text{C}_{16}\text{H}_{11}\text{F}_3\text{N}_3\text{O}$. Calculated, m/z : 318.0849.

8-Methyl-4-phenyl-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (10b). Yield 63% (DMSO), 60% (DMF), mp 174–175°C. IR spectrum, ν , cm^{-1} : 3147, 3031, 1500, 1465, 1449. ^1H NMR spectrum, δ , ppm

(J , Hz): 2.28 (3H, s, CH_3); 7.20 (1H, br. d, $J = 8.3$, H-7); 7.30 (1H, d, $J = 8.3$, H-6); 7.37–7.53 (4H, m, H-9, H-3,4,5 Ph); 7.65 (2H, d, $J = 6.1$, H-2,6 Ph); 15.76 (1H, br. s, NH). ^{13}C NMR spectrum, δ , ppm (J , Hz): 20.1; 80.7 (q, $J = 30.8$, C-4); 114.4 (br. s); 117.7; 122.9; 123.1 (q, $J = 284.7$, CF_3); 126.9; 128.6; 129.7; 131.2; 132.8; 133.7; 136.7 (br. s); 137.4 (br. s); 148.1. ^{19}F NMR spectrum, δ , ppm: 85.6 (s, CF_3). Found, m/z : 332.1006 $[\text{M}+\text{H}]^+$. $\text{C}_{17}\text{H}_{13}\text{F}_3\text{N}_3\text{O}$. Calculated, m/z : 332.1005.

8-Methoxy-4-phenyl-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (10c). Yield 78% (DMSO), 75% (DMF), mp 147–148°C. IR spectrum, ν , cm^{-1} : 3148, 3040, 1536, 1497, 1467, 1439, 1415, 1324. ^1H NMR spectrum, δ , ppm (J , Hz): 3.76 (3H, s, OCH_3); 6.96 (1H, br. d, $J = 8.7$, H-7); 7.18 (1H, br. s, H-9); 7.36 (1H, d, $J = 8.7$, H-6); 7.38–7.51 (3H, m, H-3,4,5 Ph); 7.64 (2H, d, $J = 6.4$, H-2,6 Ph); 15.81 (1H, br. s, NH). ^{19}F NMR spectrum, δ , ppm: 85.7 (s, CF_3). Found, m/z : 348.0958 $[\text{M}+\text{H}]^+$. $\text{C}_{17}\text{H}_{13}\text{F}_3\text{N}_3\text{O}_2$. Calculated, m/z : 348.0954.

6-Ethoxy-4-phenyl-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (10d). Yield 74% (DMSO), 70% (DMF), mp 144–145°C. IR spectrum, ν , cm^{-1} : 3265, 1591, 1524, 1464, 1447, 1305. ^1H NMR spectrum, δ , ppm (J , Hz): 1.55 (3H, t, $J = 7.0$, OCH_2CH_3); 4.19 (1H, dq, $J = 9.1$, $J = 7.0$ and 4.25 (1H, dq, $J = 9.1$, $J = 7.0$, OCH_2CH_3); 6.95 (1H, dd, $J = 8.2$, $J = 1.2$, H-7); 7.01 (1H, t, $J = 7.9$, H-8); 7.32 (1H, dd, $J = 7.6$, $J = 1.2$, H-9); 7.33–7.39 (3H, m, H-3,4,5 Ph); 7.76–7.81 (2H, m, H-2,6 Ph); 11.92 (1H, br. s, NH). ^{19}F NMR spectrum, δ , ppm: 83.9 (s, CF_3). Found, m/z : 362.1115 $[\text{M}+\text{H}]^+$. $\text{C}_{18}\text{H}_{15}\text{F}_3\text{N}_3\text{O}_2$. Calculated, m/z : 362.1111.

8-Bromo-4-phenyl-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (10e). Yield 74% (DMSO), 71% (DMF), mp 185–186°C. IR spectrum, ν , cm^{-1} : 3289, 1621, 1471, 1450, 1426, 1311. ^1H NMR spectrum, δ , ppm (J , Hz): 7.16 (1H, d, $J = 8.8$, H-6); 7.34–7.41 (3H, m, H-3,4,5 Ph); 7.44 (1H, dd, $J = 8.8$, $J = 2.4$, H-7); 7.71 (2H, dd, $J = 6.3$, $J = 2.5$, H-2,6 Ph); 7.89 (1H, d, $J = 2.4$, H-9); 12.06 (1H, br. s, NH). ^{13}C NMR spectrum, δ , ppm (J , Hz): 81.4 (q, $J = 32.2$, C-4); 115.8; 116.5; 119.6; 122.9 (q, $J = 285.4$, CF_3); 126.1; 127.1; 128.5; 129.7; 133.6; 133.7; 138.5; 138.6 (br. s); 150.5. ^{19}F NMR spectrum, δ , ppm: 83.7 (s, CF_3). Found, m/z : 395.9953 $[\text{M}+\text{H}]^+$. $\text{C}_{16}\text{H}_{10}\text{BrF}_3\text{N}_3\text{O}$. Calculated, m/z : 395.9954.

6,8-Dibromo-4-phenyl-4-(trifluoromethyl)-2,4-dihydrochromeno[3,4-*d*][1,2,3]triazole (10f). Yield 77% (DMSO), 74% (DMF), mp 191–192°C. IR spectrum, ν , cm^{-1} : 3290, 1449, 1429. ^1H NMR spectrum, δ , ppm (J , Hz): 7.36–7.45 (3H, m, H-3,4,5 Ph); 7.70 (1H, d, $J = 2.2$, H-7(9)); 7.78–7.88 (3H, m, H-9(7), H-2,6 Ph); 11.98 (1H, br. s, NH). ^{13}C NMR spectrum, δ , ppm (J , Hz): 82.5 (q, $J = 32.7$, C-4); 112.8; 115.8; 117.5; 122.7 (q, $J = 285.4$, CF_3); 125.2; 127.2; 128.5; 130.0; 133.0; 136.3; 138.3; 138.5; 147.5. ^{19}F NMR spectrum, δ , ppm: 83.5 (s, CF_3). Found, m/z : 475.9037 $[\text{M}+\text{H}]^+$. $\text{C}_{16}\text{H}_9\text{Br}_2\text{F}_3\text{N}_3\text{O}$. Calculated, m/z : 475.9039.

X-ray structural study of compounds 7d and 10d was performed at 22°C temperature on an Xcalibur S diffractometer with CCD detector, using the standard procedure ($\text{CuK}\alpha$ radiation, graphite monochromator,

ω -scanning, $2\theta_{\max}$ 56.6°). Crystals suitable for X-ray structural analysis were obtained by slow evaporation of acetonitrile solutions of compounds **7d** and **10d**. The structures of compounds **7d** and **10d** were solved by direct method using the SHELX97 software suite.¹¹ The positions of all non-hydrogen atoms were refined independently in anisotropic approximation, the hydrogen atom positions were calculated geometrically and refined according to the "rider" model with dependent temperature parameters. The complete X-ray structural analysis data set for compounds **7d** and **10d** was deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1527759 and CCDC 1527760, respectively).

References

- (a) De Carvalho da Silva, F.; do Carmo Cardoso, M. F.; Ferreira, P. G.; Ferreira, V. F. In *Topics in Heterocyclic Chemistry*; Dehaen, W.; Bakulev, V. A., Eds.; Springer-Verlag: Berlin, Heidelberg, 2015, Vol. 40, p. 117. (b) Lauria, A.; Delisi, R.; Mingoia, F.; Terenzi, A.; Martorana, A.; Barone, G.; Almerico, A. M. *Eur. J. Org. Chem.* **2014**, 3289.
- (a) Gimeno, N.; Martín-Rapún, R.; Rodríguez-Conde, S.; Serrano, J. L.; Folcia, C. L.; Pericás, M. A.; Ros, M. B. *J. Mater. Chem.* **2012**, *22*, 16791. (b) Yuan, J.; Fang, X.; Zhang, L.; Hong, G.; Lin, Y.; Zheng, Q.; Xu, Y.; Ruan, Y.; Weng, W.; Xia, H.; Chen, G. *J. Mater. Chem.* **2012**, *22*, 11515. (c) Ichikawa, M.; Mochizuki, S.; Jeon, H.-G.; Hayashi, S.; Yokoyama, N.; Taniguchi, Y. *J. Mater. Chem.* **2011**, *21*, 11791.
- (a) Krivopalov, V. P.; Shkurko, O. P. *Russ. Chem. Rev.* **2005**, *74*, 339. [*Usp. Khim.* **2005**, *74*, 369.] (b) Belskaya, N.; Subbotina, Ju.; Lesogorova, S. In *Topics in Heterocyclic Chemistry*; Dehaen, W.; Bakulev, V. A., Eds.; Springer-Verlag: Berlin, Heidelberg, 2015, Vol. 40, p. 51. (c) Zefirov, N. S.; Chapovskaya, N. K.; Kolesnikov, V. V. *J. Chem. Soc. D* **1971**, 1001. (d) Quiclet-Sire, B.; Zard, S. Z. *Synthesis* **2005**, 3319. (e) Quan, X.-J.; Ren, Z.-H.; Wang, Y.-Y.; Guan, Z.-H. *Org. Lett.* **2014**, *16*, 5728.
- (a) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004. (b) Kolb, H. C.; Sharpless, K. B. *Drug Discovery Today* **2003**, *8*, 1128.
- (a) Schwendt, G.; Glasnov, T. *Monatsh. Chem.* **2017**, *148*, 69. (b) Habib, P. M.; Raju, B. R.; Kavala, V.; Kuo, C.-W.; Yao, C.-F. *Tetrahedron* **2009**, *65*, 5799.
- (a) *The Chemistry of Heterocyclic Compounds: Chromans and Tocopherols*; Ellis, G. P.; Lockhart, I. M., Eds.; John Wiley & Sons: New York, 1981, Vol. 36. (b) Costa, M.; Dias, T. A.; Brito, A.; Proença, F. *Eur. J. Med. Chem.* **2016**, *123*, 487.
- (a) Korotaev, V. Yu.; Sosnovskikh, V. Ya.; Barabanov, M. A.; Yasnova, E. S.; Ezhikova, M. A.; Kodess, M. I.; Slepukhin, P. A. *Tetrahedron* **2010**, *66*, 1404. (b) Korotaev, V. Yu.; Sosnovskikh, V. Ya.; Barkov, A. Yu.; Slepukhin, P. A.; Ezhikova, M. A.; Kodess, M. I.; Shklyayev, Yu. V. *Tetrahedron* **2011**, *67*, 8685. (c) Korotaev, V. Yu.; Barkov, A. Yu.; Sosnovskikh, V. Ya. *Tetrahedron* **2013**, *69*, 9642. (d) Korotaev, V. Yu.; Barkov, A. Yu.; Moshkin, V. S.; Matochkina, E. G.; Kodess, M. I.; Sosnovskikh, V. Ya. *Tetrahedron* **2013**, *69*, 8602. (e) Korotaev, V. Yu.; Barkov, A. Yu.; Kutyashev, I. B.; Kotovich, I. V.; Ezhikova, M. A.; Kodess, M. I.; Sosnovskikh, V. Ya. *Tetrahedron* **2015**, *71*, 2658.
- Kazin, V. N.; Kuzhin, M. B.; Sirik, A. V.; Guzov, E. A. *Russ. J. Org. Chem.* **2016**, *52*, 1277. [*Zh. Org. Khim.* **2016**, *52*, 1290.]
- Korotaev, V. Yu.; Kutyashev, I. B.; Sosnovskikh, V. Ya. *Heteroat. Chem.* **2005**, *16*, 492.
- Barkov, A. Yu.; Korotaev, V. Yu.; Kotovich, I. V.; Zimnitskiy, N. S.; Kutyashev, I. B.; Sosnovskikh, V. Ya. *Chem. Heterocycl. Compd.* **2016**, *52*, 814. [*Khim. Geterotsikl. Soedin.* **2016**, *52*, 814.]
- Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112.