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Stereoselective hetero-Diels–Alder reaction of 3-nitro-2-trihalomethyl-2*H*-chromenes with 2,3-dihydrofuran and ethyl vinyl ether under solvent-free conditions

Vladislav Yu. Korotaev [a], Vyacheslav Ya. Sosnovskikh [a,*], Mikhail A. Barabanov [a], Evgeniya S. Yasnova [a], Marina A. Ezhikova [b], Mikhail I. Kodess [b], Pavel A. Slepukhin [b]

[a] Department of Chemistry, Ural State University, 620083 Ekaterinburg, Russian Federation
[b] Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620041 Ekaterinburg, Russian Federation

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ABSTRACT

3-Nitro-2-trifluoro(trichloro)methyl-2*H*-chromenes undergo heterodiene cycloaddition to 2,3-dihydrofuran and ethyl vinyl ether under solvent-free conditions producing novel cyclic nitronates with high stereoselectivity and in good yields. 3,6-Dinitro-2-trifluoromethyl-2*H*-chromene reacts with two molecules of ethyl vinyl ether to give the tandem [4+2]/[3+2] cycloaddition adduct in 48% yield. The stereochemistry of the products was established based on 2D COSY, NOESY, HSQC, and HMBC experiments and an X-ray diffraction study.

1. Introduction

Derivatives of 2*H*-1-benzopyran, also known as 2*H*-chromenes, belong to an important class of natural oxygen-containing heterocycles that are widely distributed among many plants.[1] They have considerable biological importance[2] and are useful intermediates in the synthesis of more complex natural products, such as pterocarpans.[3] In addition, 3-nitro-2*H*-chromenes have attracted considerable attention in recent years due to the possibility of using them as dipolarophiles in 1,3-cycloadditions of diazoalkanes,[4] azomethine ylides,[5] *N*-methylnitrone,[6] and sodium azide.[7]

On the other hand, considerable interest was aroused in the synthesis of partially fluorinated heterocyclic compounds, many of which have found use as agrochemicals and drugs.[8] 3-Nitro-2-trihalomethyl-2*H*-chromenes **1**, prepared by tandem condensation of appropriate salicylaldehydes[9] and ketimines[10] with 3,3,3-trichloro(trifluoro)-1-nitropropenes, have not received much attention despite their potential interest as building blocks in organic synthesis for the construction of trihalomethyl-containing heterocycles. The majority of the reactions with these compounds are nucleophilic additions at the 4-position leading to various types of 4-substituted chromans.[11] However, examples of the participation of 3-nitro-2-trihalomethyl-2*H*-chromenes **1** in any cycloaddition reactions are lacking, a fact prompting us to investigate the hetero-Diels–Alder reaction of **1** with enol ethers. This nitroolefinic system appeared to be a useful heterodiene for a convenient synthesis of CX_3-containing cyclic nitronates, which could be used as 1,3-dipoles for the preparation of novel polycyclic chroman derivatives.

Most pertinent to the present research is the [4+2] cycloaddition of 3-nitrocoumarins with electron-rich dienophiles, such as ethyl vinyl ether, 2,3-dihydrofuran, and 3,4-dihydro-2*H*-pyran, providing a straightforward route to the cyclic nitronates, which were converted into chroman-2-ols and tetrahydrofuro(pyrano)chromenes.[12] To our knowledge, this type of cycloaddition between 3-nitro-2*H*-chromenes and enol ethers has not previously been reported. Bearing in mind the electron-withdrawing force of a trihalomethyl group and the fact that hetero-Diels–Alder reactions are facilitated by the presence of such groups in the heterodiene, it was of interest to elucidate the effects of different 3-nitrochromenes **1** on the occurrence and stereoselectivity of [4+2] cycloadditions compared to those of 3-nitrocoumarins.

* Corresponding author.
E-mail address: svy@etel.ru (V.Ya. Sosnovskikh).

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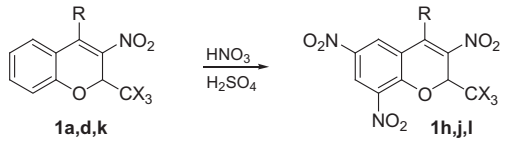
2. Results and discussion

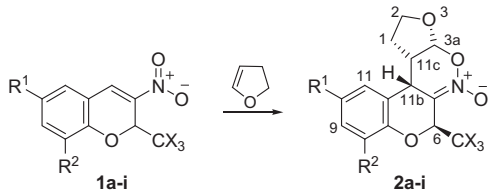
3-Nitro-2-trihalomethyl-2*H*-chromenes **1a**–**g**,**i**,**k** were prepared by the tandem reaction (conjugate addition followed by intramolecular aldol condensation) of salicylaldehydes and 2-hydroxyacetophenone imine with 3,3,3-trifluoro(trichloro)-1-nitropropenes in the presence of triethylamine reported earlier by our group.[9,10] Their reactivities can be enhanced by introducing electron-withdrawing substituents into the benzene ring. The hitherto unknown 3,6,8-trinitro-2-trihalomethyl-2*H*-chromenes **1h**,**j** were synthesized by nitration of **1a**,**d** at 125 °C in 89% and 81% yields, respectively. When the same reaction was carried out with 4-methyl-3-nitro-2-trichloromethyl-2*H*-chromene **1k**, 4-methyl-3,6,8-trinitro-2-trichloromethyl-2*H*-chromene **1l** was obtained in 65% yield (Scheme 1).



R = H, X = F (**1a,j**); R = H, X = Cl (**1d,h**); R = Me, X = Cl (**1k,l**)

Scheme 1.

We initially examined the reaction of chromenes **1** with 2,3-dihydrofuran. It was found that **1a**–**i** reacted with 2,3-dihydrofuran (2 equiv) without solvent at 40 °C for some days or at 60 °C for 10 h (with **1i**) and gave cycloadducts **2a**–**i** in 20–68% isolated yields as single diastereomeric products (Scheme 2). The results are summarized in Table 1. In a similar way to cycloaddition reactions involving 3-nitrocoumarins,[12] compounds **2a**–**i** were formed almost exclusively as the *endo*-isomers. The appearance of the *exo*-adduct in 15% (^{1}H NMR spectroscopic data) was observed only in the case of chromene **1g** with the nitro group at C-8 of the aromatic ring. The regio- and stereochemistry of these adducts can be explained by assuming that [4+2] inverse electron-demand cycloaddition of 2,3-dihydrofuran over the nitroalkene fragment of chromenes **1** occurs regioselectively, such that the oxygen atom of electron-rich dienophile is located at the 3a-position and from an *endo* transition state, which would account for the *cis*-*cis* stereochemistry observed between the H-11b, H-11c, and H-3a atoms in the newly formed ring.



Scheme 2.

Table 1
[4+2] Cycloaddition of heterodienes **1a**–**i** with 2,3-dihydrofuran

Diene	R^1	R^2	X	Adduct	Time (days)[a]	Yield (%)
1a	H	H	F	**2a**	3	47
1b	Br	H	F	**2b**	2	67
1c	NO_2	H	F	**2c**	1	68
1d	H	H	Cl	**2d**	7	20
1e	Br	H	Cl	**2e**	4	49
1f	NO_2	H	Cl	**2f**	2	40
1g	H	NO_2	Cl	**2g**	2	30[c]
1h	NO_2	NO_2	Cl	**2h**	3 h	56
1i	MeO	H	Cl	**2i**	10 h[b]	49

[a] At 40 °C.
[b] At 60 °C.
[c] As a 85:15 mixture of the *endo*- and *exo*-diastereomers.

Replacement of the trifluoromethyl group with a trichloromethyl had no effect on the *endo*-selectivity. The results obtained for 2,3-dihydrofuran showed that the more electron-withdrawing CF_3 group favors both the rate and yield of heterodiene cycloaddition, presumably because of the more electrophilic character of 2-CF_3-chromenes **1a**–**c** compared with 2-CCl_3-chromenes **1d**–**i**. The lowest yield (20%) after the longest reaction time (seven days) was obtained from chromene **1d** having no substituents in the benzene ring; this is in full agreement with the lowered reactivity of 3-nitro-2-trichloromethyl-2*H*-chromenes compared to their fluorinated analogs.[11a–d] In accordance with this, 3-nitro-2-phenyl-2*H*-chromene did not react with 2,3-dihydrofuran under the same reaction conditions. The observed difference in reactivity between 2-CX_3-chromenes **1** and 3-nitro-2-phenyl-2*H*-chromene is undoubtedly due to the fact that the presence of the trihalomethyl group in place of phenyl makes chromenes **1** more reactive mainly by lowering the energy level of the LUMO. The reaction rates show a rough trend toward increasing with the strength of the electron-withdrawing substituent in the benzene ring. However, the most reactive 3,6,8-trinitro-2-trifluoromethyl-2*H*-chromene **1j** did not give a positive result and an unidentifiable mixture of products was obtained. No reaction occurred when cycloaddition of 4-methyl-3,6,8-trinitro-2-trichloromethyl-2*H*-chromene **1l** was attempted using a similar procedure. Apparently, unfavorable steric repulsive interactions with Me group become the deciding factor in the reaction with 2,3-dihydrofuran. When 3,4-dihydro-2*H*-pyran was used instead of 2,3-dihydrofuran, no reaction proceeded with **1a**,**d** under our conditions and only starting material was recovered.

All the signals in the ^{1}H and ^{13}C NMR spectra of adducts **2** were assigned on the basis of 2D COSY, HSQC, and HMBC experiments. The stereochemistry of the fused system was assigned as 3a,11c-*cis* and 11c,11b-*cis*, since the vicinal coupling constants ($J_{3a,11c}$=7.0–7.1 and $J_{11c,11b}$=4.8–5.4 Hz) were similar to the reported ones ($J_{3a,11c}$=7.1 and $J_{11c,11b}$=4.8 Hz) of the adduct prepared from 3-nitrocoumarin and 2,3-dihydrofuran.[12] In addition, the 2D NOESY spectrum of **2a** exhibits cross-peaks between the protons H-3a, H-11c, and H-11b, indicating that they are spatially close to each other and, hence, **2a** has *endo*-structure with the *cis*–*cis* arrangement of the nodal hydrogen atoms (Fig. 1).

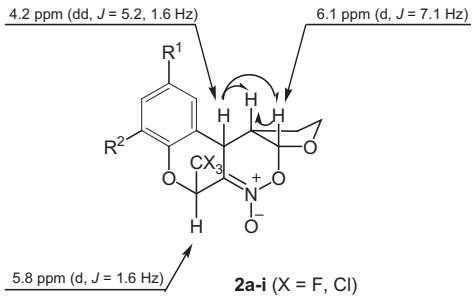


Figure 1. Diagnostic ^{1}H signals and NOE correlations of compounds **2a**–**i**.

Finally, the *endo*-structure with the *trans* arrangement of the H-11b and H-6 hydrogen atoms in fused chromans **2** was confirmed by X-ray crystallographic analysis after the isolation of **2d** as a single crystal from the reaction mixture (Fig. 2).

Next, taking into account the above results, we turned our attention to annulation with ethyl vinyl ether in order to assess the influence of this molecule on the efficiency and stereoselectivity of hetero-Diels–Alder reaction with 3-nitrochromenes **1**. In this case, the reaction of 2-CCl_3-chromenes **1d**,**f**,**h** with neat ethyl vinyl ether (2 equiv) was carried out at 40 °C in a sealed tube to give fused chromans *endo*-**3a**–**c** in 15–46% yields as the sole products without formation of the *exo*-isomers, suggesting high *endo*-selectivity in

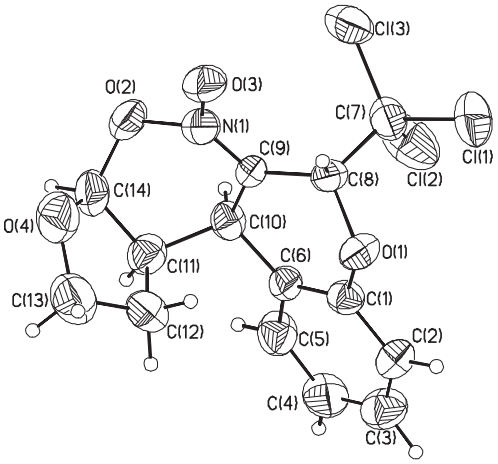
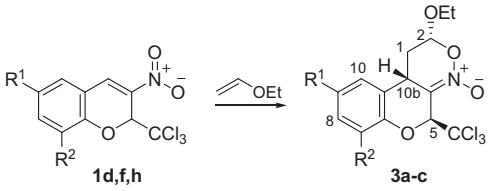


Figure 2. X-ray crystal structure of compound **2d** (thermal ellipsoids at 50% probability).

the cycloaddition reaction (Scheme 3). As expected, the reaction rates show a trend toward increasing with the number of the electron-withdrawing nitro groups in the benzene ring (Table 2).



Scheme 3.

Table 2
[4+2] Cycloaddition of heterodienes **1d**,**f**,**h** with ethyl vinyl ether

Diene	R^1	R^2	Adduct	Time (days)	Yield (%)
1d	H	H	**3a**	3	15
1f	NO_2	H	**3b**	1	35
1h	NO_2	NO_2	**3c**	3 h	46

All the signals in the ^1H and ^{13}C NMR spectra of adducts **3** were assigned on the basis of 2D HSQC and HMBC experiments. The structural assignment for compounds **3** as the 2,10b-*cis*, 10b,5-*trans* diastereomers was based on the three high-field signals of the H-2, H-10b, and H-5 protons in the ^1H NMR spectra. The signal of H-2 appeared as a doublet of doublets at δ 5.58–5.72 ppm with large and small coupling constants (^3J=7.6 and 2.8 Hz) due to coupling with the axial and equatorial protons H-1 and H-1′. Thus, the hemiacetal proton at C-2 obviously adopts a pseudo-axial position, and the ethoxy group occupies a pseudo-equatorial position. Another characteristic feature was the appearance of the signal of H-10b as a doublet of doublets at ca. 4.0 ppm with ^3J=12.2 and 7.0 Hz due to coupling with two protons of the CH_2 group. Large coupling constants of H-2 and H-10b correlate well with literature data ($^3J_{H2,H1}$=7.4 Hz and $^3J_{H10b,H1}$=12.1 Hz) for the adduct of 3-nitrocoumarin with ethyl vinyl ether[12] and revealed their axial/axial alignment. Therefore, the relative stereochemistry between these protons is *cis* as observed in adducts **2**. The H-5 signal appeared as a doublet at δ 5.95–6.14 ppm with $^4J_{H5,H10b}$=1.0–1.1 Hz and, by analogy, we can assume that in the resulting cycloadducts **3** atoms H-5 and H-10b adopt *trans* disposition with respect to each other as in the case of compound **2d**, the structure of which was established by X-ray diffraction analysis (Fig. 2). To confirm the conclusion about the stereochemistry of **3**, we carried out additionally a NOESY experiment for **3b**,**c**, which exhibits a strong cross-peak between protons H-2 and H-1, a weak one between H-2 and H-10b, but none between H-10b and H-5, all in accord with a 2,10b-*cis*, 10b,5-*trans* configuration (Fig. 3).

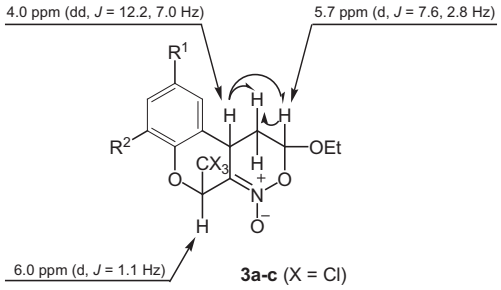
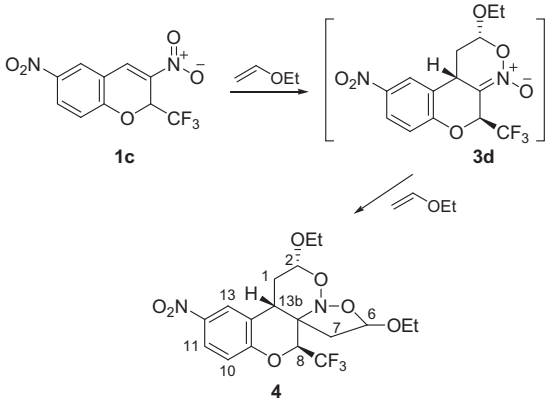


Figure 3. Diagnostic ^1H signals and NOE correlations of compounds **3a**–**c**.

Interestingly, the nature of the CX_3 group is important for the reaction with ethyl vinyl ether. Thus, chromenes **1a**,**b** bearing a trifluoromethyl group were recovered unchanged after treatment with ethyl vinyl ether (2 equiv) at 60 °C for 3 h in a sealed tube, but the more reactive 6-nitrochromene **1c** reacted readily under the same reaction conditions to give instead of the expected nitronate **3d** the tetracyclic adduct **4** in 48% yield. Clearly, this compound is formed as a result of [4+2] addition reaction across a 4π heterodiene system of **1c** by ethyl vinyl ether, which acts as an activated dienophile, and then non-isolable intermediate **3d** undergoes spontaneous [3+2] cycloaddition reaction across the nitronate function by a second molecule of ethyl vinyl ether to give bis-adduct **4** (Scheme 4). Since nitronates react much faster with electron-poor alkenes than with electron-rich alkenes,[13,14] we anticipate that CF_3-containing nitronates **3** will intercept selectively by the electron-poor alkene, such as methylacrylate. This would make it possible to prepare a set of new polycyclic chroman derivatives via three-component tandem [4+2]/[3+2] cycloaddition reaction. Further studies on the extension of this tandem reaction are in progress.



Scheme 4. Tandem [4+2]/[3+2] cycloaddition of chromene **1c** with ethyl vinyl ether.

The adduct **4** was thermally stable enough to be recrystallized from CH_2Cl_2–hexane (1:2), but it proved to be unstable in $CDCl_3$ and DMSO-d_6 solutions and the configurations at the C-6 and C-7a atoms were not determined. The structure of **4** was confirmed by its elemental and spectroscopic analyses. Besides the signals expected for the aromatic protons and two ethoxy groups, the most diagnostic signals for structural assignment of **4** are doublet of doublets of H-13b (3.06 ppm, J=14.0, 4.1 Hz), quartet of H-8 (4.98 ppm, $^3J_{H,F}$=8.4 Hz), triplet of H-2 (5.03 ppm, J=7.6 Hz), and doublet of

doublets of H-6 (5.88 ppm, J=6.4, 1.5 Hz). In the case of 2-CCl_3-chromenes **1d**,**f**,**h**, bis-adducts were not observed, most probably due to steric effects of the trichloromethyl group.

3. Conclusion

In conclusion, we have shown that the hetero-Diels–Alder reaction between 3-nitro-2-trihalomethyl-2*H*-chromenes and enol ethers under solvent-free conditions provides a regio- and stereoselective approach to the synthesis of a variety of CF_3 and CCl_3-containing cyclic nitronates, which can be considered as 1,3-dipoles for the preparation of new fused chroman derivatives of biological interest. Thus, a novel reactivity of 3-nitro-2*H*-chromenes was revealed.

4. Experimental

4.1. General

^{1}H (400 MHz), ^{13}C (100 MHz), and ^{19}F (376 MHz) NMR spectra were recorded on a Bruker DRX-400 spectrometer in DMSO-d_6 and $CDCl_3$ with TMS and C_6F_6 as internal standards, respectively. IR spectra were recorded on a Perkin–Elmer Spectrum BX-II instrument as KBr discs. Elemental analyses were performed at the Microanalysis Services of the Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences. All solvents used were dried and distilled per standard procedures. The starting 3-nitrochromenes **1a**–**g**,**i**,**k** were prepared according to described procedures.[9,10]

*4.1.1. 3,6,8-Trinitro-2-trichloromethyl-2H-chromene (**1h**).* To a mixture of chromene **1d** (3.0 g, 10.2 mmol) in conc. H_2SO_4 (10 mL) was added 65% HNO_3 (1.7 mL). The reaction mixture was heated with stirring at 125 °C for 0.5 h, cooled, and poured onto crushed ice (30 g). The precipitate that formed was filtered off, washed with water, dried, and recrystallized from ethanol. Yield 3.49 g (89%), mp 149–150 °C, yellow powder; IR (KBr) 1659, 1620, 1592, 1540, 1372, 1346 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (s, 1H, H-2), 8.19 (s, 1H, H-4), 8.53 (d, 1H, H-5, J=2.6 Hz), 8.94 (d, 1H, H-7, J=2.6 Hz). Anal. Calcd for $C_{10}H_4Cl_3N_3O_7$: C, 31.24; H, 1.05; N, 10.93. Found: C, 31.20; H, 0.77; N, 10.73.

*4.1.2. 3,6,8-Trinitro-2-trifluoromethyl-2H-chromene (**1j**).* This compound was obtained from **1a** according to the procedure for chromene **1h**. Yield 2.08 g (81%), mp 111–112 °C, yellow powder. IR (KBr) 1666, 1623, 1594, 1563, 1528, 1338 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (q, 1H, H-2, $^3J_{H,F}$=5.7 Hz), 8.22 (s, 1H, H-4), 8.56 (d, 1H, H-5, J=2.6 Hz), 8.94 (d, 1H, H-7, J=2.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ 84.27 (d, CF_3, $^3J_{F,H}$=5.7 Hz). Anal. Calcd for $C_{10}H_4F_3N_3O_7$: C, 35.84; H, 1.20; N, 12.54. Found: C, 35.80; H, 1.07; N, 12.46.

*4.1.3. 4-Methyl-3,6,8-trinitro-2-trichloromethyl-2H-chromene (**1l**).* This compound was obtained from **1k** according to the procedure for chromene **1h**. Yield 2.64 g (65%), mp 176–177 °C (hexane–$CHCl_3$, 1:3), yellow powder; IR (KBr) 1659, 1619, 1594, 1534, 1350, 1340 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (d, 3H, Me, ^5J=0.9 Hz), 6.51 (q, 1H, H-2, ^5J=0.9 Hz), 8.61 (d, 1H, H-5, J=2.6 Hz), 8.88 (d, 1H, H-7, J=2.6 Hz); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.58 (d, 3H, Me, ^5J=0.9 Hz), 7.00 (q, 1H, H-2, ^5J=0.9 Hz), 8.75 (d, 1H, H-5, J=2.6 Hz), 8.99 (d, 1H, H-7, J=2.6). Calcd for $C_{11}H_6Cl_3N_3O_7$: C, 33.15; H, 1.52; N, 10.54. Found: C, 32.86; H, 1.34; N, 10.54.

4.2. General procedure for the synthesis of fused chromans (2a–i)

A mixture of the corresponding chromene **1** (2.0 mmol) and 2,3-dihydrofuran (0.28 g, 4.0 mmol) was kept at 40 °C (60 °C for **2i**) for the appropriate time (Table 1). The resulting reaction mixture was concentrated under reduced pressure and the solid product obtained at standing was recrystallized from toluene to give compounds **2** as colorless crystals.

*4.2.1. 3a,11c-cis-6,11b-trans-11b,11c-cis-6-Trifluoromethyl-1,2,11b,11c-tetrahydro-3aH,6H-chromeno[3,4-c]furo[3,2-e][1,2]oxazin-5-oxide (**2a**).* Yield 47%, mp 162–163 °C; IR (KBr) 1629, 1588, 1492, 1457, 1380, 1350 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 (ddt, 1H, H-1, J=13.5, 7.7, 6.9 Hz), 1.76 (dddd, 1H, H-1′, J=13.5, 9.7, 7.4, 5.9 Hz), 3.36 (dtd, 1H, H-11c, J=9.7, 6.8, 5.4 Hz), 3.83 (ddd, 1H, H-2, J=9.1, 7.4, 6.9 Hz), 4.11 (ddd, 1H, H-2′, J=9.1, 7.7, 5.9 Hz), 4.12 (dd, 1H, H-11b, J=5.4, 1.6 Hz), 5.66 (qd, 1H, H-6, $^3J_{H,F}$=6.7 Hz, ^4J=1.6 Hz), 6.11 (d, 1H, H-3a, J=7.0 Hz), 7.08 (dd, 1H, H-8, J=8.2, 1.3 Hz), 7.11 (td, 1H, H-10, J=7.5, 1.3 Hz), 7.19 (dd, 1H, H-11, J=7.7, 1.8 Hz), 7.28 (ddd, 1H, H-9, J=8.2, 7.4, 1.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ 88.24 (d, CF_3, $^3J_{F,H}$=6.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.30 (C-1), 33.94 (C-11b), 46.77 (C-11c), 68.64 (q, C-6, $^2J_{C,F}$=34.3 Hz), 68.75 (C-2), 108.47 (C-3a), 116.34 (C-5a), 117.96 (C-8), 119.42 (C-11a), 122.96 (q, CF_3, $^1J_{C,F}$=287.8 Hz), 123.86 (C-10), 127.86 (C-11), 129.30 (C-9), 151.64 (C-7a); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.37 (ddt, 1H, H-1, J=13.1, 7.7, 6.7 Hz), 1.64 (dddd, 1H, H-1′, J=13.1, 9.8, 7.7, 6.1 Hz), 3.53 (dtd, 1H, H-11c, J=9.8, 6.9, 5.3 Hz), 3.74 (ddd, 1H, H-2, J=8.7, 7.7, 6.6 Hz), 3.95 (ddd, 1H, H-2′, J=8.7, 7.7, 6.1 Hz), 4.31 (dd, 1H, H-11b, J=5.3, 1.6 Hz), 6.11 (qd, 1H, H-6, $^3J_{H,F}$=7.2 Hz, ^4J=1.6 Hz), 6.16 (d, 1H, H-3a, J=6.9 Hz), 7.08 (dd, 1H, H-8, J=8.1, 1.3 Hz), 7.14 (td, 1H, H-10, J=7.7, 1.3 Hz), 7.28 (ddd, 1H, H-9, J=8.2, 7.4, 1.8 Hz), 7.41 (dd, 1H, H-11, J=7.7, 1.8 Hz); ^{19}F NMR (376 MHz, DMSO-d_6) δ 90.39 (d, CF_3, $^3J_{F,H}$=7.2 Hz). Anal. Calcd for $C_{14}H_{12}F_3NO_4$: C, 53.34; H, 3.84; N, 4.44. Found: C, 53.43; H, 3.67; N, 4.50.

*4.2.2. 3a,11c-cis-6,11b-trans-11b,11c-cis-10-Bromo-6-trifluoromethyl-1,2,11b,11c-tetrahydro-3aH,6H-chromeno[3,4-c]furo[3,2-e][1,2]oxazin-5-oxide (**2b**).* Yield 67%, mp 197–198 °C; IR (KBr) 1628, 1580, 1480, 1377, 1352 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (dq, 1H, H-1, J=13.5, 6.7 Hz), 1.81 (dddd, 1H, H-1′, J=13.5, 9.7, 7.7, 5.9 Hz), 3.35 (dtd, 1H, H-11c, J=9.7, 6.8, 5.5 Hz), 3.85 (dt, 1H, H-2, J=9.1, 7.3 Hz), 4.08 (br d, 1H, H-11b, J=3.8 Hz), 4.11 (ddd, 1H, H-2′, J=9.1, 7.9, 6.0 Hz), 5.66 (qd, 1H, H-6, $^3J_{H,F}$=6.6 Hz, ^4J=1.5 Hz), 6.10 (d, 1H, H-3a, J=7.1 Hz), 6.98 (d, 1H, H-8, J=8.7 Hz), 7.33 (d, 1H, H-11, J=2.2 Hz), 7.38 (dd, 1H, H-9, J=8.7, 2.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ 88.24 (d, CF_3, $^3J_{F,H}$=6.6 Hz). Anal. Calcd for $C_{14}H_{11}BrF_3NO_4$: C, 42.66; H, 2.81; N, 3.55. Found: C, 42.57; H, 2.66; N 3.57.

*4.2.3. 3a,11c-cis-6,11b-trans-11b,11c-cis-6-Trifluoromethyl-10-nitro-1,2,11b,11c-tetrahydro-3aH,6H-chromeno[3,4-c]furo[3,2-e][1,2]oxazin-5-oxide (**2c**).* Yield 68%, mp 175–176 °C; IR (KBr) 1636, 1588, 1532, 1514, 1485, 1381, 1348 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (dq, 1H, H-1, J=13.4, 7.5 Hz), 1.79 (dddd, 1H, H-1′, J=13.2, 9.7, 7.6, 5.5 Hz), 3.46 (dtd, 1H, H-11c, J=9.7, 7.0, 5.5 Hz), 3.86 (dt, 1H, H-2, J=9.1, 7.3 Hz), 4.14 (ddd, 1H, H-2′, J=9.1, 7.9, 5.5 Hz), 4.25 (br d, 1H, H-11b, J=4.8 Hz), 5.79 (qd, 1H, H-6, $^3J_{H,F}$=6.4 Hz, ^4J=1.6 Hz), 6.15 (d, 1H, H-3a, J=7.1 Hz), 7.22–7.26 (m, 1H, H-8), 8.18–8.21 (m, 2H, H-9, H-11); ^{19}F NMR (376 MHz, $CDCl_3$) δ 87.94 (d, CF_3, $^3J_{F,H}$=6.4 Hz). Anal. Calcd for $C_{14}H_{11}F_3N_2O_6$: C, 46.68; H, 3.08; N, 7.78. Found: C, 46.67; H, 3.04; N, 7.75.

*4.2.4. 3a,11c-cis-6,11b-trans-11b,11c-cis-6-Trichloromethyl-1,2,11b,11c-tetrahydro-3aH,6H-chromeno[3,4-c]furo[3,2-e][1,2]oxazin-5-oxide (**2d**).* Yield 20%, mp 179–180 °C (decomp.); IR (KBr) 1620, 1586, 1487, 1454, 1377 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (dq, 1H, H-1, J=13.5, 7.5 Hz), 1.74 (dddd, 1H, H-1′, J=13.5, 9.6, 7.7, 5.8 Hz), 3.35 (dtd, 1H, H-11c, J=9.6, 7.3, 5.4 Hz), 3.84 (dt, 1H, H-2, J=9.0, 7.5 Hz), 4.14 (td, 1H, H-2′, J=8.4, 5.8 Hz), 4.22 (br d, 1H, H-11b, J=5.1 Hz), 5.84 (d, 1H, H-6, J=1.3 Hz), 6.12 (d, 1H, H-3a, J=7.1 Hz),

7.05–7.10 (m, 2H, H-8, H-10), 7.16 (dd, 1H, H-11, *J*=8.0, 1.5 Hz), 7.27 (td, 1H, H-9, *J*=7.5, 1.5 Hz). Anal. Calcd for $C_{14}H_{12}Cl_3NO_4$: C, 46.12; H, 3.32; N, 3.84. Found: C, 46.14; H, 3.31; N, 3.73.

*4.2.5. 3a,11c-cis-6,11b-trans-11b,11c-cis-10-Bromo-6-trichloromethyl-1,2,11b,11c-tetrahydro-3aH,6H-chromeno[3,4-c]furo[3,2-e][1,2]oxazin-5-oxide (**2e**).* Yield 49%, mp 205–206 °C (decomp., CH_2Cl_2–hexane, 1:2); IR (KBr) 1608, 1578, 1480, 1371 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.62 (dq, 1H, H-1, *J*=13.3, 7.6 Hz), 1.80 (dddd, 1H, H-1′, *J*=13.3, 9.7, 7.6, 5.6 Hz), 3.34 (dtd, 1H, H-11c, *J*=9.7, 7.3, 5.3 Hz), 3.85 (dt, 1H, H-2, *J*=9.0, 7.4 Hz), 4.15 (ddd, 1H, H-2′, *J*=9.0, 7.9, 5.6 Hz), 4.18 (br d, 1H, H-11b, *J*=5.0 Hz), 5.84 (d, 1H, H-6, *J*=1.4 Hz), 6.11 (d, 1H, H-3a, *J*=7.0 Hz), 6.98 (d, 1H, H-8, *J*=8.7 Hz), 7.30 (d, 1H, H-11, *J*=2.3 Hz), 7.37 (dd, 1H, H-9, *J*=8.7, 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.35 (C-1), 34.74 (C-11b), 46.69 (C-11c), 68.53 (C-2), 79.04 (C-6), 98.92 (CCl_3), 108.00 (C-3a), 115.85 (C-10), 117.81 (C-5a), 119.96 (C-8), 123.17 (C-11a), 130.10 (C-11), 132.37 (C-9), 150.77 (C-7a). Anal. Calcd for $C_{14}H_{11}BrCl_3NO_4$: C, 37.91; H, 2.50; N, 3.16. Found: C, 37.86; H, 2.57; N, 3.09.

*4.2.6. 3a,11c-cis-6,11b-trans-11b,11c-cis-6-Trichloromethyl-10-nitro-1,2,11b,11c-tetrahydro-3aH,6H-chromeno[3,4-c]furo[3,2-e][1,2]oxazin-5-oxide (**2f**).* Yield 40%, mp 231–232 °C (decomp.); IR (KBr) 1651, 1619, 1582, 1522, 1478, 1343, 1331 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.58 (dq, 1H, H-1, *J*=13.2, 7.8 Hz), 1.78 (dddd, 1H, H-1′, *J*=13.2, 9.7, 7.5, 5.3 Hz), 3.44 (dtd, 1H, H-11c, *J*=9.7, 7.5, 5.3 Hz), 3.86 (dt, 1H, H-2, *J*=9.1, 7.5 Hz), 4.17 (ddd, 1H, H-2′, *J*=9.0, 8.1, 5.2 Hz), 4.35 (br d, 1H, H-11b, *J*=5.0 Hz), 5.97 (d, 1H, H-6, *J*=1.4 Hz), 6.16 (d, 1H, H-3a, *J*=7.0 Hz), 7.23 (d, 1H, H-8, *J*=8.9 Hz), 8.15 (d, 1H, H-11, *J*=2.7 Hz), 8.18 (dd, 1H, H-9, *J*=8.9, 2.7 Hz). Anal. Calcd for $C_{14}H_{11}Cl_3N_2O_6$: C, 41.05; H, 2.71; N, 6.84. Found: C, 40.89; H, 2.67; N, 6.75.

*4.2.7. 3a,11c-cis-6,11b-trans-11b,11c-cis-6-Trichloromethyl-8-nitro-1,2,11b,11c-tetrahydro-3aH,6H-chromeno[3,4-c]furo[3,2-e][1,2]oxazin-5-oxide (**2g**).* Yield 30%, mp 199–200 °C (decomp., CH_2Cl_2–hexane, 1:2); IR (KBr) 1620, 1588, 1528, 1460, 1369 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (*endo*-isomer, 85%) δ 1.68 (dq, 1H, H-1, *J*=13.1, 7.5 Hz), 1.80 (dddd, 1H, H-1′, *J*=13.1, 9.6, 7.5, 5.3 Hz), 3.38 (dtd, 1H, H-11c, *J*=9.6, 7.0, 5.3 Hz), 3.87 (dt, 1H, H-2, *J*=9.0, 7.4 Hz), 4.18 (ddd, 1H, H-2′, *J*=9.0, 8.1, 5.7 Hz), 4.33 (br d, 1H, H-11b, *J*=5.1 Hz), 6.00 (d, 1H, H-6, *J*=1.4 Hz), 6.15 (d, 1H, H-3a, *J*=7.0 Hz), 7.22 (t, 1H, H-10, *J*=7.9 Hz), 7.43 (br d, 1H, H-11, *J*=7.8 Hz), 7.84 (dd, 1H, H-9, *J*=8.1, 1.4 Hz); (*exo*-isomer, 15%) δ 2.12–2.28 (m, 2H, 2-CH_2), 3.80–3.88 (m, 1H, H-11c), 4.02 (td, 1H, H-2, *J*=8.8, 4.6 Hz), 4.14 (m, 1H, H-11b), 4.28 (q, 1H, H-2′, *J*=8.5 Hz), 5.98 (d, 1H, H-6, *J*=1.2 Hz), 6.22 (d, 1H, H-3a, *J*=7.3 Hz), 7.25 (t, 1H, H-10, *J*=7.9 Hz), 7.45 (dt, 1H, H-11, *J*=7.8, 1.3 Hz), 7.83 (dd, 1H, H-9, *J*=8.1, 1.4 Hz). Anal. Calcd for $C_{14}H_{11}Cl_3N_2O_6$: C, 41.05; H, 2.71; N, 6.84. Found: C, 40.84; H, 2.58; N, 6.70.

*4.2.8. 3a,11c-cis-6,11b-trans-11b,11c-cis-6-Trichloromethyl-8,10-dinitro-1,2,11b,11c-tetrahydro-3aH,6H-chromeno[3,4-c]furo[3,2-e][1,2]oxazin-5-oxide (**2h**).* Yield 56%, mp 219–220 °C (decomp.); IR (KBr) 1617, 1598, 1537, 1464, 1375, 1341 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.43 (dq, 1H, H-1, *J*=12.7, 7.7 Hz), 1.71–1.80 (m, 1H, H-1′), 3.67–3.74 (m, 1H, H-11c), 3.76 (dt, 1H, H-2, *J*=8.4, 7.5 Hz), 4.03 (td, 1H, H-2′, *J*=8.4, 5.5 Hz), 4.72 (br d, 1H, H-11b, *J*=5.1 Hz), 6.19 (d, 1H, H-3a, *J*=6.9 Hz), 6.49 (d, 1H, H-6, *J*=1.2 Hz), 8.70 (d, 1H, H-11, *J*=2.6 Hz), 8.82 (d, 1H, H-9, *J*=2.6 Hz). Anal. Calcd for $C_{14}H_{10}Cl_3N_3O_8$: C, 36.99; H, 2.22; N, 9.24. Found: C, 36.92; H, 2.45; N, 9.05.

*4.2.9. 3a,11c-cis-6,11b-trans-11b,11c-cis-10-Methoxy-6-trichloromethyl-1,2,11b,11c-tetrahydro-3aH,6H-chromeno[3,4-c]furo[3,2-e][1,2]oxazin-5-oxide (**2i**).* Yield 49%, mp 217–218 °C; IR (KBr) 1610, 1600, 1499, 1464, 1373, 1326 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.68 (dq, 1H, H-1, *J*=13.5, 7.5 Hz), 1.78 (dddd, 1H, H-1′, *J*=13.5, 9.7, 7.5, 6.0 Hz), 3.34 (dtd, 1H, H-11c, *J*=9.7, 7.1, 5.3 Hz), 3.79 (s, 3H, MeO), 3.84 (dt, 1H, H-2, *J*=8.6, 7.5 Hz), 4.14 (td, 1H, H-2′, *J*=8.6, 6.0 Hz), 4.15 (br d, 1H, H-11b, *J*=5.0 Hz), 5.79 (d, 1H, H-6, *J*=1.4 Hz), 6.11 (d, 1H, H-3a, *J*=7.1 Hz), 6.66 (d, 1H, H-11, *J*=2.9 Hz), 6.81 (dd, 1H, H-9, *J*=8.9, 2.9 Hz), 7.01 (d, 1H, H-8, *J*=8.9 Hz). Anal. Calcd for $C_{15}H_{14}Cl_3NO_5$: C, 45.65; H, 3.58; N, 3.55. Found: C, 45.61; H, 3.58; N, 3.46.

4.3. General procedure for the synthesis of fused chromans (3a–c)

A mixture of the corresponding chromene **1** (2.0 mmol) and ethyl vinyl ether (0.29 g, 4.0 mmol) was kept at 40 °C for the appropriate time in a sealed tube (Table 2). The resulting reaction mixture was concentrated under reduced pressure and the solid product obtained at standing was recrystallized from CH_2Cl_2–hexane (1:2) to give compounds **3** as colorless crystals.

*4.3.1. 2,10b-cis-5,10b-trans-2-Ethoxy-5-trichloromethyl-1,10b-dihydro-2H,5H-chromeno[3,4-c][1,2]oxazin-4-oxide (**3a**).* Yield 15%, mp 126–127 °C; IR (KBr) 1608, 1587, 1492, 1456, 1368 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, 3H, Me, *J*=7.1 Hz), 2.02 (ddd, 1H, H-1, *J*=13.8, 10.6, 5.3 Hz), 2.88 (ddd, 1H, H-1′, *J*=13.8, 7.3, 5.9 Hz), 3.68 (dq, 1H, OC*H*H, *J*=9.5, 7.1 Hz), 4.03–4.11 (m, 2H, OCH*H*, H-10b), 5.58 (t, 1H, H-2, *J*=5.6 Hz), 5.95 (d, 1H, H-5, *J*=1.1 Hz), 7.00–7.05 (m, 2H, H-7, H-9), 7.10 (br d, 1H, H-10, *J*=7.5 Hz), 7.23 (td, 1H, H-8, *J*=7.8, 1.7 Hz). Anal. Calcd for $C_{14}H_{14}Cl_3NO_4$: C, 45.87; H, 3.85; N, 3.82. Found: C, 45.80; H, 3.91; N, 3.78.

*4.3.2. 2,10b-cis-5,10b-trans-2-Ethoxy-9-nitro-5-trichloromethyl-1,10b-dihydro-2H,5H-chromeno[3,4-c][1,2]oxazin-4-oxide (**3b**).* Yield 35%, mp 164–165 °C; IR (KBr) 1624, 1586, 1520, 1479, 1376, 1339 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, 3H, Me, *J*=7.1 Hz), 2.27 (ddd, 1H, H-1, *J*=12.9, 12.2, 2.8 Hz), 3.35 (ddd, 1H, H-1′, *J*=12.9, 7.5, 7.0 Hz), 3.73 (dq, 1H, OC*H*H, *J*=9.5, 7.1 Hz), 3.95 (ddq, 1H, H-10b, *J*=12.2, 7.0, 1.0 Hz), 4.07 (dq, 1H, OCH*H*, *J*=9.5, 7.1 Hz), 5.69 (dd, 1H, H-2, *J*=7.6, 2.8 Hz), 5.98 (d, 1H, H-5, *J*=1.0 Hz), 7.21 (d, 1H, H-7, *J*=9.0 Hz), 8.06 (dd, 1H, H-10, *J*=2.7, 1.3 Hz), 8.17 (ddd, 1H, H-8, *J*=9.0, 2.7, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.72 (Me), 31.06 (C-10b), 36.31 (C-1), 65.63 (OCH_2), 79.86 (C-5), 99.42 (CCl_3), 104.20 (C-2), 118.36 (C-4a), 118.87 (C-7), 121.73 (C-10), 122.73 (C-10a), 124.86 (C-8), 143.48 (C-9), 156.37 (C-6a). Anal. Calcd for $C_{14}H_{13}Cl_3N_2O_6$: C, 40.85; H, 3.18; N, 6.81. Found: C, 41.00; H, 3.38; N, 6.82.

*4.3.3. 2,10b-cis-5,10b-trans-2-Ethoxy-7,9-dinitro-5-(trichloromethyl)-1,10b-dihydro-2H,5H-chromeno[3,4-c][1,2]oxazin-4-oxide (**3c**).* Yield 46%, mp 172–173 °C (yellow powder); IR (KBr) 1630, 1615, 1600, 1541, 1524, 1335 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, 3H, Me, *J*=7.1 Hz), 2.32 (td, 1H, H-1, *J*=12.4, 2.8 Hz), 3.40 (dt, 1H, H-1′, *J*=12.8, 7.3 Hz), 3.74 (dq, 1H, OC*H*H, *J*=9.6, 7.1 Hz), 4.02 (dddt, 1H, H-10b, *J*=12.1, 7.1, 1.3, 1.0 Hz), 4.07 (dq, 1H, OCH*H*, *J*=9.6, 7.1 Hz), 5.72 (dd, 1H, H-2, *J*=7.5, 2.8 Hz), 6.14 (d, 1H, H-5, *J*=1.0 Hz), 8.24 (dd, 1H, H-10, *J*=2.7, 1.3 Hz), 8.68 (dd, 1H, H-8, *J*=2.7, *J*=1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.68 (Me), 31.21 (C-10b), 36.63 (C-1), 65.85 (OCH_2), 80.23 (C-5), 98.73 (CCl_3), 104.07 (C-2), 116.37 (C-4a), 120.47 (C-8), 124.41 (C-10), 126.52 (C-10a), 139.86 (C-7), 141.97 (C-9), 149.46 (C-6a). Anal. Calcd for $C_{14}H_{12}Cl_3N_3O_8$: C, 36.83; H, 2.65; N, 9.20. Found: C, 36.79; H, 2.64; N, 9.06.

4.4. 2,6-Diethoxy-12-nitro-8-(trifluoromethyl)-1,6,7,13b-tetrahydro-2*H*-chromeno[3,4-c]isoxazolo[2,3-b][1,2]oxazine (4)

A mixture of chromene **1c** (0.58 g, 2.0 mmol) and ethyl vinyl ether (0.29 g, 4.0 mmol) was kept at 60 °C for 3 h in a sealed tube. The resulting reaction mixture was concentrated under reduced pressure and the solid product that formed was recrystallized from CH_2Cl_2–hexane (1:2) to give compound **4** as colorless crystals. Yield 0.42 g (48%), mp 148–149 °C; IR (KBr) 1590, 1528, 1487, 1449,

1375, 1348 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25, 1.27 (both t, 6H, 2Me, J=7.1 Hz), 2.27 (td, 1H, H-1, J=14.0, 8.2 Hz), 2.39 (ddd, 1H, H-1′, J=14.0, 7.0, 4.1 Hz), 2.53 (dd, 1H, H-7, J=13.3, 6.4 Hz), 2.59 (dd, 1H, H-7′, J=13.3, 1.5 Hz), 3.06 (br dd, 1H, H-13b, J=14.0, 4.1 Hz), 3.58, 3.60, 3.87, 3.99 (all dq, 4H, 2 OCH_2, J=9.7, 7.1 Hz), 4.98 (q, 1H, H-8, $^3J_{H,F}$=8.4 Hz), 5.03 (t, 1H, H-2, J=7.6 Hz), 5.88 (dd, 1H, H-6, J=6.4, 1.5 Hz), 7.11–7.14 (m, 1H, H-10), 8.07–8.11 (m, 2H, H-11, H-13); ^{19}F NMR (376 MHz, $CDCl_3$) δ 94.41 (d, CF_3, J=8.4 Hz). Anal. Calcd for $C_{18}H_{21}F_3N_2O_7$: C, 49.77; H, 4.87; N, 6.45. Found: C, 49.61; H, 4.81; N, 6.42.

4.5. Crystal data for 2d

$C_{14}H_{12}Cl_3NO_4$, M 364.60, monoclinic crystals space group $P2_1/c$, at 295(2) K, a=11.6051(15), b=16.7759(13), c=15.833(2) Å, α=90°, β=100.236(11)°, γ=90°, V=3033.3(6) $Å^3$, d_{calcd}=1.597 g cm^{-3}, absorption coefficient μ=0.620 mm^{-1}, Z=8. The intensities of 6522 independent reflections (R_{int}=0.0405) were measured on a 'Xcalibur 3' automatic four-circle diffractometer (MoK_α radiation, λ=0.71073 Å, graphite monochromator, $\omega/2\theta$ scan, $2\theta_{max}$=52°). The structure was solved by direct methods with the use of the SHELXS-97 and SHELXL-97 programs package[15] and refined by full-matrix least-squares on F^2 using all the data. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters and hydrogen atoms were included at calculated position using a ring model. The final discrepancy factors R_1=0.0375, wR_2=0.0473, GooF=1.001 for 2678 reflections with $I>2\sigma(I)$; R_1=0.1245, wR_2=0.0515 (all data). Largest different peak and hole: 0.332 and −0.349 e$Å^{-3}$. Completeness to θ=26.00° (97.7%). Deposition number CCDC 743039.

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