Chemistry of Polyhalogenated Nitrobutadienes, Part 9: Acyclic and Heterocyclic Nitroenamines and Nitroimines from 2-Nitroperchlorobuta-1,3-diene

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Various amino, diamino, aminothio, or benzotriazolo compounds derived from the exceedingly versatile 2-nitroperchlorobutadiene (**1**) gave structurally interesting and physiologically promising nitro-enamines, -imines, -amidines, and hydrazines as well as ring closure reaction products, *e. g.* pyrimidines and pyrazoles. Most of these reactions turned out to be highly selective with good to very good yields. The structure of the pyrazole precursor (*E,E*)-1-(benzotriazol-1-yl)-4,4-dichloro-3-(4-ethoxyphenylamino)-1-(4-ethoxyphenylimino)-2-nitrobut-2-ene (**30**), due to its exceptional substitution pattern, was evidenced by single-crystal X-ray diffraction analysis.

Key words: Nitro Compounds, Nucleophilic Substitution, Pyrimidines, Pyrazoles, Betaines, Click Chemistry

Introduction

In the course of our studies concerning polyhalogenated nitrodienes, in many cases 2-nitroperchlorobutadiene (**1**) [1] or nitrotrichloroethylene [2] proved themselves as appropriate precursors for a diverse variety of synthetically and/or physiologically interesting chemical compounds. Especially diene **1** is often the starting material of choice, due to its stepped reactivity in S_NVin processes. Thus, applying selective and mild reactions, this diene enables click chemistry-type syntheses [3]. In the present paper, we mainly focus on recent progress in the syntheses of acyclic and heterocyclic nitro-enamines and -imines [4, 5], such as nitropyrimidines or nitropyrazoles, or benzoannelated nitrovinylidene bisheterocycles.

Results and Discussion

The vinylic S_N reaction of 2-nitroperchlorobutadiene (**1**) with at least four equivalents of an aniline derivative that bears an electron-releasing group (ERG/Hal) in 4-position of the phenyl ring selectively affords the corresponding 1,1-bis(arylamino)-butadienes **2** – **7** with up to 95 % yield. The regiospecificity is caused by the fact that the LUMO of **1** is located preferentially at the dihalogeno-nitrovinyl fragment, and to an extent of 67 – 85 % at the C-1 carbon atom [1d]. Therefore, the first nucleophilic substitution reaction usually takes place at the C-1 position of **1** and proceeds stereospecifically with respect to the configuration of the double bonds. The ease of the second, hence twofold substitution at the C-1 atom is probably due to an extraordinary high electrophilicity of the assumed imide chloride intermediate **A** shown in Scheme 1. In fact, the reaction at this imine-type carbon atom is preferred over the nucleophilic attack at the β-carbon atom of the nitrodichlorovinylene moiety and exclusively leads to the 1,1-bisamines **2** – **7** (Scheme 1).

The substructure of a nitro-substituted enamine within compounds **2** – **7** should enable a stabilization caused by a strong hydrogen bond between an oxygen atom of the nitro group and the single proton at the aniline nitrogen atom as shown in Fig. 1 (framed structure), a behavior typical of such enamines [6, 7].

Even though nitronate or iminic structures, in detail the depicted tautomeric amidines, are plausible to occur and have been previously proven by NMR spectroscopy in case of the reaction of **1** with ani-

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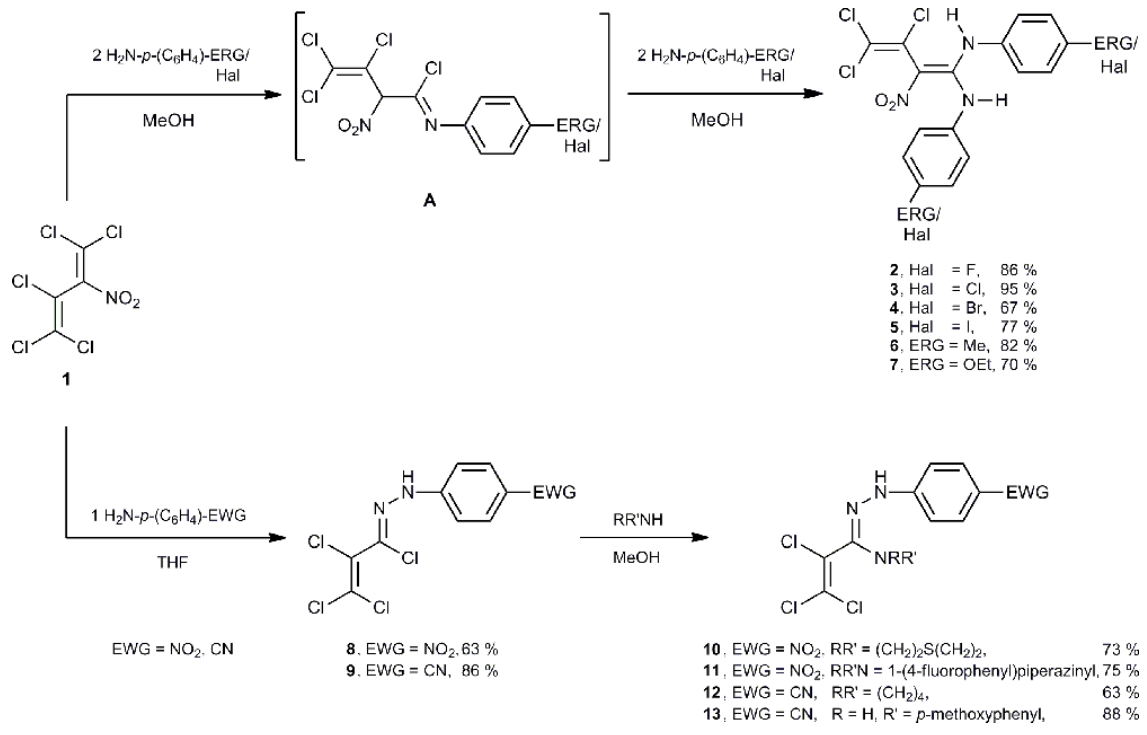
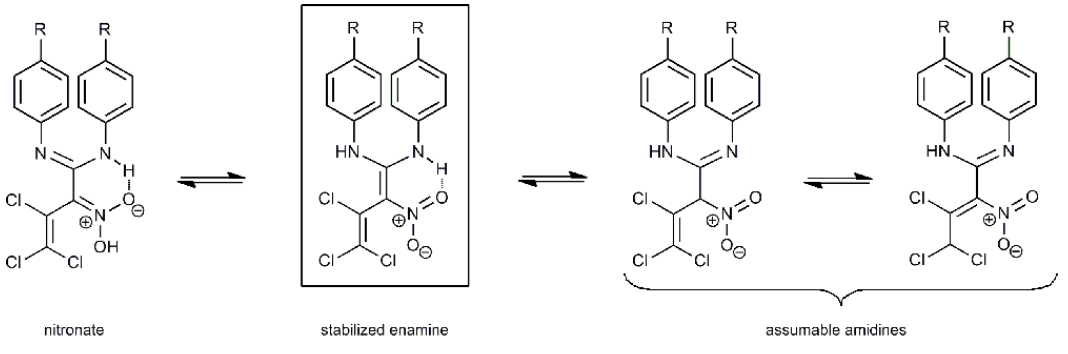


Scheme 1.

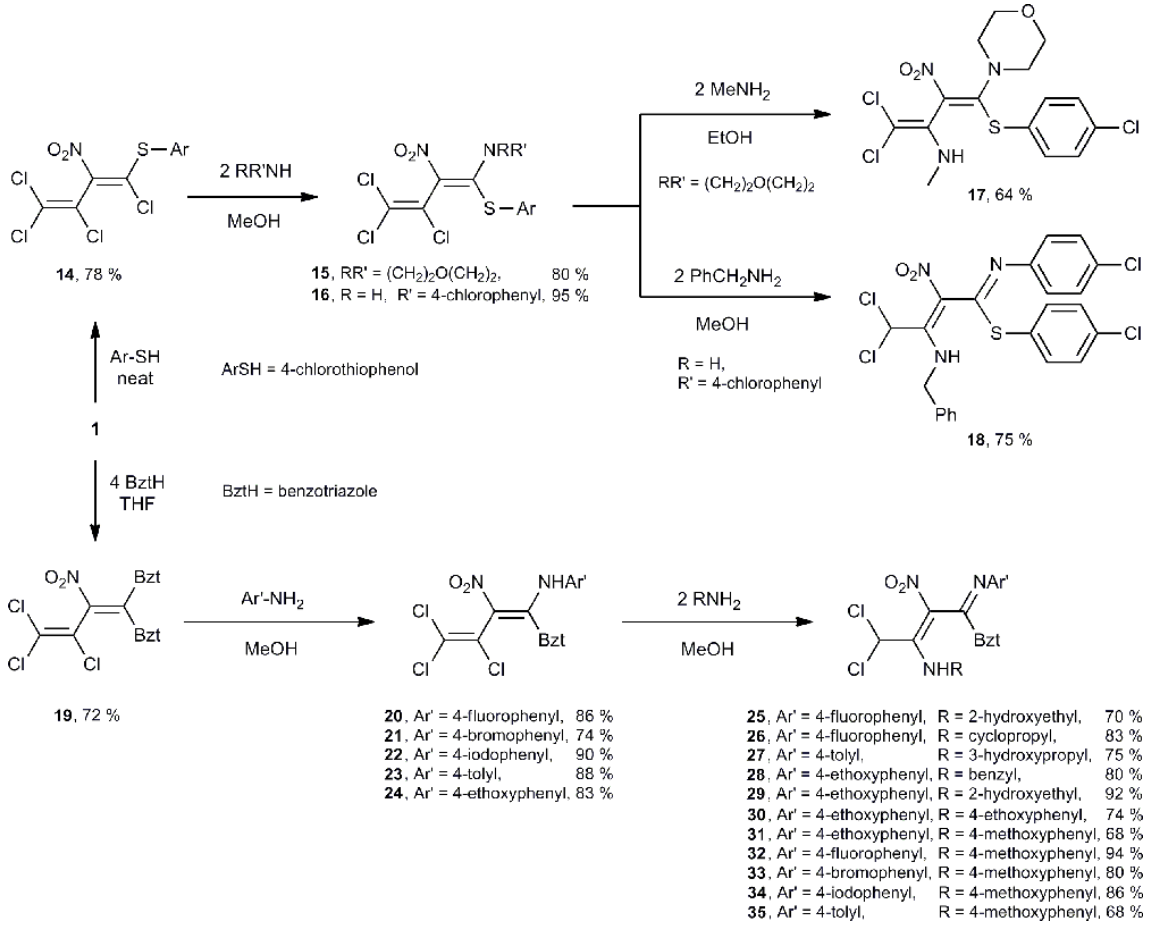


R = H, ERG/Hal as shown in Scheme 1

R = *para*-substituted phenyl as shown in Scheme 1.

Fig. 1. Tautomers of enamines **2** – **7**.

line and *o*-chloroaniline [8], in the present case the proton spectra gave no characteristic signal of such a deshielded methine proton that is located in a terminal dichloromethyl group. In contrast, applying less basic anilines with electron withdrawing groups in 4-position of the phenyl ring, *N*-tetrachloroallylidene-*N*′-arylhydrazines were obtained instead of the aforementioned 1,1-bisamination products. The reaction starts again with the initial nucleophilic substitution by the aniline derivative, but in the second step, the imidoyl chloride unit within **1** then preferentially reacts with an adjacent oxygen atom of the nitro group, *i. e.* in competition with the electron-deficient anilines. Further mechanistic aspects have been previously published by our group [9], but herein it should be explicitly stated that subsequent to the mentioned nucleophilic attack the C-1 carbon atom of the butadiene derivative **1** is lost in the form of carbon dioxide.



Scheme 2.

Thus, regarding the syntheses in this paper, the conversion of **1** with 4-nitroaniline and 4-cyanoaniline afforded the *N*-(tetrachloroallylidene)-*N′*-arylhydrazines **8** and **9**, both with a C-3 backbone. The yields of these *N*-perchloroallylidene derivatives were 63 % and 86 %, respectively (Scheme 1).

The distinct electrophilic character of the C-1 carbon within **8** and **9**, that is caused by electron withdrawal to the C=N group and in addition to the chlorine atom, prompted us to explore similar substitution reactions. Thereby, on application of aromatic or aliphatic amines, the corresponding *N*-(1-amino-2,3,3-trichloroallylidene) - *N′* - arylhydrazines **10** – **13** were obtained (yields 63 – 88 %; Scheme 1). Interestingly, quite a number of aromatic hydrazones have been found to exhibit extensive biological activity [10].

It is noteworthy that the hydrazones **10** – **12** are generated as single isomers, whereas the methoxy derivative **13** gave an inseparable 3 : 1 mixture as evidenced by ^{1}H NMR. In principle, this course observation should be expected because of the potential appearance of two tautomers of **13** as depicted in Fig. 2.

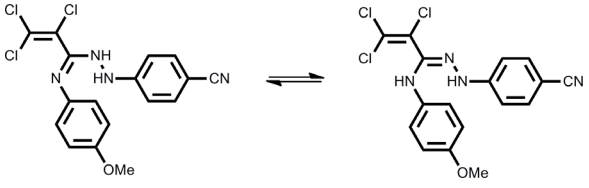


Fig. 2. Tautomers of **13**.

In addition to the aforementioned conversions of **1** applying amines, we also became interested in extending the applicability to other nucleophiles, *e. g.* sulfur compounds. As a promising example we started with 4-chlorothiophenol. The solventless reaction of butadiene **1** with one equivalent of this sulfur-nucleophile

afforded the substitution product **14** in 78 % yield (Scheme 2).

The exclusive formation of the (*E*)-isomer of **14** is in accordance with the literature [11]. However, the occurrence of the (*E*)-isomer with the opposite configuration in **15** and **16**, *i. e.* with the sulfur-substituent in *trans*-position to the nitro group, is possible due to free rotation around the single bond between C-1 and C-2 in the intermediate that is produced during the attack of the *N*-nucleophile at the C-1 carbon atom. These 1-amino-1-thiodienes **15** and **16** were obtained in 80 % and 95 % yield, respectively, upon treatment of the sulfur-substituted nitroperchlorobutadiene **14** with amines. Comparing **15** with **16**, it turned out that within **16** the remaining amine proton additionally supports the (*E*)-configuration by formation of a hydrogen bridge to the neighboring nitro substituent. Recently, in an analogous way, the double bond configuration of similar nitrovinyl compounds had been assigned [12].

With the aim to synthesize *N*,*N*,*S*-substituted dichloronitrobutadienes from **15** and **16**, we went on with S_NVin reactions. With regard to Pearson's HSAB concept [13], the monochloro-substituted α-carbon atom within the trichloro-vinyl group of these aminothiodienes should give rise to an attack of further (relatively weak) nucleophiles. Even though the application of other, preferentially different sulfur nucleophiles is on our schedule, at first we tested substitution of this single chlorine atom of the $Cl_2C{=}CCl$ fragment by amines (Scheme 2). Two different types of products appeared: the reaction of the morpholinyl derivative **15** led to dichloronitrobutadiene **17** with the expected *N*,*N*,*S*-substitution pattern, but conversion of the chlorophenylaminodiene **16** afforded the corresponding iminonitrobutene **18**. Thus, the latter product exhibits the most extended π system, *i. e.* from the chlorophenyl moiety to the push-pull-substituted olefinic double bond. Also in this case, the structural assignment was unambiguously performed applying NMR spectroscopy. In detail, even proton spectroscopy attested to the assumed structure, as the proton of the exterior $HCCl_2$ fragment within **18** gave a singlet at δ = 6.80 ppm and additionally a characteristic increase of the one-bond C,H coupling constant (from about 125 Hz to 182 Hz).

Aside from the *N*,*N*,*S* derivatives, we investigated the access to the similar *N*,*N*,*N*-trisubstituted nitrobutadienes. Therefore, the precursor **1** was subjected to reaction with four equivalents of benzotriazole in tetrahydrofuran, whereupon the aspired twofold vinylic substitution at the C-1 carbon atom of nitrodiene **1** occurred with 72 % yield (Scheme 2). Further conversions of the resulting bis(benzotriazolyl)diene **19**, each with one equivalent of a different aniline derivative under mild conditions, exclusively gave (*E*)-isomers of 1-arylamino-1-benzotriazolylnitrobutadienes **20** – **24** in good to very good yields up to 90 %. Again, the stereochemical outcome should be due to the hydrogen bond between the remaining aniline proton and the adjacent nitro group. The desired *N*,*N*,*N*-substitution pattern subsequently was completed upon reaction of **20** – **24** with two equivalents of various amines, *i. e.* more electron-rich anilines with a 4-alkoxy substituent as well as benzylamine, or non-aromatic amino compounds. Similar to the aforementioned product **18**, also comprising an imino group, a selection of (1*E*,3*E*)-1,3-diamino-1-(benzotriazolyl)-4,4-dichloro-2-nitrobut-2-enes **25** – **35** was synthesized with yields ranging from 68 % to 94 %. Biological tests of these unique compounds are underway. Some physiological potential can be expected, as even 2-nitrobut-2-enes have antiviral and also cytotoxic properties [14]. Additionally, the precursor perchloronitrobutadiene **1** was also proven to be active against cancer cells [15]. Caused by the physiological as well as synthetic key importance of these 1,1,3-triaminodichloronitro compounds, as an example an X-ray structure analysis of compound **30** was performed in addition to NMR-based structural assignments (Fig. 3).

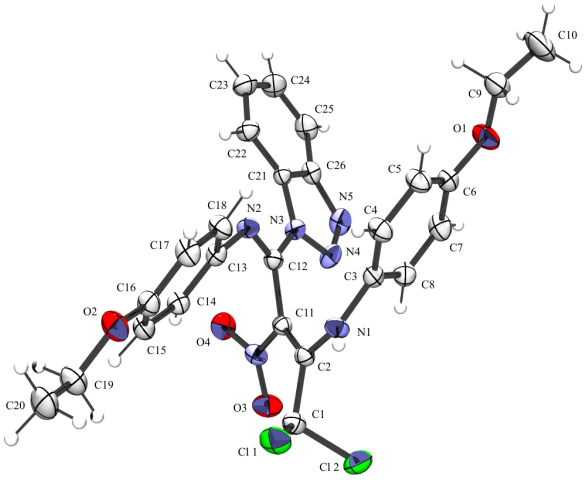
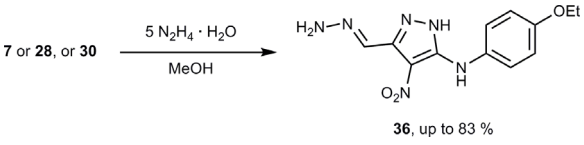


Fig. 3. Molecular structure of (*E*,*E*)-1-(benzotriazol-1-yl)-4,4-dichloro-3-(4-ethoxyphenyl-amino)-1-(4-ethoxyphenyl-imino)-2-nitrobut-2-ene (**30**) in the solid state.

In contrast to previously synthesized acyclic products, conversion of nitrobutadiene **7** or the nitrobutenes **28** and **30** with five equivalents of hydrazine hydrate in MeOH at room temperature in a multistep reaction sequence gave the interesting 5-amino-4-nitropyrazole **36**, again as a single isomer (Scheme 3).

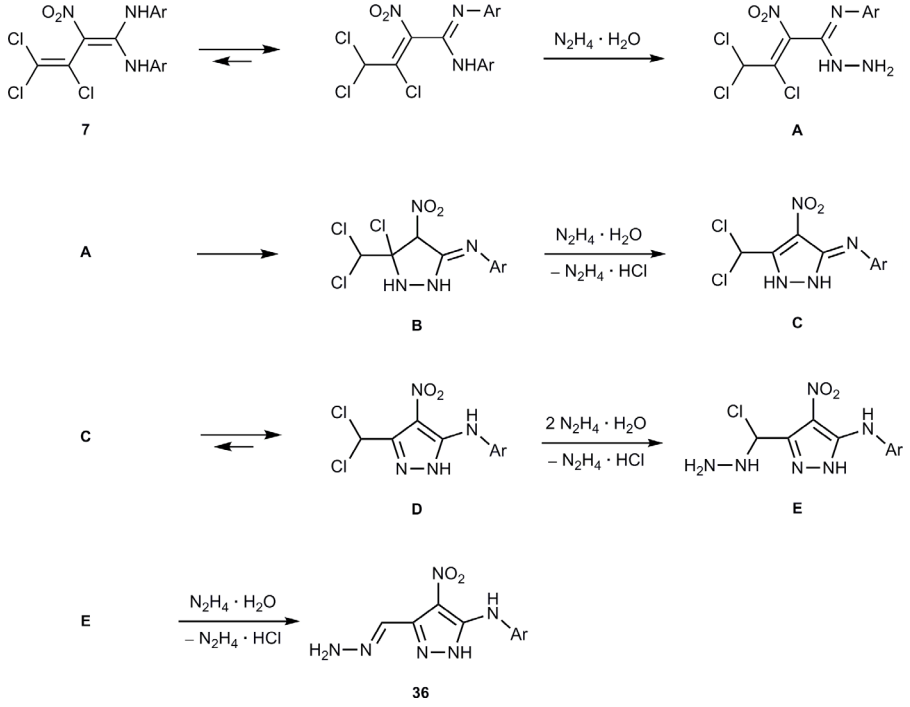


Scheme 3.

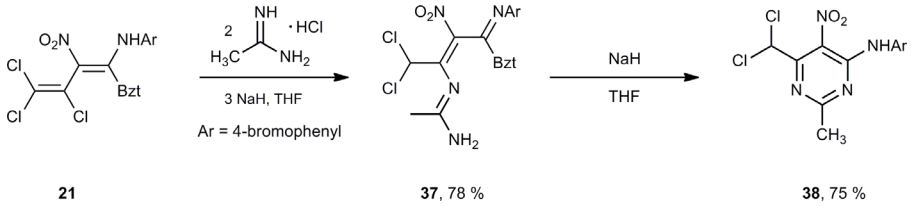
In Scheme 4 the assumed mechanistic pathway is depicted with nitrobutadiene **7** as an example, together with its amidine tautomer. However, this mechanism should also reflect the behavior of the imines **28** and **30** (see Scheme 3), as well as further examples from the entire substance pool **25** – **35**. In detail, the imino moiety initially is attacked by one equivalent of hydrazine hydrate, releasing the NHAryl group (or the benzotriazole in case of **25** – **30**). The terminal amino group of the hydrazine in intermediate **A** then forms the pyrazolidine **B**. Upon elimination of hydrochloric acid in case of **7** as the starting material (and an aniline derivative in case of **25** – **35**) which consumes a further equivalent of hydrazine hydrate in the former case, the dihydropyrazole **C** is formed. Subsequently, the imine **C** tautomerizes to the aromatic aminopyrazole **D**. The latter compound itself is then converted by a further equivalent of hydrazine hydrate (and one more as acid scavenger) to the (hydrazinomethyl)pyrazole **E** by substitution of one chlorine atom of the terminal Cl_2CH group. The newly introduced hydrazine group is transformed into the corresponding hydrazone *via* HCl elimination, again supported by one equivalent of hydrazine hydrate. The sequence ends up with the tautomerization to give **36** (Scheme 4).

It turned out to be feasible to generate not only pyrazoles, but also the rare and physiologically interesting 5-nitropyrimidines [16] starting from appropriate benzotriazolylaminodienes, such as **21** – **24**, and acetamidine. In this case, at first a bisimine **37** appeared, which upon treatment with base (sodium hydride in THF) then cyclized to the 5-nitropyrimidines **38** – **42** (Scheme 5).

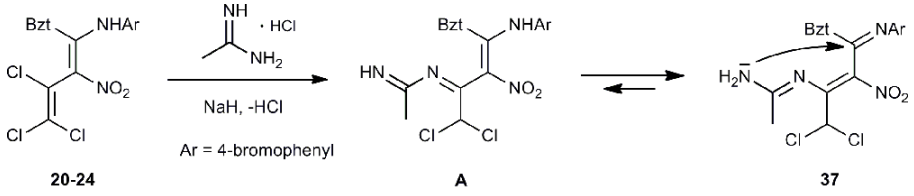
In this context, the recently proposed mechanism of this hetero ring formation [16b] can be refined

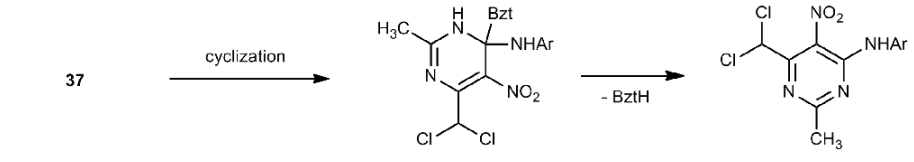


Scheme 4.

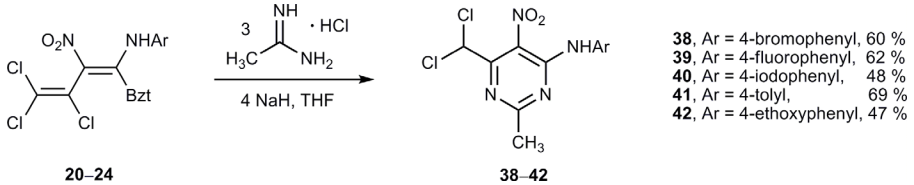


Scheme 5.





Scheme 6.

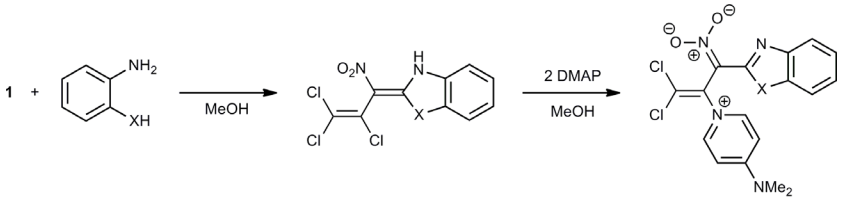


Scheme 7.

in this paper, taking into account the now isolated initial product **37**. Thus, the previous assumption that the 1-benzotriazolyl group of such a 1-amino-1-benzotriazolyl-3,4,4-trichloro-2-nitrobutadiene upon treatment with an amidine reacts in the same way as a corresponding 1,1-bisbenzotriazolyl compound, was based on the isolation of the 1-amidinyl-1-benzotriazolyl compound. However, in the present case, the 3-chloro substituent reacts faster than the 1-benzotriazolyl group. Summarizing these new findings, initially a conjugated bisimine-enamine **A** is built which then forms its tautomer **37**. The terminal amino group of the acetamidine moiety in **37** subsequently attacks the C-1 position to give intermediate **B**, *i. e.* a persubstituted 1,6-dihydropyrimidine. The mechanistic pathway ends up with an aromatization step to give the 5-nitropyrimidines **38** – **42** (Scheme 6).

To perform these syntheses more efficiently, we tested a one-step method. Indeed, the pyrimidine derivatives **38** – **42** were obtained in 47 to 69 % yield, starting from the aminobenzotriazolyldienes **20** – **24**, three equivalents of acetamidine hydrochloride, and four equivalents of the base (Scheme 7).

Moreover, treatment of nitrodiene **1** with aromatic *ortho*-substituted bisnucleophiles, such as 2-aminophenol, 2-aminothiophenol, or phenylenediamine, directly leads to bis-substitution at C-1 of the persubstituted butadiene. Good to very good yields of the resulting benzoxazoline **43**, benzthiazoline **44**, and benzimidazoline **45** up to 90 % were obtained (Scheme 8). Both of the mixed bisheterocycles, the *N,O*-derivative **43** as well as the *N,S* counterpart **44**, appear as one single isomer with (*E*)-configuration, caused by the aforementioned hydrogen bond stabilization. It is noteworthy that **45** was previously synthesized with only moderate yield and more laboriously, based on 1,3,4,4-tetrachloro-2-nitro-1-(*p*-tolylthio)buta-1,3-diene [17] or bis(benzotriazole)diene **19**, respectively. This benzimidazoline exhibits herbicidal activity and acts as a model compound, when exploring ca-



43, X = O, 88 %
44, X = S, 83 %
45, X = NH, 96 %

46, X = O, 32 %
47, X = S, 54 %
48, X = NH, 64 %

Scheme 8.

seinolytic protease as target for herbicides or growth regulators [18].

With the hope to increase the physiological performance, we also introduced the tertiary amine *N*,*N*-dimethylaminopyridine into the bisheterocycles **43** – **45**. Thus, under mild conditions at 0 °C in MeOH, the betaines **46** – **48** were synthesized in acceptable yields of up to 64 % (Scheme 8).

By affording the novel and structurally interesting cross-conjugated inner salts **46** – **48**, once again the broad synthetic applicability of 2-nitroperchlorobutadiene, especially upon reaction with *N*- or *S*-nucleophiles, is demonstrated. In conclusion, its selective and stepwise reactivity hitherto allowed for the syntheses of various classes of chemical substances and hundreds of compounds in our group [1, 2, 9, 16b], partly with remarkable physiological activity. Applying click chemistry principles, further efficient syntheses of suchlike compounds appear feasible and promising.

Experimental Section

Melting points were determined with a Büchi apparatus 520 and are uncorrected. Thin layer chromatography (tlc) was performed on Merck TLC-plates (aluminum based) silica gel 60 F 254. FTIR spectra were obtained with a Bruker Vector 22 FT-IR in the range of 400 to 4000 cm^{-1} (2.5 % pellets in KBr). Mass spectra were obtained on a Hewlett Packard MS 5989B spectrometer, usually in direct mode with electron impact (70 eV). In the case of chlorinated and brominated compounds, all peak values of molecular ions as well as fragments refer to the isotope ^{35}Cl and ^{79}Br. The elemental composition was confirmed either by combustion analysis or by high-resolution EI mass spectrometry. All HRMS results were satisfactory in comparison to the calculated accurate mass of the molecular ion (±2 ppm, R∼10000). ^1H NMR (600 MHz), ^{13}C NMR (150 MHz): Avance III 600 MHz FT-NMR spectrometer (Bruker, Rheinstetten, Germany); ^1H NMR (400 MHz), ^{13}C NMR (100 MHz): Avance 400 FT-NMR spectrometer (also Bruker). ^{14}N and ^{15}N NMR spectra were measured at their appropriate resonance frequency on the aforementioned spectrometers; ^{15}N measurements were performed as ^1H,^{15}N-HSQC or -HMBC NMR experiments (inverse detection). ^1H and ^{13}C NMR spectra were referenced to the residual solvent peak: $CDCl_3$, δ = 7.26 (^1H), δ = 77.0 (^{13}C); [D_6]DMSO, δ = 2.50 (^1H), 39.7 (^{13}C); [D_6]acetone, δ = 2.09 (^1H), 29.8 (^{13}C). ^{14}N and ^{15}N NMR spectra were referenced to nitromethane (0.0 ppm). In most cases, peak assignments were accomplished by results of HSQC- and HMBC-NMR experiments. Purifications were carried out by means of column chromatography on silica gel 60 (Merck). Petroleum ether as eluent had the boiling range 60 – 70 °C. 2-Nitropentachlorobuta-1,3-diene (**1**) was synthesized according to the literature [19] from 2*H*-pentachlorobuta-1,3-diene with a solution of 63 % HNO_3-98 % H_2SO_4 (10 : 1) in 53 % yield (b. p. 69 – 71 °C/1 mbar). Trichloroacrolein was found as a side product (8 %) and was separated by distillation (b. p. 57 – 58 °C/12 mbar).

General method 1

*3,4,4-Trichloro-N,N′-bis(4-fluorophenyl)-2-nitrobuta-1,3-diene-1,1-diamine (**2**)*

A solution of 4-fluoroaniline (5.00 g, 45 mmol) in 30 mL of MeOH was added dropwise to a solution of nitrodiene **1** (2.71 g, 10 mmol) in 30 mL of MeOH at −40 °C within 10 min. The resulting mixture was kept at the same temperature for additional 20 min with stirring. After 6 h at room temperature (r. t.) and subsequent cooling to 0 °C, 3 mL of concentrated hydrochloric acid was added. The resulting precipitate was filtered off, washed with water (2 × 30 mL) and cold MeOH (10 mL), and then dried *in vacuo* to give **2**; yield: 3.62 g (8.61 mmol, 86 %); m. p. 170 – 172 °C. – IR (KBr): ν = 3220, 3078, 2942, 1682, 1598, 1508, 1310, 1240, 1123, 835, 697, 596, 540 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 10.23 (broad s, 2 H, NH), 7.38 – 6.90 (m, 8 H). – ^{13}C NMR ([D_6]DMSO): δ = 159.8 (C-F, $^1J_{C,F}$ = 242.5 Hz), 153.1 (C-1), 134.7 (CNH, $^4J_{C,F}$ = 2.4 Hz), 126.1, 122.9 (*C*Cl=*C*Cl_2), 124.8 (CH, $^3J_{C,F}$ = 8.7 Hz), 116.1 (CH, $^2J_{C,F}$ = 22.8 Hz), 109.3 (C-NO_2). – MS: m/z (%) = 419 (3) $[M]^+$, 384 (15) $[M–Cl]^+$, 373 (8) $[M–NO_2]^+$, 290 (30) $[M–C_2Cl_3]^+$, 274 (100) $[M–C_2Cl_3–O]^+$. – HRMS ((+)-ESI):

m/z = 419.9881 (calcd. 419.9885 for $C_{16}H_{11}Cl_3F_2N_3O_2$, $[M+H]^+$).

*3,4,4-Trichloro-N,N′-bis(4-chlorophenyl)-2-nitrobuta-1,3-diene-1,1-diamine (**3**)*

General method 1, applying 4-chloroaniline and a temperature of 0 °C instead of −40 °C at the beginning; yield: 95 %; m. p. 179 – 181 °C. – IR (KBr): ν = 3195, 3058, 2934, 1625, 1575, 1489, 1413, 1307, 1125, 1013, 827, 694, 589, 507 cm^{-1}. – ^1H NMR ([D$_6$]DMSO): δ = 10.29 (broad s, 2 H, NH), 7.36 (d, J = 8.8 Hz, 4 H), 7.15 (d, J = 8.8 Hz, 4 H). – ^{13}C NMR ([D$_6$]DMSO): δ = 152.0 (C-1), 137.5 (CNH), 129.3 (CH), 129.2 (C_{aryl}-Cl), 126.0, 122.6 (CCl=CCl$_2$), 123.4 (CH), 110.0 (CNO_2). – MS: m/z (%) = 451 (6) $[M]^+$, 416 (9) $[M–Cl]^+$, 405 (6) $[M–NO_2]^+$, 322 (12) $[M–C_2Cl_3]^+$, 111 (100). – HRMS ((+)-ESI): m/z = 451.9295 (calcd. 451.9294 for $C_{16}H_{11}Cl_5N_3O_2$, $[M+H]^+$).

*N,N′-Bis(4-bromophenyl)-3,4,4-trichloro-2-nitrobuta-1,3-diene-1,1-diamine (**4**)*

General method 1, starting from 4-bromoaniline; yield: 67 %; m. p. 171 – 173 °C. – IR (KBr): ν = 3193, 3055, 2931, 1623, 1573, 1487, 1410, 1306, 1125, 1071, 1011, 822, 687, 580, 500 cm^{-1}. – ^1H NMR ([D$_6$]DMSO): δ = 10.28 (broad s, 2 H, NH), 7.48 (d, J = 8.5 Hz, 4 H), 7.09 (d, J = 8.5 Hz, 4 H). – ^{13}C NMR ([D$_6$]DMSO): δ = 151.8 (C-1), 138.0 (CNH), 132.2 (CH), 126.0, 122.5 (CCl=CCl$_2$), 123.7 (CH), 117.3 (C-Br), 110.1 (C-NO_2). – MS: m/z (%) = 539 [8] $[M]^+$, 504 (17) $[M–Cl]^+$, 471 (30), 396 (63), 109 (100). – HRMS ((+)-ESI): m/z = 539.8293 (calcd. 539.8284 for $C_{16}H_{11}Br_2Cl_3N_3O_2$, $[M+H]^+$).

*3,4,4-Trichloro-N,N′-bis(4-iodophenyl)-2-nitrobuta-1,3-diene-1,1-diamine (**5**)*

General method 1, applying 4-iodoaniline; yield: 77 %; m. p. 138 – 140 °C. – IR (KBr): ν = 3365, 3300, 1591, 1549, 1534, 1483, 1415, 1291, 1268, 1246, 1007, 817, 771, 708, 598, 490 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.30 (broad s, 1 H, NH), 7.53 (d, J = 8.7 Hz, 4 H), 6.79 (d, J = 8.7 Hz, 4 H), 6.50 (broad s, 1 H, NH). – ^{13}C NMR ($CDCl_3$): δ = 151.9 (C-1), 138.4 (CH), 135.5 (CNH), 128.4, 122.6 (CCl=CCl$_2$), 125.6 (CH), 110.6 (C-NO_2), 91.3 (C-I). – MS: m/z (%) = 635 (6) $[M]^+$, 599 (33) $[M–HCl]^+$, 565 (40) $[M–2Cl]^+$, 446 (52), 109 (100). – HRMS ((+)-ESI): m/z = 635.8002 (calcd. 635.8006 for $C_{16}H_{11}Cl_3I_2N_3O_2$, $[M+H]^+$).

*3,4,4-Trichloro-2-nitro-N,N′-di-p-tolylbuta-1,3-diene-1,1-diamine (**6**)*

General method 1, starting from *p*-toluidine; yield: 82 %; m. p. 162 – 164 °C. – IR (KBr): ν = 3194, 3027, 2925, 1665, 1631, 1577, 1514, 1417, 1376, 1321, 1116, 963, 858, 812, 698, 596, 541, 500 cm^{-1}. – ^1H NMR ([D$_6$]DMSO): δ = 10.13 (broad s, 2 H, NH), 7.09 (d, J = 8.5 Hz, 4 H), 7.02 (d, J = 8.5 Hz, 4 H), 2.23 (s, 6 H, Me). – ^{13}C NMR ([D$_6$]DMSO): δ = 152.4 (C-1), 136.0 (CNH), 134.4 (CMe), 129.6 (CH), 126.4, 122.2 (CCl=CCl$_2$), 121.9 (CH), 109.3 (C-NO_2), 20.7 (Me). – MS: m/z (%) = 411 (4) $[M]^+$, 376 (7) $[M–Cl]^+$, 365 (4) $[M–NO_2]^+$, 341 (63) $[M–2Cl]^+$, 266 (37), 91 (100). – HRMS ((+)-ESI): m/z = 412.0381 (calcd. 412.0386 for $C_{18}H_{17}Cl_3N_3O_2$, $[M+H]^+$).

*3,4,4-Trichloro-N,N′-bis(4-ethoxyphenyl)-2-nitrobuta-1,3-diene-1,1-diamine (**7**)*

General method 1, applying *p*-ethoxyaniline and −60 °C instead of −40 °C at the beginning; yield: 70 %; m. p. 126 – 128 °C. – IR (KBr): ν = 3229, 3038, 2937, 1618, 1576, 1509, 1477, 1295, 1247, 1170, 1120, 1047, 971, 922, 857, 825, 579, 548, 532 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.01 (d, J = 8.8 Hz, 4 H), 6.77 (d, J = 8.8 Hz, 4 H), 3.97 (q, J = 7.0 Hz, 4 H, CH_2), 1.38 (t, J = 7.0 Hz, 6 H, Me); the NH proton was not detected due to chemical exchange reaction. – ^{13}C NMR ($CDCl_3$): δ = 158.1 (C_{aryl}-O), 154.3 (C-1), 127.8 (CNH), 127.0, 124.0 (CCl=CCl$_2$), 126.8 (CH), 115.3 (CH), 108.9 (C-NO_2), 63.8 (CH_2), 14.6 (Me). – MS: m/z (%) = 471 (4) $[M]^+$, 436 (28) $[M–Cl]^+$, 401 (27) $[M–2Cl]^+$, 256 (45), 109 (100). – HRMS ((+)-ESI): m/z = 472.0587 (calcd. 472.0598 for $C_{20}H_{21}Cl_3N_3O_4$, $[M+H]^+$).

*N-(1,2,3,3-Tetrachloroallylidene)-N′-(4-nitrophenyl)-hydrazine (**8**)* and *N-(1,2,3,3-tetrachloroallylidene)-N′-(4-cyanophenyl)hydrazine (**9**)* were synthesized according to the literature [9]. The synthesis of nitrile **9** was optimized: A mixture of nitrodiene **1** (500 mg, 1.84 mmol) and 4-cyanoaniline (217 mg, 1.84 mmol) in anhydrous THF (20 mL) was heated at 45 – 50 °C for 6 d. After evaporation of the solvent *in vacuo*, 20 mL of water and 2 mL of conc. HCl were added. The precipitate was filtered off and washed with water. Column chromatography (petroleum ether/ethyl acetate 5:1) gave hydrazone **9** as a colorless powder; yield: 489 mg (86 %); m. p. 201 – 203 °C. NMR spectra were in accordance with the literature.

*N-(1-Amino-2,3,3-trichloroallylidene)-N′-(aryl)hydrazines (**10** – **13**)* were synthesized in MeOH at 0 °C, then r. t. from hydrazines **8** and **9**, respectively, according to a previously published method [9].

*N-(2,3,3-Trichloro-1-thiomorpholinoallylidene)-N′-(4-nitrophenyl)hydrazine (**10**)*

Yield: 73 %; m. p. 84 – 85 °C. – IR (KBr): ν = 3299, 2919, 1599, 1500, 1414, 1317, 1302, 1273, 1175, 1110, 953, 920, 850, 751, 691, 493 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 8.11 (d, J = 9.2 Hz, 2 H), 7.17 (broad s, 1 H, NH), 6.93 (d, J = 9.2 Hz, 2 H), 3.60 – 3.74 (m, 4 H, NCH_2), 2.66 –

2.79 (m, 4 H, SCH_2). – ^{13}C NMR ($CDCl_3$): δ = 150.4 (C=N), 144.7 (CNH), 139.2 (CNO_2), 126.7 (CCl), 126.2 (2 C, C_{aryl}-3,5), 117.9 (CCl_2), 111.2 (2 C, C_{aryl}-2,6), 48.5 (2 C, NCH_2), 26.5 (2 C, SCH_2). – MS: m/z (%) = 394 (45) $[M]^+$, 359 (8) $[M–Cl]^+$, 324 (4) $[M–2Cl]^+$, 285 (10), 102 (100). – HRMS ((+)-ESI): m/z = 394.9890 (calcd. 394.9903 for $C_{13}H_{14}Cl_3N_4O_2S$, $[M+H]^+$).

*{2,3,3-Trichloro-1-(4-fluorophenylpiperazin-4-yl)allylidene}-N′-(4-nitrophenyl)hydrazine (**11**)*

Yield: 75 %; m. p. 75 – 77 °C. – IR (KBr): ν = 3291, 2827, 1735, 1599, 1508, 1473, 1319, 1302, 1231, 1175, 1110, 1043, 941, 832, 751, 693, 493 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 8.14 (d, J = 9.0 Hz, 2 H), 7.20 (broad s, 1 H, NH), 6.78 – 7.08 (m, 6 H), 3.37 – 3.60 (m, 4 H, NCH_2), 3.11 – 3.33 (m, 4 H, NCH_2). – ^{13}C NMR ($CDCl_3$): δ = 155.3 (*C*F, $^1J_{C,F}$ = 242.6 Hz), 150.3 (C=N), 147.2 (*C*N, $^4J_{C,F}$ = 4.5 Hz), 144.8 (CNH), 139.4 (CNO_2), 126.7 (CCl), 126.1 (2 C, C_{aryl}-3,5), 118.5 (2 CH, $^3J_{C,F}$ = 7.4 Hz), 117.7 (CCl_2), 115.5 (2 CH, $^2J_{C,F}$ = 22.3 Hz), 111.3 (2 C, C_{aryl}-2,6), 50.2 (2 C, NCH_2), 45.9 (2 C, NCH_2). – MS: m/z (%) = (22) 471 $[M]^+$, 436 (20) $[M–Cl]^+$, 285 (12), 122 (100). – HRMS ((+)-ESI): m/z = 472.0502 (calcd. 472.0510 for $C_{19}H_{18}Cl_3FN_5O_2$, $[M+H]^+$).

*N-(2,3,3-Trichloro-1-pyrrolidinoallylidene)-N′-(4-cyanophenyl)hydrazine (**12**)*

To a suspension of hydrazone **9** (500 mg, 1.62 mmol) in MeOH (20 mL) was added a solution of pyrrolidine (0.23 g, 3.25 mmol) in MeOH (5 mL) at 0 °C within 10 min with stirring. The resulting reaction mixture then was stirred for 1 h at 0 °C and for 3 h at r. t. Subsequently, the supernatant liquid was concentrated *in vacuo* to a volume of about 5 mL, cooled to 10 °C and then treated with 5 % aqueous HCl (40 mL). The precipitate was collected. The residual solution was extracted with ethyl acetate (5 × 50 mL). Subsequently, the combined organic layers were washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent *in vacuo* gave a crude solid that was dissolved in diethyl ether. Addition of hexane (50 mL) gave the pure product that was isolated, washed with cold hexane (5 mL), and finally dried under reduced pressure. Yield: 351 mg, 63 %; m. p. 136 – 138 °C. – IR (KBr): ν = 3309, 2971, 2872, 2209 (CN), 1595, 1519, 1429, 1406, 1326, 1273, 1166, 947, 898, 824, 544 cm^{-1}.– ^1H NMR ($CDCl_3$): δ = 7.44 (d, J = 8.8 Hz, 2 H), 6.92 (d, J = 8.8 Hz, 2 H), 6.71 (broad s, 1 H, NH), 3.31 – 3.48 (m, 4 H, NCH_2), 1.93 – 2.05 (m, 4 H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 149.9 (C=N), 146.6 (CNH), 133.4 (2 C, C_{aryl}-3,5), 124.7, 120.5, 119.5 (3 C, CCl=CCl_2, C≡N), 112.3 (2 C, C_{aryl}-2,6), 99.9 (Ph(C-4)), 47.0 (2 C, NCH_2), 25.0 (2 C, CH_2). – MS: m/z (%) = 342 (68) $[M]^+$, 307 (26) $[M–Cl]^+$, 272 (25) $[M–2Cl]^+$, 116 (100). – HRMS ((+)-ESI): m/z = 343.0281 (calcd. 343.0284 for $C_{14}H_{14}Cl_3N_4$, $[M+H]^+$).

*N-(2,3,3-Trichloro-1-(4-methoxyphenylamino)allylidene)-N′-(4-cyanophenyl)hydrazine (**13**)*

A solution of *p*-anisidine (0.42 g, 3.41 mmol) in MeOH (10 mL) was added with stirring at 20 °C to a suspension of hydrazone **9** (500 mg, 1.62 mmol) in MeOH (15 mL). The resulting reaction mixture was stirred for 6 h at 45 – 50 °C. Subsequently, the supernatant liquid was concentrated *in vacuo* to a volume of about 5 mL, cooled down to 10 °C, and then treated with 5 % aqueous HCl (40 mL). After 20 min stirring, the precipitate was filtered off, washed with water (2 × 20 mL), and then dried under reduced pressure to give 564 mg (88 %) of hydrazine **13** as a 3 : 1 mixture of isomers. M. p. 70 – 72 °C. – IR (KBr): ν = 3287, 2215 (CN), 1603, 1510, 1312, 1244, 1168, 1034, 886, 829, 547 cm^{-1}. – ^1H NMR ($CDCl_3$) (major isomer): δ = 9.88 (broad s, 1 H, NH), 8.52 (broad s, 1 H, NH), 7.58 (d, J = 8.8 Hz, 2 H), 7.12 (d, J = 8.8 Hz, 2 H), 6.84 – 6.93 (m, 4 H), 3.73 (s, 3 H, OMe). – ^1H NMR ($CDCl_3$) (minor isomer): δ = 9.42 (broad s, 0.33 H, NH), 8.90 (broad s, 0.33 H, NH), 7.54 (d, J = 8.8 Hz, 0.66 H), 7.09 (d, J = 8.8 Hz, 0.66 H), 7.03 (d, J = 8.8 Hz, 0.66 H), 6.84 – 6.93 (m, 0.66 H), 3.72 (s, 1 H, OMe). – ^{13}C NMR ($CDCl_3$) (major isomer): δ = 155.5 (*C*OMe), 149.1 (CNH), 136.6 (C=N), 133.7 (2 C, CH), 133.2 (CNH), 125.5, 123.9 (2 C, CCl=CCl_2), 121.4 (2 C, CH), 120.3 (C≡N), 114.6 (2 C, CH), 112.6 (2 C, CH), 99.4 (*C*CN). – ^{13}C NMR ($CDCl_3$) (minor isomer): δ = 154.1 (COMe), 149.9 (CNH), 139.7 (C=N), 134.5 (CNH), 133.5 (2 C, CH), 125.6, 120.7 (2 C, CCl=CCl_2), 120.1 (C≡N), 119.4 (2 C, CH), 114.2 (2 C, CH), 111.8 (2 C, CH), 97.5 (*C*CN). – MS: m/z (%) = 394 (25) $[M]^+$, 359 (6) $[M–Cl]^+$, 324 (8) $[M–2Cl]^+$, 264 (16), 123 (100). – HRMS ((+)-ESI): m/z = 395.0229 (calcd. 395.0233 for $C_{17}H_{14}Cl_3N_4O$, $[M+H]^+$).

*(E)-1,3,4,4-Tetrachloro-1-(4-chlorophenylthio)-2-nitrobuta-1,3-diene (**14**)*

At r. t. 10.00 g (36.86 mmol) of nitrodiene **1** and 5.44 g (37.60 mmol) of 4-chloro-benzenethiol were combined and stirred 3 d without a solvent. The mixture then was diluted with MeOH (20 mL). The precipitate that appeared was filtered off, successively washed twice with water (50 mL each portion) and cold MeOH (2 × 50 mL), and finally dried under reduced pressure. Yield 10.91 g (78 %); m. p. 102 – 103 °C. – IR (KBr): ν = 3080, 1605, 1574, 1536 (NO_2), 1478, 1393, 1315, 1294, 1195, 1093, 1003, 923, 821, 760, 745, 685, 507 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.43 – 7.55 (m, 4 H). – ^{13}C NMR ($CDCl_3$): δ = 156.8 (C-1), 138.5 (C-2), 138.3 ($C_{quat.}$), 137.2 (2 CH), 130.0 (2 CH), 129.0, 120.9 (2 C, CCl=CCl_2), 126.9 ($C_{quat.}$). – MS: m/z (%) = 379 (5) $[M]^+$, 311 (36), 226 (29), 143 (100) [*p*-ClPhS$^+$]. – HRMS ((+)-ESI): m/z = 509.9842 (calcd. 509.9848 for $C_{18}H_{15}BrCl_2N_7O_2$, $[M+H]^+$).

General method 2

*(E)-3,4,4-Trichloro-1-(4-chlorophenylthio)-1-morpholino-2-nitrobuta-1,3-diene (**15**)*

At 0 °C a solution of 0.18 g (2.1 mmol) morpholine in 3 mL MeOH was dropwise added to a suspension of 0.38 g (1.0 mmol) sulfane **14** in 10 mL MeOH. The resulting mixture was stirred for 1 h at the same temperature, then kept at r. t. for 10 h. After cooling to 0 °C the precipitate was filtered off, washed with water (2 × 10 mL) and cold MeOH (5 mL) and finally dried under reduced pressure to yield 344 mg (80 %) of the desired product; m. p. 167 – 169 °C. – IR (KBr): ν = 2965, 2864, 1531 (NO_2), 1463, 1387, 1279 (NO_2), 1201, 1114, 1092, 1010, 890, 821, 762, 702, 646, 490 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.36 – 7.47 (m, 4 H), 3.30 – 3.70 (m, 8 H, 4 CH_2). – ^{13}C NMR ($CDCl_3$): δ = 164.6 (C-1), 136.3 ($C_{quat.}$), 133.8 (2 CH), 130.5 (2 CH), 129.1 ($C_{quat.}$), 126.3, 125.7 (2 C, CCl=CCl_2), 120.1 (C-2), 65.4 (OCH_2), 53.3 (NCH_2). – MS: m/z (%) = 428 (4) $[M]^+$, 393 (30) $[M–Cl]^+$, 358 (4) $[M–2Cl]^+$, 284 (100) [M–*p*-ClPhSH]$^+$. – HRMS ((+)-ESI): m/z = 428.9404 (428.9401 calcd. for $C_{14}H_{13}Cl_4N_2O_3S$, $[M+H]^+$).

*(E)-3,4,4-Trichloro-1-(4-chlorophenylamino)-1-(4-chlorophenylthio)-2-nitrobuta-1,3-diene (**16**)*

Following general method 2, starting from sulfane **14** and 4-chloroaniline at r. t. (10 h), then at 30 – 35 °C (3 h). Yield 95 %; m. p. 149 – 150 °C. – IR (KBr): ν = 3198, 3080, 1598, 1551 (NO_2), 1479, 1366, 1343 (NO_2), 1255, 1165, 1090, 1013, 875, 817, 757, 726, 498 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.44 (broad s, 1 H, NH), 7.17 (d, J = 8.6 Hz, 2 H), 7.12 (d, J = 8.6 Hz, 2 H), 6.95 (d, J = 8.6 Hz, 2 H), 6.90 (d, J = 8.6 Hz, 2 H). – ^{13}C NMR ($CDCl_3$): δ = 158.4 (C-1), 135.8 ($C_{quat.}$), 135.4 ($C_{quat.}$), 134.1 (2 CH), 133.4 ($C_{quat.}$), 129.5 (2 CH), 129.1 (2 CH), 128.5, 123.4 (2 C, CCl=CCl_2), 127.0 (2 CH), 126.7 ($C_{quat.}$), 121.9 (C-2). – MS: m/z (%) = 468 (4) $[M]^+$, 433 (4) $[M–Cl]^+$, 398 (4) $[M–2Cl]^+$, 325 (17) [M–*p*-ClPhS]$^+$, 111 (100). – HRMS ((+)-ESI): m/z = 468.8908 (468.8906 calcd. for $C_{16}H_{10}Cl_5N_2O_2S$, $[M+H]^+$).

*(E)-4,4-Dichloro-1-(4-chlorophenylthio)-3-methylamino-1-morpholino-2-nitrobuta-1,3-diene (**17**)*

Following general method 2 with EtOH as solvent, nitrodiene **15** and a 33 % solution of methylamine in abs. EtOH. Yield 64 %; m. p. 134 – 136 °C. – IR (KBr): ν = 3235, 3150, 2959, 1612, 1494, 1475, 1442, 1361 (NO_2), 1327, 1217, 1148, 1010, 889, 855, 827, 732, 495 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 8.25 (broad s, 1 H, NH), 7.41 (d, J = 8.0 Hz, 2 H), 7.35 (d, J = 8.0 Hz, 2 H), 3.20 – 3.80 (m, 8 H, 4 CH_2), 2.34 (s, 3 H, Me). – ^{13}C NMR ($CDCl_3$): δ = 160.9 (C-1), 133.2 ($C_{quat.}$), 132.1 ($C_{quat.}$), 131.0 (2 CH), 129.4 (2 CH), 128.4 ($C_{quat.}$), 123.1 (C-4), 106.0 (C-2), 65.5 (OCH_2), 48.8 (NCH_2), 30.6 (Me). – MS: m/z (%) = 423 (3) $[M]^+$, 388 (5) $[M–Cl]^+$, 353 (8) $[M–Cl]^+$, 286 (30), 143 (100) [*p*-ClPhS$^+$] (100). – HRMS ((+)-ESI): m/z = 424.0050 (424.0056 calcd. for $C_{15}H_{17}Cl_3N_3O_3S$, $[M+H]^+$).

*(E,E)-3-Benzylamino-4,4-dichloro-1-(4-chlorophenylimino)-1-(4-chlorophenylthio)-2-nitro-but-2-ene (**18**)*

Following general method 2, starting from nitrodiene **16** and benzylamine. Yield 75 %; m. p. 133 – 135 °C. – IR (KBr): ν = 3166, 3088, 1615, 1584 (NO_2), 1481, 1452, 1384 (NO_2), 1242, 1201, 1148, 1090, 1011, 982, 883, 825, 770, 733, 589, 503 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.35 (broad s, 1 H, NH), 7.35 – 7.47 (m, 7 H), 7.29 (d, J = 8.7 Hz, 2 H), 7.20 (d, J = 8.7 Hz, 2 H), 7.06 (d, J = 8.7 Hz, 2 H), 6.80 (s, 1 H, $CHCl_2$), 5.04 (s, 2 H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 160.5 (C-1), 151.4 ($C_{quat.}$), 146.7 ($C_{quat.}$), 137.2 (2 CH), 136.3 ($C_{quat.}$), 135.2 ($C_{quat.}$), 131.2 ($C_{quat.}$), 129.5 (4 CH), 129.1 (2 CH), 128.5 (CH), 127.3 ($C_{quat.}$), 127.1 (2 CH), 121.0 (2 CH), 119.8 (C-2), 63.3 (C-4), 49.2 (CH_2). – MS: m/z (%) = (1) 539 $[M]^+$, 504 (2) $[M–Cl]^+$, 469 (2) $[M–2Cl]^+$, 396 (5) [M–*p*-ClPhS]$^+$, 280 (4), 91 (100). – HRMS ((+)-ESI): m/z = 539.9882 (539.9874 calcd. for $C_{23}H_{18}Cl_4N_3O_2S$, $[M+H]^+$).

*Benzotriazole derivative **19***

The compound was prepared in 72 % yield from nitrobutadiene **1** in THF according to Kaberdin *et al.* [20].

General method 3

*(E)-(1-Benzotriazol-1-yl)-3,4,4-trichloro-1-(4-fluorophenylamino)-2-nitrobuta-1,3-diene (**20**)*

At 0 °C 0.117 g (1.05 mmol) 4-fluoroaniline was added to a suspension of 0.437 g (1.0 mmol) bis(benzotriazolyl) derivative **19** in MeOH (10 mL). Subsequently, the mixture was stirred for 1 h at 0 °C and at r. t. for additional 10 h. The cold mixture (10 °C) was diluted with cold water (50 mL) and conc. HCl (3 mL). The resulting precipitate was filtered off, washed with water (2 ×10 mL) and cold diethyl ether (2 × 3 mL). The product was dried under reduced pressure to give 369 mg (86 %); m. p. 118 – 119 °C. – IR (KBr): ν = 3255, 3099, 1621, 1580 (NO_2), 1503, 1461, 1378 (NO_2), 1293, 1193, 1157, 1044, 949, 878, 835, 744, 654, 496 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.60 (broad s, 1 H, NH), 8.05 (d, J = 8.0 Hz, 1 H), 7.58 – 7.29 (m, 3 H), 6.95 – 6.58 (m, 4 H). – ^{13}C NMR ($CDCl_3$): δ = 161.3 (CF, $^1J_{C,F}$ = 249.8 Hz), 146.5 (C-1), 145.2 ($C_{quat.}$), 131.8 ($C_{quat.}$), 130.6 (CNH, $^4J_{C,F}$ = 2.9 Hz), 131.3, 120.7 (2 C, CCl=CCl_2), 129.8 (CH), 125.5 (CH), 125.1 (2 CH, $^3J_{C,F}$ = 8.7 Hz), 120.7 (CH), 119.8 (CNO_2), 116.6 (2 CH, $^2J_{C,F}$ = 22.8 Hz), 109.7 (CH). – MS: m/z (%) = 427 (3) $[M]^+$, 392 (3) $[M–Cl]^+$, 357 (5) $[M–2Cl]^+$, 256 (30), 95 (100). – HRMS ((+)-ESI): m/z = 427.9892 (427.9884 calcd. for $C_{16}H_{10}Cl_3FN_5O_2$, $[M+H]^+$).

*(E)-(1-Benzotriazol-1-yl)-1-(4-bromophenylamino)-3,4,4-trichloro-2-nitrobuta-1,3-diene (**21**)*

According to general method 3 with **19** and 4-bromoaniline. Yield 74 %; m. p. 117 – 118 °C. – IR (KBr): ν = 3201, 3089, 2849, 1639, 1575 (NO_2), 1486, 1378 (NO_2), 1295, 1173, 1046, 1008, 950, 874, 811, 785, 745, 622, 497 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.56 (broad s, 1 H, NH), 8.07 (d, J = 8.0 Hz, 1 H), 7.57 – 7.34 (m, 3 H), 7.21 (d, J = 8.5 Hz, 2 H, CHCBr), 6.67 (d, J = 8.5 Hz, 2 H, C*H*CNH). – ^1H NMR ([D_6]acetone): δ = 11.70 (broad s, 1 H, NH), 8.30 – 8.12 (m, 1 H), 7.92 – 7.60 (m, 3 H), 7.47 (broad s, 2 H, CHCBr), 7.14 (broad s, 2 H, C*H*CNH). – ^{13}C NMR ($CDCl_3$): δ = 145.9 (C-1), 145.3 ($C_{quat.}$), 133.8 (CNH), 132.8 (2 C, *C*HCBr), 131.8 ($C_{quat.}$), 129.9 (CH), 129.8, 120.4 (2 C, CCl=CCl_2), 125.6 (CH), 124.3 (2 C, *C*HCNH), 121.4 (CBr), 120.9 (CH), 120.2 (CNO_2), 109.6 (CH). – MS: m/z (%) = 487 (2) $[M]^+$, 452 (3) $[M–Cl]^+$, 417 (4) $[M–2Cl]^+$, 256 (48), 91 (100). – HRMS ((+)-ESI): m/z = 487.9170 (487.9083 calcd. for $C_{16}H_{10}BrCl_3N_5O_2$, $[M+H]^+$).

*(E)-(1-Benzotriazol-1-yl)-3,4,4-trichloro-1-(4-iodophenylamino)-2-nitrobuta-1,3-diene (**22**)*

Following general method 3, applying **19** and 4-iodoaniline. Yield 90 %; m. p. 125 – 126 °C. – IR (KBr): ν = 3098, 1621, 1568 (NO_2), 1486, 1377 (NO_2), 1295, 1250, 1152, 1033, 974, 916, 872, 824, 766, 742, 613, 503 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.54 (broad s, 1 H, NH), 8.08 (d, J = 7.8 Hz, 1H), 7.56 – 7.30 (m, 3 H), 7.40 (d, J = 8.5 Hz, 2 H, C*H*CI), 6.50 (d, J = 8.5 Hz, 2 H, C*H*CNH). – ^{13}C NMR ($CDCl_3$): δ = 145.8 ($C_{quat.}$), 145.3 (C-1), 138.8 (2 C, *C*HCI), 134.6 (CNH), 131.8 ($C_{quat.}$), 130.0 (CH), 130.6, 120.4 (2 C, CCl=CCl_2), 125.6 (CH), 124.3 (2 C, *C*HCNH), 120.9 (CH), 118.5 (CNO_2), 109.6 (CH), 92.6 (CI). – MS: m/z (%) = 535 (2) $[M]^+$, 500 (2) $[M–Cl]^+$, 465 (3) $[M–2Cl]^+$, 408 (12) $[M–I]^+$, 245 (95), 91 (100).

*(E)-(1-Benzotriazol-1-yl)-3,4,4-trichloro-2-nitro-1-(4-tolylamino)buta-1,3-diene (**23**)*

Applying general method 3 with bis(benzotriazolyl) derivative **19** and *p*-toluidine. Yield 88 %; m. p. 148 – 149 °C. – IR (KBr): ν = 3254, 3020, 1627, 1580 (NO_2), 1497, 1464, 1375 (NO_2), 1295, 1256, 1176, 1048, 950, 874, 815, 785, 745, 697, 658, 489 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.70 (broad s, 1 H, NH), 8.04 (dd, J = 8.5, 0.6 Hz, 1 H), 7.51 – 7.30 (m, 3 H), 6.87 (d, J = 8.3 Hz, 2 H, C*H*CMe), 6.67 (d, J = 8.3 Hz, 2 H, C*H*CNH), 2.13 (s, 3 H, Me). – ^1H NMR ([D_6]acetone): δ = 11.68 (broad s, 1 H, NH), 8.11 (d, J = 7.9 Hz, 1 H), 7.80 (d, J = 7.9 Hz, 1 H), 7.70 – 7.57 (m, 1 H), 7.54 – 7.44 (m, 1 H), 7.02 (broad s, 4 H, $H_{arom.}$), 2.19 (s, 3 H, Me). – ^{13}C NMR ($CDCl_3$): δ = 146.4 (C-1), 145.1 ($C_{quat.}$), 137.9 (CNH), 132.0 (*C*Me), 131.8 ($C_{quat.}$), 131.6, 119.7 (2 C, CCl=CCl_2), 130.1 (2 C, *C*HCMe), 129.6 (CH), 125.3 (CH), 122.6 (2 C, *C*HCNH), 120.5 (CH), 119.3 (CNO_2), 109.9 (CH), 20.7 (Me). – MS: m/z (%) = 423 (2) $[M]^+$, 388 (2) $[M–Cl]^+$, 353 (3) $[M–2Cl]^+$, 91 (100). – HRMS ((+)-ESI): m/z = 424.0124 (424.0135 calcd. for $C_{17}H_{13}Cl_3N_5O_2$, $[M+H]^+$).

*(E)-(1-Benzotriazol-1-yl)-3,4,4-trichloro-1-(4-ethoxyphenylamino)-2-nitrobuta-1,3-diene (**24**)*

Following general method 3, applying **19** and *p*-ethoxyaniline. Yield 83 %; m. p. 137 – 139 °C. – IR (KBr): ν = 3069, 2982, 2873, 1627, 1583 (NO_2), 1498, 1466, 1373 (NO_2), 1294, 1252, 1182, 1119, 1047, 947, 872, 821, 786, 748, 584, 540 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.71 (broad s, 1 H, NH), 8.03 (d, J = 8.0 Hz, 1 H), 7.58 – 7.24 (m, 3 H), 6.74 (d, J = 9.0 Hz, 2 H, C*H*CNH), 6.56 (d, J = 9.0 Hz, 2 H, C*H*CO), 3.83 (q, J = 7.0 Hz, 2 H, OCH_2), 1.29 (t, J = 7.0 Hz, 3 H, Me). –^1H NMR ([D_6]acetone): δ = 11.66 (broad s, 1 H, NH), 8.01 (d, J = 8.2 Hz, 1 H), 7.80 – 7.67 (m, 1 H), 7.58 – 7.48 (m, 1 H), 7.47 – 7.36 (m, 1 H), 6.94 (d, J = 8.8 Hz, 2 H, C*H*CNH), 6.62 (d, J = 8.8 Hz, 2 H, C*H*CO), 3.82 (q, J = 6.9 Hz, 2 H, OCH_2), 1.19 (t, J = 6.9 Hz, 3 H, Me). – ^{13}C NMR ($CDCl_3$): δ = 158.2 (CO), 146.6 (C1), 145.1 ($C_{quat.}$), 131.9 ($C_{quat.}$), 131.7, 121.5 (2 C, CCl=CCl_2), 129.6 (CH), 127.0 (CNH), 125.3 (CH), 124.4 (2 C, *C*HCNH), 120.5 (CH), 119.5 (CNO_2), 115.1 (2 C, *C*HCO), 109.9 (CH), 63.6 (CH_2), 14.5 (Me). – MS: m/z (%) = 453 (2) $[M]^+$, 417 (4) $[M–HCl]^+$, 383 (3) $[M–2Cl]^+$, 296 (10), 119 (100) [benzotriazole]. – HRMS ((+)-ESI): m/z = 454.0204 (454.0240 calcd. for $C_{18}H_{15}Cl_3N_5O_3$, $[M+H]^+$). – HRMS ((+)-ESI): m/z = 476.0063 (476.0060 calcd. for $C_{18}H_{14}Cl_3N_5NaO_3$, $[M+Na]^+$).

*(E,E)-1-(Benzotriazol-1-yl)-4,4-dichloro-1-(4-fluorophenylimino)-3-(2-hydroxyethylamino)-2-nitrobut-2-ene (**25**)*

Following general method 2 with nitrodiene **20** and 2-aminoethanol. Yield 70 %; m. p. 121 – 123 °C. – IR (KBr): ν = 3420 (OH), 2931, 1642, 1616 (NO_2), 1503, 1449, 1378 (NO_2), 1291, 1225, 1067, 1004, 955, 839, 789, 751, 723, 669, 529 cm^{-1}. – ^1H NMR ([D_6]acetone): δ = 11.04 (broad s, 1 H, NH), 8.50 (d, J = 8.3 Hz, 1 H), 8.16 (d, J = 8.1 Hz, 1 H), 7.76 (ddd, J = 8.3, 7.0, 1.2 Hz, 1 H), 7.61 (ddd, J = 8.1, 7.0, 1.2 Hz, 1 H), 7.26 – 7.12 (m, 4 H), 7.02 (d, J = 1.6 Hz, $CHCl_2$, 1 H), 4.22 – 3.94 (m, 2 H, OCH_2), 3.93 – 3.82 (m, 2 H, NCH_2), 2.90 (broad s, 1 H, OH). – ^{13}C NMR ([D_6]acetone): δ = 162.1 (CF, $^1J_{C,F}$ = 243.1 Hz), 153.4 ($C_{quat.}$), 147.7 ($C_{quat.}$), 146.7 ($C_{quat.}$), 143.9 (CN, $^4J_{C,F}$ = 3.1 Hz), 132.2 ($C_{quat.}$), 130.5 (CH), 126.9 (CH), 123.8 (2 CH, $^3J_{C,F}$ = 8.4 Hz), 120.7 (CH), 117.2 (2 CH, $^2J_{C,F}$ = 23.0 Hz), 116.3 (CH), 114.4 (CNO_2), 64.9 ($CHCl_2$), 60.0 (OCH_2), 48.4 (NCH_2). – MS: m/z (%) = 452 (7) $[M]^+$, 406 (15) $[M–NO_2]^+$, 389 (30), 224 (100). – HRMS ((+)-ESI): m/z = 453.0648 (453.0645 calcd. for $C_{18}H_{16}Cl_2FN_6O_3$, $[M+H]^+$).

*(E,E)-1-(Benzotriazol-1-yl)-4,4-dichloro-3-cyclopropylamino-1-(4-fluorophenylimino)-2-nitrobut-2-ene (**26**)*

According to general method 2 with nitrodiene **20** and cyclopropylamine. Yield 83 %; m. p. 106 – 107 °C. – IR (KBr): ν = 3660, 3285, 3066, 2931, 3066, 1632, 1572 (NO_2), 1501, 1450, 1396 (NO_2), 1308, 1253, 1215, 1053, 952, 896, 837, 771, 755, 630, 530 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 10.66 (broad s, 1 H, NH), 8.47 (d, J = 8.3 Hz, 1 H), 8.14 (d, J = 8.1 Hz, 1 H), 7.67 (ddd, J = 8.3, 7.2, 1.2 Hz, 1 H), 7.53 (ddd, J = 8.1, 7.2, 1.2 Hz, 1 H), 7.14 – 6.97 (m, 4 H), 6.28 (d, J = 1.5 Hz, $CHCl_2$, 1 H), 3.68 – 3.40 (m, 1 H, C*H*NH), 1.26 – 0.83 (m, 4 H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 161.4 (CF, $^1J_{C,F}$ = 245.9 Hz), 153.0 ($C_{quat.}$), 146.9 ($C_{quat.}$), 145.4 ($C_{quat.}$), 141.7 (CN, $^4J_{C,F}$ = 2.9 Hz), 131.2 ($C_{quat.}$), 129.7 (CH), 126.0 (CH), 122.9 (2 CH, $^3J_{C,F}$ = 8.7 Hz), 120.2 (CH), 116.7 (2 CH, $^2J_{C,F}$ = 22.8 Hz), 115.1 (CH), 114.1 (CNO_2), 62.8 ($CHCl_2$), 28.0 (*C*HNH), 10.4 (CH_2), 10.2 (CH_2). – MS: m/z (%) = 448 (2) $[M]^+$, 402 (2) $[M–NO_2]^+$ (2), 365 (10) $[M–CHCl_2]^+$, 95 (100). – HRMS ((+)-ESI): m/z = 449.0687 (449.0696 calcd. for $C_{19}H_{16}Cl_2FN_6O_2$, $[M+H]^+$).

*(E,E)-1-(Benzotriazol-1-yl)-4,4-dichloro-3-(3-hydroxypropylamino)-2-nitro-1-(4-tolylimino)-but-2-ene (**27**)*

Following general method 2, starting from nitrodiene **23** and 3-aminopropan-1-ol. Yield 75 %; m. p. 124 – 125 °C. – IR (KBr): ν = 3520, 3016, 2935, 1642, 1601 (NO_2), 1505, 1488, 1381 (NO_2), 1290, 1221, 1192, 1128, 1074, 1005, 968, 893, 829, 788, 751, 723, 595 cm^{-1}. – ^1H NMR ([D_6]acetone): δ = 11.05 (broad s, 1 H, NH), 8.55 (d, J = 8.3 Hz, 1 H), 8.19 (d, J = 8.1 Hz, 1 H), 7.78 (ddd, J = 8.3, 7.3, 0.9 Hz, 1 H), 7.63 (ddd, J = 8.1, 7.3, 0.9 Hz, 1 H), 7.27 (d, J = 8.1 Hz, C*H*CMe, 2 H), 7.06 (d, J = 8.1 Hz, C*H*CN, 2 H), 6.96 (d, J = 1.8 Hz, $CHCl_2$, 1 H), 4.28 – 3.94 (m, 3 H, OH, OCH_2), 3.80 (t, J = 5.8 Hz, 2 H, CH_2NH), 2.32 (s, 3 H, Me), 2.02 – 1.91 (m, 2 H, CCH_2C). – ^{13}C NMR ([D_6]acetone): δ = 153.0 ($C_{quat.}$), 147.7 (C1), 146.2 ($C_{quat.}$), 144.5 (CN), 136.2 (*C*Me), 132.2 ($C_{quat.}$), 130.5 (2 C, *C*HCMe), 130.3 (CH), 126.7 (CH), 121.3 (2 C, *C*HCN), 120.5 (CH), 116.2 (CH), 114.4 (CNO_2), 64.8 ($CHCl_2$), 60.7 (*C*H_2OH), 45.4 *C*H_2NH), 32.2 (*C*H_2C), 20.9 (Me). – MS: m/z (%) = 462 (3) $[M]^+$, 416 (52) $[M–NO_2]^+$, 256 (85), 157 (100). – HRMS ((+)-ESI): m/z = 463.1047 (463.1052 calcd. for $C_{20}H_{21}Cl_2N_6O_3$, $[M+H]^+$).

*(E,E)-1-(Benzotriazol-1-yl)-3-(benzylamino)-4,4-dichloro-1-(4-ethoxyphenylimino)-2-nitro-but-2-ene (**28**)*

According to general method 2 with nitrodiene **24** and benzylamine. Yield 80 %; m. p. 131 – 132 °C. – IR (KBr): ν = 3417 (OH), 2976, 1648, 1609 (NO_2), 1501, 1449, 1381 (NO_2), 1289, 1231, 1176, 1106, 1058, 1004, 961, 893, 826, 786, 750, 699, 507 cm^{-1}. – ^1H NMR ([D_6]acetone): δ = 10.92 (broad s, 1 H, NH), 8.53 (d, J = 8.3 Hz, 1 H), 8.14 (d, J = 8.1 Hz, 1 H), 7.75 (ddd, J = 8.3, 7.2, 1.0 Hz, 1 H), 7.59 (ddd, J = 8.1, 7.2, 1.0 Hz, 1 H), 7.53 – 7.25 (m, 5 H, Ph), 7.07 (d, J = 9.0 Hz, 2 H), 7.05 (s, 1 H, $CHCl_2$), 7.03 (d, J = 9.0 Hz, 2 H), 5.21 (s, 2 H, NCH_2), 4.08 (q, J = 6.9 Hz, 2 H, OCH_2), 1.38 (t, J = 6.9 Hz, 3 H, Me). – ^{13}C NMR ([D_6]acetone): δ = 158.5 (CO), 153.0 ($C_{quat.}$), 152.8 ($C_{quat.}$), 147.7 ($C_{quat.}$), 145.3 ($C_{quat.}$), 139.7 ($C_{quat.}$), 132.2 ($C_{quat.}$), 130.3 (CH), 129.7 (2 CH), 128.9 (CH), 128.2 (2 CH), 126.7 (CH), 123.4 (2 C, *C*HCN), 120.6 (CH), 116.3 (CH), 115.8 (2 C, *C*HCO), 115.1 (CNO_2), 64.8 ($CHCl_2$), 64.2 (*C*H_2O), 49.8 (*C*H_2N), 15.1 (Me). – MS: m/z (%) = 524 (3) $[M]^+$, 489 (2) $[M–Cl]^+$, 478 (2) $[M–NO_2]^+$, 91 (100). – HRMS ((+)-ESI): m/z = 525.1218 (525.1209 calcd. for $C_{25}H_{23}Cl_2N_6O_3$, $[M+H]^+$).

*(E,E)-1-(Benzotriazol-1-yl)-4,4-dichloro-1-(4-ethoxyphenylimino)-3-(2-hydroxyethylamino)-2-nitro-but-2-ene (**29**)*

Following general method 2, applying nitrodiene **24** and 2-aminoethanol. Yield 92 %; m. p. 92 – 94 °C. – IR (KBr): ν = 3420 (OH), 2980, 2935, 1640, 1614 (NO_2), 1504, 1448, 1378 (NO_2), 1290, 1246, 1170, 1046, 1004, 954, 837, 788, 751, 723, 568, 529 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.00 (broad s, 1 H, NH), 8.49 (d, J = 8.3 Hz, 1 H), 8.13 (d, J = 8.1 Hz, 1 H), 7.66 (ddd, J = 8.3, 7.2, 1.0 Hz, 1 H), 7.52 (ddd, J = 8.1, 7.2, 1.0 Hz, 1 H), 7.02 (d, J = 9.0 Hz, 2 H), 6.90 (d, J = 9.0 Hz, 2 H), 6.25 (d, J = 1.5 Hz, 1 H, $CHCl_2$), 4.04 (q, J = 7.0 Hz, 2 H, OCH_2), 4.02 – 3.80 (m, 4 H, OCH_2CH_2N), 1.94 (broad s, 1 H, OH), 1.43 (t, J = 7.0 Hz, 3 H, Me). – ^{13}C NMR [D_6]acetone: δ = 158.4 (CO), 153.0 ($C_{quat.}$), 147.6 ($C_{quat.}$), 145.4 ($C_{quat.}$), 139.7 ($C_{quat.}$), 132.2 ($C_{quat.}$), 130.3 (CH), 126.7 (CH), 123.3 (2 CH), 120.5 (CH), 116.3 (CH), 115.7 (2 CH), 114.8 (CNO_2), 64.9 ($CHCl_2$), 64.2 (OCH_2), 59.9 ($HOCH_2$), 48.2 (NCH_2), 15.0 (Me). – MS: m/z (%) = 478 (4) $[M]^+$, 432 (2) $[M–NO_2]^+$, 256 (10), 119 (100). – HRMS ((+)-ESI): m/z = 479.1003 (479.1001 calcd. for $C_{20}H_{21}Cl_2N_6O_4$, $[M+H]^+$).

*(E,E)-1-(Benzotriazol-1-yl)-4,4-dichloro-3-(4-ethoxyphenylamino)-1-(4-ethoxyphenylimino)-2-nitro-but-2-ene (**30**)*

Following general method 2, starting from nitrodiene **24** and *p*-phenetidine. Yield 74 %; m. p. 137 – 138 °C. – IR (KBr): ν = 3328, 3054, 2978, 1626, 1604, 1565 (NO_2), 1513, 1475, 1450, 1395, 1293 (NO_2), 1240, 1170, 1086, 1048, 937, 826, 787, 752, 710, 694, 512 cm^{-1}. – ^1H NMR ([D_6]acetone): δ = 9.04 (broad s, 1 H, NH), 8.13 (d, J = 8.2 Hz, 1 H), 8.09 (d, J = 8.4 Hz, 1 H), 7.74 (s, 1 H, $CHCl_2$), 7.60 (ddd, J = 8.2, 7.0, 1.3 Hz, 1 H), 7.55 (ddd, J = 8.4, 7.0, 1.3 Hz, 1 H), 7.17 (d, J = 8.8 Hz, 2 H), 7.06 (d, J = 8.8 Hz, 2 H), 6.83 (d, J = 8.5 Hz, 2 H), 6.25 (d, J = 8.5 Hz, 2 H), 4.13 (q, J = 7.0 Hz, 2 H, OCH_2), 4.11 (q, J = 7.0 Hz, 2 H, OCH_2), 3.57 (dq, J = 9.3, 7.0 Hz, 1 H, OCH_2), 3.25 (dq, J = 9.3, 7.0 Hz, 1 H, OCH_2), 1.42 (t, J = 7.0 Hz, 3 H, Me), 1.11 (t, J = 7.0 Hz, 3 H, Me). – ^{13}C NMR

([D_6]acetone): δ = 158.7 (CO), 158.6 (CO), 153.1 ($C_{quat.}$), 153.0 ($C_{quat.}$), 147.4 ($C_{quat.}$), 143.1 ($C_{quat.}$), 139.0 ($C_{quat.}$), 131.6 ($C_{quat.}$), 129.9 (CH), 126.3 (CH), 126.0 (2 CH), 123.5 (2 CH), 120.6 (CNO_2), 120.2 (CH), 116.0 (2 CH), 115.8 (2 CH), 114.4 (2 CH), 66.1 ($CHCl_2$), 64.3 (OCH_2), 63.9 (OCH_2), 15.0 (Me), 14.7 (Me). – MS: m/z (%) = 554 (1) $[M]^+$, 519 (1) $[M–Cl]^+$, 436 (1) [M–benzotriazole]$^+$, 119 (100). – HRMS ((+)-ESI): m/z = 555.1319 (555.1314 calcd. for $C_{26}H_{25}Cl_2N_6O_4$, $[M+H]^+$).

*(E,E)-1-(Benzotriazol-1-yl)-4,4-dichloro-1-(4-ethoxyphenylimino)-3-(4-methoxyphenyl-amino)-2-nitro-but-2-ene (**31**)*

Applying general method 2 with nitrodiene **24** and *p*-anisidine. Yield 68 %; m. p. 123 – 125 °C. – IR (KBr): ν = 3314, 3058, 1625, 1605, 1568 (NO_2), 1510, 1450, 1395, 1295 (NO_2), 1242, 1170, 1048, 1005, 943, 832, 787, 753, 711, 689 cm^{-1}. – ^{1}H NMR ([D_6]acetone): δ = 9.05 (broad s, 1 H, NH), 8.13 (d, J = 7.7 Hz, 1 H), 8.09 (d, J = 7.7 Hz, 1 H), 7.75 (s, 1 H, $CHCl_2$), 7.59 (ddd, J = 7.7, 7.2, 1.0 Hz, 1 H), 7.55 (ddd, J = 7.7, 7.2, 1.0 Hz, 1 H), 7.17 (d, J = 8.9 Hz, 2 H), 7.06 (d, J = 8.9 Hz, 2 H), 6.84 (d, J = 8.5 Hz, 2 H), 6.26 (d, J = 8.5 Hz, 2 H), 4.18 – 4.05 (m, 2 H, OCH_2), 3.26 (s, 3 H, OMe), 1.41 (t, J = 7.0 Hz, 3 H, Me). – ^{13}C NMR ([D_6]acetone): δ = 159.2 (CO), 158.6 (CO), 153.0 ($C_{quat.}$), 152.9 ($C_{quat.}$), 147.3 ($C_{quat.}$), 143.1 ($C_{quat.}$), 138.9 ($C_{quat.}$), 131.5 ($C_{quat.}$), 129.8 (CH), 126.4 (CH), 126.0 (2 CH), 123.5 (2 CH), 120.7 (CNO_2), 120.1 (CH), 116.0 (2 CH), 115.70 (CH), 113.9 (2 CH), 66.1 ($CHCl_2$), 64.3 (OCH_2), 55.3 (OMe), 15.0 (Me). – MS: m/z (%) = 540 (1) $[M]^+$, 504 (1) $[M–HCl]^+$, 421 (2) [M–benzotriazole]$^+$, 119 (100). – HRMS ((+)-ESI): m/z = 541.1158 (541.1158 calcd. for $C_{25}H_{23}Cl_2N_6O_4$, $[M+H]^+$).

*(E,E)-1-(Benzotriazol-1-yl)-4,4-dichloro-1-(4-fluorophenylimino)-3-(4-methoxyphenylamino)-2-nitro-but-2-ene (**32**)*

Following general method 2, applying nitrodiene **20** and *p*-anisidine. Yield 94 %; m. p. 153 – 154 °C. – IR (KBr): ν = 3365, 3040, 1634, 1608, 1575, 1511, 1450, 1401, 1322, 1254, 1204, 1076, 1052, 1027, 833, 748 cm^{-1}. – ^{1}H NMR ([D_6]acetone): δ = 9.16 (broad s, 1 H, NH), 8.16 (d, J = 7.9 Hz, 1 H), 8.08 (d, J = 7.9 Hz, 1 H), 7.69 (s, 1 H, $CHCl_2$), 7.62 (ddd, J = 7.9, 7.2, 1.2 Hz, 1 H), 7.57 (ddd, J = 7.9, 7.2, 1.2 Hz, 1 H), 7.32 – 7.24 (m, 4 H), 6.90 (d, J = 8.5 Hz, 2 H), 6.29 (d, J = 8.5 Hz, 2 H), 3.27 (s, 3 H, OMe). – ^{13}C NMR ([D_6]acetone): δ = 162.2 (CF, $^1J_{C,F}$ = 250.3 Hz), 159.3 ($C_{quat.}$), 153.5 ($C_{quat.}$), 147.4 ($C_{quat.}$), 144.8 ($C_{quat.}$), 142.5 (CN, $^4J_{C,F}$ = 2.2 Hz), 138.4 ($C_{quat.}$), 131.5 ($C_{quat.}$), 130.2 (CH), 126.6 (CH), 126.0 (2 CH), 123.8 (CNO_2), 123.6 (2 CH, $^3J_{C,F}$ = 8.5 Hz), 120.3 (CH), 116.9 (2 CH, $^2J_{C,F}$ = 22.8 Hz), 115.6 (CH), 114.1 (2 CH), 65.9 ($CHCl_2$), 55.4 (Me). – MS: m/z (%) = 514 (3) $[M]^+$, 479 (2) $[M–Cl]^+$, 396 (3) [M–benzotriazole]$^+$, 119 (100). – HRMS ((+)-ESI): m/z = 515.0806 (515.0801 calcd. for $C_{23}H_{18}Cl_2FN_6O_3$, $[M+H]^+$).

*(E,E)-1-(Benzotriazol-1-yl)-1-(4-bromophenylimino)-4,4-dichloro-3-(4-methoxyphenylami-no)-2-nitro-but-2-ene (**33**)*

According to general method 2, starting from nitrodiene **21** and *p*-anisidine. Yield 80 %; m. p. 149 – 150 °C. – IR (KBr): ν = 3332, 3013, 1636, 1608, 1573 (NO_2), 1510, 1482, 1405, 1305 (NO_2), 1252, 1172, 1071, 1005, 945, 832, 785, 747, 514 cm^{-1}. – ^{1}H NMR ([D_6]acetone): δ = 9.18 (broad s, 1 H, NH), 8.16 (d, J = 7.7 Hz, 1 H), 8.07 (d, J = 7.7 Hz, 1 H), 7.68 (d, J = 8.9 Hz, 2 H), 7.67 (s, 1 H, $CHCl_2$), 7.62 (ddd, J = 7.7, 7.2, 1.4 Hz, 1 H), 7.58 (ddd, J = 7.7, 7.2, 1.4 Hz, 1 H), 7.17 (d, J = 8.9 Hz, 2 H), 6.92 (d, J = 8.4 Hz, 2 H), 6.30 (d, J = 8.4 Hz, 2 H), 3.27 (s, 3 H, OMe). – ^{13}C NMR ([D_6]acetone): δ = 159.3 (CO), 153.5 ($C_{quat.}$), 150.6 ($C_{quat.}$), 147.4 ($C_{quat.}$), 145.5 ($C_{quat.}$), 137.9 ($C_{quat.}$), 133.3 (2 CH, *C*HCBr), 131.5 ($C_{quat.}$), 130.3 (CH), 126.7 (CH), 126.0 (2 CH, *C*HCNH), 123.7 (2 CH, *C*HCN), 121.8 (CNO_2), 120.4 (CH), 119.7 (CBr), 115.6 (CH), 114.1 (2 CH, *C*HCO), 65.9 ($CHCl_2$), 55.4 (OMe). – MS: m/z (%) = 574 $[M]^+$ (3), 529 $[M–HNO_2]^+$ (2), 455 [M–benzotriazole]$^+$ (2), 197 (58), 119 (100). m/z $[M+H]^+$ calcd. for $C_{23}H_{18}BrCl_2N_6O_3$: 575.0001; found: 574.9999.

*(E,E)-1-(Benzotriazol-1-yl)-4,4-dichloro-1-(4-iodophenylimino)-3-(4-methoxyphenylamino)-2-nitro-but-2-ene (**34**)*

Following general method 2, applying nitrodiene **22** and *p*-anisidine. Yield 86 %; m. p. 140 – 141 °C. – IR (KBr): ν = 3329, 3017, 1637, 1608, 1574 (NO_2), 1510, 1487, 1450, 1402, 1305 (NO_2), 1251, 1069, 1050, 1002, 944, 830, 784, 747, 513 cm^{-1}. – ^{1}H NMR ([D_6]acetone): δ = 9.18 (broad s, 1 H, NH), 8.16 (d, J = 7.7 Hz, 1 H), 8.06 (d, J = 7.7 Hz, 1 H), 7.87 (d, J = 8.7 Hz, 2 H), 7.67 (s, 1 H, $CHCl_2$), 7.62 (ddd, J = 7.7, 7.1, 1.2 Hz, 1 H), 7.58 (ddd, J = 7.7, 7.2, 1.2 Hz, 1 H), 7.03 (d, J = 8.7 Hz, 2 H), 6.92 (d, J = 8.4 Hz, 2 H), 6.29 (d, J = 8.4 Hz, 2 H), 3.27 (s, 3 H, OMe). – ^{13}C NMR ([D_6]acetone): δ = 159.3 (CO), 153.5 ($C_{quat.}$), 147.4 ($C_{quat.}$), 146.1 ($C_{quat.}$), 145.1 ($C_{quat.}$), 139.3 (2 CH, *C*HCI), 139.1 ($C_{quat.}$), 131.5 ($C_{quat.}$), 130.3 (CH), 126.7 (CH), 125.9 (2 CH, *C*HCNH), 123.9 (2 CH, *C*HCN), 123.6 (CNO_2), 120.3 (CH), 115.5 (CH), 114.1 (2 CH, *C*HCO), 90.7 (CI), 65.8 ($CHCl_2$), 55.4 (OMe). – MS: m/z (%) = 622 $[M]^+$ (1), 504 [M–benzotriazole]$^+$ (2), 476 (6), 373 (10), 91 (100). m/z $[M+H]^+$ calcd. for $C_{23}H_{18}Cl_2IN_6O_3$: 622.9862; found: 622.9863.

*(E,E)-1-(Benzotriazol-1-yl)-4,4-dichloro-3-(4-methoxyphenylamino)-2-nitro-1-(4-tolylimino)-but-2-ene (**35**)*

Following the general method 2, applying nitrodiene **23** and *p*-anisidine. Yield 68 %; m. p. 144 – 145 °C. – IR (KBr):

ν = 3185, 2926, 1638, 1608, 1569 (NO_2), 1509, 1481, 1394, 1295 (NO_2), 1246, 1092, 1049, 941, 822, 757, 711 cm^{-1}. – ^1H NMR ([D_6]acetone): δ = 9.05 (broad s, 1 H, NH), 8.14 (d, J = 7.9 Hz, 1 H), 8.08 (d, J = 7.9 Hz, 1 H), 7.69 (s, 1 H, $CHCl_2$), 7.60 (ddd, J = 7.9, 7.0, 1.3 Hz, 1 H), 7.56 (ddd, J = 7.9, 7.0, 1.3 Hz, 1 H), 7.32 (d, J = 8.4 Hz, 2 H), 7.10 (d, J = 8.4 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 6.28 (d, J = 8.7 Hz, 2 H), 3.27 (s, 3 H, OMe), 2.39 (s, 3 H). – ^{13}C NMR ([D_6]acetone): δ = 159.3 (CO), 153.3 ($C_{quat.}$), 147.3 ($C_{quat.}$), 144.0 ($C_{quat.}$), 143.7 ($C_{quat.}$), 136.6 ($C_{quat.}$), 131.5 ($C_{quat.}$), 130.7 (2 CH, *C*HCMe), 130.5 ($C_{quat.}$), 130.0 (CH), 126.5 (CH), 126.0 (2 CH, *C*HCNH), 121.6 (2 CH, *C*HCN), 120.6 (CNO_2), 120.2 (CH), 115.7 (CH), 114.0 (2 CH, *C*HCO), 66.0 ($CHCl_2$), 55.3 (OMe), 21.0 (Me). – MS: m/z (%) = 510 (2) $[M]^+$, 464 (2) $[M–NO_2]^+$, 364 (10), 91 (100). – HRMS ((+)-ESI): m/z = 511.1051 (511.1052 calcd. for $C_{24}H_{21}Cl_2N_6O_3$, $[M+H]^+$).

*5-(4-Ethoxyphenylamino)-3-(hydrazonomethyl)-4-nitro-1H-pyrazole (**36**)*

To a solution of **7**, **28**, or **30** (1.0 mmol) in MeOH (10 mL) at 0 °C a solution of hydrazine hydrate (0.25 g, 5.0 mmol) in MeOH (2 mL) was added over 2 min. The resulting mixture then was stirred for 1 h at 0 °C, then at r. t. for additional 4 h in case of **28** and **30** (8 h in case of **7**). The resulting precipitate was filtered off, washed with MeOH (2 × 5 mL), and finally dried under reduced pressure to give 83 % of compound **36** by using **28**, or 54 % by using **30**, or 56 % in case of **7**. m. p. 201 – 202 °C. – IR (KBr): ν = 3423, 3300, 3222, 2971, 2868, 1603, 1572, 1513 (NO_2), 1447, 1369 (NO_2), 1284, 1258, 1233, 1120, 1052, 925, 892, 823, 767, 682, 571 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 13.22 (broad s, 1 H, NH), 8.47 (broad s, 1 H, NH), 8.13 (broad s, 2 H, NH_2), 8.07 (s, 1 H, CH=N), 7.61 (d, J = 9.0 Hz, 2 H, C*H*CNH), 6.86 (d, J = 9.0 Hz, 2 H, CHCO), 3.97 (q, J = 6.9 Hz, 2 H, OCH_2), 1.30 (t, J = 6.9 Hz, 3 H, Me). – ^{13}C NMR ([D_6]DMSO): δ = 153.4 (CO), 147.7 (C-5), 138.7 (C-3), 133.8 (CNH), 122.9 (CH=N), 119.6 (2 CH, *C*HCNH), 117.3 (CNO_2), 114.7 (2 CH, *C*HCO), 63.3 (CH_2), 14.9 (Me). – MS: m/z (%) = 290 (100) $[M]^+$, 261 (51) $[M–C_2H_5]^+$. – HRMS ((+)-ESI): m/z = 291.1203 (291.1206 calcd. for $C_{12}H_{15}N_6O_3$, $[M+H]^+$).

*(E,E,E)-4-(Benzotriazol-1-yl)-4-((4-bromophenyl)imino)-1,1-dichloro-3-nitrobut-2-en-2-yl)acetimidamide (**37**)*

To a suspension of **21** (0.49 g, 1.0 mmol) and acetamidine hydrochloride (0.19 g, 2.0 mmol) in anhydrous THF (10 mL) was added sodium hydride (0.12 g, 3.0 mmol, 60 % in mineral oil) at 0 °C within 3 min. The resulting mixture was stirred at 0 °C for 3 h. Subsequently, at the same temperature, the solvent was removed *in vacuo*. The residue was treated with cold diluted aqueous 5 % HCl (30 mL). After 20 min with stirring at r. t., the precipitate was filtered off, washed with H_2O (2 × 20 mL), Et_2O (2 × 5 mL), and dried *in vacuo* to give acetimidamide **37**; yield: 398 mg (78 %); m. p. 135 – 136 °C. – IR (KBr): ν = 3029, 2974, 2856, 1680, 1618, 1570 (NO_2), 1487, 1296 (NO_2), 1282, 1204, 1071, 1008, 945, 898, 826, 746, 498 cm^{-1}. – ^1H NMR ([D_6]acetone): δ = 8.11 (d, J = 8.3 Hz, 1 H), 7.91 (d, J = 8.3 Hz, 1 H), 7.68 (d, J = 8.8 Hz, 2 H), 7.63 – 7.56 (m, 1 H), 7.48 (s, 1 H, $CHCl_2$), 7.46 – 7.41 (m, 1 H), 7.30 (d, J = 8.8 Hz, 2 H), 7.00 (broad s, 2 H, NH_2), 2.52 (s, 3 H, Me). – ^{13}C NMR ([D_6]acetone): δ = 170.9 (*C*Me), 159.8 ($C_{quat.}$), 154.1 ($C_{quat.}$), 145.0 ($C_{quat.}$), 137.6 ($C_{quat.}$), 133.2 (2 CH, *C*HCBr), 131.5 ($C_{quat.}$), 131.0 (CH), 126.7 (CH), 126.6 (2 CH, *C*HCN), 123.4 (CNO_2), 121.3 (CH), 118.8 (CBr), 116.2 (CH), 68.1 ($CHCl_2$), 26.2 (Me). – MS: m/z (%) = 509 (1) $[M]^+$, 391 (7) [M–benzotriazole]$^+$, 324 (55), 256 (100). – HRMS ((+)-ESI): m/z = 509.9842 (509.9848 calcd. for $C_{18}H_{15}BrCl_2N_7O_2$, $[M+H]^+$).

*4-(4-Bromophenylamino)-6-dichloromethyl-2-methyl-5-nitro-pyrimidine (**38**)*

To a solution of **37** (0.51 g, 1.0 mmol) in anhydrous THF (10 mL) at 0 °C sodium hydride (44 mg, 1.1 mmol, 60 % in mineral oil) was added over 3 min. The mixture was stirred at 0 °C for 1 h and at r. t. for 10 h, then the solvent was removed at r. t. *in vacuo*. The residue was treated with aqueous 5 % HCl (30 mL). After 20 min with stirring at r. t., the precipitate was filtered off, washed with H_2O (2 × 20 mL), cold MeOH (1 × 3 mL), hexane (2 × 5 mL) and dried *in vacuo* to give pyrimidine **38**; yield: 294 mg (75 %); m. p. 165 – 166 °C. – IR (KBr): ν = 3321, 2924, 2854, 1610, 1567 (NO_2), 1509, 1377 (NO_2), 1284, 1202, 1076, 999, 856, 829, 785, 748, 734, 694, 507 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.73 (broad s, 1 H, NH), 7.54 (d, J = 9.0 Hz, 2 H, CHCBr), 7.49 (d, J = 9.0 Hz, 2 H, C*H*CNH), 7.37 (s, 1 H, $CHCl_2$), 2.69 (s, 3 H, Me). – ^{13}C NMR ($CDCl_3$): δ = 171.3 (C-2), 160.6 ($C_{quat.}$), 153.0 ($C_{quat.}$), 135.4 (CNH), 132.2 (2 C, *C*HCBr), 124.5 (2 C, *C*HCNH), 123.5 (CNO_2), 119.1 (CBr), 66.5 ($CHCl_2$), 26.5 (Me). – MS: m/z (%) = 390 (100) $[M]^+$, 355 (70) $[M–Cl]^+$, 344 (3) $[M–NO_2]^+$. – HRMS ((+)-ESI): m/z = 390.9362 (390.9364 calcd. for $C_{12}H_{10}BrCl_2N_4O_2$, $[M+H]^+$).

General method 4 (one-pot procedure)

*4-(4-Bromophenylamino)-6-dichloromethyl-2-methyl-5-nitro-pyrimidine (**38**)*

To a suspension of **21** (0.49 g, 1.0 mmol) and acetamidine hydrochloride (0.28 g, 3.0 mmol) in anhydrous THF (10 mL) sodium hydride (0.16 g, 4.0 mmol, 60 % in mineral oil) was added at 0 °C over 3 min. Subsequently, after stirring for 1 h at 0 °C and for 15 h at r. t, the solvent was removed *in vacuo* at r. t. The residue was treated with aqueous 5 % HCl (30 mL). After additional 20 min stirring at r. t., the precipitate was filtered off, washed with H_2O (2 × 20 mL), cold MeOH (1 ×

3 mL), and hexane (2 × 5 mL), and was then dried *in vacuo* to give pyrimidine **38**; yield: 235 mg (60 %). Physical data, see above.

*6-(Dichloromethyl)-4-(4-fluorophenylamino)-2-methyl-5-nitro-pyrimidine (**39**)*

Following the general method 4 with nitrodiene **20**. Yield 62 %; m. p. 152 – 153 °C. – IR (KBr): ν = 3324, 2924, 1617, 1589, 1569 (NO_2), 1511, 1385 (NO_2), 1287, 1202, 1004, 847, 783, 747, 667, 507 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.71 (broad s, 1 H, NH), 7.53 (dd, J = 8.9, 4.7 Hz, 2 H, C*H*CNH), 7.39 (s, 1 H, $CHCl_2$), 7.12 (dd, J = 8.9, 8.5 Hz, 2 H, CHCF), 2.66 (s, 3 H, Me). – ^{13}C NMR ($CDCl_3$): δ = 171.3 (C-2), 160.6 ($C_{quat.}$), 160.5 (CF, $^1J_{C,F}$ = 246.5 Hz), 153.4 ($C_{quat.}$), 132.2 (CNH, $^4J_{C,F}$ = 3.1 Hz), 125.1 (2 C, *C*HCNH, $^3J_{C,F}$ = 8.2 Hz), 123.3 (CNO_2), 115.9 (2 C, *C*HCF, $^2J_{C,F}$ = 22.8 Hz), 66.6 ($CHCl_2$), 26.5 (Me). – MS: m/z (%) = 330 (100) $[M]^+$, 313 (5) $[M–OH]^+$ (5), 296 (46) $[M–Cl+H]^+$, 284 (5) $[M–NO_2]^+$. – HRMS ((+)-ESI): m/z = 331.0163 (331.0165 calcd. for $C_{12}H_{10}Cl_2FN_4O_2$, $[M+H]^+$).

*6-(Dichloromethyl)-4-(4-iodophenylamino)-2-methyl-5-nitro-pyrimidine (**40**)*

Following general method 4, applying nitrodiene **22**. Yield 48 %; m. p. 161 – 162 °C. – IR (KBr): ν = 3322, 1613, 1568 (NO_2), 1513, 1379 (NO_2), 1285, 1204, 1002, 855, 826, 785, 749, 508 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.71 (broad s, 1 H, NH), 7.73 (d, J = 8.8 Hz, 2 H, CHCI), 7.38 (d, J = 8.8 Hz, 2 H, C*H*CNH), 7.37 (s, 1 H, $CHCl_2$), 2.69 (s, 3 H, Me). – ^{13}C NMR ($CDCl_3$): δ = 171.3 (C-2), 160.6 ($C_{quat.}$), 153.0 ($C_{quat.}$), 138.1 (2 C, CHCI), 136.1 (CNH), 124.7 (2 C, *C*HCNH), 123.5 (CNO_2), 90.0 (CI), 66.5 ($CHCl_2$), 26.5 (Me). – MS: m/z (%) = 438 (100) $[M]^+$, 404 (57) $[M–Cl+H]^+$, 370 (7). – HRMS ((+)-ESI): m/z = 438.9232 (438.9226 calcd. for $C_{12}H_{10}Cl_2IN_4O_2$, $[M+H]^+$).

*6-(Dichloromethyl)-2-methyl-5-nitro-4-(4-tolylamino)pyrimidine (**41**)*

Following general method 4 with nitrodiene **23**. Yield 69 %; m. p. 172 – 173 °C. – IR (KBr): ν = 3323, 2926, 1619, 1573 (NO_2), 1513, 1379 (NO_2), 1285, 1202, 1003, 859, 822, 785, 747, 514 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.72 (broad s, 1 H, NH), 7.45 (d, J = 8.3 Hz, 2 H, C*H*CNH), 7.39 (s, 1 H, $CHCl_2$), 7.22 (d, J = 8.3 Hz, 2 H, C*H*CMe), 2.67 (s, 3 H, Me), 2.38 (s, 3 H, Me). – ^{13}C NMR ($CDCl_3$): δ = 171.1 (C-2), 160.5 ($C_{quat.}$), 153.2 ($C_{quat.}$), 136.1 (CNH), 133.7 (*C*Me), 129.6 (2 C, *C*HCMe), 123.3 (CNO_2), 123.1 (2 C, *C*HCNH), 66.7 ($CHCl_2$), 26.5 (N_2C-*Me*), 21.9 (Me). – MS: m/z (%) = 326 (100) $[M]^+$, 309 (8) $[M–OH]^+$, 292 (32) $[M–HCl]^+$. – HRMS ((+)-ESI): m/z = 327.0415 (327.0416 calcd. for $C_{13}H_{13}Cl_2N_4O_2$, $[M+H]^+$).

*6-(Dichloromethyl)-4-(4-ethoxyphenylamino)-2-methyl-5-nitropyrimidine (**42**)*

Following the general method 4, applying nitrodiene **24**. Yield 47 %; m. p. 168 – 169 °C. – IR (KBr): ν = 3319, 2973, 1610, 1579 (NO_2), 1568, 1512, 1378 (NO_2), 1287, 1253, 1208, 1039, 1001, 858, 824, 785, 748, 672, 570, 510 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 9.80 (broad s, 1 H, NH), 7.47 (s, 1 H, $CHCl_2$), 7.42 (d, J = 8.2 Hz, 2 H, C*H*CNH), 6.93 (d, J = 8.2 Hz, 2 H, C*H*CO), 4.02 (q, J = 6.5 Hz, 2 H, OCH_2), 2.46 (s, 3 H, Me), 1.33 (t, J = 6.5 Hz, 3 H, Me). – ^{13}C NMR ($CDCl_3$): δ = 169.3 (C-2), 156.9 ($C_{quat.}$), 156.4 ($C_{quat.}$), 152.9 (CO), 130.0 (*C*NH), 125.8 (2 C, *C*HCNH), 125.0 (CNO_2), 114.4 (2 C, *C*HCO), 67.6 ($CHCl_2$), 63.4 (OCH_2), 26.2 (N_2C-*Me*), 14.9 (Me). – ^{14}N and ^{15}N NMR ($CDCl_3$): δ = −13.5 (NO_2), −123.7 (N-1), −129.2 (N-3), −270.8 (NH). – MS: m/z (%) = 356 (100) $[M]^+$, 327 (20) $[M–C_2H_5]^+$, 322 (32) $[M–HCl]^+$. – HRMS ((+)-ESI): m/z = 357.0522 (357.0521 calcd. for $C_{14}H_{15}Cl_2N_4O_3$, $[M+H]^+$).

General method 5

*(E)-2-(2,3,3-Trichloro-1-nitroallylidene)-2,3-dihydro-benzo[d]oxazole (**43**)*

At −40 °C a solution of **1** (2.71 g, 10 mmol) in 5 mL MeOH was added dropwise to a suspension of *o*-aminophenol (3.49 g, 32 mmol) in 30 mL MeOH within 5 min. The resulting mixture was kept for 1 h at this temperature, and was then allowed to warm to r. t. After 5 h stirring, the mixture was poured into a cold solution (0 °C) of 5 mL conc. hydrochloric in 250 mL of water. After 20 min, the precipitate was filtered off, washed with cold water (3 × 40 mL) and diethyl ether (2 × 10 mL). Drying *in vacuo* gave oxazole **43**; yield: 2.70 g (88 %); m. p. 134 – 135 °C. – IR (KBr): ν = 3423, 3106, 1615, 1582 (NO_2), 1473, 1427, 1368 (NO_2), 1296, 1240, 1073, 970, 925, 850, 805, 751, 587, 486, 420 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 12.26 (broad s, 1 H, NH), 7.68 (d, J = 7.3 Hz, 1 H), 7.56 (d, J = 7.5 Hz, 1 H), 7.52 – 7.33 (m, 2 H). – ^{13}C NMR ($CDCl_3$): δ = 159.0 (C-2), 146.9 (C-7a), 128.6 (C-3a), 128.4 (CCl), 126.7 (C-6), 125.5 (C-5), 120.1 (CCl_2), 113.4 (C-4), 111.2 (C-7), 107.1 (CNO_2). – UV λ_{max} (log ε_{max}) = 222 nm (4.17), 352 nm (4.25). – MS: m/z (%) = 306 (1) $[M]^+$, 271 (5) $[M–Cl]^+$, 260 (48) $[M–NO_2]^+$, 225 (100). – HRMS ((+)-ESI): m/z = 306.9444 (306.9444 calcd. for $C_{10}H_6Cl_3N_2O_3$, $[M+H]^+$).

*(E)-2-(2,3,3-Trichloro-1-nitroallylidene)-2,3-dihydro-benzo[d]thiazole (**44**)*

Following the general method 4, applying nitrodiene **1** and *o*-aminothiophenol as a 1 : 3.2 mixture. Reaction conditions: 1 h at −40 °C, then 15 h at r. t. Yield 83 %; m. p. 180 – 181 °C. – UV: λ_{max} (log ε_{max}) = 218 nm (4.38), 382 nm (4.43). – IR (KBr): ν = 3444, 3151, 3091, 2775, 1606, 1535

(NO_2), 1466, 1413, 1333 (NO_2), 1249, 1078, 1016, 946, 815, 748, 665, 588, 501 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 13.45 (broad s, 1 H, NH), 8.03 (d, J = 8.1 Hz, 1 H, H-7), 7.68 (d, J = 8.1 Hz, 1 H, H-4), 7.55 (ddd, J = 8.1, 7.1, 1.0 Hz, 1 H, H-6), 7.40 (ddd, J = 8.1, 7.1, 1.0 Hz, 1 H, H-5). – ^{13}C NMR ([D_6]DMSO): δ = 160.1 (C-2), 140.1 (C-3a), 128.2 (C-5), 127.8 (C-7a), 127.3 (CCl), 124.8 (C-6), 123.2 (C-5), 121.8 (CCl_2), 114.5 (C-4), 113.6 (CNO_2). – MS: m/z (%) = 322 (100) $[M]^+$, 287 (13) $[M–Cl]^+$), 276 (21) $[M–NO_2]$, 252 (12) [M–2Cl], 241 (100). – HRMS ((+)-ESI): m/z = 322.9210 (322.9216 calcd. for $C_{10}H_6Cl_3N_2O_2S$, $[M+H]^+$).

*2-(2,3,3-Trichloro-1-nitroallylidene)-2,3-dihydro-1H-benzo[d]imidazole (**45**)*

According to the general method 4 with nitrodiene **1** and *o*-phenylendiamine as a 1 : 2.1 mixture. Reaction conditions: 1 h at −40 °C, then 3 h at r.t. Yield 96 %; m.p. 215 – 217 °C. – UV: λ_{max} (log ε_{max}): 208 nm (4.32), 362 nm (4.33). – IR (KBr): ν = 3307, 3058, 1621, 1576 (NO_2), 1467, 1370 (NO_2), 1303, 1235, 1150, 1073, 974, 930, 844, 804, 747, 709, 586, 484, 425 cm^{-1}. – ^1H NMR ([D_6]acetone): δ = 12.26 (broad s, 2 H, NH), 7.72 – 7.51 (m, 2 H), 7.44 – 7.30 (m, 2 H). – ^{13}C NMR ([D_6]DMSO): δ = 144.6 (C-2), 131.0 (2 C, C-3a, C-7a), 126.7 (CCl), 124.2 (2 CH, C-5, C-6), 123.9 (CCl_2), 112.6 (2 C, C-4, C-7), 103.4 (CNO_2). – MS: m/z (%) = 305 (4) $[M]^+$, 270 (20) $[M–Cl]^+$, 259 (15) $[M–NO_2]^+$, 223 (73), 102 (100). – HRMS ((+)-ESI): m/z = 305.9604 (305.9604 calcd. for $C_{10}H_7Cl_3N_3O_2$, $[M+H]^+$).

*(1-(1H-Benzoxazol-2-yl)-3,3-dichloro-2-(4-(dimethylamino)pyridinium-1-yl)allylidene)azinate (**46**)*

Following general method 2, applying benzoxazole **43** and DMAP (1 : 2.1). Reaction conditions: 1 h at 0 °C and 12 h at r.t. Yield 32 %; m.p. 203 – 204 °C. – IR (KBr): ν = 3442, 3105, 1645, 1573, 1532, 1452, 1402, 1362, 1302, 1241, 1145, 1057, 914, 854, 817, 780, 744, 671, 627, 555 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 8.31 (d, J = 7.7 Hz, 2 H, NCH), 7.62 – 7.49 (m, 2 H), 7.28 – 7.14 (m, 2H), 7.06 (d, J = 7.7 Hz, 2 H, MeNCC*H*), 3.24 (s, 6 H, Me). – ^{13}C NMR ([D_6]DMSO): δ = 160.8 ($C_{quat.}$-NMe), 156.4 (NCO), 149.6 ($C_{quat.}$), 142.4 ($C_{quat.}$), 142.3 (2 CH, $N_{py}CH$), 135.7 ($N_{py}C_{quat.}$), 124.1 (CH), 122.9 (CCl_2), 122.8 (CH), 117.7 (CH), 109.9 (CH), 107.4 (2 CH, *C*HCNMe), 103.7 (CNO_2), 40.3 (Me). – MS: m/z (%) = 392 (1) $[M]^+$, 224 (4), 144 (20), 121 (100), 119 (27) [benzoxazole]$^+$. – HRMS ((+)-ESI): m/z = 393.0514 (393.0521 calcd. for $C_{17}H_{15}Cl_2N_4O_3$, $[M+H]^+$).

*(1-(1H-Benzothiazol-2-yl)-3,3-dichloro-2-(4-(dimethylamino)pyridinium-1-yl)allylidene)azinate (**47**)*

At r.t. 2.69 g (22 mmol) DMAP were added to a suspension of 3.24 g (10.0 mmol) benzothiazole **44** in 50 mL MeOH. The mixture was then stirred for 1 d at this temperature. Subsequently, after addition of 200 mL of cold water, 5 mL conc. hydrochloric acid was added dropwise. After 10 min stirring, the mixture was extracted with chloroform (3 × 100 mL). The combined organic layers were washed with brine and dried over anhydrous calcium chloride. The crude product was purified by means of column chromatography applying at first chloroform to eliminate polar side products. Afterwards, acetone was used as eluent. Evaporation of all solvents gave 2.19 g azinate **47**. Yield 54 %; m.p. 128 – 129 °C. – IR (KBr): ν = 3422, 1645, 1576, 1533, 1469, 1405, 1324, 1284, 1210, 1142, 1078, 1018, 946, 824, 791, 763, 737, 661 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 8.46 (d,

Table 1. Crystal data and numbers pertinent to data collection and structure refinement parameters for **30**.

Formula	$C_{26}H_{24}Cl_2N_6O_4$
M_r	555.41
Crystal size, mm^3	$0.29 \times 0.28 \times 0.27$
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a, Å	11.521(2)
b, Å	16.520(2)
c, Å	14.306(2)
β, deg	107.10(1)
V, $Å^3$	2602.3(6)
Z	4
D_{calc}, g cm^{-3}	1.42
$\mu(MoK_\alpha)$, mm^{-1}	0.3
$F(000)$, e	1152
Diffractometer	Stoe IPDS 2
θ range for data collection, deg	1.00 – 25.03
hkl range	±13, pm19, ±17
Reflections collected / independent / R_{int}	20756 / 4584 / 0.0837
Reflections with $I \geq 2\sigma(I)$	3225
Refined parameters	439
$R1$ [$I \geq 2\sigma(I)$] / $wR2$ (all data)	0.0543 / 0.0974
Goodness-of-fit on F^2	1.109
Peak and hole, e $Å^{-3}$	0.219 / −0.255

Table 2. Selected interatomic distances (Å), bond angles (deg), and dihedral angles (deg) in the structure of **30**.

O(1)–C(14)	1.370(3)	N(2)–N(3)	1.297(3)
O(1)–C(17)	1.438(4)	N(3)–C(10)	1.391(4)
O(2)–N(5)	1.242(3)	N(4)–C(1)	1.273(4)
O(3)–N(5)	1.238(3)	N(4)–C(11)	1.420(3)
O(4)–C(22)	1.364(4)	N(5)–C(2)	1.427(4)
O(4)–C(25)	1.432(4)	N(5)–C(3)	1.345(4)
N(1)–N(2)	1.376(3)	N(5)–C(19)	1.426(4)
N(1)–C(1)	1.413(3)	C(4)–C(19)	1.774(3)
N(1)–C(9)	1.377(3)	C(4)–C(19)	1.784(3)
N(2)–N(1)–C(1)	120.7(2)	C(3)–N(6)–C(19)	126.2(2)
N(2)–N(1)–C(9)	110.1(2)	C(9)–N(1)–C(1)	129.0(2)
N(2)–N(3)–C(10)	108.8(2)	C(22)–O(4)–C(25)	118.3(2)
N(3)–N(2)–N(1)	108.4(2)	Cl(4)–O(1)–Cl(17)	117.7(2)
N(2)–C(1)–N(1)–N(4)		166.6(1)	
C(23)–C(22)–O(4)–C(25)		179.9(1)	

J = 7.6 Hz, 2 H, NCH), 8.04 (d, J = 7.8 Hz, 1 H), 7.87 (d, J = 7.9 Hz, 1 H), 7.53 (m, 1 H), 7.37 (m, 1 H), 7.07 (d, J = 7.6 Hz, 2 H, MeNCC*H*), 3.25 (s, 6 H, Me). – ^{13}C NMR ([D$_6$]DMSO): δ = 161.5 ($C_{quat.}$NMe), 156.4 (NCS), 147.0 ($C_{quat.}$N), 142.6 (2 CH, N$^+$CH), 142.4 ($C_{quat.}$S), 133.3 (N$^+C_{quat.}$), 127.3 (CH), 124.4 (CCl_2), 124.1 (CH), 122.5 (CH), 112.0 (CH), 107.3 (2 CH, *C*HCNMe), 104.2 (CNO_2), 40.4 (Me). – MS: m/z (%) = 408 (1) [M]$^+$, 298 (8), 256 (82), 135 (80) [benzothiazole]$^+$, 112 (100). – HRMS ((+)-ESI): m/z = 409.0281 (409.0293 calcd. for $C_{17}H_{15}Cl_2N_4O_2S$, [M+H]$^+$).

*(1-(1H-Benzimidazol-2-yl)-3,3-dichloro-2-(4-(dimethylamino)pyridinium-1-yl)allylidene)azinate (**48**)*

Following general method 2, applying benzimidazole **45** and DMAP (1 : 2.1). Reaction conditions: 1 h at 0 °C and 18 h at r. t. Yield 64 %; m. p. 197 – 198 °C. – IR (KBr): ν = 3430, 3348, 3051, 1643, 1567, 1523, 1453, 1427, 1365, 1270, 1221, 1171, 1142, 1058, 983, 932, 855, 773, 751, 619, 488 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): δ = 12.12 (broad s, 1 H, NH), 8.32 (d, J = 7.8 Hz, 2 H, NCH), 7.52 – 7.39 (m, 2 H), 7.06 (d, J = 7.8 Hz, 2 H, MeNCC*H*), 7.05 – 6.91 (m, 2 H), 3.21 (s, 6 H, Me). – ^{13}C NMR ([D$_6$]DMSO): δ = 156.4 ($C_{quat.}$NMe), 148.9 (NCS), 142.2 (2 C, $C_{quat.}$N, $C_{quat.}$NH), 142.1 (2 CH, N$^+$CH), 135.0 (N$^+C_{quat.}$), 125.3 (CCl_2), 120.8 (2 CH), 120.6 (2 CH), 107.4 (2 CH, *C*HCNMe), 106.2 (CNO_2), 40.2 (Me). – MS: m/z (%) = 391 (1) [M]$^+$, 256 (36), 121 (70), 118 (35) [benzimidazole]$^+$, 112 (100). – HRMS ((+)-ESI): m/z = 392.0688 (392.0681 calcd. for $C_{17}H_{16}Cl_2N_5O_2$, [M+H]$^+$).

*X-Ray structure determination of **30***

A suitable single crystal of the title compound was selected under a polarization microscope and mounted in a glass capillary (d = 0.3 mm). The data collection was carried out with a single-crystal diffractometer (Stoe IPDS II), using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at T = 223(2) K. The structure was solved by Direct Methods using SHELXS-97 [21] and refined using alternating cycles of least-squares refinements against F^2 (SHELXL-97) [22]. All non-H atoms were located in difference Fourier maps and were refined with anisotropic displacement parameters. The H positions were determined by a final difference Fourier synthesis. For preparation of the structure drawings the programs DIAMOND [23] and POV-RAY [24] were used. Crystallographic data for **30** and details of data collection and structure refinement are given in Table 1, selected bond lengths and angles in Table 2.

CCDC 769507 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) V. A. Zapol'skii, R. Fischer, J. C. Namyslo, D. E. Kaufmann, *Bioorg. Med. Chem.* **2009**, *17*, 4206 – 4215; b) E. Nutz, V. A. Zapol'skii, D. E. Kaufmann, *Synthesis* **2009**, *16*, 2719 – 2724; c) V. A. Zapol'skii, J. C. Namyslo, A. E. W. Adam, D. E. Kaufmann, *Heterocycles* **2004**, *63,* 1281 – 1298; d) R. V. Kaberdin, V. I. Potkin, V. A. Zapol'skii, *Russ. Chem. Rev.* **1997**, *66*, 827 – 842.

[2] C. Meyer, V. A. Zapol'skii, A. E. W. Adam, D. E. Kaufmann, *Synthesis* **2008**, *16*, 2575 – 2581.

[3] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056 – 2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004 – 2021.

[4] a) A. E. Cook (Ed.) *Enamines: Synthesis, Structure, and Reactions*, Marcel Dekker Inc., New York, **1988**, pp. 165 – 699; b) Z. Rappoport (Ed.) *The Chemistry of Enamines*, Wiley, New York, **1994**.

[5] J. Barluenga, C. Valdés, *Chem. Commun.* **2005**, 4891 – 4901.

[6] V. V. Perekalin, E. S. Lipina, V. M. Berestovitskaya, D. A. Efremov, *Nitroalkenes: Conjugated Nitrocompounds*, Wiley, New York, **1994**.

[7] V. A. Zapol'skii, V. I. Potkin, N. I. Nechai, R. V. Kaberdin, M. S. Pevzner, *Russ. J. Org. Chem.* **1997**, *33*, 1461 – 1467.

[8] Y. A. Ol'dekop, R. V. Kaberdin, V. I. Potkin, I. A. Shingel, *J. Org. Chem. USSR (Engl. Transl.)* **1979**, *15*, 39 – 42.

[9] V. A. Zapol'skii, E. Nutz, J. C. Namyslo, A. E. W. Adam, D. E. Kaufmann, *Synthesis* **2006**, *17*, 2927 – 2933.

[10] a) D. L. Rector, S. D. Folz, R. D. Conklin, L. H. Nowakowski, G. Kaugarts, *J. Med. Chem.* **1981**, *24*, 532 – 538; b) P. Nuhn, A. Büge, P. Harenberg, H. Lettau, K. Moschner, M. Rauchmaul, R. Schneider, *Pharmazie* **1993**, *48*, 340 – 342.

[11] C. Ibis, M. C. Sayil, N. G. Deniz, *Acta Crystallogr.* **2006**, *E62*, o800–o801.

[12] a) G. Aydinli, C. Sayil, C. Ibis, *Spectroscopy Lett.* **2010**, *43*, 44 – 50; b) C. Ibis, Z. Gokmen, *Acta Crystallogr.* **2006**, *E62*, o2932–o2933.

[13] R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533 – 3539.

[14] a) R. R. Manam, S. Teisan, D. J. White, B. Nicholson,

J. Grodberg, S. T. Neuteboom, K. S. Lam, D. A. Mosca, G. K. Lloyd, B. C. M. Potts, *J. Nat. Prod.* **2005**, *68*, 240 – 243; b) A. Napolitano, E. Camera, M. Picardo, M. d'Ischia, *J. Org. Chem.* **2002**, *67*, 1125 – 1132.

[15] a) Z. Dai, Y. Huang, W. Sadee, P. Blower, *J. Med. Chem.* **2007,** *50,* 1896 – 1906; b) P. Blower, J. H. Chung, J. S. Verducci, S. Lin, J. K. Park, Z. Dai, C. G. Liu, T. D. Schmittgen, W. C. Reinhold, C. M. Croce, J. N. Weinstein, W. Sadee, *Mol. Cancer Ther.* **2008**, *7*, 1 – 9.

[16] a) I. M. Lagoja, *Chem. Biodiv.* **2005**, *2*, 1 – 50; b) V. A. Zapol'skii, J. C. Namyslo, C. Altug, M. Gjikaj, D. E. Kaufmann, *Synthesis* **2008**, *2*, 304 – 310.

[17] C. Ibis, Z. Goekmen, *Phosphorus Sulfur Silicon Relat. Elem.* **1998**, *143*, 67 – 75.

[18] T. Ehrhardt, A. Reindl, A. Freund, R. M. Schmidt, U. Sonnewald, N. M. Stitt, W. Lein, F. Boernke, K. Deist, *PCT Int. Appl. WO 2005054283 A2* 20050616, **2005**.

[19] V. I. Potkin, V. A. Zapol'skii, R. V. Kaberdin, *Izv. Akad. Nauk Bel., Ser. Khim. Nauk.* **1996**, *40*, 68 – 71.

[20] V. A. Zapol'skii, V. I. Potkin, N. I. Nechai, R. V. Kaberdin, *Russ. J. Org. Chem.* **1993**, *29*, 731 – 734.

[21] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473.

[22] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.

[23] K. Brandenburg, DIAMOND (version 3.0), Crystal and Molecular Structure Visualization, Crystal Impact – K. Brandenburg & H. Putz GbR, Bonn (Germany) **2004**. See also: http://www.crystalimpact.com/diamond/

[24] POV-RAY (version 3.6), Trademark of Persistence of Vision Raytracer Pty. Ltd., Williamstown, Victoria (Australia); Copyright Hallam Oaks Pty. Ltd., **2005**.