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# Synthetic Exploitation of Halogenated Alkenes Containing EWG: Benzotriazole-Mediated Synthesis of Benzoazetines and Thermal Transformations

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**Abstract**

An approach to the synthesis of stable benzoazetines (**5a-d**) based on nitrovinyl moieties has been achieved via transamination of bisbenzotriazolyl derivatives (**2a-c**). Four new heptatomic aromatic cycloheterocumulenes (azacyclohepta-1,2,4,6-tetraene) occurred at the stage of film-forming process by TVE have been suggested by rearrangement of benzoazetines. This highly strained product was characterized by IR spectroscopy.

**Keywords:** Benzoazetines, benzotriazole-mediated synthesis, seven-membered cyclic compounds, transamination reactions, heterocyclization, thermal vacuum evaporation.

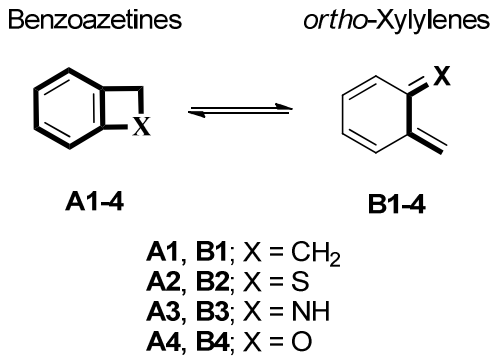
**Graphical Abstract**

## Introduction

*gem*-Dihalo nitrovinyl moieties are especially attractive building blocks owing to the synthetic versatility associated with the presence of the EWG group in vinyl moiety,[1, 2] mostly for the formation of carbon-heteroatom bonds. The presence of an EWG bonded to vinyl moiety renders these compounds more reactive toward carbon, nitrogen, sulfur, and oxygen nucleophiles.[3-8] The *gem*-dihalo nitrovinyl moiety also represents a very attractive key unit for syntheses of five- and six-membered heterocyclic compounds by selection of difunctional nucleophiles and other reagents.[9-14] Adapting these useful common precursors toward varied molecular architectures is attractive,[2, 10, 11, 13-17] not only to escape from the sameness.

The chemistry of benzo-condensed four-membered heterocyclic ring systems have been the focus of much less attention, mostly due to the instability of a series of their derivatives and complicated methods. Albeit *o*-xylylenes are versatile tools for the construction of these systems,[18] a traditional problem in the chemistry of *o*-xylylenes and their derivatives (oxy-, aza-, thio-) is the valence isomerization between the strained benzenoid form and the *o*-quinoidal form. Two real factors that is played in this process are as follow: (1) the strain of the four-membered heterocyclic ring (**A1-4**) and (2) the loss of aromaticity in the open quinoid system (**B1-4**) (Scheme 1).[19, 20] While benzocyclebutene[21, 22] (**A1**) and benzothiete[23] (**A2**) are stable under normal laboratory conditions, benzoxete (**A4**) are only stable in an argon matrix at 10 K.[24] Therefore, according to semiempirical calculations,[25] the stability of benzoazetine (**A3**) should be between that of benzocyclobutene (**A1**) and benzothiete (**A2**) on one hand and that of benzoxete (**A4**) on the other hand. The first member of the benzoazetine compounds date to the mid-1960s is 1-phenyl derivative benzoazetine system which was detected in 50% yield by Burgess and McCullagh during the UV irridation of phenylbenzotriazine derivatives in

benzene.[26] Later on, lots of methods for the synthesis of benzoazetines (**A3**) were developed by the elimination of $N_2$, $SO_2$, $H_2O$, $CO_2$, or amines from the initial molecules by the application of radiation, heat, or chemical reagents.[27] Benzoazetine derivatives (**A3**) have received much attention as potential precursors for the generation of different type products.[28-31] Although several studies on the formation of benzoazetine derivatives have appeared,[32-38] numerous efforts have therefore been made to synthesize the "stable" benzoazetines that might be convenient. These efforts have been only marginally successful. Among the synthesized compounds, all known benzoazetines contain a substituent at the nitrogen atom in described reactions up to now. In a few publications, the possibility for the formation of such compounds having an unsubstituted NH group as both stable and unstable intermediates in some reactions was postulated.[39]



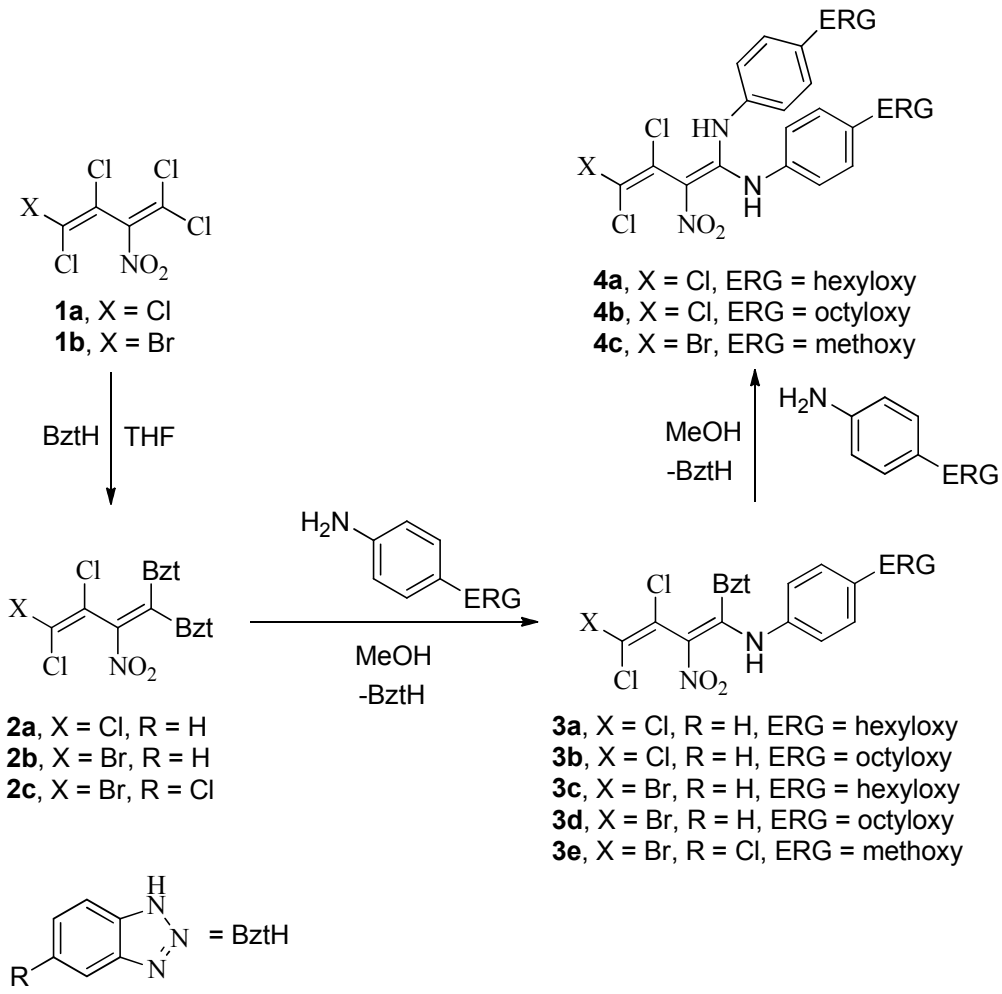

Scheme 1. Strained benzenoid form and the *o*-quinoidal form.

Benzotriazole intermediates are mostly used for the introduction of a different functional groups into molecules. The preparation of useful benzotriazolyl intermediates and the displacement by nucleophiles of the benzotriazole group in such molecules are known.[40, 41] These replacements of benzotriazole are assisted by the lone electron pair on the heteroatom substituents. Thus, initial ionization of intermediates occurs to give the reactive iminiums, which then reacts with

nucleophiles to give transamination products. In reactions of this type, the benzotriazole group and the heteroatom are connected to the same carbon. As a part of the research program, aiming at the discovery of novel heterocycles based *gem*-dihalo nitroalkene **1**, benzotriazole-mediated synthesis of benzoazetines via the transamination reactions of ketene aminals and their thermal transformations into an unstable seven-membered heterocycles is reported herein.

**Results and Discussion**

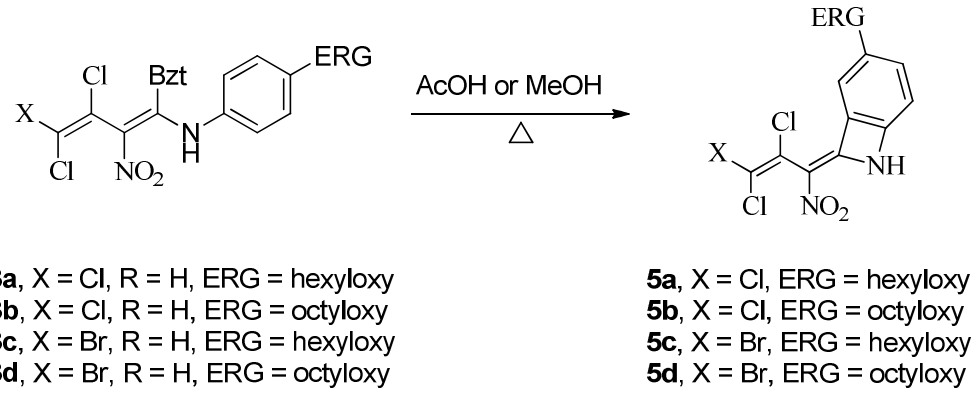
The pathway to the ketene aminals was found to be simple enough. Condensation of *gem*-dihalo nitroalkenes (**1a-b**) with a fourfold excess of benzotriazole in THF allowed replacement of two geminal chlorine atoms with benzotriazolyl substituents in the absence of catalyst to give bisbenzotriazolyl derivatives (**2a-c**)[42] and turned out to be an appropriate substrate for a transamination,[43, 44] as the azole group was an excellent leaving group. Therefore, under mild conditions, at 0 °C, in MeOH, one of the benzotriazolyl groups in **2a-c** was readily substituted with aryl amines to give enamines **3a-e** in 67-82% yields. Treatment of enamines **3a-e** in MeOH with an additional aryl amines resulted in formation of enamines **4a-c** that were isolated in 80-87% yields. The reaction pathway is believed to lead through the *in situ* formation of an imide chlorides shown in Scheme 2.[45,46,47] Transamination reactions did not proceed with aliphatic amines (ethylamine, diethylamine, and butylamine). Unfortunately, such compounds containing aliphatic amino group were not formed at all. The substructure of a nitro-substituted enamines within **3a-e** and **4a-c** compounds 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, a behavior typical of such enamines.




Scheme 2. Amination and transamination reactions of *gem*-dihalo nitroalkene **1a-b**.

Since benzotriazole is known to be good nucleophile as well as a good leaving group, benzotriazole-mediated transamination reactions would be possible for benzoazetine derivatives. The latter, when these compounds (**3a-e**) were converted by heating in proton-donating solvents such as methanol or glacial acetic acid at 55-60 °C for 12 h to the benzoazetines (**5a-d**) in a sealed tube, the corresponding azole is eliminated, and benzoazetine compounds (**5a-d**) were formed in excellent yields (Scheme 3). While reaction medium showed excellent results with temperature delivering benzoazetine compounds (**5a-d**) in up to 92% isolated yield, the application of diethyl ether and benzene was somewhat problematic. The yields were

significantly lower (no reaction and 27%, respectively) with the reaction times being longer and strong tarring was observed in both mediums. Convenient method gave the synthesis of benzoazetines with an unsubstituted amino group from *gem*-dihalo nitroalkenes which are readily prepared by sequential transformations of the commercially available trichloroethylene dimer.[48-51] the substituent ERG extremely plays an important role in syntheses of benzoazetines, in cases where this group was aniline, 4-aminobenzoic acid, 4-nitroaniline, 4-(trifluoromethyl)aniline, and 4-aminobenzonitrile attempts to synthesize benzoazetines were unsuccessful.




**3a**, X = Cl, R = H, ERG = hexyloxy
**3b**, X = Cl, R = H, ERG = octyloxy
**3c**, X = Br, R = H, ERG = hexyloxy
**3d**, X = Br, R = H, ERG = octyloxy

**5a**, X = Cl, ERG = hexyloxy
**5b**, X = Cl, ERG = octyloxy
**5c**, X = Br, ERG = hexyloxy
**5d**, X = Br, ERG = octyloxy

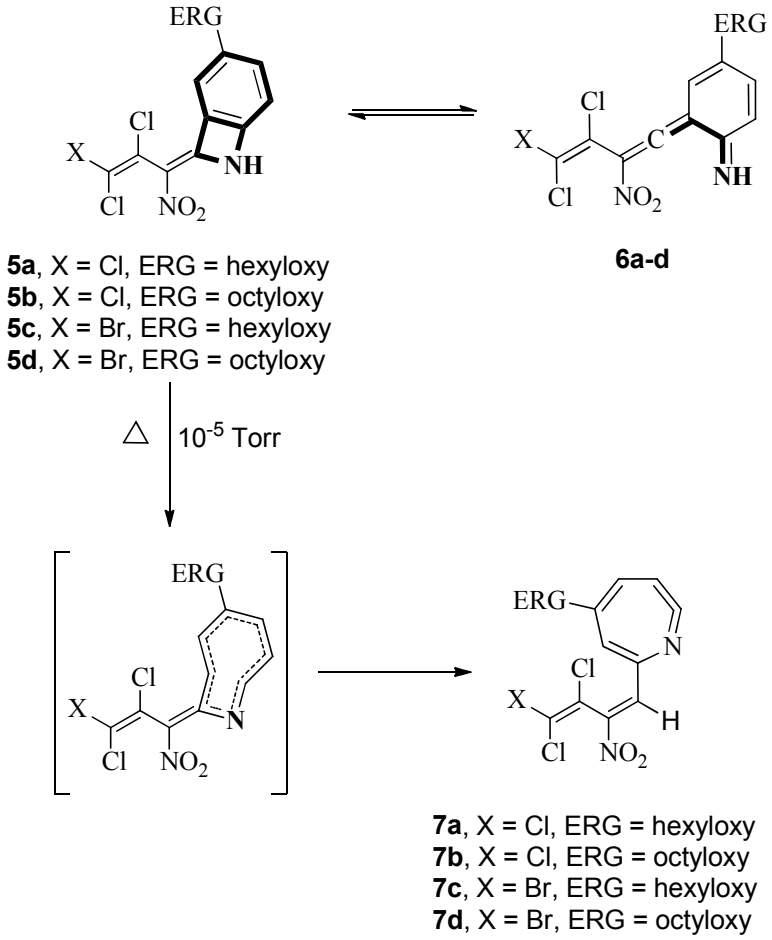
Scheme 3. Heterocyclization reactions of enamines **3a-d**.

Whereas five-, six-, and even four-membered ring systems are favored in ring constructions, the formation of seven-membered (hetero)cycles is generally more challenging due to the strain of the ring and entropic reasons.[52, 53] Very similar to five- and six-membered (hetero)cycles, there are several general methods to build up the seven-membered rings. Ring expansion, ring construction, ring-closing metathesis, isomerization, fragmentation, cycloaddition, and cyclization reactions are the most general methods.[54]

In the recent study, film-forming properties of obtained benzoazetines (**5a-d**) were investigated since heat application induces significant changes in their electronic absorption spectra.[55] During investigations on their film-forming properties, thermal vacuum evaporation (TVE) has applied on freshly synthesized benzoazetines (**5a-d**). Deposition of these structures at 150 °C and reduced pressure (1.6-1.2 x $10^{-5}$ Torr) gave rise to highly interesting compounds trapped in a chamber of the organic thin film evaporator. By TVE of 0.1 mmol (39.17-46.42 mg) samples of powdered benzoazetines (**5a-d**), mainly glossy films with a thickness of 0.62-0.74 μm that have a yellow hue have been obtained. The stability of the films at room temperature is low and varied from 1 to 5 days. Samples evaporated completely, with no residues. Application of heat under reduced pressure resulted in electrophilic ring opening to give unstable azacycloheptatetraene (**7a-d**). The reorganization of the molecules worked smoothly to give the heptatomic aromatic cycloheterocumulenes (**7a-d**). Certain isomerization of the benzoazetines and formation of the new cyclic system were observed in all compounds. The IR spectra of the obtained films were nearly similar to those of the corresponding initial samples. TVE of these compounds was accompanied by isomerization and the formation of the new cyclic system (**7a-d**).

Supposed that during the film-forming process of TVE, the benzoazetines are isomerized into the iminoketene tautomers (**6a-d**) on reversible reactions as shown in Scheme 4, as it occurs in the liquid phase for a number of benzoazetines in literature.[56, 57] According to these data, absence of some peaks on IR spectroscopy in the range of 1920-2020 $cm^{-1}$, typical for aliphatic cumulenes, and in the range of 3300-3400 $cm^{-1}$, because of stretching vibrations of >C=NH in the imine group did not matched with our results. Additionally, our findings on IR spectroscopy shows appearance of new absorption band on IR spectroscopy or growth of its intensity at around 1850 $cm^{-1}$ corresponding to the –N=C=C= of azacycloheptatetraene structure. The following scheme

(Scheme 4) of benzoazetine transformations is supposed to their TVE process on the basis of experimental data and literature.[58-60,61]




Scheme 4. Expected and obtained structures (**6a-d**) occurred during TVE process of benzoazetines **5a-d**.

## Conclusion

In summary, a straightforward synthesis of benzoazetines with an unsubstituted nitrogen atom (**5a-d**) have been developed by transamination reactions mediated by benzotriazole under mild conditions in good to excellent yields in the absence of any additives. To achieve this goal, easily leaving the property of benzotriazole was decisive in the synthesis process of highly strain

benzoazetines. Rearrangement of benzoazetines into heptatomic aromatic cycloheterocumulenes (azacyclohepta-1,2,4,6-tetraene) that is occurred at the stage of film-forming process by TVE has been shown by using IR spectroscopy.

**Experimental Section**

**General Information.** All reagents were commercially obtained commercial supplier and used without further purification unless otherwise noted. All solvents used in the reactions were distilled from appropriate drying agents prior to use according to standard procedures. Petroleum ether had a boiling range 40-60 °C. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254) based on Merck DC-plates (aluminum based). Visualization of the chromatogram was performed by UV light (254 nm). Column chromatographic separations were carried out using silica gel 60 (Merck, 63-200 μm particle sized, 60-230 mesh).

**Analysis.** $^{1}$H NMR and $^{13}$C NMR spectra were recorded either Varian$^{UNITY}$ INOVA spectrometers with 500 MHz frequency or Bruker Ultra Shield Plus with 400 MHz for $^{1}$H and 125 MHz frequency for $^{13}$C NMR in ppm ($\delta$) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. $^{1}$H NMR spectra and $^{13}$C NMR spectra in $CDCl_3$ refer to the solvent signal center at δ 7.26 and δ 77.0 ppm, respectively. Chemical shifts were reported in parts per million (ppm) and referenced in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: *s* (singlet), *br s* (broad singlet), *d* (doublet), *t* (triplet), and *m* (multiplet). Coupling constants *J* is given in Hz. IR spectra were recorded as ATR on Perkin Elmer Spectrum 100 UATR FTIR spectrometer. Microanalyses were carried out with a Carlo Erba Elemental Analyzer 1106. Mass spectra were obtained on either a Thermo Finnigan LCQ Advantage MAX MS/MS spectrometer equipped with an ESI (Electrospray

ionization) sources or a triple quadrupole mass spectrometer (LCMS-8030, Shimadzu). The LCMS-8030 triple quadrupole system was operated in the Q1 scan and Product Ion Scan modes using an electrospray ionization (ESI) source in the experiments presented here. Thermal vacuum evaporation was performed with a Vaksis Thin Film Evaporation system. Melting points (mp) were determined with an Electrothermal IA9000 series and were uncorrected.

**Procedure for Preparation of Bisbenzotriazolyl Derivatives (2a-c)**

**1,1'-(3,4,4-trichloro-2-nitrobuta-1,3-diene-1,1-diyl)bis(1*H*-benzo[*d*][1,2,3]triazole) (2a).** At room temperature, a solution of benzotriazole (5.26 g, 44.2 mmol) was added to a solution of **1a** (3 g, 11.05 mmol) in 50 mL THF. Subsequently, the mixture was stirred for 20 h and left overnight. THF was evaporated and the residue quenched with ice-water after adding 5 mL conc. HCl. The precipitate was observed immediately, aqueous layer was discarded. Organic part was taken into methanol, subsequently filtered and dried. 4.088 g, 85%, mp 137 – 138 °C (Lit.[42] 134 – 135 °C). Spectroscopic data are in accordance with reported previously.[42]

**1,1'-(4-bromo-3,4-dichloro-2-nitrobuta-1,3-diene-1,1-diyl)bis(1*H*-benzo[*d*][1,2,3]triazole) (2b).** At room temperature, a solution of benzotriazole (4.53 g, 38 mmol) was added to a solution of **2b** (3 g, 9.5 mmol) in 50 mL THF. Subsequently, the mixture was stirred for 24 h and left overnight. THF was evaporated and the residue quenched with ice-water after adding 5 mL conc. HCl. The precipitate was observed immediately, aqueous layer was discarded. Organic part was taken into methanol, subsequently filtered and dried. 3.565 g, 78%, mp 127 – 128 °C (Lit.[A] 124 – 126 °C). Spectroscopic data are in accordance with reported previously.[42]

**1,1'-(4-bromo-3,4-dichloro-2-nitrobuta-1,3-diene-1,1-diyl)bis(5-chloro-1*H*-benzo[*d*][1,2,3]triazole) (2c).** At room temperature, a solution of 5-chlorobenzotriazole (5.83 g,

38 mmol) was added to a solution of **1b** (3 g, 9.5 mmol) in 50 mL diethyl ether. Subsequently, the mixture was refluxed for 1 day and left overnight. The mixture was diluted with water. The organic layer was separated and washed with water (3 x 20 mL) and dried with $CaCl_2$ or $MgSO_4$. After evaporation of the solvent, the crude product was isolated after purification by column chromatography on silica gel as yellow solid. 2.606 g, 50%, mp 141 - 142.5 °C. IR (ATR) υ ($cm^{-1}$): 3085, 3065 ($CH_{aromatic}$), 1458, 1450 (C=C), 1590, 1245 ($NO_2$), 1077, 947. $^1H$ NMR (500 MHz, $CDCl_3$) δ = 7.29-7.38 (m, 2H, $CH_{aromatic}$), 7.69-7.87 (m, 2H, $CH_{aromatic}$), 8.26-8.36 (m, 2H, $CH_{aromatic}$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ = 115.89, 115.83, 118.13, 128.62, 129.33 ($CH_{aromatic}$), 114.85 (C4), 120.58 (C3), 132.67, 132.92, 141.26, 143.09, 149.41, 149.51 ($C_{aromatic}$), 135.41 (C2), 179.98 (C1). MS (ESI+): m/z (%) 574 (51, $[M+Na]^+$). Anal. Calcd. for $C_{16}H_6BrCl_4N_7O_2$ (549.981) (%): C, 34.94; H, 1.10; N, 17.83. Found (%): C, 35.15; H, 1.01; N, 18.06.

Alternatively, **2c** was prepared at room temperature by stirring for 1 day in THF and left overnight. The mixture was diluted with water. The organic layer was separated and washed with water (3 x 20 mL) and dried with $CaCl_2$ or $MgSO_4$. After evaporation of the solvent, the crude product was isolated after purification by column chromatography on silica gel as yellow solid. 3.920 g, 75%.

**General Experimental Method for Preparation of Amino Substituted Benzotriazolyl Derivatives (3a-e)**

**(*Z*)-N-(1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,4,4-trichloro-3-nitrobuta-1,3-dien-1-yl)-4-(hexyloxy)aniline (3a).** At 0 °C, 0.3 g (1.58 mmol) 4-(hexyloxy)aniline was added to a suspension of 0.66 g (1.50 mmol) **2a** in 10 mL MeOH. Subsequently, the mixture was stirred for 1 h at 0 °C and at room temperature for additional 8 h. The solvent was evaporated and the

residue dissolved in $CH_2Cl_2$ (20 mL). Water (50 mL) was added and the organic layer separated. The aqueous layer was then extracted with further portions of $CH_2Cl_2$ (3 × 25 mL), and the combined organic extracts were dried over $CaCl_2$ and evaporated to yield the product which could be further purified by column chromatography on silica gel as brown oil. 0.544 g, 71%. IR (ATR) υ ($cm^{-1}$): 3324 (NH), 3081, 3050 ($CH_{aromatic}$), 2961, 2924, 2854 ($CH_{aliphatic}$), 1651, 1467, 1452 (C=C), 1510, 1365, 1261 ($NO_2$), 1096, 1024, 800. $^1$H NMR (500 MHz, $CDCl_3$) δ = 0.84 (t, $^3$J = 6.83 Hz, 3H, $CH_3$), 1.15-1.42 (m, 6H, $(CH_2)_3$), 1.74 (p, 2H, $CH_2$), 3.97 (t, $^3$J = 6.83 Hz, 2H, $OCH_2$), 7.34-7.36 (m, 3H, $CH_{aromatic}$), 7.40-7.46 (m, 3H, $CH_{aromatic}$), 7.73-7.75 (m, 2H, $CH_{aromatic}$), 7.79 (broad s, 1 H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 12.99 ($CH_3$), 24.64, 27.95, 28.68, 30.51 $(CH_2)_4$, 67.94 ($OCH_2$), 101.24 (C4), 116.71 (C3), 124.18, 125.04, 127.03, 129.46 ($CH_{aromatic}$), 113.97, 130.99, 138.09, 155.58 ($C_{aromatic}$), 137.73 (C2), 156.62 (C1). MS (ESI+): m/z (%) 337 (100, $[M\text{-Bzt-}C_4H_9]^+$). Anal. Calcd. for $C_{22}H_{22}Cl_3N_5O_3$ (510.801) (%): C, 51.73; H, 4.34; N, 13.71. Found (%): C, 51.57; H, 4.30; N, 13.96.

**(*Z*)-N-(1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2,4,4-trichloro-3-nitrobuta-1,3-dien-1-yl)-4-(octyloxy)aniline (3b).** According to general experimental method with **2a** (1.16 mmol) and 4-(octyloxy)aniline (1.22 mmol). 0.4206 g, 67%. IR (ATR) υ ($cm^{-1}$): 3225 (NH), 3054 ($CH_{aromatic}$), 2961, 2924, 2853 ($CH_{aliphatic}$), 1672, 1531, 1465 (C=C), 1509, 1358, 1261, 1210 ($NO_2$), 1096, 1023, 704. $^1$H NMR (500 MHz, $CDCl_3$) δ = 0.82 (t, $^3$J = 6.83 Hz, 3H, $CH_3$), 1.19-1.40 (m, 10H, $(CH_2)_5$), 1.65 (p, 2H, $CH_2$), 3.96 (t, $^3$J = 6.83 Hz, 2H, $OCH_2$), 7.09-7.24 (m, 3H, $CH_{aromatic}$), 7.36-7.45 (m, 3H, $CH_{aromatic}$), 7.73-7.75 (m, 2H, $CH_{aromatic}$), 7.80 (broad s, 1 H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 13.06 ($CH_3$), 21.62, 24.97, 28.19, 28.29, 28.69, 30.78 $(CH_2)_6$, 67.93 ($OCH_2$), 101.19 (C4), 116.70 (C3), 121.93, 125.47, 127.08, 129.47 ($CH_{aromatic}$), 113.86, 126.96, 131.00, 155.55 ($C_{aromatic}$), 129.01 (C2), 156.63 (C1). MS (ESI+): m/z (%) 383 (59, $[M\text{-Bzt-Cl}]^+$). Anal.

Calcd. for $C_{24}H_{26}Cl_3N_5O_3$ (538.854) (%): C, 53.49; H, 4.86; N, 13.00. Found (%): C, 53.15; H, 4.70; N, 12.87.

**N-((*Z*)-1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-4-bromo-2,4-dichloro-3-nitrobuta-1,3-dien-1-yl)-4-(hexyloxy)aniline (3c).** According to general experimental method with **2b** (0.71 mmol) and 4-(hexyloxy)aniline (0.75 mmol). 0.3101 g, 79%, mp 113 - 115 °C. IR (ATR) υ ($cm^{-1}$): 3325 (NH), 3045 ($CH_{aromatic}$), 2961, 2924, 2856 ($CH_{aliphatic}$), 1659, 1489, 1449 (C=C), 1529, 1361, 1262 ($NO_2$), 1100, 1020, 802. $^1$H NMR (500 MHz, $CDCl_3$) δ = 0.85 (t, $^3$J = 6.83 Hz, 3H, $CH_3$), 1.14-1.44 (m, 6H, $(CH_2)_3$), 1.76 (p, 2H, $CH_2$), 3.99 (t, $^3$J = 6.83 Hz, 2H, $OCH_2$), 7.26 (d, $^3$J = 2.44 Hz, 1H, $CH_{aromatic}$), 7.28 (d, $^3$J = 2.93 Hz, 1H, $CH_{aromatic}$), 7.45-7.50 (m, 4H, $CH_{aromatic}$), 7.67 (t, $^3$J = 2.93 Hz, 2H, $CH_{aromatic}$), 7.92 (broad s, 1 H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 13.03 ($CH_3$), 21.57, 24.64, 27.90, 30.49 $(CH_2)_4$, 68.04 ($OCH_2$), 100.43 (C4), 117.64 (C3), 123.81, 125.32, 126.40, 130.87 ($CH_{aromatic}$), 114.00, 130.81, 134.43, 154.58 ($C_{aromatic}$), 133.44 (C2), 155.91 (C1). MS (ESI+): m/z (%) 553 (16, $[M]^+$), 517 (100, $[M\text{-}Cl]^+$), 435 (27, $[M\text{-}bzt]^+$). Anal. Calcd. for $C_{22}H_{22}BrCl_2N_5O_3$ (555.252) (%): C, 47.59; H, 3.99; N, 12.61. Found (%): C, 47.57; H, 4.28; N, 12.87.

**N-((*Z*)-1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-4-bromo-2,4-dichloro-3-nitrobuta-1,3-dien-1-yl)-4-(octyloxy)aniline (3d).** According to general experimental method with **2b** (0.73 mmol) and 4-(octyloxy)aniline (0.77 mmol). 0.348 g, 82%, mp 128 - 130 °C. IR (ATR) υ ($cm^{-1}$): 3280 (NH), 3010 ($CH_{aromatic}$), 2960, 2922, 2852 ($CH_{aliphatic}$), 1643, 1492, 1456 (C=C), 1531, 1364, 1261 ($NO_2$), 1105, 1030, 796. $^1$H NMR (500 MHz, $CDCl_3$) δ = 0.82 (t, $^3$J = 7.32 Hz, 3H, $CH_3$), 1.17-1.44 (m, 10H, $(CH_2)_5$), 1.76 (p, 2H, $CH_2$), 3.98 (t, $^3$J = 6.34 Hz, 2H, $OCH_2$), 7.27 (d, $^3$J = 2.92 Hz, 1H, $CH_{aromatic}$), 7.29 (d, $^3$J = 2.44 Hz, 1H, $CH_{aromatic}$), 7.49-7.50 (m, 4H, $CH_{aromatic}$), 7.67 (t, $^3$J = 2.93 Hz, 2H, $CH_{aromatic}$), 7.96 (broad s, 1 H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 14.33

($CH_3$), 22.88, 26.21, 29.18, 29.44, 29.52, 32.03 $(CH_2)_6$, 69.28 ($OCH_2$), 101.65 (C4), 118.94 (C3), 120.27, 122.26, 126.60, 132.06 ($CH_{aromatic}$), 113.62, 132.12, 135.64, 155.87 ($C_{aromatic}$), 134.65 (C2), 157.15 (C1). MS (ESI+): m/z (%) 606 (20, $[M+Na]^+$), 545 (46, $[M-Cl]^+$), 534 (22, $[M-NO_2]^+$), 465 (100, $[M-bzt]^+$). Anal. Calcd. for $C_{24}H_{26}BrCl_2N_5O_3$ (583.305) (%): C, 49.42; H, 4.49; N, 12.01. Found (%): C, 49.65; H, 4.60; N, 11.78.

**N-((*Z*)-4-bromo-2,4-dichloro-1-(5-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)-3-nitrobuta-1,3-dien-1-yl)-4-methoxyaniline (3e).** According to general experimental method with **2c** (0.36 mmol) and 4-methoxyaniline (0.38 mmol). 0.1392 g, 74%. IR (ATR) υ ($cm^{-1}$): 3483, 3409 (NH), 3045 ($CH_{aromatic}$), 2786 ($CH_{aliphatic}$), 1655, 1493 (C=C), 1361, 1281, 1200 ($NO_2$), 797. $^1H$ NMR (500 MHz, $CDCl_3$) δ = 3.86 (s, 3H, $OCH_3$), 7.29 (d, $^3J$ = 2.93 Hz, 1H, $CH_{aromatic}$), 7.31 (d, $^3J$ = 2.44 Hz, 1H, $CH_{aromatic}$), 7.35 (d, $^3J$ = 1.95 Hz, 1H, $CH_{aromatic}$), 7.36 (d, $^3J$ = 1.47 Hz, 1H, $CH_{aromatic}$), 7.52 (d, $^3J$ = 9.27 Hz, 2H, $CH_{aromatic}$), 7.71 (t, $^3J$ = 2.93 Hz, 2H, $CH_{aromatic}$), 7.81 (s, 1H, $CH_{aromatic}$), 7.83 (broad s, 1 H, NH). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ = 55.11 ($OCH_3$), 99.94 (C4), 115.69 (C3), 117.65, 123.58, 125.42, 126.17 ($CH_{aromatic}$), 112.55, 125.41, 130.84, 134.57, 154.55 ($C_{aromatic}$), 131.69 (C2), 156.42 (C1). MS (ESI+): m/z (%) 515 (100, $[M-H]^+$), 483 (30, $[M-Cl]^+$). MS (ESI+ MS/MS): m/z (%) 515 (45, $[M-H]^+$), 367 (61, $[M-(5\text{-chloro-bzt})]^+$), 335 (100, $[M-(5\text{-chloro-bzt})-OCH_3]^+$). Anal. Calcd. for $C_{17}H_{11}BrCl_3N_5O_3$ (519.564) (%): C, 39.30; H, 2.13; N, 13.48. Found (%): C, 38.95; H, 2.40; N, 13.71.

**General Experimental Method for Preparation of Benzoazetine Derivatives (5a-d)**

**(*Z*)-3-(hexyloxy)-8-(2,3,3-trichloro-1-nitroallylidene)-7-azabicyclo[4.2.0]octa-1(6),2,4-triene (5a).** A mixture of 0.21 g (0.41 mmol) **3a** and 20 mL glacial acetic acid was stirred for 15 h at 60 °C. It was then poured onto ice-water, and the precipitate immediately was filtered off, washed

with water, ether, and hexane. After drying in a vacuum, the crystallization was induced by adding cold chloroform-hexane mixture. 0.1401 g, 87%, mp 126 – 127.5 °C. IR (ATR) υ ($cm^{-1}$): 3302 (NH), 3189, 3105 ($CH_{aromatic}$), 2950, 2919, 2870, 2855 ($CH_{aliphatic}$), 1647, 1600, 1493, 1474, 1455 (C=C), 1529, 1389, 1361, 1277, 1227 ($NO_2$), 1105, 1024, 893, 868. $^1$H NMR (500 MHz, $CDCl_3$) δ = 0.84 (t, $^3$J = 6.83 Hz, 3H, $CH_3$), 1.16-1.44 (m, 6H, $(CH_2)_3$), 1.76 (p, 2H, $CH_2$), 3.98 (t, $^3$J = 6.83 Hz, 2H, $OCH_2$), 7.26-7.29 (m, 1H, $CH_{aromatic}$), 7.48 (d, $^3$J = 8.79 Hz, 1H, $CH_{aromatic}$), 7.66 (d, $^3$J = 2.92 Hz, 1H, $CH_{aromatic}$), 12.82 (broad s, 1 H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 13.00 ($CH_3$), 24.64, 27.92, 28.69, 30.50 $(CH_2)_4$, 68.06 ($OCH_2$), 100.44 (C4), 123.83 (C3), 117.69, 125.46, 126.71 ($CH_{aromatic}$), 123.85, 130.89, 154.74 ($C_{aromatic}$), 133.25 (C2), 155.91 (C1). MS (ESI+): m/z (%) 413 (11, $[M+Na]^+$), 391 (100, $[M+H]^+$). Anal. Calcd. for $C_{16}H_{17}Cl_3N_2O_3$ (391.030) (%): C, 49.06; H, 4.37; N, 7.15. Found (%): C, 48.62; H, 4.84; N, 7.11.

**(*Z*)-3-(octyloxy)-8-(2,3,3-trichloro-1-nitroallylidene)-7-azabicyclo[4.2.0]octa-1(6),2,4-triene (5b).** According to general experimental method with **3b** (0.93 mmol). 0.3272 g, 84%, mp 136 - 138 °C. IR (ATR) υ ($cm^{-1}$): 3302 (NH), 3196, 3079 ($CH_{aromatic}$), 2923, 2869, 2853 ($CH_{aliphatic}$), 1650, 1599, 1492, 1474, 1456 (C=C), 1531, 1389, 1364, 1278, 1228 ($NO_2$), 1108, 1022, 919, 827. $^1$H NMR (500 MHz, $CDCl_3$) δ = 0.82 (t, $^3$J = 7.32 Hz, 3H, $CH_3$), 1.19-1.44 (m, 10H, $(CH_2)_5$), 1.76 (p, 2H, $CH_2$), 3.99 (t, $^3$J = 6.83 Hz, 2H, $OCH_2$), 7.27-7.29 (m, 1H, $CH_{aromatic}$), 7.46 (d, $^3$J = 8.79 Hz, 1H, $CH_{aromatic}$), 7.67 (d, $^3$J = 2.93 Hz, 1H, $CH_{aromatic}$), 12.82 (broad s, 1 H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 13.07 ($CH_3$), 21.64, 24.97, 27.95, 28.28, 28.70, 30.79 $(CH_2)_6$, 68.08 ($OCH_2$), 100.49 (C4), 123.79 (C3), 117.61, 125.39, 126.75 ($CH_{aromatic}$), 130.91, 154.87 ($C_{aromatic}$), 133.27 (C2), 155.93 (C1). MS (ESI+): m/z (%) 441 (25, $[M+Na]^+$), 419 (100, $[M+H]^+$). Anal. Calcd. for $C_{18}H_{21}Cl_3N_2O_3$ (419.73) (%): C, 51.51; H, 5.04; N, 6.67. Found (%): C, 51.68; H, 4.99; N, 6.55.

**(*Z*)-8-(3-bromo-2,3-dichloro-1-nitroallylidene)-3-(hexyloxy)-7-azabicyclo[4.2.0]octa-1(6),2,4-triene (5c).** According to general experimental method with **3c** (0.35 mmol). 0.1445 g, 92%, mp 126 - 128 °C. IR (ATR) υ ($cm^{-1}$): 3421 (NH), 3138 ($CH_{aromatic}$), 2955, 2929, 2856 ($CH_{aliphatic}$), 1660, 1597, 1488, 1467, 1447 (C=C), 1529, 1386, 1361, 1267, 1225 ($NO_2$), 1106, 1019, 828, 802. $^1$H NMR (500 MHz, $CDCl_3$) δ = 0.83 (t, $^3J$ = 6.83 Hz, 3H, $CH_3$), 1.17-1.43 (m, 6H, $(CH_2)_3$), 1.75 (p, 2H, $CH_2$), 3.98 (t, $^3J$ = 6.83 Hz, 2H, $OCH_2$), 7.27-7.29 (m, 1H, $CH_{aromatic}$), 7.51 (d, $^3J$ = 9.27 Hz, 1H, $CH_{aromatic}$), 7.65 (t, $^3J$ = 2.92 Hz, 1H, $CH_{aromatic}$), 12.75 (broad s, 1 H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 13.00 ($CH_3$), 21.54, 24.62, 27.89, 30.47 $(CH_2)_4$, 68.00 ($OCH_2$), 100.37 (C4), 123.84 (C3), 112.29, 125.44, 130.77 ($CH_{aromatic}$), 121.10, 134.37, 154.38 ($C_{aromatic}$), 133.38 (C2), 155.84 (C1). MS (ESI+): m/z (%) 437 (100, $[M+H]^+$). Anal. Calcd. for $C_{16}H_{17}BrCl_2N_2O_3$ (436.128) (%): C, 44.06; H, 3.93; N, 6.42. Found (%): C, 44.21; H, 3.87; N, 6.17.

**(*Z*)-8-(3-bromo-2,3-dichloro-1-nitroallylidene)-3-(octyloxy)-7-azabicyclo[4.2.0]octa-1(6),2,4-triene (5d).** According to general experimental method with **3d** (0.34 mmol). 0.1432 g, 90%, mp 128 - 130 °C. IR (ATR) υ ($cm^{-1}$): 3304 (NH), 3198, 3154, 3087 ($CH_{aromatic}$), 2943, 2922, 2867, 2853 ($CH_{aliphatic}$), 1654, 1599, 1489, 1473, 1454 (C=C), 1531, 1387, 1364, 1275, 1226 ($NO_2$), 1107, 1021, 824, 796. $^1$H NMR (500 MHz, $CDCl_3$) δ = 0.82 (t, $^3J$ = 6.83 Hz, 3H, $CH_3$), 1.17-1.42 (m, 10H, $(CH_2)_5$), 1.76 (p, 2H, $CH_2$), 3.99 (t, $^3J$ = 6.83 Hz, 2H, $OCH_2$), 7.28-7.31 (m, 1H, $CH_{aromatic}$), 7.52 (d, $^3J$ = 8.78 Hz, 1H, $CH_{aromatic}$), 7.67 (t, $^3J$ = 2.93 Hz, 1H, $CH_{aromatic}$), 12.78 (broad s, 1 H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) δ = 13.09 ($CH_3$), 21.64, 24.97, 27.95, 28.20, 28.29, 30.79 $(CH_2)_6$, 68.03 ($OCH_2$), 100.35 (C4), 123.87 (C3), 113.93, 125.45, 130.87 ($CH_{aromatic}$), 123.83, 134.39, 154.45 ($C_{aromatic}$), 133.41 (C2), 155.87 (C1). MS (ESI+): m/z (%)

465 (100, $[M+H]^+$). Anal. Calcd. for $C_{18}H_{21}BrCl_2N_2O_3$ (464.181) (%): C, 46.58; H, 4.56; N, 6.04. Found (%): C, 46.37; H, 4.74; N, 6.44.

**Acknowledgments**

The author thanks the Board of Trustees of Beykent University for supplying the equipment and materials and Institute of Nanotechnology, Bilkent University for providing an instrument Vaksis Thin Film Evaporation system for thermal vacuum evaporation experiments.

**References**

1. V. A. Zapol'skii, X. N. Yang, J. C. Namyslo, M. Gjikaj and D. E. Kaufmann, *Synthesis*, 2012, 885-894.
2. C. Meyer, V. A. Zapol'skii, A. E. W. Adam and D. E. Kaufmann, *Synthesis*, 2008, 2575-2581.
3. (a) A. F. Tuyun, *Heterocycles*, 2013, **87**, 2589-2598; (b) A. F. Tuyun, *Tetrahedron Lett.*, 2014, **55**, 2085-2089.
4. (a) G. Aydinli, C. Sayil and C. Ibis, *Spectr. Lett.*, 2010, **43**, 44-50; (b) C. Ibis and A. F. Tuyun, *Phosphorus Sulfur Silicon Relat. Elem.*, 2012, **187**, 1161-1172.
5. (a) C. Ibis and H. Yildirim, *Phosphorus Sulfur Silicon Relat. Elem.*, 2009, **184**, 369-378; (b) C. Ibis and A. F. Tuyun, *Curr. Org. Synth.*, 2011, **8**, 861-871.
6. (a) C. Ibis, A. F. Tuyun and G. Aydinli, *Asian J. Chem.*, 2010, **22**, 1360-1368; (b) C. Ibis, A. F. Tuyun and G. Aydinli, *Phosphorus Sulfur Silicon Relat. Elem.*, 2010, **185**, 2014-2023.
7. Y. A. Oldekop, R. V. Kaberdin and V. I. Potkin, *Zh. Org. Khim.*, 1980, **16**, 543-547.
8. V. I. Potkin, V. A. Knizhnikov, R. V. Kaberdin and Y. A. Oldekop, *Zh. Org. Khim*, 1986, **22**, 86-89.
9. V. A. Zapol'skii, J. C. Namyslo, A. de Meijere and D. E. Kaufmann, *Beilstein J. Org. Chem.*, 2012, **8**, 621-628.
10. E. J. Vogt, V. A. Zapol'skii, E. Nutz and D. E. Kaufmann, *Z.Naturforsch.(B)*, 2012, **67**, 285-294.
11. E. Nutz, V. A. Zapol'skii and D. E. Kaufmann, *Synthesis*, 2009, 2719-2724.
12. V. A. Zapol'skii, J. C. Namyslo, C. Altug, M. Gjikaj and D. E. Kaufmanna, *Synthesis*, 2008, 304-310.
13. V. A. Zapol'skii, J. C. Namyslo, M. Gjikaj and D. E. Kaufmann, *Synlett*, 2007, 1507-1512.
14. V. A. Zapol'skii, J. C. Namyslo, B. Blaschkowski and D. E. Kaufmann, *Synlett*, 2006, 3464-3468.
15. E. J. Vogt, V. A. Zapol'skii, E. Nutz and D. E. Kaufmann, *Eur. J. Org. Chem.*, 2013, **2013**, 4285-4293.
16. V. A. Zapol'skii, J. C. Namyslo, A. E. W. Adam and D. E. Kaufmann, *Heterocycles*, 2004, **63**, 1281-1298.
17. V. A. Zapolskii, V. I. Potkin and R. V. Kaberdin, *Zh. Org. Khim.*, 1999, **35**, 469-473.

18. J. Barluenga and M. Tomas, *Adv. Heterocycl. Chem.*, 1993, **57**, 1-80.
19. M. Manoharan, F. De Proft and P. Geerlings, *J. Org. Chem.*, 2000, **65**, 7971-7976.
20. M. Manoharan, F. De Proft and P. Geerlings, *J. Chem. Soc. Perk. T. 2*, 2000, 1767-1773.
21. P. Y. Michellys, H. Pellissier and M. Santelli, *Org. Prep. Proced. Int.*, 1996, **28**, 545-&.
22. G. Mehta and S. Kotha, *Tetrahedron*, 2001, **57**, 625-659.
23. H. Meier, *J. Prak. Chem.-Chem. Ztg.*, 1996, **338**, 383-385.
24. H. Tomioka and T. Matsushita, *Chem. Lett.*, 1997, 399-400.
25. H. Kolshorn and H. Meier, *Z. Naturforsch., Teil A* 1977, **32**, 780-782.
26. E. M. Burgess and L. McCullagh, *J. Am. Chem. Soc.*, 1966, **88**, 1580.
27. V. I. Potkin and R. V. Kaberdin, *Khim. Geterotsiklicheskikh Soedin.*, 2007, 1763-1783.
28. M. Lancaster and D. J. H. Smith, *J. Chem. Soc.-Chem. Comm.*, 1980, 471-472.
29. W. Sander and J. Morawietz, *Tetrahedron Lett.*, 1993, **34**, 1913-1916.
30. C. M. Geise and C. M. Hadad, *J. Org. Chem.*, 2000, **65**, 8348-8356.
31. A. K. Sadana, R. K. Saini and W. E. Billups, *Chem. Rev.*, 2003, **103**, 1539-1602.
32. K. Okuma, T. Yasuda, K. Shioji and Y. Yokomori, *B. Chem. Soc. Jpn.*, 2007, **80**, 1824-1827.
33. K. Okuma, I. Takeshita, T. Yasuda and K. Shioji, *Chem. Lett.*, 2006, **35**, 1122-1123.
34. K. Kobayashi, K. Miyamoto, O. Morikawa and H. Konishi, *B. Chem. Soc. Jpn.*, 2005, **78**, 886-889.
35. P. Beak and G. W. Selling, *J. Org. Chem.*, 1989, **54**, 5574-5580.
36. K. K. Singal and J. Kaur, *Synth. Commun.*, 2001, **31**, 2809-2815.
37. V. I. Potkin, V. A. Zapol'skii, V. A. Knizhnikov, R. V. Kaberdin, A. A. Yanuchok and S. K. Petkevich, *Russ. J. Org. Chem.*, 2001, **37**, 689-694.
38. V. I. Potkin, V. A. Knizhnikov, A. A. Yanuchok and R. V. Kaberdin, *Russ. J. Org. Chem.*, 2001, **37**, 640-643.
39. G. Pfisterguillouzo, F. Gracian, A. Senio, M. Letulle and J. L. Ripoll, *Tetrahedron Lett.*, 1992, **33**, 5753-5756.
40. A. R. Katritzky and S. Rachwal, *Chem. Rev.*, 2011, **111**, 7063-7120.
41. A. R. Katritzky and S. Rachwal, *Chem. Rev.,* 2010, **110**, 1564-1610.
42. V. A. Zapolskii, V. I. Potkin, N. I. Nechai and R. V. Kaberdin, *Zh. Org. Khim.*, 1993, **29**, 885-888.
43. V. A. Zapolskii, V. I. Potkin, N. I. Nechai, R. V. Kaberdin and M. S. Pevzner, *Zh. Org. Khim.*, 1997, **33**, 1715-1720.
44. V. A. Zapolskii, V. I. Potkin, N. I. Nechai, R. V. Kaberdin and M. S. Pevzner, *Zh. Org. Khim.*, 1997, **33**, 1541-1547.
45. A.F. Tuyun, Tetrahedron Lett., 10.1016/j.tetlet.2014.02.038
46. V. A. Zapol'skii, J. C. Namyslo, M. Gjikaj and D. E. Kaufmann, *Z.Naturforsch.(B)*, 2010, **65**, 843-860.
47. V. I. Potkin, V. A.Zapol'skii, N. I. Nechai, R. V.Kaberdin, *Dokl. Akad. Nauk Belarusi,* 1996, **40**, 81–85
48. V. I. Potkin, R. V. Kaberdin and Y. A. Oldekop, *Zh. Org. Khim.*, 1986, **22**, 1389-1393.
49. R. V. Kaberdin, E. E. Nikolaeva, V. I. Potkin and Y. A. Oldekop, *Zh. Org. Khim.*, 1990, **26**, 2223-2224.
50. V. I. Potkin, V. I. Gogolinskii, N. I. Nechai, V. A. Zapolskii and R. V. Kaberdin, *Zh. Org. Khim.*, 1995, **31**, 1816-1822.

51. V. I. Potkin, V. A. Zapolsky and R. Y. Kaberdin, *Dokl. Akad. Nauk Belarusi*, 1996, **40**, 68-71.
52. F. Algi, T. Hokelek and M. Balci, *J. Chem. Res-S*, 2004, 658-660.
53. L. K. Sydnes, *Chem. Rev.*, 2003, **103**, 1133-1150.
54. T. V. Nguyen, J. M. Hartmann and D. Enders, *Synthesis*, 2013, 845-873.
55. A. A. Gabr, *Spectrochim. Acta A*, 1990, **46**, 1751-1757.
56. R. A. Olofson and R. K. Vandermeer, *J. Org. Chem.*, 1984, **49**, 3377-3379.
57. I. R. Dunkin, M. A. Lynch, R. Withnall, A. J. Boulton and N. Henderson, *J. Chem. Soc.-Chem. Comm.*, 1989, 1777-1778.
58. H. Tomioka, N. Ichikawa and K. Komatsu, *J. Am. Chem. Soc.*, 1993, **115**, 8621-8626.
59. A. Marcinek, E. Leyva, D. Whitt and M. S. Platz, *J. Am. Chem. Soc.*, 1993, **115**, 8609-8612.
60. A. Maltsev, T. Bally, M. L. Tsao, M. S. Platz, A. Kuhn, M. Vosswinkel and C. Wentrup, *J. Am. Chem. Soc.*, 2004, **126**, 237-249.
61. V. A. Azarko, V. I. Potkin, V. E. Agabekov, G. N. Lysenko, S. K. Petkevich, Y. K. Mikhailovskii, *Dokl. Akad. Nauk Belarusi*, 2007, **51**, 67–70.