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Synthesis of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles *via* NBS promoted addition of 1*H*-benzotriazole to alkene: Relevance in benzotriazole ring cleavage

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Graphical Abstract

Synthesis of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles *via* NBS promoted addition of 1*H*-benzotriazole to alkene: Relevance in Benzotriazole Ring Cleavage

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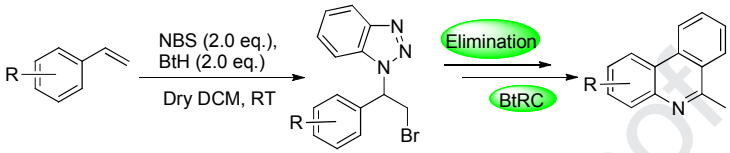
Mala Singh, Priyanka Bose, Anoop S. Singh, Vinod K. Tiwari*



A cost-effective and expeditious one-pot synthesis of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles has been devised by reacting styrene and their derivatives with 1*H*-benzotriazole in presence of *N*-bromosuccinimide in anhydrous CH_2Cl_2 at room temperature. Further, the resulted compounds undergo E_2-ellimination to afford the respective 1-(1-aryl-vinyl)-1*H*-benzotriazoles. At the end, 1-(1-phenylvinyl)-1*H*-benzotriazoles underwent benzotriazole ring cleavage (BtRC) under free radical condition to produce phenanthridine as the final product.

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Synthesis of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles *via* NBS promoted addition of 1*H*-benzotriazole to alkene: Relevance in Benzotriazole Ring Cleavage

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ABSTRACT

A cost-effective and expeditious one-pot synthesis of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles has been devised by reacting styrene and their derivatives with 1*H*-benzotriazole in presence of *N*-bromosuccinimide in anhydrous CH_2Cl_2 at room temperature. Further, the resulted compounds undergo E_2-ellimination to afford the respective 1-(1-aryl-vinyl)-1*H*-benzotriazoles. At the end, 1-(1-phenylvinyl)-1*H*-benzotriazoles underwent benzotriazole ring cleavage (BtRC) under free radical condition to produce phenanthridine as the final product.

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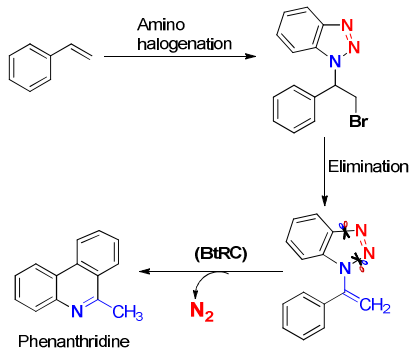
1. Introduction

Benzotriazole is pertaining significantly diverse role in organic chemistry since last four decades in the form of reagents, ligands, and intermediates to produce a large number of molecules having widespread applications.[1-3] The industrial applications in terms of utilizing the scaffold can be demonstrated as corrosion inhibitor and anti-tarnish agent for copper and its alloys[4] as fixing agents in photographic emulsions, as reagent in analytical determination of silver and use in anti-freeze and water coolant systems.[3] Remarkable bio-importance of benzotriazole moiety, such as, antibacterial, antifungal, antiviral, anti-inflammatory, antihypertensive, analgesic, etc., shows its broad relevance in the synthesis of biologically active compounds.[5-11] Molecules containing benzotriazole ring have also exhibited potential anti-tubercular,[12] anti-tumor,[13] anti-proliferative,[14] and anesthetic activities.[15] Benzotriazole ring cleavage (BtRC) methodology is one of the trending methods with the advantage of time as it is an interesting approach for an easy access to diverse series of compounds having pharmaceutical importance.[1-3,16-23] Pre-reported reaction conditions includes thermolysis, photolysis, organo-metallic reagents oxidants and free radical reagents, resulted in the desired cleavage of the relatively stable benzotriazole ring, exhibiting fascinating chemistry.[24-30] Economically effective, chemically stable and non-toxic nature of benzotriazole moiety makes it appreciable approach in the organic synthesis which has been explored to generate galaxy of libraries comprising of diverse scaffolds. Thus it plays important role in drug discovery and development.[31-43] Several research groups, most notably, the Katritzky group explored the interesting features of benzotriazole methodology since last four decades span. Previously, we also have employed BtRC approach for the synthesis of diverse benzothiazoles, benzoxazoles and amide derivatives.[18-23] Therefore, to achieve a new method to prepare benzotriazole-based reagents is of paramount importance, where benzotriazole ring cleavage has been successfully explored as a starting material in several reactions.[16-23] Herein, we wish to disclose a new synthetic protocol for the facile synthesis of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles from styrene. Further their representative application in benzotriazole ring cleavage (BtRC) aimed to respective phenanthridine under free radical condition (**Scheme 1)**.



Scheme 1. Overall synthetic route for the phenanthridine

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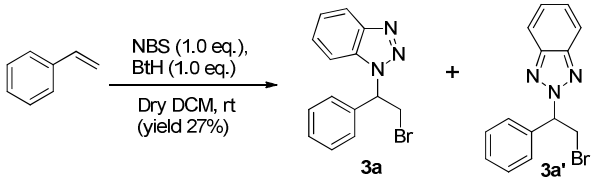
2. Results and Discussion

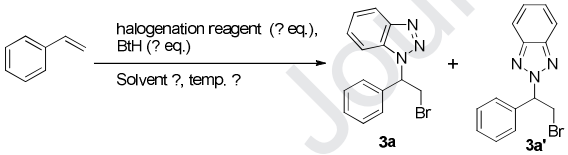
A prototype reaction for the synthesis of 1-(2-bromo-1-phenylethyl)-1*H*-benzotriazole **3a** and 1-(2-bromo-1-phenylethyl)-2*H*-benzotriazole **3a'** was set-up. For which styrene (1.0 equiv.) was treated with 1.0 equiv. of *N*-bromosuccinimide (NBS) in anhydrous dichloromethane and after 30 min, 1.0 eq. of 1*H*-benzotriazole was added and the reaction was further stirred for 5 hrs. White solid compounds **3a** and **3a´** were isolated in 27% yield **(Scheme 2)**.



Scheme 2. Prototype reaction for the synthesis of 1-(2-bromo-1-phenylethyl)-1*H* (**3a**) or 2*H*-benzotriazoles (**3b**)

Then after, we look forward for the optimization, thus the loading quantity of NBS and BtH were varied in the above prototype reaction in various solvent, where we get optimum reaction yield (90%) in entry 3. Further for the optimum reaction condition, other halogenation reagents such as I_2, NIS, NCS, KI, and KBr were trialed. The reagents NCS, NIS and I_2 provided average reaction yields, however, as expected KI and KBr failed to afford the desired product. Furthermore, in order to get the best optimum condition, we tried the reaction at high temperature and also for longer reaction time to improve the reaction yield of compound **3a,** where the result is again not the favorable one.

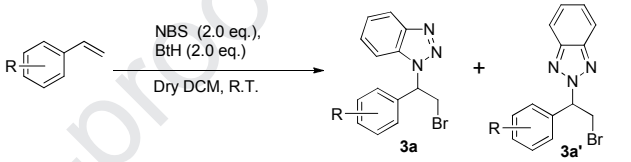
Table 1: Optimization for the synthesis of 1-(2-bromo-1-phenylethyl)-1*H*-benzotriazoles



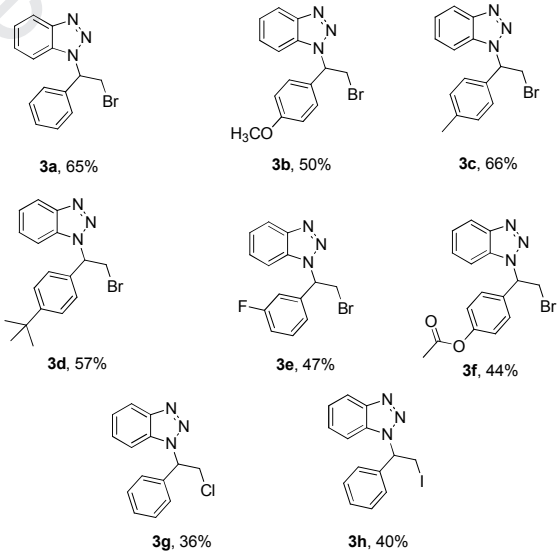
Entry[a]	Reagent (equiv.)	BtH (equiv.)	Solvent	Time	Yield[b] 3a + 3a'
1	NBS (1.0)	1.0	DCM	5	27%
2	NBS (1.5)	1.5	DCM	5	59%
3	**NBS (2.0)**	**2.0**	**DCM**	**5**	**90%**
4	NBS (2.5)	2.5	DCM	5	90%
5	NBS (2.0)	2.0	EtOAc	5	36%
6	NBS (2.0)	2.0	DMF	5	ND
7	NBS (2.0)	2.0	THF	5	10%
8	NBS (2.0)	2.0	CH_3OH	5	ND
9	NIS (2.0)	2.0	DCM	5	66%
10	NCS (2.0)	2.0	DCM	5	56%
11	I_2 (2.0)	2.0	DCM	5	40%
12	KBr (2.0)	2.0	DCM	5	ND
13	KI (2.0)	2.0	DCM	5	ND
14	NBS (2.0)	2.0	$CHCl_3$	5	80%
15	NBS (2.0)	2.0	CCl_4	5	55%
16	NBS (2.0)	2.0	EtOAc	5	36%
17	NBS (2.0)	2.0	DMF	5	ND
18	NBS (2.0)	2.0	THF	5	10%
19	NBS (2.0)	2.0	CH_3OH	5	ND
20[c]	NBS (2.0)	2.0	DCM	5	45%
21	NBS (2.0)	2.0	DCM	15	88%

Scope of Alkenes. [a]Reaction conditions: Styrene **1** (1.0 equiv.), benzotriazole **2** (X equiv.), NBS (Y equiv.), and anhydrous DCM (5 mL) at r.t. for 5 h. [b] Yield of isolated product (3a + 3a'). [c]reaction at 40 °C.

The best optimized condition for the 1-(2-bromo-1-phenylethyl)-1*H*-benzotriazoles established that involves the reaction of styrene (1.0 equiv.) with NBS (2.0 equiv.) and benzotriazole (2.0 equiv.) in anhydrous CH_2Cl_2 at room temperature for 5 hrs. Thus, we have established an efficient path for the amino-bromination of styrene after the standardization of the reaction condition (**Table 1**). The scope of styrene was explored at room temperature and the outcome has been summarized in **Figure 1**. Different derivatives of styrene such as electron-donating groups (methyl-, methoxy- and *t*-butyl-) and electron-withdrawing groups (chloro, fluoro and acetate) were used for the conversion and the product of amino-bromination was in good yield.



Developed 1-(2-bromo-1-phenylethyl)-1*H*-benzotriazoles (**3a-h**) *via* amino halogenation



Developed 1-(2-bromo-1-phenylethyl)-2*H*-benzotriazoles (**3a'-h'**) *via* amino halogination

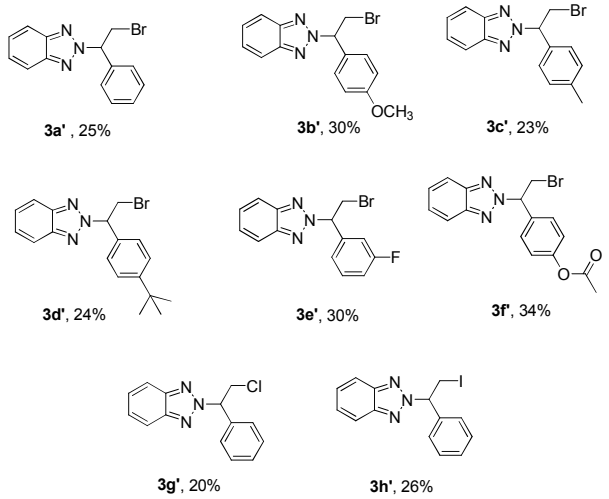


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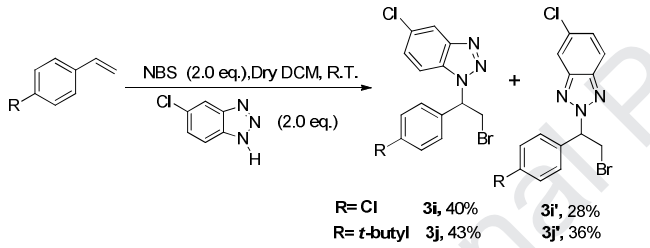
Figure 1: Scope of Alkenes. Reaction conditions: Styrene **1** (1.0 mmol), benzotriazole **2** (2.0 mmol), NBS (2.0 mmol), and anhydrous DCM (5 mL) at r.t. for 5 h. % Yield of isolated product after column chromatography (SiO_2).

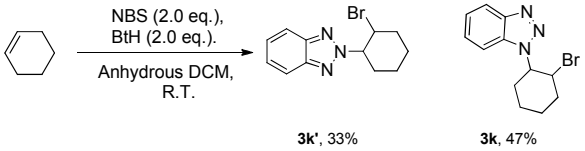
Styrene with different substituent, e.g. 4-methoxy, 4-methyl, 4-*t*-butyl has given the products in good yield (70-80%) where N1/N2 ratio was found to be around 1.5:1, here, N1 has been assigned for the yield of 1-(2-halo-1-phenylethyl)-1*H*-benzotriazoles and N2 has been assigned for the yield of 1-(2-halo-1-phenylethyl)-2*H*-benzotriazoles, respectively. The Chloro and acetate group at para position of styrene gave products in 68% and 78% yield respectively in which N1/N2 ratio was around to be 1.4:1. In case of 3-fluoro-styrene, the yield of the reaction was found to be 77% having N1/N2 (1.56:1).

For more exploration of the work, a set of benzotriazole derivatives were explored in the pre-established protocol (**Scheme 3**). When 5-chlorobenzotriazole was reacted with styrene having chloro and *t*-butyl at *p*- position, the reaction yield was 68% (N1/N2 ratio 1.42) and 79% (N1/N2 ratio 1.19), respectively.



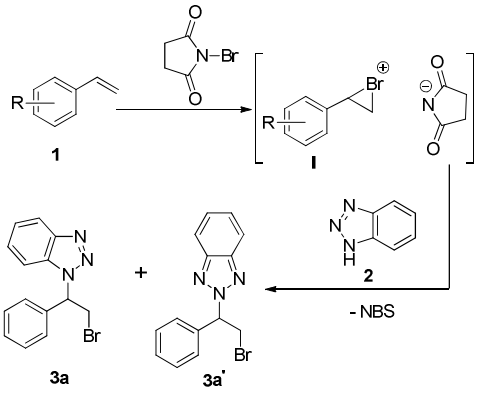
Scheme 3: Scope of reaction by varying substitution on benzotriazole ring.

Furthermore, by altering the aryl alkene with aliphatic alkene in the same reaction conditions same results have been achieved (**Scheme 4**).



Scheme 4: Scope of reaction by altering the aryl alkene with aliphatic alkene

Initially, the alkene substrate reacts with Br^+ to afford the bromonium ion intermediate **I**,[44-45] which undergoes regioselective ring opening. Further, it reacts with benzotriazole affording the desired bromo products **3**. The path of reaction proceed to the final product also has been evaluated through DFT analysis utilizing the zero point vibrational energy value supports the results obtained in the our protocol (see, the supporting information),



Scheme 5: Possible mechanism for synthesis of 1-(2-bromo-1-arylethyl)-1or 2*H*-benzotriazoles

Based on our previous experience of the benzotriazole ring cleavage, benzothiazole and benzamide were obtained from *N*-thioacyl benzotriazole and *N*-acyl benzotriazole, respectively through the cleavage of benzotriazole ring under the influence of free radical development (**Figure 2**), so we have interest to explore the resulted R(Bt)C=CH_2 in order to have the desired benz-fused heterocycle *i.e.* indole derivative, however to our surprise the isolated compound was phenanthridine, instead of the indole one.

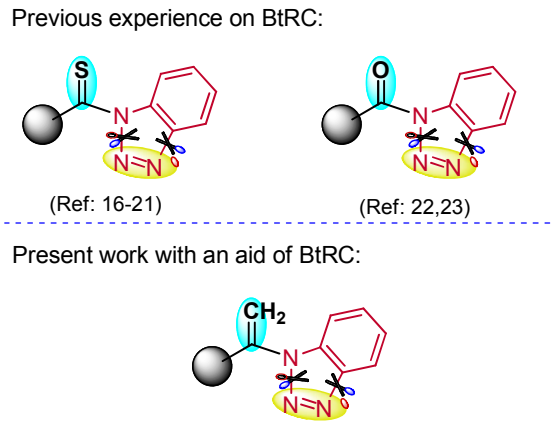


Figure 2: Exploration of benzotriazole ring cleavage (BtRC)

Thus, the end product, 1-(2-bromo-1-phenylethyl)-1*H*-benzotriazole **3a** also has been utilized for the synthesis of phenanthridine. For this, first of all E_2-ellimination on the 1-(2-bromo-1-phenylethyl)-1*H*-benzotriazole is carried out with the help of base for the formation of 1-(1-phenylvinyl)-1*H*-benzotriazole which when heated in seal tube with 2.0 equiv. of ^{n}BuSnH in presence of 0.2 equiv. of azobisisobutyronitrile (AIBN) in anhydrous toluene undergoes free radical benzotriazole ring opening to afford phenanthridine **5** as final product (**Scheme 6**).

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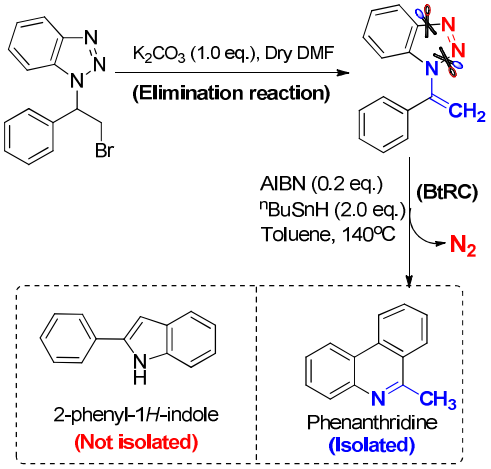

Scheme 6. Application of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles for the systematic formation of phenanthridine **5** *via* free radical reaction path.

Mechanistic consideration for BTRC:

The 1-(1-phenylethenyl)-1*H*-1,2,3-benzotriazole derivatives can easily proceed to ring cleavage by reaction with $^{n}Bu_3SnH$ in presence of azobisisobutyronitrile (AIBN), a well-known radical initiator. In such reactions, the 2-cyanoprop-2-yl radical generated from AIBN initiates the process by rapidly reacting with tin hydride to produce a tin radical, which attacks the vinylic system of 1-(1-phenylethenyl)-1*H*-1,2,3-benzotriazole **4** and propagates the reaction. Decomposition of 1-(1-phenylethenyl)-1*H*-1,2,3-benzotriazole *via* *N-N* bond cleavage through removal of the molecular nitrogen (N_2) followed by the rearrangement of the resulted biradical afforded species **B**. In the species **B**, free radical hydrogen abstracted from the another attached phenyl ring forms two phenyl radical centers as shown in species **C**.[46,47] At the end, both of the phenyl radicals in species **C** undergo cyclization to give the respective phenanthridine **5 (Figure 3)**. Moreover, the reaction carried out in presence of TEMPO, the final cyclized product was not obtained which further supports the free radical generation mechanism as presented in proposed reaction.

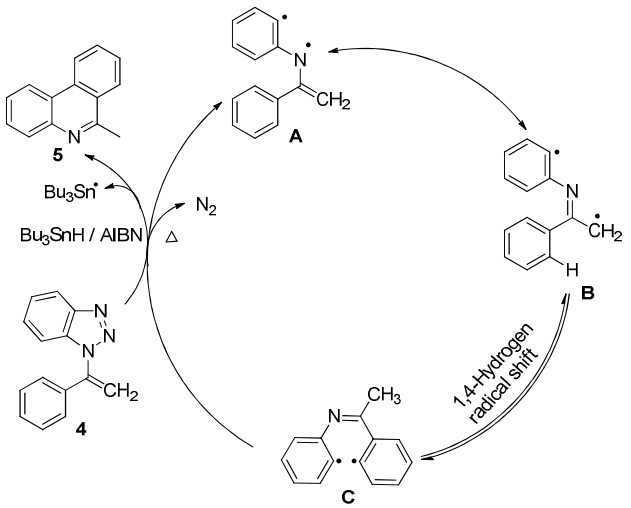

Figure 3. Plausible mechanism for the synthesis of phenanthridine **5**.

3. Conclusions

In conclusion, we have developed a practical synthesis of 1-(2-bromo-1-phenylethyl)-1*H*-benzotriazole using styrenes and 1*H*-benzotriazole, which further undergoes E_2-ellimination and free radical benzotriazole ring opening to produce phenanthridine. This approach is straightforward, easy to execute, and metal-free condition and thus can be explored in further investigation for the development of biologically relevant heterocycles.

4. Experimental

All the solvents and reagents were taken of pure grade. Thin-layer chromatography (TLC) was performed on, pre-coated aluminium plates and spots were evaluated using UltraViolet lamp (λ max = 254 nm). The solvents were evaporated at temperature < 50°C. Column chromatography was carried out using silica gel (230-400 mesh, Merck). Distilled *n*-hexane and ethyl acetate were used for the column chromatography. ^{1}H and ^{13}C NMR were recorded at 500 and 125 MHz, respectively. The chemical shifts are given in ppm downfield from internal TMS; *J* values in Hz. The Infrared spectra have been recorded as Nujol mulls in KBr palettes.

General procedure for synthesis of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles

Styrene (1.0 equiv.) in anhydrous dichloromethane (5 mL) and NBS (2.0 equiv.) was taken into RB and reaction mixture was stirred at room temperature. After 30 mins benzotriazole (2.0 equiv) dissolved in anhydrous DCM was added drop wise to the reaction mixture. After the completion of reaction as monitored by TLC, solvent was evaporated under vacuum. The reaction mixture was extracted with ethyl acetate and washed with hypo and brine solution. The organic layer obtained was dried over sodium sulphate, filtered and then evaporated under reduced pressure. Further purification was done by using flash column chromatography (SiO_2).

1-(2-Bromo-1-phenylethyl)-*1H*-benzo[d][1,2,3]triazole (3a). White Solid, yield: 188mg (65%); R_f = 0.3 (5% ethyl acetate/*n*- hexane); m.p. = 130-134°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J = 8.5Hz,* 1H), 7.43-7.40 (m, 4H), 7.36-7.34 (m, 4H), 6.02 (dd, *J = 5.5Hz, 3.5Hz,* 1H), 4.66 (t, *J = 10.5Hz,* 1H), 4.16 (dd, *J = 5.5Hz, 5.0Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 136.7, 133.2, 129.3, 129.2, 127.7, 127.0, 124.2, 120.2, 109.4, 64.9 and 32.8 ppm; HRMS m/z (M + H) calcd for $C_{14}H_{13}BrN_3$ 302.0214; Found, 302.0275.

2-(2-Bromo-1-phenylethyl)-*2H*-benzo[d][1,2,3]triazole (3a'). White Solid, yield: 72mg (25%); R_f = 0.7 (5% ethyl acetate/*n*-hexane); m.p. = 100-104°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90-7.88 (m, 2H), 7.49-7.47 (m, 2H), 7.39-7.34 (m, 5H), 6.22 (dd, *J = 4.5Hz, 5.5Hz,* 1H), 4.60 (t, *J = 10.5Hz,* 1H), 4.06 (dd, *J = 4.5Hz, 6.0Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 136.6, 129.4, 129.1, 127.1, 126.7, 118.4, 72.2 and 32.6 ppm.

1-(2-Bromo-1-(4-methoxyphenyl)ethyl)-*1H*-benzo[d][1,2,3]triazole (3b). oily, yield: 123mg (50%); R_f = 0.4 (10% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, *J*

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= 8.1Hz, 1H), 7.42-7.40 (m, 2H), 7.35-7.32 (m, 3H), 6.84 (d, *J = 8.7Hz, 2*H), 6.01-5.96 (m, 1H), 4.62 (t, *J = 10.2Hz,* 1H), 4.15-4.09 (m, 1H), 3.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9, 145.8, 132.9, 128.5, 128.1, 127.4, 123.9, 119.8, 114.3, 109.3, 64.1, 55.1 and 32.8 ppm; HRMS m/z (M + H) calcd for $C_{15}H_{15}BrN_3O$ 332.0320; Found, 332.0404.

2-(2-Bromo-1-(4-methoxyphenyl)ethyl)-*2H*-benzo[d][1,2,3]triazole (3b'). White Solid, yield: 74mg (30%); R_f = 0.7 (10% ethyl acetate/*n*-hexane); m.p. = 64-68°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88-7.86 (m, 2H), 7.44-7.33 (m, 4H), 6.86-6.83 (m, 2H), 6.18-6.17 (m, 1H), 4.57 (t, *J = 10.5Hz,* 1H), 4.05-4.01 (m, 1H), 3.72 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1, 144.2, 128.5, 128.3, 126.4, 118.4, 114.2, 71.5, 55.1 and 32.7 ppm.

1-(2-Bromo-1-(p-tolyl)ethyl)-*1H*-benzo[d][1,2,3]triazole (3c). oily, yield: 176mg (66%); R_f = 0.5 (10% ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09-8.05 (m, 1H), 7.42-7.36 (m, 2H), 7.34-7.28 (m, 3H), 7.15-7.12 (m, 2H), 6.03-5.97 (m, 1H), 4.69-4.60 (m, 1H), 4.18-4.11 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.9, 139.1, 133.5, 133.0, 129.7, 127.4, 126.7, 124.0, 119.9, 109.3, 64.5, 32.7 and 21.0 ppm; HRMS m/z (M + H) calcd for $C_{15}H_{15}BrN_3$ 316.0371; Found, 316.0448.

2-(2-Bromo-1-(p-tolyl)ethyl)-*2H*-benzo[d][1,2,3]triazole (3c'). White Solid, yield: 61mg (23%); R_f = 0.8 (10% ethyl acetate/*n*-hexane); m.p. = 74-76°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87-7.84 (m, 2H), 7.36-7.28 (m, 4H), 7.09 (d, *J = 7.8Hz,* 2H), 6.22-6.17 (m, 1H), 4.58 (t, *J = 10.5Hz,* 1H), 4.05-4.01 (m, 1H), 2.23 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.1, 139.0, 133.4, 129.4, 126.8, 126.3, 118.1, 71.6, 32.7 and 20.9 ppm.

1-(2-Bromo-1-(4-(*tert*-butyl)phenyl)ethyl)-*1H*-benzo[d][1,2,3]triazole (3d).White Solid, yield: 127mg (57%); R_f = 0.4 (5% ethyl acetate/*n*-hexane); m.p. = 134-136°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J = 8.5Hz,* 1H), 7.39-7.34 (m, 2H), 7.29-7.25 (m, 5H), 5.94 (dd, *J = 5.0Hz, 5.5Hz,* 1H), 4.59 (t, *J = 10.5Hz,* 1H), 4.06 (dd, *J = 4.5Hz, 6.0Hz,* 1H), 1.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 146.0, 133.7, 133.3, 127.6, 126.7, 126.2, 124.2, 120.2, 109.4, 64.7, 34.7, 32.9 and 31.2 ppm; HRMS m/z (M + H) calcd for $C_{18}H_{21}BrN_3$ 358.0840; Found, 357.0896.

2-(2-Bromo-1-(4-(*tert*-butyl)phenyl)ethyl)-*2H*-benzo[d][1,2,3]triazole (3d'). Oily, yield: 53mg (24%); R_f = 0.8 (5% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81-7.77 (m, 2H), 7.33-7.31 (m, 2H), 7.29-7.26 (m, 4H), 6.12 (dd, *J = 5.0Hz, 5.5Hz,* 1H), 4.52 (t, *J = 10.5Hz,* 1H), 3.96 (dd, *J = 5.0Hz, 5.5Hz,* 1H), 1.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 144.3, 133.6, 126.8, 126.6, 126.1, 118.4, 72.0, 34.7, 32.8 and 31.2 ppm.

1-(2-Bromo-1-(3-fluorophenyl)ethyl)-*1H*-benzo[d][1,2,3]triazole (3e).White Solid, yield: 123mg (47%); R_f = 0.3 (5% ethyl acetate/*n*-hexane); m.p. = 68-72°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J = 8.0Hz,* 1H), 7.48-7.31 (m, 4H), 7.21 (d, *J = 8.5Hz,* 1H), 7.15-7.13 (m, 1H), 7.05-7.01 (m, 1H), 6.01 (dd, *J = 5.5Hz, 5.0Hz,* 1H), 4.64-4.59 (m, 1H), 4.17 (dd, *J = 5.5Hz, 5.5Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8, 161.8, 145.8, 138.9, 138.8, 133.0, 130.8, 130.7, 127.8, 124.3, 122.7, 122.6, 120.1, 116.3, 116.2, 114.2, 114.0, 109.0, 64.0 and 32.2 ppm; HRMS m/z (M + H) calcd for $C_{14}H_{12}BrN_3$ 320.0120; Found, 320.0187.

2-(2-Bromo-1-(3-fluorophenyl)ethyl)-*2H*-benzo[d][1,2,3]triazole (3e'). White Solid, yield: 78mg (30%); R_f = 0.7 (5% ethyl acetate/*n*-hexane); m.p. = 76-78°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90-7.88 (m, 2H), 7.40-7.38 (m, 2H), 7.34-7.20 (m, 3H), 7.04-7.01 (m, 1H), 6.21 (dd, *J = 5.0Hz, 4.5Hz,* 1H), 4.55 (t, *J = 10.5Hz,* 1H), 4.06 (dd, *J = 4.5Hz, 6.0Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7, 161.7, 144.3, 138.66, 138.6, 130.67, 130.6, 126.7, 122.9, 122.8, 118.2, 116.4, 116.2, 114.3, 114.1, 71.2 and 32.1 ppm.

4-(1-(*1H*-benzo[d][1,2,3]triazol-1-yl)-2-bromoethyl) phenyl acetate (3f). White Solid, yield: 97mg (44%); R_f = 0.3 (10% ethyl acetate/*n*-hexane); m.p. = 148-152°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, *J = 8.5Hz,* 1H), 7.49-7.43 (m, 4H), 7.39-7.35 (m, 1H), 7.12-7.10 (m, 2H), 6.08 (dd, *J = 5.0Hz, 4.5Hz,* 1H), 4.64 (t, *J = 10.5Hz,* 1H), 4.15 (dd, *J = 5.0Hz, 5.5Hz,* 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.0, 150.9, 145.6, 133.9, 132.9, 128.0, 127.6, 124.1, 122.2, 119.8, 109.1, 63.8, 32.5 and 20.8 ppm; HRMS m/z (M + H) calcd for $C_{16}H_{15}BrN_3O_2$ 360.0269; Found, 360.0326.

4-(1-(*2H*-benzo[d][1,2,3]triazol-2-yl)-2-bromoethyl) phenyl acetate (3f'). White Solid, yield: 75mg (34%); R_f = 0.6 (10% ethyl acetate/*n*-hexane); m.p. = 126-130°C; mol. Formula = $C_{16}H_{14}BrN_3O_2$; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88-7.86 (m, 2H), 7.53-7.50 (m, 2H), 7.39-7.37 (m, 2H), 7.09-7.06 (m, 2H), 6.21 (dd, *J = 4.5Hz, 6.0Hz,* 1H), 4.57 (t, *J = 10.5Hz,* 1H), 4.03 (dd, *J = 4.5Hz, 6.5Hz,* 1H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 151.3, 144.4, 134.0, 128.4, 126.8, 122.3, 118.4, 71.5, 32.5 and 21.1 ppm.

1-(2-Chloro-1-phenylethyl)-*1H*-benzo[d][1,2,3]triazole (3g). White Solid, yield: 88mg (36%); R_f = 0.5 (10% ethyl acetate/*n*-hexane); m.p. = 118-122°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J = 7.5Hz,* 1H), 7.42-7.37 (m, 4H), 7.32-7.28 (m, 4H), 6.00 (dd, *J = 6.5Hz, 4.0Hz,* 1H), 4.80-4.76 (m, 1H), 4.28 (dd, *J = 4.5Hz, 7.0Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.0, 136.1, 133.3, 129.3, 129.2, 127.8, 127.1, 124.3, 120.1, 109.5, 64.9 and 45.5 ppm; HRMS m/z (M + H) calcd for $C_{14}H_{13}ClN_3$ 258.0719; Found, 258.0782.

2-(2-Chloro-1-phenylethyl)-*2H*-benzo[d][1,2,3]triazole (3g'). White Solid, yield: 49mg (20%); R_f = 0.8 (10% ethyl acetate/*n*-hexane); m.p. = 78-82°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89-7.87 (m, 2H), 7.48-7.46 (m, 2H), 7.38-7.31 (m, 5H), 6.19 (dd, *J = 6.0Hz, 4.5Hz,* 1H), 4.78-4.64 (m, 1H), 4.20 (dd, *J = 5.0Hz, 6.5Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 135.8, 129.2, 129.0, 127.1, 126.5, 118.2, 72.1 and 45.4 ppm.

1-(2-Iodo-1-phenylethyl)-*1H*-benzo[d][1,2,3]triazole (3h). White Solid, yield: 134mg (40%); R_f = 0.4 (5% ethyl acetate/*n*-hexane); m.p. = 132-134°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J = 7.5Hz,* 1H), 7.36-7.24 (m, 8H), 5.89 (dd, *J = 5.5Hz, 5.0Hz,* 1H), 4.37 (t, *J = 10.5Hz,* 1H), 3.94 (dd, *J = 5.0Hz, 5.5Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 137.5, 133.1, 129.3, 129.2, 127.7, 126.8, 124.2, 120.2, 109.4, 65.5 and 5.2 ppm; HRMS m/z (M + H) calcd for $C_{14}H_{13}IN_3$ 350.0075; Found, 350.0139.

2-(2-Iodo-1-phenylethyl)-*2H*-benzo[d][1,2,3]triazole (3h'). White Solid, yield: 87mg (26%); R_f = 0.8 (5% ethyl acetate/*n*-hexane); m.p. = 126-130°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89-7.87 (m, 2H), 7.48 (d, *J = 7.5Hz,* 2H), 7.39-7.31 (m, 5H), 6.19 (dd, *J = 5.5Hz, 5.0Hz,* 1H), 4.38 (t, *J = 11.5Hz,* 1H),

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3.94 (dd, *J = 5.5Hz, 6.0Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 137.4, 129.3, 129.1, 126.9, 126.7, 118.4, 72.8 and 4.9 ppm.

1-(2-Bromo-1-(4-chlorophenyl)ethyl)-5-chloro-*1H*-benzo [d][1,2,3]triazole (3i). Semi solid, yield: 107mg (40%); R_f = 0.3 (3% ethyl acetate/n-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06-8.05 (m, 1H), 7.42-7.40 (m, 1H), 7.33-7.30 (m, 5H), 5.92 (dd, *J = 5.5Hz, 4.0Hz,* 1H), 4.56 (t, *J = 10.5Hz,* 1H), 4.11 (dd, *J = 5.0Hz, 5.5Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.6, 135.6, 134.7, 130.3, 129.6, 128.9, 128.4, 127.4, 119.7, 110.1, 64.4 and 32.0 ppm; HRMS m/z (M + H) calcd for $C_{14}H_{11}BrCl_2N_3$ 368.9435; Found, 369.9501.

2-(2-Bromo-1-(4-chlorophenyl)ethyl)-5-chloro-*2H*-benzo [d][1,2,3]triazole (3i'). Oily, yield: 75mg (28%); R_f = 0.7 (3% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.75 (m, 1H), 7.69 (d, *J = 9.5Hz,* 1H), 7.30 (d, *J = 9.5Hz,* 2H), 7.22-7.19 (m, 3H), 6.06 (dd, *J = 5.5Hz, 4.5Hz,* 1H), 4.39 (t, *J = 10.5Hz,* 1H), 3.91 (dd, *J = 5.0Hz, 5.5Hz,* 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.7, 142.9, 135.6, 134.7, 132.8, 129.4, 128.6, 128.5, 119.6, 117.5, 71.5 and 32.2 ppm.

1-(2-Bromo-1-(4-(*tert*-butyl)phenyl)ethyl)-5-chloro-*1H*-benzo[d][1,2,3]triazole (3j) White Solid, yield: 105mg (43%); R_f = 0.5 (10% ethyl acetate/*n*-hexane); m.p. = 118-122^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J = 8.5Hz,* 1H), 7.41-7.30 (m, 6H), 5.89 (dd, *J = 6.0Hz, 4.5Hz,* 1H), 4.65-4.61 (m, 1H), 4.09-4.07 (m, 1H), 1.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.7, 147.2, 144.6, 134.1, 133.3, 132.0, 128.6, 126.6, 126.3, 125.4, 64.9, 34.7, 32.7 and 31.2 ppm; HRMS m/z (M + H) calcd for $C_{18}H_{20}BrClN_3$ 391.0450; Found, 392.0485.

2-(2-Bromo-1-(4-(*tert*-butyl)phenyl)ethyl)-5-chloro-*2H*-benzo[d][1,2,3]triazole (3j'). Oily, yield: 88mg (36%); R_f = 0.7 (10% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.83 (d, *J = 7.5Hz,* 1H), 7.44-7.37 (m, 4H), 7.32 (d, *J = 9.5Hz,* 1H), 6.23-6.20 (m, 1H), 4.61 (t, *J = 10.5Hz,* 1H), 4.05 (dd, *J = 5.0Hz, 5.5Hz,* 1H), 1.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.6, 144.7, 142.8, 133.4, 132.5, 128.2, 126.8, 126.1, 119.6, 117.5, 72.2, 34.7, 32.7 and 31.3 ppm.

1-(2-Bromocyclohexyl)-*1H*-benzo[d][1,2,3]triazole (3k). Semi solid, yield: 160mg (47%); R_f = 0.4 (15% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J = 8.5Hz,* 1H), 7.48 (d, *J = 6.5Hz,* 1H), 7.41-7.37 (m, 1H), 7.28-7.25 (m, 1H), 4.63-4.61 (m, 2H), 2.53-2.50 (m, 1H), 2.24-2.22 (m, 1H), 2.14-2.12 (m, 1H), 1.98-1.90 (m, 2H), 1.79-1.78 (m, 1H), 1.49-1.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.6, 133.2, 127.3, 124.0, 120.0, 109.6, 64.6, 53.8, 37.9, 33.9, 26.6 and 25.0 ppm; HRMS m/z (M + H) calcd for $C_{12}H_{15}BrN_3$ 279.0371; Found, 280.0411.

2-(2-Bromocyclohexyl)-*2H*-benzo[d][1,2,3]triazole (3k'). White Solid, yield: 112mg (33%); R_f = 0.7 (15% ethyl acetate/*n*-hexane); m.p. = 56-60^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86-7.84 (m, 2H), 7.35-7.34 (m, 2H), 4.93-4.88 (m, 1H), 4.72-4.67 (m, 1H), 2.56-2.54 (m, 1H), 2.29-2.27(m, 1H) 2.13-1.81 (m, 4H), 1.49 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 126.4, 118.2, 72.2, 52.7, 37.3, 34.5, 26.5 and 24.5 ppm.

1-(1-Phenylvinyl)-*1H*-benzo[d][1,2,3]triazole (4). Yellow oily, yield: 65mg (90%); R_f = 0.6 (5% ethyl acetate/*n*-hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99-7.97 (m, 1H), 7.29-7.14 (m, 7H), 6.95-6.93 (m, 1H), 5.66 (m, 1H), 5.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 146.1, 142.6, 134.6, 133.0, 129.8, 128.9, 127.9, 126.9, 124.3, 120.1, 111.3 and 111.2 ppm; HRMS m/z (M + H) calcd for $C_{14}H_{12}N_3$ 221.0953; Found, 222.0978.

6-Methylphenanthridine (5).[48] The 1-(1-phenylethenyl)-1*H*-1,2,3-benzotriazole **4** (1.0 equiv.) was heated with ^{n}Bu$_3$SnH (2.0 equiv.) in presence of azobisisobutyronitrile (5 mol%) in anhydrous toluene (3 mL) under sealed tube condition for 3 hours at 140 ^{0}C. Reaction mixture was evaporated under reduced pressure and subjected to column chromatography (SiO2) using gradient of ethyl acetate and hexane to afford compound **5**. Oily, yield: 34mg (40%); (R_f = 0.5, 3 % ethyl acetate/n-hexane; MS *m/z* 194 $[M + H]^+$; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 8.5Hz, 1H), 8.43 (d, *J* = 7.5Hz, 1H), 8.10 (d, *J* = 8.5Hz, 1H), 8.03 (d, *J* = 7.5Hz, 1H), 7.74-7.71 (m, 1H), 7.64-7.50 (m, 3H), 2.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 158.7, 143.6, 132.4, 130.3, 129.2, 128.5, 127.2, 126.4, 126.2, 125.8, 123.6, 122.2, 121.8 and 23.3 ppm; HRMS m/z (M + H) calcd for $C_{14}H_{12}N$ 193.0891; Found, 194.0926.

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Supporting Information

Electronic Supplementary Information (ESI) available: Copies of ^{1}H and ^{13}C NMR for all the developed compounds has been provided. Supporting information for this article is available free of charge via internet under www.

References and notes

1. Katritzky, A. R.; Lan, X.; Yang, J. Z.; Denisko, O. V. *Chem. Rev.* **1998**, *98*, 409–548.
2. Katritzky, A. R.; Rachwal, S. *Chem. Rev.* **2010**, *110*, 1564–1610.
3. Kale, R. R.; Prasad, V.; Mohapatra, P. P.; Tiwari, V. K. *Monatsh Chem.* **2010**, *141*, 1159-1182.
4. Finsgar, M.; Milosev, I. *Corrosion Sc.* **2010**, *52*, 2737–2749.
5. Khabnadideh, S.; Rezaei, Z.; Pakshir, K.; Zomorodian, K.; Ghafari, N. *Res. Pharm. Sci*., **2012**, *7*, 65-72.
6. Rezaei, Z.; Khabnadideh, S.; Pakshir, K.; Hossaini, Z.; Amiri, F.; Assadpour, E. *Eur. J. Med. Chem.* **2009**, 44, 3064-3067,.
7. Singh, R. J. *Ras. J. Chem.* **2009**, *2*, 598-601.
8. Boido, A.; Boido, C. C.; Sparatore, F. *Farmaco.* **2001**, *56*, 263-275.
9. Dawood, K. M.; Abdel-Gawad, H.; Rageb, E. A.; Ellithey, M.; Mohamed, H. A. *Bioorg. Med. Chem.* **2006**, *14*, 3672-3680.
10. Wallace, J. L. *Can. J. Physiol. Pharmacol.* **1994**, *72*, 1493-1498.
11. Sanna, P.; Carta, A.; Gherardini, L.; Nikookar, M. E. R. *Farmaco.* **2002**, *57*, 79-87.
12. Sanna, P.; Carta, A.; Nikookar, M. E. R. *Eur. J. Med. Chem.* **2000**, *35*, 535-543.
13. Handratta, V. D.; Vasaitis, T. S.; Njar, V. C. O.; Gediya, L. K.; Kataria, R.; Chopra, P.; Newman, J. D.; Farquhar, R.; Guo, Z.; Qiu, Y.; Brodie, A. M. H. *J. Med. Chem*, **2005**, *48*, 2972-84.

Journal Pre-proof

14. Carta, A.; Sanna, P.; Palomba, M.; Vargiu, L.; Colla, M. L.; Loddo, R. *Eur. J. Med. Chem.*, **2002**, *37*, 891-900.
15. Caliendo, G.; Carlo, R. D.; Greco, G.; Grieco, P.; Meli, R.; Novellino, E.; Perissutti, E.; Santagada, V. *Eur. J. Med. Chem.* **1995,** *30*, 603-612.
16. Kumar, D.; Mishra, A.; Mishra, B. B.; Bhattacharya, S.; Tiwari, V. K. *J. Org. Chem.* **2013**, *78*, 899–909.
17. Kumar, D.; Mishra, B. B.; Tiwari, V. K. *J. Org. Chem.* **2014**, *79*, 251–266.
18. Kumar, D.; Singh, A. S.; Tiwari, V. K. *RSC Adv.* **2015**, *5*, 31584–31593.
19. Singh, A. S.; Mishra, N.; Yadav, M. S.; Tiwari, V. K. *J. Heterocycl. Chem.* **2019**, *56*, 275–280.
20. Singh, A. S.; Kumar, D.; Tiwari, V. K., *ChemistrySelect* **2018**, *3*, 7809-7812.
21. Yadav, M. S.; Singh, A. S.; Agrahari, A. K.; Mishra, N.; Tiwari, V. K**.** *ACS Omega***, 2019***, 4*, 6681–6689.
22. Singh, A. S.; Kumar, D.; Mishra, N.; Tiwari, V. K. *Chemistry Sel.* **2017**, *2*, 224–229.
23. Singh, A. S.; Mishra, N.; Kumar, D.; Tiwari, V. K. *ACS Omega.* **2017**, *2*, 5044–5051.
24. Mico, X. I.; Ziegler, T.; Subramanian, L. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 1400–1403.
25. Uhde, M.; Ziegler, T. *Synth. Commun.* **2010**, *40*, 3046–3057.
26. Katritzky, A. R.; Ji, F. B.; Fan, W. Q.; Gallos, J. K.; Greenhill, J. V.; King, R. W.; Steel, P. J. *J. Org. Chem.* **1992**, *57*, 190–195.
27. Habraken, C. L.; Erkelens, C.; Mellema, J. R.; Cohen-Fernandes, P. *J. Org. Chem.* **1984**, *49*, 2197-2200.
28. Katritzky, A. R.; Akue-Gedu, R.; Vakulenko, A. V. *ARKIVOC*. **2007**, *3*, 5-12.
29. Katritzky, A. R.; Yang, B.; Dalal, N. S. *J. Org. Chem.* **1998**, *63*, 1467-1472.
30. Kim, T.; Kim, K. *Tetrahedron Lett.* **2010**, *51*, 868–871.
31. Katritzky, A. R.; Rogovoy, B. V.; Kirichenko, N.; Vvedensky, V. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1809–1811.
32. Katritzky, A. R.; Suzuki, K.; Singh, S. K.; He, H.-Y. *J. Org. Chem.* **2003**, *68*, 5720-5723.
33. Wang, X.; Zhang, Y. *Synth. Commun.* **2003**, *33*, 2627-2634.
34. Katritzky, A. R.; Abdel-Fattah, A. A. A.; Wang, M. *J. Org. Chem.* **2003**, *68*, 4932-4934.
35. Katritzky, A. R.; Abdel-Fattah, A. A. A.; Wang, M. *J. Org. Chem.* **2003**, *68*, 1443-1446.
36. Katritzky, A. R.; Cai, C.; Suzuki, K.; Singh, S. K. *J. Org. Chem.* **2004**, *69*, 811-814.
37. Katritzky, A. R.; Abdel-Fattah, A. A. A.; Gromova, A. V.; Witek, R.; Steel, P. J. *J. Org. Chem.* **2005**, *70*, 9211-9214.
38. Katritzky, A. R.; Suzuki, K.; Wang, Z. *Synlett,* **2005**, 1656-1665.
39. Lim, D.; Fang, F.; Zhou, G.; Coltart, D. M. *Org. Lett.* **2007**, *9*, 4139-4142.
40. Wang, X.; Wang, W.; Wen, Y.; He, L.; Zhu, X. *Synthesis*, **2008**, 3223-3228.
41. Zhou, G.; Lim, D.; Fang, F.; Coltart, D. M. *Synthesis,* **2009**, 3350-3352.
42. Li, J.; Sun, Y.; Chen, Z.; Su, W. *Synth. Commun.* **2010**, *40*, 3669-3677.
43. Xia, Z.; Lv, X.; Wang, W.; Wang, X. *Tetrahedron Lett.* **2011**, *52*, 4906-4910.
44. Zhu, L. L.; Xu, X. Q.; Shi, J. W.; Chen, B. L.; Chen, Z. *J. Org. Chem.* **2016**, *81*, 3568-3575.
45. Sun, K; Ma, F; Liu, L.; Sun, J.; Liu, X. Yachao Wang, Zhiguo Zhang and Guisheng Zhang. *RSC Adv.* **2015**, *5*, 82492-82495.
46. Peng, L.; Scott, L. T. *J. Am. Chem. Soc*. **2005**, *127*, 16518-16521.
47. Gulea, M.; López-Romero, J. M.; Fensterbank, L.; Malacria, M. *Org. Lett.* **2000**, *2*, 2591-2594.
48. Raju, G.; Guguloth, V.; Satyanarayana, B. *RSC Adv.* **2016**, *6*, 45036-45040.

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Highlights

- ✓ A novel and expeditious one-pot synthesis of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles has been devised by reacting styrene with 1*H*-benzotriazole in presence of NBS in anhydrous CH_2Cl_2 at room temperature.
- ✓ The resulted compounds undergo E_2-ellimination to afford respective 1-(1-phenylvinyl)-1*H*-benzotriazoles.
- ✓ 1-(1-Phenylvinyl)-1*H*-benzotriazole underwent benzotriazole ring cleavage (BtRC) under free radical condition to produce phenanthridine.

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Declaration of Interest statement

In addition to our research on Click chemistry in glycoscience for various applications (Ref: Tiwari et al, ***Chem. Rev*.., 2016,** *116*, 3086) we also focus Benzotriazole Ring Cleavage (BtRC) methodology. Recently, we have investigated *n*-Bu_3SnH/silane mediated cyclization protocol of thioacyl sugar alcohol to afford diverse 2-substituted benzothiazole glycoconjugates *via* cyclative-cleavage of benzotriazole ring (***J. Org. Chem.* 2013,** 899-909). The chemistry reported was successfully extended with different amines, thiols and aryls leading to a general route for an easy access of diverse benzothiazoles (***J. Org. Chem.* 2014,** 251-265). However, the benzylic alcohols undergo deoxygenation leading to deoxy sugar rather to cyclization (***RSC Adv.* 2015,** 31584). This BtRC chemistry has been demonstrated to UG/PG students for chemistry education purpose **(*J. Het. Chem.,* 2019**). Recently, we presented an improved *N*-acylation of 1H-benzotriazole using 2,2'-dipyridylsulfide and Ph3P (***SYNTHESIS,* 2019,** 470, https://www.organic-chemistry.org/abstracts/ lit6/674.shtm) and a practical route via Trichloroisocyanuric Acid Mediated High-Yielding Synthesis of N-Acylbenzotriazoles (***SYNTHESIS,* 2019,** 2183). Likewise, similar transformation would occur to provide *N*-phenylamides using acylbenzotriazoles under heating in presence of Bu_3SnH (***ChemistrySelect*, 2017**), where $AlCl_3$ mediated BtRC furnished respective benzoxazoles (***ACS Omega*, 2017**). Finally, A Practical and Green Synthesis of diverse Benzothiazoles utilizing a Silicon Industry Waste Polymethylhydrosiloxane-mediated BtRC has been established (***ACS Omega,* 2019**, 6681)

Herein, a cost-effective and high yield contributing method for the expeditious synthesis of 1-(2-bromo-1-arylethyl)-1*H*-benzotriazoles has been devised using alkenes and 1*H*-benzotriazole. Synthesis condition involves stirring of alkenes and 1*H*-benzotriazole in presence of NBS in one-pot in anhydrous DCM at room temperature. Further the resulted compound undergoes E_2-ellimination to afford respective 1-(1-phenylvinyl)-1*H*-benzotriazoles, which finally go through benzotriazole ring cleavage (BtRC) under free radical condition to produce phenanthridine as the final product.

The work described in the manuscript has not been previously published and no portion of it is being considered for publication elsewhere in any medium, including electronic journals, computer databases, and publicly accessible preprint Web sites.

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