JOC The Journal of Organic Chemistry

Article

Palladium-Catalyzed Synthesis of 2-Aryl-2H-Benzotriazoles from Azoarenes and TMSN3

Nilufa Khatun, Anju Modi, Wajid Ali, and Bhisma K. Patel

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.5b01706 • Publication Date (Web): 15 Sep 2015

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Palladium-Catalyzed Synthesis of 2-Aryl-*2H*-Benzotriazoles from Azoarenes and $TMSN_3$

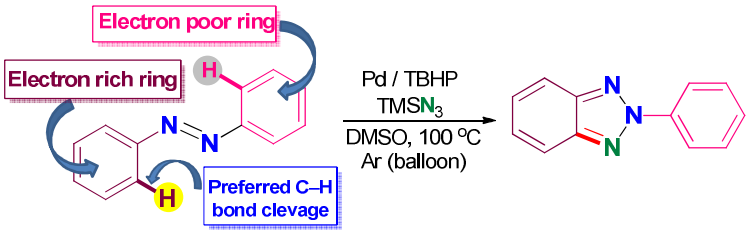
Nilufa Khatun, Anju Modi, Wajid Ali and Bhisma K. Patel*

Department of Chemistry, Indian Institute of Technology Guwahati, North Guwahati 781 039

Fax: (+91)361-26909762.

E-mail: patel@iitg.ernet.in

RECEIVED DATE (will be automatically inserted after manuscript is accepted)



ABSTRACT: Substrate directed *ortho* C–H amination of azoarenes using $TMSN_3$ as the source of nitrogen leading to the synthesis of 2-aryl-*2H*-benzotriazoles has been accomplished with the help of Pd/TBHP combinations. An intermolecular *o*-azidation (C–N bond formation) followed by an intramolecular N–N bond formation *via* nucleophilic attack of one of the azo nitrogen onto the *o*-azide nitrogen leads to cyclization with the expulsion of N_2.

INTRODUCTION

Direct C–H bond functionalization by transition metal catalysts has opened a plethora of methods in the construction of C–C, C–N and C–hetero atom bonds.[1-4] Strategies involving inert C–H bond activation are important and significant due to their step and atom economy which circumvent pre-fuctionalization of starting materials. In particular, directed C–H bond amination strategies have received a great attention recently.[5-7] A range of preactivated aminating reagents such as *N*-carboxylates,[8a] *N*-fluorobenzenesulfonimide (NFSI),[8b] *N*-tosylates,[8c] *N*-halides,[8d] benzoyl hydroxylamines,[8e] and highly active nitrene precursors, especially azides derivatives[8f-8h] have been explored as the potential aminating reagents under different metal catalysis.

Organic azides are important building blocks in synthetic chemistry and have found wide applications in medicinal chemistry, material science, polymer and biological science.[9] Generally, azide moiety is introduced into organic molecules *via* Sandmeyer reaction,[10a,b] Cu-catalyzed coupling of aryl halides/boronic acids with azides (NaN_3 or $TMSN_3$),[10c,d] coupling between organometallics and TfN_3,[10e] and metal free[10f-h] or metal mediated C–H functionalization.[10i,j] As a nitrene precursor, *ortho* azido group can participate in intramolecular cyclization after releasing a molecule of N_2. Taking advantage of this, a number of metal catalyzed protocols have been developed for the synthesis of nitrogen containing heterocycles. Prefunctionalized 2-azido substrates or the *in situ* generated *ortho* azido moiety introduced *via* cross coupling reactions or C–H functionalization often undergo intramolecular cyclizations leading to various heterocycles.[11]

2-Aryl-*2H*-benzotriazoles, are important nitrogen containing heterocycles which are found extensively in pharmaceuticals and are structural components of many UV stabilizers and organic electronic materials.[12] Compounds having 2-aryl-*2H*-benzotriazole scaffold as primary

skeleton include a seratonine/dopamine receptor ligand (**I**), human PPAR-α activator (**II**), Tinuvin-P (**III**) an ultraviolet light absorber, PCDTPBt (**IV**) an electron acceptor in organic solar cell, an ultraviolet light stabilizer (**V**) and antiviral agent (**VI**) against ssRNA positive viruses are shown in Figure 1.

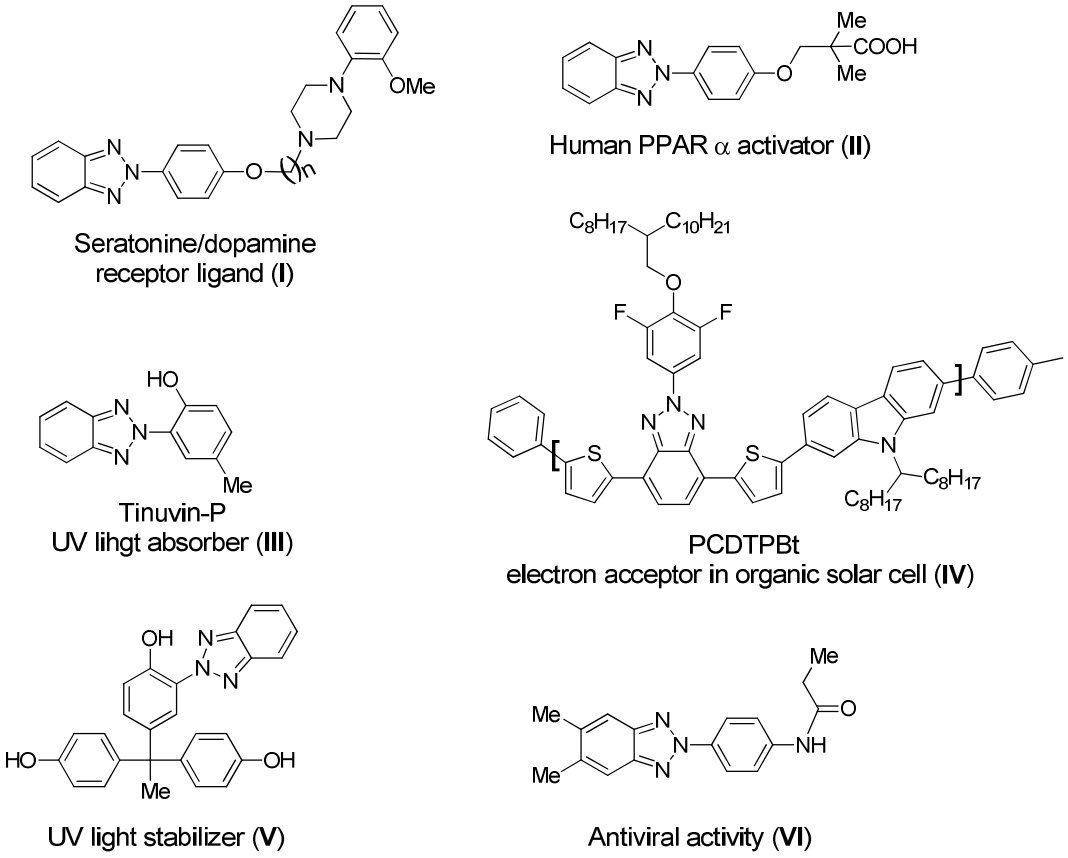
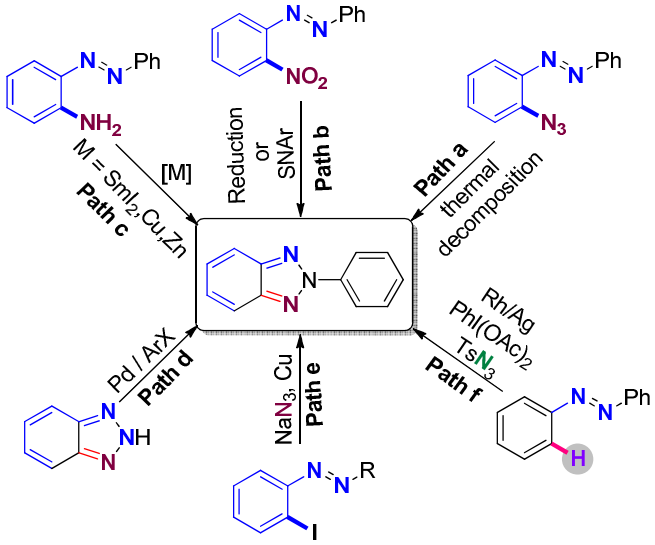


Figure 1. Important Compounds having 2-Aryl-*2H*-benzotriazole Cores

Existence of two isomeric benzotriazoles based on N^1 (N^3) and N^2 substitutions* make the selective synthetic strategies challenging. Because of the thermodynamic stability of N^1 or 1*H* isomer, compared to its N^2 or 2*H* isomer more synthetic methods have been reported for the former.[13] Traditional methods for the regioselective and direct synthesis of 2-aryl-*2H*-benzotriazoles *i.e* N^2-isomer include: thermal decomposition of 2-azidoazoarenes[14a] (Scheme 1, path a), reduction of 2-[2-nitrophenylazo] derivatives by thiourea[14b] and Zn/NH_4Cl[14c] or

nucleophilic aromatic (SNAr) substitution reaction with sodium azide[14d] (Scheme 1, path b), oxidative coupling of *ortho* substituted azoaniline (Scheme 1, path c) by metal catalysts such as SmI_2,[14e] Zn[14f] or Cu.[14g] *o*-Functionalized azoarenes are precursors in all the above strategies which often are not easily accessible. Metal-catalyzed arylation of unsubstituted benzotriazoles are associated with the formation of a regio-isomeric mixture of N^1- and N^2-benzotriazoles (Scheme 1, path d).[14h,i] Further, a copper catalyzed cross coupling of 2-haloaryltriazenes and NaN_3 leading to *2H*-benzotriazoles has also been documented (Scheme 1, path e).[14j] A Rh-catalyzed *ortho* C–H activation of azobenzenes utilizing tosyl azide (TsN_3) as the aminating source provides *2H*-benzotriazoles as depicted in Scheme 1, path f.[14k]

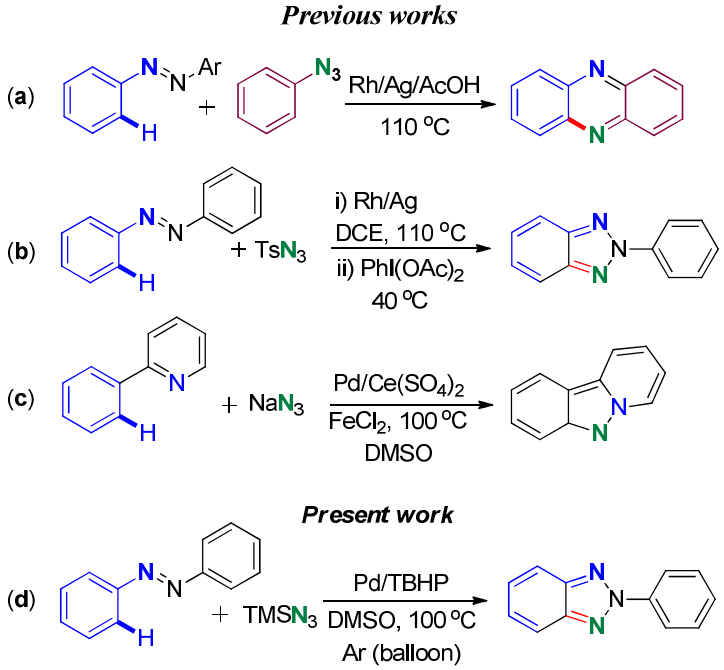
Scheme 1. Reported Strategies for the Synthesis of 2-Aryl-*2H*-benzotriazole



Aromatic azoarenes constitute an important class of conjugated molecules due to which they exhibit a diverse array of spectral properties. They find applications as industrial dyes, food additives, photochemical molecular switches, host-guest recognition, liquid crystal assemblies, biomedical image analysis, molecular motor design, materials and protein probes.[15] From

synthetic point of view, in 1971 azoarenes as the directing group were first introduced by Fahey for the *o*-halogenation *via* a C–H activation strategy.[16] However, its synthetic utility was dormant, until very recently a series of transition metals catalyzed reactions involving azoarenes as the directing substrates has been exploited. Examples include Pd-catalyzed *ortho*-aroylation,[17] *o*-nitration,[14c,18a] *o*-alkoxylation,[18b] and *o*-halogenation[18c] Rh-catalyzed alkyne annulations,[18d] allylation,[18e] *o*-acylation and its transformation to indazoles[18f] and *o*-amination.[18g,h] In addition Re and Rh catalyzed syntheses of nitrogenous heterocycles using aldehyde,[19a] α-diazo esters[19b] and diazotized Meldrum's acid[19c] have been reported. With azo as the directing group, depending upon the azides (as the source of nitrogen) either a six member or a five member heterocycle is formed using Rh catalyst. The use of aryl azide (ArN_3) provided phenazines as the sole product [Scheme 2(a)],[20] while tosyl azide gave exclusively *2H*-benzotriazoles [Scheme (2b)].[14k] Inorganic azide such as NaN_3 with 2-phenylpyridines as the directing group under a Pd-catalyzed condition gave fused heterocycle pyrido[1,2–*b*]indazoles as shown in [Scheme 2(c)].[11d] Although an elegant transformation of azoarenes to *2H*-benzotriazoles has been described by Lee group, the use of expensive combinations of catalyst $[Cp^*RhCl_2]_2$, co-catalyst $AgNTf_2$ and oxidant $PhI(OAc)_2$ make this method economically unviable.[14k] Thus, the development of an efficient, cost effective and atom-economic protocol is very much in need. With our continuing efforts to establish newer strategies for the synthesis of heterocycles through C–H activation,[21] and taking cues from the reports in Scheme 2 our investigation started. The main objective was to check whether other commercially available metal catalyst and cheaper oxidant could be replacement for the synthesis of *2H*-benzotriazoles following *o*-C–H activation of azobenzene.

Scheme 2. Metal Catalyzed *ortho* Amination of Directed Substrates with Different Azides



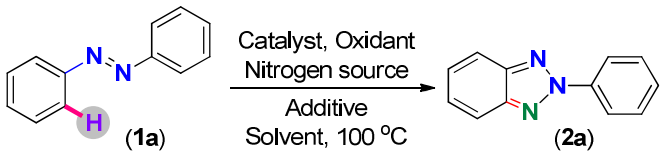
RESULTS AND DISCUSSION

With this curiosity in mind and taking cues from the previous report[11d] as shown in (Scheme 2c), an initial trial experiment was performed by treating azobenzene (**1a**) (0.5 mmol) with NaN_3 (1.0 mmol), in the presence of $Pd(OAc)_2$ (10 mol%) and oxidant $Ce(SO_4)_2$ (1.0 mmol) in DMSO at 100 ^oC. No product formation was observed even after 72 h, only starting material (**1a**) was recovered at the end of the reaction. The use of $TMSN_3$ in lieu of NaN_3 also failed to produce any positive result. Disappointingly, other common oxidants used mostly in metal catalyzed C–H functionalizations such as CAN, DDQ, $Cu(OAc)_2$, Ag_2O, $K_2S_2O_8$, Oxone® and O_2, were completely unproductive (Table 1, entry 3). Interestingly, keeping all other parameters constant the use of TBHP as oxidant (1 equiv) provided 2-phenyl-*2H*-benzotriazole (**2a**) in 42% yield (Table 1, entry 4). Encouraged by this preliminary success a series of reactions were performed by varying other reaction parameters to obtain the best possible yield of (**2a**). At first, the

catalytic efficacy of various Pd-catalysts [$Pd(OAc)_2$ (39%), $PdCl_2$ (28%), $PdBr_2$ (33%), $Pd(CH_3CN)_2Cl_2$ (21%)] were tested among which $Pd(TFA)_2$ (49%) was found to be better as shown in Table 1, entries 4–8. **Although $Pd(TFA)_2$ gave superior yield, on couple of occasions the reaction flask exploded even at room temperature which prompted us to avoid its use** and we therefore switched to the next best catalyst $Pd(OAc)_2$. The possible explosion may be due to *in situ* generation of highly explosive HN_3. The azide radical obtained by the reaction of $TMSN_3$ and TBHP is rapidly converted to HN_3 by the *in situ* generated trifluoroacetic acid from $Pd(TFA)_2$ possibly causing the explosion. When the catalyst $Pd(OAc)_2$ loading was increased to two fold *i.e* 20 mol%, the yield of the expected product improved up to 62% (Table 1, entry 9). No further significant improvement in the yield (65%) was observed even when the catalyst loading was increased up to three fold (30 mol%). Other solvents such as THF (<5%), dioxane (<5%), PhCl (41%) and DMF (48%) (Table 1, entries 11–14) tested under otherwise identical conditions were all found to be inferior to DMSO. The oxidant TBHP (in decane) was superior to other peroxide oxidants such as 70% aqueous TBHP (42%) and 30% aqueous H_2O_2 (00%) (Table 1, entries 15–16) in terms of yield. A further improvement in the product yield (70%) was observed when the oxidant (decane-TBHP) amount was increased from 1 to 2 equiv (Table 1, entry 17). No further significant enhancement in the yield was observed either by increasing the amount of aminating source *i.e* $TMSN_3$ (3 equiv) (71%) or oxidant TBHP (3 equiv) (73%) (Table 1, entries 18–19). Taking cues from previous reports,[14k,11d] effect of additives such as O_2, $PhI(OAc)_2$, $FeCl_2$ and $Cu(OAc)_2$ were also examined along with decane-TBHP as illustrated in Table 1, (entries 20–23). Unfortunately, none of the additives had any positive effects on the product yield. Interestingly, when this reaction was carried out in an argon atmosphere, the yield of the product improved up to (78%) as shown in Table 1, entry 24. By

performing the reaction at lower temperature (80 ^{o}C) led to a sluggish (36 h) reaction giving a lower yield (65%) of the product (Table 1, entry 25). It is not surprising that the reaction did not proceed either in the absence of $Pd(OAc)_2$ or TBHP suggesting the essential requirements of both (Table 1, entries 26–27). Optimally, the desired product (**2a**) was obtained in a best possible yield of 78% when the reaction was carried out using azobenzene (**1a**) (0.5 mmol), $TMSN_3$ (2 equiv), decane-TBHP (2 equiv) in DMSO (1.0 mL) at 100 ^{o}C under an atmosphere of argon. It may be mention here that both catalyst $Pd(OAc)_2$ and oxidant TBHP are not only commercially available but are also cheaper compared to catalyst $[Cp^*RhCl_2]_2$, co-catalyst $AgNTf_2$ and oxidant $PhI(OAc)_2$ combinations.

Table 1. Screening of Reaction Conditions[a]



entry	catalyst (mol%)	azide (equiv)	oxidant (equiv)	solvent	additives	yield (**2a**) (%)[b]
1	$Pd(OAc)_2$ (10)	NaN_3 (2)	$Ce(SO_4)_2$ (1)	DMSO	-	00
2	$Pd(OAc)_2$ (10)	$TMSN_3$ (2)	$Ce(SO_4)_2$ (1)	DMSO	-	00
3	$Pd(OAc)_2$ (10)	$TMSN_3$ (2)	V.O[c,d] (1)	DMSO	-	00
4	$Pd(OAc)_2$ (10)	$TMSN_3$ (2)	TBHP (1)	DMSO	-	42
5	$PdCl_2$ (10)	$TMSN_3$ (2)	TBHP (1)	DMSO	-	28
6	$PdBr_2$ (10)	$TMSN_3$ (2)	TBHP (1)	DMSO	-	33
7	$Pd(CH_3CN)_2Cl_2$(10)	$TMSN_3$ (2)	TBHP (1)	DMSO	-	21
8	$Pd(TFA)_2$ (10)	$TMSN_3$ (2)	TBHP (1)	DMSO	-	49
9	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (1)	DMSO	-	62
10	$Pd(OAc)_2$ (30)	$TMSN_3$ (2)	TBHP (1)	DMSO	-	65
11	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (1)	THF	-	< 5
12	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (1)	Dioxane	-	< 5
13	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (1)	PhCl	-	41
14	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (1)	DMF	-	48
15	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	Aq.TBHP (1)	DMSO	-	42
16	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	Aq.H_2O_2 (1)	DMSO	-	00
17	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (2)	DMSO	-	70
18	$Pd(OAc)_2$ (20)	$TMSN_3$ (3)	TBHP (2)	DMSO	-	71
19	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (3)	DMSO	-	73
20	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (2)	DMSO	O_2	61
21	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (2)	DMSO	$PhI(OAc)_2$[e]	63
22	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (2)	DMSO	$FeCl_2$[e]	61
23	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (2)	DMSO	$Cu(OAc)_2$[e]	65
24	**$Pd(OAc)_2$ (20)**	**$TMSN_3$ (2)**	**TBHP (2)**	**DMSO**	**-**	**78**[f]
25	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	TBHP (2)	DMSO	-	65[g]
26	-	$TMSN_3$ (2)	TBHP (2)	DMSO	-	00
27	$Pd(OAc)_2$ (20)	$TMSN_3$ (2)	-	DMSO	-	00

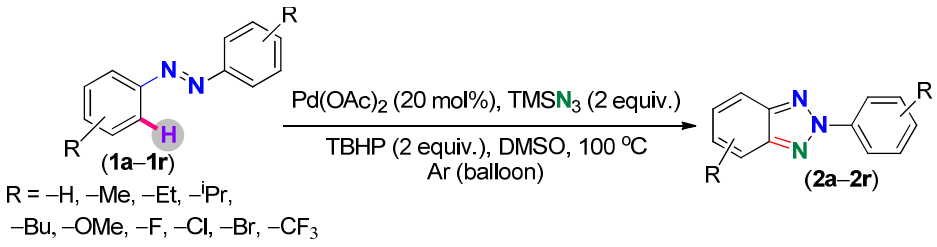
[a]Reaction condition: azobenzene (0.5 mmol), in solvent (1.0 mL) at 100 °C for 24 h. [b]Isolated yield. [c]V.O = CAN (1 equiv), DDQ (1 equiv), $Cu(OAc)_2$ (1 equiv), Ag_2O (1 equiv), $K_2S_2O_8$ (1 equiv), Oxone (1 equiv) used under air. [d]O_2 balloon. [e]20 mol% under air. [f]Reaction with argon balloon. [g]Reaction was carried out for 36 h at 80 °C.

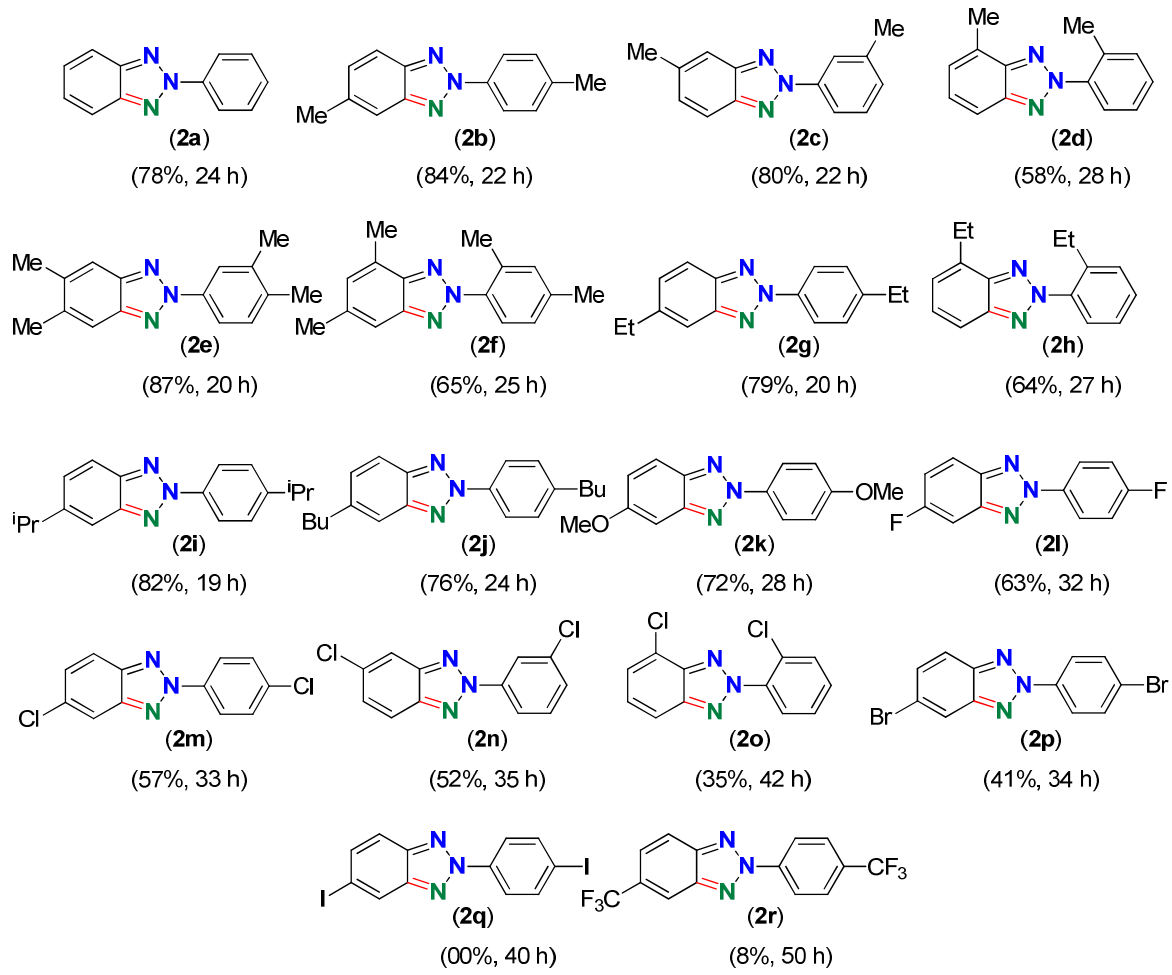
After establishing the optimized parameters, this protocol was subsequently applied to a range of substituted azoarenes to afford their corresponding *2H*-benzotriazoles. This protocol is

found to be compatible with several functional groups such as electron donating alkyl [–Me (**1b**–**1f**), –Et (**1g** and **1h**), –^{i}Pr (**1i**) and –Bu (**1j**)], methoxy (–OMe) (**1k**), moderately electron-withdrawing halogens [–F(**1l**), –Cl (**1m**–**1o**) and –Br (**1p**)] and strongly electron-withdrawing (–CF_3) (**1r**) substituents in aromatic ring of azoarenes. All the substrates in Scheme 3 (**1a**–**1r**) are symmetrically substituted azoarenes. Azoarenes possessing weakly activating substituents such as *p*-Me (**1b**), *m*-Me (**1c**) and *o*-Me (**1d**) underwent *o*-aminative-heterocyclization smoothly giving their corresponding *2H*-benzotriazoles (**2b**–**2d**) in moderate to good yields as shown in Scheme 3. Symmetrically substituted di-methylated azoarenes such as 3,4-dimethyl (**1e**) and 2,4-dimethyl (**1f**) under the optimized reaction conditions furnished their corresponding *2H*-benzotriazoles (**2e**) and (**2f**) respectively, in 87% and 65% yields (Scheme 3). Azoarenes possessing other weakly activating substituents such as 4-ethyl (**1g**) and 2-ethyl (**1h**) reacted under identical conditions to give (**2g**) and (**2h**) respectively, in 79% and 64% yields. Similarly, the reaction of 4-*iso*propyl (**1i**) and 4-butyl (**1j**) substituted symmetrical azoarenes under standard conditions afforded 82% and 76% yields of their corresponding products (**2i** and **2j**) respectively. A moderate yield (72%) of (**2k**) was obtained when both the aryl rings are electron rich due to the presence of methoxy (–OMe) (**1k**) substituent as in Scheme 3. However, the azoarenes possessing weakly deactivating substituents, irrespective of their positions in the aryl ring such as *p*-F (**1l**), *p*-Cl (**1m**), *m*-Cl (**1n**) and *o*-Cl (**1o**), provided their respective *2H*-benzotriazoles (**2l**–**2o**) in moderate to poor yields (in the range of 63-35%). Other weakly electron-withdrawing substituents such as *p*-bromo (**1p**) under the standard conditions gave only 41% yield of (**2p**), while *p*-iodo (**1q**) failed to react which is mainly because of the electronic effect of substituents and partly due to their insolubility in DMSO. Similarly, strongly electron-withdrawing substituents such as *p*-CF_3 (**1r**) furnished only low yield (8%) of (**2r**) even after 50

h which is mainly because of the electronic effect of $–CF_3$ substituent. As can be seen in Scheme 3, barring one exception (**1k**) azoarenes bearing electron-donating substituents (**1b**–**1j**) provided better yields of their products (**2b**–**2j**) compared to those bearing electron-withdrawing substituents (**1l**–**1r**). The higher yields obtained for electron-donating azoarenes could be attributed to their better chelating ability with electrophilic Pd (II) catalyst. The electronic-effect is dominated by the steric factor when the substituents are present at their *ortho* positions (**1d**, **1f**, **1h** and **1o**) giving lower yields of products (**2d**, **2f**, **2h** and **2o**) compared to their *para* and *meta* analogues as shown in Scheme 3. All the *meta* substituted azoarenes (**1c**), (**1e**) and (**1n**) gave single regioisomeric products (**2c**), (**2e**) and (**2n**) respectively. In these cases the less sterically hindered *o*-C–H (*i.e para* to the *meta* substituents) is exclusively functionalized.

Scheme 3. Substrate Scope for Symmetrical Azoarenes[a,b]





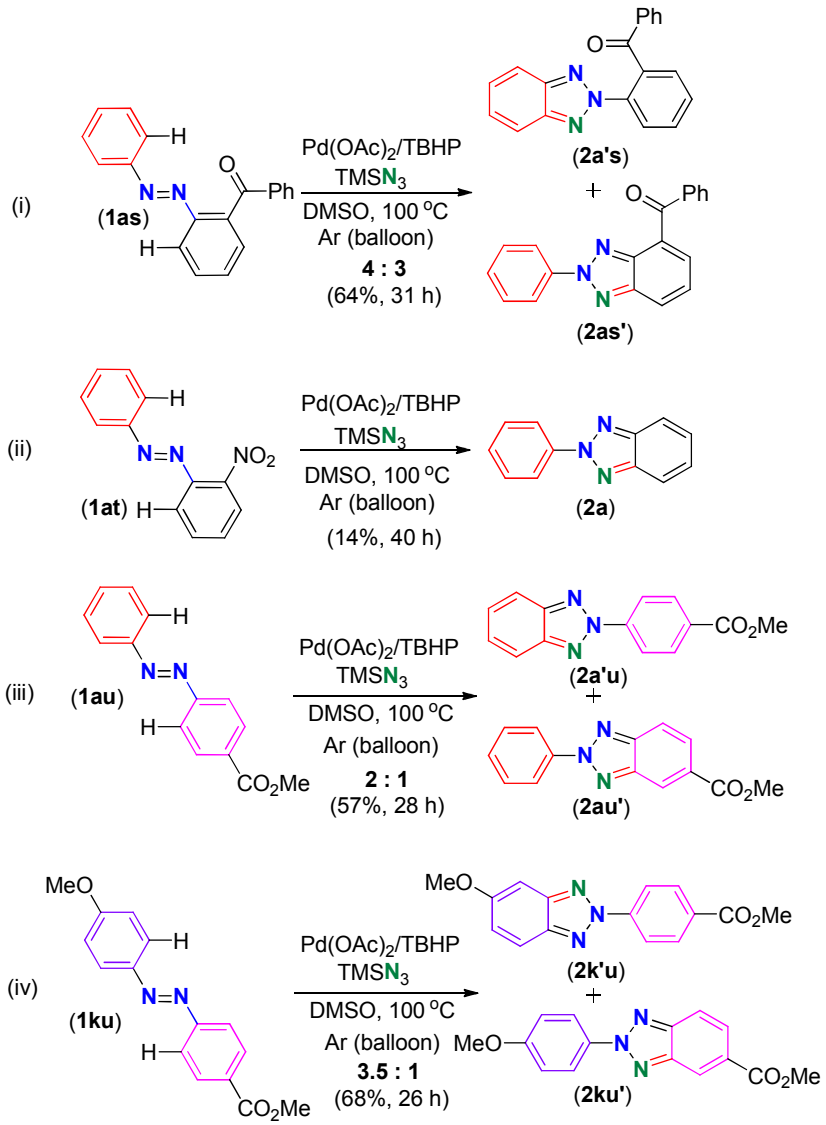
[a]Reaction condition: symmetrical azobenzene (0.5 mmol), $TMSN_3$ (2 equiv), TBHP-decane (2 equiv) in DMSO (1.0 mL) at 100 °C for 19-50 h. [b]Isolated yields of pure product.

After the successful synthesis of a series of *2H*-benzotriazoles from symmetrical azoarenes (Scheme 3) we then focused our attention on unsymmetrical azoarenes.** A query arises whether this protocol will be applicable for the regioselective *o*-aminative-heterocyclization or it

would provide a mixture of –constitutional isomeric products? Keeping the substrate reactivity trends from Scheme 3 in mind, some azoarenes were especially designed for this. These designed azoarenes possess either electron-neutral (–H) or electron-donating (–OMe) substituents in one of the aromatic ring while the other ring contains electron-withdrawing substituents such as *o*-COPh, *o*-NO_2, *p*-CO_2Me. Substrate (**1as**) bearing electron-withdrawing *o*-COPh group in one of the aromatic ring and - electron neutral (–H) substituent in the other ring, when subjected to the present reaction conditions, an inseparable constitutional isomeric mixture of *2H*-benzotriazoles (**2a′s**) and (**2as′**) were obtained in the ratio of 4 : 3 (as judged from ^{1}H NMR) in 64% yield [Scheme 4(i)]. (*E*)-1-(2-Nitrophenyl)-2-phenyldiazene (**1at**), another unsymmetrical azoarene, under the present reaction conditions gave a product (**2a**) [(Scheme 4(ii)] having no intact nitro group. This unexpected formation of product (**2a**) from unsymmetrical azoarene (**1at**) can be explained by the intermolecular nucleophilic attack (SNAr) of the *in situ* generated *o*-azido group on to the carbon attached to the nitro group. The product (**2a**) was obtained in a mere yield of 14% and the rest being unreacted starting material. Nevertheless this reaction supports the intermediacy of *o*-azido species. The failure to obtain a nitrophenyl-substituted benzotriazole from (**1at**) is possibly due to the presence of a strong deactivating *ortho* –NO_2 substituent which reduces the chelating ability of the 'azo moiety' towards electrophilic Pd (II). Another unsymmetrical substrate (**1au**) containing *p*-CO_2Me substituent in one aromatic ring and electron neutral (–H) in the other ring, furnished a mixture of inseparable constitutional isomeric products (**2a′u**) and (**2au′**) in the ratio of 2 : 1 in 57% yield (Scheme 4(iii)). Similarly, substrate (**1ku**) having *p*-CO_2Me group in one ring and *p*-OMe group in the other ring underwent *o*-aminative-heterocyclization giving inseparable products (**2k′u** and **2ku′**) in the ratio of 3.5 : 1. From the above reactions [Scheme 4(i), (iii) and (iv)] it is evident that the *o*-aminative-heterocyclization is

preferred at the aromatic rings possessing electron donating substituent (-OMe) followed by electron neutral (–H), and the electron-withdrawing substituents *p*-CO_2Me and *o*-COPh.

Scheme 4. Regioselectivity in unsymmetrical Azoarenes[a,b]

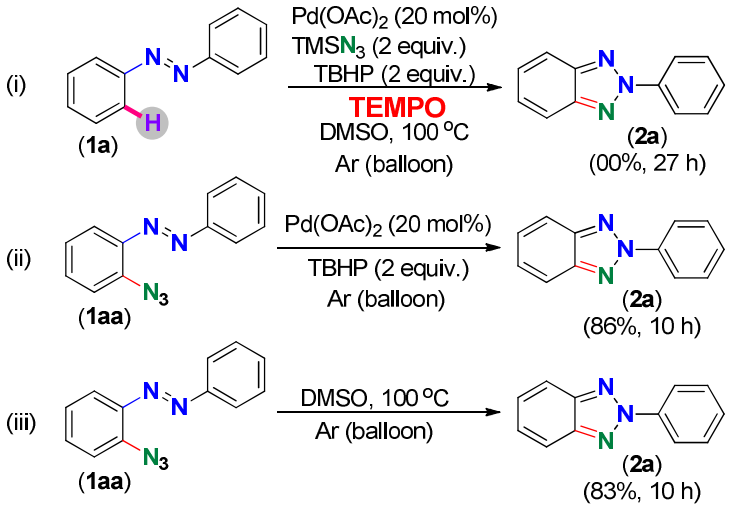


[a]Reaction condition: unsymmetrical azoarene (0.5 mmol), $TMSN_3$ (2 equiv), TBHP-decane (2 equiv) in DMSO (1 mL) at 100 °C for 26-40h. [b]Isolated yields of product(s).

Some control reactions were performed to deduce the plausible reaction mechanism for this transformation. When this reaction was carried out in the presence of a radical inhibitor TEMPO (2,2,6,6-tetramethylpiperidinooxy), no product formation (**2a**) was observed as shown in Scheme

5(i). Thus complete suppression of the product formation of (**2a**) indicates a radical pathway for this process. Formation of product (**2a**) from unsymmetrical azoarenes bearing *o*-nitro group (**1at**) [Scheme 4(ii)] can be explained if there is formation of an *o*-azido species which is possibly the intermediate in these reactions. When a pre-synthesized *ortho* azido azobenzene (**1aa**) was treated under the present reaction conditions, formation of corresponding product 2-phenyl-*2H*-benzotriazole (**2a**) was obtained in 86% yield as in Scheme 5(ii). This further supports the intermediacy of *ortho* azido species for these reactions. The thermal decomposition of (**1aa**) at 100 ^{o}C to (**2a**) in 83% yield suggests the non involvement of Pd-catalyst and oxidant (TBHP) in the final step [Scheme 5(iii)].

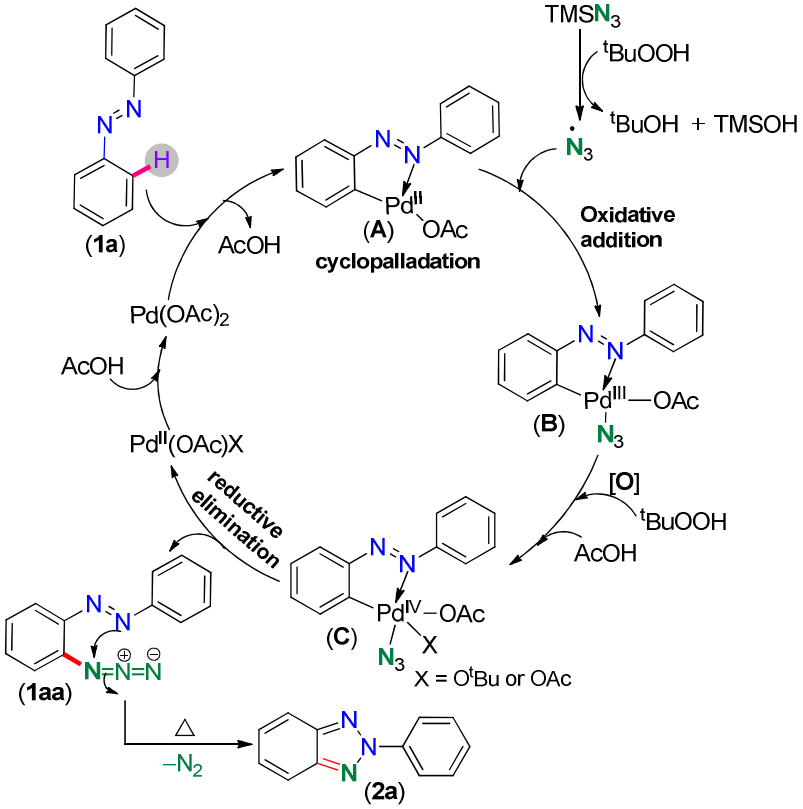
Scheme 5. Control Reactions Performed



Based on these experimental results and taking cues from the recent literature precedent,[17-18,22-23] a plausible mechanism has been proposed as shown in Scheme 6. Presumably, an initial cyclopalladation between 'azo moiety' of azobenzene and Pd(II) catalyst leads to the formation of intermediate complex (**A**). The *in situ* generated azide radical,[24] obtained by the reaction of $TMSN_3$ and TBHP, then reacts with Pd-complex (**A**), which is oxidized to give a Pd(III)[23]

intermediate (**B**) (Scheme 6). A further oxidation of intermediate (**B**) by TBHP leads to the formation of a Pd(IV)[22] intermediate (**C**). Thus TBHP is playing the dual role of an oxidant as well as a radical generator. Apart from this, the ^{t}BuO moiety generated from TBHP may act as one of the ligand for Pd^{IV} as in intermediate (**C**). A reductive elimination of intermediate (**C**) leads to the formation of an *ortho* azido azobenzene (**1aa**) and regenerating palladium (II) catalyst for the next cycle. In the final stage, attack of one of the azo nitrogen onto the *o*-azide nitrogen of the *in situ* generated *ortho* azido substrate (**1aa**) leads to cyclization giving (**2a**), with the expulsion of a molecule of N_2.

Scheme 6. Plausible Mechanism for *ortho*-Aminative Heterocyclyzation



CONCLUSION

In summary, we have developed an efficient and regioselective protocol for the synthesis of 2-aryl-*2H*-benzotriazoles *via* Pd(II)-catalyzed *ortho* sp^2 C–H activation of azoarenes using $TMSN_3$ as the nitrogen source and TBHP as the oxidant. The ligand directed intermolecular azidation (C–N bond formation) through *ortho* sp^2 C–H functionalization of azobenzenes followed by intramolecular cyclization (N–N bond formation) leads to the construction of 2-aryl-*2H*-benzotriazoles. For unsymmetrical azoarenes the heterocyclization is preferred at the aromatic ring rich in electron compared to electron neutral (–H) or electron-deficient aromatic rings. A wide range of substrates scope with tolerance of various functional groups make this method a suitable alternative to the existing methods for the synthesis of 2-aryl-*2H*-benzotriazoles.

EXPERIMENTAL SECTION

General information:

All the compounds were commercial grade and were used without further purification. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60−120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F254 (0.25 mm). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for proton NMR (600 MHz) and for ^{13}C NMR (150 MHz). HRMS spectra were recorded using ESI mode (Q-TOF type Mass Analyzer). IR spectra were recorded in KBr or neat.

*General Procedure for the Synthesis of 2-Phenyl-2H-benzo[d][1,2,3]triazole (**2a**).* Azobenzene (**1a**, 91 mg, 0.5 mmol), $Pd(OAc)_2$ (22 mg, 20 mol%), $TMSN_3$ (115 mg, 1 mmol), TBHP in decane (5-6 M) (200 μL, 1 mmol) and DMSO (1 mL) were sequentially added to a 25 mL oven

dried round-bottle flask containing a magnetic needle. Through a steady flow of argon gas the flask was sealed with a rubber septum. To maintain a positive pressure of argon, the flask was fitted with an argon balloon and the resultant reaction mixture was stirred in a preheated oil bath at 100 ^{o}C. The progress of the reaction was monitored by TLC. After the completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (10 mL). Then the reaction mixture was filtered through a small bed of celite and washed with an additional amount of ethyl acetate (20 mL). This combined organic layer of ethyl acetate (30 mL) then washed with water (2 x 5 mL). The aqueous layer was separated using a separating funnel and organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified over a column of silica gel and eluted with (95.5 : 0.5, hexane/ ethyl acetate) to give 2-phenyl-*2H*-benzo[*d*][1,2,3]triazole (**2a**) in 78%.yield (76 mg) as yellowish solid.

*2-Phenyl-2H-benzo[d][1,2,3]triazole (**2a**).* Yellowish solid; yield 76 mg, 78%; mp 98–100 ^{o}C (Lit[14k] mp 101–103 ^{o}C); ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.42–7.44 (m, 2H), 7.45 (t, 1H, *J* = 7.8 Hz), 7.56 (t, 2H, *J* = 8.4 Hz), 7.93–7.95 (m, 2H), 8.36 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 118.5, 120.8, 127.3, 129.1, 129.6, 140.5, 145.2; IR (KBr): 3063, 2924, 2854, 1643, 1594, 1564, 1488, 1460, 1445, 1412, 1339, 1318, 1288, 1221, 1070, 1020, 963, 917, 809, 760 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_{10}N_3^+$ [M + H$^+$] 196.0869; found 196.0871.

*5-Methyl-2-(p-tolyl)-2H-benzo[d][1,2,3]triazole (**2b**)*. Yellowish solid; yield 94 mg, 84%; mp 113–115 ^{o}C (Lit[14k] 121–124 ^{o}C); ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 2.43 (s, 3H), 2.51 (s, 3H), 7.23–7.26 (m, 1H), 7.33 (d, 2H, *J* = 8.4 Hz), 7.66 (s, 1H), 7.80 (d, 1H, *J* = 9 Hz), 8.20 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 21.3, 22.4, 116.7, 117.8, 120.5, 130.1, 137.3, 138.4, 139.0, 143.8, 145.6; IR (KBr): 3059, 2922, 2852, 1627, 1562, 1508, 1449, 1351, 1311, 1275, 1220, 1175, 1166, 1115, 1104, 1040, 973, 841, 764 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{14}N_3^+$ (M + H$^+$) 224.1182; found 224.1179.

*5-Methyl-2-(m-tolyl)-2H-benzo[d][1,2,3]triazole (**2c**).* Yellowish solid; yield 89 mg, 80%; mp 77–79 °C (Lit[14k] 77–80 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.48 (s, 3H), 2.51 (s, 3H), 7.24–7.26 (m, 2H), 7.42 (t, 1H, *J* = 8.0 Hz), 7.66 (s, 1H), 7.82 (d, 1H, *J* = 8.8 Hz), 8.12 (d, 1H, *J* = 8.4 Hz), 8.16 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 21.6, 22.4, 116.7, 117.8, 117.9, 121.2, 129.4, 129.7, 130.3, 137.5, 139.7, 140.6, 143.9, 145.7; IR (KBr): 3027, 2922, 2852, 1625, 1613, 1590, 1562, 1554, 1491, 1466, 1422, 1352, 1299, 1275, 1222, 1156, 1144, 1090, 1011, 972, 901, 879, 798, 780 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{14}N_3^+$ (M + H$^+$) 224.1182; found 224.1185.

*4-Methyl-2-(o-tolyl)-2H-benzo[d][1,2,3]triazole (**2d**)*. Red liquid; yield 65 mg, 58%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 2.41 (s, 3H), 2.73 (s, 3H), 7.19 (d, 1H, *J* = 6.8 Hz), 7.33–7.43 (m, 4H), 7.69 (d, 1H, *J* = 7.2 Hz), 7.79 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 17.4, 18.9, 115.8, 126.0, 126.3, 126.8, 127.3, 129.3, 129.7, 131.8, 133.7, 140.6, 144.9, 145.5; IR (KBr): 3058, 2924, 2852, 1608, 1583, 1512, 1497, 1463, 1433, 1382, 1337, 1289, 1281, 1264, 1156, 1131, 1095, 1038, 969, 874, 792, 753, 711 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{14}N_3^+$ (M + H$^+$) 224.1182; found 224.1187.

*2-(3,4-Dimethylphenyl)-5,6-dimethyl-2H-benzo[d][1,2,3]triazole (**2e**).* Yellow solid; yield 109 mg, 87%; mp 193–195 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 2.33 (s, 3H), 2.38 (s, 3H), 2.41 (s, 6H), 7.26–7.28 (m, 1H), 7.64 (s, 2H), 8.01 (d, 1H, *J* = 5.4 Hz), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 19.7, 20.1, 21.2, 116.8, 117.9, 121.5, 130.6, 137.5, 137.7, 138.1, 138.6, 144.5; IR (KBr): 3034, 2921, 2852, 1610, 1552, 1499, 1447, 1416, 1376, 1358, 1280, 1219, 1167, 1125, 1081, 1026, 1003, 971, 901, 880, 818, 720 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{18}N_3^+$ (M + H$^+$) 252.1495; found 252.1497.

*2-(2,4-Dimethylphenyl)-4,6-dimethyl-2H-benzo[d][1,2,3]triazole (**2f**).* Red Solid; yield 81 mg, 64%; mp 49–51 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 2.35 (s, 3H), 2.41 (s, 3H), 2.48 (s, 3H), 2.68 (s, 3H), 7.02 (s, 1H), 7.15 (d, 1H, *J* = 7.8 Hz), 7.18 (s, 1H), 7.52 (s, 1H), 7.55 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 17.3, 18.8, 21.3, 22.3, 113.9, 126.0, 127.4, 128.5, 128.9, 132.3, 133.2, 137.2, 138.3, 139.5, 144.1, 145.3; IR (KBr): 2947, 2921, 2854, 1697, 1623, 1579, 1510, 1498, 1447, 1380, 1335,

1286, 1264, 1248, 1237, 1158, 1141, 1041, 972, 876, 838, 775 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{18}N_3^+$ ($M + H^+$) 252.1495; found 252.1492.

*5-Ethyl-2-(4-ethylphenyl)-2H-benzo[d][1,2,3]triazole (**2g**).* Red liquid; yield 99 mg, 79%; ^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) 1.30 (t, 3H, *J* = 7.2 Hz), 1.33 (t, 3H, *J* = 7.8 Hz), 2.74 (q, 2H, *J* = 7.2 Hz), 2.81 (q, 2H, *J* = 7.8 Hz), 7.28 (dd, 1H, J_1 = 1.2 Hz, J_2 = 9.0 Hz), 7.36 (d, 2H, *J* = 8.4 Hz), 7.68 (s, 1H), 7.83 (d, 1H, *J* = 9.0 Hz), 8.23 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 15.5, 15.6, 28.7, 29.6, 115.3, 118.0, 120.6, 128.9, 129.3, 138.6, 143.7, 144.0, 145.4, 145.7; IR (KBr): 2964, 2925, 2853, 1629, 1561, 1512, 1455, 1376, 1310, 1284, 1266, 1241, 1218, 1175, 1113, 1052, 975, 965, 863, 838 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{18}N_3^+$ ($M + H^+$) 252.1495; found 252.1498.

*4-Ethyl-2-(2-ethylphenyl)-2H-benzo[d][1,2,3]triazole (**2h**).* Pale Yellow liquid; yield 80 mg, 64%; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.11 (t, 3H, *J* = 7.6 Hz), 1.42 (t, 3H, *J* = 7.6 Hz), 2.71 (q, 2H, *J* = 7.2 Hz), 3.12 (q, 2H, *J* = 7.6 Hz), 7.20 (d, 1H, *J* = 7.2 Hz), 7.36 (t, 2H, *J* = 8.0 Hz), 7.41–7.47 (m, 2H), 7.63 (d, 1H, *J* = 8.4 Hz), 7.77 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 14.3, 15.1, 25.2, 115.9, 124.1, 126.6, 126.8, 127.3, 130.0, 130.3, 135.4, 139.8, 140.2, 144.8, 145.1; IR (KBr): 3056, 2968, 2933, 2874, 1607, 1583, 1494, 1457, 1372, 1345, 1286, 1264, 1221, 1157, 1134, 1054, 971, 948, 872, 805, 754 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{18}N_3^+$ ($M + H^+$) 252.1495; found 252.1491.

*5-Isopropyl-2-(4- isopropylphenyl)-2H-benzo[d][1,2,3]triazole (**2i**).* Light red Solid; yield 114 mg, 81%; mp 58–60 ^oC; ^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) 1.30 (s, 3H), 1.31 (s, 3H), 1.34 (s, 3H), 1.35 (s, 3H), 2.96–3.02 (m, 1H), 3.03-3.09 (m, 1H), 7.33(d, 1H, *J* = 8.4 Hz), 7.40 (d, 2H, *J* = 8.4 Hz), 7.73 (s, 1H), 7.85 (d, 1H, *J* = 9.0 Hz), 8.25 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 23.9, 24.1, 34.0, 34.7, 113.8, 118.1, 120.6, 127.5, 128.1, 138.6, 144.1, 145.6, 148.3, 149.9; IR (KBr): 2956, 2925, 2866, 1562, 1513, 1463, 1453, 1430, 1383, 1362, 1354, 1307, 1276, 1253, 1216, 1146, 1106, 1052, 1032, 969, 947, 864, 840, 818, 731 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{22}N_3^+$ ($M + H^+$) 280.1808; found 280.1812.

*5-Butyl-2-(4- butylphenyl)-2H-benzo[d][1,2,3]triazole (**2j**)*. Reddish liquid; yield 117 mg, 76%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 0.93–0.97 (m, 6H), 1.32-1.44 (m, 4H), 1.61–1.72 (m, 4H), 2.69 (t, 2H, *J* = 8.0 Hz), 2.76 (t, 2H, *J* = 8.0 Hz), 7.25–7.27 (m, 1H), 7.34 (d, 2H, *J* = 8.4 Hz), 7.66 (s, 1H), 7.82 (d, 1H, *J* = 8.8 Hz), 8.21 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 14.14, 14.16, 22.49, 22.52, 33.4, 33.7, 35.5, 36.3, 116.1, 117.9, 120.5, 129.5, 129.6, 138.6, 142.3, 144.0, 144.1, 145.6; IR (KBr): 2955, 2932, 2857, 1629, 1608, 1561, 1512, 1465, 1427, 1378, 1352, 1277, 1257, 1234, 1141, 1114, 1081, 1017, 970, 953, 930, 836, 808 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{26}N_3^+$ (M + H$^+$) 308.2121; found 308.2125.

*5-Methoxy-2-(4- methoxyphenyl)-2H-benzo[d][1,2,3]triazole (**2k**)*. Yellowish solid; yield 92 mg, 72%; mp 140–142 °C (Lit[14k] 147–150 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.89 (s, 3H), 3.91 (s, 3H), 7.04 (d, 2H, *J* = 9.6 Hz), 7.09 (dd, 1H, J_1 = 2.4 Hz, J_2 = 9.2 Hz), 7.12–7.13 (m, 1H), 7.78 (d, 1H, *J* = 9.2 Hz), 8.21 (d, 2H, *J* = 9.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 55.7, 55.8, 94.9, 114.7, 119.1, 121.7, 122.1, 134.3, 141.2, 146.0, 159.3, 159.9; IR (KBr): 3002, 2972, 2924, 2840, 1630, 1610, 1566, 1453, 1439, 1405, 1359, 1289, 1256, 1225, 1207, 1190, 1169, 1133, 1108, 1087, 1025, 970, 852, 837, 827 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{14}N_3O_2^+$ (M + H$^+$) 256.1081; found 256.1080.

*5-Fluoro-2-(4- fluorophenyl)-2H-benzo[d][1,2,3]triazole (**2l**)*. Brownish solid; yield 73 mg, 63%; mp 169–171 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.26–7.29 (m, 3H), 7.55 (d, 1H, J_1 = 2.4 Hz, J_2 = 9.0 Hz), 7.94–7.96 (m, 1H), 8.34–8.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 116.6 (d, *J* = 24 Hz), 119.1 (d, *J* = 28.5 Hz), 120.3 (d, *J* = 10.5 Hz), 122.6 (d, *J* = 9 Hz), 136.7, 142.5, 145.2 (d, *J* = 15 Hz), 161.1, 162.7, 163.1 (d, *J* = 249 Hz); ^{19}F NMR ($CDCl_3$, 564.7 MHz): δ –111.9, –112.4; IR (KBr): 2958, 2923, 2853, 1663, 1614, 1603, 1568, 1509, 1429, 1409, 1353, 1303, 1279, 1222, 1158, 1121, 1096, 1085, 972, 956, 832, 803 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_8F_2N_3^+$ (M + H$^+$) 232.0681; found 232.0682.

*5-Chloro-2-(4- chlorophenyl)-2H-benzo[d][1,2,3]triazole (**2m**)*. White solid; yield 75 mg, 57%; mp 177–179 °C (Lit[14k] 185–187 °C); ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.38 (dd, 1H, J_1 = 1.8 Hz, J_2 = 9.0 Hz), 7.53 (d, 2H, *J* = 9.0 Hz), 7.86 (d, 1H, *J* = 9.0 Hz), 7.91 (s, 1H), 8.28 (d, 2H, *J* = 9.0 Hz); ^{13}C

NMR ($CDCl_3$, 150 MHz): δ (ppm) 117.6, 119.8, 122.0, 129.3, 129.9, 133.5, 135.4, 138.8, 143.9, 145.6; IR (KBr): 3062, 2922, 2851, 1617, 1589, 1557, 1491, 1482, 1415, 1397, 1319, 1304, 1267, 1244, 1218, 1171, 1139, 1112, 1092, 965, 938, 861, 828, 754 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_8{}^{35}Cl_2N_3{}^+$ ($M + H^+$) 264.0090; found 264.0092.

*5-Chloro-2-(3- chlorophenyl)-2H-benzo[d][1,2,3]triazole (**2n**).* White solid; yield 68 mg, 52%; mp 157–159 ^oC; ^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.38 (dd, 1H, J_1 = 1.2 Hz, J_2 = 9.0 Hz), 7.45 (d, 1H, J = 7.8 Hz), 7.49 (t, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 9.0 Hz), 7.92 (s, 1H), 8.24 (d, 1H, J = 7.8 Hz), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 117.6, 118.8, 119.9, 121.1, 129.4, 129.5, 130.8, 133.6, 135.6, 141.1, 143.8, 145.6; IR (KBr): 2955, 2923, 2852, 1594, 1586, 1556, 1483, 1453, 1437, 1280, 1266, 1243, 1218, 1109, 1071, 1049, 962, 938, 880, 862, 783, 762 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_8{}^{35}Cl_2N_3{}^+$ ($M + H^+$) 264.0090; found 264.0092.

*4-Chloro-2-(2- chlorophenyl)-2H-benzo[d][1,2,3]triazole (**2o**).* Colourless Gummy; yield 46 mg, 35%; ^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.41 (t, 1H, J = 7.8 Hz), 7.47–7.54 (m, 3H), 7.64 (d, 1H, J = 8.4 Hz), 7.75 (d, 1H, J = 6.6 Hz), 7.91 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 117.5, 118.8, 123.7, 126.9, 127.7, 127.8, 128.6, 131.2, 131.4, 138.7, 143.6, 145.8; IR (KBr): 2958, 2924, 2852, 1735, 1582, 1555, 1485, 1448, 1346, 1293, 1261, 1203, 1144, 1113, 1050, 1032, 979, 962, 870, 793, 704 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_8{}^{35}Cl_2N_3{}^+$ ($M + H^+$) 264.0090; found 264.0095.

*5-Bromo-2-(4- bromophenyl)-2H-benzo[d][1,2,3]triazole (**2p**).* Brown Solid; yield 72 mg, 41%; mp 160–162 ^oC; ^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.50 (dd, 1H, J_1 = 1.2 Hz, J_2 = 9.0 Hz), 7.68 (d, 2H, J = 8.4 Hz), 7.80 (d, 1H, J = 9.0 Hz), 8.10 (s, 1H), 8.22 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 119.9, 120.9, 121.4, 122.2, 123.4, 131.6, 132.8, 139.2, 143.9, 146.1; IR (KBr): 2953, 2852, 1614, 1554, 1487, 1477, 1411, 1348, 1318, 1302, 1264, 1240, 1215, 1141, 1095, 1070, 1032, 1008, 964, 927, 824, 800 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_8{}^{79}Br_2N_3{}^+$ ($M + H^+$) 351.9079; found 351.9083.

5-(Trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)-2H-benzo[d][1,2,3]triazole ***(2r)***. Gummy; yield 13 mg, 8%; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.63 (d, 1H, *J* = 8.4 Hz), 7.86 (d, 2H, *J* = 9.0 Hz), 8.07 (d, 1H, *J* = 9.0 Hz), 8.30 (s, 1H), 8.53 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 117.6 (t, *J* = 4.5 Hz), 120.2, 121.3, 123.3, 124.0, 125.9, 127.1 (t, *J* = 4.5 Hz), 130.1 (q, *J* = 33 Hz), 131.8 (q, *J* = 33 Hz), 142.5, 144.3, 146.2; ^{19}F NMR ($CDCl_3$, 564.7 MHz): δ −63.5, −63.3; IR (KBr): 2956, 2924, 2853, 1639, 1614, 1569, 1510, 1471, 1429, 1360, 1321, 1265, 1244, 1168, 1134, 1107, 1065, 1045, 967, 945, 886, 847 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_8N_3F_6^+$ (M + H$^+$) 332.0617; found 332.0620.

Phenyl (2-phenyl-2H-benzo[d][1,2,3]triazol-4-yl)methanone + (2-(2H-benzo[d][1,2,3]triazol-2-yl)phenyl)(phenyl)methanone ***(2a's + 2as')***. Yellowish solid; yield 96 mg, 64%; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.18 (t, 2H, *J* = 7.8 Hz), 7.26–7.27 (m, 3H), 7.37 (t, 1H, *J* = 3.6 Hz), 7.43–7.52 (m, 5H), 7.61–7.67 (m, 6H), 7.69–7.72 (m, 2H), 7.75 (d, 1H, *J* = 7.2 Hz), 7.92 (d, 2H, *J* = 7.8 Hz), 8.16 (d, 1H, *J* = 8.4 Hz), 8.20 (d, 1H, *J* = 7.8 Hz), 8.32 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 118.4, 121.0, 122.7, 123.0, 123.6, 126.4, 127.3, 128.2, 128.4, 128.7, 128.9, 129.47, 129.55, 130.0, 130.2, 130.5, 131.3, 132.8, 133.1, 134.2, 137.2, 137.9, 138.5, 140.2, 143.2, 145.2, 145.8, 194.3, 195.2; IR (KBr): 3038, 2923, 2852, 1668, 1654, 1596, 1578, 1566, 1489, 1462, 1448, 1440, 1428, 1347, 1331, 1321, 1308, 1288, 1233, 1218, 1181, 1156, 1061, 998, 962, 937, 849, 773 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{14}N_3O^+$ (M + H$^+$) 300.1131; found 300.1130.

Methyl 2-phenyl-2H-benzo[d][1,2,3]triazole-5-carboxylate + Methyl 4-(2H-benzo[d][1,2,3]triazol-2-yl)benzoate ***(2a'u + 2au')***. Light red solid; yield 72 mg, 57%; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 3.95 (s, 3H), 3.99 (s, 3H), 7.44 (dd, 2H, J_1 = 3.0 Hz, J_2 = 6.6 Hz), 7.48-7.50 (m, 1H), 7.57 (t, 2H, *J* = 7.8 Hz), 7.93 (dd, 2H, J_1 = 3.0 Hz, J_2 = 6.6 Hz), 7.96 (d, 1H, *J* = 9.0 Hz), 8.06 (d, 1H, *J* = 9.0 Hz), 8.23 (d, 2H, *J* = 8.4 Hz), 8.37 (d, 2H, *J* = 7.8 Hz), 8.44 (d, 2H, *J* = 8.4 Hz), 8.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 52.6, 52.7, 118.5, 118.7, 120.5, 121.0, 122.3, 122.8, 123.3, 127.3, 127.9, 129.2, 129.7, 129.8, 130.5, 130.8, 131.2, 140.3, 143.5, 144.6, 145.5, 146.9, 166.4, 166.9; IR (KBr):, 2949, 2916, 2842, 1718, 1605, 1560, 1504, 1441, 1422, 1345, 1381, 1279, 1219, 1194, 1150,

1136, 1011, 962, 855, 831, 807, 767, 747 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{12}N_3O_2^+$ ($M + H^+$) 254.0924; found 254.0923.

*Methyl 2-(4-methoxyphenyl)-2H-benzo[d][1,2,3]triazole-5-carboxylate + Methyl 4-(5-methoxy-2H-benzo[d][1,2,3]triazol-2-yl)benzoate (**2k'u** + **2ku'**).* Yellowish solid; yield 96 mg, 68%; ^1H NMR ($CDCl_3$, 600 MHz): δ (ppm) 3.89 (s, 3H), 3.91 (s, 3H), 3.96 (s, 3H), 3.98 (s, 3H), 7.06 (d, 2H, *J* = 9.0 Hz), 7.09–7.12 (m, 2H), 7.78 (d, 1H, *J* = 9.6 Hz), 8.01–8.04 (m, 2H), 8.20 (d, 2H, *J* = 9.0 Hz), 8.29 (d, 2H, *J* = 9.0 Hz), 8.37 (d, 2H, *J* = 9.0 Hz), 8.69 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 52.5, 55.8, 94.7, 114.5, 114.7, 118.2, 119.4, 119.9, 122.0, 122.4, 122.5, 123.6, 125.4, 127.0, 129.9, 130.8, 131.2, 141.9, 143.5, 146.6, 159.9, 160.8, 166.4, 166.9; IR (KBr):, 2954, 2924, 2852, 1715, 1630, 1606, 1563, 1509, 1455, 1439, 1299, 1282, 1251, 1228, 1184, 1171, 1143, 1129, 1108, 1082, 1022, 967, 950, 855, 828, 802, 766 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{14}N_3O_3^+$ ($M + H^+$) 284.1030; found 284.1030.

AUTHOR INFORMATION

Corresponding Author

*E mail: patel@iitg.ernet.in.

ACKNOWLEDGMENT

B. K. P acknowledges the support of this research by the Department of Science and Technology (DST) (SB/S1/OC-53/2013), New Delhi, and the Council of Scientific and Industrial Research (CSIR) (02(0096)/12/EMR-II). NK, AM and WA thank CSIR for fellowship.

Supporting Information

Spectral data (^1H, ^{13}C and ^{19}F) for synthesized compounds. This Supporting Information is available free of charge *via* the Internet at http://pubs.acs.org

REFERENCES

(1) (a) Goldberg, K. I.; Goldman, A. S. *Eds. Activation and Functionalization of C–H Bond*, ACS Symposium Series 885, *American Chemical Society*, Washington, DC, **2004**. (b) Chatani, N. Directed Metallation; *Springer*: Berlin, Germany, **2008**. (c) Daugulis, O.; Do, H. Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (d) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624.

(2) (a) Evans, P. A. *Modern Rhodium-Catalyzed Organic Reactions*; Wiley-VCH: Weinheim, Germany, **2005**. (b) Dyker, G. *Handbook of C−H Transformations: Applications in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, **2005**. (c) Li, C. -J. *Acc. Chem. Res.* **2009**, *42*, 335. (d) Ashenhurst, J. A. *Chem. Soc. Rev.* **2010**, *39*, 540.

(3) Yu, J.-Q.; Shi, Z.-J. *C−H Activation*; *Springer*: Berlin, **2010**.

(4) (a) (a) Santra, S. K.; Banerjee, A.; Khatun, N.; Patel, B. K. *Eur. J. Org. Chem.* **2015**, 350. (b) Khatun, N.; Banerjee, A.; Santra, S. K.; Behera, A.; Patel, B. K. *RSC Adv.* **2014**, *4*, 54532. 1307. (c) Khatun, N.; Santra, S. K.; Banerjee, A.; Patel, B. K. *Eur. J. Org. Chem.* **2015**, (d) Khatun, N.; Banerjee, A.; Santra, S. K.; Ali, W.; Patel, B. K. *RSC Adv.* **2015**, *5*, 36461 and references cited therein.

(5) Monnier, F.; Taillefer, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 6954.

(6) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651.

(7) Louillat, M.-L.; Patureau, F. W. *Chem. Soc. Rev.* **2014**, *43*, 901.

(8) (a) Ng, K.-H.; Chan, A. S. C.; Yu, W.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 12862. (b) Sun, K.; Li, Y.; Xiong, T.; Zhang, J.; Zhang, Q. *J. Am. Chem. Soc.* **2011**, *133*, 1694. (c) Chen, X.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 6790. (d) Kawano, T.; Hirano, K.; Satoh, T.; Miura, M. *J. Am. Chem. Soc.* **2010**, *132*, 6900. (e)

Yoo, E. J.; Ma, S.; Mei, T.-S.; Chan, K. S. L.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 7652. (f) Kim, J. Y.; Park, S. H.; Ryu, J.; Cho, S. H.; Kim, S. H.; Chang, S. *J. Am. Chem. Soc.* **2012**, *134*, 9110. (g) Yadav, M. R.; Rit, R. K.; Sahoo, A. K. *Org. Lett.* **2013**, *15*, 1638. (h) Kim, J.; Kim, J.; Chang, S. *Chem.-Eur. J.* **2013**, *19*, 7328 and references cited therein.

(9) (a) Bräse, S.; Banert, K. Organic Azides, Wiley-VCH, Weinheim, **2010**. (b) Voskresenska, V.; Wilson, R. M.; Panov, M.; Tarnovsky, A. N.; Krause, J. A.; Vyas, S.; Winter, A. H.; Hadad, C. M. *J. Am. Chem. Soc.* **2009**, *131*, 11535. (c) Nilov, D. I.; Komarov, D. Y.; Panov, M. S.; Karabaeva, K. E.; Mereshchenko, A. S.; Tarnovsky, A. N.; Wilson, R. M. *J. Am. Chem. Soc*. **2013**, *135*, 3423.

(10) (a) Kauer, J. C.; Carboni, R. A. *J. Am. Chem. Soc*. **1967**, *89*, 2633. (b) Ritchie, C. D.; Wright, D. J. *J. Am. Chem. Soc*. **1971**, *93*, 2429. (c) Li, Y.; Gao, L.-X.; Han, F.-S. *Chem. Eur. J*. **2010**, *16*, 7969. (d) Niu, L.; Yang, H.; Yang, D.; Fu, H. *Adv. Synth. Catal*. **2012**, *354*, 2211 and references therein. (e) Gavenonis, J.; Tilley, T. D. *Organometallics* **2002**, *21*, 5549 and references therein. (f) Deng, Q.-H.; Bleith, T.; Wadepohl, H.; Gade, L. H. *J. Am. Chem. Soc*. **2013**, *135*, 5356. (g) Kita, Y.; Tohma, H.; Inagaki, M.; Hatanaka, K.; Yakura. T. *Tetrahedron Lett*. **1991**, *32*, 4321. (h) Lubriks, D.; Sokolovs, I.; Suna, E. *J. Am. Chem. Soc*. **2012**, *134*, 15436. (i) Tang, C.; Jiao, N. *J. Am. Chem. Soc.* **2012**, *134*, 18924. (j) Xie, F.; Qi, Z.; Li, X. *Angew. Chem. Int. Ed.* **2013**, *52*, 11862.

(11) (a) Stokes, B. J.; Liu, S.; Driver, T. G. *J. Am. Chem. Soc.* **2011**, *133*, 4702 and references cited therein. (b) Lu, B.; Luo, Y.; Liu, L.; Ye, L.; Wang, Y.; Zhang, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 8358. (c) Kumar, M. R.; Park, A.; Park, N.; Lee, S. *Org. Lett.* **2011**, *13*, 3542. (d) Zheng, Q.-Z.; Feng, P.; Liang, Y.-F.; Jiao, N. *Org. Lett.* **2013**, *15*, 4262. (e)

Khatun, N.; Gogoi, A.; Basu, P.; Das, P.; Patel, B. K. *RSC Adv.* **2014**, *4*, 4080 and references cited therein

(12) (a) Catalán, J.; De Paz, J. L. G.; Torres, M. R.; Tornero, J. D. *J. Chem. Soc. Faraday Trans*. **1997**, *93*, 1691. (b) Kuila, D.; Kvakovszky, G.; Murphy, M. A.; Vicari, R.; Rood, M. H.; Fritch, K. A.; Fritch, J. R.; Wellinghoff, S. T.; Timmons, S. F. *Chem. Mater.* **1999**, *11*, 109. (c) Klein, M. F. G.; Pasker, F. M.; Kowarik, S.; Landerer, D.; Pfaff, M.; Isen, M.; Gerthsenm, D.; Lemmer, U.; Hoger, S.; Colsmann, A. *Macromolecules* **2013**, *46*, 3870. (d) Moor, O. D.; Dorgan, C. R.; Johnson, P. D.; Lambert, A. G.; Lecci, C.; Maillol, C.; Nugent, G.; Poignant, S. D.; Price, P. D.; Pye, R. J.; Storer, R.; Tinsley, J. M.; Vickers, R.; van Well, R.; Wilkes, F. J.; Wilson, F. X.; Wren, S.; Wynne, G. M. *Bioorg. Med. Chem. Lett.* **2011**, *21*, 4828. (e) Briguglio, I.; Piras, S.; Corona, P.; Gavini, E.; Nieddu, M.; Boatto, G.; Carta, A. *Eur. J. Med. Chem.* **2015**, *97*, 612 and references cited therein.

(13) (a) Zhang, F.; Moses, J. E. *Org. Lett.* **2009**, *11*, 1587. (b) Kale, R. R.; Prasad, V.; Hussain, H. A.; Tiwari, V. K. *Tetrahedron Lett*. **2010**, *51*, 5740. (c) Liu, Q.-L.; Wen, D.-D.; Hang, C.-C.; Li, Q.-L.; Zhu, Y.-M. *Helv. Chim. Acta* **2010**, *93*, 1350. (d) Zhou, J.; He, J.; Wang, B.; Yang, W.; Ren, H. *J. Am. Chem. Soc.* **2011**, *133*, 6868.

(14) (a) Hall, J. H. *J. Org. Chem.* **1968**, *33*, 2954. (b) Kamano, T.; Tanimoto, S. *Synthesis* **1986**, 647. (c) Dong, J.; Jin, B.; Sun, P. *Org. Lett.* **2014**, *16*, 4540. (d) Fischer, W.; Fritzsche, K.; Wolf, W.; Bore, L. **2002**, WO 2002024668 A1. (e) Kim, B. H.; Kim, S. K.; Lee, Y. S.; Jun, Y. M.; Baik, W.; Lee, B. M. *Tetrahedron Lett.* **1997**, *38*, 8303. (f) Liu, G.-B.; Zhao, H.-Y.; Yang, H.-J.; Gao, X.; Li, M.-K.; Thiemann, T. *Adv. Synth. Catal.* **2007**, *349*, 1637. (g) Jo, J.; Lee, H. Y.; Liu, W.; Olasz, A.; Chen, C.-H.; Lee, D. *J. Am.*

Chem. Soc. **2012**, *134*, 16000. (h) Ueda, S.; Su, M.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 8944. (i) Liu, Z.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 3198. (j) Shang, X.; Zhao, S.; Chen, W.; Chen, C.; Qiu, H. *Chem.-Eur. J.* **2014**, *20*, 1825. (k) Ryu, T.; Min, J.; Choi, W.; Jeon, W. H.; Lee, P. H. *Org. Lett.* **2014**, *16*, 2810.

(15) (a) Beharry, A. A.; Woolley, G. A. *Chem. Soc. Rev.* **2011**, *40*, 4422. (b) Lee, S.; Kang, H. S.; Park, J. K. *Adv. Mater.* **2012**, *24*, 2069. (c) García-Amorós, J.; Velasco, D. *Beilstein J. Org. Chem.* **2012**, *8*, 1003. (d) Ferri, V.; Elbing, M.; Pace, G.; Dickey, M. D.; Zharnikov, M.; Samorì, P.; Mayor, M.; Rampi, M. A. *Angew. Chem. Int. Ed.* **2008**, *47*, 3290.

(16) Fahey, D. R. *J. Organomet. Chem.* **1971**, *27*, 283.

(17) (a) Li, H. J.; Li, P. H.; Wang, L. *Org. Lett.* **2013**, *15*, 620. (b) Li, H. J.; Li, P. H.; Tan, H.; Wang, L. *Chem.-Eur. J.* **2013**, *19*, 14432. (c) Xiong, F.; Qian, C.; Lin, D.; Zeng, W.; Lu, X. *Org. Lett.* **2013**, *15*, 5444. (d) Song, H. Y.; Chen, D.; Pi, C.; Cui, X. L.; Wu, Y. J. *J. Org. Chem.* **2014**, *79*, 2955 and references cited therein

(18) (a) Majhi, B.; Kundu, D.; Ahammed, S.; Ranu, B. C. *Chem.-Eur. J.* **2014**, *20*, 9862. (b) Yin, Z.; Jiang, X.; Sun, P. *J. Org. Chem.* **2013**, *78*, 10002. (c) Ma, X.-T.; Tian, S.-K. *Adv. Synth. Catal.* **2013**, *355*, 337. (d) Muralirajan, K.; Cheng, C. H. *Chem.-Eur. J.* **2013**, *19*, 6198. (e) Deng, H.; Li, H.; Wang, L. *Org. Lett.* 2015, *17*, 2450. (f) Lian, Y.; Bergman, R. G.; Lavis, L. D.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 7122. (g) Wang, H.; Yu, Y.; Hong, X.; Tan, Q.; Xu, B. *J. Org. Chem.* **2014**, *79*, 3279. (h) Jia, X.; Han, J. *J. Org. Chem.* **2014**, *79*, 4180.

(19) (a) Geng, X.; Wang, C. *Org. Lett.*, **2015**, *17*, 2434. (b) Sharma, S.; Han, S. H.; Han, S.; Ji, W.; Oh, J.; Lee, S.-Y.; Oh, J. S.; Jung, Y. H.; Kim, I. S. *Org. Lett.* **2015**, *17*, 2852. (c) Son, J.-Y.; Kim, S.; Jeon, W. H.; Lee, P. H. *Org. Lett.* **2015**, *17*, 2518.

(20) Lian, Y.; Hummel, J. R.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 12548.

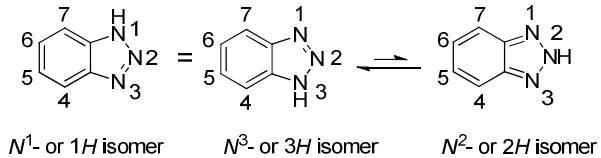
(21) (a) Guin, S.; Ghosh, T.; Rout, S. K.; Banerjee, A.; Patel, B. K. *Org. Lett.*, **2011**, *13*, 5976. (b) Gogoi, A.; Guin, S.; Rout, S. K.; Patel, B. K. *Org. Lett.*, **2013**, *15*, 1802.

(22) (a) Deprez, N. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 11234. (b) Racowski, J. M.; Dick, A. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 10974. (c) Rosewall, C. F.; Sibbald, P. A.; Liskin, D. V.; Michael, F. E. *J. Am. Chem. Soc.* **2009**, *131*, 9488. 15945. (d) Whitfield, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 15142.

(23) (a) Powers, D. C.; Geibel, M. A. L.; Klein, J. E. M. N.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 17050. (b) Powers, D. C.; Lee, E.; Ariafard, A.; Sanford, M. S.; Yates, B. F.; Canty, A. J.; Ritter, T. *J. Am. Chem. Soc.* **2012**, *134*, 12002 and references cited therein.

(24) (a) Sun, X.; Li, X.; Song, S.; Zhu, Y.; Liang, Y.-F.; Jiao, N. *J. Am. Chem. Soc.* **2015**, *137*, 6059. (b) Liang, Y.; Liang, Y.-F.; Jiao, N. *Org. Chem. Front.* **2015**, *2*, 403.

* **Benzotriazole notation**: Benzotriazole is a fused heterocyclic compound having three vicinal nitrogen atoms in its five member ring. This ring can exist in two tautomeric forms *viz.* N^1 (N^3) or 1*H* isomer and N^2 or 2*H*-isomer due to the presence of one labile proton as shown below:



The N^1 and N^3 isomers are identical due to their structural similarity. The N^1 (1*H*) isomer is predominantly present in equilibrium with N^2 (2*H*) isomer at room temperature. The

greater aromaticity of benzoid structure in N^1 (1*H*) isomer is the source of thermodynamical stability compared to the quinoid-like structure in N^2 (2*H*) isomer.

** **A general note for compounds designation**: A typical symmetrical azoarene (starting material) is designated as (**1a**) while its product is referred as (**2a**)**.** The numerical number (**1**) stands for starting material while (**2**) is for product and (**a**) for a particular substituent. For unsymmetrical azoarenes, both a numbering and two letters have been used. For instance, in (**1as**) the number (**1**) is for the starting material while the double letter (**as**) indicates the presence of two different aryl rings. The alphabet (**a**) signifies simple phenyl ring while (**s**) signifies an aryl ring having *o*-COPh substituent. The numbering (**2a's**) suggests that the *ortho*-aminative heterocyclization is taking place at the phenyl ring, while (**2as'**) indicates the *ortho*-aminative heterocyclization is at the aryl ring having *o*-COPh substituent. Similar nomenclature is followed for other symmetrical and unsymmetrical azoarenes and their products.