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Methods for direct C(sp^2)–H bonds azidation

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Direct functionalization of C–H bonds has attracted great attention in recent years from the perspectives of atom and step economy. In this context, a variety of processes have been developed for the construction of synthetically and biologically important organic azides through the oxidative C–H bonds azidation. In this review, we have summarized recent progress in the direct azidation of C(sp^2)–H bonds. The review is divided into three major sections: (i) direct azidation of aromatic C–H bonds; (ii) direct azidation of olefinic C–H bonds; and (iii) direct azidation of aldehydic C–H bonds. Mechanistic aspects of the reactions are considered and discussed in detail.

1. Introduction

Needless to say, organic azides are among the most important and versatile intermediates in organic chemistry which are diversely utilized in the synthesis of various nitrogen-containing heterocycles,[1] amines,[2] amides,[3] and imines[4] owing to the unique chemical reactivity of the azido

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functionality. Moreover, compounds bearing this valuable functional group exhibit a variety of biological activities (Scheme 1), such as anti-HIV,[5] anti-inflammatory,[6] antibiotic,[7] and anti-myeloma[8] activities. Due to the wide importance of the title compounds in organic and medicinal chemistry, a number of methods for their preparation were developed. The most commonly used methods involve: (i) coupling of organometallic reagents with azido compounds;[9] (ii) carbon-nitrogen coupling reaction between organic halides and azido compounds;[10] and (iii) decarboxylative azidation of carboxylic acids.[11] Despite their prevalence, these approaches not only require the pre-functionalized starting materials but also produce hazardous waste streams. Therefore, it is of considerable importance to develop straightforward and truly efficient procedures for the

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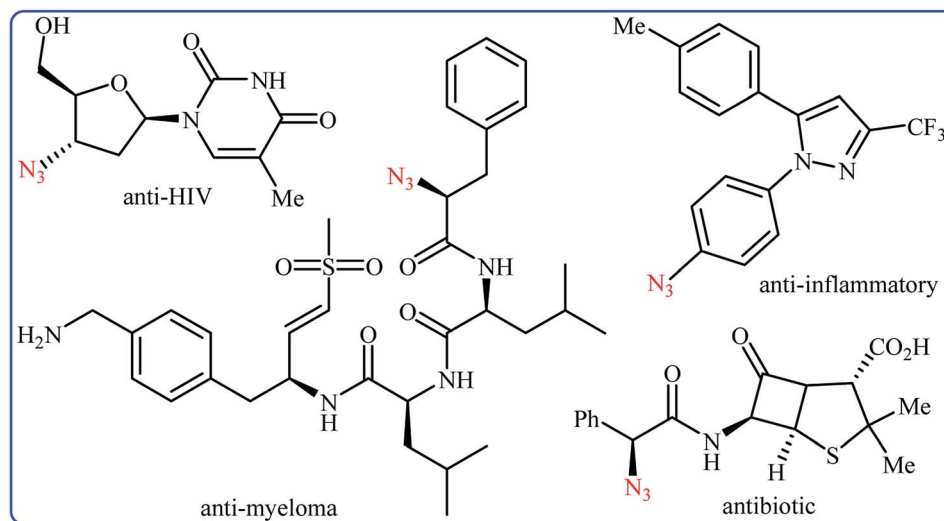
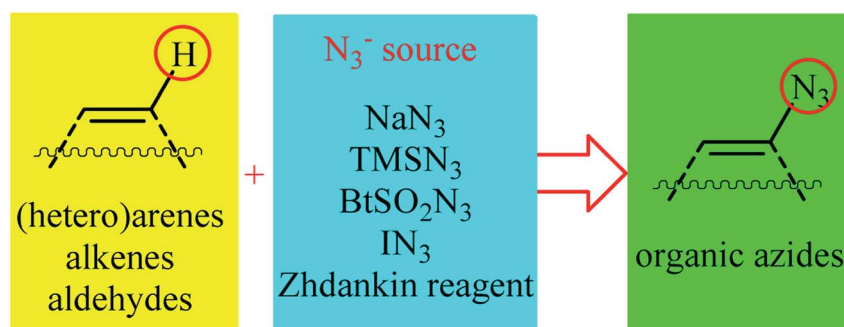**Scheme 1** Selected examples of biologically active molecules bearing azido group.

Fig. 1 Direct C(sp^2)–H bonds azidation.

fabrication of organic azides without pre-activation of starting materials.

Direct functionalization of C–H bonds represents a powerful strategy for the rapid construction of diverse C–C and C–X (X= heteroatom) bonds due to its inherent efficiency.[12] In contrast to traditional methods which rely on the use of pre-functionalized (often halogenated) starting materials, in this strategy the inactive C–H bonds act as a functional group, thereby the number of synthetic steps and chemical wastes are considerably reduced. Among various C–H bond functionalization reactions, direct C–N$_3$ bond forming reactions have attracted much attention in recent years. In connection with our recent review papers on the direct functionalization of C–H bonds[13] and cross-coupling reactions,[14] we summarize here a variety of protocols for the direct oxidative C(sp^2)–H bonds azidation reactions (Fig. 1). The review is divided into three major sections. The first section focuses exclusively on direct azidation of aromatic C–H bonds. The second will cover azidation of olefinic C–H bonds. The third section will discuss azidation of aldehydic C–H bonds. Of note, we have not discussed azidation of aliphatic C–H bonds, since it has recently been described in another publication.[15]

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2. Aromatic C–H bonds

In the present section, we'll describe the available literature on the direct azidation of (hetero)aromatic C–H bonds. For clarity,
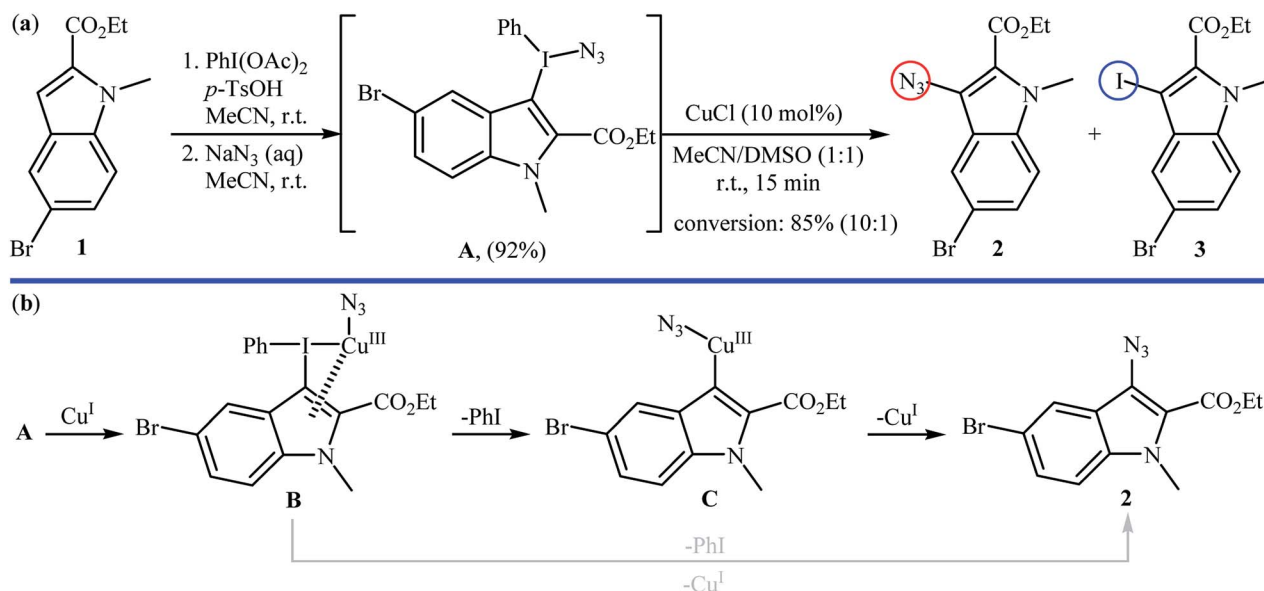
Scheme 2 (a) Suna's synthesis of indolyl azide **2**; (b) mechanistic explanation of the synthesis of indolyl azide **2**.

the reactions are classified by the type of azidation reagents (*e.g.*, NaN₃, TMSN₃, Zhdankin reagent).

2.1. NaN₃ as azide source

This subsection considers direct C–H azidation of (hetero)arene substrates utilizing inexpensive, easily available and stable sodium azide (NaN₃) as the azide source.

2.1.1. Metal-catalyzed reactions. Metal-catalyzed direct aromatic C–H bonds azidation using NaN₃ as the azide source was first demonstrated by Suna and co-workers,[16] where a functionalized indolyl azide **2** was achieved in good yield by the reaction of corresponding indole **1** with a mixture of PhI(OAc)₂, TsOH, and NaN₃ in MeCN followed by regioselective fragmentation of the resulted indolyl(phenyl)iodonium azide **A** *via* the treatment with a catalytic amount of CuCl in a 1 : 1 mixture of MeCN and DMSO at room temperature (Scheme 2a). The results proved that the choice of CuCl was critical to the success of this reaction and other metal salts (*e.g.*, Pd(OAc)₂, Zn(OTf)₂, Sc(OTf)₃, (Ph₃P)AuCl) almost failed to give the target

product. In the absence of catalyst, fragmentation of iodonium salt **A** is controlled by electronic factors, as evidenced by the formation of iodoindole **3** as the main product. The authors proposed the mechanistic pathway for the conversion of iodonium salt **A** into indolyl azide **2** shown in Scheme 2b that involves the initial formation of Cu(III) species **B** through the oxidative addition of this intermediate **A** to Cu(I) salts, which undergoes regioselective transformation to PhI and hetero-arylcopper(III) species **C**. Finally, reductive elimination of intermediate **C** leads to the expected indolyl azide **2** and regenerate the Cu(I) species. In another possibility, complex **B** can directly collapse into azide product **2** *via* the highly regio-selective coupling of the heterocycle with the azide.

The procedure was nicely applied for the synthesis of a diverse range of 1,2,3-triazoles by 1,3-dipolar cycloaddition of *in situ* generated aizdes with acetylenes **5**. As shown in Scheme 3, various electron-rich heterocycles **4** such as pyrroles, indoles, thienopyrroles, pyrrolopyridines, and pyrrolopyrimidines were applied in this transformation to give the corresponding 1,4-disubstituted 1,2,3-triazole products **6** in moderate to excellent
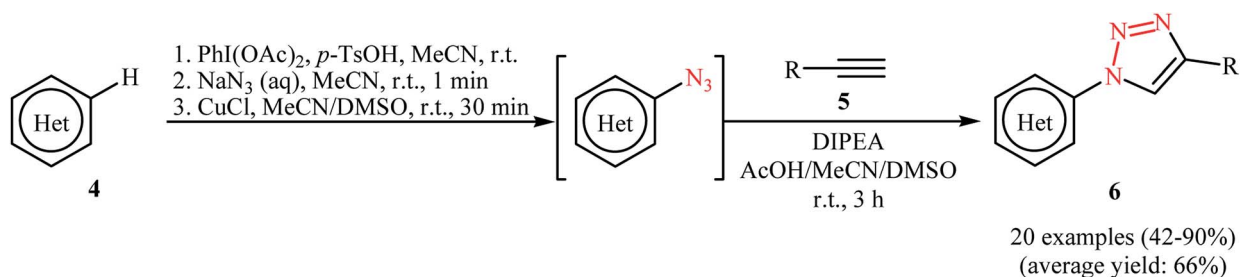
Heteroaromatics= pyrrole, indole, pyrrolo[2,3-*b*]pyridine, pyrrolo[3,2-*b*]pyridine, pyrrolo[2,3-*d*]pyrimidine, thieno[3,2-*b*]pyrrole
R= *c*Pr, C(Me)₂OH, CO₂Et, 4-OCF₃-C₆H₄, 2-Cl-C₆H₄, DAGlc (diacetone-D-glucose)

Scheme 3 . One-pot multistep synthesis of 1,4-disubstituted 1,2,3-triazoles **6**.
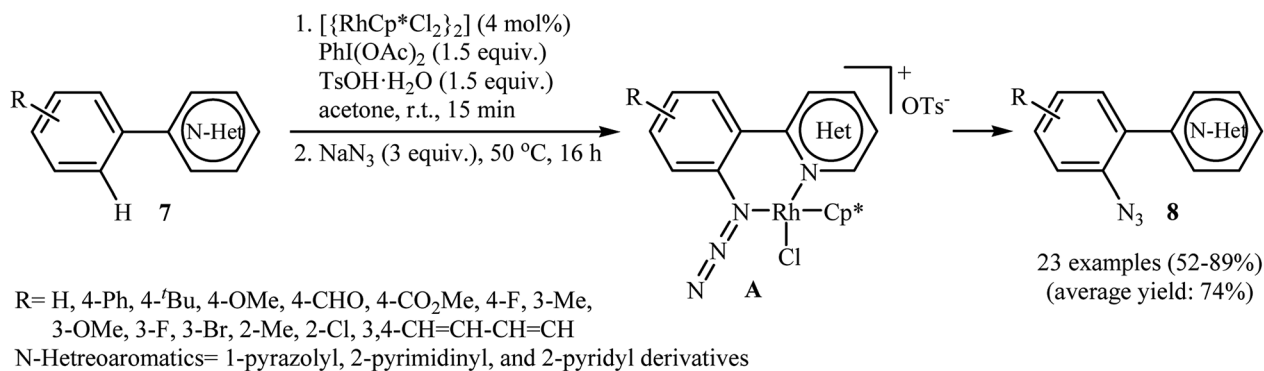
Scheme 4 Rh-catalyzed direct *ortho*-selective C–H azidation of arenes 7 with NaN$_3$.

yields. The authors also showed that *in situ* generated heteroaryl azides can be conveniently reduced to heteroarylamines by aqueous ammonium sulfide at room temperature.

Inspired by this work, Li and colleagues developed an interesting direct *ortho*-selective C–H azidation of arene substrates bearing coordinating directing groups, such as 2-pyridyl, 2-pyrimidinyl, and 1-pyrazolyl using NaN$_3$ as the azide source.[17] Thus, in the presence of [{RhCp*Cl$_2$}$_2$] as a commercially available but expensive catalyst, PhI(OAc)$_2$ as an oxidant and TsOH as an additive, various arene substrates 7 possessing electron-donating or electron-withdrawing functional groups underwent smooth *o*-azidation to afford the expected mono-azidated products 8 in 52–89% yield (Scheme 4). The authors suggested that the *N,N* chelation in intermediate **A** may account for the high selectivity of this reaction for mono-azidation. After evaluation of potential synthetic applicability of the prepared azido arenes, they found that simple heating (120 °C) of adducts in 1,4-dioxane for 10 h afforded the corresponding pyrido[1,2-*b*] indazole derivatives in almost quantitative yields. They also successfully expended their oxidative conditions to direct C–H nitration of a library of (hetero)arenes with NaNO$_2$ as a readily available nitro source. Recently, density functional theory (DFT) calculations indicated that the active Rh(III) catalyst is oxidized to Rh(v) by trivalent iodine (PhIOAc$^+$).[18] Thus it was suggested

that the reaction proceeds through an oxidation/electrophilic deprotonation/coordination/reductive elimination sequential process.

Shortly afterwards, an elegant Cu(II)-catalyzed direct azidation of azacalix[1]arene[3]pyridine derivatives with NaN$_3$ was reported by Wang *et al.*[19] The Cu(ClO)$_4$·6H$_2$O/TsOH/MeCN/DCM system was found to be optimal for this transformation, while addition of an small amount of water gave excellent results. The authors declared that water prevented precipitation of copper salts from the reaction mixture. These reaction were run under aerobic conditions at ambient temperature, tolerated various NH-free and N-protected azacalix[1]arene[3]pyridines 9, and generally provided mono-azidated products 10 in high to quantitative yields (Scheme 5). It should be mentioned that the reaction of NaN$_3$ with isolated arylcopper(II) **A** and arylcopper(III) **B** compounds indicated clearly that the arylcopper(III) **B** was an active species in this azidation reaction. Thus, an unprecedented Cu(II)–ArCu(II)–ArCu(III)–Cu(I) catalytic cycle was proposed for this synthetic strategy. Just like previous works, the synthesized azido compounds were successfully utilized as starting materials in the fabrication of amino- and 1,2,3-triazole-bearing azacalix[1]-arene[3]pyridines.
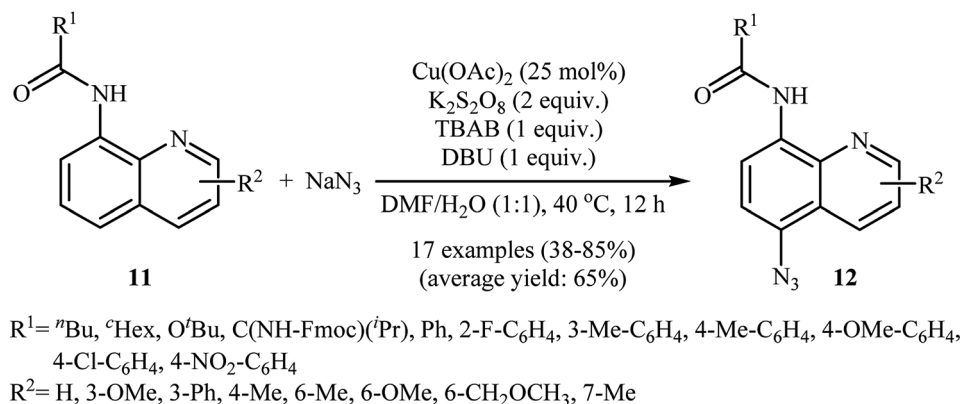
In 2016, the group of Zhu investigated Cu-catalyzed direct C–H azidation of *N*-acylated 8-aminoquinolines with NaN$_3$.[20] A
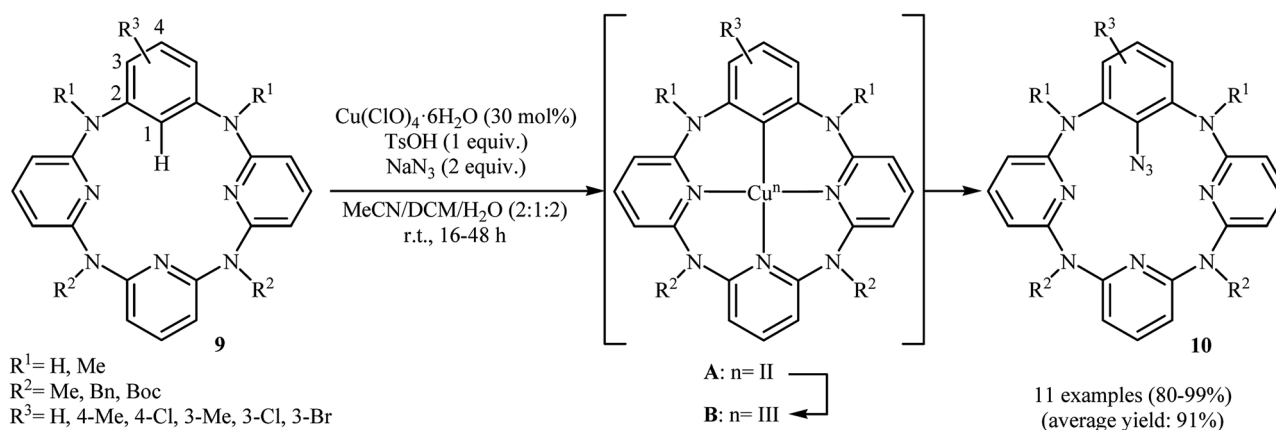
Scheme 5 Cu(II)-catalyzed direct azidation of azacalix[1]arene[3]pyridines 9 with NaN$_3$.

$R^1 = {}^nBu, {}^cHex, O^tBu, C(NH-Fmoc)({}^iPr), Ph, 2-F-C_6H_4, 3-Me-C_6H_4, 4-Me-C_6H_4, 4-OMe-C_6H_4,$
      $4-Cl-C_6H_4, 4-NO_2-C_6H_4$
$R^2 = H, 3-OMe, 3-Ph, 4-Me, 6-Me, 6-OMe, 6-CH_2OCH_3, 7-Me$

Scheme 6 Regioselective azidation of *N*-acylated 8-aminoquinolines **11** with NaN_3.

careful screening of catalysts, oxidants, additives, and solvents resulted in the optimized reaction conditions shown in Scheme 6. Under these conditions, azidation took place selectively at the 5-position of various substituted 8-aminoquinolines **11** to form C5-azidated 8-aminoquinolines **12** in almost moderate to high yields. However, the reaction failed with the C-2 substituted quinolines due to the failure formation of Cu(ɪɪ) complex coming from the steric hindrance of the *ortho*-substituted groups. The control experiments revealed that both amide N–H and quinoline nitrogen were indispensable for this reaction. Based on a series of other control experiments, the authors suggested that the reaction starts with the generation of an aryl-Cu^{II} complex **A** through the coordination of Cu(OAc)$_2$ to the nitrogen atoms of 8-aminoquinoline **11**, which is followed by reaction with the azide radical, which is generated *in situ* from the NaN$_3$ and K$_2$S$_2$O$_8$, to give the intermediate **B** *via* a single electron transfer (SET) process. Subsequently, oxidation of Cu^I

complex **B** under air leading to the formation of Cu^{II} complex **C** that, after a metal dissociation process affords the intermediate **D** and regenerates the catalyst Cu(OAc)$_2$. Finally, a proton transfer process from **D** delivers the target C5-azidated 8-aminoquinoline **12** (Scheme 7).

Recently, the same group developed an interesting Cu-catalyzed free amino group-directed C–H bond azidation of aromatic amines with NaN$_3$.[21] Thus, various electron-rich and electron-poor anilines **13** in the presence of 25 mol% of Cu(OAc)$_2$ and 2 equiv. of H$_2$O$_2$ in neat water underwent *ortho*-selective azidation and afforded the target aryl azides **14** in moderate to high yields (Scheme 8). The reaction is noteworthy in that both primary and secondary anilines are tolerated. This protocol was also successfully applied to late-stage functionalization of aniline-based drugs, such as procaine, benzocaine, and aminoglutethimide. Mechanistically, a single electron transfer process was likely involved in this transformation,
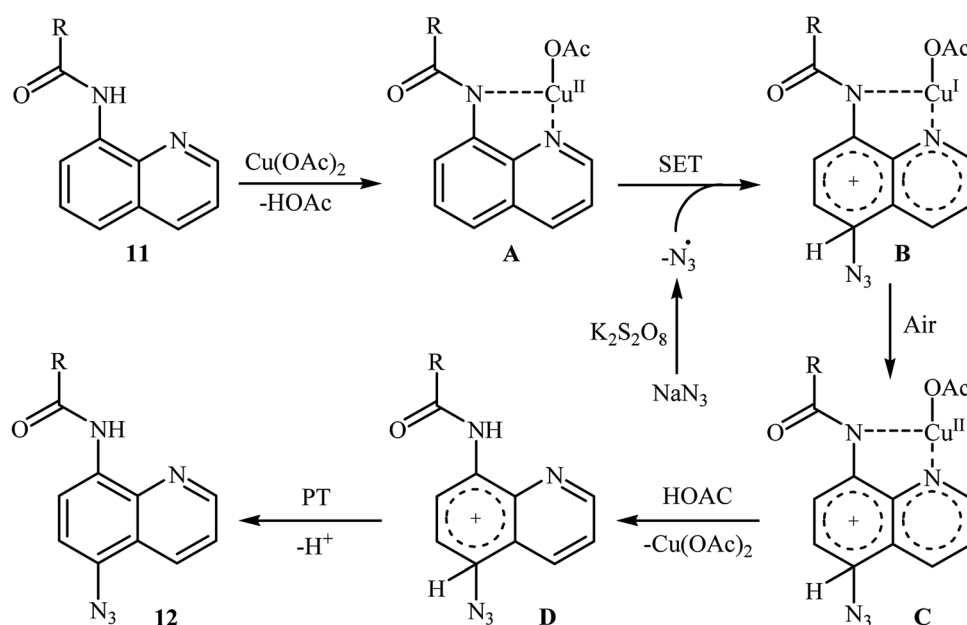
Scheme 7 The proposed mechanism for the formation of C5-azidated 8-aminoquinolines **12**.
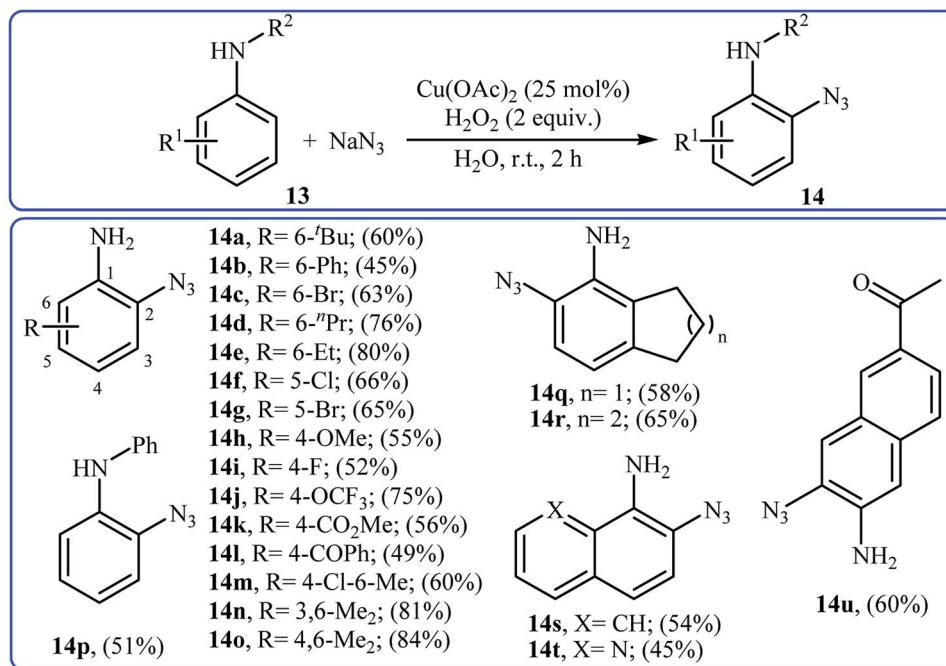
Scheme 8 *ortho*-Selective azidation of anilines **11** with NaN$_3$.

which could be completely inhibited by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), a radical scavenger.

2.1.2. Metal-free reactions. In 2016, Sudalai and colleagues reported an efficient I$_2$-mediated regioselective C3 azidation of indole derivatives **15** with NaN$_3$ under metal-free conditions at room temperature.[22] 1.0 equiv. molecular iodine and 1.0 equiv. Et$_3$N in DMSO delivered the 3-azido indole products **16** in moderate to excellent yield (Scheme 9). The protocol was highly tolerable to the substrates bearing both electron-donating and -withdrawing substituents. The results showed that NH-free

substrates furnished better yields compared to N-substituted indoles. The authors claimed that their methodology was the first example of the direct azidation of indoles at C-3 position. Under similar conditions, the azidation of a 1*H*-indazole substrate was also proceeded effectively to afford the corresponding 3-azido-1*H*-indazole in moderate yield with excellent regioselectivity. Mechanistic study revealed that the reaction starts with the formation of an iodonium ion intermediate **A** by reaction between starting indole **15** and I$_2$. Next, its ring opening with azide anion (from the preferred benzylic position)
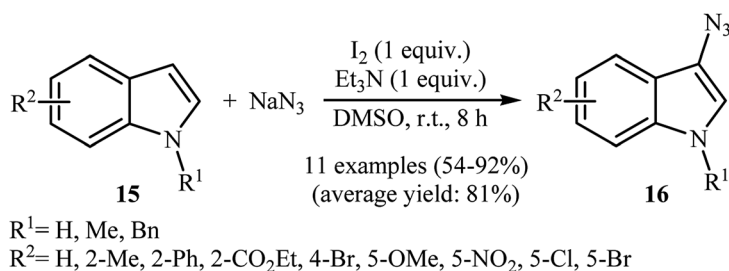
Scheme 9 I$_2$-mediated C3–H azidation of indoles **15**.
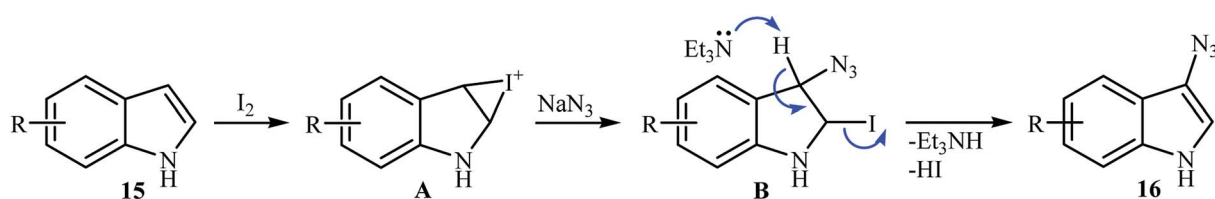
Scheme 10 Mechanistic pathway for the formation of 3-azido indoles **16**.
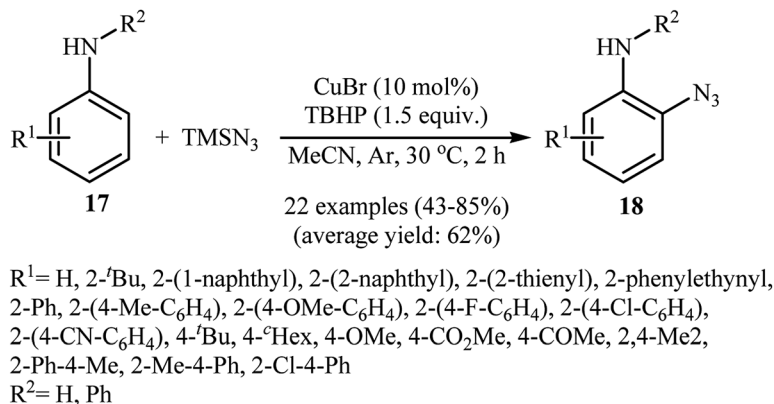
Scheme 11 Cu-catalyzed *ortho*-directed azidation of anilines **17** with TMSN$_3$.

leads to iodo-azide intermediate **B** that after HI elimination in the presence of base, affords the target 3-azido indoles **16** (Scheme 10).

2.2. TMSN$_3$ as azide source

Significant progress has been made in the azidation of organic molecules using trimethylsilyl azide (TMSN$_3$) as a versatile, commercially available azidating reagent in the past decades.[23] In this sub-section, we wish to summarize the recent developments in the direct azidation of (hetero)aromatic C–H bonds utilizing the titled reagent.

2.2.1. Metal-catalyzed reactions. In 2012, Tang and Jiao developed a copper-catalyzed *ortho*-directed azidation of anilines **17** with TMSN$_3$ under rather mild conditions to provide 2-azidobenzenamines **18** in moderate to good yields (Scheme 11).[24] The optimal conditions of the reaction involve the use of CuBr (10 mol%) as the catalyst and *tert*-butyl hydroperoxide (TBHP) as the oxidant. Among the various solvents like toluene, benzene, ethyl acetate, DMF, DCE, MeCN, MeNO$_2$; MeCN proved to be the most efficient for this transformation. The

established conditions exhibited very good functional group tolerance and regioselectivity. However, in the cases of *para*-substituted anilines, both mono- and di-azidated products were obtained. This protocol was compatible with primary and secondary amines, but not tertiary amines. According to the authors, the amino group was responsible for *ortho* C–H bond activation by coordinating with the metal center. A plausible mechanism for this C–N bond forming reaction involves the following steps (Scheme 12): (i) coordination of copper to the amino group of the substrate **17** to form intermediate **A**; (ii) combination of intermediate **A** with an azide radical, generated *in situ* from TMSN$_3$ and TBHP, to yield intermediate **B**; (iii) single electron transfer from the aryl ring of the intermediate **B** to the metal center to afford intermediate **C**; (iv) migration of the azido group into the aryl ring to give intermediate **D**; and (v) deprotonation of intermediate **D** *via* SET process to afford the final product **18**. Three years later, Lhoták and co-workers applied the similar protocol for the regioselective *meta* C–H azidation of calix[4]arene.[25] Utilizing the same catalytic system in toluene (r.t., 15 min), the desired *meta*-monoazidated calix[4]arene was obtained in 52% yield.
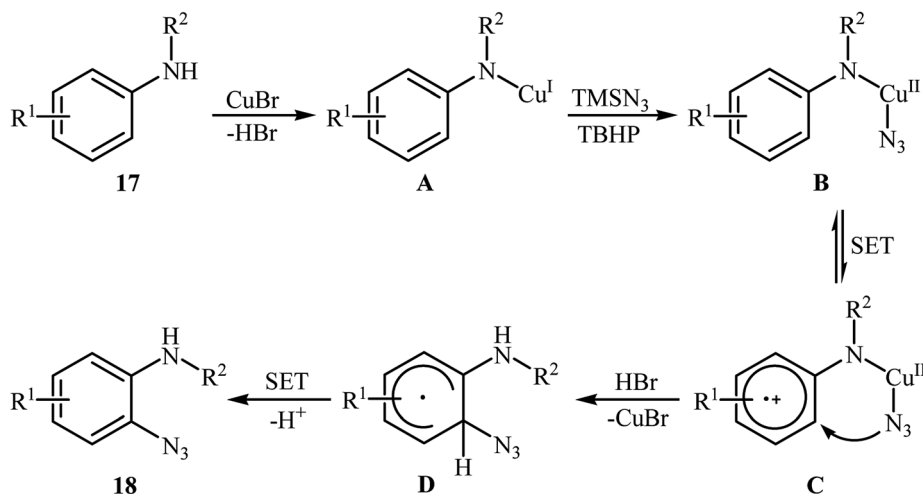
Scheme 12 Plausible mechanism for Cu(I)-catalyzed azidation of anilines **17** with TMSN$_3$.
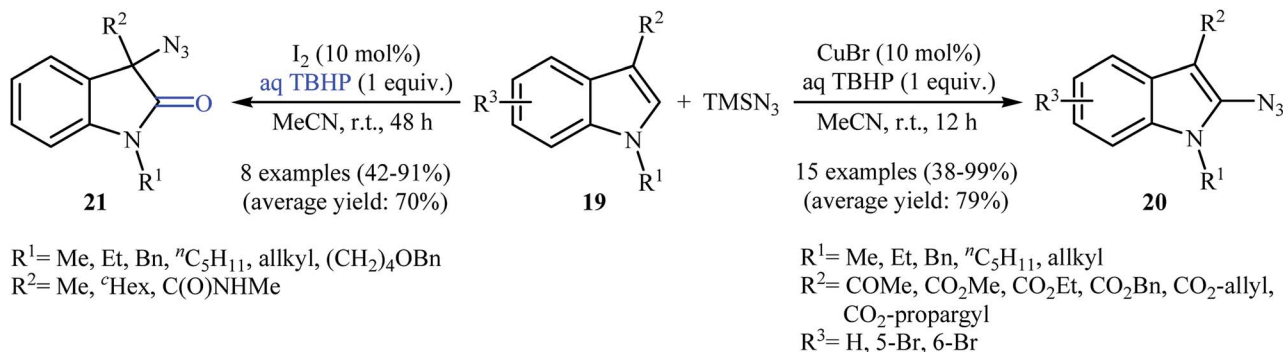
Scheme 13 Substituent-directed regioselective azidation of indoles **19** with TMSN$_3$.

Very recently, the group of Prabhu realized a similar process which extended the scope to indoles.[26] Thus, a variety of C2-azidated indoles **20** were prepared by treatment of indoles **19** bearing an ester or ketone moiety at the C3-position with TMSN$_3$ in the presence of CuBr/TBHP combination as a catalytic system at room temperature (Scheme 13). Interestingly, when the substitutions on the C3-position of indoles were less radical stabilizing groups, such as an alkyl or amide groups, the reaction preferred to furnish the 3-azidooxindole products. Noteworthy, the replacement of CuBr by molecular iodine afforded better yields of 3-azidooxindole products **21**. In this investigation, the authors found some limitation in their protocol when they attempted to react *N*-methylindole and 3-methylindole with TMSN$_3$ under the standard reaction conditions (either CuBr or I$_2$ catalysis conditions). In these cases, no desired product was observed. The application of both procedures to gram-scale synthesis was reported showing the scalability of these transformations.

2.2.2. Metal-free reactions. In 1991, Kita and co-workers successfully accomplished a hypervalent iodine reagent, phenyliodine(III) bis(trifluoroacetate) PhI(TFA)$_2$, mediated direct azidation of anisole derivatives **22** with TMSN$_3$, presenting the first example of metal-free aromatic C–H bonds azidation utilizing TMSN$_3$.[27,28] They found that the choice of solvent was critical to the success of this reaction and polar protic solvents, such as 1,1,1,3,3,3-hexafluoro-2-propanol proved to be the best choice, giving the desired mono-azidated products **23** in moderate to high yields (Scheme 14). It was suggested that the π-complex **A** was the key intermediate in this transformation. Eighteen year later, Tsarevsky applied this strategy to azidation

of polystyrene by using PhI(OAc)$_2$ as a hypervalent iodine reagent.[29] The amount of azide groups in the products was estimated to be about 1 in every 11 styrene units.

This azidation reaction was nicely extended in 2015 to quinoline N-oxides by Li *et al.*[30] They showed that functionalized quinoline N-oxides **24** can be preferentially azidated at the C2-position with TMSN$_3$ in EtOAc at room temperature (Scheme 15). This very fast reaction gave moderate to almost quantitate yields with a broad substrate scope. However, 2-substituted quinoline N-oxides failed to give the expected products under this reaction condition. Furthermore, isoquinoline N-oxide and pyridine N-oxide were incompatible in this reaction, indicating the importance of radical stabilization from the π-neighboring Ph group besides the other side of carbene. The mechanism of this azidation was proposed based on the control experiments and electron paramagnetic resonance (EPR) studies, determining that it proceeds through the following key steps (Scheme 16): (i) initial formation of two azide radicals *via* thermal hemolytic cleavage of *in situ* generated PhI(N$_3$)$_2$; (ii) single electron oxidation of quinoline N-oxide **24** with the help of the azide radical to give the radical cation **A** or **A′**; (iii) deprotonation of intermediate **A** (or **A′**) to afford the carbene stabilized N–O radical **B**; and (iv) single electron transfer from the radical **B** to TMSN$_3$ to give the target product **25** through the intermediate **C**.
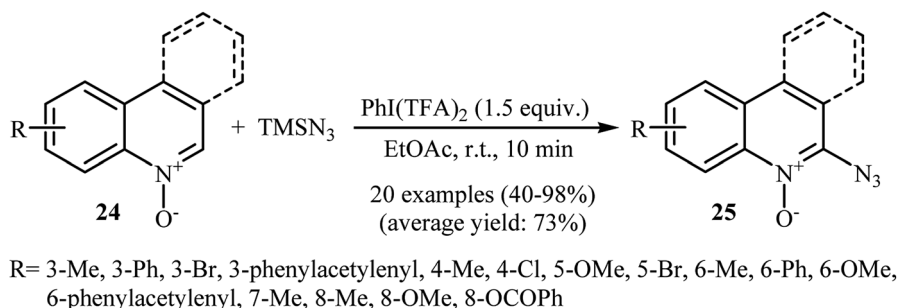
2.3. Azido-benziodoxolone as azide source

Azido-benziodoxolone (Zhdankin reagent) is a novel and valuable azidating reagent which is increasingly being used in the
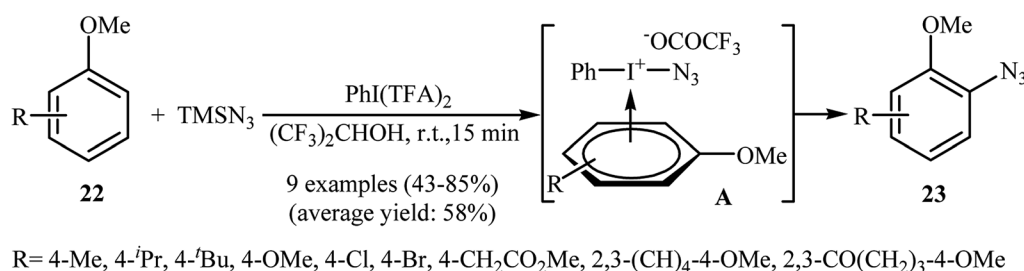
**Scheme 14** PhI(TFA)$_2$-mediated azidation of anisoles **22** with TMSN$_3$.

Scheme 15 Metal-free regioselective C–H azidation of quinoline N-oxides **24** with TMSN₃.

direct azidation of aliphatic, benzylic, olefinic, and aldehydic C–H bonds.[31] However, recently it was found that this reagent has hazardous nature.[32] The first protocol for the direct aromatic C–H bonds azidation utilizing Zhdankin reagent was reported by Hao *et al.* in 2014.[33] Catalyzed by Cu(OAc)₂, the reaction of aromatic amines **26** with azido-benziodoxolone **27** in THF furnished *ortho*-azido anilines **28** in almost moderate to high yields (Scheme 17). To compare the efficiency of this procedure to the Jiao's procedure (TMSN₃, CuBr, TBHP, MeCN, 30 °C) it can be concluded that the former methodology is superior due to it was afforded higher yields of mono-azidated products with excellent regioselectivity even for *para*-substituted anilines. Scheme 18 shows the authors proposed mechanism for this transformation. Initially, one-electron oxidation of aniline **26** by oxidative hypervalent iodine(III) reagent **27** generates the aniline radical cation and radical anion **A**. Its N–I bond cleavage by the aim of Lewis acid leads to N₃-containing 2-iodo-benzoate **B** that undergoes decomposition under the reaction conditions to form a copper(II) salt **C** and an azide radical. Subsequently, the N₃ radical preferentially attacks the aromatic ring *ortho* to the primary amino group of the aniline radical cation to give the cyclohexadienyl cation species **D** which is in equilibrium with cation species **E**. Finally,

deprotonation of **E** by 2-iodobenzoate **C** affords the target azidation product **28**.

In 2017, Wang and co-workers synthesized a library of azido-(hetero)arenes **30** in moderate to good yields through the site-selective deprotonative zincation followed by copper-catalyzed azidation of the corresponding (hetero)arenes **29** with Zhdankin reagent.[34] Among the various zincation reagents, Zn(TMP)Cl·LiCl was the most efficient for the strongly electron-deficient (hetero)arenes and LiTMP₀.₁Li[ZnEt₂(TMP)] for the non-activated and electron-rich ones. As shown in Scheme 19, the azidation took place exclusively at the most acidic position.

Recently, Chen and Wang along with their co-workers demonstrated that, in the presence of only 1 mol% of Rh₂(esp)₂ as a commercially available catalyst in DCE, various electron-rich aromatic substrates **31** undergo chemo- and regioselective azidation with Zhdankin's reagent to afford mono-azidated arenes **32** in moderate yields.[35] Interestingly, under the standard conditions, the azidation of arenes bearing alkene moieties displayed different chemoselectivities, favoring aromatic C(sp²)–H azidation over alkeneic C(sp²)–H azidation. The mild reaction conditions allowed the tolerance of various functional groups such as chloro, bromo, iodo, ether, ester, aldehyde, and ketone functionalities. Some reported examples
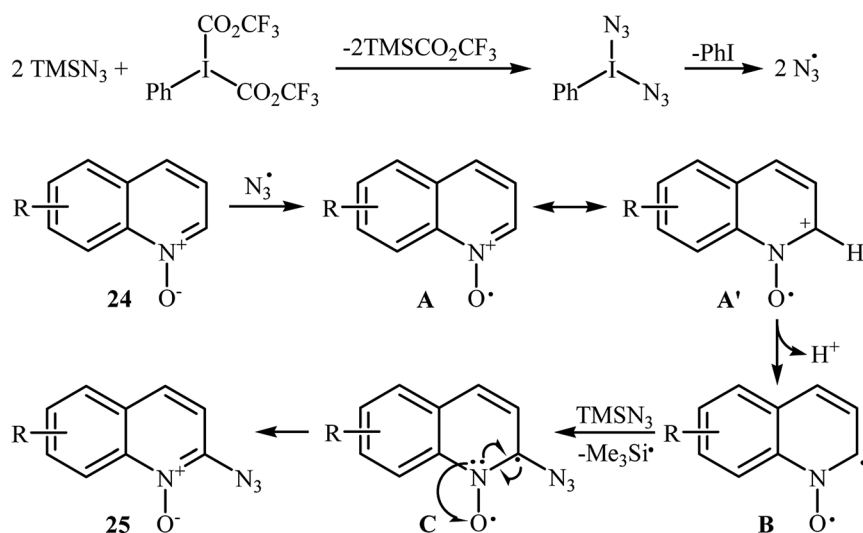
Scheme 16 Proposed mechanism for azidation of quinoline N-oxides **24** with TMSN₃.
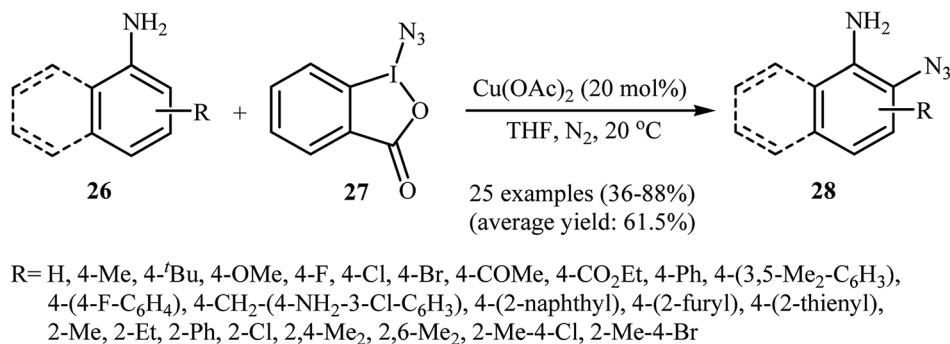
Scheme 17 Cu-catalyzed *ortho*-azidation of aromatic amines **26** with azido-benziodoxolone **27**.

are shown in Scheme 20. It was also found that the procedure is suitable for aryl amine substrates and azidation proceeded selectively at the position *para* to the amine group in MeOH. Mechanistic studies suggested that the catalyst-bound intermediate Rh$_2$(esp)$_2$N$_3$ is the key active species in the reaction.

### 2.4. Benzotriazole sulphonyl azide as azide source

In 2015, Azad and Narula revealed that the treatment of 2-phenylpyridines **33** with benzotriazole sulfonyl azide (BtSO$_2$N$_3$) as a crystalline, safe and easily available azidating agent in the presence of a catalytic amount of CuI and over-stoichiometric amount of K$_2$S$_2$O$_8$ in 1,2,3-trichloropropane (TCP) afforded the corresponding *ortho*-azide arenes **34** in moderate to excellent yields (Scheme 21).[36] The substrate scope was evaluated on 16 functionalized 2-phenylpyridines and proved that both electron-donor and -withdrawing functional groups were tolerated. Of note, other coordinating directing groups, including pyrimidine, pyrazole and thiazole were also found to similarly mediate the *ortho*-selective C–H azidation of simple arenes under this condition. The mechanistic course suggested by the authors for this azidation reaction is depicted in Scheme 22, and starts with the formation of a Cu^I complex **A** by the coordination of the copper catalyst to the 2-phenylpyridine **33** that, after reaction with BtSO$_2$N$_3$ in the presence of K$_2$S$_2$O$_8$ affords intermediate **B**. Subsequently, a single electron transfer from the metal center to the aromatic ring converts this complex into radical cation **C**, which undergoes an intramolecular azide transfer to furnish intermediate **D**. Next, another single electron transfer process along with the elimination of benzotriazole and SO$_2$ converts intermediate **D** into intermediate **E**. Finally,
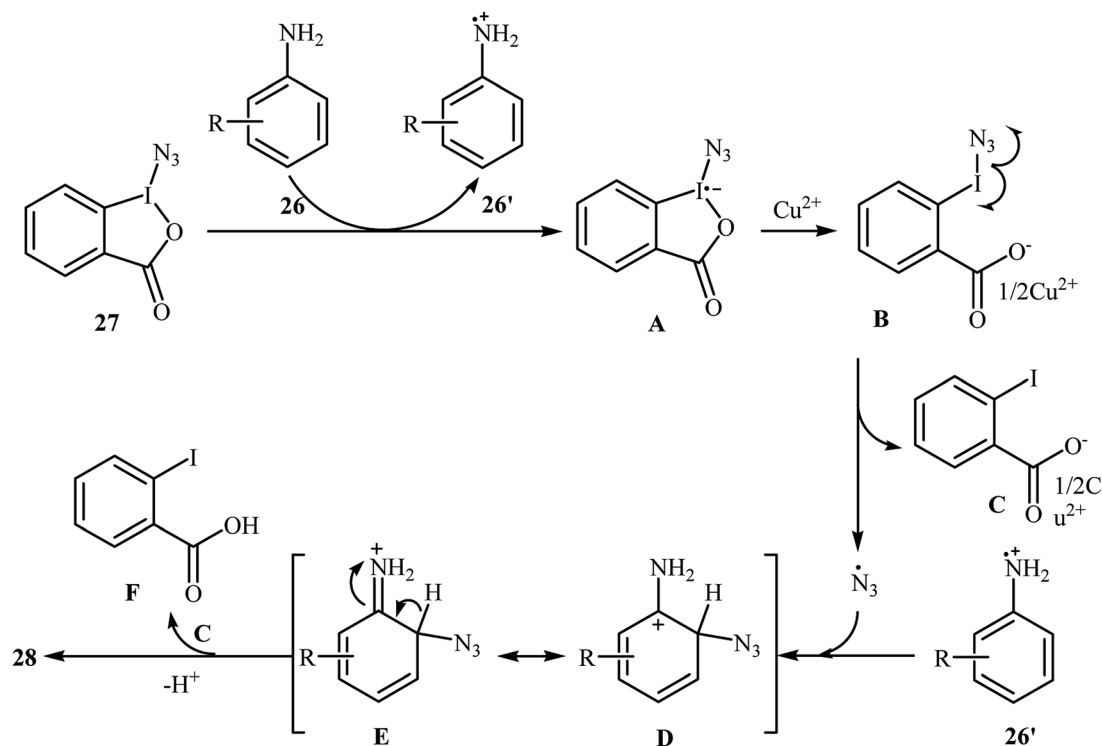
Scheme 18 Proposed mechanism of the direct azidation of aromatic amines **26** with azido-benziodoxolone **27**.
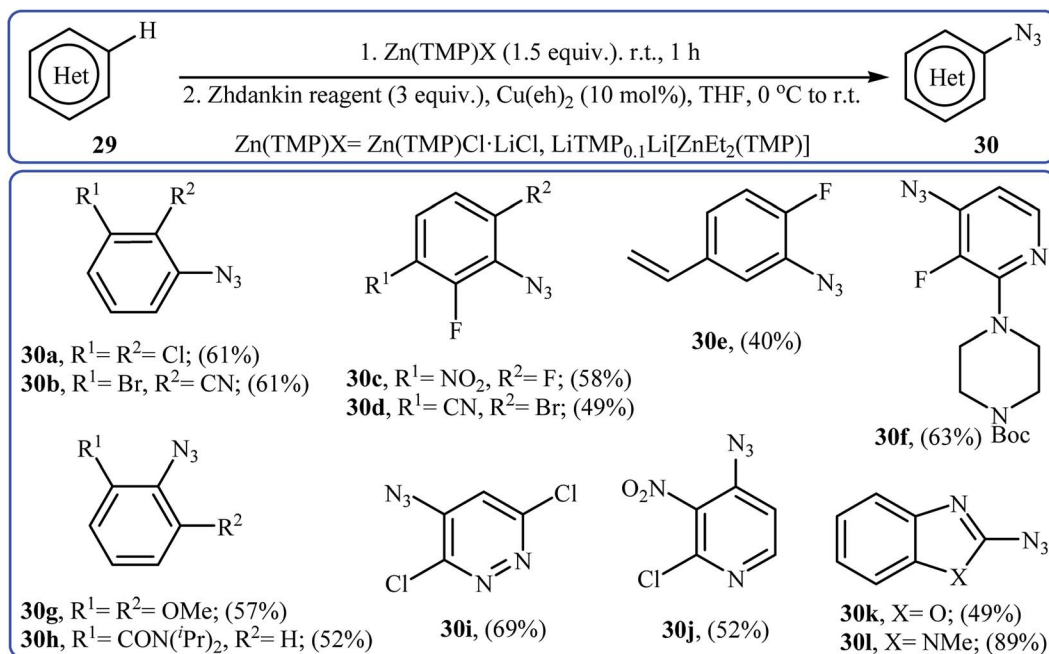
**Scheme 19** Wang's synthesis of azido-(hetero)arenes **30**.

demetallation of this intermediate affords the expected azido product **34**. To the best of our awareness, this is the only example of direct azidation of aromatic C–H bonds with benzotriazole sulfonyl azide reported so far.

3. Olefinic C–H bonds

Direct azidation of olefinic C–H bonds has been rarely studied; in fact, only three examples of such a reaction were reported in the literature thus far. In 2016, Ma, Li, and Yu reported an innovative double oxidative C–N bond formation for the synthesis of quinoxaline derivatives.[37] They found that *N*-arylenamines **35** underwent a rapid tandem oxidative azidation/ cyclization reaction with TMSN$_3$ in the presence of CuCl$_2$/

PhI(OAc)$_2$ combination as a catalytic system in DMF at room temperature. As shown in Scheme 23, a variety of electron-rich and election-poor *N*-arylenamines were applied to afford the corresponding quinoxalines **36** with yield ranging from 25% to 76%. However, ethyl 3-((2-methoxyphenyl)amino)-3-phenyl acrylate failed to enter into this reaction. It should be mentioned that the presence of electron-withdrawing CO$_2$Et group was crucial for this reaction, while the use of substrates bearing electron-donating groups (*e.g.*, Me) instead of CO$_2$Et did not lead to the desired products under the standard condition. The mechanism suggested by the authors to explain this reaction is based on the formation of vinyl azide intermediate **A**, followed by its ring closure by elimination of nitrogen gas.
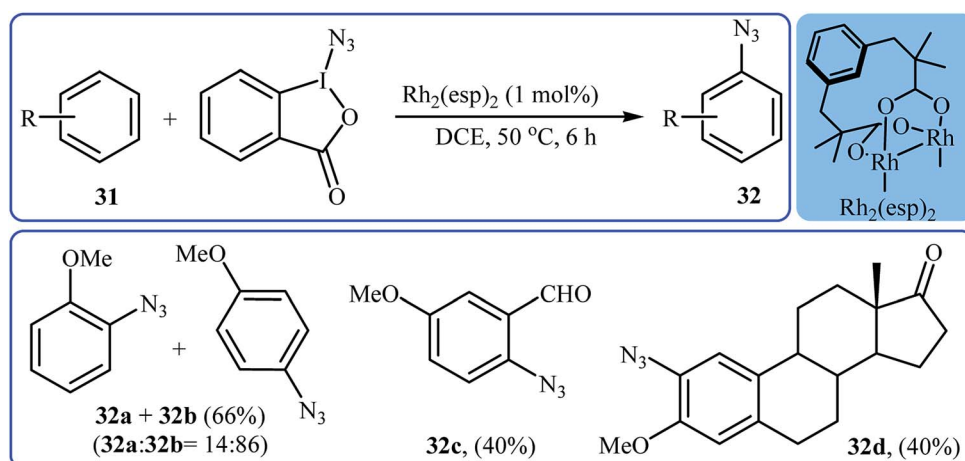

Scheme 20 Selected examples of the Rh-catalyzed direct C–H bond azidation of aromatic rings **31** with Zhdankin's reagent reported by Chen and Wang.
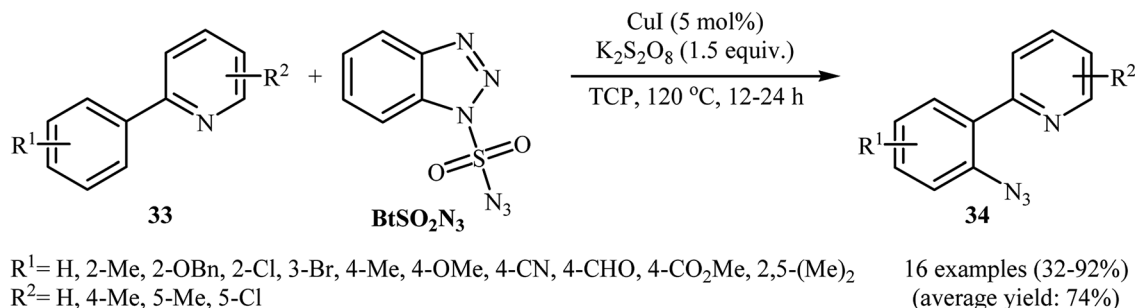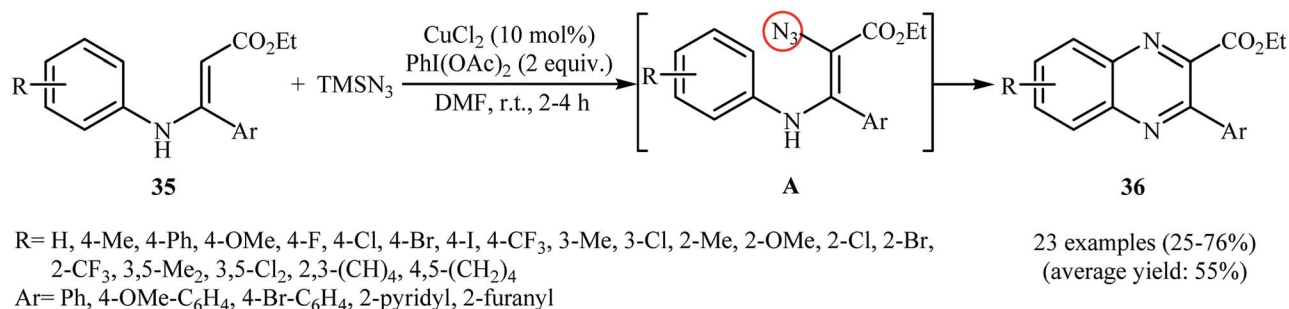
Scheme 21 Direct *ortho*-azidation of arenes **33** using benzotriazole sulphonyl azide as azidating agent.

In the same year, Yu and co-workers reported an interesting one-pot procedure for the synthesis of enamines **38** by direct azidation of the corresponding α-oxo ketene dithioacetals **37** with NaN$_3$ followed by reduction of the C–H azidation intermediate **A** by aqueous (NH$_4$)$_2$S at room temperature (Scheme 24).[38] The *in situ* generated vinyl azide intermediates were captured by phenylacetylene to produce triazoles. Interestingly, 3-amino-1,4-dithian-2-one derivatives were obtained in moderate to good yields when the (NH$_4$)$_2$S was replaced by AcO$_2$. According to the authors proposed mechanism, this reaction proceed through an azidation/ring-expansion rearrangement/thiolactonization sequential process.

Recently, Lin and co-workers presented an environmentally friendly electrochemical protocol for metal-catalyzed direct diazidation of alkenes **39** which offers a simple, mild and efficient way to synthetically important 1,2-diazides **40**.[39] The optimal system was identified using NaN$_3$ as the azide source, MnBr$_2$·4H$_2$O as the catalyst, LiClO$_4$ as the electrolyte with an undivided RVC/Pt-cell in MeCN/AcOH (9 : 1). Under the optimized conditions, various acyclic and cyclic olefins bearing sensitive functional groups such as chloro, bromo, hydroxy, amino, ester, ketone, aldehyde, acid, ether, and thioether showed high yields of the corresponding 1,2-diazide products (Scheme 25). The authors showed that several 1,2-diazides could be chemoselectively converted to the corresponding
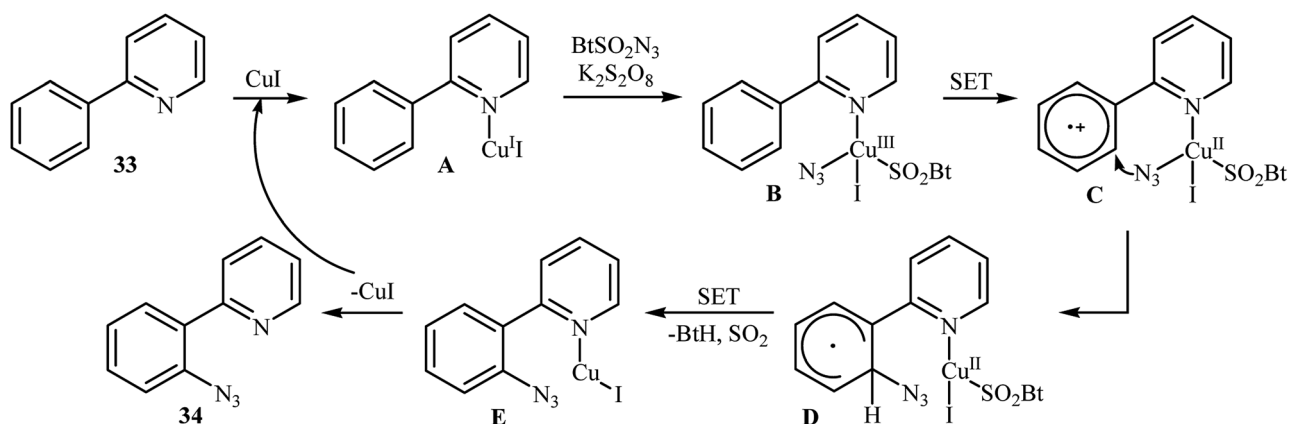
Scheme 22 Plausible reaction mechanism for the formation of *ortho*-azide arenes **34**.

R= H, 4-Me, 4-Ph, 4-OMe, 4-F, 4-Cl, 4-Br, 4-I, 4-CF$_3$, 3-Me, 3-Cl, 2-Me, 2-OMe, 2-Cl, 2-Br, 2-CF$_3$, 3,5-Me$_2$, 3,5-Cl$_2$, 2,3-(CH)$_4$, 4,5-(CH$_2$)$_4$
Ar= Ph, 4-OMe-C$_6$H$_4$, 4-Br-C$_6$H$_4$, 2-pyridyl, 2-furanyl

23 examples (25–76%)
(average yield: 55%)

Scheme 23 Synthesis of quinoxalines **36** through a tandem oxidative azidation/cyclization of *N*-arylenamines **35** with TMSN$_3$.
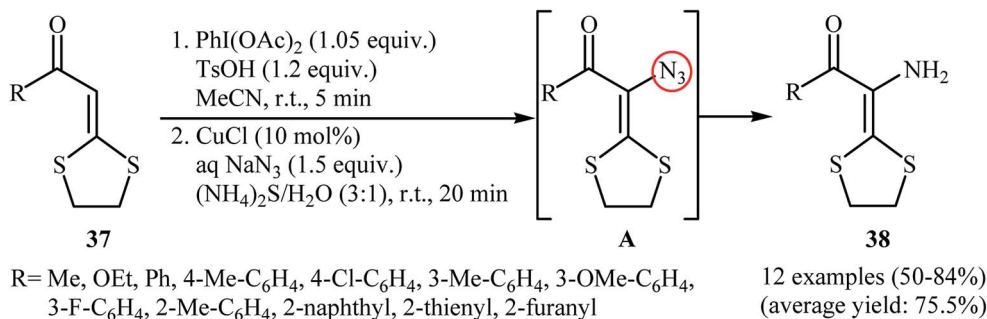
Scheme 24 Yu's synthesis of enamines **38**.
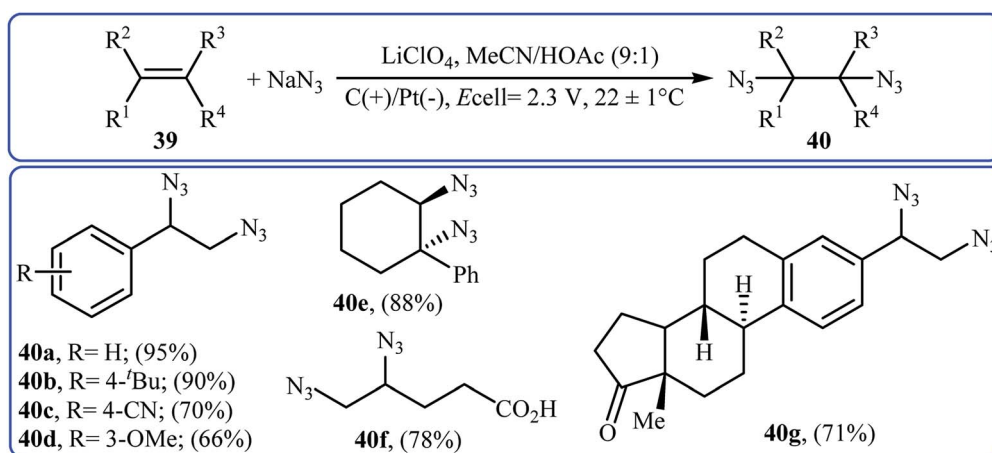
Scheme 25 Metal-catalyzed electrochemical diazidation of alkenes **39** with NaN$_3$.

biologically important 1,2-diamines by reduction under various conditions. Based on the radical clock experiments, they proposed that this azidation reaction might proceed through a radical pathway as depicted in Scheme 26.

Scheme 26 Plausible mechanism for the formation of 1,2-diazides **40**.

4.   Aldehydic C−H bonds
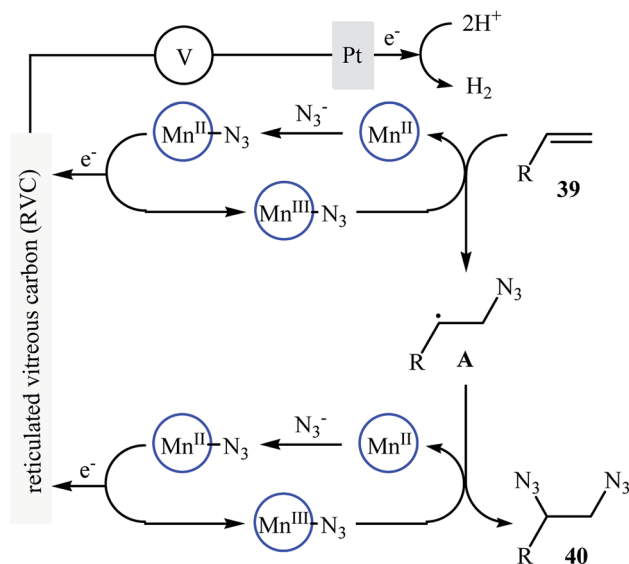
4.1.   TMSN$_3$ as azide source

In 1992, Lee and Kwak studied for the first time the direct synthesis of acyl azides from the corresponding aldehydes in a one pot reaction.[40] They showed the direct C–H bond azidation of aldehydes **41** with TMSN$_3$ in DCM at room temperature, leading to azidated products **42** in excellent yields (Scheme 27). However, toxic chromium trioxide was used as the terminal oxidant. The reaction is noteworthy in that both aromatic as well as aliphatic aldehydes were tolerated. However, a fair amount of aliphatic acyl azide products underwent rearrangement to the alkyl isocyanates under the standard conditions. The authors elegantly solved this limitation by performing the reaction at −10 °C. A plausible mechanism to explain this azidation reaction is the initial generation of the chromyl azide intermediate **A** from the reaction of CrO$_3$ with TMSN$_3$, which is subsequently reacted with aldehyde **41** to furnish the chromate ester intermediate **B**. Finally, the oxidative degradation of the chromate ester **B** leads to the observed acyl azide **42** (Scheme 28).

Eighteen years later, with the aim of designing a safer procedure to acyl azide derivatives through direct C–H azidation of aldehydes, Sarkar and Studer were able to demonstrated that a series of (hetero)aromatic acyl azides **44** could be obtained in
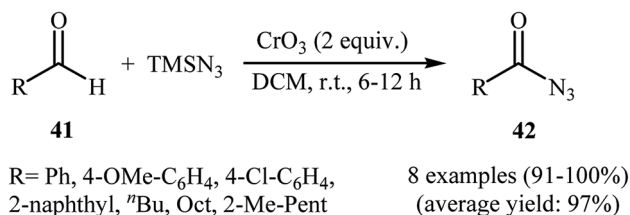
Scheme 27 CrO$_3$-mediated azidation of aldehydes **41** with TMSN$_3$.

fair to good yields from the reaction of corresponding (hetero) aromatic aldehydes **43** with TMSN$_3$ employing 1,4-dimethyl-1,2,4-triazolium iodide as a commercially available organocatalyst and DBU as a base in THF (Scheme 29).[41] Notably, under similar conditions, performing the reaction with NaN$_3$ and Bu$_4$N$^+$N$_3^-$ as azide sources gave only traces of the target products.

4.2. NaN$_3$ as azide source

After pioneering work by Elmorsy on oxidative azidation of aldehydes with triazidochlorosilane (generated *in situ* from

SiCl$_4$ and NaN$_3$) employing MnO$_2$ as the oxidant,[42] the first general report on the synthesis of acyl azids through the direct azidation of aldehydic C–H bonds with NaN$_3$ was published in 2000, by Chen *et al.*[43] They showed that various electron-rich and electron-deficient aromatic aldehydes **45** underwent relatively rapid azidation with NaN$_3$ in the presence of over-stoichiometric amounts of PhI(OAc)$_2$ as a hypervalent iodine reagent in DCM at room temperature. The corresponding aroyl azides **46** were obtained in moderate to excellent yields (Scheme 30). According to the authors proposed mechanism, this reaction proceeds *via* a free radical pathway similar to that one described in Scheme 16. Later, Bose and Reddy improved the efficiency of this reaction in the terms of reaction time and yields by replacement of PhI(OAc)$_2$ with Dess–Martin periodinane.[44]

In 2007, Akamanchi's research group reported the direct conversion of aldehydes **47** to acyl azides **48** using NaN$_3$ as a source of azide and *tert*-butyl hypochlorite (^{t}BuOCl) as an oxidant.[45] In this investigation, a series of common organic solvents (*i.e.*, cyclohexane, ^{t}BuOH, MeCN, CHCl$_3$, CCl$_4$, DCM) were used for a comparative study. The best result was obtained with CCl$_4$. In ^{t}BuOH the reaction was faster, however, a small amount of the corresponding benzoic anhydride was obtained
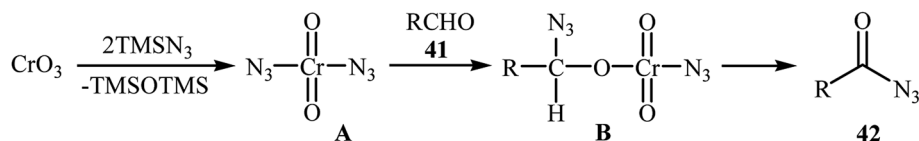
**Scheme 28** Proposed mechanisms for the C–H bond azidation of aldehydes **41** with TMSN$_3$.
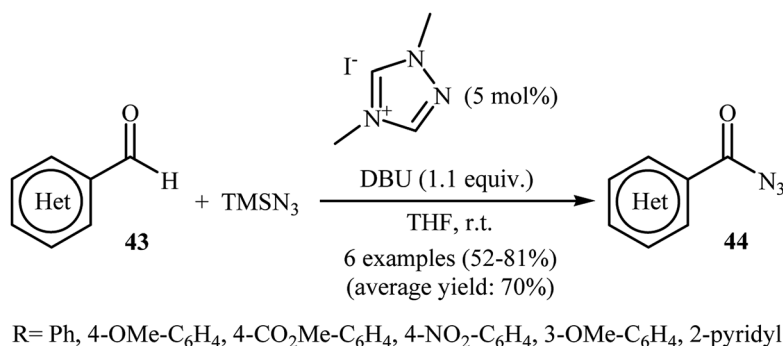
Scheme 29 NHC-catalyzed azidation of aldehydes **43** with TMSN$_3$.
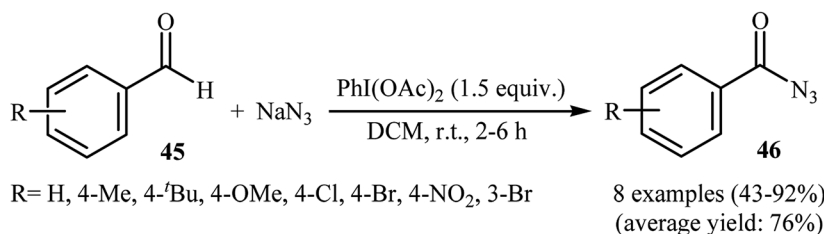
Scheme 30 Direct conversion of aldehydes **45** to acyl azides **46** using NaN$_3$ and PhI(OAc)$_2$.
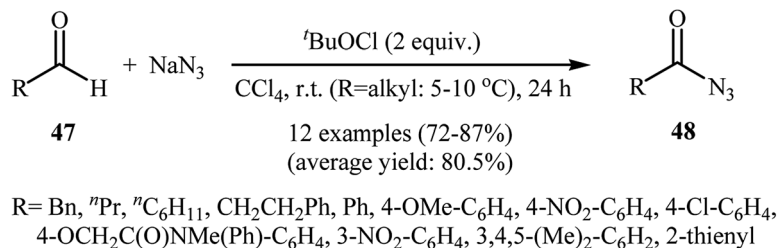
Scheme 31 Ackerman's synthesis of acyl azides **48**.
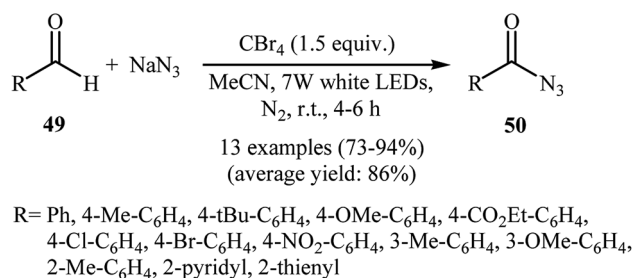
Scheme 32 Visible light-mediated azidation of aldehydes **49** with NaN$_3$.
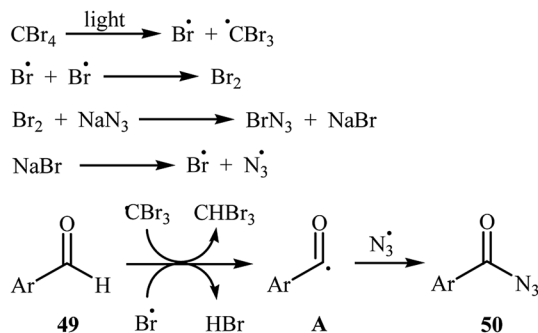
Scheme 33 Mechanism proposed to explain the synthesis of acyl azides **50**.
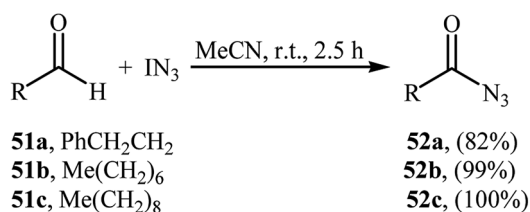
Scheme 34 Direct azidation of aliphatic aldehydes **51** with IN$_3$.

as a side product. The optimum mole ratio of aldehyde:^{t}BuOCl : NaN$_3$ was found to be 1 : 2 : 2. Various aromatic, heteroaromatic, and aliphatic aldehydes **47** were reacted well under the optimized reaction conditions to produce the corresponding acyl azides **48** in good to high yields (Scheme 31).

Later, Yadav and co-workers developed an interesting approach for visible light-mediated direct azidation of (hetero)

aromatic aldehydes **49** with NaN$_3$ using inexpensive and easily handled CBr$_4$ as a radical generator.[46] The reactions proceeded in MeCN under 7 W white LEDs, giving good to excellent yields of acyl azides **50** within 4–6 h (Scheme 32). It was noteworthy that this procedure could be applied to aromatic aldehydes with various functional groups such as OMe, Cl, Br, CO$_2$Et, and NO$_2$ groups, which provided a complementary platform for further manipulation of products to create more complex azido molecules. They nicely applied their methodology in the one-pot synthesis of carbamoyl azides (RNH–CO–N$_3$) by simple heating (80 °C) of acyl azides through Curtius rearrangement. The authors proposed mechanism for this azidation reaction is depicted in Scheme 33. First, Br$^•$ and $^•$CBr$_3$ radicals were generated via the homolytic cleavage of a C–Br bond in CBr$_4$ under irradiation of visible light. Later, abstraction of aldehydic hydrogen atom from the starting aldehyde **49** by these radicals resulted in the formation of the radical species **A**. Finally, the combination reaction of this radical with the azide radical gave the expected acyl azide **50**.

4.3. IN$_3$ as azide source

In 2003, Bols and co-workers introduced iodine azide (IN$_3$) as azidating agent for direct aldehydic C–H azidation.[47] Thus, in the absence of any catalyst and additive in MeCN at room temperature, reaction of a small series of aliphatic aldehydes **51** with IN$_3$ furnished the corresponding acyl azides **52** in high yields (Scheme 34). Notably, the synthetically important carbamoyl azides could be directly achieved by performing the process in refluxing MeCN. Twelve years later, a related transformation, using Zhdankin reagent was disclosed by Saito et al.[48] Tetrabutylammonium iodide (TBAI) served as catalyst and DCM as solvent. Noteworthy, the in situ generated IN$_3$ by reaction of Zhdankin reagent with TBAI, was acted as the azidating agent in this reaction. Various aliphatic, aromatic, heteroaromatic and bicyclic aldehydes were used to establish the general applicability of the approach.

5. Conclusion

This review provides concise overview on the direct azidation of various organic molecules (i.e., arenes, alkenes, aldehydes) via C(sp^2)–H activation. This new page to access organic azides has many potential advantages over the traditional approaches, which can be summarized as follows: (i) high pot-, atom- and step-economy; (ii) eco-friendly processes; and (iii) simple

operation. Despite the significant achievements during the past few years in this interesting and important research field, many challenges still remain to be overcome: (i) the number of reported examples in the direct azidation of olefinic C–H bonds are scarce and there is still further need to study the scope and limitations of these reactions; (ii) all of the metal-catalyzed C(sp^2)–H bonds azidation reactions covered in this review are limited to the use of rhodium and copper catalysts. Thus the exploration of other transition metal catalysts such as iron catalysts and nanosized metal catalysts are highly desirable in term of the cost and maybe the efficiency of the catalysts; (iii) synthetic application of the direct azidation of C(sp^2)–H bonds in the preparation of important and commercialized drugs should be explored. It is our hope that this review will be beneficial to elicit further research and thinking in this domain.

Conflicts of interest

There are no conflicts to declare.

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