Chem Rev Lett 8 (2025) 165-177

Review Article

Chemical Review and Letters
journal homepage: www.chemrevlett.com
ISSN (online): 2645-4947 (print) 2676-7279

Recent advances in transition-metal-catalyzed 1,2-diazidation of alkenes

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ARTICLE INFO

Article history:
Received 12 January 2025
Received in revised form 24 January 2025
Accepted 25 January 2025
Available online 15 February 2025

Keywords:
Transition-metal catalysis,
Vicinal difunctionalization,
Alkenes, organic azides, Double azidation,
1,2-Diazides, 1,2-diamines

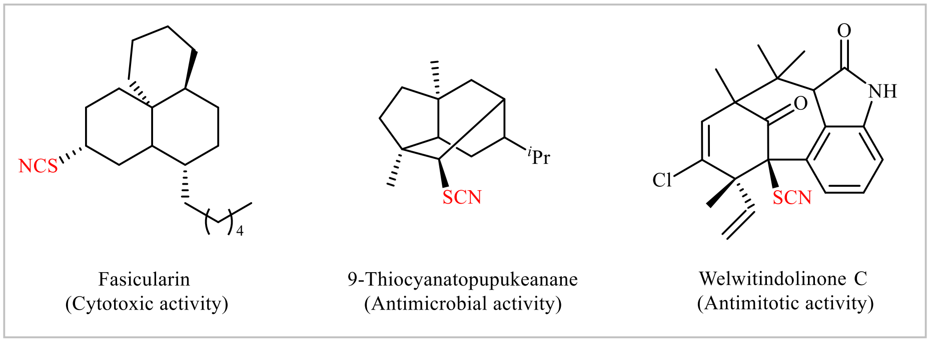
ABSTRACT

In this review, recent researches on transition-metal-catalyzed direct diazidation of alkenes into aliphatic 1,2-diazides are described. 1,2-Diazides are one of the most versatile intermediates in organic synthesis and are often employed for the preparation of biologically important 1,2-diamines.

1. Introduction

Nitrogen-containing organic molecules are crucial due to their versatility in natural and synthetic chemistry, vital across various industries, including healthcare, agriculture, and materials science [1]. Organic azides ($R-N_3$) are highly attractive and flexible synthetic intermediates, serving as precursors for numerous open-chain and heterocyclic nitrogen-containing organic molecules [2, 3]. They have also found applications as blowing agents in plastic and rubber industries. Moreover, organoazide drugs represent an important class of therapeutic agents endowed with a broad range of pharmacological activities. Particularly, aliphatic azides play an extremely important role in drug discovery, as evidenced by many FDA-approved drugs (Scheme 1) [4, 5].

Among various aliphatic azides, vicinal diazides have attracted tremendous interest and attention of medicinal chemists not only because of their potential biological properties but also their importance as precursors for the synthesis of valuable 1,2-diamines, which are prevalent skeletons in natural products, agrochemicals, and pharmaceuticals (Scheme 2) [6].



Scheme 1. Selected examples of SCN-containing biologically active natural products.

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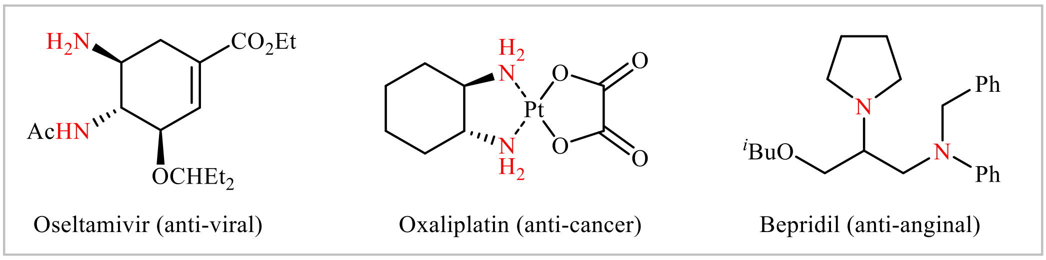
https://doi.org/ 10.22034/crl.2025.499322.1522

Traditionally, the synthesis of 1,2-diamines involves SN_2 displacements with nucleophilic azide anion, followed by reduction of vicinal azides to free primary 1,2-diamines [7]. However, these methods suffer from several inherent drawbacks, such as the requirement for pre-functionalized starting materials, unwanted byproducts, low yields, and poor functional group tolerance. An alternative and efficient protocol for the synthesis of 1,2-diazides involves the direct diazidation of widely available and readily available alkenes with various azidation reagents [8].



Scheme 2. Selected examples of 1,2-diamino-pharmaceuticals.

Traditionally, the direct vicinal diazidation of alkene substrates relied on the use of the highly explosive and toxic iodine azide (IN_3) as an azidation agent [9] or stoichiometric amounts of hazardous iodine-based oxidants such as iodosobenzene (PhIO) [10]. To overcome these limitations, various transition-metal-based catalytic systems have been developed, allowing this transformation under milder conditions with more user-friendly azidating agents and/or in the absence of external oxidants [11]. Despite significant progress that has been achieved in this attractive research area over the past few years, a comprehensive review of this topic has yet to appear in the literature. This review aims is to summarize the current literature on transition-metal-catalyzed direct vicinal diazidation of alkene substrates (Figure 1), with special emphasis on the mechanistic features of these reactions. The content is categorized around the type of catalysis, including Mn-catalyzed reactions, Pd-catalyzed reactions, Fe-catalyzed reactions, and Cu-catalyzed reactions. We hope that this review will serve as an inspiring guide for researchers working on direct difunctionalization reactions of unsaturated hydrocarbons [12, 13].

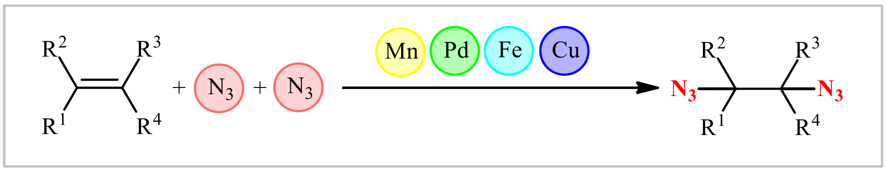
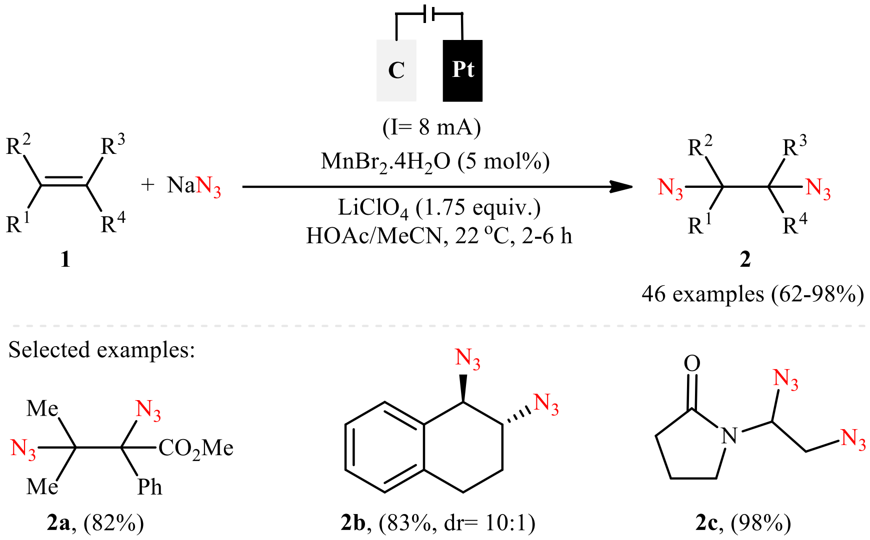


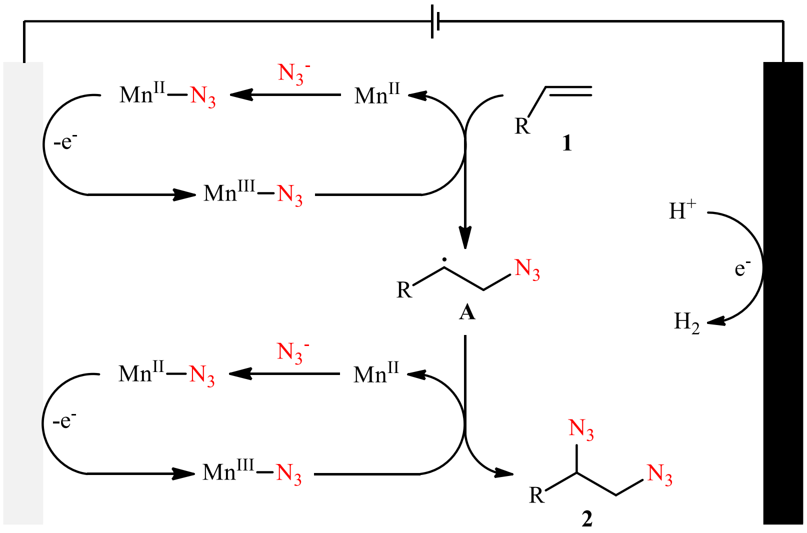
Fig. 1. Transition-metal-catalyzed 1,2-diazidation of alkenes.

2. Manganese-catalyzed reactions

Despite the fact that Mn-mediated direct vicinal diazidation of olefinic double bonds had been known since 1985 [14], it was not until 2017 that Lin and co-workers developed the first catalytic version of this transformation [15, 16]. They showed that treatment of various terminal (aliphatic and aromatic), 1,1-disubstituted, 1,2-disubstituted (cyclic and acyclic), trisubstituted and tetrasubstituted alkenes **1** with sodium azide (NaN_3) in the presence of a catalytic amount of $MnBr_2.4H_2O$ in an undivided cell assembled with a reticulated vitreous carbon (RVC) anode and a platinum (Pt) cathode under constant current conditions resulted in the corresponding 1,2-diazides **2** in good to excellent yields (Scheme 3). A diverse range of important functional groups such as fluoro, chloro, bromo, cyano, hydroxyl, acid, amide, sulfonamide, ether, thioether, ester, aldehyde, and ketone functionalities were well tolerated under these reaction conditions, thus promising further manipulation of products. Notably, this synthetic approach was also successfully extended to the preparation of vicinal diamines *via* sequential diazidation/reduction of respective alkenes without purification of the diazide intermediates. According to the authors proposed mechanism (Scheme 4), this diazidation process plausibly proceeds through a consecutive addition of two azide radicals onto C-C double bonds. Preliminary ultraviolet-visible spectroscopy data suggested that Mn(II)-N_3 formed through ligand exchange between Mn(II)-X(X, Br or OAc) and NaN_3 acts as the key azidyl transfer agent.

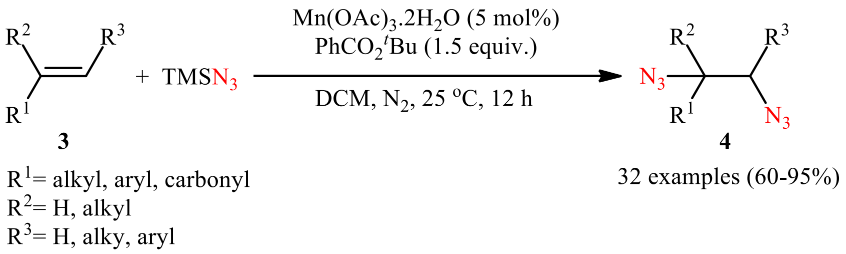


Scheme 3. Lin's synthesis of 1,2-diazides **2**.



Scheme 4. Mechanistic proposal for the formation of 1,2-diazides **2**.

Very recently, Zhao, Chen, and Ke developed a similar diazidation of alkenes using azidotrimethylsilane (TMSN$_3$) as the azide source and a combination of Mn(OAc)$_3$·2H$_2$O and PhCO$_2$^{t}Bu as the catalytic system [17]. The procedure was shown to be general and a diverse range of styrene-type alkenes, alkyl alkenes, heterocyclic compounds and α,β-unsaturated carboxylic acid derivatives **3** participated in the reaction and provided the expected 1,2-diazide products **4** in good to excellent yields, ranging from 60% to 95% (Scheme 5). Furthermore, the protocol was applicable to large-scale production of diazides as exemplified by synthesis of 1-(*tert*-butyl)-4-(1,2-diazidoethyl)benzene in 1.34 g scale in high yield of 88%.

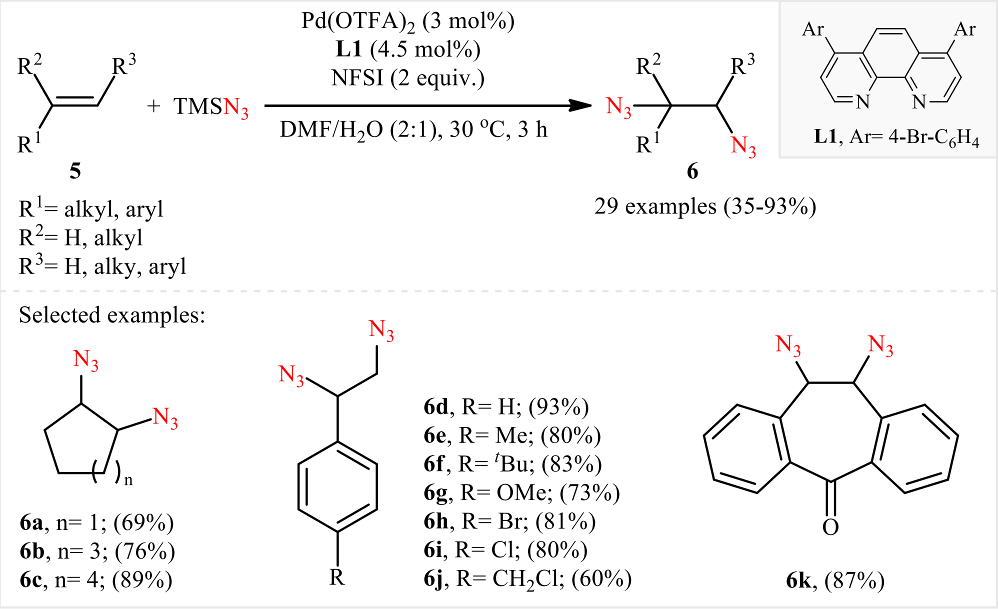


Scheme 5. Mn(OAc)$_3$·2H$_2$O-catalyzed 1,2-diazidation of alkenes **3** using TMSN$_3$.

3. Palladium-catalyzed reactions

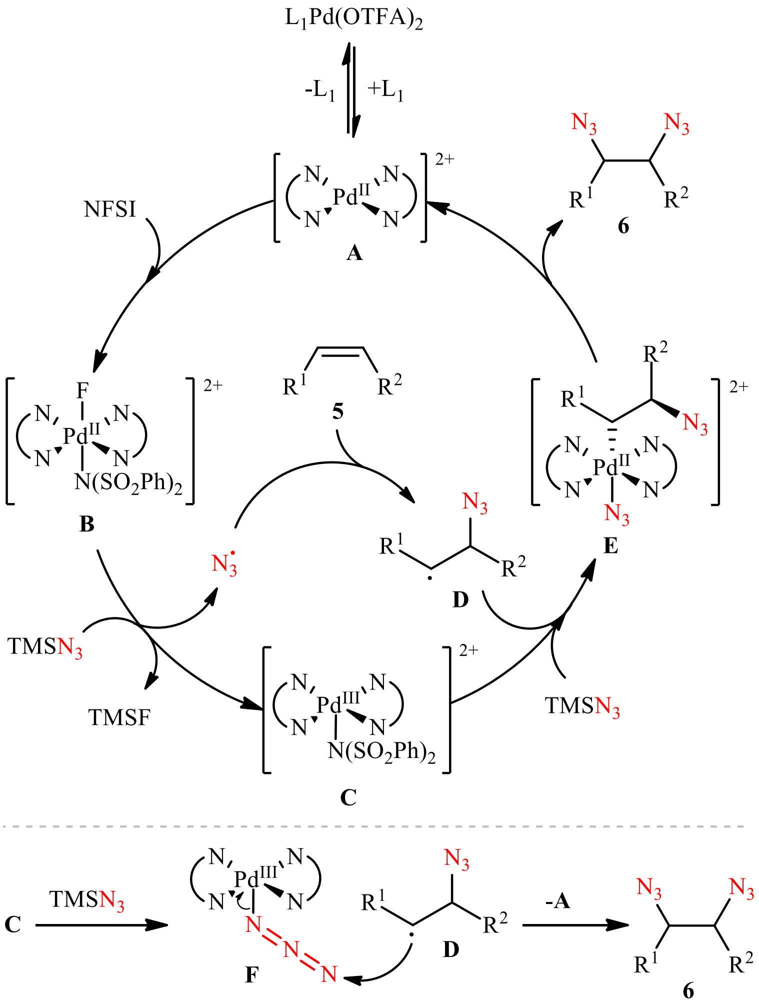
In 2017, the group of Liu demonstrated for the first time the usefulness of palladium catalysts for vicinal double azidation of alkene derivatives [18]. Thus, by using 3 mol% of $Pd(OTFA)_2$ as the catalyst and 4.5 mol% of the bidentate nitrogen ligand L1 in the presence of over-stoichiometric amounts of *N*-fluorobenzenesulfonimide (NFSI) as an oxidant in the binary solvent DMF/H_2O with ratio 2:1, the reaction of a series of activated and unactivated alkenes **5** with $TMSN_3$ furnished the corresponding 1,2-diazides **6** in poor to excellent isolated yields (Scheme 6). In order to further value the applicability of their methodology, the authors investigated diazidation of natural compounds, isopulegol and limonene 1,2-epoxide, and the expected products were obtained in 65% and 35% yield, respectively. It should be noted that besides $Pd(OTFA)_2$, other palladium catalysts such as $PdCl_2$, $Pd(OAc)_2$, and $Pd(PPh_3)_2Cl_2$ were also found to promote this difunctionalization reaction; albeit, in lower yields.

Based on several control experiments, the authors postulated a plausible reaction mechanism for this transformation as outlined in Scheme 7. The reaction starts with the oxidation of cationic $[(L1)_2Pd]^{2+}$ species **A** by NFSI to provide complex **B**, which after oxidization of $TMSN_3$ *via* a single electron transfer (SET) process renders the azido radical and $(L1)_2Pd^{III}$ species **C**. Subsequently, addition of the azido radical to alkene **5** leads to the C-centered radical **D** which is trapped by Pd^{III} species to furnish a high valent Pd^{IV} species **E**. Finally, this intermediate **E** undergoes a sequential ligand exchange and reductive elimination to afford the observed product **6** along with the regeneration of species **A** (Scheme 7, top). Alternatively, intermediate **C** might react with $TMSN_3$ to give Pd^{III}-N_3 complex **F**, which is then attacked by carbon C-centered radical **D** at external nitrogen atom to deliver the target product **6** and release $[(L1)_2Pd]^{2+}$ species **A** (Scheme 7, bottom).

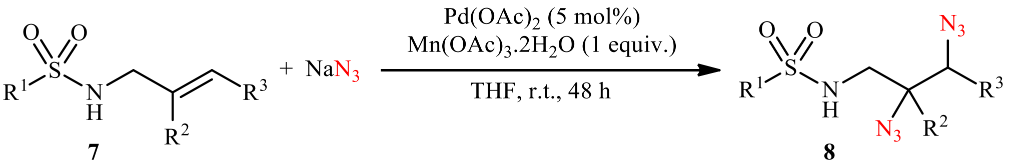


Scheme 6. Pd-catalyzed 1,2-diazidation of alkenes **5**, developed by Liu.

Quite recently, Loro and co-workers unfolded that the combinations of palladium sources and manganese sources could act as efficient catalysts for the 1,2-diazidation of olefinic double bonds under mild conditions [19]. Hence, by utilizing NaN_3 as the azide source, they reported vicinal diazidation of a series of *N*-allyl sulfonamides **7** employing a combination of $Pd(OAc)_2$ and $Mn(OAc)_3 \cdot 2H_2O$ as the catalytic system in THF at room temperature. The target 1,2-diazidation products **8** were obtained in moderate to good yields within 48 h (Scheme 8). The results indicated that the reaction was equally efficient for both aliphatic and aromatic sulfonamides bearing *ortho*, *meta* and *para* electron-donor or withdrawing substituents.



Scheme 7. The proposed pathway for the formation of aliphatic 1,2-diazides **6**.



R^1= CF_3, Ph, 4-Me-C_6H_4, 4-Cl-C_6H_4, 4-CF_3-C_6H_4, 4-NO_2-C_6H_4, 3-OMe-C_6H_4, 2-Me-C_6H_4, 2-OCF_3-C_6H_4, 2-NO_2-C_6H_4
R^2= H, Me
R^3= H, Ph

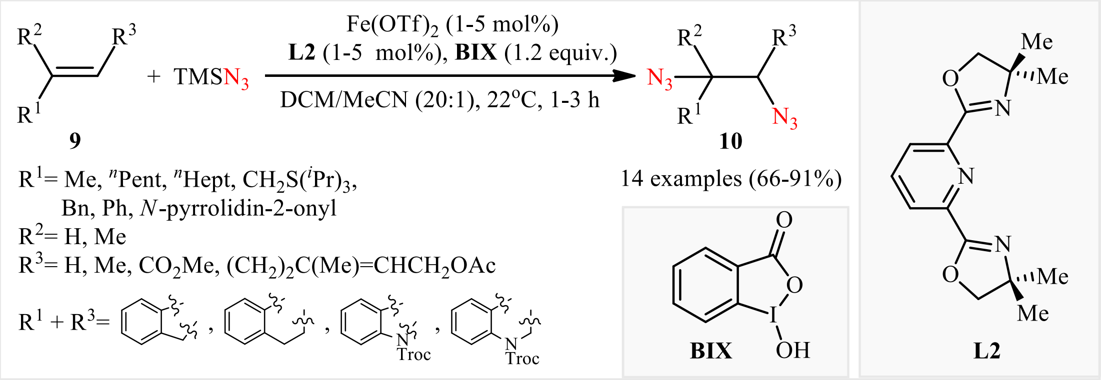
12 examples (54-76%)

Scheme 8. Loro's synthesis of sulfonamide-containing aliphatic 1,2-diazides **8**.

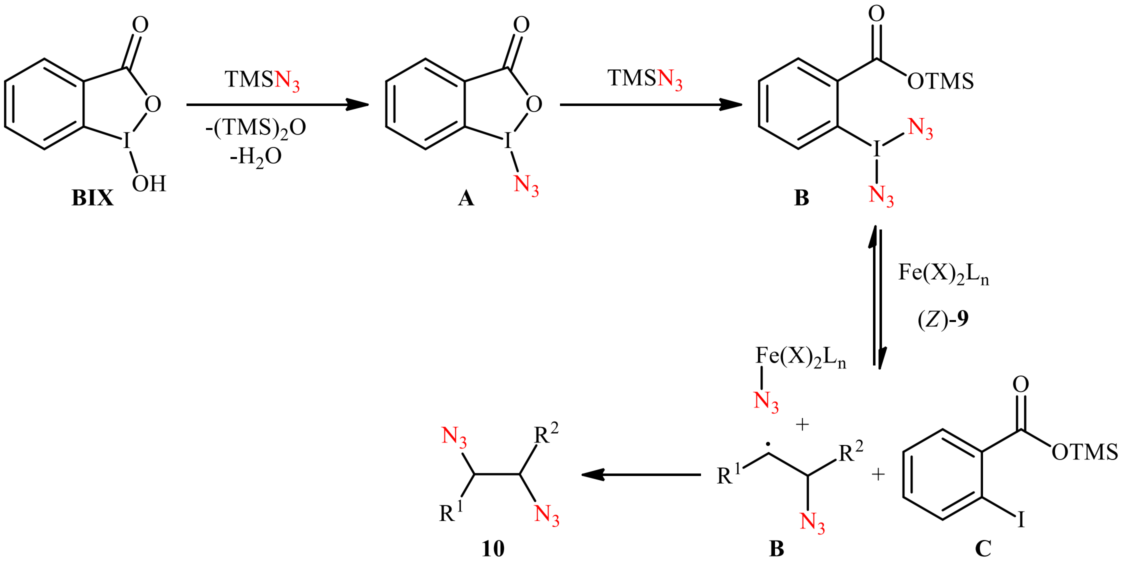
4. Iron-catalyzed reactions

The iron-catalyzed direct diazidation of alkenes is probably the area that has experienced the most growth in this field in recent years. To the best of our knowledge, Xu and co-workers first proposed the possibility of 1,2-diazidation of alkenes in the presence of Fe-based catalysts [20]. By employing indene, $TMSN_3$, and 1-hydroxy-1,2-benziodoxol-3-one (**BIX**) as the model reactants, they carefully screened several iron complexes such as $Fe(OTf)_2$, $Fe(NTf_2)_2$ and $Fe(OAc)_2$. Among them, $Fe(OTf)_2$ displayed the excellent result for this reaction, whereas 2,6-bis(4,4-dimethyl-4,5-dihydrooxazol-2-yl)pyridine (**L2**) was found to be the most effective additive among the others tested bi- and tri-dentate nitrogen ligands. Among several common solvents tested, the mixture of DCM/MeCN was found to be most effective solvent system. In their optimization study, the authors found that the presence of both $TMSN_3$ and BIX are essential for the success of this reaction. Indeed, the Lewis-acidic

TMS group is crucial for the activation of **BIX**. A range of activated and unactivated alkenes **9** were diazidated using this procedure in good to excellent yields (Scheme 9). Cyclic alkenes, such as 1*H*-indene and 1,2-dihydronaphthalene, were also compatible to give diazidated products with high diastereoselectivities (12-20:1). Additionally, complex alkene derivatives such as acetyl quinine and glycal were also reasonable substrates under these conditions. Based on a series of control experiments, the authors proposed a plausible mechanism as shown in Scheme 10. The transformation may start with the reaction of TMSN$_3$ with **BIX** to produce 1-azido-1,2-benziodoxol-3-one **A**. Subsequently, this reactive intermediate **A** may be further activated by TMSN$_3$ to generate highly reactive intermediate **B**. In the presence of the catalyst, the I-N$_3$ bond of intermediate **B** reductively cleaves and affords an azido radical **C** of alkene **9** and releases trimethylsilyl 2-iodobenzoate **D**. Finally, oxidation of azido radical **C** by the high-valent iron species through inner-sphere azido ligand transfer furnishes the observed product **10**. Subsequently, the authors extended their Fe-catalyzed azidation methodology to gram-scale diastereoselective synthesis of aliphatic diaminium salts through a tandem diazidation/diamination procedure, without purification of the diazide intermediate [21]. Four years later, a similar principle was successfully applied by Bao and colleagues to the enantioselective vicinal 1,2-diazidation of a wide range of styrene derivatives (20 examples, 54-80% yield, up to 97% *ee*) [22].

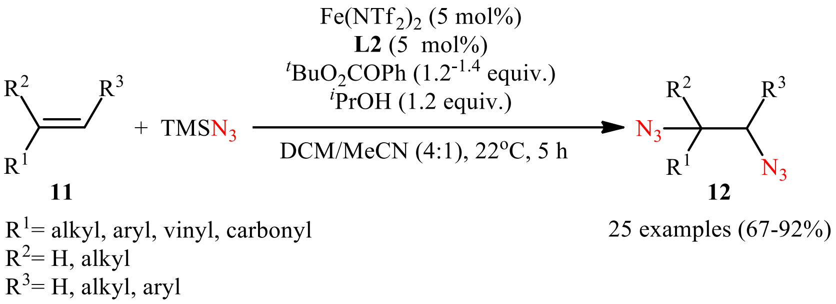


Scheme 9. Xu's synthesis of aliphatic 1,2-diazides **10**.



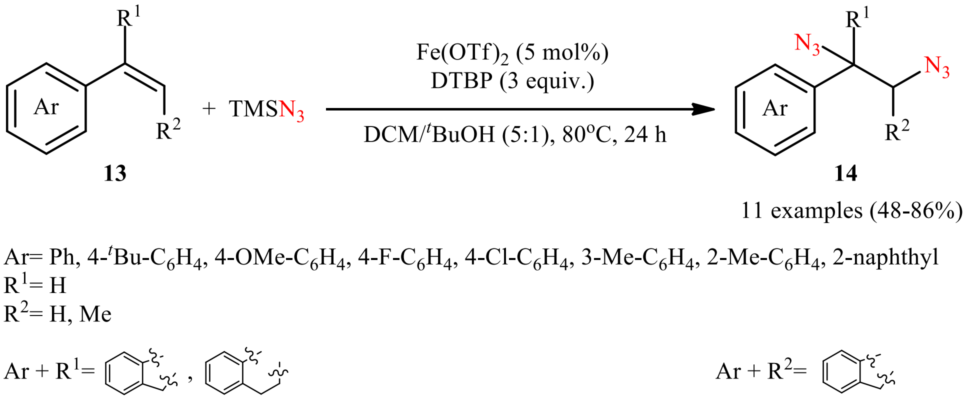
Scheme 10. Mechanism proposed to explain the synthesis of 1,2-diazides **10**.

In their subsequent studies, the innovative research group of Xu developed an alternative methodology for the Fe-catalyzed synthesis of aliphatic 1,2-diazides **12** from the corresponding alkenes **11** using TMSN$_3$ as the azide source in the presence of Fe(NTf$_2$)$_2$/**L2**/^{t}BuOOBz/^{i}PrOH combination as the catalytic system (Scheme 11) [23]. This strategy effectively addresses some of the limitations of the benziodoxole-based alkene diazidation method. Most notably, the previously problematic non-productive oxidant decomposition pathway can be suppressed. Evaluation of the substrate scope showed that the reaction was tolerant to both aliphatic and aromatic alkenes as well as 1,3-dienes. Of note, under the optimized conditions indoles and pyrroles (N-heteroaromatic compounds) underwent the direct oxidative dearomatization to form corresponding 2,3- and 2,5-diazido compounds, respectively, in good yields (5 examples, 74%-82%). Compared with the benziodoxole-based method, the current protocol presents a broader scope and higher average yields using similar substrates.



Scheme 11. Fe(NTf$_2$)$_2$-catalyzed diazidation of alkenes **11** with TMSN$_3$.

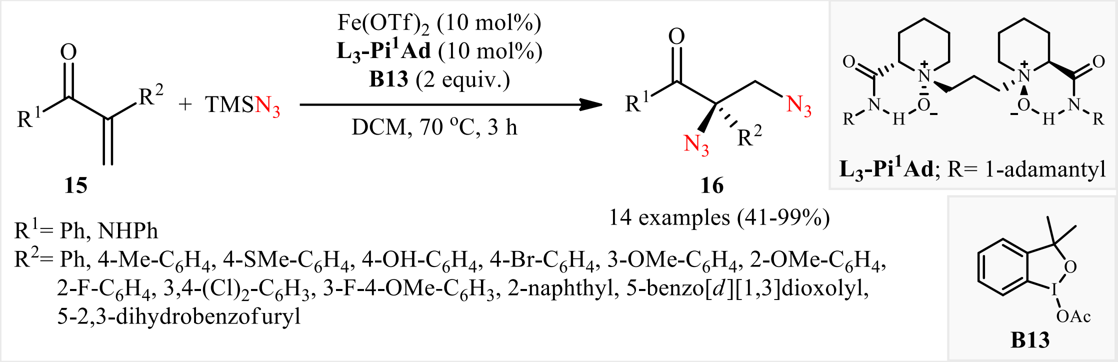
Along this line, in 2019, Chu's research group disclosed that the merge of Fe(OTf)$_2$ with di-*tert*-butyl peroxide (DTBP) can be used as effective catalytic system for selective 1,2-diazidation of styrene derivatives **13** with TMSN$_3$ without consuming any exogenous ligand [24]. The optimal reaction employed combination of DCM/^{t}BuOH as a solvent mixture. Under optimized conditions, a library of (1,2-diazidoethyl)arenes **14** were prepared in modest to high yields from the corresponding aromatic alkenes **13** (Scheme 12). Similarly, the reaction of dienes under the optimal conditions selectively afforded the corresponding internal allylic azides. Interestingly, when the same reactions were performed in DCM with higher loadings of the catalyst (10 mol%) at 110 °C, the direct vicinal carboazidation have occurred and corresponding 1-N$_3$-2-CHCl$_2$-substituted products were obtained in high yields. In this transformation, DCM playing a dual role; the solvent and the chloromethyl source.



Scheme 12. Chu's synthesis of (1,2-diazidoethyl)arenes **14**.

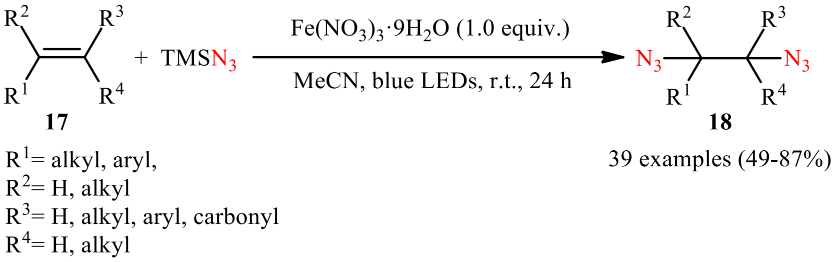
In 2021, the research group of Feng extended this diazidation methodology to enantioselective synthesis of α,β-diazidated carbonyl compounds **16** by a chiral *N*,*N*′-dioxide/Fe(OTf)$_2$ complex-catalyzed diazidation of respective α,β-unsaturated ketones and amides **15** using TMSN$_3$ as the azide source (Scheme 13) [25]. Here, Fe(OTf)$_2$ was used as the catalyst, **L$_3$-Pi^{1}Ad** as a chiral ligand, and 3,3-dimethyl-1,2-benziodoxol-1(3*H*)-yl ester (**B13**) as an oxidizing reagent. The mechanism investigation of the reaction by various control experiments and DFT calculations clarified the radical pathway and the chiral Fe(III)−N$_3$ species of this reaction.

In 2022, the research groups of Shi [26] and West [27] independently developed a unique photochemical diazidation of alkenes *via* Fe-mediated ligand-to-metal charge transfer (LMCT) process. They showed that the treatment of various alkene substrates **17** with TMSN$_3$ (4-5 equiv.) and Fe(NO$_3$)$_3$·9H$_2$O (1.0-1.2 equiv.) under irradiation of blue LEDs at room temperature afforded the corresponding aliphatic 1,2-diazides **18** in modest to high yields (Scheme 14). A range of terminal, 1,1-disubstituted, 1,2-disubstituted, tridubdtituted and tetrasubstituted alkenes were used to establish the general applicability of the method.

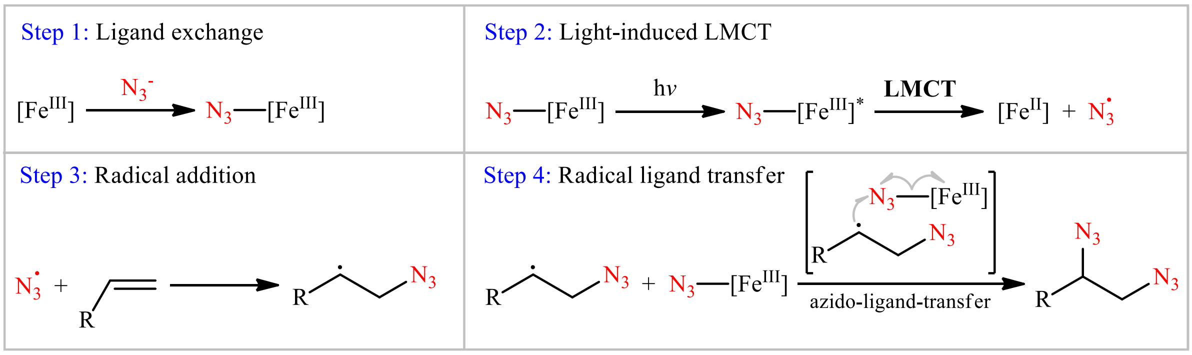


Scheme 13. Feng's synthesis of α,β-diazidated carbonyl compounds **16**.

Importantly, this methodology was also effectively applied to the late-stage diazidation of drug molecules (*e.g.*, ibuprofen, flurbiprofen, loxoprofen, isoxepac, naproxen) and natural product-derived alkenes (e.g., *L*-menthol, oleic acid, mycophenolic acid, and 18β-glycyrrhetinic acid). Mechanistic aspects of this photochemical diazidation depicted in Scheme 15. Very recently, West and co-workers improved the efficiency of this reaction in terms of yield and metal complex loading by performing the process in the presence of a catalytic amount of $Fe(OAc)_2$ (10 mol%) using Selectfluor as an additive [28].



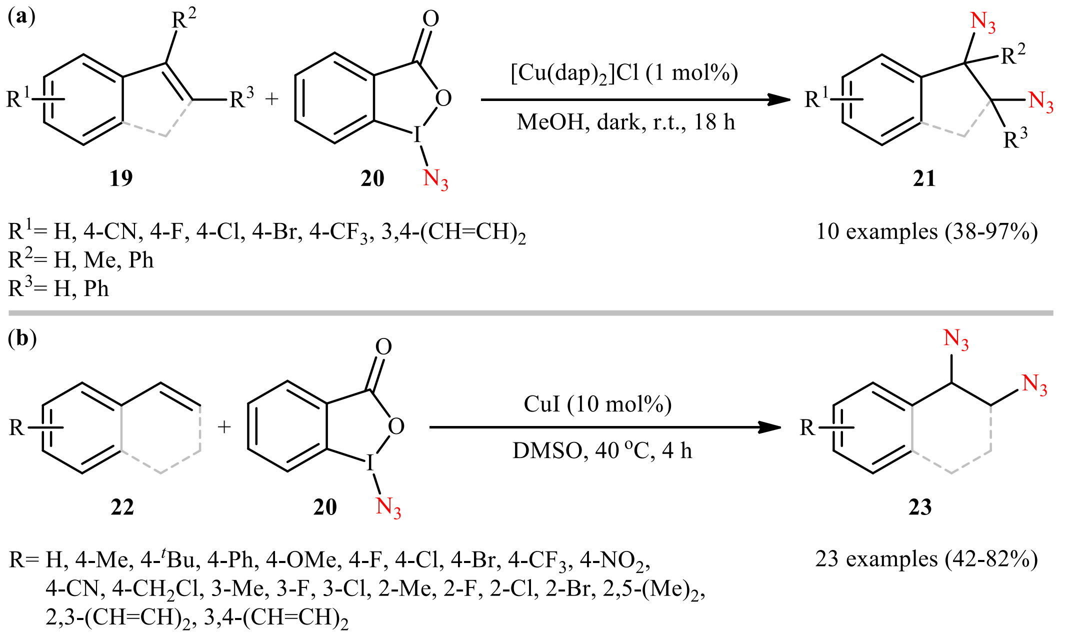
Scheme 14. West's synthesis of 1,2-diazides **18**.



Scheme 15. Plausible mechanism for Fe-mediated photochemical diazidation of alkenes **17**.

5. Copper-catalyzed reactions

One of the earliest reports of the copper-catalyzed direct vicinal diazidation of olefinic C-C double bonds, has been reported by Greaney and co-workers in 2015, when a range of vinylarenes **19** in the treatment with the hypervalent iodine reagent 1-azido-1*l*^{3}-benzo[*d*][1,2]iodaoxol-3(1*H*)-one **20** in the presence of only 1.0 mol% of [Cu(dap)2]Cl underwent selective diazidation to form the corresponding vicinal diazides **21** [29]. The reactions were carried out at room temperature under dark conditions, tolerated both open-chain and cyclic alkenes, and generally afforded the target 1,2-diazides in fair to excellent yields (Scheme 16a). The results showed that terminal alkenes afforded better yields compared to the internal ones and substrates with electron-donating substituents provided higher yields than electron-poor substrates. Interestingly, performing the same reaction under visible-light irradiation led to the corresponding methoxyazidated products through a photocatalyzed methoxy azidation process. In this case, MeOH not only acts as a solvating medium, but also as a methoxylation reagent. Concurrently, Loh's research group studied the similar diazidation of styrene derivatives **22** with hypervalent iodine reagent **20** using cheap and widely available CuI as catalyst in DMSO at 40 °C [30]. In this report, twenty-three aliphatic 1,2-diazides **23** were synthesized in modest to high yields, ranging from 42% to 82% (Scheme 16b). In addition, a tolerance for vinylarenes (*i.e.*, 2-vinylthiophene) was also demonstrated. Later, Yu and co-workers disclosed that the merge of $[Cu(dap)_2]PF_6$ with visible-light can be used as effective catalytic system for 1,2-diazidation of electron-deficient vinyl arenes with the hypervalent iodine reagent **20** [31]. However, when compared to Greaney's and Loh's protocols, this reaction presents lower average yields using similar substrates.



R^1= H, 4-CN, 4-F, 4-Cl, 4-Br, 4-CF_3, 3,4-$(CH{=}CH)_2$
R^2= H, Me, Ph
R^3= H, Ph

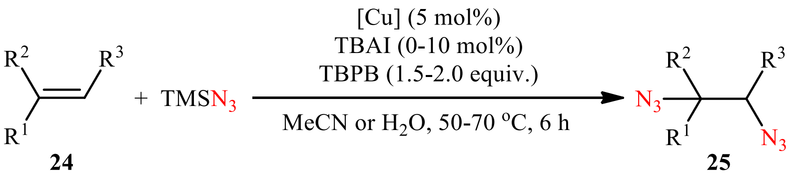
10 examples (38-97%)

R= H, 4-Me, 4-^{t}Bu, 4-Ph, 4-OMe, 4-F, 4-Cl, 4-Br, 4-CF_3, 4-NO_2, 4-CN, 4-CH_2Cl, 3-Me, 3-F, 3-Cl, 2-Me, 2-F, 2-Cl, 2-Br, 2,5-$(Me)_2$, 2,3-$(CH{=}CH)_2$, 3,4-$(CH{=}CH)_2$

23 examples (42-82%)

Scheme 16. (a) Greaney's synthesis of 1,2-diazides **21**; (b) Loh's synthesis of 1,2-diazides **23**.

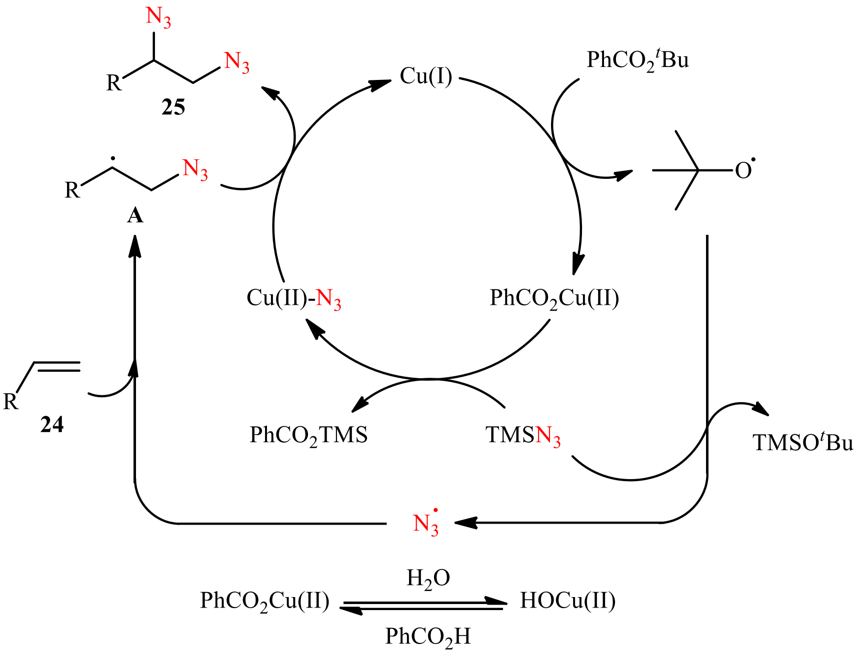
In 2017, Bao and co-workers developed an efficient protocol for the synthesis of structurally diverse 1,2-diazides **25** *via* Cu-catalyzed direct diazidation of corresponding alkenes and dienes **24** by using $TMSN_3$ as azidating agent (Scheme 17) [32]. The best conversion efficiency was obtained for the reactions containing 5 mol% of an appropriate copper catalyst (*i.e.*, CuI, Cu(OTf), CuBr·SMe_2), TBPB (1.5-2.0 equiv.), and TBAI (0-10 mol%) in MeCN (or H_2O) at 50-70 °C. Under optimized conditions, the reaction tolerated a range of important functional groups including F, Cl, Br, Ms, OH, CO_2H, ester, and ether and provided the expected diazidated products in moderate to almost quantitative yields. The protocol was also compatible for diazidation of allenes as exemplified by synthesis of (2,3-diazidoprop-1-en-1-yl)benzene from propa-1,2-dien-1-ylbenzene. Mechanistically, after a series of control experiments, it was confirmed that this difunctionalization reaction most likely proceeds *via* a radical pathway as depicted in Scheme 18.



R^1= alkyl, aryl, heteroaryl, vinyl
R^2= H, alkyl
R^3= H, alkyl, aryl

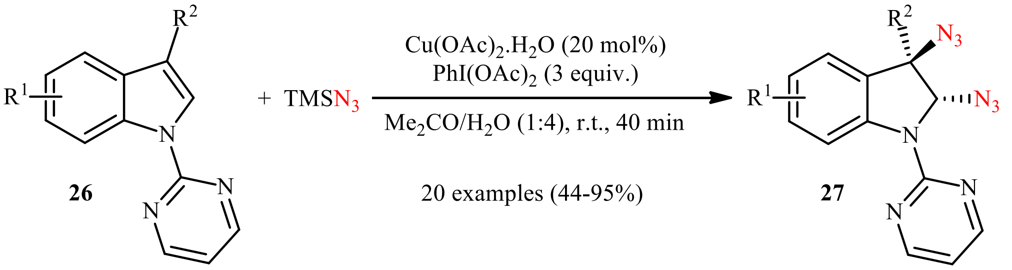
35 examples (45-98%)

Scheme 17. Bao's synthesis of 1,2-diazides **25**.



Scheme 18. Mechanistic explanation for the formation of 1,2-diazides **25**.

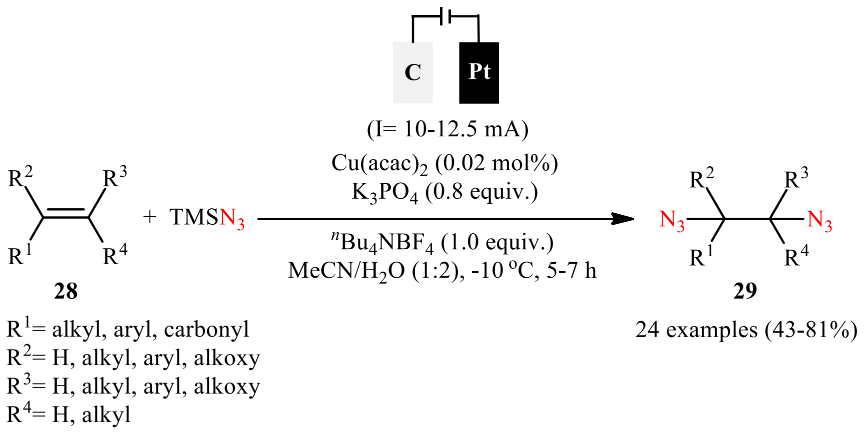
In 2020, Zhu's research team reported an interesting Cu-catalyzed directing-group-assisted diastereoselective dearomative 2,3-diazidation of indoles utilizing pyrimidyl as a coordinating directing group [33]. Careful screening of various metal catalysts such as Rh(CP)$_2$Cl$_2$, RuCl$_3$, Pd(OAc)$_2$, Cu(OAc)$_2$, CuI, CuBr; and oxidants like MnO$_2$, TBHP, K$_2$S$_2$O$_8$, H$_2$O$_2$, DCP, PIFA, PhIO, PhI(OAc)$_2$, led to Cu(OAc)$_2$/PhI(OAc)$_2$ combination as the most suitable catalytic system for this dearomative difunctionalization reaction and among the various organic solvents (*e.g.*, DMF, acetone, water); aqueous solution (contained 20% acetone) proved to be the most efficient solvent. Under optimized conditions, the C2 and C3 positions of a wide range of 2-pyrimidyl-indole derivatives **26** was selectively azidated with TMSN$_3$ and afforded the target 2,3-diazido indolines **27** in moderate to excellent yields and outstanding diastereoselectivity (Scheme 19). The results proved that the efficiency of this dearomative difunctionalization reaction strongly depended on the electronic character of the substituents on the indole ring, clearly in favor of electron-donating groups. Notably, the efficiency of this transformation was almost unaffected by the substituents in the C4, C5, C6, or C7 position (2,3-diazido-4-methyl-, -5-methyl-, -6-methyl-, and -7-methyl-indolines were obtained in 87%, 90%, 93%, and 90% yields, respectively).



R^1= H, 4-Me, 4-OMe, 4-F, 4-Cl, 4-CN, 4-NO$_2$, 5-Me, 5-F, 5-Cl, 6-Me, 6-OMe, 6-F, 6-Cl, 6-CF$_3$, 7-Me
R^2= H, Me, CH$_2$CO$_2$H, CH$_2$CO$_2$Me, CH$_2$CH(NHBoc)CO$_2$Me

Scheme 19. Zhu's synthesis of 2,3-diazido indolines **27**.

Recently, Xu and co-workers developed an efficient Cu-catalyzed electrochemical approach for direct diazidation of various terminal and internal alkenes **28** (activated, non-activated, complex natural products and drug molecules) with TMSN$_3$ at ppm catalyst loading [34]. The optimal system was identified using K$_3$PO$_4$ (0.8 equiv.) as a base and ^{n}Bu$_4$NBF$_4$ (1.0 equiv.) as a supporting electrolyte with 0.02 mol % (200 ppm) of Cu(acac)$_2$ as the catalyst in an undivided RVC/Pt-cell in aqueous acetonitrile under constant current of 10-12.5 mA at -10 °C. This electrochemical protocol efficiently provided the target aliphatic 2,3-



Scheme 20. Xu's synthesis of aliphatic 2,3-diazides **29**.

diazides **29** in modest to high yields, within 5-7 h (Scheme 20).

6. Conclusion

This review has outlined recent progress in the field of transition-metal-catalyzed direct vicinal diazidation of alkenes and shown how efficient this page of aliphatic 1,2-diazide synthesis is in terms of high yielding products and broad scope of substrates. Despite the remarkable accomplishments over the past decade (2015-2024) in this attractive and important research field, many significant challenges still remain to be overcome: (i) the reactions are generally limited to the use of manganese, palladium, iron, and copper catalysts. Therefore, the exploration of other first-row and earth abundant transition metals would be highly desirable; the majority of reported examples in the field have been performed using expensive and volatile $TMSN_3$ as the azide source. From a green chemistry point of view, there is a need for replacement of $TMSN_3$ with cheaper and less toxic NaN_3; and (iii) no reporting guideline exists for direct diazidation of 1,1-diaryl, triaryl-substituted, and tetraaryl-substituted alkenes, thus expanding of the substrate scope of this transformation to above-mentioned alkenes are necessary.

Acknowledgment

This work has been funded by the University of Zabol (Grant numbers: UOZ-GR-4188).

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