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Review

# TEMPO and its derivatives mediated reactions under transition-metal-free conditions

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ABSTRACT

2,2,6,6-Tetramethyl-1-piperidinyl-*N*-oxyl (TEMPO) and its derivatives as stable radicals can participate in many reactions. During the process, TEMPO and its derivatives could act not only as the substrates to capture or initiate new radical intermediates to provide new compounds but also as organic catalysts or oxidants for transformations of alkenes, alcohols, aldehydes and so on to synthesize various high value-added compounds. In this review, we would introduce recent advances of the transformations of different substrates mediated by TEMPO and its derivatives under transition-metal-free conditions.



## 1. Introduction

TEMPO (2,2,6,6-tetramethyl-1-piperidinyl-*N*-oxyl) as a stable radical was first synthesized in 1959 [1]. And Cella's group first realized the conversion of alcohols into the corresponding aldehydes, ketones or acids catalyzed by TEMPO with *m*-chloroperoxybenzoic acid as the oxidant [2]. Then, oxidation of alcohols in the presence of TEMPO became one of scientific hotspots. Of course, TEMPO plays many roles in organic synthesis, such as catalyst [3], radical inhibitor [4], oxidant [5] and radical capture agent [6] at present. From the viewpoint of Green Chemistry, TEMPO as a sort of organic catalyst has attracted more and more attention of the chemists. TEMPO combined with transition metal has been applied in oxidation [7,8], C-C coupling reaction [9], nitration [10], nitroxide-mediated radical polymerization [11]. Although significant progress has been made, systems involving transition metal usually are more toxic, expensive and environmentally unfriendly than transition-metal-free systems. Therefore, researchers have been paying more and more attention to transition-metal-free systems. TEMPO as a stable radical could capture or initiate free radicals, and it can be used as a catalyst, oxidant or substrate to participate in many reactions to synthesize various high value-added compounds. In this review, we want to focus on recent advances about the reactions of different substrates such as alkenes, alcohols, mediated by TEMPO and its derivatives under transition-metal-free conditions (Scheme 1).

## 2. Transformation of alkenes using TEMPO as a reagent or a catalyst

Alkenes are a highly valuable class of precursors for a variety of chemical transformations [12], such as hydrogenation [13], epoxidation [14], dihydroxylation [15], cleavage of C=C bond [16], electrophilic addition reaction [17] and radical addition reaction [18] at the C=C or C-H bond position under particular conditions. Hence, the transformation of alkenes to new compounds has stimulated researchers to pay attention to this field for searching viable approaches. In this part, we would illustrate the functionalization of alkenes with TEMPO or the transformation of alkenes mediated by TEMPO under transition-metal-free conditions.

### 2.1. The reactions of alkenes with TEMPO

Azidooxygenation, oxyarylation, aminooxygenation, and trifluoromethylaminoxylation of alkenes have been realized by radical processes in the presence of TEMPONa derived from TEMPO as the substrate [19]. Studer's group made a great contribution for this respect. In their studies, TEMPONa usually as the single electron transfer (SET) reducing reagent reacted with radical precursors, such as diazonium salts, iodanylidene malonates, and *N*-fluorobenzenesulfonimide (NFSI) to produce the

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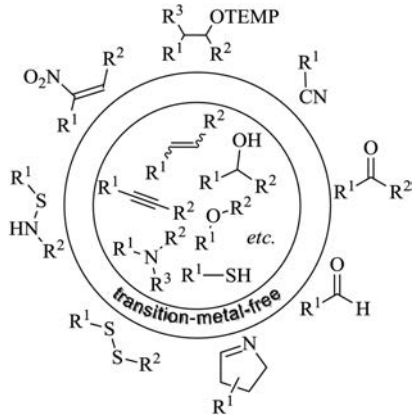
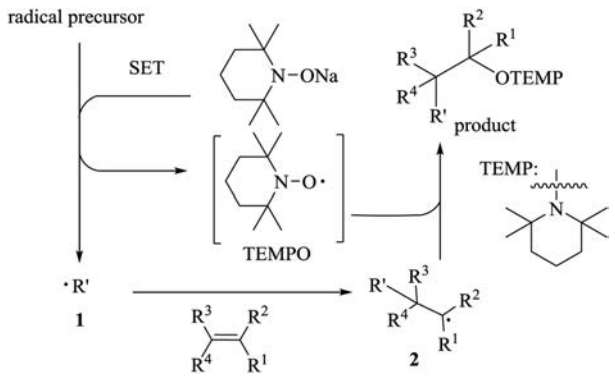


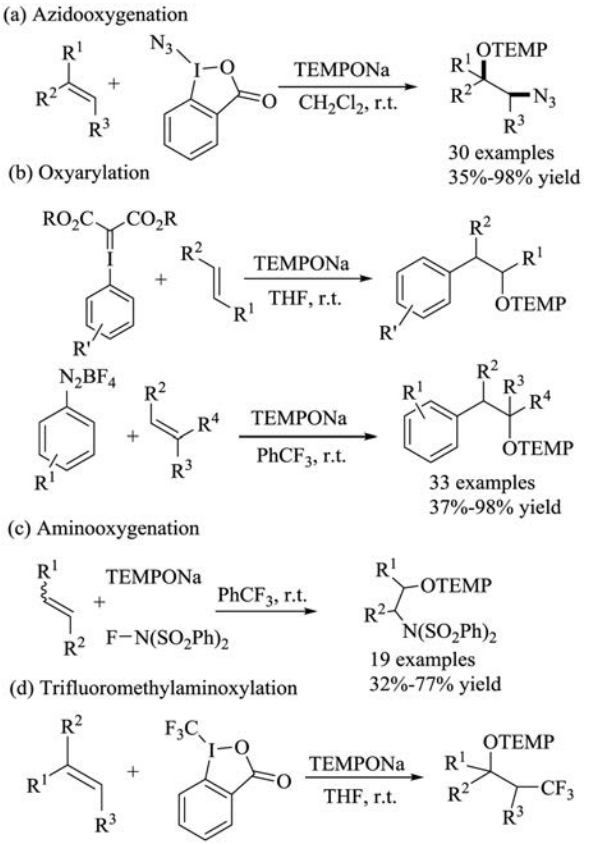

**Scheme 1.** Representative substrates and products discussed in this review.

corresponding radical **1**. Then new radicals **2** would be formed by adding radical **1** to a series of alkenes. Finally, relevant products would be generated by trapping radicals **2** with TEMPO (Scheme 2). $N_3$-radical resulting from $N_3$-iodine(III) reagent with the help of TEMPONa would react with alkenes to provide the corresponding C-radical, and good to excellent yields of the products would be obtained under mild conditions (Scheme 3a) [20]. Aryl radical generated from aryl diazonium or hypervalent iodine(III) compound addition to alkenes with subsequent TEMPO trapping provided the corresponding oxyarylation products in good to excellent yields (Scheme 3b) [21,22]. Besides, NFSI would be reduced to *N*-centered radical by TEMPONa, which would react with alkenes to give aminooxygenation products in moderate to good yields (Scheme 3c) [23]. In addition, Studer's group had found hypervalent-iodine–$CF_3$ reagent (Togni reagent) could be transformed into the $CF_3$ radical, which would be trapped by alkenes (Scheme 3d) [24]. Furthermore, a stereoselective metal-free system for *syn*-dihydroxylation of electron-rich alkenes was achieved by the reaction of alkenes with TEMPO/IBX (2-iodoxybenzoic acid) in trifluoroethanol (TFE) or hexafluoroisopropanol (HFIP) (Scheme 4) [25]. And transformation of vinyl azides to prepare various TEMPO-trapped ketones, amides, and $\alpha$-alkoxyalkyl azides has been studied as a novel strategy [26].

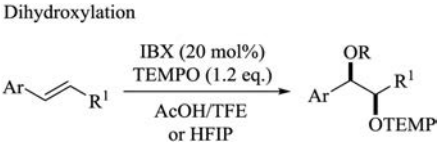
Electrochemical research involving *N*-oxyl compounds, for instance, TEMPO and related *N*-oxyl species, has attracted a lot of attention from chemists [27]. Previously mentioned azidooxygenation could also be realized through a TEMPO-$N_3$ charge-transfer complex. In electrochemical azidooxygenation, the vicinally C-O and C-N difunctionalized compounds were produced with TEMPO and




**Scheme 2.** The proposed mechanism for the reaction of TEMPONa and alkenes.

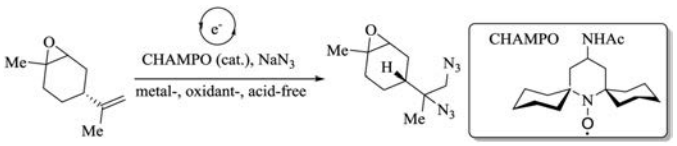



**Scheme 3.** The examples of the transformation of alkenes *via* a single electron transfer process with TEMPONa.

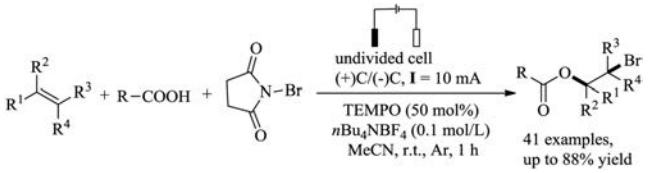



**Scheme 4.** Dihydroxylation of alkenes mediated by TEMPO.

$NaN_3$ as the substrates (the reaction was similar with Scheme 3a) [28]. Subsequently, electrochemical diazidation of alkenes was mediated by cyclohexane-substituted (4-acetamidopiperidin-1-yl)oxyl (CHAMPO) as a new aminozyl radical catalyst without any other transition metal catalysts or chemical oxidants (Scheme 5) [29]. In addition, the reactions of alkenes with acids and *N*-bromosuccinimide could be accomplished *via* a three-component electrooxidative 1,2-bromoesterification to synthesize $\beta$-bromoalkyl esters with a wide substrate and acid range by employing TEMPO as the initiator (Scheme 6) [30].




**Scheme 5.** Electrochemical diazidation of alkenes catalyzed by CHAMPO.




**Scheme 6.** Electrooxidative 1,2-bromoesterification initiated by TEMPO.

### 2.2. Cycloaddition of alkenes and compounds containing nitrogen mediated by TEMPO

TEMPO together with photocatalyst (9-mesityl-10-methylacridinium perchlorate) as the cooperative catalytic system was able to catalyze alkenes to realize selective oxidation to establish direct path for conversion of N/O-H into N/O-radicals with $O_2$ as the terminal oxidant to synthesize pyrazoline, pyridazine and isoxazoline derivatives (Scheme 7) [31]. Besides, oxidative [3 + 2] cycloaddition of organic azides with electron-deficient terminal and internal alkenes (such as chalcone) was achieved with TEMPO as the catalyst to construct a diverse array of disubstituted and trisubstituted 1,2,3-triazoles [32].

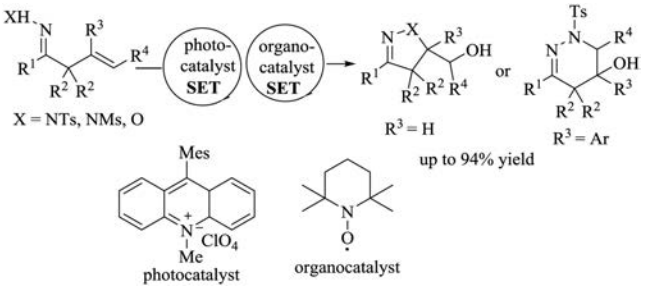
At the same time, TEMPO as the oxidant has participated in the synthesis of indolizines that have been used in biology and materials. The 1,3-dipolar cycloaddition was found in the reaction of electron-deficient alkenes and primary halogenated hydrocarbons under one-pot and transition-metal-free conditions (Scheme 8) [33].

### 2.3. Other reactions in the presence of TEMPO

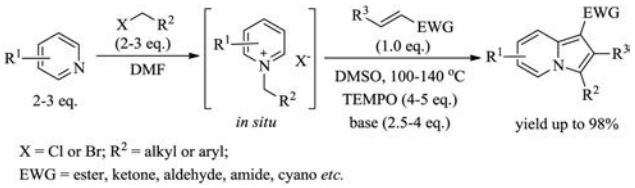
In 2013, Jiao's group developed a strategy for direct oxidative nitrogenation *via* C=C double bond cleavage catalyzed by TEMPO under metal-free conditions. In this case, it was another attractive way to synthesize various compounds containing nitrogen atom and oxygen atom such as *oxo* nitriles (Scheme 9) [34].

In addition, nitroolefins are a prominent class of synthetic intermediates and nitration could be found in the reaction between alkenes and nitrite or nitrate catalyzed by TEMPO. Maiti's group had presented the stereoselective nitration with $^t$BuONO by removing the hydrogen or other functional group such as -COOH with TEMPO as the catalyst under air [35].

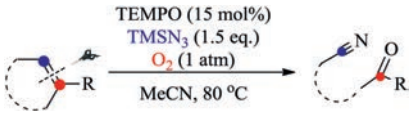
The methods for [2 + 2] cycloaddition of alkenes included light irradiation [36], transition metal-catalyzed reaction [37] and Lewis acid-mediated reaction [38]. However, the formation of dimer under transition-metal-free conditions was limited. In 2017, Shiotsuki and coworkers reported intermolecular [2 + 2] cycloaddition of norbornadienes (NBDs) using TEMPO as a catalyst and AIBN as a co-catalyst (Scheme 10) [39]. Based on the above studies, TEMPO not only acts as the catalyst, but also as the substrate to capture the radical to form compounds containing C-O bond or as an oxidant for some transformations.



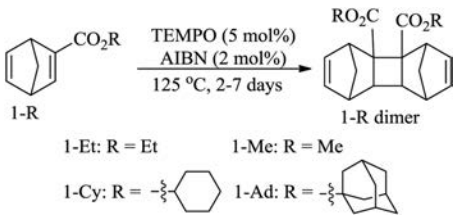

**Scheme 7.** Oxyamination and dioxygenation of alkenes catalyzed by photocatalyst and TEMPO.




**Scheme 8.** 1,3-Dipolar cycloaddition between electron-deficient alkenes and halogenated hydrocarbons.




**Scheme 9.** Direct oxidative nitrogenation *via* C=C double bond cleavage.




**Scheme 10.** Intermolecular [2 + 2] cycloaddition catalyzed by TEMPO.

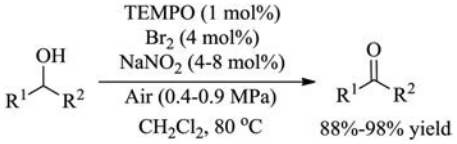
## 3. Transformation of alcohols in the presence of TEMPO

Alcohols are an important kind of organic compounds, and the transformation of them into more functionalized compounds is very significant. At present, efficient methodologies have been presented for oxidative esterification, oxidative amidation, *etc.*

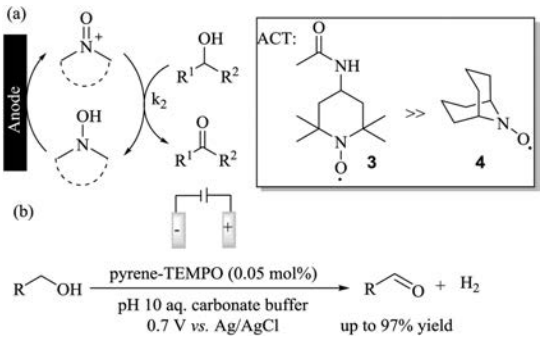
### 3.1. Transformation of alcohols into aldehydes, ketones or acids

Transition-metal-free system for aerobic oxidation of alcohols catalyzed by TEMPO has been developed rapidly since Liang and Hu reported the first example (Scheme 11) [40]. As we know, the source of halogen or nitric oxides such as $NaNO_2$, is necessary and is often used to realize the transformation of alcohols by electron transfer using TEMPO as the electron transfer mediator and oxygen as the terminal oxidant. Subsequently, many works focus on further developing the oxidation of alcohols under transition-metal-free conditions [41,42,43].

To our surprise, TEMPO has made outstanding contributions on electrochemical oxidation of alcohols. In 2015, electrocatalytic alcohol oxidation catalyzed by TEMPO and bicyclic nitroxyl derivatives (**3** and **4**) was presented (Scheme 12a). In this process, the inexpensive and readily accessible 4-acetamido-TEMPO (ACT) was selected as the better catalyst for oxidation of alcohols, exhibiting higher electrocatalytic activity than bicyclic nitroxyls




**Scheme 11.** The oxidation of alcohols catalyzed by TEMPO in transition-metal-free systems.



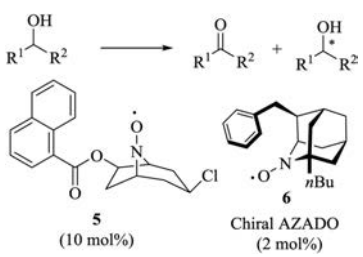

**Scheme 12.** Application of TEMPO on electrochemical oxidation of alcohols.

such as 2-azaadamantane *N*-oxyl (AZADO) and 9-azabicyclo[3.3.1] nonane *N*-oxyl (ABNO) in turnover frequencies (TOFs). And the steric effects were no match for nitroxyl/oxoammonium redox potential [44].

Different from previous studies, 4-amino TEMPO could be combined with pyrene-linked carboxylic acid derivative to form a pyrene tethered TEMPO derivative which also showed good catalytic activity for the oxidation of alcohols (Scheme 12b) [45].

In addition, chiral azabicyclo-*N*-oxyls **5** that were prepared by linking various *O*-protecting groups played excellent roles on mediating enantioselective electrooxidation of *sec*-alcohols. Through the process, the corresponding ketones were afforded and optically active alcohols could be recovered simultaneously (Scheme 13) [46]. In addition, other chirally modified AZADOs **6** as the derivatives of TEMPO have achieved oxidative kinetic resolution of racemic secondary alcohols with high enantioselectivity and a $k_{rel}$ value up to 82.2 (Scheme 13) [47]. What is more, AZADO and its derivatives exhibit different catalytic activities with different oxidants. Alcohols could be transferred to aldehydes and ketones by employing NaOCl as the oxidant [48], while vicinal diols could provide the corresponding dicarboxylic acids with $PhI(OAc)_2$ as the oxidant [49].

Recently, we also reported oxidation of secondary alcohols into ketones using TEMPO derivatives (R = *p*-H, OH, OMe, $CH_3SO_3$, (4-Me)-Ph-$SO_3$, $CH_3CONH$, $CH_3CO_2$) as the catalysts with peracetic acid as the oxidant, which was generated from $H_2O_2$ and acetic acid catalyzed by strongly acidic resins. The system proceeded well through a shortened electron-transfer cycle under metal-free conditions, avoiding the use of any other electron-transfer mediators such as halides [50]. Besides, a mild system including TEMPO and trichloroisocyanuric acid (TCCA) was applied for the transformation of primary and secondary alcohols into corresponding $\alpha$-chloro carbonyl compounds. In the reaction, TCCA could be used as an alcohol oxidant and the Cl donor [51].




**Scheme 13.** Oxidative kinetic resolution of racemic secondary alcohols mediated by TEMPO.

### 3.2. Esterification of alcohols

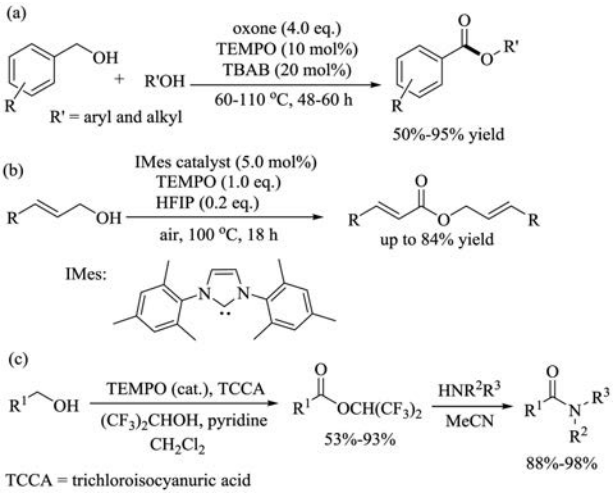
Apart from synthesis of aldehydes or ketones from alcohols, esterification of alcohols could be achieved by using TEMPO as the catalyst. In fact, the reaction procedure was aldol condensation, the alcohols combined with aldehydes or hemiacetals oxidized by oxidant and oxoammonium cation to give intermediate. Subsequently, the intermediate would incorporate with given alcohols to form the esters by cross- or self-esterification. Maiti *et al.* demonstrated an operationally simple and sustainable transition-metal-free system including catalytic amounts of TEMPO and tetra-*n*-butylammonium bromide (TBAB) in combination with oxone (potassium peroxo monosulfate) as the oxidant for "cross" esterification of alcohols (Scheme 14a) [52]. Besides, oxidative esterification of alcohols catalyzed by *N*-heterocyclic carbine with TEMPO as a stoichiometric oxidant was developed. And this reaction is an electron transfer process and does not proceed through a TEMPO ester intermediate to form esters and thioesters (Scheme 14b) [53]. Furthermore, the reaction of alcohols with $(CF_3)_2CHOH$ could afford hexafluoroisopropyl esters using TEMPO as the catalyst, which would take part in producing the amides *via* amidation in excellent yields (Scheme 14c) [54].

### 3.3. Transformation of alcohols into nitriles

Nitrile is a group of vital organic compounds, which could be applied into synthesizing intermediates in polymer materials and pharmaceuticals and make a significant effect on aromatic substances. And great progress has been made in transition metal-catalyzed transformation of alcohols into nitriles [55]. To develop better and greener methodologies, available $PhI(OAc)_2$, TEMPO and $NH_4OAc$ were employed as a system for the transformation of alcohols to nitriles, which proceeds by an oxidation-imination-aldimine oxidation sequence *in situ* under mild conditions. And this highly chemoselective ammoxidation had a wide scope of primary and secondary alcohols in high yields [56]. When TEMPO was supported, the reaction could also occur to achieve double dehydrogenation of alcohols to nitriles using recyclable MeOPEG-clicked TEMPO as the catalyst [57].

## 4. Transformation of substrates containing heteroatoms mediated by TEMPO

Heteroatomic compounds are generally important skeletons of diverse pharmaceutical intermediates. Taking advantage of TEMPO as an organic catalyst, many heteroatomic compounds could




**Scheme 14.** Oxidative esterification of alcohols.

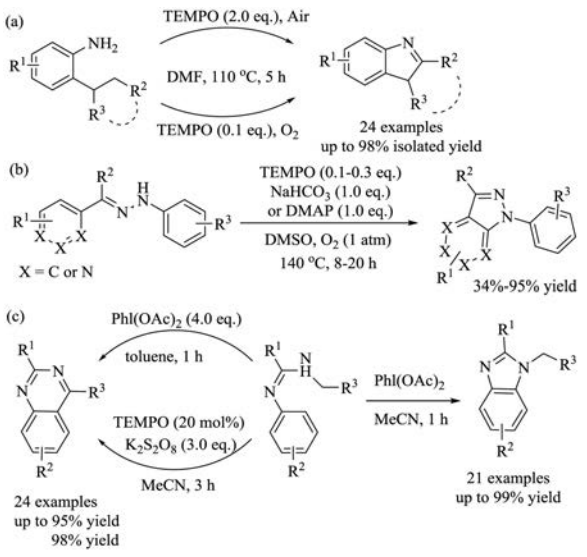
undergo different reactions to provide corresponding products in absence of transition metal.

### 4.1. Transformation of compounds containing nitrogen

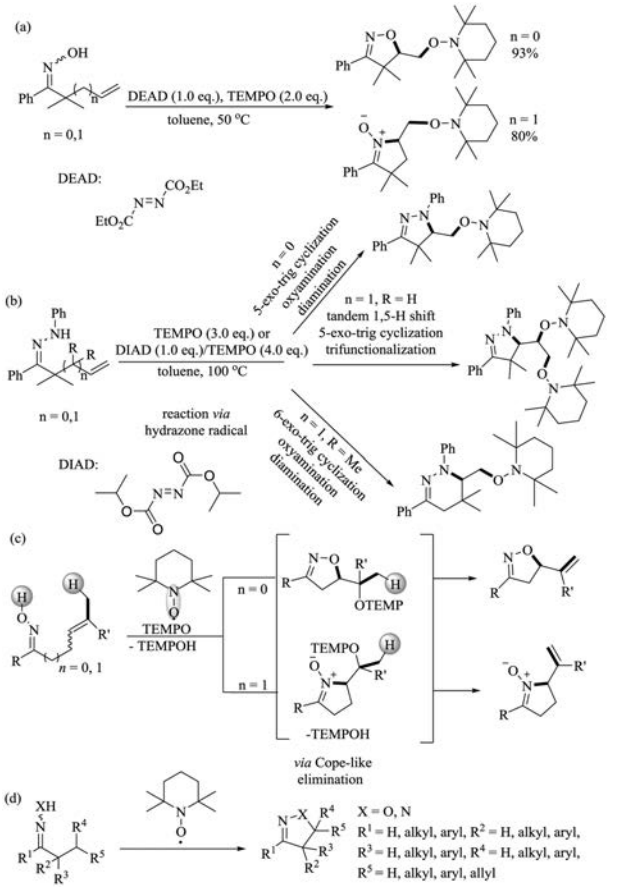
#### 4.1.1. Intramolecular cyclization reaction

The C-N bond widespread exists in organic synthetic intermediates, biomolecules, drugs and natural products. And oxidative C-H functionalization to form new C-N bonds has emerged as an atom economic and straight-forward synthetic method [58]. Intramolecular cyclizations have found wide applications in the synthesis of heterocyclic compounds. The benzimidazole scaffold, azaindazole and indazole derivatives, and quinazolines and so on are among the most common motifs present in drugs and bioactive compounds [59]. TEMPO-air/cat. TEMPO-$O_2$ system as a metal, base and additive-free system was developed for oxidative direct C($sp^3$)-H amination reaction to afford polysubstituted benzimidazoles from readily available *N*-benzyl/alkyl-1,2-phenylenediamines, giving up to 98% isolated yield (Scheme 15a) [60]. During the process, TEMPO can act as oxidant, also can play a catalytic role. Furthermore, an unprecedented method for preparing a variety of multisubstituted azaindazole and indazole derivatives through aerobic oxidative C-N coupling was developed with TEMPO as the catalyst and $O_2$ (1 atm) as the oxidant under transitional-metal-free conditions (Scheme 15b) [61]. Interestingly, iodine(III)-promoted oxidative C($sp^3$)-C($sp^2$) and C($sp^2$)-N coupling in nonpolar and polar solvents would provide multi-substituted quinazolines and benzimidazoles, while TEMPO-catalyzed C($sp^3$)-H/C($sp^2$)-H direct coupling of the amidine with $K_2S_2O_8$ as the oxidant could selectively give quinazolines in polar solvent (Scheme 15c) [62].

In 2012, the first 5-*exo*-trig cyclization of $\alpha,\beta$-unsaturated oximes was presented by Han and coworkers [63]. About the cyclization, TEMPO or DEAD (diethyl azodicarboxylate) was employed as the radical initiator to afford oxime radicals. Then the new radicals underwent radical cyclization and radical trapping to produce the isoxazolines and cyclic nitrones (Scheme 16a). Besides, this group reported another similar study about radical cyclization in 2013. Hydrazones, which would produce hydrazone radical to carry out vicinal difunctionalization of alkenes and trifunctionalization of allyls, were also incorporation with TEMPO to construct pyrazolines and tetrahydropyridazines by radical cyclization (Scheme 16b) [64].




**Scheme 15.** The formation of C-N bond mediated by TEMPO.

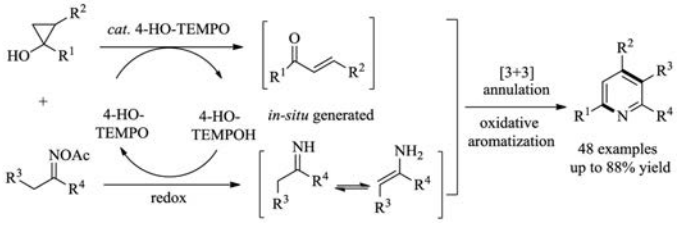



**Scheme 16.** Cyclization reaction from C—H bond activation.

Next, they reported that hydrazonyl $\sigma$ radicals could be generated from *N*-trichloroacetyl and *N*-trifluoroacetyl hydrazones by using $TEMPO^+BF_4^-$ as the oxidant and $Cs_2CO_3$ as the base. And the pyrazolines and azomethine imines were synthesized in high yields through the transformation of $\beta,\gamma$- and $\gamma,\delta$-unsaturated *N*-trifluoroacetyl and *N*-trichloroacetyl hydrazones [65]. Then isoxazoline/cyclic nitrone-featured methylenes could be afforded from the reaction of $\beta,\gamma$- and $\gamma,\delta$-unsaturated ketoximes with TEMPO *via* tandem iminoxyl radical-promoted cyclization/TEMPO-mediated Cope-like elimination. And TEMPO played dual roles as the iminoxyl radical initiator and the $\beta$-hydrogen acceptor (Scheme 16c) [66].

What is more, Chiba and coworkers also had achieved aliphatic C-H bond or allylic C-H oxidation of oximes and hydrazones mediated by TEMPO as the radical initiator to provide substituted isoxazole and pyrazole skeletons (Scheme 16d) [67,68].

Recently, the group of Han has accomplished the annulation of cyclopropanols and oxime acetates catalyzed by 4-OH-TEMPO. The redox reaction took place through $\alpha,\beta$-unsaturated ketones and imines *in situ* generated from cyclopropanols and oxime acetates. The system achieved in one pot with high chemoselectivities and an excellent functional group tolerance (Scheme 17) [69].



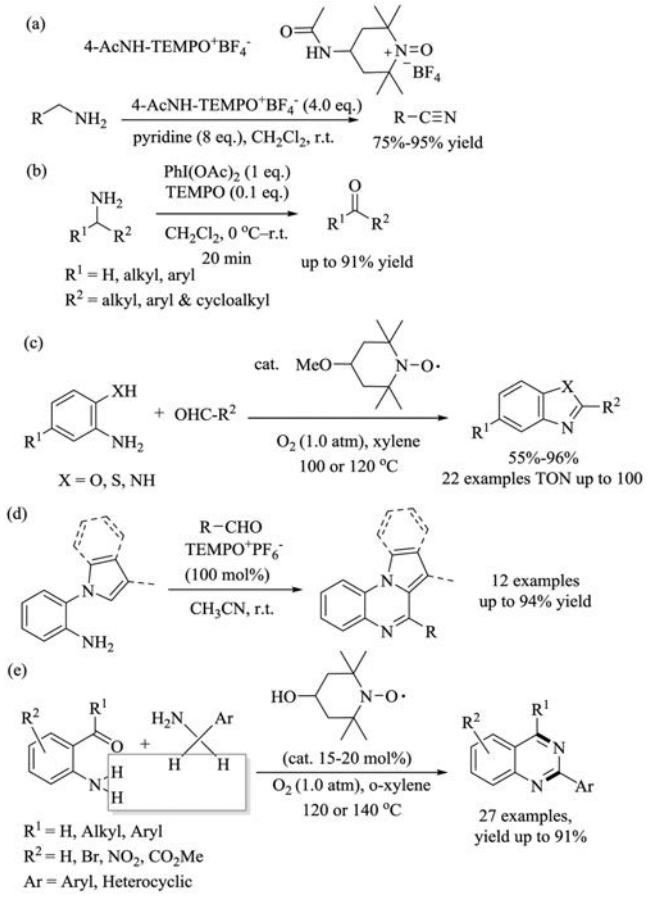

**Scheme 17.** Annulation of cyclopropanols and oxime acetates catalyzed by 4-OH-TEMPO.

*4.1.2. Transformation of amines*

Amines as a class of widely used substances are acutely sensitive to oxidation, and different products may be generated depending on the oxidant. Conversion of a primary amine to a nitrile is a particularly challenging oxidation. Wiberg and Bailey reported oxidation of primary amines in good yields mediated by a stoichiometric quantity of 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxoammonium tetrafluoroborate as the oxidant in $CH_2Cl_2$-pyridine solvent at room temperature or at gentle reflux (Scheme 18a) [70]. Then Bailey's group realized catalytic conversion of primary amines to nitriles by employing ACT as the catalyst and oxone as the terminal oxidant under mild conditions [71]. Besides, oxidative conversion of benzylamines to benzaldehydes catalyzed by TEMPO in aqueous–organic medium was also achieved with $NaIO_4$ as the oxidant [72]. On the other hand, preparation of carbonyl compounds from nitriles was mentionable. The transformation of primary and secondary amines to carbonyl compounds could be achieved using $PhI(OAc)_2$ as the oxidant and TEMPO as the catalyst under mild conditions (Scheme 18b) [73]. Then 2-substituted benzoxazoles, benzothiazoles, and benzimidazoles could be prepared by oxidative dehydrogenation catalyzed by 4-methoxy TEMPO, which undergo a one-pot reaction between aldehydes and 2-aminophenole, 2-amonothiophenol or *o*-phenylenediamine, respectively (Scheme 18c) [74].

Similarly, the primary amines could also react with aldehydes to generate pyrrolo[1,2-*a*]quinoxalines initiated by TEMPO oxoammonium salts, which drove a Pictet–Spengler reaction of imine to undergo the cyclization–dehydrogenation process for the formation of quinoxalines (Scheme 18d) [75].

Han *et al.* reported a novel and efficient aerobic protocol for the oxidative synthesis of 2-aryl quinazolines *via* benzyl C-H bond amination by a one-pot reaction of arylmethanamines with 2-aminobenzoketones and 2-aminobenzaldehydes catalyzed by 4-hydroxy-TEMPO in the absence of metal and other additives (Scheme 18e) [76].




**Scheme 18.** The conversion of primary amines.

Maruoka's group found that *in situ* generated nitrosocarbonyl compounds from hydroxamic acid derivatives could react with aldehydes to realize a highly regio- and enantioselective hydroxyamination by combination of TEMPO and benzoyl peroxide (BPO) as the oxidant and chiral binaphthyl-modified amine **7** as a catalyst (Scheme 19) [77].

Besides, pyrrolin-4-ones were ubiquitous to use in various fields. A novel *in situ* generated TEMPO oxoammonium salt as the oxidant mediated one-pot tandem reaction has been developed for the straightforward construction of pyrrolin-4-ones in good yields under mild conditions from readily available $\beta$-oxoamides with amine hydrochlorides (Scheme 20) [78].

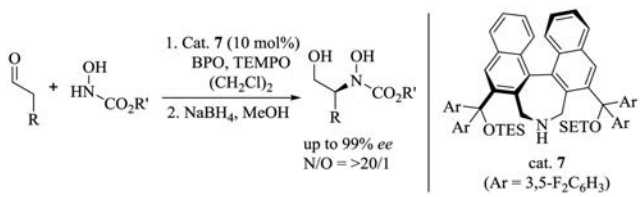
In the case of secondary amines, there are also several reported reactions. During the process in synthesis of benzothiazoles mediated by a novel magnesium base, an intermediate containing the group of secondary amine would be oxidized to imine only with TEMPO [79]. Tetrahydropyridazines, as an important class of six membered heterocycles, are widely found in many natural products and pharmaceutically active compounds. Han and coworkers reported a one-pot tandem reaction including oxidative dehydrogenation of ketohydrazones and subsequent aza-Diels-Alder reaction for the synthesis of tetrahydropyridazines in the presence of TEMPO, which plays the role of radical initiator (Scheme 21) [80]. Liu *et al.* reported direct indolation of pyridines to provide 3-(pyridin-4-yl)-1*H*-indole derivatives in moderate to excellent yields mediated by TEMPO and $(Boc)_2O$ (di-*t*-butyl dicarbonate) and the reaction could be readily applied to a large-scale synthesis [81].

Tertiary anilines are more stable and researchers often employ transition-metal catalyzed activation of inert chemical bonds (C-N bond) [82]. A catalytic metal-free system including TBN (*tert*-butyl nitrite)/TEMPO was developed for highly selective C($sp^3$)-N cleavage of tertiary anilines. The system exhibited high efficiency, good functional group tolerance under mild reaction conditions (Scheme 22) [83].

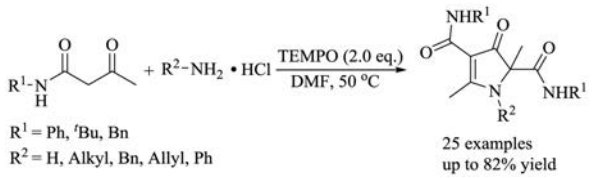
Recently, Ji paid attention to selenium functionalization of indoles and synthesized a series of 3-selenylindole derivatives catalyzed by TEMPO with $O_2$ as the green oxidant and selenium powder as the selenium source. Electron spin-resonance (ESR) studies revealed that the approach involved the formation of nitrogen-centered radicals and selenium radicals *via* oxidation of *in situ* generated selenoates (Scheme 23) [84].

*4.2. Transformation of compounds containing sulfur*

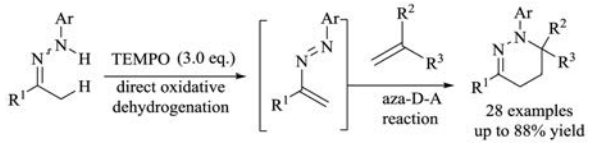
The methods for synthesizing benzimidazoles and so on mediated by TEMPO have been introduced in other part of the article. A novel metal- and reagent-free method for the synthesis of benzothiazoles and thiazolopyridines through TEMPO-catalyzed electrolytic C-H thiolation was exploited (Scheme 24). In the process, thioamide mediated by TEMPO would be transferred into an intermediate **8** containing C=N bond and S-O bond, which underwent a cleavage to release two radicals. And thioamidyl



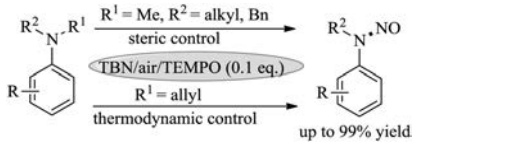

**Scheme 19.** Enantioselective hydroxyamination mediated by TEMPO.



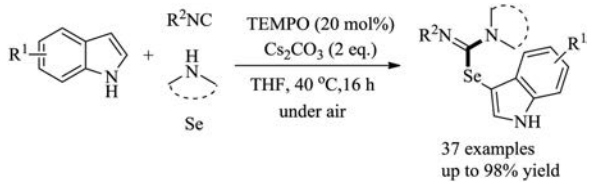

**Scheme 20.** The reaction of $\beta$-oxoamides with amine hydrochlorides to synthesize pyrrolin-4-ones.



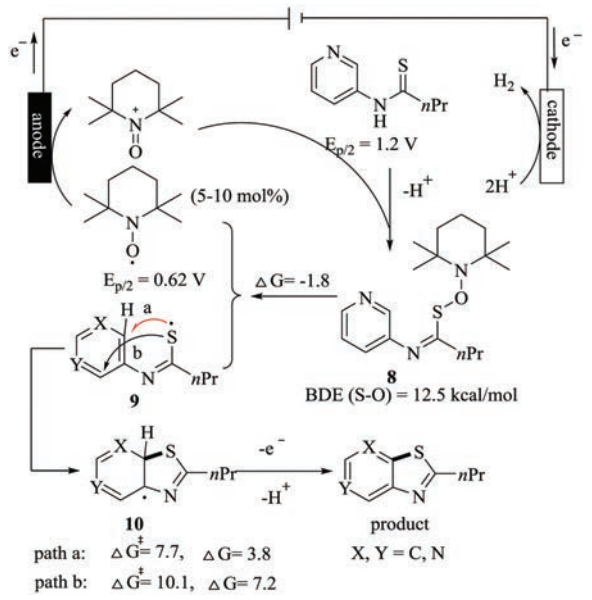

**Scheme 21.** Aza-Diels-Alder reaction of alkenes and azoalkenes initiated by TEMPO.




**Scheme 22.** Preparation of *N*-nitrosamine derivatives from tertiary anilines catalyzed by TEMPO.




**Scheme 23.** The synthesis of 3-selenylindole derivatives in presence of TEMPO.




**Scheme 24.** Electrochemical C-H thiolation utilizing TEMPO as the catalyst.

radical **9** would go through radical cyclization, the loss of electron and proton to form product thiazolopyridines [85].

Yang and coworkers had developed an environmentally friendly approach to furnish 2,2-dibenzothiazole disulfide from 2-mercaptobenzothiazole along with TEMPO in absence of metallic compounds [86]. Furthermore, the construction of sulfur –nitrogen has been demonstrated with TEMPO as the catalyst and $O_2$ as the oxidant in acetonitrile. Thiols could be generated by oxidative homocoupling and heterocoupling reactions [87].

## 5. The reactions of several other compounds in the presence of TEMPO

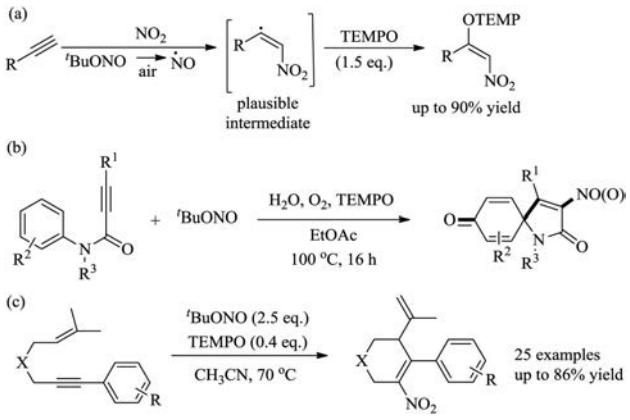
Through previous description, TEMPO has played a crucial impact on functionalization of various compounds including alkenes addition or substitution, alcohols and compounds containing heteroatom transformation. In addition, alkynes, ethers and aldehydes also could be converted into other type compounds mediated by TEMPO.

### *5.1. Nitration of alkynes*

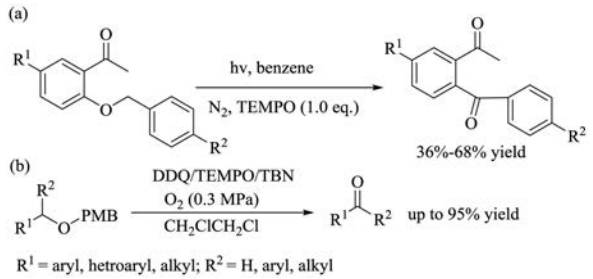
To synthesize nitro compounds, nitration of alkenes had been achieved using TEMPO as radical scavenger [88]. In this regard, alkynes have revealed excellent applications. In 2014, Matti's group presented the stereoselective nitroaminoxylation of alkynes under similar conditions compared with alkenes, which was an efficient approach to functionalized alkynes (Scheme 25a). Initially, nitro radical from $^t$BuONO oxidized by oxygen in air was added to alkynes. Subsequently, the generated vinyl radical was trapped by TEMPO to form the nitration product in high yields [89]. The addition reaction of terminal alkynes was easier than internal alkynes. Hence, it was of great significance to explore reaction of internal alkynes. Li and coworkers proposed the nitrative spirocyclization of alkynes to construct C-N/C-C bonds to produce the difunctionalized spirocyclic product with the same nitro source by employing TEMPO as the initiator (Scheme 25b) [90]. Besides, metal-free system including $^t$BuONO and TEMPO for nitrocarbocyclization of 1,6-enynes was developed by the group of Liang with similar radical mechanism (Scheme 25c) [91].

### *5.2. Transformation of ethers*

Ethers can be transferred into aldehydes, ketones or nitriles in the presence of TEMPO. A UV (Pyrex filter with a 450-W medium-pressure mercury lamp) light activation/TEMPO oxidation cascade reaction was demonstrated to be suitable for the conversion of C-O bond in *O*-acetyl aryloxy benzene derivatives to form carbonyl compounds in benzene in absence of metal (Scheme 26a) [92]. Hu




**Scheme 25.** Nitration of alkenes.




**Scheme 26.** The transformation of ethers to ketones.

and coworkers applied DDQ (2,3-dichloro-5,6-dicyano-1, 4-benzoquinone)/TEMPO/TBN as a metal-free catalytic system for direct transformation of PMB (*p*-methoxybenzyl) ethers into their corresponding aldehydes or ketones *via* a new tandem deprotection/oxidation reaction using oxygen as the oxidant (Scheme 26b) [93], and alcohols were the important intermediates of the transformation.

Water as a substrate in the reactions was very important from the development of green chemistry. Vankar exploited a simple, highly efficient and regiospecific method for the direct conversion of 3-*O*-benzylated and silylated glycals into the corresponding enones. The reaction generally proceeds in high yields (up to 86%) under mild conditions in a short time with TEMPO as the catalyst, $PhI(OCOCF_3)_2$ as the oxidant and water as the reagent (Scheme 27) [94].

It was worth noting that benzyl ethers could be directly converted into aryl nitriles. Ren and Wang developed a catalytic system including TEMPO/$HNO_3$ for the conversion by employing $NH_4OAc$ as the nitrogen source and oxygen as the terminal oxidant. The method is valuable for both the synthesis of aromatic nitriles and the deprotection of ether-protected hydroxy groups to form nitrile groups in multistep organic synthesis, in which ethers would be oxidized to aldehydes with $TEMPO^+$ [95].

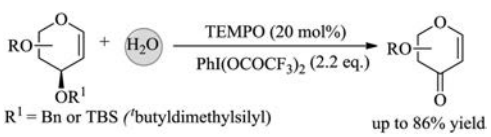
### 5.3. Conversion of aldehydes

As earlier mentioned, nitrile is an important functional group in organic synthesis. A transition-metal-free system including a catalytic amount of ACT, $NaNO_2$ and $HNO_3$ was presented for the conversion of aldehydes to nitriles. The reaction would undergo condensation with $NH_4OAc$ and aerobic oxidation [96]. Besides, Shen *et al.* employed hexamethyldisilazane (HMDS) as the nitrogen source, TEMPO as the catalyst, $NaNO_2$ or TBN as the co-catalyst, and molecular oxygen as the terminal oxidant to build an efficient system for the synthesis of nitriles from aldehydes [97].

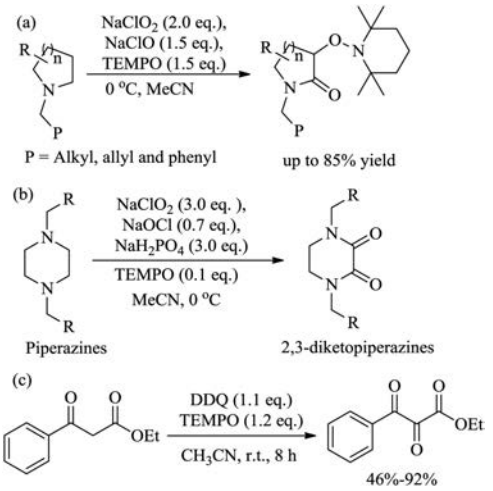
As a whole, alkynes, ethers and aldehydes could be transferred into new functionalized-compounds smoothly in presence of TEMPO by cyclization, oxidation, and so on. Hence, what we need to study is to continue to enlarge the types of compounds and make the reaction occur in more simple systems.

## 6. Functionalization of C($sp^3$)–H bond in presence of TEMPO

In general, C($sp^3$)-H is stable and nonreactive, so the activation of C-H bonds has been an important and challenging




**Scheme 27.** Synthesis of enones from ethers catalyzed by TEMPO.



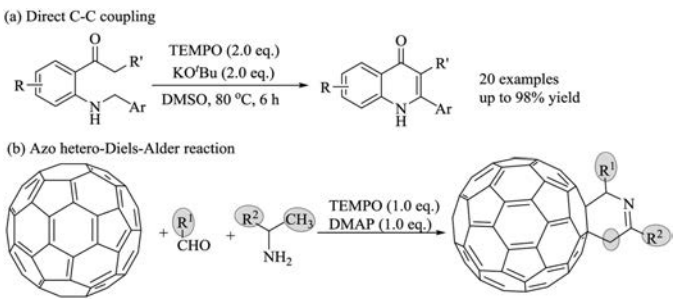

**Scheme 28.** TEMPO mediated C-H bond to carbonyl group.

investigation in organic area. And some methods for C-H bond functionalization have been proposed [98]. C($sp^3$)-H could be activated and transformed into corresponding functional groups in the presence of TEMPO and transition metals such as Pd [99] and Cu [100]. Herein, we just introduce the functionalization of C($sp^3$)-H bond to form various useful compounds mediated by TEMPO under transition-metal-free conditions.

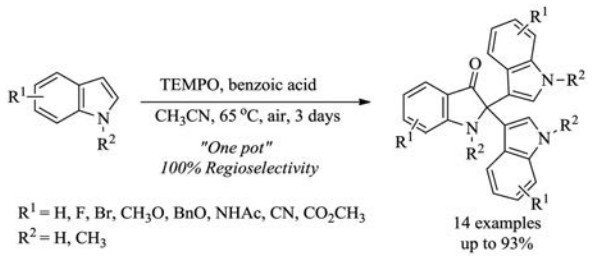
### 6.1. Formation of C=O bond from C-H

Sartillo-Piscil reported selective dual C($sp^3$)-H functionalization at the $\alpha$- and $\beta$-positions of cyclic amines to their corresponding 3-alkoxyamine lactams by employing the system including $NaClO_2$/TEMPO/NaClO in either aqueous or organic solvent (Scheme 28a). The transition-metal free system using TEMPO as the substrate is a simple, mild and non-expensive protocol, providing moderate to good yields [101]. Recently, their group continued to achieve dual C($sp^3$)-H oxidation of piperazines and morpholines to 2,3-diketopiperazines and 3-morpholinones catalyzed by TEMPO using $NaClO_2$ and NaOCl as cheap and innocuous reagents (Scheme 28b). And 2-alkoxyamino-3-morpholinone can be prepared from morpholine derivatives, which would enable further functionalization at the C2 position of the morpholine skeleton by modulating the amounts of TEMPO [102]. Besides, construction of vicinal tricarbonyl compounds from 1,3-dicarbonyl compounds was realized through DDQ-mediated oxidative activation of C($sp^3$)-H bond and subsequent coupling with TEMPO to form the key intermediate TEMPO-substrate adduct (Scheme 28c) [103].

Little and Zeng investigated the electrochemical oxidative functionalization of benzylic C-H bonds mediated by a dual bromide ion/TEMPO redox catalyst system in a two-phase electrolytic medium. The preparative scale electrolysis of




**Scheme 29.** C-C coupling reaction from C-H bond in presence of TEMPO.




**Scheme 30.** Trimeric reaction of indoles mediated by TEMPO.

tetrahydroisoquinolines afforded the corresponding dihydroisoquinolinones in moderate to good yields [104].

Besides, benzylic C($sp^3$)-H bonds of ethers and alkylarenes were successfully converted into isochromanones and xanthones with recyclable TEMPO derived sulfonic salt as the catalyst and $NaNO_2$ and HCl as the additives under aerobic conditions and the system had a broad substrate scope and functional group tolerance [105].

### *6.2. Formation of C-C bond from C-H*

Except for the oxidation of C-H bond to carbonyl compounds, there are also many systems for C-C coupling [106]. C($sp^3$)-H/C($sp^3$)-H coupling had been achieved using TEMPO as an oxidant and KO$^t$Bu as a base under transition-metal-free conditions (Scheme 29a). And this approach was suitable for providing 4-quinolone scaffold through C-C bond formation in excellent yields under mild conditions [107]. Moreover, Liu and coworkers synthesized a series of scarce tetrahydropyridinofullerenes from fullerene, $\alpha$-methylsubstituted arylmethanamines and aldehydes in the presence of TEMPO and 4-dimethylaminopyridine (DMAP) in moderate to good yields. The process underwent an azo hetero-Diels-Alder reaction, in which TEMPO induced the $\alpha$-C($sp^3$)-H of the Schiff-base imine to produce the radical intermediate. Then the intermediate was converted into azadiene in the presence of TEMPO and DMAP (Scheme 29b) [108].

Indole derivatives exhibit significant biological activities and trimerization of indoles catalyzed by TEMPO and laccases was an efficient method [109]. Recently, the tandem oxidative homocoupling reaction could be achieved by using TEMPO as the catalyst and air as the environmentally benign oxidant in the absence of metal. The trimeric reaction of indoles had broad substrates and high regioselectivity, generating products at the C3 position of indoles (Scheme 30) [110].

## 7. Conclusion and outlook

TEMPO and its derivatives as stable radicals have been utilized to participate in many reactions in absence of transition metal. TEMPO acting as a substrate or initiator usually participated in radical reactions by capturing free radicals or initiating radicals derived from the other substrates such as alkenes. On the other hand, TEMPO would play a catalytic role in most systems and electron transfer process was usually proposed during the processes under transition-metal-free conditions. And TEMPO was considered as radical or oxoammonium ion to take part in the reaction. At present, various kinds of the substrates have participated in TEMPO and its derivatives mediated reactions, including alkenes, alkynes, alcohols, aldehydes and so on. As we know, hydrocarbons are usually inert in most reactions. Activated aromatic hydrocarbons exhibited certain activities in TEMPO-catalyzed systems at present, and the activities of non-activated hydrocarbons need to be further investigated, especially under transition-metal-free conditions.

## Acknowledgments

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