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# NH-1,2,3-triazoles as versatile building blocks in denitrogenative transformations

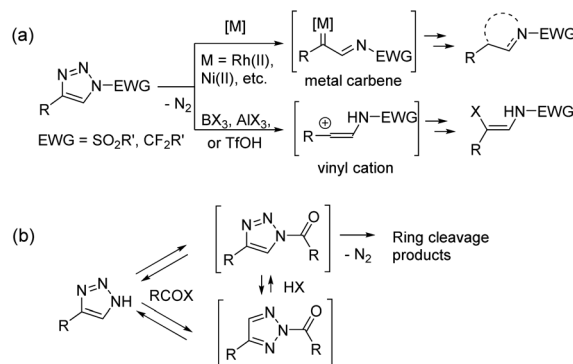
 Vladimir Motornov \* and Petr Beier \*

The utilization of NH-1,2,3-triazoles as easily accessible building blocks in denitrogenative ring cleavage transformations with electrophiles to provide multifunctionalized nitrogen heterocycles and *N*-alkenyl compounds is reviewed. Leveraging the ready availability of NH-1,2,3-triazoles, these processes provide a convenient route to a range of pharmaceutically relevant heterocyclic cores and *N*-alkenyl compounds. The synthetic usefulness of *in situ* acylated NH-1,2,3-triazoles as viable alternatives to widely explored *N*-sulfonyl-1,2,3-triazoles in ring cleavage processes is highlighted.

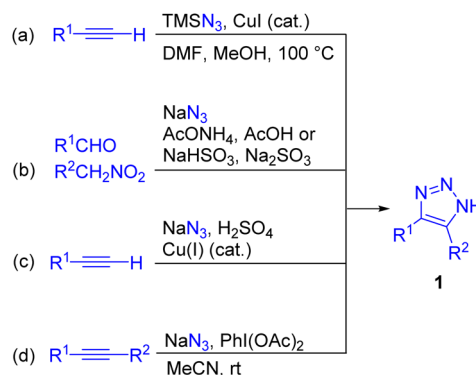
1,2,3-Triazoles are nitrogen heterocycles with versatile reactivity<sup>1</sup> and great medicinal importance.<sup>2</sup> Since the discovery of azide–alkyne click chemistry in 2002,<sup>3</sup> triazole derivatives have gained enormous attention in organic, medicinal, biomolecular, and material sciences. Among them, 1,2,3-triazoles bearing an electron-withdrawing group at position N1 are of special importance because of their propensity to undergo N1–N2 bond cleavage in denitrogenative triazole ring opening transformations (Scheme 1a).<sup>1</sup> *N*-sulfonyl-1,2,3-triazoles<sup>4</sup> and *N*-fluoroalkyl-1,2,3-triazoles<sup>5</sup> are the most explored building blocks, which undergo ring cleavage under metal catalysis or by the action of Lewis or Brønsted acids. Very recently, a new strategy based on the use of NH-1,2,3-triazoles involving the installation of an electron-withdrawing group with *in situ* ring cleavage was described and used with success (Scheme 1b). The present review features the use of free NH-1,2,3-triazoles **1** in denitrogenative transformations, proceeding *via* *N*-acyl-1,2,3-triazoles or their analogues as key intermediates.

*N*-unsubstituted NH-1,2,3-triazoles **1**, considered in the present review, are the simplest and most readily available triazoles.<sup>6</sup> They can be prepared by azide–alkyne cycloaddition<sup>6</sup> or alternative methods such as cycloaddition/elimination with activated ketones<sup>7</sup> or nitroalkenes.<sup>7</sup> In the last five years, there has been a notable surge of innovative methods for the synthesis of NH-1,2,3-triazoles and several one-pot protocols from inexpensive and commercially available reagents have been developed.<sup>6</sup> To underline the most efficient and practical routes, NH-1,2,3-triazoles were synthesized from TMSN<sub>3</sub> and alkynes *via* CuI-catalysed cycloaddition (Scheme 2a),<sup>8</sup> or sodium azide, aldehydes and nitroalkanes *via* a tandem Henry reaction/[3 + 2] cycloaddition (Scheme 2b),<sup>9a–c</sup> including recently developed green chemistry approaches.<sup>9d–h</sup> In 2022, NH-1,2,3-

triazoles became available from NaN<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> and alkynes, which is so far the simplest and the most straightforward route, although the generation of HN<sub>3</sub> raises safety concerns (Scheme



**Scheme 1** Schematic representation of the utilization of (a) *N*-sulfonyl- or *N*-fluoroalkyl-substituted 1,2,3-triazoles and (b) NH-1,2,3-triazoles in ring cleavage denitrogenative transformations.



**Scheme 2** Overview of efficient routes for the synthesis of NH-1,2,3-triazoles (a–d).

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## Review

2c).<sup>10</sup> Finally, the approach utilizing azidyl radical–alkyne cycloaddition with the use of the  $\text{NaN}_3/\text{PhI}(\text{OAc})_2$  system in mild conditions is highly efficient for complex disubstituted triazoles such as 4,5-diaryltriazoles (Scheme 2d),<sup>11a</sup> and it was also possible to efficiently synthesize these compounds without an oxidant, albeit only under harsh conditions (MW heating at 200 °C).<sup>11b</sup> More examples of novel synthetic methods to access NH-1,2,3-triazoles appeared in recent reviews.<sup>6</sup>

Due to better atom economy, the utilization of readily available NH-triazoles is advantageous compared to the use of *N*-sulfonyl- or *N*-fluoroalkyl-triazoles. Additionally, access to NH-1,2,3-triazoles was possible using “alkyne-free” methods. Both, primary nitro compounds and aromatic aldehydes are easily accessible industrial scale products.<sup>12</sup>

One of the first denitrogenative transformations of 1,2,3-NH-triazoles **1** was reported in 2014. In this process, *in situ* sulfonylation with triflic anhydride and 2,6-di(*tert*-butyl)-4-methylpyridine (DTBMP) as a base was used to generate reactive *N*-triflyl triazoles **2**.<sup>13</sup> Their ring cleavage by a chiral Rh(II) catalyst in the presence of an excess of alkene **3** afforded 2,3-dihydropyrroles **4** with low to good enantiocontrol (Scheme 3).

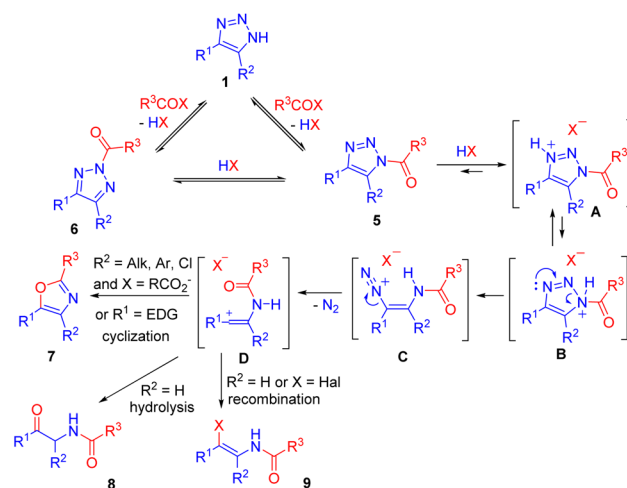
However, besides triflation, there are no other examples of *in situ* sulfonylation of NH-1,2,3-triazoles followed by denitrogenative transformations. Therefore, this reaction is limited to the extremely electron-accepting triflyl group and analogous ring cleavage did not proceed with other *N*-sulfonyl triazoles.

In contrast to sulfonylation, acylation of NH-1,2,3-triazoles is more versatile and has developed into a highly active area of research in recent years.<sup>14</sup> Tandem acylation followed by ring cleavage without isolation of *N*-acyltriazoles was performed using acyl halides or acid anhydrides. The mechanism of this transformation, recently confirmed by us,<sup>14</sup> involved the formation of N1 (**5**) and N2-acylated (**6**) triazoles in equilibrium, followed by acid-mediated cleavage of the former. Denitrogenation and formation of a vinyl cation in an irreversible step was the driving force of N2–N1-acyltriazole interconversion, which ensured the complete transformation of triazoles into ring cleavage products **7–9** (Scheme 4).

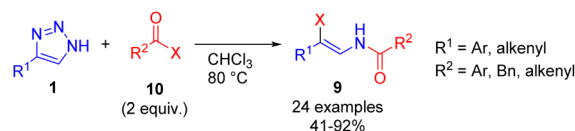
Cleavage of NH-1,2,3-triazoles **1** with an excess of acyl halides **10** ( $\text{X} = \text{Cl}, \text{Br}$ ) under elevated temperature led to the formation of  $\beta$ -enamido halides **9** in moderate to good yields (Scheme 5).<sup>15</sup>  $\beta$ -Enamido halides are difficult to access by other synthetic routes and are present in natural products, which underlines the synthetic value of the method.



Scheme 3 Synthesis of 2,3-dihydropyrroles by cleavage of NH-triazole in the presence of triflic anhydride. DTBMP – 2,6-di(*tert*-butyl)-4-methylpyridine.



Scheme 4 Mechanism of NH-triazole cleavage with electrophiles.

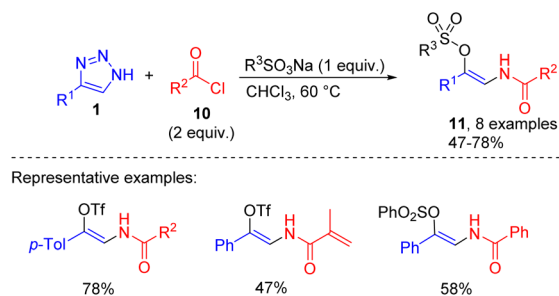


Scheme 5 Cleavage of NH-1,2,3-triazoles with acyl halides.

This transformation in the presence of sodium sulfonates was employed in the synthesis of enamido triflates or sulfonates **11**. Mainly compounds with the phenacyl group at the nitrogen were accessed by the mentioned route (Scheme 6).<sup>15</sup>

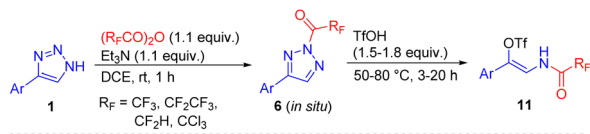
An alternative method, applicable to the synthesis of  $\beta$ -fluoroacylenamido triflates is based on the formation of N2-acyltriazoles **6** via the *in situ* acylation of NH-1,2,3-triazoles with fluorinated acid anhydrides followed by their treatment with triflic acid, which proceeds through N2–N1 acyltriazole interconversion and ring cleavage (Scheme 7).<sup>14</sup>

The products are useful building blocks, that can get involved in Pd-catalysed cross-coupling substitution reactions of the triflate group to access multifunctionalized enamide derivatives – attractive drug candidates and synthetic intermediates.<sup>16</sup> None of the methods mentioned was applicable with the less reactive alkyl-substituted acylating agents ( $\text{Ac}_2\text{O}$ ,  $\text{AcCl}$ ),

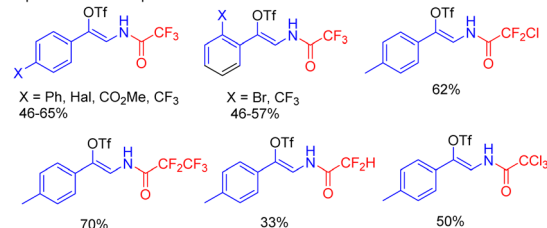


Scheme 6 Synthesis of  $\beta$ -enamido triflates and sulfonates from NH-1,2,3-triazoles, acyl halides, and sodium sulfonates.

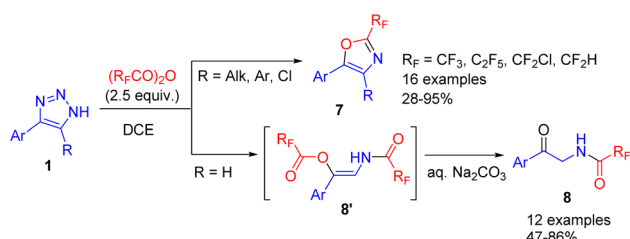




Representative examples:



Scheme 7 One-pot two step synthesis of  $\beta$ -fluoroacylenamido tri-flates. DCE = 1,2-dichloroethane.

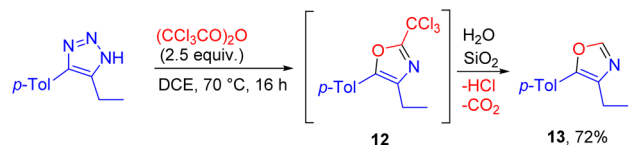


Scheme 8 Synthesis of fluoroalkylated oxazoles and 2-acylamino ketones from NH-1,2,3-triazoles with fluoroalkylated acid anhydrides.

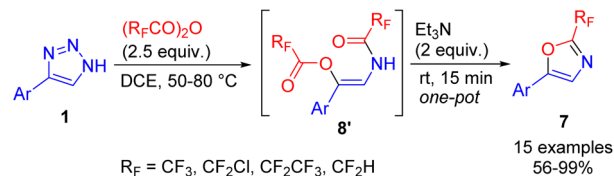
because the resulting acyltriazoles were resistant to ring cleavage even at elevated temperatures.<sup>14</sup>

The cleavage of NH-1,2,3-triazoles with an excess of fluoroalkylated acid anhydrides led to highly pharmaceutically relevant 2-fluoroalkyl oxazoles **7** (in the cases of 4,5-disubstituted triazoles) or 2-acylamino ketones (for 4-substituted triazoles, R = H) (Scheme 8).<sup>17</sup> In the first case intramolecular cyclization took place, whereas in the second, unstable  $\beta$ -acyloxyenamide **8'** formed, which underwent ester hydrolysis to 2-acylamino ketone **8** upon treatment with an aqueous base. The difference in chemoselectivity was attributed to the increased vinyl cation stability of disubstituted examples, which made them more prone to intramolecular cyclization.

4,5-disubstituted NH-1,2,3-triazole reacted with trichloroacetic anhydride to give 2-unsubstituted oxazole **13**, due to the low stability of the trichloromethyl-substituted product **12** during silica gel column chromatography. The whole transformation is a rare and unique case of a reaction involving trichloroacetic anhydride as a one-carbon building block (Scheme 9).<sup>17</sup>



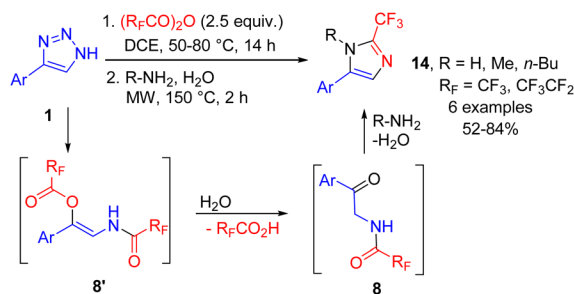
Scheme 9 Formation of 2-unsubstituted oxazole from NH-1,2,3-triazole and trichloroacetic anhydride.



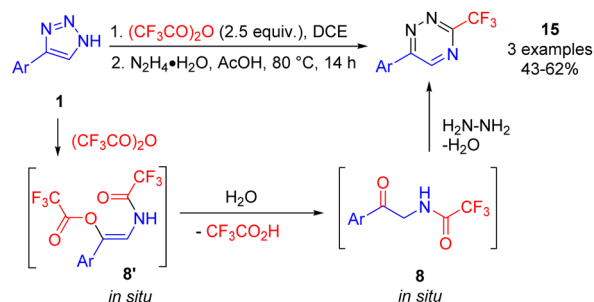
Scheme 10 One-pot synthesis of fluoroalkylated oxazoles from NH-1,2,3-triazoles, acid anhydrides and  $\text{Et}_3\text{N}$ .

The limitation of oxazole synthesis to only disubstituted triazoles was overcome by the cyclization of *in situ* formed  $\beta$ -acyloxyenamide **8'** to oxazoles **7** using  $\text{Et}_3\text{N}$  and proceeded quickly and nearly quantitatively under ambient conditions.<sup>18</sup> This one-pot triazole cleavage procedure provided an efficient access to 2-fluoroalkylated oxazoles from monosubstituted triazoles in good to excellent yields (Scheme 10).

The easy access to fluorinated 2-acylamino ketones **8** was utilized in a number of one-pot syntheses of fluoroalkylated heterocycles directly from NH-1,2,3-triazoles **1**. First, 2-fluoroalkyl imidazoles **14** were prepared by cleavage with trifluoroacetic or perfluoropropanoic anhydrides, followed by the treatment of the ketamide intermediate with an aqueous solution of the primary amine (or ammonium acetate for R = H) under microwave conditions. The acid formed after hydrolysis of the enamide to yield 2-acylamino ketone promoted the Robinson–Gabriel cyclization of the latter. This procedure afforded imidazoles **14** in moderate to good yields in a one-pot manner starting from triazoles (Scheme 11).<sup>17</sup>



Scheme 11 One-pot synthesis of 2-fluoroalkyl-imidazoles from NH-1,2,3-triazoles.



Scheme 12 Synthesis of 3-fluoroalkyl-1,2,4-triazines from NH-1,2,3-triazoles.



Alternatively, condensation of the formed acyloxyenamide **8'** with hydrazine hydrate after switching the solvent to acetic acid provided fluoroalkylated 1,2,4-triazines **15** (Scheme 12).<sup>17</sup>

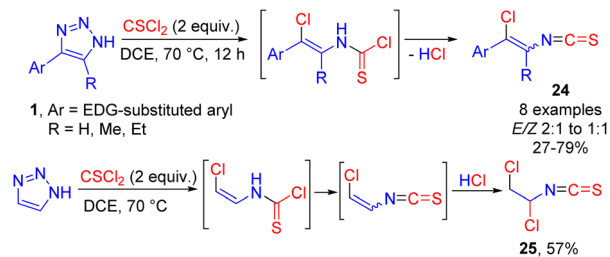
The formation of the vinyl cation intermediate in *N*-acyl-triazole cleavage was confirmed by changing the solvent from a chlorinated one to acetonitrile or propionitrile.<sup>18</sup> In one special case (Scheme 13, R = *p*-Tol) adducts **16** of the Ritter reaction were formed and hydrolysed to bis(enamides) **17**. However, this reaction was not general and in the cases of electron-rich triazoles, cyclization of the vinyl cation to oxazoles **7** took place (Scheme 13, R = H, EDG). This route is an alternative to one mentioned above (Scheme 10), and is applicable to electron-rich substrates. The straightforward formation of oxazoles **7** rather than enamides **8'** in polar MeCN was explained by the decreased stability of the vinyl cation–trifluoroacetate anion contact ion pair, which prevented recombination and favoured cyclization.<sup>18</sup>

Several efficient NH-1,2,3-triazole ring cleavage protocols were also developed for NH-benzotriazole **18**, which can be easily and regioselectively acylated on N1. The treatment of the formed *N*-acylbenzotriazole **20** with AlCl<sub>3</sub> as a Lewis acid promoter facilitated ring cleavage leading to benzoxazoles under relatively harsh conditions (Scheme 14).<sup>19</sup>

Rare examples of *ortho*-iodoacetanilide **22** formation in moderate yields from NH- and related *N*-acylbenzotriazole were reported in which the AlI<sub>3</sub>/Ac<sub>2</sub>O system or aluminium and iodine in acetonitrile were used.<sup>20</sup> These are the only cases of *N*-acetylbenzotriazole **23** ring cleavage known. Importantly, the reaction of *N*-acetylbenzotriazole **23** with AlCl<sub>3</sub> was not efficient



Scheme 15 Formation of *o*-iodoacetanilide by AlI<sub>3</sub>-mediated cleavage of N1-acetylbenzotriazole.



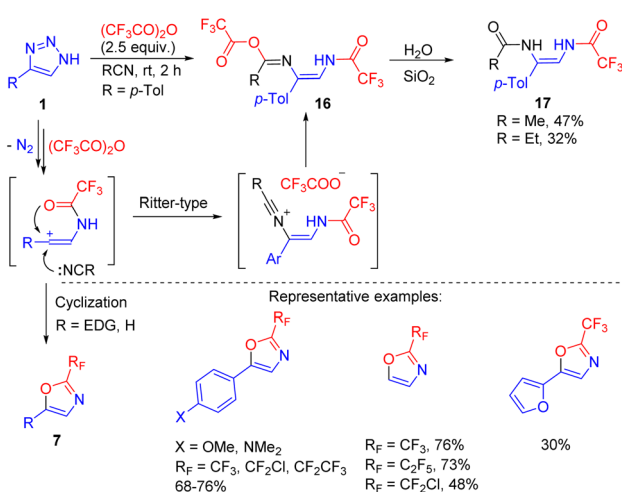
Scheme 16 Cleavage of NH-1,2,3-triazoles with thiophosgene.

and led only to deacylation, and not to the desired ring cleavage product (Scheme 15).<sup>19</sup>

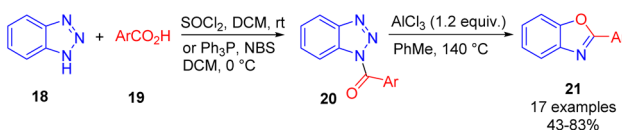
Cleavage of electron-rich 4-aryl-NH-1,2,3-triazoles **1** was successfully achieved with thiophosgene leading to the formation of vinyl isothiocyanates **24** by HCl elimination from the vinyl chloride intermediate (Scheme 16).<sup>21</sup> The vinyl isothiocyanate moiety is present in natural products with anti-fungal and antibacterial activity and is difficult to access by traditional methods. Switching from electron-rich aromatic NH-triazoles to unsubstituted NH-1,2,3-triazole afforded product **25** of HCl addition across the double bond in moderate yield.

A similar transformation with triazoles **1** bearing an electron-rich aryl or alkenyl substituent in position 4 proceeded with triphosgene.<sup>21</sup> The *in situ* formed carbamoyl chlorides **26** were treated with nucleophiles to gain access to multifunctional compounds **27**, such as *N*-alkenyl carbamates, ureas and thio-carbamates (Scheme 17).

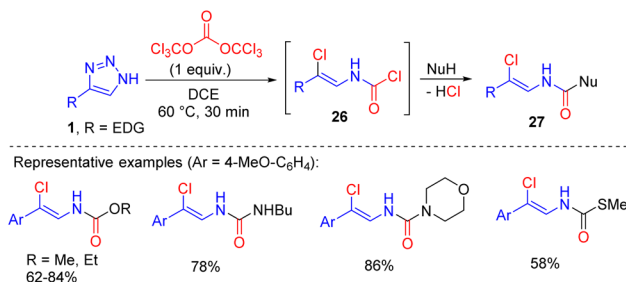
The denitrogenative transformation of NH-1,2,3-triazoles was studied also on more complex substrates such as 4-(1-hydroxycyclobutyl)-1,2,3-triazoles **28**. Their cleavage with acyl chlorides **10** catalysed by triflic acid provided efficient access to cyclic enamines **29** (Scheme 18).<sup>22</sup> The reaction proceeded *via* the cleavage of *N*-acyltriazole and semipinacol rearrangement



Scheme 13 Formation of bis(enamides) **17** and oxazoles **7** by the cleavage of NH-1,2,3-triazoles with trifluoroacetic anhydride in nitrile solvent.



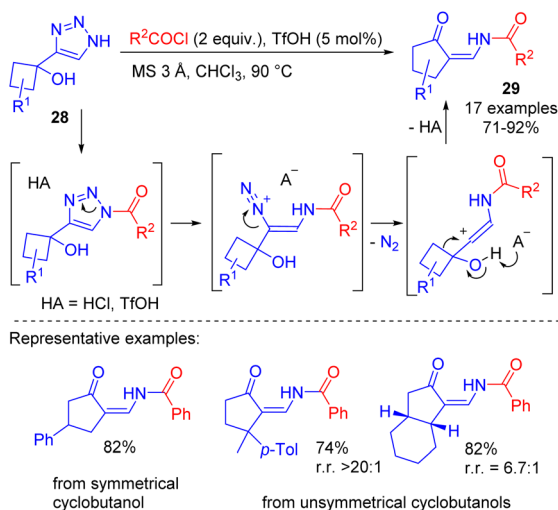
Scheme 14 Synthesis of benzoxazoles from NH-benzotriazoles.



Scheme 17 Synthesis of multifunctional *N*-alkenyl compounds by the cleavage of NH-1,2,3-triazoles with triphosgene.







**Scheme 18** Synthesis of cyclic enaminones by TfOH-catalyzed cleavage of 4-(1-hydroxycyclobutyl)-1,2,3-triazoles with acyl chlorides.

cascade. The procedure was found to be easily scalable to give multifunctional substrates in good yields.

## Conclusions

In conclusion, NH-1,2,3-triazoles are commercially available or easily synthesized starting materials that exhibit a remarkable versatility in transformations to diverse nitrogen-containing heterocycles and functionalized *N*-alkenyl compounds *via* denitrogenative cleavage. *In situ* prepared *N*-acylated 1,2,3-triazoles are key intermediates in these transformations. Acid-mediated triazole ring opening of *N*-acylated 1,2,3-triazoles, followed by nitrogen elimination affords vinyl cation intermediates, which undergo a variety of reactions such as cyclization or heteroatom capture. Further development of denitrogenation of NH-1,2,3-triazoles accompanied by C–C bond forming reactions, C–H insertion or rearrangement of the vinyl cation can be expected, providing access to a structural diversity of products with potential applications in drug development. Moreover, due to easy availability of NH-1,2,3-triazoles they are excellent starting materials for the development of new industrial synthetic processes.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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