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Triazabicyclodecene as an Organocatalyst for Regiospecific Synthesis of 1,4,5-Trisubstituted *N*-Vinyl-1,2,3-Triazoles

Dhevalapally B. Ramachary,* Jagjeet Gujral, Swamy Peraka, and G. Surendra Reddy

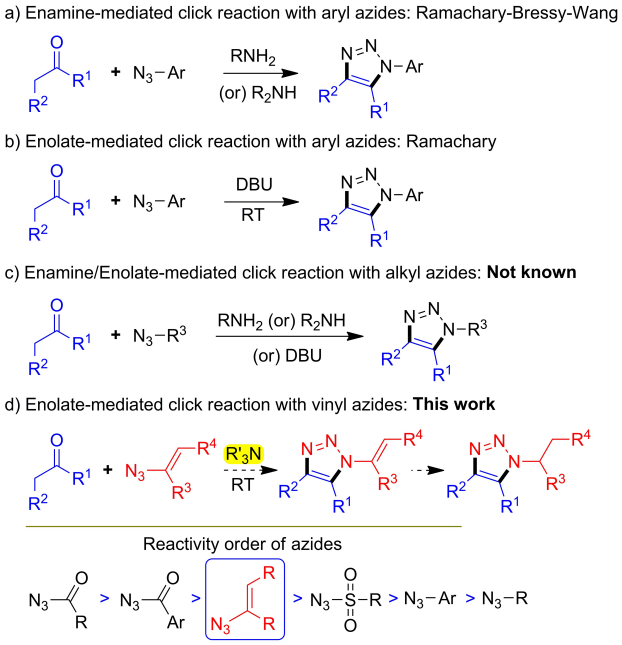
Abstract: Herein, we have reported the TBD-catalyzed enolate-mediated regiospecific synthesis of 1,4,5-trisubstituted *N*-vinyl-1,2,3-triazoles from simple activated carbonyls and *N*-vinyl azides via [3+2]-cycloaddition, which on further hydrogenation furnished the 1,4,5-trisubstituted *N*-alkyl-1,2,3-triazoles. Both organo-click and hydrogenation reactions proceeded in excellent yields with high rate and selectivity within few hours at 25 °C.

1,2,3-Triazoles have emerged as a core of considerable interest for chemists/biologists in the past few decades. This interest stems from their wide applicability in the fields of medicinal, organic, polymer and material chemistry.[1] 1,2,3-Triazoles are also capable of playing an important role as "amide isosteres" due to their bio-similarity with amide bonds in properties like relative planarity, dipole moment and amphihydrogen-bonding capability.[2] Considering these applications, high-yielding selective synthesis of variety of functionalized 1,2,3-triazoles becomes a challenge for synthetic chemists.

With the advent of the concept of "click chemistry" there has been an explosion in the number of reactions leading to the synthesis of functionalized 1,2,3-triazoles beginning from the copper-catalysed click reaction reported by Sharpless.[3] Amino acid- or amine-catalysed [3+2]-cycloaddition entering into this field has given rise to an "organocatalytic click strategy" for the synthesis of substituted 1,2,3-triazoles,[4-6] which has proved itself at par and in many cases ahead of similar metal mediated transformations in terms of atom-economy and selectivity (eq. a, Scheme 1).[4-6]

The realm of organocatalytic 1,2,3-triazole synthesis initiated by our group in 2008 was further enriched by the groups of Pons-Bressy, Wang, Dehaen, Paixão, Alves, Li and many other groups. In early years, this field witnessed a surge in enamine-mediated 1,2,3-triazole formation from different carbonyl compounds like enones, *β*-ketoesters, ketones and enals with tosyl/aryl azides.[4] In the year 2014, an approach complimentary to the enamine based strategy, an enolate-mediated functionally rich 1,2,3-triazole formation was reported by our group (eq. b, Scheme 1).[5a,b,g,h,l]

In all the previous organocatalytic reports, though a wide range of activated carbonyls substrates have been employed for the 1,2,3-triazole synthesis, the variability of the reacting partner azide has been limited to simple aryl azides and tosyl azide. Present work is an attempt to extend the scope of the azide partner beyond the aryl azides traditionally used in such reactions (Scheme 1). In our search for expanding suitable azide partner, thermal stability versus reactivity of azides was taken as a guiding light (Scheme 1).



Scheme 1: Previous work and present reaction design.

Till now these organocatalytic [3+2]-cycloadditions have been limited to thermally stable aryl azides [decomposition temperature 140-170 °C]. Moving towards the thermally less stable azides, the observance of the interplay between reactivity and stability is a worthy goal to pursue. Step towards our vision was initiated by choosing substituted vinyl azides as the click partners (eq. d, Scheme 1).[7a] Rationale for this choice has been the fact that vinyl azides are of medium thermal stability [decomposition temperature 60-70 °C] and are more reactive towards such transformations than tosyl, aryl or alkyl azides as shown in Scheme 1. Respective vinyl substituted 1,2,3-triazoles could also occupy major role in medicinal to material chemistry. According to the earlier reports,[7b-c,4f] the physicochemical or electronic factors which need to be considered for reactivity were the existence of more number of dipolar mesomeric or resonance structures from the azido moiety with attached group and it has been shown that more the number of dipolar mesomeric or resonance structures more is the reactivity of the azide partner. Due to this double-bond character between N^1-N^2 in R-N^1-N^2≡N^3 is decreased by introducing an acyl, ester or sulfonyl group in conjugation with the triazo group. Therefore acyl or sulfonyl azides are less stable than alkyl/aryl azides. This factor renders aliphatic azides though

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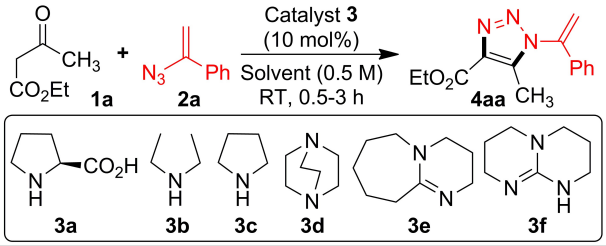
Supporting information (experimental procedures and analytical data for all new compounds) for this article is given via a link at the end of the document.

thermally highly stable, less reactive in these [3+2]-cycloaddition reactions. A fine balance of electronic and thermal factors is achieved in choosing vinyl azides as click partners. If such a transformation could be achieved this would be a very simple way of introducing an olefinic functionality directly into the 1,2,3-triazole moiety of which previous reports have been scarce.[8]

Table 1: Reaction optimization.[a]

[a] Reactions were carried out in solvent (0.5 M) with 1.5 equiv. of **2a** relative to



Entry	Catalyst **3**	Solvent	*t* [h]	Yield **4aa** [%][b]
1	**3a**	DMSO	24	–
2	**3b**	DMSO	3.0	35
3[c]	**3c**	DMSO	3.0	–
4	**3d**	DMSO	3.0	–
5	**3e**	DMSO	3.0	88
6	**3e**	DMF	3.0	85
7	**3e**	$CHCl_3$	3.0	11
8	**3e**	CH_3CN	3.0	37
9	**3f**	DMSO	3.0	98
10	K_2CO_3 **3g**	DMSO	1.5	83
11	*t*BuOK **3h**	DMSO	1.5	84
12	–	DMSO	24	–

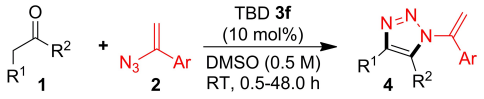
the **1a** (0.5 mmol) in the presence of 10-mol% of catalyst **3**. [b] Yield refers to the column-purified product. [c] Ethyl acetoacetate **1a** was consumed totally.

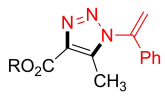
We optimized the designed organo-click reaction by screening simple organocatalysts for the [3+2]-cycloaddition of ethyl acetoacetate **1a** with 1.5 equiv. of α-azidostyrene **2a** under ambient conditions (Table 1). The reaction of **1a** with 1.5 equiv. of α-azidostyrene **2a** in DMSO under 10-mol% of proline **3a**-catalysis did not furnished the expected product **4aa** even after 24 h at 25 °C (Table 1, entry 1). The same reaction under 10-mol% of diethyl amine **3b**-catalysis furnished the 1-vinyl-1*H*-1,2,3-triazole **4aa** in only 35% yield with complete consumption of starting materials (Table 1, entry 2). The click reaction of **1a** with 1.5 equiv. of **2a** in DMSO under 10-mol% of pyrrolidine **3c**-catalysis did not furnished the expected product **4aa**; but ethyl acetoacetate **1a** is consumed totally (Table 1, entry 3). After obtaining discouraging results with the catalysts **3a-c** through enamine-mediated reaction,[4] we thought of investigating the click reaction through the in situ enolate formation,[5] for which we tested some *tert*-amines **3d-f** and base **3g-h** as the catalysts for the organo-click reaction. Organo-click reaction of **1a** with **2a** under 1,4-diazabicyclo[2.2.2]octane (DABCO) **3d**-catalysis didn't furnish the expected product **4aa** (Table 1, entry 4). Intriguingly, the reaction of **1a** with 1.5 equiv. of **2a** in DMSO under 10-mol% of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) **3e**-catalysis at 25 °C for 3.0 h furnished **4aa** in 88% yield (Table 1, entry 5). Deviating from this condition, by switching the solvent to DMF, $CHCl_3$ or CH_3CN by using 10-mol% of DBU **3e** as the catalyst was not so successful in promoting the high-yielding click reaction (Table 1, entries 6, 7, and 8).[5l] These solvent studies clearly support our hypothesis of involvement of reactive enolate formation and their stability. With these moderate results, we thought of using a strong organic base, the commercially available guanidine 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD) **3f** as the catalyst for [3+2]-cycloaddition. Because, the p*K*a value of the conjugate acid of TBD **3f** in acetonitrile is close to 26 and also TBD **3f** has been applied as a suitable catalyst for a variety of reactions, including Michael, Wittig, Henry, Strecker, transesterification and acyl transfer reactions.[9] Fascinatingly, the click reaction of **1a** with 1.5 equiv. of **2a** in DMSO under 10-mol% of TBD **3f**-catalysis at 25 °C for 3.0 h furnished the 1-vinyl-1*H*-1,2,3-triazole **4aa** in 98% yield (Table 1, entry 9). Relatively less basic *tert*-amines like DABCO [p*K*a 8.8] **3d**, and DBU [p*K*a 12.0] **3e** catalysts furnished the 1-vinyl-1*H*-1,2,3-triazole **4aa** with poor to good yields compared to TBD [p*K*a 26.0] **3f** (Table 1, entries 4 to 9), also no reaction was observed without the catalyst in DMSO for 24 h at 25 °C (Table 1, entry 12). The same click reaction under 10-mol% of non-amine bases K_2CO_3 [p*K*a 10.33] **3g** and *t*BuOK [p*K*a 29.4] **3h**-catalysis also furnished the 1-vinyl-1*H*-1,2,3-triazole **4aa** in good yields within 1.5 h at 25 °C; but which is inferior to TBD **3f**-catalysis (Table 1, entries 10-11). We finally envisioned the optimized condition to be 25 °C in DMSO under 10-mol% of TBD **3f**-catalysis which furnished the 1-vinyl-1*H*-1,2,3-triazole **4aa** in 98% yield from **1a** and **2a** (Table 1,entry 9).

With the best conditions in hand, the wider scope and the generality of the novel TBD-catalysed click reactions were investigated. A variety of functionalized activated carbonyls such as alkyl acetoacetates **1b-e**, ethyl 3-oxo-3-alkyl/aryl-propanoates **1f-k**, alkyl/aryl substituted 1,3-diketones **1l-o**, 3-oxo-3-alkyl/aryl-propanenitriles **1p-r**, chiral *N*-alkyl-3-oxo-3-phenylpropanamide **1s** and chiral alkyl 3-oxo-3-phenylpropanoate **1t** were reacted with substituted α-azidostyrenes **2a-g**, or ((2-azidoallyl)oxy)benzenes **2h-i** catalysed by 10-mol% of TBD **3f** at 25 °C in DMSO for 0.5-48 h as shown in Table 2. Interestingly, the click reaction of alkyl acetoacetates **1b-e** containing different alkyl groups like methyl, allyl, propargyl, and benzyl with α-azidostyrene **2a** under **3f**-catalysis furnished the expected 1-vinyl-1*H*-1,2,3-triazoles **4ba-ea** in excellent to good yields within 1.0-3.0 h (Table 2). In a similar manner, the TBD **3f**-catalyzed click reaction of **2a** with ethyl 3-oxo-3-alkyl/aryl-propanoates **1f-k** containing ethyl, *n*-propyl, trifluoromethyl, phenyl, 4-nitrophenyl and 4-methoxyphenyl furnished the expected functionalized 1-vinyl-1*H*-1,2,3-triazoles **4fa-ka** in excellent to moderate yields from 2.5-48.0 h (Table 2). Yields of the 1-vinyl-1*H*-1,2,3-triazole products **4fa-ga** were sustained with 93-94%, but the yields slightly decreased by increasing the reaction time with electron withdrawing groups such as trifluoromethyl, phenyl, 4-nitrophenyl and 4-methoxyphenyl compared to methyl group (Table 2). For example, instead of 10 mol% of TBD **3f**, 1.2 equiv. of DBU-catalysed click reaction of the ethyl 4,4,4-trifluoro-3-oxobutanoate **1h** with **2a** in DMSO at 25 °C for 48 h furnished the 1,2,3-triazole **4ha** in only 50% yield (Table 2). Click reaction of symmetric 1,3-diketones like pentane-2,4-dione **1l** and 1,3-diphenylpropane-1,3-dione **1m** with **2a** under 10-mol% of **3f**-catalysis furnished the selective products **4la** in 77% yield in 2.0 h and **4ma** in 70% yield in 7.0 h, respectively (Table 2).

Table 2: Substrate scope.[a]

[a] Reactions were carried out in DMSO (0.5 M) with 1.5 equiv. of **2** relative to the **1** (0.5 mmol) in the presence of 10-mol% of **3f** and yield refers to the



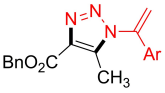


4ba: R = Me (2.5 h; 92%)
4ca: R = allyl (3.0 h; 82%)
4da: R = propargyl (1.5 h; 97%)
4ea: R = benzyl (1.0 h; 92%)

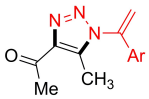
4fa: R = CH_3CH_2 (2.5 h; 94%)
4ga: R = $CH_3CH_2CH_2$ (3.0 h; 93%)
4ha: R = CF_3 (48 h; 50%)[b]
4ia: R = Ph (7.0 h; 82%)
4ja: R = 4-$NO_2C_6H_4$ (16.0 h; 90%)
4ka: R = 4-$OMeC_6H_4$ (8.0 h; 70%)

4la: R^1 = Ac, R^2 = Me (2.0 h; 77%)
4ma: R^1 = Bz, R^2 = Ph (7.0 h; 70%)
4na: R^1 = Ac, R^2 = Ph (32%) +
4'na: R^1 = Bz, R^2 = Me (21%); *t* (7.0 h)
4oa: R^1 = 3,4,5-$(OMe)_3C_6H_2CO$, R^2 = Ph (21%) +
4'oa: R^1 = Bz, R^2 = 3,4,5-$(OMe)_3C_6H_2$ (21%); *t* (5.5 h)

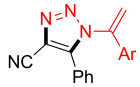
4pa: R = Ph (7.0 h; 82%)
4qa: R = 4-MeC_6H_4 (7.0 h; 87%)
4ra: R = *t*-Bu (7.5 h; 70%)



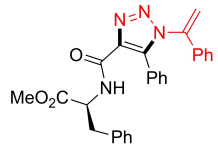
4eb: Ar = 4-FC_6H_4 (1.0 h; 96%)
4ec: Ar = 4-ClC_6H_4 (1.5 h; 90%)
4ed: Ar = 4-MeC_6H_4 (4.0 h; 80%)[c]
4ee: Ar = 2-MeC_6H_4 (2.0 h; 82%)[c]
4ef: Ar = 4-$OMeC_6H_4$ (5.0 h; 30%)[c]
4eg: Ar = 2-naphthyl (4.0 h; 80%)
4eh: Ar = 4-$PhC_6H_4OCH_2$ (0.85 h; 85%)
4ai: Ar = 4-$NO_2C_6H_4OCH_2$ (0.75 h; 90%)[d]



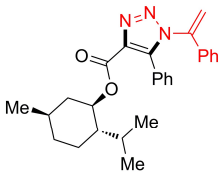
4lb: Ar = 4-FC_6H_4 (0.5 h; 91%)
4lc: Ar = 4-ClC_6H_4 (0.5 h; 90%)



4pb: Ar = 4-FC_6H_4 (4.0 h; 90%)
4pc: Ar = 4-ClC_6H_4 (4.0 h; 85%)



(+)-**4sa:** *t* (12 h); 87%



(–)-**4ta:** *t* (3 h); 80%

column-purified product. [b] 1.2 equiv. of DBU **3e** was used as catalyst. [c] Reaction performed in neat with 30 mol% of **3f**. [d] Ethyl acetoacetate **1a** was used.

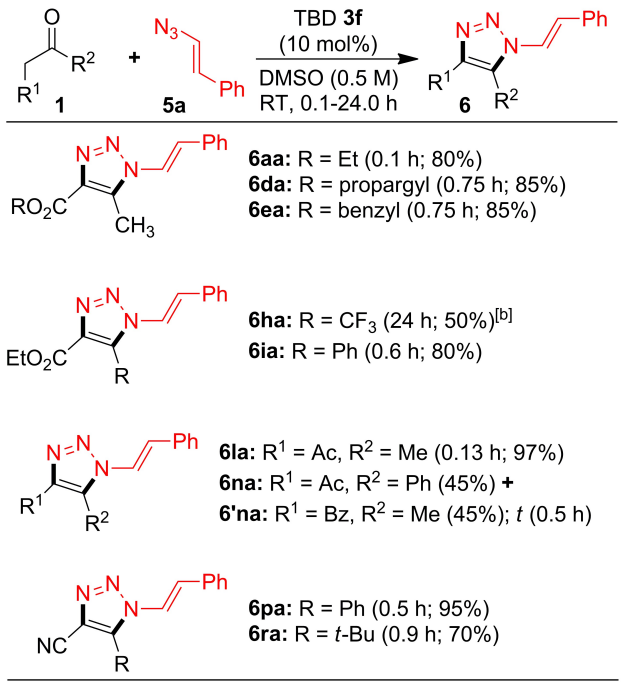
Surprisingly, click reaction of non-symmetrical 1,3-diketones like 1-phenylbutane-1,3-dione **1n** with **2a** under 10-mol% of **3f**-catalysis furnished a mixture of two products **4na** in 32% yield and **4'na** in 21% yield in 7.0 h (Table 2). Similarly, reaction of 1-phenyl-3-(3,4,5-trimethoxyphenyl)propane-1,3-dione **1o** with **2a** under 10-mol% of **3f**-catalysis furnished a mixture of two products **4oa** in 21% yield and **4'oa** in 21% yield in 5.5 h (Table 2). Interestingly, the click reaction of 3-oxo-3-phenylpropanenitrile **1p** with **2a** under 10-mol% of **3f**-catalysis for 7.0 h furnished **4pa** in 82% yield (Table 2). The **3f**-catalyzed organo-click reaction of **2a** with other two β-ketonitriles of 3-oxo-3-(*p*-tolyl)propanenitrile **1q** and 4,4-dimethyl-3-oxopentanenitrile **1r** furnished the expected products **4qa** in 87% yield and **4ra** in 70% yield, respectively (Table 2).

After clear understanding of the electronic factors of activated carbonyls **1** in the [3+2]-cycloaddition reaction, we investigated the reaction scope with different α-azidostyrenes and α-azido olefins **2b-i** with **1e** or **1a** in the presence of catalytic amount of TBD **3f** at 25 °C (Table 2). In this reaction, α-azidostyrenes **2b-f** containing different functional groups of 4-F, 4-Cl, 4-CH_3, 2-CH_3 and 4-OCH_3 were used as substrates along with **1e** for the organocatalytic click synthesis of the single isomer of 1,2,3-triazoles **4eb-ef** in excellent to good yields within 1.0-5.0 h (Table 2). Surprisingly, click reaction of α-azidostyrenes **2d-f** containing 4-CH_3, 2-CH_3 and 4-OCH_3 with **1e** under the standard conditions [10-mol% **3f** in DMSO at 25 °C] furnished the products **4ed-ef** in moderate to poor yields, but the same reaction under 30-mol% of **3f** in neat furnished the expected products **4ed-ef** in good yields (Table 2). Organo-click reaction of **1e** with 2-(1-azidovinyl)naphthalene **2g** under **3f**-catalysis at 25 °C for 4.0 h furnished the expected product **4eg** in 80% yield. With applications in mind, we performed the organo-click reaction of **1a** or **1e** with simple aliphatic α-azido olefins **2h-i** to furnish the expected click products in very good yields within 0.85 h as shown in Table 2. To test the generality of this methodology, we performed few more click reactions by using α-azidostyrenes **2b-c** containing 4-F and 4-Cl with activated carbonyls of pentane-2,4-dione **1l** and 3-oxo-3-phenylpropanenitrile **1p** to furnish the click products **4lb**, **4lc**, **4pb** and **4pc** in very good yields as shown in Table 2. With preparation of chiral functionalized 1-vinyl-1*H*-1,2,3-triazoles in mind, we performed the click reaction of (*S*)-methyl 2-(3-oxo-3-phenylpropanamido)-3-phenylpropanoate **1s** and (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-oxo-3-phenylpropanoate **1t** with **2a** under **3f**-catalysis to furnish the chiral click products (+)-**4sa** in 87% and (-)-**4ta** in 80% yield, respectively (Table 2). The results furnished in the Table 2 demonstrate the broad scope of this novel methodology covering a structurally diverse group of activated carbonyls **1a-t** and α-azidostyrenes/α-azido-olefins **2a-i**. The structure and regiochemistry of the click products **4** were established through NMR analysis and also finally confirmed by the X-ray structure analysis on **4ia** (Figure S1, see the Supporting Information).[10]

To further understand the electronic nature of azidostyrenes in the organo-click reaction, we have chosen simple (*E*)-β-azidostyrene **5a**, which is having linear conjugation (Table 3). Surprisingly, the click reaction of ethyl acetoacetate **1a** with (*E*)-β-azidostyrene **5a** under TBD **3f**-catalysis at 25 °C within 0.1 h furnished the expected 1-styryl-1*H*-1,2,3-triazole **6aa** in 80% yield (Table 3, entry 1). Likewise, the click reaction of propargyl acetoacetate **1d** and benzyl acetoacetate **1e** with (*E*)-β-azidostyrene **5a** under TBD **3f**-catalysis furnished the 1-styryl-1*H*-1,2,3-triazoles **6da** and **6ea** in 85% yield within 0.75 h, respectively (Table 3, entries 2 and 3). We have also tested six more examples of functionalized activated carbonyls **1h-r** for the organo-click reaction with (*E*)-β-azidostyrene **5a**, which furnished the expected substituted 1-styryl-1*H*-1,2,3-triazoles **6ha-6ra** in good to excellent yields (Table 3, entries 4-9). Key point to mention here in all the above nine click reactions is that the reaction rates are very high with shorter times compared to α-azidostyrene **2a**. The observed high reactivity of **5a** compared to **2a** in the [3+2]-cycloaddition is mainly due to their differences in conjugation like linear versus cross; because polarizability in **5a** is

more compared to **2a**, which is inducing the quick reaction with in situ generated enolates.

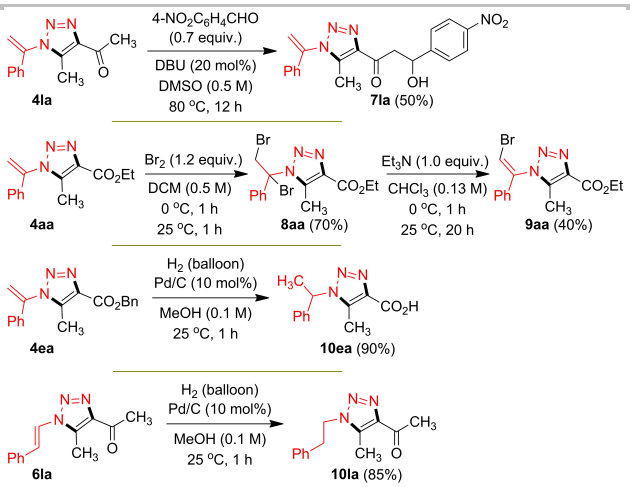
Table 3: Vinyl azide scope.[a]



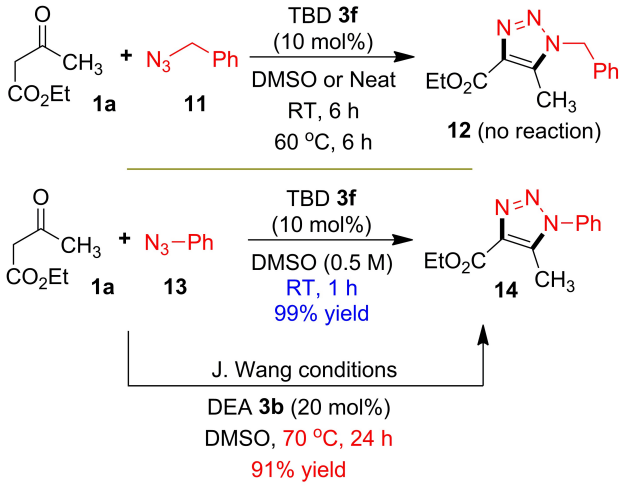
[a] Reactions were carried out in DMSO (0.5 M) with 1.5 equiv. of **5a** relative to the **1** (0.5 mmol) in the presence of 10-mol% of **3f** and yield refers to the column-purified product. [b] 1.2 equiv. of DBU **3e** was used as catalyst.

The versatility of the organo-click reaction was further exemplified by synthesizing a few useful compounds **7la**, **8aa**, **9aa**, **10ea** and **10la** (Scheme 2). We explored the utilization of **4** bearing 1,2,3-triazole-Ac in the synthesis of aldol product **7** *via* enolate-mediated aldol reaction (Scheme 2). Direct DBU-catalysed aldol reaction of 1-(5-methyl-1-(1-phenylvinyl)-1*H*-1,2,3-triazol-4-yl)ethanone **4la** with 0.7 equiv. of 4-nitrobenzaldehyde in DMSO at 80 °C for 12 h furnished the aldol product **7la** in 50% yield (Scheme 2). Aldol products containing the 1,2,3-triazole ring will be promising probes to study the medicinal and material properties.[2] As shown in Scheme 2, ethyl 1-(1,2-dibromo-1-phenylethyl)-5-methyl-1*H*-1,2,3-triazole-4-carboxylate **8aa** was synthesized in good yield from the treatment of 1.2 equiv. of bromine with 1-vinyl-1*H*-1,2,3-triazole **4aa** in DCM at 0-25 °C for 2 h; which on further treatment with 1.0 equiv. of triethylamine in $CHCl_3$ at 0-25 °C for 21 h furnished the synthetically useful triazole-based vinylbromide **9aa** in 40% yield along with fully debrominated product **4aa** in 40% yield through elimination of bromine (Scheme 2). Further, we synthesized the *N*-alkyl substituted 1,2,3-triazoles **10ea** and **10la** through hydrogenation reaction of fully substituted 1-vinyl-1*H*-1,2,3-triazole **4ea** and 1-styryl-1*H*-1,2,3-triazole **6la** using hydrogen balloon under 10-mol% of Pd/C in methanol at 25 °C for 1 h. In a single step, compound of 5-methyl-1-(1-phenylethyl)-1*H*-1,2,3-triazole-4-carboxylic acid **10ea** was isolated in 90% yield and 1-(5-methyl-1-phenethyl-1*H*-1,2,3-triazol-4-yl)ethanone **10la** was isolated in 85% yield (Scheme 2). These results highlights advantages of the organo-click reactions, which enables a quick synthesis of *N*-alkyl substituted 1,2,3-triazoles.

Scheme 2: Reaction application.



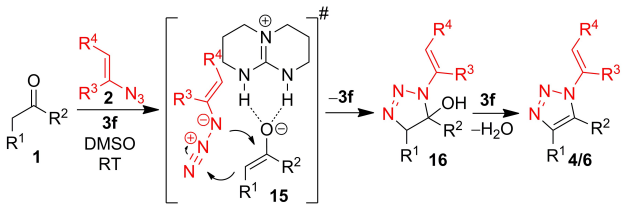
In order to further extend the understanding of catalytic power of TBD **3f** and also electronic nature of vinyl-azides **2/5**, we have done a few controlled experiments as shown in Scheme 3. Surprisingly, there is no triazole **12** formation from the reaction of ethyl acetoacetate **1a** with benzyl azide **11** under TBD **3f**-catalysis at 25 to 60 °C even after 12 h (Scheme 3). At the same time, the click reaction of ethyl acetoacetate **1a** with phenyl azide **13** under TBD **3f**-catalysis in DMSO at 25 °C within 1.0 h furnished the single isomer of 1,2,3-triazole **14** in 99% yield (Scheme 3). The same product **14** was synthesised by Wang et al in 91% yield under enamine-catalysis by using 20 mol% of diethyl amine **3b** in DMSO at 70 °C in 24 h,[4c] which is rationally inferior to the present enolate-catalysis. Many of the products **4/6** yields/selectivity obtained were excellent through enolate-intermediate compared to the previous methods and vinyl-azides reactivity towards enolates was similar to the aryl azides than aliphatic azides.



Scheme 3: Controlled experiments.

The mechanism for the selective synthesis of **4/6** through the reaction of **1**, **2/5** and **3f** is illustrated in Scheme 4.[5l] Reaction of the catalyst TBD **3f** (pK_a = 26.03 in CH_3CN) with activated carbonyls **1** generates the enolate **15**, which on in situ treatment with reactive vinyl-N_3 **2/5** furnishes selectively the functionalized 1,2,3-triazolines **16** via concerted [3+2]-cycloaddition or stepwise amination-cyclization reaction, which further transforms into the

stable 1,2,3-triazole **4/6** through rapid elimination of water induced by the basic nature of **3f**.



Scheme 4: Reaction mechanism.

In summary, for the first time we have developed the TBD-catalyzed regiospecific synthesis of 1,4,5-trisubstituted *N*-vinyl-1,2,3-triazoles **4/6** from simple activated carbonyls **1** and *N*-vinyl azides **2/5** via [3+2]-cycloaddition reaction. The click reaction proceeds in excellent yields with high rate and selectivity using TBD **3f** as the organocatalyst within a few hours at 25 °C. Further work is in progress to develop the application of these products in medicinal to material chemistry.

Experimental Section

Experimental procedures, and compound characterization data (^{1}H NMR, ^{13}C NMR, and HRMS). This material is available free of charge in the Supporting Information.

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[10] CCDC-1505414 (**4ia**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Entry for the Table of Contents

N-Vinyl-1,2,3-Triazoles (OR) Organocatalytic Click Reactions

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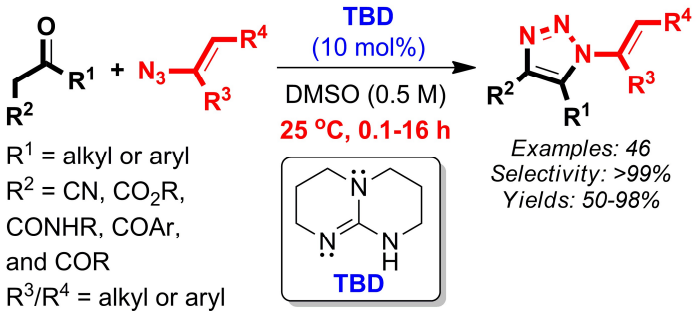
Triazabicyclodecene as an Organocatalyst for Regiospecific Synthesis of 1,4,5-Trisubstituted *N*-Vinyl-1,2,3-Triazoles



Simple organocatalyst, TBD-catalysed an enolate-mediated vinyl azide–carbonyl [3+2]-cycloaddition of various activated carbonyls with vinyl azides to furnish the functionally rich *N*-vinyl-1,2,3-triazoles.