Advanced Synthesis & Catalysis

DOI: 10.1002/adsc.201300863

# Copper-Catalyzed Oxidative Transformation of Secondary Alcohols to 1,5-Disubstituted Tetrazoles

Balaji V. Rokade,[a] Karthik Gadde,[a] and Kandikere Ramaiah Prabhu[a,*]

[a] Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, Karnataka, India
Fax: (+91)-80-2360-0529; e-mail: prabhu@orgchem.iisc.ernet.in

Received: September 24, 2013; Revised: December 13, 2013; Published online: ■■ ■■, 0000

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201300863.

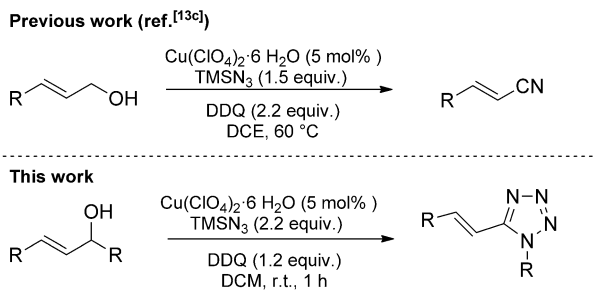
**Abstract:** A mild and convenient oxidative transformation of secondary alcohols to 1,5-disubstituted tetrazoles is uncovered by employing trimethylsilyl azide ($TMSN_3$) as a nitrogen source in the presence of a catalytic amount of copper(II) perchlorate hexahydrate [$Cu(ClO_4)_2{\cdot}6H_2O$] (5 mol%) and 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (DDQ) (1.2 equiv.) as an oxidant. This reaction is performed under ambient conditions and proceeds through C–C bond cleavage.

**Keywords:** alcohols; azides; copper; regioselectivity; tetrazoles

Metal-mediated transformations are useful and indispensable strategies for C–C and C–heteroatom bond forming reactions in organic synthesis.[1] In addition, C–N bond forming strategies are not only challenging but have a great impetus as they provide avenues for the synthesis of biologically active and therapeutically useful heterocycles.[2] Among the heterocyles, tetrazole and its derivatives form a vital class of nitrogen-containing molecules[3] due to their well-known biological activities[4] as well as vast applications in pharmaceuticals[5a] and material sciences.[5c] Traditionally, 1,5-disubstituted tetrazoles are prepared by (i) the reaction of nitriles with alkyl or aromatic azides,[6] (ii) the reaction of ketones[7] or oximes[8] with sodium azide or hydrazoic acid and (iii) the reaction of amides[9] with sodium azide in the presence of $PCl_5$ or triflic anhydride, etc. Gold-catalyzed synthesis of tetrazoles using alkynes has been recently reported by Echavarren and Gaydou.[10] Recently, Jiao and coworkers developed a method to synthesize 1,5-disubstituted tetrazoles using 1,3-diphenylpropene,[11] which requires precursors that are relatively difficult to access and require multistep synthetic sequences.[12] Additionally, this protocol uses a large excess of $TMSN_3$ (5.5 equiv.), harsh reaction conditions (80 °C), and requires additives and long reaction times.

In continuation of our investigations on the utility of azides in C–N bond forming reactions, especially leading to the formation of nitriles,[13] and in the light of Jiao's work,[11] we anticipated that secondary alcohols in the presence of a Cu salt, an excess of trimethylsilyl azide ($TMSN_3$) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), may form the corresponding azide *in situ* and then undergo a rearrangement to form the nitrilium ion, which may be trapped in a [2+3] cycloaddition fashion by the excess azide present in the reaction medium (Scheme 1). Herein, we present our detailed investigation for converting secondary alcohols directly to 1,5-disubstituted tetrazoles in a one-pot fashion under ambient conditions.

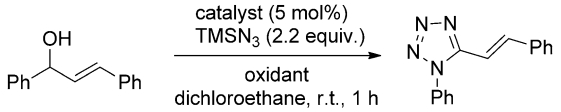
We began our study by investigating the Cu-catalyzed reaction of (*E*)-1,3-diphenylprop-2-en-1-ol **1a** with $TMSN_3$ as a nitrogen source and DDQ as an oxidant (Table 1). Preliminary studies were carried out using Cu(I) and Cu(II) salts such as CuCl, CuBr, CuI, $Cu(OAc)_2{\cdot}H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$ and $Cu(OTf)_2$. Among these copper reagents, $Cu(ClO_4)_2{\cdot}6H_2O$ and $Cu(OTf)_2$ were found to be effective catalysts, as the reactions of **1a** and $TMSN_3$ in the presence of catalytic amount of $Cu(ClO_4)_2{\cdot}6H_2O$ or $Cu(OTf)_2$ furnished the expected product (*E*)-1-phenyl-5-styryl-1*H*-tetrazole **2a** in near quantitative yields (entries 5 and 6,




**Scheme 1.**

**Table 1.** Optimization studies.[a]




1a 2a

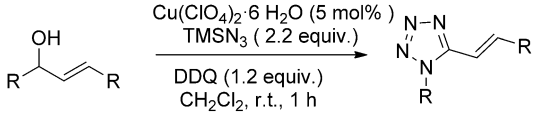
| Entry | Cu Catalyst | Oxidant (equiv.) | Yield [%][b] |
|---|---|---|---|
| 1 | CuCl | DDQ (2.2) | nd |
| 2 | CuBr | DDQ (2.2) | nd |
| 3 | CuI | DDQ (2.2) | nd |
| 4 | $Cu(OAc)_2 \cdot H_2O$ | DDQ (2.2) | nd |
| 5 | $Cu(ClO_4)_2 \cdot 6H_2O$ | DDQ (2.2) | 99 |
| 6 | $Cu(OTf)_2$ | DDQ (2.2) | 99 |
| 7 | no catalyst | DDQ (2.2) | nd |
| 8 | $Cu(ClO_4)_2 \cdot 6H_2O$ | no oxidant | nd |
| 9 | $Cu(ClO_4)_2 \cdot 6H_2O$ | DDQ (2.2) | nd[c] |
| 10 | $Cu(ClO_4)_2 \cdot 6H_2O$ | DDQ (1.5) | 99 |
| 11 | $Cu(ClO_4)_2 \cdot 6H_2O$ | DDQ (1.2) | 99 |
| 12 | $Cu(ClO_4)_2 \cdot 6H_2O$ | DDQ (1.2) | 78[d] |
| **13** | **$Cu(ClO_4)_2 \cdot 6H_2O$** | **DDQ (1.2)** | **99**[e] |
| 14 | $Cu(ClO_4)_2 \cdot 6H_2O$ | benzoquinone (1.2) | nd |
| 15 | $Cu(ClO_4)_2 \cdot 6H_2O$ | chloranil (1.2) | nd |
| 16 | $Cu(ClO_4)_2 \cdot 6H_2O$ | NaOCl (1.2) | nd |
| 17 | $Cu(ClO_4)_2 \cdot 6H_2O$ | TBHP in decane (1.2) | nd |
| 18 | $Cu(ClO_4)_2 \cdot 6H_2O$ | TBHP in water (1.2) | nd |
| 19 | CuI | DDQ (2) | nd[f] |

[a] *Reaction conditions:* **1a** (0.5 mmol), $TMSN_3$ (1.1 mmol), catalyst (0.025 mmol), oxidant, dichloroethane (2 mL) at room temperature for 1 h. nd = not detected.
[b] Isolated yield.
[c] $NaN_3$ used instead of $TMSN_3$.
[d] $CH_3CN$ used as a solvent.
[e] $CH_2Cl_2$ used as a solvent.
[f] Reaction conditions similar to those of ref.[11]

Table 1). The formation of the product tetrazole was not observed when the reaction was carried out either in the absence of $Cu(ClO_4)_2 \cdot 6H_2O$ or DDQ (entries 7 and 8, Table 1). Further studies pointed out that $NaN_3$ is not a suitable nitrogen source for this transformation as the reaction of alcohol **1a** with $NaN_3$ and DDQ did not furnish the product **2a** (entry 9, Table 1). Solvent screening studies revealed that solvents such as $CH_3CN$ and $CH_2Cl_2$ are most compatible solvents for the reaction (entries 12 and 13, Table 1). Other oxidants such as benzoquinone, chloranil, NaOCl and TBHP were found to be incompatible as these reactions did not yield the expected tetrazole **2a** (entries 14–18, Table 1).

The reaction of **1a** under Jiao's conditions (which uses 1,3-diphenylpropene) did not furnish the tetrazole **2a**, and resulted in the formation of the corresponding chalcone – 1,3-diphenyl-2-propen-1-one (entry 19, Table 1).[11] From these screening studies, the reaction of **1a** (0.5 mmol), $TMSN_3$ (1.1 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.025 mmol), DDQ (0.6 mmol), in $CH_2Cl_2$ (2 mL) at room temperature was chosen as the optimal conditions to investigate the scope of the reaction.

**Table 2.** Substrate scope for cinnamyl alcohols.[a]




1 2

| Entry | Substrate (**1**) | | Product (**2**) | Yield [%][b] |
|---|---|---|---|---|
| 1 | R = 4-$MeC_6H_4$ | **1b** | **2b** | 80 |
| 2 | R = 4-$MeOC_6H_4$ | **1c** | **2c** | 69 |
| 3 | R = 3-$BnOC_6H_4$ | **1d** | **2d** | 76 |
| 4 | R = 1-naphthyl | **1e** | **2e** | 70 |
| 5 | R = 2-$FC_6H_4$ | **1f** | **2f** | 69 |
| 6 | R = 4-$FC_6H_4$ | **1g** | **2g** | 72 |
| 7 | R = 4-$ClC_6H_4$ | **1h** | **2h** | 85 |
| 8 | R = 4-$BrC_6H_4$ | **1i** | **2i** | 74 |
| 9 | R = 2-thiophene | **1j** | **2j** | 40 |

[a] *Reaction conditions:* **1** (0.5 mmol), $TMSN_3$ (1.1 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.025 mmol), DDQ (0.6 mmol), $CH_2Cl_2$ (2 mL) at room temperature for 1 h.
[b] Isolated yield.

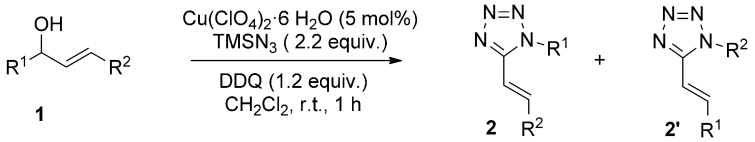
The optimized reaction conditions were found to be applicable to a wide range of substrates (Table 2 and Table 3). As depicted in Table 2, a variety of cinnamyl alcohols (substituted with the same aryl groups at the 1 and 3-positions) were converted into their corresponding tetrazoles with good to excellent yields. Substituents with electron-releasing and electron-withdrawing natures on the phenyl ring had no effect on the outcome of the reaction, as it afforded the corresponding tetrazoles **2b**, **2c**, **2d**,[14] **2e**, **2f**, **2g**, **2h** and **2i** in good to excellent yields (entries 1–8, Table 2). As can be seen, the halo-substituted tetrazoles **2h** and **2i**, which are potential precursors for further transformations, were obtained in good yields (entries 7 and 8, Table 2). Although, heterocyclic substrate such as (*E*)-1,3-di(thiophen-2-yl)prop-2-en-1-ol **1j** reacted well under the optimal conditions, the reaction furnished the corresponding tetrazole **2j** in lower yield (40%).

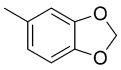
After studying the scope of allylic alcohols that are substituted with the same aryl groups at the 1 and 3 positions, the applicability of the reaction was investigated on a spectrum of unsymmetrically substituted allyl alcohols (Table 3). Reactions of alcohols containing a methyl group on the phenyl ring at the 2 and 4 positions (**1k**, **1l** and **1m)** led to the formation of the corresponding tetrazoles **2k**, **2l** and **2m** in good yields with different ratios of regiomers (entries 1–3, Table 3).

Alcohols containing electron-donating substituents on phenyl ring such as **1n** and **1o** were regioselectively transformed into their tetrazoles **2n** (12:88) and **2o**

Advanced Synthesis & Catalysis

**Table 3.** Substrate scope for cinnamyl alcohols.[a]




| Entry | Substrate (**1**) | | Product (**2:2′**) | Yield [%][b] |
|---|---|---|---|---|
| 1 | $R^1$ = Ph, $R^2$ = 2-Me$C_6H_4$ | **1k** | **2k:2k′**(55:45) | 80 |
| 2 | $R^1$ = Ph, $R^2$ = 4-Me$C_6H_4$ | **1l** | **2l:2l′** (37:63) | 73 |
| 3 | $R^1$ = 4-Me$C_6H_4$, $R^2$ = Ph | **1m** | **2m:2m′** (64:36) | 71 |
| 4 | $R^1$ = Ph, $R^2$ = 4-MeO$C_6H_4$ | **1n** | **2n:2n′** (12:88) | 62 |
| 5 | $R^1$ = Ph, $R^2$ =  | **1o** | **2o:2o′** (25:75) | 60 |
| 6 | $R^1$ = Ph, $R^2$ = 1-napthyl | **1p** | **2p:2p′** (56:44) | 73 |
| 7 | $R^1$ = Ph, $R^2$ = 2-napthyl | **1q** | **2q:2q′** (51:49) | 65 |
| 8 | $R^1$ = Ph, $R^2$ = 4-$NO_2C_6H_4$ | **1r** | **2r:2r′** (100:0) | 79 |
| 9 | $R^1$ = Ph, $R^2$ = 2-$ClC_6H_4$ | **1s** | **2s:2s′** (39:61) | 71 |
| 10 | $R^1$ = Ph, $R^2$ = 3-$ClC_6H_4$ | **1t** | **2t:2t′** (64:36) | 83 |
| 11 | $R^1$ = Ph, $R^2$ = 4-$ClC_6H_4$ | **1u** | **2u:2u′** (47:53) | 88 |
| 12 | $R^1$ = Ph, $R^2$ = 2,4-$ClC_6H_3$ | **1v** | **2v:2v′** (45:55) | 71 |
| 13 | $R^1$ = Ph, $R^2$ = 2-$FC_6H_4$ | **1w** | **2w:2w′** (39:61) | 80 |
| 14 | $R^1$ = Ph, $R^2$ = 4-$FC_6H_4$ | **1x** | **2x:2x′** (41:59) | 73 |
| 15 | $R^1$ = Ph, $R^2$ = 2-$BrC_6H_4$ | **1y** | **2y:2y′** (50:50) | 75 |
| 16 | $R^1$ = Ph, $R^2$ = 3-$BrC_6H_4$ | **1z** | **2z:2z′** (64:36) | 62 |
| 17 | $R^1$ = 4-Me$C_6H_4$, $R^2$ = 2-napthyl | **1aa** | **2aa:2aa′** (49:51) | 64 |
| 18 | $R^1$ = Me, $R^2$ = Ph | **1ab** | **2ab:2ab′** (100:0) | 54 |

[a] *Reaction conditions:* **1** (0.5 mmol), $TMSN_3$ (1.1 mmol), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 mmol), DDQ (0.6 mmol), $CH_2Cl_2$ (2 mL) at room temperature for 1 h.

[b] Isolated yield.

(25:75) in good yields (entries 4 and 5, Table 3). Alcohols such as **1p** and **1q** gave rise to the formation of tetrazoles **2p** and **2q** in moderate yields in almost the same regioisomeric ratios (entries 6-7, Table 3). An alcohol with an electron-withdrawing aryl moiety, such as (*E*)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-ol **1r**, resulted in regioselective formation (100:0) of the corresponding tetrazole, e.g., **2r** in 79% yield (entry 8, Table 3). The reaction of alcohols containing chloro as a substituent at different positions on the phenyl ring such as **1u** (4-Cl) and **1v** (2,4-Cl) furnished their corresponding tetrazoles **2u** and **2v** with poor regioselectivity (entries 11 and 12, Table 3). In contrast, alcohols **1s** and **1t** with chloro substitution at the 2- and 3-position of the phenyl ring respectively furnished corresponding tetrazoles **2s** and **2t** with the opposite regioselectivity (entries 9 and 10, Table 3). Alcohols containing fluoro and bromo substituents, such as **1w**, **1x**, **1y** and **1z** produced the corresponding tetrazoles **2w**, **2x**, **2y** and **2z** in close to 50:50 ratios in good to moderate yields (entries 13–16, Table 3). Unsymmetrical alcohol **1aa** was also converted into its tetrazole **2aa** in 64% yield in a 49:51 ratio (entry 17, Table 3). It was interesting to observe that the reaction of alcohol **1ab**, containing styryl substitution, resulted in the regioselective formation of the corresponding tetrazole **2ab** in moderate yield (entry 18, Table 3).

In addition, disubstituted benzylic alcohols are also served as good substrates under the optimized reaction conditions as alcohols such as **3a**, **3b**, **3c**, and **3d** furnished the corresponding tetrazoles in moderate yields (entries 1–4, Table 4).

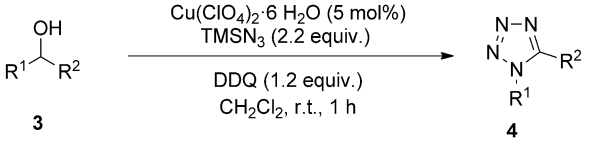
To expand the substrate scope and to examine the functional group tolerance for this reaction, the following experiments were performed. Under the optimal reaction conditions, a mixture of alcohol **1a** and ketone (**5a**) or ester (**5b**) or nitrile (**5c**) or acid (**5d**) or amide (**5e**) was subjected to this oxidative transformation. As expected, the alcohol reacted under the conditions to produce the corresponding tetrazole **2a** in almost quantitative yields and the ketone (**5a**), ester (**5b**), nitrile (**5c**), [14] acid (**5d**) or amide (**5e**) remained intact (Table 5).[15]

The suitability of this methodology for scaling up was demonstrated by carrying out the reaction on a gram scale. As can be seen, reaction of **1a** (1.05 g, 5 mmol) under the optimal conditions furnished the product **2a** in 71% yield (Scheme 2).

Several experiments were performed using a variety of substituted alcohols (see Scheme-2, Supporting Information) to understand the origin of the regioselec-

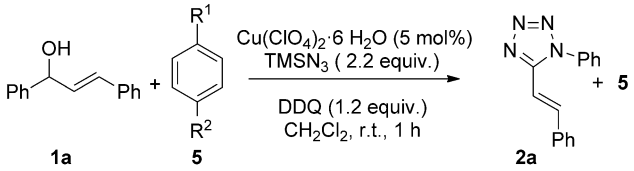
**Table 4.** Substrate scope for benzyl alcohol.[a]




| Entry | Substrate (**3**) | | Product (**4**) | Yield [%][b] |
|---|---|---|---|---|
| 1 | $R^1$=4-$MeOC_6H_4$, $R^2$=Me | **3a** | **4a** | 50 |
| 2 | $R^1$=4-$PhC_6H_4$, $R^2$=Me | **3b** | **4b** | 48[c] |
| 3 | $R^1=R^2$=4-$MeOC_6H_4$ | **3c** | **4c** | 69 |
| 4 | $R^1=R^2$=4-$Me_2NC_6H_4$ | **3d** | **4d** | 48 |

[a] *Reaction conditions:* **3** (0.5 mmol), $TMSN_3$ (1.1 mmol), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 mmol), DDQ (0.6 mmol), $CH_2Cl_2$ (2 mL) at room temperature for 1 h.
[b] Isolated yield.
[c] 8 h.

**Table 5.** Selective formation of tetrazoles.[a]




| Entry | Substrate (**5**) | Product [%][b] (**2a**) | (**5**) |
|---|---|---|---|
| 1 | **5a**: $R^1$=-C(O)$CH_3$; $R^2$=-$OCH_3$ | 42 | 58 |
| 2 | **5b**: $R^1$=-C(O)$OCH_3$; $R^2$=-H | 48 | 52 |
| 3 | **5c**: $R^1$=-CN; $R^2$=-OBn | 42 | 52 |
| 4 | **5d**: $R^1$=-COOH; $R^2$=-$OCH_3$ | 52 | 48 |
| 5 | **5e**: $R^1$=H, $R^2$ = —C(O)—N⟨ ⟩ | 47 | 53 |

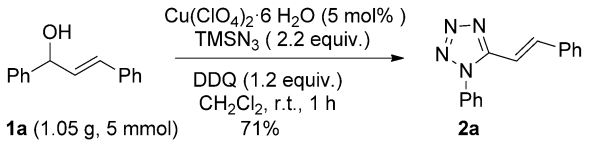
[a] *Reaction conditions:* **1a** (0.5 mmol), $TMSN_3$ (1.1 mmol), $Cu(ClO_4)_2{\cdot}6H_2O$ (0.025 mmol), DDQ (0.6 mmol), $CH_2Cl_2$ (2 mL) at room temperature for 1 h.
[b] Ratio based on $^1$H NMR data.

tivity. Based on these experiments, we believe that the electronic nature of substituent on the aromatic ring determines the regioselectivity of the reaction, which is in agreement with the observation of Jiao and co-workers.[11] We observed that the regioselective formation of azide is the determining factor, as unsymmetrically substituted alcohols preferentially furnished the azide that was benzylic to the electron-rich phenyl ring over the electron-poor phenyl ring. This phenomenon can be attributed to the stabilization of the carbocation by the electron-rich phenyl ring. Furthermore, the azide gets oxidized to the corresponding nitrilium ion, where the electron-rich group migrates to the nitrogen atom and this is emphasized by comparing the ratio of regioisomers formed in the azide stage and the tetrazole stage. Based on these observations, the overall observed migratory aptitude of a variety of substituents is as follows; *aryl group (e⁻-rich > e⁻-poor) > alkyl group > vinyl group* (see Supporting Information, Scheme-5).

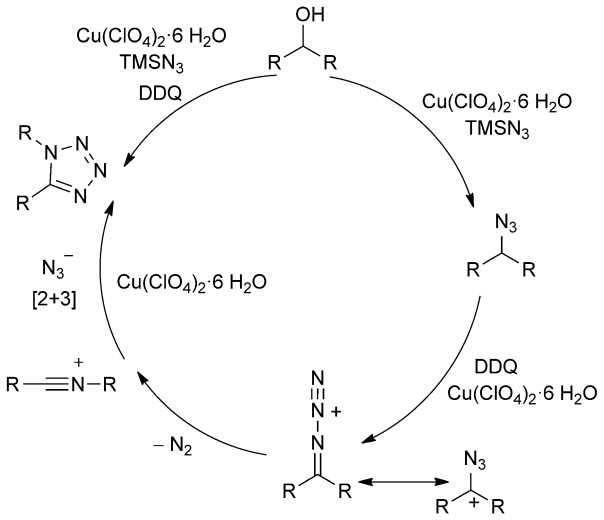
It is also noteworthy that only highly Lewis acidic copper salts such as $Cu(ClO_4)_2{\cdot}6H_2O$ and $Cu(OTf)_2$ are effective for this conversion, while the other copper salts lead to the formation of the ketone as the sole product. Also, we observed that the order of addition of reagents is crucial for the success of the reaction. If DDQ is added prior to the addition of the copper salt, the alcohol gets oxidized to the corresponding ketone and the reaction ceases.

Based on these observations (Supporting Information, Scheme-3 and Scheme-4), and in light of recent reports by Echavarren,[10] and Jiao[11,16] we believe that the reaction proceeds through the corresponding azide, which was further oxidized to the tetrazole. A tentative mechanism is presented in Scheme 3.

To summarize, we have found a mild and convenient method to synthesize 1,5-disubstituted tetrazoles using easily accessible secondary alcohols by employing $TMSN_3$ as a nitrogen source. This one-pot reaction is performed in the presence of a catalytic amount of $Cu(ClO_4)_2{\cdot}6H_2O$ using DDQ as an oxidant under ambient conditions, and tolerates a variety of functional groups such as ketone, ester, nitrile, acid and amides.




**Scheme 2.** Scaling up of the reaction.




**Scheme 3.** Plausible mechanism.

## Experimental Section

***Note:*** *Proper safety precautions should be followed when using azides.*[17]

### Typical Experimental Procedure

Trimethylsilyl azide (1.1 mmol) was added dropwise to a well-stirred mixture of alcohol (0.5 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.025 mmol) in $CH_2Cl_2$ (2 mL), after 15 min DDQ was added (0.6 mmol) and the reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was dissolved in small amount of EtOAc (2 mL), passed through alumina, and purified on a silica gel column using EtOAc/hexane as eluent.

## Acknowledgements

*KRP acknowledges IISc, CSIR (No. 01/2415/10-EMR-II) and RL Fine Chem for financial support. We thank to Dr. A. R. Ramesha for useful discussion. BVR thanks CSIR for a senior research fellowship.*

## References

[1] a) J. F. Hartwig, *Nature* **2008**, *455*, 314–322; b) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215–1292; c) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655.

[2] a) J. C. Antilla, J. M. Baskin, T. E. Barder, S. L. Buchwald, *J. Org. Chem.* **2004**, *69*, 5578–5587; b) P. Y. S. Lam, C. G. Clark, S. Saubern, J. Adams, M. P. Winters, D. M. T. Chan, A. Combs, *Tetrahedron Lett.* **1998**, *39*, 2941–2944.

[3] S. J. Wittenberger, *Org. Prep. Proced. Int.* **1994**, *26*, 499–531.

[4] a) W. Song, Y. Wang, J. Qu, M. M. Madden, Q. Lin, *Angew. Chem.* **2008**, *120*, 2874–2877; *Angew. Chem. Int. Ed.* **2008**, *47*, 2832–2835; b) W. Song, Y. Wang, J. Qu, Q. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 9654–9655; c) Y. Wang, W. J. Hu, W. Song, R. K. V. Lim, Q. Lin, *Org. Lett.* **2008**, *10*, 3725–3728; d) Y. Wang, W. Song, W. J. Hu, Q. Lin, *Angew. Chem.* **2009**, *121*, 5434–5437; *Angew. Chem. Int. Ed.* **2009**, *48*, 5330–5333.

[5] For some recent examples, see: a) A. S. Gundugola, K. L. Chandra, E. M. Perchellet, A. M. Waters, J. P. H. Perchellet, S. Rayat, *Bioorg. Med. Chem. Lett.* **2010**, *20*, 3920–3924, and references cited therein; b) P. Srihari, P. Dutta, R. S. Rao, J. S. Yadav, S. Chandrasekhar, P. Thombare, J. Mohapatra, A. Chatterjee, M. R. Jain, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 5569–5572, and references cited therein; c) M. A. Hiskey, D. Chavez, D. L. Naud, S. F. Son, H. L. Berghout, C. A. Bolme, *Proc. Int. Pyrotech. Semin.* **2000**, *27*, 3–14.

[6] a) J. S. Mihina, R. M. Herbst, *J. Org. Chem.* **1950**, *15*, 1082–1092; b) Z. P. Demko, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2214–2217; *Angew. Chem. Int. Ed.* **2002**, *41*, 2110–2113; c) Z. P. Demko, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2217–2220; *Angew. Chem. Int. Ed.* **2002**, *41*, 2113–2116; d) F. Himo, Z. P. Demko, L. Noodleman, K. B. Sharpless, *J. Am. Chem. Soc.* **2003**, *125*, 9983–9987; e) F. Couty, F. Durrat, D. Prim, *Tetrahedron Lett.* **2004**, *45*, 3725–3728; f) P. B. Palde, T. F. Jamison, *Angew. Chem.* **2011**, *123*, 3587–3590; *Angew. Chem. Int. Ed.* **2011**, *50*, 3525–3528; g) D. Cantillo, B. Gutmann, C. O. Kappe, *J. Am. Chem. Soc.* **2011**, *133*, 4465–4475.

[7] a) H. Suzuki, Y. S. Hwang, C. Nakaya, Y. Matano, *Synthesis* **1993**, 1218–1220; b) A. S. El-Ahl, S. S. Elmorsy, H. Soliman, F. A. Amer, *Tetrahedron Lett.* **1995**, *36*, 7337–7340; c) A. G. Schultz, A. Wang, C. Alva, A. Sebastian, S. D. Glick, D. C. Deecher, J. M. Bidlack, *J. Med. Chem.* **1996**, *39*, 1956–1966.

[8] R. N. Butler, D. A. O. Donoghue, *J. Chem. Res. Synop.* **1983**, 18.

[9] a) J. Zabrocki, J. B. Dunbar Jr, K. W. Marshall, M. V. Toth, G. R. Marshall, *J. Org. Chem.* **1992**, *57*, 202–209; b) E. W. Thomas, *Synthesis* **1993**, 767–768; c) A. LeTiran, J. P. Stables, H. Kohn, *Bioorg. Med. Chem.* **2001**, *9*, 2693–2708; d) J. Xiao, X. Zhang, D. Wang, C. Yuan, *J. Fluorine Chem.* **1999**, *99*, 83–85; e) A. F. Hegarty, N. M. Tynan, S. Fergus, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1328–1334.

[10] During the revision of this manuscript, Echavarran and co-workers reported a gold-catalyzed synthesis of tetrazoles. See: M. Gaydou, A. M. Echavarren, *Angew. Chem.* **2013**, *125*, 13710–13713; *Angew. Chem. Int. Ed.* **2013**, *52*, 13468–13471.

[11] F. Chen, C. Qin, Y. Cui, N. Jiao, *Angew. Chem.* **2011**, *123*, 11689–11693; *Angew. Chem. Int. Ed.* **2011**, *50*, 11487–11491. The reaction of **1a** under Jiao's conditions did not furnish the tetrazole **2a**, and resulted in the formation of the corresponding chalcone (1,3-diphenyl-2-propen-1-one) (see entry 19, Table 1).

[12] a) J. Wang, W. Huang, Z. Zhang, X. Xiang, R. Liu, X. Zhou, *J. Org. Chem.* **2009**, *74*, 3299–3304; b) Y. Liu, B. Yao, C. L. Deng, R. Y. Tang, X. G. Zhang, J. H. Li, *Org. Lett.* **2011**, *13*, 1126–1129; c) M. Mayer, W. M. Czaplik, A. Jacobi von Wangelin, *Adv. Synth. Catal.* **2010**, *352*, 2147–2152.

[13] a) M. Lamani, K. R. Prabhu, *Angew. Chem.* **2010**, *122*, 6772–6775; *Angew. Chem. Int. Ed.* **2010**, *49*, 6622–6625; b) M. Lamani, P. Devadig, K. R. Prabhu, *Org. Biomol. Chem.* **2012**, *10*, 2753–2759; c) B. V. Rokade, S. K. Malekar, K. R. Prabhu, *Chem. Commun.* **2012**, *48*, 5506–5508; d) B. V. Rokade, K. R. Prabhu, *J. Org. Chem.* **2012**, *77*, 5364–5370.

[14] Unlike the reactions of benzyl ethers with DDQ, these reactions are selective as benzyl group is tolerated under the reaction conditions.

[15] See the Supporting Information for relevant spectra.

[16] While we were preparing this manuscript Jiao and co-workers reported a silver-catalyzed nitrogenation of alkynes to access tetrazoles. See: T. Shen, T. Wang, C. quin, N. Jiao, *Angew. Chem.* **2013**, *125*, 6809–6812; *Angew. Chem. Int. Ed.* ***2013***, *52*, 6677–6680.

[17] S. Bräse, K. Banert, (Eds.), *Organic azides: Synthesis and applications*, Wiley, Chichester, **2010**. Especially relevant is: T. Keicher, S. Löbbecke, *Lab-Scale Synthesis of azido compounds: Safety measures and analysis*, *Organic azides: Synthesis and applications*, (Eds.: S. Bräse, K. Banert), Wiley, Chichester, **2010**, Chapter 1, pp 1–28.