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Copper promoted synthesis of tetrazoles and further conversion into diaryl tetrazoles through *C-N* cross-coupling approach

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Efficient tandem three component method has been demonstrated for the synthesis of substituted tetrazoles under mild reaction conditions using copper catalysis. Green solvent DMSO has been utilized and the reaction has been carried out at room temperature which establishes that our method is green synthetic approach. Variety of substrates readily undergo the optimized reaction conditions to provide their respective target products in good to excellent yields. In addition we have observed regioselective compounds depending on the substituents of phenyl ring. All the reactions are rapid, facile and are accomplished at room temperature. The reactions are of general application, clean and efficient. Furthermore we have confirmed that no other by-products could be identified during our experimental reaction process. In addition, *C-N* cross-coupling have been developed with phenyltetrazoleamines and aryl iodide under moderate reaction conditions.

Keywords: Copper catalyst, *C-N* cross-coupling reaction, one-pot reaction, room temperature, substituted tetrazoles

Tetrazoles moiety compounds (Figure 1) are very important class of heterocyclic compounds as they are resistant to metabolic degradation as well as towards chemical oxidants[1], and they are involved in many biological compounds[2]. Additionally, trazoles are found in compounds having anti-allergic/ anti-asthmatic[3], antiviral[4], anti-inflammatory[4], antineoplastic[5], and cognition disorder activities[6]. They are also used in high energy density materials (HEDM)[7] as ligands in coordination chemistry[8] and in the preparation of imidoylazides[9].

Thus, the continuous and significant efforts have been made due to their synthetic and medicinal importance. Especially, through the addition of $NaNO_2$ (Ref. 10), NaN_3 (Ref. 11,12), and *via* nucleophilic substitution by N_3^-. of (a) chlorine in R-chloroformamidines[13], which can be obtained from nitriles and alkyl halides[14], (b) the sulfite anion in aminoiminomethanesulfonic acids[15], and (c) sulfur from thioureas in the presence of mercury[16] or lead salts[17], Iodine[18]. Furthermore, 5-substituted-1*H*-tetrazoles were prepared from the cycloaddition between corresponding cyanides and NaN_3 using Zn (II) salts[19], ZnO nanocrystal[20], TBAF[21], copper catalyst[22], and cobalt catalyst[23]. Often these methods use toxic reagents[16], harsh reaction conditions, they require high temperature, they are very bad at regioselectivity[24], they frequently require unstable and/or moisture-sensitive starting materials, such as isocyanide dichlorides[17], chloroformamidines[14c], or aminoiminomethane sulfonicacids[14b].

The reported methods are really efficient enough, however, in order to overcome the above said disadvantages there is still need for a commercially available and environmentally acceptable methodology for the preparation of tetrazoles. We recently, aryl/alkyl isothiocyanates and cyanamides have been described using copper catalysis[25]. In order to continue our research work and overcome the disadvantages of tetrazole synthesis, here in, we would like to report for the construction of arylaminotetrazoles from isothiocyanates *via* the formation of thioureas in one pot reaction using copper catalysis under mild reaction conditions. Furthermore, we have also wish to demonstrate the synthesis of diaryl aminotetrazoles through inter molecular *C-N* cross-coupling reaction using copper catalysis under moderate conditions.

Results and Discussion

We investigated the construction of tetrazole compounds from isothiocyanates. The optimization of

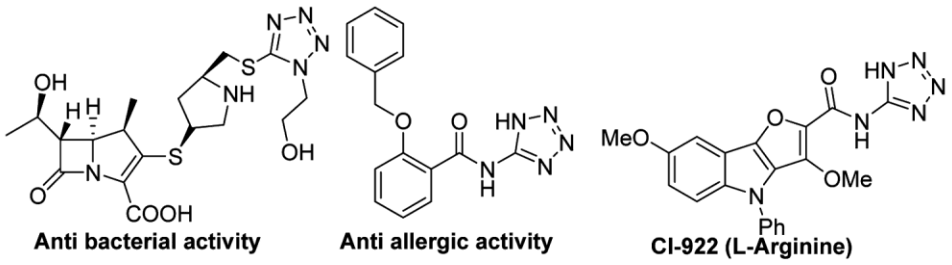


Figure 1 — Examples of biologically important tetrazole compounds

various solvents, different bases, catalysts and temperature was conducted with phenylisothiocyanate as model substrate. Phenyl isothiocyanate reacts with Aq NH_3 to give phenyl thiourea **1a** as an intermediate in complete conversion in the presence of DMSO and DMF. Phenyl thiourea **1a**, gratifyingly reacts with sodium azide using both Cu (I) & Cu (II) salts and inorganic bases and organic base (Et_3N) at room temperature to provide target product 5-amino phenyl tetrazole **2a** in complete conversion.

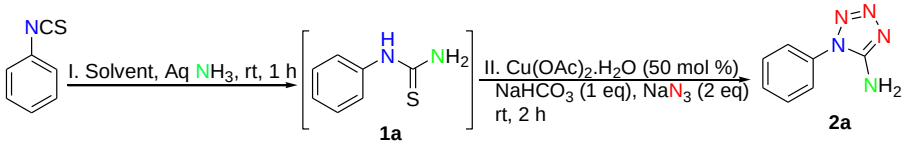
Initially, various solvents were examined and the results have been illustrated in Table I. Out of set solvents DMSO and DMF could obtain target product in high yield (Table I, entries 7-8). Other solvents such as ethanol, methanol, acetone and EtOAc could give target product in 40-55% yields (Table I, entries 1-3 and 6). Later, the reaction was examined in the presence of green solvent H_2O and no thiourea could observe. We have also performed the reaction in the presence of non poar solvents like n-hexane and n-heptane. Very unfortunately no non-polar solvent could give even thiourea also. Fianlly, the reaction was conducted in the presence of combination of solvents (DMSO and H_2O). We could observe that the solvent system DMSO:H_2O (2:1) gave final product in high yield (Table I, entry 12). The control experiment is confirmed that no thiourea**1a** as intermediate could observe in the absence of solvent (Table I, entry 13). Later base optimization was conducted (Table II), however, inorganic bases have shown greater activity than organic bases. Organic bases like triethyl amine and pyridine may form complex with copper slat to degrade the catalytic activity, whereas, inorganic bases don't have tendency to form complex, and, therefore the catalytic activity is still remained. Thus, the target product was obtained with high yield in the presence of inorganic bases.

The catalytic activity of catalyst is inserted in Table III. Initially copper sources were checked, very interestingly both Copper (I) species (CuI, CuBr, CuCl) and Copper (II) species ($CuSO_4.5H_2O$, $Cu(OAc)_2.H_2O$ and $Cu(NO_3)_2.3H_2O$) were exhibited similar activity and selectivity (Table III, entries 1-6). Other metal sources like $CoCl_2.H_2O$, $NiCl_2.H_2O$ and $FeCl_2$ catalytic activity were tested. However they are not effective for this reaction under standardized conditions (Table III, entries 7-9). Lowering the amount of copper catalyst was checked and it gave expected product in moderate yield (Table III, entry 10). The control experiment is confirmed that the reaction couldn't give desired product in the absence of catalyst (Table III, entry 11) and phenyl thiourea **1a** as an intermediate is recovered intact.

With optimized conditions established, the scope of the protocol was next explored (Scheme I). The process was found to be generally applicable; various isothiocyanates, Aq NH_3 and sodiumazide under optimized reaction conditions gave the corresponding substituted tetrazoles **2a-2l** in moderate to good yield. Aryl isothiocyanates bearing electron donating substituents (4-Me, 4-OMe and 2,4-dimethyl groups) were more reactive than those having electron withdrawing substituents (4-Cl, 4-F, 4-COOMe). Aryl ring contains electron donating groups like 4-Me, 4-OMe and 2,4-dimethyl (Table IV, entries 2-3 and entry 11) gave their respective target products in 84-93% yields. 4-Chloro and 4-Fluoro phenyl isothiocyanates could give their final tetrazoles in 83% and 75% yields, respectively. Benzyl, cyclohexyl and n-butyl isothiocyanates (Table IV, entries 12-14) readily underwent the optimized reaction conditions to provide their respective final products in 89%, 88% and 90%.

In order to reveal the mechanism (Scheme II), the control experiments were conducted. Thiourea was isolated and it was completely dissolved in DMSO solvent. To this $Cu(OAc)_2.H_2O$ was added and stirred at room temperature for 1.5 h. Later, the isolated catalyst was subjected to Powder XRD analyses (Figure 2). The signals related to 2θ = 73.65, 61.53, 42.45, 36.12, 29.59 were identified in the spectrum.

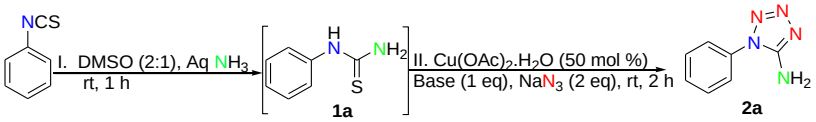
Table I — Solvent Optimization[a]



Entry	Solvent	Yield (%)[b]	
		1a	**2a**
1	Ethanol	10	50
2	MeOH	10	50
3	Acetone	20	40
4	n-Hexane	NR	NR
5	n-Heptane	NR	NR
6	EtOAc	10	55
7	DMSO	5	90
8	DMF	5	90
9	H2O	NR	NR
10	DMSO/H_2O (1:1)	40	50
11	DMSO/H_2O (1:2)	NR	NR
12	DMSO/H_2O (2:1)	5	90
13	–	NR	NR

[a] Reaction conditions: Phenyl isothiocyanate (2 mmol), solvent (4 ml), Aq NH_3 (2 ml), RT, 1 h, then, $NaHCO_3$ (1 eq), $Cu(OAc)_2.H_2O$ (50 mol %) and NaN_3 (2 eq), RT, 2 h. [b] Isolated yield.

Table II — Base Optimization for the Synthesis of Tetrazoles[a]



Entry	Base	Yield (%)[b]	
		1a	**2a**
1	Et_3N	55	35
2	Pyridine	65	30
3	NaOAc	5	90
4	NaOH	5	90
5	$NaHCO_3$	5	90
6	-	>95	NR

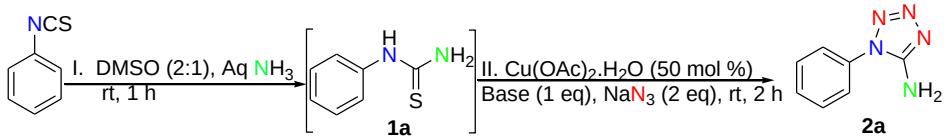
[a] Reaction conditions: Phenyl isothiocyanate (2 mmol), DMSO:H_2O (4 ml), Aq NH_3 (2 ml), rt, 1 h, then, base (1 eq), $Cu(OAc)_2.H_2O$ (50 mol %) and NaN_3 (2 eq), rt, 2 h. [b] Isolated yield.

However, the values are matched with previous reported Cu (I) species peaks[26]. Our experimental results and

literature reports[27] clearly confirmed that thiourea may reduce copper (II) species to copper (I) species which may co-ordinate with thiourea (that is provided form isothiocyanate) to give intermediate **B** *via* intermediate **A.** The intermediate **B** may give intermediate **C** along with CuS and polysulfide[1h] *via* deslphurization[28] followed by nucleophilic substitution with NaN_3[29]. The electrocyclization of **C** may proceed to give target product 5-Amino tetrazoles.

Recently our group has developed methodologies through carbon-hetero atom cross-coupling reaction using transition metal catalysis[30]. In order to continue research work on cross-coupling reactions we have focussed on inter molecular *C-N* cross-coupling using copper catalysis. In this connection the optimization was carried out with phenyl tetrazole amine and iodo

Table III — Catalyst Optimization for the Synthesis of Tetrazoles[a]



Entry	Catalyst	Yield (%)[b]	
		1a	**2a**
1	$CuSO_4.5H_2O$	5	90
2	$Cu(NO_3)_2.3H_2O$	5	90
3	$Cu(OAc)_2.H_2O$	5	90
4	CuI	5	90
5	CuBr	5	90
6	CuCl	5	90
7	$CoCl_2.H_2O$	50	40
8	$NiCl_2.H_2O$	65	27
9	$FeCl_2$	55	36
10[c]	$Cu(OAc)_2.H_2O$	5	60
11	-	NR	NR

[a] Reaction conditions: Phenyl isothiocyanate (2 mmol), DMSO:H_2O (4 ml), Aq NH_3 (2 ml), RT, 1 h, then, base (1 eq), catalyst (50 mol %) and NaN_3 (2 eq), RT, 2 h. [b] Isolated yield. [c] Catalyst (25 mol %) was used.

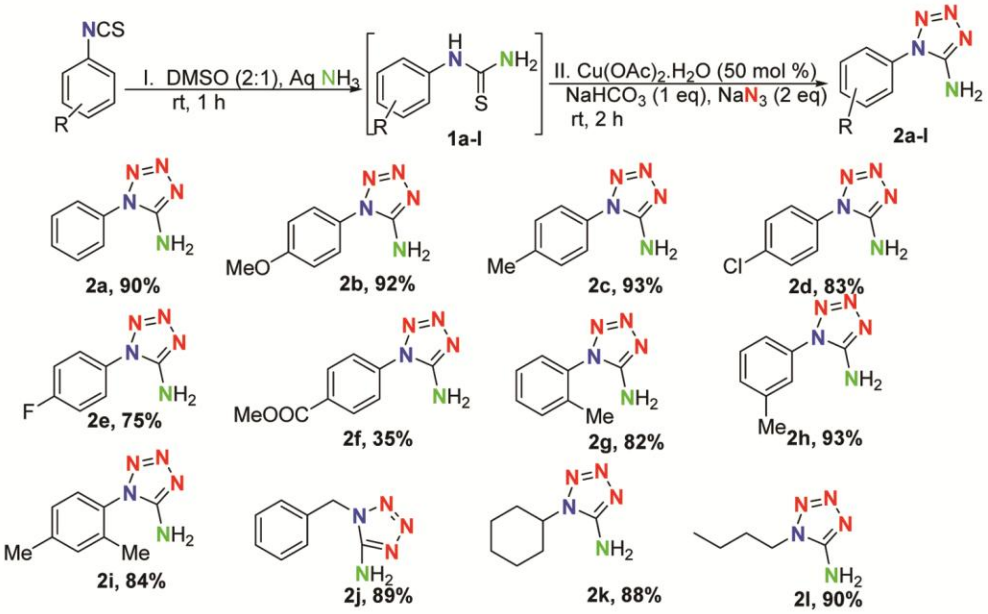
Table IV — Substantial comparison with other methods

S. No	Compd	Our Method	Other Methods
1	**2a**	Yield: 90%, Time: 3 h, Temp: RT	1 Yield:91%, Temp: 85 °C, Time: 12 h (*Tetrahedron Lett*. **2013**, *54*, 106-109) 2 Yield: 75%, Temp: RT, Time: 4 h (*Org. Biomol. Chem*. **2011**, *9*, 3235-3245) 3 Yield: 76%, Temp: 100 °C, Time: 24 h (*J. Org. Chem*. **2001**, *66*, 7945-7950) 4 Yield: 81%, Temp: 100 °C, Time: 1.5 h (*Tetrahedron* **2009,** *65*, 10715–10719)
2	**2b**	Yield: 92%, Time: 3 h, Temp: RT	1 Yield:84%, Temp: 80 °C, Time: 12 h (*Tetrahedron Lett*. **2008**, *49*, 2824-2827) 2 Yield: 86%, Temp: 100 °C, Time: 48 h (*J. Org. Chem*. **2001**, *66*, 7945-7950) 3 Yield:94%, Temp: 85 °C, Time: 12 h (*Tetrahedron Lett*. **2013**, *54*, 106-109) 4 Yield: 83%, Temp: 115 °C, Time: 65 min (*Tetrahedron* **2009,** *65*, 10715–10719)
3	**2c**	Yield: 93%, Time: 3 h, Temp: RT	1 Yield:79%, Temp: 80 °C, Time: 12 h (*Tetrahedron Lett*. **2008**, *49*, 2824-2827) 2 Yield: 73%, Temp: RT, Time: 5 h (*Org. Biomol. Chem*. **2011**, *9*, 3235-3245) 3 Yield:89%, Temp: 85 °C, Time: 12 h (*Tetrahedron Lett*. **2013**, *54*, 106-109) 4 Yield: 80%, Temp: 115 °C, Time: 65 min. (*Tetrahedron* **2009,** *65*, 10715–10719)
4	**2d**	Yield: 83%, Time: 3 h, Temp: RT	1 Yield: 79%, Temp: RT, Time: 5 h (*Org. Biomol. Chem*. **2011**, *9*, 3235-3245) 2 Yield:93%, Temp: 85 °C, Time: 12 h (*Tetrahedron Lett*. **2013**, *54*, 106-109)

(*Contd.*)

Table IV — Substantial comparison with other methods (*Contd*.)

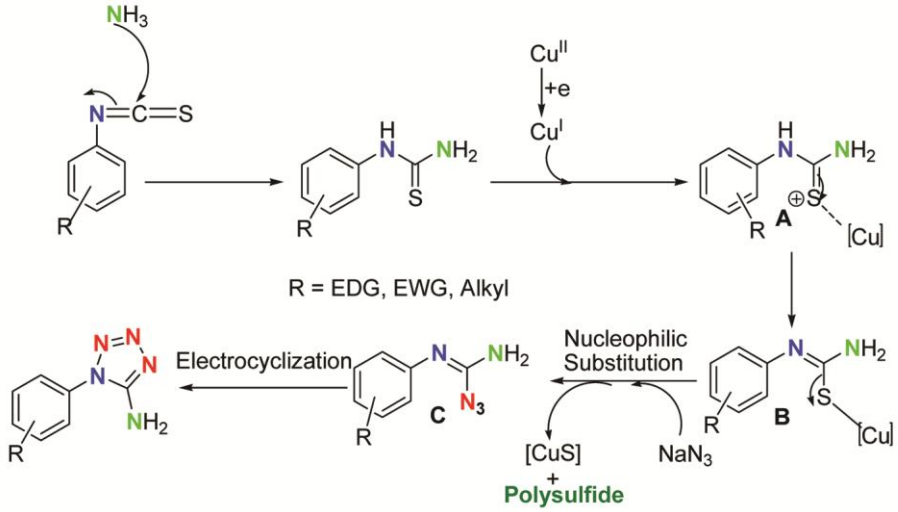
S. No	Compd	Our Method	Other Methods
5	**2e**	Yield: 75%, Time: 3 h, Temp: RT	No report is available for this compound
6	**2f**	Yield: 35%, Time: 3 h, Temp: RT	No report is available for this compound
7	**2g**	Yield: 82%, Time: 3 h, Temp: RT	1. Yield: 79%, Temp: 115 °C, Time: 65 min (*Tetrahedron* **2009,** *65*, 10715–10719)
8	**2h**	Yield: 93%, Time: 3 h, Temp: RT	No report is available for this compound
9	**2i**	Yield: 84%, Time: 3 h, Temp: RT	Yield: 81%, Temp: 115 °C, Time: 65 min (*Tetrahedron* **2009,** *65*, 10715–10719)
10	**2j**	Yield: 89%, Time: 3 h, Temp: RT	1. Yield:66%, Temp: 80 °C, Time: 24 h (*Tetrahedron Lett.* **2008**, *49*, 2824-2827) 2. Yield:74%, Temp: 85 °C, Time: 12 h (*Tetrahedron Lett.* **2013**, *54*, 106-109)
11	**2k**	Yield: 88%, Time: 3 h, Temp: RT	No report is available for this compound
12	**2l**	Yield: 90%, Time: 3 h, Temp: RT	Yield:55%, Temp: 80 °C, Time: 24 h (*Tetrahedron Lett.* **2008**, *49*, 2824-2827)
13	**3a**	Yield: 92%, Time: 12 h, Temp: 90 °C	Yield: 75%, Temp: RT, Time: 4.5 h (*Org. Biomol. Chem*. **2011**, *9*, 3235-3245)
14	**3b**	Yield: 95%, Time: 12 h, Temp: 90 °C	No report is available for this compound
15	**3c**	Yield: 95%, Time: 12 h, Temp: 90 °C	No report is available for this compound
16	**3d**	Yield: 89%, Time: 12 h, Temp: 90 °C	No report is available for this compound
17	**3e**	Yield: 72%, Time: 12 h, Temp: 90 °C	No report is available for this compound
18	**3f**	Yield: 96%, Time: 12 h, Temp: 90 °C	Yield: 74%, Temp: RT, Time: 8 h (*Org. Biomol. Chem*. **2011**, *9*, 3235-3245)
19	**3g**	Yield: 97%, Time: 12 h, Temp: 90 °C	No report is available for this compound
20	**3h**	Yield: 90%, Time: 12 h, Temp: 90 °C	No report is available for this compound



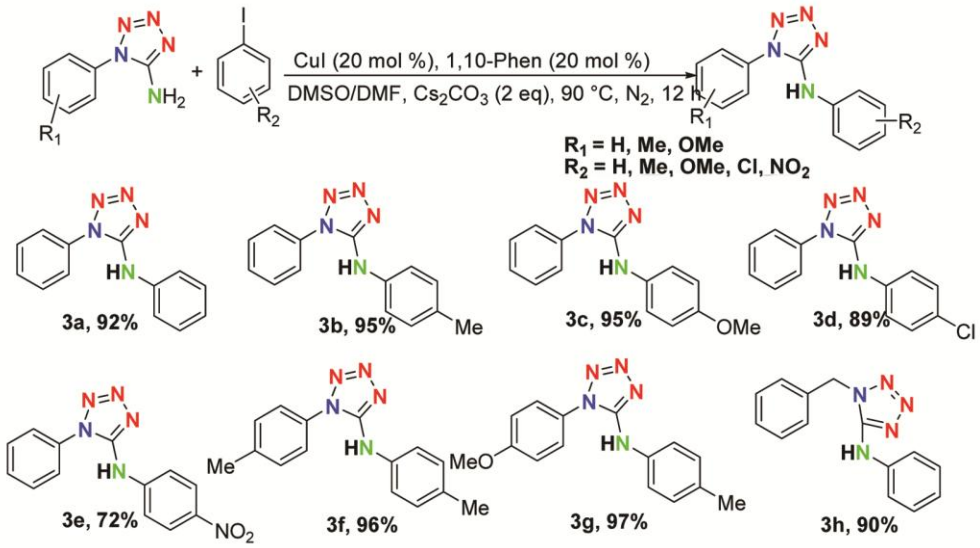
Scheme I — Substrate Scope for the Synthesis of Tetrazoles

benzene as model substrates. We glad to inform you that the reaction gave good yield using CuI (20 mol %), 1,10-Phen (20 mol%), Cs_2CO_3

(2eq) in the presence of DMSO/DMF under nitrogen atmosphere at 90 ºC (Scheme III). Substrate scope has been explored using our optimization reaction condition. Iodo benzene bearing 4-Me, 4-OMe, 4-Cl and 4-NO_2 readily carried out the reaction with phenyl tetrazoleamine to provide their respective target products **3b, 3c, 3d** and **3e** in 72-95% yields. On the other hand, phenyltetrazoleamine having substituent's like 4-Me and 4-OMe react with 4-



Scheme II — Plausible Mechanism



Scheme III — Substrate Scope for *C-N* Cross-Coupled Products

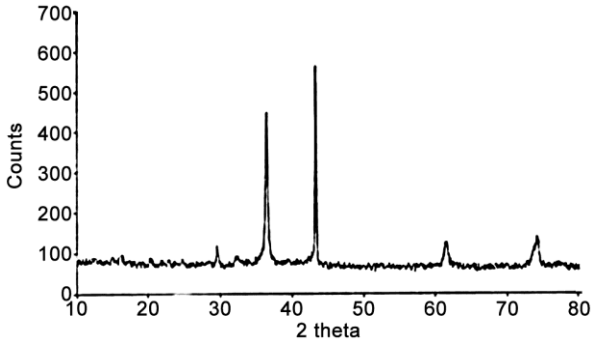


Figure 2 — XRD of Cu (I) species

Meiodobenzene to obtain desired products in 96-97% yields. In addition we have also extended the reaction with alkyl tetrazoleamine substrates. In this connection, n-butyl tetrazoleamine have provided final target product **3h** in 90%.

In addition we have compared our report with other described recent literature reported methods in terms of parameters such as temperature, time and yield of the products (Table IV). This table clearly confirmed that our method is better than others that are known. Furthermore, many of our synthesized compounds are not accomplished in recent times.

General Information

Aniline, CS_2, $CuSO_4 \cdot 5H_2O$ (98%), CuI (98%), CuBr (98%), Cu_2O (97%), $CuBr_2$ (99%), $CuCl_2 \cdot 2H_2O$ (99%) and $Cu(OAc)_2 \cdot H_2O$ (98%), Et_3N, Pyridine, sodium bicarbonate, NH_3 and NaN_3 were purchased

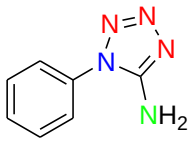
from Aldrich and used without further purification. The solvents were purchased and dried according to standard procedure prior to use. ^{1}H NMR (400MHz) spectra were recorded with a Varian 400 spectrometer. Infrared (IR) spectra recorded on a Perkin Elmer Spectrum one FT-IR spectrometer. VKSI Medico Centrifuge machine was used for our experimental procedure for the synthesis of Tetrazoles. Isothiocyanates were prepared by using our previous reported procedure[29a].

Experimental Section

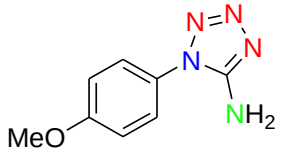
General Procedure for phenyl isothiocyanate: To a stirred solution of EtOAc/H_2O ((2:1) (4-5 ml)), aniline (2 mmol, 186 mg) was added in slowly and followed by carbon disulphide (20 mmol (10 eq), 1520 mg) and trimethylamine (2 mmol (1 eq), 202 mg) were added at room temperature. The whole reaction mixture stirred for one hour (until get the yellow color solid) at room temperature. Thiocarbomate formation was monitored by TLC. To this, $CuSO_4.5H_2O$ (50 mol %, 125 mg) was added slowly for 5 min and the reaction mixture stirred for 1 h. During this period, a black color precipitate was observed and settles at bottom of round bottom flask. The progress of the reaction was investigated by TLC (5% ethylacetate in hexane). After finishing the reaction, the reaction mixture was transferred into centrifuged tubes and the mixture was centrifuged for 10 min by using centrifugation machine. Black color solid was settled in the bottom of centrifuged tubes. The resulted clear solution was washed with ethyl acetate (10 ml) and water (7 ml) for 3 times. And organic layer was concentrated by using rotary evaporator and the crude mixture was purified by silica gel (60-120 mesh) column chromatography using 2% Ethylacetate in Hexane as eluent to obtain a Phenyl isothiocyanate as a target product, which was characterized by ^{1}H NMR and IR spectroscopy analysis.

General procedure for the synthesis of phenyl tetrazoleamine

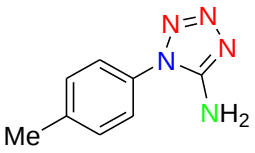
To a stirred solution of DMSO (4-5 ml)), Phenyl isothiocyanate (2 mmol, 270 mg) was added in slowly and followed by Ammonia (2 ml) was added at room temperature. The whole reaction mixture stirred for one hour at room temperature. Thiourea formation was monitored by TLC. To this, $Cu(OAc)_2.H_2O$ (50 mol %, 125 mg) and $NaHCO_3$ (1 mmol, 84 mg) were added slowly for 5 min and the reaction mixture stirred for 1 hr. During this period, a black color precipitate was observed and to that reaction mixture sodium azide (2 mmol, 130 mg). Then the reaction mixture stirred for 1 hr. The progress of the reaction was investigated by TLC (30% ethylacetate in hexane). After finishing the reaction, the reaction mixture was transferred into centrifuged tubes and the mixture was centrifuged for 10 min by using centrifugation machine. Black color solid was settled in the bottom of centrifuged tubes. The resulted clear solution was washed with ethyl acetate (10 ml) and water (7 ml) for 3 times. And organic layer was concentrated by using rotary evaporator and the crude mixture was purified by silica gel (60-120 mesh) column chromatography using 30% Ethylacetate in Hexane as eluent to obtain a Phenyl tetrazole amine as a target product, which was characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy analysis.



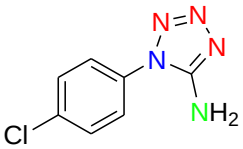
1-Phenyl-1*H*-tetrazol-5-amine 2a (Ref. 31): Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.6; yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (br S, 2H, NH_2), 7.61-7.57 (m, 2H), 7.40-7.28 (m, 2H), 7.21-7.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 130.9, 130.6, 130.1, 128.9; FT-IR (KBr) 3350, 3064, 1693, 1587, 1250, 1148, 1070, 909, 764 cm^{-1}. Anal. Calcd. for $C_7H_7N_5$: C, 52.17; H, 4.38; N, 43.45. Found: C, 52.25; H, 4.36; N, 43.39.



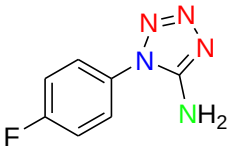
1-(4-Methoxyphenyl)-1*H*-tetrazol-5-amine 2b (Ref. 31): Analyt-ical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.6; yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2H), 6.86-6.82 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 138.6, 131.9, 127.8, 121.7, 55.4; FT-IR (KBr) 3322, 3087, 2899, 1587, 1496, 1265, 1212, 1125, 941, 808 cm^{-1}. Anal. Calcd. for $C_8H_9N_5O$: C, 50.26; H, 4.74; N, 36.63. Found: C, 50.38; H, 4.72; N, 36.56.



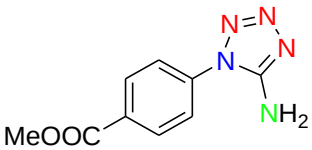
1-*p*-Tolyl-1*H*-tetrazol-5-amine 2c (Ref. 31): Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.6; yield 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (br s, 2H, NH_2), 7.50 (d, *J* = 8Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 132.4, 128.5, 124.6, 120.0, 21.3; FT-IR (KBr) 3318, 3097, 2896, 2835, 1661, 1601, 1580, 1503, 1292, 1252, 1179, 1028, 927 cm^{-1}. Anal. Calcd. for $C_8H_9N_5$: C, 54.85; H, 5.18; N, 39.98. Found: C, 54.93; H, 5.15; N, 39.93.



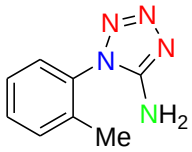
1-(4-Chlorophenyl)-1*H*-tetrazol-5-amine 2d (Ref. 31): yield 83%; Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (br, s, 2H, NH_2), 7.39 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.2, 130.8, 129.9, 124.1; FT-IR (KBr) 3399, 3076, 1670, 1505, 1250, 1114, 1046, 929, 802 cm^{-1}. Anal. Calcd. for $C_7H_6ClN_5$: C, 42.98; H, 3.09; Cl, 18.12; N, 35.80. Found: C, 43.10; H, 3.07; N, 35.75.



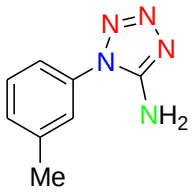
1-(4-Fluorophenyl)-1*H*-tetrazol-5-amine 2e: Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; yield 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.08 (br s, 2H, NH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 136.5, 126.2, 120.3, 114.9; FT-IR (KBr) 3359, 3056, 1654, 1554, 1459, 1352, 1235, 1140, 909, 822 cm^{-1}. Anal. Calcd. for $C_7H_6FN_5$: C, 46.93; H, 3.38; F, 10.60; N, 39.09. Found: C, 47.03; H, 3.37; N, 39.03.



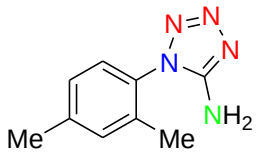
Methyl 4-(5-amino-1*H*-tetrazol-1-yl)benzoate 2f: Analytical TLC on silica gel, 4:6 ethyl acetate/hexane R_f = 0.5; yield 35%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.6 Hz, 2H), 7.38-7.33 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 142.8, 134.4, 130.5, 130.0, 129.5, 54.8; FT-IR (KBr) 3415, 3082, 1752, 1678, 1607, 1504, 1438, 1261, 1145, 1099, 872 cm^{-1}. Anal. Calcd. for $C_9H_9N_5O_2$: C, 49.31; H, 4.14; N, 31.95; O, 14.60. Found: C, 49.42; H, 4.12; N, 31.89.



1-*o*-Tolyl-1*H*-tetrazol-5-amine 2g (Ref. 31): Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; yield 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (br s, 2H, NH_2), 7.45 (d, J = 8 Hz, 2H), 7.23-7.10 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 139.6, 137.8, 134.5, 130.9, 129.9, 126.0, 20.6; FT-IR (KBr) 3375, 3065, 2920, 1656, 1490, 1379, 1229, 1125, 1036, 941, 901 cm^{-1}. Anal. Calcd. for $C_8H_9N_5$: C, 54.85; H, 5.18; N, 39.98. Found: C, 54.93; H, 5.16; N, 39.92.

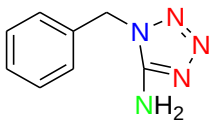


1-*m*-Tolyl-1*H*-tetrazol-5-amine 2h: Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; yield 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (br s, 2H, NH_2), 7.40-7.37 (m, 2H), 7.33-7.31 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 131.6, 131.3, 130.4, 120.3, 120.1, 115.4, 24.1; FT-IR (KBr) 3412, 3035, 2920, 2867, 1690, 1435, 1379, 1229, 1125, 1036, 941, 901 cm^{-1}. Anal. Calcd. for $C_8H_9N_5$: C, 54.85; H, 5.18; N, 39.98. Found: C, 54.92; H, 5.16; N, 39.93.

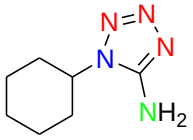


1-(2,4-Dimethylphenyl)-1*H*-tetrazol-5-amine 2i (Ref. 31): Ana-lytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; yield 84%; ^{1}H NMR (400

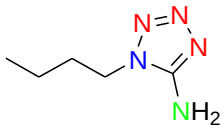
MHz, $CDCl_3$) δ 7.60 (br s, 2H, NH_2), 7.33 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 2.31 (s, 3H), 2.30 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 133.6, 133.3, 128.1, 120.3, 120.1, 116.3, 21.1, 16.1; FT-IR (KBr) 3423, 3048, 2900, 2842, 1656, 1578, 1490, 1409, 1288, 1261, 1078, 1023, 823. Anal. Calcd. for $C_9H_{11}N_5$: C, 57.13; H, 5.86; N, 37.01. Found: C, 57.20; H, 5.84; N, 36.96.



1-Benzyl-1*H*-tetrazol-5-amine 2j: Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 5H), 4.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 137.9, 130.3, 128.6, 121.0, 45.0; FT-IR (KBr) 3368, 3077, 2888, 1632, 1599, 1513, 1491, 1287, 1215, 1027, 823 cm^{-1}. Anal. Calcd. for $C_8H_9N_5$: C, 54.85; H, 5.18; N, 39.98. Found: C, 54.95; H, 5.15; N, 39.91.



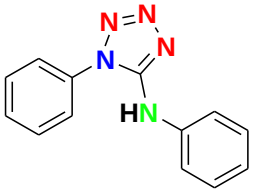
1-Cyclohexyl-1*H*-tetrazol-5-amine 2k: Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; yield 88%; ^{1}H NMR (400 MHz, DMSO) δ 6.95 (br s, 2H, NH_2), 3.54-3.50 (m, 1H), 1.64-1.56 (m, 4H), 1.43-1.34 (m, 4H), 0.96-0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 48.5, 30.8, 25.2, 19.2; FT-IR (KBr) 3412, 3052, 2898, 2833, 1602, 1583, 1491, 1287, 1146, 1027, 826 cm^{-1}. Anal. Calcd. for $C_7H_{13}N_5$: C, 50.28; H, 7.84; N, 41.88. Found: C, 50.36; H, 7.82; N, 41.82.



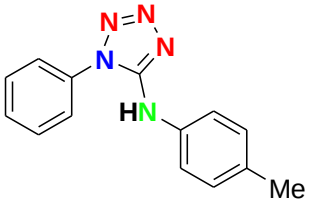
1-Butyl-1*H*-tetrazol-5-amine 2l: yield 90%; Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75-3.70 (m, 2H), 1.60-1.56 (m, 2H), 1.43-1.34 (m, 2H), 0.96-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 41.0, 30.8, 19.1, 14.2; FT-IR (KBr) 3323, 3046, 2893, 2854, 1621, 1491, 1287, 1146, 1027, 828 cm^{-1}. Anal. Calcd. for $C_5H_{11}N_5$: C, 42.54; H, 7.85; N, 49.61. Found: C, 42.61; H, 7.83; N, 49.56.

General procedure for the synthesis of diaryl tetrazoleamine

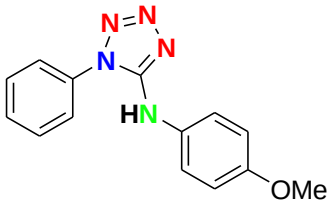
Phenyl tetrazoleamine was dissolved in DMSO at room temperature. Later, CuI (20 mol %) was added to the prior solution and followed by 1,10-Phen (20 mol%), Cs_2CO_3 (2eq) were added at room temperature. Iodo benzene was incorporated in the previous solution at room temperature. Later, the whole reaction mixture was stirred at 90 ºC for 12 h. Resulting reaction mixture was washed with ethyl acetate (10 ml) and water (7 ml) for 3 to 4 times.Organic layer was concentrated by using rotary evaporator and the crude mixture was purified by silica gel (60-120 mesh) column chromatography using 20% Ethylacetate in Hexane as eluent to obtain a diphenyl tetrazole amine as a target product, which was characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy analysis.



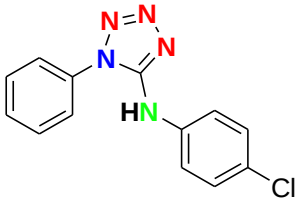
N,1-Diphenyl-1*H*-tetrazol-5-amine 3a (Ref. 32): Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.41 (m, 7H), 6.85 (d, *J* = 8.8 Hz, 3H), 6.02 (br s, 1NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 132.8, 131.6, 129.2, 128.5, 128.1, 121.5, 120.9, 117.6; FT-IR (KBr) 3426, 3097, 1645, 1631, 1567, 1512, 1491, 1287, 1250, 1146, 1027, 896 cm^{-1}. Anal. Calcd. for $C_{13}H_{11}N_5$: C, 65.81; H, 4.67; N, 29.52. Found: C, 65.88; H, 4.64; N, 29.48.



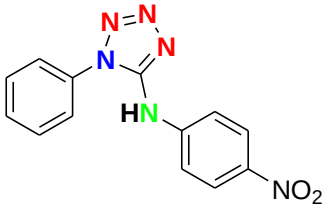
2-Phenyl-N-p-tolyl-2*H*-tetrazol-5-amine 3b: White solid; yield 95%; mp 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 6.75 (m, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 137.5, 135.6, 134.4, 132.8, 129.7, 128.8, 126.5, 124.5, 117.9, 110.1, 24.8; FT-IR (KBr) 3153, 2919, 2852, 1572, 1486, 1455, 1408, 1384, 1284, 1260, 1100, 1017 cm^{-1}. Anal. Calcd. for $C_{14}H_{13}N_5$: C, 66.92; H, 5.21; N, 27.87. Found: C, 66.99; H, 5.19; N, 27.82.



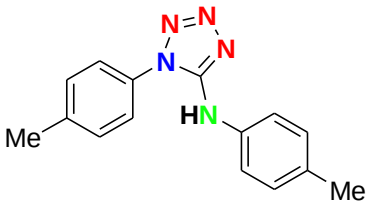
N-(4-Methoxyphenyl)-1-phenyl-1*H*-tetrazol-5-amine 3c: White solid; yield 95%; mp 111-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.22 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.88-6.61 (m, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 142.9, 133.7, 132.6, 129.7, 129.5, 129.3, 126.1, 121.4, 55.0; FT-IR (KBr) 3154, 2922, 2862, 1607, 1581, 1948, 1453, 1410, 1389, 1388, 1268, 1155, 1018 cm^{-1}. Anal. Calcd. for $C_{14}H_{13}N_5O$: C, 62.91; H, 4.90; N, 26.20; O, 5.99. Found: C, 63.03; H, 4.88; N, 26.14.



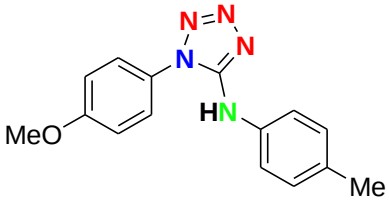
N-(4-Chlorophenyl)-1-phenyl-1*H*-tetrazol-5-amine, 3d (Ref. 32): Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; yield 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.48 (m, 4H), 7.25 (d, *J* = 6.8 Hz, 3H), 7.16 (d, *J* = 8.8 Hz, 2H), 5.96 (br s, 1NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 137.0, 132.3, 128.3, 128.1, 127.8, 127.0, 124.7, 118.1; FT-IR (KBr) 3420, 3090, 1645, 1601, 1590, 1489, 1125, 1036, 941, 854, 788, 612 cm^{-1}. Anal. Calcd. for $C_{13}H_{10}ClN_5$: C, 57.47; H, 3.71; Cl, 13.05; N, 25.78. Found: C, 57.59; H, 3.69; N, 25.71.



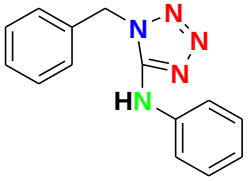
N-(4-Nitrophenyl)-2-phenyl-2*H*-tetrazol-5-amine 3e: White solid; yield 72%; mp 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.05 (m, 2H), 7.78-7.76 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.26-7.05 (m, 3H), 6.61 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 146.3, 143.8, 141.8, 137.3, 127.1, 125.6, 121.0, 120.7; FT-IR (KBr) 3278, 3177, 3058, 2958, 2863, 1633, 1545, 1499, 1422, 1377, 1292, 1195, 1114, 1023 cm^{-1}. Anal. Calcd. for $C_{13}H_{10}N_6O_2$: C, 55.32; H, 3.57; N, 29.77; O, 11.34. Found: C, 55.46; H, 3.55; N, 29.70.



N,1-Dip-tolyl-1*H*-tetrazol-5-amine 3f: White solid; yield 96%; mp 97-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8 Hz, 2H), 7.15-7.07 (m, 4H), 6.96 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ146.9, 139.5, 138.3, 137.7, 135.8, 132.6, 131.9, 130.7, 127.4, 124.3, 123.8, 117.8, 110.1, 21.7, 20.0; FT-IR (KBr) 3253, 2920, 2823, 1644, 1436, 1407, 1384, 1261, 1206, 1172, 1012 cm^{-1}. Anal. Calcd. for $C_{15}H_{15}N_5$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.97; H, 5.69; N, 26.34.



1-(4-Methoxyphenyl)-N-*p*-tolyl-1*H*-tetrazol-5-amine 3g: Analytical TLC on silica gel, 3:7 ethyl acetate/hexane R_f = 0.7; yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.22 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 1H), 6.61 (br s, 2H), 3.78 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 147.6, 144.1, 139.3, 135.6, 127.9, 127.3, 122.4, 118.0, 114.5, 107.7, 55.9, 22.3; FT-IR (KBr) 3283, 3133, 2950, 2839, 2144, 1630, 1516, 1484, 1422, 1408, 1329, 1276, 1243, 1204, 1147, 1025 cm^{-1}. Anal. Calcd. for $C_{15}H_{15}N_5O$: C, 64.04; H, 5.37; N, 24.90; O, 5.69. Found: C, 64.14; H, 5.36; N, 24.85.



N-Benzyl-1-phenyl-1*H*-tetrazol-5-amine 3h: Analytical TLC on silica gel, 4:6 ethyl acetate/hexane R_f = 0.7; yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 6.8 Hz, 3H), 7.49-7.39 (m, 4H), 6.85 (d,

J = 8.8 Hz, 3H), 6.02 (br s, 1NH), 5.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 132.8, 131.6, 129.2, 128.5, 128.1, 121.5, 120.9, 117.6, 52.6; FT-IR (KBr) 3402, 3087, 2852, 1657, 1601, 1587, 1512, 1485, 1278, 1212, 1136, 1027, 876 cm^{-1}. Anal. Calcd. for $C_{14}H_{13}N_5$: C, 66.92; H, 5.21; N, 27.87. Found: C, 67.00; H, 5.19; N, 27.81.

Conclusion

In summary, the construction of substituted tetrazoles from isothiocyanates using copper catalysis under mild reaction conditions has been accomplished. It is clean and efficient tandem three component strategy. No regioselectivity have been identified in case of electron withdrawing groups on phenyl ring, while phenyl ring having electron releasing groups have provided target products in good yield. Decent yield was observed in case of aliphatic amines. As per mechanism the proposed reaction involves simultaneously addition/desulphurization/nucleophilic substitution/electro cyclization. In order to extend our chemistry we have also developed *C-N* cross-coupling approach using copper catalyst. *C-N* cross-coupled products could be obtained in moderate to good yields from respective starting precursors under standardized reaction conditions.

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Supplementary Information

Materials, methods, experimental procedure, characterization data, and NMR spectra (^{1}H and ^{13}C) of the products are available in the website http://nopr.niscair.res.in/handle/123456789/58776.

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