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REGULAR ARTICLE

Cobalt-promoted regioselective preparation of aryl tetrazole amines

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Abstract. A highly general, efficient and simple methodology for the regioselective synthesis of aryl tetrazole amines has been explored. The present method involves consecutive desulphurization and *C-N* cross-coupling reaction. Cheap, readily available and air stable cobalt catalyst has been used for this methodology. In addition, the substrate scope has been demonstrated.

Keywords. Aryl tetrazole amines; regioselective synthesis; desulphurization; *C-N* cross-coupling reaction; consecutive reaction.

1. Introduction

Very important heterocyclic class tetrazole is found in compounds (Figure 1) having anti-asthmatic,[1] antiviral and anti-inflammatory[2] and anti-neoplastic[3] activities. In addition, tetrazoles are also used as ligands in coordination chemistry and they show medicinal applications.[4] Therefore synthetic organic chemists have drawn immense attention for the preparation of substituted tetrazoles. In this connection, researchers have developed traditional methods for the construction of tetrazoles. Especially, addition of $NaNO_2$ to amino-guanidine,[5] addition of NaN_3 to carbodiimides or cyanamides,[6] reaction of amines with a leaving group in tetrazoles 5-position,[7] nucleophilic substitution by N_3^- of (a) chlorine in α-chloroformamidines[8] and (b) sulfur from thioureas in presence of mercury[9] or lead salts[5c] or iodine.[10] 5-Substituted-1*H*-tetrazoles are also prepared from the reaction between corresponding nitriles and NaN_3 *via* [3+2] cycloaddition using Zn (II) salts[11] and ZnO nanocrystal.[12] Later, substituted tetrazoles have been prepared from the reaction between substituted nitriles and $TMSN_3$ using TBAF[13] and Copper catalyst.[14] Often these methods use either toxic reagents or harsh reaction conditions such as high temperature, toxic reagents, unavailable starting precursors and lack of regioselectivity.[15] To overcome the above-mentioned drawbacks we wish to develop a methodology for the synthesis of substituted tetrazoles from thiourea using cobalt *via* desulphurization/substitution/electro cyclization/*C-N* cross-coupling reaction. To the best of our knowledge, no report is available for the synthesis of tetrazoles from thiourea using cobalt.

2. Experimental

2.1 *General information*

CS_2, $CoCl_2 \cdot 6H_2O$, $CoSO_4 \cdot H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, Et_3N, Pyridine, sodium bicarbonate and ammonia were purchased from Aldrich and used without further purification. The solvents were purchased and dried according to standard procedure prior to use.[11]H NMR(400 MHz) spectra were recorded with a Varian 400 spectrometer. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum one FT-IR spectrometer. Elemental analyses were recorded with Perkin Elmer CHNS analyzer. VKSI Medico Centrifuge was used

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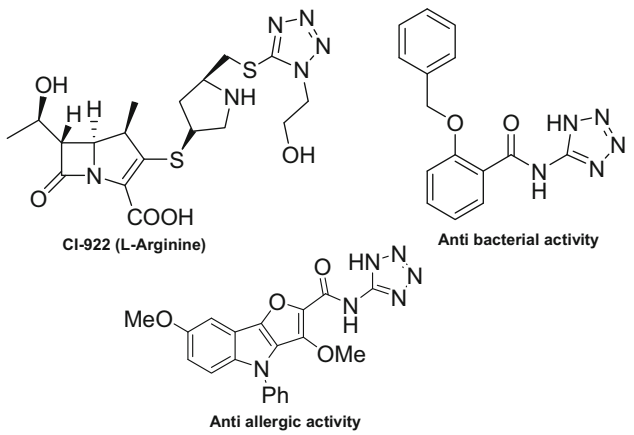
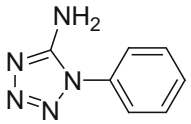


Figure 1. Some of the biological important aminotetrazoles.

for our experimental procedure for the synthesis of resulting compounds.

2.2 *Representative experimental procedure for the synthesis of Phenyl tetrazole amine (***1a***)*

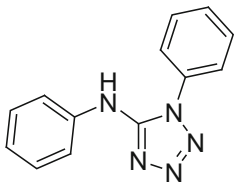
To a stirred solution of DMSO (2–3 mL), thiourea (1 mmol, 76 mg) was added in slowly and followed by Et_3N (1 mmol, 101 mg) and $CoCl_2 \cdot 6H_2O$ (50 mol%, 119 mg) at room temperature. The whole reaction mixture stirred for one hour (until black colour) at room temperature. The reaction was monitored by TLC. After completion of the reaction (monitored by TLC), add NaN_3 (2 mmol, 130 mg) and the reaction mixture stirred for 1 h. Later, iodobenzene (1 mmol, 204 mg), Cs_2CO_3 (1 mmol, 325 mg), $CoCl_2 \cdot H_2O$ (10 mol%, 23.8 mg) and 1,10-phenanthroline (20 mol%, 36 mg) were added consecutively for several min and the reaction mixture was stirred for 18 h at 85 °C. The progress of the reaction was investigated by TLC (5% ethylacetate in hexane). After completion of the reaction, the reaction mixture was transferred into centrifuge tubes and centrifuged for 10 min. Black solid settled at the bottom of centrifuge tubes. The clear solution was concentrated 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 **1a** as a white solid.



1-Phenyl-1H-tetrazol-5-amine (**1a**): Analytical TLC on silica gel, 3:7 ethyl acetate/hexane (R_f 0.6). Yield 296 mg (92%), White solid, M.p. 167–168 °C (Lit[33] M.p. 162–163 °C). ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.97 (2H, br. s, NH_2); 7.61–7.57 (m, 2H, H Ar); 7.40–7.28 (m, 2H, H Ar); 7.21–7.17 (m, 1H, H Ar). ^{13}C NMR (100 MHz, $CDCl_3$), δ, ppm: 137.8; 130.9; 130.6; 130.1; 128.9. FT-IR (KBr) cm^{-1}: 3987; 3350; 3064; 1693; 1587; 1250; 1148; 1070; 909; 764. Anal. Calcd. for $C_7H_7N_5$: C, 52.17; H, 4.38; N, 43.45. Found: C, 52.30; H, 4.34; N, 43.36.

2.3 *General procedure for the synthesis of diphenyl tetrazole amine (***1b***)*

To a stirred solution of DMSO (2–3 mL), thiourea (1 mmol, 76 mg) was added slowly, followed by Et_3N (1 mmol, 101 mg) and $CoCl_2 \cdot 6H_2O$ (50 mol%, 119 mg) was added at room temperature. The whole reaction mixture stirred for one hour (until getting the black colour) at room temperature. The reaction was monitored by TLC. After completion of the reaction (monitored by TLC), to this, NaN_3 (2 mmol, 130 mg) was added. Then, the reaction mixture stirred for 1 h. Later, iodobenzene (2 mmol, 408 mg), Cs_2CO_3 (1.5 mmol, 485 mg), $CoCl_2 \cdot H_2O$ (10 mol%, 23.8 mg) and 1,10-phenanthroline (20 mol%, 36 mg) were added consecutively for several min and the reaction mixture was stirred for 24 h at 115 °C. The progress of the reaction was investigated by TLC (5% ethylacetate in hexane). After completion of the reaction, the reaction mixture was transferred into centrifuged tubes and the mixture was centrifuged for 10 min by using centrifugation machine. Black colour solid settled at the bottom of centrifuged tubes. The clear solution 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 **1b** as a white solid.

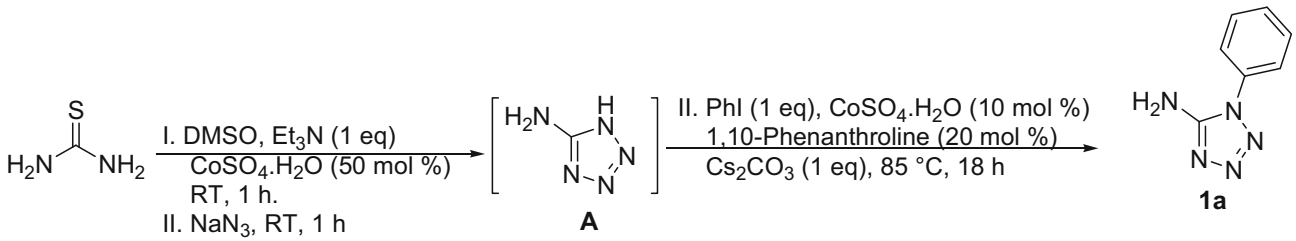


N,1-Diphenyl-1*H*-tetrazol-5-amine**1b**: Analytical TLC on silica gel, 3:7 ethyl acetate/hexane (R_f, 0.7); yield 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.41 (m, 7H), 6.85 (d, J = 8.8 Hz, 3H), 6.02 (br s, 1NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 132.8, 131.6, 129.2, 128.5, 128.1, 121.5, 120.9, 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, 65.90; H, 4.65; N, 29.45.

3. Results and Discussion

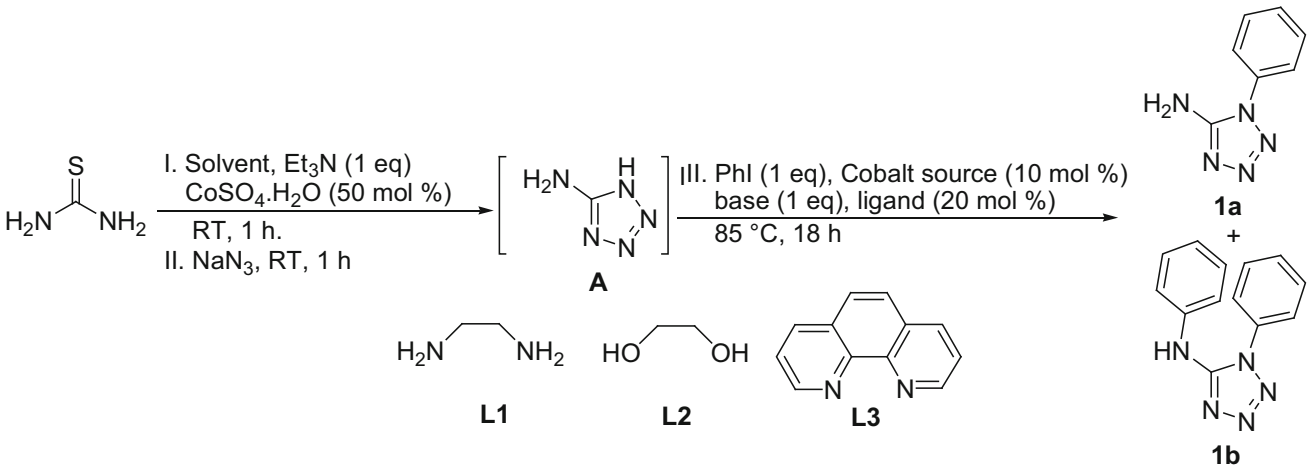
As shown below Scheme 1, thiourea gave amino tetrazole **A** as intermediate *via* desulphurization followed by cycloaddition. The intermediate **A** gave *C*-*N* cross-coupled product with aryl iodide under mild reaction conditions.

Initially, the optimization reaction condition was performed using readily available thiourea as a model substrate with various solvents, bases, ligands and cobalt sources. We were glad to observe that the reaction could give target product **1a** in complete conversion



Scheme 1. Pathway for the synthesis of phenyltetrazoleamine.

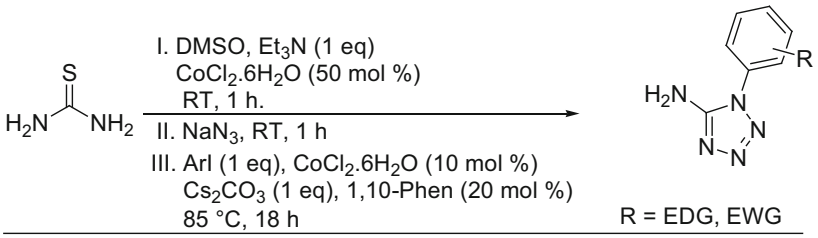
Table 1. Optimization for the synthesis of phenyltetrazoleamine[a].

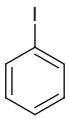
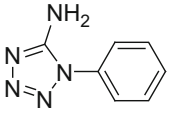
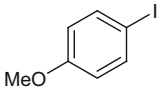
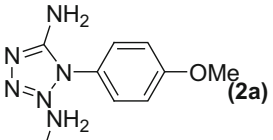
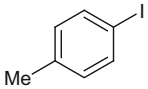
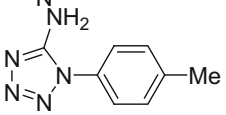
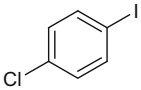
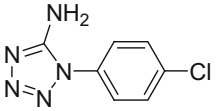
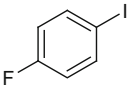
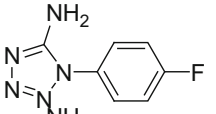
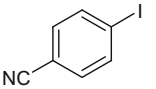
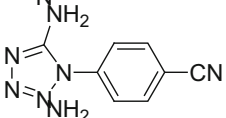
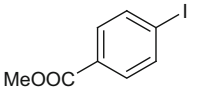
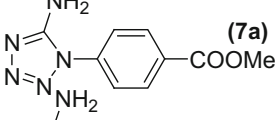
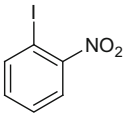
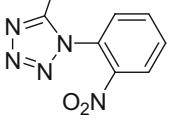
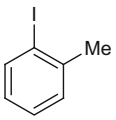
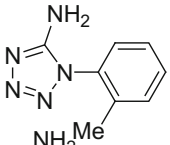
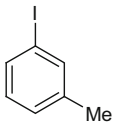
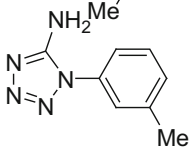
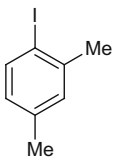
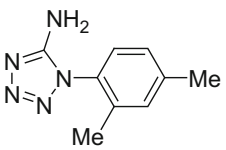


Entry	Solvent	Cobalt source	Base	Ligand	Conversion (%)[b]		
					A	**1a**	**1b**
1	EtOH	$CoCl_2 \cdot 6H_2O$	$K_3PO_4 \cdot 3H_2O$	L3	100	n.d.	n.d.
2	EtOAc	$CoCl_2 \cdot 6H_2O$	$K_3PO_4 \cdot 3H_2O$	L3	100	n.d.	n.d.
3	DMF	$CoCl_2 \cdot 6H_2O$	$K_3PO_4 \cdot 3H_2O$	L3	35	65	n.d.
4	DMSO	$CoCl_2 \cdot 6H_2O$	$K_3PO_4 \cdot 3H_2O$	L3	30	70	n.d.
5	DMSO	$CoCl_2 \cdot 6H_2O$	KOH	L3	20	80	n.d.
6	DMSO	$CoCl_2 \cdot 6H_2O$	K_2CO_3	L3	45	55	n.d.
7	DMSO	$CoCl_2 \cdot 6H_2O$	Cs_2CO_3	L3	n.d.	100	n.d.
8	DMSO	$CoCl_2 \cdot 6H_2O$	Cs_2CO_3	L1	80	20	n.d.
9	DMSO	$CoCl_2 \cdot 6H_2O$	Cs_2CO_3	L2	60	40	n.d.
10	DMSO	$CoSO_4 \cdot H_2O$	Cs_2CO_3	L3	n.d.	100	n.d.
11	DMSO	$Co(NO_3)_2 \cdot 6H_2O$	Cs_2CO_3	L3	n.d.	100	n.d.
12[c]	DMSO	$CoSO_4 \cdot H_2O$	Cs_2CO_3	L3	45	55	n.d.
13[d]	DMSO	$CoSO_4 \cdot H_2O$	Cs_2CO_3	L3	50	50	n.d.
14	DMSO	$CoSO_4 \cdot H_2O$	Cs_2CO_3	-	80	20	n.d.
15	DMSO	-	Cs_2CO_3	-	100	n.d.	n.d.
16[e]	DMSO	$CoSO_4 \cdot H_2O$	Cs_2CO_3	L3	n.d.	100	n.d.
17[f]	DMSO	$CoSO_4 \cdot H_2O$	Cs_2CO_3	L3	n.d.	85	15
18[g]	DMSO	$CoSO_4 \cdot H_2O$	Cs_2CO_3	L3	n.d.	50	50
19[h]	DMSO	$CoSO_4 \cdot H_2O$	Cs_2CO_3	L3	n.d.	n.d	100

[a]Reaction conditions: Thiourea (1 mmol), solvent (2 mL), Et_3N (1 eq), $CoSO_4 \cdot H_2O$ (50 mol%), 1 h, room temperature, then, NaN_3 (2 mmol), room temperature, then, iodo benzene (1 mmol), catalyst (10 mol%), ligand (20 mol%), base (1 mmol), 18 h, 85 °C. [b]Conversion was confirmed crude 1H NMR. [c]Cobalt source (5 mol%) used. [d]Cs_2CO_3 (0.5 equiv) used. [e]Iodobenzene (2 eq) was used. [f] Iodobenzene (2 eq) and temp 100 °C were used. [g]Iodobenzene (2 eq), temp. 100 °C and Cs_2CO_3 (1.5 eq) were used. [h]Iodobenzene (2 eq), temp 115 °C and Cs_2CO_3 (1.5 eq) were used (n.d. for not detected).

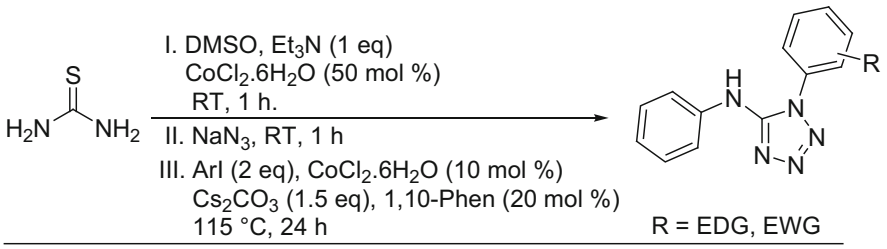
Table 2. Substrate scope for the synthesis of substituted aryltetrazoleamines[a].

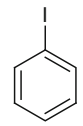
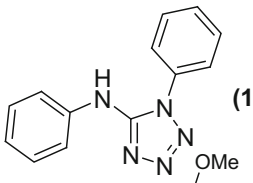
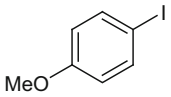
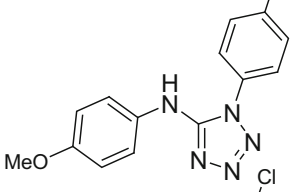
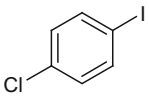
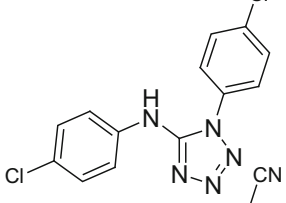
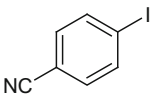
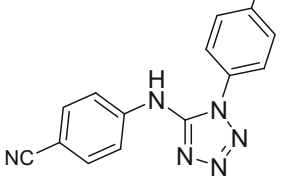
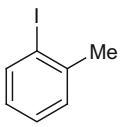
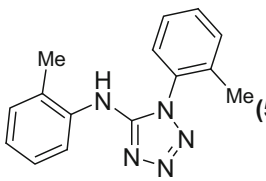
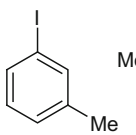
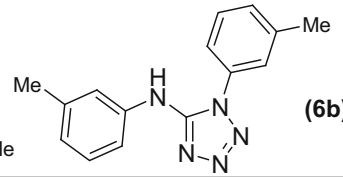


Entry	Substrate	Product	Yield[b]
1		 **(1a)**	95
2		 **(2a)**	98
3		 **(3a)**	95
4		 **(4a)**	84
5		 **(5a)**	76
6		 **(6a)**	47
7		 **(7a)**	43
8		 **(8a)**	56
9		 **(9a)**	83
10		 **(10a)**	90
11		 **(11a)**	83

[a]Reaction conditions: Thiourea (1 mmol), DMSO (2 mL), Et_3N (1 eq), $CoCl_2 \cdot 6H_2O$ (50 mol%), 1 h, room temperature, then, then, NaN_3 (2 mmol), room temperature, 1 h, then, $CoCl_2 \cdot 6H_2O$ (10 mol%), ArI (1 mmol), ligand (20 mol%), Cs_2CO_3 (1 mmol), 18 h, 85 °C. [b]Isolated yield.

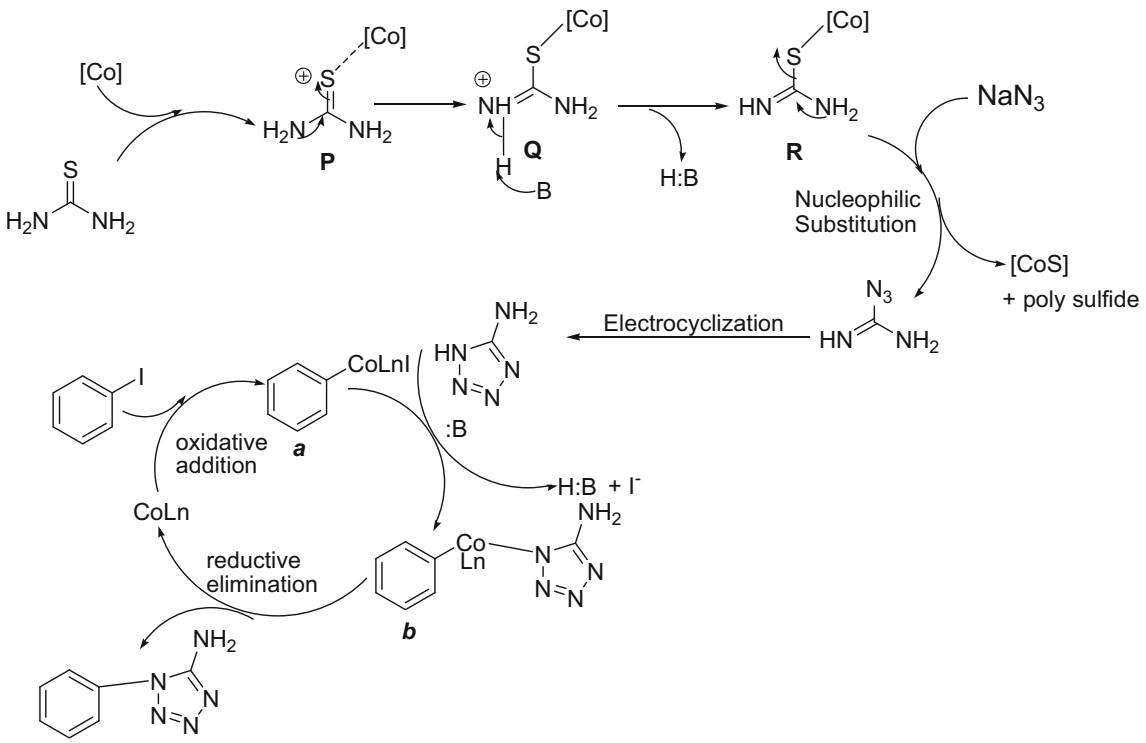
Table 3. Substrate scope for the synthesis of substituted diaryltetrazoleamines[a].



Entry	Substrate	Product		Yield[b]
1			**(1b)**	95
2			**(2b)**	95
3			**(3b)**	74
4			**(4b)**	43
5			**(5b)**	78
6			**(6b)**	82

[a]Reaction conditions: Thiourea (1 mmol), DMSO (2 mL), Et_3N (1 eq), $CoCl_2 \cdot 6H_2O$ (50 mol%), 1 h, room temperature, then NaN_3 (2 mmol, 130 mg), room temperature, 1 h, then Aryl iodide (2 mmol), $CoCl_2 \cdot 6H_2O$ (10 mol%), ligand (20 mol%), Cs_2CO_3 (1.5 mmol), 24 h, 115 °C. [b]Isolated yield.

using 10 mol% cobalt source, 20 mol% Ligand (1,10-Phenanthroline) and 1 equiv. Cs_2CO_3 at 85 °C (Table 1, entries 7 & 10–11). In case of solvent optimization, DMSO was effective to provide the target product **1a**. Other solvents such as EtOH and EtOAc could obtain amino tetrazole **A** in complete conversion, but it didn't give target product **1a** (Table 1, entries 1, 2). The reaction using Cs_2CO_3 exhibited greater reactivity compared to

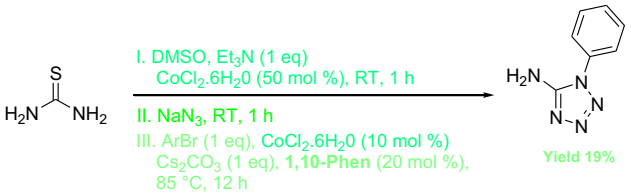


Scheme 2. Proposed mechanism.

that of $K_3PO_4 \cdot 3H_2O$, K_2CO_3 and KOH. In a set of ligands **L1**–**L3** screened, **L3** (Table 1, entry 7) was found to be the most effective in comparison to **L1, L2** (Table 1, entries 8–9). Cobalt sources ($CoCl_2 \cdot 6H_2O$, $CoSO_4 \cdot H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$) exhibited a similar catalytic activity (Table 1, entries 7 & 10,11). Lowering the amount of base (1 equiv) or the cobalt source (5 mol%) led to the *N*-arylation to afford target product in less conversion (Table 1, entries 12–13). Control experiments without ligand (Table 1, entry 14) and the cobalt source (Table 1, entry 15) confirmed that the formation of final product was not observed. Very interestingly, the above reaction condition couldn't give diphenyltetrazolamine **1b**. Therefore, we have focused for the synthesis of diphenyltetrazolamine from thiourea. In this connection, the standardization was done and the reaction could give product **1b** in complete conversion using iodobenzene (2 eq), Cs_2CO_3 (1.5 eq) at 115 °C (Table 1, entry 19).

Having the optimal conditions studied, the scope of the protocol was next explored to substituted phenyltetrazoleamines (Table 2). The substrates having both electron donating and electron withdrawing groups on the aryl rings could give their respective target products **1a**–**11a** in moderate to high yield. Aryl iodide having electron donating substituents (4-Me, 2-Me, 4-OMe and 2, 4-diMe) showed greater reactivity compared to that of bearing electron withdrawing substituents (4-Cl, 4-F, 4-CN and 4-COOMe groups). The phenyl ring having electron donating groups such as 4-methyl, 4-methoxy could give their respective aromatic cyanamides **2a, 3a** in 95–98% yield. The unsubstituted phenyl ring also gave target product **1a** in excellent yield. Electron withdrawing groups such as 4-fluoro and 4-chloro substituents provided their target products **4a** and **5a** in 76% and 84% yields, respectively. Aryl ring bearing other strong electron withdrawing substituents like nitrile, ester and nitro could give target products **6a**–**8a** in moderate yield. Aryl iodides bearing ortho and meta-substituted methyl groups readily underwent the reaction to give final products **9a**, **10a** in 83–90% yields. Di-Methyl substituent on aryl ring gave target product in 83% yield. In addition, we explored the construction of diaryltetrazolamine under optimized reaction conditions (Table 3). Aryl iodides containing both electron donating and electron withdrawing groups as well as disubstituted groups readily underwent the reaction to provide target products **1b**–**6b** in 43–95% yields.

The mechanism for the formation of substituted tetrazoles from thiourea is shown in below Scheme 2. We propose the mechanism from the experimental evidence and literature reports.[18d-i] Cobalt can co-ordinate with thiourea, followed by removal of protons to afford intermediate **R** *via* intermediates **P** and **Q**. The intermediate **R** may provide unsubstituted tetrazoles along with



Scheme 3. Reaction with Aryl bromide.

byproduct CoS and polysulphide[16] *via* desulphurization/substitution/electrocyclization.[17] On the other hand, oxidative addition of aryl iodide with cobalt complex can lead to the formation of ***a*** which can undergo intermolecular *C-N* cross-coupling reaction[18] with unsubstituted tetrazoles using the base to give the intermediate ***b*** that can complete the catalytic cycle by reductive elimination to get target product arylamino tetrazoles. In addition, the atomic absorption of the aqueous solution active cobalt salt, $CoSO_4 \cdot H_2O$ was measured to reveal the presence trace of copper[19a] which was observed in the iron-catalyzed[19b] cross-coupling reactions as the active catalyst. However, in the present protocol, no trace of copper was detected with the detection limit of 1 ppm. This experiment clearly suggests that copper doesn't involve in the present methodology.

In addition, we have also tried the reaction with aryl bromide under optimized reaction conditions (Scheme 3). Unfortunately, the reaction could give target product in 19% yield only. However, no reaction could occur with aryl chloride under optimized reaction conditions.

4. Conclusions

In conclusion, we have developed a methodology for the regioselective synthesis of aryltetrazoleamines from thiourea in one pot multistep reaction. It is a general, efficient and easy method. Although the overall isolated yields look moderate, considering that the reactions are multi processes, the yields are in fact good to excellent. Many reports are available for the preparation of aminotetrazoles. However, the simplicity, environmental acceptability and cost-effectiveness of the cobalt make this method more practical. The reactions involved desulphurization followed by intermolecular *C-N* cross-coupling reaction.

Supplementary Information (SI)

Experimental data of all synthesized compounds and ^1H & ^{13}C NMR scanned copies are available at www.ias.ac.in/chemsci.

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