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# Palladium-catalyzed *N*-Arylation of 1-substituted-1*H*-tetrazol-5-amines

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ABSTRACT

A palladium-catalyzed *N*-arylation of 1-substituted-1*H*-tetrazol-5-amines has been described for the first time. The reaction provides good yields of desired products with broad substrate scope and good functional group tolerance.



## 1. Introduction

Nitrogen-heterocyclic scaffolds are one of the most common structural motifs in pharmaceuticals [1]. As such 5-aminotetrazole is an important heterocyclic moiety of many bioactive compounds (Fig. 1). Substituted 5-aminotetrazoles exhibit versatile biological activities such as antiallergic [2], antiinflammatory [3], antidiabetic [4], antineoplastic [5] and antibiotic activity [6]. Moreover, 5-aminotetrazoles provide excellent inhibition against the corrosion of stainless steel [7] and are used as cholecystokinin B (CCK-B) receptor antagonists [8] and ligands in coordination chemistry [9]. Recent studies have described the use of 5-aminotetrazoles as photoprecursors of reactive intermediates [10].

Two main synthetic strategies for the synthesis of N5-substituted 5-aminotetrazoles are reported in the literature. The classical approach utilizes the formation of the tetrazole ring from *N*-substituted acyclic precursors (Fig. 2) [11,12], and converse approach involves N5-amino group functionalization of the previously formed 5-aminotetrazoles [2,13,14]. Recently, Bollikolla and co-workers developed copper-catalyzed double arylation of 5-aminotetrazole for the synthesis of substituted 1-aryl-5-(*N*-arylamino)-tetrazoles [15].

Palladium-catalyzed arylation of amines has emerged as powerful tool in organic synthesis and medicinal chemistry [16,17]. Of particular interest is palladium catalyzed arylation of primary amine derivatives of five- and six-membered heterocyclic compounds, which have been challenging substrates [18,19]. As we have recently demonstrated, electrostatic map potential of 5-aminotetrazoles shows that most of the electron density is located in the tetrazole ring while the amino group is in the blue region. This indicates that amino group is electron deficient and therefore less nucleophilic [20].

Herein, we report the first example of a palladium-catalyzed N-arylation of 1-substituted-1*H*-tetrazol-5-amines.

## 2. Results and discussion

In order to optimize the reaction condition, we began our study by choosing readily available 1-benzyl-1*H*-tetrazol-5-amine **1a** and bromobenzene **2a** as the model substrates with catalytic amount of $Pd_2(dba)_3$ (10 mol % Pd with respect to **2a**) as source of palladium and NaO*t*-Bu (1.2 equiv) as a base, in toluene at 105 °C. An excess amount of the 5-aminotetrazole substrate was used in the reaction in order to prevent the formation of diarylated product. Using biaryl phosphane ligand JohnPhos (20 mol % with respect to **2a**) the desired product **3a** was obtained in 8% isolated yield after 24 h reaction time (Table 1, entry 1). Unfortunately, the reaction with SPhos was inefficient (Table 1, entry 2). When the

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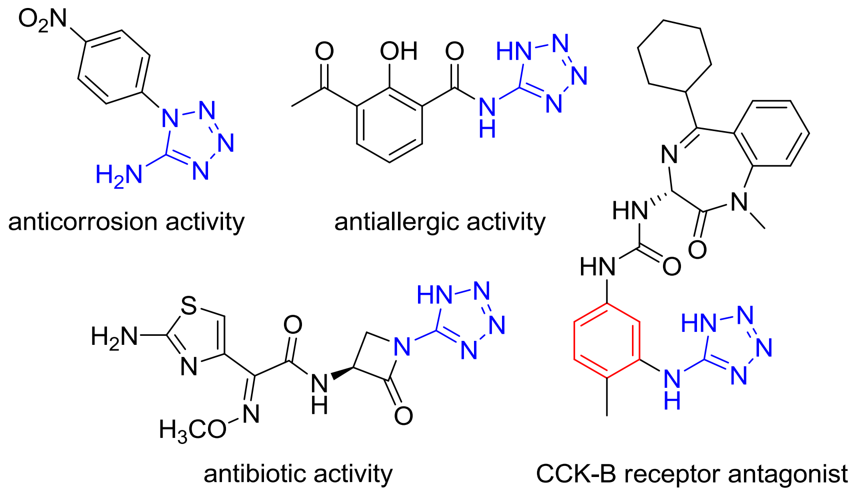



**Fig. 1.** Important molecules containing 5-aminotetrazole moiety.

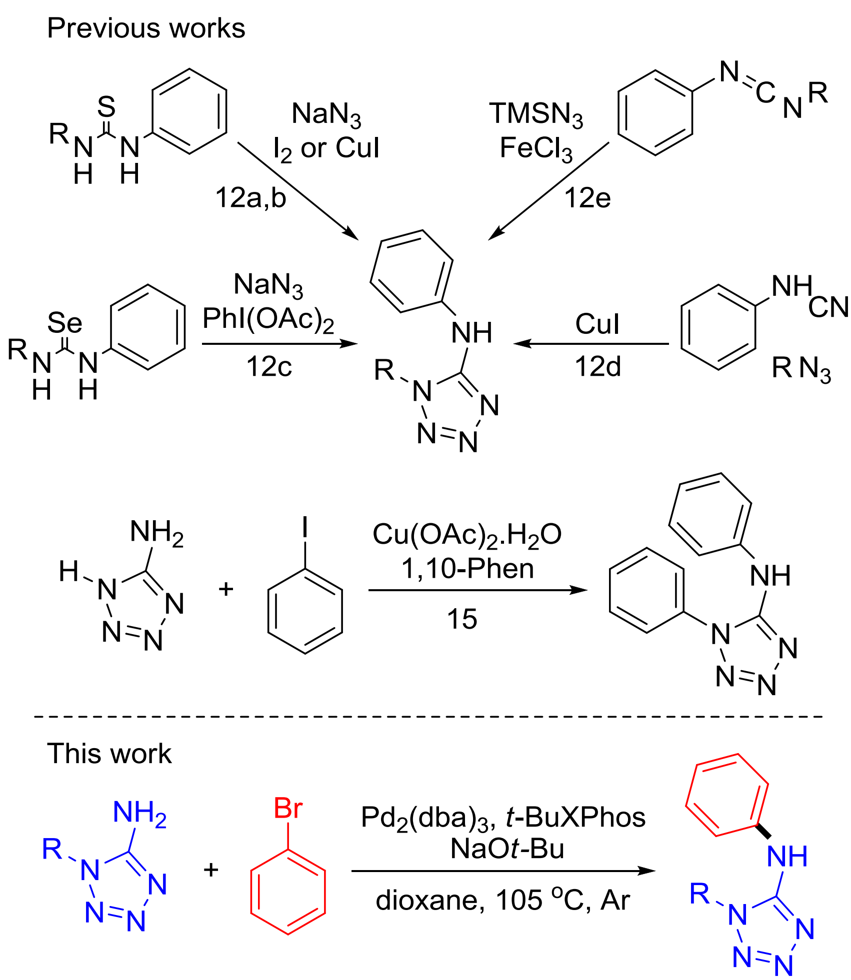
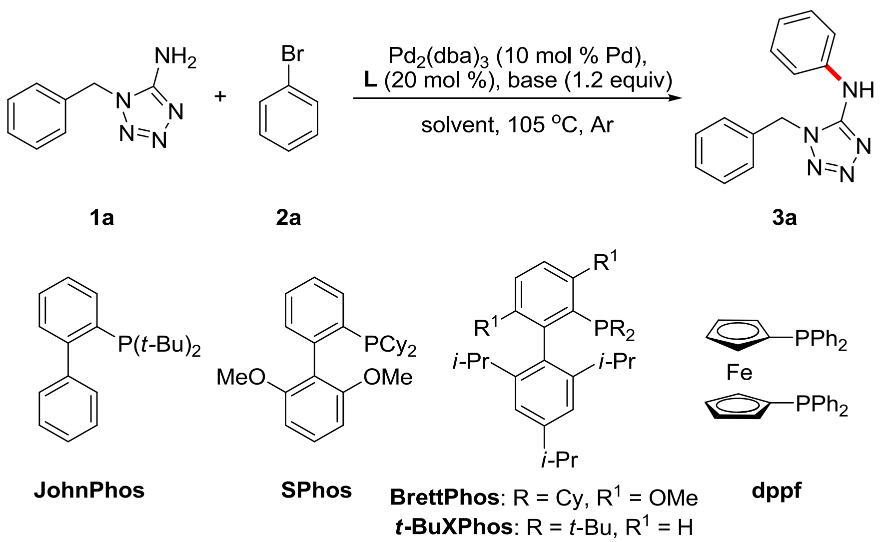



**Fig. 2.** Synthetic methods for the preparation of *N*-aryl 1-substituted-1*H*-tetrazol-5-amines.

reaction was carried out in 1,4-dioxane as solvent using JohnPhos as ligand under the same conditions, 34% of **3a** was isolated (Table 1, entry 3). To further improve the yield, different ligands were evaluated (Table 1, entries 4–6). With BrettPhos and *t*-BuXPhos significantly improved yields were observed (Table 1, entries 4 and 5). However, dppf was found to be unsuitable for the reaction (Table 1, entry 6). Moreover, shortening the reaction time from 24 h to 10 h was proven to be detrimental (Table 1, entry 7 vs entry 5). Notably, screening of the base revealed that $K_2CO_3$ was also very effective (Table 1, entry 8). On the other hand, $Cs_2CO_3$ was less effective in this reaction and resulted in lower yield (Table 1, entry 9).

**Table 1**
Optimization of the palladium-catalyzed *N*-arylation reaction conditions[a].




| entry | ligand | base | solvent | time (h) | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | JohnPhos | NaO*t*-Bu | PhMe | 24 | 8 |
| 2 | SPhos | NaO*t*-Bu | PhMe | 24 | – |
| 3 | JohnPhos | NaO*t*-Bu | dioxane | 24 | 34 |
| 4 | BrettPhos | NaO*t*-Bu | dioxane | 24 | 82 |
| **5** | ***t*-BuXPhos** | **NaO*t*-Bu** | **dioxane** | **24** | **91** |
| 6 | dppf | NaO*t*-Bu | dioxane | 24 | 18 |
| 7 | *t*-BuXPhos | NaO*t*-Bu | dioxane | 10 | 40 |
| 8 | *t*-BuXPhos | $K_2CO_3$ | dioxane | 24 | 90 |
| 9 | *t*-BuXPhos | $Cs_2CO_3$ | dioxane | 24 | 79 |

[a] Reactions were performed in a flame-dried closed reaction tube. $Pd_2(dba)_3$ (10 mol % Pd), ligand (20 mol %) and base (1.2 equiv) were added to the reaction tube followed by the solvent. The mixture was stirred under an inert atmosphere at room temperature for 5 min, after which **2a** (1.0 equiv) and **1a** (1.2 equiv) were added. The tube was sealed and the mixture was heated at 105 °C in an oil bath for the indicated reaction time.
[b] Isolated yield.

With the optimized reaction conditions in hand, we examined the substrate scope with respect to arylbromides.

As shown in Table 2, a series of arylbromides, including those with electron-donating group (–OMe) and others with electron-withdrawing groups (–$NO_2$, –CN, –$CO_2$Me, –CHO, and –$COCH_3$) were transformed into the desired products in moderate to good yields (Table 2, **3b**-**3g**), providing a potential point for further functionalization of the coupling products. In the cases of substrates with sensitive functional groups, $K_2CO_3$ was used as base (Table 2, **3d**-**3g**). In addition, with 1-bromo-4-chlorobenzene and 1-bromo-3-chlorobenzene excellent selectivity was observed (Table 2, **3h** and **3i**). Moreover, when sterically demanding 2-bromo-5-chlorotoluene was employed as substrate, the reaction provided the corresponding product **3j** in good yield. The scope of this method was further investigated by utilizing heteroaryl bromides. The present method is also applicable to 3-bromopyridine and corresponding product **3l** was obtained in 51% yield, while there was no reaction with 2-bromothiophene (Tables 2, **3k**). Notably, the reaction could be scaled up to 1 mmol scale, yielding **3a** in 91% isolated yield.

Next, we examined the substrate scope with respect to 1-substituted-1*H*-tetrazol-5-amines and arylbromides. As shown in Table 3, 1-(4-methoxybenzyl)-1*H*-tetrazol-5-amine **1b** reacted smoothly with both electron-poor and electron-rich aryl bromides and afford the corresponding desired substituted products **3m**-**3r** in moderate to excellent yields (54–95%). In addition, 4-((5-amino-1*H*-tetrazol-1-yl)methyl)benzonitrile **1c** and 1-propyl-1*H*-tetrazol-5-amine **1d** reacted with bromobenzene **2a** affording **3s** and **3t** in moderate yields. Furthermore, 1-phenyl-1*H*-tetrazol-5-amine **1e** was also reacted with **2a** and gave the desired product **3u** in 71% yield.

The reaction conditions also proved applicable to the coupling reaction of 1-benzyl-1H-tetrazol-5-amine **1a** with iodobenzene **4** and chlorobenzene **5**, and to a lesser extent to the coupling reaction of **1a** and phenyl trifluoromethanesulfonate **6** (Scheme 1).

Finally, as an expansion of this study, we explored the removal of benzyl group [21] in order to obtain *N*-phenyl-1*H*-tetrazol-5-amine. Under hydrogen atmosphere (1atm), **3a** was converted into **7a** in almost quantitative yield, using Pd/C (5 mol % Pd) as a catalyst (Scheme 2).

## 3. Conclusions

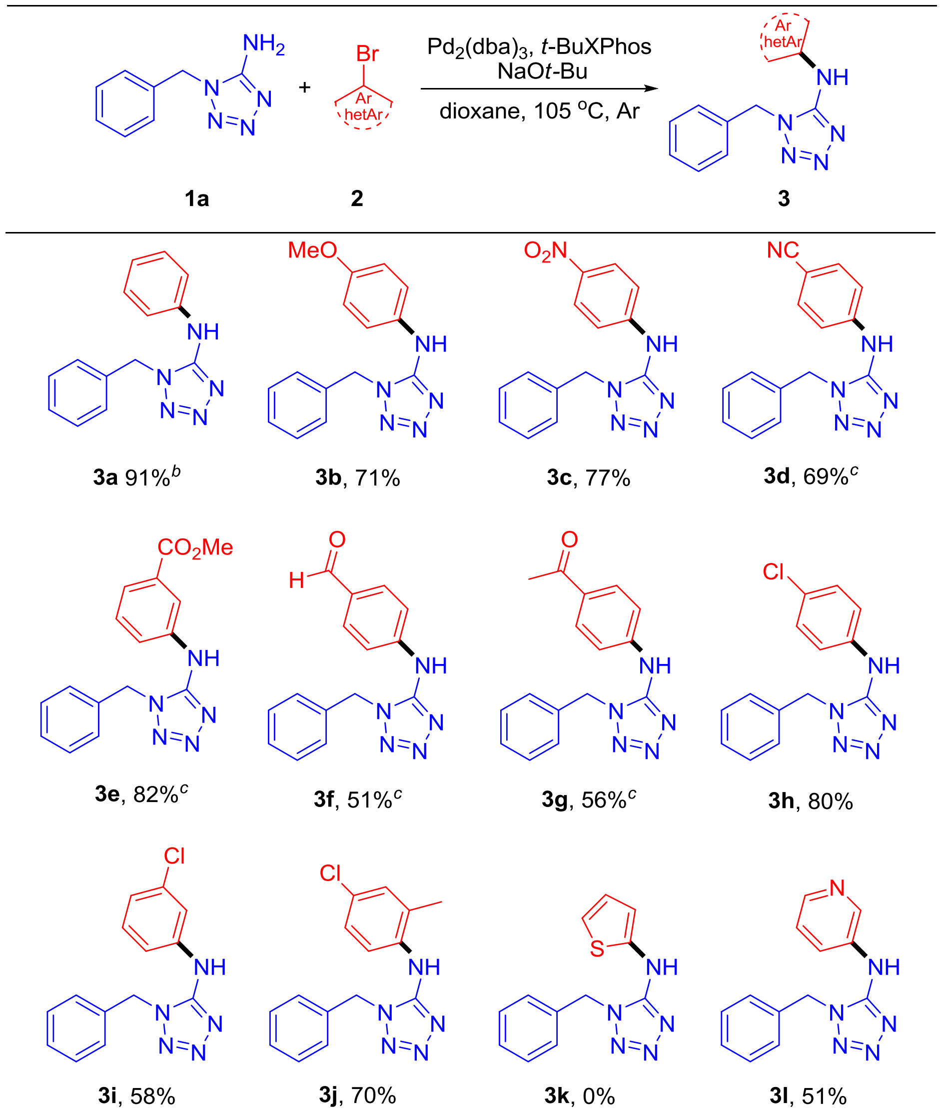
In conclusion, we have successfully developed an efficient palladium-catalyzed *N*-arylation of 1-substituted-1*H*-tetrazol-5-amines. The reaction exhibits broad substrate scope and good functional group compatibility. Considering the generality, this methodology could be of synthetic utility in the industry and drug discovery and development process.

## 4. Experimental section

### *4.1. General information*

Unless stated otherwise, all solvents and reagents were obtained

**Table 2**
Substrate scope for Pd-catalyzed *N*-arylation of 1-benzyl-1*H*-tetrazol-5-amine[a].




[a]Reactions conditions: **1a** (0.300 mmol, 1.2 equiv), **2** (0.250 mmol, 1.0 equiv), $Pd_2(dba)_3$ (0.012 mmol, 10 mol % Pd), *t*-BuXPhos (0.050 mmol, 20 mol %), NaO*t*-Bu (0.300 mmol, 1.2 equiv), 1,4-dioxane (1 mL), 105 °C, 24 h, Ar. Isolated yields are shown. [b]Reaction performed on 1.0 mmol scale. [c]$K_2CO_3$ (0.300 mmol, 1.2 equiv) and 1,4-dioxane (3.2 mL) were used. Isolated yields are shown.

from commercial sources and used without further purification. Dry-flash chromatography was performed on $SiO_2$ (0.018–0.032 mm). Melting points were determined on a Boetius PMHK apparatus and are not corrected. IR spectra were recorded on a Thermo-Scientific Nicolet 6700 FT-IR Diamond Crystal instrument. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Ultrashield Avance III spectrometer (at 500 and 125 MHz, respectively) using DMSO-$d_6$ (unless stated otherwise) as the solvent. Chemical shifts are expressed in parts per million (ppm) on the ($\delta$) scale. Chemical shifts were calibrated relative to those of the solvent. All new compounds were analyzed by high resolution tandem mass spectrometry using LTQ Orbitrap XL (Thermo Fisher Scientific Inc., USA) mass spectrometer. The sample was dissolved in MeCN and it was injected directly. Ionization was done in positive mode on heated electrospray ionization (HESI) probe. HESI parameters were: spray voltage 4.7 kV, vaporizer temperature 60 °C, sheath and auxiliary gas flow 24 and 10 (arbitrary units), respectively, capillary voltage 49 V, capillary temperature 275 °C, tube lens voltage 80 V, resolution (at *m*/*z* 400): 30000.

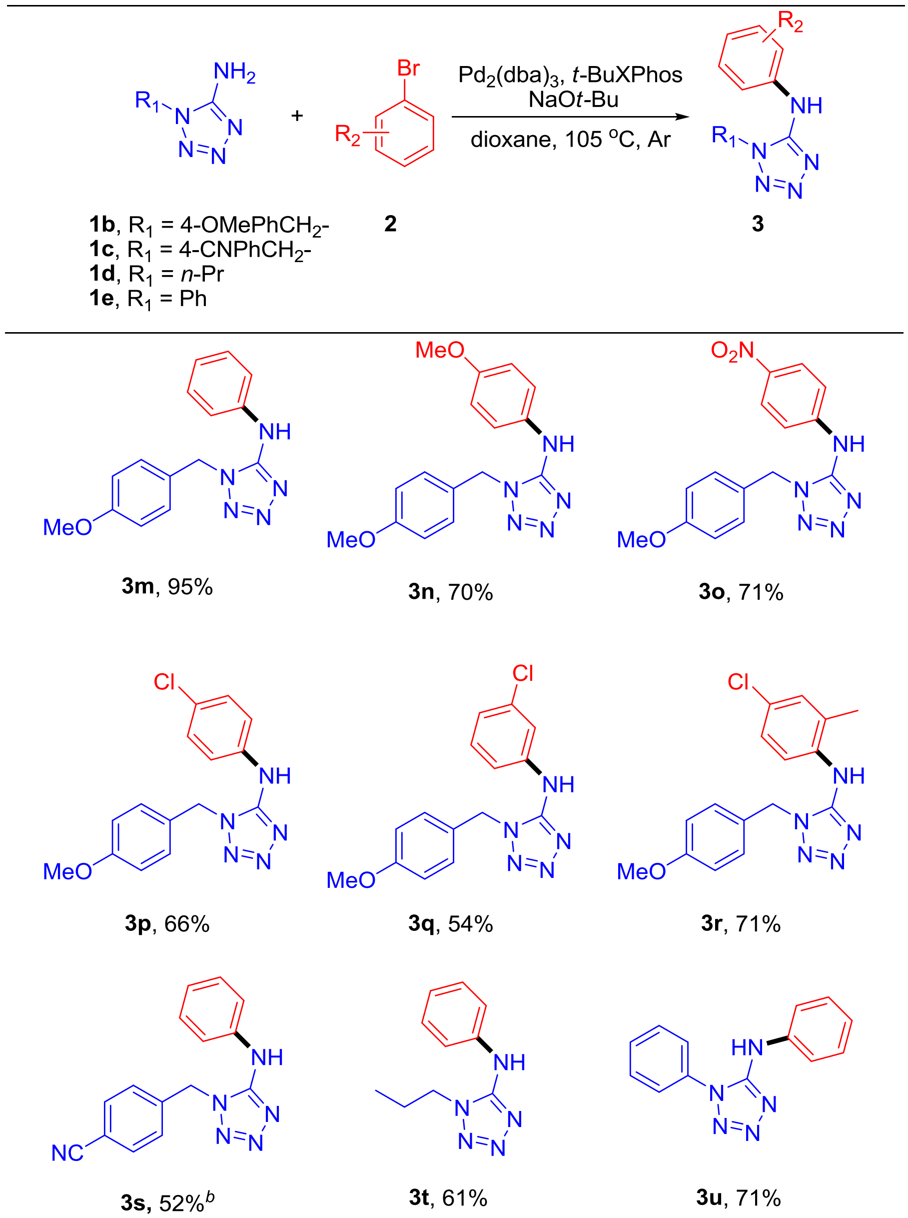
### 4.2. Synthesis

Compounds 1-benzyl-1*H*-tetrazol-5-amine (**1a**) [22], 1-propyl-1*H*-tetrazol-5-amine (**1d**) [23] and 1-phenyl-1*H*-tetrazol-5-amine (**1e**) [24] were synthesized according to the previously reported procedures.

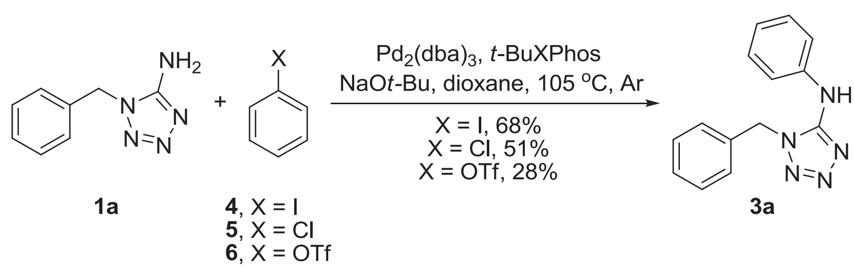
#### 4.2.1. 1-(4-Methoxybenzyl)-1H-tetrazol-5-amine (**1b**) [19].

In a flame-dried flask, CNBr (811 mg, 7.7 mmol, 2 equiv) was dissolved in dry acetonitrile (13 mL) at 0 °C. $NaN_3$ (2.373 g, 36.5 mmol, 9.5 equiv) was added at the cooled solution and the resulting mixture was stirred at 0 °C for 4 h. The precipitate was filtered on a Hirsch funnel and the filtrate was added dropwise to a stirred emulsion of (4-methoxyphenyl)methanamine (500 μL,

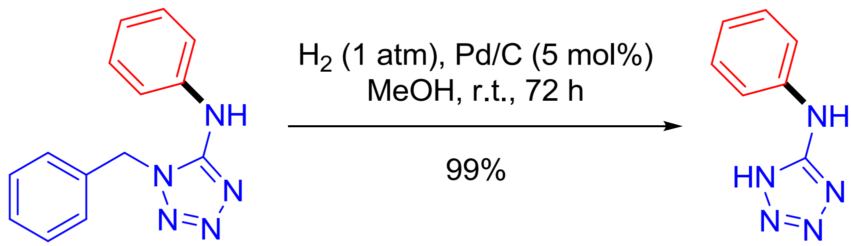
**Table 3**
Substrate scope for palladium catalyzed *N*-arylation[a].4




[a]Reactions conditions: **1** (0.300 mmol, 1.2 equiv), **2** (0.250 mmol, 1.0 equiv), $Pd_2(dba)_3$ (0.012 mmol, 10 mol % Pd), *t*-BuXPhos (0.050 mmol, 20 mol %), NaO*t*-Bu (0.300 mmol, 1.2 equiv), 1,4-dioxane (1 mL), 105 °C, 24 h, Ar. Isolated yields are shown. [b]Reactions conditions: **1** (0.180 mmol, 1.2 equiv), **2** (0.150 mmol, 1.0 equiv), $Pd_2(dba)_3$ (0.008 mmol, 10 mol % Pd), *t*-BuXPhos (0.030 mmol, 20 mol %), $K_2CO_3$ (0.180 mmol, 1.2 equiv), 1,4-dioxane (1.9 mL), 105 °C, 24 h, Ar. Isolated yields are shown.




**Scheme 1.** Reaction of 1-benzyl-1H-tetrazol-5-amine **1a** with iodobenzene **4**, chlorobenzene **5** and phenyl trifluoromethanesulfonate **6**.




**Scheme 2.** Removal of benzyl group.

3.8 mmol) in water (4 mL) at 0 °C. The resulting mixture was stirred at room temperature for 48 h. After the time has passed, the solvents were removed under the reduced pressure. The remaining residue was filtered and washed with water and acetonitrile. The product was dried under reduced pressure to afford 1-(4-methoxybenzyl)-1*H*-tetrazol-5-amine as a white crystalline solid (571 mg, 73%); m.p. 183–185 °C. IR (ATR) = 3326, 3162, 3025, 2960, 2840, 1660, 1590, 1512, 1459, 1436, 1307, 1281, 1252, 1179, 1115, 1088, 1032, 792, 763, 676, 557 $cm^{-1}$. $^{1}H$ NMR (500 Hz, DMSO-$d_6$): $\delta$ 7.21 (d, $J = 9.0$ Hz, 2H), 6.91 (d, $J = 9.0$ Hz, 2H), 6.79 (s, 2H), 5.26 (s, 2H), 3.72 (s, 3H). $^{13}C\{^{1}H\}$ NMR (125 Hz, DMSO-$d_6$): $\delta$ 159.0, 155.3, 129.2, 127.3, 114.1, 55.1, 47.1. HRMS (HESI/Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{11}N_5ONa$ 228.08613; Found 228.08524.

#### 4.2.2. 4-((5-Amino-1H-tetrazol-1-yl)methyl)benzonitrile (1c)

Following the procedure described for **1b**, compound 4-((5-amino-1H-tetrazol-1-yl)methyl)benzonitrile (**1c**) was obtained as a white powder (119 mg, 28%) starting from 283 mg (2.4 mmol) of 4-(aminomethyl)benzonitrile; m.p. 200–202 °C. IR (ATR) = 3342, 3144, 2763, 2234, 1659, 1638, 1586, 1509, 1482, 1424, 1336, 1269, 1125, 1094, 820, 698, 549 $cm^{-1}$. $^{1}H$ NMR (500 Hz, DMSO-$d_6$): $\delta$ 7.84 (d, $J = 8.5$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 6.89 (s, 2H), 5.47 (s, 2H). $^{13}C\{^{1}H\}$ NMR (125 Hz, DMSO-$d_6$): $\delta$ 155.7, 140.9, 132.7, 128.3, 118.5, 110.8, 47.1. HRMS (ESI/Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_9H_9N_6$ 201.08887; Found 201.08801.

#### 4.2.3. General procedure A for palladium catalyzed arylation of 1-substituted-1H-tetrazol-5-amines

To a flame-dried reaction tube, $Pd_2(dba)_3$ (11 mg, 0.012 mmol, 10 mol % Pd), *t*-BuXPhos (21 mg, 0.050 mmol, 20 mol %) and NaO*t*-Bu (42 mg, 0.300 mmol, 1.2 equiv) were added followed by 1,4-dioxane (1 mL). The mixture was stirred at room temperature under an inert atmosphere for 5 min, after which the aryl-bromide (0.250 mmol, 1.0 equiv) and amine (0.300 mmol, 1.2 equiv) were added, the tube was sealed and the mixture was heated at 105 °C in an oil bath for 24 h. The reaction mixture was cooled to room temperature and the mixture was diluted with EtOAc (30 mL). The mixture was washed with water (30 mL), brine (30 mL) and the organic solution was dried over anhydrous $MgSO_4$. The mixture was filtered and the solvents were removed under the reduced pressure. The crude product was purified by dry-flash column chromatography on $SiO_2$.

#### 4.2.4. General procedure B for palladium catalyzed arylation of 1-substituted-1H-tetrazol-5-amines

To a flame-dried reaction tube, $Pd_2(dba)_3$ (11 mg, 0.012 mmol, 10 mol % Pd), *t*-BuXPhos (21 mg, 0.050 mmol, 20 mol %) and $K_2CO_3$ (29 mg, 0.300 mmol, 1.2 equiv) were added followed by 1,4-dioxane (3.2 mL). The mixture was stirred at room temperature under an inert atmosphere for 5 min, after which the aryl-bromide (0.250 mmol, 1.0 equiv) and amine (0.300 mmol, 1.2 equiv) were added, the tube was sealed and the mixture was heated at 105 °C in an oil bath for 24 h. The reaction mixture was cooled to room temperature and the mixture was diluted with EtOAc (30 mL). The mixture was washed with water (30 mL), brine (30 mL) and the organic solution was dried over anhydrous $MgSO_4$. The mixture was filtered and the solvents were removed under the reduced pressure. The crude product was purified by dry-flash column chromatography on $SiO_2$.

#### 4.2.5. 1-Benzyl-N-phenyl-1H-tetrazol-5-amine (3a)

Following the general procedure A for palladium catalyzed arylation, compound **3a** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a pale yellow solid (228 mg, 91%) from 210 mg (1.2 mmol) of **1a**; m.p. 165–168 °C. IR (ATR) = 3729, 3276, 3209, 3129, 3107, 3061, 2925, 2854, 1615, 1577, 1540, 1498, 1457, 1332, 1104, 748, 716, 692 $cm^{-1}$. $^{1}H$ NMR (500 Hz, DMSO-$d_6$): $\delta$ 9.46 (s, 1H), 7.65–7.60 (m, 2H), 7.38–7.30 (m, 5H), 7.26–7.22 (m, 2H), 7.02–6.96 (m, 1H), 5.64 (s, 2H). $^{13}C\{^{1}H\}$ NMR (125 Hz, DMSO-$d_6$): $\delta$ 152.5, 139.8, 135.2, 129.0, 128.9, 128.1, 127.4, 122.0, 117.6, 48.2 ppm. HRMS (HESI/Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}N_5$ 252.12492; Found 252.12377.

*4.2.5.1. Reaction of 1-benzyl-1H-tetrazol-5-amine **1a** and iodobenzene **4**.* Following the general procedure A for palladium catalyzed arylation, compound **3a** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a pale yellow solid (12 mg, 68%) from **1a** (15 mg, 0.086 mmol) and iodobenzene **4** (8 μL, 0.071 mmol).

*4.2.5.2. Reaction of 1-benzyl-1H-tetrazol-5-amine **1a** and chlorobenzene **5**.* Following the general procedure A for palladium catalyzed arylation, compound **3a** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a pale yellow solid (9 mg, 51%) from **1a** (15 mg, 0.086 mmol) and chlorobenzene **5** (7 μL, 0.071 mmol).

*4.2.5.3. Reaction of 1-benzyl-1H-tetrazol-5-amine **1a** and phenyl trifluoromethanesulfonate **6**.* Following the general procedure A for palladium catalyzed arylation, compound **3a** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a pale yellow solid (5 mg, 28%) from **1a** (15 mg, 0.086 mmol) and phenyl trifluoromethanesulfonate **6** (16 mg, 0.071 mmol).

#### 4.2.6. 1-Benzyl-N-(4-methoxyphenyl)-1H-tetrazol-5-amine (3b)

Following the general procedure A for palladium catalyzed arylation, compound **3b** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a pale orange solid ((50 mg, 71%); 137–139 °C. IR (ATR) = 3317, 3032, 2929, 1634, 1607, 1562, 1512, 1458, 1243, 1033 $cm^{-1}$. $^{1}H$ NMR (500 Hz, DMSO-$d_6$): $\delta$ 9.26 (s, 1H), 7.54 (d, $J = 9.0$ Hz, 2H), 7.40–7.35 (m, 2H), 7.34–7.30 (m, 1H), 7.27–7.22 (m, 2H), 6.93 (d, $J = 9.0$ Hz, 2H), 5.60 (s, 2H), 3.72

(s, 3H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 154.6, 152.8, 135.2, 132.9, 128.8, 128.0, 127.4, 119.5, 114.2, 55.2, 48.0. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}N_5O$ 282.13549; Found 282.13465.

*4.2.7. 1-Benzyl-N-(4-nitrophenyl)-1H-tetrazol-5-amine (**3c**)*

Following the general procedure A for palladium catalyzed arylation, compound **3c** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 6/4) as a pale orange solid (57 mg, 77%); m.p. 245–246 °C. IR (ATR) = 3277, 3231, 3191, 3112, 3078, 2924, 1625, 1585, 1544, 1515, 1497, 1455, 1335, 1261, 1110, 856, 715 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 10.30 (s, 1H), 8.30–8.20 (m, 2H), 7.95–7.85 (m, 2H), 7.41–7.35 (m, 2H), 7.34–7.31 (m, 1H), 7.29–7.24 (m, 2H), 5.69 (s, 2H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 151.7, 146.0, 141.1, 134.8, 128.9, 128.2, 127.5, 125.4, 117.0, 48.6. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}N_6O_2$ 297.10999; Found 297.10881.

*4.2.8. 4-((1-Benzyl-1H-tetrazol-5-yl)amino)benzonitrile (**3d**)*

Following the general procedure B for palladium catalyzed arylation, compound **3d** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 6/4) as a pale yellow solid (48 mg, 69%); m.p. 220–222 °C. IR (ATR) = 3270, 3192, 3108, 3065, 2956, 2923, 2227, 1611, 1566, 1509, 1334, 844 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 10.07 (s, 1H), 7.85–7.75 (m, 4H), 7.38–7.35 (m, 2H), 7.33–7.29 (m, 1H), 7.26–7.22 (m, 2H), 5.67 (s, 2H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 151.8, 144.0, 134.9, 133.6, 128.9, 128.2, 127.4, 119.2, 117.5, 103.4, 48.5. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{13}N_6$ 277.12017; Found 277.11924.

*4.2.9. Methyl 3-((1-benzyl-1H-tetrazol-5-yl)amino)benzoate (**3e**)*

Following the general procedure B for palladium catalyzed arylation, compound **3e** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a pale yellow solid (63 mg, 82%); m.p. 142–144 °C. IR (ATR) = 3297, 3062, 2959, 2927, 2869, 1723, 1617, 1581, 1537, 1461, 1298, 1234, 1112, 756 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 9.77 (s, 1H), 8.30–8.25 (m, 1H), 8.00–7.95 (m, 1H), 7.61–7.57 (m, 1H), 7.52–7.47 (m, 1H), 7.39–7.35 (m, 2H), 7.33–7.30 (m, 1H), 7.27–7.24 (m, 2H), 5.66 (s, 2H), 3.86 (s, 3H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 166.1, 152.2, 140.2, 135.0, 130.4, 129.5, 128.8, 128.1, 127.4, 122.5, 121.9, 118.0, 52.2, 48.2. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}N_5O_2$ 310.13040; Found 310.13040.

*4.2.10. 4-((1-Benzyl-1H-tetrazol-5-yl)amino)benzaldehyde (**3f**)*

Following the general procedure B for palladium catalyzed arylation, compound **3f** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 6/4) as a yellow solid (36 mg, 51%); m.p. 192–194 °C. IR (ATR) = 3274, 3120, 3063, 2923, 2726, 1698, 1604, 1565, 1539, 1334, 1169, 834 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 10.07 (s, 1H), 9.86 (s, 1H), 7.90 (d, J = 9.0 Hz, 2H), 7.84 (d, J = 9.0 Hz, 2H), 7.39–7.35 (m, 2H), 7.34–7.29 (m, 1H), 7.27–7.23 (m, 2H), 5.68 (s, 2H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 191.3, 151.9, 145.4, 134.9, 131.2, 130.2, 128.9, 128.2, 127.5, 117.1, 48.5. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}N_5O$ 280.11984; Found 280.11891.

*4.2.11. 1-(4-((1-Benzyl-1H-tetrazol-5-yl)amino)phenyl)ethan-1-one (**3g**)*

Following the general procedure B for palladium catalyzed arylation, compound **3g** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 6/4) as a pale yellow solid (41 mg, 56%); m.p. 222–223 °C. IR (ATR) = 3278, 3194, 3119, 3061, 1678, 1603, 1563, 1538, 1455, 1270, 841 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 9.94 (s, 1H), 7.97 (d, J = 9.0 Hz, 2H), 7.77 (d, J = 9.0 Hz, 2H), 7.39–7.35 (m, 2H), 7.34–7.30 (m, 1H), 7.27–7.23 (m, 2H), 5.68 (s, 2H), 2.52 (s, 3H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 196.3, 152.0, 144.1, 135.0, 130.5, 129.9, 128.9, 128.1, 127.4, 116.7, 48.4, 26.4. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}N_5O$ 294.13549; Found 294.13406.

*4.2.12. 1-Benzyl-N-(4-chlorophenyl)-1H-tetrazol-5-amine (**3h**)*

Following the general procedure A for palladium catalyzed arylation, compound **3h** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a dark yellow solid (57 mg, 80%); m.p. 202–204 °C. IR (ATR) = 3268, 3200, 3121, 3062, 1615, 1571, 1540, 1492, 1331, 829 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 9.71 (s, 1H), 7.70–7.65 (m, 2H), 7.40–7.38 (m, 2H), 7.37–7.34 (m, 2H), 7.33–7.30 (m, 1H), 7.27–7.22 (m, 2H), 5.65 (s, 2H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 152.6, 139.2, 135.4, 129.2, 128.5, 127.8, 125.9, 119.6, 48.6. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}ClN_5$ 286.08595; Found 286.08469.

*4.2.13. 1-benzyl-N-(3-chlorophenyl)-1H-tetrazol-5-amine (**3i**)*

Following the general procedure A for palladium catalyzed arylation, compound **3i** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a yellow solid (42 mg, 58%); m.p. 173–176 °C. IR (ATR) = 3256, 3189, 3105, 3059, 1618, 1571, 1541, 1477, 1455, 1389, 1329, 1112, 785, 723 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 9.72 (s, 1H), 7.85–7.80 (m, 1H), 7.57–7.54 (m, 1H), 7.39–7.35 (m, 3H), 7.35–7.30 (m, 1H), 7.26–7.23 (m, 2H), 7.03–7.06 (m, 1H), 5.64 (s, 2H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 152.1, 141.2, 135.0, 133.4, 130.7, 128.8, 128.1, 127.4, 121.6, 116.9, 116.1, 48.3. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}ClN_5$ 286.08595; Found 286.08541.

*4.2.14. 1-Benzyl-N-(4-chloro-2-methylphenyl)-1H-tetrazol-5-amine (**3j**)*

Following the general procedure A for palladium catalyzed arylation, compound **3j** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 85/15) as an orange viscous oil (53 mg, 70%); IR (ATR) = 3269, 3031, 2926, 1611, 1492, 1452, 1095, 700 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 8.66 (s, 1H), 7.46–7.42 (m, 1H), 7.40–7.36 (m, 2H), 7.34–7.31 (m, 1H), 7.30–7.29 (m, 1H), 7.26–7.22 (m, 3H), 5.59 (s, 2H), 2.07 (s, 3H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 153.5, 136.7, 134.8, 133.5, 130.2, 128.8, 128.5, 128.2, 127.6, 126.3, 124.7, 48.4, 17.4. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}ClN_5$ 300.10160; Found 300.10036.

*4.2.15. N-(1-benzyl-1H-tetrazol-5-yl)pyridin-3-amine (**3l**)*

Following the general procedure A for palladium catalyzed arylation, compound **3l** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 3/7) as a pink solid (32 mg, 51%); m.p. 156–158 °C. IR (ATR) = 3271, 3198, 3061, 2924, 1620, 1574, 1538 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 9.74 (s, 1H), 8.85–8.80 (m, 1H), 8.25–8.19 (m, 1H), 8.14–8.10 (m, 1H), 7.40–7.36 (m, 3H), 7.34–7.31 (m, 1H), 7.28–7.25 (m, 2H), 5.65 (s, 2H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 152.3, 143.0, 139.6, 136.6, 135.0, 128.9, 128.1, 127.4, 124.4, 123.8, 48.3. HRMS (HESI/Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}N_6$ 253.12017; Found 253.11951.

*4.2.16. 1-(4-Methoxybenzyl)-N-phenyl-1H-tetrazol-5-amine (**3m**)*

Following the general procedure A for palladium catalyzed arylation, compound **3m** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a pale orange solid (67 mg, 95%); m.p. 152–155 °C. IR (ATR) = 3268, 3210, 3112, 3063, 2932, 1615, 1578, 1542, 1438, 1246, 1180, 735 $cm^{-1}$. $^1H$ NMR (500 Hz, DMSO-$d_6$): δ 9.42 (s, 1H), 7.65–7.60 (m, 2H), 7.36–7.31 (m, 2H), 7.25–7.22 (m, 2H), 7.01–6.97 (m, 1H), 6.94–6.90 (m, 2H), 5.55 (s, 2H), 3.71 (s, 3H). $^{13}C\{^1H\}$ NMR (125 Hz, DMSO-$d_6$): δ 159.1, 152.2, 139.8, 129.2, 129.0, 127.0, 121.9, 117.6, 114.2, 55.1, 47.8. HRMS (HESI/

Orbitrap) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{16}N_5O$ 282.13549; Found 282.13544.

#### 4.2.17. 1-(4-Methoxybenzyl)-N-(4-methoxyphenyl)-1H-tetrazol-5-amine (**3n**)

Following the general procedure A for palladium catalyzed arylation, compound **3n** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 6/4) as a pale yellow solid (54 mg, 70%); m.p. 123–125 °C. IR (ATR) = 3286, 2956, 2930, 1612, 1582, 1535, 1513, 1462, 1249, 1179, 1034 cm$^{-1}$. $^1$H NMR (500 Hz, DMSO-$d_6$): $\delta$ 9.22 (s, 1H), 7.60–7.50 (m, 2H), 7.25–7.20 (m, 2H), 6.95–6.90 (m, 4H), 5.50 (s, 2H), 3.72 (s, 3H), 3.71 (s, 3H). $^{13}$C{$^1$H} NMR (125 Hz, DMSO-$d_6$): $\delta$ 159.0, 154.6, 152.6, 133.0, 129.1, 127.0, 119.5, 114.2, 55.2, 55.1, 47.6. HRMS (HESI/Orbitrap) *m/z*: [M + H]$^+$ Calcd for $C_{16}N_{18}N_5O_2$ 312.14605; Found 312.14465.

#### 4.2.18. 1-(4-methoxybenzyl)-N-(4-nitrophenyl)-1H-tetrazol-5-amine (**3o**)

Following the general procedure A for palladium catalyzed arylation, compound **3o** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 6/4) as a yellow solid (58 mg, 71%); m.p. 171–173 °C. IR (ATR) = 3264, 3102, 3072, 2960, 1620, 1583, 1542, 1517, 1339, 1262, 1111, 821 cm$^{-1}$. $^1$H NMR (500 Hz, DMSO-$d_6$): $\delta$ 10.27 (s, 1H), 8.26 (d, $J$ = 9.0 Hz, 2H), 7.86 (d, $J$ = 9.0 Hz, 2H), 7.25 (d, $J$ = 8.5 Hz, 2H), 6.92 (d, $J$ = 8.5 Hz, 2H), 5.60 (s, 2H), 3.71 (s, 3H). $^{13}$C{$^1$H} NMR (125 Hz, DMSO-$d_6$): $\delta$ 159.2, 151.4, 146.0, 141.1, 129.2, 126.6, 125.4, 117.0, 114.2, 55.1, 48.2. HRMS (HESI/Orbitrap) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{14}N_6O_3Na$ 349.10251; Found 349.10096.

#### 4.2.19. N-(4-chlorophenyl)-1-(4-methoxybenzyl)-1H-tetrazol-5-amine (**3p**)

Following the general procedure A for palladium catalyzed arylation, compound **3p** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as an orange solid (52 mg, 66%); m.p. 198–200 °C. IR (ATR) = 3265, 3198, 3119, 3060, 1614, 1570, 1514, 1490, 1458, 1263, 1252, 821 cm$^{-1}$. $^1$H NMR (500 Hz, DMSO-$d_6$): $\delta$ 9.60 (s, 1H), 7.68 (d, $J$ = 9.0 Hz, 2H), 7.39 (d, $J$ = 9.0 Hz, 2H), 7.23 (d, $J$ = 8.5 Hz, 2H), 6.92 (d, $J$ = 8.5 Hz, 2H), 5.54 (s, 2H), 3.71 (s, 3H). $^{13}$C{$^1$H} NMR (125 Hz, DMSO-$d_6$): $\delta$ 159.1, 152.0, 138.8, 129.2, 128.8, 126.9, 125.5, 119.1, 114.2, 55.1, 47.8. HRMS (HESI/Orbitrap) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{14}ClN_5ONa$ 338.07846; Found 338.07687.

#### 4.2.20. N-(3-chlorophenyl)-1-(4-methoxybenzyl)-1H-tetrazol-5-amine (**3q**)

Following the general procedure A for palladium catalyzed arylation, compound **3q** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 7/3) as a yellow solid (43 mg, 54%); m.p 173–174 °C. IR (ATR) = 3266, 3195, 3116, 3063, 2997, 2927, 1617, 1568, 1540, 1514, 1459, 1310, 1261, 780 cm$^{-1}$. $^1$H NMR (500 Hz, DMSO-$d_6$): $\delta$ 9.68 (s, 1H), 7.79–7.78 (m, 1H), 7.60–7.50 (m, 1H), 7.40–7.35 (m, 1H), 7.24 (d, $J$ = 8.5 Hz, 2H), 7.05–7.00 (m, 1H), 6.92 (d, $J$ = 8.5 Hz, 2H), 5.55 (s, 2H), 3.71 (s, 3H). $^{13}$C{$^1$H} NMR (125 Hz, DMSO-$d_6$): $\delta$ 159.1, 151.8, 141.2, 133.4, 130.7, 129.2, 126.8, 121.5, 116.9, 116.0, 114.2, 55.1, 47.9. HRMS (HESI/Orbitrap) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{14}ClN_5ONa$ 338.07846; Found 338.07730.

#### 4.2.21. N-(4-chloro-2-methylphenyl)-1-(4-methoxybenzyl)-1H-tetrazol-5-amine (**3r**)

Following the general procedure A for palladium catalyzed arylation, compound **3r** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 8/2) as a yellow viscous oil (58 mg, 71%); IR (ATR) = 3237, 2962, 1612, 1590, 1516, 1488, 1253, 1162, 819 cm$^{-1}$. $^1$H NMR (500 Hz, DMSO-$d_6$): $\delta$ 8.61 (s, 1H), 7.47–7.41 (m, 1H), 7.33–7.28 (m, 1H), 7.26–7.20 (m, 3H), 6.90–6.95 (m, 2H), 5.50 (s, 2H), 3.72 (s, 3H), 2.09 (s, 3H). $^{13}$C{$^1$H} NMR (125 Hz, DMSO-$d_6$): $\delta$ 159.1, 153.3, 136.8, 133.3, 130.2, 129.2, 128.4, 126.7, 126.3, 124.6, 114.2, 55.1, 48.0, 17.4. HRMS (HESI/Orbitrap) *m/z*: [M + H]$^+$ Calcd for $C_{16}H_{17}ClN_5O$ 330.11216; Found 330.11145.

#### 4.2.22. 4-((5-(Phenylamino)-1H-tetrazol-1-yl)methyl)benzonitrile (**3s**)

Following the general procedure B for palladium catalyzed arylation, compound **3s** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 6/4) as a pale yellow solid (21 mg, 52%) from 36 mg (0.180 mmol) of **1c** and the reaction was performed in 1.9 mL of dioxane; m.p. 212–215 °C. IR (ATR) = 3266, 3208, 3107, 3067, 2928, 2234, 1616, 1577, 1540, 1499, 756 cm$^{-1}$. $^1$H NMR (500 Hz, DMSO-$d_6$): $\delta$ 9.48 (s, 1H), 7.90–7.84 (m, 2H), 7.64–7.61 (m, 2H), 7.41–7.38 (m, 2H), 7.36–7.32 (m, 2H), 7.01–6.95 (m, 1H), 5.75 (s, 2H). $^{13}$C{$^1$H} NMR (125 Hz, DMSO-$d_6$): $\delta$ 152.6, 140.6, 139.6, 132.8, 129.0, 128.2, 122.0, 118.5, 117.6, 110.8, 47.8. HRMS (HESI/Orbitrap) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{13}N_6$ 277.12017; Found 277.11983.

#### 4.2.23. N-phenyl-1-propyl-1H-tetrazol-5-amine (**3t**) [25].

Following the general procedure A for palladium catalyzed arylation, compound **3t** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 8/2) as a yellow solid (31 mg, 61%); IR (ATR) = 3288, 3208, 3124, 3055, 2963, 2927, 2874, 1611, 1574, 1532, 1501, 1457, 744, 686 cm$^{-1}$. $^1$H NMR (500 Hz, DMSO-$d_6$): $\delta$ 9.21 (s, 1H), 7.65–7.60 (m, 2H), 7.35–7.30 (m, 2H), 7.05–6.95 (m, 1H), 4.29 (t, $J$ = 7.0 Hz, 2H), 1.80 (sx, $J$ = 7.0 Hz, 2H), 0.88 (t, $J$ = 7.0 Hz, 3H).

#### 4.2.24. N,1-diphenyl-1H-tetrazol-5-amine (**3u**) [26].

Following the general procedure A for palladium catalyzed arylation, compound **3u** was obtained after dry-flash column chromatography ($SiO_2$: Hex/EtOAc = 9/1) as a colorless solid (34 mg, 71%) from 39 mg (0.242 mmol) of **1e**; IR (ATR) = 3239, 3195, 3076, 3043, 3000, 1606, 1572, 1532, 1498, 1454, 748, 692 cm$^{-1}$. $^1$H NMR (500 Hz, $CDCl_3$): $\delta$ 7.68–7.60 (m, 3H), 7.58–7.50 (m, 4H), 7.38–7.34 (m, 2H), 7.10–7.05 (m,1H), 6.34 (s, 1H).

#### 4.2.25. N-phenyl-1H-tetrazol-5-amine (**7a**) [27].

In a flame-dried flask, **3a** (23 mg, 0.092 mmol) was dissolved in deoxygenated methanol (1 mL) and Pd/C (5 mg, 0.005 mmol, 5 mol % Pd) was added. The flask was closed with a rubber septum and the reaction mixture, connected to a balloon of hydrogen, was stirred at room temperature for 72 h. The reaction mixture was filtered through a pad of Celite and washed with EtOAc (25 mL). The solvents were removed under the reduced pressure to afford the pure **7a** as a colorless solid (15 mg, 99%). IC (ATR) = 3271, 3135, 3075, 1629, 1583, 1545, 1498, 1245, 1065, 742 cm$^{-1}$. $^1$H NMR (500 Hz, $CDCl_3$): $\delta$ 9.76 (s, 1H), 7.55–7.40 (m, 2H), 7.35–7.25 (m, 2H), 7.05–6.90 (m, 1H).

## Notes

The authors declare no competing financial interest.

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## Appendix A. Supplementary data

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