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Conversion of Arylboronic Acids to Tetrazoles Catalyzed by ONO Pincer-Type Palladium Complex

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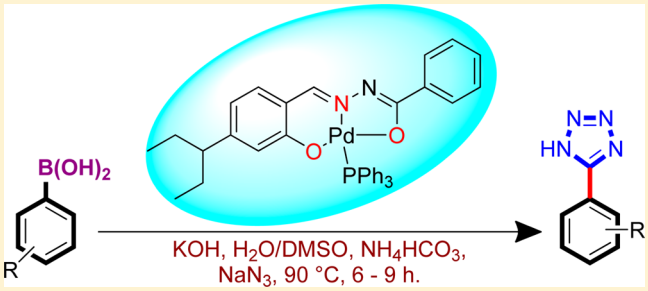
Supporting Information

ABSTRACT: A convenient synthesis of a library of tetrazoles through a novel and operationally simple protocol effecting the direct conversion of arylboronic acids catalyzed by a new ONO pincer-type Pd(II) complex under mild reaction conditions using the readily available reagents is reported. The palladium complex was reused up to four cycles in an open-flask condition.



INTRODUCTION

Direct access to target molecules in one-pot operation using readily available reagents is an attractive strategy in organic synthesis.[1] Chemistry of nitrogen-rich heterocycles gains immense importance[2] due to their diverse application.[2] Specifically, tetrazoles are an ubiquitous structural motif very often utilized in pharmaceuticals[3] (Figure 1), as ligands in coordination chemistry,[4] in organocatalysis,[5] as synthons in organic synthesis[6] as well as in various materials science applications including polymers, photosensitive agents, energy materials, and specialty explosives.[7] In the literature, a plethora of methods were reported for the synthesis of 5-substituted 1*H*-tetrazole derivatives.[8,9] Nevertheless, those protocols have some drawbacks such as, (i) high catalyst loading, (ii) expensive reagents, (iii) harsh reaction conditions; water sensitivity and the involvement of dangerous hydrazoic acid, and (iv) prolonged reaction time and elevated temperature.[8,9] Hence, development of an efficient, economical and eco-friendly[9g] one-pot methodology to construct the titled heterocyclic frame-works with wide substrate scope is a challenging scientific mission.

Consequent to the discovery of transition-metal-catalyzed cyanations,[10] the classical cyanation methods, such as Rosenmund−von Braun reaction of aryl halides[11] and diazotization of anilines followed by Sandmeyer reaction, are practically neglected.[12] On the other hand, directing group assisted C−H bond cyanation with metal precursors of the type MCN (M = Na, K, Cu, and Zn) were reported.[13] Conversely, the toxicity of cyanide salts excluded the practicality of this conversion to a larger extent in addition to the general problem associated with high affinity of cyanide toward Pd-, Ni-, and Cu-based catalysts, that often deactivates the catalytic system.[14] Hence, the development of new methodology for the cyanation of arylboronic acids using a safe cyanide source is much desirable.[14c] In this regard, we utilized DMSO and NH_4HCO_3 as harmless cyanide sources for the titled conversion.[14b,d]

Recently, several reports were documented regarding the conversion of arylboronic acids to various aryl functionalities,[15−26] such as halides (F,[15] Cl,[16] Br,[17] and I[17]), triazoles,[18] sulfinates,[19] amine,[20] nitriles,[21] nitro compounds,[22] hydroxyls,[23] azides,[24] sulfones,[25] and trifluoreomethylthiol.[26] Arylboronic acids are considered as source of aryl group owing to their stability, common availability, and often the requirement of mild conditions with wide spectrum functional group tolerance.[27] In spite of the large number of publications those deal with organic transformations using metal salts or coordination complexes, no report on the direct conversion of arylboronic acids to corresponding tetrazoles is available in the literature.[15−26] However, direct conversion of aryl halides to tetrazoles was reported earlier.[28]

In our quest to design new palladium based catalysts for C−C and C−N bond formation reactions,[29] we herein describe the synthesis and catalytic activity of a new Pd(II) complex incorporating ONO pincer-type ligand for the direct conversion of arylboronic acids to tetrazoles through a 3+2 cycloaddition of an *in situ* generated aryl nitriles with sodium azide. To the best of our knowledge, this is the maiden report on the use of Pd(II) complex catalyzed for the synthesis of tetrazoles in a simple route utilizing arylboronic acids.

RESULTS AND DISCUSSION

From the reaction of an equimolar quantity of tridentate ONO pincer-type ligand benzoic acid [4-(1-ethyl-propyl)-2-hydroxy-benzylidene]-hydrazide (H_2L1) and the precursor complex, $[PdCl_2(PPh_3)_2]$ in the presence of Et_3N, complex **1** of the

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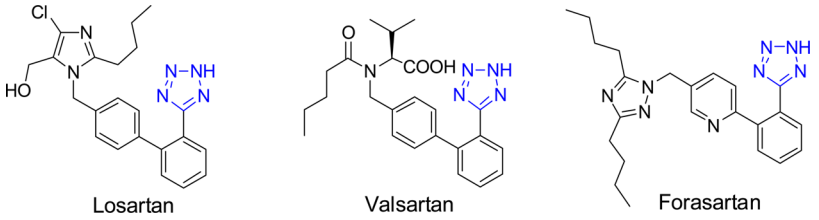
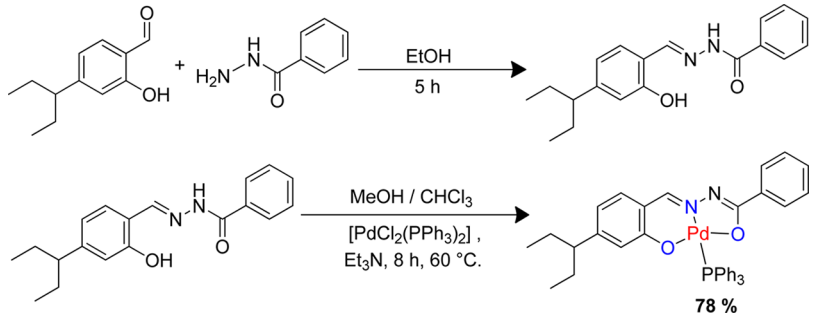


Figure 1. Tetrazole-based sartans.

Scheme 1. Synthesis of ONO Pincer-Type Ligand and the New Pd(II) Complex



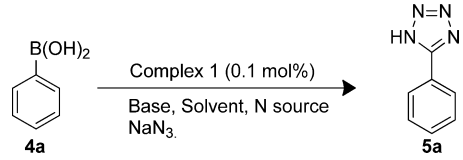
molecular formula [Pd(L) (PPh_3)] was obtained in 78% yield as sketched in Scheme 1.

The exact mode of coordination of the ligand to palladium ion in complex **1** was determined from the single-crystal X-ray structure presented in Figures S1 and S2 in SI. The Pd(II) center in complex **1** adopted a distorted square-planar geometry around the metal ion satisfied through the phenolate oxygen, azomethine nitrogen and the imidolate oxygen atoms of ONO pincer-type ligand with the fourth coordination site occupied by the triphenylphosphine molecule. From the XRD data, we inferred that the complex **1** was crystallized as monoclinic with the space group of P 1 $2_1/c_1$. Details on the data collection, structure refinements, bond angles, and bond distances were furnished in Tables S1 and S2 in SI.

Optimization of reaction conditions were undertaken by selecting a combination of phenylboronic acid (**4a**), NH_4HCO_3, and DMF as reagents for the source of CN functionality in the presence of an inorganic base in water for the tetrazole formation. In view of atom economy and for economical reasons, NaN_3 was chosen as an inexpensive azide source. As expected, the tetrazole was formed in 42% yield. To achieve higher yield of the target product, we tested the combinations of DMF−NH_4HCO_3, DMAc−NH_4HCO_3, and DMSO−NH_4HCO_3 as safe sources of CN group (Table 1 entries 4, 9, and 10) and found that only the combination of DMSO−NH_4HCO_3 was more effective for the *in situ* generation of cyanide, as reported earlier.[14b] Further, among the bases tested for the catalytic reaction, KOH served as an effective base. In our attempted tetrazole synthesis at room-temperature, no progress was observed. From the literature,[8,9] it was clear that a high yield of tetrazole synthesis required the reaction at high temperatures. Hence, we screened the reaction through the temperature range of 60−120 °C wherein the best yield of the tetrazole (92%) was achieved at 90 °C. The catalyst loading test was performed by using 0.1 mol% to 0.001 mol % and realized that 0.1 mol% of catalyst afforded 92% of the desired product. Further addition of the catalyst had not resulted in any improvement of the yield (Table 2).

To ascertain, whether the present conversion of arylboronic acids to tetrazoles could be effected only with complex **1** or also by other Pd sources, we utilized [$PdCl_2$], [$PdCl_2(PPh_3)_2$], and few previously reported[29b] Pd(II) complexes **2**, **3**, and **4** (Figure 2) as catalysts for the same reaction under identical conditions.

Table 1. Optimization of Catalytic Reaction.[a]



entry	N source	base	solvent	yield(%)
1	NH_4HCO_3	no base	H_2O/DMF	NR
2	NH_4HCO_3	NaOH	H_2O/DMF	27
3	NH_4HCO_3	Na_2CO_3	H_2O/DMF	25
4	NH_4HCO_3	KOH	H_2O/DMF	42
5	NH_4HCO_3	K_2CO_3	H_2O/DMF	36
6	NH_4HCO_3	Pyridine	H_2O/DMF	21
7	NH_4HCO_3	CH_3COONa	H_2O/DMF	19
8	NH_4HCO_3	Et3N	H_2O/DMF	15
9	NH_4HCO_3	KOH	H_2O/DMAc	52
10	NH_4HCO_3	KOH	H_2O/DMSO	71
11	NH_4Cl	KOH	H_2O/DMSO	38
12	NH_4OH	KOH	H_2O/DMSO	35
13	$(NH_4)_2SO_4$	KOH	H_2O/DMSO	24
14	NH_4HCO_3	KOH	H_2O/DMSO (10%)	45
15	NH_4HCO_3	KOH	H_2O/DMSO (20%)	57
16	NH_4HCO_3	KOH	H_2O/DMSO (30%)	71
17	NH_4HCO_3	KOH	H_2O/DMSO (40%)	84
18	**NH_4HCO_3**	**KOH**	**H_2O/DMSO (50%)**	**92**
19	NH_4HCO_3	KOH	H_2O/DMSO (60%)	86

[a]Reaction conditions: phenylboronic acid (5 mmol), base (6 mmol), NH_4HCO_3 (1.2 equiv) solvent (70:30%), and catalyst (0.1 mol%) stirred at 60−90 °C for 3−6 h. NR = No reaction.

Table 2. Effect of Catalyst Loading

entry	mol%	isolated yield (%)	TON
1	0.1	92	920
2	0.01	79	7900
3	0.001	64	64000

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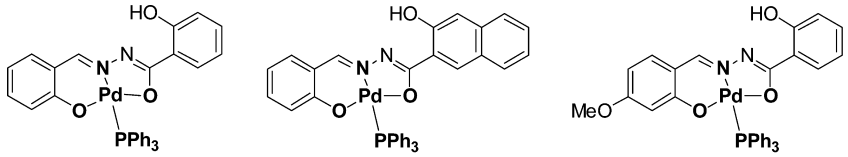


Figure 2. Structures of previously reported Pd(II) complexes.[29b]

Herein we noticed that the reaction proceeded with all the above-mentioned catalysts, but the results showed in Table 3 highlighted that complex **1** is superior for this conversion.

Table 3. Screening of Pd(II) Catalysts[a]

catalyst (0.1 mol%)	yield (%)	TON
complex **1**	92	920
complex **2**	64	640
complex **3**	72	720
complex **4**	68	680
$[PdCl_2]$	41	410
$[PdCl_2(PPh_3)_2]$	59	590

[a]Reaction conditions: phenylboronic acid (5 mmol), base (6 mmol), NH_4HCO_3 (1.2 equiv) solvent (70:30%), and catalyst (0.1 mol%) stirred at 90 °C for 6 h.

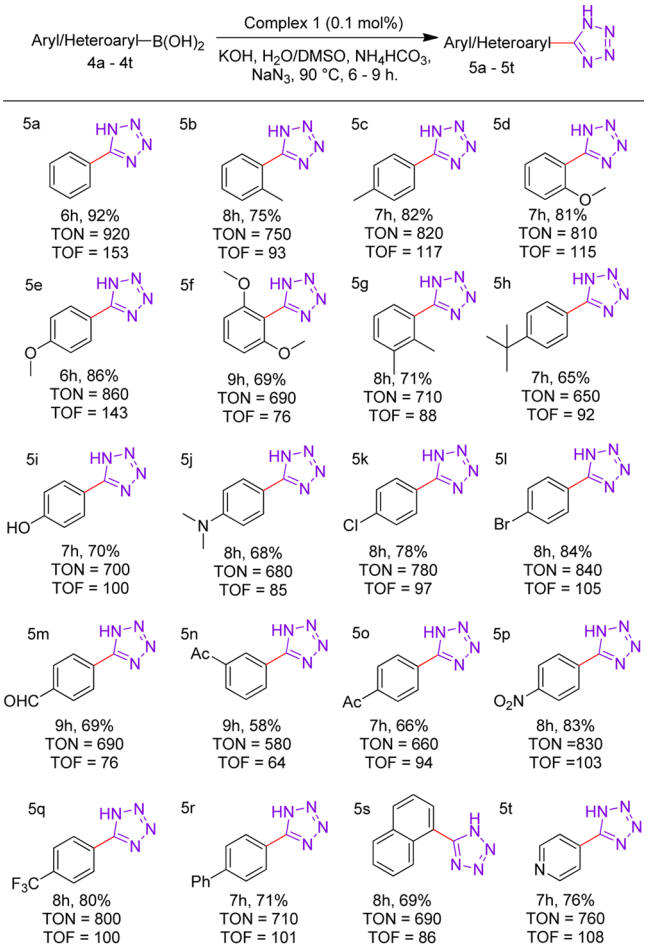
At this stage, the following optimized conditions were applied for the titled conversion: arylboronic acid (5 mmol), KOH (6 mmol), NH_4HCO_3 (1.2 equiv) H_2O/DMSO (50:50%), and complex **1** as the catalyst (0.1 mol%) at 90 °C under open-flask conditions (Table 1).

Next, we turned our attention to explore the reaction scope of arylboronic acids possessing both activating and deactivating groups. The results furnished in Table 4 revealed that a smooth conversion of arylboronic acids occurred in all the cases and delivered the target molecules **5a**−**5t** in excellent yields. It is worth to mention here that the electronic and steric effects due to the substituents of arylboronic acids did not significantly influence the outcome of the conversion process.

Arylboronic acids bearing electron-donating groups like $-CH_3$ and $-OCH_3$ at the sterically hindered *ortho* position afforded respectively 75 and 81% of products **5b** and **5d**. Moreover, sterically hindered arylboronic acids, i.e., 2, 6-dimethoxy and 2, 3-dimethylphenylboronic acids, underwent the conversion and provided 69 and 71% of the products **5f** and **5g**, respectively. Fabulously, arylboronic acids featuring $-CH_3$, $-OCH_3$, *t*-butyl, $-OH$, and $-N(CH_3)_2$ groups in *para* position too afforded the corresponding tetrazoles in 82, 86, 65, 70, and 68% yield. In addition, arylboronic acids holding moderately deactivating chloro, bromo, formyl, and acetyl functionalities also contributed well and yielded the tetrazole analogous **5k**−**5o** quantitatively. Biphenyl and naphthyl boronic acids were also converted into desired tetrazoles (**5r** and **5s**).

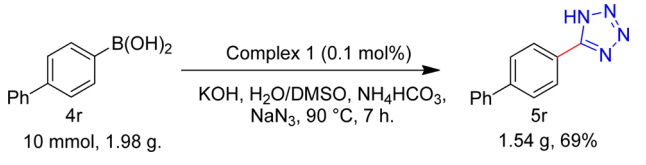
Phenylboronic acids possessing deactivating $-NO_2$ and $-CF_3$ functionalities at the *para* position also yielded the expected products in 83 and 80%, respectively. Next, utilization of a heterocyclic boronic acid (4-pyridineboronic acid) as a reagent in the palladium catalyzed conversion afforded 4-tetrazolylpyridine (**5t**) in 76% yield. In all these experiments involving the conversion of a series of arylboronic acids to tetrazoles catalyzed by the palladium complex **1**, no byproducts were obtained. In order to realize the usefulness of the current protocol for industrial application, we investigated gram scale synthesis of 5-biphenyl-4-yl-1*H*-tetrazole (**5r**) as a representative example (Scheme 2) with 69% yield.

Table 4. Scope of Arylboronic Acids[a]



[a]Reaction conditions: arylboronic acid (5 mmol), KOH (6 mmol), NH_4HCO_3 (1.2 equiv) H_2O/DMSO (50:50%), NaN_3 (5 mmol) and catalyst (0.1 mol %) stirred at 90 °C for 6−9 h. NR = No reaction, TON = turnover number = ratio of moles of the product formed to moles of the catalyst used, TOF (h^{-1}) = turnover frequency = TON/h.

Scheme 2. Gram Scale Synthesis of 5-Biphenyl-4-yl-1*H*-tetrazole (5r)



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After the completion of the reaction, the catalyst was recovered by centrifugation upon the addition of ethyl acetate and washed thoroughly with water (to remove inorganic salts) and dried under vacuum. The dried catalyst was subjected to next reaction cycles under identical conditions with fresh portions of reagents. The reusability study showed that the present palladium-based catalytic system remains active up to four consecutive runs with a gradual decrease in the activity as summarized in Figure 3.

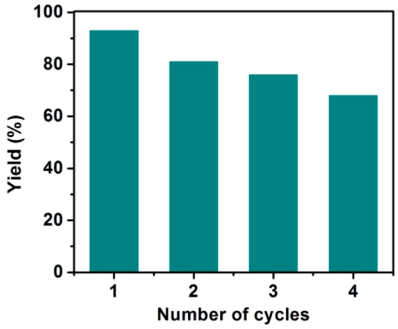
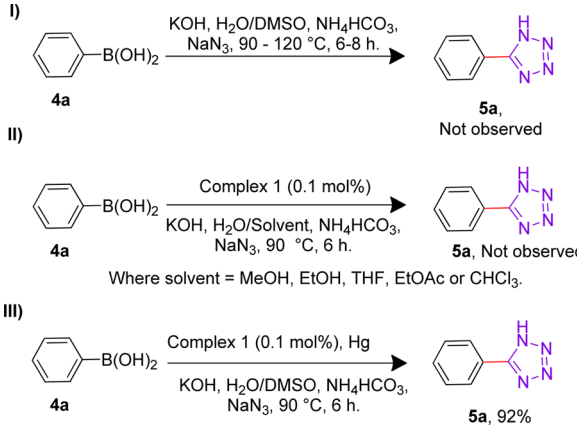


Figure 3. Reusability of the catalyst.

To understand the reaction pathway, the following control experiments were carried out (Scheme 3). One such experiment

Scheme 3. Control Experiments for Mechanistic Investigation



was performed to effect the titled conversion in the absence of catalyst, wherein no progress was observed indicating the vital role of palladium pincer-type complex. Another study conducted with several solvents excluding DMF, DMSO, or DMAc, failed to yield the product **5a**. On the other hand, use of ammonium salts such as NH_4Cl, NH_4OH, or $(NH_4)_2SO_4$ as the nitrogen source instead of NH_4HCO_3 (Table 1, entries 11, 12, and 13), successfully gave the expected tetrazoles and thus proved that the carbon atom of CN moiety was not derived from NH_4HCO_3. Besides, use of ^{13}C-labeled DMSO as a reagent confirmed that the carbon of the cyano group was originated only from DMSO but not from ammonium salts.[14b] Hg poisoning test done by adding elemental mercury revealed that no catalyst poisoning occurred and the active catalyst is likely to be a homogeneous species and not metallic palladium nanoparticles. However, we could not isolate and characterize any intermediate during the conversion of arylboronic acids to tetrazoles via the present palladium catalyzed reaction described in this manuscript. Hence, we did not propose the mechanism for the titled conversion at this point.

CONCLUSION

In summary, a robust palladium-based catalyst consisting of ONO pincer-type ligand was synthesized, characterized, (viz., UV−vis., IR, ^1H, ^{13}C NMR, and single-crystal XRD techniques), and successfully employed for the direct conversion of arylboronic acids to tetrazoles under an open-atmosphere. Mechanistic aspects of the titled reaction presented in this manuscript would definitely attract the attention of synthetic chemists who are constantly moving forward to design and develop new catalytic systems to synthesis tetrazoles from inexpensive reagents. Low catalyst loading (0.1 mol%), safe cyanide source, nonrequirement of an oxidant/additives, open-flask conditions, wide substrate scope, scalability, and reusability are the key factors of the present methodology with a definite scope for further explorations.

EXPERIMENTAL SECTION

General Experimental Considerations. Elemental analyses (C, H, and N) were performed on elemental analyzer instrument. IR spectra (4000−400 cm^{-1}) of the compounds were recorded on FT-IR spectrophotometer. Melting points were determined by melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ as solvent on 400 and 100 MHz instruments, respectively. The following abbreviations were used for multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, and dd = doublet of doublets. Mass spectra were recorded in mass spectrometer. $[PdCl_2(PPh_3)_2]$ (97%), and arylboronic acids (95−98%) were purchased from commercial suppliers and used as received. Reagent grade solvents purchased from standard suppliers were purified and dried according to standard procedures.[30]

Synthesis of the Ligand H_2L1. Pincer type ligand H_2L1 was synthesized by condensing equimolar quantity of 4-(1-ethyl-propyl)-2-hydroxy-benzaldehyde with benzhydrazide in ethanol according to literature method.[31] The reaction mixture was refluxed on a water-bath for 10 h and poured into crushed ice. The corresponding pincer-type hydrazone formed as colorless solid was filtered, washed repeatedly with distilled water, and recrystallized from ethanol with 80% (249 mg) yield.

*Synthesis of Palladium Complex **1** (Catalyst).* To a warm methanolic solution (20−30 mL) of pincer-type ligand (H_2L1) (1 equiv), a chloroform solution of $[PdCl_2(PPh_3)_2]$ (1 equiv) followed by two drops of triethylamine were added, refluxed for 8 h and kept at room temperature for crystallization. Needle like reddish brown crystals suitable for X-ray study were obtained on slow evaporation over 30−40 days.

$[Pd(L1)(PPh_3)]$ (complex **1**): Yield: 528 mg, 78%. mp 197−199 °C. Elemental analysis (%) calculated $C_{37}H_{35}N_2O_2PPd$; C, 65.63; H, 5.21; N, 4.14. Found (%) C, 65.58; H, 5.11; N, 4.17. UV−visible (solvent: DMSO, nm): 361, 399, 401, 436. Selected IR bands (KBr, ν in cm^{-1}): 1585 (C−N═N−C), 1512 (C═N), 1433 (PPh_3), 1253 (imidolate − N═C−O), 1182 (phenolate C−O). ^1H NMR ($CDCl_3$, δ ppm) 10.30 (s, 1H), 7.45 (t, J = 4.2 Hz, 4H), 7.40 (d, J = 7.6 Hz, 2H), 7.31 (s, 3H), 7.23 (t, J = 6.4 Hz, 9H), 6.68 (d, J = 8.0 Hz, 2H), 6.30−6.37 (m, 3H), 3.99 (dd, J = 2.4, 9.2 Hz, 1H), 3.69 (dd, J = 5.6, 6.0 Hz, 4H), 3.06 (t, J = 2.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, δ ppm) 162.8, 149.5, 148.4, 147.5, 146.0, 131.4, 125.0, 122.1, 114.4, 114.3, 110.8, 109.6 108.1, 100.7, 55.7, 39.4, 20.9.

General Procedure for the Catalytic Reaction. To a solvent mixture of H_2O−DMSO (50:50%), complex **1** (0.1 mol %), phenylboronic acid (4.0 mmol), KOH (6 mmol), and

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NH_4HCO_3 (1.2 mmol, 6 equiv) were added and stirred for 2 h. Later, NaN_3(4.0 mmol) was added and continuously stirred at 90 °C under open-flask condition. The progress of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was precipitated by adding ethyl acetate, centrifugated, washed thoroughly with water (to remove inorganic salts), and dried under vacuum. The identity of the products was confirmed by ^{1}H and ^{13}C NMR data.

Analytical and Spectral Data of the Products Listed in Table 4. Entry **5a**: 5-phenyl-1*H*-tetrazole:[9h] Elemental analysis (%) calculated for $C_7H_6N_4$ C, 57.53; H, 4.14; N, 38.34. Found (%) C, 57.56; H, 4.16; N, 38.40. ^{1}H − NMR: 7.34 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.13 (dd, *J* = 6.4 Hz, 2.8 Hz, 2H). ^{13}C− NMR: 161.4, 127.4, 127.3, 115.5, 115.3.

Entry **5b**: 5-*o*-tolyl-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_8H_8N_4$ C, 59.99; H, 5.03; N, 34.98. Found (%) C, 59. 98; H, 5.07; N, 35.04. ^{1}H − NMR: 7.40 (d, *J* = 8.0 Hz, 1H), 7.26 (s, 1H), 7.22 (dd, *J* = 6.4, 2.0 Hz 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 2.48 (s, 3H). ^{13}C − NMR: 153.2, 135.5, 133.7, 132.3, 130.9, 129.2, 127.5, 21.5.

Entry **5c**: 5-*p*-tolyl-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_8H_8N_4$ C, 59.99; H, 5.03; N, 34.98. Found (%) C, 60.01; H, 5.05; N, 34.96. ^{1}H − NMR: 7.42 (d, *J* = 10.0 Hz, 1H), 7.21 (t, *J* = 4.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 3H). ^{13}C − NMR: 160.6, 131.0, 128.9, 115.24, 19.9.

Entry **5d**: 5-(2-methoxy-phenyl)-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_8H_8N_4O$ C, 54.54; H, 4.58; N, 31.80. Found (%) C, 54.57; H, 4.60; N, 31.86. ^{1}H − NMR: 6.76 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 9.6 Hz, 1H), 6.63−6.65 (m, 1H), 4.21 (s, 3H). ^{13}C − NMR: 147.8, 146.5, 126.4, 122.2, 109.6, 108.3, 100.9, 58.7.

Entry **5e**: 5-(4-methoxy-phenyl)-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_8H_8N_4O$ C, 54.54; H, 4.58; N, 31.80. Found (%) C, 54.57; H, 4.60; N, 31.86. ^{1}H − NMR: 7.35 (t, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 4.26 (s, 3H). ^{13}C − NMR: 155.2, 136.4, 128.1, 127.9, 125.3, 58.0.

Entry **5f**: 5-(2,6-dimethoxy-phenyl)-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_9H_{10}N_4O_2$ C, 52.42; H, 4.89; N, 27.17. Found (%) C, 52.45; H, 4.93; N, 27.22. ^{1}H − NMR: 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 4.25 (s, 6H). ^{13}C − NMR: 161.4, 135.2, 134.0, 128.6, 127.0, 55.2.

Entry **5g**: 5-(2,3-dimethyl-phenyl)-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_9H_{10}N_4$ C, 62.05; H, 5.79; N, 32.16. Found (%) C, 62.09; H, 5.84; N, 32.18. ^{1}H − NMR: 7.27−7.35 (m, 3H), 2.78 (s, 3H), 2.22 (s, 3H). ^{13}C − NMR: 163.8, 161.7, 132.3, 127.4, 127.3, 115.5, 115.3, 23.4, 22.0.

Entry **5h**: 5-(4-*tert*-butyl-phenyl)-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_{11}H_{14}N_4$ C, 65.32; H, 6.98; N, 27.70. Found (%) C, 65.36; H, 6.99; N, 27.73. ^{1}H − NMR: 7.35 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 2H), 2.00 (s, 9H). ^{13}C − NMR: 161.1, 136.3, 127.8, 127.5, 125.1, 24.9, 19.1

Entry **5i**: 4-(1*H*-tetrazol-5-yl)-phenol:[9i] Elemental analysis (%) calculated for $C_7H_6N_4O$ C, 51.85; H, 3.73; N, 34.55. Found (%) C, 51.89; H, 3.75; N, 34.59. ^{1}H − NMR: 10.63 (s, 1H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.26 (s, 2H). ^{13}C − NMR: 163.2, 161.7, 127.3, 127.2, 115.5, 115.2.

Entry **5j**: dimethyl-[4-(1*H*-tetrazol-5-yl)-phenyl]-amine:[9k] Elemental analysis (%) calculated for $C_9H_{11}N_5$ C, 57.13; H, 5.86; N, 37.01. Found (%) C, 57.20; H, 5.89; N, 37.09. ^{1}H − NMR: 7.25−7.32 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 3.74 (s, 6H). ^{13}C − NMR: 160.0, 132.9, 132.8, 131.6, 130.8, 45.2.

Entry **5k**: 5-(4-chloro-phenyl)-1*H*-tetrazole:[9j] Elemental analysis (%) calculated for $C_7H_5ClN_4$ C, 46.55; H, 2.79; N, 31.02. Found (%) C, 46.54; H, 2.81; N, 31.08. ^{1}H − NMR: 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H). ^{13}C − NMR: 160.3, 132.9, 131.6, 130.8, 128.6.

Entry **5l**: 5-(4-bromo-phenyl)-1*H*-tetrazole:[9j] Elemental analysis (%) calculated for $C_7H_5BrN_4$ C, 37.36; H, 2.24; N, 24.90. Found (%) C, 37.38; H, 2.28; N, 24.94. ^{1}H − NMR: 7.18 (t, *J* = 6.8 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H). ^{13}C − NMR: 163.1, 131.0, 130.9, 128.8, 115.5, 115.3.

Entry **5m**: 4-(1*H*-tetrazol-5-yl)-benzaldehyde:[9j] Elemental analysis (%) calculated for $C_8H_6N_4O$ C, 55.17; H, 3.47; N, 32.17. Found (%) C, 55.18; H, 3.49; N, 32.20. ^{1}H − NMR: 9.83 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H). ^{13}C − NMR: 202.1, 159.7, 129.0, 120.3, 112.5, 110.1.

Entry **5n**: 1-[3-(1*H*-tetrazol-5-yl)-phenyl]-ethanone:[9i] Elemental analysis (%) calculated for $C_9H_8N_4O$ C, 57.44; H, 4.28; N, 29.77. Found (%) C, 57.47; H, 4.32; N, 29.78. ^{1}H − NMR: 7.38 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.22−7.27 (m, 1H), 6.86 (s, 1H), 3.78 (s, 3H). ^{13}C − NMR: 205.1, 159.7, 133.1, 133.0, 129.3, 128.4, 114.1, 113.7, 25.5.

Entry **5o**: 1-[4-(1*H*-tetrazol-5-yl)-phenyl]-ethanone:[9i] Elemental analysis (%) calculated for $C_9H_8N_4O$ C, 57.44; H, 4.28; N, 29.77. Found (%) C, 57.45; H, 4.30; N, 29.79. ^{1}H − NMR: 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H). ^{13}C − NMR: 205.1, 152.8, 132.8, 131.5, 130.7, 128.5, 21.9.

Entry **5p**: 5-(4-nitro-phenyl)-1*H*-tetrazole:[9h] Elemental analysis (%) calculated for $C_7H_5N_5O_2$ C, 43.98; H, 2.64; N, 36.64. Found (%) C, 44.01; H, 2.65; N, 36.68. ^{1}H − NMR: 6.99 (dd, *J* = 1.2, 5.2 Hz, 2H), 6.90 (d, *J* = 1.2 Hz, 2H). ^{13}C − NMR: 149.5, 148.4, 125.0, 114.5, 114.3.

Entry **5q**: 5-(4-trifluoromethyl-phenyl)-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_8H_5F_3N_4$ C, 44.87; H, 2.35; N, 26.16. Found (%) C, 44.89; H, 2.38; N, 26.19. ^{1}H − NMR: 7.31 (d, *J* = 6.8 Hz, 2H), 7.25 (d, *J* = 6.0 Hz, 2H). ^{13}C − NMR: 159.8, 133.6, 129.5, 129.0, 128.5, 126.4.

Entry **5r**: 5-biphenyl-4-yl-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_{13}H_{10}N_4$ C, 70.26; H, 4.54; N, 25.21. Found (%) C, 70.29; H, 4.55; N, 25.24. ^{1}H − NMR: 7.46 (d, *J* = 4.0 Hz, 2H), 7.44 (d, *J* = 12.4 Hz, 2H), 7.31 (s, 2H), 7.23 (t, *J* = 6.4 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H). ^{13}C − NMR: 159.6, 136.7, 132.7, 131.7, 128.5, 128.2, 127.6, 126.5, 125.8.

Entry **5s**: 5-naphthalen-2-yl-1*H*-tetrazole:[9i] Elemental analysis (%) calculated for $C_{11}H_8N_4$ C, 67.34; H, 4.11; N, 28.55. Found (%) C, 67.35; H, 4.14; N, 28.57. ^{1}H − NMR: 6.93 (d, *J* = 8.0 Hz, 2H), 6.80 (t, *J* = 4.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.56 (s, 1H), 6.11 (t, *J* = 7.6 Hz, 1H), 5.90 (s, 1H). ^{13}C − NMR: 163.8, 147.8, 147.2, 132.9, 130.8, 123.0, 121.1.

Entry **5t**: 4-(1*H*-tetrazol-5-yl)-pyridine:[9j] Elemental analysis (%) calculated for $C_6H_5N_5$ C, 48.98; H, 3.43; N, 47.60. Found (%) C, 48.95; H, 3.47; N, 47.62. ^{1}H − NMR: 6.94 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 2H). ^{13}C − NMR: 158.0, 149.5 148.4, 124.9.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02277.

^{1}H and ^{13}C NMR spectra for all compounds prepared (PDF)

X-ray crystallographic information file for complex **1** (CIF)

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Notes

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The mechanistic discussion regarding the conversion of arylboronic acids to tetrazoles, Scheme 4, and ref 30 were deleted on January 10, 2017.

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