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The sequential reactions of tetrazoles with bromoalkynes for the synthesis of (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides and 2-arylindoles†

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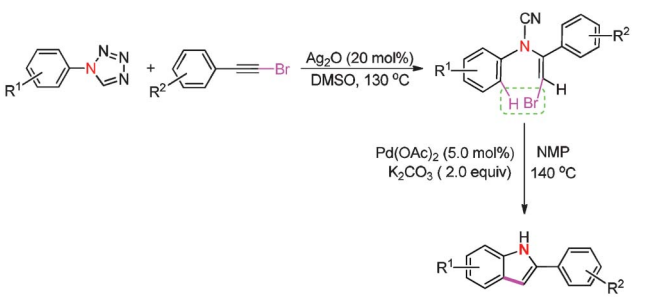
2-Arylindoles were prepared by a sequential reaction of Ag-catalyzed α-addition–Pd-catalyzed C–H bond functionalization of tetrazoles with bromoalkynes. A stereocontrolled Ag-catalyzed α-addition reaction of tetrazoles with bromoalkynes underwent smoothly to generate (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides, which were subsequently converted into 2-arylindoles through an intramolecular cyclization by Pd-catalyzed direct C–H bond functionalizations.

Nitrogen-containing heterocycles are of great importance in the pharmaceutical industry and have attracted much attention from organic chemists, as they exhibit favorable biological activity and pharmaceutical significance. Among them, indoles are important nitrogen heterocyclic compounds, which are key structural motifs in many natural products and are present in a wide range of pharmaceuticals with biologically relevant properties.[1] For the above reason, many useful and efficient synthetic methods have been developed for the synthesis of indoles.[2] To the best of our knowledge, a powerful and classic route to 2-phenylindole is the Fischer indole synthesis, which is based on the reaction of phenylhydrazine with acetophenone in the presence of a Lewis acid.[3] The other routes to 2-arylindoles are based mainly on the transition-metal-catalyzed coupling of indoles with various aryl compounds, such as halobenzenes,[4] $[Ar–I^+–Ar]BF_4^-$,[5] arylsiloxanes,[6] aryltrifluoroborate salts,[7] arylboronic acids,[8] *etc*. In addition, 2-arylindoles also can be obtained through the following methods,[9] for example, Ir-catalyzed hydroamination of internal alkynes,[9a] electrosynthesis from *o*-nitrostyrenes,[9e] Ni-catalyzed cycloaddition of anthranilic acid derivatives to alkynes,[9h] and Pd-catalyzed cascade reaction of imines with *o*-dihaloarenes or *o*-chlorosulfonates,[9i] *etc*. However, there are some drawbacks in the above methods, such as the unstable starting materials or harsh reaction conditions used in most of the cases.

1-Aryltetrazoles are stable multi-nitrogen compounds, which are widely applied in rocket propellants and explosives.[10] Apart from that, they are also used for organic transformations *via* their C–H bond functionalizations.[11] Generally, they are easily converted to *N*-arylcyanamides in the presence of a strong base. However, to the best of our knowledge, there are few reports of tetrazoles being used as synthetic equivalents of cyanamides.[12]

Bromoalkynes are obtained from terminal alkynes with NBS and used as important intermediates in coupling reactions.[13] Recently, a transition-metal-catalyzed cross-coupling and a cyclization reaction using bromoalkynes as one of the starting materials have been reported by our group.[14] In order to establish novel organic transformations, we further investigated the possibility of transition-metal-catalyzed reactions between 1-aryltetrazoles and bromoalkynes. Herein, we wish to report an Ag_2O-catalyzed α-addition of 1-aryltetrazoles to bromoalkynes, which generated (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides in good yields with excellent stereoselectivity. Furthermore, the obtained (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides undergo intramolecular cyclization to afford the corresponding 2-arylindoles in good yields *via* a palladium-catalyzed direct C–H bond functionalization process (Scheme 1).



Scheme 1

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† Electronic supplementary information (ESI) available: General information, detailed experimental procedures, and characterization data for all products. CCDC reference numbers 920810 and 920811. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ra40669e

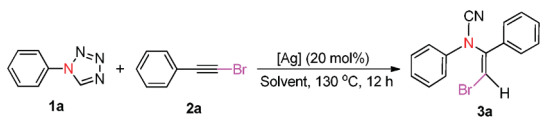
In the initial exploration of the stereocontrolled α-addition reaction of tetrazoles to bromoalkynes, 1-phenyl-1*H*-tetrazole (**1a**) and phenylethynyl bromide (**2a**) were chosen as the model substrates for the investigation and the results are shown in Table 1. Firstly, the effect of the solvent on the model reaction was examined. When the model reaction was performed in the presence of Ag_2CO_3 (20 mol%) in DMSO at 130 °C for 12 h, 80% yield of (*Z*)-*N*-(2-bromo-1-phenylvinyl)-*N*-phenylcyanamide (**3a**) was isolated with the *Z*-isomer as the sole product, and it was characterized by ^1H and ^{13}C NMR spectroscopy and HRMS analysis (Table 1, entry 1). Slightly lower yields of **3a** were obtained when CH_3CN, chlorobenzene or CH_3NO_2 was used instead of DMSO (Table 1, entries 2–4). 1,2-Dichloroethane (DCE), dioxane, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), benzene, toluene, *N*-methyl-2-pyrrolidone (NMP), and C_2H_5OH were inferior and afforded 31–63% yields of **3a** (Table 1, entries 5–12). On the other hand, the effect of the Ag source was also examined. The results indicated that Ag_2O was the most effective among the tested Ag sources. AgOAc, Ag_2SO_4 and $AgBF_4$ were inferior (Table 1, entries 13–15). Only a trace amount of the desired product **3a** was observed when AgCl or $AgNO_3$ was used in the reaction (Table 1, entries 16 and 17). When 20 mol% of Ag_2O was used, the desired product **3a** was isolated in 82% yield, but a poor yield of **3a** was obtained by decreasing the amount of Ag_2O (Table 1, entries 18–21).

Under the optimized reaction conditions, a variety of substituted tetrazoles reacted with bromoalkynes smoothly to generate the corresponding α-addition products in good yields with excellent stereoselectivity, and the results are summarized in Table 2. Clearly, 1-aryl-1*H*-tetrazoles bearing substituents on the *para*-position of the benzene ring have no obvious effect on the yields of the reactions. 1-Aryl-1*H*-tetrazoles with both electron-donating and electron-withdrawing groups, such as Me, Et, F, Cl, Br, I, NO_2, CF_3, and MeCO on the *para*-position of the benzene ring reacted with phenylethynyl bromide (**2a**) to generate the corresponding products (**3b–j**) in 72–81% yield of exclusively the *Z*-isomer (Table 2, entries 2–10). Furthermore, treatment of 3-methylphenyl-, 3-*iso*-propylphenyl-, and 3-chlorophenyl-1*H*-tetrazole with phenylethynyl bromide (**2a**) also gave the corresponding products (**3k–m**) in 75–82% yields (Table 2, entries 11–13). The effect of substituents at the *ortho*-position of tetrazoles was observed in the reaction of 2-methylphenyl- and 2-chlorophenyl-1*H*-tetrazole with **2a**, which generated the desired products (**3n** and **3o**) in 58% and 63% yields (Table 2, entries 14 and 15). The multi-substituted 1-aryl-1*H*-tetrazoles reacted with **2a** smoothly to give the corresponding products **3p** and **3q** in 73% and 84% yields (Table 2, entries 16 and 17). However, naphthalen-1-yl-tetrazole reacted with **2a** to afford the desired product **3r** in 61% yield (Table 2 entry 18). Meanwhile, the reactions of 1-phenyl-1*H*-tetrazole with a series of arylethynyl bromides, such as (4-methylphenyl)-, (4-*tert*-butylphenyl)-, (4-fluorophenyl)-, and (4-chlorophenyl)ethynyl bromide proceeded well and generated the corresponding products **3s–v** in good yields (Table 2, entries 19–22). It is important to note that aliphatic bromoalkynes, such as 1-bromohex-1-yne also could be converted to the corresponding addition product **3w** with **2a** in good yield (Table 2, entry 23).

The structure of compounds **3e** and **3f** was determined to be in the *Z*-configuration, confirmed unambiguously using single crystal X-ray analysis. The corresponding CIF data are presented in the Electronic Supplementary Information (CCDC 920810 and 920811, ESI†).[15]

With the obtained (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides (**3a–w**) in hand, the transformation of **3a–w** into the corresponding 2-arylindoles by palladium-catalyzed direct C–H bond activation and intramolecular cyclization along with the loss of the CN group was investigated. For optimization of the reaction conditions, a variety of palladium sources were tested in the presence of K_2CO_3 at 140 °C in DMF, and the results indicated that the model reaction could be catalyzed by Pd^{II} salts or Pd^0 complexes. $Pd(OAc)_2$ was found to be the most active catalyst, and **3a** was converted into 2-phenylindole (**4a**) in 44% yield (Table 3, entry 1). Other palladium sources, such as $PdCl_2$, $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ were used instead of $Pd(OAc)_2$, 20–40% yields of **4a** were obtained (Table 3, entries 2–4). The solvent also plays an important role in the reaction; 80% yield of **4a** was obtained when the reaction was performed in NMP. DMA, C_2H_5OH, DMSO, toluene, CH_3CN were inferior and afforded lower yields of **4a** (Table 3, entries 6–10). When the solvent was switched to THF, dioxane, $ClCH_2CH_2Cl$ or CH_3NO_2, no product **4a** was detected by TLC (Table 3, entries 11–14). Further investigation on various bases showed that no other bases performed better than K_2CO_3. Lower yields of **4a** (12–71%) were obtained when Na_2CO_3, KOAc, K_3PO_4, LiO^{t}Bu, KO^{t}Bu, or Cs_2CO_3 was used as a base in the reaction (Table 3, entries 15–20).

Table 1 Optimization of the reaction conditions[a]

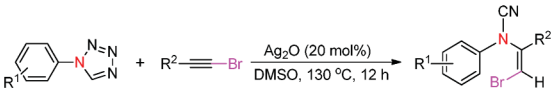


1a 2a 3a

Entry	Solvent	Ag source	Yield (%)[b]
1	DMSO	Ag_2CO_3	80
2	CH_3CN	Ag_2CO_3	74
3	Chlorobenzene	Ag_2CO_3	73
4	CH_3NO_2	Ag_2CO_3	71
5	DCE	Ag_2CO_3	60
6	DMF	Ag_2CO_3	56
7	DMA	Ag_2CO_3	53
8	Toluene	Ag_2CO_3	51
9	Benzene	Ag_2CO_3	45
10	NMP	Ag_2CO_3	44
11	Dioxane	Ag_2CO_3	38
12	C_2H_5OH	Ag_2CO_3	31
13	DMSO	AgOAc	40
14	DMSO	Ag_2SO_4	17
15	DMSO	$AgBF_4$	12
16	DMSO	AgCl	Trace
17	DMSO	$AgNO_3$	Trace
18	DMSO	Ag_2O	82
19	DMSO	Ag_2O	83[c]
20	DMSO	Ag_2O	82[d]
21	DMSO	Ag_2O	57[e]

[a] Reaction conditions: **1a** (0.50 mmol), **2a** (0.75 mmol), Ag catalyst (20 mol%), solvent (2.0 mL), 130 °C, sealed tube, air, 12 h. [b] Isolated yields. [c] 50 mol% Ag_2O was used. [d] 30 mol% Ag_2O was used. [e] 10 mol% Ag_2O was used.

Table 2 Ag_2O-catalyzed α-addition reactions of tetrazoles to bromoalkynes[a]



1 2 3

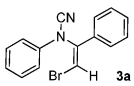
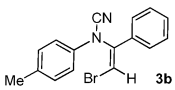
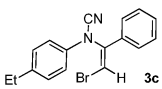
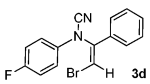
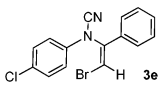
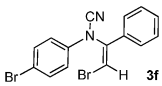
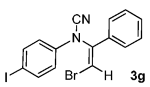
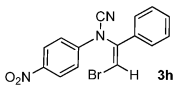
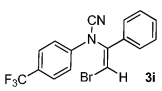
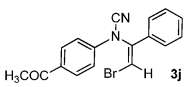
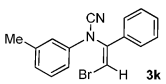
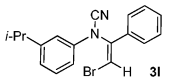
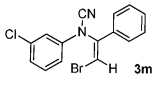
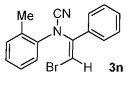
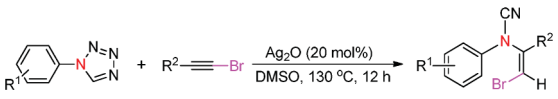
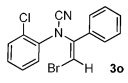
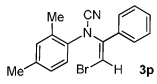
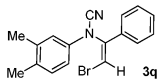
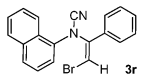
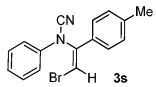
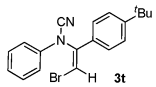
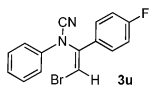
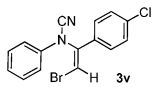
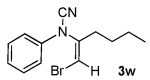
Entry	R^1	R^2	Product, **3**	Yield (%)[b]
1	H	C_6H_5	 **3a**	82
2	4-Me	C_6H_5	 **3b**	80
3	4-Et	C_6H_5	 **3c**	81
4	4-F	C_6H_5	 **3d**	72
5	4-Cl	C_6H_5	 **3e**	74
6	4-Br	C_6H_5	 **3f**	76
7	4-I	C_6H_5	 **3g**	75
8	4-NO_2	C_6H_5	 **3h**	70
9	4-CF_3	C_6H_5	 **3i**	73
10	4-CH_3CO	C_6H_5	 **3j**	71
11	3-Me	C_6H_5	 **3k**	81
12	3-(*iso*-Pr)	C_6H_5	 **3l**	82
13	3-Cl	C_6H_5	 **3m**	75
14	2-Me	C_6H_5	 **3n**	58

Table 2 (*Continued*)



1 2 3

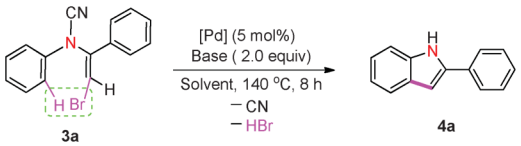
Entry	R^1	R^2	Product, **3**	Yield (%)[b]
15	2-Cl	C_6H_5	 **3o**	63
16	2,4-$(Me)_2$	C_6H_5	 **3p**	73
17	3,4-$(Me)_2$	C_6H_5	 **3q**	84
18		C_6H_5	 **3r**	61
19	H	4-MeC_6H_4	 **3s**	81
20	H	4-^{t}BuC_6H_4	 **3t**	75
21	H	4-FC_6H_4	 **3u**	85
22	H	4-ClC_6H_4	 **3v**	82
23	H	*n*-C_4H_9	 **3w**	75

[a] Reaction conditions: **1** (0.50 mmol), **2** (0.75 mmol), Ag_2O (0.10 mmol), DMSO (2.0 mL), 130 °C, sealed tube, air, 12 h. [b] Isolated yield.

Meanwhile, poor results were observed when Et_3N or pyridine was used as the base (Table 3, entries 21 and 22).

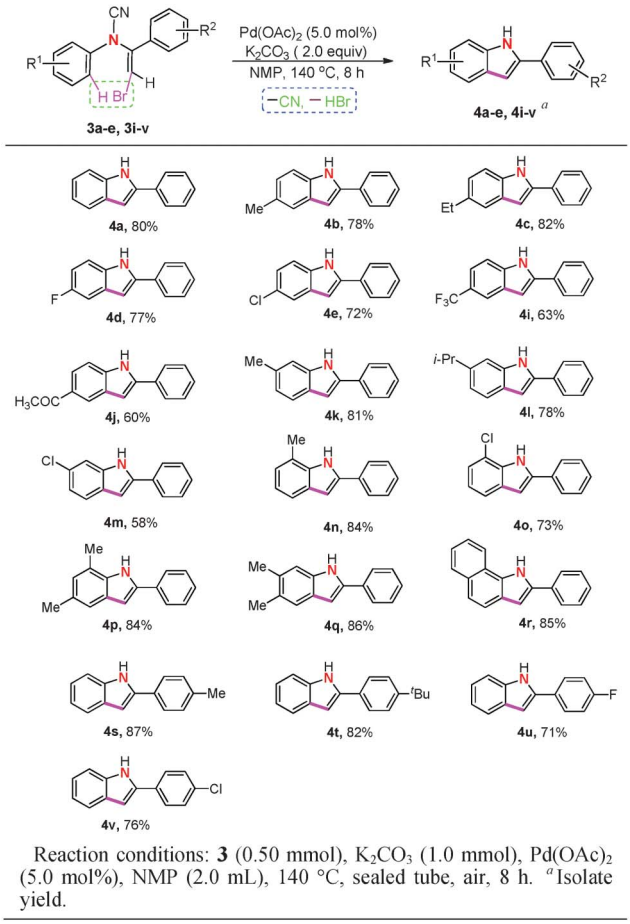
With the optimum reaction conditions for the cyclization of **3a** in hand, the prepared addition products (except **3f–h** and **3w**) underwent palladium-catalyzed intramolecular cyclization smoothly *via* the direct C–H bond functionalization to generate the corresponding 2-arylindoles along with the loss of the CN group. As can be seen from Scheme 2, substrates (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides **3** with either electron-donating or electron-withdrawing groups attached to the benzene ring were able to undergo the intramolecular cyclization reaction smoothly. Electron-donating groups on the aromatic rings of **3** gave better yields than electron-withdrawing groups on the aromatic rings of **3**

Table 3 Optimization of the reaction conditions for the palladium-catalyzed intramolecular cyclization of (*Z*)-*N*-(2-bromo-1-phenylvinyl)-*N*-phenylcyanamide (**3a**)[a]



Entry	Pd source	Base	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	K_2CO_3	DMF	44
2	$PdCl_2$	K_2CO_3	DMF	40
3	$Pd(PPh_3)_4$	K_2CO_3	DMF	29
4	$Pd(PPh_3)_2Cl_2$	K_2CO_3	DMF	20
5	$Pd(OAc)_2$	K_2CO_3	NMP	80
6	$Pd(OAc)_2$	K_2CO_3	DMA	62
7	$Pd(OAc)_2$	K_2CO_3	C_2H_5OH	17
8	$Pd(OAc)_2$	K_2CO_3	DMSO	13
9	$Pd(OAc)_2$	K_2CO_3	Toluene	10
10	$Pd(OAc)_2$	K_2CO_3	CH_3CN	7
11	$Pd(OAc)_2$	K_2CO_3	THF	ND[c]
12	$Pd(OAc)_2$	K_2CO_3	Dioxane	ND[c]
13	$Pd(OAc)_2$	K_2CO_3	DCE	NR[d]
14	$Pd(OAc)_2$	K_2CO_3	CH_3NO_2	NR[d]
15	$Pd(OAc)_2$	Na_2CO_3	NMP	71
16	$Pd(OAc)_2$	KOAc	NMP	58
17	$Pd(OAc)_2$	K_3PO_4	NMP	48
18	$Pd(OAc)_2$	LiO^tBu	NMP	15
19	$Pd(OAc)_2$	KO^tBu	NMP	13
20	$Pd(OAc)_2$	Cs_2CO_3	NMP	12
21	$Pd(OAc)_2$	Et_3N	NMP	9
22	$Pd(OAc)_2$	Pyridine	NMP	Trace

[a] Reaction conditions: **3a** (0.50 mmol), base (2.0 equiv), Pd source (5.0 mol%), solvent (2.0 mL), 140 °C, sealed tube, air, 8 h. [b] Isolated yield. [c] ND = No desired product was detected. [d] NR = No reaction.

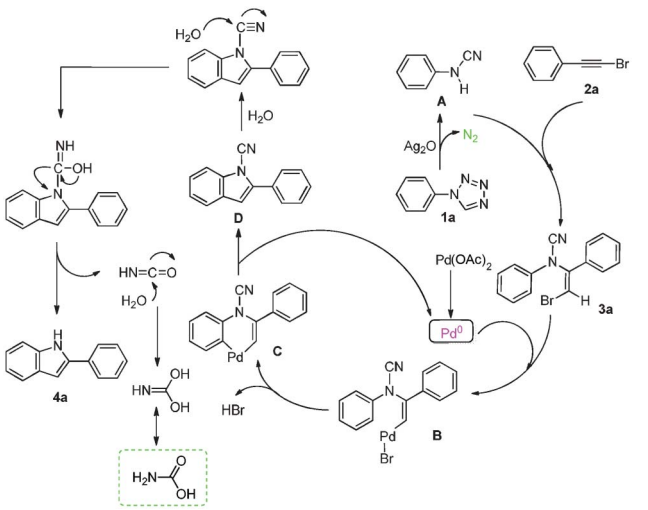


Reaction conditions: **3** (0.50 mmol), K_2CO_3 (1.0 mmol), $Pd(OAc)_2$ (5.0 mol%), NMP (2.0 mL), 140 °C, sealed tube, air, 8 h. [a] Isolate yield.

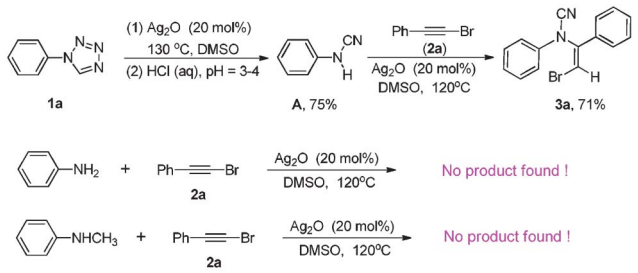
Scheme 2 Palladium-catalyzed cyclization reactions of (*Z*)-*N*-(2-bromo-1-phenylvinyl)-*N*-phenylcyanamides to 2-arylindoles.

(**4b**, **4c**, **4k**, **4l**, **4n**, **4p** and **4q** *vs.* **4d**, **4e**, **4i**, **4j**, **4m** and **4o**). It should be noted that the cyclization reactions were complicated and no desired products were obtained when (*Z*)-*N*-(4-bromophenyl)-, (*Z*)-*N*-(4-iodophenyl)- and (*Z*)-*N*-(4-nitrophenyl)-*N*-(2-bromo-1-phenylvinyl)cyanamide (**3f–h**) were used as substrates, which can be ascribed to the more sensitive groups, Br, I and NO_2 on the phenyl rings in the presence of the Pd-catalyst. Meanwhile, it is important to note that the cyclization products of **3k–m** were 6-substituted-2-phenylindoles (**4k–m**), and **3q** was 5,6-disubstituted-2-phenylindole (**4q**) with excellent regioselectivity. The *ortho*-position effect was not observed in the reaction, which generated **4n** and **4o** in 84 and 73% yields, respectively. When reactions of the substrates derived from the reactions of 1-phenyl-1*H*-tetrazole (**1a**) with substituted phenylethynyl bromides, such as (4-methylphenyl)-, (4-*tert*-butylphenyl)ethynyl-, (4-fluorophenyl)-, and (4-chlorophenyl)-bromides were carried out under the standard reaction conditions, the corresponding products were obtained in 71–87% yields (Scheme 2, **4s–v**). However, (*Z*)-*N*-(1-bromohex-1-en-2-yl)-*N*-phenylcyanamide **3w** could not give the corresponding cyclization product due to the lower reaction activity.

On the basis of our experimental results and our previous reports,[14a,16] a plausible mechanism for this sequential reaction of the addition–Pd-catalyzed cyclization reaction is proposed, as shown in Scheme 3. Firstly, *N*-phenylcyanamide (**A**) was formed by a Ag-catalyzed decomposition of 1-phenyl-1*H*-tetrazole (**1a**) with loss of N_2 (it is highly recommended that an Ace pressure tube is



Scheme 3 Proposed reaction mechanism.



Scheme 4 Controlled experiments.

employed for safety considerations),[11,12] which underwent α-addition to phenylethynyl bromide (**2a**) to generate (*Z*)-*N*-(2-bromo-1-phenylvinyl)-*N*-phenylcyanamide (**3a**) with excellent stereoselectivity. The obtained **3a** reacted with Pd^0 from its precursor $Pd(OAc)_2$ to form an intermediate **B** *via* oxidative addition. Subsequently, **B** underwent an intramolecular electrophilic aromatic palladation through C–H activation of the aromatic hydrogen, and subsequent proton abstraction, forming an intermediate **C**. This was followed by a reductive elimination to afford intermediate **D** *via* carbon–carbon bond formation and the Pd^0 was regenerated for its catalytic cycle. Finally, **D** could be transformed into the desired product 2-phenylindole (**4a**) by losing a cyano group due to a little water in the solvent.

In order to further understand the reaction process, *N*-phenylcyanamide **A** was synthesized from the reaction of 1-phenyl-1*H*-tetrazole (**1a**) in the presence of Ag_2O. Treatment of **A** with **2a** under the above reaction conditions, afforded product **3a**, which was isolated in 71% yield. It should be noted that other amines, such as aniline or *N*-methylaniline instead of **A**, could not react with **2a** to give addition product (Scheme 4).

In conclusion, we have developed a novel and efficient protocol for the synthesis of 2-arylindoles from tetrazoles and alkynyl bromides. The α-addition reactions of tetrazoles to bromoalkynes generated (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides in good yields with excellent stereoselectivity. The obtained (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides underwent intramolecular cyclization well to afford 2-arylindoles in good yields through palladium-catalyzed direct C–H bond functionalizations, involving loss of the cyano group.

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Notes and references

1 (*a*) A. Rahman and A. Basha, *Indole Alkaloids*, Harwood Academic Publishers, Amsterdam, 1998, p. 141; (*b*) S. Hibino and T. Choshi, *Nat. Prod. Rep.*, 2002, **19**, 148; (*c*) R. R. Gupta, *Heterocyclic Chemistry*, Vol. 2, Springer, New York, 1999, p. 193.

2 For recent reviews, see: (*a*) G. R. Humphrey and J. T. Kuethe, *Chem. Rev.*, 2006, **106**, 2875; (*b*) I. Nakamura and Y. Yamamoto, *Chem. Rev.*, 2004, **104**, 2127; (*c*) S. Cacchi and G. Fabrizi, *Chem. Rev.*, 2005, **105**, 2873; (*d*) R. C. Larock, in *Topics in Organometallic Chemistry Vol. 14: Palladium in Organic Synthesis*, ed. J. Tsuji, Springer, Berlin, 2005, p. 147.

3 (*a*) E. Fischer and F. Jourdan, *Ber.*, 1883, **16**, 2241; (*b*) B. Robinson, *The Fischer Indole Synthesis*, Wiley, New York, 1982; (*c*) R. S. Downing and P. J. Kunkeler, *The Fischer Indole Synthesis*, ed. R. A. Sheldon and H. Bekkum, Wiley-VCH, Weinheim, New York, 2001, pp. 178–183.

4 For selected recent examples, see: (*a*) B. S. Lane and D. Sames, *Org. Lett.*, 2004, **6**, 2897; (*b*) X. Wang, D. V. Gribkov and D. Dames, *J. Org. Chem.*, 2007, **72**, 1476; (*c*) B. Sezen and D. Sames, *J. Am. Chem. Soc.*, 2003, **125**, 5274; (*d*) L. Joucla, N. Batail and L. Djakovitch, *Adv. Synth. Catal.*, 2010, **352**, 2929; (*e*) E. T. Nadres, A. Lazareva and O. Daugulis, *J. Org. Chem.*, 2011, **76**, 471; (*f*) X. Wang, B. S. Lane and D. Sames, *J. Am. Chem. Soc.*, 2005, **127**, 4996.

5 N. R. Deprez, D. Kalyani, A. Krause and M. S. Sanford, *J. Am. Chem. Soc.*, 2006, **128**, 4972.

6 Z. Liang, B. Yao and Y. Zhang, *Org. Lett.*, 2010, **12**, 3185.

7 J. Zhao, Y. Zhang and K. Cheng, *J. Org. Chem.*, 2008, **73**, 7428.

8 S.-D. Yang, C.-L. Sun, Z. Fang, B.-J. Li, Y.-Z. Li and Z.-J. Shi, *Angew. Chem., Int. Ed.*, 2008, **47**, 1473.

9 For selected recent examples, see: (*a*) K. Gray, M. J. Page, J. Wagler and B. A. Messerle, *Organometallics*, 2012, **31**, 6270; (*b*) Y. Wei, I. Deb and N. Yoshikai, *J. Am. Chem. Soc.*, 2012, **134**, 9098; (*c*) H. Li, Z. Zhu, F. Zhang, S. Xie, H. Li, P. Li and X. Zhou, *ACS Catal.*, 2011, **1**, 1604; (*d*) P. G. Alsabeh, R. J. Lundgren, L. E. Longobardi and M. Stradiotto, *Chem. Commun.*, 2011, **47**, 6936; (*e*) P. Du, J. L. Brosmer and D. G. Peters, *Org. Lett.*, 2011, **13**, 4072; (*f*) K. Okuro, J. Gurnham and H. Alper, *J. Org. Chem.*, 2011, **76**, 4715; (*g*) R. Wang, S. Mo, Y. Lu and Z. Shen, *Adv. Synth. Catal.*, 2011, **353**, 713; (*h*) N. Maizuru, T. Inami, T. Kurahashi and S. Matsubara, *Org. Lett.*, 2011, **13**, 1206; (*i*) J. Barluenga, A. Jimenez-Aquino, F. Aznar and C. Valdes, *J. Am. Chem. Soc.*, 2009, **131**, 4031; (*j*) M. Shen, B. E. Leslie and T. G. Driver, *Angew. Chem., Int. Ed.*, 2008, **47**, 5056; (*k*) Q. Nguyen, T. Nguyen and T. G. Driver, *J. Am. Chem. Soc.*, 2013, **135**, 620; (*l*) H. H. Nguyen and M. J. Kurth, *Org. Lett.*, 2013, **18**, 362.

10 (*a*) M. Brown, *US Patent 3, 338, 915*, 1967; *Chem. Abstr.*, 1968, 87299; (*b*) V. A. Ostrovskii, M. S. Pevzner, T. P. Kofmna, M. B. Shcherbinin and I. V. Tselinskii, *Targets Heterocycl. Syst.*, 1999, **3**, 467; (*c*) M. Hiskey, D. E. Chavez, D. L. Naud, S. F. Son, H. L. Berghout and C. A. Bome, *Proc. Int. Pyrotech. Semin.*, 2000, **27**, 3.

11 M. Špulák, R. Lubojacký, P. Šenel, J. Kuneš and M. Pour, *J. Org. Chem.*, 2010, **75**, 241.

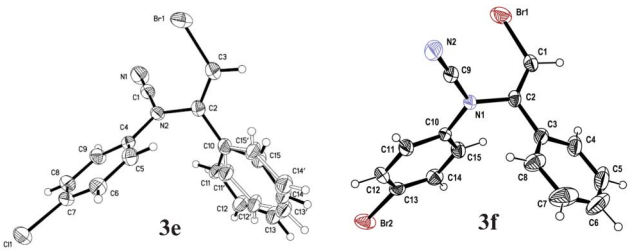
12 For the first reports on the degradation reactions of 1-substituted tetrazoles, see: (*a*) R. Stolle and F. Henke-Stark, *J. Prakt. Chem.*, 1929, **124**, 261; for selected examples, see; (*b*) A. N. Vorobiov, P. N. Gaponik, P. T. Petrov and O. A. Ivashkevich, *Synthesis*, 2006, **8**, 1307; (*c*) I. Čerňa, R. Pohl, B. Klepetářová and M. Hocek, *Org. Lett.*, 2006, **8**, 5389.

13 (*a*) F. Besseliévre and S. Piguel, *Angew. Chem., Int. Ed.*, 2009, **48**, 9553; (*b*) W. Shi, Y. Luo, X. Luo, L. Chao, H. Zhang, J. Wang and A. Lei, *J. Am. Chem. Soc.*, 2008, **130**, 14713; (*c*) K. Dooleweerdt, H. Birkedal, T. Ruhland and T. Skrydstrup, *J. Org. Chem.*, 2008, **73**, 9447; (*d*) B. Yao, Z. Liang, T. Niu and Y. Zhang, *J. Org. Chem.*, 2009, **74**, 4630; (*e*) G. A. Burley, D. L. Davies, G. A. Griffith, M. Lee and K. Singh, *J. Org. Chem.*, 2010, **75**, 980; (*f*) T. Kawano, N. Matsuyama, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*,

2010, **75**, 1764; (*g*) S. H. Kim and S. Chang, *Org. Lett.*, 2010, **12**, 1868; (*h*) H. Xu, Y. Zhang, J. Huang and W. Chen, *Org. Lett.*, 2010, **12**, 3704; (*i*) N. Matsuyama, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2009, **11**, 4156; (*j*) F. M. Istrate, A. K. Buzas, I. D. Jurberg, Y. Odabachian and F. Gagosz, *Org. Lett.*, 2008, **10**, 925; (*k*) M. O. Frederick, J. A. Mulder, M. R. Tracey, R. P. Hsung, J. Huang, K. C. M. Kurtz, L. Shen and C. J. Douglas, *J. Am. Chem. Soc.*, 2003, **125**, 2368.

14 (*a*) S. Wang, P. Li, L. Yu and L. Wang, *Org. Lett.*, 2011, **13**, 5968; (*b*) S. Wang, M. Wang, L. Wang, B. Wang, P. Li and J. Yang, *Tetrahedron*, 2011, **67**, 4800; (*c*) S. Wang, L. Yu, P. Li, L. Meng and L. Wang, *Synthesis*, 2011, 1541.

15 X-ray crystal structures of **3e** and **3f** are shown in the following, and the crystal data were deposited in the CCDC with numbers 920811 and 920810, respectively.



16 W. Zhou, Y. Zhang, P. Li and L. Wang, *Org. Biomol. Chem.*, 2012, **10**, 7184.