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Palladium-Catalyzed Reaction of Arylamine and Diarylacetylene: Solvent-Controlled Construction of 2,3-Diarylindoles and Pentaarylpyrroles

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By choosing DMF and dioxane as solvent, skeletons of indoles and pyrroles were constructed from alkynes and amines in the presence of $PdCl_2$, respectively. These Pd-catalyzed reactions were phosphane-free with high atom efficiency and

Introduction

The importance of indoles and their derivatives in natural products and pharmaceuticals^[1] has prompted the development of many useful methods for their preparation.^[2] The synthesis most often starts from o-substituted anilines or o-substituted nitrobenzenes, which need to be pre-prepared or pre-activated. Few examples start from readily available anilines or N-substituted anilines.^[3] With the development of transition-metal-catalyzed cyclizations, the transition-metal-catalyzed heteroannulation has emerged as a powerful synthetic strategy to construct the indole skeleton.^[4] Recently, Glorius et al. applied the strategy of Pdcatalyzed C-H activation in the intramolecular oxidative cyclization of N-aryl-enaminones^[5] or N-aryl-enamines,^[6] which efficiently obviated the need for o-substituted anilines. More simply, Fagnou and co-workers described an Rh-catalyzed intermolecular oxidative coupling of N-acetvlanilines and alkynes.^[7] in which the acetyl moiety acted as a directing group for o-metalation. Jiao's group also reported a Pd-catalyzed intermolecular oxidative coupling between anilines and but-2-ynedioates to form 2,3-bis(alkoxycarbonyl)indoles.^[8] In this case, the alkynes were electrondeficient, and their reaction was promoted by pivalic acid. In addition, pentaarylpyrroles have proven to be important materials in pharmaceutical and materials science.^[9] Herein, we are pleased to demonstrate a Pd-catalyzed intermolecular oxidative coupling of anilines and diarylalkynes, which furnishes 2.3-

[a] Department of Chemistry, Zhejiang University Hangzhou 310027, P. R. China Fax: +86-571-87952543 E-mail: pinglu@zju.edu.cn orgwyg@zju.edu.cn could be conducted under mild basic conditions. The proposed mechanism for the selective formation of indoles and pyrroles in different solvents is also discussed in this paper.

tions and in a manner that is controlled by one's choice of reaction solvent.

diarylindoles and pentaarylpyrroles under mild basic condi-

Results and Discussion

Pd-Catalyzed Reaction of Arylamine and Diarylacetylene for the Construction of 2,3-Diaryl-1*H*-indoles

Our investigation commenced with the reaction of 1,2diphenylethyne (1a) and aniline (2a) in the presence of PdCl₂ and Cu(OAc)₂ in N,N-dimethylformamide (DMF). To our delight, 2,3-diphenvl-1H-indole (3a) was obtained as a major product as expected.^[10] In order to have the optimized reaction conditions for the formation of 3a, we explored the source of Pd^{II}, the source of Cu salt, the base additive, the reaction solvent, and the reaction temperature. The best result (58% isolated yield of 3a) was achieved with 10 mol-% PdCl₂ and 1.0 equiv. of Cu(OAc)₂ in DMF under N₂ at 100 °C for 6 h (Table 1, Entry 1). PdCl₂, PdBr₂, and Pd(OAc)₂, without triphenylphosphane as the ligand,^[11] worked well for this reaction (Table 1, Entries 1-4). Replacing Cu(OAc)₂ by CuCl₂ or CuBr₂, the yields of 3a were decreased (Table 1, Entries 5-6). As Cu^{II} functioned as the oxidant in this reaction, 2.0 equiv. of Cu^I salt was used. Thus, CuCl, CuBr, and CuI were tested, and yields of 3a were determined to be 45%, 36%, and 32%, respectively (Table 1, Entries 7–9). Increasing the amount of $Cu(OAc)_2$ to 2.0 equiv. decreased the yield of **3a** (Table 1, Entry 10). The reaction relied heavily on the solvent. Polar aprotic solvents, such as dimethylacetamide (DMA) and dimethyl sulfoxide (DMSO), worked for the construction of the indole skeleton, but the yields were poor (Table 1, Entries 11 and 12). When acetonitrile was used as solvent, 3a was not detected, although reactant 1a disappeared completely

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(Table 1, Entry 13). In polar protic solvent, such as methanol, 3a was also not detected, although 1a was consumed (Table 1, Entry 14). When altering the solvent to 1,4-dioxane or tetrahydrofuran (THF), an interesting result was observed in that pentaphenylpyrrole $4a^{[9]}$ was obtained (Table 1, Entries 15 and 16). By decreasing the DMF ratio in the co-solvent of DMF and dioxane, the yield of 3a was diminished (Table 1, Entries 17and 18). Decreasing the reaction temperature to 60 °C, produced 3a in 43% yield, whereas **1a** could be quantitatively recovered when the reaction was conducted at room temperature (Table 1, Entries 19 and 20). In addition, the relatively stronger basicity of Cu(OAc)₂ relative to CuCl was evaluated by using a base additive. Addition of 0.25 equiv. of Na₂CO₃ to reactions mixtures involving PdCl₂/CuCl (2.0 equiv.) afforded 3a, which was isolated in 54% yield (Table 1, Entry 21), a yield comparable to that of Entry 1 in Table 1. When increasing the amount of Na₂CO₃ to 0.5 equiv., it was found that 1a failed to react and could be recovered (Table 1, Entry 22). A similar result was observed for the addition of an organic base, such as triethylamine (Et₃N) (Table 1, Entries 23 and 24). On the basis of these results it seemed advisable that a relatively weak base was necessary for this reaction to proceed. It was also noted that **1a** did not react when the reaction was conducted in the presence of air, though aniline was consumed completely (Table 1, Entry 25). Based on this fact, we tested the stability of aniline by TLC in air without diphenylacetylene (1a). It was clearly noticed that aniline was easily oxidized and consumed in DMF after 1 h.^[12]

With the reaction conditions optimized (Table 1, Entry 1), we then tested the substrate diversity for the cyclization. Various anilines (2a-2i) were suitable for this transformation. Thus, 2,3-diphenylindoles 3a-3i were prepared in yields between 36% and 64% (Figure 1). Substituents, both electron-donating (such as methyl and methoxy) and electron-withdrawing (such as fluoro, chloro, bromo), were tolerated in this reaction and failed to exert detrimental electronic effects. When the aniline was meta-substituted (2c and 2g), oxidative coupling products 3ca and 3cb were obtained regioselectively with a total yield of 47%, and the unique product 3g was isolated in 59% yield. It was also noted that 7-chloro-2,3-diphenylindole (3h) was obtained in 62% yield when 2-chloroaniline (2h) was used as a starting material. The chlorine atom was indeed retained in product **3h**. However, a Larock-type annulation^[4a,4b] occurred when either 2-bromoaniline (2i) or 2-iodoaniline (2k) reacted with 1a under the same reaction conditions (Figure 2). In these cases, **3a** was obtained.

Table 1. Optimization of reaction conditions for the formation of 3a.^[a]

		Ph-=-Ph 1a	+ PhNH₂ [Pd]/[Cu] solvent 2a base <i>T</i> , 6 h	Ph N N B 3a	
Entry	Pd ^{II}	Cu salt/	Solvent.	Temp.	Yield of $3a^{[b]}$
		[equiv.]		[0]	[/0]
1	PdCl ₂	$Cu(OAc)_2$ [1.0]	DMF	100	58
2	PdBr ₂	$Cu(OAc)_2$ [1.0]	DMF	100	53
3	$Pd(OAc)_2$	$Cu(OAc)_2$ [1.0]	DMF	100	56
4	$Pd(PPh_3)_2Cl_2$	$Cu(OAc)_2$ [1.0]	DMF	100	n.r. ^[c]
5	PdCl ₂	$CuCl_2$ [1.0]	DMF	100	33
6	PdCl ₂	CuBr ₂ [1.0]	DMF	100	24
7	PdCl ₂	CuCl [2.0]	DMF	100	45
8	PdCl ₂	CuBr [2.0]	DMF	100	36
9	PdCl ₂	CuI [2.0]	DMF	100	32
10	PdCl ₂	$Cu(OAc)_2$ [2.0]	DMF	100	50
11	PdCl ₂	$Cu(OAc)_{2}$ [1.0]	DMA	100	33
12	PdCl ₂	$Cu(OAc)_2$ [1.0]	DMSO	100	10
13	PdCl ₂	$Cu(OAc)_2$ [1.0]	CH ₃ CN	reflux	n.d. ^[d]
14	$PdCl_2$	$Cu(OAc)_{2}$ [1.0]	CH ₃ OH	reflux	n.d.
15	PdCl ₂	$Cu(OAc)_{2}$ [1.0]	dioxane	reflux	4a (12%)
16	$PdCl_2$	$Cu(OAc)_{2}$ [1.0]	THF	reflux	4a (8%)
17	$PdCl_2$	$Cu(OAc)_{2}$ [1.0]	dioxane/DMF (1:1)	reflux	3a (46%) + 4a (<5%)
18	$PdCl_2$	$Cu(OAc)_{2}$ [1.0]	dioxane/DMF (1:9)	reflux	3a(53%) + 4a(<5%)
19	$PdCl_2$	$Cu(OAc)_{2}$ [1.0]	DMF	60	43
20	$PdCl_2$	$Cu(OAc)_{2}$ [1.0]	DMF	room temp.	n.r.
21 ^[e]	PdCl ₂	CuCl [2.0]	DMF	100	54
22 ^[f]	$PdCl_2$	CuCl [2.0]	DMF	100	n.r.
23 ^[g]	PdCl ₂	CuCl [2.0]	DMF	100	50
24 ^[h]	$PdCl_2$	CuCl [2.0]	DMF	100	n.r.
25 ^[i]	PdCl ₂	Cu(OAc) ₂ [1.0]	DMF	100	n.r

[a] Conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), Pd source (0.05 mmol, 10 mol-%), solvent (2 mL), under N₂, 100 °C, 6 h. [b] Isolated yield. [c] n.r. = no reaction. [d] n.d. = not detected. [e] Na₂CO₃ (0.125 mmol, 0.25 equiv.) was the base additive in the reaction. [f] Na₂CO₃ (0.25 mmol, 0.50 equiv.) was the base additive in the reaction. [g] Et₃N (0.025 mmol, 0.05 equiv.) was the base additive in the reaction. [h] Et₃N (0.05 mmol, 0.10 equiv.) was the base additive in the reaction. Date: 25-06-12 11:36:07

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Figure 1. Formation of indoles 3a-3i from various anilines 2.



Figure 2. Larock-type indole formation of 3a from 2j or 2k.

An electronic effect was observed when the para position of the diarylethyne was substituted (Figure 3). Electronwithdrawing groups (1d and 1e) increased product yields (3k and 3l), whereas electron-donating groups decreased yields (3j). In addition, the structure of 3l was established by crystallographic analyses.^[13] No main product was detected by TLC when 1,2-bis(4-methoxyphenyl)ethyne (1c) was used, although 1c was completely consumed during the reaction. When 1,2-bis(4-acetylphenyl)ethyne (1f) was used as a reactant, it was completely recovered after 6 h of exposure to the reaction conditions. Unsymmetrical diarylacetylenes 1g-1j afforded indoles 3m-3p with no regioselectivity. Due to the relative reactivity of 1b and 1d, we envisioned that R^4 in 3 would be more electron-withdrawing when the diarylacetylene was unsymmetrical. Unfortunately, aliphatic acetylenes did not work well for the construction of the indole ring system. None of the expected product could be isolated from the reaction mixture of hex-1-ynylbenzene and 2a.

Pd-Catalyzed Reaction of Arylamines and Diarylacetylenes for the Construction of Pentaarylpyrroles

As mentioned above, 4a could be efficiently obtained from 1a and 2a when using 1,4-dioxane or THF as solvent (Table 1, Entries 15 and 16).^[9] We tried to optimize the reaction conditions and to investigate the substrate diversity for the formation of pentaarylpyrroles. The function of the Cu^I species proved to be superior to Cu^{II} (Table 2, Entries 1-6). Among these copper salts, CuCl worked the best. By adding 1.0 equiv. of Na_2CO_3 , 4a was obtained in 57% yield. Triethylamine also enhanced this reaction as a comparable yield was achieved (Table 2, Entries 7 and 8). Other Pd^{II} sources, without triphenylphosphane, also worked for the reaction (Table 2, Entries 9-11).^[11] A decreased yield of 4a was observed as the amount of DMF in the co-solvent of DMF and dioxane increased (Table 2, Entries 12 and 13). Additionally, lowering the reaction temperature was found to influence the yield of 4a (Table 2, Entries 14 and 15). When the reaction vessel was opened to air, 4a could still be obtained in 41% yield (Table 2, Entry 16); aniline in 1,4dioxane seemed relatively stable even when freely exposed to air. Finally, the optimized reaction conditions were established (Table 2, Entry 7).

With the optimized reaction conditions in hand, we next tested the scope of substrates possible for the formation of pentaarylpyrroles **4**. As shown in Figure 4, this methodology tolerated a variety of substituents at different positions on the aniline (2a-2n) when treated with diphenylacetylene (1a). Anilines with electron-withdrawing groups (such as



Figure 3. Formation of indoles 3j–3p from various alkynes 1.

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Ph

Ph

Table 2. Optimization of reaction conditions for formation of 4a.^[a]

		Ph— — —Ph + 1a	PhNH ₂ [Pd]/[Cu] base 2a 1,4-dioxane 6 h	► Ph N Ph Ph 4a	
Entry	Pd ^{II}	Cu salt	Temp.	Base	Yield of 4a ^[b]
		[equiv.]	[°C]	[equiv.]	[%]
1	PdCl ₂	CuCl [4.0]	100	_	45
2	PdCl ₂	CuBr [4.0]	100	_	39
3	PdCl ₂	CuI [4.0]	100	_	36
4	PdCl ₂	$Cu(OAc)_{2}$ [2.0]	100	_	12
5	$PdCl_2$	$CuCl_{2}$ [2.0]	100	_	< 5
6	PdCl ₂	$CuBr_{2}[2.0]$	100	_	< 5
7	$PdCl_2$	CuClb [4.0]	100	Na ₂ CO ₃ [1.0]	57
8	$PdCl_2$	CuCl [4.0]	100	Et ₃ N [0.2]	53
9	$PdBr_2$	CuCl [4.0]	100	Na_2CO_3 [1.0]	54
10	$Pd(OAc)_2$	CuCl [4.0]	100	Na_2CO_3 [1.0]	42
11	$Pd(PPh_3)_2Cl_2$	CuCl [4.0]	100	Na_2CO_3 [1.0]	n.r.
12 ^[c]	PdCl ₂	CuCl [4.0]	100	$Na_2CO_3[1.0]$	3a (37%) + 4a (26%)
13 ^[d]	$PdCl_2$	CuCl [4.0]	100	Na_2CO_3 [1.0]	3a (28%) + 4a (30%)
14	$PdCl_2$	CuCl [4.0]	60	$Na_{2}CO_{3}[1.0]$	36
15	$PdCl_2$	CuCl [4.0]	room temp.	Na_2CO_3 [1.0]	n.r.
16 ^[e]	$PdCl_2$	CuCl [4.0]	100	Na_2CO_3 [1.0]	41

[a] Conditions: **1a** (0.50 mmol), **2a** (0.25 mmol), Pd source (0.025 mmol, 10 mol-%), 1,4-dioxane (2 mL), under N_2 , 100 °C, 6 h. [b] Isolated yield. [c] A mixture of DMF/dioxane (1:1) was utilized as solvent. [d] A mixture of DMF/dioxane (1:9) was utilized as solvent. [e] Reaction conducted in the presence of air.



Figure 4. Formation of pyrroles 4a–4n from various anilines 2.

the nitro group in ortho, meta, and para positions) afforded the corresponding pentaarylpyrroles **4l–4n** in 90%, 86%, and 72% yields, respectively. The yields were apparently higher than those obtained with methyl-substituted anilines (4b-4d). Notably, *p*-methoxyaniline (2e) gave 4e in only 36% yield. Relatively low yields were also observed for anilines bearing *ortho* substituents (4d, 4j and 4n) relative to those with *para* substituents (4b, 4f and 4l). We hypothesize that this may be due to steric hindrance imposed by ortho (but not para) substituents of the aniline substrate. It was also noticeable that o-iodoaniline (2k) and o-bromoaniline (21) were suitable for the formation of the corresponding pyrroles (4k and 4l) - though again, in only moderate to poor yields. Importantly, the ability to generate 4k and 4l indicates the survival of the ortho C-I and C-Br of anilines in this Pd-catalyzed system. This is in stark contrast

to the cases of indole formation (Figure 2). Reactions involving symmetrical diarylacetylenes 1b, 1d and 1e produced 40, 4p and 4q in 48%, 67% and 62% yields, respectively (Figure 5). Reaction of 1c, containing the strong electron-donating group, failed to produce the pyrrole product, though 1c was completely consumed. Starting material 1f, with the acetyl group in the *para* position of diarylacetylene, was recovered after attempted coupling with 2a under the same reaction conditions. Reactions involving unsymmetrical diarylacetylenes 1g-1j afforded 3 kinds of isomers, which were formed with little to no regioselectivity (Figure 6). Unfortunately, neither aliphatic amines nor aliphatic acetylenes worked well for the construction of the pyrrole ring. No expected product could be isolated from either the reaction mixture of hex-1-ynylbenzene and 2a or the reaction mixture of **1a** and butan-1-amine.

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Figure 6. Formation of pyrroles 4r–4u from unsymmetrical diarylacetylenes 1g–1j.

Proposed Mechanism

Based on the survey of reaction conditions and the tolerance of substrates, possible mechanisms for the formation Scheme 1.



Scheme 1. Proposed mechanisms for the solvent-dependent formation of 3a and 4a.

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We envision that in 1,4-dioxane solution π complex **A** between **1a** and PdCl₂ is initially formed.^[14] The triple bond is thus activated and becomes electron-deficient. An aminopalladation^[15] occurs subsequently by nucleophilic attack of **2a**. In the structure of **B**, the amino group and Pd are in a *cis* configuration because of the weak coordination between the nitrogen and palladium atoms.^[16] Sufficient amounts of diphenylacetylene make the carbopalladation^[17] occur, and **C** is thus formed. For the same reasons, **C** is a cyclic structure. We envision that then intramolecular nucleophilic substitution occurs on the palladium center, thus forming **D**.^[18] Reductive elimination of Pd^{0[19]} ultimately affords pyrrole **4a**, and the active Pd^{II} complex can eventually be regenerated by oxidation with the Cu source.^[20]

In the more polar DMF solution, DMF has the potential to coordinate with palladium, especially in the presence of copper salts.^[21] Accordingly, intermediate F may be formed either through species E or B. The existence of DMF in F efficiently inhibits the coordination of B with 1a and makes the intramolecular electrophilic aromatic palladation practical, as in the cases of 2a-2i. As evidence of this, when nitroanilines 21,m were used as substrates in DMF, 1-(nitrophenyl)-2,3,4,5-tetraphenyl-1*H*-pyrroles **4**l,**m** were isolated as major adducts instead of the corresponding indoles (Figure 4). In these cases, the electron-withdrawing nature of the nitro group decreased the possibility of the intramolecular electrophilic aromatic palladation. Deprotonation of G under the mildly basic reaction conditions affords intermediate H.^[22] Consequently, reductive elimination of palladium generates indole 3a after which the resulting Pd⁰ species may be oxidized in a copper-dependent fashion to regenerate Pd^{II}.^[20]

Conclusions

We have developed a direct intermolecular oxidative coupling between diarylacetylenes and anilines that is catalyzed by Pd^{II} and copper salts under mildly basic conditions; product selectivity is dictated by one's choice of solvent. In DMF solution, the reaction furnishes 2,3-diarylindoles bypassing the *ortho*-halogenated anilines and thus providing an alternative method to the Larock indole synthesis.^[4a,b] Direct C–H activation and coordination of DMF with the palladium center are involved in this process. When 1,4-dioxane is used as solvent, the reaction affords pentaarylpyrroles. A palladium-catalyzed three-component reaction ensues. For both the DMF and 1,4-dioxane reactions both Cu^{II} and Cu^{I} work well as the oxidant. Further investigations into both of these reaction mechanisms are in process.

Experimental Section

General Methods: Melting points were recorded with a Büchi 535 apparatus. NMR spectra were obtained with a Bruker Avance DMX400 spectrometer operating at 400 MHz for ¹H NMR and

100 MHz for ¹³C NMR in CDCl₃, or a Bruker Avance DMX500 spectrometer operating at 500 MHz for ¹H NMR and 125 MHz for ¹³C NMR spectroscopy. All high-resolution mass spectra (HRMS) were recorded by using a GCT Premier CAB170 instrument. Flash column chromatography was performed by employing 300–400 mesh silica gel. Thin layer chromatography (TLC) was performed with silica gel HSGF254.

Typical Procedure for the Synthesis of 2,3-Diphenyl-1*H*-indole (3a): In a 10 mL round-bottom flask, 1a (89 mg, 0.5 mmol), 2a (70 mg, 0.75 mmol), Cu(OAc)₂ (40 mg, 0.2 mmol), and 10 mol-% of PdCl₂ (9 mg, 0.05 mmol) were dissolved in dry DMF (2 mL) at ambient temperature. The reaction mixture was degassed and then purged with nitrogen three times. The sealed flask was then heated at 100 °C for ca. 6 h. After complete consumption of the starting material as determined by TLC, the residue was dissolved in diethyl ether, washed with water (3×15 mL), and dried with Na₂SO₄. After filtration, the filtrate was distilled under reduced pressure, and the residue was purified by flash chromatography on silica gel (CH₂Cl₂/hexane, 1:10). Compound 3a (78 mg, 58%) was obtained as off-white solid. M.p. 120.6-122.0 °C; ref.^[2i] 120-121 °C. ¹H NMR (400 MHz, CDCl₃; Supporting Information, Figure S1): δ = 8.20 (br., 1 H), 7.74 (d, J = 7.9 Hz, 1 H), 7.51–7.40 (m, 7 H), 7.38– 7.26 (m, 5 H), 7.21 (dd, $J_1 = J_2 = 7.5$ Hz, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃; Supporting Information, Figure S2): δ = 135.87, 135.04, 134.06, 132.66, 130.14, 128.73, 128.65, 128.51, 128.16, 127.66, 126.22, 122.68, 120.41, 119.68, 115.01, 110.90 ppm. HRMS: calcd. for C₂₀H₁₅N [M]⁺ 269.1204; found 269.1208.

Typical Procedure for the Synthesis of 1,2,3,4,5-Pentaphenyl-1Hpyrrole (4a): In a 10 mL round-bottom flask, 1a (89 mg, 0.5 mmol), 2a (23 mg, 0.25 mmol), CuCl (93 mg, 1 mmol), Na₂CO₃ (26 mg, 0.25 mmol) and 10 mol-% of PdCl₂ (5 mg, 0.025 mmol) were dissolved in dry 1.4-dioxane (2 mL) at ambient temperature. The reaction mixture was degassed and then purged with nitrogen three times. The sealed flask was then heated at reflux for ca. 6 h. After complete consumption of the starting material as determined by TLC, the residue was dissolved in diethyl ether, washed with water $(3 \times 15 \text{ mL})$, and dried with Na₂SO₄. After filtration, the filtrate was distilled under reduced pressure, and the residue was purified by flash chromatography on silica gel (CH₂Cl₂/hexane, 1:20). Compound 4a (64 mg, 57%) was obtained as a yellowish solid. M.p. 265.8-267.4 °C. ¹H NMR (400 MHz, CDCl₃; Supporting Information, Figure S31): δ = 7.16–7.06 (m, 15 H), 6.98–6.93 (m, 10 H) ppm. ¹³C NMR (100 MHz, CDCl₃; Supporting Information, Figure S32): $\delta = 138.57, 135.25, 132.20, 131.62, 131.36, 131.06,$ 129.15, 128.22, 127.53, 127.50, 126.76, 126.39, 125.34, 122.82 ppm. HRMS: calcd. for C₃₄H₂₅N [M]⁺ 447.1987; found 447.1992.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures, characterization data, and copies of ¹H and ¹³C NMR spectra for products **3a–3p** and **4a–4u**.

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Two different kinds of Pd-catalyzed cyclizations, leading to the construction of 2,3diarylindole and pentaarylpyrrole from the same alkyne and aniline starting materials, were approached by choosing different solvents. The mechanisms for these solventcontrolled reactions are proposed and discussed. **Pd-Catalyzed Cyclization**

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Palladium-Catalyzed Reaction of Arylamine and Diarylacetylene: Solvent-Controlled Construction of 2,3-Diarylindoles and Pentaarylpyrroles

Keywords: Indoles / Pyrroles / Alkynes / Aminopalladation / Palladium catalysis / Cyclization / Solvent effects