JOC*Note*

pubs.acs.org/joc

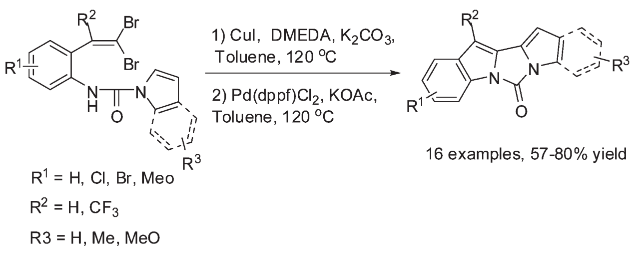
Synthesis of Unsymmetrical 2,2′-Biindolyl Derivatives by a Cu-Catalyzed *N*-Arylation/Pd-Catalyzed Direct Arylation Sequential Process

Zhi-Jing Wang,[†] Fan Yang,[†] Xin Lv,[‡] and Weiliang Bao*,[†]

[†]*Department of Chemistry, Zhejiang University, Hangzhou 310028, P. R. China, and* [‡]*Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua, Zhejiang, 321004, P. R. China*

wlbao@css.zju.edu.cn

Received September 26, 2010



A one-pot synthesis of unsymmetrical 2,2′-biindolyl derivatives through a Cu-catalyzed *N*-arylation/Pd-catalyzed direct arylation sequence was described. The reaction involved easily prepared *o*-*gem*-dibromovinyl substrates, and the desired biindolyls were obtained in moderate to good yields.

The indole framework represents a privileged structural motif of established value in biologically active natural products and pharmaceutical compounds.[1] The indole-incorporated 2,2′-biindolyls have drawn much attention because of their structural features and potential therapeutic applications. For example, 2,2′-biindolyls-derived indolocarbazole alkaloid rebeccamycin (**I**) is an inhibitor of DNA topoisomerase I,[2] while staurosporine (**II**) targets protein kinase C,[3] both of which display antitumor activity; **III** could be used for the biosynthesis of eumelanine;[4] **IV** are macrocyclic Ni(II) complexes containing the 2,2′-biindolyl moiety;[5] and **V** is claimed to be a colorimetric anion receptor[6] (Figure 1, I−V).

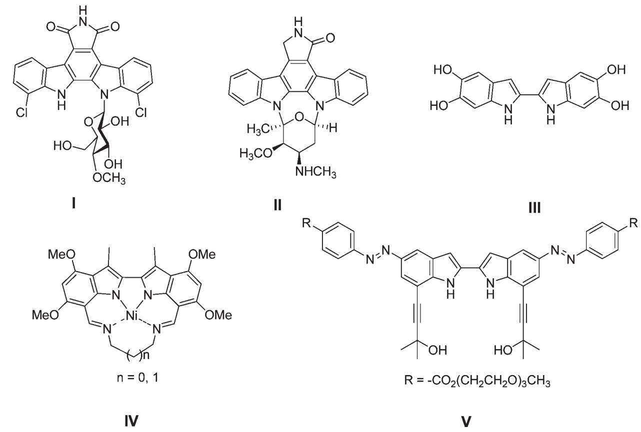


FIGURE 1. Several 2,2′-biindolyl derivatives reported as biologically active compounds and pharmaceutical products.

In this regard, the synthesis of 2,2′-biindolyls is one of the most extensive areas of research, and a number of approaches to prepare these compounds have been developed.[7] Among them, the protocol from 1,1′-carbonyldiindole was more convenient and milder.[7b] The method involved an initial step to form 1,1′-carbonyl-2,2′-biindolyl, which could easily undergo a hydrolysis to obtain 2,2′-biindolyl.[7c] But the necessity of equimolar quantity of $Pd(OAc)_2$ made large-scale synthesis by this procedure less amenable. Besides, most strategies could only synthesize symmetrical 2,2′-biindolyls, while the preparations of unsymmetrical ones were not well documented.[7c,g,h] Therefore, more efficient and economical routes to synthesize unsymmetrical 2,2′-biindolyls under mild conditions are needed.

In recent years, Cu-catalyzed reactions have been successfully applied to assemble various heterocyclic compounds via one-pot strategies, due to their efficiency and low cost.[8] The direct arylation approach has received substantial attention

(1) (a) Sundberg, R. J. *Indoles*; Academic Press: San Diego, 1996; p 175. (b) Nicolaou, K. C.; Snyder, S. A. *Classics in Total Synthesis II*; Wiley-VCH: Weinheim, 2003.

(2) (a) Nettleton, D. E.; Doyle, T. W.; Krishnan, B.; Matsumoto, G. K.; Clardy, J. *Tetrahedron Lett*. **1985**, *26*, 4011. (b) Pereira, E. R.; Belin, L.; Sancelme, M.; Prudhomme, M.; Ollier, M.; Rapp, M.; Sevère, D.; Riou, J.-F.; Fabbro, D.; Meye, T. *J. Med. Chem*. **1996**, *39*, 4471.

(3) (a) Omura, S.; Iwai, Y.; Hirano, A.; Nakagawa, A.; Awaya, J.; Tsuchiya, H.; Takahashi, Y.; Masuma, R. J. *Antibiotics* **1977**, *30*, 275. (b) Tamaoki, T.; Nomoto, H.; Takahashi, I.; Kato, Y.; Morimoto, M.; Tomita, F. *Biochem. Biophys. Res. Commun*. **1986**, *135*, 397.

(4) Napolitano, A.; Corradini, M. G.; Prota, G. *Tetrahedron Lett*. **1985**, *26*, 2805.

(5) Black, D. St C.; Kumar, N.; Wong, L. C. H. *J. Chem. Soc., Chem. Commun*. **1985**, 1174.

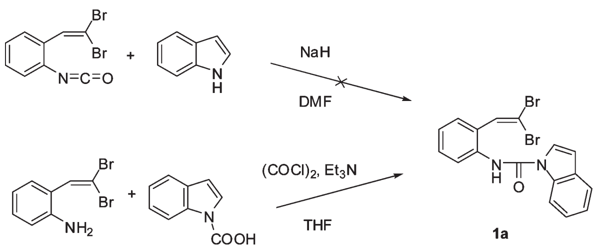
(6) Lee, G. W.; Kim, N.-K.; Jeong, K.-S. *Org. Lett*. **2010**, *12*, 2634.

(7) For selected examples of synthesis of 2,2′-biindolyls, see: (a) Madelung, W. *Ber*. **1912**, *45*, 1128. (b) Bergman, J.; Eklund, N. *Tetrahedron* **1980**, *36*, 1439. (c) Palmisano, G.; Santagostini, M. *Helv. Chim. Acta* **1993**, *76*, 2356. (d) Hudkins, R. L.; Diebold, J. L.; Marsh, F. D. *J. Org. Chem*. **1995**, *60*, 6218. (e) Shin, K.; Ogasawara, K. *Synlett* **1995**, 859. (f) Koza, D. J.; Euler, W. B. *Heterocycl. Commun*. **1999**, *5*, 399. (g) Merlic, C. A.; You, Y.; McInnes, D. M.; Zechman, A. L.; Miller, M. M.; Deng, Q. L. *Tetrahedron* **2001**, *57*, 5199. (h) Koradin, C.; Dohle, W. A.; Rodriguez, L.; Schmid, B.; Knochel, P. *Tetrahedron* **2003**, *59*, 1571.

(8) For selected examples of synthesis of heterocycles via Cu-catalyzed one-pot processes: (a) Joyce, L. L.; Evindar, G.; Batey, R. A. *Chem. Commun*. **2004**, 446. (b) Martin, R.; Rivero, M. R.; Buchwald, S. L. *Angew. Chem., Int. Ed*. **2006**, *45*, 7079. (c) Zou, B.; Yuan, Q.; Ma, D. *Org. Lett*. **2007**, *9*, 4291. (d) Zheng, N.; Buchwald, S. L. *Org. Lett*. **2007**, *9*, 4749. (e) Viirre, R. D.; Evindar, G.; Batey, R. A. *J. Org. Chem*. **2008**, *73*, 3452. (f) Yang, D.; Fu, H.; Hu, L.; Jiang, Y.; Zhao, Y. *J. Org. Chem*. **2008**, *73*, 7841. (g) Wang, B.; Lu, B.; Jiang, Y.; Zhang, Y.; Ma, D. *Org. Lett*. **2008**, *10*, 2761. (h) Yao, P.-Y.; Zhang, Y.; Hsung, R. P.; Zhao, K. *Org. Lett*. **2008**, *10*, 4275. (i) Kim, J.; Lee, S. Y.; Lee, J.; Do, Y.; Chang, S. *J. Org. Chem*. **2008**, *73*, 9454. (j) Verma, A. K.; Kesharwani, T.; Singh, J.; Tandon, V.; Larock, R. C. *Angew. Chem., Int. Ed*. **2009**, *48*, 1138. (k) Li, L.; Wang, M.; Zhang, X.; Jiang, Y.; Ma, D. *Org. Lett*. **2009**, *11*, 1309. (l) Zhu, J.; Xie, H.; Chen, Z.; Li, S.; Wu, Y. *Chem. Commun*. **2009**, 2338.

DOI: 10.1021/jo101899a Published on Web 01/12/2011

SCHEME 1. Synthesis of *o-gem*-Dibromovinyl Substrates

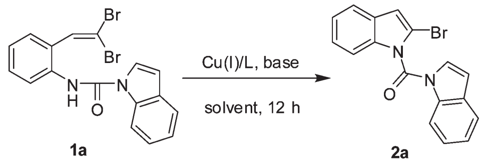


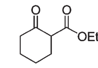
for its sustainable and environmentally benign features.[9] However, there were only limited examples of reactions in which direct arylations were coupled with another process.[10] Therefore, the combination of Cu-catalyzed coupling reactions with direct arylation to obtain structurally complex heterocyclic compounds is of significance.

o-gem-Dihalovinylanilines[11] have been recently developed for the synthesis of various 2-substituted indole derivatives via domino processes.[12−14] Our group has also reported a one-pot method to synthesize pyrimido[1,6-*a*]indol-1(2*H*)-one derivatives through a nucleophilic addition/Cu-catalyzed *N*-arylation/Pd-catalyzed C−H activation sequential process, in which the reactive ortho position of anilines underwent direct arylations.[15]

The C-2 position of indoles is also of high reactivity, on which direct arylations may easily be conducted.[16] Thus, we envisaged that indoles could also be applicable under our catalytic system.

TABLE 1. Optimization of the C−N Bond Formation Reaction Conditions[a]



entry	Cu(I)	ligand	base	temp (°C)	solvent	yield (%)
1	CuI	1,10-Phen[b]	K_2CO_3	120	Toluene	70
2	CuI	L-Proline	K_2CO_3	120	Toluene	52
3	CuI		K_2CO_3	120	Toluene	47
4	**CuI**	**DMEDA**[c]	$\mathbf{K_2CO_3}$	**120**	**Toluene**	**83**
5	CuI	No ligand	K_2CO_3	120	Toluene	45
6	CuI	DMEDA	Cs_2CO_3	120	Toluene	37
7	CuI	DMEDA	K_3PO_4	120	Toluene	22
8	CuI	DMEDA	Et_3N	120	Toluene	n.r.[d]
9	CuI	DMEDA	K_2CO_3	80	Toluene	32
10	CuI	DMEDA	K_2CO_3	100	Toluene	58
11	CuI	DMEDA	K_2CO_3	110	1,4-dioxane	75
12	CuI	DMEDA	K_2CO_3	90	CH_3CN	18
13	CuI	DMEDA	K_2CO_3	120	DMF	trace
14	CuBr	DMEDA	K_2CO_3	120	Toluene	60
15	Cu_2O	DMEDA	K_2CO_3	120	Toluene	15

[a]Unless otherwise noted, the reactions were carried out using **1a** (0.5 mmol), Cu source (0.05 mmol), ligand (0.1 mmol), and base (1.0 mmol) in solvent (4.0 mL) under N_2, for 12 h. [b]1,10-Phen = 1,10-phenanthroline. [c]DMEDA = *N*,*N*′-dimethylethylenediamine. [d]n.r. = no reaction.

TABLE 2. Optimization of the Second Cyclization: Intramolecular Direct Arylation Conditions[a]

entry	Pd catalyst	base	yield (%)
1	$PdCl_2$	K_2CO_3	55
2	Pd(dppf)Cl_2[b]	K_2CO_3	75
3	$Pd(OAc)_2$	K_2CO_3	45
4	$Pd(dba)_2$[c]	K_2CO_3	trace
5	Pd(dppf)Cl_2	Cs_2CO_3	60
6	Pd(dppf)Cl_2	K_3PO_4	62
7	**Pd(dppf)$\mathbf{Cl_2}$**	**KOAc**	**87**

[a]Unless otherwise noted, the reactions were carried out using **2a** (0.5 mmol), Pd source (0.05 mmol), and base (1.5 mmol) in solvent (4.0 mL) under N_2, at 120 °C for 24 h. [b]dppf = 1,1′-bis(diphenylphosphino)ferrocene. [c]dba = 1,5-diphenylpenta-1,4-dien-3-one.

Herein, as a part of our continuing effort, we report a novel and efficient protocol to the synthesis of unsymmetrical 1,1′-carbonyl-2,2′-biindolyls through a Cu-catalyzed *N*-arylation/Pd-catalyzed direct arylation sequential process.

Initially, *o-gem*-dibromovinylphenyl isocyanate and indole were employed as the model substrates. However, the nucleophilic addition was unsuccessful. So we decided to change the synthetic route, and *o-gem*-dibromovinylaniline and indole-1-carboxylic acid were selected as the starting materials. Indole-1-carboxylic acid was treated with oxalyl

(9) For recent reviews on direct arylation, see: (a) Dyker, G., Ed. *Handbook of C−H Transformations*; Wiley-VCH: Weinheim, 2005; Vols. 1 and 2. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (c) Seregin, I. V.; Gevorgyan, V. *Chem. Soc. Rev*. **2007**, *36*, 1173. (d) Campos, K. R. *Chem. Soc. Rev*. **2007**, *36*, 1069. (e) Li, C.-J. *Acc. Chem. Res.* **2009**, *42*, 335. (f) McGlacken, G. P.; Bateman, L. M. *Chem. Soc. Rev*. **2009**, *38*, 2447.

(10) For selected examples, see: (a) Cuny, G.; Bois-Choussy, M.; Zhu, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 4774. (b) Cuny, G.; Bois-Choussy, M.; Zhu, J. *J. Am. Chem. Soc.* **2004**, *126*, 14475. (c) Bedford, R. B.; Betham, M. *J. Org. Chem.* **2006**, *71*, 9403. (d) Thansandote, P.; Raemy, M.; Rudolph, A.; Lautens, M. *Org. Lett.* **2007**, *9*, 5255. (e) Ackermann, L.; Althammer, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 1627. (f) Watanabe, T.; Ueda, S.; Inuki, S.; Oishi, S.; Fujii, N.; Ohno, H. *Chem. Commun.* **2007**, 4516. (g) Jensen, T.; Pedersen, H.; Bang-Andersen, B.; Madsen, R.; Jørgensen, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 888. (h) Hostyn, S.; Van Baelen, G.; Lemière, G. L. F.; Maesa, B. U. W. *Adv. Synth. Catal.* **2008**, *350*, 2653. (i) Budén, M. E.; Vaillard, V. A.; Martin, S. E.; Rossi, R. A. *J. Org. Chem.* **2009**, *74*, 4490. (j) Zhu, B.; Wang, G.-W. *Org. Lett.* **2009**, *11*, 4334. (k) Pinto, A.; Neuville, L.; Zhu, J. *Tetrahedron Lett.* **2009**, *50*, 3602.

(11) Thiegles, S.; Meddah, E.; Bisseret, P.; Eustache, J. *Tetrahedron Lett.* **2004**, *45*, 907.

(12) (a) Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2005**, *7*, 3549. (b) Yuen, J.; Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2006**, *8*, 653. (c) Fayol, A.; Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2006**, *8*, 4203. (d) Fang, Y.-Q.; Karisch, R.; Lautens, M. *J. Org. Chem.* **2007**, *72*, 1341. (e) Fang, Y.-Q.; Yuen, Y.; Lautens, M. *J. Org. Chem.* **2007**, *72*, 5152. (f) Nagamochi, M.; Fang, Y.- Q.; Lautens, M. *Org. Lett.* **2007**, *9*, 2955. (g) Fang, Y.-Q.; Lautens, M. *J. Org. Chem.* **2008**, *73*, 538. (h) Bryan, C. S.; Lautens, M. *Org. Lett.* **2008**, *10*, 4633. (i) Chai, D. I.; Lautens, M. *J. Org. Chem.* **2009**, *74*, 3054. (j) Newman, S. G.; Lautens, M. *J. Am. Chem. Soc.* **2010**, *132*, 11416.

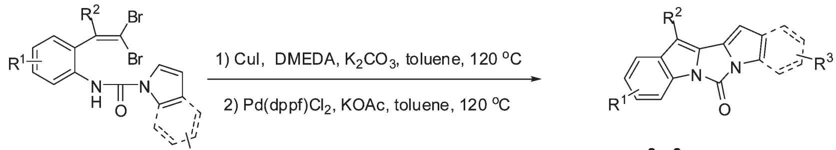
(13) Viera, T. O.; Meaney, L. A.; Shi, Y.-L.; Alper, H. *Org. Lett.* **2008**, *10*, 4899.

(14) Arthuis, M.; Pontikis, R.; Florent, J.-C. *Org. Lett.* **2009**, *11*, 4608.

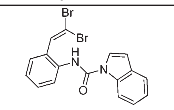
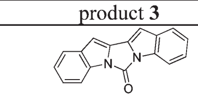
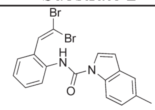
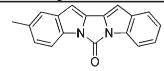
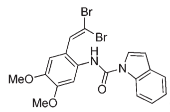
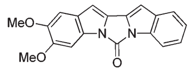
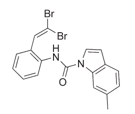
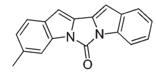
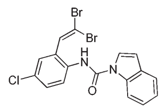
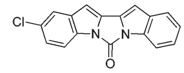
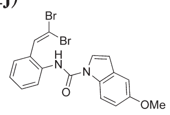
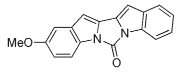
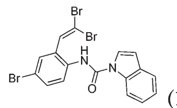
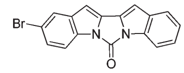
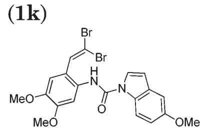
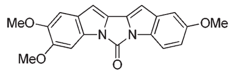
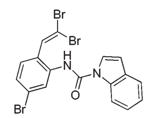
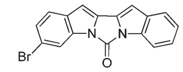
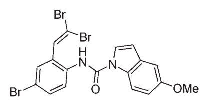
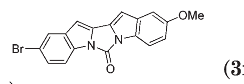
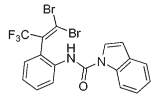
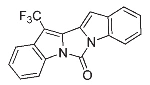
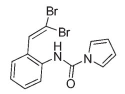
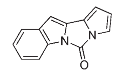
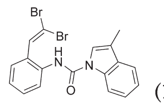
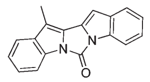
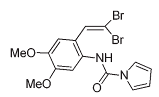
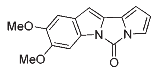
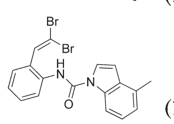
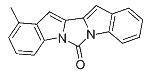
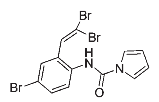
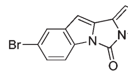
(15) Wang, Z.-J.; Yang, J.-G.; Yang., F.; Bao, W. *Org. Lett.* **2010**, *12*, 3034.

(16) For selected examples of direct arylation on the C-2 position of indoles, see: (a) Wang, X.; Lane, B. S.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 4996. (b) Lane, B. S.; Brown, M. A.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 8050. (c) Bressy, C.; Alberico, D.; Lautens, M. *J. Am. Chem. Soc.* **2005**, *127*, 13148. (d) Bremner, J. B.; Sengpracha, W. *Tetrahedron* **2005**, *61*, 5489. (e) Wang, X.; Gribkov, D. V.; Sames, D. *J. Org. Chem.* **2007**, *72*, 1476. (f) Lebrasseur, N.; Larrosa, I. *J. Am. Chem. Soc.* **2008**, *130*, 2926. (g) Zhao, J.; Zhang, Y.; Cheng, K. *J. Org. Chem.* **2008**, *73*, 7428. (h) Joucla, L.; Djakovitch, L. *Adv. Synth. Catal.* **2009**, *351*, 673.

TABLE 3. Cu-Catalyzed *N*-Arylation/Pd-Catalyzed Direct Arylation Sequential Reaction of Substituted *o-gem*-Dibromovinyl Substrates[a,b]



1a-1p **3a-3p**

entry	Substrate 2	product 3	yield (%)	entry	Substrate 2	product 3	yield (%)
1	 (**1a**)	 (**3a**)	74	9	 (**1i**)	 (**3i**)	68
2	 (**1b**)	 (**3b**)	77	10	 (**1j**)	 (**3j**)	72
3	 (**1c**)	 (**3c**)	65	11	 (**1k**)	 (**3k**)	71
4	 (**1d**)	 (**3d**)	62	12	 (**1l**)	 (**3l**)	75
5	 (**1e**)	 (**3e**)	67	13	 (**1m**)	 (**3m**)	57
6	 (**1f**)	 (**3f**)	70	14	 (**1n**)	 (**3n**)	67
7	 (**1g**)	 (**3g**)	80	15	 (**1o**)	 (**3o**)	68
8	 (**1h**)	 (**3h**)	63	16	 (**1p**)	 (**3p**)	62

[a]Unless otherwise noted, the reactions were carried out using *o-gem*-dibromovinyl substrates **1** (0.5 mmol), CuI (0.05 mmol), DMEDA (0.1 mmol), and K_2CO_3 (1.0 mmol) in toluene (4.0 mL), under N_2 at 120 °C, then Pd(dppf)Cl_2 (0.05 mmol) and KOAc(1.5 mmol), in toluene (4.0 mL), under N_2 at 120 °C. [b]For times for Cu-Catalyzed *N*-arylation and time for Pd-catalyzed direct arylation, see the Supporting Information.

chloride to form corresponding acid chloride, which reacted with *o-gem*-dibromovinylaniline to afford the desired acylation product (**1a**) successfully (Scheme 1).[17] Then we screened the reaction conditions of C−N bond formation using **1a**, and the results are shown in Table 1.

Preliminary investigation found that ligand has a significant influence on this reaction. After a range of common ligands were tested, DMEDA was selected as the optimal (Table 1, entry 4). Various bases and solvents were then screened, and K_2CO_3 and toluene proved to be the most efficient. The research also found that the yield decreased while reducing the temperature (entries 9−10). When the Cu source was switched to CuBr or Cu_2O, the result deteriorated (entries 14 and 15). Therefore, the reaction conditions described in entry 4 were the optimal.

To achieve the "one-pot" process, toluene was utilized as the solvent for the direct arylation of **2a**. Several different Pd sources were examined, and the result was remarkably improved when Pd(dppf)Cl_2 was employed for the second cyclization to produce 1,1′-carbonyl-2,2′-biindolyl (**3a**) (Table 2, entry 2). After several bases were screened, KOAc turned out to be the best base to promote the intramolecular direct arylation (entry 7).

The one-pot protocol was then examined. When the formation of **2a** completed, Pd(dppf)Cl_2 and KOAc were directly added to the reaction mixture without further purification, and **3a** were obtained successfully in good yield. Since the two steps of reactions required different metal catalysts and bases, we also attempted to use only one metal

(17) (a) Boger, D. L.; Pate1, M. *J. Org. Chem.* **1987**, *52*, 2319. (b) Boger, D. L.; Pate1, M. *J. Org. Chem.* **1987**, *52*, 3934.

catalyst such as $Pd(dppf)Cl_2$ and one of the two bases K_2CO_3 and KOAc to promote the two steps of arylations, but failed.

Under the above optimized reaction conditions, the generality of the reaction was investigated, and the results are summarized in Table 3.

All the substituted *N*-(2-(2,2-dibromovinyl)phenyl)-1*H*-indole-1-carboxamides reacted smoothly and afforded the desired products **3a−m**. The protocol proved to be a general and efficient method for the preparation of 2,2′-biindolyl derivatives. When the substituents on the phenyl ring were different from the ones on the indole ring, unsymmetrical 1,1′-carbonyl-2,2′-biindolyls were attained. *o-gem*-Dibromovinyl substrates with both electron-donating substituents (4,5-diMeO) (entry 2) and electron-withdrawing ones (4-Cl, 4-Br, 5-Br) (entries 3−5) on the phenyl ring could afford the corresponding products **3b−e**. It was noteworthy that this reaction seemed not sensitive to steric hindrance. 3-Substituted indoles **3f**,**g** could be provided from the corresponding substrates in good yields (entries 6 and 7). The reactions of substrates from electron-rich indoles(3′-Me, 4′-Me, 5′-Me, 6′-Me, 5′-MeO) afforded the corresponding products **3g−k** with good results (entries 7−11). Unsymmetrical 1,1′-carbonyl-2,2′-biindolyls with electron-donating substituents on both indole rings, or the ones bearing electron-rich substituents on one indole ring, while electron-deficient groups on the other indole ring, were obtained easily (entries 12 and 13). However, the access to unsymmetrical products bearing electron-deficient groups on the both indole rings was unsuccessful, for the indole-1-carboxylic acids with an electron-withdrawing group, such as 5-NO_2, 5-Br and 5-CN, seemed unstable, and could not be obtained. When we replaced indole with pyrrole, the reactions could also undergo smoothly to attain the products in moderate yields (entries 14−16).

In summary, we have developed a one-pot strategy for the assembly of unsymmetrical 1,1′-carbonyl-2,2′-biindolyl derivatives through a Cu-catalyzed *N*-arylation/Pd-catalyzed direct arylation sequential process. A variety of *o-gem*-dibromovinyl substrates were applicable for this process, and moderate to good yields are obtained. The products are potentially useful for their biological and pharmacological activities. Studies are ongoing in our laboratory to discover the synthetic applications.

Experimental Section

Typical Procedure for the Synthesis of 1,1′-Carbonyl-2,2′-biindolyls. To a solution of *N*-(2-(2,2-dibromovinyl)phenyl)-1*H*-indole-1-carboxamide **1a** (210 mg, 0.50 mmol) in toluene (4 mL) at rt under N_2 atmosphere were added CuI (10 mg, 0.05 mmol, 10 mol %), DMEDA (9 mg, 0.10 mmol, 20 mol %), and K_2CO_3 (138 mg, 1.0 mmol) and the mixture heated with stirring at 120 °C for 12 h. Then to the reaction mixture were added $Pd(dppf)Cl_2$ (37 mg, 0.05 mmol, 10 mol %) and KOAc (147 mg, 1.5 mmol), and the resulting mixture was stirred at 120 °C for another 24 h. After that, the reaction mixture was filtered through Celite and washed with CH_2Cl_2 (10 mL × 3), and the filtrate was evaporated under reduced pressure. The residue was purified by a quick flash chromatography on silica gel using petroleum ether/EtOAc (20:1) as eluent to afford 1,1′-carbonyl-2,2′-biindolyl **3a** as a pale yellowish-green solid (96 mg, 74%): mp 290−292 °C (lit.[7b] mp 293−294 °C); not well soluble in $CDCl_3$ or DMSO-d_6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.21 (t, $J = 7.8$ Hz, 2H), 6.70 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 102.5, 112.7, 122.5, 123.9, 126.0, 130.4, 133.2, 134.0, 144.4; EI-MS 258; IR (neat) 3052, 2904, 1756, 1607, 1475, 1303, 1009, 929, 824, 743 cm^{-1}.

Acknowledgment. This work was financially supported by the Natural Science Foundation of China (No. 21072168).

Supporting Information Available: Experimental procedure, characterization data, and copies of ^{1}HNMR and ^{13}CNMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.