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# Palladium-Catalyzed Regioselective Oxidative Coupling of Indoles and One-Pot Synthesis of Acetoxylated Biindolyls

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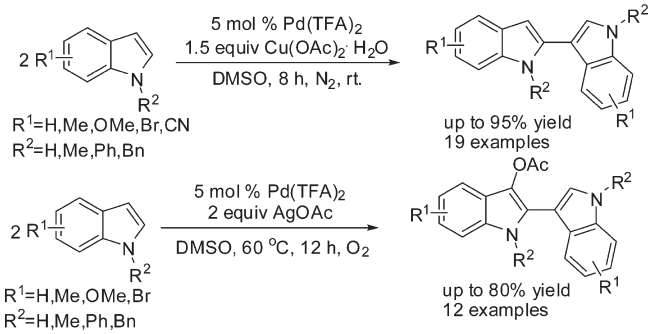


Mild conditions have been developed to achieve Pd-catalyzed homocoupling of indoles with excellent regioselectivity in the presence of $Cu(OAc)_2 \cdot H_2O$ in DMSO at room temperature in high efficiency. This method provides a simple route to 2,3′-biindolyls from the electron-rich to moderately electron-poor indoles. The reaction tolerates the bromide substituent on indoles. In addition, a one-pot approach to C3-position acetoxylated biindolyls is realized via palladium catalysis by the use of AgOAc under oxygen atmosphere as oxidants.

## Introduction

Biindolyls are useful structural units that are frequently found in pharmaceuticals and functional materials.[1] Both chemical and enzymatic synthetic methods have been reported for the construction of biindolyls,[2] and the acidic dimerization of indoles followed by dehydrogenation is the most traditional method for the preparation of biindolyls.[3] For instance, exposing the indole to anhydrous hydrogen chloride and subsequent dehydrogenation using 10 mol % Pd/C results in 2,3′-biindolyls in 65% overall yield.[4] It has been reported that 0.5 equiv of thallium(III) trifluoroacetate and 10 equiv of $BF_3 \cdot Et_2O$ can transform indoles into biindolyls.[5] On the other hand, the methods based on the transition-metal-catalyzed coupling of aryl halides with arylmetals have emerged as versatile tools for the synthesis of biaryls over the past decades,[6] and biindolyls have been

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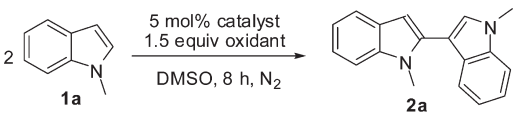
constructed facilely by Stille reaction and Suzuki reaction.[7] Recently, an efficient strategy by the palladiun-catalyzed annulation of *o*-ethynylanilines with iodoindoles was reported for the synthesis of biindolyls.[8] However, these methods require the prefunctionalization of indoles to their halide or metallic derivatives. From both scientific and environmental points of view, the development of methodology for direct activation of C−H bonds is of great significance, and metal-catalyzed C−H bond functionalization has attracted much attention currently.[9] For example, palladium-catalyzed C−H activation has been successfully applied in the homocoupling of thiophenes to approach the bithiophene units in the presence of silver salt,[10] and biindolizines have been prepared by combination of palladium catalyst and copper reagent via C−H bond cleavage.[11] As part of our ongoing investigations on selective and controllable C−H bond functionalization,[12] we studied the palladium-catalyzed oxidative coupling of indoles. Herein, we report a mild and selective method for dimerization of indoles by palladium catalysis to give 2,3′-biindolyls in high yields at room temperature. Moreover, a one-pot procedure for C3-position acetoxylated biindolyls is established by using AgOAc as oxidant at 60 °C for 12 h.

## Results and Discussion

On the outset of our study, we examined the homocoupling of *N*-methylindole in the presence of palladium catalysts. It was found that the dimerization reaction occurred by use of 5 mol % $Pd(OAc)_2$ catalyst to give the 2,3′-dimer of *N*-methylindole 1,1′-dimethyl-1*H*,1′*H*-2,3′-biindole in 40% yield in the presence of 1.5 equiv of $Cu(OAc)_2 \cdot H_2O$ in DMSO at 90 °C for 8 h (Table 1, entry 1). The derivatives of 2,2′- and 3,3′-biindolyls were not observed under the reaction conditions, showing excellent regioselectivity. A higher efficiency was observed by the use of other palladium catalysts such as $PdCl_2$, $Pd(CH_3CN)_2Cl_2$, $Pd(PPh_3)_4$, and $Pd(dba)_2$ (Table 1, entries 2−5), and the best result was obtained with $Pd(TFA)_2$ to give 80% yield (Table 1, entry 6). To our delight, when we performed the reaction at 60 °C, the yield of the product was increased under these reaction conditions (Table 1, entry 7). The reaction was further improved to afford 91% yield at room temperature (Table 1, entry 8). The reaction in the absence of palladium catalysts or copper reagents resulted in no homocoupling (Table 1, entries 10−11). Although $Cu(OAc)_2$ showed slightly higher efficiency than $Cu(OAc)_2 \cdot H_2O$ (Table 1, entry 9), $Cu(OAc)_2 \cdot H_2O$ was used as oxidant in the subsequent experiments because of its low cost and ease of handling. Silver(I) reagents such as AgOAc, $Ag_2CO_3$, and $Ag_2O$ were found to be ineffective (Table 1, entries 13−15), and only trace amounts of the product were observed when $K_2S_2O_8$, CuO, or $O_2$ were used as oxidants (Table 1, entries 12, 16, 17). The reaction in other solvents tested, including 1,4-dioxane, DMF, THF, acetone, and toluene, was sluggish (Table 1, entry 18).

**TABLE 1. Effects of Metals and Oxidants on the Dimarization[a]**




| entry | catalyst | oxidative | temp (°C) | yield (%)[b] |
|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | 40 |
| 2 | $PdCl_2$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | 69 |
| 3 | $Pd(CH_3CN)_2Cl_2$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | 75 |
| 4 | $Pd(PPh_3)_4$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | 75 |
| 5 | $Pd(dba)_2$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | 78 |
| 6 | $Pd(TFA)_2$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | 80 |
| 7 | $Pd(TFA)_2$ | $Cu(OAc)_2 \cdot H_2O$ | 60 | 86 |
| 8 | $Pd(TFA)_2$ | $Cu(OAc)_2 \cdot H_2O$ | rt | 91 |
| 9 | $Pd(TFA)_2$ | $Cu(OAc)_2$ | rt | 92 |
| 10 | | $Cu(OAc)_2 \cdot H_2O$ | rt | nr |
| 11 | $Pd(TFA)_2$ | | rt | trace |
| 12 | $Pd(TFA)_2$ | CuO | rt | trace |
| 13 | $Pd(TFA)_2$ | AgOAc | rt | 36 |
| 14 | $Pd(TFA)_2$ | $Ag_2O$ | rt | trace |
| 15 | $Pd(TFA)_2$ | $Ag_2CO_3$ | rt | trace |
| 16 | $Pd(TFA)_2$ | $K_2S_2O_8$ | rt | trace |
| 17 | $Pd(TFA)_2$ | $O_2$ | rt | trace |
| 18 | $Pd(TFA)_2$ | $Cu(OAc)_2 \cdot H_2O$ | rt | 15[c] |

[a]Reaction condition: *N*-methyl indole (1 mmol), oxidant (1.5 mmol), catalyst (0.05 mmol), DMSO (6 mL), 8 h, $N_2$. [b]Isolated yields based on *N*-methyl indole. TFA = trifluoroacetate, rt = room temperature, nr = no reaction. [c]1,4-Dioxane as the solvent instead of DMSO.

The scope of the reaction was examined and $Pd(TFA)_2$/$Cu(OAc)_2 \cdot H_2O$ is an efficient and selective catalytic system for the dimerization of various indoles as summarized in Table 2. The indoles containing electron-donating substitutes such as methyl and methoxy reacted smoothly to give 2,3′-dimers of indoles in high yields (Table 2, entries 3−6 and 13, 14). 4-Methyl-*N*-methylindole and 4-methyl-*N*-benzylindole gave relatively lower yield, possibly due to the steric hindrance (Table 2, entries 2 and 12). However, the reaction of 6-methoxy-*N*-methylindoles and 6-methoxy-*N*-benzylindole showed similar tendency of reactivity as in the direct arylation of indoles[12c] and displayed moderate reactivity (Table 2, entries 7 and 15). The presence of bromine in

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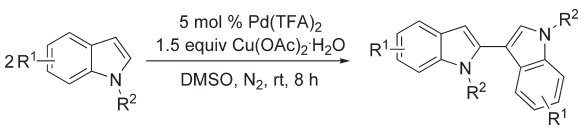
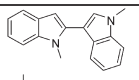
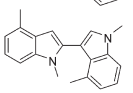
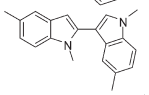
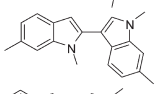
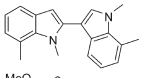
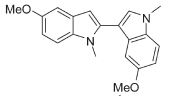
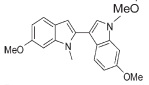
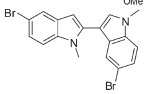
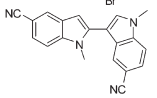
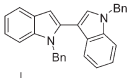
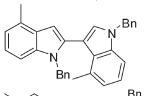
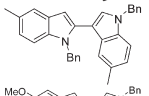
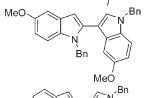
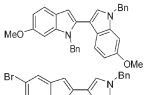
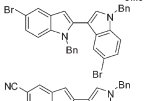
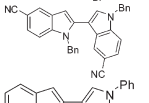
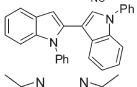
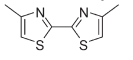
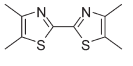
**TABLE 2. Oxidative Homocoupling of Various Substituted Indoles**[a]




| entry | indoles | $R^1$ | $R^2$ | product | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **1a** | H | Me |  | **2a**, 91 |
| 2 | **1b** | 4-Me | Me |  | **2b**, 70 |
| 3 | **1c** | 5-Me | Me |  | **2c**, 88 |
| 4 | **1d** | 6-Me | Me |  | **2d**, 88 |
| 5 | **1e** | 7-Me | Me |  | **2e**, 95 |
| 6 | **1f** | 5-OMe | Me |  | **2f**, 94 |
| 7 | **1g** | 6-OMe | Me |  | **2g**, 50 |
| 8 | **1h** | 5-Br | Me |  | **2h**, 68 |
| 9 | **1i** | 5-CN | Me |  | **2i**, 28[c] |
| 10 | **1j** | H | Ac | — | |
| 11 | **1k** | H | Bn |  | **2k**, 92 |
| 12 | **1l** | 4-Me | Bn |  | **2l**, 80 |
| 13 | **1m** | 5-Me | Bn |  | **2m**, 91 |
| 14 | **1n** | 5-OMe | Bn |  | **2n**, 93 |
| 15 | **1o** | 6-OMe | Bn |  | **2o**, 52 |
| 16 | **1p** | 5-Br | Bn |  | **2p**, 55 |
| 17 | **1q** | 5-CN | Bn |  | **2q**, 27[c] |
| 18 | **1r** | H | Ph |  | **2r**, 76[c] |
| 19 | **1s** |  | |  | **2s**, 40[d] |
| 20 | **1t** |  | |  | **2t**, 80[d] |

[a]Reaction conditions: indole derivatives (1 mmol), $Pd(TFA)_2$ (0.05 mmol), $Cu(OAc)_2 \cdot H_2O$ (1.5 mmol), DMSO (6 mL), room temperature, 8 h, $N_2$. [b]Isolated yields based on indole. [c]60 °C, 12 h. [d]$Pd(TFA)_2$ (0.05 mmol), AgOAc (1.5 mmol), 90 °C, 12 h.

indoles did not alter the reaction pathway, and moderate yields were obtained for these moderately electron-poor indoles (Table 2, entries 8 and 16). In the case of strongly electron-poor indoles, the reactivity in the homocoupling reaction dropped markedly (Table 2, entries 9 and 17), albeit the reaction temperature was enhanced and the reaction time was prolonged. A possible reason is that the presence of an electron-withdrawing group might render the indoles highly electron-deficient and retard the electrophilic palladation. Similarly, *N*-acetyl indole was incompatible with the reaction, and no desired dimerization compound was isolated (Table 2, entry 10). *N*-Benzyl and *N*-phenyl indole tolerated the reaction conditions well and generated the homocoupling products in good yields (Table 2, entries 11 and 18).

Encouraged by the successful homocoupling of indoles, the homocoupling reaction of thiazoles, which are important $\pi$-stacking five-membered rings,[13] was next examined. Unfortunately, thiazoles failed to homocouple under the above optimal reaction conditions. To our delight, the homocoupling products of thiazoles were isolated when AgOAc was used as oxidant at 90 °C for 12 h (Table 2, entries 19 and 20).

During the screening of reaction conditions for this homocoupling reaction, we isolated a small amount of C3-position acetoxylated biindolyls. Since substituted 3-oxyindoles are common scaffolds in medicinal chemistry[14] and their synthesis through direct catalytic methods is very limited,[15] we investigated the reaction conditions for selective formation of acetoxylated biindolyl products as shown in Table 3. It was found that oxygen played the key role for the acetoxylation. For example, only a trace of acetoxylated product was detected using the $Pd(OAc)_2/Cu(OAc)_2 \cdot H_2O$ catalytic system when the reaction was performed under nitrogen, but the yield of acetoxylated product increased to 38% under oxygen (Table 3, entries 1−2). Similar results were obtained by using the $Pd(TFA)_2/Cu(OAc)_2 \cdot H_2O$ system (Table 3, entries 3 and 4). In addition, the reaction efficiency was decreased when the reaction was performed at lower temperature (Table 3, entry, 5). The replacement of $Cu(OAc)_2 \cdot H_2O$ with AgOAc markedly improved the selective acetoxylation (Table 3, entries 6−12), and the best conditions for the formation of acetoxylation product was indole derivatives (1 mmol), $Pd(TFA)_2$ (0.05 mmol), and AgOAc (2 mmol) in DMSO (6.0 mL) at 60 °C for 12 h under oxygen atmosphere (Table 3, entry 13). $PhI(OAc)_2$ was ineffective under the reaction conditions (Table 3, entry 14).

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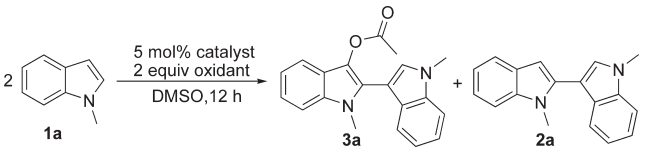
(15) (a) Sukari, M. A.; Vernon, J. M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2219–2223. (b) Mutule, I.; Suna, E.; Olofsson, K.; Pelcman, B. *J. Org. Chem*. **2009**, *74*, 7195–7198.

**TABLE 3. Optimization of Acetoxylated Biindolyls**[a]




| entry | catalyst | oxidant | temp (°C) | atmosphere | yield (%) of **3a** | yield (%) of **2a** |
|---|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | $N_2$ | trace | 40 |
| 2 | $Pd(OAc)_2$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | $O_2$ | 38 | 30 |
| 3 | $Pd(TFA)_2$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | $N_2$ | trace | 80 |
| 4 | $Pd(TFA)_2$ | $Cu(OAc)_2 \cdot H_2O$ | 90 | $O_2$ | 40 | trace |
| 5 | $Pd(TFA)_2$ | $Cu(OAc)_2 \cdot H_2O$ | 40 | $O_2$ | trace | 81 |
| 6 | $Pd(OAc)_2$ | AgOAc | 90 | $N_2$ | 44 | 25 |
| 7 | $Pd(OAc)_2$ | AgOAc | 90 | $O_2$ | 51 | < 5 |
| 8 | $Pd(OAc)_2$ | AgOAc | rt | $O_2$ | 38 | 42 |
| 9 | $Pd(TFA)_2$ | AgOAc | 90 | $N_2$ | 41 | 18 |
| 10 | $Pd(TFA)_2$ | AgOAc | rt | $N_2$ | 41 | 37 |
| 11 | $Pd(TFA)_2$ | AgOAc | 90 | $O_2$ | 41 | < 5 |
| 12 | $Pd(TFA)_2$ | AgOAc | 40 | $O_2$ | 55 | 26 |
| **13** | **$Pd(TFA)_2$** | **AgOAc** | **60** | **$O_2$** | **80** | **< 5** |
| 14 | $Pd(TFA)_2$ | $PhI(OAc)_2$ | 60 | $O_2$ | trace | 0 |

[a]Reaction conditions: indole derivative (1 mmol), catalyst (0.05 mmol), oxidant (2 mmol), DMSO (6 mL), 12 h.

The generality and scope of the acetoxylation reaction were briefly examined, and the results are summarized in Table 4. Again, the electron-rich indoles reacted smoothly to give moderate to good yields (Table 4, entries 1, 3−6, 10, 11). The steric hindrance by the methyl group in 1,4-dimethyl-1*H*-indole might explain the low yield (Table 4, entry 2). 6-Methoxy-1-methyl-1*H*-indole furnished a relatively low yield (Table 4, entry 7). Again, the presence of bromine in indoles did not alter the reaction pathway but contributed to a very low yield (Table 4, entry 8). Only traces of the dimerized and acetoxylated products were observed for electron-deficient indoles such as 1-methyl-1*H*-indole-5-carbonitrile under the reaction conditions. *N*-Benzyl indole and *N*-phenyl indole were also not so active in the acetoxylated reaction (Table 4, entries 9 and 12).

On the basis of the previous chemistry[16] and the results of our study, a plausible Pd(0)/Pd(II) mechanism for the homocoupling reaction as shown in Scheme 1 was proposed. The electrophilic palladation first occurs at the preferential C3-position of indoles and the subsequent migration of the C3-PdX bond to the 2-position leads to the formation of intermediate **1**,[17] which undergoes the electrophilic palladation with the second indole to form intermediate **2**. The following reductive elimination generates the 2,3′-dimer of indole, and the formed Pd(0) is oxidized to Pd(II) by Cu(II) or Ag(I) salts in the system to furnish the cycle. In addition, the electrophilic palladation of produced 2,3′-dimer may take place to give intermediate **3**, which undergoes the reductive elimination to afford acetoxylated product. The treatment of 2,3′-dimer in the presence of 5 mol % $Pd(TFA)_2$ and 1 equiv of AgOAc in DMSO at 60 °C for 12 h under oxygen atmosphere led to the formation of acetoxylated product in 71% yield (Scheme 2), indicating that the one-pot sequence might lead to the formation of acetoxylated biindolyls. The Pd(II)/Pd(IV) mechanism is another possible pathway for this regioselective oxidative homocoupling reaction.[18] Further research is required to elucidate the detailed reaction mechanism.

In summary, we have developed an efficient method for the homocoupling of indoles with excellent regioselectivity. The method involves the use of catalytic $Pd(TFA)_2$ and 1.5 equiv of $Cu(OAc)_2 \cdot H_2O$ and is tolerant of bromine on indoles. This new protocol provides a facile route to 2,3′-biindolyls under very mild reaction conditions. Furthermore, the C3-position acetoxylated biindolyls were prepared by a one-pot sequence. The reaction requires the presence of catalytic $Pd(TFA)_2$, 2 equiv of AgOAc, and oxygen. Only electron-rich indoles are reactive. The possible pathway for the homocoupling of indoles and one-pot formation of C3-position acetoxylated biindolyls are discussed.

## Experimental Section

**General Procedure for Homocoupling Reaction.** A mixture of indole derivative (1 mmol), $Cu(OAc)_2 \cdot H_2O$ (300 mg, 1.5 mmol), $Pd(TFA)_2$ (17 mg, 0.05 mmol), and DMSO (6 mL) was stirred at room temperature under $N_2$ for 8 h. The reaction mixture was filtered through a plug of Celite, and the residue was washed

(16) (a) Lane, B. S.; Sames, D. *Org. Lett.* **2004**, *6*, 2897–2900. (b) Lebrasseur, N.; Larrosa, I. *J. Am. Chem. Soc.* **2008**, *130*, 2926–2927. (c) Jia, C.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Org. Lett.* **1999**, *1*, 2097–2100. (d) Bellina, F.; Benelli, F.; Rossi, R. *J. Org. Chem.* **2008**, *73*, 5529–5535. (e) Deprez, N. R.; Kalyani, D.; Krause, A.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 4972–4973. (f) Yang, S.-D.; Sun, C.-L.; Fang, Z.; Li, B.-J.; Li, Y.-Z.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1473–1476. (g) Stuart, D. R.; Villemure, E.; Fagnou, K. *J. Am. Chem. Soc.* **2007**, *129*, 12072–12073. (h) Wang, X.; Gribkov, D. V.; Sames, D. *J. Org. Chem.* **2007**, *72*, 1476–1479.

(17) (a) Lane, B. S.; Brown, M. A.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 8050–8057. (b) Grimster, N. P.; Gauntlett, C.; Godfrey, C. R. A.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 3125–3129. (c) Saulnier, M. G.; Gribble, G. W. *J. Org. Chem.* **1982**, *47*, 757–761.

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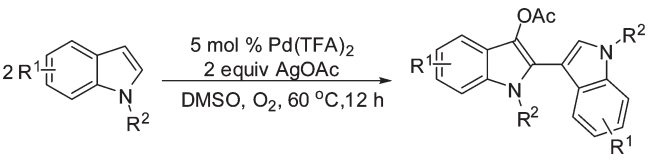
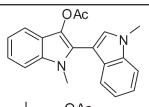
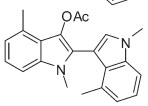
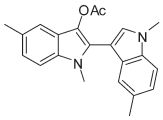
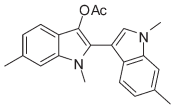
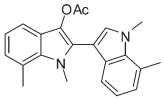
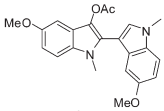
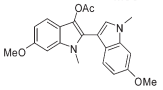
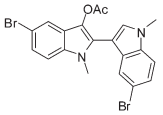
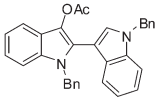
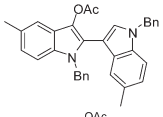
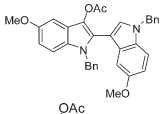
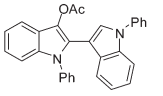
**TABLE 4. Synthesis of Acetoxylated Biindolyls**[a]

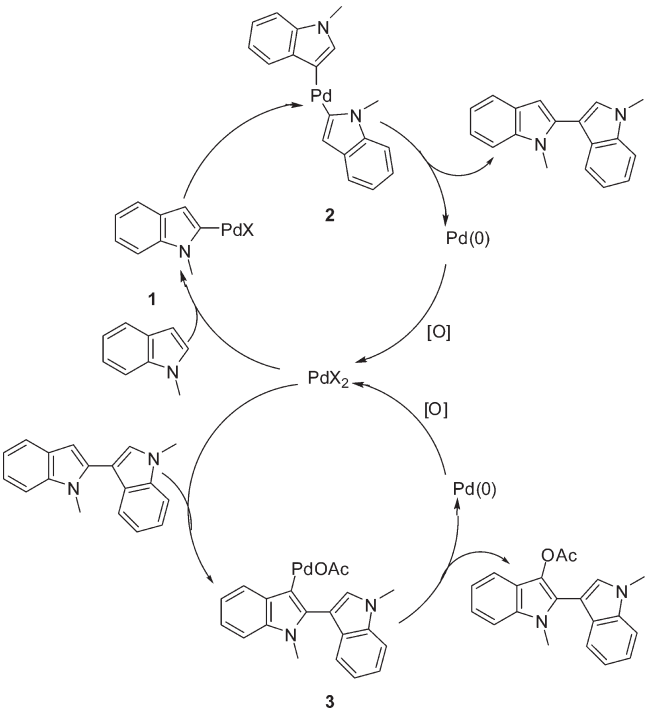



| entry | indoles | $R^1$ | $R^2$ | product | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **1a** | H | Me |  | **3a**, 80 |
| 2 | **1b** | 4-Me | Me |  | **3b**, 26 |
| 3 | **1c** | 5-Me | Me |  | **3c**, 64 |
| 4 | **1d** | 6-Me | Me |  | **3d**, 74 |
| 5 | **1e** | 7-Me | Me |  | **3e**, 78 |
| 6 | **1f** | 5-OMe | Me |  | **3f**, 71 |
| 7 | **1g** | 6-OMe | Me |  | **3g**, 40 |
| 8 | **1h** | 5-Br | Me |  | **3h**, 25 |
| 9 | **1k** | H | Bn |  | **3k**, 34 |
| 10 | **1m** | 5-Me | Bn |  | **3m**, 50 |
| 11 | **1n** | 5-OMe | Bn |  | **3n**, 60 |
| 12 | **1r** | H | Ph |  | **3r**, 44 |

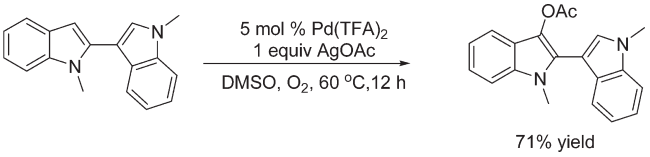
[a]Reaction conditions: indole derivatives (1 mmol), $Pd(TFA)_2$ (5 mol %), AgOAc (2 mmol), DMSO (6 mL), 60 °C, 12 h, $O_2$. [b]Isolated yields.

with diethyl ether (2 × 20 mL). The filtrate was washed with 80 mL of $H_2O$, and the organic layer was collected. The aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were washed with saturated sodium chloride solution (40 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

**SCHEME 1. Plausible Mechanism**




**SCHEME 2. Direct Acetoxylation of 2,3′-Biindolyls**




**1,1′-Dimethyl-1*H*,1′*H*-2,3′-biindole (2a).** 91% yield; white solid; mp 111−112 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.71 (d, 1H, $J$ = 8.4 Hz), 7.64 (d, 1H, $J$ = 7.2 Hz), 7.40 (d, 1H, $J$ = 8.0 Hz), 7.37 (d, 1H, $J$ = 8.4 Hz), 7.31 (m, 1H), 7.18−7.25 (m, 3H), 7.14 (m, 1H), 6.61 (br s, 1H), 3.88 (s, 3H), 3.76 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 138.0, 137.0, 135.3, 128.5, 128.4, 127.7, 122.4, 121.0, 120.4, 120.3, 120.1, 119.6, 109.6, 109.4, 107.3, 101.2, 33.0, 31.0; MS (EI) $m/z$ (%) 260 (100) [$M^+$], 245 (10), 130 (11).

**1,1′,4,4′-Tetramethyl-1*H*,1′*H*-2,3′-biindole (2b).** 70% yield; white solid; mp 154−155 °C ; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.13−7.25 (m, 4H), 7.08 (s, 1H), 6.94 (d, 1H, $J$ = 7.2 Hz), 6.90 (d, 1H, $J$ = 6.8 Hz), 6.52 (br s, 1H), 3.84 (s, 3H), 3.52 (s, 3H), 2.57 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 137.1, 137.0, 135.3, 131.2, 129.7, 129.6, 127.9, 127.1, 122.3, 121.3, 121.2, 119.7, 107.3, 107.0, 106.9, 101.8, 33.0, 30.6, 18.8, 18.5; HRMS (EI) calcd for $C_{20}H_{20}N_2$ ($M^+$) 288.1626, found 288.1620.

**1,1′,5,5′-Tetramethyl-1*H*,1′*H*-2,3′-biindole (2c).** 88% yield, white solid; mp 160−161 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.48 (s, 1H), 7.43 (s, 1H), 7.24−7.29 (m, 2H), 7.12−7.16 (m, 2H), 7.05 (d, 1H, $J$ = 8.4 Hz), 6.5 (br s, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.48 (s, 3H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 136.4, 135.4, 129.5, 128.7, 128.6, 128.4, 127.9, 123.9, 122.5, 119.9, 119.7, 109.2, 109.0, 106.8, 33.0, 31.0, 21.5, 21.5; HRMS (EI) calcd for $C_{20}H_{20}N_2$ ($M^+$) 288.1626, found 288.1622.

**1,1′,6,6′-Tetramethyl-1*H*,1′*H*-2,3′-biindole (2d).** 88% yield; white solid; mp 133−134 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.56 (d, 1H, $J$ = 8.4 Hz), 7.51 (d, 1H, $J$ = 8.0 Hz), 7.18 (s, 1H), 7.15 (s, 1H), 7.12 (s, 1H), 7.02 (d, 1H, $J$ = 8.0 Hz), 6.97 (d, 1H, $J$ = 8.0 Hz), 6.52 (br s, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 2.52 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 138.4, 137.3, 132.2, 130.7, 127.8, 126.2, 125.6, 121.9, 121.2, 120.0, 119.6, 109.5, 109.4, 107.3, 32.8, 30.9, 22.0, 21.9; HRMS (EI) calcd for $C_{20}H_{20}N_2$ ($M^+$) 288.1626, found 288.1619.

**1,1′,7,7′-Tetramethyl-1*H*,1′*H*-2,3′-biindole (2e).** 95% yield, white solid; mp 184−185 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.46 (t, 2H, $J$ = 6.4 Hz), 6.97−7.05 (m, 4H), 6.91 (d, 1H, $J$ = 7.8 Hz), 6.51 (br s, 1H), 4.13 (s, 3H), 3.93 (s, 3H), 2.82 (s, 3H), 2.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 137.0, 136.0, 135.6, 130.4, 129.2, 128.9, 124.8, 123.9, 121.5, 121.1, 120.3, 119.6, 118.4, 118.1, 107.3, 102.1, 36.9, 34.2, 20.1, 19.6; HRMS (EI) calcd for $C_{20}H_{20}N_2$ ($M^+$) 288.1626, found 288.1623.

**5,5′-Dimethoxy-1,1′-dimethyl-1*H*,1′*H*-2,3′-biindole (2f).** 94% yield; white solid; mp 165−166 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.24−7.29 (m, 2H), 7.17 (s, 1H), 7.13 (t, 2H, $J$ = 6.4 Hz), 6.96 (dd, 1H, $J$ = 2.0, 2.4 Hz), 6.90 (dd, 1H, $J$ = 2.8, 2.4 Hz), 6.50 (br s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 154.8, 154.2, 133.3, 132.1, 128.8, 128.6, 128.0, 112.9, 111.0, 110.3, 110.0, 106.9, 102.0, 101.6, 56.0, 55.9 33.1, 31.0; HRMS (EI) calcd for $C_{20}H_{20}N_2O_2$ ($M^+$) 320.1525, found 320.1524.

**6,6′-Dimethoxy-1,1′-dimethyl-1*H*,1′*H*-2,3′-biindole (2g).** 50% yield; white solid; mp 149−150 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.56 (d, 1H, $J$ = 8.4 Hz), 7.50 (d, 1H, $J$ = 8.4 Hz), 7.06 (s, 1H), 6.80−6.86 (m, 4H), 6.51 (br s, 1H), 3.90 (s, 6H), 3.80 (s, 3H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 156.8, 155.9, 138.7, 137.6, 127.1, 122.7, 122.0, 121.0, 120.5, 110.0, 109.1, 107.4, 93.4, 93.0, 55.8, 55.7, 32.9, 31.0; HRMS (EI) calcd for $C_{20}H_{20}N_2O_2$ ($M^+$) 320.1525, found 320.1523.

**5,5′-Dibromo-1,1′-dimethyl-1*H*,1′*H*-2,3′-biindole (2h).** 68% yield; light yellow solid; mp 182−183 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.78 (d, 1H, $J$ = 2.0 Hz), 7,74 (d, 1H, $J$ = 1.6 Hz), 7.38 (dd, 1H, $J$ = 2.0, 2.0 Hz), 7.30 (dd, 1 H, $J$ = 1.6, 2.0 Hz), 7.26 (d, 1H, $J$ = 9.2 Hz), 7.21 (d, 1H, $J$ = 8.4 Hz), 7.18 (s, 1H), 6.52 (br s, 1H), 3.86 (s, 3H), 3.70 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 136.6, 135.6, 135.4, 129.9, 129.4, 129.1, 125.3, 123.9, 122.6, 122.4, 113.9, 112.9, 111.1, 110.7, 106.4, 101.1, 33.2, 31.0; HRMS (EI) calcd for $C_{18}H_{14}Br_2N_2$ ($M^+$) 417.9503, found 417.9500.

**1,1′-Dimethyl-1*H*,1′*H*-2,3′-biindole-5,5′-dicarbonitrile (2i).** 28% yield; brown solid; mp 237−238 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 8.00 (s, 1H), 7.97 (s,1H), 7.55 (dd, 1H, $J$ = 1.2, 1.2 Hz), 7.47−7.49 (m, 2H), 7.41 (d, 1H, $J$ = 8.4 Hz), 7.36 (s, 1H), 6.68 (s, 1H), 3.96 (s, 3H), 3.77 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 139.7, 138.6, 135.9, 130.9, 128.1, 127.5, 125.8, 125.8, 124.7, 121.1, 120.5, 111.0, 110.5, 107.6, 104.1, 103.1, 33.7, 31.5; HRMS (EI) calcd for $C_{20}H_{14}N_4$ ($M^+$) 310.1218, found 310.1214.

**1,1′-Dibenzyl-1*H*,1′*H*-2,3′-biindole (2k).** 92% yield; white solid; mp 133−134 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.85 (d, 1H, $J$ = 8.0 Hz), 7.68 (q, 1H, $J$ = 2.8 Hz),7.13−7.33 (m, 12H), 7.05−7.08 (m, 2H), 6.95−6.97 (m, 3H), 6.77 (br s, 1H), 5.39 (s, 2H), 5.24 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 138.7, 137.7, 136.9, 136.5, 134.8, 128.8, 128.8, 128.7, 128.7, 128.1, 127.8, 127.4, 127.0, 127.0, 126.9, 126.0, 122.6, 121.3, 120.5, 120.3, 120.2, 120.0, 110.1, 110.0, 107.6, 102.3, 50.2, 47.5; HRMS (EI) calcd for $C_{30}$ $H_{24}N_2$ ($M^+$) 412.1939, found 412.1935.

**1,1′-Dibenzyl-4,4′-dimethyl-1*H*,1′*H*-2,3′-biindole (2l).** 80% yield; white solid; mp 169−170 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.23−7.24 (m, 3H), 7.17 (d, 1H, $J$ = 8.8 Hz), 7.02−7.13 (m, 8H), 6.99 (s, 1H), 6.94 (d, 1H, $J$ = 7.2 Hz), 6.89 (d, 1H, $J$ = 6.8 Hz), 6.82 (m, 2H), 6.64 (s, 1H), 5.24 (s, 2H), 5.21 (s, 2H), 2.59 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 138.5, 137.0, 136.6, 136.4, 134.9, 131.4, 129.8, 129.6, 128.8, 128.3, 128.2, 127.7, 127.2, 126.9, 126.8, 126.3, 122.4, 121.6, 121.5, 119.9, 107.8, 107.8, 107.2, 102.8, 50.2, 47.4, 18.8, 18.8; HRMS (ESI) calcd for $C_{32}H_{29}N_2$ ($M + H$)$^+$ 441.2331, found 441.2331.

**1,1′-Dibenzyl-5,5′-dimethyl-1*H*,1′*H*-2,3′-biindole (2m).** 91% yield; white solid; mp 134−135 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.54 (s, 1H), 7.47 (s, 1H), 7.24−7.27 (m, 3H), 7.19 (t, 4H, $J$ = 6.8 Hz), 7.11 (d, 1H, $J$ = 8.4 Hz), 7.03−7.05 (m, 3H), 6.96 (d, 3H, $J$ = 7.6 Hz), 6.92 (s, 1H), 6.67 (br s, 1H), 5.35 (s, 2H), 5.22 (s, 2H), 2.46 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 138.9, 137.1, 136.1, 135.1, 134.9, 129.8, 129.1, 129.0, 128.8, 128.7, 128.4, 127.7, 127.5, 127.0, 126.9, 126.0, 124.2, 122.8, 120.0, 119.9, 109.8, 109.7, 107.2, 101.7, 50.2, 47.6, 21.5, 21.5; HRMS (EI) calcd for $C_{32}H_{28}N_2$ ($M^+$) 440.2252, found 440.2255.

**1,1′-Dibenzyl-5,5′-dimethoxy-1*H*,1′*H*-2,3′-biindole (2n).** 93% yield; white solid; mp 159−160 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.17−7.28(m, 9H), 7.06−7.11 (m, 3H), 6.98 (d, 3H, $J$ = 9.2 Hz), 6.85−6.88 (m, 1H), 6.78−6.82 (m, 1H), 6.65 (br s, 1H), 5.35 (s, 2H), 5.22 (s, 2H), 3.87 (s, 3H), 3.71 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 154.9, 154.4, 138.7, 137.0, 135.7, 132.9, 131.6, 129.1, 128.8, 128.7, 128.4, 128.1, 127.8, 127.0, 126.9, 126.0, 113.1, 111.3, 110.9, 110.9, 107.3, 102.0, 101.6, 101.4, 55.9, 55.7, 50.4, 47.7; HRMS (EI) calcd for $C_{32}H_{28}N_2O_2$ ($M^+$) 472.2151, found 472.2147.

**1,1′-Dibenzyl-6,6′-dimethoxy-1*H*,1′*H*-2,3′-biindole (2o).** 52% yield; white solid; mp 129−130 °C; $^1$H NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 7.65 (d, 1H, $J$ = 9.0 Hz), 7.54 (d, 1H, $J$ = 8.5 Hz), 7.18−7.27 (m, 6H), 7.05−7.07 (m, 2H), 6.96−6.98 (m, 2H), 6.81−6.82 (m, 3H), 6.74 (d, 1H, $J$ = 1.5 Hz), 6.70 (d, 1H, $J$ = 2.0 Hz), 6.67 (br s, 1H), 5.33 (s, 2H), 5.17 (s, 2H), 3.80 (s, 3H), 3.77 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 157.1, 156.3, 138.8, 138.6, 137.5, 137.1, 134.1, 129.0, 128.9, 128.0, 127.2, 127.2, 126.3, 126.2, 123.3, 122.6, 121.2, 120.9, 110.2, 109.5, 108.1, 102.1, 94.5, 93.8, 56.0, 55.9, 50.4, 47.8; HRMS (ESI) calcd for $C_{32}$ $H_{29}$ $N_2$ $O_2$ ($M + H$)$^+$ 473.2229, found 473.2231.

**1,1′-Dibenzyl-5,5′-dibromo-1*H*,1′*H*-2,3′-biindole (2p).** 55% yield; light yellow solid; mp 165−166 °C; $^1$H NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 7.85 (d, 1H, $J$ = 2.0 Hz), 7.79 (d, 1H, $J$ = 2.0 Hz), 7.27−7.31 (m, 4H), 7.20−7.23 (m, 4H), 7.17 (d, 1H, $J$ = 8.5 Hz), 7.08 (d, 1H, $J$ = 8.0 Hz), 7.03 (t, 2H, $J$ = 3.5 Hz), 6.94 (s, 1H), 6.88−6.90 (m, 2H), 6.68 (s, 1H), 5.33 (s, 2H), 5.21 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 138.2, 136.6, 136.5, 135.4, 130.5, 129.8, 129.2, 129.1, 128.7, 128.3, 127.6, 127.1, 126.0, 125.9, 124.6, 123.0, 114.4, 113.5, 111.8, 111.7, 107.0, 102.3, 50.7, 47.8; HRMS (EI) calcd for $C_{30}H_{22}Br_2N_2$ ($M^+$) 570.0129, found 570.0139.

**1,1′-Dibenzyl-1*H*,1′*H*-2,3′-biindole-5,5′-dicarbonitrile (2q).** 27% yield; brown solid; mp 198−199 °C; $^1$H NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 8.02−8.03 (m, 2H), 7.46−7.48 (m, 1H), 7.39−7.41 (m, 2H), 7.29−7.32 (m, 4H), 7.23−7.25 (m, 3H), 7.08 (s, 1H), 7.05−7.07 (m, 2H), 6.86−6.87 (m, 2H), 6.82 (s, 1H), 5.37 (s, 2H), 5.29 (s, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 139.5, 138.2, 137.4, 135.7, 135.7, 129.9, 129.4, 129.3, 128.6, 128.4, 127.9, 127.9, 127.2, 126.0, 126.0, 125.9, 125.1, 120.9, 120.3, 111.3, 111.1, 107.8, 104.4, 103.9, 103.6, 50.9, 47.9; HRMS (ESI) calcd for $C_{32}H_{21}N_4$($M - H$)$^-$ 461.1772, found 461.1777.

**1,1′-Diphenyl-1*H*,1′*H*-2,3′-biindole (2r).** 76% yield; white solid; mp 66−67 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.98−8.00 (m, 1H), 7.71−7.73 (m, 1H), 7.52−7.54(m, 1H), 7.23−7.47 (m, 13H), 7.16−7.19 (m, 2H), 7.03 (s, 1H), 6.62 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 139.2, 138.9, 138.5, 135.9, 134.2, 129.6, 129.3, 128.9, 128.6, 127.9, 127.6, 127.1, 126.7, 124.3, 123.0, 121.8, 121.1, 120.7, 120.5, 120.1, 110.6, 110.3, 109.4, 102.8; HRMS (EI) calcd for $C_{28}H_{20}N_2$ ($M^+$) 384.1626, found 384.1629.

**4,4′-Dimethyl-2,2′-bithiazole (2s).** 40% yield; light yellow solid; mp 134−135 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 6.96 (s, 2H), 2.51 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 160.5, 153.8, 115.1, 16.8; MS (EI) $m/z$ (%) 196 (100) [$M^+$], 125 (19), 72 (84).

**4,4′,5,5′-Tetramethyl-2,2′-bithiazole (2t).** 80% yield; light yellow solid; mp 184−185 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 2.39 (s, 6H), 2.36 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 156.9, 149.4, 128.0, 14.6, 11.4; MS (EI) $m/z$ (%) 224 (100) [$M^+$], 209 (5), 191 (7), 139 (10), 112 (4), 86 (44), 71 (46), 59 (26).

**General Procedure for Acetoxylation Reaction.** A mixture of indole derivative (1 mmol), AgOAc (334 mg, 2 mmol), $Pd(TFA)_2$ (17 mg, 0.05 mmol), and DMSO (6 mL) was stirred at at 60 °C under $O_2$ for 12 h. The reaction mixture was filtered through a plug of Celite, and the residue was washed with $CH_2Cl_2$ (2 × 20 mL). The filtrate was washed with 80 mL of $H_2O$, and the organic layer was collected. The aqueous phase was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phases were washed with saturated sodium chloride solution (40 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by flash column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the corresponding products.

**1,1′-Dimethyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3a).** 80% yield; white solid; mp 156−157 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.54 (d, 1H, $J$ = 7.6 Hz), 7.44 (d, 1H, $J$ = 8.0 Hz), 7.40 (d, 1H, $J$ = 8.4 Hz), 7.36 (d, 1H, $J$ = 8.4 Hz), 7.28−7.32 (m, 1H), 7.23−7.26 (m, 1H), 7.13−7.20 (m, 3H), 3.88 (s, 3H), 3.67 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 170.3, 136.9, 135.0, 129.4, 127.5, 126.6, 124.6, 122.2, 121.8, 120.9, 120.3, 120.2, 119.7, 117.0, 109.7, 109.6, 103.3, 33.0, 30.8, 20.7; HRMS (EI) calcd for $C_{20}H_{18}N_2O_2$ ($M^+$) 318.1368, found 318.1373.

**1,1′,4,4′-Tetramethyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3b).** 26% yield; white solid; mp 206−207 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.16−7.25 (m, 3H), 7.10−7.14 (m, 2H), 6.90 (d, 1H, $J$ = 6.4 Hz), 6.87 (d, 1H, $J$ = 7.2 Hz), 3.83 (s, 3H), 3.46 (s, 3H), 2.56 (s, 3H), 2.16 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 171.2, 137.1, 134.5, 131.2, 130.4, 128.5, 128.2, 127.3, 125.5, 122.2, 121.9, 121.3, 120.8, 119.7, 107.3, 107.2, 102.5, 33.1, 30.4, 20.8, 18.5, 18.2; HRMS (EI) calcd for $C_{22}H_{22}N_2O_2$ ($M^+$) 346.1681, found 346.1675.

**1,1′,5,5′-Tetramethyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3c).** 64% yield; white solid; mp 159−160 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.30 (s, 1H), 7.26 (d, 1H, $J$ = 4.0 Hz), 7.24 (d, 1H, $J$ = 4.0 Hz), 7.22 (s, 1H), 7.10−7.12 (m, 2H), 7.04−7.07 (m, 1H), 3.83 (s, 3H), 3.62 (s, 3H), 2.46 (s, 3H), 2.43 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 170.4, 135.4, 133.6, 129.6, 129.5, 129.0, 127.9, 126.3, 124.9, 123.9, 123.5, 121.1, 120.0, 116.6, 109.5, 109.4, 103.0, 33.0, 30.9, 21.5, 20.7; HRMS (EI) calcd for $C_{22}H_{22}N_2O_2$ ($M^+$) 346.1681, found 346.1684.

**1,1′,6,6′-Tetramethyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3d).** 74% yield; white solid; mp 165−166 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.40 (d, 1H, $J$=8.0 Hz), 7.31 (d, 1H, $J$=8.0 Hz), 7.18 (s, 1H), 7.14 (s, 1H), 7.07 (s, 1H), 6.70 (t, 2H, $J$ = 5.2 Hz), 3.82 (s, 3H), 3.61 (s, 3H), 2.52 (s, 3H), 2.50 (s, 3H), 2.18 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 170.3, 137.3, 135.4, 132.1, 131.6, 128.8, 126.7, 125.5, 124.0, 122.0, 121.5, 120.0, 118.9, 116.8, 109.7, 109.5, 103.4, 32.9, 30.8, 22.0, 21.9, 20.7; HRMS (EI) calcd for $C_{22}H_{22}N_2O_2$ ($M^+$) 346.1681, found 346.1683.

**1,1′,7,7′-Tetramethyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3e).** 78% yield; white solid; mp 182−183 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.34 (d, 1H, $J$ = 8.0 Hz), 7.23−7.25 (m, 1H), 6.92−7.04 (m, 5H), 4.12 (s, 3H), 3.84 (s, 3H), 2.81 (s, 3H), 2.80 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 170.4, 135.7, 134.3, 131.3, 128.9, 127.0, 125.5, 124.9, 124.8, 121.9, 121.7, 121.6, 120.5, 120.0, 118.4, 114.9, 103.3, 37.1, 34.1, 20.6, 20.4, 19.7; HRMS (EI) calcd for $C_{22}H_{22}N_2O_2$ ($M^+$) 346.1681, found 346.1677.

**5,5′-Dimethoxy-1,1′-dimethyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3f).** 71% yield; white solid; mp 141−142 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.27 (d, 1H, $J$ = 5.6 Hz), 7.24−7.26 (m, 1H), 7.12 (s, 1H), 6.93−6.97 (m, 2H), 6.90 (dd, 1H, $J$ = 2.4, 2.4 Hz), 6.86 (d, 1H, $J$ = 3.6 Hz), 3.87 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H), 3.63 (s, 3H), 2.21 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 170.3, 154.8, 154.4, 132.1, 130.4, 129.6, 128.0, 126.4, 125.3, 120.9, 113.0, 112.3, 110.7, 110.5, 103.0, 101.3, 98.5, 55.9, 55.8, 33.2, 30.9, 20.7; HRMS (EI) calcd for $C_{22}H_{22}N_2O_4$ ($M^+$) 378.1580, found 378.1576.

**6,6′-Dimethoxy-1,1′-dimethyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3g).** 40% yield; white solid; mp 185−186 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.40 (d, 1H, $J$ = 10.0 Hz), 7.31 (d, 1H, $J$ = 9.2 Hz), 7.03 (s, 1H), 6.81−6.85 (m, 4H), 3.89 (s, 3H), 3.88 (s, 3H), 3.80 (s, 3H), 3.60 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 170.3, 156.7, 156.5, 137.6, 135.7, 128.1, 126.6, 123.2, 121.9, 121.0, 117.8, 115.5, 110.1, 109.7, 103.6, 93.4, 93.0, 55.8, 55.7, 33.0, 30.8, 20.6; HRMS (EI) calcd for $C_{22}H_{22}N_2O_4$ ($M^+$) 378.1580, found 378.1574.

**5,5′-Dibromo-1,1′-dimethyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3h).** 25% yield; white solid; mp 225−226 °C; $^1$H NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 7.65 (d, 1H, $J$ = 1.5 Hz), 7.57 (d, 1H, $J$ = 1.5 Hz), 7.37 (dd, 1H, $J$ = 1.5, 2.0 Hz), 7.31 (dd, 1H, $J$ = 2.0, 1.5 Hz), 7.25−7.26 (m, 1H), 7.21 (d, 1H, $J$=8.5 Hz), 7.16(s, 1H), 3.84 (s, 3H), 3.62 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 170.2, 135.9, 133.9, 130.7, 129.2, 126.3, 125.6, 125.4, 125.1, 123.0, 122.6, 119.9, 114.2, 113.4, 111.5, 111.4, 102.9, 33.6, 31.3, 20.8; HRMS (ESI) calcd for $C_{20}H_{17}Br_2N_2O_2$ ($M + H$) $^+$ 474.9657, found 474.9669.

**1,1′-Dibenzyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3k).** 34% yield; white solid; mp 184−185 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.56 (d, 1H, $J$ = 8.0 Hz), 7.46−7.49 (m, 1H), 7.33 (d, 1H, $J$ = 7.6 Hz), 7.12−7.28 (m, 11H), 7.05−7.07 (m, 2H), 7.02 (s, 1H), 6.92 (d, 2H, $J$ = 7.2 Hz), 5.30 (s, 2H), 5.27 (s, 2H), 2.15 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 169.8, 138.3, 136.9, 136.4, 134.7, 128.8, 128.8, 128.6, 127.8, 127.5, 127.0, 126.9, 126.0, 124.4, 122.4, 122.1, 121.4, 120.5, 120.3, 120.0, 117.3, 110.4, 110.0, 103.9, 50.2, 47.6, 20.6; HRMS (EI) calcd for $C_{32}H_{26}N_2O_2$ ($M^+$) 470.1994, found 470.1987.

**1,1′-Dibenzyl-5,5′-dimethyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3m).** 50% yield; white solid; mp 199−200 °C; $^1$H NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 7.29 (s, 1H), 7.23−7.27 (m, 4H), 7.15−7.20 (m, 4H), 7.11 (d, 1H, $J$ = 8.0 Hz), 7.01−7.04 (m, 3H), 6.96−6.99 (m, 2H), 6.92−6.93 (m, 2H), 5.26 (s, 2H), 5.23 (s, 2H), 2.44 (s, 3H), 2.36 (s, 3H), 2.15 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 170.2, 138.8, 137.3, 135.1, 133.4, 130.0, 129.5, 129.2, 129.0, 128.8, 128.4, 128.0, 127.3, 127.2, 127.0, 126.3, 124.8, 124.2, 124.0, 121.7, 120.2, 117.1, 110.4, 109.9, 103.7, 50.4, 47.8, 21.7, 21.6, 20.8; HRMS (ESI) calcd for $C_{34}H_{31}N_2O_2$ ($M + H$) $^+$ 499.2386, found 499.2387.

**1,1′-Dibenzyl-5,5′-dimethoxy-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3n).** 60% yield; white solid; mp 175−176 °C; $^1$H NMR (400 MHz, $CDCl_3$, TMS) $\delta$ 7.25−7.26 (m, 3H), 7.16−7.22 (m, 4H), 7.09 (d, 1H, $J$ = 8.8 Hz), 7.03−7.05 (m, 2H), 6.99 (s, 1H), 6.95 (d, 3H, $J$ = 8.0 Hz), 6.89 (s, 1H), 6.80−6.85 (m, 2H), 5.25 (s, 2H), 5.21 (s, 2H), 3.85 (s, 3H), 3.64 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, TMS) $\delta$ 170.0, 154.9, 154.5, 138.4, 137.0, 131.5, 130.0, 129.2, 128.8, 128.6, 128.3, 127.8, 127.2, 127.0, 126.8, 126.0, 125.2, 121.5, 113.3, 112.5, 111.5, 110.9, 103.6, 101.1, 98.8, 55.9, 55.6, 50.4, 47.6, 20.7; HRMS (ESI) calcd for $C_{34}H_{31}N_2O_4$ ($M + H$) $^+$ 531.2284, found 531.2283.

**1,1′-Diphenyl-1*H*,1′*H*-2,3′-biindol-3-yl Acetate (3r).** 44% yield; white solid; mp 166−167 °C; $^1$H NMR (500 MHz, $CDCl_3$, TMS) $\delta$ 7.68 (d, 1H, $J$ = 9.0 Hz), 7.50−7.53 (m, 2H), 7.43−7.46 (m, 2H), 7.31−7.38 (m, 7H), 7.25−7.27 (m, 2H), 7.14−7.22 (m, 4H), 6.88 (s, 1H). 2.26 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$, TMS) $\delta$ 169.9, 139.3, 138.3, 136.1, 135.9, 129.8, 129.4, 128.7,

128.5, 128.4, 128.0, 127.5, 127.0, 124.6, 124.1, 123.0, 122.9, 121.7, 121.1, 121.1, 120.9, 117.6, 110.9, 110.8, 106.6, 21.0; HRMS (ESI) calcd for $C_{30}H_{23}N_2O_2$ $(M + H)^+$ 443.1760, found 443.1769.

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**Supporting Information Available:** General experimental procedures and spectroscopic data ($^1$H NMR, $^{13}$C NMR, HRMS and MS) for the corresponding products. This material is available free of charge via the Internet at http://pubs.acs.org.