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Substrate-Controlled Regioselective Arylations of 2-Indolylmethanols with Indoles: Synthesis of Bis(indolyl)methane and 3,3′-Bisindole Derivatives

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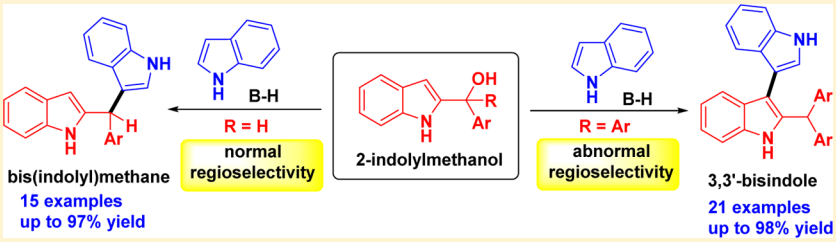
Supporting Information



ABSTRACT: A substrate-controlled regioselective arylation of 2-indolylmethanols with indoles has been established, which efficiently afforded bis(indolyl)methane and 3,3′-bisindole derivatives in high yields and with a broad substrate scope (up to 98% yield, 36 examples). This approach will not only provide an important strategy for the diversified synthesis of bis(indolyl)methane and 3,3′-bisindole derivatives but also serve as a good example for substrate-controlled regioselective reactions.

INTRODUCTION

Indole derivatives are pharmaceutically significant compounds.[1] Especially, indole derivatives containing bis(indolyl)methane or 3,3′-bisindole motifs are widely found in various bioactive natural products, synthetic compounds, and pharmaceuticals (Figure 1).[2] For example, the bis(indolyl)methane compound **I** is cytotoxic against MCF-7 cells,[2b] and compound **II** shows acetylcholinesterase inhibitory activity.[2a] In addition, the core structures of bioactive compounds **III**–**IV** and natural alkaloid **V** are 3,3′-bisindole skeletons,[3,4] which belong to a class of privileged heterocyclic frameworks. So, in recent years, continuous attentions from the chemical community have been paid to the synthesis of bis(indolyl)methanes and 3,3′-bisindoles.[3−5]

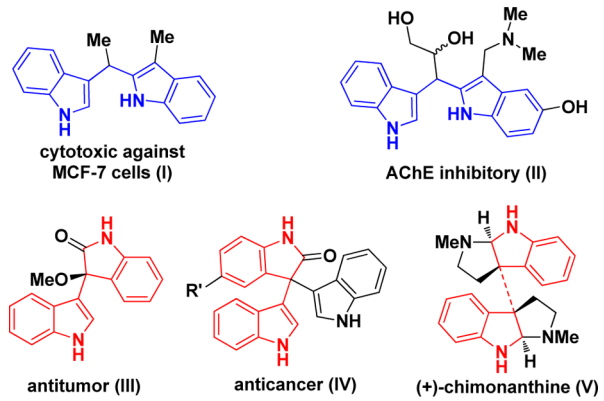


Figure 1. Selected bioactive indole derivatives containing bis(indolyl)-methane or 3,3′-bisindole motifs.

Regioselectivity is one important issue in organic synthesis, and many strategies have been developed to control the regioselectivity of the reaction.[6] Among them, substrate-controlled regioselective reaction has become a powerful method to obtain high regioselectivity or diversified regioselectivity. In this regard, it is highly desired to develop substrate-controlled regioselective reactions for the synthesis of bis(indolyl)methane and 3,3′-bisindole derivatives in a diversified mode.

Indolylmethanols have proven to be one kind of robust synthon.[7−15] Due to their characteristics of being easily converted into highly reactive resonance intermediates, numerous 3-indolylmethanol-involved reactions such as substitutions[7,8] and [3 + 2],[9] [3 + 3],[10] and [4 + 3][11] cyclizations have been developed to synthesize indole derivatives or construct indole-fused cyclic frameworks. In this context, with promising applications in the synthesis of natural products,[12] 2-indolylmethanols show great potential in the synthesis of indole derivatives. However, there are only very limited investigations focused toward the chemistry of 2-indolylmethanols.[13,14] In addition, Han and co-workers have discovered the regioselective issue in 2-indolylmethanol-involved reactions (Scheme 1a), and only the mixture of two regioisomers could be

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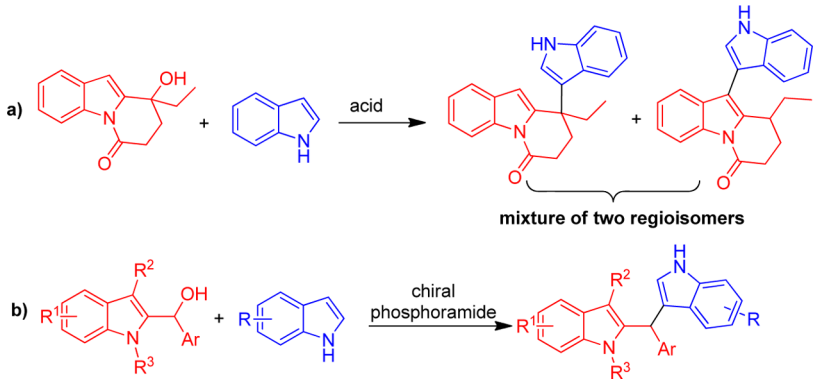
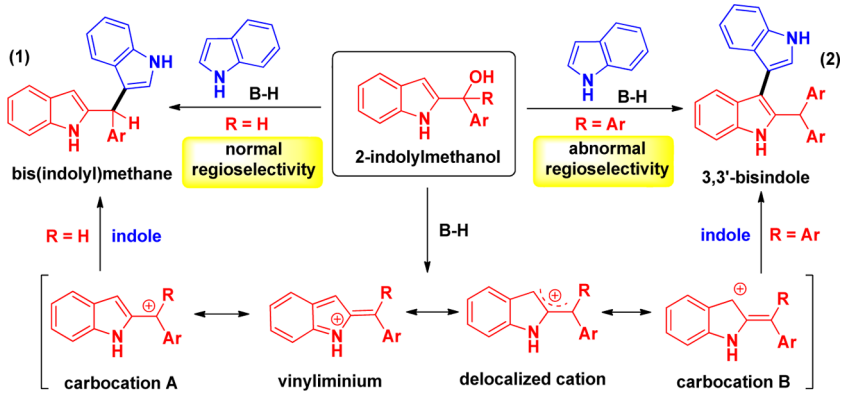
Scheme 1. Regioselective Issue in 2-Indolylmethanol-Involved Reactions



Scheme 2. Design of the Substrate-Controlled Regioselective Substitutions of 2-Indolylmethanols



obtained.[13b] When the C3-position of 2-indolylmethanol was blocked, only one regioisomer could be generated (Scheme 1b).[13d] However, by using the C3-substituted 2-indolylmethanols, the 3,3′-bisindole framework could hardly be constructed. Thus, it has become an urgent task to develop 2-indolylmethanol-involved regioselective transformations for the synthesis of biologically important indole derivatives.

In order to develop substrate-controlled regioselective reactions for the synthesis of bis(indolyl)methane and 3,3′-bisindole derivatives, as well as to discover new transformations of 2-indolylmethanols, we designed a substrate-controlled regioselective reaction based on our previous experiences in synthesizing indole derivatives.[15] As illustrated in Scheme 2, in the presence of a Brønsted acid (B−H), 2-indolylmethanols can be converted into their reactive resonant hybrids of carbocations **A**−**B**, vinyliminium, and delocalized cation intermediates. If the carbocation **A** was attacked by nucleophiles such as indole, a normal regioselective substitution would take place (eq 1). If the carbocation **B** was attacked by nucleophiles as exemplified by indole, an abnormal regioselective substitution would occur (eq 2). In this transformation, the reactivity of C3-position of indole was switched from nucleophilic to electrophilic. Traditionally, the C3-position of the indole is nucleophilic, which is the basis of indole-involved transformations. So, the abnormal regioselective transformation of carbocation **B** is a scarcely reported strategy in indole chemistry.[16] As a result, the regioselectivity of 2-indolylmethanol-involved substitutions may strongly be affected by the steric hindrance of carbocations **A** and **B**, wherein the structures of 2-indolylmethanols play an important role. When the R group of 2-indolylmethanol is an aromatic one (Ar), the two bulky Ar groups will block the attack of nucleophiles to the benzylic position, which makes the nucleophilic attack occur at the C3-position of the indole ring, thus leading to an abnormal regioselectivity (eq 2). In contrast, when the R group of 2-indolylmethanol is a hydrogen atom (H), the carbocation **A** will be more easily attacked by nucleophiles at this benzylic position, thus resulting in a normal regioselective substitution (eq 1). Based on this design, this substrate-controlled regioselective substitution of 2-indolylmethanols with indoles will be an important strategy for the diversified synthesis of bis(indolyl)methane and 3,3′-bisindole derivatives.

Herein, we report a substrate-controlled regioselective arylation of 2-indolylmethanols with indoles under Brønsted acid catalysis. By tuning the structure of 2-indolylmethanols, two series of bis(indolyl)methane and 3,3′-bisindole derivatives were selectively synthesized in high yields (up to 98% yield) and with broad substrate scopes.

RESULTS AND DISCUSSION

Initially, 2-indolylphenylmethanol **1a** was employed as a receptor to react with indole **2a** (Table 1). As expected, a normal regioselective substitution occurred and the bis(indolyl)methane product **4aa** was obtained as the sole product in the presence of a Brønsted acid **3a** (entry 1). The observed regioselectivity may be related to the less steric hindrance of the benzylic position and the fast trapping of the corresponding carbocation **A** by indole **2a**. Then, this reaction was employed as a model reaction to further optimize the conditions. After screening a series of Brønsted acids (entries 1−6), we found that *p*-methylbenzenesulfonic acid **3a** exhibited the highest catalytic activity (entry 1 vs 2−6). So, this Brønsted acid was

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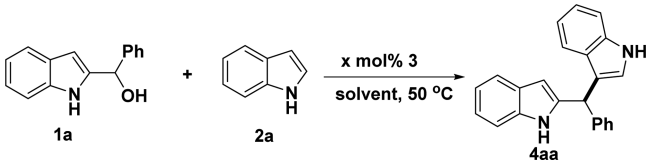
Table 1. Condition Optimization for Normal Regioselective Substitutions[a]



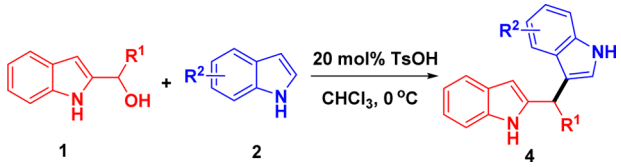
entry	cat. (3)	x	solvent	yield (%)[b]
1	TsOH (3a)	10	toluene	30
2	CF_3CO_2H (3b)	10	toluene	29
3	CH_3CO_2H (3c)	10	toluene	trace
4	CF_3SO_3H (3d)	10	toluene	28
5	HBr (3e)	10	toluene	15
6	HCl (3f)	10	toluene	17
7	TsOH (3a)	10	1,4-dioxane	27
8	TsOH (3a)	10	EtOAc	22
9	TsOH (3a)	10	acetone	trace
10	TsOH (3a)	10	CH_3CN	28
11	TsOH (3a)	10	$CHCl_3$	33
12[c]	TsOH (3a)	10	$CHCl_3$	39
13[c,d]	TsOH (3a)	10	$CHCl_3$	42
14[c,e]	TsOH (3a)	10	$CHCl_3$	61
15[c,e]	TsOH (3a)	20	$CHCl_3$	74
16[c,d]	TsOH (3a)	20	$CHCl_3$	48
17[c,e]	$InCl_3$	20	$CHCl_3$	34
18[c,e]	$InBr_3$	20	$CHCl_3$	36
19[c,e]	$Y(OTf)_3$	20	$CHCl_3$	11
20[c,e]	$Cu(OTf)_2$	20	$CHCl_3$	48

[a]Unless otherwise indicated, the reaction was carried out at the 0.1 mmol scale in a solvent (1 mL) at 50 °C for 15 h, and the molar ratio of **1a:2a** was 1:1.5. [b]Isolated yield. [c]The reaction was carried out at 0 °C. [d]**1a:2a** = 1:3. [e]**1a:2a** = 1:8.

selected as the optimal catalyst for further evaluation of the solvents (entries 7−11), which disclosed that chloroform was the most suitable solvent (entry 11). Subsequent optimization of conditions revealed that lowering the temperature or increasing the amount of substrate **2a** and the catalyst loading of **3a** could increase the yield to a high level (entries 12−15). Finally, the optimal conditions were set in line with what entry 15 illustrated (Brønsted acid **3a** as a catalyst, at 0 °C and using chloroform as a solvent), which could deliver the product **4aa** in the highest yield of 74%. Under the optimal conditions, we also tried to lower the molar ratio of **1a:2a** from 1:8 to 1:3, but the yield decreased to some extent (entry 16). Furthermore, we also tried using some Lewis acids as catalysts under the optimal conditions (entries 17−20). However, the yields in these cases were lower than that under the catalysis of Brønsted acid **3a**.

With the optimized conditions in hand, we then investigated the substrate generality of the normal regioselective substitution. As shown in Table 2, this reaction was applicable to a wide range of indoles **2** as nucleophiles bearing different R^2 groups at different positions, giving the bis(indolyl)methane products **4** in moderate to good yields (54%−89%, entries 1−6). In detail, electron-rich indoles gave higher yields in comparison with the electron-deficient fluoro-substituted indole (entries 2−4 vs 5). This phenomenon may be related to the nucleophilicities of indoles. The reactivity of C6 chloro-substituted indole was similar to that of the unsubstituted indole in terms of the yield (entry 6 vs 1). In addition, the substrate scope of 2-indolylmethanols **1** was examined (entries

Table 2. Substrate Scope of Normal Regioselective Substitutions[a]



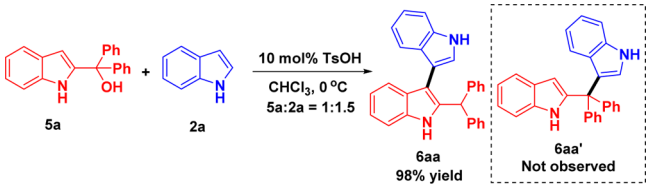
entry	4	R^1 (1)	R^2 (2)	yield (%)[b]
1	4aa	Ph (1a)	H (2a)	74
2	4ab	Ph (1a)	5-Me (2b)	69
3	4ac	Ph (1a)	5-MeO (2c)	89
4	4ad	Ph (1a)	7-Me (2d)	84
5	4ae	Ph (1a)	5-F (2e)	54
6	4af	Ph (1a)	6-Cl (2f)	74
7	4ba	*m*-MeC_6H_4 (1b)	H (2a)	83
8	4ca	*p*-MeC_6H_4 (1c)	H (2a)	71
9	4da	*p*-FC_6H_4 (1d)	H (2a)	46
10	4bg	*m*-MeC_6H_4 (1b)	6-Me (2g)	95
11	4ec	*m*-$MeOC_6H_4$ (1e)	5-MeO (2c)	85
12	4fc	*p*-$MeOC_6H_4$ (1f)	5-MeO (2c)	97
13	4jc	*n*-pentyl (1j)	5-MeO (2c)	44
14	4ka	1-naphthyl (1k)	H (2a)	56
15[c]	4la	*i*-Pr (1l)	H (2a)	31

[a]Unless otherwise indicated, the reaction was carried out at the 0.1 mmol scale in $CHCl_3$ (1 mL) in the presence of 20 mol % TsOH at 0 °C for 15 h, and the molar ratio of **1:2** was 1:8. [b]Isolated yield. [c]The reaction time was 20 h.

7−13). The property of the R^1 groups had some effect on the yields. For example, electron-rich aromatic groups (entries 7−8) were superior to an electron-deficient one (entry 9) with regard to the yield. Besides, excellent yields were observed when both electron-rich 2-indolylmethanols and indoles participated in the reaction (entries 10−12). Notably, an alkyl R^1 group could also be amenable to the reaction to give the corresponding substituted product (entry 13). When the R^1 group was replaced by bulkier groups such as 1-naphthyl and *i*-Pr (entries 14−15), the reaction could still take place with normal regioselectivity to afford the corresponding products **4ka** and **4la**, but only with moderate product yields.

Interestingly, when 2-indolyl(diphenyl)methanol **5a** was applied to similar conditions, the normal regioselective product **6aa′** was not observed. Instead, the abnormal regioselective product **6aa** was obtained in an excellent yield (Scheme 3). The

Scheme 3. 2-Indolylmethanol-Involved Abnormal Regioselective Substitution



corresponding carbocation **B** was involved in the abnormal regioselective substitution. During the whole reaction, the reactivity of C3-position of indolylmethanol **5a** was switched from nucleophilic to electrophilic. This reaction provides a new strategy for indole chemistry. And the product **6aa** possesses a

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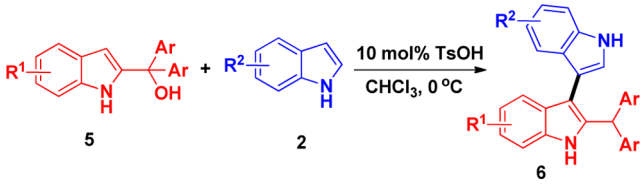
3,3′-bisindole skeleton, which is the elementary unit of some bioactive compounds and natural alkaloids.[3,4]

With this result, we carried out an investation on the substrate scope of the abnormal regioselective substitutions (Table 3). First, indoles **2** with various substituents at different

Table 3. Substrate Scope of Abnormal Regioselective Substitutions[a]

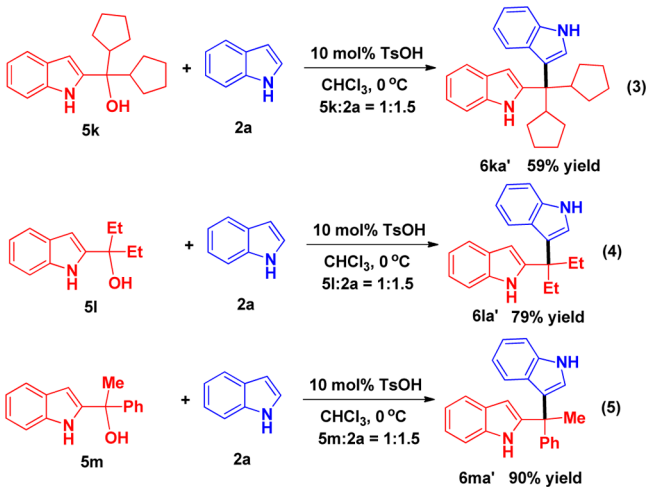


entry	6	Ar/R^1 (5)	R^2 (2)	yield (%)[b]
1	6aa	Ph/H (5a)	H (2a)	98
2	6ab	Ph/H (5a)	5-Me (2b)	86
3	6ac	Ph/H (5a)	5-MeO (2c)	86
4	6ae	Ph/H (5a)	5-F (2e)	87
5	6ag	Ph/H (5a)	6-Me (2g)	95
6	6ah	Ph/H (5a)	4-Me (2h)	76
7	6ai	Ph/H (5a)	5-Br (2i)	90
8	6aj	Ph/H (5a)	6-F (2j)	89
9	6al	Ph/H (5a)	6-Cl (2l)	82
10	6am	Ph/H (5a)	7-Me (2m)	97
11	6an	Ph/H (5a)	7-F (2n)	78
12	6ao	Ph/H (5a)	7-Cl (2o)	85
13	6ba	Ph/4-Me (5b)	H (2a)	78
14	6ca	Ph/5-Br (5c)	H (2a)	88
15	6da	Ph/6-Br (5d)	H (2a)	91
16	6ea	Ph/7-Br (5e)	H (2a)	75
17	6fa	*m*-MeC$_6$H$_4$/H (5f)	H (2a)	89
18	6ga	*m*-FC$_6$H$_4$/H (5g)	H (2a)	97
19	6ha	*p*-MeOC$_6$H$_4$/H (5h)	H (2a)	76
20	6ia	*p*-MeC$_6$H$_4$/H (5i)	H (2a)	69
21	6ja	*p*-FC$_6$H$_4$/H (5j)	H (2a)	85

[a]Unless otherwise indicated, the reaction was carried out at the 0.1 mmol scale in $CHCl_3$ (1 mL) in the presence of 10 mol % TsOH at 0 °C, and the molar ratio of **5**:**2** was 1:1.5. [b]Isolated yield.

positions were found to be suitable substrates for this reaction (entries 2−12). In particular, indoles bearing electronic-deficient groups were less nucleophilic in normal regioselective substitutions (Table 2, entries 5−6). However, in the abnormal regioselective substitutions (entries 4, 7−9, and 11−12), these substrates could successfully take part in the reaction to give the desired 3,3′-bisindole products in excellent yields (78%−90%). Second, a series of 2-indolylmethanols **5** bearing different Ar/R^1 substituents were also accommodated in the reaction (entries 13-21). It seems that the position of the substituents linked to the indole ring (R^1) had some effect on the reactivity (entries 14−16). In addition, the position of the substituents on the phenyl ring (Ar group) seems to have some influence on the yield, because *meta*-substituted Ar groups afforded the products in higher yields than their *para*-substituted counterparts (entries 17−18 vs 20−21).

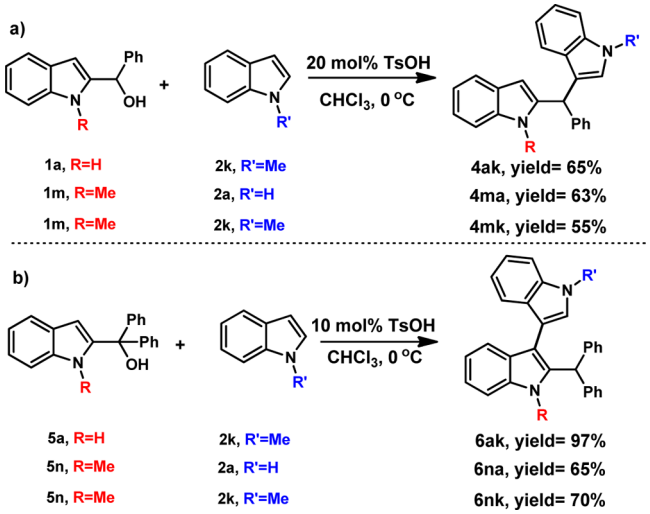
Interestingly, when substrates **5k**−**5m** bearing alkyl groups were employed to the reactions with indole **2a** under the standard conditions, the regioselectivity was switched to generate the normal regioselective products **6ka′**−**6ma′** (eqs 3−5). These results indicated that the existence of two phenyl groups in 2-indolylmethanols is necessary for performing the abnormal regioselective substitutions.



The structures of all products **4**, **6**, and **6′** were unambiguously assigned by ^{1}H and ^{13}C NMR, IR, and HR MS. Furthermore, the structure of product **6ai** was confirmed by X-ray single crystal analysis (see the Supporting Information for details).[17]

In order to gain some insights into the two regioselective substitutions, we performed two series of control experiments under the standard conditions (Scheme 4). In the case of

Scheme 4. Control Experiments To Investigate the Role of N−H Groups



normal regioselective substitution (Scheme 4a), either *N*-methyl protected 2-indolylmethanol **1m** or *N*-methyl protected indole **2k** was utilized in the reaction, which resulted in the finding that the yield of normal regioselective product **4ak** or **4ma** was decreased. Moreover, the double N-protected product **4mk** was obtained only in a low yield of 55%. These results implied that both of the N−H groups of 2-indolylmethanols **1** and indoles **2** had an important role in controlling the reactivity of the normal regioselective substitution. However, in the case of abnormal regioselective substitution (Scheme 4b), N-protected indole **2k** still displayed high reactivity with 2-indolylmethanol **5a** and gave the product **6ak** in an excellent

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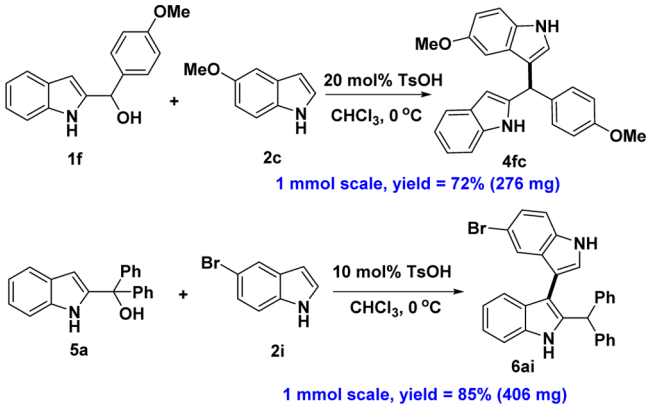
yield of 97%. In contrast, the reactivity of N-protected 2-indolylmethanol **5n** was decreased to some extent in the abnormal regioselective substitution because the yields of products **6na** and **6nk** were inferior to those of **6aa** and **6ak**. These results indicated that only the N−H group of 2-indolylmethanols **5** played an important role in controlling the reactivity of the abnormal regioselective substitution.

In addition, the two regioselective substitutions of 2-indolylmethanols and indoles could be performed at 1 mmol scale under the standard conditions to generate the corresponding bis(indolyl)methane **4fc** and 3,3′-bisindole **6ai** at good yields (Scheme 5).

Scheme 5. Preparative Scale Synthesis



CONCLUSIONS

In summary, we have established substrate-controlled regioselective arylations of 2-indolylmethanols with indoles, which efficiently afforded bis(indolyl)methane and 3,3′-bisindole derivatives in high yields and with a broad substrate scope (up to 98% yield, 36 examples). This approach will not only provide an important strategy for the diversified synthesis of bis(indolyl)methane and 3,3′-bisindole derivatives but also serve as a good example for substrate-controlled regioselective reactions. Moreover, this finding will greatly enrich the chemistry of 2-indolylmethanols which is an underdeveloped research area.

EXPERIMENTAL SECTION

^{1}H and ^{13}C NMR spectra were measured at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was $CDCl_3$ and acetone-d_6, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by an HRMS/MS instrument. Analytical grade solvents for the column chromatography were used after distillation, and commercially available reagents were used as received.

General Procedure for the Synthesis of Bis(indolyl)methane Derivatives 4. To the mixture of 2-indolylphenylmethanols **1** (0.1 mmol), indoles **2** (0.8 mmol), and TsOH **3a** (0.02 mmol) was added chloroform (1 mL), which was stirred at 0 °C for 15 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography on silica gel to afford pure products **4**.

General Procedure for the Synthesis of 3,3′-Bisindole Derivatives 6. To the mixture of 2-indolyldiphenylmethanols **5** (0.1 mmol), indoles **2** (0.15 mmol), and TsOH **3a** (0.01 mmol) was added chloroform (1 mL), which was stirred at 0 °C for 15 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography on silica gel to afford pure products **6**.

*3-((1H-Indol-2-yl)(phenyl)methyl)-1H-indole (**4aa**).* Preparative thin layer chromatography: petroleum ether/ethyl acetate = 4/1; yield: 74% (23.9 mg); yellowish solid, mp 52−53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.92 (s, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.38 (d, J = 7.0 Hz, 2H), 7.35−7.28 (m, 5H), 7.21 (t, J = 7.2 Hz, 2H), 7.16−7.09 (m, 2H), 7.08−7.02 (m, 1H), 6.75 (s, 1H), 6.25 (s, 1H), 5.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 141.0, 136.6, 136.0, 128.7, 128.6, 126.9, 126.8, 123.6, 122.4, 121.3, 120.2, 119.8, 119.7, 119.6, 117.8, 111.2, 110.7, 101.7, 42.8; IR (KBr): 3404, 3052, 2922, 2852, 1489, 1452, 1413, 1339, 1288, 1091, 1016, 744 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{18}N_2 - H)^-$ requires m/z 321.1392, found m/z 321.1380.

*3-((1H-Indol-2-yl)(phenyl)methyl)-5-methyl-1H-indole (**4ab**).* Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 69% (23.3 mg); yellowish solid, mp 48−49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.84 (s, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.35−7.32 (m, 4H), 7.32−7.28 (m, 1H), 7.26 (d, J = 3.2 Hz, 1H), 7.23 (d, J = 8.9 Hz, 2H), 7.18−7.10 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.69 (s, 1H), 6.25 (s, 1H), 5.82 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.2, 136.0, 134.9, 129.1, 128.7, 128.5, 127.0, 126.8, 124.1, 123.8, 121.3, 120.2, 119.6, 119.1, 117.3, 110.9, 110.7, 101.7, 42.6, 21.5; IR (KBr): 3404, 3025, 2919, 2853, 1488, 1453, 1415, 1288, 1094, 1020, 793, 745 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{20}N_2 - H)^-$ requires m/z 335.1548, found m/z 335.1539.

*3-((1H-Indol-2-yl)(phenyl)methyl)-5-methoxy-1H-indole (**4ac**).* Preparative thin layer chromatography: petroleum ether/ethyl acetate = 4/1; yield: 89% (31.5 mg); yellow solid, mp 55−56 °C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 10.04 (s, 1H), 10.01 (s, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.41 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.8 Hz, 4H), 7.23 (t, J = 7.2 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 2.3 Hz, 1H), 6.79 (d, J = 2.2 Hz, 1H), 6.77−6.72 (m, 1H), 6.12 (d, J = 1.0 Hz, 1H), 5.84 (s, 1H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 153.7, 143.4, 142.2, 136.8, 132.2, 128.7, 128.6, 128.2, 127.5, 126.4, 124.6, 120.6, 119.7, 118.9, 116.9, 112.0, 111.4, 110.8, 101.2, 100.7, 54.9, 42.7; IR (KBr): 3430, 1696, 1581, 1485, 1448, 1338, 1289, 1203, 1164, 1017, 780, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{20}N_2O - H)^-$ requires m/z 351.1498, found m/z 351.1496.

*3-((1H-Indol-2-yl)(phenyl)methyl)-7-methyl-1H-indole (**4ad**).* Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 84% (28.4 mg); claret-colored solid, mp 39−40 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), δ 7.88 (s, 1H), 7.55 (d, J = 7.4 Hz, 1H), 7.37−7.29 (m, 5H), 7.26−7.19 (m, 2H), 7.17−7.08 (m, 2H), 7.04 (d, J = 7.0 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.75 (s, 1H), 6.26 (d, J = 0.7 Hz, 1H), 5.84 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.1, 136.2, 136.0, 128.7, 128.6, 126.8, 126.4, 123.4, 122.9, 121.3, 120.4, 120.2, 120.0, 119.7, 118.3, 117.4, 110.7, 101.7, 42.8, 16.6; IR (KBr): 3407, 3051, 2921, 2852, 1610, 1492, 1451, 1340, 1288, 1070, 784, 740 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{20}N_2 - H)^-$ requires m/z 335.1548, found m/z 335.1545.

*3-((1H-Indol-2-yl)(phenyl)methyl)-5-fluoro-1H-indole (**4ae**).* Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 54% (18.4 mg); claret-colored solid, mp 60−61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.90 (s, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.36−7.29 (m, 5H), 7.28 (d, J = 4.3 Hz, 1H), 7.24 (s, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.07 (t, J = 7.3 Hz, 1H), 7.02−6.97 (m, 1H), 6.97−6.91 (m, 1H), 6.84 (d, J = 2.0 Hz, 1H), 6.23 (s, 1H), 5.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7 (J = 231), 141.9, 140.5, 136.1, 133.1, 128.6, 128.5, 127.0, 125.3, 121.4, 120.3, 119.7, 118.0, 111.8 (J = 10), 111.0, 110.7, 110.6, 104.7, 104.5, 101.9, 42.6; IR (KBr): 3407, 2921, 1581, 1484, 1452, 1416, 1288, 1166, 935, 794, 747, 711 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{17}FN_2 - H)^-$ requires m/z 339.1298, found m/z 339.1288.

*3-((1H-Indol-2-yl)(phenyl)methyl)-6-chloro-1H-indole (**4af**).* Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 74% (26.4 mg); yellowish solid, mp 70−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.90 (s, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 1.6 Hz, 1H), 7.35−7.27 (m, 5H), 7.26−7.22 (m,

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2H), 7.12 (t, J = 7.3 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 7.01−6.95 (m, 1H), 6.79 (d, J = 2.3 Hz, 1H), 6.22 (s, 1H), 5.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 140.5, 136.9, 136.1, 128.6, 128.4, 128.3, 127.0, 125.4, 124.2, 121.4, 120.6, 120.3, 119.7, 118.1, 111.1, 110.6, 109.9, 42.6; IR (KBr): 3407, 2921, 1486, 1452, 1406, 1335, 1290, 1090, 905, 802, 743, 675 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{17}ClN_2 - H)^-$ requires m/z 355.1002, found m/z 355.1000.

3-((1H-Indol-2-yl)(m-tolyl)methyl)-1H-indole (**4ba**). Preparative thin layer chromatography: petroleum ether/ethyl acetate = 2/1; yield: 83% (28.0 mg); claret-colored solid, mp 40−41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.91 (s, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.25−7.19 (m, 3H), 7.17 (s, 1H), 7.13 (d, J = 6.9 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.07−7.01 (m, 1H), 6.77 (d, J = 2.2 Hz, 1H), 6.25 (d, J = 0.7 Hz, 1H), 5.80 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 141.2, 138.2, 136.6, 136.0, 129.4, 128.7, 128.4, 127.6, 126.8, 125.7, 123.6, 122.3, 121.3, 120.2, 119.8, 119.7, 119.6, 117.9, 111.2, 110.7, 101.6, 42.6, 21.5; IR (KBr): 3626, 3400, 3048, 2920, 1536, 1485, 1452, 1412, 1339, 1287, 1090, 741 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{20}N_2 - H)^-$ requires m/z 335.1548, found m/z 335.1547.

3-((1H-Indol-2-yl)(p-tolyl)methyl)-1H-indole (**4ca**). Preparative thin layer chromatography: petroleum ether/ethyl acetate = 2/1; yield: 71% (23.7 mg); claret-colored solid, mp 56−57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.91 (s, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.25−7.17 (m, 4H), 7.15−7.05 (m, 4H), 7.02 (d, J = 7.8 Hz, 1H), 6.79 (d, J = 2.0 Hz, 1H), 6.24 (s, 1H), 5.80 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 139.3, 137.0, 136.6, 136.4, 136.0, 129.2, 128.6, 128.5, 127.3, 126.8, 123.6, 122.3, 121.2, 120.2, 119.7, 119.6, 118.0, 111.2, 110.6, 101.6, 42.3, 21.1; IR (KBr): 3402, 2921, 1649, 1511, 1452, 1412, 1339, 1287, 1157, 1088, 1031, 740 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{20}N_2 - H)^-$ requires m/z 335.1548, found m/z 335.1544.

3-((4-Fluorophenyl)(1H-indol-2-yl)methyl)-1H-indole (**4da**). Preparative thin layer chromatography: petroleum ether/ethyl acetate = 2/1; yield: 46% (15.7 mg); claret-colored solid, mp 55−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.91 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.31−7.27 (m, 2H), 7.23 (t, J = 7.8 Hz, 2H), 7.13 (t, J = 7.1 Hz, 1H), 7.10−7.03 (m, 2H), 7.03−6.98 (m, 2H), 6.79 (d, J = 2.2 Hz, 1H), 6.21 (s, 1H), 5.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (J = 244 Hz), 140.8, 138.0, 136.6, 136.0, 130.1 (J = 8 Hz), 128.5, 126.6, 123.5, 122.5, 121.4, 120.3, 119.9, 119.7, 119.5, 117.7, 115.3 (J = 21 Hz), 111.3, 110.7, 101.8, 41.9; IR (KBr): 3401, 2920, 1503, 1453, 1414, 1339, 1288, 1220, 1093, 1011, 807, 742 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{17}FN_2 - H)^-$ requires m/z 339.1298, found m/z 339.1299.

3-((1H-Indol-2-yl)(m-tolyl)methyl)-6-methyl-1H-indole (**4bg**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 95% (33.4 mg); claret-colored solid, mp 92−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.83 (s, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.28−7.25 (m, 1H), 7.22 (d, J = 3.2 Hz, 1H), 7.21 (d, J = 2.9 Hz, 1H), 7.16 (d, J = 5.7 Hz, 2H), 7.14 (d, J = 3.4 Hz, 1H), 7.13−7.07 (m, 3H), 6.88 (d, J = 8.1 Hz, 1H), 6.68 (s, 1H), 6.26 (s, 1H), 5.77 (s, 1H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.3, 138.1, 137.1, 136.0, 132.2, 129.4, 128.7, 128.4, 127.6, 125.7, 124.7, 123.0, 121.5, 121.2, 120.2, 119.6, 119.3, 117.7, 111.2, 110.7, 101.6, 42.7, 21.7, 21.6; IR (KBr): 3401, 2917, 1612, 1452, 1409, 1336, 1287, 1088, 1042, 798, 737, 682 cm^{-1}; ESI FTMS exact mass calcd for $(C_{25}H_{22}N_2 - H)^-$ requires m/z 349.1705, found m/z 349.1701.

3-((1H-Indol-2-yl)(3-methoxyphenyl)methyl)-5-methoxy-1H-indole (**4ec**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 1/1; yield: 85% (32.6 mg); yellowish solid, mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.92 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.25−7.20 (m, 3H), 7.12 (t, J = 7.1 Hz, 1H), 7.09−7.04 (m, 1H), 6.95−6.90 (m, 2H), 6.87−6.83 (m, 1H), 6.83−6.80 (m, 1H), 6.78−6.75 (m, 2H), 6.26 (d, J = 0.8 Hz, 1H), 5.76 (s, 1H), 3.75 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 154.0, 144.0, 140.8, 136.1, 131.7, 129.5, 128.6, 127.2, 124.4, 121.3, 121.2, 120.2, 119.6, 117.2, 114.7, 112.5, 111.9, 110.7, 101.7, 101.4, 55.8, 55.2, 42.7; IR (KBr): 3733, 3403, 2926, 1591, 1483, 1449, 1261, 1209, 1159, 1033, 747, 689 cm^{-1}; ESI FTMS exact mass calcd for $(C_{25}H_{22}N_2O_2 - H)^-$ requires m/z 381.1603, found m/z 381.1604.

3-((1H-Indol-2-yl)(4-methoxyphenyl)methyl)-5-methoxy-1H-indole (**4fc**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 1/1; yield: 97% (37.1 mg); yellow solid, mp 80−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.90 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.25 (s, 1H), 7.24 (s, 1H), 7.23−7.20 (m, 2H), 7.12 (t, J = 7.2 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H), 6.86 (d, J = 8.5 Hz, 3H), 6.77 (d, J = 2.2 Hz, 1H), 6.73 (d, J = 2.2 Hz, 1H), 6.24 (s, 1H), 5.74 (s, 1H), 3.80 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 154.0, 141.4, 136.0, 134.4, 131.7, 129.6, 128.6, 127.2, 124.3, 121.3, 120.2, 119.6, 117.8, 113.9, 112.4, 111.9, 110.7, 101.6, 101.4, 55.8, 55.3, 41.8; IR (KBr): 3403, 2926, 1582, 1509, 1452, 1292, 1247, 1212, 1173, 1026, 800, 746 cm^{-1}; ESI FTMS exact mass calcd for $(C_{25}H_{22}N_2O_2 - H)^-$ requires m/z 381.1603, found m/z 381.1607.

3-(1-(1H-Indol-2-yl)hexyl)-5-methoxy-1H-indole (**4jc**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 44% (15.3 mg); pink solid, mp 175−176 °C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 9.90 (s, 1H), 9.84 (s, 1H), 7.47 (d, J = 7.4 Hz, 1H), 7.25 (t, J = 9.3 Hz, 2H), 7.21 (s, 1H), 7.00 (d, J = 1.8 Hz, 1H), 6.98−6.90 (m, 2H), 6.76−6.70 (m, 1H), 6.41 (s, 1H), 4.40 (t, J = 7.6 Hz, 1H), 3.67 (s, 3H), 2.28−2.20 (m, 2H), 1.49−1.31 (m, 6H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 153.6, 143.5, 136.5, 132.1, 128.9, 127.4, 122.9, 120.2, 119.4, 118.7, 117.2, 111.8, 111.2, 110.6, 101.1, 98.5, 54.9, 36.4, 34.7, 31.7, 27.6, 22.4, 13.5; IR (KBr): 3410, 3296, 2924, 2857, 1486, 1451, 1290, 1210, 1174, 922, 796, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{23}H_{26}N_2O - H)^-$ requires m/z 345.1967, found m/z 345.1960.

3-((1H-Indol-2-yl)(naphthalen-1-yl)methyl)-1H-indole (**4ka**). Preparative thin layer chromatography: petroleum ether/dichlormethane = 2/1; Reaction time = 15 h; yield: 56% (21.0 mg); yellowish solid, mp 54−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.5 Hz, 1H), 7.95−7.85 (m, 3H), 7.81 (d, J = 8.2 Hz, 1H), 7.55−7.45 (m, 2H), 7.44−7.33 (m, 4H), 7.25−7.18 (m, 3H), 7.16−7.07 (m, 2H), 7.07−7.01 (m, 1H), 6.60 (s, 2H), 6.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 138.1, 136.6, 136.0, 134.0, 131.7, 128.8, 128.7, 127.7, 126.8, 126.3, 126.3, 125.7, 125.6, 124.3, 124.0, 122.4, 121.3, 120.3, 119.8, 119.7, 119.6, 117.6, 111.2, 110.7, 102.1, 38.7; IR (KBr): 3404, 1717, 1596, 1541, 1508, 1456, 1339, 1289, 1250, 789, 745 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{20}N_2 - H)^-$ requires m/z 371.1548, found m/z 371.1537.

3-(1-(1H-Indol-2-yl)-2-methylpropyl)-1H-indole (**4la**). Preparative thin layer chromatography: petroleum ether/dichlormethane = 2/1; Reaction time = 20 h; yield: 31% (9.0 mg); yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.82 (s, 1H), 7.61−7.54 (m, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 7.1 Hz, 2H), 7.12 (s, 1H), 7.10−7.00 (m, 3H), 6.48 (s, 1H), 4.19 (d, J = 7.3 Hz, 1H), 2.71−2.51 (m, 1H), 1.04 (t, J = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 136.2, 135.6, 128.7, 127.5, 122.3, 122.2, 120.8, 119.9, 119.6, 119.4, 116.4, 111.1, 110.4, 100.1, 43.8, 31.8, 21.6, 21.2; IR (KBr): 3405, 2956, 1718, 1541, 1456, 1417, 1383, 1288, 1095, 1043, 1012, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{20}H_{20}N_2 - H)^-$ requires m/z 287.1548, found m/z 287.1550.

2-Benzhydryl-1H,1′H-3,3′-biindole (**6aa**). Preparative thin layer chromatography: petroleum ether/ethyl acetate = 4/1; yield: 98% (38.9 mg); yellowish solid, mp 56−57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.86 (s, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.35−7.31 (m, 5H), 7.30−7.25 (m, 3H), 7.24 (d, J = 7.1 Hz, 1H), 7.20−7.12 (m, 6H), 6.79 (d, J = 2.1 Hz, 1H), 5.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.3, 136.2, 135.7, 129.9, 129.1, 129.0, 128.7, 128.0, 127.8, 126.8, 123.1, 122.1, 121.8, 121.0, 120.5, 119.7, 119.6, 111.2, 110.8, 110.0, 108.3, 48.4; IR (KBr): 3443, 3025, 1593, 1488, 1449, 1409, 1334, 1088, 1017, 921, 810, 740 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{22}N_2 - H)^-$ requires m/z 397.1705, found m/z 397.1709.

2-Benzhydryl-5′-methyl-1H,1′H-3,3′-biindole (**6ab**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 86% (35.5 mg); yellowish solid, mp 144−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.84 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 3.5 Hz, 2H), 7.31 (d, J = 7.6 Hz, 5H), 7.28 (d, J = 6.9

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Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.2 Hz, 4H), 7.13 (d, J = 7.7 Hz, 1H), 7.09 (d, J = 8.6 Hz, 1H), 6.80 (d, J = 2.3 Hz, 1H), 5.82 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.4, 135.7, 134.5, 129.1, 129.0, 128.8, 128.7, 128.3, 126.7, 123.7, 123.3, 121.7, 120.5, 119.6, 110.8, 110.7, 109.4, 108.4, 48.3, 21.5; IR (KBr): 3446, 2919, 1594, 1486, 1451, 1335, 1087, 1021, 922, 797, 743, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{24}N_2 - H)^-$ requires m/z 411.1861, found m/z 411.1857.

2-Benzhydryl-5′-methoxy-1H,1′H-3,3′-biindole (**6ac**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 86% (36.8 mg); yellowish solid, mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.89 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.36−7.31 (m, 4H), 7.30−7.27 (m, 3H), 7.26−7.20 (m, 2H), 7.19−7.13 (m, 4H), 7.11 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 1.9 Hz, 1H), 6.93−6.89 (m, 1H), 6.88 (d, J = 2.3 Hz, 1H), 5.84 (s, 1H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 143.1, 136.3, 135.8, 131.2, 129.0, 128.7, 128.4, 126.8, 124.0, 121.8, 120.4, 119.7, 112.8, 111.9, 110.9, 109.7, 108.3, 101.9, 55.6, 48.4; IR (KBr): 3408, 1588, 1484, 1446, 1283, 1207, 1083, 1021, 909, 801, 743, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{24}N_2O - H)^-$ requires m/z 427.1811, found m/z 427.1808.

2-Benzhydryl-5′-fluoro-1H,1′H-3,3′-biindole (**6ae**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 87% (36.0 mg); yellowish solid, mp 173−174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.87 (s, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.34 (d, J = 7.9 Hz, 4H), 7.32−7.26 (m, 4H), 7.26−7.21 (m, 2H), 7.21−7.09 (m, 5H), 7.06−6.92 (m, 1H), 6.82 (d, J = 2.2 Hz, 1H), 5.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9 (J = 233 Hz), 136.5, 135.7, 132.7, 129.0, 128.9, 128.8, 128.5, 126.9, 124.9, 121.9, 120.3, 119.9, 111.8, 111.7, 110.9, 110.7, 110.4, 110.2, 107.7, 105.8, 105.6, 48.4; IR (KBr): 3447, 2919, 1587, 1484, 1281, 1174, 1083, 1022, 914, 801, 742, 703 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{21}FN_2 - H)^-$ requires m/z 415.1611, found m/z 415.1608.

2-Benzhydryl-6′-methyl-1H,1′H-3,3′-biindole (**6ag**). Preparative thin layer chromatography: petroleum ether/ethyl acetate = 8/1; yield: 95% (39.0 mg); yellowish solid, mp 180−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.81 (s, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.35−7.28 (m, 5H), 7.27 (d, J = 7.2 Hz, 2H), 7.25−7.19 (m, 2H), 7.18−7.11 (m, 4H), 7.10 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 6.73 (d, J = 2.2 Hz, 1H), 5.83 (s, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.6, 136.2, 135.7, 131.9, 129.0, 128.7, 126.7, 125.9, 122.4, 121.7, 121.3, 120.6, 120.5, 119.6, 111.1, 110.8, 109.8, 108.4, 48.3, 21.7; IR (KBr): 3411, 2918, 1628, 1450, 1335, 1160, 1102, 1024, 926, 801, 750, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{24}N_2 - H)^-$ requires m/z 411.1861, found m/z 411.1862.

2-Benzhydryl-4′-methyl-1H,1′H-3,3′-biindole (**6ah**). Preparative thin layer chromatography: petroleum ether/ethyl acetate = 8/1; yield: 76% (31.3 mg); yellowish solid, mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.85 (s, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.38−7.32 (m, 3H), 7.30 (d, J = 7.4 Hz, 3H), 7.28 (s, 2H), 7.23−7.15 (m, 4H), 7.14 (d, J = 7.4 Hz, 2H), 7.09 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 7.0 Hz, 1H), 6.75 (d, J = 1.7 Hz, 1H), 5.77 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.5, 137.4, 136.4, 135.4, 131.8, 131.3, 129.0, 128.9, 128.7, 128.5, 127.4, 126.8, 126.6, 124.6, 122.1, 121.7, 121.0, 120.3, 119.9, 110.7, 110.0, 109.0, 108.9, 48.3, 19.1; IR (KBr): 3410, 3052, 2920, 1600, 1492, 1449, 1335, 1099, 1023, 920, 746, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{24}N_2 - H)^-$ requires m/z 411.1861, found m/z 411.1860.

2-Benzhydryl-5′-bromo-1H,1′H-3,3′-biindole (**6ai**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 90% (42.9 mg); yellowish solid, mp 165−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.87 (s, 1H), 7.70 (d, J = 0.8 Hz, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.38−7.33 (m, 4H), 7.32−7.28 (m, 2H), 7.29 (s, 1H), 7.27 (d, J = 2.5 Hz, 1H), 7.24 (d, J = 4.0 Hz, 1H), 7.21 (d, J = 7.9 Hz, 1H), 7.14 (t, J = 8.2 Hz, 5H), 6.80 (d, J = 2.3 Hz, 1H), 5.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 136.7, 135.6, 134.7, 129.8, 129.0, 128.9, 128.8, 126.9, 125.0, 124.3, 123.3, 121.9, 120.1, 120.0, 113.0, 112.6, 110.9, 109.7, 107.4, 48.4; IR (KBr): 3446, 1488, 1453, 1406, 1333, 1283, 1089, 921, 877, 793, 741, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{21}BrN_2 - H)^-$ requires m/z 475.0810, found m/z 475.0813.

2-Benzhydryl-6′-fluoro-1H,1′H-3,3′-biindole (**6aj**). Preparative thin layer chromatography: petroleum ether/ethyl acetate = 8/1; yield: 89% (36.9 mg); yellowish solid, mp 166−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.85 (s, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.52−7.45 (m, 1H), 7.40−7.30 (m, 5H), 7.28 (d, J = 6.8 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.15 (d, J = 7.4 Hz, 4H), 7.13−7.06 (m, 2H), 6.93−6.84 (m, 1H), 6.75 (d, J = 2.1 Hz, 1H), 5.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (J = 236 Hz), 142.9, 136.5, 136.1, 136.0, 135.7, 129.0, 128.9, 128.8, 126.8, 124.6, 123.2, 121.8, 121.7, 121.6, 120.3, 119.8, 110.9, 110.1, 108.4, 108.2, 107.8, 97.5, 97.2, 48.4; IR (KBr): 3414, 2921, 1492, 1450, 1333, 1236, 1136, 1084, 956, 806, 746, 701 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{21}FN_2 - H)^-$ requires m/z 415.1611, found m/z 415.1610.

2-Benzhydryl-6′-chloro-1H,1′H-3,3′-biindole (**6al**). Preparative thin layer chromatography, petroleum ether/dichloromethane = 2/1; yield: 82% (35.5 mg); yellowish solid, mp 201−202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.83 (s, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.38 (s, 1H), 7.36−7.31 (m, 1H), 7.30−7.25 (m, 5H), 7.23 (d, J = 5.2 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.17−7.11 (m, 4H), 7.10−7.02 (m, 2H), 6.75 (d, J = 1.9 Hz, 1H), 5.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 136.5, 135.6, 128.9, 128.8, 128.1, 126.8, 126.6, 123.6, 121.9, 121.7, 120.3, 120.2, 119.8, 111.0, 110.9, 110.2, 107.6, 48.4; IR (KBr): 3440, 3403, 1485, 1450, 1393, 1333, 1106, 1020, 917, 797, 749, 701 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{21}ClN_2 - H)^-$ requires m/z 431.1315, found m/z 431.1318.

2-Benzhydryl-7′-methyl-1H,1′H-3,3′-biindole (**6am**). Preparative thin layer chromatography, petroleum ether/dichloromethane = 2/1; yield: 97% (39.8 mg); yellowish solid, mp 172−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.84 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.57−7.49 (m, 1H), 7.36−7.30 (m, 6H), 7.28 (d, J = 6.0 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.20−7.14 (m, 4H), 7.13−7.05 (m, 3H), 6.76 (d, J = 2.2 Hz, 1H), 5.84 (s, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.3, 135.7, 129.0, 128.7, 127.6, 126.7, 122.8, 122.6, 121.7, 120.5, 120.3, 119.8, 119.6, 118.7, 110.8, 110.4, 108.4, 48.4, 16.7; IR (KBr): 3430, 2919, 1596, 1488, 1446, 1335, 1256, 1087, 1025, 784, 740, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{24}N_2 - H)^-$ requires m/z 411.1861, found m/z 411.1865.

2-Benzhydryl-7′-fluoro-1H,1′H-3,3′-biindole (**6an**). Preparative thin layer chromatography, petroleum ether/dichloromethane = 2/1; yield: 78% (32.4 mg); yellowish solid, mp 175−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.87 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.38−7.32 (m, 5H), 7.30 (s, 1H), 7.29−7.24 (m, 1H), 7.23 (d, J = 7.1 Hz, 1H), 7.22−7.15 (m, 4H), 7.13 (s, 1H), 7.07−6.95 (m, 2H), 6.81 (d, J = 2.3 Hz, 1H), 5.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7 (J = 242 Hz), 142.9, 136.6, 135.7, 131.7, 129.0, 128.9, 128.8, 126.9, 124.6, 124.5, 123.7, 121.9, 120.3, 119.8, 119.7, 116.7, 110.9, 110.8, 107.7, 107.0, 106.8, 48.4; IR (KBr): 3442, 1578, 1491, 1448, 1405, 1237, 1158, 1086, 1033, 912, 740, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{21}FN_2 - H)^-$ requires m/z 415.1611, found m/z 415.1609.

2-Benzhydryl-7′-chloro-1H,1′H-3,3′-biindole (**6ao**). Preparative thin layer chromatography, petroleum ether/dichloromethane = 2/1; yield: 85% (36.6 mg); yellowish solid, mp 110−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.87 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.38−7.33 (m, 5H), 7.32−7.26 (m, 3H), 7.21 (t, J = 7.5 Hz, 1H), 7.20−7.12 (m, 4H), 7.11 (d, J = 7.3 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 6.84 (d, J = 2.2 Hz, 1H), 5.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 136.6, 135.6, 133.4, 129.5, 129.0, 128.9, 128.8, 126.8, 123.7, 121.8, 121.5, 120.3, 120.2, 119.8, 119.6, 116.6, 111.1, 110.9, 107.6, 48.4; IR (KBr): 3733, 3440, 1637, 1492, 1442, 1156, 1081, 1026, 889, 780, 741, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{21}ClN_2 - H)^-$ requires m/z 431.1315, found m/z 431.1313.

2-Benzhydryl-4-methyl-1H,1′H-3,3′-biindole (**6ba**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 78% (32.0 mg); yellowish solid, mp 175−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.88 (s, 1H), 7.36 (d, J = 8.2 Hz,

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1H), 7.26 (s, 10 H), 7.17−7.12 (m, 1H), 7.05−6.98 (m, 2H), 6.89 (d, J = 6.5 Hz, 1H), 6.87−6.81 (m, 2H), 6.80 (d, J = 2.4 Hz, 1H), 6.38 (d, J = 1.9 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 142.9, 136.9, 135.5, 130.1, 129.9, 127.9, 127.7, 127.3, 126.6, 125.4, 122.2, 121.8, 121.6, 119.9, 119.8, 111.1, 108.3, 102.5, 55.3, 18.9; IR (KBr): 3407, 1486, 1448, 1407, 1336, 1238, 1101, 1021, 905, 802, 743, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{24}N_2 - H)^-$ requires m/z 411.1861, found m/z 411.1866.

2-Benzhydryl-5-bromo-1H,1′H-3,3′-biindole (**6ca**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 88% (41.9 mg); yellowish solid, mp 65−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.87 (s, 1H), 7.68 (s, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.36−7.30 (m, 4H), 7.30−7.26 (m, 4H), 7.18 (d, J = 8.9 Hz, 2H), 7.17−7.10 (m, 4H), 6.78 (d, J = 2.1 Hz, 1H), 5.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 137.8, 136.1, 134.3, 130.9, 128.9, 128.8, 127.8, 126.9, 124.6, 123.3, 122.8, 122.3, 120.6, 119.9, 113.0, 112.3, 111.2, 109.1, 108.0, 48.4; IR (KBr): 3432, 3051, 2921, 1596, 1455, 1409, 1294, 1088, 931, 796, 742, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{21}BrN_2 - H)^-$ requires m/z 475.0810, found m/z 475.0817.

2-Benzhydryl-6-bromo-1H,1′H-3,3′-biindole (**6da**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 91% (43.2 mg); yellowish solid, mp 115−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.82 (s, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.47−7.39 (m, 3H), 7.35−7.30 (m, 4H), 7.29−7.22 (m, 3H), 7.20 (d, J = 8.4 Hz, 1H), 7.18−7.12 (m, 5H), 6.76 (d, J = 1.7 Hz, 1H), 5.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 137.0, 136.4, 136.2, 128.9, 128.8, 127.9, 126.9, 123.2, 122.9, 122.3, 121.7, 120.7, 119.7, 115.2, 113.8, 111.2, 109.3, 108.4, 48.3; IR (KBr): 3421, 2918, 2850, 1492, 1451, 1404, 1331, 1087, 920, 810, 743, 699 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{21}BrN_2 - H)^-$ requires m/z 475.0810, found m/z 475.0809.

2-Benzhydryl-7-bromo-1H,1′H-3,3′-biindole (**6ea**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 75% (35.6 mg); yellowish solid, mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.87 (s, 1H), 7.69 (s, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.35−7.30 (m, 4H), 7.30−7.26 (m, 4H), 7.18 (d, J = 8.7 Hz, 2H), 7.17−7.12 (m, 4H), 6.78 (d, J = 2.2 Hz, 1H), 5.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 137.8, 136.1, 134.3, 130.9, 128.9, 128.8, 127.8, 126.9, 124.6, 123.3, 122.8, 122.3, 120.6, 119.9, 113.0, 112.3, 111.2, 109.1, 108.0, 48.4; IR (KBr): 3419, 3025, 2918, 1454, 1408, 1293, 1088, 969, 928, 795, 741, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{21}BrN_2 - H)^-$ requires m/z 475.0810, found m/z 475.0813.

2-(Di-m-tolylmethyl)-1H,1′H-3,3′-biindole (**6fa**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 89% (38.0 mg); yellowish solid, mp 43−44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.87 (s, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.44 (s, 1H), 7.37 (s, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.27−7.19 (m, 3H), 7.17−7.07 (m, 4H), 7.02−6.92 (m, 4H), 6.79 (d, J = 2.2 Hz, 1H), 5.76 (s, 1H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.4, 136.6, 136.2, 135.7, 129.7, 129.1, 128.6, 128.0, 127.5, 126.1, 123.1, 122.1, 121.6, 121.0, 120.5, 119.6, 119.5, 111.1, 110.9, 110.1, 108.1, 48.3, 21.5; IR (KBr): 3420, 3049, 2918, 1599, 1484, 1454, 1418, 1091, 1008, 804, 743, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{26}N_2 - H)^-$ requires m/z 425.2018, found m/z 425.2016.

2-(Bis(3-fluorophenyl)methyl)-1H,1′H-3,3′-biindole (**6ga**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 97% (42.2 mg); yellowish solid, mp 43−44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.81 (s, 1H), 7.62−7.53 (m, 2H), 7.43 (d, J = 8.1 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.30−7.26 (m, 2H), 7.25−7.19 (m, 2H), 7.15−7.08 (m, 2H), 7.01−6.94 (m, 2H), 6.92 (d, J = 7.7 Hz, 2H), 6.89−6.80 (m, 3H), 5.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 161.9, 144.9, 144.9, 136.2, 135.8, 134.9, 130.4, 130.3, 128.9, 127.9, 124.6, 123.1, 122.3, 122.2, 120.8, 120.6, 120.0, 119.7, 116.0, 115.8, 114.2, 114.0, 111.2, 111.9, 109.6, 108.9, 47.8; IR (KBr): 3408, 3053, 1585, 1484, 1446, 1255, 1087, 965, 926, 880, 746, 690 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{20}F_2N_2 - H)^-$ requires m/z 433.1517, found m/z 433.1519.

2-(Bis(4-methoxyphenyl)methyl)-1H,1′H-3,3′-biindole (**6ha**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 76% (34.7 mg); yellowish solid, mp 186−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.87 (s, 1H), 7.53 (d, J = 7.4 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.20−7.13 (m, 6H), 7.12−7.04 (m, 2H), 6.88−6.82 (m, 2H), 6.80−6.74 (m, 5H), 6.34 (d, J = 1.9 Hz, 1H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 144.4, 138.0, 136.9, 135.8, 130.8, 128.1, 127.3, 125.2, 122.4, 122.3, 122.1, 121.4, 120.4, 119.8, 119.6, 113.0, 111.1, 110.7, 103.8, 55.2, 53.9; IR (KBr): 3408, 2924, 1607, 1505, 1454, 1293, 1248, 1177, 1027, 811, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{26}N_2O_2 - H)^-$ requires m/z 457.1916, found m/z 457.1914.

2-(Di-p-tolylmethyl)-1H,1′H-3,3′-biindole (**6ia**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 69% (29.5 mg); yellowish solid, mp 60−61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.83 (s, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.27 (d, J = 9.4 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.15−7.08 (m, 6H), 7.04 (d, J = 8.0 Hz, 4H), 6.80 (d, J = 2.2 Hz, 1H), 5.75 (s, 1H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 136.8, 136.2, 136.2, 135.7, 129.4, 129.1, 128.8, 128.0, 123.1, 122.1, 121.6, 121.0, 120.5, 119.6, 119.5, 111.1, 110.8, 110.1, 108.0, 47.6, 21.1; IR (KBr): 3410, 2919, 1509, 1450, 1409, 1333, 1234, 1087, 1012, 905, 816, 738 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{26}N_2 - H)^-$ requires m/z 425.2018, found m/z 425.2011.

2-(Bis(4-fluorophenyl)methyl)-1H,1′H-3,3′-biindole (**6ja**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 85% (37.0 mg); yellowish solid, mp 174−175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.76 (s, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.44 (d, J = 8.1 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.30−7.26 (m, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.14−7.06 (m, 6H), 7.05−6.97 (m, 4H), 6.81 (d, J = 2.1 Hz, 1H), 5.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (J = 250 Hz), 138.5, 136.2, 135.8 (J = 10 Hz), 130.4 (J = 8 Hz), 129.0, 128.0, 123.0, 122.1 (J = 21 Hz), 120.7 (J = 23 Hz), 119.8 (J = 22 Hz), 115.6 (J = 21 Hz), 111.2, 110.9, 109.7, 108.5, 46.9; IR (KBr): 3414, 3050, 1601, 1505, 1453, 1410, 1226, 1157, 1091, 831, 746, 681 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{20}F_2N_2 - H)^-$ requires m/z 433.1517, found m/z 433.1515.

3-(Dicyclopentyl(1H-indol-2-yl)methyl)-1H-indole (**6ka′**). Preparative thin layer chromatography: petroleum ether/ethyl acetate = 4/1; yield: 59% (22.7 mg); yellowish solid, mp 232−233 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.88 (s, 1H), 7.70 (d, J = 7.2 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.24 (s, 1H), 7.19−7.12 (m, 3H), 7.10 (t, J = 5.6 Hz, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.66 (s, 1H), 6.57 (d, J = 8.0 Hz, 1H), 2.83 (s, 2H), 1.94 (s, 2H), 1.85 (d, J = 7.7 Hz, 2H), 1.49 (s, 4H), 1.38−1.20 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 136.0, 134.8, 128.1, 125.2, 122.9, 121.4, 120.7, 119.8, 119.4, 119.2, 116.7, 110.8, 110.7, 102.2, 49.0, 47.9, 24.8, 24.5; IR (KBr): 3454, 3404, 2949, 2863, 1485, 1451, 1406, 1295, 1099, 1011, 780, 741 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{30}N_2 - H)^-$ requires m/z 381.2331, found m/z 381.2327.

3-(3-(1H-Indol-2-yl)pentan-3-yl)-1H-indole (**6la′**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 79% (24.0 mg); yellowish solid, mp 76−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.1 Hz, 1H), 7.20 (d, J = 2.2 Hz, 1H), 7.16−7.04 (m, 5H), 6.83 (t, J = 7.6 Hz, 1H), 6.62 (s, 1H), 2.38−2.25 (m, 2H), 2.22−2.10 (m, 2H), 0.76 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 136.8, 135.7, 128.6, 126.1, 122.6, 122.0, 121.0, 120.8, 120.4, 119.9, 119.5, 119.2, 111.0, 110.6, 99.9, 43.2, 28.6, 8.3; IR (KBr): 3394, 2966, 2925, 1530, 1455, 1408, 1336, 1290, 1101, 1015, 790, 748 cm^{-1}; ESI FTMS exact mass calcd for $(C_{21}H_{22}N_2 - H)^-$ requires m/z 301.1705, found m/z 301.1709.

3-(1-(1H-Indol-2-yl)-1-phenylethyl)-1H-indole (**6ma′**). Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; Reaction time = 15 h; yield: 90% (30.4 mg); yellowish solid, mp 45−47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 5.8 Hz, 2H), 7.69−7.59 (m, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.33−7.27 (m, 5H), 7.21−7.15 (m, 2H), 7.15−7.08 (m, 3H), 6.97 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 1.6 Hz, 1H), 6.49 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

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146.9, 145.6, 137.0, 135.8, 128.4, 128.2, 127.6, 126.6, 126.1, 123.4, 123.1, 122.1, 121.3, 121.3, 120.3, 119.7, 119.6, 111.4, 110.8, 100.2, 44.5, 28.9; IR (KBr): 3405, 2923, 2851, 2341, 1558, 1540, 1489, 1456, 1338, 1287, 1100, 736 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{20}N_2 - H)^-$ requires m/z 335.1548, found m/z 335.1540.

*3-((1H-Indol-2-yl)(phenyl)methyl)-1-methyl-1H-indole (**4ak**).* Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 65% (21.9 mg); yellowish solid, mp 39−40 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.42−7.32 (m, 4H), 7.34−7.32 (m, 2H), 7.31−7.27 (m, 1H), 7.26 (d, J = 3.3 Hz, 1H), 7.23 (s, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.66 (s, 1H), 6.26 (d, J = 0.7 Hz, 1H), 5.85 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.2, 137.4, 136.0, 128.7, 128.6, 128.3, 127.2, 126.8, 121.9, 121.3, 120.2, 119.7, 119.6, 119.3, 116.1, 110.7, 109.3, 101.6, 42.6, 32.8; IR (KBr): 3490, 3050, 1608, 1542, 1457, 1415, 1332, 1287, 1016, 793, 742, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{20}N_2 - H)^-$ requires m/z 335.1548, found m/z 335.1546.

*2-((1H-Indol-3-yl)(phenyl)methyl)-1-methyl-1H-indole (**4ma**).* Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 63% (21.3 mg); yellowish solid, mp 53−54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.38−7.29 (m, 7H), 7.22 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.58 (d, J = 2.1 Hz, 1H), 6.02 (s, 1H), 5.81 (s, 1H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 141.9, 137.8, 136.6, 128.9, 128.5, 127.6, 126.8, 126.7, 124.0, 122.3, 121.0, 120.3, 119.6, 119.3, 117.9, 111.2, 108.9, 102.1, 41.5, 30.0; IR (KBr): 3407, 3051, 2922, 1534, 1460, 1420, 1339, 1226, 1094, 1015, 908, 739 cm^{-1}; ESI FTMS exact mass calcd for $(C_{24}H_{20}N_2 - H)^-$ requires m/z 335.1548, found m/z 335.1542.

*1-Methyl-3-((1-methyl-1H-indol-2-yl)(phenyl)methyl)-1H-indole (**4mk**).* Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 55% (19.4 mg); yellowish solid, mp 42−43 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 7.9 Hz, 1H), 7.33 (s, 1H), 7.32−7.26 (m, 6H), 7.24 (d, J = 7.3 Hz, 1H), 7.20 (d, J = 8.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.47 (s, 1H), 5.98 (s, 1H), 5.78 (s, 1H), 3.71 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 142.0, 137.7, 137.4, 128.8, 128.6, 128.4, 127.5, 127.1, 126.7, 121.7, 120.9, 120.3, 119.6, 119.2, 119.0, 116.2, 109.2, 108.8, 102.0, 41.4, 32.7, 29.9; IR (KBr): 3727, 2924, 1536, 1466, 1328, 1263, 1228, 1124, 912, 794, 740, 697 cm^{-1}; ESI FTMS exact mass calcd for $(C_{25}H_{22}N_2 - H)^-$ requires m/z 349.1705, found m/z 349.1703.

*2′-Benzhydryl-1-methyl-1H,1′H-3,3′-biindole (**6ak**).* Preparative thin layer chromatography: petroleum ether/ethyl acetate = 15/1; yield: 97% (39.8 mg); yellowish solid, mp 54−55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.59−7.53 (m, 2H), 7.38 (d, J = 8.2 Hz, 1H), 7.34−7.29 (m, 5H), 7.28−7.23 (m, 3H), 7.19−7.13 (m, 5H), 7.12−7.04 (m, 2H), 6.66 (s, 1H), 5.82 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 137.0, 136.2, 135.7, 129.1, 129.0, 128.7, 128.5, 127.8, 126.7, 121.7, 121.6, 121.0, 120.5, 119.6, 119.0, 110.7, 109.2, 108.3, 48.3, 32.8; IR (KBr): 3437, 2922, 1645, 1450, 1375, 1326, 1232, 1077, 1018, 915, 743, 701 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{24}N_2 - H)^-$ requires m/z 411.1861, found m/z 411.1860.

*2-Benzhydryl-1-methyl-1H,1′H-3,3′-biindole (**6na**).* Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 65% (26.6 mg); yellowish solid, mp 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.33−7.28 (m, 3H), 7.27−7.23 (m, 4H), 7.20−7.15 (m, 4H), 7.14−7.09 (m, 2H), 7.07 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 2.1 Hz, 1H), 6.15 (s, 1H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 138.1, 137.4, 136.1, 129.2, 128.4, 126.4, 123.4, 122.0, 121.5, 120.8, 120.4, 119.5, 119.3, 111.0, 110.4, 108.9, 108.8, 47.5, 32.0; IR (KBr): 3410, 3052, 2923, 1597, 1459, 1367, 1096, 1016, 910, 811, 744, 705 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{24}N_2 - H)^-$ requires m/z 411.1861, found m/z 411.1860.

*2-Benzhydryl-1,1′-dimethyl-1H,1′H-3,3′-biindole (**6nk**).* Preparative thin layer chromatography: petroleum ether/dichloromethane = 2/1; yield: 70% (29.7 mg); yellowish solid, mp 131−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.42−7.35 (m, 5H), 7.33−7.27 (m, 5H), 7.25−7.17 (m, 3H), 7.14 (t, J = 7.3 Hz, 1H), 6.77 (s, 1H), 6.26 (s, 1H), 3.80 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 138.1, 137.5, 137.0, 129.3, 129.0, 128.6, 128.4, 128.2, 126.4, 121.6, 120.9, 120.5, 119.4, 119.0, 109.2, 109.1, 108.9, 108.8, 47.7, 32.8, 32.0; IR (KBr): 2923, 1597, 1467, 1235, 1200, 1150, 1094, 1016, 904, 811, 737, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{31}H_{26}N_2 - H)^-$ requires m/z 425.2018, found m/z 425.2016.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02850.

Preparation procedure and the characterization data of two representative 2-indolylmethanols **1a** and **5a**; characterization data (including ^{1}H and ^{13}C NMR spectra) of products **4**, **6**, and **6′** (PDF)

Crystallographic data for **6ai** (CIF)

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Notes

The authors declare no competing financial interest.

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