JOC The Journal of Organic Chemistry

Article

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Gallium Bromide-Promoted Dearomative Indole Insertion in 3-Indolylmethanols: Chemoselective and (*Z*/*E*)-Selective Synthesis of 3,3′-Bisindole Derivatives

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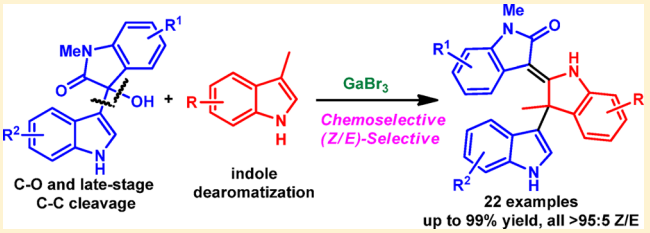
Supporting Information

ABSTRACT: Gallium bromide ($GaBr_3$)-promoted dearomative indole insertion in 3-indolylmethanols has been established, which chemoselectively constructs a biologically important 3,3′-bisindole framework bearing an all-carbon quaternary center in high yields and excellent (*Z*)-selectivities (up to 99% yield, all >95:5 *Z*/*E*). The reaction pathway was suggested to include a tandem sequence of Michael addition/C−C bond cleavage/nucleophilic addition, wherein the strong acidity of $GaBr_3$ played a crucial role in the key step of C−C bond cleavage. This reaction not only provides a new strategy for dearomatization of indoles, but also represents a new reaction category for 3-indolylmethanols, which involves a rarely reported late-stage C−C bond cleavage of 3-indolylmethanol derivatives. In addition, this approach also offers an efficient method for the synthesis of biologically important 3,3′-bisindole derivatives.

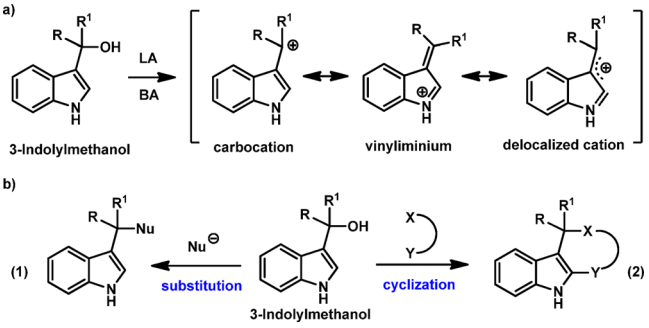


INTRODUCTION

Dearomatization reactions are powerful strategies to access the core structures of numerous natural products and pharmaceuticals from structurally simple planar aromatic substrates.[1−3] In particular, dearomatization of indoles has attracted the attention of organic chemists, due to the biological importance of indole derivatives.[4] Because of the high synthetic value of these reactions, many successful dearomative reactions of indoles have been developed based on the reactivity of the C2−C3 double bond in the indole moiety, which mainly include allylation,[5] alkylation,[6] arylation,[7] and cycloaddition reactions.[8,9] Despite great progress having been made in this field, developing new dearomative reactions of indoles has remained a long-standing goal in the chemistry community.

3-Indolylmethanols have proven to be versatile reactants for the synthesis of indole derivatives. In the presence of a Lewis acid (LA) or a Brønsted acid (BA)[10] and certain protic solvents,[11] 3-indolylmethanols can be easily attacked by nucleophiles. Owing to its reactive resonant hybrids of carbocation, vinyliminium and delocalized cation intermediates (Scheme 1a), nucleophilic substitutions of 3-indolylmethanols have been well-developed (eq 1).[12−14] Despite the low reactivity of the C-2 position in the indole moiety, 3-indolylmethanol can be used as a 3C synthon. Recently, [3+2],[15,18] [3+3],[16] and [3+4] cyclizations[17,18] of 3-indolylmethanols have been achieved to construct indole-fused cyclic frameworks (eq 2). Although elegant developments have been reported in substitutions and cyclizations of 3-indolylmethanols, other new types of reactions involving 3-indolylmethanols have scarcely been described. So, it is highly desirable to develop new reactions of 3-indolylmethanols for synthesizing structurally complex indole derivatives.

Scheme 1. Profile of 3-Indolylmethanol-Involved Reactions

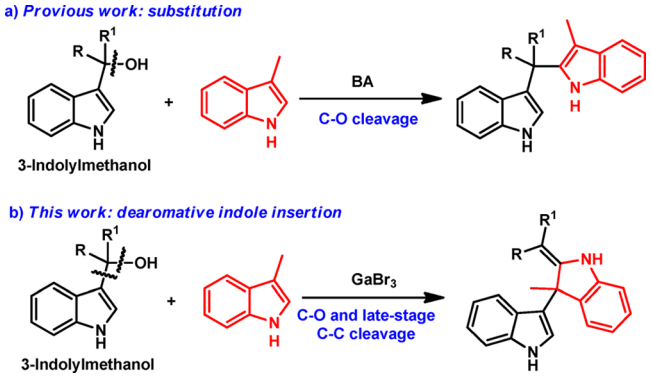


Our group has been interested in the reactions of 3-indolylmethanols for the synthesis of functionalized indoles.[13g,14a,b,15f,g,16c,d,18] In previous work, we have achieved the catalytic asymmetric arylation of 3-indolylmethanols with 3-methylindoles.[19] Under BA-catalyzed conditions, chiral indole derivatives were synthesized by enantioselective substitution of 3-methylindoles (Scheme 2a).[19] Interestingly, we recently found that when the same reaction was carried out under gallium bromide ($GaBr_3$)-promoted conditions, a dearomative indole insertion in 3-indolylmethanols occurred, which afforded a 3,3′-bisindole product in a chemoselective and (*Z*/*E*)-selective fashion (Scheme 2b). This reaction has not only

Received: September 7, 2016
Published: October 28, 2016

DOI: 10.1021/acs.joc.6b02201
J. Org. Chem. 2016, 81, 11734−11742

Scheme 2. Chemoselective Reactions of 3-Indolylmethanols with 3-Methylindoles



resulted in an unusual late-stage C−C bond cleavage of 3-indolylmethanol derivatives, rather than the more common C−O bond cleavage, but has also accomplished the dearomatization of indoles. So, this new reaction of 3-indolylmethanols will supply a new strategy for dearomatization of indoles.

In addition, the constructed 3,3′-bisindole skeleton belongs to a class of privileged heterocyclic frameworks, which constitutes the core structures of many bioactive compounds (Figure 1, compounds **I**−**II**).[20] Moreover, the 3,3′-bisindole moiety is the elementary unit of the dimeric or oligomeric hexahydropyrroloindole natural alkaloids (Figure 1, compounds **III**).[21]

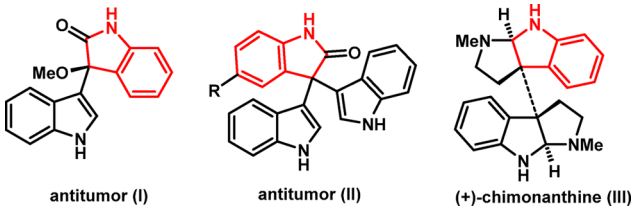


Figure 1. Selected bioactive compounds and natural alkaloids containing 3,3′-bisindole framework.

Herein, we report $GaBr_3$-promoted dearomative indole insertion in 3-indolylmethanols with 3-methylindoles, which chemoselectively constructs a biologically important 3,3′-bisindole framework bearing an all-carbon quaternary center in high yields and excellent (*Z*)-selectivities (up to 99% yield, all >95:5 *Z*/*E*).

RESULTS AND DISCUSSION

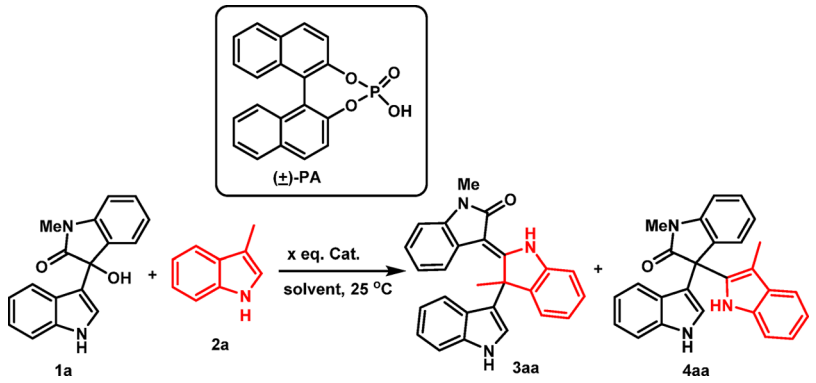
Initially, we investigated the model reaction of 3-indolylmethanol **1a** with 3-methylindole **2a**. As shown in Table 1, entries 1−3, in the presence of BAs with different acidity, the reaction only afforded the substitution product **4aa**. Then, different LAs were employed as catalysts instead of BAs. However, a weak LA failed to catalyze the reaction (entry 4), while standard LAs also afforded the substitution product **4aa** (entries 5−6). Gratifyingly, in the presence of $GaBr_3$ with stronger acidity,[22] the dearomative 3,3′-bisindole product **3aa** was obtained (entry 7). These results revealed that the acidity of the catalysts imposed some effect on the reaction, since standard acidic conditions could only facilitate the production of the substitutive product **4aa**, while $GaBr_3$, which is a stronger LA, could promote the formation of the dearomatized product **3aa**. Next, to improve the yield and chemoselectivity of **3aa**, the catalyst loading was increased (entries 7−9), which revealed that the product **3aa** could be chemoselectively generated when using 1.0 equiv $GaBr_3$ (entry 9). Subsequent evaluation of different types of solvents (entries 10−14) disclosed that 1,4-dioxane, ethyl acetate and acetone failed to promote the formation of **3aa** (entries 10−12), while acetonitrile delivered the reaction but with poor chemoselectivity (entry 13). Nevertheless, satisfyingly, the reaction in dichloromethane could chemospecifically afford the desired product **3aa** in a quantitative yield (entry 14). In addition to this, the reaction temperature was tentatively changed, which showed that either lowering or raising the temperature would reduce the yield of **3aa** (entries 15−16). So, the optimal conditions were set in line with what entry 14 illustrated. Finally, several more relevant LAs were evaluated under the optimal conditions (entries 17−20). However, these LAs failed to promote the reaction to generate the dearomative product **3aa**. Instead, the substitutive product **4aa** was formed in high yields. These results indicated that the unique catalytic activity of $GaBr_3$ played a crucial role in the generation of the dearomative product **3aa**. In addition, to illustrate the importance of $GaBr_3$ and other acid catalysts, a control experiment in the absence of $GaBr_3$ or any other acid catalysts was performed (entry 21). As expected, no reaction occurred, which demonstrated that the acid catalysts played an important role in 3-indolylmethanol-involved reactions, as illustrated in Scheme 1a.

With the known optimized condition, we then carried out an investigation on the substrate scope of the dearomative indole insertion reaction. As shown in Table 2, this reaction was amenable to a wide range of 3-indolylmethanols **1** bearing different R^1/R^2 groups, giving the 3,3′-bisindole products **3** at generally good yields and excellent (*Z*)-selectivities (52−99% yield, all >95:5 *Z*/*E*). Generally, the position and electronic properties of the R^1/R^2 groups had some effects on the yields. For example, R^1 substituents linked to the oxindole core exerted a delicate influence on the yield. For C5-substituted 3-indolylmethanols, electron-deficient groups (F and Cl) were superior to the electron-rich group (MeO) in terms of the yield (entries 3−4 vs 2). However, there was a completely opposite effect for C6- and C7-substituted 3-indolylmethanols (entries 5−11). In these cases, electron-deficient R^1 groups gave lower yields than electron-neutral ones (entries 5 and 8 vs 6−7 and 9−11). In addition, a series of 3-indolylmethanols bearing electronically different R^2 substituents at various positions of the indole moiety could easily participate in the reaction, to give the products **3** in good overall yields (entries 12−17). It appears that the electron-rich R^2 groups were superior to electron-poor ones with regard to the yield (entries 12−13 and 17 vs 14−16).

Next, the applicability of the reaction for 3-methylindoles **2** was examined (Table 3). A series of 3-methylindoles bearing either electron-donating or electron-withdrawing groups at different positions of their benzene rings were accommodated in the reaction, leading to the generation of the desired dearomatized products **3** in good yields and excellent (*Z*)-selectivities (56−99% yield, all >95:5 *Z*/*E*). It seems that the electronic nature of the substituents had little effect on the yield, since both C6-methyl and C6-chloro-substituted 3-methylindoles **2c**−**2d** delivered the products **3ac**−**3ad** in the same yield (entry 3 vs 4). However, the position of the substituents seems to have some influence on the yield, because C6-substituted 3-methylindoles afforded the products in higher

DOI: 10.1021/acs.joc.6b02201
J. Org. Chem. 2016, 81, 11734−11742

Table 1. Screening of Catalysts and Optimization of Reaction Conditions[a]



entry	cat.	x	solvent	yield (%)[b] 3aa	yield (%)[b] 4aa
1	(±)-PA	0.2	toluene	–	98
2	$PhCO_2H$	0.2	toluene	–	42
3	T_sOH	0.2	toluene	–	70
4	$Mg(OTf)_2$	0.2	toluene	–	–
5	$Zn(OTf)_2$	0.2	toluene	–	82
6	$Cu(OTf)_2$	0.2	toluene	–	95
7	$GaBr_3$	0.2	toluene	20	44
8	$GaBr_3$	0.5	toluene	27	24
9	$GaBr_3$	1.0	toluene	31	–
10	$GaBr_3$	1.0	1,4-dioxane	–	66
11	$GaBr_3$	1.0	EtOAc	–	74
12	$GaBr_3$	1.0	acetone	–	94
13	$GaBr_3$	1.0	CH_3CN	39	26
14	$GaBr_3$	1.0	CH_2Cl_2	99	–
15[c]	$GaBr_3$	1.0	CH_2Cl_2	35	15
16[d]	$GaBr_3$	1.0	CH_2Cl_2	78	–
17	$ZrCl_4$	1.0	CH_2Cl_2	–	99
18	$Sc(OTf)_3$	1.0	CH_2Cl_2	–	99
19	$Yb(OTf)_3$	1.0	CH_2Cl_2	–	62
20	$InBr_3$	1.0	CH_2Cl_2	–	90
21			CH_2Cl_2	–	–

[a]Unless otherwise indicated, the reaction was carried out at the 0.05 mmol scale in a solvent (1 mL) at 25 °C for 12 h, and the molar ratio of **1a**:**2a** was 1:1.2. [b]Isolated yield and Z/E > 95:5 in all cases for product **3aa**. [c]The reaction was carried out at 0 °C. [d]The reaction was carried out at 40 °C.

yields than their C7-substituted counterparts (entries 3−4 vs 5−6).

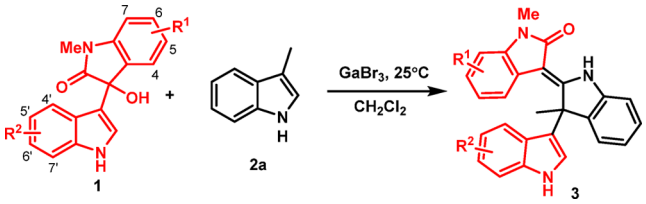
The structures of all products **3** were unambiguously assigned by ^1H and ^{13}C NMR, infrared (IR) and high-resolution mass spectrometry (HRMS). Furthermore, the structures of products **3aa** and **4aa** were confirmed by single crystal X-ray diffraction analysis (see Supporting Information for details).[23]

To gain insight into the reaction pathway, we monitored the reaction of substrates **1a** and **2a** by TLC under standard conditions (Scheme 3, eq 3). It was found that within a short reaction time of 5 min, a large amount (92% yield) of substitutive product **4aa** was generated. With prolongation of the reaction time, the amount of **4aa** was decreased, while that of dearomatized product **3aa** was increased. This therefore suggests that the final product **3aa** might be formed via the generation of **4aa**. To verify this hypothesis, compound **4aa** was subjected to the standard reaction conditions (eq 4), which indeed gave rise to product **3aa** in a quantitative yield. This outcome demonstrated that the dearomatized product **3aa** was generated via the formation of compound **4aa**.

Based on the experimental results, a possible reaction pathway was proposed for this LA $GaBr_3$-catalyzed dearomative indole insertion in 3-indolylmethanols (Scheme 4). As exemplified by the formation of product **3aa**, in the presence of $GaBr_3$, 3-indolylmethanol **1a** was easily transformed into a delocalized cation intermediate **A**, which initially reacted with 3-methylindole **2a** via a Michael addition pathway to give the intermediate product **4aa**. Next, compound **4aa** further underwent an unusual C−C bond cleavage in the presence of $GaBr_3$ as a strong LA to generate another delocalized carbocation intermediate **B**, accompanied by the release of one indole molecule. Subsequently, the released indole molecule acted as a nucleophile to attack the C3-position of the delocalized carbocation intermediate **B**, thus affording the dearomative product **3aa** bearing an all-carbon quaternary center. There may be a hydrogen-bonding interaction between the C═O group and the N−H group in the structure of intermediate **B**, which contributed to the experimentally observed (*Z*)-configuration of product **3aa**. During the process of nucleophilic addition of indole to delocalized carbocation intermediate **B**, the regioselectivity of C3-addition might be associated with steric hindrance of the oxindole moiety.

DOI: 10.1021/acs.joc.6b02201
J. Org. Chem. 2016, 81, 11734−11742

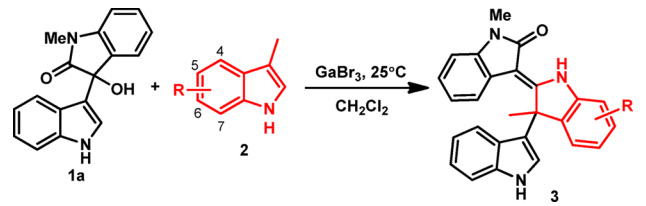
Table 2. Substrate Scope of 3-Indolylmethanols 1[a]



entry	3	R^1/R^2 (1)	Z/E[b]	yield (%)[c]
1	**3aa**	H/H (**1a**)	> 95:5	99
2	**3ba**	5-MeO/H (**1b**)	> 95:5	65
3	**3ca**	5-F/H (**1c**)	> 95:5	96
4	**3da**	5-Cl/H (**1d**)	> 95:5	83
5	**3ea**	6-Me/H (**1e**)	> 95:5	74
6	**3fa**	6-Cl/H (**1f**)	> 95:5	64
7	**3ga**	6-Br/H (**1g**)	> 95:5	70
8	**3ha**	7-Me/H (**1h**)	> 95:5	73
9	**3ia**	7-F/H (**1i**)	> 95:5	62
10	**3ja**	7-Cl/H (**1j**)	> 95:5	62
11	**3ka**	7-Br/H (**1k**)	> 95:5	61
12	**3la**	H/5′-Me (**1l**)	> 95:5	81
13	**3ma**	H/5′-MeO (**1m**)	> 95:5	84
14	**3na**	H/5′-Cl (**1n**)	> 95:5	64
15	**3oa**	H/6′-Cl (**1o**)	> 95:5	59
16	**3pa**	H/6′-Br (**1p**)	> 95:5	52
17	**3qa**	H/7′-Me (**1q**)	> 95:5	86

[a]Unless otherwise indicated, the reaction was carried out at the 0.1 mmol scale in CH_2Cl_2 (2 mL) in the presence of 1.0 eq. $GaBr_3$ at 25 °C for 12 h, and the molar ratio of **1**:**2a** was 1:1.2. [b]The ratio of Z/E was determined by ^1H nuclear magnetic resonance (NMR). [c]Isolated yield.

Table 3. Substrate Scope of 3-Methylindoles[a]

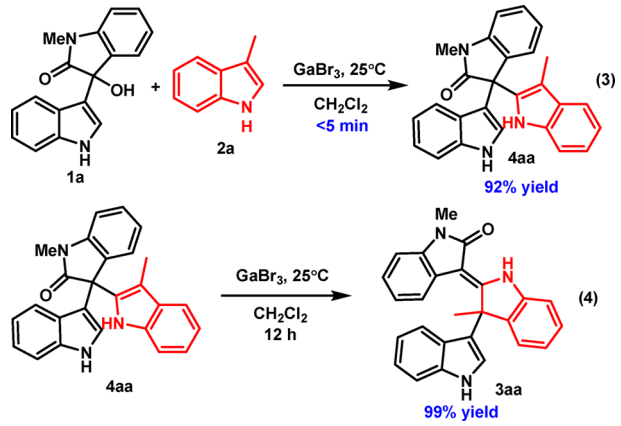


entry	3	R (**2**)	Z/E[b]	yield (%)[c]
1	**3aa**	H (**2a**)	> 95:5	99
2	**3ab**	4-F (**2b**)	> 95:5	60
3	**3ac**	6-Me (**2c**)	> 95:5	75
4	**3ad**	6-Cl (**2d**)	> 95:5	75
5	**3ae**	7-Me (**2e**)	> 95:5	63
6	**3af**	7-Cl (**2f**)	> 95:5	56

[a]Unless otherwise indicated, the reaction was carried out at the 0.1 mmol scale in CH_2Cl_2 (2 mL) in the presence of 1.0 eq. $GaBr_3$ at 25 °C for 12 h, and the molar ratio of **1a**:**2** was 1:1.2. [b]The ratio of Z/E was determined by ^1H nuclear magnetic resonance (NMR). [c]Isolated yield.

Therefore, this dearomative indole insertion in 3-indolylmethanols might include a tandem sequence of Michael addition/C−C bond cleavage/nucleophilic addition. During this process, the C−C bond cleavage was a key step that led to the formation of the final dearomatized product. Besides the acidity of the LA, $GaBr_3$ played a decisive role in the observed chemoselectivity when considering that the C−C bond cleavage could hardly take place in the presence of a weak LA.

Scheme 3. Investigation of the Reaction Pathway



To further verify the proposed reaction mechanism, two crossover experiments were carried out using different-substituted indoles **5a**−**5b** to react with the intermediate product **4aa** under the standard conditions (Scheme 5). As expected, these reactions not only afforded the dearomative product **3aa**, which was formed by self-transformation of **4aa**, but also generated the crossover products **3la** and **3qa**, which were produced via the nucleophilic addition of indoles **5a**−**5b** to the delocalized carbocation intermediate **B**. These results therefore supported that the key aspect of the reaction is an unusual C−C bond cleavage of the intermediate product **4aa**.

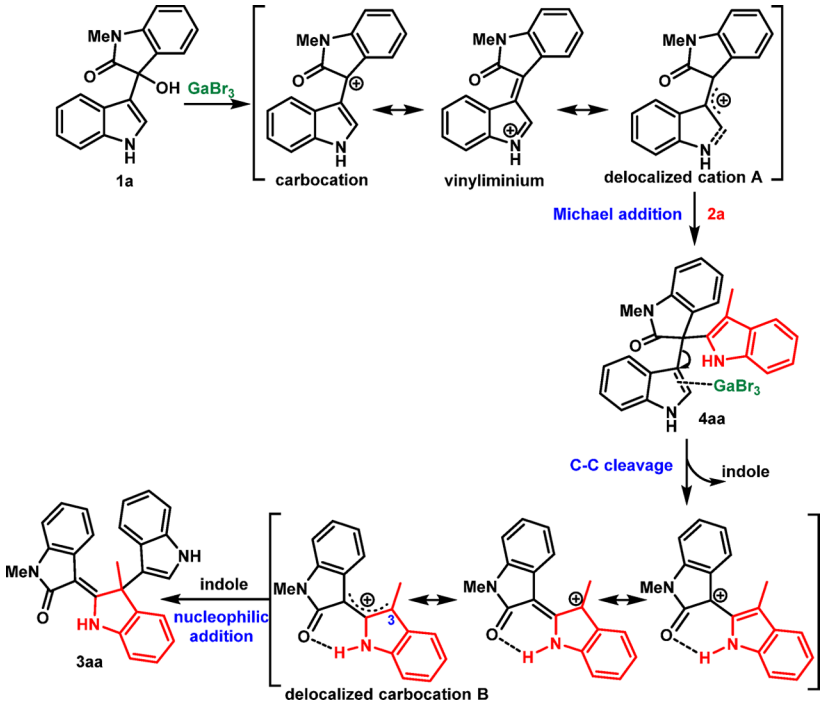
Finally, to investigate the necessity of certain structural units in the reactants, we performed some control experiments under the standard reaction conditions (Scheme 6). First, simple 3-indolyl tertiary methanol **1r** was employed as a substrate, instead of oxindole-derived 3-indolylmethanol **1a**, to react with 3-methylindole **2a** (eq 5). However, no dearomative product was generated and only a small amount of substitutive product **4ra** was formed in a 10% yield. This outcome indicated that the oxindole core in the structure of 3-indolylmethanol was very important for both the substitution reaction and the subsequent dearomative reaction. Second, *N*-protected 3-methylindole **2g** was utilized in the reaction with 3-indolylmethanol **1a** (eq 6), but no reaction occurred. This phenomenon implied that the free N−H group in the structure of 3-methylindoles played an important role in controlling the reactivity. Third, the reactant of 3-methylindole was replaced by 3-phenyl indole **2h** (eq 7) and still no reaction took place. This result demonstrated that the C3-methyl group of indoles **2** was necessary for tuning the reactivity of such reactants.

CONCLUSIONS

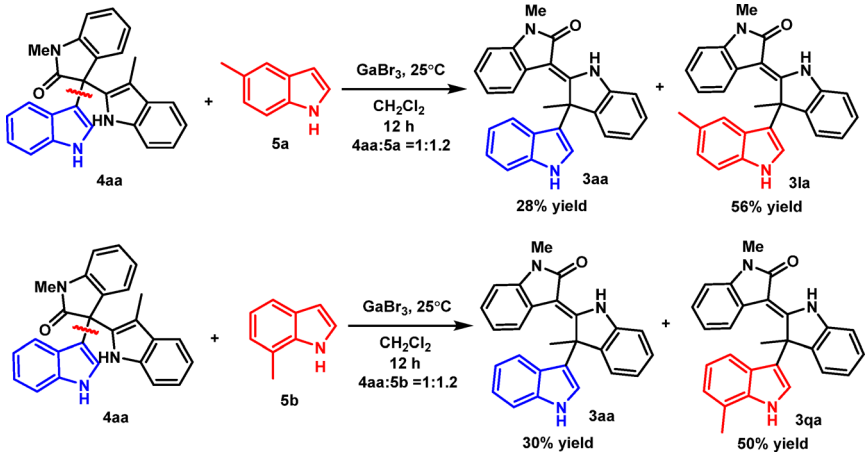
In summary, we have established $GaBr_3$-promoted dearomative indole insertion in 3-indolylmethanols, which chemoselectively constructs a biologically important 3,3′-bisindole framework, bearing an all-carbon quaternary center in high yields and excellent (*Z*)-selectivities (up to 99% yield, all >95:5 Z/E). The reaction pathway was suggested to include a tandem sequence of Michael addition/C−C bond cleavage/nucleophilic addition, wherein the strong acidity of $GaBr_3$ played a crucial role in the key step of C−C bond cleavage. This reaction not only provides a new strategy for dearomatization of indoles, but also represents a new reaction category for 3-indolylmethanols, which involves a rarely reported late-stage C−C bond cleavage of 3-indolylmethanol derivatives. In addition, this approach also

DOI: 10.1021/acs.joc.6b02201
J. Org. Chem. 2016, 81, 11734−11742

Scheme 4. Proposed Reaction Pathway



Scheme 5. Crossover Experiments To Verify the Proposed Mechanism



offers an efficient method for the synthesis of biologically important 3,3′-bisindole derivatives.

EXPERIMENTAL SECTION

^{1}H and ^{13}C NMR spectra were measured at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was DMSO-d_6 and $CDCl_3$, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a HRMS/MS instrument. Analytical grade solvents for the column chromatography were used after distillation, and commercially available reagents were used as received. Substrates **1** were synthesized according to methods described in the literature.[12a]

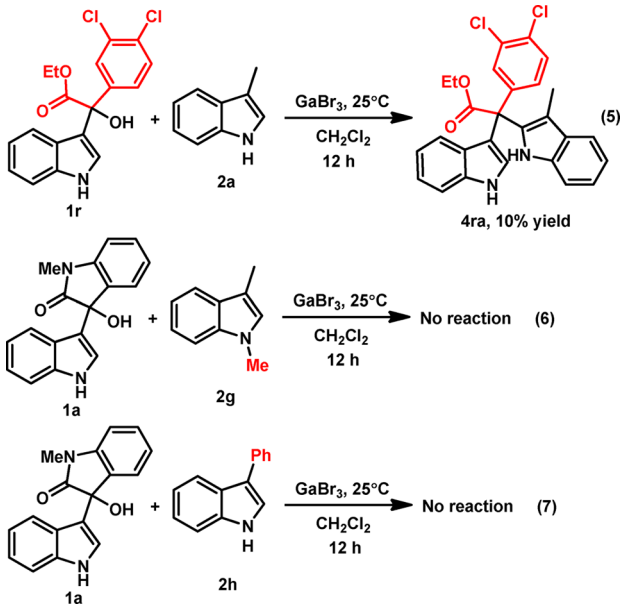
Typical Procedure for the Synthesis of 3,3′-Bisindoles 3. Under argon atmosphere, anhydrous dichloromethane (2 mL) was added to the mixture of 3-indolylmethanol **1** (0.1 mmol), 3-methylindoles **2** (0.12 mmol), and gallium bromide (0.1 mmol). Then, the reaction mixture was stirred at 25 °C for 12 h. After the completion of the reaction was indicated by TLC, the reaction mixture was directly purified through flash column chromatography on silica gel to afford pure products **3**.

(*Z*)-1,3′-Dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3aa). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time =12 h; yield: 99% (39.0 mg); > 95:5 *Z*/*E*; colorless solid, mp 197.3−198.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.19 (s, 1H), 11.21 (s, 1H), 7.89 (s, 1H), 7.40 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 8.1 Hz, 1H), 7.19−7.14 (m, 1H), 7.05−6.98 (m, 2H), 6.95−6.82 (m, 5H), 6.71−6.65 (m, 1H), 6.64−6.56 (m, 1H), 3.25 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 167.4, 141.9, 138.7, 138.5, 137.2, 128.2, 125.5, 123.7, 123.4, 122.9, 122.6, 122.4, 121.6, 121.5, 120.7, 119.1, 118.6, 114.7, 112.1, 111.5, 108.0, 100.0, 94.9, 51.7, 26.0, 22.4; IR (KBr): 3220, 2924, 2955, 2853, 1637, 1562, 1467, 1428, 1349, 1371, 1319, 1278, 1255, 1170, 1135, 1100, 738, 677 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{21}N_3O-H)^-$ requires m/z 390.1606, found m/z 390.1605.

(*Z*)-5-Methoxy-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ba). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time =12 h; yield: 65% (27.5 mg); > 95:5 *Z*/*E*; colorless solid, mp 184.7−185.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.19 (s, 1H), 11.28 (s, 1H), 7.93 (s, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.18−7.14 (m, 1H),

DOI: 10.1021/acs.joc.6b02201
J. Org. Chem. 2016, 81, 11734−11742

Scheme 6. Control Experiments



6.99 (d, J = 7.3 Hz, 1H), 6.96−6.90 (m, 2H), 6.87−6.84 (m, 1H), 6.73 (d, J = 8.5 Hz, 1H), 6.71−6.67 (m, 1H), 6.63 (s, 1H), 6.47−6.44 (m, 1H), 3.47 (s, 3H), 3.21 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 167.4, 154.4, 141.9, 138.6, 137.2, 132.7, 128.3, 125.5, 123.4, 123.1, 122.9, 122.6, 121.7, 119.1, 118.6, 115.0, 112.1, 111.5, 109.5, 108.1, 107.4, 95.5, 55.5, 51.7, 26.0, 22.6; IR (KBr): 3246, 2923, 2851, 1645, 1607, 1579, 1493, 1476, 1426, 1375, 1332, 1289, 1264, 1244, 1178, 1155, 1134, 1107, 1034, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{23}N_3O_2-H)^-$ requires m/z 420.1712, found m/z 420.1714.

(*Z*)-5-Fluoro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ca). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time =12 h; yield: 96% (39.3 mg); > 95:5 Z/E; colorless solid, mp 175.1−176.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.27 (s, 1H), 11.32 (s, 1H), 7.96 (s, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.20−7.15 (m, 1H), 7.00 (d, J = 7.3 Hz, 1H), 6.95−6.86 (m, 3H), 6.81 (dd, J = 8.4, 4.8 Hz, 1H), 6.75−6.66 (m, 3H), 3.24 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 168.5, 157.7 (d, J = 240.3 Hz), 141.8, 138.7, 137.2, 134.8, 128.3, 125.4, 123.7, 123.5 (d, J = 10.2 Hz), 122.9, 121.8, 119.2, 118.5, 114.4, 112.2, 111.9, 109.2 (d, J = 23.8 Hz), 108.4 (d, J = 23.3 Hz), 108.2 (d, J = 5.2 Hz), 94.8 (d, J = 2.7 Hz), 51.9, 26.1, 22.5; IR (KBr): 3214, 2921, 2850, 1647, 1608, 1577, 1487, 1476, 1427, 1358, 1335, 1283, 1258, 1177, 1154, 1105, 871, 742 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}FN_3O-H)^-$ requires m/z 408.1512, found m/z 408.1513.

(*Z*)-5-Chloro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3da). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time =12 h; yield: 83% (35.4 mg); > 95:5 Z/E; colorless solid, mp 146.7−147.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.26 (s, 1H), 11.36 (s, 1H), 7.93 (s, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.20−7.16 (m, 1H), 7.01−6.98 (m, 1H), 6.97−6.93 (m, 2H), 6.92−6.90 (m, 1H), 6.89−6.86 (m, 2H), 6.85−6.83 (m, 1H), 6.72−6.66 (m, 1H), 3.24 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 168.5, 141.8, 138.7, 137.2, 137.1, 128.3, 125.3, 124.8, 124.0, 123.7, 123.0, 122.9, 122.6, 121.8, 121.0, 119.2, 118.5, 114.4, 112.2, 112.0, 109.0, 94.1, 51.9, 26.1, 22.5; IR (KBr): 3215, 2923, 2852, 1648, 1607, 1578, 1477, 1459, 1431, 1365, 1334, 1281, 1255, 1166, 1137, 1105, 743 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}ClN_3O-H)^-$ requires m/z 424.1217, found m/z 424.1220.

(*Z*)-1,3′,6-Trimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ea). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time =12 h; yield: 74% (30.1 mg); > 95:5 Z/E; colorless solid, mp 173.4−174.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.15 (s, 1H), 11.34−11.22 (m, 1H), 7.92 (s, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.18−7.13 (m, 1H), 6.98 (d, J = 7.4 Hz, 1H), 6.94−6.82 (m, 4H), 6.75−6.63 (m, 3H), 3.21 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.9, 167.2, 142.0, 138.7, 137.2, 136.5, 129.1, 128.2, 125.6, 123.9, 123.8, 122.9, 122.6, 122.5, 122.4, 121.6, 119.0, 118.6, 114.8, 112.1, 111.4, 107.5, 95.1, 51.6, 26.0, 22.5, 21.5; IR (KBr): 3220, 2920, 1643, 1577, 1478, 1425, 1374, 1352, 1333, 1261, 1181, 1150, 1108, 754, 742 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{23}N_3O-H)^-$ requires m/z 404.1763, found m/z 404.1768.

(*Z*)-6-Chloro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3fa). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 64% (27.3 mg); > 95:5 Z/E; colorless solid, mp 149.3−150.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.19 (s, 1H), 11.27−11.21 (m, 1H), 7.89 (s, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.19−7.15 (m, 1H), 7.03−6.99 (m, 1H), 6.98−6.91 (m, 3H), 6.91−6.88 (m, 1H), 6.88−6.84 (m, 1H), 6.69 (s, 1H), 6.62 (dd, J = 8.3, 2.0 Hz, 1H), 3.25 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 168.0, 141.8, 139.6, 138.7, 137.2, 128.3, 127.8, 125.4, 123.8, 122.9, 122.3, 121.7, 121.2, 120.1, 119.1, 118.5, 114.3, 112.2, 111.9, 108.2, 94.1, 51.9, 26.1, 22.4; IR (KBr): 3216, 2920, 2850, 1648,1567, 1488, 1477, 1428, 1375, 1337, 1286, 1249, 1168, 1107, 1083, 943, 811, 745 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}ClN_3O-H)^-$ requires m/z 424.1217, found m/z 424.1209.

(*Z*)-6-Bromo-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ga). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 70% (32.9 mg); > 95:5 Z/E; colorless solid, mp 195.3−196.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.20 (s, 1H), 11.27−11.21 (m, 1H), 7.88 (s, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.19−7.14 (m, 1H), 7.08 (d, J = 1.8 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 6.94−6.88 (m, 3H), 6.88−6.85 (m, 1H), 6.76−6.73 (m, 1H), 6.70−6.66 (m, 1H), 3.25 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 168.2, 141.8, 139.8, 138.7, 137.2, 128.3, 125.4, 123.8, 122.9, 122.7, 121.7, 121.6, 119.1, 118.5, 115.8, 114.2, 112.2, 111.9, 110.9, 94.1, 51.9, 26.1, 22.3; IR (KBr): 3214, 2922, 2851, 1652, 1564, 1477, 1430, 1374, 1337, 1284, 1254, 1168, 1147, 1106, 939, 808, 745 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}BrN_3O-H)^-$ requires m/z 468.0711, found m/z 468.0720.

(*Z*)-1,3′,7-Trimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ha). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 73% (29.7 mg); > 95:5 Z/E; colorless solid, mp 151.5−152.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.36 (s, 1H), 11.22−11.19 (m, 1H), 7.87 (s, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.18−7.13 (m, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.96−6.89 (m, 3H), 6.87−6.83 (m, 1H), 6.71−6.67 (m, 1H), 6.60 (d, J = 7.5 Hz, 1H), 6.49−6.44 (m, 1H), 3.55 (s, 3H), 2.47 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.2, 167.2, 141.8, 138.8, 137.2, 136.4, 128.2, 127.0, 125.5, 123.5, 122.9, 122.5, 121.6, 120.5, 119.7, 119.1, 119.0, 118.7, 114.8, 112.1, 111.4, 95.0, 51.7, 29.1, 22.2, 19.4; IR (KBr): 3221, 2922, 2850, 1637, 1610, 1571, 1476, 1458, 1443, 1370, 1329, 1245, 1163, 1146, 1114, 1101, 1080, 740 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{23}N_3O-H)^-$ requires m/z 404.1763, found m/z 404.1766.

(*Z*)-7-Fluoro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ia). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 62% (25.4 mg); > 95:5 Z/E; colorless solid, mp 162.3−163.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.36 (s, 1H), 11.25 (d, J = 2.6 Hz, 1H), 7.91 (s, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.22−7.16 (m, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.99−6.83 (m, 4H), 6.76−6.67 (m, 2H), 6.62−6.53 (m, 1H), 3.46 (d, J = 2.9 Hz, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 168.4, 147.7 (d, J = 237.0 Hz), 141.6, 138.9, 137.2, 128.3, 125.7 (d, J = 5.1 Hz), 125.4, 124.7 (d, J = 8.5 Hz), 123.8, 123.0, 122.9, 121.7, 120.8 (d, J = 7.0 Hz), 119.2, 118.5, 117.7 (d, J = 2.5 Hz), 114.3, 112.2, 112.0, 110.6, 110.4, 94.5, 94.5, 52.0, 28.4 (d, J = 5.7 Hz), 22.2; IR (KBr): 2924, 2851, 1647, 1629, 1611, 1590, 1571, 1475, 1459, 1375, 1235, 1100, 742 cm^{-1}; ESI

DOI: 10.1021/acs.joc.6b02201
J. Org. Chem. 2016, 81, 11734−11742

FTMS exact mass calcd for $(C_{26}H_{20}FN_3O-H)^-$ requires m/z 408.1512, found m/z 408.1519.

(*Z*)-7-Chloro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ja). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 62% (26.4 mg); > 95:5 Z/E; colorless solid, mp 181.5−183.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.42 (s, 1H), 11.30−11.21 (m, 1H), 7.89 (s, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.20−7.16 (m, 1H), 7.06−6.99 (m, 2H), 6.97−6.85 (m, 3H), 6.85−6.82 (m, 1H), 6.69 (s, 1H), 6.59−6.54 (m, 1H), 3.62 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 141.5, 138.9, 137.2, 133.6, 128.3, 125.6, 125.3, 124.8, 123.7, 123.1, 122.9, 121.7, 121.5, 120.2, 119.2, 118.5, 114.2, 112.2, 112.0, 94.0, 52.1, 29.2, 22.1; IR (KBr): 3246, 2925, 1638, 1611, 1585, 1561, 1475, 1459, 1332, 1236, 1167, 1135, 1115, 743, 731 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}ClN_3O-H)^-$ requires m/z 424.1217, found m/z 424.1222.

(*Z*)-7-Bromo-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ka). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 61% (28.7 mg); > 95:5 *Z*/*E*; colorless solid, mp 193.0−194.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 11.28−11.23 (m, 1H), 7.90 (s, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.20−7.16 (m, 1H), 7.07 (d, J = 7.7 Hz, 1H), 7.03−6.98 (m, 2H), 6.96−6.86 (m, 3H), 6.72−6.67 (m, 1H), 6.52−6.48 (m, 1H), 3.63 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.0, 168.7, 141.5, 139.0, 137.2, 134.9, 128.3, 128.2, 125.9, 125.3, 123.7, 123.1, 122.9, 122.0, 121.7, 120.6, 119.2, 118.5, 114.2, 112.2, 112.1, 101.6, 93.9, 52.1, 29.5, 22.1; IR (KBr): 3256, 2919, 2849, 1638, 1611, 1581, 1559, 1477, 1459, 1330, 1234, 1167, 1146, 1129, 1112, 1050, 744, 728 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}BrN_3O-H)^-$ requires m/z 468.0711, found m/z 468.0715.

(*Z*)-1,3′,5″-Trimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3la). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 81% (32.9 mg); > 95:5 *Z*/*E*; colorless solid, mp 164.1−165.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.20 (s, 1H), 11.13−11.05 (m, 1H), 7.81 (s, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.20−7.14 (m, 2H), 7.05−6.97 (m, 2H), 6.91−6.83 (m, 3H), 6.82−6.68 (m, 2H), 6.64−6.59 (m, 1H), 3.25 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 167.5, 141.9, 138.8, 138.5, 135.6, 128.2, 127.3, 125.7, 123.7, 123.4, 123.3, 122.9, 122.6, 122.4, 121.6, 120.7, 118.3, 114.1, 111.9, 111.5, 108.0, 94.8, 51.7, 26.0, 22.5, 21.9; IR (KBr): 3231, 2925, 1647, 1606, 1589, 1575, 1543, 1476, 1375, 1347, 1257, 1167, 1107, 745 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{23}N_3O-H)^-$ requires m/z 404.1763, found m/z 404.1769.

(*Z*)-5″-Methoxy-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ma). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 84% (35.5 mg); > 95:5 *Z*/*E*; colorless solid, mp 172.2−173.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.22 (s, 1H), 11.10−11.02 (m, 1H), 7.86 (s, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.21−7.14 (m, 2H), 7.07 (d, J = 7.7 Hz, 1H), 7.00 (d, J = 7.3 Hz, 1H), 6.92−6.84 (m, 3H), 6.66−6.59 (m, 2H), 6.39 (s, 1H), 3.47 (s, 3H), 3.25 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 167.3, 153.0, 142.0, 138.5, 132.5, 128.3, 125.9, 124.4, 123.4, 122.9, 122.6, 122.4, 121.6, 120.7, 114.1, 112.6, 111.4, 110.5, 108.0, 101.6, 95.0, 55.4, 51.7, 26.0, 22.1; IR (KBr): 3221, 2929, 1643, 1587, 1570, 1480, 1467, 1428, 1374, 1346, 1320, 1260, 1210, 1168, 1099, 1033, 745 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{23}N_3O_2-H)^-$ requires m/z 420.1712, found m/z 420.1715.

(*Z*)-5″-Chloro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3na). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 63% (26.9 mg); > 95:5 *Z*/*E*; colorless solid, mp 162.4−163.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.19 (s, 1H), 11.51−11.44 (m, 1H), 8.02 (s, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.20−7.16 (m, 1H), 6.99 (d, J = 7.5 Hz, 2H), 6.95−6.83 (m, 5H), 6.65−6.60 (m, 1H), 3.26 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 166.7, 141.9, 138.6, 138.3, 135.7, 128.5, 126.4, 125.7, 123.6, 122.9, 122.7, 122.2, 121.7, 121.4, 120.8, 117.5, 114.6, 113.8, 111.7, 108.1, 95.0, 51.5, 26.0, 22.3; IR (KBr): 3217, 2923, 1644, 1575, 1469, 1427, 1378, 1346, 1317, 1282, 1259, 1169, 1105, 807, 746, 733, 685 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}ClN_3O-H)^-$ requires m/z 424.1217, found m/z 424.1218.

(*Z*)-6″-Chloro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3oa). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 59% (25.2 mg); > 95:5 *Z*/*E*; colorless solid, mp 178.4−179.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.18 (s, 1H), 11.42−11.34 (m, 1H), 7.96 (s, 1H), 7.40 (d, J = 7.7 Hz, 1H), 7.33 (d, J = 1.8 Hz, 1H), 7.19−7.15 (m, 1H), 7.02−6.95 (m, 2H), 6.93−6.83 (m, 4H), 6.76−6.71 (m, 1H), 6.64−6.59 (m, 1H), 3.25 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 166.9, 141.9, 138.6, 138.4, 137.6, 128.4, 126.5, 125.0, 124.2, 123.6, 122.9, 122.6, 122.2, 121.3, 120.7, 119.8, 119.5, 115.1, 111.7, 111.6, 108.0, 95.0, 51.5, 26.0, 22.4; IR (KBr): 3211, 2921, 1646, 1587, 1471, 1458, 1374, 1350, 1333, 1320, 1257, 1168, 1114, 1099, 738, 689 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}ClN_3O-H)^-$ requires m/z 424.1217, found m/z 424.1212.

(*Z*)-6″-Bromo-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3pa). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 52% (24.5 mg); > 95:5 *Z*/*E*; colorless solid, mp 170.5−171.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.18 (s, 1H), 11.44−11.35 (m, 1H), 7.95 (s, 1H), 7.49 (s, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.19−7.15 (m, 1H), 7.03−6.95 (m, 2H), 6.93−6.82 (m, 5H), 6.64−6.59 (m, 1H), 3.26 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 166.9, 141.9, 138.6, 138.4, 138.1, 128.4, 124.9, 124.5, 123.6, 122.9, 122.6, 122.2, 122.1, 121.3, 120.7, 120.2, 115.1, 114.7, 114.6, 111.6, 108.1, 95.0, 51.5, 26.0, 22.4; IR (KBr): 3170, 2921, 2850, 1644, 1589, 1577, 1535, 1469, 1429, 1376, 1346, 1319, 1257, 1168, 1142, 1101, 745 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}BrN_3O-H)^-$ requires m/z 468.0711, found m/z 468.0716.

(*Z*)-1,3′,7″-Trimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3qa). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 86% (35.0 mg); > 95:5 *Z*/*E*; colorless solid, mp 185.2−186.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.20 (s, 1H), 11.21−11.14 (m, 1H), 7.89 (s, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.17−7.13 (m, 1H), 7.09 (d, J = 7.7 Hz, 1H), 6.98 (d, J = 7.3 Hz, 1H), 6.89−6.82 (m, 3H), 6.80−6.74 (m, 1H), 6.71 (d, J = 7.0 Hz, 1H), 6.65−6.57 (m, 2H), 3.25 (s, 3H), 2.39 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 167.6, 141.9, 138.8, 138.5, 136.7, 128.2, 125.2, 123.4, 122.9, 122.5, 122.4, 122.1, 121.6, 121.2, 120.7, 119.3, 116.3, 115.1, 111.5, 108.0, 94.9, 51.8, 26.0, 22.3, 17.2; IR (KBr): 3220, 2926, 1644, 1469, 1429, 1375, 1347, 1320, 1256, 1168, 1140, 1103, 782, 746, 672 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{23}N_3O-H)^-$ requires m/z 404.1763, found m/z 404.1769.

(*Z*)-4′-Fluoro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ab). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 60% (24.6 mg); > 95:5 *Z*/*E*; colorless solid, mp 175.6−176.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.25 (s, 1H), 11.25, 7.99−7.87 (m, 1H), 7.32−7.27 (m, 2H), 7.25−7.18 (m, 1H), 7.09 (d, J = 7.7 Hz, 1H), 6.95−6.84 (m, 4H), 6.73−6.58 (m, 3H), 3.24 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 166.6, 158.3 (d, J = 245.0 Hz), 144.7 (d, J = 8.3 Hz), 138.8, 137.0, 130.8 (d, J = 8.5 Hz), 125.5, 124.6, 123.9, 123.4 (d, J = 16.3 Hz), 122.0, 121.9, 121.5, 120.8, 119.2, 118.3, 112.5, 112.2, 109.9 (d, J = 10.2 Hz), 108.1, 95.4, 50.9, 26.0, 20.0; IR (KBr): 3210, 2921, 2851, 1644, 1489, 1467, 1431, 1377, 1332, 1265, 1176, 1100, 1034, 780, 745, 734 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}FN_3O-H)^-$ requires m/z 408.1512, found m/z 408.1517.

(*Z*)-1,3′,6′-Trimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ac). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 75% (30.5 mg); > 95:5 *Z*/*E*; colorless solid, mp 157.9−158.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.15 (s, 1H), 11.20 (s, 1H), 7.87 (s, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.20 (s, 1H), 7.05−7.01 (m, 1H), 6.95−6.83 (m, 5H), 6.71−6.65 (m, 2H), 6.61 (s, 1H), 3.25 (s, 3H), 2.25 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 167.9, 142.1, 138.5, 137.7, 137.2, 136.0, 125.5, 123.6, 123.4, 123.2, 122.6, 122.4, 121.6, 121.5, 120.7, 119.0, 118.7, 114.9, 112.1, 112.0, 108.0, 94.9, 51.4, 25.9,

DOI: 10.1021/acs.joc.6b02201
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22.4, 21.6; IR (KBr): 3180, 2920, 1643, 1575, 1486, 1467, 1458, 1427, 1389, 1336, 1318, 1259, 1151, 1136, 1100, 746, 732 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{23}N_3O-H)^-$ requires m/z 404.1763, found m/z 404.1770.

(*Z*)-6′-Chloro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ad). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 75% (32.0 mg); > 95:5 *Z*/*E*; colorless solid, mp 170.1−171.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.17 (s, 1H), 11.30−11.20 (m, 1H), 7.89 (s, 1H), 7.51 (d, J = 1.8 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.98−6.83 (m, 6H), 6.75−6.68 (m, 1H), 6.65−6.58 (m, 1H), 3.24 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 166.8, 143.6, 138.9, 137.6, 137.2, 132.5, 125.4, 124.2, 123.9, 123.8, 122.1, 122.0, 121.8, 121.7, 120.8, 119.2, 118.5, 114.3, 112.2, 111.7, 108.1, 96.0, 51.2, 26.0, 22.2; IR (KBr): 3180, 2918, 1644, 1475, 1427, 1387, 1333, 1315, 1264, 1247, 1168, 1101, 1069, 732, 747, cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}ClN_3O-H)^-$ requires m/z 424.1217, found m/z 424.1221.

(*Z*)-1,3′,7′-Trimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3ae). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 63% (25.6 mg); > 95:5 *Z*/*E*; colorless solid, mp 165.3−166.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.33 (s, 1H), 11.28−11.17 (m, 1H), 7.90 (s, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.06−6.99 (m, 2H), 6.95−6.84 (m, 5H), 6.83−6.78 (m, 1H), 6.71−6.61 (m, 2H), 3.27 (s, 3H), 2.43 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.3, 167.9, 140.1, 138.4, 138.3, 137.2, 129.5, 125.5, 123.8, 123.5, 122.9, 122.2, 121.6, 121.4, 120.9, 120.7, 119.4, 119.2, 118.7, 114.4, 112.1, 108.2, 95.0, 52.0, 26.0, 22.5, 16.4; IR (KBr): 3211, 2922, 1644, 1620, 1608, 1572, 1487, 1459, 1428, 1373, 1346, 1261, 1165, 1100, 747, 734 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{23}N_3O-H)^-$ requires m/z 404.1763, found m/z 404.1767.

(*Z*)-7′-Chloro-1,3′-dimethyl-1′,3′-dihydro-1″*H*-[3,2′:3′,3″-terindol]-2(1*H*)-one (3af). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 12 h; yield: 56% (23.9 mg); > 95:5 *Z*/*E*; colorless solid, mp 96.4−97.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.18−11.02 (m, 1H), 10.25 (s, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.40−7.36 (m, 3H), 7.21−7.15 (m, 2H), 7.12−7.02 (m, 3H), 6.99−6.94 (m, 1H), 6.84−6.78 (m, 1H), 6.74 (d, J = 2.6 Hz, 1H), 3.21 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.7, 143.4, 137.5, 134.3, 132.2, 132.1, 131.6, 129.0, 126.4, 125.3, 124.6, 122.9, 121.7, 121.5, 121.3, 119.9, 119.0, 117.5, 115.6, 113.4, 112.1, 109.4, 108.7, 53.5, 26.9, 9.3; IR (KBr): 3447, 3312, 2920, 2851, 1702, 1609, 1469, 1458, 1348, 1370, 744, 669 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{20}ClN_3O-H)^-$ requires m/z 424.1217, found m/z 424.1222.

1′,3-Dimethyl-1H,1″H-[2,3′:3′,3″-terindol]-2′(1′H)-one (4aa).[19] Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; yellowish solid, mp 266.1−267.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.13 (s, 1H), 7.55−7.43 (m, 2H), 7.37 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 8.8 Hz, 1H), 7.19−7.06 (m, 5H), 7.02−6.93 (m, 2H), 6.81 (d, J = 2.0 Hz, 1H), 3.31 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ176.4, 143.1, 137.2, 134.8, 132.2, 131.1, 130.1, 128.7, 125.9, 125.5, 124.2, 123.2, 122.7, 121.8, 121.7, 120.3, 119.2, 118.6, 114.0, 111.6, 111.0, 108.6, 53.5, 26.8, 9.0; ESI FTMS exact mass calcd for $(C_{26}H_{21}N_3O-H)^-$ requires m/z 390.1601, found m/z 390.1596.

Ethyl 2-(3,4-Dichlorophenyl)-2-(1H-indol-3-yl)-2-(3-methyl-1H-indol-2-yl)acetate (4ra). Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; yellowish solid, mp 76.2−77.9 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.13 (s, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 2.2 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.24−7.17 (m, 3H), 7.16−7.11 (m, 3H), 7.01 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 2.6 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.82 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 141.0, 136.9, 134.3, 132.3, 132.0, 131.4, 131.3, 129.8, 129.7, 128.9, 126.0, 125.3, 122.6, 122.1, 120.9, 120.2, 119.3, 118.6, 115.9, 111.6, 111.1, 110.0, 62.6, 56.8, 14.1, 9.7; IR (KBr): 3680, 3401, 2924, 1719, 1547, 1462, 1421, 1376, 1333, 817, 744, 671 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{22}Cl_2N_2O_2-H)^-$ requires m/z 475.0980, found m/z 475.0976.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02201.

Characterization data (including ^{1}H and ^{13}C NMR spectra) of products **3**, **4aa**, and **4ra** (PDF)

X-ray crystallographic data of product **3aa** (CIF)

X-ray crystallographic data of product **4aa** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from National Natural Science Foundation of China (21372002 and 21232007), PAPD, TAPP, and Natural Science Foundation of Jiangsu Province (BK20160003).

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DOI: 10.1021/acs.joc.6b02201
J. Org. Chem. 2016, 81, 11734−11742