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3-Alkenylation or 3-Alkylation of Indole with Propargylic Alcohols: Construction of 3,4-Dihydrocyclopenta[*b*]indole and 1,4-Dihydrocyclopenta[*b*]indole in the Presence of Different Catalysts

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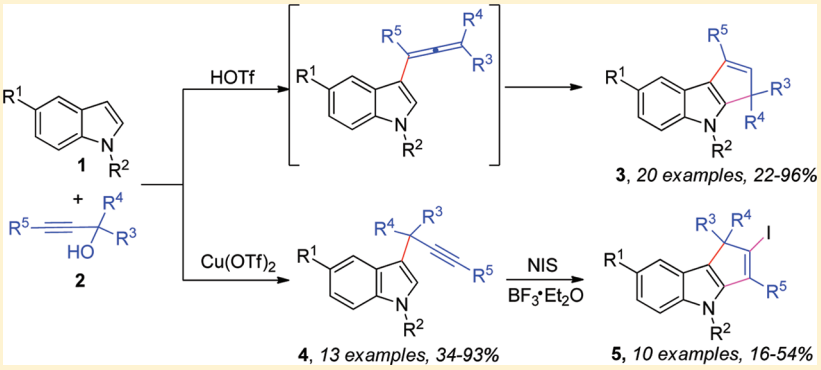
Supporting Information



ABSTRACT: 3-Alkenylation or 3-alkylation of indole with propargylic alcohols could be efficiently controlled by the catalyst. In the presence of triflic acid, 3-alkenylation of indole occurred and a 3,4-dihydrocyclopenta[*b*]indole skeleton was effectively constructed in moderate to excellent yields via a cascade process. In the presence of $Cu(OTf)_2$, 3-alkylation of indole resulted in the formation of 3-propargylic indole, which could be further converted into 2-iodo-1,4-dihydrocyclopenta[*b*]indoles in the presence of *N*-iodosuccinimide and boron trifluoride etherate. Possible mechanisms related to the 3-alkenylation or 3-alkylation of indole and their extension to the formation of 3,4-dihydrocyclopenta[*b*]indoles or 1,4-dihydrocyclopenta[*b*]indoles are postulated and discussed.

INTRODUCTION

3,4-Dihydrocyclopenta[*b*]indole and 1,4-dihydrocyclopenta[*b*]-indole are key substructures and can be extended to, respectively, indeno[2,1-*b*]indole skeleton and indeno[1,2-*b*]indole via Diels–Alder cycloaddition reaction (Scheme 1). Indeno[2,1-*b*]indole is of particularly importance as it was mapped in a route to cyanobacterial alkaloid (Fischerindole I), while indeno[1,2-*b*]indole was mapped into KSP inhibitor (Terpendole E).[1,2]

Total synthesis of Fischerindole I as well as Terpendole E is attractive because they display a broad range of bioactivities and is also challenging due to its structural complexity and the dense functionalities.[3] Baran et al.[4−6] and Gademann et al.[7] had successfully done the pioneer work in synthesizing these bioactive compounds with a spectacular protecting-group-free strategy. In the literature, the **C** ring is normally constructed by Friedel–Crafts alkylation on the 2-position of indole,[8] by Pd-catalyzed carbopalladation–annulation of indole,[9] by biradical cyclization of allenyl azide,[10,11] and by photostimulated reaction of 2-iodoaniline with the enolate anion of 2-indanone.[12] Rhodium-catalyzed[13] or silver-catalyzed[14] 3-alkylation of indole followed by sequential cyclization could also fuse the **C** ring efficiently.

RESULTS AND DISCUSSION

As a part of our ongoing research of the chemistry of propargylic alcohol under acid condition,[15−18] we tried the reaction between *N*-methylindole (**1a**) and propargylic alcohol (**2a**), which was prepared from fluorenone and phenylacetylene, in refluxing dichloromethane (DCM) for 12 h in the presence of triflic acid (TfOH) (Scheme 2). As we expected, **3a** was isolated in a yield of 66%, and the structure of **3a** was established by X-ray analysis of its single crystal (Figure 1).

In order to have a better conversion, we optimized the reaction conditions, and results are summarized in Table 1. When ytterbium triflate was used as the catalyst, 3-alkylated indole (**4a**) was formed instead of the 3-alkenylated indole (**3a**). HPLC area % of **4a** was determined to be 53% (Table 1, entry 1). Two peaks at ^{13}C NMR spectrum (91.46 and 81.34 ppm) were ascribed to two sp hybridized carbons of **4a**. Copper triflate afforded **4a** in 63% HPLC area. No desired product (**3a**) was observed (Table 1, entry 2). When silver triflate was used, **3a** could be detected except for the formation of **4a** (Table 1,

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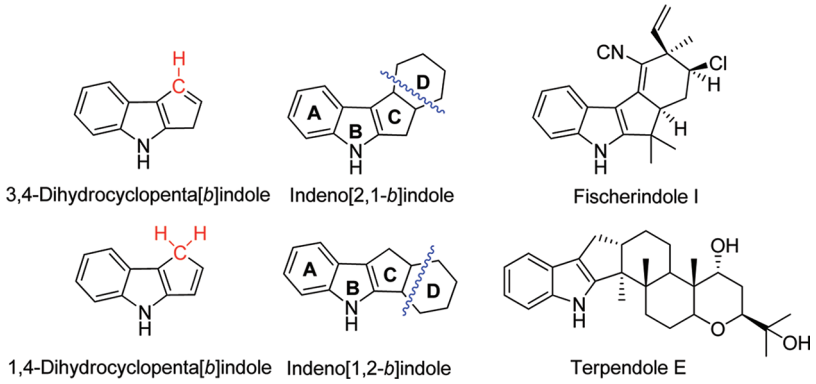
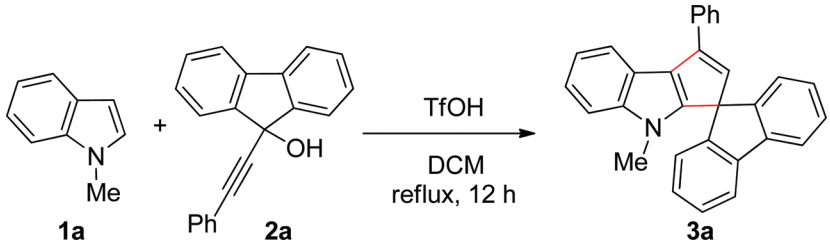
Scheme 1. Structures of 3,4-Dihydrocyclopenta[*b*]indole and 1,4-Dihydrocyclopenta[*b*]indole



Scheme 2. Formation of Cyclopenta[*b*]indoles from Propargylic Alcohols and Indoles



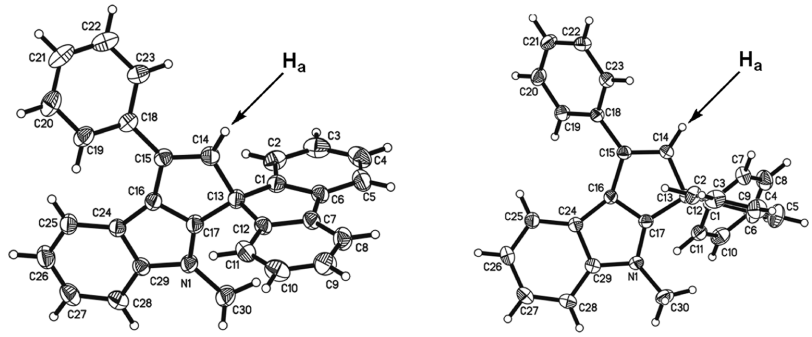


Figure 1. Crystal structures of **3a** (left) and **3c** (right).

entry 3). To our delight, when the catalyst was changed into $FeCl_3$, $AlCl_3$, $SnCl_4$, $BF_3{\cdot}Et_2O$, and TfOH, the peak area of **3a** was significantly increased (Table 1, entries 4–8). By increasing the reaction temperature to 83 °C by using dichloroethane (DCE) as the solvent, the HPLC area % of **3a** approached 91% (Table 1, entry 9). When other halogenated alkanes such as chloroform and carbon tetrachloride were used as solvent, the reaction lost its selectivity (Table 1, entries 10 and 11). The reaction could also be conducted in acetonitrile, but with relatively lower HPLC area % (Table 1, entry 12).

With the optimized reaction condition in hand (Table 1, entry 9), we test the substrate diversity for the selective formation of **3**. When we altered **1a** to *N*-methyl-5-nitroindole (**1b**), **3b** was quantitatively prepared (Table 2, entry 2). When **2b**, a benzophenone derived propargylic alcohol, reacted with the substituted indoles (**1a**–**1f**), corresponding products (**3c**–**3h**) were obtained in yields between 22% and 86% (Table 2, entries 3–8). Here it is noteworthy that indoles with electron-withdrawing groups attached at the 5 position benefitted the reaction and gave satisfactorily isolated yields (Table 1, entries 4, 7, and 8). As a comparison, methyl substituted indole (**1c**) afforded corresponding **3e** in 28% yield only. In this case, a direct 3-alkylated indole (**4b**) was formed and isolated in 9% yield. When we modified the phenylacetylene part of the propargylic alcohol, the best yield was seen for **2e** among cases of **2c**, **2d**, and **2e** (Table 2, entries 9–11). In this case, R^5 of **2e** is the *p*-fluorophenyl, with the nature of an electron-withdrawing group. Acetophenone derived alcohol (**2f**) did react with **1a**, but too many products were indicated by TLC (Table 2, entry 12) and the desired product could not be isolated. However, the reaction between **2f** and **1b** afforded **3l** in yield of 96% (Table 2, entry 13). Benzaldehyde derived alcohol (**2g**) gave the 3-alkylated indole (**4c**) in yield of 61%, while the 3-alkenylated indole derivative was not detected (Table 2, entry 14). Acetone derived alcohol (**2h**) reacted with **1b** or **1e** smoothly and produced **3m** and **3n** in yields of 56% and 57%, respectively (Table 2, entries 16 and 17). However, too many spots were observed by TLC when **2h** reacted with **1a** or **1f** (Table 2, entries 15 and 18). Yield was improved when **1b** reacted with pentafluorosubstituted propargylic alcohol (**2i**) (Table 2, entry 19). Reactions between **1b** and **2j**, **1b** and **2k**, and **1b** and **2l** afforded the corresponding cyclized products **3p**, **3q**, and **3r**, respectively (Table 2, entries 20–22). Reaction of **1b** with *n*-heptyne derived alcohol (**2m**) gave **3s** in a yield of

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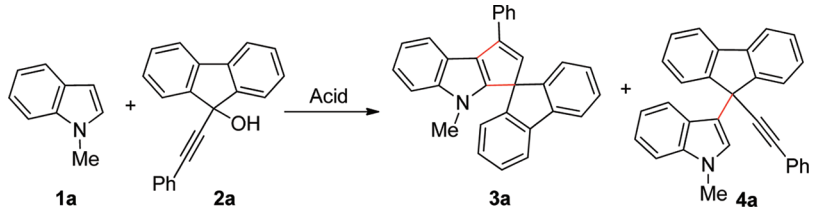
Table 1. Optimization of Reaction Conditions[a]

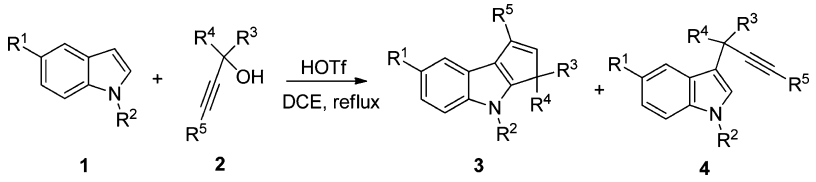


1a 2a 3a 4a

entry	acid	solvent	3a[b]	4a[c]
1	$Yb(OTf)_3$ (20 mol %)	CH_2Cl_2	2	53
2	$Cu(OTf)_2$ (20 mol %)	CH_2Cl_2	0	63
3	AgOTf (20 mol %)	CH_2Cl_2	3	39
4	$FeCl_3$	CH_2Cl_2	59	4
5	$AlCl_3$	CH_2Cl_2	82	0
6	$SnCl_4$	CH_2Cl_2	63	3
7	$BF_3{\cdot}Et_2O$	CH_2Cl_2	85	2
8	TfOH	CH_2Cl_2	83	0
9	TfOH	$ClCH_2CH_2Cl$	91	4
10	TfOH	$CHCl_3$	47	42
11	TfOH	CCl_4	21	55
12	TfOH	CH_3CN	59	0

[a] **1a** (0.25 mmol), **2a** (0.25 mmol), acid (0.25 mmol, otherwise indicated in parentheses), and 3 mL of solvent were mixed at room temperature and refluxed for 12 h. [b] HPLC peak area percentage of **3a**. C18 column was used for HPLC analysis. [c] HPLC peak area percentage of **4a**.

Table 2. Synthesis of Various 3-Alkenylated Indoles (3)[a]



1 2 3 4

entry	1 (R^1, R^2)	2 ($R^3/R^4/R^5$)	3 (%)[b] + 4 (%)[b]
1	**1a** (H, Me)	**2a**	**3a** (74)
2	**1b** (NO_2, Me)	**2a**	**3b** (93)
3	**1a**	**2b** (Ph/Ph/Ph)	**3c** (58)
4	**1b**	**2b**	**3d** (86)
5	**1c** (Me, Me)	**2b**	**3e** (28) + **4b** (9)
6	**1d** (OMe, Me)	**2b**	**3f** (22)
7	**1e** (CN, Me)	**2b**	**3g** (79)
8	**1f** (Br, Me)	**2b**	**3h** (74)
9	**1a**	**2c** (Ph/Ph/*p*-Me-Ph)	**3i** (52)
10	**1a**	**2d** (Ph/Ph/*p*-OMe-Ph)	**3j** (49)
11	**1a**	**2e** (Ph/Ph/*p*-F-Ph)	**3k** (75)
12	**1a**	**2f** (Ph/Me/Ph)	*c*
13	**1b**	**2f**	**3l** (96)
14	**1b**	**2g** (Ph/H/Ph)	**4c** (61)
15	**1a**	**2h** (Me/Me/Ph)	*c*
16	**1b**	**2h**	**3m** (56)
17	**1e**	**2h**	**3n** (57)
18	**1f**	**2h**	*c*
19	**1b**	**2i** ($Me/Me/C_6F_5$)	**3o** (74)
20	**1b**	**2j** (Me/Et/Ph)	**3p** (38)
21	**1b**	**2k** ($-(CH_2)_4-$/Ph)	**3q** (47)
22	**1b**	**2l** ($-(CH_2)_5-$/Ph)	**3r** (61)
23	**1b**	**2m** (Ph/Ph/*n*-C_5H_{11})	**3s** (41)
24	**1g** (H, H)	**2b**	*c*
25	**1h** (H, Ts)	**2b**	*c*
26	**1i** (H, $PO(OEt)_2$)	**2b**	*c*

[a] **1** (0.5 mmol), **2** (0.5 mmol), TfOH (0.5 mmol), and 5 mL of DCE were mixed at room temperature and refluxed for 12 h. [b] Isolated yield. [c] No isolable products.

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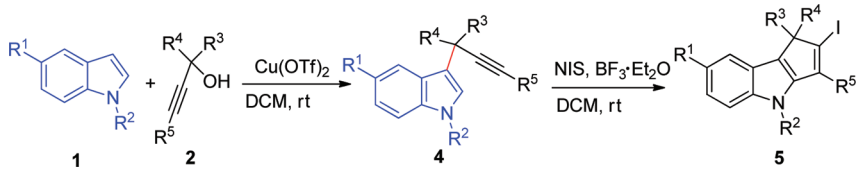
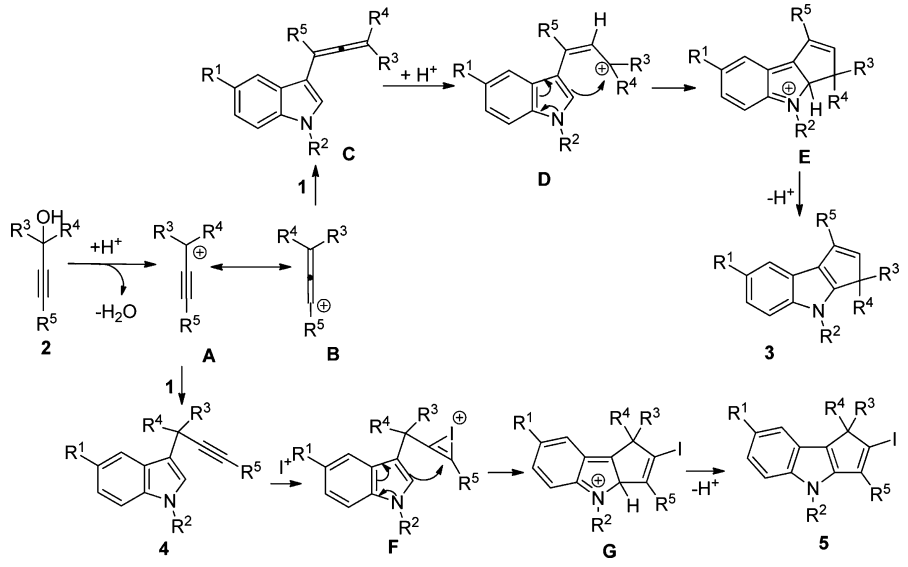
Table 3. Synthesis of 3-Alkylated Indoles (4)[a] and 2-Iodo-1,4-dihydrocyclopenta[*b*]indoles (5)[b]



entry	1 (R^1, R^2)	2 (R^3/R^4/R^5)	4 (%)[c]	5 (%)[c]
1	**1a** (H, Me)	**2a**	**4a** (68)	**5a** (46)
2	**1b** (NO_2, Me)	**2a**	**4d**[d] (84)	**5b** (31)
3	**1c** (Me, Me)	**2a**	**4e** (73)	**5c** (54)
4	**1d** (OMe, Me)	**2a**	**4f** (58)	**5d** (38)
5	**1e** (CN, Me)	**2a**	**4g** (93)	**5e** (36)
6	**1f** (Br, Me)	**2a**	**4h**[d] (86)	**5f** (43)
7	**1a**	**2b** (Ph/Ph/Ph)	**4i** (65)	**5g** (26)
8	**1a**	**2c** (Ph/Ph/*p*-Me-Ph)	**4j** (60)	**5h** (45)
9	**1a**	**2d** (Ph/Ph/ *p*-OMe-Ph)	*e*	
10	**1a**	**2e** (Ph/Ph/ *p*-F-Ph)	**4k** (34)	**5i** (39)
11	**1a**	**2f** (Ph/Me/Ph)	**4l** (84)	*e*
12	**1b**	**2n**[f]	**4m** (37)	**5j** (16)

[a]**1** (1 mmol), **2** (1 mmol), $Cu(OTf)_2$ (0.1 mmol), and 10 mL of DCM were mixed at room temperature and reacted. [b]**4** (0.5 mmol), NIS (0.5 mmol), $BF_3{\cdot}Et_2O$ (0.5 mmol), and 10 mL of DCM were mixed at room temperature and reacted. [c]Isolated yield. [d]Refluxing needed and tracked by TLC. [e]No isolable product. [f]Structure of **2n** is shown in Scheme 8.

Scheme 3. Possible Mechanism for Formation of 3, 4, and 5



41% (Table 2, entry 23). Finally we examined the substituent on the nitrogen of indole. No unsubstitution (**1g**) or substitution by sulfonyl (**1h**) or phosphoryl (**1i**) made the reaction complicated and resulted in a mixture that could not be purified by column chromatography (Table 2, entries 24–26).

As we mentioned in Table 1, 3-alkylated indole (**4a**) could be formed and isolated in the presence of catalysts such as $Yb(OTf)_3$, $Cu(OTf)_2$, AgOTf, and TfOH as well. The most suitable catalyst for the formation of **4a** was found to be $Cu(OTf)_2$ (Table 1, entry 2). We thereby tested the substrate diversity for the formation of **4** in the presence of $Cu(OTf)_2$, and the results are summarized in Table 3. Because of the large difference of the reaction activity resulted from the various substituted groups, reaction time and reaction temperature were varied and determined by TLC tracking. Similarly, the nature of the substituted group on the 5-position of the indole played a key role in the formation of **4**. With electron-withdrawing groups such as nitro, nitrile, and bromo, **1b**, **1e**, and **1f** afforded **4d**, **4g**, and **4h** in yields of 84%, 93%, and 86%, respectively (Table 3, entries 2, 5, and 6). Those with electron-donating groups, **1c** and **1d**, produced **4e** and **4f** in relatively lower yields (Table 3, entries 3 and 4). Substitute effect on the propargylic alcohols **2** was not apparent. When **2d** was used, the desired 3-alkylated product **4** could not be isolated, although the starting materials were completely consumed after a certain period (Table 3, entry 9). Acetophenone derived propargylic alcohol **2f** provided **4l** in 84% yield (Table 3, entry 11), while the reaction between **1b** and **2n** provided **4m** in 37% yield (Table 3, entry 12). With the 3-alkylated indoles **4a**–**4m** in hand, we tried to cyclize them into 2-iodo-1,4-dihydrocyclopenta[*b*]indoles (**5**). The workable method was

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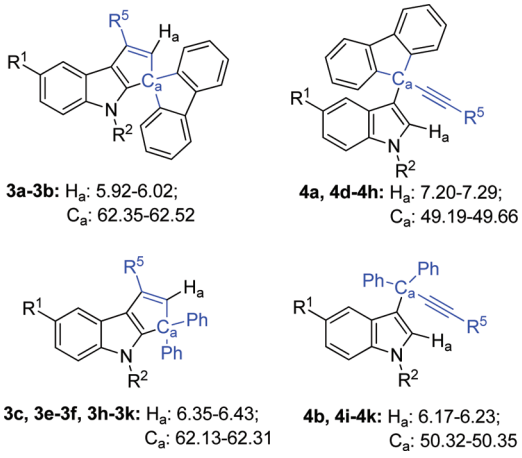
using the NIS as the electrophile in the presence of boron trifluoride etherate in DCM as solvent as shown in Table 3. In this way, **5a**−**5h** were constructed from **4a** and **4d**−**4j**, accordingly, in yields between 26% and 54%. **4l** failed to afford an isolable product (Table 3, entries 11), while **4k** and **4m** gave the corresponding **5i** and **5j** in yields of 39% and 16%, respectively (Table 3, entries 10, and12). Structure of **5j** was established by X-ray analysis of its single crystal (see Supporting Information).

On the basis of the investigation of the reaction condition and the substrate diversity, we postulated a possible mechanism for this transformation (Scheme 3). Propargylic alcohol was dehydrated under acidic condition and generated propargylic carbocation **A**, which could be directly trapped by indole (**1**) to form 3-alkylated indoles **4** in some cases. Via Meyer−Schuster rearrangement,[19,20] **A** was converted into allenylic carbocation **B**, which subsequently reacted with indole (**1**) to derive 3-allenylated indole **C**. Compound **C** undergoes protonation under the acidic conditions to form allylic carbocation **D**, which readily undergoes intramolecular cyclization to provide intermediate **E**. After deprotonation of **E**, compound **3**, with the 3,4-dihydrocyclopenta[*b*]indole skeleton, was constructed in moderate to excellent yields.

By analyzing the NMR spectra of **3** and **4** (Scheme 4), we observed the "fluorene effect". Chemical shifts of H_a in fluorene

Scheme 4. Comparative Analysis of Chemical Shifts of H_a and C_a in 3 and 4



derived **3a** and **3b** were 5.92 and 6.02 ppm, respectively. It was highly shielded by the plane of fluorene in comparison with those of analogues **3c**, **3e**−**3f**, and **3h**−**3k**, which varied from 6.35 to 6.43 ppm. The shielding effect of the fluorene could be clearly seen from the comparative images of the single crystal structures of **3a** and **3c** (Figure 1). On the other hand, chemical shifts of H_a in fluorene derived **4a** and **4d**−**4h** fell within 7.20−7.29 ppm, which was deshielded by the fluorene plane (Figure 2). In comparison, chemical shifts of H_a for **4b** and **4i**−**4k** were observed in a range of 6.17−6.23 ppm. Chemical shifts of C_a's in **3** and **4** depended upon the relative electron densities of C_a. Electron densities of **3a** and **3c** were calculated to be 0.1763 and 0.1789, while the electron densities of **4a** and **4i** were calculated to be 0.2911 and 0.2934, respectively. It is noticeable that the higher the electron density of the C_a, the lower the value of its chemical shift.

Structures of 1,3-dihydrobenzo[*cd*]indole and 1,5-dihydrobenzo[*cd*]indole could be derived into naphtho[3,2,1-*cd*]indole and naphtha[1,2,3-*cd*]indole via Diels−Alder reaction. The former compound is the key substructure of ergot analogues that are anagestic and cell-protective agents,[21−24] while the later one was the core of bioactive hapalindole G and its relatives.[25−28] Therefore, we sought to construct 1,3-dihydrobenzo[*cd*]indole and 1,5-dihydrobenzo[*cd*]indole skeletons.

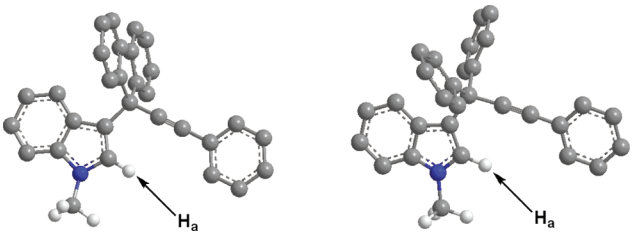
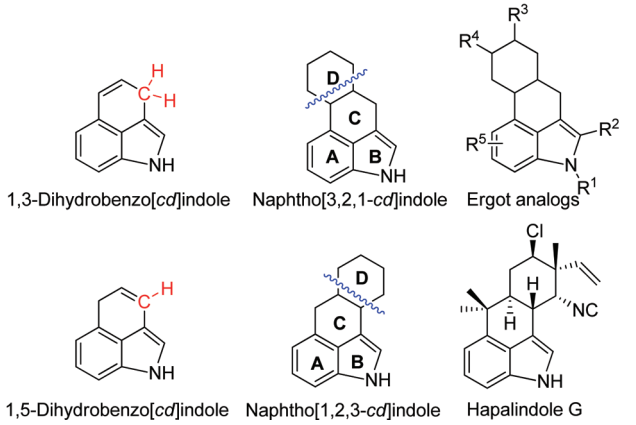


Figure 2. Optimized structures of **4a** (left) and **4i** (right), calculated with Gaussian 03 on the B3LYP Levels.

1,3-dihydrobenzo[*cd*]indole and 1,5-dihydrobenzo[*cd*]indole skeletons.



A methyl group was first used to occupy 2-position of indole, such as **1j**, to force the cyclization occurring on the C-4 of indole ring (Scheme 5) in the presence of the triflic acid. However, instead of obtaining the expected 3-alkenylated product with the 1,5-dihydrobenzo[*cd*]indole skeleton, we isolated **6** in 71% yield. Structure of **6** was established by its single crystal analysis (see Supporting Information). By postulating the possible mechanism for the formation of **6**, we found that the 3-alkenylation did occur at the beginning, and a key intermediate **J** was formed. After the subsequent protonation, **K** was formed. The problem arises because of the acidity of the allylic proton (H_a) of **K**. As a result, after the sequential deprotonation, 6π-electron electrocyclic ring closure (6π-ERC), protonation, and finally β-elimination, **6** was obtained.

Then we move our attention to other propargylic alcohols, such as **2a**, a fluorene derived propargylic alcohol. A possible depronation from **K** to **L** could be avoided. Reaction between **1j** and **2a** afforded **7a** (Scheme 6), structure of **7a** was established by the X-ray analysis of its single crystal (see Supporting Information). Meyer−Schuster rearrangement occurs, and 3-alkenylation happens on the 3-position of indole. **K′** was formed similar to the formation of **K**. However, the sequential cyclization occurred on the phenyl ring of **2a** instead of the C-4 of indole. A similar situation was observed for the reaction between **2a** and **1k**, which had the phenyl group occupied on the 2-position of indole and the methoxy group occupied on the 5-position of the indole to enrich the electron

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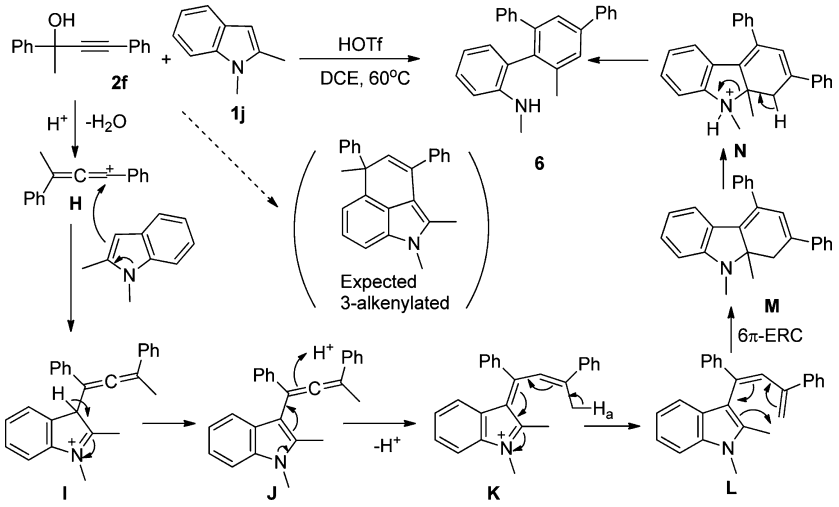
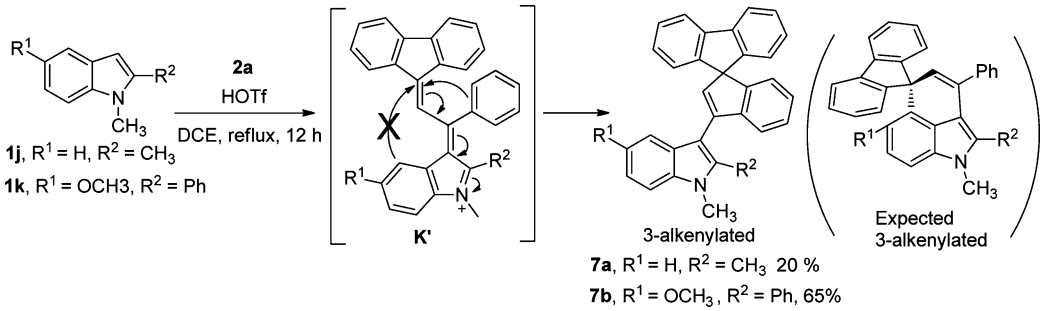
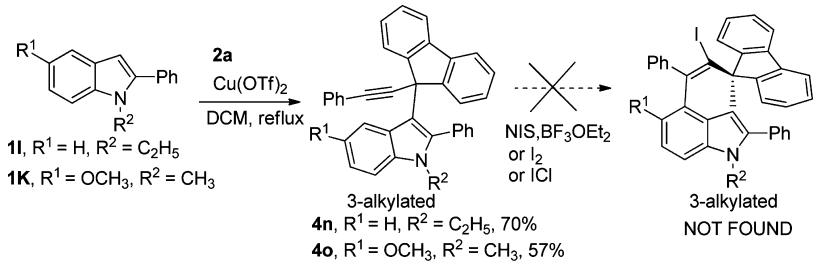
Scheme 5. Possible Mechanism for the Formation of 6



Scheme 6. Formation of 7



Scheme 7. Formation of 4n and 4o

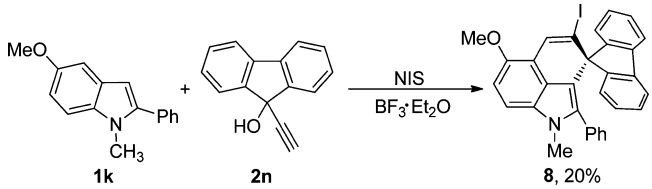


density of the indole. Still, **7b** was isolated in 65% yield. Afterward, 3-alkenylation on the 3-position of the indole ring did occur in the presence of triflic acid, but the subsequent intramolecular Friedel–Crafts alkylation on the C-4 of indole ring was not successful.

Then we tried the sequence of 3-alkylation and subsequent cyclization to construct 1,3-dihydrobenzo[*cd*]indole. In the presence of $Cu(OTf)_2$, **4n** and **4o** were isolated in yields of 70% and 57%, respectively (Scheme 7). Structure of **4n** was established by X-ray analysis of its single crystal (see Supporting Information). Unfortunately, the target molecules were not constructed from either **4n** or **4o** even though various electrophiles were tested, such as NIS, iodine, and iodine chloride.

Fortunately, when **1k** reacted with **2n**, in which the steric hindrance raised by the phenyl group was eliminated, compound **8** was constructed with the skeleton of 1,3-dihydrobenzo[*cd*]indole (Scheme 8). Structure of **8** was established by X-ray analysis of its single crystal (see Supporting Information). Enlightened by this result, we tested the reactions between **2n** and **1j** or **1l**, which resulted in complete consumption of the starting materials, but none of the desired product was isolated.

Scheme 8. Formation of 8



Larger scale reactions were carried between **1b** (880 mg, 5 mmol) and **2a** (1.41 g, 5 mmol) (Scheme 9). Thus, **3b** (1.9 g, 86%) was obtained in 1 h at room temperature in the presence of equivalent TfOH, while **4d** (1.4 g, 63%) was obtained in 3 h

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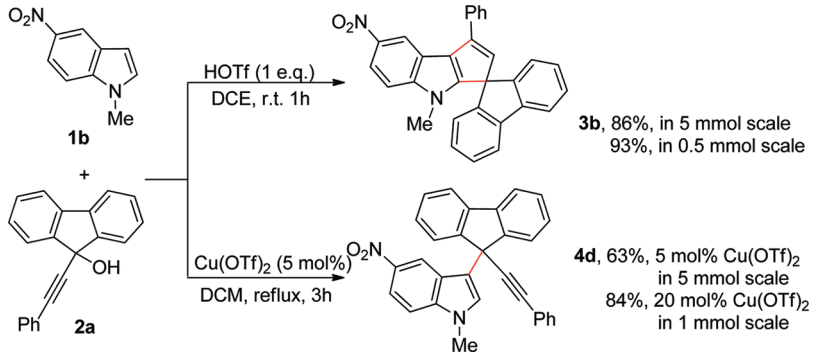
Scheme 9. Gram Scale Reactions of the 3-Alkenylation and 3-Alkylation of Indole



at refluxing temperature by decreasing the catalyst loading to 5 mol % $Cu(OTf)_2$.

CONCLUSION

In conclusion, we selectively synthesized 3,4-dihydrocyclopenta[*b*]indoles and 1,4-dihydrocyclopenta[*b*]-indoles from indoles and propargylic alcohols by the choice of the catalysts. 3-Alkenylation of indole with propargylic alcohols could be realized by the triflic acid, while 3-alkylation of indole could be accomplished by $Cu(OTf)_2$. We also attempted to construct 1,3-dihydrobenzo[*cd*]indole as well as 1,5-dihydrobenzo[*cd*]indole skeletons. Fortunately, one 1,3-dihydrobenzo[*cd*]indole was furnished by fine-tuning the electron density of the indole ring and altering the structure of the propargylic alcohol.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR spectra were recorded at 400 or 500 MHz using TMS as an internal standard and ^{13}C NMR spectra at 100 or 125 MHz using $CDCl_3$ as an internal standard. The following abbreviations are used to describe peak patterns where appropriate: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants are reported in hertz. High resolution mass spectra (HRMS) were performed on an electron ionization time-of-flight (EI-TOF) mass spectrometer. Reactions were controlled using TLC on silica. HPLC analyses were performed on a HPLC system equipped with C18 columns, detected at 273 nm. Flow phase was acetonitrile/water (95/5), and flow rate was 1.0 mL/min. Melting points were measured with a micro melting point apparatus.

The *N*-methyl-indoles and propargylic alcohols were prepared according to the published methods.[29] Other materials were purchased from common commercial sources and used without additional purification.

General Procedure for the Preparation of 3, 6, and 7. To a solution of indole **1** (0.5 mmol) and propargylic alcohol **2** (0.5 mmol) in dichloromethane (5 mL) was added a solution of triflic acid (75 mg, 0.5 mmol) in dichloromethane (3 mL) dropwise over 2 min, and the solution was stirred for 10 min at room temperature. After being stirred at reflux temperature for 6 h, the mixture was evaporated under vacuum. The product was isolated by silica gel column chromatography with a hexane/dichloromethane mixture.

4-Methyl-1-phenyl-4*H*-spiro[cyclopenta[*b*]indole-3,9′-fluorene] (3a). White solid; 146 mg, 74% yield; mp 211.7−214.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.3 Hz, 2H), 7.86 (dd, J = 5.8, 2.9 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.4 Hz, 3H), 7.24−7.13 (m, 5H), 7.10 (d, J = 7.5 Hz, 2H), 5.92 (s, 1H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 144.7, 143.1, 142.3, 141.5, 136.7, 129.1, 128.9, 128.5, 128.2, 128.1, 127.6, 124.4, 121.9, 121.0, 120.74, 120.66, 120.2, 120.0, 110.2, 62.4, 30.0; MS (ESI) (m/z) 396.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{21}N$ 395.1674, found 395.1680.

4-Methyl-7-nitro-1-phenyl-4*H*-spiro[cyclopenta[*b*]indole-3,9′-fluorene] (3b). Yellow solid; 205 mg, 93% yield; mp 174.5−175.2 °C ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, J = 2.1 Hz, 1H), 8.06 (dd, J = 9.1, 2.2 Hz, 1H), 7.86 (t, J = 7.5 Hz, 4H), 7.55 (t, J = 7.6 Hz, 2H), 7.43 (dd, J = 14.0, 6.9 Hz, 3H), 7.29−7.17 (m, 3H), 7.09 (d, J = 7.6 Hz, 2H), 6.02 (s, 1H), 3.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 143.9, 143.7, 142.3, 142.1, 141.6, 135.7, 130.7, 129.3, 128.9, 128.7, 128.3, 127.4, 124.2, 123.2, 120.9, 120.8, 116.9, 116.3, 110.0, 62.5, 30.4; MS (ESI) (m/z) 441.4 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{20}N_2O_2$ 440.1525, found 440.1528.

4-Methyl-1,3,3-triphenyl-3,4-dihydrocyclopenta[*b*]indole (3c). White solid; 115 mg, 58% yield; mp 184.7−186.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 7.4 Hz, 2H), 7.81 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.37−7.28 (m, 6H), 7.28−7.21 (m, 6H), 7.20−7.11 (m, 2H), 6.44 (s, 1H), 3.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 141.5, 141.2, 140.1, 136.5, 136.2, 128.82, 128.78, 128.6, 128.1, 127.7, 127.3, 122.0, 120.9, 120.4, 120.3, 119.1, 110.2, 62.3, 31.6; MS (ESI) (m/z) 398.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{23}N$ 397.1830, found 397.1837.

4-Methyl-7-nitro-1,3,3-triphenyl-3,4-dihydrocyclopenta[*b*]-indole (3d). Yellow solid; 190 mg, 86% yield; mp 231.4−234.3 °C ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.11 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 7.3 Hz, 2H), 7.52 (t, J = 7.3 Hz, 2H), 7.42 (t, J = 7.1 Hz, 1H), 7.38−7.21 (m, 11H), 6.53 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.9, 144.0, 142.2, 140.3, 139.1, 137.6, 135.6, 129.2, 129.0, 128.6, 128.4, 127.9, 127.4, 121.5, 120.9, 117.2, 116.4, 110.1, 62.7, 32.1; MS (ESI) (m/z) 443.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{22}N_2O_2$ 442.1681, found 442.1689.

4,7-Diethyl-1,3,3-triphenyl-3,4-dihydrocyclopenta[*b*]indole (3e). White solid; 58 mg, 28% yield; mp 171.7−173.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.4 Hz, 2H), 7.58 (s, 1H), 7.43 (t, J = 7.3 Hz, 2H), 7.35−7.10 (m, 12H), 7.00 (d, J = 8.1 Hz, 1H), 6.40 (s, 1H), 3.47 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2, 141.3, 140.2, 139.9, 136.6, 136.0, 129.5, 128.8, 128.7, 128.6, 128.0, 127.7, 127.3, 122.4, 122.1, 120.1, 118.5, 109.9, 62.1, 31.6, 22.0; MS (ESI) (m/z) 411.3 (M$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{25}N$ 411.1987, found 411.1985.

7-Methoxy-4-methyl-1,3,3-triphenyl-3,4-dihydrocyclopenta-[*b*]indole (3f). White solid; 47 mg, 22% yield; mp 189.7−190.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.41−7.17 (m, 13H), 6.86 (dd, J = 8.9, 2.4 Hz, 1H), 6.40 (s, 1H), 3.83 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 154.6, 141.1, 140.2, 136.9, 136.6, 135.8, 128.83, 128.77, 128.6, 128.1, 127.6, 127.3, 122.1, 118.5, 110.9, 110.3, 103.1, 62.2, 56.4, 31.7; MS (ESI) (m/z) 428.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{25}NO$ 427.1936, found 427.1932.

4-Methyl-1,3,3-triphenyl-3,4-dihydrocyclopenta[*b*]indole-7-carbonitrile (3g). White solid; 167 mg, 79% yield; mp 241.7−243.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.76 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.38 (ddd, J = 22.0, 11.5, 4.9 Hz, 3H), 7.31−7.23 (m, 10H), 6.50 (s, 1H), 3.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 142.8, 140.3, 139.2, 137.4, 135.7, 129.1, 129.0, 128.5, 128.4, 127.7, 127.4, 125.6, 123.8, 121.5, 121.2, 120.1, 111.1, 103.2,

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62.6, 31.9; MS (ESI) (m/z) 423.3 (M + H^+); HRMS (EI) (m/z) calcd for $C_{31}H_{22}N_2$ 422.1783, found 422.1786.

7-Bromo-4-methyl-1,3,3-triphenyl-3,4-dihydrocyclopenta[*b*]indole (3h). White solid; 176 mg, 74% yield; mp 218.7−219.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 1.6 Hz, 1H), 7.77 (d, J = 7.4 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.32−7.20 (m, 11H), 7.15 (d, J = 8.7 Hz, 1H), 6.43 (s, 1H), 3.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 140.8, 140.2, 139.7, 136.5, 136.1, 129.0, 128.9, 128.5, 128.3, 127.5, 123.7, 123.3, 122.7, 118.7, 113.8, 111.6, 62.3, 31.7; MS (ESI) (m/z) 476.1 (M + H^+); HRMS (EI) (m/z) calcd for $C_{30}H_{22}BrN$ 475.0936, found 475.0945.

4-Methyl-3,3-diphenyl-1-(*p*-tolyl)-3,4-dihydrocyclopenta[*b*]indole (3i). White solid; 107 mg, 52% yield; mp 203.5−204.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 7.7 Hz, 2H), 7.39−7.11 (m, 15H), 6.40 (s, 1H), 3.53 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 141.5, 141.1, 140.2, 137.8, 135.6, 133.6, 129.5, 128.7, 128.6, 127.6, 127.3, 122.0, 120.8, 120.4, 120.2, 119.2, 110.2, 62.2, 31.6, 21.7; MS (ESI) (m/z) 412.2 (M + H^+); HRMS (EI) (m/z) calcd for $C_{31}H_{25}N$ 411.1987, found 411.1982.

1-(4-Methoxyphenyl)-4-methyl-3,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (3j). White solid; 105 mg, 49% yield; mp 204.8−206.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.30 (t, J = 6.9 Hz, 5H), 7.27−7.11 (m, 8H), 6.98 (d, J = 8.3 Hz, 2H), 6.35 (s, 1H), 3.82 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 155.1, 141.5, 140.7, 140.3, 134.8, 129.1, 128.8, 128.7, 128.6, 127.3, 122.0, 120.8, 120.3, 120.2, 119.3, 114.2, 110.2, 62.1, 55.7, 31.6; MS (ESI) (m/z) 428.2 (M + H^+); HRMS (EI) (m/z) calcd for $C_{31}H_{25}NO$ 427.1936, found 427.1939.

1-(4-Fluorophenyl)-4-methyl-3,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (3k). White solid; 156 mg, 75% yield; mp 202.2−204.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83−7.76 (m, 2H), 7.74 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 7.3 Hz, 5H), 7.28−7.21 (m, 6H), 7.16 (ddd, J = 20.6, 16.1, 7.9 Hz, 4H), 6.38 (s, 1H), 3.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9 (d, J_{CF} = 246.7 Hz), 155.1, 141.5, 140.2, 140.0, 135.9, 132.7 (d, J_{CF} = 2.1 Hz), 129.3 (d, J_{CF} = 7.9 Hz), 128.8, 128.6, 127.4, 121.8, 121.0, 120.4, 120.1, 118.9, 115.7 (d, J_{CF} = 21.4 Hz), 110.3, 62.3, 31.6; MS (ESI) (m/z) 416.2 (M + H^+); HRMS (EI) (m/z) calcd for $C_{30}H_{22}FN$ 415.1736, found 415.1734.

3,4-Diethyl-7-nitro-1,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (3l). Yellow solid; 182 mg, 96% yield; mp 170.9−171.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 2.1 Hz, 1H), 8.06 (dd, J = 9.1, 2.2 Hz, 1H), 7.84−7.74 (m, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.34−7.22 (m, 6H), 6.22 (s, 1H), 3.62 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 143.7, 142.0, 139.4, 139.3, 138.4, 135.8, 129.2, 129.2, 128.4, 127.5, 127.3, 126.3, 121.2, 120.8, 117.0, 116.2, 109.9, 52.4, 31.5, 19.6; MS (ESI) (m/z) 381.1 (M + H^+); HRMS (EI) (m/z) calcd for $C_{25}H_{20}N_2O_2$ 380.1525, found 380.1528.

3,3,4-Trimethyl-7-nitro-1-phenyl-3,4-dihydrocyclopenta[*b*]indole (3m). Yellow solid; 89 mg, 56% yield; mp 169.0−171.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, J = 2.1 Hz, 1H), 8.04 (dd, J = 9.1, 2.1 Hz, 1H), 7.74 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 9.1 Hz, 1H), 6.04 (s, 1H), 3.95 (s, 3H), 1.57 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 143.7, 141.8, 138.9, 137.7, 136.2, 129.1, 128.2, 127.2, 120.8, 120.5, 116.8, 115.9, 109.7, 45.8, 31.6, 22.4; MS (ESI) (m/z) 391.1 (M + H^+); HRMS (EI) (m/z) calcd for $C_{20}H_{18}N_2O_2$ 318.1368, found 318.1371.

3,3,4-Trimethyl-1-phenyl-3,4-dihydrocyclopenta[*b*]indole-7-carbonitrile (3n). White solid; 85 mg, 57% yield; mp 159.6−161.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.70 (d, J = 7.4 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.44−7.30 (m, 3H), 6.01 (s, 1H), 3.93 (s, 3H), 1.56 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 142.5, 139.0, 137.4, 136.3, 129.0, 128.1, 127.2, 125.1, 123.2, 121.4, 119.0, 110.7, 102.7, 45.6, 31.4, 22.4; MS (ESI) (m/z) 299.1 (M + H^+); HRMS (EI) (m/z) calcd for $C_{21}H_{18}N_2$ 298.1470, found 298.1470.

3,3,4-Trimethyl-7-nitro-1-(perfluorophenyl)-3,4-dihydrocyclopenta[*b*]indole (3o). Yellow solid; 151 mg, 74% yield; mp 188.7−189.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, J = 2.0 Hz, 2H), 8.14 (dd, J = 9.1, 2.1 Hz, 1H), 7.32 (d, J = 9.1 Hz, 1H), 7.16 (s, 1H), 3.83 (s, 3H), 1.85 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ147.7 (d, J_{CF} = 245.5 Hz), 141.5 (d, J_{CF} = 256.0 Hz), 141.4, 140.8, 137.9 (d, J_{CF} = 251.4 Hz), 128.3, 125.1, 123.0, 118.2, 117.8, 109.7, 109.2, 100.5, 65.8, 33.5, 32.0, 30.5; MS (ESI) (m/z) 409.1 (M + H^+); HRMS (EI) (m/z) calcd for $C_{20}H_{13}F_5N_2O_2$ [M^+] 408.0897 (m/z), found 408.0893.

3-Ethyl-3,4-dimethyl-7-nitro-1-phenyl-3,4-dihydrocyclopenta[*b*]indole (3p). Yellow solid; 63 mg, 38% yield; mp 156.1−158.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, J = 2.1 Hz, 1H), 8.05 (dd, J = 9.1, 2.2 Hz, 1H), 7.80−7.70 (m, 2H), 7.51 (t, J = 7.7 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.32 (d, J = 9.1 Hz, 1H), 6.00 (s, 1H), 3.93 (s, 3H), 2.04 (dt, J = 13.9, 6.5 Hz, 2H), 1.56 (s, 3H), 0.72 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 143.8, 141.8, 140.4, 136.2, 135.4, 129.1, 128.2, 127.2, 121.7, 120.8, 116.7, 115.8, 109.6, 50.5, 31.6, 29.7, 21.2, 10.0; MS (ESI) (m/z) 333.1 (M + H^+); HRMS (EI) (m/z) calcd for $C_{21}H_{20}N_2O_2$ 332.1525, found 332.1519.

4-Methyl-7-nitro-1-phenyl-4*H*-spiro[cyclopenta[*b*]indole-3,1′-cyclopentane] (3q). Yellow solid; 81 mg, 47% yield; mp 190.2−191.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 2.1 Hz, 1H), 8.04 (dd, J = 9.1, 2.2 Hz, 1H), 7.74 (d, J = 7.1 Hz, 2H), 7.50 (t, J = 7.7 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.31 (d, J = 9.1 Hz, 1H), 6.26 (s, 1H), 3.93 (s, 3H), 2.40−2.23 (m, 2H), 2.14−1.91 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 144.0, 141.9, 138.5, 136.3, 135.7, 129.1, 128.1, 127.2, 121.4, 120.8, 116.6, 115.8, 109.6, 55.7, 33.0, 31.6, 26.7; MS (ESI) (m/z) 345.1 (M + H^+); HRMS (EI) (m/z) calcd for $C_{22}H_{20}N_2O_2$ 344.1525, found 344.1532.

4′-Methyl-7′-nitro-1′-phenyl-4′*H*-spiro[cyclohexane-1,3′-cyclopenta[*b*]indole] (3r). Yellow solid; 109 mg, 61% yield; mp 223.3−225.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 1.9 Hz, 1H), 8.02 (dd, J = 9.1, 2.0 Hz, 1H), 7.75 (d, J = 7.3 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.29 (d, J = 9.1 Hz, 1H), 6.59 (s, 1H), 3.96 (s, 3H), 2.15 (td, J = 12.9, 3.0 Hz, 2H), 1.93 (t, J = 13.6 Hz, 3H), 1.81−1.63 (m, 4H), 1.60 (d, J = 12.8 Hz, 1H), 1.50−1.35 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 143.8, 141.8, 139.9, 136.5, 132.2, 129.1, 128.2, 127.2, 120.9, 120.7, 116.7, 115.9, 109.6, 50.5, 32.2, 31.7, 26.1, 25.0; MS (ESI) (m/z) 359.3 (M + H^+); HRMS (EI) (m/z) calcd for $C_{23}H_{22}N_2O_2$ 358.1681, found 358.1685.

4-Methyl-7-nitro-1-pentyl-3,3-diphenyl-3,4-dihydrocyclopenta[*b*]indole (3s). Yellow oil; 89 mg, 41% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.09 (d, J = 8.6 Hz, 1H), 7.29 (dd, J = 28.7, 6.7 Hz, 11H), 5.80 (s, 1H), 3.82 (s, 2H), 3.34 (s, 3H), 2.15 (d, J = 6.9 Hz, 2H), 1.50−1.35 (m, 4H), 0.91 (dd, J = 14.7, 7.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 145.6, 145.3, 142.1, 133.6, 128.9, 128.3, 127.1, 122.9, 121.1, 117.7, 117.6, 117.2, 109.8, 57.0, 56.8, 32.3, 31.7, 29.4, 22.8, 14.4; MS (ESI) (m/z) 437 (M + H^+); HRMS (EI) (m/z) calcd for $C_{29}H_{28}N_2O_2$ 436.2151, found 436.2133.

General Procedure for the Preparation of 4. To a solution of indole **1** (1 mmol) and propargylic alcohol **2** (1 mmol) in dichloromethane (5 mL) was added $Cu(OTf)_2$ (72 mg, 20 mol %). After being stirred at reflux temperature for 6 h, the mixture was evaporated under vacuum. The product was isolated by silica gel column chromatography with a hexane/dichloromethane mixture.

1-Methyl-3-(9-(phenylethynyl)-9*H*-fluoren-9-yl)-1*H*-indole (4a). White solid; 269 mg, 68% yield; mp 182.5−183.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.6 Hz, 2H), 7.46−7.40 (m, 2H), 7.39−7.33 (m, 2H), 7.29 (s, 1H), 7.27−7.20 (m, 5H), 7.17 (d, J = 8.2 Hz, 1H), 7.10−7.04 (m, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 139.9, 138.1, 132.1, 128.5, 128.3, 128.2, 128.1, 125.5, 123.8, 121.8, 120.38, 120.35, 119.3, 116.0, 109.6, 91.6, 81.4, 49.6, 33.0; MS (ESI) (m/z) 396.2 (M + H^+); HRMS (EI) (m/z) calcd for $C_{30}H_{21}N$ 395. 1674, found 395. 1667.

1,5-Dimethyl-3-(1,1,3-triphenylprop-2-yn-1-yl)-1*H*-indole (4b). White solid; 37 mg, 9% yield; mp 185.7−185.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.42 (m, 6H), 7.38 (s, 1H), 7.34−7.22 (m, 9H), 7.17 (d, J = 8.3 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.17 (s, 1H), 3.62 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5,

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136.6, 132.0, 129.5, 129.0, 128.5, 128.3, 128.1, 127.2, 127.0, 124.3, 123.7, 121.9, 119.4, 109.2, 95.1, 84.8, 50.4, 33.1, 21.9; MS (ESI) (m/z) 412.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{25}N$ 411.1987, found 411.1993.

3-(1,3-Diphenylprop-2-yn-1-yl)-1-methyl-5-nitro-1*H*-indole (4c). Yellow solid; 223 mg, 61% yield; mp 155.3−156.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, J = 1.9 Hz, 1H), 8.07 (dd, J = 9.1, 2.0 Hz, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.48 (dd, J = 6.5, 2.9 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.32−7.20 (m, 5H), 7.06 (s, 1H), 5.45 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 140.8, 140.5, 132.0, 130.6, 129.1, 128.6, 128.4, 128.1, 127.6, 126.0, 123.5, 118.8, 117.8, 117.4, 109.7, 89.8, 84.3, 35.5, 33.5; MS (ESI) (m/z) 367.1 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{24}H_{18}N_2O_2$ 366.1368, found 366.1370.

1-Methyl-5-nitro-3-(9-(phenylethynyl)-9*H*-fluoren-9-yl)-1*H*-indole (4d). Yellow solid; 370 mg, 84% yield; mp 213.4−214.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.97−7.90 (m, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.51−7.44 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.33−7.22 (m, 6H), 7.11 (d, J = 9.1 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 141.5, 140.7, 139.7, 132.1, 130.7, 128.8, 128.61, 128.55, 125.3, 124.9, 123.3, 120.7, 119.5, 117.8, 117.5, 109.6, 90.4, 82.3, 49.3, 33.4; MS (ESI) (m/z) 441.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{20}N_2O_2$ 440.1525, found 440.1528.

1,5-Diethyl-3-(9-(phenylethynyl)-9*H*-fluoren-9-yl)-1*H*-indole (4e). White solid; 299 mg, 73% yield; mp 170.1−171.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.73 (m, 2H), 7.58 (dd, J = 7.5, 2.9 Hz, 2H), 7.46−7.39 (m, 2H), 7.39−7.30 (m, 2H), 7.23 (ddd, J = 6.6, 6.2, 2.0 Hz, 5H), 7.16 (d, J = 2.6 Hz, 1H), 7.06 (dd, J = 8.3, 1.9 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 6.79 (s, 1H), 3.62 (d, J = 0.8 Hz, 3H), 2.20 (d, J = 2.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 139.8, 136.6, 132.1, 128.5, 128.33, 128.28, 128.2, 128.0, 125.9, 125.5, 123.9, 123.5, 120.3, 120.2, 115.4, 109.3, 91.8, 81.4, 49.7, 33.0, 21.9; MS (ESI) (m/z) 410.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{23}N$ 409.1830, found 409.1828.

5-Methoxy-1-methyl-3-(9-(phenylethynyl)-9*H*-fluoren-9-yl)-1*H*-indole (4f). White solid; 247 mg, 58% yield; mp 172.3−173.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.48−7.42 (m, 2H), 7.38 (td, J = 7.5, 1.0 Hz, 2H), 7.31−7.24 (m, 6H), 7.08 (d, J = 8.9 Hz, 1H), 6.73 (dd, J = 8.9, 2.4 Hz, 1H), 6.30 (d, J = 2.3 Hz, 1H), 3.70 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 149.8, 139.9, 133.4, 132.2, 128.54, 128.48, 128.4, 128.3, 125.8, 125.6, 123.9, 120.2, 115.4, 112.1, 110.3, 102.1, 91.5, 81.5, 55.7, 49.6, 33.3; MS (ESI) (m/z) 426.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{23}NO$ 425.1780, found 425.1781.

1-Methyl-3-(9-(phenylethynyl)-9*H*-fluoren-9-yl)-1*H*-indole-5-carbonitrile (4g). Pale solid; 391 mg, 93% yield; mp 205.8−206.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 2H), 7.50 (dd, J = 6.8, 4.9 Hz, 2H), 7.47−7.33 (m, 5H), 7.23 (ddd, J = 18.1, 12.8, 4.9 Hz, 6H), 7.15−7.06 (m, 2H), 3.64 (d, J = 3.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 139.6, 139.4, 132.0, 130.3, 128.7, 128.53, 128.48, 128.4, 125.7, 125.2, 125.0, 124.7, 123.2, 121.0, 120.6, 117.5, 110.5, 102.2, 90.6, 81.9, 49.2, 33.1; MS (ESI) (m/z) 421.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{20}N_2$ 420.1626, found 420.1627.

5-Bromo-1-methyl-3-(9-(phenylethynyl)-9*H*-fluoren-9-yl)-1*H*-indole (4h). White solid; 407 mg, 86% yield; mp 182.7−183.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.43 (dd, J = 6.5, 2.8 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.29−7.21 (m, 5H), 7.17 (t, J = 3.7 Hz, 3H), 7.01 (d, J = 8.6 Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 139.8, 136.7, 132.1, 128.9, 128.54, 128.52, 128.4, 127.3, 125.4, 124.8, 123.6, 123.0, 120.5, 115.9, 112.8, 111.2, 91.1, 81.8, 49.4, 33.2; MS (ESI) (m/z) 474.1 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{20}BrN$ 473.0779, found 473.0782.

1-Methyl-3-(1,1,3-triphenylprop-2-yn-1-yl)-1*H*-indole (4i). White solid; 258 mg, 65% yield; mp 183.2−184.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.1 Hz, 4H), 7.44 (dd, J = 6.6, 2.9 Hz, 2H), 7.33−7.17 (m, 11H), 6.99 (t, J = 7.5 Hz, 1H), 6.23 (s, 1H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 138.2, 132.0, 129.4, 129.2, 128.5, 128.3, 128.1, 127.04, 126.96, 124.2, 122.3, 122.0, 120.1, 119.3, 109.5, 95.0, 84.9, 50.3, 33.0; MS (ESI) (m/z) 398.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{23}N$, found 397.1829.

3-(1,1-Diphenyl-3-(*p*-tolyl)prop-2-yn-1-yl)-1-methyl-1*H*-indole (4j). White solid; 247 mg, 60% yield; mp 211.1−211.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.8 Hz, 4H), 7.34 (dd, J = 8.0, 1.7 Hz, 2H), 7.31−7.17 (m, 8H), 7.05 (d, J = 7.3 Hz, 2H), 7.01−6.94 (t, 1H), 6.23 (d, J = 1.9 Hz, 1H), 3.61 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 138.2, 138.1, 131.9, 129.4, 129.2, 129.0, 128.3, 127.0, 122.3, 122.0, 121.1, 120.2, 119.3, 109.5, 94.2, 85.0, 50.3, 33.0, 21.8; MS (ESI) (m/z) 412.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{25}N$ 411.1987, found 411.1987.

3-(3-(4-Fluorophenyl)-1,1-diphenylprop-2-yn-1-yl)-1-methyl-1*H*-indole (4k). White solid; 141 mg, 34% yield; mp 192.5−193.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.1 Hz, 1H), 7.50−7.44 (m, 4H), 7.44−7.37 (m, 2H), 7.33−7.21 (m, 7H), 7.21−7.15 (m, 1H), 7.03−6.97 (m, 1H), 6.93 (td, J = 8.6, 1.7 Hz, 2H), 6.22 (d, J = 1.7 Hz, 1H), 3.62 (d, J = 1.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J_{CF} = 248.6 Hz), 145.2, 138.2, 133.8 (d, J_{CF} = 8.3 Hz), 129.4, 128.9, 128.3, 127.1, 126.9, 122.2, 122.1, 120.22, 120.20 (d, J_{CF} = 3.4 Hz), 119.4, 115.7 (d, J_{CF} = 22.0 Hz), 109.6, 94.6, 83.8, 50.3, 33.0; MS (ESI) (m/z) 416.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{22}FN$ 415.1736, found 415.1738.

3-(2,4-Diphenylbut-3-yn-2-yl)-1-methyl-1*H*-indole (4l). White solid; 281 mg, 84% yield; mp 180.8−181.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.57 (m, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.47−7.43 (m, 1H), 7.43 (d, J = 2.0 Hz, 2H), 7.34−7.22 (m, 5H), 7.23−7.19 (m, 1H), 7.19−7.13 (m, 1H), 7.00 (s, 1H), 6.99−6.93 (m, 1H), 3.74 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 138.1, 132.0, 128.5, 128.0, 127.0, 126.8, 126.6, 126.5, 124.2, 121.9, 121.6, 120.5, 119.2, 109.5, 95.5, 83.3, 40.2, 33.1, 31.4; MS (ESI) (m/z) 336.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{25}H_{21}N$ 335.1674, found 335.1675.

3-(9-Ethynyl-9*H*-fluoren-9-yl)-1-methyl-5-nitro-1*H*-indole (4m). Yellow solid; 135 mg, 37% yield; mp 203.6−204.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 9.1, 2.0 Hz, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.72 (d, J = 1.7 Hz, 1H), 7.48 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.5 Hz, 3H), 7.27 (t, J = 7.5 Hz, 2H), 7.16 (d, J = 9.1 Hz, 1H), 3.76 (s, 3H), 2.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 141.5, 140.8, 139.8, 131.1, 129.0, 128.7, 125.1, 124.5, 120.8, 118.7, 117.6, 109.6, 85.2, 70.3, 48.5, 33.6; MS (ESI) (m/z) 365.1 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{24}H_{16}N_2O_2$ 364.1212, found 364.1211.

1-Ethyl-2-phenyl-3-(9-(phenylethynyl)-9*H*-fluoren-9-yl)-1*H*-indole (4n). White solid; 340 mg, 70% yield; mp 159.8−161.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.47 (m, 4H), 7.45−6.64 (m, 18H), 3.91−3.69 (m, 2H), 1.25−1.04 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 139.7, 138.0, 135.6, 132.4, 132.1, 131.4, 128.2, 128.1, 128.0, 127.9, 127.7, 125.7, 124.0, 121.7, 121.5, 120.1, 119.6, 111.1, 109.7, 92.4, 82.4, 50.2, 38.4, 15.6; MS (ESI) (m/z) 486.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{37}H_{27}N$ 485.2143, found 485.2141.

5-Methoxy-1-methyl-2-phenyl-3-(9-(phenylethynyl)-9*H*-fluoren-9-yl)-1*H*-indole (4o). White solid; 286 mg, 57% yield; mp 179.2−180.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.5 Hz, 4H), 7.31−6.95 (m, 15H), 6.84 (d, J = 8.0 Hz, 2H), 3.59 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 150.9, 139.7, 132.2, 132.1, 131.3, 128.3, 128.1, 127.93, 127.89, 127.7, 125.7, 123.9, 120.0, 112.3, 110.7, 110.2, 102.9, 92.3, 82.5, 56.0, 50.1, 30.7; MS (ESI) (m/z) 502.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{37}H_{27}NO[M^+]$ (m/z) 501.2093, found 501.2097.

General Procedure for the Preparation of 5. To a solution of **4** (0.5 mmol) and 1-iodopyrrolidine-2,5-dione (NIS) (113 mg, 0.5 mmol) in dichloromethane (5 mL) was added a solution of $BF_3{\cdot}Et_2O$ (72 mg, 0.5 mmol) in dichloromethane (3 mL) dropwise over 3 min. After being stirred at room temperature for 2 h, the mixture was evaporated under vacuum. The product was isolated by silica gel column chromatography with a hexane/dichloromethane mixture.

2-Iodo-4-methyl-3-phenyl-4*H*-spiro[cyclopenta[*b*]indole-1,9′-fluorene] (5a). White solid; 120 mg, 46% yield; mp 210−5−211.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.5 Hz, 2H),

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7.85 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.1 Hz, 3H), 7.45 (t, J = 7.6 Hz, 3H), 7.28−7.08 (m, 6H), 7.05 (d, J = 7.6 Hz, 2H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 147.8, 143.0, 142.6, 140.7, 136.1, 129.3, 129.0, 128.7, 128.6, 128.4, 124.4, 121.9, 121.2, 121.0, 120.8, 120.4, 119.5, 110.2, 92.5, 67.7, 30.1; MS (ESI) (m/z) 522.1 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{20}IN$ 521.0640, found 521.0641.

2-Iodo-4-methyl-7-nitro-3-phenyl-4*H*-spiro[cyclopenta[*b*]-indole-1,9′-fluorene] (5b). White solid; 88 mg, 31% yield; mp 245.2−246.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 2.1 Hz, 1H), 8.05 (dd, J = 9.1, 2.2 Hz, 1H), 7.89 (t, J = 7.1 Hz, 4H), 7.60 (t, J = 7.6 Hz, 2H), 7.53 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 9.1 Hz, 1H), 7.05 (d, J = 7.5 Hz, 2H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 146.7, 143.2, 143.0, 142.3, 141.5, 135.3, 129.5, 129.3, 129.1, 128.7, 124.3, 124.0, 121.0, 120.0, 116.7, 116.5, 110.1, 95.3, 68.1, 30.6; MS (ESI) (m/z) 567.0 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{19}IN_2O_2$ 566.0491, found 566.0487.

2-Iodo-4,7-dimethyl-3-phenyl-4*H*-spiro[cyclopenta[*b*]-indole-1,9′-fluorene] (5c). White solid; 144 mg, 54% yield; mp 225.4−226.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−7.88 (m, 2H), 7.83 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.50−7.40 (m, 3H), 7.31 (s, 1H), 7.26−7.20 (m, 2H), 7.05 (dd, J = 10.3, 8.1 Hz, 3H), 6.97 (dd, J = 8.4, 1.2 Hz, 1H), 2.93 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 147.9, 142.9, 142.8, 139.1, 136.3, 129.8, 129.4, 129.0, 128.64, 128.61, 128.4, 124.4, 122.7, 121.3, 121.2, 120.7, 119.1, 109.9, 92.2, 67.7, 30.1, 21.9; MS (ESI) (m/z) 536.1 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{22}IN$ 535.0797, found 535.0800.

2-Iodo-7-methoxy-4-methyl-3-phenyl-4*H*-spiro[cyclopenta-[*b*]indole-1,9′-fluorene] (5d). White solid; 105 mg, 38% yield; mp 221.3−222.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.88 (m, 2H), 7.84 (d, J = 7.6 Hz, 2H), 7.54 (dd, J = 10.3, 4.6 Hz, 2H), 7.48−7.42 (m, 3H), 7.25−7.21 (m, 2H), 7.06 (t, J = 7.8 Hz, 3H), 7.02 (d, J = 2.4 Hz, 1H), 6.81 (dd, J = 8.9, 2.5 Hz, 1H), 3.78 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 150.4, 147.7, 142.9, 142.8, 136.1, 129.3, 129.0, 128.7, 128.6, 128.4, 124.4, 121.4, 121.3, 120.8, 110.8, 110.6, 102.2, 92.0, 67.7, 56.3, 30.2; MS (ESI) (m/z) 552.1 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{22}INO$ 551.0746, found 551.0746.

2-Iodo-4-methyl-3-phenyl-4*H*-spiro[cyclopenta[*b*]indole-1,9′-fluorene]-7-carbonitrile (5e). White solid; 98 mg, 36% yield; mp 226.8−227.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.83 (m, 5H), 7.59 (t, J = 7.4 Hz, 2H), 7.52 (d, J = 7.3 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.38 (dd, J = 8.5, 1.4 Hz, 1H), 7.31−7.21 (m, 3H), 7.04 (d, J = 7.6 Hz, 2H), 3.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 146.8, 143.0, 142.0, 141.6, 135.4, 129.4, 129.2, 129.03, 129.01, 128.6, 124.9, 124.3, 124.1, 122.6, 121.0, 121.0, 120.6, 111.0, 103.5, 94.8, 67.9, 30.4. MS (ESI) (m/z) 547.1 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{19}IN_2$ 546.0593, found 546.0590.

7-Bromo-2-iodo-4-methyl-3-phenyl-4*H*-spiro[cyclopenta[*b*]-indole-1,9′-fluorene] (5f). White solid; 129 mg, 43% yield; mp 221.8−222.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.81 (m, 4H), 7.63 (d, J = 1.8 Hz, 1H), 7.60−7.52 (m, 2H), 7.50−7.42 (m, 3H), 7.24 (qd, J = 7.7, 1.5 Hz, 3H), 7.06−7.00 (m, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 147.3, 143.0, 142.3, 139.4, 135.8, 129.2, 128.9, 128.8, 128.5, 124.4, 124.0, 122.4, 122.0, 121.4, 120.9, 113.9, 111.6, 93.3, 67.8, 30.2; MS (ESI) (m/z) 600.0 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{19}BrIN$ 598.9746, found 598.9742.

2-Iodo-4-methyl-1,3,3-triphenyl-3,4-dihydrocyclopenta[*b*]-indole (5g). Pale solid; 63 mg, 24% yield; mp 194.8−195.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.1 Hz, 2H), 7.39 (dd, J = 6.1, 3.2 Hz, 4H), 7.34−7.28 (m, 6H), 7.25 (d, J = 8.2 Hz, 1H), 7.15 (dd, J = 8.8, 6.3 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 3.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 146.1, 140.6, 138.2, 136.5, 129.5, 129.4, 128.8, 128.6, 128.5, 128.0, 121.4, 120.8, 120.5, 119.9, 119.7, 110.2, 102.8, 66.2, 31.4; MS (ESI) (m/z) 523.1 (M$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{22}IN$ 523.0797, found 523.0795.

2-Iodo-4-methyl-1,1-diphenyl-3-(*p*-tolyl)-1,4-dihydrocyclopenta[*b*]indole (5h). White solid; 121 mg, 45% yield; mp 204.6−205.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 7.9 Hz, 1H), 7.38 (dd, J = 6.6, 3.1 Hz, 4H), 7.34−7.24 (m, 9H), 7.19−7.13 (m, 1H), 7.12−7.02 (m, 1H), 3.49 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 146.0, 140.6, 138.4, 138.3, 133.6, 129.5, 129.3, 129.2, 128.7, 127.9, 121.3, 120.9, 120.5, 120.1, 119.8, 110.1, 102.4, 66.1, 31.4, 21.8; MS (ESI) (m/z) 538.1(M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{24}IN$ 537.0953, found 537.0951.

3-(4-Fluorophenyl)-2-iodo-4-methyl-1,1-diphenyl-1,4-dihydrocyclopenta[*b*]indole (5i). White solid; 105 mg, 39% yield; mp 207.1−208.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.5, 5.6 Hz, 2H), 7.42−7.24 (m, 12H), 7.23−7.13 (m, 3H), 7.09 (t, J = 7.5 Hz, 1H), 3.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J_{CF} = 247.6 Hz), 154.5, 145.2, 140.6, 138.1, 132.5 (d, J_{CF} = 3.2 Hz), 131.3 (d, J_{CF} = 8.1 Hz), 129.5, 128.8, 128.0, 121.5, 120.7, 120.6, 119. 8, 119.5, 115.6 (d, J_{CF} = 21.5 Hz), 110.3, 103.0, 66.2, 31.4; MS (ESI) (m/z) 541.1 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{30}H_{21}FIN$ 541.0703, found 541.0706.

2-Iodo-4-methyl-7-nitro-4*H*-spiro[cyclopenta[*b*]indole-1,9′-fluorene] (5j). White solid; 39 mg, 16% yield; mp 192−194 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, J = 9.0, 2.1 Hz, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 2.1 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.38 (s, 1H), 7.34 (d, J = 9.1 Hz, 1H), 7.18 (t, J = 7.4 Hz, 2H), 6.81 (d, J = 7.5 Hz, 2H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 152.2, 143.4, 143.1, 142.8, 142.1, 131.4, 128.9, 128.1, 124.2, 123.4, 121.8, 120.9, 116.2, 113.8, 111. 6, 110.4, 68.7, 31.9; MS (ESI) (m/z) 491.0(M + H$^+$); HRMS (EI) (m/z) calcd for $C_{24}H_{15}IN_2O_2$ 490.0178, found 490.0177.

***N*,6′-Diethyl-4′-phenyl-[1,1′:2′,1″-terphenyl]-2-amine (6).** White solid; 124 mg, 71% yield; mp 175−178 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 7.5 Hz, 2H), 7.54 (s, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.22−7.06 (m, 6H), 6.79 (d, J = 6.5 Hz, 1H), 6.58 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 8.1 Hz, 1H), 3.48 (s, 1H), 2.67 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 143.3, 141.8, 141.0, 140.8, 138.8, 136.1, 130.7, 129.3, 129.1, 128.6, 128.4, 127.8, 127.7, 127.4, 127.1, 126.9, 125.6, 117.0, 109.9, 31.0, 20.9; MS (ESI) (m/z) 350.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{26}H_{23}N$ 349.1830, found 349.1835.

1,2-Diethyl-3-(spiro[fluorene-9,1′-inden]-3′-yl)-1*H*-indole-(7a). White solid; 41 mg, 20% yield; mp 191.8−192.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.8 Hz, 1H), 7.35 (dd, J = 17.0, 8.0 Hz, 4H), 7.21 (dt, J = 12.0, 7.0 Hz, 4H), 7.12 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 7.4 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 7.4 Hz, 1H), 6.19 (s, 1H), 3.75 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 146.2, 145.9, 142.4, 139.9, 137.7, 137.2, 135.0, 128.01, 127.95, 127.6, 127.2, 126.3, 124.1, 122.9, 121.8, 121.4, 120.5, 120.0, 119.8, 109.1, 107.7, 67.9, 30.1, 12.0; MS (ESI) (m/z) 410.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{23}N$ 409.1830, found 409.1833.

5-Methoxy-1-methyl-2-phenyl-3-(spiro[fluorene-9,1′-inden]-3′-yl)-1*H*-indole(7b). White solid; 163 mg, 65% yield; mp 196.3−197.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.47 (d, J = 7.1 Hz, 2H), 7.39−7.26 (m, 6H), 7.17 (d, J = 2.3 Hz, 1H), 7.13 (t, J = 7.7 Hz, 3H), 7.08 (d, J = 7.3 Hz, 1H), 6.99 (dd, J = 8.8, 2.4 Hz, 1H), 6.92 (dd, J = 11.7, 7.7 Hz, 3H), 6.61 (d, J = 7.4 Hz, 1H), 6.03 (s, 1H), 3.82 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 149.0, 146.1, 145.7, 142.3, 139.9, 139.6, 138.6, 133.2, 132.3, 131.0, 128.6, 128.4, 128.2, 127.9, 127.8, 127.1, 126.0, 124.1, 122.6, 121.6, 120.3, 112.5, 110.8, 108.9, 102.7, 67.7, 56.4, 31.7; MS (ESI) (m/z) 502.2 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{37}H_{27}NO$ 501.2093, found 501.2090.

Procedure for the Preparation of 8. To a solution of indole **1k** (119 mg, 0.5 mmol), propargylic alcohol **2n** (103 mg, 0.5 mmol), and 1-iodopyrrolidine-2,5-dione (NIS) (113 mg, 0.5 mmol) in dichloromethane (5 mL) was added a solution of BF_3·Et_2O (72 mg, 0.5 mmol) in dichloromethane (3 mL) dropwise over 3 min. After being stirred at room temperature for 2 h, the mixture was evaporated under vacuum. The product was isolated by silica gel column chromatography with a hexane/dichloromethane mixture.

4-Iodo-6-methoxy-1-methyl-2-phenyl-1*H*-spiro[benzo[*cd*]-indole-3,9′-fluorene] (8). White solid; 55 mg, 20% yield; mp 212.1−213.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.29 (d, J = 7.3

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Hz, 2H), 7.27−7.14 (m, 6H), 7.12 (d, J = 8.8 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 6.80 (t, J = 7.6 Hz, 2H), 6.12 (d, J = 7.9 Hz, 2H), 3.96 (s, 3H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 148.1, 140.3, 138.6, 133.8, 130.8, 130.2, 129.6, 128.0, 127.8, 127.7, 127.4, 125.8, 124.8, 119.6, 113.8, 110.9, 110.4, 109.4, 108.2, 61.2, 57.9, 30.9; MS (ESI) (m/z) 552.1 (M + H$^+$); HRMS (EI) (m/z) calcd for $C_{31}H_{22}INO$ 551.0746, found 551.0735.

■ ASSOCIATED CONTENT

Supporting Information

HPLC reports of reaction conditions, copies of ^{1}H and ^{13}C NMR spectra, and crystallographic information in CIF format for compounds **3a**, **3c**, **4n**, **5j**, **6**, **7a**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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