

Article

Lewis-Acid-Catalyzed (3+2) Annulation of 2-Indolylmethanols with Propargylic Alcohols to Access Cyclopenta[*b*]indoles

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Abstract: Herein, a Sc(OTf)₃-catalyzed (3+2) annulation of 2-indolylmethanols with propargylic alcohols is reported. The reaction proceeds via a Friedel–Crafts-type allenylation/5-exo-annulation cascade. In the reaction, 2-indolylmethanol is used as a three-carbon synthon, and propargyl alcohol is used as a two-carbon synthon. This method provides a direct and high-yield pathway for synthetically useful cyclopenta[*b*]indoles. In general, the method features easily accessible substrates with broad scope and generality, the formation of multiple bonds with high efficiency, and easy scale-up.

Keywords: (3+2) annulation; cyclopenta[*b*]indoles; propargylic alcohols; 2-indolylmethanols



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1. Introduction

Cyclopenta[*b*]indoles, as privileged heterocyclic skeletons, are present in numerous natural alkaloids and pharmaceuticals possessing a wide range of biological activities [1–8]. Accordingly, bruceollines are traditionally used to treat parasitic diseases and malaria [5,6]. Scytonemin is a small-molecule inhibitor of polo-like kinase and has the potential to inhibit other cell cycle regulators (Figure 1) [8]. Additionally, this type of fused tricyclic structure has been used as an intermediate in pharmaceutical chemistry and in the total synthesis of natural products, such as arborisidine and 19-epi-arborisidine [9]. Owing to their important biological properties, various synthetic protocols have been developed for preparing cyclopenta[*b*]indoles. Among these protocols, the (3+2) annulation of 2-indolylmethanols and olefins is an atom-economic strategy for the synthesis of these fused indole derivatives [10–18]. In recent years, 2-indolylmethanols have become intriguing reactants because of their unique properties of electrophilicity and nucleophilicity at the C3 position [19–28]. Despite these impressive achievements, a more efficient and diversity-oriented approach for cyclopenta[*b*]indoles is still required.

Propargylic alcohols have shown promise as feedstocks for the synthesis of carbo- and heterocyclic compounds. Recently, a number of studies have specifically focused on Lewis- or Brønsted-acid-catalyzed tandem annulations of propargylic alcohols to construct diversely structured indole derivatives [29–35]. However, there have been limited studies on the annulations of propargylic alcohols with 2-indolylmethanols. In 2014, Wang [36] reported a Lewis-acid-catalyzed (3+3) annulation of propargylic alcohols and 2-indolylmethanols, providing an effective approach to obtain polysubstituted carbazole derivatives (Scheme 1a). Recently, our group developed a Brønsted-acid-catalyzed (3+4) annulation of 2-indolylmethanols and propargylic alcohols, providing a convenient method to obtain structurally diverse indole-fused oxepines (Scheme 1b) [37]. However, to the best of our knowledge, no method has been reported for the synthesis of 1,2,3-trisubstituted

cyclopenta[*b*]indoles by formal (3+2) annulation between 2-indolylmethanols and propargylic alcohols. With our continuing research interest in propargylic alcohols [38–41] and the importance of cyclopenta[*b*]indoles, herein, we describe a $\text{Sc}(\text{OTf})_3$ -catalyzed (3+2) annulation of 2-indolylmethanols with propargylic alcohols to synthesize cyclopenta[*b*]indoles (Scheme 1c).

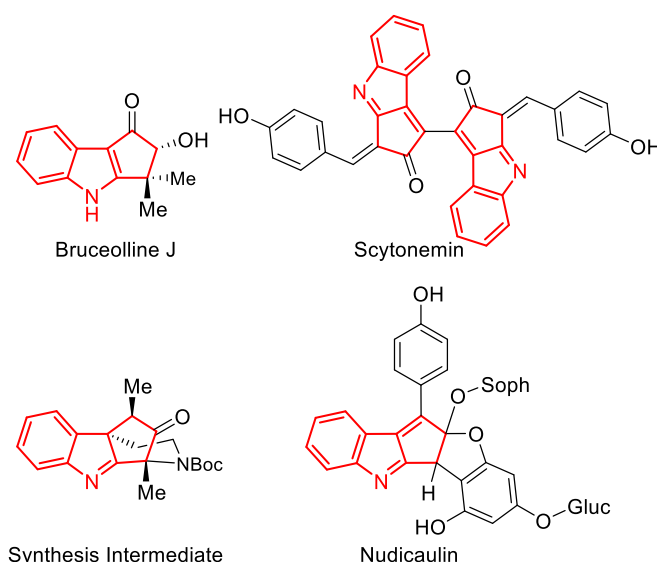
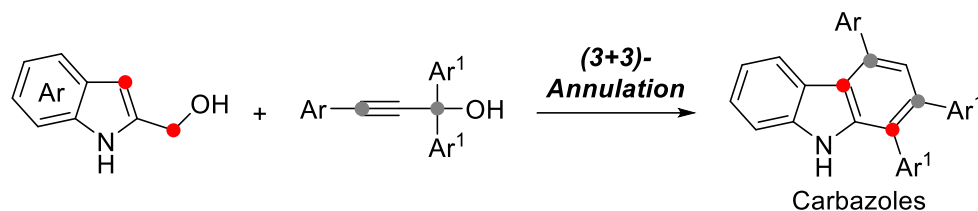
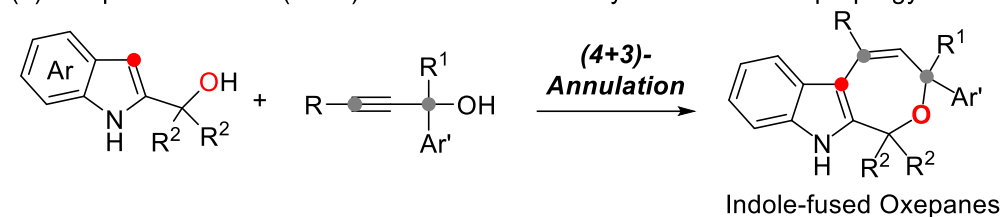


Figure 1. Representative natural product molecules.

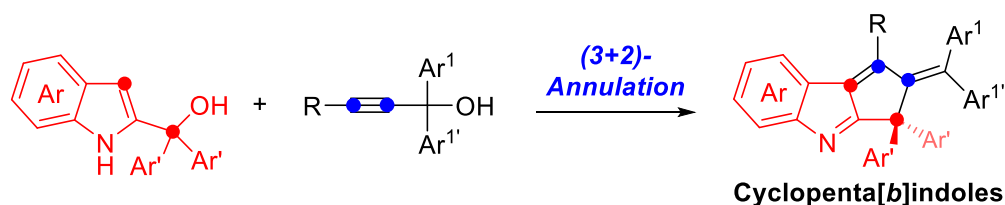
(a) Wang's work: (3 + 3)-annulation of 2-Indolylmethanols with propargylic alcohol



(b) Our previous work: (3 + 4)-annulation of 2-Indolylmethanols with propargylic alcohol



(c) This work: (3 + 2)-annulation of 2-Indolylmethanols with propargylic alcohol



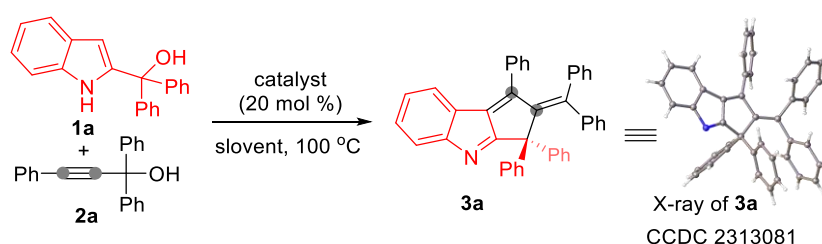
Scheme 1. Annulation of 2-indolylmethanols with propargylic alcohols.

2. Results

Initially, 2-indolylmethanol **1a** and propargylic alcohol **2a** were selected as the model substrates to explore the reaction conditions in 1,2-dichloroethane (DCE) at 100 °C (Table 1). First, a range of Lewis acids (entries 1–6) were tested. When $\text{Zn}(\text{OTf})_2$ was used as the

catalyst, the desired cyclopenta[*b*]indole **3a** was isolated in a moderate yield (entry 1, 62%). The fused tricyclic skeleton of product **3a** was determined by X-ray crystallographic analysis (CCDC 2,313,081 (**3a**) contains the supplementary crystallographic data for this paper; for details, see the Supporting Information). Other common triflates, such as Bi(OTf)₃, Yb(OTf)₃, Cu(OTf)₂, and AgNTf₂, all promoted the reaction and gave the desired cyclopenta[*b*]indole product in moderate yields (entries 2–5, 13–70%). Sc(OTf)₃ was found to be the best catalyst, and we then further evaluated the effect of the solvent (entries 6–17). Apart from dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (entries 14 and 15), many common solvents worked well, providing **3a** in moderate yields ranging from 41% to 78% (entries 8–16). Pleasingly, toluene improved the efficiency of the reaction (entry 17, 30 min, 80% yield). Increasing the equivalent amount of propargylic alcohol **2a** had a positive effect on the reaction yield (entry 18, 87% yield). Decreasing the equivalent amount of the catalyst had a negative effect on the reaction yield (entry 19, 44% yield).

Table 1. Optimization of the reaction conditions for (3+2) annulation of **1a** and **2a**.

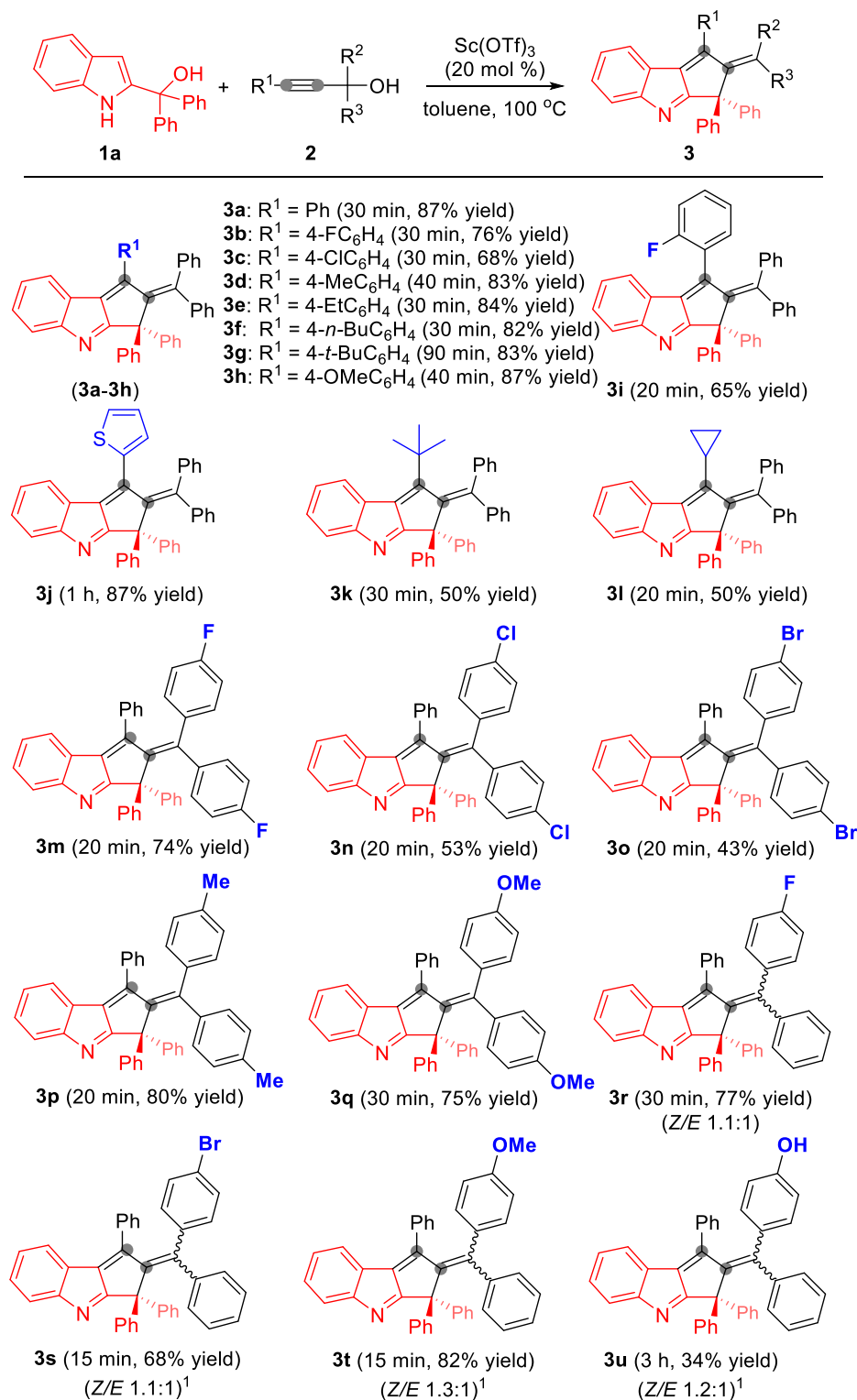


Entry	Catalyst	Solvent	Time	Yield ¹ (%)
1	Zn(OTf) ₂	DCE	2 h	62
2	Bi(OTf) ₃	DCE	3 h	70
3	Yb(OTf) ₃	DCE	2 h	64
4	Cu(OTf) ₂	DCE	2 h	63
5	AgNTf ₂	DCE	6 h	13
6	Sc(OTf) ₃	DCE	2 h	74
7	Sc(OTf) ₃	CHCl ₃	1 h	74
8	Sc(OTf) ₃	1,4-dioxane	4 h	76
9	Sc(OTf) ₃	THF	12 h	75
10	Sc(OTf) ₃	EtOH	1 h	41
11	Sc(OTf) ₃	MeCN	6 h	63
12	Sc(OTf) ₃	EA	4 h	78
13	Sc(OTf) ₃	acetone	12 h	58
14	Sc(OTf) ₃	DMF	12 h	N.R.
15	Sc(OTf) ₃	DMSO	12 h	trace
16	Sc(OTf) ₃	PhCl	40 min	78
17	Sc(OTf) ₃	toluene	30 min	80
18 ²	Sc(OTf) ₃	toluene	30 min	87
19 ³	Sc(OTf) ₃	toluene	24 h	44

Performed with **1a** (0.1 mmol) and **2a** (0.11 mmol) in the presence of catalyst (20 mol %) in solvent at 100 °C. ¹ Yield of the isolated product. ² **2a** (1.5 equiv) was used. ³ Sc(OTf)₃ (10 mol %) was used.

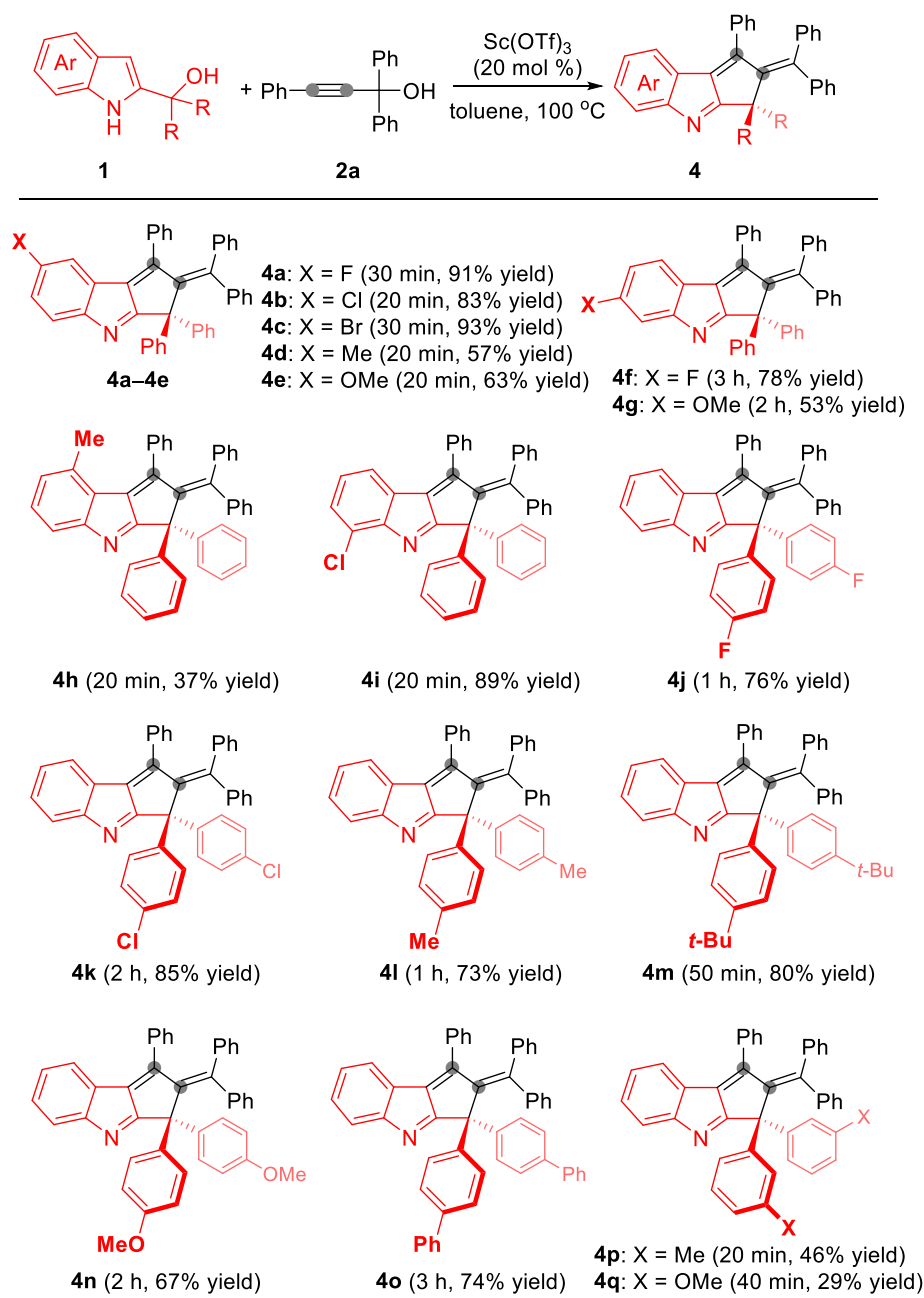
With the optimized conditions in hand, we studied the substrate scope of propargylic alcohols **2**. Various propargylic alcohols bearing different aromatic substituents gave the corresponding cyclopenta[*b*]indoles in good yields (Scheme 2). Both electron-withdrawing (Cl and F) and electron-donating (Me, Et, *n*-Bu, *t*-Bu, and MeO) groups were compatible with the reaction, affording the desired products **3a–3h** in yields ranging from 68% to 87%. Adjacent steric hindrance is unfavorable for this reaction (**2i**, 2-FC₆H₄, 65% yield). Propargylic alcohols with a heteroaryl group (2-thienyl) were also compatible with the reaction, yielding product **3g** in an 83% yield. Alkyl-substituted propargyl alcohols **2k** and **2l** (R¹ = *t*-Bu, cyclopropyl) gave the desired products **3k** and **3l** in a 50% yield. Moreover, propargylic alcohols **2m–2q**, which contained the same aromatic groups (R² = R³), were

compatible with the reaction, yielding the corresponding products **3m–3q** in moderate-to-good yields (43–80% yield). Propargylic alcohols with different aromatic groups (**2r–2u**, $R^2 \neq R^3$) provided the *E* and *Z* isomers of products **3r–3u** (*Z*:*E* = 1.1:1 to 1.3:1). Notably, when R^2 or R^3 was an alkyl group, no products were detected (for details of the examples, see the Supporting Information).



Scheme 2. Scope of propargylic alcohols. Performed at 0.2 mmol scale. ¹ Ratio of isomers determined by crude ¹H NMR.

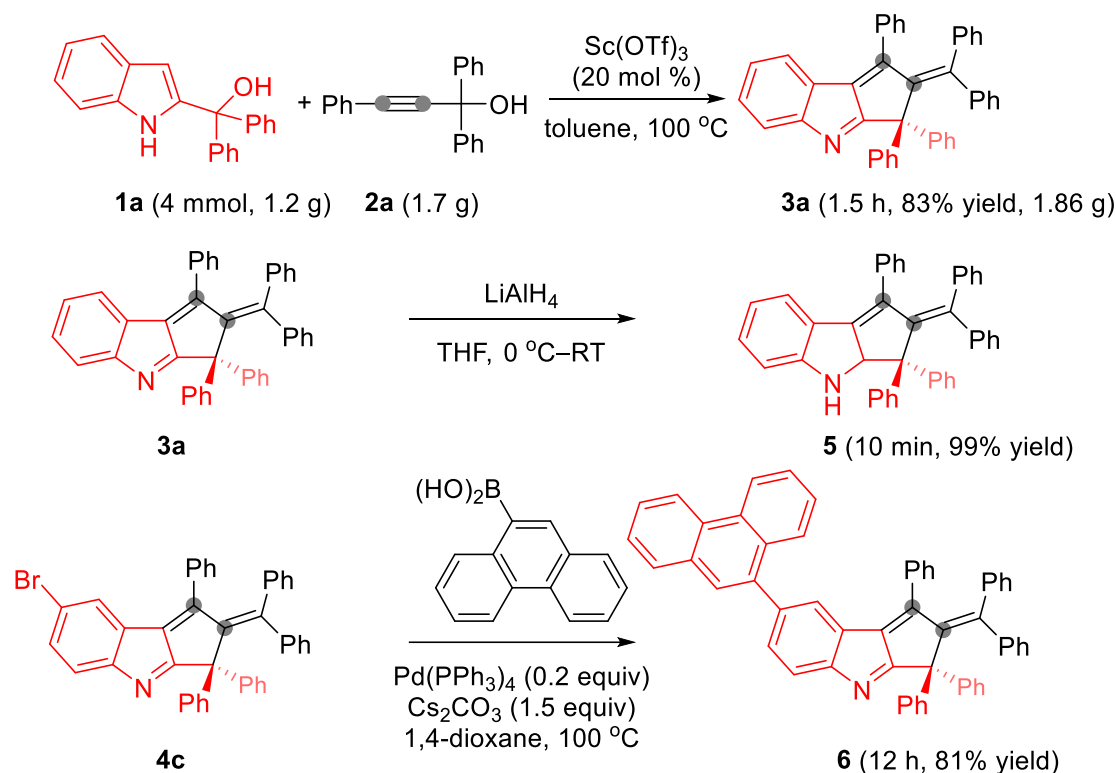
Next, we assessed the substrate scope of 2-indolylmethanols **1** in the (3+2) annulation catalyzed by $\text{Sc}(\text{OTf})_3$ (Scheme 3). A series of indolylmethanols (**1b–1j**) containing electronically diverse groups at different positions of the indole ring served as appropriate reaction partners in the tandem reaction, giving products **4a–4i** in moderate-to-good yields (37–93% yield). Moreover, indolylmethanols **1k–1r**, bearing electron-donating or electron-withdrawing Ar groups with *para*- or *meta*-substitution patterns, acted as suitable substrates, undergoing (3+2) annulation with propargylic alcohol **2a** to produce hydrobenzo[*b*]carbazoles **4j–4q** in moderate-to-high yields. Notably, when R was an alkyl group, no product was obtained.



Scheme 3. Scope of 2-indolylmethanols. Performed at 0.2 mmol scale.

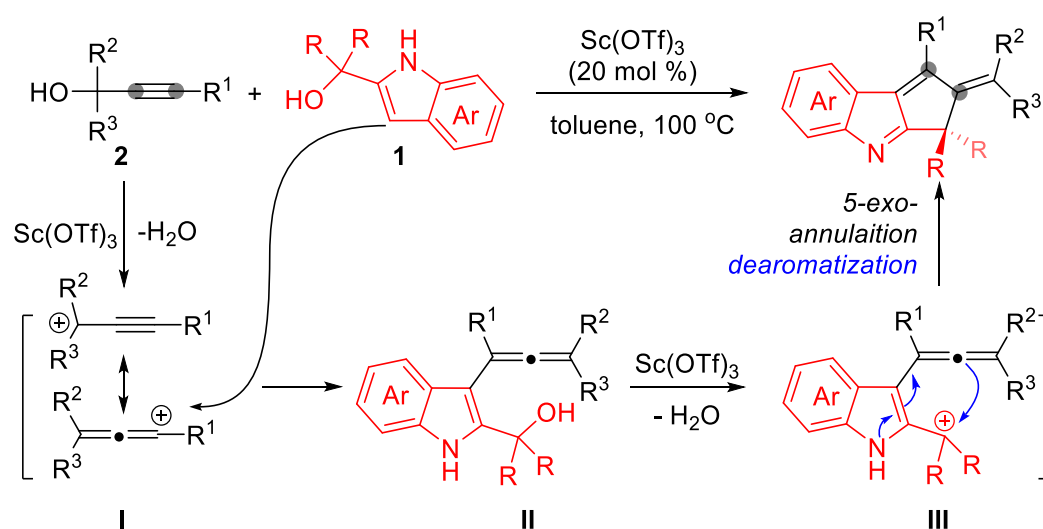
To explore the utility of this methodology, a gram-scale reaction of **3a** was carried out, affording the product **3a** in an 83% yield (Scheme 4). Treatment of **3a** with LiAlH_4 produced

compound **5** in a 99% yield. Compound **6** was obtained in an 81% yield through the Suzuki coupling reaction of **4c** and 9-phenanthrenylboronic acid.



Scheme 4. Gram-scale reaction and transformations.

A plausible mechanism for the reaction is proposed in Scheme 5. First, propargylic alcohol **2** is converted to allene carbocation **I** under Sc(OTf)_3 catalysis. This carbocation then undergoes a Friedel–Crafts-type reaction with indolylmethanol **1** to give the allene intermediate **II**. This intermediate is transformed to benzylic carbocation **III**. Intermediate **III** undergoes 5-*exo*-annulation to give the final cyclopenta[*b*]indole product.



Scheme 5. Plausible mechanism.

In conclusion, we have developed a Sc(OTf)_3 -catalyzed (3+2) annulation of 2-indolylmethanols with propargylic alcohols for the synthesis of cyclopenta[*b*]indoles. A Friedel–Crafts-type allenylation/5-*exo*-annulation cascade is involved in the reaction. This

method provides a direct and high-yield pathway to synthesize useful cyclopenta[*b*]indoles. In general, this method features easily accessible substrates with a broad scope and generality, the formation of multiple bonds with high efficiency, and easy scale-up. This work not only confirms that indolylmethanol is a good three-carbon synthon, but it also enriches the chemistry of propargyl alcohol as a two-carbon synthon.

3. Materials and Methods

Unless otherwise noted, all reagents were purchased as commercial grade (Bide, Energy Chemical, Adamas in China) and used without further purification. All products were purified by flash column chromatography using 200–300 mesh silica gel as a stationary phase. NMR spectra were recorded on a Bruker AVANCE III HD 500 device (500 MHz), using CDCl₃. Chemical shifts were denoted in ppm (δ) and calibrated by using residual undeuterated solvent CHCl₃ (7.27 ppm for ¹H NMR, 77.00 ppm for ¹³C {¹H} NMR) with Me₄Si (0.00 ppm) as an internal reference. High-resolution mass spectral analysis (HRMS) data were obtained using an Orbitrap instrument equipped with an ESI source. The 2-indolylmethanols and propargylic alcohols **2** were prepared according to the literature-reported procedures [42,43].

3.1. General Procedure for the Synthesis of **3a–4q**

Sc(OTf)₃ (0.04 mmol, 20 mol%) was added to a solution of 2-indolylmethanols **1** (0.2 mmol, 1.0 equiv) and propargylic alcohol **2** (0.3 mmol, 1.5 equiv) in toluene (2.0 mL) in a glass pressure tube (10 mL). The resulting mixture was stirred vigorously at 100 °C. The solvent was concentrated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate, giving the corresponding products **3a–4q**.

3.2. Spectroscopic Data for the Products **3a–4q**

2-(Diphenylmethylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[*b*]indole (**3a**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 95.0 mg, 87% yield, mp 270–274 °C). ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.60–7.54 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.42–7.34 (m, 4H), 7.29–7.23 (m, 1H), 7.20–7.04 (m, 9H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.88–6.80 (m, 5H), 6.77 (t, *J* = 7.8 Hz, 2H), 6.57 (d, *J* = 7.2 Hz, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 188.4, 162.9, 156.9, 152.2, 148.0, 142.4, 142.02, 141.97, 141.9, 141.8, 135.3, 130.8, 129.7, 129.6, 129.2, 129.0, 128.6, 127.9, 127.6, 127.4, 127.2, 126.7, 126.2, 125.2, 123.8, 123.0, 120.8, 62.3. IR: $\bar{\nu}$ = 2921, 2853, 1640, 1400, 1190, 1134, 1077, 756, 686, 626, 467 cm^{−1}. HRMS (ESI) *m/z*: [M + H]⁺ calcd. for C₄₂H₃₀N: 548.2373; found: 548.2371.

2-(Diphenylmethylene)-1-(4-fluorophenyl)-3,3-diphenyl-2,3-dihydrocyclopenta[*b*]indole (**3b**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 85.9 mg, 76% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.57–7.50 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.41–7.33 (m, 4H), 7.27 (td, *J* = 7.7, 1.0 Hz, 1H), 7.16–7.05 (m, 6H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.92–6.81 (m, 7H), 6.77 (t, *J* = 7.7 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 188.3, 188.2, 163.0, 161.8 (d, *J*_{C-F} = 248.1 Hz), 161.7 (d, *J*_{C-F} = 247.3 Hz), 156.5, 156.2, 152.6, 152.5, 146.6, 146.5, 142.1, 142.11, 142.09, 141.8, 141.7, 138.5, 138.0, 135.2, 132.5, 132.4, 130.94, 130.87, 130.7, 129.80, 129.77, 129.5, 129.2, 128.9, 128.7, 128.6, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 126.9, 126.4, 126.2, 125.2, 125.1, 123.8, 123.0, 120.9, 114.3, 114.19, 114.15, 114.0, 62.3. ¹⁹F NMR (471 MHz, CDCl₃) δ −111.3. IR: $\bar{\nu}$ = 2920, 2851, 1646, 1528, 1401, 1188, 1135, 1075, 757, 672, 469 cm^{−1}. HRMS (ESI) *m/z*: [M + H]⁺ calcd. for C₄₂H₂₉FN: 566.2279; found: 566.2273.

1-(*D*-chlorophenyl)-2-(diphenylmethylene)-3,3-diphenyl-2,3-dihydrocyclopenta[*b*]indole (**3c**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 79.0 mg, 68% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, *J* = 7.4 Hz, 1H), 7.60–7.53 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.42–7.34 (m, 4H), 7.30–7.22 (m, 1H), 7.21–7.05 (m, 9H), 7.03–6.99 (m, 1H), 6.98–6.92 (m, 1H), 6.88–6.80 (m, 5H), 6.77 (t, *J* = 7.8 Hz, 2H), 6.60–6.54 (m, 2H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 188.3, 163.0, 155.0, 152.0, 148.0, 142.2, 142.1, 141.69, 141.65, 134.2,

133.8, 130.7, 130.2, 130.0, 129.5, 129.1, 128.1, 127.6, 127.51, 127.47, 127.2, 126.8, 126.3, 125.0, 123.9, 122.9, 121.0, 62.3. IR: $\bar{\nu}$ = 2920, 2851, 1646, 1534, 1463, 1402, 1188, 1135, 1075, 758, 669, 474 cm⁻¹. HRMS (ESI) m/z : [M + H]⁺ calcd. for C₄₂H₂₉ClNO: 582.1983; found: 582.1978.

2-(Diphenylmethylene)-3,3-diphenyl-1-(*p*-tolyl)-2,3-dihydrocyclopenta[b]indole (**3d**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 40 min, red foam solid, 93.1 mg, 83% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, J = 7.5 Hz, 1H), 7.51–7.42 (m, 3H), 7.42–7.33 (m, 4H), 7.24 (td, J = 7.7, 1.3 Hz, 1H), 7.16–7.03 (m, 6H), 7.00 (t, J = 7.3 Hz, 1H), 6.97–6.89 (m, 3H), 6.86–6.79 (m, J = 3.0 Hz, 5H), 6.76 (t, J = 7.7 Hz, 2H), 6.57 (dd, J = 8.0, 1.4 Hz, 2H), 2.23 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 188.3, 162.9, 157.1, 152.2, 147.9, 142.4, 142.1, 141.9, 141.4, 138.6, 132.3, 130.8, 129.53, 129.45, 129.2, 129.0, 128.5, 127.5, 127.2, 127.1, 127.0, 126.6, 126.1, 125.3, 123.6, 123.0, 120.7, 62.3, 21.3. IR: $\bar{\nu}$ = 2922, 2852, 1645, 1530, 1401, 1191, 1134, 1075, 758, 672, 573, 473 cm⁻¹. HRMS (ESI) m/z : [M + H]⁺ calcd. for C₄₃H₃₂N: 562.2529; found: 562.2524.

2-(Diphenylmethylene)-1-(4-ethylphenyl)-3,3-diphenyl-2,3-dihydrocyclopenta[b]indole (**3e**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 96.6 mg, 84% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, J = 7.3 Hz, 1H), 7.52–7.44 (m, 3H), 7.42–7.32 (m, 4H), 7.25 (td, J = 7.7, 1.1 Hz, 1H), 7.17–7.03 (m, 6H), 7.01 (td, J = 7.6, 0.9 Hz, 1H), 6.99–6.90 (m, 3H), 6.86–6.79 (m, 5H), 6.76 (t, J = 7.8 Hz, 2H), 6.57 (dd, J = 8.2, 1.1 Hz, 2H), 2.53 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.6 Hz, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 188.4, 162.9, 157.1, 152.3, 147.9, 145.0, 142.3, 142.1, 141.9, 141.5, 132.5, 130.8, 129.6, 129.5, 129.21, 129.15, 127.6, 127.4, 127.21, 127.15, 126.6, 126.1, 125.3, 123.7, 123.0, 120.8, 62.3, 28.8, 15.5. IR: $\bar{\nu}$ = 2921, 2852, 1647, 1529, 1400, 1191, 1133, 1075, 759, 671, 521, 471 cm⁻¹. HRMS (ESI) m/z : [M + H]⁺ calcd. for C₄₄H₃₄N: 576.2686; found: 576.2685.

1-(4-Butylphenyl)-2-(diphenylmethylene)-3,3-diphenyl-2,3-dihydrocyclopenta[b]indole (**3f**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 98.9 mg, 82% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, J = 7.4 Hz, 1H), 7.53–7.44 (m, 3H), 7.44–7.32 (m, 4H), 7.24 (td, J = 7.7, 1.0 Hz, 1H), 7.17–7.03 (m, 6H), 7.00 (td, J = 7.6, 1.1 Hz, 1H), 6.98–6.90 (m, 3H), 6.88–6.78 (m, 5H), 6.76 (t, J = 7.8 Hz, 2H), 6.60–6.54 (m, 2H), 2.50 (t, J = 7.5 Hz, 2H), 1.58–1.44 (m, 2H), 1.33–1.22 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 188.4, 162.9, 157.2, 152.3, 147.8, 143.6, 142.4, 142.1, 141.9, 141.4, 132.5, 130.8, 129.5, 129.4, 129.2, 129.0, 128.0, 127.5, 127.2, 127.1, 126.6, 126.1, 125.3, 123.6, 123.0, 120.8, 62.3, 35.4, 33.3, 22.0, 13.9. IR: $\bar{\nu}$ = 2921, 2852, 1646, 1530, 1465, 1400, 1188, 1135, 1075, 756, 672, 470 cm⁻¹. HRMS (ESI) m/z : [M + H]⁺ calcd. for C₄₆H₃₈N: 604.2999; found: 604.2996.

1-(4-(*tert*-Butyl)phenyl)-2-(diphenylmethylene)-3,3-diphenyl-2,3-dihydrocyclopenta[b]indole (**3g**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 2 h, red foam solid, 100.0 mg, 83% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, J = 7.3 Hz, 1H), 7.53–7.45 (m, 3H), 7.41–7.34 (m, 4H), 7.32–7.22 (m, 1H), 7.18–7.04 (m, 8H), 7.03 (td, J = 7.5, 0.9 Hz, 1H), 6.98–6.91 (m, 1H), 6.84–6.73 (m, 7H), 6.57 (dd, J = 8.3, 1.3 Hz, 2H), 1.25 (s, 9H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 188.4, 162.9, 157.0, 152.4, 151.6, 147.8, 142.3, 142.1, 141.9, 141.4, 132.1, 130.8, 129.6, 129.5, 129.2, 129.0, 127.6, 127.2, 126.6, 126.1, 125.4, 124.8, 123.7, 123.1, 120.8, 62.3, 34.6, 31.0. IR: $\bar{\nu}$ = 2921, 2852, 1647, 1399, 1188, 1135, 1075, 757, 672, 576, 471 cm⁻¹. HRMS (ESI) m/z : [M + H]⁺ calcd. For C₄₆H₃₈N: 604.2999; found: 604.2998.

2-(Diphenylmethylene)-1-(4-methoxyphenyl)-3,3-diphenyl-2,3-dihydrocyclopenta[b]indole (**3h**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 40 min, red foam solid, 100.4 mg, 87% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, J = 7.5 Hz, 1H), 7.56–7.51 (m, 2H), 7.49 (d, J = 7.8 Hz, 1H), 7.39–7.34 (m, 4H), 7.30–7.23 (m, 1H), 7.15–7.04 (m, 6H), 7.03 (td, J = 7.6, 0.9 Hz, 1H), 6.99–6.91 (m, 1H), 6.90–6.79 (m, 5H), 6.77 (t, J = 7.8 Hz, 2H), 6.72–6.66 (m, 2H), 6.57 (dd, J = 8.1, 1.2 Hz, 2H), 3.76 (s, 3H). ¹³C {¹H} NMR (126 MHz, CDCl₃) δ 188.2, 162.9, 159.8, 156.8, 152.3, 147.9, 142.5, 142.2, 142.0, 140.9, 130.9, 130.8, 129.6, 129.4, 129.3, 127.7, 127.6, 127.3, 127.20, 127.17, 126.7, 126.1, 125.4, 123.6, 122.9, 120.8, 113.5, 62.4, 55.3. IR: $\bar{\nu}$ = 3117, 2920, 2852, 1647, 1529, 1401, 1188, 1135, 1074, 757, 670, 472 cm⁻¹. HRMS (ESI) m/z : [M + H]⁺ calcd. for C₄₃H₃₂NO: 578.2478; found: 578.2473.

2-(Diphenylmethylene)-1-(2-fluorophenyl)-3,3-diphenyl-2,3-dihydrocyclopenta[b]indole (**3i**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 73.4 mg, 65%

yield). ^1H NMR (500 MHz, CDCl_3) δ 7.56 (td, $J = 7.4, 1.8$ Hz, 2H), 7.50–7.30 (m, 5H), 7.30–7.25 (m, 1H), 7.20–7.07 (m, 7H), 7.07–6.97 (m, 2H), 6.97–6.81 (m, 6H), 6.80–6.72 (m, 3H), 6.57 (d, $J = 7.5$ Hz, 2H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.5, 163.0, 158.1 (d, $J_{\text{C-F}} = 249.8$ Hz), 151.7, 149.9, 147.7, 143.2, 141.7, 141.6, 130.8, 130.7, 130.44, 130.4, 130.3, 129.9, 129.6, 128.9, 128.4, 127.60, 127.42, 127.2, 126.6, 126.2, 125.0, 123.9, 123.8, 123.63, 123.60, 123.4, 120.9, 115.9, 115.8, 62.2. ^{19}F NMR (471 MHz, CDCl_3) δ -108.4. IR: $\bar{\nu} = 2920, 2851, 1646, 1528, 1399, 1188, 1135, 1075, 756, 672, 471$ cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{29}\text{FN}$ 566.2279; found: 566.2276.

2-(Diphenylmethylene)-3,3-diphenyl-1-(thiophen-2-yl)-2,3-dihydrocyclopenta[b]indole (**3j**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 1 h, red foam solid, 96.2 mg, 87% yield). ^1H NMR (500 MHz, CDCl_3) δ 8.11 (d, $J = 7.6$ Hz, 1H), 7.50 (d, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 7.3$ Hz, 4H), 7.34–7.24 (m, 3H), 7.14–7.02 (m, 7H), 6.99–6.90 (m, 6H), 6.81–6.73 (m, 3H), 6.60 (d, $J = 8.0$ Hz, 2H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.3, 162.7, 152.5, 149.0, 147.6, 143.2, 142.2, 141.9, 139.8, 136.7, 131.8, 130.6, 129.7, 129.5, 128.6, 127.6, 127.4, 127.3, 127.1, 126.9, 126.2, 124.8, 123.8, 123.7, 120.8, 62.9. IR: $\bar{\nu} = 2923, 2853, 1693, 1648, 1528, 1399, 1192, 1134, 1075, 757, 671, 474$ cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{40}\text{H}_{28}\text{NS}$: 554.1937; found: 554.1934.

1-(tert-Butyl)-2-(diphenylmethylene)-3,3-diphenyl-2,3-dihydrocyclopenta[b]indole (**3k**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 52.6 mg, 50% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, $J = 7.5$ Hz, 1H), 7.53 (d, $J = 7.7$ Hz, 1H), 7.42–7.23 (m, 7H), 7.23–6.86 (m, 12H), 6.74 (s, 3H), 1.31 (s, 9H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.5, 176.7, 162.3, 153.8, 146.7, 145.6, 143.0, 142.6, 142.2, 132.1, 130.1, 128.72, 128.70, 128.24, 128.16, 127.4, 126.9, 126.0, 125.6, 125.5, 123.4, 120.7, 65.7, 37.4, 31.0. IR: $\bar{\nu} = 2921, 2852, 1647, 1529, 1401, 1192, 1134, 1074, 758, 671, 566, 468$ cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{40}\text{H}_{34}\text{N}$: 528.2686; found: 528.2682.

1-Cyclopropyl-2-(diphenylmethylene)-3,3-diphenyl-2,3-dihydrocyclopenta[b]indole (**3l**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 51.1 mg, 50% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz, 1H), 7.47 (d, $J = 7.7$ Hz, 1H), 7.34–7.16 (m, 10H), 7.15–6.99 (m, 7H), 6.98–6.88 (m, 1H), 6.76 (t, $J = 7.8$ Hz, 2H), 6.58–6.54 (m, 2H), 1.49–1.31 (m, 3H), 0.99–0.82 (m, 2H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.4, 167.1, 162.3, 154.6, 145.8, 144.0, 142.0, 141.8, 138.7, 130.4, 129.6, 129.2, 128.6, 128.02, 128.00, 127.5, 127.2, 126.7, 126.0, 124.4, 123.8, 123.5, 120.7, 62.1, 16.1, 13.0. IR: $\bar{\nu} = 2921, 2852, 1646, 1529, 1402, 1191, 1134, 1075, 758, 671, 563, 471$ cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{39}\text{H}_{30}\text{N}$: 512.2373; found: 512.2368.

2-(Bis(4-fluorophenyl)methylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**3m**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 86.2 mg, 74% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 7.3$ Hz, 1H), 7.57–7.52 (m, 2H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.42–7.34 (m, 4H), 7.31–7.08 (m, 11H), 7.05–6.98 (m, 1H), 6.82–6.76 (m, 2H), 6.59–6.43 (m, 6H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.2, 163.0, 161.9 (d, $J_{\text{C-F}} = 248.5$ Hz), 161.8 (d, $J_{\text{C-F}} = 247.4$ Hz), 155.9, 153.0, 145.2, 142.3, 141.7, 138.3, 137.8, 135.1, 132.5, 132.4, 131.0, 130.9, 129.9, 129.5, 128.9, 128.8, 128.1, 127.7, 126.5, 125.1, 123.9, 123.1, 120.9, 114.5, 114.33, 114.28, 114.2, 62.3. ^{19}F NMR (471 MHz, CDCl_3) δ -113.7, -114.6. IR: $\bar{\nu} = 2921, 2851, 1647, 1528, 1400, 1192, 1134, 1075, 757, 671, 471$ cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{28}\text{F}_2\text{N}$: 584.2184; found: 584.2178.

2-(Bis(4-chlorophenyl)methylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**3n**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 65.2 mg, 53% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, $J = 7.4$ Hz, 1H), 7.55–7.49 (m, 2H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.41–7.33 (m, 4H), 7.27 (td, $J = 7.7, 1.1$ Hz, 1H), 7.24–7.19 (m, 3H), 7.19–7.09 (m, 6H), 7.02 (td, $J = 7.6, 0.9$ Hz, 1H), 6.83–6.70 (m, 6H), 6.52–6.46 (m, 2H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.0, 163.1, 155.5, 153.5, 144.6, 142.5, 141.5, 140.3, 140.0, 134.9, 133.5, 133.1, 131.9, 130.5, 130.1, 129.5, 128.9, 128.8, 128.2, 127.8, 127.6, 127.5, 126.5, 125.1, 124.0, 123.2, 121.0, 62.3. IR: $\bar{\nu} = 3118, 2920, 2850, 1646, 1528, 1402, 1191, 1136, 1075, 755, 670, 470$ cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{28}\text{Cl}_2\text{N}$: 616.1593; found: 616.1589.

2-(Bis(4-bromophenyl)methylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**3o**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 60.4 mg, 43% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, $J = 7.4$ Hz, 1H), 7.55–7.45 (m, 3H), 7.40–7.32 (m, 4H), 7.31–7.26 (m, 1H), 7.24–7.19 (m, 3H), 7.20–7.08 (m, 6H), 7.05–7.01 (m, 1H), 6.98–6.88 (m, 4H), 6.68 (d, $J = 8.4$ Hz, 2H), 6.43 (d, $J = 8.5$ Hz, 2H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 187.9, 163.1, 155.4, 153.5, 144.6, 142.6, 141.5, 140.6, 140.3, 134.9, 132.1, 130.7, 130.52, 130.46, 130.1, 129.5, 128.9, 128.8, 128.2, 127.8, 126.6, 125.1, 124.0, 123.2, 121.9, 121.3, 121.0, 62.3. IR: $\bar{\nu} = 2920, 2851, 1647, 1529, 1401, 1195, 1135, 1073, 756, 670, 472\text{ cm}^{-1}$. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{28}\text{Br}_2\text{N}$: 706.0563; found: 706.0561.

2-(Di-*p*-tolylmethylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**3p**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 92.0 mg, 80% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, $J = 7.5$ Hz, 1H), 7.60–7.51 (m, 2H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.38 (d, $J = 7.1$ Hz, 4H), 7.24 (td, $J = 7.7, 1.2$ Hz, 1H), 7.19–7.04 (m, 9H), 6.99 (t, $J = 7.5$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 2H), 6.59 (t, $J = 7.8$ Hz, 4H), 6.46 (d, $J = 8.0$ Hz, 2H), 2.16 (s, 3H), 2.04 (s, 3H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.5, 162.9, 157.3, 151.7, 148.4, 142.0, 141.5, 139.7, 139.3, 137.1, 136.5, 135.5, 130.8, 129.6, 129.4, 129.2, 129.0, 128.1, 127.9, 127.8, 127.5, 126.1, 125.3, 123.6, 122.9, 120.7, 62.3, 21.0, 20.9. IR: $\bar{\nu} = 3122, 2920, 2852, 1648, 1527, 1401, 1190, 1136, 1074, 756, 671, 471\text{ cm}^{-1}$. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{44}\text{H}_{34}\text{N}$: 576.2686; found: 576.2678.

2-(Bis(4-methoxyphenyl)methylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**3q**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 91.0 mg, 75% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, $J = 7.5$ Hz, 1H), 7.61–7.55 (m, 2H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.43–7.34 (m, 4H), 7.24 (td, $J = 7.7, 1.2$ Hz, 1H), 7.19 (t, $J = 7.5$ Hz, 2H), 7.17–7.05 (m, 7H), 7.00 (td, $J = 7.5, 1.0$ Hz, 1H), 6.75 (d, $J = 8.7$ Hz, 2H), 6.51 (d, $J = 8.7$ Hz, 2H), 6.38–6.29 (m, 4H), 3.65 (s, 3H), 3.58 (s, 3H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.6, 162.7, 158.9, 158.7, 157.5, 151.4, 147.8, 142.1, 141.1, 137.6, 135.5, 135.4, 134.8, 132.4, 131.6, 130.8, 129.5, 129.3, 129.0, 128.5, 128.4, 128.3, 128.2, 127.9, 127.5, 127.3, 126.1, 125.3, 123.6, 122.8, 120.7, 113.8, 113.4, 112.7, 112.5, 62.4, 55.10, 55.07. IR: $\bar{\nu} = 2921, 2851, 1649, 1529, 1400, 1195, 1135, 1073, 756, 669, 481\text{ cm}^{-1}$. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{44}\text{H}_{34}\text{NO}_2$: 608.2584; found: 608.2578.

2-((4-Fluorophenyl)(phenyl)methylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**3r**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 87.0 mg, 77% yield, Z/E = 1.1:1) ^1H NMR (500 MHz, CDCl_3) δ 7.64 (dd, $J = 7.5, 2.8$ Hz, 1H), 7.61–7.52 (m, 2H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.45–7.34 (m, 4H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.25–7.05 (m, 9H), 7.04–6.93 (m, 2H), 6.83 (s, 2H), 6.83–6.75 (m, 2H), 6.60–6.42 (m, 4H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.3, 188.2, 162.99, 162.97, 161.8 (d, $J_{\text{C-F}} = 248.1$ Hz), 161.7 ($J_{\text{C-F}} = 247.3$ Hz), 156.5, 156.2, 152.6, 152.5, 146.6, 146.5, 142.2, 142.13, 142.11, 141.8, 141.7, 138.50, 138.47, 138.04, 138.02, 135.2, 132.5, 132.4, 131.0, 130.9, 130.8, 129.81, 129.79, 129.5, 129.2, 128.9, 128.7, 128.6, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.9, 126.4, 126.3, 125.18, 125.16, 123.9, 123.1, 120.9, 114.3, 114.20, 114.15, 114.0, 62.3. ^{19}F NMR (471 MHz, CDCl_3) δ -114.0, -114.9. IR: $\bar{\nu} = 2920, 2851, 1647, 1531, 1401, 1188, 1134, 1075, 758, 672, 471\text{ cm}^{-1}$. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{29}\text{FN}$: 566.2279; found: 566.2271.

2-((4-Bromophenyl)(phenyl)methylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**3s**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 15 min, red foam solid, 85.1 mg, 68% yield, Z/E = 1.1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.64 (t, $J = 6.6$ Hz, 1H), 7.58–7.50 (m, 2H), 7.48 (dd, $J = 7.7, 1.9$ Hz, 1H), 7.43–7.33 (m, 4H), 7.26 (td, $J = 7.7, 1.0$ Hz, 1H), 7.25–7.05 (m, 9H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.99–6.88 (m, 3H), 6.83 (s, 2H), 6.78 (t, $J = 7.8$ Hz, 1H), 6.73–6.65 (m, 1H), 6.58–6.52 (m, 1H), 6.45 (d, $J = 8.5$ Hz, 1H). ^{13}C { ^1H } NMR (126 MHz, CDCl_3) δ 188.2, 188.1, 163.0, 156.3, 156.0, 152.8, 152.8, 146.2, 142.3, 141.7, 141.7, 141.4, 141.3, 140.9, 135.1, 132.2, 130.8, 130.7, 130.4, 130.3, 129.9, 129.5, 129.2, 128.9, 128.7, 128.1, 127.9, 127.8, 127.7, 127.5, 127.5, 127.3, 126.9, 126.5, 126.3, 125.2, 123.9, 123.1, 121.7, 121.1, 120.9, 62.3. IR: $\bar{\nu} = 2920, 2852, 1646, 1531, 1464, 1395, 1190, 1134, 1075, 759, 516, 468\text{ cm}^{-1}$. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{29}\text{BrNO}$: 626.1478; found: 626.1469.

2-((4-Methoxyphenyl)(phenyl)methylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**3t**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 15 min, red foam solid, 94.6 mg, 82% yield, Z/E = 1.3:1). ^1H NMR (500 MHz, CDCl_3) δ 7.65 (t, J = 7.5 Hz, 1H), 7.60–7.54 (m, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.44–7.33 (m, 4H), 7.25 (td, J = 7.7, 1.1 Hz, 1H), 7.24–7.04 (m, 9H), 7.04–6.93 (m, 2H), 6.88–6.80 (m, 3H), 6.81–6.72 (m, 2H), 6.57 (dd, J = 8.2, 1.3 Hz, 1H), 6.53–6.47 (m, 1H), 6.38–6.28 (m, 2H), 3.71 (s, 3H), 3.64 (s, 3H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 188.54, 188.50, 162.9, 158.9, 158.7, 157.1, 152.1, 151.6, 148.0, 147.8, 142.7, 142.1, 142.0, 141.9, 141.6, 135.5, 135.4, 135.1, 134.7, 132.2, 130.9, 130.7, 129.54, 129.51, 129.3, 129.0, 128.5, 128.4, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 127.1, 126.7, 126.2, 126.1, 125.28, 125.25, 123.7, 122.9, 120.8, 112.8, 112.6, 62.4, 62.3, 55.10, 55.08. IR: $\bar{\nu}$ = 2920, 2852, 1645, 1532, 1465, 1395, 1189, 1134, 1075, 758, 672, 468 cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{43}\text{H}_{32}\text{NO}$: 578.2478; found: 578.2470.

4-(Phenyl(1,3,3-triphenylcyclopenta[b]indol-2(3H)-ylidene)methyl)phenol (**3u**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 3 h, red foam solid, 38.3mg, 34% yield, Z/E = 1.2:1). ^1H NMR (500 MHz, CDCl_3) δ 7.71–7.54 (m, 5H), 7.52–7.45 (m, 2H), 7.45–7.40 (m, 2H), 7.38–7.32 (m, 2H), 7.32–7.24 (m, 5H), 7.22–7.15 (m, 2H), 7.09–6.95 (m, 4H), 6.94–6.86 (m, 1H), 6.85–6.74 (m, 1H), 6.72–6.66 (m, 1H), 6.58–6.39 (m, 3H), 4.55 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 153.4, 149.0, 145.7, 145.5, 142.8, 142.3, 141.2, 139.0, 134.3, 133.5, 128.02, 127.96, 127.93, 127.85, 127.4, 127.20, 127.15, 127.1, 126.4, 126.2, 125.6, 122.1, 120.6, 119.9, 115.9, 114.3, 111.0, 82.5, 81.5. IR: $\bar{\nu}$ = 2920, 2851, 1646, 1528, 1401, 1193, 1134, 1073, 755, 670, 471 cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{29}\text{NO}$: 564.2319; found: 564.2322.

2-(Biphenylmethylene)-7-fluoro-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**4a**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 102.8 mg, 91% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.57–7.48 (m, 2H), 7.42–7.33 (m, 5H), 7.32 (dd, J = 8.6, 2.5 Hz, 1H), 7.22–7.06 (m, 9H), 7.00–6.92 (m, 2H), 6.88–6.81 (m, 5H), 6.78 (t, J = 7.8 Hz, 2H), 6.57 (d, J = 7.2 Hz, 2H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 188.38, 188.36, 159.9 ($J_{\text{C-F}}$ = 240.8 Hz), 159.02, 159.01, 158.0, 152.0, 149.0, 142.2, 141.8, 141.7, 141.6, 141.5, 135.0, 130.8, 129.5, 129.2, 128.9, 128.8, 128.1, 127.7, 127.5, 127.4, 127.2, 126.9, 126.3, 126.23, 126.15, 121.14, 121.07, 116.0, 115.8, 110.2, 110.0, 62.4. ^{19}F NMR (471 MHz, CDCl_3) δ -119.2. IR: $\bar{\nu}$ = 2920, 2851, 1645, 1531, 1407, 1188, 1135, 1073, 755, 672, 470 cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{29}\text{FN}$: 566.2279; found: 566.2275.

3-Chloro-2-(diphenylmethylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**4b**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 96.4 mg, 83% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.57 (s, 1H), 7.54 (d, J = 7.3 Hz, 2H), 7.43–7.31 (m, 5H), 7.27–7.05 (m, 10H), 7.00–6.92 (m, 1H), 6.84 (s, 5H), 6.81–6.73 (m, 2H), 6.60–6.51 (m, 2H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 188.7, 161.3, 158.5, 152.0, 149.3, 142.2, 141.8, 141.6, 141.1, 135.0, 130.8, 129.5, 129.3, 129.20, 129.17, 129.0, 128.9, 128.1, 127.7, 127.6, 127.4, 127.2, 126.9, 126.6, 126.3, 122.9, 121.5, 62.4. IR: $\bar{\nu}$ = 2920, 2851, 1646, 1530, 1465, 1404, 1190, 1134, 1074, 759, 672, 470 cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{29}\text{ClN}$: 582.1983; found: 582.1979.

7-Bromo-2-(diphenylmethylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**4c**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 30 min, red foam solid, 116.4 mg, 93% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, J = 1.6 Hz, 1H), 7.57–7.51 (m, 2H), 7.39–7.30 (m, 6H), 7.19 (t, J = 7.5 Hz, 2H), 7.17–7.05 (m, 7H), 6.95 (t, J = 7.5 Hz, 1H), 6.87–6.80 (m, 5H), 6.77 (t, J = 7.8 Hz, 2H), 6.57 (dd, J = 8.0, 1.1 Hz, 2H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 188.5, 161.6, 158.6, 152.0, 149.3, 142.1, 141.7, 141.5, 140.9, 134.9, 132.0, 130.8, 129.4, 129.1, 129.0, 128.8, 128.1, 127.7, 127.5, 127.4, 127.2, 127.1, 126.9, 126.3, 125.7, 121.9, 117.0, 62.4. IR: $\bar{\nu}$ = 2920, 2850, 1646, 1529, 1464, 1400, 1188, 1135, 1074, 758, 672, 578, 470 cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{42}\text{H}_{29}\text{BrN}$: 626.1478; found: 626.1472.

2-(diphenylmethylene)-7-methyl-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**4d**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 64.0 mg, 57% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.60–7.52 (m, 2H), 7.43 (s, 1H), 7.41–7.32 (m, 5H), 7.17 (t, J = 7.5 Hz, 2H), 7.15–7.04 (m, 8H), 6.94 (t, J = 7.5 Hz, 1H), 6.88–6.79 (m, 5H), 6.76 (t, J = 7.8 Hz, 2H), 6.57 (dd, J = 8.1, 1.1 Hz, 2H), 2.27 (s, 3H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 187.7, 160.9, 156.2, 152.2, 147.6, 142.4, 142.1, 142.00, 141.95, 135.4, 133.4, 130.8, 130.4, 129.5,

129.2, 129.0, 128.5, 127.9, 127.6, 127.30, 127.26, 127.2, 126.7, 126.1, 125.3, 123.6, 120.4, 62.2, 21.4. IR: $\bar{\nu}$ = 2920, 2851, 1646, 1530, 1405, 1190, 1133, 1074, 758, 673, 519, 469 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{43}\text{H}_{32}\text{N}$: 562.2529; found: 562.2524.

2-(Diphenylmethylene)-7-methoxy-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**4e**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 72.6 mg, 63% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.54 (d, J = 7.2 Hz, 2H), 7.37 (d, J = 6.9 Hz, 5H), 7.22 (d, J = 2.5 Hz, 1H), 7.19–7.05 (m, 9H), 6.98–6.92 (m, 1H), 6.88–6.79 (m, 6H), 6.77 (t, J = 7.8 Hz, 2H), 6.59–6.53 (m, 2H), 3.73 (s, 3H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 187.0, 156.8, 152.2, 142.4, 142.0, 135.3, 130.8, 129.5, 129.2, 128.9, 128.6, 127.9, 127.6, 127.4, 127.2, 126.7, 126.2, 120.8, 114.3, 109.8, 62.2, 55.8. IR: $\bar{\nu}$ = 2921, 2821, 1646, 1530, 1399, 1187, 1134, 1074, 760, 672, 468 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{43}\text{H}_{32}\text{NO}$: 578.2478; found: 578.2472.

2-(Diphenylmethylene)-6-fluoro-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**4f**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 3 h, red foam solid, 88.0 mg, 78% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.63–7.49 (m, 3H), 7.39–7.33 (m, 4H), 7.22–7.07 (m, 10H), 6.96 (t, J = 7.4 Hz, 1H), 6.84 (s, 4H), 6.78 (t, J = 7.7 Hz, 2H), 6.75–6.67 (m, 1H), 6.60–6.53 (m, 2H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 190.3, 165.0, 164.7, 164.6, 164.0 (d, $J_{\text{C-F}}$ = 248.2 Hz), 156.8, 151.9, 148.3, 142.3, 141.9, 141.6, 141.0, 135.2, 130.8, 129.5, 129.2, 128.9, 128.7, 128.0, 127.7, 127.5, 127.4, 127.2, 126.8, 126.4, 123.6, 123.5, 121.4, 110.7, 110.5, 108.8, 108.6, 62.4. ^{19}F NMR (471 MHz, CDCl_3) δ -109.8. IR: $\bar{\nu}$ = 2921, 2851, 1647, 1530, 1400, 1193, 1133, 1073, 757, 671, 567, 519 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{42}\text{H}_{29}\text{FN}$: 566.2279; found: 566.2273.

2-(Diphenylmethylene)-6-methoxy-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**4g**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 2 h, red foam solid, 61.0 mg, 53% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.57–7.51 (m, 3H), 7.41–7.35 (m, 4H), 7.19–7.05 (m, 10H), 6.94 (t, J = 7.4 Hz, 1H), 6.88–6.79 (m, 5H), 6.77 (t, J = 7.7 Hz, 2H), 6.57 (d, J = 8.2 Hz, 3H), 3.78 (s, 3H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 189.9, 165.0, 161.7, 154.4, 152.0, 146.7, 142.5, 142.1, 141.9, 141.7, 135.5, 130.8, 129.6, 129.3, 128.9, 128.8, 128.5, 128.4, 128.33, 128.27, 127.8, 127.6, 127.3, 127.22, 127.19, 127.16, 126.64, 126.59, 126.2, 123.7, 117.9, 110.3, 106.3, 62.3, 55.5. IR: $\bar{\nu}$ = 2920, 2851, 1646, 1531, 1400, 1189, 1135, 1074, 759, 671, 471 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{43}\text{H}_{32}\text{NO}$: 578.2478; found: 578.2474.

2-(diphenylmethylene)-8-methyl-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**4h**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 1 h, red foam solid, 41.2 mg, 37% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.43–7.35 (m, 4H), 7.30 (d, J = 7.7 Hz, 1H), 7.23–7.10 (m, 9H), 7.05–6.98 (m, 3H), 6.91–6.86 (m, 1H), 6.85–6.81 (m, 3H), 6.80–6.76 (m, 2H), 6.75–6.68 (m, 3H), 6.56–6.49 (m, 2H), 1.57 (s, 3H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 188.7, 163.1, 155.64, 153.58, 148.1, 144.4, 142.4, 142.1, 141.8, 136.7, 135.7, 130.2, 129.6, 129.5, 129.5, 128.3, 127.6, 127.5, 127.2, 126.7, 126.6, 126.5, 126.3, 125.1, 118.3, 61.4, 21.8. IR: $\bar{\nu}$ = 2937, 2924, 1553, 1490, 1441, 1392, 1337, 785, 695, 609, 537 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{43}\text{H}_{32}\text{N}$: 562.2529; found: 562.2519.

5-chloro-2-(diphenylmethylene)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**4i**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 2 h, red foam solid, 103 mg, 89% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.60–7.48 (m, 3H), 7.42–7.36 (m, 4H), 7.28–7.23 (m, 2H), 7.21–7.05 (m, 9H), 7.00–6.90 (m, 2H), 6.84 (s, 5H), 6.78 (t, J = 7.7 Hz, 2H), 6.58–6.52 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 188.7, 159.2, 158.6, 152.3, 149.2, 142.3, 142.0, 141.8, 141.6, 135.0, 130.8, 129.9, 129.7, 129.2, 129.0, 128.8, 128.0, 127.6, 127.5, 127.4, 127.22, 127.17, 126.9, 126.31, 125.29, 124.4, 121.2, 62.7. IR: $\bar{\nu}$ = 2980, 2977, 1631, 1537, 1393, 1337, 1127, 748, 695, 488, 436 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{42}\text{H}_{29}\text{ClN}$: 582.1983; found: 582.1973.

2-(Diphenylmethylene)-3,3-bis(4-fluorophenyl)-1-phenyl-2,3-dihydrocyclopenta[b]indole (**4j**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 1 h, red foam solid, 88.6 mg, 76% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.66 (d, J = 7.5 Hz, 1H), 7.56–7.52 (m, 2H), 7.49 (d, J = 7.8 Hz, 1H), 7.38–7.26 (m, 5H), 7.20–7.15 (m, 2H), 7.14–7.11 (m, 1H), 7.07–6.98 (m, 2H), 6.89–6.79 (m, 11H), 6.60–6.54 (m, 2H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 187.9, 162.8, 161.3 (d, $J_{\text{C-F}}$ = 245.9 Hz), 156.6, 151.8, 148.2, 142.0, 141.9, 141.7, 137.60, 137.57, 135.0, 131.7, 131.0, 130.9, 130.7, 129.9, 129.0, 128.9, 128.8, 128.6, 128.24, 128.21, 127.9, 127.6, 127.5, 127.44, 127.38, 127.3, 127.1, 126.0, 125.1, 124.0, 123.1, 120.9, 114.6, 114.4, 61.0. ^{19}F NMR (471 MHz, CDCl_3) δ

-116.2. IR: $\bar{\nu}$ = 2922, 2852, 1646, 1529, 1399, 1190, 1134, 757, 672, 572, 470 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{42}\text{H}_{28}\text{F}_2\text{N}$: 584.2184; found: 584.2178.

3,3-Bis(4-chlorophenyl)-2-(diphenylmethylene)-1-phenyl-2,3-dihydrocyclopenta[b]indole (4k): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 2 h, red foam solid, 104.4 mg, 85% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.66 (d, J = 7.6 Hz, 1H), 7.57–7.51 (m, 2H), 7.49 (d, J = 7.8 Hz, 1H), 7.32–7.25 (m, 5H), 7.17 (t, J = 7.3 Hz, 2H), 7.15–7.07 (m, 5H), 7.07–6.98 (m, 2H), 6.88–6.80 (m, 7H), 6.57 (d, J = 7.3 Hz, 2H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 187.2, 162.5, 156.8, 151.2, 148.6, 141.79, 141.75, 140.1, 134.9, 132.4, 130.7, 130.0, 129.0, 128.9, 128.0, 127.9, 127.6, 127.44, 127.38, 127.2, 125.0, 124.2, 123.1, 120.9, 61.3. IR: $\bar{\nu}$ = 2919, 2851, 1644, 1540, 1406, 1260, 1190, 1133, 1076, 756, 633, 477 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{42}\text{H}_{28}\text{Cl}_2\text{N}$: 616.1593; found: 616.1589.

2-(Diphenylmethylene)-1-phenyl-3,3-di-*p*-tolyl-2,3-dihydrocyclopenta[b]indole (4l): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 1 h min, red foam solid, 83.8 mg, 73% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.62 (d, J = 7.6 Hz, 1H), 7.57–7.52 (m, 2H), 7.47 (d, J = 7.7 Hz, 1H), 7.29–7.20 (m, 6H), 7.15 (t, J = 7.4 Hz, 2H), 7.12–7.05 (m, 1H), 6.99 (td, J = 7.6, 0.9 Hz, 1H), 6.97–6.90 (m, 5H), 6.86–6.80 (m, 5H), 6.77 (t, J = 7.8 Hz, 2H), 6.58 (dd, J = 8.2, 1.1 Hz, 2H), 2.24 (s, 6H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 188.7, 163.1, 156.6, 152.4, 147.5, 142.4, 142.1, 141.9, 138.9, 135.6, 135.4, 130.8, 129.6, 129.4, 129.2, 128.9, 128.5, 128.3, 127.8, 127.3, 127.2, 127.0, 126.6, 125.3, 123.6, 122.9, 120.8, 61.8, 20.9. IR: $\bar{\nu}$ = 2921, 2852, 1645, 1542, 1398, 1266, 1187, 1135, 1077, 756, 631, 474 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{44}\text{H}_{34}\text{N}$: 576.2686; found: 576.2684.

3,3-Bis(4-*tert*-butylphenyl)-2-(diphenylmethylene)-1-phenyl-2,3-dihydrocyclopenta[b]indole (4m): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 50 min, red foam solid, 105.4 mg, 80% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 7.3 Hz, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.32–7.24 (m, 5H), 7.20–7.14 (m, 2H), 7.13–7.08 (m, 5H), 7.01 (t, J = 7.5 Hz, 1H), 6.93 (t, J = 7.4 Hz, 1H), 6.88–6.79 (m, 5H), 6.75 (t, J = 7.7 Hz, 2H), 6.60–6.53 (m, 2H), 1.26 (s, 18H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 188.8, 163.1, 156.7, 152.6, 148.6, 147.4, 142.5, 142.1, 141.9, 138.8, 135.5, 130.8, 129.6, 129.2, 129.0, 128.5, 127.8, 127.3, 127.2, 127.0, 126.4, 125.4, 124.4, 123.6, 123.0, 120.8, 61.8, 34.2, 31.3. IR: $\bar{\nu}$ = 2920, 2853, 1646, 1529, 1398, 1188, 1135, 1076, 755, 674, 472 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{50}\text{H}_{46}\text{N}$: 660.3625; found: 660.3621.

2-(Diphenylmethylene)-3,3-bis(4-methoxyphenyl)-1-phenyl-2,3-dihydrocyclopenta[b]indole (4n): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 2 h, red foam solid, 81.2 mg, 67% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.63 (d, J = 7.4 Hz, 1H), 7.57–7.52 (m, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.30–7.24 (m, 6H), 7.16 (t, J = 7.4 Hz, 2H), 7.13–7.05 (m, 1H), 7.03–6.92 (m, 2H), 6.87–6.77 (m, 7H), 6.70–6.63 (m, 4H), 6.60 (dd, J = 8.2, 1.3 Hz, 2H), 3.73 (s, 6H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 188.8, 163.1, 157.8, 156.5, 152.5, 147.5, 142.4, 142.1, 141.8, 135.4, 134.2, 130.8, 130.5, 129.6, 129.2, 128.9, 128.5, 127.9, 127.30, 127.25, 127.1, 126.7, 125.3, 123.7, 123.0, 120.8, 113.1, 61.0, 55.2. IR: $\bar{\nu}$ = 2919, 2850, 1643, 1533, 1399, 1264, 1190, 1134, 1077, 629, 471 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{44}\text{H}_{34}\text{NO}_2$: 608.2584; found: 608.2580.

3,3-Di([1,1'-biphenyl]-4-yl)-2-(diphenylmethylene)-1-phenyl-2,3-dihydrocyclopenta[b]indole (4o): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 3 h, red foam solid, 103.4 mg, 74% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.68 (d, J = 7.5 Hz, 1H), 7.64–7.58 (m, 2H), 7.57–7.46 (m, 9H), 7.45–7.34 (m, 8H), 7.34–7.24 (m, 3H), 7.21–7.14 (m, 2H), 7.10 (t, J = 7.4 Hz, 1H), 7.06–6.95 (m, 2H), 6.94–6.85 (m, 2H), 6.85–6.76 (m, 5H), 6.65 (d, J = 7.3 Hz, 2H). ^{13}C {1H} NMR (126 MHz, CDCl_3) δ 188.2, 163.0, 156.7, 152.1, 147.9, 142.2, 142.1, 142.0, 141.0, 138.9, 135.3, 130.7, 129.9, 129.8, 129.2, 129.0, 128.7, 127.9, 127.4, 127.17, 127.16, 127.1, 126.9, 126.7, 126.4, 125.3, 123.9, 123.1, 120.9, 61.9. IR: $\bar{\nu}$ = 2921, 2851, 1646, 1528, 1401, 1188, 1134, 1071, 756, 673, 470 cm^{-1} . HRMS (ESI) m/z : $[M + H]^+$ calcd. for $\text{C}_{54}\text{H}_{38}\text{N}$: 700.2999; found: 700.2996.

2-(Diphenylmethylene)-1-phenyl-3,3-di-*m*-tolyl-2,3-dihydrocyclopenta[b]indole (4p): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 20 min, red foam solid, 52.8 mg, 46% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.64 (d, J = 7.5 Hz, 1H), 7.58–7.52 (m, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.30–7.19 (m, 4H), 7.19–7.14 (m, 4H), 7.10 (t, J = 7.4 Hz, 1H), 7.07–6.98 (m, 3H), 6.95 (s, 1H), 6.90 (d, J = 7.5 Hz, 2H), 6.87–6.75 (m, 7H), 6.59 (d, J = 7.3 Hz, 2H), 2.20 (s, 6H). ^{13}C

{1H} NMR (126 MHz, CDCl₃) δ 188.6, 163.0, 156.8, 152.4, 147.6, 142.5, 142.0, 141.8, 141.7, 136.8, 135.5, 130.8, 130.6, 129.6, 129.3, 128.9, 128.5, 127.9, 127.5, 127.32, 127.27, 127.02, 126.99, 126.73, 126.67, 125.3, 123.7, 123.0, 120.8, 62.2, 21.5. IR: $\bar{\nu}$ = 2921, 2851, 1645, 1531, 1465, 1416, 1190, 1135, 1073, 758, 673, 470 cm⁻¹. HRMS (ESI) m/z : [M + H]⁺ calcd. for C₄₄H₃₄N: 576.2686; found: 576.2682.

2-(Diphenylmethylene)-3,3-bis(3-methoxyphenyl)-1-phenyl-2,3-dihydrocyclopenta[b]indole (**4q**): (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 40 min, red foam solid, 35.2 mg, 29% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, J = 7.5 Hz, 1H), 7.59–7.52 (m, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.31–7.23 (m, 1H), 7.16 (t, J = 7.4 Hz, 2H), 7.13–6.91 (m, 9H), 6.89–6.78 (m, 7H), 6.69–6.61 (m, 4H), 3.67 (s, 6H). ¹³C {1H} NMR (126 MHz, CDCl₃) δ 188.1, 163.0, 158.8, 156.6, 152.0, 147.8, 143.2, 142.3, 142.0, 141.9, 135.3, 130.8, 129.7, 129.2, 129.0, 128.6, 128.5, 127.9, 127.4, 127.1, 126.7, 125.3, 123.8, 123.0, 122.2, 120.9, 115.8, 112.0, 62.3, 55.1. IR: $\bar{\nu}$ = 2921, 2852, 1645, 1534, 1405, 1258, 1192, 1133, 1076, 756, 670, 473 cm⁻¹. HRMS (ESI) m/z : [M + H]⁺ calcd. for C₄₄H₃₄NO₂: 608.2584; found: 608.2575.

3.3. General Procedure for the Gram-Scale Synthesis of **3a**

To a solution of Sc(OTf)₃ (393.7 mg, 0.8 mmol) in toluene (40 mL) was added of **1a** (1.2 g, 4.0 mmol) and **2a** (1.7 g, 6 mmol) in glass pressure tube (100 mL). The reaction mixture was stirred for 1.5 h at 100 °C. The solvent was concentrated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (petroleum ether/ethyl acetate 10:1 to 3:1), giving the corresponding product **3a** (1.86 g, 83% yield).

3.4. General Procedure for the Synthesis of **5**

LiAlH₄ (11.4 mg, 0.3 mmol) was added to a solution of **3a** (54.7 mg, 0.1 mmol) in dry THF (1 mL) at 0 °C. The reaction mixture was stirred for 10 min. Then, water (2 mL) was added. The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (5 mL $\times$ 3). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel, giving the product **5** (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 10 min, red foam solid, 54.5 mg, 99% yield).

2-(Diphenylmethylene)-1,3,3-triphenyl-2,3,4a-tetrahydrocyclopenta[b]indole (**5**): ¹H NMR (500 MHz, CDCl₃) δ 7.64 (s, 1H), 7.41–7.29 (m, 2H), 7.19 (tt, J = 8.2, 6.6 Hz, 7H), 7.11–7.06 (m, 2H), 7.06–6.97 (m, 8H), 6.90 (ddd, J = 15.1, 11.5, 4.2 Hz, 3H), 6.83 (t, J = 7.4 Hz, 1H), 6.72 (t, J = 7.7 Hz, 2H), 6.54 (d, J = 7.2 Hz, 2H), 6.49 (d, J = 7.2 Hz, 2H), 5.65 (s, 1H). ¹³C {1H} NMR (126 MHz, CDCl₃) δ 153.0, 147.6, 145.0, 143.9, 143.6, 143.1, 142.9, 141.6, 140.8, 130.0, 128.93, 128.89, 128.8, 128.5, 128.4, 128.1, 127.44, 127.41, 127.3, 126.4, 126.3, 125.7, 125.6, 125.4, 123.3, 121.5, 119.8, 119.4, 119.1, 111.7, 62.3, 49.1. IR: $\bar{\nu}$ = 3471, 3110, 2920, 2852, 1648, 1527, 1402, 1243, 1190, 1136, 1073, 1027, 752, 671, 467 cm⁻¹. HRMS (ESI) m/z : [M + H]⁺ calcd. for C₄₂H₃₂N: 550.2529; found: 550.2525.

3.5. General Procedure for the Synthesis of **6**

Pd(PPh₃)₄ (46.2 mg, 0.2 mmol), Cs₂CO₃ (97.7 mg, 0.15 mmol), and phenanthren-9-ylboronic acid (66.6 mg, 0.15 mmol) in 1,4-dioxane (2 mL) were added to a solution of **4c** (125.3 mg, 0.312 mmol). The reaction mixture was stirred for 12 h. The residue was purified by flash chromatography on silica gel, giving the product **6** (eluent: petroleum ether/ethyl acetate 10:1 to 3:1, 12 h, red foam solid, 117.2 mg, 81% yield).

2-(Diphenylmethylene)-7-(phenanthren-9-yl)-1,3,3-triphenyl-2,3-dihydrocyclopenta[b]indole (**6**): ¹H NMR (500 MHz, CDCl₃) δ 8.70 (d, J = 8.3 Hz, 1H), 8.65 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.85–7.77 (m, 2H), 7.67–7.50 (m, 7H), 7.51–7.38 (m, 6H), 7.22–7.07 (m, 7H), 7.01 (t, J = 7.5 Hz, 2H), 6.94 (q, J = 7.4 Hz, 2H), 6.89–6.82 (m, 2H), 6.82–6.74 (m, 5H), 6.61 (d, J = 7.3 Hz, 2H). ¹³C {1H} NMR (126 MHz, CDCl₃) δ 188.8, 162.3, 157.4, 152.3, 148.3, 142.3, 142.0, 141.9, 141.8, 138.7, 136.4, 135.1, 131.5, 131.4, 131.3, 130.8, 130.5, 129.8, 129.6, 129.5, 129.22, 129.17, 128.9, 128.6, 128.5, 127.9, 127.64, 127.58, 127.4, 127.3, 127.2, 126.9, 126.77,

126.75, 126.5, 126.42, 126.39, 126.3, 126.2, 125.4, 124.6, 122.8, 122.4, 120.4, 62.5. IR: $\bar{\nu}$ = 3117, 2922, 2852, 1649, 1529, 1400, 1191, 1136, 1073, 755, 671, 469 cm^{-1} . HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{56}\text{H}_{38}\text{N}$: 724.2999; found: 724.2993.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29061251/s1>, X-ray data for products **3a**; copies of ^1H NMR, ^{13}C $\{^1\text{H}\}$ NMR spectra.

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References

1. Lim, S.-H.; Sim, K.-M.; Abdullah, Z.; Hiraku, O.; Hayashi, M.; Komiyama, K.; Kam, T.-S. Leuconoxine, Kopsinitarine, Kopsijasmine, and Kopsinone Derivatives from Kopsia. *J. Nat. Prod.* **2007**, *70*, 1380–1383. [\[CrossRef\]](#)
2. Jones, S.B.; Simmons, B.; Mastracchio, A.; MacMillan, D.W.C. Collective synthesis of natural products by means of organocascade catalysis. *Nature* **2011**, *475*, 183–188. [\[CrossRef\]](#)
3. Dethe, D.H.; Erande, R.D.; Ranjan, A. Biomimetic Total Syntheses of Borreverine and Flinderole Alkaloids. *J. Org. Chem.* **2013**, *78*, 10106–10120. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Neelamegam, R.; Hellenbrand, T.; Schroeder, F.A.; Wang, C.; Hooker, J.M. Imaging Evaluation of 5HT_{2C} Agonists, [^{11}C]WAY-163909 and [^{11}C]Vabicaserin, Formed by Pictet–Spengler Cyclization. *J. Med. Chem.* **2014**, *57*, 1488–1494. [\[CrossRef\]](#)
5. Chen, H.; Bai, J.; Fang, Z.-F.; Yu, S.-S.; Ma, S.-G.; Xu, S.; Li, Y.; Qu, J.; Ren, J.-H.; Li, L.; et al. Indole Alkaloids and Quassinoids from the Stems of *Brucea mollis*. *J. Nat. Prod.* **2011**, *74*, 2438–2445. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Scarpi, D.; Faggi, C.; Occhiato, E.G. Total Synthesis of Bruceoline I. *J. Nat. Prod.* **2017**, *80*, 2384–2388. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Tatsis, E.C.; Schaumlöffel, A.; Warskulat, A.C.; Massiot, G.; Schneider, B.; Bringmann, G. Nudicaulins, Yellow Flower Pigments of *Papaver nudicaule*: Revised Constitution and Assignment of Absolute Configuration. *Org. Lett.* **2013**, *15*, 156–159. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Ekebergh, A.; Karlsson, I.; Mete, R.; Pan, Y.; Börje, A.; Mårtensson, J. Oxidative Coupling as a Biomimetic Approach to the Synthesis of Scytonemin. *Org. Lett.* **2011**, *13*, 4458–4461. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Andres, R.; Wang, Q.; Zhu, J. Asymmetric Total Synthesis of (–)-Arborisidine and (–)-19-epi-Arborisidine Enabled by a Catalytic Enantioselective Pictet–Spengler Reaction. *J. Am. Chem. Soc.* **2020**, *142*, 14276–14285. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Vivekanand, T.; Satpathi, B.; Bankar, S.K.; Ramasastry, S.S.V. Recent metal-catalysed approaches for the synthesis of cyclopenta[b]indoles. *RSC Adv.* **2018**, *8*, 18576–18588. [\[CrossRef\]](#)
11. Haak, E. Modern Annulation Strategies for the Synthesis of Cyclo[b]fused Indoles. *Synlett* **2019**, *30*, 245–251. [\[CrossRef\]](#)
12. Yu, K.-Y.; Ge, X.-M.; Fan, Y.-J.; Liu, X.-T.; Yang, X.; Yang, Y.-H.; Zhao, X.-H.; An, X.-T.; Fan, C.-A. Iron(III)-catalyzed tandem annulation of indolyl-substituted *p*-quinone methides with ynamides for the synthesis of cyclopenta[b]indoles. *Chem. Commun.* **2022**, *58*, 8710–8713. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Ghosh, B.; Balhara, R.; Jindal, G.; Mukherjee, S. Catalytic Enantioselective Desymmetrizing Fischer Indolization through Dynamic Kinetic Resolution. *Angew. Chem. Int. Ed.* **2021**, *60*, 9086–9092. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Wu, C.; Chang, Z.; Peng, C.; Bai, C.; Xing, J.; Dou, X. Catalytic asymmetric indolization by a desymmetrizing [3+2] annulation strategy. *Chem. Sci.* **2023**, *14*, 7980–7987. [\[CrossRef\]](#)
15. Zhang, Y.-B.; Li, B.-S.; Xu, G.-J.; Sun, W.; Sun, M. Rh(III)-Catalyzed Double C–H Functionalization of Indoles with Cyclopropanones via Sequential C–H/C–C/C–H Bond Activation. *Org. Lett.* **2023**, *25*, 3922–3926. [\[CrossRef\]](#) [\[PubMed\]](#)

16. Xu, H.; Wang, H.; Xu, Z.-F.; Duan, S.; Li, C.-Y. Synthesis of Cyclopenta[b]indoles via Rhodium-Catalyzed Cascade Migration-Annulation of 1-Sulfonyl-1,2,3-triazoles and Indoles. *Adv. Synth. Catal.* **2023**, *365*, 1623–1628. [\[CrossRef\]](#)
17. Jiang, Q.; Yang, T.; Li, Q.; Liang, G.-M.; Liu, Y.; He, C.-Y.; Chu, W.-D.; Liu, Q.-Z. Synthesis of Cyclopenta[b]indoles via Sc(III)-Catalyzed Annulation of Vinyl Diazoacetates with Indole-Derived Unsaturated Imines. *Org. Lett.* **2023**, *25*, 3184–3189. [\[CrossRef\]](#)
18. Selvaraj, K.; Debnath, S.; Swamy, K.C.K. Reaction of Indole Carboxylic Acid/Amide with Propargyl Alcohols: [4+3]-Annulation, Unexpected 3- to 2- Carboxylate/Amide Migration, and Decarboxylative Cyclization. *Org. Lett.* **2019**, *21*, 5447–5451. [\[CrossRef\]](#)
19. Mei, G.-J.; Shi, F. Indolylmethanols as Reactants in Catalytic Asymmetric Reactions. *J. Org. Chem.* **2017**, *82*, 7695–7707. [\[CrossRef\]](#)
20. Zhang, Y.-C.; Jiang, F.; Shi, F. Organocatalytic Asymmetric Synthesis of Indole-Based Chiral Heterocycles: Strategies, Reactions, and Outreach. *Acc. Chem. Res.* **2020**, *53*, 425–446. [\[CrossRef\]](#)
21. Marino, P. New Perspectives in the Indole Ring Functionalization using 2-Indolylmethanols. *Adv. Synth. Catal.* **2020**, *362*, 1214–1232.
22. Yang, S.; Wang, H.-Q.; Gao, J.-N.; Tan, W.-X.; Zhang, Y.-C.; Shi, F. Lewis Acid-Catalyzed (3+2) Cycloaddition of 2-Indolylmethanols with β,γ -Unsaturated α -Ketoesters. *Eur. J. Org. Chem.* **2022**, *2022*, e202200878. [\[CrossRef\]](#)
23. Mao, J.; Zhang, H.; Ding, X.-F.; Luo, X.; Deng, W.-P. Synergistic Catalysis for Asymmetric [3+2] Cycloadditions of 2-Indolylmethanols with α,β -Unsaturated Aldehydes. *J. Org. Chem.* **2019**, *84*, 11186–11194. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Wu, J.-L.; Wang, C.-S.; Wang, J.-R.; Mei, G.-J.; Shi, F. A catalytic asymmetric interrupted Nazarov-type cyclization of 2-indolylmethanols with cyclic enaminones. *Org. Biomol. Chem.* **2018**, *16*, 5457–5464. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Wang, J.-Y.; Wu, P.; Wu, J.-L.; Mei, G.-J.; Shi, F. Chemodivergent Tandem Cyclizations of 2-Indolylmethanols with Tryptophols: C–N versus C–C Bond Formation. *J. Org. Chem.* **2018**, *83*, 5931–5946. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Xu, M.-M.; Wang, H.-Q.; Wan, Y.; Wang, S.-L.; Shi, F. Enantioselective Construction of Cyclopenta[b]indole Scaffolds via the Catalytic Asymmetric [3 + 2] Cycloaddition of 2-Indolylmethanols with *p*-Hydroxystyrenes. *J. Org. Chem.* **2017**, *82*, 10226–10233. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Zhan, S.-C.; Sun, J.; Sun, Q.; Han, Y.; Yan, C.-G. Acid-Modulated Construction of Cyclopenta[b]indole and Cyclohepta[b]indole via Unprecedented C₃/C₂ Carbocation Rearrangement. *J. Org. Chem.* **2023**, *88*, 5440–5456. [\[CrossRef\]](#)
28. Rui, K.; Gu, H.; Woldegiorgis, A.G.; Lin, X. Organocatalytic Tandem Synthesis of Chiral Hexacyclic Bisindoles from Propargylic 3-Methyleneindoles with 2-Indolylmethanols. *Org. Lett.* **2023**, *25*, 6654–6658. [\[CrossRef\]](#)
29. Khan, T.; Yaragorla, S. Iodocyclization of Propargyl Alcohols: Highly Facile Approach to Hetero/Carbocyclic Iodides. *Eur. J. Org. Chem.* **2019**, *2019*, 3989–4012. [\[CrossRef\]](#)
30. Liu, X.-Y.; Liu, Y.-L.; Chen, L. Tandem Annulations of Propargylic Alcohols to Indole Derivatives. *Adv. Synth. Catal.* **2020**, *362*, 5170–5195. [\[CrossRef\]](#)
31. Qian, H.; Huang, D.; Bi, Y.; Yan, G. 2-Propargyl Alcohols in Organic Synthesis. *Adv. Synth. Catal.* **2019**, *361*, 3240–3280. [\[CrossRef\]](#)
32. Doraghi, F.; Mahdavian, A.M.; Karimian, S.; Larijani, B.; Mahdavi, M. Recent Progress in Application of Propargylic Alcohols in Organic Syntheses. *Adv. Synth. Catal.* **2023**, *365*, 2991–3019. [\[CrossRef\]](#)
33. Wang, X.; Chen, X.; Lin, W.; Li, P.; Li, W. Recent Advances in Organocatalytic Enantioselective Synthesis of Axially Chiral Allenes. *Adv. Synth. Catal.* **2022**, *364*, 1212–1222. [\[CrossRef\]](#)
34. Du, S.; Zhou, A.-X.; Yang, R.; Song, X.-R.; Xiao, Q. Recent advances in the direct transformation of propargylic alcohols to allenenes. *Org. Chem. Front.* **2021**, *8*, 6760–6782. [\[CrossRef\]](#)
35. Song, X.-R.; Yang, R.; Xiao, Q. Recent Advances in the Synthesis of Heterocyclics via Cascade Cyclization of Propargylic Alcohols. *Adv. Synth. Catal.* **2021**, *363*, 852–876. [\[CrossRef\]](#)
36. Wang, S.; Chai, Z.; Wei, Y.; Zhu, X.; Zhou, S.; Wang, S. Lewis Acid Catalyzed Cascade Reaction to Carbazoles and Naphthalenes via Dehydrative [3+3]-Annulation. *Org. Lett.* **2014**, *16*, 3592–3595. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Qiu, Z.-W.; Li, B.Q.; Liu, H.-F.; Zhu, Z.-Q.; Pan, H.-P.; Feng, N.; Ma, A.-J.; Peng, J.-B.; Zhang, X.-Z. Formal (3+4)-Annulation of Propargylic *p*-Quinone Methides with 2-Indolylmethanols: Synthesis of Polysubstituted Indole-Fused Oxepines. *J. Org. Chem.* **2021**, *86*, 7490–7499. [\[CrossRef\]](#)
38. Zhang, X.-Z.; Qiu, Z.-W.; Wen, G.-H.; Ma, A.-J.; Bao, P.-J.; Du, J.-Y.; Xu, X.-T.; Feng, N.; Li, B.Q. Synthesis of Pyrrolo[1,2-*a*]indoles via (3+2)-Annulations of (Aza)-*para*-Quinone Methides with Indoles. *Synthesis* **2020**, *52*, 3640–3649. [\[CrossRef\]](#)
39. Zhang, X.-Z.; Li, B.Q.; Qiu, Z.-W.; Ma, A.-J.; Peng, J.-B.; Du, J.-Y.; Feng, N.; Xu, X.-T.; Pan, H.-P. Synthesis of Naphthopyrans via Formal (3+3)-Annulation of Propargylic (Aza)-*para*-Quinone Methides with Naphthols. *J. Org. Chem.* **2020**, *85*, 13306–13316. [\[CrossRef\]](#) [\[PubMed\]](#)
40. Qiu, Z.-W.; Xu, X.-T.; Pan, H.-P.; Jia, Z.-S.; Ma, A.-J.; Peng, J.-B.; Du, J.-Y.; Feng, N.; Li, B.Q.; Zhang, X.-Z. Brønsted Acid-Catalyzed Formal (3+3)-Annulation of Propargylic (Aza)-*para*-Quinone Methides with 4-Hydroxycoumarins and 1,3-Dicarbonyl Compounds. *J. Org. Chem.* **2021**, *86*, 6075–6089. [\[CrossRef\]](#)
41. Zhang, Y.-R.; Qiu, Z.-W.; Fu, Z.-J.; Chen, S.-S.; Pan, H.-P.; Li, B.-Q.; Ma, A.-J.; Zhang, X.-Z. Copper-Catalyzed Sequential C(sp²)–H/C(sp³)–H Annulation of Indoles with Propargylic Alcohols to Access Hydrobenzo[b]carbazoles. *Adv. Synth. Catal.* **2024**. [\[CrossRef\]](#)

42. Yan, Q.; Duan, M.; Chen, C.; Deng, Z.; Wu, M.; Yu, P.; He, M.-L.; Zhu, G.; Houk, K.N.; Sun, J. Organocatalytic discrimination of non-directing aryl and heteroaryl groups: Enantioselective synthesis of bioactive indole-containing triarylmethanes. *Chem. Sci.* **2022**, *13*, 5767–5773. [[CrossRef](#)] [[PubMed](#)]
43. Qian, D.; Wu, L.; Lin, Z.; Sun, J. Organocatalytic synthesis of chiral tetrasubstituted allenes from racemic propargylic alcohols. *Nat. Commun.* **2017**, *8*, 567. [[CrossRef](#)] [[PubMed](#)]

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