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# One-Pot Synthesis of Indole-Fused Scaffolds via Gold-Catalyzed Tandem Annulation Reactions of 1,2-Bis(alkynyl)-2-en-1-ones with Indoles

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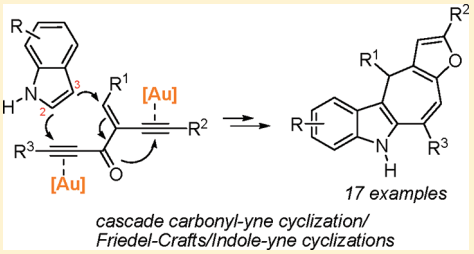
Supporting Information

**ABSTRACT:** The gold-catalyzed tandem cyclization of 1,2-bis(alkynyl)-2-en-1-ones with indoles offers an efficient and straightforward route to indole-fused polycyclic systems. The process is realized through a cascade carbonyl-yne cyclization/Friedel–Crafts/indole-yne cyclization sequence catalyzed by a single-pot catalyst of gold.




Fused heterocyclic compounds containing indole rings are present in many biologically active natural products as well as pharmaceutically important substances. For example, indole-fused seven-membered carbocycles can be found in ambiguine,[1a] ambiguine E isonitrile,[1b] silicone,[1c,d] caulersin,[1e−g] antitumor benzo[5,6]cyclohepta[*b*]-indoles,[1h] and anticancer agents of oxophenylarcyriaflavins,[1i] etc.[1] Thus, the concise methods for the construction of polycyclic indole skeletons are highly attractive. Among various synthetic approaches for indole derivatives, gold-catalyzed annulations of indole/ynes have been proven versatile in terms of efficiency and wide scope of application.[2] These include intramolecular cyclization of indoles with alkynes leading to azepino[4,5-*b*]indoles and indoloazocines,[2a−c] cycloisomerization of *N*-propargylamides to *β*-carbolinones,[2d,e] 1,2-indole migration,[2f] and cyclization of 2,3-disubstituted indoles to tetracyclic indolines,[2g] etc. We have also developed straightforward syntheses of functionalized indole derivatives through gold-catalyzed domino reactions of (*Z*)-enynols with indoles[3a] and 1,5-indole migration[3b] reactions, etc.[3] From a practical point of view, domino reactions are ideal strategies for building up complex structures because multiple bond-forming and -cleaving events could occur in one sequence, and there is no need to isolate the corresponding intermediates.[4] Inspired by these studies and our previous work of electrophilic cyclization of enynones[5] and gold-catalyzed cascade reactions of 1,6-diyne-4-en-3-ols,[6,7] we designed a new building block of 1,2-bis(alkynyl)-2-en-1-ones in which one more alkyne unit is incorporated into the enynones. We envisioned that indoles may induce double annulations of these enynones because both of the indole C-2 and C-3 can react with activated intermediates to form C−C bonds, furnishing a multiply substituted furan ring[8] and a dihydrocyclohepta[*b*]-indole framework in the same product via sequential nucleophilic attack onto the metal-coordinated alkynes (Figure 1). Herein, we report the utilization of gold as the catalyst for the cyclization of bis(alkynyl)-2-en-1-ones with indoles, which offers a convenient, general, and highly efficient approach to polycyclic indole-fused scaffolds under extremely mild reaction conditions.

The initial cyclization study of (*E*)-4-benzylidene-1,6-diphenylhexa-1,5-diyn-3-one **1a** with 2 equiv of indole was performed; to our delight, the desired polycyclic indole **3a** could be obtained in an excellent yield of 92% using 5 mol % $NaAuCl_4 \cdot 2H_2O$ (Table 1, entry 1). Obviously, the cascade cyclization occurs, and the overall domino process entails one C−O bond and a 2-fold C−C bond formation.[9] Interestingly, **3a** exhibits a strong yellow-green fluorescence in organic solvents. The use of $AuCl_3$, $Ph_3PAuNTf_2$, or gold-oxonium salt $[(Ph_3PAu)_3O]BF_4$ also provided good yields (82−90%) of **3a** (Table 1, entries 2−4). Decreasing the catalyst loading to 1 mol % resulted in the formation of **3a** and indole-substituted furan **2a** in 52 and 30% yields, respectively (Table 1, entry 5). AgOTf gave **2a** in a low yield of 30%, together with several byproducts (Table 1, entry 7).

With the optimized reaction conditions in hand, we next investigated the scope of the reaction with a variety of substituted enynones using $NaAuCl_4 \cdot 2H_2O$ as catalyst, and the results are presented in Table 2. The reaction proved to be quite general with respect to substitution of $R^1$−$R^3$ because aryl or alkyl groups were all suitable for these substituents, showing a broad diversity of the products. The cyclizations of enynones **1** with different $R^2$ and $R^3$ groups were examined first (**3a**−**i**). The reactions tolerated both electron-rich and electron-poor aryl substituents, furnishing the corresponding indole derivatives **3b**−**c** and **3f**−**h**

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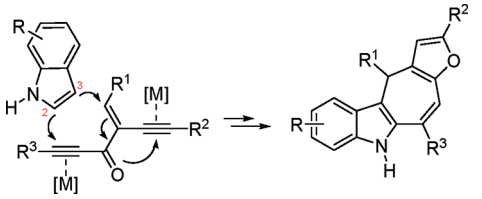
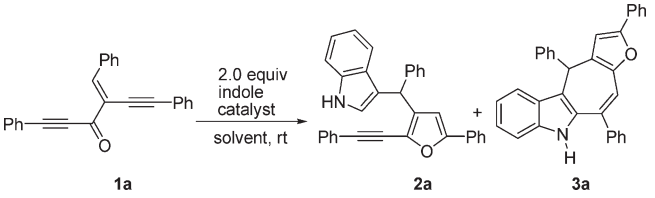


**Figure 1.** Strategy for metal-catalyzed cascade reaction for the synthesis of indole-fused polycycles.

**Table 1. Optimization Studies for the Cascade Reactions**




1a 2a 3a

| entry | catalyst | solvent | time | yield (%) of **2a**[a] | yield (%) of **3a**[a] |
|---|---|---|---|---|---|
| 1 | 5% $NaAuCl_4 \cdot 2H_2O$ | DCE | 1 h | | 92 |
| 2 | 5% $AuCl_3$ | DCE | 1 h | | 89 |
| 3 | 5% $Ph_3PAuNTf_2$ | DCE | 1 h | | 82 |
| 4 | 2% $[(Ph_3PAu)_3O]BF_4$ | DCE | 1 h | | 90 |
| 5 | 1% $NaAuCl_4 \cdot 2H_2O$ | DCE | 6 h | 30 | 52 |
| 6 | 5% $Ph_3PAuOTf$ | THF | 3 h | | *b* |
| 7 | 5% AgOTf | DCE | 5 h | 30 | |
| 8[c] | 5% TfOH | DCE | 8 h | | |

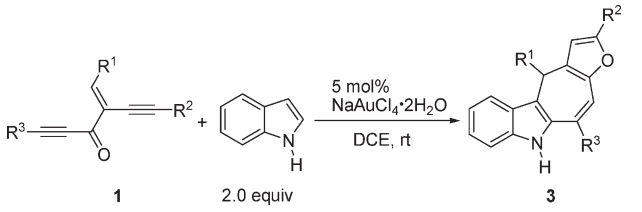
[a] Isolated yields. [b] Several products were formed. [c] **1a** was recovered in 30% yield, and some byproducts were formed.

in 56−90% yields. The functionalities of −Cl, −OMe, and $-CF_3$ were very compatible for this reaction. An alkenyl-substituent, such as 1-cyclohexenyl group, as $R^2$ produced **3d** in 41% yield. The reactions with the alkyl-substituted (either as $R^2$ or $R^3$) alkynes were also satisfactory, leading to **3e** and **3i** in 64 and 73% yields, respectively. In addition, alkyl substitution on the olefin moiety was also well accommodated; for example, methyl-substituted **3j** and **3k** could be isolated in 47 and 68% yields, respectively.

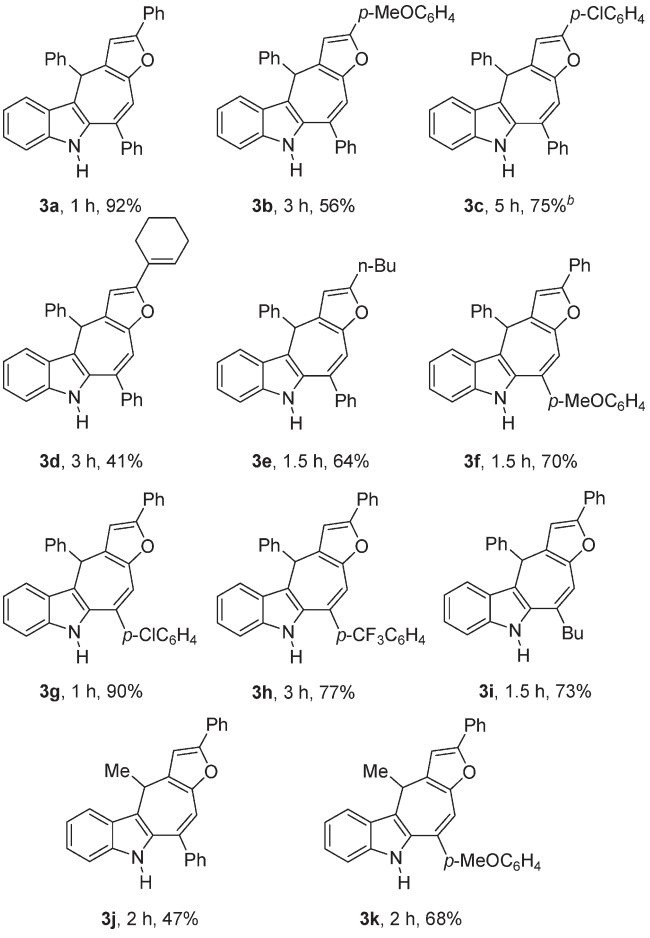
Next, we explored the cyclization reactions with various substituted indoles. Gratifyingly, the reaction could be successfully extended to indole substrates bearing −Br, −Me, −MeO, and −BnO functionalities, and high yields were realized for all cases (Table 3, entries 1−4). 4-$CO_2$Me-substituted indole afforded a moderate yield of the desired **3p** using 5 mol % of $(PPh_3)$-$AuNTf_2$ as the catalyst (Table 3, entry 5). The structure of the indole-fused carbocycle **3p** has been verified by X-ray crystallography (see Supporting Information), which clearly shows a dihydrocyclohepta[*b*]indole skeleton. It is noted that the crystals suitable for X-ray analysis should be prepared in the glovebox (vide infra).

Interestingly, when enynone **1l** bearing a siloxymethyl group was employed, an indole-tethered polycycle **4** was formed in 74% yield via the cleavage of the −OTBS group (Scheme 1, eq 1). The outcome of this experiment may be rationalized by the spontaneous reaction of the initially formed product (**3**) with the second

**Table 2. Synthesis of Polycyclic Heterocycles through Cascade Reactions**[a]




**1** 2.0 equiv **3**




[a] Isolated yields. [b] $PPh_3AuNTf_2$ (5 mol %) was used.

molecule of indole via a carbocation intermediate generated by gold-assisted ionization of the C−O bond.[10] On the other hand, it was found when a solution of **3a** in ethyl acetate was stirred in air for 5 days, a photooxygenation reaction took place, and the oxirane **5** was isolated in 50% yield as a single diastereomer (Scheme 1, eq 2). The structure of **5** was confirmed by X-ray analysis (see Supporting Information), which reveals that the phenyl ring and the oxygen atom of the oxirane are in trans orientation. This result indicates that **3a** itself may act as a photosensitizer to generate the singlet oxygen, which reacts with the furan moiety to afford diacyl oxirane **5** via the rearrangement of the unstable endoperoxide intermediate.[11]

The apparent formation of furan rings and indole-fused carbocycles in the products **3** and the observation of indole-yne **2** led us to propose a plausible reaction mechanism as depicted


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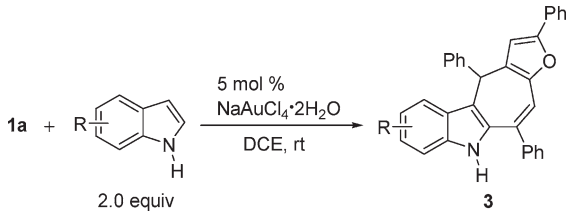
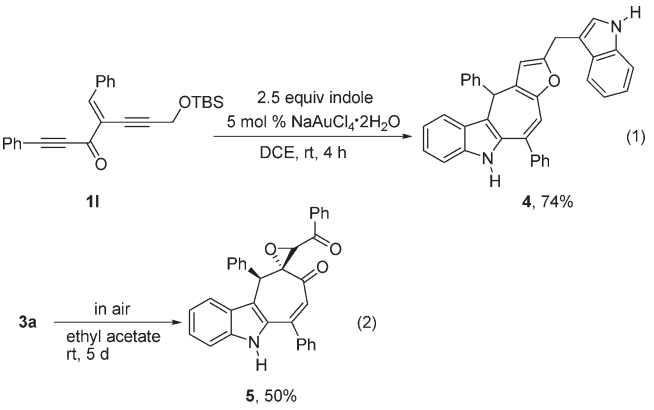
**Table 3. Formation of Various Indole-Fused Polycycles**



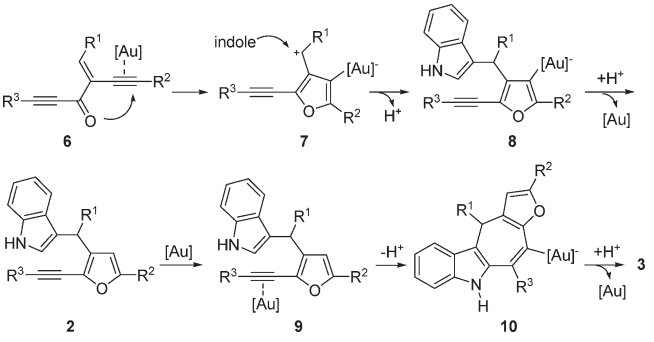

| entry | substrate | time | product | yield (%) of 3[a] |
|---|---|---|---|---|
| 1 | 5-Br-indole | 1 h | **3l** | 83 |
| 2 | 6-Me-indole | 1 h | **3m** | 82 |
| 3 | 5-MeO-indole | 1 h | **3n** | 83 |
| 4 | 5-BnO-indole | 1 h | **3o** | 85 |
| 5 | 4-COOMe-indole | 4 h | **3p** | 25 (55)[b] |

[a] Isolated yields. [b] The yield in parentheses was obtained by using 5 mol % of $(PPh_3)AuNTf_2$ for 1.5 h.

**Scheme 1**

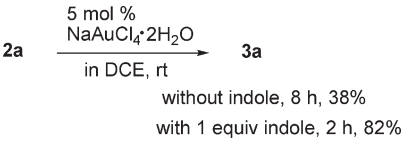



**Scheme 2**




in Scheme 2. In the first step, the alkyne moiety is activated through forming a $\pi$-complex with gold catalyst, which facilitates the nucleophilic attack by the carbonyl oxygen. Thus, the subsequent 5-*endo-dig* cyclization occurs to form a cationic intermediate **7**. The intermolecular nucleophilic attack of indole on the carbocation affords the furanyl gold **8**. This is followed by indole/yne cyclization to give gold species **10**; protonation of the resulting carbon−gold bond delivers products **3** and regenerates the gold catalyst.[12]

**Scheme 3**




To gain insight into the reaction mechanism, we subjected the indole-yne **2a** to the cyclization conditions; however, only a 38% yield of the desired product **3a** was isolated after 8 h, and **2a** was recovered in 47% yield (Scheme 3). To our surprise, when 1 equiv of indole was used as an additive, the desired **3a** was obtained in 82% yield within 2 h. The results indicated that the excess indole played an important role in the gold(III)-catalyzed cyclization of **2a** and also in the one-pot process. It has been reported that the reaction of indole with a stoichiometric amount of $NaAuCl_4 \cdot 2H_2O$ might afford a C-3 aurated indole via electrophilic metalation.[13] We postulate that this 3-indolylaurate species may be the real catalyst in our reaction, which exhibits higher catalytic activities and may be responsible for the above results. We also found when $Ph_3PAuNTf_2$ was used as a catalyst, **3a** could be formed in 82% yield for 0.5 h from **2a** without the addition of any additive.

In summary, we have developed a highly efficient gold-catalyzed double cyclization of bis(alkynyl)-2-en-1-ones with indoles. This methodology provides rapid access to heterocyclic systems fused both with indole and furan rings with diverse substitution patterns. It is anticipated that the new cascade reactions using various nucleophiles would be exploited on the basis of these findings.

## EXPERIMENTAL SECTION

**Synthesis of 1,2-Bis(alkynyl)-2-en-1-ones 1a−g, 1i, and 1l.** *Typical Procedure for the Synthesis of (E)-4-Benzylidene-1-(4-methoxyphenyl)-6- phenylhexa-1,5-diyn-3-one (**1f**).* To a solution of 1-ethynyl-4-methoxybenzene (0.79 g, 6 mmol) in THF (10 mL) was added *n*-BuLi (2.3 mL, 5.5 mmol, 2.4 M solution in hexanes) at 0 °C. After the solution was stirred at the same temperature for 0.5 h, (*E*)-2-benzylidene-4-phenylbut-3-ynal[14] (1.16 g, 5.0 mmol) was added, and then the solution was warmed up to room temperature. After the starting material was consumed, the mixture was quenched with saturated ammonium chloride solution, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel to afford (*E*)-4-benzylidene-1-(4-methoxyphenyl)-6-phenylhexa-1,5-diyn-3-ol. This alcohol was used directly for the next step.

To a solution of the above alcohol in DMSO (10 mL) was added 2-iodoxybenzoic acid (IBX) (1.82 g, 6.5 mmol) at room temperature. After the starting material was consumed, the mixture was quenched by water, filtered, extracted with ethyl acetate, and dried over $Na_2SO_4$. The solvent was evaporated in vacuo, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 10:1:1) to afford compound **1f** (1.34 g, 74%) as a yellow solid: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 3.84 (s, 3H), 6.87−6.91 (m, 2H), 7.38−7.41 (m, 3H), 7.45−7.49 (m, 3H), 7.56−7.61 (m, 4H), 8.11 (s, 1H), 8.15−8.17 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 55.4, 85.2, 87.0, 95.4, 100.2, 111.9, 114.4, 121.8, 122.8, 128.5, 128.7, 128.9, 130.9, 131.2, 131.7, 134.3, 135.2, 146.2, 161.7, 176.3. HRMS (EI) for $C_{26}H_{18}O_2$: calcd 362.1307, found 362.1312.

*(E)-4-Benzylidene-1,6-diphenylhexa-1,5-diyn-3-one (**1a**).* It was further purified by recrystallization. Yield 84%. Light yellow solid: mp 129−130 °C;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$^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 7.36−7.41 (m, 5H), 7.44−7.49 (m, 4H), 7.58−7.64 (m, 4H), 8.13 (s, 1H), 8.15−8.18 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 Hz) $\delta$ 85.0, 87.0, 94.1, 100.4, 120.1, 121.8, 122.7, 128.5, 128.6, 128.7, 129.0, 130.8, 131.0, 131.4, 131.7, 133.1, 134.2, 146.7, 176.3. HRMS (EI) for $C_{25}H_{16}O$: calcd 332.1201, found 332.1198.

*(E)-4-Benzylidene-6-(4-methoxyphenyl)-1-phenylhexa-1,5-diyn-3-one (**1b**).* Yield 93%. Brown oil: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 3.84 (s, 3H), 6.90−6.92 (m, 2H), 7.38−7.42 (m, 2H), 7.45−7.48 (m, 4H), 7.52−7.54 (m, 2H), 7.63−7.65 (m, 2H), 8.10 (s, 1H), 8.16−8.18 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 55.3, 83.9, 87.0, 94.0, 100.7, 114.1, 114.9, 120.2, 122.1, 128.6, 128.7, 130.7, 130.9, 131.2, 133.1, 135.3, 134.4, 146.0, 160.2, 176.6. HRMS (EI) for $C_{26}H_{18}O_2$: calcd 362.1307, found 362.1312.

*(E)-4-Benzylidene-6-(4-chlorophenyl)-1-phenylhexa-1,5-diyn-3-one (**1c**).* Yield 70%. Yellow oil: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 7.31−7.43 (m, 4H), 7.46−7.52 (m, 6H), 7.62−7.64 (m, 2H), 8.12−8.15 (m, 2H), 8.15 (s, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 85.8, 86.8, 94.2, 99.1, 120.0, 121.2, 121.6, 128.65, 128.73, 128.8, 130.8, 130.9, 131.5, 132.9, 133.0, 134.1, 135.0, 147.3, 176.2. HRMS (EI) for $C_{25}H_{15}ClO$: calcd 366.0811, found 366.0814.

*(E)-4-Benzylidene-6-cyclohexenyl-1-phenylhexa-1,5-diyn-3-one (**1d**).* Yield 49%. Yellow oil: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 1.62−1.74 (m, 4H), 2.17−2.22 (m, 2H), 2.28−2.31 (m, 2H), 6.31−6.35 (m, 1H), 7.38−7.50 (m, 6H), 7.63−7.66 (m, 2H), 8.03 (s, 1H), 8.10−8.13 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 21.4, 22.1, 25.8, 28.6, 82.4, 86.9, 93.8, 102.7, 120.2, 120.7, 122.1, 128.5, 128.6, 130.7, 130.8, 131.0, 133.0, 134.3, 137.0, 145.6, 176.6. HRMS (EI) for $C_{25}H_{20}O$: calcd 336.1514, found 336.1517.

*(E)-4-Benzylidene-1-phenyldeca-1,5-diyn-3-one (**1e**).* Yield 93%. Yellow oil: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 0.95 (t, $J$ = 7.2 Hz, 3H), 1.50−1.55 (m, 2H), 1.64−1.69 (m, 2H), 2.59 (t, $J$ = 7.2 Hz, 2H), 7.39−7.49 (m, 6H), 7.63−7.66 (m, 2H), 8.07 (s, 1H), 8.10−8.14 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 13.6, 19.8, 22.0, 30.4, 75.5, 86.6, 93.7, 102.9, 120.2, 122.6, 128.5, 128.6, 130.6, 130.6, 131.1, 132.9, 134.2, 146.8, 177.2. HRMS (EI) for $C_{23}H_{20}O$: calcd 312.1514, found 312.1515.

*(E)-4-Benzylidene-1-(4-chlorophenyl)-6-phenylhexa-1,5-diyn-3-one (**1g**).* It was further purified by recrystallization. Yield 62%. Light yellow solid: mp 86−87 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 7.35−7.40 (m, 5H), 7.46−7.48 (m, 3H), 7.53−7.59 (m, 4H), 8.09 (s, 1H), 8.15−8.17 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 85.0, 87.7, 92.7, 100.4, 118.6, 121.6, 122.7, 128.5, 128.7, 129.0, 129.1, 131.0, 131.5, 131.7, 134.1, 134.2, 137.2, 146.7, 176.1. HRMS (EI) for $C_{25}H_{15}ClO$: calcd 366.0811, found 366.0809.

*(E)-3-Benzylidene-1-phenyldeca-1,5-diyn-4-one (**1i**).* Yield 79%. Yellow oil: $^1$H NMR ($CDCl_3$, $Me_4Si$, 300 MHz) $\delta$ 0.93 (t, $J$ = 7.2 Hz, 3H), 1.43−1.55 (m, 2H), 1.59−1.68 (m, 2H), 2.49 (t, $J$ = 6.9 Hz, 2H), 7.35−7.38 (m, 3H), 7.43−7.46 (m, 3H), 7.55−7.59 (m, 2H), 8.07 (s, 1H), 8.10−8.14 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 75.5 MHz) $\delta$ 13.5, 18.9, 22.0, 29.7, 79.4, 84.7, 97.8, 100.3, 121.9, 122.8, 128.4, 128.6, 128.8, 130.8, 131.2, 131.6, 134.2, 147.0, 176.5. HRMS (EI) for $C_{23}H_{20}O$: calcd 312.1514, found 312.1513.

*(E)-4-Benzylidene-7-(tert-butyldimethylsilyloxy)-1-phenylhepta-1,5-diyn-3-one (**1l**).* Yield 58%. Brown oil: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 0.17 (s, 6H), 0.94 (s, 9H), 4.68 (s, 2H), 7.40−7.48 (m, 6H), 7.65−7.67 (m, 2H), 8.12−8.14 (m, 3H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ −5.2, 18.3, 25.8, 52.5, 79.5, 86.5, 94.0, 99.7, 120.1, 121.7, 128.65, 128.68, 130.8, 131.0, 131.5, 133.0, 133.9, 148.1, 176.6. HRMS (EI) for $C_{26}H_{28}O_2Si$: calcd 400.1859, found 400.1857.

**Synthesis of (*E*)-4-Benzylidene-6-phenyl-1-(4-(trifluoromethyl)phenyl)hexa-1,5-diyn-3-one (1h).** To a solution of ethynyltrimethylsilane (1.18 g, 12 mmol) in THF (20 mL) was added *n*-BuLi (4.6 mL, 11 mmol, 2.4 M solution in hexanes) at −78 °C. After the solution was stirred at the same temperature for 1 h, (*E*)-2-benzylidene-4-phenylbut-3-ynal (2.32 g, 10 mmol) was added, and the resulting solution was warmed up to room temperature and stirred for 2 h. Then, the mixture was quenched with saturated ammonium chloride solution, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel to afford (*E*)-4-benzylidene-6-phenyl-1-(trimethylsilyl)-hexa-1,5-diyn-3-ol. To a solution of the above alcohol in THF (20 mL) was added TBAF (1.0 M in THF) at room temperature. The reaction mixture was stirred until the starting material was consumed. Then, the reaction was quenched by water, extracted with ethyl acetate, and dried over $Na_2SO_4$. The solvent was evaporated in vacuo, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to afford (*E*)-4-benzylidene-6-phenylhexa-1,5-diyn-3-ol (1.4 g, 54% yield for two steps) as a yellow solid.

To a solution of (*E*)-4-benzylidene-6-phenylhexa-1,5-diyn-3-ol (0.52 g, 2.0 mmol) in triethylamine (8 mL) were added 1-iodo-4-(trifluoromethyl)benzene (0.65 g, 0.35 mL, 2.4 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol), and CuI (19 mg, 0.1 mmol) at room temperature, and then the mixture was stirred overnight. After the starting material was consumed, the mixture was quenched with $H_2O$, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum/ethyl acetate = 5:1) to afford (*E*)-4-benzylidene-6-phenyl-1-(4-(trifluoromethyl)phenyl)hexa-1,5-diyn-3-ol (290 mg, 36% yield) as a brown oil.

To a solution of the above alcohol (290 mg, 0.72 mmol) in DMSO (3 mL) was added IBX (0.26 g, 0.94 mmol) at room temperature. After the starting material was consumed, the mixture was quenched by water, filtered, extracted with ethyl acetate, and dried over $Na_2SO_4$. The solvent was evaporated in vacuo, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1) to afford compound **1h** (0.16 g, 56%) as a yellow oil: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 7.36−7.40 (m, 3H), 7.45−7.48 (m, 3H), 7.55−7.59 (m, 2H), 7.62−7.72 (m, 4H), 8.09 (s, 1H), 8.14−8.18 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 84.8, 88.2, 91.5, 100.6, 121.4, 122.1, 122.6, 123.9, 125.5 (q, $J$ = 3.5 Hz), 126.2 (q, $J$ = 272.0 Hz), 128.5, 128.7, 129.1, 131.0, 131.55, 131.60, 132.1 (q, $J$ = 32.9 Hz), 133.1, 134.0, 147.0, 175.9. HRMS (EI) for $C_{26}H_{15}F_3O$: calcd 400.1075, found 400.1078.

**Synthesis of (*E*)-1-Phenyl-4-(phenylethynyl)hex-4-en-1-yn-3-one (1j).** To a solution of phenylacetylene (0.56 g, 0.60 mL, 5.5 mmol) in THF (10 mL) was added *n*-BuLi (2.1 mL, 5.0 mmol, 2.4 M solution in hexanes) at −78 °C. After the solution was stirred at the same temperature for 1 h, (*Z*)-2-bromobut-2-enal (0.75 g, 5.0 mmol) was added. The resulting solution was warmed up to room temperature and stirred for 3 h. Then, the mixture was quenched with saturated ammonium chloride solution, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum/ethyl acetate = 5:1) to afford (*Z*)-4-bromo-1-phenylhex-4-en-1-yn-3-ol (1.04 g, 83%) as a yellow oil.

To a solution of (*Z*)-4-bromo-1-phenylhex-4-en-1-yn-3-ol (0.25 g, 1.0 mmol) in diethylamine (1.5 mL) and THF (1.5 mL) were added phenylacetylene (0.15 g, 0.16 mL, 1.5 mmol), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol), and CuI (9.5 mg, 0.05 mmol) at room temperature, and then the mixture was stirred overnight. After the starting material was consumed, the mixture was quenched with $H_2O$, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum/ethyl acetate = 8:1) to afford (*E*)-1-phenyl-4-(phenylethynyl)hex-4-en-1-yn-3-ol (200 mg, 74%) as a yellow oil.

To a solution of the above alcohol (0.2 g, 0.74 mmol) in DMSO (3 mL) was added IBX (0.27 g, 0.96 mmol) at room temperature. After the starting material was consumed, the mixture was quenched by water, filtered, extracted with ethyl acetate, and dried over $Na_2SO_4$. The solvent was evaporated in vacuo, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to afford


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compound **1j** (0.10 g, 50%) as a yellow oil: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 2.24 (d, $J$ = 7.2 Hz, 3H), 7.32−7.39 (m, 5H), 7.42−7.47 (m, 1H), 7.53−7.55 (m, 2H), 7.58−7.62 (m, 3H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 17.3, 81.9, 86.3, 93.2, 98.6, 120.0, 122.7, 128.1, 128.3, 128.60, 128.63, 130.7, 131.6, 132.9, 151.4, 175.5. HRMS (EI) for $C_{20}H_{14}O$: calcd 270.1045, found 270.1042.

**Synthesis of (*E*)-1-(4-Methoxyphenyl)-4-(phenylethynyl)-hex-4-en-1-yn-3-one (1k).** To a solution of 1-ethynyl-4-methoxybenzene (0.79 g, 6 mmol) in THF (10 mL) was added *n*-BuLi (2.3 mL, 5.5 mmol, 2.4 M solution in hexanes) at −78 °C. After the solution was stirred at the same temperature for 1 h, (*Z*)-2-bromobut-2-enal (0.75 g, 5.0 mmol) was added. The resulting solution was warmed up to room temperature and stirred for 1 h. Then, the mixture was quenched with saturated ammonium chloride solution, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel to afford (*Z*)-4-bromo-1-(4-methoxyphenyl)hex-4-en-1-yn-3-ol. To a solution of the above product in diethylamine (10 mL) and THF (10 mL) were added phenylacetylene (0.77 g, 0.83 mL, 7.5 mmol), $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol), and CuI (47.6 mg, 0.25 mmol) at room temperature, and then the mixture was stirred overnight. After the starting material was consumed, the mixture was quenched with $H_2O$, extracted with ethyl acetate, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum/ethyl acetate = 8:1) to afford (*E*)-1-(4-methoxyphenyl)-4-(phenylethynyl)hex-4-en-1-yn-3-ol (0.60 g, 40% yield for two steps) as a brown oil.

To a solution of the above alcohol (0.60 g, 2 mmol) in DMSO (10 mL) was added IBX (0.73 g, 2.6 mmol) at room temperature. After the starting material was consumed, the mixture was quenched by water, filtered, extracted with ethyl acetate, and dried over $Na_2SO_4$. The solvent was evaporated in vacuo, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15:1 to 10:1) to afford compound **1k** (0.45 g, 75%) as a yellow solid: mp 92−93 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 2.23 (d, $J$ = 6.8 Hz, 3H), 3.84 (s, 3H), 6.88−6.91 (m, 2H), 7.34−7.36 (m, 3H), 7.53−7.61 (m, 5H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 17.3, 55.3, 82.2, 86.3, 94.4, 98.4, 111.8, 114.3, 122.8, 128.1, 128.3, 128.6, 131.7, 135.0, 150.8, 161.6, 175.5. HRMS (EI) for $C_{21}H_{16}O_2$: calcd 300.1150, found 300.1151.

**Typical Procedure for Gold-Catalyzed Tandem Annulation Reactions of 1,2-Bis(alkynyl)-2-en-1-ones with Indoles.** All reactions were carried out on 0.2 or 0.3 mmol scale. To a solution of $NaAuCl_4 \cdot 2H_2O$ (6 mg, 0.015 mmol) and indole (70.3 mg, 0.6 mmol) in DCE (3 mL) was added (*E*)-4-benzylidene-1-(4-chlorophenyl)-6-phenylhexa-1,5-diyn-3-one (**1g**) (110 mg, 0.3 mmol) at room temperature. The reaction mixture was stirred until the reaction was complete as monitored by thin-layer chromatography. The solvent was evaporated under the reduced pressure, and the residue was purified by chromatography on $Al_2O_3$ (eluent: *n*-hexane/ethyl acetate = 15:1) to afford the indole-fused carbocycle **3g** (130 mg, 90%) as a light yellow crystalline solid: mp 146−147 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 5.81 (s, 1H), 6.74 (s, 1H), 6.78 (s, 1H), 7.04−7.08 (m, 1H), 7.10−7.23 (m, 6H), 7.29−7.41 (m, 8H), 7.64−7.68 (m, 3H), 7.75 (d, $J$ = 7.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 39.0, 108.7, 110.7, 116.3, 117.6, 118.4, 120.0, 123.4, 123.8, 126.4, 126.8, 127.6, 127.7, 127.8, 128.4, 128.7, 129.1, 129.2, 130.1, 130.3, 131.3, 134.1, 136.3, 136.5, 145.1, 148.0, 154.9. HRMS (EI) for $C_{33}H_{22}ClNO$: calcd 483.1390, found 483.1385.

***3a***. Yield 92%. Yellow crystalline solid: mp 208−209 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 5.83 (s, 1H), 6.75 (s, 1H), 6.84 (s, 1H), 7.04−7.22 (m, 7H), 7.31−7.45 (m, 7H), 7.52−7.54 (m, 2H), 7.65−7.67 (m, 2H), 7.76−7.79 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 75.5 MHz) $\delta$ 39.1, 108.7, 110.6, 115.9, 117.6, 118.3, 119.8, 123.3, 123.8, 126.3, 126.9, 127.5, 127.56, 127.58, 128.2, 128.4, 128.7, 128.8, 128.9, 130.4, 130.5, 131.7, 136.1, 140.2, 145.3, 148.2, 154.7. HRMS (EI) for $C_{33}H_{23}NO$: calcd 449.1780, found 449.1783.

***3b***. Yield 56% (silica gel was used instead of $Al_2O_3$). Yellow solid: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 3.76 (s, 3H), 5.83 (s, 1H), 6.63 (s, 1H), 6.84 (s, 1H), 6.88 (d, $J$ = 8.8 Hz, 2H), 7.05−7.19 (m, 6H), 7.34−7.45 (m, 5H), 7.53−7.61 (m, 4H), 7.76 (d, $J$ = 7.6 Hz, 1H), 7.78 (s, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 39.1, 55.2, 107.2, 110.6, 114.1, 115.8, 117.7, 118.3, 119.8, 123.2, 123.5, 125.3, 126.3, 126.9, 127.6, 128.1, 128.4, 128.8, 128.9, 129.8, 131.8, 136.2, 140.3, 145.4, 147.6, 154.9, 159.2. HRMS (EI) for $C_{34}H_{25}NO_2$: calcd 479.1885, found 479.1880.

***3c***. $PPh_3AuNTf_2$ (5 mol %) was used. Yield 75%. Yellow solid: mp 131−132 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 5.79 (s, 1H), 6.67 (s, 1H), 6.80 (s, 1H), 7.04−7.18 (m, 6H), 7.24−7.27 (m, 2H), 7.32−7.44 (m, 5H), 7.49−7.53 (m, 4H), 7.73−7.75 (m, 1H), 7.75 (s, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 39.1, 109.1, 110.6, 115.9, 117.3, 118.3, 119.9, 123.3, 124.9, 126.4, 126.8, 127.52, 127.54, 128.2, 128.4, 128.76, 128.79, 128.82, 128.9, 130.9, 131.6, 133.1, 136.2, 140.1, 145.3, 148.4, 153.5. HRMS (EI) for $C_{33}H_{22}ClNO$: calcd 483.1390, found 483.1394.

***3d***. Yield 41%. Yellow oil: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 1.60−1.71 (m, 4H), 2.18−2.28 (m, 4H), 5.77 (s, 1H), 6.28 (s, 1H), 6.36 (t, $J$ = 4.0 Hz, 1H), 6.78 (s, 1H), 7.06−7.19 (m, 6H), 7.31 (d, $J$ = 7.6 Hz, 2H), 7.38−7.45 (m, 3H), 7.51−7.53 (m, 2H), 7.73−7.75 (m, 1H), 7.75 (s, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 22.1, 22.3, 24.8, 25.3, 39.1, 107.4, 110.5, 115.9, 117.8, 118.3, 119.7, 123.1, 123.5, 126.2, 126.9, 127.0, 127.1, 127.6, 128.0, 128.3, 128.8, 128.9, 129.8, 131.8, 136.1, 140.3, 145.5, 147.1, 156.5. HRMS (EI) for $C_{33}H_{27}NO$: calcd 453.2093, found 453.2089.

***3e***. Yield 64%. Yellow solid: $^1$H NMR ($CDCl_3$, $Me_4Si$, 300 MHz) $\delta$ 0.90 (t, $J$ = 7.5 Hz, 3H), 1.26−1.42 (m, 2H), 1.56−1.66 (m, 2H), 2.60 (t, $J$ = 7.5 Hz, 2H), 5.75 (s, 1H), 6.10 (s, 1H), 6.75 (s, 1H), 7.03−7.18 (m, 6H), 7.29−7.43 (m, 5H), 7.50−7.52 (m, 2H), 7.74 (m, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 75.5 MHz) $\delta$ 13.8, 22.3, 28.0, 29.9, 39.0, 108.7, 110.5, 115.8, 118.0, 118.2, 119.6, 123.0, 126.1, 126.3, 126.8, 127.6, 128.0, 128.3, 128.8, 128.9, 129.0, 131.8, 136.1, 140.3, 145.6, 146.8, 158.4. HRMS (EI) for $C_{31}H_{27}NO$: calcd 429.2093, found 429.2096.

***3f***. Yield 70% (silica gel was used instead of $Al_2O_3$). Light yellow crystalline solid: mp 130−131 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 3.81 (s, 3H), 5.82 (s, 1H), 6.76 (s, 1H), 6.80 (d, $J$ = 0.4 Hz, 1H), 6.93−6.97 (m, 2H), 7.04−7.09 (m, 1H), 7.10−7.23 (m, 6H), 7.32−7.35 (m, 4H), 7.44−7.47 (m, 2H), 7.65−7.67 (m, 2H), 7.76 (d, $J$ = 7.6 Hz, 1H), 7.83 (s, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 39.0, 55.3, 108.7, 110.6, 114.2, 115.8, 116.8, 118.3, 119.8, 123.2, 123.7, 126.3, 126.9, 127.2, 127.5, 127.6, 128.4, 128.6, 130.0, 130.3, 130.4, 132.1, 132.5, 136.1, 145.3, 148.4, 154.5, 159.6. HRMS (MALDI/DHB) for $C_{34}H_{26}NO_2$ $[M + H]^+$: calcd 480.1958, found 480.1955.

***3h***. Yield 77%. Light yellow crystalline solid: mp 134−135 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 5.81 (s, 1H), 6.73 (s, 1H), 6.82 (s, 1H), 7.06 (t, $J$ = 7.2 Hz, 1H), 7.12−7.22 (m, 6H), 7.30−7.34 (m, 4H), 7.56 (d, $J$ = 8.0 Hz, 2H), 7.63−7.66 (m, 4H), 7.76 (d, $J$ = 7.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 39.0, 108.8, 110.7, 116.6, 118.3, 118.4, 120.1, 122.7, 123.6, 123.8, 125.4, 125.8 (q, $J$ = 3.5 Hz), 126.4, 126.8, 127.5, 127.8, 128.35, 128.44, 128.7, 128.95, 129.01, 130.0 (q, $J$ = 34.4 Hz), 130.2, 130.9, 136.3, 143.7, 145.0, 147.8, 155.2. HRMS (EI) for $C_{34}H_{22}F_3NO$: calcd 517.1653, found 517.1656.

***3i***. Yield 73%. Yellow solid: $^1$H NMR ($CDCl_3$, $Me_4Si$, 300 MHz) $\delta$ 0.86 (d, $J$ = 7.2 Hz, 3H), 1.23−1.35 (m, 2H), 1.45−1.61 (m, 2H), 2.39−2.71 (m, 2H), 5.72 (s, 1H), 6.58 (s, 1H), 6.69 (s, 1H), 7.00−7.62 (m, 11H), 7.62−7.72 (m, 3H), 7.97 (s, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 75.5 MHz) $\delta$ 13.9, 22.1, 31.2, 35.1, 38.7, 108.5, 110.5, 115.5, 116.2, 118.4, 119.8, 123.0, 123.6, 126.1, 126.8, 127.3, 127.8, 128.2, 128.6, 129.2, 130.5, 132.7, 136.2, 145.2, 148.4, 153.8. HRMS (EI) for $C_{31}H_{27}NO$: calcd 429.2093, found 429.2095.

***3j***. Yield 47%. Yellow solid: mp 195−196 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 300 MHz) $\delta$ 1.40 (d, $J$ = 6.9 Hz, 3H), 4.61 (q, $J$ = 6.9 Hz, 1H),


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6.69 (s, 1H), 6.85 (s, 1H), 7.13−7.24 (m, 4H), 7.35−7.49 (m, 5H), 7.57−7.59 (m, 2H), 7.68−7.71 (m, 4H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 75.5 MHz) $\delta$ 23.2, 27.9, 107.8, 110.6, 117.4, 118.0, 118.1, 119.5, 123.0, 123.7, 126.9, 127.4, 128.1, 128.7, 128.8, 128.9, 129.6, 130.5, 130.6, 130.9, 136.2, 140.3, 147.8, 154.6. HRMS (EI) for $C_{28}H_{21}NO$: calcd 387.1623, found 387.1624.

***3k***. Yield 68%. Light yellow crystalline solid: mp 123−125 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 300 MHz) $\delta$ 1.39 (d, $J$ = 6.9 Hz, 3H), 3.82 (s, 3H), 4.59 (q, $J$ = 6.9 Hz, 1H), 6.67 (s, 1H), 6.79 (s, 1H), 6.96 (d, $J$ = 8.7 Hz, 2H), 7.13−7.24 (m, 4H), 7.35 (t, $J$ = 7.5 Hz, 2H), 7.56 (d, $J$ = 8.7 Hz, 2H), 7.67−7.75 (m, 4H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 75.5 MHz) $\delta$ 23.1, 27.9, 55.3, 107.8, 110.6, 114.2, 116.6, 117.9, 118.0, 119.5, 122.9, 123.6, 126.9, 127.3, 128.6, 129.2, 130.0, 130.2, 130.6, 131.3, 132.7, 136.2, 147.9, 154.4, 159.5. HRMS (EI) for $C_{29}H_{23}NO_2$: calcd 417.1729, found 417.1725.

***3l***. Yield 83%. Orange crystalline solid: mp 150−151 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 5.73 (s, 1H), 6.77 (s, 1H), 6.88 (s, 1H), 7.04−7.12 (m, 2H), 7.18−7.27 (m, 4H), 7.31−7.49 (m, 7H), 7.54−7.56 (m, 2H), 7.68 (d, $J$ = 8.0 Hz, 2H), 7.82 (s, 1H), 7.86 (s, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 39.0, 108.6, 112.1, 113.1, 115.2, 118.4, 120.8, 123.9, 126.0, 126.5, 126.8, 127.7, 127.8, 128.4, 128.5, 128.7, 128.8, 129.1, 129.4, 130.0, 130.3, 133.1, 134.7, 139.9, 144.9, 148.0, 155.1. HRMS (EI) for $C_{33}H_{22}BrNO$: calcd 527.0885, found 527.0886.

***3m***. Yield 82%. Yellow crystalline solid: mp 110−111 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 2.37 (s, 3H), 5.80 (s, 1H), 6.73 (s, 1H), 6.80 (d, $J$ = 0.8 Hz, 1H), 6.90 (s, 1H), 6.94 (dd, $J$ = 0.8, 8.0 Hz, 1H), 7.03−7.07 (m, 1H), 7.10−7.20 (m, 3H), 7.29−7.42 (m, 7H), 7.50−7.52 (m, 2H), 7.61−7.66 (m, 4H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 21.8, 39.2, 108.7, 110.5, 115.9, 117.0, 118.0, 121.7, 123.7, 125.5, 126.2, 127.3, 127.7, 127.5, 128.1, 128.4, 128.6, 128.8, 128.9, 130.4, 130.7, 131.0, 133.3, 136.6, 140.3, 145.4, 148.3, 154.6. HRMS (EI) for $C_{34}H_{25}NO$: calcd 463.1936, found 463.1939.

***3n***. Yield 83%. Yellow crystalline solid: mp 134−135 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 3.82 (s, 3H), 5.77 (s, 1H), 6.76 (s, 1H), 6.80−6.83 (m, 2H), 7.00−7.19 (m, 2H), 7.15−7.21 (m, 4H), 7.29−7.41 (m, 7H), 7.50−7.52 (m, 2H), 7.64−7.67 (m, 3H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 39.1, 55.8, 99.9, 108.7, 111.4, 113.6, 115.6, 117.3, 123.7, 126.3, 126.8, 127.4, 127.5, 128.0, 128.1, 128.4, 128.6, 128.78, 128.84, 130.4, 130.7, 131.6, 132.6, 140.2, 145.3, 148.2, 154.2, 154.6. HRMS (EI) for $C_{34}H_{25}NO_2$: calcd 479.1885, found 479.1882.

***3o***. Yield 85%. Yellow crystalline solid: mp 119−120 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 5.08 (s, 2H), 5.73 (s, 1H), 6.74 (s, 1H), 6.80 (d, $J$ = 0.8 Hz, 1H), 6.89 (dd, $J$ = 0.8, 8.8 Hz, 1H), 7.00 (d, $J$ = 8.8 Hz, 1H), 7.04−7.08 (m, 1H), 7.13−7.21 (m, 3H), 7.24 (d, $J$ = 1.6 Hz, 1H), 7.28−7.42 (m, 10H), 7.43−7.46 (m, 2H), 7.48−7.51 (m, 2H), 7.63−7.66 (m, 3H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 39.2, 70.8, 101.7, 108.7, 111.4, 114.3, 115.7, 117.3, 123.7, 126.3, 126.8, 127.4, 127.51, 127.54, 127.7, 127.9, 128.1, 128.4, 128.5, 128.6, 128.8, 128.9, 130.4, 130.6, 131.7, 132.5, 137.5, 140.2, 145.3, 148.3, 153.3, 154.6. HRMS (EI) for $C_{40}H_{29}NO_2$: calcd 555.2198, found 555.2200.

***3p***. $PPh_3AuNTf_2$ (5 mol %) was used. Yield 55%. Light yellow crystalline solid: mp 139−140 °C; $^1$H NMR ($CDCl_3$, $Me_4Si$, 300 MHz) $\delta$ 3.90 (s, 3H), 6.51 (s, 1H), 6.90 (s, 1H), 6.91 (s, 1H), 7.01−7.22 (m, 7H), 7.26−7.43 (m, 8H), 7.61 (d, $J$ = 6.9 Hz, 1H), 7.68 (d, $J$ = 8.1 Hz, 2H), 8.10 (s, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 75.5 MHz) $\delta$ 37.4, 52.2, 109.0, 114.7, 116.4, 118.7, 121.6, 123.6, 123.8, 124.0, 124.5, 125.7, 126.9, 127.5, 127.8, 128.1, 128.6, 128.7, 128.9, 129.2, 130.46, 130.49, 135.1, 137.2, 140.1, 144.6, 148.2, 155.0, 169.1. HRMS (MALDI/DHB) for $C_{35}H_{26}NO_3$ $[M + H]^+$: calcd 508.1907, found 508.1915.

***2a***. It was synthesized from **1a** using 5 mol % AgOTf and 2.0 equiv of indole in DCE. Yield 30% (silica gel was used instead of $Al_2O_3$). Light yellow solid: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 5.75 (s, 1H), 6.59 (s, 1H), 6.82 (d, $J$ = 1.6 Hz, 1H), 7.01 (t, $J$ = 7.2 Hz, 1H), 7.16 (t, $J$ = 7.2 Hz, 1H), 7.14−7.24 (m, 2H), 7.29−7.43 (m, 13H), 7.63 (d, $J$ = 7.6 Hz, 2H), 7.92 (s, 1H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 100.6 MHz) $\delta$ 40.0, 79.2, 97.2, 107.5, 111.1, 118.3, 119.5, 119.9, 122.1, 122.5, 123.3, 124.1, 126.5, 126.9, 127.8, 128.3, 128.40, 128.43, 128.5, 128.6, 130.1, 131.3, 133.6, 135.4, 136.6, 142.8, 154.1. HRMS (EI) for $C_{33}H_{23}NO$: calcd 449.1780, found 449.1776.

***4***. 2.5 equiv of indole was used. Yield 74%. Yellow solid: $^1$H NMR ($CDCl_3$, $Me_4Si$, 400 MHz) $\delta$ 4.07 (s, 1H), 5.68 (s, 1H), 6.08 (s, 1H), 6.75 (s, 1H), 6.88 (d, $J$ = 2.0 Hz, 1H), 7.03−7.18 (m, 9H), 7.24−7.27 (m, 3H), 7.36−7.42 (m, 3H), 7.46−7.49 (m, 2H), 7.53 (d, $J$ = 11.6 Hz, 1H), 7.67−7.74 (m, 3H); $^{13}$C NMR ($CDCl_3$, $Me_4Si$, 75.5 MHz) $\delta$ 24.8, 39.0, 109.7, 110.5, 111.1, 111.7, 115.9, 118.0, 118.2, 119.1, 119.4, 119.7, 122.0, 122.6, 123.1, 126.2, 126.4, 126.9, 127.1, 127.5, 128.0, 128.3, 128.8, 128.9, 129.3, 131.8, 136.1, 136.2, 140.3, 145.5, 147.2, 156.7. HRMS (EI) for $C_{36}H_{26}N_2O$: calcd 502.2045, found 502.2044.

**Synthesis of Oxirane 5.** Compound **3a** (90 mg, 0.2 mmol) was dissolved in ethyl acetate (2 mL). The reaction mixture was stirred for 5 days. During the process, a white solid precipitated. The mixture was filtrated, and the precipitate was washed with ethyl acetate and *n*-pentane. The solid was confirmed to be oxirane **5**. Yield 50% (48 mg): mp 248−249 °C; $^1$H NMR (*d*-DMSO, $Me_4Si$, 400 MHz, $\delta$ = 2.5 ppm as internal reference) $\delta$ 5.05 (s, 1H), 5.20 (s, 1H), 5.82 (s, 1H), 7.08−7.38 (m, 5H), 7.47−7.66 (m, 12H), 7.95 (d, $J$ = 7.6 Hz, 2H), 10.89 (s, 1H); $^{13}$C NMR (DMSO-$d_6$, $Me_4Si$, 75 MHz, $\delta$ = 40.45 ppm as internal reference) $\delta$ 44.5, 66.1, 72.4, 113.8, 119.2, 120.0, 121.2, 125.5, 126.5, 128.6, 129.0, 129.1, 129.5, 129.6, 129.8, 130.6, 131.5, 134.2, 136.8, 137.0, 137.8, 140.1, 148.7, 191.5, 192.4. HRMS (EI) for $C_{33}H_{23}NO_3$: calcd 481.1678, found 481.1674.

## ■ ASSOCIATED CONTENT

**Supporting Information.** X-ray crystallography of compounds **3p** and **5** and spectroscopic characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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