# Gold(I)-Catalyzed Cascade Cyclization of Alkynyl Indoles for the Stereoselective Construction of the Quaternary Carbon Center of Akuammiline Alkaloids

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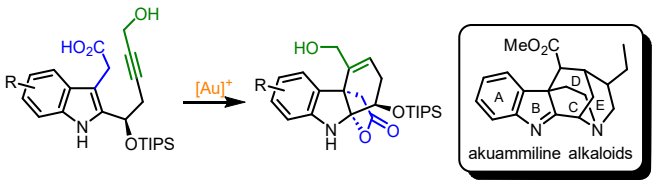
*Supporting Information Placeholder*




**ABSTRACT:** A gold-catalyzed cyclization reaction of alkynyl-indoles has been developed for the stereoselective construction of the quaternary carbon center of fused indolines. This reaction efficiently produces fused indolines via diastereoselective 6-*endo-dig* cyclization controlled by a bulky TIPS group, followed by nucleophilic attack of the carboxy group on the resulting imine. The lactone moiety of the fused indoline can be reductively cleaved to produce a tricyclic indoline, which could be useful for the synthesis of akuammiline alkaloids.

## INTRODUCTION

Akuammiline alkaloids are monoterpene indole alkaloids that are mainly isolated from oleander plants (Figure 1). More than 75 akuammiline alkaloids have been identified,[1] which often exhibit interesting biological activities, such as anticancer, antibacterial, anti-inflammatory, antitussive, and antimalarial activities.[2,3] These alkaloids have a highly fused cage-like scaffold, where the C-ring can contain different moieties, such as piperidine (**2**, **3**), tetrahydrofuran (**1**, **4**), and pyrrolidine (**5**, **6**) (shown in red in Figure 1). It is therefore highly desirable to develop efficient methods for synthesizing cage-like scaffolds for the late-stage construction of the C-ring and the structure–activity relationship study of akuammiline alkaloids. Although several efficient total syntheses of akuammiline alkaloids have been reported to date,[4-9] there are no reports on comprehensive synthetic methods for scaffolds with different C-ring moieties.

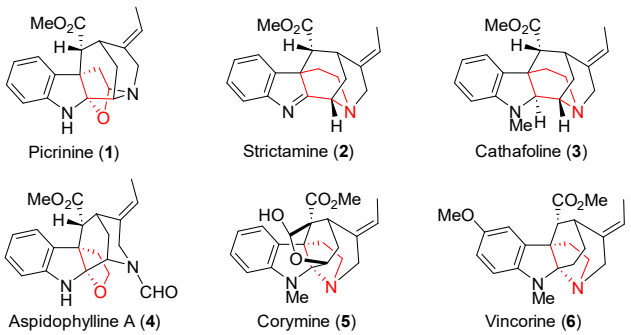


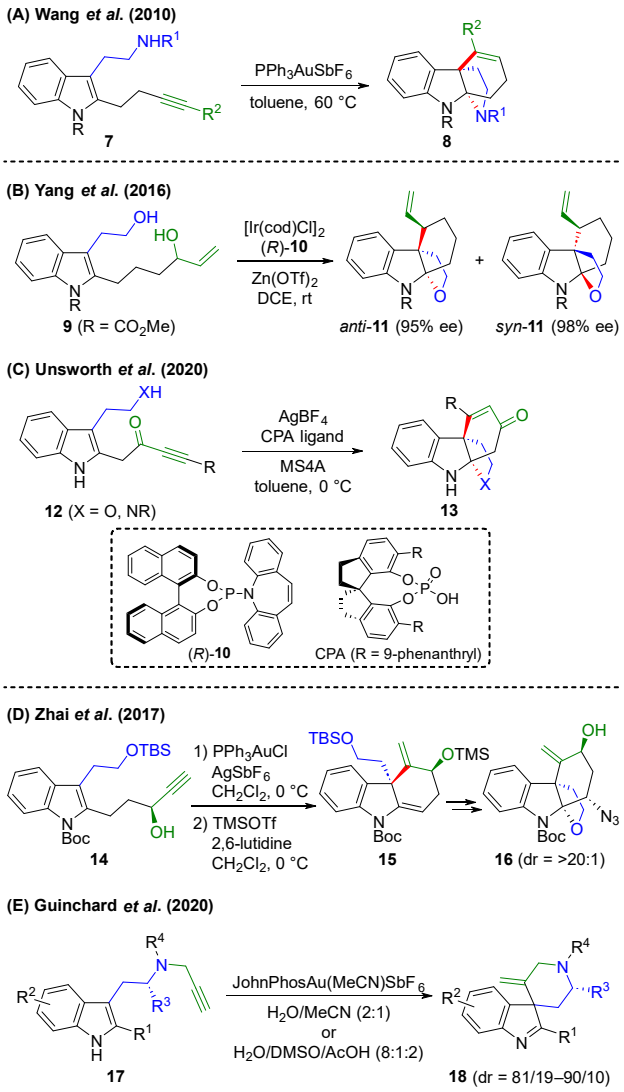

**Figure 1.** Representative akuammiline alkaloids.

Scheme 1 shows examples of methods that have been recently developed for the construction of an akuammiline-alkaloid-type fused indolenine scaffold. Wang synthesized the racemic fused indoline **8** containing a pyrrolidine ring through a gold-catalyzed cyclization of the tryptamine derivative **7** bearing an alkyne substituent at the C2-position (Scheme 1A).[10] In 2016, Yang reported the catalytic enantioselective construction of the fused indolines **11** by using a chiral iridium catalyst (Scheme 1B).[7a] Unsworth performed a catalytic asymmetric synthesis of the tetracyclic indolenines **13** by a silver-catalyzed reaction of the tryptamine derivatives **12** containing an ynone moiety in the presence of chiral phosphoric acid (CPA) (Scheme 1C).[11] By contrast, few studies have been performed on the asymmetric construction of the quaternary carbon center of fused indolines based on substrate control. In 2017, Zhai *et al*. constructed a quaternary chiral center by a gold-catalyzed cyclization of the indole **14** bearing a propargylic alcohol at the C2-position to stereoselectively produce **15**, which was subsequently transformed in several steps to the fused indoline **16** (dr = >20:1) containing a THF ring (Scheme 1D).[7c] Guinchard synthesized the spirocyclic indolenine **18** by a gold-catalyzed reaction in aqueous media of the *N*-alkynyl tryptamine or tryptophan derivative **17** (dr = 81:19–90:10, Scheme 1E).[12]

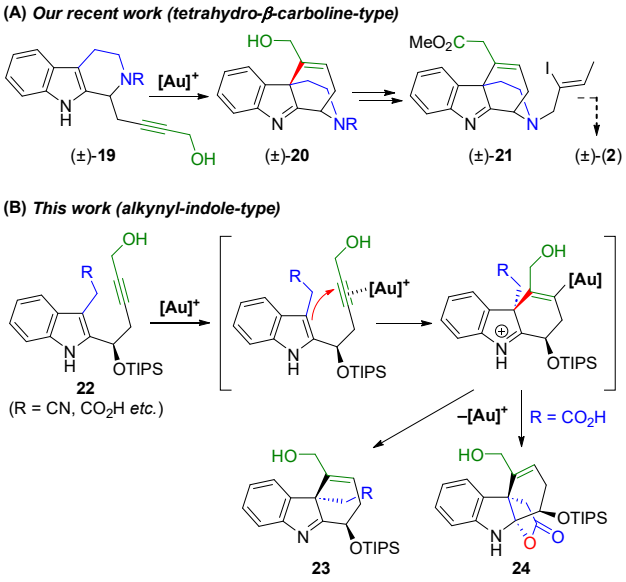
In 2016, we reported a formal total synthesis of strictamine (**2**) using a gold-catalyzed cyclization of the tetrahydro-β-carboline derivative **19** (Scheme 2A).[13,14] This reaction stereospecifically produced the tetracyclic indolenines **20**, due to the tetrahydro-β-carboline structure which determined the conformational relationship between the alkyne and indole. However, the final cyclization step from the known precursor **21** was not sufficient (5–12% yield as reported).[15] In the present study, we designed a strategy for the construction of the quaternary carbon

center of akuammiline alkaloid scaffolds, which can be used in C-ring formation at the late stage of the synthesis. Thus, a gold-catalyzed reaction of the linear alkynyl indole-type substrate **22** could be used to promote stereoselective 6-*endo-dig* cyclization, controlled by a bulky siloxy group, to stereoselectively construct the quaternary carbon (Scheme 2B). The iminium ion intermediate can then be protodeaurated to form the indolenine **23**, or alternatively, the tetracyclic indoline **24** starting with a cyclization precursor with a nucleophilic functional group, such as a carboxy group (R = $CO_2H$). This strategy is based on introducing a substituent in a high oxidation state (R = CN, $CO_2R'$, or $CO_2H$) to provide access to akuammiline alkaloids with diverse moieties on the C-ring based on the sufficient reactivity of the lactone ring in **24** (if formed). Herein, we report the stereoselective construction of a fused indoline ring with various substituents. The synthesis of a potential intermediate for akuammiline-type scaffolds is also described.

**Scheme 1. Reported Synthesis of Fused Indolenines**




**Scheme 2. Our Strategies: Gold(I)-Catalyzed Cyclization for the Construction of an Akuammiline Alkaloid Scaffold**




## RESULTS AND DISCUSSION

We initially synthesized the optically active alkynyl indole **22aa** as the cyclization precursor (Scheme 3). With some modification of the reported procedure,[16,17] the known primary alcohol **25** was prepared in 4 steps from (*S*)-(–)-glycidol. Swern oxidation of **25** and Seyferth–Gilbert alkyne synthesis afforded the diyne **26**. Tosyl-protected iodoaniline was used to carry out Sonogashira coupling–cyclization of **26a**,[18] and the tosyl group was then removed to afford the indole **28a**. Eschenmoser's salt was used to introduce a (dimethylamino)methyl group into **28a** to give **29a**, which was converted to the nitrile **30a** by treatment with iodomethane and KCN.[19] Finally, DIBAL reduction of **30a** was carried out, followed by Pinnick oxidation and removal of the TBS group to afford the acid **22aa**. Other cyclization precursors containing a nitrile, ester, or amide moiety were also synthesized through **30a** (see the Supporting Information).

Next, we investigated the gold-catalyzed cyclization of the alkynyl indole **22aa** (Table 1 and the Supporting Information). Reaction of **22aa** with a BrettPhos (**L1**) gold complex (10 mol%) efficiently afforded the bis-cyclization product **24aa** as a single diastereomer in 51% yield (Table 1, entry 1). The mono-cyclization product **23** (Scheme 2B) was not obtained. The relative configuration of the indoline **24aa** was determined by NOE analysis. The reaction was then optimized using several ligands and solvents (entries 2–9 and the Supporting Information). Among the investigated ligands, BrettPhos (**L1**) and $PPh_3$ exhibited good performance (51–52% yields, entries 1 and 3). The yield of **24aa** was improved by using silver-free conditions (entry 4). Screening of the reaction solvent revealed that the halogenated solvents dichloroethane (DCE) and 1,1,2,2-tetrachloroethane (TCE) are suitable for the reaction (entries 4 and 7). The highest yield of **24aa** (76%, entry 8) was obtained by decreasing the catalyst loading to 5 mol% and increasing the reaction temperature to 100 °C. Reducing the catalyst loading further (to 2 mol%) decreased the yield of **24aa** to 42% (entry 9). Based on these results, we selected Entry 8 as the optimized conditions.

**Scheme 3. Synthesis of the Cyclization Precursor 22aa**

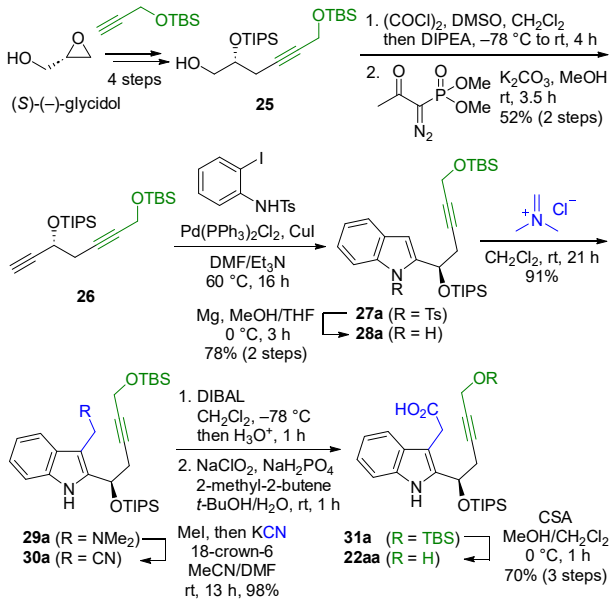
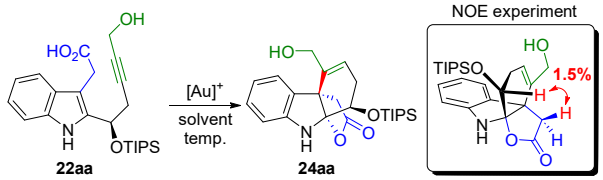
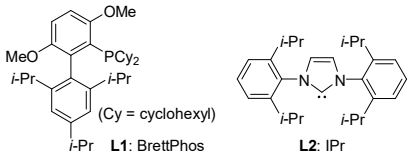



**Table 1. Optimization of Reaction Conditions**[a]



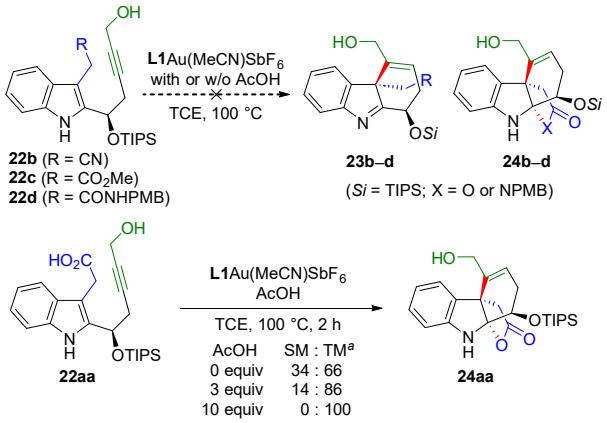

| Entry | Catalyst (mol%) | Solvent[b] (0.1 M) | Temp. (°C) | Time (h) | Yield[c] (%) |
|---|---|---|---|---|---|
| 1 | **L1**AuCl/AgSbF$_6$ (10) | DCE | 80 | 7 | 51 |
| 2 | **L2**AuCl/AgSbF$_6$ (10) | DCE | 80 | 5 | 30 |
| 3 | PPh$_3$AuCl/AgSbF$_6$ (10) | DCE | 80 | 4 | 52 |
| 4 | **L1**Au(MeCN)SbF$_6$ (10) | DCE | 80 | 3 | 65 |
| 5 | **L1**AuCl/AgSbF$_6$ (10) | MeCN | 80 | 21 | 57 |
| 6 | **L1**AuCl/AgSbF$_6$ (10) | toluene | 80 | 10 | 21 |
| 7 | **L1**Au(MeCN)SbF$_6$ (10) | TCE | 100 | 2 | 61 |
| 8 | **L1**Au(MeCN)SbF$_6$ (5) | TCE | 100 | 5 | 76 (74)[d] |
| 9 | **L1**Au(MeCN)SbF$_6$ (2) | TCE | 100 | 23 | 42 |




[a] All reactions were conducted at the 0.1 mmol scale. [b] DCE: 1,2-dichloroethane, TCE: 1,1,2,2-tetrachloroethane. [c] Isolated yields. [d] The reaction was conducted at the 12.4 mmol scale.

Using the nitrile **22b**, ester **22c**, or amide **22d** as substrates did not produce the desired cyclization products **23** or **24** (Scheme 4). Instead, the starting material was recovered or a complex mixture was produced. Considering that the carboxy group in **22aa** could act as a Brønsted acid to promote the gold-catalyzed cyclization, acetic acid was added to the reaction systems with **22b–d** as substrates; however, the desired reaction did not proceed successfully. By contrast, the reaction of the acid **22aa** was accelerated in proportion to the quantity of acetic acid added. These results suggested that the carboxy group in the substrates **22aa** not only promotes cyclization by acting as a Brønsted acid, but also plays other important roles, such as trapping the unstable intermediate.

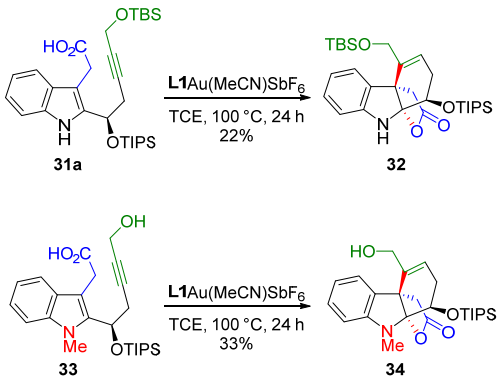
**Scheme 4. Effect of the Substrate Structure and Acid on the Reaction**




[a] Determined by $^1$H-NMR.

Next, we investigated effect of the free hydroxy and NH indole moieties on the reaction (Scheme 5). When using the TBS-protected alcohol **31a** as substrates, the cyclization products **32** was obtained in only 22% yield after 24 h. This result suggests that the free hydroxy group promotes the cyclization, presumably through a hydroxy-group-assisted coordination of alkyne to the gold catalyst.[20] In case using *N*-methylindole **33**, the yield was also decreased (33%) with prolonged reaction time, which can be attributed to the facile imine formation with NH indole in the first cyclization step.

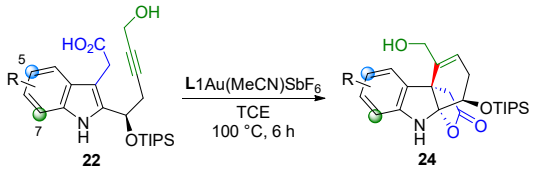
**Scheme 5. Effect of the Free Hydroxy Group and NH Indole**




We then evaluated the substrate scope of this reaction (Table 2). The acids **22ab–ad** with various halogen substituents at the indole C5-position gave the desired tetracyclic indoline (**24ab–ad**) in moderate to good yields (43–71%). Alkyl groups, such as methyl, isopropyl, and *tert*-butyl groups, were also tolerated,

affording **24ae**–**ag** in 50–57% yields. Substrates with a methoxy group at the C5- (**22ah**) or C7-position (**22ai**) produced the corresponding cyclization products **24ah** and **24ai**, which are potentially useful for the total synthesis of akuammiline alkaloids with a methoxy group.

**Table 2. Substrate Scope**[a]

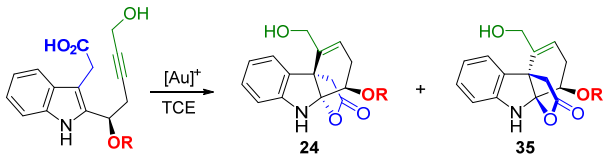



| Substrate | R | Yield (%)[b] |
|---|---|---|
| **22aa** | H | 76 |
| **22ab** | 5-Cl | 43 |
| **22ac** | 5-Br | 71 |
| **22ad** | 5-F | 53 |
| **22ae** | 5-Me | 50 |
| **22af** | 5-*i*-Pr | 53 |
| **22ag** | 5-*t*-Bu | 57 |
| **22ah** | 5-OMe | 58 |
| **22ai** | 7-OMe | 76 |

[a] The reactions were conducted at the 0.06–0.1 mmol scale using **L1**Au(MeCN)SbF$_6$ (5 mol%) in TCE at 100 °C for 6 h. [b] Isolated yields.

Next, we investigated the effect of the TIPS group on the stereoselectivity of this reaction (Scheme 6). When the substrate **22aj** containing the TBS group was used, the tetracyclic indoline **24aj** was obtained as a single diastereomer, as in the case of the TIPS-protected substrate. However, the substrate **22ak** with a methyl group gave an inseparable mixture of diastereomers (**24ak**:**35ak** = 74:26). It was thus proven that the steric effect of the hydroxy-protecting group controls the reaction stereoselectivity.

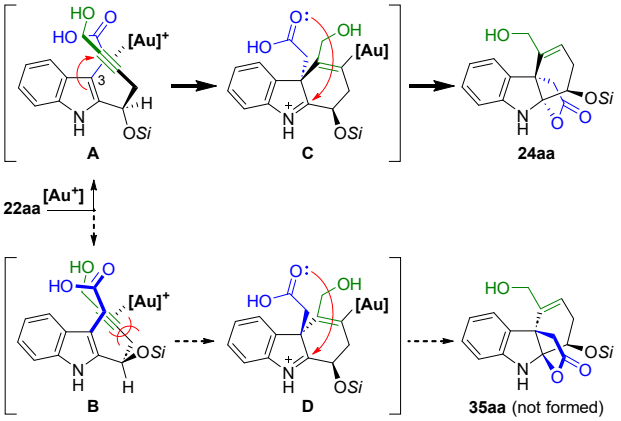
**Scheme 6. Effect of an Oxygen-Protecting Group on the Reaction Stereoselectivity**[a]




[a] Reaction conditions: **L1**Au(MeCN)SbF$_6$ (5 mol%) in TCE at 100 °C for 6 h. [b] Determined by $^1$H-NMR.

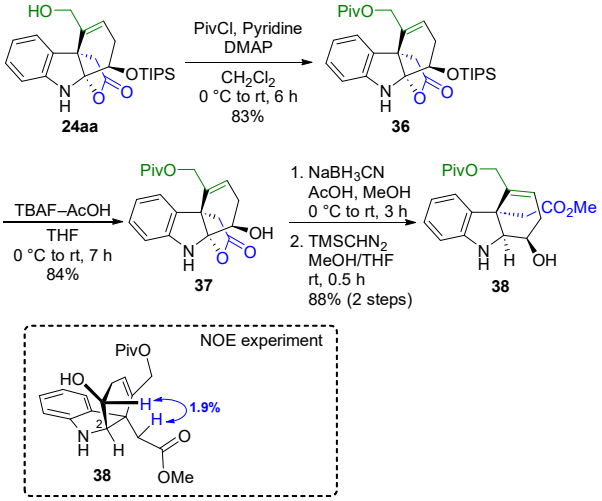
Based on the aforementioned results, the stereoselectivity of the reaction can be explained as shown in Scheme 7. The gold catalyst activates the alkyne, thereby promoting nucleophilic attack from the C3-position of the indole in a 6-*endo*-*dig* manner. The reaction proceeds exclusively from the front side of the indole, corresponding to the configuration shown in **A** rather than that shown in **B**, to circumvent steric repulsion between the TIPS and carboxymethyl groups. The subsequent nucleophilic attack of the carboxy group on the resulting imine gives the tetracyclic indoline **24aa** as a single diastereomer.

**Scheme 7. Reaction Stereoselectivity**




Finally, we investigated the ring-opening of the lactone moiety for use in akuammiline alkaloid synthesis (Scheme 8). The allyl alcohol of **24aa** was protected, the TIPS group was removed, and the lactone of **37** was reductively cleaved by sodium cyanoborohydride under acidic conditions to give carboxylic acid, which was then converted to the methyl ester **38**. The relative stereochemistry of **38** was confirmed by NOE analysis, showing that the configuration of **38** is appropriate for the synthesis of indolenine-type akuammiline alkaloids.

**Scheme 8. Reductive Ring-Opening Reaction Starting from 24aa**




## CONCLUSIONS

We developed a gold-catalyzed cyclization reaction for the stereoselective construction of the quaternary carbon center of akuammiline alkaloids. The diastereoselectivity of the reaction

was efficiently controlled by the bulky TIPS group to give cyclization products bearing various halogen or electron-donating groups. Investigations toward a comprehensive synthesis of akuammiline alkaloids based on this reaction are currently underway in our laboratory.

## EXPERIMENTAL SECTION

**General Methods**: $^1$H NMR spectra were recorded using a JEOL ECA-500 or a JEOL ECZ600R spectrometer. Chemical shifts are reported in $\delta$ (ppm) relative to $Me_4Si$ (in $CDCl_3$). $^{13}$C NMR spectra were recorded using a JEOL ECA-500 or a JEOL ECZ600R spectrometer and referenced to the residual solvent signal. IR spectra were obtained on a JASCO FT/IR-4100 spectrometer. Exact mass (HRMS) spectra were recorded on a JMS-700 mass spectrometer (FAB). Optical rotations were measured with a JASCO P-1020 polarimeter. For column chromatography, Wakogel C-300E (Wako), Chromatorex NH-DM1020 (Fuji Silysia) or COOH MB100-40/75 (Fuji Silysia) was employed. For thin layer chromatography, silica gel 70 F254 plate was employed. An oil bath was used for conventional heating.

## 1. SYNTHESIS OF SUBSTRATES

**(*R*)-2-[(Trityloxy)methyl]oxirane (S1).** To a solution of TrCl (103 g, 371 mmol) in $CH_2Cl_2$ (225 mL) were added $Et_3N$ (51.4 mL, 371 mmol) and (*S*)-(–)-glycidol (25.0 g, 337 mmol) at 0 ℃. After being stirred at room temperature for 16 h, the reaction was quenched with saturated aqueous $NH_4Cl$ and extracted with $CH_2Cl_2$ (×3). The combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was recrystallized from 2-propanol to give **S1** (91.4 g, 86%) as a white solid; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.47–7.45 (m, 6H), 7.31–7.21 (m, 9H), 3.32 (dd, $J$ = 10.0, 2.6 Hz, 1H), 3.16–3.10 (m, 2H), 2.76 (dd, $J$ = 5.2, 4.6 Hz, 1H), 2.61 (dd, $J$ = 5.2, 2.3 Hz, 1H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 143.9 (3C), 128.8 (6C), 128.0 (6C), 127.2 (3C), 86.8, 64.9, 51.2, 44.7. The spectral data were in good agreement with those previously reported.[16]

**(*R*)-6-[(*tert*-Butyldimethylsilyl)oxy]-2-[(triisopropylsilyl)oxy]hex-4-yn-1-ol (25).** *tert*-Butyldimethyl(prop-2-yn-1-yloxy)silane (15.8 mL, 77.5 mmol) was dissolved in THF (221 mL) and cooled to –78 ℃. *n*-BuLi (1.6 M in hexane; 50.0 mL, 77.5 mmol) was added dropwise to the mixture at –78 ℃. After the mixture was stirred for 30 min, a solution of **S1** (16.3 g, 51.7 mmol) in THF (207 mL) was added dropwise to the mixture. The mixture was stirred for additional 30 min, then $BF_3{\cdot}OEt_2$ (9.09 mL, 72.4 mmol) was added dropwise to the mixture, and the mixture was stirred at –78 ℃ for 2 h. After the resulting mixture was allowed to warm to room temperature, the mixture was stirred for 11 h. The mixture was diluted with saturated aqueous $NH_4Cl$ and extracted with EtOAc (×3). The combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc = 14/1 to 5/1) to give **S2** as a colorless oil. To a solution of **S2** in THF (230 mL) and DMF (115 mL) were added $Et_3N$ (17.9 mL, 129 mmol), $AgNO_3$ (10.5 g, 62.0 mmol) and TIPSCl (13.1 mL, 62.0 mmol) at 0 ℃. The resulting mixture was allowed to warm to room temperature and stirred for 12 h. The mixture was diluted with saturated aqueous $NaHCO_3$, filtered through a pad of Celite® and extracted with EtOAc (×3). The combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc = 99/1) to give **S3** as a colorless oil. The protected triol **S3** (28.8 g, 44.9 mmol) was dissolved in $CH_2Cl_2$ (180 mL) and cooled to –78 ℃. After $Et_3SiH$ (20.1 mL, 135 mmol) and $BF_3{\cdot}OEt_2$ (11.3 mL, 89.8 mmol) were added dropwise, the resulting mixture was allowed to warm to –20 ℃ over 80 min, and stirred at the same temperature for 2 h. The reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with $CH_2Cl_2$ (×3). The combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc = 49/1 to 5/1) to give **25** (12.6 g, 79% in 3 steps) as a colorless oil; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.28 (t, $J$ = 2.3 Hz, 2H), 4.01 (ddd, $J$ = 8.3, 8.3, 4.2 Hz, 1H), 3.75–3.66 (m, 2H), 2.59–2.53 (m, 1H) , 2.46–2.41 (m, 1H), 1.99 (dd, $J$ = 7.7, 4.9 Hz, 1H), 1.13–1.05 (m, 21H), 0.91 (s, 9H), 0.11 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 81.3, 80.9, 71.6, 65.4, 52.0, 25.9 (3C), 24.2, 18.3, 18.1 (6C), 12.5 (3C), –5.0 (2C). The spectral data were in good agreement with those previously reported. [17]

**(*R*)-7-[(*tert*-Butyldimethylsilyl)oxy]-3-[(triisopropylsilyl)oxy]hepta-1,5-diyne (26).** A mixture of $CH_2Cl_2$ (49.3 mL) and DMSO (1.40 mL, 19.7 mmol) was cooled to –78 ℃, and $(COCl)_2$ (1.27 mL, 14.8 mmol) was added dropwise to the mixture. After being stirred for 30 min, a solution of **25** (3.95 g, 9.87 mmol) in $CH_2Cl_2$ (9.87 mL) was added dropwise to the mixture. After the mixture was stirred for 30 min, DIPEA (8.39 mL, 49.3 mmol) was added dropwise to the mixture. After the mixture was allowed to warm to room temperature and stirred for additional 3 h, the reaction was quenched with cold water. The whole was extracted with $CH_2Cl_2$ (×3), and the combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude aldehyde was used in the next step without purification. To a solution of the crude aldehyde in MeOH (98.7 mL) were added $K_2CO_3$ (2.77 g, 20.0 mmol) and Ohira-Bestmann reagent (2.22 mL, 14.8 mmol) at 0 ℃. After being stirred at room temperature for 3.5 h, the reaction was quenched with cold water, and the whole was extracted with $Et_2O$ (×3). The combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =99/1) to give **26** (2.01 g, 52% in 2 steps) as a colorless oil; $[\alpha]^{28}_D$ –4.71 (*c* 0.85, $CHCl_3$); IR ($CDCl_3$) 2240 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.57 (td, $J$ = 6.7, 2.3 Hz, 1H), 4.30 (t, $J$ = 2.0 Hz, 2H), 2.65–2.62 (m, 2H), 2.42 (d, $J$ = 2.3 Hz, 1H), 1.17–1.07 (m, 21H), 0.91 (s, 9H), 0.12 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 84.7, 80.90, 80.83, 72.7, 62.2, 52.1, 29.9, 26.0 (3C), 18.3, 17.95 (3C), 17.93 (3C), 12.3 (3C), –5.0 (2C); HRMS (FAB) $C_{22}H_{43}O_2Si_2$ $[M + H]^+$: 395.2802; found 395.2794.

**(*R*)-2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indole (28a).** 2-Iodo-*N*-tosylaniline (4.62 g, 12.4 mmol), $Pd(PPh_3)_2Cl_2$ (789 mg, 1.12 mmol) and CuI (428 mg, 2.25 mmol) were charged in the flask under argon atmosphere. $Et_3N$ (22.5 mL) and a solution of **26** (4.43 g, 11.2 mmol) in DMF (89.8 mL) were added to them at room temperature. The mixture was heated to 60 ℃ for 16 h. After being cooled to room temperature, the reaction was quenched with saturated aqueous $NH_4Cl$, and the whole was extracted with $CH_2Cl_2$ (×3). The combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered and concen-

trated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =49/1) to give **27a** as a brown oil. Mg powder (5.94 g, 244 mmol) was added to a solution of **27a** (5.20 g, 8.13 mmol) in THF (81.3 mL) and MeOH (81.3 mL) at 0 °C. After being stirred at 0 °C for 2 h, saturated aqueous $NH_4Cl$ was added to the mixture, and the mixture was stirred at room temperature for 1 h. The mixture was extracted with EtOAc (×3). The combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/$Et_2O$ =49/1) to give **28a** (3.10 g, 78% in 2 steps) as a pale yellow oil; $[\alpha]^{26}_D$ –4.72 (*c* 0.61, $CHCl_3$); IR ($CDCl_3$) 3423 (NH), 2344 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.43 (br s, 1H), 7.56 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.35 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.15 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 7.07 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 6.37 (d, *J* = 2.3 Hz, 1H), 5.15 (dd, *J* = 6.9, 5.2 Hz, 1H), 4.28 (t, *J* = 2.0 Hz, 2H), 2.78–2.68 (m, 2H), 1.12–1.03 (m, 21H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 140.5, 135.6, 128.2, 121.5, 120.5, 119.5, 110.9, 99.2, 81.4, 81.3, 68.2, 52.0, 30.4, 25.8 (3C), 18.3, 18.0 (3C), 17.9 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{28}H_{48}NO_2Si_2$ [M + H]$^+$: 486.3224; found 486.3230.

**(*R*)-2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-chloro-1*H*-indole (28b).** Reaction was conducted according to the procedure for **28a**, using 4-chloro-2-iodo-*N*-tosylaniline instead of 2-iodo-*N*-tosylaniline. Purification was performed by column chromatography over silica gel (hexane/$Et_2O$ =49/1) to give **28b** (471 mg, 30% in 2 steps) as a colorless oil; $[\alpha]^{21}_D$ –5.30 (*c* 2.02, $CHCl_3$); IR ($CDCl_3$) 3440 (NH), 2238 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.47 (br s, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.10 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.32 (d, *J* = 1.7 Hz, 1H), 5.12 (dd, *J* = 7.2, 4.9 Hz, 1H), 4.27 (m, 2H), 2.77–2.68 (m, 2H), 1.12–1.02 (m, 21H), 0.89 (s, 9H), 0.080 (s, 3H), 0.076 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 142.0, 133.9, 129.2, 125.2, 121.8, 119.9, 111.8, 98.9, 81.6, 81.0, 68.1, 51.9, 30.3, 25.8 (3C), 18.3, 17.94 (3C), 17.88 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{28}H_{47}ClNO_2Si_2$ [M + H]$^+$: 520.2834; found 520.2836.

**(*R*)-5-Bromo-2-{5-[(*tert*-butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indole (28c).** Reaction was conducted according to the procedure for **28a**, using 4-bromo-2-iodo-*N*-tosylaniline instead of 2-iodo-*N*-tosylaniline. Purification was performed by column chromatography over silica gel (hexane/$Et_2O$ =60/1) to give **28c** (501 mg, 35% in 2 steps) as a colorless oil; $[\alpha]^{24}_D$ –3.62 (*c* 1.38, $CHCl_3$); IR ($CDCl_3$) 3473 (NH), 2238 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.48 (br s, 1H), 7.67 (s, 1H), 7.23–7.22 (m, 2H), 6.31 (d, *J* = 2.3 Hz, 1H), 5.12 (dd, *J* = 7.2, 4.9 Hz, 1H), 4.27 (s, 2H), 2.77–2.68 (m, 2H), 1.15–1.00 (m, 21H), 0.89 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 141.9, 134.1, 129.9, 124.3, 123.0, 112.7, 112.3, 98.8, 81.6, 81.0, 68.0, 51.9, 30.3, 25.8 (3C), 18.3, 17.93 (3C), 17.87 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{28}H_{47}BrNO_2Si_2$ [M + H]$^+$: 564.2329; found 564.2323.

**(*R*)-2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-fluoro-1*H*-indole (28d).** Reaction was conducted according to the procedure for the synthesis of **28a**, using 4-fluoro-2-iodo-*N*-tosylaniline instead of 2-iodo-*N*-tosylaniline. Purification was performed by column chromatography over silica gel (hexane/$Et_2O$ =60/1) to give **28d** (549 mg, 43% in 2 steps) as a colorless oil; $[\alpha]^{24}_D$ –4.63 (*c* 1.32, $CHCl_3$); IR ($CDCl_3$) 3462 (NH), 2226 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.43 (br s, 1H), 7.25–7.24 (m, 1H), 7.19 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.89 (ddd, *J* = 9.0, 9.0, 2.5 Hz, 1H), 6.33 (d, *J* = 1.7 Hz, 1H), 5.12 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.28 (s, 2H), 2.76–2.70 (m, 2H), 1.15–1.01 (m, 21H), 0.89 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 157.8 (d, $J_{C\text{-}F}$ = 233.9 Hz), 142.4, 132.0, 128.5 (d, $J_{C\text{-}F}$ = 10.8 Hz), 111.4 (d, $J_{C\text{-}F}$ = 10.8 Hz), 109.8 (d, $J_{C\text{-}F}$ = 26.4 Hz), 105.2 (d, $J_{C\text{-}F}$ = 22.8 Hz), 99.3 (d, $J_{C\text{-}F}$ = 4.8 Hz), 81.5, 81.1, 68.1, 51.9, 30.3, 25.8 (3C), 18.3, 17.95 (3C), 17.89 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{28}H_{47}FNO_2Si_2$ [M + H]$^+$: 504.3129; found 504.3134.

**(*R*)-2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-methyl-1*H*-indole (28e).** Reaction was conducted according to the procedure for the synthesis of **28a**, using 2-iodo-4-methyl-*N*-tosylaniline instead of 2-iodo-*N*-tosylaniline. Purification was performed by column chromatography over silica gel (hexane/$Et_2O$ =49/1) to give **28e** (471 mg, 37% in 2 steps) as a colorless oil; $[\alpha]^{25}_D$ –4.16 (*c* 1.62, $CHCl_3$); IR ($CDCl_3$) 3479 (NH), 2242 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.31 (br s, 1H), 7.34 (d, *J* = 1.1 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.97 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.28 (d, *J* = 1.7 Hz, 1H), 5.12 (dd, *J* = 6.9, 5.2 Hz, 1H), 4.27 (s, 2H), 2.76–2.66 (m, 2H), 2.43 (s, 3H), 1.14–1.00 (m, 21H), 0.90 (s, 9H), 0.090 (s, 3H), 0.087 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 140.7, 133.9, 128.7, 128.4, 123.0, 120.2, 110.5, 98.7, 81.4, 81.3, 68.3, 52.0, 30.4, 25.9 (3C), 21.4, 18.3, 17.97 (3C), 17.91 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{29}H_{50}NO_2Si_2$ [M + H]$^+$: 500.3380; found 500.3382.

**(*R*)-2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-isopropyl-1*H*-indole (28f).** Reaction was conducted according to the procedure for the synthesis of **28a**, using 2-iodo-4-isopropyl-*N*-tosylaniline instead of 2-iodo-*N*-tosylaniline. Purification was performed by column chromatography over silica gel (hexane/$Et_2O$ =49/1) to give **28f** (724 mg, 54% in 2 steps) as a colorless oil; $[\alpha]^{25}_D$ –8.96 (*c* 1.12, $CHCl_3$); IR ($CDCl_3$) 3479 (NH), 2324 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.34 (br s, 1H), 7.40 (d, *J* = 1.7 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.31 (d, *J* = 1.7 Hz, 1H), 5.13 (dd, *J* = 6.9, 5.2 Hz, 1H), 4.27 (s, 2H), 2.99 (hept, *J* = 6.9 Hz, 1H), 2.75–2.65 (m, 2H), 1.30 (d, *J* = 6.9 Hz, 6H), 1.15–1.01 (m, 21H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 140.7, 140.1, 134.1, 128.3, 120.7, 117.4, 110.6, 98.9, 81.4, 81.3, 68.3, 52.0, 34.2, 30.5, 25.8 (3C), 24.68, 24.64, 18.3, 18.00 (3C), 17.95 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{31}H_{54}NO_2Si_2$ [M + H]$^+$: 528.3693; found 528.3688.

**(*R*)-5-(*tert*-Butyl)-2-{5-[(*tert*-butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indole (28g).** Reaction was conducted according to the procedure for the synthesis of **28a**, using 2-iodo-4-*tert*-butyl-*N*-tosylaniline instead of 2-iodo-*N*-tosylaniline. Purification was performed by column chromatography over silica gel (hexane/$Et_2O$ =60/1) to give **28g** (695 mg, 51% in 2 steps) as a yellow oil; $[\alpha]^{21}_D$ –4.22 (*c* 3.25, $CHCl_3$); IR ($CDCl_3$) 3480 (NH), 2232 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.34 (br s, 1H), 7.56 (d, *J* = 2.3 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.24 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.33 (d, *J* = 1.7 Hz, 1H), 5.14 (dd, *J* = 6.6, 4.9 Hz, 1H), 4.27 (s, 2H), 2.75–2.66 (m, 2H), 1.38 (s, 9H), 1.16–1.02 (m, 21H), 0.90 (s, 9H), 0.092 (s, 3H), 0.085 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 142.3, 140.7, 133.7, 128.0, 119.7, 116.4, 110.3, 99.1, 81.4, 81.3, 68.3, 52.0, 34.5, 31.9 (3C), 30.5, 25.9 (3C), 18.3, 18.00

(3C), 17.96 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{32}H_{56}NO_2Si_2$ [M + H]$^+$: 542.3850; found 542.3853.

**(*R*)-2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-methoxy-1*H*-indole (28h).** Reaction was conducted according to the procedure for the synthesis of **28a**, using 2-iodo-4-methoxy-*N*-tosylaniline instead of 2-iodo-*N*-tosylaniline. Purification was performed by column chromatography over silica gel (hexane/$Et_2O$ = 30/1 to 20/1) to give **28h** (639 mg, 49% in 2 steps) as a colorless oil; $[\alpha]^{24}_D$ –2.36 (*c* 2.26, $CHCl_3$); IR ($CDCl_3$) 3424 (NH), 2242 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.31 (br s, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.30 (d, *J* = 1.7 Hz, 1H), 5.12 (dd, *J* = 6.9, 5.2 Hz, 1H), 4.28 (s, 2H), 3.84 (s, 3H), 2.77–2.68 (m, 2H), 1.15–1.01 (m, 21H), 0.90 (s, 9H), 0.090 (s, 3H), 0.088 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 154.0, 141.3, 130.7, 128.6, 111.6, 111.5, 102.4, 99.0, 81.40, 81.33, 68.3, 55.8, 52.0, 30.4, 25.8 (3C), 18.3, 17.97 (3C), 17.91 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{29}H_{50}NO_3Si_2$ [M + H]$^+$: 516.3329; found 516.3326.

**(*R*)-2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-7-methoxy-1*H*-indole (28i).** Reaction was conducted according to the procedure for the synthesis of **28a**, using 2-iodo-6-methoxy-*N*-tosylaniline instead of 2-iodo-*N*-tosylaniline. Purification was performed by column chromatography over silica gel (hexane/$Et_2O$ = 20/1) to give **28i** (532 mg, 69% in 2 steps) as a colorless oil; $[\alpha]^{23}_D$ –9.93 (*c* 1.04, $CHCl_3$); IR ($CDCl_3$) 3482 (NH), 2234 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.54 (br s, 1H), 7.16 (dd, *J* = 8.0, 0.6 Hz, 1H), 6.99 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.61 (dd, *J* = 8.0, 0.6 Hz, 1H), 6.34 (d, *J* = 2.3 Hz, 1H), 5.13–5.12 (m, 1H), 4.27 (t, *J* = 2.0 Hz, 2H), 3.95 (s, 3H), 2.78–2.67 (m, 2H), 1.15–1.01 (m, 21H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 146.1, 140.1, 129.4, 126.0, 119.8, 113.2, 101.5, 99.5, 81.30, 81.25, 68.4, 55.3, 51.9, 30.5, 25.8 (3C), 18.3, 17.97 (3C), 17.91 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{29}H_{50}NO_3Si_2$ [M + H]$^+$: 516.3329; found 516.3328.

**(*R*)-1-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (29a).** To a solution of **28a** (911 mg, 1.88 mmol) in $CH_2Cl_2$ (9.38 mL) was added Eschenmoser's salt (230 mg, 2.46 mmol) at room temperature. After being stirred at the same temperature for 21 h, the mixture was diluted with 2 N NaOH and extracted with $CH_2Cl_2$ (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over $NH_2$-silica gel (hexane/EtOAc =49/1) to give **29a** (924 mg, 91%) as a colorless oil; $[\alpha]^{23}_D$ +35.2 (*c* 0.75, $CHCl_3$); IR ($CDCl_3$) 3476 (NH), 2234 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.41 (br s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.15 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 7.08 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 5.40 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.25 (t, *J* = 2.0 Hz, 2H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.51 (d, *J* = 13.2 Hz, 1H), 2.80–2.71 (m, 2H), 2.20 (s, 6H), 1.14–1.02 (m, 21H), 0.89 (s, 9H), 0.07 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 138.1, 134.8, 128.7, 121.4, 119.4, 119.1, 110.7, 108.2, 81.6, 80.9, 66.0, 54.0, 52.0, 45.6 (2C), 30.0, 25.8 (3C), 18.3, 18.0 (3C), 17.9 (3C), 12.3 (3C), –5.1 (2C); HRMS (FAB) calcd for $C_{31}H_{55}N_2O_2Si_2$ [M + H]$^+$: 543.3802; found 543.3806.

**(*R*)-1-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-chloro-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (29b).** Reaction was conducted according to the procedure for the synthesis of **29a**. Purification was performed by column chromatography over $NH_2$-silica gel (hexane/EtOAc =49/1) to give **29b** (362 mg, 93%) as a colorless oil; $[\alpha]^{24}_D$ +38.0 (*c* 1.84, $CHCl_3$); IR ($CDCl_3$) 3475 (NH), 2230 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.42 (br s, 1H), 7.67 (d, *J* = 2.3 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.09 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.37 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.24 (s, 2H), 3.48 (s, 2H), 2.76–2.74 (m, 2H), 2.20 (s, 6H), 1.13–1.02 (m, 21H), 0.88 (s, 9H), 0.06 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 139.5, 133.2, 129.8, 124.9, 121.8, 119.0, 111.7, 108.2, 81.3, 81.1, 65.8, 53.9, 51.9, 45.5 (2C), 29.9, 25.8 (3C), 18.3, 18.0 (3C), 17.9 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{31}H_{54}ClN_2O_2Si_2$ [M + H]$^+$: 577.3412; found 577.3418.

**(*R*)-5-Bromo-1-(2-{5-[(*tert*-butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (29c).** Reaction was conducted according to the procedure for the synthesis of **29a**. Purification was performed by column chromatography over $NH_2$-silica gel (hexane/EtOAc =49/1) to give **29c** (512 mg, 97%) as a colorless oil; $[\alpha]^{24}_D$ +37.6 (*c* 1.82, $CHCl_3$); IR ($CDCl_3$) 3471 (NH), 2237 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.43 (br s, 1H), 7.83 (d, *J* = 1.1 Hz, 1H), 7.24–7.19 (m, 2H), 5.37 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.24 (s, 2H), 3.48 (s, 2H), 2.80–2.70 (m, 2H), 2.20 (s, 6H), 1.15–0.98 (m, 21H), 0.88 (s, 9H), 0.06 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 139.3, 133.4, 130.4, 124.3, 122.1, 112.5, 112.2, 108.1, 81.2, 81.1, 65.8, 53.9, 51.9, 45.5 (2C), 29.9, 25.8 (3C), 18.3, 18.0 (3C), 17.9 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{31}H_{54}BrN_2O_2Si_2$ [M + H]$^+$: 621.2907; found 621.2902.

**(*R*)-1-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-fluoro-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (29d).** Reaction was conducted according to the procedure for the synthesis of **29a**. Purification was performed by column chromatography over $NH_2$-silica gel (hexane/EtOAc = 50/1) to give **29d** (532 mg, 90%) as a colorless oil; $[\alpha]^{24}_D$ +31.3 (*c* 2.81, $CHCl_3$); IR ($CDCl_3$) 3474 (NH), 2237 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.38 (br s, 1H), 7.34 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.23 (dd, *J* = 9.2, 4.3 Hz, 1H), 6.88 (ddd, *J* = 9.2, 9.2, 2.3 Hz, 1H), 5.37 (dd, *J* = 4.9, 4.9 Hz, 1H), 4.25 (s, 2H), 3.47 (s, 2H), 2.75 (t, *J* = 4.9 Hz, 2H), 2.20 (s, 6H), 1.15–0.98 (m, 21H), 0.88 (s, 9H), 0.06 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 157.7 (d, $J_{C\text{-}F}$ = 232.7 Hz), 139.9, 131.3, 129.1 (d, $J_{C\text{-}F}$ = 9.6 Hz), 111.2 (d, $J_{C\text{-}F}$ = 9.6 Hz), 109.7 (d, $J_{C\text{-}F}$ = 26.4 Hz), 108.6 (d, $J_{C\text{-}F}$ = 4.8 Hz), 104.4 (d, $J_{C\text{-}F}$ = 24.0 Hz), 81.3, 81.0, 65.9, 54.0, 51.9, 45.5 (2C), 29.9, 25.8 (3C), 18.3, 18.0 (3C), 17.9 (3C), 12.2 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{31}H_{54}FN_2O_2Si_2$ [M + H]$^+$: 561.3708; found 561.3708.

**(*R*)-1-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-methyl-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (29e).** Reaction was conducted according to the procedure for the synthesis of **29a**. Purification was performed by column chromatography over $NH_2$-silica gel (hexane/EtOAc =49/1) to give **29e** (352 mg, 67%) as a colorless oil; $[\alpha]^{24}_D$ +36.0 (*c* 0.50, $CHCl_3$); IR ($CDCl_3$) 3475 (NH), 2240 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.28 (br s, 1H), 7.46 (d, *J* = 1.1 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.97 (dd, *J* = 8.0, 1.1 Hz, 1H), 5.37 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.24 (s, 2H), 3.51 (d, *J* = 13.2 Hz, 1H), 3.47 (d, *J* = 13.2 Hz, 1H), 2.79–2.69 (m, 2H), 2.44 (s, 3H), 2.21 (s, 6H), 1.13–1.02 (m, 21H), 0.89 (s, 9H), 0.08 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 138.3, 133.2, 129.0, 128.3, 123.0, 119.0, 110.4, 107.8, 81.7, 80.8, 66.0, 54.0, 52.0, 45.6 (2C), 30.0, 25.9 (3C), 21.5, 18.3, 18.0 (3C), 17.9 (3C),

12.3 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{32}H_{57}N_2O_2Si_2$ [M + H]$^+$: 557.3959; found 557.3957.

**(*R*)-1-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-isopropyl-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (29f).** Reaction was conducted according to the procedure for the synthesis of **29a**. Purification was performed by column chromatography over $NH_2$-silica gel (hexane/EtOAc =49/1) to give **29f** (726 mg, 91%) as a colorless oil; $[\alpha]^{23}_D$ +34.5 (*c* 2.60, $CHCl_3$); IR ($CDCl_3$) 3476 (NH), 2242 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.32 (br s, 1H), 7.49 (d, *J* = 1.7 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.05 (dd, *J* = 8.6, 1.7 Hz, 1H), 5.41 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.24 (t, *J* = 1.7 Hz, 2H), 3.52 (d, *J* = 13.7 Hz, 1H), 3.50 (d, *J* = 13.7 Hz, 1H), 3.01 (hept, *J* = 6.9 Hz, 1H), 2.78–2.68 (m, 2H), 2.21 (s, 6H), 1.31 (d, *J* = 6.9 Hz, 6H), 1.16–0.99 (m, 21H), 0.89 (s, 9H), 0.08 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 139.7, 138.4, 133.4, 128.8, 120.3, 116.4, 110.5, 107.9, 81.7, 80.8, 66.1, 53.9, 52.0, 45.6 (2C), 34.3, 30.0, 25.9 (3C), 24.7 (2C), 18.3, 18.01 (3C), 17.95 (3C), 12.3 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{34}H_{61}N_2O_2Si_2$ [M + H]$^+$: 585.4272; found 585.4265.

**(*R*)-5-(*tert*-Butyl)-1-(2-{5-[(*tert*-butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (29g).** Reaction was conducted according to the procedure for the synthesis of **29a**. Purification was performed by column chromatography over $NH_2$-silica gel (hexane/EtOAc =49/1) to give **29g** (684 mg, 97%) as a colorless oil; $[\alpha]^{23}_D$ +39.5 (*c* 2.05, $CHCl_3$); IR ($CDCl_3$) 3479 (NH), 2243 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.33 (br s, 1H), 7.63 (d, *J* = 2.3 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.23 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.42 (dd, *J* = 5.2, 5.2 Hz, 1H), 4.24 (s, 2H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.51 (d, *J* = 13.2 Hz, 1H), 2.78–2.69 (m, 2H), 2.21 (s, 6H), 1.39 (s, 9H), 1.16–1.00 (m, 21H), 0.89 (s, 9H), 0.08 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 141.8, 138.4, 132.9, 128.6, 119.6, 114.9, 110.2, 108.1, 81.8, 80.8, 66.1, 53.8, 52.0, 45.6 (2C), 34.6, 32.0 (3C), 30.0, 25.9 (3C), 18.3, 18.02 (3C), 17.96 (3C), 12.3 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{35}H_{63}N_2O_2Si_2$ [M + H]$^+$: 599.4428; found 599.4425.

**(*R*)-1-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-methoxy-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (29h).** Reaction was conducted according to the procedure for the synthesis of **29a**. Purification was performed by column chromatography over $NH_2$-silica gel (hexane/EtOAc =24/1) to give **29h** (637 mg, 95%) as a colorless oil; $[\alpha]^{23}_D$ +31.6 (*c*. 1.20, $CHCl_3$); IR ($CDCl_3$) 3470 (NH), 2249 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.28 (br s, 1H), 7.22 (d, *J* = 9.2 Hz, 1H), 7.15 (d, *J* = 2.6 Hz, 1H), 6.81 (dd, *J* = 9.2, 2.6 Hz, 1H), 5.37 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.25 (t, *J* = 1.7 Hz, 2H), 3.86 (s, 3H), 3.51 (d, *J* = 13.2 Hz, 1H), 3.48 (d, *J* = 13.2 Hz, 1H), 2.79–2.70 (m, 2H), 2.21 (s, 6H), 1.12–1.02 (m, 21H), 0.89 (s, 9H), 0.07 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 153.8, 139.0, 130.0, 129.2, 111.3 (2C), 108.0, 101.6, 81.6, 80.9, 66.0, 55.9, 54.0, 52.0, 45.5 (2C), 30.0, 25.8 (3C), 18.3, 18.0 (3C), 17.9 (3C), 12.3 (3C), –5.2 (2C); HRMS (FAB) calcd for $C_{32}H_{57}N_2O_3Si_2$ [M + H]$^+$: 573.3908; found 573.3912.

**(*R*)-1-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-7-methoxy-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (29i).** Reaction was conducted according to the procedure for the synthesis of **29a**. Purification was performed by column chromatography over $NH_2$-silica gel (hexane/EtOAc =24/1) to give **29i** (529 mg, 90%) as a colorless oil; $[\alpha]^{23}_D$ +28.1 (*c* 1.04, $CHCl_3$); IR ($CDCl_3$) 3481 (NH), 2238 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.52 (br s, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.38 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.25 (t, *J* = 2.0 Hz, 2H), 3.95 (s, 3H), 3.53 (d, *J* = 13.6 Hz, 1H), 3.49 (d, *J* = 13.6 Hz, 1H), 2.75 (dt, *J* = 5.4, 2.0 Hz, 2H), 2.20 (s, 6H), 1.10–1.03 (m, 21H), 0.88 (s, 9H), 0.072 (s, 3H), 0.068 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 146.0, 137.7, 130.0, 125.2, 119.5, 112.2, 108.8, 101.5, 81.7, 80.8, 66.2, 55.3, 54.1, 52.0, 45.5 (2C), 30.1, 25.8 (3C), 18.3, 18.0 (3C), 17.9 (3C), 12.3 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{32}H_{57}N_2O_3Si_2$ [M + H]$^+$: 573.3908; found 573.3903.

**(*R*)-2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)acetonitrile (30a).** To a solution of **29a** (11.0 g, 20.2 mmol) in MeCN (40.5 mL) was added MeI (2.52 mL, 40.4 mmol) at room temperature. After the mixture was stirred for 12 h, KCN (2.64 g, 40.4 mmol), 18-crown-6 (5.35 g, 20.2 mmol) and DMF (40.5 mL) were added to the mixture. After being stirred for additional 1 h, the mixture was diluted with water and extracted with $Et_2O$ (×3). The combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =24/1) to give **30a** (10.4 g, 98%) as a colorless oil; $[\alpha]^{27}_D$ –16.3 (*c* 2.66, $CHCl_3$); IR ($CDCl_3$) 3469 (NH), 2250 (CN/C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.39 (br s, 1H), 7.63 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.38 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.23 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.18 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 5.27 (dd, *J* = 8.6, 4.6 Hz, 1H), 4.28–4.20 (m, 2H), 3.94 (d, *J* = 18.3 Hz, 1H), 3.84 (d, *J* = 18.3 Hz, 1H), 2.85–2.80 (m, 1H), 2.74–2.72 (m, 1H), 1.17–0.99 (m, 21H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 137.4, 134.9, 127.1, 122.6, 120.1, 118.2, 117.8, 111.2, 99.5, 81.7, 80.2, 66.3, 51.9, 30.3, 25.8 (3C), 18.3, 17.9 (3C), 17.8 (3C), 13.3, 12.1 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{30}H_{49}N_2O_2Si_2$ [M + H]$^+$: 525.3333; found 525.3340.

**(*R*)-2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-chloro-1*H*-indol-3-yl)acetonitrile (30b).** Reaction was conducted according to the procedure for the synthesis of **30a**. Purification was performed by column chromatography over silica gel (hexane/EtOAc =24/1 to 5/1) to give **30b** (297 mg, 85%) as a colorless oil; $[\alpha]^{24}_D$ –18.6 (*c* 1.78, $CHCl_3$); IR ($CDCl_3$) 3348 (NH), 2254 (CN/C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.45 (br s, 1H), 7.59 (d, *J* = 2.3 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.18 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.25 (dd, *J* = 8.6, 4.6 Hz, 1H), 4.24 (s, 2H), 3.90 (d, *J* = 17.8 Hz, 1H), 3.79 (d, *J* = 17.8 Hz, 1H), 2.85–2.80 (m, 1H), 2.76–2.70 (m, 1H), 1.14–1.01 (m, 21H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 139.0, 133.2, 128.1, 126.0, 123.0, 117.8, 117.4, 112.2, 99.4, 81.9, 79.9, 66.2, 51.9, 30.2, 25.8 (3C), 18.3, 17.9 (3C), 17.8 (3C), 13.2, 12.0 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{30}H_{48}ClN_2O_2Si_2$ [M + H]$^+$: 559.2943; found 559.2935.

**(*R*)-5-Bromo-2-(2-{5-[(*tert*-butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)acetonitrile (30c).** Reaction was conducted according to the procedure for the synthesis of **30a**. Purification was performed by column chromatography over silica gel (hexane/EtOAc =24/1 to 5/1) to give **30c** (449 mg, 97%) as a colorless oil; $[\alpha]^{24}_D$ –14.9 (*c* 2.02, $CHCl_3$); IR ($CDCl_3$) 3461 (NH), 2251 (CN/C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.47 (br s, 1H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.31 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 5.25 (dd, *J* = 8.6, 4.6 Hz, 1H), 4.24 (s, 2H), 3.90 (d, *J* = 18.3 Hz, 1H), 3.79 (d, *J* = 18.3 Hz, 1H), 2.85–2.80 (m, 1H), 2.76–2.70

(m, 1H), 1.13–1.01 (m, 21H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 138.8, 133.5, 128.7, 125.6, 120.9, 117.4, 113.4, 112.7, 99.3, 81.9, 79.9, 66.1, 51.8, 30.2, 25.8 (3C), 18.3, 17.9 (3C), 17.8 (3C), 13.2, 12.0 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{30}H_{48}BrN_2O_2Si_2$ $[M + H]^+$: 603.2438; found 603.2438.

**(*R*)-2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-fluoro-1*H*-indol-3-yl)acetonitrile (30d).** Reaction was conducted according to the procedure for the synthesis of **30a**. Purification was performed by column chromatography over silica gel (hexane/EtOAc =24/1 to 5/1) to give **30d** (434 mg, 94%) as a colorless oil; $[\alpha]^{24}_D$ –20.0 (*c* 1.22, $CHCl_3$); IR ($CDCl_3$) 3472 (NH), 2252 (CN/C≡C); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.41 (br s, 1H), 7.29 (dd, $J$ = 9.2, 4.5 Hz, 1H), 7.27 (dd, $J$ = 9.2, 2.5 Hz, 1H), 6.97 (ddd, $J$ = 9.2, 9.2, 2.5 Hz, 1H), 5.25 (dd, $J$ = 8.9, 4.3 Hz, 1H), 4.28–4.20 (m, 2H), 3.90 (d, $J$ = 17.8 Hz, 1H), 3.79 (d, $J$ = 17.8 Hz, 1H), 2.85–2.80 (m, 1H), 2.74–2.72 (m, 1H), 1.17–0.99 (m, 21H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 158.0 (d, $J_{C\text{-}F}$ = 235.1 Hz), 139.3, 131.3, 127.5 (d, $J_{C\text{-}F}$ = 9.6 Hz), 117.5, 111.9 (d, $J_{C\text{-}F}$ = 9.6 Hz), 111.0 (d, $J_{C\text{-}F}$ = 26.4 Hz), 103.4 (d, $J_{C\text{-}F}$ = 24.0 Hz), 99.8 (d, $J_{C\text{-}F}$ = 4.8 Hz), 81.9, 80.0, 66.3, 51.9, 30.3, 25.8 (3C), 18.3, 17.86 (3C), 17.78 (3C), 13.4, 12.1 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{30}H_{48}FN_2O_2Si_2$ $[M + H]^+$: 543.3238; found 543.3234.

**(*R*)-2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-methyl-1*H*-indol-3-yl)acetonitrile (30e).** Reaction was conducted according to the procedure for the synthesis of **30a**. Purification was performed by column chromatography over silica gel (hexane/EtOAc =24/1 to 5/1) to give **30e** (298 mg, 87%) as a colorless oil; $[\alpha]^{25}_D$ –17.7 (*c* 2.26, $CHCl_3$); IR ($CDCl_3$) 3370 (NH), 2250 (CN/C≡C); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.29 (br s, 1H), 7.40 (d, $J$ = 1.1 Hz, 1H), 7.26 (d, $J$ = 8.6 Hz, 1H), 7.05 (dd, $J$ = 8.6, 1.1 Hz, 1H), 5.24 (dd, $J$ = 8.3, 4.3 Hz, 1H), 4.25 (d, $J$ = 15.5 Hz, 1H), 4.22 (d, $J$ = 15.5 Hz, 1H), 3.91 (d, $J$ = 18.3 Hz, 1H), 3.81 (d, $J$ = 18.3 Hz, 1H), 2.83–2.69 (m, 2H), 2.47 (s, 3H), 1.12–1.02 (m, 21H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 137.5, 133.2, 129.5, 127.3, 124.2, 117.89, 117.85, 110.9, 99.1, 81.7, 80.2, 66.4, 51.9, 30.3, 25.8 (3C), 21.5, 18.3, 17.9 (3C), 17.8 (3C), 13.3, 12.1 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{31}H_{51}N_2O_2Si_2$ $[M + H]^+$: 539.3489; found 539.3496.

**(*R*)-2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-isopropyl-1*H*-indol-3-yl)acetonitrile (30f).** Reaction was conducted according to the procedure for the synthesis of **30a**. Purification was performed by column chromatography over silica gel (hexane/EtOAc =24/1 to 5/1) to give **30f** (626 mg, 89%) as a colorless oil; $[\alpha]^{25}_D$ –17.6 (*c* 3.05, $CHCl_3$); IR ($CDCl_3$) 3474 (NH), 2250 (CN/C≡C); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.32 (br s, 1H), 7.43 (d, $J$ = 1.7 Hz, 1H), 7.30 (d, $J$ = 8.6 Hz, 1H), 7.13 (dd, $J$ = 8.6, 1.7 Hz, 1H), 5.26 (dd, $J$ = 8.6, 4.0 Hz, 1H), 4.25–4.22 (m, 2H), 3.93 (d, $J$ = 18.3 Hz, 1H), 3.83 (d, $J$ = 18.3 Hz, 1H), 3.04 (hept, $J$ = 6.9 Hz, 1H), 2.83–2.78 (m, 1H), 2.72–2.70 (m, 1H), 1.32 (d, $J$ = 6.9 Hz, 6H), 1.17–1.00 (m, 21H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 140.8, 137.5, 133.4, 127.2, 121.7, 117.9, 115.2, 111.0, 99.3, 81.7, 80.2, 66.4, 51.9, 34.3, 30.4, 25.8 (3C), 24.6 (2C), 18.3, 17.9 (3C), 17.8 (3C), 13.3, 12.1 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{33}H_{55}N_2O_2Si_2$ $[M + H]^+$: 567.3802; found 567.3795.

**(*R*)-2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-(*tert*-butyl)-1*H*-indol-3-yl)acetonitrile (30g).** Reaction was conducted according to the procedure for the synthesis of **30a**. Purification was performed by column chromatography over silica gel (hexane/EtOAc =24/1 to 5/1) to give **30g** (523 mg, 79%) as a colorless oil; $[\alpha]^{25}_D$ –20.9 (*c* 1.48, $CHCl_3$); IR ($CDCl_3$) 3472 (NH), 2249 (CN/C≡C); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.31 (br s, 1H), 7.57 (d, $J$ = 1.7 Hz, 1H), 7.33–7.30 (m, 2H), 5.27 (dd, $J$ = 8.6, 4.6 Hz, 1H), 4.27–4.20 (m, 2H), 3.94 (d, $J$ = 17.8 Hz, 1H), 3.84 (d, $J$ = 17.8 Hz, 1H), 2.83–2.78 (m, 1H), 2.74–2.68 (m, 1H), 1.40 (s, 9H), 1.17–1.00 (m, 21H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 143.1, 137.5, 133.0, 126.8, 120.9, 117.9, 113.9, 110.7, 99.5, 81.7, 80.3, 66.4, 51.9, 34.7, 31.9 (3C), 30.4, 25.8 (3C), 18.3, 17.9 (3C), 17.8 (3C), 13.3, 12.1 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{34}H_{57}N_2O_2Si_2$ $[M + H]^+$: 581.3959; found 581.3962.

**(*R*)-2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-methoxy-1*H*-indol-3-yl)acetonitrile (30h).** Reaction was conducted according to the procedure for the synthesis of **30a**. Purification was performed by column chromatography over silica gel (hexane/EtOAc =14/1 to 5/1) to give **30h** (498 mg, 83%) as a colorless oil; $[\alpha]^{24}_D$ –13.8 (*c* 1.98, $CHCl_3$); IR ($CDCl_3$) 3353 (NH), 2250 (CN/C≡C); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.28 (br s, 1H), 7.26 (d, $J$ = 8.6 Hz, 1H), 7.04 (d, $J$ = 2.3 Hz, 1H), 6.88 (dd, $J$ = 8.6, 2.3 Hz, 1H), 5.23 (dd, $J$ = 8.6, 4.6 Hz, 1H), 4.28–4.21 (m, 2H), 3.91 (d, $J$ = 18.3 Hz, 1H), 3.88 (s, 3H), 3.81 (d, $J$ = 18.3 Hz, 1H), 2.84–2.79 (m, 1H), 2.75–2.69 (m, 1H), 1.16–0.99 (m, 21H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 154.4, 138.1, 129.9, 127.5, 117.7, 112.9, 112.0, 99.9, 99.3, 81.7, 80.2, 66.4, 55.9, 51.9, 30.4, 25.8 (3C), 18.3, 17.9 (3C), 17.8 (3C), 13.4, 12.1 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{31}H_{51}N_2O_3Si_2$ $[M + H]^+$: 555.3438; found 555.3440.

**(*R*)-2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-7-methoxy-1*H*-indol-3-yl)acetonitrile (30i).** Reaction was conducted according to the procedure for the synthesis of **30a**. Purification was performed by column chromatography over silica gel (hexane/EtOAc =14/1 to 5/1) to give **30i** (482 mg, 98%) as a colorless oil; $[\alpha]^{25}_D$ –24.2 (*c* 1.66, $CHCl_3$); IR ($CDCl_3$) 3474 (NH), 2250 (CN/C≡C); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.53 (br s, 1H), 7.23 (d, $J$ = 8.0 Hz, 1H), 7.09 (dd, $J$ = 8.0, 8.0 Hz, 1H), 6.68 (d, $J$ = 8.0 Hz, 1H), 5.24 (dd, $J$ = 8.6, 4.6 Hz, 1H), 4.26–4.21 (m, 2H), 3.96 (s, 3H), 3.93 (d, $J$ = 18.3 Hz, 1H), 3.82 (d, $J$ = 18.3 Hz, 1H), 2.84–2.82 (m, 1H), 2.73–2.71 (m, 1H), 1.16–0.99 (m, 21H), 0.87 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 146.1, 137.0, 128.3, 125.4, 120.6, 117.8, 110.9, 102.5, 100.0, 81.6, 80.2, 66.5, 55.4, 51.9, 30.4, 25.8 (3C), 18.3, 17.9 (3C), 17.8 (3C), 13.5, 12.1 (3C), –5.3 (2C); HRMS (FAB) calcd for $C_{31}H_{51}N_2O_3Si_2$ $[M + H]^+$: 555.3438; found 555.3442.

**(*R*)-2-(2-{5-Hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)acetic acid (22aa).** A solution of **30a** (9.33 g, 17.8 mmol) in $CH_2Cl_2$ (355 mL) was cooled to –78 °C and DIBAL (1.0 M in toluene; 44.4 mL, 44.4 mmol) was added dropwise to the mixture. After the mixture was stirred at –78 °C for 1 h, saturated aqueous Rochelle salt and $Et_2O$ were added to the mixture, and the mixture was stirred vigorously at room temperature for 1 h. The mixture was extracted with $Et_2O$ (×3), and the combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The resulting crude aldehyde was used in the next step without purification.

To a solution of the crude aldehyde in *t*-BuOH (284 mL) and $H_2O$ (71.1 mL) were added $NaH_2PO_4$ (12.8 g, 107 mmol), 2-methyl-2-butene (113 mL, 1.07 mol) and $NaClO_2$ (4.83 g, 53.4 mmol) at room temperature. After being stirred at the same temperature for 1 h, the mixture was diluted with brine and extracted with EtOAc (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by short column chromatography over silica gel (hexane/EtOAc =5/1) to give **31a**. To a solution of **31a** in $CH_2Cl_2$ (88.8 mL) and MeOH (88.8 mL) was added (-)-10-camphor sulfonic acid (1.24 g, 5.33 mmol) at 0 ℃. After being stirred at the same temperature for 1 h, the mixture was diluted with water and extracted with EtOAc (×5). Combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 1/1 to 0/1) to give **22aa** (5.33 g, 70% in 3 steps) as a brown amorphous solid; $[\alpha]^{24}_D$ +22.3 (*c* 0.43, $CHCl_3$); IR ($CDCl_3$) 3474 (OH), 3401 (OH), 3300 (NH), 2230 (C≡C), 1708 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.38 (br s, 1H), 7.58 (d, $J$ = 8.0 Hz, 1H), 7.35 (d, $J$ = 8.0 Hz, 1H), 7.19 (dd, $J$ = 8.0, 8.0 Hz, 1H), 7.12 (dd, $J$ = 8.0, 8.0 Hz, 1H), 5.23–5.20 (m, 1H), 4.11–4.03 (m, 2H), 3.87 (d, $J$ = 16.0 Hz, 1H), 3.67 (d, $J$ = 16.0 Hz, 1H), 2.84–2.74 (m, 2H), 1.12–0.95 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.2, 137.6, 135.3, 128.1, 122.4, 119.8, 119.1, 111.1, 103.8, 81.8, 80.6, 66.2, 51.1, 30.3, 30.2, 17.9 (3C), 17.7 (3C), 12.2 (3C); HRMS (FAB) calcd for $C_{24}H_{36}NO_4Si$ $[M + H]^+$: 430.2414; found 430.2411.

**(*R*)-2-(5-Chloro-2-{5-hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)acetic acid (22ab).** Reaction was conducted according to the procedure for the synthesis of **22aa**. Purification was performed by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 1/1 to 1/4) to give **22ab** (62.4 mg, 29% in 3 steps) as a brown oil; $[\alpha]^{26}_D$ +26.6 (*c* 2.22, $CHCl_3$); IR ($CDCl_3$) 3468 (NH/OH), 3292 (NH/OH), 2229 (C≡C), 1709 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.49 (br s, 1H), 7.53 (d, $J$ = 1.7 Hz, 1H), 7.24 (d, $J$ = 8.6 Hz, 1H), 7.11 (dd, $J$ = 8.6, 1.7 Hz, 1H), 5.19 (dd, $J$ = 7.4, 5.2 Hz, 1H), 4.07 (s, 2H), 3.81 (d, $J$ = 16.0 Hz, 1H), 3.63 (d, $J$ = 16.0 Hz, 1H), 2.82–2.73 (m, 2H), 1.11–0.94 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.3, 139.0, 133.5, 129.1, 125.4, 122.5, 118.5, 112.0, 103.4, 81.5, 80.6, 66.0, 50.9, 30.1, 30.0, 17.8 (3C), 17.7 (3C), 12.0 (3C); HRMS (FAB) calcd for $C_{24}H_{35}ClNO_4Si$ $[M + H]^+$: 464.2024; found 464.2028.

**(*R*)-2-(5-Bromo-2{-5-hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)acetic acid (22ac).** Reaction was conducted according to the procedure for the synthesis of **22aa**. Purification was performed by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 1/1 to 0/1) to give **22ac** (107 mg, 30% in 3 steps) as a yellow amorphous solid; $[\alpha]^{24}_D$ +21.8 (*c* 2.67, $CHCl_3$); IR ($CDCl_3$) 3465 (NH), 3418 (OH), 2247 (C≡C), 1710 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.54 (br s, 1H), 7.69 (d, $J$ = 1.1 Hz, 1H), 7.23–7.20 (m, 2H), 5.18 (dd, $J$ = 7.4, 5.2 Hz, 1H), 4.06 (s, 2H), 3.80 (d, $J$ = 16.6 Hz, 1H), 3.63 (d, $J$ = 16.6 Hz, 1H), 2.82–2.73 (m, 2H), 1.11–0.93 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.3, 138.8, 133.7, 129.7, 125.1, 121.6, 112.9, 112.5, 103.2, 81.5, 80.6, 66.0, 50.9, 30.1, 29.9, 17.8 (3C), 17.7 (3C), 12.0 (3C); HRMS (FAB) calcd for $C_{24}H_{35}BrNO_4Si$ $[M + H]^+$: 508.1519; found 508.1515.

**(*R*)-2-(5-Fluoro-2{-5-hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)acetic acid (22ad).** Reaction was conducted according to the procedure for the synthesis of **22aa**. Purification was performed by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 2/1 to 0/1) to give **22ad** (61.4 mg, 18% in 3 steps) as a brown oil; $[\alpha]^{27}_D$ +19.8 (*c* 1.86, $CHCl_3$); IR ($CDCl_3$) 3461 (NH), 3341 (OH), 2232 (C≡C), 1710 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.44 (br s, 1H), 7.24 (dd, $J$ = 8.6, 4.0 Hz, 1H), 7.21 (dd, $J$ = 8.6, 2.3 Hz, 1H), 6.90 (ddd, $J$ = 8.6, 8.6, 2.3 Hz, 1H), 5.19 (dd, $J$ = 7.4, 5.2 Hz, 1H), 4.08–4.05 (m, 2H), 3.80 (d, $J$ = 16.0 Hz, 1H), 3.63 (d, $J$ = 16.0 Hz, 1H), 2.82–2.73 (m, 2H), 1.11–0.95 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.3, 157.9 (d, $J_{C\text{-}F}$ = 235.1 Hz), 139.3, 131.6, 128.4 (d, $J_{C\text{-}F}$ = 10.8 Hz), 111.6 (d, $J_{C\text{-}F}$ = 9.6 Hz), 110.5 (d, $J_{C\text{-}F}$ = 26.4 Hz), 104.1 (d, $J_{C\text{-}F}$ = 24.0 Hz), 103.8 (d, $J_{C\text{-}F}$ = 3.6 Hz), 81.6, 80.6, 66.1, 50.9, 30.2, 30.0, 17.8 (3C), 17.7 (3C), 11.9 (3C); HRMS (FAB) calcd for $C_{24}H_{35}FNO_4Si$ $[M + H]^+$: 448.2319; found 448.2314.

**(*R*)-2-(2-{5-Hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-methyl-1*H*-indol-3-yl)acetic acid (22ae).** Reaction was conducted according to the procedure for the synthesis of **22aa**. Purification was performed by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 1/1 to 0/1) to give **22ae** (65.3 mg, 27% in 3 steps) as a brown oil; $[\alpha]^{25}_D$ +23.0 (*c* 0.28, $CHCl_3$); IR ($CDCl_3$) 3470 (NH), 3391 (OH), 2228 (C≡C), 1710 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.30 (br s, 1H), 7.35 (d, $J$ = 1.1 Hz, 1H), 7.23 (d, $J$ = 8.6 Hz, 1H), 6.99 (dd, $J$ = 8.6, 1.1 Hz, 1H), 5.20 (dd, $J$ = 7.2, 5.4 Hz, 1H), 4.06 (s, 2H), 3.83 (d, $J$ = 16.0 Hz, 1H), 3.64 (d, $J$ = 16.0 Hz, 1H), 2.82–2.73 (m, 2H), 2.43 (s, 3H), 1.11–0.95 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.7, 137.6, 133.4, 128.9, 128.2, 123.8, 118.6, 110.7, 103.0, 81.8, 80.5, 66.1, 50.9, 30.2, 30.1, 21.5, 17.9 (3C), 17.7 (3C), 12.1 (3C); HRMS (FAB) calcd for $C_{25}H_{38}NO_4Si$ $[M + H]^+$: 444.2570; found 444.2563.

**(*R*)-2-(2-{5-Hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-isopropyl-1*H*-indol-3-yl)acetic acid (22af).** Reaction was conducted according to the procedure for the synthesis of **22aa**. Purification was performed by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 2/1 to 0/1) to give **22af** (175 mg, 37% in 3 steps) as a brown amorphous solid; $[\alpha]^{27}_D$ +17.7 (*c* 0.177, $CHCl_3$); IR ($CDCl_3$) 3344 (OH), 2107 (C≡C), 1712 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.29 (br s, 1H), 7.40 (d, $J$ = 1.1 Hz, 1H), 7.28 (d, $J$ = 8.6 Hz, 1H), 7.09 (dd, $J$ = 8.6, 1.1 Hz, 1H), 5.22 (dd, $J$ = 7.4, 5.2 Hz, 1H), 4.11–4.05 (m, 2H), 3.87 (d, $J$ = 16.0 Hz, 1H), 3.66 (d, $J$ = 16.0 Hz, 1H), 3.00 (hept, $J$ = 6.8 Hz, 1H), 2.82–2.72 (m, 2H), 1.30 (d, $J$ = 6.8 Hz, 6H), 1.12–0.96 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.4, 140.4, 137.7, 133.7, 128.0, 121.3, 116.0, 110.8, 103.2, 81.9, 80.5, 66.2, 51.1, 34.2, 30.3, 30.2, 24.7, 24.6, 17.9 (3C), 17.8 (3C), 12.1 (3C); HRMS (FAB) calcd for $C_{27}H_{42}NO_4Si$ $[M + H]^+$: 472.2883; found 472.2891.

**(*R*)-2-(5-(*tert*-Butyl)-2-{5-hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)acetic acid (22ag).** Reaction was conducted according to the procedure for the synthesis of **22aa**. Purification was performed by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 2/1 to 0/1) to give **22ag** (107 mg, 26% in 3 steps) as a brown amorphous solid; $[\alpha]^{27}_D$ +16.3 (*c* 0.080, $CHCl_3$); IR ($CDCl_3$) 3473 (NH), 3399 (OH), 2234 (C≡C), 1711 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.28 (br s, 1H), 7.55 (d, $J$ = 1.1 Hz, 1H), 7.29 (d, $J$ = 8.6 Hz, 1H), 7.27 (dd, $J$ = 8.6, 1.1 Hz, 1H), 5.22 (dd, $J$ = 7.4, 5.2 Hz, 1H), 4.09 (s, 2H), 3.88 (d, $J$ = 16.0 Hz, 1H), 3.67 (d, $J$ = 16.0 Hz, 1H), 2.82–2.72 (m, 2H), 1.38 (s, 9H), 1.09–0.97 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.4, 142.6, 137.7, 133.3,

127.7, 120.6, 114.7, 110.5, 103.3, 81.9, 80.5, 66.2, 51.1, 34.6, 31.9 (3C), 30.24, 30.22, 17.9 (3C), 17.8 (3C), 12.1 (3C); HRMS (FAB) calcd for $C_{28}H_{44}NO_4Si$ [M + H]$^+$: 486.3040; found 486.3036.

**(*R*)-2-(2-{5-Hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-5-methoxy-1*H*-indol-3-yl)acetic acid (22ah).** Reaction was conducted according to the procedure for the synthesis of **22aa**. Purification was performed by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 1/2 to 0/1) to give **22ah** (125 mg, 30% in 3 steps) as a brown oil; $[\alpha]^{26}_D$ +16.7 (*c* 0.18, $CHCl_3$); IR ($CDCl_3$) 3476 (NH), 3365 (OH), 2227 (C≡C), 1710 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.36 (br s, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.19 (dd, *J* = 6.9, 5.7 Hz, 1H), 4.07 (s, 2H), 3.82 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 3.64 (d, *J* = 16.0 Hz, 1H), 2.81–2.73 (m, 2H), 1.11–0.94 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.6, 154.0, 138.3, 130.2, 128.3, 112.2, 111.7, 103.3, 100.9, 81.8, 80.5, 66.2, 55.8, 50.9, 30.3, 30.0, 17.8 (3C), 17.7 (3C), 12.1 (3C); HRMS (FAB) calcd for $C_{25}H_{38}NO_5Si$ [M + H]$^+$: 460.2519; found 460.2519.

**(*R*)-2-(2-{5-Hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-7-methoxy-1*H*-indol-3-yl)acetic acid (22ai).** Reaction was conducted according to the procedure for the synthesis of **22aa**. Purification was performed by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 1/1 to 0/1) to give **22ai** (133 mg, 36% in 3 steps) as a brown amorphous solid; $[\alpha]^{27}_D$ +21.0 (*c* 0.18, $CHCl_3$); IR ($CDCl_3$) 3476 (NH), 3356 (OH), 3316 (OH), 2238 (C≡C), 1714 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.52 (br s, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.20 (dd, *J* = 7.4, 5.7 Hz, 1H), 4.11 (d, *J* = 16.0 Hz, 1H), 4.07 (d, *J* = 16.0 Hz, 1H), 3.94 (s, 3H), 3.85 (d, *J* = 16.0 Hz, 1H), 3.66 (d, *J* = 16.0 Hz, 1H), 2.83–2.74 (m, 2H), 1.12–0.95 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.4, 146.0, 137.1, 129.2, 125.6, 120.1, 111.8, 104.1, 102.3, 81.9, 80.5, 66.1, 55.4, 51.0, 30.4, 30.1, 17.9 (3C), 17.8 (3C), 12.1 (3C); HRMS (FAB) calcd for $C_{25}H_{38}NO_5Si$ [M + H]$^+$: 460.2519; found 460.2529.

**(*R*)-2-(2-{5-Hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)acetonitrile (22b).** To a solution of **30a** (52.3 mg, 0.0996 mmol) in MeOH (1.24 mL) was added pyridinium *p*-toluenesulfonate (7.56 mg, 0.0301 mmol) at room temperature. After being stirred at the same temperature for 12 h, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with $CH_2Cl_2$ (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =1/1) to give **22b** (36.7 mg, 90%) as a colorless oil; $[\alpha]^{28}_D$ –10.8 (*c* 1.83, $CHCl_3$); IR ($CDCl_3$) 3366 (NH/OH), 2250 (CN/C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.44 (br s, 1H), 7.62 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.39 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.24 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.18 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 5.22 (dd, *J* = 9.2, 4.6 Hz, 1H), 4.19–4.15 (m, 2H), 3.92 (d, *J* = 18.3 Hz, 1H), 3.84 (d, *J* = 18.3 Hz, 1H), 2.89–2.84 (m, 1H), 2.78–2.72 (m, 1H), 2.17 (br s, 1H), 1.15–0.98 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 137.4, 135.0, 126.9, 122.8, 120.2, 118.5, 118.2, 111.3, 99.7, 81.7, 80.6, 66.4, 51.0, 30.3, 17.8 (3C), 17.7 (3C), 13.4, 12.0 (3C); HRMS (FAB) calcd for $C_{24}H_{35}N_2O_2Si$ [M + H]$^+$: 411.2468; found 411.2472.

**Methyl (*R*)-2-(2-{5-Hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)acetate (22c).** A solution of **30a** (1.00 g, 1.91 mmol) in $CH_2Cl_2$ (38.1 mL) was cooled to –78 °C, and DIBAL (1.0 M in toluene; 4.76 mL, 4.76 mmol) was added dropwise to the mixture. After the mixture was stirred at –78 °C for 1 h, saturated aqueous Rochelle salt and $Et_2O$ were added to the mixture, and the mixture was stirred vigorously at room temperature for 1 h. The mixture was extracted with $Et_2O$ (×3), and the combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The resulting crude aldehyde was used in the next step without purification. To a solution of the crude aldehyde in *t*-BuOH (30.5 mL) and $H_2O$ (7.62 mL) were added $NaH_2PO_4$ (1.38 g, 11.5 mmol), 2-methyl-2-butene (6.07 mL, 57.2 mmol) and $NaClO_2$ (519 mg, 5.74 mmol) at room temperature. After being stirred at the same temperature for 1 h, the mixture was diluted with brine and extracted with EtOAc (×3). The combined organic layer was washed with brine (×2), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by short column chromatography over silica gel (hexane/EtOAc =4/1). To a solution of carboxylic acid in MeOH (19.1 mL) were added *N*-methylmorpholine (NMM; 419 µL, 3.81 mmol) and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM; 1.05 g, 3.81 mmol) at room temperature. After being stirred at the same temperature for 14 h, the mixture was diluted with brine and extracted with EtOAc (×3). The combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by short column chromatography over silica gel (hexane/EtOAc =4/1) to give **S4** as a pale yellow oil. To a solution of **S4** (582 mg, 1.04 mmol) in MeCN (10.4 mL) was added premixed solution of TBAF (1.0 M in THF; 5.22 mL, 5.22 mmol) and $BF_3{\cdot}OEt_2$ (655 µL, 5.22 mmol) at 0 °C. After being stirred at room temperature for 30 min, the reaction was quenched with saturated aqueous $NH_4Cl$ and extracted with $Et_2O$ (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =3/1) to give **22c** (266 mg, 31% in 4 steps) as a yellow oil; $[\alpha]^{28}_D$ +20.8 (*c* 1.38, $CHCl_3$); IR ($CDCl_3$) 3465 (NH), 3406 (OH), 2331 (C≡C), 1735 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.37 (br s, 1H), 7.58 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.35 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.18 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.12 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 5.27 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.15–4.14 (m, 2H), 3.85 (d, *J* = 15.5 Hz, 1H), 3.68 (d, *J* = 15.5 Hz, 1H), 3.67 (s, 3H), 2.80–2.78 (m, 2H), 1.98 (t, *J* = 6.0 Hz, 1H), 1.15–0.97 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 172.3, 137.4, 135.1, 128.0, 122.1, 119.6, 119.0, 111.0, 103.6, 81.9, 81.0, 66.1, 52.0, 51.2, 30.4, 30.1, 17.9 (3C), 17.8 (3C), 12.1 (3C); HRMS (FAB) calcd for $C_{25}H_{38}NO_4Si$ [M + H]$^+$: 444.2570; found 444.2569.

**(*R*)-2-(2-{5-Hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1*H*-indol-3-yl)-*N*-(4-methoxybenzyl)acetamide (22d).** A solution of **30a** (403 mg, 0.768 mmol) in $CH_2Cl_2$ (15.4 mL) was cooled to –78 °C and DIBAL (1.0 M in toluene; 1.92 mL, 1.92 mmol) was added dropwise to the mixture. After being stirred at –78 °C for 1 h, saturated aqueous Rochelle salt and $Et_2O$ was added to them and stirred vigorously at room temperature for 1 h. The mixture was extracted with $Et_2O$ (×3), combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The resulting crude aldehyde was used in the next step without purification. To a solution of the crude aldehyde in *t*-BuOH (61.4 mL) and $H_2O$ (15.4 mL) were added $NaH_2PO_4$ (571 mg, 4.76 mmol), 2-methyl-2-butene (2.45 mL, 23.0 mmol) and $NaClO_2$ (211 mg, 2.33 mmol) at room temperature. After being stirred at the same temperature

for 1 h, the mixture was diluted with brine and extracted with EtOAc (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by short column chromatography over silica gel (hexane/EtOAc =4/1). To a solution of carboxylic acid in DMF (2.56 mL) were added $PMBNH_2$ (100 μL, 0.768 mmol), DIPEA (408 μL, 2.30 mmol) and COMU (346 mg, 0.808 mmol) at 0 °C. After being stirred at room temperature for 11 h, the mixture was diluted with brine and extracted with EtOAc (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by short column chromatography over silica gel (hexane/EtOAc =3/1) to give **S5** as a yellow oil. To a solution of **S5** (329 mg, 0.496 mmol) in MeOH (4.96 mL) was added $K_2CO_3$ (354 mg, 2.56 mmol) at room temperature. After being stirred at 60 °C for 10 h, the mixture was cooled to room temperature and diluted with saturated aqueous $NH_4Cl$, followed by extraction with EtOAc (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =1/1) to give **22d** (128 mg, 28% in 4 steps) as a white amorphous solid; $[\alpha]^{28}_D$ +3.55 (*c* 0.52, $CHCl_3$); IR ($CDCl_3$) 3408 (NH), 3303 (OH), 2214 (C≡C), 1651 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.49 (br s, 1H), 7.47 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.38 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.21 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.11 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.07 (t, *J* = 6.3 Hz, 1H), 5.20 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.37 (dd, *J* = 14.9, 6.3 Hz, 1H), 4.26 (dd, *J* = 14.9, 6.3 Hz, 1H), 4.13–4.06 (m, 2H), 3.88 (d, *J* = 17.8 Hz, 1H), 3.76 (s, 3H), 3.75 (d, *J* = 17.8 Hz, 1H), 2.78–2.64 (m, 3H), 1.12–0.95 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 171.7, 158.9, 138.5, 135.1, 130.0, 128.8 (2C), 127.8, 122.5, 120.1, 118.6, 113.9 (2C), 111.3, 103.4, 81.9, 80.8, 66.6, 55.3, 50.9, 43.0, 32.7, 30.4, 17.9 (3C), 17.8 (3C), 12.1 (3C); HRMS (FAB) calcd for $C_{32}H_{45}N_2O_4Si$ [M + H]$^+$: 549.3149; found 549.3140.

**(*R*)-2-{1,5-Bis-[(*tert*-butyldimethylsilyl)oxy]-pent-3-yn-1-yl}-1*H*-indole (S6).** To a solution of **28a** (2.02 g, 4.17 mmol) in THF (83.4 mL) was added $LiAlH_4$ (1.0 M in THF; 8.34 mL, 8.34 mmol) at 0 °C. After the mixture was stirred at the same temperature for 1 h, saturated aqueous Rochelle salt and $Et_2O$ were added to the mixture, and the mixture was stirred vigorously at room temperature for 1 h. The mixture was extracted with $Et_2O$ (×3), combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =5/1 to 3/1) to give the corresponding alcohol as a colorless oil. To a solution of the alcohol (509 mg, 1.55 mmol) in DMF (15.5 mL) were added TBSCl (256 mg, 1.70 mmol) and imidazole (264 mg, 3.88 mmol) at 0 °C. After being stirred at room temperature for 27 h, the mixture was diluted with water and extracted with $Et_2O$ (×3). The combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc = 7/1) to give **S6** (420 mg, 61% in 2 steps) as a colorless oil; $[\alpha]^{24}_D$ –0.16 (*c* 1.08, $CHCl_3$); IR ($CDCl_3$) 3418 (NH), 2232 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.32 (br s, 1H), 7.51 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.31 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.11 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.04 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 6.31 (d, *J* = 2.3 Hz, 1H), 5.00 (dd, *J* = 6.3, 6.3 Hz, 1H), 4.26–4.25 (m, 2H), 2.69–2.59 (m, 2H), 0.86 (s, 18H), 0.08 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), –0.04 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 140.5, 135.5, 128.2, 121.6, 120.4, 119.6, 110.9, 98.9, 81.6, 81.0, 68.2, 51.9, 30.2, 25.9 (3C), 25.8 (3C), 18.3, 18.2, –5.0 (2C), –5.2 (2C); HRMS (FAB) calcd for $C_{25}H_{42}NO_2Si_2$ [M + H]$^+$: 444.2754; found 444.2752.

**(*R*)-1-(2-{1,5-Bis[(*tert*-butyldimethylsilyl)oxy]-pent-3-yn-1-yl}-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (S7).** To a solution of **S6** (399 mg, 0.898 mmol) in $CH_2Cl_2$ (4.49 mL) was added Eschenmoser's salt (109 mg, 1.17 mmol) at room temperature. After being stirred at the same temperature for 19 h, the mixture was diluted with 2 N NaOH and extracted with $CH_2Cl_2$ (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over $NH_2$-silica gel (hexane/EtOAc =49/1) to give **S7** (421 mg, 95%) as a colorless oil; $[\alpha]^{25}_D$ +34.4 (*c* 1.17, $CHCl_3$); IR ($CDCl_3$) 3473 (NH), 2242 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.32 (br s, 1H), 7.68 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.33 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.15 (ddd, *J* = 8.0, 8.0, 0.6 Hz, 1H), 7.09 (ddd, *J* = 8.0, 8.0, 0.6 Hz, 1H), 5.27 (dd, *J* = 5.7, 5.7 Hz, 1H), 4.28–4.27 (m, 2H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.50 (d, *J* = 13.2 Hz, 1H), 2.70–2.66 (m, 2H), 2.21 (s, 6H), 0.90 (s, 9H), 0.89 (s, 9H), 0.13 (s, 3H), 0.10 (s, 6H), –0.04 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 138.0, 134.9, 128.8, 121.5, 119.4, 119.3, 110.7, 108.2, 82.0, 80.5, 66.2, 53.7, 52.0, 45.5 (2C), 29.9, 25.9 (3C), 25.8 (3C), 18.3, 18.2, –5.0, –5.0, –5.2 (2C); HRMS (FAB) calcd for $C_{28}H_{49}N_2O_2Si_2$ [M + H]$^+$: 501.3333; found 501.3334.

**(*R*)-2-(2-{1,5-Bis[(*tert*-butyldimethylsilyl)oxy]-pent-3-yn-1-yl}-1*H*-indol-3-yl)acetonitrile (S8).** To a solution of **S7** (398 mg, 0.794 mmol) in MeCN (1.59 mL) was added MeI (98.9 μL, 1.59 mmol) at room temperature. After the mixture was stirred for 19 h, KCN (104 mg, 1.60 mmol), 18-crown-6 (210 mg, 0.794 mmol) and DMF (1.59 mL) were added to mixture. After being stirred for additional 2 h, the mixture was diluted with water and extracted with $Et_2O$ (×3). The combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =24/1 to 5/1) to give **S8** (378 mg, 99%) as a colorless oil; $[\alpha]^{25}_D$ –5.47 (*c* 1.77, $CHCl_3$); IR ($CDCl_3$) 3344 (NH), 2250 (CN/C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.38 (br s, 1H), 7.63 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.38 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.24 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.19 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 5.18 (dd, *J* = 7.4, 5.7 Hz, 1H), 4.26 (s, 2H), 3.93 (d, *J* = 17.8 Hz, 1H), 3.84 (d, *J* = 17.8 Hz, 1H), 2.77–2.74 (m, 1H), 2.69–2.67 (m, 1H), 0.90 (s, 9H), 0.89 (s, 9H), 0.14 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.01 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 137.3, 134.9, 127.1, 122.6, 120.2, 118.1, 117.8, 111.2, 99.4, 81.5, 80.5, 66.3, 51.9, 30.1, 25.8 (3C), 25.7 (3C), 18.3, 18.2, 13.1, –5.1 (2C), –5.3 (2C); HRMS (FAB) calcd for $C_{27}H_{43}N_2O_2Si_2$ [M + H]$^+$: 483.2863; found 483.2872.

**(*R*)-2-(2-{1-[(*tert*-Butyldimethylsilyl)oxy]-5-hydroxypent-3-yn-1-yl}-1*H*-indol-3-yl)acetic acid (22aj).** A mixture of **S8** (343 mg, 0.710 mmol) in $CH_2Cl_2$ (14.2 mL) was cooled to –78 °C, and DIBAL (1.0 M in toluene; 1.78 mL, 1.78 mmol) was added dropwise to the mixture. After the mixture was stirred at –78 °C for 1 h, saturated aqueous Rochelle salt and $Et_2O$ were added to the mixture, and the mixture was stirred vigorously at room temperature for 1 h. The mixture was extracted with $Et_2O$ (×3), combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The resulting crude aldehyde was used in the next step without purification. To a solution of the crude aldehyde in *t*-BuOH (11.4 mL) and $H_2O$

(2.84 mL) were added $NaH_2PO_4$ (511 mg, 4.26 mmol), 2-methyl-2-butene (4.53 mL, 42.6 mmol) and $NaClO_2$ (193 mg, 2.13 mmol) at room temperature. After being stirred at the same temperature for 1 h, the mixture was diluted with brine and extracted with EtOAc (×3). The combined organic layer was washed with brine (×2), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over $CO_2H$-silica gel (hexane/EtOAc =5/1 to 0/1) to give **S9**. To a solution of **S9** (137 mg, 0.272 mmol) in $CH_2Cl_2$ (2.72 mL) and MeOH (2.72 mL) was added (-)-10-camphor sulfonic acid (12.8 mg, 55.1 μmol) at 0 ℃. After being stirred at the same temperature for 0.5 h, the mixture was diluted with water and extracted with EtOAc (×3). Combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 1/2 to 1/4) to give **22aj** (47.6 mg, 34% in 3 steps) as a pale brown oil; $[\alpha]^{22}_D$ +21.5 (*c* 2.50, $CHCl_3$); IR ($CDCl_3$) 3403 (NH), 3335 (OH), 2230 (C≡C), 1708 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.40 (br s, 1H), 7.57 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.34 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.18 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.11 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 5.12 (dd, *J* = 6.3, 6.3 Hz, 1H), 4.10 (s, 2H), 3.84 (d, *J* = 16.0 Hz, 1H), 3.66 (d, *J* = 16.0 Hz, 1H), 2.72–2.70 (m, 2H), 0.86 (s, 9H), 0.08 (s, 3H), –0.08 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.8, 137.3, 135.1, 127.9, 122.2, 119.7, 118.9, 111.0, 103.3, 82.2, 80.3, 66.3, 51.0, 30.1, 29.8, 25.7 (3C), 18.2, –5.1, –5.2; HRMS (FAB) calcd for $C_{21}H_{30}NO_4Si$ [M + H]$^+$: 388.1944; found 388.1937.

**2-(5-[(*tert*-Butyldimethylsilyl)oxy]-1-methoxypent-3-yn-1-yl)-1*H*-indole (S10).** To a solution of **28a** (2.02 g, 4.17 mmol) in THF (83.4 mL) was added $LiAlH_4$ (1.0 M in THF; 8.34 mL, 8.34 mmol) at 0 ℃. After the mixture was stirred at the same temperature for 1 h, saturated aqueous Rochelle salt and $Et_2O$ were added to the mixture, and the mixture was stirred vigorously at room temperature for 1 h. The mixture was extracted with $Et_2O$ (×3), combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =5/1 to 3/1) to give the corresponding alcohol as a colorless oil. To a mixture of the alcohol (878 mg, 2.66 mmol) in MeOH (17.8 mL) and trimethyl orthoformate (8.88 mL) was added pyridinium *p*-toluenesulfonate (1.00 g, 4.00 mmol) at room temperature. After being stirred at the same temperature for 2 h, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with $CH_2Cl_2$ (×3). The combined organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc = 7/1) to give **S10** (265 mg, 29% in 2 steps) as a colorless oil; IR ($CDCl_3$) 3396 (NH), 2234 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.50 (br s, 1H), 7.58 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.18 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.10 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 6.46 (d, *J* = 1.7 Hz, 1H), 4.54 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.31 (t, *J* = 2.0 Hz, 2H), 3.33 (s, 3H), 2.80–2.78 (m, 2H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 137.2, 136.1, 127.8, 122.1, 120.5, 119.8, 111.0, 101.8, 81.12, 81.08, 75.6, 56.9, 52.0, 26.6, 25.8 (3C), 18.3, –5.2 (2C); HRMS (FAB) calcd for $C_{20}H_{30}NO_2Si$ [M + H]$^+$: 344.2046; found 344.2050.

**1-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-methoxypent-3-yn-1-yl}-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (S11).** To a solution of **S10** (242 mg, 0.704 mmol) in $CH_2Cl_2$ (3.52 mL) was added Eschenmoser's salt (86.1 mg, 0.919 mmol) at room temperature. After being stirred at the same temperature for 14 h, the mixture was diluted with 2 N NaOH and extracted with $CH_2Cl_2$ (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over $NH_2$-silica gel (hexane/EtOAc =39/1 to 9/1) to give **S11** (249 mg, 88%) as a colorless oil; IR ($CDCl_3$) 3328 (NH), 2359 (C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.43 (br s, 1H), 7.69 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.34 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.18 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.10 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 4.82 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.30 (t, *J* = 2.0 Hz, 2H), 3.59 (d, *J* = 13.2 Hz, 1H), 3.56 (d, *J* = 13.2 Hz, 1H), 3.30 (s, 3H), 2.83–2.71 (m, 2H), 2.24 (s, 6H), 0.90 (s, 9H), 0.10 (s, 6H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 135.3, 134.9, 128.5, 122.1, 119.43, 119.36, 111.7, 110.9, 81.3, 80.8, 73.4, 57.1, 53.4, 52.0, 45.5 (2C), 26.8, 25.8 (3C), 18.3, –5.2 (2C); HRMS (FAB) calcd for $C_{23}H_{37}N_2O_2Si$ [M + H]$^+$: 401.2624; found 401.2623.

**2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-methoxypent-3-yn-1-yl}-1*H*-indol-3-yl)acetonitrile (S12).** To a solution of **S11** (228 mg, 0.570 mmol) in MeCN (1.14 mL) was added MeI (71.0 μL, 1.14 mmol) at room temperature. After the mixture was stirred for 12 h, KCN (37.1 mg, 1.14 mmol), 18-crown-6 (151 mg, 0.570 mmol) and DMF (1.14 mL) were added to the mixture. After being stirred for additional 1.5 h, the mixture was diluted with water and extracted with $Et_2O$ (×3). The combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =14/1 to 3/1) to give **S12** (183 mg, 84%) as a colorless oil; IR ($CDCl_3$) 3356 (NH), 2249 (CN/C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.50 (br s, 1H), 7.63 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.38 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.25 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 7.19 (ddd, *J* = 8.0, 8.0, 1.1 Hz, 1H), 4.69 (dd, *J* = 7.4, 5.2 Hz, 1H), 4.27 (t, *J* = 2.3 Hz, 2H), 3.91 (d, *J* = 17.8 Hz, 1H), 3.86 (d, *J* = 17.8 Hz, 1H), 3.33 (s, 3H), 2.86–2.81 (m, 1H), 2.78–2.72 (m, 1H), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 135.2, 134.4, 126.8, 123.0, 120.3, 118.1, 117.9, 111.3, 102.5, 81.5, 80.1, 73.8, 57.4, 51.9, 26.8, 25.8 (3C), 18.3, 12.9, –5.3 (2C); HRMS (FAB) calcd for $C_{22}H_{31}N_2O_2Si$ [M + H]$^+$: 383.2155; found 383.2162.

**2-[2-(5-Hydroxy-1-methoxypent-3-yn-1-yl)-1*H*-indol-3-yl]acetic acid (22ak).** A mixture of **S12** (172 mg, 0.449 mmol) in $CH_2Cl_2$ (8.99 mL) was cooled to –78 ℃, and DIBAL (1.0 M in toluene; 1.12 mL, 1.12 mmol) was added dropwise to the mixture. After being stirred at –78 ℃ for 1.5 h, saturated aqueous Rochelle salt and $Et_2O$ were added to the mixture, and the mixture was stirred vigorously at room temperature for 1 h. The mixture was extracted with $Et_2O$ (×3), and the combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The resulting crude aldehyde was used in the next step without purification. To a solution of the crude aldehyde in *t*-BuOH (7.19 mL) and $H_2O$ (1.80 mL) were added $NaH_2PO_4$ (324 mg, 2.70 mmol), 2-methyl-2-butene (2.87 mL, 27.0 mmol) and $NaClO_2$ (122 mg, 1.35 mmol) at room temperature. After being stirred at the same temperature for 1 h, the mixture was diluted with brine and extracted with EtOAc (×3). The combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by short column chromatography over silica gel (hexane/EtOAc =1/1) to give **S13**. To a solution of **S13** in $CH_2Cl_2$ (4.49 mL) and MeOH (4.49 mL) was added (-)-10-camphor sulfonic acid (21.2 mg, 0.0913 mmol) at 0 ℃. After being stirred at the same temperature for 1 h, the mixture was diluted with

water and extracted with $CH_2Cl_2$ (×5). The combined organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 1/1 to 0/1) to give **22ak** (39.0 mg, 30% in 3 steps) as a yellow oil; IR ($CDCl_3$) 3397 (NH), 3327 (OH), 3055 (OH), 2244 (C≡C), 1709 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.76 (br s, 1H), 7.58 (dd, $J$ = 8.0, 1.1 Hz, 1H), 7.32 (dd, $J$ = 8.0, 1.1 Hz, 1H), 7.18 (ddd, $J$ = 8.0, 8.0, 1.1 Hz, 1H), 7.11 (ddd, $J$ = 8.0, 8.0, 1.1 Hz, 1H), 6.71 (br s, 1H), 4.65 (dd, $J$ = 6.0, 6.0 Hz, 1H), 4.11–4.05 (m, 2H), 3.83 (d, $J$ = 16.0 Hz, 1H), 3.70 (d, $J$ = 16.0 Hz, 1H), 3.22 (s, 3H), 2.81–2.73 (m, 2H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.5, 135.5, 134.1, 127.6, 122.6, 119.8, 118.7, 111.3, 106.7, 81.6, 80.5, 73.8, 57.0, 50.9, 29.9, 26.5; HRMS (FAB) calcd for $C_{16}H_{18}NO_4$ [M + H]$^+$: 288.1236; found 288.1236.

**(*R*)-2-(2-{5-[(*tert*-Butyldimethylsilyl)oxy]-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1-methyl-1*H*-indol-3-yl)acetonitrile (S14).** To a solution of **30a** (185 mg, 0.352 mmol) in $CH_2Cl_2$ (3.52 mL) were added NaOH (84.9 mg, 2.12 mmol) in $H_2O$ (1.76 mL) and tetrabutylammonium hydrogen sulfate (120 mg, 0.352 mmol) at 0 °C. After the mixture was stirred for 15 min, MeI (87.8μL, 1.41 mmol) was added to the mixture. After being stirred for additional 21 h, the mixture was diluted with water and extracted with $CH_2Cl_2$ (×3). The combined organic layer was washed with saturated aqueous $NH_4Cl$, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =24/1 to 5/1) to give **S14** (159 mg, 84%) as a colorless oil; $[\alpha]^{24}_D$ –9.83 (*c* 0.99, $CHCl_3$); IR ($CDCl_3$) 2246 (CN/C≡C); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.67 (dd, $J$ = 7.4, 1.1 Hz, 1H), 7.32 (dd, $J$ = 7.4, 1.1 Hz, 1H), 7.27 (ddd, $J$ = 7.4, 7.4, 1.1 Hz, 1H), 7.18 (ddd, $J$ = 7.4, 7.4, 1.1 Hz, 1H), 5.29 (dd, $J$ = 8.6, 5.2 Hz, 1H), 4.22-4.16 (m, 2H), 4.02 (d, $J$ = 17.2 Hz, 1H), 3.92 (d, $J$ = 17.2 Hz, 1H), 3.87 (s, 3H), 2.95-2.83 (m, 2H), 1.17-0.97 (m, 21H), 0.84 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 137.14, 137.10, 126.3, 122.4, 119.9, 118.4, 118.1, 109.3, 100.8, 81.5, 80.0, 67.0, 51.8, 31.0, 29.5, 25.8 (3C), 18.2, 17.9 (3C), 17.8 (3C), 13.4, 12.1 (3C), –5.3, –5.4; HRMS (FAB) calcd for $C_{31}H_{51}N_2O_2Si_2$ [M + H]$^+$: 539.3489; found 539.3494.

**(*R*)-2-(2-{5-Hydroxy-1-[(triisopropylsilyl)oxy]pent-3-yn-1-yl}-1-methyl-1*H*-indol-3-yl)acetic acid (33).** Reaction was conducted according to the procedure for the synthesis of **22aa**. Purification was performed by column chromatography over $CO_2H$-silica gel (hexane/EtOAc = 2/1 to 0/1) to give **33** (45.9 mg, 35% in 3 steps) as an orange amorphous solid; $[\alpha]^{25}_D$ +26.2 (*c* 2.29, $CHCl_3$); IR ($CDCl_3$) 3341 (OH), 2230 (C≡C), 1710 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.57 (dd, $J$ = 8.6, 1.1 Hz, 1H), 7.29 (dd, $J$ = 8.6, 1.1 Hz, 1H), 7.22 (ddd, $J$ = 8.6, 8.6, 1.1 Hz, 1H), 7.11 (ddd, $J$ = 8.6, 8.6, 1.1 Hz, 1H), 6.25 (br s, 1H), 5.31 (dd, $J$ = 8.6, 6.3 Hz, 1H), 4.01-3.90 (m, 6H), 3.66 (d, $J$ = 16.0 Hz, 1H), 2.97-2.88 (m, 2H), 1.12-0.93 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 176.4, 137.5, 136.9, 127.1, 122.1, 119.4, 119.1, 109.0, 105.0, 81.5, 80.2, 66.7, 50.8, 31.2, 30.4, 28.9, 17.9 (3C), 17.7 (3C), 12.1 (3C); HRMS (FAB) calcd for $C_{25}H_{38}NO_4Si$ [M + H]$^+$: 444.2570; found 444.2560.

## 2. SUBSTRATE SCOPE

**(4b*S*,8*R*,8a*R*)-5-(Hydroxymethyl)-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24aa).** To a solution of **22aa** (52.0 mg, 0.121 mmol) in TCE (1.21 mL) was added BrettPhosAu(MeCN)$SbF_6$ (6.12 mg, 6.05 μmol) at room temperature. After being stirred at 100 °C for 5 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =2/1) to give **24aa** (39.6 mg, 76%) as a yellow oil; $[\alpha]^{24}_D$ +46.3 (*c* 1.43, $CHCl_3$); IR ($CDCl_3$) 3447 (OH), 3343 (NH), 1761 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.23 (d, $J$ = 7.4 Hz, 1H), 7.14 (dd, $J$ = 7.4, 7.4 Hz, 1H), 6.80 (dd, $J$ = 7.4, 7.4 Hz, 1H), 6.72 (d, $J$ = 7.4 Hz, 1H), 5.59–5.58 (m, 1H), 5.13 (s, 1H), 4.30–4.24 (m, 2H), 4.13–4.11 (m, 1H), 3.32 (d, $J$ = 17.2 Hz, 1H), 2.95 (d, $J$ = 17.2 Hz, 1H), 2.46–2.44 (m, 2H), 1.21–1.11 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 174.3, 146.4, 137.4, 129.9, 129.6, 124.8, 121.4, 120.1, 110.5, 107.6, 71.1, 63.9, 55.7, 42.5, 33.1, 18.2 (6C), 12.5 (3C); HRMS (FAB) calcd for $C_{24}H_{36}NO_4Si$ [M + H]$^+$: 430.2414; found 430.2414.

**(4b*S*,8*R*,8a*R*)-3-Chloro-5-(hydroxymethyl)-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24ab).** To a solution of **22ab** (44.0 mg, 0.0948 mmol) in TCE (948 μL) was added BrettPhosAu(MeCN)$SbF_6$ (4.83 mg, 4.74 μmol) at room temperature. After being stirred at 100 °C for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =3/1) to give **24ab** (19.1 mg, 43%) as a brown oil; $[\alpha]^{26}_D$ +40.7 (*c* 0.96, $CHCl_3$); IR ($CDCl_3$) 3429 (NH), 3358 (OH), 1768 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.23 (d, $J$ = 1.7 Hz, 1H), 7.11 (dd, $J$ = 8.6, 1.7 Hz, 1H), 6.65 (d, $J$ = 8.6 Hz, 1H), 5.62 (d, $J$ = 5.2 Hz, 1H), 5.12 (s, 1H), 4.28–4.25 (m, 2H), 4.15 (d, $J$ = 13.2 Hz, 1H), 3.30 (d, $J$ = 17.8 Hz, 1H), 2.95 (d, $J$ = 17.8 Hz, 1H), 2.50–2.39 (m, 2H), 1.18–1.10 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 173.5, 144.9, 136.6, 131.7, 129.4, 124.9, 124.6, 122.0, 111.3, 107.4, 70.8, 63.9, 55.7, 42.3, 32.9, 18.0 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{24}H_{35}ClNO_4Si$ [M + H]$^+$: 464.2024; found 464.2028.

**(4b*S*,8*R*,8a*R*)-3-Bromo-5-(hydroxymethyl)-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24ac).** To a solution of **22ac** (35.8 mg, 0.0704 mmol) in TCE (704 μL) was added BrettPhosAu(MeCN)$SbF_6$ (3.59 mg, 3.55 μmol) at room temperature. After being stirred at 100 °C for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =7/3) to give **24ac** (25.3 mg, 71%) as a yellow oil; $[\alpha]^{24}_D$ +43.5 (*c* 1.26, $CHCl_3$); IR ($CDCl_3$) 3565 (NH), 3436 (OH), 1763 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.36 (d, $J$ = 2.3 Hz, 1H), 7.24 (dd, $J$ = 8.0, 2.3 Hz, 1H), 6.61 (d, $J$ = 8.0 Hz, 1H), 5.62 (d, $J$ = 5.2 Hz, 1H), 5.14 (s, 1H), 4.28-4.25 (m, 1H), 4.26 (d, $J$ = 12.6 Hz, 1H), 4.14 (d, $J$ = 12.6 Hz, 1H), 3.30 (d, $J$ = 17.8 Hz, 1H), 2.95 (d, $J$ = 17.8 Hz, 1H), 2.46–2.42 (m, 2H), 1.18–1.11 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 173.5, 145.4, 136.6, 132.3, 132.2, 127.7, 122.0, 111.8, 111.5, 107.3, 70.8, 63.8, 55.7, 42.3, 32.9, 18.0 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{24}H_{35}BrNO_4Si$ [M + H]$^+$: 508.1519; found 508.1525.

**(4b*S*,8*R*,8a*R*)-3-Fluoro-5-(hydroxymethyl)-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24ad).** To a solution of **22ad** (32.3 mg, 0.0722 mmol) in TCE (722 μL) was added BrettPhosAu(MeCN)$SbF_6$ (3.68 mg, 3.64 μmol) at room temperature. After being stirred at 100 °C for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =7/3) to give **24ad** (17.2 mg, 53%) as a brown oil; $[\alpha]^{27}_D$ +57.5 (*c* 0.86,

$CHCl_3$); IR ($CDCl_3$) 3488 (NH), 3449 (OH), 1764 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.01 (dd, $J$ = 8.3, 2.9 Hz, 1H), 6.85 (ddd, $J$ = 8.3, 8.3, 2.9 Hz, 1H), 6.64 (dd, $J$ = 8.3, 4.3 Hz, 1H), 5.62 (d, $J$ = 4.0 Hz, 1H), 5.02 (s, 1H), 4.28–4.26 (m, 1H), 4.26 (d, $J$ = 12.6 Hz, 1H), 4.14 (d, $J$ = 12.6 Hz, 1H), 3.30 (d, $J$ = 17.8 Hz, 1H), 2.94 (d, $J$ = 17.8 Hz, 1H), 2.48–2.43 (m, 2H), 1.17–1.12 (m, 21H); $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ 173.6, 157.3 (d, $J_{C\text{-}F}$ = 238.4 Hz), 142.3, 136.6, 131.2 (d, $J_{C\text{-}F}$ = 7.1 Hz), 122.0, 115.8 (d, $J_{C\text{-}F}$ = 23.2 Hz), 112.3 (d, $J_{C\text{-}F}$ = 26.0 Hz), 110.7 (d, $J_{C\text{-}F}$ = 8.7 Hz), 108.0, 70.9, 63.9, 55.8, 42.4, 33.0, 18.0 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{24}H_{35}FNO_4Si$ [M + H]$^+$: 448.2319; found 448.2322.

**(4b*S*,8*R*,8a*R*)-5-(Hydroxymethyl)-3-methyl-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24ae).** To a solution of **22ae** (39.4 mg, 0.0888 mmol) in TCE (888 μL) was added BrettPhosAu(MeCN)$SbF_6$ (4.51 mg, 4.46 μmol) at room temperature. After being stirred at 100 ℃ for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =3/1) to give **24ae** (19.6 mg, 50%) as a brown oil; [α]$^{25}_D$ +57.6 (*c* 0.71, $CHCl_3$); IR ($CDCl_3$) 3439 (NH), 3393 (OH), 1763 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.03 (d, $J$ = 1.1 Hz, 1H), 6.94 (dd, $J$ = 8.6, 1.1 Hz, 1H), 6.62 (d, $J$ = 8.6 Hz, 1H), 5.59 (dd, $J$ = 4.3, 4.3 Hz, 1H), 4.99 (s, 1H), 4.29–4.26 (m, 1H), 4.27 (d, $J$ = 13.2 Hz, 1H), 4.14 (d, $J$ = 13.2 Hz, 1H), 3.30 (d, $J$ = 17.8 Hz, 1H), 2.93 (d, $J$ = 17.8 Hz, 1H), 2.46–2.44 (m, 2H), 2.26 (s, 3H), 1.19–1.11 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 174.0, 143.9, 137.3, 129.94, 129.89, 129.3, 125.2, 121.4, 110.2, 107.8, 71.0, 63.9, 55.6, 42.4, 33.0, 20.9, 18.1 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{25}H_{38}NO_4Si$ [M + H]$^+$: 444.2570; found 444.2577.

**(4b*S*,8*R*,8a*R*)-5-(Hydroxymethyl)-3-isopropyl-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24af).** To a solution of **22af** (38.8 mg, 0.0822 mmol) in TCE (822 μL) was added BrettPhosAu(MeCN)$SbF_6$ (4.18 mg, 4.13 μmol) at room temperature. After being stirred at 100 ℃ for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =7/3) to give **24af** (20.4 mg, 53%) as a brown oil; [α]$^{27}_D$ +49.3 (*c* 1.02, $CHCl_3$); IR ($CDCl_3$) 3433 (NH), 3416 (OH), 1766 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.07 (d, $J$ = 1.7 Hz, 1H), 7.00 (dd, $J$ = 8.0, 1.7 Hz, 1H), 6.64 (d, $J$ = 8.0 Hz, 1H), 5.60 (dd, $J$ = 4.0, 4.0 Hz, 1H), 5.01 (s, 1H), 4.29–4.27 (m, 1H), 4.28 (d, $J$ = 13.2 Hz, 1H), 4.15 (d, $J$ = 13.2 Hz, 1H), 3.32 (d, $J$ = 17.2 Hz, 1H), 2.94 (d, $J$ = 17.2 Hz, 1H), 2.82 (hept, $J$ = 6.8 Hz, 1H), 2.45–2.44 (m, 2H), 1.20 (d, $J$ = 6.8 Hz, 6H), 1.15–1.13 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 174.1, 144.1, 140.9, 137.3, 129.8, 127.3, 122.6, 121.3, 110.1, 107.9, 71.1, 63.9, 55.6, 42.4, 33.7, 33.0, 24.4, 24.3, 18.1 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{27}H_{42}NO_4Si$ [M + H]$^+$: 472.2883; found 472.2888.

**(4b*S*,8*R*,8a*R*)-3-(*tert*-Butyl)-5-(hydroxymethyl)-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24ag).** To a solution of **22ag** (34.5 mg, 0.0710 mmol) in TCE (710 μL) was added BrettPhosAu(MeCN)$SbF_6$ (3.61 mg, 3.57 μmol) at room temperature. After being stirred at 100 ℃ for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =7/3) to give **24ag** (19.7 mg, 57%) as a brown oil; [α]$^{24}_D$ +42.9 (*c* 0.98, $CHCl_3$); IR ($CDCl_3$) 3448 (NH), 1766 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.23 (d, $J$ = 1.7 Hz, 1H), 7.17 (dd, $J$ = 8.0, 1.7 Hz, 1H), 6.65 (d, $J$ = 8.0 Hz, 1H), 5.60 (dd, $J$ = 4.5, 4.5 Hz, 1H), 5.02 (s, 1H), 4.28 (d, $J$ = 13.2 Hz, 1H), 4.30–4.25 (m, 1H), 4.15 (d, $J$ = 13.2 Hz, 1H), 3.33 (d, $J$ = 17.8 Hz, 1H), 2.95 (d, $J$ = 17.8 Hz, 1H), 2.46–2.43 (m, 2H), 1.27 (s, 9H), 1.19–1.11 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 174.1, 143.8, 143.1, 137.3, 129.5, 126.3, 121.4, 121.3, 109.8, 107.9, 71.1, 63.9, 55.7, 42.4, 34.3, 33.0, 31.6 (3C), 18.1 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{28}H_{44}NO_4Si$ [M + H]$^+$: 486.3040; found 486.3044.

**(4b*S*,8*R*,8a*R*)-5-(Hydroxymethyl)-3-methoxy-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24ah).** To a solution of **22ah** (28.5 mg, 0.0620 mmol) in TCE (620 μL) was added BrettPhosAu(MeCN)$SbF_6$ (3.16 mg, 3.12 μmol) at room temperature. After being stirred at 100 ℃ for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =2/1) to give **24ah** (16.6 mg, 58%) as a brown oil; [α]$^{24}_D$ + 65.8 (*c* 0.83, $CHCl_3$); IR ($CDCl_3$) 3482 (NH), 3376 (OH), 1763 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.86 (d, $J$ = 2.3 Hz, 1H), 6.71 (dd, $J$ = 8.6, 2.3 Hz, 1H), 6.64 (d, $J$ = 8.6 Hz, 1H), 5.61 (dd, $J$ = 4.3, 4.3 Hz, 1H), 4.89 (s, 1H), 4.29–4.25 (m, 1H), 4.27 (d, $J$ = 13.2 Hz, 1H), 4.14 (d, $J$ = 13.2 Hz, 1H), 3.74 (s, 3H), 3.30 (d, $J$ = 17.2 Hz, 1H), 2.93 (d, $J$ = 17.2 Hz, 1H), 2.46–2.45 (m, 2H), 1.18–1.11 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 173.8, 154.0, 140.1, 137.0, 131.1, 121.7, 114.1, 111.9, 110.7, 108.2, 71.0, 64.0, 56.1, 55.9, 42.5, 33.0, 18.1 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{25}H_{38}NO_5Si$ [M + H]$^+$: 460.2519; found 460.2524.

**(4b*S*,8*R*,8a*R*)-5-(Hydroxymethyl)-1-methoxy-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24ai).** To a solution of **22ai** (34.6 mg, 0.0753 mmol) in TCE (753 μL) was added BrettPhosAu(MeCN)$SbF_6$ (3.83 mg, 3.79 μmol) at room temperature. After being stirred at 100 ℃ for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =2/1) to give **24ai** (26.3 mg, 76%) as a brown oil; [α]$^{27}_D$ +51.6 (*c* 1.46, $CHCl_3$); IR ($CDCl_3$) 3482 (NH), 3443 (OH), 1774 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.87 (d, $J$ = 8.0 Hz, 1H), 6.79 (dd, $J$ = 8.0, 8.0 Hz, 1H), 6.74 (d, $J$ = 8.0 Hz, 1H), 5.60 (d, $J$ = 5.2 Hz, 1H), 5.14 (s, 1H), 4.30 (d, $J$ = 13.2 Hz, 1H), 4.30–4.25 (m, 1H), 4.13 (d, $J$ = 13.2 Hz, 1H), 3.83 (s, 3H), 3.31 (d, $J$ = 17.8 Hz, 1H), 2.92 (d, $J$ = 17.8 Hz, 1H), 2.51–2.45 (m, 2H), 1.19–1.11 (m, 21H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 173.9, 145.4, 137.3, 135.5, 130.5, 121.5, 120.6, 116.7, 111.2, 107.7, 71.0, 63.9, 56.4, 55.4, 42.2, 33.0, 18.1 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{25}H_{38}NO_5Si$ [M + H]$^+$: 460.2519; found 460.2530.

**(4b*S*,8*R*,8a*R*)-8-[(*tert*-Butyldimethylsilyl)oxy]-5-(hydroxymethyl)-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24aj).** To a solution of **22aj** (30.7 mg, 0.0792 mmol) in TCE (792 μL) was added BrettPhosAu(MeCN)$SbF_6$ (4.04 mg, 3.99 μmol) at room temperature. After being stirred at 100 ℃ for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =7/3) to give **24aj** (17.8 mg, 58%) as a yellow oil; [α]$^{24}_D$ +49.2 (*c* 0.85, $CHCl_3$); IR ($CDCl_3$) 3529 (NH), 3398 (OH), 1762 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.24 (dd, $J$ = 7.4, 1.1 Hz, 1H), 7.14 (ddd, $J$ = 7.4, 7.4, 1.1 Hz, 1H), 6.81 (ddd, $J$ = 7.4, 7.4, 1.1 Hz, 1H), 6.71 (dd, $J$ = 7.4, 1.1 Hz, 1H), 5.60 (d, $J$ = 5.2 Hz, 1H), 5.10 (s, 1H), 4.27 (d, $J$ = 13.2 Hz, 1H), 4.14 (d, $J$ = 13.2 Hz, 1H), 4.15–4.10 (m, 2H), 3.32 (d, $J$ = 17.8 Hz, 1H), 2.96 (d, $J$ =

17.8 Hz, 1H), 2.41–2.37 (m, 2H), 0.95 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 174.0, 146.2, 137.3, 129.8, 129.5, 124.6, 121.5, 119.9, 110.4, 107.2, 70.8, 63.9, 55.5, 42.4, 32.6, 25.8 (3C), 18.1, –4.7, –5.0; HRMS (FAB) calcd for $C_{21}H_{30}NO_4Si$ $[M + H]^+$: 388.1944; found 388.1940.

**(4b*S*,8*R*,8a*R*)-5-(Hydroxymethyl)-8-methoxy-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (24ak) and Its (4b*R*,8*R*,8a*S*)-Isomer (35).** To a solution of **22ak** (30.7 mg, 0.107 mmol) in TCE (1.07 mL) was added BrettPhosAu(MeCN)$SbF_6$ (5.43 mg, 5.37 μmol) at room temperature. After being stirred at 100 ℃ for 6 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =1/2) to give a diastereomeric mixture of **24ak** and **35** (13.6 mg, 44%) as a brown amorphous solid; IR ($CDCl_3$) 3394 (NH), 3340 (OH), 1759 (C=O); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.30 (dd, *J* = 7.4, 1.7 Hz, 0.26 H), 7.26 (dd, *J* = 7.4, 1.7 Hz, 0.74H), 7.14 (ddd, *J* = 7.4, 7.4, 1.7 Hz, 1H), 6.87 (ddd, *J* = 7.4, 7.4, 1.7 Hz, 0.26H), 6.82 (ddd, *J* = 7.4, 7.4, 1.7 Hz, 0.74H), 6.69 (dd, *J* = 7.4, 1.7 Hz, 1H), 5.64–5.62 (m, 1H), 5.23 (s, 0.74H), 4.68 (s, 0.26H), 4.28 (d, *J* = 12.6 Hz, 0.74H), 4.28 (d, *J* = 12.6 Hz, 0.26H), 4.16 (d, *J* = 12.6 Hz, 0.26H), 4.15 (d, *J* = 12.6 Hz, 0.74H), 3.84 (dd, *J* = 2.9, 2.9 Hz, 0.26H), 3.73 (dd, *J* = 10.3, 5.7 Hz, 0.74H), 3.59 (s, 2.22H), 3.45 (s, 0.78H), 3.34 (d, *J* = 17.8 Hz, 0.74H), 3.18 (d, *J* = 17.2 Hz, 0.26H), 3.13 (d, *J* = 17.2 Hz, 0.26H), 2.96 (d, *J* = 17.8 Hz, 0.74H), 2.61–2.55 (m, 1.26H), 2.33–2.27 (m, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 174.0, 146.4, 146.2, 137.3, 129.59, 129.58, 129.2, 125.0, 124.7, 121.0, 120.7, 120.1, 119.7, 110.8, 110.4, 107.3, 105.4, 78.7, 76.3, 64.2, 63.9, 59.0, 55.9, 42.3, 41.7, 29.2, 28.3; HRMS (FAB) calcd for $C_{16}H_{18}NO_4$ $[M + H]^+$: 288.1236; found 288.1229.

**(4b*S*,8*R*,8a*R*)-5-[{(*tert*-Butyldimethylsilyl)oxy}methyl]-8-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (32).** To a solution of **31a** (48.0 mg, 0.0882 mmol) in TCE (882 μL) was added BrettPhosAu(MeCN)$SbF_6$ (4.51 mg, 4.46 μmol) at room temperature. After being stirred at 100 ℃ for 24 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =10/1) to give **32** (11.0 mg, 22%) as a yellow oil; $[\alpha]^{24}_D$ +27.9 (*c* 0.74, $CHCl_3$); IR ($CDCl_3$) 3567 (NH), 1778 (C=O); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.20 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.13 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 6.81 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 6.71 (dd, *J* = 7.4, 1.1 Hz, 1H), 5.52-5.51 (m, 1H), 5.10 (br s, 1H), 4.30-4.23 (m, 2H), 4.03-4.00 (m, 1H), 3.29 (d, *J* = 17.8 Hz, 1H), 2.94 (d, *J* = 17.8 Hz, 1H), 2.48-2.38 (m, 2H), 1.20-1.11 (m, 21H), 0.94 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 174.3, 146.3, 137.1, 130.0, 129.4, 124.6, 120.4, 119.8, 110.3, 107.5, 71.0, 64.5, 55.6, 42.8, 33.0, 26.0 (3C), 18.3, 18.1 (6C), 12.4 (3C), -5.37, -5.41; HRMS (FAB) calcd for $C_{30}H_{50}NO_4Si_2$ $[M + H]^+$: 544.3278; found 544.3285.

**(4b*S*,8*R*,8a*R*)-5-(Hydroxymethyl)-9-methyl-[(triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-11-one (34).** To a solution of **33** (26.0 mg, 0.0586 mmol) in TCE (586 μL) was added BrettPhosAu(MeCN)$SbF_6$ (3.03 mg, 2.99 μmol) at room temperature. After being stirred at 100 ℃ for 24 h, the mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =2/1) to give **34** (8.6 mg, 33%) as a brown oil; $[\alpha]^{24}_D$ +46.3 (*c* 1.43, $CHCl_3$); IR ($CDCl_3$) 3447 (OH), 3343 (NH), 1761 (C=O); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.21-7.18 (m, 2H), 6.79 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 6.58 (dd, *J* = 7.4, 1.1 Hz, 1H), 5.63-5.62 (m, 1H), 4.37-4.35 (m, 1H), 4.26 (d, *J* = 13.2 Hz, 1H), 4.10 (d, *J* = 13.2 Hz, 1H), 3.31 (d, *J* = 17.8 Hz, 1H), 3.21 (s, 3H), 2.92 (d, *J* = 17.8 Hz, 1H), 2.57-2.50 (m, 1H), 2.44-2.42 (m, 1H), 1.17-1.14 (m, 21H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 173.9, 150.6, 137.3, 129.6, 129.1, 123.9, 122.2, 119.4, 108.6, 108.3, 73.2, 63.9, 56.5, 42.1, 33.2, 31.8, 18.1 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{25}H_{38}NO_4Si$ $[M + H]^+$: 444.2570; found 444.2570.

## 3. REDUCTIVE RING OPENING REACTION

**{(4b*S*,8*R*,8a*R*)-11-oxo-8-[(Triisopropylsilyl)oxy]-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-5-yl}methyl Pivalate (36).** To a solution of **24aa** (55.8 mg, 0.130 mmol) in $CH_2Cl_2$ (1.30 mL) were added pyridine (26.2 μL. 0.325 mmol), DMAP (13.5 mg, 1.10 mmol) and PivCl (31.6 μL, 0.260 mmol) at 0 ℃. After being stirred at room temperature for 6 h, the mixture was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =7/1) to give **36** (55.4 mg, 83%) as a colorless oil; $[\alpha]^{27}_D$ +28.8 (*c* 0.90, $CHCl_3$); IR ($CDCl_3$) 3408 (NH), 1777 (C=O), 1727 (C=O); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.15 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 7.12 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.82 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 6.73 (dd, *J* = 7.7, 1.1 Hz, 1H), 5.67 (dd, *J* = 5.7, 1.7 Hz, 1H), 5.12 (s, 1H), 4.67 (dd, *J* = 13.2, 1.7 Hz, 1H), 4.51 (d, *J* = 13.2 Hz, 1H), 4.30 (dd, *J* = 9.5, 6.6 Hz, 1H), 3.25 (d, *J* = 17.2 Hz, 1H), 2.93 (d, *J* = 17.2 Hz, 1H), 2.53–2.43 (m, 2H), 1.27 (s, 9H), 1.20–1.11 (m, 21H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 178.1, 173.4, 146.2, 132.9, 129.7, 129.2, 124.9, 124.4, 120.1, 110.5, 107.2, 70.7, 65.5, 55.5, 42.3, 38.8, 33.2, 27.3 (3C), 18.1 (6C), 12.4 (3C); HRMS (FAB) calcd for $C_{29}H_{44}NO_5Si$ $[M + H]^+$: 514.2989; found 514.2990.

**[(4b*S*,8*R*,8a*R*)-8-Hydroxy-11-oxo-7,8-dihydro-9*H*-8a,4b-(epoxyethano)carbazol-5-yl]methyl Pivalate (37).** To a solution of **36** (102 mg, 0.199 mmol) in THF (1.99 mL) were added a mixture of TBAF (1.0 M in THF; 477 μL, 0.477 mmol) and AcOH (27.3 μL, 0.477 mmol) at 0 ℃. After being stirred at room temperature for 7 h, the mixture was diluted with saturated aqueous $NaHCO_3$ and extracted with EtOAc (×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc = 1/2) to give **37** (60.1 mg, 84%) as a white amorphous solid; $[\alpha]^{27}_D$ +5.90 (*c* 3.01, $CHCl_3$); IR ($CDCl_3$) 3384 (NH), 1765 (C=O), 1724 (C=O); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.13 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 2H), 6.83 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 6.69 (dd, *J* = 7.4, 1.1 Hz, 1H), 5.70 (d, *J* = 4.6 Hz, 1H), 5.67 (s, 1H), 4.67 (dd, *J* = 13.8, 1.1 Hz, 1H), 4.49 (d, *J* = 13.8 Hz, 1H), 4.30 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.64 (br s, 1H), 3.26 (d, *J* = 17.8 Hz, 1H), 3.01 (d, *J* = 17.8 Hz, 1H), 2.55–2.42 (m, 2H), 1.27 (s, 9H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 178.1, 174.1, 146.2, 132.7, 129.8, 129.1, 125.1, 124.4, 120.2, 110.6, 108.1, 69.5, 65.4, 55.4, 42.1, 38.8, 30.9, 27.3 (3C); HRMS (FAB) calcd for $C_{20}H_{24}NO_5$ $[M + H]^+$: 358.1654; found 358.1656.

**[(1*R*,4a*S*,9a*S*)-1-Hydroxy-4a-(2-methoxy-2-oxoethyl)-24aa,9,9a-tetrahydro-1*H*-carbazol-4-yl]methyl pivalate (38).** To a solution of **37** (75.4 mg, 0.211 mmol) in MeOH (2.11 mL) were added AcOH (24.1 μL, 0.422 mmol) and $NaBH_3CN$ (134 mg, 2.13 mmol) at 0 ℃. After being stirred at room temperature for 3 h, the mixture was diluted with brine, acidified (pH ≈ 3) with 1 N HCl and extracted with EtOAc (×3). The combined

organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was used in the next step without purification. To a solution of crude carboxylic acid in MeOH (3.16 mL) and THF (1.05 mL) was added $TMSCHN_2$ (0.6 M in hexane; 1.41 mL, 0.844 mmol) at room temperature. After being stirred at room temperature for 0.5 h, the mixture was concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (hexane/EtOAc =1/1) to give **38** (72.8 mg, 88% in 2 steps) as a colorless oil; $[\alpha]^{24}_D$ +3.83 (*c* 0.22, $CHCl_3$); IR ($CDCl_3$) 3489 (OH), 3373 (NH), 1725 (C=O); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.09 (d, $J$ = 7.4 Hz, 1H), 7.06 (ddd, $J$ = 7.4, 7.4, 1.1 Hz, 1H), 6.71 (ddd, $J$ = 7.4, 7.4, 1.1 Hz, 1H), 6.64 (d, $J$ = 7.4 Hz, 1H), 5.81–5.80 (m, 1H), 4.66 (d, $J$ = 13.2 Hz, 1H), 4.45 (d, $J$ = 13.2 Hz, 1H), 4.31–4.28 (m, 2H), 4.10 (s, 1H), 3.61 (s, 3H), 3.02 (d, $J$ = 15.5 Hz, 1H), 2.99 (d, $J$ = 15.5 Hz, 1H), 2.59–2.53 (m, 1H), 2.40–2.34 (m, 1H), 1.19 (s, 9H); $^{13}$C{$^1$H} NMR (151 MHz, $CDCl_3$) $\delta$ 178.3, 171.2, 149.8, 132.3, 131.5, 128.8, 126.5, 123.8, 118.7, 110.4, 68.7, 66.6, 64.6, 51.7, 51.5, 41.1, 38.9, 29.6, 27.3 (3C); HRMS (FAB) calcd for $C_{21}H_{28}NO_5$ $[M + H]^+$: 374.1967; found 374.1968.

## ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

### Supporting Information

The Supporting Information is available free of charge at http://pubs.acs.org.

Synthetic scheme, optimization table and spectroscopic data copies of $^1$H, $^{13}$C NMR spectra (PDF)

### Notes

The authors declare no competing financial interest.

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