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# Synthesis of Substituted 1,4,5,6-Tetrahydrocyclopenta[*b*]pyrroles by Platinum-Catalyzed Cascade Cyclization/Ring Expansion of 2-Alkynyl-1-azaspiro[2.3]hexanes

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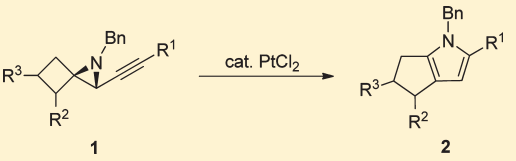
Supporting Information

**ABSTRACT:** The reaction of 2-alkynyl-1-azaspiro[2.3]hexanes with a platinum catalyst is described. 1,4,5,6-Tetrahydrocyclopenta[*b*]pyrroles having a variety of substituents were conveniently synthesized via a cascade cyclization/ring-expansion process.




## INTRODUCTION

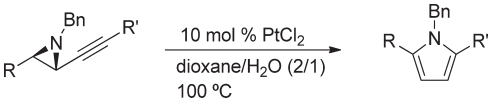
Cyclopenta[*b*]pyrroles (1,4,5,6-tetrahydrocyclopenta[*b*]pyrroles) are an important class of heteroaromatic molecules which are components of the phorbine chromophore present in all types of chlorophylls.[1] They are also utilized as synthetic intermediates for biologically active molecules having a 2-azabicyclo[3.3.0]octane skeletone.[2] Consequently, considerable effort has been devoted toward the development of an efficient methodology for the synthesis of cyclopenta[*b*]pyrroles.[3] However, few appropriate general methods for their synthesis exist.

Transition-metal-catalyzed cycloisomerization of propargylic aziridines is a useful methodology for the synthesis of substituted pyrroles.[4,5] Recently, some examples of a gold-catalyzed synthesis of pyrroles has been reported.[4] We have also found that platinum acts as a catalyst[6] for the conversion of propargylic aziridines to 2,5-disubstituted pyrroles (Scheme 1).[5a,b] As an application of this cycloisomerization reaction, we report herein a novel methodology for the synthesis of cyclopenta[*b*]pyrroles by platinum-catalyzed cascade cyclization/ring expansion of 2-alkynyl-1-azaspiro[2.3]hexanes **1**, in which various 1,4,5,6-tetrahydrocyclopenta[*b*]pyrroles **2** were synthesized with high efficiency.

## RESULTS AND DISCUSSION

The substrates **1** for the cyclization reactions were synthesized as follows (Scheme 2). After the reaction of cyclobutanone (**3a**) with benzylamine, the resulting imine was treated with the allenylzinc reagent to give the TMS-substituted propargylic aziridine **4a**.[7] Compound **4a** was subjected to the reaction with $K_2CO_3$ in MeOH to afford the desilylated compound **5a**, and then various substituents at the terminal position of the alkyne **5a** were introduced to give **1a**−**e** by the reactions with BuLi and the corresponding alkyl bromides. Compound **1f** containing a free hydroxyl group was obtained from the reaction of **1e** with TBAF. The 2-alkynyl-1-azaspiro[2.3]hexanes **1g**−**l** were also prepared from the corresponding cyclobutanones **3g**−**l** by following the same procedure.

**Scheme 1. Platinum-Catalyzed Cycloisomerization of Propargylic Aziridines**




The initial reactions for the synthesis of cyclopenta[*b*]pyrroles were attempted using the 2-pentynyl-1-azaspiro[2.3]hexane **1a** (Scheme 3). When **1a** was subjected to the reaction with 10 mol % of $PtCl_2$ in dioxane/$H_2O$ (2/1) at 100 °C following our procedure for the synthesis of pyrroles,[5a] the cyclopenta[*b*]pyrrole **2a** was produced in 84% yield. After several attempts, we found that the yield of **2a** could be increased to 97% when the reaction was carried out in dioxane.

The reactions of the various substituted 2-alkynyl-1-azaspiro[2.3]hexanes **1b**−**l** under the optimized conditions are summarized in Table 1. When the reactions of the substrates **1b** and **1c** containing an allyl and a 4-pentenyl group at the alkynyl position were carried out, the cyclopenta[*b*]pyrroles **2b** and **2c** were obtained in 91% and 90% yield, respectively (entries 1 and 2). The reactions of **1d** and **1e** having an alkynyl and a siloxy group also afforded the corresponding products **2d** and **2e** in good yields (entries 3 and 4). The substrate **1f** containing a free hydroxyl group was uneventfully transformed to the cyclopenta[*b*]pyrrole **2f** in 82% yield (entry 5). The substrate **1g**, which has a substituent on the cyclobutane ring, was successfully transformed to the product **2g** in 75% yield (entry 6). The reactions of **1h** and **1i** having 2-heptyl- and 2-phenethylcyclobutane moieties also afforded the products **2h** and **2i** in 71% and 75% yield, respectively (entries 7 and 8). The resulting **2h** and **2i** were obtained as the sole products, which indicates the predominant migration of a secondary carbon atom. When the reaction of the

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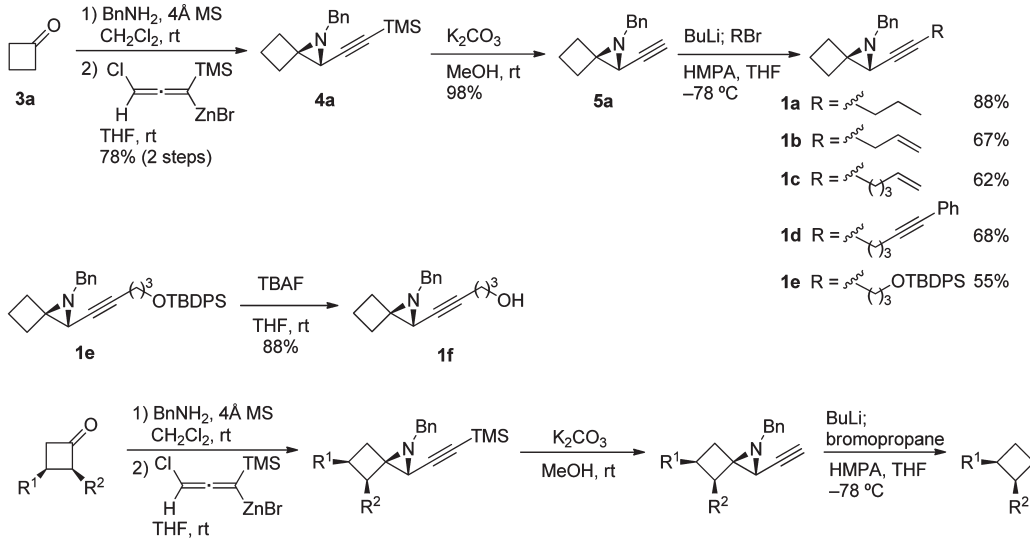
**Scheme 2. Synthesis of 2-Alkynyl-1-azaspiro[2.3]hexanes 1**



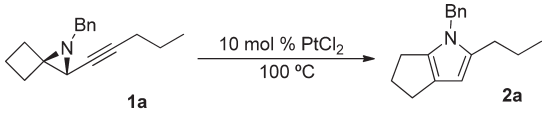

**3g** $R^1$ = 3-butenyl, $R^2$ = H
**3h** $R^1$ = H, $R^2$ = heptyl
**3i** $R^1$ = H, $R^2$ = phenethyl
**3j** $R^1+R^2$ = $-CH_2OCH_2-$
**3k** $R^1+R^2$ = $-(CH_2)_3-$
**3l** $R^1+R^2$ = $-(CH_2)_4-$

**4g** $R^1$ = 3-butenyl, $R^2$ = H 46% (2 steps)
**4h** $R^1$ = H, $R^2$ = heptyl 60% (2 steps)
**4i** $R^1$ = H, $R^2$ = phenethyl 52% (2 steps)
**4j** $R^1+R^2$ = $-CH_2OCH_2-$ 47% (2 steps)
**4k** $R^1+R^2$ = $-(CH_2)_3-$ 49% (2 steps)
**4l** $R^1+R^2$ = $-(CH_2)_4-$ 64% (2 steps)

**5g** $R^1$ = 3-butenyl, $R^2$ = H 86%
**5h** $R^1$ = H, $R^2$ = heptyl 97%
**5i** $R^1$ = H, $R^2$ = phenethyl 98%
**5j** $R^1+R^2$ = $-CH_2OCH_2-$ 98%
**5k** $R^1+R^2$ = $-(CH_2)_3-$ 89%
**5l** $R^1+R^2$ = $-(CH_2)_4-$ 87%

**1g** $R^1$ = 3-butenyl, $R^2$ = H 91%
**1h** $R^1$ = H, $R^2$ = heptyl 81%
**1i** $R^1$ = H, $R^2$ = phenethyl 52%
**1j** $R^1+R^2$ = $-CH_2OCH_2-$ 64%
**1k** $R^1+R^2$ = $-(CH_2)_3-$ 93%
**1l** $R^1+R^2$ = $-(CH_2)_4-$ 82%

**Scheme 3. Platinum-Catalyzed Cycloisomerization of Propargylic Aziridines**




| solvent | yield (%) |
|---|---|
| dioxane/$H_2O$ (2/1) | 84 |
| dioxane | 97 |

propargylic aziridine **1j** having an oxabicyclo[3.2.0]heptane ring was carried out, the tricyclic pyrrole **2j** was produced in 80% yield (entry 9). Similarly, the corresponding products **2k** and **2l** were obtained from the reactions of **1k** and **1l** containing a bicyclo[3.2.0]heptane and a bicyclo[4.2.0]octane moiety (entries 10 and 11).

A plausible mechanism for the cascade reaction of 2-alkynyl-1-azaspiro[2.3]hexanes is summarized in Scheme 4. It is presumed that the cyclopenta[*b*]pyrroles can be formed by two different pathways. The first possible one (a) involves the coordination of the platinum to the carbon−carbon triple bond as in **6**, followed by attack of the aziridine nitrogen on the alkyne, to produce the cyclized intermediate **7**. Then a regioselective 1,2-migration/ring expansion would proceed,[8] leading to the pyrrolylplatinum species **8**, which would undergo proto-demetalation to afford the cyclopenta[*b*]pyrrole **2**. As an alternative pathway (b), a ring expansion of the four-membered ring could be initially triggered by the coordination of the platinum to the aziridine nitrogen as shown in **9**, resulting in the formation of the cyclopentane imine **10**. Finally, the platinum-catalyzed cycloisomerization of **10** would take place[3d] to give the product **2**.

To further highlight the potential of this process, we next constructed 4,5,6,7-tetrahydro-1*H*-indoles by the reaction of 2-alkynyl-1-azaspiro[2.4]heptanes (Scheme 5). The 2-alkynyl-1-azaspiro[2.4]heptanes **1m** and **1n** were prepared from cyclopentanone (**3m**) by following the same procedure described for **1a** and **1e**. When the substrate **1m** was treated with 10 mol % of $PtCl_2$ in dioxane at 100 °C, the desired product **2m** was produced in 91% yield. Similarly, the reactions of **1n** having a siloxy group afforded the corresponding product **2n** in 84% yield.

## CONCLUSION

In conclusion, we have developed a methodology for the synthesis of cyclopenta[*b*]pyrroles by platinum-catalyzed cascade cyclization/ring expansion of 2-alkynyl-1-azaspiro[2.3]hexanes. The reactions afford a variety of substituted cyclopenta[*b*]pyrroles, and the process is an efficient and convenient protocol for the preparation of these derivatives.

## EXPERIMENTAL SECTION

**General Procedures.** All nonaqueous reactions were carried out under a positive atmosphere of argon in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocol. The phrase "residue upon workup" refers to the residue obtained when the organic layer was separated and dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. Cyclobutanones **3g**,[9] **3h**,[10] **3i**,[11] **3j**,[12] **3k**,[13] and **3l**,[13] were prepared according to the procedures described in the literature.

**General Procedure for the Synthesis of TMS-Substituted Propargylic Aziridines 4.** *Synthesis of* ***4a***. To a stirred solution of cyclobutanone (**3a**) (2.00 mL, 26.8 mmol) and 4 Å MS in $CH_2Cl_2$ was


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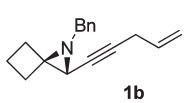
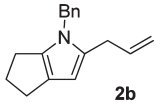
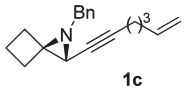
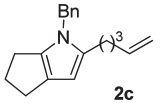
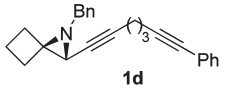
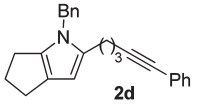
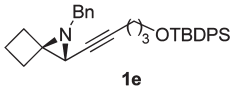
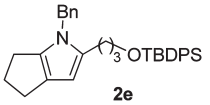
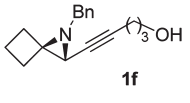
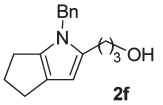
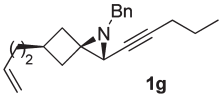
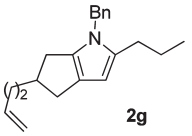
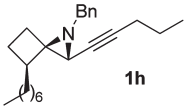
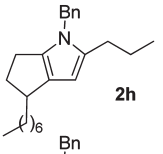
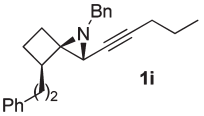
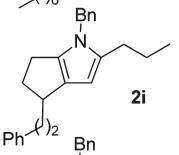
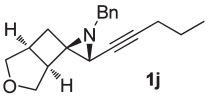
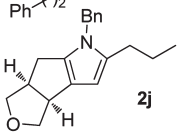
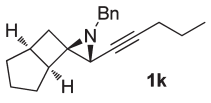
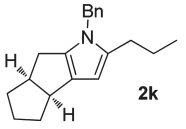
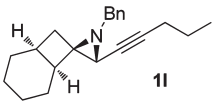
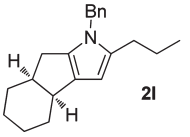
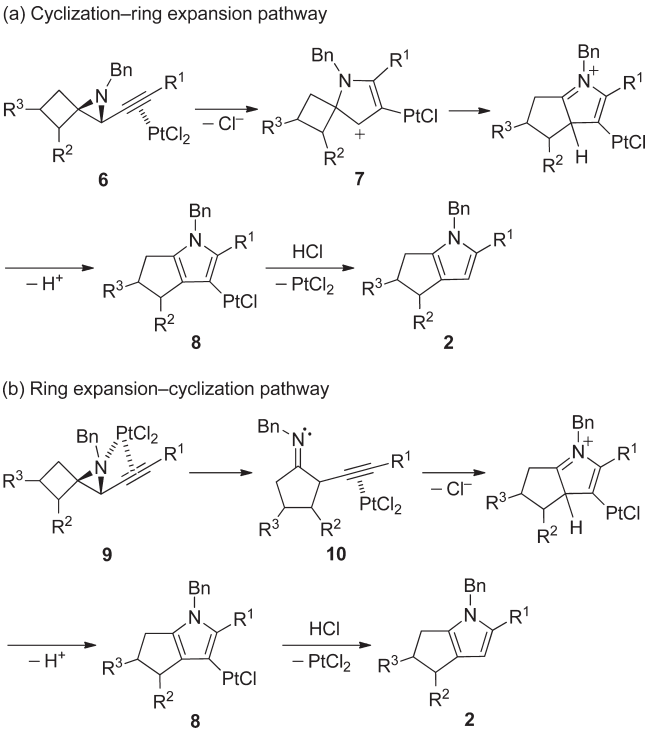
**Table 1. Reactions Using Various Substrates 1b–l**

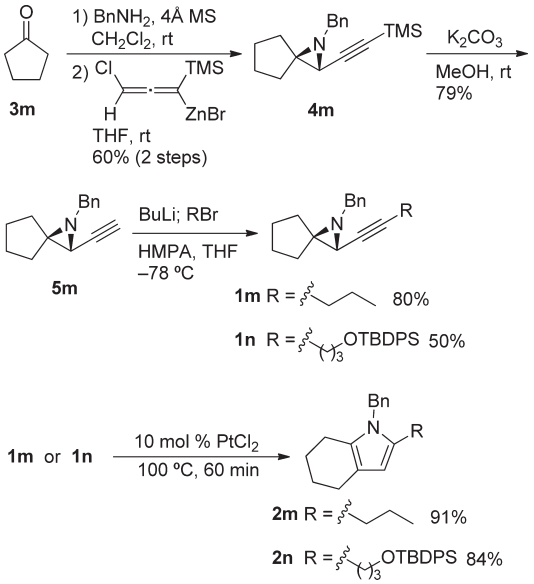
| entry | substrate **1** | product **2** | yield (%) |
|---|---|---|---|
| 1 |  **1b** |  **2b** | 91 |
| 2 |  **1c** |  **2c** | 90 |
| 3 |  **1d** |  **2d** | 79 |
| 4 |  **1e** |  **2e** | 89 |
| 5 |  **1f** |  **2f** | 82 |
| 6 |  **1g** |  **2g** | 75 |
| 7 |  **1h** |  **2h** | 71 |
| 8 |  **1i** |  **2i** | 75 |
| 9 |  **1j** |  **2j** | 80 |
| 10 |  **1k** |  **2k** | 81 |
| 11 |  **1l** |  **2l** | 52 |

[a] All reactions were carried out in the presence of 10 mol % of $PtCl_2$ in dioxane at 100 °C for 10–60 min.

**Scheme 4. Proposed Reaction Mechanisms**




**Scheme 5. Synthesis of 4,5,6,7-Tetrahydro-1*H*-indoles**




added *N*-benzylamine (2.90 mL, 26.8 mmol) at rt under argon atomosphere. After stirring was continued overnight at the same temperature, the resulting solution was filtered through a Celite pad. The filtrate was evaporated under reduced pressure to give *N*-cyclobutanbenzylimine. This crude product was used in the next steps without purification. To a stirred solution of (3-chloro-1-propynyl)trimethylsilane (4.70 g, 32.1 mmol) in THF (50 mL) was added $ZnBr_2$ (12.0 g, 53.5 mmol) at −78 °C. A freshly prepared solution of lithium diisopropylamide (1.0 M, 2.0 equiv) was slowly added dropwise to the resulting white suspension, and stirring was continued at the same temperature for 1 h to produce allenylzinc compound. *N*-Cyclobutanbenzylimine in THF (20 mL) was then added dropwise to the resulting solution of allenylzinc compound at −78 °C. The mixture was allowed to rt slowly, and further stirring was continued for 1 h at the same temperature. The resulting mixture was quenched with saturated aqueous $NH_4Cl$ and extracted with $Et_2O$. The combined organic extracts were washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (95:5, v/v) as eluent to give the TMS-substituted propargylic aziridine **4a** (5.66 g, 78%, two steps) as a yellow oil.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*1-Benzyl-2-(trimethylsilylethynyl)-1-azaspiro[2.3]hexane* (**4a**): yield 78% (two steps); yellow oil; 1:1 mixture of two invertomers; IR (neat) 2959, 1497, 1354, 1250, 1090 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.41−7.38 (m, 2H), 7.35−7.31 (m, 2H), 7.27−7.23 (m, 1H), 3.58−3.55 (m, 2H), 2.57−1.85 (m, 7H), 0.18 (s, 4.5H), 0.10 (s, 4.5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.5, 139.0, 128.23, 128.20, 128.1, 127.4, 126.7, 126.6, 103.6, 101.4, 90.8, 87.0, 57.6, 51.9, 50.2, 49.3, 38.2, 35.6, 31.4, 28.9, 25.9, 24.2, 14.6, 14.3, 0.0; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{24}NSi$ $[M + H]^+$ 270.1678, found 270.1677.

*1-Benzyl-5-(but-3-enyl)-2-(trimethylsilylethynyl)-1-azaspiro[2.3]hexane* (**4g**). Yield 46% (two steps); yellow oil; 1:1 mixture of two invertomers; IR (neat) 2959, 2922, 2151, 1454, 1250, 1092 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.40−7.37 (m, 2H), 7.35−7.31 (m, 2H), 7.27−7.23 (m, 1H), 5.85−5.74 (m, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 10.4 Hz, 1H), 3.58−3.49 (m, 2H), 2.57 (s, 0.5H), 2.45−2.19 (m, 3H), 2.07−1.88 (m, 4.5H), 1.55−1.50 (m, 2H), 0.17 (s, 4.5H), 0.16 (s, 4.5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.5, 138.9, 138.4, 128.2, 128.2, 128.1, 127.4, 126.7, 126.6, 114.5, 103.6, 101.4, 90.9, 87.0, 57.8, 52.0, 47.6, 46.6, 38.0, 37.4, 36.2, 36.1, 35.5, 34.9, 32.2, 31.6, 30.4, 28.1, 27.8, 0.0; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{30}NSi$ $[M + H]^+$ 324.2148, found 324.2143.

*1-Benzyl-4-heptyl-2-(trimethylsilylethynyl)-1-azaspiro[2.3]hexane* (**4h**): yield 60% (two steps); yellow oil; IR (neat) 2926, 2854, 2166, 1455, 1250, 843 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 3.60 (d, *J* = 13.6 Hz, 1H), 3.45 (d, *J* = 13.6 Hz, 1H), 2.48 (s, 1H), 2.38−2.22 (m, 3H), 2.08 (quint, *J* = 8.8 Hz, 1H), 1.53−1.44 (m, 2H), 1.31−1.14 (m, 11H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.18 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.6, 128.5, 128.1, 126.6, 101.7, 90.5, 52.3, 52.3, 42.4, 35.5, 31.8, 31.4, 29.6, 29.2, 26.9, 22.6, 21.8, 20.7, 14.0, 0.0; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{37}NNaSi$ $[M + Na]^+$ 390.2593, found 390.2594.

*1-Benzyl-4-phenethyl-2-(trimethylsilylethynyl)-1-azaspiro[2.3]hexane* (**4i**): yield 52% (two steps); yellow oil; 9:1 mixture of two invertomers; IR (neat) 2958, 2165, 1496, 1454, 1250 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) for the 9:1 mixture of two invertomers: $\delta$ 7.42 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 3.72 (d, *J* = 14.0 Hz, 0.1H), 3.59 (d, *J* = 13.6 Hz, 0.9H), 3.48 (d, *J* = 13.6 Hz, 0.9H), 3.33 (d, *J* = 14.0 Hz, 0.1 H), 2.55 (t, *J* = 8.0 Hz, 2H), 2.48 (s, 1H), 2.42−2.25 (m, 3H), 2.12 (quint, *J* = 8.0 Hz, 1H), 1.92−1.82 (m, 1H), 1.66−1.50 (m, 2H), 0.17 (s, 8.1H), 0.14 (s, 0.9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 142.4, 139.6, 128.5, 128.3, 128.2, 128.1, 126.7, 125.5, 101.6, 90.6, 52.3, 52.1, 41.7, 35.4, 33.4, 33.3, 21.8, 20.7, 0.0; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{31}NNaSi$ $[M + Na]^+$ 396.2123, found 396.2122. The stereochemistry of **4i** was determined unambiguously by NOE correlation.

*1-Benzyl-3-(trimethylsilylethynyl)-3′-oxaspiro(aziridine-2,6′-bicyclo-[3.2.0]heptane)* (**4j**): yield 47% (two steps); colorless needles; mp 69.2−70.6 °C [AcOEt−hexane (2:1)]; IR (neat) 2959, 2847, 2170, 1250, 1078 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 4.22 (d, *J* = 9.6 Hz, 1H), 3.90 (d, *J* = 9.6 Hz, 1H), 3.65 (d, *J* = 13.6 Hz, 1H), 3.50−3.42 (m, 2H), 3.41 (d, *J* = 13.6 Hz, 1H), 2.99−2.92 (m, 1H), 2.89−2.86 (m, 1H), 2.57 (s, 1H), 2.51 (dd, *J* = 8.4, 13.6 Hz, 1H), 2.08 (dd, *J* = 5.2, 13.6 Hz, 1H), 0.18 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.4, 128.6, 128.3, 126.8, 101.0, 91.7, 73.8, 69.8, 52.0, 48.0, 47.2, 36.7, 33.5, 28.1, 0.0; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{26}NOSi$ $[M + H]^+$ 312.1784, found 312.1781. The stereochemistry of **4j** was determined unambiguously by NOE correlation.

*1-Benzyl-3-(trimethylsilylethynyl)spiro(aziridine-2,6′-bicyclo[3.2.0]heptane)* (**4k**): yield 49% (two steps); yellow oil; IR (neat) 2955, 2360, 2173, 1250, 1075, 843 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 3.55 (d, *J* = 13.6 Hz, 1H), 3.45 (d, *J* = 13.6 Hz, 1H), 2.77−2.67 (m, 2H), 2.51 (s, 1H), 2.47 (ddd, *J* = 2.0, 8.6, 13.6 Hz, 1H), 1.82 (dd, *J* = 4.8, 12.0 Hz, 1H), 1.75 (dd, *J* = 4.8, 13.6 Hz, 1 H), 1.66−1.62 (m, 1H), 1.56−1.26 (m, 4H), 0.18 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.6, 128.5, 128.1, 126.7, 101.6, 90.9, 52.2, 48.9, 46.4, 36.7, 33.2, 32.6, 28.0, 27.9, 24.4, 0.0; HRMS (ESI) *m*/*z* calcd for $C_{20}H_{28}NSi$ $[M + H]^+$ 310.1991, found 310.1989.

*1-Benzyl-3-(trimethylsilylethynyl)spiro(aziridine-2,7′-bicyclo[4.2.0]-octane)* (**4l**): yield 64% (two steps); colorless oil; 85:15 mixture of two invertomers; IR (neat) 2931, 2854, 2165, 1452, 1250, 1068 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) for 85:15 mixture of two invertomers: $\delta$ 7.42−7.37 (m, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 4.18 (d, *J* = 14.4 Hz, 0.15H), 3.58 (d, *J* = 13.6 Hz, 0.85H), 3.50 (d, *J* = 13.6 Hz, 0.85H), 3.08 (d, *J* = 14.4 Hz, 0.15H), 2.58 (s, 0.85H), 2.52−2.41 (m, 1H), 2.31 (t, *J* = 9.2 Hz, 0.85H), 2.23−2.15 (m, 1.7H), 1.75−1.61 (m, 1.6H), 1.55−1.43 (m, 4H), 1.40−1.26 (m, 2H), 1.08−1.02 (m, 1H), 0.17 (s, 7.65H), 0.15 (s, 1.35H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.5, 128.7, 128.1, 126.7, 101.9, 90.7, 52.9, 52.0, 39.5, 35.2, 27.0, 26.1, 26.0, 23.9, 22.4, 21.4, 0.0; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{30}NSi$ $[M + H]^+$ 324.2148, found 324.2151.

*1-Benzyl-2-(trimethylsilylethynyl)-1-azaspiro[2.4]heptane* (**4m**): yield 60% (two steps); yellow oil; 1:1 mixture of two invertomers; IR (neat) 2959, 1497, 1354, 1250, 1090 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.39−7.36 (m, 2H), 7.33−7.29 (m, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 3.84−3.51 (m, 2H), 2.60 (s, 0.5H), 2.02 (s, 0.5H), 1.86−1.61 (m, 8H), 0.18 (s, 4.5H), 0.17 (s, 4.5H); $^{13}C$ NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.8, 139.3, 128.2, 128.0, 127.2, 126.5, 104.1, 101.8, 91.1, 87.4, 58.0, 54.4, 53.6, 52.1, 39.9, 37.1, 36.2, 32.7, 26.5, 25.9, 25.6, 24.9, 24.6, 24.0, 0.0; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{25}NNaSi$ $[M + Na]^+$ 306.1654, found 306.1655.

**General Procedure for the Synthesis of Terminal Alkyne 5.** *Synthesis of* **5a**. To a stirred solution of the TMS-substituted propargylic aziridine **4a** (661 mg, 2.45 mmol) in MeOH (12 mL) was added $K_2CO_3$ (678 mg, 4.91 mmol) at rt, and the stirring was continued for 0.5 h at the same temperature. The reaction mixture was then poured into $Et_2O/H_2O$ (1/1). The aqueous layer was extracted with $Et_2O$, and the combined organic extracts were washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (90:10, v/v) as eluent to give the terminal alkyne **5a** (477 mg, 98%) as yellow oil.

*1-Benzyl-2-ethynyl-1-azaspiro[2,3]hexane* (**5a**): yield 98%; yellow oil; 1:1 mixture of two invertomers; IR (neat) 3292, 3087, 3062, 3029, 2985, 2931, 2846, 2119, 1645, 1605, 1584, 1496, 1454, 1426, 1398, 1355 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.40−7.38 (m, 2H), 7.35−7.32 (m, 2H), 7.27−7.23 (m, 1H), 3.65 (d, *J* = 14.4 Hz, 0.5H), 3.61 (d, *J* = 14.4 Hz, 0.5H), 3.54 (d, *J* = 14.4 Hz, 0.5H), 3.50 (d, *J* = 14.4 Hz, 0.5H), 2.59 (d, *J* = 1.6 Hz, 0.5H), 2.51−2.10 (m, 4.5H), 2.05−1.88 (m, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.2, 138.6, 128.04, 128.03, 127.5, 127.1, 126.5, 126.4, 81.5, 78.9, 73.5, 69.9, 57.3, 51.7, 49.6, 48.6, 36.8, 34.4, 31.0, 28.7, 25.5, 24.0, 14.3, 14.0; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{15}NNa$ $[M + Na]^+$ 220.1102, found 220.1106.

*1-Benzyl-5-(but-3-enyl)-2-ethynyl-1-azaspiro[2.3]hexane* (**5g**): yield 86%; yellow oil; 1:1 mixture of two invertomers; IR (neat) 3310, 2925, 2853, 1415 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.39−7.37 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.26−7.22 (m, 1H), 5.84−5.74 (m, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 10.0 Hz, 1H), 3.65−3.44 (m, 2H), 2.59 (s, 0.5H), 2.47−2.17 (m, 4H), 2.09−1.86 (m, 4.5H), 1.55−1.50 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.4, 138.8, 138.4, 128.3, 127.9, 127.4, 126.8, 126.7, 114.5, 81.8, 79.3, 73.7, 70.1, 57.7, 52.0, 47.3, 46.2, 37.4, 37.0, 36.14, 36.10, 34.9, 34.6, 32.1, 31.5, 30.4, 28.1, 27.8; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{21}NNa$ $[M + Na]^+$ 274.1572, found 274.1567.

*1-Benzyl-2-ethynyl-4-heptyl-1-azaspiro[2.3]hexane* (**5h**): yield 97%; yellow oil; IR (neat) 3310, 2925, 2853, 1415 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 3.67 (d, *J* = 14.0 Hz, 1H), 3.45 (d, *J* = 14.0 Hz, 1H), 2.50 (d,

$J$ = 2.0 Hz, 1H), 2.38−2.24 (m, 4H), 2.08 (quint, $J$ = 8.4 Hz, 1H), 1.52−1.43 (m, 2H), 1.31−1.14 (m, 11H), 0.87 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.6, 128.4, 128.2, 126.7, 79.6, 73.3, 52.3, 52.0, 42.3, 35.5, 31.9, 31.4, 29.7, 29.2, 27.0, 22.7, 21.8, 20.9, 14.1; HRMS (ESI) $m/z$ calcd for $C_{21}H_{29}NNa$ $[M + Na]^+$ 318.2198, found 318.2197.

*1-Benzyl-2-ethynyl-4-phenethyl-1-azaspiro[2.3]hexane* (***5i***): yield 98%; colorless oil; IR (neat) 3291, 2930, 1496, 1454 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 (d, $J$ = 7.2 Hz, 2H), 7.32 (t, $J$ = 7.2 Hz, 2H), 7.24 (t, $J$ = 7.6 Hz, 3H), 7.15 (t, $J$ = 7.2 Hz, 1H), 7.09 (d, $J$ = 7.6 Hz, 2H), 3.66 (d, $J$ = 14.0 Hz, 1H), 3.47 (d, $J$ = 14.0 Hz, 1H), 2.55 (t, $J$ = 8.0 Hz, 2H), 2.50 (d, $J$ = 1.6 Hz, 1H), 2.42−2.26 (m, 4H), 2.11 (quint, $J$ = 8.0 Hz, 1H), 1.90−1.81 (m, 1H), 1.64−1.48 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.5, 139.5, 128.43, 128.40, 128.2, 128.1, 126.8, 125.6, 79.5, 73.4, 52.3, 51.9, 41.6, 34.5, 33.4, 33.3, 21.8, 20.8; HRMS (ESI) $m/z$ calcd for $C_{22}H_{24}N$ $[M + H]^+$ 302.1909, found 302.1909.

*1-Benzyl-3-ethynyl-3′-oxaspiro(aziridine-2,6′-bicyclo[3.2.0]heptane)* (***5j***): yield 98%; colorless needles; mp 64.2−65.3 °C [AcOEt−hexane (2:1)]; IR (neat) 3287, 2849, 1354, 1076, 906 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (d, $J$ = 7.2 Hz, 2H), 7.33 (t, $J$ = 7.2 Hz, 2H), 7.25 (t, $J$ = 7.2 Hz, 1H), 4.20 (d, $J$ = 9.2 Hz, 1H), 3.90 (d, $J$ = 8.8 Hz, 1H), 3.65 (d, $J$ = 13.6 Hz, 1H), 3.50−3.42 (m, 2H), 3.45 (d, $J$ = 13.6 Hz, 1H), 2.99−2.93 (m, 1H), 2.91−2.87 (m, 1H), 2.59 (s, 1H), 2.53 (ddd, $J$ = 2.0, 8.8, 13.4 Hz, 1H), 2.35 (d, $J$ = 2.0 Hz, 1H), 2.10 (dd, $J$ = 5.2, 13.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.2, 128.3, 128.2, 126.8, 78.8, 74.4, 73.7, 69.7, 51.9, 47.6, 47.1, 35.8, 33.4, 28.0; HRMS (ESI) $m/z$ calcd for $C_{16}H_{18}NO$ $[M + H]^+$ 240.1388, found 240.1386.

*1-Benzyl-3-ethynylspiro(aziridine-2,6′-bicyclo[3.2.0]heptane)* (***5k***): yield 89%; yellow oil; IR (neat) 3300, 2949, 2853, 2117, 1496, 1454, 1355, 1092 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 (d, $J$ = 7.2 Hz, 2H), 7.33 (t, $J$ = 7.2 Hz, 2H), 7.25 (t, $J$ = 7.2 Hz, 1H), 3.60 (d, $J$ = 14.0 Hz, 1H), 3.43 (d, $J$ = 14.0 Hz, 1H), 2.76−2.66 (m, 2H), 2.52 (d, $J$ = 1.6 Hz, 1H), 2.49 (ddd, $J$ = 1.6, 8.4, 13.6 Hz, 1H), 2.31 (d, $J$ = 1.6 Hz, 1H), 1.84−1.73 (m, 2H), 1.64−1.52 (m, 2H), 1.48−1.26 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.6, 128.4, 128.2, 126.8, 79.4, 73.7, 52.3, 48.6, 46.4, 35.9, 33.2, 32.6, 28.0, 27.9, 24.3; HRMS (ESI) $m/z$ calcd for $C_{17}H_{20}N$ $[M + H]^+$ 238.1596, found 238.1597.

*1-Benzyl-3-ethynylspiro(aziridine-2,7′-bicyclo[4.2.0]octane)* (***5l***): yield 87%; colorless oil; 4:1 mixture of two invertomers; IR (neat) 3296, 2930, 2854, 1496, 1451, 1356 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for 4:1 mixture of two invertomers: $\delta$ 7.42−7.37 (m, 2H), 7.35−7.31 (m, 2H), 7.26−7.23 (m, 1H), 4.19 (d, $J$ = 14.4 Hz, 0.2H), 3.62 (d, $J$ = 13.6 Hz, 0.8H), 3.50 (d, $J$ = 13.6 Hz, 0.8H), 3.07 (d, $J$ = 14.4 Hz, 0.2H), 2.60 (d, $J$ = 1.6 Hz, 1H), 2.53−2.41 (m, 1.4H), 2.35−2.29 (m, 1.6H), 2.35−2.29 (m, 2H), 2.12−1.94 (m, 0.8H), 1.78−1.60 (m, 2H), 1.56−1.43 (m, 2.2H), 1.37−1.24 (m, 2H), 1.09−0.99 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.4, 128.5, 128.2, 126.8, 79.7, 73.5, 52.9, 51.6, 39.4, 34.2, 27.0, 26.1, 26.1, 23.8, 22.4, 21.4; HRMS (ESI) $m/z$ calcd for $C_{18}H_{22}N$ $[M + H]^+$ 252.1752, found 252.1750.

*1-Benzyl-2-ethynyl-1-azaspiro[2.4]heptane* (***5m***): yield 79%; yellowish oil; 1:1 mixture of two invertomers; IR (neat): 3293, 3062, 3029, 2957, 2868, 2118, 1605, 1496, 1453, 1356 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.39 (2H, d, $J$ = 7.2 Hz), 7.34 (2H, t, $J$ = 7.2 Hz), 7.25−7.21 (1H, m), 3.77 (0.5H, d, $J$ = 14.4 Hz), 3.76 (0.5H, d, $J$ = 14.4 Hz), 3.60 (0.5H, d, $J$ = 14.4 Hz), 3.57 (0.5H, d, $J$ = 14.4 Hz), 2.62 (1H, d, $J$ = 1.6 Hz), 2.35 (1H, d, $J$ = 2.0 Hz), 2.21(1H, d, $J$ = 2.0 Hz), 2.01−1.94 (1H, m), 1.85−1.63 (6H, m); $^{13}$C NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.6, 139.1, 128.1, 127.6, 127.1, 126.5, 126.4, 82.0, 79.4, 73.9, 70.5, 57.8, 53.9, 53.0, 52.0, 38.7, 36.09, 36.04, 32.5, 26.4, 25.7, 25.5, 24.7, 24.4, 23.9; HRMS (ESI): $m/z$ calcd for $C_{15}H_{17}NNa$ $[M + Na]^+$ 234.1259; found 234.1254.

**General Procedure for the Synthesis of 2-Alkynyl-1-azaspiro[2.3]hexanes 1.** *Synthesis of* ***1a***. To a stirred solution of propargylic aziridine **5a** (1.00 g, 5.07 mmol) in THF (25 mL) was added slowly a 2.7 M hexane solution of *n*-BuLi (5.60 mL, 15.2 mmol) at −78 °C. After stirring was continued for 1 h, a solution of *n*-propyl bromide (2.70 mL, 30.4 mmol) and HMPA (3.50 mL, 30.4 mmol) in THF (5 mL) was then added dropwise to the stirred solution at the same temperature, and then the mixture was allowed gradually to rt. After being stirred for 1 h at rt, the reaction mixture was quenched with saturated aqueous $NH_4Cl$ solution and extracted with $Et_2O$. The combined organic extracts were washed with saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (90:10, v/v) as eluent to give the 2-pentynyl-1-azaspiro-[2.3]hexane **1a** (1.07 g, 88%) as colorless oil.

*1-Benzyl-2-pent-1-ynyl-1-azaspiro[2,3]hexane* (***1a***): yield 88%; colorless oil; 1:1 mixture of two invertomers; IR (neat) 3087, 3062, 3028, 2961, 2931, 2872, 2842, 2233, 1605, 1584, 1496, 1454, 1427, 1380, 1354 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for the mixture of two invertomers: $\delta$ 7.40 (d, $J$ = 7.6 Hz, 2H), 7.35−7.29 (m, 2H), 7.24 (d, $J$ = 7.6 Hz, 1H), 3.62 (d, $J$ = 14.4 Hz, 0.5H), 3.58 (d, $J$ = 14.4 Hz, 0.5H), 3.55 (d, $J$ = 14.4 Hz, 0.5H), 3.52 (d, $J$ = 14.4 Hz, 0.5H), 2.58 (s, 0.5H), 2.51−2.16 (m, 5.5H), 2.14−1.84 (m, 3H), 1.53 (dsext, $J$ = 2.8, 7.6 Hz, 2H), 0.96 (t, $J$ = 7.6 Hz, 3H); $^3$C NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.9, 139.2, 128.1, 127.8, 127.3, 126.5, 126.4, 86.2, 82.7, 77.6, 75.0, 57.6, 51.8, 49.5, 48.4, 38.1, 35.6, 31.6, 28.9, 25.8, 24.2, 22.3, 22.1, 20.8, 20.8, 14.6, 14.3, 13.4, 13.3; HRMS (ESI): $m/z$ calcd for $C_{17}H_{21}NNa$ $[M + Na]^+$ 262.1572, found 262.1570.

*1-Benzyl-2-pent-4-en-1-ynyl-1-azaspiro[2.3]hexane* (***1b***): yield 67%; colorless oil; 1:1 mixture of two invertomers; IR (neat) 3086, 3062, 3028, 2982, 2929, 2846, 2195, 1641, 1605, 1496, 1453, 1418, 1355 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.39 (d, $J$ = 7.2 Hz, 2H), 7.33 (t, $J$ = 7.2 Hz, 2H), 7.25−7.21 (m, 1H), 5.85−5.77 (m, 1H), 5.34−5.26 (m, 1H), 5.13−5.08 (m, 1H) 3.63 (d, $J$ = 14.4 Hz, 0.5H), 3.57 (d, $J$ = 14.4 Hz, 0.5H), 3.54 (d, $J$ = 14.4 Hz, 0.5H), 3.50 (d, $J$ = 14.4 Hz, 0.5H), 3.04 (t, $J$ = 7.6 Hz, 1H), 2.99 (t, $J$ = 7.6 Hz, 1H), 2.62 (s, 0.5H), 2.48−2.31 (m, 3H), 2.20−2.10 (m, 1H), 2.01−1.87 (m, 2.5H); $^{13}$C NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.8, 139.1, 132.6, 132.5, 128.2, 127.8, 127.4, 126.6, 126.5, 116.0, 115.9, 82.6, 79.9, 79.2, 77.5, 57.6, 51.9, 49.7, 48.6, 37.9, 35.5, 31.4, 29.0, 25.9, 24.3, 23.3, 23.1, 14.6, 14.3; HRMS (ESI): $m/z$ calcd for $C_{17}H_{19}NNa$ $[M + Na]^+$ 260.1415, found 260.1413.

*1-Benzyl-2-hept-6-en-1-ynyl-1-azaspiro[2.3]hexane* (***1c***): yield 62%; yellow oil; 1:1 mixture of two invertomers; IR (neat) 3063, 3029, 2930, 2857, 2232, 1640, 1605, 1496, 1453, 1354 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.39 (d, $J$ = 7.2 Hz, 2H), 7.32 (t, $J$ = 7.2 Hz, 2H), 7.25−7.21 (m, 1H), 5.84−5.73 (m, 1H), 5.05−4.96 (m, 2H), 3.60 (d, $J$ = 14.4 Hz, 0.5H), 3.57 (d, $J$ = 14.4 Hz, 0.5H), 3.52 (d, $J$ = 14.4 Hz, 0.5H), 3.50 (d, $J$ = 14.4 Hz, 0.5H), 2.58 (s, 0.5H), 2.51−2.08 (m, 8H), 2.06−1.84 (m, 2.5H), 1.60 (quint, $J$ = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.8, 139.2, 137.8, 137.6, 128.2, 127.8, 127.3, 126.6, 126.5, 115.1, 114.9, 86.0, 82.5, 77.8, 75.2, 57.6, 51.8, 49.6, 48.4, 38.0, 35.6, 32.7, 32.6, 31.3, 28.9, 28.0, 27.9, 25.8, 24.2, 18.3, 18.1, 14.6, 14.3; HRMS (ESI) $m/z$ calcd for $C_{19}H_{23}NNa$ $[M + Na]^+$ 288.1728, found 288.1722.

*1-Benzyl-2-(7-phenylhepta-1,6-diynyl)-1-azaspiro[2.3]hexane* (***1d***): yield 68%; colorless oil; 1:1 mixture of two invertomers; IR (neat) 2933, 1490 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for 1:1 mixture of two invertomers: $\delta$ 7.41−7.23 (m, 10H), 3.63−3.50 (m, 2H), 2.59−1.77 (m, 13H); $^{13}$C NMR (100 MHz, $CDCl_3$) for 1:1 mixture of two invertomers: $\delta$ 139.8, 139.2, 131.5, 128.25, 128.17, 128.14, 127.8, 127.6, 127.5, 127.4, 126.7, 126.5, 123.8, 123.8, 89.2, 88.9, 85.3, 81.8, 81.3, 81.1, 78.3, 75.8, 57.7, 51.9, 49.7, 48.6, 38.0, 35.6, 31.4, 29.0, 28.0, 25.9, 24.3, 18.6, 18.5, 18.2, 18.1, 14.7, 14.4; HRMS (ESI) $m/z$ calcd for $C_{25}H_{24}N$ $[M - H]^+$ 338.1909, found 338.1907.

*1-Benzyl-2-[5-(tert-butyldiphenylsilanyloxy)pent-1-ynyl]-1-azaspiro-[2.3]hexane* (***1e***): yield 55%; colorless oil; 1:1 mixture of two invertomers; IR (neat) 3069, 3028, 2980, 2930, 2856, 2234, 1656, 1605, 1589, 1567, 1496, 1471, 1427, 1390, 1359 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.71−7.65 (m, 4H),

7.42−7.24 (m, 10H), 7.22 (t, $J$ = 7.2 Hz, 1H), 3.73 (t, $J$ = 6.4 Hz, 2H), 3.55 (d, $J$ = 14.4 Hz, 1H), 3.45 (d, $J$ = 14.4 Hz, 1H), 2.55 (s, 0.5H), 2.50−2.31 (m, 3.5H), 2.30−2.19 (m, 2H), 2.17−1.83 (m, 3H), 1.77−1.72 (m, 2H), 1.05 (s, 4.5H), 1.04 (s, 4.5H); $^{13}$C NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.8, 139.2, 135.5, 135.5, 134.7, 133.8, 133.8, 129.5, 129.5, 129.5, 128.2, 128.2, 127.8, 127.6, 127.5, 127.5, 127.4, 126.6, 126.5, 85.9, 82.5, 77.6, 75.1, 62.5, 62.3, 57.6, 51.8, 49.6, 48.4, 38.0, 35.6, 31.84, 31.79, 31.36, 29.00, 26.82, 26.55, 25.88, 24.29, 19.20, 15.54, 15.37, 14.65, 14.33; HRMS (ESI) $m/z$ calcd for $C_{33}H_{39}NNaOSi$ $[M + Na]^+$ 516.2699, found 516.2698.

*1-Benzyl-5-(but-3-enyl)-2-(pent-1-ynyl)-1-azaspiro[2.3]hexane* (***1g***): yield 91%; colorless oil; 1:1 mixture of two invertomers; IR (neat) 2961, 2928, 1639, 1497, 1454, 1354 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.40−7.38 (m, 2H), 7.34−7.31 (m, 2H), 7.26−7.20 (m, 1H), 5.85−5.74 (m, 1H), 5.02−4.93 (m, 2H), 3.61−3.46 (m, 2H), 2.58 (s, 0.5H), 2.44−2.16 (m, 5H), 2.06−1.86 (m, 4.5H), 1.56−1.48 (m, 4H), 0.97 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.9, 139.2, 138.5, 128.2, 127.9, 127.4, 126.6, 126.5, 114.4, 86.4, 82.9, 77.7, 75.1, 57.7, 51.9, 46.9, 45.8, 38.0, 37.5, 36.3, 36.2, 35.5, 35.0, 32.1, 31.6, 30.5, 28.2, 27.8, 22.3, 22.2, 20.9, 20.8, 13.4; HRMS (ESI) $m/z$ calcd for $C_{21}H_{26}N$ $[M - H]^+$ 292.2065, found 292.2060.

*1-Benzyl-4-heptyl-2-(pent-1-ynyl)-1-azaspiro[2.3]hexane* (***1h***): yield 81%; colorless oil; IR (neat) 2959, 2926, 1455, 729 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (d, $J$ = 7.2 Hz, 2H), 7.32 (t, $J$ = 7.2 Hz, 2H), 7.23 (t, $J$ = 7.2 Hz, 1H), 3.62 (d, $J$ = 14.4 Hz, 1H), 3.41 (d, $J$ = 14.4 Hz, 1H), 2.49 (s, 1H), 2.34−2.21 (m, 5H), 2.11−2.02 (m, 1H), 1.58−1.42 (m, 5H), 1.38−1.12 (m, 10H), 0.98 (t, $J$ = 7.6 Hz, 3H), 0.87 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.0, 128.4, 128.1, 126.6, 86.0, 75.4, 52.2, 51.6, 42.3, 35.47, 31.9, 31.4, 29.7, 29.2, 27.0, 22.7, 22.4, 21.9, 20.9, 20.8, 14.1, 13.4; HRMS (ESI) $m/z$ calcd for $C_{24}H_{36}N$ $[M + H]^+$ 338.2848, found 338.2849.

*1-Benzyl-2-(pent-1-ynyl)-4-phenethyl-1-azaspiro[2.3]hexane* (***1i***): yield 92%; colorless oil; IR (neat) 2931, 1496, 1454, 733 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.42 (d, $J$ = 7.2 Hz, 2H), 7.31 (t, $J$ = 7.2 Hz, 2H), 7.26−7.22 (m, 3H), 7.15 (t, $J$ = 7.2 Hz, 1H), 7.09 (d, $J$ = 7.2 Hz, 2H), 3.61 (d, $J$ = 14.0 Hz, 1H), 3.44 (d, $J$ = 14.0 Hz, 1H), 2.55 (t, $J$ = 8.0 Hz, 2H), 2.49 (s, 1H), 2.38−2.21 (m, 5H), 2.15−2.04 (m, 1H), 1.91−1.82 (m, 1H), 1.64−1.45 (m, 4H), 0.98 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.6, 140.0, 128.4, 128.4, 128.2, 128.1, 126.6, 125.5, 86.1, 75.3, 52.2, 51.4, 41.7, 35.4, 33.5, 33.4, 22.4, 21.9, 20.9, 20.8, 13.4; HRMS (ESI) $m/z$ calcd for $C_{25}H_{29}NNa$ $[M + Na]^+$ 366.2198, found 366.2201.

*1-Benzyl-3-(pent-1-ynyl)-3′-oxaspiro(aziridine-2,6′-bicyclo[3.2.0]-heptane)* (***1j***): yield 64%; yellow oil; IR (neat) 2962, 2846, 1497,1454, 1354, 1266, 1075 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.40 (d, $J$ = 7.2 Hz, 2H), 7.32 (t, $J$ = 7.2 Hz, 2H), 7.23 (t, $J$ = 7.2 Hz, 1H), 4.21 (d, $J$ = 9.6 Hz, 1H), 3.89 (d, $J$ = 8.8 Hz, 1H), 3.60 (d, $J$ = 13.6 Hz, 1H), 3.50−3.42 (m, 2H), 3.45 (d, $J$ = 13.6 Hz, 1H), 2.97−2.91 (m, 1H), 2.88−2.85 (m, 1H), 2.58 (t, $J$ = 1.6 Hz, 1H), 2.49 (ddd, $J$ = 1.6, 8.8, 13.0 Hz, 1H), 2.23 (dt, $J$ = 1.6, 7.2 Hz, 2H), 2.06 (dd, $J$ = 4.8, 13.0 Hz, 1H), 1.53 (sext, $J$ = 7.2 Hz, 2H), 0.97 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.7, 128.4, 128.2, 126.7, 87.1, 74.7, 73.8, 69.7, 51.8, 47.2, 47.1, 36.7, 33.5, 28.1, 22.3, 20.8, 13.4; HRMS (ESI) $m/z$ calcd for $C_{19}H_{24}NO$ $[M + H]^+$ 282.1858, found 282.1862.

*1-Benzyl-3-(pent-1-ynyl)spiro(aziridine-2,6′-bicyclo[3.2.0]heptane)* (***1k***): yield 93%; yellow oil; IR (neat) 2957, 1496, 1454, 1354, 1090 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (d, $J$ = 6.8 Hz, 2H), 7.32 (t, $J$ = 6.8 Hz, 2H), 7.23 (t, $J$ = 6.8 Hz, 1H), 3.56 (d, $J$ = 14.0 Hz, 1H), 3.40 (d, $J$ = 14.0 Hz, 1H), 2.74−2.65 (m, 2H), 2.50 (d, $J$ = 1.6 Hz, 1H), 2.49 (ddd, $J$ = 2.4, 8.4, 13.4 Hz, 1H), 2.23 (dt, $J$ = 1.6, 7.2 Hz, 2H), 1.80 (dd, $J$ = 4.4, 11.8 Hz, 1H), 1.71 (dd, $J$ = 4.4, 13.4 Hz, 1H), 1.63−1.24 (m, 7H), 0.97 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 140.0, 128.5, 128.2, 126.7, 86.5, 75.3, 52.1, 48.1, 46.4, 36.8, 33.2, 32.6, 28.1, 27.9, 24.4, 22.4, 20.9, 13.4; HRMS (ESI) $m/z$ calcd for $C_{20}H_{26}N$ $[M + H]^+$ 280.2065, found 280.2065.

*1-Benzyl-3-(pent-1-ynyl)spiro(aziridine-2,7′-bicyclo[4.2.0]octane)* (***1l***): yield 82%; colorless oil; 85:15 mixture of two invertomers; IR (neat) 2930, 2854, 1496, 1452, 1355 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for 85:15 mixture of two invertomers: $\delta$ 7.41−7.38 (m, 2H), 7.34−7.30 (m, 2H), 7.25−7.21 (m, 1H), 4.17 (d, $J$ = 14.4 Hz, 0.15H), 3.58 (d, $J$ = 13.6 Hz, 0.85H), 3.46 (d, $J$ = 13.6 Hz, 0.85H), 3.08 (d, $J$ = 14.4 Hz, 0.15H), 2.59 (s, 0.85H), 2.53−2.40 (m, 1.3H), 2.32−2.14 (m, 4.85H), 1.76−1.62 (m, 1H), 1.58−1.48 (m, 7H), 1.38−1.28 (m, 2H), 0.97 (t, $J$ = 7.6 Hz, 2.55H), 0.97 (t, $J$ = 7.2 Hz, 0.45H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.9, 128.6, 128.2, 126.6, 86.2, 75.6, 52.8, 51.2, 39.4, 35.2, 27.0, 26.1, 26.1, 23.9, 22.5, 22.4, 21.5, 20.9, 13.4; HRMS (ESI) $m/z$ calcd for $C_{21}H_{27}NNa$ $[M + Na]^+$ 316.2041, found 316.2040.

*1-Benzyl-2-(pent-1-ynyl)-1-azaspiro[2.4]heptane* (***1m***): yield 80%; colorless oil; 1:1 mixture of two invertomers; IR (neat) 3086, 3063, 3029, 2968, 2932, 2872, 2233, 1605, 1587, 1496, 1451, 1429, 1382, 1354 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.37 (2H, d, $J$ = 7.2 Hz), 7.30 (2H, t, $J$ = 7.2 Hz), 7.21 (1H, t, $J$ = 7.2 Hz), 3.78 (0.5H, d, $J$ = 14.4 Hz), 3.74 (0.5H, d, $J$ = 14.4 Hz), 3.54 (0.5H, d, $J$ = 14.4 Hz), 3.53 (0.5H, d, $J$ = 14.4 Hz), 2.61 (0.5H, t, $J$ = 2.0 Hz), 2.24−2.17 (2H, m), 1.99−1.81 (1H, m), 1.79−1.70 (2H, m), 1.67−1.66 (5.5H, m), 1.56−1.50 (2H, m), 0.98 (3H, t, $J$ = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 140.1, 139.6, 128.1, 128.1, 127.8, 127.2, 126.4, 126.4, 86.6, 83.2, 77.9, 75.4, 57.9, 53.7, 52.6, 52.0, 39.8, 37.1, 36.2, 32.6, 26.6, 25.9, 25.6, 24.9, 24.6, 24.0, 22.3, 22.1, 20.9, 20.8, 13.4, 13.3; HRMS (ESI): $m/z$ calcd for $C_{18}H_{23}NNa$ $[M + Na]^+$ 276.1728, found 276.1726.

*1-Benzyl-2-[5-(tert-butyldiphenylsilyloxy)pent-1-ynyl]-1-azaspiro-[2.4]heptane* (***1n***): yield 50%; colorless oil; 1:1 mixture of two invertomers; IR (neat) 3069, 3028, 2980, 2955, 2856, 2234, 1605, 1589, 1496, 1471, 1453, 1428, 1390, 1359 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.58 (4H, d, $J$ = 7.2 Hz), 7.35−7.10 (11H, m), 3.71 (0.5H, d, $J$ = 14.4 Hz), 3.67 (2H, t, $J$ = 6.4 Hz), 3.60 (0.5H, d, $J$ = 14.4 Hz), 3.44 (0.5H, d, $J$ = 16.4 Hz), 3.40 (0.5H, d, $J$ = 14.8 Hz), 2.51 (0.5H, s), 2.36−2.27 (2H, m), 1.89−1.82 (1H, m), 1.71−1.63 (4H, m), 1.61−1.55 (5.5H, m), 0.97 (4.5H, s), 0.96 (4.5H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 140.1, 139.6, 135.5, 135.5, 133.9, 133.8, 129.5, 129.5, 128.1, 127.8, 127.6, 127.5, 127.2, 126.5, 126.4, 86.2, 82.9, 78.0, 77.2, 75.5, 62.5, 62.4, 58.0, 53.7, 52.7, 52.0, 39.8, 37.1, 36.2, 32.7, 31.8, 31.8, 26.8, 26.6, 25.9, 25.7, 24.9, 24.6, 24.1, 19.2, 15.5, 15.4, 14.1, 14.0; HRMS (ESI) $m/z$ calcd for $C_{34}H_{41}NNaOSi$ $[M + Na]^+$ 530.2855, found 530.2851.

*5-(1-Benzyl-1-azaspiro[2.3]hex-2-yl)pent-4-yn-1-ol* (***1f***). To a stirred solution of propargylic aziridine **1e** (85.0 mg, 0.172 mmol) in THF (5.0 mL) was added 1.0 M THF solution of TBAF (0.7 mL, 0.699 mmol) at 0 °C, and after that the reaction mixture was allowed to warm rt with stirring. After being stirred for 1.5 h at the same temperature, the reaction mixture was poured into aq satd $NH_4Cl$ solution. The aqueous layer was extracted with AcOEt (3 × 15 mL). The combined organic extracts were washed with brine (2 × 15 mL) and dried over $MgSO_4$. After solvent evaporation at reduced pressure, the residue was chromatographed on silica gel with hexane−AcOEt (65:35) as eluent to give the propargylic aziridine **1f** (38.7 mg, 88%) as a colorless oil as a 1:1 mixture of two invertomers: IR (neat): 3317, 3088, 3062, 3029, 2929, 2850, 2235, 1605, 1497, 1453, 1428, 1355 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 7.39−7.37 (2H, m), 7.34−7.31 (2H, m), 7.26−7.23 (1H, m), 3.71−3.65 (2H, m), 3.61 (0.5H, d, $J$ = 14.4 Hz), 3.59 (0.5H, d, $J$ = 14.4 Hz), 3.53 (0.5H, d, $J$ = 14.4 Hz), 3.49 (0.5H, d, $J$ = 14.4 Hz), 2.58 (0.5H, s), 2.49−2.25 (5H, m), 2.22−2.10 (2H, m), 2.03−1.89 (2.5H, m), 1.75−1.67 (2H, m); $^{13}$C NMR (100 MHz, $CDCl_3$) for the 1:1 mixture of two invertomers: $\delta$ 139.7, 139.0, 134.7, 128.2, 128.2, 127.7, 127.3, 126.7, 126.5, 85.6, 82.1, 78.0, 75.3, 61.3, 61.3, 57.5, 51.8, 49.7, 48.5, 38.0, 35.5, 31.5, 31.3, 31.2,

29.6, 28.9, 25.8, 24.2, 15.4, 15.3, 14.6, 14.3; HRMS (ESI) $m/z$ calcd for $C_{17}H_{21}NONa$ $[M + Na]^+$ 278.1521; found 278.1526.

**General Procedure for the Synthesis of Pyrroles from Propargylic Aziridines Using Platinum Catalyst.** *Synthesis of* ***2a****.* To a stirred solution of propargylic aziridine **1a** (90.0 mg, 0.376 mmol) in dioxane was added $PtCl_2$ (10.0 mg, 0.0380 mmol) at rt. After stirring was continued for 40 min at 100 °C, the resulting mixture was cooled to rt and diluted with a minimum amount of $Et_2O$. The solution was then filtered through a small amount of silica gel. Concentration at reduced pressure gave the residue, which was chromatographed on silica gel with hexane−AcOEt (98:2) as eluent to give the pyrrole **2a** (87.3 mg, 97%) as a yellow oil.

*1-Benzyl-2-propyl-1,4,5,6-tetrahydrocyclopenta[b]pyrrole (**2a**):* yield 97%; yellow oil; IR (neat) 3066, 3028, 2929, 2851, 1605, 1597, 1496, 1453, 1425, 1376, 1352 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.31−7.21 (m, 3H), 6.98 (d, $J$ = 7.2 Hz, 2H), 5.76 (s, 1H), 4.94 (s, 2H), 2.63 (t, $J$ = 6.8 Hz, 2H), 2.52 (t, $J$ = 7.2 Hz, 2H), 2.42 (t, $J$ = 7.2 Hz, 2H), 2.38−2.31 (m, 2H), 1.56 (sext, $J$ = 7.2 Hz, 2H), 0.92 (t, $J$ = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.7, 137.3, 136.4, 128.6, 127.0, 126.2, 124.4, 100.7, 48.4, 29.1, 28.6, 25.7, 24.8, 22.5, 14.0; HRMS (ESI) $m/z$ calcd for $C_{17}H_{21}NNa$ $[M + Na]^+$ 262.1572, found 262.1571.

*1-Benzyl-2-pent-4-enyl-1,4,5,6-tetrahydrocyclopenta[b]pyrrole (**2b**):* yield 91%; yellow oil; IR (neat) 2843, 1640, 1605, 1584, 1496, 1453, 1354 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.29 (t, $J$ = 7.2 Hz, 2H), 7.23 (t, $J$ = 7.2 Hz, 1H), 6.98 (d, $J$ = 7.2 Hz, 2H), 5.93−5.83 (m, 1H), 5.76 (s, 1H), 5.06−4.99 (m, 2H), 4.95 (s, 2H), 3.22 (d, $J$ = 6.4 Hz, 2H), 2.63 (t, $J$ = 6.8 Hz, 2H), 2.53 (t, $J$ = 6.8 Hz, 2H), 2.35 (quint, $J$ = 6.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.6, 138.1, 136.2, 133.4, 128.6, 127.1, 126.3, 124.6, 115.6, 101.9, 48.5, 31.9, 28.6, 25.7, 24.9; HRMS (ESI) $m/z$ calcd for $C_{17}H_{19}NNa$ $[M + Na]^+$ 260.1415, found 260.1413.

*1-Benzyl-2-pent-4-enyl-1,4,5,6-tetrahydrocyclopenta[b]pyrrole (**2c**):* yield 90%; yellow oil; IR (neat) 2851, 1639, 1605, 1497, 1478, 1452, 1388, 1354 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.29 (t, $J$ = 7.2 Hz, 2H), 7.22 (t, $J$ = 7.2 Hz, 1H), 6.98 (d, $J$ = 7.2 Hz, 2H), 5.80−5.70 (m, 1H), 5.76 (s, 1H), 4.99−4.91 (m, 4H), 2.63 (t, $J$ = 6.8 Hz, 2H), 2.52 (t, $J$ = 6.8 Hz, 2H), 2.43 (t, $J$ = 6.8 Hz, 2H), 2.39−2.32 (m, 2H), 2.07 (q, $J$ = 7.2 Hz, 2H), 1.62 (quint, $J$ = 7.2 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.7, 138.4, 137.4, 136.0, 128.6, 127.0, 126.2, 124.5, 114.6, 100.8, 48.4, 33.3, 28.6, 28.4, 26.3, 25.7, 24.8; HRMS (ESI): $m/z$ calcd for $C_{19}H_{23}NNa$ $[M + Na]^+$ 288.1728, found 288.1726.

*1-Benzyl-2-(5-phenylpent-4-ynyl)-1,4,5,6-tetrahydrocyclopenta[b]-pyrrole (**2d**):* yield 79%; yellow oil; IR (neat) 2934, 2850, 1490, 1452, 1388, 1353 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.34−7.20 (m, 8H), 6.98 (d, $J$ = 6.8 Hz, 2H), 5.81 (s, 1H), 4.98 (s, 2H), 2.64 (t, $J$ = 7.2 Hz, 4H), 2.55 (t, $J$ = 6.8 Hz, 2H), 2.43 (t, $J$ = 6.8 Hz, 2H), 2.39−2.32 (m, 2H), 1.82 (quint, $J$ = 6.8 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.7, 137.7, 135.2, 131.5, 128.6, 128.2, 127.5, 127.1, 126.2, 124.6, 123.9 101.2, 89.8, 81.1, 48.5, 28.7, 28.3, 26.0, 25.8, 24.9, 19.0; HRMS (ESI) $m/z$ calcd for $C_{25}H_{25}NNa$ $[M + Na]^+$ 362.1885, found 362.1881.

*1-Benzyl-2-[3-(tert-butyldiphenylsilanyloxy)propyl]-1,4,5,6-tetrahydrocyclopenta[b]pyrrole (**2e**):* yield 89%; yellow oil; IR (neat) 2926, 1589, 1517, 1471, 1453, 1359 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.63−7.61 (m, 4H), 7.40−7.38 (m, 2H), 7.36−7.32 (m, 4H), 7.27−7.23 (m, 3H), 6.96 (d, $J$ = 6.8 Hz, 2H), 5.72 (s, 1H), 4.92 (s, 2H), 3.68 (t, $J$ = 6.4 Hz, 2H), 2.63 (t, $J$ = 6.8 Hz, 2H), 2.57−2.51 (m, 4H), 2.38−2.31 (m, 2H), 1.83−1.76 (m, 2H), 1.01 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.6, 137.4, 135.9, 135.5, 133.9, 129.5, 128.6, 127.5, 127.0, 126.2, 124.4, 100.6, 63.3, 48.4, 32.2, 28.6, 26.8, 25.7, 24.8, 23.3, 19.1; HRMS (ESI) $m/z$ calcd for $C_{33}H_{39}NNaOSi$ $[M + Na]^+$ 516.2699, found 516.2694.

*1-Benzyl-2-(3-hydroxypropyl)-1,4,5,6-tetrahydrocyclopenta[b]pyrrole (**2f**):* yield 82%; yellow oil; IR (neat) 3365, 3094, 3063, 2929, 2854, 1605, 1454 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.30 (t, $J$ = 7.2 Hz, 2H), 7.21 (t, $J$ = 7.2 Hz, 1H), 6.99 (d, $J$ = 7.2 Hz, 2H), 5.78 (s, 1H), 4.96 (s, 2H), 3.64 (t, $J$ = 6.4 Hz, 2H), 2.63 (t, $J$ = 6.8 Hz, 2H), 2.57−2.52 (m, 4H), 2.39−2.32 (m, 2H), 1.78 (quint, $J$ = 7.2 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.6, 137.8, 135.3, 128.6, 127.1, 126.2, 124.5, 100.9, 62.4, 48.4, 32.1, 28.6, 25.7, 24.8, 23.2; HRMS (ESI) $m/z$ calcd for $C_{17}H_{21}NNaO$ $[M + Na]^+$ 278.1521, found 278.1520.

*1-Benzyl-5-(but-3-enyl)-2-propyl-1,4,5,6-tetrahydrocyclopenta[b]-pyrrole (**2g**):* yield 75%; yellow oil; IR (neat) 2925, 1454 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.30 (t, $J$ = 7.2 Hz, 2H), 7.23 (t, $J$ = 7.2 Hz, 1H), 6.97 (d, $J$ = 7.2 Hz, 2H), 5.87−5.77 (m, 1H), 5.73 (s, 1H), 5.02−4.91 (m, 2H), 4.93 (s, 2H), 2.86−2.77 (m, 2H), 2.69 (dd, $J$ = 7.6, 14.0 Hz, 1H), 2.41 (t, $J$ = 7.2 Hz, 2H), 2.35−2.28 (m, 1H), 2.22 (dd, $J$ = 6.4, 14.0 Hz, 1H), 2.08 (q, $J$ = 7.2 Hz, 2H), 1.68−1.51 (m, 4H), 0.92 (t, $J$ = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 139.0, 138.8, 136.1, 136.0, 128.6, 127.1, 126.2, 123.2, 114.2, 100.8, 48.3, 43.8, 36.0, 32.7, 32.4, 31.6, 29.1, 22.5, 14.1; HRMS (ESI) $m/z$ calcd for $C_{21}H_{28}N$ $[M + H]^+$ 294.2222, found 294.2224.

*1-Benzyl-4-heptyl-2-propyl-1,4,5,6-tetrahydrocyclopenta[b]pyrrole (**2h**):* yield 81%; yellow oil; IR (neat) 2926, 1672, 1455 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.31−7.21 (m, 3H), 6.97 (d, $J$ = 7.2 Hz, 2H), 5.77 (s, 1H), 4.93 (s, 2H), 2.99−2.90 (m, 1H), 2.57−2.39 (m, 5H), 1.94−1.87 (m, 1H), 1.61−1.52 (m, 2H), 1.48−1.17 (m, 12H), 0.92 (t, $J$ = 7.2 Hz, 3H), 0.89 (t, $J$ = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.8, 136.6, 135.9, 128.9, 128.6, 127.0, 126.2, 100.6, 48.3, 39.4, 37.5, 36.1, 31.9, 29.9, 29.4, 29.2, 28.2, 24.4, 22.7, 22.3, 14.1; HRMS (ESI) $m/z$ calcd for $C_{24}H_{36}N$ $[M + H]^+$ 338.2848, found 338.2850. The regiochemistry of **2h** was determined unambiguously by NOE correlation.

*1-Benzyl-4-phenethyl-2-propyl-1,4,5,6-tetrahydrocyclopenta[b]pyrrole (**2i**):* yield 75%; yellow oil; IR (neat) 2929, 1671, 1455 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.31−7.22 (m, 7H), 7.16 (t, $J$ = 6.8 Hz, 1H), 6.97 (d, $J$ = 6.8 Hz, 2H), 5.82 (s, 1H), 4.94 (s, 2H), 3.01 (quint, $J$ = 6.8 Hz, 1H), 2.84−2.69 (m, 2H), 2.59−2.40 (m, 5H), 1.98−1.72 (m, 3H), 1.57 (sext, $J$ = 7.6 Hz, 2H), 0.93 (t, $J$ = 7.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 143.1, 138.8, 136.7, 136.1, 128.6, 128.5, 128.4, 128.2, 127.0, 126.2, 125.5, 100.7, 48.3, 39.3, 39.0, 36.0, 34.5, 29.2, 24.4, 22.3, 14.1; HRMS (ESI) $m/z$ calcd for $C_{25}H_{30}N$ $[M + H]^+$ 344.2378, found 344.2376.

*1-Benzyl-2-propyl-3b,4,5,6,6a,7-hexahydro-1H-pentalenofuran-[2,1b]pyrrole (**2j**):* yield 81%; yellow oil; IR (neat) 2956, 2846, 1454, 923 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.32−7.22 (m, 3H), 6.96 (d, $J$ = 6.8 Hz, 2H), 5.72 (s, 1H), 4.91 (s, 2H), 3.95−3.90 (m, 2H), 3.72 (dd, $J$ = 4.0, 8.6 Hz, 1H), 3.66−3.61 (m, 1H), 3.49 (dd, $J$ = 5.6, 8.6 Hz, 1H), 3.37−3.29 (m, 1H), 2.76 (dd, $J$ = 8.6, 15.0 Hz, 1H), 2.40 (t, $J$ = 7.6 Hz, 2H), 2.34 (d, $J$ = 15.0 Hz, 1H), 1.55 (sext, $J$ = 7.6 Hz, 2H), 0.92 (t, $J$ = 7.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.5, 137.5, 135.4, 128.7, 127.2, 126.2, 126.0, 100.0, 75.1, 74.0, 48.5, 48.3, 45.0, 30.2, 29.2, 22.3, 14.0; HRMS (ESI) $m/z$ calcd for $C_{19}H_{24}NO$ $[M + H]^+$ 282.1858, found 282.1857.

*1-Benzyl-2-propyl-3b,4,5,6,6a,7-hexahydro-1H-pentaleno[2,1b]pyrrole (**2k**):* yield 80%; yellow oil; IR (neat) 2938, 2859, 1497, 1451, 1391, 1354 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.31−7.21 (m, 3H), 6.94 (d, $J$ = 7.6 Hz, 2H), 5.69 (s, 1H), 4.90 (s, 2H), 3.42−3.36 (m, 1H), 3.19−3.11 (m, 1H), 2.81 (dd, $J$ = 8.4, 14.6 Hz, 1H), 2.39 (t, $J$ = 7.6 Hz, 2H), 2.19 (d, $J$ = 14.6 Hz, 1H), 1.83−1.71 (m, 2H), 1.61−1.34 (m, 5H), 1.41−1.34 (m, 1H), 0.91 (t, $J$ = 7.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.9, 136.8, 135.6, 128.6, 128.4, 127.0, 126.1, 99.9, 48.2, 47.8, 43.8, 35.4, 33.5, 32.7, 29.2, 26.3, 22.3, 14.1; HRMS (ESI) $m/z$ calcd for $C_{20}H_{26}N$ $[M + H]^+$ 280.2065, found 280.2065.

*1-Benzyl-2-propyl-1,3b,4,5,6,7,7a,8-octahydroindeno[2,1b]pyrrole (**2l**):* yield 62%; yellow oil; IR (neat) 2922, 2848, 1496, 1452, 1390, 1354 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.31−7.21 (m, 3H), 6.95 (d, $J$ = 7.6 Hz, 2H), 5.74 (s, 1H), 4.94 (s, 2H), 2.87 (q, $J$ = 6.4 Hz, 1H), 2.70 (sext, $J$ = 6.4 Hz, 1H), 2.49 (dd, $J$ = 7.2, 14.0 Hz, 1H), 2.40 (t, $J$ = 7.6 Hz, 2H), 2.25 (dd, $J$ = 6.4, 14.0 Hz, 1H), 1.82−1.71 (m, 1H), 1.61−1.26 (m, 9H), 0.92 (t, $J$ = 7.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.0, 136.1, 135.1, 129.3, 128.6, 127.0, 126.1, 99.9, 48.3, 43.3, 38.8, 30.3, 30.1, 29.1, 28.8, 23.2,

23.1, 22.3, 14.1; HRMS (ESI) $m/z$ calcd for $C_{21}H_{28}N$ $[M + H]^+$ 294.2222, found 294.2224.

*1-Benzyl-2-propyl-4,5,6,7-tetrahydro-1H-indole* (**2m**): yield 91%; yellow oil; IR (neat) 2928, 2854, 1605, 1597, 1496, 1428, 1372 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.28 (t, $J$ = 7.6 Hz, 2H), 7.21 (t, $J$ = 7.6 Hz, 1H), 6.90 (d, $J$ = 7.6 Hz, 2H), 5.76 (s, 1H), 4.95 (s, 2H), 2.52 (t, $J$ = 6.0 Hz, 2H), 2.40 (t, $J$ = 7.6 Hz, 2H), 2.38 (t, $J$ = 7.6 Hz, 2H), 1.80−1.69 (m, 4H), 1.56 (sext, $J$ = 7.6 Hz, 2H), 0.92 (t, $J$ = 7.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 139.0, 131.9, 128.5, 126.9, 126.8, 125.7, 116.2, 103.9, 46.2, 28.5, 23.8, 23.4, 23.1, 22.2, 21.9, 14.1; HRMS (ESI) $m/z$ calcd for $C_{18}H_{23}NNa$ $[M + Na]^+$ 276.1728, found 276.1724.

*1-Benzyl-2-[3-(tert-butyldiphenylsilyloxy)propyl]-4,5,6,7-tetrahydro-1H-indole* (**2n**): yield 84%; yellow oil; IR (neat) 2928, 1605, 1589, 1516, 1496, 1471, 1454, 1440, 1428, 1411, 1357 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.65−7.56 (4H, m), 7.41−7.39 (2H, m), 7.38−7.31 (4H, m), 7.27−7.18 (3H, m), 6.88 (2H, d, $J$ = 7.2 Hz), 5.72 (1H, s), 4.93 (2H, s), 3.68 (2H, t, $J$ = 6.0 Hz), 2.55−2.49 (4H, m), 2.39 (2H, t, $J$ = 6.0 Hz), 1.84−1.70 (6H, m), 1.00 (9H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 138.8, 135.5, 134.0, 131.5, 129.4, 128.6, 127.5, 127.1, 126.8, 125.7, 116.2, 103.9, 63.4, 46.2, 31.9, 26.8, 23.8, 23.4, 23.1, 22.7, 21.9, 19.1; HRMS (ESI) $m/z$ calcd for $C_{34}H_{41}NNaOSi$ $[M + Na]^+$ 530.2855, found 530.2851.

## ■ ASSOCIATED CONTENT

**Supporting Information.** $^1H$ and $^{13}C$ NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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