Silylcarbocyclizations of 1,6-Diynes

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Abstract: Two types of silylcarbocyclization reactions (SiCaCs) of 1,6-diynes are discussed: (i) silylcarbocyclization−hydrosilylation (SiCaC−HS) reactions giving 3-(silylmethylene)-4-(silylmethyl)pyrrolidine, 3-(silylmethylene)-4-(silylmethyl)tetrahydrofuran, 3,4-bis(silylmethyl)-3-pyrroline, and 1,2-bis(silylmethyl)-4,4-dicarbethoxycyclopentene; and (ii) silylcarbobicyclization (SiCaB) reactions yielding a variety of carbocyclic and heterocyclic bicyclo[3.3.0] systems. Mechanisms for these SiCaC−HS and SiCaB processes are proposed.

Introduction

Transition-metal-catalyzed carbocyclization of alkenes and alkynes serves as an important and efficient reaction for the syntheses of a variety of carbocyclic and heterocyclic compounds.[1] We have been exploring the scope of the silicon-initiated carbometalation processes such as silylformylations,[2−7] silylcyclocarbonylation (SiCCa),[8] and silylcarbocyclizations (SiCaCs).[9−12] In the course of our study on the SiCaC reaction of 1,6-diynes, we discovered a novel catalytic synthesis of bicyclo[3.3.0]octenones through silylcarbobicyclization (SiCaB) reaction.[11a] We also found the SiCaB reaction of 1,6-heptadiynes yielding bicyclo[3.3.0]octa-1,5-dien-3-ones bearing a rare cyclopentanoid skeleton.[13] Although transition-metal-mediated or -catalyzed carbocyclizations of dienes and enynes have been extensively studied, only a few metal systems using palladium or nickel complexes can catalytically afford *exo*-methylenecyclopentanes, bis(*exo*-methylenecyclopentane)s, and related compounds.[1] We describe here a novel silylcarbocyclization−hydrosilylation (SiCaC−HS) reaction of 1,6-diynes as well as a full account of the SiCaB reaction of 1,6-diynes giving carbo- and heterobicyclo[3.3.0]octenone systems catalyzed by Rh and Rh−Co complexes. The products of these reactions serve as useful intermediates for cyclopentanoids, oxygen and nitrogen heterocycles, and alkaloids.

Results and Discussion

Silylcarbocyclization−Hydrosilation Reaction. SiCaC−HS reaction of dipropargylamines **1** catalyzed by rhodium complexes under ambient pressure of carbon monoxide gives 3-(silylmethylene)-4-(silylmethyl)pyrrolidine (**3**) and 3,4-bis(silylmethyl)-3-pyrroline (**4**) in fairly good yields (Scheme 1). Results are summarized in Table 1. The reaction of benzyldipropargylamine (**1a**) with $HSiMe_2Bu^t$ (4 equiv) in the presence of $Rh(acac)(CO)_2$, $Rh_2Co_2(CO)_{12}$, or $(t\text{-BuNC})_4RhCo(CO)_4$ (2 mol %) at 65 °C for 10 h afforded 1-benzyl-3-(TBS-methylene)-4-(TBS-methyl)pyrrolidine (**3a-TBS**) (TBS = *tert*-butyldimethylsilyl) as the major product and 3,4-bis(TBS-methyl)-1-benzyl-3-pyrroline (**4a-1**) as the minor product in 61−67% isolated yield. When $HSiEt_3$ (4 equiv) was used, the reaction of **1a** catalyzed by $Rh_2Co_2(CO)_{12}$ gave **3a-TES** (57%) and **4a-TES** (11%) (TES = triethylsilyl). In a similar manner, the reaction of *n*-hexyldipropargylamine (**1b**) with $HSiEt_3$ catalyzed by $Rh_2Co_2(CO)_{12}$ gave **3b-TES** and **4b-TES** (83:17) in 76% yield. It should be noted that the same reactions under nitrogen atmosphere proceed sluggishly to give the same products in very low yields. This fact indicates that a carbon monoxide atmosphere is crucial to generate active catalyst species in the SiCaC−HS reaction.

The reaction of allyldipropargylamine (**1c**) with $HSiMe_2Bu^t$ (4 equiv) catalyzed by $Rh(acac)(CO)_2$ afforded **3c-TBS** (64%) and **4c-TBS** (12%). Thus, the intramolecular carbometalation takes place exclusively with the alkyne moiety, and the alkene moiety is intact; that is, this is an extremely chemoselective process. The use of $HSiEt_3$ and $Rh_4(CO)_{12}$ as the catalyst gave **3c-TES** as the sole product in 64% yield. This reaction was

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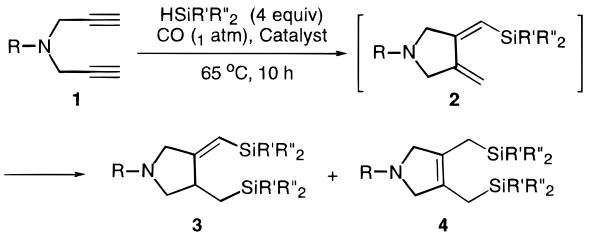
Table 1. SiCaC−HS Reaction of Dipropargylamines (**1**)

entry	substrate	R	catalyst	R′	R″	yield (%)	product ratio **3**:**4**
1	**1a**	$PhCH_2$	$Rh(acac)(CO)_2$	t-Bu	Me	64	76:24
2	**1a**	$PhCH_2$	$Rh_2Co_2(CO)_{12}$	t-Bu	Me	61	72:28
3	**1a**	$PhCH_2$	$(^tBuNC)_4RhCo(CO)_4$	t-Bu	Me	67	79:21
4	**1a**	$PhCH_2$	$Rh_2Co_2(CO)_{12}$	Et	Et	68	84:16
5	**1b**	*n*-C_6H_{13}	$Rh(acac)(CO)_2$	Et	Et	76	83:16
6	**1b**	*n*-C_6H_{13}	$Rh(acac)(CO)_2$	t-Bu	Me	60	0:100
7	**1c**	allyl	$Rh(acac)(CO)_2$	t-Bu	Me	21	100:0
8	**1c**	allyl	$Rh_4(CO)_{12}$	Et	Et	74	0:100

Scheme 1



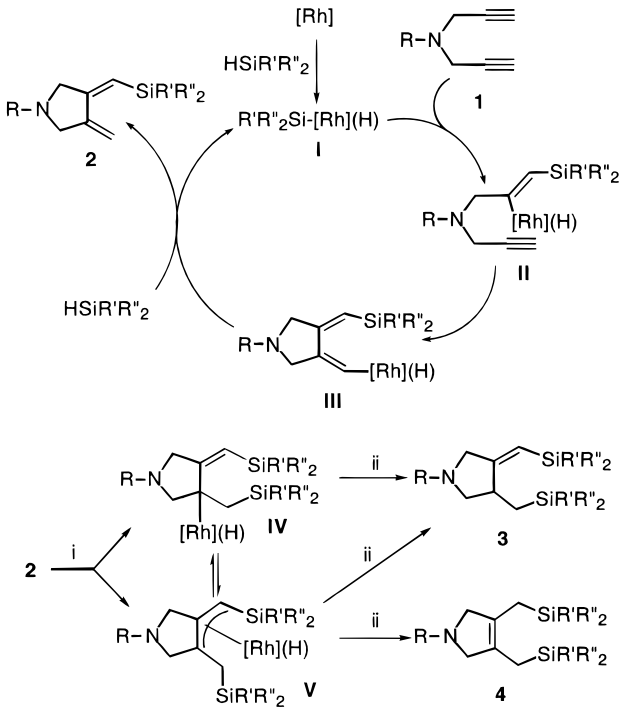
R: (a) $PhCH_2$, (b) *n*-hexyl, (c) allyl
Catalyst: $Rh(acac)(CO)_2$, $Rh_2Co_2(CO)_{12}$, $(^tBuNC)_4RhCo(CO)_4$, $Rh_4(CO)_{12}$

communicated by us earlier.[9] However, the careful reinvestigation of the structural assignment of the product revealed that the correct structure of the product should have been **3c-TES** as shown in Scheme 1.[14]

The proposed mechanism of the SiCaC−HS reaction is illustrated in Scheme 2. Oxidative addition of a hydrosilane to the rhodium catalyst species formed a silylrhodium species, R′R″$_2$Si-[Rh] (**I**). The insertion of an acetylene moiety of **1** gives a *β*-silylvinyl-[Rh] species (**II**), which undergoes intramolecular carbometalation, that is, carbocyclization, to the other acetylene moiety, yielding a pyrrolidine-*exo*-1,3-dienyl-[Rh] species (**III**). Reductive elimination of **III** regenerates the silyl-[Rh] species (**I**) and affords 3-(silylmethylene)-4-methylene-pyrrolidine (**2**). The subsequent regioselective 1,2-hydrosilylation of **2** affords **3**, while the regioselective 1,4-hydrosilylation gives **4**.

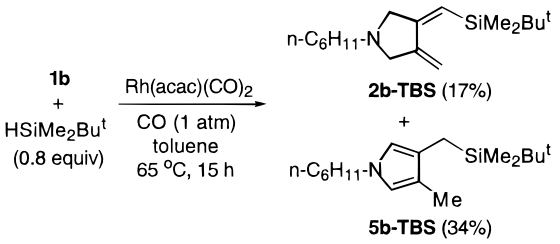
A proposed intermediate **2** was indeed isolated in an experiment using <1 equiv of a hydrosilaneto **1** otherwise under the standard conditions; that is, the reaction of **1b** with $HSiMe_2Bu^t$ (0.8 equiv) catalyzed by $Rh(acac)(CO)_2$ afforded **2b-TBS** (17% isolated yield) and its aromatized isomer **5b-TBS** (34% isolated yield) (Scheme 3). The stereochemistry of the *exo*-silylmethylene moiety of **2b-TBS** was elucidated on the basis of 1D difference NOE as well as 2D NOESY. Under the standard reaction conditions using 4 equiv of hydrosilane, the formation of pyrrole **5b-TBS** was never observed. Thus, the formation of **5b-TBS** can be ascribed to the isomerization of the two *exo*-methylenes to the energetically favorable pyrrole under the given reaction conditions. This isomerization process is completely blocked by the hydrosilylation under the standard

Scheme 2

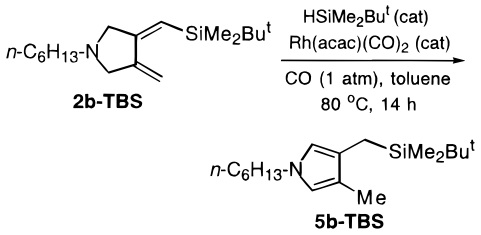


[Rh] = Rh_n or RhCo
i) R'R"$_2$Si-[Rh](H); ii) HSiR'R"$_2$ and – R'R"$_2$Si-[Rh](H)

Scheme 3



Scheme 4



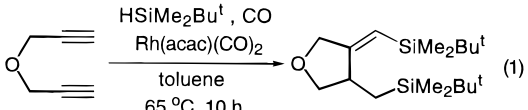
conditions, that is, in the presence of excess hydrosilane. In fact, when **2b-TBS** was treated with catalytic amounts of $Rh(acac)(CO)_2$ (0.02 equiv) and $HSiMe_2Bu^t$ (0.02 equiv) at 80 °C under carbon monoxide atmosphere, pyrrole **5b-TBS** was formed in quantitative yield (Scheme 4).

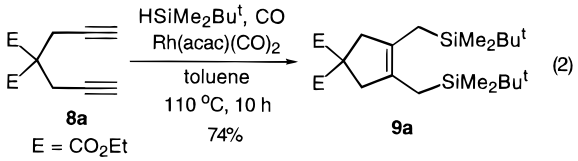
Since we were able to isolate **2b-TBS**, a control experiment was carried out to confirm the intermediacy of **2** in the formation of hydrosilylation product **4b-TBS** (see entry 6 in Table 1). Thus, the reaction of **2b-TBS** with $HSiMe_2Bu^t$ (2 equiv) in the presence of $Rh(acac)(CO)_2$ (2 mol %) in toluene at 65 °C and ambient pressure of CO overnight gave a mixture of **4b-TBS** and 1-*n*-hexyl-3-(TBS-methyl)-4-methylpyrrole (**5b-TBS**) in 34 and 33% isolated yields, respectively. When the reaction was run by premixing $HSiMe_2Bu^t$, $Rh(acac)(CO)_2$, and **1b** in toluene at 65 °C for 3 h, followed by addition of **2b-TBS**, and stirring the mixture for 18 h, **4b-TBS** was isolated as the major product

(14) In ref 9, the structures of product **4c-TES** and **11c-TES** were erroneously assigned to 1-allyl-3-(*Z*-triethylsilylmethylene)-5-(2-triethylsilylethyl)piperidin-4-one and 7-allyl-2-(triethylsilyl)-7-azabicyclo[3.3.1]non-1-ene-3,9-dione, respectively. These misassignments were caused by unfortunate mistakes at the M-H-W Laboratories for the elemental analyses of these two compounds. The erroneous elemental analyses data clearly supported the inclusion of carbon monoxide in these molecules, which played an essential role in the assignments of these incorrect structures. Unfortunately, ^1H NMR data were consistent with the incorrect structures and ^{13}C NMR data appeared to be consistent as well because of the unusually large chemical shift of C-1.

(54% isolated yield) together with **5b-TBS** (17% isolated yield) (Scheme 5). Accordingly, the intermediary of **2** in the SiCaC−HS process is unambiguously established.

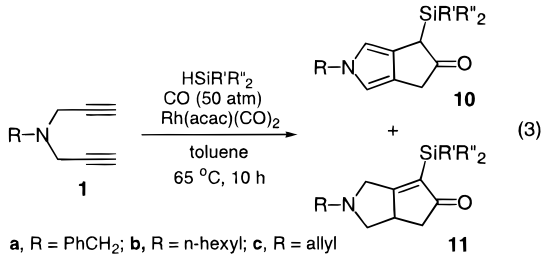
The SiCaC−HS reaction of dipropargyl ether (**6**) with $HSiMe_2Bu^t$ (4 equiv) catalyzed by $Rh(acac)(CO)_2$ under the standard conditions gave 3-(TBS-methylene)-4-(TBS-methyl)-tetrahydrofuran (**7**) exclusively, but in low yield (eq 1). The observed low yield can be ascribed to a rather facile O−C bond cleavage in a propargyl ether under the reaction conditions. On the other hand, the reaction of diethyl dipropargylmalonate (**8a**) at 110 °C afforded 1,2-bis(silylmethyl)-4,4-dicarbethoxycyclopent-1-ene (**9a**) as the sole product in good yield (eq 2).





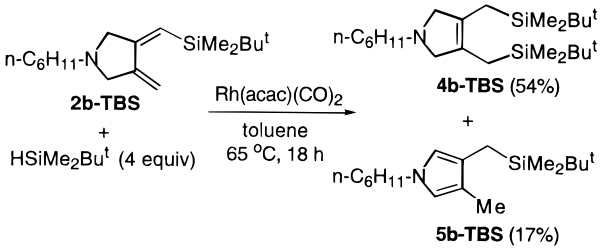
These results indicate that the C-4 position of the 1,6-diynes exerts marked influence on the product distribution; that is, the 1,2-hydrosilylation is favored with substrates with heteroatoms at the C-4 position, whereas 1,4-hydrosilylation is favored with 4,4-*gem*-disubstitution with ester groups.

Silylcarbobicyclization Reaction. As described above, under ambient carbon monoxide pressure, SiCaC reaction of a 1,6-diyne readily occurs without carbonylation, followed by hydride shift to form a bis(ex*o*-methylene)hetero- or carbocycle such as **2** as the intermediate. The subsequent regioselective 1,2- and/or 1,4-hydrosilylation of this intermediate gives SiCaC−HF products, **3**, **4**, **7**, and **9**. Under high pressure of carbon monoxide (15−50 atm), however, carbonylative carbocyclization takes place to afford bicyclo[3.3.0]octenones in excellent yields. Thus, benzyldipropargylamine (**1a**) underwent silylcarbo*bi*cylization (SiCaB) with $HSiEt_3$ (1.6 equiv) in the presence of a catalytic amount of $Rh(acac)(CO)_2$ at 65 °C and 50 atm of CO for 10 h to give a mixture of 2-TES-7-benzyl-7-azabicyclo[3.3.0]octa-5,8-dien-3-one (**10a-TES**) as the major product and 2-TES-7-benzyl-7-azabicyclo[3.3.0]oct-1-en-3-one (**11a-TES**) as the minor product (**10a-TES**/**11a-TES** = 97:3) in 66% isolated yield (eq 3).



In a similar manner, the reaction of **1a** with $HSiEt_3$ catalyzed by $(^tBuNC)_4RhCo(CO)_4$ afforded **10a-TES** (57%) and **11a-TES** (10%) and the reaction of **1a** with $HSiMe_2Bu^t$ catalyzed by $Rh(acac)(CO)_2$ afforded 2-TBS-7-benzyl-7-azabicyclo[3.3.0]-octa-5,8-dien-3-one (**10a-TBS**) (70%) and 2-TBS-7-benzyl-7-azabicyclo[3.3.0]oct-1-en-3-one (**11a-TBS**) (18%). The reaction of **1c** with $HSiMe_2Bu^t$ also gave 2-TBS-7-allyl-7-azabicyclo-

Scheme 5

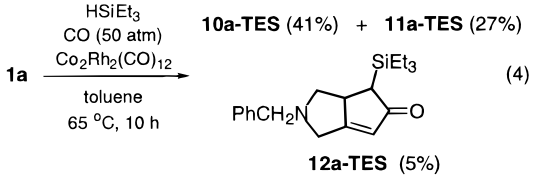


[3.3.0]octa-5,8-dien-3-one (**10c-TBS**) (56%) and 2-TBS-7-allyl-7-azabicyclo[3.3.0]oct-1-en-3-one (**11c-TBS**) (22%). It should be noted that the allyl moiety of **1c** remained intact, which indicates extremely high chemoselectivity of this reaction.

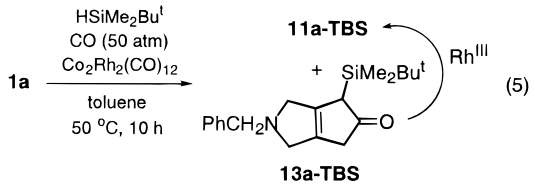
However, the reaction of dipropargyl-*n*-hexylamine (**1b**) catalyzed by $Rh(acac)(CO)_2$ under the same conditions gave 7-azabicyclo[3.3.0]octa-5,8-dien-3-one (**10b-TES**) exclusively in 58% isolated yield (eq 3). In a similar manner, the reaction of **1c** with $HSiEt_3$ catalyzed by $(^tBuNC)_4RhCo(CO)_4$ afforded **11c-TES** as the sole product in 62% isolated yield. This reaction was communicated by us earlier.[9] However, careful reinvestigation of the structural assignment of the product revealed that the correct structure of the product should have been **11c-TES** as shown in eq 3.[14]

We have reported that a mixture of **10a-TBS** (67%) and **11a-TBS** (11%) was obtained when this reaction was carried out at 120 °C.[13] Accordingly, it is strongly indicated that (i) **2a-TBS** is the precursor of bicyclic pyrrole **10a-TBS** and (ii) the double-bond isomerization takes place because of the energy gain due to aromatization.

When the reaction of **1a** with $HSiEt_3$ was carried out using $Rh_2Co_2(CO)_{12}$ as the catalyst under the same conditions, the formation of a small amount of 4-TES-7-benzyl-7-azabicyclo-[3.3.0]oct-1-en-3-one (**12a-TES**) was observed in addition to **10a-TES** and **11a-TES** (eq 4).



Reaction temperature has a certain influence on the course of the reaction as well. When the reaction of **1a** with $HSiMe_2Bu^t$ was catalyzed by $Rh_2Co_2(CO)_{12}$ or $(^tBuNC)_4RhCo(CO)_4$ at 50 °C instead of 65 °C, a small amount of 2-TBS-7-benzyl-7-azabicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**13a-TBS**) was formed in addition to **11a-TBS** (60% isolated yield) (eq 5).



The $\Delta^{1,5}$-isomer **13a-TBS** can be easily isomerized to the thermodynamically more favorable **11a-TBS**. Thus, the treatment of the mixture of **11a-TBS** and **13a-TBS** with $RhCl_3 \cdot 3H_2O$ in EtOH at 50 °C gave **11a-TBS** as the sole product in 70% isolated yield (eq 5).

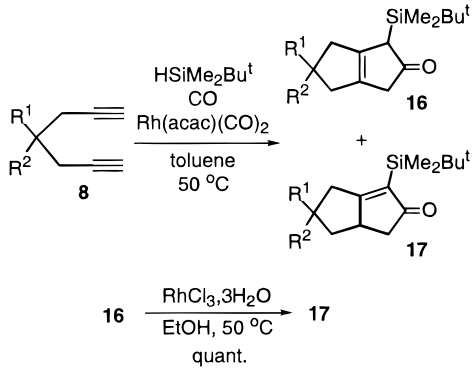
In a manner similar to the reaction of **1a** (eq 5), the reaction of dipropargyl ether (**6**) with $HSiMe_2Bu^t$ (1.6 equiv) catalyzed

Table 2. SiCaB Reaction of 1,6-Heptadines (**8**)

entry	substrate	R^1	R^2	temp (°C)	CO (atm)	time (h)	yield[a] (%)	product **16**	ratio **17**
1	**8a**	CO_2Et	CO_2Et	50	15	12	92 (98)	100	0
2	**8b**	CO_2Et	Me	50	50	20	70	100	0
3	**8c**	CO_2Et	H	50	50	12	65	74	24
4	**8d**	$AcOCH_2$	H	120	50	20	73	100	0

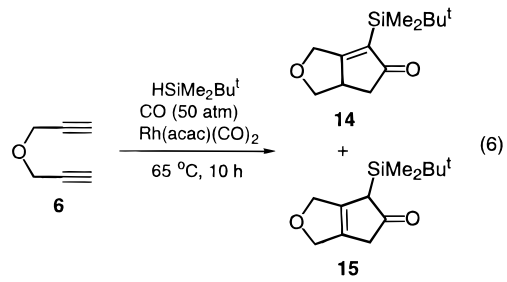
[a] The value in the parentheses is determined by GC analysis.

Scheme 6



(a) R^1, R^2 = CO_2Et; (b) R^1 = CO_2Et, R^2 = Me; (c) R^1 = CO_2Et, R^2 = H; (d) R^1 = $AcOCH_2$, R^2 = H

by $Rh(acac)(CO)_2$ under the standard conditions gave 2-TBS-7-oxabicyclo[3.3.0]oct-1-en-3-one (**14**) (22%) and 2-TBS-7-oxabicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**15**) (27%) (eq 6).

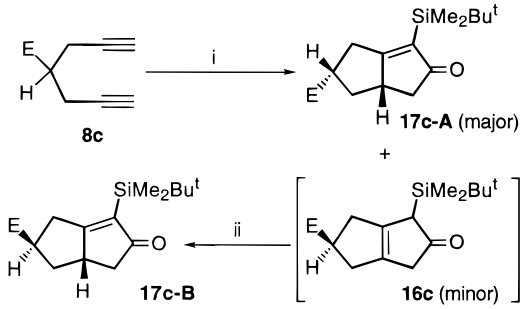


No formation of a bicyclic furan, which is equivalent to **10**, was observed at all. As mentioned for the SiCaC−HS reaction of **6**, the lower yield in this reaction can be ascribed to a rather facile C−O bond fission of **6** under the reaction conditions.

Next, the SiCaB reactions of 1,6-heptadienes **8** were investigated. The results are summarized in Table 2. In contrast to the cases of dipropargylamines **1** and dipropargyl ether (**6**), the reaction of diethyl dipropargylmalonate (**8a**) with $HSiMe_2Bu^t$ (2 equiv) catalyzed by $Rh_2Co_2(CO)_{12}$ or $Rh(acac)(CO)_2$ at 50 °C and 15 atm of CO for 12 h gave 2-TBS-7,7-dicarbethoxybicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**16a**) (Scheme 6) exclusively in 92% isolated yield (98% GC yield) (Table 2, entry 1).[15] The reaction under 50 atm of CO gave the same result. In a manner similar to the case of **13a-TBS** (eq 5), **16a** thus formed was readily isomerized to 2-TBS-7,7-dicarbethoxybicyclo[3.3.0]oct-1-en-3-one (**17a**) in quantitative yield in the presence of a catalytic amount of $RhCl_3 \cdot H_2O$ in EtOH at 50 °C for 24 h.

Bicyclo[3.3.0]octenones, very useful intermediates for a variety of biologically active cyclopentanoids, can be obtained through $Co_2(CO)_8$-promoted Pauson−Khand reaction[16−20] and

Scheme 7



i. $HSiMe_2Bu^t$, CO (50 atm), $Rh(acac)(CO)_2$, 50 °C, toluene
ii. $RhCl_3.3H_2O$, 50 °C, toluene-EtOH

via zirconocene-[21] or titanocene-mediated carbobicyclization−carbonylation of enynes.[22] However, these processes are basically stoichiometric, and only recently was a catalytic version of Pauson−Khand reaction developed.[23] Catalytic titanocene-promoted carbobicyclization−carbonylation of enynes was reported.[24a,24b] Although an isocyanide was needed as a carbonyl synthon (hydrolysis is required to obtain ketone functionality) in the original process, new processes using CO were recently develped.[24c,24d] Nickel(0)-promoted stoichiometric carbobicyclization−carbonylation also requires isocyanides as a carbonyl synthon.[1c] An efficient Pd-catalyzed carbonylative bicyclization of enynes bearing allylic acetate moieties has also been reported.[25] The SiCaB reaction provides bicyclo[3.3.0]-octenones from 1,6-diynes (not 1,6-enynes) in truly catalytic manner. In this respect, SiCaB is a very unique carbonylative bicyclization process having a high potential as a useful synthetic method that may well complement other existing methods.

It was found that $(^tBuNC)_4RhCo(CO)_4$ and $[Rh(CO)_2Cl]_2$ are active but $RhCl(PPh_3)_3$, $Rh_2(OAc)_4$, $Ru_3(CO)_{12}$, and $PdCl_2(PPh_3)_2$ were inactive for this reaction. The relative activities of rhodium complexes were found to be $Rh_2Co_2(CO)_{12} \sim Rh(acac)(CO)_2 > Rh(CN-Bu^t)_4Co(CO)_4 \gg [Rh(CO)_2Cl]_2$. For the reaction medium, toluene, ether, hexane, acetonitrile, and dioxane can be used, but the reactions in THF and CH_2Cl_2 did not show any conversion under the standard conditions at 12 h reaction period, that is, at 50 °C and 50 atm of CO, using $Rh(acac)(CO)_2$ as the catalyst.

In a similar manner, the reaction of **8b** gave 2-TBS-7-carbethoxy-7-methylbicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**16b**) in 70% isolated yield as a 1:1 mixture of two diastereomers (Table 2, entry 2), which was quantitatively isomerized to the corresponding bicyclo[3.3.0]oct-1-en-3-one **17b** in the presence of a catalytic amount of $RhCl_3 \cdot 3H_2O$.

The reaction of 4-carbethoxy-1,6-heptadiyne (**8c**) gave a mixture of 2-TBS-7-*exo*-carbethoxybicyclo[3.3.0]oct-1-en-3-one

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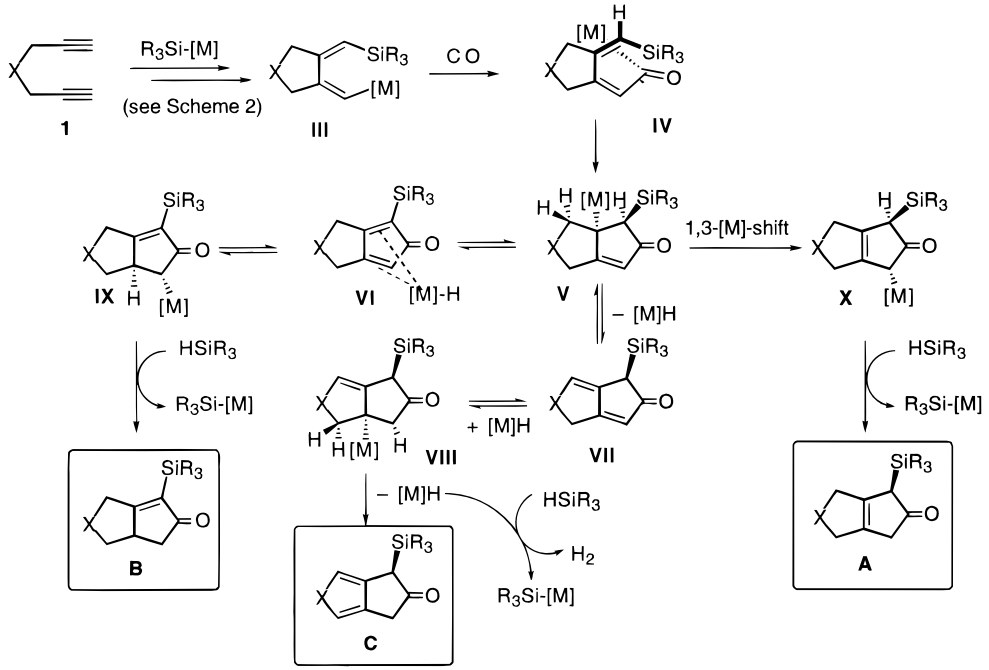
Scheme 8



(**17c-A**) (48% isolated yield) as single stereoisomer and its $\Delta^{1,5}$-isomer **16c** (17% isolated yield) (Table 2, entry 3) (Scheme 7). The isomerization of **16c** by the catalysis of $RhCl_3 \cdot 3H_2O$ gave the corresponding 7-*endo*-carbethoxybicyclo[3.3.0]oct-1-en-3-one **17c-B** as single stereoisomer in quantitative yield, which is the other diastereomer of **17c-A** (Scheme 6). The results clearly indicate that the SiCaB reaction yielding **17c-A** is stereospecific and the isomerization of **16c** to **17c-B** is extremely stereoselective.

The stereochemistries of **17c-A** and **17c-B** were unambiguously determined by ^{1}H NMR analyses on coupling constants and molecular modeling (MACROMODEL). According to MM2 calculations, **17c**−**B** is ∼3.3 kcal/mol more stable than **17c**−**A**, which means **17c**−**A** should be the kinetic product. However, when the crude reaction mixture of **17c**−**A** and **16c** was subjected to the isomerization conditions, the *endo*-isomer **17c**−**A** remained unchanged; that is, only **16c** was converted to **17c**−**B**. Thus, the isomerization of **17c**−**A** to **17c**−**B** was not observed. A possible stereoselective formation of **17c**−**A** or **17c**−**B** warrants further investigation.

The reaction of 4-(acetoxymethyl)-1,6-heptadiyne (**8d**) at 120 °C gave a 1:1 mixture of 7-*exo*- and 7-*endo*-2-TBS-7-(acetoxymethyl)bicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**25**) in 73% isolated yield (Table 2, entry 4). It should be noted that 7,7-disubstituted 2-silylbicyclo[3.3.0]octa-1,5-dien-3-ones are usually formed under these conditions when using 4,4-disubstituted 1,6-heptadienes, whereas the reaction of **8d** does not give any trace of the corresponding bicyclo[3.3.0]octa-1,5-dien-3-one. As described above, the nature of the functional group(s) at the C-4 position of 1,6-diynes exerts marked effects on the product selectivity in the SiCaB reaction. Thus, further study on the effects of the C-4 functional group(s) on the course of the reaction is clearly warranted.

A mechanism for the formation of the three kinds of bicyclo-[3.3.0] systems is proposed in Scheme 8. The intermediate **III** is formed through extremely regioselective insertion of one of the acetylene moiety of **1** to R_3Si-[M] species ([M] = [Rh_n(H)] or [RhCo(H)]) followed by carbocyclization in the same manner as that shown in Scheme 2. The subsequent carbon monoxide insertion to **III** gives acyl-[M] complex intermediate **IV**, and the carbocyclization of **IV** yields bicyclic intermediate **V**. The β-hydride elimination of **V** affords bicyclic diene-[M]H complex **VI** and/or bicyclic diene **VII**. The regioselective addition of [M]H species to the olefin moiety of **VI** in the less hindered side gives intermediate **IX**, whereas the addition of [M]H species to **VII** affords intermediate **VIII**. These β-hydride eliminations and additions of [M]H species are potentially reversible processes; that is, **IX, VI**, **V**, **VII**, and **VIII** can be in equilibrium. The reductive elimination of the R_3Si-[M] species from **IX** by the action of another molecule of the hydrosilane affords product **B**. The β-hydride elimination of **VIII** gives product **C**. This process is observed only when X is nitrogen, that is, X = R−N, forming a pyrrole, which provides a stable heteroaromatic ring system. However, it appears that energy gain by forming a furan is not large enough to promote this type of β-elimination. On the other hand, **V** is converted to **X** through the 1,3-[M] shift, and the subsequent reductive elimination affords product **A**.

Further study on the applications of the SiCaC−HS and SiCaB reactions to organic syntheses is actively underway.

Experimental Section

General Method. The ^{1}H NMR, ^{13}C NMR, COSY, NOSY, and HETCOR NMR spectra were recorded on a Bruker AC-250 or Gemini 2300 and referenced to $CDCl_3$ as the internal standard. The IR spectra were measured with a Perkin-Elmer 1600 FT-IR spectrophotometer with a Hewlett-Packard 7470A plotter using samples as neat oils or as KBr disks. High-resolution mass spectra were performed by the Mass Spectrometry Facility at University of California at Riverside. Analytical gas chromatography was performed with a Hewlett-Packard 5890 Series II gas chromatograph (FID) with a Hewlett-Packard HP 3396A

integrator using either a 15 m J&W DB-1, a 30 m J&W DB-17, or a 25 m 3% OV-101 capillary column. Elemental analyses were performed at M-H-W Laboratories, Phoenix, AZ.

Materials. All solvents were reagent grade and distilled before use. Rhodium−cobalt mixed-metal complexes $Rh_2Co_2(CO)_{12}$, $(^tBuNC)_4RhCo(CO)_4$, and $Rh_4(CO)_{12}$ were prepared according to literature methods.[26,27] Acetylacetonatorhodium dicarbonyl, $Rh(acac)(CO)_2$, was obtained from the Mitsubishi Kasei Corp. and used as received. Hydrosilanes were purchased from Aldrich Chemical Co., distilled under nitrogen, and stored over activated molecular sieves 4 Å. Silica gel used for chromatography, MN-Kieselgel 60, was purchased from Brinkman Instruments Inc. 1,6-Diynes were prepared by literature methods.[28−32] 4-Acetoxymethylhepta-1,6-diyne was prepared through the reduction of 4-carbethoxyhepta-1,6-diyne[29] with $LiAlH_4$ in ether, followed by acetylation with acetic anhydride in the presence of pyridine.

General Procedure for the Silylcarbocyclization−Hydrosilylation of 1,6-Diynes. A typical procedure is described for the reaction of benzyldipropargylamine (**1a**). To a 25 mL Pyrex round-bottom flask containing $(^tBuNC)_4RhCo(CO)_4$ (11.6 mg, 0.02 mmol) and a magnetic stir bar in toluene (15 mL) was added $HSiMe_2Bu^t$ (464 mg, 4.0 mmol) via a syringe under carbon monoxide atmosphere. A solution of benzyldipropargylamine (**1a**) (464 mg, 1.0 mmol) in 5 mL of toluene was added, and the reaction mixture was allowed to stir at 65 °C under ambient pressure of carbon monoxide for 8−10 h. The crude product was obtained after evaporation of the solvent under reduced pressure, and the mixture was submitted to GC and TLC analysis. The product was purified by flash chromatography on silica gel with mixture solvent of hexane/EtOAc to give **3a** (220 mg, 53% yield) and **4a** (58 mg, 14% yield).

1-Benzyl-3-(*tert*-butyldimethylsilylmethylene)-4-(*tert*-butyldimethylsilylmethyl)pyrrolidine (3a-TBS): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.07−0.05 (m, 12 H), 0.55 (dd, J = 14.7, 10.9 Hz, 1 H), 0.90−0.87 (br s, 18 H), 2.00 (t, J = 8.7 Hz, 1 H), 2.70 (m, 1 H), 3.02 (m, 2 H), 3.36 (br s, 1 H), 3.74−3.52 (m, 3 H), 5.33 (d, J = 2.0 Hz, 1 H), 7.33−7.25 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −5.9, −4.8, 16.1, 16.7, 17.3, 26.5, 26.6, 42.3, 59.2, 60.8, 61.9, 113.5, 127.0, 128.2, 128.6, 138.7, 165.3; IR (neat) 1630 cm^{-1}; HRMS (CI) calcd for $C_{25}H_{46}NSi_2$ (MH^+) 416.3168, found 416.3186 (Δ = −4.1 ppm).

1-Benzyl-3-(triethylsilylmethylene)-4-(triethylsilylmethyl)pyrrolidine (3a-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.53 (m, 14 H), 0.90 (m, 18 H), 1.99 (t, J = 8.8 Hz, 1 H), 2.64 (m, 1 H), 2.94 (d, J = 14.1 Hz, 1 H), 3.02 (t, J = 9.0 Hz, 1 H), 3.50 (d, J = 14.3 Hz, 1 H), 3.55 (d, J = 12.9 Hz, 1 H), 3.68 (d, J = 12.8, 1 H), 5.26 (d, J = 2.1 Hz, 1 H), 7.34−7.26 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 3.9, 4.1, 7.4, 7.5, 15.2, 42.0, 59.2, 60.8, 61.8, 112.7, 126.9, 128.2, 128.8, 138.7, 165.5; IR (neat) 1630 cm^{-1}; HRMS (CI) calcd for $C_{25}H_{46}NSi_2$ (MH^+) 416.3168, found 416.3155 (Δ = +3.3 ppm). Anal. Calcd for $C_{25}H_{45}NSi_2$: C, 72.21; H, 10.91; N, 3.37. Found: C, 72.43; H, 10.87; N, 3.37.

1-*n*-Hexyl-3-(triethylsilylmethylene)-4-(triethylsilylmethyl)pyrrolidine (3b-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.44−0.66 (m, 14 H), 0.86−0.98 (m, 23 H), 1.29 (m, 7 H), 2.38−2.51 (m, 2 H), 2.60−2.89 (m, 4 H), 3.08 (t, J = 7.0 Hz, 2 H), 5.26 (d, J = 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 2.3, 3.8, 4.1, 7.5, 14.0, 14.9, 22.5, 22.6, 26.3, 28.6, 31.9, 41.9, 57.1, 59.4, 112.3, 165.4; IR (neat) 1629 cm^{-1}; HRMS (CI) calcd for $C_{24}H_{52}NSi_2$ (MH^+) 410.3638, found 410.3621 (Δ = +4.2 ppm).

1-Allyl-3-(*tert*-butyldimethylsilylmethylene)-4-(*tert*-butyldimethylsilylmethyl)pyrrolidine (3c-TBS): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.02 (m, 12 H), 0.47 (dd, J = 14.8, 11.0 Hz, 1 H), 0.88 (br s, 18 H), 1.89 (t, J = 9.0 Hz, 1 H), 2.63 (m, 1 H), 2.84 (dd, J = 14.4, 2.2 Hz, 1 H), 3.07 (m, 4 H), 3.55 (d, J = 14.4 Hz, 1 H), 5.12 (m, 2 H), 5.30 (s, 1 H), 5.87 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −6.0, −4.9, −4.7, 16.8, 26.4, 26.5, 42.2, 59.5, 61.6, 113.5, 117.0, 135.6, 165.0; IR (neat) 1631 cm^{-1}; HRMS (CI) calcd for $C_{21}H_{44}NSi_2$ (MH^+) 366.3012, found 366.3003 (Δ = +2.5 ppm). Anal. Calcd for $C_{21}H_{43}NSi_2$: C, 68.96; H, 11.85; N, 3.83. Found: C, 68.77; H, 11.70; N, 3.83.

1-Allyl-3-(triethylsilylmethylene)-4-(triethylsilylmethyl)pyrrolidine (3c-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.50 (m, 14 H), 0.84 (m, 18 H), 1.83 (t, J = 9.0 Hz, 1 H), 2.55 (m, 1 H), 2.78 (dd, J = 14.3, 1.6 Hz, 1 H), 3.01 (m, 3 H), 3.47 (d, J = 14.3 Hz, 1 H), 5.03 (dd, J = 10.1, 1.2 Hz, 1 H), 5.12 (dd, J = 12.8, 1.2 Hz, 1 H), 5.18 (d, J = 1.6 Hz, 1 H), 5.83 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 3.8, 4.0, 7.4, 7.5, 15.0, 26.7, 42.0, 59.0, 59.2, 112.7, 117.0, 135.6, 165.2; IR (neat) 1650, 1630 cm^{-1}; HRMS (CI) calcd for $C_{21}H_{44}NSi_2$ (MH^+) 366.3012, found 366.3020 (Δ = −2.1 ppm).

1-Benzyl-3,4-bis(*tert*-butyldimethylsilylmethyl)-3-pyrroline (4a-TBS): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.42 (s, 12 H), 0.88 (s, 18 H), 1.42 (s, 4 H), 3.34 (s, 4 H), 3.75 (s, 2 H), 7.34−7.25 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −5.3, 12.5, 16.7, 26.4, 60.9, 64.8, 126.7, 127.1, 128.2, 128.6, 139.8; IR (neat) 1684 cm^{-1}. Anal. Calcd for $C_{25}H_{45}NSi_2$: C, 72.21; H, 10.91; N, 3.37. Found: C, 72.39; H, 10.86; N, 3.54.

1-Benzyl-3,4-bis(triethylsilylmethyl)-3-pyrroline (4a-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.52 (q, J = 7.7 Hz, 12 H), 0.93 (t, J = 7.7 Hz, 18 H), 1.41 (s, 4 H), 3.34 (s, 4 H), 3.75 (s, 2 H), 7.33−7.25 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 4.8, 13.8, 16.1, 61.3, 65.1, 127.4, 128.2, 128.7, 128.9, 141.2. Anal. Calcd for $C_{25}H_{45}NSi_2$: C, 72.21; H, 10.91; N, 3.37. Found: C, 72.19; H, 10.83; N, 3.21.

3,4-Bis(triethylsilylmethyl)-1-*n*-hexyl-3-pyrroline (4b-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.50 (q, J = 7.5 Hz, 12 H), 0.94 (m, 21 H), 1.27 (br s, 6 H), 1.44 (s, 4 H), 1.60 (m, 2 H), 2.46 (t, J = 7.9 Hz, 2 H), 3.66 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 4.8, 13.8, 16.1, 22.6, 26.5, 27.8, 28.5, 31.6, 43.7, 48.9, 128.5; IR (neat) 1673 cm^{-1}; HRMS (CI) calcd for $C_{24}H_{52}NSi_2$ (MH^+) 410.3638, found 410.3636 (Δ = +0.6 ppm).

1-Allyl-3,4-bis(*tert*-butyldimethylsilylmethyl)-3-pyrroline (4c-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.01 (s, 12 H), 0.87 (s, 18 H), 1.40 (s, 4 H), 3.21 (m, 2 H), 3.32 (s, 4 H), 5.13 (m, 2 H), 5.88 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.3, 12.5, 16.7, 26.4, 59.6, 64.5, 116.5, 126.9, 136.4; IR (neat) 1680 cm^{-1}; HRMS (CI) calcd for $C_{21}H_{44}NSi_2$ (MH^+) 366.3012, found 366.3000 (Δ = +0.6 ppm). Anal. Calcd for $C_{21}H_{43}N_1Si_2$: C, 68.96; H, 11.85; N, 3.83. Found: C, 68.70; H, 11.59; N, 4.00.

Isolation of 1-*n*-Hexyl-3-(*tert*-butyldimethylsilylmethyl)-4-methylenepyrrolidine (2b-TBS) and 1-*n*-Hexyl-3-(*tert*-butyldimethylsilylmethyl)-4-methylpyrrole (5b-TBS). To a 50 mL round-bottom flask equipped with a rubber septum, a stirring bar, and a needle connected to a silicone oil bubbler, containing $Rh(acac)(CO)_2$ (29.2 mg, 0.113 mmol), were added toluene (10 mL) and $HSiMe_2Bu^t$ (522 mg, 4.5 mmol) via syringe. Carbon monoxide was introduced to the mixture and allowed to flush the system for 5 min, and a solution of **1** (0.995 g, 5.62 mmol) in toluene (8 mL) was added to the mixture via syringe. The mixture was then heated at 65 °C with stirring overnight. The reaction mixture was cooled to room temperature, and the solvent and other volatile materials were removed in vacuo. The residue was submitted to column chromatography on silica gel using hexane/EtOAc (16:1) as the eluant to afford **2b-TBS** (286 mg, 17% yield) and **5b-TBS** (563 mg, 34% yield) as yellow oils.

2b-TBS: pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.12 (s, 6 H), 0.89 (br s, 12 H), 1.21−1.27(m, 6 H), 1.48 (m, 2 H), 2.41 (t, J = 7.9 Hz, 2 H), 3.32 (br s, 4 H), 5.04 (s, 1 H), 5.37 (s, 1 H), 5.53 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.6, 14.1, 17.1, 22.6, 26.3, 27.2, 28.2, 31.8, 56.7, 61.4, 64.8, 108.7, 118.9, 144.5, 153.5; IR (neat) 1610 cm^{-1}; HRMS (CI) calcd for $C_{18}H_{36}NSi$ (MH^+) 294.2617, found 294.2618 (MH^+) (Δ = +0.3 ppm). The stereochemistry of **2b-TBS** was unambiguously assigned on the basis of NOESY and 1D difference NOE NMR analyses.

1-*n*-Hexyl-3-(*tert*-butyldimethylsilylmethyl)-4-methylpyrrole (5b-TBS): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.02 (s, 3 H), 0.04 (s, 3 H), 0.87 (br s, 14 H), 1.26 (m, 6 H), 1.71 (m, 2 H), 3.25 (s, 3 H), 3.82 (t, J = 7.0 Hz, 2 H), 6.28 (s, 1 H), 6.40 (s, 1 H); ^{13}C NMR ($CDCl_3$)

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δ −6.6, −6.4, 14.0, 18.0, 22.5, 26.3, 27.0, 31.4, 31.9, 39.6, 44.2, 49.8, 112.6, 113.8, 120.0, 124.8; IR (neat) 1724 cm^{-1}; HRMS (CI) calcd for $C_{18}H_{36}NSi$ (MH^+) 294.2617, found (MH^+) 294.2637 (Δ = −6.8 ppm).

Control Experiment: Hydrosilylation of 1-*n*-Hexyl-3-(*tert*-butyldimethylsilylmethyl)-4-methylenepyrrolidine (2b-TBS). A mixture of $Rh(acac)(CO)_2$ (0.8 mg, 0.003 mmol), $HSiMe_2Bu^t$ (69.6 mg, 0.61 mmol), and **1b** (1.0 mg, 0.004 mmol) in toluene (1 mL) in a 25 mL reaction vessel was flushed with CO and heated at 65 °C for 3 h with stirring under CO. To this mixture was added a solution of bis(*exo*-methylene)pyrrolidine (**2b-TBS**) (45 mg, 0.153 mmol) in toluene (1 mL) via syringe, and the resulting solution was heated at 65 °C for 18 h with stirring. The reaction mixture was cooled to room temperature, and the solvent and other volatile materials were removed in vacuo. The residue was submitted to column chromatography on silica gel using hexane/EtOAc (16:1) as the eluant to afford **4b-TBS** (33.2 mg, 54%) and **5b-TBS** (7.6 mg, 17%) as pale yellow oils.

3-(*tert*-Butyldimethylsilylmethylidene)-4-(*tert*-butyldimethylsilylmethyl)tetrahydrofuran (7): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.03 (s, 6 H), 0.10 (m, 2 H), 0.17 (s, 6 H), 0.97 (s, 18 H), 1.60 (m, 1 H), 4.39−4.67 (m, 4 H), 6.05 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −7.7, −7.6, −4.9, −4.7, 16.9, 19.9, 22.7, 27.7, 28.0, 46.9, 49.9, 122.9, 158.9; IR 1640 cm^{-1}; GC-MS (EI) 326 (M^+).

1,2-Bis(*tert*-butyldimethylsilylmethyl)-4,4-dicarbethoxycyclopent-1-ene (9): pale yellow oil; ^1H NMR ($CDCl_3$) δ −0.53 (s, 12 H), 0.91 (s, 18 H), 1.25 (t, J = 7.1 Hz, 6 H), 1.37 (s, 4 H), 2.82 (s, 4 H), 4.17 (q, J = 7.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 16.6, 26.4, 27.1, 38.9, 45.5, 61.3, 127.0, 173.1; IR (neat) 1732, 1623 cm^{-1}; HRMS (CI) calcd for $C_{25}H_{49}O_4Si_2$ (MH^+) 469.3169, found 469.3177 (Δ = −0.4 ppm).

General Procedure for the Silylcarbobicyclization of 1,6-Diynes. A typical procedure is described for the silylcarbobicyclization of benzyldipropargylamine (**1a**). In a 25 mL Pyrex round-bottom flask containing a magnetic spinning bar and $Rh(acac)(CO)_2$ (5.2 mg, 0.02 mmol) under CO atmosphere was added a solution of $HSiEt_3$ (186 mg, 1.6 mmol) and benzyldipropargylamine (**1a**) (183 mg, 1.0 mmol) in 15 mL of toluene. The reaction vessel was placed in a 300 mL stainless steel autoclave and charged with 10 atm of CO. Carbon monoxide was released slowly, and this process was repeated twice more. The CO pressure was then adjusted to 50 atm. The reaction mixture was stirred magnetically at 65 °C and 50 atm of CO for 10 h. The autoclave was cooled in an ice bath, CO was carefully released, and the reaction mixture was submitted to GC and TLC analyses. After evaporation of the solvent under reduced pressure, the crude product was immediately submitted to flash chromatography on silica gel (hexane/EtOAc) to afford **10a-TES** (208 mg, 64% yield) and **11a-TES** (6.6 mg, 2% yield).

7-Benzyl-2-(triethylsilyl)-7-azabicyclo[3.3.0]octa-5,8-dien-3-one (10a-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.67 (q, J = 7.7 Hz, 6 H), 0.91 (t, J = 7.8 Hz, 9 H), 3.24 (m, 3 H), 5.07 (s, 2 H), 6.34 (s, 1 H), 6.50 (s, 1 H), 7.11−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 2.3, 7.3, 39.7, 43.0, 53.5, 112.8, 114.4, 121.0, 124.3, 126.6, 127.6, 128.7, 220.1; IR (neat) 1725, 1682 cm^{-1}. Anal. Calcd for $C_{20}H_{27}ONSi$: C, 73.79; H, 8.36; N, 4.30. Found: C, 73.59; H, 8.15; N, 4.33.

7-Benzyl-2-(*tert*-butyldimethylsilyl)-7-azabicyclo[3.3.0]octa-5,8-dien-3-one (10a-TBS): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.07 (s, 3 H), 0.90 (s, 9 H), 3.28 (s, 3 H), 5.05 (s, 2 H), 6.40 (s, 1 H), 6.50 (s, 1 H), 7.33−7.10 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −6.3, −6.7, 18.1, 27.0, 39.6, 44.3, 53.5, 113.3, 114.3, 120.8, 126.6, 126.7, 127.6, 128.7, 138.7, 220.0; IR (neat) 1725, 1689 cm^{-1}; HRMS (CI) calcd for $C_{20}H_{28}NOSi$ (MH^+) 326.1940, found 326.1939 (Δ = +0.4 ppm). Anal. Calcd for $C_{20}H_{27}ONSi$: C, 73.79; H, 8.36; N, 4.30. Found: C, 73.83; H, 8.49; N, 4.26.

7-*n*-Hexyl-2-(triethylsilyl)-7-azabicyclo[3.3.0]octa-5,8-dien-3-one (10b-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.64 (q, J = 7.6 Hz, 6 H), 0.85−0.95 (m, 5 H), 1.27 (m, 9 H), 1.67−2.10 (m, 9 H), 3.83 (t, J = 7.0, 2 H), 6.28 (s, 1 H), 6.41 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 2.3, 7.2, 13.9, 13.9, 22.4, 22.5, 26.3, 31.4, 31.9, 39.7, 112.1, 113.5, 120.2, 124.4, 220.7; IR (neat) 1730 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{33}NOSi$ (M^+) 319.2331, found 319.2340 (Δ = −2.3 ppm).

7-Allyl-2-(*tert*-butyldimethylsilyl)-7-azabicyclo[3.3.0]octa-5,8-dien-3-one (10c-TBS): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.02 (s, 3 H), 0.04 (s, 3 H), 0.89 (s, 9 H), 3.24 (bs, 3 H), 4.44 (d, J = 5.5 Hz, 2 H), 5.13 (m, 2 H), 5.94 (m, 1 H), 6.30 (s, 1 H), 6.41 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −6.7, −6.3, 18.0, 27.0, 39.6, 44.2, 52.2, 112.8, 113.8, 116.8, 120.5, 125.3, 134.9, 219.9; IR (neat) 1725, 1683 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{25}NOSi$ (M^+) 275.1705, found 275.1708 (Δ = −0.9 ppm).

7-Benzyl-2-(*tert*-butyldimethylsilyl)-7-azabicyclo[3.3.0]oct-1-en-3-one (11a-TBS): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.00 (s, 3 H), 0.03 (s, 3 H), 0.71 (s, 9 H), 1.83 (dd, J = 10.5, 7.8 Hz, 1 H), 1.94 (dd, J = 17.1, 4.5 Hz, 1 H), 2.40 (dd, J = 17.1, 6.3 Hz, 1 H), 3.02 (d, J = 16.9 Hz, 1 H), 3.05 (m, 1 H), 3.19 (bt, J = 7.2 Hz, 1 H), 3.59 (d, J = 13.1 Hz, 1 H), 3.68 (d, J = 13.0 Hz, 1 H), 3.88 (d, J = 18.2 Hz, 1 H), 7.21−7.12 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −5.7, 17.6, 26.6, 41.4, 47.4, 55.1, 58.0, 60.1, 127.2, 128.4, 128.6, 133.6, 138.2, 195.0, 212.9; IR (neat) 1700, 1611 cm^{-1}. Anal. Calcd for $C_{20}H_{29}ONSi$: C, 73.34; H, 8.93; N, 4.28. Found: C, 73.12; H, 8.76; N, 4.26.

7-Benzyl-2-(triethylsilyl)-7-azabicyclo[3.3.0]oct-1-en-3-one (11a-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.69 (m, 6 H), 0.90 (t, J = 7.6 Hz, 9 H), 1.96 (dd, J = 10.5, 7.9 Hz, 1H), 2.08 (dd, J = 17.1, 4.3 Hz, 1 H), 2.54 (dd, J = 17.1, 6.3 Hz, 1 H), 3.13 (d, J = 18.0 Hz, 1 H), 3.22 (m, 1 H), 3.73 (d, J = 13.1 Hz, 1 H), 3.82 (d, J = 13.0 Hz, 1 H), 4.03 (d, J = 17.9 Hz, 1 H), 7.36−7.26 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 2.7, 7.3, 41.2, 47.5, 54.9, 58.1, 60.1, 127.1, 128.4, 128.5, 133.2, 138.3, 194.9, 213.2; IR (neat) 1740, 1693, 1613 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{29}NOSi$ (M^+) 327.2018, found 327.2011 (Δ = +2.3 ppm).

7-Allyl-2-(*tert*-butyldimethylsilyl)-7-azabicyclo[3.3.0]oct-1-en-3-one (11c-TBS): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.08 (s, 3 H), 0.10 (s, 3 H), 0.87 (s, 9 H), 1.86 (dd, J = 10.8, 8.2 Hz, 1 H), 2.00 (dd, J = 17.1, 6.4 Hz, 1 H), 2.47 (dd, J = 17.1, 6.4 Hz, 1 H), 3.03 (d, J = 18.2 Hz, 1 H), 3.31−3.10 (m, 4 H), 3.95 (d, J = 18.1 Hz, 1 H), 5.11 (m, 2 H), 5.82 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.9, −5.8, 17.4, 26.5, 26.8, 41.3, 47.2, 54.7, 57.7, 58.6, 117.4, 133.5, 134.8, 194.7, 212.6; IR (neat) 1699, 1613 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{27}NOSi$ (M^+): 277.4852: found 277.4853 (Δ = −0.2 ppm).

7-Allyl-2-(triethylsilyl)-7-azabicyclo[3.3.0]oct-1-en-3-one (11c-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.73 (q, J = 7.1 Hz, 6 H), 0.90 (t, J = 7.1 Hz, 9 H), 1.94 (dd, J = 10.9, 8.3 Hz, 1 H), 2.09 (dd, J = 17.2, 4.3 Hz, 1 H), 2.56 (dd, J = 17.1, 6.6 Hz, 1 H), 3.09 (d, J = 18.5 Hz, 1 H), 3.15 (m, 1), 3.20 (dd, J = dd, J = 7.0, 1.2 Hz, 1 H), 3.34 (dd, J = 7.0, 1.2 Hz, 3.66 (dd, J = 8.3, 6.6 Hz, 1 H), 4.05 (d, J = 18.5 Hz, 1 H), 5.17 (dd, J = 10.1, 1.8 Hz, 1 H), 5.25 (dq, J = 16.0, 1.8 Hz, 1 H), 5.90 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 2.7, 7.4, 41.2, 47.2, 54.4, 57.9, 58.7, 118.2, 133.0, 134.4, 194.6, 213.2; IR (neat) 1741, 1698, 1643 cm^{-1}. Anal. Calcd for $C_{16}H_{27}ONSi$: C, 69.26; H, 9.81; N, 5.05. Found: C, 69.50; H, 9.56; N, 4.91.

7-Benzyl-4-(triethylsilyl)-7-azabicyclo[3.3.0]oct-1-en-3-one (12a-TES): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.62 (m, 6 H), 0.92 (t, J = 7.8 Hz, 9 H), 2.27 (dd, J = 11.5, 8.0 Hz, 1 H), 2.50 (d, J = 6.0 Hz, 1 H), 3.07 (d, J = 17.6 Hz, 1 H), 3.25 (bt, J = 7.4 Hz, 1 H), 3.57 (m, 1 H), 3.65 (d, J = 13.1 Hz, 1 H), 3.67 (d, J = 13.3 Hz, 2 H), 5.88 (d, J = 1.6 Hz, 1 H), 7.36−7.26 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 3.8, 7.5, 42.3, 49.3, 53.0, 57.0, 60.1, 124.3, 127.3, 128.5, 128.6, 138.2, 183.2, 211.4; IR (neat) 1739, 1707, 1691 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{29}ONSi$ (M^+) 327.2018, found 327.2013 (Δ = +1.7 ppm).

7-Benzyl-2-(*tert*-butyldimethylsilyl)-7-azabicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (13a-TBS): ^1H NMR ($CDCl_3$) δ 0.02 (s, 3 H), 0.04 (s, 3 H), 1.0 (s, 9 H), 2.82 (m, 2 H), 3.20 (m, 1 H), 3.6 (m, 4 H), 3.82 (s, 2 H), 7.2−7.3 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ −5.85, −5.67, 26.8, 42.4 (C4), 47.2 (C2), 57.8 (C6 or C8), 58.9 (C8 or C6), 60.5 (C9), 127.1, 128.4, 128.5, 134 (C5), 138 (ipso-C), 142 (C1), 218 (C3); HRMS (EI) calcd for $C_{20}H_{29}ONSi$ (M^+) 327.2018, found 327.2014 (Δ = +0.40 ppm).

2-(*tert*-Butyldimethylsilyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one (14): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.01 (s, 3 H), 0.51 (s, 3 H), 1.00 (s, 9 H), 2.79 (m, 2 H), 4.25 (m, 2 H), 4.50 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −7.8, −6.2, 18.7, 27.6, 37.7, 46.8, 66.3, 75.4, 122.9, 190.1, 209.1; IR (neat) 1741, 1701 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{22}O_2Si$ (M^+) 238.1388, found 238.1389 (Δ = −3.4 ppm).

2-(*tert*-Butyldimethylsilyl)-7-oxabicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (15): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.01 (s, 3 H), 0.51 (s, 3 H), 0.88 (s, 9 H), 2.84 (m, 1 H), 2.89 (m, 2 H), 4.55−4.60 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −5.9, −5.8, 17.7, 26.7, 41.4, 46.2, 72.8, 73.3, 133.5, 140.9,

216.7; IR (neat) 1734, 1712 cm^{-1}; HRMS (CI) calcd for $C_{13}H_{23}O_2Si$ (MH^+) 239.1467, found 239.1468 ($\Delta = -0.3$ ppm).

2-(*tert*-Butyldimethylsilyl)-7,7′-dicarbethoxybicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (16a): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.01 (s, 3 H), 0.06 (s, 3 H), 0.84 (s, 6 H), 0.88 (s, 3 H), 1.24 (t, $J = 7.0$ Hz, 6 H), 2.77 (m, 3 H), 3.06 (m, 4 H), 4.18 (q, $J = 7.1$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ −5.8, −5.7, 14.0, 17.7, 26.7, 39.2, 40.4, 43.3, 47.9, 61.1, 61.7, 133.9, 140.9, 171.9, 217.7; IR (neat) 1731, 1714, 1664 cm^{-1}; HRMS (CI) calcd for $C_{20}H_{33}O_5Si$ (MH^+) 381.2097, found 381.2103 ($\Delta = -1.5$ ppm). Anal. Calcd for $C_{20}H_{32}O_5Si$: C, 63.12; H, 8.48. Found: C, 63.30; H, 8.55.

2-(*tert*-Butyldimethylsilyl)-7,7-dicarbethoxybicyclo[3.3.0]oct-1-en-3-one (17a): ^1H NMR ($CDCl_3$) δ 0.074 (s, 3 H), 0.090 (s, 3 H), 0.082 (s, 9 H), 1.22 (t, $J = 7.3$ Hz, 6 H), 1.64 (dd, $J = 12.6$, 12.6 Hz, 1 H, 6-CH), 2.05 (dd, $J = 17.5$, 4.0 Hz, 1 H, 4-CH), 2.55 (dd, $J = 17.5$, 6.6 Hz, 1 H, 4-CH), 2.75 (dd, $J = 12.6$, 7.6 Hz, 1 H, 6-CH), 2.98 (m, 1 H, 5-CH), 3.35 (bs, 2H, 8-CH_2), 4.17 (q, $J = 7.5$ Hz, 2H), 4.22 (q, $J = 7.5$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −5.79, −5.70, 15.16, 17.42, 26.50, 36.67 (C8), 38.70 (C-6), 43.00 (C4), 46.44 (C5), 60.62 (C7), 61.90, 134.77 (C2), 170.92, 171.52, 193.97 (C1), 212.89 (C3). Anal. Calcd for $C_{20}H_{33}SiO_5$: C 62.96; H, 8.72. Found: C, 63.06; H, 8.64.

2-(*tert*-Butyldimethylsilyl)-7-carbethoxy-7-methylbicyclo[3.3.0]-oct-$\Delta^{1,5}$-en-3-one (16b). *Isomer A*: ^1H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.97 (s, 9 H), 1.2 (t, $J = 7.5$ Hz, 3 H), 1.30 (s, 3 H), 2.35 (dd, $J = 18$ Hz, 2 H), 2.90 (m, 5 H), 4.22 (q, $J = 7.5$ Hz, 2 H). *Isomer B*: ^1H NMR ($CDCl_3$) δ 0.07 (s, 3 H), 0.98 (s, 9 H), 1.22 (t, $J = 7.5$ Hz, 3 H), 1.35 (s, 3 H), 2.35 (dd, $J = 18$ Hz, 2 H), 2.90 (m, 5 H), 4.20 (q, $J = 7.5$ Hz, 2 H).

2-(*tert*-Butyldimethylsilyl)-7-carbethoxy-7-methylbicyclo[3.3.0]oct-1-en-3-one (17b). *Isomer A*: ^1H NMR ($CDCl_3$) δ 0.19 (s, 3 H), 0.21 (s, 3 H), 0.87 (s, 9 H), 1.09 (t, $J = 12.6$ Hz, 1 H, 6-CH), 1.28 (t, $J = 7.5$ Hz, 3 H), 1.36 (s, 3 H, 7-C-Me), 2.02 (dd, $J = 17.5$, 4.1 Hz, 1 H, 4-CH), 2.48 (d, $J = 18.6$ Hz, 1 H, 8-CH), 2.60 (dd, $J = 17.5$, 10.7 Hz, 1 H, 4-CH), 2.66 (dd, $J = 12.6$, 7.8 Hz, 1 H, 6-CH), 3.06 (m, 1 H, 5-CH), 3.37 (d, $J = 18.6$ Hz, 1 H, 8-CH), 4.19 (q, $J = 7.5$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −5.46, −5.29, 14.17, 17.55, 26.34 (Me-C7), 26.64, 40.61 (C8), 43.19 (C6), 43.37 (C4), 47.25 (C5), 50.69 (C7), 61.17, 134.05 (C2), 177.35, 197.06 (C1), 213.68 (C3); MS, *m*/*z* (%) 277 ($M^+ - OEt$, 26.8), 265, ($M^+ - Bu^t$, 56.3), 191 (100), 103 (12.5), 75 (70.2). Anal. Calcd for $C_{18}H_{30}SiO_3$: C67.03; H, 9.37. Found: C, 66.81; H, 9.47. *Isomer B*: ^1H NMR ($CDCl_3$) δ 0.19 (s, 3 H), 0.21 (s, 3 H), 0.86 (s, 9 H), 1.25 (t, $J = 7.5$ Hz, 3 H), 1.45 (s, 3 H, 7-C-Me), 1.65 (t, $J = 12.5$ Hz, 1 H, 6-CH), 2.08 (dd, $J = 17.4$, 4.4 Hz, 1 H, 4-CH), 2.09 (dd, $J = 12.5$, 7.3 Hz, 1 H, 6-CH), 2.49 (d, $J = 18.8$ Hz, 1 H, 8-CH), 2.60 (dd, $J = 17.4$, 6.7 Hz, 1 H, 4-CH), 3.11 (m, 1 H, 5-CH), 3.26 (d, $J = 18.8$ Hz, 1 H, 8-CH), 4.14 (q, $J = 7.5$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −5.47, −5.25, 14.17, 17.55, 26.08 (Me-C7), 26.64, 40.49 (C8), 42.18 (C6), 43.31 (C4), 46.04 (C5), 49.94 (C7), 60.95, 134.02 (C2), 176.93, 196.37 (C1), 213.39 (C3); MS, *m*/*z* (%) 277 ($M^+ - OEt$, 12.6), 265, ($M^+ - Bu^t$, 24.7), 191 (100), 103 (7.2), 75 (40). Anal. Calcd for $C_{18}H_{30}SiO_3$: C, 67.03; H, 9.37. Found: C, 66.87; H, 9.40.

2-*tert*-(Butyldimethylsilyl)-7-carbethoxybicyclo[3.3.0]oct-$\Delta^{1,5}$-en-2-one (16c). *Isomer A*: ^1H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.09 (s, 3 H), 0.87 (s, 3 H), 0.90 (s, 6 H), 1.27 (t, $J = 7.1$ Hz, 3 H), 2.72 (m, 3 H), 2.81 (m, 4 H), 3.36 (dt, $J = 15$ Hz, 7.6 Hz, 1 H), 4.17 (q, $J = 7.1$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −6.67, −5.73, 14.26, 26.69, 34.39, 35.58, 43.46, 48.01, 60.49, 60.71. *Isomer B*: ^1H NMR ($CDCl_3$) δ 0.02 (s, 3 H), 0.06 (s, 3 H), 0.89 (s, 3 H), 0.91 (s, 6 H), 1.27 (t, $J = 7.1$ Hz, 3 H), 2.72 (m, 3 H), 2.81 (m, 4 H), 3.36 (dt, $J = 15$ Hz, 7.6 Hz, 1 H), 4.17 (q, $J = 7.1$ Hz, 2 H). Anal. Calcd for $C_{17}H_{28}SiO_3$: C, 66.19; H, 9.15. Found: C, 65.92; H, 8.93 (a 1:1 mixture of diastereomers).

2-(*tert*-Butyldimethylsilyl)-7-*endo*-carbethoxybicyclo[3.3.0]oct-1-en-3-one (17c-A): ^1H NMR ($CDCl_3$) δ 0.20 (s, 3 H), 0.21 (s, 3 H), 0.80 (s, 9 H), 1.22 (t, $J = 7.2$ Hz, 3 H), 1.35 (dd, $J = 11.9$, 11.9 Hz, 1 H, 6-CH), 2.10 (dd, $J = 17.4$, 4.2 Hz, 1 H, 4-CH), 2.45 (ddd, $J = 11.9$, 6.7, 6.7 Hz, 1 H, 6-CH), 2.55 (dd, $J = 17.4$, 6.9 Hz, 1 H, 4-CH), 2.90 (d, $J = 9.3$ Hz, 2 H, 8-CH_2), 2.95 (m, 1 H, 5-CH), 3.2 (m, 1 H, 7-CH), 4.15 (q, $J = 7.20$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −5.56, −5.39, 14.20, 17.63, 26.63, 31.57 (C8), 35.26 (C6), 43.10 (C4), 44.29 (C7), 48.37 (C5), 60.84, 126.94 (C2), 134.61 (C1), 174.44, 196.24 (C3), 213.50 (C9). Anal. Calcd for $C_{17}H_{28}SiO_3$: C, 66.19; H, 9.15. Found: C, 66.00; H, 9.38.

2-(*tert*-Butyldimethylsilyl)-7-*exo*-carbethoxy[3.3.0]oct-1-en-3-one (17c-B): ^1H NMR ($CDCl_3$) δ 0.19 (s, 3 H), 0.21 (s, 3 H), 0.85 (s, 9 H), 1.27 (t, $J = 7.5$ Hz, 3 H), 1.40 (ddd, $J = 12.6$, 9.2, 9.2 Hz, 6-CH), 1.99 (dd, $J = 17.3$, 4.1 Hz, 1 H, 4-CH), 2.45 (ddd, $J = 12.6$, 7.8, 1.1 Hz, 1 H, 6-CH), 2.55 (dd, $J = 17.3$, 6.7 Hz, 1 H, 4-CH), 2.87 (dd, $J = 18.4$, 9.2 Hz, 1 H, 8-CH), 3.00 (dd, $J = 18.4$, 4.0 Hz, 1 H, 8-CH), 3.01 (m, 1 H, 5-CH), 3.18 (dddd, $J = 9.2$, 9.2, 4.1, 1.1 Hz, 1 H, 7-CH), 4.15 (q, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$) δ −5.49, −5.31, 14.18, 17.56, 26.50, 31.78 (C8), 34.20 (C6), 43.23 (C4), 43.42 (C7), 45.96 (C5), 60.76, 134.11 (C2), 175.51, 196.96 (C1), 213.75 (C3). Anal. Calcd for $C_{17}H_{28}SiO_3$: C, 66.19; H, 9.15. Found: C, 66.30; H, 9.09.

7-(Acetoxymethyl)-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (16d). *Isomer A*: pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.01 (s, 3 H), 0.06 (s, 3 H), 0.88 (s, 9 H), 2.04 (s, 3 H), 2.07 (m, 1 H), 2.15 (m, 1 H), 2.53 (m, 2 H), 2.71−2.87 (m, 4 H), 4.03 (dd, $J = 12.1$, 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −5.7, −5.6, 17.8, 21.0, 26.7, 33.8, 35.2, 38.4, 43.6, 48.2, 68.1, 135.5, 142.4, 171.2, 218.8; IR (neat) 2948−2854, 1735, 1654 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{28}O_3Si$ (M^+) 308.1808, found 308.1809 ($\Delta = -0.1$ ppm). *Isomer B*: pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.13 (s, 3 H), 0.16 (s, 3 H), 0.85 (s, 9 H), 2.04 (s, 3 H), 2.07 (m, 2 H), 2.30 (m, 2 H), 2.51−2.92 (m, 4 H), 4.07 (dd, $J = 12.6$, 6.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −5.5, −5.3, 17.7, 20.9, 26.6, 32.1, 34.8, 39.3, 43.2, 48.2, 53.1, 67.2, 129.9, 134.3, 171.1, 197.7; IR (neat) 3047, 1741, 1692, 1644, 1605 cm^{-1}; HRMS (CI) calcd for $C_{17}H_{28}O_3Si$ (M^+) 308.1808, found 308.1804 ($\Delta = +1.2$ ppm).

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