New and Efficient Catalytic Route to Bicyclo[3.3.0]octa-1,5-dien-3-ones

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The silylcarbobicyclization of 4,4-disubstituted 1,6-heptadiynes with *tert*-butyldimethylsilane catalyzed by $Rh(acac)(CO)_2$, $Co_2Rh_2(CO)_{12}$, or $(t\text{-BuNC})_4RhCo(CO)_4$ under 50 atm of carbon monoxide gives the corresponding novel 7,7-disubstituted 2-silylbicyclo[3.3.0]octa-1,5-dien-3-ones in good yields. A possible mechanism is proposed. The unique feature of this strained skeleton is discussed on the basis of ^{13}C NMR and X-ray crystallographic analyses.

Transition metal-catalyzed carbocyclizations of alkenes and alkynes provide efficient and useful methods for the syntheses of cyclic and polycyclic compounds of medicinal and theoretical interests.[1] We are interested in the silicon-initiated carbometalation processes and have been exploring the scope of silylformylations[2−7] and silylcarbocyclizations (SiCaCs).[8−11] In the course of our investigation into the SiCaC reaction of 1,6-alkadiynes, we discovered a novel catalytic synthesis of bicyclo[3.3.0]octenones.[10] Now, we have found that the silylcarbobicyclization (SiCaB) reaction of 4,4-disubstituted 1,6-heptadiynes leads to the formation of 7,7-disubstituted bicyclo[3.3.0]octa-1,5-dien-3-ones, which have a rare cyclopentanoid skeleton. Bicyclo[3.3.0]octa-1,5-dien-3-ones are attractive intermediates for the syntheses of a variety of polyfunctionalized cyclopentanoids, but their syntheses were not achieved until very recently. The first synthesis of the bicyclo[3.3.0]octa-1,5-dien-3-one skeleton was reported by Knölker and Heber in 1993 via $Fe(CO)_5$-mediated [2 + 2 + 1] cycloaddition of 1,7-TMS-diynes and carbon monoxide, followed by oxidative demetalation of the resulting (η^4-cyclopentadienone)iron tricarbonyl complexes using Me_3NO.[12] The same stoichiometric two-step process was applied for the syntheses of 2-(4-pentenyl)bicyclo[3.3.0]-octa-1,5-dien-3-ones from 12-substituted dodec-1-ene-6,11-diynes by Pearson and Perosa.[13] We wish to report here the first and efficient catalytic syntheses of bicyclo-[3.3.0]octa-1,5-dien-3-ones in one step from 1,6-heptadiynes through rhodium complex-catalyzed SiCaB reaction and the characterization of their unique skeleton by ^{13}C NMR and X-ray crystallographic analysis.

The SiCaB reaction of 4,4-(*O*-protected hydroxymethyl)hepta-1,6-diynes **1a**−**c** (1.0 mmol) with *tert*-butyldimethylsilane (2.0 mmol) catalyzed by $Rh(acac)(CO)_2$ (0.02 mmol) at 120 °C and 50 atm of carbon monoxide in toluene for 5−14 h gave 7,7-(*O*-protected hydroxymethyl)-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]octa-1,5-dien-3-ones **2a**−**c** exclusively in high isolated yields (Scheme 1). The reaction of 4,4-bis(hydroxymethyl)-hepta-1,6-diene (**1d**) catalyzed by $Rh(acac)(CO)_2$ under the standard conditions gave a mixture of 7,7-bis-(hydroxymethyl)-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]-octa-1,5-dien-3-one (**2d**) (71%) and 7,7-bis(hydroxymethyl)bicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**3d**) (7%) (Scheme 1). The reaction of **1b** catalyzed by $Co_2Rh_2(CO)_{12}$ (1.0 mol %) under the same reaction conditions gave **2b** in 72% isolated yield. The reaction of **1a** (or **1b**) proceeds at lower temperatures, e.g., 50 °C, giving the same product **2a** (or **2b**), although a much longer reaction time is necessary for the reaction to go to completion. In contrast, when the reaction of **1c** was carried out at 50 °C for 15 h, 7,7-bis(acetoxymethyl)-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**3c**) was obtained in 50% yield as the sole isolable product. The reaction of **1b** catalyzed by $(t\text{-BuNC})_4RhCo(CO)_4$ under the standard conditions, i.e., 120 °C and 50 atm of CO, gave 7,7-bis[[(triisopropylsilyl)oxy]methyl]-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**3b**) as the major product (75% yield) and **2b** as the minor product (10% yield). Thus, the nature of catalyst and

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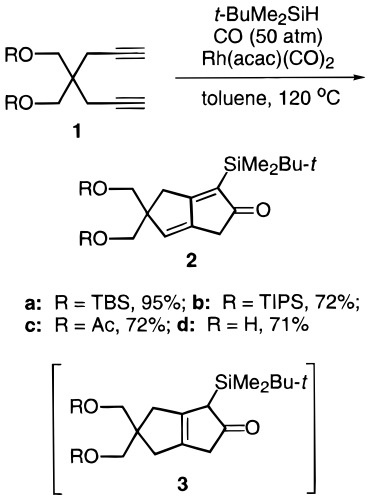
Scheme 1



substrate appears to have significant influence on the product selectivity.

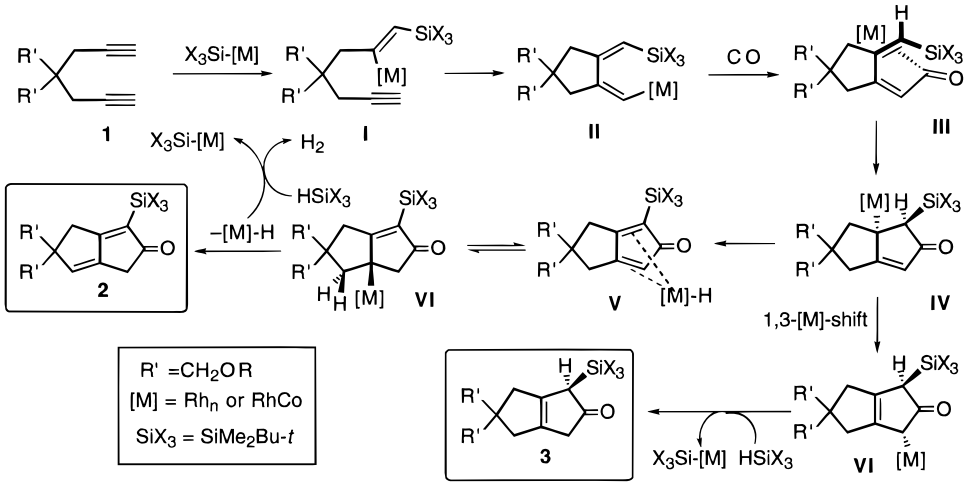
A possible mechanism for the formation of **2** and **3** is illustrated in Scheme 2. As Scheme 2 shows, one of the terminal acetylene moiety reacts with the *t*-$BuMe_2Si$−[M] species regioselectively to first form *β*-(silylethenyl)−[M] complex **I**. The carbocyclization of **I** forms **II** followed by CO insertion, and subsequent carbocyclization yields bicyclic intermediate **IV**. The *β*-hydride elimination of **IV** gives the dienone−[M]−H complex **V**, which then undergoes extremely regioselective hydrometalation of the less sterically hindered double bond, yielding **VI**. Finally, the *β*-hydride elimination of **VI** affords **2**. On the other hand, **IV** is converted to **VI** through the 1,3-[M] shift, and the reductive elimination by the action of another molecule of the hydrosilane affords **3** and regenerates the *t*-$BuMe_2Si$−[M] species. In a separate control experiment under the same reaction conditions, we found that **3b** was not converted to **2b**. Thus, it is evident that **3** is not the intermediate for the formation of **2**; i.e., **2** is formed as the kinetic product.

In order to look at the effect of substitution at the terminal acetylene moiety, an unsymmetrical 1,6-diyne, 4,4′-bis(hydroxymethyl)-1,6-octadiyne (**4**), was prepared and subjected to the same reaction conditions, i.e., 120 °C and 50 atm of CO. The reaction proceeded with extremely high regioselectivity in terms of the delivery of the TBS moiety but gave a ca. 1:1 mixture of 7,7′-bis(hydroxymethyl)-2-(*tert*-butyldimethylsilyl)-4-methylbicyclo[3.3.0]octa-1,5-dien-3-one (**5**) and 7,7′-bis(hydroxymethyl)-4-(*tert*-butyldimethylsilyl)-2-methylbicyclo[3.3.0]octa-1,5-dien-3-one (**6**) in 48% isolated yield (Scheme 3). The result clearly indicates that the initial reaction of the *t*-$BuMe_2Si$−[M] species takes place at the terminal acetylene moiety exclusively, and there are two different ways for the *β*-hydride elimination of the species like **VI** in Scheme 2. This is quite reasonable since the addition of the [M]−H species to the cyclopentadienone moiety of **V** is no longer regioselective because of the methyl group at the C-4 position in this case.

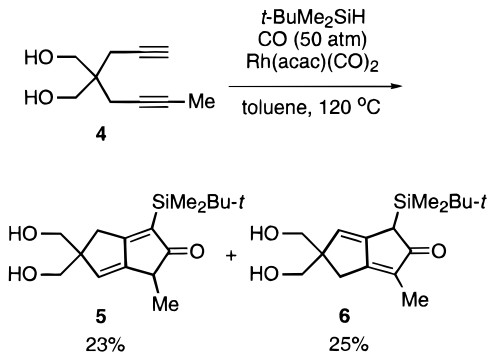
In a similar manner, the SiCaB reaction of 4,4-dimethyl-3-hydroxyhepta-1,6-diyne (**7**) catalyzed by Rh(acac)$(CO)_2$ was carried out at 75 °C and 50 atm of carbon monoxide. In this case, 7,7′-dimethyl-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]octa-1,5-dien-3-one (**8**) (40% yield) and 7,7′-dimethyl-2-(*tert*-butyldimethylsilyl)-8-hydroxybicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**9**) (27% yield) were isolated (Scheme 4). We have found that the bicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**9**) undergoes spontaneous dehydration upon standing in a flask to give bicyclo[3.3.0]octa-1,5-dien-3-one (**8**) quantitatively. It is worth mentioning that the initial SiCaB reaction is extremely regioselective since only **8** and **9** are formed; i.e., the TBS group of **9** is located in the same side as the hydroxyl group, and any double bond regioisomer of **8** is not detected. This excellent regioselectivity can be ascribed to the "hydroxy-directed" silyl-metalation; the hydroxyl group lures the *t*-$BuMe_2Si$−[M] group. The fact that the double bonds did not isomerize to give the most favorable fully conjugated system including the silyl moiety like **2** clearly indicates that **8** is a kinetic product.

It appears that the nature of the substituents at the C-4 position of 1,6-diynes exert remarkable influence on the course of the reaction. For example, in contrast to the reactions of **1a**−**d**, the reaction of 4,4-bis(ethoxycarbonyl)-1,6-heptadiyne (**10**) under the standard reaction conditions, i.e., 120 °C and 50 atm of CO, gave 7,7′-bis(ethoxycarbonyl)-2-(*tert*-butyldimethylsilyl)-bicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (**11**) in 72% yield, and only a trace amount of 7,7′-bis(ethoxycarbonyl)-2-(*tert*-

Scheme 2



Scheme 3



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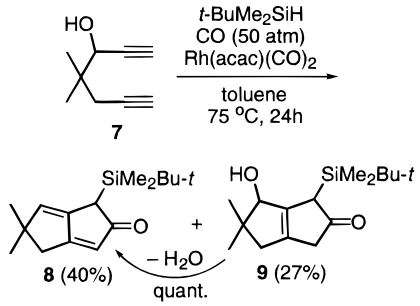
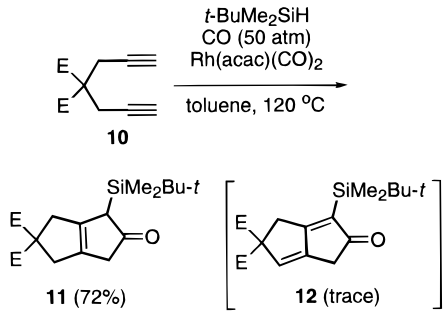


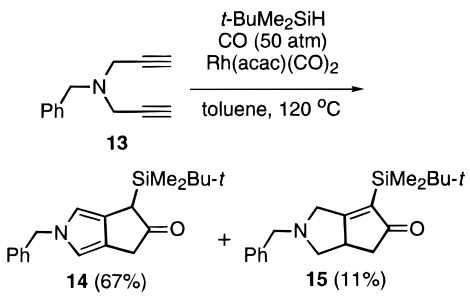
Scheme 5



butyldimethylsilyl)bicyclo[3.3.0]octa-1,5-dien-3-one (**6**) was detected (Scheme 5). As we reported previously, the reaction of **10** at 50 °C and 15−50 atm of CO gave **11** exclusively in >90% isolated yields.[10a] Even when the reaction was carried out at 140 °C and 25 atm of CO, the same result was obtained. Thus, it is obvious that the *gem*-diethoxycarbonyl moiety at C-4 prevents the formation of the bicyclo[3.3.0]octa-1,5-dien-3-one skeleton presumably by enhancing the 1,3-[M] shift in the intermediate **IV** while suppressing the β-hydride elimination from the same intermediate **IV** (see Scheme 2).

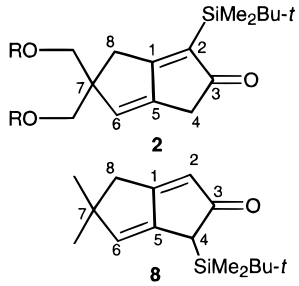
The introduction of a benzylamino moiety instead of the *gem*-disubstituted methylene group at C-4 also affects the (aza)bicyclo[3.3.0]octa-1,5-dien-3-one skeleton formation, leading the reaction to form a bicyclic pyrrole skeleton. Thus, the reaction of benzyldipropargylamine (**13**) under the standard conditions gave 2-(*tert*-butyldimethylsilyl)-7-benzyl-7-azabicyclo[3.3.0]octa-5,8-dien-3-one (**14**) as the major product (67% yield) accompanied by 2-(*tert*-butyldimethylsilyl)-7-benzyl-7-azabicyclo[3.3.0]oct-1-en-3-one (**15**) as the minor product (11% yield) (Scheme 6). In this case, the aromatization energy appears to be the driving force to form the 7-azabicyclo[3.3.0]octa-5,8-dien-3-one skeleton rather than the bicyclo[3.3.0]octa-1,5-dien-3-one skeleton. The

Scheme 6



reaction of this 1,6-diyne **13** is very sensitive to the reaction conditions as well as catalyst species used. The reaction using $Rh_2Co_2(CO)_{12}$ or $Rh(CNBu\text{-}t)_4Co(CO)_4$ as the catalyst at 50 °C and 50 atm of CO gave **15** (60% yield) and a small amount of 2-(*tert*-butyldimethylsilyl)-7-benzyl-7-azabicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one; i.e., no production of **14** was observed.[10a] In contrast, Matsuda et al. reported that the reaction catalyzed by $Rh_4(CO)_{12}$ at 95 °C and 20 atm of CO in benzene afforded a mixture of **14** (31% yield) and **15** (9% yield).[10b]

The ^{13}C NMR spectra of these novel bicyclo[3.3.0]octa-1,5-dien-3-ones (**2a**−**d** and **8**) show unique and characteristic chemical shifts, especially for the C-1 and C-3 carbons as listed below.



	C-1	C-2	C-3	C-5	C-6
2a	194.3	131.9	211.6	147.1	133.9
2b	194.5	131.5	211.6	147.1	134.1
2c	190.9	129.8	210.5	148.7	133.6
2d	198.5	133.4	215.5	149.9	137.1
8	183.2	121.9	211.5	145.2	140.4

The C-1 carbon for this unique skeleton shows an extremely large downfield shift in comparison with usual cyclic enone systems, and the carbonyl carbon (C-3) also appears in unusually low field in spite of its conjugation. This fact clearly indicates the substantial strain and high polarization of the C^1-C^2 double bond. It is also noteworthy that there is a substantial "β-silicon effect" that enhances the down field shift of the C-1 carbon by 7−11 ppm.[14] These observations prompted us to look at the X-ray crystal structure of this unique skeleton. Fortunately, **2d** gave good single crystals for X-ray analysis. The X-ray crystallographic molecular structure of **2d** is shown in Figure 1. As expected, this molecule is virtually flat ($<C^6-C^5-C^1-C^2 = 177.6°$; $<C^8-C^1-C^5-C^4 = 180.0°$), and the bond lengths of C^1-C^2 and C^5-C^6 are 1.350 and 1.322 Å, respectively. The observed C^1-C^2 and C^5-C^6 bond lengths are substantially longer and shorter, respectively, than those of ordinary double bonds (1.337 Å).[15] The C^1-C^5 bond

(14) The chemical shifts of 2-alkylbicyclo[3.3.0]octa-1,5-dien-3-one were reported to be 182−183 ppm (see ref 13). These data also confirm the β-silicon effect on the chemical shift of the C-1 carbon.

(15) The values indicated by the Chem 3D program (MM2).

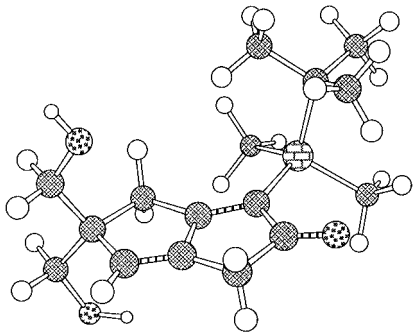


Figure 1. X-ray structure of **2d**.

length is 1.453 Å, which is substantially shorter than that of ordinary single bonds (1.503 Å).[15] These data are consistent with the ^{13}C NMR data, indicating strong polarization of the C^1-C^2 bond and the way this molecule accommodates the strain caused by the unique ring fusion.

Further study on the reactivity of these unique bicyclo[3.3.0]octa-1,5-dien-3-ones and applications to organic syntheses is actively underway.

Experimental Section

General Methods. The ^1H NMR, ^{13}C NMR, DEPT, COSY, and HETCOR NMR spectra were recorded on a Bruker AC-250 or a General Electric QE-300 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 at the University of California at Riverside mass spectrometry facility. Analytical gas chromatography was performed with a Hewlett-Packard 5890 gas chromatograph (FID) with a Hewlett-Packard HP 3396A integrator using either a 6 ft glass column packed with 3% OV-17 or with a 25 m 3% OV-101 capillary column. Elemental analyses were performed at M-H-W Laboratories, Phoenix, AZ.

Materials. Toluene, tetrahydrofuran, and diethyl ether were dried over and distilled from sodium/benzophenone ketal under nitrogen prior to use. Hexane and dichloromethane were freshly distilled from calcium hydride. All other solvents were reagent grade and used as received. Rhodium-cobalt mixed metal complexes, $Rh_2Co_2(CO)_{12}$[16] and (t-Bu-NC)$_4$RhCo(CO)$_4$,[17] were prepared by literature methods. Rh(acac)$(CO)_2$ was obtained by the Mitsubishi Kasei Corporation and used as received. All other chemicals were purchased either from Aldrich Chemical Co. or Fluka Chemical Co. *tert*-Butyldimethylsilane was distilled under nitrogen and stored under activated molecular sieves. Silica gel used for chromatography, MN-Kieselgel 60, was purchased from Brinkman Instruments Inc.

General Procedure for the Silylcarbobicyclization of 1,6-Diynes. A typical procedure is described for the silylcarbobicyclization of **1a**. To a 25 mL Pyrex reaction vessel containing a stirring bar was added a solution of 4,4-bis[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne (**1a**) (380 mg, 1.00 mmol) in 10 mL of toluene. *tert*-Butyldimethylsilane (233 mg, 2.00 mmol) and Rh(acac)$(CO)_2$ (5.2 mg, 2.0×10^{-2} mmol) were then charged under carbon monoxide atmosphere. The reaction vessel was placed in a 300 mL stainless steel autoclave, and carbon monoxide was introduced to substitute the remaining air. After the carbon monoxide pressure was adjusted to 50 atm, the reaction mixture was allowed to stir magnetically at 120 °C and 50 atm of carbon monoxide for 10 h. The carbon monoxide gas was then carefully released, and the reaction mixture was then submitted to GLC and TLC analysis. After evaporation of the solvent under the reduced pressure, the crude product was immediately submitted to flash chromatography on a silica gel using a gradient of (a) 10:1 hexane:EtOAc (100 mL), (b) 5:1 hexane:EtOAc (100 mL), and (c) 2:1 hexane:EtOAc (100 mL). 7,7-Bis[(*tert*-butyldimethylsiloxy)methyl]-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]octa-1,5-dien-3-one (**2a**) was eluted with 1:1 hexane:EtOAc solvent as a pale yellow solid (494 mg, 95% yield): mp 79−81 °C; ^1H NMR ($CDCl_3$) δ 0.01 (s, 12 H), 0.19 (s, 6 H), 0.86 (s, 27 H), 2.57 (s, 2 H), 2.84 (s, 2 H), 3.59 (s, 4 H), 5.95 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.6, −5.6, 18.0, 18.2, 25.8, 26.7, 34.6, 36.6, 61.6, 65.6, 131.9, 133.9, 147.1, 194.3 (C1), 211.6 (C3); IR (neat) 2954, 2930, 2858, 1691, 1257, 1081, 837 cm^{-1}; HRMS calcd for $C_{28}H_{54}O_3Si_3$ (MH^+) m/z 523.3489, found m/z 523.3467 ($\Delta = -1.5$ ppm).

In a similar manner, the following compounds were obtained and characterized.

7,7-Bis[(triisopropylsiloxy)methyl]-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]octa-1,5-dien-3-one (2b): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.19 (s, 6 H), 0.87 (s, 9 H), 0.93−1.10 (m, 42 H), 2.65 (s, 2 H), 2.83 (s, 2 H), 3.76 (s, 4 H), 5.99 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.6, 12.0, 17.9, 18.0, 26.8, 34.6, 36.6, 62.2, 66.5, 131.5, 134.1, 147.1, 194.5 (C1), 211.6 (C3); IR (neat) 1695, 1652, 1569 cm^{-1}. Anal. Calcd for $C_{34}H_{66}O_3Si_3$: C, 67.26; H, 10.96. Found: C, 67.10; H, 10.79.

7,7-Bis(acetoxymethyl)-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]octa-1,5-dien-3-one (2c): yellow oil; ^1H NMR ($CDCl_3$) δ 0.21 (s, 6 H), 0.88 (s, 9 H), 2.05 (s, 6 H), 2,70 (s, 2 H), 2.89 (s, 2 H), 4.11 (s, 4 H), 5.87 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.7, 17.9, 20.8, 26.6, 35.2, 36.5, 56.8, 66.6, 129.8, 133.6, 148.7, 170.7 (CO_2), 190.9 (C1), 210.5 (C3); IR (neat) 2953, 2929, 28.94, 2855, 1746, 1693, 1571, 1469, 1379, 1364, 1233, 1040.53, 837, 823, 808 cm^{-1}. Anal. Calcd for $C_{20}H_{30}SiO_5$: C, 63.46; H, 7.99. Found: C, 63.18; H, 7.92.

7,7-Bis(hydroxymethyl)-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]octa-1,5-dien-3-one (2d): white solid; mp 151−153 °C; ^1H NMR (MeOD-d_4) δ 0.01 (s, 6 H), 0.68 (s, 9 H), 2.54 (s, 2 H), 2.68 (s, 2 H), 3.41 (s, 4 H), 5.84 (s, 1 H); ^{13}C NMR (MeOD-d_4) δ −4.2, 19.8, 28.3, 36.8, 38.4, 64.1, 67.4, 133.4, 137.1, 149.9, 198.5 (C1), 215.5 (C3); IR (neat) 1670, 1638, 1558 cm^{-1}. Anal. Calcd for $C_{16}H_{26}O_3Si$: C, 65.26; H, 8.90. Found: C, 65.30; H, 8.85.

7,7′-Bis[(triisopropylsiloxy)methyl]-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]octa-$\Delta^{1,5}$-en-3-one (3b): pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.03 (s, 3 H), 0.11 (s, 3 H), 0.88 (s, 9 H), 1.10 (m, 42 H), 2.31 (m, 4 H), 2.78 (m, 3 H), 3.63 (s, 2 H), 3.75 (s, 2 H), 5.99 (s,1 H); ^{13}C NMR ($CDCl_3$) δ −5.2, −4.9, 12.7, 12.9, 17.9, 18.0, 27.4, 27.7, 40.1, 43.7, 48.5, 42.4, 66.2, 67.3, 133.8, 140.2, 215.3 (C3); IR (neat) 1720, 1709 cm^{-1}; HRMS calcd for $C_{34}H_{68}O_3Si_3$ (M^+) m/z 608.4476; found m/z 608.4498 ($\Delta = -3.6$ ppm).

7,7′-Bis(hydroxymethyl)-2-(*tert*-butyldimethylsilyl)bicyclo[3.3.0]octa-$\Delta^{1,5}$-en-3-one (3d): pale yellow oil; ^1H NMR (MeOD-d_4) δ −0.02 (s, 3 H), 0.02 (s, 3 H), 0.08 (s, 9 H), 2,18 (m, 4 H), 3.66 (s, 2 H); ^{13}C NMR (MeOD-d_4) δ −5.78, −5.70, 17.63, 26.60, 36.85, 38.15, 43.56, 48.22, 68.71, 68.96, 134.65, 141.53, 219.59 (C3); IR (neat) 1728, 1714 cm^{-1}; HRMS calcd for $C_{16}H_{29}O_3Si$ (MH^+) m/z 297.4932, found m/z 297.1885 ($\Delta = +0.3$ ppm).

7,7′-Bis(hydroxymethyl)-2-(*tert*-butyldimethylsilyl)-4-methylbicyclo[3.3.0]octa-1,5-dien-3-one (5): yellow oil; ^1H NMR ($CDCl_3$) δ 0.21 (s, 6 H), 0.90 (s, 9 H), 1.20 (d, $J = 7.7$ Hz, 3 H), 2.37(m, 2 H), 2.78 (m, 3 H), 3.74 (m, 4 H), 5.97 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ δ −6.6, −6.1, 13.9, 24.4, 30.9, 34.8, 43,1, 60.0, 71.9, 130.0, 130.7, 149.0, 190.2, 213.6; IR (neat) 1731, 1673, 1633 cm^{-1}; HRMS calcd for $C_{17}H_{29}O_3Si$ (MH^+) 309.1886, found 309.1887 ($\Delta = -0.3$ ppm).

7,7′-Bis(hydroxymethyl)-4-(*tert*-butyldimethylsilyl)-2-methylbicyclo[3.3.0]octa-1,5-dien-3-one (6): yellow oil; ^1H

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NMR ($CDCl_3$) δ δ 0.05 (s, 3 H), 0.08 (s, 3 H), 0.88 (s, 9 H), 1.79 (s, 3 H), 2.04 (br s, 2 H), 2.61 (m, 2 H), 2.83 (s, 1 H), 3.75 (m, 4 H), 5.70 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −8.9, −5.9, 8.8, 26.7, 27.2, 31.4, 40.8, 68.3, 76.5, 127.2, 130.8, 154.3, 174.0, 207.8; IR (neat) 1739, 1689, 1640 cm^{-1}; HRMS calcd for $C_{17}H_{29}O_3Si$ (MH^+) 309.1886, found 309.1878 (Δ = +2.6 ppm).

4-(*tert*-Butyldimethylsilyl)-7,7′-dimethylbicyclo[3.3.0]-octa-1,5-dien-3-one (8): pale yellow solid; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6 H), 0.08 (s, 9 H), 1.19 (s, 3 H), 1.22 (s, 3 H), 2.59 (s, 2 H), 2.81 (s, 1 H), 5.78 (s, 1 H), 5.83 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.6, 17.9, 27.0, 28.7, 28.8, 41.0, 41.4, 50.2, 121.9, 140.4, 145.2, 183.2, 211.5; IR (neat) 1697, 1655 cm^{-1}; GC−MS (EI, 70 eV) *m*/*z* 262 (M^+), 247, 205 (base peak), 191, 177, 147, 115, 73, 59.

2-(*tert*-Butyldimethylsilyl)-4,4′-dimethyl-8-hydroxy-bicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (9): pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.09 (s, 3 H), 0.08 (s, 9 H), 1.10 (s, 3 H), 1.16 (s, 3 H), 2.02 (dd, J = 16.3, 3.4 Hz, 1 H), 2.38 (d, J = 16.3 Hz, 1 H), 2.72 (d, J = 22.7 Hz, 1 H), 2.84 (t, J = 3.4 Hz, 1 H), 2.94 (d, J = 22.7 Hz, 1 H), 4.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −5.6, −5.0, 18.1, 23.1, 26.5, 27.1, 28.7, 44.0, 44.1, 44.8, 48.3, 82.9 (C6), 140.6 (C1), 144.8 (C5), 218.3 (C3); GC−MS (EI, 70 eV) *m*/*z* 280 (M^+), 262, 205, 168, 148, 133, 75, 73 (base peak), 59.

7,7′-Bis(ethoxycarbonyl)-2-(*tert*-butyldimethylsilyl)-bicyclo[3.3.0]oct-$\Delta^{1,5}$-en-3-one (11): pale yellow oil; ^{1}H 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 $C_{20}H_{32}O_5Si$ (MH^+) *m*/*z* 381.5865, found 381.2103 (Δ = −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-benzylazabicyclo[3.3.0]-octa-5,8-dien-3-one (14):[10b] pale yellow oil; ^{1}H 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 $C_{20}H_{28}ONSi$ (MH^+) 326.5378, 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.

2-(*tert*-Butyldimethylsilyl)-7-benzylazabicyclo[3.3.0]-oct-1-en-3-one (15): pale yellow oil; ^{1}H 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 (t, 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.

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Supporting Information Available: A table of X-ray crystallographic data, an ORTEP representation, and tables of all relevant parameters of **2d** (7 pages). Ordering information is given on any current masthead page.

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