Stereocomplementary Construction of Optically Active Bicyclo[4.3.0]nonenone Derivatives

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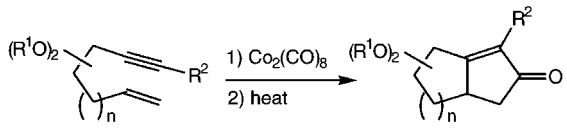
Treatment of (5*S*,6*S*)-5,6-bis(*tert*-butyldimethylsiloxy)-8-(substituted)oct-1-en-7-yne derivatives, prepared from diethyl L-tartrate, with $Co_2(CO)_8$ afforded the corresponding cobalt-complexed enynes, which were subsequently exposed to the typical Pauson−Khand conditions to furnish highly stereoselectively or exclusively (2*S*,3*S*,6*S*)-2,3-bis(*tert*-butyldimethylsiloxy)-9-(substituted)bicyclo-[4.3.0]non-1(9)-en-8-ones. On the other hand, (3*S*,4*S*)-1-(substituted)oct-7-en-1-yne-3,4-diol congeners produced, on exposure to the Pauson−Khand conditions, (2*S*,3*S*,6*R*)-2,3-dihydroxy-9-(substituted)-bicyclo[4.3.0]-non-1(9)-en-8-one derivatives in a highly stereoselective manner. The newly developed procedure has been shown to be useful for construction of the 2,3-bis(oxygenated)-7-(substituted)-bicyclo[4.3.0]non-6-en-8-one framework in a stereocomplementary as well as stereoselective fashion.

Introduction

The optically active bicyclo[*m*.3.0] ring system has been found to be a core skeleton of many natural products. Both linear and angular triquinane sesquiterpenes,[1] for instance, have the bicyclo[3.3.0]octane framework as a common structural feature. The representative natural products possessing a bicyclo[4.3.0] skeleton must be exemplified as the picrotoxanes.[2] In addition, the bicyclo-[5.3.0] and bicyclo[6.3.0] ring systems can be found in guaianolides[3] and ophiobolins,[4] respectively. An efficient and highly stereoselective general method for construction of the optically active bicyclo[m.3.0] ring system, therefore, would become a powerful tool for the total synthesis of these natural products.

The intramolecular Pauson−Khand reaction,[5] a formal [2 + 2 + 1] cyclization reaction of three components (alkyne and olefin moieties and carbon monoxide), has emerged as one of the most reliable methods for construction of the cyclopentenone-fused bicyclo compounds. During the course of our program[6] directed toward the development of stereoselective reactions mediated by alkyne−dicobalt hexacarbonyl complexes, we had envisioned that the optically active enyne derivatives **1** derived from L-tartrate would be versatile starting materials for the intramolecular Pauson−Khand reaction leading to the target bicyclo[*m*.3.0] ring system **2**. In the previous papers,[7] we succeeded in development of a new procedure for the highly stereoselective construction of

Scheme 1



1 **2**

the bicyclo[3.3.0]octenone derivatives **2** ($n = 1$) possessing two distinguishable hydroxy functionalities in line with our synthetic plan.

Our efforts[8] were then directed toward application of the newly developed method to construct the corresponding bicyclo[4.3.0]nonenone derivatives **2** ($n = 2$). We describe here a highly stereoselective as well as stereocomplementary method for preparation of the bicyclo-[4.3.0]nonenones.

Results and Discussion

Intramolecular Pauson−Khand Reaction of (5S,-6S)-5,6-Bis(oxygenated)oct-1-en-7-yne Derivatives. The required optically active enyne derivatives **5**, **6**, and **7** were easily obtained from diethyl L-tartrate. The known alcohol **3**, derived from diethyl L-tartrate according to Kotsuki's procedure,[9] was exposed to Corey's dibromoolefination[10] to give the dibromo derivative **4** in 72% yield, which was then treated with *n*-BuLi[10] affording **5a** in 78% yield. Hydrolysis of **5a** with *p*-toluenesulfonic acid (PTSA) in methanol provided the diol **6a** in 92% yield. Introduction of the *tert*-butyldimethylsilyl (TBDMS) group on the dihydroxy group of **6a** was realized by treatment with TBDMSCl in DMF to furnish **7a** in 99% yield. The other enynes **5b**,**c**, **6b**,**c**, and **7b**,**c** were obtained from

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(1) Fraga, B. M. *Nat. Prod. Chem.* **1992**, *9*, 217.
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(8) A part of this work was published in a preliminary communication: Mukai, C.; Kim, J. S.; Uchiyama, M,; Hanaoka, M. *Tetrahedron Lett.* **1998**, *39*, 7909.
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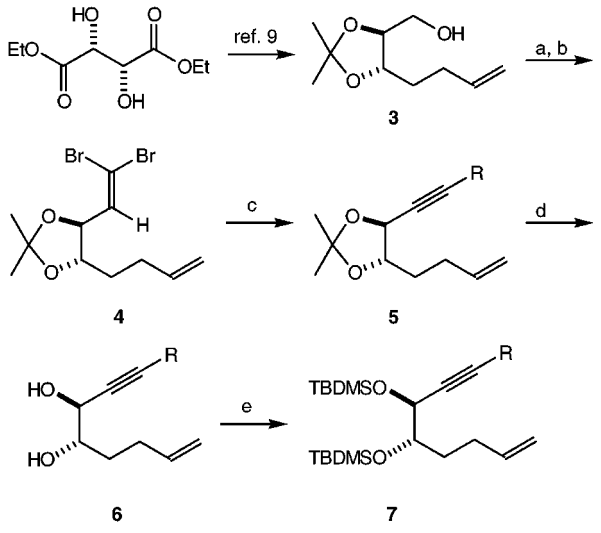
Scheme 2[a]

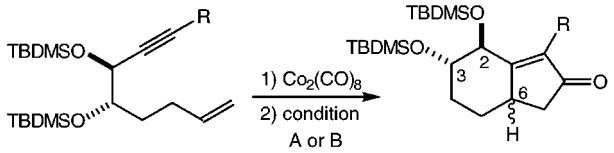


a: R = H; **b**: R = Ph; **c**: R = TMS

[a]Reaction conditions : (a) DMSO, $(COCl)_2$, Et_3N; (b) PPh_3, CBr_4, 72%; (c) *n*-BuLi, 78%; (d) PTSA, MeOH, 92%; (e) TBDMSCl, imidazole, DMF, 99%.

5a, **6a**, **7a** by conventional means (see the Experimental Section).In the previous papers,[7] the highly diastereoselective formation of the bicyclo[3.3.0]octenone skeleton was realized when the starting enynes having the TBDMSO group at the propynyl and homopropynyl positions were exposed to the typical Pauson−Khand conditions. On the basis of these results, we first investigated the Pauson−Khand reaction of **7**, hoping for highly stereoselective construction of the bicyclo[4.3.0]nonenone framework. The Pauson−Khand reaction was carried out under two conditions, the results of which are summarized in Table 1. Treatment of **7a** with dicobaltoctacarbonyl [$(Co_2(CO)_8$] in methylene chloride at room temperature gave the corresponding cobalt-complexed derivative. The complex was then heated in acetonitrile[11] at 70−75 °C (condition A) to afford the cyclized products **8a** and **9a** in a ratio of 88:12 in 85% yield. A similar result was obtained when the cobalt-complexed **7a** was exposed to trimethylamine *N*-oxide (TMANO)[12] in THF (condition B) at room temperature (Table 1, entry 2). The higher diastereoselectivity was observed in the case of the phenyl derivative **7b** where exclusive formation of **8b** could be achieved (Table 1, entries 3 and 4). It should be mentioned that the 1,3-diene derivative[13,14] **10b** was obtained in 27% yield as a byproduct in the case of **7b** under condition B. The formation of **10b** could be tentatively interpreted by the mechanism proposed by Krafft[14] recently, in which the generally acceptable metallocyclic intermediate[5] would collapse to **10b** via allylic C−H insertion instead of carbonyl insertion leading to the normal cyclopentenone derivatives. The exclusive formation of **8c** in 62 and 27% yields was also realized under conditions A and B along with the recovery of the starting enyne **7c** in 16 and 44% yields, respectively (Table 1, entries 5 and 6). These results were in good accordance with the prediction based on the previous works.[7]

Table 1. Pauson−Khand Reaction of Enyne 7

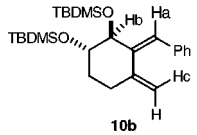


a: R = H; **b**: R = Ph; **c**: R = TMS

condition A: 70~75°C in MeCN; **condition B**: TMANO·$2H_2O$ in THF.

entry	substrate	condition	R	ratio[a] **8:9**	yield[b] (%)
1	**7a**	A	H	88:12	85
2	**7a**	B	H	88:12	86
3	**7b**	A	Ph	100:0	99
4	**7b**	B	Ph	100:0	67[c]
5	**7c**	A	TMS	100:0	62[d]
6	**7c**	B	TMS	100:0	27[e]

[a] Determined by HPLC analysis. [b] Total yield of **8** and **9**. [c] (1*S*,2*S*,3*E*)-Benzylidene-1,2-bis(*tert*-butyldimethylsilyloxy)-4-methylenecyclohexane (**10b**) was obtained in 27% yield. [d] The starting **7c** was recovered in 16% yield. [e] The starting **7c** was recovered in 44% yield.



The structure of **8** and **9** was apparent from spectral evidence (see the Experimental Section). The stereochemical assignment of the cyclized products **8** and **9** was made by examination of the ^{1}H NMR spectra. The distinguishing feature of the ^{1}H NMR spectra of **8a** and **9a** is the difference in the coupling constants between H-2 and H-3. The ^{1}H NMR spectrum of **8a** revealed a smaller coupling constant (3.4 Hz) between H-2 and H-3 due to an equatorial−equatorial coupling, while that of the corresponding 6-epimer **9a** showed a rather large value (8.3 Hz) attributable to a typical axial−axial coupling. Therefore, it is reasonable to consider that the preferred conformation of **8a** possesses two axial TBDMSO groups at the C-2 and the C-3 positions. On the other hand, **9a** must have the preferred conformer in which two TBDMSO groups should take an equatorial site. In addition, an NOE experiment with **9a** revealed 3.8% enhancement between the H-2 and the H-6 (1,3-diaxial relationship), but no enhancement between the H-2 and the H-6 could be observed in the NOE experiment with **8a**. These information from ^{1}H NMR analysis confirmed the stereochemical assignment for both **8a** and **9a**. The stereochemistry of 1,3-diene derivative **10b**, a byproduct obtained from the reaction of **7b** (Table 1, entry 4), was also determined on the basis of an NOE experiment. The fact that irradiation of the Ha produced 11.9% enhancement of the Hb while no enhancement of the Hc could be detected in its NOE experiment strongly supported the structure depicted for **10b**.

We next investigated the Pauson−Khand reaction of the enynes **6** with two free hydroxy groups at both the propynyl and homopropynyl positions. The results are

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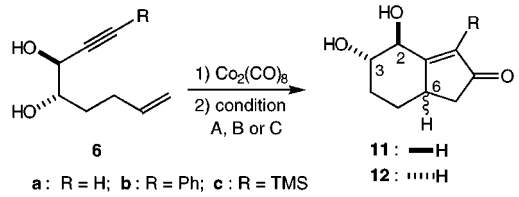
Table 2. Pauson−Khand Reaction of Enyne 6



condition A: 70~75°C in MeCN; **condition B**: TMANO·$2H_2O$ in THF; **condition C**: NMO in CH_2Cl_2

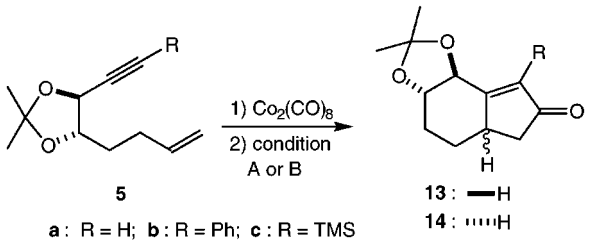
entry	substrate	condition	R	ratio[a] **11:12**	yield[b] (%)
1	**6a**	A	H	17:83	37
2	**6a**	B	H	32:68	72
3	**6b**	A	Ph	2:98	65
4	**6b**	B	Ph	15:85	88
5	**6c**	A	TMS	21:79	22[c]
6	**6c**	B	TMS	27:73	30[d]
7	**6a**	C	H	5:95	88
8	**6b**	C	Ph	1:99	94
9	**6c**	C	TMS	5:95	54[e]

[a] Determined by HPLC analysis. [b] Total yield of **11** and **12**. [c] The cobalt-complexed **6c** was recovered in 12% yield. [d] The starting **6c** was recovered in 29% yield. [e] The starting **6c** was recovered in 15% yield.

summarized in Table 2. Treatment of **6a** with $Co_2(CO)_8$ provided the corresponding cobalt-complexed **6a**, which was successively heated under the condition A to furnish a mixture of **11a** and **12a** in 37% yield (Table 2, entry 1). Although the chemical yield was rather low, the diastereoselectivity was interestingly in sharp contrast to that observed in the Pauson−Khand reaction of the enynes **7** with the sterically bulky TBDMS group on two hydroxy moieties. The similar preferential formation of **12a** over **11a** was recognized when the cyclization of **6a** was performed under the condition B (Table 2, entry 2). The phenyl and the trimethylsilyl (TMS) congeners **6b** and **6c** also showed the same bias in which the predominant formation of **12b**,**c** was constantly recorded (Table 2, entries 3−6). At this stage, we tentatively envisioned that the vicinal two hydroxy functionalities of **6** would control the diastereoselectivity resulting in the predominant production of **12**. In other words, we postulated that the transient five-membered ring possessing the two carbon appendages in a trans relationship that might be formed due to intramolecular hydrogen bonding of the vicinal hydroxy groups governs the stereochemical outcome. With the above assumption, the enyne **6a** was exposed to the condition with *N*-methylmorpholine *N*-oxide (NMO)[15] in methylene chloride (condition C)[16] where the hydrogen bonding would be expected to be more easily achieved compared to conditions A and B. Thus, treatment of the cobalt-complexed **6a** under condition C afforded **12a** in a highly stereoselective fashion (**11a**:**12a** = 9:95) in 88% yield (Table 2, entry 7) as anticipated. Similarly the highly stereoselective construction of **12b** and **12c** could be attained in the cases of **6b** and **6c** as shown in Table 2 (entries 8 and 9).

To obtain further information about the mechanism for the highly stereoselective construction of the bicyclo[4.3.0]nonenone derivative **12**, especially anticipating obtaining some supportive experimental results on the possibility of the hydrogen bonding occurring, the enyne derivative **5** was used as a substrate for the Pauson−Khand reaction. The enyne **5** has the trans dioxolane ring, which might be roughly regarded as a tightly coordinated model of hydrogen bonding. The Pauson−Khand reaction of **5a** through cobalt complexation was carried out under conditions A and B to produce **14a** exclusively as expected (Table 3, entries 1 and 2), although the yield was unsatisfactory. The phenyl congener **5b** gave the corresponding **14b** exclusively along with the recovery of the starting **5b** (Table 3, entries 3 and 4). In the case of **5c** with the terminal TMS group, exclusive formation of the corresponding **14c** was observed. However, decomplexation of the cobalt-complexed moiety became the major reaction pathway to leave almost half of the starting **5c** (Table 3, entries 5 and 6). The low chemical yield of the cyclized product **14** from **5** would be attributed to the serious ring strain arising during the carbon−carbon bond formation process giving rise to the trans-fused dioxatricyclo[7.3.0.$0^{2,6}$]dodecenone skeleton. The dioxolane ring in the enyne **5** seems to be more rigid than the plausible five-membered ring by hydrogen bonding in **6** because the carbon−oxygen bond length must be shorter than that of hydrogen bonding. This would reflect the difference observed in chemical yield between the series of **5** and **6**.

Table 3. Pauson−Khand Reaction of Enyne 5



condition A: 70~75°C in MeCN; **condition B**: TMANO·$2H_2O$ in THF;

entry	substrate	condition	R	ratio[a] **13:14**	yield[b] (%)
1	**5a**	A	H	0:100	28
2	**5a**	B	H	0:100	21
3	**5b**	A	Ph	0:100	56[c]
4	**5b**	B	Ph	0:100	32[d]
5	**5c**	A	TMS	0:100	8[e]
6	**5c**	B	TMS	0:100	2[f]

[a] Determined by HPLC analysis. [b] Total yield of **13** and **14**. [c] The starting **5b** was recovered in 22% yield. [d] The starting **5b** was recovered in 18% yield. [e] The starting **5c** was recovered in 47% yield. [f] The starting **5c** was recovered in 50% yield.

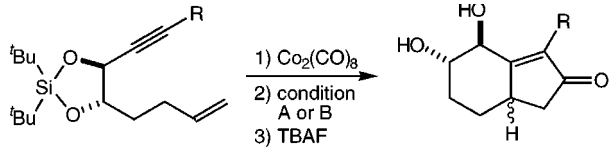
Therefore, it is of great interest to change the dioxolane ring of **5** into a dialkylated silylene ring because the silicon−oxygen bond would be more similar to the plausible hydrogen bonding. Thus, the di-*tert*-butylsilylene derivative **15**, prepared from the dihydroxy compound **6** with di-*tert*-butylsilyl triflate,[17] appeared to be an attractive substrate to see if **15** would undergo the Pauson−Khand reaction to provide selectively the cyclized product with the same stereochemistry as that of **12** and **14** in rather improved yield. The Pauson−Khand reaction of **15** was performed under the conditions according to the case of **5**. The resulting cyclized products with the silylene ring were found to be unstable for chromatographic separation. Thus, these cyclized products were immediately desilylated with tetra-*n*-butyl-

(15) NMO was employed as an amine *N*-oxide instead of TMANO·$2H_2O$ under condition C because of the poor solubility of the latter in dry methylene chloride.

(16) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289.

(17) Corey, E. J.; Hopkins, P. B. *Tetrahedron Lett.* **1982**, *23*, 4871.

Table 4. Pauson−Khand Reaction of Enyne 15



15 **11** : —H; **12** : ⋯H

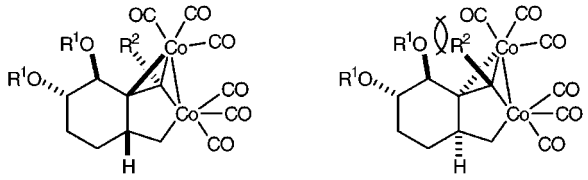
a : R = H; **b** : R = Ph; **c** : R = TMS

condition A: 70~75°C in MeCN; **condition B**: TMANO·$2H_2O$ in THF;

entry	substrate	condition	R	ratio[a] **11:12**	yield[b] (%)
1	**15a**	A	H	3:97	33
2	**15a**	B	H	1:99	54
3	**15b**	A	Ph	4:96	32[c]
4	**15b**	B	Ph	1:99	57[d]
5	**15c**	A	TMS	0:100	10[e]
6	**15c**	B	TMS		*f*

[a] Determined by HPLC analysis. [b] Total yield of **11** and **12**. [c] The desilylated enyne **6b** was recovered in 29% yield. [d] The desilylated enyne **6b** was recovered in 12% yield. [e] The desilylated enyne **6c** was recovered in 50% yield. [f] The desilylated enyne **6c** was recovered in 50% yield.

Scheme 3



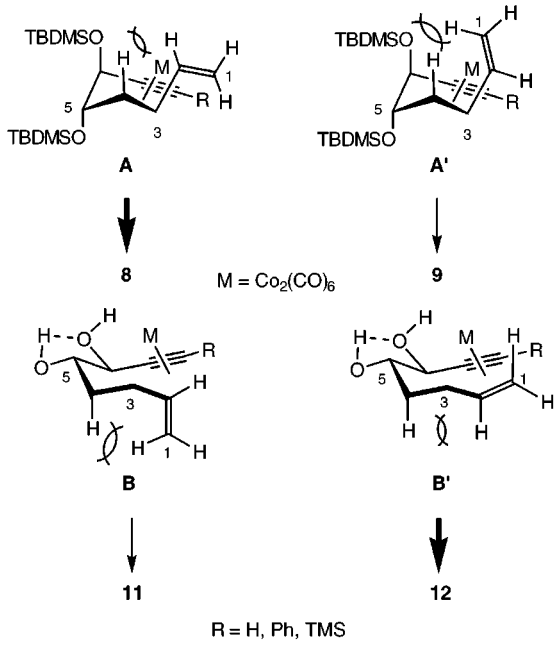
16 **17**

R^1 = TBDMS, H; R^2 = H, Ph, TMS

ammonium fluoride (TBAF) to give the corresponding dihydroxy derivative **12** in a highly stereoselective manner in a moderate yield as shown in Table 4. Combination of these results for the almost exclusive formation of **14** and **12** from **5** and **15**, respectively, with the fact that the dihydroxy derivative **6** afforded **12** in a highly stereoselective fashion strongly indicates the existence of the conformer with a five-membered ring due to hydrogen bonding during the conversion of **6** into **12**.

In the previous paper,[7b] we could interpret the stereoselective formation of the bicyclo[3.3.0]octenone derivatives possessing the same stereochemistry as that of **8** based on the mechanistic hypothesis for the intramolecular Pauson−Khand reaction proposed by Magnus.[18] Highly preferential construction of the bicyclo[4.3.0]-nonenone **8** over its epimer **9** from the enyne **7** again might be tentatively explained in terms of the intermediacy of similar cobalt-metallocycles (Scheme 3). Two plausible intermediates **16** and **17** must exist leading to compounds **8** and its epimer **9**, respectively. In the cobalt-metallocycle **17**, the hydroxy functionality (R^1 = TBDMS) at the propynyl position should have a nonbonding interaction with the substituent at the acetylenic terminus (R^2 group) due to a kind of 1,3-pseudodiaxial relationship in the sterically congested concave face of the transient cobaltabicyclo[4.3.0]nonenone skeleton; therefore, a seriously unfavorable interaction might occur. This would not be the case in the intermediate **16** where the

Scheme 4



M = $Co_2(CO)_6$

R = H, Ph, TMS

R^1 (TBDMS) group and R^2 substituent have a trans alignment. As a result, the cyclization pathway through the intermediate **16** would be preferred over that through **17**. Unfortunately, these analyses cannot be used to explain the highly diastereoselective bias observed in the Pauson−Khand reaction of **6** where the compound **12** having stereochemistry at the C-6 opposite to that of **8** was obtained in a highly stereoselective manner. The intermediate **17** (R^1 = H) derived from **6** seemed to have more serious steric repulsion between the R^1O and R^2 groups than that of **16**, resulting in the predominant formation of **11** over **12**. This prediction, however, was in sharp contrast to the results obtained (Table 2). Therefore, an alternative explanation will be required to understand the highly stereoselective and stereocomplementary construction of the bicyclo[4.3.0]nonenones **8** and **12** drawn in Tables 1 and 2.

Irradiation of the H-6 exhibited 6.6% enhancement of the H-5 in an NOE experiment with **7b**, strongly indicating that these two vicinal protons should preferentially be oriented in an gauche relationship each other (diequatorial-like positions); therefore, the two TBDMSO groups must have an antiperiplanar relation. Furthermore, the ^{1}H NMR spectrum revealed a coupling constant (4.9 Hz) that supports the above conformational analysis. Thus, the preferred conformer for **7b** would be described as the conformer **A** or **A′** shown in Scheme 4. This type of conformational analysis had already been proposed by Saito et al.[19] for the mechanism in a series of stereoselective reactions of compounds with vicinal bis-TBDMSO groups derived from L-tartrate. On the other hand, an NOE experiment with the corresponding dihydroxy compound **6b** showed a rather smaller enhancement (2.3%) between the H-5 and the H-6. In addition, enhancement

(18) (a) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851. (b) Magnus, P.; Exon, C.; Albaugh-Robertson, P. *Tetrahedron* **1985**, 41, 5861.

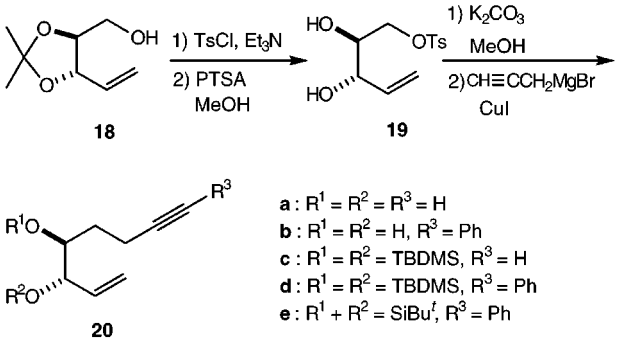
(19) (a) Saito, S.; Hirohara, Y.; Narahara, O.; Moriwake, T. *J. Am. Chem. Soc.* **1989**, *111*, 4533. (b) Saito, S.; Morikawa, Y.; Moriwake, T. *J. Org. Chem.* **1990**, *55*, 5424. (c) Saito, S.; Morikawa, Y.; Moriwake, T. *Synlett* **1990**, 523. (d) Saito, S.; Narahara, O.; Ishikawa, T.; Asahara, M.; Moriwake, T.; Gawronski, J.; Kazmierczak, F. *J. Org. Chem.* **1993**, *58*, 6292. (e) Saito, S.; Ishikawa, T.; Moriwake, T. *Synlett* **1994**, 279. (f) Ishikawa, T.; Tajima, Y.; Fukui, M.; Saito, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1863.

of the C-4 methylene protons (3.5%) could be observed when H-6 was irradiated. This was not the case in an NOE experiment with **7b** in which no enhancement of the C-4 methylene protons by irradiation of the H-6 could be recognized. It is noteworthy to mention here that the coupling constant between the H-5 and the H-6 of **6b** was shown to be the diaxial-like coupling constant (6.4 Hz). Very similar behavior was recorded in an NOE experiment with the dioxolane derivative **5b**. Namely, irradiation of the H-6 effected enhancement of the H-5 (1.1%) and the C-4 methylene protons (4.1%) as well. Furthermore, the coupling constant between the H-5 and the H-6 (7.8 Hz) is found to be closer to that of **6b** than **7b**. On the basis of these observations, we tentatively assumed that the preferred conformer for **6b** should be **B** or **B′**. To obtain further information about the mechanism for the high stereoselectivity, the NMR spectral analysis including an NOE experiment of the cobalt-complexed **6b** and **7b** was attempted several times, but only unclear and broadening peaks could be recorded presumably due to partial decomposition of the cobalt complexes that occurred during the NMR measurement.

There are two conformers, **A** and **A′**, that should be considered for the precursors of the bicyclo[4.3.0]nonenones **8** and **9**, respectively. With the conformer **A′** leading to **9**, the nonbonding interaction of the olefinic proton (H-1) with the C_3-C_4 bond (allylic 1,3-strain), especially with the axial-like H-4, can be predicted on the basis of Saito's mechanistic analysis.[19] The conformer **A** leading to **8** would suffer from a similar interaction between the H-2 and the axial-like H-4. However, the latter repulsion seems to be much less than that of the former judging from the molecular model considerations. As a result, the cyclization of **7** would proceed mainly through the conformer **A** resulting in the highly stereoselective or exclusive formation of **8**. In the case of **6**, a similar postulation would be applied for understanding the high diastereoselectivity observed. The conformer **B** ending up forming the **11** would possess the unfavorable nonbonding interaction of the olefinic proton (H-1) with the axial-like H-4. This kind of serious interaction might not be predicted with the conformer **B′**, although there is another weaker repulsion between the H-2 and the axial-like H-4. Thus, the conformer **B′** would become preferred over the conformer **B** leading to highly diastereoselective construction of **12**.

Intramolecular Pauson−Khand Reaction of (3*S*,4*S*)-3,4-Bis(oxygenated)oct-1-en-7-yne Derivatives. The Pauson−Khand reaction of (5*S*,6*S*)-bis(oxygenated)oct-1-en-7-yne derivatives **6** and **7** have successfully provided the corresponding bicyclo[4.3.0]nonenones in not only a highly stereoselective but also stereocomplementary manner by changing the protecting group on two hydroxy groups. These results prompted us to investigate the Pauson−Khand reaction of the regioisomers of **6** and **7** having two hydroxy functionalities at both allylic and homoallylic positions. The required enynes **20** were easily prepared from L-tartrate via the known alcohol **18**.[7b] Tosylation of **18** was followed by deketalization with PTSA in methanol to afford the diol **19** in 93% yield. Upon exposure to potassium carbonate, **19** underwent ring closure to provide the corresponding epoxy derivative, which was subsequently treated with propargylmagnesium bromide[20] producing **20a** in 65% yield (Scheme 5). The other enynes **20b−e** were obtained from **20a** (see the Experimental Section).

Scheme 5

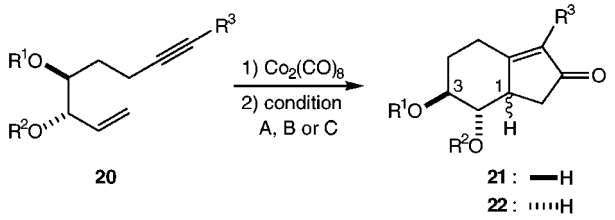


With the required regioisomeric enynes **20** in hand, the next phase in our research was now the Pauson−Khand reaction of these enynes. The dihydroxy derivative **20a** was first used as a substrate for the Pauson−Khand reaction because of anticipation of highly preferential formation of the bicyclo[4.3.0]nonenone derivative **22a** over its isomer **21a** based on the aforementioned results (see Table 2). Actually, the Pauson−Khand reaction of **20a** was carried out under condition C (NMO in methylene chloride)[16] to produce **22a** in a highly stereoselective manner together with its 1-epimer **21a** (entry 1; 81%, **21a**:**22a** = 7:93). The other results were presented in Table 5. The similar stereoselective formation of **22b** was observed in the case of **20b** (Table 5, entry 2). These results are in good agreement with those recorded in the Pauson−Khand reaction of the isomeric dihydroxy derivative **6**. The di-*tert*-butylsilylene compound **20e** also provided **22e** exclusively when exposed to condition B (TMANO in THF)[12] (Table 5, entry 7). On the other hand, the enyne **20c** possessing a bulky protecting group on two hydroxy groups has been shown to furnish **21c** stereoselectively as well as stereocomplementarily (Table 5, entries 3 and 4). In addition, the phenyl congener **20d** gave **21d** predominantly (Table 5, entries 5 and 6), although the diastereoselectivity is somewhat lower compared to the cases of compound **7** (Table 1). It is noteworthy to state that the 1,3-diene derivative **23d** was obtained as a mixture of (*E*)- and (*Z*)-isomers in the cyclization of the enyne **20d** having the phenyl substituent at the acetylenic terminus and a TBDMS protecting group on two hydroxy groups (Table 5, entries 5 and 6). Similar production of the 1,3-diene **10b** was already observed in the Pauson−Khand reaction of **7b** with the same functionalities as those of **20d** (see Table 1, entry 4). Thus, it can be roughly concluded that the behavior of enyne **20** with two hydroxy functionalities at both allylic and homoallylic positions toward the Pauson−Khand conditions is as same as that of enynes **5**, **6**, **7**, and **15** having two hydroxy functionalities at both the propynyl and homopropynyl positions.

The structure of the cyclized products **21** and **22** was elucidated by spectral evidence (see the Experimental Section). The stereochemistry of the newly created stereogenic center of these compounds was determined by ^{1}H NMR spectral considerations. In the ^{1}H NMR spectrum of **21b**, for instance, the vicinal coupling constant between the H-1 and the H-2 showed a typical equato-

(20) Huynh, C.; Derguini-Boumechal, F.; Linstrumelle, G. *Tetrahedron Lett.* **1979**, *17*, 1503.

Table 5. Pauson−Khand Reaction of Enyne 20



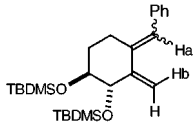
20 **21** : —H
22 : ⋯H

a : $R^1 = R^2 = R^3 = H$; **b** : $R^1 = R^2 = H$, $R^3 = Ph$
c : $R^1 = R^2 = TBDMS$, $R^3 = H$; **d** : $R^1 = R^2 = TBDMS$, $R^3 = Ph$
e : $R^1 + R^2 = SiBu^t_2$ $R^3 = Ph$

condition A: 70~75°C in MeCN; **condition B**: $TMANO{\cdot}2H_2O$ in THF; **condition C** : NMO in CH_2Cl_2

entry	substrate	condition	R1 = R2 R1 + R2	R3	ratio[a] **21:22**	yield[b] (%)
1	**20a**	C	H	H	7:93	81
2	**20b**	C	H	Ph	9:91	97
3	**20c**	A	TBDMS	H	94:6	26
4	**20c**	B	TBDMS	H	93:7	63
5	**20d**	A	TBDMS	Ph	85:15	83[c]
6	**20d**	B	TBDMS	Ph	72:28	48[d]
7	**20e**	B	$SiBu^t_2$	Ph	1:99	17[e]

[a] Determined by HPLC analysis. [b] Total yield of **21** and **22**. [c] (1*S*,2*S*)-4-Benzylidene-1,2-bis(*tert*-butyldimethylsilyloxy)-3-methylenecyclohexane (**23d**) was obtained in 4% yield as a mixture of (4*E*)- and (4*Z*)-isomers in a ratio of 88:12. [d] The 1,3-diene **23d** was obtained in 39% yield as a mixture of (4*E*)- and (4*Z*)-isomers in a ratio of 84:16. [e] The desilylated enyne **20b** was recovered in 17% yield.



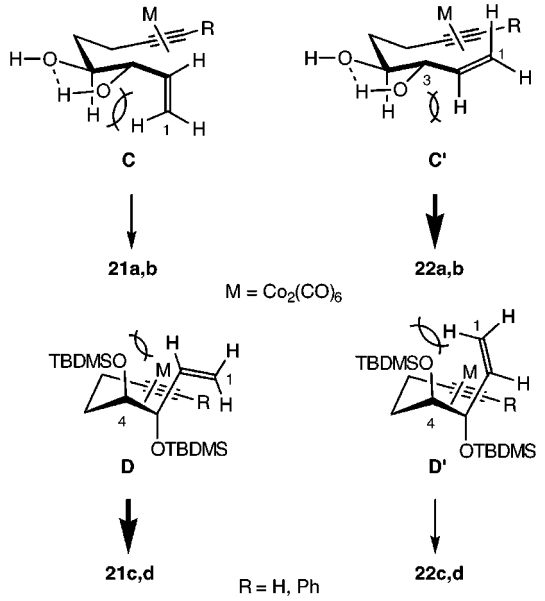
23d

rial−equatorial coupling (J = 3.4 Hz), while that of the 1-epimer **22b** was found to have a larger coupling constant (J = 9.3 Hz) strongly indicating these two protons to be axial. NOE experiments confirmed these assignments. Namely, an NOE experiment with **22b** revealed a 5.6% enhancement between the H-1 and the H-3 (1,3-diaxial relationship), and no enhancement between the H-1 and the H-3 could be observed in an NOE experiment with **21b**. The stereochemistry of **23d** was also clarified by an NOE experiment.[21]

The stereocomplementary formation of the bicyclo[4.3.0]nonenones **21** and **22** can be tentatively interpreted on the basis of the working hypothesis we used to understand the stereochemical outcome observed in a series of the Pauson−Khand reaction of enynes **5**, **6**, **7**, and **15**. Hydrogen bonding of the vicinal diol functionality of the cobalt-complexed enynes **20a**,**b** would give rise to two possible conformers, **C** and **C′**. With conformer **C**, the allylic 1,3-strain between the olefinic proton (H-1) and the C_3-C_4 bond would occur; thereby, the H-1 would also suffer from nonbonding interaction with the axial-like H-4. The conformer **C′**, however, might have much less serious interaction between the H-1 and the axial-like H-4. The highly stereoselective production of **22a**,**b**, therefore, would be rationalized by the above simple comparison of stability of these two conformers. The supportive information for this interpretation was provided by exclusive formation of **22b** from the silylene derivative **20e**. On the other hand, the preferred conformer of the cobalt-complexed **20c**,**d** can be regarded as **D** and **D′** on the basis of Saitoh's reports. The weaker repulsion between the H-2 and the axial-like TBDMSO group at C-4 might be predicted in the conformer **D**, while a very serious nonbonding interaction of the fairly bulky TBDMSO group at C-4 with the vinyl portion in the conformer **D′** would make the cyclization through the conformer **D** a predominant process. Preferential formation of **21c**,**d** over **22c**,**d** would reflect the difference in the stability of these two conformers.

(21) 6.1% enhancement of Hb by irradiation of Ha in (*E*)-**23d** was observed, while no enhancement between Ha and Hb could be detected in (*Z*)-**23d**.

Scheme 6



Conclusion

We have developed a highly stereoselective and stereocomplementary method for construction of the 2,3-bis(oxygenated)-9-(substituted)bicyclo[4.3.0]non-1(9)-en-8-one skeleton by the intramolecular Pauson−Khand reaction of (5*S*,6*S*)-5,6-bis(oxygenated)-8-(substituted)oct-1-en-7-ynes, easily derived from L-tartrate. This procedure has been found to be successfully applied for a highly stereoselective and stereocomplementary formation of 2,3-bis(oxygenated)-7-(substituted)bicyclo[4.3.0]non-6-en-8-one framework. This method would provide useful starting materials with two distinguishable hydroxy groups as well as an enone moiety for synthesis of various kinds of natural products possessing the bicyclo[4.3.0]nonane ring system as a core framework. Further studies on the mechanism for the observed stereoselectivity as well as the stereocomplementarity and its scope and limitation are now in progress.

Experimental Section

Melting points are uncorrected. IR spectra were measured in $CHCl_3$ unless otherwise mentioned. ^1H NMR spectra were taken in $CDCl_3$ unless otherwise indicated. $CHCl_3$ (7.26 ppm) was used as an internal standard for silyl compounds. TMS was employed as an internal standard for other compounds. ^{13}C NMR spectra were recorded in $CDCl_3$ with $CHCl_3$ (77.00 ppm) as an internal standard. CH_2Cl_2 was freshly distilled from phosphorus pentoxide, and THF and Et_2O from sodium diphenyl ketyl, prior to use. All reactions were carried out

under nitrogen atmosphere otherwise stated. Silica gel (silica gel 60, 230−400 mesh, Merck) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4.

(3*S*,4*S*)-1,1-Dibromo-3,4-(isopropylidenedioxy)octa-1,7-diene ((−)-4). A solution of DMSO (3.64 g, 46.6 mmol) in CH_2Cl_2 (20 mL) was added to a solution of oxalyl chloride (2.96 g, 23.3 mmol) in CH_2Cl_2 (20 mL) at −78 °C over a period of 5 min. After the mixture was stirred for 15 min, a solution of the alcohol **3**[9] (2.17 g, 11.7 mmol) in CH_2Cl_2 (20 mL) was added to the CH_2Cl_2 solution, and the reaction mixture was stirred at the same temperature for an additional hour. Et_3N (7.07 g, 69.9 mmol) was then added to the reaction mixture, which was gradually warmed to room temperature and diluted with CH_2Cl_2. The CH_2Cl_2 solution was washed with water and brine, dried, and concentrated to leave the crude aldehyde. To a solution of PPh_3 (12.2 g, 46.6 mmol) in CH_2Cl_2 (30 mL) was added a solution of CBr_4 (7.70 g, 23.3 mmol) in CH_2Cl_2 (30 mL) at 0 °C, and the reaction mixture was stirred for 10 min. A solution of the crude aldehyde in CH_2Cl_2 (20 mL) was then added to a solution of the ylide in CH_2Cl_2 solution thus adjusted at 0 °C, and stirring was continued for 3 h at room temperature. The reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2, which was washed with water and brine, dried, and concentrated to give the residual solids. The solids were washed with hexane several times, and the filtrate was concentrated to leave a residual oil, which was chromatographed with hexane−AcOEt (40:1) to give (−)-**4** (2.84 g, 72%) as a pale yellow oil: $[\alpha]^{26}_D$ −19.7 (*c* 0.21, $CHCl_3$); IR 1641 cm^{-1}; ^1H NMR δ 6.44 (d, 1H, J = 8.3 Hz), 5.82 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.05 (dd, 1H, J = 17.1, 1.5 Hz), 4.99 (dd, 1H, J = 10.3, 1.5 Hz), 4.30 (t, 1H, J = 8.3 Hz), 3.79 (dt, 1H, J = 8.3, 6.4 Hz), 2.24 (m, 1H), 2.16 (m, 1H), 1.76−1.69 (m, 2H), 1.42 (s, 3H), 1.38 (s, 3H); ^{13}C NMR δ 137.63, 135.74, 115.20, 109.40, 93.98, 80.65, 79.19, 31.16, 29.89, 27.21, 26.72; CIMS *m*/*z* 343 (M^+ + 5, 46), 341 (M^+ + 3, 100), 339 (M^+ + 1, 54). Anal. Calcd for $C_{11}H_{16}Br_2O_2$: C, 38.85; H, 4.74. Found: C, 38.88; H, 4.75.

(5*S*,6*S*)-5,6-(Isopropylidenedioxy)oct-1-en-7-yne ((−)-5a). To a solution of (−)-**4** (2.84 g, 8.36 mmol) in dry Et_2O (80 mL) was added BuLi in hexane (1.40 M, 15 mL, 20.9 mmol) at 0 °C, and the reaction mixture was stirred for 10 min, quenched by addition of saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexanes−Et_2O (30:1) to give (−)-**5a** (1.18 g, 78%) as a pale yellow oil: $[\alpha]^{27}_D$ −7.3 (*c* 0.21, $CHCl_3$); IR 3307, 1641 cm^{-1}; ^1H NMR δ 5.84 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.07 (dd, 1H, J = 17.1, 2.0 Hz), 5.00 (dd, 1H, J = 10.3, 2.0 Hz), 4.22 (dd, 1H, J = 7.3, 2.0 Hz), 4.06 (td, 1H, J = 7.3, 5.9 Hz), 2.52 (d, 1H, J = 2.0 Hz), 2.30−2.13 (m, 2H), 1.80−1.70 (m, 2H), 1.46 (s, 3H), 1.41 (s, 3H); ^{13}C NMR δ 137.48, 115.18, 109.97, 80.85, 80.70, 74.65, 70.15, 31.50, 29.69, 27.06, 26.09; MS *m*/*z* 180 (M^+, 1.3); HRMS calcd for $C_{11}H_{16}O_2$ 180.1151, found 180.1156.

(3*S*,4*S*)-Oct-7-en-1-yne-3,4-diol ((−)-6a). A solution of (−)-**5a** (700 mg, 3.88 mmol) and PTSA (74 mg, 0.39 mmol) in MeOH (40 mL) was stirred at 50 °C for 24 h, and MeOH was evaporated off. The residue was chromatographed with hexane−AcOEt (2:1) to give (−)-**6a** (503 mg, 92%) as a colorless oil: $[\alpha]^{26}_D$ −11.1 (*c* 0.21, $CHCl_3$); IR 3610, 3410, 3310, 1645 cm^{-1}; ^1H NMR δ 5.83 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.07 (dd, 1H, J = 17.1, 2.0 Hz), 4.99 (dd, 1H, J = 10.3, 2.0 Hz), 4.17 (m, 1H), 3.67 (m, 1H), 3.09 (d, 1H, J = 5.9 Hz), 2.83 (d, 1H, J = 3.9 Hz), 2.51 (d, 1H, J = 2.4 Hz), 2.27 (m, 1H), 2.18 (m, 1H), 1.78 (m, 1H), 1.59 (m, 1H); ^{13}C NMR δ 137.95, 115.10, 82.30, 74.61, 74.12, 65.86, 31.43, 29.60; MS *m*/*z* 140 (M^+, 1.9); HRMS calcd for $C_8H_{12}O_2$ 140.0837, found 140.0836.

(5*S*,6*S*)-5,6-Bis(*tert*-butyldimethylsiloxy)oct-1-en-7-yne ((−)-7a). To a solution of (−)-**6a** (180 mg, 1.28 mmol) and imidazole (525 mg, 7.70 mmol) in DMF (1.2 mL) was added TBDMSCl (579 mg, 3.84 mmol) at room temperature. The reaction mixture was heated at 50 °C for 4.5 h, quenched by addition of saturated aqueous $NaHCO_3$, and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane afforded (−)-**7a** (469 mg, 99%) as a colorless oil: $[\alpha]^{27}_D$ −26.5 (*c* 0.20, $CHCl_3$); IR 3310, 1645 cm^{-1}; ^1H NMR δ 5.83 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.03 (dd, 1H, J = 17.1, 1.5 Hz), 4.95 (dd, 1H, J = 10.3, 1.5 Hz), 4.34 (dd, 1H, J = 4.9, 2.0 Hz), 3.60 (ddd, 1H, J = 8.3, 4.9, 3.4 Hz), 2.32 (d, 1H, J = 2.0 Hz), 2.23 (m, 1H), 2.07 (m, 1H), 1.82 (m, 1H), 1.71 (m, 1H), 0.91 (s, 18H), 0.14 (s, 3H), 0.10 (s, 3H), 0.07 (s, 6H); ^{13}C NMR 138.89, 114.30, 83.06, 74.02, 73.21, 66.85, 30.89, 29.58, 25.82, 25.77, 18.17, 18.08, −4.40, −4.51, −4.67, −4.98; MS *m*/*z* 368 (M^+, 4.2). Anal. Calcd for $C_{20}H_{40}O_2Si_2$: C, 65.15; H, 10.94. Found: C, 64.80; H, 11.04.

(5*S*,6*S*)-5,6-(Isopropylidenedioxy)-8-phenyloct-1-en-7-yne ((−)-5b). To a solution of (−)-**5a** (1.00 g, 5.55 mmol) and iodobenzene (1.36 g, 6.66 mmol) in THF (55 mL) were successively added $Pd(PPh_3)_2Cl_2$ (117 mg, 0.17 mmol), CuI (63 mg, 0.33 mmol), and diisopropylamine (5.61 g, 55.5 mmol) at room temperature. The reaction mixture was stirred for 1.5 h and the precipitates were filtered off. The filtrate was concentrated to leave a residual oil, which was chromatographed with hexane-AcOEt (50:1) to afford (−)-**5b** (1.37 g, 96%) as a colorless oil: $[\alpha]^{26}_D$ −36.4 (*c* 0.20, $CHCl_3$); IR 2233, 1642 cm^{-1}; ^1H NMR δ 7.48−7.42 (m, 2H), 7.35−7.28 (m, 3H), 5.87 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.09 (dd, 1H, J = 17.1, 1.5 Hz), 5.01 (dd, 1H, J = 10.3, 1.5 Hz), 4.47 (d, 1H, J = 7.8 Hz), 4.13 (td, 1H, J = 7.8, 5.4 Hz), 2.34−2.19 (m, 2H), 1.85−1.74 (m, 2H), 1.51 (s, 3H), 1.45 (s, 3H); ^{13}C NMR δ 137.63, 131.79, 128.61, 128.25, 122.30, 115.15, 109.76, 86.49, 85.59, 80.97, 71.00, 31.61, 29.76, 27.17, 26.31; MS *m*/*z* 256 (M^+, 16). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.36; H, 8.09.

(3*S*,4*S*)-1-Phenyloct-7-en-1-yne-3,4-diol ((−)-6b). According to the procedure described for preparation of **6a** from **5a**, (−)-**6b** (36 mg, 95%) was obtained from compound (−)-**5b** (45 mg, 0.18 mmol) as a colorless oil: $[\alpha]^{27}_D$ −13.9 (*c* 0.50, $CHCl_3$); IR 3580, 3421, 2228, 1640 cm^{-1}; ^1H NMR δ 7.46−7.41 (m, 2H), 7.35−7.27 (m, 3H), 5.85 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.08 (dd, 1H, J = 17.1, 2.0 Hz), 4.99 (dd, 1H, J = 10.3, 2.0 Hz), 4.40 (d, 1H, J = 6.4 Hz), 3.76 (ddd, 1H, J = 9.3, 6.4, 2.9 Hz), 2.73 (br s, 2H), 2.32 (m, 1H), 2.22 (m, 1H), 1.85 (m, 1H), 1.66 (m, 1H); ^{13}C NMR δ 138.08, 131.72, 128.64, 128.28, 122.10, 115.06, 87.19, 86.42, 74.38, 66.69, 31.66, 29.71; MS *m*/*z* 216 (M^+, 1.9); HRMS calcd for $C_{14}H_{16}O_2$ 216.1150, found 216.1148.

(5*S*,6*S*)-5,6-Bis(*tert*-butyldimethylsiloxy)-8-phenyloct-1-en-7-yne ((−)-7b). According to the procedure described for preparation of **7a** from **6a**, (−)-**7b** (198 mg, 96%) was obtained from diol (−)-**6b** (100 mg, 0.46 mmol) as a colorless oil: $[\alpha]^{27}_D$ −51.9 (*c* 0.50, $CHCl_3$); IR 1639 cm^{-1}; ^1H NMR δ 7.43−7.38 (m, 2H), 7.32−7.27 (m, 3H), 5.85 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.04 (dd, 1H, J = 17.1, 1.5 Hz), 4.96 (dd, 1H, J = 10.3, 1.5 Hz), 4.56 (d, 1H, J = 4.9 Hz), 3.69 (ddd, 1H, J = 8.3, 4.9, 3.4 Hz), 2.25 (m, 1H), 2.11 (m, 1H), 1.86 (m, 1H), 1.76 (m, 1H), 0.93 (s, 9H), 0.92 (s, 9H), 0.19 (s, 3H), 0.14 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR δ 139.01, 131.48, 128.18, 127.96, 123.34, 114.27, 88.95, 85.23, 74.47, 67.46, 31.38, 29.60, 25.86, 18.28, 18.10, −4.31, −4.45, −4.78; MS *m*/*z* 444 (M^+, 49). Anal. Calcd for $C_{26}H_{44}O_2Si_2$: C, 70.21; H, 9.97. Found: C, 69.92; H, 10.12.

(5*S*,6*S*)-5,6-(Isopropylidenedioxy)-8-(trimethylsilyl)-oct-1-en-7-yne ((−)-5c). To a solution of (−)-**5a** (100 mg, 0.56 mmol) in THF (3.7 mL) was added BuLi in hexane (1.54 M; 0.44 mL, 0.68 mmol) at −78 °C. After being stirred at the same temperature for 10 min, TMSCl (72.7 mg, 0.68 mmol) was added to the reaction mixture. The mixture was stirred for 30 min at the same temperature, quenched by addition of saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane afforded (−)-**5c** (133 mg, 95%) as a colorless oil: $[\alpha]^{26}_D$ −21.2 (*c* 0.50, $CHCl_3$); IR 2178, 1641 cm^{-1}; ^1H NMR δ 5.84 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.06 (dd, 1H, J = 17.1, 2.0 Hz), 4.99 (dd, 1H, J = 10.3, 2.0 Hz), 4.22 (d, 1H, J = 7.8 Hz), 4.00 (m, 1H), 2.28−2.13 (m, 2H), 1.78−1.67 (m, 2H), 1.45 (s, 3H), 1.39 (s, 3H), 0.16 (s, 9H); ^{13}C NMR 137.63, 115.06, 109.70, 101.96, 91.72, 80.86, 70.84, 31.56, 29.65, 27.08, 26.22, −0.29; MS *m*/*z*

252 (M^+, 0.8). Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.39; H, 9.68.

(3*S*,4*S*)-1-(Trimethylsilyl)oct-7-en-1-yne-3,4-diol ((−)-6c). According to the procedure described for preparation **6a** from **5a**, (−)-**6c** (526 mg, 89%) was obtained from (−)-**5c** (700 mg, 2.77 mmol) as colorless solids: mp 66.0−67.0 °C (cyclohexane); $[\alpha]^{27}_D$ −10.3 (*c* 0.50, $CHCl_3$); IR 3578, 3407, 2174, 1640 cm^{-1}; ^1H NMR δ 5.84 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.07 (dd, 1H, *J* = 17.1, 1.5 Hz), 5.00 (dd, 1H, *J* = 10.3, 1.5 Hz), 4.16 (t, 1H, *J* = 5.9 Hz), 3.65 (m, 1H), 2.34 (d, 1H, *J* = 3.4 Hz), 2.27 (m, 1H), 2.26 (d, 1H, *J* = 5.9 Hz), 2.20 (m, 1H), 1.76 (m, 1H), 1.60 (m, 1H), 0.18 (s, 9H); ^{13}C NMR δ 138.08, 114.99, 103.81, 91.54, 74.20, 66.60, 31.52, 29.62, −0.27; CIMS *m*/*z* 213 (M^+ + 1, 5.4). Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49. Found: C, 62.00; H, 9.57.

(5*S*,6*S*)-5,6-Bis(*tert*-butyldimethylsiloxy)-8-(trimethylsilyl)oct-1-en-7-yne ((−)-7c). According to the procedure described for preparation of **5c** from **5a**, (−)-**7c** (1.64 g, 96%) was obtained from (−)-**7a** (1.43 g, 3.88 mmol) as a colorless oil: $[\alpha]^{27}_D$ −1.7 (*c* 0.20, $CHCl_3$); IR 1645 cm^{-1}; ^1H NMR δ 5.83 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.02 (dd, 1H, *J* = 17.1, 2.0 Hz), 4.95 (dd, 1H, *J* = 10.3, 2.0 Hz), 4.31 (d, 1H, *J* = 5.4 Hz), 3.59 (m, 1H), 2.19 (m, 1H), 2.09 (m, 1H), 1.76 (m, 1H), 1.69 (m, 1H), 0.90 (s, 9H), 0.89 (s, 9H), 0.14 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR 139.07, 114.18, 105.48, 90.03, 74.23, 67.35, 31.39, 29.47, 25.86, 18.28, 18.08, −0.21, −4.33, −4.47, −4.51, −4.74; MS *m*/*z* 440 (M^+, 1.8); HRMS calcd for $C_{23}H_{48}O_2Si_3$ 440.2962, found 440.2962.

(5*S*,6*S*)-5,6-(Di-*tert*-butylsilylenedioxy)oct-1-en-7-yne ((−)-15a). To a solution of (−)-**6a** (80.1 mg, 0.57 mmol) and 2,6-lutidine (367 mg, 1.32 mmol) in CH_2Cl_2 (1.10 mL) was added di-*tert*-butylsilyl ditriflate (0.44 mL, 1.32 mmol) at 0 °C. The reaction mixture was stirred for 6 h at room temperature and concentrated to leave residual oil, chromatography of which with hexane−AcOEt (40:1) was carried out by using 1% Et_3N containing solvent pre-eluting silica gel with to afford (−)-**15a** (140 mg, 87%) as a colorless oil: $[\alpha]^{26}_D$ −13.9 (*c* 0.51, $CHCl_3$); IR 3310, 1645 cm^{-1}; ^1H NMR 5.85 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.07 (dd, 1H, *J* = 17.1, 1.5 Hz), 4.99 (dd, 1H, *J* = 10.3, 1.5 Hz), 4.25 (dd, 1H, *J* = 8.3, 2.0 Hz), 3.97 (td, 1H, *J* = 8.3, 4.4 Hz), 2.50 (d, 1H, *J* = 2.0 Hz), 2.30 (m, 1H), 2.22 (m, 1H), 1.74 (m, 1H), 1.63 (m, 1H), 1.07 (s, 9H), 1.03 (s, 9H); ^{13}C NMR δ 137.93, 114.93, 82.09, 80.25, 74.00, 70.28, 33.69, 29.76, 26.90, 26.85, 20.97, 20.69; MS *m*/*z* 280 (M^+, 4.4). Anal. Calcd for $C_{16}H_{28}O_2Si$: C, 68.52; H, 10.06. Found: C, 68.55; H, 10.50.

(5*S*,6*S*)-5,6-(Di-*tert*-butylsilylenedioxy)-8-phenyloct-1-en-7-yne ((−)-15b). According to the procedure described for preparation of **15a** from **6a**, (−)-**15b** (153 mg, 93%) was obtained from (−)-**6b** (100 mg, 0.46 mmol) as a colorless oil: $[\alpha]^{26}_D$ −28.3 (*c* 0.19, $CHCl_3$); IR 2232, 1640 cm^{-1}; ^1H NMR δ 7.48−7.42 (m, 2H), 7.34−7.28 (m, 3H), 5.88 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.08 (dd, 1H, *J* = 17.1, 1.5 Hz), 5.00 (dd, 1H, *J* = 10.3, 1.5 Hz), 4.50 (d, 1H, *J* = 8.8 Hz), 4.06 (m, 1H), 2.34 (m, 1H), 2.26 (m, 1H), 1.80 (m, 1H), 1.70 (m, 1H), 1.10 (s, 9H), 1.06 (s, 9H); ^{13}C NMR δ 138.06, 131.84, 128.46, 128.21, 114.86, 87.17, 85.90, 80.50, 71.03, 33.89, 29.80, 26.97, 26.92, 21.04, 20.74; MS *m*/*z* 356 (M^+, 46); HRMS calcd for $C_{22}H_{32}O_2Si$ 356.2172, found 356.2166.

(5*S*,6*S*)-5,6-(Di-*tert*-butylsilylenedioxy)-8-(trimethylsilyl)oct-1-en-7-yne ((−)-15c). According to the procedure described for preparation of **15a** from **6a**, (−)-**15c** (154 mg, 92%) was obtained from (−)-**6c** (100 mg, 0.47 mmol) as a colorless oil: $[\alpha]^{27}_D$ −14.6 (*c* 0.50, $CHCl_3$); IR 2181, 1639 cm^{-1}; ^1H NMR δ 5.86 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.07 (dd, 1H, *J* = 17.1, 1.5 Hz), 4.99 (dd, 1H, *J* = 10.3, 1.5 Hz), 4.26 (d, 1H, *J* = 8.8 Hz), 3.95 (m, 1H), 2.27 (m, 1H), 2.22 (m, 1H), 1.73 (m, 1H), 1.65 (m, 1H), 1.07 (s, 9H), 1.02 (s, 9H), 0.17 (s, 9H); ^{13}C NMR δ 138.04, 114.79, 103.61, 90.89, 80.40, 70.89, 33.82, 29.69, 26.94, 26.88, 20.95, 20.69, −0.21; MS *m*/*z* 352 (M^+, 25). Anal. Calcd for $C_{19}H_{36}O_2Si_2$: C, 64.71; H, 10.29. Found: C, 64.35; H, 10.51.

General Procedure for Pauson−Khand Reaction of Enynes 5−7 and 15. Condition A. $Co_2(CO)_8$ (0.24 mmol) was added to a solution of enyne (0.20 mmol) in Et_2O (2.0 mL) at room temperature. After being stirred for 1 h, the Et_2O solution was concentrated to leave the residue, which was taken up in MeCN (2.0 mL). A solution of the crude cobalt-complexed enyne in MeCN was heated at 70−75 °C untile complete disappearance of the starting material (monitored by TLC). The reaction mixture was passed through a short pad of Celite, and the filtrate was concentrated to dryness. Chromatography of the residue with hexane−AcOEt gave cyclized products. **Condition B.** The crude cobalt-complexed enyne was dissolved in THF (10 mL) to which TMANO·$2H_2O$ (1.20 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature until complete disappearance of the starting material (monitored by TLC). Workup and chromatography as described in condition A gave product. **Condition C.** $Co_2(CO)_8$ (0.24 mmol) was added to a solution of enyne (0.20 mmol) in CH_2Cl_2 (10 mL) at room temperature. After the mixture was stirred for 2 h, NMO (2.00 mmol) was added at 0 °C, and the mixture was further stirred at 0 °C until complete disappearance of the starting material (monitored by TLC). Workup and chromatography gave products. Chemical yield and product ratio obtained under conditions A−C are summarized in Tables 1−4. In the case of enyne **15** (Table 4), the cyclized products were desilylated as follows: To a solution of the resulting cyclized products in THF (5.0 mL) was added TBAF in THF (1.0 M, 0.6 mmol, 0.6 mL) at room temperature. The reaction mixture was stirred at the same temperature untile complete disappearance of the cyclized silylene derivatives (monitored by TLC). The reaction was quenched by addition of MeOH. The reaction mixture was passed through a short pad of Celite, and the filtrate was concentrated to dryness. Chromatography of the residue with hexane−AcOEt gave products.

(2*S*,3*S*,6*S*)- and (2*S*,3*S*,6*R*)-2,3-Bis(*tert*-butyldimethylsiloxy)bicyclo[4.3.0]non-1(9)-en-8-ones ((−)-8a and (+)-9a). A mixture of (−)-**8a** and (+)-**9a** was obtained in a ratio of 88:12 (entry 1 in Table 1). The ratio was determined by HPLC analysis (hexane/2-propanol = 30:1; 1.0 mL/min; retention time of (−)-**8a** was recorded as 4.1 min and that of (+)-**9a** as 5.2 min). Compound (−)-**8a** was obtained as a colorless oil: $[\alpha]^{25}_D$ −118.7 (*c* 0.21, $CHCl_3$); IR 1704, 1631 cm^{-1}; ^1H NMR δ 5.89 (m, 1H), 4.33 (d, 1H, *J* = 3.4 Hz), 3.90 (m, 1H), 2.98 (m, 1H), 2.54 (dd, 1H, *J* = 19.0, 6.3 Hz), 2.03 (m, 1H), 1.97 (dd, 1H, *J* = 19.0, 2.0 Hz), 1.84 (m, 1H), 1.54 (m, 1H), 1.49 (m, 1H), 0.87 (s, 9H), 0.82 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR δ 209.43, 182.16, 129.15, 72.49, 70.66, 42.21, 37.13, 28.92, 27.26, 25.61, 17.97, 17.88, −4.81, −4.92, −4.98, −5.05; MS *m*/*z* 396 (M^+, 2.8). Anal. Calcd for $C_{21}H_{40}O_3Si_2$: C, 63.58; H, 10.16. Found: C, 63.20; H, 10.33. Compound (+)-**9a** was obtained as colorless solids: mp 64.0−65.0 °C (MeOH); [α +171.2 (*c* 0.22, $CHCl_3$); IR 1704, 1622 cm^{-1}; ^1H NMR δ 6.11 (t, 1H, *J* = 1.5 Hz), 4.14 (dd, 1H, *J* = 8.3, 1.5 Hz), 3.50 (ddd, 1H, *J* = 11.2, 8.3, 4.4 Hz), 2.71 (m, 1H), 2.61 (dd, 1H, *J* = 19.0, 6.8 Hz), 2.06 (m, 1H), 2.02 (dd, 1H, *J* = 19.0, 1.5 Hz), 1.97 (m, 1H), 1.54 (m, 1H), 1.04 (m, 1H), 0.93 (s, 9H), 0.89 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.00 (s, 3H); ^{13}C NMR δ 208.00, 184.69, 127.39, 77.49, 76.53, 42.07, 40.52, 33.52, 31.00, 26.04, 18.19, 18.10, −3.66, −4.27, −4.80; MS *m*/*z* 396 (M^+, 0.3); HRMS calcd for $C_{21}H_{40}O_3Si_2$ 396.2516, found 396.2520.

(2*S*,3*S*,6*S*)-2,3-Bis(*tert*-butyldimethylsiloxy)-9-phenylbicyclo[4.3.0]non-1(9)-en-8-one ((−)-8b). Compound (−)-**8b** was obtained as a colorless oil: $[\alpha]^{26}_D$ −94.7 (*c* 0.50, $CHCl_3$); IR 1695, 1646 cm^{-1}; ^1H NMR δ 7.40−7.29 (m, 5H), 4.66 (d, 1H, *J* = 3.4 Hz), 4.01 (m, 1H), 3.09 (m, 1H), 2.72 (dd, 1H, *J* = 19.0, 6.8 Hz), 2.13 (dd, 1H, *J* = 19.0, 2.0 Hz), 2.12 (m, 1H), 1.94 (m, 1H), 1.67−1.52 (m, 2H), 0.87 (s, 9H), 0.81 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H), −0.19 (s, 3H), −0.22 (s, 3H); ^{13}C NMR δ 207.37, 174.61, 139.84, 130.93, 129.27, 127.89, 127.76, 73.17, 67.85, 41.71, 35.51, 28.90, 27.60, 25.84, 25.57, 18.10, 17.83, −4.76, −4.99, −5.23; MS *m*/*z* 472 (M^+, 4.5). Anal. Calcd for $C_{27}H_{44}O_3Si_2$: C, 68.59; H, 9.38. Found: C, 68.24; H, 9.47.

(2S,3S,6S)-2,3-Bis(*tert*-butyldimethylsiloxy)-9-(trimethylsilyl)bicyclo[4.3.0]non-1(9)-en-8-one ((−)-8c). Compound (−)-**8c** was obtained as colorless solids: mp 72.0−73.0 °C (MeOH); $[\alpha]^{26}_D$ −92.2 (*c* 0.20, $CHCl_3$); IR 1680, 1599 cm^{-1}; ^1H NMR δ 4.65 (d, 1H, *J* = 3.9 Hz), 3.91 (m, 1H), 3.05 (m,

1H), 2.48 (dd, 1H, J = 19.0, 6.8 Hz), 2.07 (m, 1H), 1.90 (dd, 1H, J = 19.0, 2.4 Hz), 1.84 (m, 1H), 1.53 (m, 1H), 1.46 (m, 1H), 0.89 (s, 9H), 0.85 (s, 9H), 0.23 (s, 9H), 0.10 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.02 (s, 3H); ^{13}C NMR δ 214.16, 187.94, 139.46, 73.21, 69.69, 42.39, 38.76, 29.56, 27.32, 25.82, 25.64, 17.97, −0.34, −4.35, −4.62, −4.69, −4.96; MS m/z 468 (M^+, 35). Anal. Calcd for $C_{24}H_{48}O_3Si_3$: C, 61.48; H, 10.32. Found: C, 61.19; H, 10.53.

(2*S*,3*S*,6*S*)- and (2*S*,3*S*,6*R*)-2,3-Dihydroxybicyclo[4.3.0]-non-1(9)-en-8-ones ((−)-**11a and** (+)-**12a).** A mixture of stereoisomers (−)-**11a** and (+)-**12a** was obtained in the ratio of 17 to 83 (entry 1 in Table 2). The ratio was determined by HPLC analysis (hexane/2-propanol = 1:1; 0.5 mL/min; retention time of (−)-**11a** was recorded as 9.4 min and taht of (+)-**12a** as 10.1 min). Compound (−)-**11a** was obtained as colorless solids: mp 121−122 °C (AcOEt); $[\alpha]_D^{24}$ −287.6 (*c* 0.20, MeOH); IR (KBr) 3425, 3335, 1660, 1623 cm^{-1}; ^{1}H NMR δ (CD_3OD) 6.01 (d, 1H, J = 1.5 Hz), 4.48 (d, 1H, J = 3.4 Hz), 4.01 (m, 1H), 3.10 (m, 1H), 2.58 (dd, 1H, J = 19.0, 6.4 Hz), 2.09 (m, 1H), 1.98 (dd, 1H, J = 19.0, 2.0 Hz), 1.92 (m, 1H), 1.70 (m, 1H), 1.50 (m, 1H); ^{13}C NMR δ (CD_3OD) 212.25, 184.94, 130.67, 72.34, 70.47, 43.20, 38.56, 29.85, 27.53; MS m/z 168 (M^+, 100). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 63.90; H, 7.23. Compound (+)-**12a** was obtained as colorless solids: mp 152−153 °C (AcOEt); $[\alpha]^{26}_D$ +234.3 (*c* 0.20, MeOH); IR (KBr) 3428, 3301, 1685, 1670, 1619 cm^{-1}; ^{1}H NMR δ (CD_3OD) 6.06 (t, 1H, J = 1.5 Hz), 4.17 (br d, 1H, J = 8.8 Hz), 3.41 (ddd, 1H, J = 11.2, 8.8, 4.4 Hz), 2.84 (m, 1H), 2.62 (dd, 1H, J = 19.1, 6.3 Hz), 2.11 (m, 1H), 2.04 (dd, 1H, J = 19.1, 2.0 Hz), 2.01 (m, 1H), 1.57 (m, 1H), 1.10 (m, 1H); ^{13}C NMR δ (CD_3OD) 211.33, 187.67, 126.43, 77.43, 76.74, 42.94, 41.83, 32.90, 31.80; MS m/z 168 (M^+, 100). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 63.94; H, 7.26.

(2*S*,3*S*,6*S*)- and (2*S*,3*S*,6*R*)-2,3-Dihydroxy-9-phenylbicyclo[4.3.0]-non-1(9)-en-8-ones ((−)-11b and (+)-12b). A mixture of stereoisomers (−)-**11b** and (+)-**12b** was obtained in a ratio of 15:85 (entry 4 in Table 2). The ratio was determined by HPLC analysis (CH_2Cl_2/2-propanol = 10:1; 1.0 mL/min; retention time of (−)-**11b** was recorded as 6.0 min and that of (+)-**12b** as 4.4 min). Compound (−)-**11b** was obtained as colorless solids: mp 245−246 °C (AcOEt); $[\alpha]^{27}_D$ −133.1 (*c* 0.19, MeOH); IR (KBr) 3418, 3357, 1679, 1651 cm^{-1}; ^{1}H NMR δ (CD_3OD) 7.42−7.29 (m, 5H), 4.65 (d, 1H, J = 3.3), 4.02 (m, 1H), 3.16 (m, 1H), 2.71 (dd, 1H, J = 19.1, 6.6 Hz), 2.17 (m, 1H), 2.12 (dd, 1H, J = 19.1, 2.0 Hz), 1.98 (m, 1H), 1.74 (m, 1H), 1.60 (m, 1H); ^{13}C NMR δ (CD_3OD) 209.89, 176.98, 142.04, 132.25, 130.54, 129.12, 128.98, 72.49, 68.51, 42.84, 36.98, 29.76, 27.74; MS m/z 244 (M^+, 100); HRMS calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1096. Compound (+)-**12b** was obtained as colorless solids: mp 96−97 °C (hexane−AcOEt); $[\alpha]^{26}_D$ +120.3 (*c* 0.21, MeOH); IR (KBr) 3441, 3264, 1720, 1705, 1654, 1633 cm^{-1}; ^{1}H NMR δ (CD_3OD) 7.30−7.21 (m, 3H), 7.20−7.17 (m, 2H), 4.33 (d, 1H, J = 9.3 Hz), 3.55 (ddd, 1H, J = 11.2, 9.3, 4.4 Hz), 2.84 (m, 1H), 2.71 (dd, 1H, J = 19.0, 6.4 Hz), 2.16 (m, 1H), 2.13 (dd, 1H, J = 19.0, 1.5 Hz), 2.08 (m, 1H), 1.62 (m, 1H), 1.22 (m, 1H); ^{13}C NMR δ (CD_3OD) 210.06, 177.37, 139.85, 133.80, 131.39, 128.08, 127.99, 78.88, 76.60, 42.08, 40.84, 33.01, 32.07; MS m/z 244 (M^+, 100). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.45; H, 6.75.

(2*S*,3*S*,6*S*)- and (2*S*,3*S*,6*R*)-2,3-Dihydroxy-9-(trimethylsilyl)bicyclo[4.3.0]non-1(9)-en-8-ones ((−)-11c and (+)-12c). A mixture of stereoisomers (−)-**11c** and (+)-**12c** was obtained in a ratio of 21:79 (entry 5 in Table 2). The ratio was determined by HPLC analysis (CH_2Cl_2/2-propanol = 10:1; 1.0 mL/min; retention time of (−)-**11c** was recorded as 6.0 min and that of (+)-**12c** as 4.5 min). Compound (−)-**11c** was obtained as colorless solids: mp 118−119 °C (hexane−AcOEt); $[\alpha]^{23}_D$ −193.7 (*c* 0.20, MeOH); IR (KBr) 3422, 3288, 1681, 1591 cm^{-1}; ^{1}H NMR δ (CD_3OD) 4.72 (d, 1H, J = 3.4 Hz), 4.01 (m, 1H), 3.09 (m, 1H), 2.50 (dd, 1H, J = 19.0, 6.8 Hz), 2.11 (m, 1H), 1.91 (dd, 1H, J = 19.0, 2.4 Hz), 1.90 (m, 1H), 1.67 (m, 1H), 1.48 (m, 1H), 0.23 (s, 9H); ^{13}C NMR δ (CD_3OD) 216.42, 191.12, 141.95, 72.65, 69.92, 43.56, 40.03, 30.15, 27.62, −0.22; MS m/z 240 (M^+, 69). Anal. Calcd for $C_{12}H_{20}O_3Si$: C, 59.96; H, 8.39. Found: C, 59.57; H, 8.45. Compound (+)-**12c** was obtained as colorless solids: mp 133−134 °C (hexane−AcOEt); $[\alpha]^{24}_D$ +130.7 (*c* 0.20, MeOH); IR (KBr) 3476, 3372, 1667, 1570 cm^{-1}; ^{1}H NMR δ (CD_3OD) 4.20 (d, 1H, J = 8.8 Hz), 3.41 (ddd, 1H, J = 11.2, 8.8, 4.4 Hz), 2.71 (m, 1H), 2.54 (dd, 1H, J = 18.6, 6.8 Hz), 2.09 (m, 1H), 2.01 (m, 1H), 1.94 (dd, 1H, J = 18.6, 2.4 Hz), 1.57 (m, 1H), 1.04 (m, 1H), 0.22 (s, 9H); ^{13}C NMR δ (CD_3OD) 215.25, 193.60, 137.43, 79.28, 77.28, 43.52, 42.91, 32.97, 32.49, 1.99; MS m/z 240 (M^+, 0.4). Anal. Calcd for $C_{12}H_{20}O_3Si$: C, 59.96; H, 8.39. Found: C, 59.63; H, 8.55.

(2*S*,3*S*,6*R*)-2,3-(Isopropylidenedioxy)bicyclo[4.3.0]non-1(9)-en-8-one (14a). Compound **14a** was obtained as a labile colorless oil: IR 1706, 1647 cm^{-1}; ^{1}H NMR δ 6.60 (t, 1H, J = 1.5 Hz), 4.16 (dd, 1H, J = 9.3, 1.5 Hz), 3.45 (ddd, 1H, J = 11.7, 9.3, 3.4 Hz), 2.78 (m, 1H), 2.63 (dd, 1H, J = 19.0, 6.8 Hz), 2.32−2.22 (m, 2H), 2.02 (dd, 1H, J = 19.0, 2.4 Hz), 1.72 (m, 1H), 1.51 (s, 3H), 1.48 (s, 3H), 1.21 (m, 1H). High-resolution mass spectral analysis and combustion analysis could not be performed due to its instability.

(2*S*,3*S*,6*R*)-2,3-(Isopropylidenedioxy)-9-phenylbicyclo-[4.3.0]non-1(9)-en-8-one (14b). Compound **14b** was obtained as a labile colorless oil: IR 1704, 1662 cm^{-1}; ^{1}H NMR δ 7.41−7.21 (m, 5H), 4.30 (d, 1H, J = 9.3 Hz), 3.65 (ddd, 1H, J = 11.2, 9.3, 3.4 Hz), 2.82−2.72 (m, 2H), 2.38−2.27 (m, 2H), 2.16 (m, 1H), 1.76 (m, 1H), 1.41 (s, 3H), 1.35 (s, 3H), 1.29 (m, 1H). High-resolution mass spectral analysis and combustion analysis could not be performed due to its instability.

(2*S*,3*S*,6*R*)-2,3-(Isopropylidenedioxy)-9-(trimethylsilyl)-bicyclo-[4.3.0]non-1(9)-en-8-one ((+)-14c). Compound (+)-**14c** was obtained as colorless oil: $[\alpha]^{27}_D$ +169.5 (*c* 0.20, $CHCl_3$); IR 1692, 1605 cm^{-1}; ^{1}H NMR δ 4.21 (d, 1H, J = 9.3 Hz), 3.45 (ddd, 1H, J = 11.2, 9.3, 3.4 Hz), 2.66 (m, 1H), 2.57 (dd, 1H, J = 18.6, 7.3 Hz), 2.27−2.19 (m, 2H), 1.96 (dd, 1H, J = 18.6, 2.9 Hz), 1.70 (m, 1H), 1.48 (s, 3H), 1.47 (s, 3H), 1.16 (m, 1H), 0.25 (s, 9H); ^{13}C NMR δ 211.71, 182.55, 135.62, 110.37, 81.92, 80.41, 41.71, 41.08, 31.36, 27.71, 27.05, 26.78, 0.36; MS m/z 280 (M^+, 2.2); HRMS calcd for $C_{15}H_{24}O_3Si$ 280.1495, found 280.1495.

(1*S*,2*S*,3*E*)-3-Benzylidene-1,2-bis(*tert*-butyldimethylsiloxy)-4-methylidenecyclohexane ((−)-10b). Compound (−)-**10b** was obtained as a colorless oil: $[\alpha]^{27}_D$ -45.1 (*c* 0.20, $CHCl_3$); IR 1636 cm^{-1}; ^{1}H NMR δ 7.37−7.13 (m, 5H), 6.33 (s, 1H), 4.86 (s, 1H), 4.61 (s, 1H), 3.94 (d, 1H, J = 5.4 Hz), 3.77 (td, 1H, J = 5.4, 2.9 Hz), 2.57 (m, 1H), 2.19 (m, 1H), 2.07 (m, 1H), 1.59 (m, 1H), 0.91 (s, 9H), 0.87 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.07 (s, 3H); ^{13}C NMR δ 144.17, 142.52, 137.52, 128.82, 127.82, 126.31, 125.59, 113.05, 79.64, 73.46, 31.29, 30.91, 25.91, 25.82, 18.21, 18.04, −4.40, −4.45, −4.63, −4.81; MS m/z 444 (M^+, 92). Anal. Calcd for $C_{26}H_{44}O_2Si_2$: C, 70.21; H, 9.97. Found: C, 70.01; H, 10.15.

(2*S*,3*S*)-1-*p*-Toluenesulfonyl-4-buten-1,2,3-triol ((−)-19). *p*-TsCl (3.69 g, 19.4 mmol) was added to a solution of the known alcohol **18** (2.05 g, 12.9 mmol), Et_3N (3.93 g, 38.8 mmol), and DMAP (131 mg, 1.29 mmol) in CH_2Cl_2 (25 mL) at −20 °C. After being stirred for 2 h, the reaction mixture was quenched by addition of water and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to leave the crude tosylate. According to the procedure described for preparation of compound **6a** from **5a**, the crude tosylate was treated with PTSA (245 mg, 1.29 mmol) in MeOH (130 mL) to give (−)-**19** (3.27 g, 93%) as colorless solids: mp 52.0−53.0 °C (hexanes−Et_2O); $[\alpha]^{26}_D$ −11.5 (*c* 0.50, $CHCl_3$); IR 3563, 3416, 1646 cm^{-1}; ^{1}H NMR δ 7.80 (d, 2H, J = 8.3 Hz), 7.36 (d, 2H, J = 8.3 Hz), 5.85 (ddd, 1H, J = 17.1, 10.3, 6.4 Hz), 5.36 (d, 1H, J = 17.1 Hz), 5.27(d, 1H, J = 10.3 Hz), 4.15 (dd, 1H, J = 10.3, 4.4 Hz), 4.15 (m, 1H), 4.05 (dd, 1H, J = 10.3, 6.4 Hz), 3.78 (m, 1H), 2.49 (d, 1H, J = 5.4 Hz), 2.46 (s, 3H), 2.19 (d, 1H, J = 4.9 Hz); ^{13}C NMR δ 145.16, 136.15, 132.45, 129.94, 127.96, 118.08, 72.24, 71.81, 70.55, 21.62; FABMS m/z 273 (M^+ + 1, 17). Anal. Calcd for $C_{12}H_{16}O_5S$: C, 52.93; H, 5.92. Found: C, 52.80; H, 5.97.

(3*S*,4*S*)-Oct-1-en-7-yne-3,4-diol ((−)-20a). To a solution of (−)-**19** (1.05 g, 3.84 mmol) in MeOH (40 mL) was added K_2CO_3 (1.33 g, 9.60 mmol) at room temperature, and the reaction mixture was stirred for 10 min. MeOH was evaporated off, and the residue was diluted with water and extracted with

AcOEt. The extract was dried and concentrated to dryness. The residue was passed through a short pad of silica gel wih hexanes−Et_2O (1:1) to give the crude epoxy derivative. To a suspension of CuI (658 mg, 3.46 mmol) in Et_2O (60 mL) was added a solution of propargylmagnesium bromide in Et_2O (0.58 M; 19.9 mL; 11.5 mmol) at −78 °C. After the mixture was stirred for 5 min, a solution of crude epoxide obtained from (−)-**19** in Et_2O (60 mL) was added, and the reaction mixture was further stirred for 30 min at the same temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl, filtered through Celite, and extracted with AcOEt. The extract was washed with brine, dried, and concentrated to dryness. Chromatography of the residual oil with hexane−AcOEt (2:1) gave (−)-**20a** (350 mg, 65%) as a colorless oil: $[\alpha]^{27}_D$ −34.5 (*c* 0.20, $CHCl_3$); IR 3567, 3422, 3307, 2118, 1644 cm^{-1}; ^1H NMR δ 5.87 (ddd, 1H, J = 17.1, 10.3, 6.4 Hz), 5.37 (d, 1H, J = 17.1 Hz), 5.27 (d, 1H, J = 10.3 Hz), 3.96 (m, 1H), 3.66 (ddd, 1H, J = 9.3, 5.9, 3.4 Hz), 2.37 (m, 2H), 2.20 (br s, 2H), 1.97 (t, 1H, J = 2.4 Hz), 1.75 (m, 1H), 1.68 (m, 1H); ^{13}C NMR δ 137.23, 117.68, 83.94, 76.07, 72.90, 68.81, 31.45, 14.79; MS *m*/*z* 140 (M^+, 1.3); HRMS calcd for $C_8H_{12}O_2$ 140.0837, found 140.0840.

(3*S*,4*S*)-3,4-Bis(*tert*-butyldimethylsiloxy)oct-1-en-7-yne ((−)-20c). According to the procedure described for preparation of **7a** from **6a**, (−)-**20c** (574 mg, 98%) was obtained from (−)-**20a** (223 mg, 1.59 mmol) as a colorless oil: $[\alpha]^{27}_D$ −79.2 (*c* 0.50, $CHCl_3$); IR 3308, 2116, 1642 cm^{-1}; ^1H NMR δ 5.97 (ddd, 1H, J = 17.1, 10.7, 3.9 Hz), 5.28 (d, 1H, J = 17.1 Hz), 5.15 (d, 1H, J = 10.7 Hz), 4.18 (m, 1H), 3.77 (ddd, 1H, J = 8.8, 4.9, 3.4 Hz), 2.28 (m, 1H), 2.17 (m, 1H), 1.92 (t, 1H, J = 2.4 Hz), 1.80 (m, 1H), 1.42 (m, 1H), 0.91 (s, 9H), 0.90 (s, 9H), 0.10 (s, 3H), 0.10 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR δ 136.51, 114.88, 84.62, 74.86, 73.46, 68.32, 29.71, 25.84, 18.21, 17.99, 14.97, −4.29, −4.74, −4.80, −4.90; MS *m*/*z* 368 (M^+, 0.5); HRMS calcd for $C_{20}H_{40}O_2Si_2$ 368.2567, found 368.2566.

(3*S*,4*S*)-3,4-Bis(*tert*-butyldimethylsiloxy)-8-phenyloct-1-en-7-yne ((−)-20d). According to the procedure described for preparation of **5b** from **5a**, (−)-**20d** (540 mg, 88%) was obtained from (−)-**20c** (508 mg, 1.38 mmol) as a colorless oil: $[\alpha]^{27}_D$ −53.3 (*c* 0.50, $CHCl_3$); IR 1640 cm^{-1}; ^1H NMR δ 7.39−7.35 (m, 2H), 7.30−7.24 (m, 3H), 6.00 (ddd, 1H, J = 17.6, 10.7, 3.9 Hz), 5.30 (d, 1H, J = 17.6 Hz), 5.16 (d, J = 10.7 Hz), 4.21 (m, 1H), 3.87 (ddd, 1H, J = 9.8, 4.9, 2.9 Hz), 2.51 (ddd, 1H, J = 16.6, 6.8, 4.9 Hz), 2.40 (ddd, 1H, J = 16.6, 9.8, 6.8 Hz), 1.88 (dddd, 1H, J = 16.6, 9.8, 6.8, 2.9 Hz), 1.48 (dddd, 1H, J = 16.6, 9.8, 6.8, 4.9 Hz), 0.92 (s, 9H), 0.90 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR δ 136.59, 131.48, 128.10, 127.39, 124.15, 114.83, 90.26, 80.92, 74.93, 73.50, 29.78, 25.86, 25.81, 18.19, 18.03, 15.89, −4.27, −4.69, −4.80, −4.90; MS *m*/*z* 444 (M^+, 14). Anal. Calcd for $C_{26}H_{44}O_2Si_2$: C, 70.21; H, 9.97. Found: C, 69.83; H, 10.06.

(3*S*,4*S*)-8-Phenyloct-1-en-7-yne-3,4-diol ((−)-20b). To a solution of (−)-**20d** (447 mg, 1.00 mmol) in THF (10 mL) was added TBAF in THF (1.0 M; 2,10 mL, 2.10 mmol) at room temperature. After being stirred for 2 h at the same temperature, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (2:1) afforded (−)-**20b** (214 mg, 99%) as colorless solids: mp 45.0−46.0 °C (from hexanes−Et_2O); $[\alpha]^{26}_D$ −24.5 (*c* 0.50, $CHCl_3$); IR 3574, 3421, 1645 cm^{-1}; ^1H NMR δ 7.41−7.36 (m, 2H), 7.31−7.25 (m, 3H), 5.91 (ddd, 1H, J = 17.1, 10.3, 6.4 Hz), 5.38 (d, J = 17.1 Hz), 5.28 (d, 1H, J = 10.3 Hz), 4.01 (m, 1H), 3.73 (ddd, 1H, J = 9.3, 5.9, 3.4 Hz), 2.65−2.54 (m, 2H), 2.10 (br s, 2H), 1.85 (m, 1H), 1.76 (m, 1H); ^{13}C NMR δ 137.30, 131.48, 128.16, 127.62, 123.61, 117.65, 89.38, 81.12, 76.07, 73.19, 31.79, 15.80; MS *m*/*z* 216 (M^+, 3.5). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.50; H, 7.53.

(3*S*,4*S*)-3,4-(Di-*tert*-butylsilylenedioxy)-8-phenyloct-1-en-7-yne ((−)-20e). According to the procedure described for preparation **15a** from **6a**, (−)-**20e** (243 mg, 87%) was obtained from (−)-**20b** (170 mg, 0.78 mmol) as a colorless oil: $[\alpha]^{26}_D$ −41.7 (*c* 0.50, $CHCl_3$); IR 1645 cm^{-1}; ^1H NMR δ 7.40−7.36 (m, 2H), 7.29−7.25 (m, 3H), 5.84 (ddd, 1H, J = 17.1, 10.3, 6.4 Hz), 5.39 (d, 1H, J = 17.1 Hz), 5.23 (d, 1H, J = 10.3 Hz), 4.08 (m, 1H), 3.80 (td, 1H, J = 8.8, 2.9 Hz), 2.67 (m, 1H), 2.57 (m, 1H), 1.88 (m, 1H), 1.75 (m, 1H), 1.07 (s, 9H), 1.07 (s, 9H); ^{13}C NMR δ 136.95, 131.50, 128.18, 127.53, 123.92, 117.32, 89.65, 81.74, 80.79, 78.96, 33.14, 27.03, 26.97, 20.95, 20.74, 16.25; MS *m*/*z* 356 (M^+, 30). Anal. Calcd for $C_{22}H_{32}O_2Si$: C, 74.10; H, 9.05. Found: C, 73.87; H, 9.14.

General Procedure for Pauson−Khand Reaction of Enynes 20. According to the procedure described for the Pauson−Khand reaction of enynes **5**−**7** and **15**, enynes **20** were exposed to three conditions (conditions A−C). In the cases of cyclization of enyne **20e**, desilylation was carried out before chromatographic isolation. Chemical yield and the product ratio of **21**/**22** are summarized in Table 5.

(1*S*,2*S*,3*S*)- and (1*R*,2*S*,3*S*)-2,3-Dihydroxybicyclo[4.3.0]-non-6-en-8-ones ((−)-21a and (+)-22a). A mixture of (−)-**21a** and (+)-**22a** was obtained in a ratio of 7:93 (entry 1 in Table 5). The ratio was determined by HPLC analysis (CH_2Cl_2/2-propanol = 5:1; 1.0 mL/min; retention time of (−)-**21a** was recorded as 8.3 min and that of (+)-**22a** as 5.9 min). Compound (−)-**21a** was obtained as colorless solids: mp 181−183 °C (from AcOEt); $[\alpha]^{25}_D$ −182.3 (*c* 0.21, MeOH); IR (KBr) 3420, 3381, 1639, 1607 cm^{-1}; ^1H NMR δ (CD_3OD) 5.86 (m, 1H), 3.95−3.88 (m, 2H), 3.28 (m, 1H), 2.68 (br td, 1H, J = 13.7, 5.9 Hz), 2.60 (ddd, 1H, J = 13.7, 4.9, 2.0 Hz), 2.41 (dd, 1H, J = 18.6, 2.0 Hz), 2.34 (dd, 1H, J = 18.6, 6.4 Hz), 1.96 (tdd, 1H, J 13.7, 4.9, 2.4 Hz), 1.87 (m, 1H); ^{13}C NMR δ (CD_3OD) 213.09, 185.60, 128.71, 72.88, 70.11, 42.86, 37.81, 28.44, 25.89; MS *m*/*z* 168 (M^+, 61). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 63.88; H, 7.22. Compound (+)-**22a** was obtained as colorless solids: mp 134−135 °C (from AcOEt); $[\alpha]^{27}_D$ +52.6 (*c* 0.20, MeOH); IR (KBr) 3468, 3339, 1695, 1679, 1622 cm^{-1}; ^1H NMR δ (CD_3OD) 5.89 (m, 1H), 3.59 (ddd, 1H, J = 11.2, 9.3, 4.4 Hz), 3.00 (dd, 1H, J = 10.3, 9.3 Hz), 2.81 (ddd, 1H, J = 14.2, 4.4, 2.4 Hz), 2.76 (m, 1H), 2.59 (dd, 1H, J = 19.0, 6.4 Hz), 2.41 (br td, 1H, J = 14.2, 5.4 Hz), 2.31 (dd, 1H, J = 19.0, 1.5 Hz), 2.15 (m, 1H), (m, 1H); ^{13}C NMR δ (CD_3OD) 212.02, 183.57, 128.71, 81.56, 74.35, 48.87, 41.33, 32.92, 28.88; MS *m*/*z* 168 (M^+, 63). Anal. Calcd for $C_9H_{12}O_3$ requires C, 64.27; H, 7.19. Found: C, 63.87; H, 7.26.

(1*S*,2*S*,3*S*)- and (1*R*,2*S*,3*S*)-2,3-Dihydroxy-7-phenylbicyclo[4.3.0]non-6-en- 8-ones ((+)-21b and (−)-22b). A mixture of (+)-**21b** and (−)-**22b** was obtained in a ratio of 9:91 (entry 2 in Table 5). The ratio was determined by HPLC analysis (AcOEt; 1.0 mL/min; retention time of (+)-**21b** was recorded as 7.2 min and that of (−)-**22b** as 8.8 min). Compound (+)-**21b** was obtained as colorless solids: mp 157−158 °C (from AcOEt); $[\alpha]^{26}_D$ +33.4 (*c* 0.20, MeOH); IR (KBr) 3451, 3382, 1693, 1682, 1670, 1636, 1600 cm^{-1}; ^1H NMR δ 7.43−7.38 (m, 2H), 7.34−7.28 (m, 3H), 4.14 (m, 1H), 4.09 (m, 1H), 3.42 (m, 1H), 2.86 (ddd, 1H, J = 14.2, 4.9, 2.0 Hz), 2.70 (td, 1H, J = 14.2, 6.4 Hz), 2.59−2.56 (m, 2H), 1.99 (tdd, 1H, J = 14.2, 4.9, 2.4 Hz), 1.91 (m, 1H), 1.73 (br s, 2H); (CD_3OD) 7.40−7.35 (m, 2H), 7.32−7.24 (m, 3H), 4.00−3.94 (m, 2H), 3.36 (m, 1H), 2.75−2.63 (m, 2H), 2.55 (dd, 1H, J = 18.6, 2.4 Hz), 2.48 (dd, 1H, J = 18.6, 6.8 Hz), 1.95 (m, 1H), 1.85 (m, 1H); (D_2O; sodium 3-(trimethylsilyl)propanesulfonate was used as an internal standard) 7.52−7.41 (m, 3H), 7.32−7.28 (m, 2H), 4.14 (t, 1H, J = 3.4 Hz), 4.09 (m, 1H), 3.41 (m, 1H), 2.76 (m, 1H), 2.66 (dd, 1H, J = 19.1, 6.4 Hz), 2.65 (m, 1H), 2.56 (dd, 1H, J = 19.1, 1.5 Hz), 1.98−1.84 (m, 2H); ^{13}C NMR δ (CD_3OD) 210.17, 177.97, 139.94, 132.88, 130.36, 129.18, 128.62, 73.12, 70.28, 41.18, 37.43, 28.26, 24.27; MS *m*/*z* 244 (M^+, 100). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.37; H, 6.70. Compound (−)-**22b** was obtained as colorless solids: mp 131−132 °C (from hexane−AcOEt); $[\alpha]^{22}_D$ − 82.8 (*c* 0.20, MeOH); IR (KBr) 3400, 3344, 3274, 1677, 1628 cm^{-1}; ^1H NMR δ 7.44−7.32 (m, 3H), 7.29−7.26 (m, 2H), 3.78 (ddd, 1H, J = 13.2, 8.8, 4.4 Hz), 3.50 (br s, 1H), 3.24 (dd, 1H, J = 10.3, 8.8 Hz), 3.05 (ddd, 1H, J = 14.7, 4.4, 2.4 Hz), 2.86−2.77 (m, 2H), 2.60 (br s, 1H), 2.49 (m, 1H), 2.38 (td, 1H, J = 14.7, 5.4 Hz), 2.20 (m, 1H), 1.48 (m, 1H); (CD_3OD) 7.41−7.29 (m, 3H), 7.26−7.20 (m, 2H), 3.67 (ddd, 1H, J = 11.2, 8.8, 4.4 Hz), 3.08 (dd, 1H, J = 9.8, 8.8 Hz), 2.90 (m, 1H), 2.82 (m, 1H), 2.71 (dd, 1H, J = 19.0, 6.4 Hz), 2.45 (d, 1H, J = 19.0 Hz), 2.42 (td, 1H, J = 14.7, 5.9

Hz), 2.12 (m, 1H), 1.37 (m, 1H); (D_2O; sodium 3-(trimethylsilyl)propanesulfonate was used as an internal standard) 7.51−7.41 (m, 3H), 7.28−7.23 (m, 2H), 3.79 (ddd, 1H, J = 11.2, 9.3, 4.4 Hz), 3.24 (dd, 1H, J = 10.3, 9.3 Hz), 2.91 (m, 1H), 2.86 (m, 1H), 2.80 (dd, 1H, J = 19.1, 6.4 Hz), 2.52 (d, 1H, J = 19.1 Hz), 2.43 (td, 1H, J = 14.2, 5.4 Hz), 2.14 (m, 1H), 1.39 (m, 1H); ^{13}C NMR δ (CD_3OD) 209.20, 175.92, 139.69, 132.45, 130.29, 129.27, 128.93, 81.63, 74.55, 47.15, 40.66, 32.77, 27.29; MS m/z 244 (M^+, 100); HRMS calcd for $C_{15}H_{16}O_3$ 244.1100, found 244.1100.

(1*S*,2*S*,3*S*)- and (1*R*,2*S*,3*S*)-2,3-Bis(*tert*-butyldimethylsiloxy)bicyclo-[4.3.0]non-6-en-8-ones ((−)-21c and 22c). A mixture of (−)-**21c** and **22c** was obtained in a ratio of 94:6 (entry 3 in Table 5). The ratio was determined by HPLC analysis (hexane/AcOEt = 5:1; 1.0 mL/min; retention time of (−)-**21c** was recorded as 4.7 min and that of **22c** as 6.0 min). Compound (−)-**21c** was obtained as colorless solids: mp 80.0−81.0 °C (from MeOH); $[\alpha]^{26}_D$ −86.7 (*c* 0.20, $CHCl_3$); IR 1692, 1624 cm^{-1}; ^{1}H NMR δ 5.85 (m, 1H), 3.86 (m, 1H), 3.80 (t, 1H, J = 3.4 Hz), 3.22 (m, 1H), 2.62 (br td, 1H, J = 13.2, 5.9), 2.53 (ddd, 1H, J = 13.2, 4.9, 2.0 Hz), 2.31 (dd, 1H, J = 18.6, 6.4 Hz), 2.22 (dd, 1H, J = 18.6, 2.4 Hz), 1.92 (tdd, 1H, J = 13.2, 4.9, 2.4 Hz), 1.73 (m, 1H), 0.92 (s, 9H), 0.81 (s, 9H), 0.09 (s, 3H), 0.09 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR δ 209.41, 181.51, 128.09, 73.46, 69.85, 41.60, 37.04, 28.11, 25.72, 25.61, 24.93, 17.94, 17.85, −4.31, −4.90, −5.19; MS m/z 396 (M^+, 0.5). Anal. Calcd for $C_{21}H_{40}O_3Si_2$: C, 63.58; H, 10.16. Found: C, 63.29; H, 10.35. Compound **22c** was obtained as a labile colorless oil: IR 1706, 1626 cm^{-1}; ^{1}H NMR δ 5.86 (m, 1H), 3.70 (ddd, 1H, J = 11.2, 7.8, 3.9 Hz), 3.26 (dd, 1H, J = 8.8, 7.8 Hz), 2.73 (m, 1H), 2.59 (dd, 1H, J = 18.6, 6.4 Hz), 2.51 (m, 1H), 2.29 (m, 1H), 2.27 (dd, 1H, J = 18.6, 2.5 Hz), 2.11 (m, 1H), 1.44 (m, 1H), 0.91 (s, 9H), 0.89 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H). High-resolution mass spectral analysis and combustion analysis could not be performed due to its instability.

(1*S*,2*S*,3*S*)- and (1*R*,2*S*,3*S*)-2,3-Bis(*tert*-butyldimethylsiloxy)-8-phenylbicyclo[4.3.0]non-6-en-8-ones (21d and 22d). A mixture of **21d** and **22d** was obtained in a ratio of 85:15 (entry 5 in Table 5) as a colorless oil. The ratio was determined by HPLC analysis (hexane/2-propanol = 100:1; 0.5 mL/min; retention time of **21d** was recorded as 9.5 min and that of **22d** as 8.8 min): IR 1691, 1642 cm^{-1}; selected data for ^{1}H NMR δ 7.42−7.22 (m, 5H), 3.88 (m, 72/100 × 2H), 3.78 (ddd, 28/100H, J = 11.2, 7.8, 3.9 Hz), 3.36−3.31 (m, 1H), 0.95 (s, 72/100H × 9H), 0.92 (s, 28/100H × 9H), 0.90 (s, 28/100H × 9H), 0.83 (s, 72/100H × 9H); MS m/z 472 (M^+, 0.7). Anal. Calcd for $C_{27}H_{44}O_3Si_2$: C, 68.59; H, 9.38. Found: C, 68.50; H, 9.51.

(1*S*,2*S*,3*E*)- and (1*S*,2*S*,3*Z*)-4-Benzylidene-1,2-bis(*tert*-butyldi-methylsiloxy)-3-methylidenecyclohexanes ((*E*)-23d and (*Z*)-23d). A mixture of regioisomers **(*E*)-23d** and **(*Z*)-23d** was obtained in a ratio of 84:16 (entry 6 in Table 5) as a colorless oil. The ratio was determined by HPLC analysis (hexane; 1.0 mL/min; retention time of **(*E*)-23d** was recorded as 8.3 min and that of **(*Z*)-23d** as 9.9 min): IR 1636 cm^{-1}; selected data for ^{1}H NMR δ 7.42−7.09 (m, 5H), 6.48 (s, 84/100H), 6.27 (s, 16/100H), 5.14 (d, 84/100H, J = 2.4 Hz), 5.01 (m, 16/100H), 4.29 (m, 84/100H), 4.81 (d, 16/100H, J = 2.4 Hz), 4.02−3.98 (m, 1H), 3.77 (td, 84/100H, J = 4.9, 2.9 Hz), 3.71 (d, 16/100H, J = 5.4, 2.9 Hz), 0.93 (s, 16/100 × 9H), 0.89 (s, 84/100 × 9H); MS m/z 444 (M^+, 100). Anal. Calcd for $C_{26}H_{44}O_2Si_2$: C, 70.21; H, 9.97. Found: C, 70.05; H, 10.23.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **5a**, **6a**,**b**, **7c**, **9a**, **11b**, **14c**, **15b**, **20a**,**c**, and **22b** and ^{1}H spectra for compounds **14a**,**b** and **22c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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