Pauson−Khand Reaction of Optically Active 6,7-Bis(*tert*-butyldimethylsiloxy)non-1-en-8-ynes

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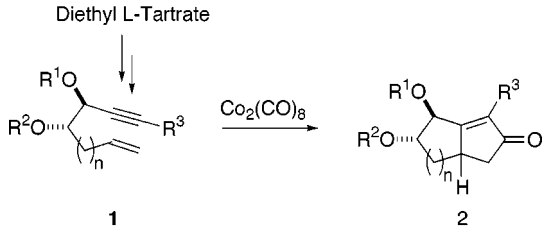
Treatment of (6*S*,7*S*)-7-bis(*tert*-butyldimethylsiloxy)non-1-en-8-ynes with dicobalt octacarbonyl gave the corresponding cobalt complex. This complex was subsequently exposed to the Pauson−Khand conditions in the presence of a promoter such as cyclohexylamine, thioanisole, methyl isopropyl sulfide, and butyl methyl sulfide ending up with the stereoselective production of the (2*S*,3*S*,6*S*,7*S*)-7-methylbicyclo[4.3.0]nonenone derivatives instead of the expected (2*S*,3*S*,7*S*)-bicyclo[5.3.0]decenone species.

Introduction

The Pauson−Khand reaction[1] is well recognized as a cobalt-mediated formal [2 + 2 + 1] cyclization of three components consisting of an alkyne and an alkene, and that of carbon monoxides on the two cobalt atoms of the cluster complex to produce cyclopentenone derivatives. The intramolecular version of this intriguing [2 + 2 + 1] cyclization procedure has emerged as one of the most convenient and reliable methods for construction of the bicyclo[*m*.3.0] frameworks (*m* = 3, 4) in one operation. In previous papers,[2] we reported an efficient procedure for the highly stereoselective construction of the optically active bicyclo[3.3.0]octenone **2** (*n* = 1)[2a,b] and bicyclo-[4.3.0]nonenone **2** (*n* = 2)[2c,d] skeletons possessing the bis-(*tert*-butyldimethlysiloxy) functionality (R^1 = R^2 = TBDMS) at both the allyl and homoallyl positions based on an intramolecular Pauson−Khand reaction of the optically active enyne **1** (*n* = 1, 2), which was easily derived from L-tartrate. This scheme could allow us to prepare the enantiomer of **2** when the commercially available D-tartrate was employed as a starting material. The next phase of this program must be to confirm whether this highly stereoselective method for preparation of the bicyclo[*m*.3.0] ring system could be applied to the formation of larger ring-sized cyclopentenone-fused systems such as bicyclo[5.3.0]decenone **2** (*n* = 3). The bicyclo[5.3.0]decenone framework thus prepared would become a promising key intermediate for synthesis of optically active natural products such as guaianolides.[3]

Scheme 1



In addition, to our knowledge, no reports on dealing with the Pauson−Khand reaction of 1-nonen-8-ynes derivatives have so far been recorded. Therefore, our efforts are directed toward investigating the intramolecular Pauson−Khand reaction of (*6S,7S*)-6,7-bis(oxygenated)-non-1-en-8-ynes, especially focusing on (*6S,7S*)-bis(*tert*-butyldimethylsiloxy)non-1-en-8-yne derivatives in line with our program.[2]

In this paper, we describe our interesting as well as unexpected results on the cyclization reaction of 1-nonen-8-yne species leading to the bicyclo[4.3.0]nonenones with a methyl group at the position α to the carbonyl moiety.

Results and Discussion

Synthesis of (6*S*,7*S*)-6,7-Bis(oxygenated)-1-nonen-8-yne Derivatives. The titled starting enynes **6**−**8** were easily prepared from diethyl L-tartrate. Activation of the primary alcohol of the known hydroxy compound **3**,[4] prepared from diethyl L-tartrate, with trifluoromethanesulfonic anhydride (Tf_2O)[5] in methylene chloride, was followed by exposure to 3-butenylmagnesium bromide in THF[6] at 0 °C to give, after desilylation with tetra-*n*-butylammonium fluoride (TBAF), the olefin derivative **4** in 72% overall yield. The Swern oxidation of **4** afforded the corresponding aldehyde, which was then converted into the dibromoolefin **5** in 71% yield under Corey's

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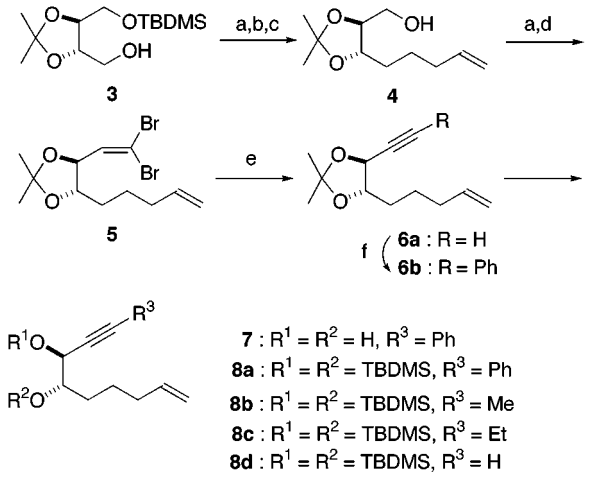
Scheme 2[a]



[a] Reaction conditions: (a) Tf_2O, $^iPr_2NEt$, CH_2Cl_2, −40 °C; (b) $CH_2{=}CH(CH_2)_2MgBr$, CuBr, THF, 0 °C; (c) TBAF, THF, rt; (d) PPh_3, CBr_4, CH_2Cl_2, 0 °C; (e) *n*-BuLi, Et_2O, −50 °C; (f) PhI, CuI, $Pd(PPh_3)_2Cl_2$, $^iPr_2NH$, THF, rt.

conditions.[7] Transformation of the dibromoolefin moiety of **5** into the triple bond was realized by exposure to *n*-butyllithium to furnish **6a** in 89% yield. Introduction of a phenyl group at the triple bond terminus was undertaken by the Sonogashira coupling[8] to provide **6b** in 87% yield. Acidic hydrolysis of the acetonide moiety of **6b** afforded **7** in 92% yield. A series of the *tert*-butyldimethylsilyl (TBDMS) group-protected enynes **8a**−**d** were prepared from **6** by conventional means (see the Experimental Section).

Pauson−Khand Reaction of (6*S*,7*S*)-6,7-Bis(oxygenated)non-1-en-8-yne Derivatives. With the required enynes **6**, **7**, and **8** for the ring-closure reaction in hand, these enynes were then submitted to the Pauson−Khand conditions. The fact[2d] that the exclusive formation of the (*6R*)-bicyclo[4.3.0]nonenone derivatives **2** (n = 2, $R^1 + R^2 = Me_2C$) had been observed when the cobalt complex of **1** (n = 2, $R^1 + R^2 = Me_2C$) was heated in acetonitrile at 75 °C (condition A)[9] or treated with trimethylamine *N*-oxide (TMANO·$2H_2O$) in THF (condition B)[10] prompted us to examine the Pauson−Khand reaction of **6** expecting the exclusive formation of (*7R*)-**2** (n = 3, $R^1 + R^2 = Me_2C$) at the inception of this program. Thus treatment of **6a** and **6b** with dicobaltoctacarbonyl [$Co_2(CO)_8$] afforded the respective corresponding cobalt complexes, which were subsequently exposed to several typical Pauson−Khand conditions[1] involving the above two conditions A and B resulting in an intractable mixture. No desired cyclized products such as the bicyclo[5.3.0]decenone derivatives **2** (n = 3) could be isolated from the reaction mixture. The dihydroxy compound **7** was also found not to be a suitable substrate for the Pauson−Khand reaction under these conditions.

Our endeavors were then directed toward the Pauson−Khand reaction of (6*S*,7*S*)-6,7-bis(*tert*-butyldimethylsiloxy)non-1-en-8-yne derivatives **8** because the enyne **1** (n = 1, 2; $R^1 = R^2$ = TBDMS) exclusively or highly stereoselectively provided the corresponding bicyclo derivatives **2** (n = 1, 2)[2d] with the (*S*)-configuration at the ring-fused carbon center when exposed to both conditions A and B. Thus the phenyl derivative **8a** was converted into the cobalt-complexed **8a**, which was successively exposed to condition A. Although a trace amount of the cyclized products was detected, the major product was unfortunately the demetalated starting material **8a** (73%). Upon treatment under condition B, the cobalt-complexed **8a** underwent ring closure to provide a mixture of the cyclized products **9a** and **10a** (**9a**:**10a** = 94:6) in 42% yield along with the recovery of **8a** (34%) (Table 1, entry 1). Interestingly as well as unexpectedly, the predicted bicyclo[5.3.0]decenone **2** (see Scheme 1; n = 3, $R^1 = R^2$ = TBDMS, R^3 = Ph), a normal intramolecular Pauson−Khand reaction product from **8a**, could never be detected in the reaction mixture. However, it did not take long to realize that the condition B could not be applicable to the other enyne substrates. Thus, the other 6,7-bis(*tert*-butyldimethylsiloxy) compounds **8b**−**d** gave only a mixture of inseparable compounds upon exposure to condition B. After searching for various kinds of Pauson−Khand conditions, we finally reached Sugihara's procedures using amines[11] or sulfides[12] as a promoter which consistently yielded compounds **9** and **10** from the enynes **8** in acceptable yields. Typical results are presented in Table 1. The cobalt-complexed **8a** was treated with cyclohexylamine in 1,2-dichloroethane at 83 °C (refluxing temperature) to afford a mixture of **9a** and **10a** in 74% yield in a ratio of 85 to 15 (entry 2). The sulfides such as thioanisole, methyl isopropyl sulfide, and *n*-butyl methyl sulfide in dichloroethane at refluxing temperature also effected the cyclization to stereoselectively furnish the bicyclo[4.3.0]nonenone derivative **9a** in acceptable yields (entries 3−5). The methyl congener **8b** produced the corresponding bicyclo[4.3.0]nonenone derivative **9b** in a stereoselective fashion (entries 6−9),

Table 1. Pauson−Khand Reaction of 8

entry	substrate	R	condition[a]	yield[b] (%)	ratio[c] **9**:**10**
1	**8a**	Ph	B	42[d]	94:6
2	**8a**	Ph	C	74	85:15
3	**8a**	Ph	D	58	96:4
4	**8a**	Ph	E	63[e]	93:7
5	**8a**	Ph	F	53[f]	95:5
6	**8b**	Me	C	74	79:21
7	**8b**	Me	D	61	84:16
8	**8b**	Me	E	71	85:15
9	**8b**	Me	F	73	80:20
10	**8c**	Et	C	72	70:30
11	**8c**	Et	D	49[g]	66:34
12	**8c**	Et	E	32[h]	61:39
13	**8c**	Et	F	63[i]	62:38
14	**8d**	H	D	34	87:13

[a] Condition B: TMANO in THF at rt. Condition C: $CyNH_2$ in $(CH_2)_2Cl_2$ at 83 °C. Condition D: PhSMe in $(CH_2)_2Cl_2$ at 83 °C. Condition E: ^{i}PrSMe in $(CH_2)_2Cl_2$ at 83 °C. Condition F: ^{n}BuSMe in $(CH_2)_2Cl_2$ at 83 °C. [b] Total yield of **9** and **10**. [c] Determined by HPLC analysis. [d] The starting **8a** was recovered in 34% yield. [e] The cobalt-complexed **8a**[17] was recovered in 8% yield. [f] The cobalt-complexed **8a**[17] was recovered in 15% yield. [g] The cobalt-complexed **8c**[17] was recovered in 26% yield. [h] The starting **8c** and its cobalt-complexed one[17] were recovered in 12 and 26% yield, respectively. [i] The starting **8c** and its cobalt-complexed one[17] were recovered in 8 and 12% yield, respectively.

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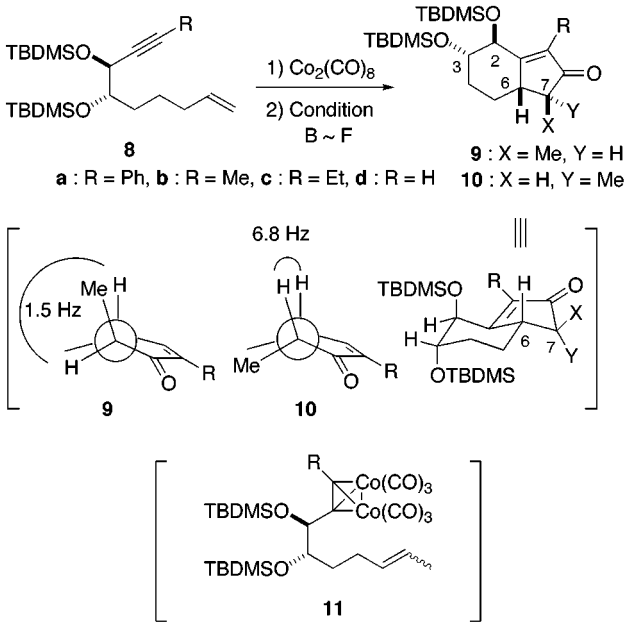
Scheme 3



although the diastereoselectivity observed was somewhat lower compared to the cases of **8a**. The Pauson−Khand reaction of the ethyl derivative **8c** also proceeded to afford a mixture of **9c** and **10c** (entries 10−13). In the case of **8d** without a substituent at the triple bond terminus, thioanisole is the only favorable promoter, for some unknown reasons, producing a mixture of **9d** and **10d** in 34% yield in a ratio of 87 to 13 (entry 14). The structure of the cyclized products **9** and **10** was determined by their spectral data. Especially, the stereochemical assignment of the bicyclo[4.3.0]nonenone framework was made by careful examination of the ^{1}H NMR spectra. For example, the coupling constant between H-2 and H-3 of both **9b** and **10b** showed the same 3.4 Hz (an equatorial−equatorial coupling), which is in good agreement with that of (*6S*)-**2** (n = 2, $R^1 = R^2$ = TBDMS; J = 3.4 Hz),[2d] while the corresponding C_6-epimer (*6R*)-**2** showed a larger coupling constant (J = 8.3 Hz)[2d] due to an axial−axial coupling. This simple comparison with the known analogues allowed us to establish the configuration of the C-6 carbon center of both **9b** and **10b** to be (*S*). The decoupling experiments further disclosed the relationship between H-6 and H-7. Irradiation of the C_7-methyl group (δ 1.14 as doublet, J = 7.8 Hz) of **9b** revealed H-7 at δ 1.89 as a doublet with a small coupling constant (J = 1.5 Hz). On the other hand, a somewhat larger coupling constant (J = 6.8 Hz) between H-6 and H-7 was observed upon irradiation of the C_7-methyl group (δ 1.07, J = 7.8 Hz) of **10b**. Thus, the diagnostic difference in the coupling constants between H-6 and H-7 of both stereoisomers could be disclosed. Examination of molecular models indicates that the dihedral angle between H-6 and H-7 of **9b** would be close to 90°, while that of **10b** would be nearly 0°. Each dihedral angle should correspond to the observed coupling constants (1.5 and 6.8 Hz, respectively) suggesting the structures of **9b** and **10b** as depicted in Scheme 3. A similar ^{1}H NMR spectral analysis of the other cyclized products established that compound **9** has a (2*S*,3*S*,6*S*,7*S*) configuration and that the absolute stereochemistry of compound **10** should be (2*S*,3*S*,6*S*,7*R*).

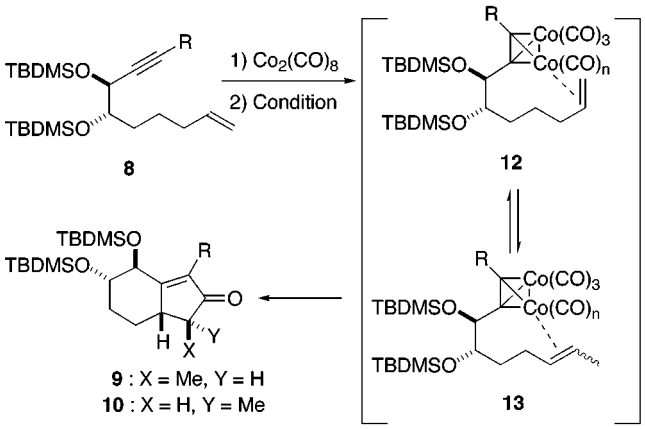
The Pauson-Khand reaction of the enyne **8** produced the 7-methylbicyclo[4.3.0]nonenones **9** and **10** instead of the anticipated bicyclo[5.3.0]decenone **2** (n = 3, $R^1 = R^2$ = TBDMS). The formation of unpredictable **9** and **10** can tentatively be postulated as follows: (i) The first step of the cyclization must be initiated by isomerization of the terminal olefin moiety of the enyne **8** and/or its cobalt-complexed form to an internal one leading to the corresponding cobalt-complexed 6,7-bis(*tert*-butyldimethylsiloxy)non-2-en-8-yne derivatives **11** (Scheme 3) under the reaction conditions used. (ii) The second step is a normal Pauson−Khand cyclization resulting in the production of a mixture of **9** and **10**.

To confirm the plausible reaction process as mentioned above, the enyne **8b** without cobalt complexation was directly exposed to the conditions C−F described in Table 1. However, no isomerization took place and the starting **8b** was recovered intact indicating that the terminal olefin moiety might be stable enough and compatible under the Pauson−Khand conditions unless the cobalt-complexed alkyne is formed. The cobalt-complexed **8b** was the next substrate for isomerization experiments. The cobalt-complexed **8b** was treated with cyclohexylamine in dichloroethane at 0 °C for 3 h. The resulting mixture was subsequently demetalated by cerium (IV) ammonium nitrate (CAN) in methanol at 0 °C to provide a mixture of **8b** and its regioisomer, demetalated **11b**,[13] in 67% yield in a ratio of ca. 70 to 30. When *n*-butyl methyl sulfide was employed as a promoter in dichloroethane at 0 °C for 3h, **8b** furnished, after treatment with CAN, demetalated **11b**[13] as a major product along with the starting **8b** (**8b**:**11b** = ca. 20:80) in 65% yield. It should be mentioned that the corresponding cyclized products **9b** and **10b** could not be detected in the reaction mixture of both experiments. These isomerization experiments strongly suggested that the cobalt-complexed alkyne functionality would interact with the terminal double bond moiety and accelerate the isomerization at a somewhat lower temperature. In addition, the resulting 7-methylbicyclo[4.3.0]nonenone derivatives **9** and **10** were found to be stable under the Pauson-Khand conditions. Thus a mixture of **9b** and **10b** (85:15) was completely recovered intact after exposure to conditions C−F or refluxing in dichloroethane in the presence of $Co_2(CO)_8$. As indicated in Table 1, the cobalt complex **11** and/or its demetalated form could not be isolated from the reaction mixture, although the starting enyne **8** and/or its cobalt-complexed form was sometimes recovered from the reaction mixture. On the basis of these experiments, the exclusive formation of the 7-methylbicyclo[4.3.0]nonenone framework **9** and **10** from the 1-nonen-8-yne derivatives **8** would be interpreted in terms of isomerization of the terminal double bond to an internal one, followed by a normal [2 + 2 + 1]-type cyclization. The promoter facilitates the formation of a vacancy on the cobalt atom of the cobalt-complexed **8**, to which the terminal olefin moiety would coordinate leading to the intermediate **12**. Insertion of the coordinated olefin moiety of this intermediate **12** must result in the formation of the bicyclo[5.3.0]decenone derivative **2** (n = 3) via the cobalt-metallocycles.[14] However, this carbon−carbon bond formation process seems to be retarded presumably due to steric reasons; thereby, the double bond migration of

(13) The ratio between (*E*)- and (*Z*)-isomers could not be determined by ^{1}H NMR and HPLC.

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

Scheme 4



12 instead of the olefin insertion process would form a favorable pathway giving rise to the isomerized cobalt complex **13**, which rapidly collapses to the 7-methylbicyclo-[4.3.0]nonenone derivatives **9** and **10** through the corresponding cobalt-metallocycles[14] at the refluxing temperature of 1,2-dichloroethane. The preferential production of compound **9** over its isomer **10** would reflect the ratio between the (*E*)-**11** and (*Z*)-**11**.[13] Sugihara and coworkers[15] reported a similar occurrence of double bond migration during their detailed experiments on the Pauson−Khand reaction using cyclohexylamine as a promoter where the cobalt-complexed (2*E*)-8-phenyloct-2-en-7-yne provided the bicyclo[4.3.0]nonenone derivative resulting from double bond migrated enyne[16] as a minor product (5%) together with the expected 4-methylbicyclo-[3.3.0]octenones (90%).

In summary, we have described a stereoselective construction of (2*S*,3*S*,6*S*,7*S*)-2,3-bis(*tert*-butyldimethylsiloxy)-7-methyl-9-substituted-bicyclo[4.3.0]nonenone derivatives **9** by the Pauson−Khand reaction of (6*S*,7*S*)-bis(*tert*-butyldimethylsiloxy)-9-substituted-non-1-en-8-ynes **8** via the double bond migration of the latter. Further studies on the mechanism of this reaction and its scope and limitation are now in progress.

Experimental Section

Melting points are uncorrected. IR spectra were measured in $CHCl_3$.^{1}H NMR spectra were taken in $CDCl_3$. $CHCl_3$ (7.26 ppm) was used as an internal standard for silyl 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 pentaoxide, and THF was from sodium diphenyl ketyl, prior to use. Et_3N and $^iPr_2NH$ were distilled from CaH_2 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.

(*2S,3S*)-2,3-(Isopropylidenedioxy)oct-7-en-1-ol ((−)-4). A solution of Tf_2O (0.91 mL, 5.43 mmol) in CH_2Cl_2 (86.0 mL) was added to a solution of **3** (1.00 g, 3.62 mmol) in CH_2Cl_2 (6.0 mL) in the presence of $^iPr_2NH$ (1.93 mL, 10.9 mmol) at −40 °C. The reaction mixture was stirred for 10 min, washed with water, saturated aqueous $NHCO_3$, and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane-AcOEt (10:1) to give the triflate. CuBr (182 mg, 1.27 mmol) was added to 3-butenylmagnesium bromide (0.5M THF solution, 21 mL, 10.5 mmol) at 0 °C. The mixture was stirred for 10 min at the same temperature, to which a solution of the crude triflate in THF (15 mL) was added. After stirring for 30 min, the reaction mixture was quenched by addition of saturated aqueous NH_4-Cl. The reaction mixture was diluted with Et_2O, which was then washed with water and brine, dried, and concentrated to dryness. To a solution of the residue in THF (35 mL) was added TBAF (1.0 M THF solution, 3.62 mL, 3.62 mmol) and the reaction mixture was stirred for 1 h at room temperature, quenched by addition of water, and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residual oil was chromatographed with hexane-AcOEt (4:1) to afford (−)-**4** (522 mg, 72%) as a colorless oil: $[\alpha]^{22}_D$ −27.5 (*c* 1.00, $CHCl_3$); IR 3594, 3450, 1640 cm^{-1}; ^{1}H NMR δ 5.78 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.00 (dd, 1H, J = 17.1, 3.4 Hz), 4.95 (m, 1H), 3.87 (m, 1H), 3.78 (dd, 1H, J = 11.7, 2.9 Hz), 3.72 (ddd, 1H, J = 8.3, 4.4, 3.4), 3.58 (dd, 1H, J = 11.7, 3.4 Hz), 2.11−2.06 (m, 2H), 1.62−1.41 (m, 4H), 1.40 (s, 3H), 1.39 (s, 3H); ^{13}C NMR δ 138.29, 114.83, 108.61, 81.42, 76.73, 62.00, 33.62, 32.38, 27.33, 27.01; MS *m*/*z* 200 (M^+, 0.5). Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.76; H, 10.20.

(3*S*,4*S*)-1,1-Dibromo-3,4-(isopropylidenedioxy)nona-1,8-diene ((−)-5). A solution of DMSO (0.76 mL, 10.6 mmol) in CH_2Cl_2 (15 mL) was added to a solution of oxalyl chloride (0.47 mL, 5.33 mmol) in CH_2Cl_2 (10 mL) at −78 °C over a period of 5 min. After the mixture was stirred for 15 min, a solution of the alcohol **4** (889 mg, 4.44 mmol) in CH_2Cl_2 (10 mL) was added to the CH_2Cl_2 solution, and the reaction mixture was stirred at the same temperature for an additional 1 h. Et_3N (3.09 mL, 22.2 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. The crude aldehyde was used directly for the next reaction. To a solution of PPh_3 (4.66 g, 17.7 mmol) in CH_2-Cl_2 (10 mL) was added CBr_4 (2.94 g, 8.88 mmol) in CH_2Cl_2 (10 mL) and Et_3N (0.62 mL, 4.44 mmol) at 0 °C, and the reaction mixture was stirred for 30 min. A solution of the crude aldehyde in CH_2Cl_2 (10 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 30 min at room temperature. The reaction mixture was quenched by addition of saturated aqueous $NaHCO_3$, and the CH_2Cl_2 solution was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane−AcOEt (40:1) to give (−)-**5** (1.11 g, 71%) as a yellow oil: $[\alpha]^{23}_D$ −10.1 (*c* 1.00, $CHCl_3$); IR 1640 cm^{-1}; ^{1}H NMR δ 6.44 (d, 1H, J = 8.3 Hz), 5.80 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.02 (dd, 1H, J = 17.1, 3.4 Hz), 4.97 (m, 1H), 4.29 (t, 1H, J = 8.3 Hz,), 3.77 (dt, 1H, J = 8.3, 7.3 Hz), 2.13−2.06 (m, 2H), 1.67−1.45 (m, 4H), 1.42 (s, 3H), 1.39 (s, 3H); ^{13}C NMR δ 138.20, 135.78, 114.88, 109.34, 93.91, 80.65, 79.79, 33.62, 31.29, 27.19, 26.72, 25.00; MS *m*/*z* 354 (M^+, 0.2). Anal. Calcd for $C_{12}H_{18}Br_2O_2$: C, 40.71; H, 5.12. Found: C, 40.72; H, 5.22.

(*6S,7S*)-6,7-(Isopropylidenedioxy)non-1-en-8-yne ((−)-6a). To a solution of **5** (3.45 g, 9.73 mmol) in Et_2O (80 mL) was added *n*-BuLi (1.63 M hexane solution, 13.1 mL, 21.4 mmol) at −50 °C, and the reaction mixture was stirred for 30 min at the same temperature. The reaction mixture was quenched by addition of water, diluted with Et_2O, and washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane-AcOEt (50:1) afforded (−)-**6a** (1.68 g, 89%) as a colorless oil: $[\alpha]^{23}_D$ −14.8 (*c* 1.00, $CHCl_3$); IR 3307, 1640 cm^{-1}; ^{1}H NMR δ 5.79 (ddt, 1H, J = 17.1, 10.3, 6.8 Hz), 5.02 (dd, 1H, J = 17.1, 3.4 Hz), 4.96 (m, 1H), 4.19 (dd, 1H, J = 7.8, 2.0 Hz,), 4.03 (dt, 1H, J = 7.8, 4.4 Hz), 2.51 (d, 1H, J = 2.0 Hz), 2.13−2.08 (m, 2H), 1.71−1.47 (m, 4H), 1.45 (s, 3H), 1.40 (s, 3H); ^{13}C NMR δ 138.17, 114.90, 109.90, 81.35, 80.77, 74.56, 70.21, 33.53, 31.68, 27.06, 26.08,

(15) Sugihara, T.; Yamaguchi, M.; Nishizawa, M. *J. Synth. Org. Chem.* **1999**, *57*, 158.

(16) Sugihara observed the partial migration of the internal (*E*)-double bond to the terminal olefin during the Pauson−Khand reaction using cyclohexylamine.

(17) The recovered cobalt-complexed enyne was converted into the corresponding enyne, whose structure was unambiguously confirmed by spectral comparison and TLC behavior.

24.87; MS *m*/*z* 194 (M^+, 0.5). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.36; H, 9.62.

(6*S*,7*S*)-6,7-(Isopropylidenedioxy)-9-phenylnon-1-en-8-yne ((−)-6b). To a solution of **6a** (450 mg, 2.32 mmol) in THF (23 mL) was successively added CuI (26.5 mg, 0.14 mmol), iodobenzene (0.57 mL, 2.78 mmol), and $Pd(PPh_3)_2Cl_2$ (48.8 mg, 0.07 mmol). After stirring for 5 min at room temperature, ^{i}-Pr_2NH (3.30 mL, 23.2 mmol) was added to the reaction mixture, which was further stirred for 2h. The resulting precipitates were filtered off and the filtrate was concentrated to leave a residual oil, which was chromatographed with hexane−AcOEt (50:1) to afford (−)-**6b** (548 mg, 87%) as a colorless oil: $[\alpha]^{23}_D$ −43.8 (*c* 1.00, $CHCl_3$); IR 2232, 1640 cm^{-1}; ^{1}H NMR δ 7.47−7.43 (m, 2H), 7.33−7.29 (m, 3H), 5.82 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.03 (dd, 1H, *J* = 17.1, 3.4 Hz), 4.97 (m, 1H), 4.45 (d, 1H, *J* = 7.8), 4.11 (dt, 1H, *J* = 7.8, 5.6 Hz), 2.17−2.11 (m, 2H), 1.75−1.55 (m, 4H), 1.51 (s, 3H), 1.45 (s, 3H); ^{13}C NMR δ 138.26, 131.79, 128.59, 128.25, 122.32, 114.90, 109.69, 86.42, 85.66, 81.47, 71.05, 33.61, 31.79, 27.17, 26.31, 24.94; MS *m*/*z* 270 (M^+, 3.7). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.82; H, 8.49.

(3*S*,4*S*)-1-Phenylnon-8-en-1-yne-3,4-diol ((−)-7). A solution of **6b** (548 mg, 2.03 mmol) in MeOH (20 mL) containing 10 drops of 10% HCl solution was heated at reflux for 1 h. MeOH was evaporated off, and the residue was taken up in $CHCl_3$ which was washed with water, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (2:1) afforded (−)-**7** (423 mg, 92%) as a colorless oil: $[\alpha]^{24}_D$ −24.2 (*c* 1.00, $CHCl_3$); IR 3567, 3413, 2228, 1640 cm^{-1}; ^{1}H NMR δ 7.45−7.42 (m, 2H), 7.35−7.28 (m, 3H), 5.81 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.02 (dd, 1H, *J* = 17.1, 3.4 Hz), 4.96 (m, 1H), 4.39 (d, 1H, *J* = 6.8), 3.74 (m, 1H), 2.74 (brs, 2H), 2.15−2.04 (m, 2H), 1.81−1.48 (m, 4H); ^{13}C NMR δ 13845, 131.72, 128.55, 128.23, 122.14, 114.68, 87.78, 86.36, 74.68, 66.52, 33.50, 32.29, 24.76; MS *m*/*z* 230 (M^+, 1.8). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.86; H, 7.97.

(6*S*,7*S*)-Bis(*tert*-butyldimethylsiloxy)-9-phenylnon-1-en-8-yne ((−)-8a). To a solution of **7** (250 mg, 1.09 mmol) and imidazole (443 mg, 6.51 mmol) in DMF (1.0 mL) was added TBDMSCl (491 mg, 3.26 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 1 h, quenched by addition of water, 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 (−)-**8a** (474 mg, 95%) as a colorless oil: $[\alpha]^{23}_D$ −11.5 (*c* 1.00, $CHCl_3$); IR 1639 cm^{-1}; ^{1}H NMR δ 7.43−7.27 (m, 5H), 5.83 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.04 (dd, 1H, *J* = 17.1, 1.5 Hz), 4.96 (m, 1H), 4.55 (d, 1H, *J* = 5.3), 3.68 (ddd, 1H, *J* = 8.2, 5.3, 3.4 Hz), 2.11−2.05 (m, 2H), 1.84−1.45 (m, 4H), 0.93 (s, 9H), 0.92 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR δ 138.99, 131.48, 128.18, 127.96, 123.38, 114.30, 89.08, 85.16, 74.95, 67.55, 33.89, 31.68, 25.88, 24.75, 18.30, 18.10, −4.33, −4.45, −4.49, −4.74; MS *m*/*z* 458 (M^+, 13.5). Anal. Calcd for $C_{27}H_{46}O_2Si_2$: C, 70.68; H, 10.11. Found: C, 70.45; H, 10.40.

(6*S*,7*S*)-Bis(*tert*-butyldimethylsiloxy)dec-1-en-8-yne ((−)-8b). To a solution of **6a** (333 mg, 1.72 mmol) in THF (17 mL) was added *n*-BuLi (1.41 M hexane solution, 1.38 mL, 2.56 mmol) at −50 °C. After stirring for 30 min at the same temperature, MeI (1.07 mL, 17.2 mL) was added to the reaction mxiture, which was then stirred at room-temperature overnight. The mixture was quenched by addition of saturated aqueous NH_4Cl, extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to give the crude product, which was successively hydrolyzed and silylated, according to the procedure described for conversion of **6b** to **8a**, to afford (−)-**8b** (479 mg, 72%) as a colorless oil: $[\alpha]^{23}_D$ −13.2 (*c* 1.00, $CHCl_3$); IR 1639 cm^{-1}; ^{1}H NMR δ 5.83 (ddt, 1H, *J* = 17.1, 10.3, 6.6 Hz), 5.00 (dd, 1H, *J* = 17.1, 3.6 Hz), 4.94 (m, 1H), 4.29 (m, 1H), 3.55 (ddd, 1H, *J* = 8.9, 5.3, 3.1 Hz), 2.07−2.06 (m, 2H), 1.82 (s, 3H), 1.73−1.35 (m, 4H), 0.90 (s, 9H), 0.90 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H), 0.06 (s, 3H), 0.06 (s, 3H); ^{13}C NMR δ 139.07, 114.20, 81.10, 78.51, 75.02, 67.23, 33.89, 31.48, 25.88, 24.78, 18.28, 18.13, 3.61, −4.35, −4.51, −4.83; MS *m*/*z* 396 (M^+, 17.8). Anal. Calcd for $C_{22}H_{44}O_2Si_2$: C, 66.60; H, 11.18. Found: C, 66.95; H, 11.46.

(6*S*,7*S*)-Bis(*tert*-butyldimethylsiloxy)undec-1-en-8-yne ((−)-8c). According to the procedure described for conversion of **6a** to **8b**, the title compound (−)-**8c** (751 mg, 71%) was obtained from **6a** (500 mg, 2.57 mmol). Compound (−)-**8c** was a colorless: $[\alpha]^{24}_D$ −9.5 (*c* 1.00, $CHCl_3$); IR 1639 cm^{-1}; ^{1}H NMR δ 5.82 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.00 (dd, 1H, *J* = 17.1, 3.4 Hz), 4.93 (m, 1H), 4.30 (dt, 1H, *J* = 5.4, 2.0 Hz), 3.56 (ddd, 1H, *J* = 7.4, 5.4, 3.9 Hz), 2.20 (qd, 2H, *J* = 7.6, 2.0 Hz), 2.08−2.03 (m, 2H), 1.75−1.35 (m, 4H), 1.12 (t, 3H, *J* = 7.6 Hz), 0.90 (s, 9H), 0.90 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H), 0.06 (s, 3H), 0.06 (s, 3H); ^{13}C NMR δ 139.07, 114.18, 86.96, 78.76, 77.47, 74.99, 67.19, 65.84, 33.89, 31.52, 25.88, 25.68, 24.67, 18.28, 18.10, 15.26, 13.77, 12.46, −4.35, −4.53, −4.78; MS *m*/*z* 410 (M^+, 8.9). Anal. Calcd for $C_{23}H_{46}O_2Si_2$: C, 67.25; H, 11.29. Found: C, 67.39; H, 11.23.

(6*S*,7*S*)-Bis(*tert*-butyldimethylsiloxy)non-1-en-8-yne ((−)-8d). According to the procedure described for conversion of **6a** to **8b**, the title compound (−)-**8d** (127 mg, 80%) was obtained from **6a** (80.7 mg, 0.42 mmol). Compound (−)-**8d** was a colorless oil: $[\alpha]^{23}_D$ −15.7 (*c* 1.00, $CHCl_3$); IR 3307, 1639 cm^{-1}; ^{1}H NMR δ 5.82 (ddt, 1H, *J* = 17.1, 10.3, 6.8 Hz), 5.01 (dd, 1H, *J* = 17.1, 3.4 Hz), 4.94 (m, 1H), 4.33 (dd, 1H, *J* = 4.8, 2.4 Hz), 3.57 (ddd, 1H, *J* = 7.8, 4.8, 3.4 Hz), 2.32 (d, 1H, *J* = 2.4 Hz), 2.09−2.04 (m, 2H), 1.77−1.37 (m, 4H), 0.90 (s, 9H), 0.90 (s, 9H), 0.13 (s, 3H), 0.09 (s, 3H), 0.06 (s, 3H), 0.06 (s, 3H); ^{13}C NMR δ 138.94, 114.30, 83.16, 74.52, 73.16, 66.92, 33.82, 31.20, 25.84, 25.77, 24.84, 18.17, 18.08, −4.42, −4.54, −4.65, −4.96; MS *m*/*z* 382 (M^+, 17.8). Anal. Calcd for $C_{21}H_{42}O_2Si_2$: C, 65.73; H, 11.06. Found: C, 65.73; H, 11.37.

General Procedure for Pauson−Khand Reaction of Eynyne. **Condition B.** $Co_2(CO)_8$ (0.24 mmol) was added to a solution of enyne (0.20 mmol) in Et_2O (2.0 mL) at room temperature. The reaction mixture was stirred for 1 h and concentrated to leave the residue. The crude cobalt-complexed enyne was dissolved in THF (5.0 mL), to which TMANO·$2H_2O$ (1.2 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature until disappearance of the starting material. The reaction mixture was concentrated and the residue was purified by silica gel chromatography with hexane-AcOEt to give cyclized products. **Condition C.** A solution of the crude cobalt-complexed enyne and $CyNH_2$ (0.80 mmol) in 1,2-dichloroethane (2.0 mL) was heated at reflux for 15 min. Workup and chromatography provided cyclized products. **Condition D.** A solution of the crude cobalt-complexed enyne and MeSPh (0.7 mmol) in 1,2-dichloroethane (2.0 mL) was heated at reflux for 1 h. Workup and chromatography provided cyclized products. **Condition E**. A solution of the crude cobalt-complexed enyne and MeSPr^i (2.00 mmol) in 1,2-dichloroethane (2.0 mL) was heated at reflux for 1 h. Workup and chromatography provided cyclized products. **Condition F**. A solution of the crude cobalt-complexed enyne and MeSBu^n (0.70 mmol) in 1,2-dichloroethane (2.0 mL) was heated at reflux for 15 min. Workup and chromatography provided cyclized products. Chemical yields and ratio between **9** and **10** are summarized in Table 1.

(2*S*,3*S*,6*S*,7*S*)- and (2*S*,3*S*,6*S*,7*R*)-Bis(*tert*-butyldimethylsiloxy)-7-methyl-9-phenylbicyclo[4.3.0]non-1(9)-en-8-ones (9a and 10a). A mixture of **9a** and **10a** was obtained in a ratio of 93:7 (entry 4 in Table 1). The ratio was determined by HPLC analysis (hexane-AcOEt=50:1; 1.0 mL/min; retention time of **9a** was recorded as 7.9 min and that of **10a** as 9.1 min). A mixture of **9a** and **10a** was a colorless oil: IR 1695, 1646 cm^{-1}; ^{1}H NMR δ 7.75−7.24 (m, 5H), 4.93 (d, 93/100 × 1H, *J* = 3.4 Hz), 4.91 (d, 7/100 × 1H, *J* = 3.9 Hz), 4.09 (m, 1H), 2.99 (m, 7/100 × 1H), 2.60 (m, 93/100 × 1H), 2.33 (m, 7/100 × 1H), 2.10 (m, 1H), 1.88 (dq, 93/100 × 1H, *J* = 7.3, 2.9 Hz), 1.70 (m, 1H), 1.60−1.51 (m, 2H), 1.21 (d, 93/100 × 3H, *J* = 7.3 Hz), 1.03 (d, 7/100 × 3H, *J* = 4.9 Hz), 0.91 (s, 93/100 × 9H), 0.87 (s, 7/100 × 9H), 0.86 (s, 7/100 × 9H), 0.83 (s, 93/100 × 9H), 0.06 (s, 93/100 × 3H), 0.02 (s, 7/100 × 3H), 0.00 (s, 93/100 × 3H), −0.02 (s, 7/100 × 3H), −0.13 (s, 7/100 × 3H), −0.14 (s, 7/100 × 3H), −0.19 (s, 93/100 × 3H), −0.21 (s, 93/100 × 3H);

MS *m*/*z* 486 (M^+, 5.3). Anal. Calcd for $C_{28}H_{46}O_3Si_2$: C, 69.08; H, 9.52. Found: C, 69.36; H, 9.80.

(2*S*,3*S*,6*S*,7*S*)- and (2*S*,3*S*,6*S*,7*R*)-Bis(*tert*-butyldimethylsiloxy)-7,9-dimethylbicyclo[4.3.0]non-1(9)-en-8-ones (9b and 10b). A mixture of **9b** and **10b** was obtained in a ratio of 80:20 (entry 9 in Table 1). The ratio was determined by HPLC analysis (hexane−AcOEt = 50:1; 1.0 mL/min; retention time of **9b** was recorded as 8.2 min and that of **10b** as 8.8 min). A mixture of **9b** and **10b** was a colorless oil: IR 1691, 1657 cm^{-1}; ^1H NMR δ 4.47 (d, 20/100 × 1H, J = 3.4 Hz), 4.46 (d, 80/100 × 1H, J = 3.4 Hz), 3.92 (m, 1H), 2.98 (m, 20/100 × 1H), 2.46 (m, 80/100 × 1H), 2.39 (m, 20/100 × 1H), 2.04 (m, 1H), 1.89 (dq, 80/100 × 1H, J = 7.3, 1.5 Hz), 1.87 (m, 1H), 1.70 (s, 80/100 × 3H), 1.69 (s, 20/100 × 3H), 1.67−1.35 (m, 2H), 1.14 (d, 80/100 × 3H, J = 7.3 Hz), 1.07 (d, 20/100 × 3H, J = 7.8 Hz), 0.87 (s, 20/100 × 9H), 0.87 (s, 80/100 × 9H), 0.81 (s, 80/100 × 9H), 0.81 (s, 20/100 × 9H), 0.07 (s, 80/100 × 3H), 0.07 (s, 20/100 × 3H), 0.04 (s, 80/100 × 3H), 0.04 (s, 20/100 × 3H), 0.02 (s, 80/100 × 3H), 0.02 (s, 20/100 × 3H), −0.02 (s, 20/100 × 3H), −0.03 (s, 80/100 × 3H); MS *m*/*z* 424 (M^+, 5.3). Anal. Calcd for $C_{23}H_{44}O_3Si_2$: C, 65.04; H, 10.44. Found: C, 65.43; H, 10.79.

(2*S*,3*S*,6*S*,7*S*)- and (2*S*,3*S*,6*S*,7*R*)-Bis(*tert*-butyldimethylsiloxy)-9-ethyl-7-methylbicyclo[4.3.0]non-1(9)-en-8-ones (9c and 10c). A mixture of **9c** and **10c** was obtained in a ratio of 62:38 (entry 13 in Table 1). The ratio was determined by HPLC analysis (hexane −AcOEt = 50:1; 1.0 mL/min; retention time of **9c** was recorded as 7.0 min and that of **10c** as 8.0 min). A mixture of **9c** and **10c** was a colorless oil: IR 1691, 1653 cm^{-1}; ^1H NMR δ 4.49 (d, 38/100 × 1H, J = 3.4 Hz), 4.48 (d, 62/100 × 1H, J = 3.4 Hz), 3.93 (m, 1H), 2.97 (m, 38/100 × 1H), 2.44 (m, 62/100 × 1H), 2.37 (m, 38/100 × 1H), 2.25−2.11 (m, 2H), 2.03 (m, 1H), 1.87 (dq, 62/100 × 1H, J = 7.3, 2.0 Hz), 1.65−1.32 (m, 3H), 1.13 (d, 62/100 × 3H, J = 7.3 Hz), 1.06 (d, 38/100 × 3H, J = 7.8 Hz), 1.05 (m, 3H), 0.88 (s, 38/100 × 9H), 0.87 (s, 62/100 × 9H), 0.83 (s, 62/100 × 9H), 0.83 (s, 38/100 × 9H), 0.09 (s, 38/100 × 3H), 0.08 (s, 62/100 × 3H), 0.05 (s, 62/100 × 3H), 0.04 (s, 38/100 × 3H), 0.04 (s, 62/100 × 3H), 0.03 (s, 38/100 × 3H), 0.00 (s, 38/100 × 3H), −0.01 (s, 62/100 × 3H); MS *m*/*z* 438 (M^+, 11.8). Anal. Calcd for $C_{24}H_{46}O_3Si_2$: C, 65.69; H, 10.57. Found: C, 65.92; H, 10.87.

(2*S*,3*S*,6*S*,7*S*)- and (2*S*,3*S*,6*S*,7*R*)-Bis(*tert*-butyldimethylsiloxy)-7-methylbicyclo[4.3.0]non-1(9)-en-8-ones (9d and 10d). A mixture of **9d** and **10d** was obtained in a ratio of 80:20 (entry 9 in Table 1). The ratio was determined by HPLC analysis (hexane−AcOEt = 50:1; 1.0 mL/min; retention time of **9d** was recorded as 10.0 min and that of **10d** as 10.5 min). A mixture of **9d** and **10d** was a colorless oil: IR 1695, 1632 cm^{-1}; ^1H NMR δ 5.89 (d, 13/100 × 1H, J = 2.0 Hz), 5.88 (d, 87/100 × 1H, J = 1.5 Hz), 4.33 (m, 1H), 3.91 (m, 1H), 3.06 (m, 13/100 × 1H), 2.54 (m, 87/100 × 1H), 2.45 (m, 13/100 × 1H), 2.03 (m, 1H), 1.96 (dq, 87/100 × 1H, J = 7.3, 2.0 Hz), 1.90 (m, 1H), 1.69−1.46 (m, 2H), 1.15 (d, 87/100 × 3H, J = 7.3 Hz), 1.07 (d, 13/100 × 3H, J = 7.8 Hz), 0.88 (s, 13/100 × 9H), 0.87 (s, 87/100 × 9H), 0.83 (s, 87/100 × 9H), 0.82 (s, 13/100 × 9H), 0.07 (s, 87/100 × 6H), 0.04 (s, 13/100 × 6H), 0.03 (s, 13/100 × 6H), 0.00 (s, 87/100 × 6H); MS *m*/*z* 410 (M^+, 15.2); HRMS calcd for $C_{22}H_{42}O_3Si_2$ 410.2672, found 410.2668.

Isomerization of 8b with $CyNH_2$. $Co_2(CO)_8$ (37.2 mg, 0.11 mmol) was added to a solution of **8b** (36.0 mg, 0.09 mmol) in Et_2O (0.9 mL) at room temperature. The reaction mixture was stirred for 1 h and concentrated to leave the residue, which was passed through a short pad of silica gel with hexane to give the residue. A solution of the crude cobalt-complexed **8b** in dichloroethane (0.9 mL) was then stirred in the presence of $CyNH_2$ (0.37 × 10^{-1} mL, 0.32 mmol) at 0 °C for 3 h, passed through a short pad of Celite with hexane to afford the residual oil, which was dissolved in MeOH (2.0 mL). CAN (200 mg, 0.36 mmol) was added to the MeOH solution, and the reaction mixture was stirred at 0 °C for 30 min. MeOH was evaporated off and the residue was taken up in Et_2O, which was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane gave a mixture of **8b** and **11b** (24.2 mg, 67%) in a ratio of 70 to 30.

Isomerization of 8b with *n*-Butyl Methyl Sulfide. A solution of the cobalt-complexed **8b**, derived from **8b** (18.3 mg, 005 mmol) and $Co_2(CO)_8$, in dichloroethane (0.5 mL) was stirred in the presence of BuSMe (0.02 mL, 0.16 mmol) at 0 °C for 3 h. Workup and CAN treatment gave, after chromatography with hexane, a mixture of **8b** and **11b** (11.8 mg, 65%) in a ratio of 20 to 80. A mixture of **8b** and **11b** was a colorless oil: selected data for ^1H NMR δ 5.82 (ddt, 20/100 × 1H, J = 17.1, 10.3, 6.8 Hz), 5.45−5.41 (m, 80/100 × 2H), 5.00 (dd, 1H, J = 17.1, 3.4 Hz), 4.93 (m, 20/100 × 1H), 4.29 (m, 1H), 3.56 (m, 1H), 1.82 (s, 3H), 1.65−1.60 (m, 20/100 × 3H); MS *m*/*z* 396 (M^+, 41.3); HRMS calcd for $C_{22}H_{44}O_2Si_2$ 396.2870, found 396.2875.

Supporting Information Available: ^1H NMR spectra for a mixture of **9d** and **10d**, and a mixture of **8b** and demetalated **11b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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