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New entry to the Pauson–Khand reaction: trimethylgermyl group at the triple bond terminus as a latent functional group

Chisato Mukai,* Takashi Kozaka, Yukihiro Suzuki and In Jong Kim

Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi 13-1, Kanazawa 920-0934 Japan

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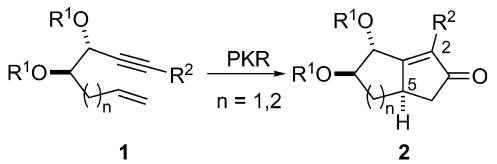
Abstract—The Pauson–Khand reaction of enynes possessing a trimethylgermyl group at the alkyne terminus afforded the corresponding bicyclo[3.3.0]octenone and bicyclo[4.3.0]nonenone skeletons in a stereoselective manner. The resulting trimethylgermyl group of the bicyclic compounds was then converted to the iodo group, which was used for further elaboration. Thus, the trimethylgermyl group at the triple bond terminus was shown to be a precursor for other appendages.

1. Introduction

The $Co_2(CO)_6$-mediated Pauson–Khand reaction (PKR)[1] is recognized as one of the most convenient and straightforward methods for the construction of bicyclo[3.3.0] as well as bicyclo[4.3.0] ring systems. Recent efforts from this laboratory[2,3] have led to the development of the highly stereoselective Pauson–Khand reaction of the enynes *ent*-**1** leading to the formation of the bicyclo[3.3.0]octenone and the bicyclo[4.3.0]nonenone derivatives *ent*-**2**[2,3] possessing two distinguishable hydroxyl groups. In particular, the exclusive formation of *ent*-**2a** (n=1,2) was observed when both substituents (R^1 and R^2) were sterically bulky silyl groups (R^1=TBDMS and R^2=TMS). However, upon exposure of the enyne **1b** (n=1) to PKR conditions, the ring-closed product **2b** (n=1) was obtained nonselectively.[2] Similarly, a decrease in stereoselectivity[3] was observed in the formation of the homologated **2b** (n=2). In addition, during the course of our program[4] directed toward the application of the newly developed stereoselective PKR to the total synthesis of bioactive compounds, the bicyclo[3.3.0]octenone derivatives **2** (n=1) with a suitable carbon appendage at the C_2-position were required as a core carbon framework. However, the PKR of the corresponding **1** (n=1) gave only a mixture of **2** (n=1) and its C_5-epimer in a moderately stereoselective manner, or nonstereoelectively (Scheme 1).[5]



a : R^1 = TBDMS, R^2 = TMS
b : R^1 = TBDMS, R^2 = H

Scheme 1.

Thus, the stereoselectivity recorded in the PKR of **1** appeared to depend in part on the bulkiness of the substituent at the triple bond terminus. In order to improve the low stereoselectivity encountered in the formation of **2b** (n=1,2)[2,3] and **2**[5] with a carbon side chain at the C_2-position, we concentrated on the silyl group at the triple bond terminus, since a bulky silyl group at the triple bond terminus might not only govern the diastereoselectivity in the PKR,[6] but could also be replaced under electrophilic substitution. Therefore, the terminal silyl moiety can be considered as a latent functional group. As a result, compound **2a** (n=1),[2] obtained from **1a** in a stereocontrolled manner, would become a versatile intermediate for the stereoselective preparation of several bicyclo[3.3.0] and bicyclo[4.3.0] skeletons **2** possessing a useful substituent at the α-position of the carbonyl functionality if efficient transformation of the vinylic TMS group into the suitable carbon tethers and hydrogen atom could be realized. However, treatment of **2a** (n=1) under typical conditions using I_2[7] or NIS,[8] showed no reaction at all and the starting **2a** (n=1) was completely recovered intact. Negishi's procedure[9] with ICl or the ICl–$AlCl_3$ system also was found not to be effective in this case. Consequently, we examined the PKR of **1** having a stannyl or germyl group instead of a silyl group at the triple bond terminus and the further transformation of the resulting **2** into the corresponding target compounds. In this paper,[10] we describe in detail the results of (i) the highly stereoselective PKR of

Keywords: Pauson–Khand reaction; Enyne; Trimethylgermyl group; Latent functional group; NIS.
* Corresponding author. Tel.: +81-76-234-4411; fax: +81-76-234-4410; e-mail address: cmukai@kenroku.kanazawa-u.ac.jp

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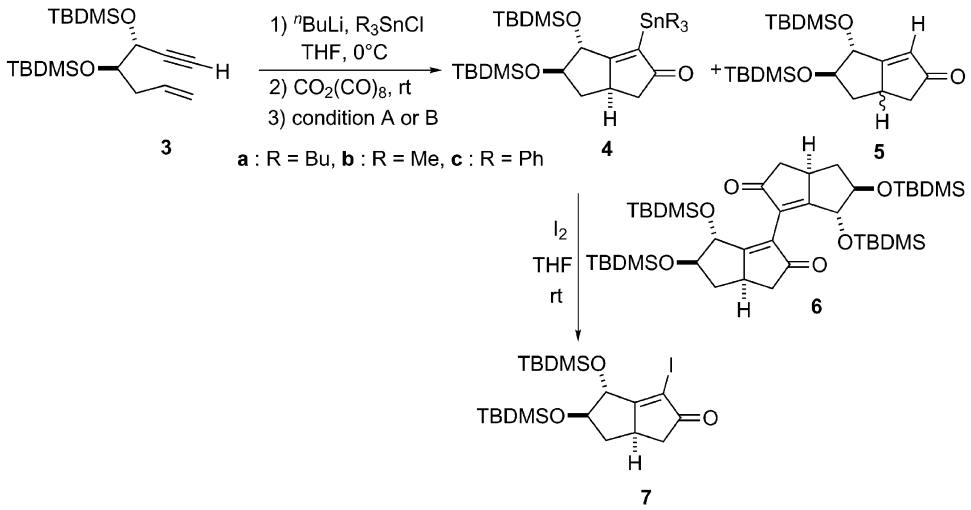
Table 1.



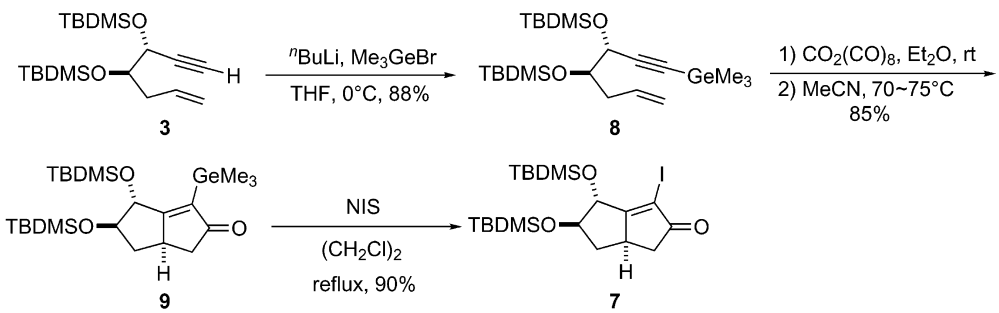
Entry	R	Condition	Yield (%)		
			4	**5**	**6**
1	Bu	A	47	14	—
2	Bu	B	65	—	—
3	Me	A	26	21	8
4	Me	B	24	24	9
5	Ph	A	27	17	—
6	Ph	B	48	Trace	—

Condition A: heated in CH_3CN at 50–55 °C. Condition B: heated in CH_3CN at 50–55 °C in the presence of 4 Å MS.

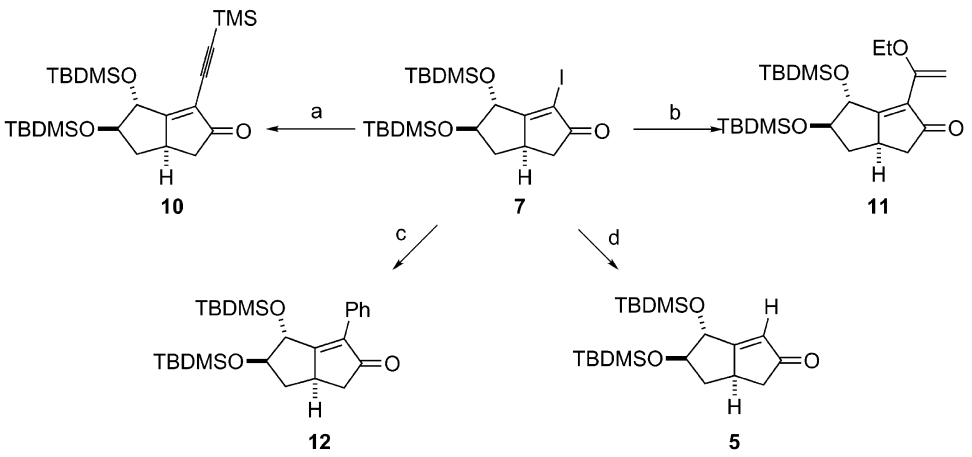
enynes having a trimethylgermyl group at the triple bond terminus and (ii) the successful transformation of the trimethylgermyl group into the desired functionalities.

We started out this study by investigating the PKR of the stannyl compounds, derived from compound **3**.[2] Treatment of the acetylide of **3** with tributyltin chloride afforded the corresponding enyne with the tributylstannyl functionality at the triple bond terminus. Because of its instability, the stannylated enyne was directly converted to the cobalt complex, which was then heated at 50–55 °C in acetonitrile[11] to provide **4a** in 47% yield in a stereoselective manner along with the nonstereoselective formation of **5** (50:50).[2b] The bicyclic compound **4a** was stable enough under PKR conditions, so that the formation of **5** could be rationalized by destannylation before the ring-closing reaction occurred. When the ring-closing reaction was carried out in the presence of 4 Å molecular sieves, **4a** was obtained in 65% yield as the sole product without detection of **5** (Table 1, entry 2). Changing the tributyl group on the tin atom to the trimethyl and triphenyl groups did not improve the chemical yield of **4** (entries 3–6). In the PKR of the trimethylstannylated derivative (entries 3 and 4), a small amount of the dimer **6** was observed. These results are summarized in Table 1. In contrast to compound **2a** with the TMS group, conversion of **4a** with the tributylstannyl group into the corresponding iodo derivative **7** (97%) was easily realized by simple treatment with I_2[7] in THF at rt.

Although the transformation of **3** into the iodide **7**, a key compound for various transformations, proceeded in a completely stereocontrolled manner via the corresponding stannylated **3** (Table 1, entry 2), this procedure (exclusive formation of **4a** without detection of **5** and **6**) could not be reproduced easily due to facile destannylation under PKR conditions. Therefore, a more reliable and reproducible method was required. To this end, we introduced a trimethylgermyl group instead of the tributylstannyl group at the alkyne terminus of **3** with the expectation that (i) the germyl group would be more reactive toward electrophilic



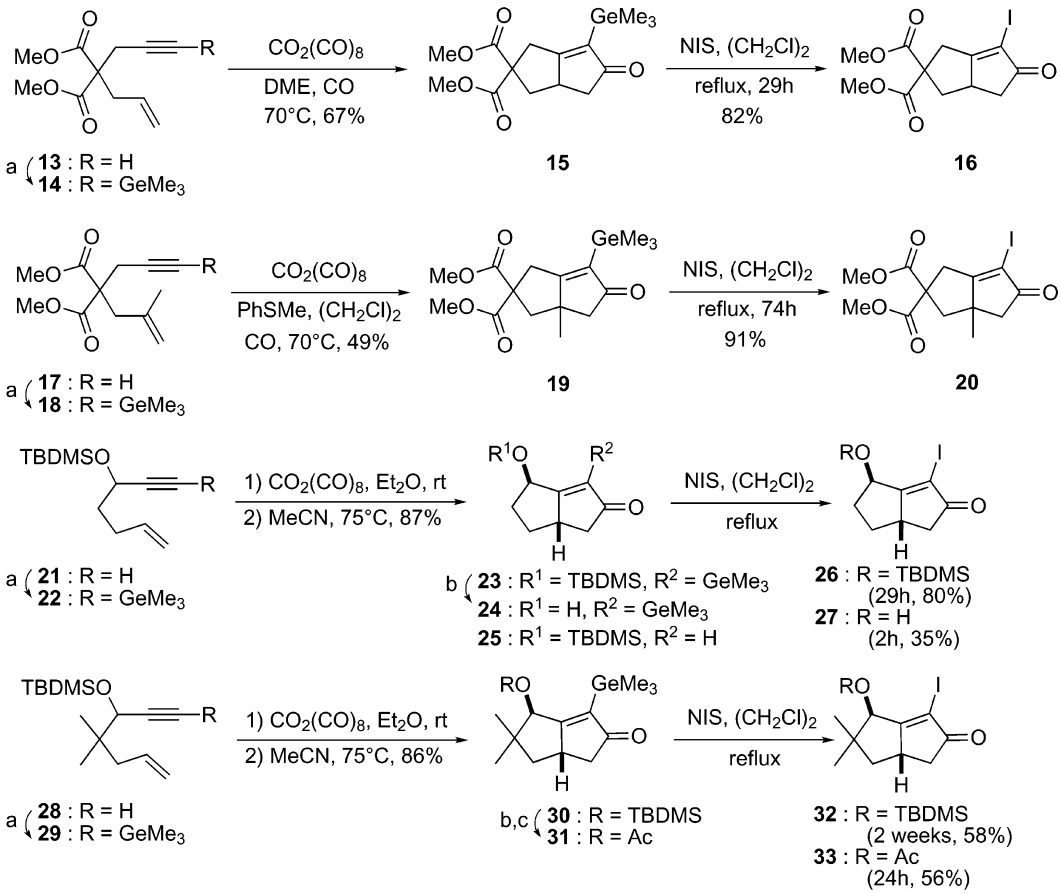
Scheme 2.



Scheme 3. Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, TMSC≡CH, $^iPr_2NH$, CuI, THF, rt, 98%; (b) $Pd(PPh_3)_2Cl_2$, (α-ethoxyvinyl)$SnMe_3$, THF, 65 °C, 84%; (c) $Pd(PPh_3)_2Cl_2$, $PhSnBu_3$, THF, reflux, 76%; (d) Bu_3SnH, THF, 55 °C, 83%.

substitution than the silyl group, and (ii) that the C–Ge bond would be stronger than the C–Sn bond and could tolerate the PKR conditions (Scheme 2). Thus, the acetylide, generated from **3**, was trapped by treatment with trimethylgermyl bromide to give **8** in 88% yield, which was subsequently exposed to $Co_2(CO)_8$. The resulting cobalt complex was heated in acetonitrile[11] to produce exclusively **9** in 85% overall yield. No formation of **5** or **6** could be detected in the reaction mixture. The 4 Å molecular sieves were not necessary in this case (Table 1, entry 2). Compound **9** was treated with NIS[8] in refluxing 1,2-dichloroethane for 36 h to furnish **7** in 90% yield. It could be predicted that the conversion of **9** to **7** required a higher reaction temperature compared to the transformation of the stannylated compound **4a** to **7**. It should be noted that the transformation of **8** to **7** via **9** under these conditions was reproduced several times.

With the iodo derivative **7** in hand, we next examined the conversion of the iodo group on the vinyl moiety of **7** to



Scheme 4. Reagents and conditions: (a) ^{n}BuLi, Me_3GeBr, THF, −78 °C, **14** (90%), **18** (81%), **22** (91%), **29** (97%); (b) TBAF, AcOH, THF, 0 °C, **24** (85%),; (c) Ac_2O, DMAP, CH_2Cl_2, 0 °C, (72%).

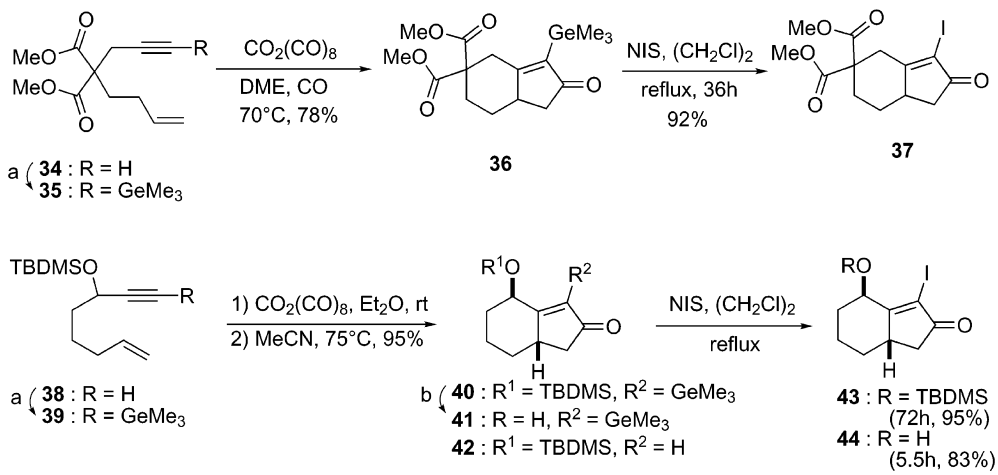
suitable functionalities (Scheme 3). Introduction of carbon side chains to the C_2-position was realized by palladium-catalyzed coupling[12] with trimethylsilylacetylene, α-(ethoxyvinyl)trimethylstannane and tributylphenylstannane to produce the corresponding coupling products **10**, **11**, and **12** in 98, 84, and 76% yield, respectively. The C_2-unsubstituted bicyclo[3.3.0]octenone derivative **5**, which had previously been nonstereoselectively obtained in 83% yield by the PKR of **3**,[2] could now be formed exclusively upon exposure of **7** to Bu_3SnH (Scheme 2).

We next investigated the PKR of several other enynes having trimethylgermyl functionality at the triple bond terminus to confirm the generality of this newly developed procedure. Scheme 4 summarizes our preparation of several bicyclo[3.3.0]octenone derivatives. The PKR[13] of the simple malonate derivative **14** possessing the trimethylgermyl functionality provided, in 67% yield, the corresponding bicyclic compound **15**, which was subsequently converted to the iodo derivative **16** in 82% yield. Under PKR conditions,[14] the enyne derivative **18** with a methyl group on the olefin moiety produced the desired **19**, although the yield (49%) was somewhat lower. Prolonged treatment of **19** with NIS furnished **20** in 91% yield, indicating tolerance of the 1,1-disubstituted olefin functionality in this transformation. Exclusive formation of **23** was realized by the PKR[11] of **22**, similar to the case of compound **9**. The enyne **21** without a terminal trimethylgermyl group was submitted to the PKR conditions[11] as a control experiment to afford a mixture of **25** along with its epimer in 79% yield in a ratio of 72 to 28. Thus, trimethylgermyl group was again found to govern the stereochemical outcome in this ring-closing reaction. Conversion of **23** into **26** under standard conditions required a relatively longer reaction time. In order to make the reaction time shorter, **23** was first desilylated to give **24**, which was subjected to the standard iodination conditions. Complete consumption of the starting material **24** was achieved within 2 h, but the yield was poor (35%).[15] Exclusive construction of **30** (86%)[11] from **29** was followed by conversion of the trimethylgermyl group to the iodo moiety to produce **32** in good yield (58%). A prolonged reaction time was required to complete the transformation of **30** into **32** under standard conditions (two weeks). Thus, adjustment of the protecting group of **30** from the bulky silyl group to the less sterically hindered acetyl group (compound **31**)[16] shortened its reaction time (24 h) and gave a similar yield.

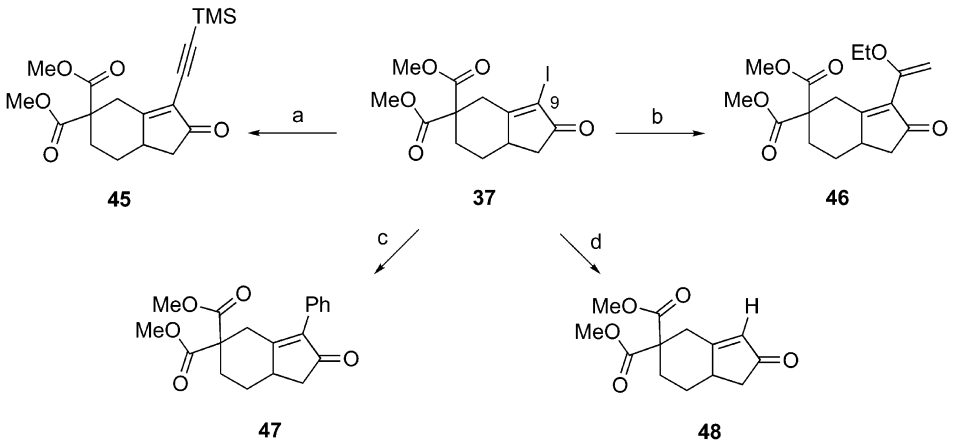
The final phase of this study was the successful application of this procedure to the synthesis of the bicyclo[4.3.0] skeleton. The homologated enyne **35** possessing the trimethylgermyl group underwent the ring-closing reaction[13] to provide the bicyclo[4.3.0]nonenone derivative **36**, which was then transformed to the corresponding iodo derivative **37** in 92% yield. On the basis of the above-mentioned preparation of compounds **9**, **23**, and **30**, it is therefore not surprising that the PKR[11] of **39** produced **40** exclusively in 95% yield. A control experiment using the unsubstituted enyne **38** produced a mixture of **42** and its epimer in 77% yield in a ratio of 92 to 8. The bicyclic derivative **40** was converted to the iodo derivative **43** in 95% yield when heated with NIS in dichloroethane for 72 h. Treatment of the alcohol (compound **41**), prepared by removal of the bulky silyl group, shortened the reaction to less than one tenth the time (5.5 h), although the yield was somewhat lower (**44**, 83%) (Scheme 5).

According to the procedure described in Scheme 3, the introduction of various carbon units at the C_9-position of **37** was achieved in the presence of a palladium catalyst[12] to furnish compounds **45**, **46**, and **47** in high yields. Reduction of **37** to **48** was also realized in 87% yield, as shown in Scheme 6.

In summary, we have developed the PKR of enynes having a trimethylgermyl group at the alkyne terminus where the stereoselective construction of the bicyclic compounds was achieved. The trimethylgermyl moiety at the α position to the carbonyl functionality of the resulting bicyclo[3.3.0]-octenone and bicyclo[4.3.0]nonenone frameworks could be converted into an iodo functionality by simple treatment with NIS in refluxing 1,2-dichloroethane. Thus, this procedure provides a new utilization of the trimethylgermyl group in PKR as a latent functional group. Further elaboration is still required and is underway in our laboratory.



Scheme 5. Reagents and conditions: (a) ^{n}BuLi, Me_3GeBr, THF, −78 °C, **35** (80%), **39** (93%); (b) TBAF, AcOH, THF, 0 °C, (87%).



Scheme 6. Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, TMSC≡CH, $^iPr_2NH$, CuI, THF, rt, 99%; (b) $Pd(PPh_3)_2Cl_2$, (α-ethoxyvinyl)$SnMe_3$, THF, 65 °C, 87%; (c) $Pd(PPh_3)_2Cl_2$, $PhSnBu_3$, THF, reflux, 88%; (d) Bu_3SnH, THF, 55 °C, 87%.

2. Experimental

Infrared spectra were measured with a Shimazu IR-460 spectrometer in $CHCl_3$, mass spectra with a Hitachi M-80 and JEOL GC mate mass spectrometers, ^1H NMR spectra with JEOL JNM-EX270 and JNM-GSX500 spectrometers for samples in $CDCl_3$, using either tetramethylsilane (for compounds without a silyl group) or $CHCl_3$ (7.26 ppm) (for compounds with a silyl group) as an internal standard, and ^{13}C NMR spectra with JEOL JNM-EX270 and JNM-GSX500 spectrometers in $CDCl_3$ with $CDCl_3$ (77.00 ppm) as an internal reference. All reactions were carried out under a 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.

2.1. General procedure for PKR of stannylated enynes

Conditions A. To a solution of enyne **3** in dry THF (0.1 M) was dropwise added *n*-BuLi in hexane (1.5 equiv.) at 0 °C. After stirring for 1 h, R_3SnCl (2.0 equiv.) was added to the reaction, which was stirred at the same temperature for 1 h. The reaction was quenched by addition of saturated aqueous NH_4Cl, extracted with Et_2O, which was then washed with H_2O and brine, dried and concentrated to dryness. The residue was directly used for the next PKR without further purification. To a solution of the crude residue in Et_2O (0.1 M) was added $Co_2(CO)_8$ (1.5 equiv.) at rt and the mixture was stirred for 1 h. Et_2O was evaporated and the residue was passed through a short pad of silica gel with hexane to give the cobalt complexed enyne derivative. A solution of the cobalt complex in acetonitrile (0.05 M) was heated at 50–55 °C for 1 h. The reaction mixture was filtered through a short pad of celite, washed with AcOEt, and concentrated to dryness. Chromatography of the residue with 2–5% AcOEt in hexane afforded **4**, **5**,[2b] and **6**.

Conditions B. The PKR of the stannylated enynes was carried out in the presence of 4Å-MS. The results were summarized in Table 1.

2.1.1. (5*R*,7*R*,8*R*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-(tributylstannyl)bicyclo[3.3.0]oct-1-en-3-one (4a). Colorless oil; $[\alpha]_D^{29}$=+78.9 (*c* 0.64, $CHCl_3$); IR 1682, 1612 cm^{-1}; ^1H NMR δ 4.34–4.31 (1H, m), 4.17 (1H, dd, *J*=6.8, 2.9 Hz), 3.32–3.24 (1H, m), 2.67 (1H, dd, *J*=17.6, 6.8 Hz), 2.57 (1H, ddd, *J*=13.2, 10.3, 6.4 Hz), 2.05 (1H, dd, *J*=17.6, 3.4 Hz),1.53–1.45 (6H, m), 1.31 (6H, sex, *J*=7.3 Hz), 1.11 (1H, ddd, *J*=13.2, 8.3, 2.9 Hz), 1.04 (6H, t, *J*=7.3 Hz), 0.88 (9H, t, *J*=7.3 Hz), 0.87 (9H, s), 0.83 (9H, s), 0.13 (3H, s), 0.07 (3H, s), 0.05(3H, s), 0.03 (3H, s); ^{13}C NMR δ 216.5, 193.8, 139.7, 80.3, 77.0, 44.5, 42.8, 39.6, 29.1, 27.3, 25.8, 25.6, 18.0, 17.9, 13.6, 9.8, −4.2, −4.3, −4.6, −4.8; MS *m/z* 672 (M^+, 0.46). HRMS calcd for $C_{32}H_{64}O_3Si_2Sn$ 672.3416, Found 672.3431.

2.1.2. (5*R*,7*R*,8*R*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-(trimethylstannyl)bicyclo[3.3.0]oct-1-en-3-one (4b). Colorless oil; $[\alpha]_D^{28}$=+85.0 (*c* 0.32, $CHCl_3$); IR 1682, 1614 cm^{-1}; ^1H NMR δ 4.37–4.33 (1H, m), 4.20–4.14 (1H, m), 3.31–3.24 (1H, m), 2.69 (1H, dd, *J*=17.6, 6.8 Hz), 2.57 (1H, ddd, *J*=13.2, 10.3, 6.4 Hz), 2.06 (1H, dd, *J*=17.6, 3.4 Hz), 1.15 (1H, ddd, *J*=13.2, 7.3, 2.0 Hz), 0.87 (9H, s), 0.82 (9H, s), 0.27 (9H, s), 0.12 (3H, s), 0.05 (3H, s), 0.04 (3H, s), 0.03 (3H, s); ^{13}C NMR δ 239.5, 216.3, 194.1, 139.4, 80.1, 76.5, 44.6, 42.5, 39.2, 25.7, 25.6, 18.0, 17.8, −4.3, −4.4, −4.6, −4.7; MS *m/z* 542 (M^+, 13.7). HRMS calcd for $C_{23}H_{46}O_3Si_2Sn$ 542.2007, Found 542.1977.

2.1.3. (5*R*,7*R*,8*R*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-(triphenylstannyl)bicyclo[3.3.0]oct-1-en-3-one (4c). Colorless oil; $[\alpha]_D^{26}$=+90.9 (*c* 0.3, $CHCl_3$); IR 1686, 1616 cm^{-1}; ^1H NMR δ 7.62–7.60 (6H, m), 7.37–7.35 (9H, m), 4.29–4.25 (1H, m), 4.11 (1H, dd, *J*=6.4, 2.0 Hz), 3.48–3.42 (1H, m), 2.80 (1H, dd, *J*=18.1, 6.8 Hz), 2.62 (1H, ddd, *J*=13.2, 10.3, 6.4 Hz), 2.20 (1H, dd, *J*=18.1, 3.4 Hz), 1.21 (1H, ddd, *J*=13.2, 7.3, 2.0 Hz), 0.80 (9H, s), 0.75 (9H, s), 0.02 (6H, s), −0.32 (3H, s), −0.33 (3H, s); ^{13}C NMR δ 215.5, 196.6, 137.8, 137.4, 137.3, 137.2, 129.1, 128.9, 128.1, 80.3, 75.6, 44.2, 4.6, 39.5, 25.8, 25.5, 17.9, 17.7, −4.6, −4.7, −4.8; MS *m/z* 732 (M^+, 32.6). HRMS calcd for $C_{38}H_{52}O_3Si_2Sn$ 732.2477, Found 732.2482.

2.1.4. Dimer 6. Colorless oil; IR 1703, 1614 cm^{-1}; ^1H NMR δ 4.96 (2H, d, *J*=2.9 Hz), 4.28 (2H, ddd, *J*=8.3, 6.8, 2.9 Hz), 3.15–3.08 (2H, m), 2.68 (2H, dd, *J*=18.1, 6.8 Hz), 2.50 (2H, dt, *J*=12.2, 6.8 Hz), 2.18 (2H, dd, *J*=18.1, 3.4 Hz), 1.24 (2H, dt, *J*=12.2, 8.3 Hz), 0.90 (18H, s), 0.81

(18H, s), 0.10 (6H, s), 0.08 (6H, s), 0.06 (6H, s), −0.07 (6H, s); ^{13}C NMR δ 207.1, 182.0, 129.1, 83.6, 76.6, 41.8, 40.9, 39.0, 25.9, 25.7, 17.97, 17.92, −3.9, −4.5, −4.6, −4.7; MS *m/z* 762 (M^+, 12.6). FABHRMS calcd for $C_{40}H_{75}O_6Si_4$ 763.4641, Found 763.4606.

2.1.5. (5*R*,7*R*,8*R*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-iodobicyclo[3.3.0]oct-1-en-3-one (7). *From compound* **4a**. A solution of **4a** (175 mg, 2.61×10^{-1} mmol) and I_2 (133 mg, 5.24×10^{-1} mmol) in dry THF (1.3 mL) was stirred at rt overnight. The reaction mixture was diluted with Et_2O, washed with saturated aqueous $Na_2S_2O_3$ and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (32:1) gave **7** (133 mg, quant.) as a colorless oil: $[\alpha]_D^{28}$=+138.3 (*c* 0.43, $CHCl_3$); IR 1715, 1632 cm^{-1}; ^{1}H NMR δ 4.40–4.35 (1H, m), 4.24 (1H, ddd, *J*=6.4, 4.4, 2.0 Hz), 3.31–3.26 (1H, m), 2.92 (1H, dd, *J*=18.1, 6.8 Hz), 2.61 (1H, ddd, *J*=13.2, 9.8, 6.4 Hz), 2.23 (1H, dd, *J*=18.1, 2.9 Hz), 1.23 (1H, ddd, *J*=13.2, 8.8, 4.4 Hz), 0.89 (9H, s), 0.85 (9H, s), 0.20 (3H, s), 0.14 (3H, s), 0.08 (3H, s), 0.05 (3H, s); ^{13}C NMR δ 204.8, 187.8, 96.3, 80.8, 78.2, 42.2, 41.5, 39.2, 25.7, 18.0, 17.8, −4.1, −4.5, −4.6, −4.8; FABMS *m/z* 509 (M^++1, 12.5). FABHRMS calcd for $C_{20}H_{38}IO_3Si_2$ 509.1404, Found 509.1409 (M^++1).

From compound **9**. A solution of **9** (6.8 mg, 1.36×10^{-2} mmol) and *N*-iodosuccinimide (4.6 mg, 2.04×10^{-2} mmol) in 1,2-dichroloethane (0.3 mL) was refluxed for 36 h in the dark. The reaction mixture was quenched by addition of water, extracted with CH_2Cl_2, which was washed with water and brine, dried and concentrated to dryness. Chromatography of the residue gave **7** (6.2 mg, 90%).

2.1.6. (4*R*,5*R*)-4,5-Bis(*tert*-butyldimethylsiloxy)-7-(trimethylgermyl)hep-1-en-6-yne (8). To a solution of **3** (50.0 mg, 1.41×10^{-1} mmol) in THF (1.4 mL) was added *n*-BuLi in hexane (1.30 M, 0.16 mL, 2.11×10^{-1} mmol) at 0 °C and the reaction mixture was stirred for 1 h at the same temperature. Me_3GeBr (0.04 mL, 2.82×10^{-1} mmol) was then added to a solution of the acetylide in THF and stirring was continued for 30 min at 0 °C. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl, extracted with Et_2O, washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane gave **8** (58.4 mg, 88%) as a colorless oil: $[\alpha]_D^{26}$=−0.20 (*c* 0.5, $CHCl_3$); IR 2170, 1639 cm^{-1}; ^{1}H NMR^{1}H NMR δ 5.87 (1H, ddt, *J*=17.6, 10.3, 7.3 Hz), 5.09–5.01 (2H, m), 4.29 (1H, d, *J*=5.4 Hz), 3.63 (1H, ddd, *J*=6.8, 5.4, 4.4 Hz), 2.48–2.33 (2H, m), 0.91 (9H, s), 0.90 (9H, s), 0.33 (9H, s), 0.14 (3H, s), 0.10 (3H, s), 0.07 (3H, s), 0.06 (3H, s); ^{13}C NMR δ 135.7, 116.7, 104.2, 90.2, 75.1, 67.1, 37.3, 25.93, 25.88, 18.3, 18.1, −0.4, −4.3, −4.42, −4.43, −4.6; MS *m/z* 472 (M^+, 41.0). HRMS calcd for $C_{22}H_{46}GeO_2Si_2$ 472.2248, Found 472.2244.

2.1.7. (5*R*,7*R*,8*R*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-(trimethylgermyl)bicyclo[3.3.0]oct-1-en-3-one (9). According to the general procedure for PKR (Conditions A), **8** (58.0 mg, 1.23×10^{-1} mmol) was treated with $Co_2(CO)_8$ (63.0 mg, 1.85×10^{-1} mmol). The resulting cobalt complex was heated at 70–75 °C in acetonitrile (1.2 mL) for 3 h. Work-up and chromatography of the residue with hexane–AcOEt (50:1) gave **9** (51.5 mg, 85%) as a colorless oil: $[\alpha]_D^{25}$=+95.9 (*c* 0.5, $CHCl_3$); IR 1686, 1622 cm^{-1}; ^{1}H NMR δ: 4.48–4.44 (1H, m), 4.16 (1H, d, *J*=5.9 Hz), 3.24–3.19 (1H, m), 3.63 (1H, dd, *J*=17.6, 6.8 Hz), 2.55 (1H, ddd, *J*=13.2, 10.3, 5.9 Hz), 3.63 (1H, dd, *J*=17.6, 3.9 Hz), 1.13 (1H, ddd, *J*=13.2, 7.3, 2.0 Hz), 0.87 (9H, s), 0.82 (9H, s), 0.36 (9H, s), 0.13 (3H, s), 0.07 (3H, s), 0.04 (3H, s), 0.02 (3H, s); ^{13}C NMR δ 215.0, 191.2, 138.7, 80.0, 75.7, 45.0, 41.4, 38.9, 25.7, 25.6, 17.9, 17.8, −1.2, −4.3, −4.6, −4.7; MS *m/z* 500 (M^+, 27.0). HRMS calcd for $C_{23}H_{46}GeO_3Si_2$ 500.2197, Found 500.2195.

2.1.8. (5*R*,7*R*,8*R*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-[2-(trimethylsilyl)ethyn-1-yl]bicyclo[3.3.0]oct-1-en-3-one (10). To a solution of **7** (20.0 mg, 3.93×10^{-2} mmol), (trimethylsilyl)acetylene (0.8×10^{-2} mL, 5.90×10^{-2} mmol), $Pd(PPh_3)_2Cl_2$ (1.7 mg, 2.36×10^{-3} mmol), and CuI (0.23 mg, 1.18×10^{-3} mmol) in THF (0.4 mL) was added *i*-Pr_2NH (0.06 mL, 3.93×10^{-1} mmol) at rt. The reaction mixture was stirred for 2 h, passed through a short pad of celite, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (5:1) gave **10** (18.5 mg, 98%) as a colorless oil: $[\alpha]_D^{28}$=+130.7 (*c* 0.26, $CHCl_3$); IR 2158, 1717, 1639 cm^{-1}; ^{1}H NMR δ 4.58–4.51 (1H, m), 4.28–4.25 (1H, m), 3.20–3.15 (1H, m), 2.77 (1H, dd, *J*=18.6, 6.8 Hz), 2.55 (1H, ddd, *J*=12.7, 9.3, 6.3 Hz), 2.15 (1H, dd, *J*=18.6, 3.4 Hz), 1.13 (1H, ddd, *J*=12.7, 9.3, 4.9 Hz), 0.89 (9H, s), 0.85 (9H, s), 0.22 (9H, s), 0.18 (3H, s), 0.11 (3H, s), 0.08 (3H, s), 0.05 (3H, s); ^{13}C NMR δ 206.2, 186.4, 122.7, 103.9, 94.7, 82.1, 75.7, 43.1, 39.3, 39.1, 25.73, 25.70, 18.0, 17.9, −0.2, −4.4, −4.6, −4.8, −4.9; FABMS *m/z* 479 (M^++1, 3.7). FABHRMS calcd for $C_{25}H_{47}O_3Si_3$ 479.2833, Found 479.2846.

2.1.9. (5*R*,7*R*,8*R*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-(1-ethoxyethen-1-yl)bicyclo[3.3.0]oct-1-en-3-one (11). A solution of **7** (99.2 mg, 1.95×10^{-1} mmol), $Pd(PPh_3)_2Cl_2$ (13.7 mg, 1.95×10^{-2} mmol) and (α-ethoxyvinyl)trimethyltin (183 mg, 7.80×10^{-1} mmol) in THF (1.0 mL) was heated at 65 °C for 6.5 h. The reaction mixture was diluted with AcOEt, which was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (50:1) gave **11** (74.1 mg, 84%) as a colorless oil: $[\alpha]_D^{28}$=+114 (*c* 0.28, $CHCl_3$); IR 1701, 1651 cm^{-1}; ^{1}H NMR δ 5.24 (1H, d, *J*=2.4 Hz), 5.03–4.96 (1H, m), 4.37 (1H, d, *J*=2.4 Hz), 4.20 (1H, dd, *J*=6.3, 2.4 Hz), 3.88–3.78 (2H, m), 3.14–3.08 (1H, m), 2.78 (1H, dd, *J*=17.6, 6.8 Hz), 2.58 (1H, ddd, *J*=13.7, 10.3, 6.3 Hz), 2.17 (1H, dd, *J*=17.6, 3.4 Hz), 1.37 (3H, t, *J*=7.3 Hz), 1.14 (1H, ddd, *J*=13.7, 7.8, 2.4 Hz), 0.86 (9H, s), 0.81 (9H, s), 0.11 (3H, s), 0.04 (3H, s), 0.03 (3H, s), 0.00 (3H, s); ^{13}C NMR δ 205.6, 177.9, 153.5, 130.9, 89.0, 81.7, 76.2, 62.0, 44.7, 39.0, 37.7, 25.9, 25.8, 18.1, 18.0, 14.6, −4.4, −4.6, −4.7; FABMS *m/z* 453 (M^++1, 4.1). FABHRMS calcd for $C_{24}H_{45}O_4Si_2$ 453.2856, Found 453.2858.

2.1.10. (5*R*,7*R*,8*R*)-7,8-Bis(*tert*-butyldimethylsiloxy)-2-phenylbicyclo[3.3.0]oct-1-en-3-one (12). A solution of **7** (17.6 mg, 3.46×10^{-2} mmol), $Pd(PPh_3)_2Cl_2$ (2.5 mg, 3.46×10^{-3} mmol) and Bu_3SnPh (45 μL, 1.38×10^{-1} mmol) in THF (0.3 mL) was refluxed for 5 h. The reaction mixture was diluted with AcOEt, which was washed with water and brine, dried, and concentrated to dryness.

Chromatography of the residue with hexane–AcOEt (26:1) gave **12** (12.0 mg, 76%) as a colorless oil: $[\alpha]_D^{26}$= +88.6 (*c* 0.42, $CHCl_3$). FABHRMS calcd for $C_{26}H_{43}O_3Si_2$ 459.2750, Found 459.2762. Spectral data were shown in ref 2b.

2.1.11. (5*R*,7*R*,8*R*)-7,8-Bis(*tert*-butyldimethylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (5). A solution of **7** (51.0 mg, 1.00×10^{-1} mmol), Bu_3SnH (0.13 mL, 5.01×10^{-1} mmol) and AIBN (a catalytic amount) in THF (0.2 mL) was heated at 55 °C for 1 h. The reaction mixture was diluted with AcOEt, which was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (20:1) gave **5** (32.0 mg, 83%) as a colorless oil: $[\alpha]_D^{26}$=+102.5 (*c* 0.3, $CHCl_3$). FABHRMS calcd for $C_{20}H_{39}O_3Si_2$ 383.2437, Found 383.2432. Spectral data are shown in Ref. 2b.

2.1.12. Dimethyl 2-allyl-2-[3-(trimethylgermyl)-2-propyn-1-yl]malonate (14). According to the procedure described for preparation of **8** from **3**, **14** (1.07 g, 90%) was obtained from **13**[17] (794 mg, 3.78 mmol) a colorless oil: IR 2174, 1736, 1641 cm^{-1}; ^1H NMR δ 5.63 (1H, ddt, *J*=10, 17, 7.6 Hz), 5.19–5.09 (2H, m), 3.72 (6H, s), 2.81–2.78 (4H, m), 0.31 (9H, s); ^{13}C NMR δ 170.2, 131.9, 119.5, 99.5, 88.0, 57.1, 52.5, 36.5, 23.9, −0.3; FABMS *m*/*z* 329 (M^++1, 10.1). FABHRMS calcd for $C_{14}H_{23}GeO_4$ 329.0808, Found 329.0814.

2.1.13. 7,7-Bis(methoxycarbonyl)-2-(trimethylgermyl)-bicyclo[3.3.0]oct-1-en-3-one (15). To a solution of enyne **14** (32.8 mg, 1.00×10^{-1} mmol) in DME (1.0 mL) was added $Co_2(CO)_8$ (41.2 mg, 1.20×10^{-1} mmol). The reaction mixture was heated at 70 °C under an atmosphere of CO for 24 h, passed through a short pad of celite, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10:1) gave **15** (23.9 mg, 67%) as colorless plates: mp 70–71 °C (hexane–Et_2O); IR 1732, 1686, 1614 cm^{-1}; ^1H NMR δ: 3.79 (3H, s), 3.75 (3H, s), 3.28, 3.16 (2H, AB-q, *J*=19 Hz), 3.10–2.98 (1H, m), 2.89–2.75 (1H, m), 2.59 (1H, dd, *J*=6.6, 17 Hz), 2.07 (1H, dd, *J*=4.0, 17 Hz), 1.68 (1H, t, *J*=13 Hz), 0.34 (9H, s); ^{13}C NMR δ 212.6, 190.7, 171.9, 171.3, 137.8, 60.6, 53.1, 52.9, 46.4, 42.5, 38.6, 35.9, −1.8; FABMS *m*/*z* 357 (M^++1, 21.8). FABHRMS calcd for $C_{15}H_{23}GeO_5$ 357.0757, Found 357.0758.

2.1.14. 2-Iodo-7,7-bis(methoxycarbonyl)bicyclo[3.3.0]-oct-1-en-3-one (16). According to the procedure described for preparation of **7** from **9**, **16** (14.0 mg, 82%) was obtained from **15** (17.4 mg, 4.78×10^{-2} mmol) as colorless needles: mp 90–91 °C (hexane–Et_2O); IR 1732, 1720, 1634 cm^{-1}; ^1H NMR δ 3.80 (3H, s), 3.77 (3H, s), 3.39, 3.13 (2H, AB-q, *J*=20 Hz), 3.26–3.12 (1H, m), 2.93–2.80 (2H, m), 2.25 (1H, dd, *J*=3.0, 18 Hz), 1.80 (1H, t, *J*=13 Hz); ^{13}C NMR δ 203.2, 188.1, 171.5, 170.7, 94.7, 59.7, 53.4, 53.2, 46.4, 39.9, 39.2, 37.3; MS *m*/*z* 364 (M^+, 20.5). Anal. Calcd for $C_{12}H_{13}IO_5$: C, 39.58; H, 3.60. Found: C, 39.57; H, 3.61.

2.1.15. Dimethyl 2-(2-methyl-2-propen-1-yl)-2-[3-(trimethylgermyl)-2-propyn-1-yl]malonate (18). According to the procedure described for preparation of **8** from **3**, **18** (742 mg, 81%) was obtained from **17**[18] (605 mg, 2.70 mmol) as a colorless oil: IR 2174, 1740, 1645 cm^{-1}; ^1H NMR δ 4.90–4.83 (2H, m), 3.72 (6H, s), 2.84 (2H, s), 2.83 (2H, s), 1.65 (3H, s), 0.30 (9H, s); ^{13}C NMR δ 170.5, 139.8, 116.0, 100.0, 88.2, 56.7, 52.5, 39.4, 23.8, 23.1, −0.4. FABMS *m*/*z* 343 (M^++1, 3.7). FABHRMS calcd for $C_{15}H_{25}GeO_4$ 343.0964, Found 343.0967.

2.1.16. 7,7-Bis(methoxycarbonyl)-5-methyl-2-(trimethylgermyl)bicyclo[3.3.0]oct-1-en-3-one (19). To a solution of enyne **18** (32.4 mg, 9.50×10^{-2} mmol) in DME (1.0 mL) was added $Co_2(CO)_8$ (39.0 mg, 1.14×10^{-1} mmol). The reaction mixture was stirred at rt for 15 min, to which PhSMe (0.04 mL, 3.33×10^{-1} mmol) was added. After being stirred for 24 h at 70 °C, the reaction mixture was passed through a short pad of celite and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10:1) gave **19** (17.1 mg, 49%) as colorless needles: mp 67–68 °C (hexane–Et_2O): IR 1732, 1693, 1618 cm^{-1}; ^1H NMR δ 3.79 (3H, s), 3.71 (3H, s), 3.41, 3.23 (2H, AB-q, *J*=17 Hz), 2.60 (1H, d, *J*=14 Hz), 2.34 (2H, s), 2.13 (1H, d, *J*=14 Hz), 1.11 (3H, s), 0.33 (9H, s); ^{13}C NMR δ 212.5, 193.7, 172.2, 172.0, 59.8, 53.3, 53.2, 52.5, 50.9, 44.3, 34.8, 27.0, −1.5; FABMS *m*/*z* 371 (M^++1, 25.4). FABHRMS calcd for $C_{16}H_{25}GeO_5$ 371.0914, Found 371.0939.

2.1.17. 2-Iodo-7,7-bis(methoxycarbonyl)-5-methylbicyclo-[3.3.0]oct-1-en-3-one (20). According to the procedure described for preparation of **7** from **9**, **20** (74.8 mg, 91%) was obtained from **19** (80.1 mg, 2.17×10^{-1} mmol) as colorless needles: mp 116–117 °C (hexane–Et_2O): IR 1732, 1720, 1636 cm^{-1}; ^1H NMR δ 3.80 (3H, s), 3.73 (3H, s), 3.56 (1H, d, *J*=18 Hz), 3.13 (1H, d, *J*=18 Hz), 2.66 (1H, d, *J*=14 Hz), 2.59, 2.47 (2H, AB-q, *J*=18 Hz), 2.27 (1H, d, *J*=14 Hz), 1.15 (3H, s); ^{13}C NMR δ 202.9, 191.0, 171.7, 171.3, 94.0, 58.8, 53.44, 53.41, 51.5, 49.5, 44.8, 36.4, 26.7; MS *m*/*z* 378 (M^+, 41.4). Anal. Calcd for $C_{13}H_{15}IO_5$: C, 41.29; H, 4.00. Found: C, 41.49; H, 4.13.

2.1.18. 5-(*tert*-Butyldimethysiloxy)hept-1-en-6-yne (21). A solution of DMSO (9.9 mL, 139 mmol) in CH_2Cl_2 (30 mL) was gradually added to a solution of oxalyl chloride (6.1 mL, 69.7 mmol) in CH_2Cl_2 (40 mL) at −78 °C. After stirring of the CH_2Cl_2 solution for 15 min, a solution of 4-penten-1-ol (3.00 g, 34.8 mmol) in CH_2Cl_2 (30 mL) was added and the reaction was stirred at −78 °C for 1 h. Et_3N (29.1 mL, 209 mmol) was added to the reaction mixture, which was then gradually warmed to rt and diluted with CH_2Cl_2. The CH_2Cl_2 solution was washed successively with water and brine, dried and concentrated to leave the crude aldehyde. *n*-BuLi in hexane (1.23 M, 42.5 mL, 52.2 mmol) was added to a solution of (trimethylsilyl)acetylene (7.4 mL, 52.2 mmol) in THF (180 mL) at −78 °C and the solution was stirred for additional 1 h. A solution of the crude aldehyde derived from 4-penten-1-ol in THF (60 mL) was then added to a solution of the acetylide in THF at −78 °C and stirring was continued for 1 h at the same temperature. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with AcOEt, which was washed successively with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10:1) gave the alcohol (5.27 g, 83%) as a pale yellow oil. To a solution of the crude alcohol (1.00 g, 5.48 mmol) and Et_3N (2.3 mL, 16.5 mmol) in CH_2Cl_2 (50 mL) was added TBSOTf (1.9 mL,

8.23 mmol) at 0 °C. The reaction mixture was stirred for 30 min at rt, quenched by addition of water, and extracted with CH_2Cl_2. The extract was washed successively with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane gave the silyl ether (1.17 g, 72%). To a solution of the silyl ether (605 mg, 2.04 mmol) in MeOH (20 mL) was added K_2CO_3 (282 mg, 2.04 mmol) at rt. The reaction mixture was stirred for 5 h at the same temperature. MeOH was evaporated off, and the residue was diluted with Et_2O, washed with water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane gave **21** (380 mg, 83%) as a colorless oil: IR 3306, 1639 cm^{-1}; ^1H NMR δ 5.82 (1H, ddt, J=10, 17, 6.6 Hz), 5.08–4.95 (1H, m), 4.36 (1H, dt, J=6.6, 2.0 Hz), 2.39 (1H, d, J=2.0 Hz), 2.24–2.16 (2H, m), 1.81–1.73 (2H, m), 0.91 (9H, s), 0.14 (3H, s), 0.11 (3H, s); ^{13}C NMR δ 137.8, 115.0, 85.4, 72.2, 62.1, 37.7, 29.3, 25.8, 18.2, −4.5, −5.1. This crude **21** was directly converted into compound **22**.

2.1.19. 5-(*tert*-Butyldimethysiloxy)-7-(trimethylgermyl)-hept-1-en-6-yne (22). According to the procedure described for preparation of **8** from **3**, **22** (512 mg, 91%) was obtained from **21** (371 mg, 1.65 mmol) as a colorless oil: IR 2166, 1639 cm^{-1}; ^1H NMR δ 5.82 (1H, ddt, J=17, 10, 6.6 Hz), 5.08–4.93 (2H, m), 4.35 (1H, t, J=6.6 Hz), 2.23–2.13 (2H, m), 1.86–1.68 (2H, m), 0.91 (9H, s), 0.33 (9H, s), 0.13 (3H, s), 0.11 (3H, s); ^{13}C NMR δ 138.1, 114.8, 106.4, 88.7, 62.8, 37.8, 29.5, 25.9, 18.3, −0.3, −4.4, −4.9; FABMS m/z 343 (M^++1, 1.5). FABHRMS calcd for $C_{16}H_{33}GeOSi$ 343.1512, Found 343.1525.

2.1.20. (5*R* *,8*R* *)-8-(*tert*-Butyldimethylsiloxy)-2-(trimethylgermyl)bicyclo[3.3.0]oct-1-en-3-one (23). According to the procedure described for preparation of **9** from **8**, **23** (320 mg, 87%) was obtained from **22** (341 mg, 1.00 mmol) as a colorless oil: IR 1686, 1616 cm^{-1}; ^1H NMR δ 4.81 (1H, dd, J=3.3, 5.6 Hz), 3.25–3.14 (1H, m), 2.64 (1H, dd, J=6.9, 18 Hz), 2.27–2.09 (2H, m), 2.04–1.82 (2H, m), 1.16–0.97 (1H, m), 0.88 (9H, s), 0.36 (9H, s), 0.12 (3H, s), 0.10 (3H, s); ^{13}C NMR δ 215.1, 193.4, 137.1, 68.9, 43.5, 43.4, 36.6, 28.0, 25.7, 17.9, −1.3, −3.8, −4.3; FABMS m/z 371 (M^++1, 8.3). FABHRMS calcd for $C_{17}H_{33}GeO_2Si$ 371.1461, Found 371.1463.

2.1.21. (5*R* *,8*R* *)-8-Hydroxy-2-(trimethylgermyl)bicyclo[3.3.0]oct-1-en-3-one (24). A mixture of TBAF in THF (1.00 M, 1.43 mL, 1.43 mmol) and AcOH (3 drops) was added to a solution of **23** (440 mg, 1.19 mmol) in THF (0.6 mL) at 0 °C. The reaction mixture was stirred for 30 h 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–AcOEt (4:1) gave **24** (257 mg, 85%) as a colorless oil: IR 3422, 1690, 1616 cm^{-1}; ^1H NMR δ 4.83 (1H, t, J=5.6 Hz), 3.22–3.07 (1H, m), 2.65 (1H, dd, J=6.3, 18 Hz), 2.50–2.38 (1H, m), 2.29–2.17 (1H, m), 2.04 (1H, dd, J=3.3, 18 Hz), 1.96–1.81 (1H, m), 1.25 (1H, s), 1.17–1.00 (1H, m), 0.89 (9H, s); ^{13}C NMR δ 215.1, 193.5, 138.2, 68.0, 44.5, 43.2, 36.3, 28.6, −1.5; FABMS m/z 257 (M^++1, 31.2). FABHRMS calcd for $C_{11}H_{19}GeO_2$ 257.0597, Found 257.0604.

2.1.22. (5*R* *,8*R* *)-8-(*tert*-Butyldimethylsiloxy)bicyclo[3.3.0]oct-1-en-3-one (25). According to the procedure described for preparation of **9** from **8**, **25** (96.1 mg, 74%) was obtained along with its stereoisomer (**25**: epimer= 72:28) from **21** (116 mg, 5.17×10^{-1} mmol). Compound **25** was a colorless oil: IR 1703, 1636 cm^{-1}; ^1H NMR δ 5.92 (1H, d, J=2.3 Hz), 4.75 (1H, dd, J=5.5, 5.6 Hz), 3.25–3.15 (1H, m), 2.67 (1H, dd, J=6.6, 18 Hz), 2.37–2.16 (2H, m), 2.06 (1H, dd, J=3.0, 18 Hz), 1.97–1.83 (1H, m), 1.17–1.04 (1H, m), 0.89 (9H, s), 0.11 (3H, s), 0.07 (3H, s); ^{13}C NMR δ 211.3, 188.4, 125.0, 68.4, 42.9, 42.8, 36.9, 28.4, 25.7, 18.1, −4.6, −4.8; MS m/z 252 (M^+, 6.7). Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.34; H, 9.82. Epimer of **25** was a colorless oil: IR 1701, 1636 cm^{-1}; ^1H NMR δ 6.02 (1H, s), 4.96 (1H, dd, J=4.9, 9.3 Hz), 2.96–2.89 (1H, m), 2.64 (1H, dd, J=6.3, 18 Hz), 2.40–2.31 (1H, m), 2.16–2.08 (2H, m), 1.88–1.81 (1H, m), 1.57–1.42 (1H, m), 0.92 (9H, s), 0.12 (3H, s), 0.11 (3H, s); ^{13}C NMR δ 210.2, 192.3, 124.4, 70.5, 43.5, 41.7, 35.4, 29.0, 25.7, 18.2, −4.8,-4.9; MS m/z 252 (M^+, 2.5). Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.33; H, 9.81.

2.1.23. (5*R* *,8*R* *)-8-(*tert*-Butyldimethylsiloxy)-2-iodobicyclo[3.3.0]oct-1-en-3-one (26). According to the procedure described for preparation of **7** from **9**, **26** (17.2 mg, 80%) was obtained from **23** (21.0 mg, 5.69×10^{-2} mmol) as a colorless oil: IR 1715, 1628 cm^{-1}; ^1H NMR δ 4.69–4.65 (1H, m), 3.34–3.24 (1H, m), 2.89 (1H, dd, J=6.6, 18 Hz), 2.43–2.14 (3H, m), 1.99–1.85 (1H, m), 1.25–1.04 (1H, m), 0.91 (9H, s), 0.18 (6H, s); ^{13}C NMR δ 205.1, 189.8, 95.2, 70.4, 44.9, 40.4, 36.6, 28.6, 25.8, 18.0, −4.2, −4.3; MS m/z 378 (M^+, 0.3). Anal. Calcd for $C_{14}H_{23}IO_2Si$: C, 44.45; H, 6.13. Found: C, 44.56; H, 6.34.

2.1.24. (5*R* *,8*R* *)-8-Hydroxy-2-iodobicyclo[3.3.0]oct-1-en-3-one (27). According to the procedure described for preparation of **7** from **9**, **27** (18.7 mg, 35%) was obtained from **24** (52.0 mg, 2.04×10^{-1} mmol) as colorless needles: mp 96–97 °C (hexane–Et_2O); IR 3418, 1715, 1628 cm^{-1}; ^1H NMR δ 4.33 (1H, t, J=6.3 Hz), 3.32–3.21 (1H, m), 2.91 (1H, dd, J=6.3, 18 Hz), 2.58–2.46 (1H, m), 2.35–2.17 (3H, m), 2.04–1.88 (1H, m), 1.25–1.05 (1H, m); ^{13}C NMR δ 204.8, 189.5, 96.0, 65.7, 45.5, 40.5, 35.2, 28.9; MS m/z 264 (M^+, 20.2). Anal. Calcd for $C_8H_9IO_2$: C, 36.39; H, 3.44. Found: C, 36.41; H, 3.57.

2.1.25. 5-(*tert*-Butyldimethysiloxy)-4,4-dimethyl-7-(trimethylgermyl)hept-1-en-6-yne (29). According to the procedure described for preparation of **8** from **3**, **29** (284 mg, 97%) was obtained from **28**[6] (200 mg, 7.92×10^{-1} mmol) as a colorless oil: IR 2166, 1638 cm^{-1}; ^1H NMR δ 5.82 (1H, ddt, J=6.3, 9.2, 17 Hz), 5.09–4.96 (2H, m), 4.00 (1H, s), 2.15–2.05 (2H, m), 0.91 (6H, s), 0.90 (9H, s), 0.33 (9H, s), 0.14 (3H, s), 0.09 (3H, s); ^{13}C NMR δ 135.5, 117.0, 105.1, 89.9, 71.0, 42.6, 39.0, 25.9, 22.7, 22.6, 18.3, −0.3, −4.2, −5.1; FABMS m/z 371 (M^++1, 1.4). FABHRMS calcd for $C_{18}H_{37}GeOSi$ 371.1825, Found 371.1862.

2.1.26. (5*R* *,8*R* *)-8-(*tert*-Butyldimethylsiloxy)-7,7-dimethyl-2-(trimethylgermyl)bicyclo[3.3.0]oct-1-en-3-one (30). According to the procedure described for preparation of **9** from **8**, **30** (656 mg, 86%) was obtained from **29**

(707 mg, 1.92 mmol) as a colorless oil: IR 1686, 1616 cm^{-1}; ^1H NMR δ 4.13 (1H, s), 3.43–3.35 (1H, m), 2.68 (1H, dd, J=6.8, 18 Hz), 2.03 (1H, t, J=12 Hz), 1.98 (1H, dd, J=3.4, 18 Hz), 1.13 (3H, s), 1.06 (1H, dd, J=5.9, 13 Hz), 0.89 (9H, s), 0.76 (3H, s), 0.36 (9H, s), 0.11 (3H, s), 0.02 (3H, s); ^{13}C NMR δ 214.9, 193.6, 136.9, 77.3, 45.6, 44.1, 42.3, 42.2, 28.5, 25.6, 24.0, 18.1, −1.3, −4.2, −4.8; FABMS m/z 397 (M^++1, 4.2). FABHRMS calcd for $C_{19}H_{37}GeO_2Si$ 397.1774, Found 397.1790.

2.1.27. (5*R* *,8*R* *)-8-Acetoxy-7,7-dimethyl-2-(trimethylgermyl)bicyclo[3.3.0]oct-1-en-3-one (31). According to the procedure described for preparation of **24** from **23**, **30** (216 mg, 5.43×10^{-1} mmol) was converted into the corresponding hydroxyl compound (118 mg, 77%). To a solution of the crude alcohol (68.6 mg, 2.42×10^{-1} mmol) and DMAP (5.9 mg, 4.85×10^{-1} mmol) in CH_2Cl_2 (2.4 mL) was added acetic anhydride (0.05 mg, 4.84×10^{-1} mmol) at 0 °C. The reaction mixture was stirred for 40 min, quenched by addition of saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (50:1) gave **31** (74.0 mg, 94%) as a colorless oil: IR 1734, 1692, 1622 cm^{-1}; ^1H NMR δ 5.35 (1H, s), 3.34–3.20 (1H, m), 2.66 (1H, dd, J=6.6, 17 Hz), 2.09 (3H, s), 2.10–1.98 (2H, m), 1.16–1.11 (1H, m), 1.07 (3H, s), 1.05 (3H, s), 0.34 (9H, s); ^{13}C NMR δ 213.8, 188.4, 170.0, 141.3, 78.0, 44.5, 44.2, 43.9, 43.6, 29.4, 23.5, 20.8, −1.5; FABMS m/z 327 (M^++1, 8.3). FABHRMS calcd for $C_{15}H_{25}GeO_3$ 327.1015, Found 327.1006.

2.1.28. (5*R* *,8*R* *)-8-(*tert*-Butyldimethylsiloxy)-2-iodo-7,7-dimethylbicyclo[3.3.0]oct-1-en-3-one (32). According to the procedure described for preparation of **7** from **9**, **32** (3.0 mg, 58%) was obtained from **30** (5.1 mg, 1.28×10^{-2} mmol) as a colorless oil: IR 1715, 1626 cm^{-1}; ^1H NMR δ 4.06 (1H, s), 3.52–3.41 (1H, m), 2.93 (1H, dd, J=6.9, 18 Hz), 2.18–2.06 (2H, m), 1.23–1.13 (1H, m), 1.13 (3H, s), 0.89 (9H, s), 0.84 (3H, s), 0.17 (3H, s), 0.10 (3H, s); ^{13}C NMR δ 205.0, 190.6, 94.3, 79.1, 44.6, 43.1, 43.0, 42.4, 28.4, 25.7, 23.8, 18.1, −4.0, −4.8; FABMS m/z 407 (M^++1, 54.2). FABHRMS calcd for $C_{16}H_{28}IO_2Si$ 407.0903, Found 407.0903.

2.1.29. (5*R* *,8*R* *)-8-Acetoxy-2-iodo-7,7-dimethylbicyclo[3.3.0]oct-1-en-3-one (33). According to the procedure described for preparation of **7** from **9**, **33** (13.7 mg, 56%) was obtained from **31** (23.7 mg, 7.29×10^{-2} mmol) as a colorless oil: IR 1740, 1720, 1634 cm^{-1}; ^1H NMR δ 5.33 (1H, s), 3.42–3.32 (1H, m), 2.96–2.88 (1H, m), 2.24–2.05 (2H, m), 2.13 (3H, s), 1.26–1.10 (1H, m), 1.13 (3H, s), 1.10 (3H, s); ^{13}C NMR δ 204.0, 185.9, 169.9, 97.9, 78.6, 44.4, 44.3, 44.0, 41.4, 28.8, 23.1, 20.6; MS m/z 334 (M^+, 21.0). HRMS calcd for $C_{12}H_{15}IO_3$ 334.0066, Found 334.0062.

2.1.30. Dimethyl 2-(3-buten-1-yl)-2-[3-(trimethylgermyl)-2-propyn-1-yl]malonate (35). According to the procedure described for preparation of **8** from **3**, **35** (273 mg, 80%) was obtained from **34** (234 mg, 1.04 mmol) as a colorless oil: IR 2174, 1732, 1641 cm^{-1}; ^1H NMR δ 5.78 (1H, ddt, J=9.9, 17, 6.3 Hz), 5.10–4.30 (2H, m), 3.72 (6H, s), 2.85 (2H, s), 2.20–1.88 (4H, m), 0.30 (9H, s); $^{13}C^{13}C$ NMR δ 170.6, 137.3, 115.0, 99.5, 88.0, 56.8, 52.5, 31.2, 28.3, 24.1, −0.3; FABMS m/z 343 (M^++1, 12.7). FABHRMS calcd for $C_{15}H_{25}GeO_4$ 343.0964, Found 343.0939.

2.1.31. 3,3-Bis(methoxycarbonyl)-9-(trimethylgermyl)-bicyclo[4.3.0]non-1(9)-en-8-one (36). According to the procedure described for preparation of **15** from **14**, **36** (410 mg, 78%) was obtained from **35** (484 mg, 1.42 mmol) as colorless needles: mp 74–75 °C (hexane–Et_2O); IR 1732, 1686, 1603 cm^{-1}; ^1H NMR δ 3.76 (3H, s), 3.70 (3H, s), 3.60 (1H, dd, J=1.7, 14 Hz), 2.70–2.44 (4H, m), 2.20–2.06 (1H, m), 2.00–1.84 (2H, m), 1.40–1.20 (1H, m), 0.38 (9H, s); ^{13}C NMR δ 211.6, 182.8, 171.6, 170.1, 141.6, 56.7, 53.0, 52.6, 42.4, 41.8, 35.2, 30.9, 30.6, −0.9; FABMS m/z 371 (M^++1, 16.6). FABHRMS calcd for $C_{16}H_{25}GeO_5$ 371.0914, Found 371.0901.

2.1.32. 9-Iodo-3,3-bis(methoxycarbonyl)bicyclo[4.3.0]-non-1(9)-en-8-one (37). According to the procedure described for preparation of **7** from **9**, **37** (70.3 mg, 92%) was obtained from **36** (74.4 mg, 2.02×10^{-1} mmol) as colorless needles: mp 119–120 °C (hexane–Et_2O); IR 1734, 1709, 1612 cm^{-1}; ^1H NMR δ 3.78 (3H, s), 3.72 (3H, s), 3.65 (1H, dd, J=2.3, 14 Hz), 2.87–2.63 (3H, m), 2.53 (1H, ddd, J=3.0, 5.6, 14 Hz), 2.20–2.02 (2H, m), 1.96 (1H, dd, J=4.0, 14 Hz), 1.38–1.16 (1H, m); ^{13}C NMR δ 201.9, 179.7, 170.9, 169.8, 102.0, 56.4, 53.2, 52.8, 42.9, 39.1, 37.4, 31.0, 30.5; MS m/z 378 (M^+, 58.6). Anal. Calcd for $C_{13}H_{15}IO_5$: C, 41.29 H, 4.00. Found: C, 41.15; H, 3.99.

2.1.33. 6-(*tert*-Butyldimethysiloxy)oct-1-en-7-yne (38). According to the procedure described for preparation of **21** from 4-penten-1-ol, **38** (495 mg, 54%) was obtained from 5-hexen-1-ol (383 mg, 3.82 mmol) as a colorless oil: IR 3308, 1639 cm^{-1}; ^1H NMR δ 5.81 (1H, ddt, J=6.6, 9.9, 17 Hz), 5.05–4.93 (2H, m), 4.35 (1H, dt, J=2.0, 6.3 Hz), 2.37 (1H, d, J=2.0 Hz), 2.12–2.04 (2H, m), 1.74–1.48 (4H, m), 0.90 (9H, s), 0.13 (3H, s), 0.11 (3H, s); ^{13}C NMR δ 138.5, 114.6, 85.5, 72.0, 62.6, 37.9, 33.3, 25.7, 24.3, 18.2, −4.6, −5.1; FABMS m/z 239 (M^++1, 1.5). FABHRMS calcd for $C_{14}H_{27}OSi$ 239.1831, Found 239.1829.

2.1.34. 6-(*tert*-Butyldimethysiloxy)-8-(trimethylgermyl)-oct-1-en-7-yne (39). According to the procedure described for preparation of **8** from **3**, **39** (147 mg, 93%) was obtained from **38** (107 mg, 4.47×10^{-1} mmol) as a colorless oil: IR 2166, 1639 cm^{-1}; ^1H NMR δ 5.81 (1H, ddt, J=6.6, 10, 17 Hz), 5.05–4.93 (2H, m), 4.33 (1H, t, J=6.6 Hz), 2.11–2.03 (2H, m), 1.72–1.45 (4H, m), 0.90 (9H, s), 0.33 (9H, s), 0.13 (3H, s), 0.11 (3H, s); ^{13}C NMR δ 138.7, 114.5, 106.6, 88.4, 63.3, 38.1, 33.3, 25.8, 24.6, 18.3, −0.3, −4.4, −4.9; FABMS m/z 355 (M^++1, 0.9). FABHRMS calcd for $C_{17}H_{35}GeOSi$ 355.1669, Found 355.1679.

2.1.35. (2*R* *,6*R* *)-2-(*tert*-Butyldimethylsiloxy)-9-(trimethylgermyl)bicyclo[4.3.0]non-1(9)-en-8-one (40). According to the procedure described for preparation of **9** from **8**, **40** (705 mg, 95%) was obtained from **39** (692 mg, 1.95 mmol) as a colorless oil: IR 1680, 1599 cm^{-1}; ^1H NMR δ 4.89 (1H, t, J=2.6 Hz), 3.16–3.07 (1H, m), 2.49 (1H, d, J=6.6, 19 Hz), 2.17–2.11 (1H, m), 2.02–1.84 (3H, m), 1.53–1.40 (2H, m), 1.26–1.08 (1H, m), 0.89 (9H, s), 0.36 (9H, s), 0.09 (3H, s), 0.01 (3H, s); ^{13}C NMR δ 213.0,

189.5, 138.6, 66.9, 42.1, 38.9, 36.6, 35.7, 25.6, 19.1, 17.9, −0.7, −4.6, −4.7; FABMS *m/z* 385 (M^++1, 9.3). FABHRMS calcd for $C_{18}H_{35}GeO_2Si$ 385.1618, Found 385.1624.

2.1.36. (2*R,6*R**)-2-Hydroxy-9-(trimethylgermyl)bicyclo[4.3.0]non-1(9)-en-8-one (41).** According to the procedure described for preparation of **24** from **23**, **41** (74.6 mg, 87%) was obtained from **40** (122 mg, 3.18×10^{-1} mmol) as colorless needles: mp 88–90 °C (hexane–Et_2O); IR 3420, 1682, 1597 cm^{-1}; ^1H NMR δ 4.91 (1H, t, *J*=2.6 Hz), 3.15–3.05 (1H, m), 2.52 (1H, dd, *J*=6.6, 19 Hz), 2.19–1.85 (6H, m), 1.64–1.49 (1H, m), 1.33–0.88 (1H, m), 0.36 (9H, s); ^{13}C NMR δ 212.9, 187.9, 139.4, 66.1, 42.3, 38.9, 35.6, 34.4, 19.1, −0.6; FABMS *m/z*: 271 (M^++1, 27.8). Anal. Calcd for $C_{12}H_{20}GeO_2$: C, 53.60; H, 7.50. Found: C, 53.49; H, 7.70.

2.1.37. (2*R,6*R**)-2-(*tert*-Butyldimethylsiloxy)bicyclo[4.3.0]non-1(9)-en-8-one (42).** According to the procedure described for preparation of **9** from **8**, **42** (81.0 mg, 71%) and its epimer (6.6 mg, 6%) were obtained from **38** (102 mg, 4.27×10^{-1} mmol). Compound **42** was a colorless oil: IR 1703, 1628 cm^{-1}; ^1H NMR δ 5.82 (1H, d, *J*=1.3 Hz), 4.73 (1H, t, *J*=2.3 Hz), 3.11–3.01 (1H, m), 2.57 (1H, dd, *J*=6.6, 19 Hz), 2.21–2.10 (1H, m), 2.04–1.86 (3H, m), 1.59–1.42 (2H, m), 1.14–0.98 (1H, m), 0.88 (9H, s), 0.07 (3H, s), 0.00 (3H, s); ^{13}C NMR δ 209.3, 183.8, 125.6, 66.7, 42.1, 37.4, 35.4, 35.3, 25.6, 19.1, 18.0, −4.9, −5.1; MS *m/z* 266 (M^+, 3.8). Anal. Calcd for $C_{15}H_{26}O_2Si$: C, 67.61 H, 9.84. Found: C, 67.27; H, 10.13. Epimer of **42** was a colorless oil: IR 1699, 1624 cm^{-1}; ^1H NMR δ 6.07 (1H, s), 4.38–4.31 (1H, m), 2.75–2.56 (2H, m), 2.17–2.01 (3H, m), 1.88–1.81 (1H, m), 1.53–1.42 (2H, m), 1.14–1.02 (1H, m), 0.91 (9H, s), 0.08 (9H, s); ^{13}C NMR δ 208.0, 186.8, 125.4, 71.6, 42.3, 40.8, 36.9, 34.4, 25.7, 23.4, 18.2, −4.8, −5.0; MS *m/z* 266 (M^+, 2.6). Anal. Calcd for $C_{15}H_{26}O_2Si$: C, 67.61 H, 9.84. Found: C, 67.37; H, 10.16.

2.1.38. (2*R,6*R**)-2-(*tert*-Butyldimethylsiloxy)-9-iodobicyclo[4.3.0]non-1(9)-en-8-one (43).** According to the procedure described for preparation of **7** from **9**, **43** (151 mg, 95%) was obtained from **40** (155 mg, 4.05×10^{-1} mmol) as a colorless oil: IR 1703, 1609 cm^{-1}; ^1H NMR δ 4.83 (1H, t, *J*=2.3 Hz), 3.24–3.14 (1H, m), 2.74 (1H, dd, *J*=6.6, 19 Hz), 2.15–1.92 (4H, m), 1.62–1.42 (2H, m), 1.25–0.98 (1H, m), 0.89 (9H, s), 0.14 (3H, s), 0.04 (3H, s); ^{13}C NMR δ 203.0, 184.4, 97.0, 69.0, 40.5, 39.4, 35.9, 35.0, 25.7, 19.3, 17.9, −4.3, −4.8; MS *m/z* 392 (M^+, 0.7). Anal. Calcd for $C_{15}H_{25}IO_2Si$: C, 45.92 H, 6.42. Found: C, 45.94; H, 6.59.

2.1.39. (2*R,6*R**)-2-Hydroxy-9-iodobicyclo[4.3.0]non-1(9)-en-8-one (44).** According to the procedure described for preparation of **7** from **9**, **44** (19.2 mg, 83%) was obtained from **41** (22.3 mg, 8.29×10^{-2} mmol) as a colorless oil: IR 3412, 1709, 1607 cm^{-1}; ^1H NMR δ 4.95–4.90 (1H, m), 3.31–3.18 (1H, m), 2.77 (1H, dd, *J*=6.6, 19 Hz), 2.18–1.90 (5H, m), 1.71–1.52 (2H, m), 1.26–1.02 (1H, m); ^{13}C NMR δ 202.9, 183.1, 98.7, 68.4, 40.5, 39.4, 35.3, 33.7, 19.4; MS *m/z* 278 (M^+, 35.9). HRMS calcd for $C_9H_{11}IO_2$ 277.9804, Found 277.9807.

2.1.40. 3,3-Bis(methoxycarbonyl)-9-[2-(trimethylsilyl)-propyn-1-yl]bicyclo[4.3.0]non-1(9)-en-8-one (45). According to the procedure described for preparation of **10** from **7**, **45** (26.6 mg, 99%) was obtained from **37** (29.1 mg, 7.70×10^{-2} mmol) as a colorless oil: IR 2160, 1732, 1713, 1624 cm^{-1}; ^1H NMR δ 3.77 (3H, s), 3.77 (1H, dd, *J*=2.3, 14 Hz), 3.71 (3H, s), 2.72–2.47 (4H, m), 2.22–1.83 (3H, m), 1.43–1.23 (1H, m), 0.22 (9H, s); ^{13}C NMR δ 203.6, 179.9, 171.3, 169.7, 125.2, 103.6, 94.0, 56.6, 53.2, 52.7, 41.1, 39.4, 34.6, 30.9, 30.8, −0.1; MS *m/z* 348 (M^+, 79.2). HRMS calcd for $C_{18}H_{24}O_5Si$ 348.1393, Found 348.1395.

2.1.41. 9-(1-Ethoxy-ethen-1-yl)-3,3-bis(methoxycarbonyl)bicyclo[4.3.0]non-1(9)-en-8-one (46). According to the procedure described for preparation of **11** from **7**, **46** (22.9 mg, 87%) was obtained from **37** (30.9 mg, 8.17×10^{-2} mm) as a colorless oil: IR 1732, 1707, 1686, 1616 cm^{-1}; ^1H NMR δ 4.10 (1H, dd, *J*=2.3, 15 Hz), 3.79–3.66 (2H, m), 3.73 (3H, s), 3.66 (3H, s), 2.73–2.39 (8H, m), 2.31–2.16 (1H, m), 2.11–1.98 (2H, m), 1.41–1.18 (2H, m); ^{13}C NMR δ 203.8, 197.4, 183.2, 170.9, 170.1, 139.4, 56.6, 53.0, 52.7, 41.6, 39.6, 34.0, 30.5, 30.4, 30.3; MS *m/z* 322 (M^+, 15.4). HRMS calcd for $C_{17}H_{22}O_6$ 322.1416, Found 322.1417.

2.1.42. 3,3-Bis(methoxycarbonyl)-9-phenylbicyclo[4.3.0]-non-1(9)-en-8-one (47). According to the procedure described for preparation of **12** from **7**, **47** (22.7 mg, 88%) was obtained from **37** (29.7 mg, 7.85×10^{-2} mmol) as colorless needles: mp 114–115 °C (hexane–Et_2O); IR 1732, 1697, 1645 cm^{-1}; ^1H NMR δ7.45–7.24 (5H, m), 3.72 (3H, s), 3.67 (1H, dd, *J*=2.3, 14 Hz), 3.53 (3H, s), 2.80–2.49 (4H, m), 2.28–1.95 (3H, m), 1.52–1.25 (1H, m); ^{13}C NMR δ 205.8, 171.4, 171.1, 170.1, 140.2, 131.0, 128.9, 128.2, 127.8, 56.2, 53.0, 52.4, 41.4, 39.0, 33.5, 30.8, 30.3; MS *m/z* 328 (M^+, 38.6). HRMS calcd for $C_{19}H_{20}O_5$ 328.1311, Found 328.1315.

2.1.43. 3,3-Bis(methoxycarbonyl)bicyclo[4.3.0]non-1(9)-en-8-one (48). According to the procedure described for preparation of **5** from **7**, **48**[19] (19.7 mg, 87%) was obtained from **37** (33.9 mg, 8.96×10^{-2} mmol).

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