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Synthesis of a Diterpene Taxoid Skeleton, Bicyclo[9.3.1]pentadecatriene

Satoshi Shibuya and Minoru Isobe*

Laboratory of Organic Chemistry, School of Bioagricultural Sciences, Nagoya University
Chikusa, Nagoya 464-8601, Japan

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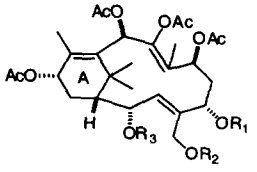
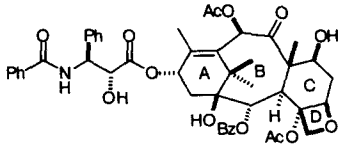
Abstract: The synthesis of bicyclo[9.3.1]pentadecatriene skeleton was investigated by employing cyclization reactions using two key precursors bearing acetylene cobalt complex. Cyclization for the synthesis of strained twelve-membered ring was achieved *via* Nicholas type reaction in reasonable yield. Reductive decomplexation of the dicobalt hexacarbonyl moiety of the cyclization product was achieved with *n*-Bu_3SnH in the presence of a catalytic amount of NBS in 1,4-cyclohexadiene solvent.

Introduction

Recently several new bicyclic taxoid diterpenoids, **1**, **2**[1,2] and **3**[3,4], were isolated from the needles of *Taxus chinensis*, or *Taxus canadensis* which have been proposed as the biosynthetic precursor[5] for taxanes. This class of compounds (**1**, **2** and **3**) bearing bicyclo[9.3.1]pentadecatriene have a similar carbon skeleton with Taxol[6] (**4**), a compound isolated from the western yew tree (*Taxus brevifolia*) in 1971 by Wall and Wani, as a potent agent against a wide range of tumor cells.



Taxachitriene A (**1**) : R_1=H, R_2=R_3=Ac
Taxachitriene B (**2**) : R_1=Ac, R_2=R_3=H
Canadensene (**3**) : R_1=R_2=H, R_3=Ac



Taxol® (**4**)

A number of organic chemists have been attracted by the multifunctional and complicated structure of Taxol itself, mode of action and a lack of natural resource. Five total syntheses of Taxol have been achieved[7-13] in the past few years. On the other hand, 10-deacetylbaccatin III is a readily available Taxol precursor isolated from Europian yew tree (*Taxus baccata*), which has been converted to Taxol in semisynthesis fashion by Holton[14] or Ojima[15] et al.

Taxol has complicated tetracyclic skeleton, which includes eight-membered ring, *gem*-dimethyl groups, fused six-membered ring and bridge head olefin against Bredt's rule. All of these compounds **1**, **2**, **3** and **4** possess the same A-ring having *gem*-dimethyl functionality, but the three formers have twelve-membered ring which is not against Bredt's rule, so that these bicyclic compounds have less strain energy than Taxol **4**. We describe here a versatile synthesis of a common bicyclo[9.3.1]pentadecane framework of **1**, **2** and **3**.

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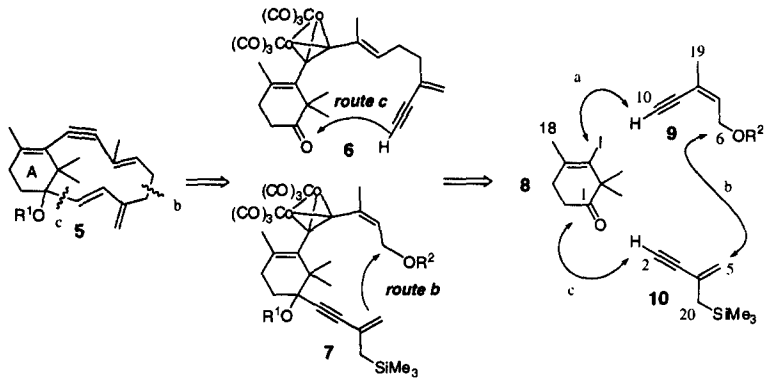
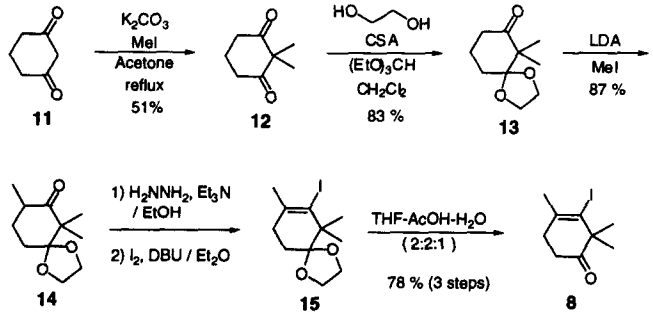


Scheme 1. Retrosynthesis of the carbon framework

To construct a bicyclo[9.3.1]pentadecane framework such as **5**, two key precursors **6** and **7** were selected for two types of cyclization reactions (***route b*** and ***c***) as shown in Scheme 1. Precursors **6** and **7** were synthesized from three common building blocks; namely, cyclohexenone ring **8** bearing *gem*-dimethyl group, two terminal acetylenes **9** and **10** having a protected alcohol or a allylsilane, respectively. Those three fragments (**8**, **9** and **10**) were synthesized[16] in short steps in high yields. The acetylene cobalt complex can be used for a carbon-carbon bond formation *via* the Nicholas reaction[17,18]. Moreover, the cobalt complex of these precursors (**6** and **7**) might be helpful for the two reaction centers to approach to each other due to the six carbonyl ligands sticking outside.

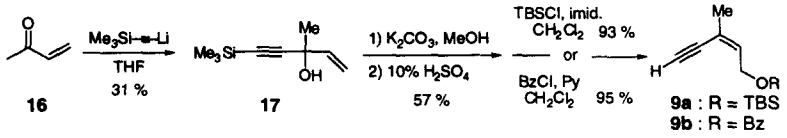
Synthesis of Three Building Blocks

The synthesis of A-ring moiety **8** was achieved in 6 steps. 1,3-Cyclohexadione **11** was treated with MeI in the presence of K_2CO_3 to give 2,2-dimethyl-1,3-cyclohexadione **12**, then its one of two ketone functionalities was transfered to cyclic acetal. Methyl group was introduced to the resulting mono cyclic acetal **13** to afford α-methyl ketone **14**. The ketone was converted to the vinyl iodide **15** using the method[19,20] that Di Grandi et al. reported. A-ring **8** was obtained from the hydrolysis of **15** using THF - AcOH - H_2O condition.



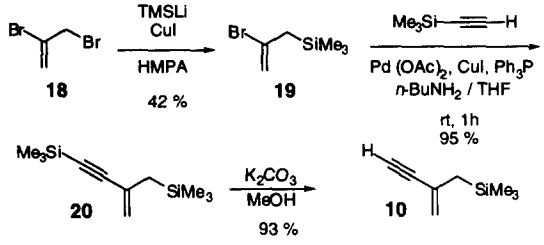
Scheme 2. Synthesis of A-ring **8**

The synthesis of allylic alcohol **9a** and **9b** were achieved in 4 steps. Methyl vinyl ketone **16** was converted to *tert*-allylic alcohol **17** on treatment with trimethylsilyl litium acetylide. Trimethylsilyl functionality of **17** was removed using K_2CO_3, then treated with 10% sulphuric acid to be isomerized[21] to give the *cis* allylic alcohol. In the case **17** was treated with acid without removing trimethylsilyl group, rearranged product was produced with a trace mixture of *trans* isomer. The allylic alcohol was protected with TBS and Bz to give **9a** and **9b**, respectively.



Scheme 3. Synthesis of protected allylic alcohol **9a** and **9b**

The synthesis of allyltrimethylsilane **10** was achieved in 3 steps. Allylsilane **19**[22] was prepared from 2,3-dibromopropene using TMSLi[23]. Vinyl bromide **19** was coupled with trimethylsilyl acetylene in the presence of palladium catalyst to give the eneyne **20**[24]. Trimethylsilyl functionality of **20** was removed using K_2CO_3 to afford allyltrimethylsilane **10**[25].

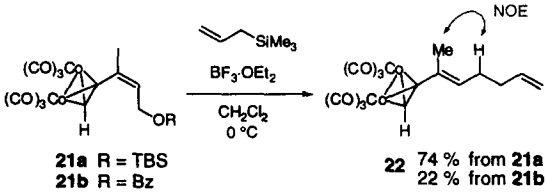


Scheme 4. Synthesis of allyltrimethylsilane **10**

Intermolecular Reaction among Three Building Blocks

Nicholas[26] reported that cobalt complex of propargyl allylic alcohol was reacted with allyltrimethylsilane in the presence of $BF_3{\cdot}OEt_2$ to give the corresponding coupling product as a single *trans* isomer.

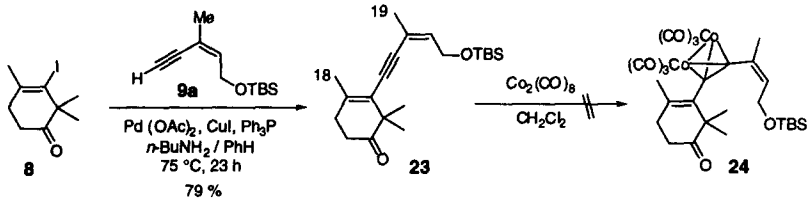
Cobalt complex **21a** and **21b** were reacted with allyltrimethylsilane in the presence of $BF_3{\cdot}OEt_2$ and **22** was obtained as a single *trans* isomer. Concentration of $BF_3{\cdot}OEt_2$ was examined at 0 °C using TBS ether **21a** and allyltrimethylsilane. In the case of 20 mM of $BF_3{\cdot}OEt_2$, the best yield was 74 %.



Scheme 5. Intermolecular Nicholas reaction

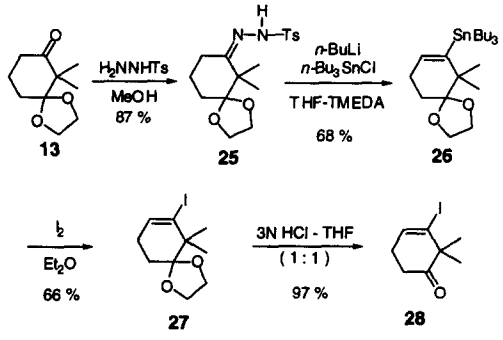
Benzoate **21b** has better leaving group than TBS ether **21a**, however, benzoate **21b** was treated with 20 mM of $BF_3{\cdot}OEt_2$ to give **22** in only 22 % yield and recovered **21b** in 64 %. Therefore, TBS ether **21a** was selected for the following sequences.

Vinyl iodide **8** (A-ring) was coupled with terminal acetylene **9a** at 75 °C for 23 h in the presence of palladium catalyst to give the dieneyne **23** in 79 % yield as shown in Scheme 6. The coupling product **23** was further treated with dicobalt octacarbonyl, but the corresponding acetylene dicobalt hexacarbonyl **24**[27] could not be obtained. This might be because the bulkiness of the substituents on both sides of acetylene. Therefore, A-ring **28** which has no methyl group at the C-18 position was used in the following sequences for obtaining the cobalt complex of corresponding coupling product.



Scheme 6. Coupling reaction between A-ring and terminal acetylene

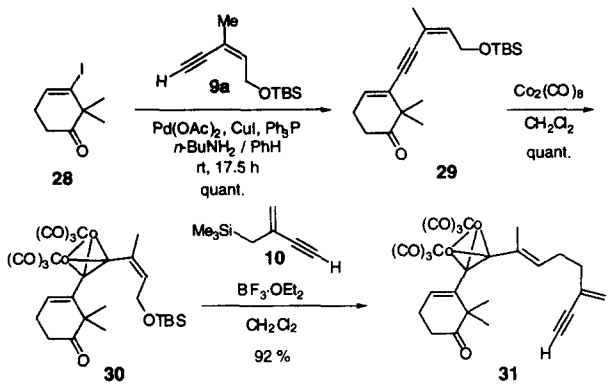
Des-methyl A-ring **28** was synthesized as shown in Scheme 7. Following by the method using for A-ring **8**, the corresponding hydrazone of **13** was unstable and low yield. Tosyl hydrazone **25** was treated with *n*-BuLi, then *n*-Bu_3SnCl to give the vinyl stannane **26**. Vinyl stannane **26** was transformed to the corresponding vinyl iodide **27**[28] using I_2 in dry ether. Cyclic acetal of **27** was hydrolyzed to give the des-methyl A-ring **28** in high yield.



Scheme 7. Synthesis of des-methyl A-ring **28**

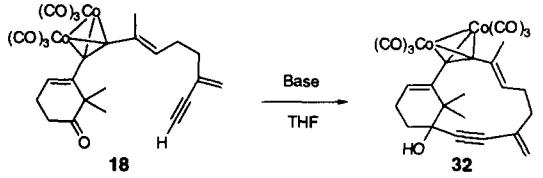
Cyclization under Basic Conditions (*route c*)

The cyclization precursor **31** was synthesized in only 3 steps in high yield by using three building blocks. Vinyl iodide **28** was mixed with terminal acetylene **9a** at room temperature for 23 h in the presence of palladium catalyst to give the dieneyne **29** in quantitative yield. Dieneyne **29** treated with dicobalt octacarbonyl gave the corresponding acetylene cobalt complex **30**. It is possible that **29** is less hinder than **23** at the C-18 position. Cobalt complex **30** was reacted with allyltrimethylsilane **10** in the presence of $BF_3{\cdot}OEt_2$ to afford **31** in 92 %.



Scheme 8. Synthesis of cyclization precursor for *route c*

Cyclization of **31** using basic condition is summarized in Table 1. High dilution condition should be necessary to avoid intermolecular reaction, so that concentration of substrate **31** was investigated using $LiN(TMS)_2$ as shown in entry 1, 2 and 3. In the case of 10 mM, cyclization product **32** was the best obtained in only 9 %. Another bases and solvents were examined using the same 10 mM concentration, the yield of **32** was not improved. One reason of low yield is instability of precursor **31** and product **32** under basic conditions, so that the bulky and weak base such as magnesium tetramethyl piperidide was used, however, it was not effective.



Entry	Substrate [mM]	Base	Yield [%]
1	5	$LiN(SiMe_3)_2$	5
2	10	$LiN(SiMe_3)_2$	9
3	20	$LiN(SiMe_3)_2$	trace
4	10	$NaN(SiMe_3)_2$	6
5	10	$KN(SiMe_3)_2$	8

Table 1. Basic conditions for cyclization

The main reason of unimproved yield is probably that the intermediate conformer **33b** is more favor than **33a** because of the freedom on its methylene bonds in Figure 1.

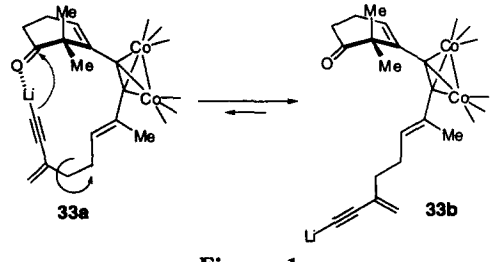
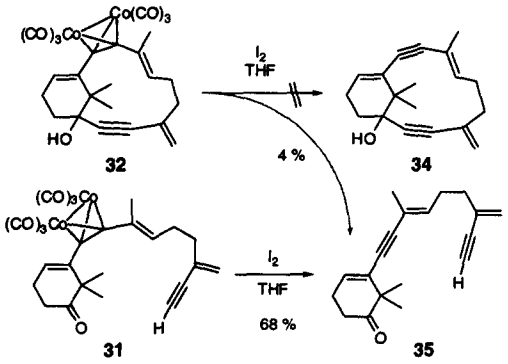


Figure 1.

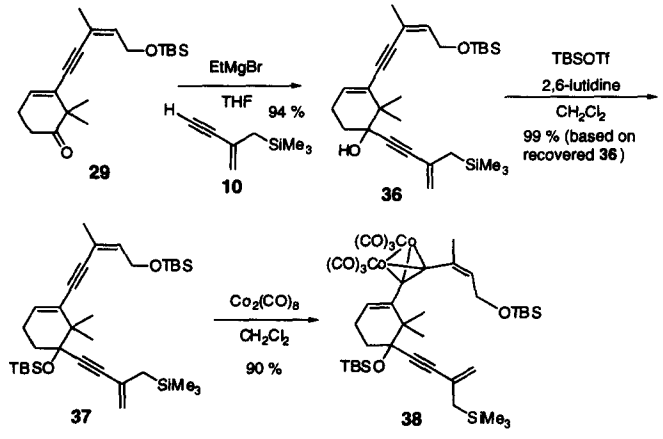
It is well known that oxidized acetylene cobalt complex reproduces its original acetylenic compound. In our case the acetylene cobalt complex **32** was treated with I_2, its corresponding acetylene **34** was not produced, but **35** was obtained in several % yield instead as shown in Scheme 9. Other oxidants such as $Ce(NH_4)_2(NO_3)_6$ and $Fe(NO_3)_3 \cdot 9H_2O$ were employed for decomplexation, however, the corresponding acetylenic compound was not formed. On the contrary, **31** was oxidised with I_2 to yield **35** in 68 %. Therefore, Bisacetylene **34** might be difficult to exist due to the highly ring strain.



Scheme 9. Oxidative decomplexation of acetylene cobalt complex

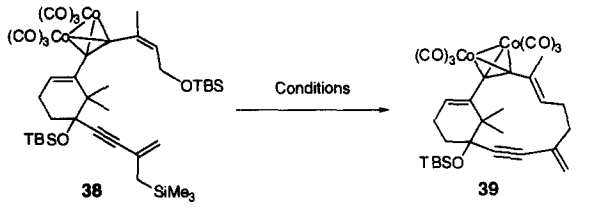
Cyclization by means of Intramolecular Nicholas Reaction[29,30] (*route b*)

The precursor **38** for intramolecular Nicholas reaction was synthesized in high yield using three common building blocks. Magnesium acetylide of **10** added to the ketone of **29** afforded the adduct **36**. The *tert*-alcohol of **36** was protected with TBS group so as to produce the mono acetylene cobalt complex in the next step[31]. The TBS ether of *tert*-alcohol **37** was treated with dicobalt octacarbonyl to give the precursor **38** in 90 %.



Scheme 10. Synthesis of cyclization precursor for *route b*

Intramolecular Nicholas reactions of **38** were examined and are summarized in Table 2. High dilution condition was necessary in order to avoid intermolecular reaction. Both the precursor **38** and the cyclization product **39** were reactive under the acidic condition so that the reaction time should be short to avoid decomposition of cyclization product **39**. Compared with the intermolecular reaction in Scheme 8 (from **30** to **31**), intramolecular Nicholas cyclizations of **38** using $BF_3{\cdot}OEt_2$ proceeded slowly. Investigation of the reaction temperature and concentration of $BF_3{\cdot}OEt_2$ showed that 4 % yield was the best. The rests were decomposed products and complexed mixture without intermolecular reaction product. Next, protic acids were examined for this cyclization in order to change the reactivity of **38**. TsOH and CSA were not effective but TfOH was gave the product **39**. The cyclization with TfOH proceeded more smoothly than with $BF_3{\cdot}OEt_2$. The yield of cyclization with TfOH in only CH_2Cl_2 was almost the same as the case with $BF_3{\cdot}OEt_2$ as acid. Using toluene as co-solvent in entry 2, the cyclization was immediately completed after addition of TfOH to improve the yield to 30 %. The rests were decomposed products and complex mixture.

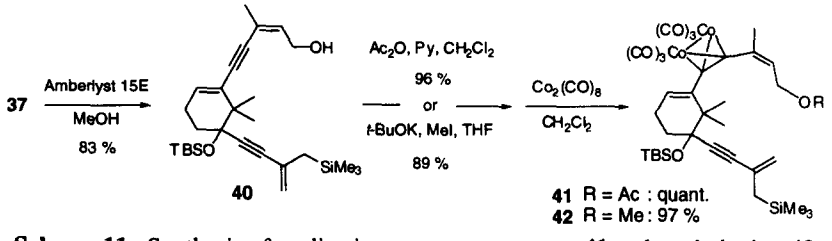


38 39

Entry	Solvent	Substrate [mM]	Acid [mM]	Temp. [°C]	Yield [%]
1	CH_2Cl_2	16	$BF_3{\cdot}OEt_2$ [16 mM]	0	4
2	CH_2Cl_2-PhMe (10 : 1)	1	TfOH [0.5 mM]	-15	30

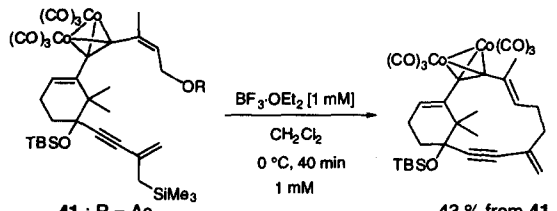
Table 2. Summary of the two best acidic conditions for cyclization of TBS ether **38**

Another improvement of the reactivity of the cyclization precursor is the selection of good leaving groups for intramolecular Nicholas reaction. Acetyl (in **41**) and methyl (in **42**) groups were selected instead of TBS ether of **38**. These two precursors were synthesized from the same intermediate **37** in 3 steps as shown in Scheme 11. TBS group of **37** was removed by Amberlyst 15E in methanol to give the alcohol **40**. The alcohol **40** was protected with acetyl group followed by treatment of dicobalt octacarbonyl to afford the precursor **41** in quantitative yield. The other precursor **42** was synthesized from **40** in 2 steps. The alcohol **40** was protected with methyl group followed by treatment of dicobalt octacarbonyl to afford the precursor **42** in 97 %.



Scheme 11. Synthesis of cyclization precursors; acetate **41** and methyl ether **42**

The best cyclization condition of **38** with $BF_3{\cdot}OEt_2$ was applied to **41** and **42**. These precursors **41** and **42** were treated with 16 mM of $BF_3{\cdot}OEt_2$ to give the cyclization product **39** in 14 % and 13 %, respectively. Under these conditions intermolecular reaction was observed, so that high dilution condition was employed.



41 : R = Ac
42 : R = Me

39 43 % from **41**
41 % from **42**

Scheme 12. Cyclization of acetate **41** and methyl ether **42**

When 1 mM of substrate and $BF_3{\cdot}OEt_2$ at 0 °C for 40 min was employed, cyclization yields of **41** and **42** were dramatically improved[32] to 43 % and 41 %, respectively. On the other hand, the best cyclization condition of **38** with TfOH in CH_2Cl_2 - toluene (10 : 1) was applied to **41** and **42**, however, the yields were less than 20 % because of side-products and complex mixture.

In Scheme 5, benzoate **21b** which has a good leaving group showed low reactivity with allyltrimethylsilane in the presence of $BF_3{\cdot}OEt_2$ and gave the coupling product in only 22 % yield. On the contrary, TBS ether **30** in Scheme 8 had excellent reactivity with allyltrimethylsilane **10** to afford the product **31** in 92 %. These results suggest that the reactivity for intramolecular Nicholas reaction depends on not only electronic effect of leaving group but also the steric effect. The ground state of this intramolecular cyclization is assumed in Figure 2, bulky acetylene cobalt complex ligands (CO ×6) turn outside and the conformation might be fixed because of less freedom than the cyclization intermediate **33** in Figure 1, thus the reaction centers face and approach to each other. This is one of the reason why cyclization of ***route c*** is better than that of ***route b***.

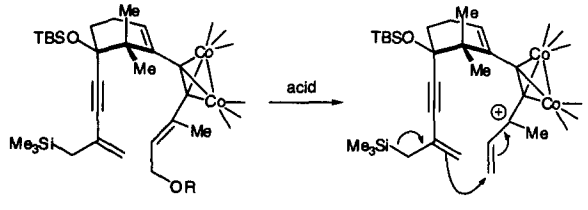
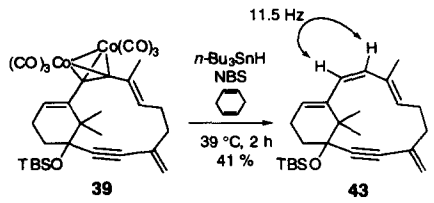


Figure 2.

Decomplexation of acetylene cobalt complex usually undergoes by oxidant such as I_2. The acetylene cobalt complex **39** in ring system, however, did not react with any oxidants to produce the corresponding acetylenic compound same as another cyclization product **32**. This may be because the strain energy will increase if free acetylene in ring system would be generated. Four reductive decomplexation methods[30,33-35] had been tried. The reductive decomplexation using *n*-Bu_3SnH[35] among those conditions was the most promising for the cyclization product **39**, then we further investigated in details. The original condition is heating of a 0.01-0.035M solution in benzene solvent at 65 °C with 10-12 equiv. *n*-Bu_3SnH for 2 h. When the same condition was employed for **39**, the corresponding product **43** was obtained in only low yield due to decomposition of both substrates **39** and **43** by heating.



Scheme 13. Reductive decomplexation of *endo*-acetylene dicobalt hexacarbonyl

Hosokawa[35] et al. reported that decomplexation reaction under n-Bu_3SnH proceeds as a radical mechanism, cobalt complex itself may act as an initiator for radical reaction. Therefore, if there is an appropriate radical initiator in the reaction mixture which works at low temperature, the problem of the decomposition by heating might be diminished. The condition of n-Bu_3SnH (3 equiv.) and catalytic amount of NBS at 39 °C for 2 h in 1,4-cyclohexadiene afforded the corresponding *cis* olefin **43** in 41 % yield. In the case of using NBS, the amount of n-Bu_3SnH can be reduced to 3 equiv. from 10-12 equiv. NBS might be a good radical initiator[36] and helpful to proceed the decomplexation reaction.

Conclusions

We designed two acetylene cobalt complexes as key intermediates and those precursors were synthesized from three common building blocks in few steps. The acetylene cobalt complex can be used for a carbon-carbon bond formation *via* the Nicholas reaction. Moreover, the cobalt complex of cyclization precursor might help for the reaction centers to face and approach to each other due to its bulkyness. Between two types of reaction conditions, intramolecular Nicholas reaction gave cyclization product in reasonable yield. Acetylene dicobalt octacarbonyl of the cyclization product was decomplexed to afford the bicyclo[9.3.1]pentadecatetraene under newly developed conditions. The synthesis of bicyclo[9.3.1]pentadecatriene skeleton for taxachitienes was achieved in 8 steps in 13 % overall yield.

Experimental

General Techniques: Infrared (IR) spectra were recorded on a JASCO FT/IR-8300 spectrophotometer and are reported in wave number (cm^{-1}). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a JEOL EX-270 (270 MHz), a Varian Gemini-2000 (300 MHz) or a BRUKER ARX-400 (400 MHz) spectrometer. The residual protio-deuterio $CDCl_3$ was referenced at 7.26 ppm for proton spectra. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a JEOL EX-270 (67.9 MHz), a Varian Gemini-2000 (75.4 MHz), a BRUKER ARX-400 (100 MHz) spectrometer. The ^{13}C signal of $CDCl_3$ was referenced at 77.0 ppm. Low-resolution mass spectra (EI, FAB) were recorded on a JEOL DX-300 spectrometer, a JEOL DX-705L or a JEOL JMS-700 spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL DX-705L or a JEOL JMS-700 spectrometer and are reported in m/z.

Preparation of cis-3-Methylpent-2-en-4-yn-1-tert-butyldimethylsilyl ether ***9a*** *from cis-3-Methylpent-2-en-4-yn-1-ol*

cis-3-Methylpent-2-en-4-yn-1-ol (26.91 g, 0.280 mol) was dissolved in DMF (300 mL) and the mixture was cooled to 0 °C. To this solution, imidazole (53.4 g, 0.784 mol) and TBDMSCl (97 % purity, 56.6 g, 0.364 mol) were subsequently added. After stirring for 2 h, the mixture was allowed to warm to rt and stirred for 21 h. The reaction mixture was treated with ice water and extracted with Et_2O (200 mL × 3). The combined organic layers were washed with water (700 mL × 3), acidic water (H_2O 600 mL + 3N HCl 20 mL) and brine (700 mL × 1), passed through a column containing sodium sulfate and a small amount of silica gel, and then evaporated *in vacuo*. The residue was purified by distillation to give the *cis*-3-Methylpent-2-en-4-yn-1-TBS ether **9a** (54.8 g, 93 %). b.p. 41-42 °C / 0.8 mmHg. IR (KBr, film) ν_{max} 3311, 2956, 2930, 2887, 2858 1256 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.08 (6H, s, $Si(CH_3)_2$), 0.90 (9H, s, $SiC(CH_3)_3$), 1.87 (3H, q, J = 1.1 Hz, CH_3), 3.14 (1H, br s, C≡C*H*), 4.38 (2H, dq, J = 6.1, 1.1 Hz, CH_2), 5.86 (1H, tq, J = 6.1, 0.9 Hz, C=C*H*-CH_2). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ -5.3, 18.3, 22.8, 25.9, 62.1, 81.8, 82.0, 117.7, 138.7. Anal. Calcd for $C_{12}H_{22}OSi$: C, 68.51; H, 10.54. Found C, 68.59; H, 10.53.

Preparation of cis-3-Methylpent-2-en-4-yn-1-benzoate ***9b*** *from cis-3-Methylpent-2-en-4-yn-1-ol*

cis-3-Methylpent-2-en-4-yn-1-ol (4.35 g, 45.2 mmol) was dissolved in CH_2Cl_2 (70 mL) and the mixture was cooled to 0 °C. To this solution, pyridine (18 mL, 0.223 mol) and BzCl (7.9 mL, 68.1 mmol) were subsequently added. After stirring for 2 h, the mixture was allowed to warm to rt and stirred for 16 h. The reaction mixture was quenched with several pieces of ice and extracted with CH_2Cl_2 (50 mL ×3). The combined organic layers were washed with saturated aqueous ammonium chloride(200 mL), dried over anhydrous sodium sulfate, and then evaporated. The residue was purified by column chromatography (silica gel 300 g, hexane : ether = 30 : 1) to give *cis*-3-Methylpent-2-en-4-yn-1-benzoate **9b** (8.63 g, 95 %). IR (KBr, film) ν_{max} 3295, 3064, 2980, 2954, 2923, 2884, 1717 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.95 (3H, br s, CH_3), 3.25 (1H, s, C≡C*H*), 5.04 (2H, br d, J = 7.0 Hz, C=CH-CH_2), 6.01 (1H, br t, J = 7.0 Hz, C=C*H*-CH_2), 7.42 (2H, td, J = 7.5, 0.5 Hz, aromatic), 7.56 (1H, tm, J = 7.5 Hz, aromatic), 8.06 (2H, dd, J = 7.5, 0.5 Hz, aromatic). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 22.9, 63.3, 81.4, 83.0, 122.4, 128.4, 129.7, 130.3, 132.3, 133.0, 166.6. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found C, 78.08; H, 6.07.

Preparation of 2-(trimethylsilylmethyl)but-1-en-3-yne ***10*** *from 2-bromo-3-trimethylsilyl-1-ene* ***19***

Palladium(II) acetate (24.8 mg, 0.110 mmol), triphenylphosphine (58.0 mg, 0.221 mmol) and copper(I) iodide (42.1 mg, 0.221 mmol) were placed in a dry 30 mL two-neck flask and the atmosphere was replaced with argon, then THF (8 mL) was added. To this flask, 2-bromo-3-trimethylsilyl-1-ene **19** (427 mg, 2.21 mmol), trimethylsilyl acetylene (0.62 mL, 4.39 mmol) and *n*-$BuNH_2$ (0.66 mL, 6.68 mmol) were added respectively. After stirring at room temperature for 1 h, the reaction mixture was poured into an ice-cold saturated aqueous ammonium chloride(20 mL), extracted with ether (10 mL ×3). The combined organic layers were washed with water (30 mL ×2) and brine (30 mL ×1). The extract was dried by passing through a column containing anhydrous sulfate and a small amount of silica gel, and evaporated under reduced pressure. The combined residues were purified by column chromatography to give 4-trimethylsilyl-2-(trimethylsilylmethyl)but-1-en-3-yne **20** (441 mg, 95 %). IR (KBr, film) ν_{max} 2959, 2899, 2146, 1597, 1419 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.07 (9H, s, $CH_2Si(CH_3)_3$), 0.17 (9H, s, C≡C$Si(CH_3)_3$), 1.67 (2H, d, J = 1.0 Hz, $CH_2Si(CH_3)_3$), 5.03 (1H, dt, J = 2.1, 1.0 Hz, C=C*H*H), 5.23 (1H, d, J = 2.1 Hz, C=CH*H*). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -1.6, -0.1, 28.2, 93.0, 107.4, 119.7, 128.9. Anal. Calcd for $C_{11}H_{22}Si_2$: C, 62.78; H, 10.54. Found C, 62.80; H, 10.49.

4-Trimethylsilyl-2-(trimethylsilylmethyl)but-1-en-3-yne **20** (14.7 g, 69.8 mmol) was dissolved in methanol (30 mL) and cooled to 0 °C. Potassium carbonate (9.65 g, 69.8 mmol) was added to this solution. After stirring 4 h, the reaction mixture was passed through a short column of silica gel to remove potassium carbonate that was suspended and the column was washed with pentane, which was poured into an ice-cold saturated aqueous ammonium chloride. The organic layer was washed with water and brine, then passed through a column containing anhydrous sodium sulfate and silica gel. After evaporation, the residue was purified by distillation under reduced pressure to give 2-(trimethylsilylmethyl)but-1-en-3-yne **10** (8.94 g, 93 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (9H, s, $CH_2Si(CH_3)_3$), 1.68 (2H, br s, $CH_2Si(CH_3)_3$), 2.85 (1H, d, J = 0.9 Hz, C≡C*H*), 5.08 (1H, m, C=C*H*H), 5.28 (1H, d, J = 2.0 Hz, C=CH*H*). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ -1.8, 27.9, 76.1, 85.8, 120.5, 128.1.

*Preparation of acetylene cobalt complex **21a** from cis-3-Methylpent-2-en-4-yn-1-tert-butyldimethylsilyl ether **9a***

To a solution of *cis*-3-Methylpent-2-en-4-yn-1-*tert*-butyldimethylsilyl ether **9a** (404 mg, 1.92 mmol) in CH_2Cl_2 (3 mL), $Co_2(CO)_8$ (788 mg, 2.30 mmol) in CH_2Cl_2 (5 mL) was added. After stirring for 5 h at room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel 30 g, only hexane) to give the product **21a** (840 mg, 88 %). IR (KBr, film) ν_{max} 2931, 2859, 2094, 2053, 2022 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.08 (6H, s, $Si(CH_3)_2$), 0.91 (9H, s, $SiC(CH_3)_3$), 2.08 (2H, q, J = 1.5 Hz, CH_3), 4.35 (2H, dq, J = 5.9, 1.5 Hz, CH_2), 5.78 (1H, tq, J = 5.9, 1.5 Hz, C=C*H*-CH_2), 6.18 (1H, br s, C≡C*H*). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -5.2, 18.4, 25.2, 25.9, 61.5, 73.8, 85.6, 130.1, 132.4, 199.5. MS (EI) *m/z* 496 (M^+), 468 (M^+-CO), 440 (M^+-2CO), 412 (M^+-3CO), 384 (M^+-4CO), 356 (M^+-5CO), 328 (M^+-6CO). HRMS (EI) calcd for $C_{17}H_{22}Co_2O_6Si$ (M-CO) 467.9849, found 467.9836.

*Preparation of acetylene cobalt complex **21b** from cis-3-Methylpent-2-en-4-yn-1-benzoate **9b***

To a solution of *cis*-3-Methylpent-2-en-4-yn-1-benzoate **9b** (514 mg, 2.57 mmol) in CH_2Cl_2 (5 mL), $Co_2(CO)_8$ (1.08 g, 3.16 mmol) in CH_2Cl_2 (5 mL) was added. After stirring for 5 h at room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel 60 g, hexane : ether = 30 : 1) to give the product **21b** (1.13 g, 91 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.16 (3H, dt, J = 1.5, 1.1 Hz, $C(CH_3)$=CH), 5.00 (2H, dq, J = 6.9, 1.1 Hz, $C(CH_3)$=CHCH_2O), 5.95 (1H, tq, J = 6.9, 1.5 Hz, $C(CH_3)$=C*H*), 6.37 (1H, s, C*H*), 7.39-7.48 (4H, m, aromatic), 7.52-7.60 (1H, m, aromatic), 8.01-8.07 (2H, m, aromatic). MS (EI) *m/z* 458 (M^+-CO), 430 (M^+-2CO), 402 (M^+-3CO), 374 (M^+-4CO), 346 (M^+-5CO), 318 (M^+-6CO). HRMS (EI) calcd for $C_{18}H_{12}Co_2O_7$: (M^+-CO) 457.9247, found 457.9225.

*Synthesis of **22** via intermolecular Nicholas reaction between cobalt complex **21a** and allyltrimethylsilane in the presence of boron trifluoride diethyl etherate*

Cobalt complex **21a** (32 mg, 0.064 mmol) and allyltrimethylsilane (10 μL, 0.063 mmol) were dissolved in CH_2Cl_2 (3 mL) and the mixture was cooled to -78 ° C. To this solution, $BF_3{\cdot}OEt_2$ (8 μL, 0.065 mmol) was added dropwise, then the reaction mixture was allowed to warm to 0 °C. After stirring for 35 min, the mixture was poured into an ice-cold saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2 (×3). The combined organic layers were passed through a column containing anhydrous sodium sulfate and silica gel, and evaporated. The residue was purified by preparative TLC (hexane : ether = 20 : 1) to give the product **22** (19 mg, 74 %). IR (KBr) ν_{max} 2928, 2092, 2051, 2018 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.08 (6H, s, $Si(CH_3)_2$), 0.91 (9H, s, $SiC(CH_3)_3$), 2.08 (2H, q, J = 1.5 Hz, CH_3), 4.35 (2H, dq, J = 5.9, 1.5 Hz, CH_2), 5.78 (1H, tq, J = 5.9, 1.5 Hz, C=C*H*-CH_2), 6.18 (1H, br s, C≡C*H*). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 18.6, 28.4, 33.2, 73.1, 96.2, 115.2, 131.5, 133.7, 137.7, 200.0. MS (EI) *m/z* 406 (M^+), 378 (M^+-CO), 350 (M^+-

2CO), 322 (M^+-3CO), 294 (M^+-4CO), 266 (M^+-5CO), 238 (M^+-6CO). HRMS (EI) calcd for $C_{15}H_{12}Co_2O_6$ 405.9298, found 405.9288.

Synthesis of ***22*** *via intermolecular Nicholas reaction between cobalt complex* ***21a*** *and allyltrimethylsilane in the presence of trifluoromethanesulfonic acid*

Cobalt complex **21a** (34 mg, 0.068 mmol) and allyltrimethylsilane (16 μL, 0.100 mmol) were dissolved in CH_2Cl_2 (3 mL) and cooled to 0 °C. Trifluoromethanesulfonic acid (3 μL, 0.034 mmol) was added dropwise to this solution. After stirring at 0 °C for 45 min, the reaction mixture was poured into an ice-cold saturated aqueous $NaHCO_3$, and then extracted with CH_2Cl_2 (×3). The combined organic layer was passed through a column containing anhydrous sodium sulfate and silica gel, and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane : ether = 20 : 1) to give the product **22** (21 mg, 77 %).

Synthesis of ***22*** *via intermolecular Nicholas reaction between cobalt complex* ***21b*** *and allyltrimethylsilane in the presence of boron trifluoride diethyl etherate*

Cobalt complex **21b** (55 mg, 0.11 mmol) and allyltrimethylsilane (18 μL, 0.11 mmol) were dissolved in CH_2Cl_2 (5 mL) and the mixture was cooled to 0 °C. $BF_3{\cdot}OEt_2$ (14 μL, 0.11 mmol) was added dropwise to this solution. After stirring for 1 h, the reaction mixture was quenched with an ice-cold saturated aqueous $NaHCO_3$ (4 mL), and then extracted with CH_2Cl_2 (×3). The combined organic layers were passed through a column containing anhydrous sodium sulfate and silica gel, and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane : ether = 2 : 1) to give the product **22** (10 mg, 22 %) and the recovered cobalt complex **21b** (35 mg, 64 %).

Synthesis of dieneyne ***23*** *from 3-iodo-2,2,4-trimethylcyclohex-3-en-1-one* ***8*** *and cis-3-Methylpent-2-en-4-yn-1-tert-butyldimethylsilyl ether* ***9a***

Palladium(II) acetate (43 mg, 0.19 mmol), triphenylphosphine (100 mg, 0.38 mmol), and copper(I) iodide (73 mg, 0.38 mmol) were placed in a dry 50 mL two neck flask and benzene (10 mL) was added under argon atmosphere. To this suspension, 3-iodo-2,2,4-trimethylcyclohex-3-en-1-one **8** (1.01 g, 3.82 mmol) in benzene (10 mL) was added, followed by *cis*-3-Methylpent-2-en-4-yn-1-*tert*-butyldimethylsilyl ether **9a** (1.45 g, 6.89 mmol) in benzene (8 mL). The whole mixture was degassed twice, then *n*-$BuNH_2$ (1.1 mL, 11.1 mmol) was added. After stirring at 75 °C for 1 day, the mixture was quenched with an ice-cold saturated aqueous ammonium chloride(30 mL), and extracted with ether (×4). The combined organic layers were washed with water and brine. The extract was dried by passing through a column containing anhydrous sodium sulfate and silica gel, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel 120 g, hexane : ether = 20 : 1) to give the dieneyne **23** (1.05 g, 79 %). IR (KBr, film) ν_{max} 2957, 2930, 2857, 1720 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.07 (6H, s, $Si(CH_3)_2$), 0.89 (9H, s, $C(CH_3)_3$), 1.28 (6H,s, $C(CH_3)_2$), 1.91 (3H, d, J = 1.5 Hz, $C(CH_3)=CHCH_2$), 1.98 (3H, s, $CH_2C(CH_3)=C$), 2.47-2.61 (4H, m, CH_2 ×2), 4.41 (2H, dd, J = 6.5, 1.2 Hz, $C(CH_3)=CHCH_2$), 5.77 (1H, td, J = 6.5, 1.5 Hz, $C(CH_3)=CHCH_2$). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -5.1, 18.4, 22.3, 23.2, 25.4, 25.9, 31.2, 35.5, 46.5, 62.5, 91.7, 92.1, 118.8, 123.6, 136.0, 139.9, 213.5. Anal. Calcd for $C_{21}H_{34}O_2Si$: C, 72.78; H, 9.89. Found C, 72.87; H, 9.95.

Synthesis of 3-iodo-2,2-dimethylcyclohex-3-en-1-one ***28*** *from 2,2-dimethylcyclohexan-1,3-dione*

2,2-Dimethylcyclohexan-1,3-dione **12** (90 % purity, 28.33 g, 0.182 mol) was dissolved in CH_2Cl_2 (450 mL). To this solution, triethylorthoformate (21.1 mL, 0.127 mol), ethylene glycol (15.2 mL, 0.272 mol) were added. After cooling to 0 °C, *DL*-CSA (4.22 g, 18.2 mmol) was added and stirred for 15 min. The reaction mixture was allowed to warm to room temperature and stirred for a further 3 days, then quenched with ice-cold

saturated aqueous $NaHCO_3$ (150 mL) and ice-cold water (50 mL) and extracted with CH_2Cl_2 (200 mL ×2). The extracts were dried over sodium sulfate and evaporated. The residue was purified by column chromatography (silica gel 300 g, hexane : ether = 5 : 1) to give 2,2-dimethyl-1,3-cyclohexanone mono ethylene acetal **13** (27.8 g, 83 %). ^1H NMR ($CDCl_3$, 270 MHz) δ 1.09 (6H, s, $C(CH_3)_2$), 1.73 (2H, m, CH_2), 1.80-1.90 (2H, m, CH_2), 2.37 (2H, t, J = 6.5 Hz, CH_2), 3.89 (4H, s, OCH_2 ×2). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 19.1, 19.8, 29.6, 36.3, 55.1, 65.3, 113.2, 212.8. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found C, 65.19; H, 8.87.

2,2-Dimethyl-1,3-cyclohexanone mono ethylene acetal **13** (10.0 g, 54.3 mmol) in MeOH (150 mL), *p*-toluenesulfonyl hydrazide (97 %, 13.0 g, 67.7 mmol) was added. After stirring at room temperature for 24 h, solvent was removed *in vacuo*. The resulting residue was washed with ether to give 2,2-dimethyl-1,3-cyclohexanone mono ethylene acetal *p*-toluenesulfonyl hydrazone **25** (16.6 g, 87 %). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.07 (6H, s, $C(CH_3)_2$), 1.56-1.68 (2H, m, CH_2), 1.68-1.78 (2H, m, CH_2), 2.25 (2H, t, J = 6.7 Hz, CH_2), 2.42 (3H, s, $PhCH_3$), 3.89 (4H, s, OCH_2 ×2), 7.30 (2H, dd, J = 8.1, 0.9 Hz, aromatic), 7.40 (1H, br, N*H*), 7.84 (2H, br d, J = 8.1, aromatic). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 19.9, 21.3, 21.5, 21.7, 48.7, 65.3, 112.6, 128.3, 129.3, 135.5, 143.8, 165.3.

2,2-Dimethyl-1,3-cyclohexanone mono ethylene acetal *p*-toluenesulfonyl hydrazone **25** (10.69 g, 30.33 mmol) was dissolved in dry THF (60 mL) and dry TMEDA (12 mL) and cooled to -78 °C. To this suspension, *n*-BuLi (1.24 M in hexane, 74 mL, 91 mmol) was added dropwise over 15 min. The reaction mixture was allowed to warm to 4 °C by means of ice-water bath. After stirring for 1 h, the mixture was cooled to -78 °C. *n*-Bu_3SnCl (95 %, 19 mL, 46 mmol) was added one portion and allowed to warm to 10 °C. After stirring at 10 °C for 30 min, one piece of ice was added to the reaction mixture, then which was poured into ice-cold water (80 mL). To the mixture, potassium sodium tartrate solution was added and stirred for 15 min, then extracted with ether (×2). The combined organic layers were washed with aqueous $CuSO_4$ (×5), water (×3) and brine (×1), passed through a column containing sodium sulfate and silica gel and concentrated under reduced pressure. The resulting residue was purified by column chromatography (silica gel 230 g, hexane : ether = 20 : 1) to give 3-tributylstannane-2,2-trimethylcyclohex-3-en-1-ethylene acetal **26** (9.37 g, 68 %). ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (9H, t, J = 7.5 Hz, $Sn((CH_2)_3CH_3)_3$), 1.05 (6H, s, $C(CH_3)_2$), 1.22-1.56 (18H, m, $Sn((CH_2)_3CH_3)_3$), 1.76 (2H, t, J = 6.5 Hz, $C{=}CHCH_2CH_2$), 2.29 (2H, td, J = 6.5, 3.5 Hz, $C{=}CHCH_2CH_2$), 3.97 (4H, m, OCH_2CH_2O), 5.65 (1H, t, J = 3.5 Hz, $C{=}CHCH_2CH_2$). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 10.9, 13.5, 25.7, 26.6, 27.4, 27.5, 29.0, 44.4, 64.9, 112.7, 134.1, 151.2.

3-Tributylstannane-2,2-trimethylcyclohex-3-en-1-ethylene acetal **26** (930 mg, 2.03 mmol) was dissolved in dry ether (15 mL) and cooled to 0 °C. I_2 (850 mg, 3.35 mmol) in ether (5 mL) was added dropwise to this solution. The reaction mixture was allowed to warm to room temperature and stirred for 20 min, then treated with an ice-cold saturated aqueous $NaHCO_3$ (10 mL). To this mixture, saturated aqueous Na_2SO_3 was added until the color of solution became yellow. The organic layer was washed with 10 % aqueous KF (×1), water (×2) and brine (×1), then passed through a column containing sodium sulfate and a small amount of silica gel and concentrated under reduced pressure. The resulting residue was purified by column chromatography (silica gel 15 g, hexane : ether = 20 : 1) to give 3-iodo-2,2-trimethylcyclohex-3-en-1-ethylene acetal **27** (393 mg, 66 %). IR (KBr) ν_{max} 2978, 2957, 2939, 2881, 1465 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.14 (6H, s, $C(CH_3)_2$), 1.81 (2H, t, J = 6.7 Hz, CH_2), 2.18 (2H, td, J = 6.7, 4.0 Hz, CH_2), 4.00 (4H, s, OCH_2 ×2), 6.33 (1H, t, J = 4.0 Hz, C=C*H*). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 25.6, 26.9, 27.9, 47.4, 65.1, 109.9, 112.9, 136.7. Anal. Calcd for $C_{10}H_{15}IO_2$: C, 40.84; H, 5.14. Found C,40.84; H,5.19.

3-Iodo-2,2-trimethylcyclohex-3-en-1-ethylene acetal **27** (6.65 g, 22.6 mmol) was dissolved in a mixture of THF (30 mL) and 3N HCl (30 mL) followed by being heated at 90 °C for 4 h. After cooling to room temperature, ether (60 mL) was added and washed with water (100 mL ×4) and brine (100 mL ×1). The organic layer was passed through a column containing sodium sulfate and a small amount of silica gel, then concentrated under reduced pressure. The resulting residue was purified by column chromatography (silica gel 85 g, hexane : ether = 20 : 1) to give 3-iodo-2,2-dimethylcyclohex-3-en-1-one **28** (5.45 g, 97 %). IR (KBr, film) ν_{max} 2970, 2929, 2844, 1716 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.26 (6H, s, $C(CH_3)_2$), 2.40 (2H, td, J = 6.8, 4.5 Hz, CH_2), 2.62 (2H, t, J = 6.8 Hz, CH_2), 6.51 (1H, t, J = 4.5 Hz, C=C*H*). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 27.2, 28.5, 35.7, 52.1, 111.7, 136.8, 208.3. MS (EI) *m/z* 250 (M^+). HRMS (EI) calcd for $C_8H_{11}IO$: 249.9854, found 249.9846. Anal. Calcd for $C_8H_{11}IO$: C, 38.42; H, 4.43. Found C, 38.44; H, 4.20.

*Synthesis of 3-(5-tert-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-one **29** from A-ring **28** and **9a***

Palladium(II) acetate (166 mg, 0.739 mmol), triphenylphosphine (387 mg, 1.48 mmol), and copper(I) iodide (281 mg, 1.48 mmol) were placed in a dry 100 mL two neck flask and benzene (35 mL) was added under argon atmosphere. To this suspension, 3-iodo-2,2-dimethylcyclohex-3-en-1-one **28** (3.69 g, 14.8 mmol) in benzene (15 mL) was added, followed by terminal acetylene **2** (6.20 g, 29.5 mmol) in benzene (9 mL). The whole mixture was degassed twice, then *n*-$BuNH_2$ (4.4 mL, 44.5 mmol) was added. After stirring at rt for 1 day, the mixture was quenched with ice-cold saturated aqueous ammonium chloride(80 mL), and extracted with ether (×3). The combined organic layers were washed with water and brine. The extract was dried by passing through a column containing anhydrous sodium sulfate and silica gel, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel 200 g, hexane : ether = 15 : 1 to 10 : 1) to give 3-(5-*tert*-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-one **29** (4.87 g, 99 %). IR (KBr, film) ν_{max} 2958, 2930, 2893, 2857, 1717 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.08 (6H, s, $Si(CH_3)_2$), 0.91 (9H, s, $SiC(CH_3)_3$), 1.31 (6H, s, $C(CH_3)_2$), 1.90 (3H, d, J = 1.5 Hz, $C(CH_3)$=$CHCH_2$), 2.46-2.62 (4H, m, CH_2 ×2), 4.39 (2H, dd, J = 6.5, 1.5 Hz, C=$CHCH_2$), 5.79 (1H, td, J = 6,5, 1.5 Hz, $(CH_3)C$=C*H*CH_2), 6.19 (1H, t, J = 4.5 Hz, C=C*H*CH_2). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ -5.1, 18.4, 23.1, 25.1, 25.5, 26.0 35.4, 47.1, 62.4, 87.7, 92.1, 118.6, 129.9, 132.3, 136.6, 213.0. MS (EI) *m/z* 332 (M^+), 317 (M^+-15). HRMS (EI) calcd for $C_{20}H_{32}O_2Si$: 332.2172, found 332.2158. Anal. Calcd for $C_{20}H_{32}O_2Si$: C, 72.23; H, 9.70. Found C, 72.10; H, 9.91.

*Synthesis of acetylene cobalt complex **30** from 3-(5-tert-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-one **29***

To a solution of 3-(5-*tert*-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-one **29** (1.16 g, 3.49 mmol) in CH_2Cl_2 (10 mL), $Co_2(CO)_8$ (1.55 g, 4.53 mmol) in CH_2Cl_2 (10 mL) was added. After stirring at room temperature for 6 h, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel 110 g, hexane : ether = 20 : 1) to give the cobalt complex **30** (2.00 g, 93 %). IR (KBr, film) ν_{max} 2955, 2931, 2888, 2859, 2088, 2051, 2025, 1718 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.02 (6H, s, Si*t*-$Bu(CH_3)_2$), 0.87 (9H, s, $SiC(CH_3)_3(CH_3)_2$), 1.32 (6H, s, $C(CH_3)_2$), 2.11 (3H, br s, $C(CH_3)$=CH), 2.60 (4H, m, CH_2 ×2), 4.10 (2H, br d, C=$CHCH_2$OTBS), 5.71 (1H, br t, J = 5.5 Hz, $C(CH_3)$=C*H*), 6.36 (1H, br t, J = 4.1 Hz, C=C*H*CH_2). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -5.4, 18.4, 24.9, 25.2, 25.9, 27.5, 34.7, 49.3, 61.7, 91.3, 94.3, 130.8, 131.7, 142.7, 199.3, 199.4, 199.6, 212.8.

*Synthesis of cyclization precursor **31** from acetylene cobalt complex **30** and allyltrimethylsilane **10***

Cobalt complex **30** (1.44 g, 2.33 mmol) was dissolved in CH_2Cl_2 (15 mL) and the mixture was cooled to -78 °C, subsequently 2-(trimethylsilylmethyl)but-1-en-3-yne **10** (711 mg, 5.14 mmol) in CH_2Cl_2 (3 mL) was added. To this solution, $BF_3{\cdot}OEt_2$ (0.57 mL, 4.6 mmol) in CH_2Cl_2 (1 mL) was added dropwise and then the mixture was allowed to warm to 0 °C. After stirring for 30 min, the reaction mixture was treated with an ice-cold saturated aqueous $NaHCO_3$ (20 mL), and extracted with CH_2Cl_2 (×3). The combined organic layers were passed through a column containing anhydrous sodium sulfate and a small amount of silica gel, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel 35 g, hexane : ether = 10 : 1) to give cyclization precursor **31** (1.18 g, 92 %). IR (KBr) ν_{max} 3310, 2977, 2930, 2850, 2086, 2046, 2018, 1717 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.32 (6H, s, $C(CH_3)_2$), 1.98 (3H, s, $C(CH_3)$=$CHCH_2$), 2.30 (2H, t, J = 7.1 Hz CH_2C(C≡CH)=CH_2), 2.44 (2H, dt, J = 7.1, 7.0 Hz, $C(CH_3)$=$CHCH_2$), 2.50-2.66 (4H, m, C=$CHCH_2CH_2C$=O), 2.90 (1H, s, C≡CH), 5.29 (1H, br s, C(C≡CH)=CHH), 5.42 (1H, br s, C(C≡CH)=CHH), 5.76 (1H, br t, J = 7.0 Hz, $C(CH_3)$=$CHCH_2$), 6.42 (1H, t, J = 4.0 Hz, C=$CHCH_2CH_2C$=O). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 19.6, 25.0, 25.1, 25.5, 27.2, 34.7, 36.5, 49.1, 77.2, 83.7, 92.6, 102.7, 123.6, 129.6, 131.5, 131.8, 133.7, 143.0, 199.7, 199.9, 213.5. MS (EI) *m/z* 552 (M^+), 378 (M^+-CO), 350 (M^+-2CO), 322 (M^+-3CO), 294 (M^+-4CO), 266 (M^+-5CO), 238 (M^+-6CO). HRMS (EI) calcd for $C_{25}H_{22}Co_2O_7$: 552.0029, found 552.0018.

*Synthesis of 3-(7-ethynyl-3-methylocta-3,7-dien-1-ynyl)-2,2-dimethylcyclohex-3-en-1-one **35** from acetylene cobalt complex **31***

Acetylene cobalt complex **31** (155 mg, 0.281 mmol) was dissolved in THF (6 mL) and the mixture was cooled to 0 °C. To this solution, I_2 (714 mg, 2.81 mmol) in CH_2Cl_2 (5 mL) was added. After stirring for 4 h, the reaction mixture was treated with a mixture of ice-cold saturated aqueous $NaHCO_3$ (3 mL) and Na_2SO_3 (3 mL), and extracted with ether (×3). The combined organic layers were washed with water (×3), brine (×1) and then passed through a column containing anhydrous sodium sulfate and silica gel, and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane : ether = 5 : 1) to give 3-(7-ethynyl-3-methylocta-3,7-dien-1-ynyl)-2,2-dimethylcyclohex-3-en-1-one **35** (51 mg, 68 %). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.29 (6H, s, $C(CH_3)_2$), 1.82 (3H, dt, J = 1.5, 0.9 Hz, $C(CH_3)$=CH), 2.24 (2H, m, CH_2), 2.36 (2H, m, CH_2), 2.44-2.52 (2H, m, CH_2), 2.52-2.60 (2H, m, CH_2), 2.90 (1H, s, C≡CH), 5.32 (1H, m, C=CHH), 5.45 (1H, m, C=CHH), 5.83 (1H, tq, J = 7.2, 1.5 Hz, $C(CH_3)$=CH), 6.15 (1H, t, J = 4.5 Hz, C=$CHCH_2$). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 17.2, 24.9, 25.3, 27.0, 35.4, 36.2, 47.2, 65.0, 77.2, 83.7, 84.1, 92.3, 118.7, 123.3, 129.9, 130.2, 131.4, 136.4, 213.3. MS (FAB) *m/z* 267 (M^++H) HRMS (EI) calcd for $C_{19}H_{22}O$: 266.1671, found 266.1750.

*Synthesis of cyclization product **32** from cyclization preursor **31***

Cobalt complex **31** (158 mg, 0.286 mmol) was dissolved in THF (29 mL). To this solution, $LiN(TMS)_2$ (1.0 M, 0.43 mL, 0.43 mmol) was added dropwise. After stirring for 30 min, the reaction mixture was treated with an ice-cold saturated aqueous ammonium chloride(20 mL), and then extracted with Et_2O (×3). The combined organic layers were washed with water (×2) and brine (×1), then passed through a column containing anhydrous sodium sulfate and a small amount of silica gel, and evaporated under reduced pressure. The residue was purified by column chromatography (hexane : ether = 20 : 1 to 5 : 1) to give the cyclization product **32** (14 mg, 9 %). IR (KBr, film) ν_{max} 3430, 2929, 2856, 2085, 2046, 2016, 1722, 1442 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.26 (3H, s, $C(CH_3)_2$), 1.33 (3H, s, $C(CH_3)_2$), 1.95-2.10 (2H, m, CH_2), 1.98 (3H, t, J = 1.5 Hz, $C(CH_3)$=CH), 2.04 (1H, s, OH), 2.16-2.26 (2H, m, CH_2), 2.36-2.58 (4H, m, CH_2 ×2), 5.31 (1H, dd, J = 1.9, 0.9 Hz, C=CHH), 5.38 (1H, d, J = 1.9 Hz, C=CHH), 5.94 (1H, t, J = 4.0 Hz, C=$CHCH_2$), 6.58 (1H, ddq, J = 10.5, 4.1, 1.5 Hz, $C(CH_3)$=$CHCH_2$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 16.7, 20.3, 24.8, 25.9,

30.0, 30.5, 37.0, 45.8, 73.5, 86.4, 93.3, 95.2, 103.5, 123.7, 129.1, 130.6, 131.0, 131.1, 142,9, 199.9, 200.7. MS (EI) *m/z* 552 (M^+), 524 (M^+-CO), 496 (M^+-2CO), 468 (M^+-3CO), 440 (M^+-4CO), 412 (M^+-5CO), 384 (M^+-6CO). HRMS (EI) calcd for $C_{25}H_{22}Co_2O_7$: 552.0029, found 552.0016.

*Synthesis of 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-tert-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-ol **36** from ketone **29** and allyltrimethylsilane **10***

2-(Trimethylsilylmethyl)but-1-en-3-yne **10** (5.37 g, 38.8 mmol) was dissolved in THF (40 mL) and cooled to 0 °C. To this solution ethylmagnesium bromide (3.0 M in diethyl ether, 12.5 mL, 37.5 mmol) was added dropwise over 5 min. After stirring at 0 °C for 1.5 h, 3-(5-*tert*-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-one **29** (4.30 g, 12.9 mmol) in THF (13 mL) was added and the mixture was stirred at 0 °C for 45 min and then allowed to warm to room temperature. After stirring for 20 min., the reaction mixture was poured into an ice-cold saturated aqueous ammonium chloride(50 mL), and then extracted with ether (50 mL ×3). The combined organic layers were washed with water (250 mL ×2) and brine (250 mL ×1), passed through a column containing anhydrous sodium sulfate and a small amount of silica gel, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel 130 g, hexane : ether = 20 : 1 to 5 : 1) to give 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-*tert*-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-ol **36** (5.70 g, 94 %). IR (KBr, film) ν_{max} 3463, 2956, 2930, 2896, 2858, 2189 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.06 (6H, s, $Si(CH_3)_3$), 0.08 (6H, s, $SiC(CH_3)_3(CH_3)_2$), 0.90 (9H, s, $SiC(CH_3)_3(CH_3)_2$), 1.28 (3H, s, $C(CH_3)_2$), 1.31 (3H, s, $C(CH_3)_2$), 1.66 (2H, br s, $CH_2Si(CH_3)_3$), 1.87 (3H, br d, J = 1.2 Hz, $C(CH_3)$=CH), 1.94-2.04 (2H, m, CH_2), 2.29 (2H, m, CH_2), 4.38 (2H, dbr d, J = 6.4, 1.2 Hz, $C(CH_3)$=CHCH_2), 5.01 (1H, m, C=C*H*H), 5.18 (1H, d, J = 1.9 Hz, C=CH*H*), 5.74 (1H, tq, J = 6.4, 1.5 Hz, $C(CH_3)$=C*H*), 6.01 (1H, t, J = 4.0 Hz, C=C*H*). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ -5.2, -1.8, 18.2, 22.6, 23.0, 23.3, 25.9, 28.0, 31.3, 41.8, 62.4, 72.6, 86.7, 87.2, 89.9, 93.8, 118.9, 119.2, 128.2, 128.3, 132.7, 135.9. MS (EI) *m/z* 470 (M^+), 455 (M^+-15). Anal. Calcd for $C_{28}H_{46}O_2Si_2$: C, 71.43; H, 9.85. Found C, 71.44; H, 10.05.

*Synthesis of 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-tert-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-tert-butyldimethylsilyl ether **37** from tert-alcohaol **36***

1-(3-(Trimethylsilyl)but-3-en-1-ynyl)-3-(5-*tert*-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-ol **36** (920 mg, 1.95 mmol) was dissolved in CH_2Cl_2 (15 mL) and cooled to -78 °C. To this solution, 2,6-lutidine (1.0 mL, 8.59 mmol) and TBDMSOTf (0.34 mL, 1.5 mmol) in CH_2Cl_2 (5 mL) were added dropwise over 3 min. The mixture was allowed to warm to 4 °C. After stirring for 15 h, the reaction mixture was poured into an ice-cold water and extracted with CH_2Cl_2 (×3). The combined extracts were washed with 1N HCl and passed through a column containing anhydrous sodium sulfate and a small amount of silica gel, and evaporated *in vacuo*. The residue was purified by column chromatography (silica gel 30 g, hexane : ether = 20 : 1 to 5 : 1) to give 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-tert-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-*tert*-butyldimethylsilyl ether **37** (880 mg, 77 %) and the recovered **36** (214 mg, 23 %). IR (KBr, film) ν_{max} 2956, 2929, 2896, 2857 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.06 (6H, s, $Si(CH_3)_3$), 0.08 (6H, s, $SiC(CH_3)_3(CH_3)_2$), 0.19 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.22 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 1.20 (3H, s, $C(CH_3)_2$), 1.26 (3H, s, $C(CH_3)_2$), 1.65 (2H, d, J = 1.0 Hz, $CH_2Si(CH_3)_3$), 1.88 (3H, dt, J = 1.5, 1.2 Hz, $C(CH_3)$=CH), 1.93 (2H, m, CH_2), 2.24 (2H, m, CH_2), 4.39 (2H, dbr d, J = 6.5, 1.2 Hz, $C(CH_3)$=CHCH_2), 5.00 (1H, dt, J = 2.0, 1.0 Hz, C=C*H*H), 5.17 (1H, d, J = 2.0 Hz, C=CH*H*), 5.72 (1H, tq, J = 6.5, 1.5 Hz, $C(CH_3)$=C*H*), 5.94 (1H, t, J = 4.0 Hz, C=C*H*). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -5.1, -3.1, -3.0, -1.6, 18.4 (×2), 23.2, 23.6, 23.9, 25.4, 25.9, 26.0, 27.8, 32.3, 43.0, 62.5, 73.9, 86.2, 88.0, 90.4, 94.5, 118.7, 119.1, 128.6, 132.4, 135.5. MS (FAB) *m/z* 453 (M+H-TBSOH). Anal. Calcd for $C_{34}H_{60}O_2Si_3$: C, 69.80; H, 10.34. Found C, 69.79; H, 10.39.

*Synthesis of acetylene cobalt complex **38** from **37***

To a solution of 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-tert-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-*tert*-butyldimethylsilyl ether **37** (1.24 g, 2.12 mmol) in CH_2Cl_2 (10 mL), $Co_2(CO)_8$ (1.56 g, 4.56 mmol) in CH_2Cl_2 (5 mL) was added. After stirring at room temperature for 14 h, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel 10 g, hexane) to give the product **38** (1.65 g, 90 %). IR (KBr, film) ν_{max} 2957, 2930, 2897, 2858, 2086, 2049, 2024, 1251 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.06 (6H, s, $CH_2Si(CH_3)_3$), 0.20 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.22 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.87 (9H, s, $SiC(CH_3)_3(CH_3)_2$), 0.90 (9H, s, $SiC(CH_3)_3(CH_3)_2$), 1.27 (3H, s, $C(CH_3)_2$), 1.30 (3H, s, $C(CH_3)_2$), 1.63 (2H, br, $CH_2Si(CH_3)_3$), 2.00 (2H, m, CH_2), 2.09 (3H, dt, J = 1.2, 1.0 Hz, $C(CH_3)$=CH), 2.30 (2H, m, CH_2), 4.29 (2H, dq, J = 5.8, 1.1 Hz, $C(CH_3)$=$CHCH_2$), 4.99 (1H, dt, J = 2.0, 1.0 Hz, C=CHH), 5.15 (1H, d, J = 2.0 Hz, C=CHH), 5.70 (1H, tq, J = 5.8, 1.2 Hz, $C(CH_3)$=CH), 6.13 (1H, t, J = 4.5 Hz, C=CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -5.2, -3.1, -3.0, -1.6, 18.3, 18.4, 23.6, 24.6, 24.8, 25.9 (×2), 27.6, 28.6, 32.0, 45.0, 61.4, 75.0, 88.1, 90.4, 93.0, 94.8, 118.8, 128.5, 131.0, 131.9, 132.2, 140.7, 200.0.

*Synthesis of cyclization product **39** from **38** in the presence of boron trifluoride diethyl etherate*

Cobalt complex **38** (22 mg, 0.025 mmol) was dissolved in CH_2Cl_2 (1.5 mL) and the mixture was cooled to -78 °C. To this solution, $BF_3{\cdot}OEt_2$ (3.0 μL, 0.024 mmol) was added one portion, then the reaction mixture was allowed to warm to 0 °C. After stirring for 30 min, the reaction mixture was treated with an ice-cold saturated aqueous $NaHCO_3$ (2 mL), and then extracted with CH_2Cl_2 (×2). The combined organic layers were passed through a column containing anhydrous sodium sulfate and a small amount of silica gel, and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane) to give the product **39** (0.7 mg, 4 %). IR (KBr, film) ν_{max} 2954, 2928, 2858, 2085, 2046, 2021, 1250 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.16 (3H, s, *t*-$BuSi(CH_3)_2$), 0.20 (3H, s, *t*-$BuSi(CH_3)_2$), 0.89 (9H, s, $Si\{C(CH_3)_3\}(CH_3)_2$), 1.21 (3H, s, $C(CH_3)_2$), 1.26 (3H, s, $C(CH_3)_2$), 1.90 (1H, dbr d, J = 13.5, 7.5 Hz, CH_2), 1.97 (3H, t, J = 1.5 Hz, $C(CH_3)$=CH), 2.02-2.22 (3H, m, CH_2), 2.30-2.55 (4H, m, CH_2 ×2), 5.28 (1H, dd, J = 2.0, 1.0 Hz, C=CHH), 5.34 (1H, d, J = 2.0 Hz, C=CHH), 5.90 (1H, t, J = 3.9 Hz, $C=CHCH_2$), 6.60 (1H, ddq, J = 10.5, 4.3, 1.5 Hz, $C(CH_3)$=$CHCH_2$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ -3.4, -3.0, -1.6, 16.6, 18.2, 20.8, 24.9, 25.8, 26.3, 30.3, 31.2, 37.0, 46.8, 74.5, 87.0, 94.0, 95.9, 103.7, 122.8, 129.0, 130.5, 131.3, 131.4, 143.1, 199.9, 200.7. MS (EI) *m/z* 666 (M^+), 638 (M^+-CO), 610 (M^+-2CO), 582 (M^+-3CO), 554 (M^+-4CO), 526 (M^+-5CO), 498 (M^+-6CO). MS (FAB) *m/z* 610 (M^+-2CO), 582 (M^+-3CO), 554 (M^+-4CO), 526 (M^+-5CO), 498 (M^+-6CO) HRMS (EI) calcd for $C_{31}H_{36}Co_2O_7Si$ (M^+-4CO): 554.1098, found 554.1082.

*Synthesis of cyclization product **39** from **38** in the presence of trifluoromethanesulfonic acid in dichloromethane-toluene (10 : 1)*

Cobalt complex **38** (40 mg, 0.046 mmol) was dissolved in freshly distilled CH_2Cl_2 (40 mL) and PhMe (4 mL), then the mixture was cooled to -15 °C. To this solution, TfOH (20 μL, 1.13 mol in $Cl_2CFCClF_2$) was added one portion. After stirring for 10 min, the reaction mixture was poured into an ice-cold saturated aqueous $NaHCO_3$ (20 mL), and then extracted with CH_2Cl_2 (×3). The combined organic layers were passed through a column containing anhydrous sodium sulfate and a small amount of silica gel, and concentrated under reduced pressure. The residue was purified by preparative column chromatography (silica gel 20 g, hexane) to give the product **39** (9 mg, 30 %).

*Synthesis of 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-hydroxy-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-tert-butyldimethylsilyl ether **40** from **37***

1-(3-Trimethylsilyl)but-3-en-1-ynyl)-3-(5-tert-butyldimethylsilyl ether-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-*tert*-butyldimethylsilyl ether **37** (851 mg, 0.33 mmol) was dissolved in MeOH (25 mL) and cooled to 0 °C. To this solution, Amberlyst 15E (2.6 g, slightly ground) was added and stirred at 0 °C for 6 h. The reaction mixture was filtrated through the pad of Super-Cell® and evaporated. The residue was purified by column chromatography (silica gel 40 g, hexane : ether = 5 : 1) to give 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-hydroxy-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-*tert*-butyldimethylsilyl ether **40** (571 mg, 83 %). IR (KBr, film) ν_{max} 3304, 2956, 2929, 2897, 2858, 1250 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.06 (6H, s, $CH_2Si(CH_3)_3$), 0.19 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.22 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.88 (9H, s, $SiC(CH_3)_3(CH_3)_2$), 1.20 (3H, s, $C(CH_3)_2$), 1.26 (3H, s, $C(CH_3)_2$), 1.65 (2H, d, J = 1.0 Hz, $CH_2Si(CH_3)_3$), 1.91 (3H, dt, J = 1.5, 1.2 Hz, $C(CH_3)$=CH), 1.93 (2H, m, CH_2), 2.25 (2H, m, CH_2), 4.43 (2H, dq, J = 6.9, 1.1 Hz, $C(CH_3)$=$CHCH_2$), 5.00 (1H, dt, J = 2.0, 1.0 Hz, C=CHH), 5.17 (1H, d, J = 2.0 Hz, C=CHH), 5.83 (1H, tq, J = 6.9, 1.5 Hz, $C(CH_3)$=CH), 5.97 (1H, t, J = 4.0 Hz, C=CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -3.2, -3.0, -1.6, 18.4, 23.3, 23.6, 23.9, 25.4, 25.9, 27.8, 32.3, 42.9, 61.5, 73.8, 85.8, 88.0, 90.2, 94.8, 118.7, 121.5, 128.4, 128.5, 133.0, 134.2. MS (EI) *m/z* 471 (M^+), 456 (M^+-15). Anal. Calcd for $C_{28}H_{46}O_2Si_2$: C, 71.43; H, 9.85. Found C, 71.28; H, 10.08.

*Synthesis of acetylene cobalt complex **41** from **40***

1-(3-(Trimethylsilyl)but-3-en-1-ynyl)-3-(5-hydroxy-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-*tert*-butyldimethylsilyl ether **40** (154 mg, 0.33 mmol) was dissolved in CH_2Cl_2 (6 mL). To this solution, acetic anhydride (1 mL, 0.011 mmol) and pyridine (1 mL, 0.012 mmol) were subsequently added and the mixture was stirred at rt for 5 h. The reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel 7 g, hexane : ether = 20 : 1) to give 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-acetoxy-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-*tert*-butyldimethylsilyl ether (157 mg, 93 %). IR (KBr, film) ν_{max} 2957, 2929, 2858, 1745, 1249, 1235 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.06 (6H, s, $CH_2Si(CH_3)_3$), 0.19 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.21 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.87 (9H, s, $SiC(CH_3)_3(CH_3)_2$), 1.19 (3H, s, $C(CH_3)_2$), 1.26 (3H, s, $C(CH_3)_2$), 1.65 (2H, d, J = 1.0 Hz, $CH_2Si(CH_3)_3$), 1.92 (3H, dt, J = 1.5, 1.0 Hz, $C(CH_3)$=CH), 1.93 (2H, m, CH_2), 2.06 (3H, s, $OCOCH_3$), 2.24 (2H, m, CH_2), 4.77 (2H, dbr d, J = 6.9, 1.0 Hz, $C(CH_3)$=$CHCH_2$), 5.00 (1H, dt, J = 2.0, 1.0 Hz, C=CHH), 5.16 (1H, d, J = 2.0 Hz, C=CHH), 5.74 (1H, tq, J = 6.9, 1.5 Hz, $C(CH_3)$=CH), 5.99 (1H, t, J = 4.0 Hz, C=CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -3.2, -3.0, -1.6, 18.4, 21.0, 23.4, 24.0, 25.4, 25.9, 27.8, 32.3, 42.9, 63.2, 73.7, 85.4, 88.0, 90.2, 95.5, 118.7, 124.2, 128.3, 128.5, 128.7, 133.3, 170.9. MS (EI) *m/z* 513 (M^+), 498 (M^+-15). Anal. Calcd for $C_{30}H_{48}O_3Si_2$: C, 70.26; H, 9.43. Found C, 70.25; H, 9.50.

To a solution of 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-acetoxy-3-methylpent-3-en-1-ynyl)-2,2-dimethyl cyclohex-3-en-1-*tert*-butyldimethylsilyl ether (110 mg, 0.214 mmol) in CH_2Cl_2 (4 mL), $Co_2(CO)_8$ (175 mg, 0.511 mmol) was added. After stirring for 2 h at room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel 4 g, hexane : ether = 1 : 0 to 20 : 1) to give the product **41** (171 mg, quant.). IR (KBr, film) ν_{max} 2956, 2930, 2897, 2858, 2088, 2050, 2023, 1746, 1250, 1230 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.05 (6H, s, $CH_2Si(CH_3)_3$), 0.20 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.22 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.87 (9H, s, $SiC(CH_3)_3(CH_3)_2$), 1.27 (3H, s, $C(CH_3)_2$), 1.29 (3H, s, $C(CH_3)_2$), 1.60 (2H, br d, J = 2.5 Hz, $CH_2Si(CH_3)_3$), 1.90-2.08 (2H, m, CH_2), 2.02 (3H, s, $OCOCH_3$), 2.13 (3H, br d, J = 1.0 Hz, $C(CH_3)$=CH), 2.31 (2H, m, CH_2), 4.69 (2H, br d, J = 7.0 Hz, $C(CH_3)$=$CHCH_2$), 4.97 (1H, m, C=CHH), 5.13 (1H, d, J = 2.0 Hz, C=CHH), 5.73 (1H, tq, J = 7.0, 1.2 Hz, $C(CH_3)$=CH), 6.12 (1H, t, J = 3.7 Hz, C=CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -3.1, -3.0, -1.7, 18.4, 20.9, 23.8, 24.5, 24.7, 25.8, 27.5, 28.4, 32.0, 45.2, 61.6, 75.0, 88.1, 90.4, 91.8, 95.0, 118.8,

123.4, 128.4, 137.8, 140.7, 170.8, 199.7, 199.9 (×2). MS (EI) *m/z* 714 (M^+-3CO), 687 (M^+-4CO), 659 (M^+-5CO), 631 (M^+-6CO).

*Synthesis of acetylene cobalt complex **42** from tert-butyldimethylsilylether **40***

1-(3-(Trimethylsilyl)but-3-en-1-ynyl)-3-(5-hydroxy-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-*tert*-butyldimethylsilylether **40** (256 mg, 0.544 mmol) was dissolved in THF (12 mL) and cooled to - 78 °C. To this solution, methyl iodide (0.34 mL, 5.44 mmol), which passed through a column containing basic Al_2O_3, was added one portion, followed by *t*-BuOK (91.6 mg, 0.816 mmol) portionwise. After stirring for 50 min at -78 °C, the mixture was allowed to warm to 0 °C and stirred for a further 10 min. The mixture was treated with ice-cold saturated aqueous ammonium chloride (8 mL) and extracted with ether (×3). The combined organic layers were washed with water (×3) and brine (×1), passed through a column containing sodium sulfate and a small amount of silica gel, then evaporated under reduced pressure. The residue was purified by column chromatography (silica gel 8 g, hexane : ether = 1 : 0 to 20 : 1) to give 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-methoxy-3-methylpent-3-en-1-ynyl)-2,2-dimethylcyclohex-3-en-1-*tert*-butyldimethylsilyl ether (246 mg, 93 %). IR (KBr, film) ν_{max} 2956, 2928, 2896, 2857, 1473, 1464, 1250 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.06 (6H, s, $CH_2Si(CH_3)_3$), 0.19 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.22 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.88 (9H, s, $SiC(CH_3)_3(CH_3)_2$), 1.20 (3H, s, $C(CH_3)_2$), 1.27 (3H, s, $C(CH_3)_2$), 1.65 (2H, d, J = 1.0 Hz, $CH_2Si(CH_3)_3$), 1.92 (3H, dt, J = 1.5, 1.1 Hz, $C(CH_3)$=CH), 1.93 (2H, m, CH_2), 2.25 (2H, m, CH_2), 3.34 (3H, s, OCH_3), 4.14 (2H, dq, J = 6.5, 1.1 Hz, $C(CH_3)$=$CHCH_2$), 5.00 (1H, dt, J = 1.9, 0.9 Hz, C=CHH), 5.17 (1H, d, J = 1.9 Hz, C=CHH), 5.74 (1H, tq, J = 6.5, 1.5 Hz, $C(CH_3)$=CH), 5.97 (1H, t, J = 4.0 Hz, C=CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -3.1, -3.0, -1.6, 18.4, 23.4, 23.6, 24.0, 25.4, 25.9, 27.8, 32.3, 43.0, 57.9, 70.9, 73.8, 86.0, 88.0, 90.3, 94.6, 118.7, 122.5, 128.5, 128.6, 131.8, 132.8. MS (EI) *m/z* 485 (M^+), 470 (M^+-15). Anal. Calcd for $C_{29}H_{48}O_2Si_2$: C, 71.84; H, 9.98. Found C, 72.09; H, 10.28.

To a solution of 1-(3-(trimethylsilyl)but-3-en-1-ynyl)-3-(5-methoxy-3-methylpent-3-en-1-ynyl)-2,2-dimethyl cyclohex-3-en-1-*tert*-butyldimethylsilyl ether (96 mg, 0.198 mmol) in CH_2Cl_2 (3 mL), $Co_2(CO)_8$ (189 mg, 1.43 mmol) in CH_2Cl_2 (10 mL) was added. After stirring for 6 h at room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel 4 g, hexane : ether = 1 : 0 to 20 : 1) to give the product **42** (146 mg, 96 %). IR (KBr, film) ν_{max} 2957, 2930, 2896, 2858, 2821, 2086, 2049, 2021 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.06 (6H, s, $CH_2Si(CH_3)_3$), 0.21 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.22 (3H, s, $SiC(CH_3)_3(CH_3)_2$), 0.88 (9H, s, $SiC(CH_3)_3(CH_3)_2$), 1.28 (3H, s, $C(CH_3)_2$), 1.30 (3H, s, $C(CH_3)_2$), 1.62 (2H, br d, J = 2.4 Hz, $CH_2Si(CH_3)_3$), 2.01 (2H, m, CH_2), 2.12 (3H, br, $C(CH_3)$=CH), 2.32 (2H, m, CH_2), 3.32 (3H, s, OCH_3), 4.03 (2H, br d, J = 6.0 Hz, $C(CH_3)$=$CHCH_2$), 5.00 (1H, m, C=CHH), 5.15 (1H, d, J = 1.9 Hz, C=CHH), 5.74 (1H, tm, J = 6.0 Hz, $C(CH_3)$=CH), 6.12 (1H, t, J = 4.0 Hz, C=CH). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -3.1, -2.9, -1.6, 18.4, 23.8, 24.7, 25.9, 27.6, 28.5, 32.0, 45.1, 58.2, 69.8, 75.0, 88.1, 90.5, 92.8, 94.8, 118.9, 126.9, 128.5, 131.6, 135.0, 140.7, 199.9. MS (FAB) *m/z* 686 (M^+-3CO), 658 (M^+-4CO), 630 (M^+-5CO), 602 (M^+-6CO). MS (EI) *m/z* 714 (M^+-2CO), 686 (M^+-3CO), 658 (M^+-4CO), 630 (M^+-5CO), 602 (M^+-6CO).

*Synthesis of cyclization product **39** from **41** in the presence of boron trifluoride diethyl etherate*

Cobalt complex **41** (30 mg, 0.038 mmol) was dissolved in CH_2Cl_2 (38 mL) and the mixture was cooled to -78 °C. To this solution, $BF_3{\cdot}OEt_2$ (4.6 μL, 0.038 mmol) was added one portion, then the reaction mixture was allowed to warm to 0 °C. After stirring for 40 min, the reaction mixture was treated with an ice-cold saturated aqueous $NaHCO_3$ (3 mL), and then extracted with CH_2Cl_2 (×2). The combined organic layers were passed through a column containing anhydrous sodium sulfate and silica gel, and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane) to give the product **39** (11 mg, 43 %).

*Synthesis of cyclization product **39** from **42** in the presence of boron trifluoride diethyl etherate*

Cobalt complex **42** (34 mg, 0.045 mmol) was dissolved in CH_2Cl_2 (45 mL) and the mixture was cooled to -78 °C. To this solution, $BF_3{\cdot}OEt_2$ (5.5 μL, 0.045 mmol) was added one portion, then the reaction mixture was allowed to warm to 0 °C. After stirring for 35 min, the reaction mixture was treated with an ice-cold saturated aqueous $NaHCO_3$ (3 mL), and then extracted with CH_2Cl_2 (×2). The combined organic layers were passed through a column containing anhydrous sodium sulfate and silica gel, and evaporated under reduced pressure. The residue was purified by preparative TLC (hexane) to give the product **39** (12 mg, 41 %).

*Synthesis of 8,15,15-trimethyl-4-methylenebicyclo[9.3.1]pentadeca-7,9,11(12)-trien-2-yn-1-ol **43** from **39** under reductive decomplexation condition*

Cobalt complex **39** (20 mg, 0.030 mmol) was dissolved in 1,4-cyclohexadiene (0.5 mL) To this solution, *n*-Bu_3SnH (25 μL, 0.093 mmol) and NBS (1 mg, 6 μmol) were added, then the reaction mixture was heated to 39 °C. After stirring for 2 h, the reaction mixture was allowed to cool to room temperature, evaporated. The residue was purified by column chromatography (silica gel 8 g, hexane) and preparative TLC (hexane) to give bicyclo[9.3.1]pentadecatetraene **43** (5 mg, 41 %). IR (KBr, film) ν_{max} 2956, 2929, 2856, 1249 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.20 (3H, s, $Si\{C(CH_3)_3\}(CH_3)_2$), 0.22 (3H, s, $Si\{C(CH_3)_3\}(CH_3)_2$), 0.90 (9H, s, $Si\{C(CH_3)_3\}(CH_3)_2$), 1.11 (3H, s, $C(CH_3)_2$), 1.16 (3H, s, $C(CH_3)_2$), 1.64 (3H, d, J = 1.5 Hz, $C(CH_3)$=CH), 1.71-1.79 (1H, m, CH_2), 2.01-2.18 (3H, m, CH_2), 2.21-2.40 (4H, m, CH_2 ×2), 5.19 (1H, d, J = 2.1 Hz, C=CHH), 5.20 (1H, tq, J = 6.5, 1.5 Hz, $C(CH_3)$=CH), 5.23 (1H, d, J = 2.1 Hz, C=CHH), 5.78 (1H, d, J = 11.5 Hz, CH=C-CH=CH), 5.83-5.93 (2H, m, CH=C-CH=CH). ^{13}C NMR ($CDCl_3$, 100 MHz) δ -3.1, -2.9, 17.0, 18.3, 21.9, 24.3, 24.8, 25.8, 29.8, 32.3, 38.4, 43.5, 74.2, 86.2, 93.4, 120.1, 122.5, 127.8, 128.9, 131.2, 132.4, 134.4, 142.0. MS (EI) *m/z* 382 (M^+), 367 (M-15). HRMS (EI) calcd for $C_{25}H_{38}OSi$: 382.2692, found 382.2712.

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32. These improvements are not only because of the leaving groups. The stability of the precursor itself also is important. Compounds **41** and **42** are more stable than **38**.
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