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One-Step Recyclization of Sugar Acetylenes to form Medium Ether Rings via Dicobalthexacarbonyl Complexes[1]

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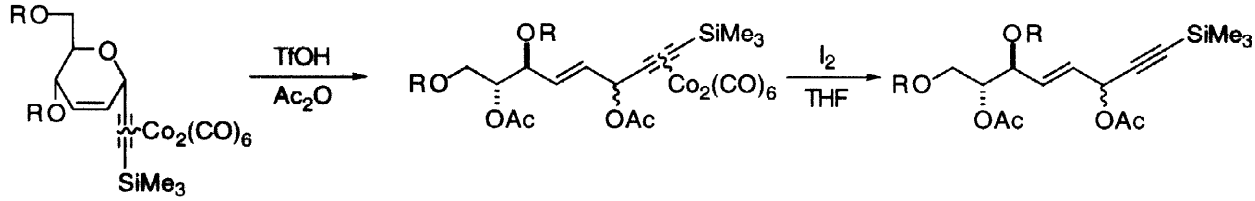
Abstract: Four C-1 alkynylated D-glucals were converted into the corresponding dicobalthexacarbonyl complexes. All of them were recyclized upon treatment with acid to form the medium size (7, 8, 9 and 10 membered) ether rings. The crucial mechanism was *cis-trans* double bond isomerization of allylic cation connected to dicobalthexacarbonyl complexes. Decomplexation was successfully achieved under high pressure hydrogenation by using rhodium catalyst.

Introduction

Medium size cyclic ethers often occur in marine polyether toxins such as brevetoxin, ciguatoxin, yessotoxin, gambierol acid and maitotoxin.[2] The medium size rings are generally difficult to synthesize via standard methodologies. We are now interested in cyclization of cyclic ethers by taking advantage of cobalt-stabilized carbocation that has been well known as Nicholas Reaction.[3]

C-Glycosidation of alkynyl group to pyranose ring is a valuable synthetic method for oxygenated carbon compounds in optically active form. Introduction of acetylenic group to D-glucals has been reported from this laboratory.[4] Recently, we described the reaction of cobalt-complexed sugar acetylene with acid to give the corresponding open-chain in which *cis-trans* isomerization of the double bond was observed as shown in Scheme 1.[5] Oxidative decomplexation of *exo*-dicobalthexacarbonyl complex by using I_2 in THF was successful.



1 R = Ac
2 R = TBDPS

3 R = Ac
4 R = TBDPS

5 R = Ac
6 R = TBDPS

Scheme 1

Focusing to *cis-trans* isomerization, we became interested in examining a possibility that glucal derivative could recyclize from 6-membered to a larger ring. Decomplexation of *endo*-dicobalthexacarbonyl

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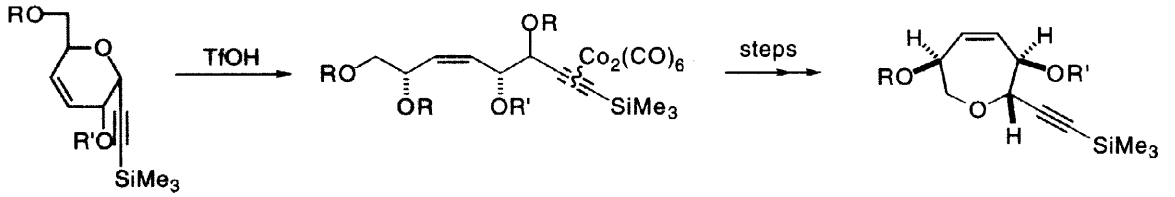
complex, which was extremely different from decomplexation of *exo*-dicobalthexacarbonyl complex,[6] was investigated under high pressure hydrogenation in the presence of Rh catalyst.[1]

In our recent publication, we could convert glucal derivative **7** to an oxepene derivative **9** via ring opening and recyclization.[7] The limitation of that method was only applicable to 7 membered ring derivative as shown in Scheme 2.



7 **8** **9**

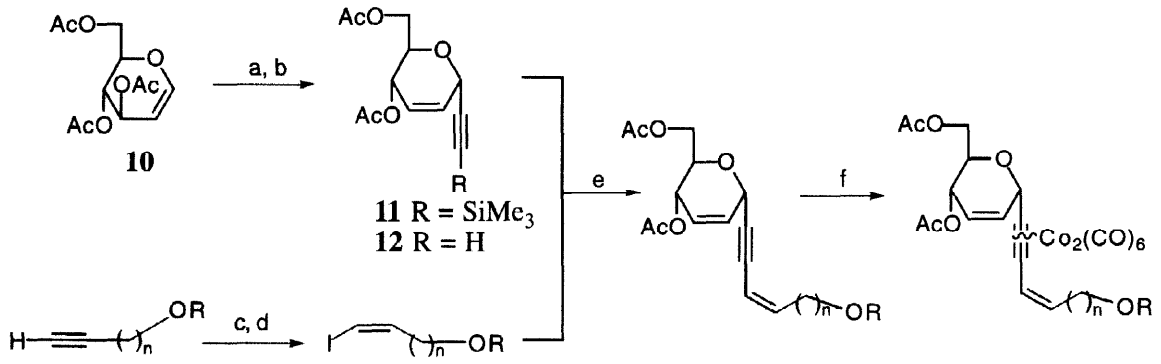
Scheme 2

In this article, we describe an efficient one-step recyclization to synthesize medium size (7, 8, 9 and 10) membered rings. We became interested in the extension of acetylenic side chain at the C-1 position of glucal derivative and making them to be dicobalthexacarbonyl complexes. After the treatment with acid the propargyl cation would have much opportunity to receive an attack by the terminal hydroxy group to form the medium size ring products (*vide infra*, Scheme 4).[8]

C-Glycosidation of glucal derivative and cobalt-complexation

C-Glycosidation of tri-*O*-acetyl-D-glucal **10** by using bistrimethylsilylacetylene and $SnCl_4$ at -40 °C gave compound **11** in high yield.[4] The silyl group was removed by treatment with tetra-*n*-butylammonium fluoride (TBAF) in a mixture of THF-H_2O (9:1) to yield **12** as shown in Scheme 3. For the next step we tried to extend side chain at the acetylenic terminal for further cyclization. In this manner, *cis* double bond was necessary for smooth cyclization. Then palladium catalyzed ene-yne coupling was the reaction of choice.[9] Vinyl iodides **14** were prepared from yn-ol in about 70% yield by treatment with I_2/morpholine and further reduction with diimide to form the corresponding *cis*-vinyl iodide derivatives.[10] In case of propargyl alcohol (n=1), it was first necessary to be protected by *tert*-butylchlorodimethylsilane (TBDMSCl) but the higher homologs being used without protection. Coupling between the acetylene **12** and vinyl iodides **14a-d** in the presence of palladium acetate ($Pd(OAc)_2$), triphenylphosphine (PPh_3), cuprous iodide (CuI) and *n*-butylamine (*n*-$BuNH_2$) in benzene as the solvent at room temperature for 5 hr[9] gave the ene-yne derivatives **15a-d** in moderate yields 65-40%. The stereochemistry of incoming double bond remained as *cis*-orientation (^1H NMR, $J_{3',4'}$ of compounds **15a,b** = 11Hz, compounds **15c,d** = 10.5 Hz). All the coupling products, **15a-d**, indicated the molecular ions in EI-MS at m/z 408, 308, 322 and 336, respectively. These products were purified on silica gel chromatography to give analytically pure materials.

Complexation of the coupling products **15** with dicobaltoctacarbonyl in dichloromethane as the solvent at room temperature afforded the corresponding dicobalthexacarbonyl complexes **16a-d** as deep-reddish brown oils. Infra red spectra of each complex showed three absorbance bands around 2092-2024 cm^{-1} as carbonyl ligands to cobalt. NMR spectral data of the complex such as **16a** showed down field shift thus H-1 from δ = 5.11 to δ = 5.49 ; H-3' from δ = 5.49 to δ = 6.48. All the compounds **16a-d** showed molecular ion (M^++1) in FAB-MS at m/z 695, 595, 609 and 623, respectively.



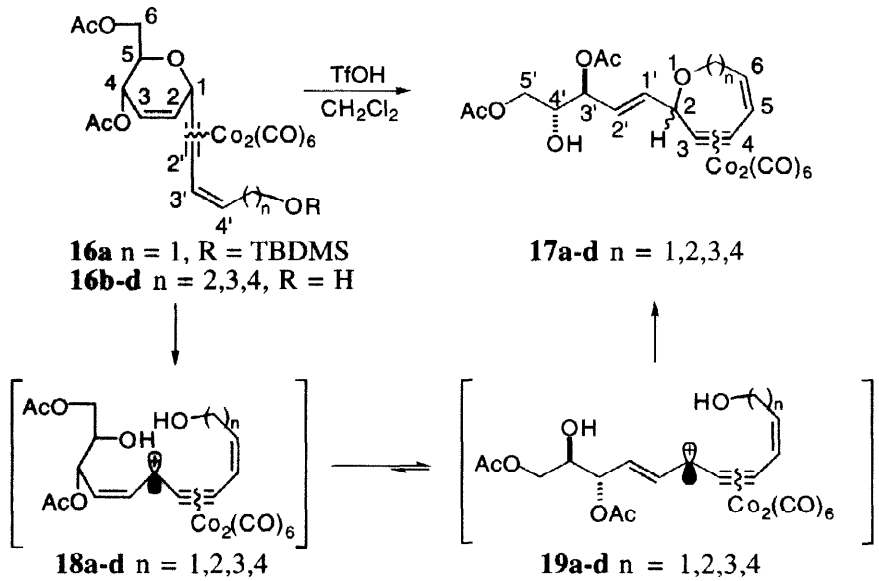
a, n = 1, R = TBDMS; **b-d**, n = 2,3,4, R = H

Reagents and conditions : a) $Me_3SiC{\equiv}CSiMe_3$, $SnCl_4$, -40 °C, 86% b) tetra-*n*-butylammonium fluoride/ tetrahydrofuran : H_2O (10:1) c) I_2 / morpholine, benzene d) KOOCN=NCOOK, AcOH, MeOH, pyridine e) $Pd(OAc)_2$, PPh_3, CuI, *n*-$BuNH_2$, rt f) 1.2 equiv. $Co_2(CO)_8$

Scheme 3

Ring-opening and recyclization

Interestingly, treatment of the cobalt complexes **16a-d** with dilute trifluoromethanesulfonic acid (TfOH, 0.1 M in 1,1,2-trichloro-1,2,2-trifluoroethane)[5] in dichloromethane as the solvent at low temperatures (-20 to -78 °C) afforded cyclization products **17a-d** as mixture of diastereomers at the C-2 position. The mechanism for this step can be explained as follows **i)** C-O bond in the glucal ring was cleaved to generate cobalt stabilized carbocation **18**,[3,5,11] **ii)** *cis-trans* isomerization[5] occurred to give unsuitable cation (**19**) for recyclization of hydroxy group at the C-5 position, **iii)** hydroxy group on the other side chain acted as a nucleophile under influence of *cis* double bond at the C-3' position and attacked at propargyl cation. In case of **16a**, protecting group (TBDMS) was easily removed in the condition of acid. For this reason we have received oxacyclic compound **17** as a major product in moderate yield except 10-membered ring (low yield, 18%), which may be because of high entropy effect in **19d**. Even though these reactions gave moderate yields, but this one-step recyclization saved several steps for manipulating the functional group.



Scheme 4

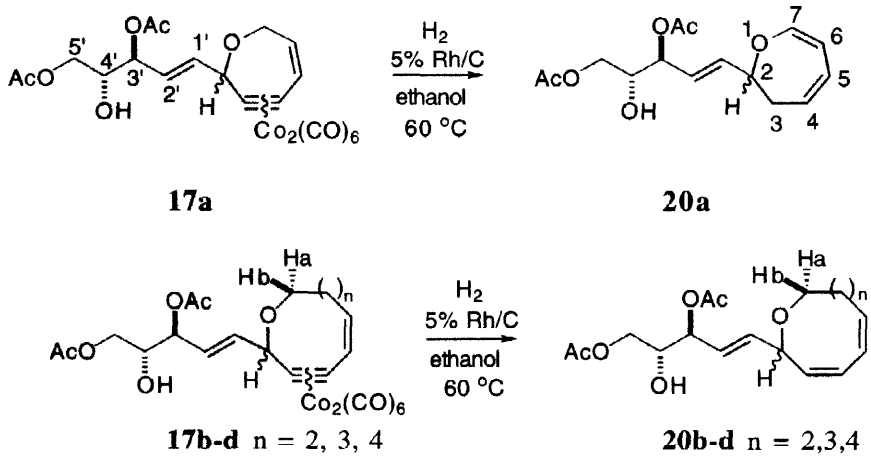
NMR spectral data of the cyclization products **17a-d** showed NOE between H-2 and H-7, H-8, H-9 and H-10 in the 7, 8, 9 and 10 membered ether rings, respectively. Some important data such as reaction conditions, yield and spectroscopic data are summarized in Table 1.

Table 1 Optimized reaction conditions, yield and some spectroscopic data of **17**.

products	ring size	temp. (°C)	TfOH (w/v)	yield (%)	selected data of products
17a	7	-40	0.2	40	m/z 581 (M^++1) NOE H-2 δ 5.30 and H-7a δ 4.32; C-3,4 δ 83.1, 83.3
17b	8	-20	0.15	43	m/z 595 (M^++1) NOE H-2 δ 5.22 and H-8a δ 3.78; C–3,4 δ 80.0, 80.4
17c	9	-40	0.25	52	m/z 609 (M^++1) NOE H-2 δ 5.26 and H-9a δ 3.61; C-3,4 δ 80.3, 80.7
17d	10	-20	0.15	18	m/z 623 (M^++1) NOE H-2 δ 5.02 and H-10a δ 3.69; C-3,4 δ 80.9, 80.1

Decomplexation

Attempted decomplexation of the cyclization products as usual way (by using I_2 in THF) was unsuccessful.[6] The *endo*-dicobalthexacarbonyl complex **17** in the ring system did not react under these oxidative conditions probably due to high ring-strain of the free acetylenic moiety. We expected that if these cobalt-complexes could decomplex due to this strain and that acetylenic parts would be reduced to double bonds, the stable cyclization products could be obtained. We examined the decomplexation of **17** by catalytic hydrogenation under high pressure hydrogen atmosphere.[12] Fortunately, we found that it could be carried out by using 5% Rh/C (rhodium on charcoal) as catalyst in ethanol solvent and heating to 60 °C for 5 hr under 100-150 kg/cm^2 hydrogen atmosphere. The decomplexation of **17a-d** yielded the corresponding colorless dienes **20a-d** in moderate yields. In seven membered case, **20a** was obtained as vinyl ether type structure after two double bond migrations. All other products **20b-d** were obtained without the double bond migration and afforded satisfactory analytical data as shown in Table 2.



17a **20a**

17b-d n = 2, 3, 4 **20b-d** n = 2,3,4

Scheme 5

Table 2 Some spectroscopic and analytical data of products **20**.

products	ring size	yield (%)	selected data of products
20a	7	53	^{1}H-NMR H-3 δ 2.61 (ddd, J = 8.5, 4.5, 1 Hz) H-2 δ 4.19 (t, J = 4.5 Hz) ^{13}C-NMR C-7 δ 155.2 C-6 δ 107.1 HRMS calcd. 296.1259 found 296.1248
20b	8	62	^{1}H-NMR H-8a δ 3.24 (ddt, J = 12.0, 8.0, 2.0 Hz) NOE with H-2 δ 4.21 (dd, J = 7.0, 5.0 Hz) HRMS calcd. 310.1416 found 310.1414
20c	9	66	^{1}H-NMR H-9a δ 3.62 (td, J = 12.0, 3.5 Hz) NOE with H-2 δ 4.28 (dd, J = 7.0, 4.0 Hz) HRMS calcd. 324.1572 found 324.1568
20d	10	57	^{1}H-NMR H-10a δ 3.65 (t, J = 3.0 Hz) NOE with H-2 δ 4.66 (dd, J = 9.0, 6.0 Hz) HRMS calcd. 338.1729 found 338.1716

Conclusion

This paper represented an issue of ring-recyclization of the 6 membered sugar *exo*-acetylene dicobalthexacarbonyl complex into larger rings of the size 7, 8, 9 and 10 membered atoms having *endo*-complex. The key step included the allylic cation intermediate, in which *cis-trans* isomerization helped the re-cyclization of the rings. Reductive decomplexation of the cobalthexacarbonyl complex of the strained acetylene is noteworthy.[1,12] This new method has recently been applied to the syntheses of ABC fragment of ciguatoxin.[13,14]

Experimental Section

General techniques

Infrared spectra were recorded on a JASCO FT/IR-8300 spectrophotometer and are reported in wave number (cm^{-1}). Proton NMR (^{1}H NMR) spectra were recorded on JEOL EX-270 (270 MHz). Underlines are used to specify NOE relationship as _____(*), * indicating the irradiated signal. Carbon NMR (^{13}C NMR) spectra were recorded on a JEOL EX-270 (67.9 MHz). Low-resolution EI and FAB mass spectra were obtained with a JEOL JMS-D 100 and a DX-705, respectively. High-resolution mass spectra (HRMS) were recorded on a JEOL DX-705L and reported in m/z. Optical rotation was determined with a JASCO DIP-370 digital polarimeter. Elemental Analysis were performed by Analytical Laboratory at Faculty of Agricultural Sciences, Nagoya University to which the authors gratefully acknowledge. Unless otherwise noted, non aqueous reaction were carried out under nitrogen or argon atmosphere. THF and CH_2Cl_2 were dried over MS 4Å. All other commercially obtained reagents were used as received. Analytical thin layer chromatography (TLC) was carried out by precoated silica gel plates (Art 5715). Preparative thin layer chromatography (PLC) was carried out by precoated silica gel plates (Art 5774), or preparative silica gel (Art 7747). Silica gel for column chromatography was supplied from Fuji Devison (BW 820-MH).

(4*S*,5*R*)-1-(2'-Trimethylsilyl-1'-ethyne)-3-deacetoxy-4,6-diacetoxy-D-glucal-2-ene (11). To a solution of **10** (1.0 g, 3.67 mmol) and bis(trimethylsilyl)acetylene (1.75 ml, 7.4 mmol) in dry

CH_2Cl_2 (30 ml) was added dropwise tin tetrachloride (0.65 ml, 5.55 mmol) at -40 °C under nitrogen atmosphere. The mixture was stirred for 2 hr at -40 °C and then poured into a mixture of saturated sodium hydrogen carbonate and saturated potassium sodium tartrate (1/1 vol/vol). After stirring for 20 minutes at 0 °C, the organic layer was separated and the water layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, brine, dried (Na_2SO_4) and evaporated to dryness. Purification of the crude oil by column chromatography (silica gel, 1:2 ether/hexane as eluent) gave compound **11** (1.06 g, 3.42 mmol, 93%) as a colorless oil. IR (KBr) ν_{max} 2165, 1746 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.20 (9H, s, TMS), 2.07 (3H, s, OAc), 2.15 (3H, s, OAc), 4.09 (1H, ddd, J = 9.0, 5.0, 3.0 Hz, H-5), 4.21 (1H, dd, *J* = 12.0 5.0 Hz, H-6), 4.25 (1H, dd, *J* = 12.0 3.0 Hz, H-6), 4.96 (1H, dt, *J* = 3.5, 2.0 Hz, H-1), 5.28 (1H, dq, *J* = 9.0, 2.0 Hz, H-4), 5.77 (1H, dt, *J* = 10.5, 2.0 Hz, H-3), 5.88 (1H, ddd, *J* = 10.5, 3.5, 2.0 Hz, H-2). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.4 (3C), 20.5, 20.8, 62.9, 64.2, 64.7, 69.9, 91.5, 100.8, 125.3, 128.9, 170.0, 170.5. FAB-MS *m/z* 251 (M^+ - OAc). $[\alpha]_D^{28}$ -78.7° (*c* 0.56, $CHCl_3$). Anal. calcd. for $C_{15}H_{22}O_5Si$: C, 58.04; H, 7.14. Found: C, 58.03; H, 7.02.

(4*S*,5*R*)-1-(1'-Ethyne)-3-deacetoxy-4,6-diacetoxy-D-glucal-2-ene (**12**). To a solution of **11** (9.59 g, 27.0 mmol) in THF/H_2O (9/1, 220 ml) was added dropwise TBAF (31 ml, 31 mmol, 1M solution in THF) at room temperature. After stirred for 12 hr, the reaction mixture was poured into sat. NH_4Cl at 0 °C and extracted with ether. The organic layer was washed with water, brine and dried over Na_2SO_4. Evaporation of the solvent gave a crude oil, which was purified by column chromatography (silica gel, 1:2 ether/hexane as eluent) to afford pure compound **12** (6.14 g, 25.8 mmol, 95%) as a colorless oil. IR (KBr) ν_{max} 3266, 2113, 1754, 1730 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 2.00 (3H, s, OAc), 2.01 (3H, s, OAc), 2.52 (1H, d, *J* = 2.5 Hz, H-2'), 4.01 (1H, ddd, *J* = 9.0, 5.0, 3.0 Hz, H-5), 4.08-4.20 (2H, m, H-6), 4.88 (1H, m, H-1), 5.20 (1H, dq, *J* = 9.0, 2.0 Hz, H-4), 5.71 (1H, dt, *J* = 10.5, 2.0 Hz, H-3), 5.82 (1H, ddd, *J* = 10.0, 3.0, 1.5 Hz, H-2). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.5, 20.7, 62.7, 63.4, 64.4, 69.7, 74.9, 79.4, 125.5, 128.6, 170.0, 170.5. $[\alpha]_D^{27}$ -30.2° (*c* 0.42, $CHCl_3$).

*Typical procedure for preparing of compound **14***

Iodine (1 eq) was dissolved in 35.5 eq of freshly distilled benzene at 45 °C and 3 eq of morpholine in benzene (3.5 eq) was added slowly to the well-stirred solution. The dark orange iodo-morpholine complex formed rapidly and after 10 minutes acetylenic compound **13** was added, and the stirring was continued at 45 °C for 24 hr. After cooling, the hydroiodide salt was removed by filtration (in vacuo) and the filtrate was diluted with ether. The organic layer was washed with 10% sodium hydrogen phosphate, 10% sodium thiosulfate, sat. sodium bicarbonate, brine, dried (Na_2SO_4) and evaporated to dryness. Iodoacetylene was obtained in quantitative yield and was used for the next step without any purification.

The crude iodoacetylene (1 eq) was dissolved in MeOH and pyridine (6 eq) and then dipotassium azodicarboxylate (3 eq) was added. Glacial acetic acid (6.3 eq) was added slowly (about 2 hr) at room temperature. After stirring for 24 hr, the reaction mixture was added 10% HCl and extracted with ether. The organic layer was neutralized with 5% $NaHCO_3$, washed with water, brine, dried (Na_2SO_4) and evaporated to dryness gave compound **14**.

3-Iodo-2-propene *tert*-butyldimethylsilyl ether (**14a**). Yield in 2 steps 70%. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.1 (6H, s, Si-Me_2), 0.91 (9H, s, t-Butyl), 4.24 (2H, dd, *J* = 5.0, 2.0 Hz, CH_2), 6.23 (1H, dt, *J* = 8.0, 2.0 Hz, H-1), 6.41 (1H, dt, *J* = 8.0, 5.0 Hz, H-2).

4-Iodo-3-butenol (14b). Yield in 2 steps 72%. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.1 (1H, s, OH), 2.43 (2H, dq, *J* = 6.5, 1.0 Hz, H-3), 3.75 (2H, t, *J* = 6.5 Hz, H-4), 6.31 (1H, q, *J* = 7.0 Hz, H-2), 6.36 (1H, dt, *J* = 7.0, 1.0 Hz, H-1).

5-Iodo-4-pentenol (14c). Yield in 2 steps 73%. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.8 (1H, brd, OH), 1.69 (2H, q, *J* = 6.5 Hz, H-4), 2.23 (2H, t, *J* = 7.0 Hz, H-3), 3.66 (2H, t, *J* = 6.5 Hz, H-5), 6.19 (2H, q, *J* = 7.0 Hz, H-2), 6.23 (1H, d, *J* = 7.0 Hz, H-1).

6-Iodo-5-hexenol (14d). Yield in 2 steps 57%. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.5-1.7 (4H, m, H-4 and 5), 1.8 (1H, brd, OH), 2.17 (2H, q, *J* = 6.5 Hz, H-3), 3.64 (2H, t, *J* = 6.5 Hz, H-6), 6.16 (1H, q, *J* = 7.0 Hz, H-2), 6.21 (1H, d, *J* = 7.0 Hz, H-1).

Typical procedure of palladium catalyzed ene-yne coupling reaction

To a degassed suspension of $Pd(OAc)_2$ (0.05 eq), PPh_3 (0.1 eq) and CuI (0.1 eq) in dry benzene were added a solution of **12** (1 eq) in dry benzene and a solution of vinyl iodide **14** (1 eq) in dry benzene. To the resulting reddish-brown solution was added *n*-$BuNH_2$ (3 eq). The solution was stirred at room temperature for 5 hr. The reddish-brown solution was poured into the saturated NH_4Cl and extracted with ether 3 times. The combined organic layer was washed with water, brine, dried (Na_2SO_4) and evaporated to dryness. After purification by column chromatography (silica gel, 1:1 hexane/ethyl acetate as eluent), the pure compound **15** was obtained.

(4*S*,5*R*)-1-(5'-*tert*-Butyldimethylsilyloxypent-3'-en-1'-yne)-3-deacetoxy-4,6-diacetoxy-D-glucal-2-ene (15a). Yield 65%. IR (film) ν_{max} 1747 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.09 (6H, s, Si-Me_2), 0.90 (9H, s, t-butyl), 2.09 (3H, s, OAc), 2.11 (3H, s, OAc), 4.10 (1H, ddd, *J* = 9.0, 5.0, 3.0 Hz, H-5), 4.21 (1H, dd, *J* = 12.0, 3.0 Hz, H-6a), 4.26 (1H, dd, *J* =12.0, 5.0 Hz, H-6b), 4.41 (2H, dd, *J* = 6.5, 2.0 Hz, H-5'), 5.11(1H, m, H-1), 5.32 (1H, dq, *J* = 9.0, 2.0 Hz, H-4), 5.54 (1H, dq, *J* = 11.0, 2.0 Hz, H-3'), 5.79 (1H, dt, *J* = 10.0, 2.0 Hz, H-3), 5.91(1H, ddd, *J* = 10.0, 3.5, 2.0 Hz, H-2), 6.08 (1H, dt, *J* = 11.0, 6.0 Hz, H-4'). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -5.1, 18.2, 20.7, 20.9, 25.8, 61.5, 62.9, 64.3, 64.6, 69.8, 82.5, 90.2, 108.0, 125.3, 129.0, 144.0, 170.1, 170.7. EI-MS *m/z* 408 (M^+). $[\alpha]_D^{28}$ -71.8° (*c* 1.02, $CHCl_3$). Anal. calcd. for $C_{21}H_{32}O_6Si$: C, 61.75; H, 7.84. Found: C, 61.71; H, 7.88.

(4*S*,5*R*)-1-(6'-Hydroxypent-3'-en-1'-yne)-3-deacetoxy-4,6-diacetoxy-D-glucal-2-ene (15b). Yield 51%. IR (film) ν_{max} 3461,1743 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.65 (1H, brd s, OH), 2.09 (3H, s, OAc), 2.10 (3H, s, OAc), 2.58 (2H, q, *J* = 7.0 Hz, H-5'), 3.72 (2H, q, *J* = 6.0 Hz, H-6'), 4.14 (1H, ddd, *J* = 9.0, 4.5, 3.5 Hz, H-5), 4.21 (1H, dd, J = 12.0, 5.0 Hz, H-6a), 4.26 (1H, dd, *J* = 12.0, 3.0 Hz, H-6b), 5.11 (1H, m, H-1), 5.29 (1H, dq, *J* = 9.0, 2.0 Hz, H-4), 5.63 (1H, dq, *J* = 11.0, 1.0 Hz, H-3'), 5.79 (1H, dt, *J* = 10.0, 2.0 Hz, H-3), 5.91 (1H, ddd, *J* = 10.0, 3.5, 2.0 Hz, H-2), 6.02 (1H, dt, *J* = 11.0, 7.5 Hz, H-4'). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.7, 20.9, 33.8, 61.5, 63.2, 64.3, 64.9, 69.7, 83.2, 89.2, 110.6, 125.3, 129.1, 140.7, 170.3, 171.0. EI-MS *m/z* 308 (M^+). $[\alpha]_D^{28}$ -177.1° (*c* 0.38, $CHCl_3$). Anal. calcd. for $C_{16}H_{20}O_6$: C, 62.34; H, 6.49. Found: C, 62.29; H, 6.49.

(4*S*,5*R*)-1-(7'-Hydroxypent-3'-en-1'-yne)-3-deacetoxy-4,6-diacetoxy-D-glucal-2-ene (15c). Yield 45%. IR ν_{max} (film) 3466 (OH), 1743 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.66 (1H, brd, OH), 1.68 (2H, p, *J* = 7.0 Hz, H-6'), 2.09 (3H, s, OAc), 2.10 (3H, s, OAc), 2.40 (2H, qd, *J* = 7.5, 1.5 Hz, H-5'), 3.65 (2H, t, *J* = 6.5 Hz, H-7'), 4.12 (1H, ddd, *J* = 9.0, 4.5, 3.5 Hz, H-5), 4.22 (1H, dd, *J* = 13.0 3.5 Hz, H-6a), 4.24 (1H, dd, *J* = 13.0, 4.5 Hz, H-6b), 5.11 (1H, m, H-1), 5.30 (1H, dq, *J* = 9.0, 2.0 Hz, H-4), 5.53 (1H, dq, *J* = 10.5, 1.5 Hz, H-3'), 5.78 (1H, dt, *J* = 10.0, 2.0 Hz, H-3), 5.91 (1H, ddd, *J* = 10.0, 3.5, 2.0 Hz, H-2), 5.99 (1H, dt, *J* = 10.5, 7.5 Hz, H-4'). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.7, 20.9, 26.5,

31.4, 61.9, 63.1, 64.3, 64.8, 69.8, 83.3, 89.0, 108.8, 125.2, 129.1, 144.3, 170.2, 170.9. EI-MS *m/z* 322 (M^+). $[\alpha]_D^{27}$ -99.8° (*c* 0.395, $CHCl_3$). Anal. calcd. for $C_{17}H_{22}O_6$: C, 63.36; H, 6.83. Found: C, 63.22; H, 6.87.

(4*S*,5*R*)-1-(8'-Hydroxypent-3'-en-1'-yne)-3-deacetoxy-4,6-diacetoxy-D-glucal-2-ene (15d).Yield 40%. IR (film) ν_{max} 3374, 1733 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 1.45-1.65 (5H, m, H-6', H-7', OH), 2.09 (3H, s, OAc), 2.10 (3H, s, OAc), 2.33 (2H, q, *J* = 7.5 Hz, H-5'), 3.65 (2H, t, *J* = 6.0 Hz, H-8'), 4.12 (1H, dt, *J* = 9.0, 4.0 Hz, H-5), 4.20-4.27 (2H, m, H-6), 5.11 (1H, m, H-1), 5.31 (1H, dq, *J* = 9.0, 2.0 Hz, H-4), 5.50 (1H, dq, *J* = 11.0, 1.5 Hz, H-3'), 5.78 (1H, dt, *J* = 10.0, 2 Hz, H-3), 5.91 (1H, ddd, *J* = 10.0, 3.5, 2.0 Hz, H-2), 5.96 (1H, dt, *J* = 11.0, 7.5 Hz, H-4'). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.7, 20.9, 24.8, 29.8, 32.0, 62.5, 63.0, 64.4, 64.8, 69.8, 83.5, 88.7, 108.6, 125.1, 129.3, 144.8, 170.3, 170.3. EI-MS *m/z* 336 (M^+). $[\alpha]_D^{27}$ -101.9° (*c* 0.11, $CHCl_3$). Anal. calcd. for $C_{18}H_{24}O_6$: C, 64.29; H, 7.14, Found: C, 64.19; H, 6.99.

Typical procedure of complexation with dicobaltoctacarbonyl

To a solution of dicobaltoctacarbonyl (1.2 eq) in dry CH_2Cl_2 was added a solution of **15** (1 eq) in CH_2Cl_2 at room temperature under argon atmosphere. After stirring for 2 hr, the reaction mixture was concentrated. The mixture was purified by column chromatography (silica gel, 1:1 hexane/ethyl acetate as eluent). Compound **16** was obtained as a reddish-brown oil.

(4*S*,5*R*)-1-(5'-*tert*-Butyldimethylsilyloxypent-3'-en-1'-yne)-3-deacetoxy-4,6-diacetoxy-D-glucal-2-ene-dicobalthexacarbonyl complex (16a). Yield 95%. IR (film) ν_{max} 2093, 2055, 2024, 1747 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.08 (6H, s, Si-Me_2), 0.91 (9H, s, t-Butyl), 2.07 (3H, s, OAc), 2.08 (3H, s, OAc), 4.15 (1H, dd, *J* = 11.0, 3.5 Hz, H-6a), 4.22 (1H, m, H-5), 4.37 (1H, dd, *J* = 11.0, 6.0 Hz, H-6b), 4.44 (2H, dd, *J* = 5.5, 2.0 Hz, H-5'), 5.19 (1H, m, H-4), 5.49 (1H, q, *J* = 2.0 Hz, H-1), 5.93 (1H, dt, *J* = 10.0, 2.0 Hz, H-3), 6.02 (1H, dt, *J* = 11.0, 5.5 Hz, H-4'), 6.07 (1H, ddd, *J* = 10.0, 2.5, 1.0 Hz, H-2), 6.48 (1H, dt, *J* = 11.0, 2.0 Hz, H-3'). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -5.3, 18.2, 20.6, 20.9, 25.8, 60.4, 62.4, 64.1, 70.7, 72.3, 82.4, 95.5, 123.5, 124.4, 131.0, 138.4, 170.4, 170.7. FAB-MS *m/z* 695 (M^++1). $[\alpha]_D^{27}$ -665° (*c* 0.60, $CHCl_3$) RSD = 3.5%. Anal. calcd. for $C_{27}H_{32}O_{12}Co_2Si$: C, 46.69; H, 4.61. Found: C, 46.59; H, 4.61.

(4*S*,5*R*)-1-(6'-Hydroxypent-3'-en-1'-yne)-3-deacetoxy-4,6-diacetoxy-D-glucal-2-ene-dicobalthexacarbonyl complex (16b). Yield 81%. IR (film) ν_{max} 3461, 2092, 2051, 2024, 1743 cm^{-1}. ^1H NMR ($CDCl_3$, 270 Hz) δ 1.75 (1H, t, *J* = 6.0 Hz, OH), 2.09 (6H, s, OAc), 2.57 (2H, m, H-5'), 3.76 (2H, ddd, *J* = 12.0, 6.0, 3.0 Hz, H-6'), 4.17 (1H, dd, *J* = 11.0, 3.5 Hz, H-6a), 4.24 (1H, m, H-5), 4.41 (1H, dd, *J* = 11.0, 6.0 Hz, H-6b), 5.17 (1H, m, H-4), 5.58 (1H, q, *J* = 2.0 Hz, H-1), 5.90 (1H, dt, *J* = 11.0, 8.0 Hz, H-4'), 5.98 (1H, ddd, *J* = 10.5, 3.5, 2.0 Hz, H-3), 6.11 (1H, ddd, *J* = 10.5, 2.5, 1.0 Hz, H-2), 6.59 (1H, dt, *J* = 11.0, 1.5 Hz, H-3'). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.7, 20.9, 32.6, 61.5, 62.3, 64.0, 71.2, 71.68, 83.8, 94.4, 124.2, 127.0, 131.5, 133.1, 170.4, 170.9. FAB-MS *m/z* 595 (M^++1). $[\alpha]_D^{27}$ -155° (*c* 0.63, $CHCl_3$) RSD = 10%. Anal. calcd. for $C_{22}H_{20}O_{12}Co_2$: C, 44.46; H, 3.37. Found: C, 44.43; H, 3.49.

(4*S*,5*R*)-1-(7'-Hydroxypent-3'-en-1'-yne)-3-deacetoxy-4,6-acetoxy-D-glucal-2-ene-dicobalthexacarbonyl complex (16c). Yield 84%. IR (film) ν_{max} 3467, 2092, 2016, 1747 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 1.60 (1H, t, *J* = 5.5 Hz, OH), 1.71 (2H, *J* = 7.0 Hz, H-6'), 2.08 (6H, two-s, OAc), 2.40 (2H, brd q, *J* = 8.0 Hz, H-5'), 3.69 (2H, q, *J* = 5.5 Hz, H-7'), 4.14 (1H, dd, *J* = 11.5, 3.5 Hz, H-6a), 4.23 (1H, td, *J* = 6.0, 3.5 Hz, H-5), 4.42 (1H, dd, *J* = 11.5, 6.0 Hz, H-6b), 5.17 (1H, m, H-4), 5.58 (1H, q, *J* = 2.0 Hz, H-1), 5.88 (1H, dt, *J* = 11.0, 7.5 Hz, H-4'), 5.94 (1H, ddd, *J* = 10.0, 3.0, 2.0 Hz, H-3),

6.07 (1H, ddd, J = 10.0, 2.0, 1.0 Hz, H-2), 6.47 (1H, dt, J = 11.0, 1.5 Hz, H-3'). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.6, 20.9, 25.6, 31.9, 62.2, 62.3, 64.1, 70.9, 71.9, 83.9, 94.8, 124.2, 124.8, 131.4, 137.1, 170.4, 170.9. FAB-MS *m/z* 609 (M^++1). $[\alpha]_D^{28}$ -71° (*c* 0.44, $CHCl_3$) RSD = 10%. Anal. calcd. for $C_{23}H_{22}O_{12}Co_2$: C, 45.41; H, 3.62. Found: C, 45.40; H, 3.54.

(4*S*,5*R*)-1-(8'-Hydroxypent-3'-en-1'-yne)-3-deacetoxy-4,6-acetoxy-D-glucal-2-ene-dicobalthexacarbonyl complex (16d). Yield 90%. IR (film) ν_{max} 3445, 2092, 2052, 2024, 1746 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 1.37 (1H, t, J = 5.5 Hz, OH), 1.5-1.7 (4H, m, H-6' and 7'), 2.08 (6H, two-s, OAc), 2.35 (2H, q, J = 7.0 Hz, H-5'), 3.66 (2H, q, J = 5.5 Hz, H-8'), 4.15 (1H, dd, J = 12.0, 3.5 Hz, H-6a), 4.23 (1H, td, J = 6.0, 3.5 Hz, H-5), 4.41 (1H, dd, J = 12.0, 6.0 Hz, H-6b), 5.18 (1H, m, H-4), 5.53 (1H, q, J = 2.0 Hz, H-1), 5.82 (1H, dt, J = 11.0, 7.0 Hz, H-4'), 5.93 (1H, t, J = 10.5, 2.0 Hz, H-3), 6.06 (1H, ddd, J = 10.5, 2.0, 1.0 Hz, H-2), 6.47 (1H, dt, J = 11.0, 1.5 Hz, H-3'). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.6, 20.9, 25.2, 28.7, 32.3, 62.4, 62.5, 64.1, 70.8, 72.1, 83.9, 95.1, 124.32, 124.37, 131.2, 138.1, 170.4, 170.9. FAB-MS *m/z* 623 (M^++1). $[\alpha]_D^{28}$ -179° (*c* 0.59, $CHCl_3$) RSD = 9%. Anal. calcd. for $C_{24}H_{24}O_{12}Co_2$: C, 46.31; H, 3.86. Found: C, 46.30; H, 3.91.

Typical procedure of recyclization

To a solution of **16** (0.05 M) in CH_2Cl_2 at various temperatures (-78, -40 and -20 °C) under nitrogen atmosphere was slowly added a solution of TfOH in $Cl_2FCCClF_2$ (0.1 M). After stirring at that temperature for 2 hours, the mixture was poured into the sat. $NaHCO_3$ at 0 °C and extracted with ether 3 times. The combined organic layer was washed with water, brine, dried (Na_2SO_4) and evaporated to dryness. The resulting product was purified by PLC (silica gel, 1:1 hexane/ethyl acetate as developing solvent) as a reddish-brown oil.

(3'*S*,4'*R*)-2-(3',5'-Diacetoxy-4'-hydroxy-1'-pentene)-oxacyclohept-5-en-3-yne-dicobalthexacarbonyl complex (17a). IR (film) ν_{max} 3420, 2091, 2049, 2020 1747, 1717 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 2.07 (3H, s, OAc), 2.10 (3H, s, OAc), 2.37 (1H, d, J = 5.0 Hz, OH), 4.01 (1H, p, J = 5 Hz, H-4'), 4.16-4.20 (2H, m, H-5'), 4.32 (1H, dt, J = 17.0, 2.5 Hz, H-7a), 4.63 (1H, dd, J = 17.0, 6.0 Hz, H-7b), 5.30 (1H, m, H-2)*, 5.42 (1H, t, J = 5.5 Hz, H-3' for one isomer), 5.45 (1H, t, J = 6 Hz, H-3' for the other isomer), 5.87-6.10 (3H, m, H-1',2',6), 6.70 (1H, dd, J = 10, 2.5 Hz, H-5). ^{13}C NMR ($CDCl_3$, 67.9 MHz) mixture of two isomers δ 20.78, [20.85, 20.88 ratio (1:1)], [64.80, 64.84 ratio (1:1)], 70.5, 70.7, [71.23, 71.27 ratio (1:1)], 74.0, 83.1, 83.3, 123.8, [127.5, 127.7 ratio (2:3)], 131.8, [134.3, 134.4 ratio (1:1)], 169.7, 171.1. FAB-MS *m/z* 581 (M^++1). Anal. calcd. for $C_{21}H_{18}O_{12}Co_2$: C, 43.46; H, 3.10. Found: C, 43.40; H, 3.17.

(3'*S*,4'*R*)-2-(3',5'-Diacetoxy-4'-hydroxy-1'-pentene)-oxacyclooct-5-en-3-yne-dicobalthexacarbonyl complex (17b). IR (film) ν_{max} 3420, 2092, 2052, 2023, 1743 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 2.07 (3H, s, OAc), 2.10 (3H, s, OAc), 2.06 (3H, s, OAc, the other isomer), 2.23 (1H, m, H-7a), 2.38 (1H, d, J= 5.0 Hz OH), 2.64 (1H, m, H-7b), 3.78 (1H, m, H-8a), 4.01 (1H, p, J = 5 Hz, H-4'), 4.18 (2H, m, H-5'), 4.26 (1H, dt, J = 12.0, 2.0 Hz, H-8b), 5.22 (1H, d, J = 4.0 Hz, H-2 for one isomer)*, 5.23 (1H, d, J = 4.0 Hz, H-2 for the other isomer)*, 5.46 (1H, t, J = 5.0 Hz, H-3'), 5.91 (1H, dd, J = 15.0, 4.0 Hz, H-2'), 5.99 (dd, J = 15.0, 4.0 Hz, H-1'), 6.01 (1H, dt, J = 11.0. 5.0 Hz, H-6), 6.56 (1H, d, J = 11.0 Hz, H-5). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.68, 20.75, 31.0, 61.4, [64.73, 64.76 ratio (3:2)], [71.20, 71.23 ratio (1:1)], [71.45, 71.58 ratio (3:2)], [73.76, 73.79 ratio (1:1)], 80.0, 80.4, [123.79, 123.89 ratio (3:2)], 128.3, 132.3, [133.86, 134.46 ratio (3:2)], 169.7, 171.0. FAB MS *m/z* 595 (M^++1). Anal. calcd. for $C_{22}H_{20}O_{12}Co_2$: C, 44.46; H, 3.37. Found: C, 44.52; H, 3.10.

(3'*S*,4'*R*)-2-(3',5'-Diacetoxy-4'-hydroxy-1'-pentene)-oxacyclonon-5-en-3-yne-dicobalthexacarbonyl complex (17c). IR (film) ν_{max} 3460, 2094, 2054, 2025, 1747, 1717 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 1.48-1.62 (2H, m, H-8), 1.87 (1H, m, H-7a), 2.05 (3H, s, OAc), 2.08 (3H, s, OAc for one isomer), 2.10 (6H, s, OAc for the other isomer), 2.42 (1H, d, *J* = 5 Hz), 2.46 (1H, m, H-7b), 3.61 (1H, brd-t, *J* = 11.0 Hz, H-9a), 3.96 (1H, dt, *J* = 11.0, 3.5 Hz, H-9b), 4.02 (1H, p, *J* = 5.0 Hz, H-4'), 4.16-4.19 (2H, m, H-5'), 5.26 (1H, d, *J* = 4.0 Hz, H-2, for one isomer)*, 5.27 (1H, d, *J* = 3.0 Hz, H-2 the other isomer)*, 5.48 (1H, m, H-3'), 5.86 (1H, td, *J* = 10.5, 8.5 Hz, H-6), 5.93 (1H, dd, *J* = 15.5, 4.0 Hz, H-2'), 6.01 (1H, dd, *J* = 15.5, 4.0 Hz, H-1'), 6.67 (1H, d, *J* = 10.5, H-5). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.79, 20.84, [24.46, 24.53 ratio (3:2)], 27.4, 64.8, [65.74, 65.79 ratio (1:1)], [71.35, 71.38 ratio (3:2)], 73.7, 73.9, 80.3, 80.7, [124.52, 124.87 ratio (1:1)], 129.8, [133.37, 133.75 ratio (1:1)], 134.3, 169.8, 171.2. FAB-MS *m/z* 609 (M^++1). Anal. calcd. for $C_{23}H_{22}O_{12}Co_2$: C, 45.41; H, 3.62. Found: C, 45.40; H, 3.68.

(3'*S*,4'*R*)-2-(3',5'-Diacetoxy-4'-hydroxy-1'-pentene)-oxacyclodec-5-en-3-yne-dicobalthexacarbonyl complex (17d). IR (film) ν_{max} 3468, 2090, 2051, 2016, 1747 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 1.50-1.85 (4H, m, H-8,9), 2.06 (3H, s, OAc), 2.10 (3H, s, OAc for one isomer), 2.07 (3H, s, OAc), 2.09 (3H, s, OAc for the other isomer), 2.15 (1H, m, H-7), 2.42 (1H, d, *J* = 5.0 Hz, OH for one isomer), 2.45 (1H, d, *J* = 5.0 Hz, OH), 2.74 (1H, m, H-7), 3.69 (1H, ddd, *J* = 12.0, 5.0, 2.0 Hz, H-10a), 4.03 (1H, p, *J* = 5.0, H-4'), 4.15-4.24 (3H, m, H-5', H-10b), 5.02 (1H, m, H-2)*, 5.52 (1H, brd-t, *J* = 5.0 Hz, H-3'), 5.74 (1H, td, *J* = 10.5, 8.0 Hz, H-6), 5.90-6.10 (2H, m, H-1',2'), 6.53 (1H, d, *J* = 10.5, H-5). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.7, 20.8, 25.6, 27.6, [28.23, 29.69 ratio (2:5)], 64.9, [71.39, 71.51 ratio (1:1)], 73.3, 73.6, [74.64, 74.70 ratio (1:1)], 80.9, 80.1, [124.62, 124.79 ratio (1:1)], 127.8, 133.6, [134.72, 134.78 ratio (5:3)], 170.0, 171.2. FAB-MS *m/z* 623 (M^++1). Anal. calcd. for $C_{24}H_{24}O_{12}Co_2$: C, 46.31; H, 3.86. Found: C, 46.31; H, 3.88.

Typical procedure of decomplexation

In the reactor, the solution of cyclization product **17** (0.2 mmol) in EtOH (10 ml) was added 5% Rh/C (70 mg). After replacing the air with N_2, the solution was taken up with high pressure hydrogen (100-150 Kg/cm^2) at 60 °C for 5 hr. Catalyst was filtered off by a short column (silica gel, ether as eluent). The solution was concentrated and purified by PLC (silica gel, 1:1 hexane/ethyl acetate as developing solvent) to obtain the decomplexation product **20** as a colorless oil.

(3'*S*,4'*R*)-7-(3',5'-Diacetoxy-4'-hydroxy-1'-pentene)-2,4-oxacycloheptadiene (20a). IR (film) ν_{max} 3450, 1739, 1232 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 2.09 (6H, s, OAc), 2.34 (1H, d, *J* = 5.0, OH), 2.61 (2H, ddd, *J* = 8.5, 4.5, 1.0 Hz, H-3), 4.00 (1H, p, *J* = 5.0 Hz, H-4'), 4.16 (2H, d, *J* = 5.0 Hz, H-5'), 4.19 (1H, t, *J* = 4.5 Hz, H-2), 5.10 (1H, d, *J* = 8.5 Hz, H-7), 5.40 (1H, dd, *J* = 7.0, 5.0 Hz, H-3'), 5.74-5.93 (3H, m, H-4, 5, 6), 6.01 (1H, dd, *J* = 16.0, 7.0 Hz, H-2'), 6.11 (1H, d, *J* = 16.0 Hz, H-1'). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.8, 21.1, 34.7, 64.8, 69.0, 71.3, 74.5, 77.1, 107.1, 122.4, 123.8, 131.6, 132.4, 155.2, 170.0, 171.1. EI-MS *m/z* 296 (M^+), 278 (M^+- H_2O). HRMS calcd. for $C_{15}H_{20}O_6$ 296.1259. Found 296.1248. $[\alpha]_D^{27}$ +29.6° (*c* 0.125, $CHCl_3$).

(3'*S*,4'*R*)-2-(3',5'-Diacetoxy-4'-hydroxy-1'-pentene)-3,5-oxacyclooctadiene (20b). IR (film) ν_{max} 3446, 1747, 1733, 1224 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 1.99 (1H, ddd, *J* = 15.0, 8.0, 1.5 Hz, H-7a), 2.05 (3H, s, OAc), 2.06 (3H, s, OAc for one isomer), 2.08 (6H, s, OAc for the other isomer), 2.50 (1H, d, *J* = 4.0 Hz, OH for one isomer), 2.52 (1H, d, *J* = 4.0, OH for the other isomer), 2.60 (1H, ddd, *J* = 15.0, 7.5, 1.0 Hz, H-7b), 3.24 (1H, ddt, *J* = 12.0, 8.0, 2.0 Hz, H-8a), 3.92-4.01 (2H, m, H-8b, 4'), 4.11

(1H, dd, J = 11.0, 2.5 Hz, H-5'a), 4.17 (1H, dd, J = 11.0, 2.5 Hz, H-5'b), 4.21 (1H, dd, J = 7.0, 5.0 Hz, H-2)*, 5.36 (1H, dd, J = 6.0, 5.0 Hz, H-3'), 5.48 (1H, dd, J = 10.5, 7.0 Hz, H-3), 5.73 (1H, dd, J = 16.0, 6.0 Hz, H-2'), 5.80 (1H, m, H-6), 5.92 (1H, dd, J = 16.0, 5.0 Hz, H-1'), 6.02-6.10 (2H, m, H-4,5). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.8, 21.0, 30.9, [64.20, 64.23 ratio (1:1)], [64.74, 64.77 ratio (1:1)], [71.16, 71.20 ratio (1:1)], [74.33, 74.77 ratio (1:1)], [75.17, 75.27 ratio (1:1)], [123.77, 123.89 ratio (1:1)], 127.5, 128.7, [129.90, 129.94 ratio (4:5)], 130.5, [136.68, 136.92 ratio (1:1)], 169.9, 171.1. EI-MS *m/z* 310 (M^+), 292 ($M^+ - H_2O$). HRMS calcd. for $C_{16}H_{22}O_6$ 310.1416. Found 310.1414.

(3'*S*,4'*R*)-2-(3',5'-Diacetoxy-4'-hydroxy-1'-pentene)-3,5-oxacyclononadiene (20c). IR (film) ν_{max} 3459, 1793, 1231 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.8 (1H, m, H-8a), 1.8 (1H, m, H-8b), 2.00 (1H, m, H-7a), 2.09 (3H, s, OAc), 2.10 (3H, s, OAc), 2.39 (1H, d, J = 5.0 Hz, OH for one isomer), 2.34 (1H, d, J = 5.0 Hz, OH for the other isomer), 2.52 (1H, qd, J = 12.0, 5.0 Hz, H-7b), 3.62 (1H, td, J = 12.0, 3.5 Hz, H-9a), 3.98 (1H, p, J = 5.0 Hz, H-4'), 4.10-4.16 (2H, m, H-5'), 4.20 (1H, m, H-9b), 4.28 (1H, dd, J = 7.0, 4.0 Hz, H-2)*, 5.36 (1H, m, H-3'), 5.60-5.90 (4H, m, H-3,6,2',1'), 5.95 (1H, brd-d, J = 12.0 Hz, H-5), 6.08 (1H, brd-d, J = 11.0 Hz, H-4). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.8, 21.1, 26.0, [28.86, 29.70 ratio (7:4)], 64.8, [71.24, 71.32 ratio (1:1)], [71.30, 73.14 ratio (1:1)], [74.37, 74.43 ratio (1:1)], [80.52, 80.58 ratio (1:1)], [122.92, 123.04 ratio (1:1)], 128.0, 131.7, [132.35, 132.40 ratio (1:1)], 133.4, [137.20, 137.64 ratio (1:1)], 169.9, 171.1. EI-MS *m/z* 324 (M^+), 306 ($M^+ - H_2O$). HRMS calcd. for $C_{17}H_{24}O_6$ 324.1572. Found 324.1568.

(3'*S*,4'*R*)-2-(3',5'-Diacetoxy-4'-hydroxy-1'-pentene)-3,5-oxacyclodecadienene (20d). IR (film) ν_{max} 3453, 1743, 1227 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.70-1.80 (2H, m, H-8), 1.95-2.10 (3H, m, H-9, 7a), 2.07 (3H, s, OAc), 2.09 (3H, s, OAc), 2.24 (1H, d, J = 5.0 Hz, OH), 2.35 (1H, d, J = 5 Hz, OH), 3.02 (1H, m, H-7b), 3.65 (1H, t, J = 3.0 Hz, H-10a), 3.68 (1H, t, J = 2.5 Hz, H-10b), 4.26 (1H, dd, J = 12.0, 6.0 Hz, H-5'), 4.30 (1H, m, H-4'), 4.34 (1H, dd, J = 12.0, 4.0 Hz, H-5'), 4.66 (1H, dd, J = 9.0, 6.0 Hz, H-2)*, 5.05 (1H, td, J = 6.0, 3.5 Hz, H-3'), 5.46 (dd, J = 11.0, 9.0 Hz, H-3), 5.60 (1H, tdd, J = 11.0, 4.0, 1.0 Hz, H-6), 5.65 (1H, dd, J = 16.0, 6.0 Hz, H-2'), 5.74 (1H, dd, J = 16.0, 6.0 Hz, H-1'), 5.82 (1H, brd-d, J = 11.0 Hz, H-5), 5.94 (1H, brd-d, J = 11.0 Hz, H-4). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ [20.76, 20.79 ratio (5:3)], 20.9, 23.0, [27.35, 27.41 ratio (1:2)], 27.8, 62.2, 68.98, 70.8, [71.21, 71.32 ratio (1:2)], 73.8, 125.7, 129.0, 129.2, [130.58, 130.77 ratio (3:2)], 133.6, 135.6, 170.3, 170.9. EI-MS *m/z* 338 (M^+), 320 ($M^+ - H_2O$). HRMS calcd. for $C_{18}H_{26}O_6$ 338.1729. Found 338.1716.

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