Pergamon

Tetrahedron Vol. 50, No. 19, pp. 5633-5644, 1994

0040-4020/94 $6.00+0.00

0040-4020(94)E0220-N

Enantiomeric Synthesis of Pyran Subunits of Marine trans-fused Polyether Toxins :Epimerization of Alkynyl Sugars through Cobalt Complexes

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Abstract: Alkynyl group attached on the C-1 position of pyranose ring was epimerized through dicobalt hexacarbonyl complex with trifluoromethanesulfonic acid. Three steps involving complexation, acidic transformation and decomplexation afforded overall epimerization. The driving force of this epimerization based on 1,3-diaxial interaction and 1,2-interaction.

Ciguatoxin (**1**) is a toxic principle of ciguatera, which is known as one of the most widespread food poisonings of dinoflagellate origin (*Gambierdiscus toxicus*).[1] In oder to open the way to immunoassay of this toxin and to obtain more reliable information on the absolute configuration, many synthetic studies are continued.[2] This highly complex molecule is characterized by having fused cyclic ether units whose size is from 5 to 9 members and with well-defined stereochemistry, usually with trans-relationship between the two substituents (H or CH_3) in the fusion of rings and cis-stereochemistry in the substituents (H or CH_3) close to the oxygen atom of cyclic ether. This is common to other marin toxins such as maitotoxin,[3] brevetoxins,[4] yessotoxin.[5] It is worthwhile to develop potentially general methodology applicable to these toxin syntheses. We believe that one of such methodologies is like biogenetic pathway,[6] in which two chiral cyclic ethers are linked with carbon chain and several rings are constructed simultaneously (**I** in Fig. 1).

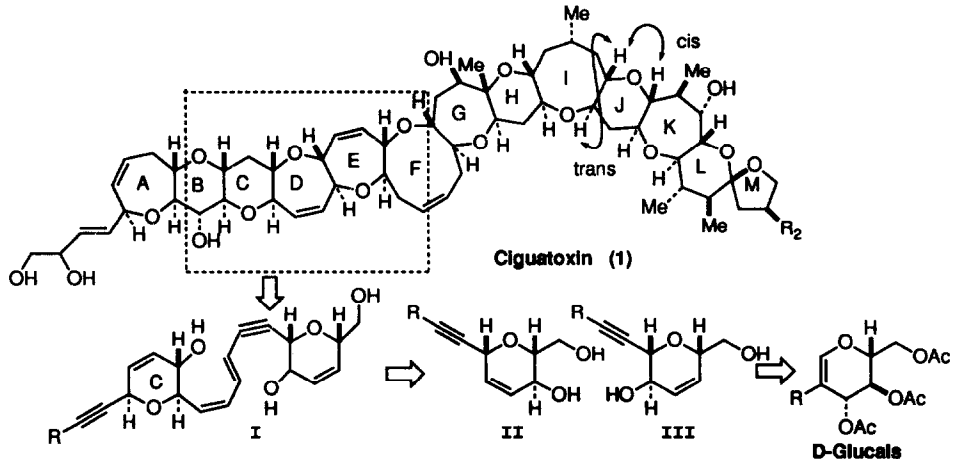
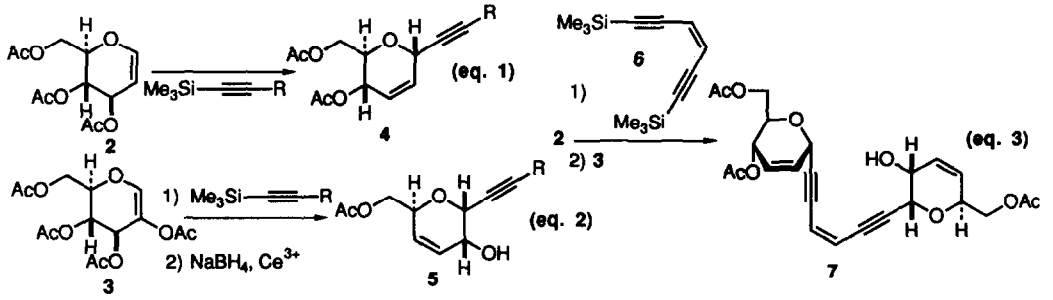


Fig. 1

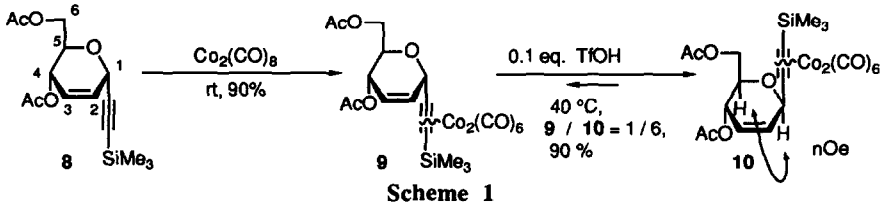
In order to develop such a method, we needed to build up a suitable cyclic ether with sufficient functionality to join the other rings. Tetrahydropyran rings are the most frequently encountered cyclic units in these toxins. The enantiomeric synthesis of such rings has been performed by the intramolecular opening of chiral epoxyalcohols[7] and the intramolecular hetero-Michael addition on chiral hydroxy-γ-benzoyloxy-α, β-unsaturated esters.[8] Although these methods are general, we became interested in using the pyranose ring of sugars which have been used as sources as well as templates in synthesis of optically active compounds.



C-Glycosidation of alkynyl group to pyranose ring is a valuable synthetic method for oxygenated carbon compounds in optically active form. Introduction of acetylenic groups to *D*-glucals (**2** or **3**) has been reported from this laboratory (eq. 1 or 2).[9] The reaction with bis(trimethylsilyl)acetylenes such as **6** made it possible to introduce two different types of pyranose rings at both ends of the bisacetylenes (eq. 3)[10]. These reactions are exclusively α-selective. Epimerization of the acetylenic groups to β-orientation would afford the simple synthetic method of sufficiently functionalized chiral pyran units (**II** or **III** in Fig. 1). On the basis of this idea, we have recently reported a short communication about the epimerization.[11] In this article, we detail the epimerization method of alkynyl sugars.

Epimerization Condition

Kende and Fujii[12] have reported a method to epimerize α-C-glycosyl alkenes under acidic conditions. However, the strongly acidic conditions weren't applicable to α-C-glycosyl alkynes. The stabilization of an intermediate cation generating at the anomeric position would allow the epimerization under milder conditions. Nicholas et al.[13] have reported that reaction of propargyl alcohols with dicobalt octacarbonyl leads to the formation of the corresponding acetylene-dicobalt hexacarbonyl complex whose propargyl cation, generated by treatment with acids such as HBF_4•Et_2O, is as stable as triphenylmethyl cation. The first complexation of glycosyl alkynes was achieved by treatment of **8**[9] with 1.2 equiv. of dicobalt octacarbonyl to afford the cobalt complex **9**[14] in 90 % yield (Scheme 1).



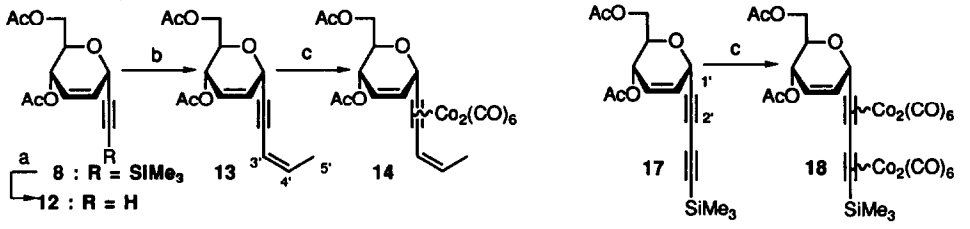
Scheme 1

Epimerization of **9** was examined using trifluoromethanesulfonic acid (TfOH). This reaction was very critical with the reaction temperatures and amount of the acid.[11] The best result was 85 % β-isomer **10**, whose

structure was confirmed with nOe between H-1 and H-5, *vs* 15 % α-isomer **9** in 90 % yield under the condition as depicted in Scheme 1. This α / β ratio was constant in equilibrium at 40 °C judging from the fact that the treatment of purified **10** with TfOH gave the mixture of **9** and **10** in the same ratio under the same condition as above.

Factors determining α / β ratio (1,3-diaxial interaction)

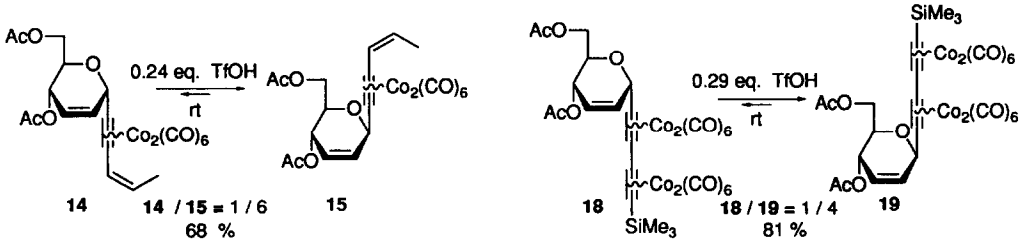
For further improvement of the equilibrium ratio 1 : 6 between **9** and **10**, other α-C-glycosyl alkynes with different acetylene moiety were examined.



Reagents : (a) n-Bu_4NF, 95 %; (b) cis-1-bromopropene, $Pd(OAc)_2$, CuI, $n\text{-}BuNH_2$, 49 %; (c) $Co_2(CO)_8$, 90 % for **14**, 71 % for **18**.

Scheme 2

The cobalt complex **14** and **18** were prepared as illustrated in Scheme 2. Treatment of **8** with tetrabutylammonium fluoride (TBAF) provided the desilylated compound **12** in 95 % yield. The end acetylene was coupled with cis-1-bromopropene using Pd catalyst[15] to afford the eneyne **13** in 49% yield. Complexation of **13** using $Co_2(CO)_8$ gave the cobalt complex **14** in 90 % yield. The biscobalt complex **18** was prepared by treatment of the silylbutadiyne **17**[9] with excess $Co_2(CO)_8$ in 71 % yield. These new cobalt complexes (**14** and **18**) were epimerized under similar condition as used for **9**. The results are shown in Scheme 3. In spite of different bulkyness of cobalt-acetylene moiety, the equilibrium ratios were almost the same.



Scheme 3

Important factor determining of the ratio was suggested from conformational analysis, thus 1) axial orientation of the acetylenic group in **8** that was confirmed from nmr data written in three dimensional structure **8a** (the coupling constant $J_{4,5}$= 9 Hz) as illustrated in Fig 2, and 2) equatorial orientation of the cobalt-acetylene moiety in **9** from *J* value (6 Hz) and nOe between H-1 and H-6 as shown in **9a**. Epimerization afforded the more stable conformer **10a** showing $J_{4,5}$= 8 Hz and nOe between H-1 and H-5. The thermodynamic difference between **9a** and **10a** seemed to depend simply upon large 1,3-diaxial interaction between H-1 and C-6, these are oriented to axial in **9a**.

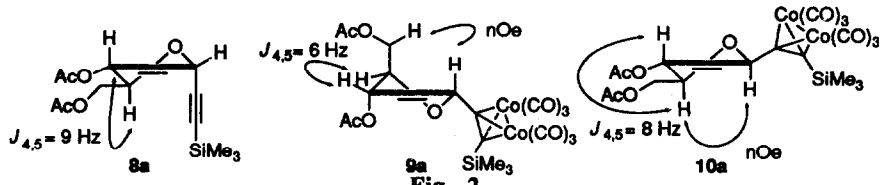
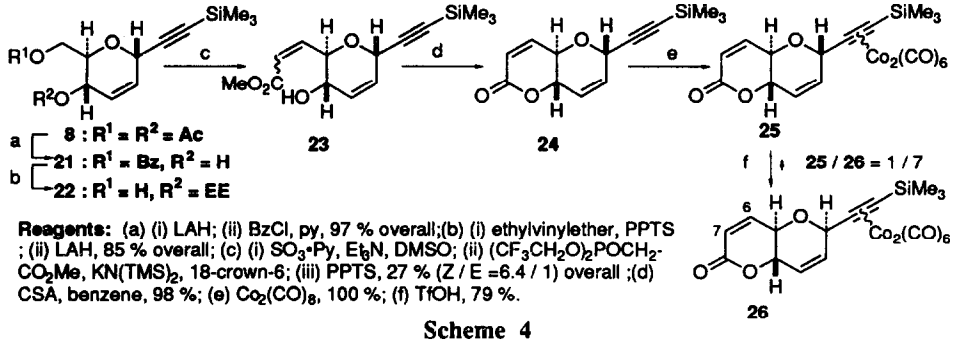


Fig. 2

If the bulkiest cobalt-acetylene moiety could be fixed in axial position in the α-isomer, the difference of thermodynamic stability between the two epimers would become larger and the equilibrium ratio in such systems would be improved. For this purpose, bicyclic lactone was synthesized as illustrated in Scheme 4. Reduction of the diacetate **8** with lithium aluminum hydride (LAH) provided the diol whose primary alcohol was protected with benzoyl chloride (BzCl) to give the monobenzoate **21** in 97 % overall yield. The remaining hydroxy function was protected with ethylvinylether and deprotection of the benzoyl group with LAH gave the alcohol **22** in 85 % overall yield. Oxidation of **22** with SO_3•pyridine followed by olefination with bis(2,2,2-trifluoroethyl)(methoxycarbonylmethyl)phosphonate[16] afforded the α, β-unsaturated ester which was further converted into the hydroxy ester **23** (Z / E = 6.4 / 1) in 27 % overall yield. Cyclization of (Z)-**23** using camphorsulfonic acid (CSA) in benzene proceeded successively to give the bicyclic lactone **24** in 98 % yield. Treatment of the lactone with $Co_2(CO)_8$ gave the cobalt complex **25** quantitatively.

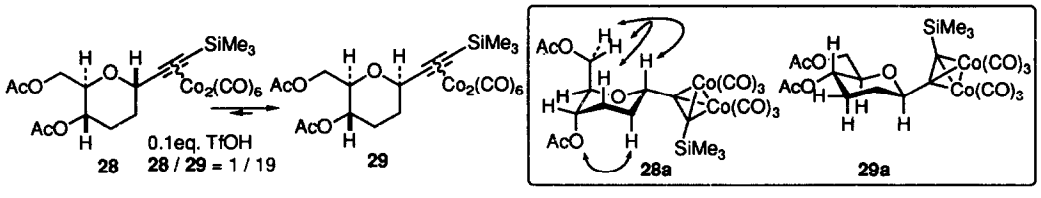


Reagents: (a) (i) LAH; (ii) BzCl, py, 97 % overall;(b) (i) ethylvinylether, PPTS ; (ii) LAH, 85 % overall; (c) (i) SO_3•Py, Et_3N, DMSO; (ii) $(CF_3CH_2O)_2POCH_2$-CO_2Me, $KN(TMS)_2$, 18-crown-6; (iii) PPTS, 27 % (Z / E =6.4 / 1) overall ;(d) CSA, benzene, 98 %; (e) $Co_2(CO)_8$, 100 %; (f) TfOH, 79 %.

Scheme 4

Epimerization of this complex with 0.1 eq. of TfOH at rt afforded the β-epimer **26**, available for the BC ring of ciguatoxin. But anticipated improvement wasn't observed in the equilibrium ratio (**25** / **26** = 1 / 7).

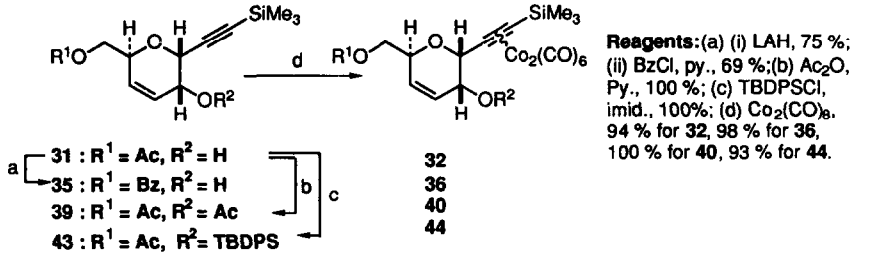
Since the cobalt complex **28**[11] has three 1,3-diaxial interactions as shown in three dimentional structure **28a** (Scheme 5), the β-isomer **29** should be the more dominant epimer in this equilibrium. Actually, epimerization of **28** at rt afforded **29** in high yield (90 %, **28** / **29** =1 / 19). The higher ratio was due to the larger energy difference (ca. 2 kcal/mol[17]) based on 1,3-diaxial interaction. Equilibrium constant (K) being theoretically 30, calculated from ΔG= -RTlnK, was roughly consistent with our observed value, K=19.



Scheme 5

Factors determining α / β ratio (1,2-interaction)

Similar experiments in the following alkynyl glycosides suggested existence of other driving force than 1,3-diaxial interaction. The alkynyl glycoside **31**[9] having different unsaturated system (Δ3,4) with oxygen function at 2-position was converted into several derivatives with a variety of protecting groups as shown in Scheme 6. LAH reduction of **31** led to the diol (75 % yield) whose primary alcohol was selectively protected with BzCl to give the monobenzoate **35** in 69 % yield. Acetylation of **31** using acetic anhydride and pyridine gave the diacetate **39** quantitatively. Silylation of **31** using *tert*-butylchlorodiphenylsilane (TBDPSCl) and imidazole afforded the silyl ether **43** in quantitative yield. These alkynyl glycosides were converted into the corresponding cobalt complexes (**32, 36, 40** and **44**) in high yields.



Scheme 6

The conformation of this type of cobalt complex was assigned as **32a** (Fig. 3) based on the nOe between H-1 and H-6. In spite of the similar 1,3-diaxial interaction as in **9a**, epimerization of the cobalt complex **32** using TfOH afforded the β-isomer **33** in better ratio (**32** : **33** = 1 : 10). This result encouraged us to investigate other derivatives such as **36, 40** and **44**. The results are summarized in Table 1.

Table 1 Epimerization of α-Complex to β-Complex at rt.

entry	Substrate (α)	TfOH (eq)	Product (β)	ratio (α:β)	yield (%)
1	**32: R1 = Ac, R2 = H**	0.3	**33**	**1 : 10**	86
2	**36: R1 = Bz, R2 = H**	0.2	**37**	**1 : 12**	95
3	**40: R1 = Ac, R2 = Ac**	0.2	**41**	**1 : 27**	94
4	**44: R1 = Ac, R2 = TBDPS**	0.2	**45**	**1 : 100**	84

The changing of C-6 protecting group to benzoyl function (entry 2) didn't effect the ratio very much. On the other hand, the changing of C-2 protecting group to acetyl function (entry 3) or TBDPS function (entry 4) gave dramatic improvement in the ratio. The even higher ratios were observed with increasing size of the protective groups (R^2) for the 2-hydroxy function. This would be due to larger 1,2-interaction[18] of the α-complex than the β-complex as shown in Newman projection (Fig. 3). Namely, the thermodynamic stability

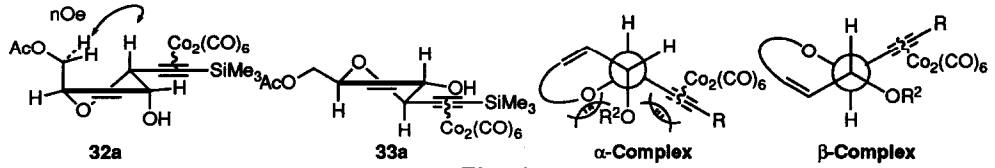
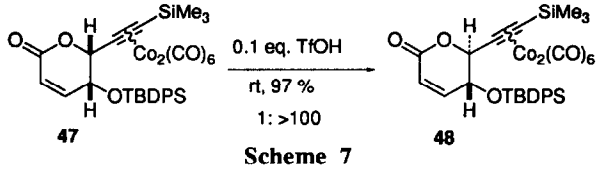


Fig. 3

difference in this system derived mainly from the strain upon the OR^2 group and the bulky cobalt-acetylene moiety. Epimerization of the cobalt complexed lactone **47** showed the importance of this 1,2-interaction. This lactone, having no 1,3-diaxial interactions anymore, was exclusively epimerized to **48** by treatment with TfOH as shown in Scheme 7.[19]

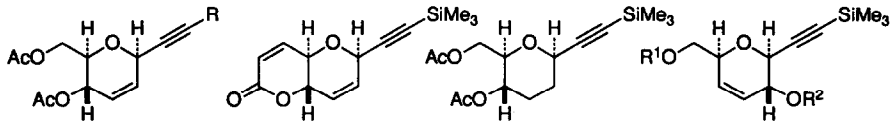


Scheme 7

Decomplexation

All of the epimerized compounds were decomplexed with iodine[12] to isolate the β-acetylenes **11, 16, 20, 27, 30, 34, 38, 42** and **46** in high yields as summarized in Table 2. In case of **15**, the trans isomerization of the olefine on side chain took place during the treatment with iodine to give **16** as main isomer (cis / trans = 1/5).

Table 2 β-Acetylenes obtained by decomplexation with iodine. (% yield from corresponding cobalt complex)



11:R=-SiMe$_3$ (100 %) **27** (84 %) **30** (90 %) **34:R^1=Ac, R^2=H** (94 %)
16:R=-(E)CH=CHMe (100 %) **38:R^1=Bz, R^2=H** (93 %)
20:R=-C≡CSiMe$_3$ (95 %) **42:R^1=R^2=Ac** (82 %)
46:R^1=Ac, R^2=TBDPS (98 %)

Efficient epimerization of alkynyl group attached on the C-1 position of pyranose ring was developed through dicobalt octacarbonyl complex. Three steps involving complexation, acidic transformation and decomplexation afforded overall epimerization. The driving force of this epimerization based on 1, 3-diaxial interaction and gauche repulsion. The current method has made it possible to prepare both α- and β-acetylenic compound on sugars, which would be of high utility for the synthesis of marine toxins such as ciguatoxin and other carbon compounds with oxygen functions.

EXPERIMENTAL SECTION

General Techniques

Melting points were recorded on a Yanaco MP-S3 melting point apparatus and are not corrected. Infrared spectra were recorded on a JASCO FT/IR-8300 spectrophotometer and are reported in wave number (cm^{-1}). Proton NMR (^1H NMR) spectra were recorded on JEOL EX-270 (270 MHz). Carbon NMR (^{13}C NMR) spectra were recorded on 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 Agriculture, Nagoya University to which the authors gratefully acknowledges.Unless otherwise noted, non aqueous reaction were carried out under nitrogen or argon atmosphere. THF was distilled from potassium metal/benzophenon ketyl. Benzene was dried over Na metal and used without distillation. DMSO was distilled from CaH_2. DMF and CH_2Cl_2 were dried over MS 4Å. Pyridine and Et_3N was dried over KOH and used without distillation. 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 prepared silica gel (Art 7747). Silica gel for column chromatography was supplied from Fuji Devison (BW 820-MH).

α-Alkynyl glycoside 13. To a solution of **8** (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 rt. After stirred for 1h, the reaction mixture was poured into saturated aqueous (sat.) NH_4Cl at 0 °C and extracted with ether.The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with ether/hexane(2/3) provided **12** (6.14 g, 25.8mmol, y. 95 %). To a degassed suspension of $Pd(OAc)_2$ (14.8 mg, 0.07 mmol), PPh_3 (34.7 mg, 0.13 mmol) and CuI (25 mg, 0.13 mmol) in THF (5 ml) was added at rt a solution of 1-bromopropene (0.76 g 6.31 mmol, cis/trans=7/1) in THF (2.5 ml). To the reulting green solution was added n-$BuNH_2$ (0.39 ml, 3.94 mmol) followed by a solution of **12** (313 mg, 1.32 mmol) in THF (5 ml). After stirred for 20h, the reaction mixture was poured into sat. NH_4Cl and extracted with ether. The extract was washed with water, sat. NH_4Cl and brine, dried and concentrated to dryness. Chromatography of the residue with ether/hexane (4/1) provided **13** (180.8 mg, 0.65 mmol, y. 49 %, cis/trans = 9/1) as a pale yellow oil: IR (KBr, cis/trans=9/1) ν_{max} 3027, 2211, 2190, 1737 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz, for cis isomer) δ 1.83 (3H, dd, *J* = 7.0, 1.5 Hz, Me), 2.05 (6H, s, OAc), 4.09 (1H, dt, *J* = 9.0, 4.0 Hz, H-5), 4.20 (2H, d, *J* = 4.0 Hz, H-6), 5.09 (1H, brm, H-1), 5.26 (1H, dq, *J* = 9.0, 2.0 Hz, H-4), 5.46 (1H, dqu, *J* = 11.0, 1.5 Hz, H-3'), 5.74 (1H, dt, *J* = 10.0, 1.5 Hz, H-3), 5.88 (1H, ddd, *J* = 10.0, 3.5, 2.0 Hz, H-2), 6.00 (1H, dq, *J* = 11.0, 7.0 Hz, H-4'). ^{13}C NMR ($CDCl_3$, 67.9 MHz, for cis isomer) δ 15.9, 20.6, 20.9, 63.0, 64.4, 64.7, 69.8, 83.3, 89.1, 109.1, 125.1, 129.3, 139.6, 170.1, 170.7. FAB-MS *m/z* 279 (M^++1). HRMS Calcd for $C_{15}H_{19}O_5$ 279.1232, found 279.1235. $[\alpha]_D^{25}$ -94.6° (*c* 0.59, $CHCl_3$, cis/trans=9/1).

Lactone 24. To a solution of **8** (1.91 g 6.16 mmol) in THF (40 ml) at 0°C was added dropwise LAH (1.6 M solution in THF, 5.8 ml 9.24 mmol). After stirred for 20min, tartaric acid aqueous solution (10 %, 25 ml) was added at 0 °C and stirred for 15 min.The mixture was extracted with ether and the extract was washed with brine, dried and concentrated to dryness. The resulting crude diol (1.51 g) was used for next reaction without further purification.To a solution of the crude diol (1.11 g) and pyridine (9 ml) in dichloromethane (2 5 ml) at -40 °C was added over 1h a solution of BzCl (0.69 ml, 5.93 mmol) in dichloromethane (5 ml). After stirred at -40 °C for 3 h, the reaction mixture was poured into ice water and extracted with ether. The extract was washed with 1.2N HCl, water and brine, dried and concentrated to dryness. Chromatography of the residue with hexane1/ethylacetate1 to afford **21** (1.44 g, 4.38 mmol, y. 97 %, 2 steps) as a colorless oil.

To a solution of **21** (1.44 g, 4.36 mmol) and pyridinium *p*-toluenesulfonate (33 mg, 0.13 mmol) in CH_2Cl_2 (20 ml) at rt was added ethylvinylether (1.25 ml, 13.1 ml). After stirred for 2 h, the reaction mixture was poured into cooled sat. $NaHCO_3$ and extracted with ether. The extract was washed with water and brine,dried and concentrated to dryness. A solution of the resulting acetal (1.65g) in THF (30 ml) at 0 °C was added dropwise LAH (1.6 M, 1.9 ml 3.04 mmol). After stirred for 20 min, the reaction mixture was added, via cannula, to cooled tartaric acid aqueous solution (10 %, 15 ml) and stirred for 15 min. The mixture was extracted with ether and the extract was washed with brine, dried and concentrated to dryness. Chromatography of the residue with hexane4/ethylacetate1 to afford **22** (1.38 g, containing benzyl alcohol which couldn't be isolated, 3.72 mmol, y. 85 % 2 steps).

To a solution of **22** (365 mg, 1.22 mmol) in DMSO (3 ml) and CH_2Cl_2 (3 ml) cooled at 0 °C was added Et_3N (0.87 ml, 6.3 mmol). SO_3• pyridine (1.0 g 6.29 mmol) was added portionwise to the reaction mixture at 0 °C and stirred for 2 h. The reaction mixture was diluted with ether and washed with water and brine, dried and concentrated to dryness. To a solution of $(CF_3CH_2O)_2POCH_2CO_2Me$ (568 mg, 1.79 mmol) and 18-crown-6 (2.36 g, 8.94 mmol) in THF (20 ml) cooled at -78°C was added $KN(TMS)_2$ (0.645 M solution in toluene, 2.77 ml, 1.79 mmol). To the resulting solution at -78 °C was added a solution of the crude

aldehyde (352.8 mg) in THF (1.5 ml). After stirred for 2 h, sat. NH_4Cl (20 ml) was added and extracted with ether. The extract was washed with brine, dried and concentrated to dryness. Chromatography of the residue with hexane3/ether1 to afford α, β– unsaturated methylester (118.7mg). A solution of the ester (118.7 mg) in CH_2Cl_2 (5 ml) and iso-propanol (2 ml) was warmed at 40 °C and stirred for 1.5 h. The reaction mixture was poured into sat. $NaHCO_3$ at 0 °C and etracted with ether, washed with water and brine , dried and concentrated to driness. The crude oil was purified by PLC (CH_2Cl_2/ether = 92/8) to afford **(Z)-23** (80.9 mg, 0.29 mmol) and **(E)-23** (12.6 mg, 0.045 mmol) in 27 % overall yield. A solution of **(Z)-23** (5.6 mg, 0.023 mmol) and CSA (2 mg, 0.009 mmol) in benzene (2 ml) was sirred at 45 °C for 20.5 h. The reaction mixture was diluted with sat. $NaHCO_3$ and extracted with ether. The extract was washed with brine, dried and concentrated to dryness. The crude product was purified by PLC (CH_2Cl_2/ether = 95/5) to give pure **24** (5.6 mg, y. 98 %) as white crystals: Mp 78-79 °C. IR (KBr) ν_{max} 2170, 1752, 1729 cm^{-1} ^1H NMR ($CDCl_3$, 270 MHz) δ 0.19 (9H, s, TMS), 4.60 (1H, dt, *J* = 10.0, 2.0, Hz, H-5), 4.70 (1H, dq, *J* = 10.0, 1.5, Hz, H-4), 5.03 (1H, q, *J* = 2.5 Hz, H-1), 5.82 (1H, ddd, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.98-6.06 (2H, m, H-3, H-7), 7.01 (1H, dd, *J* = 10.0, 1.0 Hz, H-6). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.3 (3C), 65.8, 67.3, 74.2, 92.7, 100.1, 121.1, 124.9, 128.6, 147.9, 163.1. $[\alpha]_D^{26}$ -54.8° (*c* 0.95, $CHCl_3$). Anal. Calcd for $C_{13}H_{16}O_3Si$: C, 62.87; H, 6.49. Found: C, 62.81; H, 6.48.

Monobenzoate ***35***. To a solution of LAH (0.45 g, 11.8 mmol) in THF (12 ml) was added a solution of **31** (1.59 g, 5.93 mmol) in THF (8 ml) at 0 °C. After stirred for 10min, tartaric acid aqueous solution (10 %) was slowly added to the reaction mixture which was then extracted with ether. The extract was washed with sat. $NaHCO_3$ solution and brine, dried and concentrated to give a crude diol (1.01 g,4.47 mmol, y. 75 %). To a solution of the diol (0.4 g, 1.77 mmol) in CH_2Cl_2 (10 ml) and pyridine (3 ml) at -40 °C was added over 1 h a solution of BzCl (0.21 ml,1.81 mmol) in CH_2Cl_2 (1 ml). After stirring for 3.5 h at -40 °C, the reaction mixture was gradually warmed up to rt and sttired for 3 days.The resulting mixture was poured into ice water and extracted with ether. The extract was washed with 1.2N HCl and brine, dried and concentrated to dryness. The crude oil was chromtographed with hexane/ethylacetate(4/1) to give a pure **35** (400.9 mg, 1.21 mmol; y. 69 %) as white crystals: Mp 68-69.5 °C. IR (KBr) ν_{max} 3442, 2169, 1724 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.15 (9H, s, TMS), 2.38 (1H, brd, OH), 4.22-4.30 (1H, br, H-2), 4.33 (1H, dd, *J* = 11.5, 4.5 Hz, H-6), 4.39 (1H, dd, *J* = 11.5, 5.5 Hz, H-6), 4.61-4.68 (1H, m, H-5), 4.88 (1H, d, *J* = 5.5 Hz, H-1), 5.79 (1H, brd, *J* = 10.5, Hz, H-4), 5.86 (1H, brd, *J* = 10.5, Hz, H-3), 7.33-7.41 (2H,m, aromatic), 7.45-7.53 (1H, m, aromatic), 7.96-8.02 (2H, m, aromatic). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.38 (3C), 63.2, 65.3, 67.5, 69.0, 93.6, 99.4, 126.9, 128.1 (2C), 129.4, 129.5 (2C), 129.6, 132.9, 166.1. $[\alpha]_D^{28}$ -129.6° (*c* 0.19, $CHCl_3$). Anal. Calcd for $C_{18}H_{22}O_4Si$: C, 65.42; H, 6.71. Found: C, 65.42; H, 6.69.

Diacetate ***39***. A solution of **31** (95 mg, 0.35 mmol) in Ac_2O (1 ml) and pyridine (1 ml) was stirred for 17 h at rt. Concentration of the reaction mixture with toluene gave a crude oil, which was chromatographed with hexane/ether(1/2) to furnish **39** (123 mg, y.100 %) as a colorless oil: IR (KBr) ν_{max} 2175, 1745 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.16 (9H, s, TMS), 2.07 (3H, s, OAc), 2.09 (3H, s, OAc), 4.13 (1H, dd, *J* = 12.0, 4.0 Hz, H-6), 4.20 (1H, dd, *J* = 12.0, 6.0 Hz, H-6), 4.55-4.61 (1H, m, H-5), 5.00 (1H, d, *J* = 5.0 Hz, H-1), 5.27-5.32 (1H, m, H-2), 5.84 (2H, brs, olefinic). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.29(3C), 20.8 (2C), 64.4, 64.8, 65.1, 69.4, 92.6, 99.1, 125.2, 128.8, 170.3, 170.7. FAB-MS *m/z* 311 (M^+ +1), 251 (M^+-60). HRMS calcd for $C_{15}H_{23}O_5Si$ 311.1315, found 311.1325. $[\alpha]_D^{24}$ -66.8° (*c* 0.33, $CHCl_3$).

Silyl ether ***43***. To a solution of **31** (100 mg, 0.37 mmol) and imidazole (127 mg, 1.87 mmol) in DMF (5 ml) was added TBDPSCl (0.19 ml, 0.75 mmol). After stirring for 17h at rt, the reaction mixture was poured into ice water and extracted with ether. The extract was washed with brine, dried and concentrated to dryness. The crude oil (406 mg) was used for next reaction without further purification. A small portion of the crude product was purified by PLC (hexane1/dichloromethane1) to identify. **43**: IR (KBr) ν_{max} 2174, 1747 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.28 (9H, s, TMS), 1.17 (9H, s, t-Bu), 2.04 (3H, s, OAc), 4.06 (1H, dd, *J* = 12.0, 6.5 Hz, H-6), 4.10 (1H, dd, *J* = 12.0, 4.0 Hz, H-6), 4.42-4.48 (1H, m, H-2), 4.56-4.63 (1H, m, H-5), 4.61 (1H, d, *J* = 6.0 Hz, H-1), 5.61 (1H, dt, *J* = 10.5, 2.0 Hz, H-4), 5.79 (1H, brd, *J* = 10.5 Hz, H-3), 7.36-7.48 (6H, m, aromatic), 7.72-7.79 (4H, m, aromatic). $[\alpha]_D^{26}$ -27.8° (*c* 0.67, $CHCl_3$). EI-MS *m/z* 506 (M^+). HRMS Calcd for $C_{29}H_{38}O_4Si_2$ 506.2308, found 506.2291.

Typical procedure (TP) of complexaton with dicobalt octacarbonyl (preparation of ***9, 14, 18, 25, 28, 32, 36, 40 and 44****)*

A solution of dicobalt octacarbonyl (1.2 eq) in CH_2Cl_2 was added to a solution of α-Alkynyl glycoside in CH_2Cl_2 at rt. After stirred for 2 h, the reaction mixture was concentrated. Chromatography (silica gel) of the residue provided the corresponding cobalt complex.

α-Cobalt complex ***9***. The similar treatment of **8** as TP provided the cobalt complex **9** (y. 90 %) as a reddish brown oil: IR (KBr) ν_{max} 2091, 2052, 2021, 1749 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.33 (9H, s, TMS), 2.08

(6H, s, OAc), 4.16 (1H, dd, J = 12.0, 3.5 Hz, H-6), 4.25 (1H, dt, J = 6.0, 3.5 Hz, H-5), 4.37 (1H, dd, J = 12.0, 6.0 Hz, H-6), 5.20 (1H, m, H-4), 5.45 (1H, q, J = 2.5 Hz, H-1), 5.91 (1H, dt, J = 11.0, 2.5 Hz, H-3), 6.01 (1H, brd, J = 11.0 Hz, H-2).

α-Cobalt complex 14. The similar treatment of **13** as TP provided the cobalt complex **14** (y. 90 %) as a reddish brown oil: IR (KBr, cis/trans=15/1) ν_{max} 2092, 2054, 2027, 1749 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz, for cis isomer) δ 1.86 (3H, brd, Me), 2.08 (6H, brs, OAc), 4.17 (1H, brd, J = 12.0 Hz, H-6), 4.20-4.28 (1H, m, H-5), 4.38 (1H, dd, J = 12.0, 6.0 Hz, H-6), 5.18 (1H, brs, H-4), 5.54 (1H, brs, H-1), 5.93 (1H, brd, J = 10.0 Hz, H-3), 6.00 (1H, m, H-4'), 6.06 (1H, brd, J = 10.0 Hz, H-2), 6.49 (1H, brd, J = 10.0 Hz, H-3').

α-Cobalt complex 18. The similar treatment of **17** with $Co_2(CO)_8$ (2.9 eq) provided the cobalt complex **18** as dark green crystals: Dec.>150°C. IR (KBr) ν_{max} 2098, 2078, 2053, 2009, 1995, 1752, 1736 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.40 (9H, s, TMS), 2.07 (6H, brs, OAc), 4.15-4.45 (3H, m), 5.17 (1H, brs, H-4), 5.48(1H, brs, H-1), 6.05 (1H, brd, J = 10.0 Hz, H-3), 6.17 (1H, brd, J = 10.0 Hz, H-2).

α-Cobalt complex 25. The similar treatment of **24** as TP provided **25** (y. 100 %) as a reddish brown oil: IR (KBr) ν_{max} 2092, 2052, 2026, 1751, 1731 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.33 (9H, s, TMS), 4.66 (1H, brd, J = 10.0 Hz, H-5), 4.77 (1H, dq, J = 10.0, 1.5 Hz, H-4), 5.54 (1H, q, J = 2.5 Hz, H-1), 5.91 (1H, dt, J = 10.0, 2.5 Hz, H-2), 6.03 (1H, dd, J = 10.0, 2.5 Hz, H-7), 6.16 (1H, brd, J = 10.0 Hz, H-3), 6.94 (1H, brd, J = 10.0 Hz, H-6).

α-Cobalt complex 28. Procedure was written in ref.11. **28**: IR (KBr) ν_{max} 2090, 2048, 2019, 1745cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.32 (9H, s, TMS), 1.88-2.00 (4H, m, H-2 and H-3), 2.06 (3H, s, OAc), 2.08 (3H, s, OAc), 4.09 (1H, dd, J = 11.0, 4.0 Hz, H-6), 4.10-4.18 (1H, m, H-5), 4.50 (1H, dd, 1H, J = 11.0, 7.0 Hz, H-6), 4.80-4.86 (1H, br, H-4),4.90-4.98 (1H, m, H-1).

α-Cobalt complex 32. The similar treatment of **31** as TP provided **32** (y. 94 %) as reddish brown crystals: Mp 77-78 °C. IR (KBr) ν_{max} 3458, 2089, 2051, 2021, 1745 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz), δ 0.32 (9H, s, TMS), 1.61 (1H, d, J = 10.5 Hz, OH), 2.04 (3H, s, OAc), 3.94 (1H, ddd, J = 10.5, 5.5, 2.0 Hz, H-2), 4.17 (1H, d, J = 12.0, 3.5 Hz, H-6), 4.29 (1H, dd, 1H, J = 12.0, 7.0 Hz, H-6'), 4.60-4.66 (1H, m, H-5), 5.00 (1H, d, J = 2.0 Hz, H-1), 5.91 (1H, dd, J = 10.0, 3.0 Hz, H-4), 6.27 (1H, ddd, J = 10.0, 5.5, 2.5 Hz, H-3). Anal. Calcd for $C_{19}H_{20}O_{10}SiCo_2$: C, 41.17; H, 3.64. Found: C, 41.03; H, 3.49.

α-Cobalt complex 36. The similar treatment of **35** as TP provided **36** (y. 98%) as a reddish brown oil: IR (KBr) ν_{max} 3525, 2089, 2049, 2017, 1725 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.31 (9H, s, TMS), 1.63 (1H, d, J = 11.0 Hz, OH), 3.97 (1H, ddd, J = 11.0, 6.0, 2.0 Hz, H-2), 4.41 (1H, dd, J = 12.0, 3.0 Hz, H-6), 4.65 (1H, dd, J = 12.0, 6.5 Hz, H-6), 4.75-4.81 (1H, m, H-5), 5.14 (1H, d, J = 2.0 Hz, H-1), 6.00 (1H, dd, J = 10.0, 3.0 Hz, H-4), 6.30 (1H, ddd, J = 10.0, 6.0, 2.5 Hz, H-3), 7.38-7.46 (2H, m, aromatic), 7.53-7.60 (1H, m, aromatic), 7.99-8.04 (2H, m, aromatic).

α-Cobalt complex 40. The similar treatment of **39** as TP gave **40** (y.100%) as reddish brown crystals: Mp 62-63 °C. IR (KBr) ν_{max} 2091, 2055, 2025, 1744 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.32 (9H, s, TMS), 2.04 (3H, s, OAc), 2.07 (3H, s, OAc), 4.19 (1H, dd, J = 12.0, 3.0 Hz, H-6), 4.28 (1H, d, J = 12.0, 6.0 Hz, H-6), 4.63-4.70 (1H, m, H-5), 5.06 (1H, brd, J = 5.0 Hz, H-2), 5.18 (1H, brs, H-1), 5.98 (1H, dd, J = 10.0, 2.5 Hz, H-4), 6.30-6.40 (1H, m, H-3).

α-Cobalt complex 44. The similar treatment of **43** as TP provided **44** (93 %, 2 steps) as a reddish brown viscous oil: IR (KBr) ν_{max} 2088, 2049, 2021, 1748 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz) δ 0.34 (9H, s, TMS), 1.10 (9H, s, t-Bu), 1.90 (3H, s, OAc), 3.97 (1H, dd, J = 12.0, 6.0 Hz, H-6), 4.07 (1H, d, J = 12.0, 3.0 Hz, H-6), 4.31-4.39 (1H, m, H-5), 4.84 (1H, brs, H-2), 5.25 (1H, brs, H-1), 5.43 (1H, brd, J = 10.0 Hz, H-4), 5.72 (1H, brd, J = 10.0 Hz, H-3), 7.32-7.48 (6H, m, aromatic), 7.66-7.76 (4H, m, aromatic).

*Typical procedure (TP) of epimerization with TfOH (preparation of **10, 15, 19, 26, 29, 33, 37, 41 and 45**)*

To a degassed solution (0.01 M) of α-cobalt complex in CH_2Cl_2 at rt was added dropwise a 0.1M solution of TfOH (0.1eq) in CCl_2FCClF_2. After stirred until no change observed with TLC, the mixture was poured into sat. $NaHCO_3$ at 0 °C and extracted with CH_2Cl_2. The extracted was washed with water, dried and concentrated to dryness. The resulting product was purified by silica gel column chromatography.

β-Cobalt complex 10. The similar treatment of **9** as TP at 40 °C afforded the mixture of **9** and **10** (y. 90%, **9** : **10** = 1 : 6, determined by ^1H-NMR). The mixture was purified to give **10** as a reddish brown oil: IR (KBr) ν_{max} 2091, 2052, 2027, 1748 cm^{-1}. ^1H NMR ($CDCl_3$,270 MHz) δ 0.31 (9H, s, TMS), 2.01 (3H, s, OAc), 2.10 (3H, s, OAc), 3.92 (1H, ddd, J = 9.0, 5.0, 2.0 Hz, H-5), 4.17 (1H, dd, J = 12.0, 5.0 Hz, H-6), 4.27 (1H, dd, J = 12.0, 2.5, Hz, H-6), 5.34 (1H, brd, J = 9.0 Hz, H-4), 5.33 (1H, brs, H-1), 5.84 (1H, d, J = 11.0 Hz, H-3), 5.88 (1H, d, J = 11.0 Hz, H-2).

β-Cobalt complex 15. The similar treatment of **14** with TfOH (0.24 eq) afforded the mixture of **14** and **15** (y. 68 %, **14** : **15** = 1 : 6, determined by ^{1}H-NMR). The mixture was purified by PLC to give **15** as a reddish brown oil: IR (KBr, cis/trans=15/1) ν_{max} 2092, 2053, 2028, 1747 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz), δ 1.84 (3H, dd, *J* = 12.0, 1.5 Hz, Me), 2.02 (3H, s, OAc), 2.10 (3H, s, OAc), 3.90-3.98 (1H, m, H-5), 4.17 (1H, dd, *J* = 12.0, 5.0 Hz, H-6), 4.29 (1H, dd, *J* = 12.0, 2.0 Hz, H-6), 5.36 (1H,brd, *J* = 9.0 Hz, H-4), 5.48 (1H, brs, H-1), 5.84 (1H, brd, *J* = 10.0 Hz, H-3), 5.93 (1H, brd, *J* = 10.0 Hz, H-2), 5.90-5.98 (1H, m, H-4'), 6.46 (1H, dd, *J* = 10.5, 1.5 Hz, H-3').

β-Cobalt complex 19. The similar treatment of **18** with TfOH (0.29 eq) afforded the mixture of **18** and **19** (y. 81 %, **18** : **19** = 1 : 4, determined by ^{1}H-NMR), which was used for next decomplexation without further purification. A small portion of the mixture was purified by PLC to give **19** as a dark green oil: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.39 (9H, s, TMS), 2.00 (3H, s, OAc), 2.10 (3H, s, OAc), 3.96 (1H, m, H-5), 4.16 (1H, dd, *J* = 12.0, 5.0 Hz, H-6), 4.29 (1H, dm, *J* = 12.0, Hz, H-6), 5.42 (1H, brd, *J* = 9.0 Hz, H-4), 5.44 (1H, brs, H-1), 5.95 (1H, d, *J* = 10.0 Hz, H-3), 6.04 (1H, d, *J* = 10.0 Hz, H-2).

β-Cobalt complex 26. The similar treatment of **25** with TfOH afforded the mixture of **25** and **26** (y. 79 %, **25** : **26** = 1 : 7, determined by ^{1}H-NMR). The mixture was purified by PLC to give **26** as a reddish broun oil: IR (KBr) ν_{max} 2091, 2055, 2015, 1752, 1734 cm^{-1}. ^{1}H NMR ($CDCl_3$,270 MHz) δ 0.32 (9H, s, TMS), 4.48 (1H, brd, *J* = 10.0 H-5), 4.77 (1H, brd, *J* = 10.0 Hz, H-4), 5.56 (1H, m, H-1), 5.86 (1H, dt, *J* = 10.0, 2.0 Hz, H-2), 6.02 (1H, dd, *J* = 10.0, 2.5 Hz, H-7), 6.11 (1H, brd, *J* = 10.0 Hz, H-3), 7.00 (1H, brd, *J* = 10.0 Hz, H-6).

β-Cobalt complex 29. The similar treatment of **28** with TfOH gave **28** and **29** which were purified by PLC (ether1 /hexane1) to afford **29** (y. 85.5 %) and **28** (y. 4.5 %). **29:** IR (KBr) ν_{max} 2091, 2052, 2027, 1748 cm^{-1}. ^{1}H NMR ($CDCl_3$,270 MHz) δ 0.29 (9H, s, TMS), 1.63-1.74 (2H, m, H-2 or 3), 2.00 (3H, s, OAc), 2.07 (3H, s, OAc), 2.00 (1H, m, H-3 or 2), 2.25-2.37 (1H, m, H-3 or 2), 3.77 (1H, ddd, *J* = 10.0, 5.5, 2.0 Hz, H-5), 4.10 (1H, dd, *J* = 12.0, 5.5 Hz, H-6), 4.20 (1H, dd, *J* = 12.0, 2.0 Hz, H-6), 4.52-4.57 (1H, brd, H-1), 4.72 (1H, td, *J* =10.0, 5.0 Hz, H-4).

β-Cobalt complex 33. The similar treatment of **32** with TfOH (0.3 eq) afforded the mixture of **32** and **33** (y. 87 %, **32** : **33** = 1 : 10, determined by ^{1}H-NMR). Recrystalization of the mixture from hexane gave a pure **33** as reddish brown crystals: Mp 57-58 °C. IR (KBr) ν_{max} 3465, 2089, 2051, 2025, 1724 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz), δ 0.32 (9H, s, TMS), 1.66 (1H, d, *J* = 7.0 Hz, OH), 2.01 (3H, s, OAc), 3.97-4.06 (1H, m, H-2), 4.07 (1H, dd, *J* = 12.0, 7.0 Hz, H-6), 4.16 (1H, dd, *J* = 12.0, 4.0 Hz, H-6), 4.39 (1H, d, *J* = 8.0 Hz, H-1), 4.52-4.60 (1H, m, H-5), 5.80 (1H, dt, *J* = 10.5, 1.5 Hz, H-4), 5.93 (1H, dt, *J* = 10.5, 2.0 Hz, H-3). Anal. Calcd for $C_{19}H_{20}O_{10}SiCo_2$: C, 41.17; H, 3.64. Found: C, 41.52; H, 3.52.

β-Cobalt complex 37. The similar treatment of **36** with TfOH (0.2 eq) afforded the mixture of **36** and **37** (y. 93 %, **36** : **37** = 1 : 12, determined by ^{1}H-NMR). This was used for the next reaction without purification. **37:** ^{1}H NMR ($CDCl_3$, 270 MHz), δ 0.31 (9H, s, TMS), 1.69 (1H, d, *J* = 7.0 Hz, OH), 4.01-4.10 (1H, m, H-2), 4.41 (2H, d, *J* = 4.7 Hz, H-6), 4.54 (1H, d, *J* = 8.5 Hz, H-1), 4.67-4.74 (1H, m, H-5), 5.90 (1H, dt, *J* = 10.0, 1.0 Hz, H-4), 5.97 (1H, dt, *J* = 10.0, 1.5 Hz, H-3), 7.38-7.46 (2H, m, aromatic), 7.52-7.59 (1H, m, aromatic), 8.00-8.05 (2H, m, aromatic).

β-Cobalt complex 41. The similar treatment of **40** with TfOH (0.2 eq) afforded the mixture of **40** and **41** which was purified by PLC (CH_2Cl_2) to afford **41** (y. 90.6 %) and **40** (y. 3.4 %). **41:** IR (KBr) ν_{max} 2091, 2053, 2026, 1748 cm^{-1}. ^{1}H NMR ($CDCl_3$,270 MHz) δ 0.31 (9H, s, TMS), 2.02(3H, s, OAc), 2.11 (3H, s, OAc), 4.05 (1H, dd, *J* = 12.0, 7.0 Hz, H-6), 4.17 (1H, dd, *J* = 12.0, 4.0 Hz, H-6), 4.54-4.62 (1H, m, H-5), 4.73 (1H, d, *J* = 9.0 Hz, H-1), 5.10 (1H, dq, *J* = 9.0, 1.0 Hz), 5.86 (1H, brd, *J* = 10.0 Hz, H-4), 5.94 (1H, dt, *J* = 10.0, 2.0 Hz, H-3).

β-Cobalt complex 45. The similar treatment of **44** with TfOH (0.2 eq) afforded the mixture of **44** and **45** (y. 93 %, **44** : **45** = 1 : 100, determined by ^{1}H-NMR). The mixture was purified to give **45** (y. 84 %) as a reddish brown oil: IR (KBr) ν_{max} 2090, 2052, 2019, 1747cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.32 (9H, s, TMS), 1.20 (9H, s, t-Bu), 1.96 (3H, s, OAc), 3.88 (1H, dd, *J* = 11.0, 7.0 Hz, H-6), 3.95 (1H, d, *J* = 11.0, 4.0 Hz, H-6), 4.15-4.22 (1H, m, H-5), 4.55-4.61 (1H, m, H-2),.4.81 (1H, d, *J* = 7.0 Hz, H-1), 5.34 (1H, dt, *J* = 10.0, 1.5 Hz, H-4), 5.66 (1H, dt, *J* = 10.0, 3.0 Hz, H-3), 7.32-7.48 (6H, m, aromatic), 7.70-7.78 (4H, m, aromatic).

*Typical procedure (TP) of decomplexation with iodine (preparation of **11**, **16**, **20**, **27**, **30**, **34**, **38**, **42** and **46**)*

The β–cobalt complex in THF at rt was treated, via cannula, with a solution of iodine (15 eq) in THF. After stirred for 2 h, the mixture was poured into a mixture of sat. $NaHCO_3$ and sat. Na_2SO_3 (ca.1v/1v) at 0 °C, and then extracted with ether. The extract was washed with brine, dried and concentrated to dryness. The crude product was purified by silica gel column chromatography.

β-Alkynyl glycoside 11. The similar treatment of **10** as TP afforded **11** (y. 100 %) as a colorless oil: IR (KBr) ν_{max} 2183, 1746cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.18 (9H, s, TMS), 2.07 (3H, s, OAc), 2.10 (3H, s, OAc), 3.75 (1H, ddd, *J* = 8.0, 6.0, 3.0 Hz, H-5), 4.19 (1H, dd, *J* = 12.0, 6.0 Hz, H-6), 4.23 (1H, dd, *J* = 12.0, 3.0 Hz, H-6), 4.99 (1H, m, H-1), 5.30 (1H, dq, *J* = 8.0, 2.0 Hz, H-4), 5.81 (1H, dt, *J* = 10.0, 2.0 Hz, H-3), 5.90 (1H, dt, *J* = 10.0, 5.0 Hz, H-2). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.4 (3C), 20.8, 20.9, 63.3, 64.6, 65.6, 74.5, 90.8, 101.1, 125.2, 130.0, 170.0, 170.7. $[\alpha]_D^{28}$ +219.3° (*c* 0.43, $CHCl_3$). Anal. Calcd for $C_{15}H_{22}O_5Si$: C, 58.04; H, 7.14. Found: C, 57.93; H, 7.04.

β-Alkynyl glycoside 16. The similar treatment of **15** as TP afforded **16** (cis / trans = 1 / 5, y. 100 %) as a colorless oil: IR (KBr, for cis/trans=1/5) ν_{max} 3031, 2225, 1740 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz, for trans isomer) δ 1.77 (3H, dd, *J* = 7.0, 2.0 Hz, Me), 2.06 (3H, s, OAc), 2.08 (3H, s, OAc), 3.77 (1H, ddd, *J* = 9.0, 6.5, 3.0, Hz, H-5), 4.17 (1H, dd, *J* = 12.5, 5.5 Hz, H-6), 4.22 (1H, dd, *J* = 12.5, 3.0 Hz, H-6), 5.07 (1H, brs, H-1), 5.29 (1H, dq, *J* = 9.0, 2.0 Hz, H-4), 5.49 (1H, dqu, *J* = 16.0, 2.0 Hz, H-3'), 5.78 (1H, dt, *J* = 10.0, 2.0 Hz, H-3), 5.89 (1H, dt, *J* = 10.0, 1.5 Hz, H-2), 6.19 (1H, dq, *J* = 16.0, 7.0 Hz, H-4'). ^{13}C NMR ($CDCl_3$, 67.9 MHz, for trans isomer) δ 18.6, 20.8, 20.9, 63.4, 64.7, 65.7, 74.4, 83.4, 84.5, 109.7, 125.2, 130.2, 141.3, 170.1, 170.9. FAB-MS *m/z* 279 (M^++1). HRMS Calcd for $C_{15}H_{19}O_5$ 279.1232, found 279.1238. $[\alpha]_D^{26}$ +264.1° (*c* 0.27, $CHCl_3$, for cis/trans=1/5).

β-Alkynyl glycoside 20. The similar treatment of the mixture of **18** and **19** as TP afforded **20** (y. 60 %, 2 steps) and **17** (y. 17 %, 2 steps). **20**: IR (KBr) ν_{max} 2109, 1746 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.18 (9H, s, TMS), 2.02 (3H, s, OAc), 2.09 (3H, s, OAc), 3.74 (1H, ddd, *J* = 8.5, 5.5, 3.0 Hz, H-5), 4.16 (1H, dd, *J* = 12.0, 5.5 Hz, H-6), 4.22 (1H, dd, *J* = 12.0, 3.0 Hz, H-6), 5.04 (1H, brs, H-1), 5.26 (1H, dd, *J* = 8.5, 2.5 Hz, H-4), 5.82-5.84 (2H, m, olefinic). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.6 (3C), 20.8, 20.9, 63.2, 64.4, 65.3, 70.7, 73.3, 74.3, 86.8, 88.7, 126.0, 128.5, 170.1, 170.8. FAB-MS *m/z* 335(M^++1), 275 (M^+-60). HRMS Calcd for $C_{17}H_{23}O_5Si$ 335.1315, found 335.1330. $[\alpha]_D^{28}$ +231.4° (*c* 0.39, $CHCl_3$).

β-Alkynyl glycoside 27. The similar treatment of **26** as TP gave a crude **27** which was purified by PLC (ether1/hexane2) to give **27** (y. 84 %) as white crystals: Mp 134-136°C. IR (KBr) ν_{max} 2186, 1753, 1731 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.20 (9H, s, TMS), 4.27 (1H, dt, *J* = 10.0, 2.0 Hz, H-5), 4.82 (1H, dqu, *J* = 10.0, 1.5 Hz, H-4), 5.14 (1H, q, *J* = 2.5 Hz, H-1), 5.82 (1H, dt, *J* = 10.0, 1.5 Hz, H-2), 5.99 (1H, dd, *J* = 10.0, 2.5 Hz, H-7), 6.05 (1H, brd, *J* = 10.0 Hz, H-3), 7.00(1H, dd, *J* = 10.0, 1.5 Hz, H-6). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.33 (3C), 67.3, 71.5, 73.9, 91.9, 99.9, 121.1, 125.1, 129.0, 147.2, 162.9. $[\alpha]_D^{29}$ +171.1° (*c* 0.40, $CHCl_3$). Anal. Calcd for $C_{13}H_{16}O_3Si$: C, 62.87; H, 6.49. Found: C, 62.78; H, 6.21.

β-Alkynyl glycoside 30. The similar treatment of **29** as TP gave **30** (y. 91 %) as white crystals: Mp 87-88 °C. IR (KBr) ν_{max} 2184, 1745 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.16 (9H, s, TMS), 1.40-1.58 (1H, m, H-2 or 3), 1.76-2.00 (2H, m, H-2 or 3), 2.02 (3H, s, OAc), 2.07 (3H, s, OAc), 2.17-2.28 (1H, m, H-2 or 3), 3.53 (1H, ddd, *J* = 10.0, 5.0, 2.0 Hz, H-5), 4.14 (1H, dd, *J* = 12.0, 2.5 Hz, H-6), 4.1-4.2 (1H, m, H-1), 4.20 (1H, dd, *J* = 12.0, 5.0 Hz, H-6), 4.68 (1H, dd, *J* = 10.0, 5.0 Hz, H-4). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.24 (3C), 20.9, 21.0, 29.0, 31.5, 63.3, 67.2, 68.5, 77.6, 90.1, 102.9, 169.9, 170.9. $[\alpha]_D^{27}$ +48.9° (*c* 0.33, $CHCl_3$). Anal. Calcd for $C_{15}H_{24}O_5Si$: C, 57.66; H, 7.74. Found: C, 57.67; H, 7.82.

β-Alkynyl glycoside 34. The similar treatment of **33** as TP afforded **34** (y.94%) as a colorless oil: IR (KBr) ν_{max} 3480, 2178, 1744 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.19 (9H, s, TMS), 2.07 (3H, s, OAc), 2.27 (1H, d, *J* = 5.0 Hz, OH), 4.07 (1H, d, *J* = 8.5 Hz, H-1), 4.10-4.15 (2H, m, H-6), 4.20-4.28 (1H, m, H-2), 4.36-4.43 (1H, m, H-5), 5.70 (1H, dt, *J* = 10.5, 1.8 Hz, H-4), 5.92 (1H, dt, *J* = 10.5, 2.0 Hz, H-3). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.7 (3C), 20.8, 65.6, 67.4, 70.6, 73.3, 92.3, 101.8, 126.9, 130.1, 170.9. FAB-MS *m/z* 269 (M^++1), 251 (M^+-17). HRMS calcd for $C_{13}H_{21}O_4Si$ 269.1209, found 269.1203. $[\alpha]_D^{27}$ -110.4°(*c* 0.11, $CHCl_3$).

β-Alkynyl glycoside 38. The similar treatment of the mixture of **36** and **37** as TP afforded **38** (y. 93 %) as white crystals: Mp 100-102 °C. IR (KBr) ν_{max} 3425, 2181, 1722 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.21 (9H, s, TMS), 2.30 (1H, br, OH), 4.12 (1H, d, *J* = 8.5 Hz, H-1), 4.28 (1H, brd, *J* = 8.5 Hz, H-2), 4.37 (1H, dd, *J* = 11.5, 5.0 Hz, H-6), 4.42 (1H, dd, *J* = 11.5, 5.5 Hz, H-6), 4.51-4.58 (1H, m, H-5), 5.82 (1H, brd, *J* = 10.5 Hz, H-4), 5.96 (1H, brd, *J* = 10.5 Hz, H-3), 7.40-7.47 (2H, m, aromatic), 7.52-7.60 (1H, m, aromatic), 8.02-8.07 (2H, m, aromatic). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.23 (3C), 65.9, 67.5, 70.7, 73.4, 92.3, 101.8, 127.1, 128.3 (2C), 129.7 (2C), 129.8, 130.1, 133.1, 166.3. $[\alpha]_D^{29}$ -71.3° (*c* 0.60, $CHCl_3$). Anal. Calcd for $C_{18}H_{22}O_4Si$: C, 65.42; H, 6.71. Found: C, 65.41; H, 6.63.

β-Alkynyl glycoside 42. The similar treatment of **41** as TP afforded **42** (y.82%) as a colorless oil: IR (KBr) ν_{max} 2184, 1745 cm^{-1}. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.15 (9H, s, TMS), 2.07 (3H, s, OAc), 2.08 (3H, s, OAc), 4.14 (1H, dd, *J* = 12.0, 4.5 Hz, H-6), 4.20 (1H, dd, *J* = 12.0, 6.0 Hz, H-6), 4.29 (1H, d, *J* = 8.0 Hz, H-1), 4.39-4.46 (1H, m, H-5), 5.41 (1H, dm, *J* = 8.0 Hz, H-2), 5.80 (1H, brd, *J* = 10.5 Hz, H-4), 5.84 (1H, dt, *J* = 10.5, 2.0 Hz, H-3). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.41 (3C), 20.8 (2C), 65.4, 67.1, 68.3, 73.3, 92.0, 101.0, 127.0, 128.5, 169.9, 170.8. FAB-MS *m/z* 311 (M^++1), 251 (M^+-59). HRMS calcd for $C_{15}H_{23}O_5Si$ 311.1315, found 311.1302. $[\alpha]_D^{27}$ -97.5° (*c* 0.28, $CHCl_3$).

β-Alkynyl glycoside 46. The similar treatment of **45** as TP afforded **46** (y. 98 %) as a colorless oil: IR (KBr) ν_{max} 2186, 1745 cm^{-1}. ^1H NMR($CDCl_3$, 270 MHz) δ 0.17 (9H, s, TMS), 1.08 (9H, s, t-Bu), 2.03 (3H, s, OAc), 4.01-4.10 (2H, m, H-6), 4.26 (1H, d, J = 8.0 Hz, H-1), 4.34-4.40 (1H, m, H-5), 4.44 (1H, dm, J = 8.0 Hz, H-2), 5.50 (1H, dt, J = 10.5, 1.0 Hz, H-4), 5.57 (1H, dt, J = 10.5, 1.5 Hz, H-3), 7.34-7.48 (6H, m, aromatic), 7.70-7.79 (4H, m, aromatic). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ -0.24 (3C), 19.4, 20.8, 27.0 (3C), 65.7, 68.7, 70.6, 73.3, 91.1, 103.0, 125.8, 127.59 (2C), 127.65 (2C), 129.7, 129.8, 131.3, 132.9, 134.2, 135.9 (2C), 136.1 (2C), 170.8. FAB-MS *m/z* 507 (M^++1). HRMS calcd for $C_{29}H_{39}O_4Si_2$ 507.2387, found 507.2378. $[\alpha]_D^{30}$ -32.6° (*c* 0.30, $CHCl_3$).

ACKNOWLEDGEMENTS: The authors are indebted to Dr. Y. Ichikawa for valuable discussions and helps to persuade these experiments. One of the authors S. T. is on leave from Kao Chemical and Material Research Institute.

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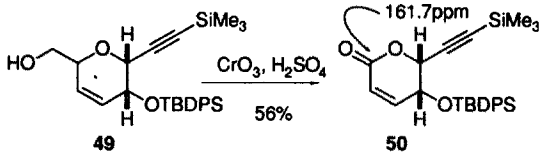
19. Unpublished data (Tanaka, S). The precursor lactone **50** was obtained by over oxidation with Jone's reagent directly from the alcohol **49** in 56 % yield.



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(*Received in Japan* 4 *February* 1994; *accepted* 25 *February* 1994)