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Pseudoenantiomeric Heteroconjugate Addition Approach for Synthesis of Spiro Segment of Tautomycin

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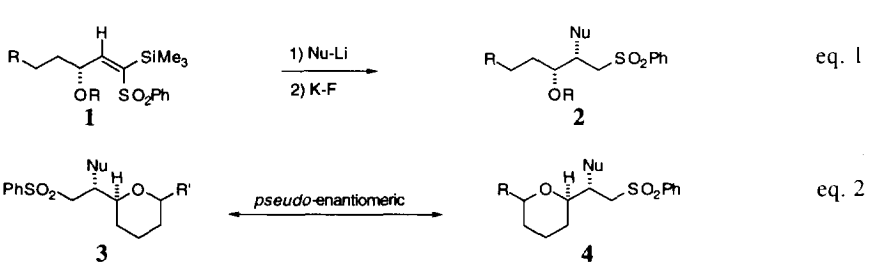
Abstract: A new synthetic method providing both enantiomers by heteroconjugate addition strategy is described for stereocontrolled synthesis of optically active compounds from D-sugar chirons. Preparation includes introduction of phenylthioacetylene, acidic epimerization *via* dicobalthexacarbonyl complex, hydrosilylation and oxidation. Addition of carbon nucleophiles to the heteroolefins extended at the C-1 position yields the product with high stereoselectivity. Mode of addition is switchable *via* α- or β-chelation control.

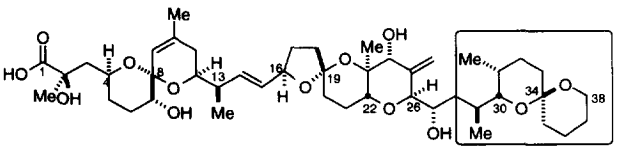
Sugars are still useful chiral source as well as carbon source in organic synthesis. We have been using sugar derivatives such as glucals that accept acetylenic carbon chain at the anomeric position in completely *alpha* orientation.[1] Such a carbon chain at the C1 position is of great interest in comparison with that at the C5 position, which is *beta* in all D-series of sugars. We became interested in extending a carbon chain at the C1 position, to which functional groups could be introduced in high stereoselectivity. The background of this concept lies on what we had employed during the syntheses of maytansine[2] and okadaic acid[3] from this laboratory to extend the chain at the C6 position. We have named this concept as "heteroconjugate addition" as exemplified in eq. 1.[2b] Nucleophile is known to be introduced in completely *syn* manner due to chelation effect of the neighboring secondary OR group.[4] When this method is applied to a ring oxygen system in sugar pyranoside, the products equivalent to **2** are **3** and **4** as shown in eq. 2, where the former extends carbon chain from the C5 position, whereas the latter does from the C1. These two drawings as **3** and **4** are enantiomeric if R equals to R'; in fact, R' is usually oxygen function and R is carbon in the hexopyranose derivative. The case is defined to be *pseudoenantiomeric*.



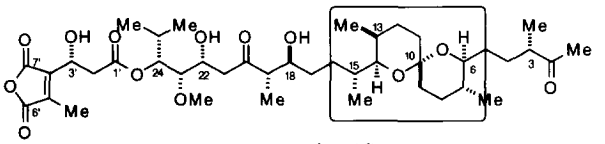
As signified in eq. 1 and 2, this system includes a hydroxy or ether function adjacent to the electrophilic olefin. Principle of the high stereocontrol lies in 3 points; thus, (i) fixation of the conformation of the heteroolefin, (ii) the metal chelation of the nucleophile with the hydroxy group (OR in **1**), (iii) so that the nucleophile will be guided from the hydroxy face of the electrophile. In this case, the conformation of the

bulky heteroolefin attains high restriction by acyclic allylic strain (AAS) which occurs at the allylic stereogenic center relative to the spacious electrophilic olefin. Stereoselectivity in this 1,2-asymmetric induction was virtually quantitative to form **2** as a single *syn*-isomer, and the switching of the diastereomeric selectivity has been established to be optional on demand.[5]

The most demanding point in such methodology that we have developed and named as "heteroconjugate addition", was the limitation of availability of L-sugars as chiral template. Namely, a new method switching the enantiomeric situation of carbohydrate synthon was awaited. Okadaic acid (**5**) was a typical example in this concept, that had led us to conclude the total synthesis mostly from D-glucose derivatives.[2] Tautomycin (**6**),[6] a current synthetic target in our group, possesses a spiro unit (indicated in the square), which is *pseudo*-enantiomeric to the spiro moiety in okadaic acid, and therein posed our next challenge to develop a new synthetic concept providing both enantiomeric structures from the same D-glucose derivative. Could this be accomplished? We have, in fact, solved this problem and have reported in a preliminary communication about this enantio switching.[7] We here describe some pertinent developments.



okadaic acid (5)

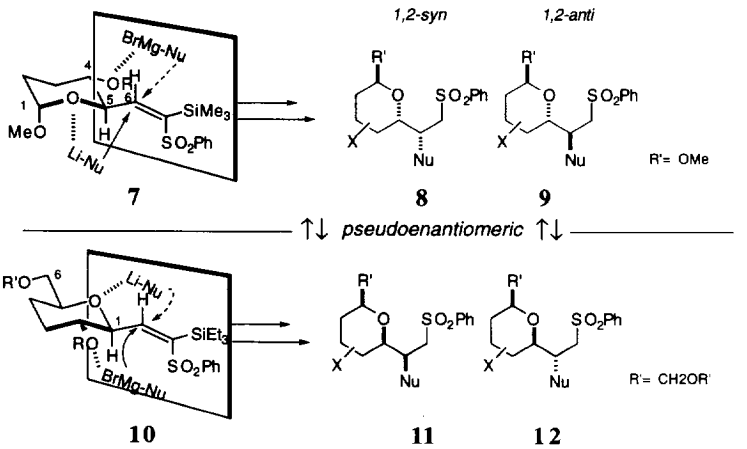


tautomycin (6)

These naturally occurring compounds (**5**, **6**) show significant inhibitory activity against protein phosphatase, the former particularly creating problems to human life since it occurs in sea food (mussels, scallops, etc.). Biological significance of tumor promotion has also prompted us to synthesize **6** to contribute solving biological problems.[6a, 8] An important synthetic problem could be solved by developing a method which would give both of the *pseudo*-enantiomer as in eq. 2, that would be derived from D-glucose as the source of the tetrahydropyrane ring.

The enantiomeric relationship of the asymmetric carbons in eq. 2, could be differentiated by the face selection of the precursor electrophilic olefin, although some portion in the carbohydrate skeleton is not necessarily identical ($R \neq R'$) as discussed above. The heteroconjugate addition strategy based on glucose derivatives has been designed to place the electrophilic olefin conjugated to heteroatom groups (= heteroolefin) at the C-6 position of carbohydrate (eq. 3), while the new method should develop the concept at the C-1 position. Equations 3 and 4 illustrate the mode of conjugate addition to the heteroolefin at the C-6 (**7**) and at the C-1' (**10**) position, respectively. The sp^2-face extending from the tetrahydropyranyl ring is conformationally restricted due to acyclic allylic strain so that the least bulky substituent at the allylic chiral center would situate in co-planarity with the sp^2-face. Addition of nucleophile to **7** was originally designed to attack from *re*-face by chelation between the α oxygen atom and lithium alkyls to give 1,2-*syn* product. To switch the *si*-face attack to produce 1,2-*anti* isomer, employment of Grignard reagent instead of lithium alkyls was more efficient in chelation with the β alkoxide. The former (α chelation control) gave, in fact,

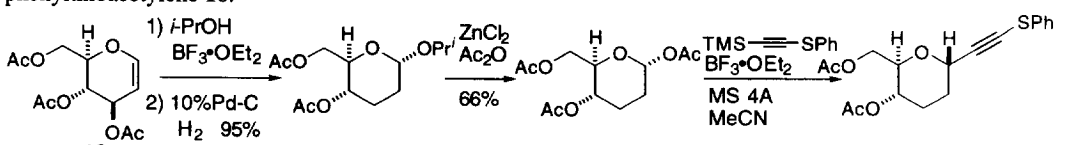
quantitatively the 1,2-*syn*-adduct **8**, while the latter (β chelation) gave the 1,2-*anti*-adduct **9** in 95% selectivity.[9] If the corresponding electrophile **10** could be prepared at the C-1 position, a similar situation could be envisioned by similar addition under the high sp^2-face selection as shown in eq. 4. Thus, the α chelation control will presumably happen from the rear *si*-face (dotted line) and the β chelation will occur on the front *re*-face through the C-2 equatorial hydroxy group with the expectation of affording **11** and **12**, (*pseudo*-enantiomeric to **8** and **9**), respectively.



eq. 3

eq. 4

Placement of this electrophile at the C-1 position has initially been examined by model study which commenced from tri-*O*-acetyl-D-glucal **13**.[1] Glycosidation of **13** with 2-propanol in the presence of boron trifluoride etherate afforded a glycoside, and following hydrogenation by the catalysis of palladium on charcoal gave the glycoside **14** in 95%. Conversion of isopropyl glycoside to acetate **15** was carried out in the presence of zinc chloride at ambient temperature in 66% yield. C-Glycosidation of glycoside acetate **15** with phenylthio(trimethylsilyl)acetylene[10] was intensively investigated with various conditions afforded α-phenylthioacetylene **16**.

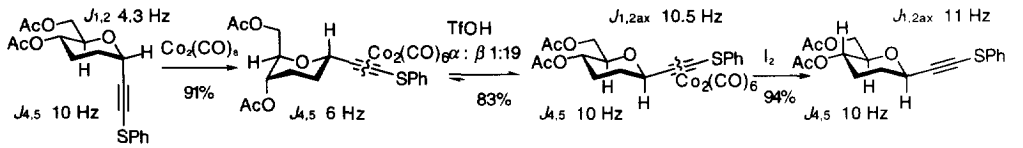


Scheme 1

There were several elements effected to C-glycosidation: 1) Protonic acids did not promote C-glycosidation in this case. 2) Boron trifluoride etherate was the most suitable Lewis acid among what we have examined. Strong Lewis acid (tin tetrachloride and titanium tetrachloride) afforded 10% of product while weak Lewis acid (zinc chloride) did not give product. Trimethylsilyl trifluoromethanesulfonate produced 24% of product whilst PPTS did not work. 3) Acetonitrile was the best among the solvents investigated and phenylnitrile gave moderate yield. 4) Lower temperature, longer reaction and the yield was decreased due to product decomposition at the prolong reaction time. Temperature at 0°C was the suitable reaction condition. 5) The relatively concentrated phenylthioacetylene led to the higher yield. 6) Enhancement of the yield was observed in the presence of molecular sieve 4Å. Based on the observed experimental facts, we concluded that

the concentrated boron trifluoride etherate, short reaction time, the presence of molecular sieve 4Å and acetonitrile as solvent are critical to the success of this reaction. Because of the sensitivity of phenylthio group toward acid along the reaction, the decomposition of product increased gradually while the formation of product was performed. The point is to enhance the velocity of the reaction at the maximum level and to prevent the loss of product through decomposition by quenching the reaction in short time, for example, 5 minutes, which led us to obtain α-epimer up to 72% yield.[11] The stereochemistry of phenylthioacetylenic group in **16** was exclusively introduced in pure *alpha* form (**Scheme 1**).

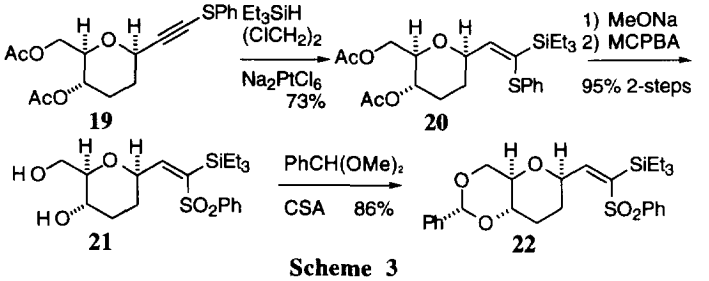
The α-phenylthioacetylenic group **16** was converted to dicobalthexacarbonyl complex **17**, which was epimerized into β-isomer **18** under an acidic condition. The ratio, for example, was 1 : 19 ($\alpha : \beta$) using trifluoromethanesulfonic acid in dichloromethane, followed by decomplexation with iodine to give **19** (**Scheme 2**).[12] Because the cobalt complexes were unstable, their elemental analysis data and their optical data are not reported in experimental section.



16 **17** **18** **19**

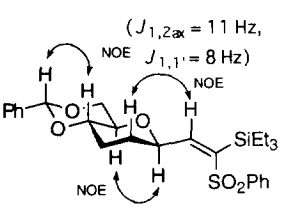
Scheme 2

The triple bond was regioselectively hydrosilylated to the vinyl sulfide **20** with triethylsilane in the presence of platinum catalyst,[13] the regioselectivity of the reaction relied on the quantity of catalyst. Deprotection with sodium methoxide and oxidation with *m*-chloroperbenzoic acid afforded **21**, which was reprotected with benzaldehyde dimethyl acetal in the presence of camphor-10-sulfonic acid to give the heteroolefin **22** as shown in **Scheme 3**. Its conformation was determined as shown in **Fig. 1** by NOE experiments and coupling constants.



19 **20** **21** **22**

Scheme 3

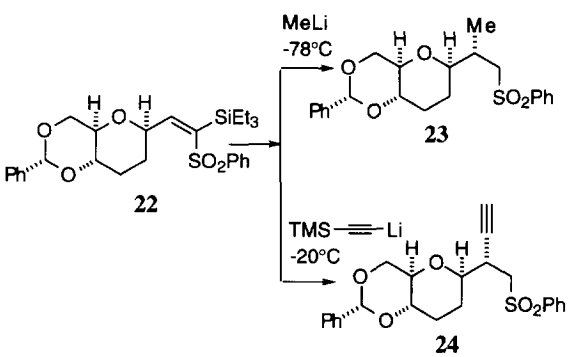


22a

Fig. 1

Two kinds of nucleophiles (MeLi•LiBr and Li-C≡C-$SiMe_3$) were used as examples to give products **23** and **24** with high stereoselectivity, respectively. The selectivity of heteroconjugate addition was highly dependent to solvents and salts as shown in **Scheme 4**, although the effects shown here are not completely systematic. In the case of LiBr free methyllithium, selectivity of *syn* to *anti* in tetrahydrofuran was 78 : 22, and addition of HMPA to the reaction medium improved the ratio to 95 : 5. When ether or hexane-ether with LiBr was employed, α-chelation controlled product **23** was observed with high selectivity. LiBr was added in ether solution. As for the addition of lithium trimethylsilylacetylide, no reaction took place in the mixed solvent of THF-HMPA, while in ether solvent 20% of product was obtained (*syn* : *anti* = 89 : 11). The best

selectivity was observed in hexane-ether solvent with LiBr, which gave 86% of product in 94 : 6 (*syn* : *anti*). All the reactions with LiBr were faster than without LiBr. These results might depend on the formation of cluster complex including substrate, reagents, salt and solvents, but the details should await for further studies. The stereochemistry of the methyl adduct **23** was assigned to be *syn* on the basis of the chemical shift of ^{13}C nmr (δ 14.6) of the methyl group, which in fact added through α-chelation.[14] The stereochemistry of the acetylene adduct **24** was also assigned to be *syn* dominant from this mechanistic point of view (**Scheme 4**).



LiBr	Solvent	yield (%)	*syn*:*anti*
no	THF	60	78 : 22
no	THF/HMPA (2:1)	95	95 : 5
12 equiv.	ether	79	>99 : 1
12 equiv.	hexane/ether (1:2)	87	>99 : 1

LiBr	Solvent	yield (%)	*syn*:*anti*
no	THF/HMPA (5:1)	no	-
no	ether	20	89 : 11
12 equiv.	hexane/ether (2:1)	86	94 : 6

Scheme 4

In **Scheme 5**, another equatorial heteroolefin **32** with a hydroxy substituent at the C-2 position is discussed. An example **32** was similarly prepared from tetra-*O*-acetyl-D-glucal (**25**) through steps involving C-glycosidation with phenylthio-trimethylsilylacetylene and reduction with sodium borohydride in the presence of cerium chloride to give a phenylthioacetylenic derivative **26** in its pure α-form. Protection of the resulting hydroxy group with bulky *t*-butyldiphenylsilyl group afforded **27**, complexation with dicobaltoctacarbonyl afforded **28** which was epimerized with trifluoromethanesulfonic acid (70 mol%) to give **29** ($\alpha : \beta$ = 1 : 7, separated ratio).

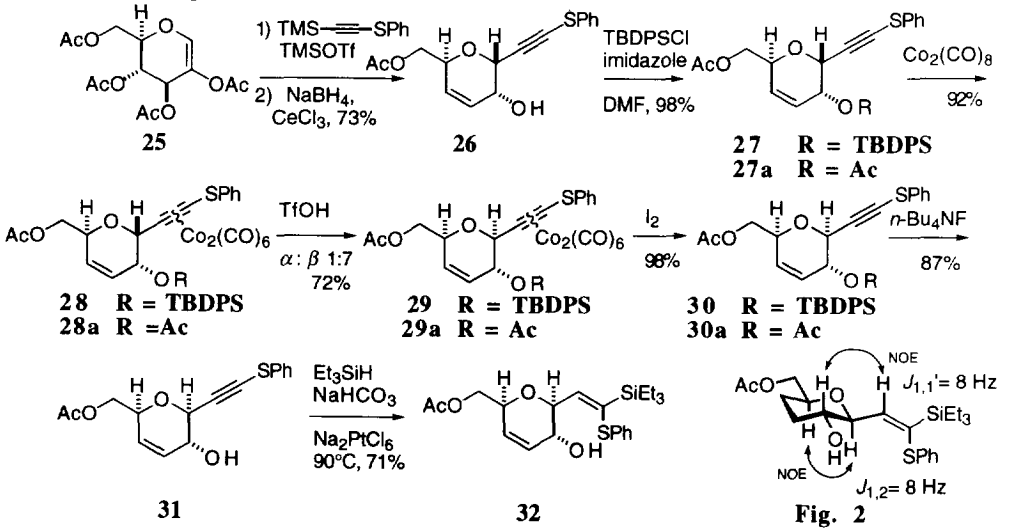
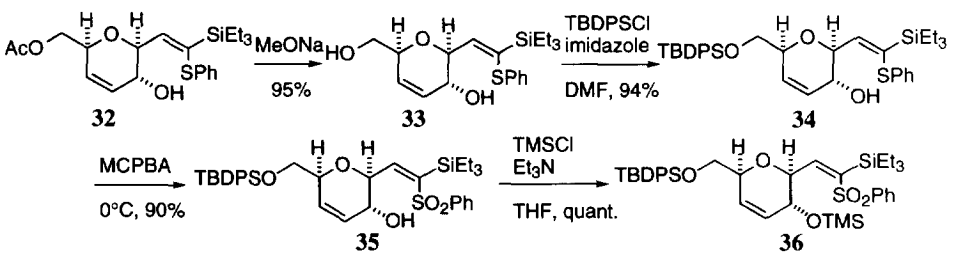


Fig. 2

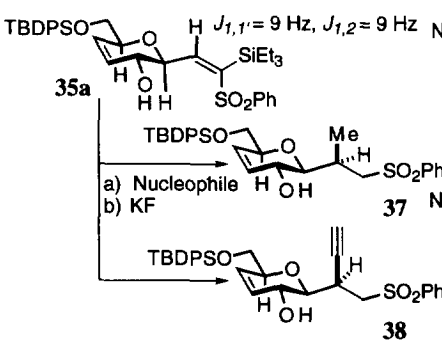
Scheme 5

The substituent effect in epimerization was obvious; for example, trifluoromethanesulfonic acid (0.01N in reaction mixture) could convert α-trimethylsilylacetylene to its β-epimer quantitatively in 30 minutes according to the observation by Tanaka *et al.*[12c] In case of phenylthioacetylenic derivative **28**, however, no reaction took place under the same condition. Additional trifluoromethanesulfonic acid to the reaction mixture (*final concentration* 0.07*N*) accelerated the reaction velocity, but it simultaneously caused the deprotection of *t*-butyldiphenylsilyl group in a substantial rate. As a result we had to quench the reaction before α-epimer was completely consumed to obtain the β-epimer in 72%. An alternative protection of *t*-butyldiphenylsilyl group is acetoxy, which is more stable in acidic media. The protection of **26** with acetic anhydride in pyridine afforded **27a**, which reacted with dicobaltoctacarbonyl to give **28a**. Epimerization with trifluoromethanesulfonic acid (0.07N) gave **29a** in the ratio of 1 : 20 (α: β). Decomplexation of **29** and **29a** with iodine afforded **30** and **30a**, respectively. Direct epimerization without protection of hydroxy at the C-2 position led to a mixture of epimers which could not be isolated. Deprotection of **30** with tetrabutylammonium fluoride afforded **31**, which was followed by hydrosilylation to give **32** with 3 ~ 10% of regioisomers varying from the quantity of the platinum catalyst (**Scheme 5**). The conformation of **32** was confirmed by NOE experiment and coupling constants (**Fig. 2**).

Following manipulation through deprotection of acetate (**32**) with sodium methoxide, selective protection of primary alcohol of **33** with *t*-butyldiphenylsilyl group (**34**) and oxidation with *m*-chloroperbenzoic acid afforded the heteroolefin **35** having free secondary hydroxy group. This hydroxy group at the C-2 position was masked with trimethylsilyl group to give **36** (**Scheme 6**).



Scheme 6



Nucleophile = Me^-

solvent	temp.	nucleophile	LiBr	yield	syn:anti
ether	-20°C	MeLi-LiBr	12eq	96%	30:70
hexane/ether	0°C	MeLi-LiBr	12eq	52%	8:92
THF	25°C	MeMgBr	---	72%	4:96

Nucleophile = TMS-C≡C-Li

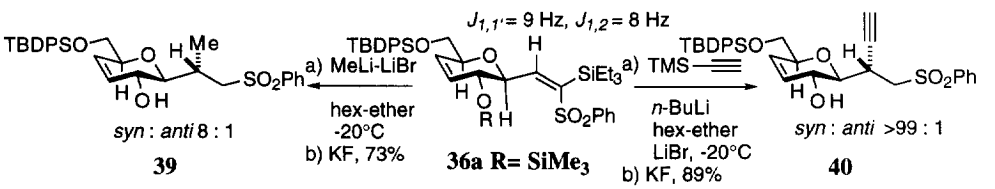
solvent	temp.	nucleophile	LiBr	yield	syn:anti
hexane/ether	-20°C	TMS—≡—Li	12 eq	30%	1:>99
THF	25°C	TMS—≡—MgBr	---	---	---
ether	0°C	TMS—≡—Li	---	63%	1:>99
hexane/ether	0°C	TMS—≡—Li	---	95%	1:>99

Scheme 7

The conformation of both electrophilic moieties (**35** and **36**) was equatorial since the coupling constant was $J_{1,2}$ = 8 Hz as shown in **Scheme 7** and **Scheme 8**. Heteroconjugate addition of methyllithium to **35a** was followed by treatment with potassium fluoride to give **37** as *anti* isomer (δ 18.7, methyl signal)[14]

through β-chelation control. The selectivity of this addition was dependent on solvent and the chelation ability of metal. As for methyllithium and lithium bromide complex, the heteroconjugate addition gave 96% of methyl adduct in the ratio of 30 : 70 (*syn* : *anti*) in ether solvent, in hexane-ether solvent the ratio improved to 8 : 92. Methylmagnesium bromide, stronger chelation agent with free alkoxide (but not with ethereal oxygen atoms) and weak nucleophile, afforded *anti* product in 20 hours in 72% with the selectivity of *syn* : *anti* being 4 : 96. Heteroconjugate addition with lithium trimethylsilylacetylide is highly selective (*syn*:*anti* 1 : >99) in ether solvent or in a mixture of hexane-ether solvent to give **38** (δ 2.09, d, J = 2 Hz, acetylenic proton). The nucleophile trimethylsilylacetylenic magnesium bromide did not give product due to its lower reactivity (**Scheme 7**).

On the other hand, heteroconjugate addition to **36** with masked β hydroxy group by trimethylsilyl was also carried out with two kinds of nucleophiles to afford *syn* isomers as dominant products. Since the protection of the free hydroxy group had blocked the β-chelation between β-hydroxy and metal ion of nucleophiles, the selectivity had been successfully switched to α-chelation controlled product. As for the nucleophile of methyllithium-lithium bromide complex, the selectivity of *syn* : *anti* was 8 : 1 in the mixture of hexane-ether solvent at -20°C to afford **39** (δ 13.6, Me), while lithium trimethylsilyl acetylide gave pure α-chelation controlled product **40** (δ 2.09, d, J = 2.5 Hz, acetylenic proton) (**Scheme 8**). Simple switching of *syn-anti* selectivity was noteworthy by protection or non-protection of the 2-hydroxy group of **35**. Assignment of the stereochemistry of the products was based on the previous studies on pseudoenantiomeric cases.[14]



Scheme 8

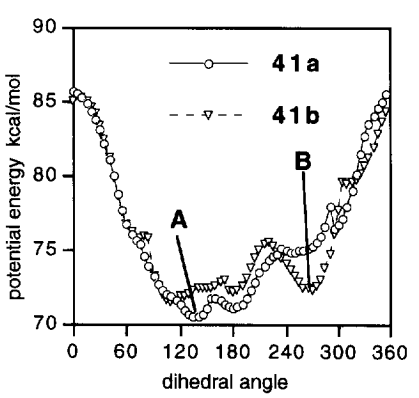


Fig. 3

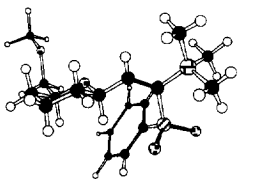


Fig. 4 A 135° 70.5 kcal

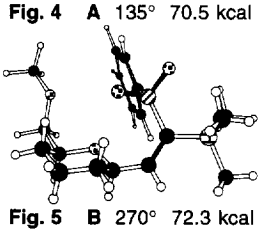
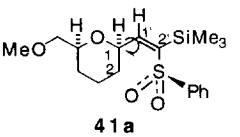
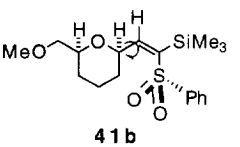


Fig. 5 B 270° 72.3 kcal



41a



41b

Mode of above heteroconjugate addition depended on two factors, the preferential conformation and the strong metal chelation as postulated earlier.[2b] The conformation of the transition state would be similar to that of the ground state. Potential energy was calculated with two rotamers of the sulfone of **41a,b** by minimizing each conformer generated in every 5° around the dihedral angle of the C_2-C_1-$C_{1'}$=$C_{2'}$ and plotted in clockwise

(**Fig. 3**). Global minimum conformation in **Fig. 3** is drawn as **A** in **Fig. 4**, which has the angle of 135° and fits with the observed NMR data ($J_{1,1'}$= 8~9 Hz). **Fig. 5** is the local minimum of another rotamer **B** (**Fig. 3**), which would not reduce the selectivity because of very little contribution due to higher energy difference (1.8 kcal/mol) from **A**. These calculations[15] ascertained the selectivity of heteroconjugate addition depending on the population of the ground state conformation of the electrophile.

The current methodology provided switching the *syn-anti* selectivity in the new preparation involving C-glycosidation and epimerization. Application of this method for the synthesis of tautomycin **6**, its diastereoisomers and other natural products is now in progress.

Experimental

Melting points were measured on a hot stage melting point apparatus. All melting points were not corrected. Infrared (IR) spectra were recorded on JASCO FT/IR 7000S and reported in wave numbers. Nuclear magnetic resonance spectra were recorded on JEOL FX-270, Bruker ARX400 and Variant Gemini 2000 (300 MHz) spectrometer. Chemical shifts were reported as δ value in parts per million relative to tetramethylsilane (0.0 ppm) as an internal standard. All samples were dissolved in $CDCl_3$ unless specified. Data are generally reported as follows: chemical shift (integrated intensity, multiplicity, coupling constants, assignment). Multiplicity is described by abbreviation; s = singlet, d = doublet, t = triplet, q = quartet or m = multiplet. Coupling constants are reported as *J* in Hz. Optical rotations were measured in 1 dm cell of 2 ml capacity by JASCO DIP-370 digital polarimeter. Because cobalt complexes were not stable, their elemental analyses are not reported.

Analytical thin layer chromatography was conducted on 0.25 mm pre-coated silica gel plate manufactured by E. Merck (Art #57515). Preparative thin layer chromatography was performed on a 0.5 mm pre-coated silica gel plate, PF254 from E. Merck (Art #5744). Column chromatography was performed with silica gel supplied by Fuji Silysia (BW-820MH). Flash chromatography was carried out with silica gel supplied by Fuji Silysia (BW-300).

Reactions were conducted under nitrogen or argon atmosphere when reactants or intermediates were sensitive to oxygen or moisture. Degassed solvent was operated using vacuum line through a 3-way valve and gas-exchange was repeated by 3 times before use. Trace of water in solvents was removed by the following methods: ether was dried by sodium wire; tetrahydrofuran was distilled over potassium metal; benzene was dried by sodium wire; chloroform and dichloromethane were dried over molecular sieve 4Å, respectively; acetonitrile was distilled in the presence of calcium hydride.

Hydrogenated isopropyl glycoside, 14

To a solution of tri-*O*-acetyl-D-glucal **13** (10.0 g, 0.037 mol) and 2-propanol (14 ml) in dichloromethane (100 ml) was added boron trifluoride etherate (1.7 ml, 0.015 mol) at ambient temperature. After stirring for 24 hours, the mixture was quenched with aqueous sodium hydrogen carbonate and extracted with ether. The organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration under reduced pressure gave crude oil of glycoside (9.8 g). A suspension of platinum (5% on charcoal, 0.5 g) and crude oil of glycoside (9.8 g, 0.036 mol) in ethyl acetate (200 ml) was kept under hydrogen atmosphere overnight. The reaction mixture was filtered through Celite and concentrated. The residue was purified by silica gel chromatography to give colorless oil, **14** (9.38 g, 95%). IR (KBr) ν_{max} 2973, 1744, 1374, 1243, 1043 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.15 (3H, d, *J* = 6.5 Hz, isopropyl), 1.23 (3H, d, *J* = 6.5 Hz, isopropyl), 1.7-2.1 (4H, m), 2.05 (3H, s, acetate), 2.1 (3H, s, acetate), 3.91 (1H, m, *J* = 7 Hz, isopropyl), 3.99 (1H, ddd, *J* = 10, 5, 3 Hz, H-5), 4.09 (1H, dd, *J* = 12, 2 Hz, H-6), 4.26 (1H, dd, *J* = 12, 5 Hz, H-6), 4.73 (1H, td, *J* = 10, 5 Hz, H-4), 4.95 (1H, s, brd, H-1). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 20.7, 21.0, 21.4, 23.2, 23.9, 29.2, 63.2, 68.0, 68.6, 70.6, 94.2, 170.0, 170.9. $[\alpha]_D^{25}$ = +109.1° (*c* 1.51, CH_2Cl_2). Anal. calcd. for $C_{13}H_{22}O_6$: C 56.92%; H 8.08%. Found: C 56.82%; H 8.12%.

Glycoside acetate, 15

To a solution of **14** (1.05 g, 3.82 mmol), acetic acid (1.1 ml) and acetic anhydride (4 ml) in dichloromethane (15 ml) was added zinc chloride (1.04 g, 7.6 mmol) at ambient temperature. After stirring

for 40 minutes, the mixture was quenched by dropwise addition of aqueous sodium hydrogen carbonate. The aqueous layer was extracted with ether. The combined organic phase was dried over anhydrous sodium sulfate and concentrated to give residue (0.73 g). The residue was subjected to silica gel chromatography to afford colorless oil, **15** (0.69 g, 66%). IR (KBr) ν_{max} 2956, 1756, 1442, 1372, 1218, 1132, 1048, 1004, 950 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.90 (m), 2.06 (3H, s, acetate), 2.08 (3H, s, acetate), 2.12 (3H, s, acetate), 4.0 (1H, ddd, J = 10, 4.6, 2 Hz, H-5), 4.10 (1H, dd, J = 12, 2 Hz, H-6), 4.27 (1H, dd, J = 12, 4.6 Hz, H-6), 4,81 (1H, td, J = 10, 4.5 Hz, H-4), 6.15 (1H, s, H-1). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 20.7, 20.9, 21.0, 23.5, 27.5, 62.6, 66.9, 70.7, 90.7, 169.2, 169.7, 170.8. Anal. calcd. for $C_{12}H_{18}O_7$: C 52.55%; H 6.62%. Found: C 52.50%; H 6.62%.

α-Phenylthioacetylene, 16

To a suspension of **15** (39.6 mg, 0.14 mmol), molecular sieve 4Å (100 mg) and phenylthiotrimethylsilylacetylene (298.0 mg, 1.44 mmol) in acetonitrile (1.5 ml) at 0°C was added boron trifluoride etherate (0.26 ml, 2.1 mmol) in one portion. After stirring for 10 minutes, the reaction mixture was quenched with aqueous sodium hydrogen carbonate dropwise and extracted with ether. The combined organic phase was concentrated under reduced pressure to afford crude oil. The residue was purified by silica gel preparative thin layer chromatography to give colorless oil, **16** (36.0 mg, 72%). IR (KBr) ν_{max} 1734, 1276 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.8-2.2 (4H, m), 2.06 (3H, s, acetate), 2.09 (3H, s, acetate), 4.11 (1H, ddd, J = 10, 5, 2 Hz, H-5), 4.13 (1H, dd, J = 12, 2 Hz, H-6), 4.3 (1H, dd, J = 12, 5 Hz, H-6), 4.72 (1H, td, J = 10, 4.3 Hz, H-4), 4.99 (1H, d, J = 4.3 Hz, H-1, anomeric), 7.36 (5H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 20.8, 21.0, 25.5, 29.5, 63.0, 65.8, 67.5, 71.9, 74.5, 95.8, 126.3, 126.8, 129.3, 132.0, 170.0, 170.9. $[\alpha]_D^{26}$ = +52.9 (c 0.23, $CHCl_3$). Anal. calcd. for $C_{18}H_{20}O_5S$: C 62.05%; H 5.79%. Found: C 61.99%; H 5.96%.

α-Dicobalthexacarbonyl complex, 17

To a dark brown solution of dicobaltoctacarbonyl (2.96 g, 8.66 mmol) in degassed dichloromethane (22 ml) under argon atmosphere was added **16** (2.07 g, 5.94 mmol) at ambient temperature. After stirring for 1 hour, the mixture was concentrated under reduced pressure and aerated for 20 minutes to yield dark brown oil. The crude oil was purified by silica gel chromatography (CH_2Cl_2) to afford pure product, **17** (3.43 g, 91%). ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.98-2.2 (4H, m), 2.10 (6H, s, acetate), 4.09 (1H, dd, J = 12, 3.5 Hz, H-6), 4.2 (1H, td, J = 7, 3.5 Hz, H-5), 4.57 (1H, dd, J = 12, 7 Hz, H-6), 4.88 (1H, m, H-4), 5.07 (1H, m, H-1), 7.4-7.5 (5H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 20.8, 21.1, 24.7, 28.8, 61.8, 67.0, 73.0, 73.1, 77.2, 129.3, 129.4, 129.8, 134.1, 134.3, 134.7, 170.3, 170.8.

β-Dicobalthexacarbonyl complex, 18

The α-epimer **17** (3.43 g, 5.41 mmol) was dissolved in degassed dichloromethane (540 ml) under argon atmosphere. To this dark brown solution was then added trifluoromethanesulfonic acid (0.1 M in $Cl_2FCCClF_2$, 5.4 ml) dropwise at ambient temperature. After stirring for 30 minutes, the reaction mixture was quenched with aqueous sodium hydrogen carbonate. The aqueous layer was extracted with ether, and the combined organic layer was dried over anhydrous sodium sulfate. After it was concentrated the residue was purified by silica gel chromatography (CH_2Cl_2 / hexane 1:1) to give β-epimer, **18** (2.86 g, 83%, α : β 1 : 19). ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.74 (m, 4H), 2.01 (3H, s, acetate), 2.08 (3H, s, acetate), 3.81 (1H, ddd, J = 10, 5.5, 2.5 Hz, H-5), 4.15 (1H, dd, J = 12, 5.5 Hz, H-6), 4.23 (1H, dd, J = 12, 2.5 Hz, H-6), 4.6 (1H, dd, J = 10.5, 2 Hz, H-1), 4.78 (1H, td, J = 10, 5 Hz, H-4), 7.5 (5H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 20.6, 21.1, 29.2, 32.0, 63.5, 68.1, 77.2, 77.5, 129.3, 129.4, 134.1, 170.1, 171.0.

Decomplexation to β-Phenylthioacetylene, 19

A solution of cobalt complex **18** (2.86 g, 4.51 mmol) and iodine (4.5 g, 0.035 mol) in tetrahydrofuran (450 ml) was stirred at ambient temperature for 1.5 hours and the mixture was quenched with aqueous sodium hydrogen carbonate and aqueous sodium hydrogen sulfite. After the aqueous phase was extracted with ether, the combined organic phase was dried and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/ether 1:1) to produce a colorless oil, **19** (1.48 g, 94%). IR (KBr) ν_{max} 2960, 1740, 1243 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.9-2.4 (4H, m), 3.6 (1H, ddd, J = 10, 5, 2.3 Hz, H-5), 4.16 (1H, dd, J = 12, 2.3 Hz, H-6), 4.24 (1H, dd, J = 12, 5 Hz, H-6), 4.4 (1H, dd, J = 11, 3 Hz, H-

4), 4.72 (1H, td, J = 10.5, 4.5 Hz, H-1, anomeric), 7.2-7.4 (5H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 20.9, 21.0, 29.1, 31.4, 31.5, 63.3, 67.1, 68.8, 73.1, 96.3, 126.4, 126.7, 129.2, 132.0, 169.9, 170.9. $[\alpha]_D^{25}$ = +60.6° (c 0.78 $CHCl_3$). Anal. calcd. for $C_{18}H_{20}O_5S$: C 62.05%; H 5.79%. Found: C 62.06%; H 5.62%.

Hydrosilylation to Vinylsulfide, 20

To a solution of **19** (89.0 mg, 0.26 mmol) and triethylsilane (1.8 ml) in 1,2-dichloroethane (2.5 ml) was added $Na_2PtCl_6 \cdot 6H_2O$ (0.021 M in isopropanol, 0.012 ml) at 90°C. After stirring for 1 hour the reaction mixture was cooled down, diluted with hexane and then filtered through Celite. The filtrate was concentrated and purified by silica gel chromatography (hexane / ether 3:1) to give pure product, **20** (88.2 mg, 73%). IR (KBr) ν_{max} 2953, 1747, 1243, 1065 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 0.53 (6H, m, CH_3CH_2Si), 0.86 (9H, t, J = 8 Hz, CH_3CH_2Si), 1.56 (2H, m), 1.78 (1H, m), 2.02 (3H, s, acetate), 2.10 (3H, s, acetate), 3.52 (1H, ddd, J = 10, 5, 2 Hz, H-5), 4.10 (1H, dd, J = 12, 2 Hz, H-6), 4.25 (1H, dd, J =12, 5 Hz, H-6), 4.61 (1H, ddd, J = 10, 7, 2.5 Hz, H-1), 4.7 (1H, td, J = 10, 4.5 Hz, H-4), 6.46 (1H, d, J =7 Hz, H-1'), 7.2 (5H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 3.2, 7.2, 20.9, 21.1, 29.1, 30.1, 63.5, 67.7, 76.7, 125.9, 128.7, 129.0, 132.9, 136.6, 151.6, 170.0, 171.0. $[\alpha]_D^{25}$ = +116.2° (c 1.51, CH_2Cl_2). Anal. calcd. for $C_{24}H_{36}O_5SSi$: C 62.03%; H 7.81%. Found: C 62.04%; H 7.75%.

Conversion to Dihydroxysulfone, 21

To a solution of **20** (0.71 g, 1.53 mmol) in methanol (15 ml) was added sodium methoxide (ca. 28% in methanol, 0.37 ml, 1.53 mmol) at 0°C. After stirring for 3 hours, the reaction mixture was neutralized with acidic ion exchange resin DOWEX 50W-X4 and filtered. The filtrate was concentrated to give crude deprotected vinylsulfide (570.0 mg). A suspension of sodium hydrogen phosphate (0.5 g) in dichloromethane (10 ml) was added to this vinyl sulfide intermediate (565.7 mg, 1.49 mmol). It was then mixed with *m*-chloroperbenzoic acid (0.95 g) at 0°C. The reaction mixture was stirred for 30 minutes, and then quenched with aqueous sodium hydrogen carbonate and aqueous sodium sulfite. The aqueous phase was extracted with ether. The combined organic phase was washed with brine and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (ether / AcOEt 5:1) to afford product, **21** (0.61 g, 99%). IR (KBr) ν_{max} 3429, 2955, 1302, 1142, 1075 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.45 (2H, m), 1.77 (1H, m), 2.05 (1H, m), 3.14 (1H, m, H-5), 3.51 (1H, m, H-4), 3.77 (2H, m, H-6), 4.88 (1H, t, brd, J = 8.5 Hz, H-1), 6.39 (1H, d, J = 8 Hz, H-1'), 7.58 (3H, m, Ar), 7.85 (2H, d, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 3.2, 7.0, 15.2, 30.5, 32.1, 63.3, 65.8, 67.0, 74.8, 80.8, 126.8, 129.0, 133.1, 142.7, 142.7, 156.0. $[\alpha]_D^{25}$ = +94.8° (c 1.05, CH_2Cl_2). Anal. calcd. for $C_{22}H_{32}O_5SSi$: C 58.22%; H 7.82%. Found: C 58.10%; H 7.79%.

β-Heteroolefin, 22

A solution of **21** (162.4 mg, 0.39 mmol) and camphor-10-sulfonic acid (91.4 mg) in dichloromethane (4 ml) was mixed with benzaldehyde dimethyl acetal (119.8 mg) at ambient temperature. After stirring for 48 hours, the mixture was quenched with aqueous sodium hydrogen carbonate and extracted with ether. The combined organic phase was concentrated under reduced pressure and purified by silica gel chromatography (hexane/ether 5:1) to yield colorless oil, **22** (170.0 mg, 86%). IR (KBr) ν_{max} 2955, 2875, 1302, 1142, 1100, 1012. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 0.75 (6H, m, CH_3CH_2Si), 0.89 (9H, m, CH_3CH_2Si), 1.53 (1H, m, H-2a), 1.75 (1H, qd, J =12, 4 Hz, H-3a), 1.96 (1H, dq, J = 13, 3 Hz, H-2e), 2.1 (1H, dq, J = 12.5, 3.5 Hz, H-3e), 3.32 (1H, ddd, J = 10, 9, 5 Hz, H-5), 3.52 (1H, ddd, J = 11, 9, 4.5 Hz, H-4), 3.65 (1H, t, J = 10 Hz, H-6), 4.17 (1H, dd, J = 10, 5 Hz, H-6), 4.97 (1H, ddd, J = 11, 8, 2.5 Hz, H-1), 5.53 (1H, s, acetal), 6.38 (1H, d, J = 8 Hz, H-1'), 7.27(m, Ar), 7.51(m, Ar), 7.89(m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 3.2, 7.0, 28.4, 30.4, 69.1, 73.0, 75.2, 77.8, 101.8, 126.1, 126.8, 126.9, 128.3, 129.00, 129.03, 133.1, 137.5, 142.7, 143.2, 155.4. $[\alpha]_D^{25}$ = +99.9° (c 0.99, CH_2Cl_2). Anal. calcd. for $C_{27}H_{36}O_5SSi$: C 64.76%; H 7.25%. Found: C 64.78%; H 7.31%.

***syn*-Methyl adduct, 23**

Compound **22** (11.1 mg, 0.022 mmol) in hexane (0.7 ml) under argon atmosphere was added lithium bromide (0.7 M in ether, 0.35 ml, 0.25 mmol) at -78°C, followed by addition of methyllithium (1.5 M in ether as complex with lithium bromide, 0.04 ml, 0.06 mmol). The reaction mixture was stirred for 20 minutes. It

was quenched with aqueous ammonium chloride and extracted with ether. The combined organic phase was concentrated under reduced pressure and dried through azeotropic evaporation with benzene to give crude oil. The crude oil in tetrahydrofuran (1 ml) was added tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 0.01 ml) at ambient temperature. The mixture was stirred for 3 hours. The usual workup and purification by silica gel thin layer chromatography (hexane : ether 1 : 1) afforded the methyl adduct, **23** (7.7 mg, 87%, *syn* : *anti* >99:1). IR (KBr) ν_{max} 2933, 2870, 1457, 1305, 1147, 1100 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.08 (3H, d, *J* = 7 Hz, CH_3), 2.1 (1H, m), 2.3 (1H, m), 2.97 (1H, dd, *J* = 14, 8 Hz, H-2'), 3.26 (1H, ddd, *J* = 10, 9, 4.5 Hz, H-4), 3.37 (1H, dd, *J* = 14, 4.5 Hz, H-2'), 3.45 (2H, m), 3.60 (1H, t, *J* = 10 Hz, H-6), 4.13 (1H, dd, *J* = 10, 5 Hz, H-6), 5.5 (1H, s, acetal), 7.3-7.9 (10H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 14.6, 26.8, 28.4, 32.7, 59.4, 69.3, 73.5, 78.3, 79.2, 101.8, 126.1, 127.8, 128.3, 129.0, 129.3, 133.6, 137.5, 140.1. $[\alpha]_D^{25}$ = -8.7° (*c* 0.51, CH_2Cl_2). Anal. calcd. for $C_{22}H_{26}O_5S$: C 65.65%; H 6.51%. Found: C 65.67%; H 6.53%.

syn-Acetylenic adduct, 24

To a solution of bis(trimethylsilyl)acetylene (42.1 mg, 0.43 mmol) in hexane (0.5 ml) was added *n*-butyllithium (1.45 M in hexane, 0.3 ml, 0.43 mmol) and lithium bromide (0.76 M in ether, 1.69 ml, 1.29 mmol) under argon atmosphere at -20°C in 30 minutes. After stirring for 50 minutes, the heteroolefin **22** (53.7 mg, 0.11 mmol) was added to this mixture and kept at -20°C overnight. The reaction was quenched with aqueous ammonium chloride and extracted with ether. The combined organic phase was dried (anhydrous sodium sulfate) and concentrated under reduced pressure. The crude oil in tetrahydrofuran (2 ml) was added tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 0.03 ml) at ambient temperature. After stirring for 1 hour, the usual workup gave crude oil, which was purified by silica gel preparative layer chromatography to afford the adduct, **24** (38.1 mg, 86%, *syn* : *anti* > 94 : 6). M.p. 180-2°C. IR (KBr) ν_{max} 3291, 2928, 2877, 1449, 1305, 1147, 1105, 1085, 1019 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.77 (m), 1.92 (m), 2.02 (1H, d, *J* = 2.5 Hz, acetylenic), 2.10 (1H, m), 3.18 (1H, m), 3.28 (1H, td, *J* = 10, 5 Hz, H-5), 3.39 (1H, dd, *J* = 14, 7.5 Hz, H-2'), 3.51 (1H, m), 3.53 (1H, dd, *J* = 14, 5 Hz, H-2'), 3.6-3.67 (1H, m), 3.67 (1H, t, *J* = 10 Hz, H-6), 4.16 (1H, dd, *J* = 10, 5 Hz, H-6), 5.5 (1H, s, acetal), 7.3-7.7 (8H, m, Ar), 7.9 (2H, d, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 27.6, 28.2, 31.9, 57.0, 69.1, 72.9, 73.6, 76.7, 77.8, 80.0, 101.7, 126.1, 128.2, 128.3, 129.0, 129.2, 133.9, 137.5, 139.4. $[\alpha]_D^{25}$ = +94.6° (*c* 0.51, CH_2Cl_2). Anal. calcd. for $C_{23}H_{24}O_5S$: C 66.97%; H 5.86%. Found: C 66.98%; H 5.85%.

2-α-Hydroxy-phenylthioacetylene, 26

To a solution of glycoside **25** (5.0 g, 15.0 mmol) and phenylthio(trimethylsilyl)acetylene (10 ml, 47.0 mmol) in dichloromethane (160 ml) was added trimetylsilyl trifluoromethanesulfonate (5.5 ml, 29.0 mmol) at 0°C. After stirring for 12 hours, the reaction mixture was poured into aqueous sodium hydrogen carbonate at 0°C and extracted with ether. The combined organic phase was concentrated under reduced pressure and filtered through silica gel to give crude oil (7.48 g). The crude oil was dissolved in methanol (40 ml) and mixed with cerium (III) chloride (15 mg, 0.04 mmol) and sodium borohydride (4.38 g, 0.116 mol, portionwise) at 0°C. After stirring for 3.5 hours, the reaction mixture was concentrated under reduced pressure and diluted with water (100 ml). The aqueous phase was extracted with ether and the combined organic layer was evaporated. The residue was purified by silica gel chromatography (CH_2Cl_2 / ether, 10:1, then 2:1) to afford yellow solid, **26** (3.35 g, 73%). IR (KBr) ν_{max} 3735, 1744, 1522 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 2.07 (3H, s, acetate), 2.5 (1H, OH), 4.15 (2H, d, *J* = 5 Hz, H-6), 4.39 (1H, m, H-5), 4.6 (1H, m, H-2), 5.10 (1H, d, *J* = 5.5 Hz, H-1), 5.7 (1H, d, *J* = 10 Hz, H-4), 5.92 (1H, d, *J* = 10 Hz, H-3), 7.32 (5H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 19.2, 20.8, 26.8, 65.4, 65.5, 68.3, 69.0, 73.5, 95.2, 125.7, 126.1, 126.4, 127.8, 127.8, 129.1, 129.9, 130.0, 131.0, 133.3, 135.7, 135.8, 170.8. $[\alpha]_D^{25}$ = -98.0° (*c* 0.33, CH_2Cl_2). Anal. calcd. for $C_{16}H_{16}O_4S$: C 63.14%; H 5.30%. Found: C 63.10%; H 5.19%.

2-α-*t*-Butyldiphenylsilyloxy-phenylthioacetylene, 27

A solution of **26** (1.91 g, 5.78 mmol) and imidazole (1.28 g, 18.8 mmol) in *N,N*-dimethylformamide (32 ml) was added *t*-butyldimethylchlorosilane (1.96 ml, 7.53 mmol) at ambient temperature. After stirring for 12 hours, the reaction mixture was quenched with aqueous sodium hydrogen carbonate. The aqueous layer was extracted with ether. The organic layer was dried (anhydrous sodium sulfate) and concentrated under

reduced pressure. The residue was purified by silica gel chromatography to give product, **27** (3.07 g, 98%). IR (KBr) ν_{max} 2929, 1583, 1472, 1256, 1111, 836 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.06 (9H, s, *t*-Bu), 2.02 (3H, s, acetate), 4.0 (1H, dd, *J* = 11.5, 7 Hz, H-6), 4.15 (1H, dd, *J* = 11.5, 4 Hz, H-6), 4.51 (1H, m), 4.6 (1H, m), 4.72 (1H, d, *J* = 6 Hz, H-1), 5.65 (1H, dt, *J* = 10.5, 2 Hz, H-4), 5.88 (1H, d, brd, *J* = 10 Hz, H-3), 7.40 (m, Ar), 7.70 (m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 19.2, 20.8, 26.8, 65.4, 65.5, 68.3, 69.0, 73.5, 95.2, 125.7, 126.1, 126.4, 127.77, 127.80, 129.1, 129.9, 130.0, 131.0, 133.3, 135.7, 135.8, 170.8. $[\alpha]_D^{27}$ = -6.19° (*c* 0.98, CH_2Cl_2). Anal. calcd. for $C_{32}H_{34}O_4SSi$: C 70.81%; H 6.31%. Found: C 70.80%; H 6.27%.

α-Dicobalthexacarbonyl complex, 28

A dark brown solution of dicobaltoctacarbonyl (1.41 g, 4.12 mmol) in degassed dichloromethane (5 ml) under argon atmosphere was added **27** (1.15 g, 2.12 mmol) in degassed dichloromethane (16 ml) at ambient temperature. The mixture was stirred for 2 hours and then concentrated. The residue was purified by silica gel chromatography (hexane / ether 10:1, then 3:1) to give brown oil **28** (1.62 g, 92%), which was not stable enough for analyses and was used for the next step.

β-Dicobalthexacarbonyl complex, 29

A solution of **28** (2.78 g, 3.35 mmol) in dichloromethane (213 ml) was degassed and added trifluoromethanesulfonic acid (1.0 M in $Cl_2FCCClF_2$, 0.96 ml) in 3 portions at ambient temperature. After stirring for 15 minutes, the reaction mixture was added aqueous sodium hydrogen carbonate (3 ml) and concentrated. The residue was purified by silica gel chromatography (hexane / CH_2Cl_2 10:1, then 1:1) to afford β–epimer **29** (1.76 g, 63%) and α-epimer, **28** (0.24 g, 9%). (total yield 72%, α : β 1:7.5), which was not stable enough for analyses and was used for the next step.

β-Phenylthioacetylene, 30

Compound **29** (1.64 g, 1.98 mmol) was dissolved in tetrahydrofuran (20 ml). Iodine (2.52 g, 19.4 mol) was added to this solution under nitrogen atmosphere at ambient temperature. After stirring for 12 hours, the mixture was quenched with aqueous sodium hydrogen carbonate and aqueous sodium sulfite. The aqueous layer was extracted with ether and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (hexane / ether 10:1, then 2:1) to give colorless oil, **30** (1.52 g, 98%). IR (KBr) ν_{max} 1749, 1560, 1540, 1507, 1231, 1113 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.05 (9H, s, *t*-Bu), 2.04 (3H, s, acetate), 4.04 (1H, d, brd, *J* = 7 Hz), 4.42 (3H, m), 5.55 (1H, d, brd, *J* = 10.5 Hz, H-3), 5.68 (1H, d, brd, *J* = 10.5 Hz, H-4), 7.36(m, Ar), 7.70(m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 19.3, 20.9, 26.8, 27.0, 65.7, 68.6, 71.0, 73.3, 74.0, 96.3, 125.8, 126.6, 126.8, 127.60, 127.65, 129.1, 129.75, 129.78, 131.5, 132.7, 133.9, 135.9, 136.1, 170.8. $[\alpha]_D^{25}$ = -30.1° (*c* 2.38, CH_2Cl_2). Anal. calcd. for $C_{32}H_{34}O_4SSi$: C 70.81%; H 6.31%. Found: C 70.61%; H 6.09%.

2-α-Hydroxy-β-phenylthioacetylene, 31

To a solution of **30** (1.0 g, 1.84 mmol) in tetrahydrofuran (18 ml) was added tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 1.8 ml) (pH = 6). After stirring for 1.5 hours, the mixture was quenched with aqueous sodium hydrogen carbonate. The aqueous layer was extracted with ether. The combined organic layer was dried (anhydrous sodium sulfate) and evaporated under reduced pressure. The residue was purified by silica gel chromatography (hexane / ether 4:1, then 1:1) to afford colorless oil, **31** (0.49 g, 87%). IR (KBr) ν_{max} 3735, 1742, 1236, 1071 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 2.09 (3H, s, acetate), 2.24 (1H, s, brd, O*H*), 4.15 (2H, d, *J* = 5.5 Hz, H-6), 4.31 (1H, d, *J* = 8.5 Hz, H-1), 4.34 (1H, m), 4.46 (1H, m), 5.75 (1H, dt, *J* =10, 1.5 Hz, H-4), 5.97 (1H, ddd, *J* = 10, 2.5, 1.5 Hz, H-3), 7.24 (1H, m, Ar), 7.35 (2H, m, Ar), 7.46 (2H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 20.9, 65.6, 67.4, 71.2, 73.4, 75.0, 95.3, 126.6, 126.9, 127.0, 129.3, 130.2, 131.7, 170.9. $[\alpha]_D^{27}$ = -72.7° (*c* 2.63, CH_2Cl_2). Anal. calcd. for $C_{32}H_{34}O_4SSi$: C 63.14%; H 5.30%. Found: C 63.10%; H 5.31%.

β-Vinylsulfide, 32

To a suspension of **31** (62.3 mg, 0.21 mmol) in 1,2-dichloroethane (4.1 ml), were added sodium hydrogen carbonate (137.6 mg, 1.64 mmol), triethylsilane (0.65 ml, 4.09 mmol) and sodium hexachloroplatinate (IV) hexahydrate (0.01 M in 2-propanol, 0.05 ml, 0.24 mol%) under argon atmosphere.

The reaction mixture was kept at 90°C for 3 hours and then cooled down. The solvent was removed by evaporation under reduced pressure with aspirator at 90°C. The residue was purified by silica gel preparative thin layer chromatography (hexane / ether 1:2) to afford colorless oil **32** (61.4 mg, 71%). IR (KBr) ν_{max} 2954, 2875, 1745, 1238, 1041 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 0.55 (6H, m, CH_3CH_2Si), 0.9 (9H, m, CH_3CH_2Si), 1.63 (1H, d, *J* = 7.5 Hz, O*H*), 2.1 (3H, s, acetate), 4.07 (1H, dd, *J* = 11.5, 4.5 Hz, H-6), 4.13 (1H, m), 4.16 (1H, dd, *J* = 11.5, 6 Hz, H-6), 4.28 (1H, m), 4.58 (1H, t, *J* = 8 Hz, H-1), 5.69 (1H, dt, *J* = 10, 1.5 Hz, H-4), 5.95 (dt, *J* =10, 2 Hz, H-3), 6.45 (1H, d, *J* = 8 Hz, H-1'), 7.26 (5H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 3.3, 7.3, 20.9, 65.9, 67.5, 72.8, 126.1, 127.1, 128.7, 129.3, 131.4, 136.4, 137.9, 148.0, 170.9. $[\alpha]_D^{27}$ = -1.92° (*c* 1.04, CH_2Cl_2). Anal. calcd. for $C_{22}H_{32}O_4SSi$: C 62.82%; H 7.67%. Found: C 62.80%; H 7.92%.

Dihydroxy-β-vinylsulfide, 33

To a solution of **32** (444.2 mg, 1.06 mmol) in methanol (21 ml) under nitrogen atmosphere at 0°C was added sodium methoxide (ca. 28%, 0.28 ml, 1.15 mmol). After stirring for 45 minutes the reaction mixture was neutralized with acidic ion exchange resin DOWEX 50W-X4 and filtered. The filtrate was concentrated and purified by silica gel chromatography (CH_2Cl_2 : ether 30 : 1, then 20:1) to afford colorless oil, **33** (379.8 mg, 95%). IR (KBr) ν_{max} 3300, 2954, 2875, 1583, 1479, 1440, 1116, 1057, 1003, 976 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 0.55 (6H, m, CH_3CH_2Si), 0.92 (9H, m, CH_3CH_2Si), 1.64 (1H, d, *J* = 7.5 Hz, O*H*), 1.92 (1H, t, *J* = 4.5 Hz, O*H*), 3.55 (1H, dd, *J* = 11, 6 Hz, H-6), 3.71 (1H, ddd, *J* = 11, 7.5, 3 Hz, H-6), 4.1 (1H, m), 4.19 (1H, m), 4.6 (1H, t, *J* = 8 Hz, H-1), 5.68 (1H, dt, *J* = 10, 1.5 Hz, H-4), 5.96 (1H, dt, *J* = 10, 2 Hz, H-3), 6.45 (1H, d, *J* = 8 Hz, H-1'), 7.25 (5H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 3.3, 7.2, 65.1, 67.7, 75.2, 76.8, 126.1, 127.5, 128.7, 129.3, 131.4, 136.4, 138.0, 148.1. $[\alpha]_D^{27}$ = +29.0° (*c* 1.35, CH_2Cl_2). Anal. calcd. for $C_{20}H_{30}O_3SSi$: C 63.45%; H 7.99%. Found: C 63.42%; H 7.70%.

2-α-Hydroxyl-β-vinylsulfide, 34

A solution of **33** (323.6 mg, 0.85 mmol), imidazole (291.5 mg) and *t*-butyldiphenylchlorosilane (256.6 mg) in *N,N*-dimethylformamide (17 ml) was kept stirring at ambient temperature for 13 hours and then quenched with aqueous sodium hydrogen carbonate. The aqueous layer was extracted with ether. The organic layer was dried by addition of benzene and by azeotropic evaporation. The crude oil was purified by silica gel chromatography to give pure product, **34** (495.4 mg, 94%). IR (KBr) ν_{max} 3735, 2956, 1595, 1473, 1302, 1144, 1085, 754 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 0.53 (6H, m, *J* = 7.5 Hz, CH_3CH_2Si), 0.88 (9H, t, *J* = 7.5 Hz, CH_3CH_2Si), 1.06 (9H, s, *t*-Bu), 1.6 (1H, d, *J* = 7.5 Hz, O*H*), 3.61 (1H, dd, *J* = 10, 6.5 Hz, H-6), 3.75 (1H, dd, *J* = 10, 6 Hz, H-6), 4.05 (1H, td, *J* = 8, 3 Hz, H-2), 4.19 (1H, m), 4.56 (1H, t, *J* = 8 Hz, H-1), 5.89 (2H, s, H-3, H-4), 6.43 (1H, d, *J* = 8 Hz, H-1'), 7.30 (m, Ar), 7.68 (m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 3.3, 7.3, 19.3, 26.8, 66.3, 67.8, 75.1, 76.8, 126.0, 127.6, 128.7, 128.9, 129.2, 129.6, 129.8, 133.5, 133.6, 135.6, 136.5, 136.9, 149.0. $[\alpha]_D^{27}$ = -26.2° (*c* 1.29, CH_2Cl_2). Anal. calcd. for $C_{36}H_{48}O_3SSi_2$: C 70.08%; H 7.84%. Found: C 70.01%; H 7.70%.

2-α-Hydroxy-β-heteroolefin, 35

To a suspension of **34** (495.0 mg, 0.80 mmol) and sodium hydrogen phosphate (797.2 mg) in dichloromethane (16 ml) was added *m*-chloroperbenzoic acid (363.4 mg) portionwise at 0°C. After stirring for 20 minutes the reaction mixture was quenched with aqueous sodium hydrogen carbonate and aqueous sodium sulfite (examined with KI-starch paper to confirm no more peroxide). The aqueous layer was extracted with ether. The organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration under reduced pressure and purification by silica gel chromatography (hexane : ether 10 : 1, then 5 : 2) afforded colorless oil, **35** (466.2 mg, 90%). IR (KBr) ν_{max} 3443, 2656, 2876, 1559, 1540, 1508, 1473, 1458, 1447, 1428, 1289, 1144, 1113 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 0.7 (6H, m, CH_3CH_2Si), 0.87 (9H, t, *J* = 7.5 Hz, CH_3CH_2Si), 1.04 (9H, s, *t*-Bu), 3.10 (1H, brd, O*H*), 3.60 (1H, dd, *J* = 10, 5.5 Hz, H-6), 3.69 (1H, dd, *J* = 10, 5.5 Hz, H-6), 3.99 (1H, d, *J* = 9 Hz, H-2), 4.13 (1H, m, H-5), 5.03 (1H, t, *J* = 9 Hz, H-1), 5.79 (1H, dt, *J* = 10,1.5 Hz, H-4), 5.97 (1H, dt, *J* = 10, 2 Hz, H-3), 6.48 (1H, d, *J* = 9 Hz, H-1'), 7.3-7.9 (15H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 3.1, 6.9, 19.3, 26.7, 66.2, 66.7, 75.2, 75.3, 126.8, 127.2, 127.6, 129.1, 129.7, 131.1, 133.1, 133.4, 133.5, 135.57, 135.63, 142.1, 144.7, 154.0.

$[\alpha]_D^{25}$ = -18.9° (*c* 1.71, CH_2Cl_2). Anal. calcd. for $C_{36}H_{48}O_5SSi_2$: C 66.62%; H 7.45%. Found: C 66.60%; H 7.50%.

2-α-Trimethylsilyloxy-β-heteroolefin, 36

To a solution of **35** (21.7 mg, 0.033 mmol) and triethylamine (0.5 ml) in tetrahydrofuran (1 ml) was added trimethylchlorosilane (0.06 ml) at ambient temperature. The mixture was stirred for 15 minutes and then concentrated under reduced pressure. The residue was purified by silica gel preparative thin layer chromatography (hexane : ether 1 : 1) to afford product, **36** (24.0 mg, 100%). IR (KBr) ν_{max} 2957, 2876, 1428, 1304, 1252, 1145, 1113 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 0.18 (9H, s, CH_3Si), 0.7 (6H, m, CH_3CH_2Si), 0.83 (9H, m, CH_3CH_2Si), 1.05 (9H, s, *t*-Bu), 3.50 (1H, dd, *J* = 10, 6 Hz, H-6), 3.65 (1H, dd, *J* = 10, 5 Hz, H-6), 4.07 (2H, m, H-2, H-5), 4.96 (1H, dd, *J* = 9, 8 Hz, H-1), 5.78 (1H, d, *J* = 11 Hz, H-4), 5.86 (1H, d, *J* = 11 Hz, H-3), 6.37 (1H, d, *J* = 9 Hz, H-1'), 7.36 (m, Ar), 7.64 (m, Ar), 7.92 (2H, d, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 0.4, 3.3, 7.1, 19.3, 26.7, 66.0, 68.7, 72.8, 75.2, 127.2, 127.6, 128.3, 128.7, 129.60, 129.65, 130.3, 132.5, 133.5, 133.6, 135.6, 143.1, 148.1, 153.3. $[\alpha]_D^{27}$ = -122.4° (*c* 0.165, CH_2Cl_2). Anal. calcd. for $C_{39}H_{56}O_5SSi_3$: C 64.95%; H 7.83%. Found: C 64.85%; H 7.74%.

***anti*-Methyl adduct, 37**

Compound **35** (10.3 mg, 0.016 mmol) in tetrahydrofuran (1 ml) under nitrogen atmosphere was added methylmagnesium bromide (1.0 N in THF, 0.07 ml) at ambient temperature. The reaction mixture was stirred for 20 hours and then quenched with aqueous sodium hydrogen carbonate. The aqueous layer was extracted with ether. The combined organic layer was concentrated and purified by silica gel preparative thin layer chromatography (hexane : ether 2 : 3) to give crude oil (8.0 mg). The addition product in methanol (0.5 ml) was added potassium fluoride (10 mg). After stirring overnight the mixture was quenched with aqueous ammonium chloride and extracted with ether. The combined organic layer was concentrated and purified by silica gel preparative thin layer chromatography (hexane : ether 2 : 3) to afford product, **37** (5.4 mg, 72%). IR (KBr) ν_{max} 3444, 2931, 2858, 1428, 1305, 1148, 1113, 1086 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.08 (9H, s, *t*-Bu), 1.16 (3H, d, *J* = 7 Hz, CH_3), 2.45 (1H, d, *J* = 8 Hz, O*H*), 2.67 (1H, m, H-1), 2.83 (1H, dd, *J* = 15, 6 Hz, H-2'), 3.4 (1H, dd, *J* = 15, 4 Hz, H-2'), 3.58 (1H, dd, *J* = 10, 5 Hz, H-6), 3.63 (1H, dd, *J* = 10, 6 Hz, H-6), 4.06 (1H, m, H-2), 4.22 (1H, m, H-5), 5.80 (1H, d, brd, *J* = 11 Hz, H-4), 5.84 (1H, d, brd, *J* = 11 Hz, H-3), 7.37 (m, Ar), 7.6 (m, Ar), 7.9 (2H, d, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 18.7, 19.2, 26.7, 28.5, 57.4, 64.5, 66.2, 76.2, 81.4, 127.57, 127.62, 127.9, 128.4, 129.4, 129.6, 130.5, 133.4, 133.5, 133.7, 135.5, 135.6, 139.5. $[\alpha]_D^{27}$ = -51.3° (*c* 0.78, CH_2Cl_2). Anal. calcd. for $C_{31}H_{38}O_5SSi$: C 67.60%; H 6.95%. Found: C 67.42%; H 6.92%.

***anti*-Acetylenic adduct, 38**

A solution of trimethylsilylacetylene (25.4 mg) in hexane (0.5 ml) and ether (0.5 ml) under nitrogen atmosphere was added *n*-butyllithium (1.45 M in hexane, 0.18 ml) at 0°C. The mixture was stirred for 15 minutes and then added **35** (17.7 mg, 0.027 mmol) in hexane (1.5 ml). After stirring for 1.5 hours the reaction mixture was quenched with aqueous ammonium chloride and extracted with ether. The combined organic layer was concentrated and purified by silica gel preparative thin layer chromatography (hexane : ether 1 : 1) to afford addition product (19.1 mg). The crude oil in methanol (1 ml) was subjected to potassium fluoride (20 mg) for 3.5 hours. Similar workup afforded acetylenic product, **38** (14.5 mg, 95%). ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.02 (9H, s, *t*-Bu), 2.09 (1H, d, *J* = 2 Hz, acetylenic), 2.51 (1H, d, *J* = 5.5 Hz, O*H*), 3.32 (1H, m, H-1'), 3.38 (1H, m), 3.46 (1H, dd, *J* = 8, 5.5 Hz, H-1), 3.56 (1H, d, *J* = 10, 6 Hz, H-6), 3.66 (m), 4.23 (2H, m, H-2, H-5), 5.79 (1H, d, brd, *J* = 10 Hz, H-4), 5.86 (1H, d, brd, *J* = 10 Hz, H-3), 7.5 (13H, m, Ar), 7.9 (2H, d, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 19.2, 26.7, 30.2, 56.7, 65.9, 66.1, 72.8, 75.9, 78.7, 81.5, 127.7, 128.3, 128.6, 129.2, 129.7, 133.3, 133.9, 135.6. $[\alpha]_D^{27}$ = -45.7° (*c* 1.29, CH_2Cl_2). Anal. calcd. for $C_{32}H_{36}O_5SSi$: C 68.54%; H 6.47%. Found: C 68.50%; H 6.52%.

***syn*-Methyl adduct, 39**

Compound **36** (7.3 mg, 0.010 mmol) in hexane (1 ml) under nitrogen atmosphere was added lithium bromide (0.5 M in ether, 0.24 ml, 0.12 mmol) at -20°C, followed by addition of methyllithium (1.5 M in ether as complex with lithium bromide, 0.013 ml). The mixture was stirred for 10 minutes and then quenched with aqueous ammonium chloride. The aqueous layer was extracted with ether. The combined organic layer

was concentrated under reduced pressure and purified by silica gel preparative thin layer chromatography (hexane : ether 1 : 1) to give addition intermediate (5.8 mg). The crude oil in methanol (0.5 ml) was subjected to potassium fluoride (10 mg) for 12 hours. Similar workup afforded product, **39** (4.0 mg, 73%). IR (KBr) ν_{max} 3460, 2930, 2858, 1428, 1305, 1148, 1113, 1085 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.02 (9H, s, *t*-Bu), 1.05 (3H, d, *J* = 7 Hz, C*H*$_3$), 1.35 (1H, d, *J* = 5.5 Hz, O*H*), 2.67 (1H, qd, *J* = 6.5, 2.5 Hz, H-1'), 3.04 (1H, dd, *J* = 14.5, 6 Hz, H-2'), 3.41 (1H, dd, *J* = 9, 2.5 Hz, H-1), 3.44 (1H, dd, *J* = 14.5, 6.5 Hz, H-2'), 3.58 (1H, dd, *J* = 10, 5 Hz, H-6), 3.66 (1H, dd, *J* = 10, 6 Hz, H-6), 4.08 (1H, m), 4.14 (1H, m), 5.81 (2H, s, H-3, H-4), 7.4 (m, Ar), 7.6 (m, Ar), 7.9 (2H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 13.6, 19.2, 26.7, 29.3, 59.8, 64.5, 66.1, 76.1, 80.0, 127.6, 127.9, 129.0, 129.3, 129.7, 130.3, 133.5, 133.6, 135.6. $[\alpha]_D^{27}$ = -69.4° (*c* 0.48, CH_2Cl_2). Anal. calcd. for $C_{31}H_{38}O_5SSi$: C 67.60%; H 6.95%. Found: C 67.55%; H 6.80%.

syn-Acetylenic adduct, 40

A solution of (trimethylsilyl)acetylene (15.8 mg, 0.16 mmol) in hexane (0.5 ml) under argon atmosphere was added *n*-butyllithium (1.45 M in hexane, 0.11 ml, 0.16 mmol) at -20°C, followed by addition of lithium bromide (0.5 M in ether, 0.39 ml, 0.19 mmol) and stirred for 30 minutes. A solution of **36** (11.6 mg, 0.016 mmol) in hexane (1.5 ml) was then added to above acetylide solution. The reaction mixture was stirred for further 40 minutes and then quenched with aqueous ammonium chloride. The aqueous layer was extracted with ether. The combined organic layer was concentrated under reduced pressure and filtered through silica gel to afford crude oil (9.0 mg). The crude oil in methanol (1 ml) was subjected to potassium fluoride (30 mg) for 10 hours. Usual workup and purification by silica gel preparative thin layer chromatography (hexane : ether 1 : 1) afforded acetylenic product, **40** (8.0 mg, 89%). IR (KBr) ν_{max} 3454, 3289, 2929, 2857, 1448, 1428, 1308, 1144, 1113, 1086 cm^{-1}. ^{1}HNMR ($CDCl_3$, 270 MHz), δ 1.08 (9H, s, *t*-Bu), 1.65 (1H, d, *J* = 7.5 Hz, O*H*), 1.99 (1H, d, *J* = 2.5 Hz, acetylenic), 3.48 (m), 3.51 (1H, dd, *J* = 13, 6 Hz, H-2'), 3.59 (m), 3.61 (1H, dd, *J* = 10.5, 5.5 Hz, H-6), 3.70 (1H, dd, *J* = 10.5, 5.5 Hz, H-6), 4.16 (1H, m, H-5), 4.37 (1H, m, H-2), 5.84 (2H, s, H-3, H-4), 7.3-7.7 (13H, m, Ar), 7.9 (2H, m, Ar). ^{13}CNMR ($CDCl_3$, 67.5 MHz), δ 19.2, 26.7, 28.9, 56.9, 65.3, 65.9, 72.7, 76.2, 77.5, 78.3, 127.6, 127.7, 128.3, 128.8, 129.3, 129.6, 129.8, 133.4, 133.8, 135.6, 135.7, 139.4. $[\alpha]_D^{27}$ = -31.6° (*c* 0.32, CH_2Cl_2). Anal. calcd. for $C_{32}H_{36}O_5SSi$: C 68.54%; H 6.47%. Found: C 68.48%; H 6.44%.

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