Studies on the Mercury-Desilylation of Chiral Cyclopropylmethylsilanes – A Stereocontrolled Access to Carba-Sugars

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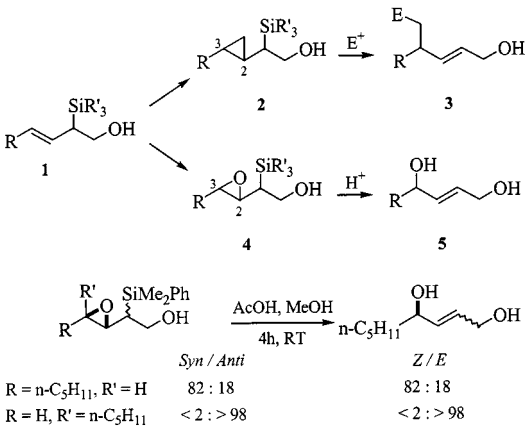
Mercury-desilylation of cyclopropylmethylsilanes affords a stereospecific access to homoallylic mercury intermediates, which can be elaborated further. This strategy is illustrated with a short access to carba-furanoses and carba-C-disaccharides.

Introduction

During the course of our studies on the epoxidation and cyclopropanation of acyclic 2-silyl-3-alkenols **1**, we have experienced unexpected problems with the determination of the stereochemistry of the cyclopropyl- and epoxysilanes **2** and **4** (Scheme 1).[1] ^{1}H NMR afforded no decisive information regarding the relative configuration between C2 and C3 and we were also unable to produce suitable crystals of **2** and **4** (as well as derivatives) for X-ray structure determination. It was thus decided to convert **2** and **4**, using a transformation of known stereochemical course, into compounds whose structure would be more amenable to ^{1}H-NMR structure determination. We thus showed that the acid-catalyzed Peterson-like ring opening of epoxides **4**[2] afforded stereospecifically the corresponding homoallylic alcohols **5** in high yields. We then reasoned that the analogous cyclopropylmethylsilanes **2** might behave similarly in the presence of electrophiles (E^+), affording stereospecifically the olefin **3**. The opening of small rings such as cyclopropanes under electrophilic conditions is usually easy, owing to the release of the angle strain energy (ca. 30 kcal mol^{-1}).[3] While the epoxymethylsilanes opened regio- and stereospecifically, previous studies indicated that the same process with cyclopropylmethylsilanes was not so clear-cut.[4] Moreover, the presence, in our case, of a β-hydroxysilyl moiety, prone to Peterson elimination,[5] represented an additional problem.

After many unsuccessful attempts, it was finally found that mercury salts efficiently mediated the ring-opening with concomitant desilylation in a stereospecific fashion and with excellent regiocontrol.[6] This method constitutes an efficient stereocontrolled SE′$_2$ alkylation of allylsilanes, since the mercury derivatives **3** (E = HgBr) can be functionalized further using radical or organometallic processes.[7] We describe here a full account of these studies and the extension of the strategy to the cyclopropanations of cyclic 2-silyl-3-alkenols and the ring-opening of their cyclopropane. The utility of this methodology is further illustrated with a short and stereocontrolled access to carba-sugars and carba-C-disaccharides.



Scheme 1

Results and Discussion

Cyclopropanation of Acyclic Allylsilanes

The cyclopropanation of acyclic 2-silyl-3-alkenols **1a−d** was carried out using Furukawa[8] conditions (CH_2I_2, $ZnEt_2$ in CH_2Cl_2) affording the desired cyclopropanes **2a−d** in good yields and with excellent diastereoselectivities (Scheme 2, Table 1). **2a−d** were assigned the *anti*-configurations as will be demonstrated below. It is noteworthy that no Peterson elimination was observed under these acidic conditions. The high level of stereocontrol was rationalized invoking a chair-like transition state such as **A** (Figure 1), where the sterically-demanding silicon group occupies a pseudo-equatorial position to minimize $A_{1,3}$ interactions.[9] Steric interactions between R and R′ and the ligands at the zinc centre (including iodine) probably prevent the cyclopropanation of (*E*)-olefin to proceed through conformation **B**, explaining the absence of the *syn*-isomer in this reaction. In the meantime, we also prepared the cyclopropanes **2e−f** lacking the OH group at C-1.[10] As reported in the litera-

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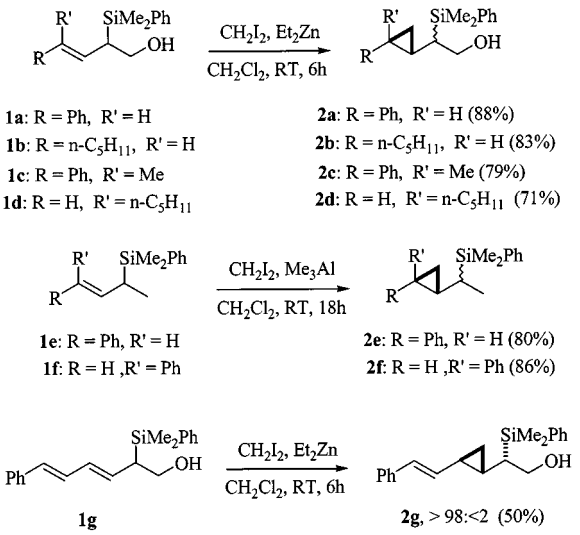
ture, the (*Z*)-olefin **1f** afforded solely the *anti* diastereomer **2f** while the (*E*)-isomer **1e** gave a mixture of the *syn* and *anti* diastereomers **2e** in a 1:1 ratio (Scheme 2).[10] Such a difference of diastereofacial selectivity between closely-related **1a−b** and **1e** may be attributed to the directing effect of the homoallylic hydroxy group in **1a−b** and the absence of such an effect in **1e.**[11] This supports the hypothesis of an internal delivery of the zinc-carbenoid in **1a−b** through conformation **A**. This hypothesis was further supported by the cyclopropanation of the acetate and the silyl ether ($SiPh_2tBu$) derivative of **1a** which both provided the Peterson elimination products and no trace of cyclopropane. Finally, cyclopropanation of the dienylsilane **1g** under the same conditions as above led to the mono-cyclopropanation product **2g** in moderate yield, but with complete diastereocontrol.



Scheme 2

Table 1. Cyclopropanation of allylsilanes **1a−f** (Scheme 2)

Entry	Allylsilane	R	R′	*anti*/*syn*[a]	Yield [%][b]
1	**1a**	Ph	H	93:7	88
2	**1b**	*n*-C_5H_{11}	H	>98:2	83
3	**1c**	Ph	Me	>98:2	79
4	**1d**	H	*n*-C_5H_{11}	>98:2	71
5	**1e**	Ph	H	50:50	80
6	**1f**	H	Ph	>98:2	86

[a] Estimated from ^{1}H NMR (400 MHz) and GC of the crude reaction mixture. − [b] Isolated yields after purification through column chromatography.

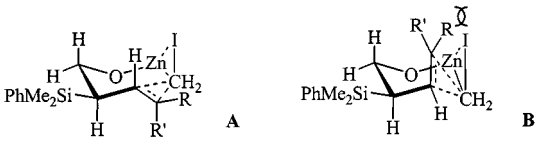
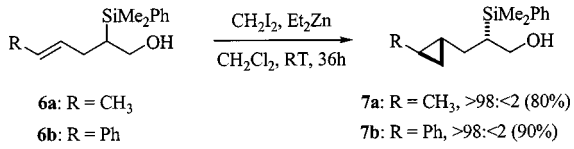


Figure 1

moallylsilanes **6a−b** have also been treated using Furukawa[8] conditions and led to the expected cyclopropanes **7a−b** in good yields but, more surprisingly, with excellent diastereoselectivities (Scheme 3). It is worthy of note that **6a−b** react much slower than the corresponding allylsilanes (36 h vs. 6 h). The directing effect of a bishomoallylic OH group is likely to be less effective than that of a homoallylic group.[11] However, the high level of diastereocontrol is indicative of such an effect. Therefore, it is reasonable to assume that similarly to **2a−g**, cyclopropanes **7a−b** possess a C2−C4 *anti*-configuration and have been formed through the chair-like transition state **C** (Figure 2).[11] As above, the bulky silicon group occupies a pseudo-equatorial position and the zinc reagent linked to the alcohol group delivers the methylene group on the *Si*-face of the olefin. An open transition state similar to that proposed recently for the hydroboration of closely-related homoallylsilanes[12] has been precluded owing to the much higher diastereocontrol observed in our case. As a comparison, hydroboration of the homoallylsilane analogue of **6a** lacking the bishomoallylic OH group led to the corresponding addition product in a 75:25 *syn*/*anti* ratio.[12]



Scheme 3

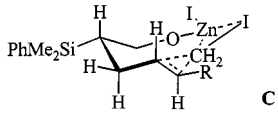
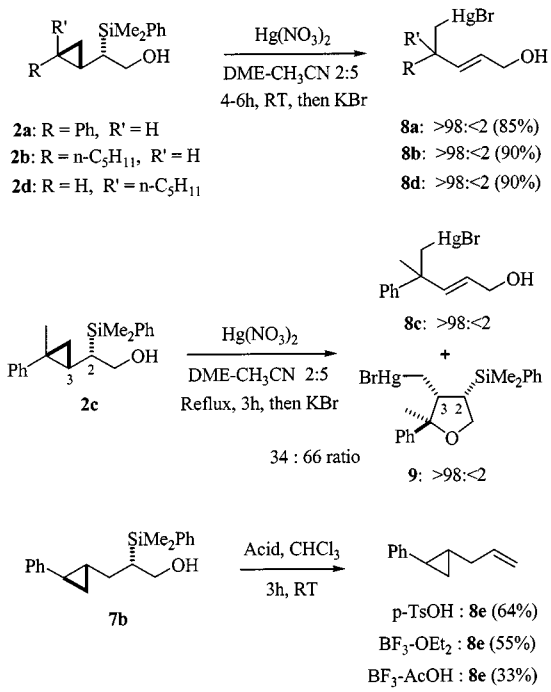


Figure 2

Our first attempts to selectively open cyclopropanes **2a−d** with concomitant desilylation were carried out using various electrophiles such as thallium salts,[13] halogens (I_2, Br_2, NIS)[14] as well as Lewis acids ($BF_3 \bullet Et_2O$).[15] All these conditions were found unsuitable and produced complex mixtures. Much better results were obtained using Collum conditions,[16] i.e. $Hg(NO_3)_2$ in a 5:2 CH_3CN/DME mixture, followed by addition of aqueous KBr. The expected olefins **8a−b** and **8d** were thus isolated in good yields. ^{1}H-NMR studies unambiguously showed that they all possess the (*E*)-stereochemistry with selectivity as high as 98:2, whatever the original configuration of the allylsilane precursors **1** (Scheme 4). Interestingly, the cyclopropane **2c** having a quaternary carbon centre afforded, under the same conditions, a mixture of the (*E*)-olefin **8c** and a tetrahydrofuran **9** as a unique diastereomer with the stereochemistry as shown (determined using difference nOe experiments). We assumed that the stereochemistry at C2 and C3 centres is conserved during the *5-endo-trig* like cyclization[17] leading to **9**, which supports the *anti* configuration for cyclopropane **2c**. The homologous cyclopropanes **7a−b** were treated similarly but gave rise to a mixture of products,

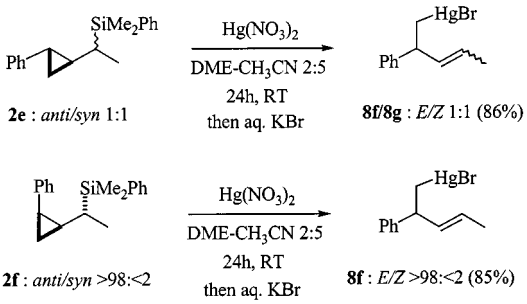
whose structures were tentatively given that of tetrahydrofurans, presumably a result of a *5-exo-trig* cyclization.[18] The attempts to separate the different isomers failed owing to the sensitivity of these mercury derivatives towards silica. Similar results were obtained when we tried to oxidize or reduce the C−HgBr bond. Finally, *p*TsOH, BF_3 • AcOH, or BF_3 • Et_2O treatment of **7b** led only to the Peterson elimination product **8e**.



Scheme 4

The stereochemistry of **9** is the first evidence that cyclopropanes **2** possess a C2−C3 *anti* configuration. However, as the stereochemistry of the electrophile mediated cyclopropane ring-opening had never been addressed before, no definitive conclusion could be drawn. Therefore, it was decided to further investigate the stereochemistry of this reaction, starting from precursors of known stereochemistry, i.e. the *anti*-cyclopropanes **2f** and the *syn-anti* mixture **2e.**[10] We thus observed that treatment of **2f**, under the same conditions as above, produced exclusively the (*E*)-olefin **8f**, whereas the 1:1 mixture of **2e** led to an equimolar amount of (*E*)- and (*Z*)-olefin **8f−g** (determined using ^1H NMR) (Scheme 5). This clearly indicates that similarly to the acid-catalysed Peterson elimination,[5] the mercury-desilylation of cyclopropylmethylsilanes is *anti*-stereospecific. Consequently, cyclopropanes **2a−f** could be assigned the *anti* configuration.

An independent proof of the stereochemistry of **2a−f** was provided by the series of experiments below (Scheme 6). Treatment of the cyclopropanes **11a−c** under the same conditions as above provided the corresponding tetrahydrofurans **12a−c** in good overall yield and with excellent stereocontrol. The stereochemistry of **12a−c** was determined through difference nOe and NOESY experiments. As the relative configuration at C2 and C3 should be retained dur-



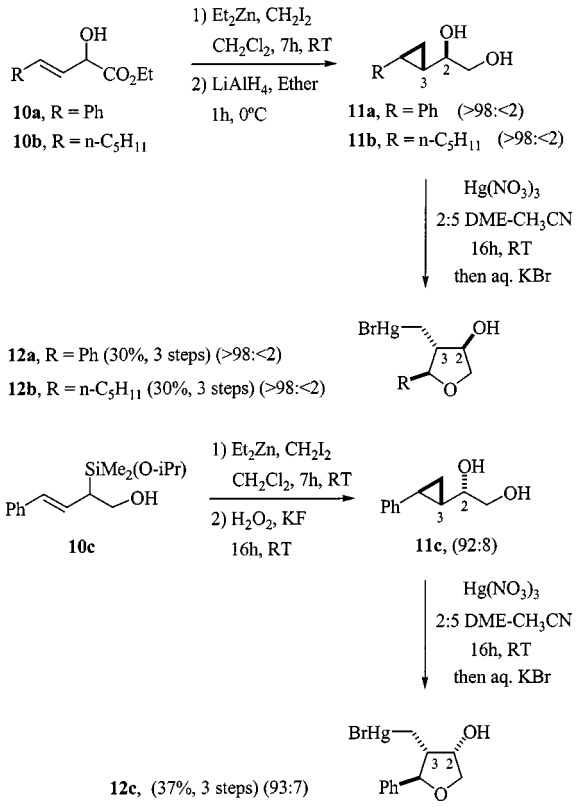
Scheme 5

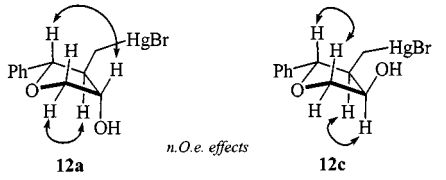
ing the *5-endo-trig* like process, the stereochemistry of the precursors **11a−c** was thus well secured. Therefore, if one assume that the oxidation of the C−Si bond occurs with retention of configuration,[19] then cyclopropanation of allylsilanes **10c** (and **1a−f**) led to products having the *anti* configuration. Cyclopropanation of the analogous allylic alcohols **10a−b** provided *syn* cyclopropanes through the well documented hydroxy-directed effect,[11] further supporting our hypothesis. The complete reversal of regioselectivity observed during ring opening of cyclopropylmethyl alcohols **11a−c**, relative to their silyl analogues is worthy of note and provides a stereospecific access to polysubstituted tetrahydrofurans.

The results above have demonstrated that our mercury-desilylation is a much more regioselective process than the Lewis acid mediated ring opening of silylcyclopropylmethylsilanes reported in the literature.[4] Such a selectivity can be tentatively rationalized as illustrated in Figure 3. The mercury-desilylation of cyclopropanes **2a−b** and **2d−f** is thought to occur through path *a*, which involves the stabilization of a nascent positive charge developing at the β-position relative to the silicon group during the C2−C3′ bond-breaking (β-silicon effect).[20] Alternatively, if the cyclopropane possesses both a quaternary carbon centre at C3 and substituents which are able to stabilize such a native positive charge (as in **2c**), then a reversal of the regioselectivity may be operative through path *b.*[17] The *5-endo-trig* cyclization process illustrated by **E** thus becomes predominant, leading to the tetrahydrofuran (i.e. **9**). This route is the only one observed with cyclopropylmethyl alcohols **11a−c** and it is noticable that the choice of the R group in **11a−c** is not restricted to aromatic groups (i.e. **11b**). Finally, the *stereospecificity* of the process may be explained assuming a conformation such as **D**, where both the C2−C3′ and the C−Si bonds, which are breaking, are in an *antiperiplanar* arrangement. Such a conformation thus resembles that generally accepted for acid-catalysed Peterson elimination.

Cyclopropanation of Cyclic Allylsilanes − Access to Carba-Sugars

Having demonstrated in acyclic series that the mercury-desilylation of cyclopropylmethylsilanes was regioselective and led to the desired homoallylic derivatives in high yield,





Scheme 6

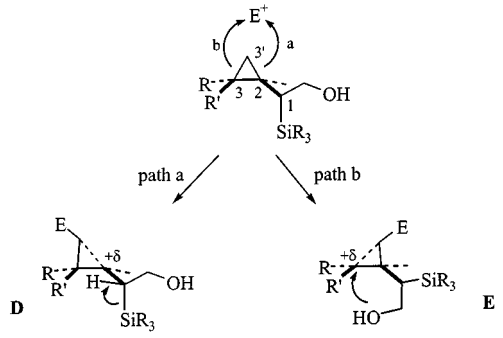
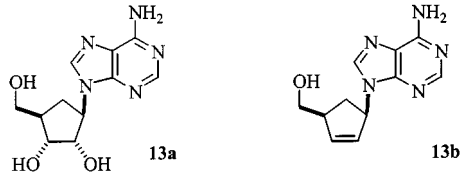
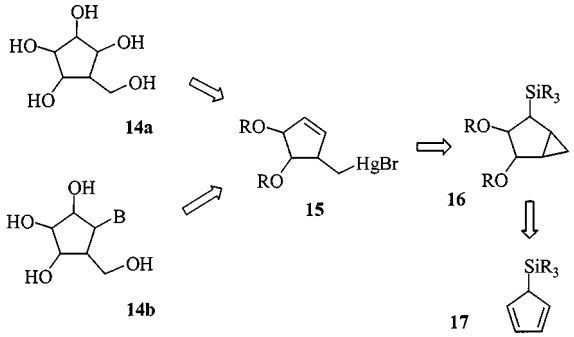


Figure 3

we then planned to extend such a strategy to cyclic series. One of our final goals was to devise a regio- and stereocontrolled access to carba-furanoses, carba-nucleosides as well as carba-C-disaccharides. Natural nucleosides and analogues have been extensively studied owing to their antiviral, antifungal, and anticancer activities.[21] However, deactivation of these substrates through phosphorylase-mediated cleavage of the *N*-glycosidic bond have hampered the utilization of such compounds for chemotherapeutic uses.[22] A better resistance to this enzymatic degradation is usually observed with the carba analogues lacking the anomeric centre.[23] Natural aristeromycin **13a**[21a] and synthetic anti-HIV agent carbovir **13b**[21a] are poor substrates for the phosphorylases and are effectively more active than their oxygenated counterparts (Scheme 7). Similar trends are observed with carba-sugars and their homologues, the carba-disaccharides.[24] These biologically relevant targets have thus been the subject of intense synthetic research.[25] Our approach would offer a new and flexible access to such targets and analogues **14a−b** as well as carba-C-disaccharides starting from readily-available cyclopentadienylsilanes **17** following the disconnection illustrated in Scheme 8. Our route involves a mercury-desilylation of the cyclopropylmethylsilane **16**, itself available through cyclopropanation and dihydroxylation of **17**. The common intermediate to all targets would be the homoallylic mercury substrate **15**, which should be easy to functionalize further.



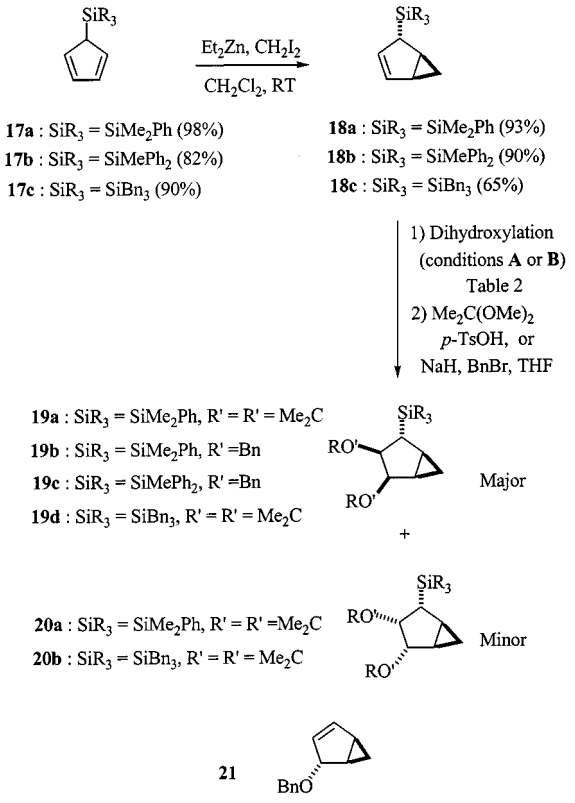
Scheme 7



Scheme 8

Cyclopentadienylsilanes **17a−c** were easily prepared in high yields through lithiation (*n*BuLi, −78°C) of cyclopentadiene and silylation with the suitable chlorosilanes (Scheme 9). It is worthy of note that using this protocol, dienylsilanes **17a−c** were obtained almost free of the isomeric vinylsilanes[26] and were used in the next step without further purifications. Cyclopropanation of **17a−c** using Furukawa conditions proceeded in high yields, leading exclusively to the *anti*-isomers **18a−c**. The remaining double bond of **18a−c** was then dihydroxylated using either Sharpless-AD conditions[27] (conditions **A**, Table 2) in which the chiral ligand was replaced by the achiral amine $Et(iPr)_2N$ or the usual OsO_4-NMMO protocol[28] (conditions **B**, Table 2). The reaction did proceed faster and with better yields using biphasic conditions **A**. The level of diastereocontrol was good with $PhMe_2Si$ and Ph_2MeSi but dropped dramatically when increasing the steric bulk at silicon, which

contrast with the observations made during the cyclopropanation and dihydroxylation of the analogous cyclohexadienylsilanes.[29] This can be rationalised invoking the conformation of the cyclopropane **18a–c**, where the cyclopropane ring is nearly perpendicular to the plane of the cyclopentene (Figure 4). Therefore, both diastereotopic faces are not so well-differentiated (as compared with those of the corresponding 6-membered ring) and the osmium reagent experience large steric interactions with both the silicon group and one hydrogen of the cyclopropane ring. Surprisingly, the use of a bulkier silicon group led to no diastereoselectivity at all. The moderate overall yield observed in entry 2 and 3 (Table 2) arise from the decomposition of the minor isomer (having the OH groups *syn* relative to the silicon group) through a base-catalyzed Peterson elimination[5] during the protection of the diol using NaH-BnBr. No trace of the *syn* isomer could be found when it was present in the crude dihydroxylation mixture. The elimination product **21** was isolated instead. On the contrary, protection of the diols as acetonides was carried out in acidic conditions and afforded a mixture of the *anti* (major) and *syn* (minor) isomers which could be separated through column chromatography (i.e. **19a**/**20a**, **19d**/**20b**).



Scheme 9

The cyclopropanes were then subjected to mercury-desilylation as described in the acyclic series. Treatment of **19a–c** with $Hg(NO_3)_2$ yielded the mercury derivatives **22a–b** in good yields, which were then converted into the corresponding alcohols **23a–b** using $NaBH_4$ in DMF under a saturated oxygen atmosphere (Scheme 10).[30] It is

Table 2. Dihydroxylation of cyclopropylsilanes **18a–d** (Scheme 9)

Entry	Substrate	Product[a]	Conditions[b]	*syn*/*anti*[c]	Yield [%][d]
1	**18a**	**19a**	**A**	8:2	60
2	**18a**	**19b**	**A**	9:1	42
3	**18b**	**19c**	**B**	9:1	40
4	**18c**	**19d**	**B**	1:1	33

[a] Major isomer. – [b] Conditions **A**: $K_2OsO_4 \cdot 2\,H_2O$, K_2CO_3, $K_3Fe(CN)_6$, $Et(iPr)_2N$, $tBuOH/H_2O$ 1:1, $CH_3SO_2NH_2$, room temp., 3d; Conditions **B**: OsO_4, NMMO, acetone/H_2O 9:1, room temp., 7–16 h. – [c] *syn*/*anti* refers to the relative stereochemistry between the diol and the silicon group. Ratio estimated from ^1H NMR (400 MHz) of the crude dihydroxylation mixture. – [d] Isolated yield of the major isomer (2 steps) after chromatography.

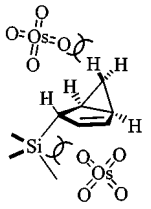
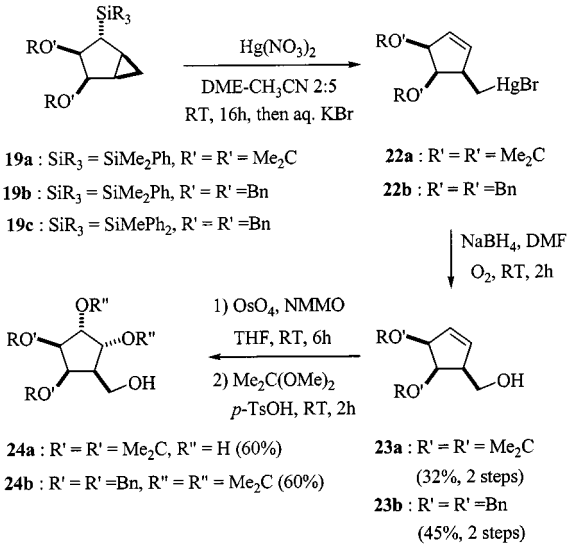


Figure 4

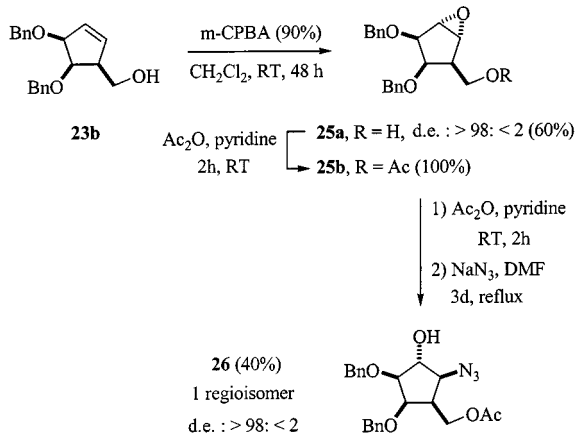
worth noticing that under the same conditions, the minor cyclopropane stereoisomer **20a** led to a complex mixture. Finally, **23a** was osmylated giving the desired diol **24a** as a unique diastereomer. Similarly, **23b** afforded a unique diol which was directly converted into its acetonide **24b**. In both cases, the osmylation occurred *anti* relative to the three substituents already on the ring. This simple route thus provides a ready access to racemic carba-sugars having 5 contiguous stereogenic centres, in only 6 steps from cyclopentadiene.



Scheme 10

This approach is also flexible and should allow for the introduction of various heteroatoms on the 5-membered ring. This was demonstrated as illustrated in Scheme 11. The homoallylic alcohol **23b** was epoxidized using *m*-CPBA

(90% after recrystallization from CH_2Cl_2) affording the epoxide **25a** as a unique diastereomer. nOe experiments unambiguously showed that the epoxidation took place *anti* relative to the three substituents and that the directing effect of the homoallylic OH group was not operative (Figure 5). **25a** was then acetylated and the epoxide opened using NaN_3 in DMF. The resulting azide **26** was obtained in a moderate yield but as a single regio- and diastereomer, thus opening a route to the synthesis of the corresponding carba-nucleoside analogues of *aristeromycin* **13a**. nOe experiments were used to establish unambiguously the structure of **26**, which showed that the N_3^- group prefers to approach away from the benzyloxy groups (Figure 5). Another route to carba-nucleoside precursors involving the conversion of the triol **24a** into the corresponding sulfate and subsequent nucleophilic displacement with adenine was attempted but led essentially to the recovery of the sulfate.



Scheme 11

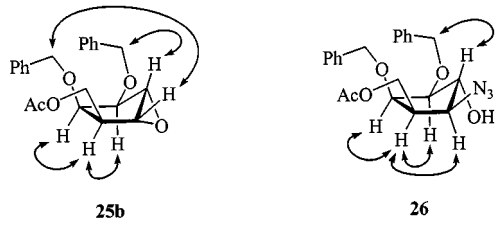
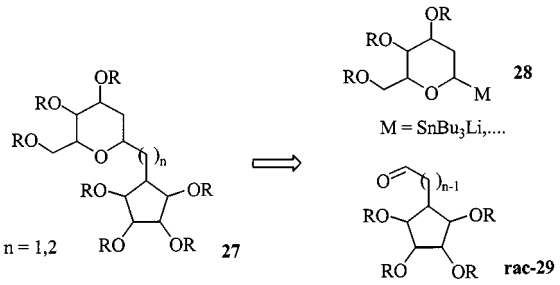


Figure 5

Preparation of Carba-C-Disaccharides

Carba-C-disaccharides have received a great deal of attention recently, owing to their potent glycosidases and glycosyltransferases inhibitory activity.[31] Recent reports suggest that better level of inhibition of the glycosidase activity should be attained using inhibitors mimicking both the glycon and the aglycon moieties.[31] Numerous approaches to carba-disaccharides and carba-C-glycosides have thus been devised,[25] leading to various types of disaccharides, but as far as we know, none of them contain a carba-furanose skeleton. We therefore initiated a study on the preparation of carba-C-disaccharides **27** possessing a sugar-pyranose moiety and a 5-membered ring carba-sugar. Our strategy was based on the utilization of the Sinaÿ−Beau[32] methodology which involves the condensation of a glycosyllithium such as **28** with aldehydes **29**, this process occurring with *retention of configuration* at the anomeric centre. Aldehydes **29** having various chain lengths ($n = 1, 2$) could be prepared using the strategy described above. As the aldehydes are racemic, their condensation with enantiopure sugars should thus lead, after oxidation or radical deoxygenation of the resulting alcohol, to a resolved 1:1 mixture of two carba-C-disaccharides which could be separated by chromatography.

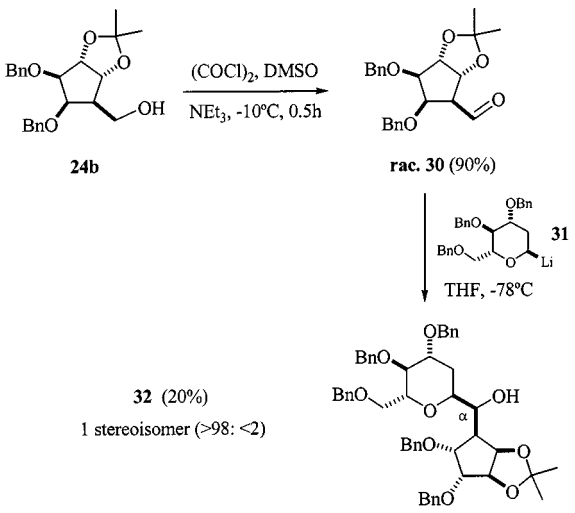


Scheme 12

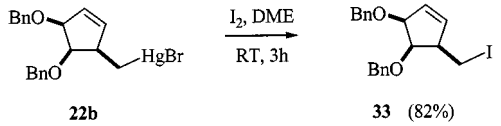
Our first attempt to prepare carba-C-disaccharides started from aldehyde **30** (chain length $n = 1$), which was easily prepared in high yield through the Swern oxidation[33] of the corresponding alcohol **24b** (Scheme 13). 2-Deoxyglucosyllithium **31** (prepared from the corresponding stannyl intermediate following literature protocol)[32a] was then condensed with racemic **30** at low temperature, leading, after purification by column chromatography to only one stereoisomer **32**. The low yield may be attributed to the high sensitivity of **30** towards bases. Deprotonation α to the aldehyde may initiate the decomposition of **30** through β-elimination (of a BnO group)[34] or condensation of the aldehyde with itself, thus leading to a complex mixture where the desired carba-C-disaccharide **32** is present only in small amounts. Nevertheless, ^{1}H-NMR studies on **32** (NOESY, COSY, ROESY) unambiguously showed that the coupling had occurred with retention of configuration at the anomeric centre. The configuration of the Cα−OH stereogenic centre could not be assigned with certainty and therefore, it has not been possible to determine which enantiomer of **30** reacted with **31**. Recent reports suggest that SmI_2-mediated coupling between a sugar-sulfone and the carba-aldehyde **30** might constitute a more suitable route and an attractive alternative to the use of strongly basic lithio-sugars.[35]

An alternative pathway was developed in parallel using, instead of the fragile aldehyde **30**, the iodide **33** prepared in one step from the corresponding mercury-intermediate **22b** (Scheme 14).[36] Condensation of the glycosyllithium **31** with **33** unfortunately did not produce the expected carba-C-disaccharide, but led to the recovery of the starting materials, under all conditions.

Much more satisfying results were obtained in the homologous series starting from an aldehyde **29** having a two-

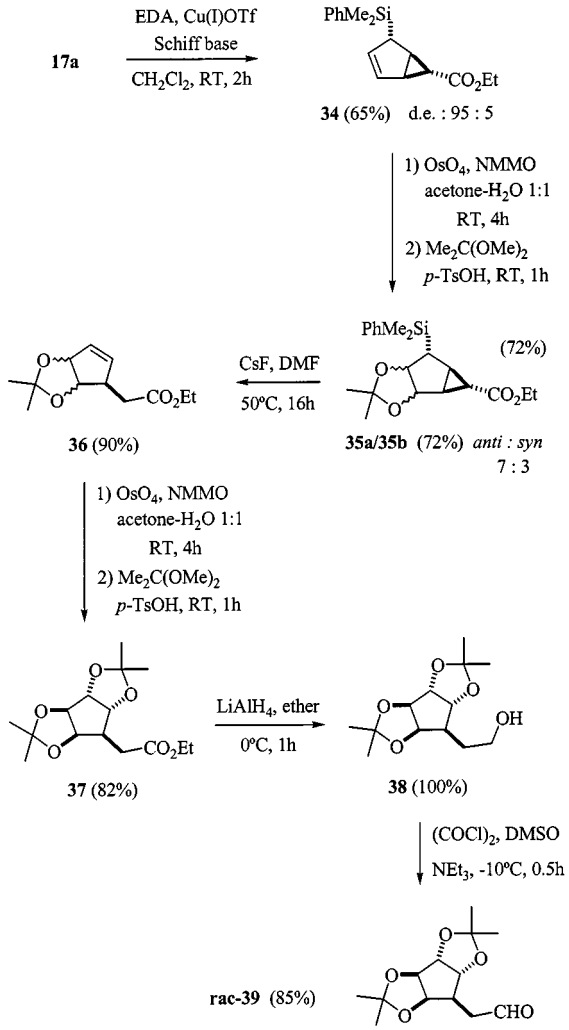


Scheme 13



Scheme 14

carbon chain (n = 2, Scheme 12). This aldehyde was prepared in racemic form in 8 steps from cyclopentadienylsilane **17a** (Scheme 15). Cyclopropanation of **17a** was carried out through $Cu^{I}OTf$ decomposition of ethyldiazoacetate (EDA)[37] in the presence of a Schiff base.[38] As above, the cyclopropanation occurred predominantly *anti* relative to the silicon group, a small amount (5%) of a stereoisomer of **34** (probably with the CO_2Et group up) also being observed. The osmylation of **34** then led to the expected diol as a 7:3 mixture of the *anti* and *syn* (relative to the silicon group) stereoisomers respectively, which were purified as their acetonides **35a−b**. As the cyclopropane is activated by an ester group, we anticipated that a nucleophilic attack at the silicon centre would assist the cyclopropane ring opening.[39] Treatment of **35a−b** with CsF in DMF effectively gave, concomitantly with the desilylation, a clean cyclopropane ring opening. The reaction was performed separately on stereoisomers *anti*-**35a** and *syn*-**35b** which afforded the corresponding esters **36** (*syn* and *anti* respectively) using 2 equivalents of CsF (50°C) for the *anti* isomer and 8 equivalents (100°C) for the *syn* isomer. **36** was then dihydroxylated and the diol protected as an acetonide, thus leading to a carba-sugar **37** having a pseudo C_2 symmetry. It is thus possible to carry out the 3 steps from **35a−b** to **37** without prior separation of the diastereomers. The ester **37** was then reduced to the alcohol **38** which was oxidized to the desired racemic aldehyde **39**, eventually obtained in 8 steps and 30% overall yield from **17a**.

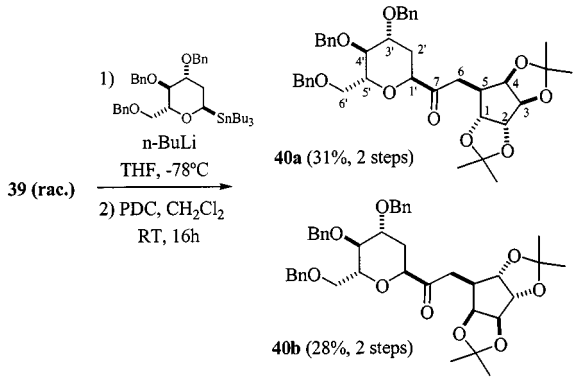


Scheme 15

The condensation of racemic **39** with 2-deoxyglucosyllithium **31** afforded a mixture of only 3 stereoisomers whose alcohol functions were directly oxidized to the ketones using PDC,[32] producing a 1:1 mixture of the desired carba-C-disaccharides **40a** and **40b**. As before, ^{1}H-NMR studies confirmed that the condensation step occurred with a complete retention of configuration at the anomeric centre. We have thus devised a short route to carba-C-disaccharides possessing a carba-furanose skeleton in 20% overall yield from cyclopentadiene. Our approach is flexible since we may envisaged the extension of the strategy to the synthesis of other carba-C-disaccharides varying the nature of the sugar unit as well as the substituents on the carba-sugar moiety.

Conclusion

As a summary, we have shown that the stereoselective cyclopropanation of allylsilanes followed by the regio- and



Scheme 16

stereospecific mercury-desilylation of the cyclopropylmethylsilanes offers an entry to homoallylic derivatives which can be versatile synthons for organic synthesis. This was demonstrated through a short and stereoselective access to carba-sugars, to precursors of carba-nucleosides and to carba-C-disaccharides. The silicon group plays a central role in this context, controlling the diastereofacial selectivity of the cyclopropanation, the regio- and also the stereoselectivity of the cyclopropane ring opening. It is also worth noting the remarkable dichotomy between the silicon and the hydroxy groups, as indicated by the reversal of regioselectivity observed during the mercury-mediated cyclopropane ring opening. This was used to devise a stereocontrolled route to diastereomeric trisubstituted tetrahydrofurans.

Experimental Section

General Remarks: ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC-250 FT (^{1}H: 250 MHz, ^{13}C: 62.9 MHz), Bruker WH-360 FT and (^{1}H: 360 MHz, ^{13}C: 90.55 MHz), Bruker ARX-400 FT (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz, respectively. − Gas chromatography was run on a Fisons Intruments, GC 8000 series. − IR spectra were recorded on a Perkin−Elmer 1710 spectrophotometer, on a Perkin−Elmer Paragon 500 FT-IR spectrophotometer or on a Perkin−Elmer Mattson Unicam 500 16PC FT-IR. − Mass spectra were recorded on a Nermag R10−10C, chemical ionization (CI) with NH_3 or Vacuum Generators micromass VG 70/70E and DS 11−250 and EI (70 eV); *m/z* (%). High resolution mass spectra were recorded on a FTICR mass spectrometer Bruker 4.7T BioApex II. − Specific rotations were recorded on a Perkin−Elmer 241 polarimeter. − Elemental analyses were performed by the I. Beetz laboratory, W-8640 Kronach (D). − Melting points were not corrected and were determined by using a Büchi Totolli apparatus. Kugelrohr distillations were carried out using a Büchi GKR-50 apparatus. − Merk silica gel 60 (70−230 mesh), (230−400 mesh ASTM) and Baker silica gel (0.063−0.200 mm) were used for flash chromatography. Slow additions were conducted using a Precidor apparatus. − CH_2Cl_2, Et_3N, $(iPr)_2NH$ were distilled from CaH_2. THF was distilled from potassium. Et_2O, hexane and DME were distilled from sodium. Chlorosilanes were distilled from magnesium.

General Procedure for the Preparation of 3,4-cyclopropylsilanes 2a−d: To a solution of allylsilane **1a−d** (0.33 mmol), in dry CH_2Cl_2 (1 mL) was added CH_2I_2 (0.442 g, 1.65 mmol) in CH_2Cl_2 (1 mL). The mixture was cooled to 0°C and a 1 M solution of Et_2Zn in hexane (1.65 mL, 1.65 mmol) was added carefully. The mixture became heterogeneous (white solid) and was stirred for 6 hours at room temp. Then, the mixture was treated with a solution of NH_4Cl, the organic layer was decanted and the aqueous layer extracted with ether (3 × 20 mL), the combined organic layers washed with brine, dried with $MgSO_4$, and the solvents were evaporated under vacuum. The yellow oil was purified by chromatography through silica gel (Petroleum ether/EtOAc/Et_3N, 95:4.5:0.5) affording the cyclopropane **2a−d** as a pale yellow oil.

Cyclopropane (2a): Following the general procedure, **2a** was obtained in 88% yield. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 3000, 1600, 1500, 1440, 1250, 1110, 840, 780, 700. − ^{1}H NMR ($CDCl_3$): δ = 7.64−6.88 (m, 10 H, aromatic H), 3.87 (dd, *J* = 4.6, 10.8 Hz, 1 H, C*H*$_a$H$_b$OH), 3.80 (dd, *J* = 7.5, 10.8 Hz, 1 H, CH$_a$*H*$_b$OH), 1.55 (dt, *J* = 4.9, 8.6 Hz, 1 H, C*H*Ph), 1.1−0.88 (m, 3 H, CH_2, CH), 0.69 (ddd, *J* = 4.6, 7.5, 15.2 Hz, 1 H, CHSi), 0.57 (dd, *J* = 4.1, 5.8 Hz, 1 H, CH$_a$*H*$_b$), 0.35 (s, 3 H, $SiCH_3$), 0.34 (s, 3 H, $SiCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 143.2 (s, aromatic C), 137.8 (s, aromatic C), 133.9 (d, aromatic CH), 129.0 (d, aromatic CH), 128.2 (d, aromatic CH), 127.8 (d, aromatic CH), 125.3 (d, aromatic CH), 125.3 (d, aromatic CH), 65.0 (t, *J* = 143 Hz, CH_2OH), 35.9 (d, *J* = 117 Hz, CHPh), 22.7 (d, *J* = 158 Hz, CHSi, CH), 17.3 (t, *J* = 161 Hz, CH_2), −3.5 (q, *J* = 120 Hz, $SiCH_3$), −3.8 (q, *J* = 120 Hz, $SiCH_3$). − MS (CI, NH_3): *m/z* (%): 279 (0.3) [M$^+$ − 17], 180 (3), 144 (21), 135 (62), 129 (100), 116 (5), 91 (22), 75 (10). − $C_{19}H_{24}OSi$ (296.48): calcd. C 76.99, H 8.17, Si 9.45; found C 75.54; H 7.93, Si 9.23.

Cyclopropane (2b): Following the general procedure, **2b** was obtained in 83% yield. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 3050, 2980, 2850, 1250, 1110, 850. − ^{1}H NMR ($CDCl_3$): δ = 7.55−7.33 (m, 5 H, aromatic H), 3.73−3.66 (m, 2 H, CH_2OH), 1.57−1.47 (m, 1 H, CHSi), 1.34−1.17 (m, 8 H, 4 × CH_2), 1.29 (t, *J* = 7.1 Hz, 3 H, CH_3), 0.52−0.38 (m, 2 H, 2 × CH), 0.38 [s, 6 H, $Si(CH_3)_2$], 0.35−0.23 (m, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 138.3 (s, aromatic C), 133.9 (d, *J* = 158 Hz, aromatic CH), 129.0 (d, *J* = 161 Hz, aromatic CH), 127.8 (d, *J* = 158 Hz, aromatic CH), 65.3 (t, *J* = 141.2 Hz, CH_2OH), 35.4 (d, *J* = 118.9 Hz, CHSi), 34.1 (t, *J* = 122.6 Hz, CH_2), 31.8 (t, *J* = 124.7 Hz, CH_2), 28.8 (d, *J* = 125 Hz, CH_2), 22.6 (t, *J* = 126 Hz, CH_2), 18.1 (d, *J* = 157 Hz, CH), 17.3 (d, *J* = 157 Hz, CH_2), 14.1 (d, *J* = 125 Hz, CH_3), 12.4 (t, *J* = 159 Hz, CH_2), −3.4 (q, *J* = 120 Hz, $SiCH_3$), −3.8 (q, *J* = 120 Hz, $SiCH_3$). − MS (CI, NH_3): *m/z* (%): 290 (5) [M$^+$], 273 (51), 245 (1), 175 (2), 152 (44), 135 (100), 110 (28), 96 (45), 81 (45). − $C_{18}H_{30}OSi$ (290.52): calcd. C 74.43, H 10.42, Si 9.64; found C 74.55, H 10.48, Si 9.69.

Cyclopropane (2c): Following the general procedure, **2c** was obtained in 79% yield. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 3000, 1630, 1510, 1475, 1275, 1110, 855, 770, 710. − ^{1}H NMR ($CDCl_3$): δ = 7.52−7.09 (m, 10 H, aromatic H), 3.85 (d, *J* = 5.6 Hz, 2 H, C*H*$_2$OH), 1.25 (s, 3 H, C*H*$_3$), 1.19 (dd, *J* = 4.1, 8.6 Hz, 1 H, C*H*$_a$H$_b$), 1.11 (ddd, *J* = 5.8, 8.6, 11.1 Hz, 1 H, CH), 0.99 (dt, *J* = 5.6, 11.1 Hz, 1 H, CHSi), 0.57 (dd, *J* = 4.1, 5.8 Hz, 1 H, CH$_a$*H*$_b$), 0.39 (s, 6 H, Si(C*H*$_3$)$_2$). − ^{13}C NMR ($CDCl_3$): δ = 147.8 (s, aromatic C), 138.0 (s, aromatic C), 134.0 (d, aromatic CH), 133.9 (d, aromatic CH), 129.1 (d, aromatic CH), 128.1 (d, aromatic CH), 127.8 (d, aromatic CH), 126.0 (d, aromatic CH), 125.3 (d, aromatic CH), 65.6 (t, CH_2OH), 29.8 (d, CHSi), 26.8 (d, *J* = 143.2 Hz, CH), 23.4 (s, *C*PhCH$_3$), 21.3 (t, *J* = 155 Hz, CH_2), 20.5 (q, *J* = 128 Hz,

CH_3), −3.3 (q, J = 120 Hz, $SiCH_3$), −3.8 (q, J = 120 Hz, $SiCH_3$). − MS (CI, NH_3): *m/z* (%): 310 (0.11) [M^+], 293 (6), 194 (4), 158 (19), 143 (88), 135 (100), 128 (19), 91 (26), 75 (11). − $C_{20}H_{26}OSi$ (310.51): calcd. C 77.38, H 8.45, Si 9.02; found C 77.42, H 8.43, Si 8.97.

Cyclopropane (2d): Following the general procedure, **2d** was obtained in 71% yield. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 3050, 2980, 2850, 1250, 1110, 840. − ^1H NMR ($CDCl_3$): δ = 7.57−7.55 (m, 2 H, aromatic H), 7.37−7.34 (m, 3 H, aromatic H), 3.76 (d, J = 4.3 Hz, 2 H, CH_2OH), 1.60 (m, 1 H, OH), 1.33−1.22 (m, 8 H, 4 × CH_2), 0.88 (t, J = 6.8 Hz, 3 H, CH_3), 0.75−0.69 (m, 5 H, 2 × CH, $-CH_2-$, CHSi), 0.39 (s, 3 H, $SiCH_3$), 0.38 (s, 3 H, $SiCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 138.4 (s, aromatic C), 134.0 (d, J = 157 Hz, aromatic CH), 129.0 (d, J = 159 Hz, aromatic CH), 127.7 (d, J = 159 Hz, aromatic CH), 65.8 (t, J = 142 Hz, CH_2OH), 31.8 (t, J = 125 Hz, CH_2), 29.5 (t, J = 125 Hz, CH_2), 29.1 (t, J = 126 Hz, CH_2), 28.4 (d, J = 121 Hz, CHSi), 22.6 (t, J = 125 Hz, CH_2), 15.7 (d, J = 163 Hz, CH), 15.3 (q, J = 124 Hz, CH_3), 14.1 (d, J = 126 Hz, CH), 10.8 (t, J = 160 Hz, CH_2), −3.3 (q, J = 120 Hz, $SiCH_3$), −4.0 (q, J = 120 Hz, $SiCH_3$). − MS (CI, NH_3): *m/z* (%): 290 [M^+] (11), 273 (81), 152 (73), 135 (100), 110 (31), 96 (52), 81 (53). − $C_{18}H_{30}OSi$ (290.52): calcd. C 74.43, H 10.42, Si 9.64; found C 74.51, H 10.31, Si 9.67.

General Procedure for the Yamamoto Cyclopropanation. − Cyclopropane (2e): To a solution of (*E*)-3-dimethylphenylsilyl-1-phenylbut-1-ene **1e** (92 mg, 0.35 mmol), in dry CH_2Cl_2 (4 mL) was added CH_2I_2 (188 mg, 0.7 mmol) in CH_2Cl_2 (1 mL). The mixture was cooled down to 0°C and a 2 M solution of Me_3Al in heptane (0.7 mmol, 0.35 mL) was carefully added. The heterogeneous reaction mixture was then stirred for 24 hours at room temp. The mixture was treated with a solution of NH_4Cl, the organic layer was decanted and the aqueous layer extracted with ether (3 × 20 mL). The combined extracts were washed with brine, dried with $MgSO_4$, and the solvents were evaporated under vacuum. The yellow oil was purified by chromatography through silica gel (Petroleum ether/EtOAc/Et_3N, 95:4.5:0.5) affording 78 mg of a 1:1 mixture of *anti*- and *syn*-cyclopropanes **2e** (80%). Spectroscopic data were in good agreement with those reported in the literature.[10a] − ^1H NMR ($CDCl_3$): δ = 7.57−7.11 (m, 20 H, aromatic H), 1.62−1.52 (m, 2 H, 2 × CHSi), 1.08 (d, J = 6.1 Hz, 3 H, CH_3), 1.06 (d, J = 6.1 Hz, 3 H, CH_3), 1.01−0.72 (m, 6 H, 6 × CH), 0.48−0.42 (m, 2 H, 2 × CH), 0.36 (s, 6 H, 2 × $SiCH_3$), 0.31 (s, 6 H, 2 × $SiCH_3$).

Cyclopropane (2f): Following the general protocol reported for **2e**, the cyclopropane **2f** was obtained from **1f** in 86% yield. Spectroscopic data were in good agreement with those reported ref.[10a] − ^1H NMR ($CDCl_3$): δ = 7.38−7.01 (m, 10 H, aromatic H), 2.18−2.11 (m, 1 H, CHSi), 1.19−1.08 (m, 1 H, CH), 0.98 (d, J = 6.1 Hz, 3 H, CH_3), 0.76−0.74 (m, 1 H, CH), 0.52−0.43 (m, 1 H, CH), 0.11 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$).

Monocyclopropane (2g): To a solution of dienol **1g** (0.41 g,1.33 mmol), in dry CH_2Cl_2 (4 mL) was added CH_2I_2 (1.42 g, 5.32 mmol) in CH_2Cl_2 (1 mL). The mixture was cooled to 0°C and a 1 M solution of Et_2Zn in hexane (5.32 mL, 5.32 mmol) was added carefully. The heterogeneous mixture was then stirred for 8 hours at room temp. Then, the mixture was treated with a solution of NH_4Cl, the organic layer was decanted, and the aqueous layer extracted with ether (3 × 20 mL). The combined organic extracts were washed with brine, dried with $MgSO_4$, and the solvents were evaporated under vacuum. The yellow oil was purified by chromatography through silica gel (Petroleum ether/EtOAc/Et_3N, 95:4.5:0.5) affording 0.55 g (98%) of **2g** as a pale yellow oil. − IR (film, KBr): $\tilde{\nu}$ = 3404 cm^{-1} (OH), 3067, 3024, 2997, 2955, 2868, 1604, 1496, 1250, 1111, 1067, 1031, 959. − ^1H NMR ($CDCl_3$): δ = 7.58−7.22 (m, 10 H, aromatic H), 6.28 (d, J = 15.8 Hz, 1 H, olefinic H), 5.71 (dd, J = 5.8, 15.8 Hz, 1 H, olefinic H), 3.85−3.72 (m, 2 H, CH_2OH), 1.60−1.52 (m, 1 H, CH), 126−1.15 (m, 1 H, CHSi), 0.85−0.74 (m, 2 H, CH_2), 0.65−0.51 (m, 1 H, CH), 0.42 (s, 6 H, $Si(CH_3)_2$). − MS (CI, NH_3): *m/z* (%): 231 (0.4) [M^+ − 17], 215 (3), 153 (6), 137 (100), 135 (94), 119 (6), 105 (11), 81 (62). − HRMS [M + Na] $C_{21}H_{26}ONaSi$: calcd. 345.1645; found 345.1644.

Cyclopropane (7a): Following the general procedure, **7a** was obtained in 80% yield. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 3050, 2980, 2850, 1250, 1110, 850, 700. − ^1H NMR ($CDCl_3$): δ = 7.55−7.51 (m, 2 H, aromatic H), 7.39−7.34 (m, 3 H, aromatic H), 3.88 (dd, J = 4.1, 10.4 Hz, 1 H, CH_aH_bOH), 3.77 (dd, J = 6.5, 10.8 Hz, 1 H, CH_aH_bOH), 1.49−1.2 (m, 4 H, OH, CHSi, CH_2), 0.98 (d, J = 5.6 Hz, 3 H, CH_3), 0.5−0.4 (m, 2 H, 2 × CH), 0.33 [s, 6 H, $Si(CH_3)_2$], 0.15−0.098 (m, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 138.4 (s, aromatic C), 133.9 (d, J = 154 Hz, aromatic CH), 129.0 (d, J = 160 Hz, aromatic CH), 127.8 (d, J = 158 Hz, aromatic CH), 64.0 (t, J = 101 Hz, CH_2OH), 32.2 (t, J = 125 Hz, CH_2), 30.9 (d, J = 115 Hz, CHSi), 20.1 (d, J = 138 Hz, CH), 18.8 (q, J = 127 Hz, CH_3), 14.0 (d, J = 152 Hz, CH), 12.9 (t, J = 158 Hz, CH_2), −3.7 (q, J = 120 Hz, $SiCH_3$), −3.8 (q, J = 120 Hz, $SiCH_3$). − MS (CI, NH_3): *m/z* (%): 231 (0.4), [M^+ − 17], 215 (3), 153 (6), 137 (100), 135 (94), 119 (6), 105 (11), 81 (62). − $C_{15}H_{24}OSi$ (248.44): calcd. C 72.52, H 9.74, Si 11.30; found C 72.52, H 9.64, Si 11.46.

Cyclopropane (7b): Following the general procedure, **7b** was obtained in 90% yield. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 3050, 2950, 2850, 1600, 1500, 1420, 1250, 1030, 840, 820, 780, 720, 700. − ^1H NMR ($CDCl_3$): δ = 7.55−7.52 (m, 2 H, aromatic H), 7.38−7.33 (m, 3 H, aromatic H), 7.24 (t, J = 7.5 Hz, 2 H, aromatic H), 7.13 (t, J = 7.4 Hz, 1 H, aromatic H), 6.99 (d, J = 7.5 Hz, 2 H, aromatic H), 3.91−3.75 (m, 2 H, CH_2OH), 1.66−1.50 (m, 2 H, CH_2), 1.35−1.20 (m, 1 H, CH), 1.13−1.04 (m, 1 H, CH), 0.94−0.83 (m, 1 H, CH), 0.81−0.76 (m, 1 H, CH), 0.73−0.67 (m, 1 H, CH), 0.34 [s, 6 H, $Si(CH_3)_2$]. − ^{13}C NMR ($CDCl_3$): δ = 143.5 (s, aromatic C), 138.2 (s, aromatic C), 133.8 (d, J = 158 Hz, aromatic CH), 128.9 (d, J = 160 Hz, aromatic CH), 128.2 (d, J = 166 Hz, aromatic CH), 127.8 (d, J = 165 Hz, aromatic CH), 125.4 (d, J = 149 Hz, aromatic CH), 125.2 (d, J = 161 Hz, aromatic CH), 63.7 (t, J = 142 Hz, CH_2OH), 32.2 (t, J = 126 Hz, CH_2), 30.7 (d, J = 117 Hz, CHSi), 24.3 (d, J = 157 Hz, CH), 23.8 (d, J = 156 Hz, CH), 16.2 (t, J = 161 Hz, CH_2), −3.7 (q, J = 120 Hz, $SiCH_3$), −3.8 (q, J = 120 Hz, $SiCH_3$). − MS (CI, NH_3): *m/z* (%): 328 [M^+ + 17], 311 [M^+], 293 (14), 277 (4), 232 (23), 214 (36), 189 (9), 175 (2), 152 (46), 135 (100), 117 (100), 91 (76). − $C_{20}H_{26}OSi$ (310.51): calcd. C 77.36, H 8.44, Si 9.04; found C 77.48, H 8.53, Si 9.04.

General Procedure for the Mercury-Desilylation of 2a−f: To a solution of cyclopropane **2a−f** (0.16 mmol) in DME (4 mL) were added successively at room temp. CH_3CN (10 mL), then mercury nitrate monohydrate (59 mg, 0.17 mmol). The resulting mixture was stirred at room temp. for 6 hours, then quenched with aqueous KBr and diluted with ether. The mixture was stirred for 2 hours at room temp. and the organic layer was decanted. The aqueous layer was extracted with ether (2 × 20 mL) and the combined extracts were washed with a solution of saturated $KHCO_3$ (twice) and water, dried with $MgSO_4$ and the solvents were evaporated under vacuum to give the crude homoallylic mercury bromides **8** in 80−90 yield. The relative instability of these organometallic compounds did not allow us to obtain satisfactory elemental analysis.

(8a): Following the general procedure, **8a** was obtained in 85% yield. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 3050, 2960, 2850, 1660, 1600, 1500, 1460, 1180, 980, 770, 700. − ^1H NMR ($CDCl_3$): δ = 7.42−7.29 (m, 5 H, aromatic H), 5.99 (ddd, *J* = 1.4, 7.15, 15.4 Hz, 1 H, C*H*=CHCH$_2$OH), 5.79 (dtd, *J* = 1.1, 5.4, 15.4 Hz, 1 H, CH=C*H*CH$_2$OH), 4.17 (d, *J* = 5.4 Hz, 2 H, CH$_2$OH), 3.88 (dd, *J* = 7.2, 7.3 Hz, 1 H, C*H*CH$_2$HgBr), 2.42 (d, *J* = 7.3 Hz, 2 H, CH$_2$HgBr). − ^{13}C NMR ($CDCl_3$): δ = 145.9 (s, aromatic C), 136.8 (d, *J* = 148 Hz, aromatic CH), 129.2 (d, *J* = 160 Hz, aromatic CH), 127.0 (d, *J* = 161 Hz, aromatic CH), 126.7 (d, *J* = 156 Hz, aromatic CH), 63.2 (t, *J* = 142 Hz, CH$_2$OH), 46.8 (d, *J* = 131 Hz, *C*HCH$_2$HgBr), 41.02 (t, *J* = 139 Hz, CH$_2$HgBr). − MS (CI, NH_3): *m*/*z* (%): 459 [M^+ + 17], 442 [M^+], 416 (58), 378 (13), 345 (6), 304 (17), 210 (13), 143 (100), 91 (74).

(8b): Following the general procedure, **8b** was obtained in 90% yield from cyclopropanes **2b** and **2d**. − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 3050, 2960, 2850, 1660, 1380, 1090, 980. − ^1H NMR ($CDCl_3$): δ = 5.71 (td, *J* = 5.5, 15.4 Hz, 1 H, CH=C*H*CH$_2$OH), 5.59 (dd, *J* = 7.8, 15.4 Hz, 1 H, C*H*=CHCH$_2$OH), 4.13 (d, *J* = 5.4 Hz, 2 H, C*H*$_2$OH), 2.17 (d, *J* = 5.5 Hz, 2 H, CH$_2$HgBr), 1.39−1.27 (m, 8 H, 4 × CH$_2$), 0.89 (t, *J* = 6.4 Hz, 3 H, CH$_3$). − ^{13}C NMR ($CDCl_3$): δ = 138.7 (d, *J* = 157 Hz, C vinyl), 128.8 (d, *J* = 153 Hz, C vinyl), 63.3 (t, *J* = 141 Hz, CH$_2$OH), 41.4 (d, *J* = 127 Hz, *C*HCH$_2$HgBr), 40.8 (t, *J* = 127 Hz, CH$_2$), 39.5 (t, *J* = 137 Hz, CH$_2$), 31.7 (t, *J* = 122 Hz, CH$_2$), 27.1 (t, *J* = 126 Hz, CH$_2$), 22.5 (t, *J* = 126 Hz, CH$_2$), 14.0 (q, *J* = 124 Hz, CH$_3$). − MS (CI, NH_3): *m*/*z* (%): 452 (M^+ + 17], 410 (100), 378 (26), 304 (15), 210 (7), 137 (67), 95 (66).

(8c) and Tetrahydrofuran (9): Following the general procedure, mercury-desilylation of **2c** produced a 34:66 mixture of **8c** and **9**, respectively which were purified by column chromatography (Petroleum ether/EtOAc/Et_3N, 95:4.5:0.5), affording **8c** in 30% yield: − IR (film, KBr): $\tilde{\nu}$ = 3400 cm^{-1} (OH), 2960, 2850, 1690, 1600, 1500, 1420, 1380, 1080, 980, 760, 700. − ^1H NMR ($CDCl_3$): δ = 7.41−7.24 (m, 5 H, aromatic H), 6.06 (dd, *J* = 1.3, 15.7 Hz, 1 H, C*H*=CHCH$_2$OH), 5.76 (td, *J* = 5.5, 15.7 Hz, 1 H, CH=C*H*CH$_2$OH), 4.22 (dd, *J* = 1.3, 5.5 Hz, 2 H, CH$_2$OH), 2.53 (d, *J* = 0.52 Hz, 2 H, CH$_2$HgBr), 1.60 (s, 3 H, CH$_3$). − ^{13}C NMR ($CDCl_3$): δ = 148.7 (s, aromatic C), 142.2 (d, aromatic CH), 128.8 (d, aromatic CH), 126.7 (d, aromatic CH), 126.4 (d, aromatic CH), 125.5 (d, aromatic CH), 63.4 (t, CH$_2$OH), 49.6 (t, CH$_2$HgBr), 44.6 (s, *C*CH$_3$Ph). − MS (CI, NH_3): *m*/*z* (%): 430 (4), 378 (2), 157 (100), 129 (59), 105 (80), 91 (85) and **9** in 60% yield: − IR (film, KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2850, 1650, 1550, 1400, 1380, 1260, 1120, 820, 800, 720. − ^1H NMR ($CDCl_3$): δ = 7.60−7.28 (m, 10 H, aromatic H), 4.23 (dd, *J* = 7.5, 10.5 Hz, 1 H, C*H*$_a$H$_b$O), 4.21 (dd, *J* = 7.5, 10.5 Hz, 1 H, CH$_a$*H*$_b$O), 3.16 (dt, *J* = 4, 5.7 Hz, 1 H, C*H*CH$_2$HgBr), 1.88 (dd, *J* = 3, 12.3 Hz, 1 H, C*H*$_a$H$_b$HgBr), 1.76 (dd, *J* = 4, 12.3 Hz, 1 H, CH$_a$*H*$_b$HgBr), 1.62 (dt, *J* = 5.7, 10.5 Hz, 1 H, CHSi), 1.46 (s, 3 H, CH$_3$), 0.41 (s, 3 H, SiCH$_3$), 0.29 (s, 3 H, SiCH$_3$). − ^{13}C NMR ($CDCl_3$): δ = 147.8 (s, aromatic C), 137.5 (s, aromatic C), 134.2 (d, aromatic CH), 133.0 (d, aromatic CH), 130.1 (d, aromatic CH), 129.2 (d, aromatic CH), 128.9 (d, aromatic CH), 128.4 (d, aromatic CH), 127.7 (d, aromatic CH), 126.6 (d, aromatic CH), 124.2 (d, aromatic CH), 87.4 (s, *C*CH$_3$Ph), 67.5 (t, *J* = 150 Hz, CH$_2$O), 49.4 (d, *J* = 131 Hz, *C*HCH$_2$HgBr), 31.2 (d, *J* = 108 Hz, CHSi), 25.7 (q, *J* = 127 Hz, CH$_3$), −2.1 (q, *J* = 103 Hz, SiCH$_3$), −3.1 (q, *J* = 103 Hz, SiCH$_3$). − MS (CI, NH_3): *m*/*z* (%): 608 [M^+ + 18], 607 [M^+ + 17], 590 [M^+], 564 (43), 526 (4), 452 (3), 378 (7), 304 (16), 255 (55), 210 (8), 152 (100), 135 (75), 105 (26).

4,5-Cyclopropan-5-phenylpentene (8e): To a solution of **7b** (53 mg, 0.17 mmol), in dry $CHCl_3$ (3 mL) was added one of the following acids [*p*TsOH (cat.) or 36% $BF_3 \cdot 2$ AcOH (1 equiv.) or 48% $BF_3 \cdot OEt_2$ (1 equiv.)]. The reaction mixture was stirred at room temp. for 3 hours and the solvent was evaporated in vacuo affording the elimination product **8e** [*p*TsOH (64%), BF_3 - 2 AcOH (33%), $BF_3 \cdot OEt_2$ (55%)]. − IR (film, KBr): $\tilde{\nu}$ = 2920 cm^{-1}, 1734, 1684, 1559, 1457, 1243, 697. − ^1H NMR ($CDCl_3$): δ = 7.36−7.04 (m, 5 H, aromatic H), 5.96−5.87 (m, 1 H, C*H*=CH$_2$), 5.13−5.98 (m, 2 H, CH=C*H*$_2$), 2.19−2.15 (m, 1 H, CH), 1.71−1.60 (m, 2 H, CH$_2$), 1.30−1.24 (m, 1 H, CH), 0.97−0.89 (m, 2 H, CH$_2$). − MS (CI, NH_3): *m*/*z* (%): 159 [M^+], 145 (8), 131 (19), 117 (48), 105 (13), 91 (30), 81 (24), 75 (2), 55 (5).

(8f): Following the general procedure, **8f** was obtained from cyclopropane **2f** in 85% yield. − IR (film, KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2850, 1650, 1080, 980. − ^1H NMR ($CDCl_3$): δ = 7.39−7.23 (m, 5 H, aromatic H), 5.74 (qdd, *J* = 1.4, 7.1, 15.1 Hz, 1 H, C*H*=CHCH$_3$), 5.62 (dqd, *J* = 0.7, 6.1, 15.1 Hz, 1 H, CH=C*H*CH$_3$), 3.82 (q, *J* = 7.1 Hz, 1 H, CHPh), 2.40 (dd, *J* = 1.4, 7.1 Hz, 2 H, CH$_2$HgBr), 1.72 (dd, *J* = 0.8, 6.1 Hz, 3 H, CH$_3$). − MS (EI): *m*/*z* (%): 360 (12), 202 (25, 145 (100), 105 (66), 91 (51), 77 (65).

(8f and 8g): Following the general procedure, mercury-desilylation of cyclopropylmethylsilane **2e** afforded a 1:1 mixture of **8f** and **8g** in 86% yield. − IR (film, KBr): $\tilde{\nu}$ = 2950 cm^{-1}, 2850, 1650, 1080, 980. − ^1H NMR ($CDCl_3$): δ = 7.56−7.23 (m, 10 H, aromatic H), 5.77−5.51 (dd, 4 H, 4 × *E*/*Z*-vinyl CH), 4.16 (q, *J* = 7.1 Hz, 1 H, *Z*-CHPh), 3.82 (q, *J* = 7.1 Hz, 1 H, E-CHPh), 2.40 (dd, *J* = 1.4, 7.1 Hz, 4 H, 2 × CH$_2$HgBr), 1.71 (d, *J* = 6.1 Hz, 6 H, 2 × CH$_3$). − MS (EI): *m*/*z* (%): 357 (6), 283 (10), 221 (7), 202 (9), 159 (16), 105 (100), 91 (40), 77 (46).

Tetrahydrofuran (12a): To a solution of **10a** (0.385 g, 1.86 mmol) in dry CH_2Cl_2 (4 mL) was added dropwise at 0°C, CH_2I_2 (2.49 g, 9.32 mmol,) then a 1 M solution of Et_2Zn in hexane (9.32 mL, 9.32 mmol). The mixture was stirred overnight at room temp. and then quenched with a saturated solution of NH_4Cl. The organic layer was decanted and the aqueous layer was extracted with ether (3 × 20 mL). The combined extracts were washed with brine, dried with $MgSO_4$, filtered and the solvents were evaporated under vacuum to give 0.371 g of the desired cyclopropane as a yellow oil (91%). This product was used in the next step without further purification. An analytical sample afforded the following structural data: − ^1H NMR ($CDCl_3$): δ = 7.31−7.29 (m, 2 H, aromatic H), 7.21−7.17 (m, 1 H, aromatic H), 7.13−7.10 (m, 2 H, aromatic H), 4.30 (q, 1 H, *J* = 7.2 Hz, CO$_2$C*H*$_a$H$_b$CH$_3$), 4.39 (q, *J* = 7.2 Hz, 1 H, CO$_2$CH$_a$*H*$_b$CH$_3$), 4.08 (d, *J* = 6.4 Hz, 1 H, C*H*OH), 3.16 (m, 1 H, OH), 2.19−2.15 (m, 1 H, CHPh), 1.49−1.43 (m, 1 H, C*H*CHOH), 1.32 (t, *J* = 7.2 Hz, 3 H, CO$_2$CH$_2$C*H*$_3$), 1.18−1.13 (m, 1 H, C*H*$_a$H$_b$), 1.02−0.98 (m, 1 H, CH$_a$*H*$_b$). − ^{13}C NMR ($CDCl_3$): δ = 171.5 (s, CO), 141.8 (s, aromatic C), 128.2 (d, *J* = 168 Hz, aromatic CH), 125.9 (d, *J* = 158 Hz, aromatic CH), 125.6 (d, *J* = 161 Hz, aromatic CH), 70.9 (d, *J* = 148 Hz, CHOH), 61.7 (t, *J* = 148 Hz, CO$_2$*C*H$_2$), 25.7 (d, *J* = 162 Hz, *C*HPh), 19.6 (d, *J* = 161 Hz, CH), 14.1 (q, *J* = 127 Hz, CO$_2$CH$_2$*C*H$_3$), 11.3 (t, *J* = 83 Hz, CH$_2$). − $C_{13}H_{16}O_3$ (220.27): calcd. C 70.89, H 7.32; found C 70.80, H 7.38. To a solution of the preceding cyclopropane in dry ether (10 mL) was added at 0°C a 1 M solution of $LiAlH_4$ in ether (1.7 mL, 1.69 mmol). The mixture was stirred at 0°C for 2 hours then quenched with a saturated solution of NH_4Cl. The organic layer was decanted and the aqueous layer extracted with ether (3 × 20 mL). The combined extracts were washed successively with a 1 M solution of HCl, sat. $NaHCO_3$ and brine, dried with $MgSO_4$, filtered, and the solvents were evaporated under vacuum, affording 0.24 g of the diol **11a** (80%): − ^1H NMR ($CDCl_3$): δ = 7.34−7.04 (m, 5 H, aromatic H), 3.81 (dd, *J* = 2.8, 11.5 Hz, 1 H, C*H*$_a$H$_b$OH),

3.64 (dd, J = 7.8, 11.5 Hz, 1 H, CH_aH_bOH), 3.38−3.33 (m, 1 H, C*H*OH), 1.91−1.84 (m, 1 H, CHPh), 1.28−1.21 (m, 2 H, CH), 1.14−1.09 (m, 1 H, CH), 1.03−0.95 (m, 1 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 141.9 (s, aromatic C), 128.3 (d, J = 159 Hz, aromatic CH), 125.8 (d, J = 148 Hz, aromatic CH), 75.5 (d, J = 142 Hz, CHOH), 66.3 (t, J = 142 Hz, CH_2OH), 24.93 (d, J = 158 Hz, *C*HPh), 20.2 (d, J = 158 Hz, CH), 13.2 (t, J = 161 Hz, CH_2). To a solution of **11a** (81 mg, 0.46 mmol) in DME (4 mL) were added successively at room temp. CH_3CN (10 mL), then mercury nitrate monohydrate (0.165 g, 0.48 mmol). The resulting mixture was stirred at room temp. overnight, then quenched with aqueous KBr and diluted with ether. The mixture was stirred for 2 hours at room temp. and the organic layer was decanted. The aqueous layer was extracted with ether (2 × 20 mL) and the combined extracts were washed with a saturated solution of $KHCO_3$ (2 ×), water, dried with $MgSO_4$, and the solvents were evaporated under vacuum. The residue was purified by chromatography through silica gel, (CH_2Cl_2/Ether, 9:1) affording 84 mg of tetrahydrofuran **12a** (40%): − ^{1}H NMR ($CDCl_3$): δ = 7.39−7.26 (m, 5 H, aromatic H), 4.27 (d, J = 10 Hz, 1 H, PhC*H*O), 4.09 (dd, J = 6.8, 8.7 Hz, 1 H, CH_aH_bO), 3.91 (m, 1 H, C*H*OH), 3.79 (dd, J = 6.5, 8.7 Hz, 1 H, CH_aH_bO), 2.16−2.14 (m, 1 H, C*H*CH_2HgBr), 1.71 (d, J = 7.9 Hz, 2 H, CH_2HgBr). − ^{13}C NMR ($CDCl_3$): δ = 139.7 (s, aromatic C), 128.9 (d, J = 161 Hz, aromatic CH), 128.6 (d, J = 161 Hz, aromatic CH), 126.7 (d, J = 158 Hz, aromatic CH), 87.5 (d, J = 148 Hz, *C*HPh), 78.0 (d, CHOH), 73.0 (t, J = 148 Hz, CH_2O), 55.1 (d, J = 132 Hz, *C*HCH_2HgBr), 29.2 (t, J = 137 Hz, CH_2HgBr). − MS (CI, NH_3): *m*/*z* (%): 476 [M^+ + 18], 475 [M^+ + 17], 457 [M^+, 0.2], 432 (15), 396 (1.3), 328 (0.9), 274 (3), 196 (45), 177 (100), 117 (66), 105 (64), 91 (63).

Tetrahydrofuran (12b): Following the procedure described for **12a**, **12b** was obtained in 30% overall yield (3 steps) from **10b**: − ^{1}H NMR ($CDCl_3$): δ = 4.01 (dd, J = 6.5, 8.9 Hz, 1 H, CH_aH_bO), 3.93−3.89 (m, 1 H, C*H*OH), 3.64 (dd, J = 5.8, 8.9 Hz, 1 H, CH_aH_bO), 3.45−3.39 (m, 1 H, CHO), 2.46 (d, J = 6 Hz, 1 H, OH), 2.12 (dd, J = 4.8, 11.2 Hz, 1 H, CH_aH_bHgBr), 2.08−1.99 (m, 2 H, C*H*CH_2HgBr), 1.76 (dd, J = 10.5, 11.2 Hz, 1 H, CH_aH_bHgBr), 1.68−1.32 (m, 8 H, 4 × CH_2), 0.90 (t, J = 6.4 Hz, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 86.1 (d, J = 140 Hz, CHOH), 79.2 (d, J = 149 Hz, CHO), 72.5 (t, J = 146 Hz, CH_2O), 52.3 (d, J = 131 Hz, *C*HCH_2HgBr), 33.8 (t, CH_2), 31.9 (t, CH_2), 25.7 (t, J = 123 Hz, CH_2), 22.6 (t, J = 128 Hz, CH_2), 14.0 (q, J = 124 Hz, CH_3). − MS (CI, NH_3): *m*/*z* (%): 451 [M^+], 381 (3), 298 (6), 202 (2), 171 (9), 135 (44), 83 (100).

Tetrahydrofuran (12c): To a solution of silyl alcohol **10c**[40] (447 mg, 1.7 mmol) in dry CH_2Cl_2 (5 mL) was added CH_2I_2 (8.5 mmol, 2.3 g). The mixture was cooled down to 0°C, then a 1 M solution of Et_2Zn in hexane (8.5 mmol, 8.5 mL) was added dropwise. The mixture was stirred at room temp. overnight, then treated with a saturated solution of NH_4Cl. The organic layer was decanted and the aqueous layer was extracted with ether (3 × 20 mL). The combined extracts were washed with brine, dried with $MgSO_4$, and the solvent was evaporated under vacuum to afford the crude cyclopropane (0.424 g, 90%) which was directly submitted to Tamao−Kumada oxidation without further purification. To a solution of the preceding cyclopropane (0.401 g, 1.45 mmol) in a 1:1 mixture of MeOH/THF (25 mL) was added at room temperature $KHCO_3$ (0.388 g, 4.41 mmol,), KF (0.227 g, 4.41 mmol), then a 30% wt. solution of H_2O_2 (2.7 mL, 30 mmol). The mixture was stirred for 16 hours at 60°C, then treated cautiously at 0°C with solid $Na_2S_2O_3$. The reaction mixture was stirred at room temp. for 30 min, then diluted with ether, filtered through celite, and the solvents were evaporated under vacuum. The residue was diluted with ether, dried with $MgSO_4$, filtered and the solvent was evaporated in vacuo to give a yellow oil, which was purified by chromatography through florisil (100−200 mesh, Petroleum ether/EtOAc, 1:1) affording the expected diol **11c** as a colourless oil (0.210 g, 82%), which was directly used in the next step: − ^{1}H NMR ($CDCl_3$): δ = 7.40−7.06 (m, 5 H, aromatic H), 3.77 (dd, J = 3.0, 11.3 Hz, 1 H, CH_aH_bOH), 3.62 (dd, J = 7.3, 11.3 Hz, 1 H, CH_aH_bOH), 3.29−3.28 (m, 1 H, C*H*OH), 1.96−1.91 (m, 1 H, CHPh), 1.29−1.23 (m, 2 H, CH_2), 0.96−0.89 (m, 1 H, C*H*CHOH). − ^{13}C NMR ($CDCl_3$): δ = 142.3 (s, aromatic C), 128.2 (d, aromatic CH), 125.8 (d, aromatic CH), 75.6 (d, CHOH), 65.9 (t, J = 145 Hz, CH_2OH), 25.0 (d, J = 159 Hz, CHPh), 20.6 (d, J = 162 Hz, CH), 12.8 (t, J = 125 Hz, CH_2). To a solution of **11c** (30 mg, 0.17 mmol,) in DME (1 mL) were added successively at room temp. CH_3CN (2.5 mL) then mercury nitrate monohydrate (61 mg, 0.18 mmol). The resulting mixture was stirred at room temp. overnight, then quenched with aqueous KBr and diluted with ether. The mixture was stirred for 2 hours at room temp. and the organic layer was decanted. The aqueous layer was extracted with ether (2 × 20 mL) and the combined extracts were washed with a saturated solution of $KHCO_3$ (2 ×) and water, dried with $MgSO_4$, and the solvents were evaporated under vacuum. The residue was purified by chromatography through silica gel, (CH_2Cl_2/Ether, 9:1) affording 38 mg of the tetrahydrofuran **12c** (50%): − ^{1}H NMR ($CDCl_3$): δ = 7.42−7.27 (m, 5 H, aromatic H), 4.51 (d, J = 10.1 Hz, 1 H, PhC*H*O), 4.37 (dd, J = 3.9, 10.1 Hz, 1 H, CH_aH_bO), 4.32 (t, J = 3.83 Hz, 1 H, C*H*OH), 3.95 (d, J = 10 Hz, 1 H, CH_aH_bO), 2.50−2.44 (m, 1 H, C*H*CH_2HgBr), 1.81−1.82 (m, 2 H, CH_2HgBr). − ^{13}C NMR ($CDCl_3$): δ = 140.0 (s, aromatic C), 129.0 (d, J = 161 Hz, aromatic CH), 128.7 (d, J = 161 Hz, aromatic CH), 126.6 (d, J = 164 Hz, aromatic CH), 86.3 (d, *C*HPh), 76.2 (t, J = 126 Hz, CH_2O), 74.2 (d, CHOH), 52.4 (d, J = 131 Hz, *C*HCH_2HgBr), 25.31 (t, CH_2HgBr). − **MS** (CI, NH_3): 476 (M^+ + 18, 25), 457 (1), 396 (2), 275 (5), 196 (49), 177 (100), 118 (25), 105 (50), 91 (62).

General Procedure for the Silylation-Cyclopropanation of Cyclopentadiene. − Cyclopropane (18a): To a solution of freshly distilled cyclopentadiene (2 g, 30 mmol) in dry THF (90 mL) was added at −80°C a 1.6 M solution of *n*BuLi in hexane (23 mL, 33.3 mmol). The mixture was stirred at −80°C for 45 minutes then a solution of dimethylphenylchlorosilane (5 mL, 30 mmol) in dry THF (10 mL) was added dropwise. The reaction mixture was stirred at −80°C for 1.5 hour, then quenched with a saturated solution of NH_4Cl and allowed to warm to room temp. The organic layer was decanted and the aqueous layer was extracted with ether (3 × 20 mL). The combined extracts were washed with brine and dried with $MgSO_4$. The solvents were evaporated in vacuo affording 5.9 g of dienylsilane **17a** (98%) which was used in the next step without further purification. − ^{1}H NMR ($CDCl_3$): δ = 7.58−7.51 (m, 2 H, aromatic H), 7.42−7.35 (m, 3 H, aromatic H), 6.62−6.52 (m, 4 H, vinylic H), 3.61 (t, J = 6.5 Hz, 1 H, CHSi), 0.20 (s, 6 H, $Si(CH_3)_2$). To a solution of **17a** (2 g, 10 mmol) in dry CH_2Cl_2 (20 mL) was added at room temp. CH_2I_2 (0.8 mL, 10 mmol,). The mixture was stirred for 5 minutes and cooled down to 0°C. A 1 M solution of Et_2Zn in hexane (10 mL, 10 mmol) was then added dropwise. The reaction mixture was stirred at room temp. for 24 hours, then quenched with a saturated solution of NH_4Cl. The organic layer was decanted and the aqueous layer was extracted with ether (3 × 20 mL). The combined extracts were washed with brine, dried with $MgSO_4$, filtered, and the solvents were evaporated under vacuum. The yellow oil was purified by chromatography through silica gel, (Petroleum ether) affording 1.98 g of **18a** as a pale yellow oil (93%). − IR (film, KBr): $\tilde{\nu}$ = 3067 cm^{-1}, 3023, 2987, 2852, 1587, 1428, 1248, 1114, 998, 874, 824, 758, 699. − ^{1}H NMR ($CDCl_3$): δ =

7.66−7.63 (m, 2 H, aromatic H), 7.46−7.43 (m, 3 H, aromatic H), 5.95−5.92 (m, 1 H, vinylic H), 5.39 (d, J = 3.9 Hz, 1 H, vinylic H), 2.26 (s, 1 H, CHSi), 1.86−1.82 (1 H, m, allylic H), 1.54−1.49 (m, 1 H, CHCHSi), 0.83−0.78 (m, 1 H, CH_aH$_b$), 0.37 (s, 3 H, SiCH$_3$), 0.36 (s, 3 H, SiCH$_3$), −0.09-(-0.12) (m, 1 H, CH$_a$$H_b$). − ^{13}C NMR (CDCl$_3$): δ = 138.1 (s, aromatic C), 134.0 (d, J = 156.6 Hz, CH:CH), 132.4 (d, J = 162 Hz, aromatic CH), 128.9 (d, J = 159 Hz, aromatic CH), 128.2 (d, J = 163 Hz, aromatic CH), 127.7 (d, J = 158 Hz, CH:CH), 38.3 (d, J = 124 Hz, SiCH), 23.7 (d, J = 170 Hz, CH), 15.6 (d, J = 166 Hz, CH), 15.1 (t, J = 161 Hz, CH$_2$), −5.0 (q, J = 120 Hz, SiCH$_3$), −5.5 (q, J = 120 Hz, SiCH$_3$). − MS (CI, NH$_3$): m/z (%): 214 [M$^+$], 197 (14), 185 (1), 159 (3), 135 (100), 121 (8), 105 (18), 91 (25), 78 (16). − $C_{14}H_{18}Si$ (214.38): calcd. C 78.44, H 8.46, Si 13.10; found C 78.44, H 8.53, Si 13.15.

Cyclopropane (18b): Following the general procedure, **18b** was obtained from cyclopentadiene in 74% yield (2 steps). − IR (film, KBr): ν̃ = 3067 cm^{-1}, 3023, 2986, 2855, 1587, 1486, 1428, 1250, 948, 792, 726. − ^{1}H NMR (CDCl$_3$): δ = 7.70−7.40 (m, 10 H, aromatic H), 5.97−5.94 (m, 1 H, CH=CHCHSi), 5.41 (d, J = 5.5 Hz, 1 H, CH=CHSi), 2.66 (d, J = 2.4 Hz, 1 H, CHSi), 1.87−1.83 (m, 1 H, CH), 1.63−1.59 (m, 1 H, CH), 0.86−0.82 (m, 1 H, CH_aH$_b$), 0.62 (s, 3 H, SiCH$_3$), −0.02-(-0.04) (m, 1 H, CH$_a$$H_b$). − ^{13}C NMR (CDCl$_3$): δ = 136.3 (s, aromatic C), 136.0 (s, aromatic C), 134.9 (d, CH), 134.8 (d, CH), 134.7 (d, CH), 132.9 (d, CH), 129.2 (d, CH), 128.1 (d, CH), 127.8 (d, CH), 127.7 (d, CH), 37.1 (d, J = 126 Hz, SiCH), 24.1 (d, J = 169 Hz, CH), 16.0 (d, J = 183 Hz, CH), 15.4 (t, J = 162 Hz, CH$_2$), −6.9 (q, J = 120 Hz, SiCH$_3$). − MS (CI, NH$_3$): m/z (%): 276 [M$^+$], 261 (5), 214 (4), 197 (100), 181 (17), 165 (8), 137 (8), 120 (49), 105 (50), 93 (17). $C_{19}H_{20}Si$ (276.45): calcd. C 82.55, H 7.29, Si 10.16; found C 82.46, H 7.34, Si 10.24.

Cyclopropane (18c): Following the general procedure, **18c** was obtained from cyclopentadiene in 59% yield (2 steps). − IR (film, KBr): ν̃ = 3067 cm^{-1}, 3022, 2987, 2853, 1585, 1428, 1249, 1114. − ^{1}H NMR (CDCl$_3$): δ = 7.38−6.92 (m, 15 H, aromatic H), 5.88−5.82 (m, 1 H, CH=CHCHSi), 5.05−4.98 (m, 1 H, CH=CHSi), 2.25−2.12 (m, 6 H, 3 × CH_2Ph), 2.09−2.06 (m, 1 H, CHSi), 1.82−1.70 (m, 1 H, CH), 1.38−1.25 (m, 1 H, CH), 0.79−0.71 (m, 1 H, CH_aH$_b$), −0.15 to −0.21 (m, 1 H, CH$_a$$H_b$). − HRMS [M + Na] $C_{21}H_{26}ONaSi$: calcd. 345.1645; found 345.1644.

General Procedure for the Sequence Dihydroxylation-Diol Protection of Cyclopropane 18a−c (Conditions A): In a 250 mL flask were placed 7.2 g of AD-mix® [K_3FeCN_6 (5 g, 15.3 mmol), K_2CO_3 (2.1 g, 15.3 mmol), (DHQ)$_2$PYR (0.05 mmol) or Et(iPr)$_2$N (0.25 mmol), K_2OsO_4 • 2 H$_2$O (19 mg, 0.05 mmol)], H$_2$O (26 mL); and tBuOH (26 mL). The solution was stirred for 5 minutes and methanesulfonamide (0.485 g, 5.1 mmol) was added. The reaction mixture was stirred for 10 minutes, then **18a** (1.1 g, 5.1 mmol) was introduced under vigorous stirring. After 3 days at room temperature, Na_2SO_3 (7.7 g) was added and the mixture was stirred at room temp. for 45 minutes. After extractions with EtOAc (5 ×), the combined extracts were washed with a 10% NaOH solution, the organic layer dried with $MgSO_4$, and the solvents were evaporated under vacuum to give a yellow oil which was directly dissolved in dimethoxypropane (8 mL). A catalytic amount of pTsOH was added and the solution was stirred for 2 hours at room temp. The solvents were then evaporated under vacuum and a saturated Na_2CO_3 solution was added. The aqueous layer was extracted with Et_2O, dried with $MgSO_4$, and the solvent was evaporated in vacuo. The residue was purified by chromatography through silica gel (Petroleum ether/EtOAc, 98:2) affording 0.885 g of the protected diol (60%, 2 steps) as a 8:2 mixture of diastereomers **19a** and **20a** respectively.

Major Diastereoisomer **19a**: − IR (film, KBr): ν̃ = 3069 cm^{-1}, 2987, 2881, 1379, 1250, 1208, 1043, 958, 864, 815, 732, 700. − ^{1}H NMR (CDCl$_3$): δ = 7.56−7.54 (m, 2 H, aromatic H), 7.41−7.37 (m, 3 H, aromatic H), 4.63 (dd, J = 5.4, 6.2 Hz, 1 H, OCH), 4.55 (d, J = 6.2 Hz, 1 H, OCHCHSi), 1.56−1.52 (m, 1 H, CH), 1.49 (s, 3 H, CH$_3$), 1.43−1.38 (m, 1 H, CH), 1.24 (s, 3 H, CH$_3$), 0.88−0.84 (m, 1 H, CH), 0.36 (s, 3 H, SiCH$_3$), 0.35 (s, 3 H, SiCH$_3$). − ^{13}C NMR (CDCl$_3$): δ = 136.9 (s, aromatic C), 133.8 (d, J = 158 Hz, aromatic CH), 129.2 (d, J = 158 Hz, aromatic CH), 127.8 (d, aromatic CH), 83.9 (d, J = 157 Hz, OCH), 82.9 (d, J = 151 Hz, OCH), 32.7 (d, J = 123 Hz, CHSi), 26.5 (q, J = 127 Hz, CH$_3$), 24.4 (q, J = 126 Hz, CH$_3$), 23.44 (d, J = 172 Hz, CH), 22.57 (d, J = 202 Hz, CH), 12.56 (t, J = 159 Hz, CH$_2$), −4.34 (q, J = 120 Hz, SiCH$_3$), −4.73 (q, J = 120 Hz, SiCH$_3$). − MS (CI, NH$_3$): m/z (%): 288 [M$^+$ − 1], 273 (4), 230 (7), 193 (5), 168 (1), 152 (20), 135 (100), 117 (64), 105 (26), 91 (20). − $C_{17}H_{24}O_2Si$ (288.46): calcd. C 70.78, H 8.39, Si 9.74; found C 70.68, H 8.22, Si 9.75. − *Minor Diastereomer* **20a**: − IR (film, KBr): ν̃ = 3069 cm^{-1}, 2987, 2881, 1379, 1250, 1208, 1043, 958, 864, 815, 732, 700. − ^{1}H NMR (CDCl$_3$): δ = 7.65−7.63 (m, 2 H, aromatic H), 7.38−7.36 (m, 3 H, aromatic H), 4.68 (dd, J = 5.3, 5.2 Hz, 1 H, OCHCHSi), 4.46 (d, J = 5 Hz, 1 H, OCH), 1.56−1.51 (m, 1 H, CH), 1.48 (s, 3 H, CH$_3$), 1.47−1.43 (m, 1 H, CH), 1.33 (d, J = 5.5 Hz, 1 H, CHSi), 1.27 (s, 3 H, CH$_3$), 0.84−0.80 (m, 1 H, CH_aH$_b$), 0.45 (s, 3 H, SiCH$_3$), 0.41 (3 H, s, SiCH$_3$), − .015-(-0.19) (m, 1 H, CH$_a$$H_b$). − ^{13}C NMR (CDCl$_3$): δ = 136.8 (s, aromatic C), 133.9 (d, J = 157 Hz, aromatic CH), 128.6 (d, J = 159 Hz, aromatic CH), 127.5 (d, J = 156 Hz, aromatic CH), 88.5 (d, J = 151 Hz, OCH), 84.6 (d, J = 152 Hz, OCH), 36.0 (d, J = 119 Hz, CHSi), 26.8 (q, J = 127 Hz, CH$_3$), 25.2 (q, J = 171 Hz, CH), 24.6 (q, J = 127 Hz, CH$_3$), 21.1 (d, J = 168 Hz, CH), 15.9 (t, J = 153 Hz, CH$_2$), −2.2 (q, J = 119 Hz, SiCH$_3$), −2.9 (q, J = 119 Hz, SiCH$_3$). − MS (CI, NH$_3$): m/z (%): 273 [M$^+$ − 17], 230 (6), 193 (9), 152 (11), 135 (100), 119 (5), 105 (12), 91 (6). $C_{17}H_{24}O_2Si$ (288.46): calcd. C 70.78, H 8.39, Si 9.74; found C 70.72, H 8.21, Si 9.88.

Dibenzyl Ether 19b (Conditions A): Following the dihydroxylation procedure **A**, cyclopropane **18a** afforded the diol, which was directly protected as a dibenzyl ether. The crude diol was then added at 0°C to a suspension of NaH (1.17 g, 48.9 mmol,) in dry THF (50 mL), then benzylbromide (4.3 mL, 34.2 mmol) and KI (cat.) were successively added. The reaction mixture was stirred overnight at room temp., then quenched with a saturated solution of NH_4Cl and extracted with Et_2O. The combined extracts were dried with $MgSO_4$ and the solvents evaporated under vacuum. The resulting oil was purified by chromatography through silica gel (Petroleum ether/EtOAc, 9:1) affording 3 g of a 9:1 mixture of diastereomer **19b** and Peterson elimination product **21** (42%, 2 steps). *Major Diastereomer* **19b**: − IR (film, KBr): ν̃ = 3067 cm^{-1}, 3028, 2956, 2815, 1606, 1587, 1496, 1453, 1249 (Si−C), 1113 (C−O), 829, 779, 764. − ^{1}H NMR (CDCl$_3$): δ = 7.53−7.51 (m, 2 H, aromatic H), 7.42−7.22 (m, 13 H, aromatic H), 4.56 (d, J = 11.9 Hz, 1 H, OCH_aH$_b$Ph), 4.48 (d, J = 11.9 Hz, 1 H, OCH$_a$$H_b$Ph), 4.38 (s, 1 H, OC$H_aH_b$Ph), 4.37 (s, 1 H, OCH$_a$$H_b$Ph), 3.98 (t, J = 5.3 Hz, 1 H, CHOBn), 3.72 (dd, J = 3.6, 5.8 Hz, 1 H, CHOBn), 1.64 (dd, J = 0.9, 3.6 Hz, 1 H, CH), 1.46−1.40 (m, 1 H, CH), 1.24−1.14 (m, 2 H, 2 × CH), 0.66−0.61 (m, 1 H, CH), 0.32 (s, 3 H, SiCH$_3$), 0.31 (s, 3 H, SiCH$_3$). − ^{13}C NMR (CDCl$_3$): δ = 138.6 (s, aromatic C), 137.6 (s, aromatic C), 133.8 (d, J = 158 Hz, aromatic CH), 129.1 (d, aromatic CH), 128.2 (d, aromatic CH), 128.1 (d, aromatic CH), 127.9 (d, aromatic CH), 127.8 (d, aromatic CH), 127.7 (d, aromatic CH), 127.4 (d, aromatic CH), 127.2 (d, aromatic CH), 80.4 (d, J = 141 Hz, CHOBn), 80.3 (d, J = 141 Hz, CHOBn), 71.3 (t, J = 141 Hz, OCH$_2$Ph), 70.9 (t, J = 142 Hz, OCH$_2$Ph), 33.8 (d, J =

121 Hz, CHSi), 19.9 (d, J = 168 Hz, CH), 15.7 (d, J = 166 Hz, CH), 11.6 (t, J = 158 Hz, CH_2), −4.1 (q, J = 119 Hz, $SiCH_3$), −4.4 (q, J = 120 Hz, $SiCH_3$). − MS (CI, NH_3): *m/z* (%): 446 [M^+ + 17], 321 (4), 241 (7), 135 (47), 91 (100), 75 (15). − $C_{28}H_{32}O_2Si$ (428.65): calcd. C 78.46, H 7.52, Si 6.55; found C 78.34, H 7.44, Si 6.63. − *Elimination product* (**21**). − IR (film, KBr): $\tilde{\nu}$ = 3062 cm^{-1}, 2988, 2859, 1592, 1496, 1454, 1362, 1066, 767, 735, 698. − ^1H NMR ($CDCl_3$): δ = 7.43−7.28 (m, 5 H, aromatic H), 6.35−6.33 (m, 1 H, vinylic H), 5.60−5.53 (m, 1 H, vinylic H), 4.67 (d, J = 11.8 Hz, 1 H, OCH_aH_bPh), 4.62 (d, J = 11.8 Hz, 1 H, OCH_aH_bPh), 4.41 (s, 1 H, C*H*OBn), 2.01−1.89 (t, 1 H, J = 5.3 Hz, CHOBn), 3.72 (dd, J = 3.6, 5.8 Hz, 1 H, CHOBn), 1.64 (dd, J = 0.9, 3.6 Hz, 1 H, CH), 1.46−1.40 (m, 2 H, 2 × CH), 1.06−1.01 (m, 1 H, CH), −0.03-(-0.06) (m, 1 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 140.6 (d, J = 164 Hz, vinylic H), 138.8 (s, aromatic C), 128.2 (d, J = 167 Hz, aromatic CH), 127.7 (d, J = 158 Hz, aromatic CH), 127.3 (d, J = 160 Hz, vinylic CH), 83.7 (d, J = 144 Hz, *C*HOBn), 69.1 (t, J = 141 Hz, O*C*H_2Ph), 22.6 (d, J = 172 Hz, CH), 22.5 (d, J = 172 Hz, CH), 20.8 (t, J = 158 Hz, CH_2). MS (CI, NH_3): *m/z* (%): 185 [M^+ − 1], 155 (6), 135 (100), 121 (5), 105 (12), 91 (78).

General Procedure for the Sequence Dihydroxylation-Diol Protection (Conditions B). − Dibenzyl Eether 19c: To a solution of **18b** (3.18 g, 11.5 mmol) and *N*-methylmorpholine oxide (NMMO) (1.71 g, 12.7 mmol,) in a 9:1 mixture of acetone/water (100 mL), was added at room temp. a solution of OsO_4 (49 mmol/l in THF) (11.7 mL, 0.57 mmol). The reaction mixture was stirred at room temp. for 16 hours and the solvent was evaporated in vacuo. The residue was treated with aqueous $Na_2S_2O_3$ and extracted with EtOAc (5 × 20 mL). The combined extracts were washed with saturated $NaHCO_3$ (2 ×) and brine, dried with $MgSO_4$ and the solvent was evaporated in vacuo. The crude diol was then added to a suspension of KH (1.09 g, 27.3 mmol) in 100 mL of THF at 0°C, then benzyl bromide (20.1 mmol, 2.4 mL) and KI (cat.) were successively added. After stirring overnight at room temperature, the solution was quenched with a saturated solution of NH_4Cl and extracted with Et_2O, dried with $MgSO_4$, and the solvents were evaporated under vacuum. The residue was purified by chromatography through silica gel (Petroleum ether/EtOAc, 95:5) affording 1.85 g of **19c** (40%). − IR (film, KBr): $\tilde{\nu}$ = 2958 cm^{-1}, 2900, 2956, 1606, 1587, 1496, 1428, 1350, 1317, 1256 (Si−C), 1193 (C−O), 1059, 844, 802, 732, 700. − ^1H NMR ($CDCl_3$): δ = 7.65−7.60 (m, 4 H, aromatic H), 7.48−7.29 (m, 14 H, aromatic H), 7.26−7.52 (m, 2 H, aromatic H), 4.61 (d, J = 12 Hz, 1 H, OCH_aH_bPh), 4.50 (d, J = 12 Hz, 1 H, OCH_aH_bPh), 4.47 (d, J = 12 Hz, 1 H, OCH_aH_bPh), 4.42 (d, J = 12 Hz, 1 H, OCH_aH_bPh), 3.97 (t, J = 5.5 Hz, 1 H, CHOBn), 3.87 (dd, J = 3.8, 5.8 Hz, 1 H, CHOBn), 2.13 (dd, J = 0.9, 2.8 Hz, 1 H, CH), 1.50−1.43 (m, 1 H, CH), 1.38−1.34 (m, 1 H, CH), 1.32−1.28 (m, 1 H, CH_aH_b), 0.76−0.71 (m, 1 H, CH_aH_b), 0.62 (s, 3 H, $SiCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 138.5 (s, aromatic C), 134.8 (d, J = 157 Hz, aromatic CH), 134.7 (d, J = 157 Hz, aromatic CH), 129.3 (d, J = 158 Hz, aromatic CH), 129.2 (d, J = 158 Hz, aromatic CH), 128.1 (d, J = 157 Hz, aromatic CH), 128.0 (d, J = 157 Hz, aromatic CH), 127.8 (d, J = 157 Hz, aromatic CH), 127.3 (d, J = 157 Hz, aromatic CH), 127.2 (d, J = 157 Hz, aromatic CH), 80.7 (d, J = 145 Hz, *C*HOBn), 80.1 (d, J = 141 Hz, *C*HOBn), 71.6 (t, J = 141 Hz, O*C*H_2Ph), 70.8 (t, J = 142 Hz, O*C*H_2Ph), 32.7 (d, J = 122 Hz, CHSi), 20.1 (d, J = 169 Hz, CH), 16.0 (d, J = 169 Hz, CH), 11.8 (t, J = 165 Hz, CH_2), −5.2 (q, J = 119 Hz, $SiCH_3$). MS (CI, NH_3); *m/z* (%): 508 [M^+ + 17], 383 (1), 303 (1), 197 (18), 165 (10), 91 (100). − $C_{33}H_{34}O_2Si$ (490.72): calcd. C 80.77, H 6.98, Si 5.72; found C 80.84, H 7.10, Si 5.80.

Dibenzyl Ether 19d and 20b: Following the general procedure (Conditions **B**) described for **19c**, the dihydroxylation-acetonide protection of **18c** afforded 0.225 g (33%) of a 1:1 mixture of diastereomers **19d** and **20b**. *Diastereomer* **19d**: − IR (film, KBr): $\tilde{\nu}$ = 3024 cm^{-1}, 2985, 2928, 1709, 1599, 1492, 1452, 1207, 1161, 1039, 912, 866, 808, 779. − ^1H NMR ($CDCl_3$): δ = 7.27−6.95 (m, 15 H, aromatic H), 4.46 (t, J = 6.1 Hz, 1 H, OCH), 4.25 (d, J = 6.7 Hz, 1 H, OC*H*CHSi), 2.23 (d, J = 17.7 Hz, 1 H, CH_aH_bPh), 2.19 (d, J = 17.7 Hz, 1 H, CH_aH_bPh) 1.59−1.57 (m, 2 H, 2 × CH), 1.44 (s, 3 H, CH_3), 1.23−1.18 (m, 1 H, CH), 1.08 (s, 3 H, CH_3), 0.75−0.64 (m, 2 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 138.4 (s, aromatic C), 128.8 (d, aromatic CH), 128.6 (d, aromatic CH), 128.6 (d, aromatic CH), 128.4 (d, aromatic CH), 128.3 (d, aromatic CH), 128.2 (d, aromatic CH), 128.1 (d, aromatic CH), 124.6 (d, aromatic CH), 124.5 (d, aromatic CH), 110.7 (s), 84.4 (d, OCH), 82.8 (d, OCH), 31.9 (d, CHSi), 26.5 (q, CH_3), 24.4 (q, CH_3), 23.0 (d, CH), 22.57 (d, CH), 21.2 (t, *C*H_2Ph), 13.6 (t, CH_2). MS (CI, CH_4); *m/z* (%): 454 [M^+], 395 (78), 377 (86), 363 (17), 301 (100), 287 (16), 227 (18), 167 (3), 123 (7), 91 (21), 79 (61). − HRMS [M + Na] $C_{30}H_{34}O_2Si$: calcd. 477.2220; found: 477.2232. − *Diastereomer* **20b**. − IR (film, KBr): $\tilde{\nu}$ = 3024 cm^{-1}, 2985, 2928, 1709, 1599, 1492, 1452, 1207, 1161, 1039, 912, 866, 808, 779. − ^1H NMR ($CDCl_3$): δ = 7.27−6.99 (m, 15 H, aromatic H), 4.40 (t, J = 5.2 Hz, 1 H, OCH), 4.36 (d, J = 4.9 Hz, 1 H, OC*H*CHSi), 2.30 (d, J = 18.4 Hz, 1 H, CH_aH_bPh), 2.19 (d, J = 18.4 Hz, 1 H, CH_aH_bPh), 1.61 (s, 3 H, CH_3), 1.53−1.46 (m, 1 H, CH), 1.26 (s, 3 H, CH_3), 1.12−1.06 (m, 1 H, CH), 1.02−1.00 (m, 1 H, CH), 0.74−0.69 (m, 1 H, CH), −0.25-(-0.35) (m, 1 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 138.7 (s, aromatic C), 128.8 (d, aromatic CH), 128.7 (d, aromatic CH), 128.6 (d, aromatic CH), 128.5 (d, aromatic CH), 128.3 (d, aromatic CH), 128.2 (d, aromatic CH), 128.1 (d, aromatic CH), 128.0 (d, aromatic CH), 126.2 (d, aromatic CH), 124.5 (d, aromatic CH), 124.1 (d, aromatic CH), 110.9 (s), 88.5 (d, OCH), 84.5 (d, OCH), 32.9 (d, CHSi), 26.8 (q, CH_3), 25.7 (q, CH_3), 24.3 (d, CH), 22.4 (t, *C*H_2Ph), 21.4 (d, CH), 16.1 (t, CH_2). MS (CI, NH_3); *m/z* (%): 379 (10), 363 (100), 301 (19), 287 (4), 255 (2), 227 (33), 149 (3), 91 (9), 79 (86). − HRMS [M + Na] $C_{30}H_{34}O_2Si$: calcd. 477.2220; found: 477.2242.

General Procedure for the Sequence Mercury-Desilylation-Oxidation of Cyclopropanes 19a−c. Following the general mercury-desilylation procedure, **22a** was obtained in 80% yield from cyclopropane **19a** and was used in the next step without further purification. **22a**: − IR (film, KBr): $\tilde{\nu}$ = 3016 cm^{-1}, 2930, 1634 (C=C), 1374 (CH_3), 1205 (C−O), 1043, 969. − ^1H NMR ($CDCl_3$): δ = 5.81−5.79 (1 H, m, vinylic H), 5.63−5.61 (m, 1 H, vinylic H), 5.11−5.09 (m, 1 H, OCH), 4.65−4.63 (m, 1 H, OCH), 3.38−3.36 (m, 1 H, CHCH_2HgBr), 2.16 (dd, J = 5.4, 12.1 Hz, 1 H, CH_aH_bHgBr), 2.03 (dd, J = 4.3, 12.1 Hz, 1 H, CH_aH_bHgBr), 1.55 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 136.8 (d, J = 162 Hz, vinylic C), 130.9 (d, J = 170 Hz, vinylic C), 110.9 (s, C), 85.6 (d, J = 141 Hz, OCH), 78.4 (d, J = 159 Hz, COH), 45.7 (d, J = 133 Hz, *C*HCH$_2$HgBr), 28.4 (t, J = 104 Hz, CH_2HgBr), 27.6 (q, J = 124 Hz, CH_3), 25.8 (q, J = 126 Hz, CH_3). In a 25 mL three necked round-bottomed flask were placed DMF (6 mL) and sodium borohydride (61 mg, 1.6 mmol,). Oxygen was then bubbled through the solution for 1 hour. A solution of **22a** in DMF (10 mL) was then added dropwise over a 1 hour period using a syringe pump. The mixture was stirred under an O_2 atmosphere for an additional 2 hours. Then, the mixture was centrifuged, quenched with a 1 M HCl solution (6 mL) and extracted with EtOAc (5 × 20 mL). The combined extracts were washed with a saturated $NaHCO_3$ solution (2 ×), brine, dried with $MgSO_4$, and the solvents were evaporated under vacuum. The residue was purified by chromatography through silica gel (Petroleum ether/EtOAc, 8:2) affording 64 mg of **23a** as a yellow oil (32%, 2 steps). − IR ($CHCl_3$): $\tilde{\nu}$ = 3391 (OH), 3065, 2934, 1633, 1372, 1047, 952, 732

cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 5.88−5.86 (m, 1 H, CH=C*H*CHO), 5.76−5.74 (m, 1 H, C*H*=CHCHO), 5.14−5.12 (m, 1 H, CH=CHC*H*O), 4.86 (dd, *J* = 5.9, 6 Hz, 1 H, OCH), 3.91 (dd, *J* = 3.8, 11.4 Hz, 1 H, CH_aH$_b$OH), 3.79 (dd, *J* = 7.1, 11.4 Hz, 1 H, CH$_a$$H_b$OH), 2.91−2.88 (m, 1 H, C*H*CH$_2$OH), 1.44 (s, 3 H, CH$_3$), 1.36 (s, 3 H, CH$_3$). − ^{13}C NMR ($CDCl_3$): δ = 133.9 (d, *J* = 167 Hz, vinylic C), 131.3 (d, *J* = 168 Hz, vinylic C), 85.4 (d, *J* = 149 Hz, OCH), 79.5 (d, *J* = 155 Hz, OCH), 61.8 (t, *J* = 139 Hz, CH$_2$OH), 49.6 (d, *J* = 131 Hz, CH), 27.1 (q, *J* = 127 Hz, CH$_3$), 25.4 (q, *J* = 124 Hz, CH$_3$). MS (CI, NH_3); *m/z* (%): 155 [M^+ − 15], 141 (7), 125 (9), 113 (18), 95 (100), 82 (87), 81 (55).

(3*R,4*S**,5*R**)-3,4-Dibenzyloxy-5-hydroxymethycyclopentene (23b):** Following the general mercury-desilylation procedure, **22b** was obtained in 85% yield from cyclopropanes **19b** and **19c**. − IR (solution, $CHCl_3$): $\tilde{\nu}$ = 3061 cm^{-1}, 3030, 1605, 1500, 1453, 1118 (C−O), 1060, 830, 780, 735, 698. − ^1H NMR ($CDCl_3$): δ = 7.44−7.30 (m, 10 H, aromatic H), 6.14 (dd, *J* = 3, 6.2 Hz, 1 H, vinylic H), 5.9 (d, *J* = 6.2 Hz, 1 H, vinylic H), 4.78 (d, *J* = 12.8 Hz, 1 H, OCH_aH$_b$Ph), 4.75 (d, *J* = 12.8 Hz, 1 H, OCH$_a$$H_b$Ph), 4.69 (d, *J* = 11.6 Hz, 1 H, OCH_aH$_b$Ph), 4.54 (d, *J* = 11.6 Hz, 1 H, OCH$_a$$H_b$Ph), 4.21 (dd, *J* = 3, 5.6 Hz, 1 H, C*H*OBn), 3.90 (dd, *J* = 6.1, 7.1 Hz, 1 H, C*H*OBn), 3.29−3.26 (m, 1 H, C*H*CH$_2$HgBr), 2.15 (dd, *J* = 5.4, 11.9 Hz, 1 H, CH_aH$_b$HgBr), 2.01 (dd, *J* = 4.4, 11.9 Hz, 1 H, CH$_a$$H_b$HgBr). MS (CI, NH_3); *m/z* (%): 592 [M^+ + 18], 576 [M^+ + 2], 548 (33), 495 (4), 312 (1), 186 (8), 91 (100). Following the general oxidation procedure, **22b** afforded the alcohol **23b** as a yellow oil (45%, 2 steps). − IR (film, KBr): $\tilde{\nu}$ = 3389 cm^{-1} (OH), 3063, 3030, 1600, 1496, 1135, 963, 736, 698. − ^1H NMR ($CDCl_3$): δ = 7.39−7.27 (m, 10 H, aromatic H), 6.09−6.07 (m, 1 H, vinylic H), 6.04 (dd, *J* = 2.9, 6.3 Hz, 1 H, vinylic H), 4.76 (d, *J* = 11.8 Hz, 1 H, OCH_aH$_b$Ph), 4.70 (s, 2 H, OCH_2Ph), 4.60 (1 H, d, *J* = 11.8 Hz, OCH$_a$$H_b$Ph), 4.33 (1 H, dd, *J* = 2.4, 5.7 Hz, CHOBn), 4.11 (1 H, dd, *J* = 5.6, 7.3 Hz, CHOBn), 3.87 (1 H, dt, *J* = 3, 11.2 Hz, CH_aH$_b$OH), 3.68 (1 H, ddd, *J* = 4.8, 8.8 Hz, 11.2, CH$_a$$H_b$OH), 3.28 (1 H, dd, *J* = 3.4, 8.8 Hz, OH), 2.94−2.90 (1 H, m, C*H*CH$_2$OH). − ^{13}C NMR ($CDCl_3$): δ = 138.1 (s, aromatic C), 136.6 (d, *J* = 168 Hz, vinylic C), 130.3 (d, *J* = 162 Hz, vinylic C), 128.4 (d, aromatic CH), 128.3 (d, aromatic CH), 127.8 (d, aromatic CH), 127.6 (d, aromatic CH), 127.5 (d, aromatic CH), 79.1 (d, *J* = 148 Hz, CHOBn), 77.8 (d, *J* = 148 Hz, CHOBn), 71.9 (t, *J* = 142 Hz, O*C*H$_2$Ph), 71.3 (t, *J* = 142 Hz, O*C*H$_2$Ph), 60.1 (t, *J* = 145 Hz, CH$_2$OH), 48.3 (d, *J* = 131 Hz, CH). MS (CI, NH_3); *m/z* (%): 328 [M^+ + 17], 311 [M^+], 281 (8), 236 (2), 220 (28), 203 (34), 142 (11), 108 (50), 91 (75). − $C_{20}H_{22}O_3$ (316.39): calcd C 77.39, H 7.14; found C 77.19, H 7.04.

Carba-Sugar (24a): To a solution of **23a** (42 mg, 0.25 mmol) in dry THF (5 mL) at room temp. was added NMMO (34 mg, 0.25 mmol) then a solution of OsO_4 (49 mmol/L in THF) (0.25 mL, 0.013 mmol). The reaction mixture was stirred at room temp. for 6 hours then quenched with aqueous $Na_2S_2O_3$. The organic layer was decanted and the aqueous layer extracted with EtOAc (5 × 10 mL). The combined extracts were washed with saturated $NaHCO_3$ (2 ×) and brine, dried with $MgSO_4$, and the solvents were evaporated in vacuo. The residue was purified by chromatography through silica gel (Petroleum ether/EtOAc, 9:1) affording 35 mg of **24a** as a white solid (60%), which was recrystallized from petroleum ether/CH_2Cl_2; m.p. 102−103°C. − IR (film, KBr): $\tilde{\nu}$ = 3391 cm^{-1} (OH), 3065, 2934, 1633, 1372, 1047, 952, 732. − ^1H NMR ($CDCl_3$): δ = 4.73 (dd, *J* = 5.8, 6.1 Hz, 1 H, OC*H*CHCH$_2$OH), 4.5 (d, *J* = 6.1 Hz, 1 H, OC*H*CHOH), 4.30 (dd, *J* = 4.2, 10.6 Hz, 1 H, OHC*H*CHCH$_2$OH), 4.05 (dd, *J* = 5.2, 11 Hz, 1 H, CH_aH$_b$OH), 4.03 (d, *J* = 4.2 Hz, 1 H, OCHC*H*OH), 3.99 (dd, *J* = 5.3, 11 Hz, 1 H, CH$_a$$H_b$OH), 2.22−2.15 (m, 1 H, C*H*CH$_2$OH), 1.42 (s, 3 H, CH$_3$), 1.28 (s, 3 H, CH$_3$). − ^{13}C NMR ($CDCl_3$): δ = 110.4 (s, C(CH$_3$)$_2$), 82.4 (d, *J* = 156 Hz, OCH), 79.2 (d, *J* = 171 Hz, OCH), 74.9 (d, *J* = 153 Hz, OCH), 72.7 (d, *J* = 147 Hz, OCH), 60.9 (t, *J* = 143 Hz, CH$_2$OH), 46.3 (d, *J* = 125 Hz, CH), 25.9 (q, *J* = 127 Hz, CH$_3$), 23.3 (q, *J* = 124 Hz, CH$_3$). MS (CI, NH_3); *m/z* (%): 155 [M^+ − 15], 141 (7), 125 (9), 113 (18), 95 (100), 82 (87), 81 (55). − $C_9H_{16}O_5$ (204.22): calcd C 52.93, H 7.90; found C 52.93, H 7.82.

Carba-Sugar (24b): To a solution of **23b** (0.387 g, 1.24 mmol) in acetone (9 mL) and water (1 mL) at room temp. was added NMMO (185 mg, 1.4 mmol) followed by a solution of OsO_4 (49 mmol/l in THF) (1.3 mL, 0.06 mmol). The reaction mixture was stirred at room temp. for 1 hour and the solvent was evaporated in vacuo. The residue was quenched with saturated $Na_2S_2O_3$ and extracted with EtOAc (5 × 20 mL). The combined extracts were washed with saturated $NaHCO_3$ (2 ×) and brine then dried with $MgSO_4$. The solvent was evaporated in vacuo affording a yellow oil, which was directly dissolved in dimethoxypropane (6 mL). A catalytic amount of *p*TsOH was added and the solution was stirred at room temp. for 2 hours. The solvents were then evaporated and a saturated Na_2CO_3 solution was added. The aqueous layer was extracted with Et_2O, the combined extracts dried with $MgSO_4$, and the solvent evaporated in vacuo. The residue was purified by chromatography through silica gel (Petroleum ether/EtOAc, 8:2) affording 0.286 g of **24b** as a pale yellow oil (60%). − IR (film, KBr): $\tilde{\nu}$ = 3452 cm^{-1} (OH), 3031, 2987, 2934, 1607, 1497, 1455, 1373, 1275, 1209, 1138, 1063, 911, 867, 734, 698. − ^1H NMR ($CDCl_3$): δ = 7.31−7.18 (m, 10 H, aromatic H), 4.70 (d, *J* = 11.7 Hz, 1 H, OCH_aH$_b$Ph), 4.67 (d, *J* = 2.1 Hz, 1 H, C*H*OBn), 4.59 (d, J *J* = 11.7 Hz, 1 H, OCH_aH$_b$Ph), 4.58 (d, *J* = 11.7 Hz, 1 H, OCH$_a$$H_b$Ph), 4.55 (dd, *J* = 1.6, 6.7 Hz, 1 H, C*H*OBn), 4.46 (d, *J* = 11.7 Hz, 1 H, OCH$_a$$H_b$Ph), 4.22 (dd, *J* = 4.8, 6.8 Hz, 1 H, CHO), 3.89 (dd, *J* = 1.6, 4.8 Hz, 1 H, CHO), 3.84 (dd, *J* = 3.3, 11.4 Hz, 1 H, CH_aH$_b$OH), 3.69−3.67 (m, 1 H, CH$_a$$H_b$OH), 2.41−2.38 (m, 1 H, C*H*CH$_2$OH), 1.38 (s, 3 H, CH$_3$), 1.25 (s, 3 H, CH$_3$). − ^{13}C NMR ($CDCl_3$): δ = 137.9 (s, aromatic C), 137.3 (s, aromatic C), 128.3 (d, *J* = 162 Hz, aromatic CH), 127.7 (d, *J* = 161 Hz, aromatic CH), 127.4 (d, *J* = 158 Hz, aromatic CH), 110 (s, C), 82.5 (d, *J* = 147 Hz, CHOBn), 82.2 (d, *J* = 156 Hz, CHOBn), 79.9 (d, *J* = 158 Hz, OCH), 79.8 (d, *J* = 141 Hz, OCH), 72.5 (t, *J* = 142 Hz, OCH$_2$Ph), 72.1 (t, *J* = 142 Hz, OCH$_2$Ph), 59.5 (t, *J* = 140 Hz, CH$_2$OH), 48.4 (d, *J* = 130 Hz, CH), 26.4 (q, *J* = 127 Hz, CH$_3$), 23.7 (q, *J* = 126 Hz, CH$_3$). MS (CI, NH_3); *m/z* (%): 385 [M^+], 293 (18), 275 (2), 235 (2), 187 (12), 155 (5), 129 (11), 91 (100). − $C_{23}H_{28}O_5$ (384.47): calcd C 71.85, H 7.34; found C 71.85, H 7.28.

Epoxide (25a): To a solution of **23b** (0.318 g, 1.03 mmol) in dry CH_2Cl_2 (10 mL) at room temp. was added *m*-CPBA (90%, 0.533 g, 3.09 mmol). The heterogeneous mixture was stirred at room temp. for 48 hours and saturated Na_2CO_3 was added. The aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed with saturated Na_2CO_3, brine, dried with $MgSO_4$, and the solvent was evaporated in vacuo. The yellow oil was purified by chromatography through florisil® (Petroleum ether/EtOAc, 9:1) affording 0.22 g of **25a** as a pale yellow oil (60%). − IR (film, KBr): $\tilde{\nu}$ = 3455 cm^{-1} (OH), 3031, 2924, 1606, 1497, 1454, 1402, 1345, 1266, 1207, 1130, 1046, 838, 737, 698. − ^1H NMR ($CDCl_3$): δ = 7.39−7.28 (m, 10 H, aromatic H), 4.82 (d, *J* = 11.6 Hz, 1 H, OCH_aH$_b$Ph), 4.71 (d, *J* = 11.6 Hz, 1 H, OCH$_a$$H_b$Ph), 4.56 (d, *J* = 11.8 Hz, 1 H, OCH_aH$_b$Ph), 4.51 (d, *J* = 11.8 Hz, 1 H, OCH$_a$$H_b$Ph), 4.09 (d, *J* = 5.3 Hz, 1 H, CHOBn), 3.97 (dd, *J* = 5.2, 7.5 Hz, 1 H, CHOBn), 3.93 (dd, *J* = 2.6, 11.7 Hz, 1 H, CHO), 3.78−3.75 (m, 1 H, CHO), 3.58 (d, *J* = 2.7 Hz, 1 H, CH_aH$_b$OH), 3.53 (d, *J* = 2.7 Hz, 1 H, CH$_a$$H_b$OH), 3.20 (s, 1 H, OH), 2.66−2.62

(m, 1 H, C*H*CH_2OH). − ^{13}C NMR ($CDCl_3$): δ = 137.7 (s, aromatic C), 137.3 (s, aromatic C), 128.5 (d, *J* = 159 Hz, aromatic CH), 128.4 (d, *J* = 159 Hz, aromatic CH), 128.1 (d, *J* = 160 Hz, aromatic CH), 127.9 (d, *J* = 160 Hz, aromatic CH), 127.8 (d, *J* = 153 Hz, aromatic CH), 127.4 (d, *J* = 201 Hz, aromatic CH), 79.1 (d, *J* = 158 Hz, CHOBn), 74.5 (d, *J* = 149 Hz, CHOBn), 73.7 (t, *J* = 142 Hz, OCH_2Ph), 72.7 (t, *J* = 142 Hz, OCH_2Ph), 58.9 (t, *J* = 142 Hz, CH_2OH), 58.4 (d, *J* = 190 Hz, OCH), 55.5 (d, *J* = 189 Hz, CHO), 42.4 (d, *J* = 133 Hz, CH). MS (CI, NH_3); *m/z* (%): 327 [M^+], 235 (5), 181 (1), 108 (5), 91 (100).

Epoxide (25b): To a solution of **25a** (35 mg, 0.11 mmol) in pyridine (2 mL) was added dropwise at room temp. acetic anhydride (1 mL) and the mixture was stirred for 2 hours. The solvents were evaporated under vacuum and the residue was purified by chromatography through silica gel, (Petroleum ether/EtOAc, 9:1) affording 45 mg of the acetate **25b** as a colourless oil (100%). − IR (film, KBr): $\tilde{\nu}$ = 3089 cm^{-1}, 3032, 2923, 1738 (C=O), 1497, 1454, 1365, 1247, 1127, 1045, 913, 840, 737, 698. − ^1H NMR ($CDCl_3$): δ = 7.37−7.28 (m, 10 H, aromatic H), 4.85 (d, *J* = 11.8 Hz, 1 H, OCH_aH_bPh), 4.62 (d, *J* = 11.9 Hz, 1 H, OCH_aH_bPh), 4.64−4.49 (m, 3 H, 2 × OCH_aH_bPh, C*H*OBn), 4.19 (dd, *J* = 10.5, 11.5 Hz, 1 H, CHO), 4.05 (d, *J* = 4.9 Hz, 1 H, CHO), 3.86 (dd, *J* = 4.9, 7.1 Hz, 1 H, CHOBn), 3.61 (d, *J* = 2.8 Hz, 1 H, CH_aH_bOAc), 3.47 (d, *J* = 2.6 Hz, 1 H, CH_aH_bOAc), 2.84−2.77 (m, 1 H, C*H*CH_2OAc), 2.07 (s, 3 H, $COCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 170.8 (s, C=O), 138.2 (s, aromatic C), 137.8 (s, aromatic C), 128.3 (d, *J* = 160 Hz, aromatic CH), 127.7 (d, *J* = 161 Hz, aromatic CH), 127.3 (d, *J* = 159 Hz, aromatic CH), 78.8 (d, *J* = 144 Hz, CHO), 75.1 (d, *J* = 150 Hz, CHO), 73.5 (t, *J* = 143 Hz, OCH_2Ph), 72.4 (t, *J* = 140 Hz, OCH_2Ph), 61.9 (t, *J* = 150 Hz, CH_2OAc), 57.9 (d, *J* = 185 Hz, OCH), 55.3 (d, *J* = 189 Hz, CHO), 39.3 (d, *J* = 137 Hz, CH), 20.8 (q, *J* = 129 Hz, $COCH_3$). − MS (CI, NH_3); *m/z* (%): 369 [M^+ + 1], 277 (13), 217 (1), 171 (5), 108 (14), 91 (100). − $C_{22}H_{24}O_5$ (368.43): calcd C 71.72, H 7.57; found C 71.56, H 6.61.

Azido-Carba Sugar (26): To a solution of **25a** (30 mg., 0.08 mmol) in DMF (5 mL) was added at room temp. NaN_3 (35 mg, 0.54 mmol). The mixture was stirred under reflux for 3 days. An aqueous solution of NH_4Cl was then added. The organic layer was extracted with EtOAc. The combined organic extracts were washed with brine, dried with $MgSO_4$, and the solvents were evaporated under vacuum. The yellow oil was purified by chromatography through silica gel (Petroleum ether/EtOAc, 8:2) affording 20 mg of the azide **26** as a colourless oil (40%). − IR (film, KBr): $\tilde{\nu}$ = 3338 cm^{-1} (OH), 3030, 2929, 2101 (N_3), 1737 (C=O), 1496, 1454, 1367, 1262, 1251, 1056, 735, 696. − ^1H NMR ($CDCl_3$): δ = 7.42−7.27 (m, 10 H, aromatic H), 4.84 (d, *J* = 11.9 Hz, 1 H, OCH_aH_bPh), 4.73 (d, *J* = 11.9 Hz, 1 H, OCH_aH_bPh), 4.60 (d, *J* = 11.9 Hz, 2 H, 2 × OCH_aH_bPh), 4.46 (dd, *J* = 5.3, 8.6 Hz, 1 H, C*H*OH), 4.33 (dd, *J* = 7.8, 11.2 Hz, 1 H, CH_aH_bOAc), 4.26 (dd, *J* = 7.2, 11.2 Hz, 1 H, CH_aH_bOAc), 3.97 (t, *J* = 3.7 Hz, 1 H, CHOBn), 3.77 (dd, *J* = 5.3, 9.3 Hz, 1 H, CHN_3), 3.63 (dd, *J* = 3.3, 8.6 Hz, 1 H, CHOBn), 2.56−2.49 (m, 1 H, CH), 2.02 (s, 3 H, CO_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 170.8 (s, C=O), 138.1 (s, aromatic C), 137.7 (s, aromatic C), 128.6 (d, aromatic CH), 128.3 (d, aromatic CH), 127.9 (d, aromatic CH), 127.8 (d, aromatic CH), 127.7 (d, aromatic CH), 127.6 (d, aromatic CH), 85.5 (d, *J* = 137 Hz, CH), 80.8 (d, *J* = 148 Hz, CHOBn), 75.9 (d, CH), 73.5 (t, *J* = 142 Hz, OCH_2Ph), 72.7 (t, *J* = 142 Hz, OCH_2Ph), 65.4 (d, *J* = 148 Hz, CH), 60.8 (t, *J* = 143 Hz, CH_2OAc), 41.0 (d, *J* = 129 Hz, CH), 20.9 (q, *J* = 129 Hz, CH_3). MS (CI, NH_3); *m/z* (%): 429 [M^+ + 18], 385 (12), 325 (7), 293 (2), 91 (100). − HRMS [M + Na] $C_{22}H_{25}N_3O_5Na$: calcd 434.16863; found 434.16692.

Carba-Aldehyde (30): To a solution of $(COCl)_2$ (0.07 mL, 0.8 mmol) in dry CH_2Cl_2 (5 mL) at −40°C was added DMSO (0.11 mL, 1.6 mmol) then alcohol **24b** (145 mg, 0.4 mmol). The solution was allowed to warm to −10°C over a period of 20 minutes and Et_3N (0.6 mL, 4 mmol) was added. Water (5 mL) was then added at room temperature and the organic layer was decanted. The aqueous layer was extracted with CH_2Cl_2, the combined extracts were washed with brine, dried with $MgSO_4$ and the solvent was evaporated under vacuum affording 0.131 g of the aldehyde **30** (90%). This sensitive product was used in the next step without further purification. − ^1H NMR ($CDCl_3$): δ = 9.89 (s, 1 H, C*H*O), 7.37−7.27 (m, 10 H, aromatic H), 5.11 (dd, *J* = 1.5, 6.5 Hz, 1 H, OCH), 4.69 (d, *J* = 12.1 Hz, 1 H, OCH_aH_bPh), 4.68 (d, *J* = 11.7 Hz, 1 H, OCH_aH_bPh), 4.54 (dd, *J* = 1.3, 6.5 Hz, 1 H, OCH), 4.43 (dd, *J* = 3.5, 7.1 Hz, 1 H, CHOBn), 3.95 (dd, *J* = 1.4, 3.5 Hz, 1 H, CHOBn), 2.91 (dd, *J* = 1.4, 7.1 Hz, 1 H, C*H*CHO), 1.41 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3).

Carba-Disaccharide (32): Into a dry 25 mL three-necked flask equipped with a thermometer, an inlet for argon and a septum, was introduced the 3-deoxyglucosyltributylstannane[32a] (0.361 g, 0.51 mmol) in anhydrous THF (10 mL). A 1.5 M solution of *n*BuLi in hexane (0.4 mL, 0.56 mmol) was then added slowly at −80°C. The aldehyde **30** (0.190 mg, 0.51 mmol) in dry THF (2 mL) was then added to the reaction mixture. After 30 minutes at −80°C, the mixture was quenched with a saturated solution of NH_4Cl. The organic layer was decanted and the aqueous layer extracted with ether (3 × 20 mL). The combined extracts were washed with brine, dried with $MgSO_4$ and the solvents were evaporated under vacuum. The crude oil was purified by chromatography through silica gel (Petroleum ether/EtOAc, 85:15) affording 82 mg of the carba-disaccharide **32** as a pale yellow oil (20%). $[\alpha]_D^{25}$ = +8.73, *c* = 0.33, $CHCl_3$. − IR (film, KBr): $\tilde{\nu}$ = 3460 cm^{-1} (OH), 3064, 3031, 2986, 2931, 1605, 1496, 1496, 1454, 1372, 1265, 1208, 1028, 866, 737, 698. − ^1H NMR ($CDCl_3$): δ = 7.39−7.25 (m, 25 H, aromatic H), 4.97 (dd, *J* = 3.6, 6.1 Hz, 1 H, CHO), 4.77 (d, *J* = 11.9 Hz, 1 H, OCH_aH_bPh), 4.75 (d, *J* = 11.6 Hz, 1 H, OCH_aH_bPh), 4.70 (d, *J* = 11.9 Hz, 1 H, OCH_aH_bPh), 4.65 (dd, *J* = 3.1, 7.1 Hz, 1 H, CHO), 4.60 (d, *J* = 11.8 Hz, 1 H, OCH_aH_bPh), 4.58 (d, *J* = 11.9 Hz, 2 H, 2 × OCH_aH_bPh), 4.56 (d, *J* = 11.8 Hz, 1 H, OCH_aH_bPh), 4.51 (d, *J* = 11.9 Hz, 1 H, OCH_aH_bPh), 4.50 (d, *J* = 11.8 Hz, 1 H, OCH_aH_bPh), 4.44 (d, *J* = 11.6 Hz, 1 H, OCH_aH_bPh), 4.21 (dd, *J* = 4.2, 5.8 Hz, 1 H, CHO), 4.16−4.12 (m, 1 H, CHO), 4.01−3.89 (dd, m, 4 H, 4 × CHO), 3.85 (dd, *J* = 5.9, 10.3 Hz, 1 H, CHO), 3.69 (dd, *J* = 4.1, 10.3 Hz, 1 H, CHO), 3.56 (t, *J* = 5.8 Hz, 1 H, CHO), 2.41−2.38 (m, 1 H, CH), 2.21 (ddd, *J* = 4.1, 7.1, 13.8 Hz, 1 H, H_2 equiv.), 1.78 (ddd, *J* = 4.3, 6.8, 13.8 Hz, 1 H, H_2 ax.), 1.45 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 138.4 (s, aromatic C), 138.3 (s, aromatic C), 138.1 (s, aromatic C), 137.6 (s, aromatic C), 128.4 (d, aromatic CH), 128.3 (d, aromatic CH), 127.9 (d, aromatic CH), 127.8 (d, aromatic CH), 127.7 (d, aromatic CH), 127.6 (d, aromatic CH), 127.5 (d, aromatic CH), 127.4 (d, aromatic CH), 111.4 (s, C), 84.6 (d, CHO), 82.8 (d, CHO), 80.9 (d, CHO), 79.6 (d, CHO), 75.5 (d, CHO), 75.0 (d, CHO), 74.3 (d, CHO), 73.1 (t, 2 × CH_2O), 72.9 (t, CH_2O), 72.0 (t, CH_2O), 71.1 (t, CH_2O), 70.4 (d, CHO), 69.2 (d, CHO), 68.8 (t, CH_2O), 49.3 (d, CH), 29.5 (t, CH_2), 26.7 (q, CH_3), 24.1 (q, CH_3). MS (CI, NH_3); *m/z* (%): 801 [M^+], 181 (3), 91 (100). HRMS [M + Na] $C_{50}H_{56}O_9Na$: calcd. 823.3816; found: 823.3813.

(3*R,4*S**,5*S**)-3,4-Dibenzyloxy-5-iodomethylcyclopentene (33):** To a solution of **22b** (0.21 g, 0.37 mmol) in dry DME (6 mL) at room temp. was added I_2 (94 mg, 0.37 mmol). The reaction mixture was stirred at room temp. for 3 hours then an aqueous solution of $Na_2S_2O_3$ was added and the mixture was stirred for 10 minutes.

The organic layer was decanted and the aqueous layer extracted with ether. The combined extracts were washed with saturated $Na_2S_2O_3$, brine, dried with $MgSO_4$, and the solvents were evaporated in vacuo. The resulting oil was purified by chromatography through silica gel (Petroleum ether/EtOAc, 95:5) affording 87 mg of the iodide **33** (82%). − IR (film, KBr): $\tilde{\nu}$ = 3062 cm^{-1}, 1500, 1453, 1357, 1106, 734, 696. − ^1H NMR ($CDCl_3$): δ = 7.42−7.29 (m, 10 H, aromatic H), 6.23 (dd, *J* = 2.7, 6.3 Hz, 1 H, CH=C*H*CHO), 6.09−6.07 (m, 1 H, C*H*=CHCHO), 4.77 (d, *J* = 11.8 Hz, 1 H, OC$H_a$$H_b$Ph), 4.73 (d, *J* = 12.1 Hz, 1 H, OC$H_a$$H_b$Ph), 4.68 (d, *J* = 12.1 Hz, 1 H, OC$H_a$$H_b$Ph), 4.66 (d, *J* = 11.8 Hz, 1 H, OC$H_a$$H_b$Ph), 4.34 (dd, *J* = 2.4, 5.2 Hz, 1 H, CHOBn), 4.00 (dd, *J* = 5.3, 6.5 Hz, 1 H, CHOBn), 3.59 (dd, *J* = 5.2, 9.4 Hz, 1 H, C$H_a$$H_b$I), 3.23 (dd, *J* = 9.4, 10.7 Hz, 1 H, C$H_a$$H_b$I), 3.07−3.02 (m, 1 H, C*H*CH_2I). − ^{13}C NMR ($CDCl_3$): δ = 138.9 (d, *J* = 165 Hz, vinylic C), 138.6 (s, aromatic C), 130.9 (d, *J* = 168 Hz, vinylic C), 128.3 (d, aromatic CH), 128.2 (d, aromatic CH), 127.6 (d, aromatic CH), 127.5 (d, aromatic CH), 80.3 (d, *J* = 144 Hz, *C*HOBn), 79.7 (d, *J* = 147 Hz, *C*HOBn), 72.3 (t, *J* = 146 Hz, O*C*H_2Ph), 71.6 (t, *J* = 142 Hz, OCH_2Ph), 49.3 (d, *J* = 133 Hz, *C*HCH_2I), 8.1 (t, *J* = 160 Hz, CH_2I). MS (CI, NH_3); *m*/*z* (%): 438 [M^+ + 18], 420 [M^+], 313 (36), 275 (1), 187 (5), 91 (100). − $C_{20}H_{21}IO_2$ (420.29): calcd C 57.16, H 5.04, I 30.19; found C 57.16, H 5.08, I 30.10.

Cyclopropane (34): A solution of $Cu^{I}OTf$−benzene complex (38 mg, 0.15 mmol) and a Schiff Base (56 mg, 0.15 mmol) in dry CH_2Cl_2 (15 mL) was stirred for 1 hour at room temp. under a nitrogen atmosphere. Then, the dienylsilane **17a** (1 g, 5 mmol) in dry CH_2Cl_2 (1 mL) was added to the green mixture and stirred for 10 minutes. Ethyl diazoacetate (0.62 mL, 6 mmol) was then added slowly over a period of 2 hours and the solvent was removed under vacuum. The resulting oil was purified by chromatography through silica gel (Petroleum Ether/EtOAc, 95:5) affording 0.587 g of **34** as a colourless oil (65%). − IR (film, KBr): $\tilde{\nu}$ = 3050 cm^{-1}, 2957, 2902, 1719 (C=O), 1380 (C−H), 1250 (Si−C), 1161, 831. − ^1H NMR ($CDCl_3$): δ = 7.56−7.53 (m, 2 H, aromatic H), 7.39−7.28 (m, 3 H, aromatic H), 5.88−5.86 (m, 1 H, vinylic H), 5.50−5.48 (m, 1 H, vinylic H), 4.11 (q, *J* = 7.1 Hz, 2 H, $CO_2C\mathit{H}_2CH_3$), 2.46−2.43 (m, 1 H, CHSi), 2.36−2.35 (m, 1 H, allylic H), 1.25 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2C\mathit{H}_3$), 0.91 (t, *J* = 2.6 Hz, 1 H, C*H*CO_2Et), 0.32 (s, 3 H, $SiCH_3$), 0.29 (s, 3 H, $SiCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 174.4 (s, C=O), 137.1 (s, aromatic C), 133.9 (d, J 157 Hz, CH=CH), 131.6 (d, *J* = 165 Hz, aromatic CH), 128.6 (d, *J* = 177 Hz, aromatic CH), 129.2 (d, *J* = 160 Hz, aromatic CH), 127.9 (d, *J* = 159 Hz, CH=CH), 60.3 (t, *J* = 143 Hz, $CO_2C\mathit{H}_2$), 39.7 (d, *J* = 123 Hz, SiCH), 35.1 (d, *J* = 176 Hz, CH), 29.1 (d, *J* = 172 Hz, CH), 27.5 (q, *J* = 127 Hz, $CO_2CH_2C\mathit{H}_3$), −5.2 (q, *J* = 120 Hz, $SiCH_3$), −5.5 (q, *J* = 120 Hz, $SiCH_3$). − MS (CI, NH_3): *m*/*z* (%): 304 [M^+], 287 [M^+], 241 (2), 208 (18), 180 (6), 152 (29), 135 (61), 119 (3), 106 (39), 91 (4). − $C_{17}H_{22}O_2Si$ (286.45): calcd. C 71.28, H 7.74; found C 71.11, H 7.76.

Protected Diols (35a−b): Following the general procedure (conditions **B**), the dihydroxylation-acetonide protection of **34** afforded **35** as a 7:3 mixture of diastereomers (72%). − *Major Diastereomer* (**35a**). − IR (film, KBr): $\tilde{\nu}$ = 3071 cm^{-1}, 3049, 2986, 1722 (C=O), 1428, 1410, 1381, 1273 (Si−C), 1208, 1179 (C−O), 1072, 1040, 814, 779, 734, 702, 649. − ^1H NMR ($CDCl_3$): δ = 7.55−7.52 (m, 2 H, aromatic H), 7.40−7.35 (m, 3 H, aromatic H), 4.55 (dd, *J* = 4.8, 6.5 Hz, 1 H, OCH), 4.50 (d, *J* = 6.5 Hz, 1 H, OCH), 4.10 (q, *J* = 7.1 Hz, 1 H, $CO_2C\mathit{H}_aH_bCH_3$), 4.07 (q, *J* = 7.1 Hz, 1 H, $CO_2CH_a\mathit{H}_bCH_3$), 2.12−2.07 (m, 2 H, 2 × CH), 1.92 (dd, *J* = 3.2, 6.6 Hz, 1 H, CH), 1.52 (s, 3 H, CH_3), 1.24 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2C\mathit{H}_3$), 1.22 (s, 3 H, CH_3), 0.38 (s, 3 H, $SiCH_3$), 0.37 (s, 3 H, $SiCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 172.8 (s, C=O), 135.9 (s, aromatic C), 133.7 (d, *J* = 158 Hz, aromatic CH), 129.5 (d, *J* = 158 Hz, aromatic CH), 127.9 (d, *J* = 158 Hz, aromatic CH), 110.8 (s, C), 109.9 (s, C), 82.9 (d, *J* = 152 Hz, CHO), 82.1 (d, *J* = 152 Hz, CHO), 60.3 (t, *J* = 151 Hz, $CO_2C\mathit{H}_2CH_3$), 33.6 (d, *J* = 175 Hz, CH), 32.8 (d, *J* = 122 Hz, CHSi), 32.5 (d, *J* = 178 Hz, CH), 26.5 (d, *J* = 155 Hz, CH), 26.4 (q, *J* = 129 Hz, CH_3), 24.3 (q, *J* = 129 Hz, CH_3), 14.2 (q, *J* = 127 Hz, $CO_2CH_2C\mathit{H}_3$), −4.5 (q, *J* = 120 Hz, $SiCH_3$), −4.7 (q, *J* = 120 Hz, $SiCH_3$). MS (CI, NH_3); *m*/*z* (%): 378 [M^+ + 18], 360 [M^+], 303 (72), 273 (4), 229 (7), 193 (40), 152 (100), 135 (57), 94 (22). − $C_{20}H_{28}O_4Si$ (360.52): calcd C 66.63, H 7.83, Si 7.79; found C 66.49, H 7.66, Si 7.68. − *Minor Diastereomer* (**35b**). − IR (film, KBr): $\tilde{\nu}$ = 2985 cm^{-1}, 2935, 1742 (C=O), 1437, 1369, 1232 (Si−C), 1038, 871, 741, 695. − ^1H NMR ($CDCl_3$): δ = 7.62−7.60 (m, 2 H, aromatic H), 7.37−7.34 (m, 3 H, aromatic H), 4.64 (t, *J* = 5.2 Hz, 1 H, OCH), 4.52 (d, *J* = 5 Hz, 1 H, OCH), 4.09 (q, *J* = 7.1 Hz, 2 H, $CO_2C\mathit{H}_2CH_3$), 2.14 (dd, *J* = 3.5, 6.7 Hz, 1 H, CH), 2.03−2.00 (m, 1 H, CH), 1.47 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 1.24 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2C\mathit{H}_3$), 1.09 (t, *J* = 3.2 Hz, 1 H, C*H*$CO_2CH_2CH_3$), 0.46 (s, 3 H, $SiCH_3$), 0.43 (s, 3 H, $SiCH_3$). − ^{13}C NMR ($CDCl_3$): δ = 172.1 (s, C=O), 138.9 (s, aromatic C), 133.9 (d, *J* = 157 Hz, aromatic CH), 128.8 (d, *J* = 159 Hz, aromatic CH), 127.6 (d, *J* = 156 Hz, aromatic CH), 110.8 (s, C), 111.2 (s, C), 87.5 (d, *J* = 153 Hz, CHO), 83.9 (d, *J* = 154 Hz, CHO), 60.4 (t, *J* = 143 Hz, $CO_2C\mathit{H}_2CH_3$), 35.7 (d, *J* = 120 Hz, CH), 35.3 (d, *J* = 175 Hz, CH), 31.4 (d, *J* = 174 Hz, CH), 30.3 (d, *J* = 171 Hz, CH), 26.7 (q, *J* = 124 Hz, CH_3), 24.6 (q, *J* = 124 Hz, CH_3), 14.1 (q, *J* = 127 Hz, $CO_2CH_2C\mathit{H}_3$), −2.3 (q, *J* = 120 Hz, $SiCH_3$), −2.9 (q, *J* = 120 Hz, $SiCH_3$). MS (CI, NH_3); *m*/*z* (%): 378 [M^+ + 18], 361 [M^+ + 1], 345 (7), 302 (76), 283 (41), 242 (16), 209 (5), 193 (18), 168 (70), 151 (100), 135 (97), 91 (27). − $C_{20}H_{28}O_4Si$ (360.52): calcd C 66.63, H 7.83, Si 7.79; found C 66.72, H 7.80, Si 7.87.

Ester (36): To a solution of **35a−b** (2.4 g, 6.4 mmol) in DMF (50 mL) at room temp. was added CsF (1.9 g, 12.8 mmol). The heterogeneous mixture was heated at 50°C overnight and water (40 mL) was added. The mixture was extracted with Et_2O (3 × 20 mL) and the combined extracts were washed with brine then dried with $MgSO_4$. The solvents were evaporated under vacuum to give a yellow oil, which was purified by chromatography through silica gel (Petroleum ether/EtOAc, 95:5) affording 1.3 g of **36** as a colourless oil (90%). − IR (film, KBr): $\tilde{\nu}$ = 3065 cm^{-1}, 2985, 2935, 1736 (C=O), 1414, 1372, 1232, 1208, 1160, 1058, 876, 733. − ^1H NMR ($CDCl_3$): δ = 5.78 (dt, *J* = 2, 5.8 Hz, 1 H, vinylic H), 5.71 (dt, *J* = 0.8, 5.8 Hz, 1 H, vinylic H), 5.09 (dd, *J* = 0.8, 5.8 Hz, 1 H, OCH), 4.77 (t, *J* = 5.8 Hz, 1 H, OCH), 4.15 (q, *J* = 7.1 Hz, 2 H, $CO_2C\mathit{H}_2CH_3$), 3.14−3.09 (m, 1 H, CH), 2.63 (dd, *J* = 8.2, 16.7 Hz, 1 H, C$H_a$$H_b$$CO_2CH_2CH_3$), 2.42 (dd, *J* = 7.1, 16.7 Hz, 1 H, $CH_a\mathit{H}_bCO_2CH_2CH_3$), 1.37 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.26 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2C\mathit{H}_3$). − ^{13}C NMR ($CDCl_3$): δ = 172.7 (s, C=O), 135.6 (d, *J* = 163 Hz, vinylic C), 130.6 (d, *J* = 168 Hz, vinylic C), 110.4 (s, C), 85.2 (d, *J* = 153 Hz, CHO), 78.6 (d, *J* = 156 Hz, CHO), 60.3 (t, *J* = 152 Hz, $CO_2C\mathit{H}_2$), 43.8 (d, *J* = 133 Hz, CH), 33.6 (t, *J* = 130 Hz, *C*H_2CO_2), 27.2 (q, *J* = 126 Hz, CH_3), 25.8 (q, *J* = 123 Hz, CH_3), 14.2 (q, *J* = 127 Hz, $CO_2CH_2C\mathit{H}_3$). MS (CI, NH_3); *m*/*z* (%): 244 [M^+ + 17], 227 [M^+, 77], 211 (41), 186 (3), 169 (100), 152 (3), 140 (10), 123 (36), 109 (2), 81 (11). − $C_{12}H_{18}O_4$ (226.27): calcd C 63.70, H 8.02; found C 63.80, H 8.08.

Bis-Acetonide (37): Following the general dihydroxylation-protection procedure, **37** was obtained from olefin **36** in 82% yield. − IR

(film, KBr): $\tilde{\nu}$ = 2987 cm^{-1}, 2938, 1736 (C=O), 1381, 1247, 1212, 1160, 1078, 984, 865, 806, 735. − ^1H NMR ($CDCl_3$): δ = 4.78 (t, *J* = 5.1 Hz, 1 H, OCH), 4.56 (d, *J* = 5.3 Hz, 1 H, OCH), 4.40−4.36 (m, 2 H, 2 × CHO), 4.16 (q, *J* = 7.1 Hz, 1 H, $CO_2CH_aH_b$), 4.15 (q, *J* = 7.1 Hz, 1 H, $CO_2CH_aH_b$), 2.65 (dd, *J* = 9.8, 16.2 Hz, 1 H, $CH_aH_bCO_2$), 2.57 (dd, *J* = 5.5, 16.2 Hz, 1 H, $CH_aH_bCO_2$), 2.48−2.41 (m, 1 H, CH), 1.47 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.27 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$). MS (CI, NH_3); *m/z* (%): 318 [M^+ + 17], 301 [M^+], 285 (52), 255 (12), 243 (19), 227 (14), 211 (3), 197 (8), 184 (15), 155 (2), 139 (9), 125 (3), 110 (14), 85 (16).

Alcohol (38): To a solution of ester **37** (0.115 g, 0.38 mmol) in dry ether (5 mL) was added at 0°C a 1 M solution of $LiAlH_4$ in ether (0.4 mL, 0.38 mmol). The reaction mixture was stirred for 2 hours at 0°C then quenched with NH_4Cl. The organic layer was decanted and the aqueous layer extracted with ether. The combined extracts were washed with a 1 M HCl solution, saturated $NaHCO_3$, brine, dried with $MgSO_4$, and the solvent was evaporated under vacuum. The yellow oil was purified by chromatography through silica gel (Petroleum ether/EtOAc, 8:2) affording 0.1 g of the alcohol **38** as a white solid (100%), recrystallized from Petroleum ether/CH_2Cl_2; m.p. 48−50°C. − IR (solution, CH_2Cl_2): $\tilde{\nu}$ = 3514 cm^{-1} (OH), 2988, 2939, 1383, 1254, 1213, 1160, 1059, 859. − ^1H NMR ($CDCl_3$): δ = 4.63 (t, *J* = 5 Hz, 1 H, OCH), 4.55 (d, *J* = 5.2 Hz, 1 H, OCH), 4.45 (dd, *J* = 5.6, 7.8 Hz, 1 H, CHO), 4.40 (d, *J* = 5.6 Hz, 1 H, OCH), 3.78−3.75 (m, 2 H, CH_2OH), 2.49 (s, 1 H, OH), 2.16−2.09 (m, 1 H, CH), 1.92−1.82 (m, 2 H, CH_2), 1.47 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 111.9 (s, C), 110.4 (s, C), 85.6 (d, *J* = 151 Hz, CHO), 84.1 (d, *J* = 146 Hz, CHO), 83.3 (d, *J* = 155 Hz, CHO), 81.3 (d, *J* = 156 Hz, CHO), 61.4 (t, *J* = 141 Hz, CH_2OH), 46.8 (d, *J* = 120 Hz, CH), 30.7 (t, *J* = 125 Hz, CH_2), 27.7 (q, *J* = 127 Hz, CH_3), 26.7 (q, *J* = 127 Hz, CH_3), 25.4 (q, *J* = 127 Hz, CH_3), 24.4 (q, *J* = 127 Hz, CH_3). MS (CI, NH_3); *m/z* (%): 259 [M^+ + 1], 243 (47), 227 (1), 185 (39), 153 (5), 143 (22), 125 (52), 113 (15), 95 (55), 85 (19). − $C_{13}H_{22}O_5$ (258.31): calcd C 60.45, H 8.58; found C 60.53, H 8.45.

Carba-Aldehyde (39): To a solution of $(COCl)_2$ (0.13 mL, 1.5 mmol) in dry CH_2Cl_2 (5 mL) at −40°C was added DMSO (0.21 mL, 3 mmol) and after 5 minutes, a solution of the alcohol **38** (0.193 g, 0.75 mmol) in CH_2Cl_2 (2 mL). The solution was allowed to warm to −10°C over a period of 20 minutes and Et_3N (1.1 mL, 7.5 mmol) was added. Water (5 mL) was then added at room temp. and the organic layer was decanted. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were washed with brine, dried with $MgSO_4$ and the solvent evaporated under vacuum. The residue was purified by chromatography through silica gel (Petroleum ether/EtOAc, 9:1) affording 0.164 g of the aldehyde **39** (85%). − IR (film, KBr): $\tilde{\nu}$ = 2988 cm^{-1}, 2936, 2726, 1725 (C=O), 1456, 1381, 1245, 1212, 1161, 1059, 858, 808, 738, 699. − ^1H NMR ($CDCl_3$): δ = 9.84 (s, 1 H, C*H*O), 4.79 (t, *J* = 5.2 Hz, 1 H, OCH), 4.59 (d, *J* = 5.3 Hz, 1 H, OCH), 4.42−4.39 (m, 2 H, 2 × OCH), 2.85 (ddd, *J* = 1.2, 9.6, 17.9 Hz, 1 H, CH_aH_bCHO), 2.72 (ddd, *J* = 1, 5.1, 17.9 Hz, 1 H, CH_aH_bCHO), 2.53−2.47 (m, 1 H, CH), 1.47 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3). MS (CI, NH_3); *m/z* (%): 274 [M^+ + 18], 257 [M^+ + 1], 241 (44), 229 (1), 216 (11), 199 (40), 183 (19), 152 (3), 123 (13), 95 (13), 85 (9).

Carba-Disaccharide (40a−b): Into a dry 25 mL three-necked flask equipped with a thermometer, an inlet for argon and a septum was introduced the 3-deoxyglucosyltributylstannane[32a] (0.346 g, 0.5 mmol,) in anhydrous THF (10 mL). A 1.5 M solution of *n*BuLi in hexane (0.4 mL, 0.54 mmol) was then added slowly at −80°C and the mixture was stirred for 0.5 hour. The aldehyde **39** (0.126 g, 0.5 mmol) in dry THF (2 mL) was then added dropwise to the resulting solution at −80°C. After 30 minutes at −80°C, the solution was quenched with a saturated solution of NH_4Cl. The organic layer was decanted and the aqueous layer extracted with ether (3 × 20 mL). The combined extracts were washed with brine, dried with $MgSO_4$ and the solvents were evaporated under vacuum. The crude oil was purified by chromatography through silica gel (Petroleum ether/EtOAc, 7:3) affording 0.260 g of a mixture of three diastereomeric alcohols, which were not separated further (78%). To a solution of the three preceding diastereomers (0.330 g, 0.46 mmol) in anhydrous CH_2Cl_2 (10 mL) was added 4 Å molecular sieves, NaOAc (85 mg, 1 mmol) and pyridinium dichromate (0.754 g, 2 mmol). After 16 hours at room temp., ether (10 mL) was added and the resulting suspension was filtered. The solvents were evaporated under vacuum and the crude product was purified by chromatography through silica gel (Petroleum ether/EtOAc, 9:1) affording 0.190 g (59%) of the carba-C-disaccharide **40** as a 1:1 mixture of two diastereomers **40a** and **40b**. **40a** (0.1 g, 31%): $[\alpha]_D^{25}$= −9.76, *c* = 0.5, $CHCl_3$. − IR (film, KBr): $\tilde{\nu}$ = 3064 cm^{-1}, 3031, 2987, 2935, 1720 (C=O), 1497, 1454, 1381, 1246, 1211, 1060, 860, 736, 698. − ^1H NMR ($CDCl_3$): δ = 7.36−7.17 (m, 15 H, aromatic H), 4.85 (dd, *J* = 12 Hz, 1 H, OCH_aH_bPh), 4.75−4.51 (m, 7 H, 2 × CHO and 5 × OCH_aH_bPh), 4.44 (dd, *J* = 2.9, 5.6 Hz, 1 H, H_1'), 4.41−4.36 (m, 2 H, 2 × CHO), 3.78−3.74 (m, 2 H, CH_2OBn), 3.72−3.65 (m, 1 H, H_3'), 3.56−3.54 (m, 2 H, 2 × CHO), 3.08 (dd, *J* = 10.3, 18.1 Hz, 1 H, CH_aH_bCO), 2.80 (dd, *J* = 4.7, 18.1 Hz, 1 H, CH_aH_bCO), 2.66 (ddd, *J* = 3.1, 4.5, 13.3 Hz, 1 H, CH_aH_b), 2.52−2.46 (m, 1 H, CH), 1.79 (ddd, *J* = 5.8, 10.3, 13.3 Hz, 1 H, CH_aH_b), 1.47 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 210.2 (s, C=O), 138.2 (s, aromatic C), 128.4 (d, aromatic CH), 128.3 (d, aromatic CH), 127.8 (d, aromatic CH), 128.7 (d, aromatic CH), 127.6 (d, aromatic CH), 127.5 (d, aromatic CH), 111.8 (s, C), 110.3 (s, C), 84.8 (d, CHO), 84.1 (d, CHO), 81.7 (d, CHO), 81.4 (d, CHO), 77.0 (d, CHO), 76.6 (d, CHO), 76.7 (d, CHO), 76.1 (d, CHO), 74.5 (t, CH_2O), 73.4 (t, CH_2O), 71.5 (t, CH_2O), 68.9 (t, CH_2O), 44.3 (d, CH), 36.9 (t, CH_2), 28.9 (t, CH_2), 27.8 (q, CH_3), 26.6 (q, CH_3), 25.5 (q, CH_3), 24.3 (q, CH_3). MS (CI, NH_3); *m/z* (%): 691 [M^+ + 17], 615 (2), 507 (1), 436 (1), 229 (2), 91 (100). HRMS [M + Na] $C_{40}H_{48}O_9Na$: calcd. 695.3190; found: 695.3191. − **40b** (90 mg, 28%): $[\alpha]_D^{25}$= +27.7, *c* = 0.46, $CHCl_3$. − IR (film, KBr): $\tilde{\nu}$ = 3064 cm^{-1}, 3031, 2987, 2935, 1720 (C=O), 1603, 1496, 1454, 1382, 1211, 1059, 911, 860, 734, 698. − ^1H NMR ($CDCl_3$): δ = 7.36−7.16 (m, 15 H, aromatic H), 4.84 (dd, *J* = 11.1 Hz, 1 H, OCH_aH_bPh), 4.74−4.51 (m, 7 H, 2 × CHO, 5 × OCH_aH_bPh), 4.41−4.34 (m, 3 H, 3 × CHO), 3.76−3.74 (m, 2 H, CH_2OBn), 3.67−3.62 (m, 2 H, 2 × CHO), 3.58−3.57 (m, 1 H, CHO), 3.14 (dd, *J* = 10.3, 18.1 Hz, 1 H, CH_aH_bCO), 2.75 (dd, *J* = 4.6, 18.1 Hz, 1 H, CH_aH_bCO), 2.62 (ddd, *J* = 3.0, 4.4, 13.2 Hz, 1 H, CH_aH_b), 2.51−2.46 (m, 1 H, CH), 1.79 (ddd, *J* = 5.9, 10.2, 13.2 Hz, 1 H, CH_aH_b), 1.47 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 210.4 (s, C=O), 138.4 (s, aromatic C), 138.0 (s, aromatic C), 128.4 (d, aromatic CH), 128.3 (d, aromatic CH), 128.2 (d, aromatic CH), 127.8 (d, aromatic CH), 127.7 (d, aromatic CH), 127.6 (d, aromatic CH), 111.9 (s, C), 110.2 (s, C), 85.0 (d, CHO), 84.1 (d, CHO), 81.5 (d, CHO), 77.8 (d, CHO), 77.2 (d, CHO), 77.1 (d, CHO), 76.7 (d, CHO), 75.6 (d, CHO), 74.4 (t, CH_2O), 73.4 (t, CH_2O), 71.6 (t, CH_2O), 68.9 (t, CH_2O), 44.2 (d, CH), 36.5 (t, CH_2), 29.2 (t, CH_2), 27.7 (q, CH_3), 26.5 (q, CH_3), 25.5 (q, CH_3), 24.2 (q, CH_3). − MS (CI, NH_3); *m/z* (%): 691 [M^+ + 17], 615 (1), 436 (1), 91 (100). HRMS [M + Na] $C_{40}H_{48}O_9Na$: calcd. 695.3190; found: 695.3192.

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