Asymmetric Total Synthesis of Taxol®**

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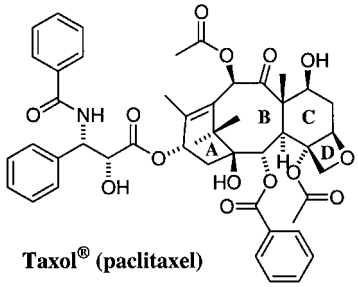
Abstract: The asymmetric total synthesis of Taxol was achieved by way of B to BC to ABC to ABCD ring construction. Optically active 8-membered ring enones **1** and **2** corresponding to the B ring of Taxol have been synthesized in high yields from the linear precursors **28** and **32**, respectively, by intramolecular aldol cyclization using SmI_2. The optically active linear polyoxy compounds **28** and **32** were obtained by way of diastereoselective aldol reaction between aldehyde **4** and ketene silyl acetal **8** catalyzed by $MgBr_2 \cdot OEt_2$. The chiral pentanal **4** was synthesized either by asymmetric aldol reaction of achiral aldehyde **7** and ketene silyl acetal **8** by means of a chiral Lewis acid or by diastereoselective aldol reaction between the chiral aldehyde **16**, derived from L-serine, and the lithium enolate derived from methyl isobutyrate. Optically active bicyclo[6.4.0]dodecanone **38**β, corresponding to the BC ring system of Taxol, was prepared from 8-membered ring enone **2** in high yield by stereoselective Michael addition and successive intramolecular aldol cyclization. Furthermore, baccatin III, the ABCD ring system of Taxol, was efficiently synthesized from the BC ring system **38**β by successive construction of the A and D rings by intramolecular pinacol coupling cyclization, introduction of the C-13 hydroxyl group and an oxetane-forming reaction. Finally, the total synthesis of Taxol was accomplished by dehydration condensation between a protected *N*-benzoylphenylisoserine **70** or **75** and 7-TES baccatin III, prepared from baccatin III. Taxol side chains **70**, **73**, **75**, and **77**, optically active protected *N*-benzoylphenylisoserines, were synthesized by enantioselective aldol reaction from two achiral starting materials, benzaldehyde and an enol silyl ether **65** derived from *S*-ethyl benzyloxyethanethioate.

Keywords: antitumor agents · cyclizations · natural products · Taxol · total synthesis

Introduction

Taxoids are diterpenoids isolated from Taxus species and have a highly oxidized tricyclic carbon framework consisting of a central 8-membered and two peripheral 6-membered rings.[2] Taxol® (paclitaxel), a taxoid isolated in 1971, has been found to have anticancer properties, and the synthesis of its highly functionalized structure has been a tempting challenge for synthetic chemists over the past two decades.[3]



Taxol® (paclitaxel)

In past few years, four US groups have reported the total synthesis of Taxol by way of independent and original pathways.[4–7] These successful syntheses of Taxol were landmarks in the field of organic synthesis and the associated methodologies represented significant developments in synthetic technology. These approaches to synthesizing the basic skeleton of Taxol can be divided into two types; that is, elaboration of naturally occurring terpenes to the AB ring system of Taxol by epoxy-alcohol fragmentation, or a convergent strategy including a B ring closure reaction of connected A – C ring systems.

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[**] The asymmetric total synthesis of Taxol is outlined in *Proc. Jpn. Acad.* **1997**,[1] and the preliminary reports of the constructions of intermediate skeletons for Taxol and related compounds have appeared in *Chem. Lett.* (**1995** – **1998**).[9–20]

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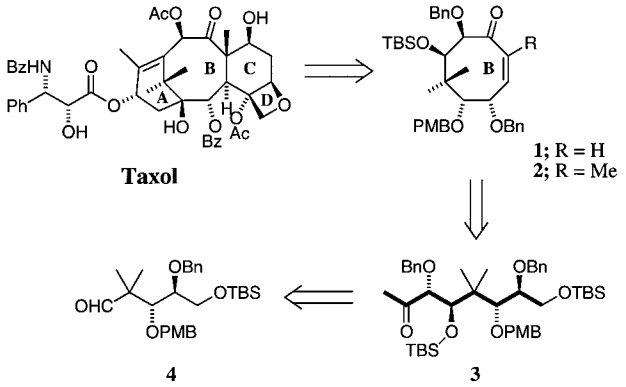
In Holton's and Wender's basic strategies, the total syntheses were achieved by a sequence of effective synthetic reactions involving formation of the AB ring by fragmentation of epoxy alcohols derived from (−)-camphor and α-pinene, respectively.[4, 7] On the other hand, the key step of B ring closure was carried out after connecting the A and C rings in the convergent approach used in Nicolaou's, Danishefsky's and Kuwajima's total syntheses.[5, 6, 8] Unlike these strategies, our preliminary reported total synthesis of Taxol was achieved by a unique pathway starting from an 8-membered ring compound by way of B to BC to ABC to ABCD ring construction.[1, 9–20] (Scheme 1).



Scheme 1. Retrosynthesis of Taxol from optically active linear compounds **3** and **4**.

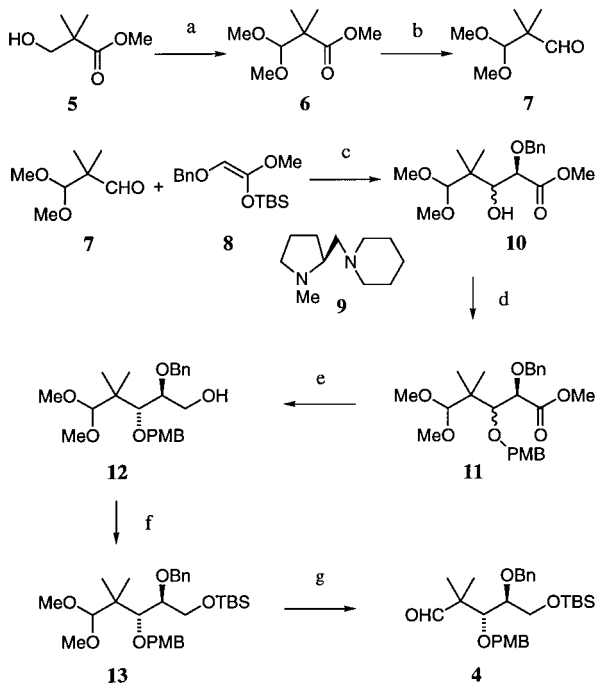
Editorial Board Member:[*] *Teruaki Mukaiyama obtained his Ph.D. from the University of Tokyo in 1957 after graduating from the Tokyo Institute of Technology. Since 1987 he has been Professor of Organic Chemistry at the Science University of Tokyo; he is also Professor Emeritus at both the University of Tokyo and the Tokyo Institute of Technology. He is a recipient of many major awards and is currently a member of the Japan Academy as well as a foreign member of the Academies of Sciences in France and Poland. His research involves exploration of new possibilities in reaction chemistry; he has published over 720 papers. These include new concepts in synthetic reactions which were eventually applied to the wide range of synthetic subjects such as carbon skeleton construction, stereoselective glycosylation and peptide and nucleotide syntheses. For the past four decades, his major interests have been focused on the fundamental subjects (e.g. exploration of new synthetic methods), but he accepted the challenge of a targeted synthesis in 1992. Five years after the start of the project, he succeeded in completing the asymmetric total synthesis of Taxol.*

[*] Members of the Editorial Board will be introduced to readers with their first manuscript.

We planned the synthesis of taxane's basic skeleton starting from the B ring of Taxol, prepared from optically active polyoxy unit **3**, and proceeding by construction of the A and C ring systems onto this framework. According to this plan, it is expected that flexible pathways in the syntheses of Taxol and its analogues are possible via B ring compounds prepared from their respective chiral linear precursors. In this paper, we would like to report our synthetic routes toward Taxol in detail.

Results and Discussion

Synthesis of optically active polyoxy linear compounds corresponding to the B ring of Taxol: In the first place, the preparation of optically active polyoxy unit **3** corresponding to the B ring of Taxol by way of asymmetric synthesis was studied.[9] Oxidation of commercially available methyl 3-hydroxy-2,2-dimethylpropionate (**5**) with Swern reagent gave the corresponding aldehyde, which in turn was converted to dimethyl acetal **6** (Scheme 2). Reduction of the ester function of **6** with $LiAlH_4$ followed by Swern oxidation gave the desired aldehyde **7**. Next, the asymmetric aldol reaction between **7** and ketene silyl acetal **8** using chiral Sn^{II} Lewis acid was examined under several reaction conditions.[21] At last, the desired optically active ester **10** was obtained in good selectivity (*anti*/*syn* = 80/20, *anti* aldol; 87–93% *ee*) by using $Sn(OTf)_2$ coordinated with chiral diamine **9**. The relative configuration of **10-*anti*** was determined by measuring the



Scheme 2. Synthesis of optically active aldehyde **4**. Reagents and conditions: a) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C to RT (89%); $HC(OMe)_3$, TsOH, MeOH, RT (93%); b) $LiAlH_4$, THF, RT (90%); $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C to RT (85%); c) $Sn(OTf)_2$, chiral diamine **9**, $nBu_2Sn(OAc)_2$, CH_2Cl_2, −23 °C (68%, *anti*/*syn* = 80/20); d) $PMBOC(CCl_3)$=NH, TfOH, Et_2O, 0 °C (95%, *anti*/*syn* = 80/20); e) $LiAlH_4$, THF, 0 °C (86% from **11-*anti***); f) TBSCl, imidazole, CH_2Cl_2, RT (93%); g) AcOH, H_2O, THF, RT (87%).

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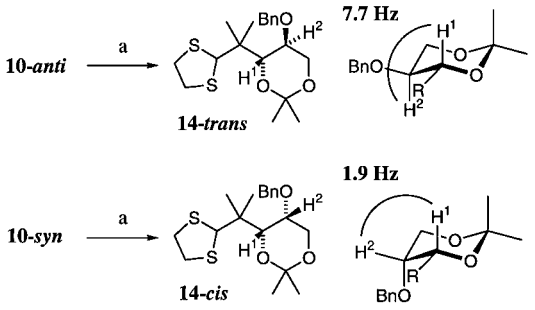
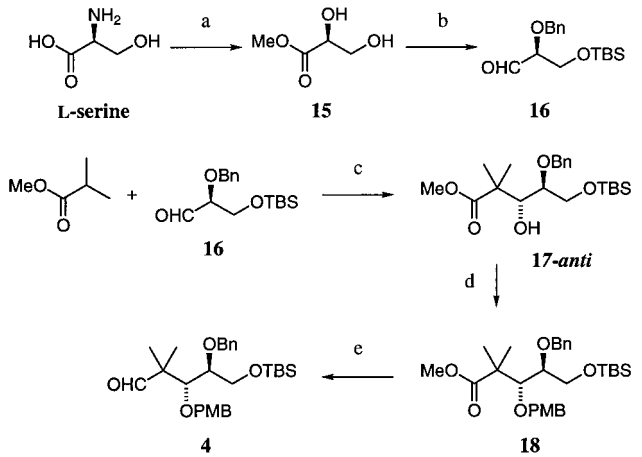
coupling constant of its derivative **14-*trans*** as shown in Scheme 3. The secondary hydroxyl group of **10** was protected by the imidate method using TfOH, and then reduction of a diastereomeric mixture of **11** gave the corresponding alcohol **12**, which was separated as a single stereoisomer. A silyl ether **13** was obtained from **12** on treatment with *tert*-butyldimethylsilyl chloride and imidazole. Finally, the acetal was deprotected by acetic acid to give desired optically active aldehyde **4**.



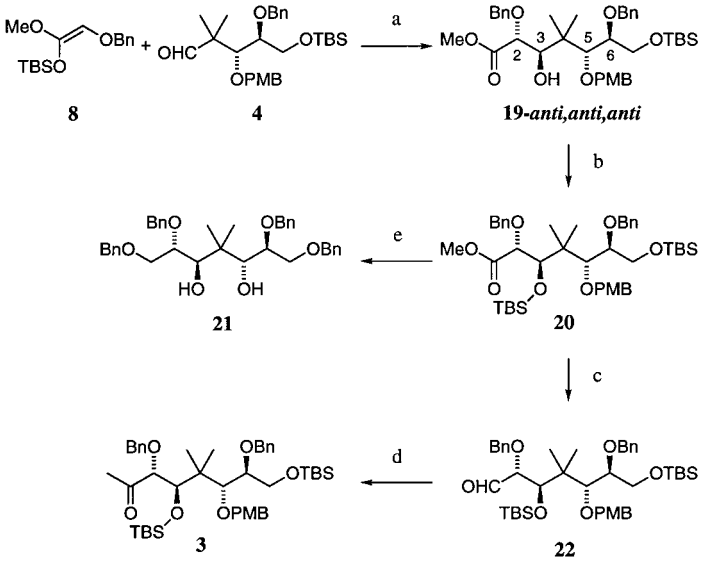
Scheme 3. Relative stereochemistries of aldols **10**. Reagents and conditions: a) $HSCH_2CH_2SH$, $BF_3 \cdot OEt_2$, CH_2Cl_2, RT (92%); $LiAlH_4$, THF, 0°C (90%); $Me_2C(OMe)_2$, CSA, CH_2Cl_2, RT (78%).

The chiral aldehyde **4** was also prepared by the following route: optically active dihydroxyester **15** was prepared from L-serine by a literature method,[22] and subsequent protections of the primary alcohol with *tert*-butyldimethylsilyl chloride and secondary alcohol with benzylimidate gave dialkoxyester, which was reduced with DIBAL to produce aldehyde **16**. The stereoselective aldol reaction between **16** and the lithium enolate derived from methyl isobutyrate smoothly proceeded to afford the aldol product **17** (*anti*/*syn* = 77/23). Successive treatment of the hydroxyl group by the imidate method, reduction of the ester function of **18** with DIBAL and Swern oxidation then gave the aldehyde **4** (Scheme 4).



Scheme 4. An alternative pathway for the synthesis of aldehyde **4**. Reagents and conditions: a) $NaNO_3$, H_2SO_4, H_2O, RT; then $HC(OMe)_3$, H_2SO_4, MeOH, 60°C (88%); b) TBSCl, imidazole, DMF, 0°C (82%); $BnOC(CCl_3)$=NH, TfOH, Et_2O, RT (100%); DIBAL, hexane, −78°C (95%); c) LDA, Et_2O, −78°C (65% of **17-*anti***, 20% of **17-*syn***); d) $PMBOC(CCl)_3$=NH, TfOH, CH_2Cl_2, 0°C (99% based on 76% conversion); e) DIBAL, hexane, −78°C (92%); $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78°C to RT (97%).

Though the aldol reaction between **4** and the lithium enolate derived from methyl benzyloxyacetate gave the corresponding adduct with poor stereoselectivity, the aldol reaction between **4** and ketene silyl acetal **8** took place rapidly in the presence of $MgBr_2 \cdot OEt_2$ to yield the desired ester **19** in good stereoselectivity (2,3,5,6-*anti,anti,anti*/three diastereomers = 81/19/0/0). On the other hand, ether-free $MgBr_2$ did not promote this aldol reaction, probably because it was not soluble in toluene. Treatment of the alcohol with *tert*-butyldimethylsilyl triflate and 2,6-lutidine afforded disiloxyester **20** in high yield. The pseudo-C_2 symmetrical structure of **20** was deduced by measuring the ^1H NMR spectrum of its derivative **21**. Reduction of the ester function of **20** with DIBAL followed by Swern oxidation gave the corresponding aldehyde **22**, and subsequent alkylation with MeMgBr and Swern oxidation then produced methyl ketone **3** (Scheme 5).



Scheme 5. Synthesis of optically active ketone **3**. Reagents and conditions: a) $MgBr_2 \cdot OEt_2$, toluene, −15°C (87% based on 88% conversion, 71% of **19-*anti,anti,anti***, 16% of **19-*syn,anti,anti***); b) TBSOTf, 2,6-lutidine, CH_2Cl_2, 0°C (100%); c) DIBAL, toluene, −78°C; $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78°C to RT (94% from **20**); d) MeMgBr, Et_2O, −78°C (99%); $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78°C to RT (97%); e) DIBAL, toluene, −78°C (81%); TBAF, THF, RT (91%); BnBr, NaH, THF, RT (87%); DDQ, MS 4 Å, CH_2Cl_2, RT (79%); 1N HCl, THF, RT (53%).

A single recrystallization of **3** thus gave optically pure methyl ketone **3**. The relative stereochemistry and pseudo-C_2 symmetrical structure of **3**, shown in Figure 1, was determined by X-ray crystallography of **3**.[23]

Attempted synthesis of 8-membered ring compounds: In 1985, Kocienski reported the formation of 8-membered ring compounds by cyclization of linear precursors containing both acetal and enol silyl ether groups by intramolecular aldol-type reaction between these two functionalities promoted by Lewis acids such as $TiCl_4$, $TiCl_2(OiPr)_2$, $BF_3 \cdot OEt_2$, $SnCl_4$, TMSOTf, etc.[24] Furthermore, it is well known that an α,β-unsaturated ketone can be formed from a β-alkylthioketone by oxidation and subsequent elimination. We therefore looked at the intramolecular aldol reaction between a dithioacetal and an

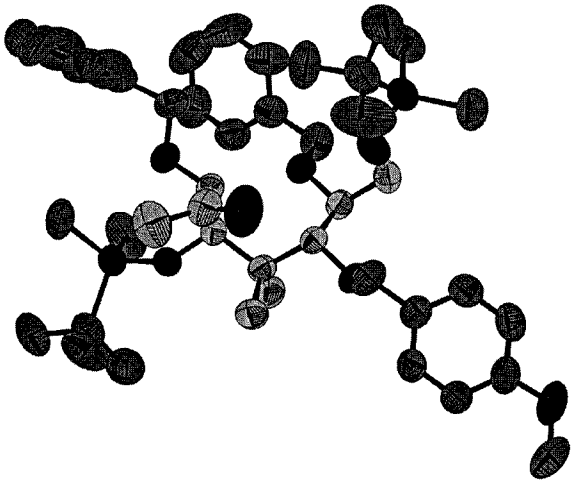
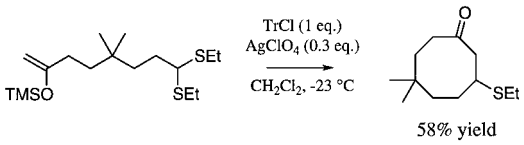


Figure 1. ORTEP drawing and relative stereochemistry of ketone **3**.

enol silyl ether in the presence of $TrClO_4$, first using a model substrate having no other oxygen-containing functionalities.[25] Actually, in the presence of a stoichiometric amount of TrCl and 30 mol% of $AgClO_4$, the intramolecular aldol reaction proceeded smoothly at $-23\,^{\circ}C$ to produce the desired β-alkylthiocyclooctanone in fairly good yield (Scheme 6).

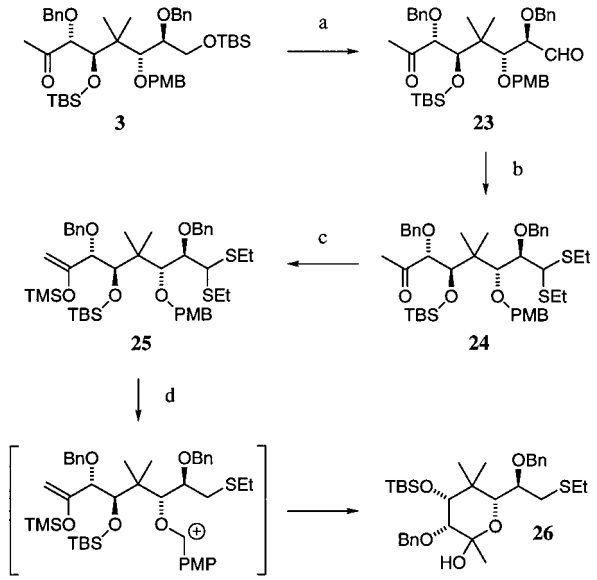


Scheme 6. Synthesis of 8-membered ring compound by means of Lewis acid.

Next, synthesis of enol silyl ether **25** was tried using optically active polyoxy unit **3** which contains all the functionalities necessary for the construction of B ring of Taxol.[10] Selective cleavage of the primary silyl ether followed by Swern oxidation afforded ketoaldehyde **23** in good yield. The aldehyde was protected as its dithioacetal, which was in turn transformed to the corresponding enol silyl ether **25**.

Then intramolecular aldol reaction of **25** was tried in the presence of $TrClO_4$ under several reaction conditions. In the above procedure, deprotection of the PMB group of **25** produced exclusively cyclic hemiketal **26**. This reaction is assumed to proceed by *p*-methoxybenzylic hydride reduction of the dithioacetal, followed by cyclization after quenching to give this undesired product (Scheme 7).

Synthesis of the B ring of Taxol: Secondly, utilization of an intramolecular aldol cyclization using SmI_2 was planned for constructing 8-membered ring compounds following the SmI_2-mediated Reformatsky cyclizations used in the syntheses of medium-membered ring compounds reported by Yamaguchi and Inanaga.[26] α-Bromoketo aldehyde **28** was obtained in high yield by bromination of the α-position of synthetic intermediate **3**, followed by deprotection of silyl ether of **27** and Swern oxidation (Scheme 8). In the presence of an excess amount of SmI_2, the cyclization reaction of **28**



Scheme 7. Attempted synthesis of 8-membered ring compound. Reagents and conditions: a) 0.8 N HCl, THF, RT (100%); $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, $-78\,^{\circ}C$ to RT (90%); b) $AgClO_4$, TMSCl, EtSTMS, toluene, $-78\,^{\circ}C$ (70%); c) LHMDS, TMSCl, THF, $-78\,^{\circ}C$ to RT (89%); d) $TrClO_4$, CH_2Cl_2, $-45\,^{\circ}C$ (48%).

proceeded quite smoothly to give a mixture of desired aldols **29**α and **29**β in high yield (**29**α/**29**β = 65/35).[10, 11] The aldols were mesylated and subsequent treatment with DBU gave the desired α,β-unsaturated cyclooctanone **1** in good yield. In order to clarify the structures of the 8-membered ring compounds, **29**α, **29**β, and **1** were transformed into bicyclic derivatives **30**α, **30**β, and **31** by transannulation, and the structures of the rigid bicyclic skeletons formed were confirmed by ^1H NMR spectroscopy.

8-Membered ring compounds are known to have many conformational peculiarities, and the above enone **1** has unique structural character as expected.[27] For example, the ^1H NMR spectrum of **1** shows that it is a mixture of two slowly interconverting conformational isomers corresponding to the broadened peaks in its spectra (in $CDCl_3$ at $25\,^{\circ}C$), as shown in Figure 2. Fast exchange of atropisomers on the ^1H NMR time scale at 270 MHz occurs at $100\,^{\circ}C$ in $[D_8]$toluene, whereas the two isomers did not interconvert at $-30\,^{\circ}C$, as demonstrated by the sharp signals detected in the ^1H NMR spectrum (57/43 in $CDCl_3$). The free energy of activation for the conformational change was estimated to be approximately 17 kcal mol^{-1} from the coalescence temperature (ca. $60\,^{\circ}C$). The 8-membered ring enone **1** was found to have the two global stable conformations depicted in Figure 3, generated by MMFF (Merck molecular force field) conformational search and minimization with PM3 molecular orbital calculation.[28]

Next, the synthesis of 8-membered ring compounds having methyl groups in their C-8 position was attempted. Methylation of the α-position of the above mentioned brominated intermediate **27** was carried out by use of LHMDS and MeI in THF. The *tert*-butyldimethylsilyl group was deprotected and Swern oxidation was carried out. The 8-membered ring closure reaction of the optically active polyoxy unit **32**

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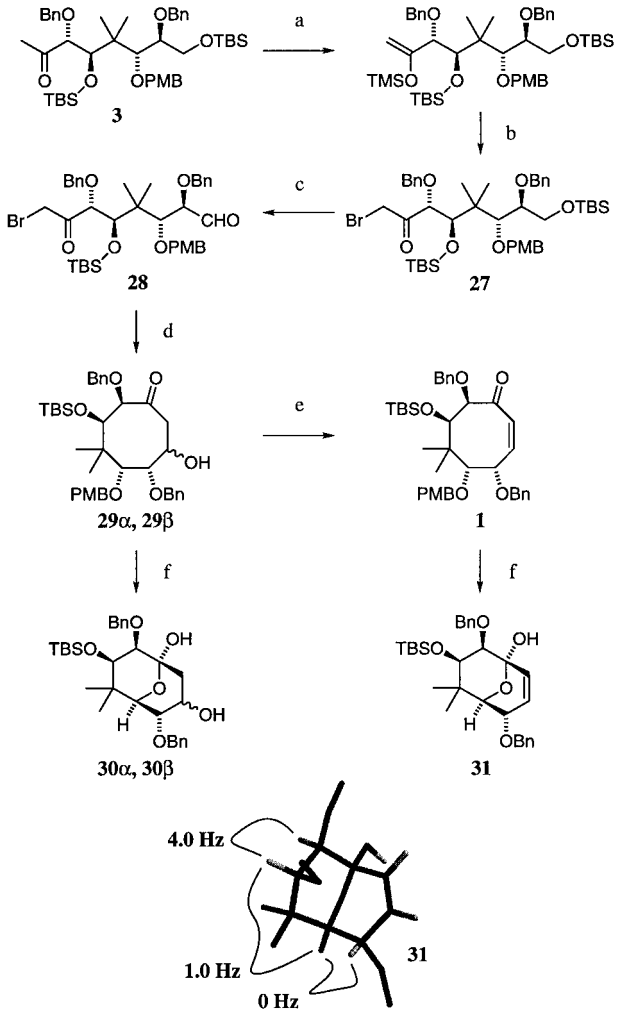


Scheme 8. Synthesis of 8-membered ring enone **1**. Reagents and conditions: a) LHMDS, TMSCl, THF, −78 °C; b) NBS, THF, 0 °C (100% from **3**); c) 1N HCl, THF, RT (99%); $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C to 0 °C (94%); d) SmI_2, THF, 0 °C (87%, **29α**/**29β** = 65/35); e) MsCl, iPr_2NEt, CH_2Cl_2, RT; then DBU, 0 °C (83%); f) DDQ, H_2O, CH_2Cl_2, RT (72% for **29α**, 55% for **29β**, 90% for **1**). Some atoms of the molecular structure of **31** have been omitted for clarity.

containing a C-8 methyl group proceeded smoothly in the presence of an excess amount of SmI_2 to give a mixture of the desired aldols in high yield with good stereoselectivity (83/17/0/0).[18] Acetylation of this mixture of isomeric alcohols with acetic anhydride and subsequent treatment with DBU gave the desired 8-membered ring enone **2** in high yield. The relative stereochemistries of major product **33α**, minor product **33β**, and 8-membered ring enone **2** were assigned by ^{1}H NMR spectroscopic measurements of their transformed products **34α**, **34β**, and **35**, respectively (Scheme 9).

It is known that generally 8-membered ring compounds are not easily available directly from simple linear precursors, except in the cases of compounds containing 5- or 6-membered rings, aromatic rings or *cis* double bonds in their backbones.[24b] The above high-yielding cyclization forming 8-membered ring compounds proceeds smoothly, presumably because the linear precursors have suitable conformations for cyclization. X-ray crystallography of methyl ketone **3** (Figure 1) and a conformational search of **3** using MMFF followed

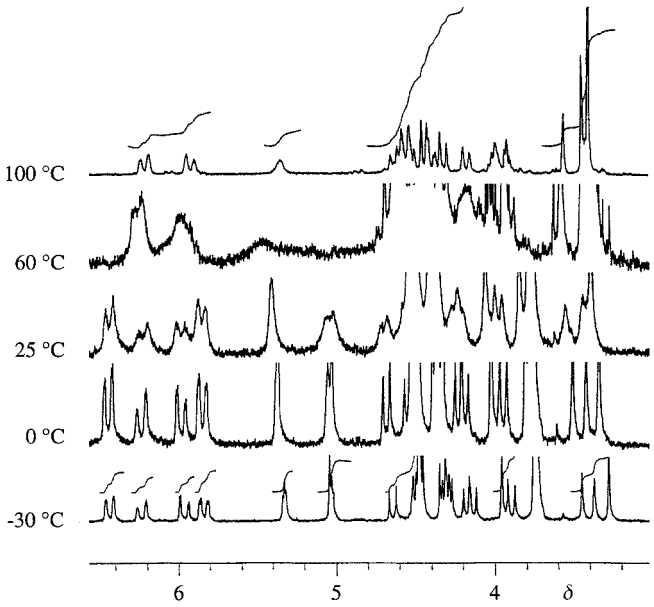


Figure 2. ^{1}H NMR spectra of 8-membered ring enone **1** at several temperatures.

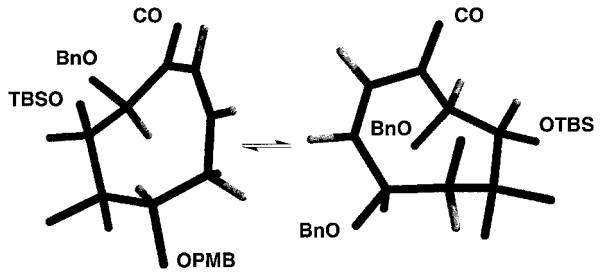
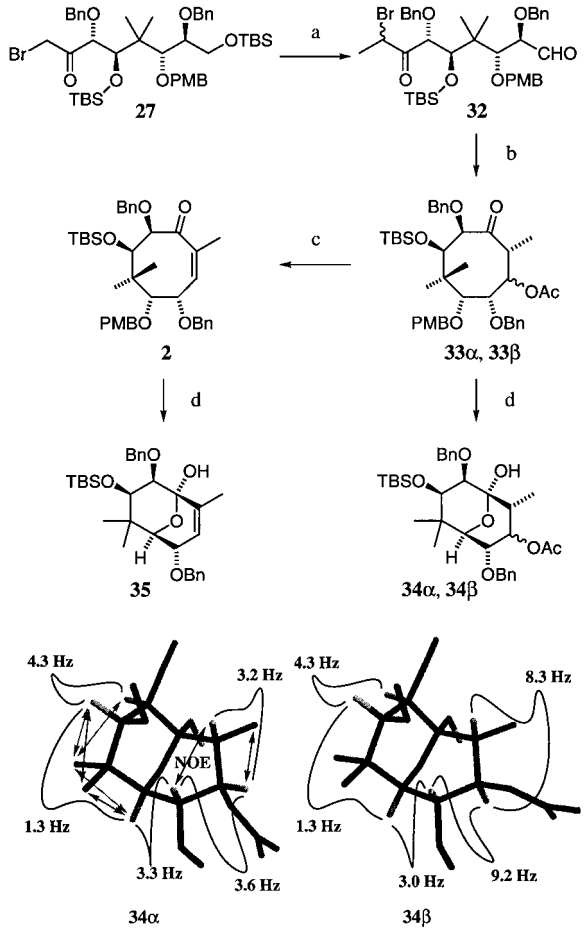


Figure 3. Stable conformations of 8-membered ring enone **1** calculated with PM3. Some atoms have been omitted for clarity.

by minimization with PM3 semiempirical molecular orbital calculations suggest that steric repulsions among the two methyl groups at C-5, *tert*-butyldimethylsiloxy group at C-4, and *p*-methoxybenzyloxy group at C-6 cause the terminal functionalities at C-1 and C-8 to come close to each other (Figure 4). Further, a conformational search of enolate anion derived from **28** (or **23**) using MMFF followed by minimization with PM3 showed that the terminal functionalities at C-1 and C-8 are located very close to one another, as depicted in Figure 4.

Synthesis of the BC ring system of Taxol: In order to build the C ring onto the 8-membered ring compounds, a three-component coupling reaction of **1** with a cuprate reagent, followed by trapping with methyl iodide, was attempted under several reaction conditions.[16] The Michael addition proceeded smoothly, employing the cuprate reagent generated in situ from 4 equiv of 2-bromo-5-(triethylsiloxy)pentene with 8.2 equiv of *t*BuLi and 2 equiv of CuCN,[29] and the desired *α*,*β*-disubstituted 8-membered ring ketone **36α** (Scheme 10) was obtained in good yield with high diastereoselectivity (91/9/0/0). The relative stereochemistry of **36α** was assigned by ^{1}H NMR spectroscopic measurement of the transannulated product. Ketoaldehyde **37α**, a precursor of the BC ring system



Scheme 9. Synthesis of 8-membered ring enone **2**. Reagents and conditions: a) LHMDS, MeI, HMPA, THF, −78 °C (100 %); 1N HCl, THF, RT (83 %); $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C to RT (95 %); b) SmI_2, THF, −78 °C (70 % plus 7 % of 10-deoxygenated 8-membered ring aldols); Ac_2O, DMAP, pyridine, RT (87 %, **33*α*/33*β*** = 83/17); c) DBU, benzene, 60 °C (91 %); d) DDQ, H_2O, CH_2Cl_2, RT (62 % for **33*α***, 51 % for **33*β***, 65 % for **2**). Some atoms of molecular structure of **34*α*** and **34*β*** have been omitted for clarity.

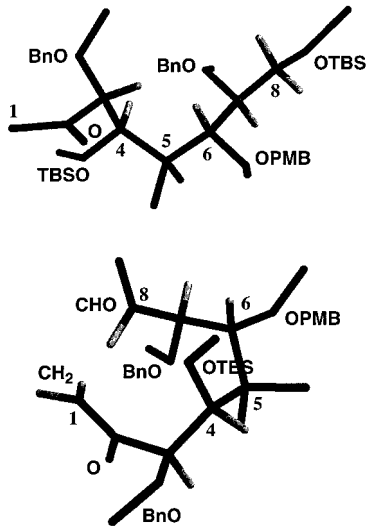
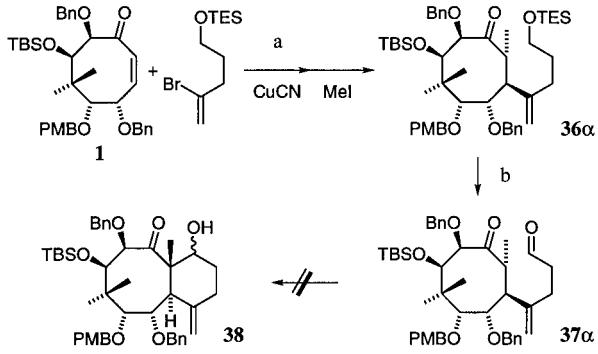


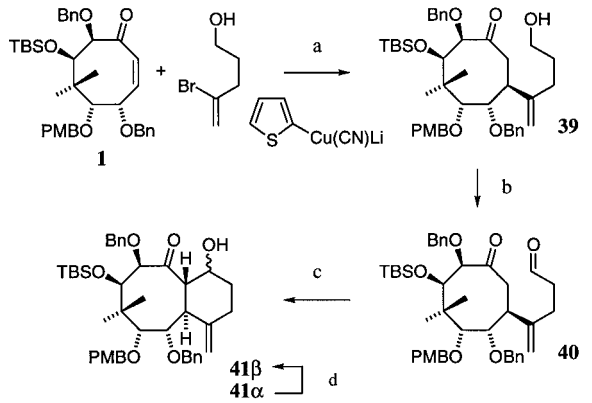
Figure 4. Stable conformations of the carbon backbone of ketone **3** (top) and of the carbon backbone of the enolate anion derived from **28** (or **23**) calculated with PM3. Some atoms have been omitted for clarity.

of Taxol, was obtained in high yield by deprotection of **36*α*** with TBAF, followed by oxidation with the TPAP and NMO combined system.[30] Next, synthesis of bicyclic compound **38** from the precursor **37*α***, which contains all the required functionalities for constructing Taxol, was attempted under several sets of reaction conditions. However, no intramolecular aldol reaction occured in any case, and ketoaldehyde **37*α*** was recovered almost quantitatively (Scheme 10).



Scheme 10. Attempted synthesis of the BC ring system **38**. Reagents and conditions: a) *t*BuLi, CuCN, THF, −78 °C to −23 °C; then MeI, HMPA, RT (77 % of **36*α***, 8 % of diastereomer); b) TBAF, THF, 0 °C (81 %); TPAP, NMO, MS 4 Å, CH_2Cl_2, 0 °C (67 % based on 78 % conversion).

At this stage, it was assumed that generation of the enolate anion from the 8-membered ring ketone **37*α*** by deprotonation did not take place under the above conditions. In order to confirm this consideration, a precursor **40** (Scheme 11), having no methyl group at C-8 of the B ring of Taxol, was



Scheme 11. Synthesis of the BC ring system **41**. Reagents and conditions. a) *t*BuLi, lithium 2-thienylcyanocuprate, Et_2O, −78 °C to 0 °C (92 % based on 99 % conversion); b) TPAP, NMO, MS 4 Å, CH_2Cl_2, 0 °C (89 %); c) NaOMe, MeOH, RT (100 %, **41*β*/41*α*** = 82/18); d) NaH, THF, 0 °C (79 % based on 61 % conversion).

employed for BC ring construction. Formation of the enolate anion from **40** was expected to proceed smoothly because there are two hydrogens at the α-position of the carbonyl group, and the enolate anion thus generated will lead to the desired bicyclic compound **41**.[16, 17]

Conjugate addition to enone **1** using a higher order cuprate reagent,[31] generated in situ from 3 equiv of 4-bromo-4-pentene-1-ol with 9 equiv of *t*BuLi and 3.3 equiv of lithium

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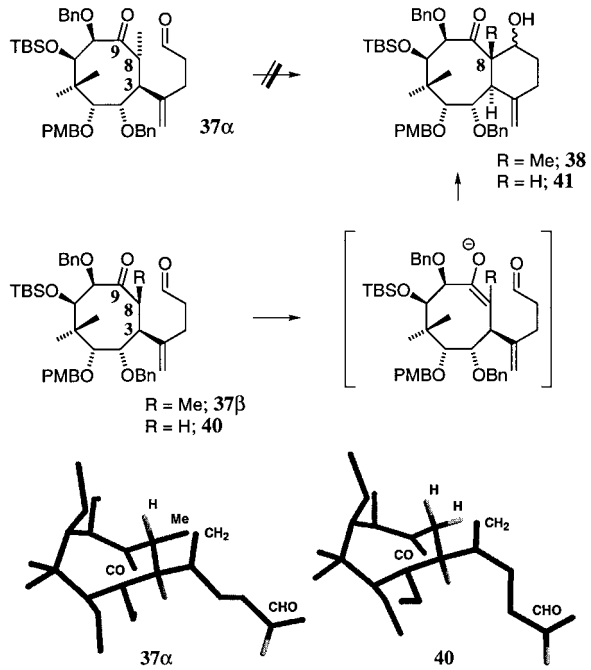
2-thienylcyanocuprate, gave the β-substituted 8-membered ring ketone **39** in high yield with perfect diastereoselectivity, though the 8-membered ring enone **1** was a mixture of two conformational isomers. Ketoaldehyde **40**, a precursor of the BC ring system of demethyltaxoids, was prepared directly by oxidation of **39** with a combination of TPAP and NMO. When intramolecular aldol reaction of the precursor **40** was tried in the presence of NaOMe at room temperature the desired reaction proceeded smoothly to afford a mixture of bicyclic compounds **41** in quantitative yield with good diastereoselectivity (82/18/0/0), as expected (Scheme 11).

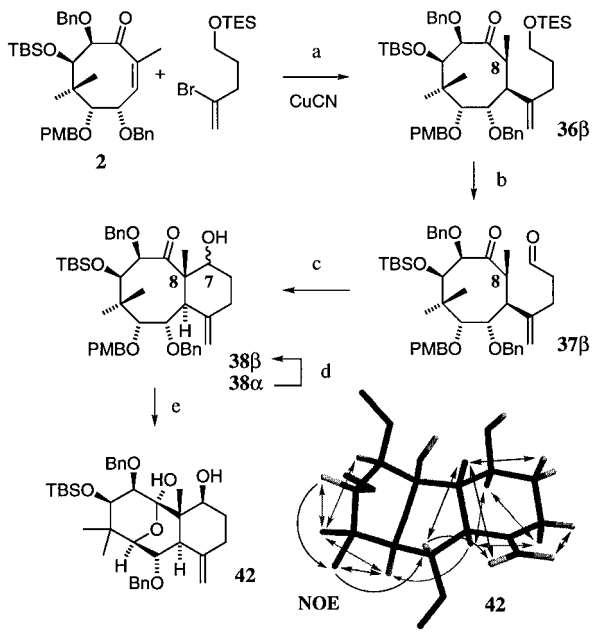
The above experimental result and a conformational search with MMFF force field of the precursors **37**α and **40** indicated that the generation of enolate anion by deprotonation from the ketoaldehyde **37**α having a C-3,8 *trans* configuration is hardly possible under the standard conditions because the dihedral angle between the H–C8–C9=O bonds is nearly antiperiplanar (Scheme 12). This suggests that a ketoaldehyde



Scheme 12. Synthesis of the BC ring systems **38** and **41** from ketoaldehydes by intramolecular aldol cyclization. Some atoms of molecular structure of **37**α and **40** have been omitted for clarity.

37β having the C-3,8 *cis* configuration should be able to generate the key enolate anion. The enolate anion thus formed should easily react with the aldehyde to form the BC ring system of Taxol by intramolecular aldol cyclization.[18, 32, 33, 7b] It was assumed that the desired ketoaldehyde **37**β having the C-3,8 *cis* configuration would be produced on α-face-selective hydrolysis of the intermediate Michael adduct, formed from 8-membered ring enone **2** and cuprate reagent (Scheme 13).

Michael addition of the cuprate reagent generated in situ from 7 equiv of 2-bromo-5-(triethylsiloxy)pentene, 14 equiv of *t*BuLi, and 3.7 equiv of copper cyanide to the enone **2** gave the 8-membered ring ketone **36**β having the C-3,8 *cis* configuration in high yield with perfect diastereoselectivity



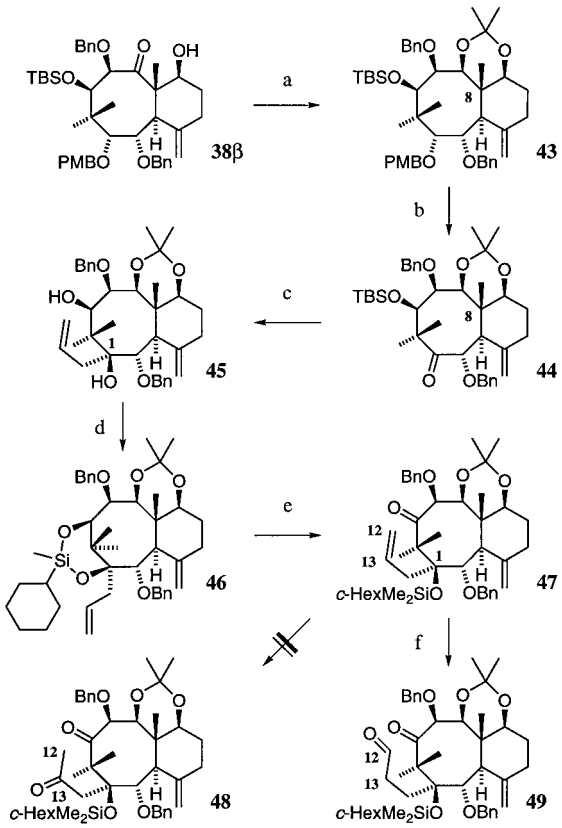
Scheme 13. Synthesis of the BC ring system **38**. Reagents and conditions: a) *t*BuLi, CuCN, Et_2O, $-23\,^{\circ}C$ (99% based on 93% conversion); b) 0.5 N HCl, THF, $0\,^{\circ}C$ (97%); TPAP, NMO, MS 4 Å, CH_2Cl_2, $0\,^{\circ}C$ (92%); c) NaOMe, MeOH, THF, $0\,^{\circ}C$ (98%, **38**β/**38**α = 92/8); d) NaOMe, THF, RT (88% based on 85% conversion); e) DDQ, H_2O, CH_2Cl_2, RT (66%). Some atoms of the molecular structure of **42** have been omitted for clarity.

by α-face selective-hydrolysis of the enolate anion. Ketoaldehyde **37**β, a precursor of the BC ring system of Taxol, was obtained in good yield by deprotection of the Michael adduct **36**β with 0.5 N HCl, followed by oxidation with a combination of TPAP and NMO. On treatment with a base, a precursor **37**β having the C-3,8 *cis* configuration was expected to generate the enolate anion, which in turn would form the desired bicyclic compound **38**. The reaction did indeed proceed smoothly to afford a mixture of bicyclic compounds **38** in nearly quantitative yield with good diastereoselectivity (92/8/0/0) when intramolecular aldol reaction of the precursor **37**β was carried out in the presence of NaOMe at $0\,^{\circ}C$. The diastereomer **38**α, which has an α-hydroxyl group at the C-7 position, could be epimerized to the desired β-alcohol **38**β in good yield on treatment with NaOMe.

Finally, the structure was confirmed as illustrated in Scheme 13 by NOE relationships and conformational analysis by MM2 calculation of a transannulated compound **42** derived from the BC ring compound **38**β. Both C-8 methyl and C-7 hydroxyl groups have the same β-configuration as Taxol.

Attempted synthesis of the ABC ring system: According to our synthetic strategy, the BC ring system **48** (Scheme 14) was regarded as the key precursor for construction of the desired ABC ring system of Taxol by intramolecular aldol cyclization.[12–14, 34] Since the BC ring system **38**β is a mixture of slowly interconverting conformational isomers, related compounds were also anticipated to exist as similar mixtures. In order to confirm the structure of these derivatives conveniently by NMR measurement at room temperature, **38**β was transformed to conformationally rigid tricyclic compounds, 7-*O*-,9-*O*-acetonides.

A mixture of two stereoisomers of the corresponding diols was formed when the aldol **38*β*** was reduced with DIBAL in hexane at room temperature. In contrast, diastereoselective reduction of the aldol **38*β*** was achieved by using AlH_3 in toluene at $-78^{\circ}C$ affording the corresponding *cis*-diol preferentially, after which protection of this *cis*-diol with isopropylidene acetal provided tricyclic compound **43**. This was converted to conformationally rigid C-1 ketone **44** by deprotection of the PMB group and successive oxidation with PDC. Though allylation of **44** by means of allylmagnesium bromide in diethyl ether afforded the homoallylic β-alcohol at the C-1 position with moderate diastereoselectivity, the desired homoallylic β-alcohol was obtained preferentially in nearly quantitative yield when the reaction was carried out in THF. Removal of the TBS group gave *cis*-diol **45**, and subsequent treatment of this diol with dichlorocyclohexylmethylsilane and imidazole yielded a silylene compound **46**, which was then converted to the trialkylsilylether at the C-1 position by way of alkylation of the bridged silicon atom with alkyllithium reagent.[12, 14, 17, 19] Oxidation of the secondary alcohol formed with PDC gave 8-membered ring ketone **47** in good yield. By the above sequential manipulations, the first target molecule **47** was efficiently synthesized from optically active 8-membered ring enone **2**. In order to prepare C-13 oxygenated compound **48**, a precursor of the ABC ring system of Taxol in our aldol strategy, we examined several oxygenation reactions of the C-13 position after model syntheses.[12, 13] However, in no case did the desired reaction take place; the C-12 position was regioselectively oxygenated to form ketoaldehyde **49** under forced Wacker oxidation conditions (Scheme 14).[35] The ^1H NMR spectrum of **47** and MMFF calculation of its conformation indicate that **47** has a rigid tricyclic structure. Comparison of the environments of the C-12 and C-13 positions in the model suggested that the C-12 position was relatively easily attacked by water because the C-13 position is considerably shielded by both the trialkylsilyl group and the exo olefin on the C ring of **47** (Figure 5).



Scheme 14. Attempted synthesis of the ABC ring system. Reagents and conditions: a) AlH_3, toluene, $-78^{\circ}C$ (94%); $Me_2C(OMe)_2$, CSA, CH_2Cl_2, RT (100%); b) DDQ, H_2O, CH_2Cl_2, RT (97%); PDC, CH_2Cl_2, RT (94% based on 96% conversion); c) allyl–MgBr, THF, $-45^{\circ}C$ (91% plus 7% of diastereomer); TBAF, THF, RT (95%); d) *c*HexMeSiCl$_2$, imidazole, DMF, $0^{\circ}C$ (97%); e) MeLi, HMPA, THF, $-78^{\circ}C$ (92%); PDC, CH_2Cl_2, RT (74% based on 86% conversion); f) $PdCl_2$, H_2O, DMF, RT (48% based on 84% conversion).

These results led to a new synthetic strategy, one of forming the ABC ring system of Taxol from intermediate **54** (Scheme 15) by A ring closure.[17, 19] In this plan, the target molecule **54** was to be prepared by the preferential oxygenation of the C-12 position of **50** by Wacker oxidation, as shown in Figure 5. Further, direct construction of the ABC ring system from diketone **54** was to be achieved by way of intramolecular pinacol coupling reaction using a low-valent titanium reagent.[36]

Total synthesis of baccatin III: Alkylation of the C-1 position of **44** with the homoallyllithium reagent in benzene produced the desired bishomoallylic β-alcohol in high yield with perfect diastereoselectivity, whereas the α-alcohol was obtained preferentially when the reaction was carried out in THF or ether. Deprotection of the TBS group resulted in formation of *cis*-diol **51**, and successive treatment with several dialkylsilyl compounds yielded silylene compounds **52a–c** in almost quantitative yields. Alkylation of these silylene compounds with methyllithium furnished compounds **53a–c** with the desired C-1-protected hydroxyl group. Oxidation of the secondary alcohols with a combination of TPAP and NMO gave the C-11 ketones **50a–c** in good yields. Oxygenation of the C-12 positions of **50a–c** proceeded smoothly to produce the desired diketones **54a–c** under forced Wacker oxidation conditions, as expected.

By the above sequence of manipulations, precursors of the ABC ring system were efficiently synthesized from the BC ring system. The ABC ring systems **55a–c** were obtained from the corresponding diketones **54a–c** by an intramolecular pinacol coupling reaction that used the low-valent titanium reagent prepared from $TiCl_2$ and $LiAlH_4$ (Scheme 15).[37] In this reaction, the desired pinacols **55a–c** were formed as the main products, along with small amounts of by-products such as partially reduced alcohols or rearranged pinacolone-type derivatives. Though the desired pinacol **55a** was obtained in up to 71% yield when the cyclization reaction was carried out with diketone **54a**, the chemical yield was not always reproducible. This was probably because the properties of the low-valent titanium reagent depended on the conditions of its preparation. The intramolecular pinacol coupling reaction with diketones **54a**, **54b**, and **54c** gave the corresponding pinacols **55a**, **55b**, and **55c** in 43–71%, 51–63%, and 42–52% yields, respectively. A conformation search with the MM2 force field and NOE relationships

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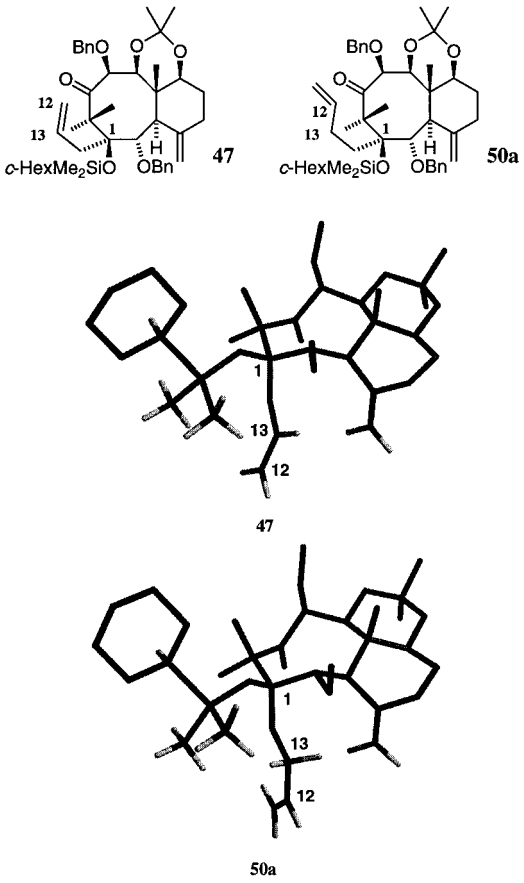
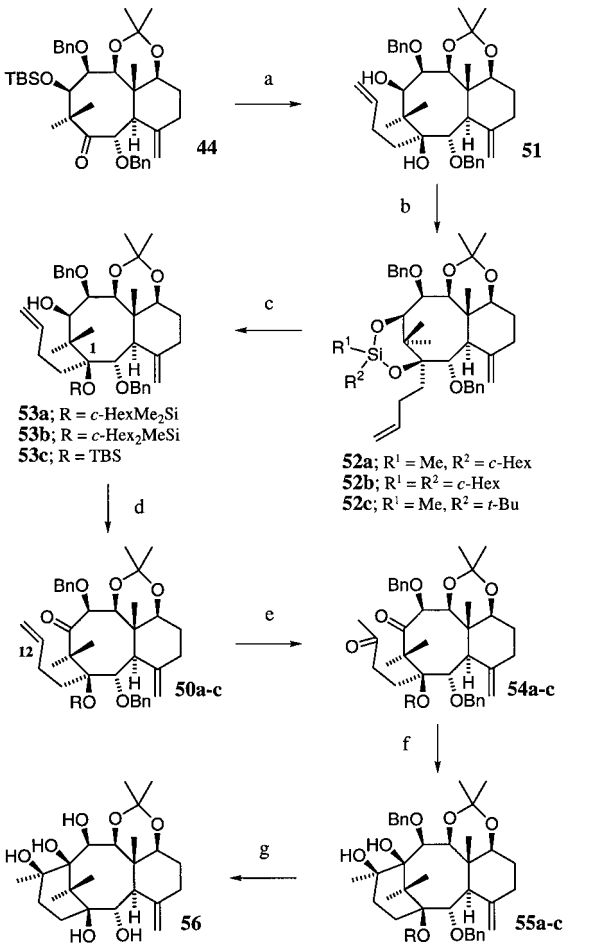


Figure 5. Stable conformations of ketones **47** and **50a** generated by calculation. Some atoms have been omitted for clarity.



Scheme 15. Synthesis of the ABC ring system **56**. Reagents and conditions: a) homoallyl–I, *s*BuLi, *c*-hexane, benzene, –23 °C to 0 °C (96 %); TBAF, THF, 50 °C (100 %); b) *c*HexMeSiCl$_2$, imidazole, DMF, RT (99 % of **52a**); *c*Hex$_2$Si(OTf)$_2$, pyridine, 0 °C (100 % of **52b**); *t*BuMeSi(OTf)$_2$, pyridine, 0 °C (100 % of **52c**); c) MeLi, HMPA, THF, –78 °C (96 % of **53a**); –45 °C (96 % of **53b**); –45 °C (96 % of **53c**); d) TPAP, NMO, MS 4 Å, CH_2Cl_2, CH_3CN, RT (80 % for **53a**, 91 % for **53b**, 85 % for **53c**); e) $PdCl_2$, H_2O, DMF, RT (98 % of **54a**, 98 % of **54b**, 91 % of **54c**); f) $TiCl_2$, $LiAlH_4$, THF, 40 °C (43–71 % of **55a**); 45 °C (51–63 % of **55b**); 35 °C (42–52 % of **55c**); g) Na, liq. NH_3, –78 °C to –45 °C; TBAF, THF, RT (100 % from **55a**, 83 % from **55b**, 93 % from **55c**).

showed the complete stereochemistry of pinacol **55c** as depicted in Figure 6.

Deprotection of the benzyl group of **55a–c** with Na/NH_3 followed by deprotection of the trialkylsilyl group with TBAF gave the desired pentaol **56** in high yields. X-ray crystallography of the pentaol **56** confirmed that it possessed the exact stereochemistry of the ABC ring system of baccatin III and Taxol as depicted in Figure 7.[23] A conformational search by MMFF suggested that there are two local minimized stable structures of pentaol **56**. The more stable conformer is almost identical to that determined by X-ray crystallography. Thus, an asymmetric synthesis of the ABC ring system of Taxol was accomplished by successive intramolecular aldol and pinacol coupling reactions from an optically active 8-membered ring compound **2**.

Successive regioselective protection of the pentaol **56** with bis(trichloromethyl) carbonate[38] and then treatment with acetic anhydride afforded the corresponding C-10 acetoxy, C-1, C-2 carbonate **57** in good yield (Scheme 16). Deprotection of the acetonide function and regioselective protection of the tetraol thus formed, followed by oxidation of this triol with a combination of TPAP and NMO, yielded C-9 ketone **58** (Scheme 16). A novel taxoid **59** was formed from the above ketone by desulfurization of the intermediate thionocarbonate with trimethylphosphite.[39] Regioselective oxygenation at the C-13 position of **59** with PCC and NaOAc gave an enone,[5a, b, e, 6, 40] which in turn was reduced to the desired α-

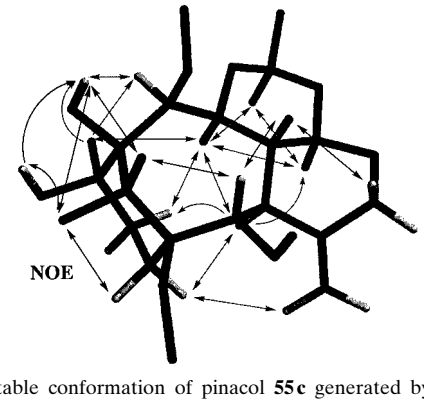


Figure 6. Stable conformation of pinacol **55c** generated by calculation. Some atoms have been omitted for clarity.

alcohol stereoselectively on treatment with K-Selectride®. On the other hand, reduction of the enone with other reducing reagents such as $NaBH_4$ and AlH_3 gave undesired β-alcohol as

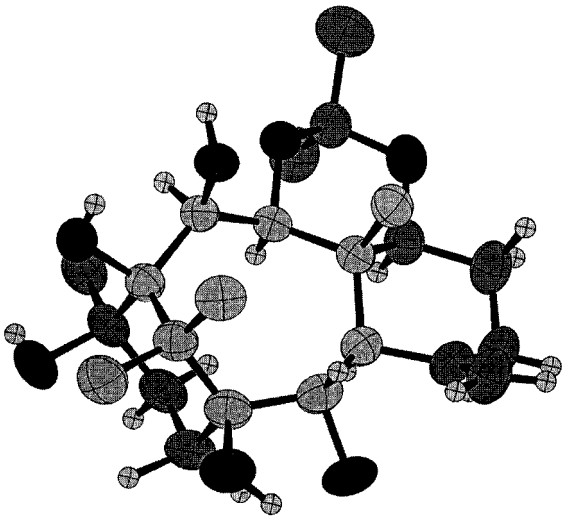


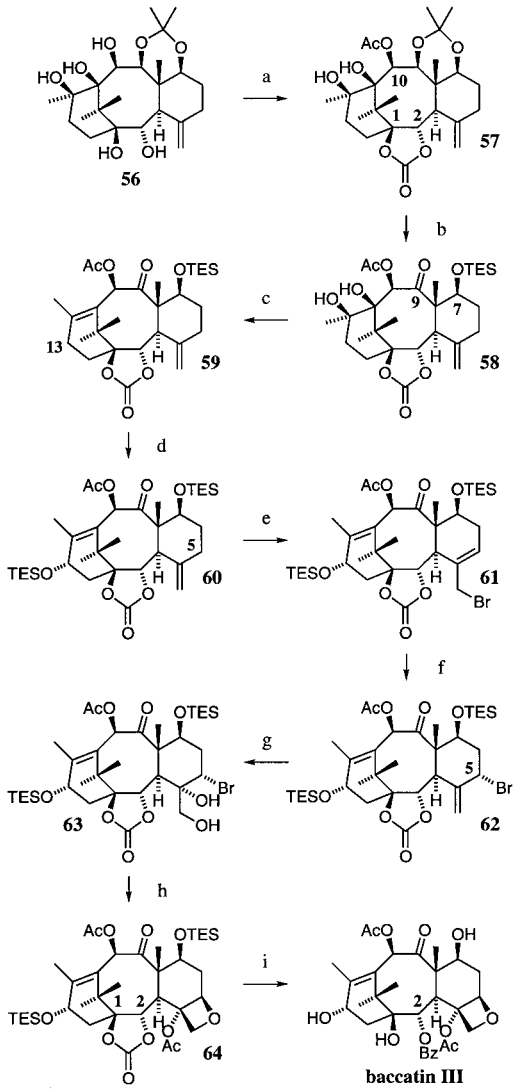
Figure 7. ORTEP drawing of pentaol **56**.

a major product. Protection of the above α-alcohol afforded tetracyclic compound **60** possessing all the functionalities necessary for the synthesis of baccatin III and Taxol. An effective method for the synthesis of baccatin III from the taxoid **60** has already been reported from our laboratory, and construction of the oxetane ring onto the ABC ring system was carried out by this procedure (Scheme 16).[15]

Allylic bromination at the C-5 position of **60** with excess amounts of CuBr and $PhCO_3tBu$ (1:1 molar ratio) gave the separable allylic bromides **61** and **62** in 62% and 15% yields, respectively.[15, 41] Furthermore, on treating the allylic bromide **61** with CuBr in CH_3CN at 50 °C, 25% of **61** and 69% of **62** were obtained, since **61** and **62** were in equilibrium under thermodynamic conditions. A conformational search using MMFF followed by minimization with PM3 and ^1H NMR experiments suggested that the most stable conformer of **62** was that shown in Figure 8. It is interesting to note that allylic bromide **62**, having an axial bromine at C-5, is more stable than its epimer with an equatorial bromine at C-5 because of allylic strain of the epimer.

Since the C ring of **62** is in the chair form, as illustrated in Figure 8, α-face-selective dihydroxylation of **62** with OsO_4 proceeded smoothly to give a dihydroxy bromide **63** in high yield as a single stereoisomer.[15, 7b] The desired oxetanol was obtained in good yield when this dihydroxy bromide **63** was treated with DBU at 50 °C in toluene. The corresponding acetate **64** was prepared by acetylation of the tertiary alcohol using acetic anhydride and DMAP in pyridine. Finally, benzoylation at the C-2 position of C-1, C-2 carbonate **64**,[4b, 5a, b, e, 6, 7b, 15, 40d] followed by desilylation of the benzoate with HF · pyridine afforded baccatin III in high yield.

Asymmetric synthesis of the side chains and total synthesis of Taxol: Total synthesis of Taxol was finally completed by the following two new synthetic procedures: 1) asymmetric synthesis of a side chain, a protected *N*-benzoylphenylisoserine, and 2) synthesis of Taxol by dehydration condensation between the side chain and 7-TES baccatin III (Scheme 17).[20]



Scheme 16. Synthesis of baccatin III. Reagents and conditions: a) $(CCl_3O)_2CO$, pyridine, CH_2Cl_2, −45 °C (100%); Ac_2O, DMAP, benzene, 35 °C (84%); b) 3 N HCl, THF, 60 °C; TESCl, pyridine, RT (83% from **57**); TPAP, NMO, MS 4 Å, CH_2Cl_2, RT (76%); c) TCDI, DMAP, toluene, 100 °C; $P(OMe)_3$, 110 °C (53% from **58**); d) PCC, NaOAc, Celite, benzene, 95 °C (78%); K-Selectride®, THF, −23 °C (87%); TESOTf, pyridine, −23 °C (98%); e) CuBr, $PhCO_3tBu$, CH_3CN, −23 °C (62% of **61**, 15% of **62**); f) CuBr, CH_3CN, 50 °C (25% of **61**, 69% of **62**); g) OsO_4, pyridine, THF, RT (96% based on 96% conversion); h) DBU, pyridine, toluene, 50 °C (81% based on 52% conversion); Ac_2O, DMAP, pyridine, RT (91%); i) PhLi, THF, −78 °C (94%); HF · pyridine, THF, RT (96%).

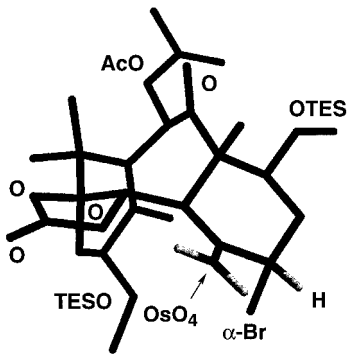


Figure 8. Stable conformation of allylic bromide **62**. Some atoms have been omitted for clarity.

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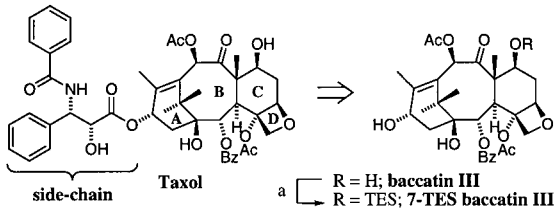
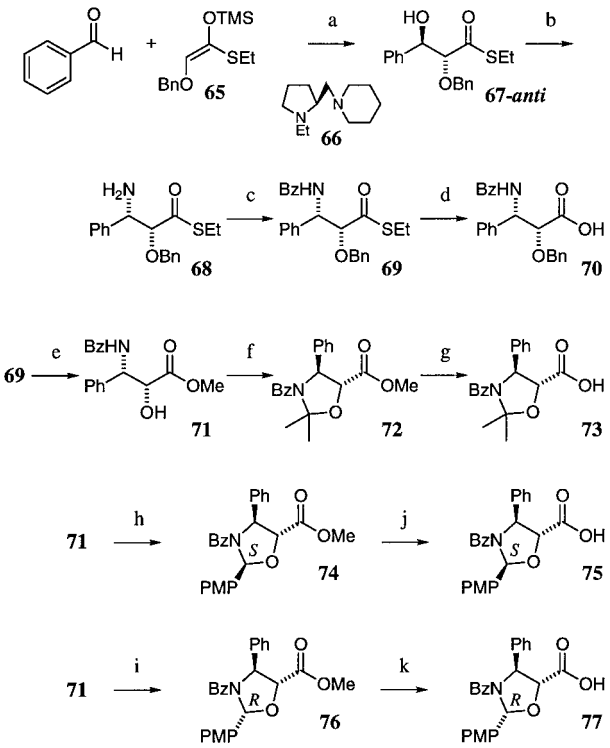


Scheme 17. Synthesis of 7-TES baccatin III from baccatin III. Reagents and conditions: a) TESCl, pyridine, RT (92% based on 95% conversion).

Although several methods for the synthesis of side chains of Taxol have been developed in the two past decades, only a few examples were reported on enantioselective synthesis.[3c] In the first place, the preparation of *S*-ethyl (2*R*,3*R*)-2-benzyloxy-3-hydroxy-3-phenylpropanethioate (**67-*anti***, Scheme 18) was attempted by the enantioselective aldol reaction previously reported from our laboratory, that is, the reaction of benzaldehyde with an enol silyl ether **65** prepared from *S*-ethyl benzyloxyethanethioate by means of a chiral promoter consisting of chiral diamine **66**, $Sn(OTf)_2$, and $nBu_2Sn(OAc)_2$; **67** was obtained in high yield with almost perfect stereoselectivity (*anti*/*syn* = 99/1, *anti* aldol; 96% *ee*).[21] The aldol product **67-*anti*** was converted to the C-3 inverted azide by a Mitsunobu reaction that employed hydrogen azide, Ph_3P, and DEAD.[42] The azide was subsequently reduced to amine **68** with Ph_3P according to a method reported by Hanaoka et al.[42] Benzoylation of the resulting amine **68** with benzoyl chloride and DMAP gave the desired amide **69** in good yield. (2*R*,3*S*)-3-Benzoylamino-2-benzyloxy-3-phenylpropionic acid (**70**), a protected Taxol side chain, was obtained by hydrolysis of the thiol ester with aqueous silver nitrate. The corresponding *N*,*O*-acetonide **72** was prepared by the sequence: 1) debenzylation of **69** with a stoichiometric amount of $SnCl_4$, 2) transesterification with MeOH and $AgOCOCF_3$, and 3) protection of the resulting alcohol **71** with 2-methoxypropene and PPTS (Scheme 18). Similarly, *N*,*O*-*p*-methoxybenzylidene acetal **74** was formed by treating **71** with *p*-methoxybenzaldehyde dimethyl acetal and CSA, and *N*,*O*-*p*-methoxybenzylidene acetal **76**, the epimer of **74** at the *N*,*O*-acetal carbon, was obtained by treating **71** with *p*-methoxybenzyl methyl ether and DDQ according to a method reported by Greene et al.[43] These esters afforded the corresponding carboxylic acids **73**, **75**, and **77** in good yields on hydrolysis with aqueous LiOH (Scheme 18).

Though Greene et al. suggested the configuration of *N*,*O*-acetal carbon of **77** is *R*,[43] we could not determine the configuration of either **74** or **75** by NOE experiments, because these compounds have broadened NMR spectra owing to the existence of amide rotamers.[44] Therefore, *N*,*O*-*p*-methoxybenzylidene acetal **80**, which has *N*-Bn group was synthesized from known aminoester **79-*syn*** by deprotection and acetalization. NOE experiment of **80** showed that the configurations of the *N*,*O*-acetal carbon atoms of **80**, **78**, **74**, and **75** are all *S*, as depicted in Scheme 19.

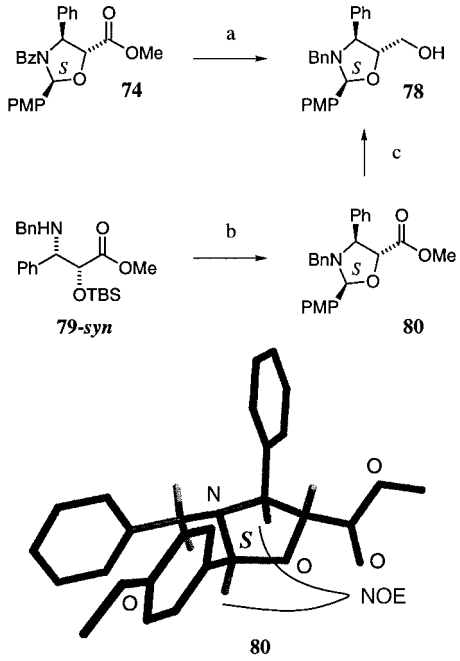
The so-called β-lactam method has been the most popular method for the introduction of side chains to 7-*O*-protected baccatin III to synthesize Taxol, and was utilized in all the reported total syntheses of Taxol.[4b, 5a, b, e, 6, 40d, 45] In addi-



Scheme 18. Synthesis of the side chains of Taxol. Reagents and conditions: a) $Sn(OTf)_2$, chiral diamine **66**, $nBu_2Sn(OAc)_2$, CH_2Cl_2, $-78\,^\circ C$ (95%); b) HN_3, Ph_3P, DEAD, benzene, RT (82%); Ph_3P, H_2O, THF, $55\,^\circ C$ (90% based on 82% conversion); c) BzCl, DMAP, CH_2Cl_2, $0\,^\circ C$ (90%); d) $AgNO_3$, H_2O, 1,4-dioxane, reflux (78%); e) $SnCl_4$, CH_2Cl_2, reflux (96%); $AgOCOCF_3$, MeOH, RT (84%); f) $CH_2C(OMe)Me$, PPTS, toluene, $80\,^\circ C$ (89%); g) LiOH, H_2O, MeOH, RT (86%); h) $PMPCH(OMe)_2$, CSA, toluene, azeotrope (79%); i) PMBOMe, DDQ, CH_3CN, $70\,^\circ C$ (75%); j) LiOH, H_2O, MeOH, $0\,^\circ C$ (83%); k) LiOH, H_2O, MeOH, RT (86%).

tion, methods for dehydration condensation between carboxylic acids and baccatin III derivatives were developed by Greene et al. and by Commerçon et al. using DPC (di(2-pyridyl) carbonate) and DMAP or using DCC and DMAP.[43a, 46, 47] Recently, Gennari et al. reported a transesterification method for the semisynthesis of Taxol using thiol esters of the side chain.[48] Since both the β-lactam method and the transesterification method were carried out under strongly basic conditions, a new method for the direct condensation reaction between 7-TES baccatin III and the side chain as its free carboxylic acid form under rather mild conditions was studied.

Esterification of 3-phenylpropionic acid with cyclohexanol was attempted as a model experiment according to a method using DPC and DMAP reported by Kim et al.,[49] which was later applied to the preparation of protected Taxol by condensation between a side chain and a baccatin III derivative by Greene et al.[46] The corresponding ester was obtained in 95% yield by the use of DPC as a dehydration reagent while the desired ester was formed in 99% yield when DPTC (*O*,*O*′-di(2-pyridyl) thiocarbonate),[50] a sulfur analog of DPC, was used as a novel coupling reagent.[51] Secondly, a dehydration condensation between the side chains and cyclohexanol was tried and, in the presence of DPTC and DMAP, side chains **70**, **73**, and **75** reacted smoothly with cyclohexanol

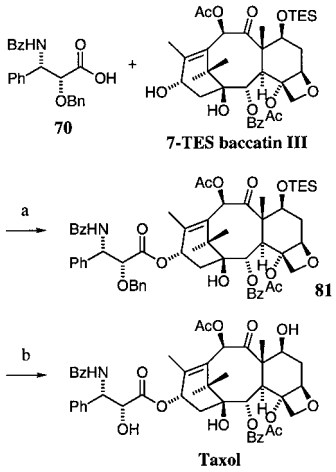


Scheme 19. Relative stereochemistry of ester **80** and carboxylic acid **75**. Reagents and conditions: a) $LiAlH_4$, THF, 0 °C (72 %) or Red-Al®, benzene, reflux (21 %); b) TBAF, THF, 0 °C (90 %); $PMPCH(OMe)_2$, CSA, toluene, azeotrope (97 %); c) $LiAlH_4$, THF, 0 °C (73 %). Some hydrogen atoms of molecular structure of **80** have been omitted for clarity.

to afford the corresponding esters in quantitative yields. On the other hand, the esterification of side chain **77** with cyclohexanol gave the coupling product in moderate yield (72 %).

The dehydration condensation between the side chains and 7-TES baccatin III was examined using a combination of DPTC and DMAP. 7-TES baccatin III was synthesized in good yield by monosilylation of baccatin III (see Scheme 17). When **70** was used in the above condensation reaction, the corresponding ester **81** was obtained in quantitative yield based on 34 % conversion after 2 h at 73 °C in toluene. There was no further reaction even when extra amounts of the side chain **70**, DPTC, and DMAP were added to the resulting reaction mixture. However, the desired ester **81** was formed when **70**, DPTC, and DMAP were added to the recovered reaction mixture after filtration through a short pad of silica gel, because the remaining 7-TES baccatin III could be completely recovered, and the overall yield was increased by repetition of the above procedure. Finally, the condensation product **81** was formed in quantitative yield based on 66 % conversion after repeating the above procedure four times. The condensation product **81** was successfully transformed to Taxol after debenzylation using palladium hydroxide on carbon under a hydrogen atmosphere and desilylation with HF·pyridine or 5 % aqueous HCl in ethanol (Scheme 20).

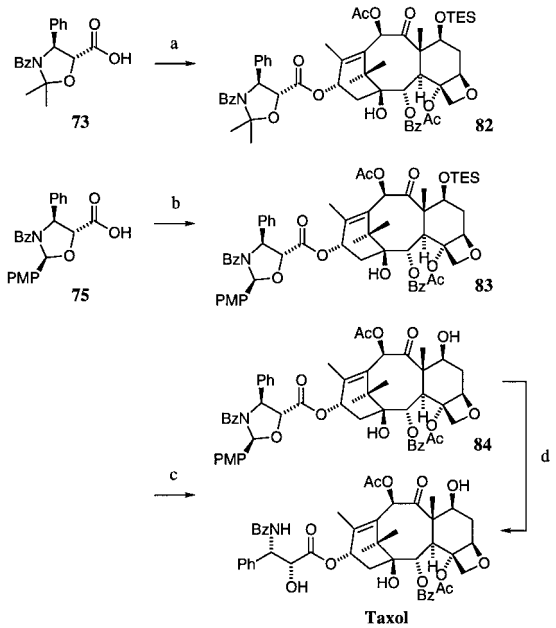
In order to increase the reactivity of the side chain, we next examined the effect of protecting groups. Side chains protected as *N,O*-cyclic acetals seemed to be more reactive because of their less hindered structure. In fact, the esterification reaction of side chain **73** with 7-TES baccatin III gave the corresponding ester **82** in 99 % yield at 64 % conversion by



Scheme 20. Synthesis of Taxol by dehydration condensation. Reagents and conditions: a) DPTC, DMAP, toluene, 73 °C (100 % based on 66 % conversion after four repetitions); b) $Pd(OH)_2/C$, H_2, EtOH, RT (76 %); HF·pyridine, THF, RT (100 %) or 5 % HCl, EtOH, RT (100 %).

one operation, although the isopropylidene group of the product is deprotection-resistant. The condensation reaction between side chain **75** and 7-TES baccatin III also proceeded smoothly to produce the desired coupling product **83** in 95 % yield at 93 % conversion. Finally, on hydrolysis under acidic conditions, the *p*-methoxybenzylidene protecting group was cleaved off smoothly to afford Taxol. It is interesting to note that side chain **75** gave the condensation product **83** in quite high yield, while the reaction did not take place when the epimer **77** was used (Scheme 21).

The completely functionalized skeleton of Taxol was revealed by X-ray crystallographic analysis of the condensa-



Scheme 21. The total synthesis of Taxol by improved method of dehydration condensation. Reagents and conditions: a) 7-TES baccatin III, DPTC, DMAP, toluene, 73 °C (99 % based on 64 % conversion); b) 7-TES baccatin III, DPTC, DMAP, toluene, 73 °C (95 % based on 93 % conversion); c) TFA, H_2O, 0 °C (93 % of Taxol, 7 % of **84**); d) TFA, H_2O, RT (94 %).

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tion product **82** (Figure 9).[23] Three carbon rings are folded up in a cup shape, and the side chain containing *N*,*O*-cyclic acetal is located outside the molecule and hangs down over the baccatin III structure.

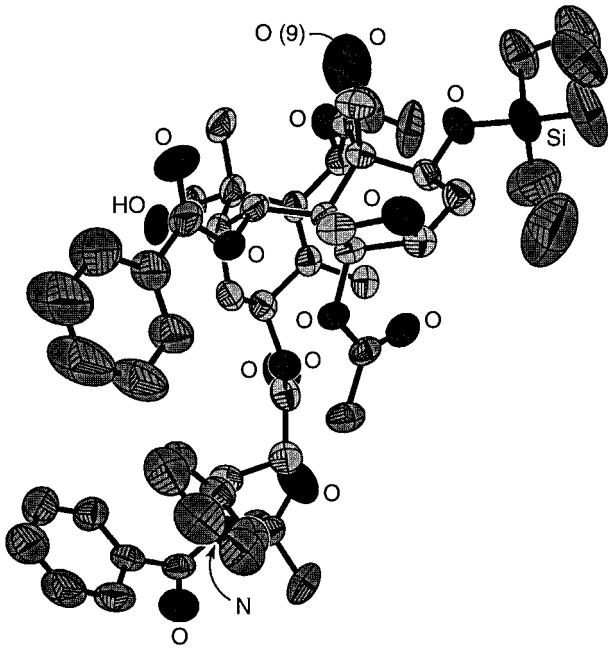


Figure 9. ORTEP drawing of protected Taxol **82**.

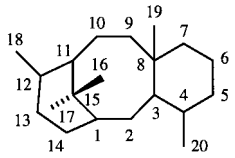
Conclusion

A new method for the asymmetric total synthesis of Taxol by way of B to BC to ABC to ABCD ring construction has been established. The optically active linear compound, precursor of the 8-membered ring compound, was synthesized by a combination of asymmetric aldol reactions. The synthesis of the 8-membered ring compound corresponding to the B ring was achieved by intramolecular aldol cyclization utilizing SmI_2. The ABC ring system of Taxol was constructed onto this B ring by successive stereoselective Michael addition, intramolecular aldol cyclization, stereoselective homoallylation, and pinacol coupling cyclization. Furthermore, a new method for the synthesis of baccatin III, the ABCD ring system of Taxol, from the ABC ring system by the introduction of a C-13 hydroxyl group and an oxetane-forming reaction has been established. Finally, a new method for the synthesis of side chains of Taxol by asymmetric aldol reaction was developed and the total synthesis of Taxol was completed by the dehydration condensation reaction using DPTC between the above side chain and 7-TES baccatin III derived from baccatin III. This synthetic method would be widely applicable to the syntheses of various derivatives of Taxol and related taxoids.

Experimental Section

General techniques: All melting points were measured on a Yanaco MP-S3 micro melting point apparatus. Optical rotations were recorded on a Jasco DIP-360 or a Jasco P-1020 digital polarimeter. IR spectra were recorded on a Horiba FT-300 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi R-1200, a JEOL JNM-EX270L, a JEOL ALPHA-500, a JEOL RAMBDA-500 or a Bruker AVANCE DPX-300 spectrometer with tetramethylsilane (TMS), chloroform (in [D]chloroform), dichloromethane (in [D_2]dichloromethane), benzene (in [D_6]benzene) or toluene (in [D_8]toluene) as internal standard. HPLC was carried out using a Hitachi LC-Organizer, L-4000 UV Detector, L-6200 Intelligent Pump, and D-2500 Chromato-Integrator. High-resolution mass spectra were recorded on a JEOL JMS-SX102A instrument with 4-nitrobenzyl alcohol as a matrix. Column chromatography was performed on silica gel 60 (Merck) or Wakogel B5F; thin-layer chromatography was performed on Wakogel B5F. All reactions were carried out under argon atmosphere in dried glassware, unless otherwise noted. Dichloromethane was distilled from diphosphorus pentoxide, then calcium hydride, and dried over MS 4 Å, benzene and toluene were distilled from diphosphorus pentoxide and dried over MS 4 Å, and THF and diethyl ether were distilled from sodium/benzophenone immediately prior to use. All reagents were purchased from Tokyo Kasei Kogyo, Kanto Chemical, or Aldrich Chemical, and used without further purification unless otherwise noted.

Carbon atoms in parentheses of ^{1}H and ^{13}C NMR spectra data of **1**, **2**, **29**–**31**, **33**–**47**, and **49**–**84** are numbered according to IUPAC taxane skeleton nomenclature.



Methyl 2,2-dimethyl-3-oxopropionate: To a solution of oxalyl chloride (10.5 g, 82.7 mmol) in dichloromethane (40 mL) at −78 °C was added a solution of DMSO (13.2 g, 169 mmol) in dichloromethane (40 mL). The reaction mixture was stirred for 10 min at −78 °C, and then a solution of methyl 3-hydroxy-2,2-dimethylpropionate (**5**) (10.0 g, 75.6 mmol) in dichloromethane (40 mL) was added. After the reaction mixture had been stirred for 1 h, triethylamine (38.3 g, 378 mmol) was added. The reaction mixture was allowed to warm to room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by distillation to afford methyl 2,2-dimethyl-3-oxopropionate (8.77 g, 89 %) as a colorless oil: b.p. 60 °C/22 mmHg; IR (neat): $\tilde{\nu}$ = 1720, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 9.56 (s, 1H, 3-CHO), 3.66 (s, 3H, MeO), 1.26 (s, 6H, Me, Me); ^{13}C NMR ($CDCl_3$): δ = 199.0 (3), 173.2 (1), 53.5 (2), 52.5 (MeO), 19.7 (Me), 19.7 (Me); HRMS: calcd for $C_6H_{11}O_3$ $[M+H]^+$ 131.0708, found 131.0718.

Methyl 3,3-dimethoxy-2,2-dimethylpropionate (**6**): To a solution of ester **5** (18.2 g, 140 mmol) and trimethyl orthoformate (29.7 g, 280 mmol) in methanol (170 mL) at room temperature was added *p*-toluenesulfonic acid (3.55 g, 14.0 mmol). The reaction mixture was stirred for 1 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. The crude product was filtered though a short pad of silica gel with diethyl ether and the filtrate was concentrated by evaporation of the solvent to afford acetal **6** (23.0 g, 93 %) as a colorless oil: b.p. 98 °C/41 mmHg; IR (neat): $\tilde{\nu}$ = 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 4.43 (s, 1H, 3-H), 3.69 (s, 3H, MeO), 3.52 (s, 6H, MeO, MeO), 1.18 (s, 6H, Me, Me); ^{13}C NMR ($CDCl_3$): δ = 176.1 (1), 110.4 (3), 58.6 (MeO), 58.6 (MeO), 51.7 (MeO), 48.4 (2), 19.5 (Me), 19.5 (Me); EIMS: calcd for $C_8H_6O_4$ $[M^+]$ 176, found 176; CIMS: calcd for $C_8H_{17}O_4$ $[M+H]^+$ 177, found 177.

3-Hydroxy-2,2-dimethylpropanal dimethyl acetal:[52] To a suspension of lithium aluminum hydride (2.16 g, 56.9 mmol) in THF (50 mL) at 0 °C was added a solution of acetal **6** (5.01 g, 28.4 mmol) in THF (50 mL). After the reaction mixture had been stirred for 2 h at room temperature, saturated aqueous sodium sulfate was added. The crude product was filtered though a short pad of Celite with diethyl ether and the filtrate was concentrated by evaporation of the solvent to afford 3-hydroxy-2,2-dimethylpropanal dimethyl acetal (4.08 g, 90 %) as a colorless oil: b.p. 120–126 °C/3.9 mmHg; IR (neat): $\tilde{\nu}$ = 3460 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 3.99 (s, 1H, 1-H), 3.51 (s, 6H, MeO, MeO), 3.41 (d, J = 5.6 Hz, 2H, 3-H, 3-H), 2.70 (t, J = 5.6 Hz, 1H, OH), 0.90 (s, 6H, Me, Me); ^{13}C NMR ($CDCl_3$): δ = 113.9 (1), 69.2 (3), 58.5

(MeO), 58.5 (MeO), 40.6 (2), 20.0 (Me), 20.0 (Me); HR MS: calcd for $C_7H_{15}O_3$ $[M-H]^+$ 147.1021, found 147.0997.

3,3-Dimethoxy-2,2-dimethylpropanal (7):[52] To a solution of oxalyl chloride (25.0 g, 197 mmol) in dichloromethane (95 mL) at $-78\,^\circ C$ was added a solution of DMSO (27.9 g, 357 mmol) in dichloromethane (95 mL). The reaction mixture was stirred for 10 min at $-78\,^\circ C$ and then a solution of 3-hydroxy-2,2-dimethylpropanal dimethyl acetal (26.5 g, 179 mmol) in dichloromethane (95 mL) was added. After the reaction mixture had been stirred for 30 min, triethylamine (72.4 g, 715 mmol) was added. The reaction mixture was allowed to warm to room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by distillation to afford aldehyde **7** (22.2 g, 85 %) as a colorless oil: b.p. 71 – 72 °C/26.0 mmHg; IR (neat): $\tilde{\nu}=1730\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta=9.60$ (s, 1H, 1-CHO), 4.21 (s, 1H, 3-H), 3.50 (s, 6H, MeO, MeO), 1.08 (s, 6H, Me, Me); ^{13}C NMR ($CDCl_3$): $\delta=205.3$ (1), 110.9 (3), 58.7 (MeO), 58.7 (MeO), 52.1 (2), 18.0 (Me), 18.0 (Me).

Benzyloxyacetic acid:[53] Sodium (25.9 g, 1.13 mol) was gradually added to benzyl alcohol (400 mL). The reaction mixture was refluxed for 2 h, and then a solution of chloroacetic acid (53.3 g, 564 mmol) in benzyl alcohol (100 mL) was added. After the reaction mixture had been refluxed for 6 h, it was concentrated by evaporation of the solvent. Water was added to the residue, and the mixture was washed with diethyl ether. Hydrochloric acid (12 M) was added to the aqueous layer and then the mixture (pH = 1) was extracted with diethyl ether. The organic layer was washed with water and brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by distillation to afford benzyloxyacetic acid (87.7 g, 94 %) as a colorless oil: b.p. 130 °C/0.4 mmHg; IR (neat): $\tilde{\nu}=3590$, 1740 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=10.88-10.59$ (br m, 1H, COOH), 7.48-7.28 (m, 5H, Ph), 4.67 (s, 2H, Bn), 4.18 (s, 2H, 2-H, 2-H).

Methyl benzyloxyacetate: To methanol (278 mL) at 0 °C was slowly added thionyl chloride (34.7 mL, 476 mmol). The reaction mixture was stirred for 15 min at 0 °C, and then a solution of benzyloxyacetic acid (65.9 g, 397 mmol) in methanol (110 mL) was added. After the reaction mixture had been stirred for 1 h at room temperature, it was concentrated by evaporation of the solvent. Dichloromethane (300 mL) and saturated aqueous sodium hydrogencarbonate (100 mL) were added to the residue, and the mixture was extracted with dichloromethane. The organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by distillation to afford methyl benzyloxyacetate (69.9 g, 98 %) as a colorless oil: b.p. 91 – 92 °C/0.8 mmHg; IR (neat): $\tilde{\nu}=1750\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta=7.51-7.22$ (m, 5H, Ph), 4.68 (s, 2H, Bn), 4.13 (s, 2H, 2-H, 2-H), 3.80 (s, 3H, MeO); HR MS: calcd for $C_{10}H_{13}O_3$ $[M+H]^+$ 181.0864, found 181.0877.

(*Z*)-2-Benzyloxy-1-methoxy-1-(*tert*-butyldimethylsiloxy)ethene (8): To a solution of diisopropylamine (3.88 mL, 19.8 mmol) in THF (8 mL) at 0 °C was added a solution of *n*-butyllithium in hexane (1.65 M, 14.4 mL, 27.7 mmol). After the reaction mixture had been stirred for 30 min at 0 °C, a solution of methyl benzyloxyacetate (3.28 g, 19.8 mmol) in THF (7 mL) and a solution of *tert*-butyldimethylsilyl trifluoromethanesulfonate (4.98 mL, 21.8 mmol) in THF (7 mL) were added at $-78\,^\circ C$. The reaction mixture was stirred for 30 min at room temperature and then triethylamine (9.07 mL, 65.1 mmol) and saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed with cold water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by distillation to afford ketene silyl acetal **8** (3.61 g, 70 %) as a colorless oil: b.p. 85 – 95 °C/1.0 mmHg; IR (neat): $\tilde{\nu}=$ 1230, 1130, 830 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=7.38-7.16$ (m, 5H, Ph), 5.21 (s, 1H, 2-H), 4.47 (s, 2H, Bn), 3.28 (s, 3H, MeO), 0.78 (s, 9H, TBS), 0.00 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=150.8$ (1), 137.9 (Ph), 128.2 (Ph), 127.7 (Ph), 127.5 (Ph), 110.5 (2), 74.6 (Bn), 55.8 (MeO), 25.8 (TBS), 20.6 (TBS), -4.7 (TBS), -4.7 (TBS); HR MS: calcd for $C_{16}H_{27}O_3Si$ $[M+H]^+$ 295.1730, found 295.1770.

Methyl (2*S*,3*R*)-2-benzyloxy-3-hydroxy-5,5-dimethoxy-4,4-dimethylpentanoate (10-*anti*) and **methyl (2*S*,3*S*)-2-benzyloxy-3-hydroxy-5,5-dimethoxy-4,4-dimethylpentanoate (10-*syn*)**: (*S*)-1-[(1-Methyl-2-pyrrolidinyl)-methyl]piperidine (**9**) was prepared by a literature method:[54] the compound is also commercially available. To a suspension of tin(II) trifluoromethanesulfonate (1.56 g, 3.74 mmol) in dichloromethane (10 mL) were added a solution of chiral diamine **9** (850 mg, 4.66 mmol) in dichloromethane (5 mL) and a solution of dibutyltin diacetate (1.47 g, 4.19 mmol) in dichloromethane (5 mL) at room temperature. After the reaction mixture had been stirred for 30 min at room temperature, a solution of ketene silyl acetal **8** (1.11 g, 3.76 mmol) in dichloromethane (10 mL) and a solution of aldehyde **7** (365 mg, 2.50 mmol) in dichloromethane (10 mL) were added at $-23\,^\circ C$. The reaction mixture was stirred for 6 h at $-23\,^\circ C$, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford a mixture of aldols **10** (*anti*/*syn* = 80/20, 556 mg, 68 %) as a colorless oil: IR (neat): $\tilde{\nu}=3490$, 1750 cm^{-1}; HR MS: calcd for $C_{17}H_{26}O_6Na$ $[M+Na]^+$ 349.1627, found 349.1622. **Aldol 10-*anti***: ^1H NMR ($CDCl_3$): $\delta=7.41-7.27$ (m, 5H, Ph), 4.62 (d, $J=11.3$ Hz, 1H, Bn), 4.38 (d, $J=11.3$ Hz, 1H, Bn), 4.10 (d, $J=6.5$ Hz, 1H, 2-H), 4.04 (s, 1H, 5-H), 3.86 (dd, $J=6.5$, 5.9 Hz, 1H, 3-H), 3.76 (s, 3H, MeO), 3.66 (d, $J=5.9$ Hz, 1H, OH), 3.47 (s, 3H, MeO), 3.40 (s, 3H, MeO), 0.97 (s, 3H, Me), 0.95 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta=172.5$ (1), 137.4 (Ph), 128.9 (Ph), 128.7 (Ph), 128.4 (Ph), 113.6 (5), 81.1 (2), 77.0 (3), 72.9 (Bn), 59.5 (MeO), 58.5 (MeO), 52.2 (MeO), 43.4 (4), 20.8 (Me), 19.3 (Me). **Aldol 10-*syn***: ^1H NMR ($CDCl_3$): $\delta=7.41-7.27$ (m, 5H, Ph), 4.85 (d, $J=11.0$ Hz, 1H, Bn), 4.34 (d, $J=11.0$ Hz, 1H, Bn), 4.17 (d, $J=$ 1.9 Hz, 1H, 2-H), 4.16 (s, 1H, 5-H), 3.81 (dd, $J=7.9$, 1.9 Hz, 1H, 3-H), 3.81 (s, 3H, MeO), 3.57 (d, $J=7.9$ Hz, 1H, OH), 3.42 (s, 3H, MeO), 3.35 (s, 3H, MeO), 0.96 (s, 3H, Me), 0.92 (s, 3H, Me).

Optical purity of aldol **10-*anti*** was determined after conversion into the corresponding acetyl derivative.

Methyl (2*R*,3*R*)-3-acetoxy-2-benzyloxy-5,5-dimethoxy-4,4-dimethylpentanoate: To a solution of mixture of aldols **10** (*anti*/*syn* = 80/20, 8.9 mg, 27.3 μmol) in dichloromethane (2.0 mL) at 0 °C were added pyridine (98.0 mg, 1.24 mmol) and acetyl chloride (330 mg, 4.20 mmol). The reaction mixture was stirred for 12 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with dichloromethane, and the organic layer was washed with saturated aqueous copper(II) sulfate, water, and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford methyl (2*R*,3*R*)-3-acetoxy-2-benzyloxy-5,5-dimethoxy-4,4-dimethylpentanoate (7.0 mg, 88 % from aldol **10-*anti***) as a colorless oil: $[\alpha]_D^{28}=+38.0$ (*c* 0.47, benzene); IR (neat): $\tilde{\nu}=1760$, 1740 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=7.35-7.28$ (m, 5H, Ph), 5.29 (d, $J=5.7$ Hz, 1H, 3-H), 4.66 (d, $J=11.6$ Hz, 1H, Bn), 4.36 (d, $J=11.6$ Hz, 1H, Bn), 4.17 (d, $J=5.7$ Hz, 1H, 2-H), 4.07 (s, 1H, 5-H), 3.73 (s, 3H, MeO), 3.43 (s, 3H, MeO), 3.40 (s, 3H, MeO), 2.00 (s, 3H, Ac), 0.94 (s, 3H, Me), 0.94 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta=170.9$ (1), 169.5 (Ac), 136.8 (Ph), 128.4 (Ph), 128.4 (Ph), 128.0 (Ph), 110.2 (5), 79.1 (3), 75.6 (2), 72.5 (Bn), 58.9 (MeO), 57.9 (MeO), 52.0 (MeO), 43.8 (4), 20.8 (Ac), 18.2 (Me), 18.0 (Me); HPLC (CHIRALCEL OD, *i*PrOH/hexane = 1/40, flow rate = 1.0 mL min^{-1}): $t_R=16.6$ min (93.3 %), $t_R=$ 38.7 min (6.7 %); HR MS: calcd for $C_{19}H_{28}O_7Na$ $[M+Na]^+$ 391.1733, found 391.1727.

Methyl (2*R*,3*R*)-2-benzyloxy-5,5-dimethoxy-3-(*p*-methoxybenzyloxy)-4,4-dimethylpentanoate (11-*anti*) and **methyl (2*R*,3*S*)-2-benzyloxy-5,5-dimethoxy-3-(*p*-methoxybenzyloxy)-4,4-dimethylpentanoate (11-*syn*)**: To a solution of a mixture of aldols **10** (*anti*/*syn* = 80/20, 100 mg, 0.306 mmol) and *p*-methoxybenzyl trichloroacetimidate (130 mg, 0.459 mmol) in diethyl ether (4.8 mL) at 0 °C was added a solution of trifluoromethanesulfonic acid (0.23 mg, 1.5 μmol) in diethyl ether (0.05 mL). The reaction mixture was stirred for 15 min at 0 °C and then triethylamine (1.6 mg, 15.3 μmol) and saturated aqueous sodium hydrogencarbonate were added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford a mixture of esters **11** (*anti*/*syn* = 80/20, 104 mg, 95 %) as a colorless oil: IR (neat): $\tilde{\nu}=1750\ cm^{-1}$; HR MS: calcd for $C_{25}H_{34}O_7Na$ $[M+Na]^+$ 469.2202, found 469.2175. **Ester 11-*anti***: ^1H NMR ($CDCl_3$): $\delta=7.40-7.18$ (m, 5H, Ph), 6.95 – 6.81 (m, 4H, Ph), 4.64 (d, $J=$ 11.4 Hz, 1H, Bn), 4.61 (d, $J=10.5$ Hz, 1H, Bn), 4.41 (d, $J=10.5$ Hz, 1H,

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Bn), 4.39 (d, $J = 11.4$ Hz, 1H, Bn), 4.26 (d, $J = 4.9$ Hz, 1H, 2-H), 4.17 (s, 1H, 5-H), 3.82 (s, 3H, MeO), 3.79 (d, $J = 4.9$ Hz, 1H, 3-H), 3.68 (s, 3H, MeO), 3.48 (s, 3H, MeO), 3.43 (s, 3H, MeO), 1.00 (s, 3H, Me), 0.91 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 172.1$ (1), 159.4 (PMP), 137.5 (Ph), 131.2 (Ph), 129.7 (Ph), 129.5 (Ph), 128.8 (Ph), 128.3 (Ph), 114.0 (PMP), 110.9 (5), 84.7 (2), 80.8 (3), 74.6 (PMB), 72.7 (Bn), 59.5 (MeO), 58.1 (MeO), 55.7 (MeO), 52.1 (MeO), 45.1 (4), 18.3 (Me), 18.1 (Me).

(3*R*,4*S*)-4-Benzyloxy-5-hydroxy-3-(*p*-methoxybenzyloxy)-2,2-dimethylpentanal dimethyl acetal (**12**): To a suspension of lithium aluminum hydride (850 mg, 22.4 mmol) in THF (200 mL) at 0 °C was added a solution of mixture of esters **11** (*anti*/*syn* = 80/20, 7.80 g, 17.2 mmol) in THF (30 mL). After the reaction mixture had been stirred for 2 h at 0 °C, water was added. The reaction mixture was allowed to warm to room temperature and then aqueous sodium hydroxide (15%) and water were added. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford alcohol **12** (5.01 g, 86% from ester **11-*anti***) as a colorless oil: $[\alpha]_D^{26} = -17.8$ (*c* 1.00, benzene); IR (neat): $\tilde{\nu} = 3450\ cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 7.40-7.27$ (m, 7H, Ph), 6.88 (d, $J = 8.7$ Hz, 2H, Ph), 4.81 (d, $J = 10.8$ Hz, 1H, Bn), 4.68 (d, $J = 11.5$ Hz, 1H, Bn), 4.54 (d, $J = 11.5$ Hz, 1H, Bn), 4.47 (d, $J = 10.8$ Hz, 1H, Bn), 4.16 (s, 1H, 1-H), 3.87 (dd, $J = 6.3$, 5.0 Hz, 2H, 5-H, 5-H), 3.82 (d, $J = 2.7$ Hz, 1H, 3-H), 3.81 (s, 3H, MeO), 3.73 (dt, $J = 5.0$, 2.7 Hz, 1H, 4-H), 3.49 (s, 3H, MeO), 3.45 (s, 3H, MeO), 2.33 (t, $J = 6.3$ Hz, 1H, OH), 0.98 (s, 3H, Me), 0.95 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 159.1$ (PMP), 138.2 (Ph), 130.8 (Ph), 129.2 (Ph), 128.4 (Ph), 127.8 (Ph), 127.7 (Ph), 113.7 (PMP), 111.0 (1), 83.6 (3), 81.2 (4), 74.6 (PMB), 71.4 (Bn), 62.6 (5), 59.1 (MeO), 57.7 (MeO), 55.2 (MeO), 43.9 (2), 18.8 (Me), 18.2 (Me); HR MS: calcd for $C_{24}H_{34}O_6Na$ $[M+Na]^+$ 441.2253, found 441.2266.

(3*R*,4*S*)-4-Benzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-2,2-dimethylpentanal dimethyl acetal (**13**): To a solution of imidazole (79.1 mg, 1.16 mmol) and *tert*-butylchlorodimethylsilane (84.0 mg, 0.557 mmol) in dichloromethane (3.5 mL) at 0 °C was added alcohol **12** (200 mg, 0.478 mmol) in dichloromethane (2 mL). After the reaction mixture had been stirred for 1 h at 0 °C, it was allowed to warm to room temperature; it was stirred for 4 h at room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford acetal **13** (238 mg, 93%) as a colorless oil: $[\alpha]_D^{24} = -17.4$ (*c* 1.07, benzene); IR (neat): $\tilde{\nu} = 2920$, 1610, 1510, 1470, 1250, 1100, 1070, 910, 840, 780, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.43-7.27$ (m, 7H, Ph), 6.90 (d, $J = 8.7$ Hz, 2H, Ph), 4.77 (d, $J = 11.8$ Hz, 1H, Bn), 4.75 (d, $J = 11.0$ Hz, 1H, Bn), 4.64 (d, $J = 11.8$ Hz, 1H, Bn), 4.45 (d, $J = 11.0$ Hz, 1H, Bn), 4.23 (s, 1H, 1-H), 4.03 (dd, $J = 11.6$, 2.1 Hz, 1H, 5-H), 3.89 (dd, $J = 11.6$, 6.7 Hz, 1H, 5-H), 3.83 (s, 3H, MeO), 3.75 (d, $J = 2.6$ Hz, 1H, 3-H), 3.70 (ddd, $J = 6.7$, 2.6, 2.1 Hz, 1H, 4-H), 3.48 (s, 3H, MeO), 3.42 (s, 3H, MeO), 0.97 (s, 3H, Me), 0.94 (s, 9H, TBS), 0.91 (s, 3H, Me), 0.09 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 159.4$ (PMP), 139.5 (Ph), 131.7 (Ph), 129.5 (Ph), 128.6 (Ph), 128.1 (Ph), 127.7 (Ph), 114.1 (PMP), 111.3 (1), 84.2 (4), 83.0 (3), 74.3 (PMB), 72.5 (Bn), 65.2 (5), 59.5 (MeO), 58.2 (MeO), 55.6 (MeO), 44.2 (2), 26.4 (TBS), 18.8 (Me), 18.7 (TBS), 18.5 (Me), −4.8 (TBS), −4.9 (TBS); HR MS: calcd for $C_{30}H_{48}O_6SiNa$ $[M+Na]^+$ 555.3118, found 555.3101.

(3*R*,4*S*)-4-Benzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-2,2-dimethylpentanal (**4**): To acetal **13** (652 mg, 1.22 mmol) was added a mixture of acetic acid (17.1 mL), water (4.3 mL), and THF (8.6 mL). The reaction mixture was stirred for 1 h at room temperature and then it was neutralized with solid sodium carbonate at 0 °C. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford aldehyde **4** (519 mg, 87%) as a colorless oil: $[\alpha]_D^{26} = +4.1$ (*c* 0.44, benzene); IR (neat): $\tilde{\nu} = 1720\ cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 9.33$ (s, 1H, 1-CHO) 7.30–7.20 (m, 7H, Ph), 6.86 (d, $J = 14.3$ Hz, 2H, Ph), 4.64 (d, $J = 10.6$ Hz, 1H, Bn), 4.55 (d, $J = 11.2$ Hz, 1H, Bn), 4.49 (d, $J = 10.6$ Hz, 1H, Bn), 4.35 (d, $J = 11.2$ Hz, 1H, Bn), 3.97–3.74 (m, 3H, 3-H, 5-H, 5-H), 3.76 (s, 3H, MeO), 3.37–3.32 (m, 1H, 4-H), 1.08 (s, 3H, Me), 0.99 (s, 3H, Me), 0.87 (s, 9H, TBS), 0.01 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 201.9$ (1), 159.2 (PMP), 137.6 (Ph), 130.4 (Ph), 129.3 (Ph), 128.2 (Ph), 128.2 (Ph), 127.6 (Ph), 113.8 (PMP), 81.1 (3 or 4), 79.8 (4 or 3), 74.9 (PMB), 71.6 (Bn), 61.8 (5), 55.3 (MeO), 49.9 (2), 25.7 (TBS), 20.7 (Me), 18.3 (Me), 16.0 (TBS), −5.3 (TBS), −5.4 (TBS); HR MS: calcd for $C_{28}H_{42}O_5SiNa$ $[M+Na]^+$ 509.2699, found 509.2708.

Methyl (2*RS*,3*RS*)-2-benzyloxy-5,5-ethylenedithio-3-hydroxy-4,4-dimethylpentanoate and **methyl (2*RS*,3*SR*)-2-benzyloxy-5,5-ethylenedithio-3-hydroxy-4,4-dimethylpentanoate**: To a solution of mixture of aldols **10** (*anti*/*syn* = 74/26, 223 mg, 0.683 mmol) and 1,2-ethanedithiol (294 mg, 3.12 mmol) in dichloromethane (10 mL) at room temperature was added boron trifluoride diethyl etherate (90.4 mg, 0.637 mmol). The reaction mixture was stirred for 45 min at room temperature and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford a mixture of methyl (2*RS*,3*RS*)-2-benzyloxy-5,5-ethylenedithio-3-hydroxy-4,4-dimethylpentanoate and methyl (2*RS*,3*SR*)-2-benzyloxy-5,5-ethylenedithio-3-hydroxy-4,4-dimethylpentanoate (*anti*/*syn* = 75/25, 225 mg, 92%) as a colorless oil: IR (neat): $\tilde{\nu} = 3500$, 1740 cm^{-1}; HR MS: calcd for $C_{17}H_{25}O_4S_2$ $[M+H]^+$ 357.1194, found 357.1183. **(2*RS*,3*RS*)-Ester**: ^{1}H NMR ($CDCl_3$): $\delta = 7.37-7.27$ (m, 5H, Ph), 4.86 (s, 1H, 5-H), 4.61 (d, $J = 11.2$ Hz, 1H, Bn), 4.42 (d, $J = 11.2$ Hz, 1H, Bn), 4.10 (d, $J = 5.6$ Hz, 1H, 2-H), 4.02 (d, $J = 5.6$ Hz, 1H, 3-H), 3.76 (s, 3H, MeO), 3.20–3.09 (m, 4H, SCH_2CH_2S), 1.07 (s, 3H, Me), 1.02 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 171.5$ (1), 136.5 (Ph), 128.1 (Ph), 127.9 (Ph), 127.7 (Ph), 80.1 (2), 77.0 (3), 72.1 (Bn), 62.4 (5), 51.7 (MeO), 43.1 (4), 38.5 (SCH_2), 38.5 (SCH_2), 20.7 (Me), 19.6 (Me). **(2*RS*,3*SR*)-Ester**: ^{1}H NMR ($CDCl_3$): $\delta = 7.37-7.27$ (m, 5H, Ph), 4.77 (s, 1H, 5-H), 4.77 (d, $J = 10.9$ Hz, 1H, Bn), 4.42 (d, $J = 10.9$ Hz, 1H, Bn), 4.17 (d, $J = 2.0$ Hz, 1H, 2-H), 3.92 (d, $J = 2.0$ Hz, 1H, 3-H), 3.80 (s, 3H, MeO), 3.20–3.09 (m, 4H, SCH_2CH_2S), 1.08 (s, 3H, Me), 0.99 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 171.5$ (1), 136.2 (Ph), 128.4 (Ph), 128.2 (Ph), 127.9 (Ph), 77.3 (2), 77.2 (3), 72.3 (Bn), 62.5 (5), 52.0 (MeO), 43.5 (4), 38.6 (SCH_2), 38.3 (SCH_2), 21.6 (Me), 19.8 (Me).

(2*RS*,3*SR*)-2-Benzyloxy-5,5-ethylenedithio-4,4-dimethyl-1,3-pentanediol and **(2*RS*,3*RS*)-2-benzyloxy-5,5-ethylenedithio-4,4-dimethyl-1,3-pentanediol**: To a suspension of lithium aluminum hydride (62.3 mg, 1.64 mmol) in THF (5 mL) at 0 °C was added a solution of a mixture of methyl (2*RS*,3*RS*)-2-benzyloxy-5,5-ethylenedithio-3-hydroxy-4,4-dimethylpentanoate and methyl (2*RS*,3*SR*)-2-benzyloxy-5,5-ethylenedithio-3-hydroxy-4,4-dimethylpentanoate (*anti*/*syn* = 75/25, 293 mg, 0.821 mmol) in THF (3 mL). After the reaction mixture had been stirred for 1 h at 0 °C, water was added. The reaction mixture was allowed to warm to room temperature, and then aqueous sodium hydroxide (15%) and water were added. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford a mixture of (2*RS*,3*SR*)-2-benzyloxy-5,5-ethylenedithio-4,4-dimethyl-1,3-pentanediol and (2*RS*,3*RS*)-2-benzyloxy-5,5-ethylenedithio-4,4-dimethyl-1,3-pentanediol (*anti*/*syn* = 75/25, 242 mg, 90%) as a colorless oil: IR (neat): $\tilde{\nu} = 3450\ cm^{-1}$; HR MS: calcd for $C_{16}H_{24}O_3S_2Na$ $[M+Na]^+$ 351.1065, found 351.1071. **(2*RS*,3*SR*)-Diol**: ^{1}H NMR ($CDCl_3$): $\delta = 7.36-7.31$ (m, 5H, Ph), 4.89 (s, 1H, 5-H), 4.60 (d, $J = 11.6$ Hz, 1H, Bn), 4.55 (d, $J = 11.6$ Hz, 1H, Bn), 3.97 (d, $J = 5.3$ Hz, 1H, 3-H), 3.89–3.85 (m, 2H, 1-H, 1-H), 3.57 (dt, $J = 5.3$, 4.0 Hz, 1H, 2-H), 3.23–3.15 (m, 4H, SCH_2CH_2S), 1.10 (s, 3H, Me), 1.05 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 138.9$ (Ph), 129.7 (Ph), 129.2 (Ph), 129.1 (Ph), 80.7 (2), 78.9 (3), 72.3 (Bn), 64.4 (5), 62.7 (1), 44.0 (4), 40.0 (SCH_2), 39.9 (SCH_2), 22.5 (Me), 21.8 (Me). **(2*RS*,3*RS*)-Diol**: ^{1}H NMR ($CDCl_3$): $\delta = 7.36-7.31$ (m, 5H, Ph), 4.87 (s, 1H, 5-H), 4.75 (d, $J = 11.2$ Hz, 1H, Bn), 4.58 (d, $J = 11.2$ Hz, 1H, Bn), 3.93–3.73 (m, 2H, 1-H, 1-H), 3.69–3.64 (m, 2H, 2-H, 3-H), 3.23–3.15 (m, 4H, SCH_2CH_2S), 1.10 (s, 3H, Me), 1.02 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 138.7$ (Ph), 129.5 (Ph), 129.2 (Ph), 129.1 (Ph), 78.5 (2), 77.7 (3), 73.0 (Bn), 64.7 (1), 64.0 (5), 44.5 (4), 40.0 (SCH_2), 39.8 (SCH_2), 22.9 (Me), 21.2 (Me).

(3*RS*,4*SR*)-4-Benzyloxy-1,1-ethylenedithio-3,5-isopropylidenedioxy-2,2-dimethylpentane (**14-*trans***) and **(3*RS*,4*RS*)-4-benzyloxy-1,1-ethylenedithio-3,5-isopropylidenedioxy-2,2-dimethylpentane** (**14-*cis***): To a solution of a mixture of (2*RS*,3*SR*)-2-benzyloxy-5,5-ethylenedithio-4,4-dimethyl-1,3-pentanediol and (2*RS*,3*RS*)-2-benzyloxy-5,5-ethylenedithio-4,4-dimethyl-1,3-pentanediol (*anti*/*syn* = 61/39, 34.3 mg, 0.104 mmol) in toluene (2 mL) and 2,2-dimethoxyethane (2 mL) at room temperature was added *p*-toluenesulfonic acid (2.0 mg, 11.6 μmol). The reaction mixture was stirred for 1 h at room temperature, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried

over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford acetonide **14-*trans*** (19.5 mg, 51%) and acetonide **14-*cis*** (10.3 mg, 27%) as colorless oils. **Acetonide 14-*trans***: IR (neat): $\tilde{\nu}=1640$, 1370, 1090 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=7.36-7.25$ (m, 5H, Ph), 4.91 (s, 1H, 1-H), 4.58 (d, $J=11.4$ Hz, 1H, Bn), 4.44 (d, $J=11.4$ Hz, 1H, Bn), 3.80 (dd, $J=12.2$, 4.0 Hz, 1H, 5-H), 3.75 (d, $J=7.7$ Hz, 1H, 3-H), 3.74 (dd, $J=12.2$, 3.9 Hz, 1H, 5-H), 3.60 (ddd, $J=7.7$, 4.0, 3.9 Hz, 1H, 4-H), 3.18–3.10 (m, 4H, SCH_2CH_2S), 1.44 (s, 3H, Me), 1.32 (s, 3H, Me), 1.03 (s, 3H, Me), 1.02 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta=137.8$ (Ph), 128.3 (Ph), 128.0 (Ph), 127.7 (Ph), 99.8 (acetonide), 76.6 (3), 75.2 (4), 70.7 (Bn), 61.7 (1), 61.6 (5), 42.8 (2), 38.9 (SCH_2), 38.7 (SCH_2), 26.3 (Me), 21.8 (Me), 21.1 (Me), 18.6 (Me); HR MS: calcd for $C_{19}H_{29}O_3S_2$ $[M+H]^+$ 369.1558, found 369.1566; HR MS: calcd for $C_{19}H_{28}O_3S_2Na$ $[M+Na]^+$ 391.1378, found 391.1378. **Acetonide 14-*cis***: IR (neat): $\tilde{\nu}=1640$, 1370, 1100 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=7.39-7.28$ (m, 5H, Ph), 4.81 (s, 1H, 1-H), 4.73 (d, $J=11.9$ Hz, 1H, Bn), 4.43 (d, $J=11.9$ Hz, 1H, Bn), 4.07 (dd, $J=12.9$, 2.2 Hz, 1H, 5-H), 3.86 (dd, $J=12.9$, 2.1 Hz, 1H, 5-H), 3.76 (d, $J=1.9$ Hz, 1H, 3-H), 3.40 (ddd, $J=2.2$, 2.1, 1.9 Hz, 1H, 4-H), 3.17–3.07 (m, 4H, SCH_2CH_2S), 1.44 (s, 3H, Me), 1.44 (s, 3H, Me), 1.20 (s, 3H, Me), 0.97 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta=138.3$ (Ph), 128.8 (Ph), 128.6 (Ph), 128.1 (Ph), 99.5 (acetonide), 76.4 (3), 71.8 (4), 70.8 (Bn), 63.0 (1), 62.2 (5), 43.4 (2), 39.3 (SCH_2), 38.9 (SCH_2), 29.4 (Me), 22.1 (Me), 19.4 (Me), 18.7 (Me); HR MS: calcd for $C_{19}H_{29}O_3S_2$ $[M+H]^+$ 369.1558, found 369.1551; HR MS: calcd for $C_{19}H_{28}O_3S_2Na$ $[M+Na]^+$ 391.1378, found 391.1384.

Methyl (*S*)-2,3-dihydroxypropionate (15):[22] To a solution of L-serine (100 g, 951 mmol) in water (225 mL) at 0 °C were added aqueous sulfuric acid (3 M, 507 mL) and aqueous sodium nitrite (6 M, 166 mL). After the reaction mixture had been stirred for 5 h at room temperature, aqueous sodium nitrite (6 M, 166 mL) was added at 0 °C. The reaction mixture was stirred for 3 days at room temperature and then aqueous sulfuric acid (3 M, 254 mL) and aqueous sodium nitrite (6 M, 166 mL) were added at 0 °C. After the reaction mixture had been stirred for 2 days at room temperature, water (1 L) was distilled under reduced pressure and a solution of sodium hydroxide (41.9 g) in water (100 mL) was added to the resulting residue at 0 °C. A mixture of methanol (300 mL) and acetone (100 mL) was added to the reaction mixture and then it was filtered through a short pad of Celite. After evaporation of the solvent, a mixture of methanol (300 mL) and acetone (100 mL) was added and then the above operation was repeated 7 times. After partial evaporation of the solvent, benzene (200 mL) was added to the residue and the solvent was removed by distillation under reduced pressure. Benzene (200 mL) was once more added to the residue and then the above operation was repeated twice. The residue was dissolved in methanol (500 mL) and acidified by concentrated sulfuric acid, and then trimethyl orthoformate (100 mL) was added to the mixture. The reaction mixture was stirred for 30 min at 60 °C and then neutralized with sodium methoxide at 0 °C. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford diol **15** (101 g, 88%) as a colorless oil: $[\alpha]_D^{25}=+6.4$ (*c* 0.20, benzene); IR (neat): $\tilde{\nu}=3470$, 1740 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=4.18$ (br s, 1H, 2-H), 3.83–3.69 (m, 2H, 3-H, 3-H), 3.72 (s, 3H, MeO), 3.41 (br s, 1H, 2-OH), 2.59 (br s, 1H, 3-OH); ^{13}C NMR ($CDCl_3$): $\delta=173.7$ (1), 71.9 (2), 64.2 (3), 53.1 (MeO); CI MS: calcd for $C_4H_9O_4$ $[M+H]^+$ 121, found 121.

Methyl (*S*)-3-(*tert*-butyldimethylsiloxy)-2-hydroxypropionate: To a solution of diol **15** (17.1 g, 142 mmol) and imidazole (22.3 g, 327 mmol) in DMF (100 mL) at 0 °C was added a solution of *tert*-butylchlorodimethylsilane (21.4 g, 142 mmol) in DMF (70 mL). The reaction mixture was stirred for 6 h at 0 °C and then phosphate buffer (pH = 7) was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford methyl (*S*)-3-(*tert*-butyldimethylsiloxy)-2-hydroxypropionate (27.5 g, 82%) as a colorless oil: $[\alpha]_D^{25}=+3.9$ (*c* 0.89, benzene); IR (neat): $\tilde{\nu}=3440$, 1740 cm^{-1}; ^1H NMR (CCl_4): $\delta=4.20-3.79$ (m, 3H, 2-H, 3-H, 3-H), 3.78 (s, 3H, MeO), 2.74 (d, $J=7.2$ Hz, 1H, OH), 0.85 (s, 9H, TBS), 0.00 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=173.1$ (1), 71.9 (2), 65.0 (3), 52.2 (MeO), 25.6 (TBS), 18.2 (TBS), −5.5 (TBS), −5.7 (TBS); HR MS: calcd for $C_{10}H_{22}O_4Si$ $[M+H]^+$ 235.1366, found 235.1378.

Methyl (*S*)-2-benzyloxy-3-(*tert*-butyldimethylsiloxy)propionate: To a solution of methyl (*S*)-3-(*tert*-butyldimethylsiloxy)-2-hydroxypropionate (1.01 g, 4.27 mmol) in dichloromethane (2 mL) at 0 °C were added a solution of benzyl trichloroacetimidate (2.16 g, 8.53 mmol) in dichloromethane (2.5 mL) and a solution of trifluoromethanesulfonic acid (32.0 mg, 0.213 mmol) in dichloromethane (0.5 mL). The reaction mixture was stirred for 10 h at room temperature and then phosphate buffer (pH = 7) was added at 0 °C. The mixture was extracted with dichloromethane, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford methyl (*S*)-2-benzyloxy-3-(*tert*-butyldimethylsiloxy)propionate (1.39 g, 100%) as a colorless oil: $[\alpha]_D^{29}=-36.0$ (*c* 1.98, benzene); IR (neat): $\tilde{\nu}=1720$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=7.34-7.24$ (m, 5H, Ph), 4.71 (d, $J=12.2$ Hz, 1H, Bn), 4.48 (d, $J=12.2$ Hz, 1H, Bn), 4.03 (t, $J=5.3$ Hz, 1H, 2-H), 3.85 (d, $J=5.3$ Hz, 2H, 3-H, 3-H), 3.70 (s, 3H, MeO), 0.83 (s, 9H, TBS), 0.00 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=171.4$ (1), 137.4 (Ph), 128.3 (Ph), 127.9 (Ph), 125.8 (Ph), 79.4 (2), 72.5 (Bn), 64.2 (3), 51.8 (MeO), 25.7 (TBS), 18.2 (TBS), −5.5 (TBS), −5.5 (TBS); HPLC (CHIRALCEL OD, *i*PrOH/hexane = 1/50, flow rate = 1.0 mL min^{-1}): $t_R=5.0$ min (97.5%), $t_R=7.4$ min (2.5%); HR MS: calcd for $C_{17}H_{29}O_4Si$ $[M+H]^+$ 325.1835, found 325.1837.

(*S*)-2-Benzyloxy-3-(*tert*-butyldimethylsiloxy)propanal (16):[55] To a solution of methyl (*S*)-2-benzyloxy-3-(*tert*-butyldimethylsiloxy)propionate (10.6 g, 32.7 mmol) in hexane (215 mL) at −78 °C was added DIBAL in hexanes (1.0 M, 42.6 mL, 42.6 mmol). The reaction mixture was stirred for 1 h at −78 °C, and then methanol (240 mL) and diethyl ether (250 mL) were added. After filtration of the mixture through a short pad of Celite and evaporation of the solvent, the crude product was purified by column chromatography to afford aldehyde **16** (9.11 g, 95%) as a colorless oil: $[\alpha]_D^{22}=-15.7$ (*c* 1.24, benzene); IR (neat): $\tilde{\nu}=1740$ cm^{-1}; ^1H NMR (CCl_4): $\delta=9.60$ (s, 1H, 1-CHO), 7.30–7.20 (m, 5H, Ph), 5.10–4.58 (m, 1H, 2-H), 4.57 (s, 2H, Bn), 4.00–3.25 (m, 2H, 3-H, 3-H), 0.85 (s, 9H, TBS), 0.00 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=202.8$ (1), 135.1 (Ph), 128.9 (Ph), 128.5 (Ph), 127.9 (Ph), 83.9 (2), 72.5 (Bn), 62.9 (3), 25.8 (TBS), 18.2 (TBS), −5.5 (TBS), −6.5 (TBS).

Methyl (3*R*,4*S*)-4-benzyloxy-5-(*tert*-butyldimethylsiloxy)-3-hydroxy-2,2-dimethylpentanoate (17-*anti*) and **methyl (3*S*,4*S*)-4-benzyloxy-5-(*tert*-butyldimethylsiloxy)-3-hydroxy-2,2-dimethylpentanoate (17-*syn*)**: To a solution of diisopropylamine (3.89 g, 38.4 mmol) in diethyl ether (347 mL) at 0 °C was added *n*-butyllithium in hexane (1.66 M, 23.2 mL, 38.5 mmol). The reaction mixture was stirred for 15 min at 0 °C, and then a solution of methyl isobutylate (3.52 g, 34.5 mmol) in diethyl ether (20 mL) was added at −78 °C. After the reaction mixture had been stirred for 30 min, a solution of aldehyde **16** (9.11 g, 30.9 mmol) in diethyl ether (20 mL) was added at −78 °C. The reaction mixture was stirred for 1 h, and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford aldol **17-*anti*** (8.01 g, 65%) and aldol **17-*syn*** (2.38 g, 20%) as colorless oils. **Aldol 17-*anti***: $[\alpha]_D^{27}=+14.5$ (*c* 1.80, benzene); IR (neat): $\tilde{\nu}=3480$, 1730 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=7.25-7.20$ (m, 5H, Ph), 4.47 (d, $J=10.9$ Hz, 1H, Bn), 4.38 (d, $J=10.9$ Hz, 1H, Bn), 3.95 (dd, $J=8.8$, 3.6 Hz, 1H, 3-H), 3.81 (dd, $J=10.6$, 4.6 Hz, 1H, 5-H), 3.73 (dd, $J=10.6$, 6.3 Hz, 1H, 5-H), 3.37 (d, $J=3.6$ Hz, 1H, OH), 3.33 (ddd, $J=8.8$, 6.3, 4.6 Hz, 1H, 4-H), 3.30 (s, 3H, MeO), 1.17 (s, 3H, Me), 1.13 (s, 3H, Me), 0.82 (s, 9H, TBS), 0.01 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=177.2$ (1), 137.9 (Ph), 128.2 (Ph), 128.1 (Ph), 127.7 (Ph), 79.0 (3 or 4), 77.9 (4 or 3), 72.6 (Bn), 64.5 (5), 51.4 (MeO), 45.3 (2), 25.8 (TBS), 23.6 (Me), 18.5 (Me), 18.1 (TBS), −5.9 (TBS), −5.9 (TBS); HPLC (CHIRALCEL AD, *i*PrOH/hexane = 1/150, flow rate = 1.0 mL min^{-1}): $t_R=11.1$ min (96.0%), $t_R=15.4$ min (4.0%); HR MS: calcd for $C_{21}H_{37}O_5Si$ $[M+H]^+$ 397.2410, found 397.2399. **Aldol 17-*syn***: IR (neat): $\tilde{\nu}=3460$, 1730 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=7.30-7.13$ (m, 5H, Ph), 4.70 (d, $J=10.8$ Hz, 1H, Bn), 4.41 (d, $J=10.8$ Hz, 1H, Bn), 3.79 (dd, $J=12.3$, 6.1 Hz, 1H, 5-H), 3.75 (dd, $J=12.3$, 6.0 Hz, 1H, 5-H), 3.57 (ddd, $J=6.1$, 6.0, 1.1 Hz, 1H, 4-H), 3.56 (dd, $J=10.5$, 1.1 Hz, 1H, 3-H), 3.32 (s, 3H, MeO), 3.19 (d, $J=10.5$ Hz, 1H, OH), 1.28 (s, 3H, Me), 1.19 (s, 3H, Me), 0.89 (s, 9H, TBS), 0.06 (s, 3H, TBS), 0.05 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=177.3$ (1), 135.8 (Ph), 128.8 (Ph), 128.4 (Ph), 128.2 (Ph), 78.1 (3 or 4), 77.2 (4 or 3), 72.7 (Bn), 63.0 (5), 51.6 (MeO), 45.0 (2), 25.9 (TBS), 23.6 (Me), 22.1 (Me), 18.1 (TBS), −5.4 (TBS), −5.4 (TBS); HR MS: calcd for $C_{21}H_{37}O_5Si$ $[M+H]^+$ 397.2410, found 397.2403.

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Methyl (3*R*,4*S*)-4-benzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-2,2-dimethylpentanoate (**18**): To a solution of aldol **17-*anti*** (6.20 g, 15.6 mmol) in dichloromethane (170 mL) at 0 °C were added a solution of *p*-methoxybenzyl trichloroacetimidate (13.3 g, 46.9 mmol) in dichloromethane (20 mL) and a solution of trifluoromethanesulfonic acid (7.0 mg, 46.6 μmol) in dichloromethane (0.47 mL). The reaction mixture was stirred for 3 h at 0 °C, and then phosphate buffer (pH = 7) was added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford ester **18** (6.03 g, 75 %) and recovered aldol **17-*anti*** (1.49 g, 24 %) as colorless oils. **Ester 18**: $[\alpha]_D^{28} = -6.5$ (*c* 1.08, benzene); IR (neat): $\tilde{\nu} = 1730\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 7.28-7.18$ (m, 7H, Ph), 6.86–6.80 (m, 2H, Ph), 4.63 (d, $J = 11.2$ Hz, 1H, Bn), 4.60 (d, $J = 10.7$ Hz, 1H, Bn), 4.52 (d, $J = 10.7$ Hz, 1H, Bn), 4.38 (d, $J = 11.2$ Hz, 1H, Bn), 3.96 (d, $J = 7.6$ Hz, 1H, 3-H), 3.92 (dd, $J = 11.6$, 2.0 Hz, 1H, 5-H), 3.76 (dd, $J = 11.6$, 5.0 Hz, 1H, 5-H), 3.75 (s, 3H, MeO), 3.37 (ddd, $J = 7.6$, 5.0, 2.0 Hz, 1H, 4-H), 3.28 (s, 3H, MeO), 1.22 (s, 3H, Me), 1.10 (s, 3H, Me), 0.87 (s, 9H, TBS), 0.06 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta =$ 176.7 (1), 159.1 (PMP), 138.3 (Ph), 130.7 (Ph), 129.2 (Ph), 128.2 (Ph), 128.0 (Ph), 127.3 (Ph), 113.7 (PMP), 82.0 (3 or 4), 80.8 (4 or 3), 74.9 (PMB), 72.3 (Bn), 62.6 (5), 55.2 (MeO), 51.3 (MeO), 45.9 (2), 25.9 (TBS), 24.2 (Me), 18.6 (Me), 18.2 (TBS), −5.1 (TBS), −5.1 (TBS); HR MS: calcd for $C_{29}H_{45}O_6Si$ $[M+H]^+$ 517.2985, found 517.2994.

(3*R*,4*S*)-4-Benzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-2,2-dimethylpentanol: To a solution of ester **18** (7.35 g, 14.2 mmol) in hexane (170 mL) at −78 °C was added DIBAL in hexanes (1.0 M, 35.6 mL, 35.6 mmol). The reaction mixture was stirred for 1 h at −78 °C and then methanol and diethyl ether were added. After filtration of the mixture through a short pad of Celite and evaporation of the solvent, the crude product was purified by column chromatography to afford (3*R*,4*S*)-4-benzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-2,2-dimethylpentanol (6.37 g, 92 %) as a colorless oil: $[\alpha]_D^{29} = -1.9$ (*c* 4.59, benzene); IR (neat): $\tilde{\nu} = 3430\ cm^{-1}$; ^1H NMR ($CDCl_3$): 7.31–7.16 (m, 7H, Ph), 6.81–6.78 (m, 2H, Ph), 4.71 (d, $J = 11.9$ Hz, 1H, Bn), 4.64 (d, $J = 10.9$ Hz, 1H, Bn), 4.52 (d, $J = 11.9$ Hz, 1H, Bn), 4.41 (d, $J = 10.9$ Hz, 1H, Bn), 3.93 (dd, $J = 11.3$, 2.6 Hz, 1H, 5-H), 3.81 (dd, $J = 11.3$, 6.4 Hz, 1H, 5-H), 3.72 (s, 3H, MeO), 3.63 (ddd, $J = 6.4$, 3.0, 2.6 Hz, 1H, 4-H), 3.46 (d, $J = 3.0$ Hz, 1H, 3-H), 3.29 (dd, $J = 11.1$, 5.3 Hz, 1H, 1-H), 3.24 (dd, $J = 11.1$, 6.9 Hz, 1H, 1-H), 2.62 (br dd, $J = 6.9$, 5.3 Hz, 1H, OH), 0.86 (s, 3H, Me), 0.84 (s, 9H, TBS), 0.79 (s, 3H, Me), 0.00 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 159.2$ (PMP), 138.5 (Ph), 130.3 (Ph), 129.7 (Ph), 128.3 (Ph), 127.8 (Ph), 127.5 (Ph), 113.8 (PMP), 85.8 (3 or 4), 81.7 (4 or 3), 74.1 (PMB), 72.4 (Bn), 71.0 (1), 64.3 (5), 55.2 (MeO), 39.2 (2), 26.0 (TBS), 22.7 (Me), 21.3 (Me), 18.3 (TBS), −5.1 (TBS), −5.1 (TBS); HR MS: calcd for $C_{28}H_{44}O_5SiNa$ $[M+Na]^+$ 511.2856, found 511.2884.

(3*R*,4*S*)-4-Benzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-2,2-dimethylpentanal (**4**): To a solution of oxalyl chloride (4.31 g, 33.9 mmol) in dichloromethane (164 mL) at −78 °C was added a solution of DMSO (3.32 g, 42.4 mmol) in dichloromethane (20 mL). The reaction mixture was stirred for 15 min at −78 °C and then a solution of (3*R*,4*S*)-4-benzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-2,2-dimethylpentanol (13.8 g, 28.3 mmol) in dichloromethane (30 mL) was added. After the reaction mixture had been stirred for 1 h, triethylamine (8.57 g, 84.6 mmol) was added. The reaction mixture was allowed to warm to room temperature and then saturated aqueous ammonium chloride was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford aldehyde **4** (13.3 g, 97 %) as a colorless oil: $[\alpha]_D^{29} = +6.6$ (*c* 2.51, benzene). Physical data of this aldehyde **4** were identical to those of the compound derived from acetal **13**, except for its optical rotation.

Methyl (2*R*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-7-(*tert*-butyldimethylsiloxy)-3-hydroxy-5-(*p*-methoxybenzyloxy)-4,4-dimethylheptanoate (**19-*anti,anti,anti***) and **methyl (2*S*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-7-(*tert*-butyldimethylsiloxy)-3-hydroxy-5-(*p*-methoxybenzyloxy)-4,4-dimethylheptanoate** (**19-*syn,anti,anti***): To a suspension of magnesium bromide diethyl etherate (13.9 g, 53.5 mmol) in toluene (89 mL) at −15 °C was added a solution of (*Z*)-2-benzyloxy-1-(*tert*-butyldimethylsiloxy)-1-methoxyethene (**8**) (6.30 g, 21.4 mmol) in toluene (107 mL). The reaction mixture was stirred for 15 min at −15 °C and then a solution of aldehyde **4** (8.00 g, 16.4 mmol) in toluene (107 mL) was added. After the reaction mixture had been stirred for 1 h at −15 °C, the mixture was poured into saturated aqueous sodium hydrogencarbonate at 0 °C. The mixture was extracted with ethyl acetate, the organic layer was washed with saturated aqueous sodium hydrogencarbonate and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford aldol **19-*anti,anti,anti*** (7.32 g, 62 %), aldol **19-*syn,anti,anti*** (1.73 g, 14 %), and recovered aldehyde **4** (1.08 g, 12 %) as colorless oils. **Aldol 19-*anti,anti,anti***: $[\alpha]_D^{28} = +0.8$ (*c* 1.85, benzene); IR (neat): $\tilde{\nu} = 3490$, 1750 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.41-7.07$ (m, 12H, Ph), 6.85 (d, $J = 10.8$ Hz, 2H, Ph), 4.72 (d, $J = 11.9$ Hz, 1H, Bn), 4.65 (d, $J = 10.8$ Hz, 1H, Bn), 4.60 (d, $J = 11.9$ Hz, 1H, Bn), 4.57 (d, $J = 11.5$ Hz, 1H, Bn), 4.30 (d, $J = 11.5$ Hz, 1H, Bn), 4.29 (d, $J = 10.8$ Hz, 1H, Bn), 4.01 (br s, 1H, 2-H), 4.00 (dd, $J = 11.6$, 1.9 Hz, 1H, 7-H), 3.85 (dd, $J = 11.6$, 6.3 Hz, 1H, 7-H), 3.80 (s, 3H, MeO), 3.80–3.69 (m, 3H, 3-H, 6-H, OH), 3.74 (s, 3H, MeO), 3.62 (d, $J = 1.7$ Hz, 1H, 5-H), 0.97 (s, 6H, Me, Me), 0.91 (s, 9H, TBS), 0.07 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 172.0$ (1), 159.4 (PMP), 138.7 (Ph), 136.6 (Ph), 129.9 (Ph), 129.6 (Ph), 128.5 (Ph), 128.4 (Ph), 128.2 (Ph), 128.1 (Ph), 127.7 (Ph), 127.4 (Ph), 113.8 (PMP), 88.0 (2), 81.9 (5), 80.7 (6), 78.1 (3), 74.1 (PMB), 72.5 (Bn), 72.2 (Bn), 64.9 (7), 55.2 (MeO), 51.8 (MeO), 40.7 (4), 25.9 (TBS), 22.4 (Me), 22.1 (Me), 18.3 (TBS), −6.5 (TBS), −6.5 (TBS); HR MS: calcd for $C_{38}H_{54}O_8SiNa$ $[M+Na]^+$ 689.3486, found 689.3487. **Aldol 19-*syn,anti,anti***: $[\alpha]_D^{25} = -23.0$ (*c* 0.48, benzene); IR (neat): $\tilde{\nu} = 3470$, 1760 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.41-7.18$ (m, 12H, Ph), 6.83 (d, $J = 11.3$ Hz, 2H, Ph), 4.82 (d, $J = 10.9$ Hz, 1H, Bn), 4.72 (d, $J = 12.2$ Hz, 1H, Bn), 4.60 (d, $J = 12.2$ Hz, 1H, Bn), 4.57 (d, $J = 10.6$ Hz, 1H, Bn), 4.36 (d, $J = 10.9$ Hz, 1H, Bn), 4.36 (d, $J = 10.6$ Hz, 1H, Bn), 4.17 (d, $J = 2.0$ Hz, 1H, 5-H), 3.97 (dd, $J = 11.4$, 2.2 Hz, 1H, 7-H), 3.85 (dd, $J = 11.4$, 3.8 Hz, 1H, 7-H), 3.85 (d, $J = 6.6$ Hz, 1H, 3-H), 3.84 (br s, 1H, OH), 3.83 (d, $J = 6.6$ Hz, 1H, 2-H), 3.78 (s, 3H, MeO), 3.78 (s, 3H, MeO), 3.63 (ddd, $J = 3.8$, 2.2, 2.0 Hz, 1H, 6-H), 0.95 (s, 3H, Me), 0.93 (s, 3H, Me), 0.80 (s, 9H, TBS), 0.05 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 172.0$ (1), 159.1 (PMP), 138.9 (Ph), 136.7 (Ph), 130.3 (Ph), 129.6 (Ph), 129.1 (Ph), 128.4 (Ph), 128.4 (Ph), 128.2 (Ph), 127.5 (Ph), 127.3 (Ph), 113.7 (PMP), 87.4 (2), 82.2 (5), 78.5 (6), 78.4 (3) 73.9 (PMB), 72.9 (Bn), 72.3 (Bn), 65.1 (7), 55.2 (MeO), 52.0 (MeO), 41.0 (4), 25.9 (TBS), 22.1 (Me), 21.2 (Me), 18.2 (TBS), −5.5 (TBS), −5.5 (TBS); HR MS: calcd for $C_{38}H_{54}O_8SiNa$ $[M+Na]^+$ 689.3486, found 689.3503.

Methyl (2*R*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-3,7-bis(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4-dimethylheptanoate (**20**): To a solution of aldol **19-*anti,anti,anti*** (4.68 g, 7.02 mmol) in dichloromethane (60 mL) were added a solution of 2,6-lutidine (2.52 g, 21.0 mmol) in dichloromethane (15 mL) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (3.81 g, 14.0 mmol) in dichloromethane (30 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford ester **20** (5.47 g, 100 %) as a colorless oil: $[\alpha]_D^{28} = -10.2$ (*c* 1.03, benzene); IR (neat): $\tilde{\nu} = 1750\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 7.36-7.23$ (m, 12H, Ph), 6.87 (d, $J = 8.6$ Hz, 2H, Ph), 4.73 (d, $J = 11.6$ Hz, 1H, Bn), 4.71 (d, $J = 10.9$ Hz, 1H, Bn), 4.53 (d, $J = 11.2$ Hz, 1H, Bn), 4.51 (d, $J = 11.6$ Hz, 1H, Bn), 4.51 (d, $J = 10.9$ Hz, 1H, Bn), 4.34 (d, $J = 2.3$ Hz, 1H, 2-H or 3-H), 4.28 (d, $J = 2.3$ Hz, 1H, 3-H or 2-H), 4.24 (d, $J = 11.2$ Hz, 1H, Bn), 4.01 (dd, $J = 11.6$, 2.0 Hz, 1H, 7-H), 3.88 (dd, $J = 11.6$, 5.7 Hz, 1H, 7-H), 3.82 (d, $J = 4.3$ Hz, 1H, 5-H), 3.79 (s, 3H, MeO), 3.68 (s, 3H, MeO), 3.64 (ddd, $J = 5.7$, 4.3, 2.0 Hz, 1H, 6-H), 1.01 (s, 3H, Me), 1.00 (s, 3H, Me), 0.92 (s, 9H, TBS), 0.90 (s, 9H, TBS), 0.06 (s, 3H, TBS), 0.06 (s, 3H, TBS), 0.04 (s, 3H, TBS), −0.01 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 171.4$ (1), 158.9 (PMP), 138.7 (Ph), 137.7 (Ph), 131.2 (Ph), 128.9 (Ph), 128.2 (Ph), 128.1 (Ph), 127.9 (Ph), 127.7 (Ph), 127.4 (Ph), 127.3 (Ph), 113.6 (PMP), 82.7 (2), 82.1 (5), 81.8 (6), 78.0 (3), 73.8 (PMB), 72.5 (Bn), 72.1 (Bn), 63.6 (7), 55.2 (MeO), 51.3 (MeO), 43.9 (4), 26.2 (TBS), 25.9 (TBS), 21.3 (Me), 18.6 (Me), 18.5 (TBS), 18.2 (TBS), −3.5 (TBS) , −4.7 (TBS), −5.3 (TBS), −5.3 (TBS); HR MS: calcd for $C_{44}H_{68}O_8Si_2Na$ $[M+Na]^+$ 803.4351, found 803.4374.

(2*S*,3*R*,5*R*,6*S*)-2,6-Dibenzyloxy-3,7-bis(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4-dimethylheptanol: To a solution of ester **20** (7.60 g, 9.73 mmol) in toluene (120 mL) at −78 °C was added DIBAL in toluene (1.0 M, 20.0 mL, 20.0 mmol). After reaction mixture was stirred for 1 h at

−78 °C, methanol was added. The mixture was allowed to warm to room temperature and then saturated aqueous potassium sodium tartrate was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with saturated aqueous potassium sodium tartrate, water and brine, and dried over sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography to afford (2*S*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-3,7-bis(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4-dimethylheptanol (5.95 g, 81%) and aldehyde **22** (1.00 g, 14%) as colorless oils. **(2*S*,3*R*,5*R*,6*S*)-2,6-Dibenzyloxy-3,7-bis-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4-dimethylheptanol**: $[\alpha]_D^{28} = -21.8$ (*c* 1.64, benzene); IR (neat): $\tilde{\nu} = 3460\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 7.36-7.17$ (m, 12H, Ph), 6.87 (d, $J = 8.6$ Hz, 2H, Ph), 4.77 (d, $J = 11.4$ Hz, 1H, Bn), 4.67 (d, $J = 10.7$ Hz, 1H, Bn), 4.49 (d, $J = 10.7$ Hz, 1H, Bn), 4.48 (d, $J = 11.4$ Hz, 1H, Bn), 4.45 (d, $J = 11.6$ Hz, 1H, Bn), 4.30 (d, $J = 11.6$ Hz, 1H, Bn), 4.25 (s, 1H, 5-H), 4.07 (d, $J = 11.1$ Hz, 1H, 7-H), 3.87 (dd, $J = 11.1$, 4.2 Hz, 1H, 7-H), 3.84–3.77 (m, 2H, 1-H, 2-H), 3.79 (s, 3H, MeO), 3.73–3.68 (m, 3H, 1-H, 3-H, 6-H), 2.25 (br s, 1H, OH), 1.05 (s, 3H, Me), 0.99 (s, 3H, Me), 0.92 (s, 9H, TBS), 0.89 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.08 (s, 3H, TBS), 0.03 (s, 3H, TBS), −0.01 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 159.5$ (PMP), 138.9 (Ph), 138.8 (Ph), 131.3 (Ph), 129.5 (Ph), 128.8 (Ph), 128.7 (Ph), 128.5 (Ph), 128.1 (Ph), 127.9 (Ph), 126.3 (Ph), 114.2 (PMP), 82.8 (5), 82.7 (2), 81.8 (6), 78.1 (3), 74.5 (PMB), 72.7 (Bn), 72.3 (Bn), 63.4 (7), 62.7 (1), 55.7 (MeO), 43.7 (4), 26.7 (TBS), 26.4 (TBS), 22.3 (Me), 20.3 (Me), 19.1 (TBS), 18.7 (TBS), −2.8 (TBS), −4.5 (TBS), −5.3 (TBS), −5.3 (TBS); HR MS: calcd for $C_{43}H_{68}O_7Si_2Na$ $[M+Na]^+$ 775.4401, found 775.4390.

(2*R*,3*R*,5*R*,6*S*)-2,6-Dibenzyloxy-3,7-bis(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4-dimethylheptanal (22): To a solution of oxalyl chloride (1.41 g, 11.1 mmol) in dichloromethane (40 mL) at −78 °C was added a solution of DMSO (1.45 g, 18.5 mmol) in dichloromethane (40 mL). The mixture was stirred for 15 min at −78 °C and then a solution of (2*S*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-3,7-bis(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4-dimethylheptanol (6.40 g, 8.49 mmol) in dichloromethane (80 mL) was added. After the reaction mixture had been stirred for 1 h, triethylamine (4.67 g, 46.1 mmol) was added. The reaction mixture was allowed to warm to room temperature and then saturated aqueous ammonium chloride was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford aldehyde **22** (6.29 g, 99%) as a colorless oil: $[\alpha]_D^{27} = -9.9$ (*c* 1.65, benzene); IR (neat): $\tilde{\nu} = 1730\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 9.70$ (d, $J =$ 3.3 Hz, 1H, 1-CHO), 7.32–7.20 (m, 12H, Ph), 6.86 (d, $J = 8.6$ Hz, 2H, Ph), 4.74 (d, $J = 11.6$ Hz, 1H, Bn), 4.68 (d, $J = 10.9$ Hz, 1H, Bn), 4.49 (d, $J =$ 10.9 Hz, 1H, Bn), 4.47 (d, $J = 11.6$ Hz, 1H, Bn), 4.45 (d, $J = 11.2$ Hz, 1H, Bn), 4.29 (d, $J = 11.2$ Hz, 1H, Bn), 4.27 (d, $J = 1.7$ Hz, 1H, 3-H), 4.02 (dd, $J = 11.6$, 2.0 Hz, 1H, 7-H), 4.00 (dd, $J = 3.3$, 1.7 Hz, 1H, 2-H), 3.84 (dd, $J = 11.6$, 5.0 Hz, 1H, 7-H), 3.79 (s, 3H, MeO), 3.74 (d, $J = 5.3$ Hz, 1H, 5-H), 3.65 (ddd, $J = 5.3$, 5.0, 2.0 Hz, 1H, 6-H), 1.02 (s, 3H, Me), 0.95 (s, 3H, Me), 0.93 (s, 9H, TBS), 0.88 (s, 9H, TBS), 0.07 (s, 3H, TBS), 0.07 (s, 3H, TBS), 0.04 (s, 3H, TBS), −0.03 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 202.8$ (1), 159.0 (PMP), 138.4 (Ph), 137.6 (Ph), 130.9 (Ph), 129.0 (Ph), 128.2 (Ph), 128.1 (Ph), 127.9 (Ph), 127.7 (Ph), 127.6 (Ph), 127.4 (Ph), 113.7 (PMP), 85.1 (2), 82.3 (5), 81.9 (6), 80.0 (3), 74.0 (PMB), 72.3 (Bn), 72.0 (Bn), 62.9 (7), 55.2 (MeO), 43.6 (4), 26.2 (TBS), 25.9 (TBS), 21.5 (Me), 19.8 (Me), 18.5 (TBS), 18.2 (TBS), −3.5 (TBS), −4.9 (TBS), −5.3 (TBS), −5.3 (TBS): HR MS: calcd for $C_{43}H_{66}O_7Si_2Na$ $[M+Na]^+$ 773.4245, found 773.4255.

(2*R*,3*S*,4*R*,6*R*,7*S*)-3,7-Dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanol and **(2*S*,3*S*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanol**: To a solution of methylmagnesium bromide in diethyl ether (3.0 M, 3.52 mL, 10.6 mmol) diluted with diethyl ether (38 mL) at −78 °C was added a solution of aldehyde **22** (3.97 g, 5.28 mmol) in diethyl ether (66 mL). The reaction mixture was stirred for 100 min at −78 °C, and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford a mixture of (2*R*,3*S*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanol and (2*S*,3*S*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanol (diastereomeric ratio 75/25, 4.01 g, 99%) as a colorless oil: IR (neat): $\tilde{\nu} = 3490\ cm^{-1}$; HR MS: calcd for $C_{44}H_{71}O_7Si_2$ $[M+H]^+$ 767.4738, found 767.4739; HR MS: calcd for $C_{44}H_{70}O_7Si_2Na$ $[M+Na]^+$ 789.4558, found 789.4538. **(2*R**,3*S*,4*R*,6*R*,7*S*)-3,7-Dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanol**: ^1H NMR ($CDCl_3$): $\delta = 7.25-6.97$ (m, 12H, Ph), 6.76 (d, $J = 8.2$ Hz, 2H, Ph), 4.62 (d, $J = 11.6$ Hz, 1H, Bn), 4.51 (d, $J = 10.9$ Hz, 1H, Bn), 4.41 (d, $J = 11.6$ Hz, 1H, Bn), 4.19 (d, $J = 11.6$ Hz, 1H, Bn), 4.19 (d, $J = 11.6$ Hz, 1H, Bn), 4.05 (d, $J = 10.9$ Hz, 1H, Bn), 4.05–3.96 (m, 1H, 3-H), 3.94 (br s, 1H, 6-H), 3.83 (dd, $J = 14.1$, 6.6 Hz, 1H, 8-H), 3.77 (dd, $J =$ 14.1, 6.1 Hz, 1H, 8-H), 3.69 (s, 3H, MeO), 3.58 (d, $J = 3.3$ Hz, 1H, 4-H), 3.58–3.45 (m, 2H, 2-H, 7-H), 3.27 (br s, 1H, OH), 1.09 (s, 3H, Me), 1.06 (d, $J = 5.0$ Hz, 3H, 1-Me), 0.98 (s, 3H, Me), 0.84 (s, 9H, TBS), 0.78 (s, 9H, TBS), 0.00 (s, 6H, TBS), −0.02 (s, 3H, TBS), −0.08 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 159.1$ (PMP), 138.4 (Ph), 138.0 (Ph), 129.0 (Ph), 128.5 (Ph), 128.4 (Ph), 128.2 (Ph), 128.1 (Ph), 128.1 (Ph), 127.9 (Ph), 127.7 (Ph), 113.7 (PMP), 82.2 (7), 81.1 (2), 80.9 (4), 79.7 (3), 73.9 (PMB), 73.1 (Bn), 72.2 (Bn), 68.8 (6), 61.8 (8), 55.2 (MeO), 43.6 (5), 26.2 (TBS), 25.9 (TBS), 22.2 (Me), 19.9 (1), 19.2 (Me), 18.7 (TBS), 18.2 (TBS), −3.5 (TBS), −3.9 (TBS), −4.6 (TBS), −4.8 (TBS).

(3*R*,4*R*,6*R*,7*S*)-3,7-Dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanone (3): To a solution of oxalyl chloride (934 mg, 7.35 mmol) in dichloromethane (17 mL) at −78 °C was added a solution of DMSO (970 mg, 12.4 mmol) in dichloromethane (18 mL). The mixture was stirred for 15 min at −78 °C and then a solution of mixture of (2*R*,3*S*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanol and (2*S*,3*S*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanol (diastereomeric ratio 75/25, 2.60 g, 3.39 mmol) in dichloromethane (6 mL) was added. After the reaction mixture had been stirred for 30 min at −45 °C, triethylamine (3.16 g, 31.2 mmol) was added. The reaction mixture was allowed to warm to room temperature, and then saturated aqueous ammonium chloride was added. The mixture was extracted with dichloromethane, the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford ketone **3** (2.53 g, 97%) as a white solid. First recrystallization of the ketone **3** thus obtained from hexane gave optically pure ketone **3**: m.p. 114 °C; $[\alpha]_D^{30} = +12.3$ (*c* 1.00, benzene); IR (KBr): 1710 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.37-6.89$ (m, 12H, Ph), 6.87 (d, $J = 8.9$ Hz, 2H, Ph), 4.74 (d, $J = 10.9$ Hz, 1H, Bn), 4.63 (d, $J =$ 10.9 Hz, 1H, Bn), 4.55 (d, $J = 10.9$ Hz, 1H, Bn), 4.42 (d, $J = 10.9$ Hz, 1H, Bn), 4.33 (d, $J = 2.3$ Hz, 1H, 3-H), 4.23 (d, $J = 11.6$ Hz, 1H, Bn), 4.18 (d, $J =$ 11.6 Hz, 1H, Bn), 4.10 (d, $J = 2.3$ Hz, 1H, 4-H), 4.09 (d, $J = 6.6$ Hz, 1H, 6-H), 4.05 (dd, $J = 11.5$, 2.0 Hz, 1H, 8-H), 3.84 (dd, $J = 11.5$, 4.0 Hz, 1H, 8-H), 3.79 (s, 3H, MeO), 3.55 (ddd, $J = 6.6$, 4.0, 2.0 Hz, 1H, 7-H), 2.24 (s, 3H, 1-Me), 1.00 (s, 3H, Me), 0.98 (s, 3H, Me), 0.95 (s, 9H, TBS), 0.90 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.09 (s, 3H, TBS), −0.05 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 212.5$ (2), 158.9 (PMP), 138.4 (Ph), 137.6 (Ph), 131.2 (Ph), 129.0 (Ph), 128.3 (Ph), 128.2 (Ph), 128.1 (Ph), 128.0 (Ph), 127.6 (Ph), 127.5 (Ph), 113.7 (PMP), 87.1 (3), 82.1 (6), 80.4 (7), 78.5 (4), 74.0 (PMB), 72.7 (Bn), 72.0 (Bn), 62.0 (8), 55.2 (MeO), 44.1 (5), 28.9 (1), 26.4 (TBS), 25.9 (TBS), 21.8 (Me), 18.7 (Me), 18.3 (TBS), 18.2 (TBS), −2.8 (TBS), −5.2 (TBS), −5.3 (TBS), −5.3 (TBS); HPLC (CHIRALCEL OD, *i*PrOH/hexane = 1/500, flow rate = 0.5 mL min^{-1}): $t_R = 15.6$ min (>99.5%), $t_R =$ 19.2 min (<0.5%); HR MS: calcd for $C_{44}H_{68}O_7Si_2Na$ $[M+Na]^+$ 787.4401, found 787.4390.

(2*S*,3*R*,5*R*,6*S*)-2,6-Dibenzyloxy-5-(*p*-methoxybenzyloxy)-4,4-dimethyl-1,3,7-heptanetriol: To a solution of (2*S*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-3,7-bis(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4-dimethylheptanol (500 mg, 0.664 mmol) in THF (9.8 mL) at room temperature was added TBAF (1.0 M, 3.32 mL, 3.32 mmol). The reaction mixture was stirred for 1 h at room temperature, and then hexane and phosphate buffer (pH = 7) were added. The mixture was extracted with ethyl acetate, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (2*S*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-5-(*p*-methoxybenzyloxy)-4,4-dimethyl-1,3,7-heptanetriol (318 mg, 91%) as a colorless oil: $[\alpha]_D^{24} = +0.1$ (*c* 1.90, benzene); IR (neat): $\tilde{\nu} = 3400\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 7.33-7.12$ (m, 12H, Ph), 6.77 (d, $J = 8.9$ Hz, 2H, Ph),

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4.70 (d, $J = 10.8$ Hz, 1H, Bn), 4.53 (d, $J = 11.4$ Hz, 1H, Bn), 4.50 (d, $J = 11.5$ Hz, 1H, Bn), 4.42 (d, $J = 11.4$ Hz, 1H, Bn), 4.39 (d, $J = 10.8$ Hz, 1H, Bn), 4.34 (d, $J = 11.5$ Hz, 1H, Bn), 3.80–3.72 (m, 5H, 1-H, 1-H, 6-H, 7-H, 7-H), 3.70 (s, 3H, MeO), 3.58 (d, 1H, $J = 2.3$ Hz, 5-H), 3.38 (d, 1H, $J = 7.3$ Hz, 3-H), 3.35 (ddd, $J = 7.3$, 5.8, 2.2 Hz, 1H, 2-H), 2.67 (br s, 1H, OH), 2.00 (br s, 1H, OH), 1.08 (s, 3H, Me), 0.97 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 159.4$ (PMP), 137.8 (Ph), 137.8 (Ph), 129.8 (Ph), 129.3 (Ph), 128.4 (Ph), 128.3 (Ph), 127.8 (Ph), 127.7 (Ph), 127.7 (Ph), 127.7 (Ph), 113.8 (PMP), 87.8 (5), 80.8 (2), 79.1 (6), 77.8 (3), 74.9 (PMB), 71.7 (Bn), 70.9 (Bn), 62.3 (7), 61.8 (1), 55.2 (MeO), 40.7 (4), 22.3 (Me), 21.3 (Me); HR MS: calcd for $C_{31}H_{41}O_7$ $[M+H]^+$ 525.2852, found 525.2855; HR MS: calcd for $C_{31}H_{40}O_7Na$ $[M+Na]^+$ 547.2672, found 547.2648.

(2*S*,3*R*,5*R*,6*S*)-1,2,6,7-Tetrabenzyloxy-5-(*p*-methoxybenzyloxy)-4,4-dimethyl-3-heptanol: To a suspension of sodium hydride (14.3 mg, 0.339 mmol) in THF (2.5 mL) at 0 °C was added a solution of (2*S*,3*R*,5*R*,6*S*)-2,6-dibenzyloxy-5-(*p*-methoxybenzyloxy)-4,4-dimethyl-1,3,-7-heptanetriol (150 mg, 0.274 mmol) in THF (3 mL). After the reaction mixture had been stirred for 15 min at 0 °C, a benzyl bromide solution (0.042 mL, 0.356 mmol) and DMF (0.55 mL) were added. The reaction mixture was stirred for 14 h at room temperature, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (2*S*,3*R*,5*R*,6*S*)-1,2,6,7-tetrabenzyloxy-5-(*p*-methoxybenzyloxy)-4,4-dimethyl-3-heptanol (174 mg, 87 %) as a colorless oil: $[\alpha]_D^{23} = -5.7$ (*c* 1.26, benzene); IR (neat): $\tilde{\nu} = 3490$ cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.28-7.17$ (m, 20H, Ph), 7.09 (d, $J = 8.6$ Hz, 2H, Ph), 6.74 (d, $J = 8.6$ Hz, 2H, Ph), 4.81 (d, $J = 11.6$ Hz, 1H, Bn), 4.80 (d, $J = 11.9$ Hz, 1H, Bn), 4.79 (d, $J = 10.4$ Hz, 1H, Bn), 4.70 (d, $J = 11.9$ Hz, 1H, Bn), 4.64 (s, 2H, Bn), 4.64 (s, 2H, Bn), 4.50 (d, $J = 11.6$ Hz, 1H, Bn), 4.43 (d, $J = 10.4$ Hz, 1H, Bn), 4.03 (dd, $J = 11.2$, 1.3 Hz, 1H, 7-H), 3.96 (ddd, $J = 5.3$, 1.3, 1.0 Hz, 1H, 6-H), 3.95 (dd, $J = 10.6$, 2.3 Hz, 1H, 1-H), 3.88 (d, $J = 11.2$, 5.3 Hz, 1H, 7-H), 3.86 (s, 3H, MeO), 3.85 (d, $J = 1.0$ Hz, 1H, 5-H), 3.79 (dd, $J = 10.6$, 5.3 Hz, 1H, 1-H), 3.76 (br d, $J = 7.3$ Hz, 1H, 3-H), 3.67 (ddd, $J = 7.3$, 5.3, 2.3 Hz, 1H, 2-H), 3.52 (br s 1H, OH), 1.07 (s, 3H, Me), 1.04 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 159.3$ (PMP), 138.7 (Ph), 138.4 (Ph), 129.9 (Ph), 129.8 (Ph), 129.8 (Ph), 128.3 (Ph), 128.3 (Ph), 128.3 (Ph), 128.3 (Ph), 128.2 (Ph), 128.2 (Ph), 128.2 (Ph), 127.9 (Ph), 127.7 (Ph), 127.7 (Ph), 127.6 (Ph), 127.5 (Ph), 127.4 (Ph), 113.8 (PMP), 87.7 (5), 80.2 (6), 79.7 (2), 77.1 (3), 74.0 (PMB), 73.4 (Bn), 73.4 (Bn), 72.3 (7), 72.1 (Bn), 71.5 (Bn), 71.4 (1), 55.2 (MeO), 40.8 (4), 22.1 (Me), 22.0 (Me); HR MS: calcd for $C_{45}H_{53}O_7$ $[M+H]^+$ 705.3791, found 705.3799; HR MS: calcd for $C_{45}H_{52}O_7Na$ $[M+Na]^+$ 727.3611, found 727.3578.

(2*S*,3*R*,5*R*,6*S*)-1,2,6,7-Tetrabenzyloxy-3,5-(*p*-methoxybenzylidenedioxy)-4,4-dimethylheptane: To a suspension of (2*S*,3*R*,5*R*,6*S*)-1,2,6,7-tetrabenzyloxy-5-(*p*-methoxybenzyloxy)-4,4-dimethyl-3-heptanol (130 mg, 0.184 mmol) and MS 4 Å (30 mg) in dichloromethane (4.2 mL) at 0 °C was added DDQ (83.5 mg, 0.368 mmol). The reaction mixture was stirred for 1 h at 0 °C and then it was allowed to warm to room temperature. After filtration of the mixture through a short pad of Celite with ethyl acetate, saturated aqueous sodium hydrogencarbonate was added to the filtrate. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (2*S*,3*R*,5*R*,6*S*)-1,2,6,7-tetrabenzyloxy-3,5-(*p*-methoxybenzylidenedioxy)-4,4-dimethylheptane (102.3 mg, 79 %) as a colorless oil: $[\alpha]_D^{23} = +4.2$ (*c* 1.37, benzene); IR (neat): $\tilde{\nu} = 1100$, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.31-7.13$ (m, 22H, Ph), 6.74 (d, $J = 8.6$ Hz, 2H, Ph) 5.55 (s, 1H, CHPMP), 4.72 (d, $J = 11.5$ Hz, 1H, Bn), 4.71 (d, $J = 11.2$ Hz, 1H, Bn), 4.50 (d, $J = 12.2$ Hz, 1H, Bn), 4.48 (d, $J = 11.5$ Hz, 1H, Bn), 4.43 (d, $J = 12.2$ Hz, 1H, Bn), 4.41 (d, $J = 12.2$ Hz, 1H, Bn), 4.39 (d, $J = 11.2$ Hz, 1H, Bn), 4.31 (d, $J = 12.2$ Hz, 1H, Bn), 3.96 (ddd, $J = 8.3$, 5.5, 3.0 Hz, 1H, 2-H or 6-H), 3.89 (d, $J = 6.6$ Hz, 1H, 5-H or 3-H), 3.79 (dd, $J = 10.2$, 2.0 Hz, 1H, 7-H or 1-H), 3.74 (dd, $J = 10.6$, 3.0 Hz, 1H, 1-H or 7-H), 3.72 (ddd, $J = 6.6$, 5.0, 2.0 Hz, 1H, 6-H or 2-H), 3.69 (s, 3H, MeO), 3.65 (dd, $J = 10.2$, 5.0 Hz, 1H, 7-H or 1-H), 3.52 (d, $J = 8.3$ Hz, 1H, 3-H or 5-H), 3.49 (dd, $J = 10.6$, 5.5 Hz, 1H, 1-H or 7-H), 1.11 (s, 3H, Me), 1.03 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 159.7$ (PMP), 138.4 (Ph), 138.3 (Ph), 131.2 (Ph), 128.3 (Ph), 128.3 (Ph), 128.3 (Ph), 128.0 (Ph), 128.0 (Ph), 127.8 (Ph), 127.8 (Ph), 127.6 (Ph), 127.6 (Ph), 127.5 (Ph), 127.5 (Ph), 127.4 (Ph), 127.4 (Ph), 127.3 (Ph), 127.3 (Ph), 113.4 (PMP), 97.6 (CHPMP), 79.6 (5 or 3), 79.0 (3 or 5), 78.2 (6 or 2), 77.4 (2 or 6), 73.4 (Bn), 73.3 (Bn), 71.8 (Bn), 71.8 (Bn), 71.1 (1 or 7), 70.4 (7 or 1), 55.2 (MeO), 37.2 (4), 21.8 (Me), 21.1 (Me); HR MS: calcd for $C_{45}H_{50}O_7Na$ $[M+Na]^+$ 725.3454, found 725.3483.

(2*S*,3*R*,5*R*,6*S*)-1,2,6,7-Tetrabenzyloxy-4,4-dimethyl-3,5-heptanediol (**21**): To a solution of (2*S*,3*R*,5*R*,6*S*)-1,2,6,7-tetrabenzyloxy-3,5-(*p*-methoxybenzylidenedioxy)-4,4-dimethylheptane (102 mg, 0.146 mmol) in THF (1.5 mL) at 0 °C was added hydrochloric acid (1 M, 1.5 mL). The reaction mixture was stirred for 6 h at room temperature, and then hexane and saturated aqueous sodium hydrogencarbonate were added at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diol **21** (57.6 mg, 53 %) as a colorless oil: $[\alpha]_D^{23} = -1.3$ (*c* 1.02, benzene); IR (neat): $\tilde{\nu} = 3680$ cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.28-7.15$ (m, 20H, Ph), 4.58 (d, $J = 11.4$ Hz, 1H, Bn), 4.58 (d, $J = 11.4$ Hz, 1H, Bn), 4.48 (s, 2H, Bn), 4.48 (s, 2H, Bn), 4.41 (d, $J = 11.4$ Hz, 1H, Bn), 4.41 (d, $J = 11.4$ Hz, 1H, Bn), 3.80 (dd, $J = 12.5$, 4.6 Hz, 1H, 1-H), 3.80 (dd, $J = 12.5$, 4.6 Hz, 1H, 7-H), 3.74 (d, $J = 1.8$ Hz, 1H, 3-H), 3.74 (d, $J = 1.8$ Hz, 1H, 5-H), 3.67 (dd, $J = 12.5$, 4.6 Hz, 2H, 1-H), 3.67 (dd, $J = 12.5$, 4.6 Hz, 2H, 7-H), 3.65 (td, $J = 4.6$, 1.8 Hz, 1H, 2-H), 3.65 (td, $J = 4.6$, 1.8 Hz, 1H, 6-H), 0.95 (s, 3H, Me), 0.95 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 138.2$ (Ph), 138.2 (Ph), 137.9 (Ph), 137.9 (Ph), 128.4 (Ph), 128.4 (Ph), 128.3 (Ph), 128.3 (Ph), 127.8 (Ph), 127.8 (Ph), 127.7 (Ph), 127.7 (Ph), 127.7 (Ph), 127.7 (Ph), 127.5 (Ph), 127.5 (Ph), 79.8 (3), 79.8 (5), 79.1 (2), 79.1 (6), 73.5 (Bn), 73.5 (Bn), 71.5 (Bn), 71.5 (Bn), 70.8 (1), 70.8 (7), 40.1 (4), 21.9 (Me), 21.9 (Me); HR MS: calcd for $C_{37}H_{45}O_6$ $[M+H]^+$ 585.3216, found 585.3201.

(3*R*,4*R*,6*R*,7*S*)-3,7-Dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-8-hydroxy-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanone: To a solution of ketone **3** (377 mg, 0.493 mmol) in THF (47 mL) at −10 °C was added hydrochloric acid (0.8 M, 31 mL). The reaction mixture was stirred for 6 h at room temperature and then hexane and saturated aqueous sodium hydrogencarbonate were added at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (3*R*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-8-hydroxy-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanone (320 mg, 100 %) as a colorless oil: $[\alpha]_D^{25} = +10.0$ (*c* 1.08, benzene); IR (neat): $\tilde{\nu} = 1710$ cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.33-7.19$ (m, 12H, Ph), 6.87 (d, $J = 8.9$ Hz, 2H, Ph), 4.72 (d, $J = 10.6$ Hz, 1H, Bn), 4.57 (d, $J = 10.6$ Hz, 1H, Bn), 4.54 (d, $J = 11.6$ Hz, 1H, Bn), 4.48 (d, $J = 11.6$ Hz, 1H, Bn), 4.37 (d, $J = 11.2$ Hz, 1H, Bn), 4.30 (d, $J = 2.6$ Hz, 1H, 4-H), 4.26 (d, $J = 11.2$ Hz, 1H, Bn), 4.03 (d, $J = 2.6$ Hz, 1H, 3-H), 3.95 (d, $J = 5.9$ Hz, 1H, 6-H), 3.89 (dd, $J = 11.9$, 2.1 Hz, 1H, 8-H), 3.78 (dd, $J = 11.9$, 2.1 Hz, 1H, 8-H), 3.78 (s, 3H, MeO), 3.59 (dt, $J = 5.9$, 2.1 Hz, 1H, 7-H), 2.25 (s, 3H, 1-Me), 1.02 (s, 3H, Me), 1.00 (s, 3H, Me), 0.93 (s, 9H, TBS), 0.06 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 211.8$ (2), 159.1 (PMP), 137.8 (Ph), 137.2 (Ph), 130.6 (Ph), 129.1 (Ph), 128.5 (Ph), 128.2 (Ph), 128.2 (Ph), 128.2 (Ph), 127.9 (Ph), 127.9 (Ph), 113.7 (PMP), 87.0 (3), 81.9 (6), 80.6 (7), 78.0 (4), 74.3 (PMB), 72.6 (Bn), 71.5 (Bn), 61.2 (8), 55.2 (MeO), 44.2 (5), 28.7 (1), 26.4 (TBS), 21.7 (Me), 18.7 (Me), 18.6 (TBS), −2.7 (TBS), −4.9 (TBS); HR MS: calcd for $C_{38}H_{54}O_7SiNa$ $[M+Na]^+$ 673.3537, found 673.3537.

(2*R*,3*R*,5*R*,6*R*)-2,6-Dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-4,4-dimethyl-7-oxooctanal (**23**): To a solution of oxalyl chloride (77.8 mg, 0.613 mmol) in dichloromethane (1 mL) at −78 °C was added a solution of DMSO (95.8 mg, 1.23 mmol) in dichloromethane (1 mL). The mixture was stirred for 15 min at −78 °C and then a solution of (3*R*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-8-hydroxy-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanone (114 mg, 0.175 mmol) in dichloromethane (2 mL) was added. After the reaction mixture had been stirred for 30 min at −78 °C, triethylamine (248 mg, 2.45 mmol) was added. The reaction mixture was allowed to warm to room temperature, and then saturated aqueous ammonium chloride was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketoaldehyde **23** (102 mg, 90 %) as a colorless oil: $[\alpha]_D^{25} = +3.5$ (*c* 1.22, benzene); IR (neat): $\tilde{\nu} = 1730$, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 9.72$ (d, $J = 1.7$ Hz, 1H, 1-CHO), 7.33–7.19 (m, 12H, Ph), 6.87 (d, $J = 8.9$ Hz, 2H, Ph), 4.67 (d, $J = 10.6$ Hz, 1H, Bn),

4.64 (d, $J=11.6$ Hz, 1H, Bn), 4.52 (d, $J=10.6$ Hz, 1H, Bn), 4.48 (d, $J=11.5$ Hz, 1H, Bn), 4.41 (d, $J=11.5$ Hz, 1H, Bn), 4.39 (d, $J=11.6$ Hz, 1H, Bn), 4.30 (d, $J=2.3$ Hz, 1H, 5-H), 4.06 (dd, $J=3.6$, 1.7 Hz, 1H, 2-H), 4.02 (d, $J=2.3$ Hz, 1H, 6-H), 3.99 (d, $J=3.6$ Hz, 1H, 3-H), 3.84 (s, 3H, MeO), 2.27 (s, 3H, 8-Me), 1.05 (s, 3H, Me), 1.01 (s, 3H, Me), 0.98 (s, 9H, TBS), 0.13 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=211.0$ (7), 201.3 (1), 159.1 (PMP), 137.2 (Ph), 137.1 (Ph), 130.2 (Ph), 129.2 (Ph), 128.4 (Ph), 128.3 (Ph), 128.3 (Ph), 128.1 (Ph), 128.1 (Ph), 127.9 (Ph), 113.7 (PMP), 87.4 (6), 84.1 (2), 84.1 (3), 77.6 (5), 73.6 (PMB), 73.0 (Bn), 72.4 (Bn), 55.2 (MeO), 44.1 (4), 28.7 (8), 26.3 (TBS), 21.2 (Me), 18.6 (Me), 18.6 (TBS), −2.8 (TBS), −4.9 (TBS); HR MS: calcd for $C_{38}H_{52}O_7SiNa$ $[M+Na]^+$ 671.3380, found 671.3392.

(3*R*,4*R*,6*R*,7*R*)-3,7-Dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-8,8-diethylthio-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanone (**24**): To a suspension of silver perchlorate (3.2 mg, 15.4 μmol) in toluene (1.5 mL) at 0 °C was added chlorotrimethylsilane (1.7 mg, 15.4 μmol) in toluene (0.5 mL). The reaction mixture was stirred for 1 h at room temperature and then a solution of ketoaldehyde **23** (50.0 mg, 77.1 μmol) and ethylthiotrimethylsilane (41.4 mg, 0.308 mmol) in toluene (2 mL) was added at −78 °C. After the reaction mixture had been stirred for 17 h at −78 °C, saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford dithioacetal **24** (40.7 mg, 70 %) as a colorless oil: $[\alpha]_D^{27}=+4.2$ (*c* 1.37, benzene); IR (neat): $\tilde{\nu}=1700$ cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=$ 7.45 – 7.41 (m, 2H, Ph), 7.27 – 7.23 (m, 8H, Ph), 7.12 – 7.08 (m, 2H, Ph), 6.88 – 6.85 (m, 2H, Ph), 5.30 (d, $J=10.6$ Hz, 1H, Bn), 4.69 (d, $J=11.4$ Hz, 1H, Bn), 4.54 (d, $J=11.4$ Hz, 1H, Bn), 4.53 (d, $J=10.6$ Hz, 1H, Bn), 4.27 (d, $J=2.6$ Hz, 1H, 3-H), 4.22 (d, $J=8.9$ Hz, 1H, 6-H), 4.21 (d, $J=2.6$ Hz, 1H, 4-H), 4.16 (d, $J=11.7$ Hz, 1H, Bn), 4.14 (s, 1H, 8-H), 4.13 (d, $J=11.7$ Hz, 1H, Bn), 3.98 (d, $J=8.9$ Hz, 1H, 7-H), 3.81 (s, 3H, MeO), 2.76 (q, $J=$ 7.4 Hz, 2H, SEt), 2.55 (q, $J=7.4$ Hz, 2H, SEt), 2.20 (s, 3H, 1-Me), 1.33 (t, $J=7.4$ Hz, 3H, SEt), 1.17 (t, $J=7.4$ Hz, 3H, SEt), 1.03 (s, 3H, Me), 0.97 (s, 3H, Me), 0.87 (s, 9H, TBS), −0.10 (s, 3H, TBS), −0.17 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=213.7$ (2), 159.0 (PMP), 137.8 (Ph), 137.6 (Ph), 128.8 (Ph), 128.4 (Ph), 128.4 (Ph), 128.3 (Ph), 128.3 (Ph), 128.0 (Ph), 127.7 (Ph), 127.5 (Ph), 113.7 (PMP), 86.4 (3), 85.3 (7), 82.1 (6), 78.5 (4), 74.8 (PMB), 74.7 (Bn), 72.7 (Bn), 55.7 (8), 55.2 (MeO), 45.0 (5), 29.0 (1), 27.6 (SEt), 26.4 (TBS), 25.6 (SEt), 22.1 (Me), 18.7 (TBS), 18.4 (Me), 14.7 (SEt), 14.5 (SEt), −2.9 (TBS), −5.6 (TBS); HR MS: calcd for $C_{42}H_{62}O_6SiNa$ $[M+Na]^+$ 777.3655, found 777.3652.

(3*R*,4*R*,6*R*,7*R*)-3,7-dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-8,8-diethylthio-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-(triethylsiloxy)octene (**25**): To a solution of hexamethyldisilazane (61.1 mg, 0.379 mmol) in THF (1.6 mL) at 0 °C was added *n*-butyllithium in hexane (1.54 M, 0.23 mL, 0.355 mmol). The reaction mixture was stirred for 30 min at 0 °C and then a solution of dithioacetal **24** (52.0 mg, 68.9 μmol) in THF (1.6 mL) was added at −78 °C. After the mixture had been stirred for 1 h at −78 °C, chlorotrimethylsilane (0.13 mL, 1.02 mmol) was added. The reaction mixture was stirred for 1 h at room temperature and then triethylamine was added. After evaporation of the solvent, the crude product was filtered through a short pad of deactivated silica gel to afford enol silyl ether **25** (51.0 mg, 89 %) as a colorless oil: $[\alpha]_D^{26}=+6.0$ (*c* 0.613, benzene); IR (neat): $\tilde{\nu}=2960$, 1610, 1510, 1460, 1250, 1090, 1030, 840 cm^{-1}; ^{1}H NMR (C_6D_6): $\delta=$ 7.56 (d, 2H, $J=6.9$ Hz, Ph), 7.32 (d, $J=8.6$ Hz, 2H, Ph), 7.26 – 7.08 (m, 8H, Ph), 6.80 (d, $J=8.6$ Hz, 2H, Ph), 5.40 (d, $J=10.9$ Hz, 1H, Bn), 4.88 (d, $J=$ 10.9 Hz, 1H, Bn), 4.78 (d, $J=10.9$ Hz, 1H, Bn), 4.76 (s, 1H, 1-H), 4.69 (d, $J=10.9$ Hz, 1H, Bn), 4.61 (d, $J=10.6$ Hz, 1H, Bn), 4.49 (d, $J=5.6$ Hz, 1H, 6-H), 4.47 (s, 1H, 8-H), 4.46 (d, $J=3.3$ Hz, 1H, 4-H), 4.45 (s, 1H, 1-H), 4.25 (d, $J=10.6$ Hz, 1H, Bn), 4.24 (d, $J=5.6$ Hz, 1H, 7-H), 4.17 (d, $J=3.3$ Hz, 1H, 3-H), 3.31 (s, 3H, MeO), 2.80 (q, $J=7.6$ Hz, 2H, SEt), 2.48 (q, $J=$ 7.3 Hz, 2H, SEt), 1.48 (s, 3H, Me), 1.33 (s, 3H, Me), 1.19 (t, $J=7.6$ Hz, 3H, SEt), 1.07 (s, 9H, TBS), 1.06 (t, $J=7.3$ Hz, 3H, SEt), 0.28 (s, 9H, TMS), −0.67 (s, 3H, TBS), −0.74 (s, 3H, TBS); ^{13}C NMR (C_6D_6): $\delta=159.6$ (2), 156.2 (PMP), 138.9 (Ph), 138.7 (Ph), 128.9 (Ph), 128.9 (Ph), 128.8 (Ph), 128.8 (Ph), 128.5 (Ph), 128.5 (Ph), 128.3 (Ph), 128.3 (Ph), 114.1 (PMP), 94.8 (1), 85.7 (7), 83.3 (3), 83.0 (6), 77.7 (4), 75.2 (PMB), 74.8 (Bn), 71.3 (Bn), 55.8 (8), 54.8 (MeO), 45.5 (5), 27.3 (SEt), 26.9 (TBS), 25.6 (SEt), 22.5 (Me), 19.4 (Me), 19.2 (TBS), 14.8 (SEt), 14.5 (SEt), 0.5 (TMS), −2.5 (TBS), −4.3 (TBS); HR MS: calcd for $C_{45}H_{70}O_6S_2Si_2Na$ $[M+Na]^+$ 849.4050, found 849.4030.

(3*R*,4*R*,6*R*,1′*R*)-3-benzyloxy-6-1′-benzyloxy-2′-ethylthioethyl-4-(*tert*-butyldimethylsiloxy)-2,5,5-trimethyl-2-oxanol (**26**): To a solution of triphenylmethyl perchlorate (21.0 mg, 61.3 μmol) in dichloromethane (1 mL) at −55 °C was added a solution of enol silyl ether **25** (50.6 mg, 61.2 μmol) in dichloromethane (0.5 mL). The reaction mixture was stirred for 3 h at −45 °C, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford hemiketal **26** (17.0 mg, 48 %) as a colorless oil: $[\alpha]_D^{26}=-12.0$ (*c* 0.59, benzene); IR (neat): $\tilde{\nu}=$ 3410 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.38-7.27$ (m, 10H, Ph), 4.97 (d, $J=$ 11.2 Hz, 1H, Bn), 4.64 (d, $J=11.2$ Hz, 1H, Bn), 4.52 (d, $J=11.2$ Hz, 1H, Bn), 4.48 (d, $J=11.2$ Hz, 1H, Bn), 3.95 (d, $J=5.3$ Hz, 1H, 6-H), 3.88 (d, $J=$ 3.3 Hz, 1H, 4-H), 3.81 (dt, $J=5.3$, 4.3 Hz, 1H, 1′-H), 3.38 (d, $J=3.3$ Hz, 1H, 3-H), 2.91 (d, $J=4.3$ Hz, 2H, 2′-H), 2.58 (q, $J=7.3$ Hz, 2H, SEt), 1.44 (s, 3H, Me), 1.23 (t, $J=7.3$ Hz, 3H, SEt), 1.07 (s, 3H, Me), 0.97 (s, 3H, Me), 0.95 (s, 9H, TBS), 0.17 (s, 3H, TBS), 0.12 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=139.3$ (Ph), 138.0 (Ph), 128.3 (Ph), 128.1 (Ph), 128.1 (Ph), 127.6 (Ph), 127.3 (Ph), 127.2 (Ph), 98.5 (2), 81.3 (3), 78.4 (1′), 75.9 (6), 75.5 (Bn), 75.1 (4), 71.5 (Bn), 38.8 (5), 33.3 (2′), 26.9 (SEt), 26.9 (Me), 26.1 (TBS), 24.7 (Me), 18.2 (TBS), 16.0 (Me), 15.0 (SEt), −3.0 (TBS), −5.1 (TBS); HR MS: calcd for $C_{32}H_{50}O_5SSiNa$ $[M+Na]^+$ 597.3046, found 597.3059.

(3*R*,4*R*,6*R*,7*S*)-3,7-Dibenzyloxy-1-bromo-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanone (**27**):

1) To a solution of hexamethyldisilazane (15.2 mL, 72.0 mmol) in THF (24 mL) at −78 °C was added *n*-butyllithium in hexane (1.6 M, 41.0 mL, 65.6 mmol). The reaction mixture was stirred for 40 min at 0 °C, and then a solution of ketone **3** (4.99 g, 6.52 mmol) in THF (54 mL) was added at −78 °C. After the mixture had been stirred for 1 h at −78 °C, chlorotrimethylsilane (12.4 mL, 97.7 mmol) in THF (24 mL) was added. The reaction mixture was stirred for 30 min at −78 °C and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water, saturated aqueous sodium hydrogencarbonate and brine, and dried over sodium sulfate. Filtration of the mixture and evaporation of the solvent afforded crude (3*R*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-trimethylsiloxyoctene.

2) To a solution of the above crude (3*R*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-4,8-bis(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-trimethylsiloxyoctene in THF (94 mL) at 0 °C was added NBS (1.41 g, 7.92 mmol). The reaction mixture was stirred for 30 min at 0 °C and then phosphate buffer (pH = 7) was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford ketone **27** (5.48 g, 100 % from ketone **3**) as a colorless solid: m.p. 127 °C; $[\alpha]_D^{30}=+5.0$ (*c* 1.07, benzene); IR (KBr): 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.68-7.04$ (m, 12H, Ph), 6.86 (d, $J=8.6$ Hz, 2H, Ph), 4.73 (d, $J=11.0$ Hz, 1H, Bn), 4.61 (d, $J=11.0$ Hz, 1H, Bn), 4.55 (d, $J=11.0$ Hz, 1H, Bn), 4.40 (d, $J=2.3$ Hz, 1H, 3-H), 4.36 (d, $J=11.0$ Hz, 1H, Bn), 4.37 (d, $J=$ 11.6 Hz, 1H, 1-H), 4.33 (d, $J=11.6$ Hz, 1H, 1-H), 4.33 (d, $J=2.3$ Hz, 1H, 4-H), 4.18 (d, $J=11.5$ Hz, 1H, Bn), 4.14 (d, $J=11.5$ Hz, 1H, Bn), 4.09 (d, $J=7.9$ Hz, 1H, 6-H), 4.07 (dd, $J=11.2$, 2.0 Hz, 1H, 8-H), 3.84 (dd, $J=11.2$, 3.0 Hz, 1H, 8-H), 3.79 (s, 3H, MeO), 3.53 (ddd, $J=7.9$, 3.0, 2.0 Hz, 1H, 7-H), 1.01 (s, 3H, Me), 0.97 (s, 9H, TBS), 0.93 (s, 3H, Me), 0.89 (s, 9H, TBS), 0.12 (s, 3H, TBS), 0.11 (s, 3H, TBS), −0.05 (s, 3H, TBS), −0.09 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta=203.8$ (2), 159.0 (PMP), 138.0 (Ph), 136.9 (Ph), 131.0 (Ph), 129.0 (Ph), 128.4 (Ph), 128.3 (Ph), 128.2 (Ph), 127.9 (Ph), 127.7 (Ph), 113.7 (PMP), 86.2 (3), 81.9 (6), 79.5 (7), 78.6 (4), 74.1 (PMB), 73.2 (Bn), 71.9 (Bn), 61.0 (8), 55.2 (MeO), 44.1 (5), 36.3 (1), 26.4 (TBS), 25.9 (TBS), 21.9 (Me), 18.7 (Me), 18.2 (TBS), 18.2 (TBS), −2.8 (TBS), −5.2 (TBS), −5.3 (TBS), −5.3 (TBS); HR MS: calcd for $C_{44}H_{67}BrO_7SiNa$ $[M+Na]^+$ 865.3506, found 865.3500.

(3*R*,4*R*,6*R*,7*S*)-3,7-Dibenzyloxy-1-bromo-4-(*tert*-butyldimethylsiloxy)-8-hydroxy-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanone: To a solution of ketone **27** (3.26 g, 3.86 mmol) in THF (110 mL) at −10 °C was added a mixture of hydrochloric acid (1 M, 228 mL) and THF (220 mL). The reaction mixture was stirred for 8 h at room temperature, and then hexane and saturated aqueous sodium hydrogencarbonate were added at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed

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with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford (3*R*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-1-bromo-4-(*tert*-butyldimethylsiloxy)-8-hydroxy-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanone (2.79 g, 99%) as a colorless oil: $[\alpha]_D^{28} = +0.1$ (*c* 1.87, benzene); IR (neat): $\tilde{\nu} = 3470$, 1730 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.30-7.12$ (m, 12H, Ph), 6.84 (d, $J = 8.6$ Hz, 2H, Ph), 4.63 (d, $J = 10.9$ Hz, 1H, Bn), 4.53 (d, $J = 10.9$ Hz, 1H, Bn), 4.52 (d, $J = 11.2$ Hz, 1H, Bn), 4.41 (d, $J = 11.2$ Hz, 1H, Bn), 4.29 (d, $J = 2.6$ Hz, 1H, 3-H), 4.28 (d, $J = 10.6$ Hz, 1H, Bn), 4.27 (d, $J = 7.9$ Hz, 1H, 1-H), 4.26 (d, $J = 7.9$ Hz, 1H, 1-H), 4.25 (d, $J = 2.6$ Hz, 1H, 4-H), 4.24 (d, $J = 10.6$ Hz, 1H, Bn), 4.19 (d, $J = 6.9$ Hz, 1H, 6-H), 3.87–3.84 (m, 2H, 8-H, 8-H), 3.76 (s, 3H, MeO), 3.54 (ddd, $J = 6.9$, 3.6, 3.3 Hz, 1H, 7-H), 1.95 (br s, 1H, OH), 0.96 (s, 3H, Me), 0.93 (s, 3H, Me), 0.89 (s, 9H, TBS), 0.01 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 203.9$ (2), 159.6 (PMP), 138.0 (Ph), 137.1 (Ph), 130.9 (Ph), 129.7 (Ph), 129.0 (Ph), 128.9 (Ph), 128.9 (Ph), 128.8 (Ph), 128.6 (Ph), 128.5 (Ph), 114.3 (PMP), 86.0 (3), 81.6 (6), 81.1 (7), 78.8 (4), 75.3 (PMB), 73.4 (Bn), 72.0 (Bn), 61.2 (8), 55.7 (MeO), 44.7 (5), 35.9 (1), 26.8 (TBS), 22.3 (Me), 19.1 (Me), 19.0 (TBS), −2.3 (TBS), −4.4 (TBS); HR MS: calcd for $C_{38}H_{53}BrO_7SiNa$ $[M+Na]^+$ 751.2642/753.2630, found 751.2660/753.2643.

(2*R*,3*R*,5*R*,6*R*)-2,6-Dibenzyloxy-8-bromo-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-4,4-dimethyl-7-oxooctanal (28): To a solution of oxalyl chloride (2.84 g, 22.4 mmol) in dichloromethane (45 mL) at −78 °C was added a solution of DMSO (2.90 g, 37.1 mmol) in dichloromethane (45 mL). The mixture was stirred for 15 min at −78 °C and then a solution of (3*R*,4*R*,6*R*,7*S*)-3,7-dibenzyloxy-1-bromo-4-(*tert*-butyldimethylsiloxy)-8-hydroxy-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-2-octanone (7.89 g, 10.8 mmol) in dichloromethane (90 mL) was added. After the reaction mixture had been stirred for 30 min at −78 °C, triethylamine (9.41 g, 93.0 mmol) was added. The reaction mixture was allowed to warm to 0 °C, and then saturated aqueous ammonium chloride was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford ketoaldehyde **28** (7.39 g, 94%) as a colorless oil: $[\alpha]_D^{27} = +0.3$ (*c* 1.01, benzene); IR (neat): $\tilde{\nu} = 1730$, 1610 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 9.67$ (d, $J = 2.0$ Hz, 1H, 1-CHO), 7.78–7.36 (m, 12H, Ph), 6.86 (d, $J = 8.9$ Hz, 2H, Ph), 4.58 (d, $J = 11.6$ Hz, 1H, Bn), 4.58 (d, $J = 10.9$ Hz, 1H, Bn), 4.47 (d, $J = 10.9$ Hz, 1H, Bn), 4.39 (d, $J = 11.5$ Hz, 1H, Bn), 4.35 (d, $J = 11.5$ Hz, 1H, Bn), 4.33 (d, $J = 11.6$ Hz, 1H, Bn), 4.30 (d, $J = 2.6$ Hz, 1H, 6-H), 4.28 (d, $J = 14.9$ Hz, 1H, 8-H), 4.23 (d, $J = 2.6$ Hz, 1H, 5-H), 4.18 (d, $J = 14.9$ Hz, 1H, 8-H), 4.01 (dd, $J = 4.3$, 2.0 Hz, 1H, 2-H), 3.88 (d, $J = 4.3$ Hz, 1H, 3-H), 3.80 (s, 3H, MeO), 0.97 (s, 3H, Me), 0.94 (s, 3H, Me), 0.93 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.06 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 202.8$ (7), 201.3 (1), 159.2 (PMP), 136.7 (Ph), 136.7 (Ph), 129.9 (Ph), 129.3 (Ph), 128.5 (Ph), 128.5 (Ph), 128.3 (Ph), 128.2 (Ph), 128.2 (Ph), 126.9 (Ph), 113.8 (PMP), 85.6 (2), 83.9 (6), 83.4 (3), 78.0 (5), 73.8 (PMB), 73.3 (Bn), 72.5 (Bn), 55.3 (MeO), 44.1 (4), 34.9 (8), 26.4 (TBS), 21.4 (Me), 18.6 (Me), 18.6 (TBS), −2.8 (TBS), −4.9 (TBS); HR MS: calcd for $C_{38}H_{51}BrO_7SiNa$ $[M+Na]^+$ 749.2485/751.2465, found 749.2518/751.2471.

(2*R*,3*R*,5*R*,6*S*,7*S*)-2,6-Dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-hydroxy-5-(*p*-methoxybenzyloxy)-4,4-dimethylcyclooctanone (29*α*) and **(2*R*,3*R*,5*R*,6*S*,7*R*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-hydroxy-5-(*p*-methoxybenzyloxy)-4,4-dimethylcyclooctanone (29*β*)**: To a solution of ketoaldehyde **28** (126.1 mg, 0.173 mmol) in THF (5 mL) at 0 °C was added samarium(II) iodide in THF (0.1 M, 9.0 mL, 0.90 mmol). The reaction mixture was stirred for 30 min at 0 °C and then aqueous phosphate buffer (pH = 7) was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford aldol **29*α*** (62.8 mg, 56%) and aldol **29*β*** (34.3 mg, 31%) as colorless oils. **Aldol 29*α***: $[\alpha]_D^{25} = +25.5$ (*c* 2.68, benzene); IR (neat): $\tilde{\nu} = 3450$, 1700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.29-6.81$ (m, 14H), 4.92–2.39 (m, 15H), 1.23–1.10 (m, 17H), 0.97–(−0.05) (m, 6H); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{38}H_{52}O_7SiNa$ $[M+Na]^+$ 671.3380, found 671.3401. **Aldol 29*β***: $[\alpha]_D^{27} = +7.4$ (*c* 1.00, benzene); IR (neat): $\tilde{\nu} =$ 3550, 1700 cm^{-1}; 1H NMR ($CDCl_3$): $\delta = 7.40-6.82$ (14H, m), 4.85–2.68 (15H, m), 1.26–0.95 (17H, m), 0.97–(−0.05) (6H, m); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{38}H_{52}O_7SiNa$ $[M+Na]^+$ 671.3380, found 671.3383.

(4*S*,5*R*,7*R*,8*R*)-4,8-Dibenzyloxy-7-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-6,6-dimethyl-2-cycloocten-1-one (1): To a solution of the mixture of aldols **29** (***α*/*β*** = 65/35, 575 mg, 0.888 mmol) in dichloromethane (30 mL) at 0 °C were added solutions of diisopropylethylamine (574 mg, 4.44 mmol) in dichloromethane (2 mL) and of methanesulfonyl chloride (348 mg, 3.04 mmol) in dichloromethane (2 mL). The reaction mixture was stirred for 10 min at room temperature, and then a solution of DBU (1.35 g, 8.87 mmol) in dichloromethane (2 mL) was added at 0 °C. After the reaction mixture had been stirred for 10 min at 0 °C, phosphate buffer (pH = 7) was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford enone **1** (464 mg, 83%) as a colorless oil: $[\alpha]_D^{27} = +87.8$ (*c* 1.38, benzene); IR (neat): $\tilde{\nu} = 1670$ cm^{-1}; ^1H NMR ($CDCl_3$): **conformer A** $\delta = 7.30-7.24$ (m, 10H, Ph), 7.16 (d, $J = 8.3$ Hz, 2H, Ph), 6.83 (d, $J = 8.9$ Hz, 2H, Ph), 6.46 (d, $J = 11.9$ Hz, 1H, 3-H), 5.88 (d, $J = 11.9$ Hz, 1H, 8-H), 5.42 (s, 1H), 4.74–3.97 (m, 7H), 3.79 (s, 3H, MeO), 3.86–3.40 (m, 2H), 1.20–0.73 (m, 15H, Me, Me, TBS), 0.06 (s, 6H, TBS); **conformer B** $\delta = 7.30-7.24$ (m, 10H, Ph), 7.16 (d, $J = 8.3$ Hz, 2H, Ph), 6.83 (d, $J = 8.9$ Hz, 2H, Ph), 6.25 (d, $J = 13.9$ Hz, 1H, 3-H), 6.01 (d, $J = 13.9$ Hz, 1H, 8-H), 5.06 (d, $J = 11.2$ Hz, 1H), 4.74–3.97 (m, 7H), 3.79 (s, 3H, MeO), 3.86–3.40 (m, 2H), 1.20–0.73 (m, 15H, Me, Me, TBS), 0.06 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{38}H_{50}O_6SiNa$ $[M+Na]^+$ 653.3274, found 653.3284.

(1*R*,3*R*,4*S*,5*R*,7*R*,8*R*)-4,8-Dibenzyloxy-7-(*tert*-butyldimethylsiloxy)-6,6-dimethyl-9-oxabicyclo[3.3.1]nonane-1,3-diol (30*α*): To a solution of aldol **29*α*** (24.3 mg, 37.5 μmol) in dichloromethane (5 mL) at 0 °C were added water (1 mL) and DDQ (12.6 mg, 55.5 μmol). The reaction mixture was stirred for 1 h at room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford hemiacetal **30*α*** (14.3 mg, 72%) as a colorless oil: $[\alpha]_D^{25} = +5.6$ (*c* 1.35, benzene); IR (neat): $\tilde{\nu} = 3450$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.45-7.36$ (m, 10H, Ph), 4.97 (d, $J = 11.2$ Hz, 1H, Bn), 4.74 (d, $J = 11.2$ Hz, 1H, Bn), 4.71 (d, $J = 11.5$ Hz, 1H, Bn), 4.60 (ddd, $J = 5.0$, 4.6, 4.3 Hz, 1H, 3-H), 4.58 (d, 1H, $J = 11.5$ Hz, Bn), 4.12 (dd, $J = 4.3$, 2.6 Hz, 1H, 2-H), 3.76 (dd, $J = 4.3$, 1.0 Hz, 1H, 11-H), 3.70 (dd, $J = 2.6$, 1.0 Hz, 1H, 1-H), 3.57 (d, $J = 4.3$ Hz, 1H, 10-H), 2.81 (dd, $J = 14.9$, 4.6 Hz, 1H, 8-H), 1.87 (dd, $J = 14.9$, 5.0 Hz, 1H, 8-H), 1.21 (s, 3H, 17-Me), 1.02 (s, 3H, 16-Me), 0.86 (s, 9H, TBS), 0.02 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 138.2$ (Ph), 137.9 (Ph), 128.7 (Ph), 128.4 (Ph), 128.1 (Ph), 128.0 (Ph), 127.9 (Ph), 127.6 (Ph), 97.2 (9), 82.4 (1), 77.6 (10), 77.5 (11), 74.2 (2), 74.1 (Bn), 71.0 (Bn), 64.6 (3), 38.8 (15), 37.2 (8), 27.5 (17), 26.2 (TBS), 22.6 (16), 18.6 (TBS), −4.1 (TBS), −4.8 (TBS); HR MS: calcd for $C_{30}H_{44}O_6Si_2Na$ $[M+Na]^+$ 551.2805, found 551.2829.

(1*R*,3*S*,4*S*,5*R*,7*R*,8*R*)-4,8-Dibenzyloxy-7-(*tert*-butyldimethylsiloxy)-6,6-dimethyl-9-oxabicyclo[3.3.1]nonane-1,3-diol (30*β*): To a solution of aldol **29*β*** (8.9 mg, 13.7 μmol) in dichloromethane (1 mL) at 0 °C were added water (0.4 mL) and DDQ (4.6 mg, 20.3 μmol). The reaction mixture was stirred for 1 h at room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford hemiacetal **30*β*** (4.0 mg, 55%) as a colorless oil: $[\alpha]_D^{27} = -8.3$ (*c* 0.78, benzene); IR (neat): $\tilde{\nu} = 3430$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.37-7.27$ (m, 10H, Ph), 4.88 (d, $J = 11.2$ Hz, 1H, Bn), 4.71 (d, $J = 11.2$ Hz, 1H, Bn), 4.71 (d, $J = 11.9$ Hz, 1H, Bn), 4.62 (d, $J = 11.9$ Hz, 1H, Bn), 4.19 (dd, $J = 7.7$, 3.2 Hz, 1H, 2-H), 4.15 (ddd, $J = 11.6$, 7.7, 6.9 Hz, 1H, 3-H), 3.73 (dd, $J = 4.0$, 1.1 Hz, 1H, 11-H), 3.62 (dd, $J = 3.2$, 1.1 Hz, 1H, 1-H), 3.43 (d, $J = 4.0$ Hz, 1H, 10-H), 2.74 (dd, $J = 14.2$, 11.6 Hz, 1H, 8-H), 1.99 (dd, $J = 14.2$, 6.9 Hz, 1H, 8-H), 1.15 (s, 3H, 17-Me), 1.10 (s, 3H, 16-Me), 0.89 (s, 9H, TBS), 0.02 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 138.7$ (Ph), 138.1 (Ph), 128.6 (Ph), 128.5 (Ph), 128.2 (Ph), 127.7 (Ph), 127.6 (Ph), 127.5 (Ph), 98.0 (9), 84.4 (1), 80.2 (2), 78.2 (11), 78.0 (10), 73.8 (Bn), 72.1 (Bn), 70.2 (3), 39.1 (15), 36.7 (8), 26.9 (17), 26.3

(TBS), 23.3 (16), 18.7 (TBS), −3.8 (TBS), −4.8 (TBS); HR MS: calcd for $C_{30}H_{44}O_6Si_2Na$ $[M+Na]^+$ 551.2805, found 551.2798.

(1*R*,4*S*,5*R*,7*R*,8*R*)-4,8-Dibenzyloxy-7-(*tert*-butyldimethylsiloxy)-6,6-dimethyl-9-oxabicyclo[3.3.1]non-2-enol (**31**): To a solution of enone **1** (24.1 mg, 38.3 μmol) in dichloromethane (1 mL) at 0 °C were added water (0.1 mL) and DDQ (12.3 mg, 54.2 μmol). The reaction mixture was stirred for 1 h at room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford hemiacetal **31** (17.6 mg, 90 %) as a colorless oil: $[\alpha]_D^{29} = +146.7$ (*c* 0.61, benzene); IR (neat): $\tilde{\nu} = 3380\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.32-7.14$ (m, 10H, Ph), 6.17 (dd, $J = 10.2$, 1.6 Hz, 1H, 8-H), 5.94 (dd, $J = 10.2$, 3.3 Hz, 1H, 3-H), 4.99 (d, $J = 10.9$ Hz, 1H, Bn), 4.61 (d, $J = 10.9$ Hz, 1H, Bn), 4.61 (d, $J = 12.2$ Hz, 1H, Bn), 4.51 (d, $J = 12.2$ Hz, 1H, Bn), 4.10 (br dd, $J = 3.3$, 1.6 Hz, 1H, 2-H), 3.96 (br d, $J = 1.0$ Hz, 1H, 1-H), 3.69 (d, $J = 4.0$ Hz, 1H, 10-H), 3.62 (dd, $J = 4.0$, 1.0 Hz, 1H, 11-H), 2.78 (br s, 1H, OH), 1.14 (s, 3H, 17-Me), 0.91 (s, 3H, 16-Me), 0.89 (s, 9H, TBS), 0.05 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 138.3$ (Ph), 138.2 (Ph), 134.1 (2), 128.7 (Ph), 128.4 (Ph), 128.1 (Ph), 127.9 (Ph), 127.7 (Ph), 127.6 (Ph), 127.6 (3), 94.2 (1), 83.1 (5), 78.3 (7), 77.3 (8), 74.0 (Bn), 70.1 (Bn), 67.9 (4), 39.8 (6), 26.9 (17), 26.0 (TBS), 22.9 (16), 18.6 (TBS), −3.8 (TBS), −5.2 (TBS); EI MS: calcd for $C_{26}H_{33}O_5Si$ $[M^+ - t\mathrm{Bu}]$ 453, found 453; HR MS: calcd for $C_{30}H_{42}O_5SiNa$ $[M+Na]^+$ 533.2699, found 533.2678.

(2*R*,4*R*,5*R*,7*R*,8*S*)-4,8-Dibenzyloxy-2-bromo-5,9-bis(*tert*-butyldimethylsiloxy)-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone and **(2*S*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5,9-bis(*tert*-butyldimethylsiloxy)-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone**: To a solution of hexamethyldisilazane (1.45 mL, 6.93 mmol) in THF (44 mL) at −78 °C was added *n*-butyllithium in hexane (1.6 M, 4.0 mL, 6.62 mmol). The reaction mixture was stirred for 40 min at 0 °C and then a solution of ketone **27** (5.28 g, 6.30 mmol) in THF (45 mL) was added at −78 °C. After the reaction mixture had been stirred for 1 h at −78 °C, iodomethane (11.7 mL, 189 mmol) and HMPA (10.9 mL, 62.7 mmol) were added. The reaction mixture was stirred for 1.5 h at −78 °C, and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford a mixture of (2*R*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5,9-bis(*tert*-butyldimethylsiloxy)-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone and (2*S*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5,9-bis(*tert*-butyldimethylsiloxy)-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone (diastereomeric ratio 80/20, 5.35 g, 100 %) as a colorless solid: IR (KBr): 1710 cm^{-1}; HR MS: calcd for $C_{45}H_{69}BrO_7Si_2Na$ $[M+Na]^+$ 879.3663/881.3654, found 879.3665/881.3622. **(2*R**,4*R*,5*R*,7*R*,8*S*)-4,8-Dibenzyloxy-2-bromo-5,9-bis(*tert*-butyldimethylsilyloxy)-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone**: ^1H NMR ($CDCl_3$): $\delta = 7.27-7.11$ (m, 12H, Ph), 6.81 (d, $J = 8.9$ Hz, 2H, Ph), 4.71 (q, $J = 6.6$ Hz, 1H, 2-H), 4.63 (d, $J = 11.2$ Hz, 1H, Bn), 4.62 (d, $J = 11.2$ Hz, 1H, Bn), 4.60 (d, $J = 2.3$ Hz, 1H, 4-H), 4.48 (d, $J = 11.2$ Hz, 1H, Bn), 4.41 (d, $J = 11.2$ Hz, 1H, Bn), 4.33 (d, $J = 11.2$ Hz, Bn), 4.28 (d, $J = 2.3$ Hz, 1H, 5-H), 4.15 (d, $J = 11.2$ Hz, 1H, Bn), 3.96 (dd, $J = 11.2$, 2.0 Hz, 1H, 9-H), 3.81 (d, $J = 5.0$ Hz, 1H, 7-H), 3.76 (dd, $J = 11.2$, 4.9 Hz, 1H, 9-H), 3.57 (ddd, $J = 5.0$, 4.9, 2.0 Hz, 1H, 8-H), 1.57 (d, $J = 6.6$ Hz, 3H, 1-Me), 0.99 (s, 3H, Me), 0.92 (s, 3H, Me), 0.86 (s, 9H, TBS), 0.84 (s, 9H, TBS), 0.01 (s, 6H, TBS), 0.00 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 204.3$ (3), 159.0 (PMP), 138.5 (Ph), 137.7 (Ph), 131.0 (Ph), 129.1 (Ph), 128.4 (Ph), 128.3 (Ph), 128.1 (Ph), 128.1 (Ph), 127.8 (Ph), 127.5 (Ph), 113.7 (PMP), 85.8 (4), 82.4 (8), 81.9 (7), 77.5 (5), 73.9 (PMB), 72.8 (Bn), 72.3 (Bn), 63.5 (9), 55.3 (MeO), 46.1 (2), 44.5 (6), 26.3 (TBS), 25.9 (TBS), 21.6 (Me), 20.8 (1), 19.1 (Me), 18.6 (TBS), 18.2 (TBS), −3.1 (TBS), −4.7 (TBS), −5.2 (TBS), −5.2 (TBS).

(2*R*,4*R*,5*R*,7*R*,8*S*)-4,8-Dibenzyloxy-2-bromo-5-(*tert*-butyldimethylsiloxy)-9-hydroxy-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone and **(2*S*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5-(*tert*-butyldimethylsiloxy)-9-hydroxy-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone**: To a solution of a mixture of (2*R*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5,9-bis(*tert*-butyldimethylsiloxy)-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone and (2*S*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5,9-bis(*tert*-butyldimethylsiloxy)-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone (diastereomeric ratio 80/20, 4.33 g, 5.01 mmol) in THF (438 mL) at 0 °C was added hydrochloric acid (1 M, 303 mL, 303 mmol). The reaction mixture was stirred for 1 h at 0 °C and then it was allowed to warm to room temperature. After the reaction mixture had been stirred for 13 h, it was diluted with hexane at room temperature and neutralized with aqueous sodium hydrogencarbonate (1 M, 303 mL, 303 mmol) at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed with saturated aqueous sodium hydrogencarbonate and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford a mixture of (2*R*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5-(*tert*-butyldimethylsiloxy)-9-hydroxy-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone and (2*S*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5-(*tert*-butyldimethylsiloxy)-9-hydroxy-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone (diastereomeric ratio 80/20, 3.19 g, 83 %) as a colorless oil: IR (neat): $\tilde{\nu} = 3430$, 1720 cm^{-1}; HR MS: calcd for $C_{39}H_{55}BrO_7SiNa$ $[M+Na]^+$ 765.2798/767.2787, found 765.2817/767.2769. **(2*R**,4*R*,5*R*,7*R*,8*S*)-4,8-Dibenzyloxy-2-bromo-5-(*tert*-butyldimethylsiloxy)-9-hydroxy-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone**: ^1H NMR ($CDCl_3$): $\delta = 7.37-7.24$ (m, 12H, Ph), 6.87 (d, $J = 8.6$ Hz, 2H, Ph), 4.82 (d, $J = 2.7$ Hz, 1H, 4-H), 4.77 (d, $J = 11.2$ Hz, 1H, Bn), 4.65 (q, $J = 6.6$ Hz, 1H, 2-H), 4.55 (d, $J = 10.3$ Hz, 1H, Bn), 4.53 (d, $J = 10.3$ Hz, 1H, Bn), 4.50 (s, 2H, Bn), 4.38 (d, $J = 2.7$ Hz, 1H, 5-H), 4.32 (d, $J = 11.2$ Hz, 1H, Bn), 3.90–3.72 (m, 6H, 7-H, 9-H, 9-H, MeO), 3.64–3.60 (m, 1H, 8-H), 1.62 (d, $J = 6.6$ Hz, 3H, 1-Me), 1.11–0.82 (m, 15H, Me, Me, TBS), 0.04 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 202.5$ (3), 159.2 (PMP), 137.8 (Ph), 137.7 (Ph), 129.3 (Ph), 129.1 (Ph), 128.4 (Ph), 128.2 (Ph), 127.7 (Ph), 127.7 (Ph), 127.6 (Ph), 127.5 (Ph), 113.8 (PMP), 85.0 (4), 81.8 (7), 80.9 (8), 77.5 (5), 74.5 (PMB), 72.4 (Bn), 71.3 (Bn), 61.3 (9), 55.1 (MeO), 45.4 (2), 44.8 (6), 26.2 (TBS), 20.9 (Me), 19.7 (1), 19.2 (Me), 18.4 (TBS), −3.3 (TBS), −4.5 (TBS).

(2*R*,3*R*,5*R*,6*R*,8*R*)-2,6-Dibenzyloxy-8-bromo-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-4,4-dimethyl-7-oxononanal (**32a**) and **(2*R*,3*R*,5*R*,6*R*,8*S*)-2,6-dibenzyloxy-8-bromo-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-4,4-dimethyl-7-oxononanal** (**32b**): To a solution of oxalyl chloride (0.85 mL, 9.74 mmol) in dichloromethane (40 mL) at −78 °C was added a solution of DMSO (1.74 mL, 24.5 mmol) in dichloromethane (20 mL). The reaction mixture was stirred for 15 min at −78 °C and then a solution of (2*R*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5-(*tert*-butyldimethylsiloxy)-9-hydroxy-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone and (2*S*,4*R*,5*R*,7*R*,8*S*)-4,8-dibenzyloxy-2-bromo-5-(*tert*-butyldimethylsiloxy)-9-hydroxy-7-(*p*-methoxybenzyloxy)-6,6-dimethyl-3-nonanone (diastereomeric ratio 80/20, 3.60 g, 4.85 mmol) in dichloromethane (40 mL) was added. After the reaction mixture had been stirred for 1 h, triethylamine (5.5 mL, 39.5 mmol) was added. The reaction mixture was allowed to warm to room temperature and saturated aqueous ammonium chloride was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford a mixture of ketoaldehydes **32** (diastereomeric ratio 80/20, 3.43 g, 95 %) as a colorless oil: IR (neat): $\tilde{\nu} = 1730\ cm^{-1}$; HR MS: calcd for $C_{39}H_{53}BrO_7SiNa$ $[M+Na]^+$ 763.2642/765.2630, found 763.2668/765.2645. **(2*R*,3*R*,5*R*,6*R*,8*R**)-2,6-Dibenzyloxy-8-bromo-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-4,4-dimethyl-7-oxononanal**: ^1H NMR ($CDCl_3$): $\delta = 9.65$ (d, $J = 2.3$ Hz, 1H, 1-CHO), 7.33–7.11 (m, 12H, Ph), 6.84 (d, $J = 8.6$ Hz, 2H, Ph), 4.74 (d, $J = 2.7$ Hz, 1H, 6-H), 4.67 (d, $J = 10.9$ Hz, 1H, Bn), 4.58 (q, $J = 6.6$ Hz, 1H, 8-H), 4.53 (d, $J = 11.9$ Hz, 1H, Bn), 4.53 (d, $J = 11.2$ Hz, 1H, Bn), 4.42 (d, $J = 10.9$ Hz, 1H, Bn), 4.31 (d, $J = 11.9$ Hz, 1H, Bn), 4.30 (d, $J = 11.2$ Hz, 1H, Bn), 4.20 (d, $J = 2.7$ Hz, 1H, 5-H), 4.02 (dd, $J = 2.6$, 2.3 Hz, 1H, 2-H), 3.77 (s, 3H, MeO), 3.72 (d, $J = 2.6$ Hz, 1H, 3-H), 1.60 (d, $J = 6.6$ Hz, 2H, 9-Me), 0.99–0.84 (m, 15H, Me, Me, TBS), 0.04 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 202.1$ (7), 201.4 (1), 159.3 (PMP), 137.7 (Ph), 137.2 (Ph), 129.5 (Ph), 129.3 (Ph), 128.4 (Ph), 128.2 (Ph), 128.1 (Ph), 127.8 (Ph), 127.8 (Ph), 127.7 (Ph), 113.8 (PMP), 84.7 (3), 84.5 (6), 84.1 (2), 77.0 (5), 74.0 (PMB), 73.5 (Bn), 72.6 (Bn), 55.2 (MeO), 45.3 (8), 44.8 (4), 26.2 (TBS), 21.0 (Me), 19.5 (9), 19.2 (Me), 18.4 (TBS), −3.1 (TBS), −4.4 (TBS).

(2*R*,3*R*,5*R*,6*S*,7*R*,8*R*)-2,6-Dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-hydroxy-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone and **(2*R*,3*R*,5*R*,6*S*,7*S*,8*R*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-hydroxy-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone**: To a solution of ketoaldehydes **32** (diastereomeric ratio 80/20, 1.40 g, 1.89 mmol) in THF

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(25 mL) at −78 °C was added samarium(II) iodide in THF (0.1M, 53.0 mL, 5.30 mmol). The reaction mixture was stirred for 20 min at −78 °C and then saturated aqueous ammonium chloride was added. The mixture was filtered through a short pad of silica gel and then the filtrate was extracted with diethyl ether. The organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford a mixture of (2*R*,3*S*,4*S*,5*R*,7*S*)-4-benzyloxy-7-(*tert*-butyldimethylsiloxy)-3-hydroxy-5-(*p*-methoxybenzyloxy)-2,6,6-trimethylcyclooctanone and (2*R*,3*R*,4*S*,5*R*,7*S*)-4-benzyloxy-7-(*tert*-butyldimethylsiloxy)-3-hydroxy-5-(*p*-methoxybenzyloxy)-2,6,6-trimethylcyclooctanone (77 mg, 7%) as a colorless oil and a mixture of (2*R*,3*R*,5*R*,6*S*,7*S*,8*R*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-hydroxy-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone and (2*R*,3*R*,5*R*,6*S*,7*R*,8*R*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-hydroxy-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone (875 mg, 70%) as a colorless oil: IR (neat): $\tilde{\nu}$ = 3530, 1700 cm^{-1}. **(2*R*,3*R*,5*R*,6*S*,7*S*,8*R*)-2,6-Dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-hydroxy-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone**: ^{1}H NMR ($CDCl_3$): δ = 7.38–7.28 (m, 10H, Ph), 7.22 (d, J = 8.6 Hz, 2H, Ph), 6.90 (d, J = 8.6 Hz, 2H, Ph), 4.97–3.60 (m, 15H), 1.30–0.74 (m, 18H), 0.09–0.00 (m, 6H); ^{13}C NMR ($CDCl_3$): very broadened spectra.

(2*R*,3*R*,5*R*,6*R*,7*S*,8*R*)-7-Acetoxy-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone (33α) and **(2*R*,3*R*,5*R*,6*R*,7*R*,8*R*)-7-acetoxy-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone (33β)**: To a solution of a mixture of (2*R*,3*R*,5*R*,6*S*,7*S*,8*R*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-hydroxy-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone and (2*R*,3*R*,5*R*,6*S*,7*R*,8*R*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-hydroxy-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone (1.36 g, 2.05 mmol) in pyridine (29 mL) at 0 °C were added acetic anhydride (5.80 mL, 61.5 mmol) and DMAP (27.1 mg, 0.222 mmol). After the reaction mixture had been stirred for 1.5 h at room temperature, phosphate buffer (pH = 7) was added at 0 °C. The mixture was extracted with ethyl acetate, and the organic layer was washed with saturated aqueous copper(II) sulfate, saturated aqueous sodium hydrogencarbonate, water, and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford a mixture of ketones **33** (α/β = 83/17, 1.26 g, 87%) as a colorless oil. **Ketone 33α**: IR (neat): $\tilde{\nu}$ = 1740, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.34–7.26 (m, 10H, Ph), 7.19 (d, J = 8.6 Hz, 2H, Ph), 6.87 (d, J = 8.6 Hz, 2H, Ph), 5.68 (dd, J = 2.8, 0.9 Hz, 1H, 3-H), 4.83 (d, J = 11.6 Hz, 1H, Bn), 4.66 (d, J = 10.9 Hz, 1H, Bn), 4.63 (d, J = 3.3 Hz, 1H, 10-H), 4.61 (d, J = 10.9 Hz, 1H, Bn), 4.45 (d, J = 10.9 Hz, 1H, Bn) 4.41 (d, J = 10.9 Hz, 1H, Bn), 4.39 (d, J = 3.3 Hz, 1H, 11-H), 4.18 (d, J = 11.6 Hz, 1H, Bn), 4.08 (dq, J = 6.6, 2.8 Hz, 1H, 8-H), 3.81 (s, 3H, MeO), 3.76 (dd, J = 1.2, 0.9 Hz, 1H, 2-H), 3.53 (d, J = 1.2 Hz, 1H, 1-H), 2.05 (s, 3H, Ac), 1.14 (d, J = 6.6 Hz, 3H, Me), 0.98–0.64 (br m, 15H, Me, Me, TBS), −0.04 (s, 3H, TBS), −0.06 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{41}H_{56}O_8SiNa$ $[M+Na]^+$ 727.3642, found 727.3611. **Ketone 33β**: IR (neat): $\tilde{\nu}$ = 1740, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.42–7.08 (br m, 12H, Ph), 6.86 (d, J = 8.6 Hz, 2H, Ph), 4.84–4.09 (br m, 10H), 3.83 (s, 3H, MeO), 3.76–3.56 (br m, 2H), 2.04 (s, 3H, Ac), 1.15 (d, J = 6.6 Hz, 3H, Me), 1.05–0.77 (br m, 15H, Me, Me, TBS), 0.06 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{41}H_{56}O_8SiNa$ $[M+Na]^+$ 727.3642, found 727.3715.

(4*S*,5*R*,7*R*,8*R*)-4,8-Dibenzyloxy-7-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-2,6,6-trimethyl-2-cycloocten-1-one (2): To a solution of mixture of ketones **33** (α/β = 83/17, 1.29 g, 1.83 mmol) in benzene (18 mL) at room temperature was added a solution of DBU (8.2 mL, 54.9 mmol) in benzene (8 mL). The reaction mixture was stirred for 1.5 h at 60 °C and then phosphate buffer (pH = 7) was added at room temperature. The mixture was extracted with ethyl acetate, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford enone **2** (1.07 g, 91%) as a colorless oil: $[\alpha]_D^{29}$ = +34.0 (*c* 1.61, benzene); IR (neat): $\tilde{\nu}$ = 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.39–7.16 (m, 12H, Ph), 6.85 (d, J = 8.7 Hz, 2H, Ph), 6.26 (br s, 1H, 3-H), 5.40 (br s, 1H, 10-H), 4.67–4.29 (m, 3H), 4.57 (d, J = 11.9 Hz, 1H, Bn), 4.43 (d, J = 11.9 Hz, 1H, Bn), 4.10 (br s, 1H), 4.02 (br d, J = 11.4 Hz, 1H), 3.90 (br s, 1H), 3.82 (s, 3H, MeO), 3.40 (br s, 1H), 1.91 (s, 3H, Me), 1.07 (s, 3H, Me), 1.02 (s, 3H, Me), 0.92 (s, 9H, TBS), 0.10 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{39}H_{52}O_6Si$ $[M^+]$ 644.3533, found 644.3535.

(1*R*,2*R*,3*R*,5*R*,6*R*,7*S*,8*R*)-7-Acetoxy-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-4,4,8-trimethyl-9-oxabicyclo[3.3.1]nonanol (34α): To a solution of ketone **33α** (38.4 mg, 54.5 μmol) in dichloromethane (8 mL) at 0 °C were added water (1.6 mL) and DDQ (16.0 mg, 70.5 μmol). The reaction mixture was stirred for 1 h at room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford hemiacetal **34α** (20.5 mg, 62%) as a colorless oil: $[\alpha]_D^{26}$ = +28.2 (*c* 1.72, benzene); IR (neat): $\tilde{\nu}$ = 3450, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.35–7.26 (m, 10H, Ph), 5.67 (dd, J = 3.6, 3.2 Hz, 1H, 3-H), 4.99 (d, J = 11.2 Hz, 1H, Bn), 4.77 (d, J = 11.2 Hz, 1H, Bn), 4.75 (d, J = 11.2 Hz, 1H, Bn), 4.45 (dd, J = 3.6, 3.3 Hz, 1H, 2-H), 4.39 (d, J = 11.2 Hz, 1H, Bn), 3.81 (dd, J = 4.3, 1.3 Hz, 1H, 11-H), 3.61 (dd, J = 3.3, 1.3 Hz, 1H, 1-H), 3.57 (d, J = 4.3 Hz, 1H, 10-H), 3.15 (dq, J = 7.3, 3.2 Hz, 1H, 8-H), 2.23 (s, 3H, Ac), 1.22 (s, 3H, 17-Me), 1.20 (d, J = 7.3 Hz, 3H, 19-Me), 1.04 (s, 3H, 16-Me), 0.89 (s, 9H, TBS), 0.04 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): δ = 171.8 (Ac), 138.0 (Ph), 138.0 (Ph), 128.8 (Ph), 128.3 (Ph), 128.2 (Ph), 128.1 (Ph), 127.7 (Ph), 127.7 (Ph), 97.6 (9), 82.4 (1), 78.8 (10), 78.3 (11), 74.8 (2), 74.3 (Bn), 71.0 (Bn), 70.7 (3), 38.8 (15), 34.4 (8), 26.8 (17), 26.1 (TBS), 22.4 (16), 21.2 (Ac), 18.5 (TBS), 12.6 (19), −4.3 (TBS), −4.6 (TBS); HR MS: calcd for $C_{33}H_{48}O_7SiNa$ $[M+Na]^+$ 607.3067, found 607.3090.

(1*R*,2*R*,3*R*,5*R*,6*R*,7*R*,8*R*)-7-Acetoxy-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-4,4,8-trimethyl-9-oxabicyclo[3.3.1]nonanol (34β): To a solution of ketone **33β** (12.0 mg, 17.0 μmol) in dichloromethane (2.5 mL) at 0 °C were added water (0.5 mL) and DDQ (5.0 mg, 22.1 μmol). The reaction mixture was stirred for 1 h at room temperature, and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford hemiacetal **34β** (5.3 mg, 51%) as a colorless oil: $[\alpha]_D^{26}$ = −27.2 (*c* 0.74, benzene); IR (neat): $\tilde{\nu}$ = 3430, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.39–7.27 (m, 10H, Ph), 5.27 (dd, J = 9.2, 8.3 Hz, 1H, 3-H), 4.84 (d, J = 11.2 Hz, 1H, Bn), 4.75 (d, J = 11.6 Hz, 1H, Bn), 4.73 (dd, J = 9.2, 3.0 Hz, 1H, 2-H), 4.72 (d, J = 11.2 Hz, 1H, Bn), 4.61 (d, J = 11.6 Hz, 1H, Bn), 3.72 (dd, J = 4.3, 1.3 Hz, 1H, 11-H), 3.68 (d, J = 4.3 Hz, 1H, 10-H), 3.56 (dd, J = 3.0, 1.3 Hz, 1H, 1-H), 2.83 (dq, J = 8.3, 7.9 Hz, 1H, 8-H), 2.03 (s, 3H, Ac), 1.22 (d, J = 7.9 Hz, 3H, 19-Me), 1.13 (s, 3H, 17-Me), 1.11 (s, 3H, 16-Me), 0.97 (s, 9H, TBS), 0.08 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): δ = 170.5 (Ac), 138.9 (Ph), 138.0 (Ph), 128.8 (Ph), 128.3 (Ph), 128.2 (Ph), 127.8 (Ph), 127.5 (Ph), 127.2 (Ph), 100.4 (9), 83.2 (1), 81.2 (10), 77.9 (11), 77.2 (3), 74.4 (2), 74.4 (Bn), 73.2 (Bn), 43.7 (8), 38.5 (15), 27.1 (17), 26.6 (TBS), 22.2 (16), 20.9 (Ac), 18.8 (TBS), 9.4 (19), −2.9 (TBS), −5.0 (TBS); HR MS: calcd for $C_{33}H_{48}O_7SiNa$ $[M+Na]^+$ 607.3067, found 607.3075.

(1*R*,4*S*,5*R*,7*R*,8*R*)-4,8-Dibenzyloxy-7-(*tert*-butyldimethylsiloxy)-2,6,6-trimethyl-9-oxabicyclo[3.3.1]non-2-enol (35): To a solution of enone **2** (28.5 mg, 44.2 μmol) in dichloromethane (6.5 mL) at 0 °C were added water (1.3 mL) and DDQ (13.0 mg, 57.3 μmol). The reaction mixture was stirred for 1 h at room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford hemiacetal **35** (15.8 mg, 65%) as a colorless oil: $[\alpha]_D^{26}$ = +96.1 (*c* 1.04, benzene); IR (neat): $\tilde{\nu}$ = 3350 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.57–7.39 (m, 10H, Ph), 5.74 (d, J = 3.0 Hz, 1H, 3-H), 5.05 (d, J = 11.2 Hz, 1H, Bn), 4.84 (d, J = 11.2 Hz, 1H, Bn), 4.76 (d, J = 11.9 Hz, 1H, Bn), 4.66 (d, J = 11.9 Hz, 1H, Bn), 4.11 (dd, J = 3.0, 1.7 Hz, 1H, 2-H), 3.93 (dd, J = 1.7, 0.9 Hz, 1H, 1-H), 4.80 (d, J = 3.6 Hz, 1H, 10-H), 4.78 (dd, J = 3.6, 0.9 Hz, 1H, 11-H), 2.13 (s, 3H, 19-Me), 1.35 (s, 3H, 17-Me), 1.10 (s, 3H, 16-Me), 0.88 (s, 9H, TBS), 0.06 (s, 3H, TBS, 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): δ = 140.9 (8), 138.5 (Ph), 138.1 (Ph), 128.9 (Ph), 128.3 (Ph), 128.2 (Ph), 127.9 (Ph), 127.7 (Ph), 127.6 (Ph), 123.2 (3), 95.9 (9), 83.2 (1), 79.6 (10), 77.4 (11), 74.1 (Bn), 69.9 (Bn), 69.2 (2), 39.7 (15), 39.7 (TBS), 27.1 (17), 26.0 (TBS), 22.9 (16), 19.6 (19), −3.6 (TBS), −5.2 (TBS); HR MS: calcd for $C_{31}H_{44}O_5SiNa$ $[M+Na]^+$ 547.2856, found 547.2852.

Ethyl 4-bromo-4-pentenoate:[29] To a solution of diisopropylamine (21.0 mL, 150 mmol) in THF (50 mL) at 0 °C was added a solution of *n*-butyllithium in *n*-hexane (1.47 M, 102 mL, 150 mmol). The reaction mixture was stirred for 30 min at 0 °C and then it was added to a suspension of ethyl acetate (14.7 mL, 150 mmol) and copper(I) iodide (57.2 g, 300 mmol) in THF (150 mL) at −110 °C. After the reaction mixture was allowed to warm to −30 °C, a solution of 1,2-dibromopropene (7.76 mL, 75.0 mmol) in THF (35 mL) was added. The reaction mixture was stirred for 1 h at −30 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. The mixture was filtered and concentrated by evaporation of the solvent to afford crude ethyl 4-bromo-4-pentenoate as a colorless oil: b.p. 110 °C/33 mmHg; IR (neat): $\tilde{\nu}$ = 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 5.59 (s, 1H, 5-H), 5.38 (s, 1H, 5-H), 4.09 (q, J = 7.1 Hz, 2H, OEt), 2.71 (t, J = 7.6 Hz, 2H, 3-H, 3-H), 2.52 (t, J = 7.6 Hz, 2H, 2-H, 2-H), 1.21 (t, J = 7.1 Hz, 3H, OEt); ^{13}C NMR ($CDCl_3$): δ = 171.8 (1), 132.1 (4), 117.5 (5), 60.5 (OEt), 36.5 (3), 32.9 (2), 14.1 (OEt).

4-Bromo-4-pentenol:[29] To a solution of the above crude ethyl 4-bromo-4-pentenoate in THF (300 mL) at 0 °C was added a solution of lithium aluminum hydride in THF (1.0 M, 100 mmol). The reaction mixture was stirred for 40 min at 0 °C and then saturated aqueous sodium sulfate was added. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford 4-bromo-4-pentenol (9.10 g, 74% from 1,2-dibromopropene) as a colorless oil: IR (neat): $\tilde{\nu}$ = 3360 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 5.57 (s, 1H, 5-H), 5.38 (s, 1H, 5-H), 3.61 (t, J = 6.4 Hz, 2H, 1-H, 1-H), 2.66 (s, 1H, OH), 2.49 (t, J = 7.4 Hz, 2H, 3-H, 3-H), 1.77 (tt, J = 7.4, 6.4 Hz, 2H, 2-H, 2-H); ^{13}C NMR ($CDCl_3$): δ = 133.8 (4), 116.8 (5), 61.0 (1), 37.6 (3), 30.7 (2).

2-Bromo-5-(triethylsiloxy)pentene: To a solution of 4-bromo-4-pentenol (9.10 g, 55.1 mmol) and imidazole (4.50 g, 66.1 mmol) in DMF (180 mL) at 0 °C was added chlorotriethylsilane (9.3 mL, 55.1 mmol). The reaction mixture was stirred for 1.5 h at 0 °C and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford methyl 2-bromo-5-(triethylsiloxy)pentene (14.4 g, 94%) as a colorless oil: IR (neat): $\tilde{\nu}$ = 1630, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 5.58 (s, 1H, 1-H), 5.40 (s, 1H, 1-H), 3.63 (t, J = 6.1 Hz, 2H, 5-H, 5-H), 2.51 (t, J = 6.9 Hz, 2H, 3-H, 3-H), 1.88 (tt, J = 6.9, 6.1 Hz, 2H, 4-H, 4-H), 0.96 (t, J = 7.9 Hz, 9H, TES), 0.59 (q, J = 7.9 Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): δ = 134.3 (2), 116.6 (1), 61.2 (5), 37.9 (3), 31.0 (4), 6.8 (TES), 4.4 (TES); HR MS: calcd for $C_{11}H_{23}OBrSi$ [M^+] 278.0701/280.0681, found 278.0660/280.0742.

(2*R*,3*R*,5*R*,6*S*,7*R*,8*R*)-2,6-Dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4,8-trimethyl-7-{1-[3-(triethylsiloxy)propyl]vinyl}cyclooctanone (36α): To a solution of 2-bromo-5-(triethylsiloxy)pentene (112 mg, 0.400 mmol) in diethyl ether (3.5 mL) at −78 °C was added *tert*-butyllithium in pentane (1.64 M, 0.5 mL, 0.820 mmol). The reaction mixture was stirred for 15 min at −78 °C and then it was added to copper(I) cyanide (17.9 mg, 0.200 mmol) with diethyl ether (2 mL) at −78 °C. After the reaction mixture had been stirred for 15 min at 0 °C, a solution of enone **1** (63.1 mg, 0.100 mmol) in diethyl ether (2 mL) was added at −78 °C. The reaction mixture was stirred for 2 h at −23 °C and then methyl iodide (2 mL, 32.1 mmol) and HMPA (1 mL, 5.75 mmol) were added at −23 °C. After the reaction mixture had been stirred for 2 h at −23 °C and it was allowed to warm to room temperature, saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketone **36α** (65.7 mg, 77%) and (2*R*,3*R*,5*R*,6*S*,7*S*,8*S*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4,8-trimethyl-7-{1-[3-(triethylsiloxy)propyl]vinyl}cyclooctanone (6.5 mg, 8%) as colorless oils. $[\alpha]_D^{24}$ = −1.1 (*c* 1.43, benzene); IR (neat): $\tilde{\nu}$ = 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.72–7.16 (m, 12H, Ph), 6.90–6.83 (m, 2H, Ph), 5.01–3.23 (m, 17H), 2.84–0.45 (m, 39H), 0.12–0.00 (m, 6H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{50}H_{76}O_7Si_2Na$ [M+Na]$^+$ 867.5027, found 867.5027.

(2*R*,3*R*,5*R*,6*S*,7*R*,8*R*)-2,6-Dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-[1-(3-hydroxypropyl)vinyl]-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone: To a solution of ketone **36α** (22.2 mg, 26.3 μmol) in THF (2 mL) at 0 °C was added TBAF (1.0 M, 0.035 mL, 35.0 μmol). The reaction mixture was stirred for 1 h at 0 °C and then phosphate buffer (pH = 7) was added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (2*R*,3*R*,5*R*,6*S*,7*R*,8*R*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-[1-(3-hydroxypropyl)vinyl]-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone (15.5 mg, 81%) as a colorless oil: $[\alpha]_D^{25}$ = −3.3 (*c* 1.39, benzene); IR (neat): $\tilde{\nu}$ = 3460, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.24–7.12 (m, 12H, Ph), 6.80–6.76 (m, 2H, Ph), 4.86–1.53 (m, 23H), 1.18–0.72 (m, 18H), 0.02–0.00 (m, 6H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{44}H_{62}O_7SiNa$ [M+Na]$^+$ 763.4163, found 763.4138.

4-[(1*S*,2*S*,3*R*,5*R*,6*R*,8*R*)-2,6-Dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-4,4,8-trimethyl-7-oxocyclooctyl]-4-pentenal (37α): To a suspension of (2*R*,3*R*,5*R*,6*S*,7*R*,8*R*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-[1-(3-hydroxypropyl)vinyl]-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone (10.3 mg, 14.1 μmol) and MS 4 Å (20 mg) in dichloromethane (0.5 mL) at 0 °C were added solutions of NMO (20.5 mg, 0.175 mmol) in dichloromethane (0.25 mL) and of TPAP (6.1 mg, 17.4 μmol) in dichloromethane (2 mL). The reaction mixture was stirred for 30 min at 0 °C and then diluted with ethyl acetate. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketoaldehyde **37α** (5.4 mg, 52%) and recovered (2*R*,3*R*,5*R*,6*S*,7*R*,8*R*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-[1-(3-hydroxypropyl)vinyl]-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone (2.3 mg, 22%) as colorless oils. $[\alpha]_D^{24}$ = −14.2 (*c* 0.54, benzene); IR (neat): $\tilde{\nu}$ = 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 9.55–9.39 (m, 1H, 7-CHO), 7.36–7.30 (m, 12H, Ph), 7.03–6.89 (m, 2H, Ph), 5.01–3.29 (m, 15H), 2.47–2.32 (m, 6H), 1.30–0.90 (m, 18H), 0.21–0.00 (m, 6H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{44}H_{60}O_7SiNa$ [M+Na]$^+$ 751.4006, found 751.3990.

(2*R*,3*R*,5*R*,6*S*,7*R*)-2,6-Dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-[1-(3-hydroxypropyl)vinyl]-5-(*p*-methoxybenzyloxy)-4,4-dimethylcyclooctanone (39): To a solution of thiophene (1.0 mL, 13.0 mmol) in THF (5 mL) at −45 °C was added *n*-butyllithium in hexane (1.65 M, 7.5 mL, 12.4 mmol). The reaction mixture was stirred for 2.5 h at −23 °C and then added to a suspension of copper(I) cyanide (1.21 g, 13.5 mmol) in THF (20.1 mL) at −78 °C. After the reaction mixture had been stirred for 60 min (20 min at −45 °C, 20 min at −20 °C and 20 min at 0 °C), it was diluted with THF (16 mL) at 0 °C. The solution of lithium 2-thienylcyanocuprate in THF (0.25 M) thus prepared was instantly used in the following reaction.

To a solution of 4-bromo-4-pentenol (490 mg, 2.97 mmol) in diethyl ether (30 mL) at −78 °C was added *tert*-butyllithium in pentane (2.0 M, 4.5 mL, 9.0 mmol). The reaction mixture was stirred for 30 min at −78 °C and then the solution of lithium 2-thienylcyanocuprate in THF (0.25 M, 13.0 mL, 3.25 mmol) was added. After the reaction mixture had been stirred for 35 min at −78 °C, a solution of enone **1** (617 mg, 0.979 mmol) in diethyl ether (20 mL) was added. The reaction mixture was stirred for 50 min (10 min at −45 °C, 20 min at −23 °C and 20 min at 0 °C) and then a mixture of saturated aqueous ammonium chloride and 28% aqueous ammonia (9/1) was added at room temperature. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford hydroxyketone **39** (642 mg, 91%) and recovered enone **1** (5.3 mg, 1%) as colorless oils. **Hydroxyketone 39**: $[\alpha]_D^{25}$ = +14.2 (*c* 1.42, benzene); IR (neat): $\tilde{\nu}$ = 3480, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.33–7.30 (m, 10H, Ph), 7.16 (d, J = 8.6 Hz, 2H, Ph), 6.83 (d, J = 8.6 Hz, 2H, Ph), 4.94 (br s, 1H, 20-H), 4.86 (br s, 1H, 20-H), 4.70 (d, J = 11.6 Hz, 1H, Bn), 4.65 (d, J = 10.6 Hz, 1H, 10-H), 4.49 (d, J = 11.2 Hz, 1H, Bn), 4.49 (d, J = 11.9 Hz, 1H, Bn), 4.36 (d, J = 11.9 Hz, 1H, Bn), 4.26 (d, J = 11.2 Hz, 1H, Bn), 4.26 (d, J = 11.6 Hz, 1H, Bn), 3.81 (s, 3H, MeO), 3.75 (d, J = 10.6 Hz, 1H, 11-H), 3.70–3.50 (m, 4H, 1-H, 2-H, 7-H, 7-H), 3.35 (br s, 1H, OH), 2.85–2.70 (m, 1H, 3-H), 2.25–2.00 (m, 3H, 5-H, 5-H, 8-H), 1.80–1.60 (m, 2H, 6-H, 6-H), 1.30–1.15 (m, 1H, 8-H), 1.13 (s, 3H, Me), 0.91 (s, 9H, TBS), 0.77 (s, 3H, Me), 0.06 (s, 3H, TBS), 0.03 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{43}H_{60}O_7SiNa$ [M+Na]$^+$ 739.4006, found 739.4014.

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4-[(1*S*,2*S*,3*R*,5*R*,6*R*)-2,6-Dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-4,4-dimethyl-7-oxocyclooctyl]-4-pentenal (40): To a suspension of hydroxyketone **39** (494 mg, 0.689 mmol), NMO (162 mg, 1.38 mmol), and MS 4 Å (379 mg) in dichloromethane (58 mL) at 0 °C was added a solution of TPAP (36.3 mg, 0.103 mmol) in dichloromethane (8 mL). The reaction mixture was stirred for 30 min at 0 °C and then cold ethyl acetate (60 mL) was added. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by column chromatography to afford ketoaldehyde **40** (437 mg, 89 %) as a colorless oil: $[\alpha]_D^{27} = +7.7$ (*c* 0.75, benzene); IR (neat): $\tilde{\nu} = 1720$, 1700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 9.61$ (br s, 1H, 7-CHO), 7.25–7.19 (m, 10H, Ph), 7.10 (d, $J = 8.6$ Hz, 2H, Ph), 6.77 (d, $J = 8.6$ Hz, 2H, Ph), 4.90 (s, 1H, 20-H), 4.74 (s, 1H, 20-H), 4.60–4.55 (m, 1H, 10-H), 4.43 (d, $J = 11.2$ Hz, 1H, Bn), 4.43 (d, $J = 11.2$ Hz, 1H, Bn), 4.31 (d, $J = 11.2$ Hz, 1H, Bn), 4.18 (d, $J = 10.2$ Hz, 1H, Bn), 4.18 (d, $J = 10.2$ Hz, 1H, Bn), 4.16 (d, $J = 11.2$ Hz, 1H, Bn), 3.84–3.50 (m, 6H, 1-H, 2-H, 11-H, MeO), 2.80–2.60 (m, 1H, 3-H), 2.50–2.30 (m, 3H, 5-H, 5-H, 8-H), 2.10–2.04 (m, 2H, 6-H, 6-H), 1.85–1.00 (br s, 4H, 8-H, Me), 0.85 (s, 9H, TBS), 0.71 (s, 3H, Me), 0.13 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{43}H_{58}O_7SiNa$ $[M+Na]^+$ 737.3850, found 737.3861.

(3*R*,4*R*,6*R*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-12-hydroxy-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-9-methylenebicyclo[6.4.0]-dodecan-2-one (41*β*) and **(3*R*,4*R*,6*R*,7*S*,8*R*,12*R*)-3,7-dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-12-hydroxy-6-(*p*-methoxybenzyloxy)-5,5-dimethyl-9-methylenebicyclo[6.4.0]dodecan-2-one (41*α*)**:

1) To a solution of ketoaldehyde **40** (561 mg, 0.785 mmol) in methanol (68 mL) at room temperature was added sodium methoxide in methanol (25 %, d 0.97, 5.2 mL, 23.4 mmol). The reaction mixture was stirred for 6 h at room temperature and then saturated aqueous ammonium chloride was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford aldol **41*β*** (462 mg, 82 %) and aldol **41*α*** (102 mg, 18 %) as colorless oils.

2) To a suspension of sodium hydride (7.4 mg, 0.308 mmol) in THF (2 mL) at −78 °C was added a solution of aldol **41*α*** (201 mg, 0.281 mmol) in THF (18 mL). The reaction mixture was stirred for 10 min at −78 °C and then allowed to warm to 0 °C. After the reaction mixture had been stirred for 1.5 h at 0 °C, saturated aqueous ammonium chloride was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford aldol **41*β*** (302 mg, 48 %) and recovered aldol **41*α*** (78.5 mg, 39 %) as colorless oils. **Aldol 41*β***: $[\alpha]_D^{26} = +49.3$ (*c* 0.80, benzene); IR (neat): $\tilde{\nu} = 3480$, 1700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.31–7.24$ (m, 10H, Ph), 7.11 (d, $J = 8.6$ Hz, 2H, Ph), 6.78 (d, $J = 8.6$ Hz, 2H, Ph), 4.98 (s, 1H, 20-H), 4.73 (s, 1H, 20-H), 4.65 (d, $J = 10.9$ Hz, 1H, Bn), 4.62 (d, $J = 11.9$ Hz, 1H, Bn), 4.61–4.56 (m, 1H, 7-H), 4.45 (d, $J = 10.6$ Hz, 1H, Bn), 4.37 (d, $J = 10.9$ Hz, 1H, Bn), 4.35 (d, $J = 11.9$ Hz, 1H, Bn), 4.29 (d, $J = 10.6$ Hz, 1H, Bn), 3.97–3.42 (m, 5H, 1-H, 2-H, 10-H, 11-H, OH), 3.78 (s, 3H, MeO), 2.59 (t, $J = 8.9$ Hz, 1H, 8-H), 2.37–2.31 (m, 1H, 3-H), 2.31–2.08 (m, 4H, 5-H, 5-H, 6-H, 6-H), 0.96 (s, 3H, Me), 0.86 (s, 9H, TBS), 0.79 (s, 3H, Me), 0.15 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{43}H_{58}O_7SiNa$ $[M+Na]^+$ 737.3850, found 737.3878. **Aldol 41*α***: $[\alpha]_D^{24} = +27.3$ (*c* 0.82, benzene); IR (neat): $\tilde{\nu} = 3490$, 1670 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.35–7.27$ (m, 10H, Ph), 7.13 (d, $J = 8.8$ Hz, 2H, Ph), 6.77 (d, $J = 8.8$ Hz, 2H, Ph), 4.98 (s, 1H, 20-H), 4.93 (d, $J = 10.8$ Hz, 1H, Bn), 4.72 (s, 1H, 20-H), 4.65 (d, $J = 11.2$ Hz, 1H, Bn), 4.62 (d, $J = 3.3$ Hz, 1H, 10-H), 4.46 (d, $J = 10.9$ Hz, 1H, Bn), 4.40 (d, $J = 10.8$ Hz, 1H, Bn), 4.40 (d, $J = 11.2$ Hz, 1H, Bn), 4.32 (d, $J = 10.9$ Hz, 1H, Bn), 4.12–3.92 (m, 1H, 7-H), 3.81 (d, $J = 3.3$ Hz, 1H, 11-H), 3.80 (s, 3H, MeO), 3.65–3.43 (m, 3H, 1-H, 2-H, OH), 3.32–3.24 (m, 1H, 8-H), 2.72–2.60 (m, 1H, 3-H), 2.21–2.17 (m, 1H, 5-H), 2.04–1.98 (m, 1H, 5-H), 1.55–1.40 (m, 1H, 6-H), 1.30–1.20 (m, 1H, 6-H), 1.16 (s, 3H, Me), 0.85 (s, 9H, TBS), 0.79 (s, 3H, Me), 0.04 (s, 3H, TBS), −0.06 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{43}H_{58}O_7SiNa$ $[M+Na]^+$ 737.3850, found 737.3854.

(2*R*,3*R*,5*R*,6*S*,7*S*,8*S*)-2,6-Dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-5-(*p*-methoxybenzyloxy)-4,4,8-trimethyl-7-{1-[3-(triethylsiloxy)propyl]vinyl}cyclooctanone (36*β*): To a solution of 2-bromo-5-(triethylsiloxy)pentene (455 mg, 1.63 mmol) in diethyl ether (22 mL) at −78 °C was added *tert*-butyllithium in pentane (1.64 M, 2.0 mL, 3.26 mmol). The reaction mixture was stirred for 20 min at −78 °C and then added to copper(I) cyanide (76.2 mg, 0.851 mmol) with diethyl ether (8 mL) at −78 °C. After the reaction mixture had been stirred for 30 min at 0 °C, a solution of enone **2** (150 mg, 0.232 mmol) in diethyl ether (22 mL) was added at −23 °C. The reaction mixture was stirred for 80 min at −23 °C and then saturated aqueous ammonium chloride (50 mL) was added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketone **36*β*** (181 mg, 92 %) and recovered enone **2** (11 mg, 7 %) as colorless oils. **Ketone 36*β***: $[\alpha]_D^{29} = +12.0$ (*c* 0.67, benzene); IR (neat): $\tilde{\nu} = 1720$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.36–7.23$ (m, 12H, Ph), 6.88 (d, $J = 8.6$ Hz, 2H, Ph), 5.05 (s, 1H, 20-H), 5.02 (s, 1H, 20-H), 4.86 (d, $J = 11.2$ Hz, 1H, Bn), 4.70 (br d, $J = 12.2$ Hz, 1H, Bn), 4.53 (d, $J = 11.2$ Hz, 1H, Bn), 4.45–3.98 (m, 5H, 1-H, 2-H, 10-H, 11-H, Bn), 4.49 (d, $J = 11.2$ Hz, 1H, Bn), 4.27 (d, $J = 11.2$ Hz, 1H, Bn), 3.84 (s, 3H, MeO), 3.60–3.45 (m, 2H, 7-H, 7-H), 2.75–2.65 (m, 1H, 8-H), 2.30–2.10 (m, 1H, 5-H), 2.10–1.95 (m, 2H, 3-H, 5-H), 1.85–1.60 (m, 2H, 6-H, 6-H), 1.14 (s, 3H, Me), 1.10 (s, 3H, Me), 1.00–0.80 (m, 12H, 19-Me, TES), 0.93 (s, 9H, TBS), 0.59 (q, $J = 7.9$ Hz, 6H, TES), 0.14 (s, 3H, TBS), 0.10 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{50}H_{76}O_7Si_2Na$ $[M+Na]^+$ 867.5027, found 867.5028.

(2*R*,3*R*,5*R*,6*S*,7*S*,8*S*)-2,6-Dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-[1-(3-hydroxypropyl)vinyl]-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone: To a solution of ketone **36*β*** (117 mg, 0.138 mmol) in THF (58 mL) at 0 °C was added hydrochloric acid (0.5 M, 0.470 mL, 0.235 mmol). After the reaction mixture had been stirred for 50 min at 0 °C, it was diluted with hexane, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and the organic layer was washed with saturated aqueous sodium hydrogencarbonate and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (2*R*,3*R*,5*R*,6*S*,7*S*,8*S*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-[1-(3-hydroxypropyl)vinyl]-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone (97.7 mg, 97 %) as a colorless oil: $[\alpha]_D^{29} = +17.6$ (*c* 1.82, benzene); IR (neat): $\tilde{\nu} = 3450$, 1720 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.33–7.21$ (m, 12H, Ph), 6.86 (d, $J = 8.6$ Hz, 2H, Ph), 5.02 (s, 1H, 20-H), 5.00 (s, 1H, 20-H), 4.83 (d, $J = 11.0$ Hz, 1H, Bn), 4.68 (br d, $J = 10.9$ Hz, 1H, Bn), 4.55 (d, $J = 11.0$ Hz, 1H, Bn), 4.53 (d, $J = 11.2$ Hz, 1H, Bn), 4.49–4.11 (m, 5H, 1-H, 2-H, 10-H, 11-H, Bn), 4.24 (d, $J = 11.2$ Hz, 1H, Bn), 3.82 (s, 3H, MeO), 3.62–3.47 (m, 2H, 7-H, 7-H), 2.77–2.62 (m, 1H, 8-H), 2.27–2.07 (m, 1H, 5-H), 2.07–1.87 (m, 2H, 3-H, 5-H), 1.77–1.57 (m, 2H, 6-H, 6-H), 1.15 (s, 3H, Me), 1.09 (s, 3H, Me), 0.96 (d, $J = 8.0$ Hz, 3H, 19-Me), 0.90 (s, 9H, TBS), 0.13 (s, 3H, TBS), 0.08 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{44}H_{63}O_7Si$ $[M+H]^+$ 731.4343, found 731.4344; HR MS: calcd for $C_{44}H_{62}O_7SiNa$ $[M+Na]^+$ 753.4163, found 753.4161.

4-[(1*S*,2*S*,3*R*,5*R*,6*R*,8*S*)-2,6-Dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-3-(*p*-methoxybenzyloxy)-4,4,8-trimethyl-7-oxocyclooctyl]-4-pentenal (37*β*): To a suspension of (2*R*,3*R*,5*R*,6*S*,7*S*,8*S*)-2,6-dibenzyloxy-3-(*tert*-butyldimethylsiloxy)-7-[1-(3-hydroxypropyl)vinyl]-5-(*p*-methoxybenzyloxy)-4,4,8-trimethylcyclooctanone (61.5 mg, 84.1 μmol) and MS 4 Å (124 mg) in dichloromethane (11 mL) at 0 °C were added solutions of NMO (20.5 mg, 0.175 mmol) in dichloromethane (2 mL) and of TPAP (6.1 mg, 17.4 μmol) in dichloromethane (2 mL). The reaction mixture was stirred for 30 min at 0 °C and then diluted with ethyl acetate. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketoaldehyde **37*β*** (56.3 mg, 92 %) as a colorless oil: $[\alpha]_D^{29} = +12.0$ (*c* 2.60, benzene); IR (neat): $\tilde{\nu} = 1720$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 9.63$ (s, 1H, 7-CHO), 7.34–7.22 (m, 12H, Ph), 6.87 (d, $J = 8.6$ Hz, 2H, Ph), 5.04 (s, 1H, 20-H), 4.95 (s, 1H, 20-H), 4.83 (d, $J = 10.9$ Hz, 1H, Bn), 4.68 (d, $J = 11.6$ Hz, 1H, Bn), 4.65–3.90 (m, 5H, 1-H, 2-H, 10-H, **11**-H, Bn), 4.55 (d, $J = 10.9$ Hz, 1H, Bn), 4.51 (d, $J = 11.8$ Hz, 1H, Bn), 4.21 (d, $J = 11.8$ Hz, 1H, Bn), 3.82 (s, 3H, MeO), 2.70–2.60 (m, 1H, 8-H), 2.60–2.10 (m, 5H, 3-H, 5-H, 5-H, 6-H, 6-H), 1.15 (s, 3H, Me), 1.10 (s, 3H, Me), 0.96 (d, $J = 6.9$ Hz, 3H, 19-Me), 0.91 (s, 9H, TBS), 0.13 (s, 3H, TBS), 0.09 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$):

very broadened spectra; HR MS: calcd for $C_{44}H_{60}O_7SiNa$ $[M+Na]^+$ 751.4006, found 751.4014.

(1*S*,3*R*,4*R*,6*R*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-12-hydroxy-6-(*p*-methoxybenzyloxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-2-one (38*β*) and **(1*S*,3*R*,4*R*,6*R*,7*S*,8*R*,12*R*)-3,7-dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-12-hydroxy-6-(*p*-methoxybenzyloxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-2-one (38*α*)**:

1) To a solution of ketoaldehyde **37*β*** (86.0 mg, 0.118 mmol) in methanol (12 mL) and THF (14 mL) at 0 °C was added sodium methoxide in methanol (28 %, d 0.93, 0.698 mL, 3.36 mmol). The reaction mixture was stirred for 1 h at 0 °C, and then hexane (15 mL) and saturated aqueous ammonium chloride were added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford aldol **38*β*** (77.1 mg, 90 %) and aldol **38*α*** (6.9 mg, 8 %) as colorless oils.

(2) To a solution of aldol **38*α*** (11.4 mg, 15.6 μmol) in THF (2 mL) at 0 °C was added sodium methoxide in methanol (28 %, d 0.93, 0.15 mL, 0.723 mmol). The reaction mixture was stirred for 5 min at 0 °C and then it was allowed to warm to room temperature. After the reaction mixture had been stirred for 1 h at room temperature, saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford aldol **38*β*** (8.6 mg, 75 %) and recovered aldol **38*α*** (1.7 mg, 15 %) as colorless oils. **Aldol 38*β***: $[\alpha]_D^{30} = +32.4$ (*c* 1.15, benzene); IR (neat): $\tilde{\nu} = 3410$, 1700 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.50$ (d, $J = 8.6$ Hz, 2H, Ph) 7.39 – 7.32 (m, 10H, Ph), 6.96 (d, $J = 8.6$ Hz, 2H, Ph), 5.27 (d, $J = 11.2$ Hz, 1H, Bn), 5.13 (s, 1H, 20-H), 4.84 (d, $J = 10.1$ Hz, 1H, Bn), 4.81 (s, 1H, 20-H), 4.69 (d, $J = 11.2$ Hz, 1H, Bn), 4.65 (d, $J = 10.1$ Hz, 1H, Bn), 4.63 (d, $J = 3.7$ Hz, 1H, 10-H), 4.48 (d, $J = 11.2$ Hz, 1H, Bn), 4.47 (d, $J = 10.1$ Hz, 1H, 1-H), 4.36 (d, $J = 11.2$ Hz, 1H, Bn), 4.20 (dd, $J = 7.3$, 6.9 Hz, 1H, 7-H), 3.96 – 3.83 (m, 1H, 2-H), 3.88 (s, 3H, MeO), 3.86 (d, $J = 3.7$ Hz, 1H, 11-H), 3.25 (s, 1H, OH), 2.96 (br d, $J = 9.0$ Hz, 1H, 3-H), 2.58 – 2.48 (m, 1H, 5-H), 2.30 – 2.16 (m, 1H, 6-H), 2.10 – 1.98 (m, 1H, 5-H), 1.68 – 1.53 (m, 1H, 6-H), 1.30 (s, 3H, Me), 1.16 (s, 3H, Me), 1.09 (s, 3H, 19-Me), 0.95 (s, 9H, TBS), 0.12 (s, 3H, TBS), 0.08 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{44}H_{60}O_7SiNa$ $[M+Na]^+$ 751.4006, found 751.4003. **Aldol 38*α***: $[\alpha]_D^{31} = +23.3$ (*c* 0.83, benzene); IR (neat): $\tilde{\nu} = 3510$, 1680 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.58 – 7.18$ (m, 12H, Ph), 6.96 (d, $J = 8.6$ Hz, 2H, Ph), 5.32 (d, $J = 11.6$ Hz, 1H, Bn), 5.10 (s, 1H, 20-H), 5.06 (d, $J = 5.3$ Hz, 1H, 10-H), 4.90 (d, $J = 5.3$ Hz, 1H, 11-H), 4.78 (s, 1H, 20-H), 4.75 (d, $J = 10.9$ Hz, 1H, Bn), 4.75 (d, $J = 9.6$ Hz, 1H, Bn), 4.71 (d, $J = 11.6$ Hz, 1H, Bn), 4.50 (d, $J = 3.3$ Hz, 1H, 2-H), 4.44 (d, $J = 3.3$ Hz, 1H, 1-H), 4.43 (d, $J = 10.9$ Hz, 1H, Bn), 4.26 (d, $J = 9.6$ Hz, 1H, Bn), 3.88 (s, 3H, MeO), 3.64 (br s, 1H, OH), 3.56 (dd, $J = 7.3$, 1.3 Hz, 1H, 7-H), 3.10 (s, 1H, 3-H), 2.76 – 2.58 (m, 1H, 5-H), 2.36 – 2.22 (m, 1H, 5-H), 2.10 – 1.92 (m, 1H, 6-H), 1.80 – 1.60 (m, 1H, 6-H), 1.29 (s, 3H, Me), 1.17 (s, 3H, Me), 0.99 (s, 3H, 19-Me), 0.95 (s, 9H, TBS), 0.16 (s, 3H, TBS), 0.10 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{44}H_{60}O_7SiNa$ $[M+Na]^+$ 751.4006, found 751.3995.

(1*R*,2*S*,3*S*,7*R*,8*S*,9*R*,11*R*,12*R*)-8,12-dibenzyloxy-11-(*tert*-butyldimethylsiloxy)-2,10,10-trimethyl-6-methylene-13-oxatricyclo[7.3.1.0^{2,7}]tridecan-1,3-diol (42): To a solution of aldol **38*β*** (12.9 mg, 17.7 μmol) in dichloromethane (2.6 mL) at 0 °C were added water (0.5 mL) and DDQ (5.2 mg, 23.0 μmol). The reaction mixture was stirred for 1 h at room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford hemiacetal **42** (7.4 mg, 66 %) as a colorless oil: $[\alpha]_D^{26} = -17.8$ (*c* 0.74, benzene); IR (neat): $\tilde{\nu} = 3490$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.41 – 7.24$ (m, 10H, Ph), 5.07 (s, 1H, 20-H), 5.01 (s, 1H, 20-H), 4.86 (dd, $J = 11.9$, 4.9 Hz, 1H, 2-H), 4.75 (s, 2H, Bn), 4.45 (d, $J = 10.9$ Hz, 1H, Bn), 4.35 (d, $J = 10.9$ Hz, 1H, Bn), 4.21 (dd, $J = 11.2$, 4.9 Hz, 1H, 7-H), 3.84 (dd, $J = 4.6$, 1.6 Hz, 1H, 11-H), 3.70 (d, $J = 4.6$ Hz, 1H, 10-H), 3.59 (dd, $J = 4.9$, 1.6 Hz, 1H, 1-H), 2.62 (d, $J = 11.9$ Hz, 1H, 3-H), 2.37 – 2.04 (m, 2H, 5-H, 5-H), 2.02 – 1.94 (m, 1H, 6-H), 1.75 – 1.59 (m, 1H, 6-H), 1.34 (s, 3H, 17-Me), 1.25 (s, 3H, 16-Me), 1.19 (s, 3H, 19-Me), 0.95 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 142.8$ (4), 139.1 (Ph), 138.1 (Ph), 128.5 (Ph), 128.3 (Ph), 128.2 (Ph), 127.8 (Ph), 127.3 (Ph), 127.2 (Ph), 110.3 (20), 102.1 (9), 85.4 (10), 81.6 (1), 77.2 (11), 75.1 (Bn), 74.3 (7), 71.1 (2), 65.0 (Bn), 48.2 (8), 47.1 (3), 38.4 (15), 34.5 (5), 30.9 (6), 28.0 (17), 26.5 (TBS), 23.1 (16), 18.7 (TBS), 10.5 (19), – 3.2 (TBS), – 4.8 (TBS); HR MS: calcd for $C_{36}H_{52}O_6SiNa$ $[M+Na]^+$ 631.3431, found 631.3442.

(1*S*,2*S*,3*S*,4*R*,6*R*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecane-2,12-diol: To a solution of lithium aluminum hydride in THF (1.0 M, 3.0 mL, 3.0 mmol) at 0 °C was added sulfuric acid (98 %, 0.080 mL, 1.5 mmol). The reaction mixture was stirred for 1 h at room temperature and then it was allowed to stand. The clear solution of aluminum hydride in THF (1.0 M) was instantly used in the following reaction without further purification.

To a solution of aldol **38*β*** (41.4 mg, 56.8 μmol) in toluene (2.2 mL) at – 78 °C was added aluminum hydride in THF (1.0 M, 0.568 mL, 0.568 mmol). The reaction mixture was stirred for 2 h at – 78 °C and then saturated aqueous potassium sodium tartrate was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (1*S*,2*S*,3*S*,4*R*,6*R*,7*S*,8*R*,12*S*)-3,7-dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecane-2,12-diol (39.0 mg, 94 %) as a colorless oil: $[\alpha]_D^{28} = +63.4$ (*c* 1.44, benzene); IR (neat): $\tilde{\nu} = 3390$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.40 – 7.20$ (m, 12H, Ph), 6.87 (d, $J = 8.5$ Hz, 2H, Ph), 5.04 (d, $J = 11.7$ Hz, 1H, Bn), 4.89 – 4.79 (br s, 1H, 7-OH), 4.83 (s, 1H, 20-H), 4.69 (s, 1H, 20-H), 4.68 (d, $J = 9.8$ Hz, 1H, Bn), 4.58 (d, $J = 11.4$ Hz, 1H, 1-H), 4.56 (d, $J = 9.8$ Hz, 1H, Bn), 4.56 (d, $J = 11.4$ Hz, 1H, Bn), 4.52 (d, $J = 11.4$ Hz, 1H, Bn), 4.29 (d, $J = 11.7$ Hz, 1H, Bn), 4.20 (br s, 1H, 9-OH), 4.02 (d, $J = 4.0$ Hz, 1H, 10-H), 3.92 – 3.77 (m, 2H, 7-H, 11-H), 3.82 (s, 3H, MeO), 3.76 – 3.60 (m, 2H, 2-H, 9-H), 2.39 – 2.28 (m, 1H, 5-H), 2.24 (d, $J = 11.3$ Hz, 1H, 3-H), 2.20 – 2.09 (m, 1H, 5-H), 2.05 – 1.90 (m, 1H, 6-H), 1.69 – 1.51 (m, 1H, 6-H), 1.28 (s, 3H, Me), 1.23 (s, 3H, Me), 1.08 (s, 3H, 19-Me), 1.00 (s, 9H, TBS), 0.15 (s, 3H, TBS), 0.10 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{44}H_{62}O_7SiNa$ $[M+Na]^+$ 753.4163, found 753.4165.

(1*S*,2*S*,3*S*,4*R*,6*R*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-2,12-(isopropylidenedioxy)-6-(*p*-methoxybenzyloxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecane (43): To a solution of (1*S*,2*S*,3*S*,4*R*,6*R*,7*S*,8*R*,12*S*)-3,7-dibenzyloxy-4-(*tert*-butyldimethylsiloxy)-6-(*p*-methoxybenzyloxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecane-2,12-diol (47.9 mg, 65.5 μmol) in dichloromethane (3.1 mL) and 2,2-dimethoxypropane (3.1 mL) at 0 °C was added CSA (3.0 mg, 12.9 μmol). After the reaction mixture had been stirred for 1 h at room temperature, triethylamine (5 drops) was added. After evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford acetonide **43** (50.3 mg, 100 %) as a colorless oil: $[\alpha]_D^{27} = +117.6$ (*c* 2.29, benzene); IR (neat): $\tilde{\nu} = 2940$, 2870 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.40 – 7.14$ (m, 10H, Ph), 7.12 (d, $J = 8.5$ Hz, 2H, Ph), 6.75 (d, $J = 8.5$ Hz, 2H, Ph), 4.77 (d, $J = 10.2$ Hz, 1H, Bn), 4.76 (d, $J = 11.0$ Hz, 1H, Bn), 4.75 (s, 1H, 20-H), 4.70 (s, 1H, 20-H), 4.63 (d, $J = 11.0$ Hz, 1H, Bn), 4.48 (d, $J = 11.2$ Hz, 1H, Bn), 4.43 (d, $J = 2.6$ Hz, 1H, 1-H), 4.39 (d, $J = 11.2$ Hz, 1H, Bn), 4.18 (d, $J = 10.2$ Hz, 1H, Bn), 3.89 (d, $J = 2.7$ Hz, 1H, 10-H), 3.87 (s, 1H, 11-H), 3.75 (s, 3H, MeO), 3.62 – 3.56 (m, 2H, 2-H, 7-H), 3.50 (d, $J = 2.7$ Hz, 1H, 9-H), 2.34 – 2.27 (m, 1H, 5-H), 2.16 (d, $J = 9.4$ Hz, 1H, 3-H), 2.18 – 2.05 (m, 1H, 6-H), 1.84 – 1.78 (m, 1H, 5-H), 1.60 – 1.49 (m, 1H, 6-H), 1.42 (s, 3H, Me), 1.36 (s, 3H, Me), 1.29 (s, 3H, Me), 1.20 (s, 3H, Me), 1.14 (s, 3H, Me), 0.91 (s, 9H, TBS), 0.03 (s, 3H, TBS), 0.00 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 159.3$ (PMP), 144.4 (4), 139.7 (Ph), 139.7 (Ph), 131.9 (Ph), 129.8 (Ph), 128.5 (Ph), 128.3 (Ph), 128.2 (Ph), 127.8 (Ph), 127.2 (Ph), 127.2 (Ph), 115.4 (20), 114.0 (PMP), 99.1 (acetonide), 93.3 (1), 82.5 (10), 82.4 (9), 79.8 (11), 77.8 (PMB), 77.1 (Bn), 76.5 (Bn), 73.8 (2), 73.1 (7), 55.7 (MeO), 50.0 (8), 46.4 (3), 39.0 (15), 30.4 (6), 26.9 (Me), 26.7 (Me), 26.4 (TBS), 25.8 (5), 21.3 (Me), 19.6 (Me), 18.5 (TBS), 9.8 (19), – 3.7 (TBS), – 4.3 (TBS); HR MS: calcd for $C_{47}H_{66}O_7SiNa$ $[M+Na]^+$ 793.4476, found 793.4479.

(1*R*,2*S*,3*R*,5*R*,6*S*,7*S*,8*S*,9*S*)-2,6-Dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3-ol: To a solution of acetonide **43** (34.3 mg, 44.5 μmol) in dichloro-

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methane (4.0 mL) and water (0.45 mL) at 0 °C was added DDQ (13.1 mg, 57.9 μmol). The reaction mixture was stirred for 1 h at room temperature and then phosphate buffer (pH = 7) was added. The reaction mixture was extracted with dichloromethane, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (1*R*,2*S*,3*R*,5*R*,6*S*,7*S*,8*S*,9*S*)-2,6-dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3-ol (28.2 mg, 97 %) as a colorless oil: $[\alpha]_D^{28} = +99.6$ (*c* 2.45, benzene); IR (neat): $\tilde{\nu} = 3380\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 7.39-7.23$ (m, 10H, Ph), 4.88 (s, 1H, 20-H), 4.87 (s, 1H, 20-H), 4.76 (d, $J = 11.2$ Hz, 1H, Bn), 4.71 (d, $J = 11.2$ Hz, 1H, Bn), 4.68 (dd, $J = 11.0$, 3.4 Hz, 1H, 1-H), 4.59 (d, $J = 11.4$ Hz, 1H, Bn), 4.34 (d, $J = 11.4$ Hz, 1H, Bn), 3.98 (s, 1H, 11-H), 3.95 (d, $J = 2.6$ Hz, 1H, 10-H), 3.75 (dd, $J = 11.7$, 3.4 Hz, 1H, 2-H), 3.69 (dd, $J = 10.2$, 7.2 Hz, 1H, 7-H), 3.60 (d, $J = 2.6$ Hz, 1H, 9-H), 2.56–2.43 (m, 1H, 5-H), 2.39 (d, $J = 11.7$ Hz, 1H, 3-H), 2.32–2.19 (m, 1H, 5-H), 2.21 (d, $J = 11.0$ Hz, 1H, OH), 1.99–1.84 (m, 1H, 6-H), 1.77–1.64 (m, 1H, 6-H), 1.47 (s, 3H, Me), 1.43 (s, 3H, Me), 1.43 (s, 3H, Me), 1.21 (s, 3H, Me), 1.04 (s, 3H, Me), 0.95 (s, 9H, TBS), 0.10 (s, 3H, TBS), 0.05 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 144.4$ (4), 139.0 (Ph), 139.0 (Ph), 128.3 (Ph), 128.1 (Ph), 128.0 (Ph), 127.3 (Ph), 127.2 (Ph), 127.0 (Ph), 115.0 (20), 98.8 (acetonide), 92.2 (1), 83.3 (10), 81.9 (9), 77.4 (11), 76.4 (Bn), 76.3 (Bn), 73.8 (2), 73.1 (7), 49.2 (8), 45.3 (3), 38.9 (15), 29.9 (6), 26.2 (Me), 25.9 (Me), 25.9 (TBS), 23.9 (5), 21.8 (Me), 19.1 (Me), 18.0 (TBS), 9.2 (19), −4.1 (TBS), −4.8 (TBS); HR MS: calcd for $C_{39}H_{58}O_6SiNa$ $[M+Na]^+$ 673.3900, found 673.3902.

(1*R*,2*S*,5*R*,6*S*,7*S*,8*S*)-2,6-Dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3-one (**44**): To a solution of (1*R*,2*S*,3*R*,5*R*,6*S*,7*S*,8*S*,9*S*)-2,6-dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3-ol (64.7 mg, 99.4 μmol) in dichloromethane (35 mL) was added PDC (748 mg, 1.99 mmol). The reaction mixture was stirred for 16 h at room temperature and then diluted with diethyl ether. After filtration of the mixture through a short pad of Celite and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketone **44** (57.8 mg, 90 %) and recovered starting material (2.7 mg, 4 %) as colorless oils. **Ketone 44**: $[\alpha]_D^{26} = +0.5$ (*c* 1.18, benzene); IR (neat): $\tilde{\nu} = 1690\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 7.37-7.19$ (m, 10H, Ph), 4.96 (s, 1H, 20-H), 4.91 (s, 1H, 20-H), 4.79 (d, $J = 10.8$ Hz, 1H, 2-H), 4.76 (d, $J = 10.9$ Hz, 1H, Bn), 4.70 (d, $J = 10.9$ Hz, 1H, Bn), 4.32 (d, $J = 11.1$ Hz, 1H, Bn), 4.19 (d, $J = 11.1$ Hz, 1H, Bn), 3.87 (s, 1H, 10-H), 3.78 (s, 1H, 9-H), 3.69 (dd, $J = 10.7$, 5.9 Hz, 1H, 7-H), 3.44 (s, 1H, 11-H), 2.75 (d, $J = 10.8$ Hz, 1H, 3-H), 2.35–2.10 (m, 2H, 5-H, 5-H), 1.85–1.10 (m, 2H, 6-H, 6-H), 1.48 (s, 3H, Me), 1.40 (s, 3H, Me), 1.38 (s, 3H, Me), 1.22 (s, 3H, Me), 1.12 (s, 3H, Me), 0.95 (s, 9H, TBS), 0.11 (s, 3H, TBS), 0.09 (s, 3H, TBS); ^{13}C NMR (C_6D_6): $\delta = 209.9$ (1), 143.3 (4), 139.0 (Ph), 138.8 (Ph), 128.8 (Ph), 128.5 (Ph), 128.4 (Ph), 128.2 (Ph), 127.9 (Ph), 127.8 (Ph), 113.1 (20), 98.9 (acetonide), 93.6 (2), 80.5 (10), 80.4 (11), 77.6 (7), 77. 6 (Bn), 75.8 (Bn), 69.2 (9), 53.8 (15), 48.1 (3), 42.0 (8), 31.8 (5), 30.5 (6), 28.1 (Me), 27.6 (Me), 26.3 (TBS), 19.5 (TBS), 19.3 (Me), 18.5 (Me), 11.3 (19), −3.6 (TBS), −4.6 (TBS); HR MS: calcd for $C_{39}H_{56}O_6SiNa$ $[M+Na]^+$ 671.3744, found 671.3772.

(1*R*,2*S*,3*S*,5*R*,6*S*,7*S*,8*S*,9*S*)-3-Allyl-2,6-dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo-[6.4.0]dodecan-3-ol: To a solution of ketone **44** (36.2 mg, 55.8 μmol) in THF (7.0 mL) at −78 °C was added allylmagnesium bromide in diethyl ether (1.0 M, 3.5 mL, 3.5 mmol). After the reaction mixture had been stirred for 15 min at −78 °C, it was allowed to warm to −45 °C. The reaction mixture was stirred for 1 h at −45 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (1*R*,2*S*,3*S*,5*R*,6*S*,7*S*,8*S*,9*S*)-3-allyl-2,6-dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo-[6.4.0]dodecan-3-ol (35.2 mg, 91 %) and (1*R*,2*S*,3*R*,5*R*,6*S*,7*S*,8*S*,9*S*)-3-allyl-2,6-dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,-4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3-ol (2.7 mg, 7 %) as colorless oils. (**1*R*,2*S*,3*S*,5*R*,6*S*,7*S*,8*S*,9*S*)-Alcohol**: $[\alpha]_D^{26} = +33.8$ (*c* 0.83, benzene); IR (neat): $\tilde{\nu} = 3370\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.42-6.99$ (m, 10H, Ph), 6.64–6.28 (br m, 1H, 13-H), 5.97–5.25 (br m, 2H), 5.25–5.02 (br m, 2H), 5.02–4.82 (br m, 3H), 4.82–4.23 (br m, 4H), 4.01–3.63 (br m, 1H), 3.55 (dd, $J = 10.2$, 5.7 Hz, 1H, 7-H), 2.99–2.68 (br m, 1H), 2.68–2.51 (m, 1H), 2.45 (s, 1H, 3-H), 2.17–2.11 (m, 1H, 5-H), 2.10–1.90 (m, 1H, 5-H), 1.75–1.62 (m, 2H, 6-H, 6-H), 1.60 (s, 3H, Me), 1.48 (br s, 6H, Me, Me), 1.33 (br s, 6H, Me, Me), 0.97 (s, 9H, TBS), 0.09 (s, 3H, TBS), 0.06 (s, 3H, TBS); ^{13}C NMR (C_6D_6): very broadened spectra; HR MS: calcd for $C_{42}H_{62}O_6SiNa$ $[M+Na]^+$ 713.4213, found 713.4196.

(1*R*,2*S*,3*S*,5*R*,6*R*,7*S*,8*S*,9*S*)-3-Allyl-2,6-dibenzyloxy-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3,5-diol (**45**): To a solution of (1*R*,2*S*,3*S*,5*R*,6*S*,7*S*,8*S*,9*S*)-3-allyl-2,6-dibenzyloxy-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3-ol (42.3 mg, 61.2 μmol) in THF (7 mL) at 0 °C was added TBAF in THF (1.0 M, 0.42 mL, 0.42 mmol). The reaction mixture was stirred for 3 h at room temperature and then phosphate buffer (pH = 7) was added at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diol **45** (33.4 mg, 95 %) as a colorless oil: $[\alpha]_D^{26} = +74.0$ (*c* 2.02, benzene); IR (neat): $\tilde{\nu} = 3520$, $3440\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.45-7.36$ (m, 2H, Ph), 7.22–6.98 (m, 8H, Ph), 6.42–6.16 (br m, 1H, 13-H), 5.84–5.49 (br m, 1H, 20-H), 5.03 (br m, 1H, 9-H or 11-H), 5.01 (br m, 1H, 20-H), 4.98 (br m, 1H, 10-H), 4.96 (d, $J = 11.2$ Hz, 1H, Bn), 4.95–4.78 (br m, 1H, 12-H), 4.93 (d, $J = 10.6$ Hz, 1H, Bn), 4.92 (br s, 1H, 2-H), 4.78 (d, $J = 10.6$ Hz, 1H, Bn), 4.77–4.61 (br m, 1H, 12-H), 4.47 (d, $J = 11.2$ Hz, 1H, Bn), 4.23 (br m, 1H, 11-H or 9-H), 3.88–3.72 (br s, 1H, OH), 3.69–3.49 (br m, 1H, OH), 3.52 (dd, $J = 10.4$, 5.4 Hz, 1H, 7-H), 2.58–2.37 (br m, 2H, 14-H, 14-H), 2.45 (br s, 1H, 3-H), 2.18–2.05 (m, 1H, 5-H), 1.97–1.82 (m, 1H, 5-H), 1.79–1.55 (m, 2H, 6-H, 6-H), 1.60 (s, 3H, Me), 1.53 (s, 3H, Me), 1.46 (s, 3H, Me), 1.29 (s, 3H, Me), 1.14 (s, 3H, Me); ^{13}C NMR (C_6D_6): very broadened spectra; HR MS: calcd for $C_{36}H_{48}O_6Na$ $[M+Na]^+$ 599.3349, found 599.3356.

(1*S*,2*S*,3*S*,4*R*,6*S*,7*S*,8*R*,12*S*)-6-Allyl-3,7-dibenzyloxy-4,6-(cyclohexylmethylsilylenedioxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecane (**46**): To a solution of diol **45** (18.7 mg, 32.4 μmol) and imidazole (153 mg, 2.24 mmol) in DMF (3 mL) at 0 °C was added dichlorocyclohexylmethylsilane (126 mg, 0.640 mmol). The reaction mixture was stirred for 1 h at 0 °C, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford silylene **46** (21.8 mg, 97 %) as a colorless oil: $[\alpha]_D^{26} = +40.6$ (*c* 1.57, benzene); IR (neat): $\tilde{\nu} = 2920$, $2850\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.62-7.42$ (m, 4H, Ph), 7.29–6.28 (m, 6H, Ph), 6.50 (dddd, $J = 16.8$, 9.1, 7.8, 6.2 Hz, 1H, 13-H), 6.02 (s, 1H, 20-H), 5.03 (d, $J = 16.8$ Hz, 1H, 12-H), 5.02 (s, 1H, 10-H), 5.01 (s, 1H, 20-H), 4.98 (s, 1H, 9-H or 11-H), 4.97 (d, $J = 11.9$ Hz, 1H, Bn), 4.91 (s, 1H, 2-H), 4.89 (d, $J = 9.1$ Hz, 1H, 12-H), 4.70 (d, $J = 11.9$ Hz, 1H, Bn), 4.21 (d, $J = 9.1$ Hz, 1H, Bn), 4.17 (s, 1H, 11-H or 9-H), 3.81 (d, $J = 9.1$ Hz, 1H, Bn), 3.51 (dd, $J = 10.7$, 4.2 Hz, 1H, 7-H), 2.97 (dd, $J = 14.9$, 6.2 Hz, 1H, 14-H), 2.69 (s, 1H, 3-H), 2.55 (dd, $J = 14.9$, 7.8 Hz, 1H, 14-H), 2.19–1.96 (m, 3H, 5-H, 5-H, 6-H), 1.95–1.42 (m, 12H, 6-H, *c*Hex), 1.76 (s, 3H, Me), 1.52 (s, 3H, Me), 1.48 (s, 3H, Me), 1.22 (s, 3H, Me), 1.17 (s, 3H, Me), 0.32 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 143.7$ (4), 140.3 (13), 139.2 (Ph), 138.3 (Ph), 129.8 (Ph), 128.2 (Ph), 128.2 (Ph), 127.5 (Ph), 127.5 (Ph), 127.4 (Ph), 116.1 (12), 114.7 (20), 99.5 (acetonide), 86.9 (1), 86.8 (2), 84.7 (10), 84.3 (11), 79.0 (Bn), 78.2 (7), 76.0 (Bn), 74.5 (9), 47.7 (15), 46.7 (8), 45.4 (14), 38.2 (3), 37.6 (5), 32.5 (6), 30.2, 29.1, 29.1, 28.4, 28.4, 28.1, 27.6, 27.6, 27.5 15.8 (16, 17, acetonide, *c*Hex), 12.8 (19), −1.0 (Me); HR MS: calcd for $C_{43}H_{60}O_6SiNa$ $[M+Na]^+$ 723.4057, found 723.4048.

(1*S*,2*S*,3*R*,4*R*,6*S*,7*S*,8*R*,12*S*)-6-Allyl-3,7-dibenzyloxy-6-(cyclohexyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-ol: To a solution of silylene **46** (21.8 mg, 31.1 μmol) in THF (4.0 mL) and HMPA (0.4 mL) at −78 °C was added methyllithium in diethyl ether (1.01 M, 0.3 mL, 0.3 mmol). The reaction mixture was stirred for 2.5 h at −78 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (1*S*,2*S*,3*R*,4*R*,6*S*,7*S*,8*R*,12*S*)-6-allyl-3,7-dibenzyloxy-6-(cyclohexyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-ol

(20.5 mg, 92%) as a colorless oil: $[\alpha]_D^{26} = +32.7$ (*c* 1.43, benzene); IR (neat): $\tilde{\nu} = 3550\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.53-6.98$ (m, 10H, Ph), 6.52–6.31 (br m, 1H, 13-H), 6.14–4.14 (br m, 12H, 2-H, 9-H, 10-H, 11-H, 12-H, 12-H, 20-H, 20-H, Bn, Bn, Bn, Bn), 3.53 (dd, $J = 8.6$, 7.3 Hz, 1H, 14-H), 3.45 (dd, $J = 8.8$, 4.7 Hz, 1H, 7-H), 3.08–2.04 (br m, 5H, 3-H, 5-H, 5-H, 6-H, 14-H), 2.01–0.95 (br m, 12H, 6-H, *c*Hex), 1.63 (s, 3H, Me), 1.53 (s, 3H, Me), 1.50 (s, 3H, Me), 1.29 (s, 3H, Me), 1.20 (s, 3H, Me), 0 19 (s, 3H, Me), 0.02 (s, 3H, Me); ^{13}C NMR (C_6D_6): very broadened spectra; HR MS: calcd for $C_{44}H_{64}O_6SiNa$ $[M+Na]^+$ 739.4370, found 739.4382.

(1*S*,2*S*,3*S*,6*S*,7*S*,8*R*,12*S*)-6-Allyl-3,7-dibenzyloxy-6-(cyclohexyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-one (**47**): To a solution of (1*S*,2*S*,3*R*,4*R*,6*S*,7*S*,8*R*,12*S*)-6-allyl-3,7-dibenzyloxy-6-(cyclohexyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-ol (21.8 mg, 30.4 μmol) in dichloromethane (10 mL) at 0 °C was added PDC (105 mg, 0.280 mmol). The reaction mixture was stirred for 5 h at room temperature and then diethyl ether (15 mL) was added. After filtration of the mixture through a short pad of Celite and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketone **47** (12.8 mg, 64%) and recovered starting material (3.1 mg, 14%) as colorless oils. **Ketone 47**: $[\alpha]_D^{25} = +63.2$ (*c* 0.84, benzene); IR (neat): $\tilde{\nu} = 1670\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.42-6.98$ (m, 10H, Ph), 6.76 (dddd, $J = 16.9$, 10.5, 8.8, 2.6 Hz, 1H, 13-H), 5.07 (d, $J = 12.6$ Hz, 1H, Bn), 5.04 (d, $J = 10.5$ Hz, 1H, 12-H), 4.97 (d, $J = 16.9$ Hz, 1H, 12-H), 4.94 (s, 1H, 20-H), 4.73 (s, 1H, 20-H), 4.67 (d, $J = 12.6$ Hz, 1H, Bn), 4.63 (d, $J = 11.0$ Hz, 1H, Bn), 4.59 (s, 1H, 2-H), 4.42 (d, $J = 11.0$ Hz, 1H, Bn), 4.42 (d, $J = 3.0$ Hz, 1H, 10-H), 4.12 (d, $J = 3.0$ Hz, 1H, 9-H), 3.72 (dd, $J = 10.2$, 7.0 Hz, 1H, 7-H), 3.13 (dd, $J = 17.4$, 2.6 Hz, 1H, 14-H), 2.83 (dd, $J = 17.4$, 8.8 Hz, 1H, 14-H), 2.31 (s, 1H, 3-H), 2.28–2.12 (m, 1H, 5-H), 2.01–1.84 (m, 2H, 5-H, 6-H), 1.82–0.67 (m, 12H, 6-H, *c*Hex), 1.78 (s, 3H, Me), 1.72 (s, 3H, Me), 1.47 (s, 3H, Me), 1.35 (s, 3H, Me), 1.22 (s, 3H, Me), 0.21 (s, 3H, Me), −0.01 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 215.4$ (11), 145.5 (4), 140.3 (13), 138.7 (Ph), 138.5 (Ph), 128.9 (Ph), 128.8 (Ph), 128.6 (Ph), 128.3 (Ph), 128.1 (Ph), 126.1 (Ph), 116.8 (12), 115.1 (20), 100.0 (acetonide), 93.7 (10), 88.7 (1), 84.1 (2), 81.0 (Bn), 76.4 (7), 74.6 (Bn), 73.5 (9), 58.0 (15), 48.7 (14), 41.0 (8), 36.4 (3), 30.6, 29.6, 29.5, 28.6, 28.6, 28.0, 27.9, 27.5, 26.5, 25.6, 23.1, 19.6 (5, 6, 16, 17, acetonide, *c*Hex), 12.7 (19), 1.1 (Me), −0.4 (Me); HR MS: calcd for $C_{44}H_{62}O_6SiNa$ $[M+Na]^+$ 737.4213, found 737.4224.

3-[(1*R*,2*S*,3*S*,6*S*,7*S*,8*S*,9*S*)-2,6-Dibenzyloxy-3-(cyclohexyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylene-5-oxobicyclo-[6.4.0]dodecan-3-yl]propanal (**49**): To a solution of ketone **47** (12.8 mg, 17.9 μmol) in DMF (3.5 mL) and water (0.5 mL) at 0 °C was added palladium(II) chloride (8.4 mg, 47.4 μmol). The reaction mixture was stirred for 1.5 h at room temperature and then phosphate buffer (pH = 7) was added at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketoaldehyde **49** (5.3 mg, 40%) and recovered ketone **47** (2.0 mg, 16%) as colorless oils. **Ketoaldehyde 49**: $[\alpha]_D^{27} = +44.9$ (*c* 0.53, benzene); IR (neat): $\tilde{\nu} = 1720$, $1670\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 9.50$ (s, 1H, 12-CHO), 7.46–7.00 (m, 10H, Ph), 4.93 (d, $J = 12.8$ Hz, 1H, Bn), 4.73 (s, 1H, 20-H), 4.60 (d, $J = 11.0$ Hz, 1H, Bn), 4.59 (d, $J = 12.8$ Hz, 1H, Bn), 4.45 (s, 1H, 20-H), 4.45 (d, $J = 2.0$ Hz, 1H, 2-H), 4.39 (d, $J = 3.2$ Hz, 1H, 10-H), 4.35 (d, $J = 11.0$ Hz, 1H, Bn), 4.10 (d, $J = 3.2$ Hz, 1H, 9-H), 3.68 (dd, $J = 10.2$, 7.0 Hz, 1H, 7-H), 3.65–3.48 (m, 1H, 13-H), 2.78–2.63 (m, 1H, 13-H), 2.59–2.44 (m, 1H, 5-H), 2.36–2.22 (m, 1H, 5-H), 2.20 (d, $J = 2.0$ Hz, 1H, 3-H), 2.15–2.01 (m, 1H, 6-H or 14-H), 1.98–1.77 (m, 2H, 6-H, 14-H), 1.76–0.63 (m, 12H, 14-H or 6-H, *c*Hex), 1.72 (s, 3H, Me), 1.69 (s, 3H, Me), 1.47 (s, 3H, Me), 1.28 (s, 3H, Me), 1.24 (s, 3H, Me), 0.07 (s, 3H, Me), −0.06 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 214.7$ (11), 201.3 (12), 147.6 (4), 140.0 (Ph), 138.3 (Ph), 128.6 (Ph), 128.6 (Ph), 128.5 (Ph), 128.4 (Ph), 128.1 (Ph), 127.9 (Ph), 113.8 (20), 99.8 (acetonide), 93.4 (10), 89.3 (1), 83.5 (2), 80.8 (Bn), 76.3 (7), 74.4 (Bn), 72.7 (9), 57.4 (15), 48.8 (13), 42.1 (8), 40.6 (3), 30.1, 28.9, 28.8, 28.2, 28.1, 27.6, 27.5, 27.2, 26.2, 25.5, 23.9, 22.7, 19.4 (5, 6, 14, 16, 17, acetonide, *c*Hex), 12.7 (19), 0.4 (Me), −1.1 (Me); HR MS: calcd for $C_{44}H_{62}O_7SiNa$ $[M+Na]^+$ 753.4163, found 753.4166.

(1*R*,2*S*,3*S*,5*R*,6*S*,7*S*,8*S*,9*S*)-2,6-Dibenzyloxy-3-(3-butenyl)-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3-ol: To a solution of *s*-butyllithium in cyclohexane (1.03 M, 0.3 mL, 0.309 mmol) at 0 °C was added 4-iodobutene (56.4 mg, 0.310 mmol). After the reaction mixture had been stirred for 25 min at −23 °C, a solution of ketone **44** (8.9 mg, 13.7 μmol) in benzene (0.8 mL) was added. The reaction mixture was stirred for 1 h at 0 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with 10% aqueous sodium thiosulfate and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (1*R*,2*S*,3*S*,5*R*,6*S*,7*S*,8*S*,9*S*)-2,6-dibenzyloxy-3-(3-butenyl)-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3-ol (9.3 mg, 96%) as a colorless oil: $[\alpha]_D^{28} = +65.2$ (*c* 1.34, benzene); IR (neat): $\tilde{\nu} = 3460\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 7.43-7.17$ (m, 10H, Ph), 5.95–5.70 (br m, 1H, 12-H), 5.65–5.28 (br m, 1H), 5.10–4.75 (br m, 5H), 4.75–4.55 (br m, 2H), 4.50–4.00 (br m, 3H), 3.75–3.45 (br m, 3H), 2.40–1.90 (br m, 6H), 1.77–1.34 (br m, 2H), 1.56 (s, 3H, Me), 1.48 (s, 3H, Me), 1.45 (s, 3H, Me), 1.35 (s, 3H, Me), 1.19 (s, 3H, Me), 0.95 (s, 9H, TBS), 0.08 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{43}H_{64}O_6SiNa$ $[M+Na]^+$ 727.4370, found 727.4387.

(1*R*,2*S*,3*S*,5*R*,6*R*,7*S*,8*S*,9*S*)-2,6-Dibenzyloxy-3-(3-butenyl)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3,5-diol (**51**): To a solution of (1*R*,2*S*,3*S*,5*R*,6*S*,7*S*,8*S*,9*S*)-2,6-dibenzyloxy-3-(3-butenyl)-5-(*tert*-butyldimethylsiloxy)-7,9-(isopropylidenedioxy)-4,4,8-trimethyl-12-methylenebicyclo[6.4.0]dodecan-3-ol (88.6 mg, 0.126 mmol) in THF (17 mL) at room temperature was added TBAF in THF (1.0 M, 3.77 mL, 3.77 mmol). The reaction mixture was stirred for 1 h at 50 °C and then phosphate buffer (pH = 7) was added at 0 °C. The mixture was extract with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diol **51** (75.9 mg, 100%) as a colorless oil: $[\alpha]_D^{30} = +58.1$ (*c* 0.92, benzene); IR (neat): $\tilde{\nu} = 3480$, $3430\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.43-7.41$ (m, 2H, Ph), 7.15–7.03 (m, 8H, Ph), 5.96 (m, 1H, 12-H), 5.78 (s, 1H, 2-H), 5.08 (s, 1H, 20-H), 5.07 (d, $J = 17.2$ Hz, 1H, 18-H), 4.99 (s, 1H, 20-H), 4.96 (d, $J = 10.6$ Hz, 1H, 18-H), 4.95 (d, $J = 10.8$ Hz, 1H, Bn), 4.94 (m, 1H, 10-H), 4.79 (d, $J = 10.8$ Hz, 1H, Bn), 4.75 (d, $J = 10.9$ Hz, 1H, Bn), 4.53 (d, $J = 10.9$ Hz, 1H, Bn), 4.25 (br m, 1H, 9-H or 11-H), 3.78 (br m, 1H, 11-H or 9-H), 3.57 (m, 1H, 7-H), 3.50 (br m, 1H, 13-H), 2.49 (br m, 1H, 13-H), 2.46 (br m, 1H, 3-H), 2.22–1.54 (m, 6H, 5-H, 5-H, 6-H, 6-H, 14-H, 14-H), 1.63 (s, 3H, Me), 1.56 (s, 3H, Me), 1.44 (s, 3H, Me), 1.30 (s, 3H, Me), 1.17 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 144.6$ (4), 140.1 (12), 138.8 (Ph), 138.3 (Ph), 129.2 (Ph), 129.1 (Ph), 129.0 (Ph), 129.0 (Ph), 128.2 (Ph), 128.2 (Ph), 114.8 (20), 113.8 (18), 99.1 (acetonide), 79.1, 79.0, 79.0, 78.9, 77.5 (1, 2, 9, 10, 11), 77.5 (7), 77.1 (Bn), 74.3 (Bn), 46.3 (3), 45.5 (8), 45.5 (15), 36.3 (14), 32.7 (5), 30.0 (Me), 30.0 (Me), 29.0 (6), 27.6 (13), 25.8 (Me), 19.3 (Me), 11.2 (19); HR MS: calcd for $C_{37}H_{51}O_6$ $[M+H]^+$ 591.3686, found 591.3698.

(1*S*,2*S*,3*S*,4*R*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(3-butenyl)-4,6-(cyclohexylmethylsilylenedioxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecane (**52a**): To a solution of diol **51** (27.7 mg, 46.9 μmol) and imidazole (319 mg, 4.69 mmol) in DMF (5.2 mL) at 0 °C was added dichlorocyclohexylmethylsilane (0.15 mL, 0.829 mmol). The reaction mixture was stirred for 15 min at room temperature and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford silylene **52a** (33.1 mg, 99%) as a colorless oil: $[\alpha]_D^{28} = +23.8$ (*c* 1.04, benzene); IR (neat): $\tilde{\nu} = 2920$, $2850\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.65-7.52$ (m, 4H, Ph), 7.30–7.06 (m, 6H, Ph), 6.14 (s, 1H, 20-H), 6.02 (dddd, $J = 17.2$, 10.2, 9.6, 6.9 Hz, 1H, 12-H), 5.17 (dd, $J = 17.2$, 0.4 Hz, 1H, 18-H), 5.07 (d, $J = 11.9$ Hz, 1H, Bn), 5.06 (dd, $J = 9.6$, 0.4 Hz, 1H, 18-H), 5.02 (d, $J = 11.6$ Hz, 1H, Bn), 4.99 (s, 1H, 20-H), 4.99 (s, 1H, 2-H), 4.92 (d, $J = 11.6$ Hz, 1H, Bn), 4.76 (d, $J = 11.9$ Hz, 1H, Bn), 4.28 (d, $J = 9.1$ Hz, 1H, 10-H), 4.23 (s, 1H, 9-H), 3.95 (d, $J = 9.1$ Hz, 1H, 11-H), 3.56 (dd, $J = 10.7$, 4.1 Hz, 1H, 7-H), 3.12–2.93 (m, 1H, 13-H), 2.88–2.70 (m, 1H, 13-H), 2.70 (s, 1H, 3-H), 2.18–1.51 (m, 17H, 5-H, 5-H, 6-H, 6-H, 14-H, 14-H, *c*Hex), 1.83 (s, 3H, Me), 1.55 (s, 3H, Me), 1.52 (s, 3H, Me), 1.28 (s, 3H, Me), 1.16 (s, 3H, Me), 0.41 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 141.5$ (4), 142.2 (12), 141.3 (Ph), 140.2 (Ph), 130.8 (Ph), 130.0 (Ph), 129.9 (Ph), 129.8 (Ph), 128.5 (Ph), 128.5 (Ph), 116.6 (18), 115.1 (20), 100.5 (acetonide), 89.1 (1), 88.0 (2), 85.1 (10), 84.2 (11), 80.1 (7), 79.3 (Bn), 77.0 (Bn), 75.6 (9), 48.7 (15), 47.5 (8), 46.3 (3), 39.1 (14), 33.1, 32.7, 32.0, 31.2, 30.1, 29.5, 29.2, 29.0, 28.7, 28.5, 29.5, 28.4,

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21.1 (5, 6, 13, 16, 17, acetonide, *c*Hex), 13.9 (19), 0.0 (Me); HR MS: calcd for $C_{44}H_{62}O_6SiNa$ $[M+Na]^+$ 737.4213, found 737.4226.

(1*S*,2*S*,3*S*,4*R*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(3-butenyl)-4,6-(dicyclohexylsilylenedioxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecane (52b): To a suspension of silver trifluoromethanesulfonate (1.08 g, 4.19 mmol) in toluene (10.4 mL) at 0 °C was added dichlorodicyclohexylsilane (0.5 mL, 2.08 mmol). The reaction mixture was stirred for 15 min at room temperature and then it was allowed to stand. The clear solution of dicyclohexylsilyl bis(trifluoromethanesulfonate) in toluene (0.2 M) was instantly used in the following reaction without further purification.

To a solution of diol **51** (74.1 mg, 0.125 mmol) in pyridine (12 mL) at 0 °C was added a solution of dicyclohexylsilyl bis(trifluoromethanesulfonate) in toluene (0.2 M, 9.0 mL, 1.8 mmol). The reaction mixture was stirred for 15 min at 0 °C, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford silylene **52b** (98.2 mg, 100 %) as a colorless oil: $[\alpha]_D^{29} = +0.3$ (*c* 1.30, benzene); IR (neat): $\tilde{\nu} = 2920$, 2850 cm^{-1}; ^1H NMR (C_6D_6): $\delta = 7.65-7.52$ (m, 4H, Ph), 7.30–7.06 (m, 6H, Ph), 6.14 (dddd, $J = 17.2$, 10.2, 9.6, 6.9 Hz, 1H, 12-H), 6.07 (s, 1H, 20-H), 5.33 (dd, $J = 17.2$, 0.4 Hz, 1H, 18-H), 5.29 (d, $J = 11.6$ Hz, 1H, Bn), 5.23 (d, $J = 11.9$ Hz, 1H, Bn), 5.12 (dd, $J = 9.6$, 0.4 Hz, 1H, 18-H), 5.10 (s, 1H, 20-H), 5.02 (d, $J = 11.6$ Hz, 1H, Bn), 4.92 (s, 1H, 20-H), 4.88 (d, $J = 11.9$ Hz, 1H, Bn), 4.25 (d, $J = 9.1$ Hz, 1H, 10-H), 4.22 (s, 1H, 9-H), 3.99 (d, $J = 9.1$ Hz, 1H, 11-H), 3.56 (dd, $J = 10.7$, 4.1 Hz, 1H, 7-H), 3.29–3.09 (m, 1H, 13-H), 2.92–2.74 (m, 1H, 13-H), 2.79 (s, 1H, 3-H), 2.18–1.51 (m, 28H, 5-H, 6-H, 6-H, 14-H, 14-H, *c*Hex, *c*Hex), 1.88 (s, 3H, Me), 1.50 (s, 3H, Me), 1.42 (s, 3H, Me), 1.22 (s, 3H, Me), 1.21 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta =$ 143.9 (4), 141.1 (12), 139.9 (Ph), 139.5 (Ph), 128.7 (Ph), 128.7 (Ph), 127.7 (Ph), 126.9 (Ph), 126.0 (Ph), 126.0 (Ph), 115.0 (18), 114.2 (20), 99.3 (acetonide), 87.2 (1), 85.6 (2), 83.9 (10), 82.9 (11), 78.8 (7), 77.6 (Bn), 75.7 (Bn), 72.9 (9), 47.3 (15), 46.2 (8), 45.3 (3), 38.0 (14), 32.0, 31.9, 31.0, 30.3, 30.1, 29.2, 29.0, 28.8, 28.4, 28.1, 27.7, 27.7, 27.7, 27.6, 27.6, 27.5, 26.5, 26.3, 20.0 (5, 6, 13, 16, 17, acetonide, *c*Hex, *c*Hex), 13.3 (19); HR MS: calcd for $C_{49}H_{70}O_6SiNa$ $[M+Na]^+$ 805.4839, found 805.4823.

(1*S*,2*S*,3*S*,4*R*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(3-butenyl)-4,6-(*tert*-butylmethylsilylenedioxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecane (52c): To a suspension of silver trifluoromethanesulfonate (257 mg, 1.00 mmol) in toluene (3.5 mL) at 0 °C was added *tert*-butyldichloromethylsilane (85.6 mg, 0.500 mmol) in toluene (1.5 mL). The reaction mixture was stirred for 15 min at room temperature and then it was allowed to stand. The clear solution of *tert*-butylmethylsilyl bis(trifluoromethanesulfonate) in toluene (0.2 M) was instantly used in the following reaction without further purification.

To a solution of diol **51** (17.4 mg, 29.5 μmol) in pyridine (4.5 mL) at 0 °C was added a solution of *tert*-butylmethylsilyl bis(trifluoromethanesulfonate) in toluene (0.2 M, 3.5 mL, 0.7 mmol). The reaction mixture was stirred for 40 min at 0 °C and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford silylene **52c** (20.0 mg, 100 %) as a colorless oil: $[\alpha]_D^{26} = +29.2$ (*c* 1.47, benzene); IR (neat): $\tilde{\nu} =$ 2940, 2870 cm^{-1}; ^1H NMR (C_6D_6): $\delta = 7.58-7.42$ (m, 4H, Ph), 7.22–6.99 (m, 6H, Ph), 6.03 (d, $J = 2.2$ Hz, 1H, 20-H), 5.98 (dddd, $J = 17.1$, 10.3, 10.1, 6.8 Hz, 1H, 12-H), 5.11 (ddd, $J = 17.1$, 2.2, 1.5 Hz, 1H, 18-H), 5.00 (d, $J =$ 11.7 Hz, 1H, Bn), 4.96 (dd, $J = 10.3$, 2.2 Hz, 1H, 18-H), 4.94 (s, 1H, 2-H), 4.92 (d, $J = 11.9$ Hz, 1H, Bn), 4.90 (d, $J = 2.2$ Hz, 1H, 20-H), 4.81 (d, $J =$ 11.7 Hz, 1H, Bn), 4.64 (d, $J = 11.9$ Hz, 1H, Bn), 4.19 (d, $J = 9.1$ Hz, 1H, 10-H), 4.17 (s, 1H, 9-H), 3.90 (d, $J = 9.1$ Hz, 1H, 11-H), 3.49 (dd, $J = 10.7$, 4.1 Hz, 1H, 7-H), 3.04–2.87 (m, 1H, 5-H), 2.80–2.66 (m, 1H, 13-H), 2.66 (s, 1H, 3-H), 2.17–1.65 (m, 4H, 5-H, 6-H, 13-H, 14-H), 1.76 (s, 3H, Me), 1.59–1.24 (m, 2H, 6-H, 14-H), 1.49 (s, 3H, Me), 1.45 (s, 3H, Me), 1.20 (s, 3H, Me), 1.18 (s, 9H, *t*Bu), 1.09 (s, 3H, Me), 0.43 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 144.0$ (4), 141.2 (12), 140.2 (Ph), 139.3 (Ph), 129.7 (Ph), 128.5 (Ph), 128.5 (Ph), 128.1 (Ph), 127.4 (Ph), 127.2 (Ph), 115.4 (18), 114.0 (20), 99.4 (acetonide), 87.5 (1), 87.2 (2), 84.4 (10), 83.1 (11), 79.0 (7), 78.3 (Bn), 76.0 (Bn), 73.7 (9), 46.7 (15), 46.3 (8), 45.0 (3), 37.6 (14), 32.0, 31.9, 31.9, 30.2, 28.6, 27.8, 27.6, 21.0, 20.1 (5, 6, 13, 16, 17, acetonide, *t*Bu), 13.1 (19), 0.0 (Me); HR MS: calcd for $C_{42}H_{60}O_6SiNa$ $[M+Na]^+$ 711.4057, found 711.4043.

(1*S*,2*S*,3*R*,4*R*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(3-butenyl)-6-(cyclohexyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-ol (53a): To a solution of silylene **52a** (76.5 mg, 0.107 mmol) in THF (12 mL) and HMPA (1.6 mL) at −78 °C was added methyllithium in diethyl ether (1.01 M, 2.1 mL, 2.08 mmol). The reaction mixture was stirred for 30 min at −78 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford alcohol **53a** (75.0 mg, 96 %) as a colorless oil: $[\alpha]_D^{27} = +14.8$ (*c* 3.75, benzene); IR (neat): $\tilde{\nu} = 3540$ cm^{-1}; ^1H NMR (C_6D_6): $\delta = 7.61-7.15$ (m, 10H, Ph), 5.99 (dddd, $J = 17.2$, 13.0, 10.3, 6.3 Hz, 1H, 12-H), 5.27 (dd, $J =$ 17.2, 1.6 Hz, 1H, 18-H), 5.21–5.01 (br m, 5H, 18-H, 20-H, 20-H, Bn, Bn), 5.01–4.49 (br m, 4H, 2-H, 11-H, Bn, Bn), 4.46–4.22 (br m, 1H, 10-H), 3.81–3.49 (br m, 2H, 7-H, 9-H), 3.04–2.79 (br m, 1H, 5-H), 2.77–2.35 (br m, 2H, 3-H, 5-H), 2.35–0.65 (br m, 17H, 6-H, 6-H, 13-H, 13-H, 14-H, 14-H, *c*Hex), 1.74 (s, 3H, Me), 1.66 (s, 3H, Me), 1.56 (s, 3H, Me), 1.43 (s, 3H, Me), 1.25 (s, 3H, Me), 0.33 (s, 3H, Me), 0.13 (s, 3H, Me); ^{13}C NMR (C_6D_6): very broadened spectra; HR MS: calcd for $C_{45}H_{66}O_6SiNa$ $[M+Na]^+$ 753.4526, found 753.4534.

(1*S*,2*S*,3*R*,4*R*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(3-butenyl)-6-(dicyclohexylmethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-ol (53b): To a solution of silylene **52b** (62.0 mg, 79.2 μmol) in THF (14 mL) and HMPA (1.54 mL) at −78 °C was added methyllithium in diethyl ether (1.01 M, 4.31 mL, 4.36 mmol). The reaction mixture was stirred for 3 h at −45 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford alcohol **53b** (60.7 mg, 96 %) as a colorless oil: $[\alpha]_D^{27} = +21.4$ (*c* 1.32, benzene); IR (neat): $\tilde{\nu} = 3550$ cm^{-1}; ^1H NMR (C_6D_6): $\delta = 7.51-6.87$ (m, 10H, Ph), 5.96–5.73 (m, 1H, 12-H), 5.24–4.61 (br m, 12H, 2-H, 9-H, 10-H, 11-H, 18-H, 18-H, 20-H, 20-H, Bn, Bn, Bn, Bn), 4.35–4.15 (br m, 1H, 7-H), 3.65–3.46 (br m, 1H, 5-H), 2.69–0.75 (br m, 30H, 3-H, 5-H, 6-H, 6-H, 13-H, 13-H, 14-H, 14-H, *c*Hex, *c*Hex), 1.63 (s, 3H, Me), 1.63 (s, 3H, Me), 1.51 (s, 3H, Me), 1.50 (s, 3H, Me), 1.28 (s, 3H, Me), 0.19 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 145.0$ (4), 140.0 (12), 139.2 (Ph), 139.0 (Ph), 129.0 (Ph), 128.9 (Ph), 128.6 (Ph) 127.2 (Ph), 126.9 (Ph), 126.7 (Ph), 115.5 (18), 114.5 (20), 99.1 (acetonide), 87.2 (1), 87.2 (2), 77.4 (10), 77.2 (Bn), 77.1 (Bn), 76.9 (11), 74.1 (9), 60.0 (7), 47.0 (15), 44.9 (14), 34.7 (8), 34.7 (3), 30.1, 30.1, 29.4, 29.0, 29.0, 29.0, 28.9, 28.8, 28.6, 28.6; 28.4, 28.4, 28.1, 27.9, 27.7, 27.5, 27.5, 20.5, 19.5 (5, 6, 13, 16, 17, acetonide, *c*Hex, *c*Hex), 14.2 (19), −2.5 (Me); HR MS: calcd for $C_{50}H_{74}O_6SiNa$ $[M+Na]^+$ 821.5152, found 821.5158.

(1*S*,2*S*,3*R*,4*R*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(3-butenyl)-6-(*tert*-butyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-ol (53c): To a solution of silylene **52c** (22.7 mg, 32.9 μmol) in THF (6.0 mL) and HMPA (0.6 mL) at −78 °C was added methyllithium in diethyl ether (1.01 M, 1.5 mL, 1.49 mmol). The reaction mixture was stirred for 40 min at −45 °C and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford alcohol **53c** (22.2 mg, 96 %) as a colorless oil: $[\alpha]_D^{27} = +0.1$ (*c* 1.53, benzene); IR (neat): $\tilde{\nu} = 3530$ cm^{-1}; ^1H NMR (C_6D_6): $\delta = 7.61-7.16$ (m, 10H, Ph), 6.18–5.98 (br m, 1H, 20-H), 5.99 (dddd, $J = 17.2$, 13.0, 10.8, 6.2 Hz, 1H, 12-H), 5.82–5.56 (br m, 1H, 20-H), 5.28 (dd, $J = 17.2$, 1.5 Hz, 1H, 18-H), 5.23–4.52 (br m, 6H, 2-H, 18-H, Bn, Bn, Bn, Bn), 4.51–4.07 (br m, 2H, 10-H, 11-H), 3.87–3.49 (br m, 2H, 7-H, 9-H), 3.06–2.55 (br m, 3H, 3-H, 5-H, 13-H), 2.43–1.99 (br m, 4H, 5-H, 6-H, 13-H, 14-H), 1.87–1.56 (br m, 2H, 6-H, 14-H), 1.76 (s, 3H, Me), 1.67 (s, 3H, Me), 1.62 (s, 3H, Me), 1.43 (s, 3H, Me), 1.29 (s, 3H, Me), 1.11 (s, 9H, TBS), 0.57 (s, 3H, TBS), 0.08 (s, 3H, TBS); ^{13}C NMR (C_6D_6): $\delta = 146.7$ (4), 139.9 (12), 139.6 (Ph), 139.4 (Ph), 128.8 (Ph), 128.8 (Ph), 128.8 (Ph); 128.1 (Ph), 128.1 (Ph), 127.3 (Ph), 115.6 (18), 114.5 (20), 99.3 (acetonide), 87.9 (1), 87.9 (2), 84.8, 83.7, 79.1, 78.3, 77.4, 73.9 (7, 9, 10, 11, Bn, Bn), 52.4, 48.4, 46.6, 43.3 (3, 8, 14, 15), 38.2, 37.8, 34.1, 33.4, 30.4, 26.1, 20.7, 19.8 (5, 6, 13, 16, 17, acetonide, TBS),

27.4 (TBS), 12.3 (19), −0.7 (TBS), −0.9 (TBS); HR MS: calcd for $C_{43}H_{64}O_6SiNa$ $[M+Na]^+$ 727.4370, found 727.4360.

(1*S*,2*S*,3*S*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(3-butenyl)-6-(cyclohexyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-one (50a): To a suspension of alcohol **53a** (19.7 mg, 26.9 μmol), NMO (10.8 mg, 92.2 μmol) and MS 4 Å (45 mg) in dichloromethane (4 mL) at 0 °C was added TPAP (3.0 mg, 8.54 μmol). Acetonitrile (0.8 mL) was added to the reaction mixture at 0 °C, and then the mixture was stirred for 1 h at room temperature. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketone **50a** (15.7 mg, 80 %) as a colorless oil: $[\alpha]_D^{26} = +45.9$ (*c* 1.86, benzene); IR (neat): $\tilde{\nu} = 1670\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.60-7.00$ (m, 10H, Ph), 6.01 (dddd, $J = 17.2$, 10.5, 8.7, 5.8 Hz, 1H, 12-H), 5.34 (dd, $J = 17.2$, 1.6 Hz, 1H, 18-H), 5.16 (dd, $J = 8.7$, 1.6 Hz, 1H, 18-H), 5.14 (d, $J = 12.7$ Hz, 1H, Bn), 5.01 (d, $J = 1.5$ Hz, 1H, 20-H), 4.86 (d, $J = 1.5$ Hz, 1H, 20-H), 4.76 (d, $J = 12.7$ Hz, 1H, Bn), 4.75 (d, $J = 11.0$ Hz, 1H, Bn), 4.63 (s, 1H, 2-H), 4.56 (d, $J = 3.2$ Hz, 1H, 10-H), 4.52 (d, $J = 11.0$ Hz, 1H, Bn), 4.28 (d, $J = 3.2$ Hz, 1H, 9-H), 3.90 (dd, $J = 10.4$, 7.1 Hz, 1H, 7-H), 3.42–3.25 (m, 1H, 13-H), 2.70–2.45 (m, 1H, 13-H), 2.44 (s, 1H, 3-H), 2.35–0.80 (m, 17H, 5-H, 5-H, 6-H, 6-H, 14-H, 14-H, *c*Hex), 1.92 (s, 3H, Me), 1.87 (s, 3H, Me), 1.61 (s, 3H, Me), 1.48 (s, 3H, Me), 1.36 (s, 3H, Me), 0.32 (s, 3H, Me), 0.16 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 215.1$ (11), 147.3 (4), 140.2 (12), 139.4 (Ph), 138.4 (Ph), 128.6 (Ph), 128.6 (Ph), 128.5 (Ph), 128.5 (Ph), 126.7 (Ph), 125.7 (Ph), 114.2 (18), 113.8 (20), 99.7 (acetonide), 93.6 (10), 89.8 (1), 83.5 (2), 80.9 (7), 76.3 (Bn), 74.4 (Bn), 72.9 (9), 57.6 (15), 48.9 (8), 40.6 (3), 30.1 (14), 30.1 (*c*Hex), 29.8 (*c*Hex), 29.0 (5), 28.8 (Me), 28.2 (Me), 27.6 (*c*Hex), 27.6 (13), 27.2 (*c*Hex), 26.2 (*c*Hex), 25.7 (*c*Hex), 22.8 (16), 19.4 (17), 12.8 (19), 0.2 (Me), −1.3 (Me); HR MS: calcd for $C_{45}H_{64}O_6SiNa$ $[M+Na]^+$ 751.4370, found 751.4348.

(1*S*,2*S*,3*S*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(3-butenyl)-6-(dicyclohexylmethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-one (50b): To a suspension of alcohol **53b** (93.4 mg, 0.117 mmol), NMO (20.6 mg, 0.176 mmol) and MS 4 Å (200 mg) in dichloromethane (12 mL) at 0 °C was added TPAP (12.3 mg, 35.1 μmol). Acetonitrile (2.6 mL) was added to the reaction mixture at 0 °C and then the mixture was stirred for 1 h at room temperature. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketone **50b** (85.2 mg, 91 %) as a colorless oil: $[\alpha]_D^{27} = +41.7$ (*c* 1.25, benzene); IR (neat): $\tilde{\nu} = 1670\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.56-6.72$ (m, 10H, Ph), 5.89 (dddd, $J = 17.1$, 9.8, 5.9, 4.9 Hz, 1H, 12-H), 5.21 (d, $J = 17.1$ Hz, 1H, 18-H), 5.07 (d, $J = 13.1$ Hz, 1H, Bn), 5.04 (d, $J = 9.8$ Hz, 1H, 18-H), 4.91 (s, 1H, 20-H), 4.78 (s, 1H, 20-H), 4.70 (d, $J = 13.1$ Hz, 1H, Bn), 4.62 (d, $J = 11.2$ Hz, 1H, Bn), 4.54 (s, 1H, 2-H), 4.41 (d, $J = 2.9$ Hz, 1H, 10-H), 4.40 (d, $J = 11.2$ Hz, 1H, Bn), 4.15 (d, $J = 2.9$ Hz, 1H, 9-H), 3.74 (dd, $J = 10.0$, 7.1 Hz, 1H, 7-H), 3.25–3.06 (m, 1H, 5-H), 2.35 (s, 1H, 3-H), 2.58–0.77 (m, 29H, 5-H, 6-H, 6-H, 13-H, 13-H, 14-H, 14-H, *c*Hex, *c*Hex), 1.82 (s, 3H, Me), 1.72 (s, 3H, Me), 1.46 (s, 3H, Me), 1.42 (s, 3H, Me), 1.22 (s, 3H, Me), 0.16 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 215.0$ (11), 147.2 (4), 140.1 (12), 139.4 (Ph), 138.3 (Ph), 128.6 (Ph), 128.4 (Ph), 128.0 (Ph), 127.8 (Ph), 126.7 (Ph), 125.6 (Ph), 114.2 (18), 114.0 (20), 99.8 (acetonide), 93.4 (10), 90.0 (1), 83.6 (2), 81.4 (7), 76.2 (Bn), 74.3 (Bn), 73.1 (9), 60.0 (15), 57.9 (8), 49.0 (3), 40.7 (14), 30.7, 30.1, 29.8, 29.5, 29.2, 29.1, 28.7, 28.4, 28.2, 28.1, 27.9, 27.4, 27.3, 26.3, 25.8, 23.0, 20.5, 19.4, 14.2 (5, 6, 13, 16, 17, acetonide, *c*Hex, *c*Hex), 12.7 (19), −3.0 (Me); HR MS: calcd for $C_{50}H_{72}O_6SiNa$ $[M+Na]^+$ 819.4996, found 819.5009.

(1*S*,2*S*,3*S*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(3-butenyl)-6-(*tert*-butyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylenebicyclo[6.4.0]dodecan-4-one (50c): To a suspension of alcohol **53c** (22.2 mg, 31.5 μmol), NMO (10.4 mg, 88.8 μmol) and MS 4 Å (60 mg) in dichloromethane (5 mL) at 0 °C was added TPAP (5.0 mg, 14.2 μmol). Acetonitrile (1.0 mL) was added to the reaction mixture at 0 °C and then the mixture was stirred for 45 min at room temperature. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketone **50c** (18.7 mg, 85 %) as a colorless oil: $[\alpha]_D^{27} = +25.2$ (*c* 1.47, benzene); IR (neat): $\tilde{\nu} = 1660\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.51-7.11$ (m, 10H, Ph), 5.95 (dddd, $J = 17.3$, 10.4, 7.5, 5.7 Hz, 1H, 12-H), 5.28 (dd, $J = 17.3$, 1.6 Hz, 1H, 18-H), 5.12 (dd, $J = 10.4$, 1.6 Hz, 1H, 18-H), 5.03 (d, $J = 13.0$ Hz, 1H, Bn), 4.98 (d, $J = 1.5$ Hz, 1H, 20-H), 4.82 (d, $J = 1.5$ Hz, 1H, 20-H), 4.70 (d, $J = 13.0$ Hz, 1H, Bn), 4.67 (d, $J = 11.1$ Hz, 1H, Bn), 4.54 (d, $J = 2.7$ Hz, 1H, 2-H), 4.51 (d, $J = 3.5$ Hz, 1H, 10-H), 4.46 (d, $J = 11.1$ Hz, 1H, Bn), 4.19 (d, $J = 3.5$ Hz, 1H, 9-H), 3.86 (dd, $J = 10.4$, 7.0 Hz, 1H, 7-H), 3.34–3.19 (br m, 1H, 13-H), 2.68–2.31 (m, 2H, 13-H, 14-H), 2.38 (d, $J = 2.7$ Hz, 1H, 3-H), 2.23–1.91 (m, 3H, 5-H, 5-H, 14-H), 1.98 (s, 3H, Me), 1.88–1.51 (m, 2H, 6-H, 6-H), 1.81 (s, 3H, Me), 1.56 (s, 3H, Me), 1.46 (s, 3H, Me), 1.31 (s, 3H, Me), 1.04 (s, 9H, TBS), 0.29 (s, 3H, TBS), 0.09 (s, 3H, TBS); ^{13}C NMR (C_6D_6): $\delta = 215.3$ (11), 147.6 (4), 140.3 (12), 139.5 (Ph), 138.6 (Ph), 128.8 (Ph), 128.8 (Ph), 128.6 (Ph), 127.6 (Ph), 126.9 (Ph), 125.7 (Ph), 114.4 (18), 114.1 (20), 99.8 (acetonide), 94.1 (10), 89.9 (1), 83.5 (2), 81.3 (7), 76.5 (Bn), 74.7 (Bn), 72.8 (9), 57.9 (15), 49.6 (8), 40.7 (3), 30.3 (14), 29.8 (5), 28.9 (6), 27.1 (TBS), 26.2, 25.5, 22.5, 20.5, 19.6 (13, 16, 17, acetonide), 15.7 (TBS), 13.2 (19), −0.7 (TBS), −1.5 (TBS); HR MS: calcd for $C_{43}H_{62}O_6SiNa$ $[M+Na]^+$ 725.4213, found 725.4197.

(1*S*,2*S*,3*S*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(cyclohexyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylene-6-(3-oxobutyl)bicyclo[6.4.0]dodecan-4-one (54a): To a solution of ketone **50a** (11.6 mg, 15.5 μmol) in DMF (4.2 mL) and water (0.6 mL) at 0 °C was added palladium(II) chloride (10.8 mg, 60.9 μmol). The reaction mixture was stirred for 3.5 h at room temperature and then phosphate buffer (pH = 7) was added at 0 °C. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diketone **54a** (11.3 mg, 98 %) as a colorless oil: $[\alpha]_D^{29} = +59.3$ (*c* 1.32, benzene); IR (neat): $\tilde{\nu} = 1720$, $1680\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.52-7.42$ (m, 2H, Ph), 7.34–7.08 (m, 8H, Ph), 5.02 (d, $J = 12.8$ Hz, 1H, Bn), 4.82 (d, $J = 1.8$ Hz, 1H, 20-H), 4.68 (d, $J = 12.8$ Hz, 1H, Bn), 4.66 (d, $J = 11.4$ Hz, 1H, Bn), 4.59 (d, $J = 1.8$ Hz, 1H, 20-H), 4.53 (d, $J = 2.5$ Hz, 1H, 2-H), 4.46 (d, $J = 3.2$ Hz, 1H, 10-H), 4.43 (d, $J = 11.4$ Hz, 1H, Bn), 4.18 (d, $J = 3.2$ Hz, 1H, 9-H), 3.75 (m, 1H, 7-H), 3.63 (m, 1H, 13-H), 2.83 (m, 1H, 13-H), 2.32 (d, $J = 2.5$ Hz, 1H, 3-H), 2.69–0.72 (m, 17H, 5-H, 5-H, 6-H, 6-H, 14-H, 14-H, *c*Hex), 1.96 (s, 3H, 18-Me), 1.79 (s, 3H, Me), 1.78 (s, 3H, Me), 1.54 (s, 3H, Me), 1.29 (s, 3H, Me), 1.15 (s, 3H, Me), 0.09 (s, 3H, Me), 0.03 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 214.8$ (11), 207.0 (12), 148.1 (4), 140.4 (Ph), 138.5 (Ph), 128.8 (Ph), 127.9 (Ph), 127.1 (Ph), 125.9 (Ph), 125.9 (Ph), 125.9 (Ph), 113.6 (20), 100.0 (acetonide), 93.6 (1), 89.7 (10), 83.7 (2), 81.1 (7), 76.5 (Bn), 74.5 (Bn), 73.0 (9), 57.7 (15), 48.9 (13), 41.1 (8), 40.8 (3), 30.3, 30.2, 29.1, 29.1, 28.4, 28.4, 27.8, 27.8, 27.4, 26.4, 25.8, 25.8, 23.0, 19.7 (5, 6, 14, 16, 17, 18, acetonide, *c*Hex), 12.9 (19), 0.6 (Me), −0.9 (Me); HR MS: calcd for $C_{45}H_{64}O_7SiNa$ $[M+Na]^+$ 767.4319, found 767.4345.

(1*S*,2*S*,3*S*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(dicyclohexylmethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylene-6-(3-oxobutyl)bicyclo[6.4.0]dodecan-4-one (54b): To a solution of ketone **50b** (4.3 mg, 5.4 μmol) in DMF (1.8 mL) and water (0.25 mL) at 0 °C was added palladium(II) chloride (6.3 mg, 35.5 μmol). The reaction mixture was stirred for 2.5 h at room temperature and then phosphate buffer (pH = 7) was added at 0 °C. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diketone **54b** (4.3 mg, 98 %) as a colorless oil: $[\alpha]_D^{28} = +43.0$ (*c* 0.85, benzene); IR (neat): $\tilde{\nu} = 1720$, $1680\ cm^{-1}$; ^1H NMR (C_6D_6): $\delta = 7.40-7.02$ (m, 10H, Ph), 5.03 (d, $J = 13.1$ Hz, 1H, Bn), 4.80 (s, 1H, 20-H), 4.69 (d, $J = 13.1$ Hz, 1H, Bn), 4.63 (s, 1H, 20-H), 4.61 (d, $J = 11.1$ Hz, 1H, Bn), 4.52 (s, 1H, 2-H), 4.39 (d, $J = 3.0$ Hz, 1H, 10-H), 4.37 (d, $J = 11.1$ Hz, 1H, Bn), 4.13 (d, $J = 3.0$ Hz, 1H, 9-H), 3.68 (dd, $J = 9.6$, 6.8 Hz, 1H, 7-H), 3.64–3.48 (m, 1H, 13-H), 2.91–2.74 (m, 1H, 13-H), 2.69–2.55 (m, 1H, 5-H), 2.50–2.33 (m, 1H, 5-H), 2.30 (s, 1H, 3-H), 2.17–0.73 (m, 26H, 6-H, 6-H, 14-H, 14-H, *c*Hex, *c*Hex), 1.91 (s, 3H, 18-Me), 1.77 (s, 3H, Me), 1.69 (s, 3H, Me), 1.46 (s, 3H, Me), 1.39 (s, 3H, Me), 1.24 (s, 3H, Me), 0.10 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): very broadened spectra; HR MS: calcd for $C_{50}H_{72}O_7SiNa$ $[M+Na]^+$ 835.4945, found 835.4917.

(1*S*,2*S*,3*S*,6*S*,7*S*,8*R*,12*S*)-3,7-Dibenzyloxy-6-(*tert*-butyldimethylsiloxy)-2,12-(isopropylidenedioxy)-1,5,5-trimethyl-9-methylene-6-(3-oxobutyl)bicyclo[6.4.0]dodecan-4-one (54c): To a solution of ketone **50c** (4.4 mg, 6.3 μmol) in DMF (1.4 mL) and water (0.2 mL) at 0 °C was added palladium(II) chloride (5.0 mg, 28.2 μmol). The reaction mixture was stirred for 4 h at room temperature and then phosphate buffer (pH = 7) was added at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diketone **54c** (4.1 mg,

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91 %) as a colorless oil: $[\alpha]_D^{26} = +29.5$ (*c* 1.36, benzene); IR (neat): $\tilde{\nu} = 1710$, 1670 cm^{-1}; ^1H NMR (C_6D_6): **conformer A** $\delta = 7.40-7.02$ (m, 10H, Ph), 4.90 (d, $J = 12.8$ Hz, 1H, Bn), 4.76 (s, 1H, 20-H), 4.59 (d, $J = 12.8$ Hz, 1H, Bn), 4.56 (d, $J = 10.9$ Hz, 1H, Bn), 4.52 (d, $J = 1.8$ Hz, 1H, 2-H), 4.42 (s, 1H, 20-H), 4.40 (d, $J = 3.4$ Hz, 1H, 10-H), 4.34 (d, $J = 10.9$ Hz, 1H, Bn), 4.08 (d, $J = 3.4$ Hz, 1H, 9-H), 3.70 (dd, $J = 10.4$, 7.0 Hz, 1H, 7-H), 3.68–3.52 (m, 1H, 13-H), 2.90–2.32 (m, 2H, 5-H, 13-H), 2.30 (d, $J = 1.8$ Hz, 1H, 3-H), 2.17–1.80 (m, 3H, 5-H, 6-H, 14-H), 1.86 (s, 3H, 18-Me), 1.76–1.25 (m, 2H, 6-H, 14-H), 1.69 (s, 3H, Me), 1.47 (s, 3H, Me), 1.35 (s, 3H, Me), 1.29 (s, 3H, Me), 1.23 (s, 3H, Me), 0.91 (s, 9H, TBS), 0.11 (s, 3H, TBS), −0.03 (s, 3H, TBS); **conformer B** $\delta = 7.40-7.02$ (m, 10H, Ph), 5.03 (d, $J = 12.3$ Hz, 1H, Bn), 4.92 (s, 1H, 20-H), 4.88 (d, $J = 12.3$ Hz, 1H, Bn), 4.70 (d, $J = 10.9$ Hz, 1H, Bn), 4.45 (d, $J = 10.9$ Hz, 1H, Bn), 4.41 (d, $J = 2.7$ Hz, 1H, 2-H), 4.40 (s, 1H, 20-H), 4.38 (d, $J = 2.1$ Hz, 1H, 10-H), 4.14 (d, $J = 2.1$ Hz, 1H, 9-H), 3.87 (dd, $J = 13.9$, 7.3 Hz, 1H, 7-H), 3.65–3.59 (m, 1H, 13-H), 2.90–2.32 (m, 2H, 5-H, 13-H), 2.25 (d, $J = 2.7$ Hz, 1H, 3-H), 2.17–1.80 (m, 3H, 5-H, 6-H, 14-H), 1.84 (s, 3H, 18-Me), 1.76–1.25 (m, 2H, 6-H, 14-H), 1.68 (s, 3H, Me), 1.58 (s, 3H, Me), 1.44 (s, 3H, Me), 1.29 (s, 3H, Me), 1.28 (s, 3H, Me), 0.96 (s, 9H, TBS), 0.33 (s, 3H, TBS), 0.15 (s, 3H, TBS); ^{13}C NMR (C_6D_6): **conformer A** $\delta = 214.8$ (11), 207.0 (12), 148.3 (4), 140.3 (Ph), 138.6 (Ph), 128.8 (Ph), 128.8 (Ph), 128.8 (Ph), 128.6 (Ph), 128.6 (Ph), 125.7 (Ph), 113.6 (20), 99.9 (acetonide), 94.0 (1), 89.7 (10), 83.4 (2), 81.3 (7), 76.6 (Bn), 74.6 (Bn), 72.7 (9), 57.8 (15), 49.4 (13), 41.1 (8), 40.7 (3), 30.3 (5), 30.2 (6), 29.0 (14), 27.1 (TBS), 26.3, 25.4, 22.5, 20.4, 19.7 (16, 17, 18, acetonide), 15.8 (TBS), 13.2 (19), −0.6 (TBS), −1.1 (TBS); **conformer B** $\delta = 215.4$ (11), 205.6 (12), 148.3 (4), 138.1 (Ph), 134.2 (Ph), 129.1 (Ph), 128.6 (Ph), 128.4 (Ph), 127.3 (Ph), 127.1 (Ph), 126.9 (Ph), 113.6 (20), 100.0 (acetonide), 93.5 (1), 87.6 (10), 84.3 (2), 81.7 (7), 76.2 (Bn), 75.8 (Bn), 66.1 (9), 59.4 (15), 46.5 (13), 42.3 (8), 41.0 (3), 32.0 (5), 29.8 (6), 27.6 (TBS), 27.4, 25.3, 24.9, 24.0, 20.5, 19.8 (14, 16, 17, 18, acetonide), 15.8 (TBS), 9.8 (19), 0.3 (TBS), −1.0 (TBS); HR MS: calcd for $C_{43}H_{62}O_7SiNa$ $[M+Na]^+$ 741.4163, found 741.4135.

(4*S*,4a*S*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-6,12-Dibenzyloxy-11-(cyclohexyldimethylsiloxy)-4,5-(isopropylidenedioxy)-4a,8,13,13-tetramethyl-1-methylenetetradecahydro-7,11-methanobenzocyclodecene-7,8-diol (55a): Titanium(II) chloride was prepared from titanium(IV) chloride and hexamethyldisilane by the procedure of Paul et al.[34] To the suspension of titanium(II) chloride thus obtained (70.0 mg, 0.589 mmol) in THF (1.47 mL) at 0 °C was added lithium aluminum hydride in THF (1.0 M, 0.13 mL, 0.13 mmol). The reaction mixture was refluxed for 20 min and then THF (0.5 mL) was added at room temperature. The suspension of low-valent titanium in THF (0.2 M) thus prepared was immediately used in the following reaction.

To a solution of diketone **54a** (2.8 mg, 3.8 μmol) in THF (1.5 mL) at 40 °C was added the suspension of low-valent titanium in THF (0.2 M, 0.4 mL, 0.080 mmol). The reaction mixture was stirred for 20 min at 40 °C and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was stirred for 10 min at room temperature and then it was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diol **55a** (2.0 mg, 71 %) as a colorless oil: $[\alpha]_D^{25} = +24.3$ (*c* 0.66, benzene); IR (neat): $\tilde{\nu} = 3570$ cm^{-1}; ^1H NMR (C_6D_6): $\delta = 7.48-7.14$ (m, 10H, Ph), 5.33 (d, $J = 12.9$ Hz, 1H, 10-Bn), 5.09 (s, 1H, 20-H-endo), 4.96 (s, 1H, 20-H-exo), 4.92 (d, $J = 13.6$ Hz, 1H, 2-Bn), 4.52 (d, $J = 13.6$ Hz, 1H, 2-Bn), 4.51 (d, $J = 12.9$ Hz, 1H, 10-Bn), 4.30 (d, $J = 4.5$ Hz, 1H, 2-H), 4.02 (d, $J = 1.5$ Hz, 1H, 9-H), 3.83 (d, $J = 1.5$ Hz, 1H, 10-H), 3.69 (dd, $J = 9.0$, 7.5 Hz, 1H, 7-H), 3.14 (s, 1H, 11-OH), 3.12 (d, $J = 4.5$ Hz, 1H, 3-H), 2.89 (s, 1H, 12-OH), 2.64–0.79 (m, 19H, 5-H, 5-H, 6-H, 6-H, 13-H, 13-H, 14-H, 14-H, *c*Hex), 1.66 (s, 3H, Me), 1.51 (s, 3H, Me), 1.40 (s, 3H, Me), 1.34 (s, 3H, Me), 1.22 (s, 3H, Me), 0.93 (s, 3H, Me), 0.26 (s, 6H, Me, Me); ^{13}C NMR (C_6D_6): $\delta = 146.5$ (4), 140.8 (Ph), 139.4 (Ph), 129.1 (Ph), 128.7 (Ph), 128.4 (Ph), 128.1 (Ph), 127.1 (Ph), 126.7 (Ph), 112.3 (20), 99.0 (acetonide), 93.9 (11), 83.2 (9), 82.5 (1), 81.1 (10), 79.8 (10-Bn), 77.2 (2), 74.4 (2-Bn), 73.0 (12), 73.0 (7), 51.3, 46.4, 40.8, 37.6, 30.4, 29.6, 29.3, 29.0, 28.8, 28.5, 28.0, 27.9, 27.7, 27.7, 27.6, 26.4, 23.5, 22.1 (3, 5, 6, 8, 13, 14, 15, 16, 17, 18, acetonide, *c*Hex), 19.2 (19), 0.4 (Me), −0.2 (Me); HR MS: calcd for $C_{45}H_{66}O_7SiNa$ $[M+Na]^+$ 769.4476, found 769.4496.

(4*S*,4a*S*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-6,12-Dibenzyloxy-11-(dicyclohexylmethylsiloxy)-4,5-(isopropylidenedioxy)-4a,8,13,13-tetramethyl-1-methylenetetradecahydro-7,11-methanobenzocyclodecene-7,8-diol (55b): To a solution of diketone **54b** (6.5 mg, 8.0 μmol) in THF (2.96 mL) at 45 °C was added the suspension of low-valent titanium in THF (0.2 M, 0.96 mL, 0.192 mmol). The reaction mixture was stirred for 5 min at 45 °C and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was stirred for 10 min at room temperature and then it was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diol **55b** (4.1 mg, 63 %) as a colorless oil: $[\alpha]_D^{26} = +49.7$ (*c* 1.57, benzene); IR (neat): $\tilde{\nu} = 3560$ cm^{-1}; ^1H NMR (C_6D_6): $\delta = 7.46-7.13$ (m, 10H, Ph), 5.32 (d, $J = 11.6$ Hz, 1H, 10-Bn), 5.15 (s, 1H, 20-H-endo), 5.02 (s, 1H, 20-H-exo), 4.92 (d, $J = 12.5$ Hz, 1H, 2-Bn), 4.53 (d, $J = 12.5$ Hz, 1H, 2-Bn), 4.51 (d, $J = 11.6$ Hz, 1H, 10-Bn), 4.36 (d, $J = 3.6$ Hz, 1H, 2-H), 4.03 (d, $J = 1.4$ Hz, 1H, 9-H), 3.86 (d, $J = 1.4$ Hz, 1H, 10-H), 3.71 (dd, $J = 9.9$, 7.3 Hz, 1H, 7-H), 3.16 (s, 1H, 11-OH), 3.15 (d, $J = 3.6$ Hz, 1H, 3-H), 2.88 (s, 1H, 12-OH), 2.65–0.80 (m, 30H, 5-H, 5-H, 6-H, 6-H, 13-H, 13-H, 14-H, 14-H, *c*Hex, *c*Hex), 1.68 (s, 3H, 17-Me), 1.66 (s, 3H, 19-Me), 1.54 (s, 3H, 16-Me), 1.51 (s, 3H, acetonide-*β*), 1.33 (s, 3H, 18-Me), 1.24 (s, 3H, acetonide-*α*), 0.32 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 146.2$ (4), 140.5 (Ph), 139.2 (Ph), 129.1 (Ph), 128.9 (Ph), 128.8 (Ph), 128.5 (Ph), 126.9 (Ph), 126.6 (Ph), 112.4 (20), 98.8 (acetonide), 94.8 (10), 83.2 (11), 82.4 (1), 80.8 (9), 79.6 (10-Bn), 77.4 (2), 74.2 (2-Bn), 72.8 (12), 72.7 (7), 51.5 (8), 46.3 (3), 40.8 (15), 37.4 (13), 30.2 (acetonide-*β*), 30.2 (5), 29.3 (14), 29.2 (*c*Hex), 29.0 (17), 29.0 (*c*Hex), 29.0 (*c*Hex), 28.8 (*c*Hex), 28.8 (*c*Hex), 28.7 (*c*Hex), 28.6 (*c*Hex), 28.3 (*c*Hex), 28.0 (*c*Hex), 27.6 (18), 27.6 (*c*Hex), 27.6 (*c*Hex), 27.5 (*c*Hex), 26.3 (6), 23.4 (16), 19.0 (acetonide-*α*), 11.0 (19), −2.9 (Me); HR MS: calcd for $C_{50}H_{74}O_7SiNa$ $[M+Na]^+$ 837.5102, found 837.5084.

(4*S*,4a*S*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-6,12-Dibenzyloxy-11-(*tert*-butyldimethylsiloxy)-4,5-(isopropylidenedioxy)-4a,8,13,13-tetramethyl-1-methylenetetradecahydro-7,11-methanobenzocyclodecene-7,8-diol (55c): To a solution of diketone **54c** (6.3 mg, 8.8 μmol) in THF (2.9 mL) at 35 °C was added the suspension of low-valent titanium in THF (0.2 M, 0.90 mL, 0.180 mmol). The reaction mixture was stirred for 5 min at 35 °C, and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was stirred for 10 min at room temperature and then extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diol **55c** (3.3 mg, 52 %) as a colorless oil: $[\alpha]_D^{26} = +20.2$ (*c* 0.82, benzene); IR (neat): $\tilde{\nu} = 3590$ cm^{-1}; ^1H NMR (C_6D_6): $\delta = 7.39-7.07$ (m, 10H, Ph), 5.21 (d, $J = 11.4$ Hz, 1H, 10-Bn), 5.06 (s, 1H, 20-H-endo), 4.98 (s, 1H, 20-H-exo), 4.92 (d, $J = 12.7$ Hz, 1H, 2-Bn), 4.54 (d, $J = 12.7$ Hz, 1H, 2-Bn), 4.47 (d, $J = 11.4$ Hz, 1H, 10-Bn), 4.33 (d, $J = 3.6$ Hz, 1H, 2-H), 3.95 (d, $J = 1.2$ Hz, 1H, 9-H), 3.79 (d, $J = 1.2$ Hz, 1H, 10-H), 3.59 (dd, $J = 10.0$, 7.1 Hz, 1H, 7-H), 3.08 (d, $J = 3.6$ Hz, 1H, 3-H), 2.99 (s, 1H, 11-OH), 2.74 (s, 1H, 12-OH), 2.74–2.61 (m, 1H, 5-H), 2.25–1.83 (m, 4H, 5-H, 6-H, 13-H, 14-H), 1.62 (s, 3H, Me), 1.58 (s, 3H, Me), 1.51–0.96 (m, 3H, 6-H, 13-H, 14-H), 1.47 (s, 3H, Me), 1.43 (s, 3H, acetonide-*β*), 1.25 (s, 3H, Me), 1.14 (s, 3H, acetonide-*α*), 0.91 (s, 9H, TBS), 0.31 (s, 3H, TBS), 0.12 (s, 3H, TBS); ^{13}C NMR (C_6D_6): $\delta = 146.2$ (4), 140.6 (Ph), 139.3 (Ph), 129.1 (Ph), 128.4 (Ph), 128.4 (Ph), 128.1 (Ph), 128.1 (Ph), 126.8 (Ph), 113.1 (20), 99.0 (acetonide), 94.0 (10), 83.6 (11), 82.5 (1), 81.0 (9), 79.5 (10-Bn), 78.1 (2), 74.3 (2-Bn), 73.4 (12), 73.1 (7), 52.0 (8), 46.4 (3), 41.3 (15), 37.5 (13), 30.4 (acetonide-*β*), 29.9 (5), 29.8 (14), 28.8 (17), 27.6 (TBS), 26.4 (18), 23.3 (6), 20.0 (16), 19.3 (acetonide-*α*), 14.6 (TBS), 11.2 (19), 0.5 (TBS), −1.0 (TBS); HR MS: calcd for $C_{43}H_{64}O_7SiNa$ $[M+Na]^+$ 743.4319, found 743.4288.

(1*S*,4a*R*,5*S*,6*S*,9*R*,10*R*,11*S*,12*S*,12a*S*)-1,12-(Isopropylidenedioxy)-9,12a,13,13-tetramethyl-4-methylenetetradecahydro-6,10-methanobenzocyclodecene-5,6,9,10,11-pentaol (56, from diol **55a)**:

1) To a solution of diol **55a** (5.0 mg, 6.7 μmol) in THF (0.5 mL) at −78 °C were added liquid ammonia (1.2 mL) and sodium (4.0 mg, 0.174 mmol). After the reaction mixture had been stirred for 1.5 h at −78 °C, it was allowed to warm to −45 °C. The reaction mixture was stirred for 30 min at −45 °C, and then solid ammonium chloride was added. After evaporation of liquid ammonia at room temperature, the residue was diluted with diethyl ether and dried over sodium sulfate. Filtration of the mixture and evaporation of the solvent afforded a crude tetraol.

2) To a solution of the above crude tetraol in THF (1.0 mL) at room temperature was added TBAF in THF (1.0 M, 0.04 mL, 40.0 μmol). The reaction mixture was stirred for 5 min at room temperature, and then the solvent was evaporated. The crude product was purified by thin-layer

chromatography to afford pentaol **56** (2.9 mg, 100% from diol **55a**) as a clear plate.

Pentaol 56 (from diol **55b**):

1) To a solution of diol **55b** (15.3 mg, 18.8 μmol) in THF (1.2 mL) at −78°C were added liquid ammonia (4.5 mL) and sodium (18.0 mg, 0.783 mmol). After the reaction mixture had been stirred for 1 h at −78°C, it was allowed to warm to −45°C. The reaction mixture was stirred for 30 min at −45°C and then solid ammonium chloride was added. After evaporation of liquid ammonia at room temperature, the residue was diluted with diethyl ether and dried over sodium sulfate. Filtration of the mixture and evaporation of the solvent afforded a crude tetraol.

2) To a solution of the above crude tetraol in THF (2.0 mL) at room temperature was added TBAF in THF (1.0 M, 0.075 mL, 75.0 μmol). The reaction mixture was stirred for 20 min at room temperature and then a small amount of methanol was added. After the solvent was evaporated, the crude product was purified by thin-layer chromatography to afford pentaol **56** (6.6 mg, 83% from diol **55b**) as a clear plate.

Pentaol 56 (from diol **55c**):

1) To a solution of diol **55c** (6.0 mg, 8.3 μmol) in THF (0.8 mL) at −78°C were added liquid ammonia (4 mL) and sodium (18.0 mg, 0.783 mmol). After the reaction mixture had been stirred for 15 min at −78°C, it was allowed to warm to −45°C. The reaction mixture was stirred for 30 min at −45°C and then solid ammonium chloride was added. After evaporation of liquid ammonia at room temperature, the residue was diluted with diethyl ether and dried over sodium sulfate. Filtration of the mixture and evaporation of the solvent afforded a crude tetraol.

2) To a solution of the above crude tetraol in THF (1.5 mL) at room temperature was added TBAF in THF (1.0 M, 0.05 mL, 50.0 μmol). The reaction mixture was stirred for 30 min at room temperature, and then a small amount of methanol was added. After the solvent was evaporated, the crude product was purified by thin-layer chromatography to afford pentaol **56** (3.3 mg, 93% from diol **55c**) as clear plates: m.p. 273–275°C; $[\alpha]_D^{28} = +4.0$ (*c* 0.49, MeOH); IR (KBr): 3530, 3390 cm^{-1}; ^1H NMR (CD_2Cl_2): $\delta = 5.10$ (s, 1H, 20-H), 4.76 (s, 1H, 20-H), 4.17 (s, 1H, OH), 4.05 (dd, $J = 8.6$, 5.6 Hz, 1H, 2-H), 3.94 (d, $J = 2.6$ Hz, 1H, 10-H), 3.69 (s, 1H, OH), 3.68 (d, $J = 2.6$ Hz, 1H, 9-H), 3.54 (dd, $J = 10.9$, 6.3 Hz, 1H, 7-H), 2.85 (d, $J = 5.6$ Hz, 1H, 2-OH), 2.79 (br s, 1H, 10-OH), 2.64 (d, $J = 8.6$ Hz, 1H, 3-H), 2.63 (s, 1H, OH), 2.27 (ddd, $J = 13.5$, 8.6, 2.6 Hz, 1H, 5-H), 2.10 (ddd, $J = 13.5$, 7.9, 1.3 Hz, 1H, 5-H), 1.98–1.42 (m, 6H, 6-H, 6-H, 13-H, 13-H, 14-H, 14-H), 1.33 (s, 3H, 18-Me), 1.32 (s, 3H, 16-Me or 17-Me), 1.31 (s, 3H, acetonide), 1.26 (s, 3H, 19-Me), 1.20 (s, 3H, 17-Me or 16-Me), 1.08 (s, 3H, acetonide); ^{13}C NMR (CD_2Cl_2): $\delta = 149.4$ (4), 113.2 (20), 98.9 (acetonide), 83.2 (10), 79.8 (11), 78.3 (9), 78.1 (1), 75.0 (7), 73.5 (12), 70.2 (2), 49.4 (3), 47.7 (8), 42.2 (15), 35.7 (13), 31.7 (5), 29.8 (acetonide), 27.8 (14), 27.7 (17), 26.9 (18), 26.3 (6), 21.9 (16), 19.5 (acetonide), 10.8 (19); HR MS: calcd for $C_{23}H_{38}O_7Na$ $[M+Na]^+$ 449.2515, found 449.2513.

(4*S*,4a*S*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-11,12-(Carbonyldioxy)-4,5-(isopropylidenedioxy)-4a,8,13,13-tetramethyl-1-methylenetetradecahydro-7,11-methanobenzocyclodecene-6,7,8-triol: To a solution of pentaol **56** (5.3 mg, 12.4 μmol) in dichloromethane (6.9 mL) and pyridine (0.05 mL, 0.618 mmol) at −45°C was added bis(trichloromethyl) carbonate (20.0 mg, 67.4 μmol). The reaction mixture was stirred for 70 min at −45°C, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and the organic layer was washed with saturated aqueous copper(II) sulfate, water, and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (4*S*,4a*S*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-11,12-(carbonyldioxy)-4,5-(isopropylidenedioxy)-4a,8,13,13-tetramethyl-1-methylenetetradecahydro-7,11-methanobenzocyclodecene-6,7,8-triol (5.6 mg, 100%) as a white foam: m.p. 254–256°C; $[\alpha]_D^{29} = -38.4$ (*c* 0.74, MeOH); IR (KBr): 3460, 1800 cm^{-1}; ^1H NMR (C_6D_6): $\delta = 5.04$ (s, 1H, 20-H), 4.95 (d, $J = 10.5$ Hz, 1H, 2-H), 4.68 (s, 1H, 20-H), 3.71 (dd, $J = 3.6$, 1.7 Hz, 1H, 10-H), 3.56 (d, $J = 1.7$ Hz, 1H, 9-H), 3.29 (dd, $J = 10.6$, 5.3 Hz, 1H, 7-H), 3.12 (s, 1H, 11-OH), 2.54 (d, $J = 2.6$ Hz, 1H, 12-OH), 2.35 (ddd, $J = 15.0$, 8.2, 0.7 Hz, 1H, 14-H), 2.26 (d, $J = 10.5$ Hz, 1H, 3-H), 2.18–2.04 (m, 1H, 5-H), 1.96 (d, $J = 3.6$ Hz, 1H, 10-OH), 1.90–1.50 (m, 6H, 5-H, 6-H, 6-H, 13-H, 13-H, 14-H), 1.69 (s, 3H, 16-Me), 1.31 (s, 3H, acetonide), 1.22 (s, 3H, 17-Me), 1.21 (s, 3H, 19-Me), 1.05 (s, 3H, acetonide), 1.03 (s, 3H, 18-Me); ^{13}C NMR (C_6D_6): $\delta =$ 152.2 (CO), 141.8 (4), 115.1 (20), 98.4 (acetonide), 91.8 (11), 83.1 (10), 79.0 (2), 78.8 (1), 77.4 (9), 72.9 (7), 73.0 (12), 45.3 (3), 45.1 (16), 44.0 (8), 34.3 (5), 33.2 (13), 29.9 (6), 29.6 (acetonide), 26.9 (17), 26.9 (18), 23.0 (14), 22.4 (16), 19.3 (acetonide), 10.2 (19); HR MS: calcd for $C_{24}H_{36}O_8Na$ $[M+Na]^+$ 475.2308, found 475.2318.

(4*S*,4a*S*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-11,12-(Carbonyldioxy)-7,8-dihydroxy-4,5-(isopropylidenedioxy)-4a,8,13,13-tetramethyl-1-methylenetetradecahydro-7,11-methanobenzocyclodecen-6-yl acetate (**57**): To a solution of (4*S*,4a*S*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-11,12-(carbonyldioxy)-4,5-(isopropylidenedioxy)-4a,8,13,13-tetramethyl-1-methylenetetradecahydro-7,11-methanobenzocyclodecene-6,7,8-triol (3.5 mg, 7.7 μmol) and DMAP (18.0 mg, 0.147 mmol) in benzene (1.5 mL) at 0°C was added acetic anhydride (0.01 mL, 0.106 mmol). The reaction mixture was stirred for 10 h at 35°C and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diol **57** (3.2 mg, 84%) as a white foam: m.p. 238–240°C; $[\alpha]_D^{28} = -4.3$ (*c* 0.59, benzene); IR (neat): $\tilde{\nu} = 3480$, 1800 cm^{-1}; ^1H NMR (C_6D_6): $\delta = 5.27$ (d, $J = 2.0$ Hz, 1H, 10-H), 5.09 (s, 1H, 20-H-endo), 5.04 (d, $J = 11.2$ Hz, 1H, 2-H), 4.79 (s, 1H, 20-H-exo), 3.82 (d, $J = 2.0$ Hz, 1H, 9-H), 3.61 (s, 1H, 11-OH), 3.28 (dd, $J = 11.5$, 5.6 Hz, 1H, 7-H), 2.64 (d, $J = 2.3$ Hz, 1H, 12-OH), 2.36–2.25 (m, 1H, 14-H), 2.21 (d, $J = 11.2$ Hz, 1H, 3-H), 2.14–2.06 (m, 1H, 5-H), 1.90–1.30 (m, 6H, 5-H, 6-H, 6-H, 13-H, 13-H, 14-H), 1.68 (s, 3H, Ac), 1.67 (s, 3H, Me), 1.28 (s, 3H, Me), 1.16 (s, 3H, Me), 1.16 (s, 3H, Me), 1.05 (s, 3H, Me), 1.04 (s, 3H, Me); ^{13}C NMR (C_6D_6): $\delta = 174.1$ (Ac), 152.0 (CO), 141.7 (4), 114.6 (20), 98.4 (acetonide), 91.6 (11), 84.2 (10), 80.1 (2), 79.0 (1), 77.4 (9), 76.5 (7), 73.2 (12), 45.9 (3), 45.1 (15), 45.0 (8), 35.7 (5), 32.4 (13), 30.5 (6), 30.2 (acetonide), 29.4 (Ac), 25.9 (17), 25.8 (18), 22.7 (14), 22.1 (16), 19.2 (acetonide), 10.5 (19); HR MS: calcd for $C_{26}H_{38}O_9Na$ $[M+Na]^+$ 517.2414, found 517.2423.

(4*S*,4a*R*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-11,12-(Carbonyldioxy)-5,7,8-trihydroxy-4a,8,13,13-tetramethyl-1-methylene-4-(triethylsiloxy)tetradecahydro-7,11-methanobenzocyclodecen-6-yl acetate:

1) To a solution of diol **57** (5.0 mg, 10.1 μmol) in THF (1 mL) at room temperature was added hydrochloric acid (3 M, 0.5 mL). The reaction mixture was stirred for 10 h at 60°C and then solid sodium hydrogencarbonate was added at 0°C. The mixture was diluted with ethyl acetate and dried over sodium sulfate. Filtration of the mixture through a short pad of silica gel and evaporation of the solvent afford a crude tetraol.

2) To a solution of the above crude tetraol in pyridine (0.75 mL) at 0°C was added chlorotriethylsilane (0.05 mL, 0.298 mmol). The reaction mixture was stirred for 40 min at room temperature, and then saturated aqueous sodium hydrogencarbonate was added at 0°C. The mixture was extracted with ethyl acetate, and the organic layer was washed with saturated aqueous copper(II) sulfate, water, and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (4*S*,4a*R*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-11,12-(carbonyldioxy)-5,7,8-trihydroxy-4a,8,13,13-tetramethyl-1-methylene-4-(triethylsiloxy)tetradecahydro-7,11-methanobenzocyclodecen-6-yl acetate (4.8 mg, 83% from diol **57**) as a colorless oil: $[\alpha]_D^{28} = -1.0$ (*c* 0.97, benzene); IR (neat): $\tilde{\nu} = 3420$, 1800, 1730 cm^{-1}; ^1H NMR (C_6D_6): $\delta = 5.89$ (s, 1H, 9-OH), 5.52 (d, $J = 2.1$ Hz, 1H, 10-H), 5.26 (d, $J = 6.3$ Hz, 1H, 2-H), 5.17 (s, 1H, 20-H-exo), 5.02 (s, 1H, 20-H-endo), 4.00 (d, $J = 2.1$ Hz, 1H, 9-H), 3.98 (s, 1H, 11-OH), 3.69 (dd, $J =$ 10.6, 6.3 Hz, 1H, 7-H), 2.69 (d, $J = 1.6$ Hz, 1H, 12-OH), 2.66 (d, $J = 6.3$ Hz, 1H, 3-H), 2.50–2.35 (m, 1H, 14-H), 2.15–2.05 (m, 1H, 5-H), 1.88–1.30 (m, 6H, 5-H, 6-H, 6-H, 13-H, 13-H, 14-H), 1.67 (s, 3H, Ac), 1.67 (s, 3H, Me), 1.31 (s, 3H, Me), 1.22 (s, 3H, Me), 1.18 (s, 3H, Me), 0.88 (t, $J = 7.9$ Hz, 9H, TES), 0.48 (q, $J = 7.9$ Hz, 6H, TES); ^{13}C NMR (C_6D_6): $\delta = 173.7$ (Ac), 152.5 (CO), 141.1 (4), 115.5 (20), 89.6 (11), 86.8 (10), 81.7 (1), 81.7 (2), 80.9 (9), 76.9 (7), 73.1 (12), 49.0 (3), 47.9 (15), 44.3 (8), 33.5 (5), 32.8 (13), 32.5 (6), 30.2 (Ac), 26.2 (17), 25.4 (18), 24.9 (14), 20.4 (16), 9.4 (19), 6.7 (TES), 5.2 (TES); HR MS: calcd for $C_{29}H_{48}O_9SiCs$ $[M+Cs]^+$ 701.2122, found 701.2108.

(4*S*,4a*S*,6*R*,7*R*,8*R*,11*S*,12*S*,12a*R*)-11,12-(Carbonyldioxy)-7,8-dihydroxy-4a,8,13,13-tetramethyl-1-methylene-5-oxo-4-triethylsiloxytetradecahydro-7,11-methanobenzocyclodecen-6-yl acetate (**58**): To a suspension of (4*S*,4a*R*,5*S*,6*S*,7*R*,8*R*,11*S*,12*S*,12a*R*)-11,12-(carbonyldioxy)-5,7,8-trihydroxy-4a,8,13,13-tetramethyl-1-methylene-4-triethylsiloxytetradecahydro-7,11-

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methanobenzocyclodecen-6-yl acetate (2.5 mg, 4.4 μmol), NMO (5.1 mg, 40.4 μmol) and MS 4 Å (5 mg) in dichloromethane (1 mL) at 0 °C was added TPAP (0.5 mg, 1.4 μmol). The reaction mixture was stirred for 1 h at room temperature and then it was diluted with ethyl acetate at 0 °C. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford dihydroxyketone **58** (1.9 mg, 76 %) as a colorless oil: $[\alpha]_D^{28} = +7.3$ (*c* 0.80, benzene); IR (neat): $\tilde{\nu} = 3450$, 1790, 1730, 1700 cm^{-1}; ^1H NMR (C_6D_6): $\delta = 5.76$ (s, 1H, 10-H), 5.26 (s, 1H, 20-H), 4.90 (s, 1H, 20-H), 4.48 (d, $J = 10.3$ Hz, 1H, 2-H), 4.16 (s, 1H, 11-OH), 3.64 (dd, $J = 5.2$, 1.6 Hz, 1H, 7-H), 2.96 (d, $J = 10.3$ Hz, 1H, 3-H), 2.40–2.20 (m, 2H, 5-H, 14-H), 2.14 (d, $J = 2.0$ Hz, 1H, 12-OH), 2.05–1.30 (m, 6H, 5-H, 6-H, 6-H, 13-H, 13-H, 14-H), 1.75 (s, 3H, Ac), 1.59 (s, 3H, Me), 1.57 (s, 3H, Me), 1.30 (s, 3H, Me), 1.03 (s, 3H, Me), 0.96 (t, $J = 7.9$ Hz, 9H, TES), 0.51 (q, $J = 7.9$ Hz, 6H, TES); ^{13}C NMR (C_6D_6): $\delta = 213.1$ (9), 173.8 (Ac), 152.2 (CO), 138.0 (4), 108.8 (20), 91.2 (10), 89.9 (11), 80.6 (1), 78.8 (2), 72.6 (7), 71.3 (12), 53.6 (8), 44.3 (3), 43.9 (15), 32.8 (5), 31.5 (13), 31.0 (6), 27.5 (Ac), 26.2 (17), 25.3 (18), 23.1 (14), 20.5 (16), 12.5 (19), 7.1 (TES), 5.7 (TES); HR MS: calcd for $C_{29}H_{46}O_9SiNa$ $[M+Na]^+$ 589.2809, found 589.2781.

(4*S*,4a*S*,6*R*,11*S*,12*S*,12a*R*)-11,12-(Carbonyldioxy)-4a,8,13,13-tetramethyl-1-methylene-5-oxo-4-triethylsiloxy-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate (**59**):

1) To a solution of dihydroxyketone **58** (1.2 mg, 2.1 μmol) in toluene (1 mL) were added TCDI (17.4 mg, 97.6 μmol) and DMAP (48.9 mg, 0.400 mmol). The reaction mixture was stirred for 4 h at 100 °C and then it was diluted with ethyl acetate at room temperature. Filtration of the mixture through a short pad of silica gel and evaporation of the solvent afforded a mixture of thionocarbonate and 12-monosubstituted intermediate. The crude mixture was dissolved in toluene (0.5 mL) and then DMAP (12.2 mg, 0.100 mmol) was added at room temperature. After the reaction mixture had been stirred for 4 h at 100 °C, it was diluted with ethyl acetate at room temperature. Filtration of mixture through a short pad of silica gel and evaporation of the solvent afforded a crude thionocarbonate (1.1 mg).

2) To the above crude thionocarbonate (0.9 mg) was added trimethyl phosphite (1 mL) at room temperature. The reaction mixture was stirred for 5 h at 110 °C and then the crude product was purified by thin-layer chromatography to afford ketone **59** (0.5 mg, 53 % from dihydroxyketone **58**) as a colorless oil: $[\alpha]_D^{28} = -55.2$ (*c* 2.00, benzene); IR (neat): $\tilde{\nu} = 1810$, 1750, 1720 cm^{-1}; ^1H NMR (C_6D_6): $\delta = 6.68$ (s, 1H, 10-H), 5.72 (s, 1H, 20-H), 4.96 (s, 1H, 20-H), 4.24 (d, $J = 5.3$ Hz, 1H, 2-H), 4.06 (dd, $J = 10.9$, 4.3 Hz, 1H, 7-H), 2.74 (d, $J = 5.3$ Hz, 1H, 3-H), 2.15–1.30 (m, 8H, 5-H, 5-H, 6-H, 6-H, 13-H, 13-H, 14-H, 14-H), 1.83 (s, 3H, 18-Me), 1.76 (s, 3H, Ac), 1.26 (s, 3H, 19-Me), 1.20 (s, 3H, 16-Me), 1.02 (t, $J = 7.6$ Hz, 9H, TES), 1.02 (s, 3H, 17-Me), 0.68 (q, $J = 7.6$ Hz, 6H, TES); ^{13}C NMR (C_6D_6): $\delta =$ 202.9 (9), 169.1 (Ac), 152.5 (CO), 142.1 (4), 140.1 (11), 131.5 (12), 115.1 (20), 92.2 (10), 81.6 (1), 76.1 (2), 74.2 (7), 62.5 (8), 48.7 (3), 37.1 (15), 32.5 (14), 30.1 (13), 29.9 (5), 26.2 (6), 23.9 (17), 21.9 (Ac), 20.4 (16), 19.1 (18), 11.5 (19), 7.1 (TES), 5.7 (TES); HR MS: calcd for $C_{29}H_{44}O_7SiNa$ $[M+Na]^+$ 555.2754, found 555.2728.

(4*S*,4a*S*,6*R*,11*S*,12*S*,12a*R*)-11,12-(Carbonyldioxy)-4a,8,13,13-tetramethyl-1-methylene-5,9-dioxo-4-triethylsiloxy-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate: To a suspension of ketone **59** (0.5 mg, 1.0 μmol), sodium acetate (2.3 mg, 28.3 μmol), and Celite (6.1 mg) in benzene (0.5 mL) at room temperature was added PCC (6.1 mg, 28.2 μmol). The reaction mixture was stirred for 7 h at 95 °C and then sodium acetate (2.3 mg, 28.3 μmol), Celite (6.1 mg), and PCC (6.1 mg, 28.2 μmol) were added at room temperature. The reaction mixture was stirred for 4 h at 95 °C and then the crude product was purified by thin-layer chromatography to afford (4*S*,4a*S*,6*R*,11*S*,12*S*,12a*R*)-11,12-(carbonyldioxy)-4a,8,13,13-tetramethyl-1-methylene-5,9-dioxo-4-triethylsiloxy-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate (0.4 mg, 78 %) as a colorless oil: $[\alpha]_D^{29} = -58.2$ (*c* 1.06, benzene); IR (neat): $\tilde{\nu} = 1820$, 1750, 1720, 1690 cm^{-1}; ^1H NMR (C_6D_6): $\delta = 6.72$ (s, 1H, 10-H), 5.59 (s, 1H, 20-H-exo), 4.87 (s, 1H, 20-H-endo), 4.21 (d, $J = 5.6$ Hz, 1H, 2-H), 3.98 (dd, $J = 10.2$, 5.0 Hz, 1H, 7-H), 2.86 (d, $J = 5.6$ Hz, 1H, 3-H), 2.66 (d, $J = 19.6$ Hz, 1H, 14-H), 2.56 (d, $J = 19.6$ Hz, 1H, 14-H), 2.20 (s, 3H, 18-Me), 1.82–1.75 (m, 1H, 5-H), 1.71 (s, 3H, Ac), 1.60–1.25 (m, 3H, 5-H, 6-H, 6-H), 1.20 (s, 3H, 19-Me), 1.07 (s, 3H, 16-Me), 0.98 (t, $J = 7.8$ Hz, 9H, TES), 0.96 (s, 3H, 17-Me), 0.62 (q, $J = 7.8$ Hz, 3H, TES), 0.61 (q, $J = 7.8$ Hz, 3H, TES); ^{13}C NMR (C_6D_6): $\delta = 200.6$ (9), 195.5 (13), 168.7 (Ac), 151.7 (CO), 149.0 (11), 141.3 (4), 139.4 (12), 115.6 (20), 88.1 (1), 80.8 (2), 76.4 (10), 74.3 (7), 63.2 (8), 49.1 (3), 41.5 (15), 40.4 (14), 36.7 (5), 32.2 (6), 31.4 (17), 20.1 (Ac), 18.2 (16), 15.0 (18), 11.5 (19), 7.0 (TES), 5.6 (TES); HR MS: calcd for $C_{29}H_{42}O_8SiCs$ $[M+Cs]^+$ 679.1703, found 679.1673.

(4*S*,4a*S*,6*R*,9*S*,11*S*,12*S*,12a*R*)-11,12-(Carbonyldioxy)-9-hydroxy-4a,8,13,13-tetramethyl-1-methylene-5-oxo-4-triethylsiloxy-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate: To a solution of K-Selectride® in THF (0.167 M, 0.24 mL, 40.1 μmol) at −23 °C was added a solution of (4*S*,4a*S*,6*R*,11*S*,12*S*,12a*R*)-11,12-(carbonyldioxy)-4a,8,13,13-tetramethyl-1-methylene-5,9-dioxo-4-triethylsiloxy-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate (2.3 mg, 4.2 μmol) in THF (0.3 mL). After the reaction mixture had been stirred for 2 h, K-Selectride® in THF (1.0 M, 0.02 mL, 20.0 μmol) was added at −23 °C. The reaction mixture was stirred for 2 h at −23 °C, and then saturated aqueous ammonium chloride was added. The mixture was extracted with diethyl ether, and aqueous hydrogen peroxide (30 %) was added to a concentrated residue of the organic layer. After the mixture had been stirred for 1 h at room temperature, saturated aqueous sodium hydrogensulfite was added, and then the mixture was neutralized with saturated aqueous ammonium chloride. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford (4*S*,4a*S*,6*R*,9*S*,11*S*,12*S*,12a*R*)-11,12-(carbonyldioxy)-9-hydroxy-4a,8,13,13-tetramethyl-1-methylene-5-oxo-4-triethylsiloxy-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate (2.0 mg, 87 %) as a colorless oil: $[\alpha]_D^{29} = -92.7$ (*c* 1.07, benzene); IR (neat): $\tilde{\nu} = 3500$, 1800, 1750, 1720 cm^{-1}; ^1H NMR (C_6D_6): $\delta = 6.78$ (s, 1H, 10-H), 5.65 (s, 1H, 20-H-exo), 5.00 (s, 1H, 20-H-endo), 4.35–4.22 (m, 1H, 13-H), 4.28 (d, $J = 5.6$ Hz, 1H, 2-H), 4.22 (dd, $J = 11.2$, 5.0 Hz, 1H, 7-H), 3.32 (d, $J = 5.6$ Hz, 1H, 3-H), 2.40–2.25 (m, 1H, 14-H), 2.26 (s, 3H, 18-Me), 2.15–1.95 (m, 3H, 5-H, 5-H, 14-H), 1.79 (s, 3H, Ac), 1.75–1.68 (m, 1H, 6-H), 1.56–1.38 (m, 1H, 6-H), 1.28 (s, 3H, 19-Me), 1.19 (s, 3H, 16-Me), 1.02 (t, $J =$ 7.9 Hz, 9H, TES), 1.00 (s, 3H, 17-Me), 0.67 (q, $J = 7.9$ Hz, 3H, TES), 0.66 (q, $J = 7.9$ Hz, 3H, TES); ^{13}C NMR (C_6D_6): $\delta = 203.1$ (9), 169.0 (Ac), 153.3 (CO), 145.8 (11), 140.8 (4), 131.3 (12), 114.7 (20), 90.3 (1), 82.0 (2), 76.4 (10), 74.2 (7), 67.4 (13), 62.7 (8), 49.2 (3), 40.5 (15), 37.4 (14), 36.7 (5), 32.6 (6), 27.4 (17), 20.4 (Ac), 19.2 (16), 17.4 (18), 11.6 (19), 7.1 (TES), 5.7 (TES); HR MS: calcd for $C_{29}H_{44}O_8SiNa$ $[M+Na]^+$ 571.2703, found 571.2714.

(4*S*,4a*S*,6*R*,9*S*,11*S*,12*S*,12a*R*)-11,12-(Carbonyldioxy)-4a,8,13,13-tetramethyl-1-methylene-5-oxo-4,9-bis(triethylsiloxy)-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate (**60**): To a solution of (4*S*,4a*S*,6*R*,9*S*,11*S*,12*S*,12a*R*)-11,12-(carbonyldioxy)-9-hydroxy-4a,8,13,13-tetramethyl-1-methylene-5-oxo-4-triethylsiloxy-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate (3.8 mg, 6.9 μmol) in pyridine (0.7 mL) at −23 °C was added triethylsilyl trifluoromethanesulfonate (0.02 mL, 90.0 μmol). The reaction mixture was stirred for 10 min at −23 °C and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and the organic layer was washed with saturated aqueous copper(II) sulfate and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketone **60** (4.5 mg, 98 %) as a colorless oil: $[\alpha]_D^{29} = -89.6$ (*c* 1.09, benzene); IR (neat): $\tilde{\nu} = 1810$, 1750, 1720 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 6.54$ (s, 1H, 10-H), 5.41 (s, 1H, 20-H), 5.00 (s, 1H, 20-H), 4.79 (ddd, $J = 9.6$, 4.2, 1.1 Hz, 1H, 13-H), 4.27 (d, $J = 5.4$ Hz, 1H, 2-H), 4.14 (dd, $J = 11.1$, 4.8 Hz, 1H, 7-H), 3.26 (d, $J = 5.4$ Hz, 1H, 3-H), 2.56 (dd, $J = 15.3$, 9.6 Hz, 1H, 14-H), 2.29–2.22 (m, 1H, 5-H), 2.21 (d, $J = 1.1$ Hz, 3H, 18-Me), 2.17 (s, 3H, Ac), 2.14 (dd, $J = 15.3$, 4.2 Hz, 1H, 14-H), 2.12–1.88 (m, 2H, 5-H, 6-H), 1.57–1.48 (m, 1H, 6-H), 1.19 (s, 3H, 19-Me), 1.13 (s, 6H, 16-Me, 17-Me), 0.98 (t, $J = 7.9$ Hz, 9H, TES), 0.89 (t, $J = 7.9$ Hz, 9H, TES), 0.65 (q, $J = 7.9$ Hz, 6H, TES), 0.51 (q, $J = 7.9$ Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 203.7$ (9), 169.2 (Ac), 153.3 (CO), 146.4 (11), 134.0 (4), 130.7 (12), 114.5 (20), 90.2 (1), 82.1 (2), 76.5 (10), 73.7 (7), 62.6 (8), 48.8 (3), 40.3 (15), 38.0 (14), 32.1 (6), 27.5 (17), 20.9 (Ac), 19.0 (16), 17.9 (18), 11.2 (19), 6.7 (TES), 6.7 (TES), 5.2 (TES), 4.8 (TES); HR MS: calcd for $C_{35}H_{58}O_8Si_2Na$ $[M+Na]^+$ 685.3568, found 685.3597.

(4*S*,4a*S*,6*R*,9*S*,11*S*,12*S*,12a*S*)-1-Bromomethyl-11,12-(carbonyldioxy)-4a,8,13,13-tetramethyl-5-oxo-4,9-bis(triethylsiloxy)-3,4,4a,5,6,9,10,11,12,12a-decahydro-7,11-methanobenzocyclodecen-6-yl acetate (**61**) and

(2*S*,4*S*,4a*S*,6*R*,9*S*,11*S*,12*S*,12a*S*)-2-bromo-11,12-(carbonyldioxy)-4a,8,13,13-tetramethyl-1-methylene-5-oxo-4,9-bis(triethylsiloxy)-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate (**62**):

1) To a mixture of copper(I) bromide (113 mg, 0.709 mmol) and *tert*-butyl perbenzoate (192 mg, 0.790 mmol) at room temperature was added acetonitrile (6 mL). The reaction mixture was stirred for 45 min at 50 °C in darkness and then cooled down to room temperature. The copper reagent in acetonitrile thus prepared was immediately used in the following reaction.

The copper reagent in acetonitrile (6 mL) was added to a solution of ketone **60** (26.2 mg, 39.5 μmol) in acetonitrile (3 mL) at −23 °C. After the reaction mixture had been stirred for 12 h at −23 °C, copper(I) bromide (157 mg, 1.185 mmol) was added. The reaction mixture was stirred for 1 h at −23 °C, and then the crude product was purified by column chromatography to afford allylic bromide **61** (18.2 mg, 62%) as a pale yellow solid and allylic bromide **62** (4.4 mg, 15%) as a pale yellow oil.

2) To a mixture of allylic bromide **61** (93.0 mg, 0.137 mmol) and copper(I) bromide (360 mg, 2.47 mmol) at room temperature was added acetonitrile (5 mL). The reaction mixture was stirred for 100 min at 50 °C and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over magnesium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford allylic bromide **62** (64.4 mg, 69%) as a pale yellow oil and recovered allylic bromide **61** (23.5 mg, 25%) as a pale yellow solid. **Allylic bromide 61**: m.p. 131–132 °C; $[\alpha]_D^{25} = -43.4$ (*c* 0.65, benzene); IR (KBr): $\tilde{\nu} = 1820, 1750, 1720\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 6.43$ (s, 1H, 10-H), 5.98–5.96 (m, 1H, 5-H), 4.90 (br dd, $J = 9.2, 5.0$ Hz, 1H, 13-H), 4.41 (d, $J = 5.0$ Hz, 1H, 2-H), 4.38 (d, $J = 10.9$ Hz, 1H, 20-H), 4.17 (d, $J = 10.9$ Hz, 1H, 20-H), 4.12 (dd, $J = 9.6, 6.3$ Hz, 1H, 7-H), 3.71 (br d, $J = 5.0$ Hz, 1H, 3-H), 2.82 (dd, $J = 15.5, 5.0$ Hz, 1H, 14-H), 2.59 (dd, $J = 15.5, 9.2$ Hz, 1H, 14-H), 2.57–2.40 (m, 1H, 6-H), 2.17 (s, 3H, Ac), 2.14 (s, 3H, 18-Me), 2.17–2.05 (m, 1H, 6-H), 1.24 (s, 3H, 19-Me), 1.21 (s, 6H, 16-Me, 17-Me), 0.99 (t, $J = 7.8$ Hz, 9H, TES), 0.90 (t, $J = 7.9$ Hz, 9H, TES), 0.67 (q, $J = 7.8$ Hz, 6H, TES), 0.57 (q, $J = 7.9$ Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 203.1$ (9), 169.1 (Ac), 152.7 (CO), 147.8 (11), 134.3 (4), 130.9 (5), 130.0 (12), 90.5 (1), 82.2 (2), 76.6 (10), 70.6 (7), 68.1 (13), 61.0 (8), 44.3 (3), 41.1 (15), 37.8 (14), 35.5 (20), 33.6 (6), 26.6 (17), 20.8 (Ac), 19.6 (16), 16.6 (18), 11.0 (19), 6.9 (TES), 6.7 (TES), 5.1 (TES), 4.8 (TES); HR MS: calcd for $C_{35}H_{57}BrO_8Si_2Na$ $[M+Na]^+$ 763.2673/765.2661, found 763.2658/765.2683. **Allylic bromide 62**: $[\alpha]_D^{29} = -18.7$ (*c* 1.28, benzene); IR (neat): $\tilde{\nu} = 1820, 1750, 1720\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 6.58$ (s, 1H, 10-H), 5.68 (d, $J = 1.7$ Hz, 1H, 20-H), 5.37 (s, 1H, 20-H), 5.01 (ddd, $J = 9.1, 6.6, 1.0$ Hz, 1H, 13-H), 4.84 (dd, $J = 4.3, 2.0$ Hz, 1H, 5-H), 4.54 (dd, $J = 10.6, 4.6$ Hz, 1H, 7-H), 4.40 (d, $J = 5.9$ Hz, 1H, 2-H), 4.05 (br d, $J = 5.9$ Hz, 1H, 3-H), 2.51 (dd, $J = 15.5, 9.1$ Hz, 1H, 14-H), 2.40 (d, $J = 1.0$ Hz, 3H, 18-Me), 2.32 (ddd, $J = 14.9, 4.6, 2.0$ Hz, 1H, 6-H), 2.30 (dd, $J = 15.5, 6.6$ Hz, 1H, 14-H), 2.18 (s, 3H, Ac), 2.12 (ddd, $J = 14.9, 10.6, 4.3$ Hz, 1H, 6-H), 1.24 (s, 3H, 19-Me), 1.22 (s, 3H, 16-Me), 1.13 (s, 3H, 17-Me), 0.97 (t, $J = 7.9$ Hz, 9H, TES), 0.90 (t, $J = 7.9$ Hz, 9H, TES), 0.67–0.53 (m, 12H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 203.3$ (9), 169.2 (Ac), 153.0 (CO), 149.0 (11), 141.0 (4), 128.6 (12), 118.4 (20), 91.0 (1), 82.0 (2), 76.3 (10), 70.0 (7), 68.1 (13), 62.4 (8), 55.9 (5), 43.8 (3), 40.8 (15), 40.5 (6), 38.2 (14), 26.2 (17), 20.9 (Ac), 20.1 (16), 17.0 (18), 11.4 (19), 6.9 (TES), 6.7 (TES), 5.2 (TES), 4.8 (TES); HR MS: calcd for $C_{35}H_{57}BrO_8Si_2Na$ $[M+Na]^+$ 763.2673/765.2661, found 763.2653/765.2653.

(1*S*,2*S*,4*S*,4a*S*,6*R*,9*S*,11*S*,12*S*,12a*R*)-2-Bromo-11,12-(carbonyldioxy)-1-hydroxy-1-hydroxymethyl-4a,8,13,13-tetramethyl-5-oxo-4,9-bis(triethylsiloxy)-1,2,3,4,4a,5,6,9,10,11,12,12a-dodecahydro-7,11-methanobenzocyclodecen-6-yl acetate (**63**): To a solution of allylic bromide **62** (10.3 mg, 13.9 μmol) and pyridine (0.072 mL, 0.890 mmol) in diethyl ether (2 mL) at 0 °C was added osmium tetraoxide in THF (0.098 M, 0.2 mL, 19.5 μmol). After the reaction mixture had been stirred for 17 h at room temperature, a mixture of sodium hydrogensulfate (530 mg), pyridine (0.3 mL), THF (2 mL), and water (3 mL) was added. The reaction mixture was stirred for 2 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with brine and dried over magnesium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford diol **63** (9.8 mg, 92%) and recovered allylic bromide **62** (0.4 mg, 4%) as pale yellow oils. **Diol 63**: $[\alpha]_D^{28} = -16.4$ (*c* 0.57, benzene); IR (neat): $\tilde{\nu} = 3490, 3460, 1810, 1750, 1710\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 6.57$ (s, 1H, 10-H), 4.96 (t, $J = 3.1$ Hz, 1H, 5-H), 4.86 (ddd, $J = 9.6, 5.0, 1.0$ Hz, 1H, 13-H), 4.48 (dd, $J = 10.7, 4.6$ Hz, 1H, 7-H), 4.29 (d, $J = 4.8$ Hz, 1H, 2-H), 4.23 (d, $J = 11.5$ Hz, 1H, 20-H), 3.68 (d, $J = 4.8$ Hz, 1H, 3-H), 3.62 (br d, $J = 11.5$ Hz, 1H, 20-H), 2.92 (dd, $J = 15.5, 5.0$ Hz, 1H, 14-H), 2.90 (s, 1H, 4-OH), 2.51 (dd, $J = 15.5, 9.6$ Hz, 1H, 14-H), 2.48 (br s, 1H, 20-OH), 2.41–2.23 (m, 2H, 6-H, 6-H), 2.34 (d, $J = 1.0$ Hz, 3H, 18-Me), 2.18 (s, 3H, Ac), 1.23 (s, 3H, 19-Me), 1.18 (s, 3H, 16-Me), 1.16 (s, 3H, 17-Me), 1.00 (t, $J = 7.8$ Hz, 9H, TES), 0.91 (t, $J = 7.9$ Hz, 9H, TES), 0.68 (q, $J = 7.8$ Hz, 6H, TES), 0.57 (q, $J = 7.9$ Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 201.6$ (9), 169.1 (Ac), 153.1 (CO), 148.6 (11), 130.6 (12), 90.4 (1), 81.9 (2), 76.0 (10), 74.8 (4), 69.2 (7), 68.3 (13), 62.7 (20), 61.3 (5), 46.4 (3), 40.8 (15), 37.3 (6), 36.9 (14), 26.6 (17), 20.8 (Ac), 19.5 (16), 17.3 (18), 12.9 (19), 6.9 (TES), 6.7 (TES), 5.0 (TES), 4.9 (TES); HR MS: calcd for $C_{35}H_{59}BrO_{10}Si_2Na$ $[M+Na]^+$ 797.2728/799.2716, found 797.2727/799.2719.

1,2-*O*,*O*-Carbonyl-7,13-*O*,*O*-bis(triethylsilyl)-4-deacetyl-2-debenzoylbaccatin III: To a mixture of diol **63** (2.7 mg, 3.5 μmol) and DBU (15.8 mg, 0.104 mmol) at room temperature was added toluene (1.3 mL). The reaction mixture was stirred for 105 min at 50 °C and then cooled down to room temperature. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford 1,2-*O*,*O*-carbonyl-7,13-*O*,*O*-bis(triethylsilyl)-4-deacetyl-2-debenzoylbaccatin III (1.0 mg, 42%) as a colorless oil and recovered diol **63** (1.3 mg, 48%) as a pale yellow oil. **1,2-*O*,*O*-Carbonyl-7,13-*O*,*O*-bis(triethylsilyl)-4-deacetyl-2-debenzoylbaccatin III**: $[\alpha]_D^{29} = -65.7$ (*c* 0.73, benzene); IR (neat): $\tilde{\nu} = 3460, 1810, 1750, 1720\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 6.42$ (s, 1H, 10-H), 4.81 (dd, $J = 9.2, 2.1$ Hz, 1H, 5-H), 4.74 (br dd, $J = 8.9, 3.3$ Hz, 1H, 13-H), 4.56 (d, $J = 8.4$ Hz, 1H, 20-H), 4.51 (d, $J = 8.4$ Hz, 1H, 20-H), 4.36 (d, $J = 5.0$ Hz, 1H, 2-H), 4.16 (dd, $J = 10.4, 7.1$ Hz, 1H, 7-H), 3.04 (d, $J = 5.0$ Hz, 1H, 3-H), 2.96 (s, 1H, OH), 2.70 (dd, $J = 15.7, 3.3$ Hz, 1H, 14-H), 2.53 (dd, $J = 15.7, 8.9$ Hz, 1H, 14-H), 2.48 (ddd, $J = 14.2, 9.2, 7.1$ Hz, 1H, 6-H), 2.18 (s, 3H, Ac), 2.13 (s, 3H, 18-Me), 1.98 (ddd, $J = 14.2, 10.4, 2.1$ Hz, 1H, 6-H), 1.64 (s, 3H, 19-Me), 1.20 (s, 3H, 16-Me), 1.14 (s, 3H, 17-Me), 1.01 (t, $J = 7.8$ Hz, 9H, TES), 0.90 (t, $J = 7.9$ Hz, 9H, TES), 0.72 (q, $J = 7.8$ Hz, 6H, TES), 0.57 (q, $J = 7.9$ Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 202.3$ (9), 169.2 (Ac), 153.1 (CO), 145.7 (11), 132.8 (12), 89.7 (1), 87.5 (5), 80.5 (2), 78.7 (20), 76.7 (10), 73.8 (4), 71.9 (7), 68.9 (13), 60.6 (8), 48.8 (3), 40.5 (15), 37.9 (6), 35.8 (14), 28.1 (17), 20.8 (Ac), 18.8 (16), 17.7 (18), 9.8 (19), 6.8 (TES), 6.7 (TES), 5.1 (TES), 4.7 (TES); HR MS: calcd for $C_{35}H_{58}O_{10}Si_2Na$ $[M+Na]^+$ 717.3466, found 717.3475.

1,2-*O*,*O*-Carbonyl-7,13-*O*,*O*-bis(triethylsilyl)-2-debenzoylbaccatin III (**64**): To a solution of 1,2-*O*,*O*-carbonyl-7,13-*O*,*O*-bis(triethylsilyl)-4-deacetyl-2-debenzoylbaccatin III (1.4 mg, 2.0 μmol) and DMAP (3.6 mg, 29.5 μmol) in pyridine (0.1 mL) was added acetic anhydride (0.037 mL, 0.392 mmol). The reaction mixture was stirred for 13 h at room temperature, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ketone **64** (1.3 mg, 91%) as a white foam: m.p. 254–256 °C; $[\alpha]_D^{29} = -46.4$ (*c* 0.87, benzene); IR (KBr): $\tilde{\nu} = 1810, 1740, 1720\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 6.43$ (s, 1H, 10-H), 5.03–4.95 (m, 1H, 13-H), 4.97 (dd, $J = 9.2, 1.3$ Hz, 1H, 5-H), 4.62 (d, $J = 8.9$ Hz, 1H, 20-H), 4.49 (d, $J = 5.9$ Hz, 1H, 2-H), 4.46 (d, $J = 8.9$ Hz, 1H, 20-H), 4.43 (dd, $J = 9.4, 6.9$ Hz, 1H, 7-H), 3.42 (d, $J = 5.9$ Hz, 1H, 3-H), 2.57 (ddd, $J = 14.5, 9.2, 6.9$ Hz, 1H, 6-H), 2.40 (dd, $J = 15.3, 9.1$ Hz, 1H, 14-H), 2.17 (s, 3H, 10-Ac), 2.16 (s, 3H, 4-Ac), 2.11 (d, $J = 1.0$ Hz, 3H, 18-Me), 2.17–2.10 (m, 1H, 14-H), 1.89 (ddd, $J = 14.5, 9.4, 1.3$ Hz, 1H, 6-H), 1.73 (s, 3H, 19-Me), 1.27 (s, 3H, 16-Me), 1.21 (s, 3H, 17-Me), 1.01 (t, $J = 7.9$ Hz, 9H, TES), 0.91 (t, $J = 7.9$ Hz, 9H, TES), 0.67 (q, $J = 7.9$ Hz, 6H, TES), 0.60 (q, $J = 7.9$ Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 202.5$ (9), 170.0 (4-Ac), 169.0 (10-Ac), 153.1 (CO), 148.6 (11), 129.5 (12), 90.5 (1), 84.1 (5), 81.6 (2), 79.4 (4), 76.3 (20), 76.3 (10), 71.4 (7), 67.5 (13), 59.9 (8), 43.7 (3), 41.2 (15), 37.8 (6), 37.0 (14), 25.3 (17), 22.3 (4-Ac), 20.9 (10-Ac), 20.8 (16), 15.5 (18), 10.0 (19), 6.9 (TES), 6.7 (TES), 5.1 (TES), 4.7 (TES); HR MS: calcd for $C_{37}H_{60}O_{11}Si_2$ $[M+H]^+$ 737.3752, found 737.3788.

7,13-*O*,*O*-Bis(triethylsilyl)baccatin III: To a solution of ketone **64** (12.7 mg, 17.2 μmol) in THF (10 mL) at −78 °C was added phenyllithium in a mixture of cyclohexane and diethyl ether (1.8 M, 0.288 mL, 0.516 mmol). The reaction mixture was stirred for 15 min at −78 °C, and then saturated

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aqueous ammonium chloride was added. The reaction mixture was extracted with diethyl ether, and the organic layer was washed with brine and dried over magnesium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford 7,13-*O,O*-bis(triethylsilyl)baccatin III (13.1 mg, 94%) as a white foam: m.p. 199–201 °C; $[\alpha]_D^{29} = -84.4$ (*c* 1.48, benzene); IR (KBr): $\tilde{\nu} = 3470$, 1740, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 8.11$ (d, $J =$ 7.6 Hz, 2H, *o*-Bz), 7.60 (t, $J = 7.6$ Hz, 1H, *p*-Bz), 7.47 (t, $J = 7.6$ Hz, 2H, *m*-Bz), 6.47 (s, 1H, 10-H), 5.63 (d, $J = 6.9$ Hz, 1H, 2-H), 4.96 (dd, $J = 9.6$, 2.0 Hz, 1H, 5-H), 4.95–4.88 (m, 1H, 13-H), 4.49 (dd, $J = 10.6$, 6.6 Hz, 1H, 7-H), 4.29 (d, $J = 8.3$ Hz, 1H, 20-H), 4.14 (d, $J = 8.3$ Hz, 1H, 20-H), 3.82 (d, $J = 6.9$ Hz, 1H, 3-H), 2.51 (ddd, $J = 14.2$, 9.6, 6.6 Hz, 1H, 6-H), 2.29 (s, 3H, 4-Ac), 2.18 (s, 3H, 10-Ac), 2.12 (d, $J = 1.0$ Hz, 3H, 18-Me), 2.26–2.03 (m, 2H, 14-H, 14-H), 1.86 (ddd, $J = 14.2$, 10.6, 2.0 Hz, 1H, 6-H), 1.67 (s, 3H, 19-Me), 1.19 (s, 3H, 16-Me), 1.11 (s, 3H, 17-Me), 1.02 (t, $J = 7.9$ Hz, 9H, TES), 0.93 (t, $J = 7.9$ Hz, 9H, TES), 0.67 (q, $J = 7.9$ Hz, 6H, TES), 0.61 (q, $J =$ 7.9 Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 202.3$ (9), 169.9 (4-Ac), 169.2 (10-Ac), 167.0 (Bz), 145.4 (11), 133.5 (Ph), 131.5 (12), 130.0 (Ph), 129.4 (Ph), 128.5 (Ph), 84.1 (5), 80.6 (1), 79.4 (4), 76.4 (20), 75.7 (10), 75.2 (2), 72.1 (7), 68.4 (13), 58.2 (8), 46.8 (3), 42.9 (15), 39.8 (14), 37.1 (6), 26.4 (17), 22.3 (4-Ac), 21.2 (16), 20.9 (10-Ac), 14.8 (18), 10.0 (19), 6.9 (TES), 6.7 (TES), 5.2 (TES), 4.8 (TES); HR MS: calcd for $C_{43}H_{67}O_{11}Si_2$ $[M+H]^+$ 815.4222, found 815.4251.

Baccatin III: To a solution of 7,13-*O,O*-bis(triethylsilyl)baccatin III (13.0 mg, 15.9 μmol) in THF (0.8 mL) at room temperature was added hydrogen fluoride·pyridine (hydrogen fluoride/pyridine = ca. 7/3, 0.16 mL). After the reaction mixture had been stirred for 1 h at room temperature, it was diluted with ethyl acetate, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with chloroform and the organic layer was washed with brine and dried over magnesium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford baccatin III (9.0 mg, 96%) as a white foam: m.p. 149–151 °C (lit. 229–231 °C,[56b] 236–238 °C[57]); $[\alpha]_D^{28} = -53.3$ (*c* 0.63, MeOH) (lit. $[\alpha]_D^{23} = -54$ (*c* 0.41, MeOH),[56b] $[\alpha]_D = -54$ (MeOH)[57]); IR (KBr): $\tilde{\nu} = 3480$, 1740, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 8.10$ (d, $J = 7.6$ Hz, 2H, *o*-Bz), 7.61 (t, $J = 7.6$ Hz, 1H, *p*-Bz), 7.48 (t, $J = 7.6$ Hz, 2H, *m*-Bz), 6.32 (s, 1H, 10-H), 5.62 (d, $J = 7.2$ Hz, 1H, 2-H), 4.98 (dd, $J = 9.7$, 2.3 Hz, 1H, 5-H), 4.91–4.85 (m, 1H, 13-H), 4.47 (dd, $J = 10.9$, 6.6 Hz, 1H, 7-H), 4.31 (d, $J = 8.3$ Hz, 1H, 20-H), 4.15 (d, $J = 8.3$ Hz, 1H, 20-H), 3.87 (d, $J = 7.2$ Hz, 1H, 3-H), 2.59 (br s, 1H, 7-OH), 2.56 (ddd, $J = 14.5$, 9.7, 6.6 Hz, 1H, 6-H), 2.38–2.10 (m, 3H, 13-H, 14-H, 14-H), 2.28 (s, 3H, 4-Ac), 2.24 (s, 3H, 10-Ac), 2.05 (d, $J =$ 1.0 Hz, 3H, 18-Me), 1.85 (ddd, $J = 14.5$, 10.9, 2.3 Hz, 1H, 6-H), 1.67 (s, 3H, 19-Me), 1.10 (s, 6H, 16-Me, 17-Me); ^{13}C NMR ($CDCl_3$): $\delta = 204.2$ (9), 171.4 (4-Ac), 170.6 (10-Ac), 167.0 (Bz), 146.5 (11), 133.7 (Ph), 131.7 (12), 130.1 (Ph), 129.3 (Ph), 128.6 (Ph), 84.4 (5), 80.7 (1), 79.0 (4), 76.4 (20), 76.2 (10), 74.9 (2), 72.3 (7), 67.9 (13), 58.6 (8), 46.1 (3), 42.6 (15), 38.7 (14), 35.5 (6), 26.9 (17), 22.6 (4-Ac), 20.9 (10-Ac), 20.9 (16), 15.6 (18), 9.4 (19); HR MS: calcd for $C_{31}H_{38}O_{11}Na$ $[M+Na]^+$ 609.2312, found 609.2313.

7-*O*-(Triethylsilyl)baccatin III: To a solution of baccatin III (15.7 mg, 26.8 μmol) in pyridine (1.3 mL) at 0 °C was added chlorotriethylsilane (121 mg, 0.803 mmol). The reaction mixture was stirred for 30 min at room temperature and then diluted with diethyl ether. The mixture was washed with water, saturated aqueous copper(II) sulfate, and brine, and dried over magnesium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford 7-*O*-(triethylsilyl)baccatin III (15.7 mg, 87%) and recovered baccatin III (0.7 mg, 5%) as white foams. **7-*O*-(Triethylsilyl)baccatin III**: m.p. 232–234 °C; $[\alpha]_D^{28} = -46.6$ (*c* 1.40, MeOH); IR (KBr): $\tilde{\nu} = 3470$, 1740, 1720, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 8.09$ (d, $J = 7.6$ Hz, 2H, *o*-Bz), 7.60 (t, $J =$ 7.6 Hz, 1H, *p*-Bz), 7.47 (t, $J = 7.6$ Hz, 2H, *m*-Bz), 6.46 (s, 1H, 10-H), 5.63 (d, $J = 6.9$ Hz, 1H, 2-H), 4.96 (dd, $J = 9.6$, 1.7 Hz, 1H, 5-H), 4.83–4.81 (m, 1H, 13-H), 4.49 (dd, $J = 10.6$, 6.6 Hz, 1H, 7-H), 4.30 (d, $J = 8.3$ Hz, 1H, 20-H), 4.14 (d, $J = 8.3$ Hz, 1H, 20-H), 3.88 (d, $J = 6.9$ Hz, 1H, 3-H), 2.53 (ddd, $J =$ 14.2, 9.6, 6.6 Hz, 1H, 6-H), 2.39 (d, $J = 5.0$ Hz, 1H, 13-OH), 2.28 (s, 3H, 4-Ac), 2.35–2.22 (m, 2H, 14-H, 14-H), 2.18 (s, 6H, 18-Me, 10-Ac), 1.87 (ddd, $J = 14.2$, 10.6, 1.7 Hz, 1H, 6-H), 1.68 (s, 3H, 19-Me), 1.19 (s, 3H, 16-Me), 1.03 (s, 3H, 17-Me), 0.92 (t, $J = 7.8$ Hz, 9H, TES), 0.58 (q, $J = 7.8$ Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 202.8$ (9), 171.1 (4-Ac), 169.8 (10-Ac), 167.5 (Bz), 144.6 (11), 134.0 (Ph), 133.0 (12), 130.5 (Ph), 129.8 (Ph), 129.0 (Ph), 84.6 (5), 81.2 (1), 79.1 (4), 76.9 (20), 76.2 (10), 75.1 (2), 72.8 (7), 68.2 (13), 59.0 (8), 47.7 (3), 43.2 (15), 38.7 (14), 37.6 (6), 27.2 (17), 23.1 (4-Ac), 21.4 (10-Ac), 20.5 (16), 15.4 (18), 10.4 (19), 7.2 (TES), 5.7 (TES); HR MS: calcd for $C_{37}H_{53}O_{11}Si$ $[M+H]^+$ 701.3357, found 701.3377.

***S*-Ethyl benzyloxyethanethioate**: Benzyloxyacetyl chloride was purchased from Aldrich or synthesized from benzyloxyacetic acid as follows: To a solution of benzyloxyacetic acid (3.00 g, 18.1 mmol) in dichloromethane (20 mL) at 0 °C was added a solution of thionyl chloride (12 mL, 164 mmol). The reaction mixture was refluxed for 10 min and then it was stirred for 10 h at room temperature. After the reaction mixture was concentrated by evaporation of the solvent, dichloromethane (30 mL) was added to the reaction mixture. The mixture was concentrated by evaporation of the solvent to afford crude benzyloxyacetyl chloride (3.33 g, 100%) as a colorless oil. The benzyloxyacetyl chloride thus prepared was used immediately in the following reaction without further purification.

To a solution of benzyloxyacetyl chloride (5.00 g, 27.1 mmol) and ethanethiol (2.2 mL, 29.7 mmol) in dichloromethane (14 mL) at 0 °C was added a solution of pyridine (2.6 mL, 32.1 mmol) in dichloromethane (7 mL). The reaction mixture was stirred for 20 h at room temperature and then concentrated by evaporation of the solvent. Water was added to the residue, and the mixture was extracted with diethyl ether. The organic layer was washed with water and brine, and dried over magnesium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by distillation to afford *S*-ethyl benzyloxyethanethioate (4.3 g, 76%) as a colorless oil: b.p. 110 °C/0.8 mmHg; IR (neat): $\tilde{\nu} = 1750$ cm^{-1}; ^{1}H NMR (CCl_4): $\delta = 7.35–7.25$ (m, 5H, Ph), 4.55 (s, 2H, Bn), 4.05 (s, 2H, 2-H, 2-H), 2.85 (q, $J = 7.0$ Hz, 2H, SEt), 1.25 (t, $J = 7.0$ Hz, 3H, SEt); HR MS: calcd for $C_{11}H_{15}O_2S$ $[M+H]^+$ 211.0793, found 211.0726.

2-Benzyloxy-1-ethylthio-1-(trimethylsiloxy)ethene (**65**): To a solution of diisopropylamine (557 mg, 5.50 mmol) in THF (20 mL) at 0 °C was added a solution of *n*-butyllithium in hexane (1.65 M, 3.33 mL, 5.50 mmol). After the reaction mixture had been stirred for 10 min at 0 °C, a solution of *S*-ethyl benzyloxyethanethioate (1.06 g, 5.04 mmol) in THF (10 mL) and a solution of chlorotrimethylsilane (598 mg, 5.50 mmol) in THF (5 mL) were added at −78 °C. The reaction mixture was allowed to warm to room temperature and then it was concentrated by evaporation of the solvent. Petroleum ether (20 mL) was added to the residue, and the suspension was filtered through a short pad of Celite under argon. The filtrate was concentrated by evaporation of the solvent to afford a mixture of enol silyl ethers **65** (*Z*/*E* = 84/16, 1.33 g, 94%) as a pale yellow oil: IR (neat): $\tilde{\nu} = 1250$, 1150, 830 cm^{-1}; HR MS: calcd for $C_{14}H_{23}O_2SSi$ $[M+H]^+$ 283.1188, found 283.1231. The crude product was used without further purification because the *E* isomer has no reactivity in the following asymmetric aldol reaction. The mixture of enol silyl ethers **65** was stored in a refrigerator to avoid isomerization from *Z* isomer to *E* isomer. **(*Z*)-2-Benzyloxy-1-ethylthio-1-(trimethylsiloxy)-ethene**: ^{1}H NMR ($CDCl_3$): $\delta = 7.53–7.26$ (m, 5H, Ph), 6.25 (s, 1H, 2-H), 4.78 (s, 2H, Bn), 2.69 (q, $J = 7.3$ Hz, 2H, SEt), 1.24 (t, $J = 7.3$ Hz, 3H, SEt), 0.16 (s, 9H, TMS); ^{13}C NMR ($CDCl_3$): $\delta = 137.1$ (1), 136.8 (Ph), 132.9 (Ph), 128.3 (Ph), 127.8 (Ph), 127.5 (2), 73.8 (Bn), 25.1 (SEt), 14.9 (SEt), −0.1 (TMS). **(*E*)-2-Benzyloxy-1-ethylthio-1-(trimethylsiloxy)ethene**: ^{1}H NMR ($CDCl_3$): $\delta = 7.53–7.26$ (m, 5H, Ph), 6.04 (s, 1H, 2-H), 4.78 (s, 2H, Bn), 2.57 (q, $J = 7.4$ Hz, 2H, SEt), 1.20 (t, $J = 7.4$ Hz, 3H, SEt), 0.22 (s, 9H, TMS); ^{13}C NMR ($CDCl_3$): $\delta = 137.1$ (1), 135.2 (Ph), 132.9 (Ph), 128.2 (Ph), 127.7 (Ph), 127.5 (2), 73.8 (Bn), 25.9 (SEt), 14.3 (SEt), 0.3 (TMS).

S*-Ethyl (2*R*,3*R*)-2-benzyloxy-3-hydroxy-3-phenylpropanethioate** (**67-*anti) and ***S*-ethyl (2*S*,3*R*)-2-benzyloxy-3-hydroxy-3-phenylpropanethioate** (**67-*syn***): Chiral diamine **66** was prepared by a literature method.[54b, c] To a suspension of tin(II) trifluoromethanesulfonate (167 mg, 0.400 mmol) in dichloromethane (1 mL) were added a solution of (*S*)-1-[(1-ethyl-2-pyrrolidinyl)methyl]piperidine (**66**) (94.2 mg, 0.480 mmol) in dichloromethane (0.5 mL) and a solution of dibutyltin diacetate (155 mg, 0.440 mmol) in dichloromethane (0.5 mL) at room temperature. After the reaction mixture had been stirred for 30 min at room temperature, a solution of enol silyl ethers **65** (*Z*/*E* = 84/16, 113 mg, 0.400 mmol) in dichloromethane (0.5 mL) and a solution of benzaldehyde (28.7 mg, 0.270 mmol) in dichloromethane (0.5 mL) were added at −78 °C. The reaction mixture was stirred for 20 h at −78 °C, and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the

solvent, the crude product was purified by thin-layer chromatography to afford a mixture of aldols **67** (*anti*/*syn* = 99/1, 82.5 mg, 96%) as a colorless oil: $[\alpha]_D^{24} = +107.2$ (*c* 0.85, benzene); IR (neat): $\tilde{\nu} = 3450, 1680\ cm^{-1}$; HPLC (CHIRALCEL AD, *i*PrOH/hexane = 1/50, flow rate = 0.5 mL min^{-1}): $t_R =$ 22.2 min (98.2%), $t_R = 26.6$ min (1.8%); anal. calcd for $C_{18}H_{20}O_3S$: C 68.33, H 6.37, S 10.13; found: C 67.84, H 6.37, S 10.07; HR MS: calcd for $C_{18}H_{20}O_3SNa$ $[M+Na]^+$ 339.1031, found 339.1018. **Aldol 67-*anti***: ^{1}H NMR ($CDCl_3$): $\delta = 7.42-7.11$ (m, 10H, Ph), 4.87 (dd, $J = 6.9$, 3.6 Hz, 1H, 3-H), 4.59 (d, $J = 11.2$ Hz, 1H, Bn), 4.20 (d, $J = 11.2$ Hz, 1H, Bn), 4.02 (d, $J =$ 6.9 Hz, 1H, 2-H), 3.19 (d, $J = 3.6$ Hz, 1H, OH), 2.85 (q, $J = 7.6$ Hz, 2H, SEt), 1.22 (d, $J = 7.6$ Hz, 3H, SEt); ^{13}C NMR ($CDCl_3$): $\delta = 203.0$ (1), 139.3 (Ph), 136.5 (Ph), 128.4 (Ph), 128.4 (Ph), 128.3 (Ph), 128.3 (Ph), 128.0 (Ph), 127.2 (Ph), 87.2 (2), 74.9 (3), 74.2 (Bn), 22.7 (SEt), 14.4 (SEt).

***S*-Ethyl (2*R*,3*S*)-3-azido-2-benzyloxy-3-phenylpropanethioate**: To a stirred mixture of sodium azide (1.50 g, 23.1 mmol), water (3.8 mL) and benzene (20.2 mL) at 0 °C was added concentrated sulfuric acid (3 mL). After the reaction mixture had been stirred for 15 min at room temperature, it was allowed to stand. The organic layer was separated and dried over sodium sulfate. The solution of hydrogen azide in benzene thus prepared was used immediately in the following reaction.

To a solution of aldols **67** (*anti*/*syn* = 99/1, 271 mg, 0.856 mmol) and triphenylphosphine (456 mg, 1.71 mmol) in benzene (8 mL) at room temperature were added the solution of hydrogen azide in benzene (1.4 mL) and DEAD in toluene (40%, 0.78 mL, 1.70 mmol). The reaction mixture was stirred for 30 min at room temperature. After filtration of the mixture through a short pad of silica gel and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford *S*-ethyl (2*R*,3*S*)-3-azido-2-benzyloxy-3-phenylpropanethioate (237 mg, 82% from aldol **67-*anti***) as a colorless oil: $[\alpha]_D^{29} = +169.8$ (*c* 1.44, benzene); IR (neat): $\tilde{\nu} = 2100, 1680\ cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 7.31-7.22$ (m, 10H, Ph), 4.92 (d, $J = 4.6$ Hz, 1H, 3-H), 4.66 (d, $J = 11.2$ Hz, 1H, Bn), 4.32 (d, $J = 11.2$ Hz, 1H, Bn), 4.07 (d, $J = 4.6$ Hz, 1H, 2-H), 2.88 (q, $J = 7.4$ Hz, 1H, SEt), 2.87 (q, $J =$ 7.4 Hz, 1H, SEt), 1.22 (t, $J = 7.4$ Hz, 3H, SEt); ^{13}C NMR ($CDCl_3$): $\delta = 200.5$ (1), 136.2 (Ph), 135.5 (Ph), 128.7 (Ph), 128.6 (Ph), 128.4 (Ph), 128.3 (Ph), 128.1 (Ph), 127.7 (Ph), 87.4 (2), 74.4 (Bn), 67.0 (3), 22.9 (SEt), 14.4 (SEt); HR MS: calcd for $C_{18}H_{19}N_3O_2SNa$ $[M+Na]^+$ 364.1096, found 364.1099.

***S*-Ethyl (2*R*,3*S*)-3-amino-2-benzyloxy-3-phenylpropanethioate (68)**: To a solution of *S*-ethyl (2*R*,3*S*)-3-azido-2-benzyloxy-3-phenylpropanethioate (75.0 mg, 0.220 mmol) and triphenylphosphine (69.0 mg, 0.264 mmol) in THF (4.5 mL) at room temperature was added water (3 drops). The reaction mixture was stirred for 6 h at 55 °C and then the solution was dried over sodium sulfate at room temperature. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford amine **68** (51.1 mg, 74%) and recovered *S*-ethyl (2*R*,3*S*)-3-azido-2-benzyloxy-3-phenylpropanethioate (13.2 mg, 18%) as colorless oils. **Amine 68**: $[\alpha]_D^{28} = +129.5$ (*c* 0.76, benzene); IR (neat): $\tilde{\nu} =$ 3320, 1680 cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 7.36-7.08$ (m, 10H, Ph), 4.53 (d, $J =$ 10.9 Hz, 1H, Bn), 4.45 (d, $J = 4.3$ Hz, 1H, 3-H), 4.04 (d, $J = 4.3$ Hz, 1H, 2-H), 4.03 (d, $J = 10.9$ Hz, 1H, Bn), 2.73 (q, $J = 7.3$ Hz, 2H, SEt), 1.51 (s, 2H, NH_2), 1.06 (t, $J = 7.3$ Hz, 3H, SEt); ^{13}C NMR (C_6D_6): $\delta = 201.4$ (1), 143.2 (Ph), 138.0 (Ph), 129.3 (Ph), 128.7 (Ph), 128.5 (Ph), 128.1 (Ph), 127.9 (Ph), 127.8 (Ph), 90.5 (2), 74.3 (Bn), 59.5 (3), 23.3 (SEt), 15.2 (SEt); HR MS: calcd for $C_{18}H_{22}NO_2S$ $[M+H]^+$ 316.1371, found 316.1375.

***S*-Ethyl (2*R*,3*S*)-3-benzoylamino-2-benzyloxy-3-phenylpropanethioate (69)**: To a solution of mixture of amine **68** (99.1 mg, 0.314 mmol) and DMAP (77.3 mg, 0.633 mmol) in dichloromethane (2.1 mL) at 0 °C was added benzoyl chloride (86.8 mg, 0.617 mmol) in dichloromethane (1.5 mL). The reaction mixture was stirred for 3 h at 0 °C and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with dichloromethane, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford amide **69** (118 mg, 90%) as a white solid: m.p. 144–145 °C; $[\alpha]_D^{26} = +66.1$ (*c* 0.77, $CHCl_3$); IR (KBr): $\tilde{\nu} = 1680,$ 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.82$ (dd, $J = 7.2$, 2.8 Hz, 2H, Bz), 7.50–7.15 (m, 14H, Ph, NH), 5.68 (dd, $J = 8.9$, 2.3 Hz, 1H, 3-H), 4.71 (d, $J =$ 11.2 Hz, 1H, Bn), 4.34 (d, $J = 11.2$ Hz, 1H, Bn), 4.27 (d, $J = 2.3$ Hz, 1H, 2-H), 2.97–2.80 (m, 2H, SEt), 1.19 (t, $J = 7.4$ Hz, 3H, SEt); ^{13}C NMR ($CDCl_3$): $\delta = 201.2$ (1), 166.4 (Bz), 138.6 (Ph), 136.1 (Ph), 134.1 (Ph), 133.1 (Ph), 131.6 (Ph), 128.5 (Ph), 128.4 (Ph), 128.2 (Ph), 128.2 (Ph), 127.6 (Ph), 127.1 (Ph), 126.7 (Ph), 86.2 (2), 74.3 (Bn), 55.1 (3), 22.8 (SEt), 14.4 (SEt); HR MS: calcd for $C_{25}H_{25}NO_3S$ $[M+H]^+$ 420.1633, found 420.1631.

(2*R*,3*S*)-3-Benzoylamino-2-benzyloxy-3-phenylpropionic acid (70): To a solution of amide **69** (84.9 mg, 0.202 mmol) in 1,4-dioxane (18.5 mL) at room temperature was added silver nitrate in water (1M, 8.7 mL, 8.7 mmol). The reaction mixture was refluxed for 10 h and then it was filtered through a short pad of Celite. The mixture was extracted with benzene, and the organic layer was dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford carboxylic acid **70** (59.1 mg, 78%) as a white foam: m.p. 184 °C; $[\alpha]_D^{26} = +5.3$ (*c* 0.35, EtOH); IR (KBr): $\tilde{\nu} = 3420, 1650,$ 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.81$ (d, $J = 8.2$ Hz, 2H, Bz), 7.52–7.28 (m, 13H, Ph), 7.14 (d, $J = 8.9$ Hz, 1H, NH), 5.81 (dd, $J = 8.9$, 2.0 Hz, 1H, 3-H), 4.76 (d, $J = 11.9$ Hz, 1H, Bn), 4.39 (d, $J = 11.9$ Hz, 1H, Bn), 4.35 (d, $J = 2.0$ Hz, 1H, 2-H), 3.30 (br s, 1H, COOH); ^{13}C NMR ($CDCl_3$): $\delta = 175.1$ (1), 167.9 (Bz), 139.0 (Ph), 137.0 (Ph), 133.6 (Ph), 131.6 (Ph), 128.3 (Ph), 128.2 (Ph), 128.1 (Ph), 127.9 (Ph), 127.5 (Ph), 127.4 (Ph), 127.3 (Ph), 126.8 (Ph), 80.4 (2), 72.6 (Bn), 54.9 (3); HR MS: calcd for $C_{23}H_{22}NO_4$ $[M+H]^+$ 376.1549, found 376.1568; HR MS: calcd for $C_{23}H_{21}NO_4Na$ $[M+Na]^+$ 398.1369, found 398.1380.

***S*-Ethyl (2*R*,3*S*)-3-benzoylamino-2-hydroxy-3-phenylpropanethioate**: To a solution of amide **69** (427 mg, 1.02 mmol) in dichloromethane (9.5 mL) at room temperature was added tin(IV) chloride (292 mg, 1.12 mmol) in dichloromethane (5 mL). The reaction mixture was refluxed for 5 h, and then saturated aqueous sodium hydrogencarbonate was added at 0 °C. The mixture was extracted with dichloromethane and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography to afford *S*-ethyl (2*R*,3*S*)-3-benzoylamino-2-hydroxy-3-phenylpropanethioate (351 mg, 96%) as a white solid: m.p. 137 °C; $[\alpha]_D^{28} = +105.5$ (*c* 0.62, EtOH); IR (KBr): $\tilde{\nu} = 3330, 1680, 1640\ cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 7.78-7.75$ (m, 2H, Bz), 7.53–7.24 (m, 9H, Ph, NH), 5.64 (dd, $J = 8.9$, 2.6 Hz, 1H, 3-H), 4.59 (d, $J = 2.6$ Hz, 1H, 2-H), 4.22 (br s, 1H, OH), 2.92–2.83 (m, 2H, SEt), 1.19 (t, $J = 7.4$ Hz, 3H, SEt); ^{13}C NMR ($CDCl_3/CD_3OD = 4/1$): $\delta = 203.4$ (1), 167.4 (Bz), 138.5 (Ph), 133.7 (Ph), 131.6 (Ph), 128.4 (Ph), 128.3 (Ph), 127.4 (Ph), 127.0 (Ph), 126.7 (Ph), 79.1 (2), 55.9 (3), 22.6 (SEt), 14.2 (SEt); HR MS: calcd for $C_{18}H_{20}NO_3S$ $[M+H]^+$ 330.1164, found 330.1165.

Methyl (2*R*,3*S*)-3-benzoylamino-2-hydroxy-3-phenylpropionate (71): To a solution of *S*-ethyl (2*R*,3*S*)-3-benzoylamino-2-hydroxy-3-phenylpropanethioate (24.1 mg, 73.2 μmol) in methanol (0.6 mL) at room temperature was added silver trifluoroacetate (61.6 mg, 0.279 mmol). The reaction mixture was stirred for 1 h at room temperature and then saturated aqueous sodium hydrogencarbonate was added. The mixture was filtered through a short pad of Celite, and the filtrate was extracted with ethyl acetate. The organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford ester **71** (18.3 mg, 84%) as a white solid: m.p. 181–183 °C; $[\alpha]_D^{27} = -52.1$ (*c* 0.57, EtOH); IR (KBr): $\tilde{\nu} = 3340, 1740, 1640\ cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 7.79-$ 7.76 (m, 2H, Bz), 7.55–7.28 (m, 8H, Ph), 6.97 (d, $J = 9.2$ Hz, 1H, NH), 5.75 (dd, $J = 9.2$, 2.0 Hz, 1H, 3-H), 4.65 (dd, $J = 4.0$, 2.0 Hz, 1H, 2-H), 3.86 (s, 3H, MeO), 3.25 (d, $J = 4.0$ Hz, 1H, OH); ^{13}C NMR ($CDCl_3/CD_3OD = 2/1$): $\delta = 177.4$ (1), 172.5 (Bz), 143.0 (Ph), 138.2 (Ph), 136.2 (Ph), 132.9 (Ph), 132.8 (Ph), 132.0 (Ph), 131.5 (Ph), 131.1 (Ph), 77.8 (2), 60.1 (3), 56.7 (MeO); HR MS: calcd for $C_{17}H_{18}NO_4$ $[M+H]^+$ 300.1236, found 300.1257.

Methyl (4*S*,5*R*)-3-benzoyl-2,2-dimethyl-4-phenyl-1,3-oxazolidine-5-carboxylate (72): To a mixture of ester **71** (43.1 mg, 0.144 mmol) and 2-methoxypropene (0.203 mL, 2.20 mmol) in toluene (2 mL) at room temperature was added PPTS (4.0 mg, 15.9 μmol). The reaction mixture was stirred for 10 h at 80 °C and then it was filtered through a short pad of silica gel with ethyl acetate. After evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford acetonide **72** (43.7 mg, 89%) as a colorless oil: IR (neat): $\tilde{\nu} = 1760, 1740, 1640\ cm^{-1}$; ^{1}H NMR ($CCl_4$): $\delta = 7.56-6.75$ (m, 10H, Ph), 5.23 (d, $J = 5.2$ Hz, 1H, 3-H), 4.38 (d, $J = 5.2$ Hz, 1H, 2-H), 3.71 (s, 3H, MeO), 1.89 (s, 3H, Me), 1.78 (s, 3H, Me); ^{13}C NMR ($CDCl_3$): $\delta = 169.6$ (1), 168.9 (Bz), 138.7 (Ph), 137.4 (Ph), 129.2 (Ph), 128.3 (Ph), 127.9 (Ph), 127.6 (Ph), 126.6 (Ph), 125.9 (Ph), 97.7 (acetonide), 81.3 (2), 65.2 (3), 52.5 (MeO), 25.3 (Me), 25.0 (Me); HR MS: calcd for $C_{20}H_{22}NO_4$ $[M+H]^+$ 340.1549, found 340.1544.

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(4*S*,5*R*)-3-Benzoyl-2,2-dimethyl-4-phenyl-1,3-oxazolidine-5-carboxylic acid (**73**): To a solution of acetonide **72** (106 mg, 0.311 mmol) in methanol (4 mL) at room temperature was added lithium hydroxide in water (1M, 0.311 mL, 0.311 mmol). The reaction mixture was stirred for 9 h at room temperature, and then hydrochloric acid (1M, 0.31 mL) was added at 0 °C. The mixture was concentrated and azeotropically dried with 2-butanone. The crude product was purified by thin-layer chromatography to afford carboxylic acid **73** (89.6 mg, 86 %) as a white solid: m.p. 213 °C; $[\alpha]_D^{28} = +99.1$ (*c* 0.36, EtOH); IR (KBr): $\tilde{\nu} = 1640$, 1620 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.28-6.80$ (m, 10H, Ph), 5.09 (br s, 1H, 3-H), 4.36 (br s, 1H, 2-H), 1.83 (br s, 6H, Me, Me); ^{13}C NMR ($CDCl_3$): $\delta = 175.6$ (1), 169.3 (Bz), 139.4 (Ph), 137.5 (Ph), 129.5 (Ph), 128.3 (Ph), 128.0 (Ph), 127.4 (Ph), 127.1 (Ph), 126.1 (Ph), 97.2 (acetonide), 82.2 (2), 65.4 (3), 25.9 (Me), 25.0 (Me); HR MS: calcd for $C_{19}H_{19}NO_4Na$ $[M+Na]^+$ 348.1212, found 348.1225.

Methyl (2*S*,4*S*,5*R*)-3-benzoyl-2-(*p*-methoxyphenyl)-4-phenyl-1,3-oxazolidine-5-carboxylate (**74**): To a mixture of ester **71** (192 mg, 0.642 mmol) and *p*-methoxybenzaldehyde dimethyl acetal (489 mg, 2.68 mmol) in toluene (21 mL) at room temperature was added CSA (4.7 mg, 20.2 μmol). The reaction mixture was concentrated by evaporation of the solvent at 130 °C. Triethylamine (6 drops) was added to the residue (ca. 5 mL) at room temperature and then the mixture was filtered through a short pad of silica gel with ethyl acetate. The crude product was purified by column chromatography to afford *N,O*-acetal **74** (212 mg, 79 %) as a white amorphous foam, *N,O*-acetal **76** (49.2 mg, 18 %) as white needles, and recovered ester **71** (3.5 mg, 2 %). ***N,O*-Acetal 74**: $[\alpha]_D^{29} = -51.4$ (*c* 0.45, benzene); IR (neat): $\tilde{\nu} = 1750$, 1650 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.40-7.20$ (m, 12H, Ph), 6.85 (d, $J = 8.6$ Hz, 2H, Ph), 6.85 (br s, 1H, CHPMP), 5.40 (br s, 1H, 3-H), 4.87 (br s, 1H, 2-H), 3.83 (s, 3H, MeO), 3.82 (s, 3H, MeO); ^{13}C NMR (C_6D_6): $\delta = 172.1$ (1), 170.5 (Bz), 160.4 (PMP), 140.1 (Ph), 136.7 (Ph), 130.8 (Ph), 130.5 (Ph), 129.3 (Ph), 128.8 (Ph), 128.6 (Ph), 128.1 (Ph), 127.5 (Ph), 127.4 (Ph), 113.8 (PMP), 91.7 (CHPMP), 82.4 (2), 65.4 (3), 54.7 (MeO), 52.0 (MeO); HR MS: calcd for $C_{25}H_{24}NO_5$ $[M+H]^+$ 418.1654, found 418.1663.

Methyl (2*R*,4*S*,5*R*)-3-benzoyl-2-(*p*-methoxyphenyl)-4-phenyl-1,3-oxazolidine-5-carboxylate (**76**): To a mixture of ester **71** (261 mg, 0.872 mmol) and *p*-methoxyphenyl methyl ether (1.19 g, 7.79 mmol) in acetonitrile (4 mL) at room temperature was added DDQ (650 mg, 2.89 mmol). After the reaction mixture had been stirred for 7 min at 70 °C, it was cooled down to room temperature. The mixture was filtered through a short pad of Celite with ethyl acetate and then the filtrate was washed with saturated aqueous sodium hydrogencarbonate and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by column chromatography and recrystallization from dichloromethane/hexane to afford *N,O*-acetal **76** (273 mg, 75 %) as slightly red needles: m.p. 160–161 °C; $[\alpha]_D^{28} = +85.9$ (*c* 0.63, benzene); IR (neat): $\tilde{\nu} = 1740$, 1640 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.26-7.13$ (m, 12H, Ph), 6.83 (br s, 2H, Ph), 6.69 (br s, 1H, CHPMP), 5.61 (br s, 1H, 3-H), 4.81 (br s, 1H, 2-H), 3.77 (s, 3H, MeO), 3.65 (s, 3H, MeO); ^{13}C NMR (C_6D_6): $\delta = 169.8$ (1), 169.6 (Bz), 160.5 (PMP), 140.2 (Ph), 137.6 (Ph), 130.9 (Ph), 130.0 (Ph), 129.3 (Ph), 127.8 (Ph), 127.6 (Ph), 127.1 (Ph), 126.9 (Ph), 126.6 (Ph), 113.8 (PMP), 93.2 (CHPMP), 83.8 (2), 65.1 (3), 54.7 (MeO), 51.8 (MeO); HR MS: calcd for $C_{25}H_{24}NO_5$ $[M+H]^+$ 418.1654, found 418.1663.

(2*S*,4*S*,5*R*)-3-Benzoyl-2-(*p*-methoxyphenyl)-4-phenyl-1,3-oxazolidine-5-carboxylic acid (**75**): To a solution of *N,O*-acetal **74** (196 mg, 0.468 mmol) in a mixture of methanol (1.5 mL) and THF (0.4 mL) at 0 °C was added lithium hydroxide (11.9 mg, 0.470 mmol) in water (1.5 mL). The reaction mixture was stirred for 20 min at 0 °C and then ethyl acetate, water, and hydrochloric acid (1M, 0.48 mL) were added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford carboxylic acid **75** (157 mg, 83 %) as a white solid: m.p. 175–178 °C; $[\alpha]_D^{29} = -37.1$ (*c* 0.93, EtOH); IR (KBr): $\tilde{\nu} = 1640$, 1610 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.72-6.50$ (br m, 16H, Ph, CHPMP, COOH), 5.36 (br s, 1H, 3-H), 4.52 (br s, 1H, 2-H), 3.70 (s, 3H, MeO); ^{13}C NMR (CD_3OD): $\delta = 177.8$ (1), 173.6 (Bz), 161.3 (PMP), 141.5 (Ph), 137.1 (Ph), 131.5 (Ph), 129.9 (Ph), 129.4 (Ph), 129.3 (Ph), 128.7 (Ph), 128.4 (Ph), 127.9 (Ph), 127.2 (Ph), 114.5 (PMP), 91.7 (CHPMP), 85.4 (2), 66.8 (3), 55.7 (MeO); HR MS: calcd for $C_{24}H_{21}NO_5Na$ $[M+Na]^+$ 426.1317, found 426.1306.

(2*R*,4*S*,5*R*)-3-Benzoyl-2-(*p*-methoxyphenyl)-4-phenyl-1,3-oxazolidine-5-carboxylic acid (**77**): To a solution of *N,O*-acetal **76** (273 mg, 0.653 mmol) in a mixture of methanol (7 mL) and THF (9 mL) at 0 °C was added lithium hydroxide (16.9 mg, 0.706 mmol) in water (3 mL). The reaction mixture was stirred for 30 min at room temperature and then ethyl acetate and hydrochloric acid (1M, 0.70 mL) were added at 0 °C. The organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography and reprecipitation from dichloromethane/hexane to afford carboxylic acid **77** (226 mg, 86 %) as a white solid: m.p. 181–183 °C; $[\alpha]_D^{27} = +66.4$ (*c* 0.56, EtOH); IR (KBr): $\tilde{\nu} = 3471$, 1628 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.58-6.08$ (br m, 15H, Ph, CHPMP), 5.34 (br s, 1H, 3-H), 4.34 (br s, 1H, 2-H), 3.70 (s, 3H, MeO); ^{13}C NMR ($CDCl_3$): $\delta = 173.2$ (1), 170.0 (Bz), 160.5 (PMP), 139.6 (Ph), 136.6 (Ph), 130.1 (Ph), 129.3 (Ph), 128.4 (Ph), 127.9 (Ph), 127.8 (Ph), 127.2 (Ph), 127.1 (Ph), 114.0 (PMP), 92.5 (CHPMP), 85.0 (2), 65.0 (3), 55.4 (MeO); HR MS: calcd for $C_{24}H_{21}NO_5Na$ $[M+Na]^+$ 426.1317, found 426.1326.

(2*S*,4*S*,5*R*)-3-Benzyl-2-(*p*-methoxyphenyl)-4-phenyl-1,3-oxazolidin-5-yl-methanol (**78**):

Method A: To a solution of *N,O*-acetal **74** (21.4 mg, 51.3 μmol) in THF at 0 °C was added lithium aluminum hydride in THF (1.0M, 0.10 mL, 0.10 mmol). The reaction mixture was stirred for 20 min at 0 °C, and then several drops of saturated aqueous sodium sulfate were added. The mixture was filtered through a short pad of Celite and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford *N,O*-acetal **78** (13.8 mg, 72 %) as a colorless oil.

Method B: To a solution of *N,O*-acetal **74** (17.5 mg, 41.9 μmol) in benzene at room temperature was added Red-Al® in toluene (65 %, 0.08 mL, 0.27 mmol). The reaction mixture was refluxed for 1.5 h and then methanol and a few drops of saturated aqueous sodium sulfate were added at room temperature. The mixture was filtered through a short pad of Celite and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford *N,O*-acetal **78** (3.3 mg, 21 %) as a colorless oil. $[\alpha]_D^{27} = -4.2$ (*c* 0.55, EtOH); IR (neat): $\tilde{\nu} = 3390$ cm^{-1}; ^1H NMR (C_6D_6): $\delta = 7.58$ (d, $J = 8.5$ Hz, 2H, Ph), 7.48 (d, $J = 7.3$ Hz, 2H, Ph), 7.19–7.08 (m, 4H, Ph), 7.00–6.93 (m, 2H, Ph), 6.97 (d, $J = 8.2$ Hz, 2H, Ph), 6.85 (d, $J = 8.2$ Hz, 2H, Ph), 5.22 (s, 1H, CHPMP), 4.08 (ddd, $J = 8.6$, 4.0, 2.7 Hz, 1H, 2-H), 3.94 (d, $J = 8.6$ Hz, 1H, 3-H), 3.58 (s, 2H, Bn), 3.57 (dd, $J = 12.2$, 2.7 Hz, 1H, 1-H), 3.39 (dd, $J = 12.2$, 4.0 Hz, 1H, 1-H), 3.35 (s, 3H, MeO); ^{13}C NMR (C_6D_6): $\delta = 161.1$ (PMP), 139.8 (Ph), 136.8 (Ph), 132.9 (Ph), 130.6 (Ph), 130.4 (Ph), 129.3 (Ph), 129.0 (Ph), 128.8 (Ph), 128.0 (Ph), 127.5 (Ph), 114.4 (PMP), 96.4 (CHPMP), 86.2 (2), 67.9 (3), 61.9 (1), 55.2 (MeO), 53.3 (Bn); HR MS: calcd for $C_{24}H_{26}NO_3$ $[M+H]^+$ 376.1913, found 376.1899.

Methyl (*tert*-butyldimethylsiloxy)acetate: To a solution of methyl hydroxyacetate (9.73 g, 108 mmol) and imidazole (22.1 g, 324 mmol) in DMF (60 mL) at 0 °C was added a solution of *tert*-butylchlorodimethylsilane (32.4 g, 215 mmol) in dichloromethane (40 mL). The reaction mixture was stirred for 12 h at room temperature and then water (120 mL) was added at 0 °C. The mixture was extracted with diethyl ether, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by distillation to afford methyl (*tert*-butyldimethylsiloxy)acetate (22.1 g, 100 %) as a colorless oil: b.p. 52 °C/1.8 mmHg; IR (neat): $\tilde{\nu} = 1770$ cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 4.20$ (s, 2H, 2-H, 2-H), 3.69 (s, 3H, MeO), 0.87 (s, 9H, TBS), 0.06 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): $\delta = 172.0$ (1), 61.6 (2), 51.6 (MeO), 25.6 (TBS), 18.3 (TBS), −5.6 (TBS), −5.6 (TBS); HR MS: calcd for $C_9H_{20}O_3SiNa$ $[M+Na]^+$ 227.1080, found 227.0998.

2-(*tert*-Butyldimethylsiloxy)-1-methoxy-1-(trimethylsiloxy)ethene: To a solution of 2,2,6,6-tetramethylpiperidine (10.9 mL, 9.12 g, 64.6 mmol) in THF (210 mL) at 0 °C was added *n*-butyllithium in hexane (1.53M, 38.7 mL, 59.2 mmol). After the reaction mixture had been stirred for 20 min at 0 °C, chlorotrimethylsilane (8.95 mL, 7.66 g, 70.5 mmol) and a solution of methyl (*tert*-butyldimethylsiloxy)acetate (11.0 g, 53.8 mmol) in THF (38 mL) were added at −95 °C. The reaction mixture was stirred for 1.5 h at room temperature and then it was concentrated by evaporation of the solvent. Petroleum ether (100 mL) was added to the residue, and then the suspension was filtered through a short pad of Celite under argon atmosphere. After evaporation of the solvent, the crude product was

purified by distillation to afford a mixture of 2-(*tert*-butyldimethylsiloxy)-1-methoxy-1-(trimethylsiloxy)ethenes (*E*/*Z* = 94/6, 6.32 g, 42%) as a colorless oil: b.p. 81 °C/3.4 mmHg; IR (neat): $\tilde{\nu}$ = 1250, 1180, 840 cm^{-1}; HR MS: calcd for $C_{12}H_{29}O_3Si_2$ $[M+H]^+$ 277.1656, found 277.1562. **(*E*)-2-(*tert*-Butyldimethylsiloxy)-1-methoxy-1-(trimethylsiloxy)ethene**: ^{1}H NMR ($CDCl_3$): δ = 5.44 (s, 1H, 2-H), 3.63 (s, 3H, MeO), 0.93 (s, 9H, TBS), 0.20 (s, 9H, TMS), 0.11 (s, 6H, TBS); ^{13}C NMR ($CDCl_3$): δ = 149.1 (1), 109.3 (2), 56.3 (MeO), 26.0 (TBS), 18.6 (TBS), 0.0 (s, TMS), −5.2 (TBS), −5.2 (TBS).

Methyl (2*RS*,3*SR*)-3-benzylamino-2-(*tert*-butyldimethylsiloxy)-3-phenylpropionate (**79-*syn***) and **methyl (2*RS*,3*RS*)-3-benzylamino-2-(*tert*-butyldimethylsiloxy)-3-phenylpropionate** (**79-*anti***):[58] To a suspension of ytterbium(III) trifluoromethanesulfonate (98.4 mg, 0.159 mmol) in dichloromethane (3 mL) at room temperature was added a solution of *N*-benzylidenebenzylamine (619 mg, 3.17 mmol) and a mixture of 2-(*tert*-butyldimethylsiloxy)-1-methoxy-1-(trimethylsiloxy)ethenes (*E*/*Z* = 94/6, 1.06 g, 2.81 mmol) in dichloromethane (6 mL). The reaction mixture was stirred for 3.5 h at room temperature and then water was added. The mixture was extracted with dichloromethane, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by silica gel chromatography to afford ester **79-*syn*** (293 mg, 23%) and ester **79-*anti*** (753 mg, 59%) as colorless oils. **Ester 79-*syn***: IR (neat): $\tilde{\nu}$ = 1750, 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.36–7.17 (m 10H, Ph), 4.23 (d, *J* = 4.6 Hz, 1H, 2-H), 4.04 (d, *J* = 4.6 Hz, 1H, 3-H), 3.84 (s, 3H, MeO), 3.77 (d, *J* = 13.5 Hz, 1H, Bn), 3.46 (d, *J* = 13.5 Hz, 1H, Bn), 2.35 (br s, 1H, NH), 0.82 (s, 9H, TBS), −0.12 (s, 3H, TBS), −0.23 (s, 3H, TBS); ^{13}C NMR ($CDCl_3$): δ = 172.4 (1), 140.4 (Ph), 139.2 (Ph), 128.3 (Ph), 128.2 (Ph), 128.1 (Ph), 128.0 (Ph), 127.5 (Ph), 126.8 (Ph), 77.4 (2), 64.2 (3), 51.6 (MeO), 52.4 (Bn), 25.6 (TBS), 18.3 (TBS), −5.5 (TBS), −5.8 (TBS); HR MS: calcd for $C_{23}H_{34}NO_3Si$ $[M+H]^+$ 400.2308, found 400.2321.

Methyl (2*RS*,3*SR*)-3-benzylamino-2-hydroxy-3-phenylpropionate: To a solution of ester **79-*syn*** (209 mg, 0.523 mmol) in THF (2 mL) at 0 °C was added TBAF in THF (1.0 M, 0.63 mL, 0.63 mmol). The reaction mixture was stirred for 30 min at 0 °C and then phosphate buffer (pH = 7) was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with brine and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford methyl (2*RS*,3*SR*)-3-benzylamino-2-hydroxy-3-phenylpropionate (135 mg, 90%) as colorless needles: m.p. 86–88 °C; IR (neat): $\tilde{\nu}$ = 3510, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.36–7.19 (m, 10H, Ph), 4.22 (d, *J* = 4.0 Hz, 1H, 2-H), 3.93 (d, *J* = 4.0 Hz, 1H, 3-H), 3.72 (d, *J* = 13.4 Hz, 1H, Bn), 3.63 (s, 3H, MeO), 3.50 (d, *J* = 13.4 Hz, 1H, Bn), 2.89 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$): δ = 174.3 (1), 140.4 (Ph), 139.9 (Ph), 129.0 (Ph), 128.7 (Ph), 128.2 (Ph), 127.5 (Ph), 75.5 (2), 63.9 (3), 52.8 (MeO), 51.0 (Bn), 25.6 (TBS), 18.3 (TBS), −5.5 (TBS), −5.8 (TBS); HR MS: calcd for $C_{17}H_{20}NO_3$ $[M+H]^+$ 286.1443, found 286.1444.

Methyl (2*RS*,4*RS*,5*SR*)-3-benzyl-2-(*p*-methoxyphenyl)-4-phenyl-1,3-oxazolidine-5-carboxylate (**80**): To a solution of methyl (2*RS*,3*SR*)-3-benzylamino-2-hydroxy-3-phenylpropionate (22.0 mg, 77.1 μmol) and *p*-methoxybenzaldehyde dimethylacetal (45.6 mg, 77.1 μmol) in toluene (10 mL) at room temperature was added CSA (0.5 mg, 2.2 μmol). The reaction mixture was concentrated by evaporation of the solvent, and then the residue was filtered through a short pad of silica gel with ethyl acetate. After evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford *N,O*-acetal **80** (30.1 mg, 97%) as a colorless oil: IR (neat): $\tilde{\nu}$ = 1740 cm^{-1}; ^{1}H NMR (C_6D_6): δ = 7.57 (d, *J* = 8.6 Hz, 2H, Ph), 7.50 (d, *J* = 8.2 Hz, 2H, Ph), 7.27–7.00 (m, 4H, Ph), 6.94–6.88 (m, 4H, Ph), 6.80 (d, *J* = 8.6 Hz, 2H, Ph), 5.48 (s, 1H, CHPMP), 4.61 (d, *J* = 7.0 Hz, 1H, 2-H), 4.19 (d, *J* = 7.0 Hz, 1H, 3-H), 3.59 (d, *J* = 13.4 Hz, 1H, Bn), 3.53 (d, *J* = 13.4 Hz, 1H, Bn), 3.33 (s, 3H, MeO), 3.27 (s, 3H, MeO); ^{13}C NMR (C_6D_6): δ = 171.9 (1), 161.1 (PMP), 140.0 (Ph), 136.3 (Ph), 130.9 (Ph), 130.7 (Ph), 130.4 (Ph), 130.1 (Ph), 129.0 (Ph); 128.8 (Ph), 128.0 (Ph), 127.4 (Ph), 114.2 (PMP), 92.5 (CHPMP), 83.1 (2), 70.2 (3), 55.0 (MeO), 52.9 (Bn), 51.7 (MeO); HR MS: calcd for $C_{25}H_{26}NO_4$ $[M+H]^+$ 404.1862, found 404.1857.

(2*RS*,4*RS*,5*SR*)-3-Benzyl-2-(*p*-methoxyphenyl)-4-phenyl-1,3-oxazolidin-5-ylmethanol (**78**): To a solution of *N,O*-acetal **80** (118 mg, 0.291 mmol) at 0 °C was added lithium aluminum hydride in THF (1.0 M, 0.30 mL, 0.30 mmol). The reaction mixture was stirred for 20 min at 0 °C and then several drops of saturated aqueous sodium sulfate were added. The mixture was filtered through a short pad of Celite and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford *N,O*-acetal **78** (79.4 mg, 73%) as a colorless oil. Physical data of this *N,O*-acetal **78** were identical to those of the compound derived from *N,O*-acetal **74** except for its optical rotation.

2′-*O*-Benzyl-7-*O*-(triethylsilyl)paclitaxel (**81**): To a suspension of carboxylic acid **70** (10.6 mg, 28.2 μmol), 7-*O*-(triethylsilyl)baccatin III (3.2 mg, 4.7 μmol) and DMAP (1.1 mg, 9.4 μmol) in toluene (0.25 mL) at room temperature was added DPTC (6.4 mg, 28.2 μmol). The reaction mixture was concentrated by evaporation of the solvent and then the residue was stirred for 1 h at 73 °C. After filtration of the mixture through a short pad of silica gel with ethyl acetate, the filtrate was concentrated and the residue was azeotropically dried with benzene.

To a suspension of the above residue, carboxylic acid **70** (10.3 mg, 27.4 μmol), and DMAP (1.1 mg, 9.4 μmol) in toluene (0.25 mL) at room temperature was added DPTC (6.5 mg, 28.6 μmol). The reaction mixture was concentrated by evaporation of the solvent and then the residue was stirred for 1 h at 73 °C. After filtration of the mixture through a short pad of silica gel with ethyl acetate, the filtrate was concentrated and the residue was azeotropically dried with benzene.

To a suspension of the above residue, carboxylic acid **70** (10.3 mg, 27.4 μmol), and DMAP (1.0 mg, 8.2 μmol) in toluene (0.30 mL) at room temperature was added DPTC (6.5 mg, 28.6 μmol). The reaction mixture was concentrated by evaporation of the solvent and then the residue was stirred for 1 h at 73 °C. After filtration of the mixture through a short pad of silica gel with ethyl acetate, the filtrate was concentrated and the residue was azeotropically dried with benzene.

To a suspension of the above residue, carboxylic acid **70** (10.3 mg, 27.4 μmol), and DMAP (1.1 mg, 9.4 μmol) in toluene (0.25 mL) at room temperature was added DPTC (6.6 mg, 29.1 μmol). The reaction mixture was concentrated by evaporation of the solvent and then the residue was stirred for 1 h at 73 °C. The crude product was purified by thin-layer chromatography to afford protected Taxol **81** (3.2 mg, 66%) and recovered 7-*O*-(triethylsilyl)baccatin III (1.1 mg, 34%) as white solids. **Protected Taxol 81**: m.p. 121–122 °C; $[\alpha]_D^{24}$ = −18.4 (*c* 0.75, MeOH); IR (KBr): $\tilde{\nu}$ = 3520, 1730, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 8.12 (dd, *J* = 7.3, 1.3 Hz, 2H, BzO), 7.77 (dd, *J* = 7.3, 1.3 Hz, 2H, BzN), 7.69–7.03 (m, 16H, Ph), 7.11 (d, *J* = 7.9 Hz, 1H, NH), 6.44 (s, 1H, 10-H), 6.26 (t, *J* = 8.9 Hz, 1H, 13-H), 5.73 (dd, *J* = 7.9, 2.3 Hz, 1H, 3′-H), 5.70 (d, 1H, *J* = 6.9 Hz, 2-H), 4.93 (dd, *J* = 8.3, 1.5 Hz, 1H, 5-H), 4.75 (d, *J* = 11.6 Hz, 1H, Bn), 4.45 (dd, *J* = 10.4, 6.2 Hz, 1H, 7-H), 4.43 (d, *J* = 2.3 Hz, 1H, 2′-H), 4.43 (d, *J* = 11.6 Hz, 1H, Bn), 4.30 (d, *J* = 8.6 Hz, 1H, 20a-H), 4.18 (d, *J* = 8.6 Hz, 1H, 20b-H), 3.80 (d, *J* = 6.9 Hz, 1H, 3-H), 2.51 (ddd, *J* = 15.8, 8.3, 6.2 Hz, 1H, 6a-H), 2.34 (dd, *J* = 15.2, 8.9 Hz, 1H, 14-H), 2.29 (s, 3H, 4-Ac), 2.18 (s, 3H, 10-Ac), 2.17 (dd, *J* = 15.2, 8.9 Hz, 1H, 14-H), 2.00 (s, 3H, 18-Me), 1.90 (ddd, *J* = 15.8, 10.4, 1.5 Hz, 1H, 6b-H), 1.77 (s, 1H, 1-OH), 1.69 (s, 3H, 19-Me), 1.23 (s, 3H, 16-Me), 1.20 (s, 3H, 17-Me), 0.93 (t, *J* = 7.9 Hz, 9H, TES), 0.58 (q, *J* = 7.9 Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): δ = 201.7 (9), 170.3 (1′), 169.9 (10-Ac), 169.3 (4-Ac), 167.1 (Bz), 167.0 (Bz), 140.5 (12), 138.2 (Ph), 135.9 (Ph), 133.9 (Ph), 133.9 (Ph), 133.7 (11), 131.8 (Ph), 130.2 (Ph), 129.2 (Ph), 128.7 (Ph), 128.6 (Ph), 128.6 (Ph), 128.4 (Ph), 128.1 (Ph), 128.0 (Ph), 127.1 (Ph), 127.0 (Ph), 126.7 (Ph), 84.2 (5), 81.1 (4), 79.0 (1), 78.8 (2′), 76.7 (20), 75.0 (10), 74.8 (2), 72.7 (Bn), 72.2 (7), 71.4 (13), 58.4 (8), 54.5 (3′), 46.7 (3), 43.3 (15), 37.2 (6), 35.3 (14), 26.6 (17), 22.7 (4-Ac), 21.3 (16), 20.9 (10-Ac), 14.4 (18), 10.1 (19), 6.7 (TES), 5.3 (TES); HR MS: calcd for $C_{40}H_{71}NO_{14}SiNa$ $[M+Na]^+$ 1080.4542, found 1080.4561.

7-*O*-(Triethylsilyl)paclitaxel: To a solution of protected Taxol **81** (3.9 mg, 3.7 μmol) in ethanol (0.5 mL) at room temperature was added palladium hydroxide on carbon (33 mg). The reaction mixture was stirred for 23 h at room temperature under hydrogen. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford 7-*O*-(triethylsilyl)paclitaxel (2.7 mg, 76%) as a white solid: m.p. 114 °C; $[\alpha]_D^{25}$ = −38.1 (*c* 0.48, MeOH); IR (KBr): $\tilde{\nu}$ = 3460, 1730, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 8.13 (d, *J* = 7.6 Hz, 2H, BzO), 7.75 (d, *J* = 7.1 Hz, 2H, BzN), 7.61 (t, *J* = 9.2 Hz, 1H, BzO), 7.52–7.33 (m, 10H, Ph), 7.04 (d, *J* = 9.0 Hz, 1H, NH), 6.42 (s, 1H, 10-H), 6.19 (t, *J* = 9.0 Hz, 1H, 13-H), 5.80 (dd, *J* = 9.0, 2.2 Hz, 1H, 3′-H), 5.68 (d, *J* = 7.1 Hz, 1H, 2-H), 4.92

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(dd, $J = 8.4$, 1.0 Hz, 1H, 5-H), 4.80 (br d, $J = 2.2$ Hz, 1H, 2′-H), 4.43 (dd, $J =$ 10.6, 6.6 Hz, 1H, 7-H), 4.30 (d, $J = 8.5$ Hz, 1H, 20a-H), 4.19 (d, $J = 8.5$ Hz, 1H, 20b-H), 3.80 (d, $J = 7.1$ Hz, 1H, 3-H), 3.62 (br s, 1H, 2′-OH), 2.52 (ddd, $J = 14.5$, 8.4, 6.6 Hz, 1H, 6a-H), 2.38 (s, 3H, 4-Ac), 2.33 (dd, $J = 15.0$, 9.0 Hz, 1H, 14a-H), 2.29 (dd, $J = 15.0$, 9.0 Hz, 1H, 14b-H), 2.18 (s, 3H, 10-Ac), 1.91 (s, 3H, 18-Me), 1.89 (ddd, $J = 14.5$, 10.6, 1.0 Hz, 1H, 6b-H), 1.70 (s, 3H, 19-Me), 1.23 (s, 3H, 16-Me), 1.18 (s, 3H, 17-Me), 0.92 (t, $J = 8.1$ Hz, 9H, TES), 0.57 (q, $J = 8.1$ Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 201.7$ (9), 172.7 (1′), 170.4 (10-Ac), 169.2 (4-Ac), 167.0 (Bz), 167.0 (Bz), 139.6 (12), 138.1 (Ph), 134.1 (Ph), 133.7 (Ph), 133.7 (11), 132.0 (Ph), 130.2 (Ph), 129.3 (Ph), 129.0 (Ph), 128.7 (Ph), 128.7 (Ph), 128.3 (Ph), 127.1 (Ph), 127.1 (Ph), 84.2 (5), 81.3 (4), 78.7 (1), 76.6 (20), 75.1 (10), 74.8 (2), 73.2 (2′), 72.5 (7), 72.3 (13), 58.6 (8), 54.9 (3′), 46.8 (3), 43.3 (15), 37.3 (6), 35.5 (14), 26.7 (17), 22.7 (4-Ac), 21.0 (16), 20.9 (10-Ac), 14.3 (18), 10.1 (19), 6.8 (TES), 5.3 (TES); HR MS: calcd for $C_{53}H_{66}NO_{14}Si$ $[M+H]^+$ 968.4253, found 968.4256.

Paclitaxel (Taxol®):

Method A: To a solution of 7-*O*-(triethylsilyl)paclitaxel (1.4 mg, 1.4 μmol) in THF (0.7 mL) at room temperature was added hydrogen fluoride · pyridine (hydrogen fluoride/pyridine = ca. 7/3, 2 drops). The reaction mixture was stirred for 3 days at room temperature and then saturated aqueous sodium hydrogencarbonate was added. The mixture was extracted with diethyl ether and the organic layer was washed with saturated aqueous copper(II) sulfate and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford paclitaxel (Taxol®) (1.2 mg, 100 %) as a white solid.

Method B: To a solution of 7-*O*-(triethylsilyl)paclitaxel (0.88 mg, 0.91 μmol) in ethanol (0.5 mL) at 0 °C was added hydrochloric acid (5 %, 0.4 mL). The reaction mixture was stirred for 2 h at room temperature, and then ethyl acetate and saturated aqueous sodium hydrogencarbonate were added at 0 °C. The mixture was extracted with dichloromethane, and the organic layer was dried over magnesium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford paclitaxel (Taxol®) (0.8 mg, 100 %) as a white solid: m.p. 172–174 °C (lit. 213–216 °C,[3a] 198–203 °C,[56] 194–197 °C,[59] 205–208 °C[57]); $[\alpha]_D^{28} = -49.5$ (*c* 0.38, MeOH) (lit. $[\alpha]_D^{20} = -49$ (MeOH),[3a] $[\alpha]_D^{23} = -42$ (*c* 0.37, MeOH),[56] $[\alpha]_D^{23} = -54$ (*c* 0.026, MeOH),[59] $[\alpha]_D = -54$ (MeOH)[57]); IR (KBr): $\tilde{\nu} = 3480$, 1730, 1650 cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 8.49$ (d, $J = 8.5$ Hz, 1H, BzO), 8.48 (d, $J = 6.6$ Hz, 1H, BzO), 7.66 (d, $J = 7.3$ Hz, 1H, BzN), 7.66 (d, $J = 8.7$ Hz, 1H, BzN), 7.56–7.50 (m, 2H, Ph), 7.35–7.21 (m, 6H, Ph), 7.10 (t, $J = 7.3$ Hz, 1H, Ph), 7.03–6.97 (m, 2H, Ph), 6.86 (d, $J = 9.2$ Hz, 1H, NH), 6.68 (s, 1H, 10-H), 6.58 (dd, $J =$ 9.2, 8.9 Hz, 1H, 13-H), 6.15 (dd, $J = 9.2$, 2.1 Hz, 1H, 3′-H), 6.04 (d, $J =$ 6.9 Hz, 1H, 2-H), 4.99 (dd, $J = 7.6$, 1.9 Hz, 1H, 5-H), 4.82–4.74 (m, 1H, 7-H), 4.76 (dd, $J = 4.6$, 2.1 Hz, 1H, 2′-H), 4.47 (s, 2H, 20-H, 20-H), 4.13 (d, $J = 6.9$ Hz, 1H, 3-H), 3.58 (d, $J = 4.6$ Hz, 1H, 2′-OH), 2.92 (d, $J = 4.0$ Hz, 1H, 7-OH), 2.74 (dd, $J = 15.7$, 8.9 Hz, 1H, 14-H), 2.62 (dd, $J = 15.7$, 9.2 Hz, 1H, 14-H), 2.74–2.61 (m, 1H, 6a-H), 2.28–2.16 (m, 1H, 6b-H), 2.26 (s, 3H, 4-Ac), 2.09 (s, 3H, 19-Me), 2.00 (s, 3H, 18-Me), 1.87 (s, 3H, 10-Ac), 1.72 (s, 1H, 1-OH), 1.19 (s, 3H, 16-Me), 1.16 (s, 3H, 17-Me); ^{13}C NMR (C_6D_6): $\delta =$ 203.4 (9), 173.4 (1′), 171.2 (Ac), 170.4 (Ac), 167.1 (Bz), 166.9 (Bz), 142.1 (12), 139.0 (Ph), 134.0 (Ph), 133.9 (Ph), 133.4 (11), 131.7 (Ph), 130.6 (Ph), 130.4 (Ph), 129.0 (Ph), 128.9 (Ph), 128.7 (Ph), 128.2 (Ph), 127.8 (Ph), 127.3 (Ph), 84.5 (5), 81.6 (4), 79.4 (1), 76.5 (20), 75.9 (10), 75.5 (2), 73.0 (2′), 72.7 (7), 72.7 (13), 59.2 (8), 55.0 (3′), 46.2 (3), 43.5 (15), 36.2 (14), 36.2 (6), 26.7 (17), 22.5 (4-Ac), 21.9 (16), 20.3 (10-Ac), 14.8 (18), 10.0 (19); HR MS: calcd for $C_{47}H_{51}NO_{14}Na$ $[M+Na]^+$ 876.3207, found 876.3219.

2′,3′-*O*,*N*-Isopropylidene-7-*O*-(triethylsilyl)paclitaxel (82): To a suspension of carboxylic acid **73** (9.7 mg, 29.8 μmol), 7-*O*-(triethylsilyl)baccatin III (3.3 mg, 4.7 μmol) and DMAP (1.3 mg, 10.6 μmol) in toluene (0.25 mL) at room temperature was added DPTC (7.1 mg, 30.6 μmol). The reaction mixture was concentrated by evaporation of the solvent and then the residue was stirred for 30 min at 73 °C. The crude product was purified by thin-layer chromatography to afford protected Taxol **82** (3.0 mg, 63 %) as white needles and recovered 7-*O*-(triethylsilyl)baccatin III (1.2 mg, 36 %) as a white solid. **Protected Taxol 82**: m.p. 172–174 °C; $[\alpha]_D^{26} = -34.0$ (*c* 0.56, MeOH); IR (KBr): $\tilde{\nu} = 3470$, 1730, 1640, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta =$ 8.00 (d, $J = 7.1$ Hz, 2H, BzO), 7.60 (t, $J = 7.5$ Hz, 1H, Ph), 7.46 (t, $J = 7.7$ Hz, 2H, BzN), 7.21–7.06 (m, 8H, Ph), 6.93 (m, 1H, Ph), 6.45 (s, 1H, 10-H), 6.23 (dd, $J = 9.1$, 7.9 Hz, 1H, 13-H), 5.64 (d, $J = 7.0$ Hz, 1H, 2-H), 5.26 (d, 1H, $J = 6.8$ Hz, 3′-H), 4.88 (dd, $J = 9.1$, 1.3 Hz, 1H, 5-H), 4.56 (d, $J = 6.8$ Hz, 1H, 2′-H), 4.46 (dd, $J = 10.5$, 6.4 Hz, 1H, 7-H), 4.23 (d, $J = 8.2$ Hz, 1H, 20a-H), 4.09 (d, $J = 8.2$ Hz, 1H, 20b-H), 3.77 (d, $J = 7.0$ Hz, 1H, 3-H), 2.50 (ddd, $J =$ 15.0, 9.1, 6.4 Hz, 1H, 6a-H), 2.20–2.05 (m, 2H, 14-H), 2.19 (s, 3H, 10-Ac), 2.20–2.05 (m, 2H, 14-H), 2.07 (s, 3H, 18-Me), 2.00 (s, 3H, acetonide), 1.93 (s, 3H, acetonide), 1.86 (s, 3H, 4-Ac), 1.85 (ddd, $J = 15.0$, 10.5, 1.3 Hz, 1H, 6b-H), 1.76 (s, 1H, 1-OH), 1.65 (s, 3H, 19-Me), 1.21 (s, 3H, 16-Me), 1.18 (s, 3H, 17-Me), 0.92 (t, $J = 8.2$ Hz, 9H, TES), 0.57 (q, $J = 8.2$ Hz, 6H, TES); ^{13}C NMR ($CDCl_3$): $\delta = 201.6$ (9), 169.9 (1′), 169.3 (10-Ac), 169.1 (4-Ac), 167.0 (Bz), 167.0 (Bz), 140.0 (12), 138.9 (Ph), 137.5 (Ph), 133.9 (Ph), 133.7 (11), 130.1 (Ph), 129.5 (Ph), 129.2 (Ph), 128.7 (Ph), 128.6 (Ph), 128.1 (Ph), 127.9 (Ph), 126.9 (Ph), 126.2 (Ph), 98.3 (acetonide), 84.2 (5), 81.3 (2′), 80.8 (4), 79.0 (1), 76.3 (20), 74.9 (10), 74.9 (2), 72.1 (7), 71.7 (13), 66.0 (3′), 58.4 (8), 46.8 (3), 43.3 (15), 37.1 (6), 35.4 (14), 26.5 (17), 26.3 (acetonide), 25.5 (acetonide), 21.7 (4-Ac), 21.1 (16), 20.9 (10-Ac), 14.3 (18), 10.1 (19), 6.7 (TES), 5.3 (TES); HR MS: calcd for $C_{56}H_{70}NO_{14}Si$ $[M+H]^+$ 1008.4566, found 1008.4552.

2′,3′-*O*,*N*-[(*S*)-(*p*-Methoxybenzylidene)]-7-*O*-(triethylsilyl)paclitaxel (83): To a suspension of carboxylic acid **75** (170 mg, 0.420 mmol), 7-*O*-(triethylsilyl)baccatin III (49.1 mg, 70.1 μmol) and DMAP (17.3 mg, 0.140 mmol) in toluene (0.5 mL) at room temperature was added DPTC (97.6 mg, 0.420 mmol). The reaction mixture was concentrated by evaporation of the solvent and then the residue was stirred for 1 h at 73 °C. The crude product was purified by thin-layer chromatography to afford protected Taxol **83** (66.9 mg, 88 %) and recovered 7-(triethylsilyl)baccatin III (3.4 mg, 7 %) as white solids. **Protected Taxol 83**: m.p. 249–251 °C; $[\alpha]_D^{29} = -61.0$ (*c* 0.89, MeOH); IR (KBr): $\tilde{\nu} = 3440$, 1740, 1730, 1720, 1650 cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 8.38$ (dd, $J = 6.8$, 2.8 Hz, 2H, BzO), 7.89 (br d, $J = 7.1$ Hz, 2H, Ph), 7.58 (d, $J = 7.3$ Hz, 1H, BzN), 7.49 (s, 1H, CHPMP), 7.44–7.36 (m, 2H, Ph), 7.36–7.15 (m, 7H, Ph), 7.03 (t, $J = 7.3$ Hz, 1H, Ph), 6.96 (s, 1H, 10-H), 6.95–6.89 (m, 4H, Ph), 6.64 (br t, $J = 9.2$ Hz, 1H, 13-H), 6.11 (d, $J = 6.9$ Hz, 1H, 2-H), 5.97 (br s, 1H, 3′-H), 5.01 (d, $J =$ 8.3 Hz, 1H, 5-H), 4.94 (dd, $J = 11.4$, 6.8 Hz, 1H, 7-H), 4.84 (br s, 1H, 2′-H), 4.46 (d, $J = 8.6$ Hz, 1H, 20a-H), 4.39 (d, $J = 8.6$ Hz, 1H, 20b-H), 4.23 (d, $J =$ 6.9 Hz, 1H, 3-H), 3.37 (s, 3H, MeO), 2.81–2.67 (m, 1H, 6a-H), 2.58 (s, 3H, 18-Me), 2.57 (dd, $J = 15.2$, 9.2 Hz, 1H, 14a-H), 2.45 (dd, $J = 15.2$, 9.2 Hz, 1H, 14b-H), 2.28–2.15 (m, 1H, 6b-H), 2.14 (s, 3H, 19-Me), 2.09 (s, 3H, 4-Ac), 1.94 (s, 3H, 10-Ac), 1.84 (br s, 1H, 1-OH), 1.37 (s, 3H, 16-Me), 1.20 (t, $J = 7.8$ Hz, 9H, TES), 1.20 (s, 3H, 17-Me), 0.44 (q, $J = 7.8$ Hz, 6H, TES); ^{13}C NMR (C_6D_6): $\delta = 201.5$ (9), 172.2 (1′), 170.8 (10-Ac), 170.3 (4-Ac), 169.0 (Bz), 167.3 (Bz), 160.8 (PMP), 140.5 (12), 139.9 (Ph), 136.4 (Ph), 135.1 (Ph), 133.7 (11), 130.9 (Ph), 130.6 (Ph), 130.5 (Ph), 130.5 (Ph), 129.5 (Ph), 129.1 (Ph), 128.9 (Ph), 128.0 (Ph), 127.9 (Ph), 127.2 (Ph), 127.1 (Ph), 114.2 (PMP), 92.0 (CHPMP), 84.4 (5), 83.1 (2′), 81.6 (4), 79.4 (1), 76.7 (20), 75.6 (2), 75.5 (10), 73.2 (7), 72.2 (13), 65.9 (3′), 59.0 (8), 54.9 (MeO), 47.5 (3), 43.7 (15), 38.1 (6), 36.1 (14), 26.8 (17), 22.1 (4-Ac), 21.3 (16), 20.7 (10-Ac), 15.4 (18), 10.6 (19), 7.4 (TES), 6.0 (TES); HR MS: calcd for $C_{61}H_{72}NO_{15}Si$ $[M+H]^+$ 1086.4671, found 1086.4659.

2′,3′-*O*,*N*-[(*S*)-(*p*-Methoxybenzylidene)]paclitaxel (84): To a mixture of protected Taxol **83** (3.3 mg, 3.0 μmol) and trifluoroacetic acid (0.125 mL, 1.62 mmol) at 0 °C was added water (3 drops). The reaction mixture was stirred for 20 min at 0 °C, and then diethyl ether and saturated aqueous sodium hydrogencarbonate were added. The mixture was extracted with ethyl acetate, and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford paclitaxel (Taxol®) (2.4 mg, 93 %) and protected Taxol **84** (0.4 mg, 7 %) as white solids. **Protected Taxol 84**: m.p. 158–160 °C; $[\alpha]_D^{28} =$ −77.2 (*c* 0.33, MeOH); IR (KBr): $\tilde{\nu} = 3470$, 1740, 1730 cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 8.35$ (dd, $J = 6.6$, 3.0 Hz, 2H, BzO), 7.98 (d, $J = 7.9$ Hz, 2H, Ph), 7.60 (d, $J = 7.3$ Hz, 2H, BzN), 7.56 (s, 1H, CHPMP), 7.50–7.16 (m, 8H, Ph), 7.03–6.91 (m, 5H, Ph), 6.65 (s, 1H, 10-H), 6.60 (t, $J = 8.9$ Hz, 1H, 13-H), 6.03 (d, $J = 6.9$ Hz, 1H, 2-H), 5.95 (s, 1H, 3′-H), 4.98 (dd, $J = 10.8$, 0.8 Hz, 1H, 5-H), 4.84–4.72 (m, 1H, 7-H), 4.72 (s, 1H, 2′-H), 4.43 (d, $J = 8.6$ Hz, 1H, 20a-H), 4.36 (d, $J = 8.6$ Hz, 1H, 20b-H), 4.14 (d, $J = 6.9$ Hz, 1H, 3-H), 3.38 (s, 3H, MeO), 3.05 (d, $J = 3.6$ Hz, 1H, 7-OH), 2.78–2.66 (m, 1H, 6a-H), 2.54 (dd, $J = 15.6$, 8.9 Hz, 1H, 14-H), 2.42 (dd, $J = 15.6$, 8.9 Hz, 1H, 14-H), 2.30–2.19 (m, 1H, 6b-H), 2.19 (s, 3H, 18-Me), 2.11 (s, 3H, 4-Ac), 2.09 (s, 3H, 19-Me), 1.90 (s, 3H, 10-Ac), 1.71 (br s, 1H, 1-OH), 1.21 (s, 3H, 16-Me), 1.20 (s, 3H, 17-Me); ^{13}C NMR (C_6D_6): $\delta = 203.6$ (9), 172.5 (1′), 171.2

(10-Ac), 170.7 (4-Ac), 170.3 (BzO), 167.2 (BzN), 160.9 (PMP), 142.4 (12), 140.3 (Ph), 136.5 (Ph), 134.0 (Ph), 133.7 (11), 131.6 (Ph), 130.6 (Ph), 130.6 (Ph), 130.4 (Ph), 129.4 (Ph), 129.1 (Ph), 129.0 (Ph), 128.9 (Ph), 128.9 (Ph), 128.1 (Ph), 127.9 (Ph), 127.7 (Ph), 127.6 (Ph), 114.3 (PMP), 91.7 (CHPMP), 84.8 (5), 83.1 (2′), 81.5 (4), 79.7 (1), 76.6 (20), 76.1 (10), 75.8 (2), 72.9 (7), 72.2 (13), 65.9 (3′), 59.5 (8), 55.0 (MeO), 46.3 (3), 43.9 (15), 36.4 (6), 36.2 (14), 27.0 (17), 22.1 (4-Ac), 22.0 (16), 20.7 (10-Ac), 15.7 (18), 10.1 (19); HR MS: calcd for $C_{55}H_{58}NO_{15}$ $[M+H]^+$ 972.3806, found 972.3831.

Paclitaxel (Taxol®): To a mixture of protected Taxol **84** (3.5 mg, 3.6 μmol) and trifluoroacetic acid (0.10 mL, 1.30 mmol) at room temperature was added water (10 drops). The reaction mixture was stirred for 15 min at room temperature, and then diethyl ether and saturated aqueous sodium hydrogencarbonate were added at 0 °C. The mixture was extracted with ethyl acetate and the organic layer was washed with water and brine, and dried over sodium sulfate. After filtration of the mixture and evaporation of the solvent, the crude product was purified by thin-layer chromatography to afford paclitaxel (Taxol®) (2.9 mg, 94 %) as a white solid. All physical data of this compound were identical to those of the compound derived from 7-*O*-(triethylsilyl)paclitaxel.

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