# Asymmetric Desymmetrization Based on an Intramolecular Haloetherification: A Highly Effective and Recyclable Chiral Nonracemic Auxiliary, 2-*exo*-Methyl-3-*endo*-phenyl-5-norbornene-2-carboxaldehyde, for *meso*-1,3- and *meso*-1,4-Diols

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**Abstract:** A new chiral auxiliary, a 3-*endo*-phenyl norbornene aldehyde derivative, which is a crystalline, very stable, and easily handled, was developed for the desymmetrization of *meso*-1,3- and *meso*-1,4-diols. The key step of the method, an intramolecular bromoetherification, proceeded in a highly diastereoselective manner. A four-step sequence, 1) acetalization, 2) intramolecular bromoetherification followed by acid hydrolysis, 3) protection of the alcohol, and 4) retrobromoetherification, transformed the *meso*-diols into optically active derivatives. The 3-*endo*-phenyl norbornene aldehyde derivative was simultaneously reformed and could be used repeatedly. This is the first chemical example of a single auxiliary that is applicable for highly enantioselective desymmetrization of *meso*-1,3- and *meso*-1,4-diols; to the best of our knowledge, this is the best chemical method available for the desymmetrization of *meso*-1,4-diols.

**Keywords:** asymmetric synthesis · chiral auxiliaries · desymmetrization · diols · norbornene

## Introduction

Desymmetrization of *meso*-diols is a very useful way to get optically active compounds and has been investigated in many ways by using chemical or enzymatic methods.[1] For the chemical methods, many good desymmetrization methods for *meso*-1,2-diols have been reported.[2] However, the desymmetrization methods for *meso*-1,3-diols are few[3] and only a few chemical desymmetrization methods for *meso*-1,4-diols, to our best knowledge, have been reported.[4] Quite recently, a new asymmetric catalyst was developed for the desymmetrization of the *meso*-1,3- and *meso*-1,4-diols by Trost and Mino.[4c]

Recently, we developed a new desymmetrization method for *meso*-1,2-diols by using the chiral nonracemic methylnorbornene aldehyde **1a** as an auxiliary.[5] We then succeeded in the optical resolution of other norbornene aldehyde derivatives and found that 3-*exo*-phenylnorbornene aldehyde **1b** is a better choice as an auxiliary for the desymmetrization of *meso*-1,2-diols because it overcomes the disadvantage of **1a**, that is, volatility.[6] In our method, the desymmetrization step of the *meso*-1,2-diols depends on the difference between the activation energies of the two transition states (**i** and **ii**) formed by the intramolecular bromoetherification of acetals derived from **1a** or **1b** and the *meso*-1,2-diols. A large difference in the activation energies between transition state **i** and transition state **ii** causes the discrimination of the two oxygen atoms of the acetals in a highly diastereoselective manner (Scheme 1).

We then applied this method to the desymmetrization of the *meso*-1,3- and *meso*-1,4-diols by using **1b**. However, the results were fruitless. The acetalization of **1b** with the *meso*-1,3-diol, *meso*-2,4-pentanediol (**2**), gave the single acetal **3**, but its intramolecular bromoetherification afforded a diastereomeric mixture of the nine-membered acetals **4** in a ratio of 6.5:1. The insufficient discrimination of the two oxygen atoms was ascertained by acid hydrolysis of **4** to give the aldehyde, which was still a 6.5:1 mixture. In the case of the *meso*-1,4-diol **5a**, acetalization did even not produce the

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains the $^{13}C$ NMR spectra of the compounds that were also analyzed by high-resolution mass spectra.

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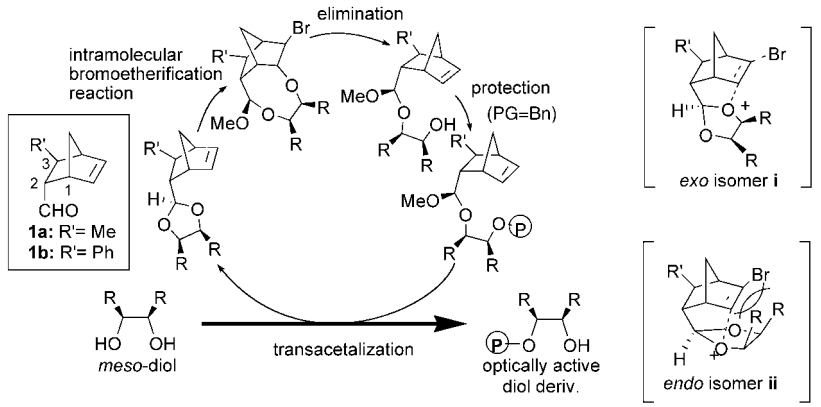
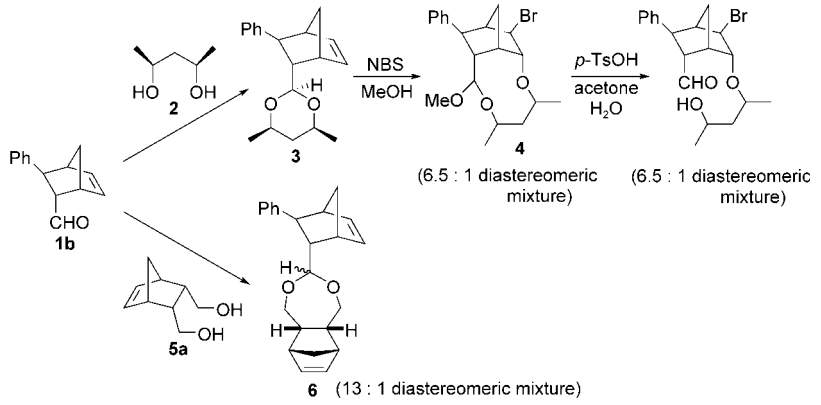


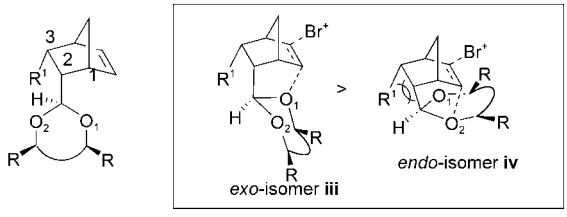

Scheme 1. Desymmetrization of *meso*-1,2-diols by using 3-*exo*-substituted norbornene aldehydes (**1a** or **1b**). PG = protecting group, Bn = benzyl, Deriv. = derivative.




Scheme 2. Desymmetrization of *meso*-1,3-diol (**2**) and *meso*-1,4-diol (**5a**) by using **1b**. NBS = *N*-bromosuccinimide, *p*-TsOH = toluene-4-sulfonic acid.

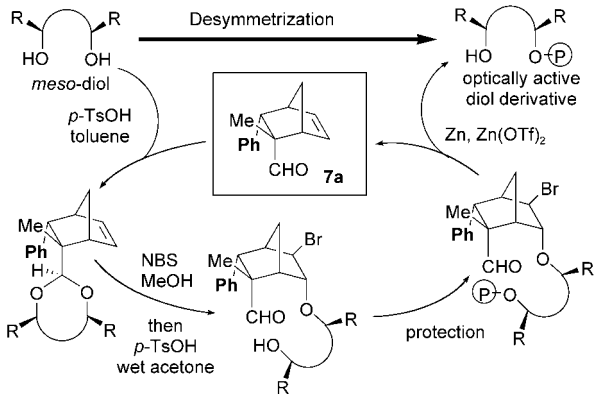
single acetal; instead acetals **6** were formed as a mixture in a ratio of 13:1. We therefore required a new auxiliary for the desymmetrization of *meso*-1,3- and *meso*-1,4-diols (Scheme 2).

Crucial steps in our method are the acetalization and discrimination of the two oxygen atoms, an intramolecular bromoetherification. Based on this requirement, especially the discrimination step, a large difference in the activation energies between the two transition states is needed to realize sufficient desymmetrization.[7] We therefore planned the synthesis of 3-*endo*-substituted norbornene aldehyde derivatives, which would produce a large difference between transition states **iii** and **iv** because the 3-*endo* substituent $R^1$ might inhibit the rotation of the acetal moiety that would lead to the formation of the *endo* isomer **iv** during the intramolecular bromoetherification (Scheme 3).




Scheme 3. Perspective view of the effect of the 3-*endo* substituent in the intramolecular bromoetherification.

Based on the above concept, we first examined the desymmetrization of *meso*-1,4-diols because the chemical methods for their desymmetrization are rare, as mentioned before.[4] We found that the 2-*endo*-aldehyde norbornene aldehyde derivative **7a** was a good auxiliary. A 2-*exo*-methyl group was introduced to prevent the epimerization of the 3-*endo*-phenyl group. The aldehyde **7a** also proved to be effective for the desymmetrization of the *meso*-1,3-diols. Scheme 4 shows a summary of our transformations: 1) acetalization of **7a** with *meso*-diols, 2) intramolecular bromoetherification in the presence of MeOH followed by acid hydrolysis, 3) protection of the alcohol, then 4) retrobromoetherification. In this transformation, **7a** was regenerated along with the optically active diol derivatives and could be used again. This is completely different from our previous method (see Scheme 1) where the ene acetals are regenerated and it makes our new method more effective. Although *exo*-substituted norbornene aldehydes **1a** and **1b** need mixed-acetal structures for good retrobromoetherification, **7a** does not need mixed-acetal structures for retrobromoetherification and aldehydes are good precursors for retrobromoetherification. This is an advantage because the retrobromoetherification of the mixed acetals requires careful reaction-temperature control (about 70 °C) to prevent reacetalization of the resulting hydroxy acetals (see Scheme 1). On the other hand, the retrobromoetherification depicted in



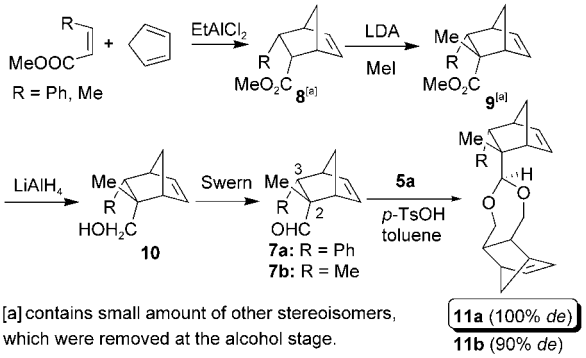

Scheme 4. Desymmetrization of *meso*-diols by using 3-*endo*-phenyl norbornene aldehyde **7a**. Tf = triflate = trifluoromethanesulfonyl.

Scheme 4 does not require careful reaction-temperature control, because the acetalization no longer occurs between the resulting **7a** and the optically active diol derivatives when one of the two hydroxy groups is protected.

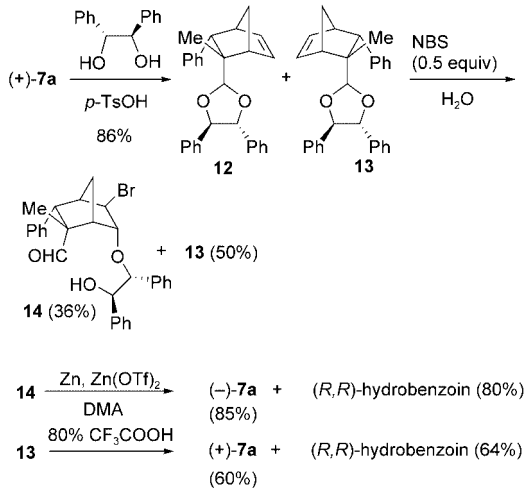
## Results and Discussion

**Design of new auxiliary**: As mentioned before (see Scheme 3), we speculated that the 3-*endo* substituent would enhance the diastereoselectivity during the key step of desymmetrization, that is, the intramolecular bromoetherification. We synthesized two 3-*endo*-substituted norbornene aldehyde derivatives, the phenyl-substituted and methyl-substituted compounds **7a** and **7b**. Aldehydes (±)-**7a**,**b** were prepared by the usual way (Scheme 5): 1) Diels–Alder reaction of methyl *Z*-cinnamate[8] or methyl isocrotonate with cyclopentadiene to give **8**, 2) methylation of **8** by treatment with LDA followed by methyl iodide to give **9**, 3) $LiAlH_4$ reduction of **9** to give **10**, and 4) Swern oxidation[9] of **10** to give (±)-**7a**,**b**. Without the 2-*exo*-methyl group, the 2-*endo*-aldehyde groups would easily epimerize to the *exo* conformation because of the steric repulsion of 3-*endo* substituents. Although acetalization of **7b** with **5a** gave the *trans*-acetal **11b** and a small amount of the *cis* isomer, the phenyl-substituted norbornene aldehyde **7a** afforded the single isomer **11a** (Scheme 5). Compound **7a** was therefore determined to be the auxiliary of choice.



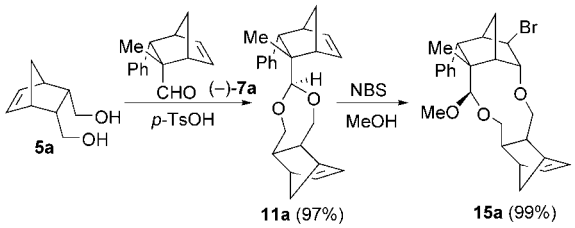

Scheme 5. Preparation of racemic 3-*endo*-substituted norbornene aldehydes **7a** and **7b** and their acetalization with **5a**. LDA = lithium diisopropylamide.

**Preparation of optically pure 2-*exo*-methyl-3-*endo*-phenyl-5-norbornene-2-carboxaldehydes (−)-7a and (+)-7a**: Optically pure **7a** was obtained from (±)-**7a** by using our recently developed method.[6] Two diastereomeric acetals **12** and **13**, obtained by the reaction of (±)-**7a** and (*R*,*R*)-hydrobenzoin[10] were treated with NBS (0.5 equiv) in the presence of $H_2O$ (5 equiv) to give the hydroxy aldehyde **14** from **12** and intact **13**. Retrobromoetherification of **14** gave the optically pure (−)-**7a** and (*R*,*R*)-hydrobenzoin. Intact **13** was hydrolyzed with 80% aqueous $CF_3COOH$ to give (+)-**7a** (Scheme 6).

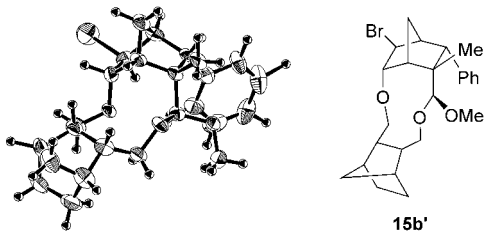



Scheme 6. Optical resolution of racemic **7a**. DMA = *N*,*N*-dimethylacetamide.

**Desymmetrization of *meso*-1,4-diols**: All of the transformations for desymmetrization of the *meso*-1,4-diols by using 5-norbornene-2-*endo*-3-*endo*-dimethanol **5a** are depicted in Schemes 7 and 9. Acetalization of (−)-**7a** with **5a** afforded the sole product **11a**, whose stereochemistry was determined to be *trans* by X-ray crystal analysis and mechanistic considerations (see below). Intramolecular bromoetherification of **11a** in the presence of MeOH gave the ten-membered mixed acetal **15a** in a highly diastereoselective manner (Scheme 7). Its stereochemistry was determined by X-ray crystal analysis of **15b′**, which was obtained by the intramolecular bromoetherification of the ene acetal from **5b** and (+)-**7a** (Scheme 8, see Table 1). Since haloetherification of the ene acetal with MeOH proceeds in an $S_N2$ manner,[5]



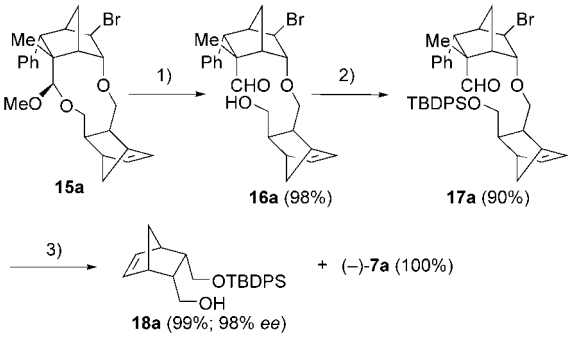

Scheme 7. Acetalization of (−)-**7a** and its intramolecular bromoetherification.




Scheme 8. X-ray crystal structure of **15b′**.

the stereochemistry of the acetal ring of **11a** was determined to be *trans* based on the X-ray crystal structure of **15b′**.[11]

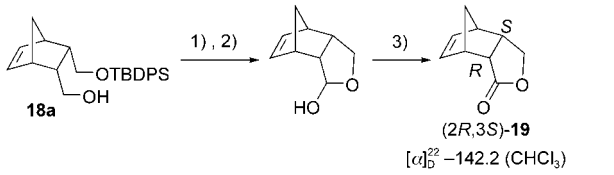
Next, we tried the retrobromoetherification reaction of **15a** by using the conditions indicated in Scheme 1 (Zn powder and $MgBr_2$ or $Zn(OTf)_2$), but the desired product was not obtained. Therefore, we developed another method of transformation as shown in Scheme 9. The hydrolysis of




Scheme 9. Conversion of **15a** into **18a**. 1) *p*-TsOH, acetone, $H_2O$; 2) TBDPSCl, imidazole; 3) Zn, $Zn(OTf)_2$, DMA. TBDPS = *tert*-butyldiphenylsilyl.

**15a** afforded the hydroxy aldehyde **16a** in high yield. Although the use of $H_2O$ in place of MeOH for the intramolecular bromoetherification directly afforded **16a**, the diastereoselectivity decreased (66% *de*), maybe as a result of the difference in nucleophilicity between MeOH and $H_2O$. Protection of the alcohol group of **16a** gave the silyl ether **17a**. Retrobromoetherification of **17a** by use of Zn powder in the presence of $Zn(OTf)_2$ afforded the optically active diol derivative **18a** and the starting aldehyde **7a**, which was reused. The absolute configuration of **18a** was determined by conversion into the known lactone **19**, as shown in Scheme 10. Thus, Swern oxidation of **18a** followed by desilylation gave the lactol, which was oxidized by PCC to give the known lactone **19**. The optical rotation value of our synthetic **19** ($[\alpha]_D^{22} = -142.2$ ($CHCl_3$)) showed the opposite sign to that of (2*S*,3*R*)-**19** ($[\alpha]_D^{20} = +143.2$ ($CHCl_3$)).[12]

Table 1 shows the results of the desymmetrization of various bicyclo-*meso*-1,4-diols (see Schemes 4, 7, and 9). In each of these cases, acetalization of (−)-**7a** with the *meso*-diols proceeded stereoselectively to give sole products, whose stereochemistries were determined as *trans* by considering the result of **5a** and the absolute configuration of the diol derivative **18a**. The subsequent intramolecular bromoetherification, protection of the alcohol, and debromoetherificatin proceeded smoothly without problems. It

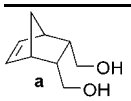
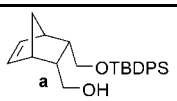
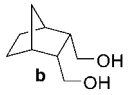
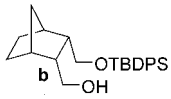
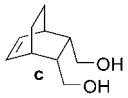
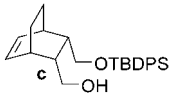
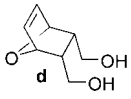
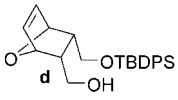



Scheme 10. Conversion of **18a** into lactone **19**. 1) Swern oxdidation; 2) TBAF; 3) PCC. TBAF = tetrabutylammonium fluoride, PCC = pyridinium chlorochromate.

is noteworthy that bromoetherification occurred only in an intramolecular fashion, not only for acetals from saturated diols but also for acetals from unsaturated diols.

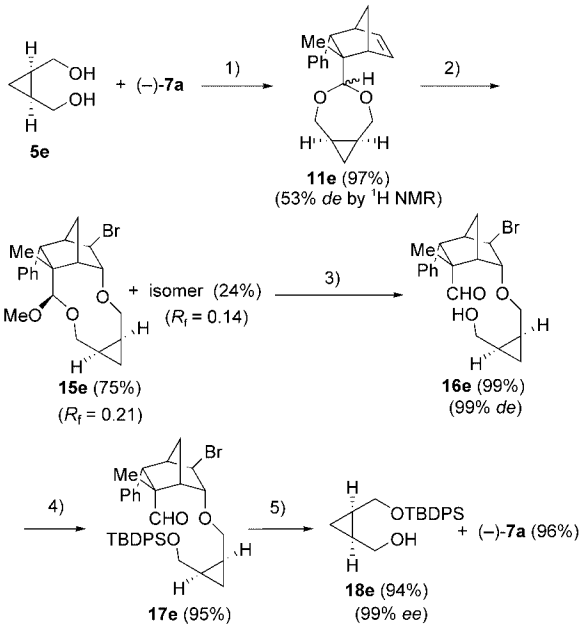
Previous chemical desymmetrizations of *meso*-1,2-bis(hydroxymethyl)cyclopropane **5e** or *meso*-4,5-bis(hydroxymethyl)cyclohexene **5f** resulted in poor enantioselectivity.[4a] However, when these compounds were used in our method, good results were obtained (Schemes 11 and 12). The acetalization of **5e** and **5f** with (−)-**7a** gave two isomers; the isomers of **11e** were difficult to separate and of **11f** were inseparable by the usual $SiO_2$ column. However, their intramolecular bromoetherification in the presence of MeOH afforded two ten-membered acetals whose $R_f$ values are different (**15e**: major 0.21, minor 0.14; **15f**: major 0.42, minor 0.35; TLC with hexane/AcOEt (10:1)). Easy separation of these isomers by using the usual $SiO_2$ column gave the pure acetals (**15e** and **15f**). In our desymmetrization cycle, three new chiral centers are formed when MeOH is used as the nucleophile in the intramolecular bromoetherification and this usually allows easy separation of the isomers. After obtaining the pure compounds, it is not difficult to get the optically pure diol derivatives (**18e** and **18f**). The optical rotation value of **18e** was in good agreement with the reported value,[13] so the absolute configuration of **18e** was determined and the relative stereochemistries of the other compounds in Scheme 11 were deduced from mechanistic considerations. The absolute and relative configurations of the compounds in Scheme 12 were tentatively determined by considering the results shown in Scheme 11.

Table 1. Desymmetrization of *meso*-1,4-diols **5** to form the optically active derivatives **18**.

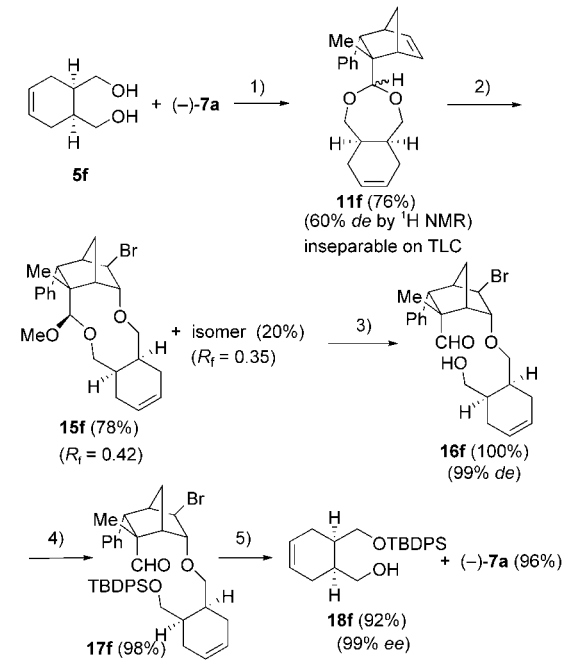
| **5** | Yield [%] | | | | **18** | Yield [%] | *ee* [%][a] |
|---|---|---|---|---|---|---|---|
| | **11** | **16** | **17** | (−)-**7a** | | | |
|  | 97 | 98 | 90 | 100 |  | 99 | ≧98 |
|  | 98 | 92 | 94 | 94 |  | 93 | ≧98 |
|  | 88 | 95 | 98 | 88 |  | 89 | ≧98 |
|  | 96 | 95 | 94 | 98 |  | 86 | ≧99 |

[a] Determined by HPLC analysis (Chiralpak AD-H or Chiralcel OD-H).

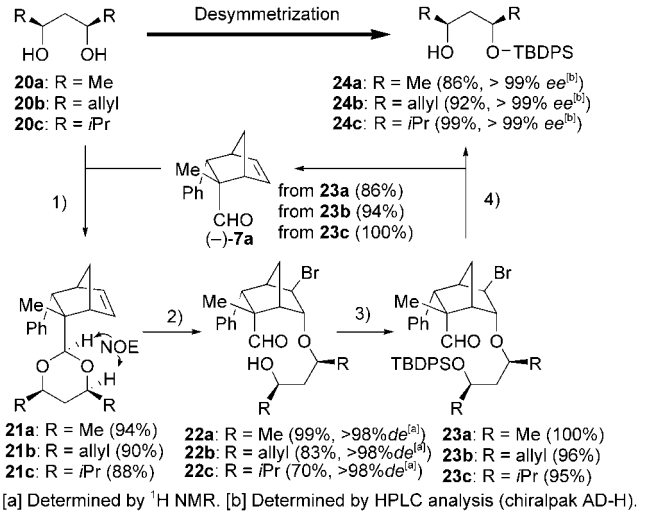



Scheme 11. Desymmetrization of *meso*-1,2-bis(hydroxymethyl)-cyclopropane (**5e**). 1) *p*-TsOH; 2) NBS, MeOH, $CH_2Cl_2$; 3) separation by $SiO_2$ column, then *p*-TsOH; 4) TBDPSCl, imidazole; 5) Zn, $Zn(OTf)_2$, DMA.




Scheme 12. Desymmetrization of *meso*-4,5-bis(hydroxymethyl)-cyclohexane (**5f**). 1) *p*-TsOH; 2) NBS, MeOH, $CH_2Cl_2$; 3) separation by $SiO_2$ column, then *p*-TsOH; 4) TBDPSCl, imidazole; 5) Zn, $Zn(OTf)_2$, DMA.

**Desymmetrization of *meso*-1,3-diols and *meso*-1,2-diols**: Since (−)-**7a** showed a high ability in the desymmetrization of *meso*-1,4-diols, we next applied it to the desymmetrization of *meso*-1,3-diols. We chose three 1,3-diols as the substrates, *meso*-2,4-pentanediol (**20a**), *meso*-1,8-nonadiene-4,6-diol (**20b**), and *meso*-2,6-dimethyl-3,5-heptanediol (**20c**). Acetalization of these diols with (−)-**7a** afforded the *cis*-acetals **21a–c**, respectively, in good yields (Scheme 13).

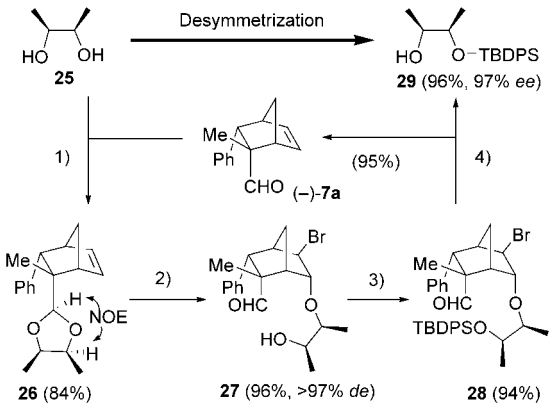



Scheme 13. Desymmetrization of *meso*-1,3-diols **20a–c**. 1) *p*-TsOH, toluene; 2) NBS, MeOH, then *p*-TsOH, acetone/$H_2O$; 3) TBDPSCl, imidazole; 4) Zn, $Zn(OTf)_2$, DMA.

Their stereochemistries were determined to be *cis* by NOE experiments. Intramolecular bromoetherification of **21a–c** in the presence of MeOH followed by acid hydrolysis gave the hydroxy aldehydes **22a–c** in a highly diastereoselective manner. The stereochemistries of compounds **22a–c** were deduced from the results of the desymmetrization of the *meso*-1,4-diols in the preceding section and from our previous results.[5] Protection of the hydroxy function of **22a–c** afforded the silyl ethers **23a–c**. Retrobromoetherification of **23a–c** with zinc in the presence of $Zn(OTf)_2$ in DMA gave the optically active diol derivatives **24a–c** with the regenerated norbornene aldehyde (−)-**7a**. The optical purities of **24a–c** were determined to be very high (>99% *ee*) by chiral HPLC analysis (Scheme 13).

As the good desymmetrization of the *meso*-1,4- and *meso*-1,3-diols has been achieved by using the 3-*endo*-phenyl norbornene aldehyde derivative (−)-**7a**, desymmetrization of the *meso*-1,2-diols was then studied. It was postulated that the possibility of (−)-**7a** working as a chiral auxiliary was low. Although *exo* isomers **1a** and **1b** needed a mixed-acetal structure for good retrobromoetherification, such structures from (−)-**7a** did not give a good retrobromoetherification for the *meso*-1,4- and *meso*-1,3-diols. To our disappointment, (−)-**7a** was only applicable for the acyclic diols, that is, *meso*-2,3-butanediol **25** (see Scheme 14). For the cyclic *meso*-1,2-diols, such as *meso*-1,2-cyclohexanediol, acetalization with (−)-**7a** under the usual conditions gave the desired products in low yields (<20%) together with unreacted (−)-**7a**. Acetalization at a higher temperature (≈50°C) afforded a mixture of stereoisomers and the aldehyde (−)-**7a** decomposed. The low reactivity of (−)-**7a** towards cyclic *meso*-1,2-diols might be due to the steric hindrance of the 3-*endo*-phenyl substituent.

The results with **25** are summarized in Scheme 14. Acetalization proceeded stereoselectively to give the *cis*-acetal **26** in high yield. The stereochemistry was determined by an NOE experiment. Intramolecular bromoetherification of **26** followed by acid hydrolysis afforded the hydroxy aldehyde

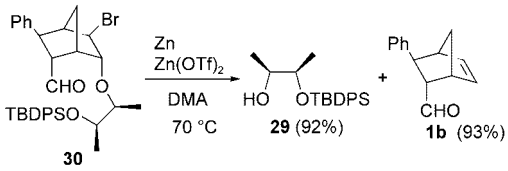



Scheme 14. Desymmetrization of *meso*-2,3-butanediol **25**. 1) *p*-TsOH, toluene, RT; 2) NBS, MeOH, then *p*-TsOH, acetone/$H_2O$; 3) TBDPSCl, imidazole; 4) Zn, $Zn(OTf)_2$, DMA.

**27** in a highly diastereoselective manner. The stereochemistry of compound **27** was deduced from the results of the desymmetrization of the *meso*-1,4-diols described in the preceding section and from our previous results.[5] Protection of the alcohol moiety as a silyl ether gave **28**. To our surprise, the retrobromoetherification reaction for **28** proceeded smoothly to give the optically active diol derivative **29** and (−)-**7a**. This result is in contrast to those obtained with **1a** and **1b**.

**Consideration of retrobromoetherification**: For the *meso*-1,4-diols and *meso*-1,3-diols, chelation structures such as **v** and **vi** (Scheme 15) do not cause any steric repulsion between the two side chains (see the reaction of **17a** to form **18a** in Scheme 9 and Table 1 for **v** and the reaction of **23a** to form **24a** in Scheme 13 for **vi**). On the other hand, the chelation structure of the acyclic *meso*-1,2-diol **vii** may cause steric repulsion between the two side chains and seems to be unfavorable. In fact, the acyclic *meso*-1,2-diol did not give the debromoetherificated product through acetal compounds like **viii**, possibly due to no formation of the chelation structure **viiib**, in our previous report,[5c] whereas mixed acetals gave the debromoetherificated products in good yields by the formation of the chelation structure **ix**, irrespective of the system being cyclic or acyclic (see Scheme 1).[5]

The results obtained here, with good retrobromoetherification even in **28** from the acyclic *meso*-1,2-diol **25** in Scheme 14, is completely different from our previous observations in ref. [5c]. A significant difference between **vii** and **viii** is that **viii** has an acetal in place of the aldehyde in **vii**. Also, **viii** might be present as **viiia** rather than **viiib** because of the steric repulsion of the acetal unit. Compound **vii** has a 3-*endo* substituent while **viii** has a 3-*exo* substituent. To recognize the actual factor required for the good retrobromoetherification of **vii**, we examined the reaction of aldehyde **30**, which is obtained from the 3-*exo*-phenyl norbornene aldehyde **1b** (see Scheme 1) and acyclic *meso*-1,2-diol **25**. The retrobromoetherification proceeded without a problem and afforded diol derivative **29** and aldehyde **1b** in high yield. When the results shown in Schemes 14 and 16 and our previous work[5c] are taken into account, steric hindrance of the acetal function in compounds like **viii** may inhibit the formation of the chelation structure **viiib** and make the retrobromoetherification difficult.



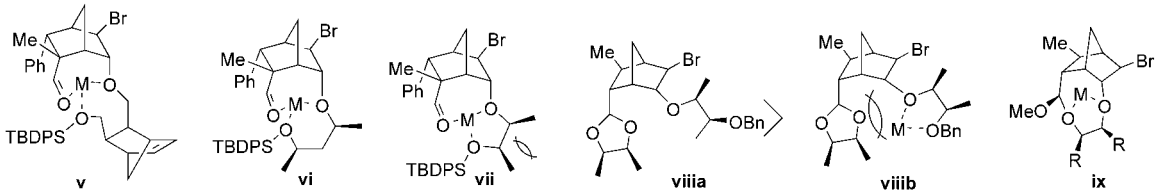

Scheme 16. Debromoetherification of 3-*exo*-phenyl compound **30**.

## Conclusion

A new auxiliary, the 3-*endo*-phenyl norbornene aldehyde derivative **7a**, was developed. It was found that this auxiliary is applicable for the desymmetrization of *meso*-1,3- and *meso*-1,4-diols. The methodology here is, to the best of our knowledge, the best chemical desymmetrization method available, especially for *meso*-1,4-diols. The significant advantage of our method is exemplified by our ability to obtain enantiopure diol derivatives of **5e** and **5f**, which were not obtained by other chemical methods.[4a] The auxiliary, **7a**, is a very stable (storage for one month at room temperature produces no decomposition) and easily handled crystal.[14] Furthermore, it is known that we can now choose the proper chiral auxiliary among the 3-*exo*- and 3-*endo*-norbornene aldehyde derivatives **1a**, **1b**, and **7a** for the highly enantioselective desymmetrization of *meso*-1,2-, *meso*-1,3-, and *meso*-1,4-diols.

## Experimental Section

All melting points are uncorrected. NMR spectra were measured on a 300 MHz spectrometer with $CDCl_3$ as the solvent and with $SiMe_4$ as an internal standard. Chemical shifts are denoted in $\delta$ (ppm). Infrared (IR) absorption spectra were recorded from KBr pellets. Optical rotations




Scheme 15. Consideration of chelation structures **v**–**ix**. M = Zn or Mg.

were measured in 0.5 dm cells with a JASCO P-1020 polarimeter. All solvents were dried and distilled according to standard procedures. $^{13}C$ NMR spectra of the compounds that were also analyzed by high-resolution mass spectra can be found in the Supporting Information.

**Methyl 3-*endo*-phenylnorbornene-2-carboxylate ((±)-8, R = Ph)**: Cyclopentadiene (3.0 mL) and $EtAlCl_2$ (44 mL, 0.98 mol in hexane) were added slowly to a stirred solution of *cis*-methyl cinnamate (7.05 g), prepared according to the literature procedure,[7] in $CH_2Cl_2$ (44 mL) at −78 °C under $N_2$. The mixture was allowed to warm to RT and stirred for an additional 12 h. Ice-water and saturated aqueous $NaHCO_3$ were added to the mixture and the resulting solution was extracted with $CH_2Cl_2$. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (20:1) as the eluent to give (±)-**8** (R = Ph; 9.68 g, 40.0 mmol, 92%, *endo*:*exo* = 17:1). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.32–7.04 (m, 5H), 6.66–6.63 (m, 1H), 6.15–6.11 (m, 1H), 3.79–3.74 (dd, $J$ = 10.8, 3.2 Hz, 1H), 3.67 (m, 1H), 3.50–3.45 (dd, $J$ = 10.8, 3.2 Hz, 1H), 3.21 (s, 3H), 3.02 (m, 1H), 1.54–1.49 ppm (m, 2H).

**Methyl 2-*exo*-methyl-3-*endo*-phenylnorbornene-2-carboxylate ((±)-9, R = Ph)**: *n*BuLi (0.68 mL) was added slowly to a stirred solution of diisopropylamine (146 mL) in THF (4.4 mL) at −78 °C under $N_2$. After 30 min, a solution of (±)-**8** (R = Ph; 198 mg) in THF (1 mL) was added dropwise to the resulting mixture at −78 °C. After 1 h, methyl iodide (0.27 mL) was added to the resulting mixture. The solution was allowed to warm to RT and stirred for 12 h. The completion of the reaction was confirmed by TLC. Ice-water was added to the mixture and the resulting solution was extracted with $Et_2O$. The organic layer was washed successively with ice-water, 10% aqueous $Na_2S_2O_3$, and brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (20:1) as the eluent to give (±)-**9** (R = Ph; 160 mg, 0.66 mmol, 76%). Colorless oil; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.25–7.02 (m, 5H), 6.72–6.69 (m, 1H), 6.19–6.16 (m, 1H), 3.19–3.18 (d, $J$ = 3.0 Hz, 1H), 3.15 (s, 3H), 2.92–2.88 (m, 2H), 1.82–1.79 (m, 1H), 1.60 (s, 3H), 1.58–1.52 ppm (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 176.1, 142.6, 140.0, 133.4, 128.4, 127.6, 126.1, 60.1, 58.4, 52.2, 50.8, 50.0, 47.9, 28.6 ppm; IR (KBr): $\tilde{\nu}$ = 1728 $cm^{-1}$; MS (EI): $m/z$: 242 [$M^+$]; HRMS (EI): $m/z$ calcd for $C_{16}H_{18}O_2$: 242.1307; found: 242.1309.

**2-*exo*-Methyl-3-*endo*-phenylnorbornene-2-methanol ((±)-10, R = Ph)**: A solution of (±)-**9** (R = Ph; 87 mg) in THF (1.0 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (20.4 mg) in THF (2.6 mL) at 0 °C under $N_2$. The mixture was allowed to warm to RT and stirred for 1 h. Excess reagent was quenched by careful addition of water and 1 N aqueous NaOH at 0 °C. The precipitate was filtered off and the filtrate was evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (5:1) as the eluent to give (±)-**10** (R = Ph; 74.3 mg, 0.35 mmol, 97%). Colorless oil; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.26–7.16 (m, 5H), 6.51–6.48 (m, 1H), 6.35–6.32 (m, 1H), 3.11–2.98 (m, 4H), 2.59 (s, 1H), 1.83–1.80 (m, 1H), 1.61–1.57 (m, 1H), 1.45 (s, 3H), 0.70 ppm (brs, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 141.4, 137.1, 134.9, 128.3, 128.1, 126.2, 68.9, 56.3, 51.8, 49.3, 49.0, 48.9, 26.5 ppm; IR (KBr): $\tilde{\nu}$ = 3362 $cm^{-1}$; MS (FAB): $m/z$: 237 [$M^+$+Na]; HRMS (FAB): $m/z$ calcd for $C_{15}H_{18}NaO$: 237.1255 [$M^+$+Na]; found: 237.1261.

**2-*exo*-Methyl-3-*endo*-phenylnorbornene-2-carbaldehyde ((±)-7a)**: DMSO (115 μL) was added carefully to a stirred solution of oxalyl chloride (70 μL) in $CH_2Cl_2$ (2.0 mL) at −78 °C under $N_2$. After 30 min, a solution of (±)-**10** (R = Ph; 43.0 mg) in $CH_2Cl_2$ (1.0 mL) was added dropwise to the resulting mixture at −78 °C. After 1 h, $Et_3N$ (335 μL) was added to the resulting solution. The solution was allowed to warm to 0 °C. Saturated aqueous $NH_4Cl$ was added to the mixture and the resulting solution was extracted with EtOAc. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (20:1) as the eluent to give (±)-**7a** (40.3 mg, 0.19 mmol, 95%). Colorless oil; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 8.99 (s, 1H,), 7.24–7.11 (m, 5H), 3.42–3.41 (m, 1H), 3.29–3.28 (m, 1H), 2.73 (brs, 1H), 1.90–1.87 (m, 1H), 1.70–1.66 (m, 1H), 1.51 ppm (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 208.0, 139.8, 137.0, 135.4, 128.5, 127.8, 126.5, 58.5, 57.6, 52.9, 49.0, 48.1, 23.8 ppm; IR (KBr): $\tilde{\nu}$ = 1715 $cm^{-1}$; MS (EI): $m/z$: 212 [$M^+$]; HRMS (EI): $m/z$ calcd for $C_{15}H_{16}O$: 212.1201; found: 212.1218; elemental analysis calcd (%) for $C_{15}H_{16}O$: C 84.87, H 7.60; found: C 84.72, H 7.65.

**Norbornene diphenyldioxolanes 12 and 13**: A catalytic amount of *p*-TsOH (0.1 equiv) was added to a solution of (±)-**7a** (54 mg) and (*R*,*R*)-hydrobenzoin (65.4 mg) in toluene (2.6 mL) under $N_2$ and the resulting mixture was stirred for 3 h at RT. After completion of the reaction (TLC check), the solution was quenched by the addition of saturated aqueous $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (20:1) as the eluent to give a 1:1 diastereomeric mixture of **12** and **13** (89.7 mg, 86%). White powder; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.36–7.05 (m, 14H), 6.62–6.35 (m, 3H), 4.88 and 4.79 (both s, total 1H), 4.64–4.61/4.50–4.47 (d, $J$ = 7.8 Hz, total 1H), 4.36–4.33/4.26–4.24 (d, $J$ = 7.8 Hz, total 1H), 3.26–3.24 (m, 1H), 3.13 (m, 1H), 2.84 (m, 1H), 1.90–1.86 (m, 1H), 1.64–1.59 (m, 1H), 1.63/1.60 ppm (both s, total 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 141.6, 141.3, 139.9, 139.6, 138.0, 137.6, 137.1, 137.0, 135.3, 135.2, 129.5, 129.1, 128.6, 128.4, 128.2, 128.0, 127.9, 127.8, 127.4, 127.2, 127.1, 126.30, 126.27, 125.9, 125.8, 124.9, 107.9, 107.4, 86.6, 85.8, 85.1, 84.6, 56.9, 56.5, 53.5, 53.3, 50.7, 50.6, 49.6, 49.1, 49.0, 48.8, 22.6, 22.2 ppm; MS (EI): $m/z$: 408 [$M^+$]; HRMS (EI): $m/z$ calcd for $C_{29}H_{28}O_2$: 408.2089; found: 408.2111; elemental analysis calcd (%) for $C_{29}H_{28}O_2$: C 85.26, H 6.91; found: C 85.22, H 6.98.

**(1*R*,2*S*,3*S*,4*S*)-2-*exo*-Methyl-3-*endo*-phenylnorbornene-2-carbaldehyde ((−)-7a)**: NBS (2.09 g, 0.5 equiv) was added to a stirred solution of **12** and **13** (9.50 g) in $CH_3CN$ containing 1% $H_2O$ (23.5 mL) at RT and the reaction mixture was stirred for 20 h at the same temperature. After completion of the reaction (checked by TLC), saturated aqueous $Na_2S_2O_3$ was added to the mixture and the resulting solution was extracted with EtOAc. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (50:1→4:1) as an eluent to give **14** (4.28 g, 8.46 mmol, 36%) and **13** (4.75 g, 11.8 mmol, 50%). **13**: $[\alpha]_D^{24}$ = −102.9 ($c$ = 1.04, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.39–7.25 (m, 10H), 7.15–7.04 (m, 3H), 6.58–6.56 (m, 1H), 6.38–6.35 (m, 2H), 4.79 (s, 1H), 4.64–4.61 (d, $J$ = 7.5 Hz, 1H), 4.36–4.33 (d, $J$ = 7.5 Hz, 1H), 3.26–3.25 (d, $J$ = 3.0 Hz, 1H), 3.12 (brs, 1H), 2.83 (brs, 1H), 1.90–1.87 (d, $J$ = 8.7 Hz, 1H), 1.62 (s, 3H), 1.61–1.58 ppm (d, $J$ = 8.7 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 141.6, 139.9, 138.0, 137.1, 135.2, 129.5, 128.6, 128.4, 128.0, 127.8, 127.2, 127.1, 125.9, 124.9, 107.4, 85.8, 85.1, 56.9, 53.3, 50.6, 49.6, 49.1, 22.2 ppm; elemental analysis calcd (%) for $C_{29}H_{28}O_2$: C 85.26, H 6.91; found: C 85.22, H 6.98.

After a solution of **14** (4.28 g, 8.46 mmol) and $Zn(OTf)_2$ (18.5 g, 50.8 mmol) in DMA (85 mL) had been stirred for 30 min at 40 °C under $N_2$, Zn powder (11.1 g) was added to the mixture and the resulting solution was stirred for 5 h at 70 °C. After completion of the reaction (checked by TLC), $Et_2O$ was added to the reaction mixture and the precipitated salt and zinc were filtered out. The filtrate was evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (10:1) as the eluent to give (−)-**7a** (1.5 g, 7.19 mmol, 85%). White crystals; m.p. 45–46 °C; $[\alpha]_D^{24}$ = −102.9 ($c$ = 1.04, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 8.99 (s, 1H), 7.24–7.11 (m, 5H), 3.42–3.41 (m, 1H), 3.29–3.28 (m, 1H), 2.73 (brs, 1H), 1.90–1.87 (m, 1H), 1.70–1.66 (m, 1H), 1.51 ppm (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 208.0, 139.8, 137.0, 135.4, 128.5, 127.8, 126.5, 58.5, 57.6, 52.9, 49.0, 48.1, 23.8 ppm; IR (KBr): $\tilde{\nu}$ = 1715 $cm^{-1}$.

**Norbornene aldehyde norbornene acetal 11a**: A catalytic amount of *p*-TsOH (0.1 equiv) was added to a solution of (−)-**7a** (320 mg) and **5a** (256 mg, 1.1 equiv) in toluene (15 mL) under $N_2$ and the resulting mixture was stirred for 24 h at RT. After completion of the reaction (checked by TLC), the solution was quenched by the addition of saturated aqueous $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (50:1) as the eluent to give **11a** (510 mg, 1.46 mmol, 97%). Colorless oil; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.26–7.11 (m, 5H), 6.51–6.48 (m, 1H), 6.24–6.21 (m, 1H), 6.02–5.99 (m, 1H), 5.89–5.86 (m, 1H), 3.99–3.93 (dd, $J$ = 12.3, 4.2 Hz, 1H), 3.58 (s, 1H), 2.98 (s, 1H), 2.95–2.90 (m, 2H), 2.88–2.84 (d, $J$ = 12.5 Hz, 1H), 2.61 (brs, 2H), 2.56–2.51 (m, 1H), 2.45 (brs, 1H), 2.42–2.37 (m, 1H), 2.10–2.06 (d, $J$ = 12.5 Hz, 1H), 1.74–1.72 (m, 1H), 1.50–1.35 (m, 3H), 1.35 ppm (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 142.5, 137.3, 135.2, 134.93, 134.91, 128.8, 127.2, 125.5, 112.4, 73.0, 71.9, 57.7, 53.0, 52.4, 51.3, 49.2, 48.9, 45.4, 45.3, 45.2, 44.9, 22.5 ppm; IR (KBr): $\tilde{\nu}$ = 2963, 1105,

742 $cm^{-1}$; MS (EI): *m/z*: 348 [$M^+$]; HRMS (EI): *m/z* calcd for $C_{24}H_{28}O_2$: 348.2089; found: 348.2119.

**10-Membered mixed acetal 15a**: NBS (48.0 mg, 0.55 equiv) was added to a stirred solution of **11a** (85.6 mg) in MeOH (2.4 mL) at −40 °C under $N_2$ and the reaction mixture was allowed to warm slowly to RT. After completion of the reaction (checked by TLC), saturated aqueous $Na_2S_2O_3$ was added to the mixture and the resulting solution was extracted with EtOAc. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (10:1) as the eluent to give **15a** (115.2 mg, 0.243 mmol, 99 %). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.27–7.17 (m, 5H), 6.09–6.04 (m, 2H), 5.11 (s, 1H), 4.62 (m, 1H), 4.35–4.32 (m, 1H), 4.08–4.05 (d, $J$ = 10.5 Hz, 1H), 3.85–3.80 (dd, $J$ = 12.6, 4.5 Hz, 1H), 3.57–3.40 (m, 2H), 2.94–2.92 (d, $J$ = 4.2 Hz, 1H), 2.84 (m, 1H), 2.78 (s, 3H), 2.70 (m, 2H), 2.57–2.56 (m, 1H), 2.41–2.38 (m, 2H), 1.99 (m, 2H), 1.43–1.41 (m, 2H), 1.24 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 139.7, 136.2, 134.0, 130.4, 127.9, 126.1, 109.7, 93.0, 74.3, 73.9, 58.3, 55.8, 55.1, 54.5, 54.4, 50.3, 48.4, 47.9, 46.0, 45.9, 42.5, 33.8, 23.8 ppm; IR (KBr): $\tilde{\nu}$ = 2963, 1117, 729 $cm^{-1}$; elemental analysis calcd (%) for $C_{25}H_{31}O_3Br$: C 65.36, H 6.80; found: C 65.47, H 6.69.

**Norbornene aldehyde norbornene alcohol 16a**: A catalytic amount of *p*-TsOH (0.1 equiv) was added to a solution of **15a** (55.8 mg) in acetone/$H_2O$ (4:1; 1 mL) and the resulting mixture was stirred at RT. After completion of the reaction (checked by TLC), the solution was quenched by the addition of saturated aqueous $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (5:2) as the eluent to give **16a** (53.6 mg, 0.120 mmol, 99 %). Colorless oil; IR (KBr): $\tilde{\nu}$ = 3398, 1710 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.46 (s, 1H), 7.37–7.09 (m, 5H), 6.07–5.99 (m, 2H), 4.18–4.10 (m, 2H), 3.41–3.34 (m, 3H), 3.18–3.13 (m, 2H), 3.07–3.02 (t, $J$ = 9 Hz, 1H), 2.82–2.76 (m, 2H), 2.48 (m, 1H), 2.41–2.29 (m, 2H), 2.14–2.10 (d, $J$ = 11.1 Hz, 1H), 1.93–1.90 (d, $J$ = 11.1 Hz, 1H), 1.51 (s, 3H), 1.40–1.24 ppm (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.8, 136.3, 135.1, 134.9, 129.1, 127.3, 126.7, 91.9, 70.6, 63.1, 56.1, 55.8, 51.1, 50.8, 50.4, 49.5, 46.2, 46.1, 44.9, 41.3, 34.0, 25.6 ppm; MS (EI): *m/z*: 444 [$M^+$]; HRMS (EI): *m/z* calcd for $C_{24}H_{29}O_3Br$: 444.1300; found: 444.1297.

**Norbornene aldehyde norbornene silylether 17a**: Imidazole (33.0 mg) and TBDPSCl (64 μL) were added to a stirred solution of **16a** (49.2 mg) in DMF (0.5 mL) at RT under $N_2$ and the resulting mixture was stirred for an additional 1 h at the same temperature. After completion of the reaction (checked by TLC), the solution was quenched by the addition of saturated aqueous $NH_4Cl$ and extracted with AcOEt. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (10:1) as the eluent to give **17a** (68.0 mg, 0.10 mmol, 99 %). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.40 (s, 1H), 7.64–7.08 (m, 15H), 5.97–5.96 (m, 1H), 5.87–86 (m, 1H), 4.13–4.12 (m, 1H), 3.99–3.96 (m, 1H), 3.52–3.46 (dd, $J$ = 9.9, 6.3 Hz, 1H), 3.35 (m, 1H), 3.20–3.14 (t, $J$ = 9.6 Hz, 1H), 3.08–3.05 (m, 2H), 2.91 (m, 1H), 2.88–2.81 (t, $J$ = 9.6 Hz, 1H), 2.72 (m, 1H), 2.38–2.21 (m, 3H), 2.08–2.04 (m, 1H), 1.86–1.83 (m, 1H), 1.47 (s, 3H), 1.39–1.19 (m, 2H), 1.04 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.6, 136.6, 135.60, 135.56, 135.3, 134.0, 129.49, 129.46, 129.0, 127.6, 127.4, 126.6, 91.9, 70.5, 63.8, 56.3, 56.1, 51.2, 51.0, 50.9, 48.9, 45.4, 45.3, 44.2, 41.3, 34.0, 26.9, 25.5, 19.2 ppm; IR (KBr): $\tilde{\nu}$ = 1712 $cm^{-1}$; MS (FAB): *m/z*: 705 [$M^+$+Na]; HRMS (FAB): *m/z* calcd for $C_{40}H_{47}BrNaO_3Si$: 705.2576 [$M^+$+Na]; found: 705.2371.

**Norbornene silylether 18a**: A solution of **17a** (82 mg) and $Zn(OTf)_2$ (262 mg) in DMA (0.37 mL) was stirred at 40 °C under $N_2$. After 30 min, Zn powder (156 mg) was added to the mixture and stirring was continued at 70 °C for 5 h. After completion of the reaction (checked by TLC), $Et_2O$ was added to the reaction mixture and the precipitated salt and zinc were filtered out. The filtrate was evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (4:1) as the eluent to give **18a** (46.6 mg, 0.118 mmol, 99 %) and (−)-**7a** (25.4 mg, 0.12 mmol, 100 %). **18a**: Colorless oil; $[\alpha]_D^{25}$ = +11.03 ($c$ = 0.67, $CHCl_3$); the optical purity of **18a** (98 % *ee*) was determined by HPLC analysis (Chiralpak AD-H, hexane/*i*PrOH (150:1), 0.5 mL $min^{-1}$ flow rate, 264 nm wavelength; retention times: 33.73 min and 37.24 min for (±)-**18a** and 37.91 min for (+)-**18a**); **7a**: $[\alpha]_D^{26}$ = −101.9 ($c$ = 0.68, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69–7.64 (m, 4H), 7.48–7.38 (m, 6H), 6.04–6.02 (m, 1H), 5.88–5.85 (m, 1H), 3.65 (br s, 1H), 3.60–3.46 (m, 4H), 2.82 (br s, 1H), 2.64 (br s, 1H), 2.62–2.49 (m, 2H), 1.59 (s, 1H), 1.36–1.35 (m, 1H), 1.04 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 135.6, 135.5, 135.1, 134.5, 129.9, 129.8, 127.80, 127.78, 65.2, 63.5, 49.8, 46.5, 46.3, 45.6, 44.8, 26.8, 19.1 ppm; IR (KBr): $\tilde{\nu}$ = 3385 $cm^{-1}$; MS (FAB): *m/z*: 393 [$M^+$+H]; HRMS (FAB): *m/z* calcd for $C_{25}H_{33}O_2Si$: 393.2250 [$M^+$+H]; found: 393.2244.

**(2*R*,3*S*)-Lactone 19**: DMSO (0.39 mL) was added carefully to a stirred solution of oxalyl chloride (0.24 mL) in $CH_2Cl_2$ (7.0 mL) at −78 °C under $N_2$. After 30 min, a solution of **18a** (272 mg) in $CH_2Cl_2$ (2.0 mL) was added dropwise to the resulting mixture at −78 °C. After 1 h, $Et_3N$ (1.16 mL) was added to the resulting solution. The solution was allowed to warm to 0 °C. Saturated aqueous $NH_4Cl$ was added to the mixture and the resulting solution was extracted with EtOAc. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (15:1) as the eluent to give the aldehyde (268 mg, 0.686 mmol, 99 %). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.40–9.39 (d, $J$ = 4.2 Hz, 1H), 7.64–7.60 (m, 4H), 7.40–7.38 (m, 6H), 6.26–6.25 (m, 1H), 6.04–6.03 (m, 1H), 3.61–3.43 (m, 2H), 3.08–2.80 (m, 4H), 1.53–1.51 (d, $J$ = 8.1 Hz, 1H), 1.39–1.36 (d, $J$ = 8.1 Hz, 1H), 1.03 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 205.7, 135.53, 135.47, 135.1, 133.55, 133.47, 129.7, 127.7, 64.3, 54.9, 49.6, 48.0, 46.2, 45.0, 26.8, 19.2; IR (KBr): $\tilde{\nu}$ = 1715 $cm^{-1}$.

TBAF (0.36 mL, 0.1 M in THF) was added to a solution of the aldehyde (141 mg) in THF (3.6 mL) at RT under $N_2$, and the mixture was stirred for 30 min at the same temperature. After completion of the reaction (checked by TLC), water was added to the mixture and the resulting solution was extracted with $Et_2O$. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was used in the next reaction without purification. A mixture of the crude product and PCC (85.4 mg) in $CH_2Cl_2$ (3.6 mL) was stirred for 3 h at RT. After completion of the reaction (checked by TLC), $Et_2O$ was added to the resulting mixture. The precipitate was removed through a short pad of Florisil. The filtrate was evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (2:3) as the eluent to give **19** (25.8 mg, 0.172 mmol, 48 % over two steps). Colorless crystals; m.p. 104–105 °C; $[\alpha]_D^{22}$ = −142.2 ($c$ = 0.99, $CHCl_3$); literature value for (2*S*,3*R*)-lactone:[12] $[\alpha]_D^{25}$ = +143.2 ($c$ = 5.2, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.30 (br s, 2H), 4.29 (dd, $J$ = 9.5, 8.2 Hz, 1H), 3.78 (dd, $J$ = 9.5, 3.1 Hz, 1H), 3.37–3.00 (m, 4H), 1.64 (br d, $J$ = 8.4 Hz, 1H), 1.45 ppm (br d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 136.9, 134.4, 70.3, 51.8, 47.6, 46.1, 45.7, 40.3 ppm; IR (KBr): $\tilde{\nu}$ = 1759 $cm^{-1}$; MS (EI): *m/z*: 150 [$M^+$]; HRMS (EI): *m/z* calcd for $C_9H_{10}O_2$: 150.0681; found: 150.067.

**Norbornene aldehyde norbornane acetal 11b**: By use of the same procedure as for **11a**, **11b** (134.0 mg, 98 %) was obtained from **5b** (67.2 mg) and (−)-**7a** (83 mg). Eluent for chromatography: AcOEt/hexane (1:50). White solid; m.p. 97 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.21–7.10 (m, 5H), 6.55–6.53 (m, 1H), 6.31–6.28 (m, 1H), 5.30 (s, 1H), 3.88–3.82 (dd, $J$ = 12.3, 4.5 Hz, 1H), 3.71 (s, 1H), 3.48–3.40 (t, $J$ = 12 Hz, 1H), 3.01 (m, 2H), 2.85–2.79 (dd, $J$ = 12.3, 4.5 Hz, 1H), 2.69–2.60 (m, 2H), 2.23–2.04 (m, 2H), 2.08 (m, 1H), 1.92 (m, 1H), 1.76–1.73 (d, $J$ = 8.6 Hz, 1H), 1.51–1.49 (d, $J$ = 8.6 Hz, 1H), 1.44–1.15 (m, 5H), 1.35 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 142.5, 137.4, 135.3, 128.9, 127.3, 125.5, 112.1, 71.0, 69.7, 57.8, 53.0, 52.4, 49.2, 49.0, 43.7, 43.4, 41.6, 39.6, 39.3, 23.0, 22.6, 22.5 ppm; IR (KBr): $\tilde{\nu}$ = 2957, 1107, 739 $cm^{-1}$; MS (EI): *m/z*: 350 [$M^+$]; HRMS (EI): *m/z* calcd for $C_{24}H_{30}O_2$: 350.2246; found: 350.2267.

**Norbornene aldehyde bicyclooctene acetal 11c**: By use of the same procedure as for **11a**, **11c** (77.1 mg, 88 %) was obtained from **5c** (44.6 mg) and (−)-**7a** (51.2 mg). Eluent for chromatography: AcOEt/hexane (1:50). White crystals; m.p. 104–105 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.21–7.09 (m, 5H), 6.50–6.48 (m, 1H), 6.25–6.22 (m, 1H), 6.07–5.94 (m, 2H), 3.81–3.75 (dd, $J$ = 12.6, 3.9 Hz, 1H), 3.55 (s, 1H), 3.51–3.07 (t, $J$ = 12 Hz, 1H), 2.99–2.98 (m, 2H), 2.81–2.75 (dd, $J$ = 12.6, 3.9 Hz, 1H), 2.60 (m, 1H), 2.32–2.04 (m, 5H), 1.74–1.72 (m, 1H), 1.33 (s, 3H), 1.49–1.09 ppm (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 142.4, 137.3, 135.2, 133.0, 132.8, 128.8, 127.3, 125.5, 111.2, 74.2, 73.3, 57.8, 53.1, 52.1, 49.2, 48.9, 45.3, 44.9, 33.1, 32.5, 25.2, 24.9, 22.5 ppm; IR (KBr): $\tilde{\nu}$ = 2936, 1111, 746 $cm^{-1}$; MS (EI): *m/z*: 362 [$M^+$]; HRMS (EI): *m/z* calcd for $C_{25}H_{30}O_2$: 362.2246; found: 362.2259.

**Norbornene aldehyde oxohexene acetal 11d**: By use of the same procedure as for **11a**, **11d** (106.0 mg, 96%) was obtained from **5d** (54.2 mg) and (−)-**7a** (67.2 mg). Eluent for chromatography: AcOEt/hexane (1:8). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.23–7.12 (m, 5H), 6.53–6.52 (m, 1H), 6.31–6.26 (m, 3H), 4.41 (s, 1H), 4.24 (s, 1H), 4.19–4.08 (m, 1H), 3.80 (s, 1H), 3.43–3.34 (t, $J$ = 12.6 Hz, 1H), 3.14–3.08 (dd, $J$ = 12.9, 5.4 Hz, 1H), 3.00 (m, 2H), 2.65–2.57 (m, 2H), 2.02–1.96 (m, 1H), 1.92–1.83 (m, 1H), 1.75–1.73 (d, $J$ = 8.4 Hz, 1H), 1.52–1.49 (d, $J$ = 8.4 Hz, 1H), 1.33 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 142.4, 137.1, 135.7, 135.4, 128.8, 127.4, 125.6, 112.4, 80.6, 80.2, 72.5, 71.3, 60.4, 57.8, 53.0, 52.3, 49.2, 49.0, 43.2, 43.1, 22.3 ppm; IR (KBr): $\tilde{\nu}$ = 2970, 1047, 739 cm$^{-1}$; MS (FAB): $m/z$: 373 [$M^+$+Na]; HRMS (FAB): $m/z$ calcd for $C_{23}H_{26}NaO_3$: 373.1780 [$M^+$+Na]; found: 373.1776.

**Norbornene aldehyde cyclopropane acetal 11e**: By use of the same procedure as for **11a**, **11e** (107.9 mg, 74%) and **11e′** (33.1 mg, 23%) were obtained from **5e** (100 mg) and (−)-**7a** (104 mg). Eluent for chromatography: AcOEt/hexane (1:30). **11e**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.26–7.10 (m, 5H), 6.53 (dd, $J$ = 5.6, 2.9 Hz, 1H), 6.23 (dd, $J$ = 5.6, 2.7 Hz, 1H), 4.15 (dd, $J$ = 12.6, 3.0 Hz, 1H), 3.60 (d, $J$ = 11.9 Hz, 1H), 3.20 (dd, $J$ = 12.9, 2.4 Hz, 1H), 3.16 (s, 1H), 3.00 (s, 1H), 3.00 (d, $J$ = 7.2 Hz, 1H), 2.61 (brs, 1H), 2.31 (d, $J$ = 13.2 Hz, 1H), 1.73 (d, $J$ = 8.4 Hz, 1H), 1.50 (dt, $J$ = 10.2, 1.8 Hz, 1H), 1.37 (s, 3H), 0.85–0.78 (m, 1H), 0.70–0.60 (m, 2H), 0.30–0.20 ppm (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 142.2, 137.0, 135.5, 129.0, 127.4, 125.6, 111.2, 68.0, 66.5, 57.5, 53.3, 52.8, 49.1, 49.0, 22.1, 16.7, 16.4, −0.2 ppm; IR (KBr): $\tilde{\nu}$ = 2968, 1083, 733 cm$^{-1}$; MS (EI): $m/z$: 296 [$M^+$]; HRMS (EI): $m/z$ calcd for $C_{20}H_{24}O_2$: 296.1776 [$M^+$]; found: 296.1769; **11e′**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.26–7.05 (m, 5H), 6.50 (dd, $J$ = 5.6, 2.9 Hz, 1H), 6.23 (dd, $J$ = 5.6, 3.0 Hz, 1H), 4.48 (dd, $J$ = 13.2, 6.6 Hz, 1H), 3.57 (s, 1H), 3.42 (dd, $J$ = 13.5, 6.6 Hz, 1H), 3.01 (s, 1H), 2.99 (brs, 1H), 2.87 (dd, $J$ = 13.2, 10.5 Hz, 1H), 2.63 (brs, 1H), 2.01 (dd, $J$ = 13.5, 10.8 Hz, 1H), 1.75 (d, $J$ = 8.7 Hz, 1H), 1.49 (dt, $J$ = 10.0, 2.0 Hz, 1H), 1.42 (s, 3H), 1.40–1.15 (m, 2H), 0.82–0.75 (m, 1H), 0.37–0.32 ppm (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 142.5, 137.2, 135.3, 128.8, 127.3, 125.5, 114.5, 74.8, 73.4, 57.8, 53.0, 52.6, 49.1, 49.0, 22.7, 18.3, 17.9, 16.5 ppm; IR (KBr): $\tilde{\nu}$ = 2966, 1092, 741 cm$^{-1}$.

**Norbornene aldehyde cyclohexene acetal 11f**: By use of the same procedure as for **11a**, **11f** and **11f′** (65.6 mg, 76%, 60% *de*) were obtained from **5f** (72.8 mg) and (−)-**7a** (54.4 mg) as an inseparable diastereomixture. Eluent for chromatography: AcOEt/hexane (1:15). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.26–7.12 (m, 5H), 6.57–6.55 (m, 1H), 6.32–6.29 (m, 1H), 6.55–6.51 (m, 2H), 3.99 (s, 1H), 3.80–3.73 (dd, $J$ = 11.9, 6.2 Hz, 1H), 3.56–3.50 (dd, $J$ = 12.2, 3.8 Hz, 1H), 3.01–2.90 (m, 3H), 2.62 (m, 1H), 2.00–1.49 (m, 9H), 1.38 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 142.4, 137.2, 135.4, 129.1, 127.5, 125.9, 125.6, 125.5, 104.4, 70.9, 70.1, 57.3, 53.4, 53.1, 49.3, 49.1, 38.3, 37.2, 27.4, 27.0, 22.0 ppm; IR (KBr): $\tilde{\nu}$ = 2964, 1134, 741 cm$^{-1}$; MS (EI): $m/z$: 336 [$M^+$]; HRMS (EI): $m/z$ calcd for $C_{23}H_{28}O_2$: 336.2089 [$M^+$]; found: 336.2084.

**Norbornene aldehyde norbornane alcohol 16b**: NBS (61.0 mg, 1.1 equiv) was added to a stirred solution of **11b** (109.2 mg) in MeOH (3.2 mL) at −40°C under $N_2$ and the reaction mixture was allowed to warm slowly to RT. After completion of the reaction (checked by TLC), saturated aqueous $Na_2S_2O_3$ was added to the mixture and the resulting solution was extracted with EtOAc. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. A catalytic amount of *p*-TsOH (0.1 equiv) was added to a solution of the crude **15b** in acetone/$H_2O$ (4:1; 1 mL) and the resulting mixture was stirred at RT. After completion of the reaction (checked by TLC), the solution was quenched by addition of saturated aqueous $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated in vacuo. The residue was purified by $SiO_2$ flash column chromatography with hexane/AcOEt (3:1) as the eluent to give **16b** (64.1 mg, 0.143 mmol, 92% over 2 steps). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.43 (s, 1H), 7.37–7.09 (m, 5H), 4.19–4.18 (m, 2H), 3.78–3.76 (m, 1H), 3.49–3.40 (m, 3H), 3.29–3.25 (m, 1H), 3.15 (m, 1H), 2.51 (m, 1H), 2.22–1.91 (m, 7H), 1.51 (s, 3H), 1.35–1.19 ppm (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.7, 136.3, 129.1, 127.3, 126.7, 91.9, 69.2, 61.3, 56.1, 55.8, 51.1, 50.7, 50.4, 43.1, 40.4, 40.2, 39.7, 39.5, 34.0, 25.6, 22.8, 22.4 ppm; IR (KBr): $\tilde{\nu}$ = 3395, 1711 cm$^{-1}$; MS (FAB): $m/z$: 447 [$M^+$+H]; HRMS (FAB): $m/z$ calcd for $C_{24}H_{32}BrO_3$: 447.1535 [$M^+$+H]; found: 447.1544.

**Norbornene aldehyde bicyclooctene alcohol 16c**: By use of the same procedure as for **16b**, **16c** (84.2 mg, 95%) was obtained from **11c** (70.0 mg) and NBS (37.8 mg). Eluent for chromatography: AcOEt/hexane (1:3). White crystals; m.p. 107–108°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.45 (s, 1H), 7.37–7.09 (m, 5H), 6.17–6.09 (m, 2H), 4.17–4.10 (m, 2H), 3.52–3.06 (m, 6H), 2.48–2.41 (m, 3H), 2.14–1.89 (m, 4H), 1.59–1.47 (m, 5H), 1.51 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.7, 136.4, 133.21, 133.18, 129.1, 127.3, 126.7, 91.9, 71.7, 64.2, 56.1, 55.9, 51.1, 50.8, 50.5, 44.9, 41.7, 34.0, 33.5, 33.4, 25.6, 25.5, 25.0 ppm; IR (KBr): $\tilde{\nu}$ = 3371, 1711 cm$^{-1}$; MS (FAB): $m/z$: 481 [$M^+$+Na]; HRMS (FAB): $m/z$ calcd for $C_{25}H_{31}BrNaO_3$: 481.1354 [$M^+$+Na]; found: 481.1358.

**Norbornene aldehyde oxohexene alcohol 16d**: By use of the same procedure as for **16b**, **16d** (51.7 mg, 95%) was obtained from **11d** (41.1 mg) and NBS (23.0 mg). Eluent for chromatography: AcOEt/hexane (1:1). White solid; m.p. 119–120°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.44 (s, 1H), 7.38–7.10 (m, 5H), 6.31 (s, 2H), 5.30 (s, 1H), 4.77 (s, 1H), 4.60 (s, 1H), 4.19 (s, 2H), 3.79 (m, 1H), 3.62–3.58 (m, 1H), 3.50–3.41 (m, 3H), 3.15 (s, 1H), 2.49 (s, 1H), 2.16–2.13 (d, $J$ = 11.1 Hz, 1H), 1.94–1.91 (d, $J$ = 11.1 Hz, 1H), 1.79–1.78 (m, 2H), 1.52 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.7, 136.4, 135.8, 135.4, 129.1, 127.3, 126.7, 92.1, 80.9, 80.7, 70.2, 62.3, 56.10, 56.07, 51.2, 50.8, 50.5, 42.1, 39.9, 34.0, 25.6 ppm; IR (KBr): $\tilde{\nu}$ = 3411, 1711 cm$^{-1}$; HRMS (FAB): $m/z$ calcd for $C_{23}H_{28}BrNaO_4$: 447.1113 [$M$+H$^+$]; found: 447.1142.

**Norbornene aldehyde cyclopropane alcohol 16e**: By use of the same procedure as for **16b**, **15e** and **15e′** (99%) were obtained from **11e** and **11e′** (132 mg) and NBS (87 mg). **15e** (138 mg, 76%) was obtained by separation with $SiO_2$ flash column chromatography with hexane/AcOEt (20:1) as the eluent. **16e** (133 mg, 100%) was obtained from **15e**. Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.46 (s, 1H), 7.39–7.11 (m, 5H), 5.58–5.57 (m, 2H), 4.21–4.09 (m, 2H), 3.46–3.41 (m, 3H), 3.32–3.27 (m, 1H), 3.19–3.14 (m, 2H), 2.76 (brs, 1H), 2.62–2.51 (m, 1H), 2.16–2.12 (m, 1H), 2.02–1.66 (m, 7H), 1.52 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 206.1, 136.4, 129.1, 127.3, 126.8, 125.63, 125.56, 91.8, 69.8, 63.1, 56.6, 56.0, 51.2, 50.9, 50.7, 37.3, 34.0, 33.3, 27.2, 25.9, 25.7 ppm; IR (KBr): $\tilde{\nu}$ = 3402, 1709 cm$^{-1}$; MS (FAB): $m/z$: 455 [$M^+$+Na]; HRMS (FAB): $m/z$ calcd for $C_{23}H_{29}BrNaO_3$: 455.1197 [$M^+$+Na]; found: 455.1189.

**Norbornene aldehyde cyclohexene alcohol 16f**: By use of the same procedure as for **16b**, **15f** and **15f′** (98%) were obtained from **11f** and **11f′** (96.4 mg) and NBS (56.0 mg). **15f** (99.6 mg, 78%) was obtained by separation with $SiO_2$ flash column chromatography with hexane/AcOEt (20:1) as the eluent. **16f** (96.4 mg, 0.224 mmol, 100%) was obtained from **15f**. Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.46 (s, 1H), 7.39–7.11 (m, 5H), 5.58–5.57 (m, 2H), 4.21–4.09 (m, 2H), 3.46–3.41 (m, 3H), 3.32–3.27 (m, 1H), 3.19–3.14 (m, 2H), 2.76 (brs, 1H), 2.62–2.51 (m, 1H), 2.16–2.12 (m, 1H), 2.02–1.66 (m, 7H), 1.52 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 206.1, 136.4, 129.1, 127.3, 126.8, 125.63, 125.56, 91.8, 69.8, 63.1, 56.6, 56.0, 51.2, 50.9, 50.7, 37.3, 34.0, 33.3, 27.2, 25.9, 25.7; IR (KBr): $\tilde{\nu}$ = 3402, 1709 cm$^{-1}$; MS (FAB): $m/z$: 455 [$M^+$+Na]; HRMS (FAB): $m/z$ calcd for $C_{23}H_{29}BrNaO_3$: 455.1197 [$M^+$+Na]; found: 455.1189.

**Norbornene aldehyde norbornane silylether 17b**: By use of the same procedure as for **17a**, **17b** (84.6 mg, 94%) was obtained from **16b** (58.4 mg), TBDPSCl (74 μL), imidazole (39.2 mg), and DMF (0.8 mL). Eluent for chromatography: AcOEt/hexane (1:10). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.35 (s, 1H), 7.64–7.07 (m, 15H), 4.13–4.01 (m, 2H), 3.75–3.69 (m, 1H), 3.56–3.50 (m, 1H), 3.34–3.31 (m, 3H), 3.22–3.16 (m, 1H), 3.09 (m, 1H), 2.35–2.28 (m, 2H), 2.17–1.98 (m, 3H), 1.87–1.83 (m, 1H), 1.46 (s, 3H), 1.27–1.19 (m, 7H), 1.02 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.6, 136.6, 135.62, 135.58, 134.1, 129.5, 129.0, 127.6, 127.5, 127.4, 126.6, 91.7, 68.5, 61.7, 56.3, 56.1, 51.2, 51.0, 50.8, 42.7, 39.7, 39.6, 39.5, 39.4, 34.0, 26.9, 25.5, 22.3, 22.1, 19.2 ppm; MS (FAB): $m/z$: 707 [$M^+$+Na]; IR (KBr): $\tilde{\nu}$ = 1713 cm$^{-1}$; HRMS (FAB): $m/z$ calcd for $C_{40}H_{49}BrNaO_3Si$: 707.2532 [$M^+$+Na]; found: 707.2542.

**Norbornene aldehyde bicyclooctene silylether 17c**: By use of the same procedure as for **17a**, **17c** (108.2 mg, 98%) was obtained from **16c** (79.2 mg), TBDPSCl (98 μL), imidazole (51.6 mg), and DMF (1.2 mL). Eluent for chromatography: AcOEt/hexane (1:10). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.39 (s, 1H), 7.64–7.08 (m, 15H), 6.11–5.96 (m, 2H), 4.12–4.10 (m, 1H), 3.99–3.96 (m, 1H), 3.54–3.49 (m, 1H), 3.36–3.34 (m, 1H), 3.28–3.16 (m, 2H), 3.10 (m, 1H), 2.92–2.86 (t, $J$ = 9 Hz, 1H), 2.63 (m, 1H), 2.42 (m, 1H), 2.32 (m, 1H), 2.07–1.97 (m, 3H), 1.86–1.82 (m, 1H), 1.46 (s, 3H), 1.43–1.02 (m, 4H), 1.03 ppm (s, 9H);

$^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.6, 136.6, 135.60, 135.56, 134.01, 133.99, 133.3, 133.2, 129.5, 129.0, 127.6, 127.4, 126.6, 91.9, 77.4, 77.0, 76.6, 70.7, 64.2, 56.3, 56.2, 51.2, 51.0, 50.9, 44.2, 41.5, 34.0, 32.3, 26.9, 25.45, 25.38, 25.0, 19.2; MS (FAB): *m/z*: 719 [$M^+$+Na]; IR (KBr): $\tilde{\nu}$ = 1713 cm$^{-1}$; HRMS (FAB): *m/z* calcd for $C_{41}H_{49}BrNaO_3Si$: 719.2732 [$M^+$+Na]; found: 719.2496.

**Norbornene aldehyde oxohexene silylether 17d**: By use of the same procedure as for **17a**, **17d** (102.2 mg, 94%) was obtained from **16d** (73.4 mg), TBDPSCl (90 μL), imidazole (47.4 mg), and DMF (1.2 mL). Eluent for chromatography: AcOEt/hexane (1:6). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.38 (s, 1H), 7.65–7.08 (m, 15H), 6.28–6.25 (m, 2H), 4.85 (s, 1H,), 4.59 (s, 1H), 4.11–4.03 (m, 2H), 3.75–3.70 (dd, *J* = 9.9, 6.0 Hz, 1H), 3.61–3.55 (t, *J* = 9.6 Hz, 1H), 3.43–3.36 (m, 2H), 3.23–3.17 (t, *J* = 9.6 Hz, 1H), 3.11–3.10 (m, 1H), 2.37–2.36 (m, 1H), 2.09–2.06 (m, 1H), 1.88–1.84 (m, 1H), 1.80–1.75 (m, 1H), 1.71–1.66 (m, 1H), 1.48 (s, 3H), 1.04 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.6, 136.6, 135.55, 135.52, 135.48, 135.4, 133.7, 133.6, 129.6, 129.0, 127.69, 127.67, 127.4, 126.6, 92.0, 80.5, 80.2, 69.9, 63.2, 56.2, 56.1, 51.3, 50.8, 50.7, 42.4, 39.7, 34.0, 26.9, 25.4, 19.2 ppm; IR (KBr): $\tilde{\nu}$ = 1713 cm$^{-1}$; MS (FAB): *m/z*: 691 [$M^+$+Li]; HRMS (FAB): *m/z* calcd for $C_{39}H_{45}BrLiO_4Si$: 691.2430 [$M^+$+Li]; found: 691.2427.

**Norbornene aldehyde cyclopropane silylether 17e**: By use of the same procedure as for **17a**, **17e** (60.1 mg, 95%) was obtained from **16e** (39.2 mg), TBDPSCl (57 μL), imidazole (29.9 mg), and DMF (0.5 mL). Eluent for chromatography: AcOEt/hexane (1:15). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.43 (s, 1H), 7.67–7.63 (m, 4H), 7.43–7.24 (m, 9H), 7.12–7.10 (m, 2H), 4.22–4.08 (m, 2H), 3.74–3.68 (m, 1H), 3.54–3.48 (m, 2H), 3.38–3.39 (m, 1H), 3.14–3.08 (m, 2H), 2.38 (br s, 1H), 2.11 (d, *J* = 11.1 Hz, 1H), 1.88 (m, 1H), 1.49 (s, 3H), 1.29–0.97 (m, 2H), 1.03 (s, 9H), 0.67–0.14 (m, 1H), 0.10–0.08 ppm (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.6, 136.6, 135.6, 134.0, 133.9, 129.5, 129.0, 127.6, 127.5, 127.4, 126.6, 91.1, 70.0, 63.9, 56.4, 56.1, 51.4, 51.2, 50.8, 34.0, 26.9, 25.6, 19.2, 17.6, 15.0, 14.2, 8.7 ppm; IR (KBr): $\tilde{\nu}$ = 1713 cm$^{-1}$; MS (FAB): *m/z*: 653 [$M^+$+Na]; HRMS (FAB): *m/z* calcd for $C_{36}H_{43}O_3BrSiNa$: 653.2028 [$M^+$+Na]; found: 653.2045.

**Norbornene aldehyde cyclohexene silylether 17f**: By use of the same procedure as for **17a**, **17f** (63.2 mg, 98%) was obtained from **16f** (41.6 mg), TBDPSCl (54 μL), imidazole (28.8 mg), and DMF (1.0 mL). Eluent for chromatography: AcOEt/hexane (1:15). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.34 (s, 1H), 7.66–7.62 (m, 4H), 7.41–7.23 (m, 9H), 7.11–7.09 (m, 2H), 5.51 (m, 2H), 4.16–4.04 (m, 2H), 3.62–3.48 (m, 2H), 3.36–3.35 (m, 1H), 3.33–3.20 (m, 2H), 3.11 (m, 1H), 2.32 (m, 1H), 2.11–1.72 (m, 8H), 1.57 (s, 3H), 1.03 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 204.3, 136.6, 135.61, 135.59, 133.89, 133.85, 129.52, 129.47, 129.0, 127.60, 127.57, 127.4, 126.6, 125.5, 125.4, 91.8, 71.5, 64.5, 56.6, 56.1, 51.4, 51.0, 50.7, 37.1, 34.9, 33.9, 26.9, 26.70, 26.66, 25.5, 19.2 ppm; IR (KBr): $\tilde{\nu}$ = 1713 cm$^{-1}$; MS (FAB): *m/z*: 693 [$M^+$+Na]; HRMS (FAB): *m/z* calcd for $C_{39}H_{47}BrNaO_3Si$: 693.2576 [$M^+$+Na]; found: 693.2362.

**Norbornane silylether 18b**: By use of the same procedure as for **18a**, **18b** (69.0 mg, 94%) and **7a** (36.5 mg, 93%) were obtained from **17b** (127.5 mg), $Zn(OTf)_2$ (405 mg), Zn (245 mg), and DMA (2.0 mL). Eluent for chromatography: AcOEt/hexane (1:5). **18b**: Colorless oil; $[\alpha]_D^{25}$ = −8.31 (*c* = 1.28, $CHCl_3$); the optical purity of **18b** (98% *ee*) was determined by HPLC analysis (Chiralpak OD-H, hexane/*i*PrOH (99:1), 0.5 mL min$^{-1}$ flow rate, 262 nm wavelength; retention times: 19.11 min and 21.68 min for (±)-**18b** and 19.68 min for (+)-**18b**); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69–7.65 (m, 4H), 7.43–7.39 (m, 6H), 4.02–3.95 (m, 2H), 3.64–3.59 (m, 3H), 2.26 (m, 3H), 2.08 (m, 1H), 1.61 (m, 1H), 1.44–1.17 (m, 5H), 1.04 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 135.5, 135.4, 132.9, 132.8, 129.8, 129.7, 127.72, 127.67, 63.8, 61.8, 43.7, 42.9, 40.8, 40.7, 40.0, 26.8, 22.8, 22.7, 19.2 ppm; IR (KBr): $\tilde{\nu}$ = 3404 cm$^{-1}$; MS (FAB): *m/z* 395 [$M^+$+H]; HRMS (FAB): *m/z* calcd for $C_{25}H_{35}O_2Si$: 395.2406 [$M^+$+H]; found: 395.2409.

**Bicyclooctene silylether 18c**: By use of the same procedure as for **18a**, **18c** (42.4 mg, 89%) and **7a** (21.8 mg, 88%) were obtained from **17c** (81.8 mg), $Zn(OTf)_2$ (256 mg), Zn (154 mg), and DMA (1.0 mL). Eluent for chromatography: AcOEt/hexane (1:5). **18c**: Colorless oil; $[\alpha]_D^{24}$ = +2.11 (*c* = 1.48, $CHCl_3$); the optical purity of **18c** (98% *ee*) was determined by HPLC analysis (Chiralpak OD-H, hexane/*i*PrOH (99:1), 0.5 mL min$^{-1}$ flow rate, 262 nm wavelength; retention times: 22.20 min and 24.33 min for (±)-**18c** and 22.24 min for (+)-**18c**); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69–7.64 (m, 4H), 7.47–7.23 (m, 6H), 6.15–5.95 (m, 2H), 3.74–3.64 (m, 3H), 3.48–3.43 (m, 2H), 2.47 (m, 1H), 2.28–2.25 (m, 3H), 1.62–1.45 (m, 2H), 1.26–1.17 (m, 2H), 1.04 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 135.6, 135.5, 134.8, 133.2, 133.0, 132.7, 129.85, 129.80, 127.77, 127.75, 66.4, 64.9, 45.8, 45.2, 34.1, 33.9, 26.8, 25.6, 25.2, 19.1 ppm; IR (KBr): $\tilde{\nu}$ = 3406 cm$^{-1}$; MS (FAB): *m/z*: 407 [$M^+$+H]; HRMS (FAB): *m/z* calcd for $C_{26}H_{35}O_2Si$: 407.2406 [$M^+$+H]; found: 407.2428.

**Oxohexene silylether 18d**:[15] By use of the same procedure as for **18a**, **18d** (67.0 mg, 86%) and **7a** (41 mg, 98%) were obtained from **17d** (135 mg), $Zn(OTf)_2$ (430 mg), Zn (260 mg), and DMA (3.0 mL). Eluent for chromatography: AcOEt/hexane (1:2). **18d**: Colorless solid; m.p. 84–85 °C; $[\alpha]_D^{20}$ = −17.73 (*c* = 1.01, $CHCl_3$); the optical purity of **18d** (99% *ee*) was determined by HPLC analysis (Chiralpak OD-H, hexane/*i*PrOH (99:1), 0.5 mL min$^{-1}$ flow rate, 259 nm wavelength; retention times: 64.40 min and 70.43 min for (±)-**18d** and 69.33 min for (+)-**18d**); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69–7.65 (m, 4H), 7.47–7.37 (m, 6H), 6.39–6.32 (m, 2H), 4.74 (s, 1H), 4.66 (s, 1H), 3.91–3.85 (m, 2H), 3.79–3.73 (m, 1H), 3.67–3.66 (m, 1H), 3.10–3.08 (m, 1H), 1.97–1.93 (m, 2H), 1.05 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 135.8, 135.6, 135.52, 135.48, 132.9, 129.9, 127.8, 81.2, 80.8, 64.4, 62.5, 42.7, 42.5, 26.8, 19.1 ppm; IR (KBr): $\tilde{\nu}$ = 3422 cm$^{-1}$; MS (FAB): *m/z*: 395 [$M^+$+Na]; HRMS (FAB): *m/z* calcd for $C_{24}H_{31}NaO_3Si$: 395.2042 [$M^+$+Na]; found: 395.2036.

**Cyclopropane silylether 18e**: By use of the same procedure as for **18a**, **18e** (33.0 mg, 92%) and **7a** (18.8 mg, 94%) were obtained from **17e** (63.2 mg), $Zn(OTf)_2$ (206 mg), Zn (122.8 mg), and DMA (0.8 mL). Eluent for chromatography: AcOEt/hexane (1:4). **18e**: Colorless oil; $[\alpha]_D^{27}$ = −12.31 (*c* = 1.14, $CHCl_3$); the optical purity of **18e** (99% *ee*) was determined by HPLC analysis (Chiralpak OD-H, hexane/*i*PrOH (99:1), 0.5 mL min$^{-1}$ flow rate, 261 nm wavelength; retention times: 16.64 min and 18.81 min for (±)-**18e** and 19.69 min for (+)-**18e**); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69–7.65 (m, 4H), 7.47–7.36 (m, 6H), 5.57–5.52 (m, 2H), 3.77–3.53 (m, 4H), 2.76 (br s, 1H), 2.12–1.88 (m, 6H), 1.06 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 135.52, 135.47, 133.0, 129.71, 129.68, 127.6, 125.5, 125.3, 65.3, 64.1, 37.9, 37.3, 27.3, 26.9, 26.6, 19.2 ppm; IR (KBr): $\tilde{\nu}$ = 3344 cm$^{-1}$; MS (FAB): *m/z*: 381 [$M^+$+H]; HRMS (FAB): *m/z* calcd for $C_{24}H_{33}O_2Si$: 381.2250 [$M^+$+H]; found: 381.2260.

**Cyclohexene silylether 18f**:[16] By use of the same procedure for **18a**, **18f** (33.0 mg, 92%) and **7a** (18.8 mg, 94%) were obtained from **17f** (63.2 mg), $Zn(OTf)_2$ (206 mg), Zn (122.8 mg), and DMA (0.8 mL). Eluent for chromatography: AcOEt/hexane (1:4). **18f**: Colorless oil; $[\alpha]_D^{27}$ = −12.31 (*c* = 1.14, $CHCl_3$); the optical purity of **18f** (99% *ee*) was determined by HPLC analysis (Chiralpak OD-H, hexane/*i*PrOH (99:1), 0.5 mL min$^{-1}$ flow rate, 263 nm wavelength; retention times: 27.69 min and 33.20 min for (±)-**18f** and 34.35 min for (+)-**18f**); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69–7.65 (m, 4H), 7.47–7.36 (m, 6H), 5.57–5.52 (m, 2H), 3.77–3.53 (m, 4H), 2.76 (br s, 1H), 2.12–1.88 (m, 6H), 1.06 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 135.52, 135.47, 133.0, 129.71, 129.68, 127.6, 125.5, 125.3, 65.3, 64.1, 37.9, 37.3, 27.3, 26.9, 26.6, 19.2 ppm; IR (KBr): $\tilde{\nu}$ = 3344 cm$^{-1}$; MS (FAB): *m/z*: 381 [$M^+$+H]; HRMS (FAB): *m/z* calcd for $C_{24}H_{33}O_2Si$: 381.2250 [$M^+$+H]; found: 381.2260.

**Norbornene aldehyde 1,3-dimethyl acetal 21a**: By use of the same procedure as for **11a**, **21a** (257 mg, 94%) was obtained from **20a** (106 mg) and (−)-**7a** (194 mg). Eluent for chromatography: AcOEt/hexane (1:50). White solid; m.p. 78–79 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.36–7.09 (m, 5H), 6.50–6.48 (m, 1H), 6.28–6.26 (m, 1H), 3.78 (s, 1H), 3.46–3.39 (m, 1H), 3.01 (br s, 2H), 2.67 (br s, 1H), 2.65–2.59 (m, 1H), 1.76–1.74 (m, 1H), 1.52–1.48 (m, 1H), 1.36 (s, 3H), 1.21–1.16 (m, 1H), 1.13–1.11 (d, *J* = 6 Hz, 3H), 0.96–0.85 (m, 1H), 0.61–0.59 ppm (d, *J* = 6 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 142.4, 137.5, 134.9, 129.1, 127.0, 125.4, 103.7, 72.2, 71.7, 57.5, 52.5, 51.2, 49.1, 48.9, 40.4, 22.4, 21.9, 20.9 ppm; IR (KBr): $\tilde{\nu}$ = 2970, 1022, 745 cm$^{-1}$; MS (EI): *m/z*: 298 [$M^+$]; HRMS (EI): *m/z* calcd for $C_{20}H_{26}O_2$: 298.1933; found: 298.1950; elemental analysis calcd (%) for $C_{20}H_{26}O_2$: C 80.50, H 8.78; found: C 80.20; H 8.80.

**Norbornene aldehyde 1,3-diallyl acetal 21b**: By use of the same procedure as for **11a**, **21b** (75.2 mg, 90%) was obtained from **20b** (50.0 mg) and (−)-**7a** (58.8 mg): Eluent for chromatography: AcOEt/hexane (1:50). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.21–7.09 (m, 5H), 6.46 (dd, *J* = 5.6, 2.4 Hz, 1H), 6.27 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.91–5.77 (m,

1H), 5.27–5.01 (m, 3H), 4.83–4.77 (m, 1H), 3.85 (s, 1H), 3.35–3.30 (m, 1H), 2.98 (brs, 2H), 2.70–2.59 (m, 2H), 2.30–2.04 (m, 2H), 1.75–1.70 (m, 3H), 1.48 (d, $J=8.4$ Hz, 1H), 1.35 (s, 3H), 1.20 (dt, $J=12.9$, 2.5 Hz, 1H), 0.99–0.91 ppm (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=142.3$, 137.6, 134.8, 134.7, 134.6, 129.0, 127.3, 125.5, 116.5, 116.0, 103.4, 75.7, 74.9, 57.5, 52.5, 51.5, 49.3, 48.8, 40.4, 39.9, 35.9, 22.4 ppm; IR (KBr): $\tilde{\nu}=2974$, 1342, 1020, 912, 742 cm$^{-1}$; elemental analysis calcd (%) for $C_{24}H_{30}O_2$: C 82.24, H 8.63; found: C 82.11, H 8.72.

**Norbornene aldehyde 1,3-diisopropyl acetal 21c**: By use of the same procedure as for **11a**, **21c** (147 mg, 88%) was obtained from **20c** (83 mg) and (−)-**7a** (100 mg). Eluent for chromatography: hexane. Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.15$–7.06 (m, 5H), 6.42–6.41 (m, 1H), 6.30–6.27 (m, 1H), 3.91 (s, 1H), 2.95–2.92 (s, 3H), 2.71 (brs, 1H), 2.38–2.35 (m, 1H), 1.72 (d, $J=8.4$ Hz, 1H), 1.57–1.55 (m, 3H), 1.43 (d, $J=8.4$ Hz, 1H), 1.32 (s, 1H), 1.27–1.12 (m, 3H), 0.95 (d, $J=6.6$ Hz, 3H), 0.84 (d, $J=6.6$ Hz, 3H), 0.46 (d, $J=6.6$ Hz, 3H), 0.31 ppm (d, $J=6.6$ Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=142.6$, 137.9, 134.7, 129.1, 127.5, 125.5, 102.9, 81.3, 80.1, 57.6, 52.9, 52.2, 49.8, 48.6, 33.2, 32.6, 31.2, 22.6, 18.4, 18.3, 17.9, 17.6 ppm; IR (KBr): $\tilde{\nu}=2959$, 1109, 746 cm$^{-1}$; elemental analysis calcd (%) for $C_{24}H_{34}O_2$: C 81.31, H 9.67; found: C 81.36, H 9.71.

**Norbornene aldehyde 1,3-dimethyl alcohol 22a**: By use of the same procedure as for **16a**, **22a** (52.5 mg, 99%) was obtained by *p*-TsOH hydrolysis of the product from the reaction of **21a** (40.0 mg), NBS (26.0 mg), and MeOH (1.5 mL). Eluent for chromatography: AcOEt/hexane (1:3). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=9.39$ (s, 1H), 7.36–7.08 (m, 5H), 4.29–4.26 (m, 1H), 4.18–4.17 (m, 1H), 3.83 (m, 1H), 3.73–3.66 (q, $J=6.2$ Hz, 1H), 3.39 (m, 1H), 3.14 (m, 1H), 2.35 (m, 1H), 2.19–2.14 (d, $J=12$ Hz, 1H), 1.93–1.89 (d, $J=12$ Hz, 1H), 1.78 (brs, 1H), 1.72–1.64 (m, 1H), 1.51 (s, 3H), 1.42–1.33 (m, 1H), 1.15–1.13 (d, $J=6.8$ Hz, 3H), 1.08–1.06 ppm (d, $J=6.8$ Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=205.1$, 136.3, 128.9, 127.2, 126.6, 89.9, 77.5, 77.0, 76.5, 75.9, 66.0, 57.8, 56.3, 51.9, 51.4, 51.2, 45.6, 34.4, 25.5, 24.0, 20.1 ppm; IR (KBr): $\tilde{\nu}=3404$, 1713 cm$^{-1}$; HRMS (EI): *m*/*z* calcd for $C_{20}H_{28}O_2Br$: 395.1221; found: 395.1218.

**Norbornene aldehyde 1,3-diallyl alcohol 22b**: By use of the same procedure as for **16a**, **22b** (66.8 mg, 87%) was obtained by *p*-TsOH hydrolysis of the product from the reaction of **21b** (61.2 mg), NBS (18.6 mg), and MeOH (1.74 mL). Eluent for chromatography: AcOEt/hexane (1:3). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=9.37$ (s, 1H), 7.35–7.07 (m, 5H), 5.79–5.57 (m, 2H), 5.10–4.99 (m, 4H), 4.30 (t, $J=3.9$ Hz, 1H), 4.21–4.19 (m, 1H), 3.71–3.63 (m, 2H), 3.37 (d, $J=3.3$ Hz, 1H), 3.14 (d, $J=1.8$ Hz, 1H), 2.33–1.87 (m, 8H), 1.65–1.50 (m, 2H), 1.49 ppm (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=204.9$, 136.3, 134.4, 133.8, 128.9, 127.2, 126.6, 118.1, 117.7, 90.2, 78.7, 68.1, 57.3, 56.2, 51.9, 51.4, 51.2, 42.0, 40.3, 37.9, 34.1, 25.2 ppm; IR (KBr): $\tilde{\nu}=3410$, 2974, 1713, 1084, 914 cm$^{-1}$; HRMS (FAB): *m*/*z* calcd for $C_{24}H_{32}O_3Br$: 447.1535 [$M^+$+H]; found: 447.1544.

**Norbornene aldehyde 1,3-diisopropyl alcohol 22c**: By use of the same procedure as for **16a**, **22c** (77 mg, 70%) was obtained by *p*-TsOH hydrolysis of the product from the reaction of **21c** (87 mg), NBS (49 mg), and MeOH (1.8 mL). Eluent for chromatography: AcOEt/hexane (1:5). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=9.29$ (s, 1H), 7.28–7.23 (m, 3H), 7.04–7.01 (m, 2H), 4.21–4.20 (m, 1H), 4.16–4.15 (m, 1H), 3.40–3.39 (m, 1H), 3.30 (m, 1H), 3.09 (s, 1H), 2.22 (brs, 1H), 2.07 (d, $J=10.8$ Hz, 1H), 1.84–1.79 (m, 2H), 1.54–1.35 (m, 3H), 1.43 (s, 3H), 1.18–1.13 (m, 2H), 0.78 (d, $J=6.9$ Hz, 3H), 0.77 (d, $J=6.9$ Hz, 3H), 0.69 (d, $J=6.9$ Hz, 3H), 0.68 ppm (d, $J=6.9$ Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=204.5$, 136.4, 128.9, 127.2, 126.6, 91.8, 86.2, 74.9, 57.5, 56.4, 52.6, 51.7, 51.5, 35.1, 34.2, 33.6, 30.2, 25.3, 18.7, 17.5, 17.3, 16.7 ppm; IR (KBr): $\tilde{\nu}=3500$, 1715 cm$^{-1}$; HRMS (FAB): *m*/*z* calcd for $C_{24}H_{36}O_3Br$: 451.1848 [$M^+$+H]; found: 451.1853.

**Norbornene aldehyde 1,3-dimethyl silylether 23a**: By use of the same procedure as for **17a**, **23a** (104.0 mg, 100%) was obtained from **22a** (65.0 mg), TBDPSCl (94 μL), imidazole (50 mg), and DMF (0.8 mL). Eluent for chromatography: AcOEt/hexane (1:15). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=9.29$ (s, 1H), 7.64–7.08 (m, 15H), 4.20–4.08 (m, 2H), 3.80–3.78 (m, 1H), 3.58–3.52 (m, 1H), 3.36 (m, 1H), 3.12 (m, 1H), 2.23 (m, 1H), 2.14–2.10 (m, 1H), 1.89–1.75 (m, 3H), 1.47 (s, 3H), 1.00 (s, 9H), 1.04–1.01 (d, $J=6.3$ Hz, 3H), 0.83–0.81 ppm (d, $J=6.3$ Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=205.1$, 136.6, 135.8, 135.7, 134.6, 134.0, 129.5, 129.4, 128.9, 127.5, 127.3, 127.3, 126.5, 89.4, 73.9, 66.8, 57.5, 56.2, 51.9, 51.2, 51.2, 46.3, 34.2, 27.0, 25.3, 23.8, 19.5, 19.2 ppm; IR (KBr): $\tilde{\nu}=3439$ cm$^{-1}$; HRMS (FAB): *m*/*z* calcd for $C_{36}H_{45}O_3BrSiNa$: 655.2219 [$M^+$+Na]; found: 655.2224.

**Norbornene aldehyde 1,3-diallyl silylether 23b**: By use of the same procedure as for **16a**, **23b** (120.2 mg, 96%) was obtained from **22b** (81.3 mg), TBDPSCl (140 μL), imidazole (75 mg), and DMF (0.5 mL). Eluent for chromatography: AcOEt/hexane (1:15). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=9.22$ (s, 1H), 7.64–7.06 (m, 15H), 5.70–5.40 (m, 2H), 4.90–4.80 (m, 4H), 4.16 (t, $J=3.9$ Hz, 1H), 4.07–4.05 (m, 1H), 3.80–3.74 (m, 1H), 3.55–3.48 (m, 1H), 3.33 (d, $J=3.3$ Hz, 1H), 3.10 (brs, 1H), 2.20–1.80 (m, 7H), 1.70–1.50 (m, 2H), 1.50 (s, 3H), 1.01 ppm (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=204.7$, 136.5, 135.8, 135.7, 134.3, 134.2, 133.9, 133.7, 129.5, 129.5, 128.9, 127.5, 127.4, 127.3, 126.6, 117.4, 117.1, 90.6, 78.1, 69.9, 57.5, 56.2, 52.1, 51.3, 51.3, 41.0, 40.2, 37.9, 34.2, 27.0, 25.2, 19.3 ppm; IR (KBr): $\tilde{\nu}=2929$, 1715, 1113, 912 cm$^{-1}$; HRMS (FAB): *m*/*z* calcd for $C_{40}H_{49}O_3BrSiNa$: 707.2532 [$M^+$+Na]; found: 707.2562.

**Norbornene aldehyde 1,3-diisopropyl silylether 23c**: By use of the same procedure for **16a**, **23c** (74 mg, 97%) was obtained from **22c** (50 mg), TBDPSCl (0.13 mL), imidazole (68 mg), and DMF (0.5 mL). Eluent for chromatography: AcOEt/hexane (1:30); white crystal. M.p. 93–94°C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta=9.07$ (s, 1H), 7.56–7.54 (m, 4H), 7.27–7.00 (m, 11H), 4.00–3.96 (m, 2H), 3.55 (m, 1H), 3.23 (brs, 1H), 3.02 (brs, 1H), 2.02–1.96 (m, 2H), 1.71–1.52 (m, 2H), 1.49–1.47 (m, 1H), 1.36 (s, 3H), 1.36–1.18 (m, 4H), 0.94 (s, 9H), 0.84 (d, $J=7.5$ Hz, 3H), 0.66 (d, $J=7.5$ Hz, 3H), 0.46 (d, $J=7.5$ Hz, 3H), 0.35 ppm ($J=7.5$ Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=204.4$, 136.5, 135.8, 135.7, 134.6, 134.3, 129.3, 129.2, 128.9, 127.3, 127.2, 126.5, 92.0, 84.9, 74.7, 57.5, 56.4, 52.7, 52.7, 51.6, 34.2, 34.2, 32.0, 29.9, 27.2, 25.1, 19.7, 18.7, 17.6, 16.6, 16.3 ppm; IR (KBr): $\tilde{\nu}=1717$, 1111 cm$^{-1}$; HRMS (FAB): *m*/*z* calcd for $C_{40}H_{53}O_3BrSiNa$: 711.2845 [$M^+$+Na]; found: 711.2816.

**1,3-Dimethyl silylether 24a**: By use of the same procedure as for **18a**, **24a** (61.2 mg, 86%) and **7a** (37.8 mg, 86%) were obtained from **23a** (132 mg), $Zn(OTf)_2$ (453 mg), Zn (273 mg), and DMA (2.0 mL). Eluent for chromatography: AcOEt/hexane (1:4). **24a**: Colorless oil; $[\alpha]_D^{24}=-16.93$ ($c=1.33$, $CHCl_3$); the optical purity of **24a** (99% *ee*) was determined by HPLC analysis (Chiralpak AD-H, hexane/*i*PrOH (150:1), 0.5 mL min$^{-1}$ flow rate, 264 nm wavelength; retention times: 20.11 min and 22.21 min for (±)-**24a** and 20.31 min for (+)-**24a**); $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.75$–7.70 (m, 4H), 7.46–7.36 (m, 6H), 4.13–4.00 (m, 2H), 3.00 (brs, 1H), 1.74–1.49 (m, 2H), 1.04 (s, 9H), 1.15–1.12 (d, $J=6.2$ Hz, 3H), 0.99–0.97 ppm (d, $J=6.2$ Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=135.8$, 135.8, 134.4, 133.5, 129.8, 129.6, 127.7, 127.5, 70.6, 67.0, 48.0, 26.9, 24.1, 23.6, 19.1 ppm; IR (KBr): $\tilde{\nu}=3439$ cm$^{-1}$; elemental analysis calcd (%) for $C_{21}H_{30}O_2Si$: C 73.63, H 8.83; found: C 73.32, H 8.69.

**1,3-Diallyl silylether 24b**: By use of the same procedure as for **18a**, **24b** (53.3 mg, 92%) and **7a** (29.3 mg, 94%) were obtained from **23b** (101.0 mg), $Zn(OTf)_2$ (321 mg), Zn (193 mg), and DMA (1.5 mL). Eluent for chromatography: AcOEt/hexane (1:15). **24b**: Colorless oil; $[\alpha]_D^{24}=-24.0$ ($c=2.03$, $CHCl_3$); the optical purity of **24b** (99% *ee*) was determined by HPLC analysis (Chiralpak AD-H, hexane, 0.5 mL min$^{-1}$ flow rate, 261 nm wavelength; retention times: 29.35 min and 32.33 min for (±)-**24b** and 29.31 min for (+)-**24b**); $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.75$–7.66 (m, 4H), 7.50–7.30 (m, 6H), 5.79–5.53 (m, 2H), 5.10–4.78 (m, 4H), 4.01–3.78 (m, 2H), 2.50 (brs, 1H), 2.20–2.06 (m, 4H), 1.70–1.56 (m, 2H), 1.06 ppm (9H, s); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta=135.9$, 134.6, 134.1, 133.6, 129.8, 129.7, 127.7, 127.5, 117.7, 117.4, 72.7, 69.1, 42.4, 42.0, 41.8, 27.0, 19.2 ppm; IR (KBr): $\tilde{\nu}=3460$, 2932, 1427, 1111, 914 cm$^{-1}$; elemental analysis calcd (%) for $C_{25}H_{34}O_2Si$: C 76.09, H 8.68; found: C 75.93, H 8.72.

**1,3-Diisopropyl silylether 24c**: By use of the same procedure as for **18a**, **24c** (99 mg, 99%) and (−)-**7a** (54 mg, 100%) were obtained from **23c** (174 mg), $Zn(OTf)_2$ (552 mg), Zn (330 mg), and DMA (2.4 mL). Eluent for chromatography: AcOEt/hexane (1:30→1:15). Colorless oil; $[\alpha]_D^{29}=+4.29$ ($c=1.43$); the optical purity of **24c** (99% *ee*) was determined by HPLC analysis (Chiralpak AD-H, hexane, 0.5 mL min$^{-1}$ flow rate, 261 nm wavelength; retention times: 25.24 min and 27.16 min for (±)-**24c** and 25.01 min for (+)-**24c**); $^1$H NMR (300 MHz, $CDCl_3$): $\delta=7.65$–7.63 (m, 4H), 7.35–7.18 (m, 6H), 6.30–6.27 (m, 1H), 3.80–3.75 (m, 1H), 3.27 (m, 1H), 1.97–1.18 (m, 4H), 1.00 (s, 9H), 0.83 (d, 6.9 Hz, 3H), 0.76

(d, 6.6 Hz, 3H), 0.74 (d, 6.6 Hz, 3H), 0.70 ppm (d, 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 136.0, 134.3, 134.2, 129.6, 129.6, 127.5, 127.5, 77.3, 74.6, 36.0, 33.5, 32.3, 27.1, 19.5, 18.4, 17.5, 17.1, 16.8 ppm; IR (KBr): $\tilde{\nu}$ = 3500, 1471, 1111 cm$^{-1}$; elemental analysis calcd (%) for $C_{25}H_{38}O_2Si$: C 75.47, H 9.80; found: C 75.32, H 9.61.

**Norbornene aldehyde 1,2-dimethyl acetal 26**: By use of the same procedure as for **11a**, **26** (65.6 mg, 84%) was obtained from **25** (50.0 mg) and (−)-**7a** (58.8 mg). Eluent for chromatography: AcOEt/hexane (1:50). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.19–7.15 (m, 5H), 6.47–6.37 (m, 2H), 4.25 (s, 1H), 3.87–3.81 (m, 1H), 3.62–3.55 (m, 1H), 3.10 (m, 1H), 3.03 (m, 1H), 2.67 (m, 1H), 1.82–1.79 (m, 1H), 1.55–1.51 (m, 1H), 1.34 (s, 3H), 1.03–1.01 (d, $J$ = 6.3 Hz, 3H), 0.92–0.90 ppm (d, $J$ = 6.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 141.6, 137.2, 135.0, 129.2, 127.2, 125.6, 105.2, 74.4, 72.8, 56.7, 53.3, 49.4, 49.2, 49.0, 22.1, 15.6, 14.8 ppm; IR (KBr): $\tilde{\nu}$ = 2972, 1094, 743 cm$^{-1}$; HRMS (EI): $m/z$ calcd for $C_{19}H_{24}O_2$: 284.1776; found: 284.1774.

**Norbornene aldehyde 1,2-dimethyl alcohol 27**: By use of the same procedure as for **16a**, **27** (56.0 mg, 96%) was obtained by *p*-TsOH hydrolysis of the product from the reaction of **26a** (43.7 mg), NBS (30 mg), and MeOH (1 mL). Eluent for chromatography: AcOEt/hexane (1:3). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.41 (s, 1H), 7.37–7.10 (m, 5H), 4.37–4.36 (m, 1H), 4.20–4.16 (m, 1H), 3.77 (br s, 1H), 3.55–3.54 (m, 1H), 3.40 (m, 1H), 3.16 (m, 1H), 2.36 (m, 1H), 2.19–2.14 (d, $J$ = 12.0 Hz, 1H), 1.93–1.89 (d, $J$ = 12.0 Hz, 1H), 1.82 (m, 1H), 1.52 (s, 3H), 1.04–0.98 ppm (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 205.2, 136.3, 129.0, 127.2, 126.6, 89.0, 79.2, 69.2, 57.5, 56.3, 51.5, 51.4, 51.0, 34.2, 25.5, 17.3, 13.0 ppm; IR (KBr): $\tilde{\nu}$ = 3456, 1710 cm$^{-1}$; MS (EI): $m/z$: 381 [$M^+$]; HRMS (EI): $m/z$: calcd for $C_{19}H_{25}O_3Br$: 381.1065; found: 381.1088.

**Norbornene aldehyde 1,2-dimethyl silylether 28**: By use of the same procedure as for **16a**, **28** (49.7 mg, 94%) was obtained from **27** (32.4 mg), TBDPSCl (49 μL), imidazole (25.5 mg), and DMF (0.6 mL). Eluent for chromatography: AcOEt/hexane (1:10). Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 9.48 (s, 1H), 7.62–7.09 (m, 15H), 4.73–4.70 (m, 1H), 4.27–4.25 (m, 1H), 3.65–3.59 (m, 2H), 3.39–3.38 (m, 1H), 3.16–3.16 (m, 1H), 2.39–2.39 (m, 1H), 2.17–2.12 (m, 1H), 1.90–1.86 (m, 1H), 1.51 (s, 3H), 0.95 (s, 9H), 0.92–0.90 (d, $J$ = 6 Hz, 3H), 0.86–0.84 ppm (d, $J$ = 6 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 205.6, 136.6, 135.9, 135.8, 129.6, 129.5, 129.0, 127.6, 127.4, 127.3, 126.6, 88.9, 78.7, 73.5, 60.4, 56.9, 56.4, 51.8, 51.6, 27.0, 25.4, 19.0, 16.6, 16.0, 14.2 ppm; IR (KBr): $\tilde{\nu}$ = 1712 cm$^{-1}$; MS (FAB): $m/z$: 641 [$M^+$+Na]; HRMS (FAB): $m/z$ calcd for $C_{35}H_{43}BrNaO_3Si$: 641.2263 [$M^+$+Na]; found: 641.2064.

**1,2-Dimethyl silylether 29**: By use of the same procedure as for **18a**, **29** (62.4 mg, 96%) and **7a** (39.9 mg, 95%) were obtained from **28** (122.1 mg), $Zn(OTf)_2$ (429 mg), Zn (258 mg), and DMA (1.5 mL). Eluent for chromatography: AcOEt/hexane (1:6). **29**: Colorless oil; $[\alpha]_D^{23} = -9.67$ ($c$ = 0.75, $CHCl_3$); the optical purity of **29a** (97% *ee*) was determined by HPLC analysis (Chiralpak OD-H, hexane/*i*PrOH (150:1), 0.5 mL min$^{-1}$ flow rate, 263 nm wavelength; retention times: 13.60 min and 14.81 min for (±)-**29** and 13.81 min for (+)-**29**); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.69–7.65 (m, 4H), 7.46–7.38 (m, 6H), 3.80–3.76 (m, 2H), 2.24 (br s, 1H), 1.70 (s, 9H), 1.05–1.03 (d, $J$ = 6 Hz, 3H), 1.00–0.98 ppm (d, $J$ = 6 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 135.8, 135.7, 134.1, 133.7, 129.8, 129.7, 127.7, 127.6, 73.0, 70.9, 27.0, 19.3, 17.2, 16.4 ppm; IR (KBr): $\tilde{\nu}$ = 3439 cm$^{-1}$; FAB MS: $m/z$: 351 [$M^+$+Na]; HRMS (FAB): $m/z$ calcd for $C_{20}H_{28}NaO_2Si$: 351.1756 [$M^+$+Na]; found: 351.1752.

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[1] For example, see: a) A. P. Davis, *Angew. Chem.* **1997**, *109*, 609–612; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 591–594; b) A. Fadel, P. Arzel, *Tetrahedron: Asymmetry* **1997**, *8*, 283–291; c) E. Schoffers, A. Golebiowski, C. R. Johnson, *Tetrahedron* **1996**, *52*, 3769–3826; d) F. Theil, *Chem. Rev.* **1995**, *95*, 2203–2227; e) L. Banfi, G. Guanti, *Synthesis* **1993**, 1029–1056; f) E. Santaniello, P. Ferraboschi, P. Grisenti, A. Manzocchi, *Chem. Rev.* **1992**, *92*, 1071–1140; g) T. Harada, A. Oku, *Synlett* **1994**, 95–104.

[2] For recent studies on desymmetrization of *meso*-1,2-diols, see: a) S. Mizuta, M. Sadamori, T. Fujimoto, I. Yamamoto, *Angew. Chem.* **2003**, *115*, 3505–3507; *Angew. Chem. Int. Ed.* **2003**, *42*, 3383–3385; b) N. Maezaki, A. Sakamoto, N. Nagahashi, M. Soejima, Y. Li, T. Imamura, N. Kojima, H. Ohishi, K. Sakaguchi, C. Iwata, T. Tanaka, *J. Org. Chem.* **2000**, *65*, 3284–3291; c) T. Oriyama, K. Imai, T. Sano, T. Hosoya, *Tetrahedron Lett.* **1998**, *39*, 3529–3533; d) M. Kinugasa, T. Harada, A. Oku, *J. Am. Chem. Soc.* **1997**, *119*, 9067–9068; e) E. Vedejs, O. Daugulis, S. T. Diver, *J. Org. Chem.* **1996**, *61*, 430–431.

[3] a) T. Harada, K. Sekiguchi, T. Nakamura, J. Suzuki, A. Oku, *Org. Lett.* **2001**, *3*, 3309–3312; b) T. Oriyama, T. Hosoya, T. Sano, *Heterocycles* **2000**, *69*, 1054–1069; c) T. Harada, Y. Ikemura, H. Nakajima, A. Oku, *Chem. Lett.* **1990**, 1441–1444; d) T. Harada, K. Sakamoto, Y. Ikemura, A. Oku, *Tetrahedron Lett.* **1988**, *29*, 3097–3100; e) J. Ichikawa, M. Asami, T. Mukaiyama, *Chem. Lett.* **1984**, 949–952.

[4] a) K. Ishihara, M. Kubota, H. Yamamoto, *Synlett* **1994**, 611–614; b) S. Yamada, H. Katsumata, *Chem. Lett.* **1998**, 995–996; c) B. M. Trost, T. Mino, *J. Am. Chem. Soc.* **2003**, *125*, 2410–2411.

[5] a) H. Fujioka, Y. Nagatomi, H. Kitagawa, Y. Kita, *J. Am. Chem. Soc.* **1997**, *119*, 12016–12017; b) H. Fujioka, Y. Nagatomi, N. Kotoku, H. Kitagawa, Y. Kita, *Tetrahedron Lett.* **1998**, *39*, 7309–7312; c) H. Fujioka, Y. Nagatomi, N. Kotoku, H. Kitagawa, Y. Kita, *Tetrahedron* **2000**, *56*, 10141–10151.

[6] a) H. Fujioka, N. Kotoku, Y. Nagatomi, Y. Kita, *Tetrahedron Lett.* **2000**, *41*, 1829–1832; b) H. Fujioka, N. Kotoku, T. Fujita, R. Inoguchi, K. Murai, Y. Nagatomi, Y. Sawama, Y. Kita, *Chirality* **2003**, *15*, 60–67.

[7] At the beginning of the work, we supposed that discrimination between the two oxygen atoms depends on the stability of the cationic intermediates from intramolecular bromoetherification. (See ref. [5], where the direction of discrimination expected from the activation energy is the same as the direction from the stability of the cationic intermediates.) Later, during the work on optical resolution (ref. [6]), the obtained direction was found to be opposite to the direction expected from the stability of the cation intermediates, but the same as the order of activation energies. We therefore suppose that the genuine factor for discrimination of the two oxygen atoms of the acetal is the difference in the activation energies of the transition states.

[8] H. Honig, P. Seufer-Wasserthal, H. Weber, *Tetrahedron* **1990**, *46*, 3841–3850.

[9] K. Omura, A. K. Sharma, D. Swern, *J. Org. Chem.* **1976**, *41*, 957–962.

[10] Chiral hydrobenzoin is readily available in both enantiomeric forms by asymmetric synthesis. See: Z.-M. Wang, K. B. Sharpless, *J. Org. Chem.* **1994**, *59*, 8302–8303.

[11] CCDC-230171 contains the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK: fax: (+44)1223-336-033; or e-mail; deposit@ccdc.cam.ac.uk).

[12] K. P. Lok, I. J. Jakovac, J. B. Jones, *J. Am. Chem. Soc.* **1985**, *107*, 2521–2526.

[13] D. Grandjean, P. Pale, J. Chuche, *Tetrahedron* **1991**, *47*, 1215–1230.

[14] Compound **7a** is stable when it stands at room temperature although it has an aldehyde functionionality. Its stability may depend on its crystallization at room temperature, although other norbornene aldehydes, such as **1a**, **1b**, and **7b**, are oils and need refrigeration for prolonged storage.

[15] K. Takano, G. Watanabe, H. Yasui, K. Tadano, *Org. Lett.* **2002**, *4*, 2941–2943.

[16] P. O'Brien, J. J. Tournayre, *Tetrahedron* **1997**, *53*, 17527–17542.

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