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Stereoselective Construction of Entire Diastereomeric Stereotetrads Based on an Asymmetric Morita-Baylis-Hillman Reaction

Hikaru Yoshimura,[a] Jun Ishihara,[a] and Susumi Hatakeyama*[b]

Abstract: A methodology for the enantio- and diastereoselective construction of all possible stereoisomers of a polypropionate stereotetrad having four contiguous stereogenic centers has been developed, which features an iterative sequence of a cinchona alkaloid-catalyzed Morita-Baylis-Hillman reaction and subsequent diastereoselective hydrogenation. By this method, benzaldehyde was successfully converted to eight diastereoisomeric 3,5-dihydroxy-2,4-dimethyl-5-phenylpentanoic acid ester derivatives with high enantiomeric purities (99% ee) in 25-67% overall yield (8 steps) in a reagent-controlled manner.

Introduction

For many decades, natural products have contributed to a broad field of drug discovery and development.[1] Polyketides, which are a class of secondary metabolites produced by certain living organisms such as bacteria, fungi, or plants, are known as one of the most fascinating subgroups of natural products because of their intriguing structures and beneficial biological activities (Figure 1).[2] It is said that about 1% of polyketides have a potential for drug-like activity which are five times higher than average.[3] The important structural motif of polyketides is a polypropionate chain consisting of alternating methyl and hydroxy groups within an aliphatic framework.[4] The unit having three, four, or five contiguous stereogenic centers is each called as stereotriad, stereotetrad, or stereopentad. In Figure 1, the stereotetrads are highlighted, and seven stereotetrads among eight possible diastereomers are actually seen in natural products.[2] From a synthetic point of view, the stereoselective construction of polypropionates is highly challenging mainly because of the stereochemical issues. Firstly, the stereoisomers exponentially increase as the stereogenic centers increase. Secondly, the stereoselective formation of a new stereogenic center is often largely affected by the exsiting stereogenic centers of the substrate. Thus, the stereoselective assembly of polypropionate structures has attracted great interest among synthetic chemists.[5] As for stereotriads, the stereoselective construction of all possible stereoisomers has been achieved by many methods based on an aldol reaction and a crotylation reaction.[4a,b,6] On the other hand, as for stereotetrads, there are a few methods applicable to the synthesis of all stereoisomers utilizing cyclic substrates for stereocontrol,[7] but there is no satisfying method for acyclic substrates.[8]

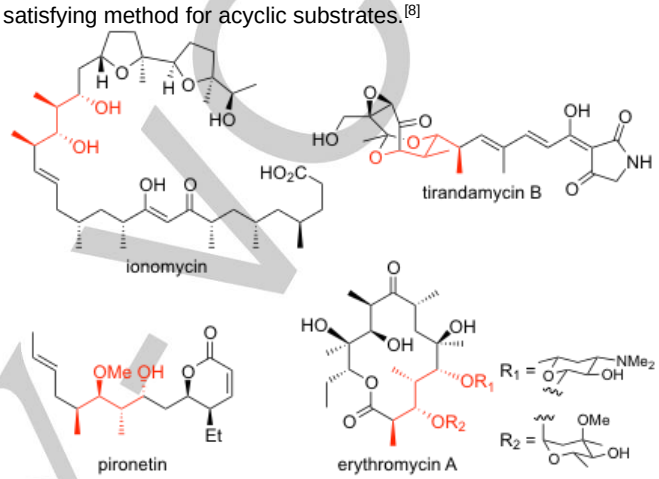

Figure 1. Examples of polyketide naturalproducts.

We have established both *S*- and *R*-selective asymmetric Morita-Baylis-Hillman (MBH) reactions of aldehydes with hexafluoroisopropyl acrylate (HFIPA) employing β-isocupreidine (β-ICD) and α-isocupreine (α-ICPN) as a catalyst, respectively (Scheme 1).[9] In addition, we have achieved the total syntheses of bioactive natural products utilizing these MBH reactions.[10] Recently, in the synthesis of the tirandamycin family of antibiotics, we devised an effective methodology to construct the essential *anti*,*anti*,*syn*-stereotetrad unit by taking advantage of our MBH reactions (Scheme 2).[11] Thus, aldehyde **1** was converted to the enantiopure adduct **2** (99% ee) by β-ICD-catalyzed MBH reaction and then the olefinic double bond was hydrogenated *syn*-selectively.[12] After conversion of **3** to aldehyde **4**, α-ICPN-catalyzed MBH reaction of **4** produced the desired adduct **5** in high diastereoselectivity (>50:1). The subsequent *anti*-selective hydrogenation[13] of **5** furnished the desired stereotetrad **6**. With this result, we then became interested in probing the possibility that the combination of the MBH reactions and *syn*- or *anti*-selective hydrogenation would enable us to secure all stereoisomers of a polypropionate stereotetrad from an aldehyde in high enantio- and diastereoselectivities. We herein report the first organocatalytic asymmetric synthesis of all diastereometric stereotetrads starting from benzaldehyde.

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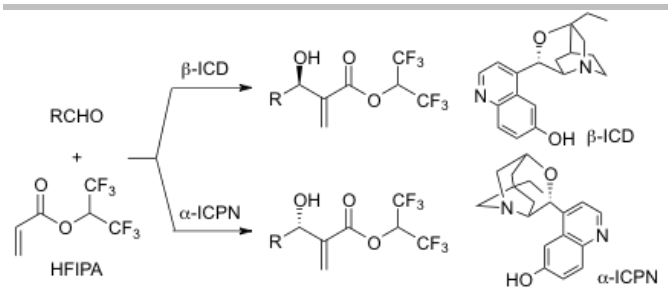
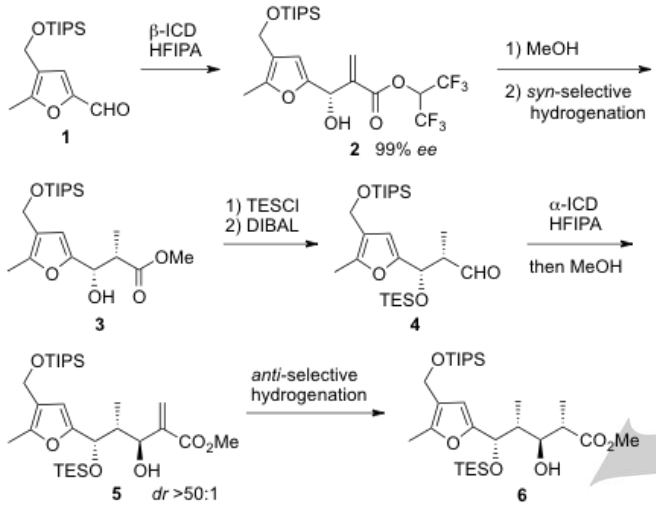


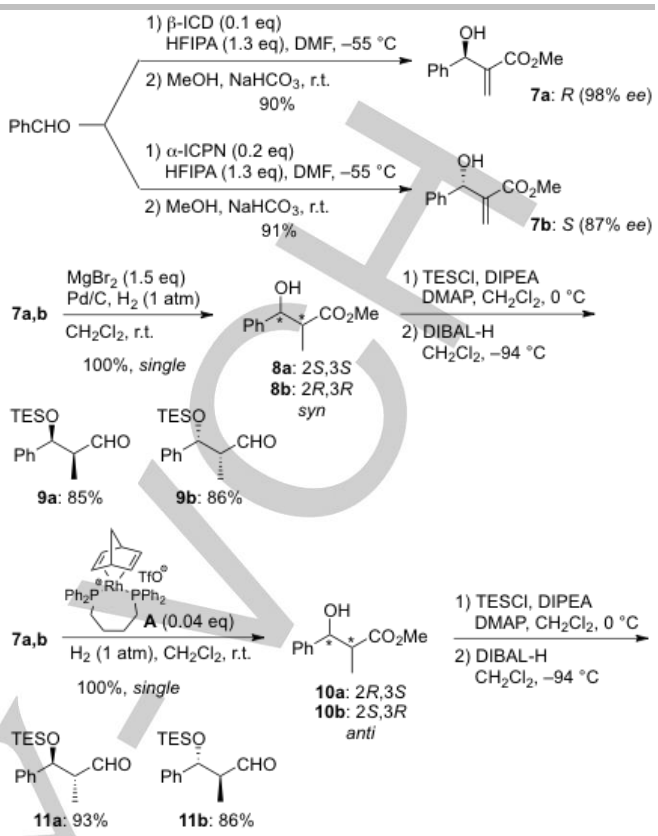
Scheme 1. Cinchona alkaloid-catalyzed Morita-Baylis-Hillman reactions.



Scheme 2. Stereoselective construction of stereotetrad **6** in the synthesis of tirandamycin.[13]

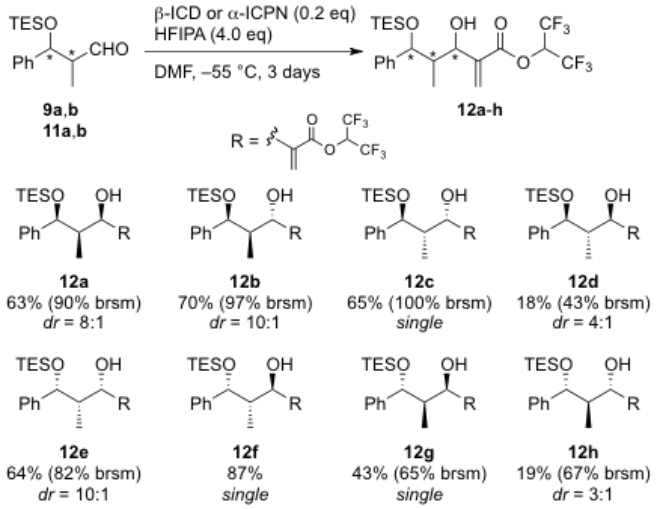
Results and Discussion

Our examination began with methyl esters (*R*)-**7a** (98% *ee*) and (*S*)-**7b** (87% *ee*) which were synthesized by β-ICD- and α-ICPN-catalyzed MBH reactions of benzaldehyde (Scheme 3).[9c,e] Thus, compounds **7a** and **7b** were hydrogenated under the conditions using H_2 (1 atm), 1.5 equiv of $MgBr_2$, and 50% wt of Pd/C in CH_2Cl_2 at room temperature to give **8a** and **8b** in excellent *syn*-selectivity, respectively.[12] On the other hand, *anti*-selective hydrogenations of **7a** and **7b** were conducted under the conditions using H_2 (1atm), 0.04 eq of rhodium catalyst **A**[13] in CH_2Cl_2 at room temperature to afford **10a** and **10b** in excellent *anti*-selectivity. Hydroxy esters **8a,b** and **10a,b**[14] were then converted to TES-protected aldehyde **9a,b** and **11a,b** by triethylsilylation followed by DIBAL-H reduction at –94°C in 85-93% yield.



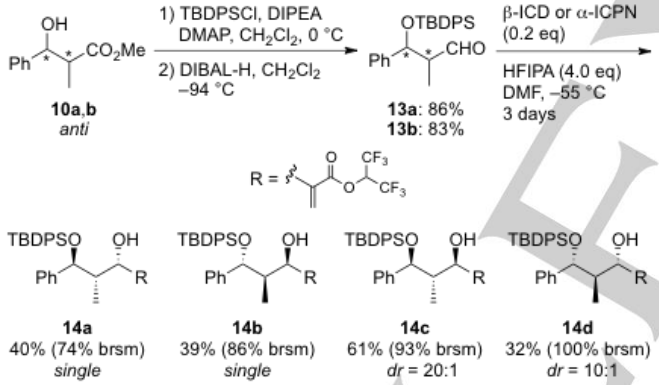
Scheme 3. Preparation of *syn*- and *anti*-aldehydes from MBH adducts.

We then investigated the synthesis of all possible eight stereotriads from *syn*-aldehydes **9a,b** and *anti*-aldehydes **11a,b** (Scheme 4). As reported previously,[11] the standard conditions using 1.3 equiv of HFIPA and 0.2 equiv of β-ICD or α-ICPN in DMF at –55 °C afforded the corresponding MBH adducts in poor yields due to the competitive production of di(hexafluoroisopropyl) 2-methyleneglutarate. However, increasing the amount of HFIPA to 4 equiv led to the production of the MBH adducts in acceptable yields and good to excellent diastereoselectivities. As a result, except for *anti,anti*-isomers **12d** and **12h,** other *syn,syn*-, *anti,syn*-, and *syn,anti*-stereotriads were successfully constructed. All of these stereoisomers were chromatographically separable and diastereomerically pure **12a-h** could be obtained. It is important to note that, although the aldehydes were recovered in most cases, no epimerization was detected after isolation.[15]



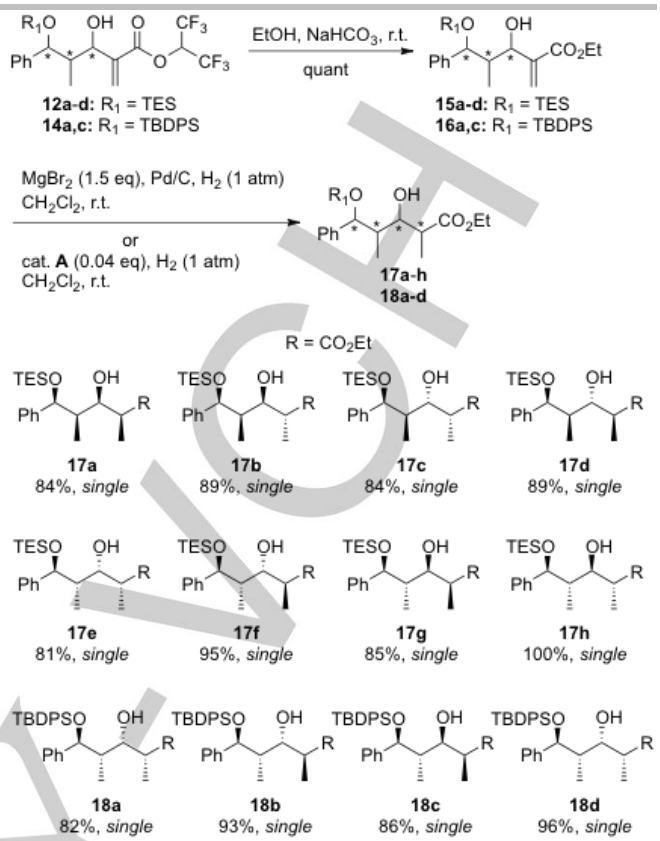
Scheme 4. MBH reactions of TES-protected *syn*- and *anti*-aldehydes.

For the preparation of *anti,anti*-stereotriads, it was found that replacing the protecting group from TES to TBDPS improves the yield and diastereoselectivity (Scheme 5). At this stage, although the reactivity and selectivity were somewhat affected by a protecting group, we succeeded in the stereoselective construction of all possible stereoisomers of stereotriads in a catalyst-controlled manner.



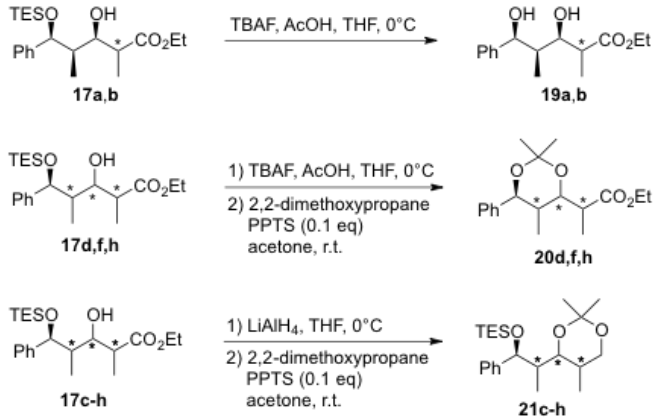
Scheme 5. MBH reactions of TBDPS-protected *anti*-aldehydes.

Finally, after ethanolysis of HFIP esters **12a-d** and **14a,c** to **15a-d** and **16a,c**, their *syn*- and *anti*-selective hydrogenations were examined under the same conditions as shown in Scheme 3 (Scheme 6). As a result, in all cases, the reactions proceeded in complete diastereoselectivities to give all patterns of stereotetrads **17a-h** and **18a-d** in good to excellent yields. Compounds **15a-d** and **16a,c** derived all the way from **7a** (98% *ee*) were found to be enantiomerically almost pure (99% *ee*) by HPLC analysis on a chiral stationary phase.[16] Interestingly, the enantiomers of **15a-d** and **16a,c** derived from **7b** (87% *ee*) turned out to be also enantiomerically pure (99% ee). These results mean that the enantiomers of **17a-h** and **18a-d** are also available in an enantiomerically pure form.



Scheme 6. Diastereoselective hydrogenations giving sterotetrads.

The stereostructures of these products were unambiguously determined as shown in Scheme 7. Compounds **17a** and **17b** were converted to the known diols **19a** and **19b** respectively, the spectral data and specific rotations of which were in good agreement with those reported.[17] For other isomers **17c-h**, the stereochemistries of C3-hydroxyl groups were determined by applying Rychnovsky's method[18] to acetonides **20d**,**f**,**h**. The stereochemistries of C2-methyl groups were determined based on $J_{2,3}$ values and NOEs in ^{1}H NMR spectra of acetonides **21c-h**.[16] The stereochemistries of **18a-d** were determined by converting to the corresponding diols and directly compared with the diols obtained from **17e-h**.



Scheme 7. Determination of the stereochemistries.

Conclusions

We have developed a new methodology for the enantio- and diastereoselective synthesis of the polypropionate stereotetrads by taking advantage of our cinchona alkaloid-catalyzed asymmetric MBH reaction. The present method enables us to construct their all pattern of configurations in a reagent-controlled manner, for the first time. Its application to the synthesis of longer polypropionate chains as well as natural products is under progress in our laboratory.

Experimental Section

General Information: Where appropriate, reactions were performed in flame-dried glassware under argon atmosphere. All extracts were dried over $MgSO_4$ and concentrated by rotary evaporation below 30 °C at 25 Torr unless otherwise noted. Commercial reagents and solvents were used as supplied with following exceptions. Dichrolomethane (CH_2Cl_2) and *N*,*N*-dimethylformamide (DMF) were distilled from CaH_2. Thin layer chromatography (TLC) was performed using precoated silica gel plates (0.2 or 0.5 mm thickness). Column chromatography was performed using silica gel (particle size 100-210 µm (regular) or 40-50 µm (flash)). Optical rotations were recorded on digital polarimeter at ambient temperature. Infrared spectra (FTIR) were measured on a Fourier transform infrared spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured using $CDCl_3$ and bezene-d_6 as solvent, and chemical shifts are reported as δ values in ppm based on internal $CHCl_3$ (^{1}H: 7.26 ppm; ^{13}C: 77.0 ppm) and bezene-d_6 (^{1}H: 7.16 ppm; ^{13}C: 128.1 ppm). Mass (MS) and high resolution mass (HRMS) spectra were taken in EI or FAB mode.

Methyl 2-((*R*)-Hydroxy(phenyl)methyl)acrylate (7a): β-ICD (2.2 g, 7.1 mmol) was dissolved in THF (10 mL) and the solution was evaporated at room temperature. After repeating this operation three times, the amorphous residue was dried under vacuum at room temperature for 10 min. A solution of the dried β-ICD and benzaldehyde (7.8 mL, 71 mmol) in DMF (237 mL) was cooled to –55 °C, and HFIPA (15.2 mL, 91 mmol) was then added. After stirring at –55 °C for 24 h, the reaction was quenched by the addition of 0.1 M HCl (140 mL). The mixture was extracted with AcOEt, washed with saturated $NaHCO_3$ and brine, dried, concentrated and chromatographed (SiO_2 300 g, hexane/AcOEt = 10:1) to give the corresponding HFIP ester (21.0 g, 64 mmol, 90%) as a colorless oil.

To a solution of the HFIP ester (3.3 g, 10 mmol) in MeOH (50 mL) was added $NaHCO_3$ (1.3 g, 15 mmol). After being stirred at room temperature for 24 h, the mixture was diluted with water (50 mL), extracted with AcOEt, washed with brine, dried, concentrated, and chromatographed (SiO_2 50 g, hexane/AcOEt = 5:1) to afford **7a** (1.9 g, 10 mmol, 100%) as colorless oil. The enantiomeric purity of **7a** was determined to be 98% *ee* by HPLC analysis; Daniced Chiralcel OJ-H, 2-propanol/hexane = 1/100 (1 mL/min), t_R = 22.7 min (**7a**) and 24.7 min (**7b**). The spectral data were identical with those reported.[9d]

Methyl 2-((*S*)-Hydroxy(phenyl)methyl)acrylate (7b): α-ICPN (620 mg, 2.0 mmol) was dissolved in THF (3 mL) and the solution was evaporated at room temperature. After repeating this operation three times, the amorphous residue was dried under vacuum at room temperature for 10 min. A solution of the dried α-ICPN and benzaldehyde (1.0 mL, 10 mmol) in DMF (33 mL) was cooled to –55 °C, and HFIPA (2.2 mL, 13 mmol) was then added. After stirring at –55 °C for 24 h, the reaction was quenched by the addition of 0.1 M HCl (20 mL). The mixture was extracted with AcOEt, washed with saturated $NaHCO_3$ and brine, dried, concentrated and chromatographed (SiO_2 100 g, hexane/AcOEt = 10:1) to give the corresponding HFIP ester (3 g, 9.1 mmol, 91%) as a colorless oil.

To a solution of the HFIP ester (2.3 g, 7 mmol) in MeOH (35 mL) was added $NaHCO_3$ (0.9 g, 11 mmol). After being stirred at room temperature for 24 h, the mixture was diluted with water (35 mL), extracted with AcOEt, washed with brine, dried, concentrated, and chromatographed (SiO_2 50 g, hexane/AcOEt = 5:1) to afford **7b** (1.3 g, 7 mmol, 100%) as a colorless oil. The enantiomeric purity of **7b** was determined to be 87% *ee* by HPLC analysis as described for **7a**. The spectral data were identical with those reported.[9e]

Methyl (2*S*,3*S*)-3-Hydroxy-2-methyl-3-phenylpropanoate (8a): To a solution of **7a** (1.36 g, 7.1 mmol) (98% ee) in CH_2Cl_2 (57 mL) were added $MgBr_2$ (1.9 g, 10.6 mmol) and 10% Pd/C (680 mg). After being stirred under hydrogen atmosphere at room temperature for 6 h, the mixture was filtered through Celite which was washed with CH_2Cl_2. The combined filtrate and washings were washed with saturated $NaHCO_3$ and brine, dried, concentrated, and chromatographed (SiO_2 40 g, hexane/AcOEt = 8:1) to give **8a** (1.36 g, 7.1 mmol, 100%) as a colorless oil: $[\alpha]_D^{23}$ –21.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 5.10 (t, *J* = 3.2 Hz, 1H), 3.66 (s, 3H), 2.98 (d, *J* = 3.2 Hz, 1H), 2.78 (dq, *J* = 3.2, 6.8 Hz, 1H), 1.12 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 141.4, 128.2, 127.5, 125.9, 73.6, 51.8, 46.4, 10.7; FTIR (neat) 3486, 2990, 1733, 1455, 1348, 1201, 1032 cm^{-1}; MS (EI) *m/z* 77, 79, 88, 105, 107, 131, 163, 176, 194 (M^+); HRMS (EI) calcd for $C_{11}H_{14}O_3$ (M^+) 194.0943, found 194.0942. The ^{1}H NMR spectrum was in good agreement with that reported for the racemic compound.[12]

Methyl (2*R*,3*R*)-3-Hydroxy-2-methyl-3-phenylpropanoate (8b): Compound **8b**, $[\alpha]_D^{23}$ +20.2 (*c* 1.00, $CHCl_3$), was obtained as a colorless oil (1.36 g, 7.1 mmol, 100%) from **7b** (1.36 g, 7.1 mmol, 87% *ee*) in the same manner as described for the synthesis of **8a**. The spectral data were identical with those of the enantiomer shown above.

Methyl (2*R*,3*S*)-3-Hydroxy-2-methyl-3-phenylpropanoate (10a): A mixture of **7a** (1.36 g, 7.1 mmol) (98% ee) and (bicyclo[2.2.1]hepta-2,5-diene)[1,4-bis(diphenylphosphino)butane]rhodium(I) trifluoromethanesulfonate (220 mg, 0.28 mmol) in CH_2Cl_2 (24 mL) was stirred at room temperature under a hydrogen atmosphere. After being stirred for 1 h, the mixture was filtered through SiO_2 which was washed with AcOEt. The filtrate and washings were concentrated and chromatographed (SiO_2 30 g, hexane/AcOEt = 8:1) to give **10a** (1.36 g, 7.1 mmol, 100%) as a colorless oil: $[\alpha]_D^{24}$ –51.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 4.72 (dd, *J* = 4.0, 8.0 Hz, 1H), 3.72 (s, 3H), 3.09 (d, *J* = 4.0 Hz, 1H), 3.00 (dq, *J* = 7.2, 8.0 Hz, 1H), 0.99 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 141.5, 128.4, 127.9, 126.6, 76.3, 51.8, 47.1, 14.4; FTIR (neat) 3460, 2948, 1733, 1455, 1372, 1250, 1023 cm^{-1}; MS (EI) *m/z* 77, 79, 88, 105, 107, 131, 176, 194 (M^+); HRMS (EI) calcd for $C_{11}H_{14}O_3$ (M^+) 194.0943, found 194.0942. The ^{1}H NMR spectrum was in good agreement with that reported for the racemic compound.[12]

Methyl (2*S*,3*R*)-3-Hydroxy-2-methyl-3-phenylpropanoate (10b): Compound **10b**, $[\alpha]_D^{23}$ +49.2 (*c* 1.00, $CHCl_3$), was obtained as a colorless oil (1.36 g, 7.1 mmol, 100%) from **7b** (1.36 g, 7.1 mmol, 87% *ee*) in the same manner as described for the synthesis of **10a**. The spectral data were identical with those of the enantiomer shown above.

Methyl (2*S*,3*S*)-3-Triethylsiloxy-2-methyl-3-phenylpropanoate: To an ice-cooled solution of **8a** (1.31 g, 7.1 mmol) in CH_2Cl_2 (14 mL) were added TESCl (2.4 mL, 14.2 mmol), DIPEA (4.8 mL, 28.3 mmol), and DMAP (86 mg, 0.7 mmol), and the mixture was stirred at 0 °C for 30 min. The mixture was diluted with CH_2Cl_2, and washed with saturated NH_4Cl, dried, concentrated, and chromatographed (SiO_2 50 g, hexane/AcOEt = 70:1) to give the TES ether (2.08 g, 6.9 mmol, 97%) as a colorless oil: $[\alpha]_D^{24}$ –23.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 5H), 5.00 (d, *J* = 6.0 Hz, 1H), 3.55 (s, 3H), 2.67 (dq, *J* = 6.0, 6.8 Hz, 1H), 1.17 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 9H), 0.51 (q, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 143.2, 127.8, 127.3, 126.2, 75.8,

51.4, 49.1, 11.7, 6.7, 4.7; FTIR (neat) 2953, 2879, 1740, 1361, 1257, 1167, 1072 cm^{-1}; MS (EI) *m/z* 87, 89, 117, 173, 221, 279 (100), 308 (M^+); HRMS (EI) calcd for $C_{17}H_{28}O_3Si$ (M^+) 308.1808, found 308.1809.

Methyl (2*R*,3*R*)-3-Triethylsiloxy-2-methyl-3-phenylpropanoate: Prepared from **8b** in the same manner as described for TES-protection of **8a**, 100%, a colorless oil; $[\alpha]_D^{23}$ +22.5 (*c* 1.00, $CHCl_3$). The spectral data were identical with those of the enantiomer shown above.

Methyl (2*R*,3*S*)-3-Triethylsiloxy-2-methyl-3-phenylpropanoate: Prepared from **10a** in the same manner as described for TES-protection of **8a**, 98%, a colorless oil; $[\alpha]_D^{25}$ –68.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 5H), 4.73 (d, *J* = 10.0 Hz, 1H), 3.72 (s, 3H), 3.00 (dq, *J* = 9.6, 10.0 Hz, 1H), 0.85-0.77 (m, 12H), 0.50-0.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 142.2, 128.1, 127.8, 127.0, 77.5, 51.4, 49.2, 13.8, 6.5, 4.6; FTIR (neat) 2953, 2879, 1740, 1361, 1257, 1167, 1072 cm^{-1}; MS (EI) *m/z* 87, 89, 117, 173, 221, 279 (100), 308 (M^+); HRMS (EI) calcd for $C_{17}H_{28}O_3Si$ (M^+) 308.1808, found 308.1812.

Methyl (2*S*,3*R*)-3-Triethylsiloxy-2-methyl-3-phenylpropanoate: Prepared from **10b** in the same manner as described for TES-protection of **8a**,100%, a colorless oil; $[\alpha]_D^{25}$ +71.0 (*c* 1.00, $CHCl_3$). The spectral data were identical with those of the enantiomer shown above.

Methyl (2*R*,3*S*)-3-*tert*-Butyldiphenylsiloxy-2-methyl-3-phenylpropanoate: Prepared from **10a** in the same manner described for TES-protection of **8a**, 94%, a colorless oil; $[\alpha]_D^{25}$ –68.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.0 Hz, 2H), 7.42-7.30 (m, 7H), 7.22 (dd, *J* = 6.0, 6.0 Hz, 1H), 7.19-7.02 (m, 5H), 4.86 (d, *J* = 8.4 Hz, 1H), 3.56 (s, 3H), 2.93 (dq, *J* = 8.0, 8.4 Hz, 1H), 0.95 (s, 9H), 0.79 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 141.0, 135.98, 135.91, 133.8, 133.2, 129.4, 129.3, 127.9, 127.6, 127.32, 127.31, 127.1, 78.0, 51.4, 48.5, 26.8, 19.3, 13.2; FTIR (neat) 2942, 2857, 1740, 1361, 1262, 1167, 1066 cm^{-1}; MS (FAB) *m/z* 89, 121, 135, 197, 213, 355, 375(100), 432 (M^+), 455 [$(M+Na)^+$]; HRMS (FAB) calcd for $C_{27}H_{32}O_3SiNa$ [$(M+Na)^+$] 455.2018, found 455.2018.

Methyl (2*S*,3*R*)-3-*tert*-Butyldiphenylsiloxy-2-methyl-3-phenylpropanoate: Prepared from **10b** in the same manner described for TES-protection of **8a**, 100%, a colorless oil; $[\alpha]_D^{24}$ +66.2 (*c* 1.00, $CHCl_3$). The spectral data were identical with those of the enantiomer shown above.

(2*S*,3*S*)-3-Triethylsiloxy-2-methyl-3-phenylpropanal (9a): To a solution of the TES ether of **8a** (1.2 g, 6.8 mmol) in CH_2Cl_2 (65 mL) was added DIBAL-H (1.02 M in hexane, 11.4 mL, 11.6 mmol) at –94 °C. After stirring at –94 °C for 1 h, the reaction was quenched by the addition of isopropanol (2 M in CH_2Cl_2, 60 mL, 120 mmol) and the mixture was allowed to warm to 0 °C. Saturated Rochelle salt (60 mL) was added and the mixture was vigorously stirred at room temperature for 6 h. The mixture was extracted with AcOEt, dried over Na_2SO_4, concentrated, and chromatographed (SiO_2 50 g, hexane/AcOEt = 50:1) to afford **9a** (1.56 g, 6.0 mmol, 88%) as a colorless oil**:** $[\alpha]_D^{24}$ –26.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.32-7.21 (m, 5H), 5.14 (d, *J* = 4.0 Hz, 1H), 2.60 (dq, *J* = 4.0, 6.8 Hz, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 8.0 Hz, 9H), 0.52 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 142.4, 128.1, 127.4, 126.1, 74.2, 54.7, 8.1, 6.6, 4.7; FTIR (neat) 2953, 2879, 1740, 1361, 1257, 1167, 1072 cm^{-1}; MS (EI) *m/z* 87, 115, 143, 221, 249, 278 (M^+); HRMS (EI) calcd for $C_{16}H_{26}O_2Si$ (M^+) 278.1702, found 278.1703.

(2*R*,3*R*)-3-Triethylsiloxy-2-methyl-3-phenylpropanal (9b): Prepared from the TES ether of **8b** in the same manner as described for the synthesis of **9a**, 86%, a colorless oil; $[\alpha]_D^{24}$ +26.8 (*c* 1.00, $CHCl_3$). The spectral data were identical with those of the enantiomer **9a**.

(2*R*,3*S*)-3-Triethylsiloxy-2-methyl-3-phenylpropanal (11a): Prepared from the TES ether of **10a** in the same manner as described for the synthesis of **9a**, 95%, a colorless oil; $[\alpha]_D^{25}$ –87.2 (*c* 2.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, *J* = 2.8 Hz, 1H), 7.32-7.26 (m, 5H), 4.78 (d, *J* = 8.0 Hz, 1H), 2.70 (m, 1H), 0.90-0.78 (m, 12H), 0.50-0.42 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 142.4, 128.1, 127.8, 126.6, 76.6, 54.7, 10.9, 6.6, 4.7; FTIR (neat) 2956, 2878, 1725, 1455, 1236, 1072, 1009 cm^{-1}; MS (EI) *m/z* 87, 115, 143, 221, 249, 278 (M^+); HRMS (EI) calcd for $C_{16}H_{26}O_2Si$ (M^+) 278.1702, found 278.1703.

(2*S*,3*R*)-3-Triethylsiloxy-2-methyl-3-phenylpropanal (11b): Prepared from the TES ether of **10b** in the same manner as described for the synthesis of **9a**, 86%, a colorless oil; $[\alpha]_D^{26}$ +85.6 (*c* 2.00, $CHCl_3$). The spectral data were identical with those of the enantiomer **11a**.

(2*R*,3*S*)-3-*tert*-Butyldiphenylsiloxy-2-methyl-3-phenylpropanal (13a): Prepared from the TBDPS ether of **10a** in the same as manner described for the synthesis of **9a**, 92%, a colorless oil; $[\alpha]_D^{28}$ –83.2 (*c* 2.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 1.2 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.45-7.30 (m, 6H), 7.22-7.15 (m, 7H), 4.88 (d, *J* = 7.2 Hz, 1H), 2.75 (dq, *J* = 7.2, 8.0 Hz, 1H), 1.00 (s, 9H), 0.76 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 141.1, 135.9, 133.3, 132.9, 129.8, 129.5, 128.1, 127.7, 127.3, 126.9, 76.7, 54.6, 26.8, 19.3, 10.3; FTIR (neat) 2934, 2858, 1726, 1108 cm^{-1}; MS (FAB) *m/z* 77, 107, 136, 154, 199, 239, 307, 402 (M^+); HRMS (EI) calcd for $C_{26}H_{30}O_2Si$ (M^+) 402.2015, found 402.2015.

(2*S*,3*R*)-3-*tert*-Butyldiphenylsiloxy-2-methyl-3-phenylpropanal (13b): Prepared from the TBDPS ether of **10b** in the same manner as described for the synthesis of **9a**, 83%, a colorless oil; $[\alpha]_D^{26}$ +80.5 (*c* 1.00, $CHCl_3$). The spectral data were identical with those of the enantiomer **13a**.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*R*,4*R*,5*S*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (12a): β-ICD (124 mg, 0.4 mmol) was dissolved in THF (2 mL) and the solution was evaporated at room temperature. After repeating this operation three times, the amorphous residue was dried under vacuum at room temperature for 10 min. A solution of the dried β-ICD and **9a** (560 mg, 2.0 mmol) in DMF (6.6 mL) was cooled to –55 °C, and HFIPA (870 µL, 5.2 mmol) was then added. After stirring at –55 °C for 36 h, HFIPA (470 µL, 2.8 mmol) was added. The mixture was further stirred at –55 °C for 36 h, and the reaction was quenched by the addition of 0.1 M HCl (6 mL). The mixture was extracted with AcOEt, washed with saturated $NaHCO_3$ and brine, dried, and concentrated. Purification of the residue by flash chromatography (SiO_2 6 g, hexane/AcOEt = 100:1 to 20:1) to give **9a** (170 mg, 30%), **12a** (558 mg, 1.12 mmol, 56%), and **12b** (70 mg, 0.14 mmol, 7%) each as a colorless oil. As a result, the MBH adducts **12b** and **12b** were obtained in 63% total yield (90% brsm) and an 8:1 diastereomeric ratio. **12a**: $[\alpha]_D^{26}$ –47.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 6.59 (s, 1H), 6.26 (s, 1H), 5.82 (septet, *J* = 6.4 Hz, 1H), 5.09 (d, *J* = 3.2 Hz, 1H), 4.88 (s, 1H), 3.52 (s, 1H), 1.95-1.85 (m, 1H), 0.90 (t, *J* = 8.0 Hz, 9H), 0.70 (d, *J* = 7.2 Hz, 3H), 0.55 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 142.7, 138.5, 130.2, 130.0, 127.4, 126.2, 120.5 (q, $^1J_{C,F}$ = 281 Hz), 80.0, 72.9, 66.6 (septet, $^2J_{C,F}$ = 35 Hz), 43.1, 6.6, 4.8, 4.5; FTIR (neat) 3498, 2960, 1752, 1385, 1234, 1109, 1001 cm^{-1}; MS (FAB) *m/z* 75, 103, 209, 221, 249, 353, 500 (M^+); HRMS (EI) calcd for $C_{22}H_{30}F_6O_4Si$ (M^+) 500.1818, found 500.1820.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*S*,4*R*,5*S*)-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (12b): Prepared by α-ICPN-catalyzed MBH reaction of **9a** in the same manner as described for the synthesis of **12a**. Compound **12b** was obtained as a colorless oil in 64% yield together with **12a** (6%) and recovered **9a** (28%). The MBH adducts **12b** and **12a** were obtained in 70% total yield (97% brsm) and a 10:1 diastereomeric ratio. **12b**: $[\alpha]_D^{26}$ –20.2 (*c* 2.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 6.51 (s, 1H), 6.12 (s, 1H), 5.81 (septet, *J* = 6.4 Hz, 1H), 5.03 (d, *J* = 2.4 Hz, 1H), 4.42 (dd, *J* = 4.4,

8.4 Hz, 1H), 4.31 (d, *J* = 4.4 Hz, 1H), 2.20-2.11 (m, 1H), 0.90 (t, *J* = 8.4 Hz, 9H), 0.67 (d, *J* = 7.2 Hz, 3H), 0.55 (q, *J* = 8.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 162.8, 141.4, 140.2, 130.6, 127.9, 127.4, 126.7, 120.4 (q, $^1J_{C,F}$ = 280 Hz), 77.0, 73.8, 66.5 (septet, $^2J_{C,F}$ = 35 Hz), 44.9, 11.6, 6.6, 4.7; FTIR (neat) 3447, 2960, 1755, 1455, 1385, 1234, 1125 cm^{-1}; MS (FAB) *m/z* 75, 103, 209, 221, 249, 353, 500 (M^+); HRMS (EI) calcd for $C_{22}H_{30}F_6O_4Si$ (M^+) 500.1818, found 500.1819.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*S*,4*S*,5*S*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (12c): Prepared by α-ICPN-catalyzed MBH reaction of **9b** in the same manner as described for the synthesis of **12a**. Compound **12c**, a colorless oil, was obtained as a single diastereomer in 65% (100% brsm) together with recovered **9b** (35%). **12c:** $[\alpha]_D^{26}$ –36.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36-7.24 (m, 5H), 6.56 (d, *J* = 1.6 Hz, 1H), 6.26 (d, *J* = 1.6 Hz, 1H), 5.71 (septet, *J* = 6.4 Hz, 1H), 4.94 (d, *J* = 3.2 Hz, 1H), 4.74 (s, 1H), 4.16 (s, 1H), 2.12-1.96 (m, 1H), 0.98-0.87 (m, 12H), 0.58 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 162.2, 142.5, 138.8, 130.4, 128.2, 127.4, 125.4, 120.5 (q, $^1J_{C,F}$ = 281 Hz), 79.9, 68.3, 66.3 (septet, $^2J_{C,F}$ = 37 Hz), 41.9, 10.6, 6.7, 4.6; FTIR (neat) 3470, 2960, 2880, 1753, 1386, 1356, 1234, 1112, 1005 cm^{-1}; MS (FAB) *m/z* 75, 103, 209, 221, 249, 353, 500 (M^+); HRMS (EI) calcd for $C_{22}H_{30}F_6O_4Si$ (M^+) 500.1818, found 500.1827.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*R*,4*S*,5*S*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (12d): Prepared by β-ICD-catalyzed MBH reaction of **9b** in the same manner as described for the synthesis of **12a**. Compound **12d** was obtained as a colorless oil in 14.5% yield together with **12c** (3.5%) and recovered **9b** (58%). The MBH adducts **12d** and **12c** were obtained in 18% total yield (43% brsm) and a 4:1 diastereomeric ratio. $[\alpha]_D^{27}$ –42.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36-7.24 (m, 5H), 6.50 (s, 1H), 6.21 (s, 1H), 5.83 (septet, *J* = 6.4 Hz, 1H), 5.02 (d, *J* = 1.2 Hz, 1H), 4.61 (d, *J* = 8.8 Hz, 1H), 4.57 (d, *J* = 8.8 Hz, 1H), 2.20-2.10 (m, 1H), 0.86 (t, *J* = 8.0 Hz, 9H), 0.55-0.41 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 162.8, 142.6, 139.9, 130.7, 128.2, 127.9, 127.2, 125.4, 120.5 (q, $^1J_{C,F}$ = 281 Hz), 81.9, 75.4, 66.6 (septet, $^2J_{C,F}$ = 37 Hz), 47.1, 13.3, 6.5, 4.6; FTIR (neat) 3453, 2960, 1753, 1386, 1234, 1114 cm^{-1}; MS (FAB) *m/z* 75, 103, 209, 221, 249, 353, 500 (M^+); HRMS (EI) calcd for $C_{22}H_{30}F_6O_4Si$ (M^+) 500.1818, found 500.1819.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*S*,4*S*,5*R*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (12e): Prepared by α-ICPN-catalyzed MBH reaction of **11a** in the same manner as described for the synthesis of **12a**. Compound **12e** was obtained as a colorless oil in 58% yield together with **12f** (6%) and recovered **11a** (22%). The MBH adducts **12e** and **12f** were obtained in 64% total yield (97% brsm) and a 10:1 diastereomeric ratio. Compound **12e**, $[\alpha]_D^{27}$ +47.1 (*c* 1.00, $CHCl_3$), exhibited identical spectral data with those of the enantiomer **12a**.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*R*,4*S*,5*R*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (12f): Prepared by β-ICD-catalyzed MBH reaction of **11a** in the same manner as described for the synthesis of **12a**. Compound **12f**, a colorless oil, $[\alpha]_D^{26}$ +21.0 (*c* 1.00, $CHCl_3$), was obtained as a single diastereomer in 87% yield. The spectral data were identical with those of the enantiomer **12b**.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*R*,4*R*,5*R*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (12g): Prepared by β-ICD-catalyzed MBH reaction of **11b** in the same manner as described for the synthesis of **12a**. Compound **12g**, a colorless oil, $[\alpha]_D^{26}$ +36.1 (*c* 1.00, $CHCl_3$), was obtained as a single diastereomer in 43% yield (65% brsm) together with recovered **11b** (34%). The spectral data were identical with those of the enantiomer **12c**.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*S*,4*R*,5*R*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (12h): Prepared by α-ICPN-catalyzed MBH reaction of **11b** in the same manner as described for the synthesis of **12a**. Compound **12h** was obtained as a colorless oil in 14% yield together with **12g** (5%) and recovered **11b** (72%). The MBH adducts **12h** and **12g** were obtained in 19% total yield (67% brsm) and a 3:1 diastereomeric ratio. Compound **12h**, $[\alpha]_D^{26}$ +42.0 (*c* 1.00, $CHCl_3$), exhibited identical spectral data with those of the enantiomer **12d**.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*S*,4*S*,5*S*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (14a): Prepared by α-ICPN-catalyzed MBH reaction of **13a** in the same manner as described for the synthesis of **12a**. Compound **14a** was obtained as a single diastereomer in 40% (74% brsm) together with recovered **13a** (46%). **14a**, a colorless oil; $[\alpha]_D^{29}$ –36.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.74 (d, *J* = 6.8 Hz, 2H), 7.48-7.30 (m, 6H), 7.29-7.18 (m, 7H), 6.51 (s, 1H), 6.14 (s, 1H), 5.80 (septet, *J* = 6.4 Hz, 1H), 4.99 (s, 1H), 4.71 (d, *J* = 6.4 Hz, 1H), 2.21 (s, 1H), 1.99 (dq, *J* = 6.4, 6.4 Hz, 1H), 1.05 (s, 9H), 0.51 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 162.2, 142.7, 139.1, 136.1, 136.0, 133.5, 132.3, 130.0, 129.9, 129.6, 128.1, 127.8, 127.3, 126.9, 120.5 (q, $^1J_{C,F}$ = 281 Hz), 79.9, 67.9, 66.5 (septet, $^2J_{C,F}$ = 37 Hz), 43.2, 27.0, 19.3, 9.2; FTIR (neat) 3482, 2935, 2860, 1753, 1386, 1358, 1268, 1109, 1054 cm^{-1}; MS (FAB) *m/z* 75, 135, 199, 305, 449, 449, 567, 624 (M^+), 647 [$(M+Na)^+$]; HRMS (FAB) calcd for $C_{27}H_{32}O_3SiNa$ [$(M+Na)^+$] 647.2028, found 647.2024.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*R*,4*R*,5*R*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (14b): Prepared by β-ICD-catalyzed MBH reaction of **13b** in the same manner as described for the synthesis of **12a**. Compound **14b** was obtained as a single diastereomer in 39% (86% brsm) together with recovered **13b** (55%). Compound **14b**, a colorless oil, $[\alpha]_D^{28}$ +35.9 (*c* 1.00, $CHCl_3$), exhibited identical spectral data with those of **14a**.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*R*,4*S*,5*S*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (14c): Prepared by β-ICD-catalyzed MBH reaction of **13a** in the same manner as described for the synthesis of **12a**. Compound **14c** was obtained in 58% yield together with **14d** (3%) and recovered **13a** (34%) each as a colorless oil. The MBH adducts **14c** and **14d** were obtained in 61% total yield (93% brsm) and a 20:1 diastereomer ratio. **14c**, $[\alpha]_D^{28}$ –33.9 (*c* 2.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.68 (d, *J* = 6.0 Hz, 2H), 7.45-7.32 (m, 6H), 7.25-7.18 (m, 7H), 6.36 (s, 1H), 5.86 (s, 1H), 5.77 (septet, *J* = 6.4 Hz, 1H), 5.03 (d, *J* = 6.0 Hz, 1H), 4.00 (dd, *J* = 6.0, 10.0 Hz, 1H), 3.13 (d, *J* = 6.0 Hz, 1H), 2.11 (ddq, *J* = 6.0, 10.0, 10.0 Hz, 1H), 1.06 (s, 9H), 0.53 (d, *J* = 10.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 163.4, 141.5, 139.9, 136.7, 134.4, 133.9, 131.5, 130.6, 130.3, 128.5, 128.3, 128.2, 128.1, 120.5 (q, $^1J_{C,F}$ = 281 Hz), 78.4, 75.6, 67.2 (septet, $^2J_{C,F}$ = 37 Hz), 46.9, 27.8, 20.1, 12.1; FTIR (neat) 3560, 2960, 1750, 1460, 1386, 1237, 1116 cm^{-1}; MS (FAB) *m/z* 75, 135, 199, 305, 449, 449, 567, 624 (M^+), 647 [$(M+Na)^+$]; HRMS (FAB) calcd for $C_{27}H_{32}O_3SiNa$ [$(M+Na)^+$] 647.2028, found 647.2024.

1,1,1,3,3,3-Hexafluoropropan-2-yl (3*S*,4*R*,5*R*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (14d): Prepared by α-ICPN-catalyzed MBH reaction of **13b** in the same manner as described for the synthesis of **12a**. Compound **14d** was obtained in 29% together with **14c** (3%) and recovered **13b** (68%) each as a colorless oil. The MBH adducts **14d** and **14c** were obtained in 32% total yield (100% brsm) and a 10:1 diastereomer ratio. Compound **14d**, $[\alpha]_D^{28}$ +35.9 (*c* 1.00, $CHCl_3$), exhibited identical spectral data with those of the enantiomer **14c**.

Ethyl (3*R*,4*R*,5*S*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (15a): To a solution of **12a** (333 mg, 0.67 mmol) in EtOH (5 mL) was added $NaHCO_3$ (112 mg, 1.33 mmol). After being

stirred at room temperature for 24 h, the mixture was diluted with water (15 mL), extracted with AcOEt, washed with brine, dried, and concentrated. Purification by chromatography (SiO_2 10 g, hexane/AcOEt = 8:1) afforded **15a** (253 mg, 0.67 mmol, 100%) as a colorless oil: $[\alpha]_D^{26}$ –54.9 (*c* 1.00, $CHCl_3$) (99% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 5H), 6.33 (s, 1H), 5.93 (s, 1H), 5.07 (d, *J* = 4.4 Hz, 1H), 4.79 (s, 1H), 4.25-4.12 (m, 2H), 3.34 (d, *J* = 1.2 Hz, 1H), 2.05-1.95 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 8.4 Hz, 9H), 0.71 (d, *J* = 7.6 Hz, 3H), 0.55 (q, *J* = 8.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 143.2, 141.2, 127.8, 127.1, 126.3, 125.2, 79.9, 73.1, 60.5, 43.4, 14.1, 6.8, 5.0, 4.8; FTIR (neat) 3514, 2957, 1714, 1456, 1265, 1173, 1094 cm^{-1}; MS (EI) *m/z* 75, 103, 209, 221, 249, 272, 349 (100), 378 (M^+); HRMS (EI) calcd for $C_{21}H_{34}O_4Si$ (M^+) 378.2226, found 378.2242. HPLC conditions: Danicel Chiralcel AD-H, 2-propanol/hexane = 1/100 (1 mL/min), t_R = 9.1 min (**15a**) and 7.3 min (enantiomer). The enantiomer of **15a**: $[\alpha]_D^{23}$ +56.3 (*c* 1.00, $CHCl_3$) (99% *ee*).

Ethyl (3*S*,4*R*,5*S*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (15b): Prepared from **12b** in the same manner as described for the synthesis of **15a**, 100%, a colorless oil; $[\alpha]_D^{26}$ –27.8 (*c* 2.00, $CHCl_3$) (99% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (m, 5H), 6.25 (s, 1H), 5.79 (s, 1H), 5.20 (d, *J* = 2.4 Hz, 1H), 4.30 (dd, *J* = 7.6, 8.0 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.89 (d, *J* = 7.6 Hz, 1H), 2.06 (ddq, *J* = 7.2, 7.6, 8.0 Hz, 1H), 1.27 (t, *J* = 6.8 Hz, 3H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.64 (d, *J* = 6.8 Hz, 3H), 0.57 (q, *J* = 8.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 143.2, 141.7, 127.7, 126.8, 126.5, 126.4, 74.9, 60.7, 45.5, 14.1, 10.6, 6.8, 4.8; FTIR (neat) 3518, 2957, 1714, 1456, 1375, 1326, 1098, 1021 cm^{-1}; MS (EI) *m/z* 75, 103, 209, 221, 249, 272, 349 (100), 378 (M^+); HRMS (EI) calcd for $C_{21}H_{34}O_4Si$ (M^+) 378.2226, found 378.2252. HPLC conditions: Danicel Chiralcel AD-H, 2-propanol/hexane = 1/100 (1 mL/min), t_R = 7.4 min (enantiomer) and 7.8 min (**15b**). The enantiomer of **15b**: $[\alpha]_D^{22}$ +27.2 (*c* 1.00, $CHCl_3$) (99% *ee*).

Ethyl (3*S*,4*S*,5*S*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (15c): Prepared from **12c** in the same manner as described for the synthesis of **15a**, 100%, a colorless oil; $[\alpha]_D^{25}$ –64.1 (*c* 1.00, $CHCl_3$) (99% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 5H), 6.32 (s, 1H), 5.92 (s, 1H), 4.92 (d, *J* = 3.6 Hz, 1H), 4.76 (s, 1H), 4.00 (q, *J* = 7.6 Hz, 2H), 3.94 (s, 1H), 2.05-1.98 (m, 1H), 1.06 (t, *J* = 7.6 Hz, 3H), 0.96-0.88 (m, 12H), 0.57 (q, *J* = 8.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 143.1, 141.5, 128.0, 127.2, 125.9, 125.5, 79.9, 68.2, 60.2, 42.2, 13.8, 10.6, 6.7, 4.7; FTIR (neat) 3493, 2957, 1719, 1456, 1276, 1091, 1007 cm^{-1}; MS (EI) *m/z* 75, 103, 209, 221, 249, 272, 349 (100), 378 (M^+); HRMS (EI) calcd for $C_{21}H_{34}O_4Si$ (M^+) 378.2226, found 378.2240. HPLC conditions: Danicel Chiralcel OD-H, 2-propanol/hexane = 1/100 (1 mL/min), t_R = 5.2 min (enantiomer) and 5.8 min (**15c**). The enantiomer of **15c**: $[\alpha]_D^{23}$ +63.0 (*c* 1.00, $CHCl_3$) (99% *ee*).

Ethyl (3*R*,4*S*,5*S*)-3-Hydroxy-5-triethylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (15d): Prepared from **12d** in the same manner as described for the synthesis of **15a**, 100%, a colorless oil; $[\alpha]_D^{25}$ –49.1 (*c* 1.00, $CHCl_3$) (99% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 5H), 6.24 (s, 1H), 5.81 (s, 1H), 4.77 (d, *J* = 7.2 Hz, 1H), 4.61 (d, *J* = 4.0 Hz, 1H), 4.35 (dd, *J* = 4.0, 8.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.19 (ddq, *J* = 7.2, 7.2, 7.6 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 9H), 0.62-0.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 142.6, 141.9, 127.9, 127.5, 127.4, 126.5, 80.0, 75.8, 60.7, 46.8, 14.1, 12.8, 6.7, 4.7; FTIR (neat) 3477, 2957, 1716, 1456, 1276, 1155, 1092, 1033 cm^{-1}; MS (EI) *m/z* 75, 103, 209, 221, 249, 272, 349 (100), 378 (M^+); HRMS (EI) calcd for $C_{21}H_{34}O_4Si$ (M^+) 378.2226, found 378.2222. HPLC conditions: Danicel Chiralcel OD-H, 2-propanol/hexane = 1/100 (1 mL/min), t_R = 5.5 min (**15d**) and 6.2 min (enantiomer). The enantiomer of **15d**: $[\alpha]_D^{23}$ +50.0 (*c* 1.00, $CHCl_3$) (99% *ee*).

Ethyl (3*S*,4*S*,5*S*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (16a): Prepared from **14a** in the same manner as described for the synthesis of **15a**, 100%, a colorless oil; $[\alpha]_D^{27}$ –48.4 (*c* 2.00, $CHCl_3$) (99% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.45-7.30 (m, 6H), 7.25-7.18 (m, 7H), 6.28 (s, 1H), 5.80 (s, 1H), 4.98 (s, 1H), 4.73 (d, *J* = 6.0 Hz, 1H), 4.18-4.08 (m, 2H), 2.19 (d, *J* = 2.8 Hz, 1H), 2.05 (dq, *J* = 6.0, 7.6 Hz, 1H), 2.05-1.98 (m, 1H), 1.17 (t, *J* = 7.6 Hz, 3H), 1.05 (s, 9H), 0.54 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 142.6, 141.3, 135.6, 133.1, 132.6, 129.3, 129.1, 127.5, 127.2, 126.8, 126.5, 124.8, 78.8, 67.7, 59.9, 43.0, 26.6, 18.9, 13.6, 8.9; FTIR (neat) 3513, 2934, 1715, 1272, 1157, 819 cm^{-1}; MS (FAB) *m/z* 77, 91, 129, 154, 327, 345, 445, 502 (M^+); HRMS (FAB) calcd for $C_{31}H_{38}O_4Si$ (M^+) 502.2539, found 502.2531. HPLC conditions: Danicel Chiralcel AD-H, 2-propanol/hexane = 1/100 (1 mL/min), t_R = 6.6 min (**16a**) and 7.4 min (enantiomer). The enantiomer of **16a**: $[\alpha]_D^{22}$ +48.9 (*c* 1.00, $CHCl_3$) (99% *ee*).

Ethyl (3*R*,4*S*,5*S*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-4-methyl-2-methylene-5-phenylpentanoate (16c): Prepared from **14c** in the same manner as described for the synthesis of **15a**, 100%, a colorless oil; $[\alpha]_D^{27}$ –38.2 (*c* 1.00, $CHCl_3$) (99% *ee*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.45-7.18 (m, 13H), 6.08 (s, 1H), 5.43 (s, 1H), 5.27 (d, *J* = 4.4 Hz, 1H), 4.61 (d, *J* = 4.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.69 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.11 (d, *J* = 9.2 Hz, 1H), 2.19 (ddq, *J* = 4.4, 6.8, 9.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.07 (s, 9H), 0.60 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 140.5, 135.8, 134.1, 133.5, 129.6, 129.4, 127.7, 127.5, 127.4, 127.3, 126.9, 126.7, 75.8, 75.7, 60.7, 45.3, 27.0, 19.4, 14.1, 10.9; FTIR (neat) 3523, 2934, 1703, 1457, 1174, 1108 cm^{-1}; MS (FAB) *m/z* 77, 91, 129, 154, 327, 345, 445, 502 (M^+); HRMS (FAB) calcd for $C_{31}H_{38}O_4Si$ (M^+) 502.2539, found 502.2521. HPLC conditions: Danicel Chiralcel AD-H, 2-propanol/hexane = 1/100 (1 mL /min), t_R = 8.4 min (**16c**) and 7.8 min (enantiomer). The enantiomer of **16c**: $[\alpha]_D^{22}$ +39.0 (*c* 1.00, $CHCl_3$) (99% *ee*).

Ethyl (2*S*,3*R*,4*R*,5*S*)-3-Hydroxy-5-triethylsiloxy-2,4-dimethyl-5-phenylpentanoate (17a): Prepared from **15a** by *syn*-selective hydrogenation in the same manner as described for the synthesis of **8a**, 84%, a colorless oil; $[\alpha]_D^{26}$ –36.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.21 (m, 5H), 4.88 (d, *J* = 4.0 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.87 (d, *J* = 8.0 Hz, 1H), 2.94 (s, 1H), 2.63 (dq, *J* = 7.6, 8.0 Hz, 1H), 1.72-1.65 (m, 1H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.90-0.81 (m, 12H), 0.52 (q, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 143.2, 127.8, 127.1, 126.3, 79.2, 75.3, 60.5, 43.8, 43.4, 14.1, 13.9, 6.8, 6.5, 4.8; FT-R (neat) 3514, 2955, 1729, 1456, 1243, 1176, 1053 cm^{-1}; MS (EI) *m/z* 75, 87, 103, 157, 209, 221, 233, 274, 351, 380 (M^+); HRMS (EI) calcd for $C_{21}H_{36}O_4Si$ (M^+) 380.2383, found 380.2383.

Ethyl (2*R*,3*R*,4*R*,5*S*)-3-Hydroxy-5-triethylsiloxy-2,4-dimethyl-5-phenylpentanoate (17b): Prepared from **15a** by *anti*-selective hydrogenation in the same manner as described for the synthesis of **10a**, 89%, a colorless oil; $[\alpha]_D^{27}$ –30.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.21 (m, 5H), 4.78 (d, *J* = 6.0 Hz, 1H), 4.19-4.08 (m, 2H), 3.62 (ddd, *J* = 4.0, 4.0, 7.6 Hz, 1H), 2.91 (d, *J* = 4.0 Hz, 1H), 2.58 (dq, *J* = 7.2, 7.6 Hz, 1H), 1.81 (ddq, *J* = 4.0, 6.0, 7.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.84 (t, *J* = 6.8 Hz, 9H), 0.52-0.42 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 143.5, 127.9, 127.2, 126.6, 78.6, 74.3, 60.5, 43.3, 42.6, 14.1, 13.8, 7.4, 6.6, 4.8; FTIR (neat) 3519, 2955, 1723, 1456, 1240, 1182, 1061 cm^{-1}; MS (EI) *m/z* 75, 87, 103, 157, 209, 221, 233, 274, 351, 380 (M^+); HRMS (EI) calcd for $C_{21}H_{36}O_4Si$ (M^+) 380.2383, found 380.2383.

Ethyl (2*R*,3*S*,4*R*,5*S*)-3-Hydroxy-5-triethylsiloxy-2,4-dimethyl-5-phenylpentanoate (17c): Prepared from **15b** by *syn*-selective hydrogenation in the same manner as described for the synthesis of **8a**, 84%, a colorless oil; $[\alpha]_D^{25}$ –40.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.21 (m, 5H), 5.21 (d, *J* = 2.4 Hz, 1H), 4.22-4.15 (m, 2H), 3.99 (ddd, *J* = 2.8, 2.8, 7.6 Hz, 1H), 3.74 (d, *J* = 2.8 Hz, 1H), 2.58 (dq, *J* = 2.4, 7.2 Hz, 1H), 1.78 (ddq, *J* = 2.4, 2.8, 7.2 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.18 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 9H), 0.67 (d, *J* = 7.2 Hz, 3H), 0.55 (q, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 143.1, 127.7, 126.8 126.6, 75.2, 72.4, 60.5, 42.8, 41.7, 14.1, 9.9, 9.1, 6.7, 4.8; FTIR (neat) 3516, 2954, 1717, 1456, 1376, 1193, 1063 cm^{-1}; MS (EI) *m/z*

75, 87, 103, 157, 209, 221, 233, 274, 351, 380 (M^+); HRMS (EI) calcd for $C_{21}H_{36}O_4Si$ (M^+) 380.2383, found 380.2385.

Ethyl (2*S*,3*S*,4*R*,5*S*)-3-Hydroxy-5-triethylsiloxy-2,4-dimethyl-5-phenylpentanoate (17d): Prepared from **15b** by *anti*-selective hydrogenation in the same manner as described for the synthesis of **10a**, 89%, a colorless oil; $[\alpha]_D^{26}$ –23.8 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.20 (m, 5H), 5.20 (d, *J* = 2.4 Hz, 1H), 4.17-4.09 (m, 2H), 3.77 (d, *J* = 8.0 Hz, 1H), 3.52 (ddd, *J* = 4.0, 8.0, 8.0 Hz, 1H), 2.67 (dq, *J* = 4.0, 6.8 Hz, 1H), 1.81 (ddq, *J* = 2.4, 6.8, 8.0 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.73 (d, *J* = 6.8 Hz, 3H), 0.55 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 143.2, 127.7, 126.8, 126.5, 75.4, 75.3, 60.3, 44.9, 41.7, 15.1, 14.1, 10.3, 6.7, 4.7; FTIR (neat) 3516, 2956, 1714, 1456, 1378, 1184, 1045 cm^{-1}; MS (EI) *m/z* 75, 87, 103, 157, 209, 221, 233, 274, 351, 380 (M^+); HRMS (EI) calcd for $C_{21}H_{36}O_4Si$ (M^+) 380.2383, found 380.2384.

Ethyl (2*R*,3*S*,4*S*,5*S*)-3-Hydroxy-5-triethylsiloxy-2,4-dimethyl-5-phenylpentanoate (17e): Prepared from **15c** by *syn*-selective hydrogenation in the same manner as described for the synthesis of **8a**, 81%, colorless oil; $[\alpha]_D^{25}$ –50.3 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 4.84 (d, *J* = 3.6 Hz, 1H), 3.98-3.92 (m, 2H), 3.81 (d, *J* = 9.6 Hz, 1H), 3.67 (brs, 1H), 2.56 (dq, *J* = 7.2, 9.6 Hz, 1H), 1.72-1.69 (m, 1H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.06 (t, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.55 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 143.0, 128.1, 127.2 125.8, 80.3, 71.4, 60.8, 44.2, 42.5, 14.4, 13.9, 11.4, 6.7, 4.6; FTIR (neat) 3503, 2956, 1731, 1457, 1374, 1177, 1053 cm^{-1}; MS (EI) *m/z* 75, 87, 103, 157, 209, 221, 233, 274, 351, 380 (M^+); HRMS (EI) calcd for $C_{21}H_{36}O_4Si$ (M^+) 380.2383, found 380.2373.

Ethyl (2*S*,3*S*,4*S*,5*S*)-3-Hydroxy-5-triethylsiloxy-2,4-dimethyl-5-phenylpentanoate (17f): Prepared from **15c** by *anti*-selective hydrogenation in the same manner as described for the synthesis of **10a**, 95%, a colorless oil; $[\alpha]_D^{25}$ –62.3 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 4.79 (d, *J* = 5.2 Hz, 1H), 4.20-4.10 (m, 2H), 4.06 (d, *J* = 9.6 Hz, 1H), 3.45 (brs, 1H), 2.53 (dq, *J* = 7.2, 9.6 Hz, 1H), 1.76 (dq, *J* = 5.2, 7.2 Hz, 1H), 1.25 (t, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 8.0 Hz, 9H), 0.51 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 143.4, 128.1, 127.2 126.2, 79.2, 71.5, 60.4, 43.6, 41.2, 14.1, 13.6, 10.3, 6.7, 4.6; FTIR (neat) 3511, 2956, 1731, 1457, 1379, 1182, 1061 cm^{-1}; MS (EI) *m/z* 75, 87, 103, 157, 209, 221, 233, 274, 351, 380 (M^+); HRMS (EI) calcd for $C_{21}H_{36}O_4Si$ (M^+) 380.2383, found 380.2383.

Ethyl (2*S*,3*R*,4*S*,5*S*)-3-Hydroxy-5-triethylsiloxy-2,4-dimethyl-5-phenylpentanoate (17g): Prepared from **15d** by *syn*-selective hydrogenation in the same manner as described for the synthesis of **8a**, 85%, a colorless oil; $[\alpha]_D^{27}$ –42.6 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 4.76 (d, *J* = 7.6 Hz, 1H), 4.25 (brs, 1H), 4.22-4.10 (m, 2H), 3.93 (d, *J* = 9.6 Hz, 1H), 2.56 (dq, *J* = 6.8, 9.6 Hz, 1H), 1.94 (dq, *J* = 6.8, 7.2 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 0.84 (t, *J* = 8.0 Hz, 9H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.58-0.41 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 142.7, 127.8, 127.5 127.4, 79.4, 74.7, 60.4, 43.3, 41.7, 14.1, 11.7, 8.7, 6.6, 4.6; FTIR (neat) 3504, 2956, 1715, 1457, 1376, 1191, 1059 cm^{-1}; MS (EI) *m/z* 75, 87, 103, 157, 209, 221, 233, 274, 351, 380 (M^+); HRMS (EI) calcd for $C_{21}H_{36}O_4Si$ (M^+) 380.2383, found 380.2383.

Ethyl (2*R*,3*R*,4*S*,5*S*)-3-Hydroxy-5-triethylsiloxy-2,4-dimethyl-5-phenylpentanoate (17h): Prepared from **15d** by *anti*-selective hydrogenation in the same manner as described for the synthesis of **10a**, 100%, a colorless oil; $[\alpha]_D^{27}$ –40.8 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H), 4.92 (d, *J* = 6.4 Hz, 1H), 4.23-4.12 (m, 2H), 3.85 (d, *J* = 6.8 Hz, 1H), 3.40 (ddd, *J* = 2.8, 6.8, 6.8 Hz, 1H), 2.73 (dq, *J* = 2.8, 6.8 Hz, 1H), 2.02 (ddq, *J* = 6.4, 6.8, 6.8 Hz, 1H), 1.28 (t, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 8.0 Hz, 9H), 0.68 (d, *J* = 6.8 Hz, 3H), 0.52-0.42 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 142.4, 127.7, 127.4 127.2, 77.2, 76.7, 60.4, 45.1, 41.7, 14.7, 14.2, 11.8, 6.7, 4.7; FTIR (neat) 3509, 2956, 1713, 1456, 1378, 1181, 1061 cm^{-1}; MS (EI) *m/z* 75, 87, 103, 157, 209, 221, 233, 274, 351, 380 (M^+); HRMS (EI) calcd for $C_{21}H_{36}O_4Si$ (M^+) 380.2383, found 380.2363.

Ethyl (2*R*,3*S*,4*S*,5*S*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-2,4-dimethyl-5-phenylpentanoate (18a): Prepared from **16a** by *syn*-selective hydrogenation in the same manner as described for the synthesis of **8a**, 82%, a colorless oil; $[\alpha]_D^{29}$ –48.3 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.8 Hz, 2H), 7.48-7.38 (m, 3H), 7.35-7.18 (m, 10H), 4.57 (d, *J* = 8.4 Hz, 1H), 4.22-4.10 (m, 3H), 2.48 (dq, *J* = 7.2, 8.4 Hz, 1H), 1.86 (dq, *J* = 7.2, 7.2 Hz, 1H), 1.66 (d, *J* = 4.4 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.08-1.01 (m, 12H), 0.50 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 143.3, 136.1, 136.0, 133.7, 133.3, 129.7, 129.3, 127.9, 127.3, 127.2, 127.1, 78.1, 71.0, 60.3, 43.8, 42.3, 27.1, 19.3, 14.1, 14.0, 8.8; FTIR (neat) 3589, 2935, 1730, 1484, 1181, 1058 cm^{-1}; MS (FAB) *m/z* 75, 131, 135, 199, 329, 345, 447, 504 (M^+); HRMS (FAB) calcd for $C_{31}H_{40}O_4Si$ (M^+) 504.2696, found 504.2668.

Ethyl (2*S*,3*S*,4*S*,5*S*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-2,4-dimethyl-5-phenylpentanoate (18b): Prepared from **16a** by *anti*-selective hydrogenation in the same manner as described for the synthesis of **10a**, 93%, a colorless oil; $[\alpha]_D^{24}$ –77.2 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.0 Hz, 2H), 7.48-7.38 (m, 3H), 7.35-7.18 (m, 10H), 4.60 (d, *J* = 6.8 Hz, 1H), 4.04 (q, *J* = 7.6 Hz, 2H), 3.90 (ddd, *J* = 2.8, 6.8, 7.0 Hz, 1H), 2.48 (dq, *J* = 6.8, 7.0 Hz, 1H), 1.78-1.70 (m, 2H), 1.16 (t, *J* = 7.6 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.04 (s, 9H), 0.66 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 142.8, 136.1, 133.7, 133.1, 129.9, 129.5, 127.9, 127.3, 127.0, 78.7, 71.2, 60.1, 43.9, 43.8, 27.1, 19.3, 14.4, 14.1, 9.7; FTIR (neat) 3594, 2935, 1729, 1457, 1371, 1177, 1107, 1053 cm^{-1}; MS (FAB) *m/z* 75, 131, 135, 199, 329, 345, 447, 504 (M^+); HRMS (FAB) calcd for $C_{31}H_{40}O_4Si$ (M^+) 504.2696, found 504.2698.

Ethyl (2*S*,3*R*,4*S*,5*S*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-2,4-dimethyl-5-phenylpentanoate (18c): Prepared from **16c** by *syn*-selective hydrogenation in the same manner as described for the synthesis of **8a**, 86%, a colorless oil; $[\alpha]_D^{28}$ –27.7 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.8 Hz, 2H), 7.48-7.32 (m, 8H), 7.28-7.18 (m, 5H), 5.28 (d, *J* = 4.4 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.90 (d, *J* = 10.0 Hz, 1H), 2.70 (d, *J* = 1.2 Hz, 1H), 2.37 (q, *J* = 6.8 Hz, 1H), 1.82 (ddq, *J* = 4.4, 6.8, 10.0 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.08 (s, 9H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 140.8, 135.9, 135.8, 134.3, 133.6, 129.6, 129.4, 127.6, 127.5, 127.4, 127.3, 126.8, 75.1, 72.1, 60.5, 42.1, 40.6, 27.1, 19.3, 14.1, 9.3, 8.5; FTIR (neat) 3526, 2935, 2857, 1713, 1459, 1381, 1191, 1108 cm^{-1}; MS (FAB) *m/z* 75, 131, 135, 199, 329, 345, 447, 504 (M^+); HRMS (FAB) calcd for $C_{31}H_{40}O_4Si$ (M^+) 504.2696, found 504.2699.

Ethyl (2*R*,3*R*,4*S*,5*S*)-3-Hydroxy-5-*tert*-butyldiphenylsiloxy-2,4-dimethyl-5-phenylpentanoate (18d): Prepared from **16c** by *anti*-selective hydrogenation in the same manner as described for the synthesis of **10a**, 96%, a colorless oil; $[\alpha]_D^{28}$ –45.1 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.8 Hz, 2H), 7.48-7.20 (m, 13H), 5.32 (d, *J* = 4.0 Hz, 1H), 4.07 (m, 2H), 2.88 (ddd, *J* = 2.4, 10.0, 10.0 Hz, 1H), 2.62 (d, *J* = 10.0 Hz, 1H), 2.50 (dq, *J* = 2.4, 6.8 Hz, 1H), 1.82 (ddq, *J* = 4.0, 7.2, 10.0 Hz, 1H), 1.20 (t, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 7.2 Hz, 3H), 1.10 (s, 9H), 0.77 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 140.6, 135.8, 135.7, 134.3, 133.7, 129.6, 129.4, 127.6, 127.5, 127.4, 127.3, 126.8, 75.3, 74.5, 60.4, 45.6, 40.6, 27.0, 19.3, 15.2, 14.1, 9.8; FTIR (neat) 3517, 2934, 2857, 1712, 1458, 1426, 1378, 1182, 1108, 1060 cm^{-1}; MS (FAB) *m/z* 75, 131, 135, 199, 329, 345, 447, 504 (M^+); HRMS (FAB) calcd for $C_{31}H_{40}O_4Si$ (M^+) 504.2696, found 504.2678.

Ethyl (2*S*,3*R*,4*R*,5*S*)-3,5-Dihydroxy-2,4-dimethyl-5-phenylpentanoate (19a): To a solution of **17a** (43 mg, 114 μmol) in THF (2 mL) was added

TBAF (1.0 M in THF, 0.23 mL, 0.23 mmol) and AcOH (4 µL, 68 µmol) at 0 °C. After stirring at 0 °C for 30 min, the reaction was quenched by the addition of saturated $NaHCO_3$ (2 mL). The mixture was extracted with AcOEt, washed with brine, dried, concentrated, and purified by preparative TLC (hexane/AcOEt = 3:1) to give **19a** (22 mg, 81 µmol, 71%) as a colorless oil**:** $[\alpha]_D^{28}$ –8.6 (*c* 1.00, $CHCl_3$) (lit.[17] $[\alpha]_D^{22}$ −8.3 (*c* 1.08, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36-7.23 (m, 5H), 4.99 (d, *J* = 2.0 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 4.07 (d, *J* = 8.8 Hz, 1H), 3.33 (brs, 1H), 3.02 (brs, 1H), 2.66 (dq, *J* = 7.2, 8.6 Hz, 1H), 1.75-1.78 (m, 1H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 175.2, 142.9, 128.2, 127.2, 125.6, 78.2, 76.9, 60.5, 43.7, 42.1, 14.1, 5.0; FTIR (neat) 3406, 2972, 1712, 1455, 1383, 1256, 1180, 1045 cm^{-1}; MS (EI) *m/z* 57, 65, 91, 107, 118, 142, 160, 220, 248, 266 (M^+); HRMS (EI) calcd for $C_{15}H_{22}O_4$ (M^+) 266.1518, found 266.1516.

Ethyl (2*R*,3*R*,4*R*,5*S*)-3,5-Dihydroxy-2,4-dimethyl-5-phenylpentanoate (19b): Prepared from **17b** in the same manner as described for the synthesis of **19a**, 70%, a colorless oil; $[\alpha]_D^{24}$ –7.2 (*c* 2.30, $CHCl_3$) (lit.[17] $[\alpha]_D^{22}$ −5.5 (*c* 1.83, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.35-7.24 (m, 5H), 5.03 (d, *J* = 3.2 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.09 (d, *J* = 7.6 Hz, 1H), 3.69 (brs, 2H), 2.62 (dq, *J* = 7.2, 7.6 Hz, 1H), 1.89-1.81 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 1H), 1.12 (d, *J* = 7.2 Hz, 3H), 0.82 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.3, 143.2, 128.1, 126.9, 125.8, 78.1, 77.4, 60.9, 43.4, 40.8, 14.1, 13.8, 4.3; FTIR (neat) 3434, 2978, 1717, 1455, 1383, 1248, 1187, 973 cm^{-1}; MS (EI) *m/z* 57, 65, 91, 107, 118, 142, 160, 220, 248, 266 (M^+); HRMS (EI) calcd for $C_{15}H_{22}O_4$ (M^+) 266.1518, found 266.1516.

Ethyl (*S*)-2-((4*S*,5*R*,6*S*)-2,2,5-Trimethyl-6-phenyl-1,3-dioxan-4-yl)propanoate (20d): To a solution of **17d** (21 mg, 56 µmol) in THF (2 mL) was added TBAF (1.0 M in THF, 0.11 mL, 0.11 mmol) and AcOH (2 µL, 34 µmol) at 0 °C. After stirring at 0 °C for 30 min, the reaction was quenched by the addition of saturated $NaHCO_3$ (2 mL). The mixture was extracted with AcOEt, washed with brine, dried, and concentrated to give the corresponding diol (16 mg). The crude diol was dissolved in acetone (1 mL), and 2,2-dimethoxypropane (0.14 mL, 1.12 mmol) and PPTS (1.4 mg, 6 µmol) were added. After stirring for 30 min, the reaction was quenched by the addition of saturated $NaHCO_3$ (1 mL). The mixture was extracted with AcOEt, dried, concentrated, and purified by preparative TLC (hexane/AcOEt = 3:1) to give **20d** (12.2 mg, 40 µmol, 72%, 2 steps) as a colorless oil**:** $[\alpha]_D^{27}$ –60.7 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36-7.20 (m, 5H), 5.07 (d, *J* = 4.8 Hz, 1H), 4.21-4.14 (m, 2H), 3.62 (dd, *J* = 6.8, 6.8 Hz, 1H), 2.66 (dq, *J* = 6.8, 6.8 Hz, 1H), 2.15 (ddq, *J* = 4.8, 6.8, 6.8 Hz, 1H), 1.44 (s, 3H), 1.36 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 7.2 Hz, 3H), 0.60 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 174.5, 139.8, 127.9, 126.6, 125.8, 101.0, 76.5, 60.3, 45.2, 39.2, 25.5, 23.5, 14.3, 13.7, 13.1; FTIR (neat) 2984, 1736, 1458, 1379, 1221, 1172, 1033 cm^{-1}; MS (EI) *m/z* 69, 107, 118, 127, 203, 248, 291, 306 (M^+); HRMS (EI) calcd for $C_{18}H_{26}O_4$ (M^+) 306.1831, found 306.1830.

Ethyl (*S*)-2-((4*S*,5*S*,6*S*)-2,2,5-Trimethyl-6-phenyl-1,3-dioxan-4-yl)propanoate (20f): Prepared from **17f** in the same manner as described for the synthesis of **20d**, 63% (2 steps), a colorless oil; $[\alpha]_D^{24}$ –70.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36-7.19 (m, 5H), 4.18-4.05 (m, 4H), 2.55 (dq, *J* = 6.0, 6.8 Hz, 1H), 2.01 (dq, *J* = 3.6, 7.2, 7.6 Hz, 1H), 1.34 (s, 3H), 1.32 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 7.6 Hz, 3H), 0.88 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 175.1, 141.9, 128.5, 127.8, 126.8, 101.5, 70.9, 60.4, 41.3, 39.7, 24.5, 23.6, 14.2, 13.3, 11.1; FTIR (neat) 2983, 1737, 1456, 1378, 1228, 1182, 887, 761 cm^{-1}; MS (EI) *m/z* 69, 107, 118, 127, 203, 248, 291, 306 (M^+); HRMS (EI) calcd for $C_{18}H_{26}O_4$ (M^+) 306.1831, found 306.1833.

Ethyl (*R*)-2-((4*R*,5*S*,6*S*)-2,2,5-Trimethyl-6-phenyl-1,3-dioxan-4-yl)propanoate (20h): Prepared from **17h** in the same manner as described for the synthesis of **20d**, 50% (2 steps), a colorless oil; $[\alpha]_D^{27}$ –49.5 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.35-7.26 (m, 5H), 4.00 (d, *J* = 10.4 Hz, 1H), 4.27-4.12 (m, 2H), 3.89 (dd, *J* = 2.4, 10.2 Hz, 1H), 2.76 (dq, *J* = 2.4, 6.8 Hz, 1H), 1.95 (ddq, *J* = 7.6, 10.2, 10.4 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.29 (t, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 7.6 Hz, 3H), 0.63 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 173.4, 140.4, 128.3, 128.1, 127.8, 98.8, 78.5, 60.3, 41.9, 37.9, 30.1, 19.4, 14.3, 12.8, 11.9; FTIR (neat) 2984, 1733, 1458, 1387, 1196, 949 cm^{-1}; MS (EI) *m/z* 69, 107, 118, 127, 203, 248, 291, 306 (M^+); HRMS (EI) calcd for $C_{18}H_{26}O_4$ (M^+) 306.1831, found 306.1830.

(4*R*,5*S*)-4-((1*S*,2*R*)-1-Triethylsiloxy-1-phenylpropan-2-yl)-2,2,5-trimethyl-1,3-dioxane (21c): To a solution of **17c** (38 mg, 100 µmol) in THF (2 mL) was added $LiAlH_4$ (8 mg, 200 µmol) at 0 °C. After stirring at 0 °C for 1 h, the reaction was quenched by the addition of saturated Rochelle salt (5 mL), and the mixture was vigorously stirred at room temperature for 6 h. The mixture was extracted with AcOEt, dried over Na_2SO_4, concentrated to give diol (30 mg). The crude diol was dissolved in acetone (1 mL), and 2,2-dimethoxypropane (0.25 mL, 2 mmol) and PPTS (2.5 mg, 10 µmol) were added at room temperature. After stirring for 30 min at room temperature, the reaction was quenched by the addition of saturated $NaHCO_3$ (1 mL). The mixture was extracted with AcOEt, dried, concentrated, and purified by preparative TLC (hexane/AcOEt = 5:1) to give **21c** (10.2 mg, 32 µmol, 32%, 2 steps) as a colorless oil**:** $[\alpha]_D^{27}$ –27.8 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.30-7.18 (m, 5H), 5.17 (s, 1H), 4.14 (dd, *J* = 2.4, 11.2 Hz, 1H), 3.88 (dd, *J* = 2.0, 8.4 Hz, 1H), 3.62 (d, *J* = 11.2 Hz, 1H), 1.55-1.46 (m, 8H), 1.00 (d, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 9H), 0.67 (d, *J* = 7.2 Hz, 3H), 0.55-0.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 145.5, 127.5, 126.4, 126.3, 98.5, 71.9, 67.2, 44.1, 30.1, 29.9, 19.5, 10.3, 6.9, 6.4, 5.1; FTIR (neat) 2956, 1456, 1381, 1238, 1198, 1101, 1007, 958 cm^{-1}; MS (EI) *m/z* 87, 115, 143, 171, 221, 249, 291, 320, 363, 378 (M^+); HRMS (EI) calcd for $C_{22}H_{38}O_3Si$ (M^+) 378.2590, found 378.2576.

(4*R*,5*R*)-4-((1*S*,2*R*)-1-Triethylsiloxy-1-phenylpropan-2-yl)-2,2,5-trimethyl-1,3- dioxane (21d): Prepared from **17d** in the same manner as described for the synthesis of **21c**, 33% (2 steps), a colorless oil: $[\alpha]_D^{25}$ –25.7 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, benzene-d_6) *δ* 7.45 (d, *J* = 8.8 Hz, 2H), 7.19 (dd, *J* = 7.2, 8.0 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 5.01 (d, *J* = 6.4 Hz, 1H), 3.46 (dd, *J* = 4.8, 11.2 Hz, 1H), 3.35 (dd, *J* = 3.6, 11.2 Hz, 1H), 3.13 (dd, *J* = 9.6, 11.2 Hz, 1H), 2.10 (ddq, *J* = 3.6, 6.4, 6.8 Hz, 1H), 1.53 (s, 3H), 1.40-1.29 (m, 4H), 1.24 (d, *J* = 6.8 Hz, 3H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.59 (q, *J* = 6.8 Hz, 6H), 0.44 (d, *J* = 2.4, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, benzene-d_6) *δ* 146.0, 127.8, 127.5, 127.4, 98.4, 78.1, 75.3, 66.1, 45.2, 32.1, 29.5, 19.7, 13.9, 13.7, 7.1, 5.5; FTIR (neat) 2957, 1457, 1375, 1198, 1062, 1001, 836 cm^{-1}; MS (EI) *m/z* 87, 115, 143, 171, 221, 249, 291, 320, 363, 378 (M^+); HRMS (EI) calcd for $C_{22}H_{38}O_3Si$ (M^+) 378.2590, found 378.2590.

(4*R*,5*S*)-4-((1*S*,2*S*)-1-Triethylsiloxy-1-phenylpropan-2-yl)-2,2,5-trimethyl-1,3-dioxane (21e): Prepared from **17e** in the same manner as described for the synthesis of **21c**, 35% (2 steps), a colorless oil: $[\alpha]_D^{27}$ –35.0 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 5H), 4.59 (d, *J* = 6.4 Hz, 1H), 4.06 (dd, *J* = 2.8, 11.6 Hz, 1H), 3.72 (dd, *J* = 2.0, 8.0 Hz, 1H), 3.57 (dd, *J* = 1.2, 11.6 Hz, 1H), 2.01 (ddq, *J* = 6.4, 6.8, 8.0 Hz, 1H), 1.80-1.72 (m, 1H), 1.36 (s, 3H), 1.34 (s, 3H), 1.12 (d, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 8.0 Hz, 9H), 0.75 (d, *J* = 6.8 Hz, 3H), 0.51-0.41 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 127.7, 127.1, 98.7, 75.7, 72.5, 67.2, 43.0, 32.2, 29.7, 19.1, 11.5, 11.4, 6.7, 4.8; FTIR (neat) 2957, 1457, 1380, 1240, 1197, 1063, 1006, 851, 740 cm^{-1}; MS (EI) *m/z* 87, 115, 143, 171, 221, 249, 291, 320, 363, 378 (M^+); HRMS (EI) calcd for $C_{22}H_{38}O_3Si$ (M^+) 378.2590, found 378.2586.

(4*R*,5*R*)-4-((1*S*,2*S*)-1-Triethylsiloxy-1-phenylpropan-2-yl)-2,2,5-trimethyl-1,3-dioxane (21f): Prepared from **17f** in the same manner as described for the synthesis of **21c**, 40% (2 steps), a colorless oil; $[\alpha]_D^{25}$ –67.5 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.31-7.22 (m, 5H), 4.45 (d, *J* = 9.2 Hz, 1H), 4.11 (dd, *J* = 1.2, 10.8 Hz, 1H), 3.72 (dd, *J* = 4.8, 11.6 Hz, 1H), 3.56 (dd, *J* = 10.8, 11.6 Hz, 1H), 1.93-1.80 (m, 2H), 1.50 (s, 3H), 1.40 (s, 3H), 0.83 (t, *J* = 8.0 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H), 0.51 (d, *J* = 7.6 Hz, 3H), 0.45-0.33 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*

144.8, 127.9, 127.4, 127.2, 97.9, 75.7, 72.8, 66.4, 42.0, 30.4, 29.8, 19.4, 12.5, 9.3, 6.9, 5.0; FTIR (neat) 2954, 1458, 1378, 1236, 1198, 1063, 1009, 834 cm^{-1}; MS (EI) *m/z* 87, 115, 143, 171, 221, 249, 291, 320, 363, 378 (M^+); HRMS (EI) calcd for $C_{22}H_{38}O_3Si$ (M^+) 378.2590, found 378.2576.

(4*S*,5*R*)-4-((1*S*,2*S*)-1-Triethylsiloxy-1-phenylpropan-2-yl)-2,2,5-trimethyl-1,3-dioxane (21g): Prepared from **17g** in the same manner as described for the synthesis of **21c**, 33% (2 steps), a colorless oil; $[\alpha]_D^{26}$ – 0.31 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 5H), 5.14 (d, *J* = 3.6 Hz, 1H), 3.95 (dd, *J* = 3.6, 12.0 Hz, 1H), 3.54 (d, *J* = 12.0 Hz, 1H), 3.30 (dd, *J* = 2.0, 10.4 Hz, 1H), 2.02 (ddq, *J* = 3.6, 6.8, 12.0 Hz, 1H), 1.46 (s, 3H), 1.32 (s, 3H), 1.36-1.28 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.89 (t, *J* = 8.4 Hz, 9H), 0.67 (d, *J* = 6.8 Hz, 3H), 0.51-0.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 127.6, 127.1, 126.7, 98.3, 75.7, 72.3, 67.1, 42.7, 30.0, 29.5, 19.4, 10.6, 7.9, 6.8, 4.9; FTIR (neat) 2957, 1457, 1381, 1195, 1090, 1007, 853, 771 cm^{-1}; MS (EI) *m/z* 87, 115, 143, 171, 221, 249, 291, 320, 363, 378 (M^+); HRMS (EI) calcd for $C_{22}H_{38}O_3Si$ (M^+) 378.2590, found 378.2581.

(4*S*,5*S*)-4-((1*S*,2*S*)-1-Triethylsiloxy-1-phenylpropan-2-yl)-2,2,5-trimethyl-1,3-dioxane (21h): Prepared from **17h** in the same manner as described for the synthesis of **21c**, 28% (2 steps), a colorless oil; $[\alpha]_D^{26}$ – 17.5 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (m, 5H), 4.76 (d, *J* = 8.4 Hz, 1H), 3.70 (dd, *J* = 4.8, 11.6 Hz, 1H), 3.58 (dd, *J* = 3.2, 10.0 Hz, 1H), 3.44 (dd, *J* = 11.6, 11.6 Hz, 1H), 2.31-2.22 (m, 1H), 2.09 (ddq, *J* = 3.2, 6.8, 8.4 Hz, 1H), 1.42 (s, 3H), 1.40 (s, 3H), 0.92-0.82 (m, 12H), 0.60 (d, *J* = 6.8 Hz, 3H), 0.48-0.38 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 127.1, 127.3, 127.0, 98.3, 77.3, 76.6, 75.8, 66.7, 43.6, 32.3, 29.5, 19.3, 13.9, 13.6, 6.8, 4.9; FT-IR (neat) 2954, 1458, 1377, 1198, 1063, 1009, 820 cm^{-1}; MS (EI) *m/z* 87, 115, 143, 171, 221, 249, 291, 320, 363, 378 (M^+); HRMS (EI) calcd for $C_{22}H_{38}O_3Si$ (M^+) 378.2590, found 378.2606.

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[14] The absolute configurations of **8a,b** and **10a,b** were determined by the comparison of the ^1H NMR spectra with those reported for racemic **8** and **10**.[12]

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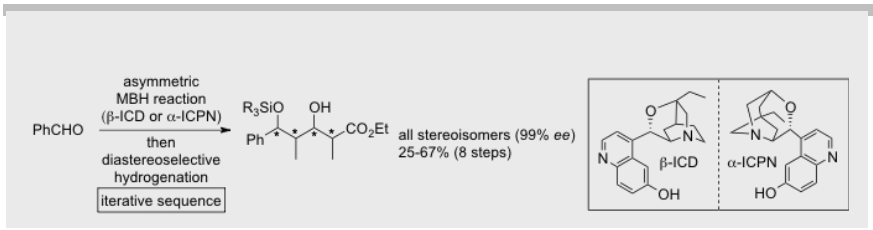

Described is a highly enantio- and diastereoselective approach to all possible stereoisomers of a polypropionate stereotetrad, which features an iterative sequence of a cinchona alkaloid-catalyzed Morita-Baylis-Hillman reaction and diastereoselective hydrogenation.

Asymmetric Synthesis

*Hikaru Yoshimura, Jun Ishihara and Susumi Hatakeyama**

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Stereoselective Construction of Entire Diastereomeric Stereotetrads Based on an Asymmetric Morita-Baylis-Hillman Reaction