Fragmentation Reactions of Optically Active Trisubstituted Cyclopropylcarbinyl Radicals

Yuki Takekawa and Kozo Shishido*

Institute for Medicinal Resources, University of Tokushima, 1-78 Sho-machi, Tokushima 770-8505, Japan

Shishido@ph2.tokushima-u.ac.jp

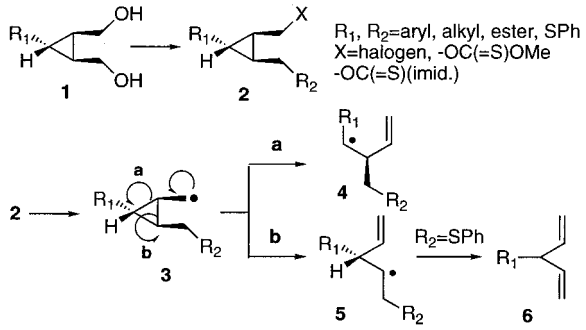
Received July 18, 2001

Fragmentation reactions of optically active trisubstituted cyclopropylcarbinyl radicals and their application to the synthesis of natural products are described. Preparation of the optically pure substrates for radical fragmentation reactions was efficiently accomplished by lipase-mediated desymmetrization of *σ*-symmetrical 3-substituted-1,2-cyclopropanedimethanols. In the presence of a radical stabilizing group, e.g., aryl, ester, or α,*β*-unsaturated ester, the fragmentation occurs selectively to generate the radical on the α-carbon of the group and provide the optically pure alkene derivatives. These derivatives possess three chemically distinct functionalities, making them excellent chiral building blocks for the construction of biologically active molecules. The synthetic usefulness of the procedure developed here has been demonstrated by an application to the enantioselective synthesis of both enantiomers of the key intermediate, 4-(3,4-methylenedioxybenzyl)dihydrofuran-2(3*H*)-one (**54**), for the total synthesis of biologically active lignans.

Introduction

Carbon−carbon bond cleavage of cyclopropanes triggered by cyclopropylcarbinyl radicals has been well-known as a method for preparing alkenyl compounds.[1] While extensive work on cyclopropylcarbinyl radicals has focused mainly on kinetic studies,[2] only a few examples of reactions from the synthetic point of view have thus far been reported.[3] In particular, systematic investigations of fragmentation reactions of optically active cyclopropylcarbinyl radicals directed toward the development of novel chiral building blocks for the enantioselective synthesis of significant molecules have yet to appear in the literature. We were therefore interested in developing the substrate-controlled selective fragmentation reactions of trisubstituted cyclopropylcarbinyl radicals as a versatile synthetic methodology. We envisioned (i) that the optically active trisubstituted cyclopropylcarbinyl radicals **3** generated from the radical precursors **2**, which would be prepared from the prochiral *σ*-symmetrical diols **1** via an enzyme-mediated desymmetrization,[4] would give either the nonracemic alkenes **4** via route a (Scheme 1) or the isomeric alkenes **5** via route b; (ii) that the direction of bond cleavage can be controlled by the choice of R_1 and R_2; (iii) that if a radical leaving group (e.g., SPh[5]) is introduced as R_2, other reaction processes, e.g., the tandem C−C bond cleavage/elimination reaction, would compete to yield the *σ*-symmetrical 3-substituted 1,4-pentadienes **6**, which would not be easy to prepare by conventional methods.[6] We reasoned that the alkenes **4** and **5** would be useful as acyclic chiral building blocks and that the skipped diene **6** would function as a *σ*-symmetrical substrate for asymmetric induction.[7]

Scheme 1



In this paper, we report general aspects for the regioselective cleavage of the carbon−carbon bond of

(1) (a) Dowd, P.; Zhang, W. *Chem. Rev.* **1993**, *93*, 2091−2115. (b) Nonhebel, D. C. *Chem. Soc. Rev.* **1993**, 347−359.

(2) For review, see: (a) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151−1176. Recent examples: (b) Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc.* **2001**, *123*, 4364−4365. (c) Tian, F.; Dolbier, W. R., Jr. *Org. Lett.* **2000**, *2*, 835−837. (d) Halgrem, T. A.; Roberts, J. D.; Horner, J. H.; Martinez, F. N.; Tronche, C.; Newcomb, M. *J. Am. Chem. Soc.* **2000**, *122*, 2988−2994. (e) Choi, S.-Y.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* **2000**, *65*, 4447, 4449. (f) Tian, F.; Bartberger, M. D.; Dolbier, W. R., Jr. *J. Org, Chem.* **1999**, *64*, 540−546. (g) Furxhi, E. F.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* **1999**, *64*, 4064−4068. (h) Kantorowski, E. J.; Eisenberg, S. W. E.; Fink, W. H.; Kurth, M. J. *J. Org. Chem.* **1999**, *64*, 570−580.

(3) (a) Handa, S.; Pattenden, G.; Li, W.-S. *Chem. Commun.* **1998**, 311−312. (b) Boffey, R. J.; Santagostino, M.; Whittingham, W. G.; Kilburn, J. D.; *Chem. Commun.* **1998**, 1875−1876. (c) Pike, K. G.; Destable, C.; Anson, M.; Kilburn, J. D. *Tetrahedron Lett.* **1998**, *39*, 5877−5880.

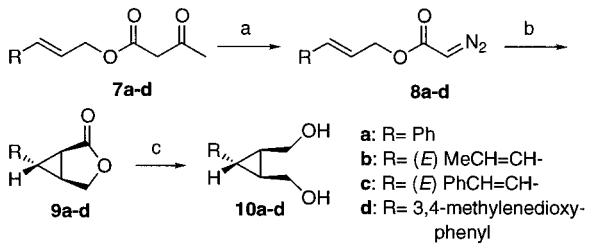
(4) (a) Faber, K. *Biotransformations in Organic Chemistry*, 3rd ed.; Springer-Verlag: Berlin, Heidelberg, 1997. (b) Schoffers, E.; Golebiowski, A.; Johnson, C. R. *Tetrahedron* **1996**, *52*, 3769−3826. (c) Itoh, T.; Mitsukura, K.; Furutani, M. *Chem. Lett.* **1998**, 903−904. (d) Itoh, T.; Emoto, S.; Kondo, M. *Tetrahedron* **1998**, *54*, 5225−5232. (e) Kirihara, M.; Takuwa, T.; Kawasaki, M.; Kakuda, H.; Hirokami, A.; Takahata, H. *Chem. Lett.* **1999**, 405−406.

(5) (a)Lythgoe, B.; Waterhouse, I. *Tetrahedron Lett.* **1977**, 4223−4226. (b)Ueno, Y.; Chino, K.; Okawara, M. *Tetrahedron Lett.* **1982**, *23*, 2575−2576. (c)Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564−5566.

(6) (a) Larock, R. C.; Gong, W. H. *J. Org. Chem.* **1989**, *54*, 2047−2057. (b) Larock, R. C.; Takagi, K. *J. Org. Chem.* **1988**, *53*, 4329−4332. (c) Trost, B. M.; Urch, C. J.; Hung, M.-H. *Tetrahedron Lett.* **1986**, *27*, 4949−4952. (d) Sheffy, F. K.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 7173−7175. (e) Yatagai, H. *J. Org. Chem.* **1980**, *45*, 1640−1644. (f) Grieco, P. A.; Wang, C.-L.; Majetich, G. *J. Org. Chem.* **1976**, *41*, 726−729.

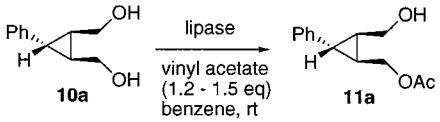
10.1021/jo010728d CCC: $20.00
Published on Web 11/16/2001

Scheme 2[a]



[a] Reagents and conditions: (a) pTsN$_3$, NaOH, ^{n}Bu$_4$NBr, CH_2Cl_2, rt; (b) $CuSO_4$, Cu(acac)$_2$, benzene, reflux; (c) $LiAlH_4$, THF, rt.

Table 1. Desymmetrization of the Diol 10a



entry	lipase	reaction time (h)	yield (%) of **11a**	ee (%)[a]
1	CAL	0.5	51	70
2	PPL	65	19	60[b]
3	Lipase PS	36	78	>99
4	Lipase AK	3	97	>99

[a] Determined by HPLC (CHIRALCEL OB column). [b] The enantiomer was obtained.

cyclopropanes triggered by cyclopropylcarbinyl radicals and enantioselective syntheses of suitably functionalized alkenes which would serve as versatile chiral building blocks for the construction of a wide variety of biologically active molecules.[8]

Results and Discussion

Fragmentation Reactions of Optically Active Trisubstituted Cyclopropylcarbinyl Radicals. The substrates for the radical reaction were synthesized from the acetoacetates **7a**−**d**, which were prepared from the corresponding allyl alcohols by transesterification with ethyl acetoacetate. Sequential treatment of **7a**−**d** with tosyl azide and sodium hydroxide produced the diazo esters **8a**−**d**, which were subjected to the Cu-catalyzed cyclopropanation.[9] The resulting bicyclic lactones **9a**−**d**[10] were reduced with $LiAlH_4$ to give the diols **10a**−**d** (Scheme 2).

We then explored the optimum conditions for desymmetrization of the σ-symmetrical diol **10a** using several lipases (Table 1). Of these, lipase AK,[11] derived from *Pseudomonas fluorescens*, proved to be the best choice in mediating transesterification using vinyl acetate as an acetyl donor in benzene at room temperature. The optically active monoacetate **11a** was obtained in 97% yield, with an enantiomeric excess over 99% as determined by HPLC on Chiralcel OB column.

Scheme 3

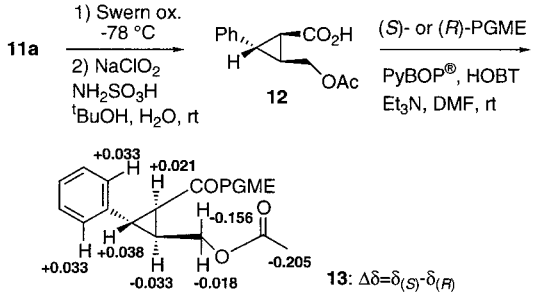
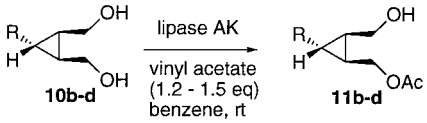


Table 2. Desymmetrization of the Diols 10b−d



entry	R	reaction time (h)	product	yield (%)	ee (%)
1	(*E*)-MeCH=CH-	2.5	**11b**	97	>99[a]
2	(*E*)-PhCH=CH-	3	**11c**	93	>99[b]
3	3,4-methylenedioxyphenyl	7	**11d**	97	>99[c]

[a] Determined by Mosher's method. [b] Determined by HPLC (CHIRALCEL OB column). [c] Determined by HPLC (CHIRALCEL OD column) after the conversion of **11d** to the corresponding TBS ether.

The absolute stereochemistry of **11a** was established as that shown in Scheme 3 using the PGME method[12] developed by Kusumi. Thus, sequential oxidation of **11a** under Swern conditions and with sodium chlorite in the presence of sulfamic acid provided the carboxylic acid **12**, which was condensed with (*R*)- and (*S*)-phenylglycine methyl ester (PGME) to give the corresponding diastereomeric amides **13*R*** and **13*S***. The $\Delta\delta$ values ($\Delta\delta = \delta S - \delta R$) calculated from the chemical shifts of the two diastereomers are shown in the Scheme 3. The systematic arrangement of + and − $\Delta\delta$ values led to the (*R*)-configuration of the carboxylic acid **12**.

Lipase-mediated desymmetrization of other diols **10b**−**d** was conducted using lipase AK under the same conditions as those for **10a**. Results are shown in Table 2. All diols were cleanly converted into the monoacetates **11b**−**d** in excellent chemical yields with high enantiomeric excesses.

These optically pure monoacetates were then converted into the radical precursors **14a**−**d**, **16**-**18**. Iodination of **11a** and bromination of **11b**−**d** gave the iodide **14a** and the bromides **14b**−**d**, respectively, in good yields. For the competitive reaction between the bond-cleavage to generate the benzyl radical[13] (route a in Scheme 1) and the tandem bond-cleavage/elimination process (route b), the iodide **16**, and the thiocarbonate **17**[14] possessing a radical leaving group (SPh) were prepared from **11a** via the sulfide **15**. Since benzenesulfonyl functions have been

(7) (a) Wallace, D. J.; Goodman, J. M.; Kennedy, D. J.; Davies, A. J.; Cowden, C. J.; Aswood, M. S.; Cottrell, I. F.; Dolling, U.-H.; Reider, P. J. *Org. Lett.* **2001**, *3*, 671−674. (b) Tanaka, M.; Imai, M.; Fujio, M.; Sakamoto, E.; Takahashi, M.; Eto-Kato, Y.; Wu, X. M.; Funakoshi, K.; Sakai, K.; Suenune, H. *J. Org. Chem.* **2000**, *65*, 5806−5816. (c) Schmidt, B.; Wildemann, H. *J. Org. Chem.* **2000**, *65*, 5817−5822. (d) Lautens, M.; Hughes, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 129−131.

(8) Takekawa, Y.; Shishido, K. *Tetrahedron Lett.* **1999**, *40*, 6817−6820.

(9) Hudlicky, T.; Reddy, D. B.; Govindan, S. V.; Kulp, T.; Still, B.; Sheth, J. P. *J. Org. Chem.* **1983**, *48*, 3422−3428.

(10) The relative stereochemistries of lactones **9a**−**d** were deduced from the coupling constants in the ^{1}H NMR spectra. The confirmation was made by the NOESY experiment, e.g., for compound **18′**.

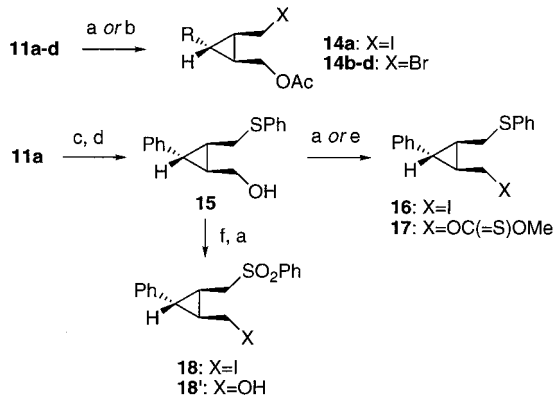
(11) Sato, K.; Yoshimura, T.; Shindo, M.; Shishido, K. *J Org. Chem.* **2001**, *66*, 309−314.

(12) Nagai, Y.; Kusumi, T. *Tetrahedron Lett.* **1995**, *36*, 1853−1856.

(13) (a) Newcomb, M.; Johnson, C. C.; Manek, M. B.; Varick, T. R. *J. Am. Chem. Soc.* **1992**, *114*, 10915−10921. (b) Martin-Esker, A. A.; Johnson, C. C.; Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc.* **1994**, *116*, 9174−9181.

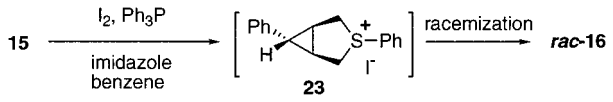
(14) (a) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574. (b) Prisbi, E. J.; Martin, J. C. *Synth. Commun.* **1985**, *15*, 401−409.

Scheme 4[a]



[a] Reagents and conditions: (a) I_2, Ph_3P, imidazole, benzene, rt; (b) CBr_4, Ph_3P, Ch_2Cl_2, rt; $CuSO_4$, $Cu(acac)_2$, benzene, reflux; (c) PhSSPh, $^nBu_3P$, pyridine, rt; (d) KOH, aq EtOH, rt; (e) $S{=}C(imid)_2$, toluene, 50 °C then MeOH, rt; (f) *m*CPBA, $KHCO_3$, CH_2Cl_2, rt.

Scheme 5



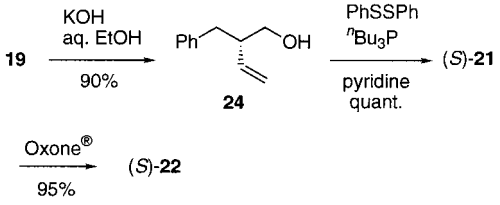
known to serve as radical leaving groups,[5a,15] we prepared the sulfone **18** from **15** by sequential oxidation with *m*CPBA and iodination (Scheme 4).

With the radical precursors in hand, we then examined the radical reactions of **14a**−**d**, **16**−**18**. When the iodide **14a** was treated with tri-*n*-butyltin hydride (2 equiv) and 2,2′-azoisobutyronitrile (0.01 equiv) in refluxing benzene, the fragmentation reaction proceeded smoothly and the alkenyl acetate **19** was obtained as a single product in 94% yield (entry 1). In like manner, the bromide **14d** was also converted cleanly under the same conditions into **20** in 92% yield (entry 4). As we had predicted, these compounds were produced via selective C−C bond cleavage to generate a stabilized benzyl radical. The optical purities of both **19** and **20** were determined to be over 99% ee by HPLC analysis, which indicated that the chirality of the starting cyclopropanes was completely retained during fragmentation. The substrates **14b**,**c** with crotyl and cinnamyl functionalities on the cyclopropane ring gave a complex mixture, probably caused by polymerization (entries 2 and 3). We next examined the radical reactions of **16**, which contains a radical leaving group (SPh) and which therefore has the possibility of competitive reactions, as shown in Scheme 1. In this instance, the product was the alkenyl sulfide **21**, obtained following the same procedure as for **14a**−**d**: however, its optical purity was surprisingly low (14% ee) (entry 5). Presumably, racemization occurred in the iodination of the alcohol **15** via the sulfonium intermediate **23**, as shown in Scheme 5.

To prove our hypothesis, the thiocarbonate **17** was subjected to the radical reaction to give the same sulfide **21**, the ee of which was >99%, thus clearly confirming the mechanism (entry 6). Furthermore, the fact that the reaction of the sulfone **18** yielded the alkenyl sulfone **22** in 88% yield with >99% ee also supports this premise (entry 7). The absolute configurations and enantiomeric

(15) (a) Phillips, E. D.; Whitham, G. H. *Tetrahedron Lett.* **1993**, *34*, 2541−2544. (b) Phillips, E. D.; Whitham, G. H. *Tetrahedron Lett.* **1993**, *34*, 2537−2540.

Scheme 6



excesses of **21** and **22**[16] were determined by comparison of the specific rotations for the enantiomers, which were synthesized as shown in Scheme 6. Hydrolysis of the acetate **19** followed by the Hata reaction[17] gave the sulfide (*S*)-**21**, which was oxidized with Oxone[18] to provide the sulfone (*S*)-**22**. The spectral properties of both are identical with those of the compounds obtained by the reactions of **17** and **18**, except for the signs of the specific rotation. Thus the absolute configurations were determined to be *R* as shown in Table 3. From these experiments, it was demonstrated that in the competitive reactions, the C−C bond cleavage to generate a benzyl radical predominates, producing the optically pure 4-aryl-3-alkyl-1-butenes selectively. In addition, a procedure for the construction of both enantiomers of sulfide **21** and sulfone **22** has been established.

We next examined the competitive C−C bond cleavage of the cyclopropane ring in compounds **26** and **27**. Radical reaction of the iodide **26** provided a 1:1 mixture of the isomeric alkenes **28** and **29** quantitatively (Scheme 7). This indicated that the radical stabilizing group is essential for selective bond cleavage. It is interesting to note that the reaction of **27** resulted in the exclusive formation of 3-phenylethyl-1,4-pentadiene **30** in 66% yield, which means that in the presence of a radical leaving group, the elimination reaction predominates over the nonstabilized radical forming process.

As an alternative radical stabilizing functionality, we chose the ester[19] and synthesized the two radical precursors **34** and **37** starting from **11b** and **25**, respectively, as shown in Scheme 8. In both cases, reactions proceeded cleanly to give the alkenyl esters **38** and **39** in quantitative and 89% yield, respectively. It was demonstrated that the ester group could control the direction of C−C bond cleavage completely.

Since it was shown that both aryl and ester functions stabilize the α-radical and control the direction of C−C bond cleavage, we then became interested in the competitive cleavage of the substrate **42** containing these two groups on the cyclopropane ring. When the iodide **42**, which was prepared from the carboxylic acid **12** via a three-step sequence, was subjected to the radical reaction, two isomeric alkenyl esters **43** and **44** were obtained as an inseparable 14:1 mixture in 86% yield (Scheme 9). Structure determination of both compounds was carried out after the reductive transformation to the alcohols (*R*)-**24** and **45** in 90% and 6% yield, respectively. From these

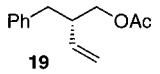
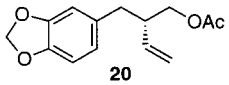
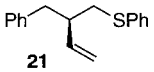
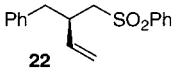
(16) The absolute configuration of **22** was further confirmed by the PGME method, after oxidative cleavage of the double bond followed by condensation of the resulting carboxylic acid with (*R*)- and (*S*)-PGME.

(17) Nakagawa, I.; Aki, K.; Hata, T. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1315−1318.

(18) Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 1287−1290.

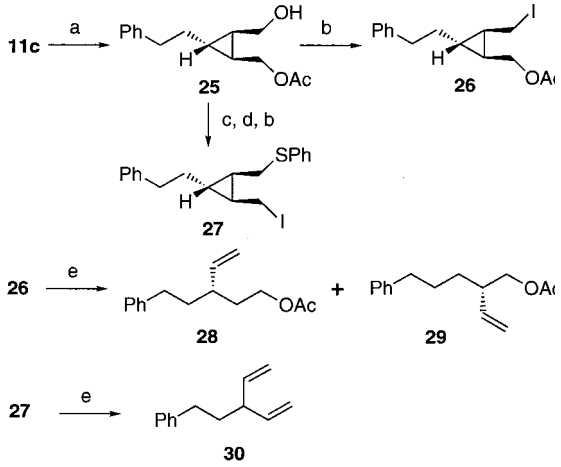
(19) Beckwith, A. L. J.; Bowry, V. W., *J. Org. Chem.* **1989**, *54*, 2681−2688.

Table 3. Radical Reactions of 14a–d, 16–18

entry	substrate	reaction time (h)	product	yield (%)	ee (%)	abs. config.
1	**14a**	1.5	 **19**	94	>99[a]	*S*
2	**14b**		complex mixt.			
3	**14c**		complex mixt.			
4	**14d**	2	 **20**	92	>99[b]	*S*
5	**16**	3	 **21**	81	14[c]	*R*
6	**17**	8	**21**	76	>99[c]	*R*
7	**18**	4	 **22**	88	>99[c]	*R*

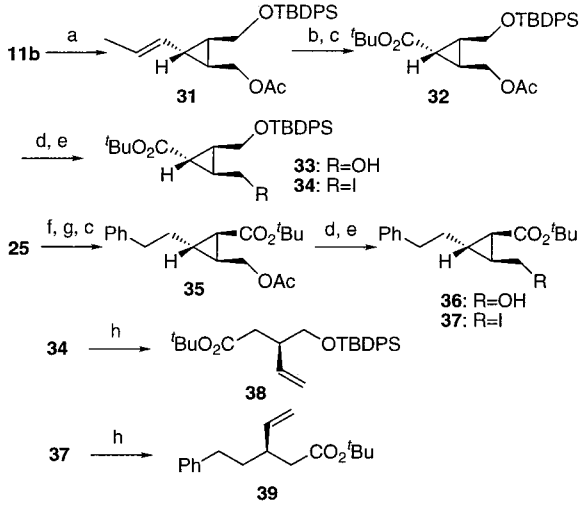
[a] Determined by HPLC (CHIRALCEL OB column). [b] Determined by HPLC (CHIRALCEL OD column) after hydrolysis of **19** to the corresponding alcohol. [c] Determined by $[\alpha]_D$.

Scheme 7



[a] Reagents and conditions: (a) H_2, 10% Pd–C, 3.5 atm, EtOH, rt; (b) I_2, Ph_3P, imidazole, benzene, rt; (c) PhSSPh, $^nBu_3P$, pyridine, rt; (d) KOH, aq EtOH, rt; (e) $^nBu_3SnH$, AIBN, benzene, reflux; (e) $LiAlH_4$, THF, rt.

Scheme 8[a]



[a] Reagents and conditions: (a) TBDPSCl, imidazole, DMAP, CH_2Cl_2, rt; (b) $RuCl_3$, $NaIO_4$, CCl_4, MeCN, H_2O, rt; (c) $Cl_3CC(=NH)O^tBu$, $BF_3{\cdot}OEt_2$, CH_2Cl_2, rt; (d) K_2CO_3, aq MeOH, rt; (e) I_2, Ph_3P, imidazole, benzene, rt; (f) Swern ox., −78 °C; (g) $NaClO_2$, NH_2SO_3H, tBuOH, H_2O, rt; (h) $^nBu_3SnH$, AIBN, benzene, reflux.

experiments, it was revealed that the radical stabilizing ability of the phenyl functionality is superior to that of the ester.

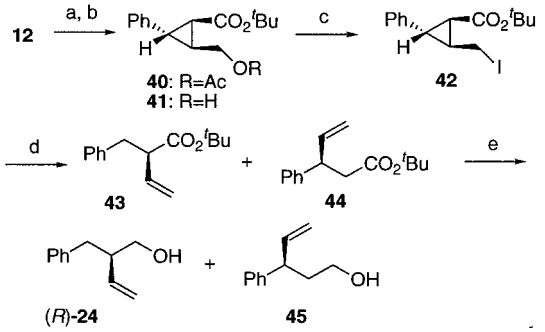
Encouraged by the results of the selective fragmentation of the radicals generated from **34** and **37**, we prepared the iodide **47** starting from **31** by a standard four-step transformation (Scheme 10). This compound contains the conjugated ester group on the cyclopropane, which can be expected to stabilize radical species. When the unsaturated ester **47** was submitted to the radical reaction, a chromatographically separable mixture of three double bond isomers (*E*)-**48**, (*Z*)-**48**, and **49** was obtained in a ratio of 5:1:1 in 80% yield. This result indicated that the bond cleavage occurs selectively to generate the stabilized radical dienolate **50** which abstracts hydrogen at the α- and γ-carbons of the ester group. The reason for the regioselectivity is not clear at this stage.

Enantioselective Synthesis of the Intermediate for Biologically Active Natural Lignans. Several naturally occurring lignans[20] have attracted considerable attention because of their cytotoxic and antileukemic activity thus making them fascinating synthetic targets. Consequently, many synthetic reports on racemic and asymmetric syntheses have been published.[21] In the enantioselective synthesis of lignans,[21b,c] the optically active lactone **54** has frequently been used as a key intermediate for total synthesis.[21c–g] Since both enanti-

(20) Keller-Juslén, C.; Kuhn, M.; von Wartburg, A.; Stähelin, H. *J. Med. Chem.* **1971**, *14*, 936–940.

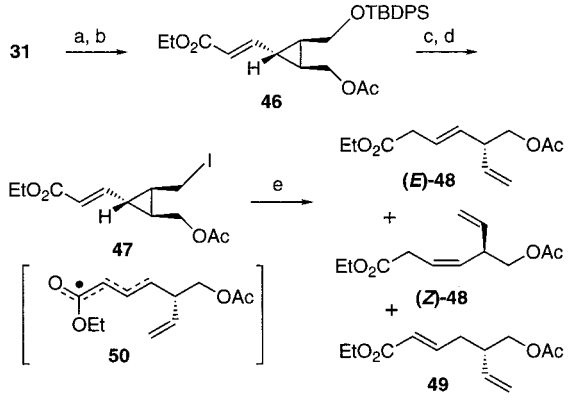
(21) (a) Ward, R. S. *Chem. Soc. Rev.* **1982**, *11*, 75–125. (b) Ward, R. S. *Synthesis* **1992**, 719–730. (c) Ward, R. S. *Tetrahedron* **1990**, *46*, 5029–5041. (d) Charlton, J. L.; Chee, G.-L. *Can. J. Chem.* **1997**, *75*, 1076–1083. (e) Bode, J. W.; Doyle, M. P.; Protopopova, M. N.; Zhou, Q.-L. *J. Org. Chem.* **1996**, *61*, 9146–9155. (f) Honda, T.; Kimura, N.; Sato, S.; Kato, D.; Tominaga, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1043–1046. (g) Tomioka, K.; Koga, K. *Tetrahedron Lett.* **1979**, *35*, 3315–3318.

Scheme 9[a]



[a] Reagents and conditions: (a) $Cl_3CC(=NH)O^tBu$, $BF_3{\cdot}OEt_2$, cyclohexane, CH_2Cl_2, rt; (b) K_2CO_3, aq MeOH, rt; (c) I_2, Ph_3P, imidazole, benzene, rt; (d) $^nBu_3SnH$, AIBN, benzene, reflux; (e) $LiAlH_4$, THF, rt.

Scheme 10[a]



[a] Reagents and conditions: (a) OsO_4, $NaIO_4$, Et_2O, H_2O, rt; (b) $(EtO)_2POCH_2CO_2Et$, $LiOH{\cdot}H_2O$, THF, rt; (c) $^nBu_4NF$, THF, rt; (d) I_2, Ph_3P, imidazole, benzene, rt; (e) $^nBu_3SnH$, AIBN, benzene, reflux.

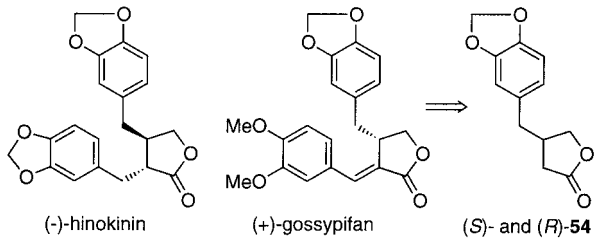


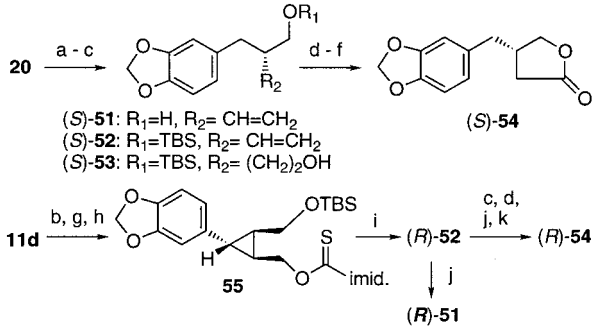
Figure 1.

omers at C-4 in the lactone ring are present in nature, e.g., (−)-hinokinin[21e−g] and (+)-gossypifan,[21d,22] the development of an enantioselective synthetic method for both enantiomers of **54** would be of significant value (Figure 1). As an application of the methodology developed here, we intended to synthesize both enantiomers of **54** starting from the fragmentation products (*S*)-**20** and (*R*)-**52**.

The acetoxy moiety of the alkenyl acetate **20**, which was derived from **14d** by radical fragmentation, was changed to a *tert*-butyldimethylsilyl ether via the alcohol (*S*)-**51** (>99% ee) and the resulting (*S*)-**52** was then submitted to hydroboration with 9-BBN to give the alcohol (*S*)-**53**. It was sequentially oxidized under Dess−Martin conditions of and with sodium chlorite and

(22) Das, B.; Das, R. *Phytochemistry* **1995**, *40*, 931−932.

Scheme 11[a]



[a] Reagents and conditions: (a) KOH, aq EtOH, rt; (b) TBSCl, imidazole, DMF, rt; (c) 9-BBN, THF, 0 °C then NaOH, H_2O_2, rt; (d) Dess−Martin ox., rt; (e) $NaClO_2$, NH_2SO_3H, ^tBuOH, H_2O, rt; (f) *p*TsOH, CH_2Cl_2, rt; (g) K_2CO_3, aq. MeOH, rt; (h) $S{=}C(imid)_2$, toluene, 50 °C; (i) $^nBu_3SnH$, AIBN, benzene, reflux; (j) $^nBu_4NF$, THF, rt; (k) PCC, CH_2Cl_2, rt.

sulfamic acid to afford the carboxylic acid, which was immediately treated with *p*-toluenesulfonic acid in dichloromethane to produce the lactone (*S*)-**54** in 59% overall yield from **53**. The spectral properties and optical rotation, $[\alpha]_D$ −3.60° (*c* = 1.09, $CHCl_3$) {lit.[21e] $[\alpha]_D$ −4.62° (*c* = 0.93, $CHCl_3$)}, were identical with those reported. On the other hand, the enantiomeric (*R*)-**54** was prepared from the monoacetate **11d**. Sequential silylation, alkaline hydrolysis, and treatment with 1,1′-thiocarbonyldiimidazole produced the imidazolide **55**, which was submitted to the radical reaction to give the alkene (*R*)-**52**. The optical purity was determined to be >99% ee by HPLC analysis (CHIRALCEL OD column) of the alcohol (*R*)-**51**, which was prepared by treatment with tetra-*n*-butylammonium fluoride. This was then converted smoothly into (*R*)-**54** [$[\alpha]_D$ +3.30° (*c* = 0.40, $CHCl_3$) {lit.[21g] $[\alpha]_D$ +5.22° (*c* = 1.13, $CHCl_3$)}] by the reaction sequence shown in Scheme 11. This synthesized compound was also identical with authentic material in all respects.

Conclusion

Fragmentation reactions of cyclopropylcarbinyl radicals were examined from a synthetic point of view. Readily available σ-symmetrical 3-substituted cyclopropane-1,2-dimethanols were converted into optically pure monoacetates by lipase-mediated desymmetrization. The fragmentation reactions of 2-aryl-3-alkylcyclopropylcarbinyl radicals proceeded selectively to generate a stabilized benzyl radical and produce the optically pure 4-aryl-3-alkyl-1-butenes exclusively. We clarified that the direction of C−C bond cleavage is also completely governed by other radical stabilizing groups on the cyclopropane ring, e.g., esters and α,β-unsaturated esters. In addition, σ-symmetrical 3-alkyl-1,4-pentadiene was synthesized via a tandem radical fragmentation and elimination of the sulfenyl radical. It was also demonstrated that the competitive reaction in the presence of both pheny and ester radical stabilizing groups on the cyclopropane led to the preferential formation of a radical on the carbon α to the phenyl ring. The synthetic usefulness of the methodology developed here was demonstrated by an application to the synthesis of both enantiomers of 4-(3,4-methylenedioxybenzyl)dihydrofuran-2(3*H*)-one, which are frequently used as key intermediates in the total synthesis of lignans. This methodology holds considerable

promise for the synthesis of other optically active biologically significant molecules.

Experimental Section

General. ^{1}H NMR were measured in $CDCl_3$ solution and referenced to TMS (0.00 ppm) using Bruker AM400, JEOL GSX400, JEOL EX400, JEOL JNM-AL400 (400 MHz), and JEOL JNM-AL-300 (300 MHz) spectrophotometers, unless otherwise noted. ^{13}C NMR were measured in $CDCl_3$ solution and referenced to $CDCl_3$ (77.0 ppm) or TMS (0.00 ppm) using Bruker AM400, JEOL GSX400, JEOL EX400 (100 MHz), JEOL JNM-AL300, and Varian Gemini 300 (75 MHz) spectrometers. IR spectra were recorded on JASCO FT/IR-410 and Perkin-Elmer 1720 FT-IR spectrometers. Mass spectra were obtained on a JEOL JMS-DX303, JMS-AX500, and JMS-SX102A. Elemental analyses were performed with Yanaco MT-3 CHN−Corder. Optical rotations were determined on JAS.CO DIP-370 and JAS.CO P-1010. Column chromatography was performed on silica gel, FUJI SILYSIA CHEMICAL BW-127ZH (100−270 mesh), Wakogel C-200E (75−150 μm), and Silica Gel 60N (70−230 mesh). Thin-layer chromatography was performed on precoated plates (0.25 mm, silica gel Merck Kieselgel 60 F_{245}). Melting points were measured with a Yanaco MP-500D melting point apparatus and are uncorrected. All reactions were performed in oven-dried glassware under positive pressure of argon or nitrogen, unless otherwise noted. Reaction mixtures were stirred magnetically.

General Procedure for the Transesterfication of Allyl Alcohol with Ethyl Acetoacetate.[9] A mixture of the allyl alcohol (1 equiv) and ethyl acetoacetate (2 equiv) were heated at 120 °C under reduced pressure (ca. 70 mmHg) for 3−9 h. After removal of excess ethyl acetoacetate, the residue was distilled or chromatographed to afford the keto ester **7**.

Cinnamyl Acetoacetate (7a). According to the general procedure, cinnamyl alcohol (21 mL, 16 mmol) was converted into the keto ester **7a** (33 g, 91%), a colorless oil, bp 155 °C/2 mmHg: IR (neat) cm^{-1} 1745, 1718, 1262, 1149, 966; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (3H, s), 3.50 (2H, s), 4.80 (2H, dd, J = 0.9, 6.4 Hz), 6.28 (1H, dt, J = 6.4, 16.0 Hz), 6.68 (1H, d, J = 16.0 Hz), 7.25 (1H, m), 7.33 (2H, t, J = 7.3 Hz), 7.39 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2 (q), 50.0 (t), 65.9 (t), 122.4 (d), 126.6 (d), 128.2 (d), 128.6 (d), 134.8 (d), 136.0 (s), 166.9 (s), 200.4 (t); MS (EI) m/z 115 (base peak), 218 (M^+); HRMS Calcd for $C_{13}H_{14}O_3$: 218.0943, found: 218.0942. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.40; H, 6.46.

5-Phenyl-*trans,trans*-2,4-pentadienyl Acetoacetate (7c). The keto ester **7c** (7.44 g, 87%), a yellow oil, was obtained from 5-phenyl-*trans,trans*-2,4-pentadien-1-ol[23] (5.6 g, 35 mmol) after purification by column chromatography (silica gel, hex/AcOEt = 90/10): IR (neat) cm^{-1} 1743, 1716, 1645, 1492, 1148, 1267, 1150, 992; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (3H, s), 3.49 (2H, s), 4.73 (2H, d, J = 6.83 Hz), 5.87 (1H, dt, J = 6.8, 15.0 Hz), 6.47 (1H, dd, J = 10.5, 15.0 Hz), 6.60 (1H, d, J = 16.0 Hz), 6.78 (1H, dd, J = 10.5, 16.0 Hz), 7.24 (1H, t, J = 7.3 Hz), 7.32 (2H, t, J = 7.3 Hz), 7.40 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2 (q), 50.0 (d), 65.6 (t), 126.0 (d), 126.5 (d), 127.5 (d), 127.9 (d), 128.6 (d), 134.2 (d), 135.2 (d), 136.8 (s), 166.8 (s), 200.4 (s); MS (EI) m/z 43 (base peak), 244 (M^+); HRMS Calcd for $C_{15}H_{16}O_3$ (M^+): 244.1099, found: 244.1080.

3,4-(Methylenedioxy)cinnamyl Acetoacetate (7d). The keto ester **7d** (5.6 g, 100%), as a yellow oil, was obtained from 3,4-(methylenedioxy)cinnamyl alcohol (3.7 g, 21 mmol) after purification by column chromatography (silica gel, hex/AcOEt = 90/10): IR (neat) cm^{-1} 1741, 1715, 1504, 1492, 1192, 1150, 964; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (3H, s), 3.49 (2H, s), 4.77 (2H, d, J = 6.8 Hz), 5.96 (2H, s), 6.11 (1H, dt, J = 6.8, 15.5 Hz), 6.58 (1H, d, J = 15.5 Hz), 6.76 (1H, d, J = 7.7 Hz), 6.83 (1H, d, J = 7.7 Hz), 6.93 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2 (q), 50.0 (t), 66.0 (t), 101.2 (t), 105.8 (d), 108.3 (d), 120.5 (d), 121.6 (d), 130.4 (s), 134.7 (d), 147.7 (s), 148.1 (s), 166.9 (s), 200.5 (s); MS (EI) m/z 131 (base peak), 262 (M^+); HRMS Calcd for $C_{14}H_{14}O_5$ (M^+): 262.0841, found: 262.0865.

General Procedure for the Preparation of the α-Diazoacetate 8.[9] A mixture of the keto ester **7** (1 equiv), tosyl azide (1 equiv), and tetrabutylammonium bromide (0.1 equiv) was stirred in CH_2Cl_2 for 30 min. To the mixture was added 10 N NaOH solution (3 equiv), the resulting mixture was stirred at room temperature for 8−14 h, washed successively with 10% KOH, water, and brine, and dried over Na_2SO_4. Removal of the solvent afforded the diazo ester **8**, after column chromatography.

Cinnamyl α-Diazoacetate (8a). According to the general procedure, the diazoacetate **8a** (4.6 g, 83%), a yellow oil, was obtained from the keto ester **7a** (6 g, 27 mmol) after purification by column chromatography (silica gel, benzene): IR (neat) cm^{-1} 2114, 1683, 1578, 1495, 1177; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (1H, br s), 4.82 (2H, dd, J = 0.9, 6.4 Hz), 6.29 (1H, dt, J = 6.4, 16.0 Hz), 6.66 (1H, d, J = 16.0 Hz), 7.26 (1H, m), 7.32 (2H, t, J = 7.7 Hz), 7.39 (2H, d, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.3 (d), 65.3 (t), 123.1 (d), 126.6 (d), 128.1 (d), 128.6 (d), 134.3(d), 136.1 (s), 166.6 (s); MS (EI) m/z 129 (base peak), 202 (M^+); HRMS Calcd for $C_{11}H_{10}N_2O_2$ (M^+): 202.0742, found: 202.0750.

5-Phenyl-*trans,trans*-2,4-pentadienyl α-Diazoacetate (8c). According to the general procedure, diazoacetate **8c** was obtained from **7c** (1.27 g, 7 mmol). Purification by column chromatography (silica gel, benzene) gave **8c** (1.06 g, 66%) as a yellow solid: mp 32−34 °C; IR ($CHCl_3$) cm^{-1} 2116, 1690, 1494, 1449, 1242, 1181; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 (2H, d, J = 6.4 Hz), 4.77 (1H, br s), 5.88 (1H, dt, J = 6.4, 15.0 Hz), 6.45 (1H, dd, J = 10.5, 15.0 Hz), 6.59 (1H, d, J = 15.5 Hz), 6.77 (1H, dd, J = 10.5, 15.5 Hz), 7.24 (1H, t, J = 7.3 Hz), 7.32 (2H, t, J = 7.3 Hz), 7.55 (2H, d, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.8 (d), 64.6 (t), 126.1 (d), 127.3 (d), 127.5 (d), 128.3 (d), 133.5 (d), 134.2 (d), 136.5 (s), 170.2 (s); MS (EI) m/z 128 (base peak), 228 (M^+); HRMS Calcd for $C_{13}H_{12}N_2O_2$ (M^+): 228.0899, found: 228.0876.

3,4-(Methylenedioxy)cinnamyl α-Diazoacetate (8d). Diazoacetate **8d** was obtained from **7d** (5.64 g, 22 mmol). Purification by column chromatography (silica gel, benzene) gave **8d** (3.97 g, 75%) as a yellow solid: mp 61.2−61.4 °C; IR ($CHCl_3$) cm^{-1} 2115, 1688, 1607, 1504, 1447, 1181, 1041; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (1H, br s), 4.78 (2H, d, J = 6.4 Hz), 5.96 (2H, s), 6.12 (1H, dq, J = 6.4, 16.0 Hz), 6.56 (1H, d, J = 16.0 Hz), 6.76 (1H, d, J = 8.2 Hz), 6.83 (1H, dd, J = 1.4, 8.2 Hz), 6.93 (1H, d, J = 1.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.3 (d), 65.4 (t), 101.2 (t), 105.8 (d), 108.3 (d), 121.2 (d), 121.6 (d), 130.5 (s), 134.2 (d), 147.7 (s), 148.1 (s), 166.7 (s); MS (EI) m/z 103 (base peak), 246 (M^+); HRMS Calcd for $C_{12}H_{10}N_2O_4$ (M^+): 246.0641, found: 246.0662.

General Procedure for the Cu-Catalyzed Cyclopropanation of Diazoacetate 8.[9] The diazo ester **8** (1 equiv) in dry benzene was added over 30 min to a refluxing slurry of anhydrous $CuSO_4$ (2.4 equiv) and $Cu(acac)_2$ (0.05 equiv) in dry benzene. The resulting mixture was further refluxed for 15 min−1 h and filtered through a pad of Celite, and the filtrate was concentrated to give a residue which was submitted to flash column chromatography followed by recrystallization or distillation to afford the cyclopropa[*c*]furan **9**.

Oxo-1,3,3a,4a-tetrahydro-4-phenylcyclopropa[*c*]furan (9a). According to the general procedure, the cyclopropa[*c*]furan **9a**[24] (1.53 g, 44%), colorless prisms, was obtained from the diazoacetate **8a** (4.06 g, 20 mmol) after purification by column chromatography (silica gel, benzene) followed by recrystallization: mp 95.6−95.8 °C (benzene/hexane); IR ($CHCl_3$) cm^{-1} 1770, 1604, 1498, 1176, 1042; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (2H, m), 2.53 (1H, dd, J = 3.7, 9.6 Hz), 4.42 (1H, d, J = 9.6 Hz), 4.47 (1H, dd, J = 4.6, 9.6 Hz), 7.07 (2H, d, J = 6.8 Hz), 7.23−7.27 (1H, m), 7.29−7.36 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2 (d), 27.4 (d), 29.4 (d), 69.7(t), 126.0 (d), 127.2 (d), 128.7 (d), 137.3 (s), 174.9 (s); MS (EI) m/z 32

(23) Barrett, A. G. M.; Doubleday: W. W.; Tustin, G. J. *Tetrahedron* **1996**, *52*, 15325−15338.

(24) Shi, H.-J.; Wei, Q.; Wu, H.-J. *Youji Huaxue* **1997**, *17*, 76−81.

(base peak), 174 (M^+); HRMS Calcd for $C_{11}H_{10}O_2$ (M^+): 174.0681, found: 174.0665. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.56; H, 5.90.

1-Oxo-4-styryl-1,3,3a,4a-tetrahydrocyclopropa[*c*]furan (9c). The cyclopropa[*c*]furan **9c** (0.44 g, 51%), colorless platelets, was obtained from the diazoacetate **8c** (1 g, 4 mmol) after purification by flash column chromatography (silica gel, hexane/AcOEt = 80/20) followed by recrystallization: mp 114.1−114.3 °C (benzene/hexane); IR ($CHCl_3$) cm^{-1} 1771, 1596, 1493, 1451, 1175, 1037; ^1H NMR (400 MHz, $CDCl_3$) δ 2.02 (1H, dt, J = 2.7, 8.7 Hz), 2.22 (1H, dd, J = 2.7, 5.9 Hz), 2.37 (1H, m), 4.34 (1H, d, J = 5.6 Hz), 4.41 (1H, dd, J = 4.6, 9.6 Hz), 5.71 (1H, dd, J = 8.7, 15.9 Hz), 6.56 (1H, d, J = 15.9 Hz), 7.24 (1H, m), 7.31 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0 (d), 25.4 (d), 28.7 (d), 69.3 (t), 125.9 (d), 125.9 (d), 127.6 (d), 128.6 (d), 131.4 (d), 136.3 (s), 174.8 (s); MS (EI) *m/z* 115 (base peak), 200 (M^+); HRMS Calcd for $C_{13}H_{12}O_2$ (M^+): 200.0837, found: 200.0847.

Oxo-4-(3,4-(methylenedioxy)phenyl)-1,3,3a,4a-tetrahydrocyclopropa[*c*]furan (9d). Cyclopropa[*c*]furan **9d** was obtained from **8d** (1.4 g, 6 mmol). Purification by column chromatography (silica gel, benzene) followed by recrystralization gave **9d** (0.73 g, 60%) as colorless needles: mp 127.9−128.3 °C (benzene/hexane); IR ($CHCl_3$) cm^{-1} 1769, 1610, 1505, 1449, 1176, 1041; ^1H NMR (400 MHz, $CDCl_3$) δ 2.26−2.30 (2H, m), 2.47 (1H, dd, J = 4.6, 9.6 Hz), 4.39 (1H, d, J = 9.6 Hz), 4.46 (1H, dd, J = 4.6, 9.6 Hz), 5.95 (2H, s), 6.52 (1H, d, J = 1.4 Hz), 6.58 (1H, dd, J = 1.4, 7.7 Hz), 6.74 (1H, d, J = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD) δ 26.0 (d), 27.4 (d), 29.5 (d), 70.1 (t), 101.3 (t), 106.4 (d), 108.5 (d), 119.7 (d), 131.0 (s), 146.9 (s), 148.1 (s), 175.8 (s); MS (EI) *m/z* 218 (base peak, M^+); HRMS Calcd for $C_{12}H_{10}O_4$ (M^+): 218.0579, found: 218.0566.

General Procedure for the Reduction of Lactone 9. The lactone **9** (1 equiv) in dry THF was added dropwise to a suspension of $LiAlH_4$ (1 equiv) in dry THF at 0 °C. The resulting mixture was stirred for 10−30 min at room temperature and then quenched with aqueous diethyl ether and stirred for 1 h at room temperature. After filtration through a pad of Celite, the filtrate was dried over $MgSO_4$ and concentrated to give a residue, which was purified by recrystallization or column chromatography to give the cyclopropanedimethanol **10**.

1α,2α,3β-3-Phenyl-1,2-cyclopropanedimethanol (10a). According to the general procedure, the cyclopropanedimethanol **10a** (1.27 g, 95%), colorless prisms, was obtained from the cyclopropa[*c*]furan **9a** (1.3 g, 7 mmol) after purification by recrystallization: mp 77−78 °C (benzene/hexane); IR (KBr) cm^{-1} 3307, 1604, 1605, 1069; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72−1.81 (3H, m), 2.55 (2H, br s, D_2O exchangeable), 3.48 (2H, m). 4.23 (2H, dd, J = 5.0, 11.8 Hz), 7.05 (2H, d, J = 7.3 Hz), 7.17 (1H, t, J = 7.3), 7.27 (2H, t, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2 (d), 28.6 (d), 61.9 (t), 125.9 (d), 125.9(d), 128.4 (d), 141.1 (s); MS (EI) *m/z* 130 (base peak), 178 (M^+); HRMS Calcd for $C_{11}H_{14}O_2$ (M^+): 178.0994, found: 178.0993. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.89; H, 7.91.

1α,2α,3β-3-(Prop-1-en-1-yl)-1,2-cyclopropanedimethanol (10b). Cyclopropanedimethanol **10b** (2.84 g, 97%), as a colorless oil, was obtained from **9b**[9] (2.86 g, 21 mmol) after purification by column chromatography (silica gel, hexane/AcOEt = 50/50): IR (neat) cm^{-1} 3336, 1438, 1066, 959; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23−1.27 (1H, m), 1.33−1.38 (2H, m), 1.64 (3H, dd, J = 1.8, 6.6 Hz), 2.12 (2H, s, D_2O exchangeable), 3.33 (2H, dd, J = 10.5, 11.9 Hz), 4.13 (2H, dd, J = 5.5, 11.9 Hz), 5.08 (1H, ddd, J = 1.8, 8.2, 15.5 Hz), 5.49 (1H, dq, J = 6.6, 15.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6 (q), 25.2 (d), 26.1 (d), 61.7 (t), 124.6 (d), 131.7 (d); MS (EI) *m/z* 55 (base peak), 142 (M^+); HRMS Calcd for $C_8H_{14}O_2$ (M^+): 142.0994, found: 142.1005.

1α,2α,3β-3-Styryl-1,2-cyclopropanedimethanol (10c). Cyclopropanedimethanol **10c** (1.65 g, 87%), as colorless leaflets, was obtained from **9c** (1.85 g, 9 mmol), after purification by recrystalization: mp 87.3−87.9 °C ($CHCl_3$/hexane); IR ($CHCl_3$) cm^{-1} 3610, 3388, 1648, 1597, 1493, 1077; ^1H NMR (400 MHz, $CDCl_3$) δ 1.47 (1H, m), 1.55 (2H, m), 2.76 (2H, br s, D_2O exchangeable), 3.40 (2H, dd, J = 10.5, 10.7 Hz), 4.18 (2H, br d, J = 10.7 Hz), 5.80 (1H, dd, J = 8.7, 15.5 Hz), 6.42 (1H, d, J = 15.5 Hz), 7.19 (1H, m), 7.31 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1 (d), 26.9 (d), 61.7 (t), 125.7 (d), 127.0 (d), 128.6 (d), 128.8 (d), 131.3 (d), 137.2 (s); MS (EI) *m/z* 91 (base peak), 204 (M^+); HRMS Calcd for $C_{13}H_{16}O_2$ (M^+): 204.1150, found: 204.1163.

1α,2α,3β-3-(3,4-Methylenedioxyphenyl)-1,2-cyclopropanedimethanol (10d). Cyclopropanedimethanol **10d** (1.91 g, 86%), as colorless platelet, was obtained from **9d** (2.1 g, 10 mmol) after purification by recrystallization: mp 104.2−104.7 °C ($CHCl_3$/hexane); IR ($CHCl_3$) cm^{-1} 3445, 1505, 1443, 1125, 1040; ^1H NMR (400 MHz, $CDCl_3$) δ 1.61−1.69 (2H, m), 1.74 (1H, t, J = 5.0 Hz), 2.36 (2H, br s, D_2O exchangeable), 3.45 (2H, dd, J = 10.5, 11.4 Hz), 4.21 (2H, dd, J = 5.5, 11.4 Hz), 5.91 (2H,s), 6.52 (1H, d, J = 1.8 Hz), 6.55 (1H, dd, J = 1.8, 7.7 Hz), 6.70 (1H, d, J = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD) δ 26.5 (d), 27.9 (d), 61.1 (t), 100.5 (t), 106.1 (d), 107.7 (d), 118.9 (d), 134.9 (s), 145.4 (s), 147.4 (s); MS (EI) *m/z* 115 (base peak), 222 (M^+); HRMS Calcd for $C_{12}H_{14}O_4$ (M^+): 222.0892, found: 222.0913.

(1*S*,2*R*,3*R*)-1-Acetoxymethyl-2-hydroxymethyl-3-phenylcyclopropane (11a). To a solution of the diol **10a** (500 mg, 2.8 mmol) in dry benzene (10 mL) were added lipase AK (250 mg) and vinyl acetate (0.28 mL, 3.0 mmol), and the mixture was stirred for 4 h at room temperature. After filtration and removal of the solvent, the resulting oil was chromatographed (hexane/AcOEt = 70/30) to afford **11a** (0.6 g, 97%) as a colorless oil: $[\alpha]^{27}_D$ = −13.8° (c = 1.5, $CHCl_3$) (>99% ee: DAICEL, CHIRALCEL OB (0.46 × 25 cm), 5% ^{i}PrOH/hex (v/v), flow rate; 1.0 mL/min; retention time, 28 min for (−)-isomer and 32 min for (+)-isomer. Eluent detection was monitored by UV absorbance at 254 nm); IR (neat) cm^{-1} 3441, 1734, 1605, 1504, 1240, 1118, 1030, 748; ^1H NMR (400 MHz, $CDCl_3$ + D_2O) δ 1.64−1.77 (2H,m), 1.80 (1H, t, J = 5.0 Hz), 3.59 (1H, dd, J = 8.7, 11.9 Hz), 4.00 (1H, dd, J = 5.5, 11.9 Hz), 4.06 (1H, dd, J = 9.1, 12.3 Hz), 4.56 (1H, dd, J = 5.5, 12.3 Hz), 7.06 (2H, d, J = 7.3 Hz), 7.18 (1H, t, 7.3 Hz), 7.29 (2H, t, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (q), 25.3 (d), 26.5 (d), 29.1 (d), 61.6 (t), 63.8 (t), 126.0 (d), 126.1 (d), 128.4 (d), 140.9 (s), 171.2 (s); MS (EI) *m/z* 43 (base peak), 220 (M^+); HRMS Calcd for $C_{13}H_{16}O_3$ (M^+): 220.1099, found: 220.1092.

(1*R*,2*S*,3*S*)-2-Acetoxymethyl-3-phenylcyclopropanecarboxylic Acid (12). To a solution of oxalyl chloride (0.78 mL, 8.9 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of dimethy sulfoxide (0.87 mL, 11.3 mmol) in CH_2Cl_2 (2 mL) and alcohol **11a** (985 mg, 4.5 mmol) in CH_2Cl_2 (8 mL) at −78 °C. Stirring was continued for 30 min at −78 °C, and NEt_3 (4.4 mL, 31.3 mmol) was added. The reaction mixture was stirred at −78 °C for 30 min and then at room temperature for 30 min and then quenched with water and extracted with CH_2Cl_2. Organic layer was washed with brine, dried over $MgSO_4$, and concentrated to give the corresponding aldehyde (1.14 g), which was used to the next reaction without further purification. The aldehyde (1.14 g) in ^{t}BuOH (10 mL) was added at 0 °C to a solution of $NaClO_2$ (6.15 g, 68 mmol) and NH_2SO_3H (6.72 g, 68 mL) in H_2O (50 mL). The mixture was stirred at room temperature for 1 h, extracted with Et_2O, washed with brine, and dried over $MgSO_4$. Removal of the solvent gave the crude carboxylic acid **12** (1.45 g), which was used to the next reaction without further purification.

(2*S*,1′*S*,2′*R*,3′*R*)-*N*-(1′-Acetoxymethyl-3′-phenyl-2′-cyclopropanecarbonyl)phenylglycine Methyl Ester (13*S*). To a stirred solution of a mixture of carboxylic acid **12** (5.4 mg, 23 μmol) and (*S*)-phenylglycine methyl ester hydrochloride ((*S*)-PGME·HCl; 5.6 mg, 28 μmol) in DMF (0.1 mL) were successively added benzotriazole-1-yl-oxy-tris(pyrrolidine)-phosphonium hexafluorophosphate (PyBOP; 14 mg, 27 μmol), 1-hydroxybenzotriazole (HOBT; 3.7 mg, 27 μmol), and NEt_3 (8 μL, 57 μmol) at 0 °C. The mixture was stirred for 14 h at room temperature, diluted with AcOEt, washed with 5% HCl and sat. $NaHCO_3$, and dried over Na_2SO_4. Removal of the solvent and column chromatography (silica gel, hexane/AcOEt = 80/20) afforded the amide **13*S*** (3.1 mg, 29% from the alcohol

11a) as colorless crystals: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87 (3H, s), 1.96 (1H, dd, J = 4.9, 8.8 Hz), 2.01 (1H, m), 2.73 (1H, t, J = 5.9 Hz), 3.74 (3H, s), 4.16 (1H, dd, J = 8.3, 11.7 Hz), 4.54 (1H, dd, J = 6.4, 11.7 Hz), 5.65 (1H, d, J = 7.3 Hz), 6.71 (1H, d, J = 7.3 Hz), 7.10 (2H, d, J = 6.8 Hz), 7.19−7.39 (8H, m).

(2*R*,1′*S*,2′*R*,33′*R*)-*N*-(1′-Acetoxymethyl-3′-phenyl-2′-cyclopropanecarbonyl)phenylglycine Methyl Ester (13*R*). Carboxylic acid **12** (6.3 mg, 27 μmol) was reacted with (*R*)-PGME·HCl (6.5 mg, 32 μmol) as described for **13*S***. The crude product was purified by preparative TLC (silica gel, hexane/AcOEt = 50/50) to give **13*R*** (5.1 mg, 42% from the alcohol **11a**) as colorless crystals: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (1H, dd, J = 4.9, 8.8 Hz), 2.05 (1H, m), 2.08 (3H, s), 2.69 (1H, t, J = 5.9 Hz), 3.74 (3H, s), 4.32 (1H, dd, J = 8.3, 11.7 Hz), 4.56 (1H, dd, J = 6.8, 11.7 Hz), 5.62 (1H, d, J = 7.3 Hz), 6.71 (1H, d, J = 6.8 Hz), 7.07 (2H, d, J = 7.3 Hz), 7.17−7.36 (8H, m).

(1*S*,2*R*,3*R*)-1-Acetoxymethyl-2-hydroxymethyl-3-(1-propenyl)cyclopropane (11b). Diol **10b** (1 g, 7 mmol) was reacted with lipase AK (0.5 g) and vinyl acetate (0.78 mL, 8.5 mmol) at room temperature for 2.5 h as described for **11a**. The crude product was purified by column chromatography (silica gel, hexane/AcOEt = 70/30) to give **11b** (1.25 g, 97%) as a colorless oil: $[\alpha]^{26}_D$ = −11.9° (c = 4.17, $CHCl_3$) (>99% ee: determined by 400 MHz ^{1}H NMR of the corresponding Mosher's ester); IR (neat) cm^{-1} 3421, 1738, 1241, 1101, 962; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23−1.38 (3H,m), 1.61 (1H, br s, D_2O exchangeable), 1.64 (3H, dd, J = 1.4, 6.4 Hz), 2.08 (3H s), 3.45 (1H, dd, J = 9.1, 11.8 Hz), 3.87 (1H, dd, J = 9.6, 11.8 Hz), 3.89 (1H, dd, J = 5.9, 11.8 Hz), 4.49 (1H, dd, J = 5.5, 11.8 Hz), 5.09 (1H, ddd, J = 1.4, 7.7, 15.1 Hz), 5.51 (1H, dq, J = 6.4, 15.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5 (q), 20.9 (q), 22.8 (d), 24.4 (d), 26.8 (d), 61.3 (t), 63.7 (t), 124.3 (d), 131.4 (d), 171.0 (s); MS (EI) m/z 43 (base peak), 184 (M^+); HRMS Calcd for $C_{10}H_{16}O_3$ (M^+): 184.1099, found: 184.1086.

(1*S*,2*R*,3*R*)-1-Acetoxymethyl-2-hydroxymethyl-3-styrylcyclopropane (11c). Diol **10c** (1 g, 5 mmol) was reacted with lipase AK (0.5 g) and vinyl acetate (0.68 mL, 7.4 mmol) at room temperature for 3 h as described for **11a**. The crude product was purified by column chromatography (silica gel, hexane/AcOEt = 60/40) to give **11c** (1.12 g, 93%) as a colorless oil: $[\alpha]^{27}_D$ = −13.94° (c = 1.36, $CHCl_3$) (>99% ee: DAICEL, CHIRALCEL OB (0.46 × 25 cm), 5% ^{i}PrOH/hex (v/v), flow rate; 1.0 mL/min; retention time, 41 min for (−)-isomer and 48 min for (+)-isomer. Eluent detection was monitored by UV absorbance at 254 nm); IR ($CHCl_3$) cm^{-1} 3572, 3490, 1735, 1597, 1493; ^{1}H NMR (400 MHz, $CDCl_3$ + D_2O) δ 1.46−1.55 (3H,m), 2.10 (3H, s), 3.53 (1H, dd, J = 8.2, 11.9 Hz), 3.94 (1H, dd, J = 6.8, 11.9 Hz), 3.98 (1H, dd, J = 8.7, 11.9 Hz), 4.50 (1H, dd, J = 5.0, 11.5 Hz), 5.82 (1H, dd, J = 7.7, 15.5 Hz), 6.44 (1H, d, J = 15.5 Hz), 7.17−7.21 (1H, m), 7.26−7.29 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (q), 23.9 (d), 25.4 (d), 27.9 (d), 61.5 (t), 63.7 (t), 125.9 (d), 127.1 (d), 128.7 (d), 129.2 (d), 131.1 (d), 137.3 (s), 171.2 (s); MS (EI) m/z 43 (base peak), 246 (M^+); HRMS Calcd for $C_{15}H_{18}O_3$ (M^+): 246.1256, found: 246.1254.

(1*S*,2*R*,3*R*)-1-Acetoxymethyl-2-hydroxymethyl-3-(3,4-(methylenedioxy)phenyl)cyclopropane (11d). Diol **10d** (100 mg, 0.9 mmol) was reacted with lipase AK (50 mg) and vinyl acetate (0.05 mL, 0.54 mmol) at room temperature for 7 h as described for **11a**. The crude product was purified by column chromatography (silica gel, hexane/AcOEt = 50/50) to give **11d** (122 mg, 97%) as a colorless oil: $[\alpha]^{27}_D$ = −13.08° (c = 1.07, $CHCl_3$); IR (neat) cm^{-1} 3421, 1735, 1505, 1111, 933; ^{1}H NMR (400 MHz, $CDCl_3$ + D_2O) δ 1.53−1.67 (2H, m), 1.75 (1H, t, J = 5.5 Hz), 2.10 (3H, s), 3.57 (1H, dd, J = 8.7, 11.8 Hz), 3.98 (1H, dd, J = 5.5, 11.8 Hz), 4.03 (1H, dd, J = 8.7, 11.8 Hz), 4.53 (1H, dd, J = 5.9, 11.8 Hz), 6.54 (1H, d, J = 1.4 Hz), 6.56 (1H, dd, J = 1.4, 7.7 Hz), 6.71 (1H, d, J = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (q), 25.0 (d), 26.3 (d), 28.8 (d), 61.6 (t), 63.8 (t), 100.9 (t), 106.6 (d), 108.2 (d), 1194 (d), 134.7 (s), 145.9 (s), 147.8 (s), 171.2 (s); MS (EI) m/z 173 (base peak), 264 (M^+); HRMS Calcd for $C_{14}H_{16}O_5$ (M^+): 264.0998, found: 264.1004.

(1*S*,2*R*,3*S*)-1-Acetoxymethyl-2-iodomethyl-3-phenylcyclopropane (14a). To a solution of **11a** (0.78 g, 3.54 mmol) in dry benzene (15.6 mL) were added successively imidazole (0.6 g, 8.8 mmol), triphenylphosphine (1.86 g, 7.1 mmol), and iodine (1.8 g, 7.1 mmol). The reaction mixture was stirred at room temperature for 15 min, washed with sat. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel, hexane/AcOEt = 95/5) to give **14a** (1.09 g, 93%) as a colorless oil: $[\alpha]^{28}_D$ = −17.19° (c = 1.69, $CHCl_3$) (>99% ee: DAICEL, CHIRALCEL OB (0.46 × 25 cm), 1% ^{i}PrOH/hex (v/v), flow rate; 1.0 mL/min; retention time, 38 min for (+)-isomer and 56 min for (−)-isomer. Eluent detection was monitored by UV absorbance at 254 nm); IR (neat) cm^{-1} 1736, 1602, 1499, 1233, 1029; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84−1.94 (3H, m), 2.10 (3H, s), 3.30 (1H, dd, J = 6.8, 9.6 Hz), 3.47 (1H, dd, J = 6.4, 9.6 Hz), 4.23 (1H, dd, J = 7.3, 11.8 Hz), 4.36 (1H, dd, J = 6.4, 11.8 Hz), 7.10 (2H, d, J = 7.3 Hz), 7.19 (1H, t, J = 7.3 Hz), 7.28 (2H, t, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.1 (t), 21.0 (q), 29.1 (d), 31.0 (d), 33.0 (d), 62.4 (t), 126.2 (d), 126.3 (d), 128.5 (d), 140.0 (s), 170.9 (s); MS (CI) m/z 203 (base peak), 331 (M^+ + 1); HRMS Calcd for $C_{13}H_{16}O_2I$ (M^+ + 1): 331.0195, found: 331.0193.

(1*S*,2*R*,3*S*)-1-Acetoxymethyl-2-bromomethyl-3-(1-propenyl)cyclopropane (14b). To a solution of **11b** (100 mg, 0.54 mmol) in dry CH_2Cl_2 (4 mL) was added triphenylphosphine (214 mg, 0.82 mmol) and carbon tetrabromide (270 mg, 0.81 mmol). After being stirred at room temperature for 15 min, the reaction mixture was quenched with sat. $NaHCO_3$. Organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated to give a residue which was submitted to column chromatography (Chromatorex/NH, hexane) to provide **14b** (111 mg, 83%) as a colorless oil: $[\alpha]^{30}_D$ = −1.2° (c = 0.77, $CHCl_3$); IR (neat) cm^{-1} 1737, 1233; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33−1.39 (1H, m), 1.42−1.55 (2H, m), 1.65 (2H, d, J = 6.2 Hz), 2.08 (3H, s), 3.35 (1H, dd, J = 8.8, 10.5 Hz), 3.62 (1H, dd, J = 6.8, 10.5 Hz), 4.09 (1H, dd, J = 7.7, 12 Hz), 4.24 (1H, dd, J = 6.6, 12.0 Hz), 5.10 (1H, dd, J = 7.7, 15.1 Hz), 5.53 (1H, dq, J = 6.6, 15.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.7 (q), 20.9 (q), 25.7 (d), 27.3 (d), 29.0 (d), 32.9 (t), 62.7 (t), 125.2 (d), 130.6 (d), 170.9 (s); MS (EI) m/z 43 (base peak), 167 (M^+ − 79); HRMS Calcd for $C_{10}H_{15}O_2$ (M^+ − 79): 167.1072, found: 176.1058.

(1*S*,2*R*,3*S*)-1-Acetoxymethyl-2-bromomethyl-3-styrylcyclopropane (14c). Bromide **14c** (87 mg, 70%), as a colorless oil, was obtained from **11c** (100 mg, 0.41 mmol), as described for **14b**, after purification by column chromatography (Chromatorex/NH, hexane): $[\alpha]^{30}_D$ = −9.0° (c = 0.95, $CHCl_3$); IR (neat) cm^{-1} 1736, 1648, 1598, 1493, 1449, 1233; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56−1.74 (3H, m), 2.09 (3H, s), 3.40 (1H, dd, J = 8.6, 10.5 Hz), 3.69 (1H, dd, J = 6.6, 10.5 Hz), 4.18 (1H, dd, J = 7.3, 12.1 Hz), 4.29 (1H, dd, J = 6.6, 12.1 Hz), 5.81 (1H, dd, J = 8.1, 15.8 Hz), 6.46 (1H, d, J = 15.8 Hz), 7.17−7.35 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9 (q), 26.4 (d), 28.1 (d), 29.8 (d), 32.4 (t), 62.5 (t), 125.7 (d), 127.1 (d), 128.5 (d), 129.5 (d), 129.8 (d), 136.8 (s), 170.9 (s); MS (EI) m/z 169 (base peak), 229 (M^+ − 79); HRMS Calcd for $C_{15}H_{17}O_2$ (M^+ − 79): 229.1228, found: 229.1273.

(1*S*,2*R*,3*S*)-1-Acetoxymethyl-2-bromomethyl-3-(3,4-(methylenedioxy)phenyl)cyclopropane (14d). Bromide **14d** (32 mg, 85%), as a colorless oil, was obtained from **11d** (30 mg, 0.11 mmol) after purification by column chromatography (Chromatorex/NH, hexane): $[\alpha]^{29}_D$ = −7.17° (c = 0.84, $CHCl_3$) IR (neat) cm^{-1} 1736, 1505, 1444, 1236, 1037; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72−1.80 (2H, m), 1.89 (1H, t, J = 5.1 Hz), 2.09 (3H, s), 3.51 (1H, dd, J = 8.0, 10.7 Hz), 3.65 (1H, dd, J = 7.3, 10.7 Hz), 4.20 (1H, dd, J = 7.2, 12.0 Hz), 4.33 (1H, dd, J = 6.6, 12.0 Hz), 5.92 (2H, s), 6.59 (1H, s), 6.60 (1H, d, J = 8.4 Hz), 6.72 (1H, d, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9 (q), 27.4 (d), 29.1 (d), 30.9 (d), 32.8 (d), 62.8 (t), 100.9 (t), 106.9 (d), 108.1 (d), 119.6 (d), 133.8 (s), 146.1 (s), 147.7 (s), 170.9 (s); MS (EI) m/z 43 (base peak), 326 (M^+), 328 (M^+ + 2); HRMS Calcd for $C_{14}H_{15}O_4Br$ (M^+): 326.0153, found: 326.0176.

(1*S*, 2*S*,3*R*)-1-Hydroxymethyl-2-phenyl-3-(phenylthiomethyl)cyclopropane (15). To a solution of the alcohol **11a**

(400 mg, 1.8 mmol) in dry pyridine (9 mL) were added diphenyl disulfide (1.19 g, 5.5 mmol) and tri-*n*-butylphosphine (1.36 mL, 5.5 mmol). After being stirred at room temperature for 1 h, the reaction mixture was diluted with Et_2O, washed with successively with 10% NaOH solution, 10% HCl solution and sat. $NaCO_3$ solution, and dried over $MgSO_4$. Removal of the solvent gave a crude oil, which was chromatographed (silica gel, hexane/AcOEt = 80/20) to afford the sulfide (574 mg, 100%) as a colorless oil: $[\alpha]^{28}_D = +23.6°$ ($c = 1.06$, $CHCl_3$); IR (neat) cm^{-1} 1733, 1605, 1503, 1233, 1092; ^1H NMR (400 MHz, $CDCl_3$) δ 1.60 (1H, m), 1.69 (1H, m), 1.82 (1H, t, $J = 5.5$ Hz), 2.08 (3H, s), 3.11 (1H, dd, $J = 7.3$, 13.2 Hz), 3.15 (1H, dd, $J = 7.7$, 13.2 Hz), 4.15 (1H, dd, $J = 8.2$, 11.8 Hz), 4.32 (1H, dd, $J = 6.8$, 11.8 Hz), 7.01 (2H, d, $J = 7.3$ Hz), 7.14−7.28 (6H, m), 7.36 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (q), 25.9 (d), 26.5 (d), 29.5 (d), 34.1 (t), 63.6 (t), 126.0 (d), 126.1 (d), 126.3 (d), 128.3 (d), 128.9 (d), 123.0 (d), 136.1 (s), 140.9 (s), 171.0 (s); MS (EI) *m*/*z* 143 (base peak), 312 (M^+); HRMS Calcd for $C_{19}H_{20}O_2S$ (M^+): 312.1184, found: 312.1169. To a solution of the sulfide (253 mg, 0.81 mmol) in EtOH (4 mL) was added 4 N KOH solution (1 mL). After being stirred at room temperature for 30 min, the mixture was concentrated, extracted with Et_2O, washed with brine, and dried over $MgSO_4$. Removal of the solvent gave a crude oil, which was chromatographed (silica gel, hexane/AcOEt = 70/30) to afford the hydroxy sulfide **15** (217 mg, 99%) as colorless solids: $[\alpha]^{28}_D = +89.2°$ ($c = 1.05$, $CHCl_3$); IR (KBr) cm^{-1} 3295, 1600, 1497, 701; ^1H NMR (400 MHz, $CDCl_3$ + D_2O) δ 1.56 (1H, m), 1.75 (2H, m), 2.87 (1H, dd, $J = 10.0$, 13.2 Hz), 3.51 (1H, dd, $J = 5.9$, 13.2 Hz), 3.58 (1H, dd, $J = 8.7$, 11.9 Hz), 4.02 (1H, dd, $J = 5.0$, 11.9 Hz), 7.01 (2H, d, $J = 7.3$ Hz), 7.15 (1H, t, $J = 7.3$ Hz), 7.24 (3H, m), 7.30 (2H, t, $J = 7.3$ Hz), 7.41 (2H, d, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5 (d), 20.0 (d), 20.7 (d), 25.1 (t), 52.7 (t), 116.9 (d), 117.0 (d), 117.7 (d), 119.4 (d), 120.0 (d), 121.3 (d), 126.3 (s), 130.2 (s); MS (EI) *m*/*z* 91 (base peak), 270 (M^+); HRMS Calcd for $C_{17}H_{18}OS$ (M^+): 270.1078, found: 270.1058.

(1*S*,2*R*,3*R*)-1-Iodomethyl-2-phenyl-3-(phenylthiomethyl)cyclopropane (16). Iodide **16** (40 mg, 99%), as a colorless oil, was obtained from **15** (30 mg, 0.11 mmol) as after purification by column chromatography (silica gel, hexane/AcOEt = 99.5/0.5): $[\alpha]^{29}_D = -1.50°$ ($c = 1.33$, $CHCl_3$); IR (neat) cm^{-1} 1602, 1583, 1497, 1480, 1437, 694; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72−1.91 (3H, m), 3.05 (1H, dd, $J = 7.3$, 13.0 Hz), 3.25−3.33 (2H, m), 3.43 (1H, dd, $J = 7.9$, 10.1 Hz), 7.04−7.06 (2H, m), 7.14−7.29 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.1 (t), 30.7 (d), 31.5 (d), 32.9 (t), 35.1 (d), 126.1 (d), 126.2 (d), 126.4 (d), 128.3 (d), 128.9 (d), 130.1 (d), 135.9 (s), 140.3 (s); MS (EI) *m*/*z* 197 (base peak), 380 (M^+); HRMS Calcd for $C_{17}H_{17}IS$ (M^+): 380.0096, found: 380.0078.

(1*S*,2*S*,3*R*)-1-Methoxythiocarbonyloxymethyl-2-phenyl-3-(phenylthiomethyl)cyclopropane (17). To a solution of alcohol **15** (57 mg, 0.21 mmol) was added 1,1-thiocarbonyldiimidazole (57 mg, 0.32 mmol), and the mixture was stirred at 50 °C for 1.5 h. Removal of the solvent and column chromatography (silica gel, hexane/AcOEt = 90/10) gave the imidazolide (84 mg, 100%) as a colorless oil: $[\alpha]^{28}_D = +8.77°$ ($c = 2.17$, $CHCl_3$); IR (neat) cm^{-1} 1229, 1093; ^1H NMR (400 MHz, $CDCl_3$) δ 1.70−78 (1H, m), 1.86−1.93 (1H, m), 1.97 (1H, t, $J = 5.4$ Hz), 3.05 (1H, dd, $J = 7.8$, 13.2 Hz), 3.28 (1H, dd, $J = 6.8$, 13.2 Hz), 4.67 (1H, dd, $J = 8.3$, 11.7 Hz), 4.97 (1H, dd, $J = 6.8$, 11.7 Hz), 7.02−7.04 (3H, m), 7.17−7.22 (2H, m), 7.25−7.29 (4H, m), 7.35−7.38 (2H, m), 7.68 (1H, t, $J = 1.5$ Hz), 8.40 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1 (d), 26.6 (d), 29.6 (d), 34.3 (t), 73.0 (t), 118.0 (d), 126.2 (d), 126.4 (d), 126.7 (d), 128.5 (d), 129.1 (d), 130.3 (d), 130.9 (d), 135.6 (s), 136.9 (d), 140.0 (s), 184.2 (s); MS (EI) *m*/*z* 115 (base peak), 380 (M^+); HRMS Calcd for $C_{21}H_{20}ON_2S_2$ (M^+): 380.1017, found: 380.1017. A solution of the imidazolide (80 mg, 0.21 mmol) in MeOH(4 mL) was stirred at room temperature for 4 h. Removal of the solvent and column chromatography (silica gel, hexane/AcOEt = 95/5) gave the thiocarbonate **17** (63 mg, 87%) as a colorless oil: $[\alpha]^{28}_D = -10.7°$ ($c = 1.27$, $CHCl_3$); IR (neat) cm^{-1} 1244; ^1H NMR (400 MHz, $CDCl_3$) δ 1.61−1.68 (1H, m), 1.78−1.85 (1H, m), 1.90 (1H, t, $J = 5.0$ Hz), 3.09 (1H, dd, $J = 7.7$, 13.2 Hz), 3.18 (1H, dd, $J = 6.8$, 13.2 Hz), 4.06 (3H, s), 4.52 (1H, dd, $J = 8.2$, 11.4 Hz), 4.73 (1H, dd, $J = 6.8$, 11.4 Hz), 7.01 (2H, d, $J = 7.7$ Hz), 7.14−7.28 (6H, m), 7.37 (2H, d, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4 (d), 26.6 (d), 29.6 (d), 34.4 (t), 59.5 (t), 72.8 (t), 126.2 (d), 126.4 (d), 126.5 (d), 128.4 (d), 129.0 (d), 130.3 (d), 136.0 (d), 140.6 (s), 196.5 (s); MS (EI) *m*/*z* 143 (base peak), 344 (M^+); HRMS Calcd for $C_{19}H_{20}O_2S_2$ (M^+): 344.0905, found: 344.0932.

(1*S*,2*R*,3*R*)-1-Iodomethyl-2-phenyl-3-(phenylsulfonylmethyl)cyclopropane (18). To a solution of **15** (30 mg, 0.11 mmol) in CH_2Cl_2 (0.6 mL) was added $KHCO_3$ (7 mg, 0.07 mmol) and *m*-chloroperbenzoic acid (*m*CPBA; 43 mg, 0.25 mmol) at room temperature. After being stirred at room temperature for 2 h, the reaction mixture was diluted with CH_2Cl_2, washed with sat. $NaHCO_3$ and brine, and dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, hexane/AcOEt = 70/30) gave sulfone (32 mg, 94%) as colorless needles: mp 119.7−119.9 °C; $[\alpha]^{27}_D = +54.4°$ ($c = 0.79$, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 3501, 1606, 1502, 1308, 1146, 1086; ^1H NMR (400 MHz, $CDCl_3$ + D_2O) δ 1.47 (1H, m), 1.64 (1H, t, $J = 5.5$ Hz), 1.82 (1H, m), 3.25 (1H, dd, $J = 9.6$, 14.6 Hz), 3.49 (1H, dd, $J = 9.6$, 12.3 Hz), 3.57 (1H, dd, $J = 5.0$, 14.6 Hz), 4.06 (1H, dd, $J = 4.1$, 12.3 Hz), 6.97 (2H, d, $J = 7.3$ Hz), 7.17 (1H, t, $J = 7.3$ Hz), 7.25 (2H, t, $J = 7.3$ Hz), 7.55 (2H, t, $J = 7.3$ Hz), 7.67 (1H, t, $J = 7.3$ Hz), 7.92 (2H, d, $J = 7.3$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3 (d), 25.7 (d), 28.7 (d), 55.7 (t), 60.9 (t), 125.8 (d), 126.2 (d), 128.2 (d), 128.4 (d), 129.4 (d), 134.0 (d), 138.2 (s), 139.9 (s); MS (EI) *m*/*z* 91 (base peak), 302 (M^+); HRMS Calcd for $C_{17}H_{18}O_3S$ (M^+): 302.0977, found: 302.0978. Iodide **18** was synthesized from the sulfone (32 mg, 0.11 mmol) as described for **14a**. Purification by column chromatography (silica gel, hexane/AcOEt = 99/1) gave **18** (42 mg, 96%) as colorless solids: mp 126 °C; $[\alpha]^{28}_D = -54.1°$ ($c = 1.37$, $CHCl_3$); IR (KBr) cm^{-1} 1499, 1301, 1172, 776, 734; ^1H NMR (400 MHz, $CDCl_3$) δ 1.63−1.71 (2H, m), 1.84 (1H, m), 3.00 (1H, dd, $J = 9.6$, 10.5 Hz), 3.06 (1H, dd, $J = 9.1$, 14.6 Hz), 3.36 (1H, dd, $J = 7.3$, 10.5 Hz), 3.67 (1H, dd, $J = 5.0$, 14.6 Hz), 6.95 (2H, d, $J = 6.8$ Hz), 7.16−7.25 (3H, m), 7.41 (2H, t, $J = 7.7$ Hz), 7.58 (1H, t, $J = 7.3$ Hz), 7.78 (2H, d, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.5 (t), 24.2 (d), 29.5 (d), 34.0 (d), 54.9 (t), 126.1 (d), 126.5 (d), 128.4 (d), 128.4 (d), 129.3 (d), 133.8 (d), 138.7 (s), 139.3 (s); MS (CI) *m*/*z* 413 (base peak, $M^+ + 1$); HRMS Calcd for $C_{17}H_{18}O_2SI$ ($M^+ + 1$): 413.0072, found: 413.0119.

General Procedure for the Radical Fragmentation Reaction. A 0.01M solution of the radical precursor (1 equiv) in dry benzene was degassed by sonication for 0.5−1 h. To the solution was added tri-*n*-butyltin hydride (2 equiv) and 2,2′-azobisisobutyronitrile (cat.), and the reaction mixture was refluxed. After the reaction was completed, removal of the solvent and chromatography gave the product.

(2*S*)-2-Vinyl-3-phenyl-1-propyl Acetate (19). According to the general procedure, the olefin **19** (29 mg, 94%), as a colorless oil, was obtained from the iodide **14a** (50 mg, 0.15 mmol) after purification by column chromatography (silica gel, hexane): $[\alpha]^{30}_D = +0.74°$ ($c = 2.7$, $CHCl_3$) (>99% ee: DAICEL, CHIRALCEL OB (0.46 × 25 cm), 0.5% ^{i}PrOH/hex (v/v), flow rate; 0.1 mL/min; retention time, 95 min for (+)-isomer and 104 min for (−)-isomer. Eluent detection was monitored by UV absorbance at 254 nm); IR (neat) cm^{-1} 3029, 1742, 1643, 1235, 1039, 920; ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (3H, s), 2.64−2.79 (3H, m), 5.01 (1H, d, $J = 17.3$ Hz), 5.05 (1H, d, $J = 10.5$ Hz), 5.70 (1H, ddd, $J = 7.3$, 10.5, 17.3 Hz), 7.15 (2H, d, $J = 7.3$ Hz), 7.19 (1H, t, $J = 7.3$ Hz), 7.27 (2H, t, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9 (q), 37.7 (t), 44.3 (d), 66.3 (t), 116.5 (t), 126.2 (d), 128.3 (d), 129.2 (d), 138.2 (d), 139.2 (d), 171.0 (s); MS (EI) *m*/*z* 91 (base peak), 204 (M^+); HRMS Calcd for $C_{13}H_{16}O_2$ (M^+): 204.1150, found: 204.1143.

(2*S*)-2-Vinyl-3-(3,4-(Methylenedioxy)phenyl)-1-propyl Acetate (20). According to the general procedure, the olefin **20** (18 mg, 92%) as a colorless oil, was obtained from the bromide **14d** (26 mg, 0.10 mmol) after purification by column chromatography (silica gel, hexane): $[\alpha]^{29}_D = -3.30°$ ($c = 1.21$, $CHCl_3$); IR (neat) cm^{-1} 1738, 1503, 1442, 1244, 926; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (3H, s), 2.56−2.71 (3H, m), 4.01 (2H, d, $J = 5.5$ Hz), 5.02 (1H, d, $J = 18.2$ Hz), 5.06 (1H,

d, J = 10.5 Hz), 5.68 (1H, ddd, J = 7.3, 10.5, 18.2 Hz), 5.92 (2H, s), 6.59 (1H, dd, J = 1.4, 8.2 Hz), 6.64 (1H, d, J = 1.4 Hz), 6.72 (1H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9 (q), 37.5 (t), 44.5 (d), 66.3 (t), 100.8 (t), 108.1 (d), 109.5 (d), 116.6 (t), 122.0 (d), 132.9 (s), 138.2 (d), 145.9 (s), 147.5 (s), 171.0 (s); MS (EI) m/z 135 (base peak), 248 (M^+); HRMS Calcd for $C_{14}H_{16}O_4$ (M^+): 248.1049, found: 248.1071.

(3*R*)-3-Phenylthiomethyl-4-phenyl-1-butene (21) from Iodide 16. According to the general procedure, the olefin **21** (34 mg, 81%) as a colorless oil, was obtained from the iodide **16** (63 mg, 0.17 mmol) after purification by column chromatography (silica gel, hexane): $[\alpha]^{30}_D = +3.10°$ (c = 1.00, $CHCl_3$); IR (neat) cm^{-1} 3062, 1640, 1584, 1495, 992, 917, 739; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (1H, m), 2.73 (1H, dd, J = 7.3, 13.7 Hz), 2.88 (1H, dd, J = 7.3, 13.7 Hz), 2.89 (1H, dd, J = 6.4, 12.8 Hz), 2.99 (1H, dd, J = 5.9, 12.8 Hz), 4.99 (1H, d, J = 16.9 Hz), 5.05 (1H, d, J = 10.5 Hz), 5.74 (1H, ddd, J = 7.5, 10.5, 16.9 Hz), 7.12−7.28 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.7 (t), 40.3 (t), 44.7 (d), 116.0 (t), 125.7 (d), 126.1 (d), 128.2 (d), 128.8 (d), 128.9 (d), 129.3 (d), 136.8 (s), 139.4 (s), 140.1 (d); MS (EI) m/z 83 (base peak), 254 (M^+); HRMS Calcd for $C_{17}H_{18}S$ (M^+): 254.1129, found: 254.1124. **From the Thiocarbonate 17.** According to the general procedure, the olefin **21** (32 mg, 76%) as a colorless oil, was obtained from the thiocarbonate **17** (56 mg, 0.16 mmol) after purification by column chromatography (silica gel, hexane): $[\alpha]^{29}_D = +23.2$ (c = 0.95, $CHCl_3$).

(3*R*)-3-Phenylsulfonylmethyl-4-phenyl-1-butene (22). The olefin **22** (30 mg, 88%) as colorless solids, was obtained from the iodide **18** (50 mg, 0.12 mmol) after purification by column chromatography (silica gel, hex/AcOEt = 80/20): mp 53−54 °C; $[\alpha]^{30}_D = -0.77°$ (c = 2.09, $CHCl_3$); IR (neat) cm^{-1} 1643, 1586, 1496, 1306, 1147, 999, 921; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (1H, dd, J = 7.3, 13.7 Hz), 2.84 (1H, dd, J = 6.8, 13.7 Hz), 2.92 (1H, m), 3.12 (1H, dd, J = 7.3, 14.6 Hz), 3.17 (1H, dd, J = 5.5, 14.6 Hz), 4.93 (1H, d), 4.97 (1H, d, J = 10.5 Hz), 5.65 (1H, ddd, J = 8.2, 10.5, 17.3 Hz), 7.06 (2H, d, J = 6.8 Hz), 7.16−7.25 (3H, m), 7.51 (2H, t, J = 7.3 Hz), 7.62 (1H, t, J = 7.3 Hz), 7.83 (2H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.8 (d), 40.8 (t), 59.4 (t), 116.4 (t), 122.2 (d), 126.5 (d), 128.0 (d), 128.4 (d), 129.2 (d), 129.3 (d), 133.6 (d), 138.0 (s), 138.5 (d), 139.9 (s); MS (EI) m/z 91 (base peak), 286 (M^+): HRMS Calcd for $C_{17}H_{18}O_2S$ (M^+); 286.1028, found: 286.1039.

(2*S*)-2-Vinyl-3-phenyl-1-propanol (24). Acetate **19** (50 mg, 0.24 mmol) was reacted with 4 N KOH solution (0.4 mL) in ethanol (0.8 mL) as described for **15**. The crude product was purified by column chromatography (silica gel, hexane/AcOEt = 90/10) to give **24** (36 mg, 90%) as a colorless oil: $[\alpha]^{29}_D = -1.88°$ (c = 1.06, $CHCl_3$); IR (neat) cm^{-1} 3354, 1604, 1496, 1030, 917; ^{1}H NMR (400 MHz, $CDCl_3$ + D_2O) δ 2.56 (1H, m), 2.66 (1H, dd, J = 7.7, 13.7 Hz), 2.75 (1H, dd, J = 6.8, 13.7 Hz), 3.48 (1H, dd, J = 7.3, 10.5 Hz), 3.60 (1H, dd, J = 5.0, 10.5 Hz), 5.09 (1H, d, J = 17.3 Hz), 5.14 (1H, d, J = 10.5 Hz), 5.71 (1H, ddd, J = 8.2, 10.5, 17.3 Hz), 7.18 (3H, m), 7.28 (2H, t, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.4 (t), 48.0 (d), 64.8 (t), 117.1 (t), 126.0 (d), 128.2 (d), 129.2 (d), 139.2 (d), 139.7 (d); MS (EI) m/z 91 (base peak), 161 ($M^+ - 1$); HRMS Calcd for $C_{13}H_{16}O_2$ (M^+): 162.1045, found: 162.1036.

(3*S*)-3-Phenylthiomethyl-4-phenyl-1-butene ((*S*)-21). (*S*)-21 was synthesized from alcohol **24** (28 mg, 0.17 mmol) as described for the sulfenylation of **11a**: $[\alpha]^{29}_D = +22.2°$ (c = 1.13, $CHCl_3$).

(3*S*)-3-Phenylsulfonylmethyl-4-phenyl-1-butene ((*S*)-22). To a solution of **(*S*)-21** (40 mg, 0.16 mmol) in methanol (1 mL) was added Oxone in water (1 mL) at 0 °C. After being stirred at room temperature for 4.5 h, the reaction mixture was diluted with water and extracted with $CHCl_3$. The organic layers were combined, washed with brine, and dried over Na_2SO_4. Removal of the solvent followed by column chromatography (silica gel, hexane/AcOEt = 90/10) gave the (*S*)-**22** (43 mg, 95%): $[\alpha]^{29}_D = +0.80°$ (c = 1.26, $CHCl_3$).

(1*S*,2*R*,3*R*)-1-Acetoxymethyl-2-hydroxymethyl-3-phenethylcyclopropane (25). A solution of **11c** (20 mg, 0.08 mmol) and Pd−C (2 mg, 10%w/w) was stirred under H_2 atmosphere (3.5 atm) at room temperature for 3 h. After filtration, the solvent was removed, and chromatography (silica gel, hexane/AcOEt = 70/30) afforded the alcohol **25** (19 mg, 95%) as a colorless oil: $[\alpha]^{28}_D = -6.19°$ (c = 1.14, $CHCl_3$); IR (neat) cm^{-1} 3433, 1736, 1496, 1454, 1027, 750; ^{1}H NMR (400 MHz, $CDCl_3$ + D_2O) δ 0.60 (1H, ddd, J = 5.0, 6.8, 11.8 Hz), 1.06 (2H, m), 1.64 (2H, dt, J = 7.3, 7.3 Hz), 2.07 (3H, s), 2.69 (2H, dd, J = 6.8, 7.8 Hz), 3.36 (1H, dd, J = 9.1, 11.8 Hz), 3.75−3.82 (2H, m), 4.41 (1H, dd, J = 5.9, 12.3 Hz), 7.16 (2H, d, J = 7.3 Hz), 7.19 (1H, t, J = 7.3 Hz), 7.28 (2H, t, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (q), 21.7 (d), 22.0 (d), 26.2 (d), 34.8 (t), 35.6 (t), 62.1 (t), 64.4 (t), 125.9 (d), 128.4 (d), 128.5 (d), 141.7 (s), 171.1 (s); MS (EI) m/z 91 (base peak), 248 (M^+); HRMS Calcd for $C_{15}H_{20}O_3$ (M^+): 248.1412, found: 248.1411.

(1*S*,2*R*,3*S*)-1-Acetoxymethyl-2-iodomethyl-3-phenethylcyclopropane (26). Iodide **26** (86 mg, 88%), as a colorless oil, was synthesized from the alcohol **25** (98 mg, 0.27 mmol), as that described for **14a**, and purified by column chromatography (silica gel, hexane/AcOEt = 90/10): $[\alpha]^{28}_D = -15.6°$ (c = 8.6, $CHCl_3$); IR (neat) cm^{-1} 1736, 1495, 1454, 1236, 1171; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.64−0.70 (1H, m), 1.24−1.39 (2H, m), 1.62 (2H, q, J = 7.0 Hz), 2.07 (3H, s), 2.72 (2H, t, J = 7.0 Hz), 3.22 (2H, m), 4.00 (1H, dd, J = 8.1, 12.0 Hz), 4.17 (1H, dd, J = 6.6, 12.0 Hz), 7.16−7.31 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.6 (t), 21.0 (q), 26.8 (d), 28.2 (d), 28.5 (d), 34.8 (t), 35.3 (t), 62.9 (t), 125.8 (d), 128.3 (d), 128.3 (d), 141.6 (s), 170.9 (s); MS (EI) m/z 91 (base peak), 231 ($M^+ - 127$); HRMS Calcd for $C_{15}H_{19}O_2$ ($M^+ - 127$): 231.1385, found: 231.1377.

(1*S*,2*R*,3*R*)-1-Iodomethyl-2-phenethyl-3-(phenylthiomethyl)cyclopropane (27). Acetate **27** (60 mg. 0.24 mmol) was converted into the corresponding sulfide as described for sulfenylation of **11a**. Purification by column chromatography (silica gel, hexane/AcOEt = 90/10) gave the sulfide (82 mg, 99%) as a colorless oil: $[\alpha]^{28}_D = -6.14°$ (c = 1.14, $CHCl_3$); IR (neat) cm^{-1} 1736, 1235, 1025, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (1H, m), 1.00−1.09 (2H, m), 1.51−1.61 (2H, m), 2.06 (3H, s), 2.65 (2H, t, J = 7.7 Hz), 2.88 (1H, dd, J = 7.7, 13.2 Hz), 3.00 (1H, dd, J = 6.8, 13.2 Hz), 3.97 (1H, dd, J = 8.2, 11.8 Hz), 4.16 (1H, dd, J = 6.8, 11.8 Hz), 7.14−7.20 (4H, m), 7.26−7.29 (4H, m), 7.33−7.35 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (q), 22.9 (d), 23.1 (d), 25.1 (d), 34.0 (t), 35.2 (t), 35.4 (t), 64.2 (t), 125.8 (d), 126.1 (d), 128.3 (d), 128.4 (d), 128.9 (d), 129.6 (d), 136.6 (s), 141.9 (s), 171.1 (s); MS (EI) m/z 91 (base peak), 340 (M^+); HRMS Calcd for $C_{21}H_{24}O_2S$ (M^+): 340.1497, found: 340.1493. The sulfenyl acetate (37 mg, 0.11 mmol) was hydrolyzed as described for **15**. Purification by column chromatography (silica gel, hexane/AcOEt = 80/20) gave the alcohol (32 mg, 100%) as a colorless oil: $[\alpha]^{28}_D = +38.3°$ (c = 2.44, $CHCl_3$); IR (neat) cm^{-1} 3420, 1455; ^{1}H NMR (400 MHz, $CDCl_3$ + D_2O) δ 0.56 (1H, m), 0.94 (1H, m), 1.05 (1H, m), 1.59 (2H, dt, J = 7.3, 7.3 Hz), 2.66 (3H, t, J = 7.3 Hz), 2.68 (1H, dd, J = 10.9, 12.8 Hz), 3.26 (1H, dd, J = 5.9, 12.8 Hz), 3.36 (1H, dd, 9.6, 11.8 Hz), 3.80 (1H, dd, J = 5.0, 11.8 Hz), 7.14−7.36 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6 (d), 24.5 (d), 26.7 (d), 34.1 (t), 35.0 (t), 35.6 (t), 62.1 (t), 125.9 (d), 126.5 (d), 128.3 (d), 128.5 (d), 129.0 (d), 130.0 (d), 135.6 (s), 141.9 (s); MS (EI) m/z 91 (base peak), 298 (M^+); HRMS Calcd for $C_{19}H_{22}OS$ (M^+): 298.1391, found: 298.1371. Iodide **27** was synthesized from the alcohol (30 mg, 0.10 mmol) as described for **14a**. Purification by column chromatography (silica gel, hexane/AcOEt = 99.5/0.5) gave **27** (33 mg, 81%) as a colorless oil: $[\alpha]^{27}_D = -1.6°$ (c =, $CHCl_3$); IR (neat) cm^{-1} 1479, 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.58 (1H, m), 1.16−1.34 (2H, m), 1.53−1.60 (2H, m), 2.69 (2H, dt, J = 2.2, 7.7 Hz), 2.84 (1H, dd, J = 8.3, 13.0 Hz), 3.13 (1H, dd, J = 6.6, 13.0 Hz), 3.21 (2H, dd, J = 2.0, 8.4 Hz), 7.16−7.36 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.6 (t), 28.1 (d), 28.8 (d), 30.8 (d), 32.8 (t), 35.1 (t), 35.3 (t), 125.7 (d), 126.1(d), 128.2 (d), 128.4 (d), 128.9 (d), 129.6 (d), 136.3 (s), 141.8 (s); MS (EI) m/z 91 (base peak), 408 (M^+); HRMS Calcd for $C_{19}H_{21}IS$ (M^+): 408.0409, found: 408.0431.

(3*S*)-3-Vinyl-5-phenyl-1-pentyl Acetate (28) and (2*R*)-2-Vinyl-5-phenyl-1-pentyl Acetate (29). The radical reaction of the iodide **26** (19 mg, 0.05 mmol) gave an inseparable mixture of the olefins, **28** and **29** (12.5 mg, 100%), as a colorless

oil, after column chromatography (silica gel, hexane to hexane/AcOEt = 99/1). Separation was done by HPLC (Hibar RT 250−25 LiChrosorb Si 60 (7μm), hex/AcOEt = 99/1 (v/v), flow rate: 10 mL/min), **28** was obtained from the fast fractions, and the slow fractions contained **29**. **28**: $[\alpha]^{29}_D = +1.8°$ (c = 0.28, $CHCl_3$); IR (neat) cm^{-1} 1740, 1496, 1455, 1257, 1173; ^1H NMR (400 MHz, $CDCl_3$) δ 1.59 (2H, m), 1.72 (2H, m), 2.20 (3H, s), 2.13 (1H, m), 2.53 (1H, ddd, J = 6.8, 10.5, 14.1 Hz), 2.66 (1H, ddd, J = 5.5, 10.0, 13.7 Hz), 4.01 (1H, dt, J = 7.3, 11.0 Hz), 4.10 (1H, ddd, J = 5.5, 7.3, 11.0 Hz), 5.03 (1H, d, J = 17.3 Hz), 5.09 (1H, d, J = 10.5 Hz), 5.58 (1H, ddd, J = 9.1, 10.5, 17.3 Hz), 7.17 (3H, m), 7.27 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (q), 33.3 (t), 33.5 (t), 36.8 (t), 40.5 (d), 62.7 (t), 116.0 (t), 125.7 (d), 128.3 (d), 128.4 (t), 141.4 (d), 142.4 (s), 171.1 (s); MS (EI) m/z 43 (base peak), 232 ($M^+ - 59$); HRMS Calcd for $C_{15}H_{20}O_2$ (M^+): 232.1464, found:232.1427. **29**: $[\alpha]^{29}_D = +1.6°$ (c = 0.43, $CHCl_3$); IR (neat) cm^{-1} 1742, 1643, 1603, 1496, 1234, 1033; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44−1.70 (4H, m), 2.03 (3H, s), 2.38 (1H, m), 2.54−2.67 (2H, m), 3.98 (2H, d, J = 6.8 Hz), 5.06 (1H, d, J = 17.3 Hz), 5.07 (1H, d, J = 10.5 Hz), 5.59 (1H, ddd, J = 8.7, 10.5, 17.3 Hz), 7−16−7.17 (3H, m), 7.27 (2H, t, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (q), 28.7 (t), 30.6 (t), 35.9 (t), 43.1 (d), 67.2 (t), 116.5 (t), 125.6 (d), 128.2 (d), 128.3 (d), 138.7 (d), 142.2 (s), 171.0 (s); MS (EI) m/z 91 (base peak), 172 ($M^+ - 60$); HRMS Calcd for $C_{13}H_{16}$ (M^+): 172.1252, found: 172.1247.

3-Vinyl-5-phenyl-1-pentene (30). According to the general procedure for the radical reaction, the diene **30** (18.2 mg, 66%) as a colorless oil, was obtained from the iodide **27** (65 mg, 0.16 mmol), after purification by the column chromatography (silica gel, hexane): IR (neat) cm^{-1} 1652, 1507, 1456; ^1H NMR (400 MHz, $CDCl_3$) δ 1.74 (2H, dt, J = 7.6, 8.0 Hz), 2.62 (2H, t, J = 7.6 Hz), 2.74 (1H, m), 5.04 (2H, d, J = 16.8 Hz), 5.05 (2H, d, J = 10.4 Hz), 5.76 (2H, m), 7.18 (2H, m), 7.27 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.5 (t), 36.1 (t), 47.4 (d), 114.5 (t), 125.6 (d), 128.2 (d), 128.3 (d), 140.8 (d), 142.2 (s); MS (EI) m/z 53 (base peak), 172 (M^+); HRMS Calcd for $C_{13}H_{16}$ (M^+): 172.1252, found:172.1258.

(1*R*,2*R*,3*S*)-1-Acetoxymethyl-2-*tert*-butyldiphenylsiloxymethyl-3-(1-propenyl)cyclopropane (31). Imidazole (106 mg, 1.56 mmol), *tert*-butyldiphenylsilyl chloride (0.41 mL, 1.58 mmol), and 4-(dimethylamino)pyridine (8 mg, 65 μmol) were added to a solution of the alcohol **11b** (250 mg, 1.36 mmol) in dry CH_2Cl_2 (5 mL). After being stirred at room temperature for 30 min, the mixture was quenched with H_2O and extracted with CH_2Cl_2. Organic layer was washed with brine, dried over $MgSO_4$, and concentrated to give a residue which was purified by column chromatography (silica gel, hexane/AcOEt = 99/1) to give the silyl ether **31** (542 mg, 95%) as a colorless oil: $[\alpha]^{27}_D = -3.45°$ (c = 3.19, $CHCl_3$); IR (neat) cm^{-1} 1739, 1240, 1110; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (9H, s), 1.25 (3H, m), 1.63 (3H, dd, J = 1.4, 6.4 Hz), 2.02 (3H, s), 3.63 (1H, dd, J = 6.4, 10.9 Hz), 3.82 (1H, dd, J = 5.0, 10.9 Hz), 4.05 (1H, dd, J = 6.8, 11.8 Hz), 4.19 (1H, dd, J = 6.8, 11.8 Hz), 5.07 (1H, m), 5.44 (1H, dq, J = 6.4, 15.0 Hz), 7.36−7.47 (6H, m), 7.65−7.68 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7 (q), 19.2 (s), 21.0 (q), 23.0 (d), 24.7 (d), 26.6 (d), 26.9 (q), 62.8 (t), 64.1 (t), 124.0 (d), 127.6 (d), 129.6 (d), 132.0 (d), 133.7 (s), 135.6 (d), 171.1 (s); MS (EI) m/z 241 (base peak), 422 (M^+); HRMS Calcd for $C_{26}H_{34}O_3Si$ (M^+): 422.2277, found: 422.2265.

(1*S*,2*R*,3*S*)-*tert*-Butyl 2-Acetoxymethyl-3-*tert*-butyldiphenylsiloxymethylcyclopropanecarboxylate (32). Ruthenium trichloride hydrate (1 mg, 5 mol %) was added to a solution of the olefin **31** (30 mg, 0.07 mmol) and sodium metaperiodate (62 mg, 0.29 mmol) in CCl_4 (0.2 mL)−CH_3CN (0.2 mL)−H_2O (0.3 mL).[25] After being stirred at room temperature for 2 h, the mixture was quenched with H_2O, extracted with Et_2O, washed with brine, and dried over $MgSO_4$. Removal of the solvent gave the crude carboxylic acid (20 mg), which was dissolved in dry CH_2Cl_2 (0.2 mL). To the solution was added *tert*-butyl trichroloacetimidate (20 mg, 0.09 mmol) in cyclohexane (0.8 mL) and boron trifluoride diethyl etherate (0.9 mL, 20 mL/mmol),[26] and it was stirred at room temperature for 30 min. After quenching with $NaHCO_3$ (solid), the mixture was filtered through a pad of Celite, and the filtrate was concentrated to give a residue which was purified by column chromatography (silica gel, hex/AcOEt = 95/5) to give the ester **32** (10 mg, 29% from olefin **31**) as a colorless oil: $[\alpha]^{28}_D = +7.2°$ (c = 2.57, $CHCl_3$); IR (neat) cm^{-1} 1742, 1720, 1258, 1154, 1112; ^1H NMR (300 MHz, $CDCl_3$) δ 0.99−1.09 (1H, m), 1.05 (9H, s), 1.44 (9H, s), 1.80 (2H, m), 2.03 (3H, s), 3.69 (1H, dd, J = 6.8, 11.4 Hz), 3.77 (1H, dd, J = 5.9, 11.4 Hz), 4.01(1H, dd, J = 7.3, 11.4 Hz), 4.19 (1H, dd, J = 6.8, 11.8 Hz), 7.20−7.48 (6H, m), 7.60−7.72 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1 (s), 20.9 (q), 23.8 (d), 24.6 (d), 26.8 (q), 27.6 (d), 28.1 (q), 61.5 (t), 62.6 (t), 80.6 (s), 127.7 (d), 129.7 (d), 133.3 (s), 135.5 (d), 135.5 (d), 170.9 (s), 171.93 (s); MS (EI) m/z 32 (base peak), 425 ($M^+ - 57$); HRMS Calcd for $C_{24}H_{29}O_5Si$ ($M^+ - 57$): 425.1784, found: 425.1789.

(1*S*,2*S*,3*R*)-*tert*-Butyl 2-*tert*-Butyldiphenylsiloxymethyl-3-hydroxymethylcyclopropanecarboxylate (33). K_2CO_3 (40 mg, 0.29 mmol) was added to a solution of the acetate **32** (94 mg, 0.19 mmol) in MeOH (1.5 mL)−H_2O (0.5 mL). After being stirred at room temperature for 1.5 h, ethanol was removed, and the residue was diluted with water, acidified with dil HCl, and extracted with AcOEt. The organic layers were combined, washed with brine, and dried over $MsSO_4$. Removal of the solvent and column chromatography (silica gel, hexane/AcOEt = 90/10) gave **33** (73 mg, 85%) as a colorless oil: $[\alpha]^{27}_D = +38°$ (c = 1.9, $CHCl_3$); IR (neat) cm^{-1} 3481, 1718, 1260, 1172, 1111; ^1H NMR (300 MHz, $CDCl_3$ + D_2O) δ 1.06 (9H, s), 1.34 (1H, t, J = 4.4 Hz), 1.40 (9H, s), 1.83 (1H, m), 1.97 (1H, m), 3.42 (2H, t, J = 11.4 Hz), 4.00 (1H, dd, J = 5.3, 11.9 Hz), 4.06 (1H, dd, J = 5.7, 11.9 Hz), 7.37−7.46 (6H, m), 7.64−7.71 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.01 (s), 25.0 (d), 26.4 (d), 26.7 (q), 27.5 (d), 28.0 (q), 61.1 (t), 62.7 (t), 80.6 (s), 127.8 (d), 129.9 (d), 123.0 (d), 132.6 (s), 132.7 (s), 135.4 (d), 135.5 (d), 171.6 (s); MS (EI) m/z 199 (base peak), 383 ($M^+ - 57$); HRMS Calcd for $C_{22}H_{27}O_4S$ ($M^+ - 57$): 383.1679, found: 383.1677.

(1*R*,2*R*,3*R*)-*tert*-Butyl 2-*tert*-Butyldiphenylsiloxymethyl-3-iodomethylcyclopropanecarboxylate (34). The iodide **34** (74 mg, 98%), a colorless oil, was obtained from the alcohol **33** (60 mg, 0.14 mmol) after purification by column chromatography (silica gel, hexane/AcOEt = 95/5): $[\alpha]^{28}_D = +3.98°$ (c = 1.76, $CHCl_3$); IR (neat) cm^{-1} 1719, 1151, 1112; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (9H, s), 1.44−1.48 (1H, m), 1.44 (9H, s), 1.89 (1H, s), 2.03 (1H, s), 3.21 (1H, dd, J = 8.7, 10.0 Hz), 3.28 (1H, dd, J = 8.2, 10.0 Hz), 3.79 (1H, dd, J = 6.4, 11.4 Hz), 3.83 (1H, dd, J = 5.5, 11.4 Hz), 7.37−7.46 (6H, m), 7.65−7.69 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.6 (t), 19.1 (s), 26.8 (q), 28.1 (q), 29.5 (d), 29.6 (d), 31.8 (d), 60.1 (t), 80.6 (s), 127.7 (d), 129.8 (d), 133.2 (s), 135.5 (d), 135.6 (d), 171.5 (s); MS (EI) m/z 57 (base peak), 493 ($M^+ - 57$); HRMS Calcd for $C_{22}H_{26}IO_3Si$ ($M^+ - 57$): 493.0696, found: 493.0734.

(1*R*,2*S*,3*S*)-*tert*-Butyl 2-Acetoxymethyl-3-phenetylcyclopropanecarboxylate (35). Swern oxidation of the alcohol **25** (577 mg, 2.3 mmol) gave the crude aldehyde (639 mg), which was oxidized with sodium chlorite to afford the carboxylic acid (611 mg). Esterification of the crude carboxylic acid (610 mg), as described for **32**, provided the *tert*-butyl ester **35** (662 mg, 89% from the alcohol **25**) as a colorless oil: $[\alpha]^{27}_D = +20°$ (c = 5.5, $CHCl_3$); IR (neat) cm^{-1} 1740, 1717, 1496, 1455, 1257, 1158; ^1H NMR (300 MHz, $CDCl_3$) δ 1.33−1.76 (5H, m), 1.44 (9H, s), 2.02 (3H, s), 2.70 (2H, t, J = 7.3 Hz), 4.02 (1H, dd, J = 8.4, 11.4 Hz), 4.42 (1H, dd, J = 5.5, 11.4 Hz), 7.14−7.30 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9 (q), 25.7 (d), 25.7 (d), 26.4 (d), 28.0 (q), 34.2 (t), 35.2 (t), 62.6 (t), 80.4 (t), 125.9 (d), 128.3 (d), 128.4 (d), 141.3 (s), 170.8 (s), 170.9 (s); MS (EI) m/z 91 (base peak), 318 (M^+); HRMS Calcd for $C_{19}H_{26}O_4$ (M^+): 318.1831, found: 318.1830.

(1*R*,2*S*,3*S*)-*tert*-Butyl 2-Hydroxymethyl-3-phenetylcyclopropanecarboxylate (36). Hydrolysis of the acetate **35**

(25) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936−3938.

(26) Armstrong, A.; Brackenridge, I.; Jackson, R. F. W.; Kirk, J. M. *Tetrahedron Lett.* **1998**, *29*, 2483−2486.

(350 mg, 1.1 mmol) gave the alcohol **36** (262 mg, 86%) as a colorless oil, after purification by column chromatography (silica gel, hexane/AcOEt = 90/10): $[\alpha]^{28}_D = +4.8°$ ($c = 3.45$, $CHCl_3$); IR (neat) cm^{-1} 3420, 1715, 1603, 1496, 1455, 1156; ^1H NMR (400 MHz, $CDCl_3 + D_2O$) δ 1.29 (1H, m), 1.42−1.50 (2H, m), 1.45 (9H, s), 1.58−1.75 (2H, m), 2.68 (1H, d, $J = 7.3$, 13.7 Hz), 2.75 (1H, dd, $J = 6.4$, 13.2 Hz), 3.69 (1H, dd, $J = 7.7$, 11.8 Hz), 3.84 (1H, dd, $J = 5.0$, 11.8 Hz), 7.15−7.21 (3H, m), 7.26−7.29 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.4 (d), 25.8 (d), 28.1 (q), 30.7 (d), 34.5 (t), 35.3 (t), 60.1 (t), 80.6 (s), 125.8 (d), 128.3 (d), 128.4 (d), 141.4 (s), 172.6 (s); MS (EI) *m/z* 91 (base peak), 276 (M^+); HRMS Calcd for $C_{17}H_{24}O_3$ (M^+): 276.1725, found: 276.1732.

(1*R*, 2*S*,3*R*)-*tert*-Butyl 2-Iodomethyl-3-phenetylcyclopropanecarboxylate (37). The iodide **37** (156 mg, 88%), a colorless oil, was obtained from the alcohol **36** (127 mg, 0.46 mmol) after purification by column chromatography (silica gel, hex/AcOEt = 99/1)**:** $[\alpha]^{29}_D = -77°$ ($c = 3.14$, $CHCl_3$); IR ($CHCl_3$) cm^{-1} 1707, 1178, 1142; ^1H NMR (400 MHz, $CDCl_3$) δ 1.39−1.44 (1H, m), 1.48 (9H, s), 1.53−1.62 (3H, m), 1.69 (1H, s), 2.71 (2H, t, $J = 7.3$ Hz), 3.38 (1H, dd, $J = 9.1$, 9.6 Hz), 3.49 (1H, dd, $J = 5.9$, 9.6 Hz), 7.14−7.20 (3H, m), 7.26−7.29 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.8 (t), 28.2 (q), 30.3 (d), 31.8 (d), 32.3 (d), 34.4 (t), 35.1 (t). 80.7 (s), 125.9 (d), 128.3 (d), 128.4 (d), 141.3 (s), 170.3 (s); MS (EI) *m/z* 203 (base peak), 313 ($M^+ - 73$); HRMS Calcd for $C_{13}H_{14}IO$ ($M^+ - 73$): 313.0089, found: 313.0124.

(3*S*)-*tert*-Butyl 3-*tert*-Butyldiphenylsiloxymethyl-pent-4-enecarboxylate (38). According to the general procedure for radical reaction, the olefin **38** (18 mg, 100%), a colorless oil, was obtained from the iodide **34** (23 mg, 0.04 mmol) after purification by column chromatography (silica gel, hex/AcOEt = 99/1): $[\alpha]^{29}_D = -4.86°$ ($c = 1.77$, $CHCl_3$); IR (neat) cm^{-1} 1730, 1259, 1171, 1111; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (9H, s), 1.42 (9H, s), 2.25 (1H, dd, $J = 8.7$, 15.0 Hz), 2.59 (1H, dd, $J = 5.5$, 15.0 Hz), 2.74 (1H, m), 3.56 (1H, dd, $J = 6.4$, 10.0 Hz), 3.64 (1H, dd, $J = 5.5$, 10.0 Hz), 5.05 (1H, d, $J = 10.0$ Hz), 5.07 (1H, d, $J = 17.3$ Hz), 5.76 (1H, ddd, $J = 7.7$, 10.0, 17.3 Hz), 7.35−7.44 (6H, m), 7.64−7.66 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3 (s), 26.8 (q), 28.1 (q), 37.3 (t), 42.9 (d), 66.4 (t), 80.2 (s), 116.0 (t), 127.6 (d), 129.6 (d), 133.6 (s), 135.6 (d), 138.3 (d), 172.0 (s); MS (EI) *m/z* 199 (base peak), 367 ($M^+ - 57$); HRMS Calcd for $C_{22}H_{27}O_3Si$ ($M^+ - 57$): 367.1729, found: 367.1748.

(3*R*)-*tert*-Butyl 5-Phenyl-3-vinylpentanoate (39). The olefin **39** (61.4 mg, 91%) as a colorless oil, was obtained from the iodide **37** (100 mg, 0.26 mmol) purification by column chromatography (silica gel, hex/AcOEt = 99/1): $[\alpha]^{28}_D = +6.8°$ ($c = 1.80$, $CHCl_3$); IR (neat) cm^{-1} 1730, 1496, 1455, 1259, 1172, 1144; ^1H NMR (400 MHz, $CDCl_3$) δ 1.42 (9H, s), 1.57−1.65 (1H, m), 1.69−1.78 (1H, m), 2.23 (1H, dd, $J = 8.2$, 14.6 Hz), 2.31 (1H, dd, $J = 6.4$, 14.6 Hz), 2.50−2.58 (2H, m), 2.66 (1H, ddd, $J = 5.5$, 10.5, 13.7 Hz), 5.07 (1H, d, $J = 11.4$ Hz), 5.08 (1H, d, $J = 15.9$ Hz), 5.68 (1H, ddd, $J = 8.7$, 114., 15.9 Hz), 7.17 (3H, m), 7.27 (2H, t, $J = 7.7$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.1 (q), 33.6 (t), 36.2 (t), 40.3 (d), 41.2 (t), 80.2 (s), 115.4 (t), 125.7 (d), 128.3 (d), 18.3 (d), 140.8 (d), 142.2 (s), 171.6 (s); MS (EI) *m/z* 91 (base peak), 260 (M^+); HRMS Calcd for $C_{17}H_{25}O_2$ (M^+): 261.1855, found: 261.1855.

(1*R*,2*S*,3*S*)-*tert*-Butyl 2-Acetoxymethyl-3-phenyl-cyclopropanecarboxylate (40). Esterification of the crude carboxylic acid **12** (1.45 g), as described for **32**, provided the *tert*-butyl ester **40** (0.96 g, 74% from the alcohol **11a**) as a colorless oil: $[\alpha]_D = +57°$ ($c = 1.62$, $CHCl_3$); IR (neat) cm^{-1} 1741, 1716, 1237, 1155, 1031; ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (9H, s), 2.02 (1H, m), 2.05 (3H, s), 2.07 (1H, dd, $J = 5.4$, 9.3 Hz), 2.59 (1H, t, $J = 5.9$ Hz), 4.22 (1H, dd, $J = 8.8$, 11.7 Hz), 4.61 (1H, dd, $J = 6.1$, 11.5 Hz), 7.09 (2H, d, $J = 7.1$ Hz), 7.21 (1H, t, $J = 7.1$ Hz), 7.29 (2H, t, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (q), 28.1 (q), 28.2 (d), 28.9 (d), 29.7 (d), 62.2 (t), 81.0 (s), 126.2 (d), 126.5 (d), 128.4 (d), 139.0 (s), 169.9 (s), 170.7 (s); MS (EI) *m/z* 43(base peak), 290 (M^+); HRMS Calcd for $C_{17}H_{22}O_4$ (M^+): 290.1518, found: 290.1501.

(1*R*,2*S*,3*S*)-*tert*-Butyl 2-Hydroxymethyl-3-phenyl-cyclopropanecarboxylate (41). Hydrolysis of acetate **40** (667 mg, 2.3 mmol) by K_2CO_3 in aqueous methanol gave the alcohol **41** (440 mg, 77%) as colorless crystals, after purification by column chromatography (silica gel, hexane/AcOEt = 90/10): mp 64−66 °C; $[\alpha]_D = +133°$ ($c = 1.49$, $CHCl_3$); IR (neat) cm^{-1} 3617, 3438, 1709, 1604, 1499, 1154; ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (9H, s), 1.94 (1H, m), 2.04 (1H, dd, $J = 5.4$, 9.0 Hz), 2.10 (1H, br s, D_2O exchangeable), 2.63 (1H, t, $J = 5.9$ Hz), 3.93 (1H, dd, $J = 7.8$, 12.0 Hz), 4.08 (1H, dd, $J = 4.9$, 12.0 Hz), 7.10 (2H, d, $J = 7.3$ Hz), 7.21 (1H, t, $J = 7.3$ Hz), 7.29 (2H, t, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1 (q), 29.3 (d), 32.3 (d), 59.8 (t), 81.2 (s), 126.1 (d), 126.4 (d), 128.4 (d), 139.6 (s), 171.5 (S); MS (EI) *m/z* 162 (base peak), 248 (M^+); HRMS Calcd for $C_{15}H_{20}O_3$ (M^+): 248.1413, found: 248.1416.

(1*R*,2*S*,3*R*)-*tert*-Butyl 2-Iodomethyl-3-phenyl-cyclopropanecarboxylate (42). Iodination of alcohol **41** (100 mg, 0.40 mmol) gave the iodide **42** (139 mg, 96%) as colorless crystals, after purification by column chromatography (silica gel, hexane/AcOEt = 90/10): mp 61−63 °C; $[\alpha]_D = +0.4°$ ($c = 1.41$, $CHCl_3$); IR (neat) cm^{-1} 1715, 1604, 1497, 1145; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (9H, s), 2.14 (1H, m), 2.23 (2H, dd, $J = 5.4$, 9.0 Hz), 2.57 (1H, dd, $J = 5.6$, 5.9 Hz), 3.57 (1H, t, $J = 9.8$ Hz), 3.71 (1H, dd, $J = 6.1$, 9.8 Hz), 7.10 (2H, d, $J = 7.0$ Hz), 7.22 (1H, t, $J = 7.3$ Hz), 7.29 (2H, t, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.7 (t), 28.3 (q), 32.9 (d), 34.1 (d), 35.8 (d), 81.3 (s), 126.1 (d), 126.6 (d), 128.5 (d), 138.8 (s), 169.4 (s); MS (EI) *m/z* 57 (base peak), 285($M^+ - 73$); HRMS Calcd for $C_{11}H_{10}IO$ ($M^+ - 73$): 284.9776, found: 284.9790.

(2*S*)-*tert*-Butyl 2-Benzylbut-3-enecarboxylate (43) and (3*R*)-*tert*-Butyl 3-Phenylpent-4-enecarboxylate (44). Radical reaction of iodide **42** (97 mg, 0.27 mmol) gave an inseparable 14:1 mixture of **43** and **44** (54 mg, 86%) as a colorless oil, after purification by column chromatography (silica gel, hexane/AcOEt = 98/2): ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (9 × 14/15 H, s), 1.35 (1/15 H, s), 2.61 (1/15 H, dd, $J = 7.8$, 15.1 Hz), 2.67 (1/15 H, dd, $J = 8.1$, 15.4 Hz), 2.81 (14/15 H, dd, $J = 6.8$, 13.7 Hz), 3.03 (14/15 H, dd, $J = 8.3$, 13.7 Hz), 3.23 (14/15 H, dd, $J = 8.1$, 15.4 Hz), 3.81 (1/15 H, dd, $J = 8.1$, 15.4 Hz), 5.08 (2H, m), 5.85 (14/15 H, ddd, $J = 8.3$, 9.5, 17.8 Hz), 5.98 (1H, ddd, $J = 7.1$, 10.0, 17.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9 (q), 27.9 (q), 38.5 (d), 41.4 (d), 45.9 (d), 52.8 (d), 80.6 (s), 114.5 (t), 117.0 (t), 126.2 (d), 126.5 (d), 127.6 (d), 128.1 (d), 128.4 (d), 129.1 (d), 136.0 (d), 138.8 (s), 140.4 (d), 172.6 (s).

(2*R*)-2-Vinyl-3-phenyl-1-propanol ((*R*)-24) and (3*R*)-3-Phenyl-pent-4-en-1-ol (45). Reduction of the mixture of **43** and **44** (54 mg, 0.23 mmol) by $LiAlH_4$ (12.2 mg, 32 mmol) in dry THF (5 mL) gave (*R*)-**24** (33 mg, 90%) and **45** (2.4 mg, 6%), after purification by column chromatography (silica gel, hexane/AcOEt = 90/10). (*R*)-**24**: $[\alpha]^{30}_D = +0.3°$ ($c = 2.87$, $CHCl_3$). **45**: $[\alpha]^{30}_D = -32°$ ($c = 0.17$, $CHCl_3$); IR (neat) cm^{-1} 3363, 1636, 915; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55 (1H, br s, D_2O exchangeable), 1.92−2.07 (2H, m), 3.48 (1H, ddd, $J = 7.3$, 7.8, 15.4 Hz), 3.62 (1H, ddd, $J = 6.3$, 10.7, 17.1 Hz), 3.63 (1H, ddd, $J = 6.3$, 10.7, 17.1 Hz), 5.05−5.11 (2H, m), 5.98 (1H, ddd, $J = 7.3$, 10.0, 17.3 Hz), 7.19−7.33 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.1 (t), 46.4 (d), 61.0 (t), 114.3 (t), 126.3 (d), 127.4 (d), 128.4 (d), 141.6 (d), 143.5 (s); MS (EI) *m/z* 117 (base peak), 162 (M^+); HRMS Calcd for $C_{11}H_{14}O$ (M^+): 162.1045, found: 162.1064.

(2′*S*,3′*R*,3*S*)-Ethyl 3-[2′-Acetoxymethyl-3′-(*tert*-butyldiphenylsilanyloxymethyl)cyclopropyl]acrylate (46). To a solution of **31** (500 mg, 1.18 mmol) in Et_2O (7.5 mL) and H_2O (7.5 mL) were added OsO_4 (cat.) and $NaIO_4$ (1.5 g, 7 mmol) at room temperature. The reaction mixture was stirred at room temperature for 18 h, filtered through a pad of Celite, extracted with Et_2O, washed with brine, and dried over $MgSO_4$. Removal of the solvent gave the crude aldehyde (357 mg), which was used for the next reaction without further purification. The mixture of the aldehyde (357 mg), triethyl phosphonoacetate (0.19 mL, 0.96 mmol), and $LiOH \cdot H_2O$ (40 mg, 0.95 mmol) in dry THF (0.9 mL) was stirred at room temperature for 14 h,[27] quenched with sat. NH_4Cl, extracted with AcOEt, washed with

(27) Bonadies, F.; Cardilli, A.; Lattanzi, A.; Orelli, L. R.; Scettri, A. *Tetrahedron Lett.* **1994**, *35*, 3383−3386.

brine, and dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, hexane/AcOEt = 95/5) gave **46** (374 mg, 66% from the olefin **31**) as a colorless oil: $[\alpha]^{30}_D$ = +9.9° (*c* = 2.19, $CHCl_3$); IR (neat) cm^{-1} 1740, 1714, 1646, 1239, 1084; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (9H, s), 1.28 (3H, t, *J* = 6.8 Hz), 1.45−1.54 (3H, m), 2.02 (3H, s), 3.72 (1H, dd, *J* = 2.9, 11.4 Hz), 3.81 (1H, dd, *J* = 5.0, 11.4 Hz), 4.11−4.17 (4H, m), 5.80 (1H, d, *J* = 15.5 Hz), 6.47 (1H, dd, *J* = 9.1, 15.5 Hz), 7.37−7.45 (6H, m), 7.65 (4H, t, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (q), 19.1 (s), 20.9 (q), 25.1 (d), 25.1 (d), 26.7 (q), 28.4 (d), 60.0 (t), 61.9 (t), 63.1 (t), 119.2 (d), 127.7 (d), 127.7 (d), 129.7 (d), 133.2 (s), 133.3 (s), 135.4 (d), 135.5 (d), 150.4 (d), 166.4 (s), 170.8 (s); MS (EI) *m*/*z* 241 (base peak), 480 (M^+); HRMS Calcd for $C_{28}H_{36}O_5Si$ (M^+): 480.2332, found: 480.2349.

(2′*S*,3′*R*,3*S*)-Ethyl 3-(2′-Acetoxymethyl-3′-iodomethyl)-cyclopropyl)acrylate (47). To the solution of **46** (200 mg, 0.42 mmol) was added tetra-*n*-butylammonium fluoride (0.54 mL, 1.0 M solution in THF) at 0 °C. After being stirred at 0 °C for 45 min then at room temperature for 30 min, the mixture was quenched with H_2O and extracted with CH_2Cl_2. Organic layer was washed with brine and dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, hexane/AcOEt = 65/35) gave the alcohol (96.4 mg, 96%) as a colorless oil: $[\alpha]^{29}_D$ = −0.53° (*c* = 0.76, $CHCl_3$); IR (neat) cm^{-1} 3445, 1739, 1714, 1644, 1238, 1145, 1082, 1033; ^1H NMR (300 MHz, $CDCl_3 + D_2O$) δ 1.28 (3H, t, *J* = 7.2 Hz), 1.49 (1H, m), 1.60 (2H, m), 2.09 (3H, s), 3.54 (1H, dd, *J* = 8.3, 11.9 Hz), 3.90 (1H, dd, *J* = 4.8, 11.9 Hz), 4.02 (1H, dd, *J* = 8.3, 11.9 Hz), 4.18 (2H, q, *J* = 7.2 Hz), 4.41 (1H, dd, *J* = 5.7, 11.9 Hz), 5.87 (1H, d, *J* = 15.6 Hz), 6.50 (1H, dd, *J* = 9.5, 15.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (q), 20.8 (q), 24.6 (d), 24.9 (d), 28.6 (d), 60.1 (t), 60.6 (t), 62.7 (t), 119.5 (d), 149.7 (s), 149.8 (d), 166.3 (s), 171.0 (s); MS (EI) *m*/*z* 43 (base peak), 242(M^+); HRMS Calcd for $C_{12}H_{18}O_5$ (M^+): 242.1155, found: 242.1187. Iodination of the alcohol (39 mg, 0.16 mmol) as described for **14a** gave the iodide **47** (52 mg, 92%) as a colorless oil, after purification by column chromatography (silica gel, hexane/AcOEt = 90/10): $[\alpha]^{30}_D$ = −2.6° (*c* = 1.48, $CHCl_3$); IR (neat) cm^{-1} 1739, 1714, 1646, 1234, 1144, 1031; ^1H NMR (300 MHz, $CDCl_3$) δ 1.28 (3H, t, *J* = 7.2 Hz), 1.52 (1H, m), 1.79 (2H, m), 2.09 (3H, s), 3.17 (1H, dd, *J* = 8.3, 10.3 Hz), 3.38 (1H, dd, *J* = 7.3, 10.3 Hz), 4.11−4.26 (4H, m), 5.89 (1H, d, *J* = 15.6 Hz), 6.47 (1H, dd, *J* = 9.5, 15.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 2.9 (t), 14.2 (q), 20.9 (q), 29.1 (d), 30.5 (d), 31.1 (d), 60.2 (t), 61.4 (t), 120.1 (d), 148.4 (d), 166.1 (s), 170.7 (s); MS (EI) *m*/*z* 43(base peak), 352(M^+); HRMS Calcd for $C_{12}H_{17}IO_4$(M^+): 352.0171, found:352.0154.

(*E*)-(3*R*)-Ethyl 5-Acetoxymethylhepta-3,6-dienoate ((*E*)-48), (*Z*)-(3*R*)-Ethyl 5-Acetoxymethylhepta-3,6-dienoate ((*Z*)-48), and (*E*)-(2*S*)-Ethyl 5-Acetoxymethylhepta-2,6-dienoate (49). Radical reaction of iodide **47** (50 mg, 0.14 mmol) gave the 5:1:1 mixture of (*E*)-**48**, (*Z*)-**48**, and **49** (26 mg, 80%) as a colorless oil. Separation was done by HPLC (Hibar RT 250−25 LiChrosorb Si 60 (7μm), hexane/AcOEt = 95/5 (v/v), flow rate; 10 mL/min (v/v), retention time; 77 min for (*Z*)-**48**, 86 min for (*E*)-**48** and 98 min for **49**. Eluent detection was monitored by UV absorbance at 215 nm). (*E*)-**48:** $[\alpha]^{30}_D$ = −0.06° (*c* = 1.02, $CHCl_3$); IR (neat) cm^{-1} 1739, 1730, 1640, 1238, 1175, 1035, 923; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (3H, t, *J* = 7.1 Hz), 2.04 (3H, s), 3.06 (2H, d, *J* = 6.8 Hz), 3.12 (1H, m), 4.06 (2H, d, *J* = 6.8 Hz), 4.14 (2H, q, *J* = 7.1 Hz), 5.11 (1H, dm, *J* = 16.4 Hz), 5.12 (1H, dm, *J* = 10.3 Hz), 5.50 (1H, dd, *J* = 7.3, 15.6 Hz), 5.66 (1H, dt, *J* = 7.3, 15.6 Hz), 5.74 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3 (q), 21.0 (q), 38.2 (t), 45.8 (d), 60.7 (t), 66.3 (t), 116.7 (s), 124.4 (d), 132.1 (d), 136.6 (d), 170.7 (s), 171.3 (s); MS (EI) *m*/*z* 43 (base peak), 181 (M^+ − 45); HRMS Calcd for $C_{10}H_{13}O_3$(M^+): 181.0865, found: 181.0869. (*Z*)-**48**: $[\alpha]^{30}_D$ = +0.9° (*c* = 0.16, $CHCl_3$); IR (neat) cm^{-1} 1740, 1638, 1240, 1176, 1036; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (3H, dt, *J* = 0.7, 7.1 Hz), 2.04 (3H, s), 3.11 (2H, dm, *J* = 7.1 Hz), 3.38 (1H, m), 4.01, (1H, dd, *J* = 7.3, 10.5 Hz), 4.05 (1H, dd, *J* = 6.6, 10.5 Hz), 4.15 (2H, dq, *J* = 0.7, 7.1 Hz), 5.11 (1H, dm, *J* = 9.0 Hz), 5.12 (1H, dm, *J* = 17.3 Hz), 5.45 (1H, dd, *J* = 9.5, 10.7 Hz), 5.68−5.80 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3 (q), 21.0 (q), 33.4 (t), 41.3 (d), 60.8 (t), 66.4 (t), 116.4 (t), 123.9 (d), 130.5 (d), 136.0 (d), 170.7 (s), 171.2 (s); MS (EI) *m*/*z* 43 (base peak), 181 (M^+ − 45); HRMS Calcd for $C_{10}H_{13}O_3$ (M^+): 181.0865, found: 181.0873. **49**:$[\alpha]^{30}_D$ = +0.3° (*c* = 0.18, $CHCl_3$); IR (neat) cm^{-1} 1743, 1719, 1232, 1177, 1042, 986, 921; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (3H, t, *J* = 7.1 Hz), 2.05 (3H, s), 2.27 (1H, m), 2.39 (1H, m), 2.57 (1H, m), 4.00 (1H, dd, *J* = 6.6, 11.0 Hz), 4.06 (1H, dd, *J* = 6.3, 11.0 Hz), 4.18 (2H, q, *J* = 7.1 Hz), 5.12 (1H, d, *J* = 17.3 Hz), 5.14 (1H, d, *J* = 10.5 Hz), 5.66 (1H, ddd, *J* = 7.8, 10.5, 17.1 Hz), 5.84 (1H, d, *J* = 15.6 Hz), 6.89 (1H, ddd, *J* = 7.3, 7.6, 15.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4 (q), 21.0 (q), 34.1 (t), 42.0 (d), 60.3 (t), 66.4 (t), 117.2 (t), 123.1 (d), 137.0 (d), 145.6 (d), 166.0 (s), 170.7 (s); MS (EI) *m*/*z* 43 (base peak), 181 (M^+ − 45); HRMS Calcd for $C_{10}H_{13}O_3$ (M^+): 181.0865, found: 181.0826.

(2*S*)-2-Vinyl-3-(3,4-(methylenedioxy)phenyl)-1-propanol ((*S*)-51). Hydrolysis of the acetate **20** (48 mg, 0.19 mmol) with KOH in aqueous ethanol gave (*S*)-**51** (39 mg, 97%) as a colorless oil after column chromatography (hexane/AcOEt = 80/20): $[\alpha]^{29}_D$ = +2.2° (*c* = 2.73, $CHCl_3$) (>99% ee: DAICEL, CHIRALCEL OB (0.46 × 25 cm), 1% ^{i}PrOH/hexane (v/v), flow rate; 1.0 mL/min; retention time; 44 min for (+)-isomer and 51 min for (−)-isomer. Eluent detection was monitored by UV absorbance at 254 nm); IR (neat) cm^{-1} 3376, 1504, 1488, 1246, 1039; ^1H NMR (400 MHz, $CDCl_3$) δ 2.49 (1H, m), 2.58 (1H, dd, *J* = 6.8, 13.7 Hz), 2.67 (1H, dd, *J* = 7.3, 13.7 Hz), 3.47 (1H, dd, *J* = 7.3, 10.5 Hz), 3.59 (1H, dd, *J* = 5.0, 10.5 Hz), 5.09 (1H, d, *J* = 17.8 Hz), 5.14 (1H, dd, *J* = 10.5 Hz), 5.69 (1H, ddd, *J* = 8.2, 10.5, 17.8 Hz), 6.61 (1H, d, *J* = 7.7 Hz), 6.66 (1H, s), 6.71 (1H, d, *J* = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.0 (t), 48.2 (d), 64.7 (t), 100.8 (t), 108.0 (d), 109.5 (d), 117.4 (t), 121.9 (d), 133.4 (s), 139.1 (d), 145.8 (s), 147.5 (s); MS (EI) *m*/*z* 135 (base peak), 206 (M^+); HRMS Calcd for $C_{12}H_{14}O_3$ (M^+): 206.0943, found: 206.0949.

(3*S*)-3-*tert*-Butyldimethylsiloxymethyl-4-(3,4-(Methylenedioxy)phenyl)-1-propene ((*S*)-52). Imidazole (24 mg, 0.35 mmol), *tert*-butyldimethylsilyl chloride (39 mg, 0.26 mmol), and 4-(dimethylamino)pyridine (cat.) were added to a solution of the alcohol (36 mg, 0.17 mmol) in dry DMF (0.8 mL). After being stirred for 1 h at room temperature, the mixture was quenched with H_2O and extracted with AcOEt. Organic layer was washed with brine and dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, hex/AcOEt = 97/3) gave the silyl ether (*S*)-**52** (53 mg, 95%) as a colorless oil: $[\alpha]^{28}_D$ = +3.75° (*c* = 1.07, $CHCl_3$); IR (neat) cm^{-1} 1504, 1488, 1041; ^1H NMR (400 MHz, $CDCl_3$) δ 0.04 (6H, s), 0.91 (9H, s), 2.40 (1H, m), 2.49 (1H, dd, *J* = 8.2, 13.7 Hz), 2.81 (1H, dd, *J* = 5.9, 13.7 Hz), 3.49 (1H, dd, *J* = 6.4, 10.0 Hz), 3.54 (1H, dd, *J* = 5.5, 10.0 Hz), 4.96 (1H, d, *J* = 18.2 Hz), 5.00 (1H, d, *J* = 10.0 Hz), 5.69 (1H, ddd, *J* = 7.7, 10.0, 18.2 Hz), 5.92 (2H, s), 6.61 (1H, d, *J* = 7.7 Hz), 6.67 (1H, s), 6.71 (1H, d, *J* = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.4 (q), −5.3 (q), 18.3 (s), 25.9 (q), 37.0 (t), 48.1 (d), 65.3 (t), 100.7 (t), 107.9 (d), 109.7 (d), 115.7 (t), 122.1 (d), 134.2 (s), 139.5 (d), 145.5 (s), 147.3 (s); MS (EI) *m*/*z* 320 (base peak, M^+); HRMS Calcd for $C_{18}H_{28}O_3Si$ (M^+): 320.1808, found: 320.1836.

(3*S*)-3-*tert*-Butyldimethylsiloxymethyl-4-(3,4-(methylenedioxy)phenyl)-1-butanol ((*S*)-53). 9-Borabicyclo[3.3.1]-nonane (0.7 mL, 0.5 M in THF) was added at 0 °C to a solution of the olefin (*S*)-**52** (56 mg, 0.17 mmol) in THF (1 mL). After being stirred at room temperature for 2 h, H_2O (0.5 mL), 3 N NaOH solution (0.2 mL), and 30% H_2O_2 solution (0.3 mL) were added to the mixture, and stirring was continued at room temperature for 2 h. The reaction mixture was extracted with AcOEt, washed with brine, and dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, hex/AcOEt = 95/5) gave the alcohol (*S*)-**53** (58 mg, 98%) as a colorless oil: $[\alpha]^{28}_D$ = −11° (*c* = 2.64, $CHCl_3$); IR (neat) cm^{-1} 3365, 1041; ^1H NMR (400 MHz, $CDCl_3 + D_2O$) δ 0.03 (3H, s), 0.04 (3H, s), 0.90 (9H, s), 1.56 (1H, m), 1.67 (1H, m), 1.88 (1H, m). 2.44 (1H, dd, *J* = 7.3, 13.7), 2.57 (1H, dd, *J* = 7.7, 13.7 Hz), 3.47 (1H, dd, *J* = 6.8, 10.0 Hz), 3.59 (1H, dd, *J* = 4.1, 10.5 Hz), 3.62 (1H, m), 3.67 (1H, m), 5.93 (2H, s), 6.60 (1H, d, *J* = 8.2 Hz), 6.66 (1H, s), 6.72 (1H, d, *J* = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ -5.6 (q), 18.2 (s), 25.8 (q), 35.4 (t), 37.7 (t),

40.8 (d), 60.9 (t), 65.6 (t), 100.7 (t), 107.9 (d), 109.4 (d), 121.9 (d), 134.2 (s), 145.6 (s), 147.5 (s); MS (EI) *m*/*z* 135 (base peak), 338 (M^+); HRMS Calcd for $C_{18}H_{30}O_4Si$ (M^+): 338.1913, found: 338.1899.

(*S*)-(−)-4-(3,4-Methylenedioxybenzyl)dihydrofuran-2(3*H*)-one ((*S*)-54). Dess−Martin periodinane (75 mg, 0.18 mmol) was added at 0 °C to a solution of the alcohol (*S*)-**53** (20 mg, 0.06 mmol) in CH_2Cl_2. After being stirred at room temperature for 1 h, the mixture was quenched with sat. $Na_2S_2O_3$ and sat. $NaHCO_3$ and stirred additional 20 min. The reaction mixture was extracted with CH_2Cl_2, washed with brine, and dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, hexane/AcOEt = 90/10) gave the aldehyde (19 mg, 94%) as a colorless oil. This aldehyde (18 mg, 0.05 mmol) was converted into the corresponding carboxylic acid (19.5 mg), which was taken up into CH_2Cl_2. *p*-Toluenesulfonic acid (cat.) was added to the solution and stirred for 2 h. The mixture was washed with brine and dried over $MgSO_4$. Removal of the solvent and chromatographic purification (silica gel, hex/AcOEt = 80/20) gave the lactone (*S*)-**54** (6.9 mg, 64% from the aldehyde) as a colorless oil: $[\alpha]^{28}_D = -3.60°$ (*c* = 1.09, $CHCl_3$); IR (neat) cm^{-1} 1775, 1243, 1172; ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (1H, dd, *J* = 6.8, 17.3 Hz), 2.60 (1H, dd, *J* = 8.2, 17.3 Hz), 2.67 (1H, dd, *J* = 8.7, 13.7 Hz), 2.71 (1H, dd, *J* = 6.8, 13.7 Hz), 2.80 (1H, m), 4.02 (1H, dd, *J* = 5.9, 9.1 Hz), 4.33 (1H, dd, *J* = 6.8, 9.1 Hz), 5.95 (2H, s), 6.60 (1H, d, *J* = 7.8 Hz), 6.63 (1H, s), 6.75 (1H, d, *J* = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.2 (t), 37.4 (d), 38.71 (t), 72.5 (t), 101.0 (t), 108.4 (d), 108.8 (d), 121.6 (d), 131.8 (s), 146.3 (s), 147.9 (s), 176.6 (s); MS (EI) *m*/*z* 135 (base peak), 220 (M^+); HRMS Calcd for $C_{12}H_{12}O_4$ (M^+): 220.0736, found: 220.0738.

(1*R*,2*S*3*S*)-1-*tert*-Butyldimethylsiloxymethyl-2-imidazolylthiocarbonyloxymethyl-3-(3,4-(methylenedioxy)-phenyl)cyclopropane (55). Silylation of the alcohol **11d** (100 mg, 0.38 mmol) as described for (*S*)-**52** gave the *tert*-butyldimethyl silyl ether (143 mg, 100%) as a colorless oil, after purification by column chromatography (silica gel, hexane/AcOEt = 90/10): $[\alpha]^{27}_D = -3.30°$ (*c* = 6.84, $CHCl_3$) (>99% ee: DAICEL, CHIRALCEL OD (0.46 × 25 cm), 1% ^{i}PrOH/hex (v/v), flow rate; 1.0 mL/min; retention time, 8 min for (+)-isomer and 13 min for (−)-isomer. Eluent detection was monitored by UV absorbance at 254 nm); IR (neat) cm^{-1} 1739, 1610, 1505, 1444, 1189; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (6H, s), 0.91 (9H, s), 1.48−1.56 (2H, m), 1.83 (1H, t, *J* = 5.0 Hz), 2.07 (3H, s), 3.69 (1H, dd, *J* = 6.8, 10.9 Hz), 3.91 (1H, dd, *J* = 5.0, 10.9 Hz), 4.19 (1H, dd, *J* = 6.8, 11.8 Hz), 4.28 (1H, 7.3, 11.8 Hz), 5.92 (2H, s), 6.55 (1H, s), 6.57 (1H, d, *J* = 7.7 Hz), 6.71 (1H, d, *J* = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −3.6 (q), 18.3 (s), 21.1 (q), 24.9 (d), 25.7 (d), 25.9 (q), 26.6 (d), 28.6 (d), 61.9 (t), 64.1 (t), 100.8 (t), 106.8 (d), 108.1 (d), 119.5 (d), 135.4 (s), 145.8 (s), 147.7 (s), 171.2 (s); MS (EI) *m*/*z* 117 (base peak), 378 (M^+); HRMS Calcd for $C_{20}H_{30}O_5Si$ (M^+): 378.1863, found: 378.1885. Hydrolysis of the silyl ether (146 mg, 0.39 mmol) as described for **33**, gave the alcohol (124 mg, 96%) as a colorless oil after purification by column chromatography (silica gel, hex/AcOEt = 95/5): $[\alpha]^{28}_D = +32.7°$ (*c* = 6.96, $CHCl_3$); IR (neat) cm^{-1} 3460, 1505, 1041; ^1H NMR (400 MHz, $CDCl_3 + D_2O$) δ 0.11 (3H,s), 0.13 (3H, s), 0.93 (9H, s), 1.50−1.57 (1H, m), 1.66−1.72 (2H, m), 3.38−3.48 (2H, m), 4.06 (1H, dd, *J* = 4.6, 11.4 Hz), 4.25 (1H, dd, *J* = 5.5, 11.4 Hz), 5.91 (2H, s), 6.51 (1H, d, *J* = 1.4 Hz), 6.54 (1H, dd, *J* = 1.4, 8.2 Hz), 6.70 (1H, d, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.5 (q), −5.3 (q), 18.2 (s), 25.9 (q), 27.0 (d), 28.4 (d), 28.9 (d), 62.3 (t), 62.9 (t), 100.9 (t), 106.4 (d), 108.1 (d), 119.1 (d), 135.1 (s), 145.8 (s), 147.8 (s); MS (EI) *m*/*z* 75 (base peak), 336(M^+); HRMS Calcd for $C_{18}H_{28}O_4Si$ (M^+): 336.1757, found: 336.1744. The imidazolide **55** (170 mg, 100%), as colorless prisms, was obtained from the alcohol (121 mg, 0.36 mmol) after purification by column chromatography (silica gel, hexane/AcOEt = 95/5): mp 40−42 °C; $[\alpha]^{30}_D = -21°$ (*c* = 2.05, $CHCl_3$); IR (neat) cm^{-1} 1505, 1464, 1232, 1094, 1040; ^1H NMR (400 MHz, $CDCl_3$) δ 0.06 (6H,s), 0.89 (9H, s). 1.64 (1H,. m), 1.74 (1H, m), 2.02 (1H, t, *J* = 5.0 Hz), 3.72 (1H, dd, *J* = 7.7, 11.4 Hz), 4.04 (1H, dd, *J* = 5.0, 11.4 Hz), 4.83 (1H, dd, *J* = 7.7, 11.4 Hz), 4.93 (1H, dd, *J* = 7.7, 11.4 Hz), 5.93 (2H, s), 6.56 (1H, s), 6.59 (1H, d, *J* = 7.7 Hz), 6.73 (1H, d, *J* = 7.7 Hz), 7.05 (1H, s), 7.67 (1H, s), 8.40 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.4 (q), −5.3 (q), 18.3 (s), 24.0 (d), 25.9 (q), 26.3 (d), 28.5 (d), 61.4 (t), 73.7 (t), 101.0 (t), 106.7 (d), 108.2 (d), 117.9 (d), 119.5 (d), 130.8 (d), 134.5 (s), 136.8 (d), 146.0 (s), 147.8 (s), 184.3 (s); MS (EI) *m*/*z* 187 (base peak), 446 (M^+); HRMS Calcd for $C_{22}H_{30}O_4N_2Si$ (M^+): 446.1696, found: 446.1702.

(3*R*)-3-*tert*-Butyldimethylsiloxymethyl-4-(3,4-(methylenedioxy)phenyl)-1-propene ((*R*)-52). According to the general procedure, the olefin **(*R*)-52** (67 mg, 55%), a colorless oil, was obtained from the imidazole **55** (169 mg, 0.38 mmol) after purification by column chromatography (silica gel, hexane/AcOEt = 99.5/0.5): $[\alpha]^{30}_D = -4.6°$ (*c* = 1.55, $CHCl_3$).

(2*R*)-2-Vinyl-3-(3,4-(methylenedioxy)phenyl)-1-propanol ((*R*)-51). The silyl ether (*R*)-**52** (19.6 mg, 0.06 mmol) was treated with tetra-*n*-butylammonium fluoride (0.07 mL, 1.0 M in THF) to give the alcohol (*R*)-**51** (12 mg, 94%), after purification by column chromatography (silica gel, hexane/AcOEt = 80/20): $[\alpha]^{30}_D = +2.6°$ (*c* = 0.33, $CHCl_3$) (>99% ee: DAICEL, CHIRALCEL OB (0.46 × 25 cm), 1% ^{i}PrOH/hexane (v/v), flow rate; 1.0 mL/min; retention time; 44 min for (+)-isomer and 51 min for (−)-isomer. Eluent detection was monitored by UV absorbance at 254 nm).

(*R*)-(−)-4-(3,4-Methylenedioxybenzyl)dihydrofuran-2(3*H*)-one ((*R*)-54). (*R*)-**52** (135 mg, 0.42 mmol) was submitted to hydroboration with 9-BBN as described for (+)-isomer, to afford the alcohol (100 mg, 70%) as a colorless oil: $[\alpha]^{28}_D = +14°$ (*c* = 4.1, $CHCl_3$). This alcohol (15 mg, 0.044 mmol) was converted into the corresponding aldehyde (14.3 mg) by Dess−Martin oxidation. This aldehyde was treated with tetra-*n*-butylammonium fluoride to give the corresponding lactol (6.2 mg). To a solution of the lactol (6 mg) was added pyridinium chlorochromate (29 mg, 0.13 mmol) at room temperature. After being stirred for 5 h, florisil (70 mg) and ether were added to the mixture. After further being stirred at room temperature for 30 min, the mixture was filtered through a pad of Celite, and the filtrate was concentrated to give a residue, which was purified by column chromatography (silica gel, hexane/AcOEt = 80/20) to give (*R*)-**54** (4 mg, 41% from the alcohol) as a colorless oil: $[\alpha]^{28}_D = +3.3°$ (*c* = 0.4, $CHCl_3$).

Acknowledgment. We are grateful to Professor Ilhyong Ryu, Osaka Prefecture University, for valuable discussions. We also thank Dr. Yoshihiko Hirose, Amano Pharmaceutical Co., Ltd., and Mr. Hidetoshi Shimizu, Novo Nordisk Bioindustry Ltd., for providing lipases PS, AK, and CAL. This work was supported in part by Grants-in-Aid for Scientific Research (No. 12877349) from the Ministry of Education, Science, Sports and Culture, Government of Japan.

JO010728D