Building a Small Polypropionate Library. Synthesis of All Possible Stereotetrads (Building Blocks for Polyketide Synthesis) from Furan

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The all diastereomeric stereotetrads (polypropionate fragments) were synthesized in a stereodivergent fashion, starting from the Diels−Alder adducts of furan with acrylic acid and (−)-2-camphanoxyacrylonitrile, respectively. The key intermediates of these sequences were the oxanorbornenic sulfones **7**, (−)-**53** and (+)-**54**. Regio- and stereocontrolled alkylative ring opening of these intermediates afforded the cyclohexenyl sulfones **14**, (+)-**55** and (−)-**58** which were transformed into the desired stereotetrads **30**, **31**, **40**, **41**, (+)-**62**, (+)-**63**, (−)-**66**, and (+)-**69**.

Introduction

The polyketides constitute an important family of natural products having a broad spectrum of biological activity such as antibiotic, antitumor, antifungal, antiparasitic, or immunomodulatory action.[1] Many of these compounds are referred to as polypropionates[2] (systems possessing units with alternating hydroxyl and methyl groups), reflecting their common biosynthesis from propionate and, to a lesser extent, acetate units.[3] The importance of these natural products as therapeutic agents and as biomedical tools together with their structural complexity has made these molecules attractive targets for synthetic organic chemists for over two decades.[4] The key to construct these systems, which possess a high level of stereochemical information, is the control of the absolute and relative stereochemistry. To this goal several strategies have been developed. Among them, sequences involving asymmetric aldol reactions[5] followed by stereoselective reduction have been successfully achieved.[6,7] The iteration of the method constitutes a biomimetic approach to these compounds. Although excellent chiral propionate reagents have been previously developed,[8] the iterative application of this methodology to the synthesis of polypropionate segments may not be ideal. In fact, such linear approaches require several synthetic steps in order to obtain the new synthon for the next propionate addition.

An alternative methodology was proposed by Hoffmann[9] with the introduction of the concept of "stereotriads". In this way "long sequences of stereocenters have

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(1) See, for instance, (a) O'Hagan, D. in *The Polyketide Metabolites*; Ellis Harwood: Chichester, 1991. (b) *Comprehensive Natural Products Chemistry*; Sankawa, V., Vol. Ed.; Barton, D. H. R.; Nakanishi, K.; Meth-Cohn, O., Gen. Eds.; Elsevier: New York, 1999, Vol. 1. For several reviews concerning the biosynthesis of polyketide metabolites, see: (c) O'Hagan, D. *Nat. Prod. Rep.* **1993**, *10*, 593. (d) Simpson, T. J. *Chem. Ind.* **1995**, 407. (e) Hopwood, D. A. *Chem. Rev.* **1997**, *97*, 2465. (f) Katz, L. *Chem. Rev.* **1997**, *97*, 2557. (g) Khosla, Ch. *Chem. Rev.* **1997**, *97*, 2577. (h) Simpson, T. J. *Top. Curr. Chem.* **1998**, *194*, 83.

(2) For selected accounts, see: (a) Masamune, S.; McCarthy, P. A. In *Macrolide Antibiotics: Chemistry, Biology and Practice*; Omura, S., Ed.; Academic Press: New York, 1984. (b) *Macrolides: Chemistry, Pharmacology and Clinical Uses*; Brysker, A. J.; Butzler, J. P.; Neu, H. C.; Tulkens, P. M., Eds.; Anette Blackwell: Paris, 1993. (c) O'Hagan, D. *Nat. Prod. Rep.* **1995**, *12*, 1. (d) Dutton, C. J.; Banks, B. J.; Cooper, C. B. *Nat. Prod. Rep.* **1995**, *12*, 165. (e) Davies-Coleman, M. T.; Garson, M. *J. Nat. Prod. Rep.* **1998**, *15*, 477.

(3) For general aspects, see: (a) Cane, D. E. *Science* **1990**, *263*, 338. (b) Staunton, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1302. (b) Robinson, J. A. In *Progress in Natural Products Chemistry*; Herz, W.; Kirby, G. W.; Steglich, W.; Tamm, C. Eds.; Springer: New York, 1991; Vol 58, pp 1−81. For the well-established mechanism of the biosynthesis of an emblematic member of this family, the erythromycin, see: (c) Mann, J. In *Chemical Aspects of Biosynthesis*; Oxford University Press: Cary, NC, 1994; p 30. (d) Cortés, J.; Wiesmann, K. E. H.; Roberts, G. A.; Brown, M. J. B.; Staunton, J.; Leadlay, P. F. *Science* **1995**, *268*, 147. (e) Pieper, R.; Luo, G.; Cane, D. E.; Khosla, Ch. *J. Am. Chem. Soc.* **1995**, *117*, 11373. (f) Kao, C. M.; Luo, G.; Katz, L.; Cane, D. E.; Khosla, Ch. *J. Am. Chem. Soc.* **1996**, *118*, 9184. (g) Jacobsen, J. R.; Hutchinson, C. R.; Cane, D. E.; Khosla, Ch. *Science* **1997**, *277*, 367.

(4) For selected reviews, see: (a) Paterson, I.; Mansuri, M. M. *Tetrahedron* **1985**, *41*, 3569. (b) Mulzer, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1452. (c) Paterson, I. *Pure Appl. Chem.* **1992**, *64*, 1281. (d) Stürmer, R.; Ritter, K.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 101.

(5) For selected recent reviews on aldolic reactions, see: (a) Bach, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 417. (b) Franklin, A. S.; Paterson, I. *Contemporary Organic Synthesis*, **1994**, *1*, 317. (c) Mukaiyama, T.; Kobayashi, S. *Org. React* **1995**, *46*, 1. (d) Mukaiyama, T. *Aldrichimica Acta* **1996**, *29*, 59. (e) Takayama, S.; Mc. Garvey, G. J.; Wong, C. H. *Chem. Soc. Rev.* **1997**, *26*, 407. (f) Cowden, C. J.; Paterson, I. *Org. React.* **1997**, *51*, 1. (g) Mahrwald, R. *Chem. Rev.* **1999**, *99*, 1095. (h) Prabhat, A.; Huiping, Q. *Tetrahedron* **2000**, *56*, 917.

(6) For recent accounts using this methodology, see: (a) Walkup, R. D.; Kahl, J. D.; Kane, R. D. *J. Org. Chem.* **1998**, *63*, 9113. (b) Paterson, I.; Cowden, C. J.; Woodrow, M. D. *Tetrahedron Lett.* **1998**, *39*, 6037, 6041. (c) Paterson, I.; Arnott, E. A. *Tetrahedron Lett.* **1998**, *39*, 7185. (d) Gennari, C.; Ceccarelli, S.; Piarulli, U.; Aboutayab, K.; Donghi, M.; Paterson, I. *Tetrahedron* **1998**, *54*, 14999. (e) Paterson, I.; Donghi, M.; Gerlach, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3315. (aldol reactions on solid support). (f) Roush, W. R.; Dilley, G. J. *Tetrahedron Lett.* **1999**, *40*, 4955. (g) Esteve, C.; Ferreró, M.; Urpí, F.; Vilarrasa, J. *Tetrahedron Lett.* **1999**, *40*, 5079, 5083. (h) Paquette, L. A.; Konetzki, I.; Duan, M. *Tetrahedron Lett.* **1999**, *40*, 7441. (i) Paterson, I.; Florence, G. J.; Gerlach, K.; Scott, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 377. (j) Paterson, I.; Doughly, V. A.; Mc Leod, M. D.; Trieselmann, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 1308. (k) Delas, Ch.; Möise, C. H. *Synlett* **2000**, 251 and references quoted in these reports.

(7) Other methods have also been used for the stereoselective construction of polypropionate chains. For some selected recent reports, see the following. Methods based on pericyclic reactions: (a) Rigby, J. H.; Fales, K. R. *Tetrahedron Lett.* **1998**, *39*, 5717 and references therein. Additions of crotyl derivatives to aldehydes: (b) Taylor, R. E.; Gavarri, J. P.; Hearn, B. R. *Tetrahedron Lett.* **1998**, *39*, 9361. (c) Chemler, S. R.; Roush, W. R. *J. Org. Chem.* **1998**, *63*, 3800 and references therein. Using epoxide chemistry: (d) Watanabe, H.; Kitahara, T. *Tetrahedron Lett.* **1998**, *39*, 8313. (e) Hayakawa, H.; Miyashita, M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3399.

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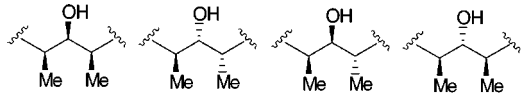


Figure 1. The stereotriads according to Hoffmann.

been conveniently analyzed in terms of subunits of three stereocenters each" (Figure 1). The strategy for the synthesis consists of the preparation of these individual building blocks conveniently functionalized at the ends in order to incorporate them as units into the target molecule.

In the same way it is possible to imagine any polypropionic sequence in terms of stereotetrads, stereopentads, etc. Two advantages become evident from this synthetic conception: the inherent convergency of the methodology and the possibility of synthesizing nonnatural analogues of any polypropionic chain, if all possible stereochemical sequences of the selected building block are available. Nevertheless, according to Hoffmann[9] "the Achilles heel of this methodology becomes apparent when the individual blocks have to be linked". However, this would not be a problem if both ends of the building block are appropriately functionalized in order to exert a high level of control of the stereochemistry of the new chiral centers created in the linkage region. Several recent examples concerning the synthesis of different polyketides using this methodology confirm this assumption.[10]

Although all possible stereotriads have been synthesized using different methods, the synthesis of the corresponding stereotetrads has received relatively little attention.[11]

In this report we wish to account for the preparation of all possible stereotetrads conveniently functionalized at both ends with the very synthetically versatile groups, formyl, and carboxymethyl. We will use as starting materials the oxabicyclo derivatives **1** and (+)-**2** (Figure 2),[12] the Diels−Alder adducts of furan and acrylic acid and (−)-2-camphanoxyacrylonitrile, respectively. It should be pointed out that the starting materials of these sequences can be available in both enantiomerically pure forms (see below). This aspect is crucial in our concept of "small polyketide library".

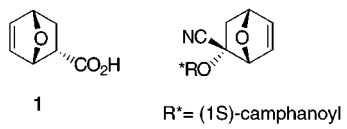


Figure 2.

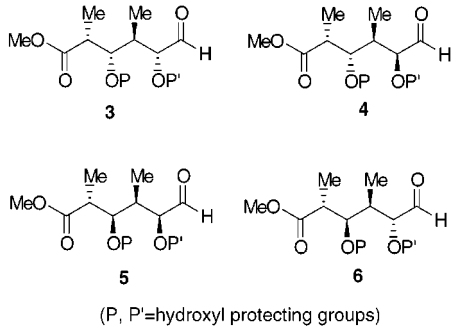


Figure 3. The 1,3-*anti*-dimethyl stereotetrads **3**−**6**.

Results and Discussion

First, we divided the stereotetrads in two groups depending on the stereochemical relationship (anti or syn) between the methyl groups.

1,3-*anti*-Dimethyl Stereotetrads. The all possible anti-stereotetrads **3**−**6** are displayed in Figure 3 (only one enantiomer is represented).

The proposed synthetic plan for the synthesis of these fragments is outlined in the Scheme 1.

Our starting material will be the Diels−Alder adduct **1** of furan and acrylic acid, and the key intermediate will be the vinyl sulfone **8**. This compound can be obtained from sulfone **7**[13] via alkylative ring opening with MeLi.[14] Thus, both the stereochemistry of the ring opening reaction (operation b; syn regarding to the oxygen bridge[14] in **7**) and of the carboxylic group in **1** (related to the methyl group in position 2 by the chemical transformation a) will determine the stereochemistry of the carbon atoms 2, 3, and 4 in the four stereotetrads. At this point, the synthetic plan diverges. Transformation of **8** into enone **9** (operation c) will give rise to the stereotetrads **3** and **4** after stereocontrolled carbonyl group reduction (operation d) followed by double bond cleavage (operation e) using the ozonolysis reaction in the Schreiber's conditions[15] and the Mitsunobu inversion

(8) See, for instance: (a) Paterson, I.; Channon, J. A. *Tetrahedron Lett.* **1992**, *33*, 797. (b) Paterson, I.; Perkins, M. V. *Tetrahedron* **1996**, *52*, 1811. (c) Szymoniak, J.; Lefrank, H.; Möise, C. *J. Org. Chem.* **1996**, *61*, 3926. (d) Grieco, P. A.; Speake, J. D.; Yeo, S. K.; Miyashita, M. *Tetrahedron Lett.* **1998**, *39*, 1125. (e) Calter, M. A.; Guo, X. *J. Org. Chem.* **1998**, *63*, 5308. (f) Kiyooka, S.; Shahid, K. A.; Hena, M. A. *Tetrahedron Lett.* **1999**, *40*, 6447. (g) Chemler, S. R.; Roush, W. R. *Tetrahedron Lett.* **1999**, *40*, 4647. (h) Hayakawa, H.; Miyashita, M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3399. (i) Watanabe, H.; Watanabe, H.; Bando, M.; Kido, M.; Kitahara, T. *Tetrahedron* **1999**, *55*, 9755.

(9) (a) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 489. (b) Hoffmann, R. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 2054.

(10) For selected recent examples, see: (a) Evans, D. A.; Kim, A. S.; Metternich, R.; Novack, V. J. *J. Am. Chem. Soc.* **1998**, *120*, 5921. (b) Marshall, J. A.; Johns, B. A. *J. Org. Chem.* **1998**, *63*, 7885. (c) Hu, T.; Takenaka, N.; Panek, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 9229. (d) Marshall, J. A.; Johns, B. A. *J. Org. Chem.* **2000**, *65*, 1501.

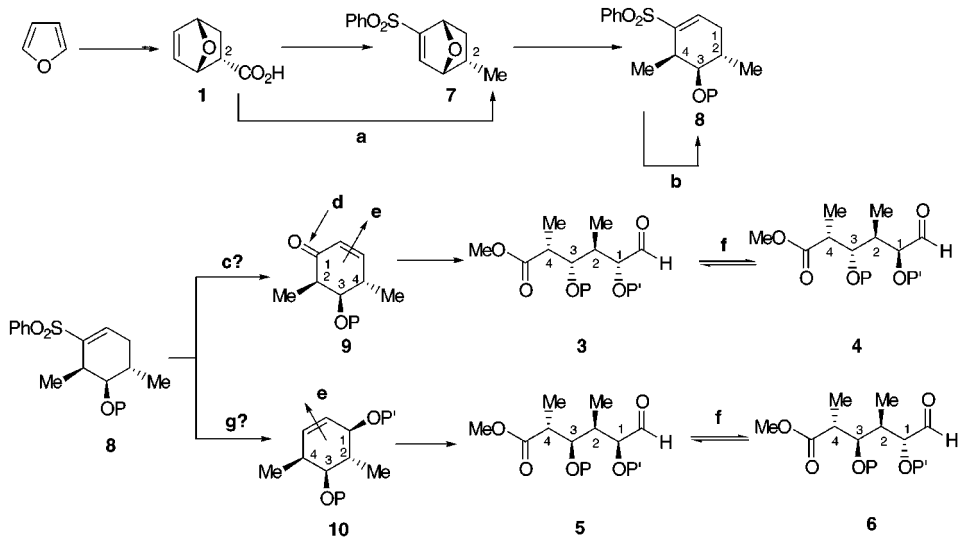
(11) For a review, see: (a) Hoffmann, R. W.; Dahmann, G.; Andersen, M. W. *Synthesis* **1994**, 629. For more recent accounts, see: (b) Domon, L.; Vogeleisen, F.; Uguen, D. *Tetrahedron Lett.* **1996**, *37*, 2773. (c) Bonini, C.; Chiummiento, L.; Funicello, M.; Marconi, L.; Righi, G. *Tetrahedron: Asymmetry* **1998**, *9*, 2559. (d) Hannessian, S.; Ma, J.; Wang, W. *Tetrahedron Lett.* **1999**, *40*, 4627, 4631. (e) Marshall, J. A.; Fitzgerald, R. N. *J. Org. Chem.* **1999**, *64*, 4477. (f) Marshall, J. A.; Manson, K. *J. Org. Chem.* **2000**, *65*, 630. The transformation of some stereotriads into the related stereopentads with good stereochemical control have also been achieved, see: (g) Chemler, S. R.; Roush, W. R. *Tetrahedron Lett.* **1999**, *40*, 4643.

(12) For other synthesis of polypropionate fragments from oxabicyclic compounds, see: (a) White, J. D.; Fukuyama, Y. *J. Am. Chem. Soc.* **1979**, *101*, 226. (b) Rama Rao, A. V.; Yadav, J. S.; Vidyasayar, V. *J. Chem. Soc., Chem. Comm.* **1985**, *55*. (c) Lautens, M.; Belter, R. K. *Tetrahedron Lett.* **1992**, *33*, 2617. (d) Lautens, M.; Chiu, P.; Colucci, J. T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 281. (e) Lautens, M.; Gadja, C.; Chiu, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1193. (f) Kernen, P.; Vogel, P. *Tetrahedron Lett.* **1993**, *34*, 2473. (g) Sevin, A. F.; Vogel, P. *J. Org. Chem.* **1994**, *59*, 5920. (h) Bialecki, M.; Vogel, P. *Tetrahedron Lett.* **1994**, *35*, 5213. (i) Lautens, M.; Chiu, P.; Ma, S.; Rooves, T. *J. Am. Chem. Soc.* **1995**, *117*, 532. (j) Kernen, P.; Vogel, P. *Helv. Chim. Acta* **1995**, *78*, 301. (k) Bialecki, M.; Vogel, P. *Helv. Chim. Acta* **1995**, *78*, 325. (l) Marchionni, C.; Vogel, P.; Roversi, P. *Tetrahedron Lett.* **1996**, *37*, 4149. (m) Ancerewicz, J.; Vogel, P. *Helv. Chim. Acta* **1996**, *79*, 1393. (n) Montaña, A. M.; García, F.; Grima, P. M. *Tetrahedron* **1999**, *55*, 5483.

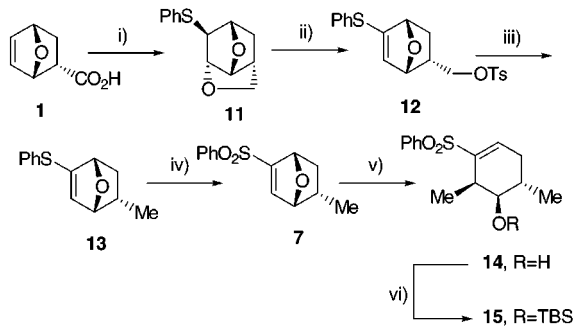
(13) All synthetic sequence starting from **1** has been achieved using the racemic material. For the optical resolution of **1** using (+)- and (−)-α-methylbenzylamine, see: Ogawa, S.; Iwasawa, Y.; Nose, T.; Suami, T.; Ohba, S.; Ito, M.; Saito, Y. *J. Chem. Soc., Perkin Trans. 1* **1985**, 903.

(14) Arjona, O.; de la Pradilla, R. F.; de Dios, A.; Plumet, J.; Viso, A. *J. Org. Chem.* **1994**, *59*, 3906 and references therein.

Scheme 1. Synthetic Plan for the Stereotetrads 3-6

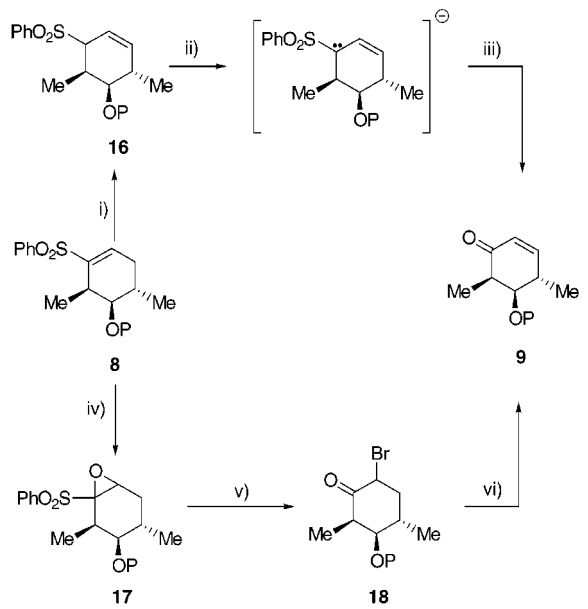


Scheme 2[a]



[a] Key: (i) two steps, 85%. See ref 16; (ii) *n*-BuLi, THF, −78 °C. Then TsCl, −78 °C to room temperature, 83%; (iii) $LiAlH_4$, Et_2O, 0 °C, 5 h, 81%; (iv) MMPP, MeOH, 0 °C to room temperature, 12 h, 86%; (v) MeLi, THF, −78 °C, 1 h, 94%; (vi) TBSOTf, Et_3N, −78 °C, 1 h, 91%.

Scheme 3[a]



[a] Key: (i) Vinyl-allyl sulfone isomerization; (ii) generation of α-sulfonyl carbanion in basic media; (iii) oxidation; (iv) nucleophilic epoxidation; (v) $MgBr_2$; (vi) HBr elimination.

at C-1 (operation f). The ozonolysis reaction will give us the necessary differentiation at both ends of the stereotetrads. On the other hand, the transformation of **8** into **10** (operation g) should afford stereotetrads **5** and **6** after double bond cleavage and Mitsunobu inversion as above. As major problems in this sequence remain the transformations of **8** into both, the enone **9**, and the allylic alcohol **10**.

Sulfone **7** was synthesized in five steps (46% overall yield) from **1**.[16] Transformation of **7** in sulfones **14** and **15** was achieved by reaction with MeLi[14] followed by protection of the resulting alcohol **14** (Scheme 2).

For the transforrmation of **8** into **9** we have considered two possibilities (Scheme 3). First, a vinyl−allyl sulfone isomerization[17] followed by oxidation of the α-sulfonyl carbanion generated from the allyl derivative **16**.[18] Alternatively, the nucleophilic epoxidation of **8**, followed by reaction of the resulting epoxysulfone **17** with $MgBr_2$ should give the α-bromoketone **18**.[19] Elimination of HBr in **18** will afford **9**. A related sequence has been used in our synthesis of (±)-cyclophellitol and (±)-epicyclophellitol.[20]

Vinyl−allyl sulfone isomerization took place smoothly by reaction of **15** with LDA to give **19** (Scheme 4).[21] However, all attempts to obtain enone **20** by oxidation of the α-sulfonyl carbanion generated from **19** (LDA, THF, −78 °C) using both bis(trimethylsilyl) peroxide

(15) (a) Schreiber, S. L.; Claus, R. E.; Reagan, J. *Tetrahedron Lett.* **1982**, *23*, 3867. (b) Claus, R. E.; Schreiber, S. L. *Org. Synth.* **1986**, *64*, 150. For some further applications, see: (c) Hayes, R.; Wallace, T. W. *Tetrahedron Lett.* **1990**, *31*, 3355. (d) Arjona, O.; Domenech, A. M.; Plumet, J. *J. Org. Chem.* **1993**, *58*, 7929.

(16) Aceña, J. L.; Arjona, O.; León, M.; Plumet, J. *Tetrahedron Lett.* **1996**, *37*, 8957.

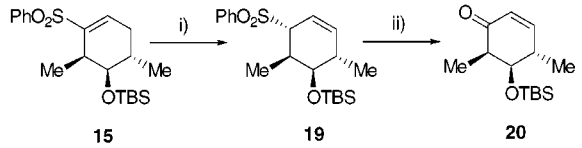
(17) See, for instance: (a) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107. (b) Lee, S. W.; Fuchs, P. L. *Tetrahedron Lett.* **1991**, *32*, 2861. (c) Domínguez, E.; Carretero, J. C. *Tetrahedron Lett.* **1993**, *34*, 5803. (d) Trost, B. M.; Ghadiri, M. R. *Bull. Soc. Chim. Fr.* **1993**, 433. (e) Fox, J. M.; Morris, C. M.; Smyth, G. D.; Whitham, G. M. *J. Chem. Soc., Perkin Trans. 1* **1994**, 731. (f) Marot, C.; Rollin, P. *Tetrahedron Lett.* **1994**, *35*, 8377.

(18) For several aspects of α-sulfonyl carbanion chemistry, see: Simpkins, N. G. In *Sulphones in Organic Synthesis*; Tetrahedron Organic Chemistry Series. Vol 10. Pergamon: New York, 1993.

(19) See, for instance: (a) Ashwell, M.; Clegg, W.; Jackson, R. F. W. *J. Chem. Soc., Perkin Trans. 1* **1991**, 897. (b) Hewkin, C. T.; Jackson, R. F. W. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3103.

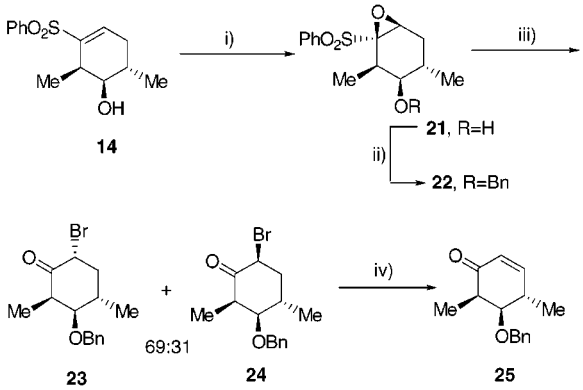
(20) Arjona, O.; Aceña, J. L.; Plumet, J. *J. Org. Chem.* **1997**, *62*, 3360.

Scheme 4[a]



[a] Key: (i) LDA, THF, −78 °C, 87%; (ii) (a) LDA, THF, −78 °C; (b) BTSP or MoOPH, 10−20%.

Scheme 5[a]



[a] Key: (i) *t*-BuO_2Li, THF, −78 °C to room temperature, 92%; (ii) BnBr, NaH, Me_4NI, THF, 0 °C to room temperature, 96%; (iii) $MgBr_2$, Et_2O, rt, 5 h, 85%; (iv) $CaCO_3$, DMF, 150 °C, 32%.

BTSP[22] or MoOPH[23] afforded **20** in 10−20% isolated yield.

These results made us move on to the second proposed approach.[24] Epoxidation of **14** with lithium *tert*-butyl hydroperoxide[25] followed by protection of the free hydroxyl group and reaction with $MgBr_2$ gave bromoketones **23** and **24** in a ratio **23**:**24**, 69:31 and 85% overall yield (Scheme 5).[26] Transformation of this mixture into enone **25** was performed using $CaCO_3$ in DMF.[20] However, and after considerable experimentation, **25** was obtained in a modest 32% isolated yield at most.

At this point we speculated that the transformation of **22** into **25** could occur in one step combining two well-known processes: the nucleophilic ring opening of α,β-epoxysulfones[27] (transformation A−B, Figure 4) and the rearrangement of epoxides to allylic alcohols using lithium amides[28] (transformation C−D, Figure 4).

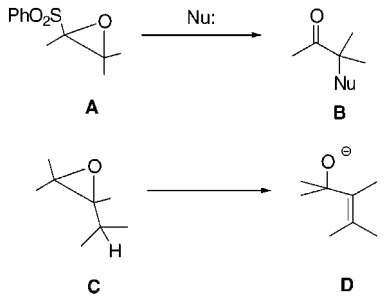
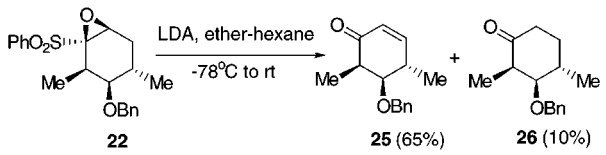


Figure 4.

Scheme 6



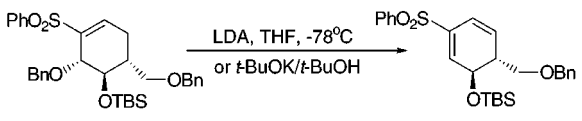
Confirmation of our speculation was obtained when the reaction of **22** with LDA in ether−hexane afforded **25** in 65% isolated yield. It should be pointed out that minor amounts of compound **26** were also isolated, probably, due to a subsequent reduction of **25** promoted by LDA.[29] These reaction conditions are critical for the success of the transformation. For instance, using THF as solvent, the reaction does not work at all and with ether as the only solvent, **25** was isolated in only 30% yield (Scheme 6).

With enone **25** in our hands the reaction sequence was continued according to our previous strategy. Thus, reduction of **25** under Luche's conditions[30] gave **27**[31] as the sole product which, after benzoylation and ozonolysis using the Schreiber's method,[15] afforded **30**. On the other hand, Mitsunobu inversion[32] of allylic alcohol **27** yielded **29**, which after ozonolysis gave rise to **31** (Scheme 7).

The transformation of epoxysulfone to enone deserves some comments. The lithium dialkylamide-mediated rearrangement of epoxides has been investigated extensively over the past several years due to its synthetic and theoretical interest.[33] Both α- or β-metalations (Scheme 8) are known to be sensitive to the choice of substrate, lithium amide, and solvent.

In the case of cyclohexene oxide both, experimental[34] and theoretical studies[35] indicate that the β-elimination

(21) This result is in clear contrast with the behavior of related compounds under the same reaction conditions. For instance, reaction of vinyl sulfone **70** with LDA or *t*-BuOK at −78 °C yield the diene **71** (see ref 20).



(22) Hwu, J. R. *J. Org. Chem*. **1983**, *48*, 4432.

(23) Little, R. D.; Myong, S. O. *Tetrahedron Lett*. **1980**, *21*, 3339.

(24) Arjona, O.; Menchaca, R.; Plumet, J. *Tetrahedron Lett*. **1998**, *39*, 6753.

(25) Clark, C.; Hermans, P.; Meh-Cohn, O.; Moore, C.; Taljard, H. C.; Van Vuuren, G. *J. Chem. Soc., Chem Commun*. **1986**, 1378. The stereochemistry of the epoxidation was governed probably by the homoallylic free hydroxyl group. However, other factors cannot be excluded. See: Aceña, J. L.; Arjona. O.; de la Pradilla, R. F.; Plumet, J.; Viso, A. *J. Org. Chem*. **1994**, *59*, 6419.

(26) Stereochemical assignments of compounds **23** and **24** was performed using ^{1}H NMR techniques. See Supporting Information. Evaluation of the mixture **23**:**24** was performed by ^{1}H NMR, 300 MHz, on well-differentiated signals. See Experimental Section.

(27) Transformations A−B have been achieved with several kinds of nucleophiles. For instance, see ref 18 and (a) Barone, A. D.; Suitman, D. L.; Watt, D. S. *J. Org. Chem*. **1978**, *43*, 2066. (b) Thanf, T. T.; Laborde, M. A.; Olesker, A.; Luckacs, G. *J. Chem. Soc., Chem. Commun*. **1988**, 1581. (c) Adamczyk, M.; Dolence, E. K.; Watt, D. S.; Christy, M. R.; Reibenspies, J. H.; Anderson, O. P. *J. Org. Chem*. **1984**, *49*, 1378.

(28) The rearrangement of epoxides to allylic alcohols using lithium amides has been reviewed; see: Crandall, J. K.; Apparu, M. *Org. React*. **1983**, *29*, 345. For a review using chiral lithium amides, see: O'Brien, P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1349. For a recent use of this reaction in the synthesis of 4-deoxyconduritols, see: Kee, A.; O'Brien, P.; Pilgram, Ch. D.; Watson, S. T. *J. Chem. Soc., Chem. Commun*. **2000**, 1521.

(29) Arjona O.; Menchaca, R.; Plumet, J. *Tetrahedron* **2000**, *56*, 3901.

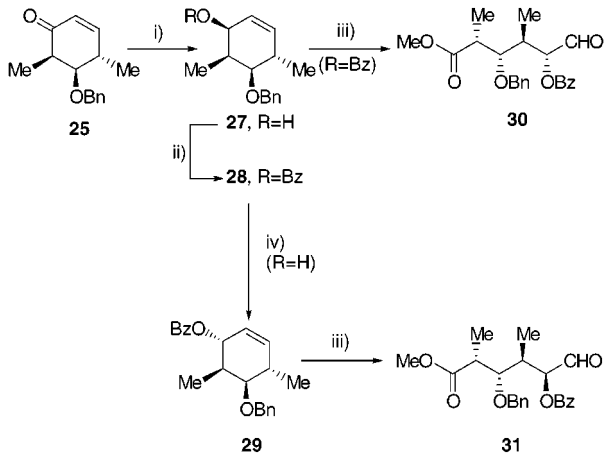
(30) Gemal, A.; Luche, J. L. *J. Am. Chem. Soc*. **1981**, *103*, 5454.

(31) The stereochemistry of compound **27** was determined using ^{1}H NMR experiments.

(32) Mitsunobu, O. *Synthesis* **1981**, 1.

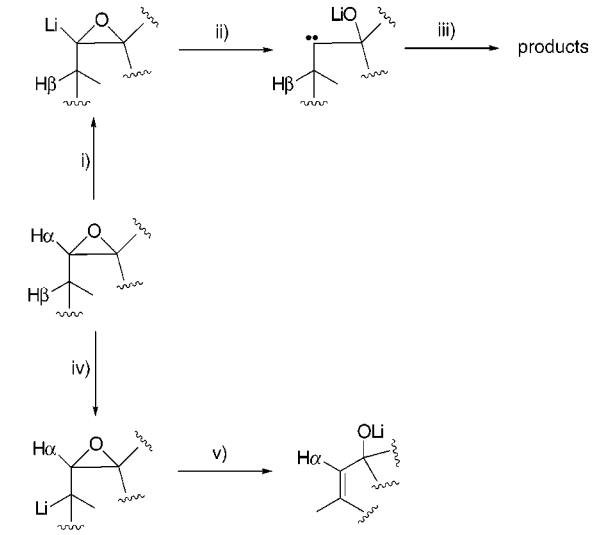
(33) See, for instance: Satoh, T. *Chem. Rev*. **1996**, *96*, 3303. See also: Doris, E.; Dechoux, L.; Miokowski, Ch. *Synlett* **1998**, 337.

Scheme 7[a]



[a] Key: (i) $NaBH_4$, $CeCl_3$, MeOH, −78 °C, 81%; (ii) BzCl, Py, CH_2Cl_2, 0 °C, 100%; (iii) (a) O_3, $NaHCO_3$, CH_2Cl_2:MeOH, 4:1, −78 °C; (b) Py, Ac_2O, CH_2Cl_2, rt, 24 h, 81% for **30** and 77% for **31**; (iv) DEAD, Ph_3P, BzOH, toluene, rt, 71%.

Scheme 8[a]

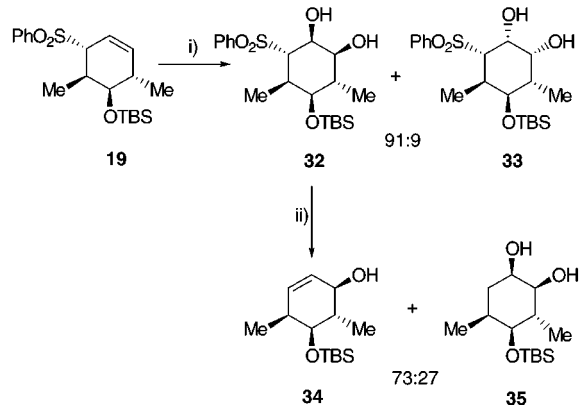


[a] Key: (i) α−metalation; (ii) generation of a carbene or carbenoid intermediate byα-elimination; (iii) C−H insertions and other reactions; (iv) *β*-metalation; (v) *β*-elimination.

appears to be the preferred pathway although the α-elimination is "not inherently less favorable". On the other hand, in the case of bicyclic epoxysulfones the α-elimination is the observed pathway.[29,36] The question remains opened for compounds such as the cyclohexanic epoxysulfones **21** and **22**.

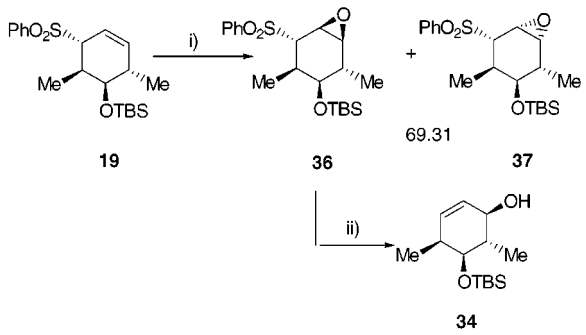
According to our synthetic plan (Scheme 1), transformation of vinyl sulfone **8** into allylic alcohol **10** was the key step in the approach to stereotetrads **5** and **6**. This transformation has been achieved as follows.[16] The OsO_4-catalyzed dihydroxylation of **19** gave a mixture 91:9 of diols **32** and **33**, from which the major diastereomer **32** was separated by column chromatography.[37] Juliá olefination[38] of this compound by treatment with Na−Hg afforded the expected allylic alcohol **34** along with the product **35** that resulted from the simple desulfonylation, in a ratio **34**:**35**, 73:27 (Scheme 9).

Scheme 9[a]



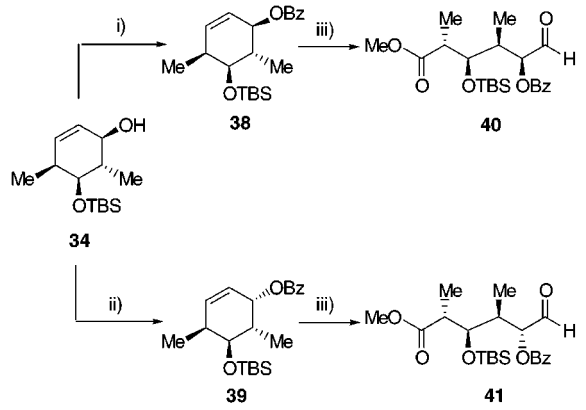
[a] Key: (i) OsO_4, $Me_3NO{\cdot}2H_2O$, Me_2CO:H_2O, 8:1, rt, 88% overall yield; (ii) Na−Hg, Na_2HPO_4, MeOH:THF, 1:1, −20 °C to room temperature, 89% overall yield.

Scheme 10[a]



[a] Key: (i) *m*-CPBA, CH_2Cl_2, 12 h, 84%, overall; (ii) Na−Hg, Na_2HPO_4, MeOH:THF, 1:1, −20 °C to room temperature, 53%.

Scheme 11[a]

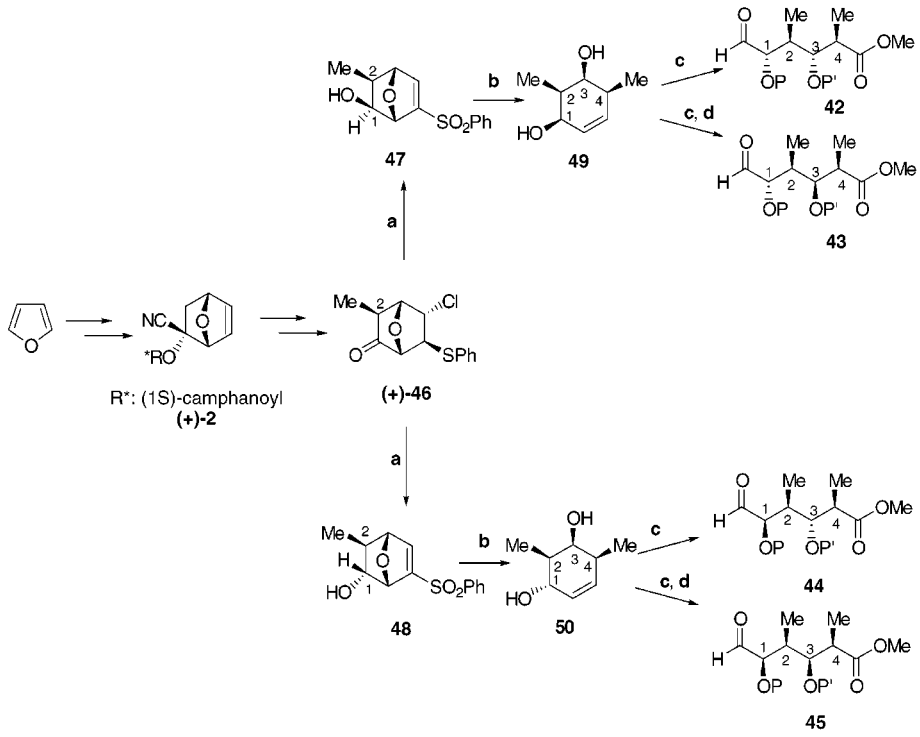


[a] Key: (i) BzCl, Py, CH_2Cl_2, 0 °C, 71%; (ii) DEAD, Ph_3P, BzOH, toluene, rt, 82%; (iii) (a) O_3, $NaHCO_3$, CH_2Cl_2:MeOH, 4:1, −78 °C; (b) Ac_2O, Py, CH_2Cl_2, rt, 85% for **40** and 61% for **41**.

Alternatively, epoxidation of **19** with *m*-CPBA yielded a mixture 69:31 of the diastereomeric oxiranes **36** and **37**.[39] After separation by column chromatography, the major product **36** was converted into allylic alcohol **34**

(34) Thummel, R. P.; Rickborn, B. *J. Am. Chem. Soc.* **1970**, *92*, 2064.
(35) See, for instance: Morgan, K. M.; Gronert, S. *J. Org. Chem.* **2000**, *65*, 1461 and references therein.
(36) (a) Ramírez, A.; Collum, D. B. *J. Am. Chem. Soc.* **1999**, *121*, 11114. (b) Dechoux, L.; Agami, C.; Doris, E.; Mioskowski, Ch. *J. Org. Chem.* **1999**, *64*, 9279 and references therein.
(37) Stereochemical assignations of compounds **32**−**33** were achieved using ^1H NMR data. See Supporting Information.
(38) (a) Juliá, M.; Paris, J. M. *Tetrahedron Lett.* **1973**, 4833. (b) Kocienzski, P. *Chem. Ind.* **1981**, 548.

Scheme 12. Synthetic Plan for the Stereotetrads 42-45



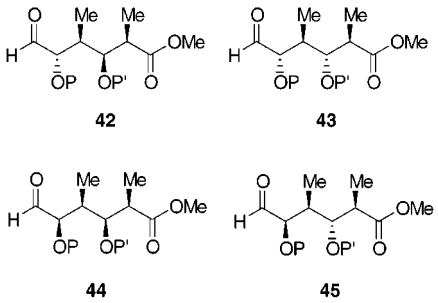


Figure 5. The 1,3-*syn*-dimethyl stereotetrads **42**−**45**.

by reaction with Na−Hg (Scheme 10) albeit only in 53% isolated yield.

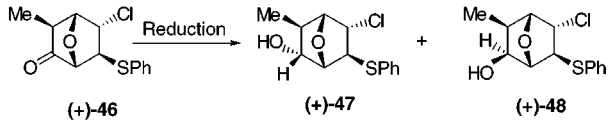
Alcohol **34** was then protected as its benzoyl derivative **38** and transformed into its epimer **39** by a Mitsunobu process. Finally, unsymmetrical ozonolysis of **38** and **39** produced the expected stereotetrads **40** and **41**, respectively (Scheme 11).

1,3-*syn*-Dimethyl Stereotetrads. The all possible syn-stereotetrads **42**−**45** are indicated in the Figure 5 (only one enantiomer is represented).

The proposed synthetic plan for the synthesis of these fragments is outlined in the Scheme 12.

Our starting material will be the compound (+)-**46** described by Vogel et al.[40] and synthesized from the Diels−Alder adduct (+)-**2** of furan and (−)-2-camphanoxyacrylonitrile (The synthesis was also performed from racemic compound **2**, Diels−Alder adduct of furan and 2-acetoxyacrylonitrile). Stereocontrolled reduction of the carbonyl group and elaboration of the chlorosulfide functionality (operation a) will allow the synthesis of the oxanorbornenic sulfones **47** and **48**. The methyl group at position 2 will be the methyl group at the same position in the final products **42**−**45**. On the other hand, by controlling the stereochemistry of the reduction of the carbonyl group at **46**, the stereochemistry of the hydroxyl group at position 1 in the final products will be fixed. The alkylative bridge opening of compounds **47** and **48** using MeLi[14] followed by desulfonylation of the resulting vinyl sulfone (operation b) will afford **49** and **50**. The stereochemistry of the incoming methyl group and of the resulting hydroxyl group will be fixed by the syn nature of the alkylative process regarding to the oxygen bridge. In this way the syn relationship between the methyl groups will be established. Finally, ozonolytic cleavage of the double bond (operation c) and Mitsunobu inversion of the hydroxyl group at position 3 (operation d) will give rise to the four desired stereotetrads.

Scheme 13[a]



i)	**1**	:	**4.6**
ii)	**6**	:	**1**

[a] Key: (i) $NaBH_4$, MeOH, 85% overall; (ii) $BH_3{\cdot}SMe_2$, THF, 96% overall.

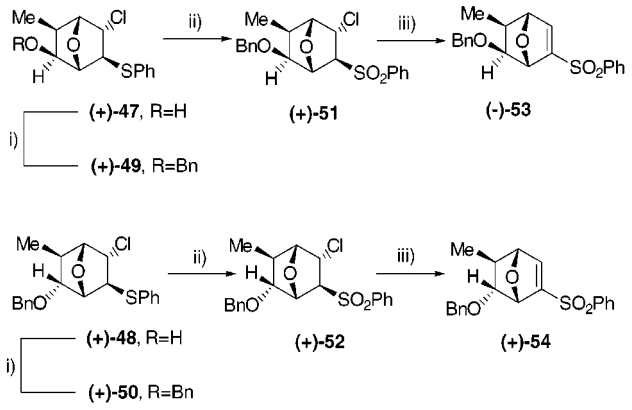
Reduction of (+)-**46** with $NaBH_4$ in MeOH gave a mixture (85% overall yield) 4.6:1 of alcohols (+)-**48** and (+)-**47**. On the other hand, using $BH_3{\cdot}SMe_2$[41] a mixture 6:1 of alcohols (+)-**47** and (+)-**48** was obtained in 96% overall yield. Both alcohols were easily separated by column chromatography (Scheme 13).

(39) Stereochemical assignations of compounds **34** and **35** was confirmed by coupling constant determinations. See Supporting Information.

(40) Vieira, E.; Vogel, P. *Helv. Chim. Acta* **1983**, *66*, 1865.

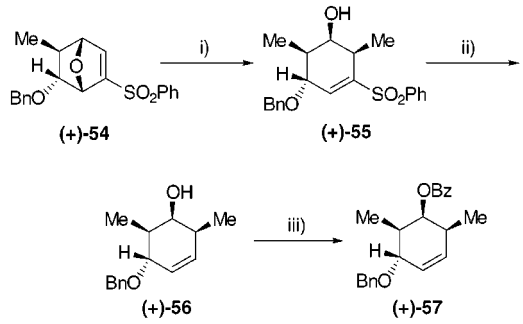
(41) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972.

Scheme 14[a]



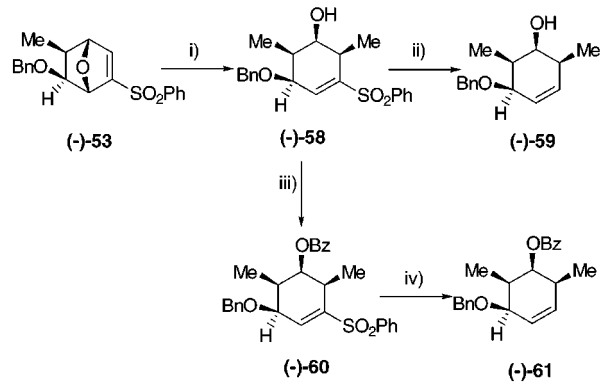
[a] Key: (i) BnBr, NaH, THF, 90% for (+)-**49** and 100% for (+)-**50**; (ii) MMPP, MeOH, 0 °C, 98% for (+)-**51** and 98% for (+)-**52**; (iii) DBU, CH_2Cl_2, 0 °C, 70% for (−)-**53** and 80% for (+)-**54**.

Scheme 15[a]



[a] Key: (i) MeLi, THF, −78 °C, 92%; (ii) Na−Hg, Na_2HPO_4, MeOH, −20 °C, 50% (method A) or SmI_2, THF, rt, 65% (method B); (iii) BzCl,Py, CH_2Cl_2, 74%.

Scheme 16[a]

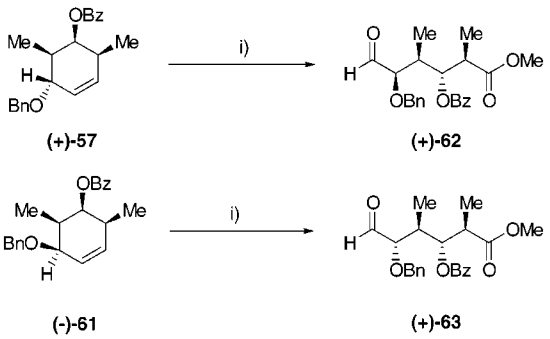


[a] Key: (i) MeLi, THF, −78 °C, 90%; (ii) different conditions (Na−Hg, SmI_2); (iii) BzCl, Py, CH_2Cl_2, 90%; (iv) Na−Hg, Na_2HPO_4, MeOH, −20 °C, 57%.

Protected vinyl sulfones (−)-**53** and (+)-**54** were synthesized in three steps (Scheme 14) consisting of protection of the hydroxyl group, sulfide oxidation to sulfone using MMPP, and final dehydrochlorination with DBU, starting from (+)-**47** and (+)-**48**, respectively.

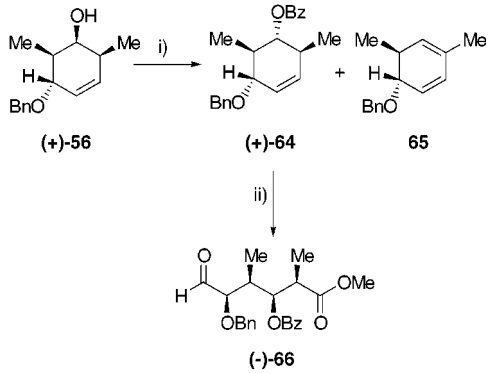
Transformation of (+)-**54** into (+)-**57** was performed in three steps (ring opening with MeLi, desulfonylation, and hydroxyl group protection (Scheme 15). The overall yield depended on the desulfonylation reagent,[42] being slightly better when using SmI_2.[43]

Scheme 17[a]



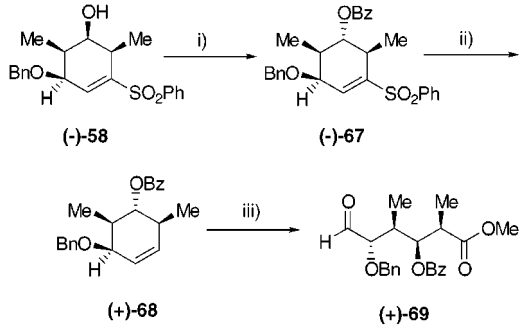
[a] Key: (i) (a) O_3, $NaHCO_3$, CH_2Cl_2:MeOH, 4:1, −78 °C; (b) Ac_2O, Py, CH_2Cl_2, rt, 67% for (+)-**62** and 61% for (+)-**63**.

Scheme 18[a]



[a] Key: (i) Method A: PBu_3, BzOH, DEAD, toluene, rt, 50% of (+)-**64** and 20−30% of **65**. Method B: PMe_3 (1 M in THF), BzOH, DEAD, toluene, rt, 74% of (+)-**64**; (ii) (a) O_3, $NaHCO_3$, CH_2Cl_2:MeOH, 4:1, −78 °C; (b) Ac_2O, Py, CH_2Cl_2, rt, 64%.

Scheme 19[a]



[a] Key: (i) PMe_3 (1 M in THF), BzOH, DEAD, toluene, rt, 49%; (ii) Na−Hg, Na_2HPO_4, MeOH, −20 °C, 46%; (iii) (a) O_3, $NaHCO_3$, CH_2Cl_2:MeOH, 4:1, −78 °C. (b) Ac_2O, Py, CH_2Cl_2, rt, 52%.

For the synthesis of the analogous cyclohexenic derivative (−)-**61** it was necessary to change the order of the synthetic steps. In this case all attempts of desulfonylation of alcohol (−)-**58** resulted in a 5−10% isolated yield of compound (−)-**59**. This drawback was circumvented by the previous benzoylation of (−)-**58** and further desulfonylation of the resulting benzoyl derivative (−)-**60** (Scheme 16).

(42) For an excellent review on desulfonylation reactions, see: Nájera, C.; Yus, M. *Tetrahedron* **1999**, *55*, 10547.

(43) (a) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. (b) Keck, G. E.; Savin, K. A.; Weglarz, M. A. *J. Org. Chem.* **1995**, *60*, 3194.

Ozonolytic cleavage under the Schreiber's conditions of compounds (+)-**57** and (−)-**61** finally afforded stereotetrads (+)-**62** and (+)-**63**, respectively (Scheme 17).

To achieve the synthesis of the last two stereotetrads it was first necessary to invert the stereochemistry of the hydroxyl group in (+)-**56**. Unfortunately, standard Mitsunobu conditions applied to (+)-**56** resulted in low yields of the desired compound (+)-**64**. As best result, we obtained (+)-**64** (50% yield) together with diene **65** in 20−30% yield (not isolated) using PBu_3, $PhCO_2H$, DEAD, and room temperature as Mitsunobu conditions. However, and to our delight, using PMe_3 (1 M in THF) instead, (+)-**64** was isolated in 90% yield. From (+)-**64**, the stereotetrad (−)-**66** was obtained as usual (Scheme 18).

Finally, the last stereotetrad was obtained in the following way: Mitsunobu inversion of sulfone (−)-**58** using PMe_3 afforded sulfone (−)-**67** which, after desulfonylation using Na−Hg and ozonolytic cleavage, afforded (+)-**69** (Scheme 19).

Conclusions

In this report we have described the first synthesis of all diastereomeric stereotetrads. The synthesis has been achieved in a stereodivergent fashion and starting from readily available materials which can be easily synthesized in both enantiomerically pure forms. Implicit in this strategy is the ready access to longer polypropionate fragments (natural and unnatural) by the selective elongation at the different ends of the chain.

Experimental Section

General. Reagents and solvents were handled by using standard syringe techniques. Tetrahydrofuran and diethyl ether were distilled from sodium and benzophenone; methylene chloride, diethylamine and diisopropylamine from calcium hydride, all under argon. The remaining solvents and chemicals were commercial and used as received. All products were purified by flash chromatography using 230−400 mesh silica gel. Analytical TLC was carried out on silica gel plates. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR were recorded for $CDCl_3$ at 300 and 75 MHz, respectively. When peak multiplicities are reported, the following abbreviations are used: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets); dt (doublet of triplets). Chemical shifts (δ) are reported in ppm from internal $(CH_3)_4Si$ and J values are given in hertz. IR spectra were recorded on a FT-IR spectrometer as thin films or KBr disks. Specific rotation $[\alpha]_D$ is given in deg per dm at 20 °C, and the concentration (c) is expressed in g per 100 mL. Elemental analyses were performed at the Universidad Complutense de Madrid.

2-(Phenylsulfenyl)-5-*endo*-(*p*-toluensulfonyloxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene (12). To a solution of **11**[44] (1.43 g, 6.11 mmol) in 30 mL of THF cooled at −78 °C, 5.73 mL of a 1.6 M *n*-BuLi solution in hexane (1.5 equiv) was added dropwise. After stirring for 1 h at −78 °C, TsCl (3.50 g, 18.3 mmol) was added and the reaction stirred for an additional 1 h and allowed to reach rt. The reaction mixture was quenched with water and extracted with AcOEt, and the organic layer was dried over $MgSO_4$. Elimination of the solvent under reduced pressure and further purification by flash chromatography of the residue eluting with hexanes/ethyl acetate (5:1) produced 1.96 g of **12** as a colorless oil (83%): IR ($CHCl_3$) υ 2980, 1710, 1365, 1190; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.73 (dd, 1 H, J = 11.6, 4.2 Hz), 1.86 (ddd, 1 H, J = 11.9, 9.4, 4.9 Hz), 2.38 (s, 3 H), 2.48−2.60 (m, 1 H), 3.42 (t, 1 H, J = 10.2 Hz), 3.91 (dd, 1 H, J = 9.9, 5.7 Hz), 4.62 (d, 1 H, J = 4.7 Hz), 4.90 (d, 1 H, J = 4.5 Hz), 5.72 (s, 1 H), 7.20−7−36 (m, 7 H), 7.70 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 28.0, 40.1, 71.9, 80.3, 80.9, 127.5, 127.8, 127.9, 129.1, 129.3, 129.9, 130.8, 131.2, 144.3, 145.0. Anal. Calcd for $C_{20}H_{19}O_4S_2$: C, 61.85; H, 5.15. Found: C, 61.70; H, 5.32.

5-*endo*-Methyl-2-(phenylsulfenyl)-7-oxabicyclo[2.2.1]-hept-2-ene (13). To a suspension of $LiAlH_4$ (124 mg, 3.25 mmol) in 6.5 mL of ether at 0 °C, 505 mg (1.30 mmol) of **12** dissolved in 6.5 mL of ether were added. After being stirred for 5h at 0 °C, the mixture was diluted with water and ether. The resulting crude was extracted over 10 h, and the combined organic extracts were dried over $MgSO_4$. Concentration under reduced pressure and purification via flash chromatography eluting with hexanes/ethyl acetate (10:1) provided 230 mg of **13** (81%) as a colorless oil: IR ($CHCl_3$) υ 2980, 2870, 1460, 1270; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.80 (dd, 1 H, J = 11.1, 4.4 Hz), 0.83 (d, 3 H, J = 6.7 Hz), 2.01 (ddd, 1 H, J = 11.1, 9.1, 5.0 Hz), 2.26−2.36 (m, 1 H), 4.68 (d, 1 H, J = 5.0 Hz), 4.81 (d, 1 H, J = 4.7 Hz), 6.10 (s, 1 H), 7.34−7−46 (m, 3 H), 7.41 (d, 2 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.9, 33.2, 34.7, 81.2, 83.3, 127.4, 129.0, 129.2, 129.6, 131.0, 142.9. Anal. Calcd for $C_{13}H_{14}OS$: C, 71.56; H, 6.42. Found: C, 71.45; H, 6.30.

5-*endo*-Methyl-2-(phenylsulfonyl)-7-oxabicyclo[2.2.1]-hept-2-ene (7). A solution of **13** (490 mg, 2.25 mmol) in 22 mL of MeOH was cooled to 0 °C, and MMPP (2.22 g, 4.50 mmol) was added. After stirring for 12 h, the reaction was quenched with saturated aqueous $NaHCO_3$ solution and concentrated in vacuo. The residue was diluted with water and extracted with AcOEt. The organic layer was dried over $MgSO_4$, and removal of the solvent under vacuum followed by purification via flash chromatography eluting with hexanes/ethyl acetate (2:1) afforded 485 mg of **7** (86%) as a white solid: mp 71−72 °C; IR (KBr) υ 2980, 1580, 1440, 1150; ^{1}H NMR ($CDCl_3$, 300 MHz) d 0.81 (d, 3 H, J = 7.1 Hz), 0.87 (dd, 1 H, J = 11.1, 4.0 Hz), 2.10 (ddd, 1 H, J = 11.4, 9.1, 4.7 Hz), 2.28−2.40 (m, 1 H), 4.87 (d, 1 H, J = 5.0 Hz), 4.90 (d, 1 H, J = 5.0 Hz), 6.97 (s, 1 H), 7.51 (t, 2 H, J = 7.7 Hz), 7.60 (t, 1 H, J = 7.1 Hz), 7.88 (d, 2 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.6, 33.2, 33.5, 79.3, 83.3, 128.0, 129.5, 134.0, 142.7, 147.0, 150.2. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.40; H, 5.60. Found: C, 62.26; H, 5.51.

(1*R,2*R**,6*S**)-3-(Phenylsulfonyl)-2,6-dimethylcyclohex-3-en-1-ol (14).** To a solution of **7** (471 mg, 1.88 mmol) in 9.4 mL of THF cooled at −78 °C, 3.53 mL of a 1.6 M MeLi solution in ether (5.63 mmol) was added dropwise. After stirring for an hour at −78 °C, the reaction was quenched with water and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude was chromatographed eluting with hexanes/ethyl acetate (1:1) to give **14** (470 mg, 94%) as a white solid: mp 112−113 °C; IR (KBr) υ 3400−3200, 1450, 1310, 720; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (d, 3 H, J = 6.4 Hz), 1.00 (d, 3 H, J = 6.7 Hz), 1.80−1.98 (m, 3 H), 2.46−2.65 (m, 2 H), 3.29 (dd, 1 H, J = 10.4, 5.0 Hz), 6.90 (dd, 1 H, J = 4.0, 2.7 Hz), 7.48 (t, 2 H, J = 7.7 Hz), 7.57 (t, 1 H, J = 7.4 Hz), 7.80 (d, 2 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 17.7, 28.3, 33.9, 34.4, 74.5, 128.0, 129.3, 133.3, 138.2, 140.2, 143.5. Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81. Found: C, 62.78; H, 6.32.

(4*S,5*R**,6*R**)-5-(*tert*-butyldimethylsilyloxy)-1-(phenylsulfonyl)-4,6-dimethyl cyclohex-1-ene (15).** To a solution of **14** (170 mg, 0.64 mmol) in 6 mL of THF, 0.18 mL of Et_3N (1.28 mmol) was added, and the solution was cooled to −78 °C. Then, 0.29 mL (1.28 mmol) of TBSOTf was added, and stirring was continued for an hour at the same temperature. The reaction was quenched with saturated aqueous NaCl solution and extracted with ether. After being dried over $MgSO_4$ and concentrated in vacuo, purification by chromatography using hexanes/ethyl acetate (10:1) afforded **15** (221 mg, 91%) as a colorless oil: IR ($CHCl_3$) υ 2960, 1450, 1260, 890; ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.17 (s, 3 H), −0.10 (s, 3 H), 0.80 (s, 9 H), 0.89 (d, 3 H, J = 6.0 Hz), 1.01 (d, 3 H, J = 7.1 Hz), 1.80−1.96 (m, 2 H), 2.40−2.58 (m, 2 H), 3.18 (dd, 1 H, J = 10.1, 4.7 Hz), 6.89 (dd, 1 H, J = 4.4, 2.4 Hz), 7.49 (t, 2 H, J = 7.0 Hz), 7.57 (t, 1 H, J = 7.0 Hz), 7.83 (d, 2 H, J = 6.7 Hz);

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^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.9, −4.6, 14.0, 18.2, 18.4, 25.9, 28.7, 34.0, 35.1, 75.1, 128.0, 129.2, 133.2, 138.0, 140.3, 143.6. Anal. Calcd for $C_{20}H_{19}O_4S_2$: C, 61.85; H, 5.15. Found: C, 61.70; H, 5.32. Anal. Calcd for $C_{20}H_{32}O_3SSi$: C, 63.11; H, 8.47. Found: C, 63.00; H, 8.38.

(3*S,4*R**,5*R**,6*R**)-4-(*tert*-Butyldimethylsilyloxy)-6-(phenylsulfonyl)-3,5-dimethylcyclohex-1-ene (19).** A solution containing diisopropylamine (0.08 mL, 0.55 mmol) in 1.25 mL of THF was cooled to −78 °C. Then, 0.35 mL of *n*-BuLi (0.55 mmol, 1.6 M solution in hexane) was added dropwise, and after being stirred for 20 min, 70 mg (0.18 mmol) of **15** dissolved in 1.25 mL of THF was added dropwise. The reaction was stirred for an hour at −78 °C and quenched with water. The organic layer was extracted with ether, dried over $MgSO_4$, and concentrated in vacuo. Purification via flash chromatography eluting with hexanes/ethyl acetate (10:1) gave 61 mg of **19** (87%) as a white solid: mp 118−119 °C; IR (KBr) υ 2930, 1450, 1310, 1260; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.01 (s, 3 H), 0.07 (s, 3 H), 0.86 (s, 9 H), 0.88 (d, 3 H, J = 7.1 Hz), 0.98 (d, 3 H, J = 7.1 Hz), 2.02−2.12 (m, 1 H), 2.32−2.45 (m, 1 H), 3.56−3.61 (m, 2 H), 5.50 (td, 1 H, J = 10.0, 3.0 Hz), 5.79 (ddd, 1 H, J = 10.0, 2.4, 1.8 Hz), 7.54 (t, 2 H, J = 7.7 Hz), 7.64 (t, 1 H, J = 7.4 Hz), 7.87 (d, 2 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.8, −4.4, 13.5, 17.7, 17.9, 25.7, 32.4, 34.4, 69.2, 72.4, 115.7, 128.8, 128.9, 133.6, 138.0, 139.0. Anal. Calcd for $C_{20}H_{32}O_3SSi$: C, 63.11; H, 8.47. Found: C, 63.37; H, 8.25.

(1*S,2*R**,3*R**,4*S**,6*S**)-1-(Phenylsulfonyl)-2,4-dimethyl-7-oxabicyclo[4.1.0]heptan-3-ol (21).** A solution containing *t*-BuOOH (0.10 mL, 0.77 mmol) in 1.5 mL of THF was cooled to −78 °C. *n*-BuLi (0.48 mL, 0.77 mmol) was added dropwise, and the resulting solution was stirred for 15 min at the same temperature. Then, 103 mg (0.39 mmol) of **14** dissolved in 1.5 mL of THF was added, and the reaction was warmed to room temperature and stirred overnight. The reaction mixture was quenched with brine, the organic layer was extracted with ether and dried over $MgSO_4$, and the solvent was removed under reduced pressure. After purification by chromatography eluting with hexanes/ethyl acetate (1:1), 100 mg (92%) of **21** were obtained as a colorless oil: IR ($CHCl_3$) υ 3600−3300, 1460, 1330, 1160; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.55 (d, 3 H, J = 7.0 Hz), 0.88 (d, 3 H, J = 5.9 Hz), 1.49−1.63 (m, 2 H), 1.83−1.90 (m, 1 H), 2.21 (q, 1 H, J = 11.0 Hz), 2.96 (quint, 1 H, J = 6.8 Hz), 3.31−3.39 (m, 1 H), 3.76 (s, 1 H), 7.55 (t, 2 H, J = 7.7 Hz), 7.67 (t, 1 H, J = 7.3 Hz), 7.88 (d, 2 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.7, 16.9, 25.7, 31.4, 32.0, 56.8, 73.6, 75.1, 129.2, 129.3, 134.4, 136.1. Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.57; H, 6.38. Found: C, 59.48; H, 6.30.

(1*S,2*R**,3*R**,4*S**,6*S**)-3-(Benzyloxy)-1-(phenylsulfonyl)-2,4-dimethyl-7-oxabicyclo[4.1.0]heptane (22).** To a solution of **21** (94 mg, 0.33 mmol) in 3.5 mL of THF cooled at 0 °C were added 20 mg (0.50 mmol, 60% mineral dispersion) of NaH, 0.08 mL (0.67 mmol) of BnBr, and 12.3 mg (0.03 mmol) of tetrabutylammonium iodide. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then, it was quenched with water, extracted with AcOEt, and dried over $MgSO_4$. The residue was chromatographed eluting with hexanes/ethyl acetate (5:1) to give 119 mg (96%) of **22** as a white solid: mp 95−96 °C; IR (KBr) υ 2830, 1580, 1340, 1270; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.58 (d, 3 H, J = 6.9 Hz), 0.93 (d, 3 H, J = 6.3 Hz), 1.53−1.68 (m, 2 H), 2.23 (dd, 1 H, J = 11.0, 4.0 Hz), 3.08−3.22 (m, 2 H), 3.78 (s, 1 H), 4.48 (syst AB, 2 H, J_{AB}= 11.4 Hz), 7.29−7.34 (m, 5H), 7.60 (tt, 2 H, J = 7.0, 1.5 Hz), 7.72 (tt, 1 H, J = 7.0, 1.5 Hz), 7.92 (d, 2 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.9, 17.3, 25.0, 28.3, 32.7, 57.1, 71.3, 75.2, 80.6, 127.7, 128.4, 129.2, 129.5, 134.4, 136.2, 136.7, 137.9. Anal. Calcd for $C_{21}H_{23}O_4S$: C, 67.92; H, 6.20. Found: C, 68.03; H, 6.36.

(2*R,3*R**,4*S**,6*R**)-3-(Benzyloxy)-6-bromo-2,4-dimethylcyclohexan-1-one (23) and (2*R**,3*R**,4*S**,6*S**)-3-(Benzyloxy)-6-bromo-2,4-dimethylcyclohexan-1-one (24).** To a suspension of $MgBr_2{\cdot}OEt_2$ (73 mg, 0.28 mmol) in 1.2 mL of ether, 70 mg (0.19 mmol) of **22** dissolved in 1.5 mL of ether was added, and the mixture was stirred for 6 h. The reaction was quenched with brine, extracted with ether, and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was chromatographed eluting with hexanes/ethyl acetate (4:1) to afford 35 mg (59%) of **23** and 16 mg (26%) of **24**, both as colorless oils. Compound **23**: IR ($CHCl_3$) υ 3020, 1730, 1570, 1100; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.15 (d, 3 H, J = 6.9 Hz), 1.16 (d, 3 H, J = 7.0 Hz), 1.77 (dd, 1 H, J = 13.9, 10.2 Hz), 2.24 (quintd, 1 H, J = 7.0, 1.8 Hz), 2.54 (dd, 1 H, J = 13.9, 5.6 Hz), 3.21 (qd, 1 H, J = 6.9, 4.0 Hz), 3.35 (dd, 1 H, J = 7.0, 4.0 Hz), 4.44 (syst AB, 2 H, J_{AB}= 11.8 Hz), 4.67 (dd, 1 H, J = 10.3, 5.7 Hz), 7.25−7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.5, 18.1, 32.2, 39.2, 44.7, 50.4, 71.1, 83.9, 127.5, 127.8, 128.4, 137.7, 203.7. Anal. Calcd for $C_{15}H_{19}O_2Br$: C, 57.88; H, 6.11. Found: C, 57.96; H, 6.06.

Compound **24**: IR ($CHCl_3$) υ 2840, 1730, 1580, 1380; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18 (d, 3 H, J = 6.6 Hz), 1.20 (d, 3 H, J = 7.7 Hz), 2.25−2.40 (m, 2 H), 2.62 (td, 1 H, J = 12.8, 4.8 Hz), 2.82 (qt, 1 H, J = 6.6, 2.8 Hz), 3.62 (td, 1 H, J = 2.9, 1.1 Hz), 4.50 (syst AB, 2 H, J_{AB}= 11.9 Hz), 4.73 (dd, 1 H, J = 12.8, 5.9 Hz), 7.26−7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.7, 15.9, 31.7, 40.0, 44.8, 52.8, 71.2, 86.1, 127.5, 128.3, 136.5, 137.9, 200.9. Anal. Calcd for $C_{15}H_{19}O_2Br$: C, 57.88; H, 6.11. Found: C, 57.96; H, 6.06.

(4*S,5*R**,6*R**)-5-(Benzyloxy)-4,6-dimethylcyclohex-2-en-1-one (25).** Method A: $CaCO_3$ (312 mg, 3.12 mmol) was suspended in 13 mL of DMF, and the mixture was heated to 150 °C. 194 mg (0.62 mmol) of a mixture of compounds **23** and **24** dissolved in 4 mL of DMF was added dropwise, and stirring was maintained for 45 min at the same temperature. After cooling to room temperature, the reaction was quenched with water, extracted with ether, and dried over $MgSO_4$. Concentration in vacuo and purification by chromatography (hexanes/ethyl acetate 10:1) afforded 46 mg (32%) of **25** as a colorless oil.

Method B: A solution containing diisopropylamine (0.09 mL, 0.63 mmol) in 1 mL of ether was cooled to −78 °C. Then, 0.40 mL of *n*-BuLi (0.64 mmol, 1.6 M solution in hexane) was added dropwise, and after being stirred for 20 min, 47 mg (0.13 mmol) of **22** dissolved in 1.3 mL of ether was added dropwise. The reaction was warmed gradually to room temperature and refluxed for an additional 3 h. The reaction was quenched with water, extracted with ether, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by purification as described above afforded 19 mg (65%) of **25** together with 3 mg (10%) of compound **26**. Compound **25**: IR ($CHCl_3$) υ 3040, 1670, 1470, 1140; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.17 (d, 3 H, J = 7.1 Hz), 1.22 (d, 3 H, J = 7.0 Hz), 2.71 (m, 1 H), 2.85 (qd, 1 H, J = 7.1, 4.0 Hz), 3.56 (dd, 1 H, J = 6.9, 4.0 Hz), 4.52 (syst AB, 2 H, J_{AB}= 11.4 Hz), 5.93 (dd, 1 H, J = 10.1, 2.1 Hz), 6.66 (dd, 1 H, J = 10.1, 3.1 Hz), 7.29−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.6, 17.0, 33.5, 43.3, 71.1, 82.3, 127.4, 127.9, 128.3, 128.5, 137.9, 151.9, 202.1. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.26; H, 7.83. Found: C, 78.14; H, 7.74.

Compound **26**: IR ($CHCl_3$) υ 2980, 1650, 1200, 840; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 (d, 3 H, J = 6.9 Hz), 1.11 (d, 3 H, J = 6.8 Hz), 1.26−1.43 (m, 2 H), 2.05−2.46 (m, 3 H), 2.59−2.65 (m, 1 H), 3.40 (dd, 1 H, J = 7.5, 6.3 Hz), 4.52 (syst AB, 2 H, J_{AB}= 1.7 Hz), 7.32−7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.2, 13.7, 18.3, 19.3, 31.3, 37.5, 72.1, 127.3, 127.4, 128.3, 128.4, 203.6. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.59; H, 8.62. Found: C, 77.46; H, 8.50.

(1*S,4*S**,5*R**,6*S**)-5-(Benzyloxy)-4,6-dimethylcyclohex-2-en-1-ol (27).** A solution of $CeCl_3{\cdot}7H_2O$ (566 mg, 1.49 mmol) dissolved in 3 mL of MeOH was cooled to −78 °C, and $NaBH_4$ (42.6 mg, 1.12 mmol) was added. After 30 min, 172 mg (0.75 mmol) of **25** dissolved in 4.5 mL of MeOH was added at the same temperature, and the reaction was warmed gradually to room temperature. After being stirred for 3 h, the reaction mixture was diluted with a 0.5 N HCl solution, extracted with ether, and dried over $MgSO_4$. Concentration in vacuo followed by purification by chromatography eluting with hexanes/ethyl acetate (10:1) afforded 140.5 mg of **27** (81%) as a colorless oil: IR ($CHCl_3$) υ 3600−3300, 1650, 1380, 1150; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.99 (d, 3 H, J = 7.3 Hz), 1.17 (d, 3 H, J = 7.0 Hz), 2.03 (m, 1 H), 2.54 (m, 1 H), 2.65 (d, 1 H, J = 10.2 Hz), 3.39 (s, 1 H), 3.87 (dt, 1 H, J = 10.3, 5.1 Hz), 4.50 (syst AB, 2 H, J_{AB}= 11.4 Hz), 5.63 (dd, 1 H, J = 10.0, 5.0 Hz), 5.88 (ddd,

1 H, J = 10.0, 4.5, 1.5 Hz), 7.29−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.9, 18.3, 32.8, 33.2, 67.9, 71.8, 83.8, 127.6, 127.7, 128.4, 128.9, 130.9, 137.3. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.59; H, 8.62. Found: C, 77.40; H, 8.56.

(3*S,4*R**,5*R**,6*S**)-5-(Benzyloxy)-3-(benzoyloxy)-4,6-dimethylcyclohex-1-ene (28).** To a solution of **27** (15 mg, 0.065 mmol) dissolved in 0.8 mL of CH_2Cl_2 cooled at 0 °C, 0.01 mL (0.13 mmol) of pyridine and 0.01 mL (0.13 mmol) of BzCl were added. After stirring for 12 h, the reaction was quenched with water. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed (hexanes/ethyl acetate, 15:1) to afford 22 mg (100%) of **28** as a colorless oil: IR ($CHCl_3$) υ 2980, 1750, 1470, 1200; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.05 (d, 3 H, J = 7.0 Hz), 1.11 (d, 3 H, J = 7.0 Hz), 2.35−2.46 (m, 1 H), 2.79−2.85 (m, 1 H), 3.35 (dd, 1 H, J = 8.8, 3.3 Hz), 4.56 (syst AB, 2 H, J_{AB}= 11.4 Hz), 5.54 (d, 1 H, J = 12.0 Hz), 5.64 (dt, 1 H, J = 12.0, 2.2 Hz), 5.69 (dd, 1 H, J = 5.5, 2.3 Hz), 7.30−7.56 (m, 7 H), 7.66−7.69 (m, 1 H), 8.05−8.19 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.5, 18.0, 29.7, 32.7, 70.9, 72.8, 81.9, 124.2, 127.8, 128.8, 129.6, 130.6, 131.4, 132.9, 134.5, 135.3, 138.5, 162.3. Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.57; H, 7.14. Found: C, 78.49; H, 7.10.

(3*R,4*R**,5*S**,6*S**)-5-(Benzyloxy)-3-(benzoyloxy)-4,6-dimethylcyclohex-1-ene (29).** To a solution of 12 mg (0.052 mmol) of **27** dissolved in toluene (1 mL) were added 27 mg (0.10 mmol) of PPh_3, 13 mg (0.10 mmol) of BzOH, and 0.02 mL (0.10 mmol) of DEAD, respectively. The reaction was stirred for 12 h and then concentrated under reduced pressure. Purification via flash chromatography (hexanes/ethyl acetate, 15:1) afforded 12.3 mg of **29** as a colorless oil (71%): IR ($CHCl_3$) υ 2980, 1750, 1380, 1150; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.04 (d, 3 H, J = 7.3 Hz), 1.14 (d, 3 H, J = 7.0 Hz), 2.33−2.45 (m, 2 H), 3.49 (dd, 1 H, J = 7.7, 3.7 Hz), 4.56 (syst AB, 2 H, J_{AB}= 11.8 Hz), 5.36 (t, 1 H, J = 3.0 Hz), 5.74 (s, 2 H), 7.28−7.47 (m, 7 H), 7.54−7.60 (m, 1 H), 7.98−8.01 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.1, 18.0, 32.7, 33.9, 70.8, 74.0, 79.8, 121.5, 122.2, 124.3, 127.6, 128.0, 128.3, 129.6, 130.4, 132.9, 136.9, 167.0. Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.57; H, 7.14. Found: C, 78.41; H, 7.03.

(2*R,3*S**,4*R**,5*R**)-Methyl 3-(Benzyloxy)-5-(benzoyloxy)-2,4-dimethyl-6-oxohexanoate (30).** To a solution of **28** (26 mg, 0.077 mmol) in 8 mL of CH_2Cl_2 and 2 mL of MeOH, 32 mg (0.39 mmol) of $NaHCO_3$ was added, and the mixture was cooled to −78 °C. O_3 was bubbled during 30 min, and then the mixture was diluted with benzene, filtered, and concentrated in vacuo. The residue was dissolved in 2 mL of CH_2Cl_2 and 0.02 mL (0.31 mmol) of pyridine, and 0.03 mL (0.39 mmol) of Ac_2O was added. After being stirred for 24 h, the mixture reaction was concentrated under reduced pressure and chromatographed eluting with hexanes/ethyl acetate (5:1) to afford 25 mg of **30** as a white solid (81%): mp: 113−114 °C; IR (KBr) υ 2840, 1740, 1580, 1220; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.14 (d, 3 H, J = 6.8 Hz), 1.24 (d, 3 H, J = 7.0 Hz), 2.64−2.76 (m, 2 H), 3.71 (s, 3 H), 4.15 (dd, 1 H, J = 10.0, 2.4 Hz), 4.45 (s, 2 H), 5.26 (d, 1 H, J = 1.9 Hz), 7.23−7.64 (m, 7 H), 7.75−7.80 (m, 1 H), 8.05−8.10 (m, 2 H), 9.30 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.0, 20.9, 29.6, 39.7, 40.7, 52.1, 72.9, 80.7, 127.7, 128.3, 128.7, 129.9, 130.1, 133.6, 134.5, 137.4, 171.2, 176.6, 196.1. Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.35; H, 6.53. Found: C, 69.28; H, 6.45.

(2*R,3*S**,4*R**,5*S**)-Methyl 3-(Benzyloxy)-5-(benzoyloxy)-2,4-dimethyl-6-oxohexanoate (31).** In a manner similar to that described for **30**, 11 mg (0.033 mmol) of **29** was allowed to react and afforded 10 mg of **31** as a colorless oil (77%): IR (CCl_4) υ 2780, 1750, 1380, 1110; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.08 (d, 3 H, J = 6.8 Hz), 1.27 (d, 3 H, J = 7.3 Hz), 2.46−2.52 (m, 1 H), 2.80 (qd, 1 H, J = 7.2, 2.9 Hz), 3.71 (s, 3 H), 3.97 (dd, 1 H, J = 9.8, 2.9 Hz), 4.36 (syst AB, 2 H, J_{AB}= 10.7 Hz)), 5.70 (d, 1 H, J = 2.4 Hz), 7.24−7.53 (m, 7 H), 7.62−7.67 (m, 1 H), 8.06−8.13 (m, 2 H), 9.61 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.4, 17.3, 29.7, 36.9, 41.0, 52.0, 74.9, 80.5, 128.1, 128.4, 128.6, 129.9, 133.5, 135.5, 136.4, 137.5, 166.1, 176.5, 198.5. Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.35; H, 6.53. Found: C, 69.26; H, 6.41.

D,L-(1,2,4,5/3,6)-4-*O*-*tert*-Butyldimethylsilyl-6-*C*-(phenylsulfonyl)-3,5-di-*C*-methylcyclohexane-1,2,4-triol (32) and D,L-(1,2,3,6/4,5)-4-*O*-*tert*-Butyldimethylsilyl-6-*C*-(phenylsulfonyl)-3,5-di-*C*-methylcyclohexane-1,2,4-triol (33). To a solution of 324 mg (0.85 mmol) of **19** in 8 mL of acetone and 1 mL of water, 195 mg (1.71 mmol) of $NMe_3O\cdot H_2O$ and 0.53 mL (0.043 mmol) of OsO_4 (2.5% solution in *t*-BuOH) were added. The reaction mixture was stirred for 48 h and was then quenched with a 10% aqueous $NaHSO_3$ solution. The mixture was concentrated under reduced pressure, and the residue was purified by chromatography (hexanes/ethyl acetate, 1:1) to afford 282 mg of **32** (80%) as a white solid and 30 mg of **33** (8%) as a colorless oil. Compound **32**: mp 141−142 °C; IR (KBr) υ 3600−3200, 1460, 1260, 840; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 3 H), 0.09 (s, 3 H), 0.87 (s, 9 H), 0.98 (d, 3 H, J = 7.3 Hz), 1.20 (d, 3 H, J = 6.8 Hz), 2.01−2.12 (m, 1 H), 2.26−2.33 (m, 1 H), 3.20 (br d, 1 H, J = 7.8 Hz), 3.28 (dd, 1 H, J = 8.3, 6.4 Hz), 3.64−3.73 (m, 3 H), 4.06 (td, 1 H, J = 6.2, 3.4 Hz), 7.55 (t, 2 H, J = 7.6 Hz), 7.64 (t, 1 H, J = 7.1 Hz), 7.91 (d, 2 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.8, −4.7, 14.8, 16.5, 17.8, 25.7, 31.6, 37.8, 66.9, 69.4, 74.0, 76.5, 128.3, 129.1, 133.7, 139.0. Anal. Calcd for $C_{20}H_{34}O_5SSi$: C, 57.94; H, 8.27. Found: C, 57.32; H, 7.94.

Compound **33**: IR ($CHCl_3$) υ 3600−3200, 1460, 1310, 1150; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.06 (s, 3 H), 0.09 (s, 3 H), 0.87 (s, 9 H), 1.04 (d, 6 H, J = 6.9 Hz), 1.67 (br s, 1 H), 1.90 (q, 1 H, J = 7.2 Hz), 1.97−2.09 (m, 1 H), 2.35 (br s, 1 H), 3.46 (t, 1 H, J = 3.7 Hz), 3.65−3.78 (m, 1 H), 3.82 (dd, 1 H, J = 7.5, 4.1 Hz), 4.24−4.35 (m, 1 H), 7.57 (t, 2 H, J = 7.6 Hz), 7.66 (t, 1 H, J = 7.2 Hz), 7.90 (d, 2 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.6, −4.4, 14.0, 15.4, 18.1, 22.5, 25.9, 29.7, 67.1, 67.5, 73.3, 74.3, 128.7, 129.3, 133.8, 138.6. Anal. Calcd for $C_{20}H_{34}O_5SSi$: C, 57.94; H, 8.27. Found: C, 58.05; H, 8.41.

(1*R,4*S**,5*S**,6*S**)-5-(*tert*-Butyldimethylsilyloxy)-4,6-dimethylcyclohex-2-en-1-ol (34) and D,L-(1,2,4,5/3)-4-*O*-(*tert*-butyldimethylsilyl)-3,5-di-*C*-methylcyclohexane-1,2,4-triol (35).** To a solution of **32** (25 mg, 0.06 mmol) in 0.45 mL of THF and 0.45 mL of MeOH cooled at −20 °C, 33 mg (0.24 mmol) of Na_2HPO_4 and 151 mg of recently prepared 6% Na−Hg were added. The mixture was gradually warmed to room temperature, and after being stirred for 4 h, another 151 mg of Na−Hg were added. After being stirred overnight, the mixture was diluted with a saturated aqueous NH_4Cl solution and extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification via flash chromatography eluting with hexanes/ethyl acetate (5:1) gave 10 mg of **34** (65%) and 4 mg of **35** (24%), both as colorless oils. Compound **34**: IR ($CHCl_3$) υ 3600−3300, 1470, 1140, 1070; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.05 (s, 3 H), 0.08 (s, 3 H), 0.89 (s, 9 H), 0.95 (d, 3 H, J = 7.0 Hz), 1.01 (d, 3 H, J = 7.2 Hz), 2.03 (qd, 1 H, J = 6.9, 4.5 Hz), 2.22−2.35 (m, 1 H), 2.54 (d, 1 H, J = 9.8 Hz), 3.64−3.74 (m, 2 H), 5.49 (dd, 1 H, J = 10.1, 3.0 Hz), 5.71 (ddd, 1 H, J = 10.1, 3.5, 2.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.6, −4.5, 15.0, 15.9, 18.1, 25.9, 32.9, 40.0, 71.1, 74.1, 127.6, 131.4. Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 64.61; H, 10.77. Found: C, 64.55; H, 10.60.

Compound **35**: IR ($CHCl_3$) υ 3600−3300, 2960, 1470, 1260; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.06 (s, 3 H), 0.11 (s, 3 H), 0.90 (m, 9 H), 0.91 (d, 3 H, J = 7.6 Hz), 0.92 (d, 3 H, J = 6.9 Hz), 1.50−1.64 (m, 2 H), 1.71−1.87 (m, 1 H), 2.35 (qt, 1 H, J = 7.6, 2.4 Hz), 2.52 (d, 1 H, J = 10.5 Hz), 3.55 (br s, 1 H), 3.59−3.75 (m, 2 H), 3.91 (d, 1 H, J = 9.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.0, −4.5, 14.7, 18.0, 18.5, 25.8, 30.5, 32.4, 41.1, 67.7, 74.7, 76.9. Anal. Calcd for $C_{14}H_{30}O_3Si$: C, 61.31; H, 10.95. Found: C, 61.19; H, 10.87.

(1*S,2*S**,3*R**,4*R**,5*S**,6*S**)-3-(*tert*-Butyldimethylsilyloxy)-5-(phenylsulfonyl)-2,4-dimethyl-7-oxabicyclo[4.1.0]-heptane (36) and (1*R**,2*S**,3*R**,4*R**,5*S**,6*R**)-3-(*tert*-Butyldimethylsilyloxy)-5-(phenylsulfonyl)-2,4-dimethyl-7-oxabicyclo[4.1.0]heptane (37).** To a solution of **19** (291 mg, 0.77 mmol) in 8 mL of CH_2Cl_2, 330 mg (1.91 mmol) of *m*-CPBA was added. After stirring for 36 h, the reaction was quenched with 5% aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$. After chromatography purification (hexanes/ethyl acetate, 5:1), 175

mg of **36** (58%) and 80 mg of **37** (26%) were obtained both as white solids. Compound **36**: mp 137−138 °C; IR (KBr) υ 2940, 1330, 1160, 840; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.09 (s, 3 H), 0.10 (s, 3 H), 0.89 (s, 9 H), 1.04 (d, 3 H, J = 7.3 Hz), 1.12 (d, 3 H, J = 7.3 Hz), 1.96−2.12 (m, 1 H), 2.37−2.49 (m, 1 H), 2.99 (d, 1 H, J = 3.5 Hz), 3.39 (d, 1 H, J = 3.4 Hz), 3.62 (br s, 1 H), 3.73 (dd, 1 H, J = 9.1, 4.4 Hz), 7.62 (t, 2 H, J = 7.6 Hz), 7.71 (t, 1 H, J = 7.2 Hz), 7.96 (d, 2 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.7, −4.3, 14.5, 17.0, 17.9, 25.7, 31.3, 32.2, 50.0, 57.9, 65.5, 72.3, 128.4, 129.5, 134.1, 138.3. Anal. Calcd for $C_{20}H_{32}O_4SSi$: C, 60.57; H, 8.13. Found: C, 60.44; H, 8.03.

Compound **37**: mp 122−123 °C; IR (KBr) υ 2870, 1470, 1330, 1090; ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.01 (s, 3 H), 0.02 (s, 3 H), 0.84 (s, 9 H), 0.92 (d, 3 H, J = 7.2 Hz), 1.15 (d, 3 H, J = 6.9 Hz), 1.85−1.99 (m, 2 H), 3.10 (td, 1 H, J = 4.0, 0.7 Hz), 3.26 (dd, 1 H, J = 3.8, 2.8 Hz, H-6), 3.33 (dd, 1 H, J = 3.5, 2.2 Hz, H-5), 3.46 (dd, 1 H, J = 7.5, 2.7 Hz), 7.56 (t, 2 H, J = 7.6 Hz), 7.63 (t, 1 H, J = 7.2 Hz), 7.98 (d, 2 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.8, −4.7, 13.8, 16.5, 17.9, 25.7, 29.2, 33.9, 51.0, 55.5, 66.0, 74.9, 128.9, 129.1, 133.7, 138.2. Anal. Calcd for $C_{20}H_{32}O_4SSi$: C, 60.57; H, 8.13. Found: C, 60.51; H, 7.95.

(3*R,4*S**,5*S**,6*S**)-3-(Benzoyloxy)-5-(*tert*-butyldimethylsilyloxy)-4,6-dimethylcyclohex-1-ene (38).** To a solution of **34** (10 mg, 0.039 mmol) in 0.4 mL of CH_2Cl_2 cooled at 0 °C, 0.01 mL (0.078 mmol) of pyridine and 0.01 mL (0.078 mmol) of BzCl were added. After stirring for 2 h, the reaction was quenched with a 0.5 N HCl solution and extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed (hexanes/ethyl acetate, 10:1) to give 10 mg of **38** (71%) as a colorless oil: IR ($CHCl_3$) υ 2960, 1710, 1280, 1070; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.06 (s, 6 H), 0.91 (s, 9 H), 1.01 (d, 3 H, J = 6.6 Hz), 1.05 (d, 3 H, J = 7.1 Hz), 2.01−2.18 (m, 1 H), 2.30−2.43 (m, 1 H), 3.66 (dd, 1 H, J = 11.0, 5.5 Hz), 5.26 (dq, 1 H, J = 9.2, 1.8 Hz), 5.57 (d, 1 H, J = 10.1 Hz), 5.79 (ddd, 1 H, J = 10.1, 5.2, 1.8 Hz), 7.42 (t, 2 H, J = 7.6 Hz), 7.54 (t, 1 H, J = 7.3 Hz), 8.04 (d, 2 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.8, −4.3, 14.3, 14.9, 18.2, 25.9, 35.9, 36.1, 72.7, 76.6, 125.2, 128.3, 129.6, 130.4, 132.9, 134.6, 166.5. Anal. Calcd for $C_{21}H_{32}O_3Si$: C, 70.00; H, 8.89. Found: C, 69.86; H, 8.83.

(2*R,3*R**,4*S**,5*S**)-Methyl 5-(Benzoyloxy)-3-(*tert*-butyldimethylsilyloxy)-2,4-dimethyl-6-oxohexanoate (40).** To a solution of **38** (10 mg, 0.030 mmol) in 1.6 mL of CH_2Cl_2 and 0.4 mL of MeOH, 13 mg (0.15 mmol) of $NaHCO_3$ was added, and the mixture was cooled to −78 °C. O_3 was bubbled during 30 min, and then the mixture was diluted with benzene, filtered, and concentrated in vacuo. The residue was dissolved in 0.5 mL of CH_2Cl_2 and 0.01 mL (0.11 mmol) of pyridine, and 0.01 mL (0.14 mmol) of Ac_2O was added After being stirred for 24 h, the mixture reaction was concentrated under reduced pressure and chromatographed eluting with hexanes/ethyl acetate (5:1) to afford 10.1 mg (85%) of **40** as a colorless oil: IR ($CHCl_3$) υ 2960, 2860, 1720, 1100; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.06 (s, 3 H), 0.10 (s, 3 H), 0.87 (s, 9 H), 1.11 (d, 3 H, J = 7.1 Hz), 1.19 (d, 3 H, J = 7.1 Hz), 2.43−2.56 (m, 1 H), 2.72−2.83 (m, 1 H), 3.55 (s, 3 H), 4.07 (t, 1 H, J = 5.1 Hz), 5.31 (d, 1 H, J = 4.2 Hz), 7.47 (t, 2 H, J = 7.7 Hz), 7.60 (t, 1 H, J = 7.5 Hz), 8.06 (d, 2 H, J = 7.7 Hz), 9.59 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.4, −4.3, 11.4, 13.1, 18.2, 25.9, 37.7, 44.8, 51.6, 74.2, 79.1, 128.5, 129.5, 129.8, 133.4, 165.9, 174.1, 197.7. Anal. Calcd for $C_{22}H_{34}O_6Si$: C, 62.56; H, 8.05. Found: C, 62.47; H, 7.96.

(3*S,4*S**,5*S**,6*S**)-3-(Benzoyloxy)-5-(*tert*-butyldimethylsilyloxy)-4,6-dimethylcyclohex-1-ene (39).** To a solution of 13 mg of **34** (0.05 mmol) in 0.5 mL of toluene were added 12 mg (0.10 mmol) of PPh_3, 27 mg (0.10 mmol) of BzOH, and 0.016 mL (0.10 mmol) of DEAD, respectively. The reaction was stirred for 12 h and then concentrated under reduced pressure. Purification via flash chromatography eluting with hexanes/ethyl acetate (10:1) produced 15 mg of **39** (82%) as a colorless oil: IR ($CHCl_3$) u 2960, 1710, 1280, 1100; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.08 (s, 3 H), 0.12 (s, 3 H), 0.92 (s, 9 H), 0.98 (d, 3 H, J = 7.0 Hz), 1.00 (d, 3 H, J = 7.1 Hz), 2.22−2.36 (m, 1 H), 2.37−2.48 (m, 1 H), 3.96 (dd, 1 H, J = 8.8, 4.8 Hz), 5.55−5.61 (m, 1 H), 5.67−5.79 (m, 2 H), 7.42 (t, 2 H, J = 7.7 Hz), 7.54 (t, 1 H, J = 7.3 Hz), 8.02 (d, 2 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.7, −4.6, 12.6, 14.3, 18.2, 25.9, 34.7, 35.4, 72.3, 72.5, 123.5, 128.3, 128.3, 129.5, 132.8, 136.0, 166.1. Anal. Calcd for $C_{21}H_{32}O_3Si$: C, 70.00; H, 8.89. Found: C, 69.81; H, 8.72.

(2*R,3*R**,4*S**,5*R**)-Methyl 5-(Benzoyloxy)-3-(*tert*-butyldimethylsilyloxy)-2,4-dimethyl-6-oxohexanoate (41).** In a manner similar to that described for **30**, 21 mg (0.058 mmol) of **39** was allowed to react and afforded 15 mg of **41** as a colorless oil (61%): IR ($CHCl_3$) υ 2960, 2860, 1720, 1460; ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.08 (s, 3 H), −0.08 (s, 3 H), 0.85 (s, 9 H), 1.06 (d, 3 H, J = 7.0 Hz), 1.16 (d, 3 H, J = 7.1 Hz), 2.19−2.33 (m, 1 H), 2.69−2.81 (m, 1 H), 3.68 (s, 3 H), 4.38 (d, 1 H, J = 8.2 Hz), 4.94 (d, 1 H, J = 9.9 Hz), 7.47 (t, 2 H, J = 7.7 Hz), 7.61 (t, 1 H, J = 7.3 Hz), 8.07 (d, 2 H, J = 7.7 Hz), 9.67 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.8, −4.5, 9.0, 14.2, 18.4, 26.0, 36.2, 45.0, 51.8, 72.1, 79.3, 128.5, 128.6, 129.8, 133.7, 166.0, 175.5, 198.0. Anal. Calcd for $C_{22}H_{34}O_6Si$: C, 62.56; H, 8.05. Found: C, 62.40; H, 7.89.

5-*endo*-Chloro-3-*exo*-methyl-6-*exo*-(phenylsulfenyl)-7-oxabicyclo[2.2.1]heptan-2-*exo*-ol, (+)-47 and 5-*endo*-Chloro-3-*exo*-methyl-6-*exo*-(phenylsulfenyl)-7-oxabicyclo[2.2.1]-heptan-2-*endo*-ol, (+)-48. Method A: A solution of (+)-**46** (1300 mg, 4.84 mmol) in 24 mL of MeOH was cooled to −20 °C. $NaBH_4$ (366 mg, 9.68 mmol) was added, and the reaction was allowed to warm to room temperature. After stirring for 3 h, the reaction was quenched with icy water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. Purification by chromatography using hexanes/ethyl acetate (10:1) afforded 917 mg of (+)-**48** (70%) as a colorless oil and 197 mg of (+)-**47** (15%) as a white solid.

Method B: To a solution of (+)-**46** (500 mg, 1.86 mmol) in 9 mL of THF, 0.44 mL of $BH_3{\cdot}SMe_2$ (4.65 mmol) was added. Stirring was continued for an hour, and then the reaction was quenched with a 5% aqueous $NaHCO_3$ solution. The organic layer was extracted with AcOEt and dried over $MgSO_4$. Purification in the same way as described above yielded 69 mg of (+)-**48** (14%) and 413 mg (82%) of (+)-**47**. Compound (+)-**47**: $[\alpha]_D$ = +78.7° (0.04 M, CH_2Cl_2); mp 128−129 °C; IR (KBr) υ 3620, 2980, 1580, 1050; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (d, 3 H, J = 7.3 Hz), 1.78 (d, 1 H, J = 9.8 Hz), 2.83 (quint, 1 H, J = 7.3 Hz), 3.06 (d, 1 H, J = 4.6 Hz), 3.91 (t, 1 H, J = 4.6 Hz), 3.97 (dd, 1 H, J = 9.8, 7.3 Hz,), 4.13 (dd, 1 H, J = 4.6, 1.1 Hz), 4.25 (s, 1 H), 7.28−7.37 (m, 3 H), 7.42−7.46 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.9, 36.3, 54.5, 61.3, 74.9, 85.5, 89.7, 127.7, 129.3, 131.8, 137.4. Anal. Calcd for $C_{13}H_{15}O_2ClS$: C, 57.67; H, 5.54. Found: C, 57.76; H, 5.62.

Compound (+)-**48**: $[\alpha]_D$ = +84.8° (0.06 M, CH_2Cl_2); IR (CCl_4) υ 3600−3200, 2960, 1470, 1310; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.16 (d, 3 H, J = 7.3 Hz), 1.99 (m, 1 H), 2.36 (qd, 1 H, J = 7.3, 2.9 Hz), 3.91 (m, 1 H), 4.02 (d, 1 H, J = 4.0 Hz), 4.08−4.14 (m, 2 H), 4.33 (d, 1 H, J = 4.8 Hz), 7.21−7.34 (m, 3 H), 7.41−7.45 (m, 2 H);^{13}C NMR ($CDCl_3$, 75 MHz) d 18.5, 38.7, 49.9, 62.6, 79.6, 86.1, 87.0, 126.9, 129.1, 130.4, 134.7. Anal. Calcd for $C_{13}H_{15}O_2ClS$: C, 57.67; H, 5.54. Found: C, 57.79; H, 5.66.

2-*exo*-(Benzyloxy)-5-*endo*-chloro-3-*exo*-methyl-6-*exo*-(phenylsulfenyl)-7-oxabicyclo[2.2.1]heptane, (+)-49. In a manner similar to that described for **22**, 500 mg (1.85 mmol) of (+)-**47** were allowed to react and afforded 598 mg of (+)-**49** as a colorless oil (90%): $[\alpha]_D$ = +46.0° (0.03 M, CH_2Cl_2); IR (CCl_4) υ 2980, 1470, 1360, 1210; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.14 (d, 3 H, J = 7.3 Hz), 2.89 (quint, 1 H, J = 7.3 Hz), 3.03 (d, 1 H, J = 4.0 Hz), 3.69 (d, 1 H, J = 7.3 Hz), 3.95 (t, 1 H, J = 4.0 Hz), 4.07 (s, 1 H), 4.17 (d, 1 H, J = 4.0 Hz), 4.40 (syst. AB, 2 H, J_{AB}= 11.8 Hz), 7.25−7.50 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.9, 30.9, 62.7, 72.3, 76.6, 82.0, 84.1, 85.5, 127.0, 127.3, 127.5, 127.8, 128.5, 129.1, 129.2, 130.8, 132.3, 134.1. Anal. Calcd for $C_{20}H_{21}O_2ClS$: C, 66.57; H, 5.82. Found: C, 66.49; H, 5.75.

2-*endo*-(Benzyloxy)-5-*endo*-chloro-3-*exo*-methyl-6-*exo*-(phenylsulfenyl)-7-oxabicyclo[2.2.1]heptane, (+)-50. In a manner similar to that described for **22**, 720 mg (2.66 mmol) of (+)-**48** was allowed to react and afforded 959 mg (100%) of

(+)-**50** as a colorless oil after chromatography eluting with hexanes/ethyl acetate (15:1): $[\alpha]_D = +48.1°$ (0.03 M, CH_2Cl_2); IR (CCl_4) υ 2980, 1600, 1560, 1300; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.14 (d, 3 H, $J = 7.3$ Hz), 2.51 (qd, 1 H, $J = 7.3$, 3.3 Hz), 3.61 (dd, 1 H, $J = 4.8$, 3.3 Hz), 4.00 (d, 1 H, $J = 4.8$ Hz), 4.07 (t, 1 H, $J = 4.8$ Hz), 4.13 (d, 1 H, $J = 4.8$ Hz), 4.41 (d, 1 H, $J = 4.8$ Hz), 4.43 (syst. AB, 2 H, J_{AB}= 11.9 Hz), 7.27−7.42 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.1, 33.6, 50.7, 62.4, 72.3, 85.0, 86.4, 87.0, 126.9, 127.4, 127.8, 128.5, 129.0, 129.1, 130.7, 137.8. Anal. Calcd for $C_{20}H_{21}O_2ClS$: C, 66.57; H, 5.82. Found: C, 66.58; H, 5.40.

2-*exo*-(Benzyloxy)-5-*endo*-chloro-3-*exo*-methyl-6-*exo*-(phenylsulfonyl)-7-oxabicyclo[2.2.1]heptane, (+)-51. In a manner similar to that described for **7**, 533 mg (1.48 mmol) of (+)-**49** was allowed to react and afforded 569 mg of (+)-**51** as a white solid after purification via flash chromatography using hexanes/ethyl acetate (4:1) (98%): $[\alpha]_D = +23.0°$ (0.02 M, CH_2Cl_2); mp 133−134 °C; IR (KBr) υ 2980, 1610, 1480, 750; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (d, 3 H, $J = 7.3$ Hz), 2.79 (quint, 1 H, $J = 7.3$ Hz), 3.01 (d, 1 H, $J = 4.9$ Hz), 3.68 (d, 1 H, $J = 7.3$ Hz), 4.16 (d, 1 H, $J = 4.9$ Hz), 4.22 (t, 1 H, $J = 4.9$ Hz), 4.57 (syst. AB, 2 H, J_{AB}= 12.2 Hz), 5.00 (s, 1 H), 7.26−7.39 (m, 5H), 7.60 (t, 2 H, $J = 7.8$ Hz), 7.68−7.73 (m, 1 H), 7.91 (d, 2 H, $J = 7.6$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.4, 36.6, 55.4, 71.9, 72.4, 80.7, 81.5, 85.3, 127.4, 127.8, 128.5, 128.8, 129.5, 134.4, 137.4, 137.6. Anal. Calcd for $C_{20}H_{21}O_4ClS$: C, 61.15; H, 5.35. Found: C, 61.35; H, 5.38.

2-*endo*-(Benzyloxy)-5-*endo*-chloro-3-*exo*-methyl-6-*exo*-(phenylsulfonyl)-7-oxabicyclo[2.2.1]heptane, (+)-52. In a manner similar to that described for **7**, 959 mg (2.66 mmol) of (+)-**50** was allowed to react and afforded 1023 mg of (+)-**52** as a white solid after purification via flash chromatography using hexanes/ethyl acetate (4:1) (98%): $[\alpha]_D = +98.3°$ (0.03 M, CH_2Cl_2); mp 99−100 °C; IR (KBr) υ 2950, 1590, 1340, 1150; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (d, 3 H, $J = 7.0$ Hz), 2.38 (qd, 1 H, $J = 7.1$, 3.3 Hz), 3.65 (dd, 1 H, $J = 4.8$, 3.3 Hz), 3.99 (d, 1 H, $J = 5.2$ Hz), 4.14 (d, 1 H, $J = 5.2$ Hz), 4.42 (s, 2 H), 4.44 (t, 1 H, $J = 5.2$ Hz), 5.04 (d, 1 H, $J = 4.8$ Hz), 7.26−7.40 (m, 5 H), 7.60 (t, 2 H, $J = 7.7$ Hz), 7.70 (t, 1 H, $J = 7.8$ Hz), 7.94 (d, 2 H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.6, 36.8, 56.1, 67.7, 72.3, 79.7, 85.3, 86.7, 127.6, 128.0, 128.5, 128.7, 129.5, 134.2, 137.1, 137.9. Anal. Calcd for $C_{20}H_{21}O_4ClS$: C, 61.15; H, 5.35. Found: C, 61.20; H, 5.41.

6-*endo*-(Benzyloxy)-5-*exo*-methyl-2-(phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-en, (+)-54. To a solution of 820 mg (2.09 mmol) of (+)-**52** cooled at 0 °C, 0.47 mL (3.14 mmol) of DBU was added dropwise. After being stirred at this temperature for 2 h, it was quenched with a 0.5 N HCl solution. The organic layer was extracted with CH_2Cl_2 and dried over $MgSO_4$. Further purification by chromatography eluting with hexanes/ethyl acetate (5:1) afforded 595 mg of (+)-**54** (80%) as a white solid: $[\alpha]_D = +47.1°$ (0.03 M, CH_2Cl_2); mp 110−111 °C; IR (KBr) υ 2980, 1580, 1350, 1210; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.17 (d, 3 H, $J = 7.3$ Hz), 1.60 (qd, 1 H, $J = 7.3$, 2.4 Hz), 3.68 (dd, 1 H, $J = 4.0$, 2.5 Hz), 4.46 (syst. AB, 2 H, J_{AB}= 12.1 Hz), 4.56 (d 1 H, $J = 1.7$ Hz), 5.15 (d, 1 H, $J = 4.0$ Hz), 7.19 (d, 1 H, $J = 1.8$ Hz), 7.28−7.34 (m, 5H), 7.48 (t, 2 H, $J = 7.8$ Hz), 7.58 (t, 1 H, $J = 7.7$ Hz), 7.94 (d, 2 H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 39.3, 60.4, 79.5, 82.9, 86.1, 127.4, 127.6, 127.7, 128.0, 128.4, 129.0, 133.5, 137.8, 139.3, 145.7. Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.41; H, 5.62. Found: C, 67.43; H, 5.66.

6-*exo*-(Benzyloxy)-5-*exo*-methyl-2-(phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene, (−)-53. In a manner similar to that described for (+)-**54**, 510 mg (1.30 mmol) of (+)-**51** was allowed to react and afforded 324 mg of (−)-**53** as a white solid (70%): $[\alpha]_D = -47.3°$ (0.01 M, CH_2Cl_2); mp 103−104 °C; IR (KBr) υ 2980, 1600, 1370, 1110; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.13 (d, 3 H, $J = 7.0$ Hz), 2.07 (quint, 1 H, $J = 7.0$ Hz), 3.75 (d, 1 H, $J = 7.0$ Hz), 4.58 (syst. AB, 2 H, J_{AB}= 12.1 Hz), 4.67 (d, 1 H, $J = 1.5$ Hz), 4.84 (s, 1 H), 7.13 (d, 1 H, $J = 1.5$ Hz), 7.32−7.39 (m, 5 H), 7.54 (t, 2 H, $J = 8.1$ Hz), 7.62 (t, 1 H, $J = 7.9$ Hz), 7.86 (d, 2 H, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 35.5, 58.1, 78.8, 82.1, 85.7, 127.5, 127.7, 127.9, 128.5, 128.6, 129.1, 134.0, 138.0, 139.2, 146.9. Anal. Calcd for $C_{20}H_{20}O_4S$: C, 67.41; H, 5.62. Found: C, 67.56; H, 5.58.

(1*R*,2*S*,3*R*,6*R*)-3-(Benzyloxy)-5-(phenylsulfonyl)-2,6-dimethylcyclohex-4-en-1-ol, (+)-55. In a manner similar to that described for **14**, 290 mg (0.81 mmol) of (+)-**54** were allowed to react and afforded 279 mg of (+)-**55** as a white solid after purification by chromatography eluting with hexanes/ethyl acetate (2:1) (92%): $[\alpha]_D = +91.4°$ (0.01 M, CH_2Cl_2); mp 118−119 °C; IR (KBr) υ 3400−3200, 3050, 1590, 1350; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.12 (d, 3 H, $J = 7.0$ Hz), 1.17 (d, 3 H, $J = 6.9$ Hz), 1.65 (m, 1 H), 1.83 (quintd, 1 H, $J = 7.0$, 3.0 Hz), 2.61 (qd, 1 H, $J = 7.0$, 3.0 Hz), 3.77 (m, 1 H), 4.12 (dt, 1 H, $J = 7.0$, 3.0 Hz), 4.64 (syst. AB, 2 H, J_{AB}= 11.4 Hz), 7.16 (t, 1 H, $J = 3.0$ Hz), 7.26−7.37 (m, 5 H), 7.61−7.50 (m, 3 H), 7.85 (d, 2 H, $J = 7.9$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.2, 21.0, 36.1, 39.7, 60.4, 71.8, 75.5, 127.4, 127.7, 127.9, 128.1, 128.5, 129.1, 133.5, 137.6, 138.9, 140.5. Anal. Calcd for $C_{21}H_{24}O_4S$: C, 67.74; H, 6.45. Found: C, 67.85; H, 6.53.

(1*S*,2*S*,3*S*,6*S*)-3-(Benzyloxy)-2,6-dimethylcyclohex-4-en-1-ol, (+)-56. Method A: To a solution of (+)-**55** (190 mg, 0.51 mmol) in 5 mL of MeOH, 290 mg (2.04 mmol) of Na_2HPO_4 was added. The mixture was cooled to −20 °C, and 510 mg of recently prepared 6% Na−Hg was added. After 30 min stirring, another 510 mg of Na−Hg was added, and the reaction was warmed gradually to 0 °C and stirred for other 2 h. The reaction was then quenched with a saturated aqueous NH_4Cl solution, extracted with ether, and dried over $MgSO_4$. Further purification by chromatography eluting with hexanes/ethyl acetate (15:1) afforded (+)-**56** (59 mg, 50%) as a colorless oil.

Method B: To a flask containig 1261 mg of Sm (8.39 mmol) dissolved in 8 mL of THF under argon, 1,2-diiodoethane (1818 mg, 6.48 mmol) was added, and the mixture was vigorously stirred until a dark blue coloration was reached. Then another 49 mL of THF was added, together with 0.49 mL of DMPU (4.03 mmol). Finally, 300 mg (0.81 mmol) of (+)-**55** dissolved in 4 mL of THF was also added. After being stirred for 3 h, the reaction mixture was quenched with water and extracted with ether. The organic layer was washed with a 0.5 N HCl solution and dried over $MgSO_4$. Further purification by using the same procedure described above afforded 122 mg (65%) of (+)-**56**: $[\alpha]_D = +235.6°$ (0.01 M, CH_2Cl_2); IR (CCl_4) υ 3600, 3300, 1650, 1290; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.08 (d, 3 H, $J = 7.3$ Hz), 1.19 (d, 3 H, $J = 7.0$ Hz), 1.59 (m, 1 H), 1.89 (quintd, 1 H, $J = 7.0$, 1.5 Hz), 2.44−2.48 (m, 1 H), 3.74 (m, 1 H), 3.89 (dd, 1 H, $J = 7.0$, 2.5 Hz), 4.59 (syst. AB, 2 H, J_{AB}= 11.4 Hz), 5.48 (dd, 1 H, $J = 9.9$, 1.5 Hz), 5.88 (dd, 1 H, $J = 9.9$, 2.5 Hz), 7.26−7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.5, 16.7, 36.2, 40.2, 65.3, 70.9, 75.3, 126.9, 127.7, 127.9, 128.3, 128.6, 140.9. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.59; H, 8.62. Found: C, 77.53; H, 8.56.

(3*S*,4*R*,5*S*,6*S*)-3-(Benzyloxy)-5-(benzoyloxy)-4,6-dimethylcyclohex-1-ene, (+)-**57.** To a solution of (+)-**56** (41 mg, 0.18 mmol) dissolved 1.7 mL of CH_2Cl_2 cooled at 0 °C, 0.03 mL (0.35 mmol) of pyridine and 0.04 mL (0.35 mmol) of BzCl were added. The reaction was gradually warmed to room temperature and stirred for 12 h. The reaction mixture was quenched with a 0.5 N HCl solution, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and flash chromatography of the crude residue (hexanes/ethyl acetate, 20:1) produced 44 mg of (+)-**57** (74%) as a colorless oil: $[\alpha]_D = +146.5°$ (0.01 M, CH_2Cl_2); IR (CCl_4) υ 3020, 2870, 1740, 1200; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (d, 3 H, $J = 7.3$ Hz), 1.10 (d, 3 H, $J = 6.4$ Hz), 2.13 (quintd, 1 H, $J = 6.4$, 2.0 Hz), 2.63 (m, 1 H), 4.00 (ddd, 1 H, $J = 6.4$, 2.1, 1.5 Hz), 4.62 (syst. AB, 2 H, J_{AB}= 11.7 Hz), 5.50 (t, 1 H, $J = 2.0$ Hz), 5.54 (dt, 1 H, $J = 10.3$, 1.5 Hz), 5.96 (dd, 1 H, $J = 10.3$, 2.1 Hz), 7.33−7.46 (m, 7 H), 7.54 (t, 1 H, $J = 7.3$ Hz), 8.07 (d, 2 H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.2, 19.1, 30.2, 36.5, 73.6, 75.1, 80.3, 126.4, 126.5, 128.7, 129.8, 130.7, 134.9, 135.4, 136.5, 137.3, 139.0, 170.4. Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.57; H, 7.14. Found: C, 78.49; H, 6.49.

(1*R*,2*S*,3*S*,6*R*)-3-(Benzyloxy)-5-(phenylsulfonyl)-2,6-dimethylcyclohex-4-en-1-ol, (−)-58. In a manner similar to that described for **14**, 150 mg (0.42 mmol) of (−)-**53** were

allowed to react and afforded 141 mg of (−)-**58** as a colorless oil after purification by chromatography eluting with hexanes/ethyl acetate (2:1) (90%): $[\alpha]_D = -107.6°$ (0.01 M, CH_2Cl_2); IR (CCl_4) υ 3650, 1600, 1470, 1110; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (d, 3 H, J = 7.0 Hz), 1.26 (d, 3 H, J = 7.0 Hz), 1.83−1.89 (m, 1 H), 2.57 (q, 1 H, J = 7.1 Hz), 3.10 (d, 1 H, J = 9.2 Hz), 3.62 (m, 1 H), 4.08 (t, 1 H, J = 4.8 Hz), 4.69 (syst. AB, 2 H, J_{AB}= 12.1 Hz), 7.29 (dd, 1 H, J = 4.8, 2.2 Hz), 7.33−7.40 (m, 5 H), 7.52 (t, 2 H, J = 7.7 Hz), 7.60 (t, 1 H, J = 7.6 Hz), 7.79 (d, 2 H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.8, 15.0, 37.1, 38.0, 72.8, 73.9, 74.2, 127.5, 127.9, 128.3, 128.6, 129.2, 133.2, 135.7, 137.3, 140.6, 145.3. Anal. Calcd for $C_{21}H_{24}O_4S$: C, 67.90; H, 6.52. Found: C, 67.74; H, 6.45.

(3*S*,4*R*,5*R*,6*R*)-3-(Benzyloxy)-5-(benzoyloxy)-1-(phenylsulfonyl)-4,6-dimethyl cyclohex-1-ene, (−)-60. In a manner similar to that described for (+)-**57**, 101 mg (0.27 mmol) of (−)-**58** was allowed to react and afforded 116 mg of (−)-**60** as a white solid after purification by chromatography eluting with hexanes/ethyl acetate (5:1) (90%): $[\alpha]_D = -59.6°$ (0.01 M, CH_2Cl_2); mp 92−93 °C IR (KBr) υ 1720, 1580, 1470, 1150; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (d, 3 H, J = 7.3 Hz), 1.15 (d, 3 H, J = 7.1 Hz), 2.40 (qd, 1 H, J = 7.1, 2.9 Hz), 2.93−3.01 (m, 1 H), 4.25 (td, 1 H, J = 3.0, 2.0 Hz), 4.69 (s, 2 H), 5.27 (dd, 1 H, J = 5.1, 3.0 Hz), 7.29 (d, 1 H, J = 2.0 Hz), 7.34−7.52 (m, 7 H), 7.59−7.67 (m, 4 H), 7.85 (d, 2 H, J = 6.8 Hz), 8.00 (d, 2 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.0, 14.1, 33.9, 35.7, 72.2, 72.8, 73.9, 127.5, 127.7, 128.2, 128.4, 129.1, 129.2, 129.7, 130.1, 132.9, 133.2, 133.7, 137.7, 141.3, 142.0, 171.8. Anal. Calcd for $C_{28}H_{28}O_5S$: C, 70.59; H, 5.88. Found: C, 70.56; H, 5.83.

(3*R*,4*R*,5*S*,6*S*)-3-(Benzyloxy)-5-(benzoyloxy)-4,6-dimethylcyclohex-1-ene, (−)-61. In a manner similar to that described for (+)-**56** (method A), 45 mg (0.094 mmol) of (−)-**60** was allowed to react and afforded 18 mg of (−)-**61** as a colorless oil after purification by chromatography eluting with hexanes/ethyl acetate (15:1) (57%): $[\alpha]_D = -11.5°$ (0.02 M, CH_2Cl_2); IR (CCl_4) υ 1730, 1320, 1050, 840; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (d, 3 H, J = 6.0 Hz), 1.18 (d, 3 H, J = 5.7 Hz), 2.23 (qdd, 1 H, J = 5.7, 3.3, 1.2 Hz), 2.56−2.64 (m, 1 H), 3.92 (dd, 1 H, J = 3.3, 2.6 Hz), 4.65 (Syst. AB, 2 H, J_{AB}= 7.6 Hz), 5.38 (dd, 1 H, J = 3.0, 1.2 Hz), 5.63 (dt, 1 H, J = 6.8, 1.2 Hz), 6.07 (ddd, 1 H, J = 6.8, 2.6, 1.7 Hz), 7.21−7.36 (m, 7 H), 7.47 (t, 1 H, J = 5.3 Hz), 8.07 (d, 2 H, J = 5.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.3, 21.2, 30.5, 33.1, 72.9, 74.2, 81.3, 126.5, 126.9, 127.4, 128.9, 129.9, 133.3, 135.5, 136.7, 138.4, 139.5, 173.3. Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.57; H, 7.14. Found: C, 78.46; H, 7.06.

(2*R*,3*R*,4*S*,5*R*)-Methyl 5-(Benzyloxy)-3-(benzoyloxy)-2,4-dimethyl-6-oxohexanoate (+)-62. In a manner similar to that described for **30**, 10 mg (0.030 mmol) of (+)-**57** were allowed to react and afforded 7 mg of (+)-**62** as a colorless oil after purification by chromatography eluting with hexanes/ethyl acetate (5:1) (67%): $[\alpha]_D = +13.0°$ (0.03 M, CH_2Cl_2); IR (CCl_4) υ 2840, 2780, 1720, 1310; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.03 (d, 3 H, J = 7.3 Hz), 1.24 (d, 3 H, J = 7.0 Hz), 2.56−2.62 (m, 1 H), 3.06 (qd, 1 H, J = 7.0, 3.6 Hz), 3.72 (s, 3 H), 3.82 (m, 1 H), 4.50 (syst. AB, 2 H, J_{AB}= 10.8 Hz), 5.51 (dd, 1 H, J = 9.0, 3.6 Hz), 7.24−7.56 (m, 7 H), 7.59 (t, 1 H, J = 7.1 Hz), 8.03 (d, 2 H, J = 6.9 Hz), 9.72 (d, 1 H, J = 1.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.9, 21.2, 29.7, 37.5, 41.1, 51.8, 73.4, 83.4, 127.9, 128.2, 128.4, 128.5, 129.8, 130.1, 133.0, 136.1, 166.5, 177.0, 194.3. Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.35; H, 6.53. Found: C, 69.41; H, 6.58.

(2*R*,3*R*,4*S*,5*S*)-Methyl 5-(Benzyloxy)-3-(benzoyloxy)-2,4-dimethyl-6-oxohexanoate (+)-63. In a manner similar to that described for **30**, 18 mg (0.053 mmol) of (−)-**61** were allowed to react and afforded 13 mg of (+)-**63** as a colorless oil after purification by chromatography eluting with hexanes/ethyl acetate (5:1) (61%): $[\alpha]_D = +19.3°$ (0.03 M, CH_2Cl_2); IR (CCl_4) υ 2980, 2780, 1720, 1200; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.08 (d, 3 H, J = 6.7 Hz), 1.20 (d, 3 H, J = 6.6 Hz), 2.00−2.05 (m, 1 H), 2.99−3.06 (m, 1 H), 3.69 (s, 3 H), 3.74 (dd, 1 H, J = 5.2, 1.3 Hz), 4.62 (syst. AB, 2 H, J_{AB}= 8.0 Hz), 5.54 (dd, 1 H, J = 5.9, 2.9 Hz), 7.32−7.51 (m, 7 H), 7.60 (t, 1 H, J = 6.9 Hz), 8.11 (d, 2 H, J = 6.9 Hz), 9.54 (d, 1 H, J = 1.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.2, 17.6, 31.1, 33.1, 47.6, 52.3, 69.9, 82.4, 129.5, 129.7, 129.9, 133.0, 133.2, 136.9, 137.5, 138.6, 168.5, 173.2, 199.5. Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.35; H, 6.53. Found: C, 69.30; H, 6.46.

(3*S*,4*R*,5*R*,6*S*)-3-(Benzyloxy)-5-(benzoyloxy)-4,6-dimethylcyclohex-1-ene, (+)-64. To a solution of 25 mg of (+)-**56** (0.11 mmol) in 1 mL of toluene were added 0.16 mL (0.16 mmol, 1 M solution in THF) of PMe_3, 20 mg (0.16 mmol) of BzOH, and 0.025 mL (0.16 mmol) of DEAD, respectively. The reaction was stirred for 12 h and then concentrated under reduced pressure. Purification via flash chromatography eluting with hexanes/ethyl acetate (10:1) produced 27 mg of (+)-**64** (74%) as a colorless oil: $[\alpha]_D = +50.6°$ (0.01 M, CH_2Cl_2); IR (CCl_4) υ 2860, 1730, 1440, 1050; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.02 (d, 3 H, J = 4.7 Hz), 1.06 (d, 3 H, J = 4.2 Hz), 2.13 (tq, 1 H, J = 6.2, 4.2 Hz), 2.53−2.61 (m, 1 H), 3.91 (ddd, 1 H, J = 6.2, 2.0, 1.2 Hz), 4.61 (syst. AB, 2 H, J_{AB}= 7.5 Hz), 4.89 (dd, 1 H, J = 7.6, 6.2 Hz), 5.61 (dt, 1 H, J = 6.8, 1.2 Hz), 5.84 (dt, 1 H, J = 6.8, 2.0 Hz), 7.29−7.38 (m, 7 H), 7.48 (t, 1 H, J = 6.5 Hz), 8.09 (d, 2 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.0, 18.1, 37.2, 40.6, 70.7, 78.5, 80.4, 127.7, 127.9, 128.4, 128.6, 129.7, 130.2, 132.6, 133.0, 136.1, 138.4, 166.5. Anal. Calcd for $C_{22}H_{34}O_6Si$: C, 62.56; H, 8.05. Found: C, 62.47; H, 7.96. Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.57; H, 7.14. Found: C, 78.41; H, 7.04.

(2*R*,3*S*,4*S*,5*R*)-Methyl 5-(Benzyloxy)-3-(benzoyloxy)-2,4-dimethyl-6-oxohexanoate, (−)-66. In a manner similar to that described for **30**, 21 mg (0.062 mmol) of (+)-**64** were allowed to react and afforded 16 mg of (−)-**66** as a colorless oil after purification by chromatography eluting with hexanes/ethyl acetate (5:1) (64%): $[\alpha]_D = -10.4°$ (0.02 M, CH_2Cl_2); IR (CCl_4) υ 2840, 2780, 1750, 1200; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (d, 3 H, J = 6.1 Hz), 1.21 (d, 3 H, J = 5.7 Hz), 2.04−2.16 (m, 1 H), 2.88 (qd, 1 H, J = 5.7, 3.0 Hz), 3.70 (s, 3 H), 4.13 (dd, 1 H, J = 4.5, 1.5 Hz), 4.58 (syst. AB, 2 H, J_{AB}= 8.1 Hz), 5.72 (dd, 1 H, J = 5.1, 3.0 Hz), 7.32−7.49 (m, 7 H), 7.60 (t, 1 H, J = 5.7 Hz), 7.98 (d, 2 H, J = 5.7 Hz), 9.67 (d, 1 H, J = 1.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.2, 19.2, 28.5, 31.3, 45.2, 52.3, 76.3, 85.1, 128.1, 129.5, 129.6, 130.4, 133.8, 134.2, 135.1, 135.3, 167.9, 175.3, 201.3. Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.35; H, 6.53. Found: C, 69.23; H, 6.38.

(3*S*,4*R*,5*S*,6*R*)-3-(Benzyloxy)-5-(benzoyloxy)-1-(phenylsulfonyl)-4,6-dimethylcyclohex-1-ene, (−)-67. In a manner similar to that described for (+)-**64**, 161 mg (0.43 mmol) of (−)-**58** was allowed to react and afforded 101 mg of (−)-**67** as a colorless oil after purification by chromatography eluting with hexanes/ethyl acetate (8:1) (49%): $[\alpha]_D = -46.5°$ (0.02 M, CH_2Cl_2);IR (CCl_4) υ 2980, 1730, 1580, 1210; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00 (d, 3 H, J = 5.3 Hz), 1.22 (d, 3 H, J = 5.0 Hz), 2.53 (sext, 1 H, J = 5.0 Hz), 3.04 (m, 1 H), 4.35 (dd, 1 H, J = 5.0, 2.3 Hz), 4.41 (syst. AB, 2 H, J_{AB} = 7.5 Hz), 5.65 (dd, 1 H, J = 7.6, 5.1 Hz), 7.13 (d, 1 H, J = 2.3 Hz), 7.30−7.43 (m, 7 H), 7.53−7.63 (m, 6 H), 7.86 (d, 2 H, J = 4.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.0, 19.3, 31.1, 32.0, 49.2, 68.1, 75.1, 125.7, 127.5, 127.7, 128.3, 128.8, 129.0, 133.2, 133.8, 137.5, 137.6, 137.8, 139.5, 140.1, 146.9, 173.1. Anal. Calcd for $C_{28}H_{28}O_5S$: C, 70.59; H, 5.88. Found: C, 70.47; H, 5.80.

(3*R*,4*R*,5*R*,6*S*)-3-(Benzyloxy)-5-(benzoyloxy)-4,6-dimethylcyclohex-1-ene, (+)-68. In a manner similar to that described for (+)-**56** (method A), 70 mg (0.15 mmol) of (−)-**67** was allowed to react and afforded 23 mg of (+)-**68** as a colorless oil after purification by chromatography eluting with hexanes/ethyl acetate (15:1) (46%): $[\alpha]_D = +15.8°$ (0.02 M, CH_2Cl_2); IR (CCl_4) υ 2960, 1730, 1470, 1150; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (d, 3 H, J = 7.3 Hz), 1.20 (d, 3 H, J = 7.1 Hz), 1.67 (m, 1 H), 2.47 (m, 1 H), 3.87 (dd, 1 H, J = 3.9, 1.2 Hz), 4.43 (syst. AB, 2 H, J_{AB}= 11.9 Hz), 5.67 (ddt, 1 H, J = 15.8, 3.9, 1.2 Hz), 5.78 (m, 1 H), 5.79 (dt, 1 H, J = 15.8, 1.2 Hz), 7.28−7.36 (m, 5 H), 7.48−7.61 (m, 3 H), 7.86 (dt, 2 H, J = 8.3, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.2, 18.2, 25.9, 33.1, 66.6, 74.5, 81.3, 127.5, 129.8, 129.9, 130.1, 135.9, 136.8, 137.5, 138.3, 144.0, 146.3, 170.0. Anal. Calcd for $C_{22}H_{24}O_3$: C, 78.57; H, 7.14. Found: C, 78.49; H, 7.10.

(2*R*,3*S*,4*S*,5*S*)-Methyl 5-(Benzyloxy)-3-(benzoyloxy)-2,4-dimethyl-6-oxohexanoate, (+)-69. In a manner similar to

that described for **30**, 18 mg (0.053 mmol) of (+)-**68** was allowed to react and afforded 11.1 mg of (+)-**69** as a colorless oil after purification by chromatography eluting with hexanes/ethyl acetate (5:1) (52%): $[\alpha]_D = +35.2°$ (0.01 M, CH_2Cl_2); IR (CCl_4) υ 2760, 1720, 1370, 1150; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (d, 3 H, $J = 7.1$ Hz), 1.24 (d, 3 H, $J = 6.4$ Hz), 2.63 (m, 1 H), 3.00 (m, 1 H), 3.68 (s, 3 H), 3.79 (ddd, 1 H, $J = 4.8$, 3.0, 1.6 Hz), 4.63 (syst. AB, 2 H, $J_{AB} = 11.2$ Hz), 5.53 (dd, 1 H, $J = 3.2$, 1.8 Hz), 7.30−7.37 (m, 7 H), 7.56 (t, 1 H, $J = 6.6$ Hz), 7.87 (dd, 2 H, $J = 6.6$, 1.6 Hz), 9.59 (d, 1 H, $J = 1.6$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.4, 17.3, 31.3, 34.7, 41.9, 53.2, 71.6, 86.9, 128.8, 129.7, 129.8, 130.1, 132.9, 133.8, 136.8, 138.3, 166.8, 179.8, 205.1. Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.35; H, 6.53. Found: C, 69.18; H, 6.42.

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Supporting Information Available: Spectroscopic data for compounds **19**, **22**−**25**, **27**, **29**−**33**, **36**−**41**, (+)-**46**−(+)-**48**, (+)-**51**, (+)-**52**, (+)-**55**, (+)-**56**, (−)-**58**, (−)-**61**-(+)-**64**, and (−)-**66**−(+)-**69**. This material is available free of charge via the Internet at http://pubs.acs.org.

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