An Intramolecular Cyclization Approach to Optically Active Cyclopentenyl Bromides

Stephane Borrelly and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

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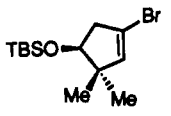
The two antipodes of 1-bromo-3,3-dimethyl-4-[(*tert*-butyldimethylsilyl)oxy]cyclopentene, the dextrorotatory form of which (1) is regarded as a potential synthetic precursor to kalmanol, have been prepared in a state of high enantiomeric purity from propargyl alcohol. The key steps in the abbreviated synthetic pathway involve the bromination–dehydrobromination of aldehyde **12** to give **7**, the conversion of alcohol **13** to the hydroxyl-substituted bromocyclopentene **18** by a novel tandem Claisen–Sakurai reaction sequence, and efficient enzymatic resolution of **18** via its chloroacetate ester. The absolute configurational assignments are based on ^{1}H NMR analyses of the (*R*)- and (*S*)-MTPA esters of (−)-**20**.

The presence of highly substituted five-membered rings in many biologically important natural products has only recently caused attention to be directed toward the synthesis of functionalized cyclopentenyllithium reagents.[1] However, the means presently available for producing these useful nucleophilic building blocks in enantiomerically enriched condition remain limited.[1,2] In the expectation that the *S* enantiomer of **1** could serve well as



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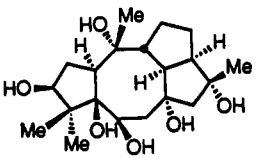

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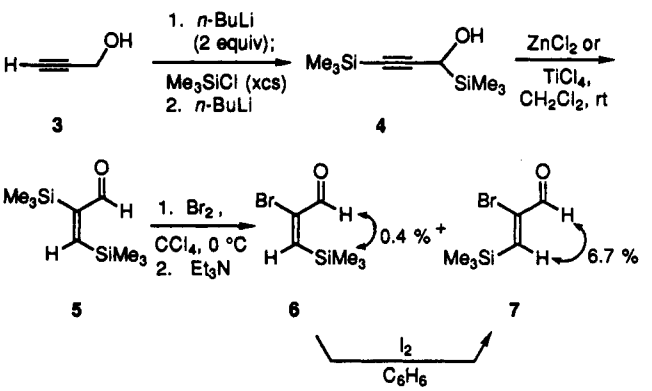
the A-ring of the distinctive tetracyclic cardiotoxic diterpenoid kalmanol (**2**),[3] we defined this bromide as the first subgoal of our synthetic endeavors. Reported here is an expedient pathway to both (+)- and (−)-**1** that capitalizes on the improvization of a tandem Claisen rearrangement/intramolecular Sakurai cyclization sequence. The process might well accommodate a reasonable level of structural variation and be serviceable in other contexts.

Results and Discussion

Consideration of (*E*)-2-Bromo-3-(trimethylsilyl)-acrolein as Intermediate. Retrosynthetic considerations led us back to the two geometric isomers of 2-bromo-3-(trimethylsilyl)propanal. A recent report[4] that the *E*-isomer of this aldehyde, viz. **6**, could be prepared isomerically pure prompted reinvestigation of the original route in order to gain information on its relative thermodynamic stability. Accordingly, propargyl alcohol (**3**) was bissilylated and subjected to silyl-Wittig rearrangement to produce **4** (Scheme I). When exposed to 10 mol % of a Lewis acid such as $ZnCl_2$ or $TiCl_4$, **4** experienced smooth conversion to **5**. However, bromination of **5** in CCl_4 at 0

Scheme I



3 **4** **5** **6** **7**

°C followed by the addition of triethylamine invariably produced mixtures containing both **6** and **7**, with the *E*-isomer predominating in most instances. It soon became apparent that **7** was considerably more thermodynamically favored than **6**. For example, full equilibration with **7** (ratio 1:20) could be rapidly established at 20 °C in benzene solution containing a catalytic quantity of iodine. In light of the lability of **6**, it is quite possible that post-equilibration was inadvertently operating during our processing of this material. At this point, the stereochemical assignments to the individual isomers were corroborated by NOE experiments as shown on the illustrated formulas.[5]

The kinetically controlled conversion of **5** to **6** introduces an interesting mechanistic dilemma. In order to realize brominative desilylation in this fashion, it is necessary that anti elimination via **8** be preceded by a totally unprecedented cis addition of bromine. Alternatively, should bromine add in conventionally trans fashion to generate **9**, ensuing reintroduction of the double bond must occur via a syn arrangement of the leaving group (Scheme II). The latter option embraces two significant features that cause us to prefer it. These are adoption of halogenation stereoselectivity demanded of bromonium ion intervention and parallelism between the syn elimination of Me_3SiBr and the anionic variant of the Peterson olefination reaction.[6]

The above findings prompted the development of a more

(1) Paquette, L. A.; Dahnke, K.; Doyon, J.; He, W.; Wyant, K.; Friedrich, D. *J. Org. Chem.* **1991**, *56*, 6199 and relevant references cited therein.
(2) Ni, Z.; Smith, G.; Heidelbaugh, T. Unpublished results from this laboratory.
(3) Burke, J. W.; Doskotch, R. W.; Ni, C.-Z.; Clardy, J. *J. Am. Chem. Soc.* **1989**, *111*, 5831.
(4) Mergardt, B.; Weber, K.; Adiwidjaja, G.; Schaumann, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1687.
(5) Our ^{1}H and ^{13}C NMR data for **5** and **6** compare closely to the chemical shift values reported in ref 4 with one exception. The vinylic proton in **6** appears at δ 7.056 (in C_6D_6) and not at δ 7.56.
(6) Ager, D. J. *Org. React.* **1990**, *38*, 1.

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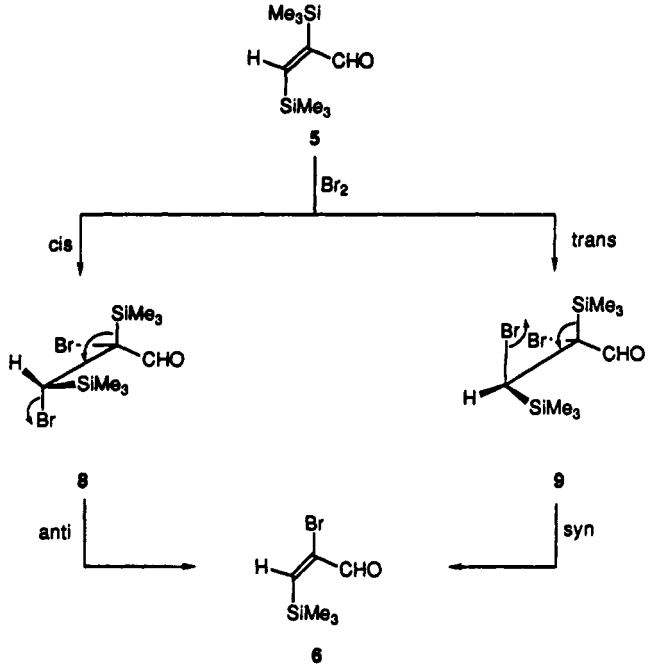
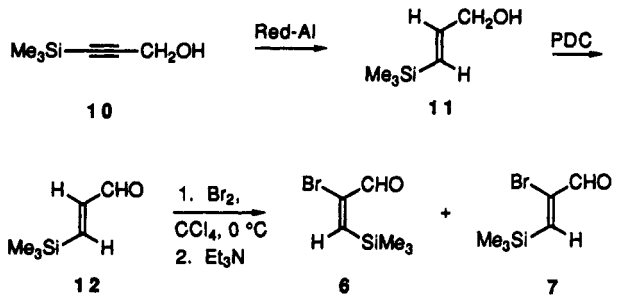
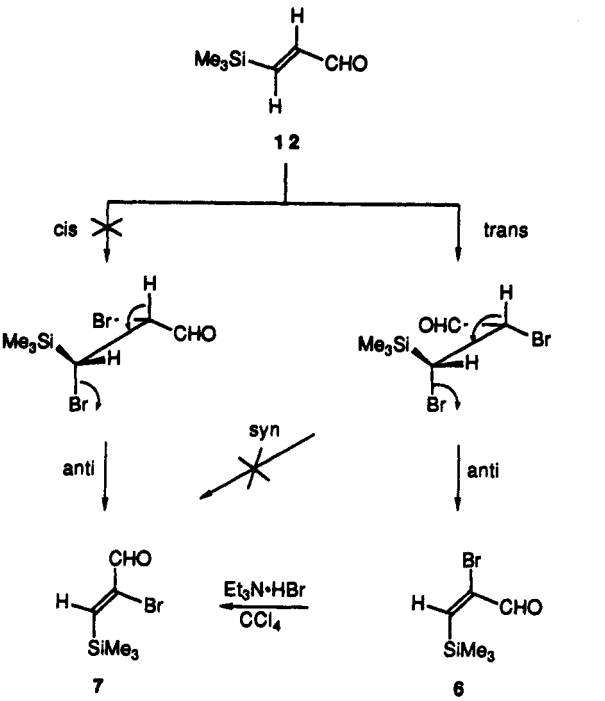
Scheme II



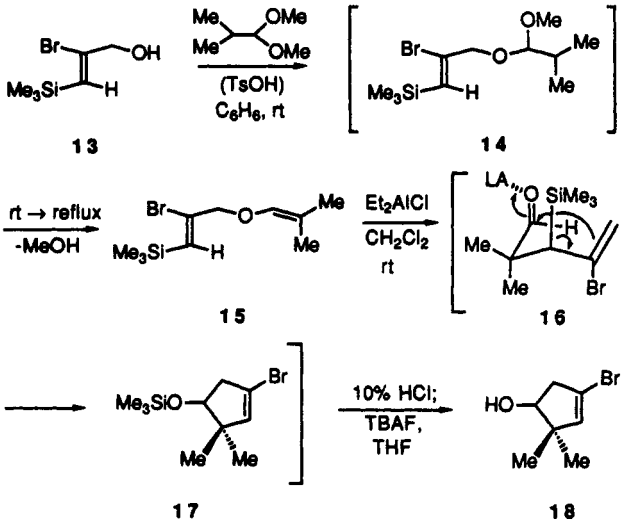
Scheme III



Scheme IV



Scheme V



efficient route to **7** that was also intended to provide added mechanistic insight.

Alternative Synthesis of the *Z*-Isomer. Reduction of alkyne **10** with Red-Al is recognized to deliver **11** exclusively[7] (Scheme III). Oxidation of this alcohol with PDC provided **12** uniquely (300-MHz ^{1}H NMR analysis).[8] Bromination–dehydrobromination[9] of **12** under conditions entirely comparable to those utilized for **5** resulted in the formation of a 1:7 mixture of **6** and **7**.

The predominance of *Z*-isomer **7** would appear once again to stand in conflict with expectations based upon trans addition followed by antiperiplanar elimination (Scheme IV). Attempts to follow the course of the bromination by performing the reaction in an NMR tube did not permit unequivocal assignments to be made to the dibromide. What was clear, however, was that the thermodynamically favored elimination product had been produced in this instance. Indeed, when enriched samples of **6** (prepared as in Scheme II) were treated with 0.65 equiv of Et_3N·HBr in CCl_4 in an effort to simulate the conditions prevailing in Scheme IV, conversion to a 1:20 mixture of **6** and **7** took place in less than 5 min. As a consequence, it would appear that, unlike **5**, the bromination–dehydrobromination of **12** proceeds conventionally to give **6**, which isomerizes to **7** under the conditions of its formation. Thus, the behavior of **9** is unique and the syn elimination of Me_3SiBr worthy of more exhaustive investigation as a mechanistic paradigm.

Tandem Claisen–Sakurai Transformations. Isomerically enriched **7** (95% purity) was reduced to **13** with Dibal-H at −78 °C (Scheme V). Care had to be exercised in this step since reductive debromination to give (*E*)-3-(trimethylsilyl)-2-propen-1-ol became competitive with the conversion to **13** if the concentration of **7** exceeded 1 mmol/20 mL. Initially, the conversion of **13** to vinyl ether **15** by the more classical methods proved problematical. However, adaptation of the Erman[10] and Baeckström protocol[11]

(7) Jones, T. K.; Denmark, S. E. *Org. Synth.* **1986**, *64*, 182.

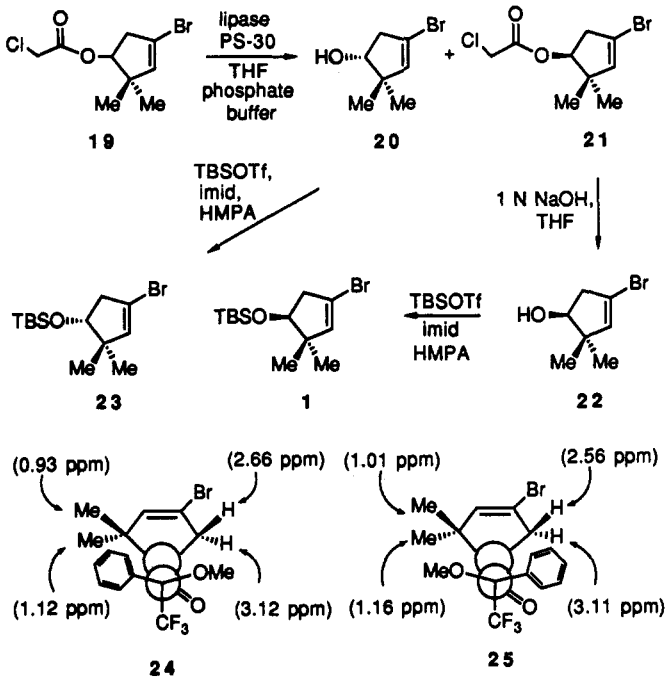
(8) Comparable oxidation of the *Z*-alcohol (Hiemstra, H.; Klaver, W. J.; Speckamp, W. N. *Rec. Trav. Chim. Pays-Bas* **1986**, *105*, 299; Ladouceur, G.; Paquette, L. A. *Synthesis* **1992**, 185) afforded mixtures of the *E*- and *Z*-aldehydes. Stereochemical integrity was also lost when MnO_2 and TPAP/NMO were the oxidants.

(9) (a) Smith, A. B., III; Branca, S. J.; Guaciaro, M. A.; Wovkulich, P. M.; Korn, A. *Org. Synth.* **1983**, *61*, 65. (b) Shih, C.; Fritzen, E. L.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 4462.

(10) Erman, W. F.; Treptow, R. S.; Bazukis, P.; Wenkert, E. *J. Am. Chem. Soc.* **1971**, *93*, 657.

(11) Baeckström, P.; Li, L.; Polec, I.; Unelius, C. R.; Wimalasiri, W. *J. Org. Chem.* **1991**, *56*, 3358.

Scheme VI



was notably successful. Thus, exposure of **13** to isobutyraldehyde dimethyl acetal in refluxing benzene containing a catalytic quantity of *p*-toluenesulfonic acid led via **14** directly to **15** (75% isolated yield).

Although the stage was now set for Claisen rearrangement, **15** was surprisingly unresponsive to thermal activation either as neat samples or when dissolved in benzene. Advantage was therefore taken of the known propensity of diethylaluminum chloride to catalyze such [3.3] sigmatropic transformations.[12] When catalysis was applied, the conversion of **15** to **17** was complete within 15 min at 25 °C (TLC analysis). Addition of 10% HCl and TBAF after 2 h afforded the colorless oily alcohol **18** in 62% yield. The discovery that the Claisen and Sakurai reactions[13] can be effectively dovetailed in this manner once again brings to the forefront the many obvious advantages associated with tandem chemical processes.[14]

Enzymatic Hydrolysis. To set the stage for resolution of the enantiomers of **18**, its chloroacetate derivative was prepared and subjected to controlled enzymatic hydrolysis with lipase PS-30 in a mixed THF–pH 7 phosphate buffer solvent system.[15] Reaction stopped after approximately 50% consumption of the racemic substrate (Scheme VI). Alcohol **20** and unreacted ester **21** were efficiently recovered by silica gel chromatography. Following the saponification of **21**, the enantiomeric excess of the alcohols was established by Mosher ester analysis[16] to be 92% for **20** and 100% for **22**. The indicated absolute configurational assignments follow from ^{1}H NMR analysis of the pair of MTPA esters prepared from (−)-**21** and the (*R*)- and (*S*)-enantiomers of α-methoxy-α-(trifluoromethyl)phenylacetic acid. As a consequence of the long-range anisotropy contributions of the phenyl substituent in the assumed ground-state conformations[16,17] of **24** and **25**, the observed ordering of the chemical shifts is uniquely consistent with the conclusion that (−)-**20** possesses the *R* configuration.

Finally, both **20** and **22** were silylated to provide the antipodal cyclopentenyl bromides **23** and **1**, respectively. We expect to report on the role played by **1** in a total synthesis of kalmanol in due course.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1320 spectrometer. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz on a Bruker AC-300 instrument. Mass spectra were recorded on a Kratos MS-30 instrument at The Ohio State University Chemical Instrument Center. Elemental analyses were performed at the Scandianavian Microanalytical Laboratory, Herlev, Denmark. The chromatographic separations were carried out either under flash conditions on Fluka silica gel H or gravimetrically on Woelm silica gel 63-200. The organic extracts were dried over anhydrous sodium sulfate. Solvents were reagent grade and in many cases dried prior to use.

(*E*)-3-(Trimethylsilyl)propenal (12). A cold (0 °C), nitrogen-blanketed, magnetically stirred solution of **11** (13.5 g, 0.092 mol) in dry CH_2Cl_2 was treated portionwise with pyridinium dichromate (41 g, 1.2 equiv) during 30 min. The cooling bath was removed, and agitation was maintained for 36 h. The reaction mixture was filtered through a pad of Celite (CH_2Cl_2 wash), washed with saturated $CuSO_4$ solution (2 × 200 mL), dried, and concentrated. Distillation of the residue afforded 7.9 g (68%) of **12**, bp 74–76 °C (35 Torr), as a colorless oil: IR (neat, cm^{-1}) 2960, 1690, 1250, 1090, 850; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.43 (d, J = 7.5 Hz, 1 H), 7.12 (d, J = 18.3 Hz, 1 H), 6.43 (dd, J = 18.3, 7.5 Hz, 1 H), 0.12 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 194.4, 158.3, 144.0, −2.2; MS *m*/*z* (M^+) calcd 128.0657, obsd 128.0628.

(*Z*)-2-Bromo-3-(trimethylsilyl)propenal (7). A cold (−5 °C), magnetically stirred solution of **12** (5.5 g, 43 mmol) in dry CCl_4 (300 mL) was treated dropwise with bromine (2.3 mL, 45 mmol), allowed to warm to rt during 1 h, and treated with triethylamine (12 mL, 86 mmol). After 2 h, the slurry was washed with water (2 × 100 mL), dried, filtered, and evaporated to give 6.2 g (70%) of a mixture of **6** and **7**. Distillation of this material after brief treatment with a catalytic quantity of iodine in benzene at rt gave pure **7** as a colorless oil, bp 28–30 °C (0.2 Torr); IR (neat, cm^{-1}) 2975, 1715, 1580, 1255, 1070, 850; ^{1}H NMR (300 MHz, C_6D_6) δ 8.60 (s, 1 H), 6.81 (s, 1 H), 0.07 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 185.4, 153.1, 139.8, −1.8; MS *m*/*z* (M^+ − Br) calcd 127.0587, obsd 127.0583.

(*Z*)-2-Bromo-3-(trimethylsilyl)propen-1-ol (13). A cold (−78 °C), magnetically stirred solution of **7** (2.0 g, 9.71 mmol) in dry CH_2Cl_2 (200 mL) was treated dropwise during 30 min with Dibal-H (9.7 mL of 1 M in hexane, 9.7 mmol). After 15 min, the reaction mixture was quenched with a saturated solution of sodium potassium tartrate (50 mL) and stirred at rt for 2 h. The separated organic phase was dried and concentrated to leave a residue that was purified by silica gel chromatography (elution with 2:1 petroleum ether–CH_2Cl_2). There was isolated 1.57 g (78%) of **13** as a colorless oil: IR (neat, cm^{-1}) 3700–3000, 2960,

(12) (a) Takai, K.; Mori, I.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 3985. (b) Stevenson, J. W. S.; Bryson, T. A. *Tetrahedron Lett.* **1982**, *23*, 3143.

(13) For previous examples of intramolecular Sakurai reactions, consult: (a) Kuwaiima, I.; Tanaka, T.; Atsumi, K. *Chem. Lett.* **1979**, 779. (b) Itoh, A.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1979**, 1783. (c) Andersen, N. H.; McCrae, D. A.; Grotjohn, D. B.; Gabbe, S. Y.; Theodere, L. J.; Ippolito, R. M.; Sarkar, T. K. *Tetrahedron* **1981**, *37*, 4069. (d) Trost, B. M.; Coppola, B. M. *J. Am. Chem. Soc.* **1982**, *104*, 6879. (e) Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655. (f) Trost, B. M.; Fray, M. J. *Tetrahedron Lett.* **1984**, *25*, 405. (g) Mikami, K.; Maeda, T.; Kishi, N.; Nakai, T. *Tetrahedron Lett.* **1984**, *25*, 5151.

(14) Ho, T. L. *Tandem Organic Reactions*: John Wiley: New York, 1992.

(15) For some examples of earlier precedent, see: (a) Schwartz, A.; Madan, P.; Whitesell, J. K.; Lawrence, R. M. *Org. Synth.* **1991**, *69*, 1. (b) Maleczka, R. E., Jr.; Paquette, L. A. *J. Org. Chem.* **1991**, *56*, 6538.

(16) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

(17) For comparable use of *O*-methylmandelate esters, see: (a) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370. (b) Paquette, L. A.; Lau, C. J. *J. Org. Chem.* **1987**, *52*, 1634. (c) Marshall, J. A.; Lebreton, J. *J. Am. Chem. Soc.* **1988**, *110*, 2925. (d) Marshall, J. A.; Robinson, E. D.; Lebreton, J. *J. Org. Chem.* **1990**, *55*, 227.

2900, 1610, 1400, 1250, 1070, 980, 840; ^{1}H NMR (300 MHz, C_6D_6) δ 6.28 (br s, 1 H), 3.88 (br s, 2 H), 1.80 (br s, 1 H), 0.20 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 141.2, 125.8, 69.5, -0.8; MS m/z (M^+) calcd 207.9910, obsd 207.9915.

The 3,5-dinitrobenzoate of **13** was obtained as a crystalline solid, mp 58–59 °C (from 10:1 pentane–ether).

Anal. Calcd for $C_{13}H_{17}BrN_2O_6Si$: C, 38.72; H, 3.75. Found: C, 38.88; H, 3.77.

1-(Trimethylsilyl)-2-bromo-6-methyl-4-oxa-1,5-heptadiene (15). A solution of **13** (100 mg, 0.485 mmol) in dry benzene (10 mL) was treated with isobutyraldehyde dimethyl acetal (172 mg, 1.46 mmol) and *p*-toluenesulfonic acid (1 crystal) and the resulting solution refluxed for 3 days under a Claisen apparatus equipped for the continuous removal of methanol. At this point, triethylamine (several drops) was introduced, and the solution was cooled to rt and concentrated to leave a residue that was purified by silica gel chromatography (elution with 5:1 petroleum ether–CH_2Cl_2). There was obtained 95 mg (75%) of **15** as a colorless oil; IR (neat, cm^{-1}) 2955, 2910, 2895, 1685, 1605, 1245, 840; ^{1}H NMR (300 MHz, C_6D_6) δ 6.42 (t, J = 1.4 Hz, 1 H), 5.58 (q, J = 1.4 Hz, 2 H), 1.69 (d, J = 0.8 Hz, 3 H), 1.40 (d, J = 0.8 Hz, 3 H), 0.17 (s, 9 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 140.1, 137.5, 128.4, 111.2, 77.1, 19.4, 15.3, -0.9; MS m/z calcd 262.0362, obsd 262.0375.

(±)-1-Bromo-3,3-dimethylcyclopenten-4-ol (18). A cold (0 °C),magnetically stirred solution of **15** (300 mg, 1.45 mmol) in dry CH_2Cl_2 (35 mL) was treated dropwise with diethylaluminum chloride (2.9 mL of 1 M in hexane, 2.9 mmol). The reaction mixture was allowed to warm to 20 °C, stirred at this temperature for 2 h, and carefully quenched with 10% HCl (5 mL). The separated organic phase was washed with brine (20 mL) and concentrated. The residue was dissolved in THF (25 mL), treated with TBAF (1.9 mL of 1 M in THF) in one portion, stirred for 15 min, and treated with saturated brine. The organic layer was dried and concentrated to leave a residue that was chromatographed on silica gel (elution with 1:1 petroleum ether–ether). There was obtained 170 mg (62%) of **18** as a colorless oil: IR (neat, cm^{-1}) 3700–3050, 2970, 2950, 1080; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (t, J = 1.8 Hz, 1 H), 4.00 (t, J = 5.6 Hz, 1 H), 2.89 (ddd, J = 16.3, 6.9, 1.8 Hz, 1 H), 1.51 (ddd, J = 16.3, 5.8, 1.8 Hz, 1 H), 1.9 (br s, 1 H), 1.06 (s, 3 H), 1.03 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.2, 117.1, 79.2, 48.6, 47.5, 26.2, 20.1; MS m/z (M^+) calcd 189.9993, obsd 190.0014.

The *p*-bromophenylurethane of **18** was obtained as colorless crystals, mp 51–52 °C (from pentane).

Anal. Calcd for $C_{14}H_{15}Br_2NO_2$: C, 43.22; H, 3.89. Found: C, 43.53; H, 4.11.

(±)-Chloroacetate 19. To a solution of **18** (100 mg, 0.526 mmol) in dry CH_2Cl_2 (10 mL) were added DMAP (5 mg) and pyridine (0.3 mL, 3 equiv). After 10 min of stirring, chloroacetyl chloride (1.4 equiv) was introduced via syringe. The reaction mixture was stirred for 24 h, quenched with saturated NH_4Cl solution (2 × 5 mL), and dried. Purification of the residue by silica gel chromatography (elution with 2:1 petroleum ether–CH_2Cl_2) gave **19** as a faintly yellow oil (123 mg, 88%): IR (near, cm^{-1}) 2980, 1715; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (t, J = 1.8 Hz, 1 H), 5.06 (dd, J = 4.2, 7.0 Hz, 1 H), 4.06 (s, 2 H), 3.08 (ddd, J = 1.9, 7.0, 13.5 Hz, 1 H), 2.62 (ddd, J = 1.8, 4.3, 14.8 Hz, 1 H), 1.13 (s, 3 H), 1.06 (s, 3 H); MS m/z ($M^+ - COCH_2Cl$) calcd 188.9915, obsd 189.1024.

Enzymatic Resolution of 18. To 35 mL of phosphate buffer (pH = 7) was added in turn 40 mg of lipase PS-30 (Amano) and a solution of **19** (400 mg, 1.5 mmol) in dry THF (3.5 mL). After 6 h, 1.5 mL of 0.5 N NaOH was added (theoretical 50% neutralization). The reaction mixture was stirred for an additional hour during which time no further change in pH was noted. Ether (50 mL) was added, the separated aqueous phase was extracted with ether (50 mL), and the combined ethereal solutions were dried and concentrated. The residue, when subjected to silica gel chromatography (elution with 1:1 petroleum ether–CH_2Cl_2), provided 170 mg (43%) of chloroacetate **21** and 125 mg (44%) of (–)-alcohol **20**, $[\alpha]^{20}_D$ -28.6° (*c* 0.21, $CHCl_3$). The chloroacetate was hydrolyzed in aqueous THF containing 1 N NaOH to give 109 mg (91%) of (+)-alcohol **22**, $[\alpha]^{20}_D$ +31.1° (*c* 0.20, $CHCl_3$).

Mosher ester analyses indicated the levorotatory alcohol to be 92% ee and the dextrorotatory alcohol to be 100% ee.

Preparation of the *O*-Silyl Derivatives. To a nitrogen-blanketed, magnetically stirred solution of either **20** or **22** (101 mg, 0.534 mmol) and imidazole (91 mg, 2.5 equiv) in dry HMPA (2 mL) was added dropwise 245 μL of *tert*-butyldimethylsilyl triflate (2 equiv). After 12 h at rt, the reaction mixture was quenched with saturated $NaHCO_3$ solution (5 mL) and diluted with pentane (10 mL). The separated organic layer was dried and concentrated, and the mixture was chromatographed on silica gel (pentane elution) to furnish 145 mg (89%) of either **23** or **1**: IR (neat, cm^{-1}) 2960, 2940, 2860, 1250, 1110; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (t, J = 1.5 Hz, 1 H), 4.01 (t, J = 7.0 Hz, 1 H), 2.71 (ddd, J = 15.7, 7.3, 1.3 Hz, 1 H), 2.58 (ddd, J = 15.7, 6.9, 2.1 Hz, 1 H), 1.04 (s, 3 H), 0.96 (s, 3 H), 0.89 (s, 9 H), 0.55 (s, 3 H), 0.50 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.2, 116.4, 79.6, 48.7, 47.2, 26.4, 25.8, 20.6, 18.1, -4.6, -5.0; MS m/z ($M^+ - t$-BuSiMe$_2$) calcd 188.9915, obsd 189.0963. For **23**: $[\alpha]^{20}_D$ -38.9° (*c* 0.11, $CHCl_3$). For **1**: $[\alpha]^{20}_D$ +42.0° (*c* 0.12, $CHCl_3$).

Anal. Calcd for $C_{13}H_{25}BrOSi$: C, 51.14; H, 8.25. Found: C, 51.43; H, 8.34.

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Supplementary Material Available: 300-MHz ^{1}H and 75-MHz ^{13}C NMR spectra of **7**, **12**, **15**, and **19** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.