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Stereodivergent Resolution of Oxabicyclic Ketones: Preparation of Key Intermediates for Platensimycin and Other Natural Products

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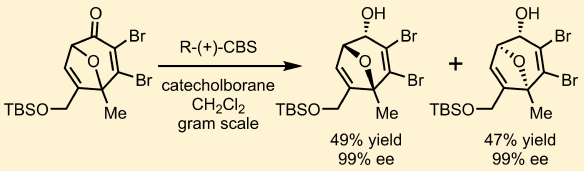
Supporting Information

ABSTRACT: An improved methodology for the preparation of enantiopure oxabicyclo[3.2.1]octadienes via a stereodivergent resolution is reported. High catalyst control proximal to the oxabridged stereocenter produces readily separable diastereomers in high yield (>92%) and with excellent optical purity (>95% ee). This resolution strategy is amenable to large-scale preparations, and the utility of the resolution was further demonstrated in the asymmetric preparation of a key intermediate used in the synthesis of the antibiotic (−)-platensimycin.



Over the past several years, we have been interested in the development of bridged bicyclic adducts derived from the condensation of perhalogenated cyclopropenes and various dienes as key intermediates for the synthesis of natural products and their analogs.[1] Of particular interest has been the oxabicyclo[3.2.1]octane adduct **1** derived in a single step through cycloaddition of furans and tetrabromocyclopropene (TBCP) that can be readily converted into the versatile dibromoenone (±)-**2** through a silver-mediated hydrolysis.[2] Compound (±)-**2** embodies a conformationally constrained cycloheptenone that is functionalized at each of the seven carbons while allowing for excellent regio- and stereochemical control in the course of synthetic elaboration. The ability to effect cleavage, annulation, and rearrangement of the bridged ether intermediate has allowed the development of routes to the meroterpenoid natural product frondosin B, the antibiotic platensimycin,[3] and the highly oxygenated eunicellin diterpenoids[4] (Figure 1). To further expand the utility of these compounds, we report here an improved preparation of several enantiopure derivatives of **2**.

We have previously reported on the resolution of the tetrabromide (±)-**1** through formation and separation of the tartrate-derived ketals.[5] Although this method provided each enantiomer of **2** in high optical purity (>95% ee) after ketal hydrolysis, the formation of the tartrate ketals involves the use of expensive air-sensitive reagents that became prohibitive on larger scale. Furthermore, cleavage of the resulting tartrate ketals required strongly acidic conditions (neat methanesulfonic acid) that would be incompatible with the incorporation of acid-sensitive functionality in more complex adducts. In order to expand the utility of these bicyclic building blocks, we set out to develop a more economical, scalable, and mild method for the preparation of both enantiomers of dibromoeneone (±)-**2**. Herein, we disclose a stereodivergent resolution strategy through the use of a divergent reduction of the racemic dibromide (±)-**2**. The utility of this resolution is further demonstrated in the asymmetric preparation of a key intermediate in the synthesis of the antibiotic (−)-platensimycin.

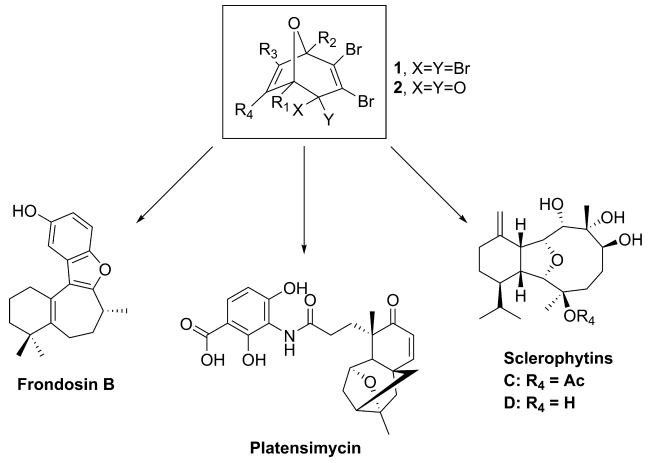


Figure 1. Examples of dibromoenone (±)-**2** derived natural products.

We were interested in the possibility of a classical kinetic resolution of enone (±)-**2** utilizing a chiral reducing agent.[6] Access to this key compound was initially improved by developing a one-pot process whereby thermal cycloaddition between furan and TBCP in dioxane could be directly treated with aqueous silver nitrate to deliver the enone directly in high yield on a multigram scale (96% on a 5 g scale) (Scheme 1). Prior to this work, we showed that Luche reduction of (±)-**2** proceeds with high diastereoselectivity giving the *endo*-alcohol as the exclusive product.[7] In accord with these studies, we envisioned a scenario whereby this diastereoselectivity could be paired with a high degree of enantio-differentiation imparted by a chiral catalyst, leading to one enantio-enriched *endo*-alcohol

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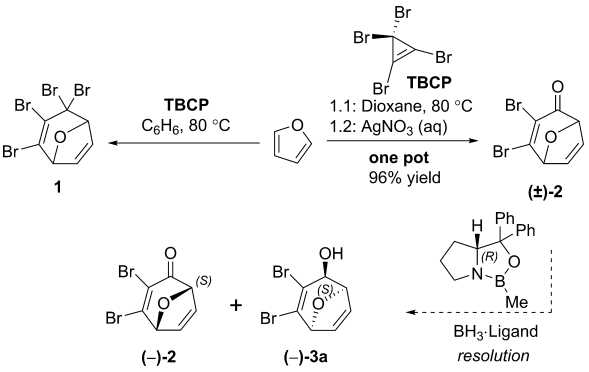
Scheme 1. An Improved One Step Synthesis of Dibromoenone (2) and Initial Strategy for Kinetic Resolution



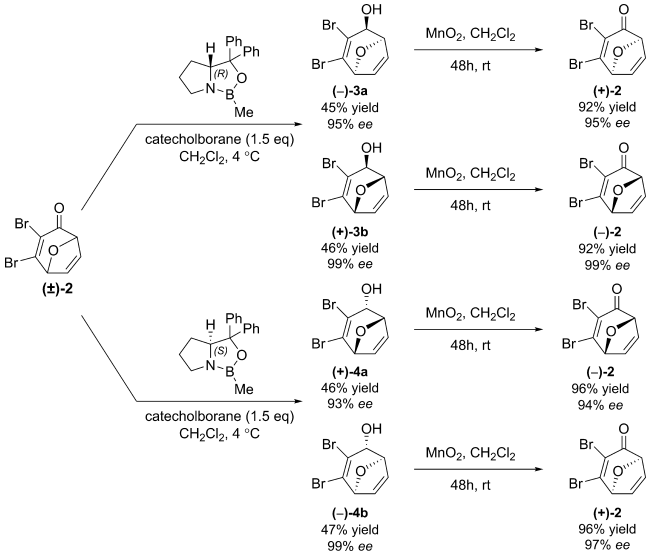
(−)-**3a** as well as recovery of the antipode of the ketone (−)-**2**. The Corey−Bakshi−Shibata (CBS) oxazaborolidine had shown prior success in reductive kinetic resolutions[8−10] and was of interest to us due to its commercial availability in both enantiomeric forms, high selectivity, and wide substrate tolerance.[11,12] Furthermore, CBS reductions of cyclic α,β-unsaturated ketones have revealed that α-substitution of the enone olefin is crucial for effective steric differentiation of the carbonyl oxygen lone pairs.[13,14] Given the α-bromo substitution in (±)-**2**, it appeared that it would be an ideal substrate for this reduction.

We first examined the reduction of dibromide (±)-**2** with *R*-(+)-CBS (0.5 equiv) and catecholborane (0.5 equiv) at −78 °C. Preliminary studies revealed that the reaction proceeded to ∼50% completion under these conditions; however, the reduction led to an ∼3:1 mixture of separable *endo*-**3a** and *exo*-**3b** alcohols. Each diastereomeric alcohol was isolated in high optical purity (>80% ee) while the starting dibromoenone was recovered in nearly racemic form.

This result was unusual given that the geometry of the oxabicyclo[3.2.1]octadiene **2** imparts significant concavity to the molecule, giving exclusively *endo*-products under Luche reduction conditions. These results suggested that catalyst control was overriding the directing effect embedded in the rigid bicyclic framework such that each enantiomer of **2** was reduced at similar rates by hydride attack from both faces of the ether bridge. The simple separation of the resulting diastereomeric *endo* and *exo* alcohols allowed us to exploit a stereodivergent resolution strategy to resolve the enantiomers of (±)-**2**.[15−18] Increasing the reaction temperature to 4 °C led to a noticeable increase in the enantiomeric excess (>90%) of both resulting alcohols. The elevated temperature allows for increased catalyst coordination to both the hydride source and the carbonyl moiety, thus suppressing any background *exo*-hydride attack.[19]

To further optimize this process, we exposed the dibromide (±)-**2** to an excess of catecholborane in the presence of the CBS catalyst and allowed the reaction to proceed until complete consumption of the starting material was observed. Pleasingly, each diastereomer was isolated in high yield with even greater optical purity (**3a**, 95% and **3b**, 99% ee) (Scheme 2). Subsequent oxidation of each individual diastereomer in the presence of MnO_2 gave the enantioenriched dibromoenones (+)-**2** and (−)-**2** in excellent yield (92%). The physical data and optical rotations of the enantiomers matched those reported from our previous studies. Likewise, exposure of

Scheme 2. Synthesis of Six Nonracemic Building Blocks from Dibromide (±)-2



dibromoenone (±)-**2** to the *S*-(−)-CBS catalyst proceeded in a similar fashion to provide the antipodal alcohols *endo*-**4a** and *exo*-**4b**. Overall, this provides direct access to six different nonracemic building blocks in only 2−3 operations from furan, while also highlighting our first synthetic method to produce *exo*-alcohols directly from (±)-**2**, a relationship required in our approach to the eunicellin diterpenes.[4]

Based on experimental evidence, preferred attack of the hydride on the carbonyl of both enantiomers of **2** likely occurs through related transition states as depicted in Figure 2. The

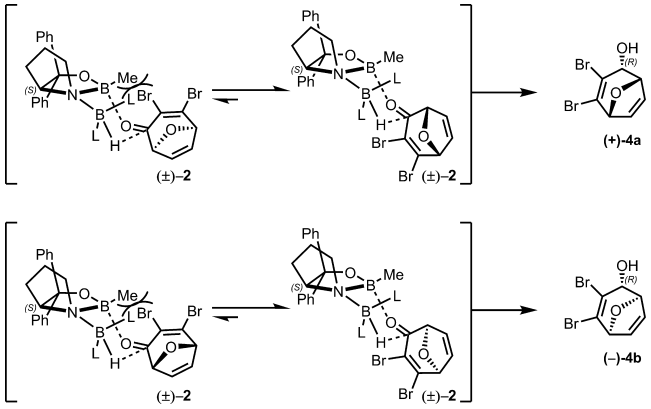


Figure 2. Transition state between *S*-(−)-CBS and (±)-**2**.

more favorable conformation positions the α-bromide *anti* to the endocyclic boron of the CBS catalyst, avoiding unfavorable steric interaction. The quasi-intramolecular hydride attack occurs from both the *endo* and *exo* face of the ether bridge, but only from a single face of the carbonyl (depending on catalyst preference). This results in a highly selective reduction without any significant control imparted from the ether bridge.

Encouraged by the success of this resolution strategy, we turned our attention to a synthetically interesting substrate that represents an early intermediate in our total synthesis of platensimycin. Dibromoenone (±)-**6** was prepared from **5** through the newly developed one-pot procedure (Scheme 3). Subjecting (±)-**6** to our resolution conditions provided *endo*-

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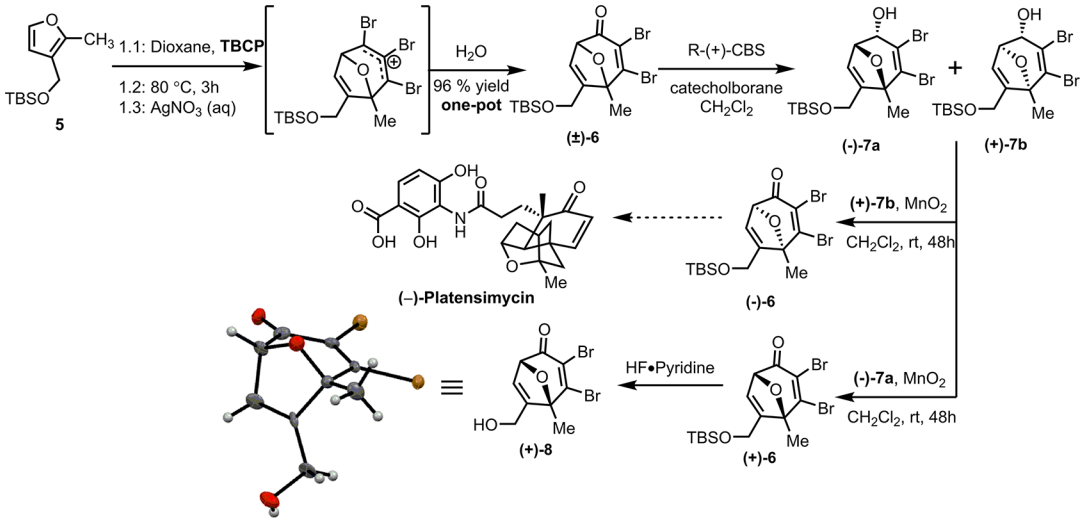
Scheme 3. Resolution of Early Intermediates for (−)-Platensimycin Synthesis and X-ray Crystal Structure of (+)-8



alcohol (−)-**7a** and *exo*-alcohol (+)-**7b** in 49% yield (99% ee) and 47% yield (99% ee), respectively. Allylic oxidation in the presence of MnO_2 provided the enantioenriched dibromides (−)-**6** and (+)-**6** in high yield. The ability to resolve this complex material at an early stage provides entry into an asymmetric synthesis of both natural and non-natural platensimycin.[20] To add further confirmation to our assignment of absolute stereochemistry, (+)-**6** was desilylated to the corresponding alcohol (+)-**8**. Alcohol (+)-**8** yielded thin plate crystals for X-ray crystallographic determination of absolute stereochemistry.

The divergent reduction of racemic bridged oxabicyclo[3.2.1]octadieneones provides direct and convenient access to several versatile enantiopure building blocks. The stereodivergent resolution strategy is greatly facilitated by the conversion to diastereomeric *endo*- and *exo*-alcohols which allows for convenient chromatographic separation. This type of process may be extendable to other bridged adducts arising from Diels−Alder and alternate cycloaddition strategies and provide a simple route to other enantiopure bicyclic building blocks.

EXPERIMENTAL SECTION

General. All reactions were carried out under an inert argon atmosphere with dry solvents under anhydrous conditions unless otherwise stated. Commercial grade reagents and solvents were used without further purification except as indicated below. High-resolution mass spectra (HRMS) were obtained by electrospray ionization time-of-flight reflectron experiments. Optical rotations were measured using a 50 mm path-length cell. The enantiomeric excess values of the *endo*-alcohols were determined by HPLC analysis in hexanes/isopropanol at a column flow rate of 1.0 mL/min on a Chiralcel OJ chiral column with detection at 254 nm. The enantiomeric excess values of the *exo*-alcohols were determined by conversion to their Mosher ester using known procedures.[21] The spectral data of (+)-**2**, (−)-**2**, (−)-**3a**, (+)-**4a**, (+)-**6**, (−)-**6**, and (+)-**8** were consistent to previous work done in the lab.[3,5]

General Procedure for One-Pot Diels−Alder and Silver Hydrolysis. To a flame-dried pressure vessel was added furan (24.6 mmol) and solvated with 1,4-dioxane (5 mL). The solution was treated with freshly distilled TBCP (8.7 g, 24.6 mmol) at rt, and the vessel was sealed. The vessel was stirred overnight at rt before being gradually heated to 80 °C and held at that temperature until all starting material was consumed, ∼1 h. After this time, the reaction was allowed to cool to rt, diluted with acetone (46 mL), and treated with two portions of $AgNO_{3(aq)}$ (8.3 g, 49.2 mmol, in 23 mL of H_2O) over 20 min. The suspension was allowed to stir at rt for 3 h before being poured over solid $NaHCO_3$ (6.2 g, 73.8 mmol). The solids were removed by filtration through Celite and washed with acetone (300 mL). The filtrate was concentrated and then extracted with Et_2O (4 × 100 mL). The combined organic layers were washed with sat. $NaHCO_3$ (2 × 100 mL), H_2O (3 × 100 mL), and brine (2 × 100 mL), dried over sodium sulfate, and concentrated. The resulting crude dibromoenone was purified by flash chromatography using 25% EtOAc in hexanes as the eluent to afford products as yellow solids. The spectral data of (±)-**2** and (±)-**6** were consistent to previous work done in the lab. Isolated with yields of (±)-**2** (96%, 23.6 mmol) and (±)-**6** (94%, 23.1 mmol).

General Procedure for CBS Reduction. To a flame-dried flask was added substrate in CH_2Cl_2 (0.2 M) followed by the (*R*)-(+)- or (*S*)-(−)-CBS catalyst (50 mol %). The solution was stirred at rt for a period of 20 min at which time the reaction was cooled to 4 °C and catecholborane (150 mol %) was added. Following the consumption of all starting material the reaction was quenched with 15% NaOH and allowed to stir at rt for 1 h. The aqueous layer was extracted with CH_2Cl_2 (3× 0.05 M). The combined organic layers were washed with 15% NaOH (3 × 0.05 M) and brine (0.05 M), dried over sodium sulfate, and concentrated. The resulting diastereomers were separated and purified by flash chromatography (SiO_2, 1:200 g) using 15% EtOAc in hexanes as the eluent to afford products as white solids.

endo-Alcohol-(−)-3a. Prepared by utilizing the (*R*)-(+)-CBS catalyst; yield based on 500 mg scale of (±)-**2**; yield = 226 mg, 45%; $[\alpha]_D^{23}$ = −63.6 (*c* 1.00, $CHCl_3$) with 95.4% ee for the major enantiomer having a T_r = 44 min.

exo-Alcohol-(+)-3b. Prepared by utilizing the (*R*)-(+)-CBS catalyst; yield based on 500 mg scale of (±)-**2**; yield = 232 mg, 47%; R_f = 0.26 (Hex/EtOAc, 3:1); IR (KBr) ν 3406, 3094, 2970, 2868, 1603, 1299, 1080, 1054, 919, 741, 692, 597 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.88 (dd, *J* = 5.9, 1.2 Hz, 1H), 6.29 (dd, *J* = 5.9, 2.1 Hz, 1H), 5.01 (d, *J* = 2.1 Hz, 1H), 4.97 (d, *J* = 1.8 Hz, 1H), 3.85 (d, *J* = 8.4 Hz, 1H), 2.75 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 131.3, 129.0, 121.6, 84.5, 83.6, 72.5. The enantiomeric excess of (+)-**3b** was determined by conversion to its Mosher ester. ^{19}F NMR (376 MHz, $CDCl_3$) δ −71.87 (s, 3F) >99% ee; HRMS (ESI) calcd for $C_7H_6Br_2O_2$ $[M+H]^+$, 280.8813; found, 280.8839; $[\alpha]_D^{23}$ = +80.5 (*c* 1.00, $CHCl_3$).

endo-Alcohol-(+)-4a. Prepared by utilizing the (*S*)-(−)-CBS catalyst; yield based on 500 mg scale of (±)-**2**; yield = 230 mg, 46%; $[\alpha]_D^{23}$ = +70.2 (*c* 1.00, $CHCl_3$) with 93.3% ee for the major enantiomer having a T_r = 36 min.

exo-Alcohol-(−)-4b. Prepared by utilizing the (*S*)-(−)-CBS catalyst; yield based on 500 mg scale of (±)-**2**; yield = 236 mg,

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47%. R_f = 0.26 (Hex/EtOAc, 3:1); IR (KBr) ν 3406, 2975, 2868, 2389, 1606, 1296, 1088, 1042, 874, 722, 694, 597 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.88 (dd, J = 5.9, 1.5 Hz, 1H), 6.29 (dd, J = 5.9, 2.0 Hz, 1H), 5.01 (d, J = 2.0 Hz, 1H), 4.97 (d, J = 1.8 Hz, 1H), 3.84 (d, J = 8.8 Hz, 1H), 2.90 (d, J = 9.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 131.2, 129.0, 121.6, 84.6, 83.5, 72.5. The enantiomeric excess of (−)-**4b** was determined by conversion to its Mosher ester. ^{19}F NMR (376 MHz, $CDCl_3$) δ −71.39 (s, 3F) >99% ee; HRMS (ESI) calcd for $C_7H_6Br_2O_2$ $[M+H]^+$, 280.8813; found, 280.8842; $[\alpha]_D^{23}$ = −79.2 (c 1.00, $CHCl_3$).

endo-Silyl-alcohol-(−)-7a. Prepared by utilizing the (*R*)-(+)-CBS catalyst; yield based on 1.75 g scale of (±)-**6**; yield = 875 mg, 49%; R_f = 0.50 (Hex/EtOAc, 3:1); IR (KBr) ν 3446, 2953, 2928, 2856, 1592, 1254, 1068, 844, 778 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.99−5.89 (m, 1H), 5.14 (d, J = 5.8 Hz, 1H), 4.53 (t, J = 5.8 Hz, 1H), 4.38 (s, 2H), 2.25 (dd, J = 9.0, 5.2 Hz, 1H, OH), 1.56 (s, 3H), 0.92 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 133.6, 126.0, 122.5, 88.1, 80.8, 70.7, 59.3, 25.8, 21.2, 18.4, −5.4; HRMS (ESI) calcd for $C_{15}H_{24}Br_2O_3Si$ [M+H]+: 438.9940; found: 438.9952; $[\alpha]_D^{22}$ = −51.6 (c 1.00, $CHCl_3$).

exo-Silyl-alcohol-(+)-7b. Prepared by utilizing the (*R*)-(+)-CBS catalyst; yield based on 1.75 g scale of (±)-**6**; yield = 827 mg, 47%; R_f = 0.43 (Hex/EtOAc, 3:1); IR (KBr) ν 3444, 2953, 2927, 2858, 1594, 1256, 1067, 844, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.97−5.88 (m, 1H), 4.94−4.88 (m, 1H), 4.40−4.30 (m, 2H), 3.81 (d, J = 8.8 Hz, 1H), 2.83 (d, J = 8.8 Hz, 1H), 1.61 (s, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 135.45, 123.4, 121.1, 87.7, 83.6, 73.4, 59.4, 25.8, 20.7, 18.3, −5.4, −5.5; HRMS (ESI) calcd for $C_{15}H_{24}Br_2O_3Si$ $[M+H]^+$, 438.9940; found, 438.9923; $[\alpha]_D^{22}$ = +65.7 (c 1.00, $CHCl_3$).

General Procedure for MnO_2 Oxidation of Separated Diastereomers. To a flame-dried flask was added an alcohol substrate in CH_2Cl_2 (0.1 M). MnO_2 (300 mol %) was added to the flask and was stirred at rt until starting material was consumed ∼48 h. Solids were filtered off through a plug of silica, and the resulting organics were condensed under reduced pressure. The solids were purified by flash chromatography (SiO_2, 2.5 g) using 10% EtOAc in hexanes as the eluent to afford the (+) or (−) dibromoenones as a white solid. Spectral data were consistent to those from work previously done in our lab. The enantiomeric excess values of (+)-**2** and (−)-**2** were determined by HPLC analysis in hexanes/isopropanol (99.5:0.5) at a column flow rate of 1.0 mL/min with detection at 254 nm.

Dibromoenone-(+)-2. Yield based on 50 mg scale of (−)-**3a**. Oxidation yielded (+)-**2** in 46 mg (92%) with an $[\alpha]_D^{23}$ = +266.3 (c 1.00, $CHCl_3$); HPLC analysis showed that (+)-**2** was formed with 94.7% ee.

Yield based on 50 mg scale of (−)-**4b**. Oxidation yielded (+)-**2** in 48 mg (96%) with an $[\alpha]_D^{23}$ = +269.4 (c 1.00, $CHCl_3$); HPLC analysis showed that (+)-**2** was formed with 96.8% ee.

Dibromoenone-(−)-2. Yield based on 50 mg scale of (+)-**4a**. Oxidation yielded (−)-**2** in 48 mg (96%) with an $[\alpha]_D^{23}$ = −268.6 (c 1.00, $CHCl_3$); HPLC analysis showed that (−)-**2** was formed with 94.1% ee.

Yield based on 50 mg scale of (+)-**3b**. Oxidation yielded (−)-**2** in 46 mg (92%) with an $[\alpha]_D^{23}$ = −295.1 (c 1.00, $CHCl_3$); HPLC analysis showed that (−)-**2** was formed with 98.6% ee.

Silyl-dibromoenone-(+)-6. Yield based on 875 mg scale of (−)-**7a**. Oxidation yielded (+)-**6** in 818 mg (94%) with an $[\alpha]_D^{21}$ = +179.7 (c 1.00, $CHCl_3$).

Silyl-dibromoenone-(−)-6. Yield based on 827 mg scale of (+)-**7b**. Oxidation yielded (−)-**6** in 790 mg (96%) with an $[\alpha]_D^{21}$ = −182.3 (c 1.00, $CHCl_3$).

Alcohol-(+)-8. To a plastic vial was added (+)-**6** (25 mg, 0.057 mmol), which was diluted with THF (0.075 mL). The solution was treated with HF·pyridine (0.03 mL, 1.14 mmol, 70% in pyridine) and stirred at rt until all starting material was consumed, ∼1 h. The reaction was quenched by the slow addition of $NaHCO_3$ and diluted with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL), and the combined organic layers were washed with $NaHCO_3$ (20 mL), H_2O (20 mL), and brine (20 mL), dried over sodium sulfate, and concentrated. The crude alcohol was purified by flash chromatography (SiO_2, 2.5 g) using 10% EtOAc in hexanes as the eluent to afford the alcohol (+)-**8** (18 mg, 0.055 mmol, 97% yield) as a white solid. The solid was crystallized by a simple diffusion method using $CHCl_3$ and pentane as diffusing solvents. All spectra were consistent with work previously done in our lab.

(±)-Dibromo-exo-alcohol for HPLC Analysis Only. Triphenylphosphine (TPP) (327 mg, 1.25 mM) was added to a 10 mL flame-dried flask, dissolved in benzene (3 mL), and cooled to 0 °C. Diisopropyl azodicarbozylate (DIAD) (0.24 mL, 1.25 mM) was added dropwise, and the solution was stirred at 0 °C for 10 min. To the resulting red solution was added 4-nitrobenzoic acid (103 mg, 0.64 mM) followed by (±)-***endo*-alcohol** (118 mg, 0.42 mM) in benzene (0.4 mL). The reaction was allowed to warm to rt and stirred until all starting material was consumed. The solvent was removed under reduced pressure, and the resulting orange solids were dissolved in Et_2O (20 mL). The organic layer was washed with sodium bicarbonate (2 × 15 mL), water (2 × 15 mL), and brine (2 × 15 mL). The organics were then dried over sodium sulfate, and the solvent was removed under reduced pressure. The resulting solids were purified by flash chromatography (SiO_2, 6 g) using 5% EtOAc in hexanes as the eluent to afford the ***exo*-nitrobenzoate** as a white solid.

The resulting ***exo*-nitrobenzoate** was taken up with THF (2 mL) and stirred with 15% NaOH at rt until all starting material was consumed. The reaction was quenched with water (3 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with sodium bicarbonate (2 × 15 mL) and brine (2 × 15 mL), and all solvent was removed under reduced pressure. The resulting solids were purified by flash chromatography (SiO_2, 6 g) using 25% EtOAc in hexanes as the eluent to afford (±)-***exo*-alcohol** as a white solid (95 mg, 80% over two steps). To develop a standard set of peaks for analysis (±)-***exo*-alcohol** was converted to its Mosher ester using known procedures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR for all new compounds and Crystallographic Information for compound (+)-**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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