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Use of 1,3-Oxazolidin-2-one Derivatives of 3-Borylpropenoic Acids as β-Hydroxy Acrylic Acid Equivalents in the Asymmetric Diels-Alder Reaction Catalyzed by a Chiral Titanium Reagent

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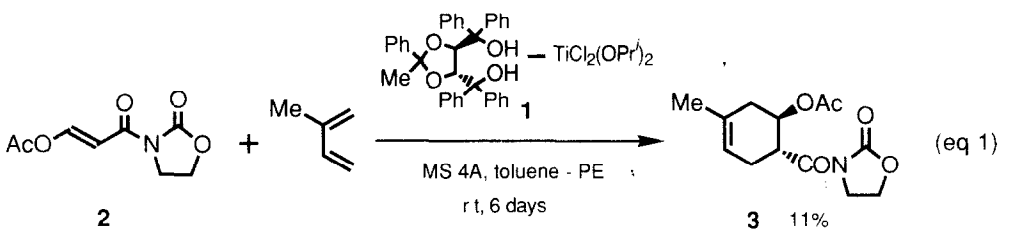
Key Words

Chiral titanium catalyst; asymmetric Diels-Alder reaction; β-hydroxyacrylic acid equivalent; 3-(3-borylpropenoyl)-1,3-oxazolidin-2-one

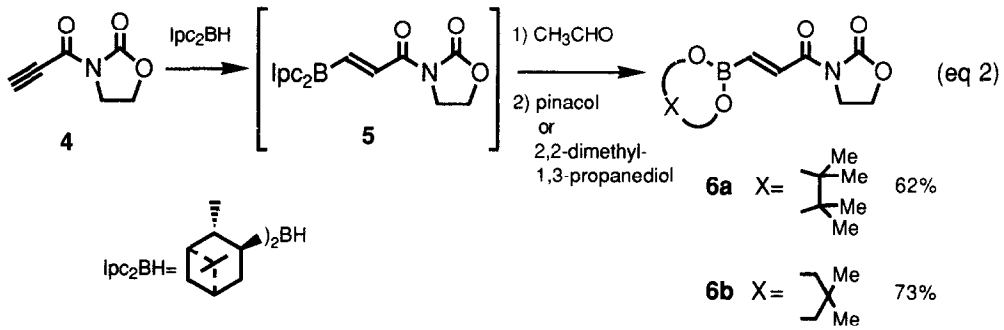
Abstract: *Catalytic asymmetric Diels-Alder reaction was developed by employing 3-(3-boryl-propenoyl)-1, 3-oxazolidin-2-one as a β-hydroxyacrylic acid equivalent. With a catalytic amount of the titanium reagent, 3-(3-borylpropenoyl)-1, 3-oxazolidin-2-ones react smoothly with various dienes in the presence of Molecular Sieves 4A to afford the adducts in high yield with high optical purity. Boryl groups of the adducts were converted to hydroxyl group oxidatively.*

The Diels-Alder reaction is one of the most useful synthetic methods in organic synthesis, and, in recent years, the main interest has been focused on the development of catalytic asymmetric reactions.[1] From our laboratory, a catalytic asymmetric Diels-Alder reaction was reported by the use of a chiral titanium catalyst prepared *in situ* from dichlorodiisopropoxytitanium and a tartrate-derived chiral 1,4-diol, (2*R*,3*R*)-1,1,4,4-tetraphenyl-2,3-*O*-(1-phenylethylidene)-1,2,3,4-butanetetrol (**1**).[2] In this reaction, high enantioselectivity is achieved by employing 1,3-oxazolidin-2-one (abbreviated as oxazolidinone) derivatives of α,β-unsaturated carboxylic acids as dienophiles. For the preparation of oxygen-functionalized Diels-Alder products, the reaction of 3-(3-acetoxypropenoyl)oxazolidinone **2** with isoprene was examined using the chiral titanium catalyst in toluene-petroleum ether (PE) mixture in the presence of Molecular Sieves (MS) 4A.[2a] But the reaction proceeded very slowly to give the adduct **3** in only 11% yield after 6 days even by the use of an equimolar amount of the titanium catalyst (eq 1).



(eq 1)

Therefore, it was necessary to design a synthetic equivalent of 3-(3-hydroxypropenoyl)oxazolidinone. Since vinylboranes are employed as good dienophiles[3] and boryl groups are readily converted to hydroxyl groups,[4] 3-(3-borylpropenoyl)oxazolidinone was chosen as a 3-hydroxypropenoyl equivalent. 3-(3-Boryl-propenoyl)oxazolidinones **6a, b** were synthesized from 3-propioloyloxazolidinone **4** (eq 2).[3b] Hydroboration of **4** with diisopinocampheylborane[5] gave a vinylborane intermediate **5**, which was treated *in situ* with excess acetaldehyde. The reaction mixture was warmed to 40 °C for 1 h and successive transesterification with pinacol or 2,2-dimethyl-1,3-propanediol afforded **6a** and **6b** in 62% and 73% yields, respectively (from **4**).



Though the boronate **6a** was slightly hydrolyzed during chromatographic purification and was isolated with contamination of pinacol, the purity of **6a** is appropriate for the successive Diels-Alder reaction. On the other hand, the boronate **6b** derived from 2,2-dimethyl-1,3-propanediol can be purified completely by recrystallization from ethanol. In the ^{13}C NMR spectra of **6a** and **6b**, signals of the α-carbons to the carbonyl group appeared at 136.4 and 134.5 ppm, respectively, which are close to that of the oxazolidinone derivative of fumaric acid (132.0 ppm). As the NMR spectral data suggested that **6a, b** would exhibit suitable reactivities as dienophiles, the asymmetric Diels-Alder reactions of the 3-(3-borylpropenoyl)oxazolidinones **6a, b** with various dienes were investigated using the chiral titanium catalyst in a mixed solvent (toluene-PE) in the presence of MS 4A.

As shown in Table 1, the boronates **6a, b** smoothly reacted with butadiene, isoprene and 2-methyl-1,3-pentadiene in the presence of a catalytic amount of the catalyst, giving the adducts **7-9** as a single isomer in good yield with high enantioselectivity (>93% ee). The reaction of **6a** with 1-acetoxy-3-methyl-1,3-butadiene afforded the cycloadducts as an inseparable mixture of the endo and exo isomers (92:8) in 80% yield and the optical purity of the endo adduct **10a** was 84% ee, while the reaction of **6b** with 1-acetoxy-3-methyl-1,3-butadiene gave selectively the endo adduct **10b** in 71% yield with 95% ee. In the reaction with cyclopentadiene, both boronates afforded the adducts **11** in high yield but with somewhat lower optical purity (66-71% ee) as compared with the acyclic dienes.

As the boronates **6**, particularly **6b**, were found to be employed successfully in the titanium catalyzed asymmetric Diels-Alder reaction, transformation of boryl groups of the cycloadducts to hydroxyl group was then investigated. By the oxidation with trimethylamine *N*-oxide dihydrate, the norbornene type adducts **11a, b** were

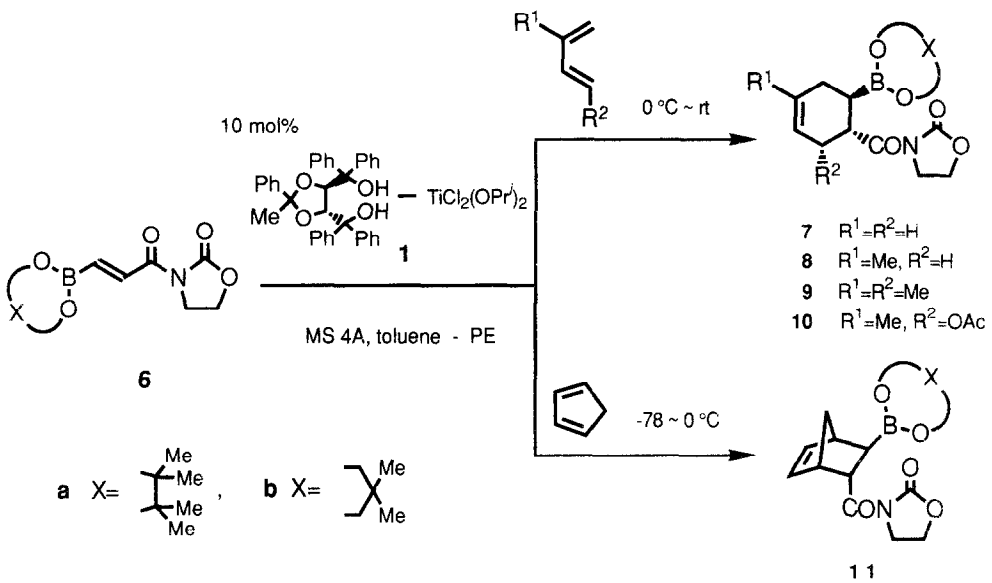
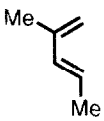
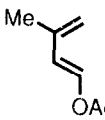
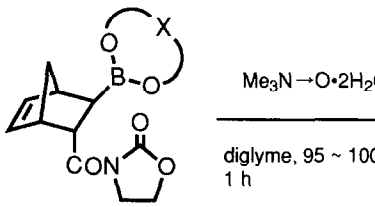


Table 1. Asymmetric Diels-Alder Reactions of 3-(3-Borylpropenoyl)oxazolidinones with Various Dienes

Diene	Dienophile	Product	Yield / %	Optical Purity / % ee
	**6a**	**7a**	88	>98
	6b	**7b**	76	>98
	**6a**	**8a**	78	>98
	6b	**8b**	74	>98
	**6a**	**9a**	93	93
	6b	**9b**	92	94
	**6a**	**10a**	80 (92 : 8) [a]	84 [b]
	6b	**10b**	71	95
	**6a**	**11a**	89 (94 : 6) [a]	66 [b]
	6b	**11b**	91 (95 : 5) [a]	71 [b]

a) Ratio of endo and exo isomers. b) Optical purity of endo isomer.

converted to the desired alcohol **12** (eq 3), but the oxidation of the cyclohexene-type adducts **7-9** gave oxazinediones **13-15** by the ring opening of oxazolidinone moiety by the nucleophilic attack of the resulting hydroxyl group (eq 4). The oxidation with *m*-chloroperbenzoic acid (*m*-CPBA) also exhibited some limitations: Treatment of **10** with *m*-CPBA afforded the alcohol **16** (eq 5), while the oxidation of **9** with *m*-CPBA preferentially gave the epoxy derivatives.

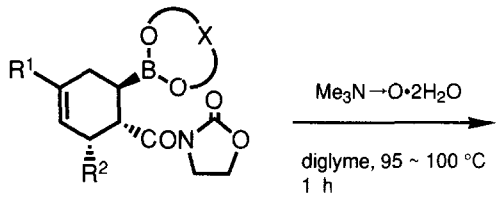


11

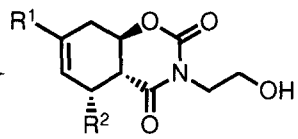
a X=  , **b** X= 

(eq 3)

	from **11a**	**11b**
12	81%	80%

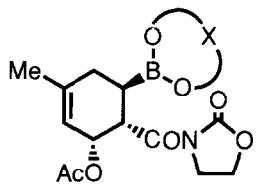


7-9

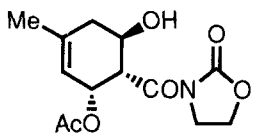


(eq 4)

		from **7a-9a**	**7b-9b**
13	$R^1=R^2=H$	75%	69%
14	R^1=Me, R^2=H	63%	70%
15	$R^1=R^2$=Me	58%	44%



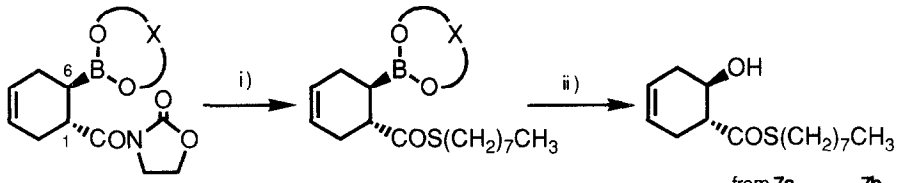
10



(eq 5)

	from **10a**	**10b**
16	81%	73%

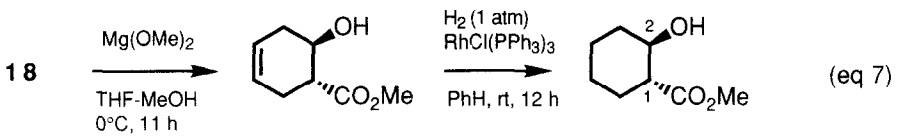
Transformation of the cycloadducts into the corresponding alcohols was performed by converting the acyloxazolidinone derivatives to the thioesters,[2c] followed by oxidation with trimethylamine *N*-oxide dihydrate. By applying this method, both **7a** and **7b** were effectively converted to the alcohol **18** in 67% and 66% total yield, respectively (eq 6).



7 17 18 from 7a 67% 7b 66%

i) $CH_3(CH_2)_7SLi$, THF, -35 ~ -10 °C, 2 ~ 3.5 h. ii) $Me_3N{\rightarrow}O{\cdot}2H_2O$, diglyme, 95 ~ 100 °C, 30 min ~ 1 h.

The optical purities of the cycloadducts were determined by ^1H NMR or ^{13}C NMR analysis of the (+)-3,3,3-trifluoro-2-methoxy-2-phenylpropionic acid (MTPA) esters[6] of the alcohols **12-16**. The absolute configuration of **7** was determined as follows. Treatment of the β-hydroxy thioester **18** with magnesium methoxide afforded methyl ester **19**, which was converted to β-hydroxy ester **20** by hydrogenation (eq 7). Comparison of the optical rotation of **20** with that in the literature[7a] determined the absolute configuration of **7** to be 1*R*, 6*R* as depicted in eq 6. This result was consistent with the prediction that *re*-face of the dienophile is attacked preferentially when the (2*R*, 3*R*)-1,4-diol **1** is employed as a chiral auxiliary.[2b] The same sense of asymmetric induction is expected to be achieved in all cases, although the absolute configurations of the adducts **8-11** were not rigorously determined.



18 quant. **19** 89% **20**

In conclusion, the Diels-Alder reactions of 3-(3-borylpropenoyl)oxazolidinones using a catalytic amount of the chiral titanium reagent proceed smoothly to afford the adducts in good yield with high optical purity. As the boryl groups of the adducts can be easily converted to hydroxyl group, 3-(3-borylpropenoyl)oxazolidinones are useful synthetic equivalents of β-hydroxyacrylic acid.

Experimental

General. Melting points and boiling points are uncorrected. ^1H NMR spectra and ^{13}C NMR spectra in $CDCl_3$ were recorded on Bruker AM500 spectrometer with $CHCl_3$ as an internal standard. ^{11}B NMR spectra in $CDCl_3$ were recorded on JEOL FX90Q spectrometer and the chemical shifts are in δ relative to boron trifluoride etherate. IR spectra were measured with Horiba FT-300S spectrometer. Optical rotations were measured with a JASCO DIP-180. High-resolution mass spectra were measured for the new compounds with JEOL JMS-SX102A mass spectrometer operating at 70 eV. Column chromatography was conducted on silica gel (Merck, 7734, 70-230 mesh). Preparative thin-layer chromatography (TLC) was carried out on a silica gel (Wakogel B-5F). Toluene and petroleum ether (PE) were distilled and stored over MS 4A. CH_2Cl_2 was distilled from P_2O_5, then from CaH_2, and dried over MS 4A. Methanol was distilled from $Mg(OMe)_2$ and dried over MS 3A. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl.

(2*R*,3*R*)-1,1,4,4-Tetraphenyl-2,3-*O*-(1-phenylethylidene)-1,2,3,4-butanetetrol (**1**)[2a] and 1-acetoxy-3-methyl-1,3-butadiene[8] were prepared according to the literature procedure.

Preparation of dichlorodiisopropoxytitanium. Under an argon atmosphere, titanium (IV) chloride (19.2 mL, 0.18 mol) was added dropwise to a toluene solution (70 mL) of titanium (IV) isopropoxide (49.8 g, 0.18 mol) at 0 °C. The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue was distilled under reduced pressure to afford dichlorodiisopropoxytitanium (57.4 g, 69%) as colorless liquid, which gradually solidified. bp 83-85 °C (1 mmHg).

Preparation of 3-propioloyl-1,3-oxazolidin-2-one (4). 3-Propioloyl-1,3-oxazolidin-2-one (**4**) was prepared from propioloyl chloride[9] and 1,3-oxazolidin-2-one according to the literature procedure.[10] **4**: mp 112 °C; IR (KBr) 3249, 2116, 1788, 1656, 1389, 1344, 1225, 1120, 1038, 756 cm^{-1}; ^1H NMR δ= 3.42 (1H, s), 4.04 (2H, t, J= 8.0 Hz), 4.43 (2H, t, J= 8.0 Hz). Anal Calcd for $C_6H_5NO_3$: C, 51.80; H, 3.62; N, 10.07. Found: C, 51.61; H, 3.68; N, 10.04.

Preparation of (*E*)-3-[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)propenoyl]-1,3-oxazolidin-2-one (6a). Under an argon atmosphere, 3-propioloyl-1,3-oxazolidin-2-one (**4**) (185 mg, 1.3 mmol) was added to a THF (0.7 mL) suspension of diisopinocampheylborane[5] (2.0 mmol) at 0 °C. After the reaction mixture was stirred at 0 °C for 1.5 h, excess acetaldehyde (1.2 mL, 21 mmol) was added to the mixture. The mixture was warmed to 40 °C and stirred for 1 h. Then the mixture was cooled to ambient temperature and pinacol (236 mg, 2.0 mmol) was added. After the reaction mixture was stirred for 14 h, solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel deactivated by 10% water using a AcOEt-hexane (5:95) mixture as an eluent to give a mixture of **6a** and pinacol. The mixture was dissolved in AcOEt and washed four times with water to remove pinacol. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give 234 mg of **6a** (62% yield, pinacol was contained (7%)). **6a**: IR (neat) 1778, 1684, 1385, 1348, 1221, 1194, 1144, 1113, 1034 cm^{-1}; ^1H NMR δ= 1.25 (12H, s), 4.05 (2H, t, J= 8.0 Hz), 4.41 (2H, t, J= 8.0 Hz), 6.89 (1H, d, J= 17.8 Hz), 7.86 (1H, d, J= 17.8 Hz); ^{13}C NMR δ= 24.74, 42.67, 62.19, 84.09, 136.39, 153.21, 164.93; ^{11}B NMR δ= 30.0 (s); HRMS Calcd for $C_{12}H_{18}BNO_5$: M, 267.1278. Found: m/z 267.1291.

Preparation of (*E*)-3-[3-(5,5-dimethyl-1,3,2-dioxaborinyl)propenoyl]-1,3-oxazolidin-2-one (6b). In the similar manner described above, hydroboration of **4** (740 mg, 5.3 mmol) with diisopinocampheylborane (8.0 mmol), followed by treatment with excess acetaldehyde (4.8 mL, 86 mmol), gave a solution of the boronate. This solution was concentrated under reduced pressure and the residue was dissolved in THF (3 mL). 2,2-Dimethyl-1,3-propanediol (833 mg, 8.0 mmol) was added to this solution and the mixture was stirred at room temperature for 3 h. After removal of the solvent under reduced pressure, ethanol was added to the residue. The resulting precipitates were filtered, washed with ether and then dried to afford the product **6b** (985 mg, 73%) as a colorless prism. **6b**: mp 154-155 °C; IR (KBr) 1765, 1674, 1483, 1340, 1300, 1271, 1221, 1188 cm^{-1}; ^1H NMR δ= 0.96 (6H, s), 3.65 (4H, s), 4.06 (2H, t, J= 8.0 Hz), 4.41 (2H, t, J= 8.0 Hz), 6.87 (1H, d, J= 17.7 Hz), 7.84 (1H, d, J= 17.7 Hz); ^{13}C NMR δ= 21.80, 31.75, 42.69, 62.14, 72.22, 134.55, 153.27, 165.29; ^{11}B NMR δ= 26.7 (s); HRMS Calcd for $C_{11}H_{16}BNO_5$: M, 253.1122. Found: m/z 253.1137. Anal. Calcd for $C_{11}H_{16}BNO_5$: C, 52.24; H, 6.38; N, 5.54. Found: C, 52.11; H, 6.33; N, 5.49.

General Procedure for the Asymmetric Diels-Alder Reaction Using a Catalytic Amount of the Titanium Reagent. 3-[((1*R*,6*R*)-4-Methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (8a). Under an argon atmosphere, the chiral diol **1**

(17.9 mg, 0.034 mmol) was added to a toluene solution (1.5 mL) of dichlorodiisopropoxytitanium (7.3 mg, 0.031 mmol) at room temperature and the reaction mixture was stirred for 1 h. MS 4A (96 mg) was then added to this solution, and the mixture was cooled to 0 °C. A toluene solution (1.7 mL) of the boronate **6a** (81.2 mg, 0.30 mmol) was added to the mixture and then PE (4 mL) and isoprene (0.78 mL) were added. The mixture was stirred overnight at 0 °C, and then pH 7 phosphate buffer was added. The mixture was filtered through Celite and the organic materials were extracted twice with AcOEt and the combined extracts were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by TLC (AcOEt : hexane = 2 : 3) to afford the adduct **8a** (79.2 mg, 78%). The optical purity was determined by analyzing the 125 MHz ^{13}C NMR of the MTPA ester of **14** prepared by oxidation of **8a**. A set of two signals appeared at 63.02 and 63.11 ppm in the spectrum of the MTPA ester prepared from the racemate, and only a signal at 63.11 ppm was observed in the spectrum of the MTPA ester prepared from the optically active **14**. **8a**: $[\alpha]^{27}_D$ -134.06° (*c* 1.58, CH_2Cl_2), >98% ee; IR (neat) 2976, 2927, 1780, 1697, 1387, 1327, 1219, 1144 cm^{-1}; ^1H NMR δ= 1.15 (6H, s), 1.18 (6H, s), 1.48 (1H, ddd, J= 11.3, 11.3, 5.8 Hz), 1.62 (3H, s), 1.92-2.07 (3H, m), 2.27-2.34 (1H, m), 3.69 (1H, ddd, J= 11.3, 11.3, 5.0 Hz), 3.94 (1H, dt, J_d= 11.0 Hz, J_t= 8.6 Hz), 3.99 (1H, dt, J_d= 11.0 Hz, J_t= 7.6 Hz), 4.36 (2H, dd, J= 8.6, 7.6 Hz), 5.34-5.38 (1H, m); ^{13}C NMR δ= 23.28, 24.42, 24.91, 29.14, 30.77, 39.44, 42.86, 61.76, 83.06, 119.17, 134.09, 153.28, 177.70; ^{11}B NMR δ= 33.8 (s). Anal. Calcd for $C_{17}H_{26}BNO_5$: C, 60.91; H, 7.82; N, 4.18. Found: C, 60.62; H, 7.83; N, 4.24.

By the same procedure described above, the cycloadducts were prepared and their spectral data and physical properties are summarized as follows.

3-[((1*R*,6*R*)-4-Methyl-6-(5,5-dimethyl-1,3,2-dioxaborinyl)-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (8b). 74% yield. In the same manner described above, the optical purity was determined by analyzing the 125 MHz ^{13}C NMR of the MTPA ester of **14** prepared by oxidation of **8b**. **8b**: $[\alpha]^{25}_D$ -118.69° (*c* 1.31, CH_2Cl_2), >98% ee; IR (neat) 2962, 2929, 1778, 1695, 1385, 1317, 1296, 1257, 1223 cm^{-1}; ^1H NMR δ= 0.87 (6H, s), 1.41 (1H, ddd, J= 11.3, 11.0, 6.1 Hz), 1.60 (3H, s), 1.89-2.03 (3H, m), 2.25-2.33 (1H, m), 3.48 (2H, d, J= 11.0 Hz), 3.51 (2H, d, J= 11.0 Hz), 3.61 (1H, ddd, J= 11.0, 10.7, 5.0 Hz), 3.93 (1H, dt, J_d= 10.7 Hz, J_t= 8.5 Hz), 3.97 (1H, dt, J_d= 10.7 Hz, J_t= 7.6 Hz), 4.35 (2H, dd, J= 8.5, 7.6 Hz), 5.30-5.35 (1H, m); ^{13}C NMR δ= 21.73, 23.31, 29.22, 31.15, 31.66, 39.48, 42.86, 61.78, 71.96, 119.01, 134.37, 153.25, 178.28; HRMS Calcd for $C_{16}H_{24}BNO_5$: M, 321.1748. Found: m/z 321.1764.

3-[((1*R*,6*R*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (7a). 88% yield. The optical purity was determined by analyzing the 125 MHz ^{13}C NMR of the MTPA ester of **13** prepared by oxidation of **7a**. A set of two signals appeared at 62.99 and 63.08 ppm in the spectrum of the MTPA ester prepared from the racemate, and only a signal at 63.08 ppm was observed in the spectrum of the MTPA ester prepared from the optically active **13**. **7a**: $[\alpha]^{25}_D$ -127.78° (*c* 0.74, CH_2Cl_2), >98% ee; IR (neat) 2978, 2920, 1780, 1695, 1389, 1365, 1325, 1217, 1144 cm^{-1}; ^1H NMR δ= 1.14 (6H, s), 1.17 (6H, s), 1.46 (1H, ddd, J= 11.5, 11.2, 5.3 Hz), 1.98-2.10 (2H, m), 2.12-2.20 (1H, m), 2.30-2.38 (1H, m), 3.76 (1H, ddd, J= 11.2, 10.4, 5.0 Hz), 3.94 (1H, dt, J_d= 11.1 Hz, J_t= 8.5 Hz), 3.99 (1H, dt, J_d= 11.1 Hz, J_t= 7.7 Hz), 4.36 (2H, dd, J= 8.5, 7.7 Hz), 5.63-5.73 (2H, m); ^{13}C NMR δ= 24.26, 24.77, 25.81, 28.58, 39.25, 42.72, 61.71, 82.94, 124.97, 126.94, 153.17, 177.31; ^{11}B NMR δ= 34.4 (s); HRMS Calcd for $C_{16}H_{24}BNO_5$: M, 321.1748. Found: m/z 321.1749.

3-[((1*R*,6*R*)-6-(5,5-dimethyl-1,3,2-dioxaborinyl)-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (7b). 76% yield. In the same manner described above, the optical purity was determined

by analyzing the 125 MHz ^{13}C NMR of the MTPA ester of **13** prepared by oxidation of **7b**. **7b**: $[\alpha]^{27}_D$ -117.41° (*c* 1.21, CH_2Cl_2), >98% ee; IR (neat) 2962, 2924, 1778, 1695, 1387, 1304, 1257, 1223, 1198 cm^{-1}; ^1H NMR δ= 0.88 (6H, s), 1.40 (1H, ddd, J= 11.4, 11.0, 5.5 Hz), 1.95-2.06 (2H, m), 2.10-2.18 (1H, m), 2.29-2.37 (1H, m), 3.49 (2H, d, J= 10.9 Hz), 3.52 (2H, d, J= 10.9 Hz), 3.70 (1H, ddd, J= 11.0, 10.5, 5.2 Hz), 3.95 (1H, dt, J_d= 10.8 Hz, J_t= 8.5 Hz), 3.98 (1H, dt, J_d= 10.8 Hz, J_t= 7.7 Hz), 4.36 (2H, dd, J= 8.5, 7.7 Hz), 5.61-5.67 (1H, m), 5.68-5.73 (1H, m); ^{13}C NMR δ= 21.64, 26.17, 28.69, 31.57, 39.30, 42.77, 61.75, 71.87, 124.87, 127.32, 153.18, 177.96; ^{11}B NMR δ= 30.4 (s); HRMS Calcd for $C_{15}H_{22}BNO_5$: M, 307.1592. Found: m/z 307.1574.

3-[((1*S*,2*R*,6*R*)-2,4-Dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (9a). 93% yield. The optical purity was determined by analyzing the ^1H NMR of the MTPA ester of **15** prepared by oxidation of **9a**. Signals of H-4a of the MTPA ester separated at 2.53 ppm (1H, dd, J= 13.0, 5.4 Hz) and 2.58 ppm (1H, dd, J= 13.1, 5.4 Hz). **9a**: $[\alpha]^{22}_D$ -171.06° (*c* 0.89, CH_2Cl_2), 93% ee; IR (neat) 2974, 2925, 1782, 1695, 1385, 1325, 1192, 1146 cm^{-1}; ^1H NMR δ= 0.74 (3H, d, J= 7.1 Hz), 1.11 (6H, s), 1.16 (6H, s), 1.52 (1H, ddd, J= 12.2, 12.1, 5.6 Hz), 1.57 (3H, s), 1.83 (1H, dd, J= 17.3, 12.1 Hz), 1.91 (1H, dd, J= 17.3, 5.6 Hz), 2.64-2.72 (1H, m), 3.70 (1H, dd, J= 12.2, 5.4 Hz), 3.88-3.98 (2H, m), 4.31-4.39 (2H, m), 5.28-5.32 (1H, m); ^{13}C NMR δ= 16.53, 23.15, 24.21, 24.68, 29.76, 30.90, 42.66, 44.62, 61.80, 82.83, 125.96, 133.01, 152.90, 176.28; ^{11}B NMR δ= 34.0 (s); HRMS Calcd for $C_{18}H_{28}BNO_5$: M, 349.2061. Found: m/z 349.2079.

3-[((1*S*,2*R*,6*R*)-2,4-Dimethyl-6-(5,5-dimethyl-1,3,2-dioxaborinyl)-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (9b). 92% yield. The optical purity was determined as described above by analyzing the ^1H NMR of the MTPA ester of **15** prepared by oxidation of **9b**. **9b**: $[\alpha]^{23}_D$ -148.03° (*c* 0.98, CH_2Cl_2), 94% ee; IR (neat) 2962, 2929, 1780, 1693, 1385, 1331, 1292, 1255, 1190 cm^{-1}; ^1H NMR δ= 0.75 (3H, d, J= 7.1 Hz), 0.89 (6H, s), 1.43 (1H, ddd, J= 12.2, 12.1, 5.6 Hz), 1.59 (3H, s), 1.87 (1H, dd, J= 17.3, 12.2 Hz), 1.94 (1H, dd, J= 17.3, 5.6 Hz), 2.62-2.70 (1H, m), 3.48 (2H, d, J= 10.6 Hz), 3.53 (2H, d, J= 10.6 Hz), 3.70 (1H, dd, J= 12.1, 5.4 Hz), 3.91 (1H, ddd, J= 10.9, 8.9, 6.0 Hz), 3.99 (1H, ddd, J= 10.9, 9.3, 8.4 Hz), 4.34 (1H, ddd, J= 8.9, 8.9, 8.4 Hz), 4.37 (1H, ddd, J= 9.3, 8.9, 6.0 Hz), 5.28-5.32 (1H, m); ^{13}C NMR δ= 16.78, 21.77, 23.26, 29.92, 31.71, 42.76, 44.36, 61.79, 71.93, 125.92, 133.38, 153.02, 176.95; ^{11}B NMR δ= 30.7 (s); HRMS Calcd for $C_{17}H_{26}BNO_5$: M, 335.1905. Found: m/z 335.1896.

3-[((1*S*,2*R*,6*R*)-2-Acetoxy-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (10a). The cycloadducts were obtained as an inseparable mixture of the endo isomer **10a** and the exo isomer (92:8) in 80% yield. The optical purity was determined by analyzing the ^1H NMR of the MTPA ester of **16** prepared by oxidation of **10a**. Signals of OCH_3 separated at 3.46 and 3.53 ppm. **10a**: 84% ee; IR (neat) 2979, 2922, 1780, 1730, 1697, 1387, 1335, 1252, 1232, 1144 cm^{-1}; ^1H NMR δ= 1.13 (6H, s), 1.18 (6H, s), 1.70 (3H, s), 1.80 (1H, ddd, J= 12.5, 12.5, 5.0 Hz), 1.91 (1H, dd, J= 17.7, 12.5 Hz), 1.92 (3H, s), 2.12 (1H, dd, J= 17.7, 5.0 Hz), 3.81 (1H, ddd, J= 10.7, 9.4, 6.5 Hz), 3.84 (1H, dd, J= 12.5, 3.1 Hz), 3.89 (1H, ddd, J= 10.7, 9.0, 7.4 Hz), 4.33-4.42 (2H, m), 5.48 (1H, d, J= 5.1 Hz), 5.65 (1H, dd, J= 5.1, 3.1 Hz); ^{13}C NMR δ= 21.09, 23.30, 24.27, 24.79, 31.20, 42.79, 44.96, 62.06, 66.19, 83.20, 118.39, 142.43, 153.52, 170.98, 173.76; ^{11}B NMR δ= 33.7 (s); HRMS Calcd for $C_{19}H_{28}BNO_7$-CH_3: M-CH_3, 378.1725. Found: m/z 378.1697.

3-[((1*S*,2*R*,6*R*)-2-Acetoxy-4-methyl-6-(5,5-dimethyl-1,3,2-dioxaborinyl)-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (10b). 71% yield. In the same manner described above, the optical

purity was determined by analyzing the ^{1}H NMR of the MTPA ester of **16** prepared by oxidation of **10b**. **10b**: $[\alpha]^{25}_D$ -159.09° (*c* 0.88, CH_2Cl_2), 95% ee; IR (neat) 2962, 2929, 1778, 1728, 1697, 1385, 1327, 1296, 1254, 1234, 1192 cm^{-1}; ^{1}H NMR δ= 0.89 (6H, s), 1.68 (1H, ddd, J= 12.7, 12.7, 5.3 Hz), 1.70 (3H, s), 1.93 (1H, dd, J= 17.7, 12.7 Hz), 1.93 (3H, s), 2.14 (1H, dd, J= 17.7, 5.3 Hz), 3.49 (2H, d, J= 10.9 Hz), 3.54 (2H, d, J= 10.9 Hz), 3.80 (1H, ddd, J= 10.7, 9.4, 6.4 Hz), 3.83 (1H, dd, J= 12.7, 3.2 Hz), 3.91 (1H, ddd, J= 10.7, 9.2, 7.4 Hz), 4.32-4.42 (2H, m), 5.45-5.49 (1H, m), 5.61-5.65 (1H, m); ^{13}C NMR δ= 21.13, 21.77, 23.33, 31.74, 31.94, 42.84, 44.70, 62.02, 66.42, 72.00, 118.25, 142.74, 153.59, 171.02, 174.29; ^{11}B NMR δ= 30.0 (s); HRMS Calcd for $C_{18}H_{26}BNO_7$: M, 379.1803. Found: m/z 379.1793.

3-[((1*S*,2*S*,3*R*,4*S*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)bicyclo[2.2.1]hept-5-en-2-yl)carbonyl]-1,3-oxazolidin-2-one (11a). The cycloadducts were obtained as an inseparable mixture of the endo isomer **11a** and the exo isomer (94:6) in 89% yield. The optical purity was determined by analyzing the ^{1}H NMR of the MTPA ester of **12** prepared by oxidation of **11a**. A set of two signals appeared at 3.04 and 3.10 ppm in the spectrum of the MTPA ester. **11a**: 66% ee; IR (neat) 2978, 1778, 1697, 1385, 1352, 1319, 1275, 1221, 1146, 1111 cm^{-1}; ^{1}H NMR δ= 1.19 (12H, s), 1.29 (1H, dd, J= 8.3, 2.0 Hz), 1.31 (1H, dd, J= 5.2, 2.1 Hz), 1.42 (1H, d, J= 8.3 Hz), 2.94 (1H, bs), 3.36 (1H, bs), 3.85-3.98 (2H, m), 4.01 (1H, dd, J= 5.2, 3.6 Hz), 4.35 (2H, dd, J= 8.4, 8.3 Hz), 5.74 (1H, dd, J= 5.5, 2.8 Hz), 6.28 (1H, dd, J= 5.5, 3.0 Hz); ^{13}C NMR δ= 24.64, 24.75, 42.99, 45.65, 45.89, 47.08, 49.26, 61.88, 83.28, 130.42, 139.63, 153.26, 174.50; ^{11}B NMR δ= 34.1 (s); HRMS Calcd for $C_{17}H_{24}BNO_5$: M, 333.1748. Found: m/z 333.1757.

3-[((1*S*,2*S*,3*R*,4*S*)-3-(5,5-dimethyl-1,3,2-dioxaborinyl)bicyclo[2.2.1]hept-5-en-2-yl)carbonyl]-1,3-oxazolidin-2-one (11b). The cycloadducts were obtained as an inseparable mixture of the endo **11b** and exo isomers (95:5) in 91% yield. The optical purity was determined as described above by analyzing the ^{1}H NMR of the MTPA ester of **12** prepared by oxidation of **11b**. **11b**: 71% ee; IR (neat) 2962, 2931, 1776, 1697, 1385, 1317, 1275, 1255 cm^{-1}; ^{1}H NMR δ= 0.89 (6H, s), 1.18 (1H, dd, J= 5.4, 1.9 Hz), 1.25 (1H, dd, J= 8.2, 1.8 Hz), 1.44 (1H, d, J= 8.2 Hz), 2.90 (1H, bs), 3.29 (1H, bs), 3.53 (4H, s), 3.84-3.96 (2H, m), 3.99 (1H, dd, J= 5.3, 3.5 Hz), 4.32-4.35 (2H, m), 5.73 (1H, dd, J= 5.5, 2.8 Hz), 6.27 (1H, dd, J= 5.5, 3.0 Hz); ^{13}C NMR δ= 21.72, 31.53, 42.96, 45.48, 45.82, 46.89, 49.13, 61.85, 71.97, 130.39, 139.85, 153.36, 174.88; ^{11}B NMR δ= 30.6 (s); HRMS Calcd for $C_{16}H_{22}BNO_5$: M, 319.1592. Found: m/z 319.1610.

General Procedure for the Oxidation of the Diels-Alder Adducts Using Trimethylamine *N*-oxide Dihydrate. (4a*R*,8a*R*)-4a,5,8,8a-Tetrahydro-7-methyl-2,4-dioxo-2*H*-1,3-benzoxazine-3(4*H*)-ethanol (14). To a solution of 3-[((1*R*,6*R*)-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (**8a**) (21.5 mg, 0.064 mmol) in diglyme (2 mL) was added trimethylamine *N*-oxide dihydrate (9 mg, 0.079 mmol) at room temperature. The mixture was heated at 95-100 °C with efficient stirring for 1 h. After removal of the solvent under reduced pressure, the residue was purified by TLC (AcOEt : hexane = 3 : 2) to afford the alcohol **14** (9 mg, 63%). By the same procedure, the oxidation of **8b** gave **14** in 70% yield. **14**: mp 109-110 °C; $[\alpha]^{25}_D$ -112.8° (*c* 0.51, CH_2Cl_2), >98% ee; IR (KBr) 3523, 3452, 1743, 1693, 1419, 1400, 1377, 1344, 1323, 1178, 1049 cm^{-1}; ^{1}H NMR δ= 1.69 (3H, s), 2.09-2.19 (1H, m), 2.26-2.34 (1H, m), 2.45 (1H, dd, J= 16.8, 6.1 Hz), 2.56-2.66 (2H, m), 3.71-3.80 (2H, m), 3.90 (1H, ddd, J= 14.0, 6.3, 4.7 Hz), 4.04 (1H, ddd, J= 14.0, 5.6, 5.1 Hz), 4.44 (1H, ddd, J= 12.5, 9.8, 6.1 Hz), 5.36-5.40 (1H, m); ^{13}C NMR δ= 22.95, 25.03, 35.36, 39.96, 44.34, 60.93, 74.10, 119.07, 130.83, 152.10, 171.18; HRMS Calcd for $C_{11}H_{15}NO_4$: M, 225.1002. Found: m/z 225.1005. Anal. Calcd for $C_{11}H_{15}NO_4$: C, 58.66; H, 6.71; N, 6.22. Found: C, 58.75; H, 6.78; N, 6.30.

By the same procedure described above, the cycloadducts **11**, **7**, **9** were oxidized. Spectral data and physical properties of the alcohols are summarized as follows.

3-[((1*S*,2*R*,3*R*,4*R*)-3-Hydroxybicyclo[2.2.1]hept-5-en-2-yl)carbonyl]-1,3-oxazolidin-2-one (12). 81% yield from **11a**. 80% yield from **11b**. **12**: $[\alpha]^{27}_D$ -36.49° (*c* 0.67, CH_2Cl_2), 71% ee; IR (KBr) 3435, 1774, 1695, 1392, 1279, 1230, 1207, 1122, 1049 cm^{-1}; ^1H NMR δ= 1.62 (1H, dd, J= 8.7, 1.6 Hz), 1.96 (1H, d, J= 8.7 Hz), 2.83 (1H, bs), 3.06 (1H, bs), 3.43 (1H, dd, J= 2.8, 2.8 Hz), 3.79 (1H, bs), 3.91 (1H, bs), 3.91-4.03 (2H, m), 4.38-4.45 (2H, m), 5.97 (1H, dd, J= 5.6, 3.3 Hz), 6.29 (1H, dd, J= 5.6, 2.7 Hz); ^{13}C NMR δ= 43.13, 44.59, 46.17, 49.97, 56.42, 62.47, 75.81, 132.39, 138.88, 154.60, 172.99; HRMS Calcd for $C_{11}H_{13}NO_4$: M, 223.0845. Found: m/z 223.0868.

(4a*R*,8a*R*)-4a,5,8,8a-Tetrahydro-2,4-dioxo-2*H*-1,3-benzoxazine-3(4*H*)-ethanol (13). 75% yield from **7a**. 69% yield from **7b**. **13**: mp 90-91 °C; $[\alpha]^{27}_D$ -104.94° (*c* 0.91, CH_2Cl_2), >98% ee; IR (KBr) 3558, 1745, 1695, 1398, 1358, 1174, 1080, 1055 cm^{-1}; ^1H NMR δ= 1.91 (1H, t, J= 5.8 Hz), 2.19-2.28 (1H, m), 2.33-2.41 (1H, m), 2.61-2.77 (3H, m), 3.76-3.87 (2H, m), 3.95 (1H, ddd, J= 14.0, 6.5, 4.4 Hz), 4.11 (1H, ddd, J= 14.0, 5.8, 4.4 Hz), 4.46 (1H, ddd, J= 12.3, 9.7, 6.0 Hz), 5.61-5.66 (1H, m), 5.69-5.74 (1H, m); ^{13}C NMR δ= 25.32, 30.71, 40.06, 44.27, 60.69, 73.73, 122.90, 125.12, 151.90, 171.07. Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.87; H, 6.20; N, 6.63. Found: C, 56.71; H, 6.16; N, 6.65.

(4a*R*,5*R*,8a*R*)-4a,5,8,8a-Tetrahydro-5,7-dimethyl-2,4-dioxo-2*H*-1,3-benzoxazine-3(4*H*)-ethanol (15). 58% yield from **9a**. 44% yield from **9b**. **15**: mp 95-98 °C; $[\alpha]^{24}_D$ -227.72° (*c* 0.81, CH_2Cl_2), 93% ee; IR (KBr) 3494, 1766, 1693, 1435, 1404, 1383, 1184, 1076 cm^{-1}; ^1H NMR δ= 0.94 (3H, d, J= 7.0 Hz), 1.70 (3H, s), 2.14 (1H, bs), 2.29 (1H, dd, J= 16.9, 9.6 Hz), 2.51 (1H, dd, J= 16.9, 6.3 Hz), 2.70 (1H, dd, J= 13.0, 5.4 Hz), 2.84-2.92 (1H, m), 3.77-3.79 (2H, m), 3.98 (1H, ddd, J= 14.0, 6.0, 4.8 Hz), 4.05 (1H, ddd, J= 14.0, 5.3, 5.3 Hz), 4.61 (1H, ddd, J= 13.0, 9.6, 6.3 Hz), 5.43-5.47 (1H, m); ^{13}C NMR δ= 16.26, 22.84, 30.27, 36.27, 44.13, 44.16, 61.02, 70.76, 126.45, 129.20, 151.92, 170.12. Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.10; H, 7.13; N, 6.00.

Oxidation of the Diels-Alder Adducts 10a and 10b Using *m*-Chloroperbenzoic Acid. 3-[((1*S*,2*R*,6*R*)-2-Acetoxy-6-hydroxy-4-methyl-3-cyclohexen-1-yl)carbonyl]-1,3-oxazolidin-2-one (16). To a cold solution (0 °C) of **10a** (44.2 mg, 0.11 mmol) in CH_2Cl_2 (3 mL) was added *m*-chloroperbenzoic acid (36.4 mg). After the solution was stirred for 1 h, *m*-chloroperbenzoic acid (15 mg) was added to the reaction mixture in three portions, and the mixture was allowed to warm to room temperature over a period of 5 h, then concentrated under reduced pressure. The residue was purified by TLC (diethylether) to afford the alcohol **16** (25.9 mg, 81%). By the same procedure, the oxidation of **10b** afforded **16** in 73% yield. **16**: $[\alpha]^{24}_D$ -235.06° (*c* 0.99, CH_2Cl_2), 95% ee; IR (neat) 3446, 1776, 1726, 1699, 1390, 1232, 1117, 1041, 1020 cm^{-1}; ^1H NMR δ= 1.75 (3H, s), 1.96 (3H, s), 2.09 (1H, dd, J= 17.6, 10.3 Hz), 2.45 (1H, dd, J= 17.6, 5.9 Hz), 3.84 (1H, ddd, J= 10.8, 9.4, 7.0 Hz), 3.87 (1H, dd, J= 10.8, 3.5 Hz), 4.00 (1H, ddd, J= 10.8, 9.2, 6.7 Hz), 4.35-4.45 (2H, m), 4.48 (1H, ddd, J= 10.8, 10.3, 5.9 Hz), 5.42-5.45 (1H, m), 5.76 (1H, dd, J= 4.4, 3.5 Hz); ^{13}C NMR δ= 20.97, 23.14, 37.85, 42.60, 51.25, 62.25, 63.73, 68.06, 117.94, 140.37, 153.32, 170.78, 171.93; HRMS Calcd for $C_{13}H_{17}NO_6$: M, 283.1066. Found: m/z 283.1070.

Transformation of 7a and 7b into β-Hydroxy Thioester 18. (a) **From 7a.** Under an argon atmosphere, a solution of Bu^nLi in hexane (1.65 M, 0.1 mL) was added dropwise to a solution of 1-octanethiol (23.8 mg, 0.16 mmol) in THF (1.8 mL) at 0 °C and the mixture was stirred for 1 h. The resulting suspension was added dropwise to a solution of **7a** (47.8 mg, 0.15 mmol) in THF (1 mL) at -30 °C. The reaction mixture

was stirred for 40 min, and then pH 7 phosphate buffer was added. The aqueous solution was extracted three times with ether. The combined ethereal solution was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give a crude product. Purification by TLC (AcOEt : hexane = 5 : 95) gave the thioester **17a** (45.3 mg, 80%) as a colorless oil. **17a**: $[\alpha]^{25}_D$ -85.94° (*c* 0.67, CH_2Cl_2); IR (neat) 2960, 2925, 2854, 1682, 1373, 1319, 1146 cm^{-1}; ^1H NMR δ= 0.85 (3H, t, J= 6.9 Hz), 1.18 (6H, s), 1.21 (6H, s), 1.19-1.35 (10H, m), 1.44 (1H, ddd, J= 10.4, 10.4, 5.5 Hz), 1.50-1.56 (2H, m), 1.96-2.04 (1H, m), 2.07-2.16 (2H, m), 2.29-2.36 (1H, m), 2.76-2.88 (3H, m), 5.62-5.72 (2H, m); ^{13}C NMR δ= 14.07, 22.61, 24.51, 24.72, 25.68, 28.56, 28.88, 29.09, 29.12, 29.67, 31.78, 49.78, 83.17, 124.93, 127.16, 203.44; HRMS Calcd for $C_{21}H_{37}BO_3S$: M, 380.2558. Found: m/z 380.2552.

Trimethylamine *N*-oxide dihydrate (16.3 mg, 0.14 mmol) was added to a solution of **17a** (45.3 mg, 0.12 mmol) in diglyme (2 mL) at room temperature and the mixture was heated at 95-100 °C with efficient stirring for 1 h. After removal of the solvent under reduced pressure, the residue was purified by TLC (AcOEt : hexane = 1 : 4) to afford the alcohol **18** (27.2 mg, 84%). **18**: $[\alpha]^{25}_D$ -84.86° (*c* 0.92, CH_2Cl_2); IR (neat) 3404, 2956, 2925, 2854, 1682, 1086, 1072 cm^{-1}; ^1H NMR δ= 0.85 (3H, t, J= 7.0 Hz), 1.19-1.37 (10H, m), 1.52-1.58 (2H, m), 2.02-2.09 (1H, m), 2.20-2.28 (1H, m), 2.38-2.46 (2H, m), 2.53 (1H, bs), 2.80 (1H, ddd, J= 11.0, 10.2, 5.6 Hz), 2.84-2.93 (2H, m), 4.13 (1H, ddd, J= 10.2, 9.8, 5.8 Hz), 5.55-5.60 (2H, m); ^{13}C NMR δ= 14.04, 22.59, 28.78, 28.81, 29.03, 29.10, 29.43, 29.70, 31.74, 33.37, 56.06, 68.15, 124.60, 124.63, 202.92; HRMS Calcd for $C_{15}H_{26}O_2S$: M, 270.1655. Found: m/z 270.1653.

(**b**) **From 7b.** In the similar manner described above, **7b** (64.9 mg, 0.21 mmol) was treated with $CH_3(CH_2)_7SLi$, prepared from a hexane solution (1.65 M, 0.13 mL) of Bu^{n}Li and 1-octanethiol (32.5 mg, 0.22 mmol), at -35 °C. The reaction mixture was allowed to warm to -10 °C over a period of 2 h, and then 1.0 M hydrochloric acid was added. The aqueous solution was extracted three times with ether. The combined ethereal solution was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to give the crude product **17b**, which was used for the next reaction without further purification. Trimethylamine *N*-oxide dihydrate (29 mg, 0.25 mmol) was added to a solution of the crude **17b** in diglyme (3 mL) at room temperature and the mixture was heated at 95 °C with efficient stirring for 30 min. After removal of the solvent under reduced pressure, the residue was purified by TLC (AcOEt : hexane = 1 : 4) to afford the alcohol **18** (37.4 mg, 66% from **7b**).

Determination of the Absolute Configuration of 7. (**a**) **Transesterification of the Thioester 18 to 19.** Under an argon atmosphere, to a suspension of Mg (10.5 mg, 0.43 mmol) in MeOH (2 mL) was added one drop of carbon tetrachloride at 0 °C and the mixture was stirred for 3.5 h to generate magnesium methoxide. When all magnesium dissolved, a solution of **18** (29.3 mg, 0.11 mmol) in THF (2 mL) was added at 0 °C and the mixture was stirred for 11 h. The reaction was quenched with saturated ammonium chloride solution and the methyl ester was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by TLC (AcOEt : hexane = 35 : 65) to give **19** (17 mg, quant.). **19**: $[\alpha]^{25}_D$ -143.67° (*c* 1.13, CH_2Cl_2); IR (neat) 3413, 1734, 1439, 1198, 1163, 1080 cm^{-1}; ^1H NMR δ= 1.99-2.07 (1H, m), 2.15-2.24 (1H, m), 2.38-2.46 (2H, m), 2.57 (1H, ddd, J= 10.6, 10.0, 5.7 Hz), 3.02 (1H, bs), 3.70 (3H, s), 4.04 (1H, ddd, J= 10.0, 9.8, 5.9 Hz), 5.52-5.63 (2H, m).

(**b**) **Hydrogenation of 19.** Under hydrogen (1 atm), a solution of **19** (17 mg, 0.11 mmol) in degassed benzene (2 mL) was added to chlorotris(triphenylphosphine)rhodium (2 mg, 0.002 mmol) at room temperature and the mixture was stirred for 12 h. After removal of the solvent, the residue was purified by TLC (AcOEt :

hexane = 2 : 3) to give **20** (15.3 mg, 89%). **20**: $[\alpha]^{28}_{D}$ -44.12° (*c* 0.89, $CHCl_3$); IR (neat) 3415, 2935, 2860, 1734, 1444, 1196, 1171, 1066, 1024 cm^{-1}; ^1H NMR δ= 1.16-1.37 (4H, m), 1.65-1.78 (2H, m), 1.96-2.04 (2H, m), 2.24 (1H, ddd, J= 12.2, 9.9, 3.8 Hz), 2.81 (1H, bs), 3.68 (3H, s), 3.73 (1H, ddd, J= 9.9, 9.9, 4.5 Hz); ^{13}C NMR δ= 24.27, 24.98, 28.05, 33.68, 51.23, 51.75, 70.88, 175.68.

These spectral data of **20** agreed with those of the literatures as follows. (1*R*, 2*R*)-**20**[7a]: $[\alpha]^{20.5}_{D}$ -47.6° (*c* 5.07, $CHCl_3$). **20**[7b]: ^1H NMR δ= 3.67 (3H, s); ^{13}C NMR ($CDCl_3$) δ= 24.51, 25.05, 28.45, 34.15, 51.69, 51.69, 70.86, 175.82. As these results show that the absolute configuration of **20** obtained is 1*R*, 2*R*, the absolute configuration of **7** is determined to be 1*R*, 6*R* as shown in eq 6.

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