Oxidative Functionalisation of SuperQuat Enamides: Asymmetric Synthesis of Homochiral 1,2 Diols

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Abstract: Homochiral (*E*)-enamides derived from (*S*)-4-phenyl-5,5-dimethyl-oxazolidin-2-one undergo highly diastereoselective epoxidation upon treatment with dimethyldioxirane (DMDO). Treatment with *m*-chloroperbenzoic acid (MCPBA) produces *syn*-(4*S*,1′*R*,2′*S*)-1′-acyloxy-2′-hydroxy derivatives with high diastereoselectivity, consistent with a mechanism involving initial epoxidation and subsequent in situ S_N1 type epoxide opening and trapping with *m*-chlorobenzoic acid. Reductive cleavage of the isolated 1′-acyloxy-2′-hydroxy derivatives generates 1,2-diols in high yields and in high ee.

Key words: homochiral 1,2-diols, SuperQuat enamides, asymmetric synthesis

Synthetic investigations concerning the oxidative functionalisation of the C=C bonds of enamines and enamides with either DMDO or MCPBA have demonstrated that oxidation occurs selectively at the C=C bond rather than at the amino functionality. Although isolation of the epoxides formed upon oxidation of enamines is generally difficult due to facile dimerisation,[1] *N*-acylation has been shown to stabilise the corresponding enamide epoxides, enabling their spectroscopic characterisation.[2] For instance, epoxidation of vinyl formamides with DMDO and in situ dehydration allows the efficient formation of epoxy isonitriles in good yield,[3] methodology which has been applied to the synthesis of isonitrin B.[4] As part of our established research programme for the direct synthesis of homochiral aldehydes and alcohols and hence carbohydrates from *N*-acyl oxazolidinones,[5] it was envisaged that stereoselective epoxidation of a SuperQuat enamide **1** to give epoxide **2**, coupled with regioselective ring opening with a suitably protected nucleophile would offer an alternative route to *O*-protected 1′-hydroxy derivatives such as **3**, with subsequent reduction leading to the formation of the corresponding 1,2-diols **4** (Figure 1). The recent publication of related studies concerning the epoxidation of chiral allenamides[6] and enamides[7] has prompted us to report our preliminary results within this area.[8]

Initial investigations were concerned with the preparation and evaluation of the potential for diastereoselective oxidation of a homochiral enamide derived from (*S*)-4-phenyl-5,5-dimethyloxazolidin-2-one (**5**). Treatment of

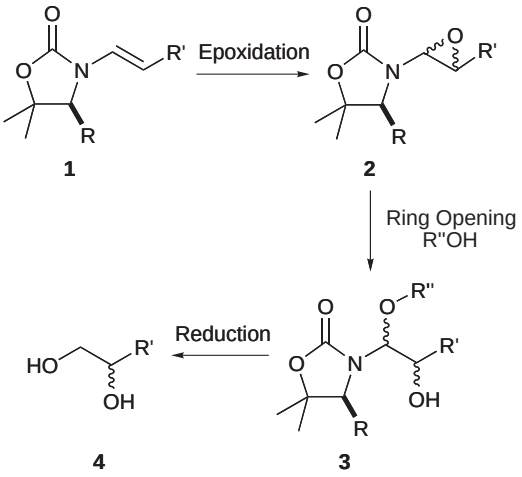

Figure 1 Proposed scheme for the asymmetric synthesis of chiral 1,2 diols.

(*S*)-4-phenyloxazolidinone **5** with phenylacetaldehyde and *p*-TSA in toluene under Dean-Stark conditions generated enamide (4*S*,1′*E*)-**6**[9] in >95% de and in 85% yield after recrystallisation, with the (1′*E*)-configuration within enamide **6** assigned on the basis of ^{1}H NMR spectroscopy from the diagnostic olefinic coupling constant (^3J = 14.5Hz).[10] To test the reactivity of the enamide functionality, oxidative functionalisation of (4*S*,1′*E*)-**6** via treatment with an acetone solution of dimethyldioxirane was evaluated,[11] with ^{1}H NMR spectroscopic analysis of the crude reaction mixture indicating that epoxide (4*S*,1′*R*,2′*S*)-**7** had been formed in 96 ± 4% de. Direct crystallisation from the crude reaction mixture gave epoxide (4*S*,1′*R*,2′*S*)-**7** in > 98% de and in 84% yield (Scheme 1).

Alternatively, functionalisation of enamide (4*S*,1′*E*)-**6** with MCPBA gave (4*S*,1′*R*,2′*S*)-3-(1′-*m*-chlorobenzoate-1′-ethyl-2′-hydroxy-2′-phenyl-4-phenyl-5,5-dimethyloxazolidin-2-one (**8**)[12] in 96 ± 4% de, with recrystallisation giving *syn*-(4*S*,1′*R*,2′*S*)-**8** in > 98% de and in 84% isolated yield (Scheme 2). The *syn*-(1′*R*,2′*S*)-configuration contained within the major diastereoisomer of 1′-*m*-chlorobenzoate-**8** was confirmed by single crystal X-ray analysis, with the absolute (4*S*,1′*R*,2′*S*)-configuration known relative to the known (*S*)-configuration of the oxazolidinone (Figure 2).[13] This *syn*-selectivity is opposite to the *anti*-stereoselectivity recently predicted by Adam et al. for oxidation with MCPBA of Evans' oxazolidinone

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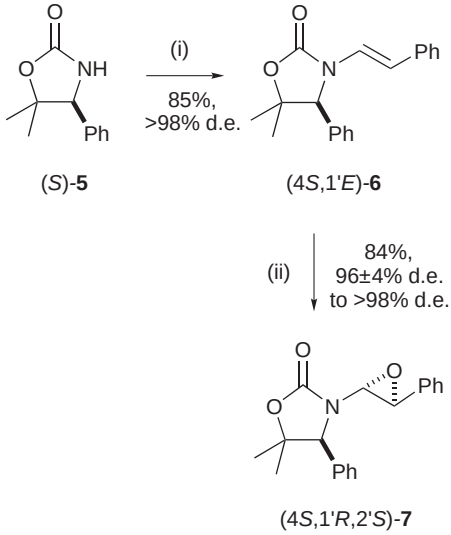
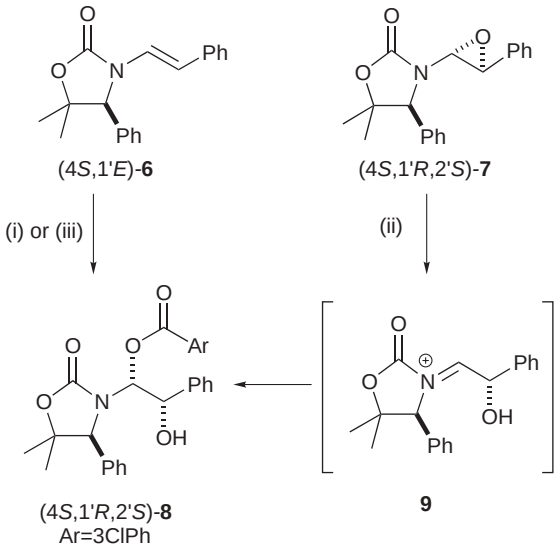


Scheme 1 *Reagents and Conditions;* (i) Phenylacetaldehyde, *p*-TSA, toluene, Δ; (ii) DMDO, acetone, 0 °C to r.t.

enamides,[7a] and is consistent with the reaction proceeding under the control of the SuperQuat auxiliary via initial diastereoselective epoxidation of enamide (4*S*,1′*E*)-**6** upon treatment with MCPBA, and subsequent epoxide opening in an S_N1 type process with retention of configuration at C(1′), presumably via *N*-acyl iminium intermediate **9**.[14] Stereoselective addition of *m*-chlorobenzoate, rather than direct regioselective S_N2 opening of epoxide-**7** at C(1′),[15] leads to *syn*-(4*S*,1′*R*,2′*S*)-**8**. In further support of this hypothesis, the addition of *m*-chlorobenzoic acid to the isolated (4*S*,1′*R*,2′*S*)-epoxide **7** resulted in the formation of 1′-*m*-chlorobenzoate-**8** in > 92% de and treatment of enamide **6** with DMDO in the presence of *m*-chlorobenzoic acid also gave *syn*-(4*S*,1′*R*,2′*S*)-**8** in >92% de.



Scheme 2 *Reagents and Conditions;* (i) MCPBA, $CHCl_3$, 0 °C to r.t.; (ii) *m*-chlorobenzoic acid, $CHCl_3$, 0 °C to r.t.; (iii) DMDO, *m*-chlorobenzoic acid, acetone, 0 °C to r.t.

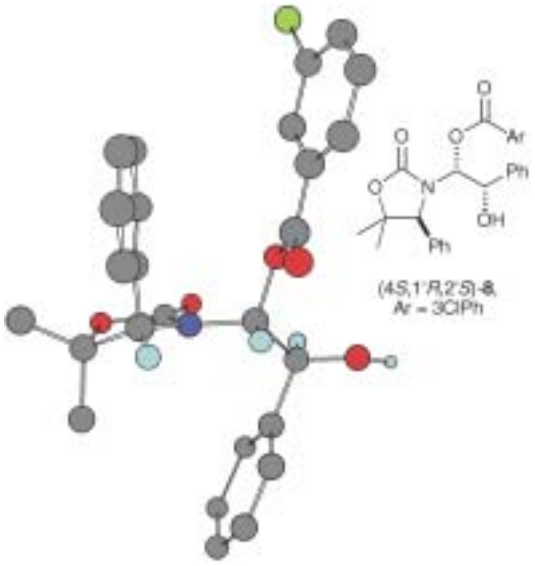
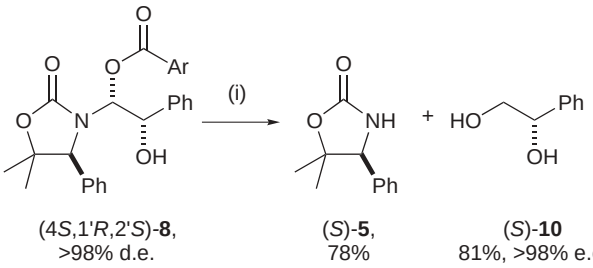


Figure 2 Chem 3D representation of the X-ray crystal structure of (4*S*,1′*R*,2′*S*)-**8** (some H omitted for clarity).

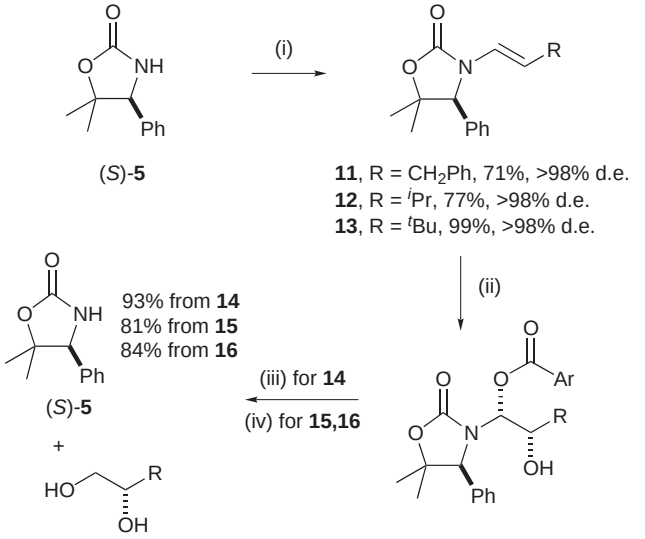
Further confirmation of the (2′*S*)-configuration within *syn*-(4*S*,1′*R*,2′*S*)-**8** was provided by reductive cleavage of the functionalised fragment from the SuperQuat chiral auxiliary. Treatment of recrystallised *syn*-(4*S*,1′*R*,2′*S*)-**8** (> 98% de) with $NaBH_4$ in MeOH furnished the parent (*S*)-4-phenyl oxazolidinone auxiliary **5** in 78% yield and (*S*)-1-phenylethanediol (**10**)[16] {$[\alpha]^{22}_D$ +64 (c 0.25, $CHCl_3$), lit., $[\alpha]^{18}_D$+66 (c 1.0, $CHCl_3$),[17] $[\alpha]^{20}_D$+63 (c 1.0, $CHCl_3$)[18]} in 81% yield, and in > 98% ee (Scheme 3).[19]



Scheme 3 *Reagents and Conditions;* (i) $NaBH_4$, MeOH, r.t.

To demonstrate the generality of this oxidative functionalisation methodology, hydrocinnamaldehyde, isovaleraldehyde and 3,3-dimethylbutyraldehyde were treated with (*S*)-**5** and catalytic *p*-TSA, furnishing the (1′*E*)-enamide derivatives (3′-phenylprop-1′-enyl)-**11**, (3′-dimethylbut-1′-enyl)-**12** and (3′,3′-dimethylbut-1′-enyl)-**13** as single diastereoisomers in 71%, 77% and 99% yield respectively. Enamide functionalisation of (3′-phenylprop-1′-enyl)-**11** and (3′-dimethylbut-1′-enyl)-**12** by treatment with MCPBA furnished the *syn*-(4*S*,1′*R*,2′*S*)-derivatives **14** and **15** in 92% and 96% de respectively, with recrystallisation giving *syn*-**14** in 60% yield and *syn*-**15** in 61% yield, and in > 98% de in each case. Treatment of 2′-benzyl-(4*S*,1′*R*,2′*S*)-**14** (>98% de) with $NaBH_4$ in MeOH returned the auxiliary (*S*)-**5** in 99% yield and (*S*)-3-phenylpropane-1,2-diol (**17**) {$[\alpha]^{24}_D$ –33.5 (c 0.93, EtOH),

lit.,[20] $[\alpha]^{20}_D$ –36 (c 1.0, EtOH)} in 93% yield after purification and in > 98% ee.[21] Although similar reduction of (4*S*,1′*R*,2′*S*)-**15** (>98% d.e.) with $NaBH_4$ led to low isolated yields of the required diol **18**, treatment with $LiAlH_4$ allowed the direct isolation of diol **18** in 56% yield {$[\alpha]^{25}_D$ +15.2 (c 0.90, $CHCl_3$), lit. *ent*-**18**; $[\alpha]^{22}_D$ –11.0 (c 1.00, $CHCl_3$)[22]; (78% yield as the bis-acetate derivative)[23] and in > 96% ee.[24] Treatment of (3′,3′-dimethylbut-1′-enyl)-**13** with MCPBA gave *syn*-(4*S*,1′*R*,2′*S*)-**16** in > 96% de, but this ester was not amenable to recrystallisation and proved extremely labile, fragmenting to a complex mixture of products upon attempted purification by chromatography. As a result, direct reduction of the crude reaction mixture with $LiAlH_4$ allowed the direct isolation of diol **19** in 51% yield (65% yield as the bis-acetate)[23] and in > 96% ee (Scheme 4).[24]



Scheme 4 *Reagents and Conditions;* (i) aldehyde, *p*-TSA, toluene, Δ; (ii) MCPBA, $CHCl_3$, 0 °C to r.t.; (iii) $NaBH_4$, MeOH, 0 °C to r.t.; (iv) $LiAlH_4$, THF, r.t. *(isolated yield of bis-acetate)

In conclusion, we have demonstrated that (*E*)-enamides may be prepared stereoselectively from (*S*)-4-phenyl-5,5-dimethyloxazolidin-2-one (**5**), which may be epoxidised selectively upon treatment with DMDO. Alternatively, treatment of the (*E*)-enamides with MCPBA generates *syn*-(4*S*,1′*R*,2′*S*)-1′-*m*-chlorobenzoate-2′-hydroxy derivatives, which upon reductive cleavage furnish homochiral 1,2-diols in high yields. The development of further methodologies for the asymmetric functionalisation of homochiral enamides are currently under investigation within our laboratory.

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(9) Experimental procedure for the synthesis (4*S*,1′*E*)-3-(2′-phenylethenyl)-5,5-dimethyl-4-phenyloxazolidin-2-one (**6**): Phenylacetaldehyde (0.44 mL, 3.77 mmol) was added to oxazolidinone (*S*)-**5** (600 mg, 3.14 mmol) in toluene (50 mL) and *p*-TSA (10 mg, 0.06 mmol) and heated under Dean–Stark conditions for three hours before concentration in vacuo. Purification by column chromatography [EtOAc/petroleum ether (40–60), 1:15] gave **6** (780 mg, 85%) as white crystals; mp 144 °C; IR (CH_2Cl_2) cm^{-1}: 1752 (C=O); $[\alpha]^{23}_D$ +7.8 (c 1, CH_2Cl_2); Found; C, 78.0; H, 6.5, N, 4.65%; $C_{19}H_{19}NO_2$ requires C, 77.8; H, 6.5, N, 4.8%; δ_H (400MHz, $CDCl_3$) 7.50–7.12 [11 H, m, ArC*H* and CH=C(2)′*H*Ph], 5.51 [1 H, d, *J* = 14.5 Hz, C(1′)*H*=CHPh], 4.81 [1 H, s, C(4)*H*], 1.66 and 1.00 [2 × 3 H, s, C(5)*Me*$_2$]; δ_C (125 MHz, $CDCl_3$) 155.2 (*C*O), 136.2, 135.0 (Ph:C_{ipso} × 2), 129.3, 129.1, 128.8, 126.8, 125.6 (Ph:*C*H), 123.4 [*C*(2′)H], 113.0 [*C*(1′)H], 82.6 [*C*(5)], 68.1 [*C*(4)H], 29.2, 24.0 [C(5)*Me*$_2$]; *m/z* (CI^+, NH_3) 294 (MH^+).

(10) (a) Based upon the related protocol for the synthesis of *N*-alkenyl lactams described in: Zezza, C. A.; Smith, M. B. *Synth. Commun.* **1987**, *17*, 729. (b) For a related protocol see: Akiba, T.; Tamura, O.; Hashimoto, M.; Kobayashi, Y.; Katoh, T.; Nakatani, K.; Kamada, M.; Hayakawa, I.; Terashima, S. *Tetrahedron* **1994**, *50*, 3905.

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(12) Experimental procedure for the synthesis of (4*S*,1′*R*,2′*S*)-3-(1′-*m*-chlorobenzoate-1′-ethyl-2′-phenyl-2′-hydroxy)-5,5-dimethyl-4-phenyloxazolidin-2-one(**8**): MCPBA (221 mg, 0.64 mmol) was added to a solution of enamide **6** (150 mg, 0.51 mmol) in $CHCl_3$ (8 mL) at 0 °C and stirred for 30 min before warming to r.t .for 2 h. H_2O (2 mL) was then added and the resulting solution concentrated in vacuo and partitioned between CH_2Cl_2 and sat. aq $NaHCO_3$. The separated organic phase was washed with sat. aq NH_4Cl and brine, dried ($MgSO_4$) and the concentrated in vacuo to afford a white solid which was purified by recrystallisation from CH_2Cl_2/hexanes to give **8** (200 mg, 84%) as white crystals; mp 106 °C; IR cm^{-1}: 1757, 1736 (C=O); $[\alpha]^{25}_D$ +94.0 (c1.0, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.97–7.04 (14 H, m, Ar*H*), 6.24 [1 H, d, *J* = 7.8 Hz, C(1′)*H*], 5.67 [1 H, d, *J* = 7.8 Hz, C(2′)*H*], 3.95 [1 H, s, C(4)*H*], 2.64 (1 H, s, O*H*), 0.99, 0.83 [2 × 3 H, s, C(5)Me_2]; δ_C (125 MHz, $CDCl_3$) 164.0 (*C*=O), 156.7 (N*C*=O), 139.4 (Ph:C_{ipso}), 135.5 (Ar*C*Cl), 134.6 (Ph:C_{ipso}), 133.8, 133.6 (Ph:*C*H), 131.2 (Ph:C_{ipso}), 130.4, 130.1, 129.9, 129.5, 129.2, 129.0, 128.9, 128.7, 128.4, 128.3, 127.3 (Ph:*C*H), 82.7 [*C*(5)Me_2], 82.3 [*C*(1′)H], 72.7 [*C*(2′)H], 71.4 [*C*(4)H], 27.9, 23.4 [C(5)Me_2]; HRMS ($APCI^+$) Found: 488.1241, $C_{26}H_{24}NO_5NaCl^+$ requires 488.1232.

(13) Data were collected using an Enraf Nonius Kappa CCD diffractometer with graphite monochromated Cu-Kα radiation using standard procedures at room temperature. The structure was solved by direct methods (SIR92), all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The crystal structure contains a molecule of solvent(pentane) and the chlorine of the *m*-chlorobenzoic ester fragment was disordered over two sites; Cl(1):Cl(34) 0.80:0.20. The model was refined using CRYSTALS.[25] Crystal Data for **8**, $C_{31}H_{35}ClNO_5$, colourless block, M = 536.73, orthorhombic, space group P 21 21 21, a = 9.8350(2) Å, b = 11.0530(2) Å, c = 27.4884(5) Å, U = 2988.2 $Å^3$, Z = 4, μ = 0.165 mm^{-1}, crystal dimensions 0.2 × 0.2 × 0.2 mm, A total of 6376 unique reflections were measured for $1 < \theta <$ 27 and 4518 reflections were used in the refinement. The final parameters were $R_1 = 0.0510$ [$I > 3\sigma(I)$] and wR_2 = 0.059. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre (CCDC 213199).

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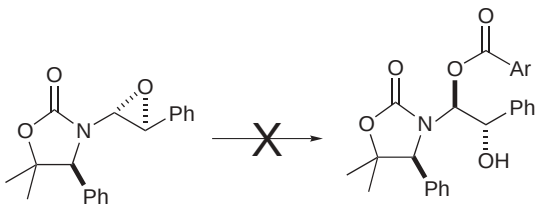
(15) Regioselective S_N2 opening of epoxide **7** at C(1′) would be expected to furnish *anti*-(4*S*,1′*S*,2′*S*)-1′-*m*-chlorobenzoate-**20** (Scheme 5).



(4*S*,1′*R*,2′*S*)-**7** (4*S*,1′*S*,2′*S*)-**20** [Ar=3ClPh]

Scheme 5

(16) Experimental procedure for the synthesis of (*S*)-1-phenylethanediol **10**: A solution of **8** (100 mg, 0.22 mmol) in MeOH (2 mL) was added to $NaBH_4$ (65 mg, 1.72 mmol) in MeOH (3 mL) and stirred at r.t. for 10 minutes before concentration in vacuo. The residue was dissolved in CH_2Cl_2 (10 mL) and HCl (1 M, 2 mL) was added and the mixture extracted with CH_2Cl_2 (3 × 10 ml), dried and concentrated in vacuo. Purification by chromatography [(40–60) petroleum ether/EtOAc, 1:2] gave auxiliary (*S*)-**5** (32mg, 78%) and alcohol **10** (24mg, 81%); $[\alpha]^{22}_D$ +64 (c 0.25, $CHCl_3$), δ_H (200 MHz, $CDCl_3$) 7.38–7.27 (5 H, m, Ar*H*), 4.82 [1 H, dd, *J* = 7.9 Hz, *J* = 3.8 Hz, C(1)*H*], 3.75–3.67 [2 H, m, C(2)H_2], 2.88 and 2.48 (2 × 1 H, br s, O*H*).

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(19) Chiral gas chromatography of diol **10** was performed on a CE Instruments Trace GC (Thermoquest) machine with an SGE Cydex-β stationary phase (25 m × 0.22 mm) with helium as the carrier gas and a flow rate of 1.5 mL per min using a FID detector. An isocratic temperature of 40 °C was followed for 120 minutes, followed by a temperature ramp of 4 °C to 140 °C for 120 minutes and comparison with an authentic racemic sample. Retention times were 159.25 min (*S*) and 159.87 min (*R*).

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(21) Chiral gas chromatography of the bis-trifluoroacetate derivative of **17** was performed on a CE Instruments Trace GC (Thermoquest) machine with an SGE Cydex-β stationary phase (25 m × 0.22 mm) with helium as the carrier gas and a flow rate of 2 mL per min using a FID detector. An isocratic temperature of 50 °C was followed for 120 minutes, followed by a temperature ramp of 4 °C to 110 °C for 60 minutes and comparison with an authentic racemic sample. Retention times were 139.38 min (*S*) and 139.89 min (*R*).

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(23) Although chromatographic purification led to the separation of diol and auxiliary, the isolated yield of the diol could be increased by acetylation of the crude reaction mixture resulting from reduction, which facilitated chromatographic purification of the bis-acetate derivative of the diol.

(24) Chiral gas chromatography of the bis-acetate derivatives was performed on a CE Instruments Trace GC (Thermoquest) machine with an SGE Cydex-β stationary phase (25 m × 0.22 mm) with helium as the carrier gas and a flow rate of 1 mL per min using a FID detector. An isocratic temperature of 40 °C was followed for 30 minutes, followed by a temperature ramp of 5 °C to 60 °C for 30 minutes, another temperature ramp of 20 °C to 190 °C for 2 minutes and comparison with an authentic racemic sample. Retention times for **18**-$(OAc)_2$ 69.41 min (*S*) and 69.45 min (*R*); for **19**-$(OAc)_2$ 51.00 (*R*) and 51.07 min (*S*).

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