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Highly enantioselective synthesis of *syn*- and *anti*-propionate aldols without diastereoselection in the chiral oxazaborolidinone-promoted aldol reaction with a silyl ketene acetal derived from ethyl 2-(methylthio)propionate

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Abstract

A mixture of *syn*- and *anti*-aldol products containing an α-methylthio group were obtained in good yields with high enantioselectivities in the chiral oxazaborolidinone-promoted aldol reactions of a novel silyl ketene acetal, derived from ethyl 2-(methylthio)propionate, with aldehydes. Subsequent desulfurization resulted in an effective preparation of essentially enantiopure *syn*- and *anti*-propionate aldols which were separable. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Enantioselective synthesis of *syn*- and *anti*-propionate aldols is quite important for the asymmetric synthesis of natural products bearing 1,3-polyol moieties. Considerable success has been reported in the field of asymmetric aldol reactions with chiral nucleophiles related to propionate synthones bound to a variety of chiral auxiliaries.[1] In spite of the development of chiral Lewis acid mediated aldol reactions, the enantioselective synthesis of propionate aldols with high diastereoselectivity is still far from attaining a practical level. For chiral borane-catalyzed (promoted) aldol reactions with silyl ketene acetals, with regard to propionate synthones, Yamamoto reported a highly enantioselective synthesis of *syn*-propionate aldols with chiral (acyloxy)borane (CAB) reagents, derived from L- or D-tartaric acid, in which the *syn* predominance is obtained independent of the geometry of the silyl ketene acetals.[2] However, the reaction using chiral oxazaborolidinones resulted in the preparation of a slight excess of *anti*-propionate

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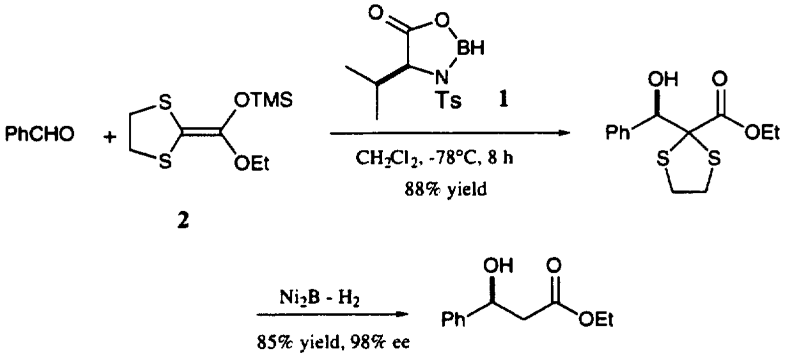
aldols with moderate enantioselectivity, but the minor *syn*-isomer showed quite high enantioselectivity.[3] In any event, to date, it seems to be difficult to produce each isomer separately with a level of high enantioselectivity by means of chiral borane-mediated aldol reactions.

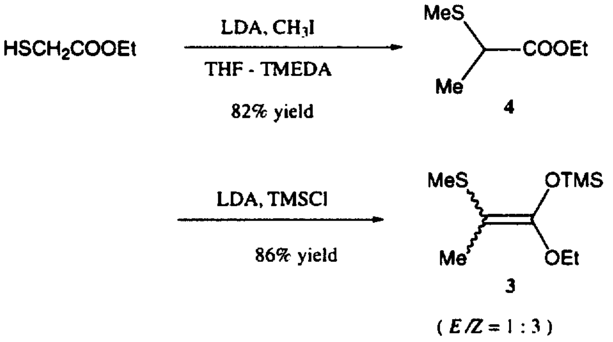
2. Results and discussion

We planned the practical enantioselective synthesis of *syn*- and *anti*-propionate aldols. We have already reported an excellent enantioselective synthesis of acetate aldols using the oxazaborolidinone **1** promoted aldol reaction with silyl ketene acetal **2**, bearing a dithiolane, in which the corresponding acetate aldol was obtained in a good yield with almost complete enantioselectivity after desulfurization with nickel boride, as shown in Eq. 1.[4] The steric bulkiness at the α-position of the nucleophiles resulted in a high enantioselectivity in the aldol reaction. The success in the preparation of enantiopure acetate aldols with **2** encouraged us to apply a silyl ketene acetal such as **3** to the enantioselective synthesis of propionate aldols.



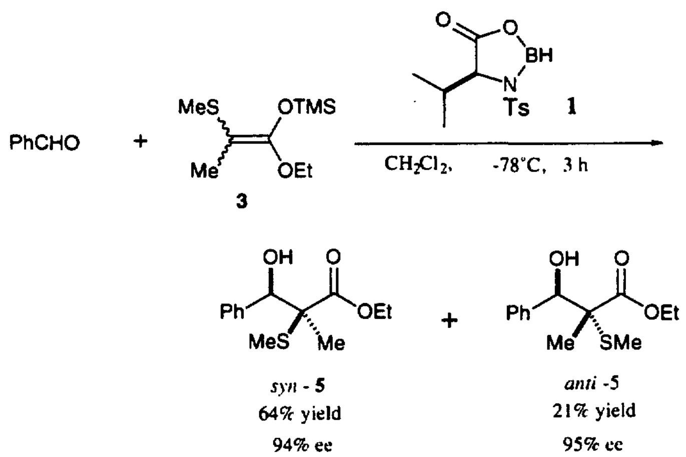
(1)

Ethyl 2-(methylthio)propionate **4** was prepared by treatment of the dianion from ethyl 2-mercaptoacetate with methyl iodide in 82% yield. The corresponding silyl ketene acetal **3** was obtained according to the usual method in 86% yield which was isolated as a mixture of geometrical isomers (the *E*:*Z* ratio was 1:3 assigned by a NOESY experiment), as shown in Eq. 2.



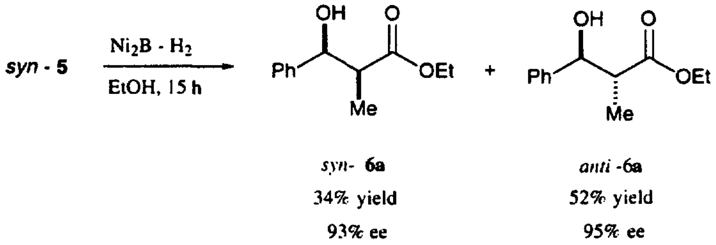
(2)

Reaction of benzaldehyde with silyl nucleophile **3** in the presence of a stoichiometric amount of **1** smoothly proceeded to give a mixture of *syn*- and *anti*-**5** in 85% yield, as shown in Eq. 3.

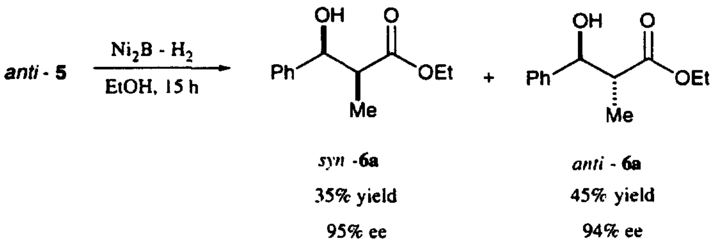


(3)

The isomers were easily separated by silica gel flash column chromatography (7% AcOEt in hexanes). The structure of *syn*- and *anti*-isomers was assigned by using the shielding effects of the phenyl ring to the methyl chemical shifts of the methylthio and methyl groups at C-2 (the methyl signals at the equatorial position resonate up-field), as depicted in Fig. 1. The enantioselectivity of *syn*-**5** was determined to be 94% ee by HPLC with Chiralcel AD (Daicel) (hexanes:2-propanol=95:5) while that of *anti*-**5** was determined to be 95% ee by using Chiralcel OD (hexanes:2-propanol=95:5). Desulfurization of **5** led to a mixture of *syn*- and *anti*-propionate aldols **6a** and **6b** in good yields by the treatment with nickel boride prepared in situ from large excesses of nickel chloride, which was finely ground to a powder, and sodium borohydride under a hydrogen atmosphere, as shown in Eqs 4 and 5.

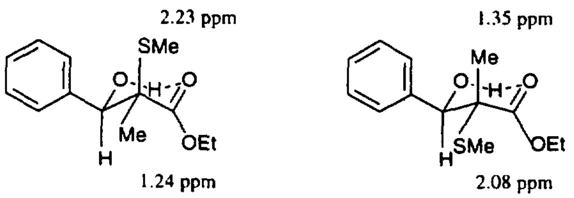


(4)



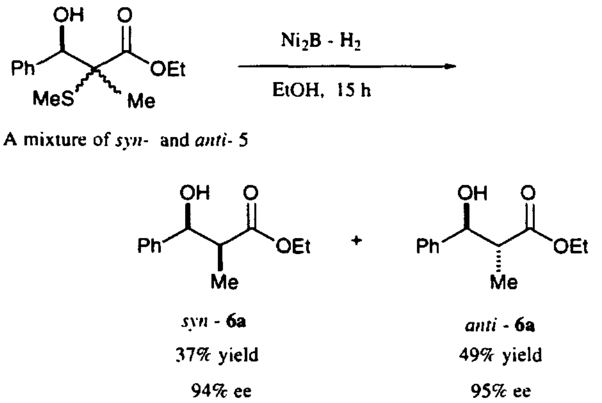
(5)

Assignment of the diastereomers was performed by comparing the carbinol resonances.[5] Scrambling of the stereochemistry at C-2 of **6** during desulfurization was observed, presumably owing to a radical process, so that similar results on the enantio- and diastereoselectivity were obtained starting from *syn*- and *anti*-**5**, however, no loss of stereochemistry at C-3 was found during the desulfurization. Direct desulfurization of a mixture of *syn*- and *anti*-**5** obtained directly from the reaction resulted in similar selectivities (Eq. 6).

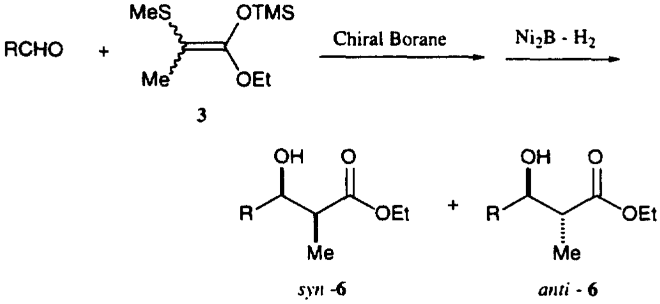


syn-**5** *anti*-**5**

Fig. 1.



(6)



(7)

Thus, from the stereochemical point of view, a successive sequence of the aldol reaction followed by desulfurization is recommended without the isolation of the sulfur-containing intermediates from the practical point of view. The successive procedure was applied to a variety of aldehydes (Eq. 7) and the results are summarized in Table 1. The enantiomeric excess of all products was determined by using Chiralcel AD and OD columns. Each reaction proceeded smoothly for the enantioselective preparation of propionate aldols. *syn*- and *anti*-Isomers of **6a**, **6b**, and **6c** could be separated by silica gel flash column chromatography, whereas separation of the isomers of **6d** was performed by preparative HPLC (YMC-Pack SIL SH-043-5 with hexanes:2-propanol=99:1). The isomers of phenyl esters of propionate aldols were found to be more easily separated by simple silica gel chromatography, but the oxazaborolodinone-promoted aldol reaction did not work with a silyl nucleophile derived from phenyl 2-(methylthio)propionate, presumably because of the steric bulkiness of the nucleophile.

In conclusion, our chiral oxazaborolidinone-promoted asymmetric aldol reaction with **3** achieved a very highly enantioselective synthesis of propionate aldols without diastereoselection. This is a quite versatile method to give both enantiomers simultaneously, for example, when both product enantiomers are required in the course of the synthesis of medicines having a complex stereochemistry. We are now engaged in a study of the enantioselective acyclic stereoselection with catalyst (promoter) based

Table 1
Enantioselective synthesis of *syn*- and *anti*-propionate aldols (Eq. 7)

Entry	R	*syn* - **6**[a]		*anti* -**6**[a]	
		% yield	% ee	% yield	% ee
1	Ph (**6a**)	34	94	39	95
2[b]	Ph (**6a**)[b]	37	95	40	96
3	$PhCH_2CH_2$ (**6b**)	35	97	32	97
4	$(CH_3)_2CH$ (**6c**)	30	98	48	95
5	$CH_3CH_2CH_2$ (**6d**)	42	99	35	98

[a] Absolute configrations of products are shown in eq.7. [b] By using a promoter derived from D-valine, the products were obtained with the opposite configration at C-2 and C-3.

stereocontrol using this aldol reaction with silyl nucleophile **3**.[6] Futhermore, we are trying to trap stereoselectively radical intermediates arising from the desulfurization process.

3. Experimental

3.1. General

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Diisopropylamine was distilled from CaH_2. Dichloromethane was distilled from P_2O_5. Tetrahydrofuran (THF) was distilled from sodium–benzophenone immediately prior to use. All reactions involving organometallic reagents were conducted under an argon atmosphere. IR spectra were determined with a JASCO FT-IR 5300 spectrometer. ^1H-NMR spectra were determined with a Hitachi R-90H (90 MHz) NMR spectrometer. ^{13}C-NMR spectra were determined with a Hitachi R-90H (22.6 MHz) NMR spectrometer. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Significant ^1H-NMR data are tabulated in order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, coupling constant(s) in hertz. Optical rotations were determined with a JASCO DIP-370 digital polarimeter. High performance liquid column chromatography (HPLC) was performed with a JASCO 875-UV/880-PU and a JASCO UV-970/PC-350/PM-350 using Daicel Chiralcel OD and AD, and YMC-A012 columns. Merck silica gel 60 (230–400 mesh) was used for flash column chromatography. *N*-*p*-Toluenesulfonyl-(*S*)-valine was prepared by the Schotten–Baumann procedure. $BH_3 \cdot THF$ (1.0 M solution in THF) was obtained from Aldrich.

3.2. Ethyl 2-(methylthio)propanoate 4

To a solution of diisopropylamine (5.6 mL, 44 mmol) in THF (40 mL) and TMEDA (6.64 mL, 44 mmol) at 0°C was added dropwise a 1.6 M solution of *n*-BuLi (27.4 mL, 44 mmol) in hexanes. After stirring for 30 min, the solution was cooled to −78°C. Ethyl 2-mercaptoacetate (2.2 mL, 20 mmol) was added dropwise to this solution over 15 min. After 1 h, CH_3I (8.0 mL, 120 mmol) was added. After stirring for 3 h at that temperature, the solution was allowed to warm to room temperature. After 1 h, the reaction mixture was quenched with a saturated NH_4Cl solution and poured into 10% HCl solution. The organic layer was extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give a crude product. The crude product was distilled under reduced pressure (75°C/25 mmHg) (82% yield). IR (neat): 1732 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.29 (t, 3H, J=7.04, 7.25), 1.44 (d, 3H, J=7.25), 2.16 (s, 3H), 3.33 (q, 1H, J=7.03, 7.25), 4.20 (q, 2H, J=7.04, 7.25).

3.3. 1-Trimethylsiloxy-1-ethoxy-2-methyl-2-methylthioethene 3

To a solution of diisopropylamine (2.12 mL, 16.2 mmol) in THF (45 mL) at 0°C was added dropwise a 1.6 M solution of *n*-BuLi (10.13 mL, 16.2 mmol) in hexanes. After stirring for 30 min, the solution was cooled to −78°C. To this solution was added ethyl 2-(methylthio)propanoate (2.0 g, 13.5 mmol) dropwise over 10 min. After 30 min, TMSCl (5.14 mL, 40.5 mmol) was added and the solution was stirred for 15 h at room temperature. After the solvent was removed with a rotary evaporator, the resulting mixture was filtered with suction through a Celite pad and washed with hexanes. The hexane extract was removed and the residue was distilled under reduced pressure (110°C–120°C/30 mmHg) to give a mixture of pure isomers (82% yield). IR (neat): 1651 cm^{-1}; ^{1}H-NMR ($CDCl_3$) of major isomer: δ 0.20 (s, 9H), 1.16 (t, 3H, J=7.03, 7.04), 1.80 (s, 3H), 2.05 (s, 3H), 3.77 (q, 2H, J=7.03, 7.04); minor isomer: δ 1.23 (t, 3H, J=7.03), 1.76 (s, 3H), 2.08 (s, 3H), 4.13 (q, 2H, J=7.2).

*3.4. General procedure for the chiral oxazaborolidinone-promoted aldol reaction with **3**. A mixture of ethyl (2S,3R)- and (2R,3R)-3-hydroxy-2-methyl-2-methylthio-3-phenylpropanoate* syn-**5** *and* anti-**5**

To a solution of *N-p*-toluenesulfonyl-(*S*)-valine (542 mg, 2.2 mmol) in 10 mL of CH_2Cl_2 at 0°C was added $BH_3 \cdot THF$ (2.0 mmol, 2.0 mL of a 1.0 M solution in THF) over 10 min and the solution was stirred for 30 min. After stirring for an additional 30 min at room tenperature, the solution was cooled to −78°C. To this solution was added benzaldehyde (212 mg, 2.0 mmol) in CH_2Cl_2 over 5 min. After stirring for 10 min, 1-trimethylsiloxy-1-ethoxy-2-methyl-2-methylthioethene (484 mg, 2.2 mmol) was added. After stirring for 3 h, the reaction mixture was quenched with a buffer solution (pH 6.8) at that temperature and extracted with CH_2Cl_2. The organic layer was washed with a saturated $NaHCO_3$ solution. The extract was dried over anhydrous $MgSO_4$ and the solvent was removed to give a crude product. The crude product was purified by flash column chromatography (7.5% AcOEt in hexanes) (85% yield). The enantiomeric excess of each isomer was determined by HPLC. IR (neat): 3489, 1714 cm^{-1}; *syn*-**5**: $[\alpha]_D^{24}$ 36.4 (c=1.24, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.25 (t, 3H, J=7.04, 7.25), 1.24 (s, 3H), 2.23 (s, 3H), 3.25 (d, 1H, J=1.54), 4.17 (q, 2H, J=7.15), 5.19 (d, 1H, J=1.31), 7.23–7.42 (m, 5H); ^{13}C-NMR ($CDCl_3$): δ 12.7, 14.0, 16.4, 53.4, 56.5, 61.1, 72.5, 127.7, 138.2, 171.4; *anti*-**5**: $[\alpha]_D^{24}$ −18.7 (c=0.79, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.32 (t, 3H, J=7.03, 7.25), 1.35 (s, 3H), 2.08 (s, 3H), 3.14 (d, 1H, J=4.83), 4.27 (q, 2H, J=7.14), 5.12 (d, 1H, J=4.62), 7.25–7.44 (m, 5H); ^{13}C-NMR ($CDCl_3$): δ 13.4, 15.0, 17.6, 54.2, 56.2, 62.4, 77.0, 128.3, 128.7, 139.5, 173.6. Anal. calcd for $C_{13}H_{18}O_3S$: C 61.39, H 7.13. Found: C 61.30, H 7.14.

3.5. General procedure for desulfurization of aldol products involving a dithiuolane. A mixture of ethyl (2S,3S)- and (2R,3S)-3-hydroxy-2-methyl-3-phenylpropanoate syn-**6a** *and* anti-**6a**

A solution of a mixture of *syn*- and *anti*-ethyl 3-hydroxy-2-methyl-2-methylthio-3-phenylpropanoate (99 mg, 0.39 mmol), obtained from the reaction (Eq. 3), in ethanol (15 mL) was kept under H_2 pressure. Anhydrous $NiCl_2$ (1.01 g, 20 equiv.) was introduced into this solution and then $NaBH_4$ (148 mg, 10 equiv.) was added rapidly at 0°C. The mixture was stirred vigorously for the next 15 h. The reaction mixture was filtered, evaporated, extracted with CH_2Cl_2, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash column chromatography (10% AcOEt in hexanes) to give a mixture of pure isomers (86% yield). IR (neat): 3454, 1716 cm^{-1}; *syn*-**6a**: $[\alpha]_D^{17}$ −22.0 (c=0.87, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.14 (d, 3H, *J*=7.26), 1.19 (t, 3H, *J*=7.04, 7.25), 2.63–2.91 (dq, 1H, *J*=3.96, 7.26), 2.97 (d, 1H, *J*=3.08), 4.11 (q, 2H, *J*=7.03, 7.25), 5.02–5.10 (dd, 1H, *J*=3.08, 3.96), 7.31 (br.s, 5H); ^{13}C-NMR ($CDCl_3$): δ 11.0, 14.1, 53.4, 60.6, 73.7, 126.0, 127.3, 128.1, 141.5, 175.5; *anti*-**6a**: $[\alpha]_D^{17}$ −15.3 (c=1.11, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.02 (d, 3H, *J*=7.25), 1.20 (t, 3H, *J*=7.03, 7.25), 2.71–2.88 (dq, 1H, *J*=7.25, 8.24), 3.03 (d, 1H, *J*=4.61), 4.17 (q, 2H, *J*=7.03, 7.25), 4.67–4.81 (dd, 1H, *J*=4.61, 8.24), 7.32 (br.s, 5H). ^{13}C-NMR ($CDCl_3$): δ 14.9, 15.2, 47.9, 61.4, 77.0, 127.3, 128.6, 129.0, 142.3, 176.3. Anal. calcd for $C_{12}H_{16}O_3$: C 69.21, H 7.74. Found: C 70.02, H 7.77.

3.6. Ethyl (2S,3R)- and (2R,3R)-3-hydroxy-2-methyl-5-phenylpentanoate 6b

IR (neat): 3447, 1730 cm^{-1}; *syn*-**6b**: $[\alpha]_D^{25}$ 22.3 (c=2.20, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.18 (d, 3H, *J*=7.5), 1.25 (t, 3H, *J*=7.0), 1.6–2.1 (m, 2H), 2.52 (dq, 1H, *J*=3.8, 7.0), 2.5–3.1 (m, 2H), 2.65 (d, 2H, *J*=4.6), 3.87 (dt, 1H, *J*=3.95, 7.0), 4.14 (q, 2H, *J*=7.0), 7.21 (s, 5H); *anti*-**6b**: $[\alpha]_D^{25}$ 9.2 (c=1.97, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.20 (d, 3H, *J*=7.5), 1.24 (t, 3H, *J*=7.0), 1.6–2.0 (m, 3H), 1.7–2.0 (m, 2H), 2.55 (quint, 1H, *J*=7.3), 2.7–3.1 (m, 2H), 2.76 (d, 2H, *J*=5.05), 3.66 (dt, 1H, *J*=6.5, 7.0), 4.16 (q, 2H, *J*=7.0), 7.22 (s, 5H).

3.7. Ethyl (2S,3R)- and (2R,3R)-2,4-dimethyl-3-hydroxypentanate 6c

IR (neat): 3497, 1718 cm^{-1}; *syn*-**6c**: $[\alpha]_D^{25}$ 5.16 (c=0.775, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.87 (d, 3H, *J*=6.6), 1.00 (d, 3H, *J*=6.6), 1.17 (d, 3H, *J*=7.0), 1.26 (t, 3H, *J*=7.2), 1.68 (2×q, 1H, *J*=6.6), 2.50 (d, 1H, *J*=3.0), 2.64 (dq, *J*=3.5, 7.0), 3.55 (dd, 1H, *J*=3.5, 7.5), 4.15 (q, 2H, *J*=7.2); *anti*-**6c**: $[\alpha]_D^{25}$ −6.0 (c=1.66, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.92 (d, 3H, *J*=6.6), 0.96 (d, 3H, *J*=6.6), 1.21 (d, 3H, *J*=7.0), 1.27 (t, 3H, *J*=7.2), 1.5–2.0 (m, 1H), 2.5–2.9 (m, 1H), 2.60 (d, 1H, *J*=7.0), 3.36 (dd, 1H, *J*=5.7, 7.0), 4.16 (q, 2H, *J*=7.2).

3.8. Ethyl (2S,3R)- and (2R,3R)-3-hydroxy-2-methylhexanate 6d

IR (neat): 3447, 1732 cm^{-1}; *syn*-**6d**: $[\alpha]_D^{25}$ 5.4 (c=1.48, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.93 (t, 3H, *J*=6.5), 1.17 (d, 3H, *J*=7.2), 1.27 (t, 3H, *J*=7.0), 1.4–1.7 (m, 4H), 3.4–3.8 (m, 1H), 4.08 (q, 2H, *J*=7.0); *anti*-**6d**: $[\alpha]_D^{25}$ −55.5 (c=0.59, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.93 (t, 3H, *J*=6.5), 1.20 (d, 3H, *J*=7.2), 1.27 (t, 3H, *J*=7.2), 1.3–1.6 (m, 4H), 2.4–2.8 (m, 2H), 3.6–3.9 (m, 1H), 4.17 (q, 2H, *J*=7.0).

Acknowledgements

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