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Enantioselective Diastereospecific Synthesis of *anti*-α-Alkyl-β-hydroxy Esters through Cuprate Opening of Glycidic Esters

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A diastereospecific chain elongation of the aldehydes **1** to *anti*-α-alkyl-β-hydroxy esters **2** via the intermediates **4** – **7** is described. By means of the *Sharpless* epoxidation, **2** may be obtained with >90% ee in either enantiomer.

Enantioselektive diastereospezifische Synthese von *anti*-α-Alkyl-β-hydroxycarbonsäureestern durch Cuprat-Ringöffnung von Glycidestern

Eine über die Zwischenglieder **4** – **7** ablaufende diastereospezifische Kettenverlängerung von Aldehyden **1** zu *anti*-α-Alkyl-β-hydroxyestern **2** wird beschrieben. Durch Verwendung der *Sharpless*-Epoxidierung kann **2** mit Enantiomerenüberschüssen von >90% in Form beider Antipoden erhalten werden.

A variety of methods[1)] is available for the synthesis of *anti*- and *syn*-α-alkyl-β-hydroxy esters (**2**/**3**) from aldehydes (**1**). Although amazingly high diastereo and enantio control can be achieved in certain cases, this selectivity is substrate dependent and may drop significantly on substituent variation. We report here a synthesis of **2** from **1**, which is characterized by a strictly mechanism-controlled and hence substrate independent stereochemistry. As shown in Scheme 1, the epoxy esters **7** are easily available from **1** in ca. 60% overall yield in five routine steps without the need of extensive purification or characterization of the intermediates **4** – **6**. The diastereomeric purity of **7**, which is crucial to the stereo control of the overall sequence, was carefully secured by 270-MHz ^{1}H NMR spectroscopy and shown to be >99% in all cases. The ring opening of **7a** – **d** with *Lipshutz* cuprates[2)] proceeded with perfect regio and stereo control to give the esters **2** in about 60% isolated yield. However, **7e** and **f**, both having α-branched substituents in the R^1-position, were inert and could be reisolated unchanged.

The diastereomeric purity of **2a** – **j** was checked by ^{13}C NMR comparison with **2**/**3** mixtures prepared from **1** and the carboxylic acid dianions **8** and subsequent esterification with ethereal diazomethane. As <1% of **3** could have been detected, we conclude that the reaction **7**→**2** occurred with >99% inversion at C-2.

Enantio control in either direction with predictable sense of asymmetric induction can easily be exerted by using *Sharpless*' procedure[3)] in the epoxidation step **5**→**6**, which is amply documented to afford reliable ee-values of 90 – 95%[4)]. Spe-

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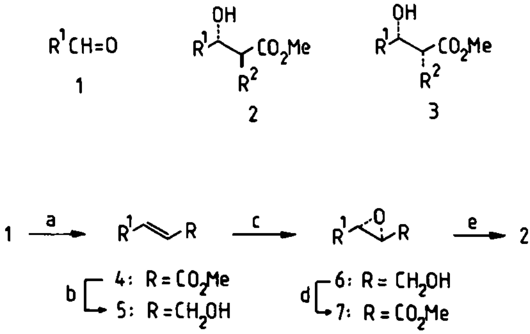
cifically, (2*S*,3*S*)-**6c**, (2*R*,3*S*)-**7c**, and (2*S*,3*S*)-**2h** were prepared in 92% ee from **5c** using diethyl (*R*,*R*)-tartrate as the chiral inductor. If only racemates are desired, the sequence may be abbreviated by epoxidizing the α,β-unsaturated acids (or esters) immediately, as exemplified in the synthesis of **7a** from (*E*)-crotonic acid.

Scheme 1



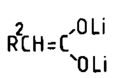
1,4,5,6,7	R^1	2, 3	R^1	R^2	2, 3	R^1	R^2
a	Me	**a**	Me	Ph	**g**	n-C_3H_7	Ph
b	Et	**b**	Me	Me	**h**	n-C_3H_7	n-C_4H_9
c	n-C_3H_7	**c**	Me	n-C_4H_9	**i**	n-C_5H_{11}	Ph
d	n-C_5H_{11}	**d**	Et	Ph	**j**	n-C_5H_{11}	n-C_4H_9
e	$CHMe_2$	**e**	Et	Me			
f	*t*Bu	**f**	Et	n-C_4H_9			

a. $(EtO)_2POCH_2CO_2Me$, NaH, diglyme; b. $(i\mathrm{Bu})_2AlH$, Et_2O, −78°C; c. *m*-chloroperbenzoic acid, CH_2Cl_2, 0°C or (+)-diethyl tartrate, *t*BuOOH, $Ti(OiPr)_4$, CH_2Cl_2, −20°C; d. RuO_4, CH_3CN, CCl_4, H_2O; CH_2N_2, Et_2O; e. $R^2_2CuCNLi_2$, Et_2O, −78°C.

The regiospecific ring opening of **7** at C-2 deserves some comment. For various 2,3-epoxy acids it has been demonstrated that nitrogen and sulfur nucleophiles can be directed to C-3 by $Ti(OiPr)_4$ catalysis, whereas they react unselectively in the absence of the catalyst[5]. Organoaluminium compounds attack epoxy esters like **7** at C-3 preferentially[6]. For cuprate agents, two cases of regio controlled C-2 openings of **7** have been reported, however, without stereochemical assignment[7]. Most recently, *Sharpless* and co-worker described the reaction of epoxy acids with cuprate derivatives[8] and found a 6−30 : 1 preference for C-2 opening in the case of the *trans*-isomer, whereas the *cis*-epoxy acid shows a preference of up to 17:1 for C-3 attack. Epoxy alcohols like **6** generally show a tendency towards C-2 addition[9,4,5], which is, however, strongly modulated[4,5] by the influence of R^1.

On applying organometallics other than cuprates to **7**, side reactions began to dominate. For instance, **7a** reacted with one mol equivalent of phenyllithium to form a 4 : 1 mixture of **9a** and **10**; similarly 2,4,5-trimethoxyphenyllithium produced **9b** from **7a**. On treatment with vinylmagnesium bromide and one mol equivalent of CuI **7a** gave 90% of the iodo ester **11b**. The reaction of *trans*-2,3-epoxybutyric acid with methylmagnesium iodide furnished the corresponding acid

11a. Obviously, not the formal carbanion but the iodide is the strongest nucleophile in this system. The β-position of the iodine in **11b** clearly follows from the ^1H NMR spectrum, which shows $J = 6$ Hz for the OH,2-H coupling constant.



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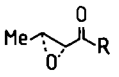
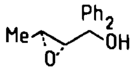


9a: R = Ph
9b: R = 2,4,5-$(CH_3O)_3C_6H_2$



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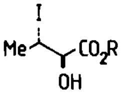

11 a: R = H
b: R = Me

In conclusion, we have presented a six-step (four-step in the case of racemic **2a**–**c**) chain elongation of **1** to **2**, which to our knowledge represents the only *anti*-diastereospecific and enantioselective solution to the Reformatsky problem. Within the limitations that a) R^1 must be unbranched in the α-position and b) R^2 must form a stable cuprate, our procedure should be a welcome supplement to the aldol methodology[10] which despite great efforts recently[11] is much more suitable for generating the *syn*-diastereomers **3**.

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Experimental Part

Melting points are uncorrected. – ^1H NMR spectra: Bruker WH 270, PW 80, Varian EM 360 and A 60. – ^{13}C NMR spectra: Bruker WP 80, WH 270. – IR: Perkin Elmer IR 580 B. – HPLC: Knauer HPLC pump 64, RI and UV detection. – The organometallic reactions were performed in absolute diethyl ether under argon. All reactions were monitored with TLC (Merck 5554). Preparative column chromatography by flash technique on silica gel Merck 60.

The α,β-unsaturated esters **4**[12], the allylic alcohols **5**[13] and the epoxy alcohols **6**[14] were prepared by routine procedures. The oxidation of **5** to the epoxy acids was performed according to *Sharpless*[15]. 2,3-Epoxybutyric acid was prepared from crotonic acid as described[16]. The esterification with diazomethane in ether gave quantitative yields of **7**. Some analytical and spectral data of **6** and **7** are compiled in Tables 1 and 2.

Table 1. Names, yields (from **1**) and elemental analyses of **7**

7	Methyl *trans*-2,3-Epoxy-	Yield (%)	Formula (Mol. Weight)	Calcd. C	Calcd. H	Found C	Found H
b	-pentanoate	62	$C_6H_{10}O_3$ (130.1)	55.38	7.75	54.85	7.65
c	-hexanoate	57	$C_7H_{12}O_3$ (144.2)	58.32	8.39	58.31	8.49
d	-octanoate	60	$C_9H_{16}O_3$ (172.2)	62.77	9.36	62.30	9.44
e	-4-methylpentanoate	65	$C_7H_{12}O_3$ (144.2)	58.32	8.39	58.05	8.29
f	-4,4-dimethylpentanoate	70	$C_8H_{14}O_3$ (158.2)	60.74	8.92	60.02	8.77

Table 2. Some spectral data of compounds **6**, **7**, **9**, **10**, **11**

	^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ =	IR (cm^{-1}) (neat)
6a	1.33 (d, $^3J_{3,4}$ = 5 Hz, 3H, 4-H); 2.90 (ddd, $^3J_{1A,2}$ = 5, $^3J_{1B,2}$ = $^3J_{2,3}$ = 3 Hz, 1H, 2-H); 3.03 (dq, $^3J_{2,3}$ = 3, $^3J_{3,4}$ = 5 Hz, 1H, 3-H); 3.36 (s, broad, 1H, OH); 3.59, 3.87 (dd, $^3J_{1A,2}$ = 5, $^3J_{1B,2}$ = 3, $^2J_{1A,B}$ = 13 Hz, 2H, 1-H)	
6b	1.00 (t, $^3J_{4,5}$ = 7 Hz, 3H, 5-H); 1.62 (mc, 2H, 4-H); 2.86 (s, broad, 1H, OH); 2.95 (mc, 2H, 3-H); 3.61, 3.90 (dd, $^3J_{1A,2}$ = 5, $^3J_{1B,2}$ = 3, $^2J_{1A,B}$ = 13 Hz, 2H, 1-H)	
6c	0.95 (t, $^3J_{5,6}$ = 7 Hz, 3H, 6-H); 1.51 (mc, 4H, 4-, 5-H); 2.93 (mc, 2H, 2-, 3-H); 3.12 (s, broad, 1H, OH); 3.57, 3.87 (dd, $^3J_{1A,2}$ = 5, $^3J_{1B,2}$ = 3, $^2J_{1A,B}$ = 13 Hz, 2H, 1-H)	
6d	0.90 (t, $^3J_{7,8}$ = 7 Hz, 3H, 8-H); 1.22, 1.45, 1.56 (3 × mc, 8H, 4-, 5-, 6-, 7-H); 2.34 (t, $^3J_{1,OH}$ = 7 Hz, 1H, OH); 2.94 (mc, 2H, 2-, 3-H); 3.62, 3.92 (ddd AB, $^3J_{1,OH}$ = 7, $^3J_{1A,2}$ = 5, $^3J_{1B,2}$ = 3, $J_{A,B}$ = 13 Hz, 2H, 1-H)	
7a	1.40 (d, $^3J_{3,4}$ = 5 Hz, 3H, 4-H); 3.18 (d, $^3J_{2,3}$ = 2 Hz, 1H, 2-H); 3.23 (qd, $^3J_{2,3}$ = 2, $^3J_{3,4}$ = 5 Hz, 1H, 3-H); 3.75 (s, 3H, OCH_3)	
7b	1.02 (t, $^3J_{4,5}$ = 7 Hz, 3H, 5-H); 1.69 (mc, 2H, 4-H); 3.16 (dt, $^3J_{2,3}$ = 2, $^3J_{3,4}$ = 5 Hz, 1H, 3-H); 3.25 (d, $^3J_{2,3}$ = 2 Hz, 1H, 2-H); 3.77 (s, 3H, OCH_3)	3050–2860 s (sat. CH); 1760 s (C=O); 1455, 1450 m (CH-def.); 1355 m (CH_3-def.); 1295, 1215 s (C–O); 1250, 895, 825 m (epoxide-CO and -CH); 1080 m; 995 m; 825 m
7c	0.98 (t, $^3J_{5,6}$ = 7 Hz, 3H, 6-H); 1.43–1.51 (m, 4H, 5-, 4-H); 3.13 (dt, $^3J_{2,3}$ = 2, $^3J_{3,4}$ = 5 Hz, 1H, 3-H); 3.20 (d, $^3J_{2,3}$ = 2 Hz, 1H, 2-H); 3.74 (s, 3H, OCH_3)	3050–2885 s (sat. CH); 1750 s (C=O); 1450 s (CH-def.); 1345 m (CH_3-def.); 1295, 1210 s (C–O); 1255, 905, 790 m (epoxide-CO and -CH); 1055 m; 1025 m
7d	0.90 (t, $^3J_{7,8}$ = 7 Hz, 3H, 8-H); 1.34 (mc, 4H, 7-, 6-H); 1.48 (mc, 2H, 5-H); 1.62 (mc, 2H, 4-H); 3.16 (dt, $^3J_{2,3}$ = 2, $^3J_{3,4}$ = 5 Hz, 1H, 3-H); 3.23 (d, $^3J_{2,3}$ = 2 Hz, 1H, 2-H); 3.77 (s, 3H, OCH_3)	3040–2870 s (sat. CH); 1750 s (C=O); 1450 s (CH-def.); 1345 m (CH_3-def.); 1293, 1205 s (C–O); 1255, 893, 798 m (epoxide-CO and -CH); 1028 m

Table 2 (*Continued*)

	^1H NMR (270 MHz, $CDCl_3$, TMS) δ =	IR (cm^{-1}) (neat)
7e	1.00, 1.05 (2 × d, $^3J_{4,5}$ = $^3J_{1',4}$ = 7 Hz, 6H, CH_3); 1.66 (t, $^3J_{4,5}$ = $^3J_{1',4}$ = 7 Hz, 1H, 4-H); 2.98 (dd, $^3J_{2,3}$ = 2, $^3J_{3,4}$ = 7 Hz, 1H, 3-H); 3.28 (d, $^3J_{2,3}$ = 2 Hz, 1H, 2-H); 3.78 (s, 3H, OCH_3)	3060–2840 s (sat. CH); 1750 s (C=O); 1475, 1450 s (CH-def.); 1373, 1360 m (CH_3-def.); 1292, 1203 s (C–O); 1220, 900, 820 m (epoxide-CO and -CH)
7f	0.97 (s, 9H, 5-H, CH_3); 3.00 (d, $^3J_{2,3}$ = 2 Hz, 1H, 3-H); 3.33 (d, $^3J_{2,3}$ = 2 Hz, 1H, 2-H); 3.78 (s, 3H, OCH_3)	3040–2860 s (sat. CH); 1750 s (C=O); 1485, 1468 (sh); 1450 s (CH-def.); 1370, 1340 m (CH_3-def.); 1290 m, 1205 s (C–O); 1245 m, 903 m, 700 w (epoxide-CO and -CH); 1038, 1008 m
9a	(80 MHz, $CDCl_3$, TMS): 1.52 (d, $^3J_{3,4}$ = 5.5 Hz, 3H, 4-H); 3.46 (dq, $^3J_{2,3}$ = 2, $^3J_{3,4}$ = 5.5 Hz, 1H, 3-H); 3.96 (d, $^3J_{2,3}$ = 2 Hz, 1H, 2-H); 7.31–7.75, 7.95–8.11 (m, 5H, Ph)	3100–3000 m (unsat. CH); 3000–2950 m (sat. CH); 1690 s (C=O); 1605 m, 1475 s (C=C-aromat.); 1245 s
9b	(60 MHz, $CDCl_3$, TMS): 1.50 (d, $^3J_{3,4}$ = 5.5 Hz, 3H, 4-H); 3.17 (dq, $^3J_{2,3}$ = 2, $^3J_{3,4}$ = 5.5 Hz, 1H, 3-H); 3.88, 3.98 (2 × s, 9H, OCH_3); 4.07 (d, $^3J_{2,3}$ = 2 Hz, 1H, 2-H); 6.55, 7.40 (2 × s, 2H, C_6H_2)	(KBr): 3100–2840 m (unsat. and sat. CH); 1645 s (C=O); 1600, 1505 s (C=C-aromat.); 1460, 1435 m (CH-def.); 1350 m (CH_3-def.); 1265 s, 1210 s (C–O); 1170 m; 1130 m; 1015 s
10	(80 MHz, $CDCl_3$, TMS): 1.33 (d, $^3J_{3,4}$ = 5.5 Hz, 3H, 4-H); 2.76 (s, broad, 1H, OH); 3.24 (dq, $^3J_{2,3}$ = 2, $^3J_{3,4}$ = 5.5 Hz, 1H, 3-H); 3.51 (d, $^3J_{2,3}$ = 2 Hz, 1H, 2-H); 7.37 (mc, 5H, Ph)	(KBr): 3400 s, broad (OH); 3100, 3000 w (unsat. CH); 3000–2850 m (sat. CH); 1575, 1490 m (C=C-aromat.); 1315 m (OH-def.); 1175, 945, 750 m (epoxide-CO and -CH); 860 s, 740 s; 700 s
11a	(270 MHz, [D_6]acetone, TMS): 1.87 (d, $^3J_{3,4}$ = 7 Hz, 3H, 4-H); 4.29 (d, $^3J_{2,3}$ = 3.5 Hz, 1H, 2-H); 4.55 (dq, $^3J_{2,3}$ = 3.5, $^3J_{3,4}$ = 7 Hz, 1H, 3-H)	(KBr): 3400 s, broad (OH); 2980, 2930 s (sat. CH); 1723 s (C=O); 1441, 1387 m (CH-def.); 1265 s, 1220 s, 1129 m, 1093 s, 1068 s (OH-def. and C–O-val.); 985 m; 892 m; 867 m; 756 m; 502 m (C–I); 415 m
11b	1.87 (d, $^3J_{3,4}$ = 7 Hz, 4-H); 3.54 (d, $^3J_{H,OH}$ = 6 Hz, 1H, OH); 3.85 (s, 3H, OCH_3); 4.24 (dd, $^3J_{H,OH}$ = 6, $^3J_{2,3}$ = 3.6 Hz, 1H, 2-H); 4.46 (dq, $^3J_{2,3}$ = 3.6, $^3J_{3,4}$ = 7 Hz, 1H, 3-H)	3770–3100 s (broad, OH); 2940 m (sat. CH); 1725 s (C=O); 1425 m (OH-def.); 1245, 1200 m (C–O); 1120 m, 1015 m

Ring Opening of **7** *with Cuprates. General Procedure:* 30 mmol of CuI was suspended in ether at −78°C and treated dropwise with the organolithium compound (10 mmol; MeLi in ether, BuLi in hexane, PhLi in ether). While stirring the mixture for 1 h, the temp. was raised to −50°C. After recooling to −78°C **7** (10 mmol) was added dropwise and the mixture was stirred at −30°C overnight. Then 2 N H_2SO_4 was added, the organic phase was separated, washed with water, dried ($MgSO_4$), and evaporated. The crude hydroxy esters **2a**−**j** were purified by chromatography (ethyl acetate/hexane 1 : 2). Names of the products, yields, analytical and spectral data are listed in Tables 3 and 4. The absence of regioisomers was secured by careful analysis of the ^1H NMR spectra, e. g., absence of $CH(CH_3)_2$ signals in **2b** or of $CH(OH)CO_2CH_3$ signals in **2a**−**j**. For a stereochemical comparison **2**/**3**-mixtures were prepared from carboxylic acid dianions and **1** as described earlier[17].

Table 3. Names, melting points, yields (from **7**), and elemental analyses of **2**

2	Methyl *anti*-	m. p. (°C)	Yield (%)	Formula (Mol. Weight)	Calcd./Found C	H
a	3-hydroxy-2-phenylbutyrate	56−57	55	$C_{11}H_{14}O_3$ (194.2)	68.02 67.79	7.27 7.37
b	3-hydroxy-2-methylbutyrate	oil	50	$C_6H_{12}O_3$ (132.2)	54.53 53.76	9.15 9.16
c	2-butyl-3-hydroxybutyrate	oil	57	$C_9H_{18}O_3$ (174.2)	62.04 62.04	10.41 10.57
from **2d**	3-acetoxy-2-phenylpentanoate	oil	60	$C_{14}H_{18}O_4$ (250.3)	67.18 67.36	7.25 7.38
e	3-hydroxy-2-methylpentanoate	oil	55	$C_7H_{14}O_3$ (146.2)	57.51 57.24	9.65 9.31
f	2-butyl-3-hydroxypentanoate	oil	61	$C_{10}H_{20}O_3$ (188.3)	63.80 63.34	10.71 10.81
g	3-hydroxy-2-phenylhexanoate	52−53	71	$C_{13}H_{18}O_3$ (222.3)	70.25 70.17	8.16 8.22
h	2-butyl-3-hydroxyhexanoate	oil	57	$C_{11}H_{22}O_3$ (202.3)	65.31 64.88	10.96 11.15
i	3-hydroxy-2-phenyloctanoate	45−46	65	$C_{15}H_{22}O_3$ (250.3)	71.97 71.84	8.86 9.12
j	2-butyl-3-hydroxyoctanoate	oil	51	$C_{13}H_{26}O_3$ (230.3)	67.78 68.17	11.38 11.44

Methyl (2R,3S)-2,3-Epoxyhexanoate [(2*R*,2*S*)-**7c**]: (*E*)-2-Hexen-1-ol (**5c**) (5.00 g, 50 mmol) was epoxidized with diethyl (*R*,*R*)-tartrate (8.03 g, 55 mmol), *tert*-butyl hydroperoxide (4.95 g, 55 mmol), and $Ti(O\mathit{i}Pr)_4$ (15.62 g, 55 mmol) in dichloromethane (200 ml) at −20°C for 14 h as described[4]. Hydrolytic workup followed by distillation under reduced pressure yielded 5.20 g (90%) of the optically active 2,3-epoxyhexanol (2*S*,3*S*)-**6c**, $[\alpha]^{22}_{D} = -44.6$ ($c = 2$, $CHCl_3$). The optical purity of the product was determined[18] by acylating 450 mg (3.88 mmol) of (2*S*,3*S*)-**6c** with (−)-methoxyphenyl(trifluoromethyl)acetyl chloride ((−)-MTPA chloride) (970 mg, 3.88 mmol) in pyridine (10 ml) for 14 h at 22°C. Usual workup with water and ether furnished 1.23 g (96%) of the MTPA ester. Likewise, racem. **6c** was converted into the MTPA ester. Comparison of the ^1H and ^{13}C NMR spectra revealed an ee-value of 92 ± 2%.

(−)-MTPA Ester of racem. **6c**: ^1H NMR (270 MHz, $CDCl_3$, TMS): $\delta = 0.93$ (t, J = 7 Hz, 3H, 6-H); 1.37−1.55 (m, 4H, 4-, 5-H); 2.81 (dt, J = 2 and 6 Hz, 1H, 3-H); 2.95 (ddd,

Table 4. ^{1}H (270 MHz, $CDCl_3$, TMS), ^{13}C NMR (25.2 MHz, $CDCl_3$, TMS), and IR spectra of **2**/**3a**–**j**

	^{1}H NMR δ =	^{13}C NMR δ =	IR (cm^{-1}) (neat)
2a	1.04 (d, $^3J_{3,4}$ = 6 Hz, 3H, 4-H); 3.50 (d, $^3J_{2,3}$ = 9 Hz, 1H, 2-H); 3.59 (s, broad, 1H, OH); 3.64 (s, 3H, OCH_3); 4.32 (dq, $^3J_{3,4}$ = 6, $^3J_{2,3}$ = 9 Hz, 1H, 3-H); 7.27 (mc, 5H, Ph)	20.6 (C-4); 52.4 (OCH_3); 60.4 (C-2); 69.8 (C-3); 127.6, 128.2, 128.6, 136.2 (Ph); 173.6 (C-1)	(KBr): 3260 m (OH); 3065, 3035 w (unsat. CH); 2980, 2940 m (sat. CH); 1780 s (C=O); 1605 w, 1495 w (C=C-aromat.); 1467, 1437 m (CH-def.); 1355 m (CH_3-def.); 1280 m (OH-def.); 1202 m, 1165 s (C–O); 1130 m; 1100 m; 1095 m; 1010 m; 950 m; 735, 702 m (CH-aromat, out of plane)
3a	1.22 (d, $^3J_{3,4}$ = 6 Hz, 3H, 4-H); 3.04 (s, broad, 1H, OH); 3.52 (d, $^3J_{2,3}$ = 6.5 Hz, 1H, 2-H); 3.65 (s, 3H, OCH_3); 4.35 (dq, $^3J_{3,4}$ = 6, $^3J_{2,3}$ = 6.5 Hz, 1H, 3-H); 7.27 (mc, 5H, Ph)	21.0 (C-4); 52.2 (OCH_3); 58.8 (C-2); 68.6 (C-3); 127.6, 128.0, 128.6, 134.8 (Ph); 172.8 (C-1)	
2b	1.15 (d, $^3J_{1',2}$ = 7 Hz, 3H, CH_3); 1.20 (d, $^3J_{3,4}$ = 7 Hz, 3H, 4-H); 2.48 (q, $^3J_{1',2}$ = $^3J_{2,3}$ = 7 Hz, 1H, 2-H); 3.37 (s, broad, 1H, OH); 3.68 (s, 3H, OCH_3); 3.89 (q, $^3J_{2,3}$ = $^3J_{3,4}$ = 7 Hz, 1H, 3-H)	13.6 (CH_3); 20.4 (C-4); 47.0 (C-2); 51.7 (OCH_3); 69.3 (C-3); 176.0 (C-1)	3500 s (OH); 2985, 2945 s (sat. CH); 1725 s (C=O); 1465, 1442 m (CH-def.); 1383 m (CH_3-def.); 1265 m, 1211 s (C–O-val.); 915 m
3b	1.16 (d, J = 7 Hz, 3H, CH_3); 1.18 (d, $^3J_{3,4}$ = 7 Hz, 3H, 4-H); 2.50 (dq, $^3J_{2,3}$ = 5, $^3J_{3,4}$ = 7 Hz, 1H, 2-H); 3.48 (s, broad, 1H, OH); 3.68 (s, 3H, OCH_3); 4.01 (dq, $^3J_{2,3}$ = 5, $^3J_{3,4}$ = 7 Hz, 1H, 3-H)	12.0 (OCH_3); 20.5 (C-4); 46.5 (C-2); 51.6 (OCH_3); 68.3 (C-3); 176.0 (C-1)	
2c	0.90 (t, $^3J_{3',4'}$ = 7 Hz, 3H, 4'-H); 1.21 (d, $^3J_{3,4}$ = 6 Hz, 3H, 4-H); 1.24–1.37 (m, 4H, 2'-, 3'-H); 1.48–1.70 (m, 2H, 1'-H); 2.38 (ddd, $^3J_{1'a,2}$ = 10, $^3J_{1'b,2}$ = 7, $^3J_{2,3}$ = 6 Hz, 1H, 2-H); 3.37 (s, broad, 1H, OH); 3.68 (s, 3H, OCH_3); 3.88 (qui., $^3J_{2,3}$ = $^3J_{3,4}$ = 6 Hz, 1H, 3-H)	13.8 (C-4'); 21.3 (C-4); 22.6 (C-3'); 28.9 (C-2'); 29.6 (C-1'); 51.4 (OCH_3); 53.2 (C-2); 68.4 (C-3); 175.8 (C-1)	3460 s (OH); 2970 s, 2945 s, 2880 m (sat. CH); 1730 s (C=O); 1462, 1440 m (CH-def.); 1383 m (CH_3-def.); 1275 m (OH-def.); 1200, 1173 s (C–O-val.); 1125 m

Table 4 (*Continued*)

	^{1}H NMR δ =	^{13}C NMR δ =	IR (cm^{-1}) (neat)
3c	0.90 (t, J = 7 Hz, 3H, 4′-H); 1.91 (d, J = 7 Hz, 3H, 4-H); 1.25 – 1.39 (m, 4H, 2′-, 3′-H); 1.51 – 1.73 (m, 2H, 1′-H); 2.36 – 2.46 (m, 1H, 2-H); 3.89 (s, broad, 1H, OH); 3.67 (s, 3H, OCH_3); 3.39 (qui, J = 6 Hz)	13.8 (C-4′); 20.6 (C-4); 22.6 (C-3′); 27.7 (C-2′); 29.9 (C-1′); 51.4 (OCH_3); 52.9 (C-2); 68.3 (C-3); 175.4 (C-1)	
2d[a)]	0.80 (t, $^3J_{4,5}$ = 7 Hz, 3H, 5-H); 1.30 (dq, $^2J_{4,4}$ = 15, $^3J_{3,4}$ = 7, $^3J_{4,5}$ = 7 Hz, 1H, 4-H); 1.55 (dq, $^2J_{4,4}$ = 15, $^3J_{3,4}$ = 3.5, $^3J_{4,5}$ = 7 Hz, 1H, 4-H); 2.06 (s, 3H, CH_3); 3.62 (s, 3H, OCH_3); 3.80 (d, $^3J_{2,3}$ = 11 Hz, 1H, 2-H); 5.53 (3 × d, $^3J_{2,3}$ = 11, $^3J_{3,4a}$ = 3.5, $^3J_{3,4b}$ = 7 Hz, 1H, 3-H); 7.27 – 7.37 (m, 5H, Ph)	(67.88 MHz, $CDCl_3$): 8.5 (C-5); 20.8 (C-2′); 24.3 (C-4); 51.9 (OCH_3); 55.5 (C-2); 75.3 (C-3); 127.9, 128.6, 128.8, 134.9 (Ph); 170.0 (C-1′); 172.0 (C-1)	3070, 3040 w (unsat. CH); 2980 s, 2880 w (sat. CH); 1745 s (C=O); 1605 w, 1500 m (C=C-aryl); 1458, 1437 m (CH-def.); 1375 s (CH_3-def.); 1275, 1245, 1203, 1170 (C–O-val.); 1092 m, 1030 m, 968 m; 740 m, 705 m (C–H-aryl, out of plane)
3d	0.91 (t, $^3J_{4,5}$ = 7 Hz, 3H, 5-H); 1.28 (m, 1H, 4-H); 1.64 (m, 1H, 4-H); 1.78 (s, 3H, CH_3); 3.64 (s, 3H, OCH_3); 3.76 (d, $^3J_{2,3}$ = 8 Hz, 1H, 2-H); 5.50 (m, 1H, 3-H); 7.21 – 7.34 (m, 5H, Ph)	(67.88 MHz, $CDCl_3$): 9.5 (C-5); 20.5 (C-2′); 25.9 (C-4); 52.0 (OCH_2); 55.4 (C-2); 74.5 (C-3); 127.6, 128.3, 128.9, 135.2 (Ph); 170.0 (C-1′); 171.8 (C-1)	
2e	0.99 (t, $^3J_{4,5}$ = 7 Hz, 3H, 5-H); 1.19 (d, $^3J_{1',2}$ = 7 Hz, 3H, 1′-H); 1.40 – 1.62 (m, 2H, 4-H); 2.57 (q, $^3J_{1',2;2,3}$ = 7 Hz, 1H, 2-H); 3.62 (ddd, $^3J_{2,3}$ = 7, $^3J_{3,4a}$ = 8, $^3J_{3,4b}$ = 4 Hz, 1H, 3-H); 3.70 (s, 3H, OCH_3); 4.59 (s, broad, 1H, OH)	(67.88 MHz, $CDCl_3$): 9.8 (C-1′); 14.1 (C-5); 27.5 (C-4); 44.8 (C-2); 51.6 (OCH_3); 74.6 (C-3); 176.4 (C-1)	3500 s, broad (OH); 2985 s, 2945 s, 2880 m (sat. CH); 1733 s (C=O); 1470, 1443 m (CH-def.); 1255 s, 1205 s, 1177 s (C–O-val.); 1037 m; 985 m; 897 m
3e	0.96 (t, $^3J_{4,5}$ = 7 Hz, 3H, 5-H); 1.19 (d, $^3J_{1',2}$ = 7 Hz, 3H, 1′-H); 1.38 – 1.66 (m, 2H, 4-H); 2.56 (q, $^3J_{1',2;2,3}$ = 7 Hz, 1H, 2-H); 3.06 (s, broad, 1H, OH); 3.70 (s, 3H, OCH_3); 3.78 (m, 1H, 3-H)	(67.88 MHz, $CDCl_3$): 10.2 (C-1′); 10.6 (C-5); 26.8 (C-4); 44.0 (C-2); 51.6 (OCH_3); 73.3 (C-3); 176.5 (C-1)	

Table 4 (*Continued*)

	${}^1H$ NMR δ =	${}^{13}C$ NMR δ =	IR (cm^{-1}) (neat)
2f	0.89 (t, ${}^3J_{3',4'}$ = 7 Hz, 3H, 4'-H); 0.97 (t, ${}^3J_{4,5}$ = 7 Hz, 3H, 5-H); 1.20−1.77 (m, 8H, 4-H, 1'-, 2'-, 3'-H); 2.45 (dt, ${}^3J_{1',2}$ = 6, ${}^3J_{2,3}$ = 9 Hz, 1H, 2-H); 2.71 (s, broad, 1H, OH); 3.58 (m, slightly covered, 1H, 3-H); 3.67 (s, 3H, OCH_3)	(67.88 MHz, $CDCl_3$): 9.9 (C-5); 13.8 (C-4'); 22.5 (C-3'); 28.4 (C-2'); 29.2 (C-1'); 29.6 (C-4); 50.6 (C-2); 51.4 (OCH_3); 73.7 (C-3); 176.2 (C-1)	3480 s, broad (OH); 2965 s, 2940 s, 2880 m, 2870 m (sat. CH); 1760 s (C=O); 1462, 1438 m (CH-def.); 1380 m (CH_3-def.); 1270 m, 1197, 1173 s (C−O-val.); 1125 m; 980 m
3f	0.89 (t, ${}^3J_{3',4'}$ = 7 Hz, 3H, 4'-H); 0.97 (t, ${}^3J_{4,5}$ = 7 Hz, 3H, 5-H); 1.18−1.77 (m, 8H, 4-H, 1'-, 2'-, 3'-H); 2.46 (m, 1H, 2-H); 2.83 (s, broad, 1H, OH); 3.55−3.76 (m, 1H, 3-H); 3.66, 3.69 (2 × s, 3H, OCH_3 *anti/syn*)	(67.88 MHz, $CDCl_3$): 10.0 (C-5); 13.6 (C-4'); 22.5 (C-3'); 26.9 (C-4); 27.3 (C-2'); 29.8 (C-1'); 51.0 (C-2); 51.2 (OCH_3); 73.5 (C-3); 175.8 (C-1)	
2g	0.81 (t, ${}^3J_{5,6}$ = 7 Hz, 3H, 6-H); 1.19−1.37, 1.44−1.59 (2 sm, 4H, 5-, 4-H); 3.13 (s, broad, 1H, OH); 3.58 (d, ${}^3J_{2,3}$ = 9 Hz, 1H, 2-H); 3.65 (s, 3H, OCH_3); 4.17 (mc, 1H, 3-H); 7.23−7.33 (m, 5H, Ph)	(67.88 MHz, $CDCl_3$): 13.7 (C-6); 18.5 (C-5); 31.1 (C-4); 52.1 (OCH_3); 58.6 (C-2); 76.5 (C-3); 127.6, 128.4, 128.8, 129.6, 136.3 (Ph); 174.2 (C-1)	3450 s, broad (OH); 3095 w, 3070 w, 3038 w (unsat. CH); 2962 s, 2880 m (sat. CH); 1732 s (C=O); 1602 m, 1500 m (C=C-aryl-val.); 1457 s, 1437 s (CH-def.); 1355 (CH_3-def.); 1313 m, 1285, 1270 m, 1230 m, 1200 s, 1167 s (C−O-val. and OH-def.); 1127 m; 1025 m; 739, 703 s (CH-aryl-def.)
3g	0.91 (t, ${}^3J_{5,6}$ = 7 Hz, 3H, 6-H); 1.18−1.60 (m, 4H, 5-, 4-H); 2.96 (s, broad, 1H, OH); 3.56 (d, ${}^3J_{2,3}$ = 4 Hz, 1H, 2-H); 3.65 (s, 3H, OCH_3); 4.16 (m, 1H, 3-H); 7.29−7.35 (5H, Ph)	(67.88 MHz, $CDCl_3$): 13.8 (C-6); 18.9 (C-5); 36.6 (C-4); 52.0 (OCH_3); 57.3 (C-2); 72.0 (C-3); 127.7, 128.7, 129.2, 136.3 (Ph); 174.1 (C-1)	
2h	0.88, 0.92 (2 × t, ${}^3J_{3',4'}$ = ${}^3J_{5,6}$ = 7 Hz, 6H, 4'-, 6-H); 1.19−1.77 (3 × m, 10H, 3'-, 2'-, 1'-H and 4-, 5-H); 2.42 (dt, ${}^3J_{1',2}$ = 6, ${}^3J_{2,3}$ = 9 Hz, 1H, 2-H); 2.54 (d, broad, 1H, OH); 3.58−3.72 (m, covered, 1H, 3-H); 3.68 (s, 3H, OCH_3)	(67.88 MHz, $CDCl_3$): 13.8 (C-6); 13.9 (C-4'); 18.8 (C-3'); 22.5 (C-2'); 29.3 (C-1'); 29.6 (C-5); 37.8 (C-4); 51.1 (C-2); 51.4 (OCH_3); 72.0 (C-3); 176.2 (C-1)	3500 s, broad (OH); 2970, 2945 s, 2885 s (sat. CH); 1730 s (C=O); 1462, 1440 s (CH-def.); 1380, 1370 m (CH_3-def.); 1265 m, 1230 m, 1197 s, 1272 s, 1130 m (C−O-val. and OH-def.); 1027 m

Table 4 (*Continued*)

	^{1}H NMR δ =	^{13}C NMR δ =	IR (cm^{-1}) (neat)
3h	0.89, 0.91 (2 × t, $^3J_{3',4'}$ = $^3J_{5,6}$ = 7 Hz, 6H, 4'-, 6-H); 1.21 – 1.77 (m, 10H, 3'-, 2'-, 1'-H and 4-, 5-H); 3.43 (mc, 1H, 3-H); 2.93 (s, broad, 1H, OH); 3.63 – 3.80 (m, covered, 1H, 3-H); 3.67 (s, 3H, OCH_3)	(67.88 MHz, $CDCl_3$): 13.8 (C-6); 13.8 (C-4'); 19.0 (C-3'); 22.6 (C-2'); 26.8 (C-1'); 29.9 (C-5); 36.5 (C-4); 51.2 (C-2); 51.4 (OCH_3); 71.9 (C-3); 176.0 (C-1)	
2i	0.82 (t, $^3J_{7,8}$ = 7 Hz, 3H, 8-H); 1.19, 1.28, 1.50 (3 × mc, 6H, 7-, 6-, 5-, 4-H); 3.20 (d, broad, $^3J_{H,OH}$ = 5 Hz, 1H, OH); 3.60 (d, $^3J_{2,3}$ = 9 Hz, 1H, 2-H); 3.66 (s, 3H, OCH_3); 4.19 (m, 1H, 3-H); 7.24 – 7.35 (m, 5H, Ph)	(67.88 MHz, $CDCl_3$): 13.8 (C-8); 22.4 (C-7); 24.9 (C-6); 31.5 (C-5); 33.8 (C-4); 51.9 (OCH_3); 58.6 (C-2); 73.3 (C-3); 127.6, 128.3, 128.7, 136.2 (Ph); 174.2 (C-1)	(KBr): 3500 – 3430 s, broad (OH-val.); 3065 w, 3038 w (unsat. CH); 2960, 2938, 2862 s (sat. CH); 1737 s (C=O); 1603 w, 1500 m (C=C-aryl-val.); 1457, 1437 s (CH-def.); 1353 m (CH_3-def.); 1307 m, 1282 m, 1255 m, 1232 m, 1203 m, 1169 s (C – O-val. and OH-def.); 1135 m; 732, 700 s (CH-aryl, def.)
3i	0.87 (t, $^3J_{7,8}$ = 7 Hz, 3H, 8-H); 1.06 – 1.57 (m, 8H, 7-, 6-, 5-, 4-H); 2.66 (s, broad, 1H, OH); 3.55 (d, $^3J_{2,3}$ = 6 Hz, 1H, 2-H); 3.60 (s, 3H, OCH_3); 4.13 (m, 1H, 3-H); 7.18 – 7.31 (m, 5H, Ph)	(67.88 MHz, $CDCl_3$): 13.8 (C-8); 22.5 (C-7); 25.3 (C-6); 31.6 (C-5); 34.5 (C-4); 51.9 (OCH_3); 57.3 (C-2); 72.2 (C-3); 127.7, 128.6, 129.2, 135.3 (Ph); 173.6 (C-1)	
2j	0.89 (t, $^3J_{7,8}$ = $^3J_{3',4'}$ = 7 Hz, 6H, 8-, 4'-H); 1.30, 1.46, 1.60, 1.68 (4 × mc, 14H, 7-, 6-, 5-, 4-H and 3'-, 2'-, 1'-H); 2.43 (dt, $^3J_{1',2}$ = 6, $^3J_{2,3}$ = 9 Hz, 1H, 2-H); 2.60 (s, broad, 1H, OH); 3.66 (mc, covered, 1H, 3-H); 3.69 (s, 3H, OCH_3)	(67.88 MHz, $CDCl_3$): 13.8 (C-8); 13.9 (C-4'); 22.5 (C-7, -3'); 25.3 (C-6); 29.2 (C-2'); 29.6 (C-1'); 31.7 (C-5); 35.6 (C-4); 51.0 (C-2); 51.4 (OCH_3); 72.3 (C-3); 176.1 (C-1)	3500 s, broad (OH); 2965, 2940 s, 2870 s (sat. CH); 1732 s (C=O); 1462, 1440 m (CH-def.); 1382 m (CH_3-def.); 1265 m, 1230 m, 1198 s, 1173 s (C – O-val. and OH-def.); 1132 m
3j	0.88 (t, $^3J_{7,8}$ = $^3J_{3',4'}$ = 7 Hz, 6H, 8-, 4'-H); 1.29, 1.43, 1.65 (3 × mc, 14H, 7-, 6-, 5-, 4-H and 3'-, 2'-, 1'-H); 2.42 (m, 1H, 2-H); 2.70 (s, broad, 1H, OH); 3.61 – 3.74 (m, 1H, 3-H); 3.66 (s, 3H, OCH_3)	(67.88 MHz, $CDCl_3$): 13.8 (C-8); 13.9 (C-4'); 22.2, 22.6 (C-7, -3'); 25.5 (C-6); 26.7 (C-2'); 29.9 (C-1'); 31.7 (C-5); 34.3 (C-4); 51.2 (C-2); 51.4 (OCH_3); 72.2 (C-3); 176.0 (C-1)	

J = 2, 3.5, and 6 Hz, 2-H of diast. A); 2.99 (ddd, J = 2, 3.5, and 6 Hz, 1H, 2-H of diast. B); 3.54 (s, 3H, OCH_3); 4.16 (dd, J = 12 and 6 Hz, 1H, 1-H of diast. A); 4.19 (dd, J = 12 and 6 Hz, 1H, 1-H of diast. B); 4.50 (dd, J = 12 and 3.5 Hz; 1H, 1-H of diast. A); 4.55 (dd, J = 12 and 3.5 Hz; 1H, 1-H of diast. B); 7.34, 7.49 (2 mc, 5 phenyl-H). – ^{13}C NMR (67.88 MHz, $CHCl_3$, TMS): δ = 13.7, 19.1, 33.4, 54.5, 55.4, 56.4, 56.5, 66.0, 66.2, 123.3, 127.4, 128.4, 129.7, 132.1, 166.4.

(–)-MTPA Ester of (2*S*,3*S*)-**6c**: ^{1}H NMR (270 MHz, $CDCl_3$, TMS): δ = 0.92 (t, J = 7 Hz, 3H, 6-H); 1.34–1.55 (m, 4H, 4-, 5-H); 2.81 (dt, J = 2 and 5 Hz, 1H, 3-H); 3.00 (ddd, J = 2, 3.5, and 6 Hz, 1H, 2-H); 3.55 (s, 3H, OCH_3); 4.17 (dd, J = 6 and 12 Hz, 1H, 1-H); 4.55 (dd, J = 3.5 and 12 Hz, 1H, 1-H); 7.34, 7.50 (2 m, 5 phenyl-H). – ^{13}C NMR (67.88 MHz, $CDCl_3$, TMS): δ = 13.7, 19.1, 33.4, 54.5, 55.4, 56.4, 66.0, 123.3, 127.4, 128.4, 129.7, 132.1, 166.4.

The further conversion of (2*S*,3*S*)-**6c** into (2*R*,3*S*)-**7c** ($[\alpha]_D^{20}$ = –23.8; c = 2.6, $CHCl_3$) and (2*S*,3*S*)-**2h** ($[\alpha]_D^{20}$ = –13.8; c = 1.2, $CHCl_3$) was performed as described for the racemic material.

To make sure that no optical activity has been lost on the way to the final product, (2*S*,3*S*)-**2h** was also converted into the MTPA ester and this was compared with a sample obtained from racemic **2h**. ^{13}C NMR and HPLC-analysis congruently revealed an ee-value of 90 ± 2%.

(–)-MTPA Ester of (2*S*,3*S*)-**2h**: ^{13}C NMR (67.88 MHz, $CDCl_3$, TMS): δ = 13.7, 17.6, 22.5, 27.8, 29.5, 33.1, 48.8, 51.5, 55.3, 76.9, 123.4, 127.5, 128.3, 129.5, 132.3, 166.0, 173.2.

(–)-MTPA Ester of racem. **2h**: ^{13}C NMR (67.88 MHz, $CDCl_3$, TMS): δ = 13.7, 17.5, 18.0, 22.5, 27.5, 27.7, 29.5, 33.1, 33.3, 48.7, 48.8, 51.4, 51.5, 55.3, 76.7, 123.4, 127.5, 128.3, 129.5, 132.3, 165.9, 173.1, 173.2. – HPLC (Waters Porasil 10 µ, 3.9 × 300, ethyl acetate/hexane 1.5 : 98.5): τ(diastereomer A) = 8.91 min; τ(diastereomer B) = 9.73 min; ratio 95 : 5, flow 2 ml/min, 63 bar.

Reaction of **7a** *with Organometallic Reagents other than Cuprates (^{1}H NMR and IR data of the products see Table 2)*

a) ***With Phenyllithium:*** **7a** (1.00 g, 8.62 mmol) in ether (20 ml) was treated dropwise with phenyllithium (1 M in ether, 10 ml, 10 mmol) at –70°C. After 3 h at –15°C the mixture was quenched with NH_4Cl solution, the organic phase was separated, washed with water, dried ($MgSO_4$), and evaporated to give 1.28 g (84%) of a 4 : 1 mixture of **9a** and **10**, which were separated by fractional crystallization from ether/pentane.

trans-2,3-Epoxy-1-phenyl-1-butanone (**9a**): Colorless platelets of m. p. 62–63°C.

$C_{10}H_{10}O_2$ (162.2) Calcd. C 74.05 H 6.21 Found C 73.98 H 6.10

trans-2,3-Epoxy-1,1-diphenyl-1-butanol (**10**): Colorless needles of m. p. 158–159°C.

$C_{16}H_{16}O_2$ (240.2) Calcd. C 79.97 H 6.71 Found C 80.27 H 6.67

b) ***With 2,4,5-Trimethoxyphenyllithium:*** 1-Bromo-2,4,5-trimethoxybenzene (1.00 g, 4.00 mmol) was converted into the lithium derivative by reaction with *n*-butyllithium (2.86 ml of a 1.4 M solution in hexane, 4.00 mmol) in ether (20 ml) at –78°C for 1.5 h. Then **7a** (350 mg, 3.02 mmol) was added in ether (2 ml). After 12 h at –30°C the mixture was worked up as described in a) to give 378 mg (50%) of *trans-2,3-epoxy-1-(2,4,5-trimethoxyphenyl)-1-butanone* (**9b**) as colorless crystals of m. p. 129–130°C.

$C_{13}H_{16}O_5$ (252.3) Calcd. C 61.89 H 6.39 Found C 61.76 H 6.10

c) *With Vinylmagnesium Bromide/CuI:* CuI (380 mg, 2.00 mmol) in absol. THF (5 ml) was treated with 2 ml of a 1.2 M solution of vinylmagnesium bromide in THF at −78°C for 2 h. Then **7a** (232 mg, 2.00 mmol) was added in THF (2 ml) and the mixture was stirred at −10°C for 15 h. Workup as described furnished methyl *anti*-2-hydroxy-3-iodobutyrate (**11b**) (440 mg, 90%) identical in all respects with a sample obtained from diazomethane esterification of the corresponding acid (see below).

Reaction of trans-2,3-Epoxybutyric Acid with Methylmagnesium Iodide: trans-2,3-Epoxybutyric acid (1.0 g, 10.0 mmol) in ether (50 ml) was treated with 10 ml of a 1 M solution of methylmagnesium iodide in ether for 10 h at 20°C. After usual workup 1.84 g (80%) of *anti-2-hydroxy-3-iodobutyric acid* (**11a**) was isolated as colorless crystals of m. p. 95−96°C.

$C_4H_7IO_3$ (230.0) Calcd. C 20.89 H 3.07 Found C 21.30 H 3.10

Esterification with ethereal diazomethane furnished a quantitative yield of **11b**.

CAS Registry Numbers

1a: 75-07-0 / **1b**: 123-38-6 / **1c**: 123-72-8 / **1d**: 66-25-1 / **1e**: 78-84-2 / **1f**: 630-19-3 / (±)-**2a**: 100939-25-1 / (±)-**2b**: 65781-33-1 / (±)-**2c**: 100939-26-2 / (±)-**2d**: 100939-27-3 / (±)-**2e**: 100992-75-4 / (±)-**2f**: 100945-78-6 / (±)-**2g**: 100946-31-4 / (±)-**2h**: 100939-28-4 / **2h**: 100992-82-3 / **2h** (MTPA ester): 100939-37-5 / (*R,R*)-**2h** (MTPA ester): 100992-83-4 / (±)-**2i**: 100939-29-5 / (±)-**2j**: 100939-30-8 / **4a**: 623-43-8 / **4b**: 15790-88-2 / **4c**: 13894-63-8 / **4d**: 7367-81-9 / **4e**: 20515-15-5 / **4f**: 20664-51-1 / **5a**: 504-61-0 / **5b**: 1576-96-1 / **5c**: 928-95-0 / **5d**: 18409-17-1 / **5e**: 69143-05-1 / **5f**: 64081-43-2 / (±)-**6a**: 55058-23-6 / (±)-**6b**: 100992-76-5 / (±)-**6c**: 89395-00-6 / **6c**: 89459-98-3 / **6c** (MTPA ester): 100992-80-1 / (*R,R*)-**6c** (MTPA ester): 100992-79-8 / (±)-**6d**: 100992-77-6 / (±)-**6e**: 89459-99-4 / (±)-**6f**: 101052-71-5 / (±)-**7a**: 83057-88-9 / (±)-**7b**: 101052-72-6 / (±)-**7c**: 100939-31-9 / **7c**: 100992-81-2 / (±)-**7d**: 100939-32-0 / (±)-**7e**: 100939-33-1 / (±)-**7f**: 100939-34-2 / (±)-**9a**: 100939-35-3 / (±)-**9b**: 100945-79-7 / (±)-**10**: 100992-78-7 / (±)-**11a**: 100939-36-4 / (±)-**11b**: 100946-32-5 / (−)-MTPA chloride: 39637-99-5 / $(EtO)_2P(O)CH_2CO_2Me$:1067-74-9

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