Synthesis of Enantioenriched Methyl *vic*-Dihydroxystearates

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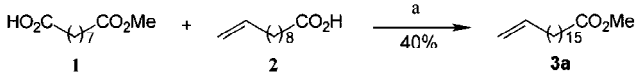
Abstract: Several enantioenriched methyl *vic*-dihydroxystearates **4** have been synthesized from methyl octadecenoates by enantioselective dihydroxylation in good yields (85–97%) and with satisfactory enantiomeric excess (ee 80–97%). The enantioenriched *anti*-9,10-dihydroxystearates (*anti*-**4c**) were prepared by HPLC separation of the corresponding dicamphanyl esters *anti*-**6**. Their ee was determined by HPLC of the corresponding diastereoisomeric carbamates **7**, and their configuration was assigned by relation to a described compound or by applying the mnemonic device of Sharpless.

Key words: enantioselective dihydroxylation, methyl *vic*-dihydroxystearates, methyl octadecenoates, separation of diastereoisomers, Kolbe electrolysis

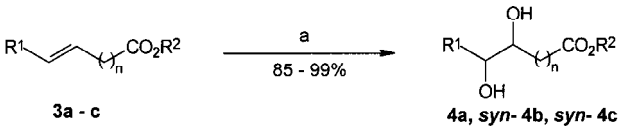
Monolayers of chiral amphiphiles can spontaneously separate into chiral domains.[1] Most of the amphiphiles, studied so far bear chiral polar head groups. We wanted to explore how the monolayer behavior of methyl stearates is influenced by stereogenic centers located at different positions in the alkyl chain. For this purpose enantioenriched methyl *vic*-dihydroxystearates were prepared using the Sharpless[2] method for the enantioselective dihydroxylation of olefins. The corresponding methyl octadecenoates were synthesized by Kolbe electrolysis[3] or Wittig reaction. Methyl octadec-17-enoate **(3a)** has been obtained in 40% yield by coelectrolysis of one equivalent of undec-10-enoic acid **(2)** with four equivalents of methyl azelate **(1)**[4] (Scheme 1) at platinum electrodes in methanol in an undivided cell.[5] Ethyl *trans*-octadec-2-enoate **(3b)** was synthesized by a Wittig reaction from hexadecanal and (ethoxycarbonylmethylene)triphenylphosphorane in 74% yield.



a) 4 equiv. **1**, 1 equiv. **2**, MeOH, 5 % NaOMe, -e (electrolysis, Pt-anode)

Scheme 1

The synthesis of chiral vicinal diols by enantioselective dihydroxylation has been described for a variety of olefins;[2] however, to our knowledge this powerful conversion has not yet been applied to the synthesis of chiral *vic*-dihydroxy fatty acid esters. The enantioselective dihydroxylation of **3a**,**b** and of commercially available methyl *trans*-octadec-9-enoate **(3c)** led in excellent yield (85–97%) and satisfactory to high enantiomeric excess (ee 84–97%) to methyl *vic*-dihydroxystearates **4** (Scheme 2, Table 1). As reagents for the dihydroxylations commercially available AD-Mix-α and AD-Mix-β were used.[6]

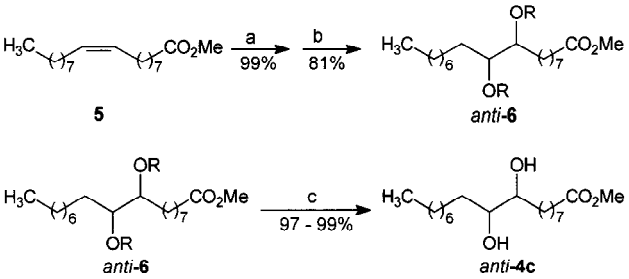


a) AD-mix-α / AD-mix-β, $MeSO_2NH_2$, H_2O, *t*-BuOH, 0 °C

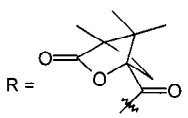
3/4	a	b	c
R1	H	$(CH_2)_{14}CH_3$	$(CH_2)_7CH_3$
R^2	Me	Et	Me
n	15	0	7

Scheme 2

In the case of methyl oleate **(5)** the enantiomeric excess of the dihydroxylation was very low, which has been reported before for the dihydroxylation of nearly symmetrical *cis*-olefins.[7] The synthesis of enantioenriched methyl *anti*-9,10-dihydroxystearates was then achieved by HPLC separation of the corresponding diastereoisomeric dicamphanyl esters *anti*-**6** (Scheme 3). For this purpose methyl oleate **(5)** was treated with OsO_4 to yield the methyl *anti*-9,10-dihydroxystearates (*anti*-**4c**).[8] The diastereoisomers *anti*-**6** were obtained by diesterification of *anti*-**4c** with (–)-camphanic acid chloride, as described by Mohr and Rosini,[9] followed by HPLC separation and partial hydrolysis to the methyl *anti*-9,10-dihydroxystearates (–)-(9*S*,10*S*)-**4c** and (+)-(9*R*,10*R*)-**4c** (Scheme 3, Table 2).



a) OsO_4, $K_3Fe(CN)_6$, K_2CO_3, H_2O, *t*-BuOH; b) RCl, pyridine;
c) 1. HLPC separation of the diastereoisomers, 2. KOH, MeOH



Scheme 3

To determine their enantiomeric purity, the dihydroxy esters **4a**, *syn*-**4b** and *anti*-**4c** were transformed into their diastereoisomeric carbamates **7** by refluxing them in toluene with (*S*)-1-phenylethyl isocyanate (Scheme 4). The crude

Table 1. Enantioenriched Methyl *vic*-Dihydroxystearates **4** Prepared by Enantioselective Dihydroxylation of Unsaturated Methyl Esters **3**

Methyl Octadecenoate	Reagent	*vic*-Dihydroxy Stearate	Yield (%)	$[\alpha]_D^{20}$	ee (%)	mp (°C)
3a	AD-Mix-α	(+)-(17*S*)-**4a**	90	+0.4 (*c* = 2, $CHCl_3$)	92[a]	88
3a	AD-Mix-β	(–)-(17*R*)-**4a**	90	–0.4 (*c* = 2, $CHCl_3$)	84[a]	88
3b	AD-Mix-α	(+)-(2*R*,3*S*)-**4b**	85	+8.0 (*c* = 2, $CHCl_3$)	95[a]	64
3b	AD-Mix-β	(–)-(2*S*,3*R*)-**4b**	85	–8.0 (*c* = 2, $CHCl_3$)	91[a]	64
3c	AD-Mix-α	(–)-(9*S*,10*S*)-**4c**	97	–21.3 (*c* = 1, MeOH)	95[b]	68–69
3c	AD-Mix-β	(+)-(9*R*,10*R*)-**4c**	95	+21.9 (*c* = 1, MeOH)	97[b]	68–69

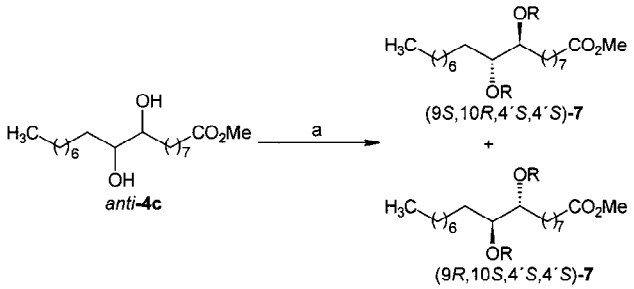
[a] By HPLC analysis of the corresponding diastereomeric carbamates **7** (Scheme 4) on a Merck LiChroSpher RP-18 ec column.
[b] By comparison with the specific rotation of (+)-(9*R*,10*R*)-**4c** $[\alpha]_D^{20}$ 22.5 (*c* = 1.2, MeOH) prepared from methyl ricinoleate.[10]

Table 2. Enantioenriched Methyl *vic*-Dihydroxystearates *anti*-**4c** Prepared by HPLC Separation of the Dicamphanic Esters *anti*-**6**

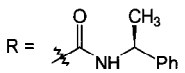
Methyl Dihydroxystearate	Yield[a] (%)	$[\alpha]_D^{20}$ [b]	ee[c] (%)	mp (°C)
(+)-(9*R*,10*S*)-**4c**	77	+0.7 (*c* = 1, MeOH)	80	106–107
(–)-(9*S*,10*R*)-**4c**	79	–0.9 (*c* = 1, MeOH)	99	106–107

[a] For three steps: **5** → *anti*-**4c**.
[b] Lit.[10]: (–)-(9*S*, 10*R*)-**4c**: –0.12 (*c* = 1.1, MeOH).
[c] By HPLC analysis of the corresponding diastereomeric carbamates **7** (Scheme 4) on a Knauer Nucleosil 100-3 column.

products were filtered over silica gel and the carbamates were separated by HPLC to determine their diastereoisomeric excess (Tables 1 and 2). The absolute configuration of the methyl 9,10-dihydroxystearates (–)-(9*S*,10*S*)-**4c** and (+)-(9*R*,10*R*)-**4c** were assigned by comparison of their specific optical rotations with the values reported by Morris and Crouchman.[10] They correspond to the configurations predicted by the mnemonic device proposed by Sharpless.[2] The absolute configuration of the methyl dihydroxystearates (+)-(17*S*)-**4a**, (–)-(17*R*)-**4a**, (+)-(2*R*,3*S*)-**4b** and (–)-(2*S*,3*R*)-**4b** were assigned applying this mnemonic device.



a) toluene, Δ, (1*S*)-1-phenylethylisocyanate



Scheme 4

In summary, unsaturated *trans*-fatty acid esters can be enantioselectively dihydroxylated to *vic*-dihydroxy esters in good yields and high enantiomeric excess by the Sharpless method.[2] The methyl *anti*-9,10-dihydroxystearates *anti*-**4c** have been prepared by HPLC separation of their diastereoisomeric dicamphanoyl esters *anti*-**6**. Results on the chiral discrimination of monolayers of (–)-(9*S*,10*S*)-**4c** and (+)-(9*R*,10*R*)-**4c** as determined by Brewster angle microscopy on the Langmuir trough and the formation of gels consisting of helical fibers as observed by atomic force microscopy are reported elsewhere.[11]

The solvents were purified and dried, if necessary. Analytical TLC: Merck aluminium foils covered with silica gel 60 F_{254}. Preparative column chromatography: Merck silica gel 60 (70–230 mesh). Analytical GLC: Hewlett–Packard 5890 series II with integrator HP 3396, HP 5 (25 m × 0.25 mm) or HP 1 (25 m × 0.31 mm) capillary columns, carrier gas: N_2. Optical rotations: Perkin–Elmer P 241 polarimeter. IR spectra: Bruker IFS 28 spectrophotometer. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) spectra: Bruker WM 300. MS: Varian Saturn II (Ion trap), Finnigan MAT 8230 with Varian GC 3400 (EI, 70 eV) or Finnigan MAT 312 (direct inlet). HPLC: Shimadzu LC-10-HPLC-system with Merck LiChroSpher RP-18 ec column, system of Knauer pump 64 with Knauer refractometer type 5178 and Knauer Nucleosil 100-5 (250 mm × 16 mm) or Nucleosil 100-3 (250 mm × 8 mm) columns.

Methyl Octadec-17-enoate (3a):
A solution of **1** (2.24 g, 12 mmol), **2** (553 mg, 3 mmol) and NaOMe (80 mg, 1.5 mmol) in MeOH (40 mL) was electrolyzed at 40–45 °C with a current density of 200 mA/cm^2 at platinum electrodes in an undivided cell.[5] To prevent passivation of the electrodes their polarity was reversed every 30 s. After current consumption of 1 F/mol the electrolysis was stopped, the cell was rinsed with MeOH (50 mL) and petroleum ether (50 mL). To the combined organic layers was added petroleum ether (100 mL) and they were then washed with 0.5 N HCl (4 × 50 mL), dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/Et_2O 30:1). Yield: 356 mg (40%); mp 25–27 °C; R_f 0.23 (petroleum ether/Et_2O 30:1).

Ethyl *trans*-Octadec-2-enoate (3b):
To a stirred solution of (ethoxycarbonylmethylene)triphenylphosphorane (5.57 g, 16 mmol) in toluene (150 mL) a solution of hexadecanal (3.12 g, 13 mmol) in toluene (20 mL) was added at 60 °C. The mixture

Table 3. Spectroscopic Data[a]

Compound	IR (KBr/film) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS (70eV) *m/z* (%)
3a	3078, 2925, 2854, 1744, 1640, 1466, 1437, 1364, 1171, 1114, 994, 909, 721	1.18–1.40 (m, 24H, H-4–H-15), 1.60 (m_c, 2H, H-16), 2.02 (m_c, 2H, H-3), 2.27 (t, ^3J = 7.6, 2H, H-2), 3.64 (s, 3H, OCH_3), 4.90 (ddt, $^3J_{cis}$ = 10.1, $^2J_{gem}$ = 2.2, $^4J_{allyl}$ = 1.2, 1H, H-18_a), 4.96 (ddt.$^3J_{trans}$ = 17.0, $^2J_{gem}$ = 2.2, $^4J_{allyl}$ = 1.4, 1H, H-18_b), 5.78 (ddt, $^3J_{cis}$ = 10.1, $^3J_{trans}$ = 17.0, ^3J = 6.7, 1H, H-17)	25.0 (C-3), 28.9, 29.1, 29.2, 29.5, 29.6 (C-4–C-15), 33.8, 34.1 (C-2, C-16), 51.4 (OCH_3), 114.1 (C-18), 139.2 (C-17), 174.3 (C-1)	296 (M^+, 10), 265 (M^+-CH_3O, 60), 264 (M^+-$HOCH_3$, 100), 235 (3), 222 (40), 180 (28), 152 (18), 111 (36), 97 (68), 87 (85), 83 (71), 74 (98), 69 (88), 55 (99), 43 (63), 41 (69)
3b	3075, 2916, 2853, 1724, 1655, 1466, 1437, 1367, 1309, 1179, 1127, 1046, 980, 721	0.86 (t, ^3J = 6.9, 3H, H-18), 1.18–1.35 (m_c, 26H, H-5–H-17), 1.43 (t, ^3J = 7.1, 3H, OCH_2CH_3), 2.16 (ddt, $^4J_{allyl}$ = 1.7, ^3J = 7.2, ^3J = 7.2, 2H, H-4), 4.16 (q, ^3J = 7.1, 2H, OCH_2CH_3), 5.78 (dt, $^3J_{trans}$ = 15.7, $^4J_{allyl}$ = 1.7, 1H, H-2), 6.94 (dt, ^3J = 6.9, $^3J_{trans}$ = 15.7, 1H, H-3) lit.[12]	14.1, 14.3 (OCH_2CH_3, C-18), 22.7, 28.0, 29.2, 32.0, 32.2 (C-4–C-17), 60.0 (OCH_2), 121.3 (C-2), 149.5 (C-3), 166.8 (C-1)	310 (M^+, 16), 265 (M^+-C_2H_5O, 28), 264 (M^+-C_2H_5OH, 34), 222 (18), 155 (20), 141 (14), 127 (25), 101 (61), 88 (46), 83 (34), 69 (36), 57 (52), 55 (80), 43 (100), 41 (60)
4a	3327, 2917, 2850, 1737, 1471, 1437, 1254, 1204, 1196, 1104, 719	1.15–1.36 (m, 24H, H-4–H-15), 1.42 (m_c, 2H, H-3), 1.60 (m_c, 2H, H-16), 2.28 (t, ^3J = 7.6, 2H, H-2), 1.95 (s_c, br, OH-17, OH-18), 3.41 (dd, ^3J = 7.5, $^2J_{gem}$ = 10.8, 1H, H-18_a), 3.64 (dd, ^3J = 3.1, $^2J_{gem}$ = 10.8, 1H, H-18_b), 3.65 (s, 3H, OCH_3), 3.70 (m_c, 1H, H-17)	24.1, 24.8 (C-3, C-15), 28.2, 28.3, 28.4, 28.7, 28.8, 28.9, 29.2, 29.4, 29.7 (C-4–C-14), 32.6, 33.1 (C-2, C-16), 50.3 (OCH_3), 65.9 (C-17), 71.3 (C-18), 173.1 (C-1)	[b]459 (M^+-CH_3, 5), 443 (M^+-OCH_3, 4), 371 (M^+-CH_2OSiMe_3, 100), 147 (26), 109 (12), 95 (20), 83 (22), 73 (58), 69 (24), 55 (28), 43 (16)
syn-**4b**	3387, 3204, 2920, 2848, 1737, 1716, 1463, 1398, 1293, 1113, 1034, 862, 724	0.86 (t, 3H, H-18), 1.16–1.30 (m, 26H, H-5–H-17), 1.35 (t, ^3J = 7.2, 3H, OCH_2CH_3), 1.58 (m_c, 2H, H-4), 1.98 (d_c, ^3J = 8.8, 1H, OH-3), 3.07 (d_c, ^3J = 5.5, 1H, OH-2), 3.85 (m_c, 1H, H-3), 4.05 (dd, ^3J = 5.5, ^3J = 2.2, 1H, H-2), 4.28 (q, ^3J = 7.2, 2H, $OCCH_2CH_3$)	14.1, 14.2 (C-18, OCH_2CH_3), 22.7 (C-17), 25.7, 25.8, 29.4, 29.6, 29.7 (C-5–C-15), 32.0 (C-16), 33.8 (C-4), 62.1 (OCH_2CH_3), 72.6, 73.1 (C-2, C-3), 173.3 (C-1)	[b]473 (M^+-CH_3, 10), 415 (M^+-$SiMe_3$, 5), 383 (5), 313 (60), 248 (100), 176 (5), 147 (18), 83 (6), 73 (40), 69 (3), 55 (4), 43 (3)
syn-**4c**	3404, 2917, 2847, 1739	0.85 (t, 3H, H-18), 1.15–1.63 (m, 26H, H-3–H-8, H-11–H-17), 2.07 (s_c, 1H, OH), 2.08 (s_c, 1H, OH), 2.27 (t, 2H, H-2), 3.36 (m_c, 2H, H-9–H-10), 3.64 (s, 3H, OCH_3)	14.1 (C-18), 22.7, 24.9, 25.6, 25.7, 29.0, 29.1, 29.3, 29.4, 29.6, 29.7, 31.9, 33.6, 33.7, 34.1 (C-2–C-8, C-11–C-17), 51.4 (OCH_3), 74.5 (C-9–C-10), 174.3 (C-1); in agreement with lit.[8]	[b]459 (M^+-CH_3, 4), 442 (6), 332 (20), 259 ($Me_3SiOC_8H_{15}CO_2Me^+$, 100), 215 ($C_9H_{18}OSiMe_3^+$, 62), 147 (10), 73 (20), 55 (10)
anti-**4c**	3277, 2916, 2849, 1736	0.86 (t, 3H, H-18), 1.20–1.65 (m, 26H, H-3–H-8, H-11–H-17), 1.75 (s_c, 2H, OH), 2.28 (t, 2H, H-2), 3.57 (m_c, 2H, H-9–H-10), 3.64 (s, 3H, OCH_3)	14.1 (C-18), 22.7, 24.9, 25.9, 26.0, 29.0, 29.1, 29.2, 29.4, 29.5, 29.7, 31.2, 31.3, 31.9, 34.1 (t, C-2–C-8, C-11–C-17), 51.5 (OCH_3), 74.7 (C-9–C-10), 175.9 (C-1); in agreement with lit.[8]	
anti-**6**[c]	2931, 2857, 1795, 1738, 1453, 1314, 1270, 1168, 1060, 1017, 992, 959, 932, 898, 739	0.85 (t, ^3J = 6.8, 3H, H-18), 0.92, 0.99, 1.05, 1.08 (s, 18H, H-8', H-9', H-10'), 1.20–1.40 (m, 20H, H-4–H-7, H-12–H-17), 1.50–1.62 (m, 8H, H-8, H-11, H-3, camph.-H), 1.81–2.08 (m, 4H, camph.-H), 2.29 (t, ^3J = 7.6, 2H, H-2), 2.31–2.45 (m, 2H, camph.-H), 3.64 (s, 3H, OCH_3), 5.07–5.12, 5.20–5.26 (m, 2H, H-9, H-10)	9.7, 14.1, 16.7 (C-18, C-8', C-9', C-10'), 22.7, 24.9, 25.5, 25.6, 28.5, 29.0, 29.2, 29.4, 29.5, 31.0, 31.8, 34.1, 51.5, 54.2, 54.4, 54.9, 55.0 (C-2–C-8, C-11–C-17, camph.-CH_2), 51.5 (OCH_3), 65.9 (camph.-CH_2), 75.2, 75.8 (C-9, C-10), 91.0, 91.2 (C-1'), 167.4, 174.2, 178.2, 178.3 (camph.-C=O, C-1)	691 (M^++H, 1), 659 (M^+-OCH_3, 2), 644 (1), 617 (1), 493 (10), 448 (10), 311 (8), 294 (10), 263 (8), 164 (12), 153 (30), 136 (50), 125 (40), 109 (80), 97 (50), 83 (100), 55 (60), 41 (30)
anti-**7**[c]	3335, 2924, 2852, 1734, 1685, 1528, 1466, 1248, 1075, 1029, 757, 699	0.87 (t, ^3J = 6.8, 3H, H-18), 1.09–1.61 (m, 32H, H-5', H-3–H-7, H-11–H-17), 2.27 (t, ^3J = 7.6, 2H, H-2), 3.58 (s, 3H, OCH_3), 4.47 (m_c, 6H, H-9, H-10, H-3', H-4'), 7.11–7.31 (m, 10H, H_{arom})	14.0 (C-18), 22.6, 24.8, 25.3, 29.0, 29.2, 29.4, 29.5, 31.8, 34.0 (C-2–C-8, C-11–C-17, C-5'), 50.5 (C-4'), 51.3 (OCH_3), 75.1 (C-9, C-10), 125.9, 127.1, 128.5, 145.0 (C_{arom}), 155.4 (C-2'), 174.2 (C-1)	624 (M^+, 1), 609 (M^+-CH_3, 1), 460 (20), 444 (8), 335 (6), 313 (4), 281 (6), 262 (2), 166 (40), 147 (40), 132 (82), 105 (100), 77 (40), 55 (20)

[a] Satisfactory elemental analyses were obtained for all new compounds except for **3a** (C: ± 0.06–0.30, H: ± 0.02–0.23, N: ± 0.15).
[b] MS spectra of the bistrimethylsilyl ether.
[c] The ^1H NMR, ^{13}C NMR and mass spectra of the mixture and the isolated two diastereoisomers are identical.

was refluxed for 4 h and then allowed to cool. After removal of the solvent and addition of petroleum ether (20 mL) the Ph_3PO was filtered off. The ether layer was evaporated in vacuum and the residue purified by flash chromatography (petroleum ether/Et_2O 30:1). Yield: 2.54 g (63%); mp 25–27 °C; R_f 0.26 (petroleum ether/Et_2O 30:1).

Enantioselective Dihydroxylation; General Procedure:[2]
A mixture of *t*-BuOH (5 mL), water (5 mL), AD-Mix-α or AD-Mix-β (1.4 g) and $MeSO_2NH_2$ (95 mg, 1 mmol) was stirred at r.t. until both phases were clear and then cooled to 0 °C. The unsaturated fatty ester **3 (**1 mmol) was added and, after stirring for 24 h at 0 °C, the reaction was quenched by addition of Na_2SO_3 (1.5 g, 12 mmol). The mixture was allowed to warm up and extracted with EtOAc (3 × 15 mL). The organic layer was washed with 2 N NaOH (15 mL), dried ($MgSO_4$) and evaporated in vacuo. The dihydroxy esters **4** were purified by flash chromatography (EtOAc/cyclohexane 5:2) (Table 1).

Preparation of Methyl (–)-(9*S*,10*R*)- and (+)-(9*R*,10*S*)-9,10-Dihydroxystearate [(–)-(9*S*,10*R*)-4c, (+)-(9*R*,10*S*)-4c]:
To a solution of *anti*-**4c** (388 mg, 1.17 mmol) in pyridine (10 mL) a solution of (–)-ω-camphanic acid chloride (1.3 g, 6.35 mmol) in CH_2Cl_2 (10 mL) was added at 0 °C. The mixture was allowed to warm up and stirred at r.t. for 15 h. After addition of 2 N HCl (50 mL) and water (30 mL) it was extracted with Et_2O (3 × 30 mL). The organic layer was washed with $NaHCO_3$ (30 mL), dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/Et_2O 1:1) to give *anti*-**6**. Yield: 660 mg (81%); R_f 0.35 (petroleum ether/Et_2O 1:1).

Part of *anti*-**6** was separated into the diastereoisomers (–)-(9*S*,10*R*,1′*S*,1′*S*)-**6** ($[a]_D^{20}$ –7.89 (*c* = 3.0, MeOH)) and (–)-(9*R*,10*S*,1′*S*,1′*S*)-**6** ($[a]_D^{20}$ –14.96 (*c* = 3.0, MeOH)) by HPLC (Knauer Nucleosil 100-5 column, cyclohexane/EtOAc, 6:1). The ^1H, ^{13}C NMR spectra and MS of the mixture of the two diastereoisomers and the separated diastereoisomers are identical and are given in Table 3. Solutions of (–)-(9*R*,10*S*,1′*S*,1′*S*)-**6** (132 mg, 0.92 mmol), KOH (260 mg, 4.64 mmol) in MeOH (10 mL) and of (9*S*,10*R*,1′*S*,4′R,1′*S*,4′*R*)-**6** (125 mg, 0.87 mmol), KOH (250 mg, 4.46 mmol) in MeOH (10 mL) were stirred for 30 min at r.t. After addition of water (10 mL) the mixtures were neutralized with 2 N HCl and extracted with Et_2O (3 × 10 mL). The organic layers were washed with $NaHCO_3$ (10 mL), dried ($MgSO_4$) and evaporated to yield (+)-**4c** and (–)-**4c** (Table 2). For the synthesis of (+)-**4c** and (–)-**4c** from methyl ricinoleate see lit.[10]

Preparation of the Carbamates 7; General Procedure:
A solution of the dihydroxy ester **4** (1 mmol) and (*S*)-1-phenylethyl isocyanate (0.28 mL, 2 mmol) in toluene (5 mL) was refluxed for 48 h. After evaporation in vacuo the product was filtered over silica gel (Et_2O) and the filtrate was concentrated in vacuo. By HPLC analysis of the diastereoisomeric carbamates **7** the enantiomeric excess of the dihydroxy esters **4** was determined (Tables 1 and 2).

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