Synthesis and Anionically Induced Domino Reactions of Chiral α-Bromo α,β-Unsaturated Esters☆

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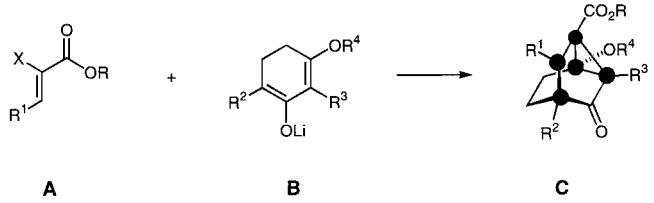
The chiral α-bromo α,β-unsaturated esters **3** and **9** are prepared by asymmetric Sharpless dihydroxylation (AD) of **5** and from ester **7** and the chiral diols **8** by transacetalization, respectively. Both types of α-bromo α,β-unsaturated ester react with the kinetic lithium dienolates of enone **10** to give functionalized tricyclo[3.2.1.0^{2,7}]octanes **11**. Esters **3** give one single diastereomer (*de* ≥ 95%), whereas mixtures of diastereomers (*de* 28 to 46%) are obtained with the esters **9**.

Domino reactions[1] are very efficient in the construction of complex carbon skeletons, especially for the synthesis of natural products and their analogues. Of particular interest are anionically-induced domino reactions starting with a Michael-type addition[2] of lithium dienolate **B** to an α-bromo α,β-unsaturated ester **A** under aprotic conditions.[3] This leads, after a second intramolecular Michael addition and subsequent γ-elimination, directly to tricyclo-[3.2.1.0^{2,7}]octanes **C** (Scheme 1):

Scheme 1



A **B** **C**

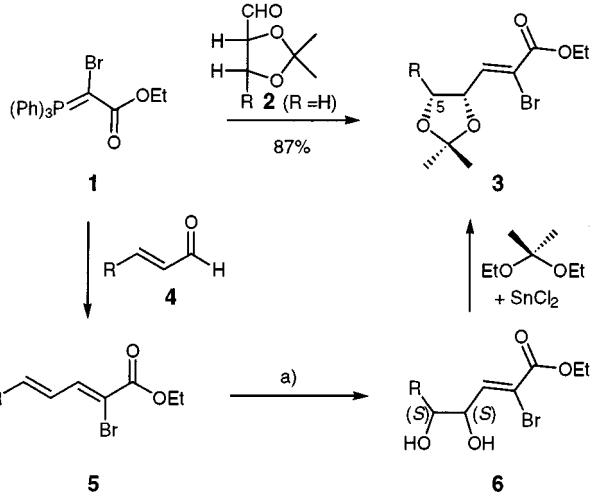
Three C−C bonds are formed and up to five quaternary centers are created in a single chemical operation.[4] We set out to achieve stereochemical control at the new centers using chiral α-bromo α,β-unsaturated esters as Michael acceptors. These esters can be conveniently prepared by Wittig or Horner-Emmons reactions.[5]

Synthesis of Chiral α-*Bromo* α,β-*Unsaturated Esters:*

(a) Esters of Type **3**: Both the chiral (*Z*)-α-bromo α,β-unsaturated ester **3a**[6] and the prochiral α-bromo α,β,γ,δ-unsaturated esters **5** are available by Wittig olefination from (ethoxycarbonyl)bromomethylene-triphenylphosphorane (**1**)[7] and the appropriate aldehydes **2** (R = H, derived from D-mannitol) and **4**, respectively (Scheme 2).

[*] The term "domino reaction" instead of "tandem" or "cascade reactions" may be used for sequential reactions in one pot.

Scheme 2



a) AD-mix α/H_2O/*tert*-butyl alcohol (1+1)/CH_3 SO_2NH_2/room temp.

3,**4**,**5**,**6**	R	**6** *ee* (yield)
a	H	–
b	Me	94% (73%)
c	Ph	99% (90%)

The geometries of the α,β-bonds [(*Z*)/(*E*)] in **3** and **6** were determined by measuring the $^3J(^{13}C,^1H)$ coupling constants (carbonyl-C and β-H), typical values for which are around 4.8 Hz for (*Z*)- and up to 12 Hz for (*E*)-diastereomers (see also Table 3).[8] Similar compounds such as **2** (R ≠ H) are not available in the chiral pool, but can be made by Sharpless asymmetric dihydroxylation ("AD")[9] from the corresponding prochiral (*Z*)-α-bromodienecarboxylates **5**. The diols **6** are transformed (yield: 70−90%) into the dioxolanes

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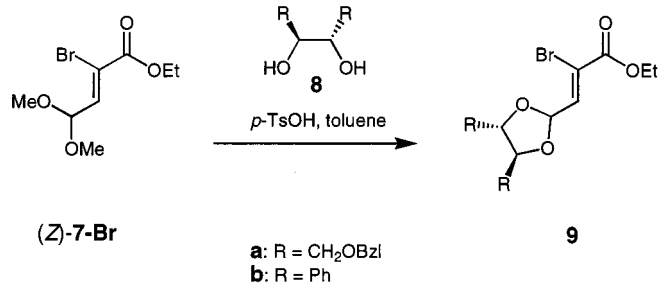
3 by treatment with 2,2-diethoxypropane in glyme in the presence of a Lewis acid ($SnCl_2$). This reaction sequence is useful for the generation of the 5-substituted α-bromo α,β-unsaturated esters **3b**,**c**, but it was not possible to prepare the ester **3a** by this Sharpless oxidation because of the rapid polymerization of the bromopentadienoate **5a**. The enantiomeric excesses of the diols **6b**,**c** obtained using AD-mix α (*ee* > 94%) were determined by HPLC on a chiral column (CHIRALCEL OD, Daicel) using racemic mixtures as references. The oxidation takes place very regioselectively at the γ,δ-double bond of the esters **5**; no oxidation of the electron-poor $\Delta^{2,3}$ double bond was observed.[10] The absolute stereochemistries of the hydroxylated products (face selectivity of the AD-mix α or β, respectively) were predicted with the "mnemonic device" suggested by Sharpless[11] and later proven by the subsequent transformations leading to the crystalline tricyclic compound **11c**-OMe[12].

(b) Esters of Type **9**: Acid-catalyzed (*p*-toluenesulfonic acid) transacetalization of (*Z*)-**7** (Wittig olefination: bromophosphorane **1** and 2,2-dimethoxyethanal) with the chiral diols **8a** and **8b** in boiling toluene gave the α-bromo esters **9** in good yields (81−87%) (Scheme 3).

Scheme 3



The corresponding (*Z*)/(*E*)-**7**-Cl, -I, however, were obtained by a "one-pot" Horner-Emmons olefination/halogenation sequence. The diol **8a** was prepared via an established route from L-tartaric acid [13] and diol **8b** by Sharpless dihydroxylation of *trans*-stilbene[14] with AD-mix α. The synthesis of the pure methyl ester (*E*)-**9a** was achieved similarly, starting from methyl ester (*E*)-**7**[15] (obtained from 2,5-dihydro-5-methoxy-2-furanone).

Domino Reaction of Esters **3** *and* **9** *with Lithium Dienolates* Li-**10**: The reaction of esters **3** and **9** with the dienolates Li-**10** generated under kinetic control (from the corresponding enones **10** using LDA) gives functionalized tricyclo[3.2.1.$0^{2,7}$]octanes **11** with a central "push-pull" substituted cyclopropane[16] moiety, which permits further simple modifications (e.g. retro aldol reaction to form bicyclo[3.2.1]octanes[17]). The chiral (*Z*)-ester **3a** reacts with high diastereoselectivity (*de* ≥ 95%) to afford enantiopure tricyclo[3.2.1.$0^{2,7}$]octane **11a**-Me.[18] The homologous esters **3b** and **3c** behave similarly and form with the dienolate Li-**10** single adducts **11b**, **c** (Scheme 4, Table 1).

Esters of type **9**, however, give a different picture: In all cases, upon reaction with the dienolate Li-**10** (R = Bzl), we obtained mixtures of the diastereomeric tricycles **11**/**11′** (Scheme 4, Table 2).

Table 2. Diastereomeric excesses (*de*) and yields of **11** from esters (*Z*)-**9a**,**b**

	ester **9a**	ester **9b**
Li-**10**; R = OBzl	**11d/11′d**, *de* ≥ 28% (62%)	**11e/11′e**, *de* ≥ 46% (40%)

This result indicates that the stereogenic center adjacent to the β-carbon of the acceptor plays an important role in determining the diastereoselectivity of the first step (Michael addition, *ul*-diastereoface selection[19]) of this anionically-induced domino reaction. Clearly, the additional (*S*)-configured stereogenic center at C-5 of the di-

Scheme 4

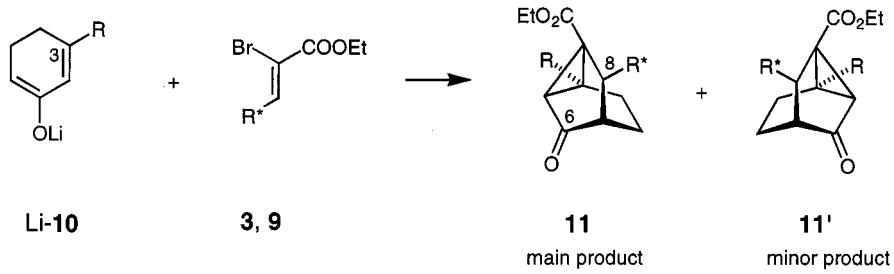


Table 1. Diastereomeric excesses (*de*) and yields of **11** from esters (*Z*)-**3a−c** (*these combinations were not investigated

	ester **3a**	ester **3b**	ester **3c**
Li-**10**; R = Me	**11a**-Me, *de* ≥ 95% (68%)	− *	**11c**-Me, *de* ≥ 95% (59%)
Li-**10**; R = OMe	− *	**11b**-OMe, *de* ≥ 95% (48%)	**11c**-OMe, *de* ≥ 95% (29%)

oxolane moiety in the Michael acceptor **3b**,**c** does not influence the course of the initial diastereoselection. It seems that in the reaction of ester (*Z*)-**3c** with different dienolates Li-**10**, the yields depend to some extent on the steric demand of the group R at C-3 of enone **10**: the ester (*Z*)-**3c** did not react with Li-**10-**OBzl, but upon reaction with Li-**10-**OMe gave the adduct **11c-**OMe (29%).

Determination of the absolute configurations of the tricyclo[3.2.1.$0^{2,7}$]octanes **11** and **11′** was possible by comparing their CD spectra with that of the known[20] *tert*-butyl (1*S*,2*R*,5*S*,7*S*,8*R*,4′*S*)-2-benzyloxy-8-(2′,2′-dimethyl-1,3-dioxolan-4′-yl)-6-oxotricyclo[3.2.1.$0^{2,7}$]octane-1-carboxylate, which shows a positive Cotton effect (similar size) as **11**, in contrast to **11′**, which has a negative Cotton effect (n → π* at approx. λ_{max} = 287 nm). This interpretation is strongly supported by the X-ray structure of **11c-**OMe.[12]

The relative stereochemistry at C-8 (*anti* position of R* and keto group at C-6) of the tricycles **11d**, **e** and **11′d**, **e** was deduced by ^{1}H-NMR analysis [long-range coupling (^4J = 1.4 to 1.7 Hz) between 4-H and 8-H] and was supported by MM2[21] calculations. There is no such coupling in the 8-*epi* series, e.g. in the methyl ester of 8-*epi*-**11d/11d′**.

The chiral induction is remarkably high (*de* > 95%) in the above anionic domino reaction with the acceptors of type (*Z*)-**3**. With the esters (*Z*)-**9**, however, the chiral induction in the tricyclo[3.2.1.$0^{2,7}$]octanes **11** is disappointingly low (*de* 28 to 46%). Unfortunately,[22] this was also observed with the methyl ester (*E*)-**9a**. Its reaction with the dienolate Li-**10**; R = OBzl also gave a diastereomeric mixture of methyl esters of 8-*epi*-**11d/11′d** (*de* 38%). As yet, we have not been able to achieve chromatographic separation of the diastereomeric pairs **11d/11′d**, **11e/11′e,** and 8-*epi*-**11d/11′d** on a preparative scale, although the pairs **11d/11′d**, **11e/11′e** could be separated on an analytical chiral HPLC column (CHIRALCEL OD, eluent *n*-hexane/2-propanol).

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Experimental Section

THF was dried over benzophenone/sodium and distilled prior to use. − ^{1}H- and ^{13}C-NMR spectra: Bruker WM-250 (all spectra were recorded at 250 and 62.89 MHz, unless otherwise stated), or on a Varian Unity INOVA-300 instrument at 300 and 75.42 MHz, respectively; the ^{1}H-coupled ^{13}C-NMR spectra were measured using the "gated decoupling method" at 75.48 MHz (ARX-300) with a digital resolution of 0.4 Hz. − IR: Philips infrared spectrophotometer PU9516. − UV/Vis: Hewlett-Packard 8452A diode-array spectrophotometer. − MS: Varian MAT 311 A, EI, 70 eV, low and high resolution. − Polarimetry: Perkin-Elmer polarimeter 241. − CD: Jasco spectropolarimeter J-500A. − GC: GC 8000 Series, Fisons Instruments, fused silica capillary column: DB 1, 10 m, methylsilicon rubber, nitrogen as carrier gas. − Melting points (not corrected): Büchi SMP-20. − TLC: DC aluminum foil, silica gel 60 F_{254}, Merck, Darmstadt. − Column chromatography: silica gel 60, 0.063−0.200 mm (70−220 mesh ASTM), Merck, Darmstadt. − Short-path distillation: Kugelrohr GKR-50, Fa. Büchi, Buchs, Switzerland; temperatures are path temperatures. − Elemental analyses: Mikroanalytisches Laboratorium, Universität Stuttgart.

(+)-Ethyl (Z)-2-Bromo-3-[(4S,5S)-2,2,5-trimethyl-1,3-dioxolan-4-yl]-2-propenoate (**3b**): To a solution of 1.39 g (5.5 mmol) of diol (+)-**6b** in 10 ml of 1,2-dimethoxyethane was added 0.80 g (6.05 mmol) of 2,2-diethoxypropane and 30 mg of anhydrous $SnCl_2$ and the mixture was refluxed for 1.5 h. Then, 60 µl pyridine was added, the solvents were distilled off, and the remaining oil was chromatographed on silica gel (eluent: diethyl ether/petroleum ether, 1:1). Concentration of the eluate gave an oil, which was distilled. Yield: 1.15 g (71%), colorless liquid, b.p. 85°C/0.006 Torr (kugelrohr). − IR (film): ν = 2990 cm^{-1}, 2940, 2910 (CH), 1725 (C=O), 1635 (C=C), 1590, 1450, 1385, 1375, 1265, 1240, 1180, 1100, 1040, 980, 940, 865, 815, 760. − UV/Vis (methanol): λ_{max} (lg ε) = 209 nm (3.737), 239 (3.882), 277 (3.731). − ^{1}H NMR ($CDCl_3$): δ = 1.35 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.38 (d, *J* = 6.1 Hz, 3 H, 6-H), 1.44 and 1.46 [s, each 3 H, $C(CH_3)_2$], 3.97 (dq, *J* = 6.1 Hz, 8.2 Hz, 1 H, 5-H), 4.30 (dq, *J* = 1.0 Hz, 7.1 Hz, 2 H, OCH_2CH_3), 4.53 (dd, $J_1 = J_2$ = 8.2 Hz, 1 H, 4-H), 7.22 (d, *J* = 8.2 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 13.99 (q, OCH_2CH_3), 17.31 (q, C-6), 26.56 and 27.18 [q, $C(CH_3)_2$], 62.75 (t, OCH_2CH_3), 76.23 (d, C-5), 81.16 (d, C-4), 109.72 [s, $C(CH_3)_2$], 118.44 (s, C-2), 141.51 (d, C-3), 161.62 (s, C-1). − GC-MS (70 eV); *m/z* (%): 293/295 (0.1) [M^+ + H], 292/294 (0.05) [M^+], 277/279 (81) [$M^+ - CH_3$], 248/250 (63), 235/237 (84), 190/192 (90), 162/164 (100), 139 (70), 117 (80), 97 (63), 82 (83), 59 (91). − $[\alpha]_D^{24}$= +5.1 (*c* = 0.76 in $CHCl_3$). − HRMS: calcd. 277.0075 [$M^+ - CH_3$] ≡ [$C_{10}H_{14}O_4{}^{79}Br$]; found 277.0069.

(+)-(Z)-Ethyl 2-Bromo-3-[(4S,5S)-(2,2-dimethyl-5-phenyl-1,3-dioxolan-4-yl]-2-propenoate (**3c**): Prepared as described above from 1.73 g (5.5 mmol) of (−)-**6c** in 10 ml of 1,2-dimethoxyethane, 0.80 g (6.05 mmol) of 2,2-diethoxypropane, and 30 mg of anhydrous $SnCl_2$. Yield: 1.83 g (94%) of a pale-yellow liquid; b.p. 165°C/0.05 Torr (kugelrohr). This compound underwent decomposition on standing. − IR (film): ν = 3040 cm^{-1}, 2990, 2940 (CH), 1730 (C=O), 1630 (C=C), 1500, 1455, 1375, 1260, 1235, 1170, 1095, 1070, 1055, 910, 870, 820, 755 (C_6H_5), 710 (C_6H_5). − UV/Vis (methanol): λ_{max} (lg ε) = 208 nm (4.098), 236 (3.898), 324 (3.954). − ^{1}H NMR ($CDCl_3$): δ = 1.33 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.56 and 1.61 [s, each 3 H, $C(CH_3)_2$], 4.28 (q, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 4.73−4.83 (m, 2 H, 4-H and 5-H), 7.30−7.39 (m, 6 H, 3-H and C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 14.03 (q, OCH_2CH_3), 26.84 and 26.98 [q, $C(CH_3)_2$], 62.82 (t, OCH_2CH_3), 81.92 (d, C-4 and C-5), 110.54 [s, $C(CH_3)_2$], 119.46 (s, C-2), 126.53, 128.53 and 128.58 (d, C_6H_5), 136.13 (s, C_6H_5), 140.23 (d, C-3), 161.69 (s, C-1). − MS (70 eV) *m/z* (%): 339/341 (5) [$M^+ - CH_3$], 297/299 (11), 280/282 (5), 248/250 (63), 190/192 (73), 162/164 (87), 139 (45), 129 (37), 115 (41), 105 (60) [$C_7H_5O^+$], 91 (60) [$C_7H_7^+$], 79 (28) [Br^+], 77 (65) [$C_6H_5^+$], 43 (100) [$C_3H_7^+$], 29 (91) [$C_2H_5^+$]. − $[\alpha]_D^{24}$= +8.3 (*c* = 1.65 in $CHCl_3$). − HRMS: calcd. 339.0232 [$M^+ - CH_3$] ≡ [$C_{15}H_{16}O_4{}^{79}Br$]; found 339.0243.

Ethyl 2-Bromo-2,4-pentadienoate (**5a**): To a solution of 10.68 g (25 mmol) of (ethoxycarbonyl)bromomethylenetriphenylphosphorane (**1**) in 80 ml of dichloromethane, 1.40 g (25 mmol) of propenal (**4a**) was added at room temp. and the mixture was stirred for 12 h. The solvent was then removed by distillation, and the remaining partially polymerized product was chromatographed on silica gel (eluent: diethyl ether/petroleum ether, 2:1) to give 0.79 g (15%) of

5a in the form of a liquid, as an 89:11 (*Z*)/(*E*) mixture (GC), which was distilled (kugelrohr); b.p. 80°C/0.04 Torr. **5a** polymerizes very rapidly on standing. − (*Z*)/(*E*): IR (film): ν̃ = 2990 cm^{-1}, 2940, 2910 (CH), 1725 (C=O), 1620 (C=C), 1580 (C=C), 1450, 1420, 1395, 1370, 1250, 1180, 1100, 1050, 1000, 940, 825, 770. − UV/Vis (methanol): λ_{max} (lg ε) = 207 nm (3.520), 267 (3.706). − HRMS: calcd. $C_7H_9O_2{}^{79}Br$: 203.9786; found 203.9779. − (*Z*)-**5a**: ^1H NMR ($CDCl_3$): δ = 1.35 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 4.30 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 5.68 (ddd, *J* = 0.8 Hz, 1.5 Hz, 10.3 Hz, 1 H, 5-H_{cis}), 5.79 (ddd, *J* = 0.8 Hz, 1.5 Hz, 17.0 Hz, 1 H, 5-H_{trans}), 6.76 (ddd, $J_1 = J_2$ = 10.3 Hz, J_3 = 17.0 Hz, 1 H, 4-H), 7.66 (ddd, *J* = 0.8 Hz, 10.3 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 14.09 (q, OCH_2CH_3), 62.44 (t, OCH_2CH_3), 115.40 (s, C-2), 127.76 (t, C-5), 133.82 (d, C-4), 141.01 (d, C-3), 161.10 (s, C-1). − $^3J(^{13}C,^1H)$: 4.5 Hz. − GC-MS (70 eV); *m/z* (%): 204/206 (60) [M^+], 176/178 (81) [$M^+ - C_2H_4$], 159/161 (43) [$M^+ - C_2H_5O$], 131/133 (52), 125 (25) [M^+ − Br], 119/121 (4), 105/107 (8), 97 (100), 79 (35) [Br^+], 69 (20).

(*E*)-**5a**: GC-MS (70 eV); *m/z* (%): 204/206 (19) [M^+], 176/178 (55) [$M^+ - C_2H_4$], 159/161 (10) [$M^+ - C_2H_5O$], 131/133 (15), 119/121 (5), 105/107 (2), 97 (100), 79 (11) [Br^+], 69 (10).

Ethyl 2-Bromo-2,4-hexadienoate (**5b**): Prepared as described above from a solution of 10.68 g (25 mmol) phosphorane **1** in 80 ml dichloromethane and 1.75 g (25 mmol) of (*E*)-butenal (**4b**). Yield: 3.67 g (67%) of **5b**[23] after distillation, b.p. 85°C/0.05 Torr (kugelrohr), colorless oil, (2*Z*,4*E*):(2*E*,4*E*) = 89:11 (GC). − IR (film): ν̃ = 2990 cm^{-1}, 2940, 2910 (CH), 1720 (C=O), 1635 (C=C), 1590 (C=C), 1450, 1395, 1370, 1315, 1265, 1235, 1170, 1100, 1050, 980, 935, 825, 760. − ^1H NMR ($CDCl_3$): δ = 1.34 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.91 (dd, *J* = 6.6 Hz, 1.4 Hz, 3 H, 6-H), 4.28 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 6.34 (dq, *J* = 6.6 Hz, 15.2 Hz, 1 H, 5-H), 6.50 (ddq, *J* = 1.4 Hz, 10.3 Hz, 15.2 Hz, 1 H, 4-H), 7.32 (d, *J* = 10.3 Hz, 1 H, 3-H).

Ethyl 2-Bromo-5-phenyl-2,4-pentadienoate (**5c**): Prepared as described for **5a** from a solution of 10.68 g (25 mmol) of **1** and 3.30 g (25 mmol) of (2*E*)-3-phenyl-2-propenal (**4c**) in 80 ml of ethanol at room temp. Yield: 6.16 g (88%) after distillation (kugelrohr, 150°C/0.005 Torr), white crystals, m.p. 41−43°C, (2*Z*,4*E*):(2*E*,4*E*) = 9:1 (GC). − IR (KBr): ν̃ = 3060 cm^{-1}, 3030, 2980, 2880 (CH), 1710 (C=O), 1610 (C=C), 1580 (C=C), 1270, 1230, 750 (C_6H_5), 700 (C_6H_5). − UV/Vis (methanol): λ_{max} (lg ε) = 206 nm (4.169), 234 (3.951), 324 (4.523). − ^1H NMR ($CDCl_3$): δ = 1.35 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 4.30 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 7.03 (d, *J* = 15.6 Hz, 1 H, 5-H), 7.16 (dd, *J* = 10.0 Hz, 15.6 Hz, 1 H, 4-H), 7.29−7.53 (m, 5 H, C_6H_5), 7.81 (d, *J* = 10.0 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 14.14 (q, OCH_2CH_3), 62.33 (t, OCH_2CH_3), 114.35 (s, C-2), 125.23, 127.49 and 128.82 (d, C_6H_5), 129.50 (d, C-5), 135.86 (s, C_6H_5), 141.08 (d, C-4), 142.60 (d, C-3), 162.90 (s, C-1). − $C_{13}H_{13}O_2Br$ (281.15): calcd. C 55.54, H 4.66, Br 28.42; found C 56.13, H 4.80, Br 28.12.

(+)-Ethyl (Z)-(4S,5S)-2-Bromo-4,5-dihydroxy-2-hexenoate [(+)-**6b**]: To a stirred two-phase solution of 5.60 g AD-mix α (Aldrich) in a mixture of 20 ml of *tert*-butanol and 20 ml of water, 0.38 g (4 mmol) of methanesulfonamide, and 0.88 g (4 mmol) of ethyl ester **5b** were added at room temp. After stirring for 16 h, 6 g of sodium sulfite was added and stirring was continued for a further 45 min. The organic phase was separated and the aqueous phase was extracted with dichloromethane (3 × 30 ml). The combined organic phases were washed with 10 ml of 2 M potassium hydroxide solution, dried ($MgSO_4$), filtered through silica gel (30 g), and eluted with diethyl ether/petroleum ether (3:1). Evaporation of the solvents gave 0.74 g (73%) of (+)-**6b** as a colorless, viscous oil. − IR (film): ν̃ = 3400 cm^{-1} (OH), 2980, 2940, 2910 (CH), 1720 (C=O), 1630 (C=C), 1450, 1395, 1375, 1270, 1235, 1140, 1040, 1005, 930, 905, 875, 765. − UV/Vis (methanol): λ_{max} (lg ε) = 212 nm (3.627), 236 (3.788). − ^1H NMR ($CDCl_3$): δ = 1.25 (d, *J* = 6.4 Hz, 3 H, 6-H), 1.34 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 2.78 (d, *J* = 3.4 Hz, 1 H, OH), 3.17 (d, *J* = 4.3 Hz, 1 H, OH), 3.85 (m, 1 H, 5-H), 4.30 (qd, *J* = 0.8 Hz, 7.1 Hz, 2 H, OCH_2CH_3), 4.39 (m, 1 H, 4-H), 7.25 (d, *J* = 8.3 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 14.02 (q, OCH_2CH_3), 18.89 (q, C-6), 62.89 (t, OCH_2CH_3), 69.77 (d, C-5), 75.61 (d, C-4), 117.97 (s, C-2), 143.50 (d, C-3), 163.23 (s, C-1). − $^3J(^{13}C,^1H)$: 4.7 Hz. − MS (70 eV) *m/z* (%): 253/255 (1) [M^+ + H], 208/210 (28) [$M^+ + H - C_2H_5O$], 179/181 (21) [$M^+ - C_3H_5O_2$], 162/164 (33), 151 (28), 135 (13), 105 (12), 83 (15), 71 (16), 55 (36), 45 (100) [$C_2H_5O^+$]. − $[\alpha]_D^{24}$ = +3.0 (*c* = 1.13 in $CHCl_3$). − *ee*: ≥ 94% (HPLC: CHIRALCEL OD, eluent: *n*-hexane:2-propanol, 95:5, flow rate: 0.5 ml/min., λ = 254 nm). − HRMS: calcd. 207.9735 [$M^+ + H - C_2H_5O$] ≡ [$C_6H_9O_3{}^{79}Br$]; found 207.9740. − $C_8H_{13}O_4Br$ (253.09): calcd. C 37.97, H 5.18, Br 31.57; found C 38.58, H 5.21, Br 31.98.

(−)-Ethyl (Z)-(4R,5R)-2-Bromo-4,5-dihydroxy-2-hexenoate [(−)-**6b**]: Prepared analogously using AD-mix β. Yield: 0.43 g (43%), viscous oil. − $[\alpha]_D^{24}$ = −1.3 (*c* = 1.07 in $CHCl_3$). − *ee*: ≥ 16%.

(−)-Ethyl (Z)-(4S,5S)-2-Bromo-4,5-dihydroxy-5-phenyl-2-pentenoate [(−)-**6c**]: Prepared as described above from 5.60 g of AD-mix α (Aldrich) in a mixture of 20 ml of *tert*-butanol and 20 ml of water, 0.38 g (4 mmol) of methanesulfonamide, and 1.12 g (4 mmol) of 2-bromopentadienoate **5c** at room temp. Yield: 1.17 g (90%), white needles, m.p. 115−117°C (diethyl ether/petroleum ether). − IR (KBr): ν̃ = 3420 cm^{-1} (OH), 3300 (OH), 3090, 3060, 3050, 3030, 2990, 2930, 2910 (CH), 1720 (C=O), 1630 (C=C), 1500, 1475, 1450, 1370, 1340, 1270, 1250, 1220, 1185, 1100, 1080, 1030, 995, 900, 885, 835, 785, 765, 745, 725, 705. − UV/Vis (methanol): λ_{max} (lg ε) = 210 nm (4.032), 236 (3.897), 322 (3.115). − ^1H NMR ($CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 2.84 (d, *J* = 4.8 Hz, 1 H, OH), 2.97 (d, *J* = 4.8 Hz, 1 H, OH), 4.25 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 4.68 (ddd, J_1 = 7.9 Hz, $J_2 = J_3$ = 4.8 Hz, 1 H, 4-H), 4.77 (dd, $J_1 = J_2$ = 4.8 Hz, 1 H, 5-H), 7.32 (d, *J* = 7.9 Hz, 1 H, 3-H), 7.32−7.39 (m, 5 H, C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 14.03 (q, OCH_2CH_3), 62.85 (t, OCH_2CH_3), 75.56 and 75.60 (d, C-4, C-5), 117.85 (s, C-2), 126.46, 128.26 and 128.48 (d, C_6H_5), 139.47 (s, C_6H_5), 143.16 (d, C-3), 161.90 (s, C-1). − $^3J(^{13}C,^1H)$: 4.8 Hz. − MS (70 eV) *m/z* (%): 280/282 (12) [M^+ − 2OH], 251/253 (6), 208/210 (70), 162/164 (27), 129 (50), 107 (100), 79 (93), 77 (77) [$C_6H_5{}^+$]. − $[\alpha]_D^{24}$ = −16.2 (*c* = 0.61 in $CHCl_3$). − *ee*: ≥ 99% (HPLC: CHIRALCEL OD, eluent: *n*-hexane:2-propanol, 9:1, flow rate: 0.5 ml/min., λ = 254 nm). − $C_{13}H_{15}O_4Br$ (315.16): calcd. C 49.54, H 4.80, Br 25.35; found C 49.53, H 4.81, Br 25.19.

(+)-Ethyl (Z)-(4R,5R)-2-Bromo-4,5-dihydroxy-5-phenyl-2-pentenoate [(+)-**6c**]: Prepared analogously using AD-mix β (Aldrich). Yield: 1.15 g (89%), white needles, m.p. 115−117°C (diethyl ether/petroleum ether). − $[\alpha]_D^{24}$ = +17.2 (*c* = 0.70 in $CHCl_3$). − *ee*: ≥ 99%.

Ethyl (Z)/(E)-2-Chloro-4,4-dimethoxy-2-butenoate (**7**-Cl): Prepared analogously to a published procedure[5] from 6.72 g (30 mmol) of triethyl phosphonoacetate, 1.44 g (60 mmol) of NaH in 80 ml THF, 4.01 g (30 mmol) of *N*-chlorosuccinimide, and 6.95 g (30 mmol) of a 45% solution of 1,1-dimethoxyethanal in *tert*-butyl methyl ether at 25°C. Yield: 4.45 g (85.4%), pale-yellow liquid, b.p. 135°C, 15 Torr (kugelrohr), (*Z*)/(*E*): 66:34 (GC). − IR (film): ν̃ = 1730 cm^{-1} (C=O), 1640 (C=C). − HRMS: calcd. 177.0319 [$M^+ - OCH_3$] ≡ [$C_7H_{10}O_3{}^{35}Cl$]; found 177.0320. − (*Z*)-**7**-Cl: ^1H NMR

($CDCl_3$): δ = 1.34 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 3.41 (s, 6 H, OCH_3), 4.30 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 5.25 (d, *J* = 6.7 Hz, 1 H, 4-H), 6.98 (d, *J* = 6.7 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 13.97 (q, OCH_2CH_3), 53.49 (q, OCH_3), 62.64 (t, OCH_2CH_3), 100.01 (d, C-4), 127.44 (s, C-2), 135.99 (d, C-3), 161.73 (s, C-1). − (*E*)-**7**-Cl: ^1H NMR ($CDCl_3$): δ = 1.36 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 3.39 (s, 6 H, OCH_3), 4.31 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 5.56 (d, *J* = 6.9 Hz, 1 H, 4-H), 6.34 (d, *J* = 6.9 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 13.91 (q, OCH_2CH_3), 53.49 (q, OCH_3), 62.40 (t, OCH_2CH_3), 99.09 (d, C-4), 126.38 (s, C-2), 137.77 (d, C-3), 161.88 (s, C-1).

Ethyl (Z)-2-Bromo-4,4-dimethoxy-2-butenoate (**7**-Br): Prepared as described for **5** from 12.81 g (30 mmol) of **1** in 180 ml of dichloromethane and 6.95 g (30 mmol) of a 45% solution of 1,1-dimethoxyethanal in *tert*-butyl methyl ether at room temp. The solvents were distilled off after 24 h, the residue was redissolved in 50 ml of diethyl ether and chromatographed on silica gel (eluent: diethyl ether/petroleum ether, 1:1). Yield: 6.57 g (87%), liquid, b.p. 145°C/15 Torr (kugelrohr), (*Z*)/(*E*): 90:10 (GC). Horner-Emmons reaction in THF with 5.34 g (30 mmol) of *N*-bromosuccinimide gave **7**-Br as a 71:29 (*Z*)/(*E*) mixture (GC) in 87% yield (see procedure for **7**-Cl). − IR (film): ν = 1730 cm^{-1} (C=O), 1635 (C=C). − HRMS: calcd. 220.9813 [$M^+ - OCH_3$] ≡ [$C_7H_{10}O_3{}^{79}Br$]; found 220.9815. − (*Z*)-**7**-Br: ^1H NMR ($CDCl_3$): δ = 1.34 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 3.41 (s, 6 H, OCH_3), 4.30 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 5.18 (d, *J* = 6.5 Hz, 1 H, 4-H), 7.23 (d, *J* = 6.5 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 13.90 (q, OCH_2CH_3), 53.42 (q, OCH_3), 62.73 (t, OCH_2CH_3), 101.93 (d, C-4), 118.59 (s, C-2), 139.65 (d, C-3), 161.64 (s, C-1). − (*E*)-**7**-Br: ^1H NMR ($CDCl_3$): δ = 1.36 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 3.37 (s, 6 H, OCH_3), 4.30 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 5.44 (d, *J* = 6.5 Hz, 1 H, 4-H), 6.53 (d, *J* = 6.5 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 13.81 (q, OCH_2CH_3), 53.42 (q, OCH_3), 62.38 (t, OCH_2CH_3), 99.62 (d, C-4), 115.42 (s, C-2), 140.88 (d, C-3), 162.28 (s, C-1).

Ethyl (Z)/(E)-2-Iodo-4,4-dimethoxy-2-butenoate (**7**-I): Prepared by Horner-Emmons reaction with 6.75 g (30 mmol) of *N*-iodosuccinimide as described for **7**-Cl. Yield: 6.45 g (71.7%), pale-yellow liquid [(*Z*)/(*E*): 79:21 (GC)]. − IR (film): ν = 1725 (C=O), 1630 (C=C). − HRMS: calcd. 299.9859 ($C_8H_{13}O_4I$); found 299.9860. − (*Z*)-**7**-I: ^1H NMR ($CDCl_3$): δ = 1.33 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 3.42 (s, 6 H, OCH_3), 4.29 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 5.03 (d, *J* = 6.2 Hz, 1 H, 4-H), 7.23 (d, *J* = 6.2 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 13.84 (q, OCH_2CH_3), 53.30 (q, OCH_3), 62.82 (t, OCH_2CH_3), 96.60 (s, C-2), 105.36 (d, C-4), 146.12 (d, C-3), 162.04 (s, C-1). − (*E*)-**7**-I: ^1H NMR ($CDCl_3$): δ = 1.34 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 3.35 (s, 6 H, OCH_3), 4.27 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 5.33 (d, *J* = 5.9 Hz, 1 H, 4-H), 6.69 (d, *J* = 5.9 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 13.71 (q, OCH_2CH_3), 53.16 (q, OCH_3), 62.20 (t, OCH_2CH_3), 88.88 (s, C-2), 100.11 (d, C-4), 147.64 (d, C-3), 163.56 (s, C-1).

Table 3. Vicinal (^3J) $^{13}C,^1H$-coupling of **7** [Hz] in $CDCl_3$

	7-Cl (*Z*)/(*E*)	**7-Br** (*Z*)/(*E*)	**7-I** (*Z*)/(*E*)
^3J(C,H)	4.5/10.7	4.5/10.9	5.4/11.8

Ethyl (Z)-3-[(4S′,5S′)-4′,5′-Bis(benzyloxymethyl)-1′,3′-dioxolane-2′-yl]-2-bromo-2-propenoate [(*Z*)-**9a**]: A solution of 10.12 g (40 mmol) of (*Z*)-**7**-Br, 12.08 g (40 mmol) of (2*S*,3*S*)-butanediol **8a** and 50 mg of *p*-toluenesulfonic acid in 170 ml of toluene was stirred under reflux for 30 min. The reflux condenser was then replaced by a Vigreux column and the methanol formed was distilled off (azeotropic mixture: toluene/methanol). The remaining toluene solution was cooled to room temp., washed with 20 ml of saturated sodium bicarbonate solution, dried ($MgSO_4$), and concentrated to give an oil, which was chromatographed on silica gel (eluent: petroleum ether/diethyl ether, 4:1). Yield: 15.87 g (81%), viscous oil. − IR (film): ν = 3040 cm^{-1}, 2880 (CH), 1730 (C=O), 1640 (C=C), 1500, 1460, 1375, 1305, 1265, 1245, 1095, 1035, 995, 910, 865, 745 (C_6H_5), 705 (C_6H_5). − UV/Vis (methanol): λ_{max} (lg ε) = 214 nm (4.172), 234 (3.883). − ^1H NMR ($CDCl_3$): δ = 1.30 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 3.61−3.65 (m, 4 H, $CHCH_2$), 4.16−4.18 (m, 2 H, 4′-H and 5′-H), 4.27 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 4.57 and 4.59 (s, each 2 H, $OCH_2C_6H_5$), 5.90 (d, *J* = 6.7 Hz, 1 H, 2′-H), 7.19 (d, *J* = 6.7 Hz, 1 H, 3-H), 7.26−7.37 (m, 10 H, C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 14.03 (q, OCH_2CH_3), 62.88 (t, OCH_2CH_3), 69.82 and 69.87 (t, $OCH_2C_6H_5$), 73.50 (t, $CHCH_2$), 77.74 (d, C-4′), 78.18 (d, C-5′), 101.98 (d, C-2′), 120.28 (s, C-2), 127.57, 127.62, 127.72, 128.39 and 128.51 (d, C_6H_5), 137.72 (s, C_6H_5), 139.36 (d, C-3), 161.69 (s, C-1). − MS (70 eV); *m*/*z* (%): 490/492 (3) [M^+], 444/446 (1) [$M^+ - C_2H_5O$], 411 (4) [M^+ − Br], 401/399 (18) [$M^+ - C_7H_7$], 305 (23), 293/295 (31), 207/209 (21), 162 (16), 105/107 (23), 92 (64), 91 (100) [$C_7H_7{}^+$], 87 (59), 69 (19), 65 (26), 43 (20). − $[\alpha]^D_{24}$ = +6.7 (*c* = 2.17 in $CHCl_3$). − $C_{24}H_{27}O_6Br$ (491.38): calcd. C 58.66, H 5.54, Br 16.26; found C 58.52, H 5.54, Br 16.17.

Methyl (E)-3-[(4′S,5′S)-4′,5′-Bis(benzyloxymethyl)-1′,3′-dioxolane-2′-yl]-2-bromo-2-propenoate [(*E*)-**9a**]: Prepared as described above for (*Z*)-**9a** from 9.56 g (40 mmol) of (*E*)-**7**-Br, 12.08 g (40 mmol) of (2*S*,3*S*)-butanediol **8a**, and 30 mg of *p*-toluenesulfonic acid in 170 ml of toluene. The crude product was purified by chromatography on silica gel (eluent: petroleum ether/diethyl ether, 2:1). Yield: 13.64 g (72%), viscous liquid. − IR (film): ν = 3090 cm^{-1}, 3070, 3040, 2960, 2870 (CH), 1730 (C=O), 1625 (C=C), 1500, 1455, 1440, 1370, 1310, 1270, 1235, 1100, 1035, 995, 920, 815, 750 (C_6H_5), 710 (C_6H_5). − UV/Vis (methanol): λ_{max} (lg ε) = 211 nm (4.227), 232 (3.732). − ^1H NMR ($CDCl_3$): δ = 3.60−3.62 (m, 4 H, $CHCH_2$), 3.78 (s, 3 H, OCH_3), 4.09−4.18 (m, 2 H, 4′-H and 5′-H), 4.56 (s, 4 H, $OCH_2C_6H_5$), 6.14 (d, *J* = 6.9 Hz, 1 H, 2′-H), 6.59 (d, *J* = 6.9 Hz, 1 H, 3-H), 7.21−7.39 (m, 10 H, C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 53.20 (q, OCH_3), 69.83 (t, $OCH_2C_6H_5$), 73.41 and 73.45 (t, $CHCH_2$), 77.36 (d, C-4′), 78.03 (d, C-5′), 99.40 (d, C-2′), 116.88 (s, C-2), 127.51, 127.58, 127.63 and 128.33 (d, C_6H_5), 137.68 and 137.74 (s, C_6H_5), 142.16 (d, C-3), 162.46 (s, C-1). − MS (70 eV); *m*/*z* (%): 476/478 (8) [M^+], 461/463 (3) [$M^+ - CH_3$], 444/446 (2) [$M^+ - CH_4O$], 397 (7) [M^+ − Br], 385/387 (31) [$M^+ - C_7H_7$], 291 (50), 279/281 (51), 223 (21), 203 (40), 187 (24), 181 (47), 161/163 (17), 105/107 (49), 92 (77), 91 (100) [$C_7H_7{}^+$], 87 (73), 79/81 (20) [Br^+], 69 (43), 65 (50), 43 (38). − $[\alpha]_D{}^{24}$ = +9.6 (*c* = 1.30 in $CHCl_3$). − $C_{23}H_{25}O_6Br$ (477.35): calcd. C 57.87, H 5.28, Br 16.74; found C 58.31, H 5.44, Br 16.57.

Ethyl (Z)-2-Bromo-3-[(4S′,5S′)-4′,5′-diphenyl-1′,3′-dioxolane-2′-yl]-2-propenoate [(*Z*)-**9b**]: Prepared as described for **9a** from 1.93 g (9 mmol) of (1*S*,2*S*)-1,2-diphenylethanediol (**8b**) and 2.28 g (9 mmol) of (*Z*)-**7**-Br in 60 ml toluene in the presence of 30 mg of *p*-toluenesulfonic acid. The crude product was purified chromatographically on silica gel (eluent: diethyl ether/petroleum ether, 1:1). Yield: 3.14 g (87%), viscous liquid. − IR (film): ν = 3070 cm^{-1}, 3040, 2990, 2910 (CH), 1730 (C=O), 1685 (C=C), 1635, 1605, 1500, 1455, 1395, 1375, 1305, 1270, 1245, 1135, 1100, 1035, 925, 880, 775 (C_6H_5), 710 (C_6H_5), 660. − UV/Vis (methanol): λ_{max} (lg ε) = 214 nm (4.222), 234 (4.010). − ^1H NMR ($CDCl_3$): δ = 1.37 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 4.34 (q, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 4.83 (s, 2 H, 4′-H and 5′-H), 6.29 (d, *J* = 6.6 Hz, 1

H, 2′-H), 7.22−7.38 (m, 10 H, C_6H_5), 7.44 (d, *J* = 6.6 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 14.07 (q, OCH_2CH_3), 62.99 (t, OCH_2CH_3), 85.16 (d, C-4′), 86 62 (d, C-5′), 102.38 (d, C-2′), 120.62 (s, C-2), 126.46, 126.73, 128.49 and 128.63 (d, C_6H_5), 136.36 (s, C_6H_5), 139.36 (d, C-3), 161.82 (s, C-1). − MS (70 eV); *m/z* (%): 401/403 (0.2) [M^+ − H], 357/359 (0.5) [M^+ − C_2H_5O], 296/298 (20), 217 (17), 190/192 (100), 162/164 (74), 155 (42), 111 (40), 105 (56) [$C_7H_5O^+$], 77 (27) [$C_6H_5^+$]. − $[\alpha]_D^{24}$= −9.8 (*c* = 1.18 in $CHCl_3$). − $C_{20}H_{19}O_4Br$ (403.27): calcd. C 59.57, H 4.75, Br 19.81; found C 59.86, H 4.90, Br 19.69.

Ethyl (1S,2R,5S,7S,8R,4′S,5′S)-2-Methoxy-8-(2′,2′,5′-trimethyl-1′,3′-dioxolan-4′-yl)-6-oxotricyclo[3.2.1.0^{2,7}]octane-1-carboxylate (**11b**-OMe): To a cooled (−78°C), stirred solution of 3.3 mmol LDA [prepared from 0.33 g (3.3 mmol) diisopropylamine and 3.3 mmol butyllithium] in 15 ml THF under an Ar atmosphere, a solution of 0.38 g (3.0 mmol) of 3-methoxycyclohex-2-enone (**10**-OMe) in 4 ml of THF was added by means of a syringe. After 30 min. at −78°C, a solution of 1.07 g (3.0 mmol) of bromo ester (*Z*)-**3b** in 4 ml of THF was added dropwise from a syringe. The reaction mixture was kept at −78°C for a further 30 min. and was then allowed to warm to room temp. The reaction was terminated by the addition of 10 ml of saturated ammonium chloride solution. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3 × 30 ml). The combined organic phases were dried ($MgSO_4$), concentrated, and the residue was chromatographed on silica gel (eluent: diethyl ether/petroleum ether, 1:1). Yield: 0.49 g (48%), oil, *de*: ≥ 95% (estimated from the ^{1}H-NMR spectrum of the crude product). − IR (film): ν = 2990 cm^{-1}, 2940, 2840 (CH), 1735 (C=O), 1460, 1385, 1350, 1305, 1235, 1180, 1155, 1125, 1080, 1030, 945, 880, 825, 780. − UV/Vis (methanol): λ_{max} (lg ε) = 208 nm (3.808), 260 (3.052), 340 (2.821). − ^{1}H NMR ($CDCl_3$): δ = 1.29 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.33 (d, *J* = 5.6 Hz, 3 H, CH_3), 1.40 [s, 3 H, $C(CH_3)_2$], 1.42 [s, 3 H, $C(CH_3)_2$], 1.61 (m, 1 H, 4-H), 2.18−2.66 (m, 3 H, 3-H and 4-H), 2.32 (m, 1 H, 5-H), 2.65 (d, *J* = 1.5 Hz, 1 H, 7-H), 2.75 (m, *J* = 5.3 Hz, 1 H, 8-H), 3.38 (s, 3 H, OCH_3), 4.02−4.27 (m, 2 H, 4′-H and 5′-H), 4.15−4.27 (m, *J* = 7.1 Hz, 2 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$): δ = 13.99 (q, OCH_2CH_3), 18.88 (q, CH_3), 20.02 (t, C-3), 20.51 (t, C-4), 27.23 [q, $C(CH_3)_2$], 27.25 [q, $C(CH_3)_2$], 41.15 (d, C-8), 42.50 (s, C-1), 43.25 (d, C-5), 44.36 (d, C-7), 55.40 (q, OCH_3), 61.22 (t, OCH_2CH_3), 75.52 (d, C-4′), 76.12 (s, C-2), 80.86 (d, C-5′), 108.14 (s, C-2′), 167.97 (s, COO), 206.98 (s, C-6). − MS (70 eV); *m/z* (%): 338 (0.4) [M^+], 323 (16) [M^+ − CH_3], 294 (3), 280 (70), 251 (14), 235 (17), 223 (15), 207 (53), 195 (99) [$C_{10}H_{11}O_4^+$], 182 (57), 163 (36), 149 (37), 135 (33), 121 (52), 115 (47), 109 (35), 105 (49), 91 (49), 77 (41), 58 (74), 56 (58), 54 (73), 42 (97), 29 (100) [$C_2H_5^+$]. − CD (methanol): λ_{max} (Θ/Δε) = 287.5 nm (+7197/+2.18). − $[\alpha]_D^{24}$= −5.1 (*c* = 1.02 in $CHCl_3$). − $C_{18}H_{26}O_6$ (338.40): calcd. C 63.89, H 7.74; found C 63.68, H 7.75.

Ethyl (1S,2R,5S,7S,8R,4′S,5′S)-2-Methoxy-8-(2′,2′-dimethyl-5′-phenyl-1′,3′-dioxolan-4′-yl)-6-oxotricyclo[3.2.1.0^{2,7}]octane-1-carboxylate (**11c**-OMe): Prepared analogously from 3.3 mmol of LDA in 15 ml THF, 0.38 g (3.0 mmol) of **10**-OMe in 4 ml of THF, and 1.07 g (3.0 mmol) of bromo ester (*Z*)-**3c** in 4 ml of THF. Yield: 0.35 g (29%), white crystals, m.p. 102−104°C (diethyl ether/petroleum ether). − *de*: ≥ 95% (based on the ^{1}H-NMR spectrum of the crude reaction product). − IR (KBr): ν = 3060 cm^{-1}, 3030, 2980, 2940, 2880 (CH), 1730 (C=O), 1605, 1495, 1455, 1385, 1370, 1350, 1235, 1175, 1160, 1120, 1085, 1070, 1050, 1030, 970, 945, 890, 875, 830, 770 (C_6H_5), 710 (C_6H_5). − UV/Vis (methanol): λ_{max} (lg ε) = 214 nm (4.059), 252 (3.387), 280 (2.868). − ^{1}H NMR ($CDCl_3$): δ = 1.19 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.56 [s, 3 H, $C(CH_3)_2$], 1.58 [s, 3 H, $C(CH_3)_2$], 1.62 (m, 1 H, 4-H), 2.21−2.42 (m, 2 H, 3-H and 4-H), 2.46 (m, 1 H, 5-H), 2.58−2.69 (m, 2 H, 3-H and 8-H), 2.62 (d, *J* = 1.4 Hz, 1 H, 7-H), 3.23 (s, 3 H, OCH_3), 4.04−4.17 (m, *J* = 7.1 Hz, 2 H, OCH_2CH_3), 4.61 (dd, *J* = 4.8 Hz, 8.8 Hz, 1 H, 4′-H), 4.81 (d, *J* = 8.8 Hz, 1 H, 5′-H), 7.29−7.39 (m, 5 H, C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 13.85 (q, OCH_2CH_3), 20.39 (t, C-4), 20.61 (t, C-3), 26.58 [q, $C(CH_3)_2$], 27.10 [q, $C(CH_3)_2$], 38.58 (d, C-8), 42.41 (s, C-1), 42.85 (d, C-5), 44.07 (d, C-7), 55.23 (q, OCH_3), 61.01 (t, OCH_2CH_3), 76.16 (s, C-2), 80.54 (d, C-5′), 80.69 (d, C-4′), 108.81 (s, C-2′), 126.82, 128.36 and 128.53 (d, C_6H_5), 137.37 (s, C_6H_5), 167.70 (s, COO), 206.82 (s, C-6). − MS (70 eV); *m/z* (%): 400 (0.6) [M^+], 385 (2) [M^+ − CH_3], 342 (25), 326 (5), 297 (6), 269 (10), 253 (19), 223 (36), 205 (32), 195 (100) [$C_{10}H_{11}O_4^+$], 182 (46), 148 (45), 119 (35), 91 (82) [$C_7H_7^+$], 54 (38). − CD (methanol): λ_{max} (Θ/Δε) = 288.5 nm (+12143/+3.68). − $[\alpha]_D^{24}$= −13.0 (*c* = 1.24 in $CHCl_3$). − $C_{23}H_{28}O_6$ (400.47): calcd. C 68.98, H 7.05; found C 68.83, H 7.15.

Ethyl (1S,2S,5S,7R,8R,4′S,5′S)-2-Methyl-8-(2′,2′-dimethyl-5′-phenyl-1′,3′-dioxolan-4′-yl)-6-oxotricyclo[3.2.1.0^{2,7}]octane-1-carboxylate (**11c**-Me): Prepared analogously from 3.3 mmol LDA in 15 ml of THF, 0.33 g (3.0 mmol) of 3-methylcyclohex-2-enone (**10**-Me) in 4 ml of THF, and 1.07 g (3.0 mmol) of (*Z*)-**3c** in 4 ml of THF. Chromatography (silica gel, diethyl ether/petroleum ether, 1:1) gave 0.68 g (59%), oil. − *de*: ≥ 95% (based on the ^{1}H-NMR spectrum of the crude reaction product). − IR (film): ν = 3060 cm^{-1}, 3030, 2990, 2940, 2880 (CH), 1730 (C=O), 1600, 1500, 1455, 1385, 1375, 1350, 1270, 1240, 1215, 1180, 1145, 1095, 1055, 1035, 975, 920, 890, 875, 830, 770 (C_6H_5), 710 (C_6H_5). − UV/Vis (methanol): λ_{max} (lg ε) = 214 nm (4.035), 252 (3.650), 292 (3.006). − ^{1}H NMR ($CDCl_3$): δ = 1.15 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.28 (s, 3 H, CH_3), 1.54 [s, 3 H, $C(CH_3)_2$], 1.56 [s, 3 H, $C(CH_3)_2$], 1.82−1.89 (m, 2 H, 3-H and 4-H), 2.01 (m, 1 H, 3-H), 2.15 (d, *J* = 1.5 Hz, 1 H, 7-H), 2.26 (m, 1 H, 4-H), 2.43 (m, 1 H, 5-H), 2.78 (t, *J* = 5.4 Hz, 1 H, 8-H), 3.98−4.07 (m, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 4.57 (dd, *J* = 5.4 Hz, 8.7 Hz, 1 H, 4′-H), 4.87 (d, *J* = 8.7 Hz, 1 H, 5′-H), 7.28−7.38 (m, 5 H, C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 13.91 (q, OCH_2CH_3), 20.32 (q, CH_3), 24.69 (t, C-3), 25.41 (t, C-4), 26.83 [q, $C(CH_3)_2$], 27.18 [q, $C(CH_3)_2$], 37.77 (d, C-8), 41.80 (s, C-2), 42.00 (s, C-1), 44.13 (d, C-7), 45.15 (d, C-5), 60.95 (t, OCH_2CH_3), 80.75 (d, C-5′), 80.80 (d, C-4′), 108.77 (s, C-2′), 127.05, 128.45 and 128.59 (d, C_6H_5), 137.73 (s, C_6H_5), 169.81 (s, COO), 210.80 (s, C-6). − MS (70 eV); *m/z* (%): 384 (0.2) [M^+], 369 (1) [M^+ − CH_3], 326 (8), 310 (6), 282 (4), 179 (7), 148 (74), 109 (13), 105 (16), 91 (28) [$C_7H_7^+$], 86 (58), 84 (81), 51 (45), 49 (100). − CD (methanol): λ_{max} (Θ/Δε) = 288 nm (+12379/+3.75). − $[\alpha]_D^{24}$= −9.1 (*c* = 1.16 in $CHCl_3$). − HRMS: calcd. 326.1518 [M^+ − CH_3 − CH_3 − CO] ≡ [$C_{20}H_{22}O_4$]; found 326.1555.

Ethyl 2-Benzyloxy-8-[4′,5′-bis(benzyloxymethyl)-1′,3′-dioxolan-2′-yl]-6-oxotricyclo[3.2.1.0^{2,7}]octane-1-carboxylate (**11d/11′d**): Prepared analogously from 5.5 mmol of LDA in 20 ml of THF, 1.01 g (5.0 mmol) of 3-benzyloxycyclohex-2-enone (**10**-OBzl) in 5 ml of THF, and 2.46 g (5.0 mmol) of (*Z*)-**9a** in 5 ml of THF. Chromatography (silica gel, diethyl ether/petroleum ether, 2:1) of the crude product gave 1.89 g (62%), yellow oil. *de*: ≥ 28% (based on the ^{1}H-NMR spectrum of the crude mixture). Separation of the diastereomers: HPLC, CHIRALCEL OD, eluent: *n*-hexane/2-propanol, 85:15, flow rate: 0.9 ml/min., λ = 254 nm. − IR (film): ν = 3090 cm^{-1}, 3070, 3040, 2990, 2910, 2870 (CH), 1735 (C=O), 1605, 1500, 1455, 1370, 1350, 1310, 1275, 1235, 1205, 1155, 1130, 1095, 1035, 950, 925, 875, 830, 750 (C_6H_5), 710 (C_6H_5). − MS; *m/z* (%): 612 (0.5) [M^+], 583 (0.1) [M^+ − C_2H_5], 567 (0.2) [M^+ − C_2H_5O], 521 (3) [M^+ − C_7H_7], 493 (1), 475 (0.8), 352 (2), 327 (3), 313 (10), 237 (3), 209 (2), 181 (19), 115 (4), 92 (23), 91 (100) [$C_7H_7^+$], 69 (9), 44 (6). − UV/Vis (methanol): λ_{max} (lg ε) = 214 nm (4.245), 256

(3.129), 284 (2.674). – $[\alpha]_D^{24}$= +3.5 (*c* = 0.71 in $CHCl_3$). – $C_{37}H_{40}O_8$ (612.72): calcd. C 72.53, H 6.58; found C 72.63, H 6.62. – Main product: (1*S*,2*R*,5*S*,7*S*,8*R*,4′*S*,5′*S*)-**11d**. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.55 (m, 1 H, 4-H), 2.10 (m, 1 H, 4-H), 2.26 (m, 1 H, 3-H), 2.38 (m, 1 H, 5-H), 2.58 (m, 1 H, 3-H), 2.67 (d, *J* = 1.6 Hz, 1 H, 7-H), 2.92 (ddd, J_1 = 1.2 Hz, J_2 = J_3 = 4.4 Hz, 1 H, 8-H), 3.62–3.68 (m, 4 H, $CHCH_2$), 3.98–4.22 (m, 4 H, OCH_2CH_3, 4′-H and 5′-H), 4.56 (s, 2 H, $OCH_2C_6H_5$), 4.57 (d, *J* = 11.2 Hz, 1 H, $OCH_2C_6H_5$), 4.58 (s, 2 H, $OCH_2C_6H_5$), 4.68 (d, *J* = 11.2 Hz, 1 H, $OCH_2C_6H_5$), 5.54 (d, *J* = 4.4 Hz, 1 H, 2′-H), 7.25–7.39 (m, 15 H, C_6H_5). – ^{13}C NMR (75.42 MHz, $CDCl_3$): δ = 14.01 (q, OCH_2CH_3), 20.28 (t, C-4), 21.61 (t, C-3), 42.49 (s, C-1), 42.82 (d, C-8), 43.19 (d, C-5), 43.59 (d, C-7), 61.25 (t, OCH_2CH_3), 70.27 (t, $OCH_2C_6H_5$), 73.53 (t, $CHCH_2$), 75.40 (s, C-2), 76.88 (d, C-4′), 78.49 (d, C-5′), 102.71 (d, C-2′), 127.38, 127.53, 127.58, 127.70, 128.30 and 128.41 (d, C_6H_5), 137.53, 137.84 and 137.95 (s, C_6H_5), 167.74 (s, COO), 207.29 (s, C-6). – CD (methanol): λ_{max} (Θ/Δε) = 286.5 nm (+4814/+1.46). – $[\alpha]_{365}^{24}$ = +42.7 (*c* = 0.15 in methanol). – Minor product: (1*R*,2*S*,5*R*,7*R*,8*S*,4′*S*,5′*S*)-**11′d**. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.52 (m, 1 H, 4-H), 2.12–2.29 (m, 2 H, 3-H and 4-H), 2.39 (m, 1 H, 5-H), 2.60 (m, 1 H, 3-H), 2.69 (d, *J* = 1.6 Hz, 1 H, 7-H), 2.90 (ddd, J_1 = 1.7 Hz, J_2 = J_3 = 4.6 Hz, 1 H, 8-H), 3.61–3.68 (m, 4 H, $CHCH_2$), 4.05–4.17 (m, 4 H, OCH_2CH_3, 4′-H and 5′-H), 4.54 (s, 2 H, $OCH_2C_6H_5$), 4.56 (d, *J* = 11.4 Hz, 1 H, $OCH_2C_6H_5$), 4.58 (s, 2 H, $OCH_2C_6H_5$), 4.66 (d, *J* = 11.4 Hz, 1 H, $OCH_2C_6H_5$), 5.58 (d, *J* = 4.6 Hz, 1 H, 2′-H), 7.26–7.37 (m, 15 H, C_6H_5). – ^{13}C NMR (75.42 MHz, $CDCl_3$): δ = 14.00 (q, OCH_2CH_3), 20.36 (t, C-4), 21.67 (t, C-3), 42.45 (s, C-1), 42.89 (d, C-8), 42.96 (d, C-5), 43.48 (d, C-7), 61.27 (t, OCH_2CH_3), 70.31 and 70.41 (t, $OCH_2C_6H_5$), 73.53 (t, $CHCH_2$), 75.51 (s, C-2), 77.09 (d, C-4′), 78.03 (d, C-5′), 102.59 (d, C-2′), 127.37, 127.57, 127.67, 127.78, 128.28 and 128.41 (d, C_6H_5), 137.47, 137.72 and 137.95 (s, C_6H_5), 167.92 (s, COO), 207.34 (s, C-6). – CD (methanol): λ_{max} (Θ/Δε) = 287 nm (–9291/–2.82). – $[\alpha]_{365}^{24}$ = –121.8 (*c* = 0.06 in methanol).

Ethyl 2-Benzyloxy-8-(4′,5′-diphenyl-1′,3′-dioxolane-2′-yl)-6-oxotricyclo[3.2.1.0^{2,7}]octane-1-carboxylate (**11e/11′e**): Prepared analogously from 5.5 mmol of LDA in 20 ml of THF, 1.01 g (5.0 mmol) 3-benzyloxycyclohex-2-enone (**10-**OBzl) in 5 ml of THF, and 2.02 g (5.0 mmol) of (*Z*)- **9b** in 5 ml of THF. Chromatography (silica gel, diethyl ether/petroleum ether, 1:1) of the crude product gave 1.04 g (40%), viscous oil, mixture of diastereomers. *de*: ≥ 46% (based on the ^{1}H-NMR spectrum of the crude mixture). Separation of the diastereomers: HPLC: CHIRALCEL OD, eluent *n*-hexane/2-propanol, 95:5, flow rate: 0.5 ml/min., λ = 254 nm. – IR (film): ν = 3090 cm^{-1}, 3070, 3040, 2990, 2940, 2910, 2890 (CH), 1735 (C=O), 1605, 1500, 1455, 1370, 1350, 1295, 1275, 1235, 1200, 1155, 1130, 1090, 1030, 880, 775, 750 (C_6H_5), 710 (C_6H_5). – MS (70 eV); *m/z* (%): 524 (0.4) [M^+], 479 (2) [$M^+ - C_2H_5O$], 418 (9), 328 (9), 237 (31), 225 (36), 209 (18), 197 (41), 165 (18), 135 (7), 105 (47) [$C_7H_5O^+$], 91 (100) [$C_7H_7^+$], 77 (28). – UV/Vis (methanol): λ_{max} (lg ε) = 214 nm (4.244), 252 (3.602), 284 (2.980). – $[\alpha]_D^{24}$= –1.5 (*c* = 4.48 in $CHCl_3$). – $C_{33}H_{32}O_6$ (524.61): calcd. C 75.55, H 6.15; found C 75.12, H 6.31. – Major product: (1*S*,2*R*,5*S*,7*S*,8*R*,4′*S*,5′*S*)-**11e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.72 (m, 1 H, 4-H), 2.20–2.39 (m, 2 H, 3-H and 4-H), 2.55 (m, 1 H, 5-H), 2.68 (m, 1 H, 3-H), 2.75 (d, *J* = 1.5 Hz, 1 H, 7-H), 3.19 (ddd, J_1 = 0.7 Hz, J_2 = J_3 = 4.1 Hz, 1 H, 8-H), 4.09–4.27 (m, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 4.59 and 4.74 (d, *J* = 11.5 Hz, each 1 H, $OCH_2C_6H_5$), 4.79 and 4.84 (d, *J* = 8.0 Hz, each 1 H, 4′-H and 5′-H), 5.98 (d, *J* = 4.1 Hz, 1 H, 2′-H), 7.22–7.39 (m, 15 H, C_6H_5). – ^{13}C NMR (75.42 MHz, $CDCl_3$): δ = 14.05 (q, OCH_2CH_3), 20.54 (t, C-4), 21.70 (t, C-3), 42.64 (s, C-1), 42.77 (d, C-8), 43.70 (d, C-5), 43.88 (d, C-7), 61.42 (t, OCH_2CH_3), 70.29 (t, $OCH_2C_6H_5$), 75.44 (s, C-2), 84.44 (d, C-4′), 87.45 (d, C-5′), 103.63 (d, C-2′), 126.17, 126.83, 127.25, 127.66, 128.18, 128.31 and 128.63 (d, C_6H_5), 136.38, 137.60 and 138.64 (s, C_6H_5), 167.75 (s, COO), 206.94 (s, C-6). – CD (methanol): λ_{max} (Θ/Δε) = 287 nm (+7841/+2.38). – $[\alpha]_{365}^{24}$ = +47.2 (*c* = 0.13 in methanol). – Minor product: (1*R*,2*S*,5*R*,7*R*,8*S*,4′*S*,5′*S*)-**11′e** (7:3 mixture). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.71 (m, 1 H, 4-H), 2.20–2.45 (m, 2 H, 3-H and 4-H), 2.57 (m, 1 H, 5-H), 2.67 (m, 1 H, 3-H), 2.73 (d, *J* = 1.6 Hz, 1 H, 7-H), 3.18 (ddd, J_1 = 0.7 Hz, J_2 = J_3 = 5.4 Hz, 1 H, 8-H), 4.03–4.21 (m, *J* = 7.2 Hz, 2 H, OCH_2CH_3), 4.58 and 4.76 (d, *J* = 11.3 Hz, each 1 H, $OCH_2C_6H_5$), 4.81 and 4.88 (d, *J* = 8.1 Hz, each 1 H, 4′-H and 5′-H), 5.92 (d, *J* = 5.4 Hz, 1 H, 2′-H), 7.22–7.39 (m, 15 H, C_6H_5). – ^{13}C NMR (75.42 MHz, $CDCl_3$): δ = 14.05 (q, OCH_2CH_3), 20.53 (t, C-4), 21.58 (t, C-3), 42.64 (s, C-1), 42.75 (d, C-8), 43.70 (d, C-5), 44.47 (d, C-7), 65.20 (t, OCH_2CH_3), 70.45 (t, $OCH_2C_6H_5$), 75.14 (s, C-2), 84.75 (d, C-4′), 87.11 (d, C-5′), 103.85 (d, C-2′), 126.18, 126.95, 127.03, 127.37, 127.73, 128.52, 128.59 and 128.66 (d, C_6H_5), 136.10, 137.46 and 138.22 (s, C_6H_5), 167.74 (s, COO), 206.95 (s, C-6). – CD (methanol, 7:3 mixture): λ_{max} (Θ/Δε) = 288 nm (–254/–0.08). – $[\alpha]_{365}^{24}$ = –7.4 (*c* = 0.10 in methanol, 7:3 mixture).

☆ Dedicated to Professor Dr. *Wolfgang Steglich*, Ludwig-Maximilians-Universität München, on the occasion of his 65th birthday.

[1] L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136; L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137–170; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131; M. Ihara, K. Fukumoto, *Angew. Chem.* **1993**, *105*, 1059–1071; *Angew. Chem. Int. Ed. Engl.* **1993**, 1010–1022.

[2] H. Hagiwara, T. Komoda, H. Kosugi, H. Uda, *J. Chem. Soc., Chem. Commun.* **1976**, 413; R. A. Lee, *Tetrahedron Lett*. **1973**, 3333–3336.

[3] L. Hadjiarapoglou, I. Klein, D. Spitzner, A. de Meijere, *Synthesis* **1996**, 525–528; R. M. Cory, R. M. Renneborg, *J. Org. Chem.* **1984**, *49*, 3898–3904; H. Hagiwara, H. Uda, T. Kodama, *J. Chem. Soc., Perkin Trans. 1* **1980**, 963–977.

[4] R. A. Holton, A. D. Williams, R. M. Kennedy, *J. Org. Chem*. **1986**, *51*, 5480–5482; S. F. Martin, *Tetrahedron* **1980**, *36*, 419–460.

[5] N. A. Braun, I. Klein, D. Spitzner, B. Vogler, S. Braun, H. Borrmann, A. Simon, *Liebigs Ann.* **1995**, 2165–2169.

[6] H.-D. Ambrosi, W. Duczek, M. Ramm, E. Gründemann, B. Schulz, K. Jähnisch, *Liebigs Ann. Chem.* **1994**, 1013–1018.

[7] L. I. Vereshchagin, S. P. Korshunov, R. L. Bol′shedvorskaya, T. V. Lipovich, *J. Org. Chem. USSR (Engl. Transl.)* **1966**, *2*, 524–529; *Zh. Org. Khim*. **1966**, *2*, 522–528; G. Märkl, *Chem. Ber*. **1961**, *94*, 2996–3004.

[8] L. F. Tietze, U. Beifuss, M. Ruther, *J. Org. Chem*. **1989**, 3120–3129; U. Vogeli, W. v. Philipsborn, *Org. Magn. Res.* **1975**, *7*, 617–627. We thank Dr. *S. Braun*, TH Darmstadt, for performing these experiments.

[9] H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483–2547. We thank Professor *K. B. Sharpless* for helpful discussions.

[10] H. Becker, M. A. Soler, K. B. Sharpless, *Tetrahedron* **1995**, *51*, 1345–1376.

[11] H. C. Kolb, P. G. Andersson, K. B Sharpless, *J. Am. Chem. Soc.* **1994**, *116*, 1278–1291.

[12] K. Peters, E.-M. Peters, N. A. Braun, I. Klein, D. Spitzner, *Z. Kristallogr. NCS* **1997**, *212*, 131–132.

[13] E. A. Mash, K. A. Nelson, S. Van Deusen, S. B. Hemperly, *Org. Synth.* **1989**, *68*, 92–103.

[14] K. B. Sharpless, W. Amberg, Y. L. Bennani, G. A. Crispino, J. Hartung, K.-S. Jeong, H.-L. Kwong, K. Morikawa, Z.-M. Wang, D. Xu, X.-L. Zhang, *J. Org.Chem*. **1992**, *57*, 2768–2771.

[15] F. Farina, M. R. Martin, M. V. Martin, *An. Quim*. **1979**, *75*, 144–149; F. Farina, M. R. Martin, M. V. Martin, *An. Quim*. **1978**, *74*, 799–805.

[16] H.-U. Reißig, *Top. Curr. Chem.* **1988**, *144*, 73−135.
[17] L. Hadjiarapoglou, A. de Meijere, H.-J. Seitz, I. Klein, D. Spitzner, *Tetrahedron Lett.* **1994**, *35*, 3269−3272; D. Spitzner, A. Engler, P. Wagner, A. de Meijere, G. Bengtson, *Tetrahedron* **1987**, *43*, 3213−3223; D. Spitzner, A. Engler, T. Liese, G. Splettstösser, A. de Meijere, *Angew. Chem.* **1982**, *94*, 799−800; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 785; *Angew. Chem. Suppl.* **1982**, 1722−1729.
[18] N. A. Braun, N. Stumpf, D. Spitzner, *Synthesis* **1997**, 917−920.
[19] J. Mulzer, M. Kappert, G. Huttner, I. Jibril, *Tetrahedron Lett.* **1985**, *26*, 1631−1634; D. Horton, T. Machinani, *J. Chem. Soc., Chem. Commun*. **1981**, 88.
[20] N. A. Braun, I. Klein, D. Spitzner, B. Vogler, H. Borrmann, A. Simon, *Tetrahedron Lett*., **1995**, *36*, 3675−3678.
[21] PCMODEL 4.0, Serena Software, Bloomington, IN, USA.
[22] H. Nagaoka, K. Shibuya, K. Kobayashi, I. Miura, M. Muramatsu, Y. Yamada, *Tetrahedron Lett*. **1993**, *34*, 4039−4042.
[23] D. F. Shellhamer, V. L. Heasley, J. E. Foster, J. K. Luttrull, G. E. Heasley, *J. Org. Chem*., **1977**, *42*, 2141−2145.

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