Stereoselective Total Synthesis of Multiplolide A and of a Diastereoisomer

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A stereoselective total synthesis of multiplolide A (**1**) and of its diastereoisomer **2** was described from easily accessible starting materials (*Schemes 2–4*). The synthetic strategy involves a *Jacobsen* resolution, *Sharpless* epoxidation, *Swern* oxidation, *Yamaguchi* reaction, and ring-closing metathesis (RCM).

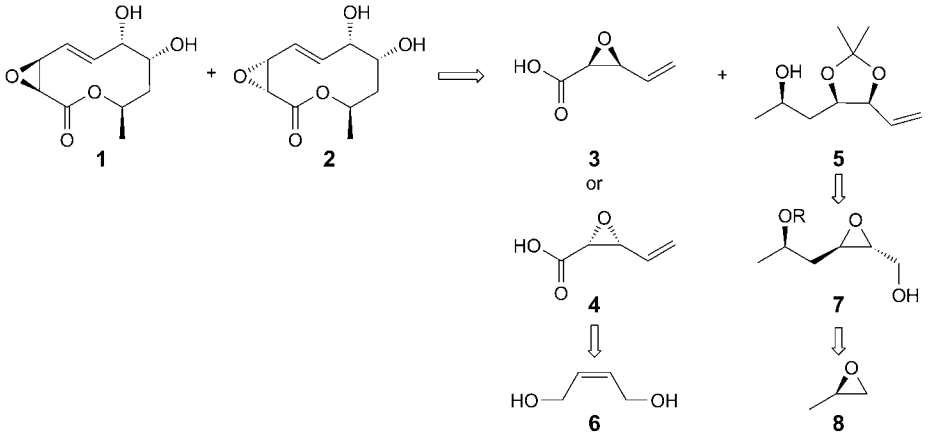
Introduction. – Natural products are a versatile source for therapeutic agents. Among them, lactone containing molecules are often shown to possess a wide spectrum of biological activity [1]. Particularly, ten-membered lactones, formerly called decanolides, are abundant in nature and display a wide range of biological properties such as, antifungal and antibacterial achivity and the inhibition of cholesterol biosynthesis [2].

Multiplolides A (**1**) and B are ten-membered lactones, which have been isolated from the culture broth of *Xylaria multiplex* in 2001 [3]. They exhibit antifungal activity against *Candida albicans* with an IC_{50} value of 7 and 2 μg/ml, respectively. *Ramana* and co-workers reported the first total synthesis [4] and absolute configuration of multiplolide A. Their synthetic strategy was based on the use of chiral starting material and ring-closing methathesis (RCM). Recently, we have initiated a research programme for the total synthesis of bioactive natural products from achiral sources [5]. Our approach to the total synthesis of multiplolide A (**1**) and its diastereoisomer **2** involves the use of commercially available 2-methyloxirane and (2*Z*)-but-2-ene-1,4-diol as starting materials.

Results and Discussions. – The retrosynthetic analysis of lactones **1** and **2** is shown in *Scheme 1*. The cleavage of the lactone leads to the oxiranecarboxylic acids **3** and **4** and (protected) olefinic alcohol **5**, which in turn could be obtained from (2*Z*)-but-2-ene-1,4-diol (**6**) and (2*R*)-2-methyloxirane (**8**) *via* **7**, respectively (*Scheme 1*).

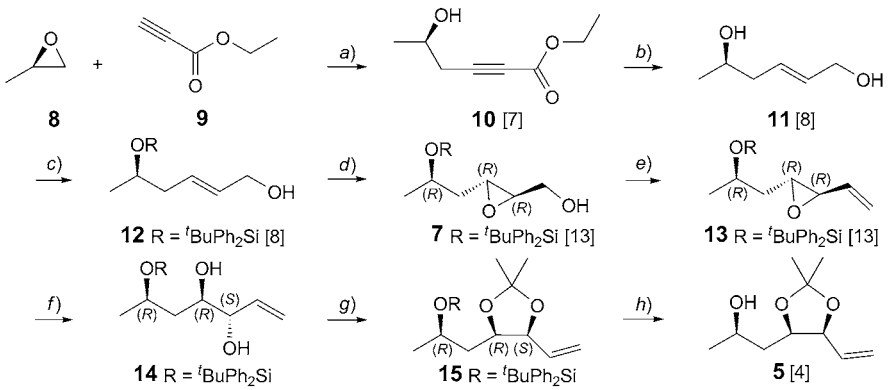
The synthesis of fragment **5** began with the kinetic resolution of 2-methyloxirane with (*R*,*R*)-*Jacobsen* catalyst (**A**) [6]. The chiral oxirane **8** was then opened with ethyl prop-2-ynoate (**9**) in the presence of BuLi at −78° to give hydroxyalkynoate **10** in 81% yield [7] (*Scheme 2*). The selective reduction of the alkyne and ester moiety of **10** with $LiAlH_4$ furnished allylic alcohol **11** in 78% yield [8]. The primary-alcohol moiety of **11** was protected by treatment with pivaloyl chloride (81% yield), then the secondary-alcohol moiety was protected as ^{t}BuPh$_2$Si ether (91% yield), and finally the pivaloyl

Scheme 1. *Retrosynthetic Analysis of Multiplolide A* (**1**) *and of Its Diastereoisomer* **2**

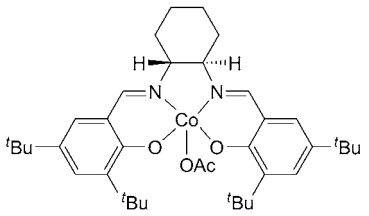


group was deprotected with K_2CO_3 in MeOH leading to the ^{t}BuPh$_2$Si-protected allylic alcohol **12** in 88% yield. The latter was transformed into oxirane alcohol **7** *via Sharpless* epoxidation [9]. Conversion of oxirane alcohol **7** into **13** was accomplished in good yield by *Swern* oxidation [10] followed by a one-C-atom homologation [11] with Ph_3(Me)PI (60% overall yield after 2 steps). Treatment of the ethenyloxirane alcohol **13** with Sc(OTf)$_3$ in THF/H_2O 10:1 (0.25M) cleanly afforded olefinic diol **14** in 70% yield [12]. Protection of **14** with 2,2-dimethoxypropane and camphorsulfonic acid (CSA) in CH_2Cl_2 at 0° gave ethenyl-1,3-dioxol **15** in 90% yield. Removal of the ^{t}BuPh$_2$Si group with Bu_4NF in THF led to the required olefinic alcohol **5** in 88% yield [4] (*Scheme 2*).

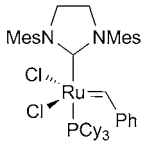
Scheme 2



a) BuLi, $BF_3 \cdot Et_2O$,THF, −78°, 2 h; 81%. *b*) $LiAlH_4$, THF, 0° to 80°, 2 h; 78%. *c*) 1. Pivalolyl chloride, *N*,*N*-dimethylpyridin-4-amine (DMAP),CH_2Cl_2, 0°, 2 h; 81%; 2. ^{t}BuPh$_2$SiCl, 1*H*-imidazole, CH_2Cl_2, r.t.; 91%; 3. K_2CO_3, MeOH, r.t., 10 h; 88%. *d*) (−)-Diisopropyl tartrate ((−)-DIPT), Ti(^{i}PrO)$_4$, ^{t}BuOOH, CH_2Cl_2, 4-Å molecular sieves, −20°; 90%. *e*) 1. $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78°, 1 h; 2. Ph_3(Me)PI, sodium hexamethyldisilazanide (NaHMDS), 0°, 1 h; 80%. *f*) Sc(OTf)$_3$, THF/H_2O 10:1, r.t., 2.5 h; 70%. *g*) 2,2-dimethoxypropane, CSA, CH_2Cl_2, 0°, 30 min; 90%. *h*) Bu_4NF, THF, r.t., 2 h; 88%.



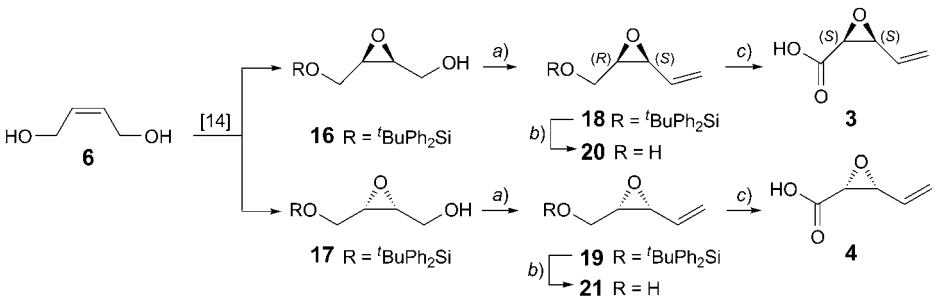
(*R*,*R*)-*Jacobsen* catalyst (**A**)



2nd-Generation *Grubbs* catalyst (**B**)

The synthesis of oxiranecarboxylic acids **3** and **4** started from the known (2*Z*)-but-2-ene-1,4-diol (**6**) (*Scheme 3*). Thus, selective monoprotection of the OH group with ^{t}BuPh$_2$SiCl in CH$_2$Cl$_2$ at room temperature gave the mono ^{t}BuPh$_2$Si ether in 86% yield, which on further *Sharpless* epoxidation [14] with (+)- and (−)-diisopropyl tartrate ((+)- and (−)-DIPT) gave enantiomeric oxirane alcohols **16** and **17** in 90% yield, respectively. *Swern* oxidation of primary alcohols **16** and **17** gave the corresponding aldehydes, which on further one-C-atom homologation furnished ethenyloxiranes **18** and **19** in good yield (60% overall yield after 2 steps). Deprotection of the ^{t}BuPh$_2$Si ether was achieved by treatment with Bu$_4$NF in THF to give **20** and **21** [15], which on further oxidation [16] with 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) and [bis-(acetoxy)iodo]benzene (BAIB) gave the required 3-ethenyloxirane-2-carboxyclic acids **3** and **4**, respectively, in 84% yield (overall yield for 2 steps).

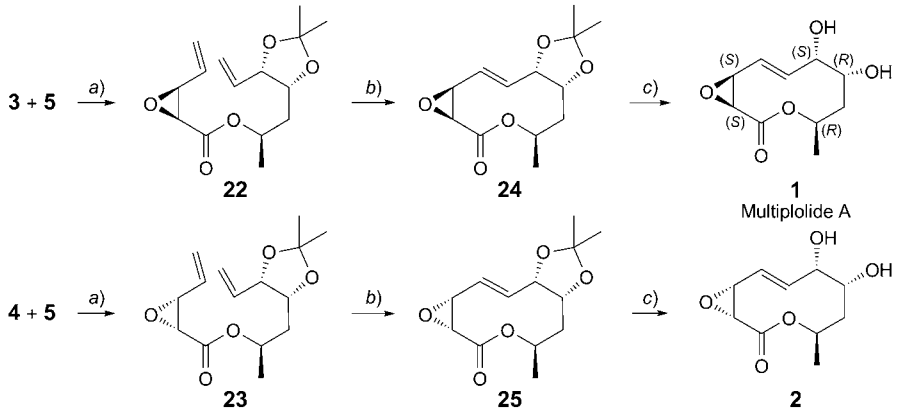
Scheme 3



a) 1. (COCl)$_2$, DMSO, Et$_3$N, CH$_2$Cl$_2$, −78°, 1 h; 2. Ph$_3$(Me)PI, NaHMDS, 0°, 1 h; 80%. *b*) Bu$_4$NF, THF, r.t., 2 h; 88%. *c*) TEMPO, BAIB, MeCN/H$_2$O 1:1; 78%.

The esterification of **3** and **4** with olefinic alcohol **5** under *Yamaguchi* reaction conditions [17] (2,4,6-trichlorobenzoyl chloride) gave compounds **22** and **23** in 80% yield (*Scheme 4*). The RCM reaction [18] of bis-olefins **22** and **23** with *Grubbs* second-generation catalyst (**B**; 10 mol-%) afforded the penultimate compounds **24** and **25** [4], respectively, in 65% yield, which after deprotection of the acetonide with CF$_3$COOH gave target molecules **1** and **2** in good yield (70%). The prepared synthetic multiplolide A (**1**) and its diastereoisomer **2** were identical (IR, ^{1}H- and ^{13}C-NMR, and MS) with the natural product and its diastereoisomer and also had optical rotations ($[\alpha]_D^{25} = +25.8$ ($c = 0.4$, CHCl$_3$) for **1** and $[\alpha]_D^{25} = -12.1$ ($c = 0.59$, CHCl$_3$) for **2**) in good agreement with the literature values ($[\alpha]_D^{25} = +22.6$ ($c = 0.3$, CHCl$_3$) for **1** and $[\alpha]_D^{25} = -11.8$ ($c = 0.5$, CHCl$_3$) for **2** [4]).

Scheme 4



a) 2,4,6-Trichlorobenzoyl chloride, THF, Et_3N, r.t.,6 h, DMAP, toulene, r.t., 14 h; 80%. *b*) 2nd-Generation *Grubbs* catalyst (**B**), benzene, reflux 2 h; 65%. *c*) CF_3COOH, CH_2Cl_2, r.t., 10 h; 70%.

In summary, a new stereoselective total synthesis of multiplolide A (**1**) and its diastereoisomer **2** was achieved from inexpensive and commercially available starting materials. The synthesis is highlighted by *Jacobsen* resolution, *Sharpless* epoxidation, *Swern* oxidation, *Yamaguchi* reaction, and RCM reactions as key steps.

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Experimental Part

General. All reactions were carried out without any special precautions in an atmosphere of air. Chemicals were purchased from *Fluka* and *S. D. Fine Chemicals*. TLC: precoated silica gel plates *60 F_{254}* (SiO_2, 0.2 mm layer; *Merck*). Column chromatography (CC): SiO_2 60–120 mesh (*Merck*) ^{1}H-NMR Spectra: *Varian-200* or *Bruker-300* spectrometer; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. MS: *VG Autospec*; in *m*/*z*.

*Ethyl (5*R*)-5-Hydroxyhex-2-ynoate* (**10**) [7]. A soln. of **9** (6.3 g, 64.2 mmol) in dry THF (100 ml) was stirred at $-78°$, then 1.6M BuLi in hexane (40.0 ml, 64.2 mmol) was added, and the mixture was stirred for 30 min at $-78°$. $BF_3 \cdot Et_2O$ (8.2 ml, 64.2 mmol) was added followed by a soln. of **8** (2.5 g, 43.0 mmol) in dry THF (20 ml) and stirred at $-78°$ for 2 h. The reaction was quenched by sat. aq. NH_4Cl soln. and extracted with Et_2O. The org. layer was washed with brine, dried (Na_2SO_4), and concentrated and the residue purified by CC (SiO_2, 10% AcOEt/hexane): **10** (8.11 g, 81%). $[\alpha]_D^{25} = -9.85$ ($c = 3.05$, $CHCl_3$). IR(KBr): 3457, 2954, 2858, 1738, 1254, 1118. ^{1}H-NMR (300 MHz): 1.06–1.22 (*m*, 6 H); 2.30–2.41 (*m*, 2 H); 3.82–3.96 (*m*, 1 H); 3.99–4.14 (*m*, 2 H). ^{13}C-NMR (75 MHz): 13.4; 21.9; 28.3; 61.5; 65.0; 74.1; 86.2; 153.4. ESI-MS: 156 (M^+). ESI-HR-MS: 156.1818 ($C_8H_{12}O_3^+$; calc. 156.1814).

*(2*E,*5*R*)-Hex-2-ene-1,5-diol* (**11**) [8]. To a stirred soln. of $LiAlH_4$ (5.4 g, 143 mmol) in dry THF (130 ml) at 0°, **10** (10.14 gm, 65 mmol) was added dropwise in THF (130 ml) for 10 min. Then, the temp. was increased to r.t. and then to reflux for 2 h. The reaction was quenched by ice and sat. aq. Na_2SO_4 soln. the mixture and stirred for 1 h at r.t. The mixture was filtered through *Celite*, the *Celite* washed with MeOH, the combined org. layer concentrated, and the residue purified by CC (SiO_2, 70% AcOEt/hexane): **11** (5.88 g, 78%). $[\alpha]_D^{25} = -11.8$ ($c = 1.6$, $CHCl_3$). IR (KBr): 3417, 2925, 1646, 1545, 1235. ^{1}H-NMR (300 MHz): 1.19 (*d*, $J = 6.04$, 3 H); 2.00–2.30 (*m*, 2 H); 3.80–3.84 (*m*, 1 H); 4.10 (*d*, $J = 3.77$,

2 H); 5.68–5.70 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 25.2; 44.2; 66.2; 70.3; 128.7; 129.3. ESI-MS: 139 ($[M+Na]^+$). ESI-HR-MS: 139.1492 ($C_6H_{12}O_2Na^+$; calc. 139.1498).

*(2*E*,5*R*)-5-{[(1,1-Dimethylethyl)diphenylsilyl]oxy}hex-2-en-1-ol* (**12**) [8]. To a stirred soln. of **11** (5.3 g, 45.68 mmol) in CH_2Cl_2 (182 ml), Et_3N (13.88 ml, 100.5 mmol), DMAP (cat.), and pivaloyl chloride (5.3 ml, 45.68 mmol) were sequentially added at 0° and stirred at r.t. for 1 h. The mixture was diluted with H_2O (30 ml) and extracted with AcOEt (4 × 25 ml). The combined org. layer was washed with brine (20 ml), dried (Na_2SO_4), and concentrated and the residue purified by CC (SiO_2 20% AcOEt/hexane): primary-alcohol-protected pivaloyl compound (7.4 g, 81%). IR (KBr): 3404, 3067, 2957, 2929, 2858, 1692, 1604, 1258. ^{1}H-NMR (300 MHz): 1.18 (*d*, *J* = 6.04, 3 H); 1.17 (*s*, 9 H); 2.01–2.25 (*m*, 2 H); 3.78 (*sext.*, *J* = 6.04, 1 H); 4.50 (*d*, *J* = 6.04, 2 H); 5.53–5.80 (*m*, 2 H). ^{13}C-NMR (75 MHz): 22.9; 27.3; 38.7; 42.2; 64.6; 66.9; 127.6; 131.3; 177.8. ESI-MS: 223 ($[M+Na]^+$).ESI-HR-MS: 223.2678 ($C_{11}H_{20}O_3Na^+$; calc. 223.2677).

To a stirred soln. of this pivaloyl compound (5.6 g, 28 mmol) in CH_2Cl_2 (112 ml), 1*H*-imidazole (4.0 gm, 61.6 mmol) and ^{t}BuPh$_2$SiCl (8.46 g, 30.8 mmol) were subsequently added at 0° and stirred at r.t. for 30 min. The mixture was diluted with H_2O and extracted with AcOEt (4 × 20 ml). The combined org. layer was washed with brine, dried (Na_2SO_4), and concentrated and the residue purified by CC (SiO_2, AcOEt/hexane): secondary-alcohol-protected ^{t}BuPh$_2$Si compound (11.16 g, 91%). Liquid. $[\alpha]_D^{25} = +20.1$ (*c* = 2.0, $CHCl_3$). IR (KBr): 3069, 2928, 2857, 1679, 1222, 1102. ^{1}H-NMR (300 MHz): 1.04 (*s*, 9 H); 1.18 (*s*, 9 H); 1.27 (*d*, *J* = 9.82, 3 H); 2.15–2.22 (*m*, 2 H); 3.80–3.97 (*m*, 1 H); 4.42 (*d*, *J* = 5.85, 2 H); 5.40–5.53 (*m*, 1 H); 5.59–5.72 (*m*, 1 H); 7.28–7.42 (*m*, 6 H); 7.60–7.67 (*m*, 4 H). ^{13}C-NMR (75 MHz): 19.2; 22.9; 27.0; 27.1; 38.8; 42.3; 64.8; 69.0; 126.4; 127.4; 127.5; 129.5; 131.5; 135.8; 175.4. ESI-MS: 438 (M^+). ESI-HR-MS: 438.6822 ($C_{27}H_{38}O_3Si^+$; calc. 438.6824).

To a soln. of the above ^{t}BuPh$_2$Si compound (8.7 g, 20 mmol) in MeOH (100 ml) was added K_2CO_3 (3.6 g, 26 mmol) and stirred at r.t. for 10 h. The mixture was then passed through *Celite* and the MeOH evaporated. The residue was extracted with AcOEt (3 × 10 ml), the extract washed with brine (20 ml), dried (Na_2SO_4), and concentrated, and the residue purified by CC (SiO_2, 5% AcOEt/hexane): **12** (6.2 g, 88%). Colorless liquid. $[\alpha]_D^{25} = +42.7$ (*c* = 1.4, $CHCl_3$). IR (KBr): 3463, 3047, 1589, 1470, 1427, 1107. ^{1}H-NMR (300 MHz):1.08 (*d*, *J* = 6.04, 3 H); 1.10 (*s*, 9 H); 2.11–2.23 (*m*, 2 H); 3.82–3.92 (*m*, 1 H); 3.98 (*d*, *J* = 3.58, 2 H); 5.52–5.57 (*m*, 2 H); 7.31–7.45 (*m*, 6 H); 7.62–7.70 (*m*, 4 H). ^{13}C-NMR (75 MHz): 19.2; 23.1; 27.0; 42.2; 63.6; 69.2; 127.4; 129.2; 129.5; 131.3; 134.4; 135.9. ESI-MS: 377 ($[M+Na]^+$). ESI-HR-MS: 377.5547 ($C_{22}H_{30}O_2Na^+Si$; calc. 377.5542).

*(2*R*,3*R*)-3-{(2*R*)-2-{[(1,1-Dimethylethyl)diphenylsilyl]oxy}propyl}oxirane-2-methanol* (*=2,3-Anhydro-4,6-dideoxy-5-*O*-[(1,1-dimethylethyl)diphenylsilyl]-*D*-*arabino*-hexitol*; **7**). To a stirred suspension of activated 4-Å molecular sieves (1.0 g) in CH_2Cl_2 (80 ml) was added (−)-D-DIPT (0.338 ml, 1.3 mmol) and Ti(^{i}PrO)$_4$ (0.316 ml, 0.356 mmol) with stirring, and the resulting mixture was stirred for 30 min at −20°. Then **12** (4.0 g, 11.29 mmol) in dry CH_2Cl_2 (42 ml) was added dropwise, and the resulting mixture was stirred for another 30 min at −20°. ^{t}BuOOH (6.8 ml, 3.0M in toluene, 22.58 mmol) was then added and the resulting mixture stirred at −20° for 8 h. After warming to 0°, the mixture was quenched with H_2O (1 ml) and stirred for 2 h at r.t. Aq. NaOH soln. (30%, sat. with NaCl) was then added and the mixture stirred vigorously for another 30 min at r.t. The mixture was filtered through *Celite*, the filtrate extracted with CH_2Cl_2 (3 × 10 ml), washed with brine, dried (Na_2SO_4), and concentrated, and the residue purified by CC (SiO_2, AcOEt/hexane 0.5:9.5); **7** (3.75 g, 90%). Colorless viscous liquid. $[\alpha]_D^{25} = +23$ (*c* = 0.8, CH_2Cl_2). IR (KBr): 3068, 2926, 2854, 1690, 1602, 1299, 1178. ^{1}H-NMR (300 MHz): 1.05 (*s*, 9 H); 1.14 (*d*, *J* = 6.23, 3 H); 1.58–1.68 (*m*, 1 H); 1.72–1.81 (*m*, 1 H); 2.80–2.85 (*m*, 1 H); 3.05–3.09 (*td*, *J* = 2.33, *J* = 3.11, 1 H); 3.84 (*m*, 1 H); 4.48 (*d*, *J* = 6.23, 2 H); 7.34–7.46 (*m*, 6 H); 7.64–7.70 (*m*, 4 H). ^{13}C-NMR (75 MHz): 21.7; 26.9; 40.9; 52.9; 58.1; 67.3; 70.4; 127.5; 129.5; 129.6; 135.7. EI-MS: 393 ($[M+Na]^+$). ESI-HR-MS: 393.5539 ($C_{22}H_{30}O_3Na^+Si$; calc. 393.553).

*(2*R*,3*R*)-2-{[2*R*)-2-{[1,1-Dimethylethyl)diphenylsilyl]oxy}propyl}-3-ethenyloxirane* (**13**). To a soln. of oxalyl chloride (0.82 ml, 7.5 mmol) in CH_2Cl_2 (10 ml) at −78° was added DMSO (1.13 ml, 16.0 mmol) within 20 min. The resulting mixture was stirred for an additional 15 min. Then **7** (1.85 g, 5 mmol) in CH_2Cl_2 (10 ml) was added dropwise. The mixture was stirred for 30 min, Et_3N (3.47 ml, 25 mmol) was added dropwise, and the mixture was warmed to r.t. for 30 min. After completion of the reaction, the mixture was quenched with H_2O (30 ml) and the aq. phase extracted with CH_2Cl_2

(2×20 ml). The combined org. layer was washed with brine, dried (Na_2SO_4), and concentrated: aldehyde (1.472 g, 80%) as a colorless liquid.

To a soln. of Ph_3(Me)PI (4.84 g, 12.0 mmol) in dry THF (35 ml) was added 1.6M NaHMDS in hexane (7.5 ml) at 0° and stirred for 2 h at 0°. A soln. of the aldehyde (0.560 g, 4.0 mmol) in THF (15 ml) was added *via* cannula to the mixture at 0° and stirred for 30 min. The reaction was quenched with sat. aq. NH_4Cl soln., and the mixture extracted with AcOEt (3×40 ml). The combined org. extract was washed with brine (30 ml), dried (Na_2SO_4), and concentrated, and the residue purified by CC (SiO_2, 5% AcOEt/hexane): **13** (1.17 g, 80%). Yellow syrup. $[\alpha]_D^{25} = +15$ ($c = 0.67$, CH_2Cl_2). IR (KBr): 3029, 2985, 2851, 1555, 1229, 1056. ^{1}H-NMR (300 MHz): 1.06 (*s*, 9 H); 1.15 (*d*, $J = 6.00$, 3 H); 1.61–1.83 (*m*, 2 H); 2.94–3.01 (*m*, 1 H); 3.02 (*d*, $J = 8.00$, 1 H); 4.04–4.11 (*sext.*, $J = 6.00$, 1 H); 5.22–5.28 (*m*, 1 H); 5.41–5.47 (*d*, $J = 16.01$, 1 H); 5.49–5.59 (*m*, 1 H); 7.34–7.47 (*m*, 6 H); 7.64–7.73 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.3; 26.9; 41.4; 57.3; 58.4; 67.4; 119.2; 127.4; 127.5; 129.5; 129.6; 135.8. ESI-MS: 366 (M^+). ESI-HR-MS: 366.5754 ($C_{23}H_{30}O_2Si^+$; calc. 366.5755).

(3S,4R,6R)-6-{[(1,1-Dimethylethyl)diphenylsilyl]oxy}hept-1-ene-3,4-diol (**14**). To a stirred soln. of **13** (1.3 g, 3.36 mmol) in THF/H_2O 10:1 (8 ml) was added $Sc(OTf)_3$ (0.20 equiv., 310 mg, 0.68 mmol), and the mixture was stirred at r.t. for 2.5 h. The resulting diol was extracted with AcOEt (20 ml), the extract washed sequentially with sat. aq. NH_4Cl soln. and brine, dried (Na_2SO_4), and concentrated, and the residue purified by flash chromatography (AcOEt/hexane 2:8): **14** (0.903 g, 70%). Pale yellow syrup. $[\alpha]_D^{25} = -9.0$ ($c = 0.5$, $CHCl_3$). IR (KBr): 3348, 3070, 2961, 2858, 1589, 1467, 1108, 999. ^{1}H-NMR (300 MHz): 1.04 (*s*, 9 H); 1.12 (*d*, $J = 6.0$, 3 H); 1.56–1.78 (*m*, 2 H); 3.84–3.93 (*m*, 1 H); 4.07–4.20 (*m*, 2 H); 5.20–5.35 (*dd*, $J = 10.5$, 17.3, 2 H); 5.77–5.90 (*m*, 1 H); 7.35–7.47 (*m*, 6 H); 7.66–7.77 (*m*, 4 H). ^{13}C-NMR (75 MHz): 19.1; 24.0; 26.8; 40.2; 65.8; 70.4; 75.5; 116.9; 127.5; 127.7; 129.7; 135.9; 136.2. ESI-MS: 407 ($[M + Na]^+$). ESI-HR-MS: 407.5812 ($C_{23}H_{32}O_3Na^+Si$; calc. 407.5805).

(4R,5S)-4-{(2R)-2-{[(1,1-Dimethylethyl)diphenylsilyl]oxy}propyl}-5-ethenyl-2,2-dimethyl-1,3-dioxolane (**15**). To a soln. of **14** (768 mg, 2 mmol) in CH_2Cl_2 (10 ml) was added CSA (cat.) and 2,2-dimethoxypropane (0.96 ml, 6 mmol) at 0°, and the mixture was stirred for 15–20 min. The reaction was quenched with Et_3N (1 or 2 drops), the mixture concentrated, and the residue purified by CC (SiO_2, AcOEt/hexane 0.5:9.5): **15** (0.804 g, 90%). Pale yellow syrup. $[\alpha]_D^{25} = -9.8$ ($c = 0.9$, $CHCl_3$). IR (KBr): 3434, 3081, 2981, 2930, 1642, 1457, 1375, 1217, 1042. ^{1}H-NMR (300 MHz): 1.05 (*s*, 9 H); 1.13 (*d*, $J = 6.0$, 3 H); 1.25 (*s*, 3 H); 1.28 (*s*, 3 H); 1.68–1.90 (*m*, 2 H); 3.93–3.99 (*m*, 1 H); 4.06–4.32 (*m*, 2 H); 5.03–5.34 (*m*, 2 H); 5.56–5.91 (*m*, 1 H); 7.32–7.44 (*m*, 6 H); 7.64–7.75 (*m*, 4 H). ^{13}C-NMR (75 MHz): 19.1; 24.0; 26.9; 29.7; 40.1; 70.5; 75.5; 85.3; 107.3; 117.0; 127.5; 127.7; 129.6; 129.8; 135.8; 136.1. ESI-MS: 447 ($[M + Na]^+$). ESI-HR-MS: 424.2435 ($C_{26}H_{36}O_3Na^+Si$; calc. 424.2433).

(2R,3S)-2-{{[(1,1-Dimethylethyl)diphenylsilyl]oxy}methyl}-3-ethenyloxirane (**18**). To a soln. of oxalyl chloride (1.3 ml, 15 mmol) in CH_2Cl_2 (70 ml) at −78° was added DMSO (1.4 ml, 20 mmol) within 20 min. The mixture was stirred for an additional 15 min. Then **16** (3.42 g, 10 mmol) in CH_2Cl_2 (30 ml) was added dropwise. After 30 min stirring, Et_3N (7 ml, 50 mmol) was added dropwise. The mixture was allowed to warm to r.t. and stirred for 30 min. After completion of the reaction, the mixture was quenched with H_2O (30 ml) and the aq. phase extracted with CH_2Cl_2 (2×30 ml). The combined org. layer was washed with brine, dried (Na_2SO_4), and concentrated: aldehyde (3.06 g, 90%). Colorless liquid.

To a soln. of Ph_3(Me)PI (14.9 g, 54.0 mmol) in dry THF (65 ml) was added a 1.6M NaHMDS in hexane (36 ml) at 0° and stirred for 2 h at 0°. A soln. of the aldehyde (3.06 g, 9.0 mmol) in THF (35 ml) was added *via* cannula at 0° and stirred for 30 min. The reaction was quenched with sat. aq. NH_4Cl soln. and the mixture extracted with AcOEt (3×40 ml). The combined org. layer was washed with brine (30 ml), dried (Na_2SO_4), and concentrated and the residue purified by CC (SiO_2, 10% AcOEt/hexane): **18** (2.43 g, 80%). Yellow syrup. $[\alpha]_D^{25} = +5.9$ ($c = 1.2$, $CHCl_3$). IR (KBr): 3064, 2962, 2931, 1469, 1259, 1103. ^{1}H-NMR (300 MHz): 1.06 (*s*, 9 H); 3.32 (*q*, $J = 5.0$, 1 H); 3.42–3.45 (*m*, 1 H); 3.76 (*d*, $J = 5.0$, 2 H); 5.20 (*d*, $J = 10.0$, 1 H); 5.40 (*d*, $J = 18.0$, 1 H); 5.55–5.61 (*m*, 1 H); 7.45–7.60 (*m*, 6 H); 7.75–7.80 (*m*, 4 H). ^{13}C-NMR (75 MHz): 19.0; 26.7; 56.4; 59.2; 65.9; 119.4; 129.4; 130.9; 134.6; 134.9. ESI-MS: 338 (M^+). ESI-HR-MS: 338.1700 ($C_{21}H_{26}O_2Si^+$; calc. 338.1702).

*(2S,3R)-2-{{[(*tert*-Butyl)diphenylsilyl]oxy}methyl-3-ethenyloxirane* (**19**). As described for **18**: **19**. Liquid. $[\alpha]_D^{25} = -2.3$ ($c = 2.5$, $CHCl_3$). IR (KBr): 3064, 2992, 2931, 1457, 1259, 1105. ^{1}H-NMR (200 MHz):

1.07 (*s*, 9 H); 3.28 (*dd*, *J* = 4.5, 5.2, 1 H); 3.38–3.43 (*m*, 1 H); 3.75 (*d*, *J* = 5.2, 2 H); 5.23 (*dd*, *J* = 1.5, 8.3, 1 H); 5.37 (*dd*, *J* = 1.5, 15.8, 1 H); 5.47–5.60 (*m*, 1 H); 7.32–7.46 (*m*, 6 H); 7.63–7.71 (*m*, 4 H). ^{13}C-NMR (75 MHz): 19.1; 26.8; 56.4; 59.0; 65.9; 119.4; 129.4; 130.9; 134.5; 134.9. ESI-MS: 338 (M^+). ESI-HR-MS: 338.1696 ($C_{21}H_{26}O_2Si^+$; calc. 338.1702).

*(2*R*,3*S*)-3-Ethenyloxirane-2-methanol* (**20**). To **18** (2.028 g, 6 mmol) in dry THF (20 ml) was added 1M Bu_4NF in THF (3.48 ml, 12 mmol), dropwise at 0°, and the mixture was stirred at r.t. for 30 min. H_2O (2 ml) was added and the mixture extracted with AcOEt (2 × 20 ml). The org. layer was washed with brine, dried (Na_2SO_4), and concentrated and the residue purified by CC (SiO_2, AcOEt/hexane 0.5:9.5): **20** (528 mg, 88%). Liquid. $[\alpha]_D^{25} = +8.0$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3433, 3076, 2986, 2871, 1639, 1453, 1379, 1216, 1056, 925, 758. ^{1}H-NMR (200 MHz): 1.27 (*s*, 6 H); 2.20–2.23 (*m*, 2 H); 3.73–3.78 (*m*, 1 H); 3.95–3.99 (*m*, 2 H); 5.05–5.08 (*m*, 2 H); 5.82–5.86 (*m*, 1 H). ^{13}C-NMR (75 MHz): 57.1; 58.1; 60.7; 121.1; 134.5. ESI-MS: 100 (M^+). ESI-HR-MS: 100.1170 ($C_5H_8O_2^+$; calc. 100.1173).

*(2*S*,3*R*)-3-Ethenyloxirane-2-methanol* (**21**). As described for **20**: **21**. Liquid. $[\alpha]_D^{25} = -10.0$ ($c = 0.9$, $CHCl_3$). IR (KBr): 3427, 3011, 1619, 1276, 1041. ^{1}H-NMR (200 MHz): 1.27 (*s*, 6 H); 2.20–2.22 (*m*, 2 H); 3.73–3.77 (*m*, 1 H); 3.95–3.97 (*m*, 2 H); 5.05–5.07 (*m*, 2 H); 5.82–5.88 (*m*, 1 H). ^{13}C-NMR (75 MHz): 55.4; 56.8; 59.4; 122.6; 133.4. ESI-MS: 100 (M^+). ESI-HR-MS: 100.1171 ($C_5H_8O_2^+$; calc. 100.1173).

*(2*S*,3*S*)-3-Ethenyloxirane-2-carboxylic Acid* (**3**). To a vigorously stirred soln. of **20** (400 mg, 4 mmol) in MeCN (4 ml) and H_2O (4 ml) was added TEMPO (0.150 g, 0.8 mmol) and BAIB (3.41 g, 8.8 mmol). Stirring was continued until complete conversion of **20** to **3** (TLC monitoring). The reaction was quenched by sat. aq. $Na_2S_2O_3$ soln. (5 ml), the mixture then extracted with AcOEt (2 × 10 ml), the combined org. layer dried (Na_2SO_4) and concentrated, and the residue purified by CC (SiO_2, AcOEt/hexane 3:7): pure **3** (0.358 g, 78%). Colorless liquid. $[\alpha]_D^{25} = +15.0$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3422, 3006, 1724, 1618, 1570, 1256, 1099. ^{1}H-NMR (300 MHz): 3.65 (*dd*, *J* = 4.0, 5.0, 1 H); 3.72 (*d*, *J* = 5.0, 1 H); 5.47 (*d*, *J* = 10.0, 1 H); 5.67 (*d*, *J* = 18.0, 1 H); 5.80–5.89 (*m*, 1 H). ^{13}C-NMR (75 MHz): 56.5; 58.2; 116.3; 136.1; 174.4. EI-MS: 115 ($[M+1]^+$). ESI-HR-MS: 114.0318 ($C_5H_6O_3^+$; calc. 114.0316).

*(2*R*,3*R*)-3-Ethenyloxirane-2-carboxylic Acid* (**4**). As described for **3**: **4**. Liquid. $[\alpha]_D^{25} = -12.1$ ($c = 0.8$, $CHCl_3$). IR (KBr): 3429, 3016, 1745, 1620, 1496, 1255, 1079. ^{1}H-NMR (300 MHz): 3.52 (*dd*, *J* = 2.2, 4.5, 1 H); 3.72–3.75 (*m*, 1 H); 5.37 (*d*, *J* = 10.5, 1 H); 5.52 (*d*, *J* = 17.3, 1 H); 5.75–5.78 (*m*, 1 H). ^{13}C-NMR (75 MHz): 56.6; 58.6; 116.4; 135.6; 173.4. EI-MS: 115 ($[M+1]^+$). ESI-HR-MS: 114.0321 ($C_5H_6O_3^+$; calc. 114.0316).

*(2*R*)-2-[(4*R*,5*S*)-5-Ethenyl-2,2-dimethyl-1,3-dioxolan-4-yl]-1-methylethyl (2*S*,3*S*)-3-Ethenyloxirane-2-carboxylate* (**22**). To a stirred soln. of **3** (0.114 g, 1 mmol) in dry CH_2Cl_2 (10 ml) were added Et_3N (0.40 g, 2 mmol) and a soln. of 2,4,6-trichlorobenzoyl chloride (0.55 g, 1.5 mmol) in dry CH_2Cl_2 (10 ml) and stirred at 0° for 20 min. A soln. of **5** (0.204 g, 1.1 mmol) in dry CH_2Cl_2 (5 ml) and DMAP (cat.) were added and stirred for 6 h at r.t. After completion of the reaction (TLC monitoring), the solvent was evaporated and the residue purified by CC (SiO_2 (60–120 mesh) 10% AcOEt/hexane): **22** (0.226 g, 80%). Colorless liquid. $[\alpha]_D^{25} = +8.9$ ($c = 0.6$, $CHCl_3$). IR (KBr): 3030, 1714, 1616. ^{1}H-NMR (300 MHz): 1.24 (*d*, *J* = 5.9, 3 H); 1.34 (*s*, 6 H); 1.83–1.87 (*m*, 2 H); 3.67–3.69 (*m*, 1 H); 4.10–4.14 (*m*, 1 H); 4.20–4.22 (*m*, 1 H); 4.50 (*t*, *J* = 6.9, 1 H); 5.05–5.09 (*m*, 1 H); 5.20–5.36 (*m*, 4 H); 5.72–5.83 (*m*, 2 H). ^{13}C-NMR (75 MHz): 21.9; 27.0; 35.6; 56.7; 66.1; 69.9; 85.4; 113.4; 117.0; 118.1; 135.6; 139.2; 172.7. EI-MS: 283 ($[M+1]^+$). ESI-HR-MS: 282.3364 ($C_{15}H_{22}O_5^+$; calc. 282.3366).

*(1*R*)-2-[(4*R*,5*S*)-5-Ethenyl-2,2-dimethyl-1,3-dioxolan-4-yl]-1-methylethyl 3-(2*R*,3*R*)-3-Ethenyloxirane-2-carboxylate* (**23**). As described for **22**: **23**. Liquid. $[\alpha]_D^{25} = -2.1$ ($c = 0.49$, $CHCl_3$). IR (KBr): 3016, 1724, 1612, 1489, 1058. ^{1}H-NMR (300 MHz): 1.27 (*d*, *J* = 6.1, 3 H); 1.33 (*s*, 6 H); 1.75–1.89 (*m*, 2 H); 3.45–3.47 (*m*, 1 H); 4.10–4.12 (*m*, 1 H); 4.19–4.22 (*m*, 1 H); 4.53 (*t*, *J* = 5.2, 1 H); 5.01–5.02 (*m*, 1 H); 5.23–5.36 (*m*, 4 H); 5.68–5.80 (*m*, 2 H). ^{13}C-NMR (75 MHz): 21.7; 26.9; 35.3; 56.8; 66.6; 69.8; 85.2; 113.1; 116.8; 118.0; 135.5; 139.1; 172.4. EI-MS: 283 ($[M+1]^+$). ESI-HR-MS: 282.3360 ($C_{15}H_{22}O_5^+$; calc. 282.3366).

*(1a*S*,4*R*,5a*R*,8a*S*,9*E*,10a*S*)-1a,4,5,5a,8a,10a-Hexahydro-4,7,7-trimethyl-2*H*-[1,3]dioxolo[4,5-g]oxireno[c]oxecin-2-one* (= *(4*E*)-2,3-Anhydro-4,5,8,10-tetradeoxy-6,7-*O*-(1-methylethylidene)*-D-glycero-D-manno-*dec-4-enonic Acid 9-Lactone*; **24**). To a soln. of **22** (0.056 g, 0.2 mmol) in freshly distilled degassed anh. benzene (0.5 ml) was added *Grubbs* second generation catalyst (**B**; 0.017 mg, 0.02 mmol) and stirred at 25° for 2 h under Ar until complete consumption of the starting material (TLC

monitoring). The solvent was evaporated and the brown residue purified by CC (SiO_2, 10% AcOEt/hexane): **24** (33 mg, 65%). Colorless oil. $[\alpha]_D^{25} = +14.6$ ($c = 0.6$, $CHCl_3$). IR (KBr): 3025, 2992, 1757, 1605, 1222, 1128. ^{1}H-NMR (300 MHz): 1.34 (*d*, *J* = 6.0, 3 H); 1.47 – 1.49 (*m*, 6 H); 1.51 – 1.68 (*m*, 2 H); 3.33 (*d*, *J* = 5.2, 1 H); 3.81 – 3.97 (*m*, 2 H); 4.19 – 4.21 (*m*, 1 H); 4.61 – 4.67 (*m*, 1 H); 5.77 (*dd*, *J* = 9.8, 15.8, 1 H); 5.82 (*dd*, *J* = 6.7, 15.8, 1 H). ^{13}C-NMR (75 MHz): 21.6; 26.6; 34.1; 56.9; 57.1; 67.8; 67.9; 85.9; 112.6; 126.6; 129.5; 171.4. ESI-MS: 254 (M^+). ESI-HR-MS: 254.2825 ($C_{13}H_{18}O_5^+$; calc. 254.2829).

*(1a*R*,4*R*,5a*R*,8aS,9*E*,10a*R*)-1a,4,5,5a,8a,10a-Hexahydro-4,7,7-trimethyl-2*H*-[1,3]dioxolo[4,5-*g*]oxireno[*c*]oxecin-2-one* (= *(4*E*)-2,3-Anhydro-4,5,8,10-tetradeoxy-6,7-*O*-(1-methylethylidene)-*D*-glycero-*D*-allo-dec-4-enonic Acid 9-Lactone*; **25**). As described for **24**: **25**. Oil. IR (KBr): 3070, 2999, 1734, 1615, 1479, 1254, 1110, 1025. $[\alpha]_D^{25} = -9.3$ ($c = 0.4$, $CHCl_3$). ^{1}H-NMR (300 MHz): 1.32 (*d*, *J* = 6.9, 3 H); 1.40 – 1.43 (*m*, 6 H); 1.58 – 1.61 (*m*, 2 H); 3.41 (*d*, *J* = 5.7, 1 H); 3.67 – 3.89 (*m*, 2 H); 4.21 – 4.24 (*m*, 1 H); 4.47 – 4.49 (*m*, 1 H); 5.72 (*dd*, *J* = 8.9; 16.1, 1 H); 5.82 (*dd*, *J* = 6.6, 16.1, 1 H). ^{13}C-NMR (75 MHz): 21.0; 26.2; 33.8; 56.8; 57.0; 67.9; 67.6; 85.4; 112.1; 126.0; 129.25; 170.9. ESI-MS: 254 (M^+). ESI-HR-MS: 254.2822 ($C_{13}H_{18}O_5^+$; calc. 254.2829).

Multiplolide A (= *(4*E*)-2,3-Anhydro-4,5,8,10-tetradeoxy*-*D*-glycero-*D*-manno-*dec-4-enonic Acid 9-Lactone*; **1**). To a stirred soln. of **24** (0.025 g, 0.1 mmol) in dry CH_2Cl_2 (2 ml), CF_3COOH (0.10 ml) was added and the mixture stirred for 6 h at 0° (TLC monitoring). The solvent was evaporated and the residue purified by CC (SiO_2, 10% AcOEt/hexane): **1** (0.014 g, 70%). Colorless liquid. $[\alpha]_D^{25} = +25.8$ ($c = 0.4$, $CHCl_3$). IR (KBr): 3425, 3070, 2932, 2858, 1740, 1590, 1467, 1262, 1108, 1045. ^{1}H-NMR (300 MHz): 1.34 (*d*, *J* = 6.9, 3 H); 1.62 – 1.91 (*m*, 2 H); 3.40 (*d*, *J* = 4.6, 1 H); 3.88 – 3.90 (*m*, 1 H); 3.99 – 4.01 (*m*, 1 H); 4.67 – 4.69 (*m*, 1 H); 5.07 – 5.10 (*m*, 1 H); 5.66 (*dd*, *J* = 1.1, 15.8, 1 H); 5.90 (*dd*, *J* = 2.2, 15.8, 1 H). ^{13}C-NMR (75 MHz): 20.5; 35.1; 53.7; 55.1; 67.7; 68.2; 72.1; 117.9; 135.1; 169.1. ESI-MS: 214 (M^+). ESI-HR-MS: 214.0837 ($C_{10}H_{14}O_5^+$; calc. 214.0841).

*(4*E*)-2,3-Anhydro-4,5,8,10-tetradeoxy*-*D*-glycero-*D*-alloo-*dec-4-enonic Acid 9-Lactone* (**2**). As described for **1**: **2**. Liquid. $[\alpha]_D^{25} = -12.1$ ($c = 0.59$, $CHCl_3$). IR (KBr): 3425, 3070, 2932, 2858, 1740, 1590, 1467, 1262, 1108, 1045. ^{1}H-NMR (300 MHz): 1.37 (*d*, *J* = 6.7, 3 H); 1.81 – 1.83 (*m*, 2 H); 3.30 – 3.33 (*m*, 1 H); 3.88 – 3.89 (*m*, 1 H); 3.99 (*dd*, *J* = 2.1, 6.7, 1 H); 4.51 – 4.54 (*m*, 1 H); 5.05 – 5.08 (*m*, 1 H); 5.72 (*dd*, *J* = 2.1, 16.0, 1 H); 5.89 (*dd*, *J* = 1.7, 16.0, 1 H). ^{13}C-NMR (75 MHz): 21.2; 35.0; 53.3; 54.7; 67.4; 68.1; 72.0; 117.7; 135.3; 170.0. ESI-MS: 214 (M^+). ESI-HR-MS: 214.0834 ($C_{10}H_{14}O_5^+$; calc. 214.0841).

REFERENCES

[1] G. Rousseau, *Tetrahedron* **1995**, *51*, 2777; L. S. Longo Jr., F. I. Bombonato, H. M. C. Ferraz, *Quim. Nova* **2007**, *30*, 415; I. Shiina, *Chem. Rev.* **2007**, *107*, 239; H. M. C. Ferraz, F. I. Bombonato, M. K. Sano, L. S. Longo Jr., *Quim. Nova* **2008**, *31*, 885.

[2] G. Dräger, A. Kirschning, R. Thiericke, M. Zerlin, *Nat. Prod. Rep.* **1996**, *13*, 365; M. C. Ferraz, F. I. Bombonato, L. S. Longo Jr., *Synthesis* **2007**, 3261; V. B. Riatto, R. A. Pilli, M. M. Victor, *Tetrahedron* **2008**, *64*, 2279.

[3] S. Boonphong, P. Kittakoop, M. Isaka, D. Pittayakhajonwut, M. Tantichareon, Y. Thebtaranonth, *J. Nat. Prod.* **2001**, *64*, 965.

[4] C. V. Ramana, T. P. Khaladkar, S. Chatterjee, M. K. Gurjar, *J. Org. Chem.* **2008**, *73*, 3817.

[5] B. C. Reddy, H. M. Meshram, *Tetrahedron Lett.* **2010**, *51*, 4020; P. Ramesh, H. M. Meshram, *Tetrahedron Lett.* **2011**, *52*, 2443; H. M. Meshram, D. A. Kumar, P. Ramesh, *Helv. Chim. Acta* **2010**, *93*, 1422.

[6] S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, *124*, 1307; L. J. Theodore, W. L. Nelson, *J. Org. Chem.* **1987**, *52*, 1309.

[7] N. P. H. Tan, C. D. Donner, *Tetrahedron* **2009**, *65*, 4007.

[8] T.-L. Wang, X. E. Hu, J. M. Cassady, *Tetrahedron Lett.* **1995**, *36*, 9301; D. K. Reddy, V. Shekhar, P. Prabhakar, D. C. Babu, D. Ramesh, B. Siddhardha, U. S. N. Murthy, Y. Venkateswarlu, *Bioorg. Med. Chem. Lett.* **2011**, *21*, 997.

[9] T. Katsuki, K. B. Sharpless, *J. Am. Chem. Soc.* **1980**, *102*, 5974; Y. Gao, J. M. Klunder, R. M. Hanson, H. Masamune, S. Y. Ko, K. B. Sharpless, *J. Am Chem. Soc.* **1987**, *109*, 5765; B. Tirupathi, R. R. Gundapaneni, D. K. Mohapatra, *Synlett* **2011**, 2667.
[10] T. Mukaiyama, H. Arai, I. Shiina, *Chem. Lett.* **2000**, *5*, 580.
[11] E. J. Corey, A. Martaf, B. C. Laguzza, *Tetrahedron Lett.* **1981**, *22*, 3339; R. M. Garbaccio, S. J. Stachel, D. K. Baeschlin, S. J. Danishefsky, *J. Am. Chem. Soc.* **2001**, *123*, 10903.
[12] P.-Y. Dakas, R. Jogireddy, G. Valot, S. Barluenga, N. Winssinger, *Chem. – Eur. J.* **2009**, *15*, 11490.
[13] R. M. Garbaccio, S. J. Danishefsky, *Org. Lett.* **2000**, *2*, 3127.
[14] T. Katsuki, V. S. Martin, *Org. React.* **1996**, *48*, 1 – 300; C. Bonini, R. D. Fabio, *Tetrahedron Lett.* **1988**, *29*, 815; T. Ayad, Y. Génnison, M. Baltas, *Org. Biomol. Chem.* **2005**, *3*, 2626; F. Yakushiji, J. Maddaluno, M. Yoshida, K. Shisshido, *Tetrahedron Lett.* **2009**, *50*, 1504.
[15] D. Diez, A. B. Anton, J. Perna, P. Garcia, N. M. Garrido, I. S. Marcos, F. Sanz, P. Basabe, J. G. Urones, *Tetrahedron: Asymmetry* **2010**, *21*, 786; V. Jäger, D. Schröter, B. Koppenhoefer, *Tetrahedron* **1991**, *47*, 2195.
[16] J. B. EPP, T. S. Widlanski, *J. Org. Chem.* **1999**, *64*, 293.
[17] J. Inanga, K. Hirata, H. Saeki, T. Katsuki, M. Yamaguchi, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1989; T. Okino, S. Qi, H. Matsuda, M. Murakami, K. Yamaguchi, *J. Nat. Prod.* **1997**, *60*, 158.
[18] D. K. Mohapatra, D. K. Ramesh, M. A. Giardello, M. S. Chorghade, M. K. Gurjar, R. H. Grubbs, *Tetrahedron Lett.* **2007**, *48*, 2621; T. Mahapatra, T. Das, S. Nanda, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 511.

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