154. Asymmetric Dihydroxylations of β-Substituted *N*-(α,β-Enoyl)bornane-10,2-sultams

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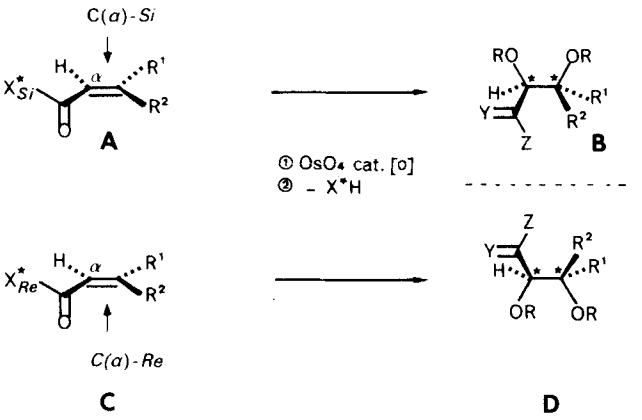
Pure (*E*)- or (*Z*)-enoylsultams **2** were oxidized with OsO_4/*N*-methylmorpholine *N*-oxide in a stereospecific and highly π-face-selective manner. Acetalization of the resulting 1,2-diols furnished, after purification, the stable, crystalline acetals **6** in > 99% d.e. and in 63–74% overall yield from **2**. Reductive or hydrolytic cleavage of **6** gave enantiomerically pure alcohols **8** or carboxylic acids **9** with recovery of the sultam auxiliary **1**.

Introduction. – Stoichiometric or catalytic oxidations of olefins by OsO_4 provide a reliable and stereospecific route to vicinal diols [1]. Asymmetric versions of this process deserve particular attention considering the value of enantiomerically and diasteroisomerically pure diol derivatives **B** and **D** as building blocks for syntheses of polyoxygenated compounds. Promising π-face differentiations have already been achieved by osmylations of either prochiral alkenes in the presence of chiral ligands [2] or of olefinic bonds attached to a removable chiral auxiliary [3][4]. As a follow-up of preliminary reports [5][6], we describe here a practical C(α)-*Re*-face-selective dihydroxylation of β-substituted enoyl derivatives **C**→**D** which complements the existing methodology.

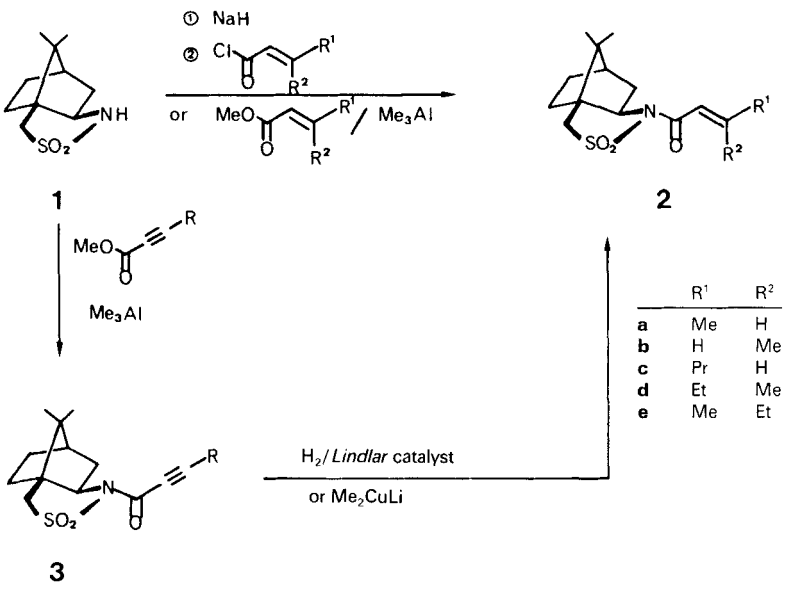
Exploiting the topological bias of the sultam chirophor **1** ($X^*_{Re}H$) [6] and taking into account that both enantiomers of **1** are readily and commercially available, both topicities C(α)-*Si* and C(α)-*Re* can be efficiently achieved (*cf.* **A**→**B** and **C**→**D**, respectively; *Scheme 1*).

Scheme 1



Preparation and Dihydroxylation of *N*-Enoylsultams 2. – Sultam **1** was conveniently acylated by treatment with either NaH and enoyl chlorides or with methyl enoates/Me_3Al to give enoylsultams **2** in good yields. The latter, also available *via* the alkynoylsultams **3** by partial hydrogenation (→**2b**) or 1,4-addition of Me_2CuLi (→**2e**), were easily purified by crystallization *(Scheme 2)*.

Scheme 2



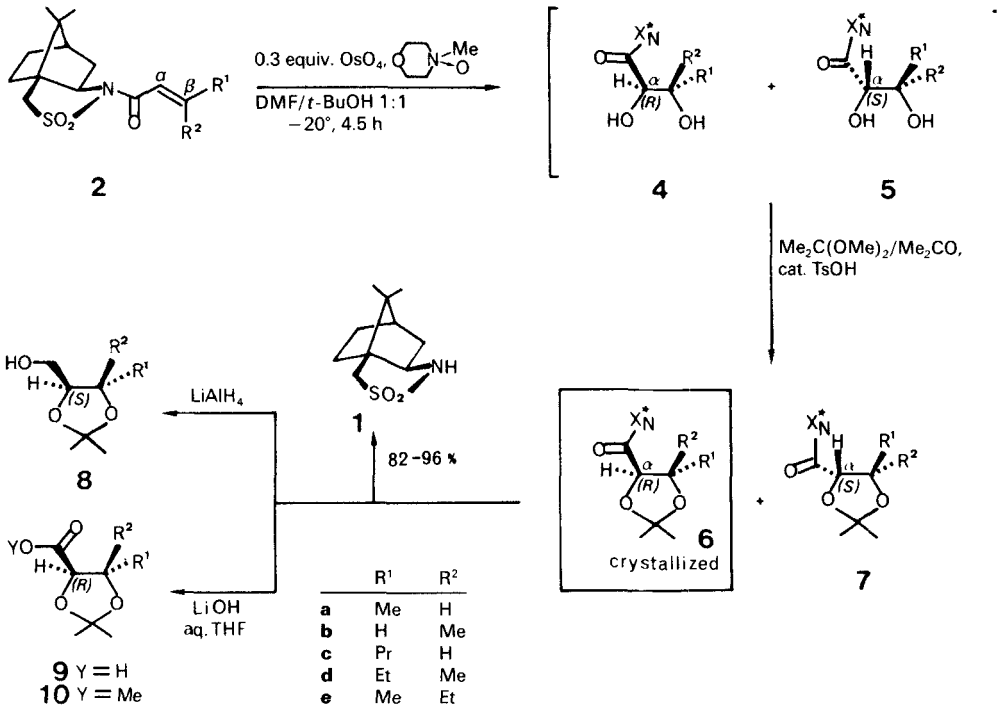
Oxidation of the β-substituted (α,β-enoyl)sultams **2** with OsO_4 (0.3 mol-equiv., DMF/*t*-BuOH, −20°, 5 h) in the presence of *N*-methylmorpholine *N*-oxide monohydrate (2 mol-equiv.) provided glycols **4/5** which were converted ($Me_2C{=}O/Me_2C(OMe)_2$ 1:1, cat. TsOH) to the corresponding dimethyl acetals **6/7** *(Scheme 3, Table)*.

The reaction mixtures were directly analyzed by capillary GC showing product ratios **6/7** of 90:10 to 95:5. Analogous osmylations of **2** using trimethylamine *N*-oxide as a secondary oxidant [1] proceeded slower to furnish similar ratios of diasteroisomers **6/7**. Facile separation of the latter by flash chromatography *(Entries a, c–e)* or crystallization *(Entry b)* gave the crystalline major products **6** in > 99% d.e. (63–79% yields from **2**). Depending on the (*E*/*Z*)-configuration of the enoylsultam **2**, the formation of a tertiary

Table. *Asymmetric Dihydroxylations/Acetalizations* **2**→**4/5**→**6/7**

Entry	R^1	R^2	Yield [%] **6/7** (crude)	Ratio **6/7** (crude)	Yield [%] **6** (pure)	d.e. [%] **6** (pure)
a	Me	H	84	90 :10	74	> 99
b	H	Me	90	91 : 9	66	> 99
c	Pr	H	89	91.5: 8.5	79	> 99
d	Et	Me	78	95 : 5	63	> 99
e	Me	Et	78	90 :10	67	> 99

Scheme 3



or quaternary center at C(β) could be directed in either sense with comparable selectivity *(cf. Entries a/b, d/e)*. Reductive ($LiAlH_4$, THF) or hydrolytic (LiOH, aq. THF, r.t.) cleavage of **6** regenerated the sultam **1** (82–96%) and gave enantiomerically pure alcohols **8** (75–82%) or carboxylic acids **9** (92–94%), respectively. The absolute configurations of **8** and **9** were assigned by comparing their optical rotations with values reported in the literature.

To explain the observed π-face differentiations we postulate a reactive conformation *(Scheme 4)* of **2** featuring a *'syn'*-orientation of the C=O and SO_2 groups, s-*cis*-related C=O/C(α)–C(β) bonds, and an approach of the reagent from the less hindered C(α)-*Re* (bottom) face[1]). Such a conformation would suffer from repulsion between an α-substituent and the bornane skeleton. It was, therefore, not unexpected that tigloylsultam **11** underwent analogous osmylation much slower with low (*ca.* 20% d.e.) π-facial selectivity to give after acetalization a mixture of products **12** and **13**[2]).

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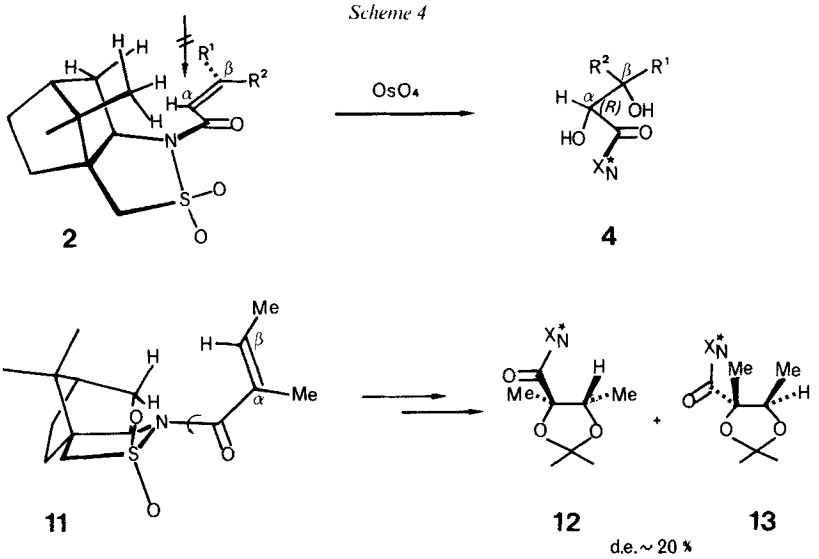
[1]) The postulated *'syn'*-disposition of the C=O and SO_2 groups may be due to a chelation by an Os-atom. An alternative explanation for the observed π-facial discrimination implies a conformation of **2** with *'anti'*-disposed C=O and SO_2 groups, s-*cis*-related C=O/C(α)–C(β) bonds and a stereoelectronically controlled attack by OsO_4 from the top face.

[2]) For presumably similar reasons catalytic hydrogenations [7] or 1,4-hydride additions [8] of *N*-(α,β-enoyl)bornane-10,2-sultams showed π-face differentiations to depend significantly on the presence or absence of a substituent at C(α). In contrast, tiglate esters of chiral secondary alcohols could be dihydroxylated with up to 67% stereoface selectivity consistent with the s-*trans*-relation of C=O/C(α)–C(β) bonds [4].

Scheme 4



Conclusion. – We conclude that the described asymmetric dihydroxylations of enoyl derivatives **2** exemplify the general advantages associated with the sultam chirophor **1** [6]. The preparative value of this methodology is highlighted by the demonstrated potential of acetals **8** and **9** (as well as of their antipodes) as intermediates for the syntheses of enantiomerically pure deoxy- [9] and amino-sugars [10] (*e.g.* daunosamine, acosamine), of (–)-viridofloric acid [11], (–)-dihydromahubanolide B [12], biopterin [13], *Scolytus-multistriatus* pheromone [14], fungal metabolite LLP-880β [15], and α,β-dihydroxy-methylvaleric acid [16].

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Experimental Part

General. All reactions were carried out under Ar with magnetic stirring, unless otherwise specified. Solvents were dried by distillation from drying agents as follows: Et_2O; THF (Na); toluene (K); *t*-BuOH *(Fluka)* was stirred in the presence of $KMnO_4$ at r.t. for 2 d, filtered, and distilled over $KMnO_4$. CuI was purified by continuous extraction with THF over 48 h using a *Soxhlet* extractor in the dark. 'Workup' denotes extraction with an org. solvent, washing of the org. phase with sat. aq. NaCl soln., drying ($MgSO_4$), and removal of solvent by distillation *in vacuo* using a rotatory evaporator. Column flash chromatography (FC): SiO_2 *(Merck 9385)*. GC: *Hewlett-Packard 5790A*, integrator *HP 3390*, capillary column (fused silica, 0.2 mm i.d. 12 m), *OV-1*, 10 psi H_2, unless otherwise specified; t_R in min (area %). M.p.: *Kofler* hot stage; uncorrected. [α]: *Perkin-Elmer-241* polarimeter; in $CHCl_3$, unless otherwise specified; IR: *Perkin-Elmer 257*, $CHCl_3$ unless otherwise specified. ^{1}H-NMR at 360 MHz, unless otherwise specified; ^{13}C-NMR at 50 MHz, unless otherwise specified; standard TMS (= 0 ppm); *J* in Hz. MS: *m/z* (rel. %).

Preparation of *N*-Enoylsultams 2. – *(2R)-Bornane-10,2-sultam* (**1**). Auxiliary **1** was prepared from (+)-(1*S*)-camphor-10-sulfonyl chloride following the procedure described for the preparation of its antipode [17]. M.p. 182–184°. $[\alpha]_D = -31.3°$, $[\alpha]_{578} = -32.8°$, $[\alpha]_{546} = -37.6°$, $[\alpha]_{436} = -66.2°$, $[\alpha]_{365} = -109.3°$ ($c = 1.00$, $T = 22°$). IR, ^{1}H-NMR, and MS: identical to those reported for the antipode [17].

N-[(E)-2-Butenoyl]bornane-10,2-sultam (**2a**). A soln. of **1** (2.25 g, 10.5 mmol) in toluene (25 ml) was added dropwise at r.t. to a stirred suspension of NaH (55–60% dispersion in mineral oil, 0.685 g, 15.8 mmol). After 30 min, a soln. of (*E*)-crotonoyl chloride (1.296 g, 12.4 mmol) in toluene (5 ml) was added slowly and the mixture was stirred at r.t. for 90 min. Addition of ice water (30 ml), extraction of the aq. phase with AcOEt, drying of the combined org. phases ($MgSO_4$), evaporation, and chromatography (hexane/AcOEt 7:3), and crystallization from MeOH gave **2a** (2.40 g, 81%). GC (150°→10°/min→270°): 5.0. M.p. 186–187°. $[\alpha]_D = -99.5°$, $[\alpha]_{578} = -104.0°$, $[\alpha]_{546} = -118.7°$, $[\alpha]_{436} = -209.7°$, $[\alpha]_{365} = -369.0°$ (*c* = 1.04, *T* = 22°). IR: 2960, 1685, 1643, 1335, 1295, 1260, 1230, 1210, 1135. ^{1}H-NMR: 0.98 (*s*, 3 H); 1.18 (*s*, 3 H); 1.3–1.4 (2 H); 1.8–2.0 (6 H); 2.05–2.2 (2 H); 3.45 (*d*, *J* = 13.5, 1 H); 3.52 (*d*, *J* = 13.5, 1 H); 3.95 (*dd*, *J* = 5, 7.5, 1 H); 6.61 (*dq*, *J* = 15, 2, 1 H); 7.11 (*sext.*, *J* = 7, 1 H). ^{13}C-NMR: 164.0 (*s*); 145.94 (*d*); 122.42 (*d*); 65.14 (*d*); 53.17 (*t*); 48.44 (*s*); 47.77 (*s*); 44.75 (*d*); 38.52 (*t*); 32.87 (*t*); 26.50 (*t*); 20.81 (*q*); 19.88 (*q*); 18.26 (*q*). MS: 283 (3, $C_{14}H_{21}NO_3S^+$), 204 (10), 134 (8), 69 (100), 41 (25). HR-MS: 283.1244 ($C_{14}H_{21}NO_3S^+$, calc. 283.1242).

N-[(E)-2-Hexenoyl]bornane-10,2-sultam (**2c**). Oxalyl chloride (7.425 g, 60 mmol) was added dropwise to a soln. of (*E*)-2-hexenoic acid (3.40 g, 30 mmol) in Et_2O (10 ml). Stirring of the mixture for 14 h at r.t., evaporation of Et_2O, and distillation of the residue furnished (*E*)-2-hexenoyl chloride (3.58 g, 90%). Following the procedure described for **2a**, acylation of **1** (2.00 g, 9.3 mmol) with (*E*)-2-hexenoyl chloride (1.54 g, 11.7 mmol) followed by crystallization (hexane) furnished **2c** (2.18 g, 75%). GC (200°): 4.23. M.p. 96–97°. $[\alpha]_D = -93.82°$, $[\alpha]_{578} = -97.97°$, $[\alpha]_{546} = -111.86°$, $[\alpha]_{436} = -198.15°$, $[\alpha]_{365} = -349.60°$ (*c* = 4.125, $CHCl_3$, *T* = 20°). IR: 2960, 2880, 1685, 1640, 1460, 1335, 1270, 1120, 1060, 980. ^{1}H-NMR: 0.94 (*t*, *J* = 7.5, 3 H); 0.98 (*s*, 3 H); 1.19 (*s*, 3 H); 1.3–1.45 (2 H); 1.52 (*sext.*, *J* = 7.5, 2 H); 1.8–2.0 (3 H); 2.05–2.2 (2 H); 2.23 (*dq*, *J* = 1, 7.5, 2 H); 3.42 (*d*, *J* = 14, 1 H); 3.50 (*d*, *J* = 14, 1 H); 3.92 (*dd*, *J* = 5, 7.5, 1 H); 6.55 (*dt*, *J* = 15.5, 1.5, 1 H); 7.07 (*dt*, *J* = 15.5, 7.5, 1 H). ^{13}C-NMR: 164.09 (*s*); 150.62 (*d*); 120.93 (*d*); 65.06 (*d*); 53.09 (*t*); 48.40 (*s*); 47.73 (*s*); 44.67 (*d*); 38.48 (*t*); 34.46 (*t*); 32.79 (*t*); 26.45 (*t*); 21.25 (*t*); 20.84 (*q*); 19.85 (*q*); 13.65 (*q*). MS: 311 (6, $C_{16}H_{25}NO_3S^+$), 204 (40), 97 (100), 68 (12), 55 (100). HR-MS: 311.1544 ($C_{16}H_{25}NO_3S^+$, calc. 311.1555).

Methyl (E)-3-Methyl-2-pentenoate. At −40°, 0.9N EtLi in Et_2O (42 ml, 37.8 mmol) was added dropwise over 15–20 min to a suspension of CuI (7.18 g, 37.8 mmol) in THF (120 ml). Stirring of the mixture at −40° for 30 min followed by slow addition of a soln. of methyl 2-butynoate (3.37 g, 34 mmol; over 1 h using a syringe pump) in THF (10 ml) at −78°, stirring at −78° for another 90 min, addition of MeOH (2 ml), warming up to −20°, addition of sat. aq. $(NH_4)_2SO_4$ soln. (5 ml), filtration through *Celite*, extraction of the aq. phase with Et_2O, washing of the combined org. phases with 25% aq. NH_3 and aq. sat. NaCl soln., drying ($MgSO_4$), evaporation, and bulb-to-bulb-distillation of the residue furnished methyl (*E*)-3-methyl-2-pentenoate (3.49 g, 79%). B.p. (bath) 95–105°/12 Torr. GC (5 psi, 50°): 4.57 (95%). ^{1}H-NMR: 1.08 (*t*, *J* = 7.5, 3 H); 1.57 (*d*, *J* = 1, 3 H); 2.16 (*q*, *J* = 7.5, 2 H); 3.69 (*s*, 3 H); 5.67 (*s*, 1 H). MS: 128 (60, $C_7H_{12}O_2^{+\cdot}$), 114 (22), 97 (100), 81 (13), 69 (27), 59 (15), 53 (13).

(E)-3-Methyl-2-pentenoic Acid. A mixture of methyl (*E*)-3-methyl-2-pentenoate (1.28 g, 10 mmol), NaOH (16.5 mmol), $NaHCO_3$ (1.65 mmol), MeOH (5 ml), and H_2O (11 ml) was stirred at r.t. for 20 h. Acidification of the mixture with 2N H_2SO_4 to pH 2–3, extraction with AcOEt and workup yielded (*E*)-3-methyl-2-pentenoic acid (1.11 g, 97%). M.p. 44–45°. IR: 3000, 1690, 1650, 1425, 1380, 1300, 1260, 1175, 1120, 1075, 870. ^{1}H-NMR: 1.08 (*t*, *J* = 7.5, 3 H); 2.19 (*q*, *J* = 7.5, 2 H); 2.15 (*s*, 3 H); 5.67 (*s*, 1 H). MS: 114 (77, $C_6H_{10}O_2^{+\cdot}$), 99 (50), 85 (15), 81 (23), 69 (61), 41 (100).

N-[(E)-3-Methyl-2-pentenoyl]bornane-10,2-sultam (**2d**). Following the procedure described for **2c**, (*E*)-3-methyl-2-pentenoic acid was converted into its acyl chloride which served to acylate **1** (860 mg, 4.0 mmol) to give, after crystallization (hexane), **2d** (720 mg, 58%). GC (180°): 7.10. M.p. 96–97°. $[\alpha]_D = -80.0°$, $[\alpha]_{578} = -83.3°$, $[\alpha]_{546} = -94.3°$, $[\alpha]_{436} = -155.6°$, $[\alpha]_{365} = -243.2°$ (*c* = 0.664, *T* = 20°). IR: 2970, 2880, 1680, 1630, 1330, 1270, 1130, 1060, 1040, 1030, 990. ^{1}H-NMR: 0.97 (*s*, 3 H); 1.10 (*t*, *J* = 7.5, 3 H); 1.20 (*s*, 3 H); 1.25–1.5 (2 H); 1.8–2.0 (3 H); 2.05–2.2 (2 H); 2.17 (*d*, *J* = 1.8, 3 H); 2.24 (*q*, *J* = 7.5, 2 H); 3.45 (*d*, *J* = 14, 1 H); 3.52 (*d*, *J* = 14, 1 H); 3.94 (*dd*, *J* = 7.5, 5.0, 1 H); 6.35 (*q*, *J* = 1.8, 1 H). ^{13}C-NMR (50 MHz): 164.62 (*s*); 163.90 (*s*); 114.46 (*d*); 64.99 (*d*); 53.08 (*t*); 48.09 (*s*); 47.68 (*s*); 44.64 (*d*); 38.64 (*t*); 34.06 (*t*); 32.79 (*t*); 26.50 (*t*); 20.79 (*q*); 19.84 (*q*); 19.79 (*q*); 11.80 (*q*). MS: 311 (0.43, $C_{16}H_{25}NO_3S^+$), 98 (12), 97 (100), 69 (10). HR-MS: 311.1552 ($C_{16}H_{25}NO_3S^+$, calc. 311.1555).

N-(2-Butynoyl)bornane-10,2-sultam (**3**, R = Me). A 2M soln. of Me_3Al in hexane (5.5 ml, 11 mmol) was added dropwise to a soln. of **1** (2.15 g, 10 mmol) in toluene (20 ml). Stirring of the mixture for 20 min followed by addition of methyl tetrolate (1.5 ml, 15 mmol), heating of the mixture at 60° for 20 h, careful hydrolysis with 1N aq. HCl, workup, and crystallization (EtOH) afforded **3** (R = Me; 1.96 g, 70%). GC (150°–10°/min→270°): 5.40. M.p. 185–186°. $[\alpha]_D = -115.9°$, $[\alpha]_{578} = -121.1°$, $[\alpha]_{546} = -138.6°$, $[\alpha]_{436} = -250.2°$, $[\alpha]_{365} = -443.1°$ (*c* = 1.041, *T* = 20°). IR: 3000, 2970, 2920, 2890, 2130, 1660, 1485, 1460, 1395, 1375, 1345, 1300, 1250, 1160, 1140, 1100, 1055, 1000. ^{1}H-NMR: 0.98 (*s*, 3 H); 1.17 (*s*, 3 H); 1.3–1.5 (2 H); 1.85–2.0 (3 H); 2.10 (*m*, 1 H); 2.07 (*s*, 3 H); 2.23 (*m*, 1 H); 3.45 (*d*, *J* = 14, 1 H); 3.52 (*d*, *J* = 14, 1 H); 3.88 (*dd*, *J* = 5, 8, 1 H). ^{13}C-NMR: 149.79 (*s*); 92.31 (*s*); 72.85 (*s*); 64.95

(*d*); 53.03 (*t*); 48.45 (*s*); 47.78 (*s*); 44.82 (*d*); 38.29 (*t*); 32.84 (*t*); 26.41 (*t*); 20.85 (*q*); 19.84 (*q*); 4.24 (*q*). MS: 281 (0.25, $C_{14}H_{19}NO_3S^{+\cdot}$), 134 (10), 108 (7), 93 (7), 79 (7), 67 (100), 55 (7). HR-MS: 281.1102 ($C_{14}H_{19}NO_3S^{+\cdot}$, calc. 281.1085).

N-*[(Z)-2-Butenoyl]bornane-10,2-sultam* (**2b**). A soln. of **3** (R = Me; 2.0 g, 12 mmol) in benzene (60 ml) was stirred under H_2 (1 atm.) in the presence of *Lindlar* catalyst (200 mg). After the uptake of 170 ml of H_2, filtration through *Celite*, evaporation, and medium-pressure chromatography (*LiChroprep Si60*, hexane/AcOEt 4:1) gave pure **2b** (1.27 g, 63%). GC (150°→10°/min→270°): 4.71. M.p. 89–90° (on attempted recrystallization, **2b** underwent partial *cis/trans*-isomerization). $[\alpha]_D = -85.8°$, $[\alpha]_{578} = -89.2°$, $[\alpha]_{546} = -100.8°$, $[\alpha]_{436} = -167.7°$, $[\alpha]_{365} = -267.1°$ (c = 1.868, $CHCl_3$, T = 20°). IR: 2980, 2920, 2880, 1680, 1640, 1440, 1330, 1265, 1230, 1210, 1160, 1130, 1110, 1060, 1035, 985. ^{1}H-NMR: 0.98 (*s*, 3 H); 1.19 (*s*, 3 H); 1.3–1.5 (2 H); 1.8–2.0 (3 H); 2.05–2.25 (4 H); 3.44 (*d*, J = 13, 1 H); 3.50 (*d*, J = 13, 1 H); 3.94 (*dd*, J = 5, 7.5, 1 H); 6.38–6.54 (2 H). ^{13}C-NMR: 164.19 (*s*); 146.64 (*d*); 120.32 (*d*); 64.96 (*d*); 53.07 (*t*); 48.29 (*s*); 47.74 (*s*); 44.67 (*d*); 38.59 (*t*); 32.82 (*t*); 26.52 (*t*); 20.83 (*q*); 19.87 (*q*); 16.17 (*q*). MS: 283 (5, $C_{14}H_{21}NO_3S^{+\cdot}$), 204 (5), 135 (6), 108 (3), 93 (3), 69 (100). HR-MS: 283.1245 ($C_{14}H_{21}NO_3S^{+\cdot}$, calc. 283.1242).

N-*(2-Pentynoyl)bornane-10,2-sultam* (**3**, R = Et). Following the procedure described for **3** (R = Me), treatment of **1** (1.077 g, 5 mmol) with Me_3Al (5.5 mmol) and methyl 2-pentynoate [18] (0.841 g, 7.5 mmol) followed by chromatography and crystallization (hexane/AcOEt 9:1) gave **3** (R = Et; 952 mg, 65%). GC (170°): 9.50. M.p. 123–124°. $[\alpha]_D = -113.0°$. $[\alpha]_{578} = -118.2°$, $[\alpha]_{546} = -135.4°$, $[\alpha]_{436} = -243.6°$, $[\alpha]_{365} = -428.6°$ (c = 1.26, T = 20°). IR: 2990, 2970, 2920, 2890, 2230, 1660, 1460, 1415, 1375, 1345, 1320, 1300, 1290, 1250, 1170, 1145, 1105, 1065, 1055. ^{1}H-NMR: 0.94 (*s*, 3 H); 1.15 (*s*, 3 H); 1.21 (*t*, J = 8, 3 H); 1.25–1.45 (2 H); 1.8–2.0 (3 H); 2.05 (*dd*, J = 14, 8, 1 H); 2.22 (*m*, 1 H); 2.41 (*q*, J = 8, 2 H); 3.42 (*d*, J = 14, 1 H); 3.49 (*d*, J = 14, 1 H); 3.87 (*dd*, J = 5, 8, 1 H). ^{13}C-NMR: 149.91 (*s*); 97.19 (*s*); 72.93 (*s*); 64.87 (*d*); 52.92 (*t*); 48.42 (*s*); 47.73 (*s*); 44.73 (*d*); 38.33 (*t*); 32.77 (*t*); 26.35 (*t*); 20.83 (*q*); 19.80 (*q*); 12.75 (*t*); 12.14 (*q*). MS: 295 (0.41, $C_{15}H_{21}NO_3S^{+\cdot}$), 135 (10), 134 (10), 81 (100), 53 (28). HR-MS: 295.1231 ($C_{15}H_{21}NO_3S^{+\cdot}$, calc. 295.1242).

N-*[(Z)-3-Methyl-2-pentenoyl]bornane-10,2-sultam* (**2e**). A 1.5N soln. of MeLi in Et_2O (3 ml, 4.5 mmol) was added dropwise at −5° to a stirred suspension of CuI (433 mg, 2.27 mmol). Stirring of the mixture at −5° for additional 10 min followed by slow addition of a soln. of **3** (R = Et; 610 mg, 2.06 mmol) in THF (6 ml) at −95°, stirring of the mixture for further 10 min at −95°, addition of MeOH (1 ml), warming to −20° over 90 min, addition of aq. sat. NH_4Cl soln. (10 ml), workup, and FC (CH_2Cl_2/hexane 3:1) afforded **2e** ((*Z*)/(*E*) = 99:1; 304 mg, 47%). GC (180°): 6.15. M.p. 100–101°. $[\alpha]_D = -60.8°$, $[\alpha]_{578} = -63.1°$, $[\alpha]_{546} = -70.9°$, $[\alpha]_{436} = -111.8°$, $[\alpha]_{365} = -164.1°$ (c = 1.46, T = 20°). IR: 2970, 2890, 1680, 1630, 1450, 1330, 1280, 1260, 1190, 1160, 1130, 1120, 1060, 1040, 990, 910. ^{1}H-NMR: 0.98 (*s*, 3 H); 1.06 (*t*, J = 7.5, 3 H); 1.16 (*s*, 3 H); 1.28–1.45 (2 H); 1.8–1.95 (3 H); 1.93 (*d*, J = 1.5, 3 H); 2.0–2.15 (2 H); 2.53 (*dq*, J = 13, 7.5, 1 H); 2.61 (*dq*, J = 13, 7.5, 1 H); 3.43 (*d*, J = 14, 1 H); 3.48 (*d*, J = 14, 1 H); 3.93 (*dd*, J = 5, 7.5, 1 H); 6.30 (*s*, 1 H). ^{13}C-NMR: 164.51 (*s*); 163.96 (*s*); 115.41 (*d*); 65.03 (*d*); 53.14 (*t*); 48.105 (*s*); 47.68 (*s*); 44.66 (*d*); 38.65 (*t*); 32.81 (*t*); 27.56 (*t*); 26.53 (*t*); 25.06 (*q*); 20.78 (*q*); 19.85 (*q*); 12.45 (*q*). MS: 311 (0.74, $C_{16}H_{25}NO_3S^{+\cdot}$), 97 (100), 96 (8), 69 (7.5). HR-MS: 311.1543 ($C_{16}H_{25}NO_3S^{+\cdot}$, calc. 311.1555).

N-*[(E)-2-Methyl-2-butenoyl]bornane-10,2-sultam* (**11**). Following the procedure described for **2a**, acylation of **1** (4 g, 18.6 mmol) with (*E*)-2-methyl-2-butenoyl chloride (2.7 g, 23 mmol), subsequent FC (hexane/AcOEt 4:1), and crystallization (MeOH) furnished **11** (4.52 g, 82%). M.p. 181–182°. $[\alpha]_D = -76.0°$, $[\alpha]_{578} = -79.6°$, $[\alpha]_{546} = -91.8°$, $[\alpha]_{436} = -174.2°$, $[\alpha]_{365} = -339.6°$ (c = 2.488, T = 20°). IR: 3020, 2965, 2885, 1680, 1650, 1520, 1330, 1292, 1285, 1182, 1170, 1130, 1110, 1062, 1045, 1032, 925. ^{1}H-NMR: 1.00 (*s*, 3 H); 1.23 (*s*, 3 H); 1.3–1.5 (2 H); 1.83 (*d*, J = 7, 3 H); 1.87 (*s*, 3 H); 1.8–1.98 (4 H); 2.2 (*dd*, J = 7, 13, 1 H); 3.39 (*d*, J = 14, 1 H); 3.4 (*d*, J = 14, 1 H); 4.07 (*dd*, J = 4, 8, 1 H); 6.38 (*q*, J = 7, 1 H). ^{13}C-NMR: 172.20 (*s*); 137.44 (*d*); 131.37 (*s*); 65.26 (*d*); 53.43 (*t*); 47.77 (*s*); 47.58 (*s*); 45.10 (*d*); 38.13 (*t*); 33.08 (*t*); 26.45 (*t*); 21.22 (*q*); 19.81 (*q*); 14.01 (*q*); 12.60 (*q*). MS: 297 (3.5, $C_{15}H_{23}NO_3S^{+\cdot}$), 282 (1), 233 (2), 218 (4), 205 (2.5), 190 (2), 134 (2.5), 108 (2), 84 (100), 55 (40). HR-MS: 297.1382 ($C_{15}H_{23}NO_3S^{+\cdot}$, calc. 297.1398).

Transformations of *N*-Enoylsultams 2 to Acetals 6/7. – *General Procedure for Dihydroxylation/Acetalization.* A 0.4M soln. of OsO_4 (0.3 mol-equiv., stabilized by the addition of a few drops of 30% aq. H_2O_2 soln.) in *t*-BuOH was added at −20° to a stirred soln. of **2** or **11** (1 mol-equiv.) and *N*-methylmorpholine *N*-oxide monohydrate (2 mol-equiv.) in *t*-BuOH/DMF 1:1 (10 ml per mmol of **2**). Stirring of the mixture at −20° for 4 to 6 h, addition of aq. sat. $NaHSO_3$ soln., extraction of the aq. phase with AcOEt, drying ($MgSO_4$) of the combined org. phases, and evaporation of the solvent furnished **4/5** as an oil. The crude mixture of **4/5** (4 mmol) was then stirred in acetone/2,2-dimethoxypropane 1:1 (20 ml) in the presence of TsOH (3 mg) at r.t. for 2 h. Successive addition of aq. sat. $NaHCO_3$ soln., shaking with CH_2Cl_2/H_2O, washing of the org. phase with sat. aq. NaCl soln., drying ($MgSO_4$), and evaporation furnished **6/7** which were analyzed by capillary GC and separated as described below. *To control*

the GC data, the racemic acids **9** were prepared by submitting the corresponding (*E*)- or (*Z*)-methyl enoates to the general osmylation/acetalization procedure followed by saponification. Treatment of racemic **9** with oxalyl chloride and acylation of **1** with NaH and the resulting acyl chlorides gave mixtures **6**/**7** which, on GC analysis, showed 2 peaks superimposable with those from the reaction mixtures obtained by osmylation/acetalization of **2**.

N-[(4R,5S)-2,2,5-Trimethyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam (**6a**) *and N-[(4S,5R)-2,2,5-Trimethyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam* (**7a**). Following the general oxidation/acetalization procedure, **2a** (1.13 g, 4 mmol) was converted to a 90:10 mixture **6a**/**7a** (1.47 g) which, on separation by medium-pressure chromatography (*Merck LOBAR*, hexane/AcOEt 4:1), furnished the major isomer **6a** (1.049 g, 74%). Crystallization of **6a** (770 mg, hexane) yielded colorless crystals (733 mg). GC (150°–10°/min→270°): 6.35. M.p. 120–121°. $[\alpha]_D = -94.7°$, $[\alpha]_{578} = -98.7°$, $[\alpha]_{546} = -111.9°$, $[\alpha]_{436} = -188.3°$, $[\alpha]_{365} = -295.8°$ ($c = 2.124$, T = 20°). IR: 3000, 2970, 2890, 1710, 1460, 1415, 1385, 1340, 1270, 1170, 1140, 1100, 1060, 1035, 980, 910, 850. ^{1}H-NMR: 1.00 (*s*, 3 H); 1.20 (*s*, 3 H); 1.3–1.5 (2 H); 1.42 (*d*, *J* = 6, 3 H); 1.47 (*s*, 3 H); 1.49 (*s*, 3 H); 1.85–2.05 (3 H); 2.11 (*dd*, *J* = 8, 14, 1 H); 2.18 (*m*, 1 H); 3.44 (*d*, *J* = 14, 1 H); 3.55 (*d*, *J* = 14, 1 H); 3.95 (*dd*, *J* = 5, 8, 1 H); 4.5–4.6 (2 H). ^{13}C-NMR: 170.00 (*s*); 111.06 (*s*); 80.14 (*d*); 75.34 (*d*); 65.6 (*d*); 53.18 (*t*); 48.64 (*s*); 47.72 (*s*); 44.74 (*d*); 38.40 (*t*); 33.01 (*t*); 27.49 (*q*); 26.33 (*t*); 25.93 (*q*); 21.02 (*q*); 19.86 (*q*); 18.28 (*q*). MS: 342 (15, $C_{17}H_{27}NO_5S^{+\cdot}-CH_3$), 216 (5), 151 (5), 135 (11), 116 (7), 115 (100), 97 (5), 79 (5), 67 (5). HR-MS: 342.1385 ($C_{17}H_{27}NO_5S-CH_3^+$, calc. 342.1375).

The above-described medium-pressure chromatography afforded also the minor product **7a** (153 mg, 11%) which was recrystallized (hexane). GC (150°–10°/min→270°): 7.05. M.p. 135–136°. ^{1}H-NMR: 1.00 (*s*, 3 H); 1.15 (*s*, 3 H); 1.40 (*m*, 1 H); 1.43 (*d*, *J* = 6, 3 H); 1.50 (*s*, 3 H); 1.54 (*s*, 3 H); 1.8–2.2 (5 H); 3.47 (*d*, *J* = 14, 1 H); 3.52 (*d*, *J* = 14, 1 H); 3.96 (*dd*, *J* = 5, 8, 1 H); 4.25 (*dq*, *J* = 7, 6, 1 H); 4.73 (*d*, *J* = 7, 1 H). ^{13}C-NMR: 170.25 (*s*); 111.52 (*s*); 80.45 (*d*); 65.42 (*d*); 53.19 (*t*); 48.60 (*s*); 47.83 (*s*); 44.73 (*d*); 38.42 (*t*); 32.92 (*t*); 27.68 (*q*); 26.43 (*t*); 26.16 (*q*); 20.85 (*q*); 19.86 (*q*); 18.04 (*q*).

N-[(4R,5R)-2,2,5-Trimethyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam (**6b**). Following the general oxidation/acetalization procedure, **2b** (566 mg, 2.0 mmol) was converted to a 91:9-mixture **6b**/**7b** (745 mg), GC (150°→10°/min→270°): 6.85 (91%), 7.45 (9%). Filtration through SiO_2 (hexane/EtOAc 7:3) and crystallization (hexane) yielded the major product **6b** (470 mg, 66%). GC (150°–10°/min→270°): 6.85. M.p. 126–127°. $[\alpha]_D = -69.9°$, $[\alpha]_{578} = -73.0°$, $[\alpha]_{546} = -83.4°$, $[\alpha]_{436} = -147.8°$, $[\alpha]_{365} = -251.4°$ ($c = 4.092$, $T = 20°$). IR: 2990, 2960, 2880, 1660, 1455, 1410, 1380, 1335, 1270, 1165, 1135, 1080, 1060, 855. ^{1}H-NMR: 0.98 (*s*, 3 H); 1.18 (*s*, 3 H); 1.26 (*d*, *J* = 6, 3 H); 1.3–1.5 (2 H); 1.38 (*s*, 3 H); 1.59 (*s*, 3 H); 1.8–2.0 (3 H); 2.13 (*dd*, *J* = 8, 14, 1 H); 2.31 (*m*, 1 H); 3.45 (*d*, *J* = 14, 1 H); 3.54 (*d*, *J* = 14, 1 H); 3.91 (*dd*, *J* = 5, 8, 1 H); 4.65 (*dq*, *J* = 7, 6, 1 H); 5.21 (*d*, *J* = 6, 1 H). ^{13}C-NMR: 167.93 (*s*); 110.24 (*s*); 76.80 (*d*); 74.26 (*d*); 65.66 (*d*); 53.12 (*t*); 48.85 (*s*); 47.78 (*s*); 44.70 (*d*); 38.53 (*t*); 32.98 (*t*); 26.91 (*q*); 26.26 (*t*); 25.38 (*q*); 21.04 (*q*); 19.85 (*q*); 16.48 (*q*). MS: 342 (13, $C_{17}H_{27}NO_5S^{+\cdot}-CH_3$), 135 (10), 115 (100), 59 (26), 57 (10). HR-MS: 342.1378 ($C_{17}H_{27}NO_5S^{+\cdot}-CH_3$, calc. 342.1375).

N-[(4R,5S)-2,2-Dimethyl-5-propyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam (**6c**) *and N-[(4S,5R)-2,2-Dimethyl-5-propyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam* (**7c**). Following the general oxidation/acetalization procedure (but extending the acetalization to 15 h), **2c** (1.24 g, 4 mmol) was converted to a 91.5:8.5 mixture **6c**/**7c** (1.63 g) which, on FC (hexane/AcOEt 4:1), furnished the pure major product **6c** (1.22 g, 79%). GC (200°): 6.17. M.p. 110–111°. $[\alpha]_D = -101.1°$, $[\alpha]_{578} = -105.3°$, $[\alpha]_{546} = -119.4°$, $[\alpha]_{436} = -200.6°$, $[\alpha]_{365} = -313.1°$ ($c = 2.602$, $T = 20°$). IR: 2960, 2870, 1690, 1450, 1410, 1370, 1335, 1265, 1160, 1130, 1050. ^{1}H-NMR: 0.95 (*t*, *J* = 7.5, 3 H); 1.00 (*s*, 3 H); 1.21 (*s*, 3 H); 1.3–1.5 (4 H); 1.45 (*s*, 3 H); 1.49 (*s*, 3 H); 1.65–1.75 (2 H); 1.85–2.0 (3 H); 2.05–2.25 (2 H); 3.44 (*d*, *J* = 14, 1 H); 3.54 (*d*, *J* = 14, 1 H); 3.96 (*dd*, *J* = 5, 8, 1 H); 4.49 (*q*, *J* = 7, 1 H); 4.57 (*d*, *J* = 6.5, 1 H). ^{13}C-NMR: 170.24 (*s*); 111.07 (*s*); 78.97 (*d*); 78.65 (*d*); 65.65 (*d*); 53.22 (*t*); 48.66 (*s*); 47.73 (*s*); 44.82 (*d*); 38.42 (*t*); 35.00 (*t*); 33.09 (*t*); 27.50 (*q*); 26.32 (*t*); 25.90 (*q*); 21.09 (*q*); 19.89 (*q*); 18.93 (*t*); 13.94 (*q*). MS: 370 (15, $C_{19}H_{31}NO_5S^{+\cdot}-CH_3^+$), 151 (9), 143 (100), 113 (15), 85 (15), 59 (40). HR-MS: 370.1674 ($C_{19}H_{31}NO_5S^{+\cdot}-CH_3$, calc. 370.1688).

Further elution furnished the more polar, minor product **7c** (115 mg, 8%). GC (200°): 7.66. M.p. 116–118°. $[\alpha]_D = -56.5°$, $[\alpha]_{578} = -58.8°$, $[\alpha]_{548} = -67.0°$, $[\alpha]_{436} = -115.4°$, $[\alpha]_{365} = -190.0°$ ($c = 1.555$, $T = 20°$). IR: 2980, 2960, 2870, 1700, 1450, 1375, 1335, 1265, 1160, 1130, 1100, 1050. ^{1}H-NMR: 0.93 (*t*, *J* = 7.5, 3 H); 1.00 (*s*, 3 H); 1.16 (*s*, 3 H); 1.3–1.5 (4 H); 1.49 (*s*, 3 H); 1.54 (*s*, 3 H); 1.65–1.8 (2 H); 1.85–2.08 (4 H); 2.13 (*dd*, *J* = 7,5, 14, 1 H); 3.39 (*d*, *J* = 14, 1 H); 3.44 (*d*, *J* = 14, 1 H); 3.97 (*dd*, *J* = 5, 8, 1 H); 4.23 (*dt*, *J* = 5.5, 7.5, 1 H); 4.74 (*d*, *J* = 7.5, 1 H). ^{13}C-NMR: 170.49; 111.50; 80.63; 78.97; 65.34; 53.15; 48.50; 47.73; 44.61; 38.32; 34.33; 32.86; 27.56; 26.38; 26.07; 20.70; 19.84; 18.77; 13.85. MS: 370 (18, $C_{19}H_{31}NO_5S^{+\cdot}-CH_3$), 143 (100), 113 (11), 85 (18), 59 (46). HR-MS: 370.1679 ($C_{19}H_{31}NO_5S^{+\cdot}-CH_3$, calc. 370.1688).

N-[(4R,5S)-5-Ethyl-2,2,5-trimethyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam (**6d**) *and N-[(4S,5R)-5-Ethyl-2,2,5-trimethyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam* (**7d**). Following the general oxidation/acetalization procedure (but extending the acetalization to 4 h at 50°), **2d** (137 mg, 0.44 mmol) was converted to a 95:5

mixture **6d**/**7d** which, on FC (hexane/AcOEt 4:1), furnished the less polar, major product **6d** (105 mg, 63%). GC (200°): 5.92. M.p. 122–123°. $[\alpha]_D = -97.6°$, $[\alpha]_{578} = -101.7°$, $[\alpha]_{546} = -115.6°$, $[\alpha]_{436} = -197.9°$, $[\alpha]_{365} = -319.2°$ ($c = 2.905$, $T = 20°$). IR: 2980, 2880, 1705, 1455, 1410, 1375, 1335, 1270, 1165, 1130, 1090, 1055, 990. ^{1}H-NMR: 0.99 (*s*, 3 H); 1.00 (*t*, $J = 7.5$, 3 H); 1.20 (*s*, 3 H); 1.30 (*s*, 3 H); 1.32–1.4 (2 H); 1.45 (*s*, 3 H); 1.60 (*s*, 3 H); 1.77–2.0 (5 H); 2.12 (*dd*, $J = 7.5, 14$, 1 H); 2.23 (*m*, 1 H); 3.44 (*d*, $J = 14$, 1 H); 3.54 (*d*, $J = 14$, 1 H); 3.96 (*dd*, $J = 5, 8$, 1 H); 4.90 (*s*, 1 H). ^{13}C-NMR: 169.61 (*s*); 111.15 (*s*); 85.38 (*s*); 81.86 (*d*); 65.98 (*d*); 53.38 (*t*); 48.62 (*s*); 47.74 (*s*); 44.74 (*d*); 38.77 (*t*); 33.12 (*t*); 32.99 (*t*); 28.24 (*q*); 28.18 (*q*); 26.35 (*t*); 21.72 (*q*); 21.07 (*q*); 19.88 (*q*); 7.85 (*q*). MS: 370 (18, $C_{19}H_{31}NO_5S^+-CH_3$), 310 (25), 143 (53), 112 (26), 85 (100), 59 (77). HR-MS: 370.1690 ($C_{19}H_{31}NO_5S^+-CH_3$, calc. 370.1688).

Further elution gave a 70:30 mixture **6d**/**7d** (26 mg), showing the following properties of **7d**: GC (200°): 7.82. ^{1}H-NMR: 0.99 (*s*, 3 H); 1.00 (*t*, $J = 7.5$, 3 H); 1.15 (*s*, 3 H); 1.23 (*s*, 3 H); 1.3–1.4 (2 H); 1.44 (*s*, 3 H); 1.62 (*s*, 3 H); 1.7–2.07 (5 H); 2.07–2.3 (2 H); 3.45 (*d*, $J = 14$, 1 H); 3.54 (*d*, $J = 14$, 1 H); 3.97 (*dd*, $J = 5, 8$, 1 H); 5.03 (*s*, 1 H).

N-*[(4*R,*5*R*)-5-Ethyl-2,2,5-trimethyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam* (**6e**) *and* N-*[(4*S,*5*S*)-5-Ethyl-2,2,5-trimethyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam* (**7e**). Following the general oxidation/acetalization procedure, **2e** (198 mg, 0.635 mmol) was converted to a 90:10 mixture **6e**/**7e** which, on FC (hexane/AcOEt 17:3) gave the less polar, major product **6d** (165 mg, 67%). GC (200°): 5.40. M.p. (hexane) 135–136°. $[\alpha]_D = -59.0°$, $[\alpha]_{578} = -61.6°$, $[\alpha]_{546} = -70.1°$, $[\alpha]_{436} = -121.3°$, $[\alpha]_{365} = -198.4°$ ($c = 2.38$, $T = 20°$). IR: 2980, 2970, 2880, 1700, 1455, 1410, 1380, 1340, 1265, 1165, 1130, 1090, 1055, 990, 925, 860. ^{1}H-NMR: 0.88 (*t*, $J = 7.5$, 3 H); 0.92 (*s*, 3 H); 1.14 (*s*, 3 H); 1.25–1.6 (3 H); 1.40 (*s*, 3 H); 1.43 (*s*, 3 H); 1.50 (*s*, 3 H); 1.70 (*dq*, $J = 14, 7.5$, 1 H); 1.8–2.0 (3 H); 2.07 (*dd*, $J = 7.5, 14$, 1 H); 2.17 (*m*, 1 H); 3.42 (*d*, $J = 14$, 1 H); 3.51 (*d*, $J = 14$, 1 H); 3.95 (*dd*, $J = 5, 8$, 1 H); 4.82 (*s*, 1 H). ^{13}C-NMR: 168.88 (*s*); 110.51 (*s*); 85.06 (*s*); 83.18 (*d*); 66.08 (*d*); 53.37 (*t*); 48.53 (*s*); 47.70 (*s*); 44.72 (*d*); 38.78 (*t*); 33.10 (*t*); 29.16 (*t*); 27.97 (*q*); 27.93 (*q*); 26.30 (*t*); 24.46 (*q*); 21.05 (*q*); 19.85 (*q*); 8.08 (*q*). MS: 370 (3.62, $C_{19}H_{31}NO_5S^+-CH_3$), 310 (8), 143 (49), 135 (32), 112 (28), 109 (9), 107 (17), 97 (10), 96 (9), 93 (25), 91 (9), 86 (12), 85 (100), 79 (16), 69 (14), 67 (16), 59 (78), 57 (14), 55 (21). HR-MS: 370.1697 ($C_{19}H_{31}NO_5S^+-CH_3$, calc. 370.1688).

Further elution afforded the more polar, minor product **7e** (9 mg, 4%). GC (200°): 7.00. M.p. (hexane) 149–151°. IR: 3000, 2980, 2890, 1710, 1450, 1410, 1380, 1370, 1340, 1270, 1239, 1195, 1135, 1060, 910. ^{1}H-NMR: 0.90 (*t*, $J = 7.5$, 3 H); 0.93 (*s*, 3 H); 1.08 (*s*, 3 H); 1.1–1.25 (2 H); 1.25–1.5 (1 H); 1.40 (*s*, 3 H); 1.42 (*s*, 3 H); 1.52 (*s*, 3 H); 1.75 (*dq*, $J = 14, 7.5$, 1 H); 1.8–2.0 (4 H); 2.09 (*dd*, $J = 7.5, 14$, 1 H); 3.49 (*d*, $J = 14$, 1 H); 3.52 (*d*, $J = 14$, 1 H); 3.97 (*dd*, $J = 5, 8$, 1 H); 5.00 (*s*, 1 H). ^{13}C-NMR: 168.62 (*s*); 110.36 (*s*); 84.27 (*s*); 83.12 (*d*); 65.44 (*d*); 53.12 (*t*); 48.23 (*s*); 47.75 (*s*); 44.46 (*d*); 38.19 (*t*); 32.79 (*t*); 29.50 (*t*); 28.10 (*q*); 27.93 (*q*); 26.41 (*t*); 24.09 (*q*); 20.60 (*q*); 19.86 (*q*); 7.87 (*q*). MS: 370 (3.5, $C_{19}H_{31}NO_5S^+-CH_3$), 356 (2), 310 (6), 143 (35), 135 (25), 112 (27), 107 (14), 93 (20), 86 (10), 85 (100), 79 (13), 67 (14), 59 (87), 57 (19), 55 (25). HR-MS: 370.1687 ($C_{19}H_{31}NO_5S^+-CH_3$, calc. 370.1688).

N-*[(4*R,*5*S*)-2,2,4,5-Tetramethyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam* (**12**) *and* N-*[(4*S,*5*R*)-2,2,4,5-Tetramethyl-1,3-dioxolane-4-carbonyl]bornane-10,2-sultam* (**13**). Following the general procedure, **11** (60 mg, 0.2 mmol) was oxidized at –20° for 42 h and acetalized for 1.5 h to give 60% of unchanged **11**, **12** and **13** (24% and 16% which were not assigned). GC (180°): 4.46 (60%), 8.89 (24%), 9.28 (16%).

Another oxidation of **11** was carried out following a similar procedure but oxidizing **11** (119 mg, 0.4 mmol) at r.t. for 7 h to give, after acetalization, a 1.3:1 mixture **12**/**13** (not assigned, 91 mg, 63%). GC (180°), 9.32 (55%), 9.72 (41%). IR: 3000, 2970, 2890, 1678, 1460, 1348, 1170, 1150, 1127, 1110, 1062. ^{1}H-NMR (200 MHz): 0.97 (*s*, 2.6 H); 1.00 (*s*, 3.4 H); 1.18 (*s*, 2.6 H); 1.21 (*s*, 3.4 H); 1.3–1.42 (22 H); 1.48 (*s*, 2.6 H); 1.49 (*s*, 3.4 H); 1.8–2.1 (10 H); 3.3–3.6 (4 H); 3.95–4.1 (2 H); 4.24 (*q*, $J = 6.5$, 1.2 H); 4.54 (*q*, $J = 6.5$, 0.8 H). MS: 356 (4, $C_{18}H_{29}NO_5S^+-CH_3$), 263 (9), 216 (8), 190 (1), 151 (1), 129 (100), 99 (9), 71 (37), 59 (22).

Nondestructive Removal of the Auxiliary Group. – *Methyl (4*R,*5*S*)-2,2,5-Trimethyl-1,3-dioxolane-4-carboxylate* (**10a**). A mixture of **6a** (355 mg, 0.994 mmol) and LiOH. H_2O (355 mg, 8.46 mmol) in THF/H_2O 2:1 (6 ml) was stirred at r.t. for 13 h. Addition of H_2O, extraction with CH_2Cl_2, drying ($MgSO_4$) of the org. phases, and evaporation furnished **1** (205 mg, 96%). The aq. phase was acidified to pH 2–3 with 1N HCl, saturated with NaCl and extracted with AcOEt. Drying ($MgSO_4$) and evaporation of the extracts furnished **9a** (146 mg) which was treated with a slight excess of CH_2N_2 in Et_2O. Evaporation of the ether and bulb-to-bulb distillation of the residue afforded **10a** (144 mg, 83% from **6a**). B.p. (bath) 90–110°/70 Torr, which was purified by prep. GC (*Carlo Erba Fractovap 2400*, 15 mm × 2 m, 10% *Carbowax* on *Chromosorb W*, 1 kg N_2/cm^2, 100°). GC (60°): 2.95. $[\alpha]_D = +18.9°$, $[\alpha]_{578} = +19.7°$, $[\alpha]_{546} = +22.7°$, $[\alpha]_{436} = +41.9°$, $[\alpha]_{365} = +71.8°$ ($c = 1.240$, $T = 20°$); [10b]: $[\alpha]_D$ (enantiomer of **10a**) $= -18.7°$ ($c = 4.1$, $CHCl_3$, $T = 20°$). IR (film): 2990, 2960, 2940, 1765, 1740, 1440, 1380, 1370, 1290, 1250, 1205, 1170, 1125, 1100, 850. ^{1}H-NMR: 1.43 (*d*, $J = 6$, 3 H); 1.44 (*s*, 3 H); 1.47 (*s*, 3 H); 3.75 (*s*, 3 H);

4.03 (*d*, *J* = 8, 1 H); 4.17 (*dq*, *J* = 8, 6, 1 H). ^{13}C-NMR: 170.88 (*s*); 110.55 (*s*); 80.32 (*d*); 75.04 (*d*); 52.31 (*q*); 27.08 (*q*); 25.63 (*q*); 18.43 (*q*). MS: 159 (100, $C_8H_{14}O_4^+-CH_3$), 130 (8), 115 (45), 99 (28), 85 (12), 73 (78), 59 (85). HR-MS: 159.0661 ($C_8H_{14}O_4^+-CH_3$, calc. 159.0657).

(4S,5R)-2,2,5-Trimethyl-1,3-dioxolane-4-methanol (**8b**). A mixture of **6b** (255 mg, 071 mmol) and $LiAlH_4$ (40 mg, 1.05 mmol) in THF (5 ml) was stirred at r.t. for 1 h. Quenching of the mixture by adding several drops of sat. aq. Na_2SO_4 soln., drying ($MgSO_4$), careful evaporation, and trituration of the residue with pentane gave the recovered **1** as an insoluble, solid residue (125 mg, 82%). Evaporation of the pentane solution and bulb-to-bulb distillation of the residue furnished **8b** (78 mg, 75%). GC (60°): 2.10. B.p. (bath) 100–110°/10 Torr. $[\alpha]_D = -52.5°$, $[\alpha]_{578} = -54.6°$, $[\alpha]_{546} = -61.8°$, $[\alpha]_{436} = -102.7°$, $[\alpha]_{365} = -156.5°$ (*c* = 3.667, *T* = 20°); [14]: $[\alpha]_D$ (enantiomer of **8b**) = +52° (*c* = 1.0, $CHCl_3$, *T* = 20°). IR: 3580, 3470, 2980, 2930, 2880, 1450, 1380, 1370, 1360, 1305, 1240, 1170, 1085, 1035, 990, 930, 900, 855, 830. ^{1}H-NMR: 1.25 (*d*, *J* = 7, 3 H); 1.37 (*s*, 3 H); 1.48 (*s*, 3 H); 1.92 (*t*, *J* = 6, 1 H); 3.61 (*t*, *J* = 6, 2 H); 4.15 (*q*, *J* = 6, 1 H); 4.37 (*dq*, *J* = 6, 7, 1 H). ^{13}C-NMR: 107.99 (*s*); 78.01 (*d*); 72.56 (*d*); 61.81 (*t*); 28.12 (*q*); 25.38 (*q*); 14.46 (*q*). MS: 131 (44, $C_7H_{14}O_3^+-CH_3$), 115 (32), 101 (8), 71 (23), 61 (14), 59 (100), 58 (15), 57 (16), 45 (13). HR-MS: 131.0713 ($C_7H_{14}O_3^+-CH_3$, calc. 131.0708).

(4S,5S)-2,2-Dimethyl-5-propyl-1,3-dioxolane-4-methanol (**8c**). Using the procedure described for **8b**, reductive cleavage of **6c** (771 mg, 2.0 mmol) with $LiAlH_4$ gave recovered **1** (374 mg, 87%) and, after bulb-to-bulb distillation, **8c** (285 mg, 82%). GC (50°): 9.80. B.p. (bath) 100–110°/1 Torr. $[\alpha]_D = -27.9°$, $[\alpha]_{578} = -29.0°$, $[\alpha]_{546} = -32.5°$, $[\alpha]_{436} = -50.8°$, $[\alpha]_{365} = -71.9°$ (*c* = 4.192, *T* = 20°); [15]: $[\alpha]_D = -27.8°$ (*c* = 5.7, $CHCl_3$, *T* = 25°). IR (film): 3450, 2980, 2960, 2930, 2870, 1460, 1375, 1365, 1245, 1215, 1165, 1100, 1040, 985, 900, 860, 830. ^{1}H-NMR: 0.93 (*t*, *J* = 7.5, 3 H); 1.39 (*s*, 3 H); 1.41 (*s*, 3 H); 1.3–1.65 (4 H); 2.40 (br. *s*, 1 H); 3.57 (*dd*, *J* = 4.5, 11.5, 1 H); 3.73 (*m*, 1 H); 3.75 (*dd*, *J* = 3, 11.5, 1 H); 3.85 (*m*, 1 H). ^{13}C-NMR: 108.49 (*s*); 81.48 (*d*); 76.62 (*d*); 62.01 (*t*); 35.09 (*t*); 27.28 (*q*); 26.94 (*q*); 19.16 (*t*); 14.02 (*q*). MS: 159 (37, $C_9H_{18}O_3^+-CH_3$), 143 (13), 85 (16), 81 (44), 59 (100), 57 (24), 55 (32). HR-MS: 159.1018 ($C_9H_{18}O_3^+-CH_3$, calc. 159.1021).

(4R,5S)-5-Ethyl-2,2,5-trimethyl-1,3-dioxolane-4-carboxylic Acid (**9d**). Using similar conditions as described for the saponification of **6a**, **6d** (100 mg, 0.26 mmol) was hydrolyzed at r.t. within 7 h to give **1** (55 mg, 98%) and **9d** (46 mg, 94%) which was sublimed at 55–60° (bath)/0.5 Torr to give colorless crystals (37 mg). M.p. 49–50° ([19]: 46.5–49°). $[\alpha]_D = +33.3°$, $[\alpha]_{578} = +34.9°$, $[\alpha]_{546} = +39.4°$, $[\alpha]_{436} = +66.9°$, $[\alpha]_{365} = +103.2°$ (*c* = 0.619, *T* = 20°); [19]: $[\alpha]_D = +26.0°$ (*c* = 0.84, $CHCl_3$, *T* = 20°). IR: 3300–2500 (br.), 3000, 2940, 1780, 1740, 1460, 1380, 1360, 1130, 1100, 1000, 875. ^{1}H-NMR: 1.04 (*t*, *J* = 7.5, 3 H); 1.24 (*s*, 3 H); 1.42 (*s*, 3 H); 1.58 (*s*, 3 H); 1.75–1.95 (2 H); 4.46 (*s*, 1 H); 6.4–7.5 (1 H). ^{13}C-NMR: 173.03 (*s*); 109.80 (*s*); 83.58 (*s*); 80.13 (*d*); 32.20 (*t*); 28.40 (*q*); 27.16 (*q*); 21.91 (*q*); 8.06 (*q*). MS: 173 (28, $C_9H_{16}O_4^+-CH_3$), 116 (12), 113 (48), 95 (17), 85 (16), 71 (12), 59 (100), 57 (20), 55 (12). HR-MS: 173.0821 ($C_9H_{16}O_4^+-CH_3$, calc. 173.0814).

(4R,5R)-5-Ethyl-2,2,5-trimethyl-1,3-dioxolane-4-carboxylic Acid (**9e**). Using the conditions described for the saponification of **6a**, hydrolysis of **6e** (96 mg, 0.249 mmol) at r.t. for 5.5 h gave **1** (54 mg, 100%) and **9e** (44 mg, 94%) which, on sublimation at 50–60° (bath)/0.5 Torr, gave colorless crystals (31 mg). M.p. 96–97° ([16]: 93–94.5°). $[\alpha]_D = +58.9°$, $[\alpha]_{578} = +61.1°$, $[\alpha]_{546} = +69.1°$, $[\alpha]_{436} = +113.3°$, $[\alpha]_{365} = +168.0°$ (*c* = 1.485, *T* = 20°); [16]: $[\alpha]_D = +58.6°$ (*c* = 3.0, $CHCl_3$, *T* = 20°). IR: 3440, 3400–2700 (br.), 2980, 2940, 2880, 1775, 1730, 1520, 1380, 1350, 1130, 1090, 1020, 980, 930, 900, 860. ^{1}H-NMR: 0.92 (*t*, *J* = 7.5, 3 H); 1.37 (*m*, 1 H); 1.38 (*s*, 3 H); 1.42 (*s*, 3 H); 1.50 (*s*, 3 H); 1.65 (*sext.*, *J* = 7.5, 1 H); 4.42 (*s*, 1 H); 7.3–8.9 (1 H). ^{13}C-NMR: 172.48 (*s*); 109.55 (*s*); 83.15 (*s*); 82.53 (*d*); 28.16 (*t*); 27.97 (*q*); 27.10 (*q*); 23.30 (*q*); 7.37 (*q*). MS: 173 (7, $C_9H_{16}O_4^+-CH_3$), 161 (14), 113 (17), 85 (10), 73 (9), 59 (100), 57 (10). HR-MS: 173.0819 ($C_9H_{16}O_4^+-CH_3$, calc. 173.0814).

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