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The asymmetric ene reaction of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam with 1-pentene and 1-hexene †

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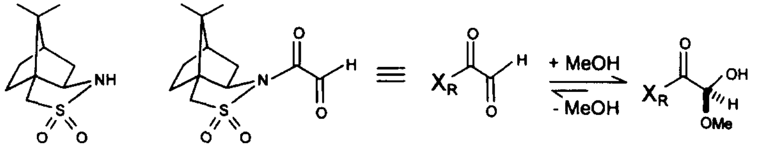
Abstract: The asymmetric ene reaction of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **2** and its hemiacetal **3** with 1-pentene **4** and 1-hexene **5** in the presence of Lewis acids is reported. All the ene reactions studied led to diastereoisomeric mixtures of olefins **6** and **7** or **8** and **9**, with predominance of products of the (*S*) absolute configuration on the newly formed stereogenic center. The absolute configuration (*via* X-ray analysis of **6** and chemical correlation) and the extent of asymmetric induction were established. Stereochemical models are proposed. © 1997 Elsevier Science Ltd

There is a growing interest in synthetic applications of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **2**,[1–9] readily available from Oppolzer's (2*R*)-bornane-10,2-sultam **1**[10] (Scheme 1). Recently, we have described the successful application of compound **2** to the highly stereocontrolled hetero-Diels–Alder[1,6] and Danishefsky's cyclocondensation[8] reactions, leading to convenient intermediates for the synthesis of natural products.[2,6,7] These facts prompted us to initiate systematic studies on the ene reaction with the use of chiron **2**. In this paper we report on the asymmetric ene reaction of compound **2** or its hemiacetal **3** with commercially available 1-pentene **4** or 1-hexene **5**, in the presence of various Lewis acids as catalysts.



1 X$_R$H **2** **3**

Scheme 1.

The reaction of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **2** with 1-pentene **4**, in the presence of a Lewis acid, afforded a mixture of two diastereoisomeric products **6** and **7**, which was easily separated into single diastereoisomers *via* flash chromatography. The latter fact allowed precise determination of the composition of the reaction mixture. Analogously, the catalytic reaction of **2** with 1-hexene **5** gave a diastereoisomeric mixture of products **8** and **9** (Scheme 2). The results of asymmetric ene reactions of compounds **2** or **3** with olefins **4** or **5**, carried out under various conditions, are presented in Table 1.

After the determination of the extent of asymmetric induction, we studied its direction by X-ray analysis as well as by chemical correlation. The major diastereoisomer **6**, obtained from the reaction of **2** with **4**, followed by chromatographic separation, was finally crystallized. Its absolute configuration (14*S*) was established using X-ray analysis. The results are presented in Figure 1 which also shows the intramolecular hydrogen bond between the hydroxy and carbonyl groups.

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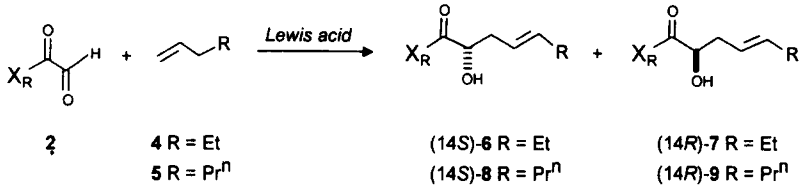


Scheme 2.

The absolute configuration of both diastereoisomeric products (14*S*)-**6** and (14*R*)-**7** were independently confirmed by chemical correlations in two ways, with compounds (2*S*)-**12** and (2*R*)-**14**, respectively (Scheme 3). The first comprises hydrogenation in the presence of the Pd/C in ethyl acetate as a solvent, giving intermediates (14*S*)-**10** and (14*R*)-**11**, respectively, which after lithium aluminum hydride reduction afforded compounds (2*S*)-**12** and (2*R*)-**14**, respectively.

The second, one-step route is based on hydrogenation of compounds (2*S*)-**6** and (2*R*)-**7** in the presence of the Adams catalyst in the same solvent. The reduction of the amide and alkene functionalities afforded directly the vicinal diols (2*S*)-**12** and (2*R*)-**14**, respectively. Similarly, compounds (14*S*)-**8** and (14*R*)-**9**, obtained from the reaction of **2** or **3** with **5** followed by chromatographic separation, were chemically correlated *via* the second route with compounds (2*S*)-**13** and (2*R*)-**15**, respectively.

Several aspects of the data shown in Table 1 are noteworthy. The reaction of **2** with **4**, carried out in the presence of $SnCl_4$, and in nitromethane as a solvent, afforded the mixture of diastereoisomeric products (14*S*)-**6** and (14*S*)-**7** in a good yield, but with poor (10% d.e.) asymmetric induction (Entry 1). Therefore, we decided to enhance asymmetric induction by changing the solvent used. Indeed, the reaction performed in methylene chloride gave also products in a very good yield, but the diastereoselectivity was much higher (42% d.e.) as shown in Entry 2. Changes of the reaction temperature caused the expected changes in asymmetric induction (Entries 2–4). The reaction of **2** with **5**, carried out under analogous conditions as that from Entry 4, led to the similar (50% d.e.) results (Entry 5). When instead of **2** we used hemiacetal **3**, the result of asymmetric induction was slightly lower (38% d.e.), as shown in Entry 6, or slightly better (56% d.e.), in the case of higher (3 equiv) concentration of the catalyst used (Entry 7). The application of $TiCl_4$ instead of $SnCl_4$ as the catalyst, failed to change substantially the diastereoisomeric composition of the product, and what was more, the chemical yield was much lower (Entries 8–11). The best results in terms of diastereoisomeric excess were obtained when reactions of **2** with **4** (80% d.e., Entry 12), and with **5** (78% d.e., Entry 14) were carried out at 5°C in the presence of $ZnBr_2$ as the catalyst. Reactions with the use of **3** as the enophile, performed under the same conditions, afforded the products with slightly lower diastereoselectivity (Entries 13,15–16). The application of nonchelating Lewis acids such as $BF_3 \cdot Et_2O$, $AlCl_3$, and $EtAlCl_2$ failed to enhance the diastereoselectivity of the reactions studied (Entries 17–19). On the other hand, the use of $Eu(fod)_3$, weak chelating Lewis acid, led to the products with high yield and diastereoselectivity (Entry 20).

Rationalization of our results obtained for the ene reaction may be based on two concepts: 1) the sterically controlled approach of an ene to the thermodynamically more stable SO_2/CO *anti*-periplanar, CO/CHO s-*cis* planar conformer A, as proposed by Oppolzer *et al.*,[10,11] and by Curran *et al.*,[12] for the noncatalyzed [4+2]cycloaddition with the use of *N*-acryloyl- and *N*-crotonoyl-(2*R*)-bornane-10,2-sultam,; and 2) the high reactivity of the less stable SO_2/CO *syn*-periplanar, CO/CHO s-*cis* planar conformer B (Scheme 4), reinforced by the cooperative stereoelectronic effect, as recently formulated by Chapuis *et al.*[6,13]

As suggested by X-ray analysis of *N*-acryloyl- and *N*-crotonoyl-(2*R*)-bornane-10,2-sultam,[10–12] for *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **2** the more stable conformer A should be preferred over conformer B due to electrostatic and/or dipole–dipole repulsion between the sultam oxygen and the glyoxyloyl moiety.[14]

Table 1. The asymmetric ene reaction of enophiles **2** or **3** with enes **4** or **5**

Entry	Enophile	Ene	Catalyst (equiv)	Solvent	Temp. [°C]	Time [h]	Yield [%]	Diastereoisomeric composition (*S*) : (*R*)
1	**2**	**4**	$SnCl_4$ (1.1)	CH_3NO_2	5	36	95.0	55 : 45
2	**2**	**4**	$SnCl_4$ (1.1)	CH_2Cl_2	5	8	89.5	71 : 29
3	**2**	**4**	$SnCl_4$ (1.1)	CH_2Cl_2	20	2	86.0	66 : 34
4	**2**	**4**	$SnCl_4$ (1.1)	CH_2Cl_2	-78	48	77.8	84 : 16
5	**2**	**5**	$SnCl_4$ (1.1)	CH_2Cl_2	-78	48	93.3	75 : 25
6	**3**	**5**	$SnCl_4$ (1.1)	CH_2Cl_2	-78	48	94.6	69 : 31
7	**3**	**5**	$SnCl_4$ (3.0)	CH_2Cl_2	-78	24	96.0	78 : 22
8	**2**	**5**	$TiCl_4$ (1.1)	CH_2Cl_2	-78	48	42.0	83 : 17
9	**3**	**5**	$TiCl_4$ (1.1)	CH_2Cl_2	-78	48	40.0	79 : 21
10	**3**	**5**	$TiCl_4$ (2.0)	CH_2Cl_2	-78	48	63.0	77 : 23
11	**3**	**5**	$TiCl_4$ (3.0)	CH_2Cl_2	-78	48	57.0	77 : 23
12	**2**	**4**	$ZnBr_2$ (1.1)	CH_2Cl_2	5	48	50.5	90 : 10
13	**3**	**4**	$ZnBr_2$ (1.1)	CH_2Cl_2	5	54	46.0	88 : 12
14	**2**	**5**	$ZnBr_2$ (1.1)	CH_2Cl_2	5	48	43.0	89 : 11
15	**3**	**5**	$ZnBr_2$ (1.1)	CH_2Cl_2	5	60	43.0	85 : 15
16	**3**	**5**	$ZnBr_2$ (1.1)	CH_2Cl_2	20	48	46.0	82 : 18
17	**3**	**5**	$BF_3 \cdot Et_2O$ (1.1)	CH_2Cl_2	5	80	65.0	65 : 35
18	**3**	**5**	$AlCl_3$ (2.0)	CH_2Cl_2	5	80	78.0	84 : 16
19	**3**	**5**	$EtAlCl_2$ (2.0)	CH_2Cl_2	5	80	42.0	76 : 24
20	**3**	**4**	$Eu(fod)_3$ (0.02)	CH_2Cl_2	5	120	87.0	83 : 17

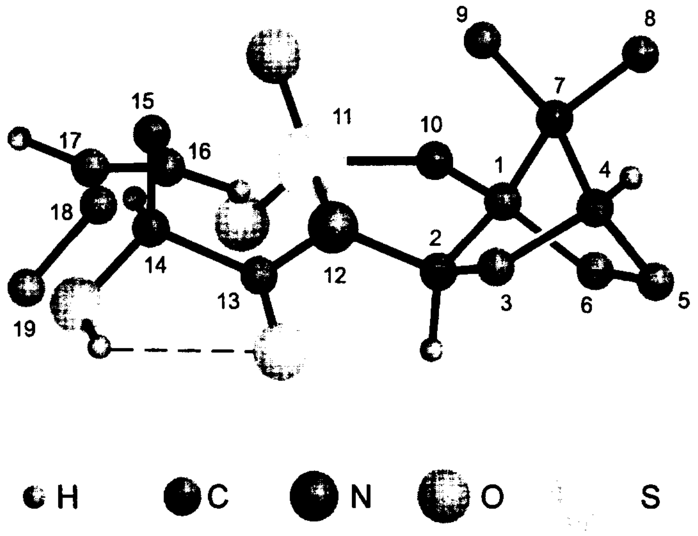
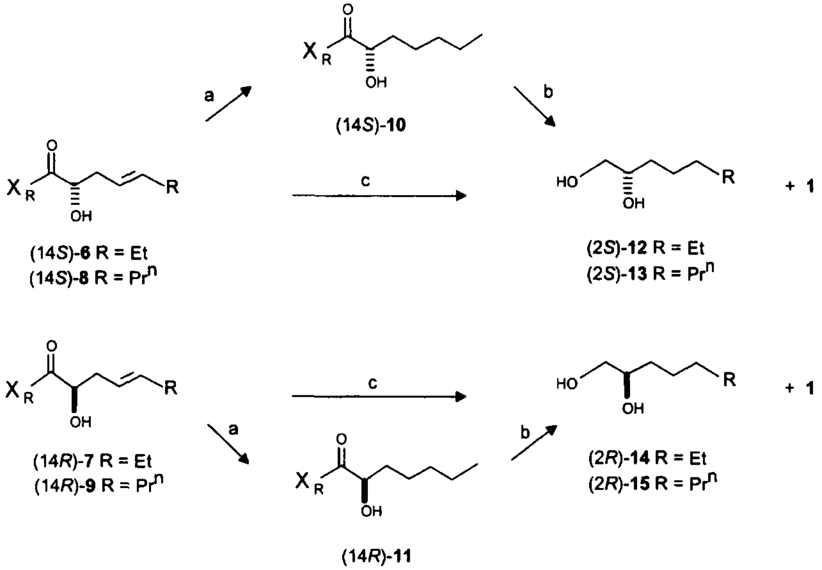
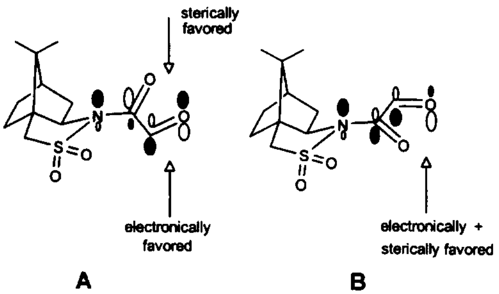


Figure 1. Molecular structure of compound (14*S*)-**6**.



Scheme 3. Reaction conditions: a) H_2, Pd/C, AcOEt, 20°C, 3 h; b) LAH, THF, 0°C→RT, 2 h; c) H_2, Pt, AcOEt, 20°C, 3 h.

It is also noteworthy that under high-pressure conditions, the CO/CHO s-*cis* conformation of the chiral glyoxylates is favored.[15,16] Therefore, the approach of an ene to the derivative **2** should occur from the top side of the bornane skeleton. Recent calculations at the semiempirical PM3 and *ab initio* STO3-21G level of theory,[13] suggest that among the conformations of low energy, the conformer B is the most reactive species in term of LUMO level and atomic coefficients.[17,18] This conformer thus could participate to the stereoselectivity outcome of the ene reaction by kinetical driving the thermodynamic equilibrium on its side, similarly as it was proposed for the Diels–Alder reaction.[6] Furthermore, the N, (CO), C_α, and O atomic coefficients of the LUMO are nonequivalent with respect to both $C_{\alpha\text{-re}}$ and $C_{\alpha\text{-si}}$ faces, favoring, independently of the conformation, the attack on the opposite face to the nitrogen lone pair. This stereoelectronic effect is thus mismatching the steric



Scheme 4. The stereochemical models (LUMO level) for asymmetric induction in the reaction of heteroenophile **2** with ene **4** or **5**.

effect in the conformer A, while being additive in conformer B, reinforcing its higher reactivity. The stereoelectronic effect is certainly depending on the electronic conjugation of the π system, which is reflected in part by the CO/CHO dihedral or 'twisting' angle.[19] The conformational equilibrium may be even more complicated in view of, as recently proposed by Pindur *et al.*,[20] reactive SO_2/CO *anti*-periplanar, CO/CH=CH_2 s-*trans* planar conformation which cannot be excluded in our case,[1] due to the sterically less demanding reactive HC=O double bond as compared with the entropically more favored HC=CH_2 double bond.

Further work directed to the asymmetric ene reaction of *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam with substituted olefins is in progress.

Experimental

General

Melting points were determined using a Kofler hot stage apparatus and are uncorrected. Rotations were recorded using a JASCO DIP-360 polarimeter with a thermally jacketed 10 cm cell. IR spectra were obtained on a Perkin–Elmer 1640 FTIR spectrophotometer in KBr pellets. ^{1}H NMR spectra were recorded using a Varian Gemini (200 MHz) spectrometer, and ^{13}C NMR spectra were recorded with DEPT editing as necessary, using also a Varian Gemini (50 MHz) spectrometer. All chemical shifts are quoted in parts per milion relative to tetramethylsilane (δ, 0.00 ppm), and coupling constants (J) are measured in Hertz. Mass spectra were recorded on an AMD-604 Intectra instrument using the electron impact (EI) technique. Single-crystal X-ray diffraction analysis was performed on an Enraf–Nonius CAD-4 diffractometer. Flash-column chromatography was undertaken according to Still *et al.*[21] on silica gel (Kieselgel-60, Merck, 200-400 mesh). Commercially available 1-pentene **4** and 1-hexene **5** were distilled before use. *N*-Glyoxyloyl-(2*R*)-bornane-10,2-sultam **2** and its hemiacetal **3** were prepared according to our own methodology.[9]

*Preparation of (*2R,*14*S,*16*E*)-*N*-(14-hydroxy-16-heptenoyl)bornano-10,2-sultam* **6** *and (*2R,*14*R,*16*E*)-*N*-(14-hydroxy-16-heptenoyl)bornano-10,2-sultam* **7**

Hemiacetal **3** (205.7 mg, 0.79 mmol) was heated at 100–110°C/0.1 mm Hg over a period of 2 h to afford free aldehyde **2** which was immediately subjected to the reaction. A solution of heterodienophile **2** in CH_2Cl_2 (10 mL) was cooled to −78°C. Excess of 1-pentene, which had been precooled to −78°C, was added, followed by 0.09 mL (0.79 mmol) of $SnCl_4$ in 1 mL CH_2Cl_2. The reaction mixture was stirred at −78°C for 48 h, then it was quenched with 20 mL of saturated NH_4F, extracted with Et_2O (3×20 mL), and the combined organic layers were dried ($MgSO_4$). After evaporation, the residue was purified by flash chromatography (hexanes–ethyl acetate 9:1→6:4) to afford the crystalline diastereoisomer (14*S*)-**6** (93 mg) and oily diastereoisomer (14*R*)-**7** (18 mg) (84:16, 78% overall yield).

Analytical and spectral data for (14*S*)-**6**: mp 109–110°C (from n-hexane–isopropanol); $[\alpha]_D^{20}=-87.6$ (c 2.42, EtOH); ν_{max} (film)/cm^{-1} 3522, 2986, 2960, 2935, 2888, 1687, 1459, 1373, 1295, 1211,

Table 2. Crystal data and measurement conditions for compound (14*S*)-**6**

Formula	$C_{17}H_{27}NO_4S$
Molecular weight	341.46
Crystal system	monoclinic
a [Å]	7.442(1)
b [Å]	9.248(1)
c [Å]	13.486(1)
β [deg]	101.46(1)
V [Å^3]	909.6(3)
Molecular multiplicity	*Z*=2
Calculated density [g cm^{-3}]	1.25
Space group	*P*2
Radiation (graphite monochromated)	Mo K$_\alpha$
Wavelength [Å]	1.54178
Linear absorption coeff. μ [cm^{-1}]	1.63
Number of electrons *F* (000)	324
Crystal size [mm]	0.28×0.35×0.40
Temperature [°C]	22±1
Scan mode	ω/ 2θ
Scan range (2θ) [deg]	0-150
Number of collected data:	
total measured	1826
unique [with *I* >2σ]	1585
R	0.0492

1134, 1055, 768, 532; δ_H (200 MHz; $CDCl_3$) 5.61 (dt, J_1=15.4, J_2=6.1, 1H), 5.31 (dt, J_1=15.3 J_2=7.4, 1H), 4.82 (ddd, J_1=7.9, J_2=5.9, J_3=4.6, 1H), 3.90 (dd, J_1=7.7, J_2=5,1, 1H), 3.49 (ABq, J=13.7, 2H), 3.01 (d, J=7.9, 1H), 2.61 (dt, J_1=14.5, J_2=4.7, J_3=1.0, 1H), 2.45 (dt, J_1=14.5, J_2=6.4, J_3=0.9, 1H), 2.16–1.82 (m, 7H), 1.52–1.28 (m, 2H), 1.15 (s, 3H), 0.98 (s, 3H), 0.95 (t, 3H); δ_C (50 MHz; $CDCl_3$) 174.4, 136.8, 121.9, 70.8, 64.9, 52.9, 48.8, 47.8, 44.6, 38.7, 38.2, 32.7, 26.4, 25.6, 20.7, 19.6, 13.6; m/z (EIHR) calculated for $C_{17}H_{27}NO_4S$ $(M)^+$ 341.1661, found 341.1661.

X-ray structure determination of compound 6

Crystal data and measurement conditions are given in Table 2. The positions of the hydrogen atoms bonded to carbon atoms were generated from assumed geometries. The structure was solved by the SHELXS86[22] and refined with the SHELXL76[23] programs.

Distances between donor (D)–acceptor (A) and hydrogen (H)–acceptor are 2.71 and 2.38 Å, respectively.

Lists of the fractional atomic coordinates, isotropic thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

*Analytical and spectral data for (14*R*)-7*

$[\alpha]_D^{20}$ −55.0 (c 2.78, EtOH); ν_{max} (film)/cm^{-1} 3505, 2961, 2884, 1692, 1456, 1413, 1333, 1280, 1136, 969; δ_H (200 MHz; $CDCl_3$) 5.64 (dt, J_1=15.3, J_2=6.1, 1H), 5.43 (dt, J_1=15.3, J_2=6.9, 1H), 4.60 (dt, J_1=7.4, J_2=4.6, 1H), 3.90 (dd, J_1=7.7, J_2=5.0, 1H), 3.20 (ABq, J=13.8, 2H), 3.05 (d, J=7.5, 1H), 2.58 (dt, J_1=14.5, J_2=5.9, 1H), 2,41 (dt, J_1=14.4, J_2=6.8, 1H), 2.28–2.14 (m, 2H), 2.14–1.80 (m, 5H), 1.51–1.33 (m, 2H), 1.15 (s, 3H), 0.97 (s, 3H), 0.97 (t, J=7.5, 3H); δ_C (50 MHz; $CDCl_3$) 172.0, 136.6, 122.9, 70.6, 65.3, 52.8, 49.1, 47.9, 44.4, 38.0, 35.9, 32.7, 26.4, 25.6, 20.7, 19.8, 13.6; m/z (EIHR) calculated for $C_{17}H_{27}NO_4S$ $(M)^+$ 341.1661, found 341.1661.

*Preparation of (2R,14S,16E)-N-(14-hydroxy-16-octenoyl)bornano-10,2-sultam **8** and (2R,14R,16E)-N-(14-hydroxy-16-octenoyl)bornano-10,2-sultam **9***

Compounds **8** and **9** were prepared in similar way as in the former case, using $ZnBr_2$ as a catalyst at 5°C (cf. Table 1, Entry 14). Final chromatographic separation afforded pure crystalline diastereoisomers (14*S*)-**8** and (14*R*)-**9** (89:11, 43% overall yield).

Analytical and spectral data for (14S)-8

mp 109°C (from n-hexane–isopropanol); $[\alpha]_D^{20}$ −81.4 (c 2.50, EtOH); ν_{max} (film)/cm^{-1} 3515, 3299, 2985, 2901, 1815, 1709, 1518, 1429, 1418, 1387, 1349, 1250, 1231, 1179, 1145, 1070, 985, 885, 770; δ_H (200 MHz; $CDCl_3$) 5.54 (dt, J_1=15.4, J_2=6.4, 1H), 5.37 (dt, J_1=16.1, J_2=7.2, 1H), 4.68 (dt, J_1=7.7, J_2=5.6, 1H), 3.50 (dd, J_1=7,7, J_2=5,0, 1H), 3.20 (ABq J=16.1, 2H), 3.11 (d, J=1.3, 1H), 2.60 (dt, J_1=17.5, J_2=5.6, 1H), 4.87 (dt, J_1=17.2, J_2=6.3, 1H), 2.18–1.78 (m, 7H), 1.53–1.22 (m, 4H), 1.14 (s, 3H), 0.98 (s, 3H), 0.92 (t, J=7.4, 3H); δ_C (50 MHz; $CDCl_3$) 174.1, 134.8, 122.9, 70.6, 64.7, 52.7, 48.7, 47.6, 44.4, 38.0, 35.9, 34.5, 32.5, 26.2, 22.2, 20.5, 19.7, 13.5; m/z (EIHR) calculated for $C_{18}H_{29}NO_4S$ $(M)^+$ 355.1817, found 355.1819.

Analytical and spectral data for (14R)-9

mp 209°C (from n-hexane–isopropanol); $[\alpha]_D^{20}$ −88.8 (c 0.30, EtOH); ν_{max} (film)/cm^{-1} 3510, 2960, 2880, 1745, 1700, 1459, 1419, 1395, 1375, 1335, 1280, 1240, 1220, 1369, 1335, 1060, 970, 875, 759; δ_H (200 MHz; $CDCl_3$) 5.59 (dt, J_1=16.1, J_2=6.4, 1H), 5.42 (dt, J_1=16.2, J_2=6.7, 1H), 4.60 (dt, J_1=7.4, J_2=4.7, 1H), 3.90 (dd, J_1=7.7, J_2=5.1, 1H), 3.49 (ABq J=13.4, 2H), 3.04 (d, J=7.5, 1H), 2.68–2.32 (m, 2H), 2.29–1.80 (m, 7H), 1.52–1.20 (m, 4H), 1.14 (s, 3H), 0.97 (s, 3H), 0.88 (t, J=7.4, 3H); δ_C (50 MHz; $CDCl_3$) 168.5, 134.9, 124.0, 72.5, 65.2, 53.0, 48.5, 47.8, 44.6, 38.4, 35.9, 34.7, 32.8, 26.4, 25.0, 20.8, 19.9, 13.6; m/z (EIHR) calculated for $C_{18}H_{29}NO_4S$ $(M)^+$ 355.1817, found 355.1819.

*Preparation of (2R,14S)-(14-hydroxyheptanoyl)bornano-10,2-sultam (14S)-**10***

To the ene adduct (14*S*)-**6** (270 mg, 0.79 mmol) dissolved in ethyl acetate (15 mL), 10% palladium-on-charcoal (100 mg) was added, and the reaction mixture was stirred for 3 h under hydrogen atmosphere. Then the catalyst was removed, the solvent was evaporated and the residue was chromatographed (n-hexane–Et_2O, 9:1) to afford the product (14*S*)-**10** (242 mg, 89%) as an oil:

$[\alpha]_D^{20}$ −88.6 (c 1.67, EtOH); ν_{max} (film)/cm^{-1} 3499, 2957, 1691, 1458, 1413, 1474, 1334, 1137, 1060, 766, 544; δ_H (200 MHz; $CDCl_3$) 4.76–4.64 (m, 1H), 3.93 (dd, J_1=7.4, J_2=5.1, 1H), 3.49 (ABq J=13.9, 2H), 3.06–2.94 (m, 1H), 2.17–1.78 (m, 6H), 1.50–1.22 (m, 9H), 1.13 (s, 3H), 0.98 (s, 3H), 0.88 (t, J_1=6.5, 3H); δ_C (50 MHz; $CDCl_3$) 175.2, 71.2, 64.9, 52.8, 48.8, 47.8, 44.5, 38.1, 35.6, 32.6, 31.3, 26.4, 24.3, 22.4, 20.5, 19.8, 13.9; m/z (EIHR) calculated for $C_{12}H_{18}NO_4S$ $(M\text{-}C_5H_{11})^+$ 272.0957, found 272.0956.

*Preparation of (2R,14R)-N-(14-hydroxyheptanoyl)bornano-10,2-sultam (14R)-**11***

The ene adduct (14*R*)-**7** (201 mg, 059 mmol) was hydrogenated as described above to afford 176 mg (87%) of (14*R*)-**11** as on oil: $[\alpha]_D^{20}$ −79.4 (c 2.78, EtOH); ν_{max} (film)/cm^{-1} 3504, 2957, 1696, 1457, 1413, 1374, 1332, 1136, 1061, 765; δ_H (200 MHz; $CDCl_3$) 4.61–4.49 (m, 1H), 3.89 (dd, J_1=7.7, J_2=5.1, 1H), 3.49 (ABq J=13.8, 2H), 3.01 (d, J=7.2, 1H), 2.28–1.79 (m, 6H), 1.70–1.24 (m, 9H), 1.15 (s, 3H), 0.92 (s, 3H), 0.89 (t, J=6.5, 3H); δ_C (50 MHz; $CDCl_3$) 172.6, 70.8, 65.1, 52.7, 49.0, 47.8, 44.3, 37.9, 32.6, 32.6, 31.4, 26.3, 24.6, 22.4, 20.6, 19.7, 13.9; m/z (EIHR) calculated for $C_{12}H_{18}NO_4S$ $(M\text{-}C_5H_{11})^+$ 272.0957, found 272.0956.

*Preparation of (2S)-heptanediol-1,2 (**12**) and (2R)-heptanediol-1,2 (**14**)*

To a solution of compound (14*S*)-**10** (156 mg, 0.46 mmol) in Et_2O (20 mL) lithium aluminum hydride (950 mg) was added portionwise at 0°C. After stirring at room temperature over a period of 3 h, the reaction mixture was treated with an aqueous solution of sodium potassium tartrate (10 mL) and stirring was continued for additional 2 h. The post-reaction mixture was transferred into a separatory funnel and the aqueous layer was extracted with Et_2O (3 x 20 mL). The organic layers were combined, dried ($MgSO_4$), and evaporated *in vacuo*. The oily residue was treated with a mixture of Et_2O and n-hexane to give crystalline (2*R*)-bornane-10,2-sultam (**1**) in 80% yield. The mother liquor was evaporated and the oily residue was chromatographed (n-hexane–ethyl acetate, 7:3→4:6) to afford the desired product (2*S*)-heptanediol **12** (45 mg, 75% yield) as an oil. Analytical and spectral data for enantiomer (2*S*)-**12**: $[\alpha]_D^{20}$ −17.5 (c 2.92 EtOH), Lit.[24] $[\alpha]_D^{20}$=−16.1 (c 11,7, EtOH); ν_{max} (film)/cm^{-1} 3382, 2955, 2930, 2871, 2860, 1741, 1724, 1657, 1462, 1260, 1072, 1036, 871; δ_H (200 MHz, $CDCl_3$, 50°C) 3.71–3.62 (m, 1H), 3.59 (dd, J_1=10.9, J_2=2.8, 1H), 3.35 (dd, J_1=10.9, J_2=7.4, 1H), 2.54 (bs, 1H), 1.45–1.15 (m, 8H), 0.85 (bt, 3H); δ_C (50 MHz, $CDCl_3$, 50°C) 72.3, 66.7, 33.1, 31.8, 25.2, 22.5, 13.9; EIMS (m/z) (%) 131$(M-H)^+$ (0.65), 101$(M-CH_2OH)^+$ (33), 83 (100), 61 (13), 55 (87), 41 (18). enantiomer (2*R*)-**14**: $[\alpha]_D^{20}$ +17.1 (c 1,22, EtOH), Lit.[25] $[\alpha]_D^{20}$ +17.1° (c 2, EtOH).

Preparation of (2S)-octanediol-1,2 (13) and (2R)-octanediol-1,2 (15)

To a solution of compound (14*S*)-**8** in anhydrous ethyl acetate (20 mL), under argon atmosphere, PtO_2 (20 mg) was added, and the reaction mixture was stirred under hydrogen atmosphere at room temperature over a period of 3 h. Then the catalyst was removed, the solvent was evaporated and the residue was chromatographed (n-hexane–ethyl acetate, 7:3→4:6) to afford the product (2*S*)-**13** (42.5 mg, 92% yield) as an oil; Analytical and spectral data for enantiomer (2*S*)-**13**: $[\alpha]_D^{20}$ −16.4 (c 2.20 EtOH), Lit.[26] $[\alpha]_D^{20}$ −16.3 (c 2.10, EtOH); ν_{max} (film)/cm^{-1} 3373, 2928, 2857, 1652, 1466, 1378, 1071, 1039, 860, 724; δ_H (200 MHz, $CDCl_3$) 3.75–3.69 (m, 1H), 3.64 (dd, J_1=10.9, J_2=2.8, 1H), 3.41 (dd, J_1=11.2, J_2=7.7, 1H), 3.01 (bs, 1H), 1.55–1.15 (m, 10H), 0.88 (bt, 3H); δ_C (50 MHz, $CDCl_3$) 72.4, 66.7, 33.1, 31.7, 29.3, 25.5, 22.6, 14.0; EIMS (m/z) (%) 145$(M-H)^+$ (0.2), 129 (0.3), 115$(M-CH_2OH)^+$ (30), 97 (86), 69 (21), 55 (100), 43 (20)

Enantiomer (2*R*)-**15**: $[\alpha]_D^{20}$ +15.6 (c 1.15, EtOH), Lit.[26] $[\alpha]_D^{20}$ +14.5 (c 2.21, EtOH), $[\alpha]_D^{20}$ +16.7 (c 2.42, EtOH).

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