Synthesis and [4 + 2] Cycloaddition of (2*R*,2′*R*)-*N*,*N*′-Fumaroylbis[fenchane-8,2-sultam] (= (2*E*)-1,4-Bis[(3a*S*,6*S*,7a*R*)-1,4,5,6,7,7a-hexahydro-7,7-dimethyl-2,2-dioxido-3*H*-3a,6-methano-2,1-benzothiazol-1-yl]but-2-ene-1,4-dione) to Cyclopentadiene

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The now corrected X-ray structure of (2*R*)-bornane-10,2-sultam ((−)-**1a**), as well as that of its already published *N*-crotonoyl derivative (−)-**1d**, were compared with those of the newly synthesized (2*R*)-fenchane-8,2-sultam ((+)-**5a**), as well as its *N*-crotonoyl derivative (−)-**5d**. Also the *N*-methyl- and *N*-acryloylfenchane-8,2-sultams (−)-**5b**,**c** were prepared, and both the reactivity and diastereoselectivity imparted by the new chiral auxiliary to *N*,*N*′-fumaroylbis[fenchane-8,2-sultam] (−)-**5e** were compared with those of (−)-**1a** by addition of cyclopenta-1,3-diene to (−)-**5e**, in various solvents and at different temperatures under $TiCl_4$-mediated and uncatalyzed conditions. The determining influence of these factors is rationalized by the loss of the masked C_2 symmetry earlier attributed to camphor-derived sultams as well as transition-state dipolar stabilization by the solvent of the thermodynamically less stable *syn*-s-*cis* conformer.

Introduction. – We recently presented and compared the X-ray structure analyses of both the (2*R*)-bornane-10,2-sultam ((−)-**1a**) and its six-membered ring homologue (2*R*)-10a-homobornane-10a,2-sultam [1]. We discussed the stereoelectronic influence of the N lone pair (lp) as well as the steric influence of the Me(8) substituent on the N pyramidalization as well as conformations and diastereoselectivities imparted by these structural changes during the [4 + 2] cycloaddition of cyclopenta-1,3-diene to their N,N′-fumaroylbis[sultam] derivatives in different solvents [2]. For further comparison, we also wish to present the X-ray crystal-structure analysis of a new chiral auxiliary derived from (1*R*)-fenchone (−)-**2** and to comparatively discuss its influence on both the reactivity and diastereoselectivity of its *N*,*N*′-fumaroyl-derived dienophile[2]).

Results. – Two years ago, after submission of our paper describing the structure of the camphor-derived sultam (−)-**1a** [1], Prof. *King* [6] suggested that there was a typographical error in which the S−N (1.750(3) Å) and S−C (1.688(4) Å) bond lengths had accidentally become swapped because there is no other crystallographic evidence in the literature to suggest that the S−C bond length would be shorter than that of S−N[3]). We confirmed to him our original results but, after lengthy discussion, decided

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[2]) For previous asymmetric [4 + 2] cycloadditions of fumaroyl derivatives, see ref. cit. in [3]. For recent examples involving chiral dienophiles and chiral catalysts, see [4] and [5], resp.
[3]) For this functionality, the longest S−N bond length (1.723(3) Å, see footnote 22 in [1]) was measured for a (2*R*)-*N*-fluoro-2-methylbornane-10,2-sultam [7].

it best to redetermine the structure of (−)-**1a**[4]). The new results reported here (*Fig. 1*, *Table 1*) reveal quite normal bond lengths with S−N < S−C. Subsequently, a careful investigation of the original crystal-structure determination revealed that the unexpected geometric parameters were the result of an overlooked accidental interchange of the quite similar unit cell *b* and *c* parameters, which, in fact, led to many other unusual but at the time undetected bond lengths in the structure.

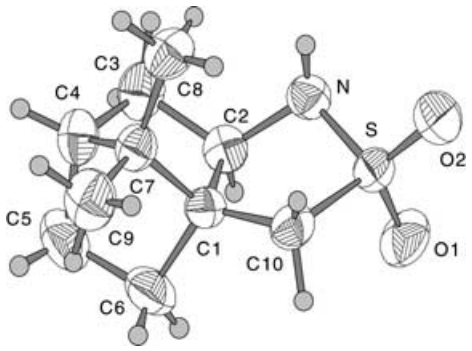

Fig. 1. *ORTEP Representation of (−)-***1a** *with arbitrary atom numbering*. Ellipsoids are represented at the 50% probability level.

Having effected this adjustment, we then turned our attention to the synthesis of the analogous fenchane (=1,3,3-trimethylbicyclo[2.2.1]hexane) derivative.

Starting from (1*R*)-fenchone ((−)-**2**)[5]), we encountered some difficulties in obtaining a satisfying yield of 2-oxofenchane-8-sulfonic acid ((−)-**3a**) using the original SO_3 conditions [11]. For this reason, we followed a recent and more practical procedure developed by Swedish authors [12] (Ac_2O, H_2SO_4), and were able to isolate the sulfonic acid (−)-**3a** in 66% yield (*Scheme*). Transformation to its corresponding sulfonyl chloride (−)-**3b** (66%) with $SOCl_2$ prior to sulfonamidation to (−)-**3c** (89%) with NH_4OH was also in accord with precedents [11]. Cyclization under acidic conditions (HCl) afforded the known unsaturated fenchanesultam (−)-**4** [11] (58%). The ultimate reduction, performed with $NaBH_4$ in MeOH/H_2O, furnished the new saturated fenchanesultam (+)-**5a** in 83% isolated yield. Its solid-state structure is represented in *Fig. 2*, and selected bond lengths and angles are given in *Table 1*.

To study the pyramidalization of the N-atom in the absence of a H-bond, we prepared the *N*−methyl analogue (−)-**5b** (NaH, THF, MeI; yield 60%) but were unable to grow suitable crystals[6]). For comparison with analogous known X-ray crystal-structure data of dienophiles (−)-**1c**,**d** obtained from the camphor-derived sultam [13][14], we also acylated sultam (+)-**5a** with the corresponding acyl chlorides

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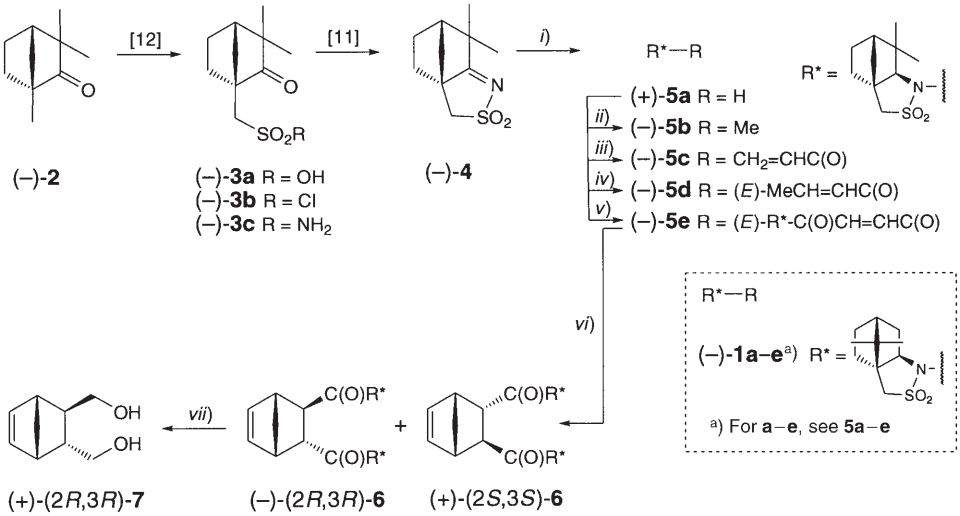
[4]) See acknowledgements as well as footnote 17 in [8].

[5]) The absolute configuration of (+)-(1*S*)-fenchone was earlier ascertained by chemical correlation with both (−)-(2*S*)-2-isopropyl-5-oxohexanoic acid and (−)-(2*S*)-2-isopropylglutaric acid [9], as well as by an X-ray structure analysis of (1*S*)-2-bromo-2-nitrofenchane [10]. Either the chiroptical properties or the absolute configurations reported in [11b][11c] are incorrect and inconsistent with [11a][12]. For (−)-**3a**, the following chiroptical properties were measured: $[\alpha]_D^{20} = -30.6$ ($c = 1.0$, acetone).

[6]) The corresponding *N*-fluorofenchanesultam may be more relevant.

Scheme



i) $NaBH_4$, MeOH, H_2O; 83%. *ii*) NaH, toluene, MeI; 60%. *iii*) NaH, toluene, acryloyl chloride; 32%. *iv*) NaH, toluene, crotonoyl chloride; 63%. *v*) NaH, toluene, fumaroyl chloride; 63%. *vi*) Cyclopentadiene, CH_2Cl_2, $-78°$; 92%. *vii*) $LiAlH_4$, THF; 44%.

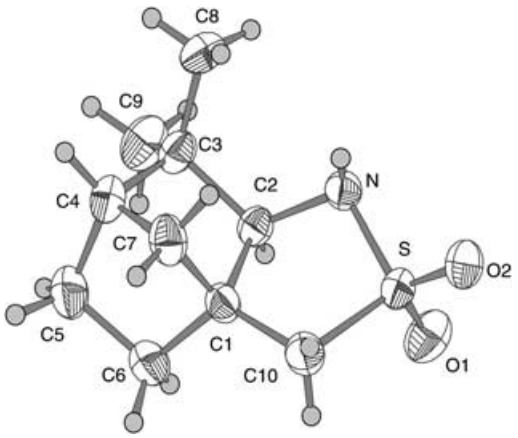


Fig. 2. *ORTEP Representation of (+)-***5a** *with arbitrary atom numbering.* Ellipsoids are represented at the 50% probability level.

(NaH, toluene) to isolate the unreported *N*-acryloyl fenchanesultam (–)-**5c** (32%), its *N*-crotonoyl analogue (–)-**5d** (63%), as well as its *N*,*N*′-fumaroyl derivative (–)-**5e** (63%). Crystals of (–)-**5d** suitable for X-ray analysis could be obtained. Its crystallographic structure is depicted in *Fig. 3*, and selected bond lengths and angles are given in *Table 1*.

To avoid problems of *endo*/*exo* selectivity, we initially chose the symmetric dienophile (–)-**5e** for the [4+2] cycloaddition to cyclopenta-1,3-diene. When the

Table 1. *Selected Bond Lengths* [Å] *and Angles* [°] *for (−)-***1a**,**d**, *(+)-***5a**, *and (−)-***5d**

	(−)-**1a**	(+)-**5a**	(−)-**1d** [14]	(−)-**5d**
S=O(1)	1.4267(17)	1.4287(15)	1.423(5)	1.4257(19)
S=O(2)	1.4292(17)	1.4332(13)	1.430(5)	1.4287(19)
S–N	1.6418(19)	1.6541(14)	1.694(4)	1.6787(16)
S–C(10)	1.799(2)	1.7883(19)	1.795(7)	1.760(2)
N–C(2)	1.478(3)	1.484(2)	1.475(7)	1.479(2)
N–H	0.85(3)	0.89(2)		
N–C(11)			1.384(6)	1.398(3)
O(3)–C(11)			1.218(6)	1.212(3)
C(11)–C(12)			1.463(8)	1.477(3)
C(12)–C(13)			1.333(7)	1.316(3)
O(1)=S=O(2)	117.84(11)	117.79(8)	117.6(4)	117.62(13)
C(2)–N–S	104.94(14)	104.22(10)	112.0(3)	113.92(13)
C(2)–N–H	115.7(19)	115.5(12)		
S–N–H	110.7(19)	102.2(13)		
C(2)–N–C(11)			119.9(4)	119.48(16)
S–N–C(11)			121.3(3)	123.46(14)
O(3)–C(11)–N			118.4(5)	119.5(2)
N–C(11)–C(12)			117.6(4)	116.77(19)
C(11)–C(12)–C(13)			121.1(5)	120.8(2)
C(12)–C(13)–C(14)			125.0(5)	125.5(3)
C(2)–N–S=O(1)	76.4(16)	75.43(12)	103.5(4)	124.03(16)
C(2)–N–S=O(2)	−153.97(15)	−154.98(11)	−125.9(4)	−105.50(16)
C(3)–C(2)–N–S	157.14(16)	161.73(12)	142.4(4)	128.44(16)
H–N–S=O(1)	−157.93(16)	−164.48(12)		
C(11)–N–S=O(1)			−47.3(5)	−35.8(2)
O(3)–C(11)–C(12)–C(13)			−5.9(8)	0.3(4)
S–N–C=O(3)			150.7(4)	153.44(17)
ΔhN	0.376(3)	0.447(2)	0.230(5)	0.155(2)
Puckering parameters q_2	0.558	0.675	0.651	0.670
S–N–C(2)–C(1)–C(10) ϕ_2	305.8	299.0	271.4	252.4

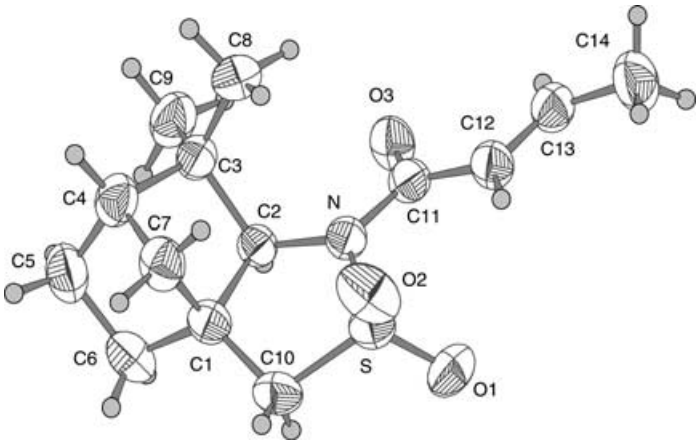


Fig. 3. *ORTEP Representation of (−)-***5d** *with arbitrary atom numbering*. Ellipsoids are represented at the 50% probability level.

reaction was performed in CH_2Cl_2 at $-78°$ in the presence of 2.5 mol-equiv. of $TiCl_4$ [15], cycloadduct (2*S*,3*S*)-**6** was obtained in 25% d.e. (*Table 2*, *Entry 1*), while an equimolar amount of this chelating *Lewis* acid resulted in a quantitative yield, albeit with a drop to 20% d.e. (*Entry 2*). This indicates that the poor diastereoselection in the latter case does not result from a mismatching co-operation [16] of both prosthetic groups in a chelated/unchelated disposition. When the reaction was repeated in the absence of *Lewis* acid, the diastereoselectivity (82% d.e., *Table 2*, *Entry 3*) was slightly lower than that promoted by (2*R*)-bornane-10,2-sultam (−)-**1a**. The sense of induction was established by the chiroptical properties of diol (+)-(2*R*,3*R*)-**7** ($[\alpha]_D^{20} = +14.93$ ($c = 0.6$, $CHCl_3$); [17]: $[\alpha]_D^{20} = +23.0$ ($c = 0.6$, $CHCl_3$)), obtained in 44% yield after $LiAlH_4$ reduction and chromatographic purification with recuperation of the chiral prosthetic group (94% yield), while its numerical value as well as the conversion were measured by ^{1}H-NMR analysis (500 MHz; ±2%) of the olefinic protons of the crude reaction mixture. Indeed, cycloadduct (−)-(2*R*,3*R*)-**6** exhibits ^{1}H-NMR resonances at δ 6.45 and 6.03, while its minor (+)-(2*S*,3*S*) stereoisomer **6** shows signals at δ 6.45 and 6.10, and the starting material (−)-**5e** appears as a *s* at δ 7.52. We then studied at 20° the solvent-polarity ($E_T(30)$ [18]) dependency and found that in polar DMF or MeCN, the diastereoselectivity decreased to 68 and 65% d.e., respectively, while in $CHCl_3$ 72% d.e. was reached. Indeed, less polar solvents such as THF (54% d.e.) or CCl_4 (59% d.e.) also resulted in erosion of the diastereoselectivity. In practically all cases, the conversions observed with this new chiral auxiliary were slightly inferior to those of the analogous more reactive camphor-derived sultam dienophile (−)-**1e**. We also observed that the induction was neither better in CH_2Cl_2 at $-78°$ nor a simple function of the solvent polarity, as earlier observed for (−)-**1e** [15], and that slightly better performances were obtained in CH_2Cl_2 (85% d.e.) and toluene (76% d.e.) at 20°, as compared to (−)-**1e**. Based on these seven solvents whose solvatochromic parameters are available [19], we found that the square of the *Hildebrand* index [20], the H-bond donor parameter α[7]), as well as the H-bond acceptor parameter β, were statistically not relevant and could be omitted in the *Abboud–Abraham–Kamlet–Taft* solvent model [21]. Thus, based on only π^* and δ, a good correlation was found between experimental and calculated diastereoselectivities ($\log(dr)$, dr = diastereoisomer ratio) for the cycloaddition of (−)-**5e** to cyclopenta-1,3-diene at 20°. When this linear regression was applied to a series of 27 solvents that we earlier tested with (−)-**1e** [2a], we predicted that the best diastereoselectivities should be observed in pyridine and nitrobenzene. These two aromatic solvents resulted in 76 and 85% d.e., respectively. As expressed by *Fig. 4*, a correlation coefficient of 0.85 ($n = 9$) was found with a standard deviation of 0.12 when the regression was fitted with the parameters of *Eqn 1*. It is noteworthy that the π^* parameter measures the ability of a solvent to stabilize a neighboring dipole by virtue of nonspecific dielectric interaction, and is thus nearly proportional to the dipole moment of the solvent. An empirically variable polarizability parameter δ must be added to correct the π^* term [21][8]).

$$\log(dr) = 0.321 + 0.493\ \pi^* + 0.268\ \delta \quad (1)$$

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[7]) This is normal since protic solvents were not tested.

[8]) See [2] for the values of π^*, δ, α, and β parameters of the different solvents used.

Table 2. *Comparative $TiCl_4$-Mediated and Uncatalyzed Cycloadditions of (−)-***1e** *and (−)-***5e** *to Cyclopenta-1,3-diene with Dependence of the Diastereoselectivity on the Solvent Polarity and Temperature*

Solvent	T [°]	$E_T(30)$ [18]	(−)-**1e** [2a][15]			(−)-**5e**		
		[kcal/mol]	Conv. [%]	d.e. [%]	Abs. conf.	Conv. [%]	d.e. [%]	Abs. conf.
CH_2Cl_2	−78	2.5 ($TiCl_4$)	>99	98	(2*R*,3*R*)	34	25	(2*S*,3*S*)
CH_2Cl_2	−78	1.0 ($TiCl_4$)	>99	98	(2*R*,3*R*)	>99	20	(2*S*,3*S*)
CH_2Cl_2	−78	40.7	95	89	(2*R*,3*R*)	92	82	(2*R*,3*R*)
MeCN	20	45.6	100	88	(2*R*,3*R*)	98	65	(2*R*,3*R*)
DMF	20	43.2	69	84	(2*R*,3*R*)	>99	68	(2*R*,3*R*)
$PhNO_2$	20	41.2	100	83	(2*R*,3*R*)	>99	85	(2*R*,3*R*)
CH_2Cl_2	20	40.7	100	84	(2*R*,3*R*)	>99	85	(2*R*,3*R*)
Pyridine	20	40.5	100	74	(2*R*,3*R*)	>99	76	(2*R*,3*R*)
$CHCl_3$	20	39.1	100	76	(2*R*,3*R*)	71	72	(2*R*,3*R*)
THF	20	37.4	100	75	(2*R*,3*R*)	>99	54	(2*R*,3*R*)
Toluene	20	33.9	100	64	(2*R*,3*R*)	>99	76	(2*R*,3*R*)
CCl_4	20	32.4	100	58	(2*R*,3*R*)	96	59	(2*R*,3*R*)

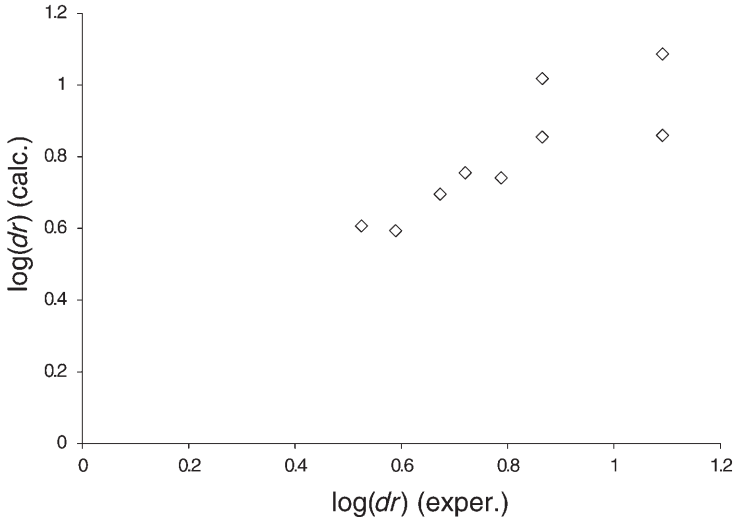

Fig. 4. *Experimental* vs. *predicted diastereoselectivity of (−)-***5e** *based on the* Abboud – Abraham – Kamlet – Taft *model* (*dr* = diastereoisomer ratio)

These results demonstrate a significant influence of the temperature, the solvent dipole moment, as well as chelation on the diastereoselectivity induced by this new fenchanesultam auxiliary (+)-**5a**.

Discussion. – X-Ray structure analysis of the free sultam (+)-**5a** (see *Fig. 2*) shows an intermolecular H-bond between the NH and the pseudoequatorial S=O(2)[9]) moiety of a neighboring molecule, in contrast to (−)-**1a** which prefers to make a H-

[9]) N–H 0.85(2) Å, H···O(2) 2.25(2) Å, N···O(2) 3.092(2) Å, N–H···O(2) 168.6(19)°.

bond with the corresponding pseudoaxial S=O(1) moiety[10]). The N-atom of (+)-**5a** is more pyramidalized than that of (−)-**1a** as expressed by either their respective ΔhN values[11]) (*Table 1*) or than in case of additive substituents angles (321.92° for (+)-**5a** and 331.34° for (−)-**1a** as compared to 360° for a planar sp^2 N-atom [22]). Both the N-tilting as well as the S=O(1) pseudoaxial orientation are similar in both free sultams (−)-**1a** and (+)-**5a**, indicating that the presence of a Me(8) substituent at position C(7) is not the primordial feature for the orientation of either the S=O or the N−H bonds, both involved in and directed by H-bonding. The situation is quite different with the sterically more demanding *N*-acyloylsultam (−)-**5d**. Indeed, due to a strong 1,5-repulsion with the Me(8) substituent at C(3), the *N*-crotonoyl side chain is obliged to adopt an identical orientation, imposing a similar but less pronounced N-tilting as compared to (−)-**1d** due to a second 1,5-repulsion with the Me(9) substituent at C(3). The C(11)=O(3) is similarly in an *anti*-periplanar orientation with respect to the SO_2 moiety as earlier rationalized by both a dipole–dipole repulsion [14b] and stereoelectronic influence [23][24]. The C(12)=C(13) bond is s-*cis* coplanar due to a severe steric interaction with either the SO_2 or the geminal Me groups at C(3) in either the *anti*- or *syn*-s-*trans* conformations, respectively. As a result, the orientation of S=O(2) is now modified, pointing in the pseudoaxial direction due to the absence of the Me(8) substituent at C(7) as well as the steric influence of the bisecting H−C(12)[12]). These features break the masked C_2 symmetry, a steric concept earlier proposed by *Kim* and *Curran* [25][13]). B3LYP/6-31G** DFT Calculations [26] suggest that the unchelated *syn*-s-*cis* conformer of (−)-**5d** (S−N−C=O −21.0°, O(3) bisecting the O(1)=S=O(2) angle[14]) and orientating the S=O(2) in a pseudoaxial direction) is thermodynamically 6.75 kcal/mol less stable than its *anti*-s-*cis* conformer (S−N−C=O 157.9°) (*Table 3*). This difference of energy is four times higher than that calculated for the corresponding conformers of (−)-**1d** [23][15]).

We were particularly astonished by the sense of induction under either chelating or thermal conditions. Indeed, according to *Curran*'s postulate [25], the *Lewis* acid chelated *syn*-s-*cis* disposition should induce the C(α)-*re* face attack at C(12) since similar orientation of the C(2)−C(3) substituent accumulates both steric and stereoelectronic influence for each of the (−)-**1d** and (−)-**5d** sultam prosthetic groups [28]. For the new dienophile (−)-**5d**, the topology should be inverted in the unchelated thermodynamically more stable *anti*-s-*cis* conformers. Indeed, in the case of (−)-**1d**, the

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[10]) N−H 0.85(3) Å, H···O(1) 2.39(3) Å, N···O(1) 3.194(3) Å, N−H···O(1)) 158(3)°.

[11]) Orthogonal distance separating the N-atom from the plane defined by its three substituents.

[12]) H···O(1) 2.62(2) Å, H···O(2) 2.85(2) Å.

[13]) The conformation of the dienophile side chain of *N*-crotonoylsultam (−)-**5d** is very close to the *N*-acryloylsultam (−)-**1c** [13] (O(3)−C(11)−C(12)−C(13) 1.0(9)°, S−N−C=O(3) 153.9(4), C(11)−N−S=O(1) −51.4(4)°, C(2)−N−S=O(1) 99.6(4)°, and C(2)−N−S=O(2) −131.1(4)°) which, like (−)-**1d**, possesses a more pyramidalized N-atom (ΔhN 0.226(3) Å) due to the steric influence of the pseudoequatorial S=O(2) and absence of C(3) substituents as well as a possibly more efficient *anti*-periplanar as compared to *syn*-periplanar stereoelectronic contribution of the N lp with the pseudoaxial S−O σ* bond [24].

[14]) This value is close to the dihedral angle of −25.6(7)° observed in the X-ray-analysis of the *syn*-s-*cis* chelated $TiCl_4$/(−)-**1d** complex [14b].

[15]) For a nonchelated *syn* conformer (S−N−C=O −9.3(8)°) imposing a greater planarity to the N-atom, see [27].

Table 3. *Conformational Energy of the* N-*Crotonoyl Side Chain of (−)-***5d**

S−N−C(11)=O(3) [°]	O(3)=C(11)−C(12)=C(13) [°]	*E* [kcal/mol]
− 90	159.2	16.95
− 90	− 5.5	14.68
90	0.7	10.10
90	− 179.4	9.03
− 21.0	− 8.0	6.75
157.9	− 4.9	0.0
− 33.4[a])	− 7.2	$TiCl_4$
− 6.5[b])	1.1	$TiCl_4$

[a]) Chelation of $TiCl_4$ with O(2) forced into a pseudo equatorial orientation is 3.2 kcal/mol higher in energy than for the situation given in *Footnote b*. [b]) Chelation of $TiCl_4$ with the pseudoequatorial O(1).

approach directed opposite to the pseudoaxial S=O(1) occurs on the same C(α)-*re* face with mismatching steric/stereoelectronic influences [28], while for (−)-**5d**, the reverse C(α)-*si* attack is expected, due to both the Me(8)−C(3) and proximate pseudoaxial S=O(2) substituents, benefiting from both cooperative steric/stereoelectronic influences, which no longer differentiate the reactivity of the *syn*- or now much more stable *anti*-s-*cis* conformers as initially suggested by us for (−)-**1d** [23][28]. Since the observed topology is completely the opposite and does not fit the simple steric view of *Curran*'s postulate [25], we were obliged to look for another rationalization. In the *Lewis* acid chelated *syn*-s-*cis* conformation[16]), either the additional π-facial steric influence of the Me(9)−C(3) substituent or the competition of reactive C=O coordinated but unchelated *anti*-s-*cis* conformers[17]) can rationalize a lower and opposite diastereoselectivity as compared to (−)-**1e** [14]. Alternatively, the poor selectivity may also be rationalized by the steric shielding of both π faces by either the Me(8)−C(3) substituent on the C(α)-*si* face or one apical Cl-atom on the C(α)-*re* face, due to the down orientation of the pseudoequatorial S=O(1), chelation with S=O(2) forced in a pseudoequatorial orientation being 3.2 kcal/mol higher in energy (*Table 3*). Under uncatalyzed conditions, the sense of induction is compatible with our initial hypothesis of a competitive reactive *syn*-s-*cis* conformation [23], the S−N−C=O dihedral angle being less planar than in the chelated case (see *Table 3*), the C(α)-*re* face would not be sterically influenced by the Me(9)−C(3) substituent. Additional more dipolar orthogonal SO_2−N−C=O conformations [2b], due to the presence of the geminal Me groups at C(3), seem statistically less relevant in view of their thermodynamically higher conformational constraints (see *Table 3*)[18]). These considerations may be similarly extended to the *N*-acryloyl or *N*,*N*′-fumaroyl dienophiles of type (−)-**5c**,**e**. Indeed, these rationales are consistent with the detrimental influence of a lower temperature on the diastereoselectivity observed in the case of (−)-**5e**, as compared to

16) The influence of either H-bond-donor solvents or other chelating and nonchelating *Lewis* acids under catalyzed and stoichiometric conditions shall be reported in due course.

17) For reactive out-of-plane complexation of the enone by *Lewis* acids in the *Diels–Alder* reaction, see [29].

18) For the X-ray structure analysis of a (2*R*,2′*R*)-*N*,*N*′-(2-ethylfumaroylbis[bornane-10,2-sultam] showing identical partial respective conformations as compared to (2*R*)-*N*-crotonoyl- [14] and (2*R*)-*N*-methacryloylbornane-10,2-sultam [30], see [31].

(−)-**1e**, by statistically increasing the *anti*-s-*cis* conformation in a competitive non-C_2 C(α)-*si* directing environment.

Conclusion. – Under $TiCl_4$-mediated chelating conditions, dienophile (−)-**5e**, derived from fenchanesultam (+)-**5a**, behaves differently than its camphor-derived sultam analogue (−)-**1e**, with 20–25% d.e. in favor of the (2*S*,3*S*)-cycloadduct **6**. Under uncatalyzed conditions, the temperature, the solvent dipole moment, and the aromaticity strongly influence the observed diastereoselectivity in favor of the diastereoisomeric (2*R*,3*R*)-cycloadduct **6**, with up to 85% d.e. in CH_2Cl_2 or $PhNO_2$. The loss of the masked C_2 symmetry imparted by camphor-derived sultam (−)-**1a** [25] as depicted in the X-ray-analysis of *N*-crotonoylfenchane-sultam (−)-**5d** may partially explain this inversion of the sense of induction. Indeed, in this case, in contrast to the X-ray crystal structure of (−)-**1d**, the O(1) atom adopts a pseudoequatorial orientation, while the absence of the Me(8)–C(7) substituent allows the O(2) atom to point in a pseudoaxial direction. Both the C=O functionality, *anti*-periplanar with respect to the SO_2 moiety, and the N-tilting remain identical as compared to the camphor-derived *N*-crotonoylsultam (−)-**1d**, despite the more planar N-atom of (−)-**5d** and the *syn*-periplanarity of its lp with the S=O(2) bond. The chameleon-like nature of the N-atom [1] incorporated in a sultam functionality allows its pitching to be modulated by H-bond, steric and/or stereoelectronic factors. The sense and extent of chiral induction generated by this new fenchanesultam (+)-**5a** is consistent with our hypothesis of *anti*-s-*cis*/*syn*-s-*cis* competitive reactive conformations [23]. Besides the loss of pseudo-C_2 symmetry, dienophiles derived from (+)-**5a**, as compared to (−)-**1a**, are also differentiated by the absence of mismatching steric/stereoelectronic influences in the thermodynamically much more stable *anti*-s-*cis* disposition. Both enantiomers of fenchone of high optical purities are commercially available, and the scope of this new, crystalline, and readily recovered chiral auxiliary is actually under investigation in our laboratory. Finally, (−)-isofenchone [32] or (−)-1-methylnorcamphor [33] could also be instructive as comparative sultam precursors lacking geminal Me groups at both C(3) and C(7).

The X-ray analyses of (−)-**1a**, (+)-**5a**, and (−)-**5d** were recorded by the crystallographic department of the University of Warsaw. We are also indebted to Dr. *G. Bernardinelli*, University of Geneva, for fruitful discussions, as well as to a referee for having found the origin of the error in the crystallographic data refinement.

Experimental Part

General. See [34].

X-Ray Crystal-Structure Analyses. Crystal data for structures (−)-**1a**, (+)-**5a**, and (−)-**5d**, are given in *Table 4*. All measurements of crystals were performed on a *Kuma-KM4CCD k*-axis diffractometer with graphite-monochromated MoK_α radiation. The crystal was positioned at 65 mm from the *KM4CCD* camera. The data were corrected for *Lorentz* and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the *Kuma* diffraction (Wroclaw) programs. The structure was solved by direct methods [35] and refined by means of SHELXL [36]. The refinement was based on F^2 for all reflections, except for those with very negative F^2. For (−)-**1a**, the H-atoms were located at isotropically refined positions, except for the Me groups. For (+)-**5a**, the H-atoms were located at calculated positions, except for NH. For (−)-**5d**, all the H-atoms were located at calculated positions. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in [37]. The known configurations of the asymmetric centers of the sultam unit were

confirmed by the *Flack*-parameter refinement [38]. The *Cremer* and *Pople* puckering parameters [39] (*Table 1*) were calculated according to [40]. CCDC 260372, 260373, and 260371 contain the supplementary crystallographic data for (−)-**1a**, (+)-**5a**, and (−)-**5d**, respectively. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.can.ac.uk/data_request/cif.

Table 4. *Crystal Data and Structure Refinement of Compounds (−)-***1a**, *(+)-***5a**, *and (−)-***5d**

		(−)-**1a**	(+)-**5a**	(−)-**5d**
Empirical formula		$C_{10}H_{17}NO_2S$	$C_{10}H_{17}NO_2S$	$C_{14}H_{21}NO_3S$
M_r		215.31	215.31	283.38
Temp. [°K]		293(2)	250(2)	293(2)
Wavelength [Å]		0.71073	0.71073	0.71073
Crystal system		orthorhombic	tetragonal	orthorhombic
Space group		$P2_12_12_1$	$P4_32_12$	$P2_12_12_1$
Unit-cell dimensions	a [Å]	9.2612(10)	7.8267(7)	7.6118(15)
	b [Å]	10.4082(11)	7.8267(7)	10.0412(17)
	c [Å]	11.1876(12)	34.959(4)	18.959(3)
Volume [Å^3]		1078.4(2)	2141.5(3)	1449.0(4)
Z		4	8	4
Density [Mg/m^3]		1.326	1.336	1.299
Absorption coeff. [mm^{-1}]		0.275	0.277	0.227
$F(000)$ electrons		464	928	608
Crystal size [mm]		$0.32 \times 0.18 \times 0.07$	$0.43 \times 0.23 \times 0.05$	$0.36 \times 0.21 \times 0.07$
θ Range for data [°]		2.67 to 28.70	2.85 to 28.78	2.88 to 28.80
Index ranges		$-12 \le h \le 12$	$-10 \le h \le 10$	$-10 \le h \le 10$
		$-13 \le k \le 13$	$-10 \le k \le 10$	$-13 \le k \le 13$
		$-14 \le l \le 15$	$-46 \le l \le 47$	$-25 \le l \le 25$
Reflections collected		20117/2691	40349/2731	26908/3619
R(int)		0.0486	0.0488	0.0523
Refinement method		Full-matrix least-squares on F^2 in all cases		
Data/restraints/parameters		2691/0/174	2731/0/133	3619/0/176
Goodness-of-fit on F^2		1.093	1.106	1.046
$R(F)$ ($I > 2\sigma(I)$)		0.0418	0.0345	0.0430
$wR(F^2)$(all data)		0.1220	0.0943	0.1190
Abs. structure parameter		−0.03(9)	−0.03(9)	0.00(9)
Extinction coefficient		0.211(14)	0.0137(15)	0.030(3)
Largest peak and holes [eÅ^{-3}]		0.382, −0.393	0.180, −0.201	0.349, −0.283

*(2*R*)-Fenchane-8,2-sultam* (*=(3a*S*,6*S*,7a*R*)-1,4,5,6,7,7a-Hexahydro-7,7-dimethyl-3*H*-3a,6-methano-2,1-benzothiazole 2,2-Dioxide*; (+)-**5a**). $NaBH_4$ (0.23 g, 6.05 mmol) was added in one portion to a soln. of unsaturated sultam (−)-**4** (1.2 g, 5.6 mmol) in MeOH/H_2O 3:1 (80 ml) at 5°. After 24 h at 20°, the mixture was evaporated and the residue dissolved in CH_2Cl_2 (5 ml). The CH_2Cl_2 soln. was poured onto 2N H_2SO_4 (10 ml), the aq. phase extracted with CH_2Cl_2 (2 × 10 ml), the org. layer dried ($MgSO_4$) and evaporated, and the crude product purified by crystallization (EtOH): (+)-**5a** (83%). Colorless crystals. M.p. 162–166° (Et_2O). $[\alpha]_D^{20} = +24.02$ ($c = 1$, $CHCl_3$). IR: 3252, 2957, 2876, 1482, 1458, 1409, 1387, 1321, 1280, 1185, 1142, 1068, 1039, 845, 799, 763, 722, 555, 526, 510. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.03 (*s*, 3 H); 1.11 (*s*, 3 H); 1.38 (*d*, *J* = 10.5, 1 H); 1.44 (*m*, 1 H); 1.58 (*m*, 1 H); 1.75 (*m*, 2 H); 1.85 (*m*, 1 H); 2.16 (*dd*, *J* = 10.3, 1.5, 1 H); 2.95 (*dd*, *J* = 7, 1.5, 1 H); 3.23 (*d*, *J* = 13.5, 1 H); 3.32 (*d*, *J* = 13, 1 H); 4.32 (*d*, *J* = 6.5, 1 H). ^{13}C-NMR: 24.0 (*q*); 24.2 (*t*); 26.3 (*q*); 30.5 (*t*); 40.3 (*t*); 42.0 (*s*); 48.5 (*d*); 53.8 (*s*); 53.9 (*t*); 71.5 (*d*). ESI-MS: 238 ($[M + Na]^+$). HR-ESI-MS: 238.0849 ($C_{10}H_{17}NO_2SNa^+$; calc. 238.0878). Anal. calc. for $C_{10}H_{17}NO_2S$: C 55.78, H 7.96, N 6.51, S 14.89; found: C 55.80, H 7.82, N 6.50, S 14.99.

*(2*R*)-*N*-Methylfenchane-8,2-sultam* (*=(3a*S*,6*S*,7a*R*)-1,4,5,6,7,7a-Hexahydro-1,7,7-trimethyl-3*H*-3a,6-methano-2,1-benzothiazole 2,2-Dioxide*; (−)-**5b**). A soln. of (+)-**5a** (100 mg, 0.46 mmol) in toluene (2 ml) was added dropwise at 0° to a 60% suspension of NaH in mineral oil (46 mg, 1.15 mmol) in toluene (3 ml). After 30 min, a soln. of MeI (150 µl, 0.46 mmol) in toluene (2 ml) was added dropwise. The resulting mixture was stirred

overnight at 20°. H_2O was added, and the aq. phase was extracted with CH_2Cl_2. The org. phase was dried ($MgSO_4$) and evaporated and the crude material purified by CC (SiO_2, AcOEt/cyclohexane 7:3): (−)-**5b** (60%). M.p. 68–72° (Et_2O). $[\alpha]_D^{20} = -15.33$ ($c = 1.0$, $CHCl_3$). IR: 3426, 2953, 2880, 1465, 1370, 1306, 1274, 1207, 1166, 1132, 1072, 1004, 987, 792, 773, 726, 685, 555, 536, 453. ^{1}H-NMR: 1.12 (*d*, *J* = 8, 6 H); 1.34 (*s*, 1 H); 1.41–1.36 (*m*, 1 H); 1.62–1.55 (*m*, 1 H); 1.78–1.68 (*m*, 2 H); 1.84 (*d*, *J* = 4.5, 1 H); 2.25 (*dd*, *J* = 8.5, 1.5, 1 H); 2.46 (*d*, *J* = 1, 1 H); 2.66 (*s*, 3 H); 3.19 (*AB*('*d*'), *J* = 12.5, 1 H); 3.37 (*AB*('*d*'), *J* = 13, 1 H). ^{13}C-NMR: 23.5 (*q*); 24.0 (*t*); 26.6 (*q*); 31.9 (*t*); 32.8 (*q*); 40.7 (*t*); 43.1 (*s*); 48.1 (*s*); 49.7 (*d*); 52.4 (*t*); 78.9 (*d*). ESI-MS: 230 ($[M+H]^+$), 252 ($[M+Na]^+$). HR-ESI-MS: 230.1185 ($C_{11}H_{20}NO_2S^+$, $[M+H]^+$; calc. 230.1215).

*(2*R*)*-N-*Acryloylfenchane-8,2-sultam* (=*1-[(3a*S*,6*S*,7a*R*)-1,4,5,6,7,7a-Hexahydro-7,7-dimethyl-2,2-dioxido-3*H*-3a,6-methano-2,1-benzothiazol-1-yl]prop-2-en-1-one* (−)-**5c**). As described for (−)-**5e**: (−)-**5c** (32%). M.p. 107–112° (AcOEt/hexane). $[\alpha]_D^{20} = -57.8$ ($c = 1.0$, $CHCl_3$). IR: 3431, 2971, 2878, 1675, 1619, 1469, 1411, 1338, 1313, 1286, 1269, 1253, 1174, 1147, 1035, 974, 799, 774, 544, 523. ^{1}H-NMR: 0.91 (*s*, 3 H); 1.27 (*s*, 3 H); 1.33 (*d*, *J* = 10.5, 1 H); 1.42 (*m*, 1 H); 1.63 (*m*, 1 H); 1.77 (*dt*, *J* = 11.5, 4, 1 H); 1.86 (*m*, 1 H); 1.89 (*m*, 1 H); 2.42 (*d*, *J* = 10.5, 1 H); 3.43 (*AB*('*d*'), *J* = 14, 1 H); 3.49 (*AB*('*d*'), *J* = 14, 1 H); 3.65 (*s*, 1 H); 5.85 (*d*, *J* = 12, 1 H); 6.48 (*d*, *J* = 16, 1 H); 6.78 (*dd*, *J* = 12, 16, 1 H). ^{13}C-NMR: 22.7 (*q*); 23.7 (*t*); 25.1 (*q*); 32.1 (*t*); 39.4 (*t*); 44.9 (*s*); 46.3 (*s*); 49.0 (*d*); 54.7 (*t*); 73.8 (*d*); 128.7 (*d*); 130.3 (*t*); 165.4 (*s*). ESI-MS: 292 ($[M+Na]^+$). HR-ESI-MS: 292.0982 ($C_{13}H_{19}NNaO_3S^+$, $[M+Na]^+$; calc. 292.0983).

*(2*R*)*-N-*Crotonoylfenchane-8,2-sultam* (=*(2*E*)-1-[3a*S*,6*S*,7a*R*)-1,4,5,6,7,7a-Hexahydro-7,7-dimethyl-2,2-dioxido-3*H*-3a,6-methano-2,1-benzothiazol-1-yl]but-2-en-1-one*; (−)-**5d**). As described for (−)-**5e**: (−)-**5d** (63%). M.p. 154–158° (hexane/AcOEt). $[\alpha]_D^{20} = -42.25$ ($c = 1.0$, $CHCl_3$). IR: 3435, 2979, 2878, 1674, 1633, 1443, 1333, 1289, 1230, 1172, 1147, 1086, 1023, 967, 806, 774, 644, 545, 521. ^{1}H-NMR: 0.90 (*s*, 3 H); 1.26 (*s*, 3 H); 1.32 (*d*, *J* = 10.5, 1 H); 1.41 (*m*, 1 H); 1.61 (*m*, 1 H); 1.76 (*dt*, *J* = 12.5, 4, 1 H); 1.86 (*m*, 2 H); 1.94 (*dd*, *J* = 5, 1.5, 2 H); 2.42 (*m*, 1 H); 3.40 (*AB*('*d*'), *J* = 12.5, 1 H); 3.47 (*AB*('*d*'), *J* = 12.5, 1 H); 3.63 (*d*, *J* = 1, 1 H); 6.48 (*d*, *J* = 14, 1 H); 7.04 (*dq*, *J* = 14, 5, 1 H). ^{13}C-NMR: 18.3 (*q*); 22.8 (*q*); 23.7 (*t*); 25.1 (*q*); 32.0 (*t*); 39.4 (*t*); 44.9 (*s*); 46.2 (*s*); 49.0 (*d*); 54.7 (*t*); 73.7 (*d*); 123.3 (*d*); 145.1 (*d*); 165.5 (*s*). ESI-MS: 306 ($[M+Na]^+$); 589 ($[2M+Na]^+$). HR-ESI-MS: 306.1131 ($C_{14}H_{21}NO_3NaS^+$, $[M+Na]^+$; calc. 306.1140).

*(2*R*,2′*R*)*-N,N′-*Fumaroylbis[fenchane-8,2-sultam]* (=*(2*E*)-1,4-Bis[3a*S*,6*S*,7a*R*)-1,4,5,6,7,7a-Hexahydro-7,7-dimethyl-2,2-dioxido-3*H*-3a,6-methano-2,1-benzothiazol-1-yl]but-2-ene-1,4-dione*; (−)-**5e**). A soln. of (+)-**5a** (100 mg, 0.46 mmol) in toluene (2 ml) was added dropwise at 0° to a 60% suspension of NaH in mineral oil (46 mg, 1.15 mmol) in toluene (2 ml). After 30 min, but-2-enedioyl dichloride (85 µl, 0.29 mmol) was added dropwise. The resulting mixture was stirred overnight at 20°. Workup as described for (−)-**5b** and CC (SiO_2, AcOEt/hexane 9:1 → 6:4) afforded (−)-**5e** (63%). R_f (toluene/AcOEt 7:3) 0.67. M.p. 208–211° (MeOH/AcOEt). $[\alpha]_D^{20} = -93.01$ ($c = 1$, $CHCl_3$). IR: 3430, 2957, 2877, 1671, 1470, 1324, 1213, 1169, 1149, 1087, 1045, 1023, 955, 771, 648, 546, 521. ^{1}H-NMR: 0.91 (*s*, 6 H); 1.27 (*s*, 6 H); 1.33 (*d*, *J* = 10, 4 H); 1.59 – 1.66 (*m*, 2 H); 1.75–1.81 (*m*, 2 H); 1.84–1.90 (*m*, 4 H); 2.43 (*d*, *J* = 9.5, 2 H); 3.42 (*AB*('*d*'), *J* = 13, 2 H); 3.49 (*AB*('*d*'), *J* = 12.5, 2 H); 3.63 (*s*, 2 H); 7.52 (*s*, 2 H). ^{13}C-NMR: 22.8 (*q*); 23.7 (*t*); 25.0 (*q*); 32.1 (*t*); 39.4 (*t*); 45.0 (*s*); 46.4 (*s*); 48.9 (*d*); 54.6 (*t*); 73.9 (*d*); 132.6 (*d*); 163.6 (*s*). ESI-MS: 533 ($[M+Na]^+$), 1042 ($[2M+Na]^+$). HR-ESI-MS: 533.1754 ($C_{24}H_{34}N_2O_6NaS_2^+$, $[M+Na]^+$; calc. 533.1756).

*[(2*S*,3*S*)-Bicyclo[2.2.1]hept-5-ene-2,3-diyl]bis[[3a*S*,6*S*,7a*R*)-1,4,5,6,7,7a-hexahydro-7,7-dimethyl-2,2-dioxido-3*H*-3a,6-methano-2,1-benzothiazol-1-yl]methanone]* ((+)-(2*S*,3*S*)-**6**). To a soln. of (−)-**5e** (51 mg, 0.1 mmol) in CH_2Cl_2 (2 ml), 1M $TiCl_4$ in CH_2Cl_2 (100 µl, 0.1 mmol) was added. Then, the mixture was cooled to −78°, and cyclopenta-1,3-diene (83 µl, 1.0 mmol) was added slowly along the wall of the flask. After 24 h at −78°, the mixture was quenched with NH_4F and equilibrated to 20°. After addition of H_2O, the mixture was extracted with CH_2Cl_2. The org. phase was dried ($MgSO_4$), and evaporated. Both conversion and d.e. were measured by integration of the olef. protons in the ^{1}H-NMR of the crude material. Pure material was obtained after purification by CC (SiO_2, from toluene to toluene/AcOEt 95:5): (+)-(2*S*,3*S*)-**6**. Oil. R_f (toluene/AcOEt 7:3) 0.74. $[\alpha]_D^{20} = +18.15$ ($c = 1$, $CHCl_3$). IR: 3442, 2953, 2876, 1681, 1472, 1333, 1280, 1223, 1169, 1146, 1087, 1046, 1021, 820, 757, 619, 539, 518. ^{1}H-NMR: 0.84 (*s*, 3 H); 0.90 (*s*, 3 H); 1.23 (*s*, 3 H); 1.29 (*s*, 3 H); 1.35–1.39 (*m*, 3 H); 1.54–1.62 (*m*, 4 H); 1.70–1.76 (*m*, 2 H); 1.81–1.87 (*m*, 4 H); 2.08 (*d*, *J* = 8.5, 1 H); 2.30 (*dd*, *J* = 2.0, 8.5, 2 H); 2.99 (*dd*, *J* = 1.5, 1.0, 1 H); 3.20 (*d*, *J* = 1.5, 1 H); 3.41–3.48 (*m*, 5 H); 3.53 (*s*, 1 H); 3.58 (*s*, 1 H); 3.81 (*dd*, *J* = 3.0, 2.0, 1 H); 6.10 (*dd*, *J* = 3.0, 2.5, 1 H); 6.45 (*dd*, *J* = 3.5, 2.5, 1 H). ^{13}C-NMR: 22.7 (2 C); 23.7; 25.0; 32.1; 32.2; 39.3; 44.9 (2 C); 46.05(2 C); 46.8; 47.3; 49.1; 50.5 (2 C); 52.4; 54.7; 74.2; 74.3; 134.8; 137.8; 173.8; 174.3. ESI-MS: 599 ($[M+Na]^+$), 1175 ($[2M+Na]^+$). HR-ESI-MS: 599.2220 ($C_{29}H_{40}N_2O_6NaS_2^+$, $[M+Na]^+$; calc. 599.2226).

*[(2*R*,3*R*)-Bicyclo[2.2.1]hept-5-ene-2,3-diyl]bis[(3a*S*,6*S*,7a*R*)-1,4,5,6,7,7a-hexahydro-7,7-dimethyl-2,2-dioxido-3*H*-3a,6-methano-2,1-benzothiazol-1-yl]methanone]* ((−)-(2*R*,3*R*)-**6**). Cyclopenta-1,3-diene (83 µl, 1 mmol) was added to a soln. of (−)-**5e** (51 mg, 0.1 mmol) in the desired solvent (2 ml; see *Table 2*) at −78°

(or 20°, see *Table 2*). After 24 h at this temp., the solvent was evaporated and the product filtered through a short SiO_2 column to remove polymers. Both conversion and d.e. were measured by means of ^{1}H-NMR. Pure material was obtained after CC (SiO_2, toluene → toluene/AcOEt 95:5): (−)-(2*R*,3*R*)-**6**. R_f (toluene/AcOEt 7:3) 0.56. M.p. 237–240° (MeOH/CH_2Cl_2). $[\alpha]_D^{20} = -188.0$ ($c = 1$, $CHCl_3$). IR: 3441, 2978, 2877, 1691, 1472, 1335, 1270, 1219, 1166, 1146, 1116, 1086, 1041, 1020, 861, 773, 714, 552, 525. ^{1}H-NMR: 0.87 (*s*, 3 H); 0.91 (*s*, 3 H); 1.20 (*s*, 3 H); 1.24 (*s*, 3 H); 1.28–1.38 (*m*, 4 H); 1.48 (*dd*, *J* = 7.5, 1, 1 H); 1.55–1.63 (*m*, 2 H); 1.70–1.77 (*m*, 2 H); 1.79–1.87 (*m*, 5 H); 2.45 (*d*, *J* = 10.5, 2 H); 3.29 (*d*, *J* = 1.0, 1 H); 3.34 (*d*, *J* = 4.5, 1 H); 3.37 (*d*, *J* = 5, 1 H); 3.45 (*d*, *J* = 4.5, 1 H); 3.47 (*d*, *J* = 4, 1 H); 3.52 (*s*, 1 H); 3.56 (*d*, *J* = 8.5, 2 H); 3.80 (*dd*, *J* = 3.5, 1 H); 4.53 (*t*, *J* = 4, 1 H); 6.03 (*dd*, *J* = 3.0, 2.5, 1 H); 6.45 (*dd*, *J* = 3.0, 3.5, 1 H). ^{13}C-NMR: 22.6; 22.9; 23.7 (2 C); 25.0 (2 C); 32.3 (2 C); 39.3; 39.35; 44.9; 45.1; 45.9 (2 C); 47.8; 48.4; 49.0; 49.4; 54.5 (2 C); 74.2; 74.5; 134.6; 137.8; 172.9; 173.7. ESI-MS: 599 ($[M + Na]^+$), 1175 ($[2M + Na]^+$). HR-ESI-MS: 599.2223 ($C_{29}H_{40}N_2O_6NaS_2^+$, $[M + Na]^+$; calc. 599.2226).

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