99. Non-destructive Removal of the Bornanesultam Auxiliary in α-Substituted *N*-Acylbornane-10,2-sultams under Mild Conditions: An Efficient Synthesis of Enantiomerically Pure Ketones and Aldehydes

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α-Substituted *N*-acylbornane-10,2-sultams **6**, **9**, and **10** can be converted into enantiomerically pure ketones **5**, **13**, and **14**, respectively, *via* a two-step procedure involving a known mercaptolysis reaction followed by an [Fe(acac)$_3$]-mediated coupling of the resulting *S*-benzyl thioesters with *Grignard* reagents. Futhermore, enantiomerically pure aldehydes **23** can be obtained from α-substituted *N*-acylbornane-10,2-sultams **6** *via* a one-step reduction with (i-Bu)$_2$AlH. No epimerization at the α-chiral center is observed during the cleavage reaction whereby the chiral auxiliary, bornane-10,2-sultam **1** or *ent*-**1**, was recovered. By using this methodology, several natural products or precursors thereof can be prepared.

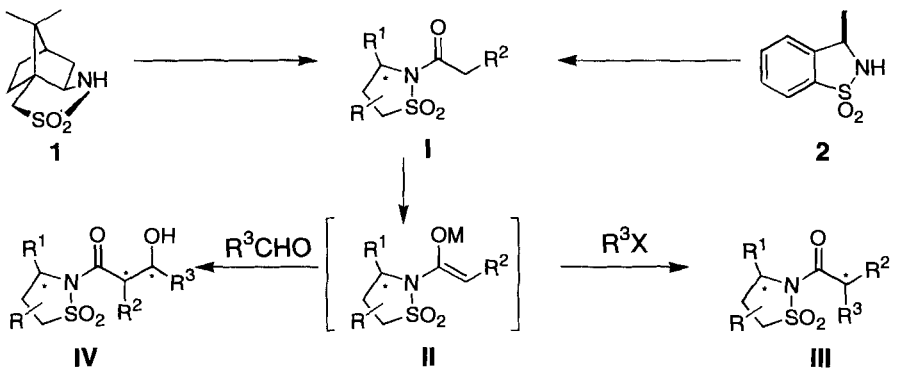
Introduction. – The asymmetric α-alkylation of carbonyl compounds is a fundamental and one of the more important transformations in organic chemistry [1]. The chiral RAMP and SAMP hydrazone auxiliaries of *Enders et al.* have defined one of the standards in the field for more than a decade: RAMP or SAMP hydrazones derived from acyclic ketones can be alkylated, followed by ozonolytic or hydrolytic cleavage of the auxiliary to yield α-substituted, enantiomerically enriched, acyclic ketones [2]. Since 1980, the generation of an 'acyclic' stereogenic center *via* face-selective alkylations of chiral enolates with electrophiles has been impressively addressed [1]. However, the transformation of the corresponding auxiliary-based carboxylic-acid derivatives into chiral ketones or aldehydes is not always straightforward. In this context, the pseudoephedrine auxiliary of *Meyers et al.* is worthwhile mentioning, because the pseudoephedrine amides can function as direct precursors to chiral aldehydes and ketones of high enantiomeric purity using alkoxyaluminum hydride and alkyllithium reagents, respectively [3].

In our laboratory, we developed the use of sultams **1**, **2**, and their antipodes as chiral auxiliaries [4]. Readily available in both antipodal forms[2]) they provide exceptionally high π-facial discrimination in most of the reactions of their 'enolate' derivatives [4a]. Two reactions are well studied: *i*) the diastereoselective alkylation of the enolates derived from the corresponding *N*-acylsultams **I**, even with unactivated alkyl halides (**II** → **III**) [4b] [5], and *ii*) the diastereoselective aldol condensation of the enolates **II**, producing either *syn*- or *anti*-aldol products with high diastereoisomeric purity (**II** → **IV**) [4b] [6]. In

[1]) Deceased, March 15, 1996.

[2]) Manufactured by *Oxford Chirality*, Oxford, UK.

Scheme 1

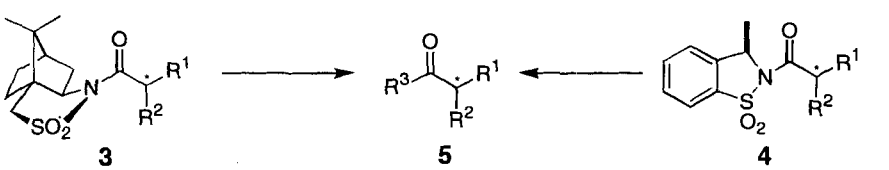


addition, the products **III** and **IV** are readily transformed into carboxylic acids, esters and primary alcohols (*Scheme 1*).

We report herein an efficient synthesis of enantiomerically pure aldehydes and ketones *via* a non-destructive cleavage of the sultam auxiliary in the alkylated *N*-acylsultams **III** or aldol products **IV**.

Enantiomerically Pure Ketones from α-Alkylated *N*-Acylbornane-10,2-sultams. – We recently reported that *N*-acyltoluenesultams such as **4** undergo smooth displacement of the sultam group by a variety of dilithiated alkyl phenyl sulfones, giving, after reductive removal of the sulfonyl group (SmI_2 or Al(Hg)), the corresponding ketones **5** without racemization at C(α) [7]. On the other hand, the cleavage of *N*-acylbornane-10,2-sultams such as **3** with dilithiated ethyl phenyl sulfone is relatively slow and occurs with partial racemization at C(α) (*Scheme 2*) [7b].

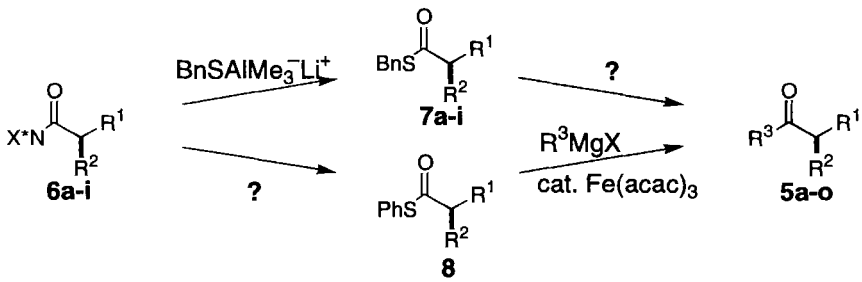
Scheme 2



Since the bornane-10,2-sultam derivatives are more readily available than their toluenesultam counterparts [4b], we sought an alternative strategy for the transformation of *N*-acylbornane-10,2-sultam derivatives **3** into ketones **5**. We were thereby attracted by a recent report by *Naito* and coworkers, who describe a selective and original cleavage of diastereoisomerically pure sultam- or oxazolidinone-based amides into *S*-benzyl thioesters by the action of an 'ate' complex, $BnSAlMe_3Li$, prepared *in situ* from trimethylaluminum and lithium benzylthiolate [8]. The corresponding thioesters **7** were obtained without concomitant racemization at C(α) (*Scheme 3*).

On the other hand, *Marchese* and coworkers reported an efficient synthesis of achiral or racemic ketones *via* an Fe^{III}-mediated coupling of *S*-phenyl thioesters with *Grignard* reagents (**8** → **5**) [9]. A combination of these two methods would thus provide a two-step procedure for the conversion of *N*-acylbornane-10,2-sultams into ketones.

Scheme 3



It turns out that the phenylthiol-derived 'ate' complex failed to displace the bornanesultam moiety in **6**. On the contrary, thioesters **7a–i** could be prepared in good yields by treatment of the *N*-acylsultams **6a–i** with the aluminum thiobenzyloxy 'ate' complex according to [8] (*Scheme 3* and *Table 1*).

Table 1. *Synthesis of* S-*Benzyl Thioesters* **7a–i** *by Mercaptolysis of* N-*Acylbornane-10,2-sultams* **6a–i**

Entry	Acylsultam	R^1	R^2	Time [h]	Sultam [%][a])	Thioester [%][a])	$[\alpha]_D$ ($CHCl_3$)
1	**6a**	Bn	Me	1.45	*ent*-**1** (89)	**7a** (92)	– 94.9
2	**6b**	Me	Bn	2	**1** (73)	**7b** (85)	+ 94.8
3	**6c**	Et	Me	1	**1** (94)	**7c** (96)	– 27.9
4	**6d**	Me	Et	2	*ent*-**1** (99)	**7d** (95)	+ 28.3
5	**6e**	Ph	Me	3.75	**1** (94)	**7e** (96)	– 95.1
6	**6f**	Me	Ph	3	*ent*-**1** (99)	**7f** (95)	+ 94.9
7	**6g**	(*E*)-$CH_2CMe{=}CHMe$	Me	2	*ent*-**1** (85)	**7g** (91)	– 17.8
8	**6h**	Me	(*E*)-$CH_2CMe{=}CHMe$	2	**1** (87)	**7h** (99)	+ 17.7
9	**6i**	(*E*)-$CH_2CMe{=}CHEt$	Me	0.5	*ent*-**1** (70)	**7i** (89)	– 18.3

[a]) Isolated yields of analytically pure compounds.

In most cases, both enantiomers of **7a–i** were prepared starting from the enantiomeric bornane-10,2-sultams[3]). Moreover, the chiral auxiliary was always recovered in excellent yields (73–99%).

The stage was now set to probe the crucial Fe^{III}-mediated coupling reaction of *S*-benzyl thioesters with a variety of *Grignard* reagents (**7a–i** → **5a–o**). Our results are summarized in *Table 2*.

Thus, treatment of the *S*-benzyl thioesters **7a–i** with *Grignard* reagents in the presence of a catalytic amount of $[Fe(acac)_3]$ (10 mol-%) gave the corresponding ketones in excellent yields (68–99%). The undesirable tertiary alcohols were not detected. The reaction works well with primary (Et, hexyl), secondary (i-Pr), and aromatic (Ph) *Grignard* reagents. Unfortunately, with more reactive *Grignard* reagents such as MeMgBr, (vinyl)MgBr, or (allyl)MgBr, the tertiary alcohol was the predominant product, even at

[3]) The α-alkylated *N*-acylbornane-10,2-sultams **6** are prepared according to [4b] and described in the *Exper. Part*.

Table 2. *Synthesis of Ketones* **5a**–**o** *by* Fe^{III}*-Mediated Coupling of* S*-Benzyl Thioesters* **7a**–**i** *with* Grignard *Reagents*

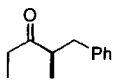
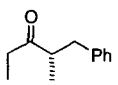
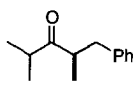
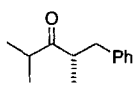
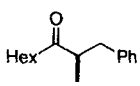
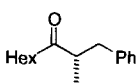
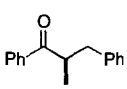
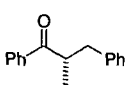
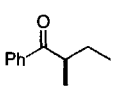
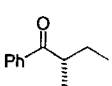
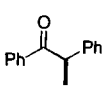
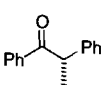
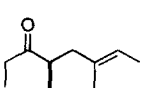
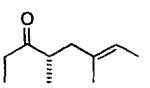
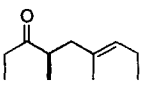
Entry	Thioester	Conditions	Product		Yield [%][a]	Conf.	ee [%]	$[\alpha]_D$[e]	$[\alpha]_D$[e] (ref.)
1	**7a**	EtMgBr (1.2 equiv.) – 35°, 4.5 h		**5a**	94	(*R*)	> 98[b])	– 54.9	–
2	**7b**	EtMgBr (1.6 equiv.) 0°, 0.5 h		**5b**	90	(*S*)	> 97[b])	+ 54.6	–
3	**7a**	(i-Pr)MgCl (1.2 equiv.) – 35°, 4.5 h		**5c**	92	(*R*)	> 99[b])	– 83.8	–
4	**7b**	(i-Pr)MgCl (1.6 equiv.) 0°, 3 h		**5d**	82	(*S*)	> 98[b])	+ 83.6	–
5	**7a**	(Hex)MgBr (2.6 equiv.) – 10°, 4 h		**5e**	75	(*R*)	> 99[c])	– 53.0	–
6	**7b**	(Hex)MgBr (1.6 equiv.) – 20°, 1.5 h		**5f**	86	(*S*)	> 99[c])	+ 53.2	–
7	**7a**	PhMgBr (1.2 equiv.) – 35°, 3 h		**5g**	87	(*R*)	–	– 71.7	–
8	**7b**	PhMgBr (2.2 equiv.) – 20°, 1.5 h		**5h**	81	(*S*)	–	–	–
9	**7c**	PhMgBr (1.5 equiv.) – 10°, 2 h		**5i**	77	(*R*)	> 99[b])	– 36.9	– 27.9
10	**7d**	PhMgBr (2.25 equiv.) 0°, 3 h		**5j**	77	(*S*)	> 99[b])	+ 36.8	+ 36.6
11	**7e**	PhMgBr (2.25 equiv.) – 20°, 4 h		**5k**	84	(*R*)	60[d])	– 150.5	–
12	**7f**	PhMgBr (2.25 equiv.) – 20°, 4 h		**5l**	84	(*S*)	58[d])	+ 144.9	+ 257 ([2f])
13	**7g**	EtMgB (1.8 equiv.) – 35°, 3.5 h		**5m**	69	(*R*)	94[b])	–	– 33.0 ([2f])

Table 2 (cont.)

Entry	Thioester	Conditions	Product		Yield [%][a]	Conf.	ee [%]	$[\alpha]_D$[e]	$[\alpha]_D$[e] (ref.)
14	**7h**	EtMgBr (2.1 equiv.) – 35°, 3 h		**5n**	70	(*S*)	93[b]	–	+ 31.6 ([2f])
15	**7i**	EtMgBr (1.7 equiv.) – 35°, 3 h		**5o**	99	(*R*)	> 99[b]	– 29.9	– 23.9 ([13b,c])

[a]) Isolated yields of analytically pure compounds. [b]) By chiral GC using *Lipodex E* as column. [c]) By chiral GC using *Lipodex D* als column. [d]) Deduced from the rotation. [e]) In $CHCl_3$ exept **5k**, **5l** measured in EtOH, and **5i**, **5j** in Et_2O.

very low temperatures, and no ketones could be isolated from the reaction mixture[4]). The enantiomeric excess (ee) was determined and proved to be, within the limits of detection, better than 93–99%, indicating that no epimerization at C(α) had occurred in the course of deprotection. In special cases, however, with a Ph group directly attached to C(α) (**5k**, **l**) the enantiomeric excess drops distinctly to 58–60% (*Entries 11* and *12*). This phenomenon was also observed using *Meyers* or *Enders* auxiliaries. However, our results still compare favorably with those previously published where the enantiomeric excess was 10% using *Enders*' method [2f] and 20% using *Meyers*' procedure [10].

Furthermore, the efficiency of this two-step cleavage is illustrated by the synthesis of the defensive substance of 'Daddy Longlegs' **5m**, **n** (*Leiobumum vittatum* [11] and *L. Calcar* [12]) in 94% ee (*Entries 13* and *14*)[5]) and of ethyl ketone **5o** (*Entry 15*), an intermediate in the synthesis of the marine polypropionates denticulatins A and B [13], in 99% ee. It is also worthwhile mentioning that no migration of the isolated C=C bonds was observed. Ethyl ketone **5o** was previously prepared starting from the corresponding *N*-acyltoluenesultam in 95% ee *via* displacement of the sultam moiety with dilithiated ethyl phenyl sulfone, followed by reductive removal of the sulfonyl group [13a][6]).

Scheme 4 and *Table 3* show that the same procedure is equally efficient for the formation of ketones starting from the bornanesultam-containing aldol products **9** and **10**.

The moderate-to-good yields of the isolated *S*-benzyl thioesters **11a**, **b** and **12a–c** extend the scope of the *Naito* procedure, tolerating functionalities such as β-alkoxy substituents. It is noteworthy that even esters are tolerated in the molecule, giving a smooth chemoselective mercaptolysis of the amide bond without elimination or cleavage of the β-acyloxy substituent (*Entries 2* and *5*). Subjecting **11a**, **b** and **12a–c** to the

[4]) Preliminary experiments show that reaction of thioesters **7** with *Gilman*'s cuprate (Me_2CuLi) would allow access to the corresponding methyl ketones: reaction of **7b** with Me_2CuLi in THF at – 20° gave the corresponding methyl ketone in 80% yield without apparent racemization at C(α). The use of vinyl or allyl cuprates (Mg counterion), however, resulted still in formation of the tertiary alcohol.

[5]) For a previously reported synthesis of **5m**, **n** in 97% ee, see [2e].

[6]) The synthesis of ethyl ketone **5o** was also described by *Hoffmann* and coworkers [13b], and *Ziegler* and *Becker* [13c] in their synthesis of denticulatins A and B, albeit in lower optical purity (80–89% ee)

Scheme 4

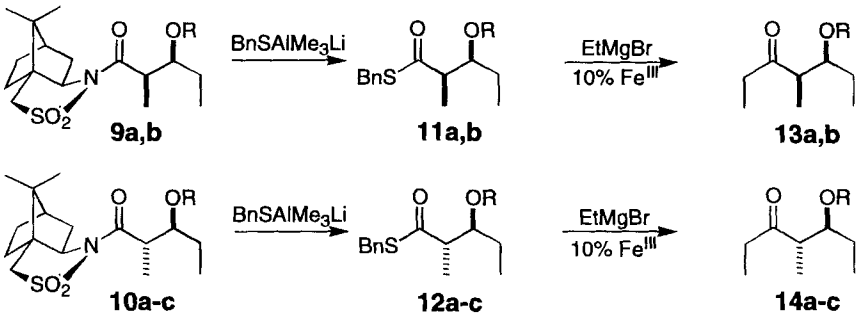


Table 3. *Transformation of* syn- *and* anti-*Aldols* **9** *and* **10** *to Ketones* **13** *and* **14** via S-*Benzyl Thioesters* **11** *and* **12** (TBS = (*t*-Bu)Me_2Si, TMS = Me_3Si)

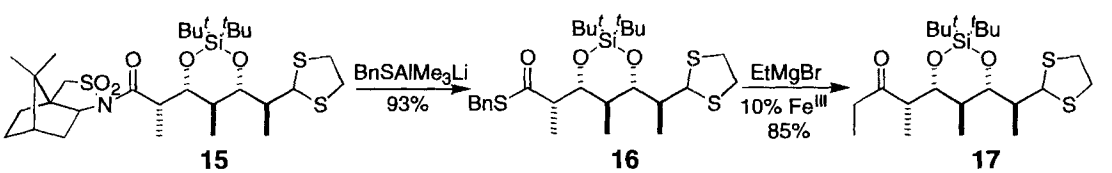
Entry	Aldol Product	Conditions	Sultam **1** [%][a])	Thioester ([%][a])	EtMgBr [equiv.]	Time [h]	Ketone ([%])[a])	de[b]) [%]	$[\alpha]_D$ ($CHCl_3$)
1	**9a** (R=TBS)	0°, 10 h	54	**11a** (61)	2.0	30	**13a** (65)	> 97	– 31.6
2	**9b** (R=COEt)	– 40°, 0.5 h	85	**11b** (80)	2.1	2	**13b** (83)	> 97	– 49.3
3	**10a** (R=TBS)	– 20°, 1 h	–	**12a** (80)	2.0	0.5	**14a** (78)	> 97	+ 62.3
4	**10b** (R=TMS)	– 10°, 2 h	89	**12b** (90)	1.9	0.5	**14b** (72)	–	+ 65.5
5	**10c** (R=COEt)	– 40°, 4.5 h	65	**12c** (46)	1.5	2.5	**14c** (85)	> 97	+ 27.0

[a]) Isolated yields of analytically pure compounds. [b]) Determined by comparison of ^{1}H-NMR spectra of diastereoisomers.

Fe^{III}-mediated coupling with EtMgBr gave the corresponding ketones in good yields (65–85%) and with high diastereoisomeric excess (> 97%), indicating that no racemization at C(α) had occurred. Compounds **13a, b** are protected forms of the aggregation pheromone of the rice and the maize weevil (Sitophilure: **13**, R = H) [14].

An impressive illustration of the effectiveness of this method is the efficient, two-step transformation of the highly functionalized stereopentad **15** into ethyl ketone **17** (*Scheme 5*).

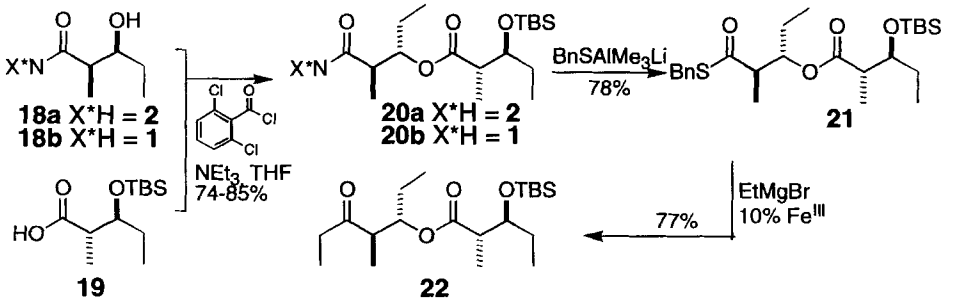
Scheme 5



Ethyl ketone **17** is a useful intermediate in the synthesis of the marine polypropionates denticulatins A and B. We previously reported the preparation of **17** *via* a lengthy four-step sequence involving the reductive cleavage of the bornanesultam auxiliary ($LiEt_3BH$), a *Swern* oxidation, a *Grignard* addition of EtMgBr, and another *Swern* oxidation [13a]. Applying the more practical two-step sequence described above, **17** was obtained from sultam derivative **15**, *via* thioester **16**, in 79% overall yield.

Recently, we reported a short efficient synthesis of the sex pheromone component of the Cigarette Beetle, (−)-serricorole, *via* key intermediate **22** (*Scheme 6*) [7a].

Scheme 6



The intermediate **22** was obtained after displacement of the toluenesultam moiety in **20a** by lithiated ethyl phenyl sulfone followed by reductive removal of the SO_2 group. The choice of the more readily removable toluenesultam auxiliary proved to be crucial for this transformation. However, by using the methodology described in this paper, it is now possible to use also **20b**, embedding the less expensive bornane-10,2-sultam auxiliary, instead of **20a**.

Indeed, treatment of **20b**, obtained *via Yamagushi* esterification [15] between aldol **18b** [6a] and carboxylic acid **19** [7a], with *Naito*'s 'ate' complex [8] gave clean displacement of the bornanesultam moiety, providing thioester **21** without concomitant cleavage of the ester group. Finally, Fe^{III}-mediated coupling of thioester **21** with EtMgBr produced the key intermediate **22**.

Optically Active Aldehydes from Reductive Cleavage of *N*-Acylbornane-10,2-sultams. – The cleavage of amide-bound chiral auxiliaries to obtain enantiomerically pure aldehydes is rare [16]. Generally, it proceeds with moderate yields [16a,b] or *via* a two-step procedure [16c–d]. Recently, *Meyers et al.* described a one-step reductive cleavage of pseudoephedrine-amide derivatives into chiral aldehydes of high optical purity using triethoxyaluminum hydride as the reducing agent [3]. Herein, we report an efficient, one-step, reductive cleavage of *N*-acylbornane-10,2-sultam derivatives with commercially available $(i\text{-Bu})_2AlH$ (DIBAL) affording enantiomerically pure aldehydes.

Thus, treatment of diastereoisomerically pure *N*-acylsultams **6a**, **b**, **j**–**o** with 1 equiv. of DIBAL in CH_2Cl_2 at −78° for 2 h afforded aldehydes **23a**–**h** in high yields (79–95%) and enantiomeric excess (90–99% ee). The chirophore **1** or its enantiomer *ent*-**1** were recovered in high yields (*Scheme 7* and *Table 4*).

As depicted in *Table 4*, the reduction took place without apparent racemization at C(α) except when C(α) was substituted with a Ph group (*Entries 7* and *8*). Exactly the same extent of racemization (~ 5%) was observed by *Meyers et al.* on reducing identically substituted pseudoephedrine-based amides with triethoxyaluminum hydride [3]. It is interesting to note that *Brown*'s reducing agent, triethoxyaluminum hydride [17], was inactive for the reductive cleavage of *N*-acylbornane-10,2-sultam derivatives **6**, whereby the starting material was recovered unchanged.

Scheme 7

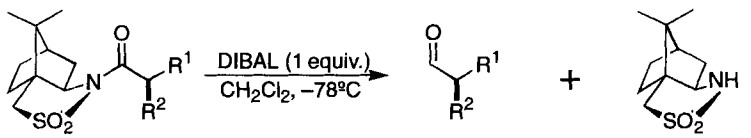


Table 4. *Synthesis of Aldehydes* **23a–h** *by DIBAL Reduction of* N-*Acylbornanesultams* **6**

Entry	Sultam	R^1	R^2	de of **6** [%][a])	Sultam ([%][b])	Aldehyde [%][a])	Conf.	ee [%][c])	$[\alpha]_D$ ($CHCl_3$)
1	**6a**	Bn	Me	94	*ent*-**1** (95)	**23a** (85)	(*R*)	94	–
2	**6b**	Me	Bn	99	**1** (88)	**23b** (83)	(*S*)	94	–
3	**6j**	$CH_2CH{=}CMe_2$	Isopropenyl	92	*ent*-**1** (95)	**23c** (79)	(*S*)	92	+ 95
4	**6k**	Isopropenyl	$CH_2CH{=}CMe_2$	95	**1** (95)	**23d** (87)	(*R*)	95	– 128
5	**6l**	Me	Octyl	97	**1** (86)	**23e** (95)	(*S*)	97	+ 21.7
6	**6m**	Octyl	Me	99	**1** (95)	**23f** (93)	(*R*)	99	– 20.2
7	**6n**	Et	Ph	98	*ent*-**1** (95)	**23g** (90)	(*S*)	91	+ 128
8	**6o**	Ph	Et	98	**1** (89)	**23h** (87)	(*R*)	90	– 128

[a]) By GC or ^{1}H-NMR. [b]) Isolated yields of analytically pure compounds. [c]) By chiral GC; *Lipodex C* or *Lipodex D* columns.

Conclusion. – In summary, the described two-step transformation of diastereoisomerically pure *N*-acylbornane-10,2-sultams into enantiomerically pure ketones represents a convenient and powerful procedure involving a mercaptolysis of the sultam derivatives with an *in situ* prepared 'ate' complex, followed by an Fe^{III}-mediated coupling of the resulting *S*-benzyl thioesters with *Grignard* reagents. This transformation, which compares very favorably with those already published, takes place under mild conditions without racemization at C(α) (except in some particular cases) and tolerates several functional groups such as double bonds, esters, and silyl protecting groups. The potential of this method is illustrated by the synthesis of complex intermediates *en route* to natural products.

Furthermore, we presented a particular attractive, one-step, reductive cleavage of *N*-acylbornane-10,2-sultam derivatives by using the commercially available DIBAL as the reducing agent. The corresponding optically active aldehydes were obtained without significant racemization at C(α).

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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/benzophenone), toluene (Na metal), CH_2Cl_2, HMPA, pyridine, Et_3N (CaH_2). Workup denotes extraction with an org. solvent, drying ($MgSO_4$), filtration, and evaporation *in vacuo*. Column flash chromatography (FC): SiO_2 (*Merck, Kieselgel 60*, 0.040–

0.060 mm). TLC: *Merck 60F254*, 0.025 mm. HPLC: *Waters 501 UV 481*, column *Lichrosorb Si60* (*Merck*, 5 mm), UV detector (λ = 254 nm); t_R in min (area %). GC: *Hewlett-Packard 5790A*, integrator *HP3390*, capillary column *OV-1* (11 m × 0.1 mm), 10 psi H_2, t_R in min (area %); chiral GC: *Lipodex D* or *E* columns (25 m × 0.25 mm). M.p.: *Kofler* hot stage apparatus, uncorrected. $[\alpha]_D$: *Perkin-Elmer-241* polarimeter. IR: *Perkin-Elmer 1600FT-IR* on KBr pallets. NMR-Spectra in $CDCl_3$, unless otherwise specified; standard: $CHCl_3$ (δ = 7.27 ppm); ^1H and ^{13}C were recorded on a *Bruker AMX-400* spectrometer at operating frequencies of 400.1 and 100.6 MHz, respectively. MS: *Varian CH-4* or *Finnigan 4023* at 70 eV, *m/z* (rel. %). HR-MS: *VG 707-E*.

Starting Materials. (2R)-N-{*(2S,3S)-3[(*tert-*Butyl)dimethylsilyloxy]-2-methylpentanoyl}bornane-10,2-sultam* (**10a**) [7a], *(2S,3S)-3[(*tert-*Butyl)dimethylsilyloxy]-2-methylpentanoic Acid* (**19**) [7a], *(2R)*-N-{*(2R,3S)-3-[(*tert-*Butyl)dimethylsilyloxy]-2-methylpentanoyl}bornane-10,2-sultam* (**9a**) [6a], *(2S)*-N-{*(2S)-2-[(4R,5S,6S)-2,2-Di(*tert-*butyl)-6[(1S)-1-([1,3]dithiolan-2-ylethyl]-5-methyl[1,3,2]dioxasilinan-4-yl]propan-1-oyl}bornane-10,2-sultam* (**15**) [13a].

(2R)-N-*[(2R,3S)-2-Methyl-3-(propionyloxy)pentanoyl]bornane-10,2-sultam* (**9b**). Propionyl chloride (0.180 ml, 2.00 mmol) was added at 0° to a soln. of *(2R)*-N-*[(2R,3S)-3-hydroxy-2-methylpentanoyl]bornane-10,2-sultam* (**9**, R = H) [6a] (0.520 g, 1.56 mmol) in CH_2Cl_2/pyridine. The mixture was stirred at 0° for 20 h, then 0.1M aq. HCl was added to the mixture. Workup and FC (hexane/Et_2O 95:5) gave **9b** (0.570 g, 95%). M.p. 86–88°. $[\alpha]_D$ = – 79.9; $[\alpha]_{578}$ = – 102.2; $[\alpha]_{546}$ = – 116.6; $[\alpha]_{436}$ = – 198.4; $[\alpha]_{365}$ = – 314.5 (*c* = 1.23, $CHCl_3$, 21.5°). IR: 1730, 1698, 1461, 1378, 1305, 1270, 1219, 1133, 1059, 938, 552. ^1H-NMR: 0.87 (*t*, *J* = 7.4, 3 H); 0.97 (*s*, 3 H); 1.10–1.25 (*m*, 9 H); 1.30–1.50 (*m*, 2 H); 1.50–1.70 (*m*, 2 H); 1.80–1.90 (*m*, 3 H); 2.00–2.10 (*m*, 2 H); 2.40 (*dd*, *J* = 15.6, 7.7, 2 H); 3.20–3.30 (*m*, 1 H); 3.50 (*m*, 2 H); 3.90–4.00 (*m*, 1 H); 5.25 (*m*, 1 H). ^{13}C-NMR: 174.00 (*s*); 173.51 (*s*); 74.63 (*d*); 65.17 (*d*); 53.21 (*t*); 48.35 (*s*); 47.78 (*s*); 44.68 (*d*); 43.97 (*d*); 38.37 (*t*); 32.87 (*t*); 27.76 (*t*); 26.44 (*t*); 25.84 (*q*); 20.80 (*q*); 19.86 (*q*); 15.02 (*s*); 9.71 (*q*); 9.25 (*q*). MS: 57 (65), 69 (14), 97 (100), 135 (10), 171 (22), 328 (0.7), 386 (0.2, $[M + 1]^+$). HR-MS: 328.1567 ($[C_{19}H_{31}NO_5S - C_3H_5O]^{+\cdot}$; calc. 328.1583).

(2R)-N-*[(2S,3S)-2-Methyl-3-(trimethylsilyloxy)pentanoyl]bornane-10,2-sultam* (**10b**). Me_3SiCl (TMSCl, 0.20 ml, 1.6 mmol) was added at 0° to a soln. of *(2R)*-N-*[(2S,3S)-3-hydroxy-2-methylpentanoyl]bornane-10,2-sultam* (**10**, R = H) [7a] (0.400 g, 1.26 mmol) and Et_3N (0.34 ml, 2.43 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at r.t. for 3 h, then 0.1M aq. HCl was added to the mixture. Workup and FC (hexane/Et_2O 9:1) gave **10b** (0.48 g, 98%). M.p. 88–91°. $[\alpha]_D$ = + 62.8; $[\alpha]_{578}$ = + 66.2; $[\alpha]_{546}$ = + 76.4; $[\alpha]_{436}$ = + 144.9; $[\alpha]_{365}$ = + 265.3 (*c* = 2.04, $CHCl_3$). IR: 2961, 1693, 1458, 1394, 1331, 1270, 1214, 1133, 1062, 842, 536. ^1H-NMR: 0.10 (*s*, 9 H); 0.86 (*t*, *J* = 7.4, 3 H); 0.94 (*s*, 3 H); 1.07 (*d*, *J* = 6.8, 3 H); 1.15 (*s*, 3 H); 1.25–1.55 (*m*, 4 H); 1.80–2.00 (*m*, 3 H); 2.00–2.10 (*m*, 2 H); 3.25 (*quint*, *J* = 6.8, 1 H); 3.39 (*d*, *J* = 13.8, 1 H); 3.48 (*d*, *J* = 13.8, 1 H); 3.90 (*m*, 1 H); 3.95–4.05 (*m*, 1H). ^{13}C-NMR: 174.62 (*s*); 74.68 (*d*); 65.23 (*d*); 53.10 (*t*); 48.11 (*s*); 47.69 (*s*); 45.29 (*d*); 44.69 (*d*); 38.61 (*t*); 32.80 (*t*); 26.48 (*t*); 25.30 (*t*); 20.87 (*q*); 19.87 (*q*); 11.99 (*q*); 8.37 (*q*); 0.32 (*q*). MS: 55 (15), 69 (15), 73 (100), 74 (10), 75 (26), 79 (10), 93 (13), 107 (11), 131 (75), 135 (23), 150 (17), 157 (23), 187 (14), 343 (24), 386 (16, $[M^+ - 15]$). HR-MS: 386.1860 ($[C_{19}H_{35}O_4SiSN - CH_3]^{+\cdot}$; calc. 386.1821).

(2R)-N-*[(2S,3S)-2-Methyl-3-(propionyloxy)pentanoyl]bornane-10-2-sultam* (**10c**). Propionyl chloride (0.172 ml, 1.914 mmol) was added at 0° to a soln. of *(2R)*-N-*[(2S,3S)-3-hydroxy-2-methylpentanoyl}bornane-10,2-sultam* (**10**, R = H) [7a] (0.485 g, 1.472 mmol) in CH_2Cl_2/pyridine. The mixture was stirred at 0° for 18 h, then 0.1M aq. HCl was added to the mixture. Workup and FC (hexane/Et_2O 4:7) gave **10c** (0.506 g, 89%). M.p. 140–142°. $[\alpha]_D$ = – 48.8; $[\alpha]_{578}$ = – 51.2; $[\alpha]_{546}$ = – 58.1; $[\alpha]_{436}$ = – 102.2; $[\alpha]_{365}$ = – 170.1 (*c* = 1.22, $CHCl_3$, 20.5°). IR: 2967, 2903, 2880, 1736, 1689, 1458, 1409, 1394, 1337, 1216, 1186, 1133. ^1H-NMR: 0.88 (*t*, *J* = 7.5, 3 H); 0.98 (*s*, 3 H); 1.12 (*t*, *J* = 7.5, 3 H); 1.18 (*d*, *J* = 7.1, 3 H); 1.19 (*s*, 3 H); 1.30–1.45 (*m*, 2 H); 1.50–1.60 (*m*, 1 H); 1.74–2.00 (*m*, 5 H); 2.08 (*dd*, *J* = 8.0, 13.7, 1 H); 2.24 (*dt*, *J* = 7.5, 16.4, 1 H); 2.31 (*dt*, *J* = 7.5, 16.4, 1 H); 3.38 (*dq*, *J* = 7.1, 8.4, 1 H); 3.44 (*d*, *J* = 13.7, 1 H); 3.52 (*d*, *J* = 13.7, 1 H); 3.88 (*dd*, *J* = 7.5, 4.9, 1 H); 5.13 (*dt*, *J* = 3.5, 8.4, 1 H). ^{13}C-NMR: 173.64 (*s*); 173.45 (*s*); 76.55 (*d*); 65.41 (*d*); 53.19 (*t*); 48.25 (*s*); 47.73 (*s*); 44.78 (*d*); 43.17 (*d*); 38.62 (*t*); 32.94 (*t*); 27.57 (*t*); 26.46 (*t*); 24.21 (*t*); 20.88 (*q*); 19.89 (*q*); 13.79 (*q*); 9.20 (*q*); 8.71 (*q*). MS: 57 (69), 69 (9), 93 (5), 97 (100), 108 (2), 134 (4), 135 (11), 171 (41), 172 (4), 216 (3), 271 (4), 300 (2), 312 (1.5). HR-MS: 312.1624 ($[C_{19}H_{31}O_5NS - C_3H_5O_2]^{+\cdot}$; calc. 312.1633).

General Procedure for the Asymmetric Alkylation of N-*Acylbornanesultams.* A 1.6M soln. of BuLi (hexane, 1.17 equiv.) was added over 2 h to a soln. of *N*-acylbornanesultam (1 equiv.) in THF (38 ml/10 mmol) at –78°. The mixture was stirred at –78° for 1 h, and a soln. of halide (3 equiv.) in HMPA (3 equiv.) was added at –78°, and stirring was continued for 1/2 to 15 h at –70° to –50°. Hydrolysis with a 1M. aq. soln. of HCl, workup (Et_2O), and purification by FC and/or crystallization furnished alkylation products **6a–o**.

(2S)-N-*[(2R)-2-Methyl-3-phenylpropionyl]bornane-10,2-sultam* (**6a**). Alkylation of (2*S*)-*N*-propionylbornane-10,2-sultam (0.500 g, 1.844 mmol) with $PhCH_2I$ (0.75 ml, 5.532 mmol) gave, after workup followed by FC (hexane/Et_2O 99:1) and recrystallization (hexane), pure **6a** (0.59 g, 89%). $[\alpha]_D$ = + 3.6; $[\alpha]_{578}$ = + 3.3;

$[\alpha]_{546} = +3.1$; $[\alpha]_{436} = -2.0$; $[\alpha]_{365} = -18.3$ ($c = 1.09$, $CHCl_3$, 21°). M.p. 119–120°. IR: 3030, 3005, 2988, 2954, 2878, 1699, 1606, 1466, 1409, 1394, 1325, 1282, 1223, 1136, 1116, 1060, 975. ^{1}H-NMR: 0.70 (*s*, 3 H); 0.88 (*s*, 3 H); 1.21 (*d*, $J = 6.6$, 3 H); 1.25–1.38 (*m*, 2 H); 1.68–1.98 (*m*, 5 H); 2.70 (*dd*, $J = 7.1$, 12.8, 1 H); 3.01 (*dd*, $J = 12.8$, 8.4, 1 H); 3.36 (*d*, $J = 13.7$, 1 H); 3.41 (*d*, $J = 13.7$, 1 H); 3.46 (*ddq*, $J = 6.6$, 7.1, 8.4, 1 H); 3.81 (*dd*, $J = 4.9$, 8.0, 1 H); 7.15–7.27 (*m*, 5 H). ^{13}C-NMR: 175.58 (*s*); 138.61 (*s*); 129.34 (*d*); 128.22 (*d*); 126.39 (*d*); 65.12 (*d*); 53.12 (*t*); 48.07 (*s*); 47.54 (*s*); 44.64 (*d*); 41.76 (*d*); 41.28 (*t*); 38.34 (*t*); 32.85 (*t*); 26.42 (*t*); 20.51 (*q*); 19.80 (*q*); 16.64 (*q*). MS: 361 (7), 297 (1), 282 (1), 254 (1), 147 (10), 135 (5), 119 (60), 118 (58), 108 (5), 91 (100). HR-MS: 361.1683 ($[C_{20}H_{27}O_3NS]^{+\cdot}$; calc. 361.1712).

(2R)-N-[(2S)-2-Methyl-3-phenylpropionyl]bornane-10,2-sultam (**6b**). Alkylation of (2*R*)-*N*-propionylbornane-10,2-sultam (2.5 g, 9.2 mmol) with $PhCH_2I$ (3.8 ml, 27.5 mmol) gave, after workup followed by FC (hexane/Et_2O 99:1) and recrystallization (hexane), pure **6b** (1.7 g, 81%) showing the same m.p., IR, NMR, and MS as compound **6a**.

(2R)-N-[(2R)-2-Methylbutanoyl]bornane-10,2-sultam (**6c**). Alkylation of (2*R*)-*N*-butanoylbornane-10,2-sultam (0.400 g, 1.406 mmol) with MeI (0.26 ml, 4.218 mmol) gave, after workup followed by FC (hexane/Et_2O 99:1) and recrystallization (hexane), pure **6c** (0.362 g, 86%). M.p. 188–189°. $[\alpha]_D = -106.2$; $[\alpha]_{578} = -110.8$; $[\alpha]_{546} = -125.8$; $[\alpha]_{436} = -211.9$; $[\alpha]_{365} = -331.1$ ($c = 1.68$, $CHCl_3$, 20°). IR: 2990, 2964, 2930, 2874, 1686, 1463, 1413, 1394, 1325, 1285, 1225, 1135, 1062. ^{1}H-NMR: 0.92 (*t*, $J = 7.5$, 3 H); 0.92 (*s*, 3 H); 1.16 (*s*, 3 H); 1.20 (*d*, $J = 6.6$, 3 H); 1.30–1.50 (*m*, 3 H); 1.65–1.97 (*m*, 4 H); 2.00–2.10 (*m*, 2 H); 2.99 (*sext.*, $J = 6.9$, 1 H); 3.44 (*d*, $J = 13.7$, 1 H); 3.50 (*d*, $J = 13.7$, 1 H); 3.90 (*t*, $J = 6.4$, 1 H). ^{13}C-NMR: 176.31 (*s*); 65.06 (*d*); 53.20 (*t*); 48.22 (*s*); 47.71 (*s*); 44.61 (*d*); 41.86 (*d*); 38.46 (*t*); 32.81 (*t*); 26.44 (*t*); 25.65 (*t*); 20.80 (*q*); 19.87 (*q*); 18.61 (*q*); 11.74 (*q*). MS: 299 (5), 271 (38), 220 (10), 207 (10), 152 (38), 151 (23), 150 (13), 136 (15), 135 (39), 134 (41), 109 (14), 108 (35), 107 (16), 94 (11), 85 (91), 57 (100). HR-MS: 299.1546 ($[C_{15}H_{25}O_3NS]^{+\cdot}$; calc. 299.1555).

(2S)-N-[(2S)-2-Methyl]bornane-10,2-sultam (**6d**). Alkylation of (2*S*)-*N*-butanoylbornane-10,2-sultam (0.500 g, 1.75 mmol) with MeI (0.33 ml, 0.525 mmol) gave, after workup followed by FC (hexane/Et_2O 99:1) and recrystallization (hexane), pure **6d** (0.491 g, 94%) showing the same m.p., IR, NMR, and MS as compound **6c**. $[\alpha]_D = +106.1$; $[\alpha]_{578} = +110.6$; $[\alpha]_{546} = +125.4$; $[\alpha]_{436} = +210.5$ ($c = 9.53$, $CHCl_3$, 20°). HR-MS: 299.1550 ($[C_{15}H_{25}O_3NS]^{+\cdot}$; calc. 299.1555).

(2R)-N-[(2R)-2-Phenylpropionyl]bornane-10,2-sultam (**6e**). Alkylation of (2*R*)-*N*-benzoylbornane-10,2-sultam (0.350 g, 1.050 mmol) with MeI (0.43 ml, 3.15 mmol) gave, after workup followed by FC (hexane/AcOEt 7:1) and recrystallization (hexane), pure **6e** (0.296 g, 81%). M.p. 118–120°. $[\alpha]_D = -62.8$; $[\alpha]_{578} = -64.8$; $[\alpha]_{546} = -74.0$; $[\alpha]_{436} = -118.2$; $[\alpha]_{365} = -173.4$ ($c = 1.16$, $CHCl_3$, 20°). IR: 3079, 3032, 2966, 2931, 2887, 1690, 1602, 1493, 1458, 1384, 1322, 1267, 1218, 702. ^{1}H-NMR: 0.99 (*s*, 3 H); 1.21 (*s*, 3 H); 1.25–1.45 (*m*, 2 H); 1.59 (*d*, $J = 7.1$, 3 H); 1.80–1.90 (*m*, 3 H); 2.00–2.20 (*m*, 2 H); 3.44 (*d*, $J = 13.7$, 1 H); 3.54 (*d*, $J = 13.7$, 1 H); 3.86 (*dd*, $J = 4.9$, 7.5, 1 H); 4.45 (*q*, $J = 7.1$, 1 H); 7.20–7.50 (*m*, 5 H). ^{13}C-NMR: 174.11 (*s*); 139.14 (*s*); 128.42 (*d*); 128.25 (*d*); 127.19 (*d*); 65.45 (*d*); 53.18 (*t*); 48.35 (*s*); 47.78 (*s*); 45.29 (*d*); 44.67 (*d*); 38.49 (*t*); 32.88 (*t*); 26.42 (*t*); 20.92 (*q*); 20.05 (*q*); 19.89 (*q*). MS: 348 (19), 347 (72), 242 (12), 214 (11), 136 (12), 135 (71), 132 (45), 107 (14), 106 (42) 105 (100), 104 (33), 103 (17), 93 (20), 91 (10), 79 (40), 77 (31), 67 (12) 55 (11). HR-MS: 347.1544 ($[C_{19}H_{25}O_3NS]^{+\cdot}$; calc. 347.1555).

(2S)-N-[(2S)-2-Phenylpropionyl]bornane-10,2-sultam (**6f**). Alkylation of (2*S*)-*N*-benzoylbornane-10,2-sultam (0.350 g, 1.050 mmol) with MeI (0.43 ml, 3.150 mmol) gave, after workup followed by FC (hexane/AcOEt 7:1) and recrystallization (hexane), pure **6f** (0.31 g, 85%) showing the same m.p., IR, NMR, and MS as the compound **6e**. $[\alpha]_D = +62.6$; $[\alpha]_{578} = +64.9$; $[\alpha]_{546} = +73.4$; $[\alpha]_{436} = +117.3$; $[\alpha]_{365} = +170.1$ ($c = 1.70$, $CHCl_3$, 20°).

(2S)-N-[(2R,E)-2,4-Dimethylhex-4-en-1-oyl]bornane-10,2-sultam (**6g**). Alkylation of (2*S*)-*N*-propionylbornane-10,2-sultam (0.100 g, 0.367 mmol) with (*E*)-1-bromo-2-methylbut-2-ene (172 mg, 1.10 mmol) in the presence of 2 equiv. of HMPA using sodium hexamethyldisilazide as base (1.13 equiv.) gave, after workup and FC (hexane/AcOEt 15:1), pure **6g** (89.9 mg, 72%) which was recrystallized from MeOH (65.3 mg, 52%) showing the same m.p., IR, NMR, and MS as **6h**. $[\alpha]_D = +53.5$; $[\alpha]_{578} = +56.4$; $[\alpha]_{546} = +63.1$; $[\alpha]_{436} = +104.4$; $[\alpha]_{365} = +162.1$ ($c = 0.76$, $CHCl_3$, 20°).

(2R)-N-[(2S,E)-2,4-Dimethylhex-4-en-1-oyl]bornane-10,2-sultam (**6h**). Alkylation of (2*R*)-*N*-propionylbornane-10,2-sultam (0.100 g, 0.367 mmol) with (*E*)-1-bromo-2-methylbut-2-ene (172 mg, 1.101 mmol) in the presence of 2 equiv. of HMPA using as base sodium hexamethyldisilazide (1.13 equiv.) gave, after workup and FC (hexane/AcOEt 15:1), pure **6h** (86.5 mg, 70%) which was recrystallized from MeOH (74.5 mg, 60%). M.p. 88–90°. $[\alpha]_D = -53.4$; $[\alpha]_{578} = -56.2$; $[\alpha]_{546} = -63.0$; $[\alpha]_{436} = -104.0$; $[\alpha]_{365} = -161.7$ ($c = 1.15$, $CHCl_3$, 20°). IR: 2978, 2930, 2888, 1685, 1648, 1458, 1395, 1333, 1282, 1273, 1240, 1166, 1135, 1063. ^{1}H-NMR: 0.96 (*s*, 3 H); 1.12 (*s*, 3 H); 1.13 (*d*, $J = 6.6$, 3 H); 1.30–1.45 (*m*, 2 H); 1.51 (*d*, $J = 6.6$, 3 H); 1.64 (*s*, 3 H); 1.75–2.10 (*m*, 6 H);

2.45 (*m*, 1 H); 3.25–3.38 (*m*, 1 H); 3.41 (*d*, *J* = 13.7, 1 H); 3.48 (*d*, *J* = 13.7, 1 H); 3.88 (*dd*, *J* = 7.5, 4.9, 1 H); 5.22 (*q*, *J* = 6.3, 1 H). ^{13}C-NMR: 176.24 (*s*); 132.95 (*s*); 121.29 (*d*); 65.24 (*d*); 53.23 (*t*); 48.13 (*s*); 47.68 (*s*); 45.66 (*t*); 44.79 (*d*); 38.46 (*t*); 38.35 (*d*); 32.87 (*t*); 26.49 (*t*); 20.57 (*q*); 19.87 (*q*); 16.68 (*q*); 15.30 (*q*); 13.33 (*q*). MS: 55 (100), 93 (33), 94 (11), 96 (96), 97 (100), 107 (27), 108 (15), 109 (22), 124 (34), 125 (67), 126 (8), 134 (28), 135 (88), 136 (16), 151 (5), 156 (6), 271 (17), 324 (2). HR-MS: 339.1862 ($[C_{18}H_{29}O_3NS]^{+\cdot}$; calc. 339.1868).

(2S)-N-*[(2*R,E*)-2,4-Dimethylhept-4-en-1-oyl]bornane-10,2-sultam* (**6i**). Alkylation of (2*S*)-*N*-propionylbornane-10,2-sultam (3.48 g, 12.83 mmol) with (*E*)-1-bromo-2-methylpent-2-ene (1.9 g, 11.66 mmol) in the presence of 3 equiv. of HMPA using sodium hexamethyldisilazide (1.13 equiv.) as a base for 16 h at −60°, gave, after workup, the crude crystalline sultam **6i** (4.14 g, 100%) which was > 98.3% diastereoisomerically pure as judged by GC (*OV*-1; 140° (2 min), 10°/min increase, 270°). The crude mixture was recrystallized from MeOH to give, after 3 recrystallizations, 2.85 g (8.07 mmol, 69%) of the white crystalline product **6i**. M.p. 110.5–112°. $[\alpha]_D$ = + 56.3; $[\alpha]_{578}$ = + 58.5; $[\alpha]_{546}$ = + 66.7; $[\alpha]_{436}$ = + 111.4; $[\alpha]_{365}$ = + 174.4 (*c* = 1.23, $CHCl_3$). IR: 2964, 2932, 2878, 1682, 1459, 1395, 1333, 1282, 1272, 1238, 1224, 1165, 1135, 1116, 1062, 770, 544, 532. ^{1}H-NMR (200 MHz): 0.91 (*t*, *J* = 7.5, 3 H); 0.96 (*s*, 3 H); 1.12 (*d*, *J* = 6.6, 3 H); 1.13 (*s*, 3 H); 1.31–1.47 (*m*, 2 H); 1.63 (br.*s*, 3 H); 1.80–2.13 (*m*, 8 H); 2.45 (*dd*, *J* = 8.3, 12.6, 1 H); 3.30 (*ddq*, *J* = 6.6, 6.6, 8.3, 1 H); 3.40 (*d*, *J* = 13.7, 1 H); 3.50 (*d*, *J* = 13.7, 1 H); 3.88 (*dd*, *J* = 5.6, 6.9, 1 H); 5.15 (br. *t*, *J* = 7.0, 1 H). ^{13}C-NMR (50 MHz): 176.19 (*s*); 131.39 (*s*); 129.38 (*d*); 65.27 (*d*); 53.22 (*t*); 48.15 (*s*); 47.67 (*s*); 45.62 (*t*); 44.73 (*d*); 38.49 (*t*); 38.23 (*d*); 32.85 (*t*); 26.49 (*t*); 21.17 (*t*); 20.71 (*q*); 19.86 (*q*); 16.58 (*q*); 15.40 (*q*); 14.08 (*q*). MS: 353 (1, $M^{+\cdot}$), 271 (24), 139 (19), 136 (10), 135 (75), 134 (19), 111 (26), 110 (12), 107 (13), 95 (24), 93 (16), 81 (12), 79 (14), 69 (100), 67 (24), 57 (12), 56 (11), 55 (70), 53 (13). HR-MS: 353.2027 ($[C_{19}H_{31}NO_3S]^{+\cdot}$; calc. 353.2025). Anal. calc. for $C_{19}H_{31}NO_3S$: C 64.55, H 8.84, N 3.96; found: C 64.37, H 8.79, N 4.03.

(2S)-N-*[(2S)-5-Methyl-2-(1-methylethenyl)hex-4-enoyl]bornane-10,2-sultam* (**6j**). Alkylation of (2*S*)-*N*-(3-methylbut-3-enoyl)bornane-10,2-sultam (218 mg, 0.73 mmol) with isoprenyl bromide gave, after workup and recrystallization (hexane), pure **6j** (245 mg, 81%, d.e. > 92%; ^{1}H-NMR) as white crystals showing the same m.p., IR, NMR, and MS as compound **6k**.

*(2*R*)*-N-*[(2*R*)-5-Methyl-2-(1-Methylethenyl)hex-4-enoyl]bornane-10,2-sultam* (**6k**). Alkylation of (2*R*)-*N*-(3-methylbut-3-enoyl)bornane-10,2-sultam (200 mg, 0.67 mmol) with isoprenyl bromide, gave after workup and recrystallization (hexane), pure **6k** (203 mg, 89%, d.e. > 95%; ^{1}H-NMR) as white crystals. M.p. 161–162°. $[\alpha]_D$ = − 103.8, $[\alpha]_{578}$ = − 108.3, $[\alpha]_{546}$ = − 123.9, $[\alpha]_{436}$ = − 213.3, $[\alpha]_{365}$ = −346.8 (*c* = 1.17, $CHCl_3$, 20°). IR: 2965, 1687, 1333. ^{1}-H-NMR: 0.96 (*s*, 3 H); 1.15 (*s*, 3 H); 1.29–1.42 (*m*, 2 H); 1.61 (*s*, 3 H); 1.63 (*s*, 3 H); 1.84 (*s*, 3 H); 1.82–1.92 (*m*, 3 H); 1.95–2.10 (*m*, 2 H); 2.29 (*m*, 1 H); 2.62 (*m*, 1 H); 3.47 (*AB*, *J* = 14, 2 H); 3.76 (*dd*, *J* = 6.0, 9.0, 1 H); 3.88 (*dd*, *J* = 5.0, 8.0, 1 H); 4.94 (*m*, 1 H); 5.02 (*s*, 1 H); 5.12 (*m*, 1 H). ^{13}C-NMR: 172.7 (*s*); 141.8 (*s*); 133.9 (*s*); 120.0 (*d*); 113.9 (*t*); 65.5 (*d*); 53.2 (*t*); 52.1 (*d*); 48.1 (*s*); 47.7 (*s*); 44.8 (*s*); 38.5 (*t*); 33.0 (*t*); 32.1 (*t*); 26.4 (*t*); 25.7 (*q*); 21.4 (*q*); 20.7 (*q*); 19.9 (*q*); 17.7 (*q*). MS: 365 (15, $[C_{20}H_{31}NO_3S]^{+\cdot}$), 296 (15), 218 (9), 151 (24), 150 (18), 135 (24), 124 (13), 123 (100). HR-MS: 365.2014 ($[C_{20}H_{31}NO_3S]^{+\cdot}$; calc. 365.2024).

*(2*R*)*-N-*[(2S)-2-Methyldecanoyl]bornane-10,2-sultam* (**6l**). Alkylation of (2*R*)-*N*-propanoylbornane-10,2-sultam (350 mg, 1.29 mmol) with octyl iodide gave, after workup and FC, pure **6l** (192 mg, 39%, de = 97%; GC, *OV-1*, 50-2-20-270) as an oil. $[\alpha]_D$ = − 42, $[\alpha]_{578}$ = − 45.5, $[\alpha]_{546}$ = − 50.3, $[\alpha]_{436}$ = − 85.2, $[\alpha]_{365}$ = − 134. (*c* = 1.1, $CHCl_3$, 20°). IR: 3025, 2961, 2928, 2856, 1692, 1462, 1331. ^{1}H-NMR: 0.85–0.88 (*m*, 3 H); 0.98 (*s*, 3 H); 1.16 (*d*, *J* = 6.4, 3 H); 1.18 (*s*, 3 H); 1.20–1.45 (*m*, 14 H); 1.70 (*m*, 1 H); 1.82–1.95 (*m*, 3 H); 2.00–2.10 (*m*, 2 H); 3.10 (*m*, 1 H); 3.47 (*AB*, *J* = 14, 2 H); 3.90 (*dd*, *J* = 5.6, 6.8, 1 H). ^{13}C-NMR: 176.8 (*s*); 65.3 (*d*); 53.2 (*t*); 48.2 (*s*); 47.7 (*s*); 44.7 (*d*); 39.9 (*d*); 38.6 (*t*); 35.5 (*t*); 32.9 (*t*); 31.8 (*t*); 29.4 (*t*); 29.2 (*t*); 27.0 (*t*); 26.5 (*t*); 22.6 (*t*); 20.8 (*q*); 19.9 (*q*); 16.6 (*q*); 14.1 (*q*). MS: 382 (1, $[C_{21}H_{36}NO_3S]^{+\cdot}$), 271 (100), 169 (58), 135 (74), 85 (87).

*(2*R*)*-N-*[(2*R*)-2-Methyldecanoyl]bornane-10,2-sultam* (**6m**). Alkylation of (2*R*)-*N*-decanoylbornane-10,2-sultam (730 mg, 2 mmol) with MeI gave, after workup and FC, pure **6m** (480 mg, 63%, de > 99%, GC, *OV-1*, 50-2-20-270) as an oil. $[\alpha]_D$ = − 83.5, $[\alpha]_{578}$ = − 87.0, $[\alpha]_{546}$ = − 99.5, $[\alpha]_{436}$ = − 168, $[\alpha]_{365}$ = − 262. (*c* = 0.73, $CHCl_3$, 20°). IR: 3024, 2961, 2927, 2856, 1693, 1459, 1332. ^{1}H-NMR: 0.85–0.88 (*m*, 3 H); 0.97 (*s*, 3 H); 1.16 (*s*, 3 H); 1.20 (*d*, *J* = 7.1, 3 H); 1.20–1.45 (*m*, 14 H); 1.76 (*m*, 1 H); 1.84–1.96 (*m*, 3 H); 2.02–2.07 (*m*, 2 H); 3.04 (*m*, 1 H); 3.47 (*AB*, *J* = 14, 2 H); 3.90 (*m*, 1 H). ^{13}C-NMR: 176.5 (*s*); 52 (*d*); 53.3 (*t*); 48.3 (*s*); 47.8 (*s*); 44.7 (*d*); 40.4 (*d*); 38.5 (*t*); 32.9 (*t*); 32.7 (*t*); 31.9 (*t*); 29.7 (*t*); 29.4 (*t*); 29.3 (*t*); 27.3 (*t*); 26.5 (*t*); 22.6 (*t*); 20.8 (*q*); 19.9 (*q*); 19.0 (*q*); 14.1 (*q*).

(2S)-N-*[(2S)-2-Phenylbutanoyl]bornane-10,2-sultam* (**6n**). Alkylation of (2*S*)-*N*-{2-phenylethanoyl}bornane-10,2-sultam (117 mg, 0.35 mmol) with EtI gave, after workup and FC, pure **6n** (108 mg, 85%, de = 98.5%; GC, *OV-1*, 60-2-20-270) as an oil. $[\alpha]_D$ = + 69, $[\alpha]_{578}$ = + 72, $[\alpha]_{546}$ = + 80, $[\alpha]_{436}$ = + 138, $[\alpha]_{365}$ = + 218 (*c* = 0.64, $CHCl_3$, 20°). IR: 3030, 2966, 2878, 2358, 1690, 1456, 1333. ^{1}H-NMR: 0.94 (*t*, *J* = 7.2, 3 H); 0.98 (*s*, 3 H); 1.22 (*s*, 3 H); 1.25–1.35 (2 H); 1.82–1.93 (4 H); 2.05–2.20 (3 H); 3.47 (*AB*, *J* = 14, 2 H); 3.85 (*dd*, *J* = 4.9, 7.3, 1 H);

(*t*, J = 7.5, 1 H); 7.20–7.32 (3 H), 7.44–7.46 (2 H). ^{13}C-NMR: 173.5 (*s*); 137.9 (*s*); 128.9 (*d*); 128.2 (*d*); 127.2 (*d*); 65.5 (*d*); 53.2 (*t*); 52.8 (*d*); 48.2 (*s*); 47.7 (*s*); 44.7 (*d*); 38.6 (*t*); 33.0 (*t*); 29.4 (*t*); 26.4 (*t*); 20.9 (*q*); 19.9 (*q*); 12.2 (*q*). MS: 361 (96, $[C_{20}H_{27}NO_3S]^{+\cdot}$), 304 (27), 242 (42), 146 (20), 119 (69), 91 (100).

(2R)-N-[(2R)-2-Phenylbutanoyl]bornane-10,2-sultam (**6o**). Alkylation of (2*R*)-*N*-{2-phenylethanoyl}-bornane-2,10-sultam (147 mg, 0.44 mmol) with EtI gave, after workup and FC, pure **6o** (127 mg, 80%, d.e. = 98.5%; GC, *OV-1*, 60-2-20-270) as an oil. $[\alpha]_D = -71$, $[\alpha]_{578} = -74$, $[\alpha]_{546} = -89$, $[\alpha]_{436} = -146$, $[\alpha]_{365} = -212$ (c = 0.65, $CHCl_3$, 20°).

General Procedure for the Synthesis of S-*Benzyl Thioesters* **7**, **11**, *and* **12**. To a stirred soln. of benzenethiol (1.5 equiv.) in Et_2O (7 ml/mmol of sultam **6**) was added at 0° BuLi (1.6M in hexane, 1.5 equiv.) followed after 5 min by Me_3Al (2M in toluene, 1.5 equiv.). After stirring for 20 min at 0°, the sultam derivative **6**, **9**, or **10** (1.0 equiv.) in toluene (13 ml/mmol) was added dropwise, and stirring was continued at 0° during the indicated time (*Table 1*). The mixture was diluted with an org. solvent and 0.1N HCl was added dropwise. The aq. layer was extracted with Et_2O, and the combined org. layers were washed with 1N NaOH, sat. aq. NH_4Cl, dried, and concentrated to give the crude thioester **7**, **11**, or **12** which was purified by FC. The bornanesultam auxiliaries **1** or *ent*-**1** can be recovered by basification of the aq. layer (aq. HCl) followed by extraction with CH_2Cl_2, drying ($MgSO_4$), filtration, and purification by FC or crystallization from MeOH.

S-*Benzyl (2R)-2-Methyl-3-phenylpropanethioate* (**7a**). Mercaptolysis of **6a** (0.150 g, 0.415 mmol) gave pure **7a** (oil, 0.103 g, 92%) and the recovered *ent*-**1** (89%). $[\alpha]_D = -94.9$; $[\alpha]_{578} = -99.6$; $[\alpha]_{546} = -115.0$; $[\alpha]_{436} = -272.4$; $[\alpha]_{365} = -411.0$ (c = 0.75, $CHCl_3$, 20°). IR: 3085, 3061, 3028, 2971, 2931, 2872, 1685, 1602, 1496, 1454, 966, 699. ^{1}H-NMR: 1.18 (*d*, J = 7.1, 3 H); 2.67 (*dd*, J = 13.5, 7.7, 1 H); 2.92 (*sext*, J = 7.1, 1 H); 3.07 (*dd*, J = 13.5, 6.8, 1 H); 4.06 (*d*, J = 13.7, 1 H); 4.11 (*d*, J = 13.7, 1 H); 7.20–7.40 (*m*, 10 H); ^{13}C-NMR: 202.33 (*s*); 138.86 (*s*); 137.59 (*s*); 129.05 (*d*); 128.77 (*d*); 128.66 (*d*); 128.36 (*d*); 127.15 (*d*); 126.36 (*d*); 50.11 (*d*); 39.96 (*t*); 32.98 (*t*); 17.21 (*q*). MS: 270 (7), 246 (5), 181 (5), 147 (50), 119 (90), 118 (70), 91 (100), 77 (10) 65 (27). HR-MS: 270.1079 ($[C_{17}H_{18}OS]^{+\cdot}$; calc. 270.1079).

S-*Benzyl (2S)-2-Methyl-3-phenylpropanethioate* (**7b**). Mercaptolysis of **6b** (0.800 g, 3.20 mmol) gave pure **7b** (oil, 0.51 g, 85%) showing the same IR, NMR, and MS as the **7a**, and the recovered (*R*)-bornanesultam **1** (73%). $[\alpha]_D = +94.8$; $[\alpha]_{578} = +99.3$; $[\alpha]_{546} = +114.7$; $[\alpha]_{436} = +271.7$; $[\alpha]_{365} = +410.1$ (c = 2.38, $CHCl_3$, 20°). HR-MS: 270.1092 ($[C_{17}H_{18}OS]^{+\cdot}$; calc. 270.1079).

S-*Benzyl (2R)-2-Methylbutanethioate* (**7c**). Mercaptolysis of **6c** (0.150 g, 0.501 mmol) gave pure **7c** (oil, 0.101 g, 96%) and the recovered (*R*)-**1** (94%). $[\alpha]_D = -27.9$; $[\alpha]_{578} = -29.1$; $[\alpha]_{546} = -33.5$; $[\alpha]_{436} = -62.3$; $[\alpha]_{365} = -111.5$ (c = 1.52, $CHCl_3$, 20°). IR: 3062, 3029, 2967, 2931, 2875, 1686, 1602, 1496, 1454, 970, 699. ^{1}H-NMR: 0.91 (*t*, J = 7.5, 3 H); 1.73 (*d*, J = 7.1, 3 H); 1.40–1.55 (*m*, 1 H); 1.65–1.80 (*m*, 1 H); 2.50–2.65 (*m*, 1 H); 4.09 (*d*, J = 13.7, 1 H); 4.13 (*d*, J = 13.7, 1 H); 7.20–7.40 (*m*, 5 H); ^{13}C-NMR: 203.05 (*s*); 137.81 (*s*); 128.80 (*d*); 128.57 (*d*); 127.13 (*d*); 49.92 (*d*); 32.89 (*t*); 27.19 (*t*); 17.10 (*q*); 11.54 (*q*). MS: 208 (11), 91 (48), 85 (37), 65 (14), 57 (100), 45 (20). HR-MS: 208.0926 ($[C_{12}H_{16}OS]^{+\cdot}$; calc. 208.0922).

S-*Benzyl (2S)-2-Methylbutanethioate* (**7d**). Mercaptolysis of **6d** (0.100 g, 0.334 mmol) gave pure **7d** (oil, 0.066 g, 95%) and the recovered (*S*)-**1** (99%) showing the same IR, NMR, and MS as **7c**. $[\alpha]_D = +28.3$; $[\alpha]_{578} = +30.0$; $[\alpha]_{546} = +34.1$; $[\alpha]_{436} = +62.5$; $[\alpha]_{365} = +112.0$ (c = 1.32, $CHCl_3$, 20°). HR-MS: 208.0919 ($[C_{12}H_{16}OS]^{+\cdot}$; calc. 208.0922).

S-*Benzyl (2R)-2-Phenylpropanethioate* (**7e**). Mercaptolysis of **6e** (0.150 g, 0.432 mmol) gave pure **7e** (oil, 0.101 g, 96%) and the recovered (*R*)-**1** (94%). $[\alpha]_D = -95.1$; $[\alpha]_{578} = -99.9$; $[\alpha]_{546} = -116.5$; $[\alpha]_{436} = -231.6$; (c = 3.70, $CHCl_3$, 20°). IR: 3085, 3061, 3028, 2976, 2931, 2871, 1686, 1601, 1495, 1453, 997, 945, 698. ^{1}H-NMR: 1.57 (*d*, J = 7.1, 3 H); 3.91 (*q*, J = 7.1, 1 H); 4.04 (*d*, J = 13.7, 1 H); 4.14 (*d*, J = 13.7, 1 H); 7.20–7.35 (*m*, 10 H). ^{13}C-NMR: 200.52 (*s*); 139.69 (*s*); 137.32 (*s*); 128.80 (*d*); 128.67 (*d*); 128.56 (*d*); 127.96 (*d*); 127.48 (*d*); 127.19 (*d*); 54.04 (*d*); 33.49 (*t*); 18.38 (*q*). MS: 256 (19), 106 (29), 105 (100), 104 (20), 103 (11), 91 (59), 79 (19), 77 (25), 65 (12), 51 (10), 45 (14). HR-MS: 256.0928 ($[C_{16}H_{16}OS]^{+\cdot}$; calc. 256.0922).

S-*Benzyl (2S)-2-Phenylpropanethioate* (**7f**). Mercaptolysis of **6f** (0.100 g, 0.334 mmol) gave pure **7f** (oil, 0.066 g, 95%) and the recovered (*S*)-**1** (99%) showing the same IR, NMR, and MS as **7e**. $[\alpha]_D = +94.9$; $[\alpha]_{578} = +99.7$; $[\alpha]_{546} = +116.1$; $[\alpha]_{436} = +230.0$; $[\alpha]_{365} = +468.0$ (c = 1.19, $CHCl_3$, 20°). HR-MS: 256.0911 ($[H_{16}H_{16}OS]^{+\cdot}$; calc. 256.0922).

S-*Benzyl (2R,E)-2-4-Dimethylhex-4-enethioate* (**7g**). Mercaptolysis of **6g** (0.050 g, 0.147 mmol) gave pure **7g** (oil, 0.033 g, 91%) and the recovered (*S*)-**1** (0.0268 g, 85%) showing the same m.p., IR, NMR, and MS as **7h**. $[\alpha]_D = -17.8$; $[\alpha]_{578} = -18.9$; $[\alpha]_{546} = -21.9$; $[\alpha]_{436} = -39.9$; $[\alpha]_{365} = -77.6$ (c = 0.67, $CHCl_3$, 20°). HR-MS: 248.1242 ($[C_{15}H_{20}OS]^{+\cdot}$; calc. 248.1235).

S-*Benzyl (2S,E)-2,4-Dimethylhex-4-enethioate* (**7h**). Mercaptolysis of **6h** (0.070 g, 0.205 mmol) gave pure **7h** (oil, 0.0506 g, 99%) and the recovered (*R*)-**1** (0.0382 g, 87%). $[\alpha]_D = +17.7$; $[\alpha]_{578} = +18.8$; $[\alpha]_{546} = +21.8$;

$[\alpha]_{436} = +39.6$; $[\alpha]_{365} = +76.9$ ($c = 0.84$, $CHCl_3$, 20°). IR: 3085, 3062, 3029, 2972, 2931, 2959, 1688, 1602, 1496, 1454, 1380, 1072, 961, 700. ^{1}H-NMR: 1.12 (*d*, *J* = 7.1, 3 H); 1.54 (*d*, *J* = 7.1, 3 H); 1.57 (*s*, 3 H); 2.04 (*dd*, *J* = 13.5, 7.7, 1 H); 2.43 (*dd*, *J* = 13.5, 6.9, 1 H); 2.80 (*sext.*, *J* = 7.1, 1 H); 4.06 (*d*, *J* = 13.7, 1 H); 4.14 (*d*, *J* = 13.7, 1 H); 5.17–5.30 (*m*, 1 H); 7.20–7.35 (*m*, 5 H). ^{13}C-NMR: 202.83 (*s*); 137.82 (*s*); 132.26 (*s*); 128.78 (*d*); 128.56 (*d*); 127.12 (*d*); 121.64 (*d*); 46.64 (*d*); 44.19 (*t*); 32.91 (*t*); 17.06 (*q*); 15.43 (*q*); 13.36 (*q*). MS: 55 (100), 65 (23), 69 (81), 70 (5), 79 (6), 81 (16), 83 (5), 91 (64), 96 (31), 97 (84), 98 (7), 124 (11), 125 (10), 157 (49), 158 (5), 248 (0.7). HR-MS: 248.1230 ($[C_{15}H_{20}OS]^{+\cdot}$; calc. 248.1235).

S-*Benzyl 2,4-Dimethylhept-4-enethioate* (**7i**). Mercaptolysis of **6i** (97 mg, 0.275 mmol) gave pure **7i** (oil, 64 mg, 89%) and recovered (*S*)-**1** (41 mg, 70%). $[\alpha]_D = -18.3$; $[\alpha]_{578} = -19.0$; $[\alpha]_{546} = -22.0$; $[\alpha]_{436} = -43.0$; $[\alpha]_{365} = -86.9$ ($c = 1.07$, $CHCl_3$). IR: 2963, 2931, 2872, 1688, 1495, 1454, 963. ^{1}H-NMR: 0.93 (*t*, *J* = 7.3, 3 H); 1.14 (*d*, *J* = 7.0, 3 H); 1.59 (br. *s*., 3 H); 1.98 (*dq*, *J* = 7.0, 7.3, 2 H); 2.05 (*dd*, *J* = 8.1, 13.6, 1 H); 2.44 (*dd*, *J* = 7.0, 13.6, 1 H); 2.82 (*ddq*, *J* = 7.0, 7.0, 8.1, 1 H); 4.09 (*d*, *J* = 13.6, 1 H); 4.14 (*d*, *J* = 13.6, 1 H); 5.18 (br. *t*, *J* = 7.0, 1 H); 7.22–7.33 (*m*, 5 H). ^{13}C-NMR: 202.69 (*s*); 137.81 (*s*); 130.83 (*s*); 129.67 (*d*); 128.78 (*d*); 128.55 (*d*); 127.11 (*d*); 46.71 (*d*); 44.13 (*t*); 32.96 (*t*); 21.19 (*t*); 17.00 (*q*); 15.60 (*q*); 14.12 (*q*). MS: 180 (3.5), 172 (2), 171 (21), 138 (7), 111 (14), 110 (8), 95 (10), 91 (29), 69 (100), 55 (40), 45 (12). HR-MS: 180.0608 ($[C_{10}H_{12}OS]^{+\cdot}$; calc. 180.0609), 171.0848 ($[C_9H_{15}OS]^{+\cdot}$; calc. 171.0844). Anal. cal. for $C_{16}H_{22}OS$: C 73.24, H 8.45; found: C 73.40, H 8.24.

S-*Benzyl (2R,3S)-3[(*tert-*Butyl)dimethylsilyloxy]-2-methylpentanethioate* (**11a**). Mercaptolysis of **9a** (0.230 g, 0.519 mmol) gave pure **11a** (oil, 0.092 g, 61%) and the recovered (*R*)-**1** (0.060 g, 54%) at a conversion of 83%. $[\alpha]_D = -12.1$; $[\alpha]_{578} = -13.2$; $[\alpha]_{546} = -15.5$; $[\alpha]_{436} = -32.8$; $[\alpha]_{365} = -70.1$ ($c = 1.91$, $CHCl_3$, 21°). IR: 3030, 1685, 1496, 1454, 1361, 1255, 1101, 1053, 1011, 961, 868, 835, 775, 700. ^{1}H-NMR: 0.03 (*s*, 3 H); 0.05 (*s*, 3 H); 0.88 (*s*, 9 H); 0.88 (*t*, *J* = 7.5, 3 H); 1.20 (*d*, *J* = 6.9, 3 H); 1.42–1.58 (*m*, 2 H); 2.77 (*qd*, *J* = 6.9, 5.5, 1 H); 3.95 (*q*, *J* = 5.6, 1 H); 4.11 (*s*, 2 H); 7.20–7.40 (*m*, 5 H). ^{13}C-NMR: 201.66 (*s*); 137.56 (*s*); 128.85 (*d*); 128.57 (*d*); 127.15 (*d*); 74.57 (*d*); 52.62 (*d*); 33.13 (*t*); 27.83 (*t*); 25.85 (*q*); 18.10 (*s*); 12.42 (*q*); 9.13 (*q*); −4.32 (*q*); −4.65 (*q*). MS: 73 (82), 77 (75), 91 (10), 115 (30), 181 (65), 237 (55, $[M - (t\text{-Bu})Me_2Si]^{+\cdot}$); 295 (50, $[M - t\text{-Bu}]^+$); 337 (5, $[M - Me]^+$).

(1S,2R)-3-(Benzylsulfanyl)-1-ethyl-3-oxopropyl Propanoate (**11b**). Mercaptolysis of **9b** (0.540 g, 1.40 mmol) at −40° gave pure **11b** (oil, 0.33 g, 80%) and the recovered (*R*)-**1** (0.260 g, 85%). $[\alpha]_D = -50.7$; $[\alpha]_{578} = -53.0$; $[\alpha]_{546} = -60.9$; $[\alpha]_{436} = -111.2$; $[\alpha]_{365} = -195.6$ ($c = 1.40$, $CHCl_3$, 20°). IR: 3029, 2976, 2930, 1732, 1683, 1455, 1220, 1190, 1072, 969. ^{1}H-NMR: 0.90 (*t*, *J* = 7.0, 3 H); 1.10 (*t*, *J* = 7.3, 3 H); 1.20 (*d*, *J* = 7.0, 3 H); 1.60 (*m*, 2 H); 2.20–2.40 (*m*, 2 H); 2.80–3.00 (*m*, 1 H); 4.10 (*s*, 2 H); 5.2–5.1 (*m*, 1 H); 7.20–7.30 (*m*, 5 H). ^{13}C-NMR: 199.99 (*s*); 173.83 (*s*); 137.37 (*s*); 128.77 (*d*); 128.59 (*d*); 127.40 (*d*); 75.25 (*d*); 51.23 (*d*); 33.15 (*t*); 27.67 (*t*); 24.83 (*t*); 12.99 (*q*); 9.83 (*q*); 9.20 (*q*). MS: 45 (42), 55 (14), 57 (100), 58 (81), 65 (22) 69 (55), 97 (100), 98 (16), 171 (63), 294 (0.24). HR-MS: 294.1269 ($[C_{16}H_{22}O_3S]^{+\cdot}$; calc. 294.1290).

S-*Benzyl (2S,3S)-3[(*tert-*Butyl)dimethylsilyloxy]-2-methylpentanethioate* (**12a**). Mercaptolysis of **10a** (0.120 g, 0.27 mmol) at −20° gave pure **12a** (oil, 0.080 g, 80%). IR: 3064, 2975, 2925, 2882, 2857, 1690, 1495, 1454, 1377, 1360, 1252, 1123, 1079, 1022, 962, 834, 775, 700. ^{1}H-NMR: 0.05 (*m*, 3 H); 0.10 (*s*, 3 H); 0.80–0.90 (*m*, 12 H); 1.10 (*d*, *J* = 7.0, 3 H); 1.40–1.60 (*m*, 2 H); 2.80 (*m*, 1 H); 4.00 (*m*, 1 H); 4.10 (*m*, 2 H); 7.20–7.40 (*m*, 5 H). ^{13}C-NMR: 201.53 (*s*); 137.47 (*s*); 128.85 (*d*); 128.55 (*d*); 127.13 (*d*); 74.18 (*d*); 53.38 (*d*); 33.17 (*t*); 25.80 (*q*); 25.68 (*t*); 18.05 (*s*); 12.63 (*q*); 8.17 (*q*); −4.39 (*q*); −5.00 (*q*).

S-*Benzyl (2S,3S)-Methyl-3-(trimethylsilyloxy)pentanethioate* (**12b**). Mercaptolysis of **10b** (0.480 g, 1.20 mmol) at −10° gave pure **12b** (oil, 0.335 g, 90%) and the recovered (*R*)-**1** (0.131 g, 89%). $[\alpha]_D = +62.8$; $[\alpha]_{578} = +66.2$; $[\alpha]_{546} = +76.4$; $[\alpha]_{436} = +144.5$; $[\alpha]_{365} = +265.3$ ($c = 2.04$, $CHCl_3$, 20°). IR: 2962, 1687, 1495, 1454, 1376, 1250, 1122, 1077, 1025, 963, 879, 840, 700. ^{1}H-NMR: 0.12 (*s*, 9 H); 0.90 (*t*, *J* = 7.4, 3 H); 1.10 (*d*, *J* = 7.0, 3 H); 1.20–1.75 (*m*, 2 H); 2.80 (*qd*, *J* = 7.2, 14.2, 1 H); 3.90 (*dt*, *J* = 3.8, 6.8, 1 H); 4.06 (*d*, *J* = 13.7, 1 H); 4.16 (*d*, *J* = 13.7, 1 H); 7.20–7.40 (*m*, 5 H). ^{13}C-NMR: 201.79 (*s*); 137.51 (*s*); 128.86 (*d*); 128.57 (*d*); 127.14 (*d*); 74.93 (*d*); 54.22 (*d*); 33.13 (*t*); 26.25 (*t*); 13.25 (*q*); 9.04 (*q*); 0.22 (*q*). MS: 69 (15), 73 (100), 74 (15), 75 (28), 91 (79), 117 (29), 131 (62), 143 (27), 181 (11), 187 (17), 310 (2). HR-MS: 310.1403 ($[C_{16}H_{26}O_2SSi]^{+\cdot}$; calc. 310.1423).

*(1S,2S)-(3-*S*-Benzylsulfanyl)-1-ethyl-3-oxopropyl Propanoate* (**12c**). Mercaptolysis of **10c** (0.054 g, 0.14 mmol) at −40° gave pure **12c** (oil, 0.018 g, 46%) and the recovered (*R*)-**1** (0.0196 g, 65%). $[\alpha]_D = 0$; $[\alpha]_{578} = 0$; $[\alpha]_{546} = 0$; $[\alpha]_{436} = 0$; $[\alpha]_{365} = 0$ ($c = 0.80$, $CHCl_3$, 20°). IR: 3028, 2976, 2938, 2879, 1740, 1689, 1603, 1496, 1454, 1379, 1272, 1182, 1072, 906, 701. ^{1}H-NMR: 0.88 (*t*, *J* = 7.3, 3 H); 1.08 (*t*, *J* = 7.5, 3 H); 1.18 (*d*, *J* = 7.1, 3 H); 1.45–1.70 (*m*, 2 H); 2.10–2.30 (*m*, 1 H); 2.95 (*quint.*, *J* = 7.3, 2 H); 4.07 (*d*, *J* = 13.7, 1 H); 4.15 (*d*, *J* = 13.7, 1 H); 5.11 (*td*, *J* = 8.0, 3.5, 1 H); 7.20–7.30 (*m*, 5 H). ^{13}C-NMR: 199.96 (*s*); 173.62 (*s*); 137.64 (*s*); 128.80 (*d*); 128.57 (*d*); 127.21 (*d*); 75.28 (*d*); 51.09 (*d*); 33.09 (*t*); 27.56 (*t*); 24.02 (*t*); 13.59 (*q*); 9.13 (*q*); 9.03 (*q*). MS: 45 (34), 51 (6), 55 (13), 57 (100), 65 (19), 69 (37), 70 (5), 77 (5), 91 (100), 92 (6), 97 (100), 115 (5), 122 (7), 123 (7), 171 (69), 172 (7), 294 (0.25). HR-MS: 294.1313 ($[C_{16}H_{22}O_3S]^{+\cdot}$; calc. 294.1290).

General Procedure for the Synthesis of Chiral Ketones **5**, **13**, *and* **14** *from Thioesters* **7**, **11**, *and* **12**. To a stirred soln. of thioesters **7**, **11**, and **12** in dry THF (17 ml/mmol) was added [Fe(acac)$_3$] (*10* mol-%), followed by the dropwise addition of *Grignard* reagent (as THF or ether soln.) at the indicated temperatures. When the conversion was complete, dil. HCl (0.01M) was added dropwise to the mixture, and the aq. layer was extracted with Et_2O. The combined org. layers were washed with sat. aq. $NaHCO_3$, dil. HCl, sat. aq. NH_4Cl, dried, and concentrated. The ketones **5**, **13**, and **14** were purified by FC.

(2R)-2-Methyl-1-phenylpentan-3-one (**5a**). Reaction of **7a** (0.020 g, 0.074 mmol) with 1.2 equiv. of EtMgBr (1M in THF) in the presence of [Fe(acac)$_3$] at −35° for 4.5 h gave, after workup and FC (hexane/Et_2O 95:5), **5a** (oil, 12.2 mg, 94%). $[\alpha]_D = -54.9$; $[\alpha]_{578} = -57.2$; $[\alpha]_{546} = -66.2$; $[\alpha]_{436} = -126.1$; $[\alpha]_{365} = -253.0$ ($c = 0.96$, $CHCl_3$, 20°). IR: 3063, 3028, 2968, 2927, 2874, 2854, 1714, 1604, 1496, 1454, 1375, 700. ^{1}H-NMR: 0.98 (*t*, *J* = 7.3, 3 H); 1.09 (*d*, *J* = 6.6, 3 H); 2.27 (*dq*, *J* = 7.1, 18.0, 1 H); 2.44 (*dq*, *J* = 7.1, 18.0, 1 H); 2.58 (*dd*, *J* = 13.3, 7.1, 1 H); 2.85 (*sext.*, *J* = 7.1, 1 H); 2.98 (*dd*, *J* = 13.3, 7.5, 1 H); 7.10–7.30 (*m*, 5 H). ^{13}C-NMR: 214.73 (*s*); 139.87 (*s*); 128.93 (*d*); 128.38 (*d*); 126.19 (*d*); 47.90 (*d*); 39.29 (*t*); 35.14 (*t*); 16.60 (*q*); 7.59 (*q*). MS: 51 (12), 57 (100), 65 (15), 77 (7), 91 (100), 119 (25), 147 (20), 161 (5), 176 (16). HR-MS: 176.1205 ($[C_{12}H_{16}O]^{+\cdot}$; calc. 176.1201). Chiral GC (*Lipodex E*; 100°): ee > 98% ((*R*)-enantiomer: t_R 9.09 min; (*S*)-enantiomer: t_R 9.50 min; flow: 50).

(2S)-2-Methyl-1-phenylpentan-3-one (**5b**). Reaction of **7b** (0.05 g, 0.185 mmol) with 1.6 equiv. of EtMgBr (1M in THF) in the presence of [Fe(acac)$_3$] at 0° for 1/2 h gave, after workup and FC (hexane/Et_2O 95:5), **5b** (oil, 30 mg, 90%) showing the same IR, NMR, and MS as **5a**. $[\alpha]_D = +54.6$; $[\alpha]_{578} = +57.2$; $[\alpha]_{546} = +66.1$; $[\alpha]_{436} = +126.4$; $[\alpha]_{365} = +253.6$ ($c = 1.65$, $CHCl_3$, 20°). HR-MS: 176.1205 ($[C_{12}H_{16}O]^{+\cdot}$; calc. 176.1201). Chiral GC (*Lipodex E*; 100°): ee > 97% ((*R*)-enantiomer: t_R 11.9 min; (*S*)-enantiomer: t_R 12.50 min; flow: 40).

(2R)-2,4-Dimethyl-1-phenylpentan-3-one (**5c**). Reaction of **7a** (0.020 g, 0.074 mmol) with 1.2 equiv. of (i-Pr)MgBr (2M in THF) in the presence of [Fe(acac)$_3$] at −35° for 4.5 h gave, after workup and FC (hexane/Et_2O) **5c** (oil, 12.9 mg, 92%). $[\alpha]_D = -83.8$; $[\alpha]_{578} = -88.8$; $[\alpha]_{546} = -102.9$; $[\alpha]_{436} = -199.2$; $[\alpha]_{365} = -401.1$ ($c = 1.07$, $CHCl_3$, 20°). IR: 3062, 3028, 2967, 2927, 2871, 1712, 1604, 1495, 1451, 1382, 1015, 700. ^{1}H-NMR: 0.87 (*d*, *J* = 6.6, 3 H); 1.01 (*d*, *J* = 6.6, 3 H); 1.08 (*d*, *J* = 6.6, 3 H); 2.45–2.60 (*m*, 2 H); 2.90–3.05 (*m*, 2 H); 7.10–7.30 (*m*, 5 H). ^{13}C-NMR: 217.76 (*s*); 140.01 (*s*); 129.01 (*d*); 128.32 (*d*); 126.16 (*d*); 46.52 (*d*); 40.38 (*d*); 39.53 (*t*); 18.00 (*q*); 17.71 (*q*); 17.13 (*q*). MS: 51 (12), 65 (20), 71 (65), 77 (10), 91 (100), 119 (75), 131 (85), 147 (35), 173 (5), 190 (15), 191 (15). HR-MS: 190.1350 ($[C_{13}H_{18}O]^{+\cdot}$; calc. 190.1357). Chiral GC (*Lipodex E*; 90°): ee > 99% ((*R*)-enantiomer: t_R 18.3 min; (*S*)-enantiomer: t_R 19.0 min; flow: 50).

(2S)-2,4-Dimethyl-1-phenylpentan-3-one (**5d**). Reaction of **7b** (0.047 g, 0.174 mmol) with 1.6 equiv. of (i-Pr)MgBr (2M in THF) in the presence of [Fe(acac)$_3$] at 0° for 3 h gave, after workup and FC (hexane/Et_2O), **5d** (oil, 27 mg, 82%) showing the same IR, NMR, and MS as **5c**. $[\alpha]_D = +83.6$; $[\alpha]_{578} = +87.9$; $[\alpha]_{546} = +101.6$; $[\alpha]_{436} = +195.7$; $[\alpha]_{365} = +395.0$ ($c = 1.08$, $CHCl_3$, 21°). HR-MS: 190.1345 ($[C_{13}H_{18}O]^{+\cdot}$; calc. 190.1357). Chiral GC (*Lipodex E*; 90°): ee > 98% ((*R*)-enantiomer: t_R 21.80 min; (*S*)-enantiomer: t_R 22.97 min; flow: 40).

(2R)-2-Methyl-1-phenylnonan-3-one (**5e**). Reaction of **7a** (0.012 g, 0.044 mmol) with 2.6 equiv. of (Hex)MgBr (0.4M in THF) in the presence of [Fe(acac)$_3$] at −10° for 4 h gave, after workup and FC (hexane/Et_2O), **5e** (oil, 7.8 mg, 75%). $[\alpha]_D = -53.0$; $[\alpha]_{578} = -55.6$; $[\alpha]_{546} = -64.9$; $[\alpha]_{436} = -124.5$; $[\alpha]_{365} = -248.7$ ($c = 0.60$, $CHCl_3$, 20°). IR: 3085, 3062, 3027, 2956, 2928, 2856, 1713, 1604, 1496, 1454, 1375, 700. ^{1}H-NMR: 0.87 (*t*, *J* = 7.1, 3 H); 1.08 (*d*, *J* = 6.8, 3 H); 1.15–1.35 (*m*, 6 H); 1.40–1.55 (*m*, 2 H); 2.26 (*dt*, *J* = 7.5, 16.8, 1 H); 2.39 (*dt*, *J* = 7.5, 16.8, 1 H); 2.56 (*dd*, *J* = 7.5, 13.3, 1 H); 2.84 (*sext.*, *J* = 7.1, 1 H); 2.98 (*dd*, *J* = 7.1, 13.3, 1 H); 7.10–7.30 (*m*, 5 H). ^{13}C-NMR: 214.36 (*s*); 138.89 (*s*); 128.96 (*d*); 128.33 (*d*); 126.18 (*d*); 48.08 (*d*); 42.03 (*t*); 39.17 (*t*); 31.58 (*t*); 28.85 (*t*); 23.46 (*t*); 22.46 (*t*); 16.53 (*q*); 13.99 (*q*). MS: 57 (30), 65 (15), 77 (5), 85 (35), 91 (100), 113 (60), 120 (30), 147 (15), 162 (5), 232 (4). HR-MS: 232.1825 ($[C_{16}H_{24}O]^{+\cdot}$; calc. 232.1827). Chiral GC (*Lipodex D*; 105°): ee > 99% ((*R*)-enantiomer: t_R 78.00 min; (*S*)-enantiomer: t_R 80.74 min; flow: 60).

(2S)-2-Methyl-1-phenylnonan-3-one (**5f**). Reaction of **7b** (0.02 g, 0.074 mmol) with 1.6 equiv. of (Hex)MgBr (1M in THF) in the presence of [Fe(acac)$_3$] at −20° for 1.5 h gave, after workup and FC (hexane/Et_2O), **5f** (oil, 37 mg, 86%) showing the same IR, NMR, and MS as **5e**. $[\alpha]_D = +53.2$; $[\alpha]_{578} = +55.9$; $[\alpha]_{546} = +64.7$; $[\alpha]_{436} = +125.1$; $[\alpha]_{365} = +250.4$ ($c = 2.38$, $CHCl_3$, 20°). HR-MS: 232.1819 ($[C_{16}H_{24}O]^{+\cdot}$; calc. 232.1827). Chiral GC (*Lipodex D*, 105°): ee > 99% ((*R*)-enantiomer: t_R 78.00 min; (*S*)-enantiomer: t_R 80.74 min; flow: 60).

(2R)-2-Methyl-1,3-diphenylpropan-1-one (**5g**). Reaction of **7a** (0.020 g, 0.74 mmol) with 1.2 equiv. of PhMgBr (3M in Et_2O) in the presence of [Fe(acac)$_3$] at −35° for 3 h gave, after workup and FC (hexane/Et_2O) **5g** (oil, 14.4 mg, 87%). $[\alpha]_D = -71.7$; $[\alpha]_{578} = -74.5$; $[\alpha]_{546} = -88.0$; $[\alpha]_{436} = -196.5$; ($c = 0.84$, $CHCl_3$, 20°). IR: 3081, 3060, 3026, 2979, 2953, 2925, 2868, 1681, 1595, 1578, 1493, 1446, 1362, 1332, 1234, 1179, 1080, 97, 700. ^{1}H-NMR: 1.22 (*d*, *J* = 6.8, 3 H); 2.70 (*dd*, *J* = 13.7, 7.5 H, 1 H); 3.18 (*dd*, *J* = 13.7, 6.2, 1 H); 3.76 (*m*, 1 H); 7.15–7.30 (*m*, 5 H); 7.44–7.58 (*m*, 3 H); 7.92–7.95 (*m*, 2 H). ^{13}C-NMR: 203.71 (*s*); 139.95 (*s*); 136.51 (*s*); 132.88 (*d*); 129.07 (*d*); 128.61 (*d*); 128.36 (*d*); 128.27 (*d*); 126.18 (*d*); 42.76 (*d*); 39.38 (*t*); 17.38 (*q*). MS: 71 (23), 91 (19), 105 (100), 224 (34). HR-MS: 224.1196 ($[C_{16}H_{16}O]^{+\cdot}$; calc. 224.1201).

(2S)-2-Methyl-1,3-diphenylpropan-1-one (**5h**). Reaction of **7b** (0.04 g, 0.15 mmol) with 2.2 equiv. of PhMgBr (3M in Et_2O) in the presence of $[Fe(acac)_3]$ at $-20°$ for 1.5 h gave, after workup and FC (hexane/Et_2O), **5h** (oil, 27 mg, 81%) showing the same IR, NMR, and MS as **5g**. HR-MS: 224.1210 ($[C_{16}H_{16}O]^{+\cdot}$; calc. 224.12012).

(2R)-1-Phenyl-2-methylbutan-1-one (**5i**). Reaction of **7c** (0.05 g, 0.240 mmol) with 1.5 equiv. of PhMgBr (3M in Et_2O) in the presence of $[Fe(acac)_3]$ at $-10°$ for 2 h gave, after workup and FC (hexane/Et_2O), **8a** (oil, 29.9 mg, 77%). $[\alpha]_D = -36.9$; $[\alpha]_{578} = -38.6$; $[\alpha]_{546} = -44.2$; $[\alpha]_{436} = -81.2$; ($c = 0.64$, Et_2O, 20°). IR: 3062, 2966, 2932, 2875, 1682, 1596, 1580, 1448, 1372, 1218, 972, 700. ^{1}H-NMR: 0.92 (*t*, $J = 7.5$, 3 H); 1.20 (*d*, $J = 6.8$, 3 H); 1.42–1.56 (*m*, 1 H); 1.75–1.90 (*m*, 1 H); 3.41 (*sext.*, $J = 6.7$, 1 H); 7.15–8.05 (*m*, 5 H). ^{13}C-NMR: 204.46 (*s*); 136.88 (*s*); 132.75 (*d*); 128.58 (*d*); 128.22 (*d*); 42.14 (*d*); 26.67 (*t*); 16.74 (*q*); 11.75 (*q*). MS: 51 (65), 57 (25), 77 (95), 78 (10), 85 (5), 91 (8), 105 (100), 134 (20), 145 (5), 162 (30), 163 (20). HR-MS: 162.1041 ($[C_{11}H_{14}O]^{+\cdot}$; calc. 162.1045). Chiral GC (*Lipodex E*; 60°): ee > 99% ((*R*)-enantiomer: t_R 55.46 min; (*S*)-enantiomer: t_R 59.50 min; flow: 55).

(2S)-1-Phenyl-2-methylbutan-1-one (**5j**). Reaction of **7d** (0.035 g, 0.168 mmol) with 2.25 equiv. of PhMgBr (3M in Et_2O) in the presence of $[Fe(acac)_3]$ at 0° for 3 h gave, after workup and FC (hexane/Et_2O), **5j** (oil, 21.0 mg, 77%) showing the same IR, NMR, and MS as **5i**. $[\alpha]_D = +36.8$; $[\alpha]_{578} = +39.1$; $[\alpha]_{546} = +43.8$; $[\alpha]_{436} = +75.7$; ($c = 0.30$, Et_2O, 20°). HR-MS: 162.1040 ($[C_{11}H_{14}O]^{+\cdot}$; calc. 162.1045). Chiral GC (*Lipodex E*; 60°): ee > 99% ((*R*)-enantiomer: t_R 55.46 min; (*S*)-enantiomer: t_R 59.50 min; flow: 55).

(2R)-1,2-Diphenylpropan-1-one (**5k**). Reaction of **7e** (0.035 g, 0.137 mmol) with 2.25 equiv. of PhMgBr (3M in Et_2O) in the presence of $[Fe(acac)_3]$ at $-20°$ for 4 h gave, after workup and FC (hexane/Et_2O), **5k** (oil, 24 mg, 84%). $[\alpha]_D = -150.2$; $[\alpha]_{578} = -158.6$; $[\alpha]_{546} = -186.9$; $[\alpha]_{436} = -412.8$ ($c = 1.55$, EtOH, 20°). IR: 3061, 3027, 2975, 2930, 1682, 1597, 1582, 1493, 1448, 1222, 952, 698. ^{1}H-NMR: 1.55 (*d*, $J = 6.8$, 3 H); 4.70 (*q*, $J = 6.8$, 1 H); 7.20–7.98 (*m*, 10 H). ^{13}C-NMR: 200.29 (*s*); 141.44 (*s*); 136.49 (*s*); 132.71 (*d*); 128.93 (*d*); 128.72 (*d*); 128.43 (*d*); 127.73 (*d*); 126.84 (*d*); 47.87 (*d*); 19.44 (*q*). MS: 51 (15), 77 (45), 105 (100), 165 (2), 210 (5). HR-MS: 210.1046 ($[C_{15}H_{14}O]^{+\cdot}$; calc. 210.1045). ee 60% (deduced from the rotation of the pure compound).

(2S)-1,2-Diphenylpropan-1-one (**5l**). Reaction of **7f** (0.022 g, 0.086 mmol) with 2.25 equiv. of PhMgBr (3M in Et_2O) in the presence of $[Fe(acac)_3]$ at $-20°$ for 4 h gave, after workup and FC (hexane/Et_2O), **5l** (oil, 15.2 mg, 84%) showing the same IR, NMR, and MS as **5k**. $[\alpha]_D = +144.9$; $[\alpha]_{578} = +152.7$; $[\alpha]_{546} = +179.9$; $[\alpha]_{436} = +394.9$ ($c = 1.20$; EtOH, 20°). ee 58% (deduced from the rotation of the pure compound).

(4R)-4,6-Dimethyloct-6-en-3-one (**5m**). Reaction of **7g** (0.023 g, 0.093 mmol) with 1.8 equiv. of EtMgBr (1M in THF) in the presence of $[Fe(acac)_3]$ at $-35°$ for 3.5 h gave, after workup and FC (hexane/EtO 9:1), **5m** (oil, 9.9 mg, 69%) showing the same IR, NMR, and MS as **5n**. Chiral GC (*Lipodex E*; 60°): ee 94% ((*R*)-enantiomer: t_R 9.72 min; (*S*)-enantiomer: t_R 11.01 min; flow: 50).

(4S)-4,6-Dimethyloct-6-en-3-one (**5n**). Reaction of **7f** (0.040 g, 0.161 mmol) with 2.1 equiv. of EtMgBr (1M in THF) in the presence of $[Fe(acac)_3]$ at $-35°$ for 3.5 h gave, after workup and FC (hexane/EtO 9:1), **5n** (oil, 17.4 mg, 70%). IR: 2973, 2934, 1714, 1456, 1377, 1105. ^{1}H-NMR: 1.01 (*d*, $J = 7.1$, 3 H); 1.03 (*t*, $J = 7.3$, 3 H); 1.56 (*d*, $J = 6.6$, 3 H); 1.59 (*s*, 3 H); 1.90–2.00 (*m*, 1 H); 2.25–2.34 (*m*, 1 H); 2.44 (*qd*, $J = 7.3$, 1.8, 2 H); 2.70 (*quint.*, $J = 7.1$, 1 H); 5.20 (*qq*, $J = 6.6$, 0.9, 1 H). ^{13}C-NMR: 215.17 (*s*); 132.92 (*s*); 121.01 (*d*); 44.30 (*d*); 43.31 (*t*); 34.33 (*t*); 16.13 (*q*); 15.49 (*q*); 13.35 (*q*); 7.69 (*q*). MS: 53 (10), 55 (100), 56 (7), 57 (96), 67 (9), 69 (51), 70 (4), 81 (10), 85 (5), 86 (41), 96 (10), 97 (91), 98 (8), 105 (2), 107 (5), 111 (2), 125 (45), 126 (4), 154 (18), 155 (2). HR-MS: 154.1347 ($[C_{10}H_{18}O]^{+\cdot}$; calc. 154.1358). Chiral GC (*Lipodex E*; 60°): ee 93% ((*R*)-enantiomer: t_R 9.72 min; (*S*)-enantiomer: t_R 11.01 min; flow: 50).

(4R,E)-4,6-Dimethylnon-6-en-3-one (**5o**). Reaction of **7i** (55 mg, 0.21 mmol) with 1.7 equiv. of EtMgBr (1M in THF) in the presence of $[Fe(acac)_3]$ at $-35°$ for 3 h gave, after workup and FC (AcOEt/hexane 1:7), pure **5o** (35 mg, 99%). $[\alpha]_D = -29.9$; $[\alpha]_{578} = -31.4$; $[\alpha]_{546} = -37.2$; $[\alpha]_{436} = -76.7$; $[\alpha]_{365} = -170.5$ ($c = 2.22$, $CHCl_3$). IR: 2966, 2932, 2867, 1710, 1456, 1265, 738. ^{1}H-NMR: 0.92 (*t*, $J = 7.3$, 3 H); 1.01 (*d*, $J = 7.0$, 3 H); 1.03 (*t*, $J = 7.3$, 3 H); 1.58 (br. *s*, 3 H); 1.93 (*dd*, $J = 7.7$, 13.6, 1 H); 1.97 (*dq*, $J = 7.0$, 7.3, 2 H); 2.30 (*dd*, $J = 7.0$, 13.6, 1 H); 2.38–2.50 (*m*, 2 H); 2.70 (*dq*, $J = 7.0$, 14.0, 1 H); 5.12 (br. *t*, $J = 7.0$, 1 H). ^{13}C-NMR (50 MHz): 215.26 (*s*); 131.45 (*s*); 129.12 (*d*); 44.28 (*d*); 43.37 (*t*); 34.45 (*t*); 21.21 (*t*); 16.14 (*q*); 15.67 (*q*); 14.25 (*q*); 7.68 (*q*). MS: 168 (11, $M^{+\cdot}$), 139 (20), 11 (22), 86 (63), 83 (43), 69 (100), 57 (81), 55 (58). HR-MS: 168.1513 ($[C_{11}H_{20}O]^{+\cdot}$; calc. 168.1514). Anal. calc. for $C_{11}H_{20}O$: C 78.51, H 11.98; found: C 78.29, H 11.74. Chiral GC (*Lipodex E*; 70°): ee > 99% ((*R*)-enantiomer: t_R 11.3 min; (*S*)-enantiomer: t_R 12.0 min).

*(4R,5S)-5-[(*tert*-Butyl)dimethylsilyloxy]-4-methylheptan-3-one* (**13a**). Reaction of **11a** (0.025 g, 0.071 mmol) with 2.0 equiv. of EtMgBr (1M in THF) in the presence of $[Fe(acac)_3]$ at $-20°$ for 30 h gave, after workup and FC (hexane/Et_2O 9:1), **13a** (oil, 11.8 mg, 65%). $[\alpha]_D = -31.6$; $[\alpha]_{578} = -34.6$; $[\alpha]_{546} = -40.7$; $[\alpha]_{436} = -84.5$; $[\alpha]_{365} = -103.8$ ($c = 0.59$, $CHCl_3$, 21°). IR: 2931, 2857, 1713, 1462, 1379, 1256, 1100, 1053, 1005, 836, 775. ^{1}H-NMR: 0.05 (*s*, 3 H); 0.06 (*s*, 3 H); 0.87 (*t*, $J = 7.4$, 3 H); 0.89 (*s*, 9 H); 1.03 (*t*, $J = 7.4$, 3 H); 1.06 (*d*, $J = 7.0$,

3 H); 1.26–1.57 (*m*, 2 H); 2.45 (*dq*, *J* = 7.3, 18.0, 1 H); 2.58 (*dq*, *J* = 7.4, 18.0, 1 H); 2.68 (*dq*, *J* = 5.1, 7.0, 1 H); 3.84 (*m*, 1 H). ^{13}C-NMR: 214.01 (*s*); 74.83 (*d*); 50.64 (*d*); 35.75 (*t*); 27.42 (*t*); 25.84 (*q*); 18.07 (*s*); 12.09 (*q*); 9.67 (*q*); 7.55 (*q*); −4.35 (*q*); −4.56 (*q*).

(1S,2R)-1-Ethyl-2-methyl-3-oxopentyl Propanoate (**13b**). Reaction of **11b** (0.070 g, 0.24 mmol) with 2.1 equiv. of EtMgBr (1M in THF) in the presence of [Fe(acac)$_3$] at −20° for 2 h gave, after workup and FC (hexane/Et$_2$O 96:4), **13b** (oil, 37 mg, 83%) showing the same IR, NMR, and MS as the compound described in [7b]. $[\alpha]_D$ = − 49.3; $[\alpha]_{578}$ = − 51.5, $[\alpha]_{546}$ = − 59.6; $[\alpha]_{436}$ = − 112.8 (*c* = 1.17, CHCl$_3$, 21.5°).

*(4S,5S)-5-[(*tert*-Butyl)dimethylsilyloxy]-4-methylheptan-3-one* (**14a**). Reaction of **12a** (0.065 g, 0.19 mmol) with 2.0 equiv. of EtMgBr (1M in THF) in the presence of [Fe(acac)$_3$] at −20° for 0.5 h gave, after workup and FC (hexane/Et$_2$O 9:1), **14a** (oil, 36 mg, 78%). $[\alpha]_D$ = + 62.3; $[\alpha]_{578}$ = + 65.2; $[\alpha]_{546}$ = + 75.1; $[\alpha]_{436}$ = + 138.4; (*c* = 1.83, CHCl$_3$, 21°). ^{1}H-NMR: 0.01 (*s*, 3 H); 0.06 (*s*, 3 H); 0.88 (*s*, 9 H); 0.90 (*t*, *J* = 7.3, 3 H); 0.97 (*d*, *J* = 7.0, 3 H); 1.02 (*t*, *J* = 7.2, 3 H); 1.20–1.60 (*m*, 2 H); 2.50 (*q*, *J* = 7.2, 2 H); 2.65–2.90 (*m*, 1 H); 3.85 (*m*, 1 H). ^{13}C-NMR: 214.50 (*s*); 74.51 (*d*); 49.78 (*d*); 36.87 (*t*); 26.07 (*t*); 25.77 (*q*); 17.98 (*s*); 12.68 (*q*); 7.52 (*q*); 7.32 (*q*); −4.39 (*q*); −5.00 (*q*).

(4S,5S)-4-Methyl-5-(trimethylsilyloxy)heptan-3-one (**14b**). Reaction of **12b** (0.220 g, 0.74 mmol) with 1.9 equiv. of EtMgBr (1M in THF) in the presence of [Fe(acac)$_3$] at −20° for 1/2 h gave, after workup and FC (hexane/Et$_2$O 96:4), **14b** (oil, 110 mg, 72%). $[\alpha]_D$ = + 65.5; $[\alpha]_{578}$ = + 68.7; $[\alpha]_{546}$ = + 78.7; $[\alpha]_{436}$ = + 145.5; $[\alpha]_{365}$ = + 269.5 (*c* = 1.19, CHCl$_3$, 20°). IR: 2963, 1718, 1458, 1376, 1250, 1120, 1068, 1026, 882, 840. ^{1}H-NMR: 0.06 (*s*, 9 H); 0.89 (*t*, *J* = 7.6, 3 H); 0.94 (*d*, *J* = 7.0, 3 H); 1.02 (*t*, *J* = 7.2, 3 H); 1.26–1.60 (*m*, 2 H); 2.48 (*q*, *J* = 7.3, 2 H); 2.60–2.80 (*m*, 1 H); 3.75–3.90 (*m*, 1 H). ^{13}C-NMR: 214.84 (*s*); 75.42 (*d*); 50.73 (*d*); 37.05 (*t*); 26.61 (*t*); 13.04 (*q*); 8.53 (*q*); 7.32 (*q*); −0.22 (*q*). MS: 69 (15), 73 (100), 74 (15), 75 (28), 91 (79), 117 (29), 131 (62), 143 (27), 181 (11), 187 (17).

(1S,2S)-1-Ethyl-2-methyl-3-oxopentyl Propanoate (**14c**). Reaction of **12c** (0.037 g, 0.125 mmol) with 1.5 equiv. of EtMgBr (1M in THF) in the presence of [Fe(acac)$_3$] at −20° for 2.5 h gave, after workup and FC (pentane), **14c** (oil, 21.4 mg, 85%). $[\alpha]_D$ = + 27.0; $[\alpha]_{578}$ = + 28.0; $[\alpha]_{546}$ = + 33.0; $[\alpha]_{436}$ = + 66.9 (*c* = 1.10, CHCl$_3$, 20°). IR: 2975, 2940, 2881, 1738, 1716, 1462, 1377, 1186, 1099, 1081, 1000. ^{1}H-NMR: 0.88 (*t*, *J* = 7.5, 3 H); 1.04 (*t*, *J* = 7.1, 3 H); 1.06 (*d*, *J* = 7.1, 3 H); 1.12 (*t*, *J* = 7.5, 3 H); 1.40–1.80 (*m*, 2 H); 2.29 (*qd*, *J* = 7.5, 2.1, 2 H); 2.49 (*qd*, *J* = 7.5, 2.1, 2 H); 2.87 (*quint.*, *J* = 7.1, 1 H); 5.07 (*td*, *J* = 7.5, 3.5, 1 H). ^{13}C-NMR: 212.24 (*s*); 173.76 (*s*); 75.52 (*d*); 49.03 (*d*); 34.92 (*t*); 27.72 (*t*); 23.71 (*t*); 12.20 (*q*); 9.20 (*q*); 9.16 (*q*); 7.61 (*q*). MS: 57 (100), 70 (45), 86 (20), 97 (40), 115 (3), 126 (10), 131 (16), 143 (5), 171 (2). HR-MS: 171.1021 ([$C_{11}H_{20}O_3$ − Et]$^+$; calc. 171.1021).

*5-Benzyl (2S)-2-{(4*R*,5*S*,6*S*)-2,2-Di(*tert*-butyl)-6-[(1*S*)-1-([1,3]dithiolan-2-yl)ethyl]-5-methyl-1,3-dioxa-2-silacyclohexan-4-yl}propanoate* (**16**). To a stirred soln. of phenylmethanethiol (51 ml, 0.476 mmol) in Et$_2$O (2 ml) was added at 0° BuLi (2.7M in heptane; 0.176 ml, 0.476 mmol). After stirring for 5 min at 0°, Me$_3$Al (2M in toluene; 0.238 ml, 0.476 mmol) was added dropwise, and stirring was continued for 20 min after which a pre-cooled soln. (0°) of **15** [13a] (200 mg, 0.317 mmol) in toluene (2 ml + 2 ml rince) was added *via* cannula. After stirring for 12 h at 0°, 2% aq. HCl (6 ml) was added and the aq. phase extracted with Et$_2$O. The combined org. layers were washed with brine, dried, and concentrated. The residue was purified by FC (CH$_2$Cl$_2$/hexanes 1:4 to 1:2) to give pure **16** (160 mg, 93%). $[\alpha]_D$ = − 15.7; $[\alpha]_{578}$ = − 16.2; $[\alpha]_{546}$ = − 18.4; $[\alpha]_{436}$ = − 27.4; $[\alpha]_{365}$ = − 29.5 (*c* = 1.15, CHCl$_3$). IR: 2966, 2931, 2857, 1698, 1473, 1454, 1136, 1055, 1018, 955, 863, 826, 702, 652. ^{1}H-NMR: 0.80 (*d*, *J* = 7.0, 3 H); 0.96 (*s*, 9 H); 1.02 (*s*, 9 H); 1.24 (*d*, *J* = 7.0, 3 H); 1.25 (*d*, *J* = 6.6, 3 H); 2.00 (*ddq*, *J* = 7.0, 9.6, 9.6, 1 H); 2.27 (*ddq*, *J* = 1.8, 5.2, 6.6, 1 H); 2.87 (*dq*, *J* = 2.6, 7.0, 1 H); 3.06–3.25 (*m*, 4 H); 3.81 (*dd*, *J* = 1.8, 9.6, 1 H); 4.14 (*s*, 2 H); 4.36 (*dd*, *J* = 2.6, 9.6, 1 H); 4.77 (*d*, *J* = 5.2, 1 H); 7.18–7.31 (*m*, 5 H). ^{13}C-NMR: 200.88 (*s*); 137.89 (*s*); 128.82 (*d*); 128.49 (*d*); 127.04 (*d*); 83.05 (*d*); 80.73 (*d*); 53.68 (*d*); 51.31 (*d*); 41.14 (*d*); 38.72 (*d*); 38.61 (*t*); 38.31 (*t*); 32.89 (*t*); 27.77 (*q*); 27.14 (*q*); 23.20 (*s*); 20.18 (*s*); 16.41 (*q*); 12.50 (*q*); 8.39 (*q*). MS: 485 (13), 484 (19), 483 (57), 351 (28), 349 (17), 303 (27), 275 (13), 237 (13), 236 (15), 235 (92), 117 (12), 105 (100), 101 (45), 91 (75), 77 (14), 75 (30). HR-MS: 483.1513 ([$C_{23}H_{35}O_3S_3Si$]$^+$; calc. for 483.1518). Anal. calc. for $C_{27}H_{44}O_3S_3Si$: C 59.95, H 8.20; found: C 60.14, H 8.25.

*(2S)-2-{(4*R*,5*S*,6*S*)-2,2-Di(*tert*-butyl)-6-[(1*S*)-1-([1,3]dithiolan-2-yl)ethyl]-5-methyl-1,3-dioxa-2-silacyclohexan-4-yl}pentan-3-one* (**17**). To a stirred soln. of **16** (79 mg, 0.146 mmol) in THF (2.5 ml) containing [Fe(acac)$_3$] (5 mg) was added at −30° EtMgBr (1M in THF; 0.190 ml, 0.190 mmol). After stirring for 50 min between −30° and −20°, another 0.7 equiv. of EtMgBr (1M in THF; 0.1 ml, 0.1 mmol) was added and stirring continued for 1 h. The mixture was quenched by the slow addition of 2% aq. HCl (4 ml) after which the aq. phase was extracted with hexanes. The combined org. phases were washed with brine, dried, and concentrated to give a residue which was purified by FC (CH$_2$Cl$_2$/hexanes 1:2 to 2:1) to give pure **17** (55 mg, 85%). $[\alpha]_D$ = + 4.9; $[\alpha]_{578}$ = + 5.2; $[\alpha]_{546}$ = + 6.2; $[\alpha]_{436}$ = + 15.4; $[\alpha]_{365}$ = + 40.8 (*c* = 0.61, CHCl$_3$). IR: 2967, 2932, 2858, 1716,

1473, 1386, 1276, 1131, 1056, 1005, 864, 826, 652. ^{1}H-NMR: 0.82 (*d*, *J* = 7.0, 3 H); 0.98 (*s*, 9 H); 1.02 (*s*, 9 H); 1.06 (*dd*, *J* = 7.3, 7.3, 3 H); 1.16 (*d*, *J* = 7.0, 3 H); 1.26 (*d*, *J* = 7.0, 3 H); 2.02 (*ddq*, *J* = 7.0, 9.6, 9.6, 1 H); 2.28 (*ddq*, *J* = 1.8, 7.0, 7.0, 1 H); 2.53 (*dq*, *J* = 7.3, 18.0, 1 H); 2.58 (*dq*, *J* = 7.3, 18.0, 1 H); 2.62 (*dq*, *J* = 2.6, 7.0, 1 H); 3.09–3.26 (*m*, 4 H); 3.82 (*dd*, *J* = 1.8, 9.6, 1 H); 4.29 (*dd*, *J* = 2.6, 9.6, 1 H); 4.79 (*d*, *J* = 5.2, 1 H). ^{13}C-NMR: 213.07 (*s*); 83.08 (*d*); 80.94 (*d*); 53.68 (*d*); 49.69 (*d*); 41.13 (*d*); 38.70 (*t*); 38.64 (*d*); 38.34 (*t*); 33.37 (*t*); 27.19 (*q*); 27.10 (*q*); 23.18 (*s*); 20.21 (*s*); 16.34 (*q*); 12.52 (*q*); 7.97 (*q*); 7.73 (*q*). MS: 446 (0.6, $M^{+\cdot}$), 389 (9), 303 (37), 258 (14), 257 (71), 256 (15), 255 (79), 235 (53), 215 (24), 107 (12), 105 (100), 101 (25), 77 (10); 75 (17), 57 (24). HR-MS: 389.1610 ($[C_{18}H_{33}O_3S_2Si]^{+\cdot}$; calc. 369.1640).

*(2*R*)-*N*-{(2*R*,3*S*)-3-{(2*R*,3*S*)-3-[(*tert*-Butyl)dimethylsilyloxy]-2-methylpentanoyloxy}-2-methylpentanoyl}-bornane-10,2-sultam* (**20b**). A mixture of **19** [7a] (0.300 g, 1.20 mmol), 2,6-dichlorobenzoyl chloride (0.18 ml, 1.27 mmol), and Et_3N (0.186 ml, 1.34 mmol) in THF (3 ml) was stirred at r.t. for 20 h. Then, the mixture was filtered under N_2, the filtrate evaporated, and the residue dissolved in toluene (10 ml). Addition of **18b** [6a] (0.342 g, 1.05 mmol) followed by a solution of 4-(dimethylamino)pyridine (DMAP, 0.150 mg, 1.2 mmol) in CH_2Cl_2 (2 ml), stirring at r.t. for 20 h, filtration, evaporation, and FC (hexane/AcOEt) furnished pure **20b** (oil, 0.412 mg, 74%). ^{1}H-NMR: 0.02 (*s*, 6 H); 0.85 (*s*, 9 H); 0.99 (*s*, 3 H); 0.80–1.00 (*m*, 5 H); 1.05–1.30 (*m*, 10 H); 1.30–1.75 (*m*, 6 H); 1.75–1.95 (*m*, 3 H); 1.96–2.10 (*m*, 2 H); 2.62 (*dq*, *J* = 5.3, 7.1, 1 H); 3.22 (*dq*, *J* = 7.0, 7.1, 1 H); 3.40 (*d*, *J* = 13.9, 1 H); 3.50 (*d*, *J* = 13.9, 1 H); 3.80–4.00 (*m*, 2 H); 5.10–5.30 (*m*, 1 H). ^{13}C-NMR: 173.85 (*s*); 173.42 (*s*); 74.45 (*d*); 74.09 (*d*); 65.08 (*d*); 53.13 (*t*); 48.30 (*s*); 47.72 (*s*); 45.44 (*d*); 44.54 (*d*); 43.73 (*d*); 38.30 (*t*); 32.77 (*t*); 26.39 (*t*); 25.94 (*t*); 25.83 (*q*); 25.59 (*t*); 20.77 (*q*); 19.82 (*q*); 18.03 (*s*); 15.27 (*q*); 11.26 (*q*); 9.68 (*q*); 9.55 (*q*); −4.62 (*q*). MS: 55 (18), 57 (12), 69 (42), 73 (63), 75 (55), 79 (11), 93 (17), 97 (48), 107 (15), 114 (22), 115 (35), 135 (65), 173 (75), 174 (12), 189 (16), 199 (15), 229 (14), 285 (11), 312 (100), 313 (32), 314 (11), 528 (1). HR-MS: 528.2783 ($[C_{28}H_{51}O_6SiSN - Et]^{+\cdot}$; calc. 528.2815).

*(1S,2R)-3-(Benzylsulfanyl)-1-ethyl-2-methylpropyl (2S,3S)-3-[(*tert*-Butyl)dimethylsilyloxy]-2-methylpentanoate* (**21**). Mercaptolysis of **20b** (0.300 g, 0.540 mmol) for 1 h at 0° according to the *General Procedure* gave pure **2f** (oil, 0.195 g, 78%) and the recovered (*R*)-**1** (0.110 g, 91%). $[\alpha]_D = -14.6$; $[\alpha]_{578} = -15.3$; $[\alpha]_{546} = -17.7$; $[\alpha]_{436} = -32.8$; $[\alpha]_{365} = -58.2$ (*c* = 1.60, $CHCl_3$, 22°). IR: 2930, 1739, 1690, 1455, 1382, 1255, 1182, 1109, 1049, 969, 836, 775, 702. ^{1}H-NMR: 0.06 (*s*, 3 H); 0.07 (*s*, 3 H); 0.88 (*t*, *J* = 7.2, 3 H); 0.80 (*t*, *J* = 7.3, 3 H); 0.89 (*s*, 9 H); 1.10 (*d*, *J* = 7.1, 3 H); 1.21 (*d*, *J* = 7.1, 3 H); 1.30–1.50 (*m*, 2 H); 1.50–1.70 (*m*, 2 H); 2.65 (*dq*, *J* = 4.8, 7.1, 1 H); 2.87 (*dq*, *J* = 7.0, 7.0, 1 H); 3.95 (*dt*, *J* = 4.5, 6.9, 1 H); 4.11 (*s*, 2 H); 5.10 (*dt*, *J* = 6.2, 6.2, 1 H); 7.20–7.30 (*m*, 5 H). ^{13}C-NMR: 199.85 (*s*); 173.61 (*s*); 137.31 (*s*); 128.79 (*d*); 128.60 (*d*); 127.26 (*d*); 75.30 (*d*); 74.21 (*d*); 51.06 (*d*); 45.54 (*d*); 33.18 (*t*); 25.84 (*q*); 25.61 (*t*); 24.87 (*t*); 18.06 (*s*); 13.14 (*q*); 10.91 (*q*); 9.92 (*q*); 9.78 (*q*); −4.58 (*q*); −4.67 (*q*). MS: 45 (16), 55 (21), 59 (10), 69 (33), 70 (10), 73 (65), 75 (65), 91 (100), 92 (16), 97 (25), 115 (25), 117 (10), 134 (10), 173 (29), 189 (59), 221 (20), 467 (0.24, $[M + 1]^+$). HR-MS: 409.1860 ($[C_{25}H_{42}O_4SiS - (t\text{-Bu})]^{+\cdot}$; calc. 409.1890).

*(1R,2R)-1-Ethyl-2-methyl-3-oxopentyl (2S,3S)-3-[(*tert*-Butyl)dimethylsilyloxy]-2-methylpentanoate* (**22**). Reaction of **21** (0.130 g, 0.28 mmol) with 1.6 equiv. of EtMgBr (1M in THF) in the presence of $[Fe(acac)_3]$ using the *General Procedure* gave, after workup and FC (hexane/Et_2O), **22** (oil, 80 mg, 77%) showing the same IR, NMR, and MS as the compound described in [7a]. $[\alpha]_D = -14.6$; $[\alpha]_{578} = -15.3$; $[\alpha]_{546} = -17.7$; $[\alpha]_{436} = -32.8$; $[\alpha]_{365} = -58.2$ (*c* = 1.60, $CHCl_3$, 22°).

General Procedure for the Cleavage of N*-Acylbornane-10,2-sultams* **6** *into Aldehydes* **23**. A 0.3M soln. of DIBAL (1 equiv.) in CH_2Cl_2 at −78° was added to a 0.1M soln. of **6** (1 equiv.) in CH_2Cl_2 at −78°. Then, the mixture was stirred for 2 h at −78° and MeOH (20 equiv.) added within 1 min to the soln. at −78° and stirred again for 10 min. After that, a 1M aq. soln. of HCl was added to the soln. at −78° and warmed to r.t. The soln. was extracted with CH_2Cl_2, dried, concentrated, and purified by FC to give **23** as an oil and the recovered **1** or *ent*-**1** as a solid.

*(2*R*)-2-Methyl-3-phenylpropanal* (**23a**). Reduction with DIBAL of **6a** (120 mg, 0.33 mmol) gave, after purification, (*S*)-**1** (69 mg, 95%) as a solid and **23a** (42 mg, 85%) as an oil. IR: 3026, 2937, 1709, 1496, 1454. ^{1}H-NMR: 1.10 (*d*, *J* = 6.8, 3 H); 2.55–2.70 (*m*, 2 H); 3.10 (*m*, 1 H); 7.15–7.35 (*m*, 5 H); 9.73 (*s*, 1 H). ^{13}C-NMR: 204.3 (*d*); 138.8 (*s*); 129.0 (*d*); 128.5 (*d*); 126.4 (*d*); 48.0 (*d*); 36.7 (*t*); 13.2 (*q*). MS: 148 (7, $[C_{10}H_{12}O]^{+\cdot}$); 118 (52), 91 (100), 65 (12). Chiral GC (*Lipodex D*; 80°): ee 94% ((*R*)-enantiomer: t_R 23.0 min; (*S*)-enantiomer: t_R 23.8 min; flow: 63).

*(2*S*)-2-Methyl-3-phenylpropanal* (**23b**). Reduction with DIBAL of **6b** (120 mg, 0.33 mmol) gave, after purification, (*R*)-**1** (63 mg, 88%) as a solid and **23b** (41 mg, 83%) as an oil showing the same IR, NMR, and MS as **23a**. Chiral GC (*Lipodex D*; 75°): ee 94% ((*R*)-enantiomer: t_R 31.1 min; (*S*)-enantiomer: t_R 33.9 min; flow: 63).

(2S)-5-Methyl-2-(1-methylethenyl)hex-4-enal (**23c**). Reduction with DIBAL of **6j** (130 mg, 0.35 mmol) gave, after purification (*S*)-**1** (81 mg, 95%) as a solid and **23c** (43 mg, 79%) as an oil showing the same IR, NMR, and

MS as **23d**. $[\alpha]_D = +95$, $[\alpha]_{578} = +101$, $[\alpha]_{546} = +119$, $[\alpha]_{436} = +257$, $[\alpha]_{365} = +646$ ($c = 0.30$, $CHCl_3$, 20°). Chiral GC (*Lipodex D*; 60°): ee 92% ((*R*)-enantiomer: t_R 12.9 min; (*S*)-enantiomer: t_R 13.6 min; flow: 60).

(2R)-5-Methyl-2-(1-methylethenyl)hex-4-enal (**23d**). Reduction with DIBAL of **6k** (140 mg, 0.38 mmol) gave, after purification, (*R*)-**1** (80 mg, 95%) as a solid and **23d** (51 mg, 87%) as an oil. $[\alpha]_D = -128$, $[\alpha]_{578} = -135$; $[\alpha]_{546} = -161$, $[\alpha]_{436} = -348$, $[\alpha]_{365} = -876$, ($c = 0.73$, $CHCl_3$, 20°). IR: 2972, 2917, 2857, 2725, 1720, 1451, 1377. ^{1}H-NMR: 1.63 (*s*, 3 H); 1.68 (*s*, 3 H); 1.72 (*s*, 3 H); 2.25 (*m*, 1 H); 2.50 (*m*, 1 H); 2.96 (*m*, 1 H); 4.90 (*s*, 1 H); 5.04 (*m*, 1 H); 5.06 (*m*, 1 H); 9.51 (*d*, $J = 2.2$, 1 H). ^{13}C-NMR: 201.3 (*d*); 140.2 (*s*); 133.7 (*s*); 120.6 (*d*); 115.3 (*t*); 60.7 (*d*); 25.9 (*t*); 25.7 (*q*); 21.3 (*q*); 17.9 (*q*). MS: 152 (5, $[C_{10}H_{16}O]^{+\cdot}$), 123 (13), 109 (20), 84 (31), 69 (100). Chiral GC (*Lipodex D*; 55°): ee 95% ((*R*)-enantiomer: t_R 34.7 min; (*S*)-enantiomer: t_R 36.8 min; flow: 63).

(2S)-2-Methyldecanal (**23e**). Reduction with DIBAL of **6l** (66 mg, 0.17 mmol) gave, after purification, (*R*)-**1** (32 mg, 86%) as a solid and **23e** (28 mg, 95%) as an oil. $[\alpha]_D = +21.7$, $[\alpha]_{578} = +23.3$, $[\alpha]_{546} = +26.7$, $[\alpha]_{436} = +58.1$, $[\alpha]_{365} = +139$ ($c = 0.58$, $CHCl_3$, 20°). IR: 3020, 2958, 2929, 2856, 1720, 1465. ^{1}H-NMR: 0.87–0.90 (*m*, 3 H); 1.09 (*d*, $J = 7.1$, 3 H); 1.20–1.40 (*m*, 13 H); 1.70 (*m*, 1 H); 2.33 (*m*, 1 H); 9.62 (*d*, $J = 2.2$, 1 H). ^{13}C-NMR: 205.3 (*d*); 46.3 (*d*); 31.8 (*t*); 30.6 (*t*); 29.6 (*t*); 29.4 (*t*); 29.2 (*t*); 26.9 (*t*); 22.6 (*t*); 14.1 (*q*); 13.3 (*q*). MS: 186 (19), 143 (47), 129 (62), 101 (19), 87 (89), 74 (100). Chiral GC (*Lipodex D*; 70°): ee 97% ((*R*)-enantiomer: t_R 29.9 min; (*S*)-enantiomer: t_R 32.8 min; flow: 60).

(2R)-2-Methyldecanal (**23f**). Reduction with DIBAL of **6m** (90 mg, 0.24 mmol) gave, after purification, (*R*)-**1** (48 mg, 95%) as a solid and **23f** (37 mg, 93%) as an oil. $[\alpha]_D = -20.2$, $[\alpha]_{578} = -20.5$, $[\alpha]_{546} = -23.5$, $[\alpha]_{436} = -47.2$, $[\alpha]_{365} = -104$ ($c = 0.62$, $CHCl_3$, 20°). Chiral GC (*Lipodex D*; 70°): ee 99% ((*R*)-enantiomer: t_R 29.9 min; flow: 60).

(2S)-2-Phenylbutanal (**23g**). Reduction with DIBAL of **6n** (54 mg, 0.15 mmol) gave, after purification, (*S*)-**1** (31 mg, 95%) as a solid and **23g** (20 mg, 90%) as an oil. $[\alpha]_D = +128$, $[\alpha]_{578} = +135$, $[\alpha]_{546} = +158$, $[\alpha]_{436} = +326$, $[\alpha]_{365} = +751$ ($c = 0.30$, $CHCl_3$, 20°). IR: 3030, 2968, 2935, 2877, 1721, 1492, 1454. ^{1}H-NMR: 0.89–0.93 (*m*, 3 H); 1.75 (*m*, 1 H); 2.12 (*m*, 1 H); 3.41 (*m*, 1 H); 7.18–7.40 (*m*, 5 H); 9.68 (*d*, $J = 2.0$, 1 H). ^{13}C-NMR: 201.0 (*d*); 136.4 (*s*); 129.0 (*d*); 128.8 (*d*); 127.5 (*d*); 60.9 (*d*); 23.0 (*t*); 11.7 (*q*). MS: 148 (8, $[C_{10}H_{12}O]^+$), 119 (54), 91 (100), 77 (16), 65 (22), 51 (23). Chiral GC (*Lipodex C*; 40°): ee 91% ((*S*)-enantiomer: t_R 85.8 min; (*R*)-enantiomer: t_R 91.9 min; flow: 55).

(2R)-2-Phenylbutanal (**23h**). Reduction with DIBAL of **6o** (70 mg, 0.20 mmol) gave, after purification, (*R*)-**1** (37 mg, 89%) as a solid and **23h** (25 mg, 87%) as an oil. $[\alpha]_D = -128$, $[\alpha]_{578} = -134$, $[\alpha]_{546} = -158$, $[\alpha]_{578} = -327$, $[\alpha]_{365} = -754$ ($c = 0.52$, $CHCl_3$, 20°). Chiral GC (*Lipodex C*, 40°): ee 90% ((*S*)-enantiomer: t_R 85.5 min; (*R*)-enantiomer: t_R 91.9 min; flow: 55).

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