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DIASTEREO- AND ENANTIOSELECTIVE SYNTHESIS OF α,α'-DISUBSTITUTED SPIROACETALS USING THE SAMP-/RAMP-HYDRAZONE METHOD[+]

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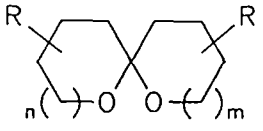
Abstract: α,α'-Disubstituted spiroacetals were synthesized with excellent enantiomeric excesses and in good overall yields from symmetrical ketones employing the SAMP-/RAMP-hydrazone-method for asymmetric α,α'-alkylation.

The spiroacetal moiety **I** is part of many natural products with a broad spectrum of biological activities. Among them are for instance, antiparasitic agents (avermectins[1-3] and milbemycins[4]), antibiotics (calcimycin[5]) and many volatile spiroacetals with simple substituents used by insects as pheromones[6-8] (e.g. *chalcogran*[9,10]). Polyether antibiotics with a spiroacetal substructure are monensin[11], iso-dianemycin[12], which contains two spiroacetal entities one of which is substituted at both carbons next to the spirocarbon and salinomycin[13] with its trioxadispiroketal system. Further compounds carrying the spiroacetal moiety as a crucial structural feature are the talaromycins[14], which are a class of mycotoxins, and okadaic acid[15].



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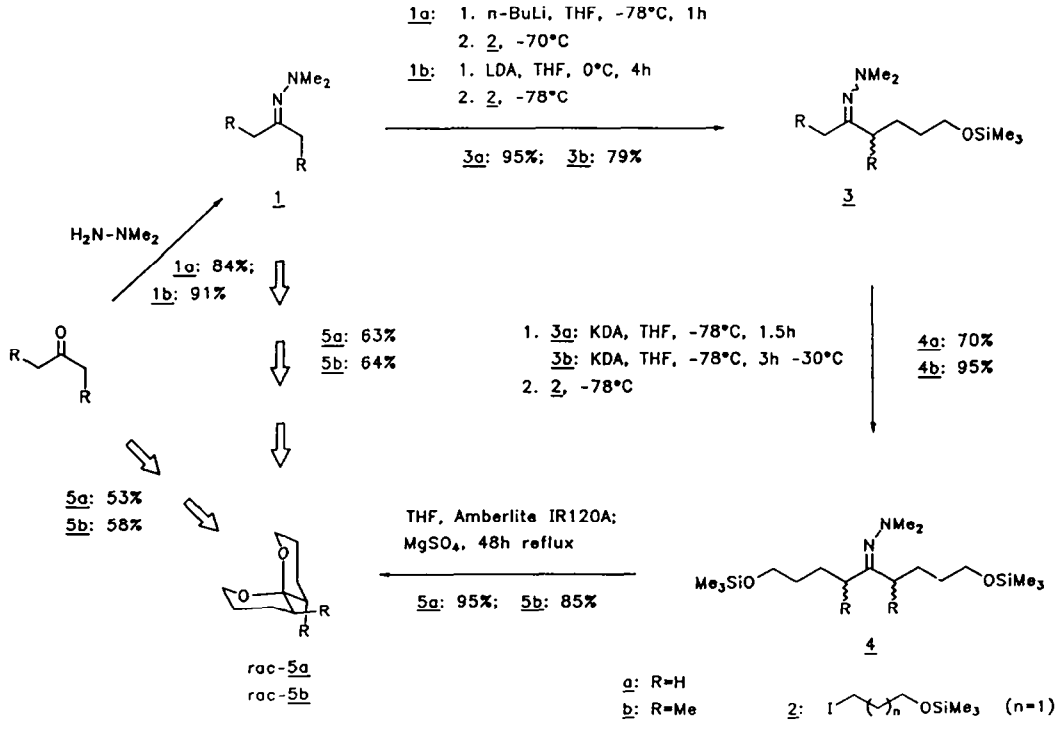
An important aspect in dealing with spiroacetals are steric and anomeric effects, which have profound influence on their conformations. Equatorial substituents are favoured, as usual, over axial substituents due to steric effects and axial C-O-bonds over equatorial C-O-bonds due to the anomeric effect[16,17], thus making

[+] Dedicated to Professor W.D.Ollis on the occasion of his 65th birthday.

it possible to predict the conformations of products formed in thermodynamically controlled reactions, especially in acid catalyzed spirocyclizations of dihydroxyketones[8].

In recent years, numerous spiroacetal syntheses have been designed[7,8,18,19]. Most of them involve the acid catalyzed ring closure of dihydroxyketones or their equivalents. Deslongchamps et al.[16] synthesized 5,11-dimethyl-1,7-dioxaspiro[5.5]undecane [**5b**] by hydrolysis of the appropriate ketodiacetate and acid catalyzed spiroacetalization, thus providing three isomers, whose ratio could be predicted by calculation of their energies with respect to the anomeric effect.

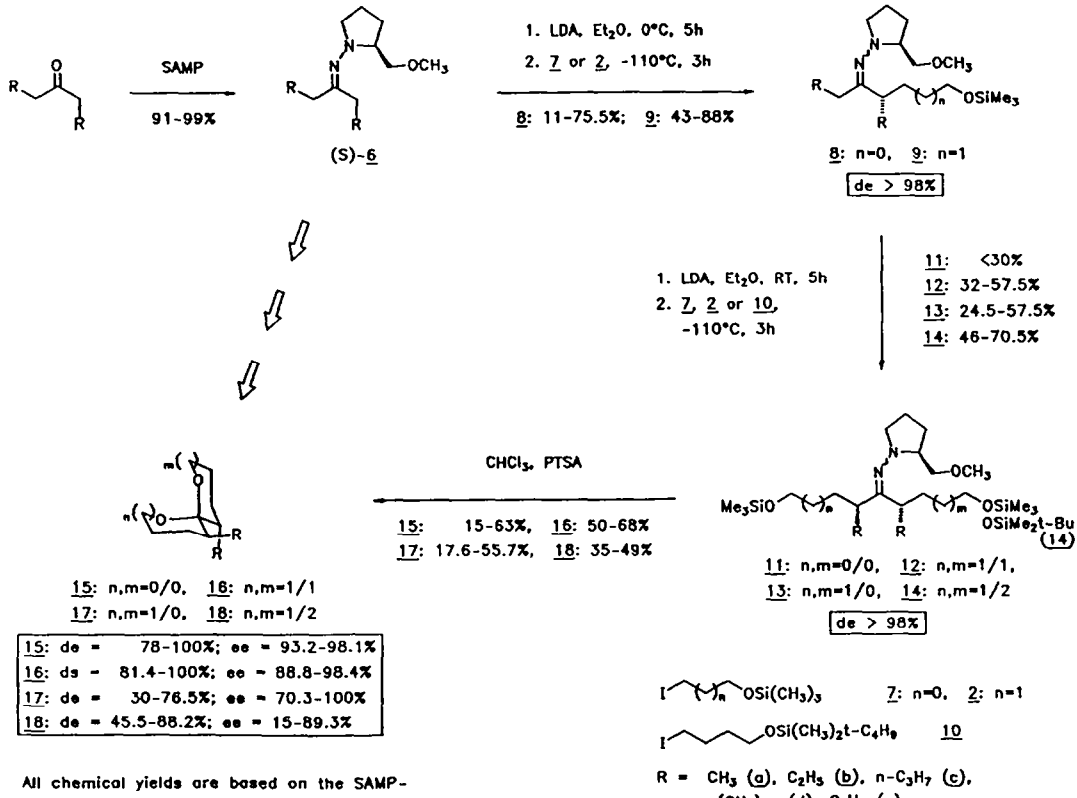
Other appropriate precursors are α,α'-alkylated dimethylhydrazones used by us to synthesize the bark-beetle pheromone *chalcogran* via bisalkylation of acetone dimethylhydrazone with oxiranes and subsequent acidic cleavage and cyclization[20]. A similar approach was used by Reddy and Mitra[21] in the synthesis of 1,7-dioxaspiro[5.5]undecane [**5a**]. Instead of oxiranes they used THP-protected 3-bromo-1-propanol as alkylating agent. We synthesized rac-**5a**, the sex pheromone of the olive fruit-fly *Dacus oleae*, and 5,11-dimethyl-1,7-dioxaspiro[5.5]undecane [rac-**5b**] by using 1-iodo-3-trimethylsilyloxy-propane[22] [2] as electrophile in 53 and 58% overall yield respectively from acetone and pentane-3-one (scheme 1)[23]. The appropriate dimethylhydrazones were synthesized according to known procedures[24,25]. Metalations and alkylations were



- Scheme 1 -

carried out in THF, acidic cleavage and cyclization was effected by refluxing with amberlite IR 120 A and $MgSO_4$ for two days, thus yielding the isomers with axial C-O-bonds and equatorial methylgroups exclusively.

Evans et al.[26,27] also used the alkylation of a dimethylhydrazone in their calcimycin synthesis. The stereocentre adjacent to the central spirocarbon atom was installed by an equilibration step, which took advantage of the enolizability and epimerizability of this position in protic media and lead to the most stable configuration. Employing our SAMP-/RAMP-hydrazone-method[28-32] we now report on an efficient and flexible diastereo- and enantioselective synthesis of α,α'-disubstituted spiroacetals[33]. Herein we hoped to generate the two α and α'-stereocenters by double alkylation of symmetrical SAMP-hydrazones **6**, whereas the absolute configuration at the central spirocarbon atom should be controlled by the steric and anomeric effects mentioned above.



15:	de = 78-100%; ee = 93.2-98.1%
16:	ds = 81.4-100%; ee = 88.8-98.4%
17:	de = 30-76.5%; ee = 70.3-100%
18:	de = 45.5-88.2%; ee = 15-89.3%

All chemical yields are based on the SAMP-hydrazones 6, except those of 12a-d, which are based on 9a-d.

- Scheme 2 -

As is depicted in scheme 2, the SAMP-hydrazones **6**, synthesized according to literature procedures[28-31] with chemical yields ranging from 83 to 99%, were deprotonated by LDA in Et_2O at 0°C and alkylated with 1-iodo-2-trimethylsilyloxyethane[34] [7] or 1-iodo-3-trimethylsilyloxypropane [2] at -110°C. The chemical

Table 1. Monoalkylated SAMP-hydrazones **8** and **9**

Product	R	n	yield[a] (%)	$[\alpha]_D$ (°)	de[b] (%)	E/Z[b]
(*S,S*)-**8a**	CH_3	0	75[c]	+153.6 (23°C, c = 0.93, $CHCl_3$)	>98	only Z[c]
(*S,S*)-**8b**	C_2H_5	0	75.5[c]	+140.7 (23°C, c = 1.70, $CHCl_3$)	>98	1:21.4[c]
(*S,S*)-**8c**	n-C_3H_7	0	41[c]	+140.3 (23°C, c = 1.08, $CHCl_3$)	>98	1:31.5[c]
(*S,S*)-**8d**	-$(CH_2)_3$-	0	34[c]	+116.5 (23°C, c = 1.43, $CHCl_3$)	>98	1:4.5[c]
(*S,R*)-**8e**	C_6H_5	0	11[c]	+2.5 (23°C, c = 0.94, $CHCl_3$)	>98	only E[c]
(*S,S*)-**9a**	CH_3	1	88[d]	+158.6 (23°C, neat)	>98	1:7[d]
(*S,S*)-**9b**	C_2H_5	1	87.5[d]	+136.4 (21°C, neat)	>98	1:6[d]
(*S,S*)-**9c**	n-C_3H_7	1	64.5[c]	+125.9 (26°C, neat) +153.0 (26°C, c = 1.48, C_6H_6)	>98	only Z[c]
(*S,S*)-**9d**	-$(CH_2)_3$-	1	91[d]	+155.8 (26°C, c = 1.41, C_6H_6)	>98	1:1.4[d]
(*S,R*)-**9e**	C_6H_5	1	43[c]	+16 (28°C, c = 0.62, C_6H_6)	>98	only E[c]

[a]Based on the unalkylated SAMP-hydrazones **6**. - [b]Determined by ^{13}C NMR spectroscopy. - [c]After chromatography (SiO_2; ether:pentane = 1:1-1:4). - [d]After distillation (Kugelrohr).

yields of the colourless to light yellow monoalkylated SAMP-hydrazones **8** and **9** ranged from 11 to 75.5% and 43 to 91% after distillation or flash-chromatography (SiO_2) (Table 1). The diastereomeric excesses were >98% according to ^{13}C NMR spectroscopy. The determination was simplified by careful work-up and chromatographic purification (SiO_2), so that the hydrazones **8** and **9** were obtained almost exclusively as (Z)-isomers.

To obtain the bisalkylated SAMP-hydrazones **11**, **12**, **13** and **14** the compounds **8** and **9** were again metalated with LDA in Et_2O at room-temperature and alkylated with **2**, **7** or 4-iodo-1-(*tert*-butyldimethylsilyloxy)propane[35] [**10**] at -110°C. Flash-chromatography (SiO_2) provided **11**, **12**, **13** and **14** as colourless to pale yellow oils of >98% de, but with lower chemical yields (**11**: <30%, **11c** (R = n-C_3H_7) decomposed completely; **12**: 32-57.5%; **13**: 24.5-57.5%; **14**: 46-70.5%) due to partial decomposition during chromatography (Table 2). So, we could demonstrate that the SAMP-/RAMP-hydrazone-method is not only applicable for overall enantioselective monoalkylations, but for α,α'-bisalkylations of ketones too. Using two different electrophiles in the mono- and bisalkylations could have produced (E/Z)-mixtures. However, the products we obtained were homogeneous concerning this aspect. In view of the proposed mechanism for the α-alkylation of SAMP-/RAMP-hydrazones, we presume that after the alkylation the SAMP-hydrazone group and the alkyl group last introduced are in syn-position to each other and that (E/Z)-isomerization takes place very slowly.

Table 2. Bisalkylated SAMP-hydrazones **11**, **12**, **13** and **14**

Product	R	n/m	Yield[a] (%)	$[\alpha]_D$ (°)	de[b] (%)
(*S,S,S*)-**11a**	CH_3	0/0	30	+165.1 (24°C, c = 1.05, $CHCl_3$)	>98
(*S,S,S*)-**11b**	C_2H_5	0/0	17.5	+131.4 (23°C, c = 0.86, $CHCl_3$)	>98
(*S,S,S*)-**12a**	CH_3	1/1	48.5	+167.2 (24°C, c = 1.14, C_6H_6) +135.3 (24°C, neat)	>98
(*S,S,S*)-**12b**	C_2H_5	1/1	39	+126.9 (23°C, c = 1.20, C_6H_6)	>98

Table 2. (continued)

Product	R	n/m	Yield[a] (%)	$[\alpha]_D$ (°)	de[b] (%)
(*S,S,S*)-**12c**	n-C_3H_7	1/1	57.5	+131.8 (22°C, c = 1.12, C_6H_6) +102.1 (22°C, neat)	> 98
(*S,S,S*)-**12d**	-$(CH_2)_3$-	1/1	32	+120.9 (26°C, c = 1.05, C_6H_6)	> 98
(*S,R,R*)-**12e**	C_6H_5	1/1	37.5	+179.6 (26°C, c = 1.02, C_6H_6)	> 98
(*S,S,S*)-**13a**	CH_3	1/0	42.5	+141.5 (24°C, c = 0.99, $CHCl_3$)	> 98
(*S,S,S*)-**13b**	C_2H_5	1/0	57.5	+104.2 (29°C, c = 1.58, $CHCl_3$)	> 98
(*S,S,S*)-**13c**	n-C_3H_7	1/0	25.5	+103.1 (28°C, c = 1.88, $CHCl_3$)	> 98
(*S,S,S*)-**13d**	-$(CH_2)_3$-	1/0	24.5	+82.2 (24°C, c = 0.97, $CHCl_3$)	> 98
(*S,R,R*)-**13e**	C_6H_5	1/0	41	+146.1 (28°C, c = 1.67, $CHCl_3$)	> 98
(*S,S,S*)-**14a**	CH_3	1/2	70.5	+124.5 (23°C, neat)	> 98
(*S,S,S*)-**14b**	C_2H_5	1/2	63.5	+90.4 (24°C, c = 1.03, $CHCl_3$)	> 98
(*S,S,S*)-**14c**	n-C_3H_7	1/2	68.5	+86.0 (27°C, c = 1.65, $CHCl_3$)	> 98
(*S,S,S*)-**14d**	-$(CH_2)_3$-	1/2	46	+62.7 (26°C, c = 1.04, $CHCl_3$)	> 98

Table 2. (continued)

Product	R	n/m	Yield[a] (%)	[α]D (°)	de[b] (%)
(*S,R,R*)-**14e**	C_6H_5	1/2	53.5	+ 121.3 (27°C, c = 1.10, $CHCl_3$)	> 98

[a]After flash-chromatography (SiO_2; ether:pentane = 1:1-1:4); for (*S,S,S*)-**12a-d** based on the monoalkylated SAMP-hydrazones **9a-d**; for all other compounds based on the unalkylated SAMP-hydrazones **6**, because the monoalkylated SAMP-hydrazones were used as crude products. - [b]Determined by ^{13}C NMR spectroscopy.

The last step of the procedure was the acidic cleavage and cyclization of the hydrazones **11**, **12**, **13** and **14**. As previously mentioned, the α,α'-positions of spiroacetals are enolizable under acidic conditions. Thus, in our work the main difficulty was to avoid the epimerization of the two established stereocentres in protic media. To reach our goal, we finally used p-toluenesulphonic acid (PTSA) (Table 3). Typically, approximately 1.5 eq of PTSA were required for reaction to occur with crude **11**, **12**, **13** or **14** in $CHCl_3$. In some cases, excess PTSA was added to the hydrazone solution in one portion and work-up (saturated $NaHCO_3$) followed after 5 minutes; in other cases PTSA was added in small portions and the solution was stirred for 5 minutes each time; if enough PTSA had been added the reaction occured immediately (TLC-control) and work-up followed at once to avoid epimerization. Purification was carried out by flash-chromatography (SiO_2). PTSA as cyclization agent had already been used by Deslongchamps et al.[16] in their synthesis of 5.11-dimethyl-1,7-dioxaspiro[5.5]undecane [**5b**] and later Ireland et al.[36] also found, that using PTSA just for some minutes avoids epimerization.

Table 3. α,α'-Disubstituted Spiroacetals **15**, **16**, **17** and **18**[a]

Product	R n/m	Yield[b,c] (%)	[α]D	de[d] (%)	de[c] (%)	ee (%)
(*S,R,S*)-**15a**	CH_3 0/0	63	-98.7° (22°C, c = 1.60, EtOH)	100	100	93.2
(*S,R,S*)-**15b**	C_2H_5 0/0	39	-62.8° (22°C, c = 1.02, EtOH)	93	100	97.8
(*S,R,S*)-**15c**	n-C_3H_7 0/0	15	-25.2° (22°C, c = 0.51, EtOH)	78	100	98.1

Table 3. (continued)

Product	R n/m	Yield[b,c] (%)	$[\alpha]_D$	de[d] (%)	de[c] (%)	ee (%)
(*S,R,S*)-**16a**	CH_3 1/1	68	-113.4° (22°C, c = 0.97, EtOH)	81.4[e]	100	97.4
(*S,S,S*)-**16a**	CH_3 1/1	16[f]		14.3[e]	86[e]	97.4
rac-(*S,S,R*)/ (*R,R,S*)-**16a**	CH_3 1/1			4.2[e]	14[e]	0
(*S,R,S*)-**16b**	C_2H_5 1/1	50	-46.1° (22°C, c = 0.95, EtOH)	100	100	95
(*S,R,S*)-**16c**	n-C_3H_7 1/1	62	-15.8° (22°C, c = 1.10, EtOH)	100	100	[h]
(*S,R,S*)-**16d**	-$(CH_2)_3$-	65	+31.3° (22°C, c = 0.99, EtOH)	95.9[e]	100	98.4
rac-(*S,R,R*)/ (*R,S,S*)-**16d**	-$(CH_2)_3$- 1/1	12	0°	4.1[e]	100	0
(*R,R,R*)-**16e**	C_6H_5 1/1	59	-43.2° (22°C, c = 0.94, EtOH)	100	100	88.8
(*S,R,S*)-**17a**	CH_3 1/0	32.3	-91.5° (25°C, c = 0.92, EtOH)	57.2	100	96.5
(*S,S,S*)-**17a**	CH_3 1/0	11.2	+106.3° (25°C, c = 0.87, EtOH)		100	100
(*S,R,S*)-**17b**	C_2H_5 1/0	47.0	-47.8° (24°C, c = 0.96, EtOH)	76.5	100	98.6
(*S,S,S*)-**17b**	C_2H_5 1/0	5.3	+78.5° (23°C, c = 1.18, EtOH)		100	98.4
(*S,R,S*)-**17c**	n-C_3H_7 1/0	60.1	-18.7° (22°C, c = 0.94, EtOH)	72.6	90.4	98.2

Table 3. (continued)

Product	R n/m	Yield[b,c] (%)	[α]D	de[d] (%)	de[e] (%)	ee (%)
(*S,S,S*)-**17c**	n-C_3H_7 1/0	9.3	+126.9° (21°C, c = 0.79, EtOH)		100	97.8
(*S,R,S*)-**17d**	-$(CH_2)_3$- 1/0	25.8	-43.2° (22°C, c = 0.63, EtOH)	30[h]	100	70.3
(*R,R,R*)-**17e**	C_6H_5 1/0	55.7	-14.1° (23°C, c = 0.82, EtOH)	77.9[e]	100	100
(*R,S,R*)-**17e**	C_6H_5 1/0	14.5[f]		14.6[e]	35.0	100
(*S,R,R*)-**17e**	C_6H_5 1/0			7.6[e]		54.3
(*S,R,S*)-**18a**	CH_3 1/2	35	+61.6° (28°C, c = 0.90, EtOH)	68.5	100	89.3
(*S,R,S*)-**18b**	C_2H_5 1/2	49	+36.6° (26°C, c = 0.59, EtOH)	88.2	100	82.0
(*S,R,S*)-**18d**	-$(CH_2)_3$- 1/2	46	0°	45.5	100	15

[a]Cleavage-Methods: A: PTSA is added in several small portions, TLC-control after 5 min each time: **16a, 16c, 16e, 17a, 17e, 18a, 18d**; B: PTSA is added in one portion (1.3-1.5 eq.), work-up after 5 min: **15a, 15b, 15c, 16b, 16d, 17b, 17c, 17d, 18b**. - [b]Based on the unalkylated SAMP-hydrazones **6**. - [c]After chromatography (SiO_2; ether:pentane = 1:10-1:30). - [d]Determined by GC on crude product. - [e]Diastereoselectivity (ds)[37,38] is given. - [f] Diastereomers not separable. - [g] So far we couldn't determine the ee of this spiroacetal. We suppose its value is within the scope of those of (*S,R,S*)-**16a** and (*S,R,S*)-**16b**.- [h]Other diastereomer could not be isolated.

Diastereomeric and enantiomeric excesses were determined by gas chromatography; the latter by using chiral cyclodextrin-phases[39-42] (Fig. 1-4). Racemic products to test the separation were easily obtained by treatment of the synthesized spiroacetals with PTSA for a longer period of time.

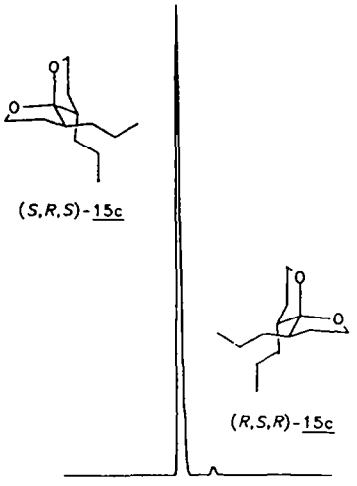


Fig.1. ee-Determination of (*S,R,S*)-**15c**. Fused-silica capillary with 10% heptakis-(2,3,6-tri-O-methyl)-ß-cyclodextrin in OV-1701. 110°C; 1 bar H_2.

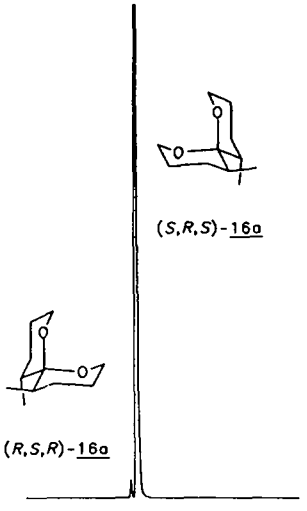


Fig.2. ee-Determination of (*S,R,S*)-**16a**. Fused-silica capillary with 10% heptakis-(2,3,6-tri-O-methyl)-ß-cyclodextrin in OV-1701. 110°C; 0.8 bar H_2.

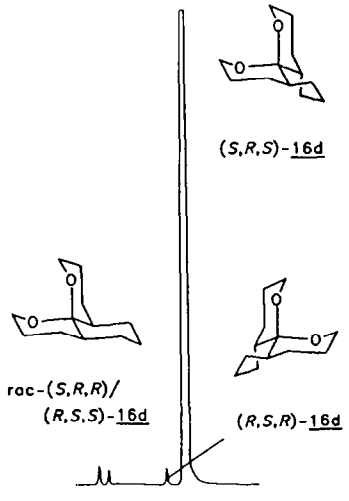


Fig.3. ee-Determination of (*S,R,S*)-**16d**. Fused-silica capillary with 10% heptakis-(2,3,6-tri-O-methyl)-ß-cyclodextrin in OV-1701. 110°C; 0.8 bar H_2.

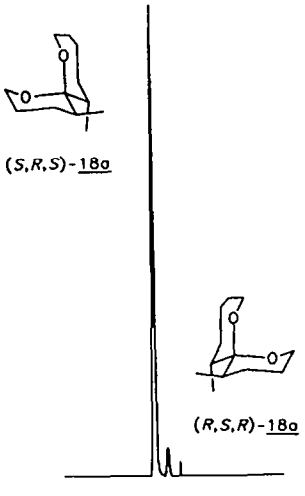


Fig.4. ee-Determination of (*S,R,S*)-**18a**. Fused-silica capillary with 10% heptakis-(2,3,6-tri-O-methyl)-ß-cyclodextrin in OV-1701. 110°C; 1 bar H_2.

The configurations of the synthesized spiroacetals were deduced taking steric and anomeric effects into account. Actually, we found only axial C-O-bonds in our products. Further evidence was taken from the inspection of the received ^{13}C NMR spectra. Though it should be possible to calculate the ^{13}C chemical shift data[43,44], we found it much easier and more reliable to make comparisons of the ^{13}C NMR data within our series of spiroacetals and to draw our own conclusions. The signals easiest to be found and on which we heavily relied were those of the central spirocarbon (**OCO**) in the area from 95 to 115 ppm, the carbons next to oxygen (**CH_2O**) in the area from 59 to 67 ppm and the substituted carbons (**CH**) in the area from 30 to 55 ppm, which could be distinguished from other signals with the help of a J-modulated spinecho-experiment. ^{13}C NMR spectra were especially simple, when the spiroacetal molecule possessed C_2-symmetry (Table 4).

We found that δ(OCO) normally showed no large dependence upon the substituent R. However, for the 4,10-disubstituted 1,6-dioxaspiro[4.5]decanes [**17**] compared to stereoisomer A δ(OCO) is about 2 ppm larger in stereoisomer B (entry 12-21).

For δ(CH_2O) we found the following relationships:

- no big dependence upon the substituent R
- change from 6-ring, R_{eq} to 5-ring, R_{eq}: ca. +5 to +6 ppm
- change from 6-ring, R_{ax} to 5-ring, R_{ax}: ca. +4 ppm
- change from 6-ring, R_{eq} to 6-ring, R_{ax}: ca. +0.5 ppm
- change from 5-ring, R_{eq} to 5-ring, R_{ax}: ca. -0.7 to -1.2 ppm

Furthermore we found for δ(CH) the following dependences:

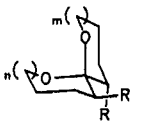
- change from 6-ring, R_{eq} to 5-ring, R_{eq}: ca. +4.5 ppm
- change from 6-ring, R_{ax} to 5-ring, R_{ax}: ca. +9 ppm
- change from 6-ring, R_{eq} to 6-ring, R_{ax}: ca. -3 ppm
- change from 5-ring, R_{eq} to 5-ring, R_{ax}: ca. +1.5 ppm
- change from 6-ring, R_{eq} (n/m:1/1) to 6-ring, R_{eq} (n/m:1/2): ca. +1 ppm
- change from 6-ring, R_{eq} to 7-ring, R_{eq}: ca. +9 to +13 ppm

With R = CH_3 in the 1,7-dioxaspiro[5.5]undecane-system [**16a**] three diastereomers were detected by gas chromatography. The main product was as expected the most stable stereoisomer (*S,R,S*)-**16a** (A) with two axial C-O-bonds, thus gaining maximium anomeric stabilization, and two equatorial methyl groups. The enantiomeric excess of (*S,R,S*)-**16a**, which could be separated from the two other stereoisomers by chromatography on silica-gel, was determined to be 97.4% ee (Fig. 2). By reversal of the configuration at the central spiro-C-atom, the thermodynamically least stable stereoisomer (*S,S,S*)-**16a** (**B**), showing the same ee was formed. The third diastereomer rac-(*S,S,R*)/(*R,R,S*)-**16a** (C, ee: 0%) was a result of the epimerization of the established stereocentres. Similar situations could be found concerning the 4,10-disubstituted 1,6-dioxaspiro[4.5]decanes [**17**].

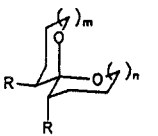
Table 4. Some ^{13}C-NMR data δ(ppm) of synthesized spiroacetals 15-18

	abs. conf.	R CH	n/m CH_2O	conf.	OCO	6-Ring, R_{eq} CH	6-Ring, R_{eq} CH_2O	6-Ring, R_{ax} CH	6-Ring, R_{ax} CH_2O	5/7-Ring, R_{eq} CH	5/7-Ring, R_{eq} CH_2O	5-Ring, R_{ax} CH	5-Ring, R_{ax} CH_2O
1	(*S,R,S*)-15a	CH_3	0/0	A[a]	114.84					37 46	65 99		
2	(*S,R,S*)-15b	C_2H_5	0/0	A[a]	114 64					45.55	66.06		
3	(*S,R,S*)-15c	n-C_3H_7	0/0	A[a]	114.87					43.37	66.13		
4	(*S,R,S*)-16a	CH_3	1/1	A[a]	99 75	34 44	59.88						
5	(*S,S,S*)-16a	CH_3	1/1	B[a]	99.34			31.92	60 67				
6	rac-(*S,S,R*)/ (*R,R,S*)-16a	CH_3	1/1	C	100.02	35.92	59.40	35.78	60.53				
7	(*S,R,S*)-16b	C_2H_5	1/1	A[a]	100.30	40.94	59.79						
8	(*S,R,S*)-16c	C_3H_7	1/1	A[a]	100.29	38 75	59.79						
9	(*S,R,S*)-16d	-$(CH_2)_3$-	1/1	A[a]	98 43	35.12	61 62						
10	rac-(*S,S,R*)/ (*R,R,S*)-16d	-$(CH_2)_3$-	1/1	C	96 86	44.86[c]	60.01[c]	38.51[c]	60.32[c]				
11	(*R,R,R*)-16e	C_6H_5	1/1	A[a]	99.19	48 86	59.92						
12	(*S,R,S*)-17a	CH_3	1/0	A	107.27	33.59	60.50			37 97	65.59		
13	(*S,S,S*)-17a	CH_3	1/0	B	109.47			30 46	60.99			39.52	65 02
14	(*S,R,S*)-17b	C_2H_5	1/0	A	107.47	40 76	60.34			45.50	65.55		
15	(*S,S,S*)-17b	C_2H_5	1/0	B	109.53			37.87	60 78			47.02	64 87
16	(*S,R,S*)-17c	C_3H_7	1/0	A	107.59	38 63	60.34			43.29	65.62		
17	(*S,S,S*)-17c	C_3H_7	1/0	B	109.62			35 58	60 80			44.65	64.90
18	(*S,R,S*)-17d	-$(CH_2)_3$-	1/0	A	106.30	41.56[c]	61.06[c]			42.61[c]	64.78[c]		
19	(*R,R,R*)-17e	C_6H_5	1/0	A	106.17	47.58	60.66			50.59	65.58		
20	(*R,S,R*)-17e	C_6H_5	1/0	B	109.27			43.53	61.06			52 98	65 71
21	(*S,R,R*)-17e	C_6H_5	1/0	C	109.20	47.95	62.63					54.93	66 60
22	(*S,R,S*)-18a	CH_3	1/2	A	103.24	35.40	[b]			45.55	[a]		
23	(*S,R,S*)-18b	C_2H_5	1/2	A	103.66	42.27	[b]			53.89	[a]		
24	(*S,R,S*)-18d	-$(CH_2)_3$-	1/2	A	100.56	36 02	[b]			44 76	[a]		

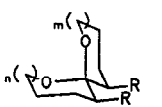
[a]Molecule possesses C_2-symmetry. - [b]Shift-data too similar, assignment not possible. - [c]Uncertain assignment.



A



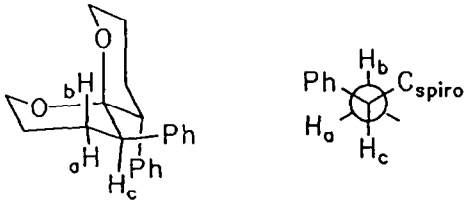
B



C

By cleavage of (*S,S,S*)-**12d** two diastereomers were formed. Using 1.5 eq PTSA (3 min) the diastereoselectivity was 95.9%. The stereoisomers could be separated by chromatography. We mainly got the desired stereoisomer (*S,R,S*)-**16d** (A) with its C6-ring in twist conformation thus possessing C2-symmetry and a ^{13}C NMR spectrum with just 7 signals. The ee-value turned out to be 98.4% (Fig. 3). Under the prolonged influence of the protic medium it epimerized to form its thermodynamically more stable diastereomer rac-(*S,S,R*)/(*R,R,S*)-**16d** (C) with all rings in chair conformation, and not its enantiomer. So, on lengthening the cleavage time with PTSA, diastereoselectivity decreased, but the optical rotation of the fraction containing the C_2-isomer always showed the same value and an ee of about 98.4%, whereas the other fraction showed no rotation and 0% ee (Fig. 3).

The ^1H NMR spectra of (*R,R,R*)-**16e** deserves a more detailed examination (Fig. 5). The signal for the protons H_c can be found at 2.53 ppm. Coupling with H_b ($J^{ax\text{-}ax}(H_b\text{-}H_c) = 12.9Hz$) and H_a ($J^{eq\text{-}ax}(H_a\text{-}H_c) = 3.9Hz$) splits H_c into two doublets. For H_b the following coupling-constants can be found: $J^{gem}(H_a\text{-}H_b) = J^{ax\text{-}ax}(H_b\text{-}H_c) = J^{ax\text{-}ax}(H_b\text{-}H_d) = 12.9Hz$ and $J^{ax\text{-}eq}(H_b\text{-}H_e) = 4.8Hz$. These result from a q/d-splitting of the H_b-signal at 2.1 ppm. So, the ^1H NMR spectra is in accordance with the given conformation.



(*R,R,R*)-16e

Fig. 5

All absolute configurations shown in the scheme and listed in the tables are in accordance with the postulated mechanism for SAMP-/RAMP-alkylations[28-32].

In summary, the diastereo- and overall enantioselective α,α'-bisalkylation of ketones via their corresponding SAMP-/RAMP-hydrazones opens up an efficient and flexible entry into the important class of spiro - acetals.

EXPERIMENTAL

Optical rotation values were measured using a Perkin-Elmer P241 polarimeter. Microanalyses were obtained using a Heraeus CHN-O-Rapid. IR-spectra were recorded on a Beckman Acculab 4 spectrophotometer. ^{1}H- and ^{13}C-NMR-spectra were obtained using a Varian VXR 300 spectrometer. MS spectra were recorded on a Varian MAT 212 spectrometer. ee-values were determined by gaschromatography on heptakis-(2,3,6-tri-O-methyl)-beta-[41] and octakis-(3-O-methyl-2,6-di-O-pentyl)-gamma-cyclodextrin-phases[42].

1. Dimethylhydrazones 1 and SAMP-hydrazones 6 (general procedure)

1.5 eq of N,N-dimethylhydrazine and 1 eq of ketone or 1 eq of SAMP and 1.25 eq of ketone in 70 ml cyclohexane are heated under reflux while the reaction water is removed via a Dean Stark trap. After 12 h the reaction is complete (TLC control) and the solvent is removed in vacuo. The residue is dissolved in Et_2O, washed three times with a little water, dried over $MgSO_4$ and evaporated in vacuo. The crude hydrazone is purified by distillation under reduced pressure or chromatography.

2. Metalation of DMH-hydrazones by n-BuLi and alkylation (general procedure):

In a dried, argon-filled round-bottomed flask fitted with a septum cap, the ketone-hydrazone is solved in anhydrous THF. The solution is cooled to -78°C and n-Butyllithium (1.1 eq, 1.6 M solution in n-hexane) is added dropwise. After 1 h further stirring **2** (1.4 eq) is added dropwise at -70°C and the mixture is allowed to warm up to room temperature slowly (about 15 h). THF is removed under reduced pressure, ether/pentane (1:1) is added and filtered over Al_2O_3. The crude product is purified by distillation.

3. Metalation of DMH- and SAMP-hydrazones by LDA and alkylation (general procedure):

In a dried, argon-filled round-bottomed flask fitted with a septum cap, anhydrous Et_2O (**1b**: THF) (4-7 ml/mmol) is cooled to 0°C and diisopropylamine (1.1 eq) and then n-Butyllithium (1.1 eq, 1.6 M solution in n-hexane) are added to form a LDA-solution. After 15 min the hydrazone (**1b, 6, 8** or **9**) is added dropwise and the mixture stirred for 5 h at 0°C (**1b, 6**) or room-temperature (**8** and **9**). The solution of metalated hydrazone is cooled to -110°C (**1b**: -78°C), **2, 7** or **10** (1.1 eq) is added dropwise, and the mixture is stirred for 3 h at -110°C (**1b**: -78°C) and then warmed slowly to room temperature (about 15 h). Et_2O (40 ml/mmol) is added, washed three times with a little water, dried ($MgSO_4$) and evaporated under reduced pressure. The crude product **8, 9, 11, 12, 13** or **14** is purified by distillation or column chromatography (silica gel, Et_2O/pentane, 1:2-1:4) to give a colorless to pale yellow oil. Concerning the workup of **3b** THF is removed under reduced pressure, ether/pentane (1:1) is added and filtered over Al_2O_3. The crude product is purified by distillation.

4. Metalation of DMH-hydrazones by KDA and alkylation (general procedure):

In a dried, argon-filled round-bottomed flask fitted with a septum cap, kalium-tert.-butylate is dissolved in anhydrous THF. The solution is cooled to -78°C and diisopropylamine (1.1 eq) and n-Butyllithium (1.1 eq, 1.6 M solution in n-hexane) are added dropwise. After 30 min further stirring **3a** or **3b** is added dropwise at -78°C and stirred for 1 h at -78°C (**3a**) or 4 h at 0°C (**3b**). To the solution of metalated hydrazone **2** is added at -70°C (**3a**) or -78°C (**3b**). After warm-up THF is removed under reduced pressure, ether/pentane (1:1) is added and filtered over Al_2O_3. The crude product is purified by distillation.

5. Acidic Cleavage and Spiroacetalization of DMH-hydrazones 4 (general procedure):

The bisalkylated DMH-hydrazone **4** is dissolved in THF (7 ml/mmol) and amberlite IR 120 A (1.5 g/mmol) and $MgSO_4$ (1 g/mmol) are added. After refluxing for 48 h the mixture is filtered and amberlite and $MgSO_4$ are washed several times with THF. The solvent is removed in vacuo, ether is added and the solution is washed with saturated sodium bicarbonate, pH-7-buffer and water. After drying ($MgSO_4$), the crude product is purified by distillation.

6. Acidic Cleavage and Spiroacetalization of SAMP-hydrazones 11, 12, 13 and 14 (general procedure):

To a solution of crude bisalkylated SAMP-hydrazone **11**, **12**, **13** or **14** in $CHCl_3$ (15 ml/mmol) p-toluenesulphonic acid (about 1.5 eq) is added in:

A: several small portions, stirred for 5 min each time and controlled by TLC or in

B: one portion and stirred for 5 min.

The reaction is quenched by adding saturated sodium bicarbonate. The aqueous phase is extracted with $CHCl_3$ three times, the organic phase is washed with saturated sodium bicarbonate, dried (Na_2SO_4), evaporated under reduced pressure and purified by column chromatography (silica gel, ether/pen-pentane = 1:10-1:30) to give colorless oils.

6-Trimethylsilyloxy-hexanone-2-dimethylhydrazone [**3a**]. 2 g (20 mmol) **1a** and 7.23 g (28 mmol) 1-iodo-3-trimethylsilyloxy-propane [**2**]. 4.4 g (95 %) of a light yellow liquid after distillation, b.p. 56°C/0.5 torr; IR (film): 2990-2780 (CH), 1640 (CN), 1470, 1462, 1455, 1432, 1390, 1360, 1252, 1160, 1100, 1028, 975, 875, 855, 755, 645 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz): δ = 0 (s, 9H, $Si(CH_3)_3$), 1.32-1.55 (m, 4H, $(CH_2)_2$), 1.78 (s, 3H, CH_3CN), 1.95-2.15 (m, 2H, CH_2CN), 2.21 (s, 6H, $N(CH_3)_2$), 3.37-3.57 (m, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 22.63 MHz): δ = -0.85, 15.90, 22.07 (E/Z), 22.90, 31.90, 38.20, 46.59, 47.07 (E/Z), 61.85, 167.04, 168.82 (E/Z) ppm; MS: m/z (r.I. %) = 231 (16, $M^+ + 1$), 230 (84, M^+), 215 (13, M^+-CH_3), 186 (38, $M^+ + 1$-$(CH_3)_3$), 185 (17, M^+-$(CH_3)_3$), 172 (40), 171 (87), 113 (22), 100 (42), 98 (46), 75 (29), 73 (100, $Si(CH_3)_3$), 60 (52), 58 (35), 45 (32), 44 (52). (High resolution MS, Found: 230.1814. Calc for $C_{11}H_{26}N_2OSi$: 230.1806).

4-Methyl-7-trimethylsilyloxy-heptanone-3-dimethylhydrazone [**3b**]. 3.2 g (25 mmol) **1b** and 7 g (27.5 mmol) 1-iodo-3-trimethylsilyloxy-propane [**2**]. 5.1 g (79 %) of a yellow liquid after distillation, b.p. 85°C/0.08 torr (Kugelrohr); IR (film): 2960-2780 (CH), 1635 (CN), 1475, 1465, 1455, 1395, 1380, 1265, 1255, 1200, 1165, 1105, 1030, 970, 875, 845, 755, 695 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz): δ = 0 (s, 9H, $Si(CH_3)_3$), 0.9 (d, 3H, CH_3), 0.99 (t, 3H, CH_3), 1.27-1.42 (m, 4H, $(CH_2)_2$), 1.93-2.21 (m, 3H, CH_2CN, CHCN), 2.21 (s, 6H, $N(CH_3)_2$), 3.34-3.58 (m, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 20 MHz): δ = -0.48, 11.97, 18.15, 23.87, 30.51, 30.87, 33.70, 39.82 (E/Z), 47.59, 47.73 (E/Z), 62.30, 62.69 (E/Z), 176.19 ppm; MS: m/z (r.I. %) = 259 (7, $M^+ + 1$), 258 (33, M^+), 214 (29, M^+-$N(CH_3)_2$), 200 (18), 199 (24), 128 (34), 126 (21), 124 (15), 109 (36), 98 (47), 84 (55), 75 (25), 73 (68, $Si(CH_3)_3$), 60 (70), 44 (100). (Found: C, 60.01; H, 11.73; N, 10.88. Calc for $C_{13}H_{30}N_2OSi$ (258.54): C, 60.39; H, 11.72; N, 10.84 %).

1,9-Bis(trimethylsilyloxy)-nonanone-5-dimethylhydrazone [**4a**]. 3.91 g (17 mmol) **3a** and 4.38 g (17 mmol) 1-iodo-3-trimethylsilyloxy-propane [**2**]. 4.3 g (70 %) of a yellow oil after distillation, b.p. 110°C/0.4 torr; IR (film): 2970-2790 (CH), 1640 (CN), 1470, 1460, 1445, 1380, 1270, 1250, 1145, 1100, 1025, 845, 770, 755, 695 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz): δ = 0 (s, 18H, $2Si(CH_3)_3$), 1.32-1.58 (m, 8H, $4CH_2$), 1.98-2.20 (m, 4H, $2CH_2CN$), 2.20 (s, 6H, $N(CH_3)_2$), 3.38-3.58 (m, 4H, $2CH_2OSi$) ppm.

4,6-Dimethyl-1,9-bis(trimethylsilyloxy)-nonanone-5-dimethylhydrazone [**4b**]. 2.58 g (10 mmol) **3b** and 2.84 g (11 mmol) 1-iodo-3-trimethylsilyloxy-propane [**2**]. 3.7 g (95 %) of a yellow oil after distillation, b.p. 110°C/0.05 torr (Kugelrohr); IR (film): 2960-2780 (CH), 1625 (CN), 1460, 1450, 1440, 1380, 1250, 1240, 1090, 1035, 1015, 975, 955, 935, 855, 835, 740, 680 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 90 MHz): δ = 0.07 (s, 18H, $2Si(CH_3)_3$), 0.95-1.13 (2d, 6H, $2CH_3$), 1.30-1.62 (m, 8H, $4CH_2$), 1.70-1.97 (m, 1H, CHCN), 2.28 (s, 6H, $N(CH_3)_2$), 3.39-3.77 (m, 5H, $2CH_2OSi$, CHCN) ppm; ^{13}C-NMR ($CDCl_3$, 20 MHz): δ = -0.46, -0.42, 17.54, 17.60, 20.30, 21.00, 29.97, 30.23, 30.89, 30.98, 31.01, 31.05, 31.96, 33.00, 33.99, 34.02, 34.33, 34.64, 47.68, 62.45, 62.85, 62.88, 179.64, 179.86 ppm; MS: m/z (r.I. %) = 389 (12, $M^+ + 1$), 388 (39, M^+), 373 (14, M^+-CH_3), 344 (71, M^+-$N(CH_3)_2$), 258 (15), 229 (25), 228 (19), 149 (41), 139 (32), 138 (13), 129 (49), 124 (16), 103 (22), 75 (27), 73 (100, $Si(CH_3)_3$), 72 (16), 69 (53), 60 (93), 59 (23), 46 (21), 45 (29), 44 (62), 41 (38). (Found: C, 58.77; H, 11.46; N, 7.14. Calc for $C_{19}H_{44}N_2O_2Si_2$ (388.72): C, 58.70; H, 11.41; N, 7.20 %).

rac-1,7-Dioxaspiro[5.5]undecane [**rac-5a**]. 1.80 g (5 mmol) **4a**, 7.5 g amberlite IR 120 A and 5 g $MgSO_4$. 1.48 g (95 %) of a colorless liquid after distillation, b.p. 69°C/12 torr; IR (film): 2970-2860 (CH), 1460, 1455, 1430, 1385, 1370, 1355, 1340, 1290, 1280, 1260, 1230, 1210, 1180, 1105, 1100, 1070, 1045, 990, 935, 915, 880, 800 cm^{-1}: ^{1}H-NMR (CCl_4, 90 MHz): δ = 1.12-2.09 (m, 12H, H_{aliph}), 3.28-3.79 (m, 4H, $2CH_2O$) ppm; ^{13}C-NMR ($CDCl_3$, 22.63 MHz): δ = 18.73, 25.58, 35.94, 60.26 (CH_2O), 94.90 (OCO) ppm; MS: m/z (r.I. %) = 156 (18, M^+), 111 (12), 101 (100), 100 (61), 98 (70), 83 (31), 55 (27). (Found: C, 68.94; H, 10.39. Calc for $C_9H_{16}O_2$ (156.22): C, 69.19; H, 10.32 %).

rac-5,11-Dimethyl-1,7-dioxaspiro[5.5]undecane [rac-**5b**]. 3 g (7.7 mmol) **4b**, 11.5 g amberlite IR 120 A and 7.7 g $MgSO_4$. 1.2 g (85 %) of a colorless liquid after distillation, b.p. 120°C/15 torr. Spectroscopical data were in accordance with those of (*S,R,S*)-**16a**.

(+)-(2*S*,2'*S*)-1-(1-Ethyl-2-methyl-4-trimethylsilyloxy-butylideneamino)-2-methoxymethyl-pyrrolidine [(*S,S*)-**8a**]. 5.1 g (25.7 mmol) (*S*)-**6a** and 6.91 g (28.3 mmol) 1-iodo-2-trimethylsilyloxy-ethane [7]. 6.05 g (75 %) of a pale yellow oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{23}$ = +153.6° (c = 0.93, $CHCl_3$); IR (film): 2995-2820 (CH), 1630 (CN), 1460, 1450, 1380, 1350, 1300, 1250, 1200, 1185, 1130, 1100, 1030, 1020, 1000, 970, 910, 880, 840, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.10 (s, 9H, $Si(CH_3)_3$), 1.02-1.14 (d, t, 6H, $2CH_3$), 1.50-1.67 (m, 2H, H_{aliph}), 1.53-2.08 (m, 4H, 2βNCH$_2$), 2.16 (q, 2H, CH_2CN), 2.39 (m, 1H, NCHH), 2.91-3.45 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.32 (s, 3H, OCH_3), 3.48-3.60 (m, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.23, 12.06, 17.83, 21.68, 23.54, 26.66, 31.25 (Z-CHCN), 37.26, 55.02, 58.85, 60.80, 65.74, 75.76, 175.07 ppm; MS: m/z (r.I. %) = 315 (2, M^+ + 1), 314 (7, M^+), 299 (3, M^+-CH_3), 271 (6), 270 (21), 269 (100, M^+-CH_2OCH_3), 200 (3), 199 (5), 198 (38), 197 (3), 154 (3), 153 (29), 145 (8), 142 (3), 129 (7), 128 (44), 127 (10), 119 (4), 115 (5), 114 (27), 112 (5), 110 (21), 104 (8), 103 (89), 91 (6), 89 (8), 85 (4), 84 (13), 83 (4), 82 (11), 75 (15), 74 (8), 73 (85, $Si(CH_3)_3$), 71 (5), 70 (35), 69 (4), 68 (5), 59 (7), 56 (20), 55 (32), 45 (15), 42 (5), 41 (15). (Found: C, 60.97; H, 10.64; N, 9.17. Calc for $C_{16}H_{34}N_2O_2Si$ (314.55): C, 61.10; H, 10.90; N, 8.91 %).

(+)-(2*S*,2'*S*)-1-(2-Ethyl-4-trimethylsilyloxy-1-propyl-butylideneamino)-2-methoxymethyl-pyrrolidine [(*S,S*)-**8b**]. 5.3 g (23.4 mmol) (*S*)-**6b** and 6.3 g (25.7 mmol) 1-iodo-2-trimethylsilyloxy-ethane [7]. 6.1 g (76 %) of a colorless oil after after flash-chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{23}$ = +140.65° (c = 1.70, $CHCl_3$); IR (film): 2995-2820 (CH), 1630 (CN), 1460, 1385, 1355, 1250, 1225, 1200, 1190, 1110, 1050, 970, 920, 880, 845, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (s, 9H, $Si(CH_3)_3$), 0.85-0.98 (2t, 6H, $2CH_3$), 1.30-2.07 (m, 10H, $6H_{aliph}$, 2βNCH$_2$), 2.07 (t, 2H, CH_2CN), 2.38 (m, 1H, NCHH), 2.92-3.45 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.32 (s, 3H, OCH_3), 3.48-3.59 (m, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.30, 12.29, 14.00, 20.32, 21.62, 25.11, 26.78, 32.73, 35.28, 38.43 (Z-CHCN), 46.01 (E-CHCN), 54.96, 58.76, 60.95, 65.83, 75.93, 173.32 ppm; MS: m/z (r.I. %) = 343 (4, M^+ + 1), 342 (14, M^+), 297 (8, M^+-CH_2OCH_3), 259 (3), 258 (14), 229 (3), 228 (16), 227 (4), 226 (24), 186 (6), 181 (4), 170 (11), 159 (6), 138 (7), 115 (4), 114 (38), 113 (4), 112 (14), 103 (22), 96 (3), 91 (4), 89 (5), 84 (4), 82 (5), 75 (14), 74 (6), 73 (58, $Si(CH_3)_3$), 70 (30), 69 (100), 59 (4), 55 (7), 45 (14), 42 (4), 41 (21). (Found: C, 63.22; H, 11.32; N, 8.05. Calc for $C_{18}H_{38}N_2O_2Si$ (342.60): C, 63.11; H, 11.18; N, 8.18).

(+)-(2*S*,2'*S*)-1-(1-Butyl-4-trimethylsilyloxy-2-propyl-butylideneamino)-2-methoxymethyl-pyrrolidine [(*S,S*)-**8c**]. 9 g (40 mmol) (*S*)-**6c** and 10.7 g (44 mmol) 1-iodo-2-trimethylsilyloxy-ethane [7]. 6.1 g (41 %) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{23}$ = +140.3° (c = 1.08,

$CHCl_3$); IR (film): 2990-2820 (CH), 1630 (CN), 1460, 1380, 1250, 1200, 1185, 1130, 1100, 1045, 975, 955, 920, 880, 845, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (s, 9H, $Si(CH_3)_3$), 0.87-0.95 (2t, 6H, $2CH_3$), 1.16-2.05 (m, 14H, $10H_{aliph}$, $2\beta NCH_2$), 2.10 (t, 2H, CH_2CN), 2.38 (m, 1H, NCHH), 2.92-3.44 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.33 (s, 3H, OCH_3), 3.48-3.56 (m, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.16, 13.89, 14.25, 21.10, 21.72, 22.89, 26.95, 29.64, 30.75, 34.70, 35.55, 36.90 (Z-CHCN), 43.00 (E-CHCN), 55.07, 58.94, 61.12, 65.86, 76.09, 174.12 ppm; MS: m/z (r.I. %) = 371 (3, $M^+ + 1$), 370 (9, M^+), 355 (5, $M^+ - CH_3$), 327 (7), 326 (26), 325 (100, $M^+ - CH_2OCH_3$), 256 (3), 255 (7), 254 (43), 225 (3), 212 (3), 209 (12), 200 (11), 173 (3), 168 (5), 166 (4), 157 (4), 156 (16), 155 (4), 141 (3), 140 (24), 129 (3), 114 (21), 103 (17), 101 (4), 91 (3), 89 (4), 84 (11), 83 (38), 82 (4), 75 (13), 74 (3), 73 (35, $Si(CH_3)_3$), 71 (3), 70 (17), 69 (3), 68 (3), 59 (5), 57 (6), 56 (3), 55 (27), 45 (15), 43 (4), 42 (5), 41 (25). (Found: C, 65.02; H, 11.49; N, 7.44. Calc for $C_{20}H_{42}N_2O_2Si$ (370.66): C, 64.81; H, 11.42; N 7.56).

(+)-(2*S*,2'*S*)-2-Methoxymethyl-1-(2-(2-trimethylsilyloxyethyl)-cyclohexylideneamino)-pyrrolidine [(*S*,*S*)-**8d**]. 8.6 g (40.9 mmol) (*S*)-**6d** and 11 g (45 mmol) 1-iodo-2-trimethylsilyloxy-ethane [7]. 4.5 g (34 %) of a pale yellow oil after flash-chromatography (SiO_2, ether:pentane = 2:1); $[\alpha]_D^{23}$ = +116.5° (c = 1.43, $CHCl_3$); IR (film): 2985-2800 (CH), 1630 (CN), 1460, 1450, 1390, 1350, 1300, 1250, 1200, 1190, 1100, 1050, 1010, 970, 940, 920, 880, 845, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (s, 9H, $Si(CH_3)_3$), 1.30-2.50 (m, 14H, $8H_{aliph}$, $2\beta NCH_2$, CH_2CN), 2.39 (m, 1H, NCHH), 2.96-3.47 (m, 5H, NCHH, NCH, CHCN, CH_2O), 3.33 (s, 3H, OCH_3), 3.54-3.66 (m, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.14, 20.67, 21.92, 27.20, 28.05, 31.33, 31.71, 33.37 (Z-CHCN), 34.17, 40.75 (E-CHCN), 55.31, 58.97, 60.85, 65.69, 76.29, 173.50 ppm; MS: m/z (r.I. %) = 327 (3, $M^+ + 1$), 326 (11, M^+), 311 (2, $M^+ - CH_3$), 283 (6), 282 (22), 281 (100, $M^+ - CH_2OCH_3$), 213 (3), 212 (18), 211 (9), 210 (58), 198 (4), 196 (3), 182 (12), 166 (4), 165 (31), 142 (3), 133 (5), 124 (4), 122 (20), 120 (10), 114 (14), 103 (13), 96 (4), 95 (4), 84 (3), 82 (3), 81 (6), 80 (3), 79 (3), 75 (12), 74 (4), 73 (38, $Si(CH_3)_3$), 71 (3), 70 (27), 68 (4), 67 (5), 59 (6), 55 (10), 53 (3), 45 (14), 42 (6), 41 (19). (Found: C, 62.70; H, 10.61; N, 8.43. Calc for $C_{17}H_{34}N_2O_2Si$ (326.56): C, 62.53; H, 10.49; N, 8.58).

(+)-(2*S*,2'*R*)-1-(1-Benzyl-4-trimethylsilyloxy-2-phenyl-butylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*R*)-**8e**]. 6.45 g (20 mmol) (*S*)-**6e** and 5.47 g (22 mmol) 1-iodo-2-trimethylsilyloxyethane [7]. 0.97 g (11 %) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{23}$ = +2.5° (c = 0.94, $CHCl_3$); IR (film): 3090-3010 (CH_{arom}), 2990-2810 (CH), 1730, 1630 (CN), 1600, 1585, 1500, 1460, 1385, 1350, 1250, 1200, 1100, 1060, 1035, 955, 910, 840, 765, 705 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.05 (s, 9H, $Si(CH_3)_3$), 1.65-1.94 (m, 4H, $2\beta NCH_2$), 2.09 (m, 1H, CHHCH), 2.31 (m, 1H, CHHCH), 2.51 (m, 1H, NCHH), 2.84 (d, 1H, J = 14.4Hz, CHHCN), 3.00-3.55 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.41 (s, 3H, OCH_3), 3.53-3.57 (m, 2H, CH_2OSi), 4.32 (d, 1H, J = 14.4Hz, CHHCN), 7.00-7.30 (m, 10H, H_{arom}) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.01, 22.03, 26.71, 36.54, 36.86, 46.26 (E-CHCN), 54.49, 59.12, 60.57, 66.32, 75.84, 126.14, 126.47, 128.33, 128.36, 128.38, 129.33, 137.62, 142.34, 167.42 ppm; MS: m/z (r.I. %) = 439 (1, $M^+ + 1$), 438 (3, M^+), 423 (1, $M^+ - CH_3$), 394 (6), 393 (18, $M^+ - CH_2OCH_3$), 366 (3), 323 (5), 322

(22), 321 (25), 278 (7), 277 (34), 190 (3), 117 (5), 115 (3), 114 (7), 105 (13), 103 (21), 92 (8), 91 (100, $C_7H_7^+$), 89 (3), 73 (8, $Si(CH_3)_3$), 70 (12), 65 (5), 45 (11), 41 (5). (Found: C, 71.35; H, 8.55; N, 6.44. Calc for $C_{26}H_{38}N_2O_2Si$ (438.69): C, 71.19; H, 8.73; N, 6.39 %).

(+)-(2*S*,2'*S*)-1-(1-Ethyl-2-methyl-5-trimethylsilyloxy-pentylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*S*)-**9a**]. 8.46 g (42.7 mmol) (*S*)-**6a** and 12.12 g (46 mmol) 1-iodo-3-trimethylsilyloxy-propane [2]. 12.3 g (88 %) of a pale yellow oil after distillation, b.p. 120°C/0.02 torr (Kugelrohr); $[\alpha]_D^{23}$ = +158.6° (neat); IR (film): 2985-2820 (CH), 1630 (CN), 1460, 1450, 1380, 1360, 1290, 1250, 1200, 1190, 1110, 1070, 1040, 1000, 970, 920, 900, 840, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (s, 9H, $Si(CH_3)_3$), 1.01-1.15 (d, t, 6H, $2CH_3$), 1.39 (m, 4H, H_{aliph}), 1.60-2.08 (m, 4H, 2ßNCH$_2$), 2.14 (q, 2H, CH_2CN), 2.38 (m, 1H, NCHH), 2.94-3.42 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.32 (s, 3H, OCH_3), 3.56 (t, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.13, 12.19, 18.12, 21.77, 23.42, 26.60, 30.44, 30.49, 34.13 (Z-CHCN), 39.73 (E-CHCN), 55.05, 58.89, 62.33, 65.94, 75.66, 175.28 ppm; MS: m/z (r.I. %) = 329 (2, M^+ + 1), 328 (8, M^+), 313 (3, M^+-CH_3), 285 (5), 284 (21), 283 (96, M^+-CH_2OCH_3), 134 (9), 129 (13), 128 (7), 103 (28), 98 (5), 75 (8), 73 (34, $Si(CH_3)_3$), 70 (21), 69 (100), 56 (6), 45 (8), 41 (20). (Found: C, 61.86; H, 11.34; N, 8.64. Calc for $C_{17}H_{36}N_2O_2Si$ (328.57): C, 62.14; H, 11.04; N, 8.53 %).

(+)-(2*S*,2'*S*)-1-(2-Ethyl-5-trimethylsilyloxy-1-propyl-pentylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*S*)-**9b**]. 9.5 g (42 mmol) (*S*)-**6b** and 11.93 g (46 mmol) 1-iodo-3-trimethylsilyloxy-propane [2]. 13.1 g (87.5 %) of a pale yellow oil after distillation, b.p. 115°C/0.02 torr (Kugelrohr); $[\alpha]_D^{21}$ = +136.4° (neat); IR (film): 2990-2820 (CH), 1630 (CN), 1460, 1385, 1360, 1250, 1200, 1190, 1110, 1050, 980, 925, 870, 845, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (s, 9H, $Si(CH_3)_3$), 0.85-0.97 (2t, 6H, $2CH_3$), 1.23-2.08 (m, 12H, 2ßNCH$_2$, 8H_{aliph}), 2.05 (t, 2H, CH_2CN), 2.39 (m, 1H, NCHH), 2.94-3.42 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.32 (s, 3H, OCH_3), 3.56 (t, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.03, 12.66, 14.32, 20.80, 21.84, 25.54, 26.79, 28.37, 30.46, 32.87, 41.50 (Z-CHCN), 47.32 (E-CHCN), 55.15, 59.00, 62.57, 66.16, 75.85, 174.11 ppm; MS: m/z (r.I. %) = 357 (2, M^+ + 1), 356 (7, M^+), 341 (3, M^+-CH_3), 313 (5), 312 (23), 311 (100, M^+-CH_2OCH_3), 173 (3), 148 (11), 142 (8), 129 (7), 114 (5), 103 (21), 91 (7), 89 (3), 84 (6), 83 (73), 75 (8), 73 (25, $Si(CH_3)_3$), 70 (18), 69 (100), 56 (3), 55 (40), 45 (7), 43 (7), 41 (12). (Found: C, 64.10; H, 11.24; N, 7.90. Calc for $C_{19}H_{40}N_2O_2Si$ (356.63): C, 63.99; H, 11.31; N 7.86).

(+)-(2*S*,2'*S*)-1-(1-Butyl-5-trimethylsilyloxy-2-propyl-pentylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*S*)-**9c**]. 5.1 g (20 mmol) (*S*)-**6c** and 5.7 g (22 mmol) 1-iodo-3-trimethylsilyloxy-propane [2]. 5.0 g (64.5 %) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:3); $[\alpha]_D^{26}$ = +125.9° (neat), $[\alpha]_D^{26}$ = +153.0° (c = 1.48, C_6H_6); IR (film): 2990-2820 (CH), 1630 (CN), 1460, 1380, 1250, 1200, 1185, 1100, 1045, 970, 870, 845, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (s, 9H, $Si(CH_3)_3$), 0.88-0.94 (2t, 6H, $2CH_3$), 1.16-2.08 (m, 16H, 2ßNCH$_2$, 12H_{aliph}), 2.07 (t, 2H, CH_2CN), 2.38 (m, 1H, NCHH), 2.92-3.41 (m,

5H, NCHH, NCH, CH_2O, CHCN), 3.35 (s, 3H, OCH_3), 3.56 (t, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.25, 13.82, 14.26, 21.13, 21.62, 22.82, 26.55, 28.42, 29.50, 30.29, 30.50, 34.91, 39.58 (Z-CHCN), 54.92, 58.70, 62.29, 65.93, 75.59, 174.06 ppm; MS: m/z (r.I. %) = 385 (3, $M^+ + 1$), 384 (10, M^+), 369 (4, $M^+ - CH_3$), 341 (7), 339 (100, $M^+ - CH_2OCH_3$), 162 (8), 156 (6), 129 (5), 114 (5), 103 (13), 98 (4), 97 (38), 91 (4), 89 (3), 84 (5), 82 (3), 75 (9), 73 (19, $Si(CH_3)_3$), 70 (12), 69 (6), 59 (3), 57 (3), 55 (37), 45 (7), 43 (4), 42 (3), 41 (11). (Found: C, 65.65; H, 11.55; N, 7.45. Calc for $C_{21}H_{44}N_2O_2Si$ (384.68): C, 65.57; H, 11.53; N 7.28).

(+)-(2*S*,2'*S*)-2-Methoxymethyl-1-(2-(3-trimethylsilyloxy-propyl)-cyclohexylideneamino)-pyrrolidine [(*S*,*S*)-**9d**]. 4.3 g (20.4 mmol) (*S*)-**6d** and 5.8 g (22.4 mmol) 1-iodo-3-trimethylsilyloxy-propane [2]. 6.3 g (91 %) of a pale yellow oil after distillation, b.p. 115°C/0.05 torr (Kugelrohr); $[\alpha]_D^{26}$ = +155.8° (c = 1.41, C_6H_6); IR (film): 2985-2800 (CH), 1630 (CN), 1460, 1450, 1390, 1360, 1290, 1250, 1200, 1190, 1100, 1050, 970, 860, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (s, 9H, $Si(CH_3)_3$), 1.30-2.10 (m, 14H, 2βNCH$_2$, 10H$_{aliph}$), 2.12-2.40 (m, 2H, CH_2CN), 2.42 (m, 1H, NCHH), 2.95-3.45 (m, 5H, NCHH, NCH, CHCN, CH_2O), 3.35 (s, 3H, OCH_3), 3.60 (t, 2H, CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.23, 20.49, 21.79, 26.77, 26.93, 28.08, 29.88, 31.23, 31.59, 36.06 (Z-CHCN), 43.64 (E-CHCN), 55.13, 58.74, 62.24, 65.72, 75.76, 171.19 (E-CN), 173.61 (Z-CN) ppm; MS: m/z (r.I. %) = 341 (2, $M^+ + 1$), 340 (8, M^+), 325 (3, $M^+ - CH_3$), 297 (6), 296 (23), 295 (100, $M^+ - CH_2OCH_3$), 227 (4), 226 (18), 210 (5), 196 (11), 165 (3), 142 (4), 140 (11), 136 (37), 135 (8), 134 (53), 132 (5), 129 (5), 119 (9), 114 (12), 110 (7), 108 (6), 103 (20), 95 (17), 94 (8), 93 (11), 91 (14), 85 (13), 82 (10), 79 (7), 75 (20), 74 (7), 73 (67, $Si(CH_3)_3$), 70 (70), 67 (15), 59 (8), 55 (20), 45 (14), 42 (8), 41 (23). (Found: C, 63.70; H, 10.61; N, 8.13. Calc for $C_{18}H_{36}N_2O_2Si$ (340.59): C, 63.48; H, 10.65; N, 8.22).

(+)-(2*S*,2'*R*)-1-(1-Benzyl-5-trimethylsilyloxy-2-phenyl-pentylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*R*)-**9e**]. 7.26 g (22.5 mmol) (*S*)-**6e** and 6.52 g (25.3 mmol) 1-iodo-3-trimethylsilyloxypropane [2]. 4.4 g (43 %) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{28}$ = +16° (c = 0.62, C_6H_6); IR (film): 3090-3010 (CH_{arom}), 2990-2810 (CH), 1720, 1630 (CN), 1600, 1585, 1500, 1465, 1385, 1350, 1290, 1250, 1200, 1190, 1100, 1035, 1010, 975, 915, 850, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.05 (s, 9H, $Si(CH_3)_3$), 1.10-2.20 (m, 8H, 2βNCH$_2$, 4H$_{aliph}$), 2.50 (m, 1H, NCHH), 2.81 (d, 1H, J = 14.4Hz, CHHCN), 3.00-3.55 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.40 (s, 3H, OCH_3), 3.53-3.58 (m, 2H, CH_2OSi), 4.32 (d, 1H, J = 14.4Hz, CHHCN), 7.00-7.30 (m, 10H, H$_{arom}$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.52, 21.98, 26.66, 29.83, 30.64, 36.77, 49.82 (E-CHCN), 54.47, 59.10, 62.57, 66.30, 75.82, 126.17, 126.43, 128.27, 128.36, 128.39, 129.31, 137.68, 142.75, 167.38 ppm; MS: m/z (r.I. %) = 453 (4, $M^+ + 1$), 452 (11, M^+), 437 (2, $M^+ - CH_3$), 409 (6), 408 (22), 407 (67, $M^+ - CH_2OCH_3$), 361 (3), 196 (7), 132 (11), 131 (100), 129 (7), 116 (5), 115 (4), 114 (5), 103 (7), 92 (4), 91 (54, $C_7H_7^+$), 89 (5), 75 (7), 74 (4), 73 (18, $Si(CH_3)_3$), 70 (15), 59 (5), 55 (4), 45 (15), 41 (7), 28 (4). (Found: C, 71.45; H, 8.79; N, 6.39. Calc for $C_{27}H_{40}N_2O_2Si$ (452.71): C, 71.64; H, 8.91; N, 6.19 %).

(+)-(2*S*,3'*S*,5'*S*)-2-Methoxymethyl-1-(3,5-dimethyl-1,7-bis(trimethylsilyloxy)-4-heptylideneamino)-pyrrolidine [(*S*,*S*,*S*)-**11a**]. 3.15 g crude (*S*,*S*)-**8a** and 2.68 g (11 mmol) 1-iodo-2-trimethylsilyloxyethane [7]. 1.21 g (30.0 % based on (*S*)-**6a**) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{24}$ = +165.1° (c = 1.05, $CHCl_3$); IR (film): 2995-2810 (CH), 1630 (CN), 1460, 1380, 1350, 1250, 1200, 1100, 1030, 990, 970, 910, 880, 840, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.11 (2s, 18H, $2Si(CH_3)_3$), 1.04-1.10 (2d, 6H, $2CH_3$), 1.46-2.08 (m, 8H, $2\beta NCH_2$, $4H_{aliph}$), 2.36 (m, 1H, NCHH), 2.55 (m, 1H, CHCN), 2.90-3.54 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.33 (s, 3H, OCH_3), 3.56 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.04, 17.54, 21.80, 21.86, 27.01, 30.71, 31.66, 36.92, 38.28, 55.11, 59.09, 60.74, 60.97, 65.89, 76.23, 177.87 ppm; MS: m/z (r.I. %) = 431 (5, M^+ + 1), 430 (13, M^+), 416 (4), 415 (12, M^+-CH_3), 385 (11, M^+-CH_2OCH_3), 384 (31), 383 (100), 316 (5), 315 (13), 314 (55), 297 (6), 270 (6), 269 (27), 246 (4), 245 (10), 244 (42), 200 (8), 199 (8), 198 (57), 172 (10), 157 (5), 156 (31), 153 (8), 147 (5), 145 (13), 129 (6), 128 (4), 115 (5), 114 (38), 110 (7), 104 (6), 103 (58), 91 (7), 89 (8), 84 (9), 82 (10), 75 (22), 73 (100, $Si(CH_3)_3$), 71 (5), 70 (30), 69 (3), 68 (5), 67 (3), 59 (9), 56 (6), 55 (34), 47 (4), 45 (25), 43 (4), 42 (6), 41 (17). (Found: C, 58.52; H, 10.70; N, 6.59. Calc for $C_{21}H_{46}N_2O_3Si_2$ (430.78): C, 58.55; H, 10.76; N, 6.50 %).

(+)-(2*S*,3'*S*,5'*S*)-1-(3,5-Diethyl-1,7-bis(trimethylsilyloxy)-4-heptylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*S*,*S*)-**11b**]. 3.8g crude (*S*,*S*)-**8b** and 3g (12.2 mmol) 1-iodo-2-trimethylsilyloxy-ethane [7]. 0.85 g (17.5 % based on (*S*)-**6b**) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{23}$ = +131.4° (c = 0.86, $CHCl_3$); IR (film): 2995-2810 (CH), 1625 (CN), 1460, 1380, 1350, 1250, 1200, 1100, 1050, 940, 920, 880, 845, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (2s, 18H, $2Si(CH_3)_3$), 0.90 (2t, 6H, $2CH_3$), 1.38-2.10 (m, 12H, $2\beta NCH_2$, $8H_{aliph}$), 2.31 (m, 1H, CHCN), 2.38 (m, 1H, NCHH), 2.88-3.40 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.33 (s, 3H, OCH_3), 3.58 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.06, 11.59, 12.98, 21.88, 24.62, 27.11, 27.32, 34.65, 36.14, 38.22, 39.31, 55.35, 59.05, 60.91, 61.41, 66.01, 76.34, 175.87 ppm; MS: m/z (r.I. %) = 459 (2, M^+ + 1), 458 (5, M^+), 443 (6, M^+-CH_3), 415 (6), 414 (17), 413 (50, M^+-CH_2OCH_3), 344 (3), 343 (6), 342 (23), 298 (4), 297 (16), 259 (6), 258 (26), 229 (5), 228 (25), 227 (6), 226 (36), 186 (9), 181 (5), 170 (12), 159 (8), 147 (3), 138 (7), 115 (4), 114 (39), 113 (4), 112 (14), 104 (3), 103 (26), 101 (3), 96 (3), 91 (4), 89 (5), 84 (3), 82 (4), 75 (12), 74 (5), 73 (55, $Si(CH_3)_3$), 70 (29), 69 (100), 59 (4), 55 (6), 45 (12). (Found: C, 60.25; H, 10.82; N, 6.38. Calc for $C_{23}H_{50}N_2O_3Si_2$ (458.84): C, 60.21; H, 10.98; N, 6.11 %).

(+)-(2*S*,4'*S*,6'*S*)-2-Methoxymethyl-1-(4,6-dimethyl-1,9-bis(trimethylsilyloxy)-5-nonylideneamino)-pyrrolidine[(*S*,*S*,*S*)-**12a**]. 3g (9.1 mmol) (*S*,*S*)-**9a** and 2.58 g (10 mmol) 1-iodo-3-trimethylsilyloxypropane [2]. 2.03 g (48.5 %) of a pale yellow oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{24}$ = +135.3° (neat), $[\alpha]_D^{24}$ = +167.2° (c = 1.14, C_6H_6); IR (film): 2995-2810 (CH), 1630 (CN), 1460, 1390, 1350, 1250, 1200, 1185, 1100, 1045, 990, 965, 945, 860, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.11 (2s, 18H, $2Si(CH_3)_3$), 1.01-1.10 (2d, 6H, $2CH_3$), 1.30-2.08 (m, 12H, $2\beta NCH_2$, $8H_{aliph}$), 2.31 (m, 1H, CHCN), 2.35 (m, 1H, NCHH), 2.90-3.50 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.32 (s, 3H, OCH_3), 3.56 (m, 4H,

$2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.45, 17.63, 21.67, 21.80, 26.68, 30.02, 30.55, 30.96, 31.50, 33.81, 34.22, 54.87, 58.89, 62.36, 62.79, 65.86, 75.85, 178.17 ppm; MS: m/z (r.I. %) = 459 (2, $M^+ + 1$), 458 (7, M^+), 443 (3, M^+-CH_3), 415 (12), 414 (33), 413 (95, M^+-CH_2OCH_3), 344 (5), 258 (15), 186 (4), 171 (4), 170 (16), 160 (6), 159 (32), 132 (7), 131 (5), 129 (8), 114 (6), 103 (30), 96 (6), 91 (6), 75 (12), 73 (33, $Si(CH_3)_3$), 70 (22), 69 (100), 67 (5), 55 (6), 45 (7), 44 (10), 43 (6), 41 (16). (Found: C, 60.35; H, 11.09; N, 6.09. Calc for $C_{23}H_{50}N_2O_3Si_2$ (458.84): C, 60.21; H, 10.98; N, 6.11 %).

(+)-(2*S*,4'*S*,6'*S*)-1-(4,6-Diethyl-1,9-bis(trimethylsilyloxy)-5-nonylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*S*,*S*)-**12b**]. 4 g (11.2 mmol) (*S*,*S*)-**9b** and 3.2 g (12.4 mmol) 1-iodo-3-trimethylsilyloxy-propane [2]. 2.13 g (39 %) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{23}$ = +126.9° (c = 1.20, C_6H_6); IR (film): 2995-2810 (CH), 1620 (CN), 1460, 1390, 1355, 1250, 1200, 1190, 1100, 1055, 970, 930, 860, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (2s, 18H, $2Si(CH_3)_3$), 0.90 (2t, 6H, $2CH_3$), 1.20-2.20 (m, 17H, 2ßNCH$_2$, 12H$_{aliph}$, CHCN), 2.36 (m, 1H, NCHH), 2.90-3.40 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.32 (s, 3H, OCH_3), 3.58 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.46, 11.78, 13.08, 21.84, 24.75, 26.91, 27.28, 27.47, 29.49, 30.86, 30.90, 41.20, 41.98, 55.24, 59.00, 62.51, 63.01, 66.07, 76.11, 176.35 ppm; MS: m/z (r.I. %) = 487 (4, $M^+ + 1$), 486 (9, M^+), 471 (5, M^+-CH_3), 443 (11), 442 (30), 441 (83, M^+-CH_2OCH_3), 372 (5), 369 (4), 272 (13), 200 (6), 185 (2), 184 (12), 174 (3), 173 (21), 129 (5), 114 (7), 110 (3), 103 (20), 91 (7), 89 (4), 84 (9), 83 (100), 75 (11), 73 (34, $Si(CH_3)_3$), 70 (18), 55 (43), 45 (10), 41 (12). (Found: C, 61.57; H, 11.30; N, 5.88. Calc for $C_{25}H_{54}N_2O_3Si_2$ (486.89): C, 61.67; H, 11.18; N, 5.75 %).

(+)-(2*S*,4'*S*,6'*S*)-2-Methoxymethyl-1-(1,9-bis(trimethylsilyloxy)-4,6-dipropyl-5-nonylideneamino)-pyrrolidine [(*S*,*S*,*S*)-**12c**]. 3.8 g (10 mmol) (*S*,*S*)-**9c** and 2.8 g (11 mmol) 1-iodo-3-trimethylsilyloxy-propane [2] 2.96 g (57.5 %) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{22}$ = +102.1° (neat), $[\alpha]_D^{22}$ = +131.8° (c = 1.12, C_6H_6); IR (film): 2995-2810 (CH), 1620 (CN), 1460, 1385, 1350, 1250, 1200, 1100, 1045, 970, 880, 845, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.10 (2s, 18H, $2Si(CH_3)_3$), 0.84-0.94 (2t, 6H, $2CH_3$), 1.17-2.28 (m, 21H, 2ßNCH$_2$, 16H$_{aliph}$, CHCN), 2.36 (m, 1H, NCHH), 2.93-3.39 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.38 (s, 3H, OCH_3), 3.54 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.23, 14.11, 14.24, 20.32, 21.38, 21.60, 26.65, 27.72, 29.69, 30.66, 30.70, 33.96, 37.06, 39.41, 39.74, 54.95, 58.68, 62.23, 62.73, 65.82, 75.83, 176.57 ppm; MS: m/z (r.I. %) = 516 (8, $M^+ + 1$), 515 (19, M^+), 501 (3), 500 (8, M^+-CH_3), 473 (5), 472 (15), 470 (100, M^+-CH_2OCH_3), 401 (7), 288 (4), 287 (13), 214 (5), 198 (12), 187 (11), 130 (3), 129 (6), 124 (3), 114 (9), 103 (14), 98 (6), 97 (68), 91 (5), 89 (4), 84 (3), 83 (3), 82 (4), 75 (11), 73 (33, $Si(CH_3)_3$), 70 (17), 69 (8), 55 (48), 45 (10), 43 (5), 41 (9). (Found: C, 63.09; H, 11.42; N, 5.46. Calc for $C_{27}H_{58}N_2O_3Si_2$ (514.95): C, 62.98; H, 11.35; N, 5.44 %).

(+)-(2*S*,2'*S*,6'*S*)-2-Methoxymethyl-1-(2,6-bis(3-trimethylsilyloxy-propyl)-cyclohexylideneamino)-pyrrolidine[(*S*,*S*,*S*)-**12d**]. 2.9g (8.5 mmol) (*S*,*S*)-**9d** and 2.4g (9.4 mmol) 1-iodo-3-trimethylsilyloxypropane [2]. 1.28 g (32 %) of a pale yellow oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{26}$ = +120.9° (c = 1.05, C_6H_6); IR (film): 3000-2800 (CH), 1630 (CN), 1480, 1460, 1450, 1390, 1360, 1290, 1250, 1200, 1190, 1100, 1050, 970, 915, 860, 740 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (s, 18H, 2Si(CH_3)$_3$), 0.95-2.30 (m, 19H, 2βNCH_2, 14H_{aliph}, CHCN), 2.32 (m, 1H, NC<u>H</u>H), 2.90-3.48 (m, 5H, NCH<u>H</u>, NCH, CHCN, CH_2O), 3.32 (s, 3H, OCH_3), 3.59 (m, 4H, 2CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.48, 21.03, 21.83, 26.78, 27.10, 27.40, 30.00, 30.85, 31.96, 35.82, 36.08, 39.67, 54.80, 58.94, 62.44, 63.16, 66.12, 76.05, 173.44 ppm; MS: m/z (r.I. %) = 471 (8, M^+ + 1), 470 (21, M^+), 455 (7, M^+-CH_3), 427 (13), 426 (32), 425 (100, M^+-CH_2OCH_3), 357 (10), 356 (29), 340 (4), 326 (6), 268 (5), 267 (10), 266 (44), 250 (4), 176 (18), 130 (9), 129 (13), 114 (11), 103 (13), 95 (6), 93 (7), 91 (7), 89 (8), 85 (6), 81 (9), 79 (7), 75 (27), 74 (8), 73 (77, Si(CH_3)$_3$), 70 (32), 67 (11), 59 (8), 55 (14), 45 (13), 41 (15). (Found: C, 61.36; H, 10.58; N, 6.12. Calc for $C_{24}H_{50}N_2O_3Si_2$ (470.85): C, 61.22; H, 10.70; N, 5.95 %).

(+)-(2*S*,4'*R*,6'*R*)-2-Methoxymethyl-1-(1,9-bis(trimethylsilyloxy)-4,6-diphenyl-5-nonylideneamino)-pyrrolidine [(*S*,*R*,*R*)-**12e**]. 6g crude (*S*,*R*)-**9e** and 2.3g (8.8 mmol) 1-iodo-3-trimethylsilyloxypropane [2]. 1.2 g (37.5 % based on (*S*)-**6e**) of a pale yellow oil after flash-chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{26}$ = +179.6° (c = 1.02, C_6H_6); IR (film): 3090-3010 (CH_{arom}), 3000-2820 (CH), 1630 (CN), 1600, 1590, 1500, 1480, 1460, 1395, 1360, 1290, 1250, 1210, 1190, 1100, 1040, 980, 920, 850, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (s, 18H, 2Si(CH_3)$_3$), 1.25-2.20 (m, 12H, 2βNCH_2, 8H_{aliph}), 2.62 (m, 1H, NC<u>H</u>H), 3.12-3.67 (m, 9H, NCH<u>H</u>, NCH, CH_2O, CHCN, 2CH_2OSi), 3.38 (s, 3H, OCH_3), 4.69 (d, d, 1H, CHCN), 6.92 (m, 10H, H_{arom}) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.48, 21.99, 26.54, 26.95, 30.39, 31.30, 33.07, 45.51, 47.91, 55.54, 59.03, 62.48, 62.65, 66.45, 75.16, 125.28, 126.01, 127.29, 127.67, 127.74, 128.83, 138.76, 142.89, 172.63 ppm; MS: m/z (r.I. %) = 584 (3, M^+ + 1), 583 (7, M^+), 568 (2, M^+-CH_3), 540 (7), 539 (17), 538 (38, M^+-CH_2OCH_3), 468 (6), 361 (7), 232 (4), 132 (11), 131 (100), 129 (7), 116 (6), 114 (6), 103 (5), 91 (19, $C_7H_7^+$), 75 (6), 73 (20, Si(CH_3)$_3$), 70 (13), 59 (4), 55 (3), 45 (15), 41 (4), 28 (4). (Found: C, 67.74; H, 9.62; N, 4.68. Calc for $C_{33}H_{54}N_2O_3Si_2$ (582.98): C, 67.99; H, 9.34; N, 4.81 %).

(+)-(2*S*,3'*S*,5'*S*)-2-Methoxymethyl-1-(3,5-dimethyl-1,8-bis(trimethylsilyloxy)-4-octylideneamino)-pyrrolidine[(*S*,*S*,*S*)-**13a**]. 5.2g crude (*S*,*S*)-**9a** and 4.24g (17.4 mmol) 1-iodo-2-trimethylsilyloxyethane [7]. 3.1g (42.5 % based on (*S*)-**6a**) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{24}$ = +141.5° (c = 0.99, $CHCl_3$); IR (film): 2995-2810 (CH), 1630 (CN), 1460, 1380, 1350, 1250, 1200, 1100, 1040, 1025, 990, 970, 910, 875, 840, 735 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.12 (2s, 18H, 2Si(CH_3)$_3$), 1.07 (2d, 6H, 2CH_3), 1.30-2.08 (m, 10H, 2βNCH_2, 6H_{aliph}), 2.35 (m, 2H, NC<u>H</u>H, CHCN), 2.89-3.40 (m, 5H, NCH<u>H</u>, NCH, CH_2O, CHCN), 3.33 (s, 3H, OCH_3), 3.53 (m, 4H, 2CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.09, 17.54, 21.74, 21.76, 26.90, 31.01, 31.40, 31.66, 34.30, 36.88, 55.00, 59.02, 61.22, 62.82, 65.83, 76.11, 178.05 ppm; MS: m/z (r.I. %) = 445 (2, M^+ + 1), 444 (5, M^+), 429 (4, M^+-CH_3), 400 (17), 399

(54, M^+-CH_2OCH_3), 330 (4), 329 (7), 328 (27), 284 (7), 283 (30), 259 (4), 258 (18), 244 (8), 214 (6), 198 (3), 172 (3), 170 (10), 160 (3), 159 (18), 156 (10), 145 (8), 143 (3), 130 (6), 129 (10), 124 (4), 115 (4), 114 (26), 105 (3), 104 (6), 103 (59), 101 (4), 96 (5), 91 (8), 89 (7), 85 (6), 84 (5), 83 (4), 82 (7), 75 (16), 74 (7), 73 (76, $Si(CH_3)_3$), 71 (4), 70 (35), 69 (100), 68 (3), 67 (3), 59 (6), 56 (3), 55 (19), 45 (14), 42 (4), 41 (21). (Found: C, 59.55; H, 10.96; N, 6.40. Calc for $C_{22}H_{48}N_2O_3Si_2$ (444.81): C, 59.41; H, 10.88; N, 6.30 %).

(+)-(2*S*,3'*S*,5'*S*)-1-(3,5-Diethyl-1,8-bis(trimethylsilyloxy)-4-octylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*S*,*S*)-**13b**]. 7.0g crude (*S*,*S*)-**9b** and 5.3g (21.6 mmol) 1-iodo-2-trimethylsilyloxy-ethane [7]. 5.34 g (57.5 % based on (*S*)-**6b**) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:3); $[\alpha]_D^{29}$ = +104.2° (c = 1.58, $CHCl_3$); IR (film): 2995-2810 (CH), 1625 (CN), 1460, 1380, 1350, 1250, 1200, 1100, 1050, 970, 920, 880, 840, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.11 (2s, 18H, $2Si(CH_3)_3$), 0.90 (2t, 6H, $2CH_3$), 1.37-2.20 (m, 15H, 2ßNCH_2, 10H_{aliph}, CHCN), 2.37 (m, 1H, NCHH), 2.88-3.40 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.32 (s, 3H, OCH_3), 3.55 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.46, 11.68, 12.98, 21.84, 24.68, 27.10, 27.19, 29.49, 30.87, 34.64, 39.12, 41.58, 55.31, 59.08, 61.49, 62.97, 66.00, 76.35, 176.13 ppm; MS: m/z (r.I. %) = 472 (2, M^+), 457 (2, M^+-CH_3), 429 (5), 428 (12), 427 (35, M^+-CH_2OCH_3), 358 (5), 357 (6), 356 (24), 312 (7), 311 (29), 273 (4), 272 (17), 259 (3), 258 (11), 243 (6), 242 (28), 200 (6), 186 (6), 184 (11), 173 (17), 170 (11), 159 (8), 157 (3), 152 (4), 147 (4), 130 (7), 129 (12), 115 (4), 114 (38), 110 (5), 104 (4), 103 (40), 101 (5), 96 (3), 91 (10), 89 (8), 85 (7), 84 (12), 83 (100), 82 (6), 75 (20), 74 (7), 73 (81, $Si(CH_3)_3$), 71 (5), 70 (40), 69 (85), 68 (4), 67 (4), 59 (6), 56 (4), 55 (50), 45 (19). (Found: C, 60.84; H, 11.18; N, 5.75. Calc for $C_{24}H_{52}N_2O_3Si_2$ (472.87): C, 60.96; H, 11.08; N, 5.92 %).

(+)-(2*S*,3'*S*,5'*S*)-2-Methoxymethyl-1-(1,8-bis(trimethylsilyloxy)-3,5-dipropyl-4-octylideneamino)-pyrrolidine [(*S*,*S*,*S*)-**13c**]. 4.4 g crude (*S*,*S*)-**9c** and 4.3 g (17.7 mmol) 1-iodo-2-trimethylsilyloxy-ethane [7]. 1.43 g (25.5 % based on (*S*)-**6c**) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:3); $[\alpha]_D^{28}$ = +103.1° (c = 1.88, $CHCl_3$); IR (film): 2995-2810 (CH), 1625 (CN), 1460, 1380, 1350, 1250, 1200, 1100, 1045, 975, 945, 920, 880, 840, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.11 (2s, 18H, $2Si(CH_3)_3$), 0.87 (2t, 6H, $2CH_3$), 1.17-2.25 (m, 19H, 2ßNCH_2, 14H_{aliph}, CHCN), 2.38 (m, 1H, NCHH), 2.89-3.40 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.32 (s, 3H, OCH_3), 3.54 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.01, 14.24, 14.44, 20.51, 21.49, 21.82, 27.15, 29.92, 30.97, 34.01, 34.99, 37.09, 37.21, 40.06, 55.23, 59.11, 61.44, 62.99, 65.91, 76.41, 176.85 ppm; MS: m/z (r.I. %) = 501 (4, M^+ + 1), 500 (11, M^+), 486 (3), 485 (8, M^+-CH_3), 457 (9), 456 (24), 455 (64, M^+-CH_2OCH_3), 384 (8), 383 (14), 382 (51), 367 (4), 340 (7), 339 (27), 287 (3), 286 (12), 272 (10), 271 (6), 270 (27), 214 (4), 200 (4), 198 (11), 187 (8), 184 (12), 173 (4), 147 (7), 130 (7), 129 (9), 124 (4), 115 (4), 114 (31), 103 (22), 101 (7), 98 (5), 97 (51), 91 (7), 89 (10), 85 (6), 84 (10), 83 (38), 82 (9), 75 (29), 73 (100, $Si(CH_3)_3$), 71 (7), 70 (35), 69 (12), 67 (7), 59 (11), 56 (7), 55 (97), 45 (31), 43 (12), 42 (8), 41 (29). (Found: C, 61.91; H, 11.31; N, 5.80. Calc for $C_{26}H_{56}N_2O_3Si_2$ (500.92): C, 62.34; H, 11.27; N, 5.59 %).

(+)-(2*S*,2'*S*,6'*S*)-2-Methoxymethyl-1-(2-(2-trimethylsilyloxy-ethyl)-6-(3-trimethylsilyloxy-propyl)-cyclohexylideneamino)-pyrrolidine [(*S*,*S*,*S*)-**13d**]. 5.3 g crude (*S*,*S*)-**9d** and 4.2 g (17.2 mmol) 1-iodo-2-trimethylsilyloxyethane [7]. 1.75 g (24.5 % based on (*S*)-**6d**) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{24}$ = +82.2° (c = 0.97, $CHCl_3$); IR (film): 2990-2820 (CH), 1630 (CN), 1480, 1460, 1450, 1410, 1390, 1350, 1260, 1250, 1200, 1190, 1100, 1050, 1020, 970, 910, 875, 845, 810, 740 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.11 (s, 18H, $2Si(CH_3)_3$), 1.40-2.18 (m, 16H, 2ßNCH_2, 12H_{aliph}), 2.20-2.38 (m, 2H, NC<u>H</u>H, CHCN), 2.90-3.42 (m, 5H, NCH<u>H</u>, NCH, CHCN, CH_2O), 3.34 (s, 3H, OCH_3), 3.56 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.04, 21.16, 21.92, 27.11, 27.14, 30.89, 31.97, 33.39, 34.63, 35.67, 39.88, 54.94, 59.10, 60.97, 63.20, 66.05, 76.49, 173.22 ppm; MS: m/z (r.I. %) = 457 (2, M^+ + 1), 456 (6, M^+), 441 (4, M^+-CH_3), 413(8), 412 (20), 411 (61, M^+-CH_2OCH_3), 343 (5), 342 (15), 340 (10), 312 (7), 296 (3), 295 (13), 254 (4), 253 (7), 252 (33), 224 (4), 163 (4), 162 (23), 136 (10), 134 (6), 130 (5), 129 (8), 120 (7), 114 (27), 108 (6), 105 (4), 103 (18), 97 (10), 95 (6), 93 (8), 91 (7), 89 (8), 85 (7), 84 (6), 83 (6), 82 (7), 81 (10), 80 (5), 79 (9), 75 (28), 74 (10), 73 (100, $Si(CH_3)_3$), 71 (6), 70 (39), 67 (13), 59 (10), 55 (18), 45 (17), 41 (19). (Found: C, 60.80; H, 10.58; N, 6.17. Calc for $C_{23}H_{48}N_2O_3Si_2$ (456.82): C, 60.47; H, 10.59; N, 6.13 %).

(+)-(2*S*,3'*R*,5'*R*)-2-Methoxymethyl-1-(1,8-bis(trimethylsilyloxy)-3,5-diphenyl-4-octylideneamino)-pyrrolidine [(*S*,*R*,*R*)-**13e**]. 8.1 g crude (*S*,*R*)-**9e** and 5.44 g (22.3 mmol) 1-iodo-2-trimethylsilyloxypropane [7]. 4.1 g (41.0 % based on (*S*)-**6e**) of a pale yellow oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{28}$ = +146.1° (c = 1.67, $CHCl_3$); IR (film): 3090-3010 (CH_{arom}), 3000-2820 (CH), 1650 (CN), 1600, 1580, 1495, 1455, 1385, 1250, 1200, 1190, 1100, 1050, 970, 950, 910, 880, 845, 760, 735, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.08 (s, 18H, $2Si(CH_3)_3$), 1.40-2.33 (m, 10H, 2ßNCH_2, 6H_{aliph}), 2.64 (m, 1H, NC<u>H</u>H), 3.15-3.52 (m, 5H, NCH<u>H</u>, NCH, CH_2O, CHCN), 3.37 (s, 3H, OCH_3), 3.61 (m, 4H, $2CH_2OSi$), 4.66 (d, d, 1H, CHCN), 6.93 (m, 10H, H_{arom}) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -0.03, 22.06, 26.64, 27.05, 30.46, 39.48, 43.76, 45.87, 55.62, 59.08, 60.46, 62.53, 66.46, 75.25, 125.35, 126.02, 127.32, 127.75, 127.86, 128.94, 138.90, 142.57, 172.62 ppm; MS: m/z (r.I. %) = 568 (15, M^+), 554 (3), 553 (6, M^+-CH_3), 525 (10), 523 (49, M^+-CH_2OCH_3), 454 (9), 453 (11), 452 (30), 407 (10), 361 (7), 320 (7), 232 (4), 132 (12), 131 (100), 129 (8), 117 (13), 116 (6), 115 (5), 114 (28), 105 (5), 104 (7), 103 (43), 91 (19, $C_7H_7^+$), 89 (5), 84 (5), 82 (5), 75 (10), 73 (44, $Si(CH_3)_3$), 70 (18), 59 (4), 55 (5), 45 (23), 44 (6), 41 (5). (Found: C, 67.74; H, 9.26; N, 4.86. Calc for $C_{32}H_{52}N_2O_3Si_2$ (568.95): C, 67.56; H, 9.21; N, 4.92 %).

(+)-(2*S*,4'*S*,6'*S*)-1-(10-tert-Butyl-dimethylsilyloxy-4,6-dimethyl-1-trimethylsilyloxy-5-decylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*S*,*S*)-**14a**]. 3 g crude (*S*,*S*)-**9a** and 3.14 g (10 mmol) 4-tert-butyl-dimethylsilyloxy-1-iodo-butane [**10**]. 3.71 g (70.5 % based on (*S*)-**6a**) of a pale yellow oil after flash-chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{23}$ = +124.5° (neat); IR (film): 2990-2810 (CH), 1625 (CN), 1460, 1390, 1360, 1250, 1200, 1185, 1100, 1045, 1010, 980, 960, 940, 840, 780 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.04 (s, 6H, $Si(CH_3)_2$), 0.11 (s, 9H, $Si(CH_3)_3$), 0.89 (s, 9H, $SiC(CH_3)_3$), 1.05 (2d, 6H, $2CH_3$), 1.18-2.08 (m, 14H, 2ßNCH_2, 10H_{aliph}), 2.34 (m, 2H, NC<u>H</u>H, CHCN), 2.90-3.52 (m, 5H, NCH<u>H</u>, NCH, CH_2O, CHCN),

3.32 (s, 3H, OCH_3), 3.57 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -5.34, -0.08, 17.56, 18.24, 21.72, 21.85, 23.75, 25.89, 26.72, 30.97, 31.55, 33.00, 33.76, 33.90, 34.58, 54.93, 58.94, 62.82, 63.03, 65.91, 75.88, 178.38 ppm; MS: m/z (r.I. %) = 515 (2, $M^+ + 1$), 514 (14, M^+), 500 (3), 499 (6, M^+-CH_3), 471 (5), 471 (16), 469 (100, M^+-CH_2OCH_3), 457 (4), 400 (3), 184 (9), 170 (10), 159 (14), 133 (5), 129 (5), 115 (8), 114 (9), 110 (3), 103 (15), 101 (6), 96 (4), 91 (4), 89 (22), 84 (8), 83 (59), 82 (5), 81 (4), 75 (26), 74 (6), 73 (64, $Si(CH_3)_3$), 71 (4), 70 (28), 69 (60), 68 (3), 67 (5), 59 (8), 56 (5), 55 (40), 45 (12), 43 (4), 42 (5), 41 (25). (Found: C, 62.90; H, 11.59; N, 5.74. Calc for $C_{27}H_{58}N_2O_3Si_2$ (514.95): C, 62.98; H, 11.35; N, 5.44 %).

(+)-(2*S*,4'*S*,6'*S*)-1-(10-tert-Butyl-dimethylsilyloxy-4,6-diethyl-1-trimethylsilyloxy-5-decylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*S*,*S*)-**14b**]. 2 g crude (*S*,*S*)-**9b** and 1.9 g (6.17 mmol) 4-tert-butyl-dimethylsilyloxy1-iodo-butane [**10**]. 1.84 g (63.5 % based on (*S*)-**6b**) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:6); $[\alpha]_D^{24}$ = +90.4° (c = 1.03, $CHCl_3$); IR (film): 2995-2810 (CH), 1620 (CN), 1460, 1390, 1360, 1250, 1200, 1190, 1100, 1050, 1005, 970, 940, 920, 875, 840, 780 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.04 (s, 6H, $Si(CH_3)_2$), 0.1 (s, 9H, $Si(CH_3)_3$), 0.89 (s, 9H, $SiC(CH_3)_3$), 0.89 (2t, 6H, $2CH_3$), 1.20-2.19 (m, 19H, $2\beta NCH_2$, $14H_{aliph}$, CHCN), 2.38 (m, 1H, NCHH), 2.90-3.40 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.31 (s, 3H, OCH_3), 3.59 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -5.32, -0.49, 11.75, 13.03, 18.27, 21.80, 24.13, 24.63, 25.92, 26.86, 27.25, 29.48, 30.77, 31.23, 33.19, 41.25, 42.34, 55.20, 58.90, 62.92, 63.11, 66.05, 76.05, 176.32 ppm; MS: m/z (r.I. %) = 543 (12, $M^+ + 1$), 542 (25, M^+), 527 (7, M^+-CH_3), 500 (4), 499 (18), 497 (100, M^+-CH_2OCH_3), 485 (6), 481 (7), 428 (6), 328 (7), 200 (5), 198 (13), 185 (2), 184 (10), 174 (2), 173 (14), 133 (5), 129 (5), 115 (6), 114 (10), 110 (3), 103 (11), 97 (36), 91 (4), 89 (13), 84 (7), 83 (45), 75 (19), 74 (5), 73 (47, $Si(CH_3)_3$), 70 (21), 69 (6), 59 (5), 55 (55), 45 (11), 41 (14). (Found: C, 64.31; H, 11.56; N, 5.32. Calc for $C_{29}H_{62}N_2O_3Si_2$ (543.00): C, 64.15; H, 11.51; N, 5.16 %).

(+)-(2*S*,4'*S*,6'*S*)-1-(10-tert-Butyl-dimethylsilyloxy-1-trimethylsilyloxy-4,6-dipropyl-5-decylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*S*,*S*)-**14c**]. 3.2 g crude (*S*,*S*)-**9c** and 2.86 g (9.1 mmol) 4-tert-butyl-dimethylsilyloxy-1-iodo-butane [**10**]. 3.02 g (68.5 % based on (*S*)-**6c**) of a colorless oil after flash-chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{27}$ = +86.0° (c = 1.65, $CHCl_3$); IR (film): 2995-2800 (CH), 1620 (CN), 1460, 1380, 1360, 1350, 1250, 1200, 1185, 1100, 1110, 970, 940, 920, 880, 840, 780, 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.04 (s, 6H, $Si(CH_3)_2$), 0.10 (s, 9H, $Si(CH_3)_3$), 0.89 (s, 9H, $SiC(CH_3)_3$), 0.84-0.92 (2t, 6H, $2CH_3$), 1.18-2.26 (m, 23H, $2\beta NCH_2$, $18H_{aliph}$, CHCN), 2.37 (m, 1H, NCHH), 2.88-3.37 (m, 5H, NCHH, NCH, CH_2O, CHCN), 3.30 (s, 3H, OCH_3), 3.57 (m, 4H, $2CH_2OSi$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -5.36, -0.13, 14.20, 14.34, 18.21, 20.45, 21.51, 21.73, 24.07, 25.87, 26.85, 29.83, 30.79, 31.63, 33.11, 33.96, 37.18, 39.66, 40.26, 55.10, 58.83, 62.87, 63.04, 65.93, 76.03, 176.91 ppm; MS: m/z (r.I. %) = 572 (7, $M^+ + 1$), 571 (16, M^+), 556 (5, M^+-CH_3), 529 (6), 528 (17), 527 (44), 526 (100, M^+-CH_2OCH_3), 457 (8), 343 (11), 270 (5), 243 (5), 214 (8), 212 (17), 198 (14), 187 (19), 133 (7), 130 (6), 129 (9), 124 (4), 115 (9), 114 (21), 111 (34), 103 (16), 101 (9), 98 (7), 97 (84), 91 (8), 89 (21), 85 (5), 84 (8), 83 (9), 82 (10), 81 (5), 75

(48), 74 (7), 73 (67, $Si(CH_3)_3$), 71 (5), 70 (40), 69 (98), 67 (10), 59 (9), 57 (9), 56 (8), 55 (90), 45 (21), 43 (10), 41 (24). (Found: C, 65.36; H, 11.74; N, 4.99. Calc for $C_{31}H_{66}N_2O_3Si_2$ (571.06): C, 65.20; H, 11.65; N, 4.91 %).

(+)-(2*S*,2'*S*,6'*S*)-1-(6-(4-tert-Butyl-dimethylsilyloxy-butyl)-2-(3-trimethylsilyloxypropyl)-2-methoxymethyl-cyclohexylideneamino)-pyrrolidine [(*S*,*S*,*S*)-**14d**]. 2.0 g crude (*S*,*S*)-**9d** and 2.0 g (6.5 mmol) 4-tert-butyl-dimethylsilyloxy1-iodo-butane [**10**]. 1.34 g (46.0 % based on (*S*)-**6d**) of a pale yellow oil after flash-chromatography (SiO_2, ether:pentane = 1:6); $[\alpha]_D^{26}$ = +62.7° (c = 1.04, $CHCl_3$); IR (film): 3000-2800 (CH), 1630 (CN), 1470, 1460, 1450, 1390, 1360, 1250, 1200, 1185, 1100, 1005, 970, 940, 915, 870, 840, 775, 760 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.04 (s, 6H, $Si(CH_3)_2$), 0.11 (s, 9H, $Si(CH_3)_3$), 0.89 (s, 9H, $SiC(CH_3)_3$), 0.95-2.10 (m, 20H, 2ßNCH_2, 16H_{aliph}), 2.21 (m, 1H, CHCN), 2.31 (m, 1H, NCHH), 2.90-3.45 (m, 5H, NCHH, NCH, CHCN, CH_2O), 3.32 (s, 3H, OCH_3), 3.58 (m, 4H, 2CH_2OSi) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -5.31, -0.46, 18.25, 21.09, 21.86, 23.27, 25.92, 26.81, 27.17, 30.87, 31.15, 31.86, 33.05, 35.91, 36.56, 39.77, 54.84, 58.93, 63.03, 63.17, 66.20, 76.07, 173.48 ppm; MS: m/z (r.I. %) = 527 (9, M^+ + 1), 526 (20, M^+), 511 (6, M^+-CH_3), 483 (14), 482 (39), 481 (100, M^+-CH_2OCH_3), 469 (5), 413 (4), 412 (11), 322 (5), 280 (7), 190 (6), 129 (3), 114 (4), 103 (3), 89 (5), 75 (10), 74 (3), 73 (25, $Si(CH_3)_3$), 70 (10), 67 (4), 55 (5), 45 (3), 41 (5). (Found: C, 63.86; H, 11.33; N, 5.61. Calc for $C_{28}H_{58}N_2O_3Si_2$ (526.96): C, 63.82; H, 11.09; N, 5.32 %).

(+)-(2*S*,4'*R*,6'*R*)-1-(10-tert-Butyl-dimethylsilyloxy-1-trimethylsilyloxy-4,6-diphenyl-5-decylideneamino)-2-methoxymethyl-pyrrolidine [(*S*,*R*,*R*)-**14e**]. 3 g crude (*S*,*R*)-**9e** and 2.3 g (7.3 mmol) 4-tert-butyl-dimethylsilyloxy-1-iodo-butane [**10**]. 2.23 g (53.5 % based on (*S*)-**6e**) of a pale yellow oil after flash-chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{27}$ = +121.3° (c = 1.10, $CHCl_3$); IR (film): 3090-3010 (CH_{arom}), 3000-2800 (CH), 1630 (CN), 1600, 1585, 1495, 1470, 1460, 1455, 1390, 1360, 1290, 1250, 1200, 1185, 1100, 1030, 1010, 970, 940, 875, 840, 780, 760, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.03 (s, 6H, $Si(CH_3)_2$), 0.07 (s, 9H, $Si(CH_3)_3$), 0.88 (s, 9H, $SiC(CH_3)_3$), 1.22-2.16 (m, 14H, 2ßNCH_2, 10H_{aliph}), 2.63 (m, 1H, NCHH), 3.13-3.67 (m, 9H, NCHH, NCH, CH_2O, CHCN, 2CH_2OSi), 3.37 (s, 3H, OCH_3), 4.70 (d, d, 1H, CHCN), 6.88-7.00 (m, 10H, H_{arom}) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = -5.28, -0.04, 18.24, 22.00, 23.47, 25.92, 26.97, 30.00, 31.08, 32.99, 33.08, 45.85, 47.97, 55.54, 58.99, 62.63, 62.96, 66.40, 76.16, 125.25, 125.94, 127.26, 127.64, 127.70, 128.86, 138.75, 142.87, 172.84 ppm; MS: m/z (r.I. %) = 639 (1, M^+ + 1), 638 (5, M^+), 623 (2, M^+-CH_3), 595 (6), 593 (28, M^+-CH_2OCH_3), 525 (3), 524 (6), 376 (1), 361 (4), 277 (7), 246 (4), 232 (4), 221 (5), 145 (31), 132 (11), 131 (100), 129 (10), 117 (14), 116 (6), 115 (8), 114 (12), 104 (4), 103 (5), 91 (30, $C_7H_7^+$), 89 (8), 75 (11), 73 (35, $Si(CH_3)_3$), 70 (20), 59 (4), 55 (4), 45 (14), 41 (4). (Found: C, 69.65; H, 9.98; N, 4.48. Calc for $C_{37}H_{62}N_2O_3Si_2$ (639.09): C, 69.64; H, 9.78; N, 4.38 %).

(-)-(4*S*,5*R*,9*S*)-4,9-Dimethyl-1,6-dioxaspiro[4.4]nonane [(*S*,*R*,*S*)-**15a**]. 0.7 g crude (*S*,*S*,*S*)-**11a** and approx. 1.5 eq PTSA in one portion. 140 mg (63 % based on (*S*)-**6a**) of a pale yellow liquid after chromatography (SiO_2, ether:pentane = 1:2); $[\alpha]_D^{22}$ = -98.7° (c = 1.60, EtOH); IR (film): 2995-2860 (CH), 1460, 1380, 1345, 1230, 1180, 1160, 1140, 1105, 1070, 1030, 990, 920 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.03 (d, 6H, J = 6.4Hz, $2CH_3$), 1.76 (m, 2H, 2CH), 2.02 (m, 4H, $2CH_2$), 3.69 (d, d, d, 2H, J_1 = 6.7Hz, J_2 = 8.1Hz, J_3 = 9.4Hz, 2CHHO); 3.99 (t, d, 2H, J_1 = 9.1Hz, J_2 = 2.4Hz, 2CHHO) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 12.96 (CH_3), 32.50 (CH_2), 37.46 (CH), 65.99 (CH_2O), 114.84 (OCO) ppm; MS: m/z (r.I. %) = 157 (0.3, $M^+ + 1$), 156 (0.6, M^+), 112 (6), 111 (35), 102 (6), 101 (100), 100 (5), 86 (4), 83 (16), 73 (11), 69 (4), 59 (3), 57 (28), 56 (18), 55 (27), 45 (7), 43 (11), 42 (3), 41 (19). (Found: C, 69.22; H, 10.33. Calc for $C_9H_{16}O_2$ (156.23): C, 69.19; H, 10.32 %).

(-)-(4*S*,5*R*,9*S*)-4,9-Diethyl-1,6-dioxaspiro[4.4]nonane [(*S*,*R*,*S*)-**15b**]. 1.5 g crude (*S*,*S*,*S*)-**11b** and approx. 1.5 eq PTSA in one portion. 204 mg (39 % based on (*S*)-**6b**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{22}$ = -62.8° (c = 1.02, EtOH); IR (film): 2995-2860 (CH), 1465, 1450, 1380, 1175, 1155, 1140, 1070, 1030, 1000, 980, 960, 940, 900 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.96 (t, 6H, J = 7.4Hz, $2CH_3$), 1.30-1.64 (m, 4H, $2CH_3$-CH_2-CH), 1.70 (m, 2H, 2CH), 1.86 (m, 2H, 2CHH), 2.07 (m, 2H, 2CHH), 3.68 (d, d, d, 2H, J_1 = 7.1Hz, J_2 = 8.1Hz, J_3 = 9.4Hz, 2CHHO); 3.99 (t, d, 2H, J_1 = 8.7Hz, J_2 = 2.7Hz, 2CHHO); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 13.13 (CH_3), 21.89, 30.49, 45.55 (CH), 66.06 (CH_2O), 114.64 (OCO) ppm; MS: m/z (r.I. %) = 185 (0.4, $M^+ + 1$), 184 (0.6, M^+), 183 (0.7), 139 (4), 126 (4), 125 (34), 116 (11), 115 (100), 112 (3), 97 (9), 84 (3), 73 (4), 71 (4), 70 (10), 69 (26), 59 (4), 57 (16), 55 (27), 45 (17), 43 (6), 42 (16), 41 (24), 39 (7). (Found: C, 71.68; H, 11.07. Calc for $C_{11}H_{20}O_2$ (184.28): C, 71.70; H, 10.94 %).

(-)-(4*S*,5*R*,9*S*)-4,9-Dipropyl-1,6-dioxaspiro[4.4]nonane [(*S*,*R*,*S*)-**15c**]. 2 g crude (*S*,*S*,*S*)-**11c** and approx. 1.5 eq PTSA in one portion. 92 mg (15 % based on (*S*)-**6c**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:4); $[\alpha]_D^{22}$ = -25.2° (c = 0.51, EtOH); IR (film): 2995-2860 (CH), 1470, 1455, 1380, 1360, 1330, 1245, 1220, 1180, 1140, 1110, 1040, 1030, 1010, 980, 950, 930, 885, 735 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.95 (t, 6H, J = 6.7Hz, $2CH_3$), 1.38 (m, 8H, H_{aliph}), 1.71 (m, 2H, CH), 1.93 (m, 2H, 2CHH); 2.00 (m, 2H, 2CHH), 3.66 (d, d, d, 2H, J_1 = 7.1, J_2 = 8.1, J_3 = 9.4, 2CHHO), 3.99 (t, d, 2H, J_1 = 8.6, J_2 = 2.4, 2CHHO) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 14.40 (CH_3), 21.87, 30.85, 31.20, 43.37 (CH), 66.13 (CH_2O), 114.87 (OCO) ppm; MS: m/z (r.I. %) = 213 (0.2, $M^+ + 1$), 212 (0.4, M^+), 139 (8), 130 (7), 129 (100), 84 (5), 83 (14), 71 (4), 69 (6), 67 (2), 59 (2), 57 (3), 56 (8), 55 (18), 45 (4), 43 (5), 42 (4), 41 (9). (Found: C, 73.42; H, 11.50. Calc for $C_{13}H_{24}O_2$ (212.34): C, 73.54; H, 11.39 %).

(-)-(5*S*,6*R*,11*S*)-5,11-Dimethyl-1,7-dioxaspiro[5.5]undecane [(*S*,*R*,*S*)-**16a**]. 0.40 g crude (*S*,*S*,*S*)-**12a** and approx. 1.5 eq PTSA in several small portions (TLC control). 133.5 mg (68 % based on (*S*)-**6a**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:30); $[\alpha]_D^{22}$ = -113.4° (c = 0.97, EtOH); IR (film):

2995-2860 (CH), 1465, 1450, 1440, 1390, 1380, 1360, 1345, 1290, 1240, 1195, 1180, 1150, 1100, 1085, 1060, 1045, 1030, 990, 945, 920, 900 cm^{-1}: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.87 (d, 6H, J = 6.8Hz, $2CH_3$), 1.37-1.65 (m, 8H, H_{aliph}), 1.74-1.87 (m, 2H, 2CH), 3.52-3.65 (m, 4H, $2CH_2O$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 16.13 (CH_3), 26.32, 27.22, 34.44 (CH), 59.88 (CH_2O), 99.75 (OCO) ppm; MS: m/z (r.I. %) = 185 (4, $M^+ + 1$), 184 (33, M^+), 142 (11), 139 (3), 126 (10), 116 (7), 115 (100), 114 (48), 111 (4), 99 (3), 97 (18), 70 (7), 69 (28), 59 (6), 57 (11), 56 (3), 55 (18), 45 (17), 43 (8), 42 (18), 41 (22). (Found: C, 71.60; H, 11.26. Calc for $C_{11}H_{20}O_2$ (184.28): C, 71.70; H, 10.94 %).

(5*S*,6*S*,11*S*)-5,11-Dimethyl-1,7-dioxaspiro[5.5]undecane [(*S*,*S*,*S*)-**16a**]. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.01 (d, 6H, J = 7Hz, $2CH_3$), 1.2-2.2 (m, 10H, H_{aliph}), 3.50-3.72 (m, 4H, $2CH_2O$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 13.54 (CH_3), 19.53, 25.30, 31.92 (CH), 60.67 (CH_2O), 99.34 (OCO) ppm.

rac-(5*S*,6*S*,11*R*)/(5*R*,6*R*,11*S*)-5,11-Dimethyl-1,7-dioxaspiro[5.5]undecane [rac-(*S*,*S*,*R*)/(*R*,*R*,*S*)-**16a**]. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.98 (d, 3H, J = 6.7Hz, $2CH_3$), 1.09 (d, 3H, J = 7.4Hz, $2CH_3$), 1.2-2.2 (m, 10H, H_{aliph}), 3.50-3.72 (m, 4H, $2CH_2O$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 16.73 (CH_3), 17.42 (CH_3), 20.54, 24.76, 26.57, 29.19, 35.78 (CH), 35.92 (CH), 59.40 (CH_2O), 60.53 (CH_2O), 100.02 (OCO) ppm.

(-)-(5*S*,6*R*,11*S*)-5,11-Diethyl-1,7-dioxaspiro[5.5]undecane [(*S*,*R*,*S*)-**16b**]. 0.52 g crude (*S*,*S*,*S*)-**12b** and approx. 1.5 eq PTSA in one portion. 138 mg (50 % based on (*S*)-**6b**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:30); $[\alpha]_D^{22}$ = -46.1° (c = 0.95, EtOH); IR (film): 2995-2860 (CH), 1465, 1450, 1390, 1295, 1240, 1195, 1170, 1150, 1100, 1070, 1050, 1020, 950, 875, 840 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.85 (t, 6H, J = 7.4Hz, $2CH_3$), 1.13 (m, 4H, $2CH_3$-CH_2-CH), 1.38-1.71 (m, 10H, H_{aliph}), 3.57 (m, 4H, $2CH_2O$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 11.97 (CH_3), 22.80, 23.42, 26.16, 40.94 (CH), 59.79 (CH_2O), 100.30 (OCO) ppm; MS: m/z (r.I. %) = 213 (5, $M^+ + 1$), 212 (32, M^+), 197 (2, M^+-CH_3), 167 (2), 156 (5), 154 (2), 141 (8), 139 (2), 130 (7), 129 (100), 128 (24), 126 (5), 113 (6), 111 (6), 100 (10), 98 (3), 84 (2), 83 (23), 71 (5), 69 (6), 59 (3), 57 (4), 56 (7), 55 (20), 45 (6), 43 (5), 42 (4), 41 (14). (Found: C, 73.68; H, 11.27. Calc for $C_{13}H_{24}O_2$ (212.34): C, 73.54; H, 11.39 %).

(-)-(5*S*,6*R*,11*S*)-5,11-Dipropyl-1,7-dioxaspiro[5.5]undecane [(*S*,*R*,*S*)-**16c**]. 1.03 g crude (*S*,*S*,*S*)-**12c** and approx. 1.5 eq PTSA in several small portions (TLC control). 198 mg (62 % based on (*S*)-**6c**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:30); $[\alpha]_D^{22}$ = -15.8° (c = 1.10, EtOH); IR (film): 2995-2860 (CH), 1465, 1450, 1390, 1380, 1340, 1295, 1240, 1230, 1190, 1170, 1140, 1100, 1070, 1050, 1040, 1030, 950, 875, cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.89 (t, 6H, J = 6.7Hz, $2CH_3$), 1.04-1.22 (m, 4H, $2CH_3$-CH_2), 1.31-1.76 (m, 14H, H_{aliph}), 3.51-3.65 (m, 4H, $2CH_2O$) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 14.39 (CH_3), 20.38, 24.06, 26.12, 32.42, 38.75 (CH), 59.79 (CH_2O), 100.29 (OCO) ppm; MS: m/z (r.I. %) = 241 (2, $M^+ + 1$), 240 (14, M^+), 210 (14), 153 (3), 144 (8), 143 (100), 142 (8), 141 (12), 140 (5), 125 (3), 113

(12), 101 (3), 100 (15), 98 (11), 97 (29), 85 (3), 83 (4), 71 (6), 70 (4), 69 (9), 67 (4), 59 (4), 56 (6), 55 (39), 46 (5). (Found: C, 74.47; H, 11.81. Calc for $C_{15}H_{28}O_2$ (240.39): C, 74.95; H, 11.74 %).

(+)-(6*S*,1*R*,10*S*)-2,14-Dioxatricyclo[8.4.0.0^{1,6}]tetradecane [(*S*,*R*,*S*)-**16d**]. 0.51 g crude (*S*,*S*,*S*)-**12d** and approx. 1.5 eq PTSA in one portion. 131.5 mg (65 % based on (*S*)-**6d**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:30); $[\alpha]_D^{22}$ = +31.3° (c = 0.99, EtOH); IR (film): 2995-2840 (CH), 1460, 1450, 1380, 1370, 1350, 1330, 1300, 1290, 1260, 1240, 1200, 1190, 1165, 1140, 1100, 1070, 1045, 1030, 1000, 970, 950, 940, 930, 890, 880 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.40-1.92 (m, 16H, 7CH_2, 2CH), 3.53-3.62 (m, 2H, 2CHHO), 3.94-4.04 (m, 2H, 2CHHO) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 20.41, 22.78, 24.05, 28.34, 35.12 (CH), 61.62 (CH_2O), 98.43 (OCO) ppm; MS: m/z (r.I. %) = 197 (6, M^+ + 1), 196 (51, M^+), 166 (5), 152 (6), 151 (52), 150 (3), 139 (17), 138 (98), 137 (32), 124 (6), 123 (11), 114 (7), 113 (100), 110 (19), 109 (6), 101 (7), 100 (59), 99 (7), 97 (7), 96 (4), 95 (29), 93 (4), 91 (4), 86 (4), 83 (3), 82 (4), 81 (9), 79 (7), 77 (4), 71 (5), 69 (10), 68 (9), 67 (19), 56 (4), 55 (24), 54 (7), 53 (7), 43 (11), 42 (4), 41 (39). (Found: C, 73.30; H, 10.30. Calc for $C_{12}H_{20}O_2$ (196.29): C, 73.43; H, 10.27 %).

rac-(1*S*,10*S*,6*R*)/(1*R*,10*R*,6*S*)-2,14-Dioxatricyclo[8.4.0.0^{1,6}]tetradecane [rac-(*S*,*S*,*R*)/(*R*,*R*,*S*)-**16d**]. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.17-2.20 (m, 16H, 7CH_2, 2CH), 3.28-3.78 (m, 4H, 2CH_2O) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 19.96, 23.25, 24.52, 25.67, 26.56, 27.86, 29.48, 38.51 (CH), 44.86 (CH), 60.01 (CH_2O), 60.32 (CH_2O), 96.86 (OCO) ppm.

(-)-(5*R*,6*R*,11*R*)-5,11-Diphenyl-1,7-dioxaspiro[5.5]undecane [(*R*,*R*,*R*)-**16e**]. 0.53 g crude (*S*,*S*,*S*)-**12e** and approx. 1.5 eq PTSA in several small portions (TLC control). 144.2 mg (59 % based on (*S*)-**6e**) of a colorless solid after chromatography (SiO_2, ether:pentane = 1:30); m.p. 150-152°C; $[\alpha]_D^{22}$ = -43.2° (c = 0.94, EtOH); IR (KBr): 3100-3020 (CH_{arom}), 2980-2840 (CH), 1600, 1490, 1450, 1440, 1380, 1350, 1330, 1290, 1240, 1220, 1170, 1150, 1100, 1080, 1065, 1040, 970, 950, 910, 880, 850, 810, 760, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.45-1.52 (m, 6H, 2H_a, 2H_d, 2H_e), 2.1 (d, q, 2H, 2H_b, $J(H_a\text{-}H_b) = J(H_b\text{-}H_c) = J(H_b\text{-}H_d) = 12.9$Hz, $J(H_b\text{-}H_e) = 4.8$Hz), 2.53 (d, d, 2H, 2H_c, $J(H_b\text{-}H_c) = 12.9$Hz, $J(H_a\text{-}H_c) = 3.9$Hz), 3.8 (m, 4H, 2CH_2O), 7.27 (m, 10H, H_{arom}) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 26.27, 27.95, 48.86 (CH), 59.92 (CH_2O), 99.19 (OCO), 126.20, 127.67, 129.87, 142.93 ppm; MS: m/z (r.I. %) = 309 (6, M^+ + 1), 308 (24, M^+), 178 (4), 177 (25), 176 (19), 132 (5), 131 (9), 117 (11), 115 (5), 105 (11), 104 (100), 103 (6), 91 (10, $C_7H_7^+$), 78 (6), 77 (4), 51 (3). (Found: C, 81.88; H, 7.69. Calc for $C_{21}H_{24}O_2$ (308.42): C, 81.78; H, 7.84 %).

(-)-(4*S*,5*R*,10*S*)-4,10-Dimethyl-1,6-dioxaspiro[4.5]undecane [(*S*,*R*,*S*)-**17a**]. 1 g crude (*S*,*S*,*S*)-**13a** and approx. 1.5 eq PTSA in several small portions (TLC control). 142.8 mg (32.3 % based on (*S*)-**6a**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:10); $[\alpha]_D^{25}$ = -91.5° (c = 0.92, EtOH); IR (film): 2995-2840 (CH), 1460, 1375, 1240, 1210, 1190, 1160, 1145, 1085, 1070, 1030, 1010, 990, 980, 970, 930, 900

cm^{-1}: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.86 (d, 3H, J = 6.7Hz, CH_3), 1.00 (d, 3H, J = 6.7Hz, CH_3), 1.45-1.83 (m, 6H, H_{aliph}), 1.95 (m, 1H, CH), 2.12 (m, 1H, CH), 3.57 (m, 1H, CHHO), 3.71-3.93 (m, 3H, CHHO, CH_2O) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 12.68 (CH_3), 16.59 (CH_3), 26.34, 28.94, 31.67, 33.59 (CH), 37.97 (CH), 60.50 (CH_2O), 65.59 (CH_2O), 107.27 (OCO) ppm; MS: m/z (r.I. %) = 170 (1, M^+), 129 (3), 128 (36), 101 (9), 99 (5), 98 (73), 97 (46), 96 (12), 95 (11), 84 (7), 83 (100), 81 (6), 71 (11), 70 (13), 69 (13), 68 (8), 67 (12), 66 (9), 57 (9), 56 (47), 55 (35), 54 (17), 53 (8), 45 (62), 44 (4), 43 (25), 42 (31), 41 (61), 40 (17), 39 (34). (Found: C, 70.68; H, 10.26. Calc for $C_{10}H_{18}O_2$ (170.25): C, 70.55; H, 10.66 %).

(+)-(4*S*,5*S*,10*S*)-4,10-Dimethyl-1,6-dioxaspiro[4.5]decane [(*S*,*S*,*S*)-**17a**]. 49.6 mg (11.2 % based on (*S*)-**6a**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:10); $[\alpha]_D^{25}$ = +106.3° (c = 0.87, EtOH); IR (film): 2995-2850 (CH), 1470, 1450, 1380, 1360, 1210, 1160, 1145, 1100, 1090, 1070, 1050, 1020, 1000, 960, 925, 890 cm^{-1}: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.91 (d, 3H, J = 7.1Hz, CH_3), 1.11 (d, 3H, J = 6.7Hz, CH_3), 1.21-2.40 (m, 8H, 6H_{aliph}, 2CH), 3.56 (m, 1H, CHHO), 3.76-4.02 (m, 3H, CHHO, CH_2O) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 14.70 (CH_3), 15.72 (CH_3), 19.79, 26.36, 30.46 (CH), 31.57, 39.52 (CH), 60.99 (CH_2O), 65.02 (CH_2O), 109.47 (OCO) ppm; MS: m/z (r.I. %) = 170 (1, M^+), 128 (2), 125 (8), 115 (14), 112 (15), 102 (5), 101 (100), 100 (17), 97 (7), 83 (14), 71 (8), 70 (5), 69 (14), 57 (25), 56 (11), 55 (24), 45 (10), 43 (11), 42 (13), 41 (22), 39 (7).

(-)-(4*S*,5*R*,10*S*)-4,10-Diethyl-1,6-dioxaspiro[4.5]decane [(*S*,*R*,*S*)-**17b**]. 2 g crude (*S*,*S*,*S*)-**13b** and approx. 1.5 eq PTSA in one portion. 429,9 mg (47.0 % based on (*S*)-**6b**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:10); $[\alpha]_D^{24}$ = -47.8° (c = 0.96, EtOH); IR (film): 2995-2850 (CH), 1465, 1450, 1380, 1230, 1210, 1190, 1160, 1140, 1085, 1040, 1020, 980, 955, 910, 885, 845, 740 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, 3H, J = 7.4Hz, CH_3), 0.93 (t, 3H, J = 7.7Hz, CH_3), 1.02-1.84 (m, 10H, H_{aliph}), 2.00 (m, 2H, 2CH), 3.53 (m, 1H, CHHO) 3.69-3.91 (m, 3H, CHHO, 2CH_2O) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 11.94 (CH_3), 13.23 (CH_3), 21.69, 23.31, 25.30, 26.17, 29.71, 40.76 (CH), 45.40 (CH), 60.34 (CH_2O), 65.55 (CH_2O), 107.47 (OCO) ppm; MS: m/z (r.I. %) = 199 (4, M^+ + 1), 198 (23, M^+), 183 (1, M^+-CH_3), 153 (9), 140 (8), 139 (9), 130 (3), 129 (30), 125 (10), 116 (8), 115 (100), 114 (9), 112 (9), 111 (5), 97 (6), 84 (3), 83 (7), 69 (6), 55 (4), 40 (7). (Found: C, 72.68; H, 11.21. Calc for $C_{12}H_{22}O_2$ (198.31): C, 72.68; H, 11.18 %).

(+)-(4*S*,5*S*,10*S*)-4,10-Diethyl-1,6-dioxaspiro[4.5]decane [(*S*,*S*,*S*)-**17b**]. 48,5 mg (5.3 % based on (*S*)-**6b**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:10); $[\alpha]_D^{23}$ = +78.5° (c = 1.18, EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.90 (2t, 6H, J = 6.7Hz, J = 6.4Hz, 2CH_3), 1.20-1.98 (m, 11H, 10H_{aliph}, CH), 2.17 (m, 1H, CH), 3.57 (m, 1H, CHHO) 3.76-3.95 (m, 3H, CHHO, CH_2O) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 11.90 (CH_3), 11.97 (CH_3), 19.77, 19.84, 20.67, 20.87, 27.11, 37.87 (CH), 47.02 (CH), 60.78 (CH_2O), 64.87 (CH_2O), 109.53 (OCO) ppm; MS: m/z (r.I. %) = 199 (1, M^+ + 1), 198 (9, M^+), 153 (6), 140 (7), 139 (7), 130 (2), 129 (22), 125 (8), 116 (7), 115 (100), 114 (7), 112 (9), 111 (3), 97 (4), 84 (5), 83 (9), 71 (4), 69 (16), 57 (9), 56 (8), 55 (19), 45 (10), 43 (5), 42 (7), 41 (19).

(-)-(4*S*,5*R*,10*S*)-4,10-Dipropyl-1,6-dioxaspiro[4.5]decane [(*S*,*R*,*S*)-**17c**]. 1 g crude (*S*,*S*,*S*)-**13c** and approx. 1.5 eq PTSA in one portion. 211.6 mg (60.1 % based on (*S*)-**6c**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:15); $[\alpha]_D^{22}$ = -18.7° (c = 0.94, EtOH); IR (film): 2995-2840 (CH), 1470, 1460, 1210, 1190, 1160, 1090, 1060, 1035, 1015, 960, 890, cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.91 (2t, 6H, J = 7.0Hz, J = 7.0Hz, $2CH_3$), 1.02-1.81 (m, 14H, H_{aliph}), 2.04 (m, 2H, 2CH), 3.55 (m, 1H, CHHO), 3.69-3.93 (m, 3H, CHHO, CH_2O) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 14.37 (CH_3), 14.45 (CH_3), 20.48, 21.95, 26.01, 26.19, 29.98, 31.02, 32.94, 38.63 (CH), 43.29 (CH), 60.34 (CH_2O), 65.62 (CH_2O), 107.59 (OCO) ppm; MS: m/z (r.I. %) = 227 (2, M^+ + 1), 226 (13, M^+), 197 (4), 153 (4), 144 (3), 143 (36), 139 (7), 130 (11), 129 (100), 128 (8), 127 (5), 126 (8), 111 (4), 99 (4), 98 (5), 97 (11), 86 (6), 84 (7), 83 (20), 71 (7), 70 (5), 69 (10), 67 (4), 59 (4), 57 (4), 56 (8), 55 (33), 45 (5), 43 (8), 42 (7), 41 (19). (Found: C, 73.99; H, 11.60. Calc for $C_{14}H_{26}O_2$ (226.36): C, 74.29; H, 11.58 %).

(+)-(4*S*,5*S*,10*S*)-4,10-Dipropyl-1,6-dioxaspiro[4.5]decane [(*S*,*S*,*S*)-**17c**]. 32.7 mg (9.3 % based on (*S*)-**6c**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:15); $[\alpha]_D^{21}$ = +126.9° (c = 0.79, EtOH); δ = 0.93 (2t, 6H, J = 7.0Hz, J = 7.0Hz, $2CH_3$), 1.12-1.84 (m, 14H, H_{aliph}), 1.91 (m, 1H, CH), 2.17 (m, 1H, CH), 3.55 (m, 1H, CHHO) 3.76-3.96 (m, 3H, CHHO, CH_2O) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 14.10 (CH_3), 14.24 (CH_3), 19.92, 20.31, 20.42, 21.19, 27.66, 29.05, 30.08, 35.58 (CH), 44.65 (CH), 60.80 (CH_2O), 64.90 (CH_2O), 109.62 (OCO) ppm.

(-)-(6*S*,1*R*,10*S*)-2,13-Dioxatricyclo[8.3.0.0^{1,6}]tridecane [(*S*,*R*,*S*)-**17d**]. 0.8 g crude (*S*,*S*,*S*)-**13d** and approx. 1.5 eq PTSA in one portion. 80.9 mg (25.8 % based on (*S*)-**6d**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:10); $[\alpha]_D^{22}$ = -43.2° (c = 0.63, EtOH); IR (film): 2995-2820 (CH), 1450, 1380, 1350, 1340, 1285, 1270, 1260, 1240, 1210, 1170, 1160, 1145, 1105, 1070, 1045, 1020, 995, 970, 960, 930, 920, 890, 880 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.00-1.78 (m, 12H, $6CH_2$), 1.88 (m, 1H, CH), 2.24 (m, 1H, CH), 3.58 (m, 1H, CHHO), 3.82-4.04 (m, 3H, CHHO, CH_2O) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 25.12, 26.18, 26.79, 29.27, 29.67, 30.54, 41.56 (CH), 42.61 (CH), 61.06 (CH_2O), 64.78 (CH_2O), 106.30 (OCO) ppm; MS: m/z (r.I. %) = 183 (5, M^+ + 1), 182 (43, M^+), 165 (6), 164 (46), 163 (11), 154 (5), 152 (8), 151 (6), 150 (4), 149 (31), 139 (4), 138 (14), 137 (76), 136 (10), 135 (20), 125 (11), 124 (100), 123 (16), 121 (6), 114 (3), 113 (32), 110 (8), 109 (10), 108 (5), 107 (5), 100 (33), 99 (52), 98 (5), 97 (8), 96 (32), 95 (18), 93 (9), 91 (7), 87 (5), 86 (70), 85 (6), 83 (4), 82 (4), 81 (15), 79 (11), 77 (5), 69 (12), 68 (10), 67 (23), 58 (8), 56 (4), 55 (36), 54 (10), 53 (10), 43 (11), 42 (7), 41 (44), 40 (4), 39 (20). (Found: C, 72.25; H, 9.75. Calc for $C_{11}H_{18}O_2$ (182.26): C, 72.49; H, 9.95 %).

(-)-(4*R*,5*R*,10*R*)-4,10-Diphenyl-1,6-dioxaspiro[4.5]decane [(*R*,*R*,*R*)-**17e**]. 1 g crude (*S*,*S*,*S*)-**13e** and approx. 1.5 eq PTSA in several small portions (TLC control). 309 mg (55.7 % based on (*S*)-**6e**) of a colorless oil after chromatography (SiO_2, ether:pentane = 1:20); $[\alpha]_D^{28}$ = -14.1° (c = 0.82, EtOH); IR (KBr):

3100-3020 (CH_{arom}), 2980-2840 (CH), 1600, 1490, 1455, 1440, 1380, 1355, 1320, 1300, 1270, 1230, 1210, 1180, 1140, 1100, 1070, 1050, 1030, 1015, 970, 950, 910, 880, 820, 760, 740, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.50-2.44 (m, 6H, $3CH_2$), 2.75 (m, 2H, 2CH), 3.74 (m, 2H, CH_2O), 4.05 (m, 2H, CH_2O), 7.30 (m, 10H, H_{arom}) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 26.07, 28.97, 31.49, 47.58 (CH), 50.59 (CH), 60.66 (CH_2O), 65.58 (CH_2O), 106.17 (OCO), 126.52, 126.59, 127.74, 128.13, 129.48, 129.97, 138.38, 142.85 ppm; MS: m/z (r.I. %) = 295 (2, $M^+ + 1$), 294 (10, M^+), 163 (9), 162 (7), 132 (13), 131 (3), 119 (4), 118 (31), 117 (27), 115 (7), 105 (11), 104 (100), 103 (6), 91 (11, $C_7H_7^+$), 78 (6), 77 (4), 51 (3). (Found: C, 81.28; H, 7.46. Calc for $C_{20}H_{22}O_2$ (294.40): C, 81.60; H, 7.53 %).

(4*R*,5*S*,10*R*)-4,10-Diphenyl-1,6-dioxaspiro[4.5]decane [(*R*,*S*,*R*)-**17e**] and (4*S*,5*R*,10*R*)-4,10-Diphenyl-1,6-dioxaspiro[4.5]decane [(*S*,*R*,*R*)-**17e**]. 80.2 mg (14.5 % based on (*S*)-**6e**) of a colorless solid after chromatography (SiO_2, ether:pentane = 1:20) containing 2 diastereomers; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 19.45, 27.85, 33.15, 43.53 (CH), 52.98 (CH), 61.06 (CH_2O), 65.71 (CH_2O), 109.27 (OCO), 125.68, 125.78, 127.40, 127.45, 128.44, 129.42, 138.08, 142.05 ppm for (*R*,*S*,*R*)-**14e**; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 26.01, 29.50, 30.23, 47.95 (CH), 54.93 (CH), 62.63 (CH_2O), 66.60 (CH_2O), 109.02 (OCO), 125.96, 126.43, 127.17, 127.66, 128.47, 129.64, 138.00, 141.89 ppm for (*S*,*R*,*R*)-**14e**.

(+)-(5*S*,6*R*,12*S*)-5,12-Dimethyl-1,7-dioxaspiro[5.6]dodecane [(*S*,*R*,*S*)-**18a**]. 0.5 g crude (*S*,*S*,*S*)-**14a** and approx. 1.5 eq PTSA in several small portions (TLC control). 68.9 mg (35 % based on (*S*)-**6a**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:30); $[\alpha]_D^{28}$ = +61.6° (c = 0.90, EtOH); IR (film): 2995-2840 (CH), 1460, 1440, 1380, 1360, 1290, 1240, 1220, 1180, 1160, 1150, 1130, 1100, 1080, 1060, 1035, 990, 960, 940, 920 cm^{-1}: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.93 (d, 3H, J = 6.7Hz, CH_3), 1.05 (d, 3H, J = 7.4Hz, CH_3), 1.20-1.90 (m, 12H, $5CH_2$, 2CH), 3.58 (m, 3H, CH_2O, CHHO), 3.78 (m, 1H, CHHO) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 17.54 (CH_3), 18.81 (CH_3), 26.21, 28.48, 30.36, 30.39, 32.83, 35.40 (CH), 45.55 (CH), 60.44 (CH_2O), 60.67 (CH_2O), 103.24 (OCO) ppm; MS: m/z (r.I. %) = 199 (3, $M^+ + 1$), 198 (20, M^+), 156 (9), 140 (15), 139 (12), 129 (37), 128 (10), 126 (16), 125 (11), 116 (8), 115 (100), 114 (6), 112 (11), 111 (21), 102 (4), 98 (6), 97 (18), 83 (17), 69 (16), 55 (9), 44 (6), 41 (5), 40 (4). (Found: C, 72.42; H, 11.30. Calc for $C_{12}H_{22}O_2$ (198.31): C, 72.68; H, 11.18 %).

(+)-(5*S*,6*R*,12*S*)-5,12-Diethyl-1,7-dioxaspiro[5.6]dodecane [(*S*,*R*,*S*)-**18b**]. 0.5 g crude (*S*,*S*,*S*)-**14b** and approx. 1.5 eq PTSA in one portion. 92.5 mg (49 % based on (*S*)-**6b**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:30); $[\alpha]_D^{26}$ = +36.6° (c = 0.59, EtOH); IR (film): 2995-2840 (CH), 1460, 1440, 1380, 1290, 1260, 1230, 1215, 1180, 1160, 1150, 1110, 1090, 1070, 1045, 1010, 995, 975, 950, 880, 835 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.82 (t, 3H, J = 7.4Hz, CH_3), 0.96 (t, 3H, J = 7.0Hz, CH_3), 1.08-1.70 (m, 15H, $7CH_2$, CH), 1.84 (m, 1H, CH), 3.58 (m, 3H, CH_2O, CHHO), 3.79 (m, 1H, CHHO) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 11.26 (CH_3), 13.36 (CH_3), 23.09, 23.28, 24.68, 25.99, 28.71, 30.37, 30.90, 42.27 (CH), 53.89 (CH), 60.58 (CH_2O), 60.68 (CH_2O), 103.60 (OCO) ppm; MS: m/z (r.I. %) = 227 (2, $M^+ + 1$), 226

(14, M^+), 211 (1, M^+-CH_3), 197 (3), 170 (6), 168 (4), 167 (6), 155 (5), 154 (6), 143 (48), 140 (6), 139 (6), 130 (7), 129 (100), 128 (3), 126 (7), 125 (12), 114 (5), 113 (5), 112 (5), 111 (8), 98 (8), 97 (27), 84 (7), 83 (34), 73 (5), 71 (11), 69 (15), 67 (5), 59 (7), 57 (9), 56 (14), 55 (54), 53 (4), 46 (9). (Found: C, 73.94; H, 11.42. Calc for $C_{14}H_{26}O_2$ (226.36): C, 74.29; H, 11.58 %).

(+)-(7*S*,1*R*,11*S*)-2,15-Dioxatricyclo[9.4.0.$0^{1,7}$]pentadecane [(*S*,*R*,*S*)-**18d**]. 0.66 g crude (*S*,*S*,*S*)-**14d** and approx. 1.5 eq PTSA in several small portions (TLC control). 114.9 g (46 % based on (*S*)-**6d**) of a colorless liquid after chromatography (SiO_2, ether:pentane = 1:10); IR (film): 2995-2850 (CH), 1470, 1440, 1380, 1370, 1355, 1290, 1260, 1245, 1210, 1190, 1150, 1130, 1110, 1090, 1065, 1050, 1030, 1005, 960, 945, 930, 900, 890 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 1.17-1.92 (m, 19H, 8CH_2, 1CH), 2.14 (m, 1H, CH), 3.55 (m, 2H, 2CHHO), 3.80 (m, 2H, 2CHHO) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 20.44, 21.10, 24.31, 28.48, 29.54, 30.25, 30.59, 32.18, 36.02 (CH), 44.76 (CH), 59.95 (CH_2O), 60.91 (CH_2O), 100.56 (OCO) ppm; MS: m/z (r.I. %) = 211 (15, M^+ + 1), 210 (90, M^+), 181 (3), 180 (16), 165 (4), 152 (17), 151 (78), 139 (16), 138 (42), 137 (20), 127 (4), 124 (5), 123 (6), 114 (12), 113 (100), 110 (9), 109 (13), 101 (15), 100 (64), 99 (5), 97 (10), 96 (4), 95 (20), 93 (5), 91 (5), 83 (4), 82 (4), 81 (15), 79 (8), 77 (4), 71 (5), 69 (8), 68 (6), 67 (19), 56 (3), 55 (25), 54 (7), 53 (7), 43 (8), 42 (6). (Found: C, 74.01; H, 10.70. Calc for $C_{13}H_{22}O_2$ (210.32): C, 74.24; H, 10.54 %).

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