Enantioselective Synthesis of Polyfunctional Small Building Blocks with a Quaternary Stereogenic Center

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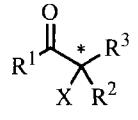
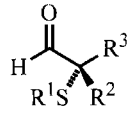
Application of the SAMP-/RAMP-hydrazone method offers an efficient and flexible access to compounds with a quaternary stereogenic center. Examples bearing silyl, thio, phenyl, aldo, keto, ester, and alkyl functionalities are described. The 2-phenylaldehydes and -ketones and the β-keto esters **4** were obtained in good overall yields and with variable enantiomeric excesses. The synthesis of the thiolated 2-formyl and 3-formyl carboxylic esters **12** was achieved in high overall yields and with high enantiomeric excesses. The silylated carboxylic ester and acids **16** were produced in moderate to high overall yields and with moderate to excellent enantiomeric excesses, depending on the electrophile used for the quaternization. The absolute configurations of the compounds **12** and **16** were determined by X-ray structure analyses, and the mechanism of the quaternization is postulated.

The design of asymmetric syntheses for molecules with a quaternary carbon center as chirons for the generation of natural products and biologically active compounds is an attractive and challenging field in synthetic organic chemistry. Since Martin's review[1] of the creation of quaternary carbon centers a number of efforts have been made during the last decade to extend the range of enantioselective methods[2]. Since highly regio-, diastereo-, and enantioselective electrophilic substitutions at the C_α position of the carbonyl group of ketones and aldehydes by the SAMP-/RAMP-hydrazone method[3] are well established, it was decided to explore the high potential of this methodology in the asymmetric creation of small polyfunctional building blocks bearing a quaternary carbon center[3a,4]. Our research group has already reported on a highly enantioselective synthesis of 2-alkyl-2-cyanocycloalkanones **D** with a quaternary stereogenic center[5] and demonstrated in a short communication[6] an efficient enantioselective route to quaternary 2-formyl esters and carboxylic acids. The enantioselective synthesis of the small polyfunctional building blocks **A**, **B**, and **C** using the SAMP-/RAMP-hydrazone method is described in this paper in full detail.



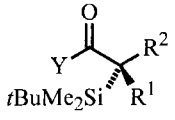
A

X : Ph, CO_2Me, CO_2Et
R^1: H, Me
R^2: Me
} -$(CH_2)_3$-, -$(CH_2)_4$-
R^3: Me, Et, Allyl, *n*-Pr



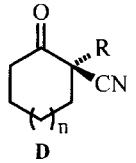
B

R^1: Me, Ph
R^2: Et, *n*-Pr, *n*-Bu, *n*-Hex, *n*-Oct, *n*-Dec, *n*-Undec, $CH_2C_6H_2(OMe)_3$
R^3 : CO_2Me, CH_2CO_2Me



C

Y : H, OH
R^1: Me, Et, *n*-Pr, *n*-Bu, *n*-Hex, *n*-Oct, *n*-Undec, *n*-Dodec
R^2: CO_2Me, Me, Et, *n*-Pr, *i*-Pr,



D

R: Me, Et, *n*-Pr, *n*-Bu, *n*-Hex
n: 1, 3

The racemic 2-phenyl aldehydes and ketones and the racemic 2-oxo carboxylic acids were easily transformed into the corresponding SAMP- and the (*S*)-1-amino-2-{[(methoxyethoxy)methoxy]methyl}pyrrolidine (SAMEMP)-hydrazones **2** (for the synthesis of SEMEMP see scheme 2). The β-keto ester SAMP-hydrazones exist as a 1:2 mixture of the hydrazone/ene hydrazine tautomeric form. The 2-phenyl derivatives **2a–c** were added to a solution of LDA in THF at −78°C and after alkylation with alkyl halides at −100°C the 2-phenylhydrazones **3a–d** were prepared in good yields. Metalation of the β-keto ester SAMP- and the SAMEMP-hydrazones[3a,4] with *n*BuLi in THF at −100°C followed by trapping of the intermediate aza-allyl anion with alkyl halides furnished the corresponding hydrazones **3e–l** in good yields. After hydrazone cleavage (**3a**, **b**: acidic hydrolysis via the methiodide in a two-phase system; **3c**, **d**: acidic hydrolysis in a two-phase system; **3d–l**: ozonolysis) the optically active 2-phenyl aldehydes and ketones and the β-keto esters **4** were obtained in good yields (53–80%) with

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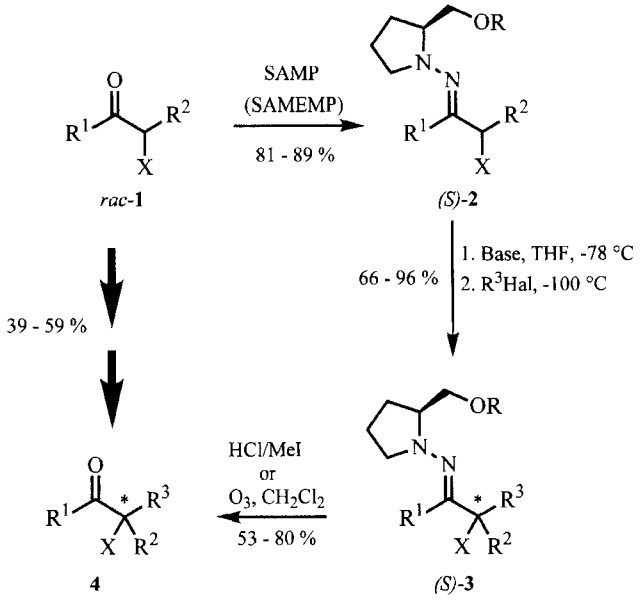
enantiomeric excesses ranging between 18 and 93% (Scheme 1).

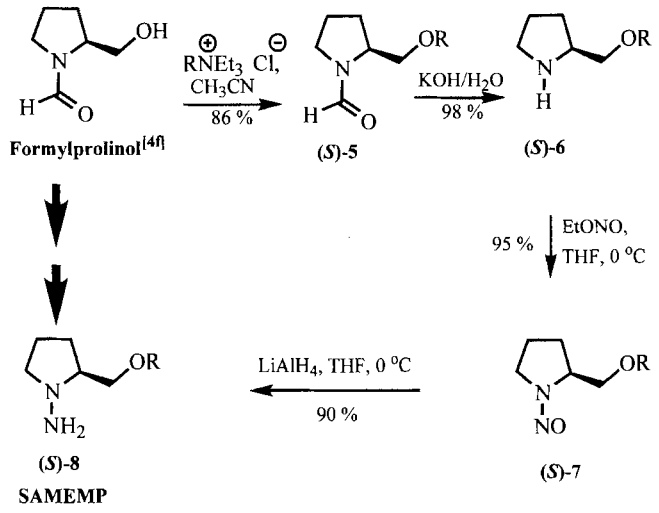
Scheme 1



X : Ph, CO_2Me, CO_2Et
R : CH_3, $CH_2OCH_2CH_2OCH_3$
R^1: H, Me; R^2: Me } $-(CH_2)_3-$, $-(CH_2)_4-$
R^3: Me, Et, Allyl, *n*-Pr

The diastereomeric and the enantiomeric excesses of the hydrazones **3** and the quaternary carbonyl compounds **4** were determined by LIS-NMR techniques using the achiral shift reagent $Eu(fod)_3$ and the chiral shift reagent $Eu(hfc)_3$, respectively. The absolute configuration of the hydrazones **3** were not determined.

Scheme 2



R = $CH_2OCH_2CH_2OCH_3$

SAMEMP **8** was used as a chiral auxiliary in an attempt to achieve a stronger chelation by the increased number of oxygens in the pyrrolidine side chain. A comparison of the results (**3a** versus **3k**, **3b** versus **3l**) revealed no significant effect on the degree of asymmetric induction (Table 1). Although the ee values of the quaternary carbonyl compounds **4** are in general relatively low (18–93%) the excep-

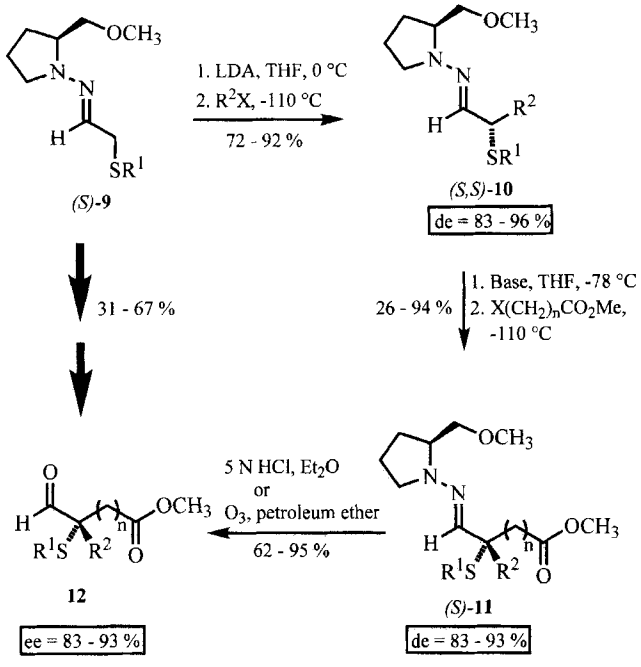
Table 1. SAMP- and SAMEMP-hydrazones **3** and α-quaternary carbonyl compounds **4**

2[a]	R^1	R^2	X	**3**[a]	R^3	yield [%]	α_D^{RT} neat or (*c*, C_6H_6)	de[b] [%]	**4**[a]	yield [%]	$[\alpha]_D^{RT}$ (*c*, $CHCl_3$)	ee[c] [%]
(*S*)-**2a**	H	Me	Ph	(*S*)-**3a**	Allyl	85	–76.6	30	**4a**	64	–35.2 (1.39)	30
(*S*)-**2b**	H	Me	Ph	(*S*)-**3b**	Et	83	–78.9	28	**4b**[d]	76	–2.9 (4.19)	25
(*S*)-**2c**	$-(CH_2)_3-$		Ph	(*S*)-**3c**	Me	69	+289.5 (1.19)	[e]	**4c**[d]	73	+69.5 (1.24)[f]	77
(*S*)-**2d**	$-(CH_2)_4-$		Ph	(*S*)-**3d**	Me	66	+402.8 (1.42)	[e]	**4d**[d]	80	+200.4(2.38)[g]	93
(*S*)-**2e**	$-(CH_2)_3-$		CO_2Me	(*S*)-**3e**	Me	85	+240.2	60	**4e**	78	–7.4 (1.16)	60
(*S*)-**2f**	$-(CH_2)_3-$		CO_2Me	(*S*)-**3f**	Et	96	+233.5	23	**4f**	73	+3.7 (1.21)	18
(*S*)-**2g**	$-(CH_2)_4-$		CO_2Me	(*S*)-**3g**	Et	93	+211.6	42	**4g**	68	+67.6 (3.04)	43
(*S*)-**2h**	Me	Me	CO_2Et	(*S*)-**3h**	Et	85	+232.7	[e]	**4h**	62	+1.8 (1.33)	27
(*S*)-**2i**	$-(CH_2)_4-$		CO_2Et	(*S*)-**3i**	Allyl	73	+163.8	20	—	—	—	—
(*S*)-**2j**[h]	Me	Me	CO_2Et	(*S*)-**3j**[h]	*n*-Pr	83[i]	+193.5	[e]	**4i**[h]	76	+2.1 (1.46)	31
(*S*)-**2k**[h]	H	Me	Ph	(*S*)-**3k**[h]	Allyl	86	–62.5	[e]	**4a**[h]	76	–27.6 (1.17)	24
(*S*)-**2l**[h]	H	Me	Ph	(*S*)-**3l**[h]	Et	90	–66.0	[e]	**4b**[d,h]	53	–3.2 (1.36)	28

[a] The absolute configuration was not determined. – [b] Determined by $Eu(fod)_3$ shift. – [c] Determined by $Eu(hfc)_3$ shift. – [d] The absolute configuration was determined to be (*R*) by a comparison with literature data[16,17]. – [e] Not determined. – [f] Measured in CH_3CH_2OH. – [g] Measured in C_6H_{12}. – [h] SAMEMP [(*S*)-**8**] was used instead of SAMP as auxiliary [*R* = $CH_2OCH_2CH_2OCH_3$]. – [i] 50% of the substance was starting material.

tional case of (*R*)-**4d** (ee = 93%) demonstrated the possibility of high induction by using the SAMP-/RAMP-hydrazone method. This prompted us to optimize the results of this method not only by a variation of the reaction parameters (temperature, solvent, cosolvent, base) but also by changing the neighboring anion-stabilizing groups. Instead of phenyl and ester groups, thio, silyl, and cyano[5] groups were investigated.

Scheme 3



R^1: Me, Ph

R^2: Et, *n*-Pr, *n*-Bu, *n*-Hex, *n*-Oct, *n*-Dec, *n*-Undec, $CH_2C_6H_2(OMe)_3$

n : 0, 1

Table 2. SAMP- and RAMP-hydrazones **11** and thiolated 2-formyl and 3-formyl methyl esters **12**

11	R^1	R^2	n	yield [%]	α_D^{RT} neat or (*c*, C_6H_6)	de[a] [%]	**12**	yield [%]	$[\alpha]_D^{RT}$ (*c*,C_6H_6)	ee[b] [%]
(*S,R*)-**11a**	Ph	Et	0	91	−22.9 (1.13)	90	(*R*)-**12a**	90	+155.6 (1.06)	90
(*R,S*)-**11a**[c]	Ph	Et	0	69	+23.3 (1.00)	92	(*S*)-**12a**[c]	95	−161.7 (1.03)	92
(*S,R*)-**11b**	Ph	*n*-Pr	0	91	−27.1	92	(*R*)-**12b**	80	+127.8 (0.98)	92
(*S,R*)-**11c**	Ph	*n*-Bu	0	90	−25.3	92	(*R*)-**12c**	83	+162.7 (1.10)	92[d]
(*R,S*)-**11c**[c]	Ph	*n*-Bu	0	73	+9.9 (0.87)	92	(*S*)-**12c**[c]	75	−158.5 (1.05)	92
(*S,R*)-**11d**	Ph	*n*-Hex	0	85	−11.7 (1.06)	92	(*R*)-**12d**	95	+136.1 (0.98)	92
(*S,R*)-**11e**	Ph	*n*-Oct	0	77	−19.2	92	(*R*)-**12e**	95	+112.7 (1.15)	92
(*S,R*)-**11f**	Ph	*n*-Dec	0	94	−14.4	91	(*R*)-**12f**	83	+100.8 (1.07)	91
(*S,R*)-**11g**	Ph	*n*-Undec	0	91	−14.5	93	(*R*)-**12g**	82	+109.4 (1.20)	93
(*S,R*)-**11h**	Ph	[e]	0	60	−26.3 (1.14)	93	(*R*)-**12h**	62	+141.9 (0.94)	93
(*S,R*)-**11i**	Me	Et	0	82	−85.0	88	(*R*)-**12i**	79	+109.9 (1.38)	88
(*S,S*)-**11j**	Me	Et	1	26	−79.3 (1.13)	91	(*S*)-**12j**	80	−20.9 (0.23)	91
(*S,S*)-**11k**	Ph	Et	1	75	−31.1 (0.97)	83	(*S*)-**12k**	63	−62.6 (1.01)	83
(*S,S*)-**11l**	Ph	*n*-Hex	1	64	−15.9 (1.06)	87	(*S*)-**12l**	25[f]	−57.5 (1.05)	87

[a] Determined by ^{13}C-NMR spectroscopy. – [b] Indirectly determined by ^{13}C-NMR spectroscopy of the hydrazone **11**. – [c] RAMP was used instead of SAMP as auxiliary. – [d] Determined by ^{19}F-NMR spectroscopy of the Mosher ester[8] of the corresponding alcohol. – [e] R^2: $CH_2C_6H_2(OMe)_3$. – [f] Byproduct methyl 3-formylnon-3-enoate.

The α-thiolated hydrazones **9**[7], easily prepared from the corresponding aldehyde and SAMP, were metalated with LDA in THF at 0°C and the lithio derivatives converted diastereoselectively to the hydrazones **10**[7] (de = 83–96%) in high yields (72–92%) by alkylation with various electrophiles at −110°C. Deprotonation with a base (*n*BuLi, LDA, or MeLi) in THF at −78°C followed by quaternization of the azaallyl anion with methyl chloroformate or methyl bromoacetate at −110°C yielded the α-thiolated hydrazones **11**. Acylation with methyl chloroformate furnished the 2-formyl ester derivatives **11a–i** in good yields (60–94%) and with high diastereomeric excesses (de = 88–93%). The quaternization with methyl bromoacetate afforded the hydrazones **11j–l** with good diastereomeric excesses (de = 83–91%) but only in moderate yields (26–75%) due to the lower reactivity of methyl bromoacetate compared with methyl chloroformate. The hydrazones **11a–i** were hydrolytically cleaved with 5 N HCl in a two-phase system with diethyl ether to the enantiomerically enriched 2- and 3-formyl esters **12a–i** (ee = 88–93%) in good yields (62–95%). Since the hydrolytic cleavage of **11l** led to the formation of methyl 3-formylnon-3-enoate as a byproduct, resulting in a low yield (25%) of the desired product **12k**, the hydrazone **11k** was oxidatively cleaved with ozone. The antipodes of the *R* enantiomers of the 2-formyl esters were synthesized by using RAMP instead of SAMP as a chiral auxiliary [(*R*)-**12a** versus (*S*)-**12a** and (*R*)-**12c** versus (*S*)-**12c**].

The diastereomeric excesses of hydrazones **10** and **11** were determined by ^{13}C-NMR spectroscopy. The enantiomeric excesses of the 2- and 3-formyl esters **12** were determined indirectly by ^{13}C-NMR spectroscopy of the hydrazones **11**. The hydrolytic cleavage of the quaternary hydrazones took place without racemization, as proven by the determination of the enantiomeric excess of (*R*)-**12c** by ^{19}F-NMR spectroscopy of the 3,3,3-trifluoro-2-methoxy-2-phenylpropionic acid ester (Mosher's ester[8]) of the corresponding alcohol, which was obtained by reduction of (*R*)-**12c** with $NaBH_4$ in ethanol.

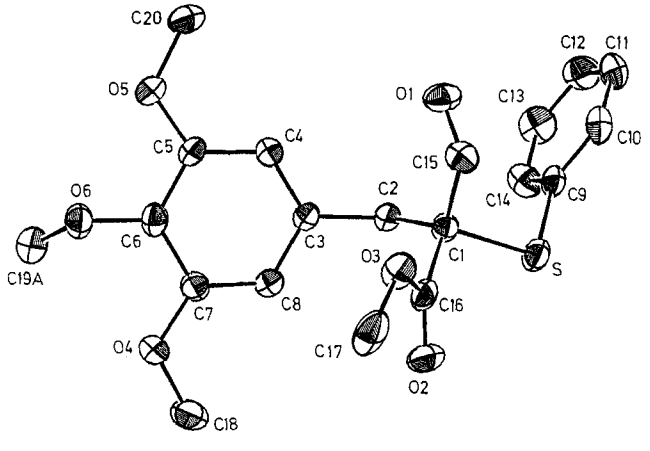


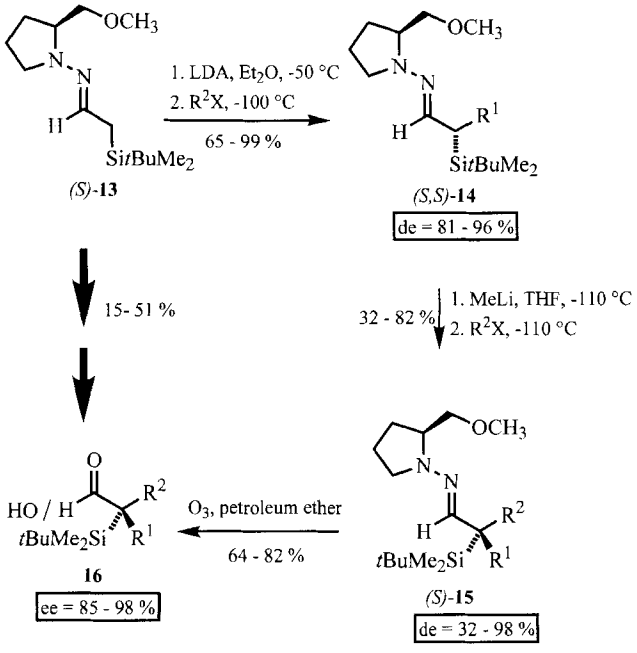
Figure 1. Molecular structure of (*R*)-**12g** in the solid state[9]. Only one component of the disordered carbon atom C19 is shown (ORTEP[10] plot)

Since all 2- and 3-formyl esters **12** were previously unknown in optically pure form, the absolute configuration

needed to be determined. Suitable crystals of (*R*)-**12g** for the X-ray structure analysis were obtained from diethyl ether/petroleum ether (1:2) at room temperature (Figure 1). The *R* configuration found at the quaternary stereogenic center confirmed the postulated mechanism for electrophilic substitutions via SAMP-/RAMP-hydrazones[3a,11].

The α-silylated hydrazone **13**[6] was prepared by silylation of the deprotonated acetaldehyde SAMP-hydrazone with *tert*-butyldimethylsilyl chloride. Metalation of this hydrazone with LDA in diethyl ether at −50°C and subsequent reaction with different alkyl iodides at −100°C afforded the α-alkylated α-silylated hydrazones **14** in good yields (65−96%) and with high enantiomeric excesses (81−96%). After deprotonation of **14** with MeLi and quaternization with various electrophiles, the hydrazones **15** were obtained with moderate to excellent diastereomeric excesses (de = 32−98%) and in good yields (32−82%). After oxidative cleavage with ozone, the 2-formyl esters **16a−f** were obtained in good yields (66−82%) and with high enantiomeric excesses (ee = 90−98%). Ozonolysis of hydrazones **15g**, **j**, **l**, and **m** (R^2: alkyl) gave the corresponding carboxylic acids instead of the aldehydes. The α-quaternary carboxylic acids **16g−j** were obtained in good yields (64−74%) and with high enantiomeric excesses (85−93%).

Scheme 4



R^1: Me, Et, *n*-Pr, *n*-Bu, *n*-Hex, *n*-Oct, *n*-Undec, *n*-Dodec

R^2: CO_2Me, Me, Et, *n*-Pr, *i*-Pr

The highest diastereomeric excesses for the quaternary hydrazones **15** were obtained by treatment with methyl chloroformate as the electrophile (de = 90−98%), but only moderate yields were achieved (32−62%) because of a competing *N*-acylation of the metalated species, providing the corresponding methyl *N*-[2-(*tert*-butyldimethylsilyl)-1-alkenyl]-*N*-SMP-carbamate. Concerning quaternization with alkyl iodides, the best results were obtained with ethyl iodide (Table 3). Using starting materials with a short side chain such as **14a**, **c**, and **d**, we synthesized the hydrazones **15g**, **i**, and **j** in good yields (79−82%) and with high diastereomeric excesses (de = 85−93%). If starting materials with a long side chain were used for the alkylation with ethyl iodide the resultant yields were lower (39−41%), whereas the diastereomic excesses were in a similar range (de = 84−88%). In comparison with ethyl iodide, the use of the other homologues (propyl and methyl iodide) and the branched homologue (isopropyl iodide) resulted in lower chemical yields (39−41%), but with still high asymmetric inductions (de = 84−93%). Quaternization with methyl iodide proceeded only in moderate yields (32−48%) with low diastereomeric excesses (de = 63−66%). The diastereomeric excesses of the hydrazones **14** and **15** were determined by ^{13}C-NMR spectroscopy. The enantiomeric excesses of the 2-formyl ester and carboxylic acids **16** were determined indirectly by ^{13}C-NMR spectroscopy of the hydrazones **15**. Racemization by oxidative cleavage with ozone was not observed[3].

Table 3. SAMP- and RAMP-hydrazones **15** and silylated quaternary carbonyl compounds **16**

15	R^1	R^2	yield [%]	$[\alpha]_D^{RT}$ neat or (*c*, C_6H_6)	de[a] [%]	**16**	yield [%]	$[\alpha]_D^{RT}$ (*c*, C_6H_6)	ee[b] [%]
(*S,R*)-**15a**	Et	CO_2Me	56	+7.1 (1.48)	90	(*R*)-**16a**	77	−183.1 (1.00)	90
(*S,R*)-**15b**	*n*-Pr	CO_2Me	47	−12.0	96	(*R*)-**16b**	66	−167.9 (0.97)	96
(*S,R*)-**15c**	*n*-Bu	CO_2Me	62	+7.1 (0.98)	97	(*R*)-**16c**	82	−124.9 (1.18)	97
(*S,R*)-**15d**	*n*-Hex	CO_2Me	52	0.0 (0.95)	98	(*R*)-**16d**	75	−126.1 (0.93)	98
(*S,R*)-**15e**	*n*-Oct	CO_2Me	43	+4.3 (1.20)	96	(*R*)-**16e**	75	−131.1 (0.97)	96
(*R,S*)-**15e**[c]	*n*-Oct	CO_2Me	32	−5.6 (1.18)	98	(*S*)-**16e**[c]	73	+107.6 (1.22)	98
(*S,R*)-**15f**	*n*-Undec	CO_2Me	62	+4.1 (1.02)	96	(*R*)-**16f**	74	−112.1 (1.00)	96
(*S,S*)-**15g**	Me	Et	82	−120.5 (1.00)	93	(*S*)-**16g**	70[d]	+2.3 (0.97)	93
(*S,R*)-**15g**	Et	Me	66	−68.7 (1.07)	32	—	—	—	—
(*S,R*)-**15h**	*n*-Bu	Me	63	−55.6 (1.18)	48	—	—	—	—
(*S,R*)-**15i**	*n*-Pr	Et	87	−75.0 (1.09)	86	—	—	—	—
(*S,S*)-**15i**	Et	*n*-Pr	66	−96.6 (1.04)	79	—	—	—	—
(*S,R*)-**15j**	*n*-Bu	Et	79	−78.8 (1.03)	85	(*R*)-**16h**	74[d]	+9.0 (0.92)	85
(*S,S*)-**15j**	Et	*n*-Bu	69	−91.7 (1.03)	75	—	—	—	—
(*S,R*)-**15k**	*n*-Oct	Et	39	−61.3 (0.97)	84	—	—	—	—
(*S,R*)-**15l**	*n*-Dodec	Et	41	−57.4 (1.03)	88	(*R*)-**16i**	64[d]	+11.6 (1.09)	88
(*S,S*)-**15m**	*n*-Dodec	*i*-Pr	41	−85.7 (1.05)	93	(*S*)-**16j**	66[d]	+8.7 (0.98)	93

[a] Determined by ^{13}C-NMR spectroscopy. − [b] Indirectly determined by ^{13}C-NMR spectroscopy of the hydrazone **15**. − [c] RAMP was used instead of SAMP as auxiliary. − [d] The corresponding carboxylic acid was isolated instead of the aldehyde after ozonolysis.

The absolute configurations of the 2-formyl esters and carboxylic acids **16** were determined by X-ray structure analysis of the carboxylic acid (*S*)-**16g** (Figure 2). The *S* configuration found at the new stereogenic center was in agreement with that predicted by the postulated mechanism for electrophilic substitutions via SAMP-/RAMP-hydrazones[3a,11].

In conclusion, the application of the SAMP-/RAMP-hydrazone method to asymmetric syntheses of highly enantiomerically enriched polyfunctional chirons bearing a quaternary stereogenic center has been shown. The absolute configuration of **B** and **C** and the mechanism of the electro-

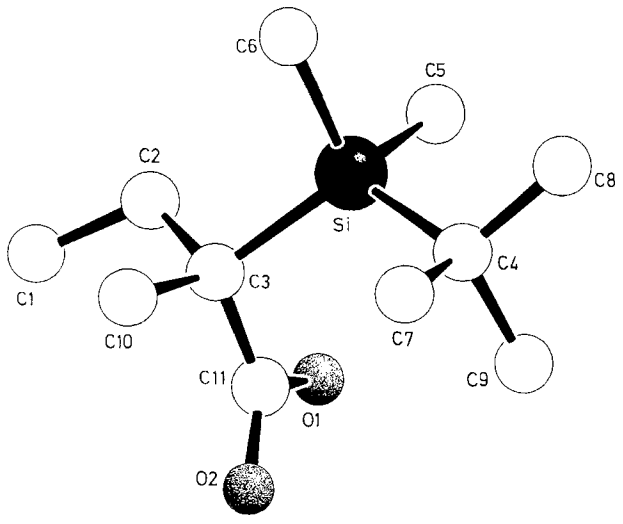


Figure 2. Molecular structure of (*S*)-**16g**[9] in the solid state (SCHAKAL[12] plot)

philic substitution to give a quaternary carbon center by using SAMP-/RAMP-hydrazone has been proven. The use of these building blocks for the enantioselective synthesis of β,β-disubstituted γ-lactones and γ-quaternary oxiranes has already been investigated[4e]. Further applications to the enantioselective synthesis of biologically active compounds and natural products can now be studied.

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Experimental

^1H and ^{13}C NMR: in $CDCl_3$, TMS as internal reference, Varian XL 100, Varian EM-390, Varian VXR 300 or a Unity 500. – IR: Beckman Acculab 4 or Perkin-Elmer Infracord 337. – MS: Kratos MS-30 or Varian MAT 212 (70 eV). – Optical rotation: Room temperature, Perkin Elmer P 241 polarimeter. – Microanalyses: Heraeus CHN-O-RAPID element analyzer. – Ozonolyses: Fischer ozone generator type 502. – TLC analyses: Merck TLC plates silica gel 60 F_{254}. – All solvents were dried and distilled according to standard procedures. – Bromoacetaldehyde diethyl acetal was purchased from Janssen, Beerse, Belgium. (*S*)- and (*R*)-1-Amino-2-(methoxymethyl)pyrrolidine (SAMP and RAMP) were synthesized according to the literature procedure[11a] from (*S*)- and (*R*)-proline.

(S)-1-Formyl-2-{[(2-methoxyethoxy)methoxy]methyl}pyrrolidine (**5**): To a solution of 1.29 g (10 mmol) of *N*-formylprolinol in 20 ml of acetonitrile was added a solution of 3.39 g (15 mmol) of triethyl[(2-methoxyethoxy)methyl]ammonium chloride[13] in 25 ml of acetonitrile. After refluxing of the reaction mixture for 14 h and storage at 2°C overnight the precipitate of triethylammonium chloride was filtered, washed with diethyl ether, and the combined organic phases were concentrated in vacuo. Reduced-pressure distillation of the residue afforded 1.86 g (86%) of a colorless oil; b.p. 121–122°C/0.25 Torr, $\alpha_D^{22} = -31.0$ (neat). – IR (neat): $\tilde{\nu} = 2930\ cm^{-1}$, 2880, 2810, 1665, 1455, 1410, 1380, 1345, 1240, 1110, 1040, 845, 750, 720. – ^1H NMR ($CDCl_3$): δ = 2.03 (m, 4H, CH_{2pyr}), 3.32–3.97 (m, 8H, NCH_2, OCH_2, OCH_2CH_2O), 3.54 (s, 3H, OCH_3), 4.00–4.20 (m, 1H, NCH), 4.84 (s, 2H, OCH_2O), 8.39, 8.46 (s, 1H, CHO, *E*/*Z* = 3:1). – MS, *m/z* (%): 218 (1) [M^+ + 1], 217 (2) [M^+], 112 (73), 111 (53), 98 (100) [$C_5H_8NO^+$], 70 (90), 68 (27), 59 (72), 55 (28), 45 (39), 43 (45), 41 (49). – $C_{10}H_{19}NO_4$ (217.3): calcd. C 55.28, H 8.81, N 6.45; found C 54.85, H 8.81, N 6.70.

(S)-2-{[(2-Methoxyethoxy)methoxy]methyl}pyrrolidine (**6**): To a solution of 6.31 g (112.5 mmol) of KOH in 55 ml of water was added slowly 16.30 g (75 mmol) **5**. The resultant mixture was refluxed for 4 h until completion of the reaction (TLC control). After repeated extraction with CH_2Cl_2 the combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. Reduced-pressure distillation of the residue afforded 13.88 g (98%) of a colorless oil; b.p. 78°C/0.15 Torr, $\alpha_D^{22} = -3.5$ (neat). – IR (neat): $\tilde{\nu} = 3350$ (NH) cm^{-1}, 2930, 2875, 1455, 1410, 1365, 1280, 1240, 1195, 1170, 1110, 1045, 980, 930, 845. – ^1H NMR ($CDCl_3$): δ = 1.75 (m, 4H, CH_{2pyr}), 2.06 (s, 1H, NH), 2.90 (m, 2H, NCH_2), 3.06–3.82 (m, 7H, OCH_2, NCH, OCH_2-CH_2O), 3.40 (s, 3H, OCH_3), 4.71 (s, 2H, OCH_2O). – MS, *m/z* (%): 190 (1) [M^+ + 1], 114 (24) [$C_6H_{12}NO^+$], 84 (42) [$C_5H_{10}N^+$], 70 (100) [$C_4H_8N^+$], 59 (31), 55 (32), 45 (41), 43 (35), 41 (32). – $C_9H_{19}NO_2$ (189.5): calcd. C 57.11, H 10.21, N 7.40; found C 56.85, H 10.08, N 7.20.

(S)-2-{[(2-Methoxyethoxy)methoxy]methyl}-1-nitrosopyrrolidine (**7**): 12.36 g of a 85% solution of ethyl nitrite (140 mmol) was dissolved in 50 ml of THF and the solution cooled to 0°C. To this solution was added dropwise 13.31 g (70.33 mmol) of **6**. The reaction mixture was allowed to warm to room temp. overnight and stirred for 22 h at this temp. (TLC control). After concentration in vacuo the product was distilled under reduced pressure to afford 14.61 g (95%) of a yellow oil; b.p. 118°C/0.1 torr, $\alpha_D^{22} = -65.6$ (neat). – IR (neat): $\tilde{\nu} = 2930\ cm^{-1}$, 2880, 2820, 1665, 1450, 1415, 1360, 1300, 1195, 1170, 1150, 1110, 1040, 980, 965, 940, 890, 845, 805, 770. – ^1H NMR ($CDCl_3$): δ = 2.06 (m, 4H, CH_{2pyr}), 3.20–3.82 (m, 6H, NCH_2, OCH_2-CH_2O), 3.43 (s, 3H, OCH_3), 3.96 (d, 2H, OCH_2), 4.52–4.83 (m, 1H, NCH), 4.74 (s, 2H, OCH_2O). – MS, *m/z* (%): 218 (<1) [M^+], 89 (27), 70 (37), 59 (100), 55 (39), 45 (63), 42 (37), 41 (55). – $C_9H_{12}N_2O_4$ (189.5): calcd. C 49.53, H 8.31, N 12.84; found C 49.76, H 8.41, N 12.49.

(S)-1-Amino-2-{[(2-methoxyethoxy)methoxy]methyl}pyrrolidine (SAMEMP)[4a] (**8**): In a 250-ml three-necked flask 5.28 g (139.1 mmol) of $LiAlH_4$ was suspensed in 120 ml of THF, then 14.02 g (64.24 mmol) of **7** in 30 ml of THF was added dropwise to the suspension during 2 h. The resultant reaction mixture was refluxed for 4 h and stirred overnight. After hydrolysis with 2 ml of a 10% KOH solution and 18 ml of water, the resulting slurry was filtered with suction, and the precipitate was refluxed in THF (150 ml) for 4 h, filtered and then the process repeated with fresh THF (150 ml). The combined THF extracts were concentrated in vacuo. The resultant oil was dissolved in CH_2Cl_2 and the solution dried with Na_2SO_4. After concentration of the solution, reduced-pressure distillation of the residue afforded 11.85 g (90%) of a colorless oil; b.p. 87–88°C/0.1 Torr, $\alpha_D^{22} = -71.5$ (neat). – IR (neat): $\tilde{\nu} = 3350$ (NH_2) cm^{-1}, 3150, 2930, 2880, 2820, 1605, 1460, 1410, 1365, 1280, 1240, 1200, 1170, 1110, 1050, 980, 930, 850. – ^1H NMR ($CDCl_3$): δ = 1.75 (m, 4H, CH_{2pyr}), 2.40 (m, 2H, NCH_2), 2.82–3.86 (m, 7H, NCH, OCH_2O, OCH_2CH_2O), 3.18 (s, 2H, NCH_2), 3.42 (s, 3H, OCH_3), 4.76 (s, 2H, OCH_2O). – ^{13}C NMR ($CDCl_3$): δ = 20.9 (NCH_2CH_2), 26.6 (CH_2CH), 58.8 (OCH_3), 60.2 (CH_2N), 66.8 (CH_2OCH_3), 68.3 (CH), 70.3 (CH_2O), 71.9 (OCH_2CH_2), 95.8 (OCH_2O). – MS, *m/z* (%): 205 (2) [M^+ + 1], 204 (12) [M^+], 97 (40), 85 (79), 83 (52), 70 (100) [$C_4H_8N^+$], 68 (30), 59 (51), 45 (37), 44 (20), 41 (56). – $C_9H_{20}N_2O_3$ (204.3): calcd. C 52.92, H 9.87, N 13.72; found C 52.90, H 9.94, N 13.36.

(RS,S)-2-(Methoxymethyl)-1-[(2-phenylpropyliden)amino]pyrrolidine (**2a**): To 2.60 g (20 mmol) of SAMP was added dropwise 2.68 g (20 mmol) of (±)-2-phenylpropanal at 0°C. After refluxing at 60°C until completion of the reaction (TLC control) the reaction mixture was extracted with CH_2Cl_2/H_2O (4:1). The organic phase was dried with $NaSO_4$ and concentrated in vacuo. Reduced-pressure distillation of the residue afforded 4.30 g (87%) of a light yellow oil; b.p. 112–113°C/0.15 Torr, $\alpha_D^{22} = -91.5$ (neat). – IR (neat): $\tilde{\nu} = 3080$–$2780\ cm^{-1}$, 1600, 1490, 1450, 1370, 1355, 1300, 1280, 1190, 1140–1080, 1050, 1010, 970, 900, 760, 695. – ^1H NMR (CCl_4): δ = 1.35 (d, 3H, CH_3), 1.80 (m, 4H, NCH_{2pyr}), 2.65 (m, 1H, NCH_2), 2.95–3.75 (m, 5H, NCH_2, NCH, CH_2O, CH), 3.25 (s, 3H, OCH_3), 6.48 (d, 1H, CHN), 7.15 (m, 5H, C_6H_5). – MS, *m/z* (%): 246 (3) [M^+], 201 (100) [$M^+ - CH_2OCH_3$], 105 (47), 70 (33). – $C_{15}H_{22}N_2O$ (246.4): calcd. C 73.13, H 9.00, N 11.37; found C 73.10, H 8.71, N 11.33.

(RS,S)-2-(Methoxymethyl)-1-[(2-phenylcyclopentyliden)amino]pyrrolidine (**2c**): 7.25 g (89%) of **2c** was prepared from 3.91 g (30 mmol) of SAMP and 4.81 g (30 mmol) of (±)-2-phenylcyclopentanone according to the procedure described for the synthesis of **2a**; b.p. 135°C/0.2 Torr, $\alpha_D^{22} = +234.8$ (neat). – IR (neat): $\tilde{\nu} = 3080\ cm^{-1}$, 3055, 3020, 2960, 2870, 2820, 2720, 1640 (CN), 1600, 1490, 1445, 1420, 1375, 1335, 1270, 1190, 1100, 1040, 1025, 1000, 960, 905, 840, 750, 695. – ^1H NMR ($CDCl_3$): δ = 1.14–2.88 (m, 11H, NCH_{2pyr}, NCH_2, CH_2), 2.90–3.94 (m, 5H, NCH_2, NCH, CH_2O, CH), 3.33, 3.37 (s, 3H, OCH_3), 7.33 (m, 5H, C_6H_5). – MS, *m/z* (%): 273 (2) [M^+ + 1], 272 (8) [M^+], 227 (100) [$M^+ - CH_2OCH_3$], 158 (70) [$C_{11}H_{12}N^+$], 117 (83), 115 (23), 91 [$C_7H_7^+$], 70 (47), 45 (23). – $C_{17}H_{24}N_2O$ (272.4): calcd. C 74.96, H 8.88, N 10.29; found C 75.10, H 8.75, N 10.25.

(RS,S)-2-(Methoxymethyl)-1-[(2-phenylcyclohexyliden)amino]-pyrrolidine (**2d**): 6.92 g (81%) of **2d** was prepared from 3.91 g (30 mmol) of SAMP and 5.23 g (30 mmol) of (±)-2-phenylcyclohexanone by the same procedure as described for the synthesis of **2a**; b.p. 132–133°C/0.03 Torr, $\alpha_D^{24} = +234.6$ (neat). – IR (neat): $\tilde{\nu} = 3090\ cm^{-1}$, 3060, 3030, 2940, 2860, 1635 (CN), 1600, 1495, 1450, 1195, 1125, 1050, 1030, 1000, 970, 920, 845, 770, 725, 700. – ^1H NMR ($CDCl_3$): δ = 1.40–2.08 (m, 10H, NCH_{2pyr},

CH_2), 2.20–2.68 (m, 3H, NCH_2, CH_2), 2.90–3.56 (m, 4H, NCH, NCH_2, CH_2O), 3.32, 3.37, 3.39 (s, 3H, OCH_3), 3.75, 4.85 (m, 1H, CH, *E*/*Z*), 7.30 (m, 5H, C_6H_5). – MS, *m/z* (%): 286 (<1) [M^+], 172 (83), [$C_{12}H_{14}N^+$], 171 (42), 145 (53), 144 (93), 129 (27), 91 (36), 82 (40), 70 (82) [$C_4H_8N^+$], 45 (100) [$CH_2OCH_3^+$], 41 (43). – $C_{18}H_{26}N_2O$ (286.4): calcd. C 75.48, H 9.15, N 9.78; found C 75.22, H 9.02, N 9.69.

(RS,S)-1-{[2-(Methoxycarbonyl)cyclopentyliden]amino}-2-(methoxymethyl)pyrrolidine (**2e**): 7.52 g (84%) of **2e** was prepared from 4.56 g (35 mmol) of SAMP and 4.47 ml (36 mmol) of methyl (±)-2-oxocyclopentanecarboxylate by the same procedure as described for **2a**. The product was a 2:1 mixture of the ene-hydrazine (A)/hydrazone (B) tautomers. The optical rotation was measured directly after distillation; b.p. 111–113°C/0.03 Torr, $\alpha_D^{22} = -39.6$ (neat). – IR (neat): $\tilde{\nu}$ = 3270 (NH, A) cm^{-1}, 2950, 2875, 1735 (C=O, B), 1665 (C=O, A), 1605 (CN, B), 1460, 1430, 1385, 1335, 1300, 1270, 1185, 1120, 1040, 920, 770. – ^1H NMR ($CDCl_3$): δ = 1.56–2.14 (m, 6H, NCH_{2pyr}, CH_2), 2.40–2.97 (m, 6H, NCH_2, CH_2), 3.10–3.52 [m, ≈ 3.3H, NCH, CH_2O, CH (B)], 3.34, 3.35 (s, 3H, OCH_3, A:B ≈ 2:1), 3.68 (s, 3H, CO_2CH_3), 7.72 [br s, ≈0.7H, NH(A)]. – MS, *m/z* (%): 255 (1) [M^+ + 1], 254 (1) [M^+], 209 (24), 177 (31), 151 (100) [$M^+ - CH_2OCH_3 - CO_2H_3$], 82 (81), 70 (56), 55 (32). – $C_{13}H_{22}N_2O_3$ (254.3): calcd. C 61.39, H 8.72, N 11.02; found C 61.59, H 8.70, N 10.89.

(RS,S)-1-{[2-(Methoxycarbonyl)cyclohexyliden]amino}-2-(methoxymethyl)pyrrolidine (**2g**): 9.43 g (87%) of **2g** was prepared from 5.21 g (40 mmol) of SAMP and 6.40 g (41 mmol) of methyl (±)-2-oxocyclohexanecarboxylate by the same procedure as described for **2a**. The product was a 2:1 mixture of the ene-hydrazine (A)/hydrazone (B) tautomers; b.p. 115°C/0.07 Torr, $\alpha_D^{22} = +24.5$ (neat). – IR (neat): $\tilde{\nu}$ = 3220, 3160 (NH, A) cm^{-1}, 2940, 2860, 1735 (C=O, B), 1655 (C=O, A), 1595 (CN, B), 1445, 1380, 1240, 1185, 1170, 1120, 1070, 1060, 1005, 980, 965, 910, 880, 855, 820, 770, 630. – ^1H NMR ($CDCl_3$): δ = 1.34–2.97 (m, 13H, NCH_{2pyr}, CH_2, NCH_2), 3.02–3.58 (m, 4H, NCH_2, NCH, OCH_2), 3.38 (s, 3H, OCH_3), 3.70, 3.73 (s, 3H, CO_2CH_3, A/B ≈ 2:1), 4.60 [m, ≈0.3H, CH (B)], 9.42 [br s, ≈0.7H, NH (A)]. – MS, *m/z* (%): 269 (2) [M^+ + 1], 268 (14) [M^+], 223 (100) [$M^+ - CH_2OCH_3 - CO_2H_3$], 122 (56), 100 (28), 94 (69), 70 (65), 55 (41), 45 (53). – $C_{14}H_{24}N_2O_3$ (268.4): calcd. C 62.66, H 9.01, N 10.44; found C 62.45, H 8.98, N 10.46.

(RS,S)-1-{[2-(Ethoxycarbonyl)-1-methylpropyliden]amino}-2-(methoxymethyl)pyrrolidine (**2j** with SAMP): 4.00 g (16.5 mmol) of (*RS,S*)-1-{[2-(ethoxycarbonyl)-1-methylethyliden]amino}-2-(methoxymethyl)pyrrolidine, which was prepared from SAMP and ethyl 3-oxobutyrate according to the procedure described for **2a**, was metalated with *n*BuLi (16.5 mmol) at −78°C for 30 min and alkylated with 1.03 ml (17 mmol) of methyl iodide at −78°C. After stirring at this temp. for 3 h the reaction mixture was allowed to warm to room temp. The reaction was quenched with diethyl ether/water (2:1). After twofold extraction of the aqueous phase with diethyl ether, the combined organic phases were dried with $MgSO_4$. The product was purified by reduced-pressure distillation yielding 3.76 g (89%) of a yellow oil; b.p. 95–96°C/0.3 Torr, $\alpha_D^{22} = +252.7$ (neat). – IR (neat): $\tilde{\nu}$ = 2980 cm^{-1}, 2940, 2880, 2830, 2730, 1730 (C=O), 1635, 1595, 1450, 1365, 1325, 1295, 1250, 1180, 1095, 1020, 990, 965, 910, 860. – ^1H NMR ($CDCl_3$): δ = 1.24 (t, 3H, OCH_2CH_3), 1.30 (d, 3H, CH_3), 1.50–2.13 (m, 4H, NCH_{2pyr}), 1.88 (s, 3H, CH_3), 2.42 (m, 1H, NCH_2), 2.80–3.56 (m, 5H, NCH_2, NCH, OCH_2, CH), 3.35 (s, 3H, OCH_3), 4.15 (q, 2H, OCH_2CH_3). – MS; *m/z* (%): 257 (2) [M^+ + 1], 256 (9) [M^+], 211 (100) [$M^+ - CH_2OCH_3$], 73 (42), 70 (40), 55 (27), 45 (30), 42 (62). – $C_{13}H_{24}N_2O_3$ (256.3): calcd. C 60.91, H 9.44, N 10.93; found C 61.02, H 9.57, N 10.84.

(RS,S)-1-{[2-(Ethoxycarbonyl)cyclohexyliden]amino}-2-(methoxymethyl)pyrrolidine (**2i**): 2.50 g (89%) of **2i** was prepared from 1.30 g (10 mmol) of SAMP and 1.87 g (11 mmol) of ethyl (±)-2-oxocyclohexanecarboxylate by the same the procedure as described for **2a**. The product was a 2:1 mixture of the ene-hydrazine (A)/hydrazone (B) tautomeres; b.p. 118–119°C/0.25 Torr, $\alpha_D^{22} = +46{,}4$ (neat). – IR (neat): $\tilde{\nu}$ = 3220, 3160 (NH, A) cm^{-1}, 2975, 2930, 2860, 1730 (C=O, B), 1650 (C=O, A), 1590 (CN, B), 1445, 1420, 1360, 1340, 1240, 1170, 1120, 1090, 1070, 1060, 970, 910, 986, 770. – ^1H NMR ($CDCl_3$): δ = 1.24 (t, 3H, CH_3), 1.35–2.98 (m, 13H, NCH_{2pyr}, CH_2, NCH_2), 3.00–3.62 (m, 4H, NCH_2, NCH, OCH_2), 3.31 (s, 3H, OCH_3), 4.08, 4.12 (q, 2H, OCH_2CH_3), 4.56 [m, ≈0.3H, CH (B)], 9.25 [br s, ≈0.7H, NH (A)]. – MS, *m/z* (%): 282 (4) [M^+], 137 (41) [$M^+ - CH_2OCH_3$], 122 (32), 94 (34), 70 (54), 55 (29), 45 (68), 44 (36). – $C_{15}H_{26}N_2O_3$ (282.4): calcd. C 63.80, H 9.28, N 9.92; found C 64.01, H 9.30, N 9.87.

(RS,S)-1-{[2-(Ethoxycarbonyl)-1-methylpropyliden]amino}-2-{[(2-methoxyethoxy)methoxy]methyl}pyrrolidine (**2j** with SAMEMP): To a solution of 2.57 g (8.12 mmol) of (*RS,S*)-1-{[2-(ethoxycarbonyl)-1-methylethyliden]-amino}-2-{[2-(methoxyethoxy)methoxy]methyl}pyrrolidine (prepared from SAMEMP and ethyl 3-oxobutyrate according to the procedure described for **2a**) in 20 ml of THF was added 5.1 ml (8.12 mmol) of *n*BuLi at −78°C. After stirring for 30 min at this temp. 0.60 (10 mmol) of methyl iodide was added. The reaction was quenched with CH_2Cl_2/water (2:1). After extraction of the aqueous phase twice with CH_2Cl_2, the combined organic phases were dried with Na_2SO_4. Reduced-pressure distillation yielded 2.14 g (80%) of a light yellow oil; b.p. 130°C/0.08 Torr, $\alpha_D^{22} = +191.7$ (neat). – IR (neat): $\tilde{\nu}$ = 2980 cm^{-1}, 2940, 2880, 1735 (C=O), 1640, 1455, 1365, 1330, 1250, 1175, 1115, 1045, 930, 855. – ^1H NMR ($CDCl_3$): δ = 1.24 (t, 3H, OCH_2CH_3), 1.30 (d, 3H, CH_3), 1.48–2.20 (m, 4H, NCH_{2pyr}), 1.86 (s, 3H, CH_3), 2.44 (m, 1H, NCH_2), 2.80–3.80 (m, 9H, NCH_2, NCH, OCH_2, CH, OCH_2-CH_2O), 3.42 (s, 3H, OCH_3), 4.12 (q, 2H, OCH_2CH_3), 4.70 (s, 2H, OCH_2O). – MS, *m/z* (%): 331 (1) [M^+ + 1], 330 (3) [M^+], 211 (100) [$M^+ - CH_2OCH_2$-$OCH_2CH_2OCH_3$], 125 (22), 70 (33), 59 (59), 55 (30), 45 (30), 42 (55), 41 (39). – $C_{16}H_{30}N_2O_5$ (330.4): calcd. C 58.16, H 9.15, N 8.48; found C 58.40, H 9.25, N 8.50.

(RS,S)-2-{[(2-Methoxyethoxy)methoxy]methyl}-1-[(2-phenylpropyliden)amino]pyrrolidine (**2k**): 4.22 g (82%) of **2k** was prepared from 3.27 g (16 mmol) of SAMEMP and 2.15 g (16 mmol) of (±)-2-phenylpropanal by the same the procedure as described for **2a**; b.p. 150–170°C/0.03 Torr, $\alpha_D^{22} = -77.6$ (neat). – IR (neat): $\tilde{\nu}$ = 3095 cm^{-1}, 3070, 3035, 2980, 2940, 2880, 2825, 1605 (CN), 1495, 1455, 1410, 1365, 1340, 1300, 1280, 1240, 1200, 1115, 1045, 930, 850, 760, 700. – ^1H NMR ($CDCl_3$): δ = 1.43 (d, 3H, CH_3), 1.85 (m, 4H, NCH_{2pyr}), 2.75 (m, 1H, NCH_2), 3.16–3.96 (m, 9H, NCH_2, NCH, CH, OCH_2, OCH_2CH_2O), 3.41, 3.42 (s, 3H, OCH_3), 4.76, 4.78 (s, 2H, OCH_2O), 6.72 (d, 1H, CHN), 7.34 (m, 5H, C_6H_5). – MS, *m/z* (%): 321 (1) [M^+ + 1], 320 (4) [M^+], 201 (58), 105 (100) [$C_8H_9^+$], 77 (23). – $C_{18}H_{28}N_2O_3$ (320.4): calcd. C 67.47, H 8.81, N 8.74; found C 67.74, H 8.82, N 8.53.

(S)-1-[(2-Allyl-2-phenylpropyliden)amino]-2-(methoxymethyl)pyrrolidine (**3a**): To 5.05 mmol of LDA in 30 ml of THF at −78°C was added 1.23 g (5 mmol) of **2a**. After warming to 0°C and stirring for 7 h at this temp. the reaction mixture was cooled to −100°C, and 0.50 ml (5.8 mmol) of 3-bromopropene was added. After stirring at this temp. for 3 h the reaction mixture was allowed to warm to room temp. The reaction mixture was poured into diethyl ether/water (2:1) and the aqueous layer extracted twice with diethyl ether. After drying of the combined organic phases with Na_2SO_4 the product was purified by reduced-pressure distillation, yielding 1.22 g (85%) of a light yellow oil; b.p. 140°C/0.06 Torr, $\alpha_D^{22} = -76.6$ (neat); de = 30% [Eu(fod)$_3$ shift]. – IR (neat): $\tilde{\nu}$ = 3075 cm^{-1}, 3060, 3025, 2975, 2930, 2875, 2825, 2730 (CH), 1640 (CN), 1600, 1490, 1460, 1440, 1370, 1340, 1300, 1280, 1190, 1120, 1070, 1030, 990, 970, 910, 760, 700. – ^1H NMR ($CDCl_3$): δ = 1.46 (s, 3H, CH_3), 1.90 (m, 4H, CH_{2pyr}), 2.62 (d, 2H, $CH_2CH=CH_2$), 2.85 (m, 1H, NCH_2), 3.10–3.74 (m, 4H, NCH_2, CH, OCH_2), 3.40 (s, 3H, OCH_3), 4.80–5.12 (m, 2H, $CH=CH_2$), 5.35–5.88 (m, 1H, $CH=CH_2$), 6.68 (s, 1H, CHN), 7.00–7.48 (m, 5H, C_6H_5). – MS, *m/z* (%): 245 (33) [$M^+ - CH_2CH=CH_2$], 241 (100) [$M^+ - CH_2OCH_3$], 200 (30), 130 (100) [$C_9H_8N^+$], 114 (55), 103 (53), 70 (79), 45 (94), 41 (70). – $C_{18}H_{26}N_2O$ (286.4): calcd. C 75.48, H 9.15, N 9.78; found C 75.60, H 9.20, N 9.80.

(S)-2-(Methoxymethyl)-1-[(2-methyl-2-phenylbutyliden)amino]pyrrolidine (**3b**): 1.23 g (5.0 mmol) of **2a** was transformed by treatment with 5.05 mmol of *n*BuLi and 0.46 ml (5.8 mmol) of iodoethane into 1.14 g (83%) of **3b** by the same procedure as described for **3a**; b.p. 150–160°C/0.05 Torr, $\alpha_D^{22} = -78.9$ (neat); de = 28% [Eu(fod)$_3$ shift]. – IR (neat): $\tilde{\nu}$ = 3090 cm^{-1}, 3060, 3025, 2970, 2930, 2880, 2825 (CH), 1600, 1490, 1455, 1380, 1340, 1300, 1190, 1120, 1070, 1030, 970, 900, 760, 700. – ^1H NMR ($CDCl_3$): δ = 0.78 (t, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.92 (m, 6H, CH_{2pyr}, CH_2), 2.72 (m, 1H, NCH_2), 3.10–3.85 (m, 4H, NCH_2, CH, OCH_2), 3.41 (s, 3H, OCH_3), 6.72 (s, 1H, CHN), 7.04–7.52 (m, 5H, C_6H_5). – MS, *m/z* (%): 275 (2) [M^+ + 1], 274 (7) [M^+], 229 (100) [$M^+ - CH_2OCH_3$], 133 (58), 130 (54), 117 (39), 103 (30), 91 (76) [$C_7H_7^+$], 77 (28), 70 (73), 55 (33), 45 (45). – $C_{17}H_{26}N_2O$ (274.4): calcd. C 74.41, H 9.55, N 10.21; found C 74.65, H 9.55, N 9.73.

(S)-2-(Methoxymethyl)-1-[(2-methyl-2-phenylcyclopentyliden)amino]pyrrolidine (**3c**): 1.36 g (5.0 mmol) of **2c** was transformed by treatment with 4.9 mmol of *n*BuLi and 0.31 ml (5.1 mmol) of methyl iodide into 0.97 g (69%) of **3c** by the same procedure as described for **3a**. The product was purified by flash chromatography (SiO_2, diethyl ether); $[\alpha]_D^{22} = +289.5$ (*c* = 1.19, C_6H_6). – IR (neat): $\tilde{\nu}$ = 3085 cm^{-1}, 3060, 3020, 2960, 2925, 2870, 2825, 2730 (CH), 1640 (CN), 1600, 1490, 1445, 1420, 1370, 1340, 1275, 1195, 1120, 1045, 1030, 970, 940, 910, 760, 700. – ^1H NMR ($CDCl_3$): δ = 1.17–2.88 (m, 11H, CH_{2pyr}, CH_2, NCH_2), 1.45, 1.46 (s, 3H, CH_3), 3.00–3.64 (m, 4H, NCH_2, CH, OCH_2), 3.40, 3.41 (s, 3H, OCH_3), 7.01–7.52 (m, 5H, C_6H_5). – MS, *m/z* (%): 287 (2) [M^+ + 1], 286 (7) [M^+], 241 (71) [$M^+ - CH_2OCH_3$], 172 (70) [$C_{12}H_{14}N^+$], 131 (69), 130 (30), 104 (97), 103 (30), 91 (100) [$C_7H_7^+$], 78 (32), 77 (37), 70 (60), 45 (67) [$CH_2OCH_3^+$], 41 (67). – $C_{18}H_{26}N_2O$ (286.4): calcd. C 75.48, H 9.15, N 9.78; found C 75.65, H 9.09, N 9.73.

(S)-2-(Methoxymethyl)-1-[(2-methyl-2-phenylcyclohexyliden)amino]pyrrolidine (**3d**): 1.43 g (5.0 mmol) of **2d** was transformed by treatment with 4.5 mmol of *n*BuLi and 0.31 ml (5.1 mmol) of methyl iodide into 0.89 g (66%) of **3d** by the same procedure as described for **3a**. The product was purified by flash chromatography (SiO_2, diethyl ether/*n*-pentane, 1:1); $[\alpha]_D^{22} = +402.8$

(*c* = 1.42, C_6H_6). – IR (neat): $\tilde{\nu}$ = 3090 cm^{-1}, 3060, 3025, 2965, 2935, 2860, 2825 (CH), 1630 (CN), 1600, 1490, 1450, 1370, 1195, 1120, 1025, 1000, 970, 910, 760, 700. – ^1H NMR ($CDCl_3$): δ = 1.28 (s, 3H, CH_3), 1.30–2.16 (m, 10H, CH_{2pyr}, CH_2), 2.28–2.70 (m, 3H, CH_{2pyr} NCH_2), 2.90–3.65 (m, 4H, NCH_2, CH, OCH_2), 3.39 (s, 3H, OCH_3), 7.20 (m, 5H, C_6H_5). – MS, *m/z* (%): 301 (12) [M^+ + 1], 300 (50) [M^+], 255 (100) [M^+ – CH_2OCH_3], 188 (42), 186 (99) [$C_{13}H_{16}N^+$], 130 (97), 117 (44), 105 (87), 104 (56), 91 (79) [$C_7H_7^+$], 70 (71). – $C_{19}H_{28}N_2O$ (300.4): calcd. C 75.95, H 9.39, N 9.33; found C 75.73, H 9.34, N 9.05.

(S)-1-{[2-(Methoxycarbonyl)-2-methylcyclopentyliden]amino}-2-(methoxymethyl)pyrrolidine (**3e**): 1.27 g (5.0 mmol) of **2e** was dissolved in 20 ml of THF and the solution cooled to –100°C. To this 5.5 mmol of *n*BuLi was added dropwise. To complete the metalation the reaction mixture was stirred at –100°C for 5 min. Alkylation was performed with 0.35 ml (5.7 mmol) of methyl iodide and purification according to the procedure described for **3a** yielding 1.14 g (85%) of a yellow oil; b.p. 130–140°C/0.1 Torr, α_D^{22} = +240.2 (neat); de = 60% [Eu(fod)$_3$ shift]. – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2870, 2825, 2730 (CH), 1735 (C=O), 1685, 1650, 1560, 1460, 1430, 1370, 1340, 1310, 1265, 1190, 1150, 1050, 1010, 970, 905, 870, 835, 760, 740. – ^1H NMR ($CDCl_3$): δ = 1.40 (s, 3H, CH_3), 1.52–2.10 (m, 7H, CH_{2pyr} CH_2), 2.10–2.73 (m, 4H, CH_{2pyr} CH_2), 3.08–3.56 (m, 4H, NCH_2, CH, OCH_2), 3.36 (s, 3H, OCH_3), 3.68 (s, 3H, CO_2CH_3). – MS, *m/z* (%): 269 (2) [M^+ + 1], 268 (16) [M^+], 223 (100) [M^+ – CH_2OCH_3], 122 (36), 94 (47), 70 (87), 69 (32), 55 (34), 45 (43), 42 (33), 41 (82). – $C_{14}H_{24}N_2O_3$ (268.4): calcd. C 62.66, H 9.01, N 10.44; found C 63.08, H 9.05, N 10.41.

(S)-1-{[2-Ethyl-2-(methoxycarbonyl)cyclopentyliden]amino}-2-(methoxymethyl)pyrrolidine (**3f**): 1.27 g (5.0 mmol) of **2e** was transformed by treatment with 5.5 mmol of *n*BuLi and 0.46 ml (5.8 mmol) of iodoethane into 1.34 g (96%) of **3f** by the same procedure as described for **3e**; b.p. 130–150°C/0.3 Torr, α_D^{22} = +233.5 (neat); de = 23% [Eu(fod)$_3$ shift]. – IR (neat): $\tilde{\nu}$ = 2970 cm^{-1}, 2880, 2730 (CH), 1730 (C=O), 1640, 1460, 1430, 1380, 1330, 1290, 1230, 1190, 1145, 1095, 1000, 970, 910, 840, 800, 770. – ^1H NMR ($CDCl_3$): δ = 0.88 (t, 3H, CH_3), 1.48–2.80 (m, 13H, CH_{2pyr} CH_2, CH_2CH_3, NCH_2), 3.08–3.60 (m, 4H, NCH_2, CH, OCH_2), 3.34, 3.36 (s, 3H, OCH_3), 3.70, 3.71 (s, 3H, CO_2CH_3). – MS, *m/z* (%): 283 (4) [M^+ + 1], 282 (21) [M^+], 237 (100) [M^+ – CH_2OCH_3], 108 (41), 70 (92). – $C_{15}H_{26}N_2O_3$ (282.4): calcd. C 63.80, H 9.28, N 9.92; found C 63.75, H 9.29, N 9.88.

(S)-1-{[2-Ethyl-2-(methoxycarbonyl)cyclohexyliden]amino}-2-(methoxymethyl)pyrrolidine (**3g**): 1.34 g (5.0 mmol) of **2g** was transformed by treatment with 5.5 mmol of *n*BuLi and 0.46 ml (5.8 mmol) of iodoethane into 1.38 g (93%) of **3g** by the same procedure as described for **3e**; b.p. 160–180°C/0.4 Torr, α_D^{22} = +211.6 (neat); de = 42% [Eu(fod)$_3$ shift]. – IR (neat): $\tilde{\nu}$ = 2940 cm^{-1}, 2875, 2730 (CH), 1730 (C=O), 1630, 1450, 1375, 1340, 1290, 1275, 1245, 1215, 1115, 1050, 995, 970, 940, 920, 810, 790, 740. – ^1H NMR ($CDCl_3$): δ = 0.90 (t, 3H, CH_3), 1.16–2.72 (m, 15H, CH_{2pyr} CH_2, CH_2CH_3, NCH_2), 2.75–3.58 (m, 4H, NCH_2, CH, OCH_2), 3.37 (s, 3H, OCH_3), 3.72 (s, 3H, CO_2CH_3). – MS, *m/z* (%): 297 (3) [M^+ + 1], 296 (14) [M^+], 251 (100) [M^+ – CH_2OCH_3], 165 (41), 150 (49), 122 (47), 96 (33), 70 (54), 55 (27). – $C_{16}H_{28}N_2O_3$ (296.4): calcd. C 64.83, H 9.52, N 9.45; found C 65.32, H 9.48, N 9.45.

(S)-1-{[2-(Ethoxycarbonyl)-1,2-dimethylbutyliden]amino}-2-(methoxymethyl)pyrrolidine (**3h**): 1.28 g (5.0 mmol) of **2h** was transformed by treatment with 5.5 mmol of *n*BuLi and 0.42 ml (5.3 mmol) of iodoethane into 1.21 g (85%) of **3h** by the same procedure as described for **3e**; b.p. 120–140°C/0.03 Torr, α_D^{22} = +232.7 (neat). – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2935, 2875, 2825, 2730 (CH), 1730 (C=O), 1630, 1460, 1360, 1295, 1235, 1110, 1050, 965, 910, 855, 760. – ^1H NMR ($CDCl_3$): δ = 0.82, 0.84 (t, 3H, OCH_2CH_3), 1.23, 1.25 (t, 3H, OCH_2CH_3), 1.32, 1.34 (s, 3H, CH_3), 1.50–2.20 (m, 6H, CH_{2pyr}, CH_2CH_3), 1.83, 1.88 (s, 3H, CH_3), 2.40 (m, 1H, NCH_2), 3.02–3.64 (m, 4H, NCH_2, CH, OCH_2), 3.38 (s, 3H, OCH_3), 4.38, 4.39 (q, 2H, OCH_2CH_3). – MS, *m/z* (%): 285 (2) [M^+ + 1], 284 (7) [M^+], 239 (39) [M^+ – CH_2OCH_3], 153 (98), 85 (63), 73 (38), 70 (46), 58 (53), 57 (71), 43 (44), 42 (100). – $C_{15}H_{28}N_2O_3$ (284.4): calcd. C 63.35, H 9.92, N 9.85; found C 63.06, H 9.08, N 10.26.

(S)-1-{[2-Allyl-2-(ethoxycarbonyl)cyclohexyliden]amino}-2-(methoxymethyl)pyrrolidine (**3i**): 2.80 g (10 mmol) of **2i** was transformed by treatment with 5.5 mmol of *n*BuLi/11 mmol of HMPA and 1.20 g (10 mmol) of 3-bromopropene into 2.35 g (73%) of **3i** by the same procedure as described for **3e**; b.p. 125–135°C/0.02 Torr, α_D^{20} = +163.8 (neat); de = 20% [Eu(fod)$_3$ shift]. – IR (neat): $\tilde{\nu}$ = 3080–2780 cm^{-1} (CH), 1730 (CO), 1640 (C=C), 1460, 1450, 1370, 1290, 1270, 1220, 1140, 1130, 1100, 1040, 1010, 980, 920. – ^1H NMR ($CDCl_3$): δ = 1.23 (t, 3H, CH_2CH_3), 1.40–2.75 (m, 14H, CH_2, CH_{2pyr}, $CH_2CH{=}CH_2$), 2.85–3.60 (m, 5H, NCH_2, CH, OCH_2), 3.35 (s, 3H, OCH_3), 4.10 (q, 2H, OCH_2CH_3), 4.82–5.14 (m, 2H, $CH{=}CH_2$), 5.50–6.15 (m, 1H, $CH{=}CH_2$). – MS, *m/z* (%): 322 (0.5) [M^+], 307 (23), 277 [100, M^+ – OC_2H_5], 210 (41), 136 (30), 70 (42), 45 (23). – $C_{18}H_{30}N_2O_3$ (322.4): calcd. C 67.05, H 9.37, N 8.68; found C 67.12, H 9.64, N 9.08.

(S)-1-{[2-(Ethoxycarbonyl)-1,2-dimethylpentyliden]amino}-2-{[(2-methoxyethoxy)methoxy]methyl}pyrrolidine (**3j**): 1.65 g (5.0 mmol) of **2j** was metalated with 3.15 ml (5 mmol) of *n*BuLi according to the procedure described for **3e**. At –100°C 0.59 ml (6 mmol) of 1-iodopropane was added, and the reaction mixture was stirred for another 30 min at this temp. After warming to room temp. overnight the product was purified by the procedure described for **3a**. Distillation yielded 1.55 g (83%) of a yellow oil which consisted of 50% starting material. A small amount of this sample was purified by flash chromatography (SiO_2, diethyl ether); α_D^{22} = +193.5 (neat). – IR (neat): $\tilde{\nu}$ = 2965 cm^{-1}, 2940, 2880 (CH), 1730 (C=O), 1630, 1570, 1460, 1365, 1240, 1200, 1175, 1120, 1045, 980, 930, 850. – ^1H NMR ($CDCl_3$): δ = 0.88 (t, 3H, $CH_2CH_2CH_3$), 1.00–1.46 (m, 8H, CH_3, $CH_2CH_2CH_3$, OCH_2CH_3), 1.46–2.16 (m, 9H, CH_{2pyr} CH_3, $CH_2CH_2CH_3$), 2.40 (m, 1H, NCH_2), 2.95–3.80 (m, 8H, NCH_2, OCH_2, CH, OCH_2CH_2O), 3.40 (s, 3H, OCH_3), 4.10, 4.12 (q, 2H, OCH_2CH_3), 4.70 (s, 2H, OCH_2O). – MS, *m/z* (%): 372 (6) [M^+], 254 (13), 253 (100) [M^+ – $CH_2OCH_2OCH_2CH_2OCH_3$], 140 (39), 112 (33), 85 (66), 70 (83), 59 (93), 58 (60), 57 (71), 55 (47), 41 (81). – $C_{19}H_{36}N_2O_5$ (372.5): calcd. C 61.26, H 9.74, N 7.72; found C 60.65, H 9.64, N 7.87.

(S)-1-[(2-Allyl-2-phenylpropyliden)amino]-2-{[(2-methoxyethoxy)methoxy]methyl}pyrrolidine (**3k**): 1.28 g (4.0 mmol) of **2k** was metalated at –78°C with 2.81 ml (4.4 mmol) of *n*BuLi for 30 min and alkylated with 0.41 ml (4.8 mmol) of 3-bromopropene at –110°C according to the procedure described for **3e**. After warming to room temp. overnight the product was purified by the procedure described for **3a** yielding 1.24 g (86%) of a yellow oil; b.p. 180°C/0.08 torr, α_D^{22} = –62.5 (neat). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 3030, 2930, 2880 (CH), 1640, 1600, 1490, 1450, 1410, 1375, 1365, 1340, 1320, 1300, 1280, 1240, 1200, 1115, 1050, 910, 850, 760, 700, 640. – ^1H NMR ($CDCl_3$): δ = 1.44 (s, 3H, CH_3), 1.90 (m, 4H, CH_{2pyr}), 2.54–2.97 (m, 3H, NCH_2, $CH_2CH{=}CH_2$), 3.10–3.96 (m, 8H, NCH_2, OCH_2, NCH, OCH_2CH_2O), 3.42 (s, 3H, OCH_3), 4.78 (s, 2H, OCH_2O), 4.85–5.17 (m, 2H, $CH{=}CH_2$), 5.40–5.92 (m, 1H, $CH{=}CH_2$), 6.72 (s, 1H, CHN), 7.05–7.48 (m, 5H, C_6H_5). – MS, *m/z* (%): 361 (1) [M^+ + 1], 360 (1.5) [M^+], 319 (80), 241 (100) [M^+ – $CH_2OCH_2OCH_2CH_2OCH_3$], 201 (99), 188 (27), 145 (36), 130 (48), 117 (23), 112 (47), 105 (77), 91 (37), 89 (30), 70 (67), 59 (63). – $C_{21}H_{32}N_2O_3$ (360.5): calcd. C 69.96, H 8.95, N 7.77; found C 70.39, H 9.15, N 7.72.

(S)-2-{[(2-Methoxyethoxy)methoxy]methyl}-1-[(2-methyl-2-phenylbutyliden)amino]pyrrolidine (**3l**): 1.28 g (4.0 mmol) of **2k** was metalated at –78°C with 2.81 ml (4.4 mmol) of *n*BuLi for 30 min and alkylated with 0.38 ml (4.8 mmol) of iodoethane at –110°C according to the procedure described for **3e**. After warming to room temp. overnight the product was purified by the procedure described for **3a** yielding 1.25 g (90%) of a yellow oil; b.p. 160–180°C/0.03 torr, α_D^{22} = –66.0 (neat). – IR (neat): $\tilde{\nu}$ = 3085 cm^{-1}, 3060, 3030, 2965, 2930, 2880, 2820 (CH), 1600, 1490, 1450, 1410, 1380, 1360, 1340, 1280, 1240, 1200, 1170, 1150, 1115, 1095, 1045, 930, 900, 850, 760, 700. – ^1H NMR ($CDCl_3$): δ = 0.74 (t, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.85 (m, 6H, CH_2, CH_{2pyr}), 2.70 (m, 1H, NCH_2), 3.12–3.92 (m, 8H, NCH_2, OCH_2, NCH, OCH_2CH_2O), 3.38 (s, 3H, OCH_3), 4.72 (s, 2H, OCH_2O), 6.68 (s, 1H, CHN), 7.08–7.45 (m, 5H, C_6H_5). – MS, *m/z* (%): 349 (1) [M^+ + 1], 348 (4) [M^+], 229 (100) [M^+ – $CH_2OCH_2OCH_2CH_2OCH_3$], 201 (16), 91 (16). – $C_{20}H_{32}N_2O_3$ (348.5): calcd. C 68.93, H 9.26, N 8.04; found C 68.85, H 9.25, N 7.79.

(–)-2-Methyl-2-phenylpent-4-enal (**4a**). – a) *Cleavage of the SAMP Hydrazone* **3a**: 1.25 ml (20 mmol) of methyl iodide was added to 0.74 g (2.58 mmol) of **3a**, and the mixture was refluxed for 10 h at 60°C (TLC control). After cooling to room temp. the methyl iodide was removed under reduced pressure, and the precipitated hydrazonium iodide was dissolved in 12.5 ml of 6 N HCl. After stirring of the solution for 5 min 50 ml of *n*-pentane was added, and the mixture was stirred vigorously for another 30 min. After separation of the phases the organic layer was washed twice with water, dried with Na_2SO_4, and concentrated in vacuo. Reduced-pressure distillation of the residue yielded 0.29 g (64%) of a colorless liquid; b.p. 60–70°C/0.3 Torr (ref.[14] 120°C/16 Torr), $[\alpha]_D^{22}$ = –35.2 (*c* = 1.39, $CHCl_3$); ee = 30% [Eu(hfc)$_3$ shift]. The spectroscopic data were in agreement with the literature data[14,15]. – b) *Cleavage of the SAMEMP Hydrazone* **3k**: According to the procedure described under a) 0.85 g (3.10 mmol) of **3k** was refluxed with methyl iodide (20 h) and cleaved with 6 N HCl. Reduced-presure distillation yielded 0.38 g (76%) of a colorless liquid: b.p. 90–100°C/0.6 Torr, $[\alpha]_D^{22}$ = –27.6 (*c* = 1.17, $CHCl_3$); ee = 24% [Eu(hfc)$_3$ shift]. The spectroscopic data were in agreement with those obtained from the cleavage of **3a**.

(R)-(–)-2-Methyl-2-phenylbutanal (**4b**). – a) *Cleavage of the SAMP Hydrazone* **3b**: 0.85 g (3.10 mmol) of **3b** was refluxed with methyl iodide for 20 h. Cleavage with 6 N HCl by the procedure described for **4a** yielded 0.38 g (76%) of a colorless liquid; b.p. 110–130°C/2 Torr (ref.[16] 65°C/0.5 Torr), $[\alpha]_D^{22}$ = –2.9 (*c* = 4.19, $CHCl_3$); ee = 25% [Eu(hfc)$_3$ shift]. The spectroscopic data were in agreement with the literature data[16]. – b) *Cleavage of the SAMEMP Hydrazone* **3l**: According to the procedure described for **4a** 0.97

g (2.78 mmol) of **3l** was refluxed with methyl iodide (24 h). Cleavage with 6 N HCl and reduced-pressure distillation yielded 0.24 g (53%) of a colorless liquid; b.p. 100–120°C/1.5 Torr, $[\alpha]_D^{22} = -3.2$ (c = 1.36, $CHCl_3$); ee = 28% [Eu(hfc)$_3$ shift]. The spectroscopic data were in agreement with those obtained from the cleavage of **3b**.

(R)-(+)-2-Methyl-2-phenylcyclopentanone (**4c**): 10 ml of 12 N HCl was added to 0.52 g (1.82 mmol) of **3c**, and the mixture was stirred vigorously for 10 min (TLC control). After extraction with diethyl ether (3 × 50 ml) the combined organic phases were dried with K_2CO_3 and concentrated in vacuo. Reduced-pressure distillation of the residue yielded 0.23 g (73%) of a colorless oil; b.p. 100–120°C/0.5 Torr (ref.[17] 80–83°C/0.63 Torr), $[\alpha]_D^{22} = +69.5$ (c = 1.24, C_2H_5OH); ee = 77% [Eu(hfc)$_3$ shift]. The spectroscopic data were in agreement with the literature data[17].

(R)-(+)-2-Methyl-2-phenylcyclohexanone (**4d**): 0.66 g (2.20 mmol) of **3d** was cleaved with 10 ml of 12 N HCl by the procedure described for **4c** yielding 0.33 g (80%) of a colorless oil; b.p. 100–120°C/0.1 Torr (ref.[18] 98°C/1.5 Torr), $[\alpha]_D^{22} = +200.4$ (c = 2.38, C_6H_{12}); ee = 93% [Eu(hfc)$_3$ shift]. The spectroscopic data were in agreement with the literature data[18].

(–)-Methyl 1-Methyl-2-oxocyclopentanecarboxylate (**4e**): 0.77 g (2.87 mmol) of **3e** was dissolved in 30 ml of CH_2Cl_2, and the solution was cooled to –78°C. Ozone was bubbled into this solution at the same temp. Upon complete conversion (TLC control) excess ozone was removed by passing argon through the solution, which was then warmed to room temp. The solvent was removed by evaporation under reduced pressure, and flash chromatography (SiO_2, diethyl ether) of the residue yielded (0.35 g (78%) of a colorless liquid; $[\alpha]_D^{22} = -7.4$ (c = 1.16, $CHCl_3$); ee = 60% [Eu(hfc)$_3$ shift]. – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2880, 1750 (C=O), 1450, 1430, 1405, 1370, 1315, 1270, 1235, 1190, 1150, 1060, 980, 940, 870, 840, 810, 770. – ^{1}H-NMR ($CDCl_3$): δ = 1.32 (s, 3H, CH_3), 1.64–2.20 (m, 3H, CH_2), 2.20–2.70 (m, 3H, CH_2), 3.74 (s, 3H, OCH_3). – MS, *m/z* (%): 157 (2) [M$^+$ + 1], 156 (11) [M$^+$], 128 (87), 113 (41), 101 (51), 97 (40), 83 (93), 69 (100) [$C_4H_5O^+$], 55 (40), 41 (70). – $C_8H_{12}O_3$ (156.2): calcd. C 61.52, H 7.75; found C 61.54, H 7.78.

(+)-Methyl 1-Ethyl-2-oxocyclopentanecarboxylate (**4f**): 1.24 g (4.39 mmol) of **3f** was cleaved by the procedure described for **4e**. Flash chromatography (SiO_2, diethyl ether) yielded 0.55 g (73%) of a colorless liquid; $[\alpha]_D^{22} = +3.7$ (c = 1.21, $CHCl_3$); ee = 18% [Eu(hfc)$_3$ shift]. The spectroscopic data were in agreement with the literature data[19].

(+)-Methyl Ethyl-2-oxocyclohexanecarboxylate (**4g**): 1.19 g (4.01 mmol) of **3g** was cleaved according to the procedure described for **4e**. Flash chromatography (SiO_2, diethyl ether) yielded 0.50 g (68%) of a colorless liquid; $[\alpha]_D^{22} = +67.6$ (c = 3.04, $CHCl_3$); ee = 43% [Eu(hfc)$_3$ shift]. The spectroscopic data were in agreement with the literature data[20].

(+)-Ethyl 2-Acetyl-2-methylbutanoate (**4h**): 1.00 g (3.52 mmol) of **3h** was cleaved by the procedure described for **4e**. Flash chromatography (SiO_2, diethyl ether) yielded 0.38 g (62%) of a colorless liquid; $[\alpha]_D^{22} = +1.8$ (c = 1.33, $CHCl_3$); ee = 27% [Eu(hfc)$_3$ shift]. – IR (neat): $\tilde{\nu}$ = 2980 cm^{-1}, 2950, 2890, 1740, 1715 (2 C=O), 1460, 1380, 1360, 1305, 1260, 1245, 1150, 1060, 1020, 865. – ^{1}H NMR ($CDCl_3$): δ = 0.91 (t, 3H, CH_2CH_3), 1.18 (t, 3H, OCH_2CH_3), 1.24 (s, 3H, CH_3), 1.75 (q, 2H, CH_2CH_3), 2.08 (s, 3H, CH_3), 4.09 (q, 2H, OCH_2CH_3). – MS, *m/z* (%): 172 [M$^+$], 130, 127, 116, 115, 102, 88, 87, 85, 73, 69, 57, 55, 45, 43. – $C_9H_{16}O_3$ (172.2): calcd. C 62.76, H 9.37; found C 62.72, H 9.36.

(+)-Ethyl 2-Acetyl-2-methylpentanoate (**4i**): Oxidative cleavage of 1.15 g (3.09 mmol) of **3j** with ozone according to the procedure described for **4e** yielded, after purification of the crude product by flash chromatography, 0.44 g (76%) of a colorless oil; $[\alpha]_D^{22} = +2.1$ (c = 1.46, $CHCl_3$); ee = 31% [Eu(hfc)$_3$ shift]. – IR (neat): $\tilde{\nu}$ = 3440 cm^{-1}, 3420, 2960, 2940, 2875, 1735, 1710, 1460, 1375, 1355, 1295, 1275, 1230, 1200, 1145, 1075, 1040, 970, 910, 855. – ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 3H, CH_2CH_3), 1.01–1.38 (m, 2H, CH_2CH_3), 1.18 (t, 3H, OCH_2CH_3), 1.26 (s, 3H, CH_3), 1.68 (t, 2H, $CH_2CH_2CH_3$), 2.12 (s, 3H, CH_3), 4.14 (q, 2H, OCH_2CH_3). – MS, *m/z* (%): 186 [M$^+$], 144, 141, 115, 99, 87, 85, 70, 69, 57, 45. – $C_{10}H_{18}O_3$ (186.3): calcd. C 64.49, H 9.74; found C 64.56, H 9.70.

(S,R)-(–)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)butyliden]-amino}-2-(methoxymethyl)pyrrolidine (**11a**): To 9 mmol of *n*BuLi in 21 ml of THF was added at –78°C 1.75 g (6 mmol) of (*S,S*)-2-(methoxymethyl)-1-{[2-(phenylthio)butyliden]amino}pyrrolidine[7] (**10a**). After warming to room temp. overnight the reaction mixture was cooled to –110°C, and 0.96 g (10.2 mmol) of methyl chloroformate was added with stirring. The reaction mixture was stirred for another 30 min at this temp. and then allowed to warm slowly to room temp. overnight. The solution was diluted with diethyl ether and washed with pH 7 buffer, then water. After drying with $MgSO_4$ and concentration of the solution in vacuo the crude product was purified by flash chromatography (SiO_2, diethyl ether/petroleum ether, 1:2) yielding 1.91 g (91%) of a yellow oil; $[\alpha]_D^{25} = -22.9$ (c = 1.13, C_6H_6); de = 90% (^{13}C-NMR). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 3020–2800, 1725 (C=O), 1580 (CN), 1470, 1460–1440, 1370, 1340, 1320, 1295, 1230, 1110, 1025, 1015, 775, 750, 710, 690. – ^{1}H NMR ($CDCl_3$): δ = 0.97 (t, J = 7.4 Hz, 3H, CH_2CH_3), 1.74–1.96 (m, 4H, CH_{2pyr}), 2.03 (d/q, J = 13.8/7.1 Hz, 1H, CH_2CH_3), 2.25 (d/q, J = 13.8/7.4 Hz, 1H, CH_2CH_3), 2.80 (m, 1H, NCH_2), 3.15–3.50 (m, 4H, OCH_2, NCH_2, NCH), 3.33 (s, 3H, OCH_3), 3.69 (s, 3H, CO_2CH_3), 6.49 (s, 1H, CHN), 7.24–7.45 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 9.9 (CH_3), 22.1 (NCH_2CH_2), 26.9 (CH_2CH), 27.8 (CH_2CH_3), 48.9 (CH_2N), 52.2 (CO_2CH_3), 59.1 (OCH_3), 62.5 (C), 62.8 (CH), 74.5 (CH_2O), 128.4, 129.1, 130.7 (CH_{arom}), 131.1 (C_{arom}), 137.2 (CHN), 172.0 (CO_2). – MS, *m/z* (%): 350 (3) [M$^+$], 241 (100) [M$^+$ – SPh], 218 (41), 185 (45), 183 (46), 110 (44), 109 (47), 105 (31), 77 (27), 70 (74), 55 (35), 43 (37), 41 (60). – $C_{18}H_{26}N_2O_3S$ (350.5): calcd. C 61.69, H 7.48, N 7.99; found C 61.46, H 7.77, N 8.02.

(R,S)-(+)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)butyliden]amino}-2-(methoxymethyl)pyrrolidine (**11a**): 1.17 g (4.0 mmol) of hydrazone (*R,R*)-**10a**[7] was transformed by treatment with 6 mmol of *n*BuLi and 0.64 g (6.8 mmol) of methyl chloroformate into 0.96 g (69%) of a yellow oil by the procedure described for (*S,R*)-**11a**; $[\alpha]_D^{25} = +23.3$ (c = 1.00, C_6H_6); de = 92% (^{13}C NMR). The spectroscopic data were in agreement with those described for (*S,R*)-**11a**.

(S,R)-(–)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)pentyliden]amino}-2-(methoxymethyl)pyrrolidine (**11b**): 0.92 g (3 mmol) of (*S,S*)-2-(methoxymethyl)-1-{[2-(phenylthio)pentyliden]amino}pyrrolidine[7] (**10b**) was transformed by treatment with 4.5 mmol of LDA and 0.48 g (5.1 mmol) of methyl chloroformate into 1.00 g (91%) of a yellow oil by the procedure described for (*S,R*)-**11a**; $\alpha_D^{25} = -27.1$ (neat), de = 92% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 3000–2800, 1725 (C=O), 1580 (CN), 1435, 1340, 1320, 1295, 1215, 115, 1020, 970, 750, 705, 690. – ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, J = 7.4 Hz, 3H, CH_2CH_3), 1.24–2.56 (m, 2H, CH_2CH_3), 1.72–1.98 (m, 5H, CH_{2pyr}, $CH_2CH_2CH_3$), 2.09–2.20 (m, 1H, $CH_2CH_2CH_3$), 2.79 (m, 1H, NCH_2), 3.14–3.46 (m, 4H, OCH_2, NCH_2, NCH), 3.34 (s, 3H, OCH_3), 3.69 (s, 3H, CO_2CH_3), 6.49 (s, 1H, CHN), 7.25–7.46 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 14.4 (CH_3), 11.7 (CH_2), 22.1 (NCH_2CH_2), 26.9 (CH_2CH), 37.0 (CH_2), 48.9 (CH_2N), 52.2 (CO_2CH_3), 59.1 (OCH_3), 61.8 (C), 62.8 (CH), 74.5 (CH_2O), 128.4, 129.1, 131.1 (CH_{arom}), 131.2 (CHN), 137.2 (C_{arom}), 172.1 (CO_2). – MS, *m/z* (%): 364 (1) [M$^+$], 255 (100) [M$^+$ – SPh], 114 (24), 70 (79). – $C_{19}H_{28}N_2O_3S$ (364.5): calcd. C 62.61, H 7.74, N 7.69; found C 62.39, H 7.89, N 7.57.

(S,R)-(–)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)hexyliden]amino}-2-(methoxymethyl)pyrrolidine (**11c**): 7.68 g (24 mmol) of (*S,S*)-2-(methoxymethyl)-1-{[2-(phenylthio)hexyliden]amino}pyrrolidine[7] (**10c**) was transformed by treatment with 36 mmol of *n*BuLi and 3.63 g (38.4 mmol) of methyl chloroformate into 8.20 g (90%) of a yellow oil by the procedure described for (*S,R*)-**11a**; $\alpha_D^{23} = -25.3$ (neat); de = 92% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 3000–2800, 1725 (C=O), 1580 (CN), 1460, 1435, 1340, 1305, 1260, 1240, 1205, 1120, 1025, 970, 750, 705, 690. – ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, J = 7.4 Hz, 3H, CH_2CH_3), 1.23–1.45 [m, 4H, $(CH_2)_2CH_3$], 1.72–2.01 [m, 5H, CH_{2pyr}, $CH_2(CH_2)_2CH_3$], 2.15 [m, 1H, $CH_2(CH_2)_2CH_3$], 2.78 (m, 1H, NCH_2), 3.24–3.50 (m, 4H, OCH_2, NCH_2, NCH), 3.33 (s, 3H, OCH_3), 3.69 (s, 3H, CO_2CH_3), 6.48 (s, 1H, CHN), 7.24–7.46 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3), 22.1 (NCH_2CH_2), 23.0 (CH_2), 26.9 (CH_2CH), 27.5 (CH_2), 34.5 (CH_2), 48.9 (CH_2N), 52.2 (CO_2CH_3), 59.1 (OCH_3), 61.8 (C), 62.8 (CH), 74.5 (CH_2O), 128.4, 129.1, 131.1 (CH_{arom}), 131.2 (C_{arom}), 137.2 (CHN), 172.1 (CO_2). – MS, *m/z* (%): 378 (1) [M$^+$], 269 (100) [M$^+$ – SPh], 114 (21), 70 (62). – $C_{20}H_{30}N_2O_3S$ (378.5): calcd. C 63.46, H 7.99, N 7.40; found C 63.02, H 7.98, N 7.96.

(R,S)-(–)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)hexyliden]amino}-2-(methoxymethyl)pyrrolidine (**11c**): 6.00 g (18.75 mmol) of (*R,R*)-**10c**[7] was transformed by treatment with 28.1 mmol of *n*BuLi and 2.84 g (30 mmol) of methyl chloroformate into 5.17 g (73%) of a yellow oil by the procedure described for (*S,R*)-**11a**; $[\alpha]_D^{25} = +9.9$, (c = 0.87, C_6H_6); de = 92% (^{13}C NMR). The spectroscopic data were in agreement with those described for (*S,R*)-**11c**.

(S,R)-(–)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)octyliden]amino}-2-(methoxymethyl)pyrrolidine (**11d**): 4.70 g (13.5 mmol) of (*S,S*)-2-(methoxymethyl)-1-{[2-(phenylthio)octyliden]amino}pyrrolidine[7] (**10d**) was transformed by treatment with 20.3 mmol of *n*BuLi and 2.04 g (21.6 mmol) of methyl chloroformate into 4.66 g (85%) of a yellow oil by the procedure described for (*S,R*)-**11a**; $[\alpha]_D^{25} = -11.7$ (c = 1.06, C_6H_6); de = 92% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 3000–2800, 1730 (C=O), 1580 (CN), 1445, 1320, 1295, 1240, 1190, 1130, 750, 705, 690. – ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, J = 7.4 Hz, 3H, CH_2CH_3), 1.24–1.44 [m, 8H, $(CH_2)_4CH_3$], 1.74–2.01 [m, 5H, CH_{2pyr}, $CH_2(CH_2)_4CH_3$], 2.17 [m, 1H, $CH_2(CH_2)_4CH_3$], 2.78 (m, 1H, NCH_2), 3.12–3.48 (m, 4H, OCH_2, NCH_2, NCH), 3.33 (s, 3H, OCH_3), 3.69 (s, 3H, CO_2CH_3), 6.48 (s, 1H, CHN), 7.24–7.54 (m, 5H,

C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.1 (NCH_2CH_2), 22.5 (CH_2), 25.2 (CH_2), 26.9 (CH_2CH), 29.5 (CH_2), 31.6 (CH_2), 34.8 (CH_2), 48.9 (CH_2N), 52.2 (CO_2CH_3), 59.1 (OCH_3), 61.8 (C), 62.8 (CH), 74.5 (CH_2O), 128.4, 129.1, 131.1 (CH_{arom}), 131.2 (C_{arom}), 137.2 (CHN), 172.1 (CO_2). – MS, *m/z* (%): 406 (1) [M^+], 297 (100) [M^+ – SPh], 114 (19), 70 (52). – $C_{22}H_{34}N_2O_3S$ (406.6): calcd. C 64.99, H 8.43, N 6.89; found C 64.70, H 8.47, N 6.83.

(S,R)-(–)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)decyliden]amino}-2-(methoxymethyl)pyrrolidine (**11e**): 1.13 g (3.0 mmol) of (*S,S*)-2-(methoxymethyl)-1-{[2-(phenylthio)decyliden]amino}pyrrolidine[7] (**10e**) was transformed by treatment with 4.5 mmol of *n*BuLi and 0.48 g (5.1 mmol) of methyl chloroformate into 1.00 g (77%) of a yellow oil by the procedure described for (*S,R*)-**11a**; α_D^{23} = –19.2 (neat); de = 92% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 3000–2800, 1725 (C=O), 1580 (CN), 1460, 1435, 1340, 1300, 1225, 1195, 1120, 1065, 1020, 750, 705, 690. – ^1H NMR ($CDCl_3$): δ = 0.87 (br t, 3H, CH_2CH_3), 1.20–1.52 [m, 12H, $(CH_2)_6CH_3$], 1.74–1.99 [m, 5H, CH_{2pyr}, $CH_2(CH_2)_6CH_3$], 2.16 [m, 1H, $CH_2(CH_2)_6CH_3$], 2.78 (m, 1H, NCH_2), 3.12–3.48 (m, 4H, OCH_2, NCH_2, NCH), 3.33 (s, 3H, OCH_3), 3.69 (s, 3H, CO_2CH_3), 6.48 (s, 1H, CHN), 7.24–7.54 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.0 (NCH_2CH_2), 22.7 (CH_2), 25.2 (CH_2), 26.8 (CH_2CH), 29.2 (CH_2), 29.3 (CH_2), 29.9 (CH_2), 31.9 (CH_2), 34.7 (CH_2), 48.9 (CH_2N), 52.2 (CO_2CH_3), 59.1 (OCH_3), 61.8 (C), 62.8 (CH), 74.5 (CH_2O), 128.4, 129.1, 131.1 (CH_{arom}), 131.1 (C_{arom}), 137.2 (CHN), 172.1 (CO_2). – MS, *m/z* (%): 434 (1) [M^+], 325 (100) [M^+ – SPh], 114 (25), 70 (58). – $C_{24}H_{38}N_2O_3S$ (434.6): calcd. C 66.32, H 8.81, N 6.45; found C 66.48, H 8.78, N 6.81.

(S,R)-(–)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)dodecyliden]amino}-2-(methoxymethyl)pyrrolidine[7] (**10f**) was transformed by treatment with 4.5 mmol of LDA and 0.48 g (5.1 mmol) of methyl chloroformate into 1.30 g (94%) of a yellow oil by the procedure described for (*S,R*)-**11a**; α_D^{25} = –14.4 (neat); de = 91% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 3000–2800, 1730 (C=O), 1580 (CN), 1460, 1445, 1435, 1340, 1315, 1295, 1230, 1195, 1125, 1020, 970, 750, 705, 690. – ^1H NMR ($CDCl_3$): δ = 0.88 (br t, 3H, CH_2CH_3), 1.22–1.31 [m, 16H, $(CH_2)_8CH_3$], 1.74–2.00 [m, 5H, CH_{2pyr}, $CH_2(CH_2)_8CH_3$], 2.16 [m, 1H, $CH_2(CH_2)_8CH_3$], 2.79 (m, 1H, NCH_2), 3.12–3.48 (m, 4H, OCH_2, NCH_2, NCH), 3.34 (s, 3H, OCH_3), 3.69 (s, 3H, CO_2CH_3), 6.48 (s, 1H, CHN), 7.25–7.55 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.1 (NCH_2CH_2), 22.7 (CH_2), 25.3 (CH_2), 26.9 (CH_2CH), 29.4 (CH_2), 29.60 (CH_2), 29.63 (CH_2), 29.9 (CH_2), 32.0 (CH_2), 34.8 (CH_2), 49.0 (CH_2N), 52.2 (CO_2CH_3), 59.2 (OCH_3), 61.9 (C), 62.8 (CH), 74.5 (CH_2O), 128.4, 129.1, 131.2 (CH_{arom}), 131.3 (C_{arom}), 137.2 (CHN), 172.2 (CO_2). – MS, *m/z* (%): 462 (<1) [M^+], 353 (100) [M^+ – SPh], 114 (24), 70 (68), 41 (21). – $C_{26}H_{42}N_2O_3S$ (462.7): calcd. C 67.49, H 9.15, N 6.05; found C 67.32, H 9.20, N 6.63.

(S,R)-(–)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)tridecyliden]amino}-2-(methoxymethyl)pyrrolidine (**11g**): 1.25 g (3.0 mmol) of (*S,S*)-2-(methoxymethyl)-1-{[2-(phenylthio)tridecyliden]amino}pyrrolidine[7] (**10g**) was transformed by treatment with 4.5 mmol of *n*BuLi and 0.48 g (5.1 mmol) of methyl chloroformate into 1.30 g (91%) of a yellow oil by the procedure described for (*S,R*)-**11a**; α_D^{24} = –14.5 (neat); de = 93% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 3000–2800, 1725 (C=O), 1580 (CN), 1460, 1440, 1360, 1240, 1195, 1120, 1025, 910, 750, 730, 705, 690. – ^1H NMR ($CDCl_3$): δ = 0.88 (br t, 3H, CH_2CH_3), 1.16–1.52 [m, 18H, $(CH_2)_9CH_3$], 1.74–2.01 [m, 5H, CH_{2pyr}, $CH_2(CH_2)_9CH_3$], 2.17 [m, 1H, $CH_2(CH_2)_9CH_3$], 2.78 (m, 1H, NCH_2), 3.12–3.50 (m, 4H, OCH_2, NCH_2, NCH), 3.33 (s, 3H, OCH_3), 3.68 (s, 3H, CO_2CH_3), 6.48 (s, 1H, CHN), 7.24–7.54 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.1 (NCH_2CH_2), 22.7 (CH_2), 25.3 (CH_2), 26.9 (CH_2CH), 29.4 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 29.9 (CH_2), 32.0 (CH_2), 34.8 (CH_2), 48.9 (CH_2N), 52.2 (CO_2CH_3), 59.1 (OCH_3), 61.8 (C), 62.8 (CH), 74.5 (CH_2O), 128.4, 129.0, 131.1 (CH_{arom}), 131.3 (C_{arom}), 137.2 (CHN), 172.1 (CO_2). – MS, *m/z* (%): 476 (2) [M^+], 415 (22), 367 (100) [M^+ – SPh], 269 (33), 168 (28), 114 (32), 110 (57), 109 (30), 77 (20), 70 (93), 55 (52), 43 (44), 41 (73). – $C_{27}H_{44}N_2O_3S$ (476.7): calcd. C 68.03, H 9.39, N 5.88; found C 67.89, H 9.41, N 6.24.

(S,R)-(–)-1-{[2-(Methoxycarbonyl)-2-(phenylthio)-3-(3,4,5-trimethoxyphenyl)propyliden]amino}-2-(methoxymethyl)pyrrolidine (**11h**): 2.66 g (6.0 mmol) of (*S,S*)-2-(methoxymethyl)-1-{[2-(phenylthio)-3-(3,4,5-trimethoxyphenyl)propyliden]amino}pyrrolidine[21] (**10h**) dissolved in 2 ml of THF was transformed by treatment with 9 mmol of *n*BuLi and 0.96 g (10.2 mmol) of methyl chloroformate into 1.80 g (60%) of a yellow oil by the procedure described for (*S,R*)-**11a**; $[\alpha]_D^{28}$ = –26.3 (*c* = 1.14, C_6H_6); de = 93% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3040 cm^{-1}, 2920, 2860, 2815, 1720 (C=O), 1580 (CN), 1495, 1450, 1320, 1230, 1190, 1105, 1040, 1000, 965, 900, 830, 770, 740, 720, 685. – ^1H NMR ($CDCl_3$): δ = 1.73–2.00 (m, 4H, CH_{2pyr}), 2.79 (m, 1H, NCH_2), 3.10–3.52 (m, 4H, OCH_2, NCH_2, NCH), 3.35 (s, 3H, CH_2OCH_3), 3.66 (s, 3H, CO_2CH_3), 3.76 (s, 6H, OCH_3), 3.79 (s, 3H, OCH_3), 6.43–6.52 (m, 3H, CHN, C_6H_2), 7.26–7.52 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 22.1 (NCH_2CH_2), 27.2 (CH_2CH), 41.6 (CH_2), 49.0 (CH_2N), 52.2 (CO_2CH_3), 55.9 (OCH_3), 59.2 (OCH_3), 60.8 (OCH_3), 61.9 (C), 62.7 (CH), 74.6 (CH_2O), 108.0, 128.4, 129.0, 131.1 (CH_{arom}), 131.3 (C_{arom}), 132.7 (C_{arom}), 136.6 (C_{arom}), 137.4 (CHN), 152.4 (C_{arom}), 171.5 (CO_2). – MS, *m/z* (%): 457 (1) [M^+ – CH_2OCH_3], 394 (23) [M^+ – CO_2CH_3], 393 (100) [M^+ – SPh], 361 (38), 278 (25), 181 (34) [$(H_3CO)_3C_6H_2CH_2^+$], 129 (20), 114 (13) [$NC_6H_{12}O^+$], 70 (37) [$NC_4H_8^+$]. – $C_{26}H_{34}N_2O_6S$ (502.6): calcd. C 62.13, H 6.82, N 5.57; found C 61.05, H 6.90, N 5.86.

(S,R)-(–)-1-{[2-(Methoxycarbonyl)-2-(methylthio)butyliden]amino}-2-(methoxymethyl)pyrrolidine (**11i**): 0.345 g (1.5 mmol) of (*S,R*)-2-(methoxymethyl)-1-{[2-(methylthio)butyliden]amino}pyrrolidine[22] (**10i**) was transformed by treatment with 2.25 mmol of MeLi and 0.24 g (2.55 mmol) of methyl chloroformate into 0.353 g (82%) of a yellow oil by the procedure described for (*S,R*)-**11a**; α_D^{25} = –85.0 (neat); de = 88% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3020–2800 cm^{-1}, 1740, 1585, 1465, 1440, 1350, 1240, 1120, 1025. – ^1H NMR ($CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 3H, CH_2CH_3), 1.75–2.25 (m, 6H, CH_{2pyr}, CH_2CH_3), 2.05 (s, 3H, SCH_3), 2.85 (m, 1H, NCH_2), 3.30–3.60 (m, 4H, OCH_2, NCH_2, NCH), 3.35 (s, 3H, OCH_3), 3.76 (s, 3H, CO_2CH_3), 6.55 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = 9.5 (CH_3), 12.3 (SCH_3), 22.1 (NCH_2CH_2), 26.6 (CH_2CH), 27.1 (CH_2), 49.2 (CH_2N), 52.4 (CO_2CH_3), 58.6 (C), 59.2 (OCH_3), 63.1 (CH), 7.74 (CH_2O), 131.8 (CHN), 172.2 (CO_2). – MS, *m/z* (%): 288 (4) [M^+], 243 (33), 241 (79), 195 (27), 114 (21), 87 (32), 70 (100). – $C_{13}H_{24}N_2O_3S$ (288.4): calcd. C 54.21, H 8.39, N 9.73; found C 54.04, H 8.50, N 9.85.

(S,S)-(–)-1-{{[2-(Methoxycarbonyl)methyl]-2-(methylthio)butyliden}-amino}-2-(methoxymethyl)pyrrolidine (**11j**): 0.345 g (1.5 mmol) of **10i**[22] was transformed by treatment with 2.25 mmol of MeLi and 0.36 g (2.55 mmol) of methyl bromoacetate into 0.119 g (26%) of a yellow oil by the procedure described for (*S,R*)-**11a**; $[\alpha]_D^{26}$ = –79.3 (*c* = 1.13, C_6H_6); de = 91% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3020–2800 cm^{-1}, 1745, 1595, 1450, 1350, 1300, 1250, 1100, 1025, 950. – ^1H NMR ($CDCl_3$): δ = 1.00 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.75–2.05 (m, 6H, CH_{2pyr}, CH_2CH_3), 1.95 (s, 3H, SCH_3), 2.77 (m, 3H, CH_2CO_2, NCH_2), 3.30–3.60 (m, 4H, OCH_2, NCH_2, NCH), 3.37 (s, 3H, OCH_3), 3.68 (s, 3H, CO_2CH_3), 6.43 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = 8.7 (CH_3), 11.0 (SCH_3), 21.9 (NCH_2CH_2), 26.5 (CH_2CH), 28.5 (CH_2), 37.4 (CH_2CO_2), 49.7 (CH_2N), 51.3 (CO_2CH_3), 51.9 (C), 59.2 (OCH_3), 63.7 (CH), 74.4 (CH_2O), 138.2 (CHN), 171.3 (CO_2). – MS, *m/z* (%): 302 (1) [M^+], 255 (38) [M^+ – SCH_3], 209 (100), 108 (25), 70 (52). – $C_{14}H_{26}N_2O_3S$ (302.4): calcd.C 55.59, H 8.67, N 9.26; found C 55.36, H 8.54, N 9.16.

(S,S)-(–)-1-{{[2-(Methoxycarbonyl)methyl]-2-(phenylthio)butyliden}-amino}-2-(methoxymethyl)pyrrolidine (**11k**): 0.88 g (3.0 mmol) of (*S,S*)-**10a**[7] was transformed by treatment with 4.5 mmol of MeLi and 0.78 g (5.1 mmol) of methyl bromoacetate into 0.82 g (75%) of a yellow oil by the procedure described for (*S,R*)-**11a**; $[\alpha]_D^{28}$ = –31.1 (*c* = 0.97, C_6H_6); de = 83% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3075 cm^{-1}, 3060, 2960–2830, 1740 (CO), 1585, 1475, 1460, 1440, 1340, 1290, 1200, 1175, 1125, 750, 695. – ^1H NMR ($CDCl_3$): δ = 1.06 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.64–2.12 (m, 6H, CH_{2pyr}, CH_2CH_3), 2.64 (m, 1H, NCH_2), 2.78 (m, 3H, CH_2CO_2), 2.94–3.04 (m, 1H, NCH_2), 3.20–3.28 (m, 3H, OCH_2, NCH), 3.28 (s, 3H, OCH_3), 3.67 (s, 3H, CO_2CH_3), 6.43 (s, 1H, CHN), 7.22–7.47 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 9.0 (CH_3), 22.1 (NCH_2CH_2), 26.6 (CH_2CH), 29.2 (CH_2), 38.5 (CH_2CO_2), 49.2 (CH_2N), 51.2 (CO_2CH_3), 56.8 (C), 59.1 (OCH_3), 63.1 (CH), 74.4 (CH_2O), 128.3, 128.8, 137.2 (CH_{arom}), 131.3 (C_{arom}), 137.7 (CHN), 171.3 (CO_2). – MS, *m/z* (%): 333 (2) [M^+ – OCH_3], 255 (100) [M^+ – SPh], 223 (26), 209 (50), 114 (22) [$NC_6H_{12}O^+$], 110 (46), 109 (15) [$SC_6H_5^+$], 70 (45) [$NC_4H_8^+$]. – $C_{19}H_{28}N_2O_3S$ (364.5): calcd. C 62.60, H 7.74, N 7.69; found C 62.67, H 7.72, N 7.60.

(S,S)-(–)-1-{{[2-(Methoxycarbonyl)methyl]-2-(phenylthio)octyliden}-amino}-2-(methoxymethyl)pyrrolidine (**11l**): 1.03 g (3.0 mmol) of (*S,S*)-**10d**[7] was transformed by treatment with 4.5 mmol of MeLi and 0.73 g (4.8 mmol) of methyl bromoacetate into 0.80 g (64%) of a yellow oil by the procedure described for (*S,R*)-**11a**; $[\alpha]_D^{25}$ = –15.9 (*c* = 1.06, C_6H_6); de = 87% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 2950–2850, 1740 (CO), 1590, 1455, 1435, 1340, 1300, 1280, 1200, 1170, 1120, 1020, 970, 910, 750, 730. – ^1H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_2CH_3), 1.27–2.08 [m, 14H, CH_{2pyr}, $(CH_2)_5$], 2.58–2.67 (m, 1H, NCH_2), 2.77 (d, *J* = 1.7 Hz, 3H, CH_2CO_2), 2.90–3.01 (m, 1H, NCH_2), 3.20–3.37 (m, 3H, OCH_2, NCH), 3.27 (s, 3H, OCH_3), 3.66 (s, 3H, CO_2CH_3), 6.42 (s, 1H, CHN), 7.21–7.45 (m, 5H, C_6H_5). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.1 (NCH_2CH_2), 22.7 (CH_2), 24.4 (CH_2), 26.5 (CH_2CH), 29.7 (CH_2), 31.7 (CH_2), 36.5 (CH_2), 38.9 (CH_2CO_2), 49.1 (CH_2N), 51.1 (CO_2CH_3), 56.4 (C), 59.1 (OCH_3), 63.1 (CH), 74.4 (CH_2O), 128.2, 128.8, 137.3 (CH_{arom}), 131.4 (C_{arom}), 137.7 (CHN), 171.3 (CO_2). – MS, *m/z* (%): 389 (1) [M^+ – OCH_3], 311 (100) [M^+ – SPh], 265 (52), 114 (15) [$NC_6H_{12}O^+$], 110 (52), 109 (15) [$SC_6H_5^+$], 70 (39) [$NC_4H_8^+$]. – $C_{23}H_{36}N_2O_3S$ (420.6): calcd. C 65.58, H 8.63, N 6.66; found C 65.85, H 8.64, N 6.56.

(R)-(+)-Methyl 2-Formyl-2-(phenylthio)butanoate (**12a**): 0.70 g (2.0 mmol) of (*S,R*)-**11a** was cleaved with 18 ml of 5 N HCl (18.5 h) by the

procedure described for **4c**. The combined ethereal extracts were washed with pH 7 buffer and water. After drying with $MgSO_4$, the organic phase was concentrated in vacuo and the crude product purified by flash chromatography (SiO_2, diethyl ether/petroleum ether, 2:3) yielding 0.43 g (90%) of a colorless oil; $[\alpha]_D^{25} = +155.6$ ($c = 1.04$, C_6H_6); ee = 90% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu} = 3420$ cm^{-1}, 3060, 2970, 2950, 2880, 2850, 1720 (CO), 1585, 1575, 1470, 1440, 1385, 1330, 1300, 1240, 1130, 1095, 1070, 1025, 800, 750, 705, 690. – ^{1}H NMR ($CDCl_3$): $\delta = 0.96$ (t, $J =$ 7.4 Hz, 3H, CH_3), 1.96 (m, 2H, CH_2), 3.73 (s, 3H, OCH_3), 7.26–7.47 (m, 5H, C_6H_5), 9.60 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 9.4$ (CH_3), 24.7 (CH_2), 52.8 (OCH_3), 66.5 (C), 128.1 (C_{arom}), 129.1, 130.2, 137.3 (CH_{arom}), 168.8 (CO_2), 190.7 (CHO). – MS, *m/z* (%): 238 (24) [M^+], 210 (45), 178 (58), 151 (33), 149 (82), 109 (100) [SPh^+], 105 (94), 77 (29), 73 (48), 69 (34), 65 (61). – $C_{12}H_{14}O_3S$ (238.3): calcd. C 60.48, H 5.92; found C 60.78, H 5.92.

(S)-(–)-Methyl 2-Formyl-2-(phenylthio)butanoate (**12a**): 0.35 g (1.0 mmol) of (*R,S*)-**11a** was cleaved with 9 ml of 5 N HCl (18.5 h) by the procedure described for (*R*)-**12a** yielding 0.23 g (95%) of a colorless oil; $[\alpha]_D^{22} = -161.7$ ($c = 1.03$, C_6H_6); ee = 92% (^{13}C-NMR analysis of the starting material). The spectroscopic data were in agreement with those described for (*R*)-**12a**.

(R)-(+)-Methyl 2-Formyl-2-(phenylthio)pentanoate (**12b**): 0.47 g (1.3 mmol) of (*S,R*)-**11b** was cleaved with 12 ml of 5 N HCl (18 h) by the procedure described for (*R*)-**12a** yielding 0.25 g (80%) of a colorless oil; $[\alpha]_D^{23} = +127.8$ ($c = 0.98$, C_6H_6); ee = 92% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu} = 3410$ cm^{-1}, 3060, 2960, 2920, 2860, 1745, 1720, 1580, 1460, 1435, 1380, 1295, 1260, 1230, 1130, 1070, 1020, 910, 750, 735, 705, 690. – ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, $J = 7.4$ Hz, 3H, CH_3), 1.24–1.44 (m, 2H, CH_2), 1.77–1.97 (m, 2H, CH_2), 3.71 (s, 3H, OCH_3), 7.21–7.50 (m, 5H, C_6H_5), 9.59 (d, $J = 0.7$ Hz, 1H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 14.2$ (CH_3), 18.3 (CH_2), 33.2 (CH_2), 52.7 (OCH_3), 66.8 (C), 128.1 (C_{arom}), 129.1, 130.2, 137.2 (CH_{arom}), 168.9 (CO_2), 190.7 (CHO). – MS, *m/z* (%): 252 (91) [M^+], 224 (93), 223 (42), 192 (100), 163 (87), 135 (52), 113 (41), 110 (50), 109 (95) [SPh^+], 105 (99), 65 (46). – $C_{13}H_{16}O_3S$ (252.3): calcd. C 61.88, H 6.39; found C 61.90, H 6.52.

(R)-(+)-Methyl 2-Formyl-2-(phenylthio)hexanoate (**12c**): 6.80 g (18 mmol) of (*S,R*)-**11c** was cleaved with 162 ml of 5 N HCl (18 h) by the procedure described for (*R*)-**12a** yielding 3.98 g (83%) of a colorless oil; $[\alpha]_D^{23} = +162.7$ ($c = 1.10$, C_6H_6); ee = 92% (^{19}F- and ^{1}H-NMR analysis of the MTPA ester[8] of the corresponding alcohol). – IR (neat): $\tilde{\nu} = 3060$ cm^{-1}, 2950, 2930, 2860, 2740, 1725, 1470, 1440, 1305, 1270, 1240, 1210, 1130, 1030, 750, 695. – ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 3H, CH_3), 1.23–1.42 (m, 4H, CH_2), 1.80–2.07 (m, 2H, CH_2), 3.71 (s, 3H, OCH_3), 7.28–7.49 (m, 5H, C_6H_5), 9.59 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 13.8$ (CH_3), 22.9 (CH_2), 26.9 (CH_2), 30.9 (CH_2), 52.7 (OCH_3), 65.8 (C), 128.1 (C_{arom}), 129.1, 130.2, 137.2 (CH_{arom}), 168.9 (CO_2), 190.8 (CHO). – MS, *m/z* (%): 267 (13) [$M^+ + 1$], 266 (74) [M^+], 238 (100), 206 (85), 177 (68), 135 (55), 110 (66), 109 (65) [SPh^+], 105 (45), 55 (25), 41 (52). – $C_{14}H_{18}O_3S$ (266.3): calcd. C 63.13, H 6.81; found C 63.08, H 6.85.

(S)-(–)-Methyl 2-Formyl-2-(phenylthio)hexanoate (**12c**): 4.76 g (12.6 mmol) of (*R,S*)-**11c** was cleaved with 63 ml of 5 N HCl (18 h) by the procedure described for (*R*)-**12a** yielding 2.51 g (75%) of a colorless oil; $[\alpha]_D^{25} = -158.5$ ($c = 1.05$, C_6H_6); ee = 92% (^{13}C-NMR analysis of the starting material). The spectroscopic data were in agreement with those described for (*R*)-**12c**.

(R)-(+)-Methyl 2-Formyl-2-(phenylthio)octanoate (**12d**): 0.44 g (1.1 mmol) of (*S,R*)-**11d** was cleaved with 9 ml of 5 N HCl (16.5 h) by the procedure described for (*R*)-**12a** yielding 0.30 g (95%) of a colorless oil; $[\alpha]_D^{21} = +136.1$ ($c = 0.98$, C_6H_6); ee = 92% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu} = 3420$ cm^{-1}, 3060, 2950, 2920, 2860, 1745, 1720, 1580, 1440, 1380, 1240, 1195, 1130, 1095, 1070, 1045, 1025, 1000, 920, 750, 690. – ^{1}H NMR ($CDCl_3$): $\delta = 0.86$ (t, $J = 6.7$ Hz, 3H, CH_3), 1.25 (m, 8H, CH_2), 1.89 (m, 2H, CH_2), 3.72 (s, 3H, OCH_3), 7.25–7.48 (m, 5H, C_6H_5), 9.59 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 14.0$ (CH_3), 22.5 (CH_2), 24.8 (CH_2), 29.4 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 52.7 (OCH_3), 65.8 (C), 128.1 (C_{arom}), 129.1, 130.2, 137.2 (CH_{arom}), 169.0 (CO_2), 190.8 (CHO). – MS, *m/z* (%): 294 (63) [M^+], 267 (83), 235 (64), 206 (42), 135 (40), 123 (44), 109 (63) [SPh^+], 105 (47), 95 (100), 55 (59), 41 (48). – $C_{16}H_{22}O_3S$ (294.4): calcd. C 65.28, H 7.53; found C 65.51, H 7.52.

(R)-(+)-Methyl 2-Formyl-2-(phenylthio)decanoate (**12e**): 0.69 g (1.6 mmol) of (*S,R*)-**11e** was cleaved with 15 ml of 5 N HCl (15.5 h) by the procedure described for (*R*)-**12a** yielding 0.49 g (95%) of a colorless oil; $[\alpha]_D^{20} = +112.7$ ($c = 1.15$, C_6H_6); ee = 92% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu} = 3420$ cm^{-1}, 3060, 2950, 2920, 2850, 1720, 1580, 1470, 1440, 1380, 1230, 1190, 1140, 1090, 1070, 1025, 910, 750, 735, 690. – ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (t, $J = 7.1$ Hz, 3H, CH_3), 1.24 (m, 12H, CH_2), 1.79–2.02 (m, 2H, CH_2), 3.70 (s, 3H, OCH_3), 7.26–7.53 (m, 5H, C_6H_5), 9.59 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3), 22.6 (CH_2), 24.8 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.7 (CH_2), 31.2 (CH_2), 31.8 (CH_2), 52.7 (OCH_3), 65.8 (C), 128.1 (C_{arom}), 129.1, 130.2, 137.2 (CH_{arom}), 168.9 (CO_2), 190.8 (CHO). – MS, *m/z* (%): 322 (60) [M^+], 294 (100), 262 (64), 235 (53), 164 (43), 135 (42), 123 (61), 110 (73), 109 (69) [SPh^+], 105 (42), 91 (38), 81 (63), 69 (61), 67 (51), 55 (64), 41 (83). – $C_{18}H_{26}O_3S$ (322.5): calcd. C 67.05, H 8.13; found C 67.02, H 8.27.

(R)-(+)-Methyl 2-Formyl-2-(phenylthio)dodecanoate (**12f**): 0.90 g (2.0 mmol) of (*S,R*)-**11f** was cleaved with 18 ml of 5 N HCl (17 h) by the procedure described for (*R*)-**12a** yielding 0.58 g (83%) of a colorless oil; $[\alpha]_D^{23} = +100.8$ ($c = 1.07$, C_6H_6); ee = 91% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu} = 3420$ cm^{-1}, 3060, 2970, 2920, 2850, 1745, 1720, 1580, 1460, 1440, 1380, 1240, 1190, 1140, 1090, 1070, 1025, 1000, 815, 750, 705, 690. – ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 3H, CH_3), 1.24 (m, 16H, CH_2), 1.89 (m, 2H, CH_2), 3.72 (s, 3H, OCH_3), 7.25–7.47 (m, 5H, C_6H_5), 9.59 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3), 22.7 (CH_2), 24.8 (CH_2), 29.25 (CH_2), 29.30 (CH_2), 29.47 (CH_2), 29.54 (CH_2), 29.7 (CH_2), 31.2 (CH_2), 31.9 (CH_2), 52.8 (OCH_3), 65.8 (C), 128.1 (C_{arom}), 129.1, 130.2, 137.2 (CH_{arom}), 169.0 (CO_2), 190.8 (CHO). – MS, *m/z* (%): 350 (45) [M^+], 322 (100), 290 (60), 263 (39), 164 (38), 135 (30), 123 (32), 110 (62), 109 (43) [SPh^+], 105 (39), 95 (59), 83 (33), 81 (42), 69 (40), 67 (36), 55 (63), 43 (67). – $C_{20}H_{30}O_3S$ (350.5): calcd. C 68.53, H 8.63; found C 68.53, H 8.70.

(R)-(+)-2-Methyl 2-Formyl-2-(phenylthio)tridecanoate (**12g**): 0.88 g (1.9 mmol) of (*S,R*)-**11g** was cleaved with 22 ml of 5 N HCl (17 h) by the procedure described for (*R*)-**12a** yielding 0.55 g (82%) of a colorless oil; $[\alpha]_D^{23} = +109.4$ ($c = 1.20$, C_6H_6); ee = 93% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu} = 3420$ cm^{-1}, 3060, 2950, 2920, 2850, 1745, 1720, 1580, 1465, 1440, 1380, 1240, 1130, 1090, 1070, 1025, 750, 705, 690. – ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, $J = 7.1$ Hz, 3H, CH_3), 1.24 (m, 18H, CH_2), 1.89 (m, 2H, CH_2), 3.71 (s, 3H, OCH_3), 7.26–7.54 (m, 5H, C_6H_5), 9.59 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3), 22.7 (CH_2), 24.8 (CH_2), 29.25 (CH_2), 29.34 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 31.2 (CH_2), 31.9 (CH_2), 52.7 (OCH_3), 65.8 (C), 128.1 (C_{arom}), 129.1, 130.2, 137.2 (CH_{arom}), 169.0 (CO_2), 190.8 (CHO). – MS, *m/z* (%): 364 (41) [M^+], 336 (100), 304 (54), 277 (36), 164 (35), 135 (29), 123 (34), 110 (57), 109 (41) [SPh^+], 105 (36), 95 (42), 83 (37), 69 (38), 67 (35), 57 (40), 55 (66), 43 (69), 41 (71). – $C_{21}H_{32}O_3S$ (364.5): calcd. C 69.19, H 8.85; found C 68.93, H 8.96.

(R)-(+)-Methyl 2-Formyl-2-(phenylthio)-3-(3,4,5-trimethoxyphenyl)propanoate (**12h**): 1.19 g (2.4 mmol) of (*S,R*)-**11h** was cleaved with 20 ml of 5 N HCl (18 h) by the procedure described for (*R*)-**12a** yielding 0.57 g (62%) of a colorless solid; m.p. 92–93°C, $[\alpha]_D^{21} = +141.9$ ($c = 0.94$, C_6H_6); ee = 93% (^{13}C-NMR analysis of the starting material). – IR (KBr): $\tilde{\nu} = 3060$ cm^{-1}, 2960–2820, 1740, 1705, 1590, 1510, 1470, 1425, 1335, 1320, 1260, 1245, 1235, 1130, 755, 695. – ^{1}H NMR ($CDCl_3$): $\delta = 3.24$ (d, $J = 13.5$ Hz, 1H, CH_2), 3.25 (d, $J = 13.8$ Hz, 1H, CH_2), 3.61 (s, 3H, OCH_3), 3.79 [s, 9H, $(CH_3O)_3C_6H_2$], 6.43 [s, 2H, $(CH_3O)_3C_6H_2$], 7.29–7.54 (m, 5H, C_6H_5), 9.64 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 37.8$ (CH_2), 52.7 (CO_2CH_3), 56.0 (OCH_3), 60.8 (OCH_3), 65.8 (C), 107.5 ($CH_{arom}COCH_3$), 127.8 (C_{arom}), 129.2, 130.5, 137.4 (CH_{arom}), 130.5 ($C_{arom}CHOCH_3$), 152.8 ($C_{arom}OCH_3$), 168.5 (CO_2), 190.9 (CHO). – MS, *m/z* (%): 391 (3) [$M^+ + 1$], 390 (11) [M^+], 181 (100) [$(CH_3O)_3C_6H_2CH_2^+$], 168 (5). – $C_{20}H_{22}O_6S$ (390.4): calcd. C 61.52, H 5.68; found C 61.49, H 5.65.

(R)-(+)-Methyl 2-Formyl-2-(methylthio)butanoate (**12i**): 0.285 g (0.99 mmol) of (*S,R*)-**11i** was cleaved with 9 ml of 5 N HCl (10 h) by the procedure described for (*R*)-**12a** yielding 0.135 g (79%) of a colorless liquid; $[\alpha]_D^{21} = +109.9$ ($c = 1.38$, C_6H_6); ee = 88% (^{13}C-NMR analysis of the starting material). – IR (KBr): $\tilde{\nu} = 3000–2800$ cm^{-1}, 1760–1700, 1465, 1440, 1385, 1300, 1250, 1135, 1025, 810. – ^{1}H NMR (neat): $\delta = 0.97$ (t, $J = 7.4$ Hz, 3H, CH_3), 1.85–2.20 (m, 2H, CH_2), 1.95 (s, 3H, SCH_3), 3.85 (s, 3H, OCH_3), 9.32 (s, 1H, CHO). – MS, *m/z* (%): 176 (6) [M^+], 148 (70), 147 (46), 116 (100) [$M^+ - C_2H_4O_2$], 115 (34), 91 (39), 88 (40), 87 (62), 73 (69), 59 (36), 45 (45). – $C_7H_{12}O_3S$ (176.2): calcd. C 47.71, H 6.86; found C 47.71, H 6.63.

(S)-(–)-Methyl 3-Formyl-3-(methylthio)pentanoate (**12j**): 0.070 g (0.37 mmol) of (*S,R*)-**11j** was cleaved with of 5 ml 6 N HCl (10 h) by the procedure described for (*R*)-**12a** yielding 0.035 g (80%) of a colorless liquid; $[\alpha]_D^{20} = -20.9$ ($c = 0.23$, C_6H_6); ee = 91% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu} = 2960$ cm^{-1}, 1740, 1715, 1440, 1410, 1340, 1260, 1150–1000, 910, 800, 735. – ^{1}H NMR ($CDCl_3$): $\delta = 1.01$ (t, $J = 7.5$ Hz, 3H, CH_3), 1.80 (s, 3H, SCH_3), 1.75–1.95 (m, 2H, CH_2), 2.70 (s, 2H, CH_2CO_2), 3.70 (s, 3H, OCH_3), 9.05 (s, 1H, CHO). – MS, *m/z* (%): 190 (<1) [M^+], 162 (45), 129 (46), 115 (37), 101 (100), 61 (29), 59 (29), 55 (46). – $C_8H_{14}O_3S$ (190.3): calcd. C 50.50, H 7.42; found C 50.63, H 7.34.

(S)-(–)-Methyl 3-Formyl-3-(phenylthio)pentanoate (**12k**): 0.50 g (1.4 mmol) of (*S,R*)-**11k** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.22 g (63%) of a colorless oil; $[\alpha]_D^{20} = -62.6$ ($c = 1.01$, C_6H_6); ee = 83% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu} = 3070$ cm^{-1}, 2970, 2950, 2880, 2820, 2720, 1740, 1720,

1475, 1440, 1340, 1290, 1205, 1180, 755, 695. – ^{1}H NMR ($CDCl_3$): δ = 1.04 (t, *J* = 7.4 Hz, 3H, CH_3), 1.79 (d/q, *J* = 14.9/7.4 Hz, 1H, CH_2), 1.92 (d/q, *J* = 14.9/7.4 Hz, 1H, CH_2), 2.60 (d, *J* = 15.9 Hz, 1H, CH_2CO_2), 2.67 (d, *J* = 15.9 Hz, 1H, CH_2CO_2), 3.65 (s, 3H, OCH_3), 7.25–7.42 (m, 5H, C_6H_5), 9.30 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = 8.3 (CH_3), 23.3 (CH_2), 34.9 (CH_2CO_2), 51.9 (OCH_3), 61.3 (C), 128.3 (C_{arom}), 129.2, 130.0, 137.5 (CH_{arom}), 170.2 (CO_2), 192.9 (CHO). – MS, *m/z* (%): 253 (2) [M^+ + 1], 252 (11) [M^+], 224 (92), 191 (51), 163 (83), 135 (65), 115 (40), 110 (100), 108 (45), 83 (44), 65 (32), 55 (54). – $C_{13}H_{16}O_3S$ (252.3): calcd. C 61.88, H 6.39; found C 61.79, H 6.41.

(S)-(–)-Methyl 3-Formyl-3-(phenylthio)nonanoate (**12l**): 0.77 g (2.2 mmol) of (*S,R*)-**11l** was cleaved with 20 ml of 5 N HCl by the procedure described for (*R*)-**12a** yielding 0.13 g (25%) of **8l** and 0.07 g (16%) of methyl 3-formylnon-3-enoate. Data for **8l**: $[\alpha]_D^{28}$ = –57.5 (*c* = 1.05, C_6H_6); ee = 87% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1}, 2950–2850, 2700, 1735, 1435, 1345, 1190, 1175, 750, 695. – ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.21–1.39 (m, 7H, CH_2), 1.55–1.92 (m, 3H, CH_2), 2.61 (d, *J* = 16.2 Hz, 1H, CH_2CO_2), 2.67 (d, *J* = 16.2 Hz, 1H, CH_2CO_2), 3.80 (s, 3H, OCH_3), 7.26–7.43 (m, 5H, C_6H_5), 9.30 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6 (CH_2), 23.8 (CH_2), 29.5 (CH_2), 30.4 (CH_2), 31.6 (CH_2), 35.2 (CH_2CO_2), 51.8 (OCH_3), 60.6 (C), 128.4 (C_{arom}), 129.1, 130.0, 137.5 (CH_{arom}), 170.2 (CO_2), 192.8 (CHO). – MS, *m/z* (%): 309 (2) [M^+ + 1], 308 (8) [M^+], 280 (58), 219 (41), 139 (44), 110 (100), 109 (50), 67 (34), 55 (37). – $C_{17}H_{24}O_3S$ (308.4): calcd. C 66.20, H 7.84; found C 66.19, H 7.77.

(S,S)-(–)-1-{[(2-(tert-Butyldimethylsilyl)propyliden]amino}-2-(methoxymethyl)pyrrolidine (**14a**): To 10.5 mmol of LDA in 20 ml of diethyl ether was added dropwise at –50°C a solution of 2.70 g (10 mmol) of (*S*)-1-{[2-(*tert*-butyldimethylsilyl)ethyliden]amino}-2-(methoxymethyl)pyrrolidine (**13a**)[6] in 10 ml of diethyl ether. After stirring for 5 h at this temp. the reaction mixture was cooled to –100°C, and 1.56 g (11 mmol) of methyl iodide was added. The reaction mixture was allowed to warm to room temp. overnight. After dilution with diethyl ether the organic phase was washed twice with water, then brine and dried with $MgSO_4$. The crude product was purified by flash chromatography yielding 2.49 g (88%) of a yellow oil; $[\alpha]_D^{24}$ = –114.4 (*c* = 1.25, C_6H_6); de = 81% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 2950–2820 cm^{-1}, 1460, 1365, 1340, 1250, 1200, 1120, 1010, 990, 970, 900, 830, 810, 770. – ^{1}H NMR ($CDCl_3$): δ = –0.03 [s, 3H, $Si(CH_3)_2$], –0.02 [s, 3H, $Si(CH_3)_2$], 0.93 [s, 9H, $SiC(CH_3)_3$], 1.16 (d, *J* = 7.1 Hz, 3H, CH_3), 1.72–1.99 (m, 4H, CH_{2pyr}), 2.00 (d/q, *J* = 7.4/7.4 Hz, 1H, CH), 2.69 (m, 1H, NCH_2), 3.28–3.60 (m, 4H, NCH, NCH_2, OCH_2), 3.35 (s, 3H, OCH_3), 6.73 (d, *J* = 7.4 Hz, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –7.2 [$Si(CH_3)_2$], –7.1 [$Si(CH_3)_2$], 13.7 (CH_3), 17.6 (C), 22.0 (NCH_2CH_2), 25.8 (CH), 26.6 (CH_2CH), 27.3 [$SiC(CH_3)_3$], 50.8 (NCH_2), 59.1 (OCH_3), 63.8 (NCH), 74.8 (CH_2O), 144.3 (CHN). – MS, *m/z* (%): 284 (16) [M^+], 239 (100) [$M^+ - CH_2OCH_3$], 123 (31), 115 (16) [$SiC_6H_{15}^+$], 114 (92) [$NC_6H_{12}O^+$], 73 (100), 70 (16) [$NC_4H_8^+$]. – $C_{15}H_{32}N_2OSi$ (284.5): calcd. C 63.32, H 11.34, N 9.85; found C 63.15, H 11.28, N 9.45.

(S,S)-(–)-1-{[2-(tert-Butyldimethylsilyl)butyliden]amino}-2-(methoxymethyl)pyrrolidine (**14b**): 1.89 g (7.0 mmol) of (*S*)-**13a**[6] was transformed by treatment with 15 mmol of LDA and 2.34 g (11 mmol) of iodomethane into 2.03 g (97%) of a yellow oil by the procedure described for (*S,S*)-**14a**; $[\alpha]_D^{23}$ = –87.4 (*c* = 1.06, C_6H_6); de = 96% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3020–2780 cm^{-1}, 1620, 1595, 1460, 1410, 1390, 1360, 1340, 1300, 1280, 1250, 1195, 1115, 1035, 1005, 970, 935, 885, 830, 805, 770, 685. – ^{1}H NMR ($CDCl_3$): δ = –0.02 [s, 3H, $Si(CH_3)_2$], 0.02 [s, 3H, $Si(CH_3)_2$], 0.95 [s, 9H, $SiC(CH_3)_3$], 0.97 (t, *J* = 7.4 Hz, 3H, CH_3), 1.51–2.04 (m, 7H, CH_2, CH, CH_{2pyr}), 2.78 (m, 1H, NCH_2), 3.32–3.62 (m, 4H, NCH, NCH_2, OCH_2), 3.39 (s, 3H, OCH_3), 6.71 (d, *J* = 8.4 Hz, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.8 [$Si(CH_3)_2$], –6.7 [$Si(CH_3)_2$], 14.5 (CH_3), 17.6 (C), 21.6 (CH_2), 21.9 (NCH_2CH_2), 26.5 ($NCHCH_2$), 27.2 [$SiC(CH_3)_3$], 34.3 (CH), 51.3 (NCH_2), 59.1 (OCH_3), 63.9 (NCH), 74.9 (CH_2O), 144.6 (CHN). – MS, *m/z* (%): 298 (21) [M^+], 253 (100) [$M^+ - CH_2OCH_3$], 128 (30), 115 (13) [$SiC_6H_{15}^+$], 114 (14) [$NC_6H_{12}O^+$], 73 (56), 70 (13) [$NC_4H_8^+$]. – $C_{16}H_{34}N_2OSi$ (298.5): calcd. C 64.37, H 11.48, N 9.38; found C 64.35, H 11.35, N 9.73.

(S,S)-(–)-1-{[2-(tert-Butyldimethylsilyl)pentyliden]amino}-2-(methoxymethyl)pyrrolidine (**14c**): 2.08 g (7.7 mmol) of (*S*)-**13a**[6] was transformed by treatment with 15 mmol of LDA in THF and 2.55 g (15 mmol) of 1-iodopropane into 2.41 g (99%) of a yellow oil by the procedure described for (*S,S*)-**14a**; $[\alpha]_D^{23}$ = –89.7 (*c* = 0.95, C_6H_6); de = 93% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1615, 1460, 1390, 1375, 1360, 1250, 1195, 1120, 1060, 1050, 970, 935, 835, 820, 805, 770, 680. – ^{1}H NMR ($CDCl_3$): δ = –0.02 [s, 3H, $Si(CH_3)_2$], 0.02 [s, 3H, $Si(CH_3)_2$], 0.88–0.96 (m, 3H, CH_3), 0.95 [s, 9H, $SiC(CH_3)_3$], 1.20–2.00 (m, 9H, CH_2, CH, CH_{2pyr}), 2.77 (m, 1H, NCH_2), 3.30–3.46 (m, 4H, NCH, NCH_2, OCH_2), 3.38 (s, 3H, OCH_3), 6.67 (d, *J* = 8.4 Hz, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.8 [$Si(CH_3)_2$], –6.7 [$Si(CH_3)_2$], 14.0 (CH_3), 17.6 (C), 21.9 (NCH_2CH_2), 22.9 (CH_2), 26.5 ($NCHCH_2$), 27.3 [$SiC(CH_3)_3$], 30.7 (CH_2), 32.1 (CH), 51.2 (NCH_2), 59.1 (OCH_3), 63.8 (NCH), 74.9 (CH_2O), 144.5 (CHN). – MS, *m/z* (%): 312 (14) [M^+], 267 (91) [$M^+ - CH_2OCH_3$], 142 (34), 115 (22) [$SiC_6H_{15}^+$], 114 (19) [$NC_6H_{12}O^+$], 73 (100). – $C_{17}H_{36}N_2OSi$ (312.6): calcd. C 65.33, H 11.61, N 8.96; found C 65.23, H 11.56, N 9.01.

(S,S)-(–)-1-{[2-(tert-Butyldimethylsilyl)hexyliden]amino}-2-(methoxymethyl)pyrrolidine (**14d**): 2.16 g (8.0 mmol) of (*S*)-**13a**[6] was transformed by treatment with 12 mmol of LDA in THF and 2.21 g (12 mmol) of 1-iodobutane into 2.30 g (88%) of a yellow oil by the procedure described for (*S,S*)-**14a**; α_D^{22} = –61.7 (neat); de = 91% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1620, 1460, 1390, 1380, 1360, 1250, 1200, 1120, 1035, 1005, 970, 935, 830, 820, 805, 770, 680. – ^{1}H NMR ($CDCl_3$): δ = 0.03 [s, 3H, $Si(CH_3)_2$], 0.06 [s, 3H, $Si(CH_3)_2$], 0.88–0.98 (m, 3H, CH_3), 0.95 [s, 9H, $SiC(CH_3)_3$], 1.18–2.02 (m, 11H, CH_2, CH, CH_{2pyr}), 2.77 (m, 1H, NCH_2), 3.31–3.62 (m, 4H, NCH, NCH_2, OCH_2), 3.39 (s, 3H, OCH_3), 6.68 (d, *J* = 8.4 Hz, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.8 [$Si(CH_3)_2$], –6.7 [$SiC(CH_3)_2$], 14.0 (CH_3), 17.6 (C), 21.9 (NCH_2CH_2), 22.6 (CH_2), 26.4 ($NCHCH_2$), 27.2 [$Si(CH_3)_3$], 28.0 (CH_2), 32.0 (CH_2), 32.2 (CH), 51.2 (NCH_2), 59.1 (OCH_3), 63.8 (NCH), 74.8 (CH_2O), 144.6 (CHN). – MS, *m/z* (%): 326 (11) [M^+], 281 (69) [$M^+ - CH_2OCH_3$], 115 (25) [$SiC_6H_{15}^+$], 114 (22) [$NC_6H_{12}O^+$], 73 (100), 70 (24) [$NC_4H_8^+$], 59 (31). – $C_{18}H_{38}N_2OSi$ (326.6): calcd. C 66.20, H 11.73, N 8.58; found C 66.23, H 11.67, N 8.89.

(S,S)-(–)-1-{[2-(tert-Butyldimethylsilyl)octyliden]amino}-2-(methoxymethyl)pyrrolidine (**14e**): 10.38 g (34 mmol) of (*S*)-**13a**[6] was transformed by treatment with 51 mmol of LDA in THF and 8.41 g (51 mmol) of 1-bromohexane into 9.77 g (81%) of a yellow oil by the procedure described for (*S,S*)-**14a**; α_D^{25} = –30.4 (neat): de = 92% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3020–2780 cm^{-1}, 1620, 1460, 1390, 1375, 1360, 1340, 1250, 1195, 1120, 1040, 1005, 970, 935, 830, 805, 770, 680. – ^{1}H NMR ($CDCl_3$): δ = –0.01 [s, 3H, $Si(CH_3)_2$], 0.01 [s, 3H, $Si(CH_3)_2$], 0.88–0.98 (m, 3H, CH_3), 0.95 [s, 9H, $SiC(CH_3)_3$], 1.21–2.01 (m, 15H, CH_2, CH, CH_{2pyr}), 2.77 (m, 1H, NCH_2), 3.30–3.61 (m, 4H, NCH, NCH_2, OCH_2), 3.39 (s, 3H, OCH_3), 6.71 (d, *J* = 8.4 Hz, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.8 [$Si(CH_3)_2$], –6.7 [$Si(CH_3)_2$], 14.1 (CH_3), 17.6 (C), 21.9 (NCH_2CH_2), 22.7 (CH_2), 26.5 ($NCHCH_2$), 27.3 [$SiC(CH_3)_3$], 28.4 (CH_2), 29.3 (CH_2), 29.8 (CH_2), 31.8 (CH_2), 32.3 (CH), 51.2 (NCH_2), 59.2 (OCH_3), 63.9 (NCH), 74.9 (CH_2O), 144.7 (CHN). – MS, *m/z* (%): 354 (21) [M^+], 309 (100) [$M^+ - CH_2OCH_3$], 115 (9) [$SiC_6H_{15}^+$], 114 (13) [$NC_6H_{12}O^+$], 73 (42). – $C_{20}H_{42}N_2OSi$ (354.6): calcd. C 67.73, H 11.94, N 7.90; found C 67.75, H 12.25, N 8.15.

(S,S)-(–)-1-{[2-(tert-Butyldimethylsilyl)decyliden]amino}-2-(methoxymethyl)pyrrolidine (**14f**): 2.70 g (10 mmol) of (*S*)-**13a**[6] was transformed by treatment with 15 mmol of LDA in THF and 3.60 g (15 mmol) of 1-iodooctane into 3.64 g (95%) of a yellow oil by the procedure described for (*S,S*)-**14a**; α_D^{23} = –53.0 (neat); de = 93% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1620, 1460, 1390, 1375, 1360, 1250, 1195, 1120, 1005, 965, 935, 830, 820, 805, 770. – ^{1}H NMR ($CDCl_3$): δ = –0.02 [s, 3H, $Si(CH_3)_2$], 0.02 [s, 3H, $Si(CH_3)_2$], 0.91 (t, *J* = 6.7 Hz, 3H, CH_3), 0.95 [s, 9H, $SiC(CH_3)_3$], 1.20–2.02 (m, 19H, CH_2, CH, CH_{2pyr}), 2.77 (m, 1H, NCH_2), 3.30–3.62 (m, 4H, NCH, NCH_2, OCH_2), 3.39 (s, 3H, OCH_3), 6.71 (d, *J* = 8.4 Hz, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.8 [$Si(CH_3)_2$], –6.7 [$Si(CH_3)_2$], 14.1 (CH_3), 17.6 (C), 21.9 (NCH_2CH_2), 22.7 (CH_2), 26.4 ($NCHCH_2$), 27.3 [$SiC(CH_3)_3$], 28.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 31.9 (CH_2), 32.3 (CH), 51.2 (NCH_2), 59.2 (OCH_3), 63.8 (NCH), 74.9 (CH_2O), 144.9 (CHN). – MS, *m/z* (%): 382 (19) [M^+], 337 (91) [$M^+ - CH_2OCH_3$], 115 (22) [$SiC_6H_{15}^+$], 114 (32) [$NC_6H_{12}O^+$], 73 (100). – $C_{22}H_{46}N_2OSi$ (382.7): C 69.05, H 12.12, N 7.32; found C 69.2, H 12.03, N 7.64.

(R,R)-(–)-1-{[2-(tert-Butyldimethylsilyl)decyliden]amino}-2-(methoxymethyl)pyrrolidine (**14f**): 0.81 g (3.0 mmol) of (*R*)-**13a**[6] was transformed by treatment with 6 mmol of LDA in THF and 1.44 g (6 mmol) of 1-iodooctane into 0.92 g (80%) of a yellow oil by the procedure described for (*S,S*)-**14a**; $[\alpha]_D^{25}$ = +59.4 (*c* = 1.05, C_6H_6); de = 93% (^{13}C NMR). The spectroscopic data were in agreement with those described for (*S,S*)-**14f**.

(S,S)-(–)-1-{[2-(tert-Butyldimethylsilyl)tridecyliden]amino}-2-(methoxymethyl)pyrrolidine (**14g**): 2.03 g (7.5 mmol) of (*S*)-**13a**[6] was transformed by treatment with 7.9 mmol of LDA in THF and 2.33 g (8.25 mmol) of 1-iodoundecane into 2.92 g (96%) of a yellow oil by the procedure described for (*S,S*)-**14a**; α_D^{23} = –51.2 (neat); de = 92% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1460, 1390, 1380, 1360, 1340, 1250, 1195, 1120, 1005, 970, 935, 830, 805, 770, 735. – ^{1}H NMR ($CDCl_3$): δ = 0.03 [s, 3H, $Si(CH_3)_2$], 0.05 [s, 3H, $Si(CH_3)_2$], 0.92 (t, *J* = 6.7 Hz, 3H, CH_3), 0.95 [s, 9H, $SiC(CH_3)_3$], 1.20–2.02 (m, 25H, CH_2, CH, CH_{2pyr}), 2.77 (m, 1H, NCH_2), 3.30–3.62 (m, 4H, NCH, NCH_2, OCH_2), 3.39 (s, 3H, OCH_3), 6.71 (d, *J* = 8.4 Hz, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.8 [$Si(CH_3)_2$], –6.7 [$Si(CH_3)_2$], 14.1 (CH_3), 17.6 (C), 21.9 (NCH_2CH_2), 22.7 (CH_2), 26.4 ($NCHCH_2$), 27.3 [$SiC(CH_3)_3$], 28.4 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.68 (CH_2), 29.72 (CH_2), 29.8 (CH_2), 32.0 (CH_2), 32.3 (CH), 51.2 (NCH_2), 59.2 (OCH_3), 63.8 (NCH), 74.9 (CH_2O), 144.8 (CHN). – MS, *m/z* (%): 424 (18)

$[M^+]$, 379 (100) $[M^+ - CH_2OCH_3]$, 310 (28), 115 (13) $[SiC_6H_{15}^+]$, 114 (28) $[NC_6H_{12}O^+]$, 73 (61). – $C_{25}H_{52}N_2OSi$ (424.8): calcd. C 70.69, H 12.34, N 6.60; found C 70.71, H 12.30, N 7.18.

(S,S)-(–)-1-{[2-(tert-Butyldimethylsilyl)tetradecyliden]amino}-2-(methoxymethyl)pyrrolidine (**14h**): 3.21 g (11.9 mmol) of (*S*)-**13a**[6] was transformed by treatment with 17.9 mmol of LDA in THF and 4.46 g (17.9 mmol) of 1-bromododecane into 3.39 g (65%) of a yellow oil by the procedure described for (*S,S*)-**14a**; $[\alpha]_D^{21} = -62.5$ (c = 1.12, C_6H_6); de = 96% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 2960–2850 cm^{-1}, 1460, 1365, 1340, 1245, 1195, 1120, 1010, 970, 905, 830, 805, 770. – ^1H NMR ($CDCl_3$): δ = 0.02 [s, 3H, $Si(CH_3)_2$], 0.03 [s, 3H, $Si(CH_3)_2$], 0.92 (t, J = 7.1 Hz, 3H, CH_3), 0.95 [s, 9H, $SiC(CH_3)_3$], 1.17–2.06 (m, 27H, CH_2, CH, CH_{2pyr}), 2.76 (m, 1H, NCH_2), 3.09–3.58 (m, 4H, NCH, NCH_2, OCH_2), 3.38 (s, 3H, OCH_3), 6.67 (d, J = 8.4 Hz, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.8 $[Si(CH_3)_2]$, –6.7 $[Si(CH_3)_2]$, 14.1 (CH_3), 17.6 (C), 21.9 (NCH_2CH_2), 22.7 (CH_2), 26.4 ($NCHCH_2$), 27.3 $[SiC(CH_3)_3]$, 28.4 (CH_2), 29.4 (CH_2), 29.58 (CH_2), 29.60 (CH_2), 29.67 (CH_2), 29.73 (CH_2), 29.80 (CH_2), 29.81 (CH_2), 30.5 (CH_2), 32.0 (CH_2), 32.3 (CH), 51.1 (NCH_2), 59.1 (OCH_3), 63.9 (NCH), 74.9 (CH_2O), 144.4 (CHN). – MS, *m/z* (%): 439 (7) $[M^+ + 1]$, 438 (18) $[M^+]$, 393 (100) $[M^+ - CH_2OCH_3]$, 324 (32), 115 (15) $[SiC_6H_{15}^+]$, 114 (34) $[NC_6H_{12}O^+]$, 73 (73). – $C_{26}H_{54}N_2OSi$ (438.8): calcd. C 71.17, H 12.40, N 6.38; found C 70.76, H 12.37, N 6.25.

(S,R)-(+)-1-{[2-(tert-Butyldimethylsilyl)-2-(methoxycarbonyl)-butyliden]amino}-2-(methoxymethyl)pyrrolidine (**15a**): 3.37 g (11.3 mmol) of (*S,S*)-**14b** was added at –110°C to a solution of 50 mmol of MeLi in 35 ml of THF. After stirring for 1 h at this temp. the reaction mixture was allowed to warm to room temp. overnight. The metalated hydrazone was cooled to –110°C, and 7.56 g (80 mmol) of methyl chloroformate was added. After stirring for 3 h at this temp. the reaction mixture was allowed to warm to room temp. overnight. It was subsequently diluted with diethyl ether, washed with pH 7 buffer, then with water and dried with $MgSO_4$. Flash chromatography yielded 2.27 g (56%) of a yellow oil; $[\alpha]_D^{24} = +7.1$ (c = 1.48, C_6H_6); de = 90% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1705, 1590, 1460, 1450, 1370, 1320, 1295, 1220, 1130, 1110, 1020, 970, 825, 820, 770, 690, 665. – ^1H NMR ($CDCl_3$): δ = 0.03 [s, 3H, $Si(CH_3)_2$], 0.11 [s, 3H, $Si(CH_3)_2$], 0.83 (t, J = 7.1 Hz, 3H, CH_3), 0.89 [s, 9H, $SiC(CH_3)_3$], 1.73–2.22 (m, 6H, CH_2, CH_{2pyr}), 2.76 (m, 1H, NCh_2), 3.28–3.65 (m, 4H, NCH, NCH_2, OCH_2), 3.37 (s, 3H, OCh_3), 3.69 (s, 3H, CO_2CH_3), 7.14 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.7 $[Si(CH_3)_2]$, –6.5 $[Si(CH_3)_2]$, 10.2 (CH_3), 19.3 $[SiC(CH_3)_3]$, 21.9 (NCH_2CH_2), 23.7 (CH_2), 26.5 (CH_2CH), 27.6 $[SiC(CH_3)_3]$, 49.7 (NCH_2, C), 51.1 (CO_2CH_3), 59.2 (OCH_3), 63.6 (NCH), 74.9 (CH_2O), 147.4 (CHN), 175.1 (CO_2). – MS, *m/z* (%): 357 (16) $[M^+ + 1]$, 356 (63) $[M^+]$, 311 (100) $[M^+ - CH_2OCH_3]$, 115 (15) $[SiC_6H_{15}^+]$, 73 (63). – $C_{18}H_{36}N_2O_3Si$ (356.6): calcd. C 60.63, H 10.18, N 7.86; found C 60.59, H 10.28, N 7.63.

(S,R)-(–)-1-{[2-(tert-Butyldimethylsilyl)-2-(methoxycarbonyl)-pentyliden]amino}-2-(methoxymethyl)pyrrolidine (**15b**): 0.74 g (2.4 mmol) of (*S,S*)-**14c** was transformed by treatment with 11.8 mmol of MeLi and 1.19 g (18.9 mmol) of methyl chloroformate to 0.42 g (47%) of a yellow oil by the procedure described for (*S,R*)-**15a**; $\alpha_D^{26} = -12.0$ (neat), de value = 96% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1710, 1590, 1460, 1435, 1390, 1360, 1340, 1295, 1250, 1210, 1110, 1020, 970, 905, 835, 825, 805, 775, 690, 665. – ^1H NMR ($CDCl_3$): δ = 0.03 [s, 3H, $Si(CH_3)_2$], 0.12 [s, 3H, $Si(CH_3)_2$], 0.87 (t, J = 7.4 Hz, 3H, CH_3), 0.89 [s, 9H, $SiC(CH_3)_3$], 1.00–1.52 (m, 2H, CH_2), 1.73–2.08 (m, 6H, CH_2, CH_{2pyr}), 2.78 (m, 1H, NCH_2), 3.27–3.62 (m, 4H, NCH, NCH_2, OCH_2), 3.36 (s, 3H, OCH_3), 3.68 (s, 3H, CO_2CH_3), 7.16 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.6 $[Si(CH_3)_2]$, –6.5 $[Si(CH_3)_2]$, 14.7 (CH_3), 19.0 (CH_2), 19.3 $[SiC(CH_3)_3]$, 21.9 (NCH_2CH_2), 26.4 (CH_2CH), 27.6 $[SiC(CH_3)_3]$, 33.0 (CH_2), 33.0 (CH_2), 49.2 (C), 49.6 (NCH_2), 51.1 (CO_2CH_3), 59.2 (OCH_3), 63.7 (NCH), 74.7 (CH_2O), 137.7 (CHN), 175.2 (CO_2). – MS, *m/z* (%): 370 (12) $[M^+]$, 325 (35) $[M^+ - CH_2OCH_3]$, 115 (25) $[SiC_6H_{15}^+]$, 114 (10) $[NC_6H_{12}O^+]$, 89 (28), 73 (100), 70 (40) $[NC_4H_8^+]$. – $C_{19}H_{38}N_2O_3Si$ (370.6): calcd. C 61.58, H 10.33, N 7.56; found C 61.60, H 10.56, N 7.80.

(S,R)-(+)-1-{[2-tert-(Butyldimethylsilyl)-2-(methoxycarbonyl)-hexyliden]amino}-2-(methoxymethyl)pyrrolidine(**15c**): 0.70 g (2.15 mmol) of (*S,S*)-**14d** was transformed with 10.7 mmol of MeLi and 1.62 g (17.2 mmol) of methyl chloroformate into 0.51 g (62%) of a yellow oil by the procedure described for (*S,R*)-**15a**; $[\alpha]_D^{21} = +7.1$ (c = 0.98, C_6H_6); de = 97% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1710, 1590, 1460, 1430, 1390, 1380, 1360, 1340, 1240, 1200, 1110, 1030, 1010, 855, 835, 800, 770, 690, 665. – ^1H NMR ($CDCl_3$): δ = 0.03 [s, 3H, $Si(CH_3)_2$], 0.12 [s, 3H, $Si(CH_3)_2$], 0.88 (t, J = 7.4 Hz, 3H, CH_3), 0.89 [s, 9H, $SiC(CH_3)_3$], 0.87–1.50 (m, 4H, CH_2), 1.76–2.11 (m, 6H, CH_2, CH_{2pyr}), 2.76 (m, 1H, NCH_2), 3.29–3.62 (m, 4H, NCH, NCH_2, OCH_2), 3.36 (s, 3H, OCH_3), 3.68 (s, 3H, CO_2CH_3), 7.16 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.6 $[Si(CH_3)_2]$, –6.5 $[Si(CH_3)_2]$, 14.0 (CH_3), 19.3 $[SiC(CH_3)_3]$, 21.8 (NCH_2CH_2), 21.9 (CH_2), 26.4 (CH_2CH), 27.6 $[SiC(CH_3)_3]$, 27.9 (CH_2), 30.5 (CH_2), 49.1 (C), 49.6 (NCH_2), 51.1 (CO_2CH_3), 59.2 (OCH_3), 63.7 (NCH), 74.7 (CH_2O), 137.7 (CHN), 175.2 (CO_2). – MS, *m/z* (%): 385 (13) $[M^+ + 1]$, 384 (43) $[M^+]$, 339 (100) $[M^+ - CH_2OCH_3]$, 115 (24) $[SiC_6H_{15}^+]$, 114 (11) $[NC_6H_{12}O^+]$, 73 (86), 70 (35) $[NC_4H_8^+]$. – $C_{20}H_{40}N_2O_3Si$ (384.6): calcd. C 62.45, H 10.48, N 7.28; found C 62.43, H 10.42, N 7.38.

(S,R)-1-{[2-(tert-Butyldimethylsilyl)-2-(methoxycarbonyl)octyliden]-amino}-2-(methoxymethyl)pyrrolidine (**15d**): 3.55 g (10 mmol) of (*S,S*)-**14e** was transformed by treatment with 50 mmol of MeLi and 7.56 g (80 mmol) of methyl chloroformate into 2.15 g (52%) of a yellow oil by the procedure described for (*S,R*)-**15a**; $[\alpha]_D^{20} = 0.0$ (c = 0.95, C_6H_6); de = 98% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3000–2780 cm^{-1}, 1710, 1460, 1390, 1380, 1360, 1340, 1220, 1190, 1110, 1040, 1005, 970, 860, 835, 805, 770, 690, 665. – ^1H NMR ($CDCl_3$): δ = 0.03 [s, 3H, $Si(CH_3)_2$], 0.12 [s, 3H, $Si(CH_3)_2$], 0.87 (t, J = 7.1 Hz, 3H, CH_3), 0.89 [s, 9H, $SiC(CH_3)_3$], 1.21–1.34 (m, 8H, CH_2), 1.79–2.10 (m, 6H, CH_2, CH_{2pyr}), 2.77 (m, 1H, NCH_2), 3.27–3.63 (m, 4H, NCH, NCH_2, OCH_2), 3.37 (s, 3H, OCH_3), 3.68 (s, 3H, CO_2CH_3), 7.15 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.6 $[Si(CH_3)_2]$, –6.5 $[Si(CH_3)_2]$, 14.1 (CH_3), 19.3 $[SiC(CH_3)_3]$, 21.9 (NCH_2CH_2), 22.7 (CH_2), 25.6 (CH_2), 26.5 (CH_2CH), 27.6 $[SiC(CH_3)_3]$, 30.0 (CH_2), 30.8 (CH_2), 31.8 (CH_2), 49.2 (C), 49.6 (NCH_2), 51.1 (CO_2CH_3), 59.2 (OCH_3), 63.7 (NCH), 74.8 (CH_2O), 137.8 (CHN), 175.2 (CO_2). – MS, *m/z* (%): 413 (19) $[M^+ + 1]$, 412 (63) $[M^+]$, 367 (100) $[M^+ - CH_2OCH_3]$, 115 (15) $[SiC_6H_{15}^+]$, 114 (9) $[NC_6H_{12}O^+]$, 73 (55). – $C_{22}H_{44}N_2O_3Si$ (412.7): calcd. C 64.03, H 10.75, N 6.79; found C 64.18, H 10.66, N 7.22.

(S,R)-(+)-1-{[(2-tert-Butyldimethylsilyl)-2-(methoxycarbonyl)-decyliden]amino}-2-(methoxymethyl)pyrrolidine (**15e**): 1.91 g (5.0 mmol) of (*S,S*)-**14f** was transformed by treatment with 25 mmol of MeLi and 3.78 g (40 mmol) of methyl chloroformate into 0.95 g (43%) of a yellow oil by the procedure described for (*S,R*)-**15a**; $[\alpha]_D^{21} = +4.3$ (c = 1.20, C_6H_6); de = 96% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1710, 1460, 1390, 1380, 1360, 1340, 1250, 1220, 1170, 1115, 835, 820, 770. – ^1H NMR ($CDCl_3$): δ = 0.02 [s, 3H, $Si(CH_3)_2$], 0.11 [s, 3H, $Si(CH_3)_2$], 0.87 (t, J = 7.1 Hz, 3H, CH_3), 0.89 [s, 9H, $SiC(CH_3)_3$], 1.25 (m, 12H, CH_2), 1.75–2.09 (m, 6H, CH_2, CH_{2pyr}), 2.76 (m, 1H, NCH_2), 3.29–3.63 (m, 4H, NCH, NCH_2, OCH_2), 3.37 (s, 3H, OCH_3), 3.68 (s, 3H, CO_2CH_3), 7.15 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.6 $[Si(CH_3)_2]$, –6.5 $[Si(CH_3)_2]$, 14.1 (CH_3), 19.3 $[SiC(CH_3)_3]$, 21.9 (NCH_2CH_2), 22.7 (CH_2), 25.7 (CH_2), 26.5 (CH_2CH), 27.6 $[SiC(CH_3)_3]$, 29.4 (CH_2), 29.6 (CH_2), 30.4 (CH_2), 30.8 (CH_2), 31.9 (CH_2), 49.1 (C), 49.6 (NCH_2), 51.1 (CO_2CH_3), 59.2 (OCH_3), 63.7 (NCH), 74.8 (CH_2O), 137.8 (CHN), 175.2 (CO_2). – MS, *m/z* (%): 441 (19) $[M^+ + 1]$, 440 (59) $[M^+]$, 395 (100) $[M^+ - CH_2OCH_3]$, 115 (17) $[SiC_6H_{15}^+]$, 114 (10) $[NC_6H_{12}O^+]$, 73 (65). – $C_{24}H_{48}N_2O_3Si$ (440.7): calcd. C 65.41, H 10.98, N 6.36; found C 65.48, H 11.00, N 6.70.

(R,S)-(–)-1-{[2-(tert-Butyldimethylsilyl)-2-(methoxycarbonyl)-decyliden]amino}-2-(methoxymethyl)pyrrolidine (**15e**): 0.76 g (2.0 mmol) of (*R,R*)-**14f** was transformed by treatment with 10 mmol of MeLi and 1.51 g (16 mmol) of methyl chloroformate into 0.28 g (32%) of a yellow oil by the procedure described for (*S,R*)-**15a**; $[\alpha]_D^{25} = -5.6$ (c = 1.18, C_6H_6); de = 98% (^{13}C NMR). The spectroscopic data were in agreement with those described for (*S,R*)-**15e**.

(S,R)-(+)-1-{[2-(tert-Butyldimethylsilyl)-2-(methoxycarbonyl)tridecyliden]amino}-2-(methoxymethyl)pyrrolidine (**15f**): 0.85 g (2.0 mmol) of (*S,S*)-**14g** was transformed by treatment with 10 mmol of MeLi and 1.51 g (16 mmol) of methyl chloroformate into 0.60 g (62%) of a yellow oil by the procedure described for (*S,R*)-**15a**; $[\alpha]_D^{21} = +4.1$ (c = 1.02, C_6H_6); de = 96% (^{13}C NMR): – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1710, 1460, 1390, 1380, 1360, 1340, 1250, 1220, 1115, 860, 835, 805, 770. – ^1H NMR ($CDCl_3$): δ = 0.02 [s, 3H, $Si(CH_3)_2$], 0.11 [s, 3H, $Si(CH_3)_2$], 0.88 (t, J = 7.1 Hz, 3H, CH_3), 0.89 [s, 9H, $SiC(CH_3)_3$], 1.25 (m, 18H, CH_2), 1.75–2.13 (m, 6H, CH_2, CH_{2pyr}), 2.76 (m, 1H, NCH_2), 3.29–3.62 (m, 4H, NCH, NCH_2, OCH_2), 3.36 (s, 3H, OCH_3), 3.68 (s, 3H, CO_2CH_3), 7.15 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = –6.7 $[Si(CH_3)_2]$, –6.5 $[Si(CH_3)_2]$, 14.1 (CH_3), 19.3 $[SiC(CH_3)_3]$, 21.8 (NCH_2CH_2), 22.6 (CH_2), 25.7 (CH_2), 26.4 (CH_2CH), 27.6 $[SiC(CH_3)_3]$, 29.4 (CH_2), 29.6 (CH_2), 29.67 (CH_2), 29.70 (CH_2), 29.74 (CH_2), 30.4 (CH_2), 30.8 (CH_2), 31.9 (CH_2), 49.1 (C), 49.6 (NCH_2), 51.1 (CO_2CH_3), 59.2 (OCH_3), 63.7 (NCH), 74.8 (CH_2O), 137.7 (CHN), 175.2 (CO_2). – MS, *m/z* (%): 483 (25) $[M^+ + 1]$, 482 (70) $[M^+]$, 437 (100) $[M^+ - CH_2OCH_3]$, 115 (15) $[SiC_6H_{15}^+]$, 114 (11) $[NC_6H_{12}O^+]$, 73 (63). – $C_{27}H_{54}N_2O_3Si$ (482.8): calcd. C 67.17, H 11.27, N 5.80; found C 67.26, H 11.27, N 6.35.

(S,S)-(–)-1-{[2-(tert-Butyldimethylsilyl)-2-methylbutyliden]amino}-2-(methoxymethyl)pyrrolidine (**15g**): 2.84 g (10 mmol) of (*S,S*)-**14b** was metalated with 50 mmol of MeLi and alkylated with 12.50 g (80 mmol) of iodoethane by the procedure described for (*S,R*)-**15a**. The reaction mixture was diluted with diethyl ether, washed with brine, then with water and dried with $MgSO_4$. Flash chromatography yielded 2.57 g (82%) of a yellow oil; $[\alpha]_D^{23} = -120.5$ (c = 1.00, C_6H_6); de = 93% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 2960–2820 cm^{-1}, 1460, 1380, 1360, 1340, 1250, 1200, 1120, 1010, 970, 830,

765, 665. – ^{1}H NMR ($CDCl_3$): δ = −0.03 [s, 3H, $Si(CH_3)_2$], −0.02 [s, 3H, $Si(CH_3)_2$], 0.80 (t, *J* = 7.3 Hz, 3H, CH_3), 0.92 [s, 9H, $SiC(CH_3)_3$], 1.11 (s, 3H, CH_3), 1.53 (d/q, *J* = 14.5/7.3, 1H, CH_2), 1.72–2.00 (m, 5H, CH_2, CH_{2pyr}), 2.68 (m, 1H, NCH_2), 3.24–3.65 (m, 4H, NCH, NCH_2, OCH_2), 3.36 (s, 3H, OCH_3), 6.67 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = −7.18 [$Si(CH_3)_2$], −7.15 [$Si(CH_3)_2$], 8.1 (CH_3), 17.3 (CH_3), 19.0 [$SiC(CH_3)_3$], 21.9 (NCH_2CH_2), 26.5 (CH_2CH), 27.6 (CH_2), 28.3 [$SiC(CH_3)_3$], 33.1 (C), 50.6 (NCH_2), 59.2 (OCH_3), 63.9 (NCH), 75.0 (CH_2O), 146.2 (CHN). – MS, *m/z* (%): 312 (12) [M^+], 267 (10) [$M^+ - CH_2OCH_3$], 198 (90) [$M^+ - NC_6H_{12}O$], 197 (21) [$M^+ - SiC_6H_{15}$], 142 (36), 115 (15) [$SiC_6H_{15}^+$], 114 (23) [$NC_6H_{12}O^+$], 73 (100). – $C_{17}H_{36}N_2OSi$ (312.6): calcd. C 65.33, H 11.61, N 8.96; found C 65.38, H 11.87, N 8.98.

(S,R)-(−)-1-{[2-(tert-Butyldimethylsilyl)-2-methylbutyliden]amino}-2-(methoxymethyl)pyrrolidine (**15g**): 0.45 g (1.5 mmol) of (*S,S*)-**14c** was transformed by treatment with 7.5 mmol of MeLi and 1.70 g (12 mmol) of methyl iodide into 0.31 g (66%) of a yellow oil by the procedure described for (*S,S*)-**15g**; $[\alpha]_D^{22}$ = −68.7 (*c* = 1.07, C_6H_6); de = 32% (^{13}C NMR). The spectroscopic data were in agreement with those described for (*S,S*)-**15g**.

(S,R)-(−)-1-{[2-(tert-Butyldimethylsilyl)-2-methylhexyliden]amino}-2-(methoxymethyl)pyrrolidine (**15h**): 0.66 g (2.0 mmol) of (*S,S*)-**14d** was transformed by treatment with 9.1 mmol of MeLi and 1.70 g (12 mmol) of methyl iodide into 0.43 g (63%) of a yellow oil by the procedure described for (*S,S*)-**15g**; $[\alpha]_D^{23}$ = −55.6 (*c* = 1.18, C_6H_6); de = 48% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 2960–2820 cm^{-1}, 1460, 1375, 1360, 1340, 1250, 1195, 1120, 825, 765. – ^{1}H NMR ($CDCl_3$): δ = −0.03 [s, 3H, $Si(CH_3)_2$], −0.02 [s, 3H, $Si(CH_3)_2$], 0.85–0.97 [m, 12H, $CH_3SiC(CH_3)_3$], 1.15 (s, 3H, CH_3), 1.15–1.97 (m, 10H, CH_2, CH_{2pyr}), 2.61–2.74 (m, 1H, NCH_2), 3.19–3.65 (m, 4H, NCH, NCH_2, OCH_2), 3.37 (s, 3H, OCH_3), 6.76 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = −7.2 [$Si(CH_3)_2$], −7.1 [$Si(CH_3)_2$], 14.1 (CH_3), 17.9 (CH_3), 19.2 [$SiC(CH_3)_3$], 21.8 (NCH_2CH_2), 23.6 (CH_2), 26.1 (CH_2), 26.4 (CH_2CH), 28.4 [$SiC(CH_3)_3$], 33.3 (C), 35.2 (CH_2), 50.7 (NCH_2), 59.1 (OCH_3), 64.1 (NCH), 74.7 (CH_2O), 147.5 (CHN). – MS, *m/z* (%): 340 (21) [M^+], 295 (10) [$M^+ - CH_2OCH_3$], 226 (100) [$M^+ - NC_6H_{12}O$], 225 (19) [$M^+ - SiC_6H_{15}$], 115 (22) [$SiC_6H_{15}^+$], 114 (28) [$NC_6H_{12}O^+$], 73 (88), 70 (27) [$NC_4H_8^+$]. – $C_{19}H_{40}N_2OSi$ (340.6): calcd. C 67.00, H 11.84, N 8.22; found C 66.57, H 11.81, N 8.24.

(S,R)-(−)-1-{[2-(tert-Butyldimethylsilyl)-2-ethylpentyliden]amino}-2-(methoxymethyl)pyrrolidine (**15i**): 2.81 g (9.0 mmol) of (*S,S*)-**14c** was transformed by treatment with 45 mmol of MeLi and 11.03 g (72 mmol) of iodoethane into 2.68 g (87%) of a yellow oil by the procedure described for (*S,S*)-**15g**; $[\alpha]_D^{20}$ = −75.0 (*c* = 1.09, C_6H_6); de = 86% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 2960–2820 cm^{-1}, 1460, 1390, 1380, 1360, 1340, 1250, 1200, 1120, 1010, 970, 830, 805, 765, 670. – ^{1}H NMR ($CDCl_3$): δ = 0.01 [s, 3H, $Si(CH_3)_2$], 0.03 [s, 3H, $Si(CH_3)_2$], 0.85 (t, *J* = 7.4 Hz, 3H, CH_3), 0.89 (t, *J* = 7.4 Hz, 3H, CH_3), 0.91 [s, 9H, $SiC(CH_3)_3$], 1.20–1.97 (m, 10H, CH_2, CH_{2pyr}), 2.61–2.71 (m, 1H, NCH_2), 3.21–3.63 (m, 4H, NCH, NCH_2, OCH_2), 3.36 (s, 3H, OCH_3), 6.68 (s, 1H, CHN). – ^{13}C-NMR ($CDCl_3$): δ = −5.4 [$Si(CH_3)_2$], −5.3 [$Si(CH_3)_2$], 9.0 (CH_3), 15.1 (CH_3), 17.8 (CH_2), 19.3 [$SiC(CH_3)_3$], 21.9 (NCH_2CH_2), 24.5 (CH_2), 26.5 (CH_2CH), 28.3 [$SiC(CH_3)_3$], 34.2 (CH_2), 37.2 (C), 50.5 (NCH_2), 59.1 (OCH_3), 63.9 (NCH), 75.0 (CH_2O), 146.8 (CHN). – MS, *m/z* (%): 340 (7) [M^+], 295 (3) [$M^+ - CH_2OCH_3$], 226 (64) [$M^+ - NC_6H_{12}O$], 225 (15) [$M^+ - SiC_6H_{15}$], 73 (100). – $C_{19}H_{40}N_2OSi$ (340.6): calcd. C 67.00, H 11.84, N 8.22; found C 66.70, H 11.99, N 8.25.

(S,S)-(−)-1-{[2-(tert-Butyldimethylsilyl)-2-ethylpentyliden]amino}-2-(methoxymethyl)pyrrolidine (**15i**): 2.99 g (10 mmol) of (*S,S*)-**14b** was transformed by treatment with 50 mmol of MeLi and 13.60 g (80 mmol) of 1-iodopropane into 2.27 g (66%) of a yellow oil by the procedure described for (*S,S*)-**15g**; $[\alpha]_D^{21}$ = −96.6 (*c* = 1.04, C_6H_6); de = 79% (^{13}C NMR). The spectroscopic data were in agreement with those described for (*S,R*)-**15i**.

(S,R)-(−)-1-{[2-(tert-Butyldimethylsilyl)-2-ethylhexyliden]amino}-2-(methoxymethyl)pyrrolidine (**15j**): 4.57 g (14 mmol) of (*S,S*)-**14d** was transformed by treatment with 70 mmol of MeLi and 15.80 g (101 mmol) of iodoethane into 3.92 g (79%) of a yellow oil by the procedure described for (*S,S*)-**15g**; $[\alpha]_D^{21}$ = −78.8 (*c* = 1.03, C_6H_6); de = 85% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 2980–2810 cm^{-1}, 1590, 1465, 1390, 1380, 1360, 1340, 1250, 1200, 1125, 1010, 975, 830, 810, 765. – ^{1}H NMR ($CDCl_3$): δ = 0.02 [s, 3H, $Si(CH_3)_2$], 0.03 [s, 3H, $Si(CH_3)_2$], 0.86 (t, *J* = 7.4 Hz, 3H, CH_3), 0.89–0.94 [m, 12H, CH_3, $SiC(CH_3)_3$], 1.15–1.98 (m, 12H, CH_2, CH_{2pyr}), 2.68 (m, 1H, NCH_2), 3.22–3.64 (m, 4H, NCH, NCH_2, OCH_2), 3.36 (s, 3H, OCH_3), 6.69 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = −5.4 [$Si(CH_3)_2$], −5.3 [$Si(CH_3)_2$], 9.1 (CH_3), 14.2 (CH_3), 19.4 [$SiC(CH_3)_3$], 21.9 (NCH_2CH_2), 23.8 (CH_2), 24.4 (CH_2), 26.4 (CH_2CH), 26.7 (CH_2), 28.3 [$SiC(CH_3)_3$], 31.5 (CH_2), 37.1 (C), 50.5 (NCH_2), 59.1 (OCH_3), 63.9 (NCH), 74.9 (CH_2O), 146.9 (CHN). – MS, *m/z* (%): 354 (15) [M^+], 309 (5) [$M^+ - CH_2OCH_3$], 240 (100) [$M^+ - NC_6H_{12}O$], 239 (21) [$M^+ - SiC_6H_{15}$], 115 (16) [$SiC_6H_{15}^+$], 114 (21) [$NC_6H_{12}O^+$], 73 (85), 70 (27) [$NC_4H_8^+$]. – $C_{20}H_{42}N_2OSi$ (354.65): calcd. C 67.73, H 11.94, N 7.90; found C 67.63, H 11.91, N 7.93.

(S,S)-(−)-1-{[2-(tert-Butyldimethylsilyl)-2-ethylhexyliden]amino}-2-(methoxymethyl)pyrrolidine (**15j**): 2.21 g (7.4 mmol) of (*S,S*)-**14b** was transformed by treatment with 37 mmol of MeLi and 10.85 g (55.2 mmol) of 1-iodobutane into 1.81 g (69%) of a yellow oil by the procedure described for (*S,S*)-**15g**; $[\alpha]_D^{21}$ = −91.7 (*c* = 1.03, C_6H_6); de = 75% (^{13}C NMR). The spectroscopic data were in agreement with those described for (*S,R*)-**15j**.

(S,R)-(−)-1-{[2-(tert-Butyldimethylsilyl)-2-ethyldecyliden]amino}-2-(methoxymethyl)pyrrolidine (**15k**): 1.91 g (5.0 mmol) of (*S,S*)-**14f** was transformed by treatment with 25 mmol of MeLi and 6.13 g (39 mmol) of iodoethane into 0.80 g (39%) of a yellow oil by the procedure described for (*S,S*)-**15g**; $[\alpha]_D^{22}$ = −61.3 (*c* = 0.97, C_6H_6); de = 84% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 2960–2850 cm^{-1}, 1460, 1390, 1380, 1365, 1340, 1250, 1200, 1120, 830, 810, 765. – ^{1}H NMR ($CDCl_3$): δ = 0.02 [s, 3H, $Si(CH_3)_2$], 0.03 [s, 3H, $Si(CH_3)_2$], 0.83–0.94 (m, 6H, CH_3), 0.91 [s, 9H, $SiC(CH_3)_3$], 1.20–1.99 (m, 20H, CH_2, CH_{2pyr}), 2.62–2.70 (m, 1H, NCH_2), 3.21–3.63 (m, 4H, NCH, NCH_2, OCH_2), 3.36 (s, 3H, OCH_3), 6.68 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = −5.4 [$Si(CH_3)_2$], −5.3 [$Si(CH_3)_2$], 9.1 (CH_3), 14.1 (CH_3), 19.4 [$SiC(CH_3)_3$], 21.9 (NCH_2CH_2), 22.8 (CH_2), 24.5 (CH_2), 26.5 (CH_2CH), 28.4 [$SiC(CH_3)_3$], 29.5 (CH_2), 29.7 (CH_2), 30.9 (CH_2), 31.9 (CH_2), 32.0 (CH_2), 37.2 (C), 50.5 (NCH_2), 59.1 (OCH_3), 64.0 (NCH), 75.0 (CH_2O), 146.8 (CHN). – MS, *m/z* (%): 410 (16) [M^+], 365 (4) [$M^+ - CH_2OCH_3$], 296 (100) [$M^+ - NC_6H_{12}O$], 295 (15) [$M^+ - SiC_6H_{15}$], 115 (19) [$SiC_6H_{15}^+$], 114 (24) [$NC_6H_{12}O^+$], 73 (94). – $C_{24}H_{50}N_2OSi$ (410.8): calcd. C 70.18, H 12.27, N 6.82; found C 69.91, H 12.34, N 6.53.

(S,R)-(−)-1-{[2-(tert-Butyldimethylsilyl)-2-ethyltetradecyliden]amino}-2-(methoxymethyl)pyrrolidine (**15l**): 3.76 g (8.6 mmol) of (*S,S*)-**14h** was transformed by treatment with 43 mmol of MeLi and 10.73 g (68.8 mmol) of iodoethane into 1.65 g (41%) of a yellow oil by the procedure described for (*S,S*)-**15g**; $[\alpha]_D^{21}$ = −57.4 (*c* = 1.03, C_6H_6); de = 88% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 2960–2850 cm^{-1}, 1465, 1390, 1380, 1365, 1340, 1250, 1200, 1120, 830, 810, 765. – ^{1}H NMR ($CDCl_3$): δ = 0.01 [s, 3H, $Si(CH_3)_2$], 0.02 [s, 3H, $Si(CH_3)_2$], 0.86 (t, *J* = 7.4 Hz, 3H, CH_3), 0.85–0.94 [m, 12H, CH_3, $SiC(CH_3)_3$], 1.26 (m, 20H, CH_2), 1.53–2.00 (m, 8H, CH_2, CH_{2pyr}), 2.67 (m, 1H, NCH_2), 3.21–3.63 (m, 4H, NCH, NCH_2, OCH_2), 3.36 (s, 3H, OCH_3), 6.68 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = −5.4 [$Si(CH_3)_2$], −5.3 [$Si(CH_3)_2$], 9.1 (CH_3), 14.1 (CH_3), 19.4 [$SiC(CH_3)_3$], 21.9 (NCH_2CH_2), 22.7 (CH_2), 24.56 (CH_2), 24.64 (CH_2), 26.6 (CH_2CH), 28.4 [$SiC(CH_3)_3$], 29.4 (CH_2), 29.71 (CH_2), 29.74 (CH_2), 29.8 (CH_2), 30.9 (CH_2), 32.0 (CH_2), 37.2 (C), 50.5 (NCH_2), 59.1 (OCH_3), 64.0 (NCH), 75.1 (CH_2O), 146.7 (CHN). – MS, *m/z* (%): 466 (17) [M^+], 421 (4) [$M^+ - CH_2OCH_3$], 352 (100) [$M^+ - NC_6H_{12}O$], 351 (14) [$M^+ - SiC_6H_{15}$], 185 (29), 114 (22) [$NC_6H_{12}O^+$], 73 (69). – $C_{28}H_{58}N_2OSi$ (466.9): calcd. C 72.04, H 12.52, N 6.00; found C 72.02, H 12.53, N 5.75.

(S,S)-(−)-1-{[2-(tert-Butyldimethylsilyl)-2-isopropyltetradecyliden]amino}-2-(methoxymethyl)pyrrolidine (**15m**): 2.89 g (6.6 mmol) of (*S,S*)-**14h** was transformed by treatment with 32 mmol of MeLi and 8.98 g (68.8 mmol) of 2-iodopropane into 1.65 g (41%) of a yellow oil by the procedure described for (*S,S*)-**15g**; $[\alpha]_D^{21}$ = −85.7 (*c* = 1.05, C_6H_6); de = 93% (^{13}C NMR). – IR (neat): $\tilde{\nu}$ = 2960–2840 cm^{-1}, 1465, 1385, 1365, 1340, 1250, 1195, 1120, 825, 760. – ^{1}H NMR ($CDCl_3$): δ = 0.05 [s, 3H, $Si(CH_3)_2$], 0.09 [s, 3H, $Si(CH_3)_2$], 0.88 (t, *J* = 7.1 Hz, 3H, CH_3), 0.92 [s, 9H, $SiC(CH_3)_3$], 0.96 (d, *J* = 7.1 Hz, 3H, CH_3), 1.00 (d, *J* = 6.8 Hz, 3H, CH_3), 1.26 (m, 20H, CH_2), 1.59–2.00 (m, 6H, CH_2, CH_{2pyr}), 2.25 [sep, *J* = 6.8 Hz, 1H, $CH(CH_3)_2$], 2.69 (m, 1H, NCH_2), 3.20–3.64 (m, 4H, NCH, NCH_2, OCH_2), 3.37 (s, 3H, OCH_3), 6.77 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ = −3.8 [$Si(CH_3)_2$], −3.6 [$Si(CH_3)_2$], 14.1 (CH_3), 19.2 (CH_3), 19.8 [$SiC(CH_3)_3$], 20.8 (CH_3), 21.8 (NCH_2CH_2), 22.7 (CH_2), 26.1 (CH_2), 26.5 (CH_2CH), 28.5 [$SiC(CH_3)_3$], 29.4 (CH_2), 29.70 (CH_2), 29.71 (CH_2), 29.74 (CH_2), 29.8 (CH_2), 30.9 (CH_2), 31.1 (CH_2), 31.3 (CH), 32.0 (CH_2), 41.2 (C), 50.5 (NCH_2), 59.2 (OCH_3), 63.9 (NCH), 75.1 (CH_2O), 145.4 (CHN). – MS, *m/z* (%): 480 (26) [M^+], 435 (5) [$M^+ - CH_2OCH_3$], 366 (100) [$M^+ - NC_6H_{12}O$], 365 (26) [$M^+ - SiC_6H_{15}$], 199 (29), 142 (47), 115 (29) [$SiC_6H_{15}^+$], 114 (22) [$NC_6H_{12}O^+$], 73 (80). – $C_{29}H_{60}N_2OSi$ (480.9). calcd. C 72.43, H 12.58, N 5.83; found C 72.85, H 12.81, N 5.60.

(R)-(−)-Methyl 2-(tert-Butyldimethylsilyl)-2-formylbutanoate (**16a**): 2.24 g (6.3 mmol) of (*S,R*)-**15a** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 1.19 g (77%) of a colorless liquid; $[\alpha]_D^{21}$ = −183.1 (*c* = 1.00, C_6H_6); ee = 90% (^{13}C NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 2960–2860 cm^{-1}, 2750, 1730, 1715, 1695, 1475, 1470, 1440, 1370, 1335, 1305, 1255, 1230, 1155, 1115, 845, 825, 810, 780, 715. – ^{1}H NMR ($CDCl_3$): δ = 0.09 [s, 3H, $Si(CH_3)_2$], 0.16 [s, 3H, $Si(CH_3)_2$], 0.79 (t, *J* = 7.1 Hz, 3H, CH_3), 0.92 [s, 9H, $SiC(CH_3)_3$], 1.92 (d/q, *J* = 14.4/7.1 Hz, 1H, CH_2), 2.14 (d/q, *J* = 13.6/7.1 Hz, 1H, CH_2), 3.80 (s, 3H, OCH_3), 10.19 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = −7.0 [$Si(CH_3)_2$], −6.8 [$Si(CH_3)_2$], 11.2 (CH_3), 19.3 [$SiC(CH_3)_3$], 22.0 (CH_3), 27.1 [$SiC(CH_3)_3$], 51.5 (OCH_3), 64.1 (C), 172.2 (CO_2), 200.8 (CHO). – MS, *m/z* (%): 245 (1) [$M^+ + 1$], 244 (2) [M^+], 203 (38), 187 (39), 89 (100), 75 (14), 73 (24). – $C_{12}H_{24}O_3Si$ (244.4): calcd. C 58.97, H 9.90; found C 58.95, H 10.08.

(R)-(−)-Methyl 2-(tert-Butyldimethylsilyl)-2-formylpentanoate (**16b**): 0.37 g (1.0 mmol) of (*S,R*)-**15b** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.17 g (66%) of a colorless liquid; $[\alpha]_D^{25} = -167.9$ (*c* = 0.97, C_6H_6); ee = 96% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 2950 cm^{-1}, 2920, 2850, 2740, 1700, 1460, 1430, 1260, 1200, 1110, 930, 905, 860, 840, 820. – ^{1}H NMR ($CDCl_3$): δ = 0.09 [s, 3H, $Si(CH_3)_2$], 0.17 [s, 3H, $Si(CH_3)_2$], 0.87 (t, *J* = 7.4 Hz, 3H, CH), 0.92 [d, *J* = 0.7 Hz, 9H, $SiC(CH_3)_3$], 1.06–1.31 (m, 2H, CH_2), 1.77–1.88 (m, 1H, CH_2), 1.99–2.10 (m, 1H, CH_2), 3.78 (d, *J* = 0.7 Hz, 3H, OCH_3), 10.22 (d, *J* = 1.3 Hz, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = −7.0 [$Si(CH_3)_2$], −6.7 [$Si(CH_3)_2$], 14.5 (CH_3), 19.3 [$SiC(CH_3)_3$], 20.0 (CH_2), 27.1 [$SiC(CH_3)_3$], 31.1 (CH_2), 51.5 (OCH_3), 63.3 (C), 172.5 (CO_2), 201.0 (CHO). – MS, *m/z* (%): 257 (2) [M^+ − 1], 201 (61), 89 (100), 73 (33), 59 (25) [$CH_3CO_2^+$], 44 (19). – $C_{13}H_{26}O_3Si$ (258.4): calcd. C 60.42, H 10.14; found C 59.93, H 10.31.

(R)-(−)-Methyl 2-(tert-Butyldimethylsilyl)-2-formylhexanoate (**16c**): 0.35 g (0.90 mmol) of (*S,R*)-**15c** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.20 g (82%) of a colorless liquid; $[\alpha]_D^{25} = -124.9$ (*c* = 1.18, C_6H_6); ee = 97% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 2960–2850 cm^{-1}, 2745, 1705, 1465, 1430, 1365, 1245, 1205, 1115, 900, 840, 820, 770, 675. – ^{1}H NMR ($CDCl_3$): δ = 0.09 [s, 3H, $Si(CH_3)_2$], 0.17 [s, 3H, $Si(CH_3)_2$], 0.86 (t, *J* = 7.1 Hz, 3H, CH_3), 0.92 [s, 9H, $SiC(CH_3)_3$], 1.01–1.40 (m, 4H, CH_2), 1.80–1.91 (m, 1H, CH_2), 2.02–2.13 (m, 1H, CH_2), 3.79 (s, 3H, OCH_3), 10.22 (d, *J* = 1.3 Hz, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = −7.0 [$Si(CH_3)_2$], −6.8 [$Si(CH_3)_2$], 13.8 (CH_3), 19.3 [$SiC(CH_3)_3$], 23.2 (CH_2), 27.1 [$SiC(CH_3)_3$], 28.8 (CH_2), 29.0 (CH_2), 51.5 (OCH_3), 63.3 (C), 172.5 (CO_2), 201.0 (CHO). – MS, *m/z* (%): 272 (1) [M^+], 271 (4) [M^+ − 1], 215 (44) [$M^+ - (CH_2)_3CH_3$], 89 (100), 75 (46), 73 (55), 59 (30) [$CH_3CO_2^+$], 57 (34). – $C_{14}H_{28}O_3Si$ (272.5): calcd. C 61.72, H 10.36; found C 61.16, H 10.47.

(R)-(−)-Methyl 2-(tert-Butyldimethylsilyl)-2-formyloctanoate (**16d**): 0.33 g (0.80 mmol) of (*S,R*)-**15d** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.18 g (75%) of a colorless liquid; $[\alpha]_D^{20} = -126.1$ (*c* = 0.93, C_6H_6); ee = 98% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 3000–2800°C, 1710, 1690, 1465, 1430, 1410, 1390, 1365, 1230, 1190, 1110, 1040, 1005, 930, 875, 840, 820, 770, 675. – ^{1}H NMR ($CDCl_3$): δ = 0.09 [s, 3H, $Si(CH_3)_2$], 0.17 [s, 3H, $Si(CH_3)_2$], 0.86 (t, *J* = 6.7 Hz, 3H, CH_3), 0.92 [s, 9H, $SiC(CH_3)_3$], 1.00–1.35 (m, 8H, CH_2), 1.78–1.90 (m, 1H, CH_2), 2.01–2.11 (m, 1H, CH_2), 3.78 (s, 3H, OCH_3), 10.22 (d, *J* = 1.7 Hz, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = −7.0 [$Si(CH_3)_2$], −6.7 [$Si(CH_3)_2$], 14.0 (CH_3), 19.3 [$SiC(CH_3)_3$], 22.6 (CH_2), 27.1 [$SiC(CH_3)_3$], 26.7 (CH_2), 29.0 (CH_2), 29.8 (CH_2), 31.6 (CH_2), 51.5 (OCH_3), 63.3 (C), 172.5 (CO_2), 201.0 (CHO). – MS, *m/z* (%): 300 (1) [M^+], 243 (100) [$M^+ - (CH_2)_3CH_3$], 89 (61), 73 (31). – $C_{16}H_{32}O_3Si$ (300.5): calcd. C 63.95, H 10.73; found C 63.85, H 10.82.

(R)-(−)-Methyl 2-(tert-Butyldimethylsilyl)-2-formyldecanoate (**16e**): 0.50 g (1.1 mmol) of (*S,R*)-**15e** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.27 g (75%) of a colorless liquid; $[\alpha]_D^{23} = -131.1$ (*c* = 0.97, C_6H_6); ee = 96% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1710, 1690, 1460, 1430, 1410, 1390, 1360, 1250, 1225, 1110, 1070, 1000, 930, 910, 835, 820, 770, 675. – ^{1}H NMR ($CDCl_3$): δ = 0.09 [s, 3H, $Si(CH_3)_2$], 0.17 [s, 3H, $Si(CH_3)_2$], 0.87 (t, *J* = 7.1 Hz, 3H, CH_3), 0.92 [s, 9H, $SiC(CH_3)_3$], 1.00–1.35 (m, 12H, CH_2), 1.78–1.89 (m, 1H, CH_2), 2.00–2.11 (m, 1H, CH_2), 3.78 (s, 3H, OCH_3), 10.22 (d, *J* = 1.7 Hz, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = −7.0 [$Si(CH_3)_2$], −6.7 [$Si(CH_3)_2$], 14.1 (CH_3), 19.2 [$SiC(CH_3)_3$], 22.7 (CH_2), 26.8 (CH_2), 27.1 [$SiC(CH_3)_3$], 29.0 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 30.1 (CH_2), 31.8 (CH_2), 51.5 (OCH_3), 63.3 (C), 172.4 (CO_2), 201.0 (CHO). – MS, *m/z* (%): 329 (31) [M^+ + 1], 313 (41), 183 (46), 89 (100), 81 (31), 73 (70), 59 (42), 57 (70), 55 (49), 44 (77), 43 (65). – $C_{18}H_{36}O_3Si$ (328.6): calcd. C 65.80, H 11.04; found C 65.80, H 11.34.

(S)-(+)-Methyl 2-(tert-Butyldimethylsilyl)-2-formyldecanoate (**16e**): 0.23 g (0.50 mmol) of (*R,S*)-**15e** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.12 g (73%) of a colorless liquid; $[\alpha]_D^{28} = +107.6$ (*c* = 1.22, C_6H_6); ee = 98% (^{13}C-NMR analysis of the starting material). The spectroscopic data were in agreement with those of (*R*)-**16e**.

(R)-(−)-Methyl 2-(tert-Butyldimethylsilyl)-2-formyltridecanoate (**16f**): 0.37 g (0.80 mmol) of (*S,R*)-**15f** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.21 g (74%) of a colorless liquid; $[\alpha]_D^{21} = -112.1$ (*c* = 1.00, C_6H_6); ee = 96% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 3000–2800 cm^{-1}, 1710, 1690, 1460, 1430, 1410, 1390, 1360, 1250, 1230, 1115, 840, 820, 770, 675. – ^{1}H NMR ($CDCl_3$): δ = 0.09 [s, 3H, $Si(CH_3)_2$], 0.17 [s, 3H, $Si(CH_3)_2$], 0.88 (t, *J* = 7.1 Hz, 3H, CH_3), 0.92 [s, 9H, $SiC(CH_3)_3$], 1.00–1.35 (m, 18H, CH_2), 1.75–1.90 (m, 1H, CH_2), 2.00–2.11 (m, 1H, CH_2), 3.78 (s, 3H, OCH_3), 10.22 (d, *J* = 1.7 Hz, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = −6.9 [$Si(CH_3)_2$], −6.7 [$Si(CH_3)_2$], 14.1 (CH_3), 19.3 [$SiC(CH_3)_3$], 22.7 (CH_2), 26.8 (CH_2), 27.1 [$SiC(CH_3)_3$], 29.1 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 30.2 (CH_2), 32.0 (CH_2), 51.5 (OCH_3), 63.3 (C), 172.5 (CO_2), 201.0 (CHO). – MS, *m/z* (%): 370 (1) [M^+], 314 (100), 313 (63), 253 (28), 89 (86), 75 (36), 73 (85), 59 (34). – $C_{21}H_{42}O_3Si$ (370.65): calcd. C 68.05, H 11.42; found C 68.04, H 11.37.

(S)-(+)-2-(tert-Butyldimethylsilyl)-2-methylbutanoic Acid (**16g**): 0.72 g (2.3 mmol) of (*S,S*)-**15g** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.35 g (70%) of a colorless solid; m.p. 122–124°C, $[\alpha]_D^{23} = +2.3$ (*c* = 0.97, C_6H_6); ee = 93% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 3500–3050 cm^{-1}, 2970, 2940, 2905, 2890, 2860, 1670, 1470, 1320, 1265, 1200, 1160, 1135, 860, 840, 825, 810, 775. – ^{1}H NMR ($CDCl_3$): δ = 0.06 [s, 3H, $Si(CH_3)_2$], 0.10 [s, 3H, $Si(CH_3)_2$], 0.88 (t, *J* = 7.2 Hz, 3H, CH_3), 0.95 [s, 9H, $SiC(CH_3)_3$], 1.23 (s, 3H, CH_3), 1.39 (d/q, *J* = 13.8/7.2 Hz, 1H, CH_2), 2.15 (d/q, *J* = 13.7/7.3 Hz, 1H, CH_2), 12.31 (br s, 1H, OH). – ^{13}C NMR ($CDCl_3$): δ = −7.2 [$Si(CH_3)_2$], −7.1 [$Si(CH_3)_2$], 8.8 (CH_3), 16.4 (CH_3), 19.4 [$SiC(CH_3)_3$], 27.5 (CH_2), 27.7 [$SiC(CH_3)_3$], 37.8 (C), 185.1 (CO_2). – MS, *m/z* (%): 216 (1) [M^+], 159 (25), 84 (24), 75 (100), 73 (36), 69 (20). – $C_{11}H_{24}O_2Si$ (216.4): calcd. C 61.06, H 11.18; found C 61.08, H 11.14.

(R)-(+)-2-(tert-Butyldimethylsilyl)-2-ethylhexanoic Acid (**16h**): 1.04 g (2.94 mmol) of (*S,R*)-**15j** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.56 g (74%) of a colorless liquid; $[\alpha]_D^{22} = +9.0$ (*c* = 0.92, C_6H_6); ee = 85% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 3500–3050 cm^{-1}, 2960–2800, 2605, 1670, 1465, 1390, 1380, 1365, 1250, 1220, 830, 820, 810, 770, 735, 685. – ^{1}H NMR ($CDCl_3$): δ = 0.08 [s, 3H, $Si(CH_3)_2$], 0.09 [s, 3H, $Si(CH_3)_2$], 0.72–0.89 [m, 15H, CH_3, $SiC(CH_3)_3$], 1.12–1.24 (m, 4H, CH_2), 1.45–1.80 (m, 3H, CH_2), 1.87 (d/q, *J* = 14.7/7.5, 1H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = −5.5 [$Si(CH_3)_2$], −5.4 [$Si(CH_3)_2$], 10.1 (CH_3), 14.1 (CH_3), 19.7 [$SiC(CH_3)_3$], 23.7 (CH_2), 23.9 (CH_2), 27.6 (CH_2), 27.8 [$SiC(CH_3)_3$], 30.6 (CH_2), 42.1 (C), 184.5 (CO_2). – MS, *m/z* (%): 258 (2) [M^+], 199 (26), 109 (23), 83 (50), 75 (100), 73 (59), 55 (26). – $C_{14}H_{30}O_2Si$ (258.5): calcd. C 65.06, H 11.70; found C 64.67, H 11.47.

(R)-(+)-2-(tert-Butyldimethylsilyl)-2-ethyltetradecanoic Acid (**16i**): 0.70 g (1.5 mmol) of (*S,R*)-**15l** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.36 g (64%) of a colorless liquid; $[\alpha]_D^{21} = +11.6$ (*c* = 1.09, C_6H_6); ee = 88% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 3330–3050 cm^{-1}, 2960, 2930, 2860, 2620, 1675, 1465, 1390, 1380, 1360, 1260, 1250, 835, 820, 810, 770. – ^{1}H NMR ($CDCl_3$): δ = 0.11 [s, 6H, $Si(CH_3)_2$], 0.88 (t, *J* = 7.1 Hz, 3H, CH_3), 0.91 (t, *J* = 7.1 Hz, 3H, CH_3), 0.94 [s, 9H, $SiC(CH_3)_3$], 1.26 (m, 20H, CH_2), 1.64–1.90 (m, 3H, CH_2), 1.98 (d/q, *J* = 14.6/7.4, 1H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = −5.50 [$Si(CH_3)_2$], −5.46 [$Si(CH_3)_2$], 10.1 (CH_3), 14.1 (CH_3), 19.6 [$SiC(CH_3)_3$], 22.7 (CH_2), 23.8 (CH_2), 25.4 (CH_2), 27.7 [$SiC(CH_3)_3$], 29.4 (CH_2), 29.6 (CH_2), 29.69 (CH_2), 29.72 (CH_2), 30.7 (CH_2), 30.9 (CH_2), 32.0 (CH_2), 42.2 (C), 184.5 (CO_2). – MS, *m/z* (%): 370 (5) [M^+], 299 (40), 157 (24), 83 (61), 75 (100), 73 (63), 55 (29). – $C_{22}H_{46}O_2Si$ (370.7): calcd. C 71.28, H 12.51; found C 71.05, H 12.59.

(S)-(+)-2-(tert-Butyldimethylsilyl)-2-isopropyltetradecanoic Acid (**16j**): 0.96 g (2.0 mmol) of (*S,S*)-**15m** was oxidatively cleaved with ozone according to the procedure described for **4e** yielding 0.52 g (66%) of a colorless liquid; $[\alpha]_D^{23} = +8.7$ (*c* = 0.98, C_6H_6); ee = 93% (^{13}C-NMR analysis of the starting material). – IR (neat): $\tilde{\nu}$ = 3200–3060 cm^{-1}, 2960, 2930, 2860, 2620, 1675, 1470, 1390, 1370, 1265, 1255, 835, 820, 810, 770. – ^{1}H NMR ($CDCl_3$): δ = 0.09 [s, 3H, $Si(CH_3)_2$], 0.12 [s, 3H, $Si(CH_3)_2$], 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 0.96 [s, 9H, $SiC(CH_3)_3$], 1.03 (d, *J* = 7.1 Hz, 6H, CH_3), 1.21–1.78 (m, 22H, CH_2), 2.54 (sep, *J* = 7.1, 1H, CH). – ^{13}C NMR ($CDCl_3$): δ = −5.2 [$Si(CH_3)_2$], −4.1 [$Si(CH_3)_2$], 14.1 (CH_3), 19.7 (CH_3), 20.0 [$SiC(CH_3)_3$], 22.1 (CH), 22.7 (CH_2), 27.5 (CH_2), 28.3 [$SiC(CH_3)_3$], 29.4 (CH_2), 29.6 (CH_2), 29.70 (CH_2), 29.72 (CH_2), 29.74 (CH_2), 29.77 (CH_2), 31.5 (CH_2), 32.0 (CH_2), 47.0 (C), 183.8 (CO_2). – MS, *m/z* (%): 384 (8) [M^+], 327 (38), 229 (23), 213 (47), 140 (28), 109 (22), 98 (43), 97 (81), 95 (29). – $C_{23}H_{48}O_2Si$ (384.7): calcd. C 71.81, H 12.58; found C 71.58, H 12.60.

X-Ray Structure Determination of **12g**[9]: Crystals of sufficient quality were obtained from diethyl ether/petroleum ether (1:1) at room temp. The compound crystallizes in the monoclinic space group $P2_1$, *a* = 9.126(3), *b* = 5.885(2), *c* = 18.511(4) Å. *Z* = 2, *V* = 991.35 Å^3, M_r = 390.5, resulting in a calculated density of $\rho_{calcd.}$ = 1.308 gcm^{-1}, while the total number of electrons per cell amounts to *F*(000) = 412. $\sin\Theta/\lambda_{max}$ = 0.65 for solution and refinement. The structure was solved by direct methods as implemented in the Xtal3.0 package of crystallographite programs[23], employing GENSIN[24] to generate structure-invariant relationships and GENTAN[25] for the general tangent-phasing procedure. A total number of 5653 reflections was collected in the range ±*h* +*k* +*l*, ±*h* −*k*−*l* at 0°C with an Enraf-Nonius CAD4 diffractometer, R_{av} = 0.012, graphite-monochromated Mo-K_α (λ = 0.71069 Å), μ = 1.86 cm^{-1}, no absorption correction. 3435 reflections with $I > 2\sigma(I)$ were used in the full-matrix least-squares refinement process of

254 variables terminating at $R = 0.053$ [$R_w = 0.046$, $w = 1/\sigma^2(F)$] with a final shift/error smaller than 0.0013. Residual electron density 0.3. 15 hydrogen positions were located in a difference Fourier map and 7 hydrogen atomic coordinates were calculated by employing idealized geometric parameters. One methoxy group of the molecule is disordered in that carbon atom C19 occurs in two positions with almost equal site occupation parameters (C19A: 0.567, C19B: 0.43).

X-Ray Structure Determination of **16g**[9]: Crystals of sufficient quality were obtained from diethyl ether at room temperature. The compound crystallizes in the orthorhombic space group $P2_12_12$, $a = 10.849(2)$, $b = 11.717(1)$, $c = 10.943(1)$ Å. $Z = 4$, $V = 1391.04$ Å^3, $M_r = 216.4$, resulting in a calculated density of $\rho_{calcd.} = 1.033$ gcm^{-1}, while the total number of electrons per cell amounts to $F(000) = 480$. $\sin\Theta/\lambda_{max} = 0.631$ for solution and refinement. The structure was solved by direct methods as implemented in the Xtal2.6 package of crystallographic programs[26], employing GENSIN[27] to generate structure-invariant relationships and GENTAN[28] for the general tangentphasing procedure. A total number of 5787 reflections was collected in the range $+h +k +l$, $-h -k -l$ at -10°C with an Enraf-Nonius CAD4 diffractometer, $R_{av} = 0.0147$, graphite-monochromated Mo-K_α ($\lambda = 0.71069$ Å), $\mu = 1.43$ cm^{-1}, no absorption correction. 3862 reflections with $I > 2\sigma(I)$ were used in the full-matrix least-squares refinement process of 127 variables terminating at $R = 0.070$ [$R_w = 0.059$, $w = 1/\sigma^2(F)$] with a final shift/error smaller than 0.00026. Residual electron density 0.3. The positions of the hydrogen atoms were calculated and held fixed during the refinement process.

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[96/94]