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Stereoselective Reduction of Prochiral Ketones, Using Aluminum Hydride Reagents Prepared from $LiAlH_4$ and Chiral Diethanolamines.

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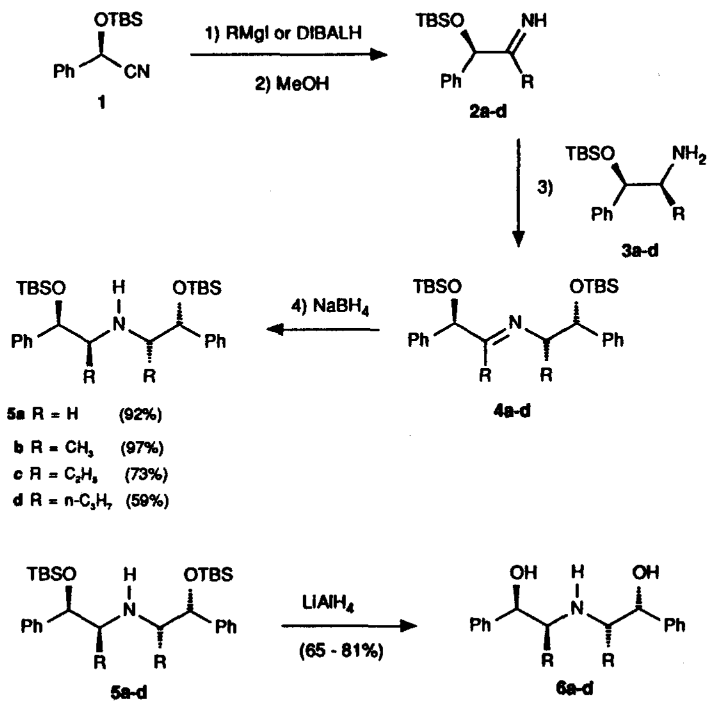
Abstract: The asymmetric reduction of prochiral ketones to chiral secondary alcohols by $LiAlH_4$, modified with optically active diethanolamines, was studied. Asymmetric inductions of up to 94% were obtained with these reagents. The stereoselectivity of the reaction was found to depend both upon the temperature at which the reduction was performed and upon the conditions under which the chiral aluminum hydride reagent had been prepared. By changing the substituents at the carbon atom α to nitrogen in the chiral auxiliary, either the (*R*)- or the (*S*)-enantiomer of the secondary alcohol could be obtained in excess.

INTRODUCTION

Synthesis of optically pure compounds from achiral starting materials, using easily recoverable chiral auxiliaries, has been a major focus in organic chemistry in recent years. A substantial part of this research has been directed towards the synthesis of chiral secondary alcohols *via* asymmetric reduction of prochiral ketones.[1,2] For this purpose simple reducing agents, such as $LiAlH_4$, have been modified by various chiral alcohols, amines, and ethanolamines. The asymmetric induction obtained ranged from a few percent to over 90%.[2] The stereoselectivity of the reduction is low in those cases where disproportionation of the chiral aluminum hydride complex occurs, resulting in the regeneration of $LiAlH_4$, which is a stronger reducing agent than the chiral complex.[3] The presence of non-equivalent hydrides in the aluminum hydride complex can also be a reason for reduced stereoselectivity.[4] Since optically active diethanolamines are able to form thermodynamically stable tridentate complexes with $LiAlH_4$, possessing a single reactive hydride, they would seem to be suitable chiral modifiers. Surprisingly, only a few examples of chiral aluminum hydride reagents containing a diethanolamine



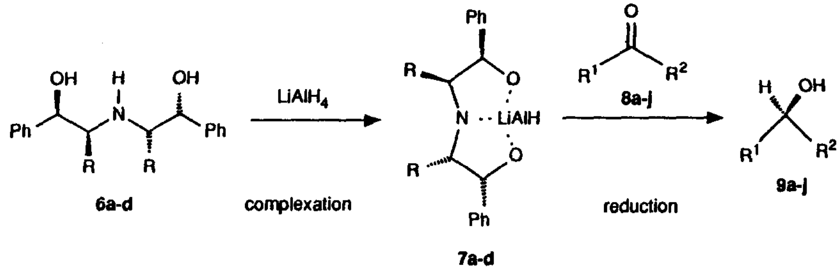
Scheme I: *Synthesis of chiral diethanolamines from optically active cyanohydrins.*

moiety have been reported.[5]

Recently, we have prepared a series of optically active diethanolamines, having two, three, or four stereogenic centers in the diethanolamine backbone. These were used as chiral building blocks in the synthesis of diaza-crown ethers.[6] The synthetic route followed allowed systematic variation of the substitution pattern. We now report the asymmetric reduction of prochiral ketones, using $LiAlH_4$ modified with chiral diethanolamines **6a-d**. These diethanolamines possess a C_2-axis of symmetry and differ only in the substituents attached to the carbon atoms α to nitrogen. Systematic variation of these substituents was expected to provide valuable information about the nature of the transition state of the reduction reaction.

RESULTS and DISCUSSION

Chiral O-protected diethanolamines **5a-d** were prepared from optically active O-protected cyanohydrin **1**[7] *via* a one-pot Grignard-transimination-reduction[8] or a one-pot reduction-transimination-reduction[9] procedure, as previously reported.[6] Thus, **1** was treated with a Grignard reagent or with DIBALH to form an imine-metal complex (Scheme I). Dry methanol was added to protonate the imine anion and to destroy the excess of Grignard reagent or DIBALH. Upon addition of an excess of



Scheme II: *Asymmetric reduction of prochiral ketones by $LiAlH_4$ modified with diethanolamines.*

optically active ethanolamine **3a-d**,[10] transimination of the free primary imine **2a-d** to the thermodynamically more stable secondary imine **4a-d** occurred rapidly. The latter was stereoselectively reduced *in situ* to give protected diethanolamines **5a-d**. The overall yields of these four-step one-pot procedures were high when the substituents R were small, but the yields decreased with increasing size of R. Probably, the equilibrium of the transimination step is shifted towards the side of the primary imine for substrates with large R substituents. This may be due to steric interactions between the R substituents in **4**, which results in destabilization of the secondary imine. A diethanolamine **5**, with R = benzyl, could not be prepared at all by this procedure. Ethanolamine **3** was isolated as the sole reaction product. The de's of the protected diethanolamines, determined by ^1H NMR (**5b-d**) or HPLC-analysis (**5a**), were at least 88%. After reductive removal of the TBS-groups with $LiAlH_4$,[10] unprotected diethanolamines **6a-d** were obtained in almost quantitative yield. Recrystallization yielded diastereomerically pure **6a-d** in 65-81% (de > 96%).

Reduction of acetophenone (**8a**) by $LiAlH_4$, modified with diethanolamine **6b**, was carried out under various reaction conditions (Scheme II). Table 1 shows that the stereoselectivity of the reduction depends both on the temperature at which the reduction step is performed and on the conditions under which the chiral aluminum hydride reagent is prepared. As expected, lowering the temperature of the reduction step results in a higher asymmetric induction (entry 1-3). The dependence of the stereoselectivity of the reduction on the reaction conditions used to form the chiral aluminum reagent is more complex. When the chiral hydride reagent was prepared *in situ* by refluxing $LiAlH_4$ with diethanolamine **6b** in THF for 2 hours, reduction afforded (R)-1-phenylethanol (**9a**) with an ee of 49% (entry 3). If, on the other hand, the preparation of the aluminum complex was performed by refluxing the reagents in THF for only 30 min, product **9a** was obtained with an ee of 65% (entry 4). The fact that a lower asymmetric induction is obtained, when the aluminum hydride reagent is refluxed for a longer period of time, may be due to disproportionation of the chiral reducing agent upon heating.[3] However, when the aluminum complex was prepared by stirring $LiAlH_4$ with **6b** in THF at room temperature for 30 min, alcohol **9a** was obtained with an ee of only 56% (entry 5).

Apparently, for the formation of a good chiral reducing agent, it is necessary to heat the reaction mixture for a short period of time. To investigate this feature, the amount of H_2-gas, that was evolved, when $LiAlH_4$ was allowed to react with an equimolar amount of **6b**, was measured. When a solution of

Table 1: *Asymmetric Reduction of Acetophenone 8a by $LiAlH_4$, Modified with 6b under Various Conditions.*

	complexation			reduction		
entry	T (°C)	time (h)	solv	T (°C)	yield (%)[a]	ee (%)[b]
1	66	2	THF	-40	86	33
2	66	2	THF	-80	84	46
3	66	2	THF	-100	80	49
4	66	0.5	THF	-100	90	65
5	20	0.5	THF	-100	95	56
6	35	0.5	ether	-100	90	54

a) Isolated yields b) Determined by HPLC-analysis, using a CHIRALCEL OD column (flow rate: 1 mL/min; eluent: 2-propanol/n-hexane = 1/9).

6b in THF was slowly added to a suspension of $LiAlH_4$ in THF at room temperature, just over two equivalents of H_2-gas were rapidly evolved. Stirring the reaction mixture at room temperature for another hour did not result in the formation of more H_2-gas. However, when this reaction mixture was refluxed for 30 min, almost another equivalent of H_2-gas was evolved, bringing the total amount to three. These results indicate that the secondary amine group of **6b** is not or only partially deprotonated by $LiAlH_4$ at room temperature. To deprotonate both hydroxyl groups as well as the secondary amine function of **6b** with $LiAlH_4$, heating of the reaction mixture is required.

Next, the asymmetric reduction of several prochiral ketones (**8a-j**) to the corresponding chiral secondary alcohols (**9a-j**) by $LiAlH_4$ modified with diethanolamines **6a-d** was investigated (Scheme II). All these reactions were carried out under the same conditions: first, chiral aluminum hydride complexes **7a-d** were prepared *in situ* by refluxing $LiAlH_4$ with **6a-d** in THF for 30 min, then ketones **8a-j** were reduced by this reagent at -100 °C for 6 hours. The results of these reductions, summarized in Table 2, show that ketones **8a-i**, having an aromatic ring attached to the carbonyl group, were reduced in good chemical yields and in optical yields varying from moderate to excellent (46-94%). Reduction of the aliphatic ketone **8j** by $LiAlH_4$, modified with **6c**, gave only poor asymmetric induction (24%). Ketones **8f** and **8g**, that have an electron donating substituent at the aromatic ring, were reduced more selectively than ketones **8h** and **8i**, carrying an electron withdrawing chlorine substituent at the aromatic ring. This effect might be due to the higher electron density on the carbonyl oxygen atom in **8f** and **8g**, compared to **8h** and **8i**, which causes tighter complexation of the oxygen atom with the lithium ion in the chiral lithium aluminum hydride complex (*vide infra*).

One aspect of major importance in these asymmetric reductions is the ease with which the chiral auxiliary can be regenerated. For all asymmetric reductions described here, the chiral auxiliary used

Table 2: ***Results of the Reduction of Ketones 8a-j by $LiAlH_4$, Modified with Diethanolamines 6a-d, under Standard Conditions[a].***

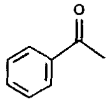
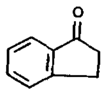
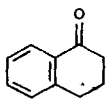
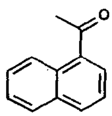
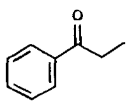
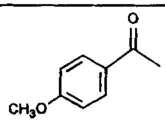
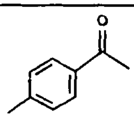
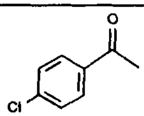
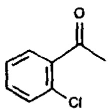
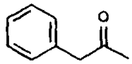
ketone no	structure	ligand	conv (%)	yield (%)[b]	ee (%)[c]	$[\alpha]^{20}_D$ (c=1,$CHCl_3$)	config[d]
8a		6a	88	90	46	-23	S
		6b	89	90	65	+35	R
		6c	90	98	82	+45	R
		6d	83	83	79	+45	R
8b		6a	88	93	72	+19	S
		6c	70	96	93	-26	R
		6d	72	83	94	-29	R
8c		6a	70	86	68	+20	S
		6c	81	98	70	-20	R
		6d	67	88	87	-28	R
8d		6a	78	87	46	-31	S
		6c	75	95	71	+49	R
		6d	76	90	70	+46	R
8e		6b	88	90	59	+30	R
		6c	93	87	72	+35	R
8f		6c	57	83	86	+45	R
8g		6c	63	79	76	+39	R
8h		6c	85	95	70	+30	R

Table 2: *Continued.*

ketone no	structure	ligand	conv (%)	yield (%)[b]	ee (%)[c]	$[\alpha]^{20}_D$ (c=1,$CHCl_3$)	config[d]
8i		**6c**	78	88	67	+41	R
8j		**6c**	100	85	24	-8	R

a) Chiral aluminum hydride complex **7** was prepared *in situ* by refluxing $LiAlH_4$ with **6a-d** in THF for 30 min. The reduction step was carried out at -100 °C for 6 h. b) Isolated yields, based upon the amount of converted starting material. c) Determined by HPLC-analysis (See Experimental). d) Determined by the sign of the optical rotation. **9a-e**, ref. 11; **9f-h**, ref. 12; **9i**, ref. 13; **9j**, ref. 14.

(**6a-d**) could be recovered after the reaction in high yield (85-95%) by recrystallization from $CHCl_3$/pentane. When studying the influence of the R substituent in chiral auxiliaries **6a-d** on the stereoselectivity of the reaction, the following order of selectivity was observed: H > Me > Et ≈ n-Pr. The most striking observation, however, was that, when chiral auxiliary **6a**, with R = H, was employed in the asymmetric reduction, the (*S*)-enantiomer of the product was formed in excess, whereas, when chiral diethanolamines **6b-d**, with R = alkyl, were used, the (*R*)-isomer of the product was obtained as the major enantiomer.

In an attempt to explain these features, the model depicted in Figure 1 was developed. In this model the lithium rather than the aluminum ion is coordinated to both oxygen atoms and the nitrogen atom of the diethanolamine. This postulate is supported by the evidence available in literature.[2,15] The bicyclic lithium-diethanolamine structure most likely will adopt a conformation, in which both large phenyl substituents occupy pseudo-equatorial positions, thereby forcing the R substituents to occupy a pseudo-axial position.[16] Aluminum, with the one remaining hydride, is also bound to the two oxygen atoms of the diethanolamine. The fourth coordination site of aluminum is probably occupied by a solvent molecule. The carbonyl group of the ketone is activated for reduction by complexation to the lithium ion.[15] The ketone complexes in such a manner that the large aromatic substituent is as far away from the bulky complex as possible. If the R substituents of the diethanolamine are alkyl groups, the alkyl group of the ketone will be oriented in the direction of the benzylic proton of the diethanolamine to avoid steric interaction with these R substituents. This results in formation of the (*R*)-alcohol upon reduction. If, on the other hand, the R substituents of the diethanolamine are as small as hydrogen, the steric interaction between the benzylic proton of the chiral auxiliary and the alkyl group of the ketone will be larger than the steric interaction between the R substituents of the ligand and the alkyl group

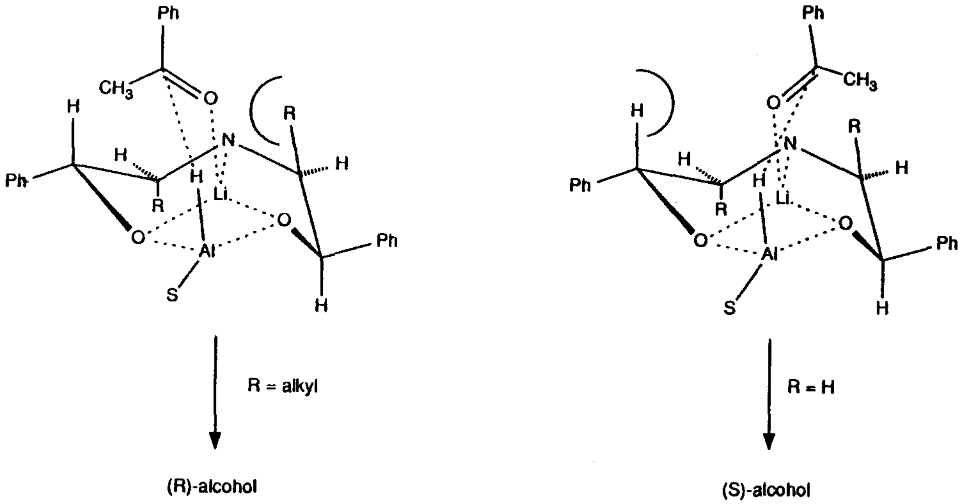


Figure 1: *Transition state model of the asymmetric reduction of acetophenone by diethanolamine modified $LiAlH_4$.*

of the ketone. The latter will now be oriented towards the R substituent of the diethanolamine and thus upon reduction the (*S*)-alcohol will be formed predominantly.

In conclusion, it can be said that chiral aluminum hydride complexes, prepared from $LiAlH_4$ and optically active diethanolamines, can be highly stereoselective reagents in the reduction of prochiral aromatic ketones. Both enantiomers of the product can be obtained by using diethanolamines, having either hydrogen or alkyl substituents at the carbon atoms α to nitrogen, as the chiral modifiers. By systematic variation of these substituents, more insight was obtained in the nature of the transition state complex.

EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-200 instrument. Samples were measured in $CDCl_3$, with TMS as internal standard for ^1H NMR, and $CDCl_3$ as internal standard for ^{13}C NMR. De's were determined by integration of the ^1H NMR signals of the benzylic protons, or by HPLC using a CHIRALCEL OD column (eluent: 2-propanol/n-hexane = 0.25/99.75). Mass spectrometry experiments were performed on a Finnigan MAT TSQ-70 equipped with an Electrospray interface. Experiments were done in positive ionization mode. Samples were dissolved in CH_2Cl_2 and diluted in methanol/water (80/20) with 1% acetic acid, and were introduced by means of constant infusion at a flowrate of 1 μL/min. Optical rotations were measured on a Propol automatic polarimeter. Melting points are uncorrected.

Chemicals

Commercially available chemicals were used, with the exception of **1**,[7] **3a-e**,[10] **5a-c**,[6] and **6b,c**,[6] which were synthesized by methods described before. THF was freshly distilled from $LiAlH_4$ prior to use. Diethyl ether was dried on sodium wire. Methanol was dried on molecular sieves (3Å). All reactions were carried out in a nitrogen atmosphere.

Bis[(1*R*,2*S*)-1-{(*tert.*-butyldimethylsilyl)oxy}-1-phenylpentan-2-yl]amine (5d)

To a solution of 36 mmol of $CH_3CH_2CH_2MgI$ in 50 mL of anhydrous ether was added a solution of 4.40 g (18 mmol) of **1** in 50 mL of ether. After 3 h of reflux, 15 mL of dry methanol and a solution of 15.0 g (51 mmol) of **3d** in 15 mL of methanol were added successively at 0 °C. The reaction mixture was stirred at ambient temperature for 3.5 h. Then, at 0 °C, 1.40 g (36 mmol) of $NaBH_4$ was added in small portions, after which the reaction mixture was stirred overnight at room temperature. After adding 300 mL of water, the mixture was extracted with ether (3 x 150 mL). The combined organic layers were washed with 200 mL of a saturated NaCl solution, dried on $MgSO_4$, and concentrated *in vacuo*. Flash column chromatography (eluent: triethylamine/petroleum ether 40-60 = 3/97) afforded 6.00 g (59%) of **5d** and 11.4 g of **3d** (81% of the excess).

$[\alpha]^{20}_D$ -31 (c=1, $CHCl_3$); de 88% (^1H NMR).

^1H NMR δ(ppm) 7.26 (m, 10H, Ph), 4.48 (d, 2H, J = 5.4 Hz, CHO), 3.48 (m, 2H, CHN), 1.55 (bs, 1H, NH), 1.3-0.9 (m, 8H, CH_2), 0.84 (s, 18H, *t*-Bu), 0.74 (t, 6H, J = 7.1 Hz, CH_3), -0.02 (s, 6H, $SiCH_3$), -0.29 (s, 6H, $SiCH_3$).

^{13}C NMR δ(ppm) 143.4, 127.6, 127.3, 126.9 (Ph), 77.6 (CHO), 61.3 (CHN), 31.8 (CH_2), 25.9 ($C(CH_3)_3$), 18.1 ($C(CH_3)_3$), 18.1 (CH_2), 14.6 (CH_3), -4.5, -5.0 ($SiCH_3$).

MS (EI) m/z 570 (100%, $[M+H]^+$), 438 (5%, $[M+H-TBSOH]^+$), 306 (86%, $[M+H-2(TBSOH)]^+$), 277 (11%, $[PhCH(OTBS)CH^+CH_2CH_2CH_3]$).

Anal. Calcd for $C_{34}H_{59}NO_2Si_2$: C, 71.64; H, 10.43; N, 2.46. Found: C, 71.68; H, 10.29; N, 2.20.

Bis[(1*R*)-1-hydroxy-phenylethan-2-yl]amine (6a)

To a suspension of 1.20 g (31 mmol) of $LiAlH_4$ in 10 mL of freshly distilled THF was added a solution of 3.80 g (7.8 mmol) of **5a** in 30 mL of THF at 0 °C. After 4 h of reflux, the reaction mixture was cooled to 0 °C. Successively 1.3 mL of water in 5 mL of THF, 2.4 mL of 4 M NaOH, and 3.6 mL of water were added. The suspension was stirred at room temperature for 1 h. After $MgSO_4$ was added, the suspension was stirred for another 30 min and filtered. The residue was washed three times with 50 mL of ether. The combined filtrates were concentrated *in vacuo*. The crude product was then recrystallized from $CHCl_3$/pentane.

Yield: 1.63 g (81%); $[\alpha]^{20}_D$ -75 (c=1, $CHCl_3$); mp 90-93 °C.

^1H NMR δ(ppm) 7.34 (m, 10H, Ph), 4.74 (dd, 2H, J = 4.1 Hz, J = 8.0 Hz, CHO), 2.90 (dd, 2H, J = 4.1 Hz, J = 12.3 Hz, CHN), 2.81 (dd, 2H, J = 8.0 Hz, J = 12.3 Hz, CHN).

^{13}C NMR δ(ppm) 142.4, 128.2, 127.4, 125.7 (Ph), 71.9 (CHO), 56.5 (CHN).

Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.42; H, 7.39; N, 5.36.

Bis[(1*R*,2*S*)-1-hydroxy-1-phenylpentan-2-yl]amine (6d)

Prepared as described for **6a**, using **5d** as the starting material.

Yield: 65%; $[\alpha]_D$ -9.5 (c=1, $CHCl_3$); mp 121-122 °C; de > 96% (^1H NMR).

^1H NMR δ(ppm) 7.33 (m, 10H, Ph), 4.87 (d, 2H, J = 3.3 Hz, CHO), 2.90 (m, 2H, CHN), 1.7-1.1 (m, 8H, CH_2), 0.80 (t, 6H, J = 6.6 Hz, CH_3).

^{13}C NMR δ(ppm) 141.6, 128.1, 127.0, 125.8 (Ph), 72.9 (CHO), 60.3 (CHN), 30.4, 19.6 (CH_2), 14.1 (CH_3).

Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.38; H, 9.15; N, 4.10. Found: C, 77.30; H, 9.21; N, 3.88.

General procedure for the reduction of ketones with diethanolamine modified $LiAlH_4$.

To a suspension of 219 mg (5.8 mmol) of $LiAlH_4$ in 10 mL of freshly distilled THF was slowly added a solution of 5.8 mmol of diethanolamine **6a-d** in 10 mL of THF at 0 °C. The reaction mixture was refluxed for 30 min, after which the suspension was cooled to -100 °C. A solution of 1.9 mmol of ketone **8a-j** in 10 mL of THF was added and the reaction mixture was stirred for 6 h at this temperature. After the reaction was quenched at -100 °C by the addition of 3 mL of methanol, 0.20 mL of water, 0.40 mL of 4 M NaOH, and 0.60 mL of water were added successively. The suspension was stirred for another 2 h at room temperature, after which it was dried on $MgSO_4$ and filtered. The residue was washed three times with 15 mL of ether. The combined filtrates were concentrated *in vacuo*. Pure diethanolamine **6a-d** was recovered by recrystallization from $CHCl_3$/pentane in a yield of 85-95%. The mother liquor was concentrated *in vacuo*. After purification of the crude product by flash column chromatography (eluent: petroleum ether 40-60/ether = 1/1) chiral alcohols **9a-j** were obtained. The optical purity of the products was determined by HPLC-analysis, using a CHIRALCEL OD column (flow rate: 1 mL/min; eluent: **9c,f,g,h,i**: 2-propanol/n-hexane = 1/99, **9b,e,j**: 2-propanol/n-hexane = 3/97, **9a,d**: 2-propanol/n-hexane = 10/90).

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