Enantioselective Synthesis of α-Phosphanyl Ketones and 2-Phosphanyl Alcohols☆

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An efficient, highly enantioselective methodology for the synthesis of α-phosphanyl ketones **7** and 2-phosphanyl alcohols **12** and **13**, important hemilable ligands for enantioselective homogeneous catalysis and chiral building blocks in general, has been developed. The key step of this first enantioselective synthesis of α-phosphanyl ketones is the diastereoselective phosphanylation of SAMP hydrazones **2** to produce α-phosphanyl hydrazones, isolated as the more stable borane adducts **6**. Subsequent ozonolysis afforded α-phosphanyl ketones **7**. The enantioselective synthesis of 2-phosphanyl alcohols **12** and **13** has been accomplished by two fundamentally different procedures: the phosphanylation of unsubstituted chiral aldehyde hydrazones **9** and the alkylation of α-diphenylphopshanyl acetaldehyde SAMP hydrazone **10**. After separation of the minor diastereomer, the borane-protected α-phosphanyl aldehyde hydrazones **11** were converted to unprotected 2-phosphanyl alcohols **13** by ozonolysis, reduction and removal of the borane group. The absolute configuration of the functionalized phosphanes was determined by X-ray analysis, NOE experiments or polarimetry.

Introduction

1. Functionalized phosphanes containing an additional oxygen donor functionality, e.g. esters[1], ketones[2], ethers[3] and alcohols[4], are used as hemilabile ligands in homogeneous catalysis[5]. α-Phosphanyl ketones are successfully used as ligands in the **S**hell **H**igher **O**lefin **P**rocess (SHOP)[6]. Phosphanyl alcohols are especially interesting as they may be used either directly or after further transformation to ethers or phosphites. Despite the utility of enantiopure α-phosphanyl ketones and phosphanyl alcohols for enantioselective catalysis, asymmetric syntheses of these important classes of compounds have hardly been investigated.

Shaw[7] and Brunner[8] obtained achiral α-phosphanyl ketones by nucleophilic addition of phosphides to α-halogeno ketones. Braunstein[9] as well as Demerseman and Dixneuf[10] synthesized α-phosphanyl ketones by electrophilic substitution of ketones with chlorodiphenylphosphane. In a similar way, Shaw[11] and Cole-Hamilton[12] isolated diastereo- and enantiomerically pure 3-*endo*-diphenylphosphanyl camphor starting from camphor or 3-*endo*-bromocamphor. Synthetic access to enantiomerically enriched phosphanyl alcohols or the related phosphanyl ethers has most frequently been provided by nucleophilic addition of phosphides to chiral oxiranes[13] or by selective substitution of hydroxy groups from chiral pool substances[14]. Brunner developed the first enantioselective synthesis of a diphosphanyl alcohol[15] starting from cinnamic alcohol by Sharpless epoxidation and subsequent addition of a phosphide. Kagan reported on the isolation of enantiomerically pure 2-phosphanyl alcohols by addition of diphenylphosphide to racemic oxiranes and subsequent enzymatic resolution[16]. The reaction of (*S*)-styrene oxide with lithium diphenylphosphide gave two enantiomerically pure regioisomers[17]. Börner and Kagan synthesized enantiomerically pure *cis*- and *trans*-diphenylphosphanyl tetrahydrofurans starting from L-ascorbic and D-isoascorbic acid[18], respectively. Especially remarkable are Hayashi's enantiomerically pure, axially chiral phosphanyl ethers[19] and Takaya's phosphane phosphite BINAPHOS[20] which are synthesized via the corresponding phosphanyl alcohol.

In continuation of our efforts to explore the utility of the SAMP/RAMP hydrazone methodology[21], we have recently reported on the first enantioselective synthesis of α-phosphanyl ketones by asymmetric carbon–phosphorus bond formation at an α-position to a carbonyl group[22]. Furthermore, we have accomplished a novel enantioselective access to 2-phosphanyl alcohols[23]. We now wish to report on these novel procedures in detail and on alternative routes to 2-phosphanyl alcohols.

Results and Discussion

For the enantioselective synthesis of α-phosphanyl ketones, the ketones **1** were reacted with (*S*)-1-amino-2-methoxymethylpyrrolidine (SAMP) affording the corresponding SAMP hydrazones (*S*)-**2** (Table 1)[21]. After deprotonation with LDA at 0 °C for 4 h in THF, the resulting azaenolates were cooled to −78 °C before treatment with chlorodiphenylphosphane. After 14 h at −78 °C and aqueous work-up at 0 °C, the (*Z*)-configured α-phosphanyl hydrazones (*S,R*)-**3**

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were isolated in good yields (70–79%) and with good diastereomeric excess (*de* = 80–85%) (Scheme 1, Table 2).

Table 1. Ketone SAMP hydrazones **2** prepared

	R^1	R^2	yield [%]
(*S*)-**2a**	Et	Me	85
(*S*)-**2b**	Pr	Et	76
(*R*)-**2b** [a]	Pr	Et	77
(*S*)-**2c**	Bu	Pr	75
(*S*)-**2d**	Ph	Me	87

[a] RAMP was used as chiral auxiliary.

Scheme 1. Synthesis of α-phosphanyl ketone SAMP hydrazones (*S,R*)-**3** and hydrazone cleavage experiments

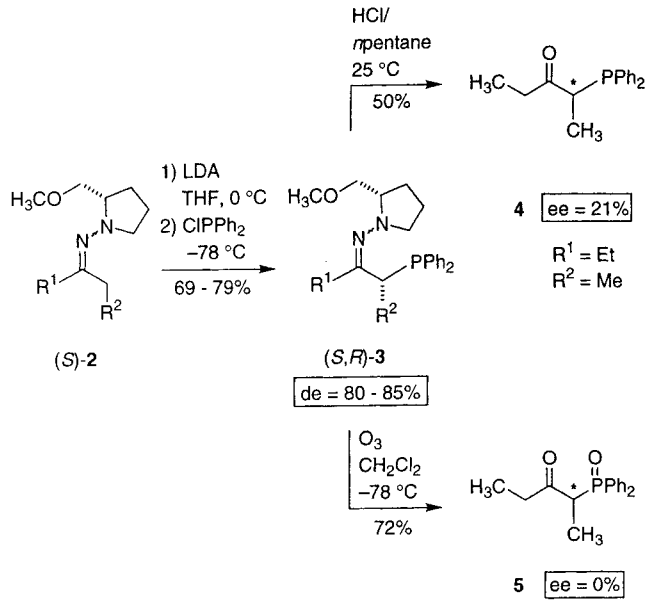


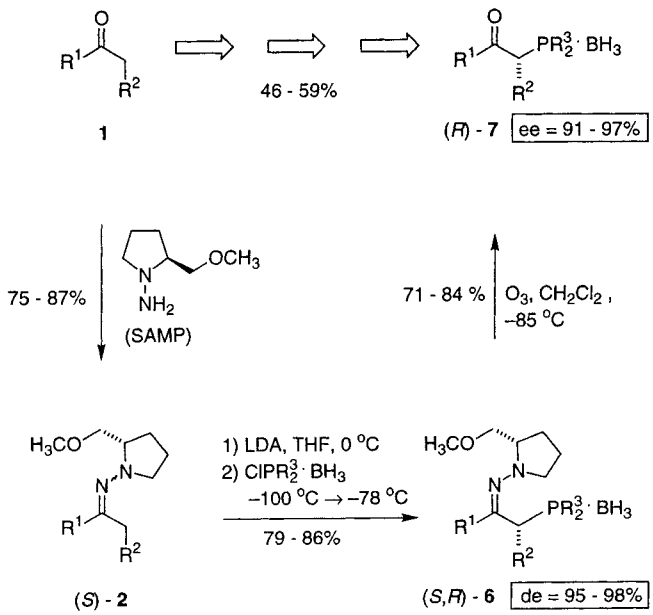
Table 2. α-Phosphanyl ketone hydrazones **3** prepared by phosphanylation of ketone SAMP hydrazones **2** with chlorodiphenylphosphane

entry	R^1	R^2	yield [%]	*de* (*Z*) [%]
(*S,R*)-**3a**	Et	Me	70	80
(*S,R*)-**3b**	Pr	Et	69	80
(*S,R*)-**3c**	Ph	Me	79	85

The subsequent cleavage of the chiral auxiliary was investigated with the phosphanyl hydrazone (*S,R,Z*)-**3a** (*de* = 80%). The best non-oxidative method for the cleavage of the C=N double bond was acid hydrolysis in the two-phase system 2.5 N HCl/*n*-pentane, which gave the α-phosphanyl ketone **4** in 50% yield but only 21% *ee*. Ozonolysis gave the corresponding phosphane oxide **5** in 72% yield as a racemic mixture. As ozonolysis is one of the mildest methods for regenerating the carbonyl function from SAMP hydrazones, the racemization of the phosphane oxide was presumably due to oxidation of the phosphorus to produce the analogous 1,3-dicarbonyl system **5** and not due to the C=N bond cleavage.

The well-documented stability of phosphane-borane adducts under oxidative conditions was used to prevent oxidation of the phosphorus during ozonolysis[24]. The phosphorus–boron bond was formed by the reaction of the chlorophosphanes with a borane source such as the borane-methyl sulfide complex as reported by Schmidbaur[25]. Reaction of these electrophiles with the deprotonated ketone SAMP hydrazones (*S*)-**2** at −100 °C and aqueous work-up at 0 °C gave the airstable, borane-protected α-phosphanyl-hydrazones (*S,R*)-**6** mainly as (*Z*)-isomers with regard to the C=N-double bond (Scheme 2). After flash chromatography the (*Z*)-configured isomers were isolated in good yields (79–86%) and with excellent diastereomeric excesses (*de* = 95–98%). The (*E*)-configured isomers were obtained in 2 to 10% yield and with diastereomeric excesses of 0 to 10% (**6a,b,d**) and 56% (**3c**), respectively. Only the diisopropylphosphanyl hydrazone **6e** isomerized to the thermodynamically favored (*E*)-form without epimerisation (Table 3).

Scheme 2. Enantioselective synthesis of borane-protected α-phosphanyl ketones (*R*)-**7**



Ozonolysis of the (*Z*)-configured hydrazones (*S,R*)-**6** gave the α-phosphanyl ketones **7** in 71–84% yield as colourless crystals (**7a–c**) or oils (**7d, e**) (Table 4). The enantiomeric excesses (91–97%) were almost as high as the diastereomeric excesses of the hydrazones (*S,R*)-**6**. The optical antipodes (*S*)-**7** are synthesized by simply using the enantiomeric hydrazine RAMP instead of SAMP as chiral auxiliary as shown in example **7b**.

The diastereomeric excesses of the α-phosphanyl hydrazones **6** were determined by ^1H and ^{13}C NMR spectroscopy. The enantiomeric excesses of the α-phosphanyl ketones were measured by ^1H NMR experiments using (−)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as chiral cosolvent and by

Table 3. Borane-protected α-phosphanyl ketone SAMP hydrazones **6** prepared by phosphinylation of ketone SAMP hydrazones **2** with chlorophosphane-borane adducts

entry	R^1	R^2	R^3	yield (*Z*) [%]	yield (*E*) [%]	yield (*Z*+*E*) [%]	$[\alpha]_D^{22}$ (*c* = 1, $CHCl_3$)	*de* (*Z*) [%]
(*S*,*R*)-**6a**	Et	Me	Ph	81	10	91	+95.2	96
(*S*,*R*)-**6b**	Pr	Et	Ph	86	2	88	+130.9	98
(*R*,*S*)-**6b** [a]	Pr	Et	Ph	85	3	88	−132.1	98
(*S*,*R*)-**6c**	Bu	Pr	Ph	79	8	87	+114.2	98
(*S*,*R*)-**6d**	Ph	Me	Ph	86	2	88	+297.5	95
(*S*,*R*)-**6e**	Pr	Et	*i*Pr	b	b	80	+261.8 [c]	96 [d]

[a] RAMP was used as chiral auxiliary. – [b] Only total yield determined. – [c] Optical rotation of the (*E*)-isomer; (*Z*)-isomer is always contaminated with ca. 10% of the (*E*)-isomer. – [d] Compound isomerizes without epimerisation.

Table 4. α-Phosphanyl ketones **7** prepared by ozonolysis of α-phosphanyl ketone hydrazones **6**

entry	R^1	R^2	R^3	yield [%]	$[\alpha]_D^{22}$ (*c* = 1, C_6H_6)	*ee* [%]
(*R*)-**7a**	Et	Me	Ph	84	+71.7	94
(*R*)-**7b**	Pr	Et	Ph	78	+78.8	97
(*S*)-**7b** [a]	Pr	Et	Ph	77	−81.4	97
(*R*)-**7c**	Bu	Pr	Ph	76	+73.1	97
(*R*)-**7d**	Ph	Me	Ph	71	+14.9	91
(*R*)-**7e**	Pr	Et	*i*Pr	78	+201.5	92

[a] RAMP was used as chiral auxiliary.

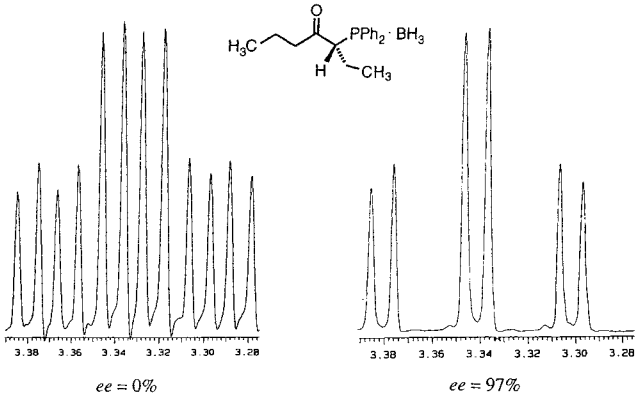
comparison with the racemic mixtures prepared via the corresponding *N*,*N*-dimethylhydrazones[26].

Figure 1 shows the determination of the enantiomeric excesses of the α-phosphanyl ketone (*R*)-**7b**. The signal of the methine proton is split into a doublet of doublets of doublets by coupling to the diastereotopic methylene protons (J = 11.8 Hz, J = 2.9 Hz) and to phosphorus ($^2J_{HP}$ = 11.8 Hz). The ^{1}H-NMR shift spectrum of the racemate shows separate signals for each enantiomer, whereas the ^{1}H-NMR shift spectrum of the α-phosphanyl ketone (*R*)-**7b** synthesized by the method described in this paper only shows the signal of one enantiomer (*ee* = 97%).

The absolute configuration of the newly generated stereogenic centre was determined by X-ray analysis and NOE experiments. The X-ray analysis of the (*E*)-configured minor diastereomer of the hydrazone **6b** showed the (*S*)-configuration at the newly generated stereogenic centre (Figure 2)[27].

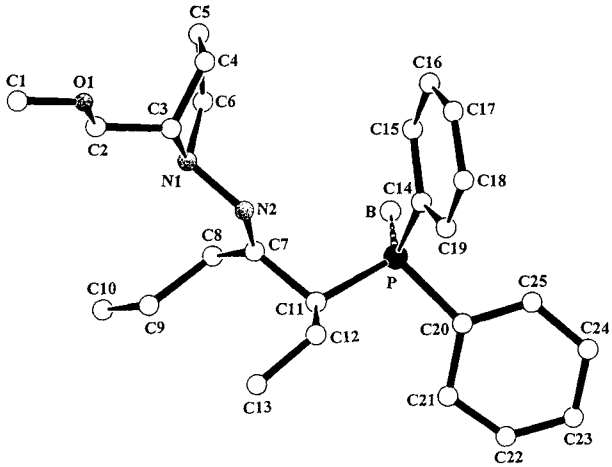
NOE experiments on both of the (*Z*)-configured diastereomers[28] of the hydrazone **6b** are in agreement with the results of the X-ray analysis (Figure 3). Both diastereomers show an NOE effect between the CH_2O protons and the BH_3 protons, indicating a donor-acceptor-interaction between oxygen and the borane-protected phosphanyl group. In the major diastereomer (*S*,*R*)-**6b**, an NOE effect between

Figure 1. Determination of the enantiomeric excess of the α-phosphanyl ketone (*R*)-**7b**



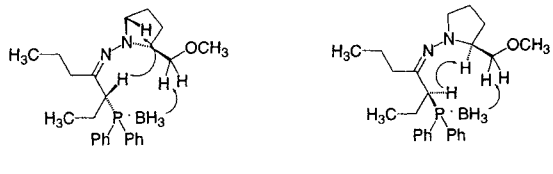
ee = 0% *ee* = 97%

Figure 2. Structure of the (*E*)-configured minor diastereomer (*S*,*S*)-**6b** (Schakal plot)



the proton at the newly generated stereogenic centre and the CH_2N proton *cis* to the OCH_3 group was observed. The minor diastereomer (*S*,*S*)-**6b** showed an NOE effect between the protons at both stereogenic centres. Based on the assumption of a uniform reaction mechanism the stereogenic centres of the α-phosphanyl ketones synthesized by phosphinylation of SAMP hydrazones have the (*R*)-configuration, in agreement with the postulated mechanism for electrophilic substitutions of SAMP/RAMP hydrazones[29].

Figure 3. Decisive NOE effects on both diastereomers of the (*Z*)-configured α-phosphanyl hydrazone **6b**



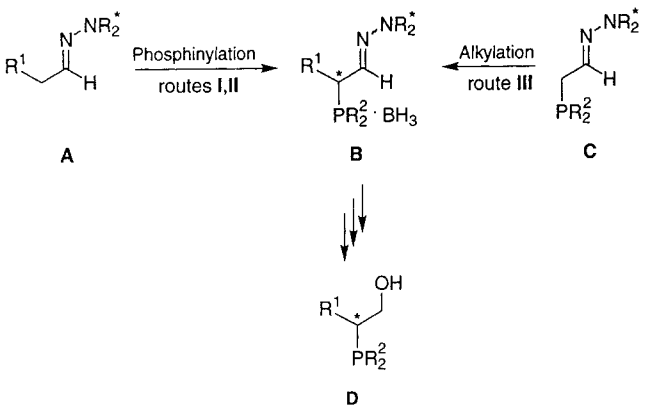
major diastereomer (*S*,*R*,*Z*)-**6b** minor diastereomer (*S*,*S*,*Z*)-**6b**

The deprotection of the phopshane functionality, feasible by reaction with amines[24c,30] or acids, was investigated with the α-phosphanyl ketone (*R*)-**7a** (ee = 94%). The mildest basic method, the reaction with DABCO[31], gave the

unprotected α-phosphanyl ketone **4**[10] with only 20% enantiomeric excess. Reaction with $HBF_4 \cdot OEt_2$ in CH_2Cl_2 as described in the literature[32] did not give the α-phosphanyl ketone **4** but the corresponding alcohol in variable but low diastereomeric excesses. The best way turned out to be the reaction with $HBF_4 \cdot OEt_2$ in acetone which gave the target compound **4** in 81% yield and 68% enantiomeric excess.

The enantioselective synthesis of 2-phosphanyl alcohols **D** was accomplished using borane-protected α-phosphanyl aldehyde hydrazones **B** as key intermediates (Scheme 3). After oxidative cleavage of the chiral auxiliary, in situ reduction and removal of the borane protecting group, the unprotected 2-phosphanyl alcohols **D** were obtained. Two fundamentally different approaches were investigated for the synthesis of α-phosphanyl aldehyde hydrazones **B**: the electrophilic phosphanylation of aldehyde hydrazones **A** (routes I, II) and the alkylation of phosphanyl acetaldehyde SAMP hydrazones **C** (route III). The phosphanylation of unsubstituted aldehyde hydrazones **A** was carried out with the chlorodiphenylphosphane–borane adduct (route **I**) and with chlorophosphanes and subsequent phosphorus–boron bond formation (route **II**).

Scheme 3. Synthetic plan to 2-phosphanyl alcohols **D**



Aldehydes **8** were converted into the corresponding hydrazones **9**[21] by reaction with the hydrazine reagents SAMP, RAMP or (*S*)-(1)-amino-2-(1′-methoxy-1′-ethylpropyl)pyrrolidine (SAEP)[33] (Table 5). After deprotonation of the SAMP hydrazones (*S*)-**9** with LDA for 4 h at 0 °C, the resulting azaenolates were trapped with the chlorodiphenylphosphane–borane adduct (route **I**) at −100 °C (Scheme 4). After allowing the mixture to warm to room temperature overnight and aqueous work-up, the borane-protected α-phosphanyl aldehyde hydrazones (*S*,*R*)-**11** were isolated in moderate yields (38–56%) and with good diastereomeric excesses (*de* = 73–80%) (Table 6) as (*E*/*Z*)-mixtures with regard to the C=N double bond. The (*Z*)-isomers isomerised to the thermodynamically favored (*E*)-configured compounds within days or weeks.

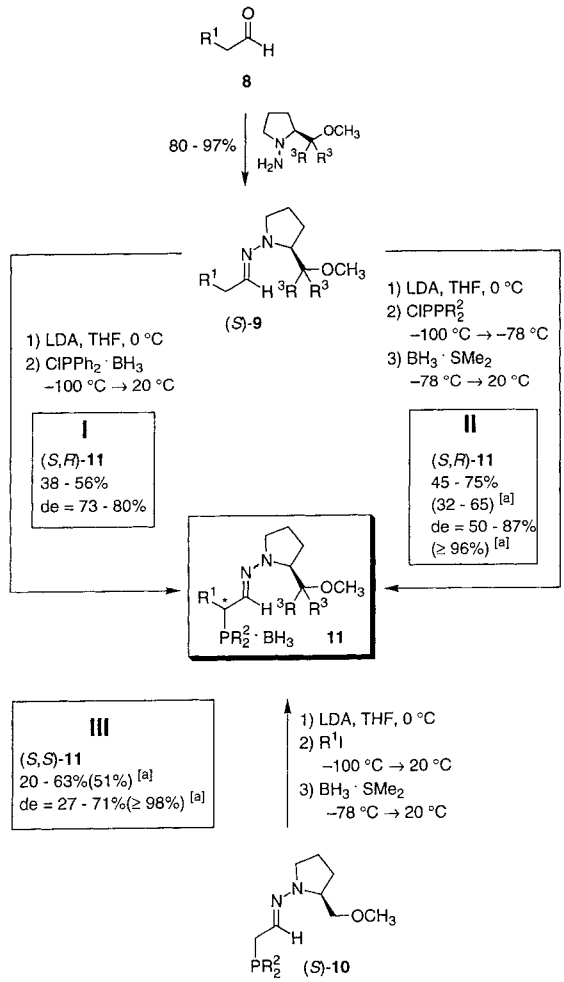
Alternatively, the azaenolates of SAMP, RAMP or SAEP hydrazones **9** were trapped with chlorodiphenylphosphane or chlorodiisopropylphosphane at −100 °C. After reaction at −78 °C overnight, the phosphorus–boron bond was formed by addition of the borane–methyl sulfide complex

Table 5. Chiral aldehyde hydrazones **9** prepared

	R^1	R^3	yield [%]
(*S*)-**9a**	H	H	90
(*S*)-**9b**	Me	H	82
(*S*)-**9c**	Me	Et	80
(*S*)-**9d**	Et	H	97
(*S*)-**9e**	Pr	H	93
(*R*)-**9e** [a]	Pr	H	80
(*S*)-**9f**	Bu	H	81
(*S*)-**9g**	Pent	H	93
(*S*)-**9h**	Oct	H	85

[a] RAMP was used as chiral auxiliary.

Scheme 4. Synthetic routes to borane-protected α-phosphanyl aldehyde hydrazones **11**: route **I**: phosphanylation of aldehyde hydrazones **9** with the chlorodiphenylphosphaneborane adduct; route **II**: phosphanylation of aldehyde hydrazones **9** with chlorophosphanes and subsequent addition of the borane-methyl sulfide complex; route **III**: alkylation of α-diphenylphosphanyl acetaldehyde SAMP hydrazone **10** and subsequent addition of the borane-methyl sulfide complex



[a] after separation of the minor diastereomer

Table 6. Borane-protected α-phopshanyl aldehyde SAMP hydrazones (*S,R*)-**11** prepared by phosphanylation of aldehyde hydrazones **9** with the chlorodiphenylphosphane-borane adduct (route **I**)

entry	R^1	yield [%]	$[\alpha]_D^{22}$ (*E*) ($c = 1$, $CHCl_3$)	*de* [%]
(*S,R*)-**11b**	Me	56	+43.2	73
(*S,R*)-**11d**	Et	40	+80.8	80
(*S,R*)-**11e**	Pr	40	+77.9	77
(*S,R*)-**11f**	Bu	39	+69.9	77
(*S,R*)-**11g**	Pent	41	+35.9	80
(*S,R*)-**11h**	Oct	38	+50.7	79

and warming the mixtures to room temperature. Upon aqueous work-up and flash chromatography the air-stable α-phosphanyl hydrazones **11** were isolated in better yields (45–75%) and diastereomeric excesses (*de* = 50–87%), predominantly as (*Z*)-isomers with regard to the C=N double bond (Table 7).

Table 7. Borane-protected α-phosphanyl aldehyde SAMP hydrazones (*S,R*)-**11** prepared by phosphanylation of aldehyde hydrazones **9** with chlorophosphanes and subsequent addition of the borane-methyl sulfide complex (route **II**)

entry	R^1	R^2	R^3	yield [a] [%]	$[\alpha]_D^{22}$ (*Z*) [d]	*de* [a,b] [%]
(*S,R*)-**11a**	Me	iPr	H	74	+180.0	87
(*S,R*)-**11b**	Me	Ph	H	45(32)	+157.6	50(≥98)
(*S,R*)-**11c**	Me	Ph	Et	75(65)	+85.9 [e]	73(≥96)
(*S,R*)-**11d**	Et	Ph	H	67(50)	+136.2	79(≥98)
(*S,R*)-**11e**	Pr	Ph	H	68(60)	+114.1	86(≥98)
(*R,S*)-**11e** [c]	Pr	Ph	H	66(59)	−112.2	86(≥98)
(*S,R*)-**11f**	Bu	Ph	H	69(55)	+121.7	80(≥98)
(*S,R*)-**11g**	Pent	Ph	H	70(57)	+125.9	81(≥98)
(*S,R*)-**11h**	Oct	Ph	H	66(45)	+110.8	80(≥98)

[a] In parentheses: after purification of the major diastereomer by crystallization, HPLC or flash chromatography (**11c**). – [b] Determined by ^1H and ^{13}C NMR spectroscopy. – [c] RAMP was used as chiral auxiliary. – [d] Optical rotations of the diastereomerically pure compounds (except **11a**). – [e] (*E*)-isomer.

The (*Z*)-configured major diastereomers of the diphenylphosphanyl SAMP hydrazones **11b,d–h** were crystallized from ether/pentane at −20 °C. Further separation of diastereomers from the mother liquor by HPLC afforded diastereomerically pure diphenylphosphanyl SAMP hydrazones **11d–h** in 45–60% yield (*de* = 96%). In the case of the diphenylphosphanyl-propanal-hydrazones **11b,c** the change of the chiral auxiliary from SAMP to SAEP provided far higher yields of diastereomerically pure substance (**11b**: 32% yield; **11c**: 65% yield). Diastereomeric enrichment was found to be impossible for the diisopropylphosphanyl hydrazone **11a**[23].

An alternative route to α-phosphanyl aldehyde hydrazones **11** was by alkylation of α-diphenylphosphanyl acetaldehyde SAMP hydrazone (*S*)-**10**, yielding products with different stereochemistry at the newly generated stereogenic centre. The starting material was synthesized in 68% yield by phosphanylation of acetaldehyde SAMP hydrazone (*S*)-**9a** with chlorodiphenylphosphane and subsequent purification of the (*E*)-configured compound by flash chromatography under argon.

After deprotonation of (*S*)-**10** with LDA at 0 °C for 5 h, the resulting azaenolate was trapped with alkyl iodide at −100 °C and warmed to room temperature. Conversion to the phosphane-borane adducts by addition of borane–methyl sulfide complex at −78 °C and warming to room temperature afforded α-diphenylphosphanyl aldehyde hydrazones (*S,S*)-**11** in good yields (60–63%) and good diastereomeric excesses (*de* = 68–71%) as (*E/Z*)-mixtures after flash chromatography (Table 8). The major diastereoisomer of hydrazone **11e** was purified by preparative HPLC.

Table 8. Borane-protected α-phosphanyl aldehyde SAMP hydrazones (*S,S*)-**11** prepared by alkylation of α-diphenylphosphanyl acetaldehyde SAMP hydrazone (*S*)-**10** and subsequent addition of the borane–methyl sulfide complex (route **III**)

entry	R^1	yield [%]	*de* [%]
(*S,S*)-11b	Me	60	69
(*S,S*)-11d	Et	63	71
(*S,S*)-11e	Pr	62 (51) [a]	68 (≥98) [a]
(*S,S*)-11f	Bu	62	70

[a] In parentheses: after purification of the major diastereomer by HPLC.

Ozonolysis and in situ reduction of the generated aldehydes with borane–methyl sulfide complex gave the air-stable protected 2-diphenylphosphanyl alcohols **12** in good yields (67–83%) (Table 9). Reaction with DABCO afforded the unprotected 2-phosphanyl alcohols **13** in very good yields (85–91%) and enantiomeric excesses (*ee* = 96%) (Scheme 5, Table 10).

The enantiomeric excesses of the 2-phosphanyl alcohols **13** were derived from the ^1H and ^{13}C NMR spectra of the corresponding MTPA esters[34] and by comparison with the racemic mixtures[35]. Figure 4 shows the determination of the enantiomeric excess of the 2-phosphanyl alcohol **13c**. Each diastereomer shows a triplet for the methyl group of the alcohol moiety. In the ^1H NMR spectrum of the MTPA-ester synthesized from 2-phosphanyl alcohol (*R*)-**13c**, only one triplet can be seen (*ee* = 98%).

The absolute configuration of the newly generated stereogenic centre was determined by comparison of the optical rotations of compound **12b** generated by the new method described here and from (*S*)-1,2-propanediol (**14**) in four steps (Scheme 6). After protection of the primary hydroxyl function with *tert*-butyldimethylsilyl chloride, the secondary hydroxyl function was sulfonylated with mesyl chloride. Substitution of the mesylate with $KPPh_2$ (S_N2), formation of the phosphane-borane adduct (*R*)-**16** by addition of borane–methyl sulfide complex and tetrabutylammonium fluoride mediated removal of the silyl group afforded com-

Table 9. Ozonolysis and in situ reduction of the α-phosphanyl aldehyde hydrazones **11** to borane-protected 2-phosphanyl alcohols **12**

entry	R^1	R^2	yield [%]	$[\alpha]_D^{22}$ ($c = 1$, $CHCl_3$)	*ee* [e] [%]
(*R*)-**12a**	Me	iPr	72	−2.7	84 [f]
(*R*)-**12b** [a]	Me	Ph	73	−34.4	≥96 [f]
(*R*)-**12b** [b]	Me	Ph	68	−31.2	≥96 [f]
(*R*)-**12c**	Et	Ph	67	−29.4	98
(*R*)-**12d**	Pr	Ph	75	−45.0	≥96
(*S*)-**12d** [c]	Pr	Ph	72	+46.1	≥96
(*S*)-**12d** [d]	Pr	Ph	69	+46.5	≥96
(*R*)-**12e**	Bu	Ph	77	−46.7	98
(*R*)-**12f**	Pent	Ph	75	−41.7	≥96 [f]
(*R*)-**12g**	Oct	Ph	83	−37.1	≥96

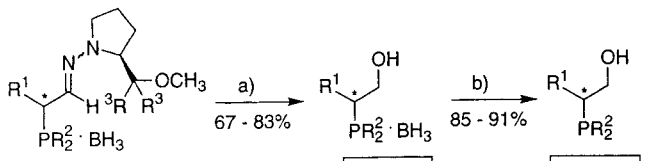
[a] Starting material: (*S,R*)-**11b**. – [b] Starting material: (*S,R*)-**11c**. – [c] Starting material: (*R,S*)-**11e**. – [d] Starting material: (*S,S*)-**11e**. – [e] Determined by ^1H and ^{13}C NMR spectroscopy of the MTPA esters of the unprotected 2-phosphanyl alcohols **13**. – [f] Determined by ^1H and ^{13}C NMR spectroscopy of the MTPA esters.

Table 10. Unprotected 2-phosphanyl alcohols **13**

entry	R^1	yield [%]	$[\alpha]_D^{22}$ (c, CH_2Cl_2)	*ee* [c] [%]
(*R*)-**13b**	Me	85	−7.9 (2.2)	≥96 [d]
(*R*)-**13c**	Et	85	+4.0 (2.0)	98
(*R*)-**13d**	Pr	91	−9.2 (2.0)	≥96
(*S*)-**13d** [a]	Pr	92	+9.4 (2.2)	≥96
(*R*)-**13e**	Bu	91	−14.3 (2.7)	98
(*R*)-**13f**	Pent	86	−12.8 (1.1) [b]	≥96 [d]
(*R*)-**13g**	Oct	85	−12.2 (2.0)	≥96

[a] Starting material: (*S*)-**12d**. – [b] Solvent: $CHCl_3$. – [c] Determined by ^1H and ^{13}C NMR spectroscopy of the MTPA esters. – [d] Determined by ^1H and ^{13}C NMR spectroscopy of the MTPA esters after reconversion to phosphane–borane adducts **12**.

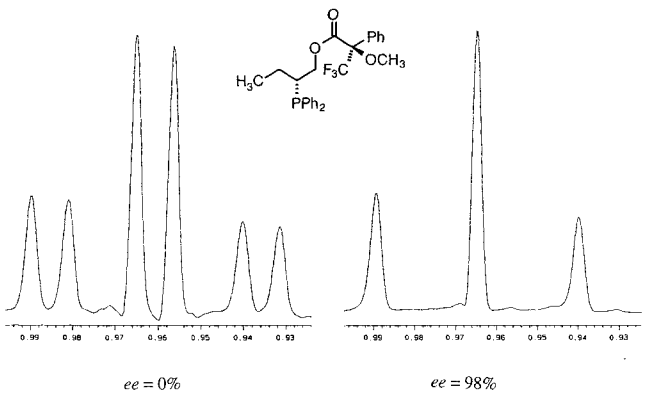
Scheme 5. Synthesis of 2-phosphanyl alcohols **12** and **13** from α-phosphanyl aldehyde hydrazones **11**



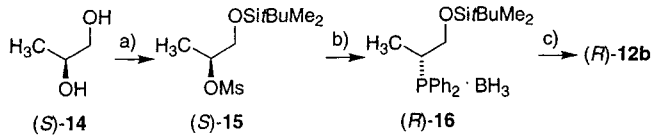
a) 1. O_3, CH_2Cl_2/ *n*pentane, −78 °C, 2. $BH_3 \cdot SMe_2$, −78 °C → 25 °C
b) DABCO, Et_2O, 25 °C, 48h

pound (*R*)-**12b** in 38% overall yield; $[\alpha]_D^{RT} = -33.8$ ($c = 1$, $CHCl_3$); *ee* = 98%. Compound **12b**, prepared by phosphanylation of propanal SAMP hydrazone **9b**, gave $[\alpha]_D^{RT} = -34.4$ ($c = 1$, $CHCl_3$). Based on the assumption of a uniform reaction mechanism, the 2-phosphanyl alcohols prepared by phosphanylation of aldehyde SAMP hydrazones (*S*)-**9** have the configuration (*R*). The optical antipodes can be obtained without change of the chiral auxiliary by alkylation of the α-diphenylphosphanyl aldehyde SAMP hydrazone (*S*)-**10** or by the phosphanylation of RAMP hydrazones (*R*)-**9** (see examples **13d**). The assigned configurations are in agreement with the mechanism for electrophilic substitutions of SAMP/RAMP hydrazones[29].

Figure 4. Determination of the enantiomeric excess of the 2-phosphanyl alcohol **13c**



Scheme 6. Synthesis of 2-phosphanyl alcohol (*R*)-**12b** from (*S*)-1,2-propanediol (**14**)



a) 1. $ClSiMe_2tBu$, NEt_3, DMF, 73%, 2. MsCl, CH_2Cl_2, 80%; b) 1. $KPPh_2$, THF, 2. $BH_3 \cdot SMe_2$, 80%; c) TBAF, THF, 82%

In summary, we have presented the first enantioselective synthesis of α-phosphanyl ketones by asymmetric carbon-phosphorus bond formation. Furthermore, we have reported on novel synthetic routes to virtually enantiopure 2-phosphanyl alcohols in both configurations by asymmetric phosphanylation of unsubstituted chiral hydrazones or by alkylation of α-diphenylphosphanyl acetaldehyde SAMP hydrazone. The highly enantiomerically enriched functionalized phosphanes described in this paper are useful synthetic building blocks and important hemilabile (P,O) ligands for asymmetric homogeneous catalysis.

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Experimental Section

All reactions were carried out using standard Schlenk techniques under argon unless otherwise stated. Solvents were dried and purified by conventional methods prior to use. THF (over potassium)

and dichloromethane (over CaH_2) were distilled under argon. All reagents were distilled and/or stored under argon. – Column chromatography: Merck silica gel 60, 0.040–0.063 mm (230–400 mesh). – Preparative HPLC: Gilson with a Merck, Packed column RT, 25 × 250 mm, LiChrosorb, Si60 (7 μm), ether/*n*-pentane (1:3), UV detector. – IR spectra: Perkin-Elmer FT/IR 1750. – ^1H and ^{13}C NMR spectra: Varian VXR 300, Varian Gemini 300, Varian Unity 500. – Mass spectra: Varian MAT 212 (EI), Finnigan MAT 95 (HRMS). – Microanalyses: Heraeus CHN-O-Rapid.

General Procedure 1 (GP 1) for the Formation of Chlorophosphane–Borane Adducts: 12 mmol of borane–methyl sulfide complex was added to 12 mmol of chlorophosphane in THF (2 ml/mmol) at 0 °C under argon. The resultant solution of the chlorophosphane–borane adduct was stirred for 1 h and then used without purification.

General Procedure 2 (GP 2) for the Metallation of Chiral Hydrazones **2**, **3** *and* **10**: To a solution of diisopropylamine (1.56 ml, 11 mmol) in THF (2 ml/mmol hydrazone) at 0 °C under argon, was added a solution of *n*BuLi in hexane (6.9 ml, 1.6 mol/l, 11 mmol). After stirring for 15 min at 0 °C, hydrazone (10 mmol) [**2** or **9**: neat; **10**: dissolved in THF (3 ml/mmol)] was added and the mixture was stirred for an additional 4 h at this temperature.

General Procedure 3 (GP 3) for the Phosphanylation of Ketone SAMP Hydrazones **2** *with Chlorodiphenylphosphane:* To a solution of metallated ketone hydrazone **2** (10 mmol) at −78 °C, was added chlorodiphenylphosphane (12 mmol). After stirring for 12 h at this temperature the reaction mixture was quenched with aqueous NH_4Cl, extracted with *n*-pentane, dried ($MgSO_4$), filtered and the solvent was evaporated at 0 °C.

General Procedure 4 (GP 4) for the Phosphanylation of Ketone SAMP Hydrazones **2** *with Chlorophosphane–Borane Adducts:* To a solution of metallated ketone hydrazone **2** at −100 °C, was added the chlorophosphane-borane adduct in THF (1.2 equiv., 2 ml/mmol). After stirring for 1 h at this temperature the reaction mixture was allowed to warm to −78 °C and stirred for an additional 12 h. It was then quenched with aqueous NH_4Cl, extracted with ether, dried ($MgSO_4$) and filtered, and the solvent was evaporated. The (*Z*)-configured hydrazones **6** were purified by flash chromatography (SiO_2, ether/*n*-pentane, 1:4).

General Procedure 5 (GP 5) for the Phosphanylation of Aldehyde SAMP Hydrazones **9** *with the Chlorodiphenylphosphane–Borane Adduct:* To a solution of metallated aldehyde hydrazone **9** at −100 °C, was added the chlorodiphenylphosphane–borane adduct in THF (1.2 equiv., 2 ml/mmol). After stirring for 1 h at this temperature the reaction mixture was first allowed to warm to −78 °C and then to room temperature. It was then quenched with aqueous NH_4Cl, extracted with ether, dried ($MgSO_4$) and filtered, and the solvent was evaporated. The hydrazones **11** were isolated by flash chromatography (SiO_2, ether/*n*-pentane, 1:4).

General Procedure 6 (GP 6) for the Phosphanylation of Chiral Aldehyde Hydrazones **9** *with Chlorophosphanes and Subsequent Conversion to Phosphane–Borane Adducts:* To a solution of metallated aldehyde hydrazone **9** at −100 °C, was added the chlorophosphane in THF (1.2 equiv., 2 ml/mmol). After stirring for 1 h at this temperature the reaction mixture was allowed to warm to −78 °C overnight. Borane-methyl sulfide complex (1.2 equiv.) was added and the mixture was warmed to room temperature. The reaction mixture was quenched with aqueous NH_4Cl at 0 °C, extracted with ether, dried ($MgSO_4$) and filtered, and the solvent was evaporated. The hydrazones **11** were isolated by flash chromatography (SiO_2, ether/*n*-pentane, 1:4) and evaporation of the solvent at 0 °C. The (*Z*)-configured major diastereomers were crystallized from ether/pentane at −20 °C. From the mother liquor diastereomerically pure diphenylphosphanyl SAMP hydrazones were obtained by preparative HPLC.

General Procedure 7 (GP 7) for the Alkylation of the Diphenylphosphanylacetaldehyde SAMP Hydrazone **10**: To a solution of metallated hydrazone **10** at −100 °C, was added the alkyl iodide. After stirring for 1 h at this temperature the reaction mixture was allowed to warm to room temperature overnight. Borane–methyl sulfide complex (1.2 equiv.) was added at −78 °C and the mixture allowed to warm to room temperature. The reaction mixture was quenched with aqueous NH_4Cl at 0 °C, extracted with ether, dried ($MgSO_4$) and filtered, and the solvent was evaporated. The hydrazones **11** were isolated by flash-chromatography (SiO_2, ether/*n*-pentane, 1:4). The major diastereomer was purified by preparative HPLC.

General Procedure 8 (GP 8) for the Ozonolysis of Borane-Protected α-Phosphanyl Ketone Hydrazones **6**: The (*Z*)-configured, borane-protected α-phosphanyl ketone hydrazones **6** were dissolved in dichloromethane (130 ml/mmol). At −85 °C, a stream of ozone was passed through the stirred solution until completion of the oxidative cleavage (TLC control). After removal of excess ozone by a stream of argon the mixture was warmed to room temperature. The solvent was removed in vacuo and the α-phosphanylated ketones **7** were isolated by column chromatography (SiO_2, ether/*n*-pentane, 1:6). All glassware was carefully cleaned to remove all traces of alkali and acids (i. dil. aqueous HCl, ii. H_2O, iii. 12 h at 100 °C). The temperature of solutions of the products was not allowed to exceed 20 °C.

General Procedure 9 (GP 9) for the Ozonolysis of Borane-Protected α-Phosphanyl Aldehyde Hydrazones **11** *and in situ Reduction:* The borane-protected α-phosphanyl aldehyde hydrazones **11** were dissolved in a mixture of dichloromethane (200 ml/mmol) and *n*-pentane (200 ml/mmol). At −78 °C, a stream of ozone was passed through the stirred solution until the reaction was complete (TLC control). The generated aldehydes were reduced in situ with borane-methyl sulfide complex (30 mmol/mmol) at −78 °C. After warming the reaction mixture to room temperature and hydrolysis of excess borane–methyl sulfide complex with aq. NH_4Cl (150 ml), the crude products **12** were concentrated in vacuo and purified by flash chromatography (SiO_2, Et_2O/pentane, 1:4).

General Procedure 10 (GP 10) for the Cleavage the Borane Group: To a solution of protected alcohol **12** in ether (5 ml/mmol) at room temperature DABCO (5 mmol/mmol alcohol) was added and the mixture was stirred for 48 h (TLC control). Alcohols **13** were purified by column chromatography under argon (SiO_2, Et_2O/pentane, 1:3).

General Procedure 11 (GP 11) for the Synthesis of Racemic Unprotected 2-Phosphanyl Alcohols **13**: To a solution of 11 mmol LDA in THF (1 ml/mmol) was added 10 mmol diphenylphopshanyl ethyl acetate at 0 °C. After 1 h, 15 mmol of the alkyl iodide was added at −78 °C and the mixture was warmed to room temperature. The mixture was added to a suspension of 5 equiv. LAH in THF at 0 °C (2 ml/mmol) (TLC control). After hydrolysis of the excess LAH, the crude alcohols **13** were concentrated in vacuo and purified by flash chromatography (SiO_2, Et_2O/pentane, 1:3) under argon.

(−)-(S)-2-(1'-Methoxy-1'-ethylpropyl)-1-(1'-propylideneamino)pyrrolidine [(*S*)-**9c**]: 2.9 g (50 mmol) Propanal and 9.3 g (50 mmol) SAEP were reacted analogously to a literature procedure[21], yielding 9.4 g (80%) of **9c** as a colourless liquid. – $[\alpha]_D^{22} = -5.1$ ($l = 0.1$, neat). – IR (neat): $\tilde{\nu}$ 2966, 2938, 2880, 2825 (s, CH_2, CH_3), 1606 (m, C=N), 1459 (s, br.), 1138 (s), 1124 (s),

1087 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.87, 0.90 (t, *J* = 7.4 Hz, 3H, $CH_3CH_2C_q$), 1.05 (t, *J* = 7.6 Hz, 3H, CH_3CH_2CHN), 1.45–2.00 (m, 8H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$, $CH_3CH_2C_q$), 2.20 (qd, *J* = 7.4 Hz, *J* = 4.9 Hz, 2H, CH_3CH_2CHN), 2.70 (m, 1H, NCHH), 3.27 (s, 3H, OCH_3), 3.34 (m, 1H, NCHH), 3.54 (m, 1H, NCH), 6.60 (t, *J* = 4.9 Hz, 1H, HC=N). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 7.95, 8.53 (s, $CH_3CH_2C_q$), 11.98 (s, CH_3CH_2CHN), 23.88, 23.95, 24.52, 26.28, 26.40 (s, CH_3CH_2CN, 2 $CH_3CH_2C_q$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 50.52 (s, OCH_3), 51.88 (s, NCH_2), 69.17 (s, NCH), 80.45 [s, $(Et_2)CO$], 137.90 (s, C=N). – MS (70 eV); *m/z* (%): 226 (3) [M^+], 126 (9), 125 (100) [$M^+ - Et_2COCH_3$], 70 (16) [$C_4H_8N^+$]. – $C_{13}H_{26}N_2O$ (226.36): calcd. C 68.98, H 11.58, N 12.38; found C 69.08, H 11.59, N 12.38.

(–)-(S)-1-(1'-Heptylideneamino)-2-methoxymethylpyrrolidine [(*S*)-**9g**]: 5.7 g (50 mmol) heptanal and 6.5 g (50 mmol) SAMP were reacted analogously to a literature procedure[21], yielding 19.8 g (93%) of **9g** as a colourless liquid. – b.p. 105–107°C (1 mbar), $[\alpha]_{D}^{22}$ = –106.6 (*l* = 0.1, neat); $[\alpha]_{D}^{22}$ = –127.0 (*c* = 1, C_6H_6). – IR (neat): ṽ 2955–2855 (s, CH_2, CH_3), 1606 (m, C=N), 1461 (m), 1378 (m), 1340 (m), 1302 (s), 1282 (s), 1197 (m), 1120 (s, br., C–O), 973 (m), 903, 726 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.75 (t, *J* = 6.9 Hz, 3H, CH_3), 1.16–1.33 (m, 8H, CH_2), 1.64–1.78 (m, 4H, $CH_{2\ PYRR}$), 2.07 (m, 2H, CH_2CHN), 2.58 (m, 1H, NCHH), 3.23–3.29 (m, 3H, CH_2O, NCHH), 3.27 (s, 3H, OCH_3), 3.43 (m, 1H, NCH), 6.51 (t, *J* = 5.6 Hz, 1H, HC=N). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 13.90 (CH_3), 22.07, 27.75, 28.84, 31.66, 33.07 (CH_2), 22.52 ($NCH_2CH_2CH_2$), 26.50 ($NCH_2CH_2CH_2$), 50.32 (NCH_2), 59.03 (OCH_3), 63.44 (NCH), 74.79 (CH_2O), 139.05 (C=N). – MS (70 eV); *m/z* (%): 226 (6) (M^+), 181 (100) ($M^+ - C_2H_5O$), 82 (8), 70 (64) ($C_4H_8N^+$), 55 (10), 45 (8), 43 (30), 41 (20). – $C_{13}H_{26}N_2O$ (226.36): calcd. C 68.98, H 11.58, N 12.38; found C 69.29, H 11.61, N 12.20.

(–)-(S)-1-(1'-Decylideneamino)-2-methoxymethylpyrrolidine [(*S*)-**9h**]: 7.8 g (50 mmol) decanal and 6.5 g (50 mmol) SAMP were reacted analogously to a literature procedure[21], yielding 18.9 g (85%) of **9h** as a colourless liquid. – b.p. 156–158°C (1 mbar), $[\alpha]_{D}^{22}$ = –90.2 (*l* = 0.1, neat), $[\alpha]_{D}^{22}$ = –97.8 (*c* = 1, C_6H_6). – IR (neat): ṽ 2955–2855 (s, CH_2, CH_3), 1606 (m, C=N), 1460 (m), 1379 (m), 1340 (m), 1301 (s), 1282 (s), 1197 (m), 1121 (s, br., C–O), 973 (m), 903, 722 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.79 (t, *J* = 6.7 Hz, 3H, CH_3), 1.18–1.37 (m, 14H, CH_2), 1.68–1.83 (m, 4H, $CH_{2\ PYRR}$), 2.11 (m, 2H, CH_2CHN), 2.62 (m, 1H, NCHH), 3.28–3.34 (m, 3H, CH_2O, NCHH), 3.27 (s, 3H, OCH_3), 3.47 (m, 1H, NCH), 6.56 (t, *J* = 5.6 Hz, 1H, HC=N). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): 14.08 (CH_3), 22.13, 27.85, 29.23, 29.30, 29.50, 29.54, 31.89, 33.12 (CH_2), 22.67 ($NCH_2CH_2CH_2$), 26.56 ($NCH_2CH_2CH_2$), 50.43 (NCH_2), 59.11 (OCH_3), 63.56 (NCH), 74.85 (CH_2O), 139.33 (C=N). – MS (70 eV); *m/z* (%): 268 (5) (M^+), 223 (100) ($M^+ - C_2H_5O$), 70 (43) ($C_4H_8N^+$), 55 (6), 45 (5), 43 (19), 41 (11). – $C_{16}H_{32}N_2O$ (268.44): calcd. C 71.59, H 12.02, N 10.44; found C 71.34, H 12.34, N 10.71.

(–)-(S)-1-[(2'-Diphenylphosphanyl)-1'-ethylideneamino]-2-methoxymethylpyrrolidine [(*S*)-**10**]: 7.8 g (50 mmol) hydrazone **9a** and 11.0 g (50 mmol) $ClPPh_2$ were reacted according to *GP 3*. After heating to 100°C for 3 h the crude product was purified by column chromatography under argon, yielding 11.56 g (68%) of (*S*)-**10** as a colourless oil. – $[\alpha]_{D}^{22}$ = –109.8 (*c* = 1.0, $CHCl_3$). – IR (neat): ṽ 3069, 3052 (m, C–$H_{arom.}$), 2973, 2923, 2876, 2825 (s, CH_2, CH_3), 1586 (m), 1575 (m), 1481, 1460 (m), 1434 (s, P–Ph), 1341, 1196 (m), 1119 (s, P–Ph), 1097, 742, 698 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.60–1.86 (m, 4H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.54 (m, 1H, NCHH), 2.99 (d, br., *J* = 5.7 Hz, 2H, CH_2P), 3.09–3.41 (m, 4H, NCH, NCHH, CH_2O), 3.23 (s, 3H, OCH_3), 6.44 (dq, $^3J_{HP}$ = 5.7 Hz, *J* = 5.7 Hz, 1H, HC=N), 7.18–7.28 (m, 6H, $H_{meta,para}$), 7.32–7.42 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.07 (s, $NCH_2CH_2CH_2$), 25.49 (s, $NCH_2CH_2CH_2$), 32.08 (d, $^1J_{CP}$ = 14 Hz, CH_2P), 48.99 (s, NCH_2), 58.14 (s, OCH_3), 62.28 (s, NCH), 73.59 (s, CH_2O), 127.29 (d, $^3J_{CP}$ = 7 Hz, C_{meta}), 127.50 (d, $^2J_{CP}$ = 3 Hz, C=N), 131.14, 131.28 (s, C_{para}), 131.82, 131.94 (d, $^2J_{CP}$ = 18 Hz, C_{ortho}), 137.03, 137.13 (d, $^1J_{CP}$ = 14 Hz, C_{ipso}). – MS (70 eV); *m/z* (%): 340 (11) (M^+), 295 (6) ($M^+ - C_2H_5O$), 183 (7), 156 (11), 155 (100) ($M^+ - Ph_2P$), 121 (6), 112 (11), 109 (5) ($PhPH^+$), 80 (10), 71 (14), 55 (7), 45 (8) ($C_2H_5O^+$), 41 (8). – $C_{20}H_{25}N_2OP$ (340.40): calcd. C 70.57, H 7.40, N 8.28; found C 70.85, H 7.53, N 8.51.

(2S,2'R,Z)-1-[(2'-Diphenylphosphanyl)-pent-3'-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R,Z*)-**3a**]: 1.98 g (10 mmol) hydrazone (*S*)-**2a** and 2.43 g (11 mmol) $ClPPh_2$ were reacted according to *GP 3*, yielding 2.67 g (70%) of (*S,R,Z*)-**3a** as a colourless oil. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.02 (t, *J* = 7.3 Hz, 3H, CH_3CH_2), 1.16 (dd, $^3J_{HP}$ = 15.8 Hz, ^3J = 7.1 Hz, 3H, CH_3CHP), 1.56–2.48 (m, 7H, NCH_2CH_2CHH, $NCH_2CH_2CH_2$, NCHH, CH_3CH_2), 2.89–3.39 (m, 4H, NCHH, CH_2O, NCH), 3.34/3.27 (s, 3H, OCH_3), 4.12/4.71 (dq, $^2J_{HP}$ = 7.3 Hz, ^3J = 7.3 Hz, 1H, CH_3CHP), 7.23–7.31 (m, 6H, $H_{meta,para}$), 7.46–7.56 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDcl_3$, TMS): δ = 11.24/11.27 (s, CH_3CH_2), 15.01/14.43 (d, $^2J_{CP}$ = 15 Hz, CH_3CHP), 21.36/20.75 (s, NCH_2CH_2), 25.24 (d, $^3J_{CP}$ = 13 Hz, CH_3CH_2), 26.59/25.47 (s, $NCHCH_2$), 34.29/33.82 (d, $^1J_{CP}$ = 12 Hz, CH_3CHP), 54.48/53.98 (s, NCH_2), 58.09/57.90 (s, OCH_3), 65.75/64.78 (s, NCH), 75.94 (s, CH_2O), 127.07, 127.36 (d, $^3J_{CP}$ = 7 Hz, C_{meta}), 132.02, 133.19 (d, $^2J_{CP}$ = 20 Hz, C_{ortho}), 167.98/173.61 (d, $^2J_{CP}$ = 9 Hz, C=N). – MS (70 eV); *m/z* (%): 382 (7) (M^+), 198 (12), 197 (100) ($M^+ - Ph_2P$), 183 (6), 114 (15), ($C_6H_{12}N^+$), 109 (6) ($PhPH^+$), 84 (11) ($C_5H_{10}N^+$), 70 (6) ($C_4H_8N^+$), 56 (34) ($C_4H_8^+$), 41 (8) (C_2H_5O).

(2S,2'R,Z)-1-[(2'-Diphenylphosphanyl)-hept-4'-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R,Z*)-**3b**]: 2.26 g (10 mmol) hydrazone **2b** and 2.43 g (11 mmol) $ClPPh_2$ were reacted according to *GP 3*, yielding 3.24 g (79%) of (*S,R,Z*)-**3b** as a colourless oil. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.72, 0.78 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.19–2.28 (m, 10H, 5 CH_2), 2.36 (m, 1H, NCHH), 2.81 (m, 1H, CHHO), 3.17 (s, 3H, OCH_3), 2.95–3.13 (m, 3H, NCHH, CHHO, NCH), 4.13/4.39 (m, 1H, CH_3CH_2CHP), 7.10–7.28 (m, 6H, $H_{meta,para}$), 7.39, 7.51 (m, 2H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 12.53 (d, $^3J_{CP}$ = 9 Hz, CH_3CH_2CHP), 13.10 (s, $CH_3CH_2CH_2$), 19.48 (s, $CH_3CH_2CH_2$), 22.32 (s, NCH_2CH_2), 22.72 (d, $^2J_{CP}$ = 18 Hz, Ch_3CH_2CHP), 26.47 (s, $NCH_2CH_2CH_2$), 34.70 (d, $^2J_{CP}$ = 10 Hz, $CH_3CH_2CH_2$), 40.85 (d, $^1J_{CP}$ = 16 Hz, CH_3CH_2CHP), 54.46/53.93 (s, NCH_2), 57.92/57.85 (s, OCH_3), 65.66/64.94 (s, NCH), 75.28 (s, CH_2O), 126.99, 127.42 (d, $^3J_{CP}$ = 7 Hz, C_{meta}), 128.20 (s, C_{para}), 132.36, 133.48 (d, $^2J_{CP}$ = 19 Hz, C_{ortho}), 166.56 (d, $^2J_{CP}$ = 8 Hz, C=N).

(2S,2'R,Z)-1-[(2'-Diphenylphosphanyl)-1'-phenyl-1'-propylideneamino]-2-methoxymethylpyrrolidine [(*S,R,Z*)-**3c**]: 2.46 g (10 mmol) hydrazone **2d** and 2.43 g (11 mmol) $ClPPh_2$ were reacted according to *GP 3*, yielding 3.40 g (79%) of (*S,R,Z*)-**3c** as a colourless oil. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.46 (dd, $^3J_{HP}$ = 14.8 Hz, ^3J = 7.4 Hz, 3H, CH_3CHP), 1.60–2.20 (m, 4H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.65 (m, 1H, NCHH), 3.20–3.58 (m, 4H, NCH, CH_2O, NCHH), 3.38 (s, 3H, OCH_3), 4.38/4.94 (dq, $^2J_{HP}$ = 14.8 Hz, ^3J = 7.4 Hz, 1H, CH_3CHP), 7.20–7.50 (m, 15H, $H_{arom.}$). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 15.93/15.85

(d, $^2J_{CP}$ = 20 Hz, CH_3CHP), 21.96 (s, $NCH_2CH_2CH_2$), 26.66 (s, $NCH_2CH_2CH_2$), 33.66 (d, $^1J_{CP}$ = 16 Hz, CH_3CHP), 55.42 (s, NCH_2), 58.16 (s, OCH_3), 66.07 (s, NCH), 75.85 (s, CH_2O), 126.68, 127.12, 127.71, 128.11 ($C_{arom.}$), 127.19, 126.92, 127.43 (d, $^3J_{CP}$ = 7 Hz, C_{Pmeta}), 132.23, 132.99 (d, $^2J_{CP}$ = 20 Hz, C_{Portho}), 135.80, 136.35 (d, $^2J_{CP}$ = 16 Hz, C_{Pipso}), 163.43 (d, $^2J_{CP}$ = 10 Hz, C=N).

Chlorodiphenylphosphane–Borane Adduct: 2.65 g (12 mmol) Ph_2PCl and 1.2 ml (12 mmol) $BH_3 \cdot SMe_2$ were reacted according to *GP 1*, yielding $ClPPh_2 \cdot BH_3$ as a colourless oil. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = ca. 1.3 (q, $^1J_{HB} \approx$ 100 Hz, 3H, BH_3), 7.39 (m, 4H, H_{meta}), 7.47 (m, 2H, H_{para}), 7.71 (m, 4H, H_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = 92.9 (q, $^1J_{PB}$ = 50 Hz).

Chlorodiisopropylphosphane–Borane Adduct: 1.83 g (12 mmol) iPr_2PCl and 1.2 ml (12 mmol) $BH_3 \cdot SMe_2$ were reacted according to *GP 1*, yielding $ClPiPr_2 \cdot BH_3$ as a colourless liquid. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = ca. 0.65 (q, $^1J_{HB} \approx$ 100 Hz, 3H, BH_3), 1.22, 1.25 [dd, *J* = 8.6 Hz, *J* = 7.0 Hz, 12H, $(CH_3)_2$CHP], 2.25 [m, 2H, $(CH_3)_2CHP$]. – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = 136.9 (q, $^1J_{PB}$ = 46 Hz).

(+)-(2S,2′R,Z)-1-[(2′-Boranatodiphenylphopshanyl)-pent-3′-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R,Z*)-**6a**]: 1.98 g (10 mmol) hydrazone (*S*)-**2a** and 2.81 g (12 mmol) $ClPPh_2 \cdot BH_3$ were reacted according to *GP 4*, yielding 3.21 g (81%) (*S,R,Z*)-**6a** as a colourless oil. – $[\alpha]_D^{22}$ = +95.2 (*c* = 1.0, $CHCl_3$). – IR (neat): $\tilde{\nu}$ 3058 (m, C–H_{arom}), 2972, 2933, 2872, 2833, 2811 (s, CH_2, CH_3), 2381 (s, B–H), 2346 (sh), 1619 (C–$C_{arom.}$), 1588 (C=N), 1458 (m), 1437 (s, P–Ph), 1125, 1098, 1061, 742, 699, 693 (s) cm^{-1}. – ^{1}H NMR (500 MHz, C_6D_6, TMS): δ = 0.98 (t, *J* = 7.3 Hz, 3H, CH_3CH_2), 1.34 (dd, $^3J_{HP}$ = 16.8 Hz, ^3J = 7.3 Hz, 3H, CH_3CHP), 1.60 (m, 3H, NCH_2CH_2CHH, NCH_2CH_2CHH), 2.02 (m, 1H, NCH_2CH_2CHH), 2.25 (m, 1H, NCHH), 2.50 (m, 2H, CH_3CH_2), 2.98 (m, 1H, NCHH), 3.21 (s, 3H, OCH_3), 3.29, 3.43 (m, 1H, CH_2O), 3.54 (m, 1H, NCH), 4.67 (dq, $^2J_{HP}$ = 14.7 Hz, ^3J = 7.3 Hz, 1H, CH_3CHP), 7.01–7.19 (m, 6H, $H_{meta,para}$), 7.99, 8.66 (m, 2H, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 11.10 (s, CH_3CH_2), 14.04 (d, $^2J_{CP}$ = 3 Hz, CH_3CHP), 22.81 (s, NCH_2CH_2), 27.25 (d, $^3J_{CP}$ = 1 Hz, CH_3CH_2), 27.55 (s, $NCHCH_2$), 33.47 (d, $^1J_{CP}$ = 31 Hz, CH_3CHP), 56.16 (s, NCH_2), 58.99 (s, OCH_3), 67.70 (s, NCH), 76.55 (s, CH_2O), 128.71, 128.94 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 129.91, 130.87 (d, $^1J_{CP}$ = 53 Hz, C_{ipso}), 131.15, 131.49 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.92, 133.42 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 165.66 (s, C=N). – ^{31}P NMR (202 MHz, C_6D_6, TMS): δ = 22.4 (s, br.). – MS (70 eV); *m/z* (%): 396 (2) (M^+), 395 (4) (M^+ – H), 282 (95) ($M^+ - NC_6H_{12}O$), 201 (41), 197 (54) ($M^+ - Ph_2P \cdot BH_3$), 185 (25) (Ph_2P^+), 153 (56) ($M^+ - Ph_2P \cdot BH_3 - C_2H_4O$), 114 (66) ($C_6H_{12}N^+$), 109 (26) ($PhPH^+$), 84 (45) ($C_5H_{10}N^+$), 70 (42) ($C_4H_8N^+$), 56 (100) ($C_4H_8^+$), 41 (28) C_2H_5O). – $C_{23}H_{34}BN_2OP$ (396.32): calcd. C 69.70, H 8.65, N 7.07; found C 69.98, H 8.88, N 7.06.

(+)-(2S,2′R,Z)-1-[(2′-Boranatodiphenylphosphanyl)-hept-4′-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R,Z*)-**6b**]: 2.26 g (10 mmol) hydrazone (*S*)-**2b** and 2.81 g (12 mmol) $ClPPh_2 \cdot BH_3$ were reacted according to *GP 4*, yielding 3.65 g (86%) (*S,R,Z*)-**6b** as a colourless oil. – $[\alpha]_D^{22}$ = +130.9 (*c* = 1.0, $CHCl_3$). – IR (neat): $\tilde{\nu}$ 3058, 3022 (m, C–$H_{arom.}$), 2963, 2929, 2872, 2829 (s, CH_2, CH_3), 2395 (s, B–H), 2345 (sh), 1618 (C–$C_{arom.}$), 1590 (C=N), 1459 (m), 1437 (s, P–PH), 1126, 1097, 1061, 740, 702, 694 (s) cm^{-1}. – ^{1}H NMR (500 MHz, C_6D_6, TMS): δ = 0.73 (t, ^3J = 7.3 Hz, 3H, CH_3CH_2CHP), 0.79 (t, ^3J = 7.3 Hz, 3H, $CH_3CH_2CH_2$), 1.40 (m, 1H, CH_3CHHCH_2), 1.65 (m, 4H, NCH_2CH_2CHH, NCH_2CH_2CHH, CH_3CHHCH_2), 1.87 (m, 1H, $CH_3CHHCHP$), 2.05 (m, 1H, NCH_2CH_2CHH), 2.13 (m, 1H, $CH_3CHHCHP$), 2.35 (m, 2H, NCHH, CH_3CH_2CHH), 2.46 (m, 1H, CH_3CH_2CHH), 3.12 (m, 2H, CHHO, NCHH), 3.18 (s, 3H, OCH_3), 3.23 (m, 1H, CHHO), 3.42 (m, 1H, NCH), 4.75 (dt, $^2J_{HP}$ = 15.1 Hz, ^3J = 7.3 Hz, 1H, CH_3CH_2CHP), 7.03–7.13 (m, 6H, $H_{meta,para}$), 8.01, 8.19 (m, 2H, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 13.74 (d, $^3J_{CP}$ = 9 Hz, CH_3CH_2CHP), 13.86 (s, $CH_3CH_2CH_2$), 19.74 (s, $CH_3CH_2CH_2$), 22.44 (d, $^2J_{CP}$ = 3 Hz, CH_3CH_2CHP), 22.56 (s, NCH_2CH_2), 27.23 (s, $NCH_2CH_2CH_2$), 35.84 (s, $CH_3CH_2CH_2$), 39.81 (d, $^1J_{CP}$ = 30 Hz, CH_3CH_2CHP), 55.72 (s, NCH_2), 59.06 (s, OCH_3), 66.98 (s, NCH), 75.86 (s, CH_2O), 128.26, 128.82 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 128.99, 129.64 (d, $^1J_{CP}$ = 54 Hz, C_{ipso}), 131.14, 131.26 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 133.75, 133.54 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 164.21 (s, C=N). – ^{31}P NMR (202 MHz, C_6D_6, H_3PO_4): δ = 20.9 (s, br.). – MS (70 eV); *m/z* (%): 424 (3) (M^+), 423 (9) (M^+ – H), 311 (23), 310 (100) ($M^+ - NC_6H_{12}O$), 309 (26), 226 (23), 225 (20) ($M^+ - Ph_2P \cdot BH_3$), 185 (10) (Ph_2P^+), 181 (9) ($M^+ - Ph_2P \cdot BH_3 - C_2H_4O$), 114 (15) ($C_6H_{12}N^+$), 70 (16) ($C_4H_8N^+$). – $C_{25}H_{38}BN_2OP$ (424.37): calcd. C 70.76, H 9.03, N 6.60; found C 70.71, H 8.93, N 6.47.

(+)-(2R,2′S,Z)-[(2′-Boranatodiphenylphosphanyl)-hept-4′-ylideneamino]-2-methoxymethylpyrrolidine [(*R,S,Z*)-**6b**]: 2.26 g (10 mmol) hydrazone (*R*)-**2b** and 2.81 g (12 mmol) $ClPPh_2 \cdot BH_3$ were reacted according to *GP 4*, yielding 3.60 g (85%) (*R,S,Z*)-**6b** as a colourless oil. – $[\alpha]_D^{22}$ = –132.1 (*c* = 1.0, $CHCl_3$). The other analytical data corresponded with those of [(*S,R,Z*)-**6b**].

(+)-(2S,2′R,Z)-1-[(2′-Boranatodiphenylphosphanyl)-non-5′-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R,Z*)-**6c**]: 2.54 g (10 mmol) hydrazone (*S*)-**2c** and 2.81 g (12 mmol) $ClPPh_2 \cdot BH_3$ were reacted according to *GP 4*, yielding 3.57 g (79%) (*S,R,Z*)-**6c** as a colourless oil. – $[\alpha]_D^{22}$ = +114.2 (*c* = 1.0, $CHCl_3$). – IR (neat): $\tilde{\nu}$ 3077, 3057, 3024 (m, C–$H_{arom.}$), 2958, 2930, 2871 (s, CH_2, CH_3), 2384 (s, B–H), 2346 (sh), 1550 (C=N), 1484, 1460 (m), 1437 (s, P–Ph), 1130, 1111, 1062, 739, 698 (s) cm^{-1}. – ^{1}H NMR (300 MHz, C_6D_6, TMS): δ = 0.70 (t, ^3J = 7.3 Hz, 3H, $CH_3CH_2CH_2CHP$), 0.83 (t, ^3J = 7.3 Hz, 3H, $CH_3CH_2CH_2CH_2$), 1.08–2.55 (m, 15H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$, NCHH, CH_2), 3.13 (m, 2H, CHHO, NCHH), 3.18 (s, 3H, OCH_3), 3.26 (m, 1H, CHHO), 3.44 (m, 1H, NCH), 4.93 (dt, $^2J_{HP}$ = 15.1 Hz, ^3J = 7.4 Hz, 1H, $CH_3CH_2CH_2CHP$), 7.00–7.15 (m, 6H, $H_{meta,para}$), 8.03, 8.24 (m, 2H, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 14.15, 14.23 (s, CH_3), 22.75 (d, $^3J_{CP}$ = 7 Hz, $CH_3CH_2CH_2CHP$), 22.75 (s, NCH_2CH_2), 22.93 (s, $CH_3CH_2CH_2$), 27.34 (s, $NCH_2CH_2CH_2$), 28.49 (s, $CH_3CH_2CH_2CH_2$), 32.04 (d, $^2J_{CP}$ = 3 Hz, $CH_3CH_2CH_2CHP$), 34.05 (s, $CH_3CH_2CH_2CH_2$), 38.79 (d, $^1J_{CP}$ = 29 Hz, $CH_3CH_2CH_2CHP$), 56.15 (s, NCH_2), 58.94 (s, OCH_3), 67.75 (s, NCH), 75.92 (s, CH_2O), 128.47, 129.98 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 130.10, 131.35 (d, $^1J_{CP}$ = 53 Hz, C_{ipso}), 131.13, 131.25 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 133.13, 133.65 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 164.91 (s, C=N). – ^{31}P NMR (202 MHz, C_6D_6, H_3PO_4): δ = 21.0 (q, $^1J_{PB}$ = 50 Hz). – MS (70 eV); *m/z* (%): 452 (1) (M^+), 339 (11), 338 (54) ($M^+ - NC_6H_{12}O$), 337 (11), 253 (100) ($M^+ - Ph_2P \cdot BH_3$), 209 (10) ($M^+ - Ph_2P \cdot BH_3 - C_2H_4O$), 201 (9), 185 (12) ($Ph_2P^+$), 183 (17), 114 (17) ($C_6H_{12}N^+$), 108 (12) ($PhP^+$), 84 (26) ($C_5H_{10}N^+$), 70 (11) ($C_4H_8N^+$). – $C_{27}H_{421}BN_2OP$ (452.43): calcd. C 71.68, H 9.36, N 6.19; found C 71.98, H 9.62, N 6.45.

(+)-(2S,2′R,Z)-1-[(2′-Boranatodiphenylphosphanyl)-1′-phenyl-1′-propylideneamino]-2-methoxymethylpyrrolidine [(*S,R,Z*)-**6d**]: 2.54 g (10 mmol) hydrazone (*S*)-**2d** and 2.81 g (12 mmol) $ClPPh_2 \cdot BH_3$ were reacted according to *GP 4*, yielding 3.82 g (86%) (*S,R,Z*)-**6d** as a colourless oil. – $[\alpha]_D^{22}$ = +297.5 (*c* = 1.0, $CHCl_3$).

– IR (neat): ṽ 3078, 3057, 3024 (m, C–H$_{arom.}$), 2968, 2927, 2872, 2828 (s, CH$_2$, CH$_3$), 2384 (s, B–H), 1589, 1574, 1487, 1438 (s, P–Ph), 1131, 1107 (s, P–Ph), 1062, 740, 698 (s) cm^{-1}. – ^{1}H NMR (300 MHz, C_6D_6, TMS): δ = 1.58 (m, 3H, NCH$_2$C*H*$_2$CH$_2$, NCH$_2$CH$_2$CH*H*), 1.68 (dd, $^3J_{HP}$ = 16.4 Hz, ^3J = 7.5 Hz, 3H, C*H*$_3$CHP), 2.01 (m, 1H, NCH$_2$CH$_2$C*H*H), 2.41 (m, 1H, NC*H*H), 3.18 (m, 1H, NCH*H*), 3.22 (s, 3H, OCH$_3$), 3.38, 3.53 (m, 1H, CH$_2$O), 3.71 (m, 1H, NCH), 4.99 (dq, $^2J_{HP}$ = 15.1 Hz, ^3J = 7.5 Hz, 1H, CH$_3$C*H*P), 6.96–7.12 (m, 9H, H$_{meta,para}$), 7.45 (m, 2H, H$_{Cortho}$), 7.81–8.04 (m, 2H, H$_{Portho}$). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 15.10 (d, $^2J_{CP}$ = 4 Hz, *C*H$_3$CHP), 23.35 (s, NCH$_2$*C*H$_2$CH$_2$), 27.53 (s, NCH$_2$CH$_2$*C*H$_2$), 33.65 (d, $^1J_{CP}$ = 29 Hz, CH$_3$*C*HP), 57.02 (s, NCH$_2$), 59.01 (s, OCH$_3$), 68.01 (s, NCH), 76.41 (s, CH$_2$O), 128.31, 128.90 (s, C$_{ortho,Cmeta}$), 128.37, 128.83 (d, $^3J_{CP}$ = 10 Hz, C$_{meta}$), 131.03, 131.21 (d, $^4J_{CP}$ = 2 Hz, C$_{para}$), 133.10, 133.83 (d, $^2J_{CP}$ = 9 Hz, C$_{ortho}$), 137.92 (s, C$_{Cipso}$), 161.30 (s, C=N). – ^{31}P NMR (202 MHz, C_6D_6, H_3PO_4): δ = 24.6 (s, br.). – MS (70 eV); *m/z* (%): 444 (2) (M$^+$), 443 (6) (M$^+$ – H), 331 (18), 330 (88) (M$^+$ – NC$_6$H$_{12}$O), 329 (24), 246 (23), 245 (46) (M$^+$ – Ph$_2$P · BH$_3$), 214 (13), 213 (11), 201 (27) (M$^+$ – Ph$_2$P · BH$_3$ – C$_2$H$_4$O), 186 (11), 185 (41) (Ph$_2$P$^+$), 183 (34), 142 (17), 141 (22), 140 (16), 133 (12), 132 (100) (M$^+$ – Ph$_2$P · BH$_3$ – C$_6$H$_{11}$NO), 129 (18), 114 (56) (C$_6$H$_{12}$N$^+$), 109 (23) (PhPH$^+$), 104 (28), 91 (14), 84 (17) (C$_5$H$_{10}$N$^+$), 77 (36), 70 (11) (C$_4$H$_8$N$^+$). – $C_{27}H_{34}BN_2OP$ (444.36): calcd. C 72.98, H 7.71, N 6.30; found C 73.05, H 7.87, N 6.43.

(+)-(2S,2′R)-1-[(2′-Boranatodiisopropylphosphanyl)-hept-4′-ylideneamino]-2-methoxymethylpyrrolidine [(*S*,*R*)-**6e**]: 2.26 g (10 mmol) hydrazone (*S*)-**2b** and 2.00 g (12 mmol) Cl*i*Pr$_2$P · BH$_3$ were reacted according to *GP 4*, yielding 2.85 g (80%) (*S*,*R*)-**6e** as a colourless oil. – m.p. 37°C (*E*), $[\alpha]_D^{22}$ (*E*) = +261.8 (*c* = 1.0, $CHCl_3$). – IR (KBr): ṽ 2970, 2931, 2873, 2826 (s, CH$_2$, CH$_3$), 2378 (s, B–H), 2344 (sh), 1630 (C–C$_{arom.}$), 1630 (C=N), 1460 (m), 1385, 1369, 1348, 1282, 1269, 1238 (m), 1127, 1097, 1067, 1042, 972, 928 (s) cm^{-1}. – ^{1}H NMR (300 MHz, C_6D_6, TMS): (*Z*): δ = 0.74 (t, ^3J = 7.3 Hz, 3H, C*H*$_3$CH$_2$CH$_2$CHP), 0.97 (t, ^3J = 7.3 Hz, 3H, C*H*$_3$CH$_2$CH$_2$), 1.03–1.22 (m, 12H, PCHC*H*$_3$), 1.52–2.04 (m, 10H), 2.23 (m, 3H), 2.63 (m, 1H), 3.12 (s, 3H, OCH$_3$), 3.04–3.42 (m, 4H, NCH, CH$_2$O, NC*H*H), 3.55 (ddd, $^2J_{HP}$ = 15.1 Hz, *J* = 12.4 Hz, *J* = 3.0 Hz, 1H, CH$_3$CH$_2$C*H*P). – ^{1}H NMR (300 MHz, C_6D_6, TMS): (*E*): δ = 0.86, 0.90 (t, ^3J = 7.3 Hz, 3H, CH$_3$), 1.01, 1.05, 1.10, 1.26 (dd, $^3J_{HP}$ = 14 Hz, ^3J = 12 Hz, 3H, PCHC*H*$_3$), 1.40–2.18 (m, 9H), 2.29–2.65 (m, 4H), 2.92–3.06 (m, 2H), 3.24 (s, 3H, OCH$_3$), 3.26–3.36 (m, 2H, NCH, CH*H*O), 3.60 (m, 1H, C*H*HO). – ^{13}C NMR (75 MHz, C_6D_6, TMS): (*Z*): δ = 13.16 (d, $^3J_{CP}$ = 13 Hz, *C*H$_3$CH$_2$CHP), 14.34 (s, *C*H$_3$CH$_2$CH$_2$), 17.37, 17.75, 18.40, 18.68 (d, $^2J_{CP}$ = 2 Hz, *C*H$_3$CHP), 19.56 (s, CH$_3$CH$_2$CH$_2$), 21.57 (d, $^2J_{CP}$ = 1 Hz, CH$_3$*C*H$_2$CHP), 21.56, 23.73 (d, $^1J_{CP}$ = 30 Hz, CH$_3$*C*HP), 22.50 (s, NCH$_2$*C*H$_2$), 26.35 (s, NCH$_2$CH$_2$*C*H$_2$), 35.76 (d, $^1J_{CP}$ = 22 Hz, CH$_3$CH$_2$*C*HP), 36.50 (s, CH$_3$CH$_2$*C*H$_2$), 55.49 (s, NCH$_2$), 58.74 (s, OCH$_3$), 67.96 (s, NCH), 74.97 (s, CH$_2$O), 164.87 (d, $^2J_{CP}$ = 4 Hz, C=N). – ^{13}C NMR (75 MHz, C_6D_6, TMS): (*E*): δ = 13.81 (d, $^3J_{CP}$ = 9 Hz, *C*H$_3$CH$_2$CHP), 14.99 (s, *C*H$_3$CH$_2$CH$_2$), 17.32 (s), 17.85 (s), 18.19 (d, $^2J_{CP}$ = 4 Hz), 19.27 (s) (PCH*C*H$_3$), 19.82 (d, $^2J_{CP}$ = 1 Hz, CH$_3$*C*H$_2$CHP), 20.07, 21.06 (d, $^1J_{CP}$ = 29 Hz, PC*H*CH$_3$), 22.69 (s, CH$_3$*C*H$_2$CH$_2$), 22.75 (s, NCH$_2$*C*H$_2$), 27.62 (s, NCH$_2$CH$_2$*C*H$_2$), 36.79 (s, CH$_3$CH$_2$*C*H$_2$), 41.84 (d, $^1J_{CP}$ = 23 Hz, CH$_3$CH$_2$*C*HP), 55.70 (s, NCH$_2$), 58.95 (s, OCH$_3$), 67.16 (s, NCH), 76.02 (s, CH$_2$O), 167.80 (d, $^2J_{CP}$ = 2 Hz, C=N). – ^{31}P NMR (202 MHz, C_6D_6, H_3PO_4) (*E*): δ = 37.0 ($^1J_{PB}$ = 69 Hz). – MS (70 eV); *m/z* (%): 356 (4) (M$^+$), 355 (8) (M$^+$ – H), 243 (14), 242 (100) (M$^+$ – NC$_6$H$_{12}$O), 241 (24), 226 (17) (M$^+$ – *i*Pr$_2$P · BH$_3$), 181 (15) (M$^+$ – *i*Pr$_2$P · BH$_3$ – C$_2$H$_4$O), 114 (31) (C$_6$H$_{12}$N$^+$), 112 (30), 84 (6) (C$_5$H$_{10}$N$^+$), 75 (9) (*i*PrPH$^+$), 70 (46) (C$_4$H$_8$N$^+$), 41 (23) (C$_2$H$_5$O$^+$). – $C_{19}H_{42}BN_2OP$ (356.34): calcd. C 64.04, H 11.88, N 7.86; found C 64.26, H 11.89, N 7.89.

(+)-(R)-2-Boranatodiphenylphosphanyl-3-pentanone [(*R*-**7a**]: Hydrazone [(*S*,*R*)-**6a**] (396 mg, 1 mmol) was ozonolyzed according to *GP 8*, yielding 239 mg (84%) of [(*R*)-**7a**] as colourless crystals. – m.p. 59°C, $[\alpha]_D^{22}$ = +71.7 (*c* = 1.0, C_6H_6). – IR (KBr): ṽ 3079, 3059, 3007 (m, C–H$_{arom.}$), 2978, 2938, 2904, 2878 (s, CH$_2$, CH$_3$), 2389 (s, B–H), 2350 (sh), 1713 (s, C=O), 1589 (w, C–C$_{arom.}$), 1456 (s), 1438 (s, P–Ph), 1378, 1350 (m), 1107 (s, P–Ph), 1064, 741 (s) cm^{-1}. – ^{1}H NMR (300 MHz, C_6D_6, TMS): δ = 0.82 (t, *J* = 7.2 Hz, 3H, C*H*$_3$CH$_2$), 1.16 (dd, $^3J_{HP}$ = 15.4 Hz, ^3J = 7.2 Hz, 3H, C*H*$_3$CHP), 2.12 (qd, ^3J = 7.2 Hz, $^4J_{HP}$ = 0.8 Hz, 2H, CH$_3$C*H*$_2$), 3.39 (dq, $^2J_{HP}$ = 12.3 Hz, ^3J = 7.2 Hz, 1H, CH$_3$C*H*P), 6.92–7.06 (m, 6H, H$_{meta,para}$), 7.69, 7.88 (m, 2H, H$_{ortho}$). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 7.55 (s, *C*H$_3$CH$_2$), 12.69 (s, *C*H$_3$CHP), 36.98 (s, CH$_3$*C*H$_2$), 44.69 (d, $^1J_{CP}$ = 24 Hz, CH$_3$*C*HP), 128.82, 128.87 (d, $^3J_{CP}$ = 10 Hz, C$_{meta}$), 131.37, 131.51 (d, $^4J_{CP}$ = 2 Hz, C$_{para}$), 133.27, 133.66 (d, $^2J_{CP}$ = 9 Hz, C$_{ortho}$), 207.07 (d, $^2J_{CP}$ = 1 Hz, C=O). – ^{31}P NMR (202 MHz, C_6D_6, H_3PO_4): δ = 22.0 (q, $^1J_{PB}$ = 62 Hz). – MS (70 eV); *m/z* (%): 284 (2) (M$^+$), 283 (11) (M$^+$ – H), 271 (19), 270 (100), 255 (16) (M$^+$ – BH$_3$ – CH$_3$), 214 (32), 213 (25) (Ph$_2$PCHCH$_3^+$), 203 (25), 202 (8), 198 (12), 187 (10), 186 (67) (Ph$_2$P$^+$), 185 (53), 183 (66), 165 (10), 152 (10), 135 (15), 109 (41), 108 (55) (PhP$^+$), 91 (9) (C$_7$H$_7^+$), 77 (7) (C$_6$H$_5^+$), 41 (30). – $C_{17}H_{22}BOP$ (284.14): calcd. C 71.86, H 7.80; found C 71.57, H 8.30.

(+)-(R)-3-Boranatodiphenylphosphanyl-4-heptanone [(*R*)-**7b**]: Hydrazone [(*S*,*R*)-**6b**] (424 mg, 1 mmol) was ozonolyzed according to *GP 8*, yielding 244 mg (78%) of [(*R*)-**7b**] as colourless crystals. – m.p. 63°C, $[\alpha]_D^{22}$ = +78.8 (*c* = 1.0, C_6H_6). – IR (neat): ṽ 3100, 3057, 3032 (m, C–H$_{arom.}$), 2966, 2933, 2875 (s, CH$_2$, CH$_3$), 2414, 2373, 2346 (s, B–H), 1712 (s, C=O), 1587, 1577 (w, C–C$_{arom.}$), 1437 (s, P–Ph), 1106, 744, 737, 695 (s) cm^{-1}. – ^{1}H NMR (300 MHz, C_6D_6, TMS): δ = 0.64 (t, ^3J = 7.2 Hz, 3H, C*H*$_3$CH$_2$CH$_2$), 0.65 (t, ^3J = 7.2 Hz, 3H, C*H*$_3$CH$_2$CHP), 1.40 (m, 2H, CH$_3$C*H*$_2$CH$_2$), 1.65 (m, 1H, CH$_3$CH*H*CHP), 2.06 (m, 1H, CH$_3$C*H*HCHP), 2.13 (t, ^3J = 7.2 Hz, 2H, CH$_3$CH$_2$C*H*$_2$), 3.40 (ddd, $^2J_{HP}$ = 11.8 Hz, ^3J = 11.8 Hz, ^3J = 2.9 Hz, 1H, CH$_3$CH$_2$C*H*P), 6.94–7.08 (m, 6H, H$_{meta,para}$), 7.74, 7.96 (m, 2H, H$_{ortho}$). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 13.56 (s, *C*H$_3$CH$_2$CH$_2$), 13.56 (d, $^3J_{CP}$ = 12 Hz, *C*H$_3$CH$_2$CHP), 16.81 (s, CH$_3$CH$_2$CH$_2$), 22.22 (s, CH$_3$CH$_2$CHP), 47.41 (s, CH$_3$CH$_2$*C*H$_2$), 53.03 (d, $^1J_{CP}$ = 24 Hz, CH$_3$CH$_2$*C*HP), 128.82, 128.90 (d, $^3J_{CP}$ = 10 Hz, C$_{meta}$), 131.40, 131.54 (d, $^4J_{CP}$ = 2 Hz, C$_{para}$), 133.29, 133.81 (d, $^2J_{CP}$ = 9 Hz, C$_{ortho}$), 206.77 (d, $^2J_{CP}$ = 2 Hz, C=O). – ^{31}P NMR (202 MHz, C_6D_6, H_3PO_4): δ = 19.7 (q, $^1J_{PB}$ = 55 Hz). – MS (70 eV); *m/z* (%): 312 (2) (M$^+$), 311 (8) (M$^+$ – H), 298 (50) (M$^+$ – BH$_3$), 269 (7) (M$^+$ – BH$_3$ – C$_2$H$_5$), 227 (7) (Ph$_2$PCHC$_2$H$_5^+$), 214 (12), 203 (13), 198 (7), 187 (15), 186 (100) (Ph$_2$P$^+$), 185 (31), 183 (26), 113 (7) (M$^+$ – Ph$_2$P · BH$_3$), 109 (16), 108 (28) (PhP$^+$), 89 (7), 55 (15). – $C_{19}H_{26}BOP$ (312.12): calcd. C 73.10, H 8.39; found C 72.94, H 8.43.

(–)-(S)-3-Boranatodiphenylphosphanyl-4-heptanone [(*S*)-**7b**]: Hydrazone [(*R*,*S*)-**6b**] (424 mg, 1 mmol) was ozonolyzed according to *GP 8*, yielding 240 mg (77%) of [(*S*)-**7b**] as colourless crystals. – $[\alpha]_D^{22}$ = –81.4 (*c* = 1.0, C_6H_6). The other analytical data corresponded with those of [(*R*)-**7b**].

(+)-(R)-4-Boranatodiphenylphosphanyl-5-nonanone [(*R*)-**7c**]: Hydrazone [(*S*,*R*)-**6c**] (452 mg, 1 mmol) was ozonolyzed according to *GP 8*, yielding 340 mg (76%) of [(*R*)-**7c**] as a colourless oil. – m.p. 99°C, $[\alpha]_D^{22}$ = +73.1 (*c* = 1.0, C_6H_6). – IR (neat): ṽ 3079,

3026, 3008 (m, C–$H_{arom.}$), 2959, 2932, 2872 (s, CH_2, CH_3), 2390 (s, B–H), 2351 (sh), 1711 (s, C=O), 1589 (w, C–$C_{arom.}$), 1464, 1437 (s, P–Ph), 1380, 1345, 1106, 1061, 740, 696 (s) cm^{-1}. – ^1H NMR (300 MHz, C_6D_6, TMS): δ = 0.62 (t, ^3J = 7.2 Hz, 3H, $CH_3CH_2CH_2CH_2$), 0.72 (t, ^3J = 7.2 Hz, 3H, $CH_3CH_2CH_2CHP$), 0.98–1.74 (m, 10H, 5 CH_2), 3.56 (ddd, $^2J_{HP}$ = 11.8 Hz, ^3J = 11.8 Hz, ^3J = 2.6 Hz, 1H, $CH_3CH_2CH_2CHP$), 6.96–7.10 (m, 6H, $H_{meta,para}$), 7.77, 8.00 (m, 2H, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 13.71 (s, $CH_3CH_2CH_2CH_2$), 14.00 (s, $CH_3CH_2CH_2CHP$), 22.24 (s, $CH_3CH_2CH_2CH_2$), 22.56 (d, $^3J_{CP}$ = 11 Hz, $CH_3CH_2CH_2CHP$), 22.48 (s, $Ch_3CH_2CH_2CH_2$), 30.70 (s, $CH_3CH_2CH_2CHP$), 45.33 (s, $CH_3CH_2CH_2CH_2$), 51.26 (d, $^1J_{CP}$ = 23 Hz, $CH_3CH_2CH_2CHP$), 128.86, 128.92 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.45, 131.59 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 133.32, 133.85 (d, $^2J_{CP}$ = 10 Hz, C_{ortho}), 206.94 (d, $^2J_{CP}$ = 2 Hz, C=O). – ^{31}P NMR (202 MHz, C_6D_6, H_3PO_4): δ = 19.8 (q, $^1J_{PB}$ = 57 Hz). – MS (70 eV); *m/z* (%): 340 (1) (M^+), 339 (5) (M^+ – H), 226 (40) (M^+ – BH_3), 297 (4) (M^+ – BH_3 – C_2H_5), 283 (7) (M^+ – BH_3 – C_3H_7), 241 (8) ($Ph_2PCHC_3H_7^+$), 227 (6) ($Ph_2PCHC_2H_5^+$), 214 (16), 213 (9), 203 (18), 198 (8), 187 (19), 186 (100) (Ph_2P^+), 185 (37), 183 (56), 141 (14) (M^+ – $Ph_2P \cdot BH_3$), 109 (14), 108 (27) (PhP^+), 89 (6), 55 (11). – $C_{21}H_{30}BOP$ (340.25): calcd. C 73.10, H 8.39; found C 72.94, H 8.43.

(+)-(R)-2-Boranatodiphenylphosphanyl-1-phenyl-1-propanone [(*R*)-**7d**]: Hydrazone [(*S,R*)-**6d**] (444 mg, 1 mmol) was ozonolyzed according to *GP 8*, yielding 236 mg (71%) of [(*R*)-**7d**] as colourless crystals. – m.p. 75°C, $[\alpha]_D^{22}$ = +14.9 (*c* = 1.0, C_6H_6). – IR ($CHCl_3$): ṽ 3060, 3009 (m, C–$H_{arom.}$), 2935 (s, CH_3), 2390 (s, B–H), 1678 (s, C=O), 1596 (w, C–$C_{arom.}$), 1448 (s), 1438 (s, P–Ph), 1377, 1217 (s), 1107 (s, P–Ph), 1065, 757 (s) cm^{-1}. – ^1H NMR (300 MHz, C_6D_6, TMS): δ = 1.43 (dd, $^3J_{HP}$ = 15.4 Hz, ^3J = 7.1 Hz, 3H, CH_3CHP), ca. 1.9 (q, $^1J_{BH}$ = 90 Hz, 3H, BH_3), 4.49 (dq, $^2J_{HP}$ = 8.7 Hz, ^3J = 7.1 Hz, 1H, CH_3CHP), 6.80–7.08 (m, 9H, $H_{arom.}$), 7.70, 8.13 (m, 2H, H_{orthoP}). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 14.16 (s, CH_3CHP), 40.03 (d, $^1J_{CP}$ = 27 Hz, CH_3CHP), 126.69 (d, $^1J_{CP}$ = 53 Hz, C_{ipsoP}), 128.56, 128.78 (d, $^2J_{CP}$ = 10 Hz, C_{meta}), 128.54, 128.67 ($C_{arom.C}$), 131.08, 131.57 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 133.00 (s, $C_{arom.C}$), 133.24, 133.68 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 137.62 (s, C_{ipsoC}), 198.26 (d, $^2J_{CP}$ = 5 Hz, C=O). – ^{31}P NMR (202 MHz, C_6D_6, H_3PO_4): δ = 25.1 (q, $^1J_{PB}$ = 55 Hz). – MS (70 eV); *m/z* (%): 332 (2) (M^+), 331 (3) (M^+ – H), 319 (21), 318 (100) (M^+ – BH_3), 317 (37), 214 (10), 213 (9) ($Ph_2PCHCH_3^+$), 202 (22), 201 (8), 187 (7), 186 (49) (Ph_2PH^+), 185 (34), 183 (39), 155 (7), 152 (7), 133 (6) (M^+ – $Ph_2P \cdot BH_3$), 109 (18), 108 (29) (PhP^+), 91 (19) ($C_7H_7^+$), 77 (28) ($C_6H_5^+$), 65 (10), 41 (15). – $C_{21}H_{22}BOP$ (332.19): calcd. C 75.93, H 6.68; found C 75.97, H 7.06.

(+)-(R)-3-Boranatodiisopropylphosphanyl-4-heptanone [(*R*)-**7e**]: Hydrazone [(*S,R*)-**6e**] (356 mg, 1 mmol) was ozonolyzed according to *GP 8*, yielding 190 mg (78%) of [(*R*)-**7e**] as a colourless oil. – $[\alpha]_D^{22}$ = +201.5 (*c* = 1.0, C_6H_6). – IR (neat): ṽ 2965, 2935, 2876 (s, CH_2, CH_3), 2381 (s, B–H), 2345 (sh), 1709 (s, C=O), 1462, 1388, 1370 (s), 1322 (m), 1068, 1041, 687 (s) cm^{-1}. – ^1H NMR (300 MHz, C_6D_6, TMS): δ = 0.66 (t, ^3J = 7.2 Hz, 3H, $CH_3CH_2CH_2$), 0.88 (t, ^3J = 7.2 Hz, 3H, CH_3CH_2CHP), 0.90, 0.95, 1.00, 1.06 (dd, $^2J_{HP}$ = 15 Hz, ^3J = 7 Hz, 3H, $PCHCH_3$), 1.32 (m, 1H, CH_3CHHCH_2), 1.65 (m, 2H, CH_3CH_2CHP), 1.75 (m, 1H, $PCHCH_3$), 1.94 (m, 1H, $CH_3CHHCHP$), 2.01 (m, 1H, $PCHCH_3$), 2.19 (ddd, *J* = 18.0 Hz, *J* = 7.5 Hz, *J* = 6.7 Hz, 1H, CH_3CH_2CHH), 2.74 (ddd, *J* = 12.2 Hz, *J* = 10.6 Hz, *J* = 2.1 Hz, 1H, CH_3CH_2CHP), 2.92 (ddd, *J* = 18.0 Hz, *J* = 7.5 Hz, *J* = 5.0 Hz, 1H, CH_3CH_2CHH). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 13.79 (s, $CH_3CH_2CH_2$), 13.94 (d, $^3J_{CP}$ = 9 Hz, CH_3CH_2CHP), 17.03 (s, $CH_3CH_2CH_2$), 16.34, 16.69, 17.22, 17.36, 17.38, 17.62, 17.65, 18.47 ($PCHCH_3$), 20.79, 20.90, 21.84, 21.21 ($PCHCH_3$), 21.27 (s, CH_3CH_2CHP), 48.79 (d, $^1J_{CP}$ = 17 Hz, CH_3CH_2CHP), 48.99 (s, $CH_3CH_2CH_2$), 206.77 (s, C=O). – ^{31}P NMR (202 MHz, C_6D_6, H_3PO_4): δ = 35.8 (q, $^1J_{PB}$ = 59 Hz). – MS (70 eV); *m/z* (%): 244 (5) (M^+), 243 (31) (M^+ – H), 231 (10), 230 (54), (M^+ – BH_3), 215 (21), 202 (15), 201 (28) (M^+ – BH_3 – C_2H_5), 188 (18) (M^+ – BH_3 – C_3H_6), 187 (11), 159 (28), 146 (39), 145 (14), 135 (46), 119 (16), 118 (100) (iPr_2H^+), 117 (22), 76 (22), 75 (15), 55 (19), 43 (16), 41 (13). – $C_{13}H_{30}BOP$ (244.16): calcd. C 63.95, H 12.39; found C 63.98, H 12.50.

2-Diphenylphosphanyl-3-pentanone (**4**): a) To a solution of 382 mg (1 mmol) hydrazone (*S,R*)-**3a** in 10 ml *n*-pentane, was added 5 ml of 2.5 M HCl under argon. After stirring for 30 min at room temperature, the organic phase was washed with pH 7 buffer, extracted with *n*-pentane and concentrated in vacuo, yielding 186 mg (50%) of **4** as a colourless oil.

b) To a solution of 142 mg (0.5 mmol) 2-boranatodiphenylphosphanyl-3-pentanone (*R*)-**7a** in 2 ml toluene, was added 112 mg (1 mmol) DABCO at room temperature. After extraction of the excess DABCO with HCl (0.1 M) the organic phase was washed with pH 7 buffer, extracted with *n*-pentane and concentrated in vacuo, yielding 70 mg (52%) of (*R*)-**4** as a colourless oil.

c) To a solution of 142 mg (0.5 mmol) 2-boranatodiphenylphosphanyl-3-pentanone (*R*)-**7a** in 1 ml acetone, was added 240 mg (1.5 mmol) $HBF_4 \cdot Et_2O$. After stirring for 30 min at room temperature, the organic phase was washed with pH 7 buffer, extracted with *n*-pentane and concentrated in vacuo, yielding 109 mg (82%) of (*R*)-**4** as a colourless oil. – $[\alpha]_D^{22}$ = +102.2 (*c* = 1.0, $CDCl_3$). – IR (neat): ṽ 3061, 3041 (m, C–$H_{arom.}$), 2960, 2920, 2863 (s, CH_2, CH_3), 1700 (s, C=O), 1563 (m, C–$C_{arom.}$), 1476 (s), 1450, 1430 (s, P–Ph), 1371, 1340 (s), 1107 (s, P–Ph), 1088, 1021, 943, 741 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.85 (t, *J* = 7.2 Hz, 3H, CH_3CH_2), 1.21 (dd, $^3J_{HP}$ = 13.4 Hz, ^3J = 6.7 Hz, 3H, CH_3CHP), 2.25 (m, 2H, CH_3CH_2), 3.49 (qd, ^3J = 6.8 Hz, $^2J_{HP}$ = 4.8 Hz, 1H, CH_3CHP), 7.22–7.50 (m, 10H, $H_{arom.}$). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 7.54 (s, CH_3CH_2), 14.00 (d, $^2J_{CP}$ = 15 Hz, CH_3CHP), 35.48 (d, $^3J_{CP}$ = 4 Hz, CH_3CH_2), 46.55 (d, $^1J_{CP}$ = 21 Hz, CH_3CHP), 128.32, 128.35 (d, $^3J_{CP}$ = 7 Hz, C_{meta}), 128.99 (d, $^4J_{CP}$ = 9 Hz, C_{para}), 132.95, 133.31 (d, $^2J_{CP}$ = 20 Hz, C_{ortho}), 138.98, 195.85 (d, $^1J_{CP}$ = 16 Hz, C_{ipso}), 211.31 (d, $^2J_{CP}$ = 8 Hz, C=O). – ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ = –0.6 (s). – MS (70 eV); *m/z* (%): 271 (18) (M^+ + H), 270 (98) (M^+), 269 (39) (M^+ – H), 255 (22) (M^+ – CH_3), 214 (8), 213 (43) ($Ph_2PCHCH_3^+$), 203 (48), 202 (18), 187 (8), 186 (61), 185 (29) (Ph_2P^+), 183 (54), 152 (9), 135 (30), 109 (100), 108 (35) (PhP^+), 91 (14) ($C_7H_7^+$), 77 (6) ($C_6H_5^+$). – $C_{17}H_{19}OP$: calcd. 270.11735; found 270.11738 (MS).

2-Diphenylphosphinoyl-3-pentanone (**5**): Hydrazone [(*S,R*)-**3a**] (382 mg, 1 mmol) was ozonolyzed according to *GP 8*. The phosphorus was completely oxidized in the crude product. Chromatography yielded 202 mg (70%) of **5** as colourless crystals. – m.p. 83°C. – IR (KBr): ṽ 3055, 3023 (m, C–$H_{arom.}$), 2976, 2896, 2877 (s, CH_2, CH_3), 1708 (s, C=O), 1591 (m, C–$C_{arom.}$), 1485 (s), 1439 (s, P–Ph), 1408 (s), 1379, 1350 (s), 1210 (12), 1181, 1120, 1074 (s, P–Ph), 1074, 1043, 1027, 1011, 990, 950 (s), 721, 711, 701 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.81 (t, *J* = 7.2 Hz, 3H, CH_3CH_2), 1.31 (dd, $^3J_{HP}$ = 16.2 Hz, ^3J = 7.2 Hz, 3H, CH_3CHP), 2.48 (q, 3H, *J* = 7.2 Hz, CH_3CH_2), 3.61 (dq, $^2J_{HP}$ = 14.3 Hz, ^3J = 7.0 Hz, 1H, CH_3CHP), 7.36–7.50 (m, 6H, $H_{meta,para}$), 7.66–7.79 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 7.52 (s, CH_3CH_2), 11.54 (d, $^2J_{CP}$ = 4 Hz, CH_3CHP), 36.43 (s, CH_3CH_2), 50.44 (d, $^1J_{CP}$ = 58 Hz, CH_3CHP), 128.73, 128.75 (d, $^3J_{CP}$ = 12 Hz, C_{meta}), 131.36, 131.39 (d, $^2J_{CP}$ =

9 Hz, C_{ortho}), 132.24, 132.19 (d, $^4J_{CP}$ = 3 Hz, C_{para}), 208.15 (d, $^2J_{CP}$ = 2 Hz, C=O). – ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ = 31.0 (s). – MS (70 eV); *m/z* (%): 286 (38) (M^+), 231 (9), 230 (51), 229 (32) ($Ph_2POCHCH_3^+$), 220 (11), 219 (81), 203 (10), 202 (78), 201 (100) (Ph_2PO^+), 155 (16), 141 (9), 105 (12), 77 (38) ($C_6H_5^+$), 51 (18), 47 (22). – $C_{17}H_{19}O_2P$ (286.31): calcd. C 71.32, H 6.69; found C 71.09, H 6.83.

(+)-(2S,2'R)-1-[(2'-Boranatodiisopropylphosphanyl)prop-1'-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R*)-**11a**]: 1.70 g (10 mmol) hydrazone (*S,R*)-**9b** was reacted with 1.98 g (13 mmol) ($ClPiPr_2$ and 1.3 ml (13 mmol) $BH_3 \cdot SMe_2$ according to *GP 6*, yielding 2.22 g (74%) of **11a** as a colourless oil. IR (neat): ṽ 2963, 2933, 2874, 2827 (s, CH_2, CH_3), 2373 (s, B–H), 2341 (sh), 1589 (C=N), 1461 (m), 1369, 1342, 1303, 1197 (m), 1123, 1069 (s), 1035 (m), 926, 885, 755, 692 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS) (*Z*): δ = 1.24, 1.28 (dd, $^3J_{HP}$ = 13.7 Hz, *J* = 7.1 Hz, 6H, [$(CH_3)_2$CHP]), 1.39 (dd, $^3J_{HP}$ = 14.1 Hz, *J* = 7.2 Hz, 3H, CH_3CHP), 1.54–2.20 (m, 6H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$, [$(CH_3)_2$CHP]), 2.58 (m, 1H, NCHH), 3.24–3.53 (m, 5H, NCH, NCHH, CH_2O, CH_3CHP), 3.33 (s, 3H, OCH_3), 6.87 (dd, *J* = 9.4 Hz, *J* = 5.1 Hz, 1H, HC=N). – ^{1}H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 1.17–1.28 (m, 12H, [$(CH_3)_2$CHP]), 1.36 (dd, $^3J_{HP}$ = 13.5 Hz, *J* = 7.4 Hz, 3H, CH_3CHP), 1.75–2.20 (m, 6H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$, [$(CH_3)_2$CHP]), 2.79 (m, 1H, NCHH), 3.02 (m, 1H, CH_3CHP), 3.22–3.46 (m, 3H, NCHH, CH_2O), 3.37 (s, 3H, OCH_3), 3.54 (m, 1H, NCH), 6.57 (dd, *J* = 6.9 Hz, *J* = 2.9 Hz, 1H, HC=N). – ^{13}C NMR (75 MHz, C_6D_6, TMS) (*Z*): δ = 13.95 (s, CH_3CHP), 17.31, 18.13 (d, $^2J_{CP}$ = 1 Hz), 17.70, 18.26 (s) [$(CH_3)_2$CHP], 21.85, 22.21 (d, $^1J_{CP}$ = 30 Hz, [$(CH_3)_2$CHP]), 23.30 (s, $NCH_2CH_2CH_2$), 26.94 (s, $NCH_2CH_2CH_2$), 28.03 (d, $^1J_{CP}$ = 26 Hz, CH_3CHP), 56.76 (s, NCH_2), 59.00 (s, OCH_3), 67.14 (s, NCH), 75.94 (s, CH_2O), 151.72 (d, $^2J_{CP}$ = 2 Hz, C=N). – ^{13}C NMR (75 MHz, C_6D_6, TMS) (*E*): δ = 14.04 (s, CH_3CHP), 17.62, 17.85, 17.91, 18.04 [$(CH_3)_2$CHP], 21.63, 22.75 (d, $^1J_{CP}$ = 30 Hz, [$(CH_3)_2$CHP], 22.15 (s, $NCH_2CH_2CH_2$), 26.68 (s, $NCH_2CH_2CH_2$), 31.20 (d, $^1J_{CP}$ = 29 Hz, CH_3CHP), 50.00 (s, NCH_2), 59.24 (s, OCH_3), 63.32 (s, NCH), 74.65 (s, CH_2O), 134.45 (d, $^2J_{CP}$ = 2 Hz, C=N). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4) (*E*): δ = 36.8 (q, $^1J_{PB}$ = 72 Hz). – MS (70 eV); *m/z* (%): 300 (26) (M^+), 299 (17), 255 (100) ($M^+ - C_2H_5O$), 186 (24) ($M^+ - NC_6H_{12}O$), 169 (35) ($M^+ - iPr_2P \cdot BH_3$), 126 (12), 125 (22) ($M^+ - iPr_2P \cdot BH_3 - C_2H_4O$), 117 (18) ($iPr_2P^+$), 84 (6) ($C_5H_{10}N^+$), 75 (9) ($iPrPH^+$), 70 (20) ($C_4H_8N^+$), 45 (23) ($C_2H_5O^+$). – $C_{15}H_{34}BN_2OP$ (300.23): calcd. C 60.01, H 11.42, N 9.33; found C 59.98, H 11.25, N 7.65.

(+)-(2S,2'R,E)-1-(2'-Boranatodiphenylphosphanyl)prop-1'-ylideneamino]-2-(1'-methoxy-1'-ethylpropyl)pyrrolidine [(*S,R,E*)-**11c**]: 2.26 g (10 mmol) hydrazone (*S,R*)-**9c** was reacted with 2.87 g (13 mmol) $ClPPh_2$ and 1.3 ml (13 mmol) $BH_3 \cdot SMe_2$ according to *GP 6*. After isomerisation to the (*E*)-form, flash chromatography afforded 2.78 g (65%) of the major diastereomer of (*S,R,E*)-**11c** as a colourless oil. – $[\alpha]_D^{22}$ = +85.9 (*c* = 1.0, $CHCl_3$). – IR (neat): ṽ 3078, 3058 (m, C–$H_{arom.}$), 2969, 2936, 2879, 2826 (s, CH_2, CH_3), 2384 (s, B–H), 2347 (sh), 1586 (C=N), 1482, 1455 (m), 1437 (s, P–Ph), 1346, 1205 (m), 1107 (s, P–Ph), 1065, 740, 696 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.82, 0.83 (t, *J* = 7.2 Hz, 3H, CH_3CH_2), 1.32 (dd, $^3J_{HP}$ = 15.1 Hz, ^3J = 7.2 Hz, 3H, CH_3CHP), 1.38–1.94 (m, 8H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$, CH_3CH_2), 2.54 (m, 1H, NCHH), 3.18–3.23 (m, 2H, NCH, NCHH), 3.19 (s, 3H, OCH_3), 3.52 (m, 1H, CH_3CHP), 6.36 (dd, *J* = 7.4 Hz, *J* = 3.7 Hz, 1H, HC=N), 7.33–7.51 (m, 6H, $H_{meta,para}$), 7.75 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 8.57, 7.80 (s, CH_3CH_2), 13.24 (d, $^2J_{CP}$ = 2 Hz, CH_3CHP), 23.65, 24.33 (s, CH_3CH_2, $NCH_2CH_2CH_2$), 26.15 (s, $NCH_2CH_2CH_2$), 34.72 (d, $^1J_{CP}$ = 34 Hz, CH_3CHP), 50.41 (s, OCH_3), 50.98 (s, NCH_2), 68.39 (s, NCH), 80.18 (s, $(Et_2)CO$), 128.22, 128.68 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 129.87 (s, C=N), 130.92, 131.13 (d, $^4J_{CP}$ = 3 Hz, C_{para}), 133.78, 133.31 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (121 MHz, $CDCl_3$, H_3PO_4): δ = 22.1 (q, $^1J_{PB}$ = 64 Hz). – MS (70 eV); *m/z* (%): 424 (3) (M^+), 323 (100) ($M^+ - Et_2COCH_3$), 310 (10), 309 (46) ($Et_2COCH_3 - BH_3$), 240 (12), 225 (4) ($M^+ - Ph_2P \cdot BH_3$), 185 (7) (Ph_2P^+), 183 (7), 125 (16), 109 (10) ($PhPH^+$), 101 (14), 70 (14) ($C_4H_8N^+$), 45 (10), 41 (10). – $C_{25}H_{38}BN_2OP$ (424.37): calcd. C 70.76, H 9.03, N 6.60; found C 71.26, H 9.32, N 6.38.

(+)-(2S,2'R)-1-[(2'-Boranatodiphenylphosphanyl)prop-1'-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R*)-**11b**]: a) 1.70 g (10 mmol) hydrazone (*S*)-**9b** was reacted with 3.05 g (13 mmol) $ClPPh_2 \cdot BH_3$ according to *GP 5*, yielding 2.06 g (56%) of (*S,R*)-**11b** as a colourless oil.

b) 1.70 g (10 mmol) hydrazone (*S*)-**9b** was reacted with 2.87 g (13 mmol) $ClPPh_2$ and 1.3 ml (13 mmol) $BH_3 \cdot SMe_2$ according to *GP 6*, yielding 1.80 g (49%) of (*S,R*)-**11b** as a colourless oil. After crystallization of the (*Z*)-configured major diastereomer and preparative HPLC of the mother liquor, 1.18 g (32%) of diastereomerically pure (*S,R*)-**11b** was isolated. – m.p. (*Z*) 136°C, $[\alpha]_D^{22}$ = +157.6 (*c* = 1, $CHCl_3$) (*Z*, *de* = 98%). – IR (KBr): ṽ 3058 (m, C–$H_{arom.}$), 2966, 2923, 2873, 2855, 2831, 2809 (s, CH_2, CH_3), 2373 (s, B–H), 2346 (sh), 1622 (C–$C_{arom.}$), 1575 (C=N), 1479, 1452 (m), 1438 (s, P–Ph), 1331, 1196 (m), 1108 (s, P–Ph), 1068, 1038, 1025, 969, 900, 744, 692 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS) (*Z*): δ = 1.31 (dd, $^3J_{HP}$ = 16.6 Hz, ^3J = 7.4 Hz, 3H, CH_3CHP), 1.60–2.15 (m, 4H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.65 (m, 1H, NCHH), 3.13–3.52 (m, 4H, NCH, NCHH, CH_2O), 3.35 (s, 3H, OCH_3), 3.98 (ddq, $^2J_{HP}$ = 14.1 Hz, ^3J = 9.4 Hz, ^3J = 7.1 Hz, 1H, CH_3CHP), 6.93 (dd, ^3J = 9.4 Hz, $^3J_{HP}$ = 5.1 Hz, 1H, HC=N), 7.37–7.54 (m, 6H, $H_{meta,para}$), 7.68–7.79 (m, 4H, H_{ortho}). – ^{1}H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 1.30 (dd, $^3J_{HP}$ = 16.2 Hz, ^3J = 7.2 Hz, 3H, CH_3CHP), 1.64–1.95 (m, 4H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.51 (m, 1H, NCHH), 3.04–3.46 (m, 4H, NCH, NCHH, CH_2O), 3.30 (s, 3H, OCH_3), 3.60 (ddq, $^2J_{HP}$ = 14.8 Hz, ^3J = 7.4 Hz, ^3J = 7.2 Hz, 1H, CH_3CHP), 6.43 (dd, ^3J = 7.4 Hz, $^3J_{HP}$ = 3.4 Hz, 1H, HC=N), 7.33–7.52 (m, 6H, $H_{meta,para}$), 7.76 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS) (*Z*): δ = 14.04 (s, CH_3CHP), 23.24 (s, $NCH_2CH_2CH_2$), 27.34 (s, $NCH_2CH_2CH_2$), 30.97 (d, $^1J_{CP}$ = 34 Hz, CH_3CHP), 56.80 (s, NCH_2), 59.18 (s, OCH_3), 67.11 (s, NCH), 76.24 (s, CH_2O), 127.61, 127.94 (d, $^1J_{CP}$ = 54 Hz, C_{ipso}), 128.60, 128.83 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.47 (s, C_{para}), 132.69, 133.80 8d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 150.97 (s, C=N). – ^{13}C NMR (75 MHz, C_6D_6, TMS) (*E*): δ = 13.51 (d, $^2J_{CP}$ = 2 Hz, CH_3CHP), 22.13 (s, $NCH_2CH_2CH_2$), 26.37 (s, $NCH_2CH_2CH_2$), 34.59 (d, $^1J_{CP}$ = 35 Hz, CH_3CHP), 49.83 (s, NCH_2), 59.06 (s, OCH_3), 63.35 (s, NCH), 76.43 (s, CH_2O), 128.17, 128.71 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 130.94, 131.14 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 131.54 (s, C=N), 132.61, 133.18 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4) (*Z*): δ = 25.0 (q, $^1J_{PB}$ = 63 Hz). – MS (70 eV); *m/z* (%): 368 (29) (M^+), 323 (70) ($M^+ - C_2H_5O$), 254 (58) ($M^+ - NC_6H_{12}O$), 185 (25) (Ph_2P^+), 183 (17), 169 (100) ($M^+ - PH_2P \cdot BH_3$), 125 (22) ($M^+ - Ph_2P \cdot BH_3 - C_2H_4O$), 114 (14) ($NC_6H_{12}O^+$), 109 (25) ($PhPH^+$), 84 (10) ($C_5H_{10}N^+$), 70 (40) ($C_4H_8N^+$), 45 (55) ($C_2H_5O^+$). – $C_{21}H_{30}BN_2OP$ (368.26): calcd. C 68.49, H 8.21, N 7.61; found C 68.38, H 8.35, N 7.65.

(+)-(2S,2'S,E)-1-[(2'-Boranatodiphenylphosphanyl)prop-1'-ylideneamino]-2-methoxymethylpyrrolidine [(*S,S*)-**11b**]: 340 mg (1 mmol) hydrazone (*S*)-**10a** was reacted with 213 mg (1.5 mmol) MeI and 0.1 ml (1 mmol) $BH_3 \cdot SMe_2$ according to *GP 7*, yielding 221

mg (60%) of (*S,S*)-**11b** as a colourless oil. – $[\alpha]_D^{22}$ = +140.4 (*c* = 1, $CHCl_3$). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = ca. 1.0 (q, $^1J_{HB}$ = 90 Hz, BH_3), 1.29 (dd, $^3J_{HP}$ = 16.2 Hz, ^3J = 7.2 Hz, 3H, CH_3CHP), 1.65–1.96 (m, 4H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.76 (m, 1H, NC*H*H), 3.07–3.45 (m, 4H, NCH, NCH*H*, CH_2O), 3.29 (s, 3H, OCH_3), 3.57 (ddq, $^2J_{HP}$ = 14.8 Hz, ^3J = 7.4 Hz, ^3J = 7.2 Hz, 1H, CH_3CHP), 6.38 (dd, ^3J = 7.4 Hz, $^3J_{HP}$ = 3.6 Hz, 1H, HC=N), 7.36–7.49 (m, 6H, $H_{meta,para}$), 7.77 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 13.94 (d, $^2J_{CP}$ = 2 Hz, CH_3CHP), 21.99 (s, $NCH_2CH_2CH_2$), 26.76 (s, $NCH_2CH_2CH_2$), 34.42 (d, $^1J_{CP}$ = 35 Hz, CH_3CHP), 49.33 (s, NCH_2), 59.18 (s, OCH_3), 62.80 (s, NCH), 74.55 (s, CH_2O), 128.54 (d, $^1J_{CP}$ = 55 Hz, C_{ipso}), 128.40, 128.76 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 130.98, 131.16 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 131.95 (s, C=N), 132.78, 133.17 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}).

The other analytical data corresponded with those of hydrazone (*S,R*)-**11b**.

(+)-(2S,2′R)-1-[(2′-Boranatodiphenylphosphanyl)but-1′-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R*)-**11d**]: a) 1.84 g (10 mmol) hydrazone (*S*)-**9d** was reacted with 3.05 g (13 mmol) $ClPPh_2 \cdot BH_3$ according to *GP 5*, yielding 1.53 g (40%) of (*S,R*)-**11d** as a colourless oil.

b) 1.84 g (10 mmol) hydrazone (*S*)-**9d** was reacted with 2.87 g (13 mmol) $ClPPh_2$ and 1.3 ml (13 mmol) $BH_3 \cdot SMe_2$ according to *GP 6*, yielding 2.56 g (67%) [1.91 g (50%) after purification of the major diastereomer] of (*S,R*)-**11d** as a colourless oil. – m.p. (*Z*) 113°C, $[\alpha]_D^{22}$ = +136.2 (*c* = 1, $CHCl_3$) (*Z*, *de* = 98%). – IR (KBr): $\tilde{\nu}$ 3077, 3057, 3024 (m, C–$H_{arom.}$), 2965, 2930, 2873, 2826 (s, CH_2, CH_3), 2383 (s, B–H), 2347 (sh), 1626 (C–$C_{arom.}$), 1587 (C=N), 1483, 1459 (m), 1437 (s, P–Ph), 1340, 1197 (m), 1107 (s, P–Ph), 1061, 739, 696 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*Z*): δ = 0.94 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.49 (m, 1H, CH_3CHH), 1.71–2.04 (m, 5H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$, CH_3CHH), 2.70 (m, 1H, NC*H*H), 2.76–3.50 (m, 4H, NCH, NCH*H*, CH_2O), 3.28 (s, 3H, OCH_3), 3.92 (m, 1H, CH_3CH_2CHP), 6.78 (dd, *J* = 9.7 Hz, *J* = 4.1 Hz, 1H, HC=N), 7.35–7.55 (m, 6H, $H_{meta,para}$), 7.69–7.85 (m, 4H, H_{ortho}). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 0.94 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.50–1.95 (m, 6H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$, CH_3CH_2), 2.48 (m, 1H, NC*H*H), 3.01–3.48 (m, 5H, NCH, NCH*H*, CH_2O, CH_3CH_2CHP), 3.31 (s, 3H, OCH_3), 6.36 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, *J* = 3.8 Hz, 1H, HC=N), 7.29–7.48 (m, 6H, $H_{meta,para}$), 7.69–7.85 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*Z*): δ = 13.33 (d, $^3J_{CP}$ = 11 Hz, CH_3), 21.94 (d, $^2J_{CP}$ = 2 Hz, CH_3CH_2), 23.25 (s, $NCH_2CH_2CH_2$), 27.26 (s, $NCH_2CH_2CH_2$), 38.00 (d, $^1J_{CP}$ = 31 Hz, CH_3CH_2CHP), 55.71 (s, NCH_2), 59.03 (s, OCH_3), 66.87 (s, NCH), 75.88 (s, CH_2O), 128.46, 128.86 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.30, 131.46 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.76, 133.12 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 148.02 (s, C=N). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*E*): δ = 13.51 (d, $^3J_{CP}$ = 13 Hz, CH_3), 21.92 (d, $^2J_{CP}$ = 3 Hz, CH_3CH_2), 22.75 (s, $NCH_2CH_2CH_2$), 26.91 (s, $NCH_2CH_2CH_2$), 42.36 (d, $^1J_{CP}$ = 35 Hz, CH_3CH_2CHP), 50.61 (s, NCH_2), 59.72 (s, OCH_3), 64.02 (s, NCH), 75.04 (s, CH_2O), 128.73, 129.36 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.48, 131.78 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.47 (s, C=N), 133.16, 133.76 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4) (*Z*): δ = 23.3 (q, $^1J_{PB}$ = 61 Hz). – MS (70 eV); *m/z* (%): 382 (39) (m^+), 381 (20), 338 (21), 337 (89) ($M^+ - C_2H_5O$), 268 (25) ($M^+ - NC_6H_{12}O$), 212 (12), 185 (31) (Ph_2P^+), 183 (100) ($M^+ - Ph_2P \cdot BH_3$), 151 (14), 141 (12), 139 (17) ($M^+ - Ph_2P \cdot BH_3 - C_2H_4O$), 126 (20), 114 (27) ($NC_6H_{12}O^+$), 109 (17) ($PhPH^+$), 108 (14), 84 (21) ($C_5H_{10}N^+$), 70 (87) ($C_4H_8N^+$), 55 (34). – $C_{22}H_{32}BN_2OP$ (382.29): calcd. C 69.12, H 8.44, N 7.33; found C 69.46, H 8.61, N 7.03.

(+)-(2S,2′S,E)-1-[(2′-Boranatodiphenylphosphanyl)but-1′-ylideneamino]-2-methoxymethylpyrrolidine [(*S,S*)-**11d**]: 340 mg (1 mmol) hydrazone (*S*)-**10** was reacted with 234 mg (1.5 mmol) EtI and 0.1 ml (1 mmol) $BH_3 \cdot SMe_2$ according to *GP 7*, yielding 241 mg (63%) of hydrazone (*S,S,E*)-**11d** as a colourless oil. – $[\alpha]_D^{22}$ = +114.1 (*c* = 1, $CHCl_3$). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 0.93 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.50–1.95 (m, 6H, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$, CH_3CH_2), 2.78 (m, 1H, NC*H*H), 3.01–3.48 (m, 5H, NCH, NCH*H*, CH_2O, CH_3CH_2CHP), 3.27 (s, 3H, OCH_3), 6.30 (dd, *J* = 8.0 Hz, *J* = 3.7 Hz, 1H, HC=N), 7.32–7.52 (m, 6H, $H_{meta,para}$), 7.69–7.83 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*E*): δ = 12.81 (d, $^3J_{CP}$ = 13 Hz, CH_3), 21.21 (d, $^2J_{CP}$ = 3 Hz, CH_3CH_2), 21.95 (s, $NCH_2CH_2CH_2$), 26.76 (s, $NCH_2CH_2CH_2$), 41.53 (d, $^1J_{CP}$ = 35 Hz, CH_3CH_2CHP), 49.53 (s, NCH_2), 59.15 (s, OCH_3), 62.73 (s, NCH), 74.57 (s, CH_2O), 128.31, 128.76 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.86, 131.11 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.16 (s, C=N), 133.65, 133.16 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = 19.5 (s, br.).

The other analytical data corresponded with those of (*S,R*)-**11d**.

(+)-(2S,2′R)-1-[(2′-Boranatodiphenylphosphanyl)pent-1′-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R*)-**11e**]: a) 1.96 g (10 mmol) hydrazone (*S*)-**9e** was reacted with 3.05 g (13 mmol) $ClPPh_2 \cdot BH_3$ according to *GP 5*, yielding 1.58 g (40%) of (*S,R*)-**11e** as a colourless oil.

b) 1.96 g (10 mmol) hydrazone (*S*)-**9e** was reacted with 2.87 g (13 mmol) $ClPPh_2$ and 1.3 ml (13 mmol) $BH_3 \cdot SMe_2$ according to *GP 6*, yielding 2.73 g (69%) of (*S,R*)-**11e** as a colourless oil. After crystallization of the (*Z*)-configured major diastereomer and preparative HPLC of the mother liquor, 2.38 g (60%) of diastereomerically pure (*S,R*)-**11e** was isolated. – m.p. (*Z*) 79°C, $[\alpha]_D^{22}$ = +114.1 (*c* = 1, $CHCl_3$) (*Z*, *de* = 98%). – IR (neat): $\tilde{\nu}$ 3078, 3057, 3024 (m, C–$H_{arom.}$), 2959, 2931, 2872, 2826 (s, CH_2, CH_3), 2384 (s, B–H), 2349 (sh), 1587 (C=N), 1483, 1461 (m), 1437 (s, P–Ph), 1341, 1197 (m), 1108 (s, P–Ph), 1061, 739, 695 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*Z*): δ = 0.84 (t, ^3J = 7.3 Hz, 3H, CH_3), 1.19–2.01 (m, 8H, CH_3CH_2, $CH_3CH_2CH_2$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.70 (m, 1H, NC*H*H), 2.77, 2.99 (m, 1H, CH_2O), 3.20 (m, 1H, NCH*H*), 3.27 (s, 3H, OCH_3), 3.37 (m, 1H, NCH), 4.04 (m, 1H, $CH_3CH_2CH_2CHP$), 6.79 (dd, *J* = 9.5 Hz, *J* = 3.9 Hz, 1H, HC=N), 7.34–7.54 (m, 6H, $H_{meta,para}$), 7.68–7.86 (m, 4H, H_{ortho}). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 0.84 (t, ^3J = 7.0 Hz, 3H, CH_3), 1.20–1.97 (m, 8H, CH_3CH_2, $CH_3CH_2CH_2$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.47 (m, 1H, NC*H*H), 2.97–3.53 (m, 5H, CH_2O, NCH*H*, NCH, $CH_3CH_2CH_2CHP$), 3.33 (s, 3H, OCH_3), 6.36 (dd, *J* = 7.8 Hz, *J* = 3.5 Hz, 1H, HC=N), 7.31–7.50 (m, 6H, $H_{meta,para}$), 7.69–7.84 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*Z*): δ = 14.11 (s, CH_3), 21.93 (d, $^3J_{CP}$ = 10 Hz, CH_3CH_2), 23.23 (s, $NCH_2CH_2CH_2$), 27.19 (s, $NCH_2CH_2CH_2$), 30.80 (d, $^2J_{CP}$ = 2 Hz, $CH_3CH_2CH_2$), 36.68 (d, $^1J_{CP}$ = 32 Hz, $CH_3CH_2CH_2CHP$), 55.53 (s, NCH_2), 58.99 (s, OCH_3), 66.88 (s, NCH), 75.80 (s, CH_2O), 127.93, 128.16 (d, $^1J_{CP}$ = 54 Hz; C_{ipso}), 128.41, 128.85 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.26, 131.48 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.75, 133.07 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 147.91 (s, C=N). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*E*): δ = 13.61 (s, CH_3), 21.27 (d, $^3J_{CP}$ = 12 Hz, CH_3CH_2), 23.19 (s, $NCH_2CH_2CH_2$), 26.35 (s, $NCH_2CH_2CH_2$), 29.83 (d, $^2J_{CP}$ = 3 Hz, $CH_3CH_2CH_2$), 39.83 (d, $^1J_{CP}$ = 35 Hz, CH_3CH_2CHP), 50.10 (s, NCH_2), 59.16 (s, OCH_3), 63.50 (s, NCH), 74.54 (s, CH_2O), 128.14, 128.78 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 130.88, 131.21 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.31 (s, C=N), 132.75, 133.07 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4) (*Z*): δ = 23.0 (q, $^1J_{PB}$ = 64 Hz). – MS (70 eV); *m/z* (%): 396 (56) (M^+), 395 (21), 352 (23), 351 (97) ($M^+ - C_2H_5O$), 282 (24) (M^+ –

$NC_6H_{12}O$), 212 (8), 198 (20), 197 (100) ($M^+ - Ph_2P \cdot BH_3$), 185 (27) (Ph_2P^+), 183 (26), 153 (14) ($M^+ - Ph_2P \cdot BH_3 - C_2H_4O$), 151 (14), 141 (12), 126 (19), 123 (16), 114 (23) ($NC_6H_{12}O^+$), 109 (11) ($PhPH^+$), 108 (12), 84 (25) ($C_5H_{10}N^+$), 70 (72) ($C_4H_8N^+$), 55 (24). – $C_{23}H_{34}BN_2OP$ (382.29): calcd. C 69.71, H 8.65, N 7.07; found C 69.51, H 8.84, N 7.30.

(–)-(2R,2'S)-1-[(2'-Boranataodiphenylphosphanyl)pent-1'-ylideneamino]-2-methoxymethylpyrrolidine [(*R,S*)-**11e**]: 1.96 g (10 mmol) hydrazone (*R*)-**9e** was reacted with 2.87 g (13 mmol) $ClPPh_2$ and 1.3 ml (13 mmol) $BH_3 \cdot SMe_2$ according to *GP 6*, yielding 2.63 g (66%) of (*R,S*)-**11e** as a colourless oil. After crystallization of the (*Z*)-configured major diastereomer and preparative HPLC of the mother liquor, 2.35 g (59%) of diastereomerically pure (*R,S*)-**76e** was isolated. – $[\alpha]_D^{22} = -112.2$ (*c* = 1, $CHCl_3$) (*Z*, *de* = 98%).

The other analytical data corresponded with those of hydrazone (*S,R*)-**11e**.

(+)-(2S,2'S)-1-[(2'-Boranatodiphenylphosphanyl)pent-1'-ylideneamino]-2-methoxymethylpyrrolidine [(*S,S*)-**1e**]: 340 mg (1 mmol) hydrazone (*S*)-**10** was reacted with 255 mg (1.5 mmol) *n*PrI and 0.1 ml (1 mmol) $BH_3 \cdot SMe_2$ according to *GP 7*, yielding 245 mg (62%) of hydrazone (*S,S*)-**11e** as a colourless oil. After preparative HPLC, 206 mg (52%) of diastereomerically pure (*S,S*)-**11e** was isolated. – $[\alpha]_D^{22} = +173.4$ (*c* = 1.1, $CHCl_3$) (*Z*). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*Z*): δ = 0.85 (t, *J* = 7.3 Hz, 3H, CH_3), 1.19–1.92 (m, 8H, CH_3CH_2, $CH_3CH_2CH_2$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.37 (m, 1H, NC*H*H), 3.16–3.39 (m, 4H, NCH*H*, CH_2O, NCH), 3.32 (s, 3H, OCH_3), 4.19 (m, 1H, $CH_3CH_2CH_2CHP$), 7.14 (dd, *J* = 9.1 Hz, *J* = 3.3 Hz, 1H, HC=N), 7.30–7.90 (m, 10H, $H_{arom.}$). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 0.83 (t, *J* = 7.0 Hz, 3H, CH_3), 1.20–1.95 (m, 8H, CH_3CH_2, $CH_3CH_2CH_2$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.76 (m, 1H, NC*H*H), 3.00–3.53 (m, 5H, CH_2O, NCH*H*, NCH, $CH_3CH_2CH_2CHP$), 3.27 (s, 3H, OCH_3), 6.32 (dd, *J* = 7.8 Hz, *J* = 3.5 Hz, 1H, HC=N), 7.31–7.52 (m, 6H, $H_{meta,para}$), 7.69–7.84 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*Z*): δ = 13.92 (s, CH_3), 21.20 (d, $^3J_{CP}$ = 12 Hz, CH_3CH_2), 22.67 (s, $NCH_2CH_2CH_2$), 26.57 (s, $NCH_2CH_2CH_2$), 31.00 (s, $CH_3CH_2CH_2$), 36.46 (d, $^1J_{CP}$ = 33 Hz, $CH_3CH_2CH_2CHP$), 54.88 (s, NCH_2), 58.97 (s, OCH_3), 66.92 (s, NCH), 75.32 (s, CH_2O), 126.13 (d, $^1J_{CP}$ = 55 Hz, C_{ipso}), 128.49, 129.08 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.25, 131.89 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.79, 133.23 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 152.87 (s, C=N). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*E*): δ = 13.66 (s, CH_3), 21.15 (d, $^3J_{CP}$ = 12 Hz, CH_3CH_2), 21.94 (s, $NCH_2CH_2CH_2$), 26.75 (s, $NCH_2CH_2CH_2$), 29.76 (d, $^2J_{CP}$ = 3 Hz, $CH_3CH_2CH_2$), 39.55 (d,m $^1J_{CP}$ = 34 Hz, $CH_3CH_2CH_2CHP$), 49.51 (s, NCH_2), 59.12 (s, OCH_3), 62.70 (s, NCH), 74.54 (s, CH_2O), 128.30, 128.74 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 130.84, 131.15 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.58 (s, C=N), 132.66, 133.17 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}).

The other analytical data corresponded with those of (*S,R*)-**11e**.

(+)-(2S,2'R)-1-[(2'-Boranatodiphenylphosphanyl)hex-1'-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R*)-**11f**]: a) 2.10 g (10 mmol) hydrazone (*S*)-**9f** was reacted with 3.05 g (13 mmol) $ClPPh_2$ BH_3 according to *GP 5*, yielding 1.60 g (39%) of (*S,R*)-**11e** as a colourless oil.

b) 2.10 g (10 mmol) hydrazone (*S*)-**9f** was reacted with 2.87 g (13 mmol) $ClPPh_2$ and 1.3 ml (13 mmol) $BH_3 \cdot SMe_2$ according to *GP 6*, yielding 2.83 g (69%) of (*S,R*)-**11e** as a colourless oil. After crystallization of the (*Z*)-configured major diastereomer and preparative HPLC of the mother liquor, 2.26 g (55%) of diastereomerically pure (*S,R*)-**11f** was isolated. – m.p. (*Z*) 89 °C, $[\alpha]_D^{22} = +121.7$ (*c* = 1, $CHCl_3$) (*Z*, *de* = 98%). – IR (neat): $\tilde{\nu}$ 3078, 3057 (m, C–$H_{arom.}$), 2956, 2928, 2871 (s, CH_2, CH_3), 2386 (s, B–H), 2350 (sh), 1588 (C=N), 1484, 1461 (m), 1437 (s, P–PH), 1341, 1196 (m), 1107 (s, P–Ph), 1062, 739, 696 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*Z*): δ = 0.80 (t, ^3J = 7.0 Hz, 3H, CH_3), 1.11–2.04 (m, 10H, CH_3CH_2, $CH_3CH_2CH_2$, $CH_3CH_2CH_2CH_2$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.70 (m, 1H, NC*H*H), 2.77, 2.97 (m, 1H, CH_2O), 3.20 (m, 1H, NCH*H*), 3.28 (s, 3H, OCH_3), 3.37 (m, 1H, NCH), 3.99 (m, 1H, $CH_3CH_2CH_2CH_2CHP$), 6.78 (dd, *J* = 9.6 Hz, *J* = 3.8 Hz, 1H, HC=N), 7.35–7.57 (m, 6H, $H_{meta,para}$), 7.67–7.87 (m, 4H, H_{ortho}). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 0.81 (t, ^3J = 7.1 Hz, 3H, CH_3), 1.10–1.95 (m, 10H, CH_3CH_2, $CH_3CH_2CH_2$, $CH_3CH_2CH_2CH_2$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.47 (m, 1H, NC*H*H), 3.02 (m, 1H, $CH_3CH_2CH_2CHP$), 3.19–3.52 (m, 4H, CH_2O, NCH*H*, NCH), 3.34 (s, 3H, OCH_3), 6.37 (dd, *J* = 8.0 Hz, *J* = 3.6 Hz, 1H, HC=N), 7.32–7.52 (m, 6H, $H_{meta,para}$), 7.64–7.84 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS) (*Z*): δ = 13.74 (s, CH_3), 22.67 (s, CH_3CH_2), 23.26 (s, $NCH_2CH_2CH_2$), 27.23 (s, $NCH_2CH_2CH_2$), 28.42 (d, $^2J_{CP}$ = 2 Hz, $CH_3CH_2CH_2CH_2$), 30.75 (d, $^3J_{CP}$ = 10 Hz, $CH_3CH_2CH_2CH_2CHP$), 36.76 (d, $^1J_{CP}$ = 32 Hz, $CH_3CH_2CH_2CH_2CHP$), 55.52 (s, NCH_2), 59.02 (s, OCH_3), 66.85 (s, NCH), 75.84 (s, CH_2O), 128.44, 128.85 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.27, 131.46 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.79, 133.13 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 148.07 (s, C=N). – ^{13}C NMR (75 MHz, C_6D_6, TMS) (*E*): δ = 13.83 (s, CH_3), 22.16, 22.21 (s, CH_3CH_2, $NCH_2CH_2CH_2$), 26.27 (s, $NCH_2CH_2CH_2$), 27.45 (d, $^2J_{CP}$ = 2 Hz, $CH_3CH_2CH_2CH_2$), 30.23 (d, $^3J_{CP}$ = 12 Hz, $CH_3CH_2CH_2CH_2CHP$), 39.98 (d, $^1J_{CP}$ = 35 Hz, $CH_3CH_2CH_2CH_2CHP$), 50.15 (s, NCH_2), 59.18 (s, OCH_3), 63.56 (s, NCH), 74.48 (s, CH_2O), 128.13, 128.79 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 130.87, 131.20 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.52 (s, C=N), 132.61, 133.20 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4) (*Z*): δ = 23.2 (s, br.). – MS (70 eV); *m/z* (%): 410 (35) (M^+), 409 (16), 366 (19), 365 (100) ($M^+ - C_2H_5O$), 296 (31) ($M^+ - NC_6H_{12}O$), 212 (27), 211 (100) ($M^+ - Ph_2P \cdot BH_3$), 185 (25) (Ph_2P^+), 183 (24), 167 (14) ($M^+ - Ph_2P \cdot BH_3 - C_2H_4O$), 165 (9), 141 (11), 126 (15), 123 (15), 114 (23) ($NC_6H_{12}O^+$), 109 (10) ($PhPH^+$), 108 (12), 84 (18) ($C_5H_{10}N^+$), 70 (61) ($C_4H_8N^+$), 55 (30). – $C_{24}H_{36}BN_2OP$ (410.34): calcd. C 70.25, H 8.84, N 6.83; found C 70.61, H 8.82, N 7.08.

(+)-(2S,2'S)-1-[(2'-Boranatodiphenylphosphanyl)hex-1'-ylideneamino]-2-methoxymethylpyrrolidine [(*S,S*)-**11f**]: 340 mg (1 mmol) hydrazone (*S*)-**10** was reacted with 276 mg (1.5 mmol) *n*BuI and 0.1 ml (1 mmol) $BH_3 \cdot SMe_2$ according to *GP 7*, yielding 254 mg (62%) of hydrazone (*S,S*)-**11f** as a colourless oil. – $[\alpha]_D^{22}$ (*E*) = +96.3 (*c* = 1, $CHCl_3$). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 0.80 (t, *J* = 7.1 Hz, 3H, CH_3), 1.00–1.95 (m, 10H, CH_3CH_2, $CH_3CH_2CH_2$, $CH_3CH_2CH_2CH_2$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.76 (m, 1H, NC*H*H), 2.99–3.52 (m, 5H, $CH_3CH_2CH_2CH_2CHP$, CH_2O, NCH*H*, NCH), 3.27 (s, 3H, OCH_3), 6.32 (dd, *J* = 8.0 Hz, *J* = 3.4 Hz, 1H, HC=N), 7.30–7.52 (m, 6H, $H_{meta,para}$), 7.68–7.82 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 13.82 (s, CH_3), 21.94, 22.18 (s, CH_3CH_2, $NCH_2CH_2CH_2$), 26.77 (s, $NCH_2CH_2CH_2$), 27.35 (d, $^2J_{CP}$ = 3 Hz, $CH_3CH_2CH_2CH_2$), 30.16 (d, $^3J_{CP}$ = 12 Hz, $CH_3CH_2CH_2CH_2CHP$), 39.76 (d, $^1J_{CP}$ = 35 Hz, $CH_3CH_2CH_2CH_2CHP$), 49.55 (s, NCH_2), 59.13 (s, OCH_3), 62.70 (s, NCH), 74.54 (s, CH_2O), 128.30, 128.74 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 130.86, 131.13 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.59 (s, C=N), 132.70, 133.19 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4) (*E*): δ = 19.7 (s, br.).

The other analytical data corresponded with those of (*S,R*)-**11f**.

(+)-(2S,2'R)-1-[(2'-Boranatodiphenylphosphanyl)hept-1'-ylideneamio]-2-methoxymethylpyrrolidine [(*S,R*)-**11g**]: a) 2.26 g (10

mmol) hydrazone (*S*)-**9g** was reacted with 3.05 g (13 mmol) $ClPPh_2$ BH_3 according to *GP 5*, yielding 1.74 g (41%) of (*S,R*)-**11g** as a colourless oil.

b) 2.26 g (10 mmol) hydrazone (*S*)-**9g** was reacted with 2.87 g (13 mmol) $ClPPh_2$ and 1.3 ml (13 mmol) $BH_3 \cdot SMe_2$ according to *GP 6*, yielding 2.96 g (70%) of (*S,R*)-**11g** as a colourless oil. After crystallization of the (*Z*)-configured major diastereomer and preparative HPLC of the mother liquor, 2.42 g (57%) of diastereomerically pure (*S,R*)-**11g** was isolated. – m.p. (*Z*) 92°C, $[\alpha]_D^{22} = +125.9$ (*c* = 1, $CHCl_3$) (*Z*, *de* = 98%). – IR (KBr): $\tilde{\nu}$ 3078, 3057 (m, C–$H_{arom.}$), 2955, 2928, 2870 (s, CH_2, CH_3), 2386 (s, B–H), 2350 (sh), 1588 (C=N), 1483, 1460 (m), 1437 (s, P–Ph), 1340, 1196 (m), 1107 (s, P–Ph), 1062, 739, 696 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*Z*): δ = 0.80 (t, ^3J = 6.3 Hz, 3H, CH_3), 1.15–2.05 (m, 12H, CH_3CH_2, $CH_3CH_2CH_2$, $CH_3CH_2CH_2CH_2$, $CH_3CH_2CH_2CH_2CH_2$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.70 (m, 1H, NC*H*H), 2.77, 2.99 (m, 1H, CH_2O), 3.19 (m, 1H, NCH*H*), 3.28 (s, 3H, OCH_3), 3.37 (m, 1H, NCH), 4.00 (m, 1H, $CH_3CH_2CH_2CH_2CH_2CHP$), 6.79 (dd, *J* = 9.5 Hz, *J* = 4.0 Hz, 1H, HC=N), 7.35–7.55 (m, 6H, $H_{meta,para}$), 7.67–7.85 (m, 4H, H_{ortho}). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 0.82 (t, ^3J = 6.7 Hz, 3H, CH_3), 1.10–1.95 (m, 12H, CH_3CH_2, $CH_3CH_2CH_2$, $CH_3CH_2CH_2CH_2$, $CH_3CH_2CH_2CH_2CH_2$, $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$), 2.47 (m, 1H, NC*H*H), 3.02 (m, 1H, CHP), 3.18–3.52 (m, 4H, CH_2O, NCH*H*, NCH), 3.34 (s, 3H, OCH_3), 6.36 (dd, *J* = 8.0 Hz, *J* = 3.6 Hz, 1H, HC=N), 7.32–7.52 (m, 6H, $H_{meta,para}$), 7.68–7.86 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*Z*): δ = 13.93 (s, CH_3), 22.29 (s, CH_3CH_2), 23.25 (s, $NCH_2CH_2CH_2$), 27.23 (s, $NCH_2CH_2CH_2$), 28.28 (d, $^3J_{CP}$ = 10 Hz, CH_2), 28.63 (d, $^2J_{CP}$ = 2 Hz, CH_2), 31.69 (s, $CH_3CH_2CH_2$), 36.76 (d, $^1J_{CP}$ = 32 Hz, CHP), 55.52 (s, NCH_2), 59.02 (s, OCH_3), 66.85 (s, NCH), 75.84 (s, CH_2O), 128.42, 128.84 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.27, 131.47 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.77, 133.10 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 148.13 (s, C=N). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*E*): δ = 13.98 (s, CH_3), 22.20, 22.41 (s, CH_3CH_2, $NCH_2CH_2CH_2$), 26.28 (s, $NCH_2CH_2CH_2$), 27.69, 31.24 (s, CH_2), 27.78 (d, $^3J_{CP}$ = 9 Hz, CH_2), 40.00 (d, $^1J_{CP}$ = 35 Hz, CHP), 50.15 (s, NCH_2), 59.18 (s, OCH_3), 63.55 (s, NCH), 74.80 (s, CH_2O), 128.13, 128.77 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 128.73 (d, $^1J_{CP}$ = 55 Hz, C_{ipso}), 130.86, 131.19 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.47 (s, C=N), 132.62, 133.22 (d, $^2J_{CP}$ = 8 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4) (*Z*): δ = 23.0 (d, $^1J_{PB}$ = 50 Hz). – MS (70 eV); *m/z* (%): 424 (31) (M^+), 423 (15), 380 (19), 379 (100) (M^+ – C_2H_5O), 310 (32) (M^+ – $NC_6H_{12}O$), 226 (21), 225 (100) (M^+ – $Ph_2P \cdot BH_3$), 185 (23) (PH_2P^+), 183 (21), 181 (11) (M^+ – $Ph_2P \cdot BH_3$ – C_2H_4O), 179 (6), 141 (8), 126 (12), 123 (12), 114 (18) ($NC_6H_{12}O^+$), 109 (8), 108 (8) ($PhPH^+$), 84 (13) ($C_5H_{10}N^+$), 70 (48) ($C_4H_8N^+$), 55 (21). – $C_{25}H_{38}BN_2OP$ (424.37): calcd. C 70.76, H 9.03, N 6.60; found C 70.49, H 9.32, N 6.63.

(+)-(2S,2'R)-1-[(2'-Boranatodiphenylphosphanyl)dec-1'-ylideneamino]-2-methoxymethylpyrrolidine [(*S,R*)-**11h**]: a) 2.68 g (10 mmol) hydrazone (*S*)-**9h** was reacted with 3.05 g (13 mmol) $ClPPh_2$ BH_3 according to *GP 5*, yielding 1.77 g (38%) of (*S,R*)-**11h** as a colourless oil.

b) 2.68 g (10 mmol) hydrazone (*S*)-**9h** was rected with 2.87 g (13 mmol) $ClPPh_2$ and 1.3 ml (13 mmol) $BH_3 \cdot SMe_2$ according to *GP 6*, yielding 3.08 g (66%) of (*S,R*)-**11h** as a colourless oil. After crystallization of the (*Z*)-configured major diastereomer, 2.01 g (45%) of diastereomerically pure (*S,R*)-**11h** was isolated. – m.p. (*Z*) 66°C, $[\alpha]_D^{22} = +110.8$ (*c* = 1, $CHCl_3$) (*Z*, *de* = 98%). – IR (neat): $\tilde{\nu}$ 3078, 3058 (m, C–$H_{arom.}$), 2926, 2855 (s, CH_2, CH_3), 2385 (s, B–H), 2350 (sh), 1588 (C=N), 1482, 1462 (m), 1437 (s, P–Ph), 1196 (m), 1108 (s, P–Ph), 1062, 739, 696 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*Z*): δ = 0.86 (t, *J* = 6.9 Hz, 3H, CH_3), 1.08–2.05 (m, 18H, CH_2), 2.69 (m, 1H, NC*H*H), 2.77, 2.99 (m, 1H, CH_2O), 3.20 (m, 1H, NCH*H*), 3.28 (s, 3H, OCH_3), 3.37 (m, 1H, NCH), 4.00 (m, 1H, CHP), 6.79 (dd, *J* = 9.6 Hz, *J* = 4.1 Hz, 1H, HC=N), 7.35–7.56 (m, 6H, $H_{meta,para}$), 7.68–7.86 (m, 4H, H_{ortho}). – ^1H NMR (300 MHz, $CDCl_3$, TMS) (*E*): δ = 0.86 (t, ^3J = 6.7 Hz, 3H, CH_3), 1.14–1.92 (m, 18H, CH_2), 2.47 (m, 1H, NC*H*H), 3.03 (m, 1H, CHP), 3.19–3.51 (m, 4H, CH_2O, NCH*H*, NCH), 3.28 (s, 3H, OCH_3), 6.35 (dd, *J* = 7.9 Hz, *J* = 3.5 Hz, 1H, HC=N), 7.31–7.50 (m, 6H, $H_{meta,para}$), 7.70–7.84 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS) (*Z*): δ = 14.08 (s, CH_3), 22.60 (s, CH_2), 23.25 (s, $NCH_2CH_2CH_2$), 27.23 (s, $NCH_2CH_2CH_2$), 28.55, 28.68, 29.12, 29.18, 29.54, 31.74 (CH_2), 36.75 (d, $^1J_{CP}$ = 31 Hz, CHP), 55.53 (s, NCH_2), 59.02 (s, OCH_3), 66.85 (s, NCH), 75.84 (s, CH_2O), 128.43, 128.84 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.26, 131.45 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.77, 133.11 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}), 148.15 (s, C=N). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS) (*E*): δ = 14.85 (s, CH_3), 22.20, 22.63 (s, CH_2, $NCH_2CH_2CH_2$), 26.32 (s, $NCH_2CH_2CH_2$), 27.72 (d, $^2J_{CP}$ = 3 Hz, CH_2), 28.08 (d, $^3J_{CP}$ = 12 Hz, CH_2), 29.04, 29.18, 29.30, 31.81 (CH_2), 40.01 (d, $^1J_{CP}$ = 35 Hz, CHP), 50.12 (s, NCH_2), 59.17 (s, OCH_3), 63.54 (s, NCH), 74.52 (s, CH_2O), 128.14, 128.77 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 130.86, 131.18 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.45 (s, C=N), 132.66, 133.23 (d, $^2J_{CP}$ = 8 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4) (*Z*): δ = 23.1 (s, br.). – MS (70 eV); *m/z* (%): 466 (51) (M^+), 465 (21), 422 (28), 421 (94) (M^+ – C_2H_5O), 352 (29) (M^+ – $NC_6H_{12}O$), 267 (100) (M^+ – $Ph_2P \cdot BH_3$), 226 (8), 223 (15) (M^+ – $Ph_2P \cdot BH_3$ – C_2H_4O), 185 (36) (Ph_2P^+), 183 (31), 154 (10), 141 (18), 126 (23), 123 (17), 114 (32) ($NC_6H_{12}O^+$), 109 (13), 108 (18) ($PhPH^+$), 84 (28) ($C_5H_{10}N^+$), 70 (94) ($C_4H_8N^+$), 55 (38). – $C_{28}H_{44}BN_2OP$ (466.45): calcd. C 72.10, H 9.51, N 6.01; found C 71.70, H 9.83, N 6.50.

(S)-1-(tert-Butyldimethylsilyloxy)-2-(methylsulfonyl)propane [(*S*)-**15**]: To a solution of 2.28 g (30 mmol) (*S*)-1,2-propanol in 30 ml DMF were added 4.08 g (60 mmol) imidazole and 4.76 g (31.5 mmol) *tert*-butyldimethylsilyl chloride at 0°C. After stirring for 20 h at room temperature the reaction mixture was quenched with NH_4Cl solution, extracted with ether, dried ($MgSO_4$) and concentrated in vaco. To a solution of the product in 30 ml CH_2Cl_2 were added 3.75 g (33 mmol) mesyl chloride and 6.06 g (60 mmol) triethylamine at 0°C. After warming to room temperature overnight, the reation mixture was quenched with NH_4Cl solution, extracted with ether, dried ($MgSO_4$) and concentrated in vacuo. Upon column chromatography (SiO_2, ether/*n*-pentane, 1:10) 4.66 g (58%) of (*S*)-**15** was isolated as a colourless liquid. – $[\alpha]_D^{22} = +5.2$ (*c* = 1.1, $CHCl_3$). – IR (neat): $\tilde{\nu}$ 3027 (m, C–$H_{arom.}$), 2955, 2932, 2886, 2858 (s, CH_3), 1473, 1464 (m), 1358, 1256, 1179, 1109 (s), 839, 780 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.08, 0.09 (s, 3H, $SiCH_3$), 0.91 (s, 9H, *t*Bu), 1.37 (d, *J* = 6.3 Hz, 3H, H_3CCHOS), 3.03 (s, 3H, H_3CS), 3.68 (m, 2H, CH_2O), 4.74 (m, 1H, CH_3CHOS). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = –5.49, –5.42 ($SiCH_3$), 17.62 (H_3CCHOS), 25.84 (*t*Bu), 38.35 (H_3CS), 66.00 (H_2COSi), 80.48 (H_3CCHOS). – MS (70 eV); *m/z* (%): 155 (8), 153 (100) (M^+ – *t*BuMe_2Si), 89 (9), 75 (22), 73 (18), 59 (10), 41 (10). – $C_{10}H_{24}O_4SSi$ (268.35): calcd. C 44.74, H 9.01; found C 44.75, H 9.20.

(R)-2-Boranatodiphenylphosphanyl-1-(tert-butyldimethylsilyloxy)propane [(*R*)-**16**]: To a solution of 268 mg (1 mmol) mesylated diol (*S*)-**15** in 5 ml THF, was added 1.5 mmol $KPPh_2$ in THF (0.5 mmol/ml) at 0°C. After stirring at room temperature for 1 h, 0.2 ml (2 mmol) $BH_3 \cdot SMe_2$ was added at 0°C. After 10 min., the reaction mixture was quenched with NH_4Cl solution, extracted with ether, dried ($MgSO_4$) and concentrated in vacuo. Upon column chromatography (SiO_2, ether/*n*-pentane, 1:10), 290 mg (79%)

of (*R*)-**16** was isolated as colourless crystals. – m.p. 69 °C, $[\alpha]_D^{22}$ = −1.7 (*c* = 1.0, $CHCl_3$). – IR (neat): ṽ 3060 (m, C−$H_{arom.}$), 2952, 2928, 2879, 2856 (s, CH_3, CH_2), 1485, 1470 (m), 1438 (s, P−Ph), 1389 (m), 1107 (s), 1093, 1071 (s), 1014 (m), 837, 784, 742, 693 (s). – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.04, 0.07 (s, 3H, $SiCH_3$), 0.81 (s, 9H, *t*Bu), 1.16 (dd, $^3J_{HP}$ = 16.1 Hz, *J* = 7.0 Hz, 3H, CH_3CHP), 2.80 (m, 1H, CH_3CHP), 3.69−3.88 (m, 2H, CH_2O), 7.44−7.57 (m, 6H, $H_{meta,para}$), 7.75−7.91 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = −5.51 ($SiCH_3$), 11.99 (CH_3CHP), 25.81 (*t*Bu), 31.98 (d, $^1J_{CP}$ = 35 Hz, CHP), 63.81 (d, $^2J_{CP}$ = 9 Hz, CH_2OSi), 128.60 (d, $^1J_{CP}$ = 54 Hz, C_{ipso}), 128.69 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.06, 131.09 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.53, 132.59 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – MS (70 eV); *m/z* (%): 372 (M^+), 359 (16), 315 (44) (M^+ − *t*Bu), 301 (15) (M^+ − *t*Bu − BH_3), 256 (14), 255 (89), 254 (21), 187 (19), 186 (100) (Ph_2P^+), 185 (56), 173 (17), 151 (11), 150 (33), 135 (25), 117 (17), 115 (12), 109 (37), 108 (50) (PhP^+), 107 (19), 89 (11), 87 (15), 75 (23), 73 (73), 71 (12), 59 (34), 57 (24), 55 (13), 43 (16), 41 (21). – $C_{21}H_{34}$BOPSi (372.37): calcd. C 67.74, H 9.20; found C 67.70, H 9.31.

(−)-(R)-2-Boranatodiisopropylphosphanyl-1-propanol [(*R*)-**12a**]: 300 mg (1 mmol) hydrazone (*S,R*)-**11a** was ozonolysed and reduced according to *GP 9*. For the separation of the SMP-nitrosamine, the crude product was reacted with 468 mg (2 mmol) (*S*)-MTPA-Cl and 360 mg (3 mmol) DMAP. After flash chromatography (SiO_2, ether/*n*-pentane, 1:10), the MTPA-ester was dissolved in 5 ml MeOH and treated with 276 mg (2 mmol) K_2CO_3, yielding after chromatography (SiO_2, ether/*n*-pentane, 1:2) 137 mg (72%) of (*R*)-**12a** as a colourless oil. – $[\alpha]_D^{22}$ = −2.7 (*c* = 1.0, $CHCl_3$). – IR (neat): ṽ 3456 (s, br., OH), 2965, 2937, 2877 (s, CH_2, CH_3), 2373 (s, B−H), 1257, 1142 (m), 1068 (s, C−O), 1024 (s), 885, 756 (m), 691 (s), 651 (m) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = ca. 0.4 (q, br., *J* = 90 Hz, 3H, BH_3), 1.17−1.31 [m, 15H, CH_3CHP, PCH(CH_3)$_2$], 2.04−2.26 [m, 3H, CH_3CHP, PC*H*(CH_3)$_2$], 3.75 (ddd, *J* = 13.6 Hz, *J* = 13.0 Hz, *J* = 5.1 Hz, C*H*HOH), 3.90 (ddd, *J* = 14.0 Hz, *J* = 13.6 Hz, *J* = 5.9 Hz, CH*H*OH). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 12.89 (d, $^2J_{CP}$ = 4 Hz, CH_3), 17.36, 17.54 [d, $^2J_{CP}$ = 3 Hz, (CH_3)$_2$CHP], 20.35, 21.82 [d, $^1J_{CP}$ = 32 Hz, (CH_3)$_2$*C*HP], 29.00 (d, $^1J_{CP}$ = 28 Hz, CH_3CHP), 64.78 (d, $^2J_{CP}$ = 2 Hz, CH_2). – MS (70 eV); *m/z* (%): 190 (2) (M^+), 189 (4) (M^+ − H), 177 (12), 176 (100) (M^+ − BH_3), 146 (8), 145 (20) (*i*Pr_2PCHCH$_3$), 134 (20) (*i*Pr_2POH$^+$), 119 (9), 118 (68) (*i*Pr_2P^+), 117 (10), 104 (14), 92 (25), 89 (9), 76 (26), 75 (22), 74 (13), 69 (9), 61 (11). – C_9H_{24}BOP (190.07): calcd. C 56.87, H 12.73; found C 57.01, H 12.39.

(−)-(R)-2-Boranatodiphenylphosphanyl-1-propanol [(*R*)-**12b**]: a) 368 mg (1 mmol) hydrazone (*S,R*)-**11b** was ozonolyzed and reduced according to *GP 9*. For the separation of the SMP-nitrosamine, the crude product was reacted with 468 mg (2 mmol) (*S*)-MTPA-Cl and 360 mg (3 mmol) DMAP. After flash chromatography (SiO_2, ether/*n*-pentane, 1:10), the MTPA ester was dissolved in 5 ml MeOH and treated with 276 mg (2 mmol) K_2CO_3, yielding after chromatography (SiO_2, ether/*n*-pentane, 1:3) 188 mg (73%) of (*R*)-**12b** as colourless crystals. – $[\alpha]_D^{22}$ = −34.4 (*c* = 1.0, $CHCl_3$).

b) 424 mg (1 mmol) hydrazone (*S,R*)-**11c** was ozonolysed and reduced according to *GP 9*, yielding 175 mg (68%) of (*R*)-**12b** as colourless crystals. – $[\alpha]_D^{22}$ = −31.2 (*c* = 1.0, $CHCl_3$).

c) To a solution of 186 mg (0.5 mmol) (*R*)-1-(*tert*-butyldimethylsilyl)-2-boranatodiphenylphosphanylpropane (*R*)-**16** in 1 ml THF, was added 1.5 ml (1.5 mmol) tetrabutylammonium fluoride solution at room temperature and the mixture was stirred for 1 h (TLC-control). It was then quenched with aq. NH_4Cl at 0 °C, extracted with ether, dried ($MgSO_4$), filtered and evaporated, yielding 106 mg (82%) of (*R*)-**12b** after chromatography as colourless crystals. – m.p. 67−68 °C, $[\alpha]_D^{22}$ = −33.8 (*c* = 1.0, $CHCl_3$). – IR (KBr): ṽ 3512 (s, OH), 3435 (s, br., OH), 3083, 3058, 3033 (m, C−$H_{arom.}$), 2971, 2955, 2932, 2917, 2886 (s, CH_2, CH_3), 2382 (s, B−H), 2343 (sh), 2113, 1971, 1902, 1890, 1828, 1779, 1763, 1664, 1589, 1575 (m), 1482 (m), 1437 (s, P−Ph), 1396, 1379, 1317 (s), 1279, 1253, 1206, 1186, 1120 (s), 1040 (s, C−O), 960, 740, 690 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = ca. 1.0 (q, br., *J* = 90 Hz, 3H, BH_3), 1.18 (dd, $^3J_{HP}$ = 15.6 Hz, ^3J = 7.1 Hz, 3H, CH_3), 2.01 (s, br., 1H, OH), 2.84 (m, 1H, CH_3CHP), 3.78 (m, 2H, CH_2), 7.40−7.52 (m, 6H, $H_{meta,para}$), 7.69−7.82 (m, 4h, H_{ortho}). – ^{13}C NMR (75 MHz, C_6D_6, TMS): δ = 11.92 (d, $^2J_{CP}$ = 1 Hz, CH_3), 31.74 (d, $^1J_{CP}$ = 35 Hz, CH_3CHP), 63.55 (d, $^2J_{CP}$ = 6 Hz, CH_2), 128.11 (d, $^1J_{CP}$ = 55 Hz, C_{ipso}), 128.83, 128.93 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.37 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.40, 132.69 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = 18.9 (q, $^1J_{PB}$ = 67 Hz). – MS (70 eV); *m/z* (%): 258 (1) (M^+), 257 (7) (M^+ − H), 244 (100) (M^+ − BH_3), 213 (11) (Ph_2P−$C_2H_4^+$), 202 (27), 186 (34) (Ph_2PH^+), 185 (24) (Ph_2P^+), 183 (53), 155 (10), 152 (7) ($Ph_2PCHCH_2OH^+$), 136 (5) ($PhPCHCH_3^+$), 109 (27), 108 (49) (PhP^+), 89 (6). – $C_{15}H_{20}$BOP (258.11): calcd. C 69.80, H 7.81; found C 69.80, H 8.02.

(−)-(R)-2-Boranatodiphenylphosphanyl-1-butanol [(*R*)-**12c**]: 382 mg (1 mmol) hydrazone (*S,R*)-**11d** was ozonolyzed and reduced according to *GP 9*, yielding 182 mg (67%) of (*R*)-**12c** as a colourless oil. – $[\alpha]_D^{22}$ = −29.4 (*c* = 1, $CHCl_3$). – IR ($CHCl_3$): ṽ 3513 (s, br., OH), 3078, 3058, 3006 (m, C−$H_{arom.}$), 2965, 2933, 2877 (s, CH_2, CH_3), 2384 (s, B−H), 2350 (sh), 1484, 1461 (m, C−$C_{arom.}$), 1437 (s, P−Ph), 1333, 1312 (m), 1106 (s, P−Ph), 1065 (s, C−O), 1046, 1030 (s), 740, 697 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.00 (t, *J* = 7.4 Hz, 3H, CH_3), ca. 1.1 (q, br., *J* = 90 Hz, 3H, BH_3), 1.46 (m, 1H, CH_3CHH), 1.71 (m, 1H, CH_3CHH), 2.16 (s, br., 1H, OH), 2.55 (m, 1H, CH_3CH_2CHP), 3.84 (m, 1H, C*H*HO), 3.93 (ddd, *J* = 11.5 Hz, *J* = 11.5 Hz, *J* = 5.1 Hz, 1H, CH*H*O), 7.43−7.54 (m, 6H, $H_{meta,para}$), 7.69−7.82 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 12.71 (d, $^3J_{CP}$ = 11 Hz, CH_3), 19.08 (d, $^2J_{CP}$ = 2 Hz, CH_3CH_2), 38.40 (d, $^1J_{CP}$ = 35 Hz, CH_3CHP), 59.88 (d, $^2J_{CP}$ = 3 Hz, CH_2), 127.87 (d, $^1J_{CP}$ = 55 Hz, C_{ipso}), 128.83, 128.96 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.39 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.40, 132.72 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = 18.5 (1, $^1J_{PB}$ = 67 Hz). – MS (70 eV); *m/z* (%): 272 (2) (M^+), 271 (9) (M^+ − H), 259 (20), 258 (100) (M^+ − BH_3), 213 (11) (Ph_2P−$C_2H_4^+$), 202 (14), 186 (33) (Ph_2PH^+), 185 (23) (Ph_2P^+), 183 (24), 154 (7), 136 (6), 109 (22) ($PhPH^+$), 108 (55) (PhP^+), 107 (15), 89 (8), 55 (10), 51 (6). – $C_{16}H_{21}$BOP (M^+ − H): calcd. 271.1423; found 271.1426 (MS).

(−)-(R)-2-Boranatodiphenylphosphanyl-1-pentanol [(*R*)-**12d**]: 396 mg (1 mmol) hydrazone (*S,R*)-**11e** was ozonolysed and reduced according to *GP 9*, yielding 215 mg (75%) of (*R*)-**12d** as a colourless oil. – $[\alpha]_D^{22}$ = −45.0 (*c* = 1, $CHCl_3$). – IR (neat): ṽ 3514 (s, br., OH), 3078, 3058, 3006 (m, C−$H_{arom.}$), 2959, 2932, 2872 (s, CH_2, CH_3), 2383 (s, B−H), 2350 (sh), 1483, 1464 (m, C−$C_{arom.}$), 1437 (s, P−Ph), 1382, 1336, 1314 (m), 1106 (s, P−Ph), 1064 (s, C−O), 1039, 1030 (s), 740, 696 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.85 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.29 (m, 2H, CH_3CH_2), 1.57, 1.73 (m, 1H, $CH_3CH_2CH_2$), 2.14 (s, br., 1H, OH), 2.64 (m, 1H, CH_3CHP), 3.84 (m, 2H, CH_2O), 7.41−7.54 (m, 6H, $H_{meta,para}$), 7.70−7.83 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 13.89 (s, CH_3), 21.11 (d, $^3J_{CP}$ = 10 Hz, CH_3CH_2), 27.77 (s, $CH_3CH_2CH_2$), 36.51 (d, $^1J_{CP}$ = 34 Hz, CHP), 60.35 (d, $^2J_{CP}$ = 3 Hz, CH_2), 127.87 (d, $^1J_{CP}$ = 56 Hz, C_{ipso}), 128.83, 128.96 (d, $^3J_{CP}$ = 9 Hz, C_{meta}), 131.38 (d, $^4J_{CP}$ = 2 Hz, C_{para}), 132.41, 132.74 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = 18.6 (q, $^1J_{PB}$ = 64 Hz). – MS (70 eV);

m/z (%): 286 (3) (M^+), 285 (10) ($M^+ - H$), 273 (20), 272 (100) ($M^+ - BH_3$), 230 (37) ($Ph_2P-C_2H_4OH^+$), 214 (11), 212 (46) ($Ph_2P-C_2H_4^+$), 202 (6), 187 (10), 186 (54) (Ph_2PH^+), 185 (20) (Ph_2P^+), 183 (42), 154 (7), 152 (10), 136 (6), 110 (8), 109 (24), 108 (65) (PhP^+), 107 (29), 89 (8), 55 (6), 51 (6). – $C_{17}H_{24}BOP$ (286.16): calcd. C 71.35, H 8.45; found C 71.36, H 8.79.

(+)-(S)-2-Boranatodiphenylphosphanyl-1-pentanol [(*S*)-**12d**]: a) 396 mg (1 mmol) hydrazone (*R,S*)-**11e** was ozonolysed and reduced according to *GP 9*, yielding 206 mg (72%) of (*S*)-**12d** as a colourless oil. – $[\alpha]_D^{22} = +46.1$ ($c = 1$, $CHCl_3$).

b) 396 mg (1 mmol) hydrazone (*S,S*)-**11e** was ozonolysed and reduced according to *GP 9*, yielding 197 mg (69%) of (*S*)-**12d** as a colourless oil. – $[\alpha]_D^{22} = +46.5$ ($c = 1$, $CHCl_3$). The other analytical data corresponded with those of (*R*)-**12d**.

(−)-(R)-2-Boranatodiphenylphosphanyl-1-hexanol [(*R*)-**12e**]: 410 mg (1 mmol) hydrazone (*S,R*)-**11f** was ozonolysed and reduced according to *GP 9*, yielding 231 mg (77%) of (*R*)-**12e** as a colourless oil. – $[\alpha]_D^{22} = -46.7$ ($c = 1$, $CHCl_3$). – IR ($CHCl_3$): ṽ 3513 (s, br., OH), 3078, 3058, 3007 (m, C–$H_{arom.}$), 2957, 2932, 2871 (s, CH_2, CH_3), 2384 (s, B–H), 2350 (sh), 1483, 1466 (m, C–$C_{arom.}$), 1437 (s, P–Ph), 1380, 1335, 1313 (m), 1107 (s, P–Ph), 1064 (s, C–O), 1030 (s), 757, 741, 696 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.81 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.29–1.82 (m, 6H, 3 CH_2), 2.15 (s, br., 1H, OH), 2.62 (m, 1H, CH_3CHP), 3.82 (m, 1H, C*H*HO), 3.91 (ddd, J = 12.3 Hz, J = 12.1 Hz, J = 5.2 Hz, 1H, CH*H*O), 7.41–7.54 (m, 6H, $H_{meta,para}$), 7.70–7.83 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 13.83 (s, CH_3), 22.50 (s, CH_3CH_2), 25.33 (d, $^2J_{CP}$ = 2 Hz, CH_2), 30.12 (d, $^3J_{CP}$ = 10 Hz, CH_2), 36.71 (d, $^1J_{CP}$ = 34 Hz, CHP), 60.30 (d, $^2J_{CP}$ = 3 Hz, CH_2), 127.87 (d, $^1J_{CP}$ = 54 Hz, C_{ipso}), 128.82, 128.95 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.36, 131.40 (d, $^4J_{CP}$ = 3 Hz, C_{para}), 132.39, 132.73 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = 18.6 (q, $^1J_{PB}$ = 66 Hz). – MS (70 eV); *m/z* (%): 300 (3) (M^+), 299 (10) ($M^+ - H$), 287 (21), 286 (100) ($M^+ - BH_3$), 230 (27) ($Ph_2P-C_2H_4OH^+$), 214 (11), 213 (46) ($Ph_2P-C_2H_4^+$), 187 (21), 186 (88) (Ph_2PH^+), 185 (27) (Ph_2P^+), 183 (42), 152 (7), 110 (8), 109 (21), 108 (39) (PhP^+), 107 (17), 89 (5), 55 (16), 43 (11), 41 (17). – $C_{18}H_{25}BOP$ ($M^+ - H$): calcd. 299.1736; found 299.1734 (MS).

(−)-(R)-2-Boranatodiphenylphosphanyl-1-heptanol [(*R*)-**12f**]: 424 mg (1 mmol) hydrazone (*S,R*)-**11g** was ozonolysed and reduced according to *GP 9*, yielding 236 mg (75%) of (*R*)-**12f** as a colourless oil. – $[\alpha]_D^{22} = -41.7$ ($c = 1$, $CHCl_3$). – IR ($CHCl_3$): ṽ 3507 (s, br., OH), 3079, 3060, 3008 (m, C–$H_{arom.}$), 2956, 2930, 2860 (s, CH_2, CH_3), 2384 (s, B–H), 2350 (sh), 1484 (m, C–$C_{arom.}$), 1438 (s, P–Ph), 1107 (s, P–Ph), 1064 (s, C–O), 1030 (m), 757, 696 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.82 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.10–1.80 (m, 8H, 4 CH_2), 2.22 (s, br., 1H, OH), 2.63 (m, 1H, CH_3CHP), 3.80 (m, 1H, C*H*HO), 3.91 (ddd, J = 12.3 Hz, J = 12.1 Hz, J = 5.2 Hz, 1H, CH*H*O), 7.41–7.54 (m, 6H, $H_{meta,para}$), 7.70–7.83 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 13.93 (s, CH_3), 22.37 (s, CH_3CH_2), 25.66 (d, $^2J_{CP}$ = 2 Hz, CH_2), 27.64 (d, $^3J_{CP}$ = 10 Hz, CH_2), 31.53 (s, CH_2), 36.74 (d, $^1J_{CP}$ = 33 Hz, CHP), 60.41 (d, $^2J_{CP}$ = 3 Hz, CH_2), 127.88 (d, $^1J_{CP}$ = 56 Hz, C_{ipso}), 128.79, 128.93 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.34, 131.37 (d, $^4J_{CP}$ = 3 Hz, C_{para}), 132.39, 132.71 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = 18.6 (q, $^1J_{PB}$ = 68 Hz). – MS (70 eV); *m/z* (%): 314 (3) (M^+), 313 (8) ($M^+ - H$), 301 (15), 300 (67) ($M^+ - BH_3$), 243 (11), 230 (18) ($Ph_2P-C_2H_4OH^+$), 214 (7), 213 (30) ($Ph_2P-C_2H_4^+$), 187 (22), 186 (100) (PH_2PH^+), 185 (21) (Ph_2P^+), 183 (24), 152 (5), 110 (6), 109 (20), 108 (54) (PhP^+), 107 (18), 91 (7), 55 (13), 43 (7), 41 (13). – $C_{19}H_{28}OBP$ (314.21): calcd. C 72.63, H 8.98; found C 72.80, H 8.82.

(−)-(R)-2-Boranatodiphenylphosphanyl-1-decanol [(*R*)-**12g**]: 466 mg (1 mmol) hydrazone (*S,R*)-**11h** was ozonolysed and reduced according to *GP 9*, yielding 295 mg (83%) of (*R*)-**12b** as a colourless oil. – $[\alpha]_D^{22} = -37.1$ ($c = 1$, $CHCl_3$). – IR (neat): $[\alpha]_D^{22} = 3512$ (s, br., OH), 3078, 3059, 3007 (m, C–$H_{arom.}$), 2953, 2926, 2855 (s, CH_2, CH_3), 2384 (s, B–H), 2350 (sh), 1483, 1465 (m, C–$C_{arom.}$), 1437 (s, P–Ph), 1206 (m), 1107 (s, P–Ph), 1064 (s, C–O), 1029 (m), 758, 695 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.86 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.10–1.80 (m, 14H, 4 CH_2), 2.15 (s, br., 1H, OH), 2.62 (m, 1H, CH_3CHP), 3.83 (m, 1H, C*H*HO), 3.91 (ddd, J = 12.5 Hz, J = 12.3 Hz, J = 5.3 Hz, 1H, CH*H*O), 7.41–7.54 (m, 6H, $H_{meta,para}$), 7.70–7.83 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 14.09 (s, CH_3), 22.63, 29.16, 29.30, 29.35, 31.80 (s, CH_2), 25.62 (d, $^2J_{CP}$ = 1 Hz, CH_2), 27.95 (d, $^3J_{CP}$ = 10 Hz, CH_2), 36.75 (d, $^1J_{CP}$ = 34 Hz, CHP), 60.38 (d, $^2J_{CP}$ = 3 Hz, CH_2), 127.86 (d, $^1J_{CP}$ = 55 Hz, C_{ipso}), 128.82, 128.95 (d, $^3J_{CP}$ = 10 Hz, C_{meta}), 131.36, 131.39 (d, $^4J_{CP}$ = 3 Hz, C_{para}), 132.40, 132.70 (d, $^2J_{CP}$ = 9 Hz, C_{ortho}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = 18.6 (q, $^1J_{PB}$ = 70 Hz). – MS (70 eV); *m/z* (%): 356 (3) (M^+), 355 (7) ($M^+ - H$), 343 (13), 342 (52) ($M^+ - BH_3$), 243 (8), 230 (14) ($Ph_2P-C_2H_4OH^+$), 214 (5), 213 (20) ($Ph_2P-C_2H_4^+$), 187 (19), 186 (100) (Ph_2PH^+), 185 (18) (Ph_2P^+), 183 (23), 109 (11), 108 (34) (PhP^+), 107 (8), 55 (7), 43 (6), 41 (7). – $C_{22}H_{34}BOP$ (356.29): calcd. C 74.16, H 9.62; found C 73.85, H 9.93.

(−)-(R)-2-Diphenylphosphanyl-1-propanol [(*R*)-**13b**]: 129 mg (0.5 mmol) borane-protected alcohol (*R*)-**12b** was reacted with 280 mg (2.5 mmol) DABCO according to *GP 10*, yielding 104 mg (85%) of (*R*)-**13b** as a colourless oil. – $[\alpha]_D^{22} = -7.9$ ($c = 2.2$, CH_2Cl_2). – IR ($CHCl_3$): ṽ 3350 (s, br., OH), 3065, 3045 (m, C–$H_{arom.}$), 2950, 2920, 2860 (s, CH_2, CH_3), 1570 (m), 1475 (s), 1430 (s, P–Ph), 1175 (m), 1090 (s), 1028 (s, br., C–O), 740, 693 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.10 8dd, $^3J_{HP}$ = 13.7 Hz, ^3J = 6.9 Hz, 3H, CH_3), 2.12 (s, br., 1H, OH), 2.58 (m, 1H, CH_3CHP), 3.53 (dm, J = 11 Hz, 1H, C*H*H), 3.71 (ddd, J = 11 Hz, J = 8.5 Hz, J = 4.5 Hz, 1H, CH*H*), 7.32 (m, 6H, $H_{meta,para}$), 7.49 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 14.21 (d, $^2J_{CP}$ = 15 Hz, CH_3), 33.84 (d, $^1J_{CP}$ = 11 Hz, CH_3CHP), 65.55 (d, $^2J_{CP}$ = 23 Hz, CH_2), 128.40, 128.49 (d, $^3J_{CP}$ = 7 Hz, C_{meta}), 128.89 (d, $^4J_{CP}$ = 6 Hz, C_{para}), 133.33, 133.83 (d, $^2J_{CP}$ = 20 Hz, C_{ortho}), 135.96, 136.58 (d, $^1J_{CP}$ = 13 Hz, C_{ipso}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = −9.9 (s). – MS (70 eV); *m/z* (%): 244 (100) (M^+), 230 (5) ($M^+ - CH_2$), 213 (19) ($Ph_2PC_2H_4^+$), 202 (33) (Ph_2POH^+), 201 (10), 186 (39) (Ph_2PH^+), 185 (19) (Ph_2P^+), 183 (39), 155 (13), 152 (5) ($Ph_2PCHCH_2OH^+$), 133 (6) ($PhPCHCH_3^+$), 125 (7), 109 (50), 108 (67) (PhP^+), 91 (8), 77 (8), 65 (6), 51 (7), 43 (20), 41 (6). – $C_{15}H_{17}OP$: calcd. 244.1017; found 244.1015 (MS).

(+)-(R)-2-Diphenylphosphanyl-1-butanol [(*R*)-**13c**]: 136 mg (0.5 mmol) borane-protected alcohol (*R*)-**12c** was reacted with 280 mg (2.5 mmol) DABCO according to *GP 10*, yielding 110 mg (85%) of (*R*)-**13c** as a colourless oil. – $[\alpha]_D^{22} = +4.0$ ($c = 2.0$, CH_2Cl_2). – IR ($CHCl_3$): ṽ 3392 (s, br., OH), 3072, 3055, 3012 (m, C–$H_{arom.}$), 2963, 2930, 2875 (s, CH_2, CH_3), 1480 (m), 1461 (m), 1434 (s, P–Ph), 1217, 1093, 1027 (s, br., C–O), 749, 698 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.02 (t, ^3J = 7.3 Hz, 3H, CH_3), 1.54 (m, 2H, CH_3CH_2), 2.39 (s, br., 1H, OH), 2.39 (m, 1H, CH_3CH_2CHP), 3.63 (ddd, J = 11.6 Hz, J = 8.5 Hz, J = 5.5 Hz, 1H, C*H*HO), 3.77 (ddd, J = 11.6 Hz, J = 11.5 Hz, J = 4.6 Hz, 1H, CH*H*O), 7.28–7.36 (m, 6H, $H_{meta,para}$), 7.45–7.55 (m, 4H,

H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 12.21 (d, $^3J_{CP}$ = 10 Hz, CH_3), 21.18 (d, $^2J_{CP}$ = 16 Hz, CH_3CH_2), 40.70 (d, $^1J_{CP}$ = 12 Hz, CH_3CHP), 62.14 (d, $^2J_{CP}$ = 16 Hz, CH_2), 128.40, 128.49 (d, $^3J_{CP}$ = 4 Hz, C_{meta}), 128.87 (d, $^4J_{CP}$ = 7 Hz, C_{para}), 133.56, 133.60 (d, $^2J_{CP}$ = 20 Hz, C_{ortho}), 136.12, 136.51 (d, $^1J_{CP}$ = 13 Hz, C_{ipso}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = −13.2 (s). – MS (70 eV); *m/z* (%): 259 (15), 258 (98) (M^+), 230 (8) ($M^+ - C_2H_4$), 213 (41) ($Ph_2P-C_2H_4^+$), 202 (29), 201 (10), 186 (57) (Ph_2PH^+), 185 (26) (Ph_2P^+), 183 (65), 155 (13), 154 (12), 133 (9), 125 (9), 109 (32) ($PhPH^+$), 108 (100) (PhP^+), 107 (32), 91 (9), 77 (9), 55 (6), 47 (12). – $C_{16}H_{19}OP$: calcd. 258.1174; found 258.1170 (MS).

(−)-(R)-2-Diphenylphosphanyl-1-pentanol [(*R*)-**13d**]: 143 mg (0.5 mmol) borane-protected alcohol (*R*)-**12d** was reacted with 280 mg (2.5 mmol) DABCO according to *GP 10*, yielding 124 mg (91%) of (*R*)-**13d** as a colourless oil. – $[\alpha]_D^{22}$ = −9.2 (*c* = 2.0, CH_2Cl_2). – IR ($CHCl_3$): ṽ 3385 (s, br., OH), 3071, 3054, 3002 (m, $C-H_{arom.}$), 2957, 2930, 2870 (s, CH_2, CH_3), 1480, 1465 (m), 1434 (s, P−Ph), 1217 (m), 1093 (m, P−Ph), 1028 (s, br., C−O), 698 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.85 (t, *J* = 7.0 Hz, 3H, CH_3), 1.30−1.60 (m, 4H, CH_2), 1.96 (s, br., 1H, OH), 2.46 (m, 1H, CH_2CHP), 3.58 (ddd, 1H, *J* = 11.5 Hz, *J* = 8.7 Hz, *J* = 5.8 Hz, $CHHO$), 3.74 (ddd, 1H, *J* = 11.5 Hz, *J* = 11.5 Hz, *J* = 4.4 Hz, $CHHO$), 7.26−7.35 (m, 6H, $H_{meta,para}$), 7.46−7.55 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 14.21 (s, CH_3), 20.86 (d, $^3J_{CP}$ = 10 Hz, CH_3CH_2), 30.52 (d, $^2J_{CP}$ = 15 Hz, CH_2), 38.83 (d, $^1J_{CP}$ = 12 Hz, CHP), 62.60 (d, $^2J_{CP}$ = 15 Hz, CH_2), 128.37, 128.42 (d, $^3J_{CP}$ = 7 Hz, C_{meta}), 128.80 (d, $^4J_{CP}$ = 6 Hz, C_{para}), 133.53, 133.57 (d, $^2J_{CP}$ = 19 Hz, C_{ortho}), 136.14, 136.51 (d, $^1J_{CP}$ = 13 Hz, C_{ipso}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = −12.3. – MS (70 eV); *m/z* (%): 273 (12), 272 (65) (M^+), 230 (41) ($M^+ - C_3H_6$), 229 (13), 213 (100) ($Ph_2P-C_2H_4^+$), 202 (10), 201 (6), 186 (48) (Ph_2PH^+), 185 (17) (Ph_2P^+), 183 (56), 155 (5), 152 (7), 133 (6), 125 (6), 109 (20) ($PhPH^+$), 108 (71) (PhP^+), 107 (25), 91 (7), 77 (5), 47 (7), 41 (12). – $C_{17}H_{21}OP$: calcd. 272.1330; found 272.1327 (MS).

(+)-(S)-2-Diphenylphosphanyl-1-pentanol [(*S*)-**13d**)]: 143 mg (0.5 mmol) borane-protected alcohol (*S*)-**12d** was reacted with 280 mg (2.5 mmol) DABCO according to *GP 10*, yielding 125 mg (92%) of (*S*)-**13d** as a colourless oil. – $[\alpha]_D^{22}$ = +9.4 (*c* = 2.2, CH_2Cl_2).

The other analytical data corresponded with those of (*R*)-**13d**.

(−)-(R)-2-Diphenylphosphanyl-1-hexanol [(*R*)-**13e**]: 150 mg (0.5 mmol) borane-protected alcohol (*R*)-**12e** was reacted with 280 mg (2.5 mmol) DABCO according to *GP 10*, yielding 130 mg (91%) of (*R*)-**13e** as a colourless oil. – $[\alpha]_D^{22}$ = −14.3 (*c* = 2.7, CH_2Cl_2). – IR ($CHCl_3$): ṽ 3375 (s, br., OH), 3070, 3053, 3015, 3000 (m, $C-H_{arom.}$), 2955, 2928, 2870, 2859 (s, CH_2, CH_3), 1480, 1466 (m), 1434 (s, P−Ph), 1379 (m), 1094 (m, P−Ph), 1028 (s, br., C−O), 1000 (s), 742, 698 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.84 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.20−1.60 (m, 6H, 3 CH_2), 1.90 (s, br., 1H, OH), 2.48 (m, 1H, CH_2CHP), 3.60 (ddd, *J* = 11.2 Hz, *J* = 8.7 Hz, *J* = 5.7 Hz, 1H, $CHHO$), 3.76 (ddd, *J* = 11.3 Hz, *J* = 11.3 Hz, *J* = 4.4 Hz, 1H, $CHHO$), 7.18−7.28 (m, 6H, $H_{meta,para}$), 7.37−7.47 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 13.95 (s, CH_3), 22.82 (s, CH_3CH_2), 28.00 (d, $^2J_{CP}$ = 15 Hz, CH_2), 29.88 (d, $^2J_{CP}$ = 10 Hz, CH_2), 39.90 (d, $^1J_{CP}$ = 11 Hz, CH_2CHP), 62.63 (d, $^2J_{CP}$ = 15 Hz, CH_2), 128.39, 128.45 (d, $^3J_{CP}$ = 7 Hz, C_{meta}), 128.83 (d, $^4J_{CP}$ = 7 Hz, C_{para}), 133.59 (d, $^2J_{CP}$ = 19 Hz, C_{ortho}), 136.19, 136.58 (d, $^1J_{CP}$ = 14 Hz, C_{ipso}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = −12.4 (s). – MS (70 eV); *m/z* (%): 287 (12), 286 (57) (M^+), 243 (21) ($M^+ - C_3H_7$), 229 (13) ($M^+ - C_4H_9$), 213 (86) ($Ph_2P-C_2H_4^+$), 202 (8), 201 (6), 186 (100) (Ph_2PH^+), 185 (19) (Ph_2P^+), 183 (54), 154 (6), 152 (7), 133 (6), 125 (6), 109 (20) ($PhPH^+$), 108 (82) (PhP^+), 107 (24), 91 (7), 77 (6), 47 (8), 41 (11). – $C_{18}H_{23}OP$: calcd. 286.14869; found 286.14865 (MS).

(−)-(R)-2-Diphenylphosphanyl-1-heptanol [(*R*)-**13f**]: 157 mg (0.5 mmol) borane-protected alcohol (*R*)-**12f** was reacted with 280 mg (2.5 mmol) DABCO according to *GP 10*, yielding 147 mg (86%) of (*R*)-**13f** as a colourless oil. – $[\alpha]_D^{22}$ = −12.8 (*c* = 1.1, $CHCl_3$). – IR ($CHCl_3$): ṽ 3400 (s, br., OH), 3078, 3051 (m, $C-H_{arom.}$), 2954, 2930, 2871, 2858 (s, CH_2, CH_3), 1480, 1467 (m), 1434 (s, P−Ph), 1380 (m), 1091 (m, P−Ph), 1030 (s, br., C−O), 741, 698 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.84 (t, ^3J = 7.4 Hz, 3H, CH_3), 1.15−1.60 (m, 8H, 4 CH_2), 1.70 (s, br., 1H, OH), 2.45 (m, 1H, CH_2CHP), 3.60 (ddd, *J* = 11.3 Hz, *J* = 8.8 Hz, *J* = 5.4 Hz, 1H, $CHHO$), 3.76 (ddd, *J* = 11.5 Hz, *J* = 11.3 Hz, *J* = 4.7 Hz, 1H, $CHHO$), 7.28−7.37 (m, 6H, $H_{meta,para}$), 7.46−7.55 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 14.02 (s, CH_3), 22.49, 31.92 (s, CH_2), 27.37 (d, $^3J_{CP}$ = 10 Hz, CH_2), 28.28 (d, $^2J_{CP}$ = 15 Hz, CH_2), 39.15 (d, $^1J_{CP}$ = 12 Hz, CHP), 62.67 (d, $^2J_{CP}$ = 15 Hz, CH_2), 128.40, 128.46 (d, $^3J_{CP}$ = 7 Hz, C_{meta}), 128.86 (d, $^4J_{CP}$ = 3 Hz, C_{para}), 133.56, 132.60 (d, $^2J_{CP}$ = 19 Hz, C_{ortho}), 136.13, 136.55 (d, $^1J_{CP}$ = 13 Hz, C_{ipso}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = −12.4 (s). – MS (70 eV); *m/z* (%): 301 (7), 300 (34) (M^+), 243 (25) ($M^+ - C_4H_9$), 230 (30) ($M^+ - C_5H_{10}$), 229 (9) ($M^+ - C_5H_{11}$), 213 (72) ($Ph_2P-C_2H_4^+$), 202 (7), 201 (6), 186 (100) (Ph_2PH^+), 185 (22) (Ph_2P^+), 183 (50), 152 (6), 133 (7), 109 (20) ($PhPH^+$), 108 (77) (PhP^+), 107 (16), 91 (7), 77 (6), 55 (11), 47 (8), 41 (16). – $C_{19}H_{25}OP$: calcd. 300.1643; found 300.1644 (MS).

(−)-(R)-2-Diphenylphosphanyl-1-decanol [(*R*)-**13g**]: 178 mg (0.5 mmol) borane-protected alcohol (*R*)-**12g** was reacted with 280 mg (2.5 mmol) DABCO according to *GP 10*, yielding 145 mg (85%) of (*R*)-**13g** as a colourless oil. – $[\alpha]_D^{22}$ = −12.2 (*c* = 2.0, CH_2Cl_2). – IR ($CHCl_3$): ṽ 3343 (s, br., OH), 3055 (m, $C-H_{arom.}$), 2954, 2925, 2854 (s, CH_2, CH_3), 1480, 1466 (m), 1436 (s, P−Ph), 1380 (m), 1176 (s), 1118 (s), 1028 (s, br., C−O), 746, 697 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.87 (t, *J* = 7.4 Hz, 3H, CH_3), 1.17−1.60 (m, 14H, 4 CH_2), 1.95 (s, br., 1H, OH), 2.45 (m, 1H, CH_2CHP), 3.58 (m, 1H, $CHHO$), 3.74 (ddd, *J* = 11.6 Hz, *J* = 11.3 Hz, *J* = 4.6 Hz, 1H, $CHHO$), 7.18−7.25 (m, 6H, $H_{meta,para}$), 7.35−7.47 (m, 4H, H_{ortho}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 14.13 (s, CH_3), 22.67, 29.25, 29.44, 29.76, 31.86 (s, CH_2), 27.69 (d, $^3J_{CP}$ = 10 Hz, CH_2), 28.30 (d, $^2J_{CP}$ = 15 Hz, CH_2), 39.14 (d, $^1J_{CP}$ = 12 Hz, CHP), 62.65 (d, $^2J_{CP}$ = 15 Hz, CH_2), 128.39, 128.45 (d, $^3J_{CP}$ = 7 Hz, C_{meta}), 128.83 (d, $^4J_{CP}$ = 6 Hz, C_{para}), 133.60, 133.62 (d, $^2J_{CP}$ = 19 Hz, C_{ortho}), 136.24, 136.62 (d, $^1J_{CP}$ = 13 Hz, C_{ipso}). – ^{31}P NMR (202 MHz, $CDCl_3$, H_3PO_4): δ = −12.4. – MS (70 eV); *m/z* (%): 343 (7), 342 (31) (M^+), 243 (21) ($M^+ - C_7H_{15}$), 230 (30) ($M^+ - C_8H_{16}$), 229 (9) ($M^+ - C_8H_{17}$), 213 (42) ($Ph_2P-C_2H_4^+$), 202 (14), 201 (9), 186 (100) (Ph_2PH^+), 185 (18) (Ph_2P^+), 183 (39), 109 (12) ($PhPH^+$), 108 (44) (PhP^+), 107 (11), 91 (8), 77 (5), 69 (6), 55 (9), 47 (7), 41 (16). – $C_{22}H_{31}OP$: calcd. 342.2113; found 342.2111 (MS).

☆ Dedicated to Professor *Hans Paulsen* on the occasion of his 75th birthday.

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[27] [27a] For the synthesis and isolation of compound (*S,S,E*)-**6b**, the (*Z*)-configured SAMP hydrazone (*S,R*)-**6b** was refluxed in benzene under complete epimerisation of the newly generated stereogenic centre. The obtained (*E*)-configured diastereomers were separated by column chromatography. One of the (*E*)-configured compounds was isolated as an oil, the other one was obtained as crystals. In order to determine which of the (*E*)-configured diastereomers had the same configuration at the newly generated centre as the (*Z*)-configured major diastereomer, both the (*E*)-isomers and the (*Z*)-isomer were treated with ozone to yield the ketones **7b**. By comparison of the optical rotations and the ^{1}H NMR shift experiments the crystalline compound was identified as minor diastereomer (*S,S,E*)-**6b**. Appropriate crystals were obtained from diethyl ether/petroleum ether (1/5) at −20 °C. $C_{25}H_{38}BN_2OP$ (424.37), monoclinic, a = 11.972(4) Å, b = 9.428(2) Å, c = 12.019(3) Å, β = 109.85(2)°, V = 1275.93 Å^3, Z = 2, = 1.105 g·cm^{-3}, no. of electrons per unit cell F(000) = 460, space group $P2_1(4)$. CAD4-Enraf-Nonius, CuK_α-radiation (λ = 1.54179 Å), graphite monochromator, crystal size ca. 0.5 × 0.5 × 0.5 mm, ν/2°, 10.97° < Θ < 32.99°, 3887 reflections measured, 2867 independent reflections, 2240 observed ($I > 2\sigma(I)$), absorption coefficient μ = 10.61 cm^{-1}. Solution with direct methods (GENSIN/GENTAN XTAL 3.2[27b], hydrogen positions calculated, 271 parameters refined, R = 0.107, R_W = 0.076, rest electron density −0.6/+0.7 e·Å^{-3}. Further details on the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-406005, the names of the authors and the journal citation. – [27b] *XTAL3.2 Reference Manual* (Ed.: S. R. Hall, H. D. Flack, J. M. Stewart, Universities of Western Australia, Geneva and Maryland), Lamb, Perth, **1992**.
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[35] Ethyl acetate was metalated with LDA and phosphinylated with chlorodiphenylphosphane. The resulting diphenylphosphanyl ethyl acetate[11a,b] was deprotonated again with LDA, followed by alkylation with alkyl iodides and subsequent LAH reduction to afford the alcohols **13** as racemic mixtures.

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