Syntheses of New Chiral Phosphane Ligands by Diastereoselective Conjugate Addition of Phosphides to Enantiomerically Pure Acceptor-Substituted Olefins from the Chiral Pool

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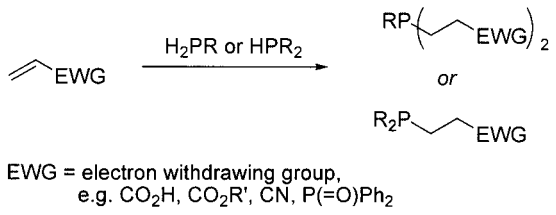
A variety of new chiral phosphanes were prepared by highly diastereoselective additions of phosphanes to α,β-unsaturated carbonyl compounds and related acceptor-substituted olefins derived from myrtenal as *ex chiral pool* source. Monophosphanes with astereogenic as well as stereogenic phosphorus are described. In addition diphosphanes were prepared by a highly diastereoselective double conjugate addition of a secondary diphosphane.

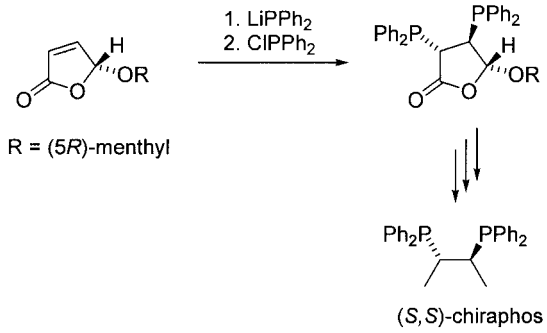
Introduction

In modern organic synthesis, a variety of enantioselective reactions are successfully applied that are promoted by transition metal catalysts containing chiral ligands.[1] Especially phosphane ligands are extremely valuable as they are highly variable both with respect to their electronic and steric properties.[2] Therefore, the development of new methods or strategies for the synthesis of enantiomerically pure phosphanes is of great importance.[3] So far, phosphorus is most often introduced by nucleophilic substitution reactions with alkali phosphides.[4] Far less attention has been paid to the conjugate addition of phosphanes to electron-deficient olefins, especially to α,β-unsaturated carboxylic acid derivatives according to Scheme 1, leading to potentially useful phosphane ligands with one or two additional functional groups.



Scheme 1. Conjugate additions of phosphanes.

There are several reports on the preparation of achiral or racemic phosphanes via conjugate addition to achiral enoates.[5] However, prior to our work reactions with chiral, enantiomerically pure substrates were only carried out by Jansen and Feringa who employed this approach for a synthesis of the ligand *chiraphos* using as key steps diastereoselective addition of lithium diphenylphosphide to a γ-alkoxybutenolide and trapping of the resulting enolate with PPh_2Cl (Scheme 2).[6]



Scheme 2. Asymmetric synthesis of *chiraphos* via conjugate addition.

Afterwards, the concept of the diastereoselective conjugate addition of phosphides as a simple route to novel ligands was further elaborated in our group. In contrast to Jansen and Feringa we directly used the addition products as ligands and selected the chiral starting materials from *ex chiral pool* sources in order to assure enantiomeric purity and relative configuration of the new phosphane ligands. In this way it was possible to obtain enantiomerically pure *trans*-3-(diphenylphosphanyl)myrtanic acid[7] in only two steps: addition of lithium diphenylphosphide to *tert*-butyl myrtenate which is easily accessible from commercial, cheap myrtenal followed by cleavage of the ester (Scheme 3).[8] In the meantime related diastereoselective conjugate additions to EWG-substituted olefins to give enantiomerically pure P,N-ligands were described by Knochels group.[9] Further-

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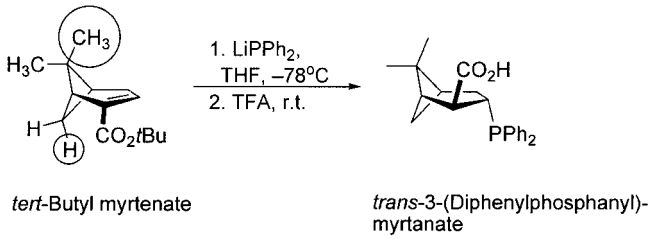
more, enantioselective additions of phosphanes under control of asymmetric catalysts have been achieved by Togni et al.[10]



Scheme 3. Synthesis of *trans*-3-(diphenylphosphanyl)myrtanic acid, an excellent ligand for Pd-catalyzed allylic substitutions, by diastereoselective conjugate addition.

trans-3-(Diphenylphosphanyl)myrtanic acid is an excellent ligand for Pd-catalyzed allylic substitutions.[11] Minami et al. described an alternative approach to enantiomerically pure β-phosphanylcarboxylic acids via a multi-step synthesis of a racemate followed by enantiomer resolution by crystallization of diastereomeric salts.[12]

Both the butenolide-derived as well as the myrtane-based system impressively demonstrate that phosphane additions on such rigid, cyclic cores proceed with a high degree of diastereoselectivity and at a high reaction rate. The almost unlimited availability of a large variety of enantiomerically pure enones, enoates and enals, therefore, offers the possibility to generate libraries of structurally diverse ligands. This consideration and the high efficiency of *trans*-3-(diphenylphosphanyl)myrtanic acid as ligand in Pd-catalyzed allylic alkylation reactions[8] prompted us to examine the conjugate addition more thoroughly. To begin with, the following aspects were most relevant:

1. The torsion angle between the phosphanyl and the carboxyl group of phosphanylcarboxylic acids can be systematically varied by choosing appropriate conjugated acceptors. As shown in Scheme 4 phosphanylcarboxylic acids with torsion angles between 0° and 120° could be realized starting from camphor, menthone and myrtenal as cheap *ex chiral pool* compounds.

2. The scope of the stereoselective conjugate addition of phosphides to carboxylic acid derivatives was examined. The reaction was possible with a α,β–unsaturated amide, the nitrile as well as oxazolines derived from myrtenic acid. Further transformation of the acceptor groups by reduction gave hydroxy- and amino-phosphanes. Thus, chiral mono- and bidentate ligands with sterically and electronically variable functionalities are accessible.

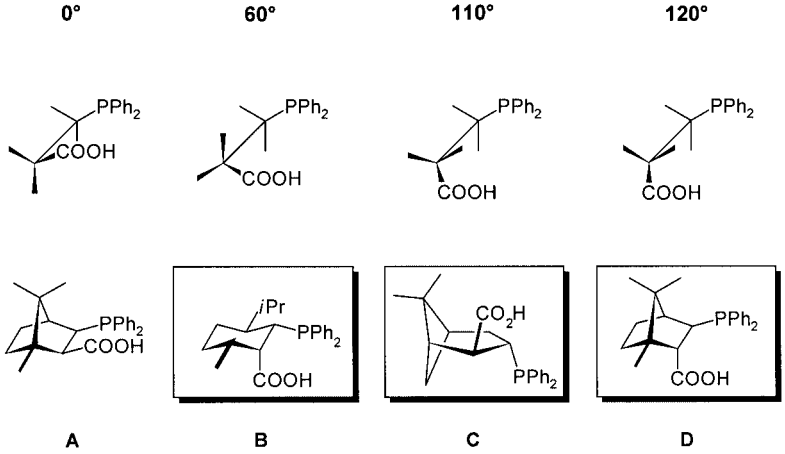
3. Addition of diphosphanes [HP(R)CH_2CH_2P(R)H] as well as unsymmetrically substituted phosphanes (HRR′P) allows the generation of polydentate ligands and the fine tuning of the steric and electronic properties of the phosphanyl group.

In this report, syntheses with α,β–unsaturated carboxylic acid derivatives derived from myrtenal are described. The conjugate addition of the phosphanes under a variety of conditions as well as derivatizations of the resulting phosphanylcarboxylic esters will be presented. As mentioned above, applications of *trans*-3-(diphenylphosphanyl)myrtanate in catalysis were already reported.[8,11] Syntheses of phosphane ligands with a menthane and a camphane skeleton and asymmetric syntheses with the new phosphane ligands will be reported separately.

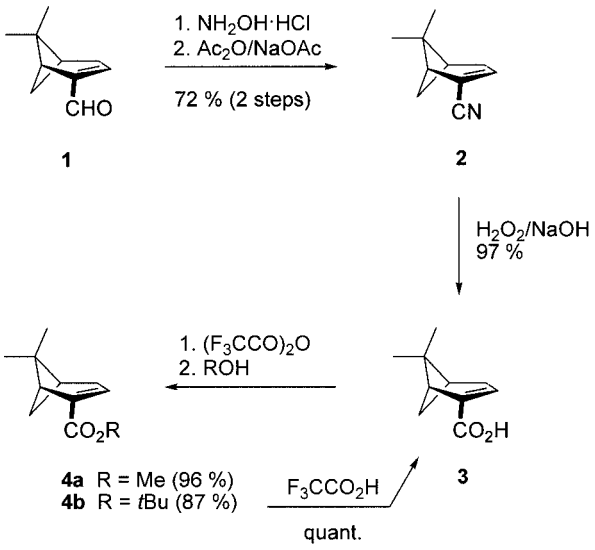
Results and Discussion

1. Synthesis of the Requisite α,β-Unsaturated Carboxylic Acid Derivatives

The synthesis of myrtenic acid (**3**) (Scheme 5) followed a route described by Semmler,[13] starting from commercially available (1*R*)-myrtenal (**1**) by oxime formation, dehydratisation of this to give the nitrile **2** and subsequent hydrolysis. For the hydrolysis of nitrile **2** to give acid **3** we obtained superior results by modifying the original procedure and use of alkaline aqueous hydrogen peroxide solution under reflux (97% yield).

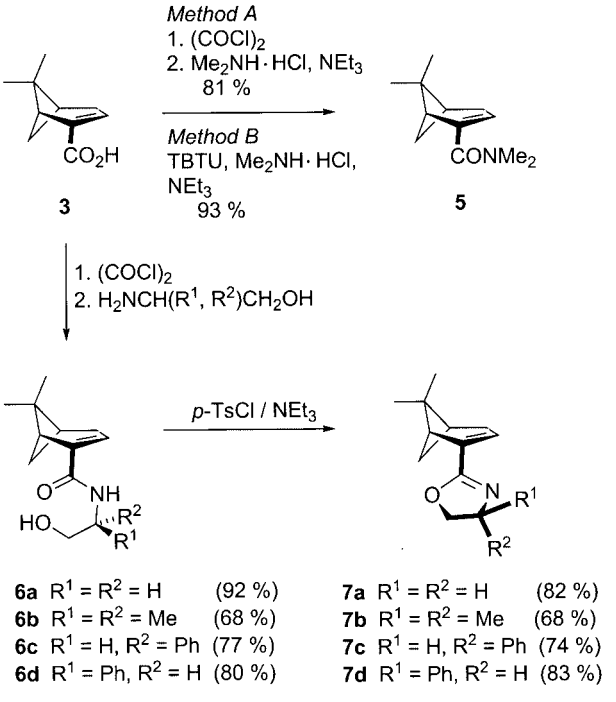


Scheme 4. β-Phosphanylcarboxylic acids with different torsion angles (HOOC)–C–C–P.



Scheme 5. Synthesis of myrtenic acid (**3**) and myrtenic acid esters **4a** and **4b**.

Esters **4a** and **4b** were prepared from acid **3** by reaction with trifluoroacetic acid anhydride according to Kuivila[14] followed by in situ reaction either with methanol or *tert*-butyl alcohol (Scheme 5). The methyl ester **4a** could also be obtained directly from myrtenal by oxidation with MnO_2/NaCN under Corey conditions.[15] For large scale synthesis (100–200 g), however, the stepwise synthesis was preferred as it avoids the handling of large amounts of cyanides. The enantiomeric purity of the *tert*-butyl ester **4b** could be enhanced to >99% *ee* by crystallization from cold *n*-pentane. The ester **4b** was transformed to the enantiomerically pure

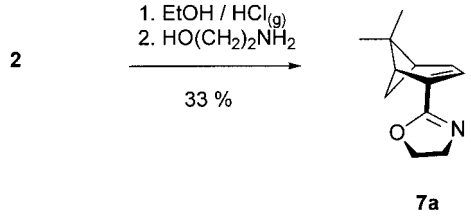


Scheme 6. Synthesis of myrtenic acid amide 5 and the dihydrooxazoles **7a**–**7d**.

carboxylic acid **3** in quantitative yield using trifluoroacetic acid.

The amide **5** was prepared by activation of the acid **3** with oxalyl chloride followed by reaction with dimethylamine, or in one step by in situ activation with 2-(1*H*-benzotriazol-1-yl)-1,1,3,3- tetramethyluronium tetrafluoroborate (TBTU) and subsequently reaction with dimethylamine (Scheme 6). Dihydrooxazoles **7a**–**7d** were obtained via amides **6a**–**6d** which were cyclized in a one-pot procedure by treatment with tosyl chloride and base.[16]

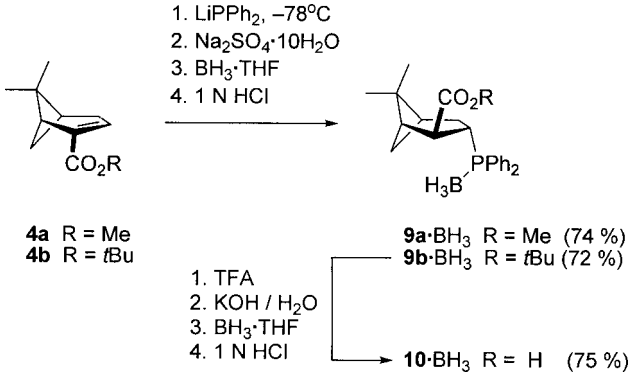
Alternatively, the synthesis of dihydrooxazoles was carried out by transforming nitrile **2** to an imidate[17] and condensation of this with the amino alcohol (Scheme 7). The dihydrooxazole **7a** was obtained in 33% yield using this procedure.



Scheme 7. One-pot synthesis of dihydrooxazole **7a**.

2. Addition of Diphenylphosphane

The rate of addition of diphenylphosphane (**8a**) to the various α,β-unsaturated carboxylic acid derivatives differs considerably; thus, variation of reaction conditions and optimization are required. The reaction of lithium diphenylphosphide with the esters **4a** and **4b** at –78 °C proceeded with quantitative yield (Scheme 8). For easier purification and storage, the phosphanylcarboxylic acid esters **9a** and **9b** were transformed into the oxidation-stable borane adducts **9a**·BH_3 and **9b**·BH_3.



Scheme 8. Synthesis of phosphanyl carboxylic acid esters **9a**·BH_3 and **9b**·BH_3 and of the phosphanyl carboxylic acid **10**·BH_3.

The corresponding phosphanylcarboxylic acid **10**·BH_3 can be obtained as follows (Scheme 8). Treatment of the *tert*-butyl ester **9b**·BH_3 with trifluoroacetic acid initially gives the complex **10**·BH_2(OOCCF$_3$) according to ^{31}P

NMR monitoring. Upon treatment with aqueous KOH during work-up **10** is produced which is treated with BH_3·THF to furnish **10**·BH_3 in 75% yield. Alkaline saponification of the methyl ester **9a**·BH_3 gives the phosphane **10** in 70% yield, i.e., this reaction also proceeds with loss of the BH_3 group. In addition, the formation of 11% each of myrtenic acid and $HPPh_2$ signifies accompanying elimination, most likely of $HPPh_2BH_3$ which further reacts.

The configuration of **10** was confirmed by X-ray analysis of the phosphane oxide **10**·oxide (Figure 1). A noteworthy feature of this structure is an envelope conformation of the six-membered ring. As a consequence a very large torsion angle (HOOC)–C–C–P of 110° is found in the X-ray structure.

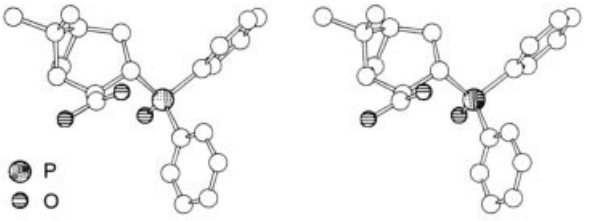
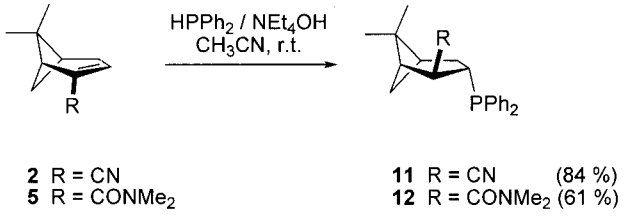


Figure 1. Stereoview of the X-ray crystal structure of phosphane oxide **10**·oxide.

Lithium diphenylphosphide did not yield an addition product with the dihydrooxazoles **7a**-**7d** and amide **5**. The addition proceeded smoothly with diphenylphosphane at room temperature under catalysis with tetraethylammonium hydroxide (Scheme 9, Scheme 10).[18] The configuration of the phosphane **12** was confirmed by X-ray analysis (Figure 2). In the case of the dihydrooxazole **7a** it was demonstrated by ^{31}P NMR that the addition also proceeds under acidic conditions with camphorsulfonic acid as catalyst.

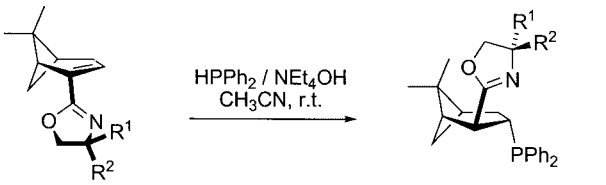


2 R = CN
5 R = $CONMe_2$

11 R = CN (84 %)
12 R = $CONMe_2$ (61 %)

Scheme 9. Conjugate addition of diphenylphosphane to myrtenic acid derivatives.

Excepting the formation of dihydrooxazole **7d**, the additions proceeded with diastereoselectivities >95:5 (^1H NMR, ^{31}P NMR). In the course of the synthesis of the phosphanyl dihydrooxazole **13d** slow epimerization of the benzylic position of the dihydrooxazole ring occurred because of the basic reaction conditions. This led to contamination of the desired product **13d** by its epimer **13c** (**13d**/**13c** ≈ 20:1). Attempts to separate the isomers by crystallization or MPLC were not successful.



7a $R^1 = R^2 = H$
7b $R^1 = R^2 = Me$
7c $R^1 = H$, $R^2 = Ph$
7d $R^1 = Ph$, $R^2 = H$

13a $R^1 = R^2 = H$ (58 %)
13b $R^1 = R^2 = Me$ (61 %)
13c $R^1 = H$, $R^2 = Ph$ (80 %)
13d $R^1 = Ph$, $R^2 = H$ (60 %,
13d:**13c** ~20:1)

Scheme 10. Conjugate addition of diphenylphosphane to dihydrooxazole derivatives of myrtenic acid (3).

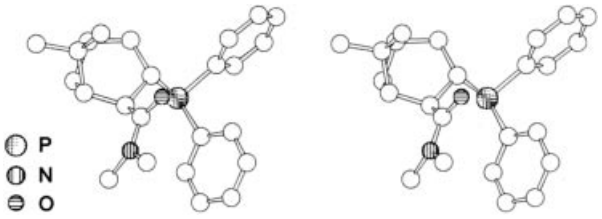
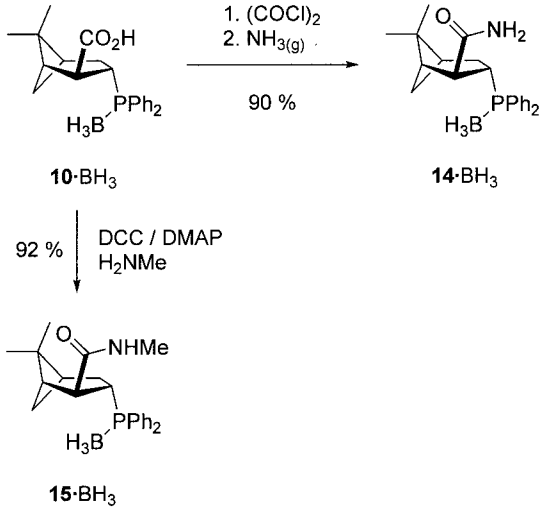


Figure 2. Stereoview of the X-ray crystal structure of phosphane 12.

3. Phosphanes Obtained by Functional Group Interconversion

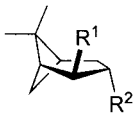
Due to the presence of the carboxyl group, the phosphanes described above could be easily modified and, therefore, generation of further ligands was possible. Thus, transformation of **10**·BH_3 to the acid chloride and reaction of this with anhydreous ammonia gave the amide **14**·BH_3, and the *N*-methyl-amide **15**·BH_3 was obtained under DCC coupling conditions (Scheme 11). However, under the same reaction conditions, attempted DCC coupling of **10**·BH_3 with the secondary amine piperidine did not yield the desired amide but the corresponding *N*-acyl urea resulting from rearrangement.



10·BH_3 **14**·BH_3 **15**·BH_3

Scheme 11. Preparation of derivatives of the phosphanyl carboxylic acid **10**·BH_3.

Reduction of ester **9a**·BH_3 and nitrile **11** with lithium aluminium hydride gave the alcohol **16**·BH_3 in 94% and the ammonium salt **17** in 52% yield, respectively.



16·BH_3 $R^1 = CH_2OH$, $R^2 = PPh_2{\cdot}BH_3$
17 $R^1 = CH_2NH_3^+$ 4-$(CH_3)C_6H_4SO_3^-$, $R^2 = PPh_2$

4. Addition of Unsymmetric Secondary Phosphanes and Diphosphanes

Encouraged by the results obtained in the addition of diphenylphosphane (**8a**) to myrtenic esters, additions of the unsymmetric secondary phosphanes (2-biphenyl)-phenylphosphane (**8b**), (1-naphthyl)-phenylphosphane (**8c**) and methyl-phenylphosphane (**8d**) were examined (Scheme 12). The phosphanes were prepared by known procedures.[19] Their additions to esters **4** were relatively slow and reversible, presumably because of the steric bulk of these phosphanes. It was important to add the lithium phosphide at –78 °C and hydrolyze the resultant enolate at –78 °C with a *pre-cooled solution* of methanol in THF. The crude phosphanyl carboxylic esters were transformed into the air-stable borane adducts. For **20**·BH_3 this was possible by directly adding BH_3·THF to the reaction mixture. In the case of **18**·BH_3 and **19**·BH_3, however, complexation only occurred after removal of salts from the crude phosphanes by filtration through silica.

In all the reactions described above, only two diastereomers were formed in every case according to ^{31}P NMR analysis of the crude products. These were *P*-epimers which were formed with a low degree of diastereoselectivity (Scheme 12). On the other hand, all additions proceeded highly diastereoselectively in favor of the *trans*-isomers (*dr* > 95:5 according to ^{31}P NMR).

Whilst (R_P)- and (S_P)-diastereomers of borane adducts **18**·BH_3 and **19**·BH_3 could be separated by flash chromatography, this was not possible in the case of **20**·BH_3; only diastereomerically pure (S_P)-**20**·BH_3 could be isolated, by crystallization from PE/ethyl acetate. Similarly, in the case of **21**·BH_3 only diastereomerically pure (R_P)-**21**·BH_3 could be obtained by chromatography. Ester (R_P)-**21**·BH_3 was converted to carboxylic acid (R_P)-**22**·BH_3 by treatment with trifluoroacetic acid.

Configurations of the borane-protected epimers of the phosphanyl carboxylic esters **19**·BH_3, **20**·BH_3 and **21**·BH_3 were determined by X-ray crystal structure analysis (Figure 3). Tentative assignment of the configuration of the *P*-epimers of **18** is based on comparison of ^{31}P NMR chemical shifts with those of the epimers of **19** and **20** (Table 1).

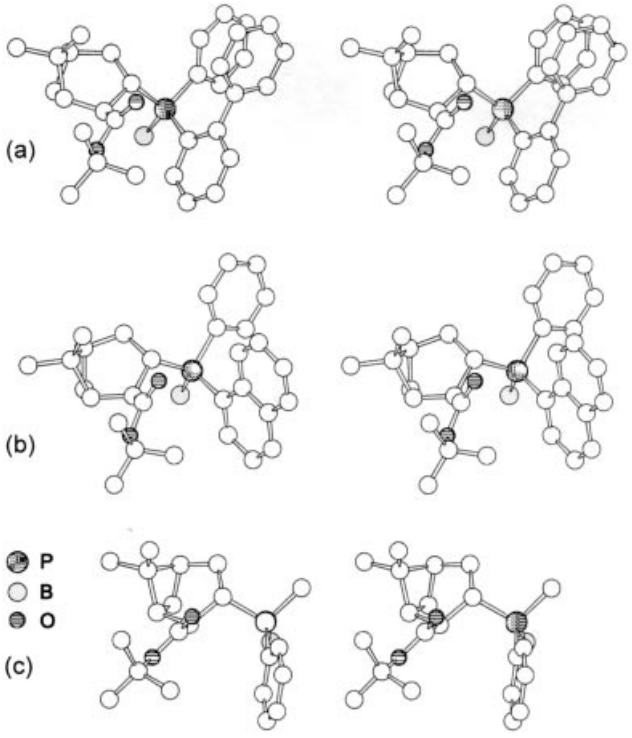
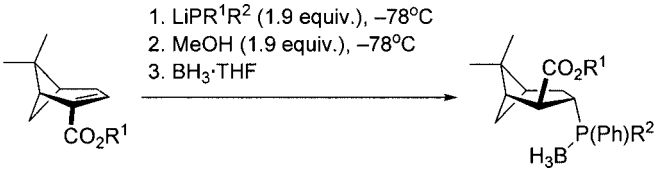


Figure 3. Stereoviews of the X-ray crystal structures of borane-protected phosphanyl carboxylic esters: (a) (S_P)-**19**·BH_3, (b) (S_P)-**20**·BH_3, (c) (R_P)-**21**·BH_3.

Propensities of phosphanes[20] (S_P)-**18**, (S_P)-**19** and (S_P)-**20** towards P-epimerization were assessed by ^{31}P NMR spectroscopy. In the temperature range room temp. –100 °C, spectra of toluene solutions were recorded at 10 °C intervals



4a R^1 = Me
4b R^1 = *t*Bu

18·BH_3 R^1 = Me, R^2 = 2-Bp (55 %, R_p : S_p 73:27)
19·BH_3 R^1 = *t*Bu, R^2 = 2-Bp (78 %, R_p : S_p 57:42)
20·BH_3 R^1 = *t*Bu, R^2 = 1-Naph (68 %, R_p : S_p 75:25)
21·BH_3 R^1 = *t*Bu, R^2 = Me (22 %, R_p : S_p 61:39)

1. TFA
2. BH_3·THF → **22**·BH_3 R^1 = H, R^2 = Me (75 %)

Scheme 12. Synthesis of phosphanyl carboxylic esters with stereogenic phosphorus (2-Bp = 2-biphenyl). Yields refer to the sum of the pure diastereomers, the ratio refer to ^{31}P integration.

Table 1. ^{31}P NMR chemical shifts of phosphanes **18**–**21**.

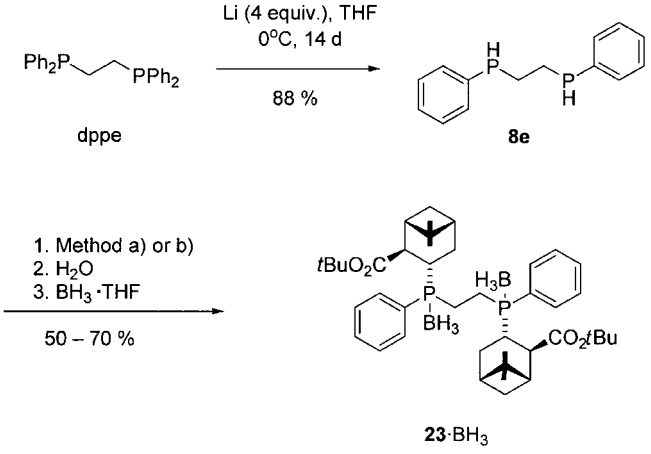
Compound	(S_P)-**18**/(R_P)-**18**	(S_P)-**19**/(R_P)-**19**	(S_P)-**20**/(R_P)-**20**	(R_P)-**21**
δ [ppm]	–4.7/ –1.4 32.1/30.2[a]	–5.1/ –1.5 32.0/29.1[a]	–8.5/ –4.5	–12.1

[a] Chemical shifts of borane complexes.

over a time period of 5 min at every stage. The diarylphosphanes were configurationally stable up to 80 °C; at temperatures higher than 90 °C isomerization became apparent. The dialkylmonoarylphosphane (R_P)-**21** did not isomerize (15 h at 110 °C, toluene) under these conditions.

5. Double Conjugate Addition of Secondary Diphosphanes

Stimulated by the encouraging results described above, the preparation of diphosphane ligands by double conjugate addition of secondary diphosphanes was examined. The requisite diphosphane **8e** was prepared according to Brookham et al. by reductive cleavage of dppe with lithium at 0 °C (Scheme 13).[21] In the reaction between the dianion of **8e** and the enoate, the diphosphide could not be used in excess because of the formation of the undesired monoaddition product. Good results were obtained using either of the following methods:



Scheme 13. Synthesis of **23**·BH_3 by double conjugate addition to acceptor **8e**. Methods a and b see text.

(a) Deprotonation of **8e** with two equivalents of *n*BuLi at –78 °C, followed by addition of two equivalents of **4b**;

(b) Addition of **8e** to **4b** catalyzed by tetraethylammonium hydroxide at room temperature according to the method Blinn et al.[18]

In both cases the resultant diphosphanes were transformed into the air stable borane adducts **23**·BH_3. Under both conditions, P-diastereoisomeric products **23a-c** and corresponding borane adducts were formed with a remarkably high degree of diastereoselection. Thus, from the reaction according to method (a) (R_P,S_P)-**23a**·BH_3, (S_P,S_P)-**23b**·BH_3 and (R_P,R_P)-**23c**·BH_3 were obtained pure (flash chromatography) in 45, 3 and < 1% yield, respectively. Similarly, the reaction according to method (b) gave the three isomers in 43, ca. 5 and 0.6% yield, respectively. The mono addition product was not observed under either conditions.

For preparation of (S_P,S_P)-**23** and (R_P,R_P)-**23** in substantial amounts, crude phosphanes were isomerized by heating at 110 °C for eight hours. Epimers were obtained in the ratio (R_P,S_P)-**23**:(S_P,S_P)-**23**:(R_P,R_P)-**23** = 32:39:29 (^{31}P NMR). Borane adducts of the isomers were separated by standard flash chromatography. Investigation of the rate of P-epimerization of phosphanes **22** showed that these compounds are configurationally stable up to a temperature of 100 °C.

Relative configurations of the isomers as given above were determined by X-ray crystal structure analysis and NMR spectroscopy as follows. The C_1-symmetric diastereomer (R_P,S_P)-**23a**·BH_3 displays two sets of signals both in the ^{1}H NMR as well as in the ^{31}P NMR spectrum. The configurations of the two C_2-symmetric epimers could be assigned by X-ray structure analysis of (S_P,S_P)-**23**·BH_3 (Figure 4).

Experimental Section

General Methods: All reactions requiring anhydrous conditions were carried out in dried flasks under a positive pressure of argon or nitrogen. Melting points were determined in open glass capillaries and are not corrected. If not stated otherwise, ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 500 [500 MHz (^{1}H), 125 MHz (^{13}C)], or a Bruker Avance 300 spectrometer [300 MHz (^{1}H), 75 MHz (^{13}C)], ^{31}P NMR and ^{11}B NMR spectra were recorded on a Bruker AC-200 spectrometer [81 MHz (^{31}P), 64 MHz (^{11}B), $CDCl_3$]. Chemical shifts are reported in δ (ppm) relative to

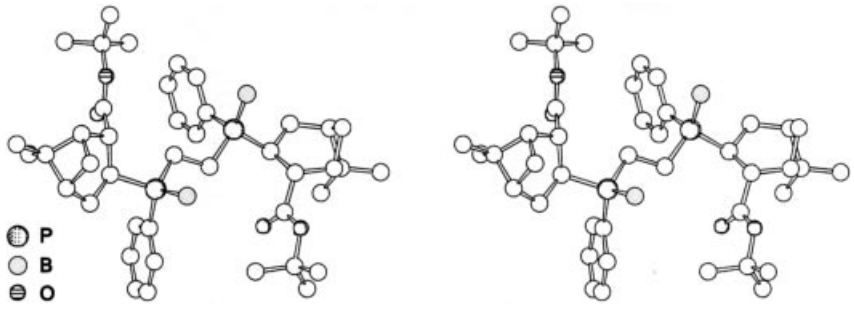


Figure 4. X-ray crystal structure of (S_P,S_P)-**23b**·BH_3.

tetramethylsilane (TMS). High resolution MS were obtained on a vacuum Generators ZAB 2F (EI) or JEOL JMS-700 (FAB) spectrometer. Optical rotations were measured with a Perkin–Elmer PE 241 polarimeter. For TLC Machery–Nagel PolygramSil G/UV_{254} plates were used with spot detection by I_2 vapour, UV light or phosphomolybdic acid in ethanol followed by heating. If not stated otherwise, ICN Kieselgel S (0.032–0.063 mm) was used for flash chromatography. For MPLC columns of type C (N = 10000) according to Helmchen and Glatz[22] were used.

Materials: Commercially available reagents were used without further purification. (–)-(1*R*)-Myrtenal was purchased from Acros or Aldrich,[23] borane-THF complex from Aldrich, *n*BuLi from Metallgesellschaft. Petroleum ether (PE) and ethyl acetate (Merck, Darmstadt) were distilled through a 1 m Vigreux column. Diethyl ether, dioxane and THF were dried by distillation from sodium/benzophenone. Methylene chloride and chloroform were distilled from CaH_2. All anhydrous solvents were stored under nitrogen over 4-Å molecular sieves. For reactions and work-up involving phosphanes carefully deoxygenated solvents and reagents were used.

General Procedure for Conjugate Addition of Lithium Phosphides Derived from Secondary Phosphanes (GP 1): Under nitrogen, *n*BuLi (1.9 mmol, 1.6 M in hexane) was added dropwise to a solution of the phosphane (2.0 mmol) in anhydrous THF (1.5 mL) at –78 °C. After stirring at –78 °C for 30 min, a cold (–78 °C) solution of the acceptor-substituted olefin (1.0 mmol) in anhydrous THF (2.5 mL) was added via double-ended needle transfer. The mixture was stirred at –78 °C and conversion was monitored by TLC and ^{31}P NMR spectroscopy.[24] Work-up was initiated by adding at –78 °C a cold (–78 °C) deoxygenated solution of methanol (3 mmol) in THF (1.5 mL).[25] Subsequently borane adducts were formed as described below for individual compounds.

General Procedure for Conjugate Addition of Secondary Phosphanes by Use of Catalytic Amounts of Et_4NOH (GP 2): All operations were carried out under strict exclusion of oxygen. To a degassed solution of Et_4NOH (15 drops, 40% in water) in degassed acetonitrile (2 mL) the acceptor-substituted olefin (1.0 mmol) was added. After addition of the phosphane (1.0 mmol) the mixture was stirred at room temp. for 1–4 days. Conversion was monitored by TLC and ^{31}P NMR and was >90% in all cases. For work-up, the solvent was removed under reduced pressure, water was added and the product was extracted with CH_2Cl_2. The combined organic layers were washed three times with water at 0 °C and dried over deoxygenated Na_2SO_4. After filtration, the solvent was removed in vacuo and the product purified.

General Procedure for Amide Formation (GP 3): Oxalyl chloride (1.5 mmol) was added to a cooled (0 °C) solution of the carboxylic acid (1.0 mmol) and a catalytic amount of anhydrous DMF (2 drops) in anhydrous toluene (2 mL) and the mixture was stirred overnight at room temp. The mixture was evaporated down under reduced pressure and the residue was repeatedly dissolved in toluene (2 mL) and concentrated in vacuo in order to remove traces of oxalyl chloride. The crude acid chloride was then dissolved in dioxane (1 mL) and the solution added to a solution of the amino alcohol (1.2 mmol) and NEt_3 (5 mmol) in dioxane (1 mL) at 10 °C. After stirring overnight water (1 mL) was added and the mixture concentrated in vacuo. The residue was extracted with CH_2Cl_2 or ethyl acetate. The combined organic layers were successively washed with 1 N HCl, 1 N NaOH and brine, dried over Na_2SO_4, filtered and the solvent was removed in vacuo.

General Procedure for Cyclization of β-Hydroxy Amides to Dihydro-1,3-oxazoles (GP 4): To a cold (0 °C) solution of the β-hydroxy amide (1.0 mmol) and NEt_3 (5.0 mL) in anhydrous CH_2Cl_2 or $CHCl_3$ (8 mL) *p*TsCl (1.1 mmol) was added. The reaction mixture was allowed to warm to room temp. and stirred until TLC indicated complete conversion. The mixture was then cooled to 0 °C and a catalytic amount of DMAP and water (3.0 mmol) were added. After stirring overnight the solution was washed successively with 1 N HCl, 1 N NaOH and brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The dihydro-1,3-oxazoles were purified by flash chromatography.

(–)-(1*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carbonitrile (2): $NH_2OH{\cdot}HCl$ (50.7 g, 729 mmol) was added in small portions to a solution of $NaHCO_3$ (61.3 g, 729 mmol) in water (50 mL). When the evolution of CO_2 had ceased water (64 mL) was added, the solution was cooled to 0 °C and a solution of (–)-(1*R*)-myrtenal (**1**) (97.0 g, 646 mmol) in ethanol (1250 mL) was added. The mixture was heated at reflux for 20 h, then most of the ethanol was removed in vacuo and 2 N HCl was added (pH < 2). The residual aqueous mixture was extracted with diethyl ether (4 × 200 mL). The combined organic layers were dried (Na_2SO_4) and the solvent removed in vacuo to give crude crystalline oxime. This was treated with acetic acid anhydride (165.1 g, 1615 mmol) and sodium acetate (53.2 g, 646 mmol) and the mixture was stirred for 5 d at 100 °C. The reaction mixture was then neutralized by addition of 2 N NaOH (900 mL) and extracted with diethyl ether (5 × 150 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuo. Kugelrohr distillation of the crude product [95–98 °C/10 mbar (ref.[13b] 95–98 °C, 8.5 Torr)] gave the nitrile **2** (67.9 g, 72%) as colorless oil. $[\alpha]_D^{22}$ = –55.2 (c = 1.00, $CHCl_3$) (ref.[13b] $[\alpha]_D$ = 55, neat). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.87 (s, 3 H, 8-H), 1.24 (d, $J_{7a,7b}$ = 9.3 Hz, 1 H, 7-H_a), 1.32 (s, 3 H, 9-H), 2.16 (m_c, 1 H, 5-H), 2.39–2.42 (m, 3 H, 4-H, 7-H_b), 2.54 (m, 1 H, 1-H), 6.55 (m_c, 1 H, 3-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.96 (q, C-8), 25.64 (q, C-9), 31.26, 32.63 (2t, C-4, C-7), 38.18 (s, C-6), 39.84, 44.56 (2d, C-1, C-5), 118.46 (s, C-2), 120.96 (s, CN), 142.06 (d, C-3).

(–)-(1*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carboxylic Acid (3): Nitrile **2** (10.00 g, 67.9 mmol) was added at 0 °C to a stirred solution of sodium hydroxide (8.00 g, 200 mmol) in aqueous hydrogen peroxide (10%, 150 mL). After stirring for 3 h at room temperature the solution was heated at reflux for 4 d. After cooling to room temperature the mixture was extracted with diethyl ether and the organic phase discarded. The aqueous layer was acidified (pH < 2) and extracted three times with diethyl ether (400 mL). The combind organic layers were dried (Na_2SO_4) and the solvent was removed. Kugelrohr distillation [160 °C /4 mbar (ref.[13b] 149–152 °C, 9 Torr)] of the residue gave **3** (10.99 g, 97%) as slightly yellow oil.

Trifluoroacetic acid (5.93 mL) was added to the *tert*-butyl ester **4b** (1.00 g, 4.50 mmol) in a pre-dried flask, and the reaction mixture was stirred for 30 min under argon atmosphere. Excess of trifluoroacetic acid was removed in vacuo, and the residue was treated with an aqueous solution of potassium hydroxide (5.93 mL, 3 M). The aqueous phase was extracted with diethyl ether (2 × 30 mL) and the organic phase discarded. The aqueous phase was acidified with HCl (6 M) to pH 2 and extracted with diethyl ether (4 × 40 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated in vacuo. The carboxylic acid **3** (755.1 mg, 100%) of was isolated as pale yellow oil. $[\alpha]_D^{22}$ = –40.2 (c = 1.01, $CHCl_3$), $[\alpha]_D^{22}$ = –47.1 (c = 4.22, EtOH) [ref.[14] $[\alpha]_D^{22}$ = –60.4 (c = 4.36, EtOH)]. ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.79 (s, 3 H, 8-H), 1.12 (d, $J_{7a,7b}$ = 9.2 Hz, 1 H, 7-H_a), 1.33 (s, 3 H, 9-H), 2.13 (m_c, 1 H, 5-H), 2.36–2.53 (m, 3 H, 4-H, 7-H_b), 2.78 (ddd, J = 5.6, J = 5.6, $J_{1,3}$ = 1.5 Hz, 1 H, 1-H), 6.99 (m, 1 H, 3-H), 11.4 (br. s, 1 H, COOH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.91 (q, C-8), 25.83

(q, C-9), 31.24, 32.35 (2t, C-4, C-7), 37.67 (s, C-6), 40.25, 40.90 (2d, C-1, C-5), 139.39 (d, C-3), 139.71 (s, C-2), 171.55 (s, COOH).

(–)-(1*R*)-Methyl 6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carboxylate (4a): Diazomethane in diethyl ether was added to a solution of **3** (500 mg, 3.01 mmol) in diethyl ether (20 mL) until the yellow color persisted, and excess diazomethane was destroyed by addition of acetic acid. Then 2 N NaOH was added and the solution was extracted with diethyl ether (3 × 50 mL), and the combined organic layers were dried over Na_2SO_4. Kugelrohr distillation at 160 °C/10 mbar gave **4a** (520 mg, 96%) as colorless liquid. $[\alpha]_D^{22} = -35.4$ (*c* = 1.29, $CHCl_3$) [ref.[14] $[\alpha]_D^{22} = -45.8$ (*c* = 1.71, $CHCl_3$)]. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.76 (s, 3 H, 8-H), 1.08 (d, $J_{7a,7b}$ = 9.0 Hz, 1 H, 7-H_a), 1.29 (s, 3 H, 9-H), 2.06–2.10 (m, 1 H, 5-H), 2.36–2.47 (m, 3 H, 4-H, 7-H_b), 2.76 (ddd, *J* = 5.7, *J* = 5.7, *J* = 1.5 Hz, 1 H, 1-H), 3.69 (s, 3 H, OCH_3), 6.80 (m_c, 1 H, 3-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.69 (q, C-9), 25.65 (q, C-8), 31.08, 31.92 (2t, C-4, C-7), 37.41 (s, C-6), 40.07, 41.02 (2t, C-1, C-5), 51.25 (q, CO-O*C*H_3), 136.23 (d, C-3), 139.85 (s, C-2), 166.47 (s, *C*OOCH$_3$).

(–)-(1*R*)-*tert*-Butyl 6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carboxylate (4b): Trifluoroacetic anhydride (100.9 g, 0.480 mol) was added to a solution of **3** (20.0 g, 0.120 mol) in anhydrous benzene (170 mL). After stirring for 40 min at room temperature *t*BuOH (143.1 g, 1.929 mol) was added. Conversion was monitored by TLC [PE/EE, 10:1, R_f(**3**) = 0.09, R_f(**4b**) = 0.57]. After 3.5 h aqueous NaOH (15%, 110 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 200 mL). The combined organic phases were dried over Na_2SO_4. The solvent was removed in vacuo and the product was purified by chromatography (500 g of silica gel, PE/diethyl ether, 10:1). Kugelrohr distillation gave **4b** (23.2 g, 87%) as colorless oil. B.p. 160 °C, 10 mbar. $[\alpha]_D^{21} = -32.1$ (*c* = 1.00, $CHCl_3$, 96% *ee*), [ref.[14] $[\alpha]_D^{21} = -34.1$ (*c* = 3.25, $CHCl_3$)]. GC: column Chrompac Permethyl-β-CD (50 m × 0.25 mm), oven temp.: 110 °C, He (1 bar), injector temp.: 250 °C, detector temp.: 250 °C, t_R[(1*R*)-**4b**] = 26.8 min, t_R[(1*S*)-**4b**] = 28.0 min. The oil crystallized after some time. Crystallization from a saturated solution in ether or *n*-pentane by cooling with a dry ice bath and removal of the mother liquor with a syringe gave material of >99% *ee* in 55% yield. M.p. 34–34.5 °C. $[\alpha]_D^{21} = -38.9$ (*c* = 1.13, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.76 (s, 3 H, 8-H), 1.08 (d, $J_{7a,7b}$ = 8.8 Hz, 1 H, 7-H_a), 1.30 (s, 3 H, 9-H), 1.46 [s, 9 H, C(CH_3)$_3$], 2.08 (m, 1 H, 5-H), 2.33–2.45 (m, 3 H, 4-H, 7-H_b), 2.73 (ddd, *J* = 6.9, *J* = 6.9, $J_{1,3}$ = 1.5 Hz, 1-H), 6.67 (m_c, 1 H, 3-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.85 (q, C-8), 25.93 (q, C-9), 28.14 [q, C(*C*H$_3$)$_3$], 31.29, 31.96 (2t, C-4, C-7), 37.58 (s, C-6), 40.37, 41.16 (2d, C-1, C-5), 79.69 [s, *C*(CH$_3$)$_3$], 134.84 (d, C-3), 141.67 (s, C-2), 165.62 [s, *C*OOC(CH$_3$)$_3$].

(–)-(1*R*)-*N*,*N*,6,6-Tetramethylbicyclo[3.1.1]hept-2-ene-2-carboxamide (5): *Method A*: According to GP 3, carboxylic acid **3** (10.0 g, 60.2 mmol) was converted into the acid chloride. This was dissolved in anhydrous $CHCl_3$ (20 mL) and the solution added dropwise to a mixture of dimethylamine hydrochloride (7.36 g, 90.3 mmol) and anhydrous NEt_3 (40 mL, 289 mmol) in anhydrous $CHCl_3$ (100 mL) at –10 °C. The resulting brown suspension was stirred overnight. After aqueous work-up the crude product was purified by flash chromatography (silica gel, PE/ethyl acetate, 7:3) and kugelrohr distillation afforded **5** (9.40 g, 81%) as colorless oil.

Method B: TBTU (1.60 g, 5.00 mmol) and NEt_3 (1.92 mL, 13.6 mmol) were added to a cooled (ice bath) solution of the carboxylic acid **3** (755.1 mg, 4.54 mmol) and dimethylamine hydrochloride (741 mg, 9.09 mmol) in anhydrous dichloromethane (14 mL), and the suspension was stirred for 1 h at 0 °C. The ice-bath was removed and dichloromethane (70 mL) was added. The organic phase was washed with an aqueous solution of $NaHSO_4$ (3 × 10 mL), $NaHCO_3$ (3 × 10 mL), brine (10 mL), and dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography (pre-dried silica gel, *n*-pentane/diethyl ether, 1:1) to afford the amide **5** (818.5 mg, 93%) as a pale yellow oil. B.p. = 100–120 °C, 0.01 mbar. $[\alpha]_D^{21} = -44.5$ (*c* = 2.18, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (s, 3 H, 8-H), 1.24 (d, $J_{7a,7b}$ = 8.8 Hz, 1 H, 7-H_a), 1.28 (s, 3 H, 9-H), 2.09–2.15 (m, 1 H, 5-H), 2.28–2.41 (m, 3 H, 1-H, 4-H), 2.48 (ddd, $J_{7a,7b}$ = 8.8, $J_{1,7b}$ = 5.6, $J_{5,7b}$ = 5.6 Hz, 1 H, 7-H_b), 2.95 [bs, 6 H, N(CH$_3$)$_2$; at –50 °C: 2.91, 2.98 [2s, each 3 H, N(CH$_3$)$_2$], 5.79–5.82 (m, 1 H, C=CH). ^{13}C NMR ($CDCl_3$): δ = 21.09 (q, C-8), 25.93 (q, C-9), 31.53, 31.65 (2t, C-4, C-7), 34.92, [bq, N(CH$_3$)$_2$], 37.79 (s, C-6), 38.23 [bq, N(CH$_3$)$_2$], 40.36 (d, C-5), 44.23 (d, C-1), 125.81 (d, C=*C*H), 143.67 (s, *C*=CH), 171.20 (s, C=O). $C_{12}H_{19}NO$ (193.32): calcd. C 74.55, H 9.93, N 7.25; found C 74.28, H 9.89, N 7.20.

(–)-(1*R*)-*N*-(2-Hydroxyethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-carboxamide (6a): Carboxylic acid **3** (14.0 g, 84.2 mmol) and 2-aminoethanol (6.18 g, 101 mmol) were transformed into the title compound according to GP 3 [TLC: PE/*i*PrOH, 9:1, R_f(**3**) = 0.46, R_f(**6a**) = 0.21]. The crude product was purified by flash chromatography (silica gel, CH_2Cl_2/MeOH, 95:5) to give **6a** (16.2 g, 92%) as colorless oil $[\alpha]_D^{23} = -37.7$ (*c* = 1.37, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75 (s, 3 H, 8-H), 1.07 (d, $J_{7a,7b}$ = 9.0 Hz, 1 H, 7-H_a), 1.27 (s, 3 H, 9-H), 2.08–2.15 (m, 1 H, 5-H), 2.28–2.39 (m, 2 H, 4-H), 2.45 (ddd, $J_{7a,7b}$ = 9.0, $J_{1,7b}$ = 5.7, $J_{5,7b}$ = 5.7 Hz, 1 H, 7-H_b), 2.62 (ddd, $J_{1,5}$ = 5.5, $J_{1,7b}$ = 5.5, $J_{1,3}$ = 1.5 Hz, 1 H, 1-H), 3.44 (q, *J* = 5.0 Hz, 2 H, CH_2N; after H/D exchange: t, 5.0 Hz), 3.70 (t, *J* = 5.0 Hz, 2 H, CH_2O), 3.80 (br. s, 1 H, OH, H/D), 6.38–6.45 (m, 1 H, C=CH), 6.48–6.58 (m, 1 H, NH, H/D). ^{13}C NMR ($CDCl_3$): δ = 20.70 (q, C-8), 25.71 (q, C-9), 31.17 (t, C-7), 31.52 (t, C-4), 37.51 (s, C-6), 40.16 (d, C-5), 41.66 (d, C-1), 42.33 (t, CH_2N), 61.85 (t, CH_2O), 129.59 (d, C=*C*H), 143.03 (s, *C*=CH), 168.23 (s, C=O). $C_{12}H_{19}NO_2$ (209.32): calcd. C 68.85, H 9.17, N 6.69; found C 68.62, H 9.16, N 6.58.

(–)-(1*R*)-*N*-(2-Hydroxy-1,1-dimethylethyl)-6,6-dimethylbicyclo-[3.1.1]hept-2-ene-2-carboxamide (6b): Carboxylic acid **3** (3.50 g, 21.1 mmol) and 2-amino-2-methylpropanol (2.23 g, 25.0 mmol) were transformed into the title compound according to GP 3 [TLC: PE/*i*PrOH, 95:5, R_f(**3**) = 0.31, R_f(**6b**) = 0.14]. The crude product was purified by flash chromatography (silica gel, PE/ethyl acetate, 95:5) and crystallized from ethyl acetate/hexane to give **6b** (3.41 g, 68%) as colorless needles. M.p. 83.5–84.5 °C. $[\alpha]_D^{20} = -38.2$ (*c* = 1.30, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (s, 3 H, 8-H), 1.13 (d, $J_{7a,7b}$ = 9.0 Hz, 1 H, 7-H_a), 1.30 [s, 6 H, NC(CH$_3$)$_2$], 1.32 (s, 3 H, 9-H), 2.09–2.15 (m, 1 H, 5-H), 2.28–2.46 (m, 2 H, 4-H), 2.45 (ddd, $J_{7a,7b}$ = 9.0, $J_{1,7b}$ = 5.9, $J_{5,7b}$ = 5.9 Hz, 1 H, 7-H_b), 2.59 (ddd, $J_{1,5}$ = 5.5, $J_{1,7b}$ = 5.5, $J_{1,3}$ = 1.8 Hz, 1 H, 1-H), 3.57 (d, *J* = 6.0 Hz, 2 H, CH_2O; after H/D exchange: s), 5.07 (t, *J* = 5.9 Hz, 1 H, OH, H/D), 5.75 (br. s, 1 H, NH, H/D), 6.29–6.37 (m, 1 H, C=CH). ^{13}C NMR ($CDCl_3$): δ = 20.68 (q, C-8), 24.46, 24.55 [2d, NC(*C*H$_3$)$_2$], 25.69 (d, C-9), 31.15, 31.42 (2t, C-4, C-7), 37.51 (s, C-6), 40.11 (d, C-5), 41.89 (d, C-1), 55.73 [s, N*C*(CH$_3$)$_2$], 70.68 (t, CH_2O), 128.88 (d, C=*C*H), 143.81 (s, *C*=CH), 168.01 (s, C=O). $C_{14}H_{23}NO_2$ (237.38): calcd. C 70.83, H 9.79, N 5.90; found C 70.81, H 9.68, N 5.87.

(–)-(1*R*)-*N*-[2-Hydroxy-(1*R*)-phenylethyl]-6,6-dimethylbicyclo-[3.1.1]hept-2-ene-2-carboxamide (6c): Carboxylic acid **3** (20.0 g, 120.3 mmol) and (*R*)-phenylglycinol (19.8 g, 144.3 mmol) were converted into the title compound according to GP 3 [TLC: PE/*i*PrOH, 95:5, R_f(**3**) = 0.31, R_f(**6c**) = 0.18]. Crystallization of the crude product from ethyl acetate gave **6c** (26.4 g, 77%) as needles. M.p. 165–

167 °C. $[\alpha]_D^{20}$ = –46.5 (*c* = 3.10, MeOH). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (s, 3 H, 8-H), 1.13 (d, $J_{7a,7b}$ = 9.0 Hz, 1 H, 7-H_a), 1.31 (s, 3 H, 9-H), 2.12–2.19 (m, 1 H, 5-H), 2.30–2.43 (m, 2 H, 4-H), 2.48 (ddd, $J_{7a,7b}$ = 9.2, $J_{1,7b}$ = 5.9, $J_{5,7b}$ = 5.9 Hz, 1 H, 7-H_b), 2.68 (ddd, $J_{1,5}$ = 5.7, $J_{1,7b}$ = 5.7, $J_{1,3}$ = 1.5 Hz, 1 H, 1-H), 3.08 (br. s, 1 H, OH, H/D), 3.88 [m, 2 H, CH_2O; after H/D exchange: 3.85 (dd, *J* = 11.2, *J* = 4.2 Hz, 1 H, CH_2O)], 3.91 [dd, *J* = 11.2, *J* = 5.7 Hz, 1 H, CH_2O], 5.09 (dd, *J* = 11.0, *J* = 5.8 Hz, 1 H, CHN; after H/D exchange: t, *J* = 5.0 Hz), 6.38–6.48 (m, 2 H, C=CH, NH, H/D; after H/D exchange: m, 1 H, C=CH), 7.23–7.39 (m, 5 H, Ph-H). ^{13}C NMR ($CDCl_3$): δ = 20.73 (q, C-8), 25.70 (q, C-9), 31.19 (t, C-7), 31.55 (t, C-4), 37.57 (s, C-6), 40.22 (d, C-5), 41.78 (d, C-1), 55.96 (d, CHN), 66.62 (t, CH_2O), 126.47, 127.61, 128.68 (3d, Ph-C), 129.47 (d, C=*C*H), 139.04 (s, Ph-C), 143.30 (s, *C*=CH), 167.60 (s, C=O). $C_{18}H_{23}NO_2$ (285.42): C 75.74, H 8.14, N 4.91; found C 75.54, H 8.07, N 4.85.

(–)-(1*S*)-*N*-[2-Hydroxy-(1*S*)-phenylethyl]-6,6-dimethylbicyclo-[3.1.1]hept-2-ene-2-carboxamide (6d): The title compound was prepared from carboxylic acid **3** (15.1 g, 90.8 mmol) and (*S*)-phenylglycinol (15.0 g, 109.3 mmol) according to GP 3 [TLC: PE/*i*PrOH, 9:1, R_f(**3**) = 0.31, R_f(**6d**) = 0.20]. Crystallization of the crude product from ethyl acetate gave **6d** (20.8 g, 80%) as colorless needles. M.p. 121.5–122.0 °C. $[\alpha]_D^{20}$ = –20.4 (*c* = 1.36, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (s, 3 H, 8-H), 1.10 (d, $J_{7a,7b}$ = 9.0 Hz, 1 H, 7-H_a), 1.30 (s, 3 H, 9-H), 2.11–2.18 (m, 1 H, 5-H), 2.30–2.43 (m, 2 H, 4-H), 2.48 (ddd, $J_{7a,7b}$ = 8.8, $J_{1,7b}$ = 5.6, $J_{5,7b}$ = 5.6 Hz, 1 H, 7-H_b), 2.63 (ddd, $J_{1,5}$ = 5.5, $J_{1,7b}$ = 5.5, $J_{1,3}$ = 1.4 Hz, 1 H, 1-H), 3.15 (br. s, 1 H, OH, H/D), 3.81–3.88 [m, 2 H, CH_2O; after H/D exchange: 3.80 (d, *J* = 5.1 Hz)], 5.00–5.05 [m, 1 H, CHN; after H/D exchange: 5.05 (t, *J* = 5.0 Hz)], 6.40–6.48 (m, 1 H, C=CH), 6.57 (bd, *J* = 6.7 Hz, 1 H, NH, H/D), 7.28–7.38 (m, 5 H, Ph-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.98 (q, C-8), 25.95 (q, C-9), 31.42 (t, C-7), 31.77 (t, C-4), 37.79 (s, C-6), 40.40 (d, C-5), 41.92 (d, C-1), 56.01 (d, CHN), 66.49 (t, CH_2O), 126.67, 127.71, 128.80 (3d, Ph-C), 129.95 (d, C=*C*H), 139.39 (s, Ph-C), 143.32 (s, *C*=CH), 167.78 (s, C=O). $C_{18}H_{23}NO_2$ (285.42): calcd. C 75.74, H 8.14, N 4.91; found C 75.55, H 8.04, N 4.85.

(–)-2-[(1*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]-4,5-dihydro-1,3-oxazole (7a): According to GP 4, **6a** (7.10 g, 33.9 mmol) was converted into crude dihydrooxazole **7a** [TLC: PE/*i*PrOH, 9:1, R_f(**4b**) = 0.22, R_f(**7a**) = 0.49, R_f(*p*TsCl) = 0.58]. This was purified by flash chromatography (PE/ethyl acetate, 95:5, then 8:2) and kugelrohr distillation to give **7a** (5.31 g, 82%) as colorless oil. $[\alpha]_D^{21}$ = –26.5 (*c* = 1.61, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (s, 3 H, 8-H), 1.13 (d, $J_{7a,7b}$ = 9.0 Hz, 1 H, 7-H_a), 1.29 (s, 3 H, 9-H), 2.09–2.17 (m, 1 H, 5-H), 2.32–2.50 (m, 3 H, 4-H, 7-H_b), 2.80 (ddd, $J_{1,5}$ = 5.6, $J_{1,7b}$ = 5.6, $J_{1,3}$ = 1.2 Hz, 1 H, 1-H), 3.87 (t, *J* = 9.3 Hz, 2 H, CH_2N), 4.32 (t, *J* = 9.1 Hz, 2 H, CH_2O), 6.42–6.48 (m, 1 H, C=CH). ^{13}C NMR ($CDCl_3$): δ = 20.66 (q, C-8), 25.67 (q, C-9), 31.17 (t, C-7), 31.80 (t, C-4), 37.47 (s, C-6), 40.26 (d, C-5), 42.35 (d, C-1), 54.43 (t, CH_2N), 66.79 (t, CH_2O), 130.81 (d, C=*C*H), 136.42 (s, *C*=CH), 164.19 (s, C=N). $C_{12}H_{17}NO$ (191.30): calcd. C 75.34, H 8.98, N 7.32; found C 75.15, H 9.04, N 7.29.

(–)-2-[(1*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]-4,4-dimethyl-4,5-dihydro-1,3-oxazole (7b): According to GP 4, **6b** (3.40 g, 14.3 mmol) was converted into crude dihydrooxazole **7b** [TLC: PE/*i*PrOH, 95:5, R_f(**6b**) = 0.17, R_f(**7b**) = 0.40, R_f(*p*TsCl) = 0.51]. This was purified by flash chromatography (PE/$CHCl_3$, 6:4) and kugelrohr distillation to give **7b** (2.10 g, 68%) as colorless oil. $[\alpha]_D^{19}$ = –22.4 (*c* = 2.35, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (s, 3 H, 8-H), 1.13 (d, $J_{7a,7b}$ = 9.0 Hz, 1 H, 7-H_a), 1.23, 1.24 [2s, each 3 H, $NC(CH_3)_2$], 1.27 (s, 3 H, 9-H), 2.09–2.13 (m, 1 H, 5-H), 2.24–2.48 (m, 3 H, 4-H, 7-H_b), 2.81 (td, $J_{1,5}$ = 5.5, $J_{1,7b}$ = 5.5, $J_{1,3}$ = 1.5 Hz, 1 H, 1-H), 3.88 (s, 2 H, CH_2O), 6.37–6.39 (m, 1 H, C=CH). ^{13}C NMR ($CDCl_3$): δ = 20.57 (q, C-8), 25.61 (q, C-9), 28.09, 28.16 [2q, $NC(CH_3)_2$], 31.21 (t, C-7), 31.79 (t, C-4), 37.45 (s, C-6), 40.26 (d, C-5), 42.14 (d, C-1), 66.85 [s, $NC(CH_3)_2$], 78.23 (t, CH_2O), 130.48 (d, C=*C*H), 136.73 (s, *C*=CH), 161.48 (s, C=N). $C_{14}H_{21}NO$ (219.36): calcd. C 76.65, H 9.67, N 6.39; found C 76.45, H 9.83, N 6.24.

(+)-2-[(1*R*)-6,6-Dimethyl-bicyclo[3.1.1]hept-2-en-2-yl]-(4*R*)-phenyl-4,5-dihydro-1,3-oxazole (7c): According to GP 4, **6c** (1.60 g, 5.61 mmol) was converted into the dihydrooxazole **7c** [TLC: PE/*i*PrOH, 95:5, R_f(**6c**) = 0.20, R_f(**7c**) = 0.39, R_f(TsCl) = 0.51]. Flash chromatography (silica gel, PE/ethyl acetate, 95:5) and kugelrohr distillation yielded **7c** (1.12 g, 74%) as colorless oil. $[\alpha]_D^{19}$ = +50.3 (*c* = 0.96, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 3 H, 8-H), 1.20 (d, $J_{7a,7b}$ = 9.0 Hz, 1 H, 7-H_a), 1.33 (s, 3 H, 9-H), 2.14–2.21 (m, 1 H, 5-H), 2.38–2.56 (m, 3 H, 4-H, 7-H_b), 2.94 (ddd, $J_{1,5}$ = 5.5, $J_{1,7b}$ = 5.5, $J_{1,3}$ = 1.4 Hz, 1 H, 1-H), 4.11 (t, *J* = 8.2 Hz, 1 H, CH_2O), 4.64 (dd, *J* = 10.0, *J* = 8.1 Hz, 1 H, CH_2O), 5.23 (dd, *J* = 10.0, *J* = 8.1 Hz, 1 H, CHN), 6.58–6.60 (m, 1 H, C=CH), 7.20–7.38 (m, 5 H, Ph-H). ^{13}C NMR ($CDCl_3$): δ = 20.97 (q, C-8), 25.90 (q, C-9), 31.52 (t, C-7), 32.21 (t, C-4), 37.79 (s, C-6), 40.52 (d, C-5), 42.62 (d, C-1), 69.96 (d, CHN), 74.34 (t, CH_2O), 126.77, 127.48, 128.66 (3d, Ph-C), 131.81 (d, C=*C*H), 136.69 (s, *C*=CH), 142.57 (s, Ph-C), 164.41 (s, C=N). $C_{18}H_{21}NO$ (267.40): calcd. C 80.85, H 7.93, N 5.24; found C 80.83, H 7.92, N 5.28.

(–)-2-[(1*R*)-6,6-Dimethyl-bicyclo[3.1.1]hept-2-en-2-yl]-(4*S*)-phenyl-4,5-dihydro-1,3-oxazole (7d): According to GP 4, **6d** (18.3 g, 64.1 mmol) was converted into the dihydrooxazole **7d** [TLC: PE/*i*PrOH, 95:5, R_f(**6d**) = 0.21, R_f(**7d**) = 0.39, R_f(*p*TsCl) = 0.51]. Flash chromatography (silica gel, PE/ethyl acetate, 95:5) yielded **7d** (14.2 g, 83%) as crystalline compound. M. p. 70–71 °C. $[\alpha]_D^{21}$ = –119.1 (*c* = 1.27, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (s, 3 H, 8-H), 1.23 (d, $J_{7a,7b}$ = 9.0 Hz, 1 H, 7-H_a), 1.33 (s, 3 H, 9-H), 2.13–2.20 (m, 1 H, 5-H), 2.38–2.55 (m, 3 H, 4-H, 7-H_b), 2.94 (ddd, $J_{1,5}$ = 5.5, $J_{1,7b}$ = 5.5, $J_{1,3}$ = 1.4 Hz, 1 H, 1-H), 4.11 (t, *J* = 8.3, 1 H, CH_2O), 4.64 (dd, *J* = 10.0, *J* = 8.3 Hz, 1 H, CH_2O), 5.23 (t, *J* = 9.0 Hz, 1 H, CHN), 6.63–6.70 (m, 1 H, C=CH), 7.23–7.39 (m, 5 H, Ph-H). ^{13}C NMR ($CDCl_3$): δ = 20.97 (q, C-8), 25.90 (q, C-9), 31.52 (t, C-7), 32.21 (t, C-4), 37.79 (s, C-6), 40.52 (d, C-5), 42.62 (d, C-1), 69.96 (d, CHN), 74.34 (t, CH_2O), 126.77, 127.48, 128.66 (3d, Ph-C), 131.81 (d, C=*C*H), 136.69 (s, *C*=CH), 142.57 (s, Ph-C), 164.41 (s, C=N). $C_{18}H_{21}NO$ (267.40): calcd. C 80.85, H 7.93, N 5.24; found C 80.74, H 7.66, N 5.26.

(–)-(1*S*,2*R*,3*S*)-Methyl 3-(Boranatodiphenylphosphanyl)-6,6-dimethylbicyclo[3.1.1]heptane-2-carboxylate (9a·BH_3): A solution of **4a** (9.00 g, 50.0 mmol) in degassed THF (75 mL) was reacted with diphenylphosphane (**8a**) (18.64 g, 100.0 mmol) according to GP 1 (reaction time: 30 min). Conversion was monitored by TLC [PE/ethyl acetate, 98:2, R_f(**4**) = 0.20, R_f(**9a**) = 0.14]. The mixture was cooled to –78 °C, BH_3·THF (1 M in THF, 150 mL, 150 mmol) was added and conversion was monitored by TLC [PE/ethyl acetate, 95:5, R_f(**9a**) = 0.23, R_f(**9a**·BH_3) = 0.15]. The mixture was allowed to warm to room temperature and excess borane was hydrolyzed by addition of 1 N HCl (150 mL). The mixture was then extracted with diethyl ether, the organic layer dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, PE/ethyl acetate/CH_2Cl_2, 85:7.5:7.5) to give **9a**·BH_3 (14.0 g, 74%) as colorless needles. M. p. 119–120 °C. $[\alpha]_D^{20}$ = –84.4 (*c* = 1.77, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (s, 3 H, 8-H), 1.17 (s, 3 H, 9-H), 1.58 (ddd, $J_{7a,7b}$ = 9.9, *J* = 3.5, *J* = 3.5, 1 H, 7-H_a), 1.90 (m, 1 H, 5-H), 1.98–2.17 (m, 2 H, 4-

H), 2.30–2.34 (m, 2 H, 1-H, 7-Hb), 3.22 (ddd, $J_{2,P}$ = 20.2, J = 6.8, J = 2.0 Hz, 1 H, C*H*COOCH$_3$), 3.23 (s, 3 H, COOCH$_3$), 4.00 (m, 1 H, CHP), 7.28–7.41 (m, 3 H, Ar-H), 7.44–7.54 (m, 3 H, Ar-H), 7.63–7.75 (m, 2 H, Ar-H), 7.93–7.99 (m, 2 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 21.82 (q, C-8), 22.87 [dd, J(C,P) = 36.1 Hz, CHP], 27.06 (q, C-9), 27.86 (td, $J_{C,P}$ = 3.3 Hz, C-4), 29.61 (t, C-7), 38.99 (s, C-6), 40.47 (dd, $J_{C,P}$ = 4.4 Hz, C-1 or C-2 or C-5), 44.30 (dd, $J_{C,P}$ = 5.2 Hz, C-1 or C-2 or C-5), 45.22 (dd, $J_{C,P}$ = 4.4 Hz, C-1 or C-2 or C-5), 51.57 (q, COO*C*H$_3$), 127.86 (d, $J_{C,P}$ = 58 Hz, Ar-C), 128.05–133.41 (10 Ar-C), 174.64 (d, $J_{C,P}$ = 2.7 Hz, *C*OOCH$_3$). ^{31}P NMR ($CHCl_3$): δ = +27. ^{11}B NMR ($CDCl_3$): δ = –39. $C_{23}H_{30}O_2PB$ (380.28): calcd. C 72.65, H 7.95, P 8.15; found C 72.68, H 8.01, P 8.18.

(–)-(1*S*,2*R*,3*S*)-*tert*-Butyl 3-(Boranatodiphenylphosphanyl)-6,6-dimethylbicyclo[3.1.1]heptane-2-carboxylate (9b·BH$_3$): All reagents and solvents were carefully dried and degassed. Under nitrogen, a solution of *n*BuLi (1.6 M solution in *n*-hexane, 91 mL, 145 mmol) was added dropwise over a period of 20 min to a stirred solution of diphenylphosphane (**8a**) (27.9 g, 150 mmol) in THF (250 mL) cooled to –78 °C. The mixture was allowed to warm up to room temperature and was 15 min later cooled again to –78 °C. The resultant cold, dark red solution was dropped via double-ended needle transfer into a cooled (–78 °C) solution of ester **4b** (30.0 g, 135 mmol) in THF (300 mL). Conversion was monitored by TLC [PE/ethyl acetate, 98:2, R_f(**4b**) = 0.23, R_f(**9b**) = 0.20]. The mixture was stirred for 30 min at –78 °C and was then treated with a cold (–20 °C) solution of methanol (9.0 g, 281 mmol) in THF (100 mL). The cooling bath was removed for 20 min and then the mixture was again cooled to –78 °C and dropwise treated with BH$_3$·THF (1 M solution in THF, 400 mL, 400 mmol) (ATTENTION: gas evolution). The mixture was then stirred for 1 h at –78 °C and 2 h at 0 °C. TLC showed that conversion was complete [PE/ethyl acetate, 95:5, R_f(HPPh·BH$_3$) = 0.33, R_f(**9b**·BH$_3$) = 0.39]. Excess borane was destroyed by cautious addition of 1 N HCl (ca. 300 mL) at 0 °C (ATTENTION: gas evolution). The mixture was extracted with diethyl ether and the organic layer washed with 1 N HCl, sat. $NaHCO_3$ solution and sat NaCl solution, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, PE/ethyl acetate/CH_2Cl_2, 85:7.5:7.5) to give **9b**·BH$_3$ (41.2 g, 72%) as colorless glassy solid. $[\alpha]_D^{20}$ = –85 (c = 1.4, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (s, 3 H, 8-H), 1.12 [s, 9 H, C(C*H*$_3$)$_3$], 1.17 (s, 3 H, 9-H), 1.64 (d, $J_{7a,7b}$ = 10.0 Hz, 1 H, 7-H$_a$), 1.90 (m, 1 H, 5-H), 1.96–2.14 (m, 2 H, 4-H), 2.24–2.34 (m, 2 H, 1-H, 7-H$_b$), 3.10 (ddd, $J_{2,P}$ = 20.8, J = 6.3, J = 2.6 Hz, 1 H, C*H*COO*t*Bu), 4.05 (m, 1 H, CHP), 7.27–7.37 (m, 3 H, Ar-H), 7.46–7.51 (m, 3 H, Ar-H), 7.70–7.76 (m, 2 H, Ar-H), 7.94–8.00 (m, 2 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 21.74 (dd, $J_{C,P}$ = 36.7 Hz, CHP), 21.80 (q, C-8), 27.19 (q, C-9), 27.73 [q, C(*C*H$_3$)$_3$], 27.83 (td, $J_{C,P}$ = 3.9 Hz, C-4), 29.06 (t, C-7), 39.09 (s, C-6), 40.38 (dd, $J_{C,P}$ = 4.0 Hz, C-1 or C-2 or C-5), 44.49 (dd, $J_{C,P}$ = 4.5 Hz, C-1 or C-2 or C-5), 45.76 (dd, $J_{C,P}$ = 4.5 Hz, C-1 or C-2 or C-5), 80.34 [s, *C*(CH$_3$)$_3$], 127.81–133.53 (12 Ar-C), 173.28 (d, $J_{C,P}$ = 2.9 Hz, *C*OO*t*Bu). ^{31}P NMR ($CDCl_3$): δ = +26.5. ^{11}B NMR ($CDCl_3$): δ = –39.5. HR-MS (EI+) $C_{26}H_{33}O_2P$ (M^+ – BH$_3$) calcd. 408.2218; found 408.2239.

(–)-(1*S*,2*R*,3*S*)-3-(Boranatodiphenylphosphanyl)-6,6-dimethylbicyclo[3.1.1]heptane-2-carboxylic Acid (10·BH$_3$): All operations were carried out under strict exclusion of oxygen. A solution of **9b**·BH$_3$ (30.8 g, 73.0 mmol) in degassed trifluoroacetic acid (120 mL) was stirred at room temperature for 1 h while strong evolution of gas occurred. The solvent was removed in vacuo (0.01 Torr) and the residue was dissolved in diethyl ether (100 mL). At 0 °C first 2 M KOH (40 mL) was added and then solid KOH until the mixture was alkaline (ATTENTION: gas evolution). After 40 min the reaction mixture was extracted thrice with diethyl ether. The combined organic layers were washed with water, dried over Na_2SO_4 and filtered. The filtrate was cooled to –78 °C and treated with BH$_3$·THF (1 M in THF) (220 mL, 220 mmol). After stirring for 1 h 1 N HCl (200 mL) was added and stirring was continued until gas evolution ceased. The aqueous layer was removed and extracted with diethyl ether. The combined organic phases were washed with water to remove HCl, dried and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, PE/ethyl acetate/CH_2Cl_2, 84:8:8) to give **10**·BH$_3$ (19.6 g, 75%) as colorless needles.[26] M.p. 172–173.5 °C. $[\alpha]_D^{20}$ = –99.2 (c, 2.11, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50–1.50 (br. s, 3 H, BH$_3$), 0.90 (s, 3 H, 8-H), 1.17 (s, 3 H, 9-H), 1.60 (d, J = 10.4 Hz, 1 H, 7-H$_a$), 1.89–1.95 (m, 1 H, 5-H), 1.91–2.21 (m, 2 H, 4-H), 2.28–2.38 (m, 1 H, 7-H$_b$), 2.40–2.47 (m, 1 H, 1-H), 3.19 (ddd, $J_{2,P}$ = 20.2, J = 6.4, J = 2.7 Hz, 1 H, 2-H), 3.84–3.98 (m, 1 H, CHP), 7.24–7.37 (m, 3 H, Ph-H$_{m,p}$), 7.48–7.58 (m, 3 H, Ph-H$_{m,p}$), 7.67–7.76 (m, 2 H, Ph-H$_o$), 7.91–8.00 (m, 2 H, Ph-H$_o$), 9.70 (br. s, 1 H, COOH, H/D). ^{13}C NMR ($CDCl_3$): δ = 21.35 (q, C-8), 22.03 (d, $J_{C,P}$ = 36.1 Hz, CHP), 26.62 (q, C-9), 27.59 (td, $J_{C,P}$ = 3.4 Hz, C-4), 28.81 (t, C-7), 38.81 (s, C-6), 39.95 (dd, $J_{C,P}$ = 4.0 Hz, C-5), 43.92 (dd, $J_{C,P}$ = 4.5 Hz, C-1), 44.32 (dd, $J_{C,P}$ = 4.0 Hz, C-2), 127.42 (dd, $J_{C,P}$ = 55.4 Hz, Ph-C$_i$), 127.90 (d, $J_{C,P}$ = 9.6 Hz, Ph-C$_m$), 128.05 (d, $J_{C,P}$ = 52.0 Hz, Ph-C$_i$), 128.68 (dd, $J_{C,P}$ = 9.6 Hz, Ph-C$_m$), 130.92 (dd, $J_{C,P}$ = 2.8 Hz, Ph-C$_p$), 131.27 (dd, $J_{C,P}$ = 2.2 Hz, Ph-C$_p$), 132.82 (dd, $J_{C,P}$ = 8.5 Hz, Ph-C$_o$), 133.98 (dd, $J_{C,P}$ = 8.5 Hz, Ph-C$_o$), 179.87 (d, $J_{C,P}$ = 3.4 Hz, C=O). ^{31}P NMR ($CDCl_3$): δ = +27.3. ^{11}B NMR ($CDCl_3$, 64.21 MHz): δ = –39.9. $C_{22}H_{28}O_2PB$ (366.25): calcd. C 72.15, H 7.70, P 8.46; found C 71.93, H 7.88, P 8.23.

(–)-(1*S*,2*R*,3*S*)-3-Diphenylphosphanyl-6,6-dimethylbicyclo[3.1.1]heptane-2-carbonitrile (11): Nitrile **2** [11.1 g (75.4 mmol)] was reacted with diphenylphosphane according to GP2 [TLC: PE/ethyl acetate, 9:1, R_f(**2**) = 0.43, R_f(**11**) = 0.31, R_f(HPPh$_2$) = 0.66]. After work-up nitrile **11** was obtained as an oil which slowly solidified (21.0 g, 84%). M.p. 56.5–58.0 °C. $[\alpha]_D^{22}$ = –50.9 (c = 1.78, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28, 1.30 (2s, each 3 H, 8-H, 9-H), 1.43 (d, $J_{7a,7b}$ = 10.4 Hz, 1 H, 7-H$_a$), 1.78 (dddd, J = 18.7, J = 14.0, J = 4.1, J = 4.1 Hz, 1 H, 4-H$_a$), 1.94–2.00 (m, 1 H, 5-H), 2.20–2.37 (m, 3 H, 1-H, 4-H$_b$, 7-H$_b$), 2.96 (ddd, $J_{2,P}$ = 14.5, J = 5.2, J = 2.7 Hz, 1 H, 2-H), 3.03–3.13 (m, 1 H, CHP), 7.34–7.39 (m, 6 H, Ph-H$_{m,p}$), 7.54–7.67 (m, 4 H, Ph-H$_o$). ^{13}C NMR ($CDCl_3$): δ = 21.69 (q, C-8), 26.11 (q, C-9), 26.73 (dd, $J_{C,P}$ = 11.5 Hz, CHP), 28.58 (td, $J_{C,P}$ = 2.0 Hz, C-7), 30.60 (td, $J_{C,P}$ = 18.3 Hz, C-4), 33.11 (dd, $J_{C,P}$ = 23.7 Hz, C-2), 38.20 (d, $J_{C,P}$ = 1.4 Hz, C-6), 40.01 (dd, $J_{C,P}$ = 2.0 Hz, C-5), 43.80 (dd, $J_{C,P}$ = 2.0 Hz, C-1), 122.76 (d, $J_{C,P}$ = 4.8 Hz, CN), 128.61 (dd, $J_{C,P}$ = 6.8 Hz, Ph-C$_m$), 128.71 (dd, $J_{C,P}$ = 7.5 Hz, Ph-C$_m$), 129.15 (d, Ph-C$_p$), 129.87 (dd, $J_{C,P}$ = 1.2 Hz, Ph-C$_p$), 133.29 (dd, $J_{C,P}$ = 19.0 Hz, Ph-C$_o$), 134.02 (d, $J_{C,P}$ = 20.3 Hz, Ph-C$_o$), 135.66 (d, $J_{C,P}$ = 15.6 Hz, Ph-C$_i$), 136.05 (d, $J_{C,P}$ = 13.5 Hz, Ph-C$_i$). ^{31}P NMR ($CDCl_3$): δ = +6.1 (**11**), δ = +34.9 (**11**-oxide). $C_{22}H_{24}NP$ (333.44): calcd. C 79.24, H 7.27, N 4.20, P 9.29; found C 78.96, H 7.23, N 4.14, P 9.12.

(–)-(1*S*,2*R*,3*S*)-*N*,*N*,6,6-Tetramethyl-3-diphenylphosphanylbicyclo[3.1.1]heptane-2-carboxamide (12): Amide **5** (5.00 g, 25.9 mmol) was reacted with diphenylphosphane according to GP 2. In the course of the reaction the product precipitated and a thick suspension formed. For work-up, the reaction mixture was concentrated to about 1/4 of its original volume and the remaining solvent was removed with a syringe. The crystalline residue was suspended in CH_3CN (3 × 5 mL) and the washing liquid removed each time with a syringe. The residue was dissolved in CH_2Cl_2 and the solution treated as described in GP 2. Crystallization from CH_3CN gave **12**

(5.61 g, 61%) as colorless needles. M.p. 158–160 °C. $[\alpha]_D^{21}$ = –124.5 (*c* = 1.94, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (s, 3 H, 8-H), 1.14 (s, 3 H, 9-H), 1.24 (d, $J_{7a,7b}$ = 9.9 Hz, 1 H, 7-H_a), 1.83 (dddd, *J* = 19.9, *J* = 14.0, *J* = 5.5, *J* = 3.0 Hz, 1 H, 4-H_a), 1.96–2.60 (m, 2 H, 1-H, 5-H), 2.34–2.43 (m, 2 H, 4-H_b, 7-H_b), 2.42, 2.55 [2bs, each 3 H, N(CH_3)$_2$], 2.98 (ddd, $J_{2,P}$ = 16.5, *J* = 6.5, *J* = 1.8 Hz, 1 H, 2-H), 3.86–3.97 (m, 1 H, CHP), 7.20–7.25 (m, 3 H, Ph-$H_{m,p}$), 7.30–7.40 (m, 3 H, Ph-$H_{m,p}$), 7.49–7.58 (m, 2 H, Ph-H_o), 7.63–7.70 (m, 2 H, Ph-H_o). ^{13}C NMR ($CDCl_3$): δ = 22.43 (q, C-8), 23.55 (dd, $J_{C,P}$ = 5.5 Hz, CHP), 27.58 (q, C-9), 31.48 (td, $J_{C,P}$ = 22.1 Hz, C-4), 31.90 (t, C-7), 35.51, 36.33 [2bq, N(CH_3)$_2$], 38.83 (d, $J_{C,P}$ = 1.7 Hz, C-6), 41.51 (dd, $J_{C,P}$ = 4.0 Hz, C-5), 44.19 (dd, $J_{C,P}$ = 4.5 Hz, C-1), 46.73 (dd, $J_{C,P}$ = 20.3 Hz, C-2), 127.29 (dd, $J_{C,P}$ = 7.9 Hz, Ph-C_m), 128.11 (dd, $J_{C,P}$ = 6.8 Hz, Ph-C_m), 128.49 (d, Ph-C_p), 128.85 (dd, $J_{C,P}$ = 1.1 Hz, Ph-C_p), 133.09 (dd, $J_{C,P}$ = 18.1 Hz, Ph-C_o), 134.65 (dd, $J_{C,P}$ = 20.3 Hz, Ph-C_o), 137.11 (d, $J_{C,P}$ = 15.8 Hz, Ph-C_i), 137.31 (d, $J_{C,P}$ = 14.1 Hz, Ph-C_i), 172.80 (d, $J_{C,P}$ = 2.3 Hz, C=O). ^{31}P NMR ($CDCl_3$): δ = +8.1 (**12**), δ = +35.8 (**12**-oxide). $C_{24}H_{30}NOP$ (379.52): calcd. C 75.95, H 7.98, N 3.69, P 8.16; found C 75.89, H 7.99, N 3.61, P 8.20.

(–)-2-[(1*S*,2*R*,3*S*)-3-Diphenylphosphanyl-6,6-dimethylbicyclo[3.1.1]-hept-2-yl]-4,5-dihydro-1,3-oxazole (13a): Dihydrooxazole **7a** (2.75 g, 14.4 mmol) was reacted with diphenylphosphane according to GP 2. Under argon, the crude oil obtained after work-up was dissolved in diethyl ether and filtered. The product crystallized upon standing at 5 °C for several days to give **13a** (3.30 g, 58%) as large, octahedral crystals. M.p. 102–104 °C. $[\alpha]_D^{21}$ = –88.7 (*c* = 1.76, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (s, 3 H, 8-H), 1.15 (s, 3 H, 9-H), 1.36 (d, $J_{7a,7b}$ = 8.8 Hz, 1 H, 7-H_a), 1.80 (dddd, *J* = 18.2, *J* = 14.2, *J* = 4.1, *J* = 4.1 Hz, 1 H, 4-H_a), 1.92–1.98 (m, 1 H, 5-H), 2.27–2.43 (m, 3 H, 1-H, 4-H_b, 7-H_b), 2.84–2.96 (m, 1 H, 2-H), 3.26–3.39 (m, 1 H, CH_2N), 3.49–3.61 (m, 1 H, CH_2N), 3.63–3.73 (m, 1 H, CHP), 3.78 (td, *J* = 10.5, *J* = 8.1 Hz, 1 H, CH_2O), 3.91 (td, *J* = 10.3, *J* = 8.0 Hz, 1 H, CH_2O), 7.18–7.25 (m, 3 H, Ph-$H_{m,p}$), 7.30–7.41 (m, 3 H, Ph-$H_{m,p}$), 7.50–7.57 (m, 2 H, Ph-H_o), 7.64–7.71 (m, 2 H, Ph-H_o). ^{13}C NMR ($CDCl_3$): δ = 21.54 (q, C-8), 24.19 (dd, $J_{C,P}$ = 8.5 Hz, CHP), 26.98 (q, C-9), 29.73 (td, $J_{C,P}$ = 1.7 Hz, C-7), 30.94 (td, $J_{C,P}$ = 18.0 Hz, C-4), 38.79 (d, $J_{C,P}$ = 2.2 Hz, C-6), 41.00 (dd, $J_{C,P}$ = 2.2 Hz, C-5), 43.00 (dd, $J_{C,P}$ = 20.8 Hz, C-2), 43.96 (dd, $J_{C,P}$ = 4.0 Hz, C-1), 53.75 (t, CH_2N), 66.59 (t, CH_2O), 127.41 (dd, $J_{C,P}$ = 7.4 Hz, Ph-C_m), 128.32 (dd, $J_{C,P}$ = 6.8 Hz, Ph-C_m), 128.69 (dd, $J_{C,P}$ = 1.1 Hz, Ph-C_p), 128.79 (d, Ph-C_p), 133.75 (dd, $J_{C,P}$ = 18.6 Hz, Ph-C_o), 134.64 (dd, $J_{C,P}$ = 19.2 Hz, Ph-C_o), 136.84 (d, $J_{C,P}$ = 13.5 Hz, Ph-C_i), 137.40 (d, $J_{C,P}$ = 16.4 Hz, Ph-C_i), 169.91 (d, $J_{C,P}$ = 4.0 Hz, C=N). ^{31}P NMR($CDCl_3$): δ = +7.8 (**13a**), δ = +36.6 (**13a**-oxide). $C_{24}H_{28}NOP$ (377.50): calcd. C 76.35, H 7.49, N 3.71, P 8.20; found C 76.21, H 7.52, N 3.61, P 8.10.

(–)-2-[(1*S*,2*R*,3*S*)-3-Diphenylphosphanyl-6,6-dimethylbicyclo-[3.1.1]hept-2-yl]-4,4-dimethyl-4,5-dihydro-1,3-oxazole (13b): Dihydrooxazole **7b** (3.82 g, 17.4 mmol) was reacted with diphenylphosphane according to GP 2. The oil obtained after work-up crystallized upon standing. The product was purified by suspending the crystals at –78 °C under argon in a small amount of *n*-hexane. The residue was dissolved in diethyl ether, filtered and the solvent was removed to give **13b** (4.33 g, 61%) as needles. M.p. 91–92 °C. $[\alpha]_D^{20}$ = –77.8 (*c* = 2.62, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 [s, 3 H, NC(CH_3)$_2$], 0.99 (s, 3 H, 8-H), 1.07 [s, 3 H, NC(CH_3)$_2$], 1.16 (s, 3 H, 9-H), 1.55 (d, $J_{7a,7b}$ = 9.5 Hz, 1 H, 7-H_a), 1.78 (dddd, *J* = 20.2, *J* = 14.0, *J* = 3.7, *J* = 3.7 Hz, 1 H, 4-H_a), 1.92–1.98 (m, 1 H, 5-H), 2.27–2.43 (m, 3 H, 1-H, 4-H_b, 7-H_b), 2.92 (ddd, $J_{2,P}$ = 17.6 Hz *J* = 4.8 Hz *J* = 2.6 Hz, 1 H, 2-H), 3.48 (d, *J* = 7.7 Hz, 1 H, CH_2O), 3.62 (d, *J* = 7.7 Hz, 1 H, CH_2O), 3.60–3.74 (m, 1 H, CHP), 7.18–7.25 (m, 3 H, Ph-$H_{m,p}$), 7.30–7.41 (m, 3 H, Ph-$H_{m,p}$), 7.55–7.62 (m, 2 H, Ph-H_o), 7.64–7.71 (m, 2 H, Ph-H_o). ^{13}C NMR ($CDCl_3$): δ = 21.80 (q, C-8), 23.35 (dd, $J_{C,P}$ = 7.9 Hz, CHP), 26.85 (q, C-9), 27.46, 27.49 [2q, NC(CH_3)$_2$], 28.70 (td, $J_{C,P}$ = 2.8 Hz, C-7), 30.70 (td, $J_{C,P}$ = 18.1 Hz, C-4), 38.81 (d, $J_{C,P}$ = 2.3 Hz, C-6), 40.95 (dd, $J_{C,P}$ = 2.2 Hz, C-5), 42.88 (dd, $J_{C,P}$ = 20.4 Hz, C-2), 44.14 (dd, $J_{C,P}$ = 3.4 Hz, C-1), 66.46 [s, NC(CH_3)$_2$], 78.63 (t, CH_2O), 127.55 (dd, $J_{C,P}$ = 7.4 Hz, Ph-C_m), 128.24 (dd, $J_{C,P}$ = 6.8 Hz, Ph-C_m), 128.49 (d, Ph-C_p), 128.85 (dd, $J_{C,P}$ = 1.1 Hz, Ph-C_p), 133.81 (dd, $J_{C,P}$ = 18.6 Hz, Ph-C_o), 134.70 (d, $J_{C,P}$ = 19.2 Hz, Ph-C_o), 137.20 (d, $J_{C,P}$ = 13.5 Hz, Ph-C_i), 137.48 (d, $J_{C,P}$ = 17.0 Hz, Ph-C_i), 167.39 (d, $J_{C,P}$ = 5.0 Hz, C=N). ^{31}P NMR ($CDCl_3$): δ = +9.6 (**13b**), δ = +37.5 (**13b**-oxide). $C_{26}H_{32}NOP$ (405.56): calcd. C 76.99, H 7.97, N 3.45, P 7.64; found C 76.81, H 7.94, N 2.32, P 7.71.

(–)-2-[(1*S*,2*R*,3*S*)-Diphenylphosphanyl-6,6-dimethylbicyclo[3.1.1]-hept-2-yl]-(4*R*)-phenyl-4,5-dihydro-1,3-oxazol (13c): Dihydrooxazole **7c** (2.90 g, 10.8 mmol) was reacted with diphenylphosphane according to GP 2. In the course of the reaction the product precipitated and acetonitrile (15 mL) was added to allow stirring. The solid obtained after work-up (ca. 4.3 g) was suspended in *n*-hexane (20 mL) under reflux, followed by slow addition of ethyl acetate until a clear solution was obtained. Upon slow cooling in an oil bath 2.60 g of **13c** precipitated. Further crystallization from the mother liquid yielded additional 1.31 g of **13c** (80% overall yield) as thick needles. M.p. 118–120 °C. $[\alpha]_D^{20}$ = –47.6 (*c* = 0.90, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (s, 3 H, 8-H), 1.21 (s, 3 H, 9-H), 1.69 (d, $J_{7a,7b}$ = 10.1 Hz, 1 H, 7-H_a), 1.83 (dddd, *J* = 19.8, *J* = 14.0, *J* = 3.7, *J* = 3.7 Hz, 1 H, 4-H_a), 1.96–2.03 (m, 1 H, 5-H), 2.28–2.55 (m, 3 H, 1-H, 4-H_b, 7-H_b), 3.08–3.19 (m, 1 H, 2-H), 3.73 (dd, *J* = 9.6, *J* = 8.3 Hz, 1 H, CH_2O), 3.76–3.86 (m, 1 H, CHP), 4.39 (dd, *J* = 9.9, *J* = 8.4 Hz, 1 H, CH_2O), 4.97 (t, *J* = 9.8 Hz, 1 H, CHN), 6.89–6.94 (m, 2 H, Ph-H), 7.17–7.33 (m, 6 H, Ph-H), 7.34–7.42 (m, 3 H, Ph-H), 7.56–7.66 (m, 2 H, Ph-H_o), 7.68–7.72 (m, 2H Ph-H_o). ^{13}C NMR ($CDCl_3$): δ = 21.21 (q, C-8), 23.81 (dd, $J_{C,P}$ = 9.0 Hz, CHP), 26.83 (q, C-9), 28.25 (td, $J_{C,P}$ = 4.5 Hz, C-7), 30.65 (td, $J_{C,P}$ = 17.0 Hz, C-4), 38.78 (d, $J_{C,P}$ = 2.3 Hz, C-6), 40.82 (dd, $J_{C,P}$ = 1.7 Hz, C-5), 42.35 (dd, $J_{C,P}$ = 20.4 Hz, C-2), 44.27 (dd, $J_{C,P}$ = 2.8 Hz, C-1), 69.41 (d, CHN), 74.26 (t, CH_2O), 126.81, 127.21 (2d, Ph-C), 127.99 (dd, $J_{C,P}$ = 6.8 Hz, Ph-C_m), 128.32 (dd, $J_{C,P}$ = 6.8 Hz, Ph-C_m), 128.49 (d, Ph-C), 128.75 (dd, $J_{C,P}$ = 1.1 Hz, Ph-C_p), 128.80 (d, Ph-C_p), 133.93 (d, $J_{C,P}$ = 18.6 Hz, Ph-C_o), 134.50 (dd, $J_{C,P}$ = 19.8 Hz, Ph-C_o), 137.11 (d, $J_{C,P}$ = 13.6 Hz, Ph-C_i), 137.58 (d, $J_{C,P}$ = 17.5 Hz, Ph-C_i), 142.00 (s, Ph-C), 170.98 (d, $J_{C,P}$ = 5.6 Hz, C=N). ^{31}P NMR ($CDCl_3$): δ = +9.2 (**13c**), δ = +37.8 (**13c**-oxide). $C_{30}H_{32}NOP$ (453.60): calcd. C 79.43, H 7.13, N 3.09, P 6.83; found C 79.21, H 7.22, N 3.03, P 6.76.

(–)-2-[(1*S*,2*R*,3*S*)-3-Diphenylphosphanyl-6,6-dimethylbicyclo-[3.1.1]hept-2-yl]-(4*S*)-phenyl-4,5-dihydro-1,3-oxazole (13d): Dihydrooxazole **7d** (390 mg, 1.46 mmol) was reacted with diphenylphosphane according to GP 2. After work-up, an oily mixture of diastereomers, **13c/13d** = 20:1 (398 mg, 60%) was obtained. $[\alpha]_D^{20}$ = –47.4 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (s, 3 H, 8-H), 1.20 (s, 3 H, 9-H), 1.42 (d, $J_{7a,7b}$ = 9.6 Hz, 1 H, 7-H_a), 1.78–1.88 (m, 1 H, 4-H_a), 1.96–2.03 (m, 1 H, 5-H), 2.33–2.53 (m, 3 H, 1-H, 4-H_b, 7-H_b), 2.93–3.37 (m, 1 H, 2-H), 3.65 (t, *J* = 8.5 Hz, 1 H, CH_2O), 3.73–3.86 (m, 1 H, CHP), 4.15 (dd, *J* = 10.3, *J* = 8.1 Hz, 1 H, CH_2O), 4.60–4.69 (m, 1 H, CHN), 7.04–7.08 (m, 2 H, Ph-H), 7.24–7.40 (m, 9 H, Ph-H), 7.58–7.64 (m, 2 H, Ph-H), 7.66–7.71 (m, 2 H, Ph-H). ^{13}C NMR ($CDCl_3$): δ = 22.15 (q, C-8), 24.17 (dd, $J_{C,P}$ = 8.4 Hz, CHP), 27.11 (q, C-9), 30.06 (td, $J_{C,P}$ = 2.2 Hz, C-7), 31.20 (td, $J_{C,P}$ = 18.6 Hz, C-4), 39.06 (d, $J_{C,P}$ = 2.2 Hz, C-6), 41.34 (dd, $J_{C,P}$ = 1.7 Hz, C-5), 43.51 (dd, $J_{C,P}$ = 20.9 Hz, C-2), 44.58 (dd, $J_{C,P}$ = 3.4 Hz, C-1), 69.64 (d, CHN), 74.07 (t,

CH_2O), 126.80, 127.34 (2d, Ph-C), 127.50 (dd, $J_{C,P}$ = 7.4 Hz, Ph-C_m), 128.34 (dd, $J_{C,P}$ = 6.8 Hz, Ph-C_m), 128.51 (d, Ph-C), 128.80 (d, Ph-C_p), 128.86 (dd, $J_{C,P}$ = 1.1 Hz, Ph-C_p), 133.73 (dd, $J_{C,P}$ = 18.6 Hz, Ph-C_o), 134.96 (dd, $J_{C,P}$ = 19.8 Hz, Ph-C_o), 137.02 (d, $J_{C,P}$ = 14.1 Hz, Ph-C_i), 137.42 (d, $J_{C,P}$ = 17.0 Hz, Ph-C_i), 142.46 (s, Ph-C), 170.63 (d, $J_{C,P}$ = 3.4 Hz, C=N). ^{31}P NMR ($CDCl_3$): δ = +8.5 (**13d**), δ +36.3 (**13d**-oxide). $C_{30}H_{32}NOP$ (453.60): calcd. C 79.43, H 7.13, N 3.09, P 6.83; found C 79.41, H 7.14, N 3.05, P 6.67.

(–)-(1*R*)-3-(Boranatodiphenylphosphanyl)-6,6-dimethylbicyclo-[3.1.1]heptane-2-carboxamide (14·BH$_3$): Oxalyl chloride (320 mg, 2.52 mmol) was added dropwise to a cold (–20 °C) solution of **10**·BH_3 (780 mg, 2.13 mmol) and 3 drops of anhydrous DMF in anhydrous toluene (5 mL). The mixture was allowed to warm to r. t. and stirred for 3 h. Residual oxalyl chloride and the solvent were removed in vacuo. The crude acid chloride was dissolved in anhydrous dioxane (10 mL) and dry NH_3 gas was introduced under cooling with an ice-water bath. The solvent was removed and the residue suspended in PE/ethyl acetate/*i*PrOH, 2:1:1. After filtration the solvent was removed. The product was purified by flash chromatography (silica gel, PE/ethyl acetate/*i*PrOH, 90:5:5) to give **14**·BH_3 (700 mg, 90%) as a colorless solid. M.p. 139–142 °C. $[\alpha]_D^{20}$ = –77.3 (*c* = 19.9, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50–1.50 (br. s, 3 H, BH_3), 1.02 (s, 3 H, 8-H), 1.17 (s, 3 H, 9-H), 1.64 (d, $J_{7a,7b}$ = 10.3 Hz, 1 H, 7-H_a), 1.91–1.97 (m, 1 H, 5-H), 2.01–2.20 (m, 3 H, 1-H, 4-H), 2.29–2.38 (m, 1 H, 7-H_b), 3.04 (ddd, $J_{2,P}$ = 20.6, *J* = 6.6, *J* = 2.6 Hz, 1 H, 2-H), 4.18–4.35 (m, 1 H, CHP), 4.80, 4.94 (2bs, 2 H, NH_2, H/D), 7.30–7.44 (m, 3 H, Ph-$H_{m,p}$), 7.48–7.55 (m, 3 H, Ph-$H_{m,p}$), 7.76–7.85 (m, 2 H, Ph-H_o), 7.94–8.02 (m, 2 H, Ph-H_o). ^{13}C NMR ($CDCl_3$): δ = 21.31 (dd, $J_{C,P}$ = 36.8 Hz, CHP), 21.76 (q, C-8), 27.11 (qd, $J_{C,P}$ = 1.2 Hz, C-9), 27.53 (td, $J_{C,P}$ = 3.4 Hz, C-4), 29.58 (t, C-7), 39.00 (s, C-6), 40.28 (dd, $J_{C,P}$ = 4.5 Hz, C-5), 45.68 (dd, $J_{C,P}$ = 5.6 Hz, C-1), 46.08 (dd, $J_{C,P}$ = 4.5 Hz, C-2), 127.89 (dd, $J_{C,P}$ = 9.6 Hz, Ph-C_m), 128.30 (d, $J_{C,P}$ = 53.0 Hz, Ph-C_i), 128.49 (d, $J_{C,P}$ = 54.2 Hz, Ph-C_i), 128.59 (dd, $J_{C,P}$ = 9.6 Hz, Ph-C_m), 130.94 (dd, $J_{C,P}$ = 2.3 Hz, Ph-C_p), 131.07 (dd, $J_{C,P}$ = 2.3 Hz, Ph-C_p), 132.70 (dd, $J_{C,P}$ = 8.4 Hz, Ph-C_o), 133.32 (dd, $J_{C,P}$ = 8.5 Hz, Ph-C_o), 175.00 (d, $J_{C,P}$ = 2.8 Hz, C=O). ^{31}P NMR ($CDCl_3$): δ = +26.3. ^{11}B NMR ($CDCl_3$): δ = –42.3. HR-MS (FAB+) $C_{22}H_{28}BNOP$ ($M^+ + H - H_2$) calcd. 365.2069; found 365.2002.

(–)-(1*S*,2*R*,3*S*)-3-(Boranatodiphenylphosphanyl)-*N*,6,6-trimethylbicyclo[3.1.1]heptane-2-carboxamide (15·BH$_3$): Methylamine hydrochloride (150 mg, 2.22 mmol) and DCC (355 mg, 1.72 mmol) were added to a cooled (–60 °C) solution of **10**·BH_3 (600 mg, 1.64 mmol) and DMAP (210 mg, 1.72 mmol) in anhydrous CH_2Cl_2 (5 mL). The mixture was allowed to slowly warm to room temperature and further stirred for 2 days [TLC: PE/ethyl acetate/*i*PrOH, 90:3:3, R_f(**10**·BH_3) = 0.47, R_f(**15**·BH_3) = 0.41]. The resultant suspension was filtered through celite (eluent: CH_2Cl_2) and the filtrate was washed with 1 N HCl, sat. hydrogencarbonate solution, water and brine. The organic layer was dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified by flash chromatography (silica gel, PE/ethyl acetate/*i*PrOH, 90:3:3) to give **15**·BH_3 (570 mg, 92%) as amorphous powder. M.p. 167–169 °C. $[\alpha]_D^{22}$ = –55.6 (*c* = 1.16, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50–1.50 (br. s, 3 H, BH_3), 1.08 (s, 3 H, 8-H), 1.15 (s, 3 H, 9-H), 1.55 (d, $J_{7a,7b}$ = 10.3 Hz, 1 H, 7-H_a), 1.88–1.97 (m, 1 H, 5-H), 2.05–2.18 (m, 3 H, 1-H, 4-H), 2.29–2.35 (m, 1 H, 7-H_b), 2.29 (d, *J* = 4.8 Hz, 3 H, NCH_3; after H/D exchange: s), 2.96 (ddd, $J_{2,P}$ = 20.2, *J* = 7.0, *J* = 2.2 Hz, 1 H, 2-H), 4.12–4.35 (m, 1 H, CHP), 4.89 (bd, *J* = 4.8 Hz, 1 H, NH, H/D), 7.27–7.40 (m, 3 H, Ph-$H_{m,p}$), 7.47–7.52 (m, 3 H, Ph-$H_{m,p}$), 7.77–7.84 (m, 2 H, Ph-H_o), 7.91–7.99 (m, 2 H, Ph-H_o). ^{13}C NMR ($CDCl_3$): δ = 21.72 (dd, $J_{C,P}$ = 37.3 Hz, CHP), 22.38 (q, C-8), 25.94 (q, NCH_3), 27.29 (q, C-9), 27.57 (td, $J_{C,P}$ = 4.1 Hz, C-4), 30.37 (t, C-7), 38.86 (s, C-6), 40.45 (dd, $J_{C,P}$ = 5.1 Hz, C-5), 45.80 (dd, $J_{C,P}$ = 6.2 Hz, C-1), 47.45 (dd, $J_{C,P}$ = 4.5 Hz, C-2), 128.03 (dd, $J_{C,P}$ = 9.6 Hz, Ph-C_m), 128.30 (d, $J_{C,P}$ = 54.8 Hz, Ph-C_i), 128.39 (d, $J_{C,P}$ = 52.0 Hz, Ph-C_i), 128.84 (dd, $J_{C,P}$ = 9.6 Hz, Ph-C_m), 131.06 (dd, $J_{C,P}$ = 2.3 Hz, Ph-C_p), 131.30 (dd, $J_{C,P}$ = 2.3 Hz, Ph-C_p), 132.72 (dd, $J_{C,P}$ = 8.5 Hz, Ph-C_o), 133.50 (dd, $J_{C,P}$ = 9.0 Hz, Ph-C_o), 173.61 (d, $J_{C,P}$ = 2.3 Hz, C=O). ^{31}P NMR ($CDCl_3$): δ = +25.5. ^{11}B NMR ($CDCl_3$): δ = –42.5. $C_{23}H_{31}BNOP$ (379.33): calcd. C 72.82, H 8.25, N 3.69, P 8.16; found C 72.78, H 8.20, N 3.61, P 8.13.

(–)-(1*S*,2*R*,3*S*)-[3-(Boranatodiphenylphosphanyl)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methanol (16·BH$_3$): A solution of **9a**·BH_3 (12.80 g, 33.7 mmol) in THF was added dropwise to a suspension of $LiAlH_4$ (4.00 g, 105.4 mmol) in THF (200 mL) at 0 °C. Then the mixture was warmed to room temperature and conversion monitored by TLC [PE/ethyl acetate, 7:3, R_f(**9a**·BH_3) = 0.73, R_f(**16**·BH_3) = 0.32]. After dilution with diethyl ether (200 mL) the reaction mixture was worked up according to the procedure of Mihailovic.[27] The resulting suspension was filtered and the residue washed thoroughly with diethyl ether. The filtrate was dried over Na_2SO_4, filtered and the solvent removed in vacuo. The product was purified by flash chromatography (silica gel, PE/EE, 8:2). Recrystallization from hexane/ethyl acetate gave **16**·BH_3 (11.1 g, 94%) as colorless plates. M.p. 122–123 °C. $[\alpha]_D^{21}$ = –63.4 (*c* = 1.47, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50–1.50 (br. s, 3 H, BH_3), 1.02 (s, 3 H, 8-H), 1.08 (s, 1 H, OH, H/D), 1.18 (s, 3 H, 9-H), 1.23 (m, 1 H, 7-H_a), 1.85–1.92 (m, 1 H, 5-H), 1.98 (dddd, $J_{4a,4b}$ = 14.0, *J* = 3.1, *J* = 3.1, *J* = 3.1 Hz, 1 H, 4-H_a), 2.06–2.19 (m, 1 H, 4-H_b), 2.20–2.30 (m, 2 H, 1-H, 7-H_b), 2.48–2.78 (m, 3 H, 2-H, CHP, CH_2O), 3.34 (t, *J* = 10.3 Hz, 1 H, CH_2O), 7.35–7.54 (m, 6 H, Ph-$H_{m,p}$), 7.67–7.74 (m, 2 H, Ph-H_o), 7.84–7.90 (m, 2 H, Ph-H_o). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 23.03 (q, C-8), 25.44 (d, $J_{C,P}$ = 32.8 Hz, CHP), 27.06 (q, $J_{C,P}$ = 1.7 Hz, C-9), 28.82 (t, $J_{C,P}$ = 1.7 Hz, C-4), 29.20 (t, C-7), 38.95 (s, C-6), 40.44 (d, $J_{C,P}$ = 4.0 Hz, C-5), 41.24 (d, $J_{C,P}$ = 6.2 Hz, C-1), 44.18 (d, $J_{C,P}$ = 2.8 Hz, C-2), 65.66 (t, $J_{C,P}$ = 1.7 Hz, CH_2O), 127.64 (s, $J_{C,P}$ = 54.2 Hz, Ph-C_i), 128.50 (d, *J* = 9.6 Hz, Ph-C_m), 128.66 (d, *J* = 9.6 Hz, Ph-C_m), 129.74 (d, *J* = 51.4 Hz, Ph-C_i), 131.17 (d, $J_{C,P}$ = 2.3 Hz, Ph-C_p), 131.26 (d, $J_{C,P}$ = 2.3 Hz, Ph-C_p), 132.50 (d, $J_{C,P}$ = 7.9 Hz, Ph-C_o), 133.10 (d, $J_{C,P}$ = 7.9 Hz, Ph-C_o). ^{31}P NMR ($CDCl_3$): δ = +27.0. ^{11}B NMR ($CDCl_3$): δ = –40.9. $C_{22}H_{30}BOP$ (352.30): calcd. C 75.00, H 8.60, P 8.79; found C 74.94, H 8.89, P 8.86.

(–)-(1*S*,2*R*,3*S*)-[3-Diphenylphosphanyl-6,6-dimethylbicyclo[3.1.1]-hept-2-yl]methanaminium 4-Methylbenzenesulfonate (17): A solution of **11** (6.90 g, 207 mmol) in diethyl ether (80 mL) was added dropwise within 1 h to a cooled (0 °C), stirred suspension of $LiAlH_4$ (7.90 g, 208 mmol) in diethyl ether (130 mL). The mixture was then allowed to reach room temperature and progress of the reaction was monitored by TLC [PE/ethyl acetate, 9:1, R_f(**11**) = 0.31, R_f(**17**) = ca. 0.0]. After 12 h diethyl ether (200 mL) was added and the reaction mixture was worked up according to the procedure of Mihailovic involving controlled precipitation of aluminum oxide.[27] This was filtered off and the residue was thoroughly washed with diethyl ether. The filtrate was dried over Na_2SO_4 and concentrated in vacuo. The residue was dissolved in diethyl ether (20 mL). On 5 mL of this solution a layer of a solution of *p*-toluenesulfonic acid (950 mg, 5.00 mmol) in THF (10 mL) was placed, avoiding mixing as far as possible. The product crystallized upon standing over a period of several days. The crystals were washed with a small amount of cold (0 °C) THF. A second crop was obtained from the mother liquor to give an overall yield of **17** (1.33 g, 53%) as colorless needles. M.p. 232–236 °C (dec.). $[\alpha]_D^{21}$ = –11.9 (*c* = 1.72,

$CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.81 (d, $J_{7a,7b}$ = 9.6 Hz, 1 H, 7-H_a), 0.96 (s, 3 H, 8-H), 1.04 (s, 3 H, 9-H), 1.68–1.85 (m, 2 H, 4-H_a, 5-H), 2.11–2.31 (m, 4 H, 1-H, 4-H_b, 7-H_b, CHP), 2.32–2.49 (m, 1 H, CH_2N), 2.38 (s, 3 H, Ar-CH_3), 2.59–2.73 (m, 1 H, CH_2N), 7.17–7.33 (m, 5 H, Ph-H, Ar-H), 7.34–7.42 (m, 3 H, Ph-H), 7.56–7.66 (m, 4 H, Ph-H), 7.74 (d, J = 8.1 Hz, 2 H, Ar-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.15 (q, Ar-CH_3), 22.17 (q, C-8), 26.35 (q, C-9), 28.15 (dd, $J_{C,P}$ = 14.2 Hz, CHP), 29.67 (t, C-7), 31.27 (td, $J_{C,P}$ = 13.0 Hz, C-4), 38.72 (d, $J_{C,P}$ = 1.1 Hz, C-6), 40.9, 41.09 (2d, C-1, C-5), 42.93 (dd, $J_{C,P}$ = 6.2 Hz, C-2), 43.16 (t, CH_2N), 126.09 (d, Ar-C), 128.33 (dd, $J_{C,P}$ = 6.8 Hz, Ph-C_m), 128.73 (dd, $J_{C,P}$ = 7.0 Hz, Ph-C_m), 128.79 (d, Ar-C), 129.01, 129.13 (2d, Ph-C_p), 133.04 (dd, $J_{C,P}$ = 18.6 Hz, Ph-C_o), 134.36 (dd, $J_{C,P}$ = 19.2 Hz, Ph-C_o), 135.68 (d, $J_{C,P}$ = 15.8 Hz, Ph-C_i), 137.37 (d, $J_{C,P}$ = 17.5 Hz, Ph-C_i), 139.87, 141.68 (2s, Ar-C). ^{31}P NMR ($CDCl_3$): δ = +4.8 (**17**), δ = +43.5 (**17**-oxide). $C_{29}H_{36}NO_3PS$ (509.69): calcd. C 68.33, H 7.13, N 2.75, P 6.08, S 6.29; found C 68.30, H 7.40, N 2.76, P 6.10, S 6.29.

Methyl (1*S*,2*R*,3*S*)-3-[Boranatobiphenyl-2-yl(phenyl)phosphanyl]-6,6-dimethylbicyclo[3.1.1]heptane-2-carboxylate (18·BH_3): Ester **4a** (1.50 g, 8.30 mmol) and phosphane **8b** (4.30 g, 16.4 mmol) were reacted according to GP 1 (reaction time: 6 h). After filtration of the reaction mixture through a pad of silica gel (PE/ethyl acetate, 70:1) and evaporation of the solvent, the crude product was dissolved in anhydrous THF (120 mL) and BH_3·THF (1 M in THF) (16.4 mL, 16.4 mmol) was added at –78 °C. After stirring overnight residual borane was hydrolyzed by addition of water. Then brine (100 mL) was added and the mixture was extracted with THF (5 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The diastereomeric phosphanes were separated by flash chromatography {silica gel, PE/THF, 50:1, R_f[(S_P)-**18**·BH_3] = 0.18, R_f[(R_P)-**18**·BH_3] = 0.14}. Crystallization of these compounds was achieved by adding a layer of hexane on to a concentrated solution in THF/ethyl acetate. This gave (S_P)-**18**·BH_3 (1.14 g, 30%) as colorless hexagon-shaped crystals and (R_P)-**18**·BH_3 (0.98 g, 25%) as colorless, rectangular crystals.

(S_P)-18·BH_3: M.p. 145–146 °C. $[\alpha]_D^{20}$ = +93.4 (c = 0.99, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.5–1.5 (br. s, 3 H, BH_3), 0.93 (s, 3 H, 8-H), 1.14 (s, 3 H, 9-H), 1.23 (d, $J_{7a,7b}$ = 9.9 Hz, 1 H, 7-H_a), 1.81 (m_c, 1 H, 5-H), 1.90–2.31 (m, 4 H, 1-H, 4-H, 7-H_b), 3.29 (s, 3 H, OCH_3), 3.35 (ddd, $J_{P,H}$ = 13.6, J = 6.3, J = 4.1 Hz, 1 H, 2-H), 3.88 (m, 1 H, 3-H), 7.01–7.09, 7.11–7.18, 7.19–7.27 (3m, 11 H, Ar-H), 7.33–7.34 (m, 2 H, Ar-H), 8.11 (m_c, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 21.91 (q, C-8), 23.12 (dd, $J_{C,P}$ = 34.5 Hz, C-3), 27.05 (dd, $J_{C,P}$ = 1.1 Hz, C-9), 28.30 (t, C-4), 29.54 (t, C-7), 39.06 (s, C-6), 40.49 (dd, $J_{C,P}$ = 3.9 Hz, C-5), 44.54 (dd, $J_{C,P}$ = 5.7 Hz, C-1), 45.57 (dd, $J_{C,P}$ = 5.1 Hz, C-2) 51.56 (q, COOCH_3), 126.35, 126.66, 126.81, 126.84, 126.99, 127.14, 127.51, 127.88, 127.99, 128.12, 129.08, 129.73, 129.76, 130.53, 130.56, 132.07, 132.15, 132.71, 132.82, 135.37, 135.58, 141.26, 141.30, 147.58, 147.59 (Ar-C), 174.66 (d, $J_{C,P}$ = 2.8 Hz, COOCH$_3$). ^{31}P NMR ($CDCl_3$): δ = +32.1 [(S_P)-**18**·BH_3], –5.2 [(S_P)-**18**]. ^{11}B NMR ($CDCl_3$): δ = +39. $C_{29}H_{34}O_2BP$ (456.37): calcd. C 76.32, H 7.51, P 6.79; found C 76.14, H 7.50, P 6.79.

(R_P)-18·BH_3: M.p. 200–201 °C. $[\alpha]_D^{20}$ = +39.7 (c = 0.99, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.4–1.4 (br. s, 3 H, BH_3), 0.96 (s, 3 H, 8-H), 1.18 (s, 3 H, 9-H), 1.72 (d, $J_{7a,7b}$ = 9.1 Hz, 1 H, 7-H_a), 1.92 (br. s, 1 H, 5-H), 2.07–2.30 (m, 4 H, 1-H, 4-H, 7-H_b), 3.25 (m_c, 1 H, 2-H), 3.20 (s, 3 H, OCH_3), 3.98 (m_c, 1-H, 3-H), 6.81 (br. s, 2 H, Ar-H), 7.11–7.19 (m, 2 H, Ar-H), 7.23–7.34 (m, 2 H, Ar-H), 7.35–7.49 (m, 3 H, Ar-H), 7.53–7.62 (m, 3 H, Ar-H), 8.12–8.19 (m, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 21.91 (q, C-8), 23.15 (dd, $J_{C,P}$ = 32.3 Hz, C-3), 27.15 (q, C-9), 28.33 (dt, $J_{C,P}$ = 3.4 Hz, C-4), 29.37 (t, C-7), 39.09 (s, C-6), 40.54 (dd, $J_{C,P}$ = 4.5 Hz, C-5), 44.72 (dd, $J_{C,P}$ = 5.7 Hz, C-1), 45.20 (dd, $J_{C,P}$ = 4.3 Hz, C-2), 51.40 (q, COOCH_3), 126.16, 126.84, 127.04, 127.15, 127.38, 127.59, 127.81, 127.94, 129.65, 129.76, 130.33, 130.61, 130.64, 130.74, 130.77, 132.65, 132.76, 133.33, 133.43, 133.55, 140.86, 140.91, 148.56, 148.67 (Ar-C), 174.40 (s, COOCH$_3$). ^{31}P NMR ($CDCl_3$): δ = +30.2 [(R_P)-**18**·BH_3], –1.6 [(R_P)-**18**]. ^{11}B NMR ($CDCl_3$): δ = –42. $C_{29}H_{34}O_2BP$ (456.37): calcd. C 76.32, H 7.51, P 6.79; found C 76.48, H 7.61, P 6.82.

***tert*-Butyl (1*S*,2*R*,3*S*)-3-[Boranatobiphenyl-2-yl(phenyl)phosphanyl]-6,6-dimethylbicyclo[3.1.1]heptane-2-carboxylate (19·BH_3):** Ester **4b** (1.70 g, 7.66 mmol) and phosphane **8b** (4.00 g, 15.26 mmol) were reacted according to GP 1 (reaction time: 6 h). The crude product was dissolved in THF and the solution cooled to –78 °C, stirred and dropwise treated with BH_3·THF (1 M in THF, 15.3 mL, 15.3 mmol). Stirring was continued for 15 h and residual borane hydrolyzed by addition of water and then brine (50 mL). The mixture was extracted with THF (5 × 100 mL) and the combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was dissolved in PE/ethyl acetate, 70:1 and the solution filtered through silica gel. The crude product was dissolved in anhydrous THF (40 mL) and BH_3·THF (1 M in THF) (15.3 mL, 15.3 mmol) was added at –78 °C. After stirring overnight residual borane was hydrolyzed by addition of water. Upon addition of brine (100 mL) the mixture was extracted with THF (5 × 100 mL), and the organic layers dried over Na_2SO_4, filtered and concentrated in vacuo. The diastereomeric products were separated by flash chromatography {600 g of silica gel, PE/ethyl acetate, 70:1, R_f[(S_P)-**19**·BH_3] = 0.12, R_f[(R_P)-**19**·BH_3] = 0.09} to give (S_P)-**19**·BH_3 (1.98 g, 44%) and (R_P)-**19**·BH_3 (1.52 g, 34%), both colorless powders.

(S_P)-19·BH_3: M.p. 155–157 °C. $[\alpha]_D^{20}$ = –88.6 (c = 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.5–1.7 (br. s, 3 H, BH_3), 0.99 (s, 3 H, 8-H), 1.16 [s, 9 H, C(CH_3)$_3$], 1.18 (s, 3 H, 9-H), 1.54 (d, $J_{7a,7b}$ = 10.3 Hz, 1 H, 7-H_a), 1.85 (m_c, 1 H, 5-H), 1.77–2.37 (m, 4 H, 1-H, 4-H, 7-H_b), 3.30 (ddd, J = 21.1, J = 6.9, J = 2.2 Hz, 1 H, 2-H), 3.99 (ddt, $J_{P,H}$ = 17.8, $J_{3,4}$ = 11.4, $J_{2,3}$ = 6.6 Hz, 1 H, 3-H), 6.93–7.05 (m, 5 H, Ar-H), 7.11–7.21 (m, 6 H, Ar-H), 7.35–7.42 (m, 2 H, Ar-H), 8.14–8.26 (m, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 22.14 (q, C-8), 22.35 (dd, $J_{C,P}$ = 34.5 Hz, C-3), 27.30 (q, C-9), 27.80 [q, C(CH_3)$_3$], 28.50 (t, C-4), 29.20 (t, C-7), 39.20 (s, C-6), 40.48 (dd, $J_{C,P}$ = 3.5 Hz, C-5), 44.88 (dd, $J_{C,P}$ = 5.6 Hz, C-1), 46.23 (dd, J = 5.1 Hz, C-2), 80.13 [s, C(CH_3)$_3$], 126.62, 126.66, 126.81, 127.22, 127.32, 127.41, 127.88, 128.01, 128.08, 129.10, 129.45, 129.48, 130.59, 130.62, 131.99, 132.09, 132.47, 132.59, 135.57, 135.78, 141.50, 141.54, 147.77 (Ar-C), 173.19 [d, $J_{C,P}$ = 2.8 Hz, COOC(CH_3)$_3$]. ^{31}P NMR ($CDCl_3$): δ = +32.0 [(S_P)-**19**·BH_3], δ –5.1 [(S_P)-**19**]. ^{11}B NMR ($CDCl_3$): δ = –38. $C_{32}H_{40}O_2BP$ (498.45): calcd. C 77.11, H 8.09, P 6.21; found C 76.97, H 8.21, P 6.24.

(R_P)-19·BH_3: M.p. 59–60 °C. $[\alpha]_D^{20}$ = –3.8 (c = 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.1–1.2 (br. s, 3 H, BH_3), 0.94 (s, 3 H, 8-H), 1.10 [s, 9 H, C(CH_3)$_3$], 1.16 (s, 3 H, 9-H), 1.76 (d, $J_{7a,7b}$ = 10.0 Hz, 1 H, 7-H_a), 1.88 (br. s, 1 H, 5-H), 1.29–2.33 (m, 4 H, 1-H, 4-H, 7-H_b), 3.07 (m, 1 H, 2-H), 4.08 (m, 1 H, 3-H), 7.10 (m, 1 H, Biph-H), 7.23–7.31 (m, 3 H, Ar-H), 7.31–7.41 (m, 2 H, Ar-H), 7.46–7.63 (m, 5 H, Ar-H), 7.68–7.77 (m, 1 H, Ar-H), 7.93–8.01 (m, 1 H, Ar-H), 8.11–8.18 (m, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 21.92 (q, C-8), 22.91 (dd, $J_{C,P}$ = 35.3 Hz, C-3), 27.20 (q, C-9), 27.74 [q, C(CH_3)$_3$], 28.50 (t, C-4), 29.06 (t, C-7), 39.10 (s, C-6), 40.46 (dd, $J_{C,P}$ = 4.5 Hz, C-5), 44.96 (dd, $J_{C,P}$ = 4.6 Hz, C-1), 46.65

(dd, $J_{C,P}$ = 10.9 Hz, C-2), 80.08 [s, $C(CH_3)_3$], 121.67–148.95 (Ar-C), 173.54 [d, $J_{C,P}$ = 2.8 Hz, $COOC(CH_3)_3$]. ^{31}P NMR ($CDCl_3$): δ = +29.1 [(R_P)-**19**·BH_3], δ –1.5 [(R_P)-**19**]. ^{11}B NMR ($CDCl_3$): δ = –41. $C_{32}H_{40}O_2BP$ (498.45): calcd. C 77.11, H 8.09, P 6.21; found C 76.82, H 7.94, P 6.33.

***tert*-Butyl (1*S*,2*R*,3*S*)-6,6-Dimethyl-3-[boranato(1-naphthyl)phenylphosphanyl]bicyclo[3.1.1]heptane-2-carboxylate (20·BH_3):** Ester **4b** (0.47 g, 2.11 mmol) and phosphane **8c** (1.00 g, 4.23 mmol) were reacted according to GP 1 (reaction time: 7 h). The cold reaction mixture was dropwise treated with BH_3·THF (1 M in THF, 5.00 mL, 5.00 mmol) and the mixture stirred overnight and allowed to reach room temperature. Residual borane was hydrolyzed by addition of water. Upon addition of brine (30 mL) the mixture was extracted five times with THF, the organic layers dried over Na_2SO_4, filtered and concentrated in vacuo. The product was purified by flash chromatography [silica gel, PE/ethyl acetate, 30:1, R_f(**20**·BH_3) = 0.12] to give **20**·BH_3 (0.70 g, 68%) as mixture of diastereomers. Recrystallization from PE/ethyl acetate gave 0.23 g (21%) of (S_P)-**20**·BH_3 as colorless, cubic crystals. M.p. 147–149 °C. $[\alpha]_D^{20}$ = –103.7 (c = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.5–1.5 (br. s, 3 H, BH_3), 0.88 [s, 9 H, $C(CH_3)_3$], 0.98 (s, 3 H, 8-H), 1.17 (s, 3 H, 9-H), 1.42 (m, 1 H, 7-H_a), 1.98 (m, 1 H, 5-H), 2.22 (m, 2 H, 1-H, 4-H_a), 2.45–2.62 (m, 2 H, 4-H_b, 7-H_b), 3.08 (ddd, $J_{P,H}$ = 21.7, $J_{2,3}$ = 6.6, $J_{1,2}$ = 1.8 Hz, 2 H, 2-H), 4.35 (m, 1 H, 3-H), 7.33 (m, 1 H, Naph-H), 7.33–7.52 (m, 6 H, Naph-H), 7.73–7.79 (m, 3 H, Ar-H), 7.93 (d, J = 8.1 Hz, 1 H, Naph-H), 8.10 (d, J = 8.1 Hz, 1 H, Naph-H), 8.27 (dd, J = 13.4, J = 7.4 Hz, 1 H, Naph-H). ^{13}C NMR ($CDCl_3$): δ = 22.02 (q, C-8), 22.17 (dd, $J_{C,P}$ = 34.4 Hz, C-3), 27.17 (q, C-9), 27.34 [q, $C(CH_3)_3$], 28.51 (dt, $J_{C,P}$ = 1.1 Hz, C-4), 29.04 (t, C-7), 39.09 (s, C-6), 40.52 (dd, $J_{C,P}$ = 3.4 Hz, C-5), 44.65 (dd, $J_{C,P}$ = 7.4 Hz, C-1), 46.93 (dd, $J_{C,P}$ = 5.0 Hz, C-2), 79.95 [s, $C(CH_3)_3$], 124.48, 124.54, 124.65, 125.17, 125.91, 126.301, 127.05, 127.11, 128.71, 128.81, 128.84, 130.03, 130.66, 130.69, 130.75, 132.51, 132.62, 132.84, 132.88, 133.75, 133.80, 133.92, 134.01, 136.31, 136.47, (Ar-C), 172.38 [d, $J_{C,P}$ = 3.0 Hz, $COOC(CH_3)_3$]. ^{31}P NMR ($CDCl_3$): δ = +31.5 [(S_P)-**20**·BH_3], –4.9 [(S_P)-**20**]. ^{11}B NMR ($CDCl_3$): δ = –39. $C_{24}H_{34}O_2BP$ (472.41): calcd. C 76.27, H 8.11, P 6.56; found C 76.09, H 8.19, P 6.59.

***tert*-Butyl (1*S*,2*S*,3-*R*,R_P)-6,6-Dimethyl-3-(boranatomethylphenylphosphanyl)bicyclo[3.1.1]heptane-2-carboxylate [(R_P)-21·BH_3]:** A solution of methyldiphenylphosphane (3.38 g, 16.9 mmol) in THF (20 mL) was treated with powdered lithium (239 mg, 34.7 mmol). After stirring for 12 h at room temperature the mixture was filtered and the filtrate treated with a solution of *tert*-butyl chloride (1.29 g, 15.3 mmol) in THF (7 mL). The solution of lithium methylphenylphosphide obtained in this way was heated to reflux for 10 min and was then directly used in the reaction with ester **4b** (2.82 g, 12.7 mmol) in degassed THF (35 mL) according to GP 1 (reaction time: 3 h). Conversion was monitored by TLC [PE/ethyl acetate/*i*PrOH, 99:0.5:0.5, R_f(**21**) = 0.20, R_f(**8d**) = 0.14]. The reaction mixture was cooled to –78 °C, BH_3·THF (1 M in THF, 60 mL, 60 mmol) was added and progress of the reaction monitored by TLC [PE/ethyl acetate/*i*PrOH, 99:0.5:0.5, R_f[(R_P)-**21**·BH_3] = 0.37, R_f[(S_P)-**21**·BH_3] = 0.27, R_f(PhMePH·BH_3) = 0.27]. After 1 h the mixture was allowed to warm to room temperature overnight and excess borane was destroyed by addition of 1 N HCl (20 mL). The reaction mixture was extracted with diethyl ether, the organic layer dried over Na_2SO_4, filtered and the filtrate was concentrated in vacuo. The product was purified by flash chromatography (silica gel, PE/ethyl acetate/*i*PrOH, 99:0.5:0.5) to give (R_P)-**21**·BH_3 (1.01 g, 22%) as colorless needles. M.p. 129 °C. $[\alpha]_D^{20}$ = +1.7 (c = 0.96, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.25–1.25 (br. s, 3 H, BH_3), 0.84 (s, 3 H, 8-H), 1.12 [s, 9 H, $COOC(CH_3)_3$], 1.08–1.18 (m, 1 H, 7-H_a), 1.15 (s, 3 H, 9-H), 1.21 (d, J = 9.0 Hz, 4-H_a), 1.58 (d, J = 10.0 Hz, PCH_3), 1.90–1.96 (m, 1 H, 5-H), 2.07–2.25 (m, 3 H, H-1, 4-H_b, 7-H_b), 2.79 (ddd, $^3J_{2,P}$ = 21.1, J = 6.7, J = 2.3 Hz, 1 H, 2-H), 3.27–3.38 (m, 1 H, 3-H), 7.35–7.44 (m, 3 H, 3′-H, 4′-H), 7.72–7.78 (m, 2 H, 2′-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 9.05 (dq, J = 38.6 Hz, C-1′′), 21.62 (q, C-8), 24.42 (dd, J = 34.9 Hz, C-3), 26.65 (dq, J = 2.8 Hz, C-9), 27.14 (t, C-7), 27.66 [3q, $COOC(CH_3)_3$], 29.28 (t, C-4), 38.89 (s, C-6), 40.20 (dd, J = 4.7 Hz, C-5), 44.16 (dd, J = 4.7 Hz, C-1), 46.27 (dd, J = 2.8 Hz, C-2), 80.29 [s, $COOC(CH_3)_3$], 128.10 (ds, J = 51.8 Hz, C-1′), 128.28 (dd, J = 9.4 Hz, C-3′), 131.27 (dd, J = 2.8 Hz, C-4′), 132.83 (dd, J = 8.5 Hz, C-2′), 173.05 (ds, J = 2.4 Hz, $COOtBu$). ^{31}P NMR ($CDCl_3$): δ = +19.95 [(R_P)-**21**·BH_3], –12.07 [(R_P)-**21**]. ^{11}B NMR ($CDCl_3$): δ = –40.33. $C_{21}H_{34}BO_2P$ (360.24): calcd. C 70.01, H 9.51; found C 70.27, H 9.55.

(–)-(1*R*,2*S*,3*R*)-6,6-Dimethyl-3-(R_P)-(boranatomethylphenylphosphanyl)bicyclo[3.1.1]heptane-2-carboxylic Acid (22·BH_3): A solution of (R_P)-**21**·BH_3 (250 mg, 0.691 mmol) in degassed trifluoroacetic acid (1 mL) was stirred for 30 min at room temperature (CAUTION! Strong evolution of gas.). The solvent was removed and the residue was dissolved in diethyl ether (10 mL). After addition of 2 M aqueous KOH (1 mL) the mixture was stirred for 30 min (evolution of gas). The reaction mixture was extracted thrice with diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was dissolved in THF, the solution cooled to –78 °C and BH_3·THF (1 M in THF) (2.0 mL, 2.0 mmol) was added. After stirring for 1 h 1 M HCl (2 mL) was added at –78 °C and the mixture was allowed to warm to room temperature. It was then extracted with diethyl ether (4 × 5 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (silica gel, PE/ethyl acetate/*i*PrOH, 98:1:1) gave **22**·BH_3 (153 mg, 73%) as colorless needles. M.p. 183–184 °C. $[\alpha]_D^{21}$ = –10.4 (c = 0.99, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.2–1.4 (br. s, 3 H, BH_3), 0.83 (s, 3 H, 8-H), 1.14 (d, $^2J_{7a,7b}$ = 10.2 Hz, 1 H, 7-H_a), 1.15 (s, 3 H, 9-H), 1.59 (d, J = 9.9 Hz, PCH_3), 1.94–2.01 (m, 1 H, 5-H), 2.11–2.25 (m, 3 H, 7-H_b, 4-H_a, 4-H_b), 2.31–2.40 (m, 1 H, 1-H), 2.92 (ddd, $^3J_{2,1}$ = 2.5, $^3J_{2,3}$ = 6.5, $^3J_{2,P}$ = 20.2 Hz, 1 H, 2-H), 3.16–3.24 (m, 1 H, 3-H), 7.24–7.42 (m, 3 H, 3′-H, 4′-H), 7.70–7.74 (m, 2 H, 2′-H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 8.75 (dq, J = 39.5 Hz, C-1′′), 21.39 (q, C-8), 24.61 (dd, J = 34.8 Hz, C-3), 26.78 (t, C-4), 26.79 (q, C-9), 29.23 (t, C-7), 38.86 (s, C-6), 40.02 (dd, J = 3.7 Hz, C-5), 43.79 (dd, J = 3.7 Hz, C-1), 44.96 (dd, J = 1.8 Hz, C-2), 127.74 (ds, J = 51.8 Hz, C-1′), 128.32 (dd, J = 10.3 Hz, C-3′), 131.47 (dd, J = 1.9 Hz, C-4′), 132.64 (dd, J = 8.5 Hz, C-2′), 179.62 (ds, J = 2.8 Hz, COOH). ^{31}P NMR ($CDCl_3$): δ = +21.35 (**22**·BH**3**); –15.44 (**22**). ^{11}B NMR ($CDCl_3$): δ = –41.9. HMS (FAB+): $C_{17}H_{26}BO_2P$ calcd. 304.1763, found 304.1764.

Di-*tert*-butyl 3,3′-[Ethane-1,2-diylbis(boranatophenylphospanediyl)]-bis[(1*S*,2*R*,3*S*)-6,6-dimethylbicyclo[3.1.1.]heptane-2-carboxylate] (23). A. Preparation of 23a–c by Conjugate Addition/Epimerization: Under nitrogen, five drops of aqueous Et_4NOH (40%) were added to a solution of **8e** (2.00 g, 8.12 mmol) in degassed acetonitrile (80 mL). The mixture was stirred for 15 min at room temperature, then **4b** (3.61 g, 16.24 mmol) was added and stirring was continued for 36 h. Then the solvent was removed and the residue dissolved in degassed toluene (50 mL). The solution was heated to reflux for 8 h, then cooled to –78 °C and treated with BH_3·THF (1 M in THF) (16.2 mL, 16.2 mmol). After stirring for 16 h excess of borane was destroyed by addition of water. Brine (50 mL) was added and the mixture was extracted with THF. The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuo. The product was purified by repeated flash chromatography {silica, pe-

troleum ether/ethyl acetate, 30:1, R_f[(R_P,S_P)-**23a**·BH_3] = 0.09, R_f[(S_P,S_P)-**23b**·BH_3] = 0.08, R_f[(R_P,R_P)-**23c**·BH_3] = 0.06} to give (R_P,S_P)-**23a**·BH_3 (1.17 g, 20%), (S_P,S_P)-**23b**·BH_3 (1.84 g, 32%), (R_P,R_P)-**23c**·BH_3 (0.46 g, 8%) and a mixture of (R_P,S_P)-**23a**·BH_3 and (S_P,S_P)-**23b**·BH_3 (0.42 g, 7%) as white colorless powders.

B. Selective Preparation of 23a by Conjugate Addition of Diphosphane 8e Catalyzed by NEt_4OH: In the same way as described above, diphosphane **8e** (0.50 g, 2.0 mmol) was treated with ester **4b** (910 mg, 4.01 mmol). The crude phosphanes were reacted with BH_3·THF by stirring overnight, avoiding P-epimerization. After work-up as described above, flash chromatography yielded (R_P,S_P)-**23a**·BH_3 (630 mg, 43%), (S_P,S_P)-**23b**·BH_3 (70 mg, 5%) and (R_P,R_P)-**23c**·BH_3 (10 mg, 0.7%).

C. Selective Preparation of 23a by Conjugate Addition of the Dilithio Derivative of 8e: A cold (–78 °C) solution of **8e** (0.50 g, 2.0 mmol) in THF (20 mL) was treated with *n*BuLi (4.10 mmol, 1.6 M solution in *n*-hexane). The mixture was then stirred at room temperature for 15 min, cooled to –78 °C and then ester **4b** (910 mg, 4.10 mmol) was added. After 3 days, complexation with borane and work-up according to GP 1 followed by flash chromatography as described above gave of (R_P,S_P)-**23a**·BH_3 (650 mg, 45%) and (S_P,S_P)-**23b**·BH_3 (50 mg, 3%).

(R_P,S_P)-23a·BH_3: M.p. 254 °C (dec.). $[\alpha]_D^{21}$ = –10.0 (c = 1.01, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.2–0.9 (br. s, 6 H, BH_3), 0.72, 1.06 (2d, J = 7.6 Hz, 2 H, 7-H_a, 7′-H_a), 0.74, 0.75 (2s, 6 H, 9-H, 9′-H), 1.05, 1.08 (2s, 6 H, 8-H, 8′-H), 1.07, 1.20 [2s, 18 H, $C(CH_3)_3$], [1.46–1.80 (6H), 1.81–1.93 (1H), 1.98–2.10 (2H), 2.11–2.19 (2H), 2.23–2.41 (3H), (5 m, 1-H, 4-H, 5-H, 7-H_b, 13-H, 1′-H, 4′-H, 5′-H, 7′-H_b, 13′-H)], 2.71 (ddd, J = 20.3, J = 6.5, J = 2.4 Hz, 1 H, 2′-H), 2.86 (ddd, J = 20.9, J = 6.7, J = 2.7 Hz, 1 H, 2-H), 3.19 (ddd, J = 22.4, J = 12.1, J = 6.0 Hz, 1 H, 3′-H), 3.36 (ddd, J = 23.2, J = 11.5, J = 6.0 Hz, 1 H, 3-H), 7.35–7.43(m, 3 H, Ar-H), 7.44–7.53 (m, 3 H, Ar-H), 7.67, 7.80 (2t, J = 8.2 Hz, each 2 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 16.29, 17.09 (2dt, $J_{C,P}$ = 33.9, $J_{C,P}$ = 32.2 Hz, PCH_2), 21.57, 21.61 (2q, C-8, C-8′), 23.97, 24.41 (2dd, $J_{C,P}$ = 35.6, $J_{C,P}$ = 33.9 Hz, C-3, C-3′), 26.79, 27.15 (2t, C-4, C-4′), 27.00, 27.07 (2q, C-9, C-9′), 27.64, 27.76 [2q, $C(CH_3)_3$], 29.03, 29.09 (2t, C-7, C-7′), 38.85, 38.89 (2s, C-6, C-6′), 40.06, 40.09 (2d, C-5, C-5′), 43.96, 44.14 (2dd, $J_{C,P}$ = 4.2, $J_{C,P}$ = 3.4 Hz, C-1, C-1′), 46.06, 46.07 (2d, C-2, C-2′), 80.40, 80.97 [2s, $C(CH_3)_3$], 125.00, 126.31 (2d, $J_{C,P}$ = 48.3, $J_{C,P}$ = 50.9 Hz, C_i, C'_i), 128.57, 129.01 (2dd, $J_{C,P}$ = 9.3, $J_{C,P}$ = 9.3 Hz, C_m, C'_m), 131.57, 131.74 (2d, C_p, C'_p), 132.89, 133.61 (2dd, $J_{C,P}$ = 7.6, $J_{C,P}$ = 7.6 Hz, C_o, C'_o), 172.74, 173.39 [2s, $COOC(CH_3)_3$]. ^{31}P NMR ($CDCl_3$): δ = +32.5 (**23a**·BH_3); 6.7, 7.3 (each d, $J_{P,P}$ = 16.2 Hz) (**23a**). ^{11}B NMR ($CDCl_3$): δ = –47. $C_{42}H_{66}O_4P_2B_2$ (718.55): calcd. C 70.21, H 9.26, P 8.62; found C 69.99, H 9.25, P 8.53.

(S_P,S_P)-23b: M.p. 234 °C (dec.). $[\alpha]_D^{20}$ = –18.6 (c = 1.02, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.2–1.0 (br. s, 6 H, BH_3), 0.71 (s, 6 H, 9-H), 1.09 (s, 6 H, 8-H), 1.34 (d, $J_{7a,7b}$ = 10.2 Hz, 2 H, 7-H_a), 1.39 [s, 18 H, $C(CH_3)_3$], 1.48–1.62 (m, 4 H, 4-H_a, PCH_2), 1.64–1.76 (m, 4 H, 4-H_b, 5-H), 1.84 (m_c, 2 H, PCH_2), 2.17 (ddd, $J_{7a,7b}$ = 10.3, $J_{1,7b}$ = 6.2, $J_{5,7b}$ = 6.2 Hz, 2 H, 7-H_b), 2.38 (br. s, 2 H, 1-H), 3.00 (ddd, $J_{P,H}$ = 20.2, $J_{2,3}$ = 6.2, $J_{1,2}$ = 2.7 Hz, 2 H, 2-H), 3.25 (ddd, $J_{P,H}$ = 23.9, $J_{3,4}$ = 11.5, $J_{2,3}$ = 6.0 Hz, 2 H, 3-H), 7.37 (t, J = 7.5 Hz, 4 H, Ar-H), 7.50 (m_c, 6 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 17.45 (dt, $J_{C,P}$ = 32.2 Hz, PCH_2), 21.49 (q, C-8), 23.81 (dd, $J_{C,P}$ = 35.6 Hz, C-3), 26.92 (q, C-9), 26.97 (t, C-4), 27.94 [q, $C(CH_3)_3$], 28.76 (t, C-7), 38.79 (s, C-6), 39.97 (d, C-5), 43.85 (d, C-1), 45.89 (d, C-2), 81.18 [s, $C(CH_3)_3$], 126.95 (d, $J_{C,P}$ = 50.9 Hz, C_i), 128.69, 128.73 (2dd, $J_{C,P}$ = 4.2, $J_{C,P}$ = 5.1 Hz, C_m), 131.47 (d, C_p), 132.58, 132.61 (2dd, $J_{C,P}$ = 4.2, $J_{C,P}$ = 4.2 Hz, C_o), 173.84 [s, $COOC(CH_3)_3$]. ^{31}P NMR ($CDCl_3$): δ = +32.5 (**23b**·BH_3), +5.2 (**23b**). ^{11}B NMR ($CDCl_3$): δ = –45. $C_{42}H_{66}O_4P_2B_2$ (718.55): calcd. C 70.21, H 9.26, P 8.62; found C 70.17, H 9.35, P 8.53.

(R_P,R_P)-23c·BH_3: M.p. 225 °C (dec.). $[\alpha]_D^{20}$ = –17.2 (c = 0.50, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.3–1.0 (br. s, 6 H, BH_3), 0.76 (s, 6 H, 8-H), 1.05 [s, 18 H, $C(CH_3)_3$], 1.08 (s, 6 H, 9-H), 1.21 (d, $J_{7a,7b}$ = 7.6 Hz, 2 H, 7-H_a), 1.69–1.74 (br. s, 2 H, 13-H_a), 1.89 (br. s, 2 H, 5-H), 2.09–2.32 (m, 10 H, 1-H, 4-H, 7-H_b, 13-H_b), 2.68 (ddd, $J_{P,H}$ = 20.6, $J_{2,3}$ = 6.4, $J_{1,2}$ = 1.8 Hz, 2 H, 2-H), 3.25 (ddd, $J_{P,H}$ = 23.9, $J_{3,4}$ = 11.5, $J_{2,3}$ = 6.0 Hz, 2 H, 3-H), 7.34 (t, J = 7.3 Hz, 4 H, H_m), 7.44 (t, J = 7.3 Hz, 2 H, H_p), 7.54 (br. s, 4 H, H_o). ^{13}C NMR ($CDCl_3$): δ = 16.92 (dt, $J_{C,P}$ = 35.5 Hz, C-13), 21.54 (q, C-8), 23.83 (dd, $J_{C,P}$ = 34.5 Hz, C-3), 26.82 (t, C-4), 27.07 (q, C-9), 27.59 [q, $C(CH_3)_3$], 29.20 (t, C-7), 38.86 (s, C-6), 40.11 (d, C-5), 44.17 (d, C-1), 46.12 (d, C-2), 80.28 [s, $C(CH_3)_3$], 125.27 (d, $J_{C,P}$ = 49.8 Hz, C_i), 128.32, 128.36 (2dd, $J_{C,P}$ = 4.6, $J_{C,P}$ = 4.0 Hz, C_m), 131.66 (d, C_p), 133.59, 133.62 (2dd, $J_{C,P}$ = 4.0, $J_{C,P}$ = 3.3 Hz, C_o), 172.93 [s, $COOC(CH_3)_3$]. ^{31}P NMR ($CDCl_3$): δ = +32.3 (**23c**·BH_3), +5.9 (**23c**). ^{11}B NMR ($CDCl_3$): δ = –45. $C_{42}H_{66}O_4P_2B_2$ (718.55): calcd. C 70.21, H 9.26, P 8.62; found C 70.15, H 9.38, P 8.52.

Crystal Structure Determinations: Crystal data were recorded on a AED II diffractometer for **10-O**, and on a Enraf–Nonius KappaCCD diffractometer for **12**, on a Siemens/Stoe Syntex R3 diffractometer for (S_P)-**19**·BH_3 and (S_P)-**20**·BH_3, and on a Bruker Smart CCD diffractometer for (R_P)-**21**·BH_3 and **23b**·BH_3; Mo-$K\alpha$ radiation (μ = 0.71073 Å); temperature 150(2) K for **12**, and 200(2) K for (R_P)-**21**·BH_3 and **23b**·BH_3, otherwise room temperature; χ-scans, absorption correction based on multi-scans for **12** and **23b**·BH_3 or else ψ-scans; the structures were solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL (5.10) software package, except for the structure **12** which was solved using the direct methods program SIR92 and refined against F with a full-matrix least-squares refinements using CRYSTALS program suite; all non hydrogen atoms were refined anisotropically, hydrogen atoms were treated by using appropriate riding models, except of the cyclonutyl hydrogens in **12** and the hydrogen atoms of the BH_3 in (S_P)-**19**·BH_3, (S_P)-**20**·BH_3, (R_P)-**21**·BH_3 and **23b**·BH_3 which were refined isotropically.

Crystal Data of 10-O: $C_{22}H_{25}O_3P$, M_r = 368.39, crystal dimension 0.40 × 0.60 × 0.70 mm^3, orthorhombic, space group $P2_12_12_1$, a = 10.501(5) Å, b = 11.278(6) Å, c = 17.780(9) Å, V = 2105.7(18) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.162 $g\,cm^{-3}$, $F(000)$ = 784, μ = 0.147 mm^{-1}, $T_{min.}$ = 0.93, $T_{max.}$ = 1.00, 3.0° ≤ 2Θ ≤ 52.5°, 3995 reflections measured, 3995 unique, 2528 observed [$I > 2\sigma(I)$], 240 parameters refined, 0.1(2) Flack parameter (absolute structure), final residual values $R(F)$ = 0.052, w$R(F^2)$ = 0.116 for observed reflections (mm^3), orthorhombic, sp residual electron density –0.20 to 0.17 e·$Å^{-3}$.

Crystal Data of 12: $C_{24}H_{30}NOP$, M_r = 379.48, crystal dimension 0.14 × 0.44 × 0.44 mm^3, monoclinic, space group $P2_1$, a = 11.1636(3) Å, b = 6.6031(2) Å, c = 14.4940(5) Å, V = 1056.44(6) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.193 $g\,cm^{-3}$, $F(000)$ = 408, μ = 0.143 mm^{-1}, $T_{min.}$ = 0.94, $T_{max.}$ = 0.98, 5.0° ≤ 2Θ ≤ 27.5°, 11284 reflections measured, 4547 unique, 3727 observed [$I > 3\sigma(I)$], 261 parameters refined, Flack parameter (absolute structure) –0.03(8), final residual values $R(F)$ = 0.0362, w$R(F)$ = 0.0413 for observed reflections, residual electron density –0.34 to 0.29 e·$Å^{-3}$.

Crystal Data of (S_P)-19·BH_3: $C_{32}H_{40}BO_2P$, M_r = 498.45, crystal dimension 0.50 × 0.95 × 0.99 mm^3, space group $P2_12_12_1$, a = 11.498(2) Å, b = 11.863(3) Å, c = 21.620(5) Å, V = 2949(1) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.12 $g\,cm^{-3}$, $F(000)$ = 1072, μ = 0. 12 mm^{-1}, $T_{min.}$ = 0.85, $T_{max.}$ = 1.00, 3.0° ≤ 2Θ ≤ 60°, 6158 reflections measured,

6158 unique, 4553 observed [$I > 2\sigma(I)$], 336 parameters refined, Flack parameter (absolute structure) 0.0(1), final residual values $R(F) = 0.059$, $wR(F^2) = 0.131$ for observed reflections, residual electron density –0.26 to 0.23 e·Å^{-3}.

Crystal Data of (S_P)-20·BH$_3$: $C_{30}H_{38}BO_2P$, M_r = 472.38, crystal dimension 0.40 × 0.40 × 0.45 mm^3, orthorhombic, space group $P2_12_12_1$, a = 10.700(2) Å, b = 13.555(3) Å, c = 19.284(4) Å, V = 2797(1) Å^3, Z = 4, $\rho_{calcd.}$ = 1.12 g cm^{-3}, $F(000)$ = 1016, μ = 0.12 mm^{-1}, $T_{min.}$ = 0.93, $T_{max.}$ = 1.00, 3.0° ≤ 2Θ ≤ 45°, 3172 reflections measured, 3172 unique, 2197 observed [$I > 2\sigma(I)$], 317 parameters refined, Flack parameter (absolute structure) –0.1(2), final residual values $R(F)$ = 0.067, $wR(F^2)$ = 0.117 for observed reflections, residual electron density –0.20 to 0.18 e·Å^{-3}.

Crystal Data of (R_P)-21·BH$_3$: $C_{21}H_{34}BO_2P$, M_r = 360.26, crystal dimension 0.48 × 0.24 × 0.14 mm^3, polyhedron, space group $P2_1$, a = 9.6722(1) Å, b = 9.6698(1) Å, c = 12.435(5) Å, V = 1094.18(16) Å^3, $\rho_{calcd.}$ = 1.093 g cm^{-3}, μ = 0.136 mm^{-1}, $T_{min.}$ = 0.76, $T_{max.}$ = 0.98, 3.4° ≤ 2Θ ≤ 54.8°, 11069 reflections measured, 4988 unique, 4376 observed [$I > 2\sigma(I)$], 276 parameters refined, Flack parameter (absolute structure) 0.05(6), final residual values $R(F)$ = 0.035, $wR(F^2)$ = 0.081 for observed reflections, residual electron density –0.19 to 0.23 e·Å^{-3}.

Crystal Data of 23b·BH$_3$: M_r = 718.51, crystal dimension 0.10 × 0.37 × 0.38 mm^3, monoclinic, space group $P2_1$, a = 10.653(2) Å, b = 17.468(4) Å, c = 23.914(4) Å, β = 98.40(2) °, V = 4402(1) Å^3, Z = 4, $\rho_{calcd.}$ = 1.08 g cm^{-3}, $F(000)$ = 1560, μ = 0.14 mm^{-1}, $T_{min.}$ = 0.86, $T_{max.}$ = 1.00, 3.0° ≤ 2Θ ≤ 51.2°, 20475 reflections measured, 13652 unique [R(int) = 0.0235], 10817 observed [$I > 2\sigma(I)$], 957 parameters refined, Flack parameter (absolute structure) –0.02(6), final residual values $R(F)$ = 0.048, $wR(F^2)$ = 0.096 for observed reflections, residual electron density –0.24 to 0.18 e·Å^{-3}.

CCDC-147755 (for **10-O**), -261244 (for **12**), -147752 [for (S_P)-**19**·BH$_3$], -147753 [for (S_P)-**20**·BH$_3$], -166021 [for (R_P)-**21**·BH$_3$] and -147754 (for **23b**·BH$_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[24] For ^{31}P NMR monitoring samples (0.3 mL) were quickly transferred into a cooled (–78 °C) NMR tube, kept under nitrogen, charged with dry, degassed methanol (0.1 mL).

[25] In earlier experiment we used quenching with deoxygenated $Na_2SO_4 \cdot 10H_2O$. It is then necessary to remove solid material by filtering before adding $BH_3 \cdot THF$.
[26] Should small amounts of the corresponding phosphane oxide be formed could this to some extent be removed via crystallization, otherwise via column chromatography {silica gel, PE/diethyl ether/DCM/*i*PrOH, 70:15:15:1, R_f(**4b**) = 0.63, R_f(**10**·BH_3) = 0.25, R_f(**10**-oxide) = 0.14}.
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