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Novel chiral diphosphine ligands with a pinene core obtained via an allylphosphinite–allylphosphine oxide rearrangement

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Abstract—A number of new chiral diphosphine ligands with a pinene framework were synthesized and tested in some transition metal-catalyzed asymmetric reactions (enantioselectivities up to 84% ee were achieved). The [2,3]-sigmatropic allylphosphinite–allyl phosphine oxide rearrangement was applied as a key step of the synthesis. An improved procedure for the phosphine oxide reduction and a new protocol for the deprotection of phosphine–borane complexes were developed.
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1. Introduction

Chiral diphosphine ligands have been extensively studied and used over the last few decades as ligands for transition metals in catalytic processes for the synthesis of enantiopure compounds.[1] Natural homochiral terpenes present an inexpensive and reliable source for the synthesis of new ligands, although so far, most of the known syntheses of chiral ligands from terpenes start from camphor.[2]

More than 50 years ago, Arbuzov and Nikonorov, discovered the thermal rearrangement of allyldiarylphosphinites to allyldiphenylphosphine oxides.[3] We have shown that this reaction proceeds highly diastereoselectively and is a convenient tool for the transformation of easily available chiral allylic alcohols into chiral diarylphosphines. Several new chiral ligands were synthesized in this way.[4,5] Herein, we report the application of this reaction to the synthesis of new chiral diphosphines starting from naturally occurring allylic alcohols. Thermal [2,3]-sigmatropic rearrangement of diphenylphosphinites,[4] obtained in situ from chiral myrtenol and *trans*-pinocarveol gave the corresponding allylphosphine oxides in excellent yields. Hydroboration–oxidation gave diphenylphosphinoyl alcohols as single diastereomers, which were transformed into the corresponding diphosphines in four synthetic steps. The short retrosynthetic analysis of the pinene-derived ligands is shown in Figure 1.

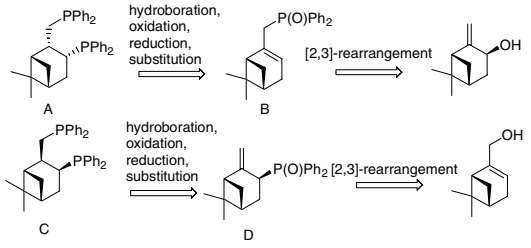

Figure 1. Retrosynthetic pathway for the pinene-derived ligands.

Starting from pinene-derived alcohols, myrtenol, and pinocarveol, we were able to obtain two types of ligands with the opposite configuration of the phosphorus-containing substituents, attached to the pinene scaffold (Fig. 2).

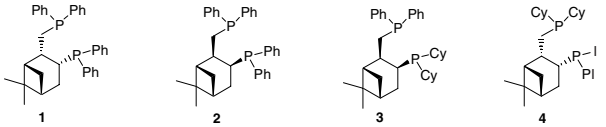

Figure 2. Ligands obtained from pinene-derived alcohols.

Novel diphosphine ligands were tested in a number of transition-metal catalyzed asymmetric reactions. Enantioselectivities up to 84% ee were achieved.

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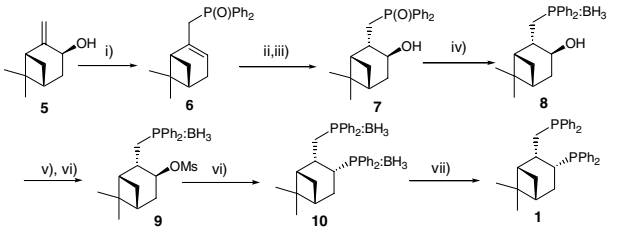
2. Results and discussion

2.1. Synthesis of (2*R*,3*R*)-2-diphenylphosphanyl-3-[(diphenylphosphanyl)-methyl]-bicyclo[3.1.1]heptane

The elaboration of the remaining asymmetric centers in the synthesis of ligand **1** (Scheme 1) is based on the known hydroboration of pinenes, which occurs with high diastereoselectivity.[6] The formation of diphenylphosphinite from *trans*-pinocarveol[22] **5** and its thermal rearrangement were performed in toluene according to a one-pot procedure,[5] and gave allylphosphine oxide **6**. The hydroboration[7,8] of the allylphosphine oxide with borane–dimethyl sulfide readily occurred in toluene at 60 °C. We found that for the oxidation[9] of the borane adduct, *m*-chloroperbenzoic acid in CH_2Cl_2 is much more efficient than the conventional NaOH–H_2O_2 mixture. After the removal of the excess of the acids (aq $Na_2S_2O_5$, then NaOH) and the usual work-up, the desired diphenylphosphinoyl alcohol was crystallized from ether in 62% overall yield. Its relative configuration of the single diastereomer formed was established by X-ray analysis (Fig. 3).[10]



Scheme 1. Reagents and conditions: (i) Ph_2PCl, DMAP, toluene, 80 °C, 6 h; (ii) BH_3–Me_2S, 60 °C, 6 h; (iii) *m*CPBA, CH_2Cl_2, 10–15 °C, 62% overall; (iv) PMHS, Ti(O*i*-Pr)$_4$, PhMe, 100 °C, 2 h, BH_3–Me_2S, then 25% HF, 25 °C, 12 h, 96%; (v) MsCl, Et_3N, CH_2Cl_2, −20 °C, 2 h; (vi) Ph_2PH, *t*-BuOK, THF, 50 °C, 18 h, BH_3–Me_2S, 55% for two steps; (vii) *N*,*N*′-bis-(3-aminopropyl)-piperazine, 100 °C, 2 h, 95%.

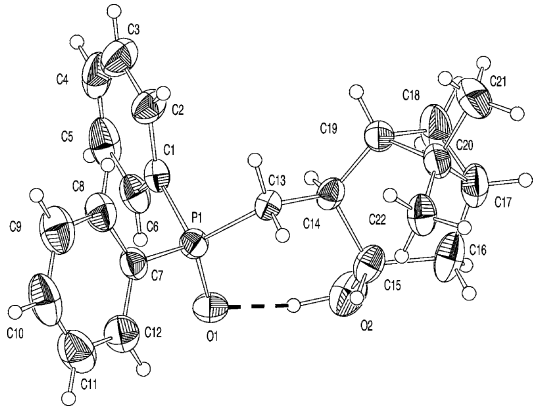


Figure 3. ORTEP diagram of alcohol **7**.

Phosphine oxide **7** was reduced quantitatively into the corresponding phosphine by a mixture of polymethylhydrosiloxane–Ti(O*i*-Pr)$_4$, although under the originally described conditions[11] (THF, reflux) the reaction was very sluggish. In toluene at 100 °C however we could obtain full conversion within 1–2 h. Since the reaction mixture is homogeneous, it can be conveniently monitored by ^{31}P NMR. Excess of PMHS and its oxidized derivates of various polarity made the chromatographical purification of the product troublesome until we found that stirring of the mixture after the reaction with 20–25% HF completely removed both the titanium and silicon compounds, leaving the borane protection intact. By this method, alcohol **8** was obtained in nearly quantitative yield.

Alcohol **8** was converted into the mesylate by treatment with excess methanesulfonyl chloride and triethylamine in cold CH_2Cl_2. Dilution of the reaction mixture with ether, filtration through silica gel and removal of the excess of MsCl in vacuo afforded the unstable mesylate sufficiently pure for direct use in the next step.

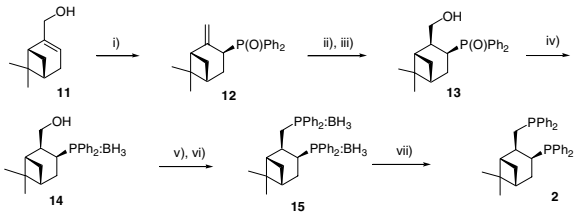
Reaction of the mesylate with diphenylphosphine and *t*-BuOK in THF followed by protection gave the desired diphosphine–borane in an acceptable yield. The product was purified by flash chromatography (Al_2O_3, CH_2Cl_2–pentane) and recrystallized from Et_2O in 55% overall yield, mp 195–196 °C. Attempts to use more convenient phosphine-borane nucleophiles in polar aprotic solvents[12] proved unsuccessful, with only the starting material being recovered.

Whereas deprotection of monophosphine–boranes normally proceeds easily, bis-phosphine boranes, especially electron-rich, can present a significant problem for deprotection. Although a complementary acid-mediated method of their decomplexation is known,[12,13] we were looking for a simplified procedure avoiding the use of aqueous solutions, which usually contaminates the product with the phosphine oxide. Inexpensive *N*,*N*′-bis-3-(aminopropyl)-piperazine turned out to be an excellent solution: complete deprotection of the bis-borane could be performed at 100 °C within 1 h. Dilution of the mixture with ether, filtration through dry silica in argon and evaporation gave the desired diphosphine in nearly quantitative yield.

2.2. Synthesis of (2*S*,3*S*)-2-diphenylphosphanyl-3-[(diphenylphosphanyl)-methyl]-bicyclo[3.1.1]heptane

The rearrangement of the diphenylphosphinite, obtained from myrtenol (Scheme 2) required harsher conditions (100 °C, 48 h against 6 h at 80 °C) compared to the *trans*-pinocarveol derivative, but led to the desired allylphosphine oxide in excellent yield. Hydroboration of product **12** with borane in THF gave a diastereomeric mixture of products in 3:1 ratio. Use of more bulky 9-BBN [14] gave after oxidation, alcohol **13** as a single diastereomer. The anticipated *cis*-configuration of the substituents was confirmed by X-ray analysis (Fig. 4).[15] Interestingly, the borane adduct of alkene **12** and 9-BBN is unusually air-stable crystalline solid, which can be easily purified by recrystallization.

The remaining steps of the synthesis were performed using the same sequence as for the ligand **1**. In this way,



Scheme 2. Reagents and conditions: (i) Ph_2PCl, DMAP, PhMe, 100 °C, 48 h, 90%; (ii) 9-BBN, THF, 75 °C, 48 h; (iii) *m*CPBA, CH_2Cl_2, 10–15 °C, 67% for two steps; (iv) PMHS, Ti(O*i*-Pr)$_4$, PhMe, 100 °C, 2 h, BH_3–Me_2S, then 25% HF, 25 °C, 12 h, 95%; (v) MsCl, Et_3N, CH_2Cl_2, −20 °C, 2 h; (vi) Ph_2PH, *t*-BuOK, THF, 50 °C, 18 h, BH_3–Me_2S, 48% for two steps; (vii) *N*,*N*′-bis-(3-aminopropyl)-piperazine, 100 °C, 2 h, 96%.

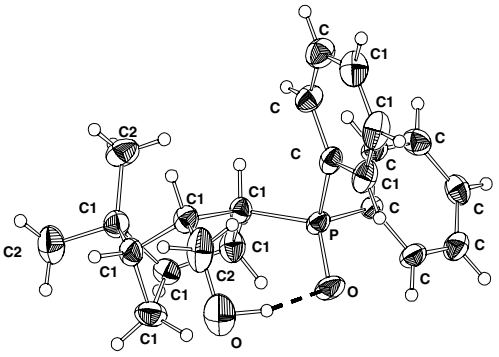


Figure 4. ORTEP diagram of alcohol **13.**

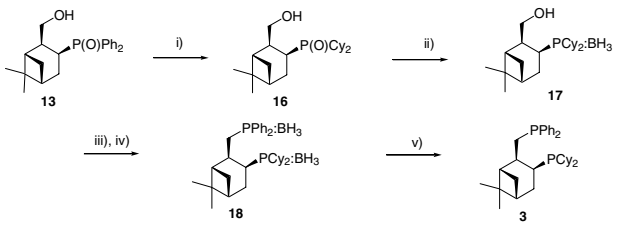
chiral diphosphine **2** with the opposite configuration of the phosphine substituents on the pinene core was obtained.

2.3. Synthesis of diphenyphosphanyl–dicyclohexylphosphanyl 'mixed' ligands

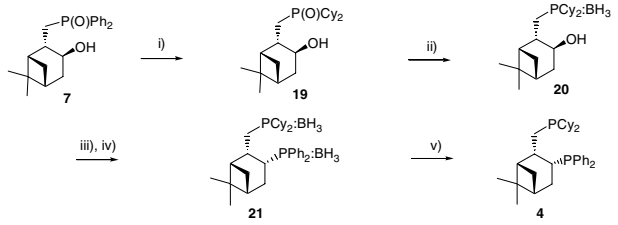
The introduction of the dicyclohexylphosphine moiety instead of diarylphosphine often significantly changed the ligands properties due to steric reasons and different electron densities on the phosphorus atom.[16,17] Hydrogenation[18] of diphenylphosphinoyl alcohols **7** and **13** proceeded quantitatively over Raney Ni in methanol. Reduction of the products with PMHS–Ti(O*i*-Pr)$_4$ followed by borane protection, formation of the mesylates, and nucleophilic substitution with the phosphide anion gave the desired phosphine–borane complexes, which were finally deprotected by heating with bis-3-(aminopropyl)-piperazine to obtain the corresponding phosphines in slightly less (44–48%) overall yields than for the bis-(diphenylphosphine) analogs. The syntheses of new 'mixed' phosphines are given on Schemes 3 and 4.

2.4. Asymmetric catalysis

We examined the performances of the newly synthesized ligands in the Rh-catalyzed asymmetric reduction of three substrates: methyl acetamidocinnamate, dimethyl itaconate, and methyl acetamidoacrylate. Since the



Scheme 3. Reagents and conditions: (i) Raney Ni, MeOH, H_2, 50 bar, 50 °C, 48 h, 97%; (ii) PMHS, Ti(O*i*-Pr)$_4$, PhMe, 100 °C, 2 h, BH_3–Me_2S, then 25% HF, 25 °C, 12 h, 93%; (iii) MsCl, Et_3N, CH_2Cl_2, −20 °C, 2 h; (iv) Ph_2PH, *t*-BuOK, THF, 50 °C, 18 h, BH_3–Me_2S, 44% for two steps; (v) *N*,*N*′-bis-(3-aminopropyl)-piperazine, 100 °C, 12 h, 96%.



Scheme 4. Reagents and conditions: (i) Raney Ni, MeOH, H_2, 50 bar, 50 °C, 48 h, 98%; (ii) PMHS, Ti(O*i*-Pr)$_4$, PhMe, 100 °C, 2 h, BH_3–Me_2S, then 25% HF, 25 °C, 12 h, 94%; (iii) MsCl, Et_3N, CH_2Cl_2, −20 °C, 2 h; (iv) Ph_2PH, *t*-BuOK, THF, 50 °C, 18 h, BH_3–Me_2S, 48% for two steps; (v) *N*,*N*′-bis-(3-aminopropyl)-piperazine, 100 °C, 12 h, 95%.

enantiomeric excess of the hydrogenation reaction is strongly dependent on the solvent, we performed the optimization of the solvent system for these reactions with ligand **7** as the model compound. Hydrogenation of methyl (*Z*)-acetamidocinnamate was performed at room temperature and 1 bar pressure, with $Rh(COD)_2BF_4$ as the metal source, using 2 mol% of the preformed catalyst. Screening of the solvents (Table 1) showed that the highest enantioselectivities were achieved in a toluene–methanol 10:1 mixture. This mixture was used for the testing of all other ligands in the Rh-catalyzed hydrogenation of acetamidocinnamic and acetamidoacrylic esters.

Solvent optimization for the hydrogenation of dimethyl itaconate showed that methanol and toluene–THF mixtures give similar results (Table 2). The further

Table 1. Solvent optimization for Rh-catalyzed hydrogenation of methyl acetamidocinnamate

Entry	Solvent system	Enantiomeric excess (%)
1	MeOH	38
2	CH_2Cl_2–MeOH 10:1	29
3	THF–MeOH 10:1	47
4	PhMe–MeOH 1:1	52
5	PhMe–THF 5:1	49
6	**PhMe–MeOH 10:1**	**78**

Reagents and conditions: 0.5 mmol methyl acetamidocinnamate, 0.01 mmol $Rh(COD)_2BF_4$, 0.011 mmol of ligand **7** in 5 mL solvent, rt, 1 bar H_2, 12 h.

Table 2. Solvent optimization for Rh-catalyzed hydrogenation of dimethyl itaconate

Entry	Solvent system	Enantiomeric excess (%)
1	PhMe	58
2	PhMe–MeOH	66
3	PhMe–THF	78
4	**MeOH**	**81**

Reagents and conditions: 0.5 mmol dimethyl itaconate, 0.01 mmol $Rh(COD)_2BF_4$, 0.011 mmol of ligand **7**, 5 mL of solvent, rt, 1 bar H_2, 12 h.

testing reactions for this substrate with other ligands were performed in methanol.

Test results for our ligands in Rh-catalyzed catalytic asymmetric hydrogenation of acetamidocinnamic ester are given in Table 3. Reactions were performed at 1 bar H_2 pressure and room temperature for 12 h. In all cases, full conversion was achieved. As we can conclude from the testing data, the additional steric hindrance created by the methyl groups of pinene core forces the phosphorus atom to take a more advantageous position for high enantioselectivity. Introduction of cyclohexyl rings instead of phenyl impairs the enantioselectivity of the reaction in both cases.

Table 3. Rh-catalyzed asymmetric hydrogenation of methyl acetamidocinnamate

Entry	Ligand	Enantiomeric excess (%)
1	**1**	84 (*R*)
2	**2**	78 (*S*)
3	**3**	51 (*R*)
4	**4**	46 (*S*)

Reagents and conditions: 0.5 mmol methyl acetamidocinnamate, 0.01 mmol $Rh(COD)_2BF_4$, 0.011 mmol of ligand in 5 mL PhMe–MeOH (10:1), rt, 1 bar H_2, 12 h.

For the hydrogenation of acetamidoacrylic ester (Table 4, the same reaction conditions) the situation changed significantly: both ligands **1** and **2** essentially gave the same enantioselectivity, while the introduction of cyclohexyl rings led to an improvement of ee in one case (ligand **3)** and a dramatic drop in another (ligand **4**). Conversely to the reaction with acetamidocinnamic ester, all the ligands gave the same enantiomer of the product.

Table 4. Rh-catalyzed asymmetric hydrogenation of methyl acetamidoacrylate

Entry	Ligand	Enantiomeric excess (%)
1	**1**	60 (*R*)
2	**2**	61 (*R*)
3	**3**	79 (*R*)
4	**4**	7 (*R*)

Reagents and conditions: 0.5 mmol of methyl acetamidoacrylate, 0.01 mmol $Rh(COD)_2BF_4$, 0.011 mmol of ligand, 5 mL PhMe–MeOH (10:1), rt, 1 bar H_2, 12 h.

Table 5. Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate

Entry	Ligand	Enantiomeric excess (%)
1	**1**	18 (*S*)
2	**2**	81 (*S*)
3	**3**	17 (*R*)
4	**4**	54 (*S*)

Reagents and conditions: 0.5 mmol dimethyl itaconate, 0.01 mmol $Rh(COD)_2BF_4$, 0.011 mmol of ligand in 5 mL MeOH, rt, 1 bar H_2, 12 h.

Data of hydrogenation of dimethyl itaconate reveal a very strong difference between the diastereomeric bisdiphenylphosphine ligands **1** and **2**: 18% and 81% ee, correspondingly (Table 5).

Introduction to the ligand **1** cyclohexyl groups in place of the phenyls (ligand **3**) caused dramatical changes in the reaction course, leading to the opposite enantiomer of the product.

Besides the application of the newly synthesized ligands in hydrogenation of C=C double bonds, we examined their performance in the asymmetric hydrogenation of C=O and C=N bonds. For Ru-catalyzed catalytic hydrogenation of benzoyl acetate (0.5 mol% $Ru(COD)(C_4H_7)_2$, 0.5 mol% ligand **2**, 0.3 M HBr in MeOH, 50 bar H_2, rt, 16 h)[19] the product was obtained with full conversion, but only 37% ee. Full conversion, but poor enantioselectivity was achieved in the Rh-catalyzed hydrogenation of acetophenone benzoylhydrazone with ligand **1** (1 mol% ligand, 1 mol% $Rh(COD)_2BF_4$, MeOH, 50 bar H_2, rt, 16 h, 30% ee,[20] and Pd-catalyzed allylic substitution of 1,3-diphenylpropenyl acetate with dimethyl malonate (1 mol% $[Pd(allyl)Cl]_2$, 2 mol% of ligand, 5 mol% KOAc, 3 equiv BSA, rt, 1 h, 33% ee).[21]

3. Conclusion

Starting from naturally occurring terpenes, we have synthesized a number of new chiral diphosphine ligands with a pinene framework and tested them in some transition metal-catalyzed asymmetric reactions. For the catalytic asymmetric hydrogenations, enantioselectivities up to 84% ee were achieved. In the key step of the synthesis, we applied the [2,3]-sigmatropic allylphosphinite–allyl phosphine oxide rearrangement, which afforded a simple one-step conversion of allylic alcohols into phosphine oxides. A formerly reported method for phosphine oxide reduction has been significantly improved upon in terms of easiness and scalability. We also reported a new, simple and practical protocol for the deprotection of phosphine–borane complexes, suitable for preparation of diphosphines, including polyalkyl-substituted electron-rich ones.

4. Experimental

All reactions were carried out under argon using standard Schlenk techniques. ^1H and ^{13}C NMR spectra were

recorded on a Bruker AMX 300 instrument. ^{31}P NMR spectra were recorded on a VARIAN Mercury 200 instrument. Chemical shifts (δ) are given as ppm relative to the residual solvent peak. IR spectra were recorded on a Perkin–Elmer 1420 Infrared Spectrometer. Mass spectra were recorded on a FINNIGAN MAT 95 Q spectrometer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. Column chromatography was performed on MERCK silica gel 60 (230–400 mesh ASTM). Thin layer chromatography was performed on MERCK TLC-plates silica gel 60 F-254. Enantiomeric excesses were determined by by chiral GC (Chiralsil L-Val and TFA–cyclodextrine columns).

4.1. Typical procedure for the conversion of phosphine oxides into phosphine–borane complexes

Into a 50 mL Schlenk flask was placed a phosphine oxide (5 mmol), dry toluene (20 mL), polymethylhydrosiloxane (2 mL, 33 mmol), and titanium isopropoxide (1.5 mL, 20 mmol). The mixture was heated at 100 °C for 2–4 h, until ^{31}P NMR showed complete reduction, after which it was cooled and BH_3–Me_2S (1 mL, 10 mmol) then added. After 5 min, the mixture was carefully poured into a 250 mL Erlenmeyer flask with methanol (5 mL). When gas evolution ceased, the solution was transferred into a 250 mL Nalgene® bottle with a mixture of 48% HF (20 mL) and H_2O (20 mL), and stirred for 12 h at room temperature. The aqueous phase was extracted with toluene (15 mL) and the combined organic phases washed with saturated $NaHCO_3$, brine, dried over $MgSO_4$, and evaporated. The residue was redissolved in a small amount of ether and filtered through silica gel, washed with ether, and evaporated and dried in vacuo to obtain a phosphine–borane complex as a viscous oil, which gradually solidified. Yields 93–96%.

4.2. Typical procedure for the synthesis of bis-phosphine boranes from phosphine–borane alcohols

Into a 100 mL Schlenk flask was placed a phosphine–borane alcohol (5 mmol) and dry dichloromethane (40 mL). Cooled to −20 °C, dry triethylamine (2.4 mL, 17 mmol) was added. Methanesulfonyl chloride (1.2 mL, 17 mmol) was added at this temperature dropwise with good stirring. The mixture was left at −20 °C for 2 h and, while still cold, poured into dry ether (200 mL). After 5 min, the white precipitate was filtered off through a pad of silica gel, the filter cake washed with ether (100 mL), and the filtrate concentrated on rotary evaporator to about 10 mL. The residual solvents and the excess MsCl were removed by oil pump vacuo during 5 h. The mesylate was used in the next step without further purification.

In a 100 mL Schlenk flask, *t*-BuOK (1.40 g, 12.5 mmol) was dissolved in THF (25 mL), and diphenylphosphine (2.33 g, 12.5 mmol) then added. The orange solution was cooled to −20 °C and the solution of the mesylate in 10 mL THF slowly added. The mixture was heated at 50 °C for 18 h. BH_3–Me_2S (2.0 mL, 20 mmol) was added and the reaction mixture transferred into a 250 mL Erlenmeyer flask with methanol (10 mL). When gas evolution ceased, saturated NH_4Cl (50 mL) was added and the aqueous layer extracted twice with dichloromethane (20 mL portions). The combined organic extracts were washed with saturated brine, dried over $MgSO_4$, and evaporated. The residue was dissolved in a small amount of a dichloromethane–pentane mixture (1:1) and passed through alumina (Fluka, Brockmann grade III). The filtrate was concentrated on a rotary evaporator to dryness and treated as specified for the substance. Yields 44–55%.

4.3. Typical procedure for the deprotection of a phosphine–borane with *N*,*N*′-bis(3-aminopropyl)-piperazine

A phosphine–borane (1 mmol) was placed into a 10 mL Schlenk tube and dissolved in toluene (2 mL). To the solution, *N*,*N*′-bis(3-aminopropyl)-piperazine (1 mL, excess) was added. The mixture was heated at 100 °C for the time stated, cooled down and diluted with ether (10 mL). The solution was filtered under an Ar atmosphere through a pad of previously dried silica and evaporated. The resulting phosphine was obtained as white foam or very viscous oil and stored under argon. Yields 95–96%.

4.4. Typical procedure for the hydrogenation of a diphenylphosphine oxide over Raney Ni

Raney Ni (6.0 g, 50% in water, Acros) was washed three times with 20 mL portions of methanol and transferred in methanol into a 200 mL stainless steel autoclave. The diphenylphosphine oxide (8 mmol) was added, and the autoclave charged with hydrogen to 50 bar pressure. Hydrogenation was performed at 50 °C for 48 h, the autoclave depressurized, the contents filtered through a pad of Celite and the precipitate washed successively with methanol. The filtrate was evaporated to give the product as a colourless solid in practically quantitative yield.

4.5. Synthesis of [(1*S*,2*R*,3*R*,5*R*)-3-(diphenylphosphino)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-methyl(diphenyl)-phosphine 1

4.5.1. (1*S*,2*R*,3*S*,5*R*)-2-(Diphenylphosphinoylmethyl)-6,6-dimethyl-bicyclo[3.1.1]heptan-3-ol 7. 4-Dimethylaminopyridine (10.2 g, 84 mmol) was placed into a 250 mL Schlenk flask and dissolved under argon in dry toluene (100 mL). *trans*-Pinocarveol (12.7 g, 84 mmol) was added, the mixture cooled to −30 °C, at which point diphenyl chlorophosphine (15.2 mL, 84 mmol, Strem 98%, distilled in vacuo prior to use) was added dropwise in 5 min. The mixture was allowed to reach ambient temperature and heated at 80 °C for 6 h. ^{31}P NMR showed complete rearrangement (diphenylphosphinite: 126 ppm, diphenylphosphine oxide: 29 ppm). The hot mixture was filtered through a pad of Celite and the filter cake washed

with toluene. The filtrate was concentrated to about 70 mL and borane–dimethyl sulfide complex (12 mL, 120 mmol) was added carefully. The solution was heated at 50 °C for 6 h, cooled down and carefully poured into a 1 L Erlenmeyer flask with methanol (70 mL). After 4 h, the solution was evaporated in vacuo and the residue redissolved in dichloromethane (80 mL). *meta*-Chloroperbenzoic acid (70–75%, Acros, 25 g, 106 mmol) was dissolved separately in dichloromethane (200 mL), the solution was dried over $MgSO_4$ and placed into 0.5 L two-necked flask with a dropping funnel and thermometer. The flask was immersed into an acetone–dry ice cooling bath and the solution of the hydroborated adduct added slowly so that the temperature didn't exceed 15 °C. After completion of the addition, the mixture was stirred for 1 h, and filtered. The filtrate was stirred with a solution of 80 g of $Na_2S_2O_5$ in 200 mL H_2O for 10 min, the layers separated and the organic phase washed twice with 100 mL portions of 2 M NaOH, then with saturated brine, dried, and evaporated. The semi-solid residue was stirred 24 h with ether (200 mL), the precipitate filtered off, washed with ether, and dried in vacuo. Yield 18.4 g (62%), white solid.

Mp 200–200.5 °C, $[\alpha]_D = -4.2$ (*c* 0.75, $CHCl_3$); IR (KBr): $\bar{\nu}$ 3351 (br s), 1438 (s), 1173 (vs), 1120 (s), 740 (vs), 546 (s). ^{1}H NMR ($CDCl_3$): δ 7.71–7.63 (m, 4H), 7.50–7.36 (m, 6H), 5.56 (br s, 1H), 4.34–4.24 (m, 1H), 3.64 (br s, 1H), 2.56–2.38 (m, 2H), 2.29–2.13 (m, 2H), 1.94–1.86 (m, 1H), 1.14 (s, 3H), 0.99 (s, 1H), 0.96 (s, 1H), 0.91 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 134.6, 133.2, 132.7, 132.4–132.3 (m), 131.5 (d, $J = 9.2$ Hz), 130.8 (d, $J = 9.2$ Hz), 129.3 (m), 129.1 (m), 70.2, 51.3 (d, $J = 14.4$ Hz), 48.3, 41.8, 38.7, 38.0 (d, $J = 69$ Hz), 37.0, 34.5, 27.9, 24.2. ^{31}P NMR (81 MHz, $CDCl_3$): δ 36.0. MS (EI, 70 eV) *m*/*z* (%): 155(20), 201(78), 202(100), 215(32), 311(57). HRMS: 355.1809 ($C_{22}H_{28}O_2P$, $[M+H]^+$).

A sample of [(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]methyl-(diphenyl)-phosphine oxide **6** was taken from the reaction mixture after the rearrangement reaction finished and purified by column chromatography (CH_2Cl_2–Et_2O 1:1). White hygroscopic solid.

Mp 50–52 °C, $[\alpha]_D = -10.1$ (*c* 0.85, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 2984 (m), 2914 (s), 1437 (s), 1194 (vs), 1119 (s), 735 (m), 719 (s), 696 (s), 533 (m). ^{1}H NMR ($CDCl_3$): δ 7.73–7.63 (m, 4H), 7.43–7.30 (m, 6H), 5.30–5.25 (m, 1H), 3.07–2.95 (m, 2H), 2.15–2.02 (m, 2H), 1.90–1.82 (m, 1H), 1.08 (s, 3H), 0.86 (s, 1H), 0.83 (s, 1H), 0.62 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.6 (d, $J = 11$ Hz), 134.5 (d, $J = 28$ Hz), 133.2 (d, $J = 28$ Hz), 131.8, 131.4, 131.3, 131.2, 128.9–128.6 (m), 122.3 (d, $J = 11$ Hz), 47.4, 40.5, 39.8, 38.9, 38.4, 31.9 (d, $J = 9$ Hz), 26.5, 21.4. ^{31}P NMR (81 MHz, $CDCl_3$): δ 29.4. MS (EI, 70 eV) *m*/*z* (%): 77 (17), 91 (16), 155 (19), 201 (55), 202 (100), 203 (22), 293 (12), 321 (18), 336 (17). HRMS: 336.1660 ($C_{22}H_{25}OP$, $[M]^+$).

4.5.2. (1*S*,2*R*,3*S*,5*R*)-2-(Diphenylphosphanylmethyl)-6,6-dimethyl-bicyclo[3.1.1]heptan-3-ol-borane complex 8. Compound **8** was obtained from **7** according to Section 4.1. Yield 1.69 g (96%), colourless semi-solid mass, slowly crystallized during the storage.

Mp 107–107.5 °C, $[\alpha]_D = 13.0$ (*c* 0.75, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3432 (br s), 3255 (br s), 2922 (s), 2386 (s), 1436 (vs), 1105 (m), 1062 (m), 1031 (m), 736 (vs), 691 (s). ^{1}H NMR ($CDCl_3$): δ 7.78–7.62 (m, 4H), 7.56–7.40 (m, 6H), 4.20–4.10 (br s, 1H), 2.70–2.40 (m, 1H), 2.48 (br s, 1H), 2.33–2.20 (m, 2H), 1.93 (s, 1H), 1.86 (s, 1H), 1.79 (s, 1H), 1.75 (s, 1H), 1.17 (s, 3H), 1.15 (s, 1H), 1.11 (s, 1H), 0.96 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 132.8 (d, $J = 8.8$ Hz), 132.3 (d, $J = 8.8$ Hz), 131.8, 131.6, 131.1, 129.3 (d, $J = 4.7$ Hz), 129.2 (d, $J = 4.7$ Hz), 128.8, 71.1 (d, $J = 5.6$ Hz), 48.5, 48.4, 41.1, 38.1, 33.8, 33.3, 32.5, 27.4, 24.1. ^{31}P NMR (81 MHz, $CDCl_3$): δ 15.4 (br s). MS (EI, 70 eV) *m*/*z* (%): 108 (16), 183 (34), 185 (17), 186 (11), 199 (100), 200 (82), 338 (11). HRMS: 351.2051 ($C_{22}H_{29}BOP$, $[M-H]^+$).

4.5.3. (1*S*,2*R*,3*R*,5*R*)-3-Diphenylphosphanyl-2-[(diphenylphosphanyl)-methyl]-6,6-dimethyl-bicyclo[3.1.1]heptane bis-borane complex 10. Compound **8** was transformed into the corresponding bis-phosphine borane **10** according to Section 4.2. The residue after evaporation was quickly dissolved in ether (25 mL). Within minutes, crystallization of the product started. After 12 h, the crystals were filtered off, washed with a small amount of ether, and dried in vacuo. Yield 1.47 g (55%), colourless crystals.

Mp 195–196 °C, $[\alpha]_D = +17.9$ (*c* 0.48, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3435 (br s), 2919 (w), 2401 (s), 2383 (s), 1436 (s), 1106 (m), 1054 (m), 739 (s), 698 (vs), 500 (m). ^{1}H NMR ($CDCl_3$): δ 7.93–7.79 (m, 2H), 7.71–7.50 (m, 4H), 7.47–7.21 (m, 8H), 7.22–7.00 (m, 4H), 6.90–6.77 (m, 2H), 3.70–3.45 (m, 1H), 3.26 (br s, 1H), 3.10–2.85 (m, 1H), 2.16–1.90 (m, 1H), 1.80–0.73 (m, 6H), 0.91 (s, 3H), 0.87 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 131.5, 131.4, 131.2, 131.1, 130.7, 130.4, 130.2, 130.0 (d, $J = 8.8$ Hz), 129.8, 129.6 (m), 129.4, 129.3, 129.3, 129.2, 129.0, 128.8, 128.5 (d, $J = 9.4$ Hz), 128.1, 127.6 (d, $J = 10.0$ Hz), 127.3 (d, $J = 10.0$ Hz), 44.5, 38.9, 37.2, 33.9, 32.7, 28.1, 27.2 (d, $J = 10.6$ Hz), 26.8 (d, $J = 10.6$ Hz), 25.6 (d, $J = 8.5$ Hz), 19.9.); ^{31}P NMR (81 MHz, $CDCl_3$): δ 17.5 (br s), 19.0 (br s). MS (EI, 70 eV) *m*/*z* (%): 183 (24), 185 (14), 262 (11), 429 (100), 430 (30), 519 (17). HRMS: 534.2953 ($C_{34}H_{42}B_2P_2$, $[M]^+$).

4.5.4. (1*S*,2*R*,3*R*,5*R*)-[3-(Diphenylphosphino)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-methyl(diphenyl)-phosphine 1. Compound **1** was obtained from **10** according to Section 4.3. Yield 0.48 g (95%), colourless, very viscous oil.

$[\alpha]_D = +19.8$ (*c* 1.25, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3436 (br s), 2912 (s), 1479 (w), 1433 (s), 696 (s), 741 (vs), 513 (m). ^{1}H NMR ($CDCl_3$): δ 7.49–7.36 (m, 4H), 7.25–7.00 (m, 16H), 6.85–6.78 (m, 2H), 3.24–3.10 (m, 1H), 2.53–2.37 (m, 3H), 2.36–2.32 (m, 1H), 2.10–2.00 (m, 1H), 1.76 (br s, 1H), 1.58–1.40 (m, 2H), 1.27 (d, $J = 10.1$ Hz, 1H), 1.10 (s, 3H), 0.91 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.3 (d, $J = 14.1$ Hz), 138.2 (d, $J = 11.8$ Hz), 137.4 (d, $J = 13.5$ Hz), 137.0 (d, $J = 14.7$ Hz), 133.4 (d, $J = 20.8$ Hz), 132.1 (d, $J = 19.4$ Hz), 131.4 (d,

$J = 18.5$ Hz), 127.9–127.0 (m), 124.3, 45.3 (d, $J = 14.4$ Hz), 40.1, 37.2, 35.1–34.8 (m), 31.7 (d, $J = 17.0$ Hz), 29.8–29.3 (m), 27.2–27.0 (m), 26.6, 26.1, 20.0. ^{31}P NMR (81 MHz, $CDCl_3$): δ −15.6 (d, $J = 3.4$ Hz), −16.2 (d, $J = 3.4$ Hz). MS (EI, 70 eV) m/z (%): 183 (25), 185 (11), 262 (9), 429 (100), 431 (27). HRMS: 506.2288 ($C_{34}H_{36}P_2$, $[M]^+$).

4.6. Synthesis of (1*S*,2*S*,*S*,*R*)-3-(diphenylphosphino)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-methyl(diphenyl)-phosphine 2

4.6.1. (1*R*,3*S*,5*R*)-6,6-dimethyl-2-methylenebicyclo-[3.1.1]hept-3-yl](diphenyl)phosphine oxide 12. Into a 250 mL Schlenk flask under argon was placed 4-dimethylaminopyridine (7.60 g, 62 mmol) in toluene (120 mL). (−)-Myrtenol (9.50 g, 62 mmol) (Dragoco, >99% ee) was added and the solution cooled down to −30 °C. At this temperature, diphenylchlorophosphine (11.2 mL, 62 mmol, Strem 98%, distilled in vacuo prior to use) was added dropwise in 5 min. The mixture was allowed to reach room temperature and heated at 100 °C for 48 h, then filtered hot through a pad of Celite and the precipitate was washed with 50 mL of hot toluene. The filtrate evaporated in vacuo, the residue filtered off and washed with ether. Yield 20.8 g (90%), white crystalline solid.

Mp 189.5–190 °C, $[\alpha]_D = -35.0$ (c 1.05, CH_2Cl_2). IR (KBr): $\bar{\nu}$ 3435 (br s), 3054 (w), 2981 (m), 2920 (s), 1631 (w), 1437 (s), 1174 (s), 1116 (s), 720 (s), 701 (vs), 538 (s), 606 (m). ^{1}H NMR ($CDCl_3$): δ 7.88–7.82 (m, 4H), 7.50–7.43 (m, 6H), 4.56 (d, $J = 3.4$ Hz, 1H), 3.91 (s, 1H), 3.64 (br s, 1H), 2.41–1.94 (m, 6H), 1.24 (s, 3H), 0.77 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.4 (d, $J = 8.5$ Hz), 134.5 (d, $J = 10.0$ Hz), 133.2 (d, $J = 13.2$ Hz), 132.2 (d, $J = 8.5$ Hz), 131.7 (m), 131.5 (d, $J = 8.5$ Hz), 129.1 (d, $J = 11.2$ Hz), 128.6 (d, $J = 11.2$ Hz), 112.3 (d, $J = 7.6$ Hz), 52.0, 41.0, 39.9, 34.9 (d, $J = 67$ Hz), 26.9, 26.5, 26.1, 21.7. ^{31}P NMR (81 MHz, $CDCl_3$): δ 37.0. MS (EI, 70 eV) m/z (%): 155 (19), 201 (68), 202 (100), 203 (76), 267 (33), 293 (22), 335 (29), 336 (28). HRMS: 336.1647 ($C_{22}H_{25}OP$, $[M]^+$).

4.6.2. (1*S*,2*S*,3*S*,5*R*)[3-(Diphenylphosphinoyl)-6,6-dimethyl-bicyclo[3.1.1]hept-2-yl]-methanol 13. Phosphine oxide **12** (8.0 g, 20 mmol) was dissolved under argon in 0.5 M THF solution of 9-BBN (Aldrich, 50 mL, 25 mmol) and the mixture heated at 70 °C in a sealed tube for 12 h. Into a 0.5 L three-necked flask was placed the dried solution of *meta*-chloroperbenzoic acid (25 g, 106 mmol, 70–75% Acros) in dichloromethane (250 mL), the flask was cooled to 15 °C in acetone–dry ice cooling bath and the solution of the hydroborated phosphine oxide added at such a rate that temperature did not exceed 20 °C. After the end of the addition, the mixture was stirred for 1 h and filtered. The filtrate was stirred for 15 min with a solution of 80 g $Na_2S_2O_5$ in 200 mL H_2O. The layers were separated and the organic phase washed twice with 100 mL portions of 2 M NaOH, then with saturated brine, dried, and evaporated. The semi-solid residue was stirred 24 h with ether (100 mL), the precipitate was filtered off, washed with ether, and dried in vacuo. Yield 5.65 g (67%), white solid.

Mp 185.5–186 °C, $[\alpha]_D = +56.6$ (c 0.66, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3370 (br s), 2882 (s), 1437 (s), 1162 (s), 720 (s), 700 (s), 538 (vs), 1117 (m). ^{1}H NMR ($CDCl_3$): δ 7.94–7.82 (m, 2H), 7.80–7.67 (m, 2H), 7.50–7.23 (m, 6H), 4.81 (br s, 1H), 3.83 (br s, 1H), 3.52–3.25 (m, 2H), 2.58 (br s, 1H), 2.27 (br s, 1H), 2.12–1.90 (m, 2H), 1.87–1.65 (m, 3H), 1.19 (s, 3H), 0.98 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 135.9, 134.6, 134.2, 132.9, 132.0, 131.7, 131.1 (d, $J = 8.7$ Hz), 130.4 (d, $J = 8.7$ Hz), 129.5 (d, $J = 11.0$ Hz), 129.1 (d, $J = 11.0$ Hz), 89.0, 65.4 (d, $J = 12.0$ Hz), 46.1, 41.5 (d, $J = 3.8$ Hz), 40.0 (d, $J = 5.0$ Hz), 39.5, 29.4, 29.0, 28.7, 28.5, 27.0, 21.3. ^{31}P NMR ($CDCl_3$): δ 39.1. MS (EI, 70 eV) m/z (%): 155 (17), 201 (42), 202 (100), 203 (22), 255 (19), 324 (72), 325 (18). HRMS: 335.1825 ($C_{22}H_{28}OP$, $[M]^+$).

4.6.3. (1*S*,2*S*,3*R*,5*S*)[3-(Diphenylphosphanyl)-6,6-dimethyl-bicyclo[3.1. 1]hept-2-yl]-methanol-borane complex 14. Compound **13** was transformed according to Section 4.1 into the corresponding phosphine–borane complex **14**. Yield 1.68 g (95%), colourless, very viscous oil.

$[\alpha]_D = +86.8$ (c 1.15, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3434 (s, br s), 2932 (s), 2387 (m), 1437 (s), 1105 (vs), 1070 (vs), 1027 (s), 740 (m), 695 (vs). ^{1}H NMR ($CDCl_3$): δ 7.82–7.72 (m, 2H), 7.61–7.52 (m, 2H), 7.41–7.32 (m, 3H), 7.27–7.18 (m, 3H), 3.55–3.35 (m, 2H), 2.61 (br s, 1H), 2.17–2.00 (m, 2H), 1.94–1.77 (m, 2H), 1.43–0.99 (m, 4H), 1.12 (s, 3H), 0.95 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 132.8 (d, $J = 8.8$ Hz), 132.3 (d, $J = 8.8$ Hz), 131.8, 131.6, 131.1, 129.3 (d, $J = 4.7$ Hz), 129.2 (d, $J = 4.7$ Hz), 128.8, 71.1 (d, $J = 5.6$ Hz), 48.5, 48.4, 41.1, 38.1, 33.8, 33.3, 32.5, 27.4, 24.1. ^{31}P NMR (81 MHz, $CDCl_3$): δ 21.0 (br s). MS (EI, 70 eV) m/z (%): 40 (48), 108 (55), 183 (100), 185 (41), 186 (69), 213 (80), 267 (85). HRMS: 351.2047 ($C_{22}H_{29}BOP$, $[M-H]^+$).

4.7. (1*S*,2*S*,3*S*,5*R*)-3-(Diphenylphosphino)-6,6-dimethyl-bicyclo[3.1.1]hept-2-yl]-methyl(diphenyl)-phosphine bis-borane complex 15

Bis-phosphine borane **15** was synthesized from **14** according to Section 4.2. The residue after evaporation was quickly dissolved in 25 mL of ether. Within minutes, crystallization of the product started; after 12 h the crystals were filtered off, washed with small amount of ether and dried in vacuo. Yield 1.29 g (48%), colourless crystals.

Mp 195.5–196 °C, $[\alpha]_D = -47.3$ (c 0.69, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3436 (m, br s), 2919 (m), 2383 (s), 2401 (s), 1437 (s), 1106 (m), 1054 (m), 739 (s), 698 (vs), 500 (m). ^{1}H NMR ($CDCl_3$): δ 7.90–7.80 (m, 2H), 7.62–7.53 (m, 2H), 7.52–7.44 (m, 2H), 7.33–7.09 (m, 10H), 7.10–6.98 (m, 2H), 6.86–6.73 (m, 2H), 3.58–3.35 (m, 1H), 3.13–2.81 (m, 2H), 2.25–2.00(m, 1H), 1.99–1.86 (m, 1H), 1.77 (br s, 1H), 1.64 (br s, 1H), 1.20 (d, $J = 10.3$ Hz), 1.09 (s, 1H), 0.87 (s, 3H), 0.71 (s, 1H), 0.50 (s, 3H). ^{13}C NMR

($CDCl_3$): δ 133.5 (d, $J = 9.4$ Hz), 133.0, 132.9, 132.8, 132.7, 132.1, 131.8, 131.7, 131.6, 131.3, 131.0, 130.9–130.7 (m), 130.2 (d, $J = 10.3$ Hz), 129.9 (d, $J = 9.7$ Hz), 129.5, 129.1, 129.0, 128.2, 44.2, 40.7 (d, $J = 8.5$ Hz), 39.1, 37.4, 29.0, 28.5, 27.9, 27.5, 27.2, 23.0. ^{31}P NMR (81 MHz, $CDCl_3$): δ 17.4 (br s), 19.0 (br s). MS (EI, 70 eV) m/z (%): 183 (24), 185 (14), 262 (10), 429 (100), 430 (30), 519 (17). HRMS: 534.2926 ($C_{34}H_{42}B_2P_2$, $[M]^+$).

4.7.1. (1*S*,2*S*,3*S*,5*R*)-3-(Diphenylphosphino)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-methyl(diphenyl)-phosphine 2. Compound **15** was transformed into the corresponding phosphine **2** according to the Section 4.3. Heating time 2 h. Yield 0.49 g (96%), colourless, very viscous oil.

$[\alpha]_D = +4.0$ (c 0.75, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3436 (m, br s), 2929 (vs), 2854 (m), 2371 (w), 1448 (w), 1064 (w). ^{1}H NMR ($CDCl_3$): δ 7.55–7.47 (m, 2H), 7.45–7.35 (m, 2H), 7.33–7.23 (m, 2H), 7.22–7.10 (m, 10H), 7.10–7.00 (m, 2H), 6.84–6.74 (m, 2H), 3.22 (t, $J = 9.1$ Hz, 1H), 2.65 (t, $J = 13.1$ Hz, 1H), 2.54–2.40 (m, 2H), 2.32–2.21 (m, 1H), 2.14–2.03 (m, 1H), 1.82–1.71 (m, 1H), 1.69–1.58 (m, 1H), 1.28 (d, $J = 9.8$ Hz, 1H), 1.08 (s, 3H), 1.04 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.8 (d, $J = 12.9$ Hz), 137.9 (d, $J = 12.6$ Hz), 137.1 (d, $J = 13.5$ Hz), 136.7 (d, $J = 14.7$ Hz), 133.3 (d, $J = 20.8$ Hz), 132.1, 131.8, 131.6, 128.1–126.7 (m), 43.6 (d, $J = 13.5$ Hz), 40.1, 38.6–38.3 (m), 38.2, 30.3–29.2 (m), 27.1–26.6 (m), 26.6 (d, $J = 31.7$ Hz), 22.2. ^{31}P NMR (81 MHz, $CDCl_3$): δ −15.7 (d, $J = 3.2$ Hz), −16.3 (d, $J = 3.2$ Hz). MS (EI, 70 eV) m/z (%): 201 (29), 262 (24), 276 (20), 321 (21), 429 (100), 430 (29). HRMS: 506.2288 ($C_{34}H_{36}P_2$, $[M]^+$).

4.8. Synthesis of (1*S*,2*S*,3*S*,5*R*)-dicyclohexyl(2-[(diphenylphosphino)methyl]-6,6-dimethylbicyclo-[3.1.1]hept-3-yl-phosphine 3

4.8.1. (1*S*,2*S*,3*S*,5*R*)-3-(Dicyclohexylphosphoryl)-6,6-dimethyl-bicyclo[3.1.1]hept-2-yl]methanol 16. According to the Section 4.4, compound **13** was transformed into adduct **16**. Yield 2.87 g (98%), white solid.

Mp 164–165 °C, $[\alpha]_D = +12.9$ (c 1.35, CH_2Cl_2). IR (KBr): ν 3401 (m, br s), 3281 (m, br s), 2954 (vs), 2928 (s), 1447 (m), 1143 (s), 1060 (w), 567 (w). ^{1}H NMR ($CDCl_3$): δ 6.05 (br s, 1H), 3.92 (br s, 1H), 3.66–3.48 (m, 1H), 3.00–2.78 (m, 1H), 2.59 (br s, 1H), 2.31–1.05 (m, 36H), 0.94 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 65.8, 46.3, 42.7, 39.7, 39.1, 37.8, 37.0, 35.6, 34.8, 28.3, 27.3, 27.2–24.9 (m), 20.5. ^{31}P NMR (81 MHz, $CDCl_3$): δ 62.0. MS (EI, 70 eV) m/z (%): 214 (45), 241 (30), 267 (31), 335 (22), 283 (32), 336 (100), 337 (33). HRMS: 367.2767 ($C_{22}H_{40}PO_2$, $[M+H]^+$).

4.8.2. (1*S*,2*S*,3*S*,5*R*)-3-(Dicyclohexylphosphoryl)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methanol borane complex (17). Compound **17** was obtained from phosphine oxide **16** according to Section 4.1. Yield 1.72 g (94%), colourless, very viscous oil.

$[\alpha]_D = +2.6$ (c 0.91, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3436 (s, br s), 2930 (vs), 2380 (m), 1634 (w, br s), 1449 (m), 1070 (m). ^{1}H NMR ($CDCl_3$): δ 4.01–3.92 (m, 1H), 3.80–3.70 (m, 1H), 3.00–2.80 (m, 1H), 2.55–2.37 (m, 1H), 2.31–1.06 (m, 33H), 1.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 63.3, 49.3, 43.5, 41.3, 40.0, 37.1, 33.2, 32.8, 32.4, 28.8, 28.0, 27.7, 27.2–27.0 (m), 25.2, 21.3, 21.0, 20.4. ^{31}P NMR ($CDCl_3$): δ 17.2 (br s). MS (EI, 70 eV) m/z (%): 117 (31), 170 (35), 198 (47), 225 (35), 279 (39), 319 (49), 333 (58), 334 (53), 361 (100), 377 (77). HRMS: 363.3014 ($C_{22}H_{41}BOP$, $[M-H]^+$).

4.9. (1*S*,2*S*,3*S*,5*R*)-Dicyclohexyl(2-[(diphenylphosphino)-methyl]-6,6-dimethylbicyclo-[3.1.1]hept-3-ylphosphine borane complex 18

Compound **17** was transformed into the corresponding bis-phosphine borane **18** according to the Section 4.2. The residue after evaporation was dissolved in dichloromethane (10 mL). Methanol (50 mL) was added and the solution concentrated on a rotary evaporator to half volume and left in a fridge at 0 °C. After 12 h, the precipitate was filtered off, washed with a small amount of ether, and dried in vacuo. Yield 1.31 g (48%), colourless crystals.

Mp 204–205 °C (dec.), $[\alpha]_D = +14.4$ (c 0.73, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3436 (m, br s), 2930 (vs), 2853 (m), 2378 (s), 1437 (m), 1070 (m), 738 (m), 695 (m). ^{1}H NMR ($CDCl_3$): δ 7.98–7.88 (m, 2H), 7.68–7.58 (m, 2H), 7.51–7.42 (m, 3H), 7.35–7.23 (m, 3H), 3.68–3.42 (m, 1H), 3.09–2.91 (m, 1H), 2.43–2.14 (m, 4H), 1.91–0.57 (m, 31H), 0.53–0.29 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 132.7 (d, $J = 8.3$ Hz), 131.9, 131.2, 131.1, 130.4, 129.9 (d, $J = 9.6$ Hz), 129.7, 129.0, 129.0 (d, $J = 9.6$ Hz), 44.8, 41.0, 39.3, 37.4, 34.7 (d, $J = 32.0$ Hz), 32.7 (d, $J = 32.0$ Hz), 28.2–25.8 (m), 23.4, 22.0–21.3 (m). ^{31}P NMR ($CDCl_3$): δ 16.8 (br s), 28.7 (br s). MS (EI, 70 eV) m/z (%): 183 (7), 435 (100), 436 (27), 530 (14), 531 (42), 532 (19). HRMS: 531.3467 ($C_{34}H_{50}BP_2$, $[M-BH_4]^+$).

4.10. (1*S*,2*S*,3*S*,5*R*)-Dicyclohexyl(2-[(diphenylphosphino)-methyl]-6,6-dimethylbicyclo-[3.1.1]hept-3-ylphosphine 3

Phosphine **3** was obtained from the borane complex **18** according to the Section 4.3. Heating time 12 h. Yield 0.49 g (95%), colourless, very viscous oil.

$[\alpha]_D = +4.5$ (c 0.93, CH_2Cl_2), IR (KBr): $\bar{\nu}$ 2923 (vs), 2849 (s), 1447 (m), 1434 (m), 1262 (m), 1096 (m), 1027 (m), 738 (s), 696 (s). ^{1}H NMR ($CDCl_3$): δ 7.64–7.52 (m, 2H), 7.47–7.35 (m, 2H), 7.35–7.21 (m, 3H), 7.20–7.10 (m, 3H), 3.40–3.20 (m, 1H), 2.60–2.23 (m, 3H), 2.22–2.08 (m, 1H), 1.98–1.81 (m, 1H), 1.80–0.46 (m, 32H). ^{13}C NMR ($CDCl_3$): δ 138.8 (d, $J = 12.3$ Hz), 137.4 (d, $J = 13.8$ Hz), 133.3 (d, $J = 20.8$ Hz), 131.7 (d, $J = 18.8$ Hz), 128.2–126.8 (m), 43.4 (d, $J = 12.3$ Hz), 40.8–39.7 (m), 38.0, 32.8–32.1 (m), 29.7 (d, $J = 17.6$ Hz), 29.0 (d, $J = 12.3$ Hz), 28.9–28.4 (m), 28.0 (d, $J = 10.3$ Hz), 27.1, 27.0–26.0 (m), 25.4 (d, $J = 17.0$ Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ −3.4 (s), −17.4 (s). MS

(EI, 70 eV) m/z (%): 41(5), 55 (7), 183 (6), 185 (5), 435 (100), 436 (26), 437 (4), 451 (8). HRMS: 518.3222 ($C_{34}H_{48}P_2$, $[M]^+$).

4.11. Synthesis of (1*S*,2*R*,3*R*,5*R*)-Dicyclohexyl-[3-(diphenylphosphino)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methylphosphine 4

4.11.1. (1*S*,2*R*,3*S*,5*R*)-2-[(Dicyclohexylphosphinoyl)-methyl]-6,6-dimethylbicyclo[3.1.1]heptan-3-ol 19. According to the Section 4.4, compound **7** was transformed into adduct **19**. Yield 2.84 g (97%), white solid.

Mp 160–161 °C, $[\alpha]_D = -20.8$ (c 0.85, CH_2Cl_2). IR (KBr): $\bar{\nu}$ 3435 (m, br s), 3231 (m, br s), 2927 (vs), 2854 (s), 1450 (m), 1147 (s), 1028 (m). ^{1}H NMR ($CDCl_3$): δ 5.94 (s, 1H), 4.05 (bs, 1H), 2.49–2.19 (m, 3H), 2.08–1.54 (m, 17H), 1.52–1.06 (m, 14H), 1.16 (s, 3H), 0.90 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 70.9, 51.0, 50.2, 42.9, 39.8, 38.7, 38.1, 37.7 (d, $J = 14.7$ Hz), 36.8, 35.2, 31.7 (d, $J = 57.5$ Hz), 28.9, 28.3–26.7 (m), 26.3, 25.3. ^{31}P NMR (81 MHz, $CDCl_3$): δ 61.0. MS (EI, 70 eV) m/z (%): 39 (6), 55 (10), 146 (9), 214 (18), 268 (6), 323 (100), 324 (23). HRMS: 367.2728 ($C_{22}H_{40}PO_2$, $[M+H]^+$).

4.11.2. (1*S*,2*R*,3*S*,5*R*)-2-[(dicyclohexylphosphoryl)-methyl]-6,6-dimethylbicyclo[3.1.1]heptan-3-ol-borane complex 20. Phosphine oxide **19** was transformed according to Section 4.3 into the corresponding phosphine–borane complex **20**. Yield 1.70 g (93%), colourless solid.

Mp 103–104 °C, $[\alpha]_D = -13.6$ (c 1.03, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 1435 (vs, br s), 2915 (m, br s), 1637 (w, br s), 1435 (m), 1183 (w, br s), 695 (s). ^{1}H NMR ($CDCl_3$): δ 4.01–3.92 (m, 1H), 2.50–2.08 (m, 4H), 1.97–1.47 (m, 19H), 1.42–1.05 (m, 18H), 0.84 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 69.4, 47.7, 47.4, 39.7, 36.5 (d, $J = 24.3$ Hz), 32.1–30.3 (m), 26.6–24.3 (m), 22.8. ^{31}P NMR (81 MHz, $CDCl_3$): δ 34 (br s). MS (EI, 70 eV) m/z (%): 55 (33), 130 (76), 131 (47), 212 (100), 251 (26), 323 (27), 350 (31). HRMS: 363.2978 ($C_{22}H_{41}BOP$, $[M-H]^+$).

4.11.3. 1*S*,2*R*,3*R*,5*R*)-Dicyclohexyl[3-(diphenylphosphino)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methylphosphine bis-borane complex 21. Compound **20** was converted into the corresponding bis-phosphine borane **21** according to the Section 4.2. The residue after evaporation was quickly dissolved in ether (25 mL). In some minutes, crystallization of the product starts. After 12 h, the precipitate was filtered off, washed with small amount of ether, and dried in vacuo. Yield 1.21 g (44%), colourless crystals.

Mp 228–229 °C, $[\alpha]_D = +206.6$ (c 0.49, CH_2Cl_2); IR (KBr): $\bar{\nu}$ 3436 (m, br s), 2930 (vs), 2852 (m), 2380 (s), 1436 (m), 1069 (w), 1056 (w), 742 (w), 695 (m). ^{1}H NMR ($CDCl_3$): δ 7.79–7.69 (m, 4H), 7.48–7.37 (m, 6H), 3.29–3.00 (m, 3H), 2.60–2.45 (m, 1H), 2.28–2.08 (m, 2H), 2.07–1.79 (m, 8H), 1.78–1.56 (m, 6H), 1.55–1.05 (m, 18H), 1.02 (s, 3H), 1.00 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 132.5 (d, $J = 9.4$ Hz), 132.2, 132.0 (d, $J = 8.8$ Hz), 131.5, 131.2, 131.0, 130.3, 129.1 (d, $J = 10.0$ Hz), 128.9 (d, $J = 10.0$ Hz), 46.9, 40.8, 38.4, 35.9, 34.6 (d, $J = 30.8$ Hz), 33.9 (d, $J = 27.8$ Hz), 30.2, 29.7, 29.4, 29.2, 28.8, 28.4–27.5 (m), 26.4 (d, $J = 22.0$ Hz), 24.6–24.0 (m), 21.5. ^{31}P NMR (81 MHz, $CDCl_3$): δ 16.0 (br s), 33.5 (br s). MS (EI, 70 eV) m/z (%): 185 (5), 435 (100), 436 (33), 531 (25), 532 (9). HRMS: 531.3499 ($C_{34}H_{50}BP_2$, $[M-BH_4]^+$).

4.11.4. (1*S*,2*R*,3*R*,5*R*)-Dicyclohexyl-{[3-(diphenylphosphino)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methyl}phosphine 4. Phosphine **4** was obtained from compound **21** according to the Section 4.3. Heating time 12 h. Yield 0.50 g (96%), viscous oil.

$[\alpha]_D = +26.5$ (c 1.8, CH_2Cl_2); IR (KBr): ν 2921 (vs), 2850 (s), 1446 (m), 1433 (m), 737 (m), 696 (s), 511 (w). ^{1}H NMR ($CDCl_3$): δ 7.42–7.32 (m, 4H), 7.26–7.17 (m, 6H), 2.73–2.60 (m, 3H), 2.49–2.20 (m, 7H), 2.07–1.37 (m, 16H), 1.29–0.98 (m, 15H), 0.94 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.4 (d, $J = 11.5$ Hz), 137.8 (d, $J = 14.1$ Hz), 132.4 (d, $J = 19.1$ Hz), 131.8 (d, $J = 18.2$ Hz), 127.5, 127.4–126.8 (m), 55.5, 52.4, 46.3, 40.4, 39.9, 37.2, 36.4, 32.7–30.3 (m), 29.6, 29.3, 28.2, 27.7, 27.4–26.3 (m), 25.5 (d, $J = 23.8$ Hz), 24.4–23.7 (m), 20.3. ^{31}P NMR (81 MHz, $CDCl_3$): δ −3.8 (s), −17.5 (s). MS (EI, 70 eV) m/z (%): 41(6), 55 (8), 183 (6), 185 (5), 435 (100), 436 (25). HRMS: 518.3240 ($C_{34}H_{48}P_2$, $[M]^+$).

4.12. Typical procedure for the catalytic asymmetric hydrogenation reaction

In a 10-mL Schlenk tube, $Rh(COD)_2BF_4$ (4.1 mg, 0.01 mmol) and of the tested phosphine (0.011 mmol) were stirred in dry CH_2Cl_2 (1 mL) for 10 min. The solvent was removed in vacuo and the residue dissolved in 5 mL of MeOH. In a 10 mL Schlenk flask under Ar, 0.5 mmol of the substrate was dissolved in 5 mL of the appropriate solvent (toluene for acetamidocinnamic and acetamidoacrylic esters, methanol for dimethyl itaconate), and the flask was filled with hydrogen. The catalyst solution (0.5 mL, 1 μmol, 2 mol%) was added and the mixture stirred for 12 h in hydrogen atmosphere. The products were isolated by flash chromatography and analyzed by chiral GC.

Methyl *N*-acetylphenylalaninate: column Chiralsil L-Val (Chrompak, 25 m × 0.12 μm × 0.22 μm); 140 °C const. Retention time: (*R*)-enantiomer 10.5 min, (*S*)-enantiomer 11.3 min.

Methyl *N*-acetylalaninate: column Chiralsil L-Val, 120 °C const., (*R*)-enantiomer 1.94 min, (*S*)-enantiomer 2.06 min.

Dimethyl itaconate: column TFA–cyclodextrine; 60 °C for 3 min, then ramp 2 °C/min to 100 °C, (*R*)-enantiomer 19.0 min, (*S*)-enantiomer 19.6 min.

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