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Preparation of polyfunctional phosphines using zinc organometallics

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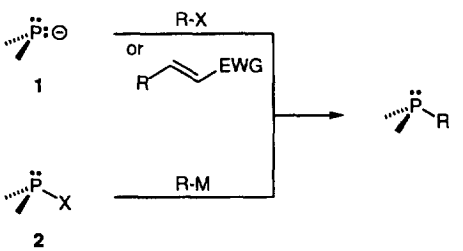
Abstract: The reaction of functionalized diorganozincs with chlorodiorganophosphines provides polyfunctional phosphines in good yields. Especially attractive is the hydroboration/boron–zinc exchange sequence which allows the conversion of functionalized olefins into polyfunctional phosphines in a one-pot procedure. Several new chiral phosphines have been prepared starting from readily available chiral olefins (terpenes) and their efficiency in asymmetric hydrogenation reactions has been evaluated. © 1997 Elsevier Science Ltd. All rights reserved.

Introduction

Phosphines are an important class of ligands for transition metal complexes.[1] Chiral phosphines have proved especially useful for the preparation of chiral transition metal catalysts of interest for asymmetric catalysis.[1,2] Two general methods involving the formation of a carbon–phosphorus bond are available for the synthesis of phosphines: (i) the reaction of a nucleophilic phosphorus entity of type **1** with an organic electrophile or (ii) the reaction of a nucleophilic organic reagent with an electrophilic phosphorus entity of type **2** via a nucleophilic displacement at the phosphorus (Scheme 1).[3]



Scheme 1.

The nucleophilic reagent used in this last reaction pathway is often an organometallic species which implies some drawbacks. It is often a highly reactive organolithium or organomagnesium compound which precludes the presence of functionalities in both the organometallic reagent and in the electrophilic phosphorus species **2**. The low selectivity of the magnesium and lithium reagents often leads to side reactions and results in moderate yields.[3] The use of more selective organometallics like organozinc compounds gives better results and a few unfunctionalized arylzinc reagents have been used with success.[4] Herein, we report the results of a general study showing that a range of polyfunctional organozinc iodides RZnI **3** and diorganozincs R_2Zn **4** react with phosphino halides of type **5** providing, after protection with BH_3, the polyfunctional phosphineborane complexes **6** in good to excellent yields (Scheme 2).[5] This methodology is also well suited for the preparation of chiral phosphines using readily available terpene derivatives as precursors. Finally, we report the results of

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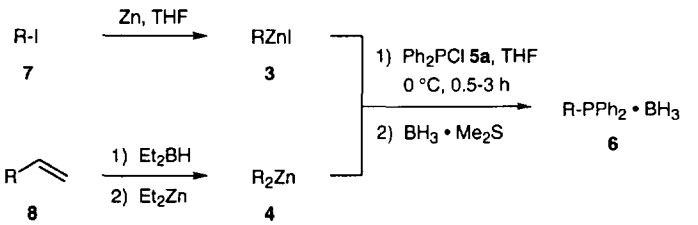
ruthenium catalyzed asymmetric hydrogenations performed with some of the newly prepared chiral phosphines as ligands.[6]



Scheme 2. Preparation of diphenylphosphine–borane complexes **6** using zinc organometallics.

Results and discussion

Alkylzinc iodides **3** are obtained in high yields by the reaction of 1,2-dibromoethane and TMSCl activated zinc dust with alkyl iodides **7** in THF (40°C, 1–3 h).[7] The reaction of chlorodiphenylphosphine **5a** with these organozinc reagents **3** proceeds smoothly at 0°C in THF and is complete within a few hours at this temperature. After completion, the crude reaction mixture is treated with $BH_3 \cdot Me_2S$[8] affording the air stable protected phosphines **6a–k** (Scheme 2 and Table 1) which can be readily purified by flash-chromatography. Secondary alkylzinc iodides like cyclohexylzinc iodide **3b** react as well furnishing the corresponding phosphine–borane complex **6b**. Alternatively, diorganozincs **4** prepared from olefins **8** via a hydroboration/boron–zinc exchange sequence[9] may also be used. Thus, the reaction of octylzinc iodide **3a** or dioctylzinc **4b** (0.5 equiv) with Ph_2PCl **5a** furnishes, after protection with borane, diphenyloctylphosphine–borane complex **6a** in 89% and 96% yields respectively (entries 1 and 2 of Table 1). Importantly, both organic groups of the diorganozinc are transferred to phosphorus.

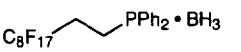
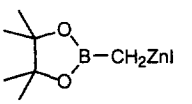
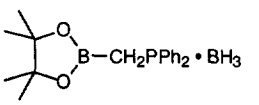
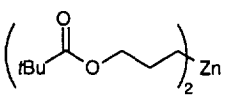
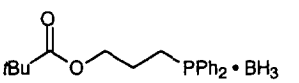
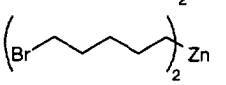
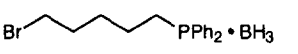
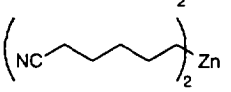
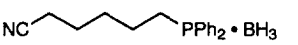
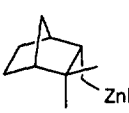
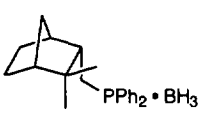
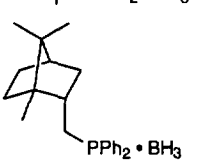
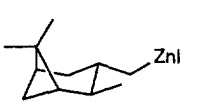
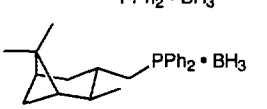
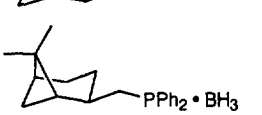
Polyfluorinated alkylzinc reagents are very useful for introducing a perfluorinated carbon chain in a molecule.[10] The polyfluorinated zinc reagent **3c** is prepared by direct insertion of zinc dust in THF and reacts with Ph_2PCl **5a** leading to the polyfluorinated phosphine **6c** in 81% yield (entry 4 of Table 1).[11,12] The corresponding diorganozinc **4a** (Scheme 3) can be prepared via a hydroboration/boron–zinc exchange procedure or an iodine/zinc exchange. However, the hydroboration of perfluorohexylethylene with Et_2BH is very sluggish leading to the diethyl(2-(perfluorohexyl)ethyl)borane in only 18% yield. The perfluorinated zinc reagent **4a** reacts well with PCl_3, $PhPCl_2$ and $Cl_2P(CH_2)_2PCl_2$ providing the expected phosphines **9a–c** respectively in 80%, 75% and 63% yield. Both **9b** and **9c** have some solubility in perfluorinated solvents like bromoperfluorooctane and constitute potential ligands for the preparation of transition metal complexes for use in perfluorinated solvents.[12]

A range of functional groups like a boronic ester (entry 5), an ester (entry 6), a bromide (entry 7) and a cyanide (entry 8) can be present in the starting zinc organometallics.[7] This provides an expeditious entry to polyfunctional phosphines (entries 5–8 of Table 1).

Various chiral terpene derived organozincs (**3e–g** and **4f**) have been prepared and reacted with Ph_2PCl **5a** resulting in the corresponding phosphines **6h–k** in 72–90% yield (entries 9–12 of Table 1). Whereas **4f** can be prepared stereospecifically by the hydroboration of β-pinene followed by a boron–zinc exchange reaction[5] in almost quantitative yield, moderate diastereoselectivities are observed for the hydroboration of camphene **10** and 2-methylenebornane **11**. The zinc reagents **3e–g** could however be prepared with high stereoselectivity by converting **10** and **11** to the carboxylic acids **12** and **13** (CH_3CO_3H, 50°C, 5d).[13a] After several recrystallizations from hexane pure *endo*-acids **12** and **13** were obtained in 16–20% yield.

Although the terpene derivative *endo*-**12** was obtained as a racemate by this procedure, the *endo*-acid **13** was enantiomerically pure.[13b,c] Both acids were reduced to the corresponding alcohols with $LiAlH_4$ (ether, 40°C, 12 h) and converted to the alkyl iodides **14** and **15** in respectively 27% and 89%

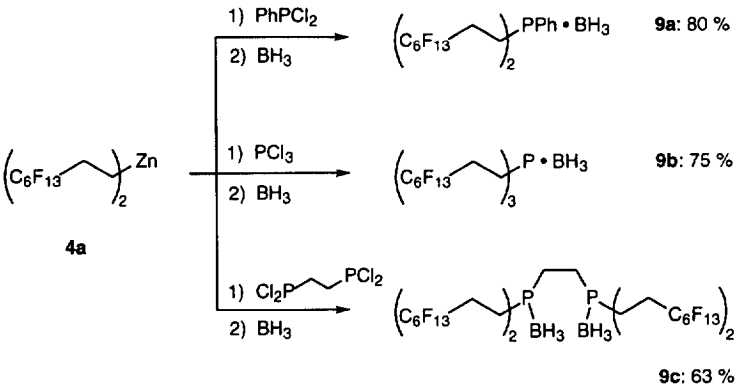
Table 1. Diphenylalkylphosphine–borane complexes **6a–k** obtained by the reaction of Ph_2PCl **5a** with zinc organometallics **3** or **4**

entry	zinc organometallic 3 or 4		product 6		yield (%)[a]
1	OctZnI	**3a**	$OctPPh_2 \cdot BH_3$	**6a**	89
2	Oct_2Zn	**4b**	$OctPPh_2 \cdot BH_3$	**6a**	96
3	*c*-HexZnI	**3b**	*c*-$HexPPh_2 \cdot BH_3$	**6b**	90
4	$C_8F_{17}CH_2CH_2ZnI$	**3c**		**6c**	81
5		**3d**		**6d**	86
6		**4c**		**6e**	83
7		**4d**		**6f**	82
8		**4e**		**6g**	86
9		**3e**		**6h**	72
10		**3f**		**6i**	75
11		**3g**		**6j**	83
12		**4f**		**6k**	90

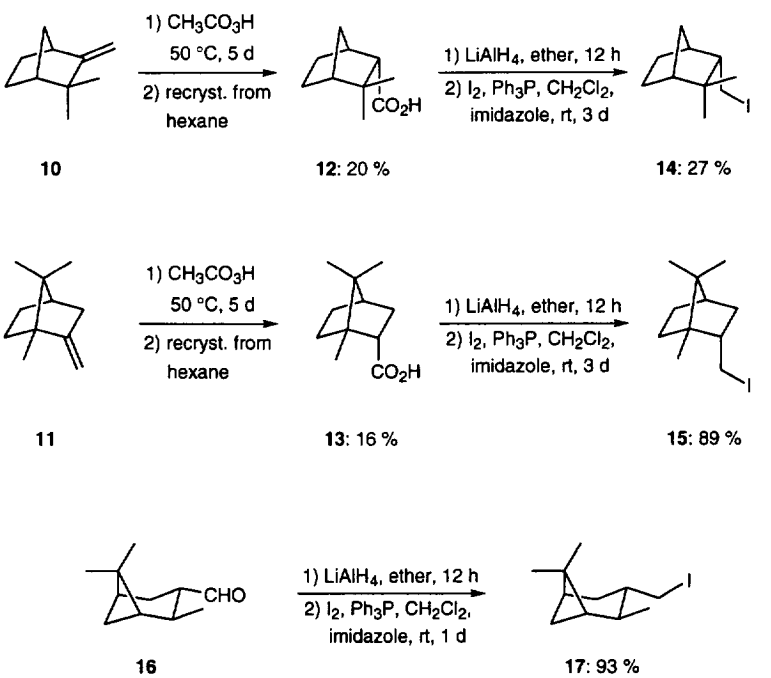
[a]Isolated yields of analytically pure products.

yield (I_2, Ph_3P, imidazole, rt, 3d).[14] Homochiral formylpinane **16**[15] was reduced with $LiAlH_4$ (ether, 40°C, 12 h) and converted as described above to the primary alkyl iodide **17** (Scheme 4).

Benzylic, alkenyl, alkynyl and arylzinc halides also react with various chlorophosphines furnishing the substituted phosphine–borane complexes **6l–6p** (Table 2). The hydroboration of stilbene with Et_2BH[5] followed by a boron–zinc exchange with Et_2Zn gives the benzylic zinc reagent **4g** which



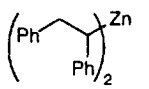
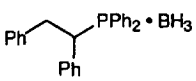
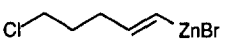
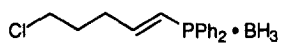
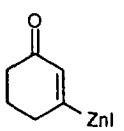
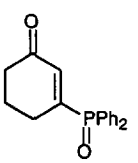
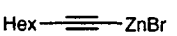
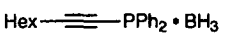
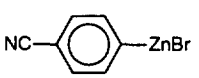
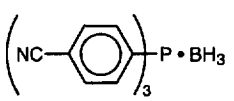
Scheme 3. Synthesis of the polyfluorinated phosphines **9**.



Scheme 4. Preparation of terpenic alkyl iodides **14**, **15** and **17**.

reacts with Ph_2PCl **5a** leading to the benzylic phosphine–borane complex **6l**. Alkenylzinc halides were prepared either by an iodine–lithium exchange followed by a transmetalation with $ZnBr_2$ like **3h**[16] or by the direct insertion of zinc dust to an activated alkenyl iodide such as 3-iodo-2-cyclohexen-1-one[17] The reaction of **3h** with Ph_2PCl **5a** produces the unsaturated phosphine–borane complex **6m** in 72% yield (entry 2 of Table 2). The zinc reagent **3i** bearing an enone function reacts with Ph_2PCl **5a** leading to a ketophosphine which cannot be cleanly converted to the borane complex due to a partial reduction of the ketone function. This phosphine was isolated after an aqueous H_2O_2 oxidation furnishing the phosphine oxide **6n** (entry 3 of Table 2). The alkynylzinc bromide **3j** reacts with Ph_2PCl **5a** giving the alkynyldiphenylphosphine–borane complex **6o** in 80% yield. The functionalized arylzinc, *p*-cyanophenylzinc bromide obtained from the corresponding aryllithium and transmetallation with $ZnBr_2$[16,18] reacts readily with PCl_3 affording the triarylphosphine **6p** in 65% yield.

Table 2. Unsaturated phosphine–borane complexes **6l–6p** obtained by the reaction of Ph_2PCl **5a** or PCl_3 with zinc organometallics **3** or **4**

entry	zinc organometallic 3 or 4		product 6		yield (%)[a]
1		**4g**		**6l**	83
2		**3h**		**6m**	72
3		**3i**		**6n**	60[b]
4		**3j**		**6o**	80
5		**3k**		**6p**	65[c]

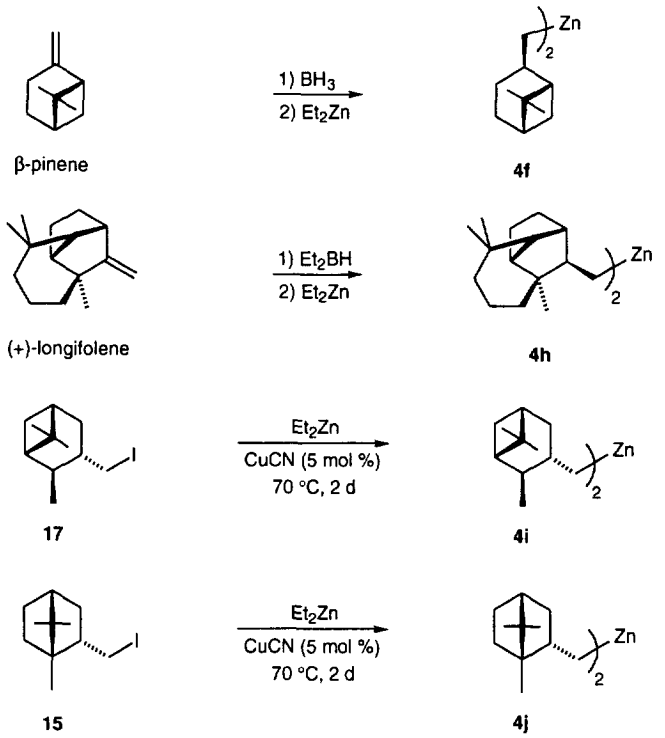
[a]Isolated yield of analytically pure product. [b]The crude phosphine was oxidized with dilute aqueous H_2O_2 leading to the phosphine oxide. [c]The arylzinc bromide was quenched with PCl_3.

The terpenylzinc reagents **4f**, **4h–j** prepared by boron–zinc exchange[5] or by iodine–zinc exchange[18] were treated with 1,2-bis(dichlorophosphino)ethane **18** and 1,4-bis(dichlorophosphino)butane[19] **19** leading to diphosphines of type **20** and **21** (Schemes 5 and 6).

To obtain the sterically hindered diphosphines **20** and **21**, heating of the diorganozincs **4** with the *bis*(dichlorophosphino)alkanes **18** or **19** to 50°C for 5 d was necessary. After borane protection and purification by recrystallization, the compounds **20–21** were obtained as white crystalline solids. The use of the more reactive lithium reagents proved to be advantageous in several cases and led to the desired diphosphines **20c–d** and **21c–d** in substantially higher yields and shorter reaction times. Treatment of the alkyl iodides **15** and **17** with *t*-BuLi (2 equiv)[20] in ether at −78°C for 0.5 h, followed by the addition of the *bis*(dichlorophosphino)alkanes **18** and **19** (−80°C to 25°C, 3 h) and protection with borane provides the diphosphine–borane complexes **20c–d** and **21c–d** (67–79% yield; Scheme 7).

The phosphine–borane complexes prepared can readily be converted into free phosphines by the treatment with an excess of diethylamine at 50°C (50 equiv, 6 h), removing the volatiles by vacuum and repeating this process a second time. Under these conditions, the phosphine–borane complexes **6a** and **6l** were converted to the free phosphines **22** and **23** in quantitative yields (Scheme 8).

The activity of the chelating diphosphines **20a–d** and **21a** as ligands for asymmetric catalysis was investigated, especially the Ru(II) catalyzed hydrogenation of ethyl acetylacetate **24** and (*E*)-2-methyl-3-phenyl-2-propen-1-ol **25**.[2c,31] Thus, by using (*p*-cymene)ruthenium(II) chloride dimer (0.5 mol%) in the presence of the chiral diphosphine (1 mol%), the unsaturated substrates **24–25** were



Scheme 5. Preparation of diorganozincs derived from terpenes.

reduced (100 bar H_2, methanol, 50°C, 14 h) leading to the expected products **26–27** with moderate enantioselectivity (Scheme 9 and Table 3).

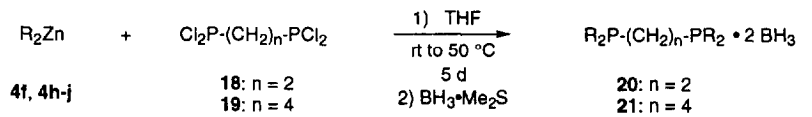
The diphosphine **20a** gives the best results and using a longer bridge between the two phosphorus atoms (four carbon chain in the case of **21a**) leads to a lower enantioselectivity (21% *ee*; see entry 2 of Table 3). These disappointing results may be explained by the remote position of the stereogenic centers in the phosphine ligand.[6]

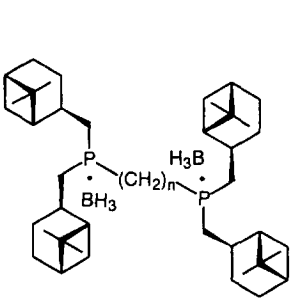
In summary, we have developed an efficient preparation of polyfunctional phosphines by using the reaction of functionalized organozinc iodides or diorganozincs with chlorophosphines. By using chiral organozinc species derived from naturally occurring terpenes, it was possible to prepare chiral phosphines and chiral diphosphines which lead to moderate enantioselectivities in hydrogenation reactions.

Experimental section

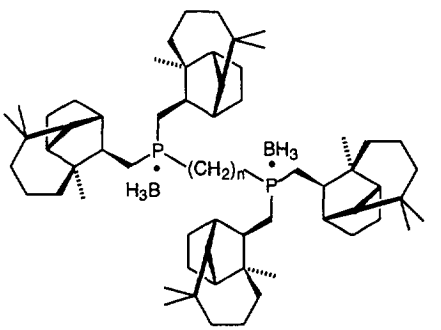
General considerations

Unless otherwise indicated all reactions were carried out under argon. Solvents (THF, ether, hexanes) were dried and freshly distilled over sodium/benzophenone. Reactions were monitored by gas chromatography (GC) or thin-layer chromatography (TLC) analysis of hydrolyzed aliquots. For the hydrogenation experiments, freshly distilled and carefully degassed methanol, methylene chloride and diethylamine were used. (*p*-Cymene)ruthenium(II) chloride dimer was purchased from Aldrich Chemical Co. Deprotection of the borane phosphines and all hydrogenation experiments were carried out in a glove box if not otherwise mentioned.

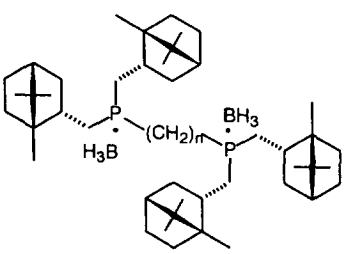




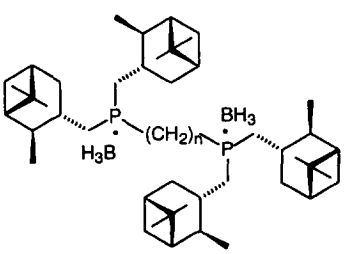
20a: n = 2; 70 %
21a: n = 4; 62 %



20b: n = 2; 45 %
21b: n = 4; 40 %



20c: n = 2; 46 %
21c: n = 4; 47 %



20d: n = 2; 63 %
21d: n = 4; 61 %

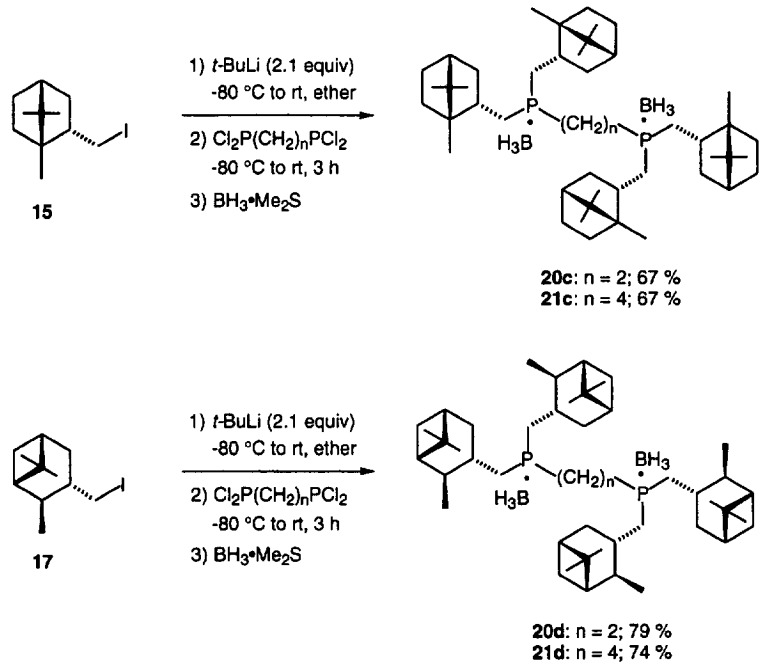
Scheme 6. Chiral diphosphines **20a–d** prepared from terpenoid zinc reagents.

Starting materials

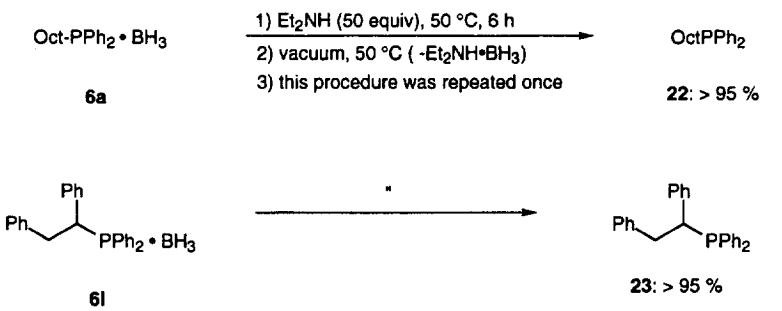
The following substances were purchased and directly used or in some cases after short-path distillation: Borane–methyl sulfide complex, 1,2-bis-(dichlorophosphino)ethane, *p*-bromobenzonitrile, *t*-BuLi (solution in pentane), camphene, chlorodiphenylphosphine (**5a**), cyclohexyl iodide, dichloro(phenyl)phosphine, diethylamine, (+)-(1*S*,2*S*,3*S*)-3-formyl-2,6,6-trimethylbicyclo[3.1.1]heptane (**16**, ca. 62% *ee*) (+)-longifolene, octyl iodide, 1-octene, 1-octyne, 2-(perfluorohexyl)ethene, 2-(perfluorohexyl)ethyl iodide, 2-(perfluorooctyl)ethyl iodide, phosphorus trichloride, (1*S*)-(−)-β-pinene, *trans*-stilbene.

The following starting materials were prepared according to literature procedures: allyl pivalate[21], *bis*(diethylamino)chlorophosphine[22], 5-bromo-1-pentene[23], 5-chloro-1-iodo-1-pentene[24], 5-hexenenitrile[25], 3-iodo-2-cyclohexen-1-one[26], 2-methylenebornane[27], 4,4,5,5-tetramethyl-3,1,2-dioxaborolylmethyl iodide[28].

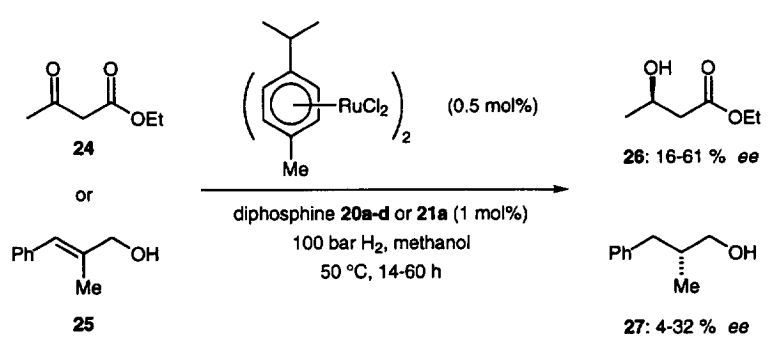
Following zinc reagents were prepared according to literature procedures: 5-chloro-1-pentenylzinc bromide **3h**[16], 4-cyanophenylzinc bromide **3k**[16], 1-cyclohexen-3-on-1-ylzinc iodide **3i**[17].



Scheme 7. Chiral diphosphines **20c–d** and **21c–d** obtained from terpenoid lithium reagents.



Scheme 8. Deprotection of phosphine boranes to free phosphines.



Scheme 9. Asymmetric hydrogenation using the new ligands.

Table 3. Ruthenium(II) catalyzed hydrogenations of **24** and **25** using the chiral diphosphine ligands **20a–d** and **21a**

entry	phosphine	substrate	time (h)	H_2 (bar)	conv. (%)[a]	*ee* (%)[b]
1	**20a**	**24**	14	100	76	61
2	**21a**	**24**	60	100	97	21
3	**20d**	**24**	14	100	76	38
4	**20c**	**24**	18	100	93	16
5	**20a**	**25**	14	100	76	32
6	**21a**	**25**	14	100	65	12
7	**20d**	**25**	14	100	78	5
8	**20c**	**25**	18	100	93	4

[a]determined by ^{1}H-NMR-analysis.

[b]determined by GC (Chirasil-DEX CB) for **26** and HPLC (Chiralcel OD, hexane/*i*-PrOH 95:5, flow 0.9 mL/min, detection at 215 nm) for **27**.

*Typical procedure A for the insertion of zinc into alkyl iodides and subsequent reaction with chlorodiphenylphosphine **5a**: preparation of 2-(perfluorooctyl)ethylzinc iodide **3c** and diphenyl(2-(perfluorooctyl)ethyl)phosphine–borane complex **6c***

a) A dry three-necked, 50 mL flask equipped with an argon inlet, a magnetic stirring bar and a low temperature thermometer was charged with zinc dust (0.98 g, 15 mmol) and flushed with argon. 1,2-Dibromoethane (200 mg) in THF (3 mL) was added. The zinc suspension was heated to ebullition with a heat gun, allowed to cool and heated again. This process was repeated three times. Then Me_3SiCl (0.15 mL) was added, and after 10 min of stirring, a solution of 2-(perfluorooctyl)ethyl iodide (2.87 g, 5 mmol) in THF (3 mL) was added dropwise over 15 min. During the addition, the temperature rose to 40°C. The reaction mixture was stirred for an additional 15 min at rt. THF (5 mL) was added and the zinc powder was allowed to settle for 3 h. GC analysis of a reaction aliquot indicates complete conversion of the alkyl iodide to the zinc organometallic. No side products were detected and the yield was estimated to be ≥ 95 %.

b) The clear alkylzinc iodide solution was transferred to a 50 mL Schlenk-flask, cooled to 0°C and chlorodiphenylphosphine **5a** (0.88 g, 4.0 mmol, 0.8 equiv) was added and the reaction mixture was stirred for 3 h at 0°C. $BH_3 \cdot Me_2S$ (0.30 g, 4 mmol) was added to protect the free phosphine. After 1 h of stirring at rt, the mixture was worked up as usual and the crude product was purified by chromatography (hexanes/CH_2Cl_2/ether 15:4:1) providing pure **6c**. Yield: 2.09 g (81%).

*Typical procedure B for the hydroboration of alkenes with diethylborane, subsequent boron–zinc exchange and reaction with chlorodiphenylphosphine **5a**: Preparation of di(5-bromopentyl)zinc (**4d**) and 5-bromopentyldiphenylphosphine–borane complex **6f***

a) 5-Bromo-1-pentene (1.49 g, 10.0 mmol) was cooled to 0°C and Et_2BH (10.0 mmol solution in ether, prepared from $BH_3 \cdot Me_2S$ (3.80 g, 50 mmol) and Et_3B (9.80 g, 100 mmol) and ether (14.8 g)) was slowly added via syringe. After 3 h at rt, the solvents were removed under vacuum (0.1 mmHg,

0°C, 0.5 h) affording the expected 5-bromopentyl(diethyl)borane (2.02 g, 92% yield) as a colorless oil having ca. 95% purity as shown by ^1H and ^{13}C NMR analysis.

b) The organoborane (1.84 g, 8.4 mmol) was transfered to a 50 mL Schlenk-flask, cooled to 0°C and Et_2Zn (1.04 g, 16.8 mmol, 2 equiv) was added. After 0.5 h at 0°C, the excess of Et_2Zn and formed Et_3B was pumped off (0.1 mmHg, 0°C, 3 h). The resulting colorless di(5-bromopentyl)zinc **4d** was diluted with THF (5 mL) and cooled to 0°C. Chlorodiphenylphosphine **5a** (1.67 g, 7.6 mmol, 0.9 equiv) was added and the reaction mixture was stirred for 3 h at 0°C. $BH_3 \cdot Me_2S$ (0.58 g, 7.6 mmol) was added to protect the free phosphine. After 1 h stirring at rt, the mixture was worked up as usual and the crude product was purified by chromatography (hexanes/CH_2Cl_2/ether 15:4:1) providing pure **6f**. Yield: 2.16 g (82%).

*Bis(2-(perfluorohexyl)ethyl)zinc **4a***

a) Diethyl(2-(perfluorohexyl)ethyl)borane was prepared according to typical procedure B using perfluorohexylethene (17.3 g, 50.0 mmol) and diethylborane (50.0 mmol, 1 equiv). Reaction conditions: 5 d at 80°C, yield: 3.70 g (18%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=2.23 (sept, J=9.0 Hz, 2H), 1.50 (q, J=8.0 Hz, 2H), 1.26 (q, J=7.5 Hz, 4H), 0.99 (t, J=7.5 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=125.0–105.0 (m, 6C), 26.5 (t, J=22.9 Hz), 19.4 (br), 16.6 (br), 7.6.

b) Bis(2-(perfluorohexyl)ethyl)zinc **4a** was prepared from diethyl(2-(perfluorohexyl)ethyl)borane (1.25 g, 3.0 mmol) and diethylzinc (0.74 g, 6.0 mmol, 2 equiv). ^1H NMR (200 MHz, $CDCl_3$): δ=2.34 (sept, J=8.9 Hz, 4H), 0.47 (t, J=7.6 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=125–105 (m, 12C), 27.7 (t, J=22.7 Hz), 0.6 (t, J=6.8 Hz).

*Typical procedure C for the iodine/zinc exchange of alkyl iodides with diethylzinc: Preparation of bis(2-(perfluorohexyl)ethyl)zinc **4a***

2-(Perfluorohexyl)ethyl iodide (23.7 g 50 mmol), diethylzinc (9.26 g, 75 mmol, 1.5 equiv) and CuCN (0.05 g, 0.5 mmol) were heated to 70°C for 12 h. After cooling to rt, all volatiles were pumped off under high vacuum for 6 h. The resulting gray oil was purified by dissolution in THF (20 mL), allowing the solids to settle, transferring the resulting clear and colorless supernate into a different flask and pumping off the solvent. Yield of **4a**: 18.6 g (98%) as a colorless liquid. ^1H NMR (200 MHz, $CDCl_3$): δ=2.34 (sept, J=8.9 Hz, 4H), 0.47 (t, J=7.6 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=125–105 (m, 12C), 27.7 (t, J=22.7 Hz), 0.6 (t, J=6.8 Hz).

*Dimyrtanylzinc **4f***

a) Trimyrtanylborane was prepared by hydroboration of (1*S*)-(−)-β-pinene (13.6 g, 100 mmol, 3.3 equiv) in ether (10 mL) with $BH_3 \cdot Me_2S$ (2.28 g, 30 mmol, 1 equiv). Reaction conditions: 1d at rt, yield: 12.6 g (99%) as a white solid. Purification by recrystallization from hexane. ^1H NMR (200 MHz, $CDCl_3$): δ=2.45–2.15 (m, 6H), 1.80 (m, 12H), 1.55 (m, 3H), 1.32 (m, 9H), 1.09 (s, 9H), 0.98 (s, 9H), 0.81 (d, J=9.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=49.2, 41.3, 38.8, 38.4, 34.4, 28.3, 26.8, 25.3, 23.4.

b) Trimyrtanylborane (12.5 g, 29.6 mmol) was reacted with diethylzinc (7.32 g, 59.3 mmol, 2 equiv) according to typical procedure B. Yield of **4f**: 15.0 g (99%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=2.30 (m, 4H), 2.19–1.70 (m, 10H), 1.53–1.34 (m, 2H), 1.21 (s, 6H), 1.10 (s, 6H), 0.86 (d, J=9.2 Hz, 2H), 0.61 (dd, J=7.5 Hz, 9.0 Hz, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=52.2, 41.4, 40.1, 39.0, 34.8, 28.9, 28.7, 27.8, 27.0, 23.6.

*Dilongifolylzinc **4h***

a) Diethyl(longifolyl)borane was prepared according to typical procedure B using (+)-longifolene (20.4 g, 100 mmol) and diethylborane (100 mmol, 1 equiv). Reaction conditions: 2 d at 40°C. Yield: 22.3 g (81%) as a white insoluble solid.

b) Diethyl(longifolyl)borane (22.0 g, 80.2 mmol) was reacted with diethylzinc (19.8 g, 160 mmol, 2 equiv). Yield of **4h**: 17.2 g (90%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=2.05 (m, 2H),

1.95–1.15 (m, 26H), 1.04 (s, 6H), 1.01 (s, 12H), 0.56 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=64.7, 54.5, 49.8, 46.0, 44.8, 39.5, 38.0, 34.5, 33.0, 32.3, 31.7, 31.6, 25.2, 21.6, 19.0.

Bis((+)-(1S,2S,3S)-2,6,6-trimethylbicyclo[3.1.1]hept-3-ylmethyl)zinc ***4i***

Prepared according to typical procedure C from alkyl iodide **17** (27.8 g, 100 mmol), diethylzinc (24.7 g, 200 mmol) and CuCN (0.45 g, 5 mmol). Reaction conditions: 2 d at 70°C. Yield of **4i**: 18.4 g (100%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.43–2.27 (m, 4H), 2.10–1.88 (m, 4H), 1.78 (m, 2H), 1.62 (dt, *J*=1.7 Hz, 7.1 Hz, 2H), 1.44 (ddd, *J*=2.2 Hz, 6.5 Hz, 13.0 Hz, 2H), 1.21 (s, 6H), 1.07 (d, *J*=7.0 Hz, 6H), 1.03 (s, 6H), 0.85 (d, *J*=9.3 Hz, 4H), 1.05–0.75 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=49.6, 48.8, 42.7, 41.1, 38.6, 36.1, 35.3, 30.4 (br), 28.4, 23.1, 21.8.

Bis((1S,2S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylmethyl)zinc ***4j***

Prepared according to typical procedure C from alkyl iodide **15** (5.56 g, 20 mmol), diethylzinc (4.94 g, 40 mmol) and CuCN (0.09 g, 1 mmol). Reaction conditions: 2 d at 70°C. Yield of **4j**: 3.31 g (90%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.25–1.95 (m, 4H), 1.80–1.50 (m, 6H), 1.35–1.00 (m, 4H), 0.91 (s, 12H), 0.80 (s, 6H), 0.57 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=48.9, 48.7, 45.8, 41.7, 41.5, 29.0, 27.8, 20.5, 18.7, 17.5 (br), 14.7.

*Diphenyl(octyl)phosphine–borane complex (****6a****)*

Prepared according to typical procedure A from octylzinc iodide (**3a**) (using activated zinc dust (0.65 g, 10 mmol) in THF (5 mL) and octyl iodide (neat, 1.20 g, 5 mmol). Reaction conditions: 15 min at 35°C, ca. 95% yield), chlorodiphenylphosphine (**5a**) (1.10 g, 5.0 mmol) and $BH_3 \cdot Me_2S$ (0.38 g, 5.0 mmol). Reaction conditions: 0°C, 1 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6a**: 1.39 g (89%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.74 (m, 4H), 7.48 (m, 6H), 2.25 (m, 2H), 1.70–1.25 (m, 12H), 0.91 (t, *J*=6.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=131.9 (d, *J*=9.1 Hz), 130.9 (d, *J*=2.5 Hz), 129.5 (d, *J*=54.9 Hz), 128.5 (d, *J*=9.6 Hz), 31.5, 30.9 (d, *J*=13.6 Hz), 28.8, 28.7, 25.4 (d, *J*=36.7 Hz), 22.7, 22.4, 13.9. IR (neat): 2930 (s), 2385 (s), 1435 (s), 1110 (s), 1060 (s), 735 (s), 695 (s) cm^{-1}. MS (EI): 298 (39), 229 (39), 2163 (33), 199 (100), 186 (76), 108 (58). Anal. calcd. for $C_{20}H_{30}BP$: C, 76.93%; H 9.68%. Found C, 76.81%; H, 9.73%.

Diphenyl(octyl)phosphine–borane complex ***6a***

a) Diethyl(octyl)borane was prepared according to typical procedure B using 1-octene (1.12 g, 10.0 mmol) and diethylborane (10.0 mmol, 1 equiv). Reaction conditions: 3 h at 0°C. Yield: 1.73 g (95%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.24 (m, 16H), 0.91 (t, *J*=7.6 Hz, 6H), 0.85 (t, *J*=6.7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=33.0, 32.1, 29.7, 29.4, 28.4 (br), 24.6, 22.8, 19.0 (br), 14.1, 8.1.

b) Dioctylzinc **4b** was prepared from diethyl(octyl)borane (1.73 g, 9.5 mmol) and diethylzinc (2.35 g, 19.0 mmol, 2 equiv) and was reacted with chlorodiphenylphosphine **5a** (2.10 g, 9.5 mmol) and $BH_3 \cdot Me_2S$. Reaction conditions: 0°C, 1 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6a**: 2.84 g (96%). See above for the analytical data.

Cyclohexyldiphenylphosphine–borane complex ***6b***

Prepared according to typical procedure A from cyclohexylzinc iodide **3b** (using activated zinc dust (1.96 g, 30 mmol) in THF (10 mL) and cyclohexyl iodide (neat, 2.10 g, 10 mmol). Reaction conditions: 30 min at 40°C, ca. 97% yield). The zinc reagent **3a** was reacted with chlorodiphenylphosphine **5a** (2.10 g, 10.0 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Reaction conditions: 0°C, 3 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6b**: 2.53 g (90%) isolated as white crystals (m.p. 92°C). ^{1}H NMR (200 MHz, $CDCl_3$): δ=8.35 (m, 4H), 7.70 (m, 6H), 2.73 (m, 1H), 2.10–1.40 (m, 10H), 2.00–0.50 (br (BH_3), 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=132.4 (d, *J*=8.7 Hz), 130.8 (d, *J*=2.5 Hz), 128.5 (d, *J*=9.5 Hz), 128.2 (d, *J*=53.2 Hz), 33.3 (d, *J*=36.3 Hz), 26.5, 26.3, 25.6 (d, *J*=1.2 Hz). IR (KBr): 2940 (s), 2385 (s), 1435 (s), 1110 (m), 1065 (m), 735 (s), 690 (s) cm^{-1}.

MS (EI): 55 (19), 108 (67), 186 (56), 213 (20), 268 (100). Anal. calcd. for $C_{18}H_{24}BP$: C, 76.62%; H, 8.57%. Found: C, 77.01%; H, 8.71%.

Diphenyl(2-(perfluoroctyl)ethyl)phosphine–borane complex ***6c***

Prepared according to typical procedure A from 2-(perfluorohexyl)ethylzinc iodide (**3c**, 5.0 mmol). The zinc reagent **3c** was reacted with chlorodiphenylphosphine **5a** (0.88 g, 4.0 mmol) and $BH_3 \cdot Me_2S$ (0.30 g, 4.0 mmol). Reaction conditions: 0°C, 1 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6c**: 2.09 g (81%) as a white solid (m.p. 71°C). ^1H NMR (200 MHz, $CDCl_3$): δ=7.73 (m, 4H), 7.52 (m, 6H), 2.60–2.25 (m, 4H), 2.10–0.40 (br (BH_3), 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=132.1 (d, *J*=9.5 Hz), 131.8 (d, *J*=2.5 Hz), 129.1 (d, *J*=9.9 Hz), 127.8 (d, *J*=56.1 Hz), 25.6 (t, *J*=23.1 Hz), 17.1 (d, *J*=38.8 Hz). IR (KBr): 2395 (m), 1440 (m), 1240 (s), 1205 (s), 1145 (s) cm^{-1}. MS (EI): 632 (100), 201 (21), 185 (92), 183 (44). Anal. calcd. for $C_{22}H_{17}BF_{17}P$: C, 40.90%; H, 2.65%. Found: C, 40.76%; H, 2.65%.

4,4,5,5-Tetramethyl-1,3,2-dioxaborolanylmethyldiphenylphosphine–borane complex ***6d***

Prepared according to typical procedure A from 4,4,5,5-tetramethyl-1,3,2-dioxaborolylmethylzinc iodide **3d** (using activated zinc dust (0.98 g, 15 mmol) in THF (5 mL) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolylmethyl iodide (neat, 1.34 g, 5 mmol). Reaction conditions: 1 h at 30°C, ca. 95% yield). The zinc reagent **3d** was reacted with chlorodiphenylphosphine **5a** (0.88 g, 4.0 mmol) and $BH_3 \cdot Me_2S$ (0.38 g, 5.0 mmol). Reaction conditions: 0°C, 1 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6d**: 1.17 g (86%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=7.68 (m, 4H), 7.39 (m, 6H), 1.80 (d, *J*=14.8 Hz, 2H), 1.07 (s, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=131.8 (d, *J*=9.9 Hz), 130.9 (d, *J*=55.3 Hz), 130.6 (d, *J*=2.5 Hz), 128.2 (d, *J*=9.9 Hz), 83.8, 24.4, 9.5 (br). IR (neat): 2980 (s), 2410 (s), 2355 (s), 1325 (s), 1145 (s), 1050 (s), 735 (s), 700 (s) cm^{-1}. MS (EI): 326 (100), 215 (31), 201 (30), 183 (29), 105 (20). Anal. calcd. for $C_{19}H_{27}B_2O_2P$: C, 67.12%; H, 8.00%. Found: C, 66.97%; H, 7.98%.

3-Pivaloxypropyldiphenylphosphine–borane complex ***6e***

a) Tri(3-pivaloxypropyl)borane was prepared by hydroboration of allyl pivalate (2.13 g, 15.0 mmol, 3 equiv) with $BH_3 \cdot Me_2S$ (0.38 g, 5.0 mmol, 1 equiv). Reaction conditions: 2d at 35°C. Yield: 1.23 g (56%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=3.94 (t, *J*=6.5 Hz, 6H), 1.67 (quin, *J*=7.8 Hz, 6H), 1.20 (s, 27H), 0.84 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=178.4, 66.2, 38.6, 27.1, 26.0, 23.6 (br).

b) Di(3-pivaloxypropyl)zinc **4c** was prepared according to typical procedure B from tri(3-pivaloxypropyl)borane (1.14 g, 2.6 mmol) and diethylzinc (1.92 g, 15.5 mmol, 6 equiv) and was reacted with chlorodiphenylphosphine **5a** (1.82 g, 7.0 mmol) and $BH_3 \cdot Me_2S$ (0.61 g, 8.0 mmol). Reaction conditions: 0°C, 1 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6e**: 2.00 g (83%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=7.60 (m, 4H), 7.31 (m, 6H), 3.95 (t, *J*=6.1 Hz, 2H), 2.15 (m, 2H), 1.75 (m, 2H), 1.06 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=177.8, 131.7 (d, *J*=9.1 Hz), 131.0 (d, *J*=2.5 Hz), 128.7 (d, *J*=54.9 Hz), 128.6 (d, *J*=9.9 Hz), 63.8 (d, *J*=15.1 Hz), 48.3, 38.4, 26.9, 22.4 (d, *J*=4.5 Hz), 21.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ=17.1. IR (neat): 2970 (s), 2385 (s), 1725 (s), 1285 (s), 1155 (s), 740 (s), 700 (s) cm^{-1}. MS (EI): 328 (62), 243 (100), 217 (63), 199 (55), 183 (62), 91 (53), 57 (87). Anal. calcd. for $C_{20}H_{28}BO_2P$: C, 70.19%; H, 8.25%. Found: C, 69.94%; H, 8.48%.

5-Bromopentyldiphenylphosphine–borane complex ***6f***

a) 5-Bromopentyldiethylborane was prepared according to typical procedure B using 5-bromo-1-pentene (1.49 g, 10.0 mmol) and diethylborane (10 mmol, 1 equiv). Reaction conditions: 3 h at 0°C. Yield: 2.02 g (92%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=3.34 (t, *J*=6.9 Hz, 2H), 1.80 (m, 2H), 1.35 (m, 4H), 1.13 (q, *J*=7.3 Hz, 6H), 0.87 (t, *J*=7.3 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=33.9, 32.8, 31.3, 27.7 (br), 23.6, 19.8 (br), 8.0.

b) Di(5-bromopentyl)zinc **4d** was prepared from 5-bromopentyldiphenylborane (1.84 g, 8.4 mmol) and diethylzinc (1.04 g, 16.8 mmol, 2 equiv) and was reacted with chlorodiphenylphosphine **5a** (1.67 g, 7.6 mmol) and $BH_3 \cdot Me_2S$ (0.58 g, 7.6 mmol). Reaction conditions: 0°C, 1 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6f**: 2.16 g (82%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=7.63 (m, 4H), 7.39 (m, 6H), 3.28 (t, *J*=7.6 Hz, 2H), 2.21 (m, 2H), 1.76 (quin, *J*=6.8 Hz, 2H), 1.47 (m, 4H), 1.50–0.40 (br (BH_3), 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=131.9 (d, *J*=9.0 Hz), 131.0 (d, *J*=2.1 Hz), 129.3 (d, *J*=54.9 Hz), 128.7 (d, *J*=9.8 Hz), 33.3, 31.9, 29.4 (d, *J*=14.0 Hz), 25.4 (d, *J*=37.1 Hz), 22.1. IR (neat): 2945 (s), 2380 (s), 1435 (s), 1110 (s), 1060 (s), 735 (s), 700 (s) cm^{-1}. MS (EI): 255 (100), 214 (10), 199 (9), 183 (13), 109 (13). Anal. calcd. for $C_{17}H_{23}BBrP$: C, 58.50%; H, 6.64%. Found: C, 58.22%; H, 6.56%.

5-Cyanopentyldiphenylphosphine–borane complex ***6g***

a) 5-Cyanopentyldiethylborane was prepared according to typical procedure B using 5-hexenenitrile (0.95 g, 10.0 mmol) and diethylborane (10 mmol, 1 equiv). Reaction conditions: 3 h at 0°C. Yield: 1.46 g (88%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=2.28 (t, *J*=7.0 Hz, 2H), 1.59 (m, 2H), 1.40–1.00 (m, 10H), 0.86 (t, *J*=7.3 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=119.6, 25.2, 27.0 (br), 25.2, 23.7, 19.0 (br), 16.9, 7.9.

b) Di(5-cyanopentyl)zinc **4e** was prepared from 5-cyanopentyldiphenylborane (1.39 g, 8.4 mmol) and diethylzinc (1.04 g, 16.8 mmol, 2 equiv) and was reacted with chlorodiphenylphosphine **5a** (1.67 g, 7.6 mmol) and $BH_3 \cdot Me_2S$ (0.58 g, 7.6 mmol). Reaction conditions: 0°C, 1 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6g**: 1.92 g (86%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=7.45 (m, 4H), 7.22 (m, 6H), 2.03 (t, *J*=6.6 Hz, 2H), 1.31 (s, 8H), 0.30–1.50 (m (BH_3), 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=132.5 (d, *J*=9.6 Hz), 131.7 (d, *J*=2.7 Hz), 129.9 (d, *J*=44.2 Hz), 129.2 (d, *J*=3.7 Hz), 120.0, 30.3 (d, *J*=14.9 Hz), 26.1, 25.4 (d, *J*=8.0 Hz), 22.8, 17.4. IR (neat): 2935 (s), 2865 (s), 2380 (s), 2245 (m), 1440 (s) cm^{-1}. MS (EI): 294 (12), 281 (70), 257 (50), 241 (100), 199 (56), 36 (56). Anal. calcd. for $C_{18}H_{23}BNP$: C, 73.25%; H, 7.85%; N, 4.75%. Found: C, 73.08%; H, 7.81%; N, 4.69%.

endo-*2,2-Dimethyl-3-(diphenylphosphinomethyl)bicyclo[2.2.1]heptane* ***6h***

Prepared according to typical procedure A from *endo*-2,2-dimethylbicyclo[2.2.1]hept-3-ylmethylzinc iodide **3e** (using activated zinc dust (1.65 g, 25.2 mmol) in THF (10 mL) and *endo*-2,2-dimethyl-3-(iodomethyl)bicyclo[2.2.1]heptane (neat, 3.33 g, 12.6 mmol). Reaction conditions: 8 h at 40°C, ca. 90% yield). The zinc reagent **3e** was reacted with chlorodiphenylphosphine **5a** (1.94 g, 8.8 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Reaction conditions: rt, 6 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6h**: 2.13 g (72%) as a colorless solid (m.p. 98°C). ^1H NMR (200 MHz, $CDCl_3$): δ=7.76 (m, 4H), 7.44 (m, 6H), 2.50–2.10 (m, 2H), 2.05–1.70 (m, 3H), 1.60–1.45 (m, 2H), 1.30–1.00 (m, 4H), 0.90 (s, 3H), 0.88 (s, 3H), 1.50–0.50 (br (BH_3), 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=131.9 (dd, *J*=9.1 Hz, 23.5 Hz), 130.7 (dd, *J*=1.0 Hz, 4.5 Hz), 130.0 (dd, J=12.0 Hz, 53.6 Hz), 128.3 (dd, *J*=6.6 Hz, 9.5 Hz), 48.1, 44.9, 44.3 (d, *J*=1.7 Hz), 37.6 (d, *J*=10.7 Hz), 36.6, 31.2, 24.3, 22.4 (d, *J*=36.7 Hz), 22.0, 19.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ=17.0. IR (KBr): 2950 (s), 2390 (s), 2340 (s), 1435 (s), 1065 (s), 735 (s), 695 (s) cm^{-1}. MS (EI): 322 (48), 186 (100), 108 (41). Anal. calcd. for $C_{22}H_{30}BP$: C, 78.58%; H, 8.99%. Found: C, 78.45%; H, 9.30%. $[\alpha]_D$: 0.3 ($CHCl_3$; c=5.0).

(+)-Diphenyl-((1S,2S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylmethyl)phosphine–borane complex ***6i***

Prepared according to typical procedure A from ((1*S*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylmethyl)methylzinc iodide **3f** (using activated zinc dust (0.65 g, 10.0 mmol) in THF (5 mL) and ((1*S*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylmethyl)methyl iodide (neat, 1.39 g, 5.0 mmol). Reaction conditions: 8 h at 40°C, ca. 90% yield). The zinc reagent **3f** was reacted with chlorodiphenylphosphine **5a** (0.88 g, 5.0 mmol) and $BH_3 \cdot Me_2S$ (0.38 g, 4.0 mmol). Reaction conditions: rt, 6 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6i**: 1.05 g (75%) as a

colorless solid (m.p. 114°C). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.73 (m, 4H), 7.47 (m, 6H), 2.37 (m, 1H), 2.25–1.95 (m, 2H), 1.90–1.45 (m, 4H), 1.40–1.25 (m, 1H), 1.20–0.95 (m, 1H), 0.84 (s, 3H), 0.76 (s, 3H), 0.75 (s, 3H), 0.62 (dd, *J*=4.2 Hz, 12.7 Hz, 1H), 2.00–0.00 (br (BH_3), 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=131.9 (dd, *J*=3.7 Hz, 9.1 Hz), 130.8, 129.3 (dd, *J*=19.4 Hz, 54.9 Hz), 128.4 (dd, *J*=3.7 Hz, 9.9 Hz), 49.0, 48.8, 47.7, 45.0, 37.7, (d, *J*=9.5 Hz), 28.3 (d, 36.7 Hz), 28.2, 28.1, 19.4, 18.1, 13.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ=16.9. IR (neat): 2950 (vs), 2390 (vs), 1435 (s), 1065 (s), 735 (s), 695 (s) cm^{-1}. MS (EI): 336 (65), 186 (100), 108 (25). Anal. calcd. for $C_{23}H_{32}BP$: C, 78.86%; H, 9.21%. Found: C, 78.55%; H, 8.83%. $[\alpha]_D$: 22.3 ($CHCl_3$; c=4.3).

(+)-(1S,2S,3S)-3-Diphenylphosphinomethyl-2,6,6-trimethylbicyclo[3.1.1]heptane–borane complex ***6j***

Prepared according to typical procedure A from (1*S*,2*S*,3*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-ylmethylzinc iodide **3g** (using activated zinc dust (0.65 g, 10.0 mmol) in THF (5 mL) and (1*S*,2*S*,3*S*)-3-iodomethyl-2,6,6-trimethylbicyclo[3.1.1]heptane (neat, 1.39 g, 5.0 mmol). Reaction conditions: 8 h at 40°C, ca. 90% yield). The zinc reagent **3f** was reacted with chlorodiphenylphosphine **5a** (0.88 g, 4.0 mmol) and $BH_3 \cdot Me_2S$ (0.38 g, 5.0 mmol). Reaction conditions: rt, 6 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6j**: 1.16 g (83%) as a colorless solid (m.p. 74°C). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.79 (m, 4H), 7.43 (m, 6H), 2.60–2.00 (m, 5H), 1.80 (m, 3H), 1.32 (dd, *J*=5.8 Hz, 13.5 Hz, 1H), 1.16 (s, 3H), 0.99 (d, *J*=7.3 Hz, 3H), 0.95 (s, 3H), 0.78 (d, *J*=9.5 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=131.9 (dd, *J*=9.1 Hz, 16.1 Hz), 130.8 (d, *J*=2.5 Hz), 130.1 (dd, *J*=5.4 Hz, 53.6 Hz), 128.4 (dd, *J*=3.7 Hz, 9.9 Hz), 41.6, 38.1, 36.6, (d, *J*=33.8 Hz), 35.9, 34.7, 32.1, 27.9, 22.7, 20.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ=14.4. IR (neat): 2920 (s), 2385 (s), 1440 (s), 1055 (s) 750 (s), 695 (s) cm^{-1}. MS (EI): 336 (47), 267 (44), 199 (35), 186 (100), 108 (35). Anal. calcd. for $C_{23}H_{32}BP$: C, 78.86%; H, 9.21%. Found: C, 78.73%; H, 9.27%. $[\alpha]_D$: 40.4 ($CHCl_3$; c=4.8).

Myrtanyldiphenylphosphine–borane complex ***6k***

a) Diethyl(myrtanyl)borane was prepared according to typical procedure B using (1*S*)-(−)-β-pinene (2.73 g, 20.0 mmol) and diethylborane (20 mmol, 1 equiv). Reaction conditions: 3 h at 0°C. Yield: 3.91 g (95%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.35–1.13 (m, 14H), 1.12 (s, 3H), 1.01 (s, 3H), 0.88 (t, *J*=7.5 Hz, 6H), 0.82 (d, *J*=9.6 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=49.2, 41.2, 38.7, 37.9, 34.1, 28.3, 26.7, 25.0, 23.2, 20.0 (br), 8.0.

b) Dimyrtanylzinc **4f** was prepared according to typical procedure B from diethyl(myrtanyl)borane (1.14 g, 4.0 mmol) and diethylzinc (0.99 g, 8.0 mmol, 2 equiv) and was reacted with chlorodiphenylphosphine **5a** (0.88 g, 4.0 mmol) and $BH_3 \cdot Me_2S$ (0.30 g, 4.0 mmol). Reaction conditions: 0°C, 1 h. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6k**: 1.21 g (90%) as a white solid (m.p. 72°C). ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.76 (m, 4H), 7.47 (m, 6H), 2.55 (m, 3H), 2.26 (m, 1H), 2.25–1.70 (m, 4H), 1.48 (m, 2H), 1.13 (s, 3H), 1.10 (s, 3H), 0.88 (d, *J*=9.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=131.9 (t, *J*=9.4 Hz), 130.7 (dd, *J*=2.9 Hz, 4.5 Hz), 130.1 (dd, *J*=21.4 Hz, 54.4 Hz), 128.4 (dd, *J*=1.2 Hz, 9.5 Hz), 47.3 (d, *J*=8.2 Hz), 40.5, 38.1, 35.7, 34.2 (d, *J*=34.6 Hz), 32.6, 27.4, 26.0, 23.7 (d, *J*=6.2 Hz), 23.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ=15.5. IR (KBr): 2935 (s), 2370 (s), 1435 (s), 1055 (s), 735 (s), 700 (s) cm^{-1}. MS (EI): 333 (16), 322 (100), 279 (23), 199 (55), 186 (43), 108 (52). Anal. calcd. for $C_{22}H_{30}BP$: C, 78.58%; H, 8.99%. Found: C, 78.33%; H, 8.98%. $[\alpha]_D$: −13.2 ($CHCl_3$; c=3.4).

(1,2-Diphenylethyl)diphenylphosphine–borane complex ***6l***

a) Diethyl(1,2-diphenylethyl)borane was prepared according to typical procedure B using *trans*-stilbene (2.82 g, 15.6 mmol) and diethylborane (15.6 mmol, 1 equiv). Reaction conditions: 3 d at 50°C. Yield: 3.10 g (79%) as a colorless oil.

b) *Bis*(1,2-diphenylethyl)zinc **4g** was prepared from diethyl(1,2-diphenylethyl)borane (2.50 g, 10.0 mmol) and diethylzinc (2.47 g, 20.0 mmol, 2 equiv) and was reacted with chlorodiphenylphosphine **5a** (2.21 g, 10.0 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Reaction conditions: 0°C, 1 h. Purification by recrystallization (ether/CH_2Cl_2 3:1). Yield of **6l**: 3.16 g (83%) as a white solid (m.p. 163°C). ^{1}H

NMR (200 MHz, $CDCl_3$): δ=8.06 (m, 2H), 7.56 (m, 3H), 7.45–7.05 (m, 13H), 6.90 (m, 2H), 3.98 (ddd, *J*=3.0 Hz, 11.5 Hz, 16.0 Hz, 1H), 3.31 (dddd, *J*=3.0 Hz, 11.5 Hz, 15.6 Hz, 43.0 Hz, 2H), 2.00–0.50 (br (BH_3), 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=139.2 (d, *J*=13.6 Hz), 135.0, 132.7 (dd, *J*=8.2 Hz, 27.6 Hz), 131.1 (dd, *J*=2.5 Hz, 38.8 Hz), 130.0 (d, *J*=4.5 Hz), 128.4, 128.3 (dd, *J*=9.5 Hz, 42.5 Hz), 128.0, 127.7 (d, *J*=2.1 Hz), 127.6 (d, *J*=52.0 Hz), 127.0 (d, *J*=2.5 Hz), 126.1, 45.3 (d, *J*=29.7 Hz), 36.4 (d, *J*=5.5 Hz). IR (KBr): 2405 (s), 1435 (s), 1070 (s), 745 (s), 695 (s) cm^{-1}. MS (EI): 380 (4), 366 (40), 275 (16), 181 (100), 103 (32). Anal. calcd. for $C_{26}H_{26}BP$: C, 82.12%; H, 6.89%. Found: C, 81.99%; H, 6.99%.

5-Chloro-1-pentenyldiphenylphosphine–borane complex ***6m***

5-Chloro-1-pentenylzinc bromide **3h**[16] was prepared from 5-chloro-1-iodo-1-pentene (1.38 g, 6.0 mmol) in ether (5 mL), *n*-BuLi (1.6 N in hexane, 3.75 mL, 6.0 mmol) and zinc bromide (1.35 g, 6.0 mmol) in THF (5 mL) at −100°C. The reaction mixture was warmed to −50°C and chlorodiphenylphosphine **5a** (1.10 g, 5.0 mmol) was added. After stirring for 2 h at rt, protection with $BH_3 \cdot Me_2S$ (0.38 g, 5 mmol) and additional stirring for 3 h at rt, the product was obtained after usual workup and purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6m**: 1.09 g (72%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=7.64 (m, 4H), 7.46 (m, 6H), 6.65 (m, 1H), 6.27 (m, 2H), 3.54 (t, *J*=6.4 Hz, 2H), 2.47 (q, *J*=7.1 Hz, 2H), 1.95 (quin, *J*=6.9 Hz, 2H), 2.00–0.00 (br (BH_3), 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=150.6 (d, *J*=8.1 Hz), 131.9 (d, *J*=9.5 Hz), 130.8 (d, *J*=2.1 Hz), 129.5 (d, *J*=59.0 Hz), 128.4 (d, *J*=10.3 Hz), 119.4 (d, *J*=57.3 Hz), 43.8, 31.5 (d, *J*=15.3 Hz), 30.2. IR (neat): 3075 (w), 2955 (w), 2385 (s), 1435 (s), 1060 (s), 735 (s), 695 (s) cm^{-1}. MS (EI): 301 (2), 288 (61), 253 (100), 239 (27), 183 (20). Anal. calcd. for $C_{17}H_{21}BClP$: C, 67.48%; H, 6.99%. Found: C, 67.36%; H, 7.10%.

3-Oxocyclohexenyldiphenylphosphine oxide ***6n***

Prepared according to typical procedure A from 1-cyclohexen-3-on-1-ylzinc iodide **3i**[17] using activated zinc dust (0.98 g, 15.0 mmol) in THF (5 mL) and 3-iodo-2-cyclohexen-1-one[26] (neat, 1.10 g, 5.0 mmol). Reaction conditions: 15 min at 35°C, ca. 95% yield). The zinc reagent **3i** was reacted at 0°C for 1 h with chlorodiphenylphosphine **5a** (0.88 g, 5.0 mmol). The product was not treated with borane but oxidized with aqueous H_2O_2 (35%, 2 mL) at rt for 5 min affording the corresponding phosphine oxide. Purification by flash chromatography (hexanes/CH_2Cl_2/ether 7:2:1). Yield of **6n**: 0.71 g (60%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=7.65–7.65 (m, 10H), 6.10 (d, *J*=18.5 Hz, 1H), 2.40 (m, 4H), 2.00 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=195.0 (d, *J*=16.1 Hz), 152.2 (d, *J*=86.1 Hz), 136.6 (d, *J*=7.0 Hz), 132.4 (d, *J*=2.9 Hz), 131.5 (d, *J*=9.9 Hz), 129.1 (d, *J*=103.9 Hz), 128.7 (d, *J*=12.4 Hz), 37.6, 25.1 (d, *J*=7.4 Hz), 22.7 (d, *J*=8.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ=25.6. IR (neat): 3055 (s), 2950 (s), 1685 (s), 1440 (s), 1190 (s), 1120 (s) cm^{-1}. MS (EI): 296 (100), 267 (17), 240 (15), 201 (38), 185 (25), 77 (29). Anal. calcd. for $C_{18}H_{17}O_2P$: C, 72.96%; H, 5.78%. Found: C, 72.86%; H, 5.81%.

1-Octinyldiphenylchlorophosphine–borane complex ***6o***

1-Octyne (0.55 g, 5.0 mmol) in ether (5 mL) was cooled to −80°C and a solution of *n*-BuLi (1.35 N in hexane; 3.71 mL; 5.0 mmol) was added. After 5 min, zinc bromide (1.27 g, 5.0 mmol) in THF (10 mL) was added at −60°C. The reaction mixture was warmed to −30°C and diphenylchlorophosphine (1.11 g, 5.0 mmol) was added. After stirring for 2 h at rt, protection with $BH_3 \cdot Me_2S$ (0.38 g, 5 mmol) and additional stirring for 3 h at rt, the product was obtained after usual workup and purification by flash chromatography (hexanes/CH_2Cl_2/ether 15:4:1). Yield of **6o**: 1.23 g (80%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=7.68 (m, 4H), 7.28 (m, 6H), 2.27 (dt, *J*=3.0 Hz, *J*=7.0 Hz, 2H), 1.46 (quin, *J*=7.0 Hz, 2H), 1.35–1.00 (m, 6H), 0.74 (t, *J*=6.6 Hz, 3H), 2.50–0.00 (br (BH_3), 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=131.5 (d, *J*=11.1 Hz), 131.1 (d, *J*=2.5 Hz), 129.4 (d, *J*=63.9 Hz), 128.5 (d, *J*=11.1 Hz), 112.6 (d, *J*=17.3 Hz), 69.7 (d, *J*=114.2 Hz), 30.8, 28.1, 27.4 (d, *J*=1.2 Hz), 22.2, 19.8 (d, *J*=2.1 Hz), 13.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ=4.5. IR (neat): 2930 (s), 2390 (s), 2195 (s),

1440 (s), 1105 (s), 1055 (s), 735 (s), 695 (s) cm^{-1}. MS (EI): 294 (100), 237 (47), 186 (27), 108 (34), 91 (23). Anal. calcd. for $C_{20}H_{26}BP$: C, 77.94%; H, 8.50%. Found: C, 77.72%; H, 8.21%.

Tri(4-cyanophenyl)phosphine–borane complex ***6p***

4-Cyanophenylzinc bromide **3k**[16], was prepared from *p*-bromobenzonitrile (2.46 g, 13.5 mmol) in THF (12.5 mL), *n*-BuLi (1.6 N in hexane, 8.40 mL, 13.5 mmol) and zinc bromide (3.04 g, 13.5 mmol) in THF (7 mL) at −80°C.[16] The reaction mixture was warmed to −30°C and phosphorus trichloride (0.69 g, 4.0 mmol) was added. After stirring for 12 h at rt, protection with $BH_3 \cdot Me_2S$ (0.38 g, 5 mmol) and additional stirring for 3 h at rt, the phosphine–borane complex **6p** was obtained after usual workup and purification by flash chromatography (hexanes/CH_2Cl_2/ether 10:4:1). Yield of **6p**: 0.91 g (65%) as a colorless solid (m.p. 100°C). ^1H NMR (200 MHz, $CDCl_3$): δ=8.01 (m, 12H), 2.00–0.00 (br (BH_3) 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=135.1 (d, *J*=102.3 Hz), 132.3 (d, *J*=4.1 Hz), 132.1 (d, *J*=2.1 Hz), 117.1 (d, *J*=1.7 Hz), 116.3 (d, *J*=3.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ=30.8. IR (KBr): 1690 (s), 1440 (s), 1190 (s), 720 (s), 695 (s), 545 (s) cm^{-1}. MS (EI): 296 (100), 201 (44), 185 (37), 77 (40). Anal. calcd. for $C_{21}H_{15}BN_3P$: C, 71.83%; H, 4.31%; N, 11.97%. Found: C, 71.55%; H, 4.46%; N, 12.05%.

Di(2-(perfluorohexyl)ethyl)(phenyl)phosphine–borane complex ***9a***

Di((2-perfluorohexyl)ethyl)zinc (**4a**, 1.14 g, 1.5 mmol) in THF (3 mL) was cooled to 0°C and dichloro(phenyl)phosphine (0.54 g, 3.0 mmol) was added. After stirring at 70°C for 5 h, protection with $BH_3 \cdot Me_2S$ (0.23 g, 3.0 mmol) and additional stirring for 3 h at rt, the product was obtained after usual workup and purification by flash chromatography (hexanes/CH_2Cl_2/ether 10:4:1). Yield of **9a**: 1.95 g (80%) as a white solid (m.p. 78°C). ^1H NMR (200 MHz, $CDCl_3$): δ=7.77 (m, 2H), 7.60 (m, 3H), 2.60–1.90 (m, 8H), 2.00–0.10 (br (BH_3), 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=132.8 (d, *J*=2.5 Hz), 132.0 (d, *J*=9.5 Hz), 129.6 (d, *J*=9.9 Hz), 124.7 (d, *J*=52.0 Hz), 125–105 (m, 12 C), 25.3 (t, *J*=23.7 Hz), 17.3 (d, *J*=38.4 Hz). IR (KBr): 2390 (m), 1370 (m), 1240 (s), 1230 (s), 1185 (s), 950 (m) cm^{-1}. MS: 801 (100), 780 (26), 455 (21), 127 (100), 109 (65), 91 (68). Anal. calcd. for $C_{22}H_{16}BF_{26}P$: C, 32.38%; H, 1.98%. Found: C, 32.22%; H, 2.13%.

Tri(2-(perfluorohexyl)ethyl)phosphine–borane complex ***9b***

Di((2-perfluorohexyl)ethyl)zinc (**4a**, 8.20 g, 10.8 mmol) in THF (5 mL) was cooled to 0°C and phosphorus trichloride (0.74 g, 5.4 mmol) was added. After stirring at 50°C for 24 h, protection with $BH_3 \cdot Me_2S$ (0.41 g, 5.4 mmol) and additional stirring for 3 h at rt, the product was obtained by usual workup in CH_2Cl_2 and purification by sublimation. Yield of **9b**: 4.40 g (75%) as a white solid (m.p. 95–97°C). ^1H NMR (200 MHz, THF-d_8): δ=2.48 (m, 6H), 2.18 (m, 6H), 1.0–0.0 (br (BH_3), 3H). ^{13}C NMR (50 MHz, THF-d_8): δ=125.0–105.0 (m, 18 C), 25.2 (t, *J*=22.3 Hz), 14.7 (d, *J*=34.8 Hz). ^{31}P NMR (162 MHz, THF-d_8): δ=23.6. IR (KBr): 1240 (s), 1190 (s), 1145 (s), 945 (m), 710 (m), 650 (m) cm^{-1}. MS (EI): 1086 (2), 1073 (95), 1054 (39), 742 (29), 726 (28), 69 (100). Anal. calcd. for $C_{24}H_{15}BF_{39}P$: C, 26.54%; H, 1.39%. Found: C, 26.25%; H, 1.57%.

1,2-Bis((di-(2-(perfluorohexyl)ethyl)phosphino)ethane–diborane complex ***9c***

Di((2-perfluorohexyl)ethyl)zinc (**4a**, 22.79 g, 30.0 mmol) in THF (10 mL) was cooled to 0°C and 1,2-bis(dichlorophosphino)ethane (2.31 g, 10.0 mmol) was added. After stirring at 50°C for 3 d, protection with $BH_3 \cdot Me_2S$ (1.52 g, 20.0 mmol) and additional stirring for 6 h at rt, the product was obtained after usual workup using CH_2Cl_2 as solvent and purification by sublimation. Yield of **9c**: 9.49 g (63%) as a white solid (m.p. 208°C). ^1H NMR (200 MHz, THF-d_8 at 50°C): δ=2.47 (m, 8H), 2.13 (m, 8H), 2.06 (m, 4H), 1.00–0.00 (br (BH_3), 6H). ^{13}C NMR (50 MHz, THF-d_8 at 50°C): δ=122.0–107.0 (m, 24 C), 25.9 (t, *J*=22.7 Hz), 17.2 (m), 14.6 (m). ^{31}P NMR (162 MHz, THF-d_8 at 50°C): δ=25.8. IR (KBr): 1240 (s), 1190 (s), 1145 (s), 940 (m), 745 (m), 710 (m), 650 (m) cm^{-1}. MS (EI): 1506 (14), 1491 (100), 1147 (22). Anal. calcd. for $C_{34}H_{26}B_2F_{52}P_2$: C, 27.12%; H, 1.74%. Found: C, 26.99%; H, 2.01%.

endo-2,2-Dimethylbicyclo[2.2.1]heptane-3-carboxylic acid **12**[13a]

Acetic anhydride (108 g, 1.06 mol) was cooled to 0°C and aqueous H_2O_2 (36%, 100 g, 1.06 mol) was slowly added providing peracetic acid (conc. ca. 38%). After stirring overnight at rt, camphene (57.7 g, 424 mmol) in ethyl acetate (60 mL) was added dropwise within a period of 6 h at 45°C to the peracid. The reaction mixture was heated to 50°C for 4 d and to 70°C for 1 d. It was diluted with ether (500 mL) and neutralized with aqueous KOH solution (56.0 g KOH in 400 mL H_2O) in a separation funnel. After extraction with aqueous KOH solution (28.0 g KOH in 200 mL H_2O and then 28.0 g KOH in 400 mL H_2O), the combined aqueous phase was acidified with H_3PO_4 (85%, 67 mL), extracted with ether (5×100 mL) and the combined organic phase was dried over $MgSO_4$. The solvents were removed to give the crude product (49 g) which slowly crystallized within 2 d at rt and was recrystallized four times from hexane. Yield of **12**: 14.3 g (20%) as a colorless solid (m.p. 95°C). ^{1}H NMR (200 MHz, $CDCl_3$): δ=11.92 (s, 1H), 2.46–2.33 (m, 2H), 2.05–1.91 (m, 1H), 1.85 (m, 1H), 1.63–1.58 (m, 2H), 1.48–1.22 (m, 5H), 1.12 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=180.8, 56.1, 48.9, 40.7, 38.4, 37.5, 31.8, 24.5, 22.7, 21.4. $[\alpha]_D$: −0.2 ($CHCl_3$, c=13.8).

(1S,2S)-1,7,7-Trimethylbicyclo[2.2.1]heptane-2-carboxylic acid **13**[13b,c]

Preparation according to the procedure for **12** from 2-methylenebornane (75.1 g, 0.5 mol) and peracetic acid (246 g, 1.25 mol). Yield of **13** after recrystallization four times from hexane: 14.6 g (16%) as a white solid (m.p. 82°C). ^{1}H NMR (200 MHz, $CDCl_3$): δ=12.20 (s (br), 1H), 2.68 (ddd, *J*=2.0 Hz, 5.0 Hz, 11.0 Hz, 1H), 1.97–1.80 (m, 1H), 1.75–1.65 (m, 3H), 1.50–1.35 (m, 2H), 1.35–1.18 (m, 1H), 1.03 (s, 3H), 0.89 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=182.5, 50.0, 49.9, 49.7, 45.0, 31.1, 30.4, 27.7, 19.1, 18.8, 14.8. $[\alpha]_D$: 16.8 (benzene; c=7.7).

endo-*2,2-Dimethyl-3-iodomethylbicyclo[2.2.1]heptane* **14**

a) *endo*-2,2-Dimethyl-3-hydroxymethylbicyclo[2.2.1]heptane[29]: acid **12** (45.0 g, 267 mmol) in ether was slowly added to a suspension of $LiAlH_4$ (30.0 g, 792 mmol) in ether (160 mL) at a rate sufficient to maintain a gentle reflux. The reaction mixture was heated to reflux overnight. Ice (200 mL) was carefully added in small portions and the resulting slurry was treated with aqueous H_2SO_4 (25%, 300 mL). The phases were separated and the aqueous layer was extracted with ether (7×150 mL). The combined organic phase was washed with $NaHCO_3$ solution (2×15 mL) and NaCl solution (30 mL) and dried over $MgSO_4$. Yield: 40.8 g (99%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.55 (d, *J*=1.5 Hz, 1H), 3.51 (d, *J*=3.3 Hz, 1H), 2.69 (s, 1H), 2.22 (s, 1H) 1.68 (s, 1H), 1.65–1.45 (m, 3H), 1.37–1.10 (m, 4H), 0.93 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=60.5, 52.3, 48.9, 39.6, 36.9, 36.6, 32.4, 24.4, 20.3, 20.1. $[\alpha]_D$: 0.3 ($CHCl_3$; c=4.6).

b) Triphenylphosphine (12.1 g, 46.0 mmol) was dissolved in CH_2Cl_2 (32 mL) and iodine (11.4 g, 45 mmol) was added in small portions at 0°C. Imidazole (2.88 g, 41.9 mmol) and *endo*-2,2-dimethyl-3-hydroxymethylbicyclo[2.2.1]heptane (6.46 g, 41.9 mmol) in CH_2Cl_2 (20 mL) were added to the yellow suspension and the reaction mixture was kept at 0°C for 3 d. It was poured into hexanes (350 mL) and stirred with water (10 mL) until two phases had formed. The aqueous phase was extracted with hexanes (3×50 mL). The combined organic layer was washed with $Na_2S_2O_3$ solution (1 mL), NaCl solution (3×20 mL) and dried over $MgSO_4$. The solvents were removed under reduced pressure and the product was distilled in high vacuum over copper powder (b.p. (0.2 mmHg) 85°C). Yield of **14**: 13.3 g (27%) as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.30–3.10 (m, 2H), 2.39 (s (br), 1H), 2.00–1.85 (m, 2H), 1.73–1.55 (m, 2H), 1.35–1.15 (m, 4H), 0.99 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=53.2, 50.1, 43.2, 38.6, 36.2, 32.0, 24.4, 20.3, 19.3, 7.1. IR (neat): 2955 (s), 2880 (m), 1465 (m), 1195 (m), 1185 (m) cm^{-1}. MS (EI): 137 (63), 95 (49), 81 (100), 67 (37), 55 (22), 41 (29) Anal. calcd. for $C_{10}H_{17}I$: C, 45.47%; H, 6.49%. Found: C, 45.12%; H, 6.50%. $[\alpha]_D$: 0.1 ($CHCl_3$; c=12.9).

(+)-(1S,2S)-1,7,7-Trimethyl-2-iodomethylbicyclo[2.2.1]heptane ***15***

a) (+)-(1*S*,2*S*)-1,7,7-Trimethyl-2-hydroxymethylbicyclo[2.2.1]heptane[13b] was prepared from acid **13** (7.13 g, 39.1 mmol) and $LiAlH_4$ (4.45 g, 117 mmol) using the same procedure as for **14**. Yield: 6.38 g (97%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ=3.67 (m, 1H), 3.50 (m, 1H), 2.75 (s (br), 1H), 2.05–1.75 (m, 2H), 1.75–1.50 (m, 2H), 1.45–1.20 (m, 2H), 1.15–0.95 (m, 1H), 0.95–0.75 (m, 1H), 0.82 (s, 3H), 0.81 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=65.5, 48.9, 46.9, 45.7, 44.9, 34.3, 28.8, 28.2, 18.8, 18.4, 14.8. $[\alpha]_D$: 46.4 ($CHCl_3$; c=3.2).

b) Iodide **15** was prepared from triphenylphosphine (9.23 g, 35.2 mmol), iodine (8.93 g, 35.2 mmol), imidazole (2.42 g, 35.2 mmol) and (+)-(1*S*,2*S*)-1,7,7-trimethyl-2-hydroxymethylbicyclo[2.2.1]heptane (5.92 g, 35.2 mmol) using the same procedure as for **14**. Yield of **15** after distillation over copper powder (b.p. (0.2 mmHg) 70–72°C): 8.67 g (89%) as a colorless liquid. ^1H NMR (200 MHz, $CDCl_3$): δ=3.30 (dd, *J*=3.2 Hz, 9.0 Hz, 1H), 3.06 (dd, *J*=9.0 Hz, 11.3 Hz, 1H), 2.30–2.00 (m, 2H), 1.80–1.57 (m, 2H), 1.52–1.37 (m, 1H), 1.33–1.22 (m, 1H), 1.18–1.02 (m, 1H), 0.88 (m, 1H), 0.85 (s, 3H), 0.83 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=49.8, 49.6, 47.9, 44.7, 38.2, 28.4, 27.8, 19.8, 18.4, 14.2, 11.9. IR (neat): 2985 (m), 2950 (s), 2875 (m), 1460 (m), 1390 (m), 1180 (m) cm^{-1}. MS (EI): 151 (50), 109 (50), 95 (100), 81 (45), 69 (32), 55 (35). Anal. calcd. for $C_{11}H_{19}I$: C, 47.50%; H, 6.88%. Found: C, 47.49%; H, 7.06%. $[\alpha]_D$: 74.7 ($CHCl_3$; c=7.4).

(+)-(1S,2S,3S)-3-Formyl-2,6,6-trimethylbicyclo[3.1.1]heptane ***16****, (trivial name: 3-formylpinane)*[15]

a) 2,4,6-Tris((1*S*,2*S*,3*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl)-1,3,5-trioxacyclohexane by acid catalyzed trimerisation: 3-formylpinane (ca. 62% *ee*, 360 g, 2.17 mol) in ethyl acetate (400 mL) was acidified with HCl solution (saturated in ether, 2 mL) and kept at −30°C overnight. The cloudy solution was slowly warmed to rt and a precipitate was formed. The suspension was recooled to −30°C and the precipitate (49 g) was filtered. HCl solution (2 mL) and $MgSO_4$ (2 g) was added to the mother liquid. It was stirred for 2 h at 0°C with some precipitation and kept for 7 d at −30°C. The precipitate was filtered and extracted with hot ethyl acetate. During cooling to rt, the trimer slowly precipitated (150 g, 42%) and was recrystallized from ethyl acetate. ^1H NMR (200 MHz, $CDCl_3$): δ=4.68 (d, *J*=4.2 Hz, 3H), 2.22–1.72 (m, 21H), 1.19 (s, 9H), 1.12 (d, *J*=6.2 Hz, 9H), 1.01 (s, 9H), 0.91 (d, *J*=9.5 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=106.0, 47.8, 41.0, 40.1, 38.8, 37.1, 32.7, 28.4, 28.0, 23.0, 22.5. $[\alpha]_D$: 11.1 ($CHCl_3$; c=2.36); $[\alpha]_D$: 49.5 (benzene; c=4.96).

b) Acid catalyzed cleavage: The trimer (15.0 g, 30.0 mmol) was heated with a crystal of *p*-toluenesulfonic acid to 100°C under reduced pressure in a distillation apparatus until the entire solid was molten. Then the monomer **16** was distilled off under high vacuum (b.p. (0.2 mmHg) 60°C). Yield of **16**: 13.5 g (90%) as a colorless liquid. ^1H NMR (200 MHz, $CDCl_3$): δ=9.53 (d, *J*=2.0 Hz, 1H), 2.45 (m, 1H), 2.24 (m, 2H), 2.03 (m, 2H), 1.90 (m, 1H), 1.78 (m, 1H), 1.14 (s, 3H), 1.07 (d, *J*=7.3 Hz, 3H), 0.95 (s, 3H), 0.62 (d, *J*=10.0 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=202.5, 48.7, 46.8, 40.2, 39.0, 35.8, 32.9, 27.6, 26.1, 22.7, 21.7. $[\alpha]_D$: 27.9 (neat).

(+)-(1S,2S,3S)-3-Iodomethyl-2,6,6-trimethylbicyclo[3.1.1]heptane ***17***

a) (+)-(1*S*,2*S*,3*S*)-3-Hydroxymethyl-2,6,6-trimethylbicyclo[3.1.1]heptane was prepared from formylpinane **16** (13.3 g, 80.0 mmol) and $LiAlH_4$ (3.04 g, 80.0 mmol) using the same procedure as for **13**. Yield after distillation (b.p. (0.2 mmHg) 70°C): 13.0 g (97%) as a colorless liquid. ^1H NMR (200 MHz, $CDCl_3$): δ=3.90 (s, 1H), 3.48 (m, 1H), 3.33 (m, 1H), 2.25–1.95 (m, 2H), 1.90–1.43 (m, 5H), 1.11 (s, 3H), 0.99 (d, *J*=7.2 Hz, 3H), 0.93 (s, 3H), 0.67 (d, *J*=9.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=69.4, 47.5, 41.2, 39.2, 38.7, 38.6, 33.1, 31.0, 27.8, 22.7, 21.9. $[\alpha]_D$: 39.3 ($CHCl_3$; c=4.2).

b) Iodide **17** was prepared from triphenylphosphine (18.6 g, 71.0 mmol), iodine (18.0 g, 71.0 mmol), imidazole (4.89 g, 71.0 mmol) and (+)-(1*S*,2*S*,3*S*)-3-hydroxymethyl-2,6,6-trimethylbicyclo[3.1.1]heptane (12.0 g, 71.0 mmol) using the same procedure as for **14**. Yield of **17** after distillation over copper powder (b.p. (0.2 mmHg) 75°C): 18.4 g (93%) as a colorless liquid. ^1H NMR (200 MHz, $CDCl_3$): δ=3.37 (dd, *J*=4.3 Hz, 9.3 Hz, 1 H), 3.10 (t, *J*=8.8 Hz, 1H), 2.20 (m, 2H),

1.93 (m, 2H), 1.70 (m, 2 H), 1.52 (ddd, *J*=2.3 Hz, 6.0 Hz, *J*=13.3 Hz, 1 H), 1.19 (s, 3H), 1.07 (d, *J*=7.0 Hz, 3H), 0.98 (s, 3H), 0.84 (d, *J*=9.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=47.6, 43.5, 41.6, 38.7, 38.5, 35.5, 33.3, 27.8, 22.6, 21.4, 19.4. IR (neat): 2905 (s), 1450 (m), 1385 (m), 1165 (m), 620 (m) cm^{-1}. MS (EI): 278 (1), 151 (13), 95 (100), 83 (52), 69 (76). Anal. calcd. for $C_{11}H_{19}I$: C, 47.50%; H, 6.88%. Found: 47.50%; H, 7.20%. $[\alpha]_D$: 50.1 (neat), 54.3 ($CHCl_3$; c=7.1).

1,4-Bis(dichlorophosphino)butane ***19***[19]

Butan-1,4-diyldimagnesium dibromide (50 mmol) was prepared from magnesium (2.67 g, 110 mmol) and 1,4-dibromobutane (10.8 g, 50 mmol) in THF (100 mL) in a usual manner. The resulting clear Grignard solution was transfered into a 250 mL three-necked flask equipped with a mechanical stirrer and cooled to −25°C furnishing a gray suspension. *Bis*(diethylamino)chlorophosphine[22] (21.1 g, 100 mmol) in THF (25 mL) was added within 1.5 h. The reaction mixture was stirred overnight at rt and dry dioxane (65 mL) was added. The precipitate was filtered under argon and washed with hexanes (3×50 mL). The solvents were evaporated at 30°C under reduced pressure and the residue was diluted with ether (200 mL) and transfered into a 1 L three-necked flask with a mechanical stirrer. Methyl orange was added as indicator and dry HCl gas was passed through the solution until the color of the indicator changed to dark red. The reaction mixture was stirred for 2 h at rt and the excess of HCl was removed by passing argon through the suspension. The precipitate was filtered under argon, washed with ether (4×50 mL). After removal of the ether under normal pressure, the product was distilled in high vacuum with an oil diffusion pump (b.p. (1.3×10^{-2} mbar) 75–78°C). Yield of **19**: 8.16 g (63%) as a clear colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.38 (m, 4H), 1.88 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=42.2 (d, *J*=45.0 Hz), 23.7 (dd, *J*=9.5 Hz, 13.2 Hz).

Typical procedure D for the synthesis of the chiral diphosphines ***20a–d*** *and* ***21a–d*** *from dialkylzincs (Scheme 7): Preparation of 1,2-bis(dimyrtanylphosphino)ethane–diborane complex* ***20a***

Dimyrtanylzinc (**4f**, 2.04 g, 6.0 mmol) in THF (3 mL) was cooled to 0°C and 1,2-bis(dichlorophosphino)ethane (0.46 g, 2.0 mmol) was added. After 30 min, the reaction mixture was stirred for 3 d at 50°C. $BH_3\cdot Me_2S$ (0.30 g, 4.0 mmol) was added at 0°C and the suspension was stirred at rt overnight. It was poured into CH_2Cl_2 (400 mL) and carefully quenched with $NaSO_4\cdot 10\ H_2O$ (1 g). After washing with H_2O, drying over $MgSO_4$ and removal of the solvent, the crude product was purified by recrystallization from ethyl acetate. Yield of **20a**: 0.93 g (70%) as a white solid (m.p. 148°C). ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.40–2.20 (m, 8H), 2.20–1.96 (m, 4H), 1.96–1.60 (m, 28H), 1.55–1.35 (m, 4 H), 1.16 (s, 12H), 0.99 (s, 12H), 0.90 (d, *J*=10.0 Hz, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=48.0 (quin, *J*=4.0 Hz), 40.6, 38.2, 35.7 (d, *J*=2.1 Hz), 32.8, 32.7 (dd, *J*=10.7 Hz, 30.9 Hz), 27.7 (d, *J*=1.2 Hz), 26.0, 24.2, 23.2, 17.3 (d, *J*=30.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ=19.2. IR (KBr): 2905 (s), 2365 (s), 1565 (m), 1060 (s) cm^{-1}. MS (EI): 652 (85), 501 (63), 365 (100), 333 (31), 229 (20), 69 (46). Anal. calcd. for $C_{42}H_{78}B_2P_2$: C, 75.67%; H, 11.79%. Found: C, 75.44%; H, 11.71%. $[\alpha]_D$: −43.3 ($CHCl_3$; c=3.6).

1,2-Bis(dilongifolylphosphino)ethane–diborane complex ***20b***

Preparation according to typical procedure D from dilongifolylzinc (**4h**, 3.81 g, 8.0 mmol), 1,2-bis(dichlorophosphino)ethane (0.46 g, 2.0 mmol) and $BH_3\cdot Me_2S$ (0.38 g, 5.0 mmol). Yield of **20b**: 0.84 g (45%) as a colorless solid (m.p. 105–110°C). ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.00 (s, 8H), 1.90–1.10 (m, 56H), 0.97 (s, 24H), 0.94 (s, 12H), 1.50–0.00 (br (BH_3), 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=64.4, 49.6 (d, *J*=9.5 Hz), 46.2 (m), 45.1 (d, *J*=10.3 Hz), 44.7, 38.8 (d, *J*=6.6 Hz), 37.0, 33.3, 32.8, 32.0, 31.6 (d, *J*=3.3 Hz), 31.2, 26.1 (d, *J*=32.2 Hz), 24.8, 20.8, 18.0 (d, *J*=29.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ=24.0. IR (KBr): 2940 (s), 2385 (s), 1435 (s), 1110 (m), 1065 (m), 735 (s), 690 (s) cm^{-1}. MS (EI): 921 (25), 705 (100), 557 (13), 501 (26), 470 (13). Anal. calcd. for $C_{62}H_{106}B_2P_2$: C, 79.30%; H, 11.81%. Found: C, 79.30%; H, 11.94%. $[\alpha]_D$: −13.0 ($CHCl_3$; c=3.7).

(+)-1,2-Bis(bis((1S,2S)-1,7,7-trimethylbicyclo[2.2.1]heptane-2-ylmethyl)phosphino)ethane–diborane complex ***20c***

Preparation according to typical procedure D from *bis*((1*S*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylmethyl)zinc (**4j**, 1.84 g, 5.0 mmol), 1,2-bis(dichlorophosphino)ethane (0.23 g, 1.0 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Yield of **20c**: 0.33 g (46%) as a white solid (m.p. 252°C). ^1H NMR (200 MHz, $CDCl_3$): δ=2.20–2.00 (m, 4H), 1.95–1.75 (m, 4H), 1.75–1.15 (m, 32H), 1.15–0.95 (m, 4H), 0.83 (s, 24H), 0.73 (s, 12H), 2.00–(−0.50) (br (BH_3), 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=49.0 (m, 2C), 48.0 (d, *J*=0.9 Hz), 45.3 (d, *J*=2.0 Hz), 38.4 (d, *J*=21.8 Hz), 37.8 (d, *J*=24.2 Hz), 28.2 (dd, *J*=5.2 Hz, 11.6 Hz), 26.3–25.9 (m), 19.5 (d, *J*=2.5 Hz), 18.3, 18.2 (d, *J*=31.2 Hz), 13.9 (d, *J*=2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ=21.7. IR (KBr): 2950 (vs), 2370 (s), 1460 (m), 1060 (s) cm^{-1}. MS (EI): 722 (2), 707 (100), 641 (11), 543 (72), 393 (21), 95 (32). HRMS calcd. for $C_{46}H_{86}B_2P_2$: 722.6357, found: 722.6374. $[\alpha]_D$: 56.8 ($CHCl_3$; c=4.8).

(+)-1,2-Bis(bis((1S,2S,3S)-2,6,6-trimethylbicyclo[3.1.1]hept-3-ylmethyl)phosphino)ethane–diborane complex ***20d***

Preparation according to typical procedure D from bis((+)-(1*S*,2*S*,3*S*)-2,6,6-trimethylbicyclo[3.1.1]-hept-3-ylmethyl)zinc (**4i**, 3.67 g, 10.0 mmol), 1,2-bis(dichlorophosphino)ethane (0.46 g, 2.0 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Yield of **20d**: 0.91 g (63%) as a white solid (m.p. 171°C). ^1H NMR (200 MHz, $CDCl_3$): δ=2.33 (m, 8H), 2.15–1.48 (m, 32H), 1.19 (s, 12H), 1.12 (d, *J*=10.5 Hz, 12H), 1.01 (s, 12H), 0.75 (d, *J*=9.8 Hz, 4H), 2.00–0.00 (br (BH_3), 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ=48.0, 46.3 (m), 41.9, 38.4, 36.9, (d, *J*=8.7 Hz), 35.4 (m), 34.9, 32.4 (d, *J*=13.2 Hz), 28.0 (d, *J*=1.2 Hz), 23.0, 21.0 (d, *J*=4.5 Hz), 19.3 (d, *J*=29.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ=17.2. IR (KBr): 2905 (s), 2360 (s), 1060 (s) cm^{-1}. MS (EI): 722 (7), 708 (100), 626 (24), 556 (25), 543 (40), 361 (32). Anal. calcd. for $C_{46}H_{86}B_2P_2$: C, 76.44%; H, 11.99%. Found: C, 76.70%; H, 11.98%. $[\alpha]_D$: 90.6 ($CHCl_3$; c=5.1).

Typical procedure E for the synthesis of the chiral diphosphines ***20c–d*** *and* ***21c–d*** *from lithium reagents (Scheme 8): Preparation of (+)-1,2-*bis(bis*((1S,2S)-1,7,7-trimethylbicyclo[2.2.1]heptane-2-ylmethyl)phosphino)ethane–diborane complex* ***20c***

The alkyl iodide **15** (2.64 g, 10.0 mmol) in ether (20 mL) was cooled to −110°C and *t*-BuLi (1.34 N in pentane, 15.7 mL, 21 mmol) was added whithin 5 min. The light yellow suspension was stirred at −80°C for 30 min and then warmed to rt to quench the excess *t*-BuLi. At −100°C, 1,2-*bis*(dichlorophosphino)ethane (0.29 g, 1.25 mmol) was added and the suspension was warmed slowly to rt. After 30 min, $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol) was added and the reaction mixture was treated for workup according to typical procedure D. Yield of **20c**: 0.61 g (67%). See above for the analytical data.

(+)-1,2-Bis(bis((1S,2S,3S)-2,6,6-trimethylbicyclo[3.1.1]hept-3-ylmethyl)phosphino)ethane–diborane complex ***20d***

Preparation according to typical procedure E from alkyl iodide **17** (2.78 g, 10 mmol), *t*-BuLi (21 mmol), 1,2-bis(dichlorophosphino)ethane (0.29 g, 1.25 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Yield of **20d**: 0.72 g (79%). See above for the analytical data.

1,4-Bis(dimyrtanylphosphino)butane–diborane complex ***21a***

Preparation according to typical procedure D from dimyrtanylzinc (**4f**, 9.86 g, 29.0 mmol), 1,4-bis(dichlorophosphino)butane (1.88 g, 7.3 mmol) and $BH_3 \cdot Me_2S$ (1.52 g, 20.0 mmol). Yield of **21a**: 3.13 g (62%) as a white solid (m.p. 207°C). ^1H NMR (200 MHz, $CDCl_3$): δ=2.40–2.25 (m, 8H), 2.18–2.02 (m, 4H), 2.00–1.80 (m, 14H), 1.78–1.68 (m, 8 H), 1.57–1.40 (m, 14H), 1.13 (s, 12H), 0.97 (s, 12H), 0.88 (d, *J*=9.8 Hz, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=48.3 (dd, *J*=7.9 Hz, 12.2 Hz), 40.9, 38.5, 35.8, 33.1 (dd, *J*=12.8 Hz, 31.1 Hz), 32.9, 27.9, 26.2, 24.5 (m, 3C), 23.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ=16.1. IR (KBr): 2945 (s), 2905 (s), 2350 (m), 1465 (m), 1060 (m) cm^{-1}. MS (EI): 680

(2), 679 (5), 529 (100), 393 (13), 361 (10), 69 (7). HRMS calcd. for $C_{44}H_{82}B_2P_2$: 694.6046, found: 694.6062. Anal. calcd. for $C_{44}H_{82}B_2P_2$: C, 76.07%; H, 11.90%. Found: C, 75.72%; H, 12.30%. $[\alpha]_D$: −20.9 ($CHCl_3$; c=0.77).

1,4-Bis(dilongifolylphosphino)butane–diborane complex ***21b***

Preparation according to typical procedure D from dilongifolylzinc (**4h**, 8.57 g, 18.0 mmol), 1,4-bis(dichlorophosphino)butane (1.56 g, 6.0 mmol) and $BH_3 \cdot Me_2S$ (0.91 g, 12.0 mmol). Yield of **21b**: 2.32 g (40%) as a white solid (m.p. 198°C). ^1H NMR (200 MHz, $CDCl_3$): δ=1.98 (s, 8H), 1.80–1.46 (m, 32H), 1.45–1.10 (m, 32H), 0.95 (s, 24H), 0.92 (s, 12H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=64.3, 49.5 (d, *J*=4.2 Hz), 46.1 (dd, *J*=4.3 Hz, 8.6 Hz), 45.0, 44.7, 38.7, 36.9, 33.2 (d, *J*=3.7 Hz), 32.8 (d, *J*=1.2 Hz), 31.9 (d, *J*=4.3 Hz), 31.5 (d, *J*=7.3 Hz), 31.1 (d, *J*=4.9 Hz), 26.1 (dd, *J*=23.2 Hz, 33.0 Hz), 24.7, 24.5 (d, *J*=12.8 Hz), 23.5 (d, *J*=32.3 Hz), 20.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ=20.7. IR (KBr): 2950 (s), 2375 (s), 1460 (s), 1060 (s) cm^{-1}. MS (EI): 967 (1), 953 (30), 734 (100), 529 (27), 498 (22), 470 (13). HRMS calcd. for $C_{64}H_{111}B_1P_2$ (M^+-14 (BH_3)): 952.8302, found: 952.8278. $[\alpha]_D$: −23.8 ($CHCl_3$; c=2.85), −23.5 ($CHCl_3$; c=4.6).

(+)-1,2-Bis(bis((1S,2S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylmethyl)phosphino)butane–diborane complex ***21c***

Preparation according to typical procedure D from bis((1*S*,2*S*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylmethyl)zinc (**4j**, 1.84 g, 5.0 mmol), 1,4-bis(dichlorophosphino)butane (0.26 g, 1.0 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Yield of **21c**: 0.35 g (47%) as a white solid (m.p. 228°C). ^1H NMR (200 MHz, $CDCl_3$): δ=2.20–1.98 (m, 4H), 1.95–1.75 (m, 4H), 1.75–1.15 (m, 36H), 1.15–0.95 (m, 4H), 0.83 (s, 24H), 0.73 (s, 12H), 2.00–(−0.50) (br (BH_3), 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=49.0 (d, *J*=3.3 Hz), 48.9 (d, *J*=4.0 Hz), 48.0, 45.3, 38.2 (d, *J*=10.8 Hz), 37.7 (m), 28.2 (m), 26.0 (dd, *J*=3.7 Hz, 33.5 Hz), 24.6 (d, *J*=12.9), 24.2 (d, *J*=33.2 Hz), 19.5 (d, *J*=2.4 Hz), 18.3, 13.9 (d, *J*=2.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ=18.5. IR (KBr): 2950 (vs), 2360 (s), 1460 (m), 1065 (s) cm^{-1}. MS (EI): 735 (62), 571 (100), 420 (29), 389 (42). Anal. calcd. for $C_{48}H_{90}B_2P_2$: C, 76.79%; H, 12.08%. Found: C, 76.60%; H, 11.97%. $[\alpha]_D$: 53.8 ($CHCl_3$; c=4.7).

(+)-1,2-Bis(bis((1S,2S)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylmethyl)phosphino)butane–diborane complex ***21c***

Preparation according to typical procedure E from alkyl iodide **15** (2.64 g, 10 mmol), *t*-BuLi (21 mmol), 1,4-bis(dichlorophosphino)butane (0.33 g, 1.25 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Yield of **21c**: 0.63 g (67%). See above for the analytical data.

(+)-1,4-Bis(bis((1S,2S,3S)-2,6,6-trimethylbicyclo[3.1.1]hept-3-ylmethyl)phosphino)butane–diborane complex ***21d***

Preparation according to typical procedure D from bis((+)-(1*S*,2*S*,3*S*)-2,6,6-trimethylbicyclo[3.1.1]-hept-3-ylmethyl)zinc (**4i**, 3.67 g, 10.0 mmol), 1,4-bis(dichlorophosphino)butane (0.52 g, 2.0 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Yield of **21d**: 0.92 g (61%) as a white solid (m.p. 141°C). ^1H NMR (200 MHz, $CDCl_3$): δ=2.35 (m, 8H), 2.15–1.40 (m, 36H), 1.15 (s, 12H), 1.01 (s, 12H), 0.98 (s, 12H), 0.73 (d, *J*=9.8 Hz, 4H), 2.00–0.00 (br (BH_3), 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=47.8, 46.2 (m), 41.8, 38.2, 36.6, (d, *J*=8.7 Hz), 35.4 (d, *J*=6.2 Hz), 34.7, 32.2 (m), 28.0 (d, *J*=1.2 Hz), 25.4, 24.7, 24.4, 22.9 (d, *J*=1.7 Hz), 20.8 (d, *J*=5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ=14.3. IR (KBr): 2920 (s), 2385 (s), 2355 (s), 2325 (s), 1065 (s), 850 (s) cm^{-1}. MS (EI): 751 (4), 655 (14), 572 (100), 422 (34). Anal. calcd. for $C_{48}H_{90}B_2P_2$: C, 76.79%; H, 12.08%. Found: C, 76.48%; H, 12.14%. $[\alpha]_D$: 83.0 ($CHCl_3$; c=4.4).

(+)-1,4-Bis(bis((1S,2S,3S)-2,6,6-trimethylbicyclo[3.1.1]hept-3-ylmethyl)phosphino)butane–diborane complex ***21d***

Preparation according to typical procedure E from alkyl iodide **17** (2.78 g, 10 mmol), *t*-BuLi (21 mmol), 1,4-bis(dichlorophosphino)butane (0.33 g, 1.25 mmol) and $BH_3 \cdot Me_2S$ (0.76 g, 10.0 mmol). Yield of **21d**: 0.69 g (74%). See above for the analytical data.

Octyldiphenylphosphine ***22***[30]

Phosphine **6a** (0.31 g, 1.0 mmol) was stirred with diethylamine (3.66 g, 50 mmol) at 50°C for 6 h. All volatiles were removed in high vacuum at 50°C for 3 h. This process was repeated to ensure complete deprotection of the phosphine. Yield of **22**: 0.30 g (100%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.35–7.15 (m, 10H), 1.95 (t, *J*=7.5 Hz, 2H), 1.32 (m, 4H), 1.15 (s, 8H), 0.78 (t, *J*=6.3 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=139.0 (d, *J*=13.2 Hz), 132.6 (d, *J*=18.1 Hz), 128.3, 128.2, 31.7, 31.2 (d, *J*=12.8 Hz), 29.1 (d, *J*=2.9 Hz), 28.0 (d, *J*=11.8 Hz), 25.9 (d, *J*=17.0 Hz), 22.6, 14.0.

Diphenyl(1,2-diphenylethyl)phosphine ***23***

Phosphine **6l** (0.38 g, 1.0 mmol) was stirred with diethylamine (3.66 g, 50 mmol) at 50°C for 6 h. All volatiles were removed in high vacuum at 50°C for 3 h. This process was repeated to ensure complete deprotection of the phosphine. Yield of **23**: 0.37 g (100%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.65 (m, 2H), 7.31 (m, 3H), 6.97 (s, 1H), 6.72 (m, 2H), 3.54 (m, 1H), 2.93 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ=140.3 (d, *J*=8.7 Hz), 140.2 (d, *J*=13.2 Hz), 137.0 (d, *J*=14.4 Hz), 136.7 (d, *J*=15.7 Hz), 134.2 (d, *J*=20.6 Hz), 133.0 (d, *J*=17.7 Hz), 129.4, 129.3, 129.2, 128.7, 128.6, 128.1, 128.0, 127.9, 127.8, 127.7, 126.1 (d, *J*=2.5 Hz), 125.8, 47.8 (d, *J*=14.0 Hz), 39.7 (d, *J*=22.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ=0.0.

Typical procedure E for the deprotection of the chiral diphosphine–diborane complexes ***20a–d*** *and* ***21a****: preparation of 1,2-bis(dimyrtanylphosphino)ethane*

1,2-Bis(dimyrtanylphosphino)ethane–diborane complex (**20a**, 133 mg, 0.2 mmol) was heated with diethylamine (5 mL) overnight to 55°C. All volatiles were removed under high vacuum and another 5 mL of diethylamine was added. The suspension was stirred at 55°C for 3 h and all volatiles were removed under high vacuum. This procedure was repeated three times.

Typical procedure F for the enantioselective hydrogenation reactions: hydrogenation of ethyl 3-oxobutanoate

A solution (10^{-2} N) of the free chiral diphosphine in CH_2Cl_2 (1.06 mL, 10.6 μmol) was added to a solution of (*p*-cymene)ruthenium(II) chloride dimer (3.1 mg, 5.06 μmol) in methanol (5 mL). The resulting red solution was stirred at rt for 30 min and transfered into a steel autoclave. Methanol (14 mL) and ethyl 3-oxobutyrate (0.13 mL, 1.0 mmol) were added, the autoclave was closed and taken out of the glove box. The inert gas was replaced by hydrogen at a pressure of 100 bar. The autoclave was heated to 50°C for 14 h and the pressure carefully was released. The crude product was distilled under reduced pressure furnishing (*R*)-ethyl 3-hydroxybutanoate (85% yield determined by ^{1}H NMR). The enantiomeric excess was determined by GC (61% *ee*, Chirasil-DEX CB).

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