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# Chiral boronates—versatile reagents in asymmetric synthesis

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Dedicated to Professor Dr. Dr.h.c. L.F. Tietze, Göttingen, on the occasion of his 60th birthday

**Abstract**

The new, axially chiral borates **2**, **9**, and **11** and boronates **3**–**6** and **12** are synthesized in good yields. They are representatives of three different structural types. The bicyclic borates **2** and **9** are homochiral propeller compounds; their exclusive formation is used to increase the enantiomerical purity of **1**. Especially the borates are efficient Lewis acidic catalysts for stereoselective Diels–Alder reactions. The new seven-membered boron compounds **4**, **5**, **6**, and **12** are interesting reagents for different asymmetric synthetic steps. Activated vinylboronates **31** can serve as efficient cyclophiles in [3+2] cycloaddition reactions with methylenecyclopropane **27** giving borylated methylenecyclopentanes **32**. 

*Keywords:* Boronates; Biaryls; Asymmetric synthesis; [3+2] Cycloadditions; Cyclopentanes

## 1. Introduction

The synthesis and application of axially chiral biaryls has been the subject of many research reports over the last years [1]. The biaryl unit is both, an important structural feature of many natural products and the conformationally stable backbone of powerful chiral catalysts and reagents in asymmetric synthesis. Chiral boronates have proved their great importance in stereoselective synthesis during the last decades, [2]. Therefore, we have synthesized new borates and boronates with a chiral biaryl backbone for stoichiometric and catalytic asymmetric syntheses, [3] (Schemes 1 and 2).

## 2. Results and discussion

### 2.1. Synthesis and catalysis

The reaction of biarylols with boron compounds is complex and dependent on both, the boron substituents and the substitution pattern of the biarylol. When 2,2′-dihydroxy-1,1′-binaphthyl (β-binaphthol, **1**) is reacted with borane complexes, hydrohaloboranes or boric acid, the bicyclic homochiral bisborate propeller compounds **2** with axially chiral 1,1-binaphthyl groups as 'blades' is formed exclusively in very good yields [4]. Introduction of either a bromo or trimethylsilyl substituent in 3,3′-position of the β-binaphthol exclusively leads to the formation of the seven-membered dioxadihydroborepine system **3** to avoid additional steric strain.

Seven-membered ring systems are also formed exclusively when allyl, phenyl (additional structure proof by X-ray) or vinyl boranes are reacted with **1**. The product structures strongly depend on the substitution pattern of the biarylol. In case of the 2,2′-dihydroxy-1,1′-dibenzofuranyl (**8**) [5] another propeller type compound **9** is formed. Two biphenylols **10a/b** with both, H or methyl [6] in 6-position, were also reacted. Possibly due to the

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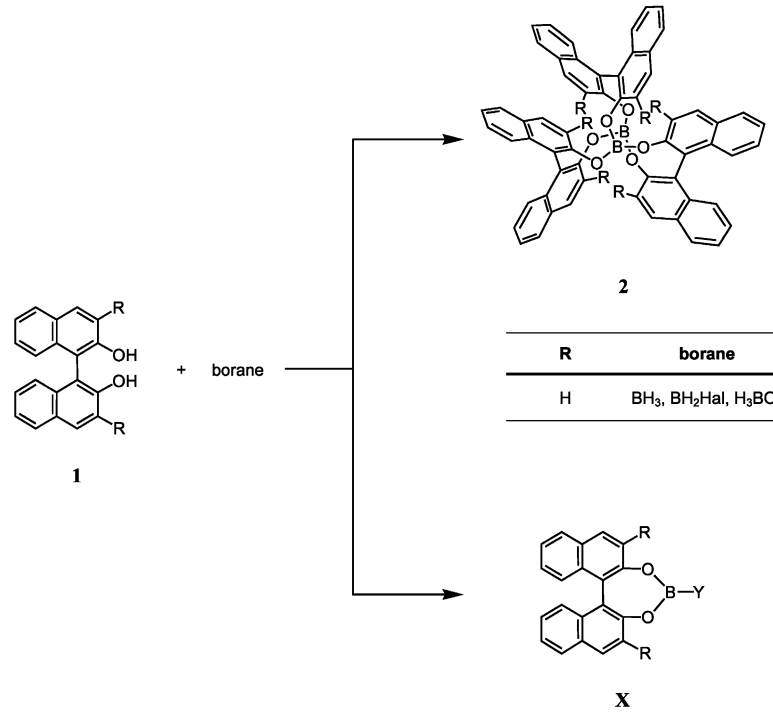
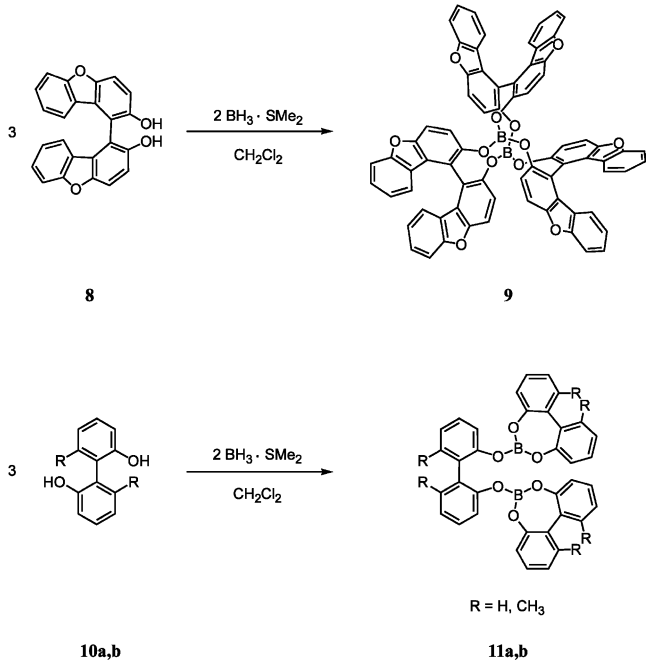


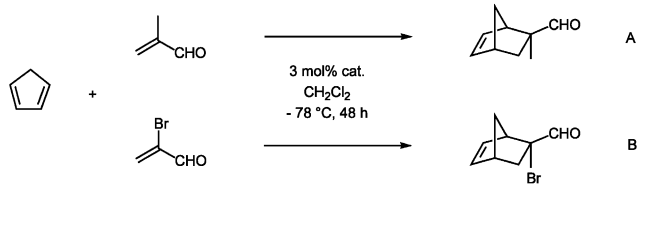

| R | borane |
|---|---|
| H | $BH_3$, $BH_2Hal$, $H_3BO_3$ |

| X | R | borane | Y |
|---|---|---|---|
| **3a,b** | TMS, Br | $BHal_3$ | Hal |
| **4** | H | $Allyl_3B$ | Allyl |
| **5** | H | $PhB(OH)_2$ | Ph |
| **6** | H | $VinylBCl_2$ | Vinyl |
| **7** | H | $(PhO)_3B$ | OPh |

Scheme 1. Reaction of β-binaphthols **1** with boranes.




Scheme 2. Reaction of biarylols **8** and **10** with borane–dimethyl sulfide.




| catalyst | yield [%] | | *exo/endo* | |
|---|---|---|---|---|
| | A | B | A | B |
| without catalyst | < 5 | 38 | 86 : 14 | 22 : 78 |
| **2** | 90 | 51 | 96 : 4 (*ee* 90 %) | 6 : 94 |
| **11a** | 97 | 61 | 96 : 4 | 5 : 95 |
| **5** | 80 | 48 | 93 : 7 | 10 : 90 |
| **7** | 91 | 56 | 96 : 4 | 6 : 94 |

Scheme 3. Boron Lewis acid catalyzed Diels–Alder reactions.

different dihedral angles the first examples **11a**,**b** of a twofold formation of a seven-membered ring system **11** were observed. The attempted borylation reaction of the isomers 3,3′-dihydroxy-4,4′-biphenanthryl and 10,10′-dihydroxy-9,9′-biphenanthryl led to the formation of polymeric material, only.

Since a number of boranes with a chiral biaryl backbone has already been successfully employed as effective Lewis acidic catalysts in stereoselectively induced Diels–Alder reactions [7], we have examined the applicability of the chiral borates **2**, **5**, **7**, and **11a** to the reaction of cyclopentadiene with either methacrolein or bromoacrolein. Whereas the uncatalyzed cycloadditions provided only a poor yield even at 20 °C and a modest *exo*-selectivity, conducting the reaction in dichloromethane at −78 °C in the presence of 3 mol% of the borates led to the isolation of the cycloadducts in 48–97%. In general, the observed *exo*-selectivity is very high (A: 96%); it is dropping distinctly (90–93%) though, when the phenyl boronate **5** is used (Scheme 3).

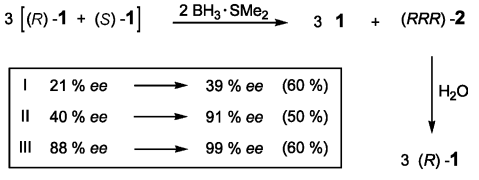
### 2.2. Increase of the enantiomerical purity of *1*

Optically active β-binaphthols are extremely useful $C_2$-symmetric compounds employed as chiral auxiliaries or chiral catalysts in asymmetric synthesis.

Several methods such as optical resolution by separation of diastereomers [8], asymmetric synthesis from 2-naphthol [9], and by separation of inclusion complexes [10] are available to obtain **1** in enantiopure form. However, the procedures often give only partially resolved **1** and a further purification step is required.

It has been mentioned in the beginning, that the reaction of racemic **1** with borane complexes results in the formation of enantiomers of the $C_3$-symmetric propeller compound **2**. It appears that the β-binaphthol tends to form the homochiral (*SSS*) and (*RRR*) enantiomers rather than the unsymmetrical (*SRR*) and (*RSS*) isomers. This fact can be applied to increase the optical purity of partially resolved **1** without using another chiral source simply by formation of the propeller compound **2** and separating it from the rest of **1**.

For our investigation we have carried out several experiments with initial enantiomeric excesses of 20–80% and in the presence of excess **1**. The results are summarized in Scheme 4. In a typical procedure, two equivalents of $BH_3 \cdot SMe_2$ were added to a solution of six equivalents of partially resolved **1** in dichloromethane at 0 °C. The mixture was allowed to warm to room temperature and stirred for 6 h. Dichloromethane was removed under reduced pressure and the residue was dissolved in ether to precipitate **2**. Filtered **2** was redissolved in dichloromethane and treated with water




Scheme 4. Increase of the enantiomeric purity of β-binaphthol (*R*)-**1**.

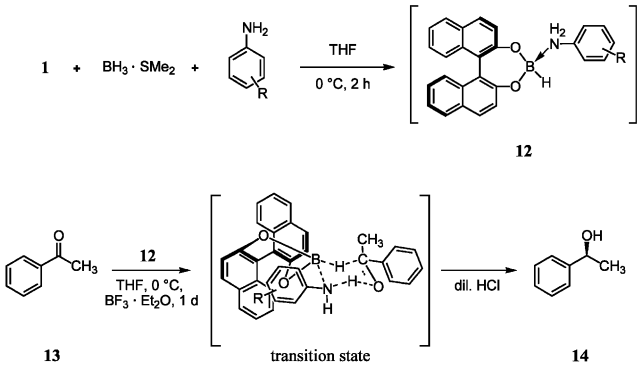
to obtain the optically enriched β-binaphthol **1**. In conclusion, a simple and efficient procedure to increase the enantiomeric excess of partially resolved **1** was developed.

### 2.3. Asymmetric hydroborane reduction

The asymmetric reduction of prochiral ketones is a useful method for the preparation of chiral alcohols. A number of enantioselective reduction methods with chiral hydride reagents have been published [11].

We describe the asymmetric reduction of a prochiral ketone with a hydroborane reagent bearing optically pure **1** as a chiral ligand. The chiral reagent was generated in situ from **1**, $BH_3 \cdot SMe_2$, and a primary aromatic amine. Treatment of acetophenone **13** with **12** in THF gave 1-phenylethanol in good to excellent yield in each case. The effect of added amine on the enantioselection was examined by using various aromatic amines and DBU. Results are summarized in Scheme 5. The presence of all amines enhanced the optical yield to some extent. The highest degree of enantioselectivity was achieved by the use of *m*-nitroaniline. DBU being more basic was less effective than the *N*-arylamines in the extent of selection. These facts suggest that both the amino group and the aromatic ring influence the enantioselective reduction.

It is likely that a six-membered transition state is formed during the reaction of acetophenone and **12** containing an *N*-arylamine as illustrated in Scheme 5. The structure suggests a π–π-interaction between the naphthyl π-system and the π-system of the *N*-arylamine.




| Amine | yield [%] | *ee* [%] |
|---|---|---|
| - | 90 | 5 |
| β-$C_{10}H_7NH_2$ | 93 | 35 |
| *p*-$C_6H_4(NO_2)NH_2$ | 75 | 45 |
| *m*-$C_6H_4(NO_2)NH_2$ | 76 | 54 |

Reactions were performed by using 2 equ. of chiral reducing reagent **12**, equimolar amounts of $BF_3 \cdot Et_2O$ in THF at 0 °C for 24 h.

Scheme 5. Asymmetric reduction of acetophenone **13** with chiral hydroborane–amine complexes **12**.

The interaction can be enhanced by attaching an electron withdrawing group to the *N*-aryl ring.

### 2.4. Binaphthyl based boronates

Starting material for all routes to binaphthyl boronates **4**–**6** was the easily available β-binaphthol **1**. Several synthetic pathways were tried; the optimized ones are reported. When reacting **1** with triallylborane the corresponding allylbinaphthyl boronate **4** was formed in 78% yield. Preparation of the phenyl substituted derivative **5** was readily accomplished by treatment of **1** with phenylboronic acid **16** in toluene at reflux. Reaction of dichlorovinylborane and β-binaphthol in dichloromethane afforded the vinylboronic ester **6**.

#### 2.4.1. Asymmetric allylboration

Allylboration of aldehydes is an important method for the synthesis of chiral homoallylic alcohols [12]. The reason for high levels of stereoselectivity observed in additions of chiral allyl organometallics to carbonyl compounds is a chair like six-membered transition state.

Carbonyl addition was carried out by reacting benzaldehyde **18** with the allyl reagent **4** at low temperature in ether and working up with dilute hydrochloric acid, followed by extraction with ether. The chiral auxiliary was easily recycled by precipitation with hexane. Allylboration of benzaldehyde with **4** produced the homoallylic alcohol **19** in high chemical yield and with an enantioselectivity of 88%.

#### 2.4.2. Asymmetric synthesis via an (α-chloromethyl)boronic ester

The discovery of the class of (α-haloalkyl)boronic esters in high enantiomeric purity has led to a novel method of asymmetric synthesis of broad scope [13]. The asymmetric insertion of a CHCl group into a B–C bond can be controlled precisely if the chiral ligand is appropriately chosen. The chlorine is readily replaced by the alkyl group of a Grignard reagent or by other nucleophiles. The resulting boronic esters can be further homologated by introducing a second carbon atom.

Optically pure **1** was used as the chiral directing group and the starting boronic ester **5** was easily obtained. (Dichloromethyl)lithium was prepared from butyllithium and dichloromethane in THF at −100 °C and then treated with **5**. The resulting clear solution was allowed to warm to ambient temperature in order to rearrange the intermediate borate compas isolated by filtering off the precipitated lithium chloride. The solution was then cooled to −78 °C and treated with methylmagnesium bromide and kept at 20 °C overnight. Peroxidic oxidation of **23** gave 1-phenylethanol **14** in almost quantitative yield and with an *ee* of 92%.

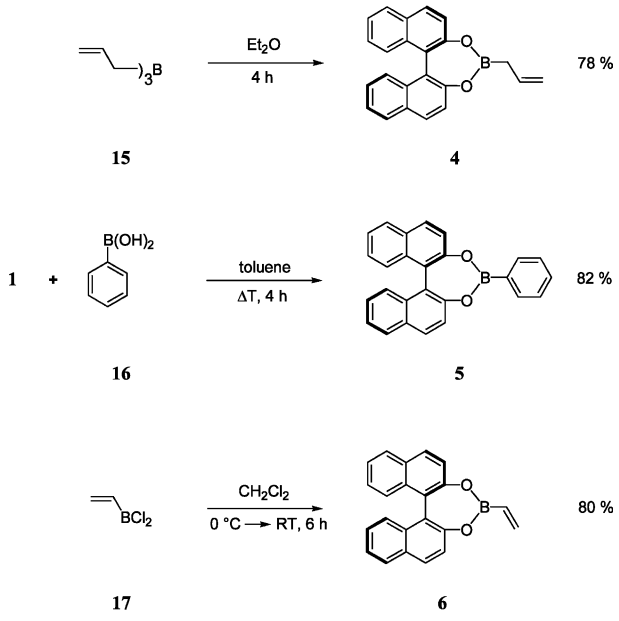
#### 2.4.3. Nickel(0)-catalyzed [3+2] cycloadditions with vinylboronates

The construction of cyclopentane systems is still gaining much attention due to the biological significance of many natural products possessing these structural units [14].

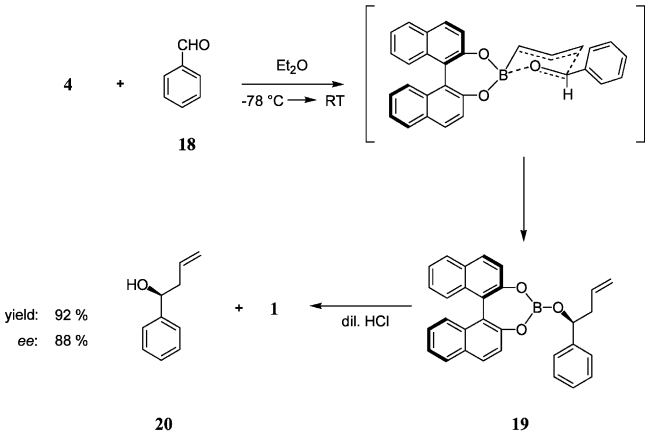
Trimethylenemethane (TMM) is an excellent synthon for preparing a wide range of methylenecyclopentanes directly by [3+2] cycloadditions with suitable alkenes [15]. The idea to modify the alkene by replacing one of the olefinic hydrogens by an activating boronic ester group is synthetically attractive, because, the cycloadducts can be transformed stereoselectively into alcohols, amines and several other classes of compounds. Another option includes the aspect of asymmetry by the use of an optically active diol as a chiral auxiliary. Vinylboronic esters are easily accessible. Especially those derived from pinacol are very stable to oxidation and moisture and can be even purified by column chromatography [16].

Our initial cycloaddition studies focused on the parent methylenecyclopropane **24** as a TMM precursor and the vinylboronates **6** or **28** derived from **1** or pinacol. The binaphthyl vinylboronate (**6**) was prepared in good yields using the sequence outlined in Schemes 6–9. The reaction of **6** with **24** was carried out in the presence of catalytic amounts (5 mol%) of $Ni(COD)_2$ at −15 °C in toluene.

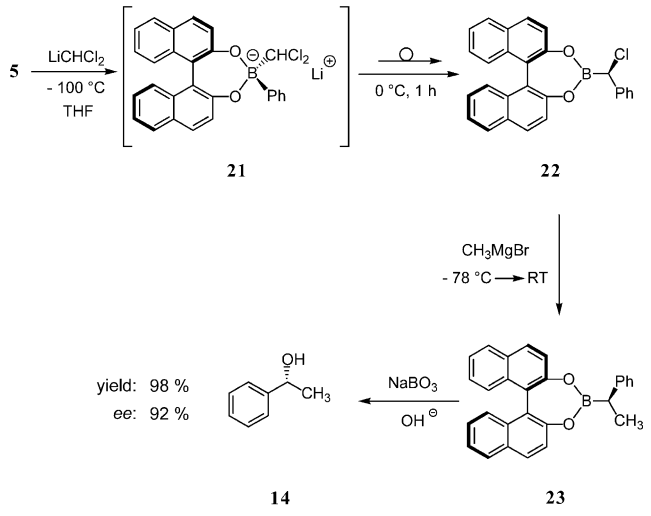
Cycloadditions of methylenecyclopropane **24** catalyzed with 'naked' $Ni(COD)_2$ usually favour proximal cleavage of the cyclopropane C–C bond [17]. Accordingly, the formation of the corresponding cycloadduct **25** was expected. However, this alkenylboronate did not afford the desired [3+2] cycloadduct. The only identifiable products from the reaction mixture were recovered



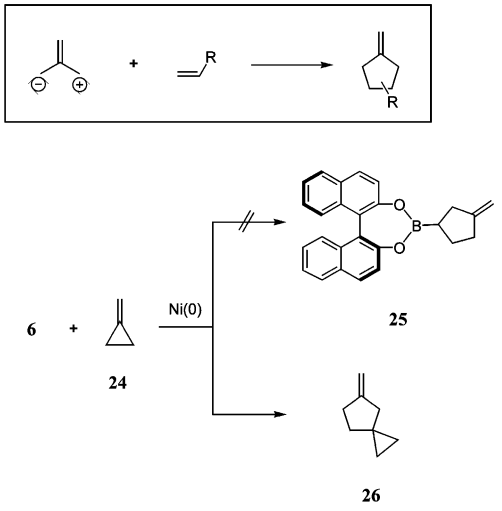

Scheme 6. Synthesis of β-binaphthyl based boronate reagents **4**–**6**.




Scheme 7. Allylboration of benzaldehyde **18**.




Scheme 8. Asymmetric synthesis of phenylethanol **14** via an (α-chloromethyl)boronic ester **22**.




Scheme 9. Attempted [3+2] cycloaddition of the vinyl boronate **6** with methylenecyclopropane **24**.

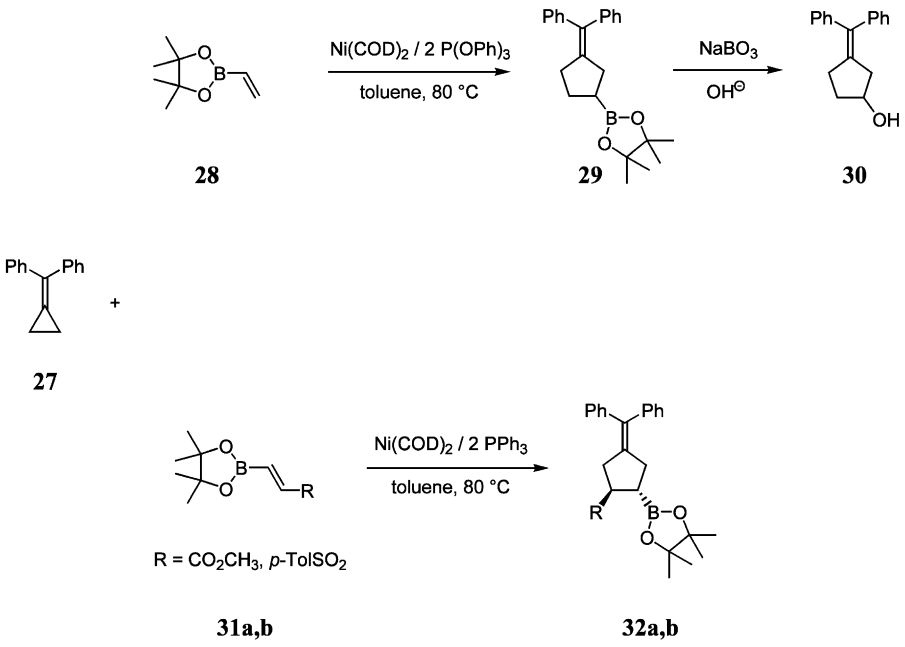
starting material **6** and the cyclodimerization product **26** of methylenecyclopropane itself.

Compared with the parent compound **24** double bond substituted cyclopropanes often give better results in cycloaddition reactions with a wider range of alkenes. Mono- and di-substituted alkylidenecyclopropanes react with nickel(0) catalysts exclusively by distal ring opening. Moreover, they are also less sensitive to self-oligomerization. Therefore, less reactive alkenes, which do not undergo [3+2] cycloadditions with the parent methylenecyclopropane do react in this manner with double bond substituted species.

For our further investigation we selected diphenylmethylene-cyclopropane **27**—showing excellent regioselectivity and giving exclusively diphenylidenecyclopentanes without scrambling of the phenyl groups—and vinylboronate **28**. The reaction proceeded at 60 °C, and without any phosphorous ligand present only 5% of the desired cycloadduct **29** was formed. The use of triphenylphosphine or triarylphosphite modified nickel(0) catalysts permits higher reaction temperatures and led to an increase of the yield up to 65%. All of the cycloaddition studies described in this area utilized the same convenient catalyst system prepared in situ from $Ni(COD)_2$ by addition of either triphenylphosphine or triphenylphosphite (Ni:P ratio 1:2). The cycloadditions were performed by simply heating the substrates in toluene in the presence of 2 mol% of this catalyst mixture. The product **29** is stable towards air and water and can be purified by column chromatography.

The use of vinylboronate **28** as an acceptor was unsatisfactory due to its lack of reactivity. Therefore, we decided to increase the reactivity of the vinylboronate by introducing an, electron withdrawing group $\beta$ to the boryl group, such as $-CO_2Me$ or $-SO_2$-*p*-Tol [18]. Attempted cycloadditions of **27** to the vinylboronates **31a/b** were successful, in particular the reactions with the sulfonylated vinylboronate derivate **31b**. This vinylboronate was shown to react already at room temperature with **27**, thus showing the activating effect of the arylsulfonyl group. By heating the reaction mixture at 80 °C the yield of **32b** raised up to 95%. The cycloaddition reactions of the (*E*)-vinylboronic esters **31a/b** were highly stereoselective and yielded exclusively the corresponding *trans*-products.

The carbon–boron bond of these cycloaddition products can be further transformed stereoselectively by oxidation to the corresponding cyclopentanols as it has been illustrated exemplary by **29**. This borylated cyclopentane was easily oxidized by sodium perborate in THF in the presence of sodium hydroxide (Scheme 10) giving **30**. Therefore, vinylboronates serve as synthetic equivalents of enols.




Scheme 10. [3+2] Cycloaddition of vinyl boronates **28** and **31** with diphenylmethylene–cyclopropane **27**.

## 3. Conclusions

We have described the synthesis of several new boronates **3**–**6** and **12** and borates **2**, **9**, and **11** with an axially chiral backbone. They belong to the three different structural types **2**, **11** and **X**. As the bicyclic borates **2** and **9** are homochiral propeller compounds, their exclusive formation can be used to increase the enantiomerical purity of biarylols like β-binaphthol **1**. Especially the borates can serve as efficient Lewis acidic catalysts for stereoselective Diels–Alder reactions.

We have shown that the new seven-membered boron reagents **4**, **5**, **6**, and **12** are easily available and may be used for asymmetric reductions, allylborations, synthesis of (α-chloromethyl)boronic esters, and [3+2] cycloadditions of vinylborates with methylenecyclopropanes. The use of twofold activated vinylboronates **31** opens an efficient and easy access to boryl substituted cyclopentanes **32**, interesting precursors for natural product chemistry.

## 4. Experimental

### 4.1. General data

All manipulations were carried out under a dry nitrogen atmosphere using standard vacuum techniques. The solvents were purified by conventional means and distilled under nitrogen prior to use. The elemental analyses were performed by the Microanalytical Laboratory of the Institut für Pharmazeutische Chemie der Universität Braunschweig.

The NMR spectra were recorded on a Bruker AMX 400 and AC 200F spectrometer ($^1$H: 400 and 200 MHz—$^{13}$C: 100 and 50 MHz—$^{11}$B: 128 MHz) with tetramethylsilane as internal and $BF_3 \cdot Et_2O$ as external standard; $\delta$ values are given in ppm, $J$ values in Hz. Multiplicities of $^{13}$C-NMR signals were determined by the DEPT sequence and are reported as follows: +, for CH or $CH_3$; −, for $CH_2$ and o, for C. Mass spectra were obtained with a Hewlett Packard 5898B (at 70 eV); high resolution mass spectra were recorded with a Varian MAT 311A spectrometer with pre-selected molecular ion peak matching at $R \gg 10\,000$ to be within $\pm 2$ ppm of the exact masses. Melting points (m.p.) are uncorrected.

#### 4.1.1. Hexanaphthohexaoxa-1,8-diborabicyclo[6.6.6]-eicosa-3,5,10,12,16,18-hexaene (2)

Borane–dimethyl sulfide (0.2 ml, 2 mmol) is added dropwise to a cooled (0 °C) solution of β-binaphthol (858 mg, 3 mmol) **1** in 60 ml $CH_2Cl_2$. The solution is allowed to warm up to room temperature (r.t.) and is stirred for 14 h. After evaporation of all volatile compounds the residue is washed with diethyl ether (30 ml). The product is dried in vacuo; colorless crystals; m.p.: 348 °C; yield: 855 mg (98%). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta = 7.74$ (d, $^3J = 8.0$, 2H, $H_{aromat}$), 7.47 (dd, $^3J = 8.1$, 6.7, 2H, $H_{aromat}$), 7.22 (dd, $^3J = 8.3$, 6.7, 2H, $H_{aromat}$), 7.06 (d, $^3J = 8.3$, 2H, $H_{aromat}$), 6.64 (AB-System, $^3J = 8.8$, 4H, $H_{aromat}$). $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta = 120.2$ (+, 2C, $C_{aromat}$), 121.7 (o, 2C, $C_{aromat}$), 124.2 (+, 2C, $C_{aromat}$), 125.4 (+, 2C, $C_{aromat}$), 125.8 (+, 2C, $C_{aromat}$), 127.6 (+, 2C, $C_{aromat}$), 127.8 (+, 2C, $C_{aromat}$), 130.3 (o, 2C, $C_{aromat}$), 133.3 (o, 2C,

$C_{aromat}$), 147.7 (o, 2C, $C_{aromat}$). $^{11}$B-NMR (128 MHz, $CDCl_3$): $\delta = 15.6$ (bs). MS (70 eV); *m/z* (%): 874 (38) [$M^+$], 680 (3), 606 (5), 562 (2), 437 (16) [$M^{2+}$], 386 (4), 342 (47), 312 (76), 294 (33), 268 (100), 239 (87).

#### 4.1.2. Bis-(3-trimethylsilylnaphtho)[2,1-a:1′,2′-c]-1-chloro-1,3,2-dioxaborepin (**3a**)

Procedure see **2**: 2,2′-Dihydroxy-3,3′-bis(trimethylsilyl)binaphthyl (60 mg, 0.14 mmol); 8 ml $CH_2Cl_2$; $BH_2Cl \cdot SMe_2$ (0.14 mmol); crystallization from $CH_2Cl_2$–hexane (1:1); colorless crystals; m.p.: 193 °C; yield: 57 mg (86%); $^1$H-NMR (200 MHz, $CDCl_3$): $\delta = 0.00$ (s, 18H, $Si(CH_3)_3$), 6.97 (d, $^3J = 8.0$, 2H, $H_{aromat}$), 7.10 (ddd, $^3J = 8.5$, 6.8, $^4J = 1.4$, 2H, $H_{aromat}$), 7.32 (ddd, $^3J = 7.8$, 7.0, $^4J = 1.0$, 2H, $H_{aromat}$), 7.81 (d, $^3J = 8.0$, 2H, $H_{aromat}$), 7.97 (s, 2H, $H_{aromat}$). $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta =$ 1.8 (+, 6C, $Si(CH_3)_3$), 123.6 (+, 2C, $C_{aromat}$), 124.8 (o, 2C, $C_{aromat}$), 126.7, 127.3 und 127.9 (+, 6C, $C_{aromat}$), 132.6, 132.9 und 133.9 (o, 6C, $C_{aromat}$), 134.0 (+, 2C, $C_{aromat}$), 152.3 (o, 2C, $C_{aromat}$). $^{11}$B-NMR (128 MHz, $CDCl_3$): $\delta = 23.5$ (s). MS (70 eV); *m/z* (%): 474 (62) [$M^+$], 425 (40), 417 (19), 413 (11), 381 (12), 367 (11), 351 (16), 323 (9), 309 (21), 291 (11), 281 (10), 279 (20), 277 (17), 265 (35), 263 (26), 250 (7), 167 (15), 93 (52), 73 (100). HRMS ($C_{26}H_{28}BClO_2Si_2$): 474.1409 (calc. and found).

#### 4.1.3. Hexa(dibenzofuranyl)hexaoxa-1,8-diborabicyclo-[6.6.6]eicosa-3,5,10,12,16,18-hexaene (**9**)

Procedure see **2**: 2,2′-dihydroxy-1,1′-bisdibenzofuranyl (366 mg, 1 mmol) **8**; 30 ml $CH_2Cl_2$; $BH_3 \cdot SMe_2$ (67 µl, 0.67 mmol); crystallization from $CH_2Cl_2$–hexane (1:1); colorless crystals; m.p.: > 350 °C; yield: 370 mg (quant). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta = 6.5$ (d, $^3J =$ 8.1, 6H, $H_{aromat}$), 6.60 (bs, 12H, $H_{aromat}$), 6.83 (t, $^3J =$ 7.1, 6H, $H_{aromat}$), 7.23 (t, $^3J = 7.5$, 6H, $H_{aromat}$), 7.56 (d, $^3J = 8.1$, 6H, $H_{aromat}$). $^{11}$B-NMR (128 MHz, $CDCl_3$): $\delta = 18.6$ (s). MS (70 eV); *m/z* (%): 1114 (4) [$M^+$], 766 (6), 558 (5), 456 (100), 410 (4), 347 (33), 263 (8), 228 (25).

#### 4.1.4. 2,2′-Bis(dibenzo[a,c]-1,3,2-dioxaborepin-2-yloxy)biphenyl (**11a**)

Procedure see **2**: 2,2′-Dihydroxybiphenyl (279 mg, 1.5 mmol) **10a**; 30 ml $CH_2Cl_2$; $BH_3 \cdot SMe_2$ (50 µl, 0.5 mmol); crystallization from $CH_2Cl_2$–hexane (1:1); colorless crystals; m.p.: 148 °C; yield: 280 mg (97%). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta = 6.77$ (d, $^3J = 7.8$, 6H, $H_{aromat}$), 6.98–7.18 (m, 12H, $H_{aromat}$), 7.25 (d, $^3J = 7.5$, 6H, $H_{aromat}$). $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta = 120.9$ (+, 6C, $C_{aromat}$), 124.2 (+, 6C, $C_{aromat}$), 127.4 (o, 6C, $C_{aromat}$, C-1,1′), 129.5 (+, 6C, $C_{aromat}$), 130.1 (+, 6C, $C_{aromat}$), 151.5 (+, 6C, C–$O_{aromat}$, C-2,2′). $^{11}$B-NMR (128 MHz, $CDCl_3$): $\delta = 19.3$ (bs). MS (70 eV); *m/z* (%): 574 (95) [$M^+$], 406 (39), 380 (30), 287 (11, M2+), 121 (31), 168 (100), 139 (51). Calculated elemental analysis (Anal. Calc.) for $C_{36}H_{24}B_2O_6$ (574.18): C, 75.30; H, 4.21. Found: C, 75.21; H, 4.14%.

#### 4.1.5. Catalyzed Diels–Alder reactions

##### 4.1.5.1. General procedure for the reaction of cyclopentadiene with methacrolein and α-bromoacrolein.

A solution of the dienophile in $CH_2Cl_2$ is added to the solution of 3 mol% of the boron catalyst in $CH_2Cl_2$ (−78 °C). After stirring for 15 min to form the dienophile-catalyst complex the cyclopentadiene is added. The reaction mixture is stirred for 1 day at −78 °C, then it is allowed to warm slowly to 0 °C and hydrolyzed with a saturated $NaHCO_3$-solution. The aqueous phase is extracted 3 × with $CH_2Cl_2$, then dried with $Na_2SO_4$. Yield and *exo*/*endo* ratio are determined by GC (internal standard 2-methylnaphthalene). The products are identified by GC–MS and compared with authentic materials.

#### 4.1.6. Increase of the enantiomerical purity of β-binaphthol (**1**)

Fifty-two microliters (0.5 mmol) $BH_3 \cdot SMe_2$ is added dropwise to a solution of 430 mg (1.5 mmol) of enantiomerically enriched (88% *ee*) (+)-β-binaphthol (**1**) in 15 ml $CH_2Cl_2$ at 0 °C. The solution is allowed to warm to r.t. and kept at this temperature for 6 h. The solvent is removed in vacuo, the residue treated with 15 ml diethyl ether and stirred for 15 min; during this time the excess β-binaphthol is solved. The diborate propeller molecule **2** is filtered and dried in vacuo. Before hydrolysis the purity is checked by $^1$H-NMR. Compound **2** is then hydrolyzed in a solution of $CH_2Cl_2$. The phases are separated, the solvent is removed and the product dried in vacuo. Yield: 130 mg (60%) (+)-**1**; $\alpha_D^{20} = 34°$, 99% *ee*; 300 mg (+)-**1**, $\alpha_D^{20} = 23.4°$, 69% *ee*.

#### 4.1.7. Asymmetric reduction of acetophenone (**13**) with hydroborane–amine complexes

A solution of 1.56 g (5.46 mmol) (+)- or (−)-β-binaphthol **1** in 15 ml THF is dropwise added to a solution of 0.56 ml (5.91 mmol) borane–dimethyl sulfide in 2 ml THF at 0 °C. The mixture is stirred at 0 °C for 1 h, then a solution of 5.59 mmol of the amine in THF is added and the mixture is stirred for another h at 0 °C. Afterwards a solution of 0.29 ml (2.46 mmol) acetophenone und 0.3 ml (2.46 mmol) boron trifluoride–ethylether in 0.5 ml THF is added. The reaction mixture is kept for 12 h at 0 °C, the conversion is checked by GC. The reaction is worked up by adding 2 ml 6 N HCl. The product is isolated by Kugelrohr-distillation and identified by GC–MS, the *ee* is determined by GC.

a) 799.37 mg (5.59 mmol) β-naphthylamine; yield: 279.1 mg (93%) **14**, 35% *ee*.
b) 771.42 mg (5.59 mmol) *p*-nitroaniline; yield: 225.0 mg (75%) **14**, 45% *ee*.
c) 771.42 mg (5.59 mmol) *m*-nitroaniline; yield: 228.1 mg (76%) **14**, 54% *ee*.

d) 0.83 ml (5.59 mmol) DBU; yield: 216.0 mg (72%) **14**, 24% *ee*.
e) Without amine; yield: 270.1 mg (90%) **14**, 5% *ee*.

#### 4.1.8. Dinaphtho[2,1-a;1′,2′-c]-1-allyl-1,3,2-dioxaborepin (**4**)

A mixture of 0.19 ml (1 mmol) triallylborane **15** and 286 mg (1 mmol) (+)- or (−)-β-binaphthol **1** in 8 ml diethyl ether is stirred at r.t. After their gas evolution has ceased the mixture is stirred for another 2 h. The solvent is removed in vacuo and the product crystallized from diethyl ether–hexane; colorless oil, slowly solidifying; yield: 262 mg (78%). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta = 1.26$ (d, $^3J = 7.5$, 2H, 3-$H_{allyl}$), 4.41 (dd, $^2J = 10.3$, $^3J = 9.3$, 2H, 1-$H_{allyl}$), 5.12 (m, 1H, 2-$H_{allyl}$), 6.99 (d, $^3J = 8.0$, 2H, $H_{aromat}$), 7.18–7.29 (m, 4H, $H_{aromat}$), 7.34 (ddd, $^3J = 7.9$, 7.1, $^4J = 1.0$, 2H, $H_{aromat}$), 7.83 (d, $^3J = 7.8$, 2H, $H_{aromat}$), 7.98 (d, $^3J = 9.0$, 2H, $H_{aromat}$).

$^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta = 23.0$ (b, +, 1C, $C_{allyl}$-3, C–B), 120.9 (+, 2C, $C_{aromat}$), 121.2 (o, 2C, $C_{aromat}$), 125.5, 125.8, 127.5, 128.4 (+, 8C, $C_{aromat}$), 131.0 (o, 2C, $C_{aromat}$), 131.1 (+, 2C, $C_{aromat}$), 133.8 (+, 1C, $C_{allyl}$-2), 133.9 (2C, $C_{aromat}$), 150.6 (o, 2C, $C_{aromat}$). $^{11}$B-NMR (128 MHz, $CDCl_3$): $\delta = 28.2$ (bs). MS (70 eV); *m*/*z* (%): 336 (100) [$M^+$], 295 (37), 294 (41), 286 (66), 268 (27), 267 (43), 239 (50). HRMS ($C_{23}H_{17}BO_2$): 336.1322 (calc.) 336.1321 (found).

#### 4.1.9. Allylboration of benzaldehyde: 1-phenyl-3-buten-1-ol (**20**)

Twenty-four microliters (0.24 mmol) benzaldehyde **18** is added to a solution of 100 mg (0.30 mmol) of the allyl boronate **4** in 0.5 ml diethyl ether at −78 °C. The reaction mixture is stirred at −78 °C for 2 h, then warmed to r.t. and poured into 1 ml of dil. HCl. The product is extracted with 2 ml diethyl ether. The combined ether extracts are treated with $NaHCO_3$ and saturated NaCl solution and dried with $Na_2SO_4$. The solution is concentrated to a third of its original volume and then diluted with hexane to precipitate the β-binaphthol. The solution is separated, the solvent is removed in vacuo and the product purified by chromatography ($SiO_2$, petrol ether:diethyl ether 5:1); colorless oil; yield: 40 mg (94%) 88% *ee* (GC). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta = 2.28$ (s, 1H, OH), 2.45–2.51 (m, 2H, 2-H), 4.69 (t, $^3J = 6.4$, 1H, 1-H), 5.11 (d, $^3J = 10.0$, 1H, 4-H), 5.13 (d, $^3J = 7.1$, 1H, 4-H), 5.78 (ddt, $^3J = 7.1$, 10.0, 17, 1H, 3-H), 7.22–7.37 (m, 5H, $H_{aromat}$). $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta = 43.7$ (−, 1C, C-2), 73.2 (+, 1C, C-1), 118.3 (−, 1C, C-4), 125.8 (+, 1C, $C_{aromat}$), 127.4 (+, 2C, $C_{aromat}$), 128.3 (+, 2C, $C_{aromat}$), 134.4 (+, 1C, C-3), 143.8 (o, 1C, $C_{aromat}$). MS (70 eV); *m*/*z* (%): 148 (3) [$M^+$], 131 (4), 107 (96), 79 (100), 51 (46).

#### 4.1.10. Dinaphtho[2,1-a;1′,2′-c]-1-phenyl-1,3,2-dioxaborepin (**5**) [19]

A mixture of β-binaphthol (1.38 g, 4.8 mmol) **1** and phenylboronic acid (588.0 mg, 4.8 mmol) **16** in 25 ml toluene is refluxed with a water separator for 4 h. The solvent is removed in vacuo; crystallization from $CH_2Cl_2$–hexane (1:1); colorless crystals; yield: 82.6 mg (76%). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta = 7.19$–$7.28$ (m, 4H, $H_{aromat}$), 7.35–7.44 (m, 3H, $H_{aromat}$), 7.50 (d, $^3J = 9.0$, 4H, $H_{aromat}$), 7.91 (t, $^3J = 8.4$, 4H, $H_{aromat}$), 8.22 (dd, $^3J = 7.9$, $^4J = 1.4$, 2H, $H_{aromat}$). $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta = 121.3$ (o, 2C, $C_{aromat}$), 124.6, 125.9, 127.0 (+, 6C, $C_{aromat}$), 127.3 (+, 1C, $C_{aromat}$), 127.9, 128.0, 130.1 (+, 6C, $C_{aromat}$), 130.8 (o, 2C, $C_{aromat}$), 132.6 (+, 2C, $C_{aromat}$), 134.9 (o, 2C, $C_{aromat}$), 135.8 (+, 2C, $C_{aromat}$), 152.1 (o, 2C, $C_{aromat}$–O). $^{11}$B-NMR (128 MHz, $CDCl_3$): $\delta = 26.4$ (bs). MS (70 eV); *m*/*z* (%): 372 (96) [$M^+$], 357 (18), 294 (18), 268 (64), 239 (100), 120 (19), 104 (35), 78 (21). HRMS ($C_{26}H_{17}BO_3$): 372.1322 (calc.) 372.1321 (found).

#### 4.1.11. (α-Chloromethyl)boronic ester

##### 4.1.11.1. Asymmetric synthesis of 1-phenylethanol (**14**).

*4.1.11.1.1. Lithiodichloromethane.* To a rapidly stirred solution of 0.8 ml $CH_2Cl_2$ in 20 ml THF at −100 °C a precooled solution of 6.6 ml (9.25 mmol, 1.4 M solution in hexane) *n*-BuLi is added in such a manner, that the temperature does not rise. After the addition is completed the solution is kept at this low temperature for 30 min.

*4.1.11.1.2. (α-Chloromethyl)boronic ester.* Thirty milliliters THF is now slowly added to the above solution, the temperature is kept at −100 °C. Compound **5** (3.3 g, 8.85 mmol) is added in small portions. The solution gets clear. The reaction mixture is allowed to warm to r.t. overnight. The THF is removed in vacuo and the residue is washed with $CH_2Cl_2$ to precipitate LiCl. The $CH_2Cl_2$ is removed in vacuo and solved in 30 ml THF again.

*4.1.11.1.3. Methylation.* Methyl lithium (6.7 ml, 10.6 mmol, 1.6 M solution in diethyl ether) is added dropwise to a solution of the chloromethylboronic ester **22** in THF at −78 °C. The reaction mixture is allowed to warm to r.t. and the solvent is removed in vacuo. The residue is treated with diethyl ether. The lithium chloride is filtered off and a solution of 0.79 g (9.73 mmol) sodium perborate and 0.18 g (4.42 mmol) NaOH in 10 ml water is added dropwise. The reaction mixture is rapidly stirred for 16 h. The phases are separated; the ether is removed in vacuo and the product is purified by Kugelrohr-distillation; colorless oil; yield: 1.06 g (99%) **13**, 92% *ee* (GC). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta = 1.19$ (d, $^3J = 6.4$, 3H, $CH_3$), 2.42 (s, 1H, O*H*), 4.81 (q, $^3J = 6.4$, 1H, C*H*), 7.21–7.33 (m, 5H, $H_{aromat}$). $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta = 25.0$ (+, 1C, C-2), 70.3 (+, 1C, C-1),

125.3 (+, 1C, $C_{aromat}$), 127.3 (+, 2C, $C_{aromat}$), 128.4 (+, 2C, $C_{aromat}$), 145.8 (o, 1C, $C_{aromat}$).

#### 4.1.12. Dinaphtho[2,1-a:1′,2′-c]-1-vinyl-1,3,2-dioxaborepin (6) [20]

A solution of 112.40 mg (1.03 mmol) dichlorovinylborane **17** in 5 ml $CH_2Cl_2$ is slowly added dropwise to a solution of 295.2 mg (1.03 mmol) β-binaphthol **1** in 12 ml $CH_2Cl_2$ at 0 °C. The reaction mixture is warmed to r.t. and stirred for 6 h. The solvent is removed in vacuo and the residue crystallized from toluene; colorless solid; yield: 265.3 mg (80%). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta = 5.43$ (dd, $^3J_{(E)} = 18.6$, $^3J_{(Z)} = 13.5$, 1H, =C*H*), 5.78 (ddd, $^3J_{(E)} = 18.2$, $^3J_{(Z)} = 14.2$, $^2J_{(gem)} = 3.8$, 2H, =C*H*$_2$), 6.99 (d, $^3J = 8.6$, 2H, $H_{aromat}$), 7.10–7.20 (m, 2H, $H_{aromat}$), 7.23 (d, $^3J = 8.8$, 2H, $H_{aromat}$), 7.30 (ddd, $^3J = 8.0$, 7.0, $^4J = 1.2$, 2H, $H_{aromat}$), 7.78 (d, $^3J = 8.3$, 2H, $H_{aromat}$), 7.84 (d, $^3J = 9.0$, 2H, $H_{aromat}$). $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta = 119.8$ (+, 2C, $C_{aromat}$), 121.4 (o, 2C, $C_{aromat}$), 124.8, 126.0, 127.2, 128.1 (+, 8C, $C_{aromat}$), 130.6 (o, 2C, $C_{aromat}$), 131.0 (+, 2C, $C_{aromat}$), 133.6 (2C, $C_{aromat}$), 136.2 (+, 1C, $=CH_2$), 152.3 (o, 2C, $C_{aromat}$). $^{11}$B-NMR (128 MHz, $CDCl_3$): $\delta = 24.5$ (bs). MS (70 eV); *m*/*z* (%): 322 (37) [$M^+$], 307 (6), 295 (8), 286 (30), 268 (22), 257 (9), 239 (36), 226 (4), 213 (4), 147 (8), 119 (14), 84 (100), 66 (89). HRMS ($C_{22}H_{15}BO_2$): 322.1165 (calc.) 322.1164 (found).

#### 4.1.13. Nickel(0)-catalyzed [3+2] cycloadditions of vinylboronates with methylenecyclopropanes

*4.1.13.1. General procedure.* A mixture of 2–5 mol% $Ni(COD)_2$, two equivalents arylphosphine or arylphosphite and the vinylboronate is stirred in toluene at r.t. for 15 min, then the methylenecyclopropane is added. The reaction mixture is warmed up and the conversion is followed by GC or DC. After completion the solvent is removed in vacuo and the product purified.

#### 4.1.14. Diphenylidenecyclopentane-3-boronic acid (2,3-dimethylbutan-2,3-diyl)ester (29)

Six hundred milligrams (2.91 mmol) **27**, 448.5 mg (2.91 mmol) **28**, 24.0 mg ($8.74 \times 10^{-5}$ mol, 3 mol%) $Ni(COD)_2$, 54.1 mg ($1.75 \times 10^{-4}$ mol, two equivalents) $P(OPh)_3$, 5 ml toluene, 1.5 d, 100 °C. The product is purified by chromatography ($SiO_2$, petrol ether:ethyl ether 10:1; colorless oil; yield: 562 mg (54%, conversion (GC): 65%). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta = 1.23$ (s, 12H, C(C*H*$_3$)$_2$), 1.56 (m, 2H, 4,4′-H), 1.92 (quintett, $^3J = 8.3$, 1H, 3-H), 2.44 (m, 4H, H-5,5′,2,2′), 7.16–7.27 (m, 10H, $H_{aromat}$). $^1$H-NMR (200 MHz, $C_6D_6$): $\delta = 1.16$ (s, 12H, C(C*H*$_3$)$_2$), 1.63 (m, 1H, 3-H), 1.89 (m, 1H, 4-H), 2.09 (m, 1H, 4′-H), 2.60 (m, 2H, 5,5′-H), 2.88 (m, 2H, 2,2′-H), 7.13–7.46 (m, 10H, $H_{aromat}$).

$^{13}$C-NMR (50 MHz, $C_6D_6$): $\delta = 25.2$ (+, 4C, C(CH$_3$)$_2$), 30.1 (−, 1C, C-4), 35.1 (−, 1C, C-2), 36.3 (−, 1C, C-5), 83.3 (o, 2C, *C*(CH$_3$)$_2$), 126.7 (+, 2C, $C_{aromat}$, C-4,4′), 128.7 (+, 4C, $C_{aromat}$, C-2,2′,6,6′), 130.1 (+, 4C, $C_{aromat}$, C-3,3′,5,5′), 133.8 (o, 2C, $C_{aromat}$, C-1,1′), 144.3 (o, 1C, C-6), 144.6 (o, 1C, C-1). $^{11}$B-NMR (128 MHz, $C_6D_6$): $\delta = 34.0$ (bs). GC–MS (70 eV); *m*/*z* (%): 360 (45) [$M^+$], 275 (11), 260 (15), 232 (100), 193 (33), 167 (51), 129 (16), 115 (32), 101 (28), 91 (37), 85 (47). HRMS ($C_{24}H_{19}BO_2$): 360.2261 (calc.) 360.2260 (found).

#### 4.1.15. Diphenylmethylene-cyclopentan-3-ol (30)

Two hundred milligram (0.55 mmol) **29** in 8 ml diethyl ether; 324.6 mg (2.11 mmol) sodium perborate, 55 mg–1.38 mmol NaOH in 4 ml water; reaction time: 6 h. The product was purified by chromatography ($SiO_2$, petrol ether:ethyl ether 10:1); colorless oil, slowly solidifying; yield: 61 mg (95%). $^1$H-NMR (200 MHz, $C_6D_6$): $\delta = 1.52$ (m, 2H, 4-H), 2.22 (m, 2H, 5-H), 2.46 (ddd, $^3J = 17.3$, 5.4, 2.3, 1H, 2-H), 2.63 (ddd, $^3J = 17.3$, 8.5, 6.1, 1H, 2′-H), 3.94 (quintett, $^3J = 4.4$, 1H, 3-H), 7.02–7.10 (m, 2H, $H_{aromat}$), 7.12–7.18 (m, 4H, $H_{aromat}$), 7.20–2.24 (m, 4H, $H_{aromat}$). $^{13}$C-NMR (50 MHz, $C_6D_6$): $\delta = 31.0$ (−, 1C, C-5), 35.9 (−, 1C, C-4), 43.4 (−, 1C, C-2), 73.4 (+, 1C, C-3), 127.2 (+, 2C, $C_{aromat}$, C-4,4′), 128.6 (+, 4C, $C_{aromat}$, C-3,3′,5,5′), 130.3 (+, 4C, $C_{aromat}$, C-2,2′,6,6′), 135.7 (o, 2C, $C_{aromat}$, C-1,1′), 141.3 (o, 1C, C-6), 144.1 (o, 1C, C-1). MS (70 eV); *m*/*z* (%): 250 (19) [$M^+$], 232 (100), 215 (42), 204 (96), 191 (49), 178 (12), 165 (21), 152 (23), 141 (16), 128 (32), 115 (34), 107 (22), 101 (57), 91 (40), 89 (25), 77 (29), 63 (14), 51 (19). HRMS ($C_{18}H_{18}O$): 250.1358 (calc.) 250.1357 (found).

#### 4.1.16. Diphenylidenecyclopentane-trans-3-carboxylic acid methylester 4-boronic acid (2,3-dimethylbutan-2,3-diyl)ester (32a)

Compound **31a** (45.4 mg, 0.31 mmol), 63.6 mg (0.31 mmol) **27**, 4.26 mg ($1.55 \times 10^{-5}$ mol, 5 mol%) $Ni(COD)_2$, 8.12 mg ($3.1 \times 10^{-5}$ mol, two equivalents) $PPh_3$, 1.5 ml toluene, 12 h, 100 °C. The product was purified by chromatography ($SiO_2$, petrol ether:ethyl ether 10:1); yellow oil, slowly solidifying; yield: 83 mg (64%, conversion (GC): 87%). $^1$H-NMR (200 MHz, $C_6D_6$): $\delta = 1.23$ (s, 12H, C(C*H*$_3$)$_2$, 1.56 (m, 1H, H-4), 2.52 (m, 2H, H-5,5′), 2.73 (m, 2H, H-2,2′), 2.89 (m, 1H, H-3), 3.65 (s, 3H, $CO_2CH_3$), 7.15–7.35 (m, 10H, $H_{aromat}$). $^{13}$C-NMR (50 MHz, $C_6D_6$): $\delta = 25.1$ (+, 4C, C(*C*H$_3$)$_2$), 35.4 (−, 1C, C-5), 37.4 (−, 1C, C-2), 47.5 (+, 1C, C-3), 52.0 (+, 1C, $CO_2CH_3$), 83.8 (o, 2C, *C*(CH$_3$)$_2$), 126.6 (+, 2C, $C_{aromat}$, C-4,4′), 128.5 (+, 4C, $C_{aromat}$, C-2,2′,6,6′), 129.5 (+, 4C, $C_{aromat}$, C-3,3′,5,5′), 134.3 (o, 2C, $C_{aromat}$, C-1,1′), 141.4 (o, 1C, C-6), 143.4 (o, 1C, C-1), 175.8 (o, 1C, *C*O$_2$CH$_3$). $^{11}$B-NMR (128 MHz, $C_6D_6$): $\delta = 33.7$ (bs). MS (70 eV); *m*/*z* (%): 418 (11) [$M^+$], 358 (16), 318 (6), 219 (14), 258 (9), 323 (31), 230 (33), 215 (22), 204 (15), 191 (13), 167 (22), 152 (13), 100 (34), 67 (26), 57 (100). HRMS ($C_{26}H_{31}BO_4$): 418.2316 (calc.) 418.2315 (found).

#### 4.1.17. Diphenylidenecyclopentane-trans-3-p-toluolsulfonyl-4-boronic acid (2,3-dimethylbutan-2,3-diyl)ester (**32b**)

Compound **31b** (67.7 mg, 0.22 mmol), 45.3 mg (0.22 mmol) **27**, 3.0 mg ($1.1 \times 10^{-5}$ mol, 5 mol%) $Ni(COD)_2$, 5.8 mg ($2.2 \times 10^{-5}$ mol, two equivalents) $PPh_3$, 1.5 ml toluene, 12 h, 80 °C. The solvent is removed in vacuo and the residue washed with hexane to remove excess **27** and triphenylphosphine. When the product is treated with ether the nickel precipitates. The solution is decanted and the solvent removed. The residue is crystallized from ethyl ether–hexane 1:1; colorless oil, slowly solidifying; yield: 107 mg (95%). $^1$H-NMR (400 MHz, $CDCl_3$): $\delta = 1.11$ (s, 6H, $C(CH_3)_2$), 1.13 (s, 6H, $C(CH_3)_2$), 1.87 (q, $^3J = 9.1$, 1H, H-4), 2.36 (s, 3H, Ph–$CH_3$ and m, 1H, H-5′), 2.68 (m, 2H, H-2,5′), 2.85 (ddd, $^2J = 17.4$, $^3J = 7.9$, 4.0, 1H, H-2), 3.74 (q, $^3J = 8.4$, 1H, H-3), 7.28 ($^3J = 8.1$, 2H, $H_{aromat}$), 7.26–7.32 (m, 10H, $H_{aromat}$), 7.72 (d, $^3J = 8.3$, 2H, $H_{aromat}$). $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta = 22.0$ (+, 1C, Ph–$CH_3$), 25.0 und 25.1 (+, 4C, $C(CH_3)_2$), 34.5 (−, 1C, C-5), 34.8 (−, 1C, C-2), 67.0 (+, 1C, C-3), 84.2 (o, 2C, $C(CH_3)_2$), 128.5 (+, 3C, $C_{aromat}$), 129.3 (+, 6C, $C_{aromat}$), 130.1 (+, 6C, $C_{aromat}$), 135.4 (o, 3C, $C_{aromat}$), 142.5 (o, 1C, C-6), 144.6 (o, 1C, C-1). CI–MS ($CH_4$); *m/z* (%): 557 (11) $[M^+ + C_3H_7]^+$, 543 (9) $[M^+ + C_2H_5]^+$, 515 (88) $[M^+ + 1]^+$, 499 (3), 443 (8), 415 (36), 387 (11), 359 (100), 307 (22), 279 (98), 271 (5), 201 (4).

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