# Planar chiral hydroxy derivatives of [2.2]paracyclophane as auxiliaries for asymmetric allylboration

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Allylboronic esters with various structures were synthesized for the first time based on [2.2]paracyclophane derivatives containing one or two hydroxy groups. It was demonstrated that these esters can be used as chiral inductors in the asymmetric allylboration of benzaldehyde. The highest enantiomeric excess of 1-phenylbut-3-en-1-ol (60%) was achieved in the reactions with acyclic bis-*O*,*O*′-(paracyclophanyl) allylboronates based on (*S*)-4-hydroxy- and (*S*)-12-bromo-4-hydroxy[2.2]paracyclophanes. (*S*)-4-Hydroxy[2.2]paracyclophane was studied by X-ray diffraction.

**Key words:** [2.2]paracyclophanes, allylboration, asymmetric synthesis, planar chirality, chiral auxiliaries, homoallylic alcohols, X-ray diffraction study.

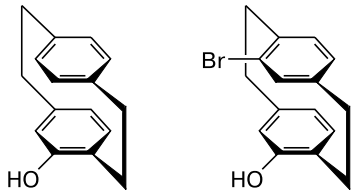
The allylboration of aldehydes is one of the most widely used approaches to the stereoselective C—C bond formation.[1—4] Generally, enantiomerically pure compounds (diols, diamines, sulfamides, and amino alcohols) possessing central[4] or (more rarely) axial chirality[5] are used for the design of reagents for the asymmetric allylboration.

Earlier,[6,7] we have demonstrated for the first time that planar chiral [2.2]paracyclophane derivatives can be used in this reaction. For example, diastereomerically pure diallylborinate **2** was synthesized starting from 4-acetyl[2.2]paracyclophane (**1**)[8,9] (Scheme 1).

Compound **2** was used in the allylboration of 4-formyl[2.2]paracyclophane (**4**) (*de* of *rel*-($R_p$,*R*)-4-(1-hydroxybut-3-enyl)[2.2]paracyclophane (**5**) 50%) and benzaldehyde (**6**) (*ee* of 1-phenylbut-3-en-1-ol (**7**) was 18%). Homoallylic alcohol **3** produced in the reaction is a recyclable auxiliary because it again gives ester **2** in the reaction with triallylborane (see Scheme 1).

In alcohol **3**, the hydroxy group is two bonds from the paracyclophane moiety. In the present study, we investigated the influence of the distance between the functional group and the paracyclophane moiety on the stereochemical result of asymmetric allylboration of benzaldehyde. For this purpose, we examined for the first time the possibility of designing reagents for the asymmetric allylboration based on chiral phenols, *viz.*, (*S*)-4-hydroxy[2.2]paracyclophane (**8**) and (*S*)-12-bromo-4-hydroxy[2.2]paracyclophane (**9**), in which the hydroxy group is directly fixed in the aromatic ring of [2.2]paracyclophane.

An important feature, which distinguishes phenols **8** and **9** from alcohol **3** containing two stereogenic centers,




(*S*)-**8** (*S*)-**9**

is that they contain only one (planar) chirality center, which eliminates the question about the possible cooperative effect of the planar and central chirality in the asymmetric process.

## Results and Discussion

**Synthesis of starting phenols 8 and 9.** Racemic phenol **8** was synthesized according to a known procedure.[10] To synthesize its enantiomers, we have developed[11—14] a procedure for the resolution of *rac*-**8** into enantiomers through esters with (1*S*)-(−)-camphanic acid **10** (Scheme 2).[15,16]

Diastereomeric esters **10** were separated by fractional crystallization[15] followed by the preparative separation of the mother liquor by silica gel column chromatography.[16]

In the present study, we improved the procedure for the isolation of enantiomers of phenol **8** from diastereomerically pure esters by using the hydrolysis with KOH in an aqueous methanolic mixture (see Scheme 2) instead of the reduction of esters **10** with a large excess of $LiAlH_4$ in anhydrous THF (the yield of **8** was 93%).[15] In this case, the refluxing of individual diastereomers of **10** in a Soxhlet apparatus during a long period of time (6—12 h) is not

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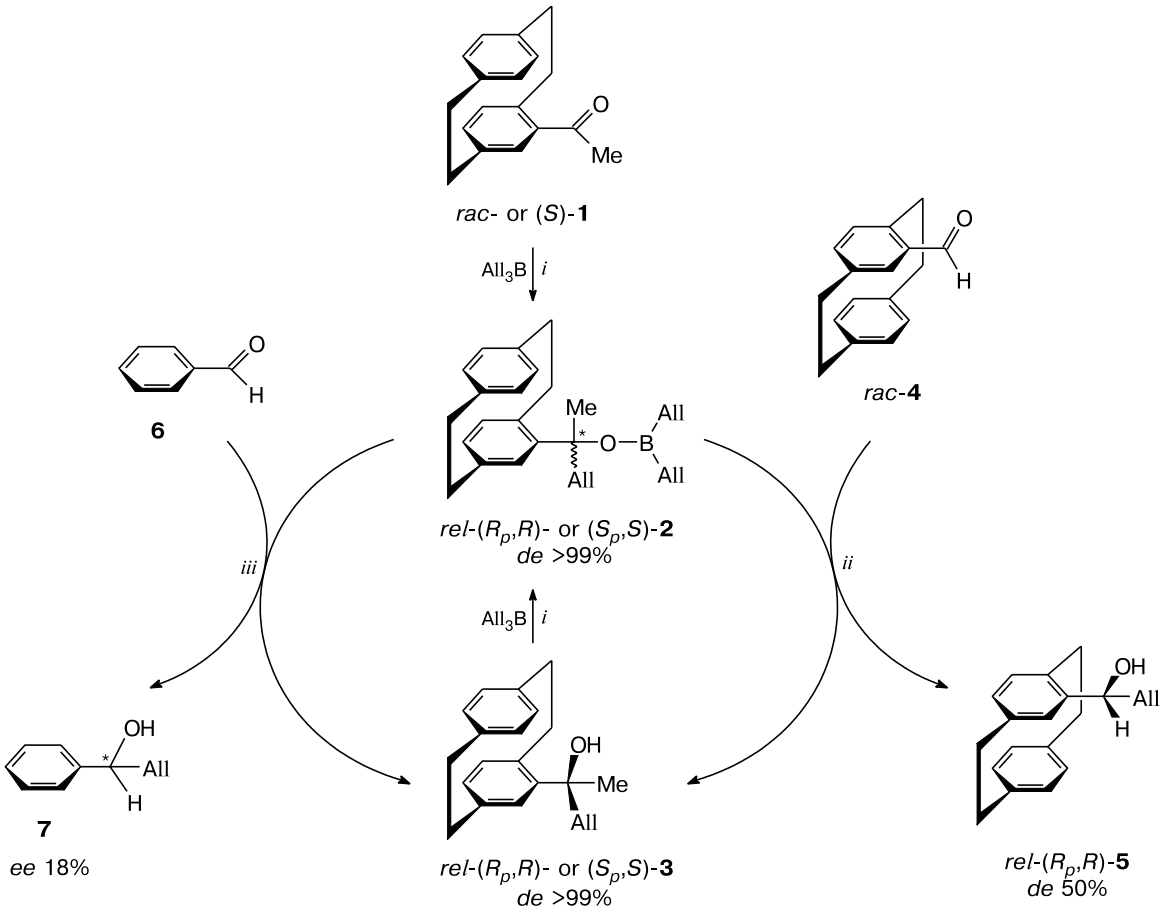
**Scheme 1**




**Reagents and conditions:** *i*. $CH_2Cl_2$, 40 °C, 5 h. *ii*. *rel*-($R_p$,*R*)-**2** and **4**, $CH_2Cl_2$, −70 °C; 0.5 h, ~20 °C; then MeOH and NaOH in $H_2O$, the yield of *rel*-($R_p$,*R*)-**3** was 96%, the yield of **5** was 92%. *iii*. ($S_p$,*S*)-**2** and **6**, THF, −70 °C, 17 h; then $NaBH_4$ in EtOH, 1 h; then MeOH and NaOH in $H_2O$, ~20 °C, the yield of ($S_p$,*S*)-**3** was 86%, the yield of **7** was 97%.

required; the hydrolysis is completed in 2 h at room temperature and gives enantiomers of phenol **8** in almost quantitative yield.

Earlier, we have synthesized[17] racemic bromo phenol **9** in high yield by the selective monolithiation of 4,12-dibromo[2.2]paracyclophane with BuLi in THF followed by the replacement of the Li atom by the B atom in the reaction of the Li intermediate with $B(OMe)_3$ and the oxidation of boronic ester with the $H_2O_2$/NaOH system.[17—19] The procedure, which we have developed earlier[18,19] for the resolution of bromophenol **9** into enantiomers, also involves the synthesis and chromatographic separation of its esters with (1*S*)-(−)-camphanic acid followed by hydrolysis of individual diastereomers.

The (*R*)-enantiomer of **8** was studied by X-ray diffraction. The structure of **8** contains two crystallographically independent molecules (**8A** and **8B**). In one molecule (**8A**), the hydrogen atom of the OH group is disordered over two positions (Fig. 1).

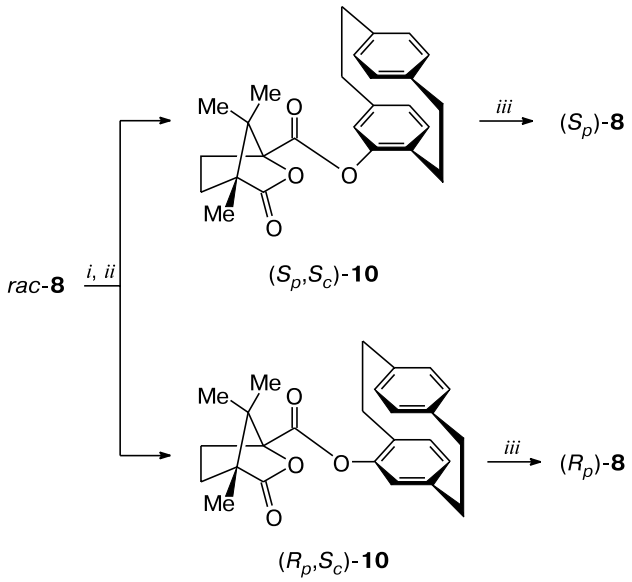
The geometric parameters of molecules **8A** and **8B** are given in Table 1. As can be seen from this table, the independent molecules are structurally identical.

The crystal structure consists of isolated hydrogen-bonded tetrameric associates (Fig. 2).

**Allylborating agents based on phenol 8.** With the aim of synthesizing allylborating agents starting from phenol **8**, we studied the reaction of the latter with triallylborane (Scheme 3).

The formation of allylboronic esters **11—13** was monitored by $^{11}B$ NMR spectroscopy because the chemical shifts of boranes and boronic esters with one, two, or three B—O bonds are substantially different.[20] When phenol **8** and $All_3B$ were used in a ratio of 1 : 1.1 ($CH_2Cl_2$, ~20 °C, 2 h), the $^{11}B$ NMR spectrum ($CH_2Cl_2$) of the reaction mixture measured after distillation of excess $All_3B$ showed only one signal at δ 51 corresponding to diallylborinate **11**. The yield of ester **11** (>99%) was determined based on the yield of 1-phenylbut-3-en-1-ol (**7**), which

**Scheme 2**




**Reagents and conditions:** *i*. (1*S*)-(−)-Camphanoyl chloride, Py, ~20 °C, 6 h, the yield of **10** was 95%. *ii*. Crystallization (AcOEt) and silica gel chromatography, the yields of $(S_p,S_c)$-**10** and $(R_p,S_c)$-**10** were up to 40%. *iii*. KOH, MeOH, ~20 °C, 2 h, the yields of $(S_p)$-**8** or $(R_p)$-**8** were 95%.

was prepared by the subsequent reaction with benzaldehyde (see below). To synthesize allylboronate **12**, the ratio of **8** to $All_3B$ was increased to 2.2 : 1, which required more drastic conditions (2 h, toluene, 110 °C). In this case, the $^{11}B$ NMR spectrum (toluene) shows the main signal at δ 27 corresponding to allylboronate **12** and a minor signal at δ 15 assigned to borate **13**. The yield of ester **12** was 80%. When the **8** : $All_3B$ ratio was increased to 3 : 1 and the protolysis time was increased to 5 h (toluene, 110 °C), triparacyclophanyl borate **13** was ob-

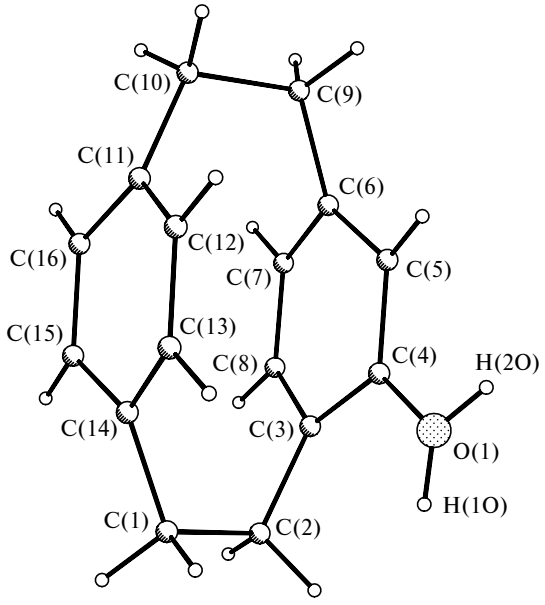



**Fig. 1.** Molecular structure of (*R*)-4-hydroxy[2.2]paracyclophane (**8A**).

**Table 1.** Bond lengths (*d*) and selected bond angles (ω) in compound **8**

| Parameter | **8A** | **8B** |
|---|---|---|
| Bond | *d*/Å | |
| C(4)—O(1) | 1.386(2) | 1.377(3) |
| C(4)—C(5) | 1.387(3) | 1.384(3) |
| C(7)—C(8) | 1.379(3) | 1.382(3) |
| C(12)—C(13) | 1.382(3) | 1.389(3) |
| C(15)—C(16) | 1.386(3) | 1.385(3) |
| C(3)—C(4) | 1.396(3) | 1.398(3) |
| C(3)—C(8) | 1.400(3) | 1.401(3) |
| C(6)—C(5) | 1.392(3) | 1.384(3) |
| C(6)—C(7) | 1.396(3) | 1.402(3) |
| C(11)—C(12) | 1.396(3) | 1.398(3) |
| C(11)—C(16) | 1.395(3) | 1.393(3) |
| C(14)—C(13) | 1.391(3) | 1.396(3) |
| C(14)—C(15) | 1.404(3) | 1.393(3) |
| C(2)—C(3) | 1.510(3) | 1.512(3) |
| C(6)—C(9) | 1.511(3) | 1.508(3) |
| C(1)—C(14) | 1.517(3) | 1.512(3) |
| C(10)—C(11) | 1.511(3) | 1.510(3) |
| C(1)—C(2) | 1.583(3) | 1.587(3) |
| C(9)—C(10) | 1.580(3) | 1.589(3) |
| Angle | ω/deg | |
| O(1)—C(4)—C(3) | 120.5(2) | 120.5(2) |
| O(1)—C(4)—C(5) | 117.3(2) | 117.6(2) |

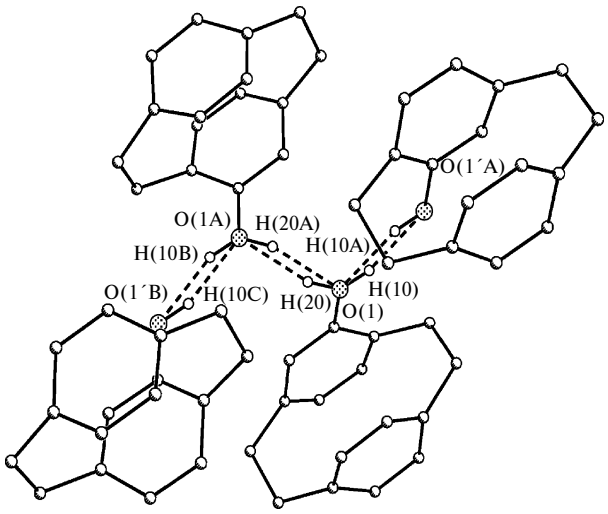
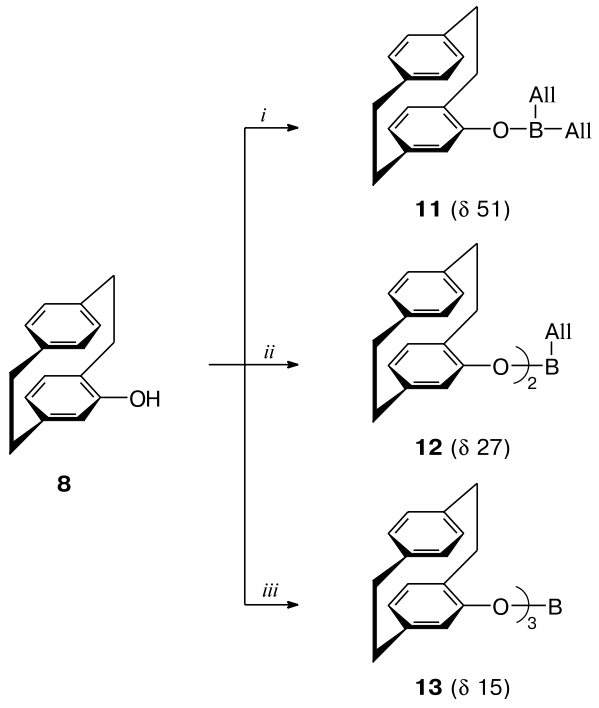



**Fig. 2.** Tetrameric associate in the crystal structure of **8**. The hydrogen bond parameters for the O(1)—H(10)...O(1´A) $(-x+2, y+1, -z+1)$, O(1)—H(20)...O(1A) $(-x+2, y, -z+1)$, and O(1´A)—H(10A)...O(1) bonds: the O...O and O...H distances are 2.796(2), 2.801(3), 2.796(2) Å and 1.98, 1.99, 2.00 Å, respectively, the O—H—O angles are 159, 160, and 156°, respectively.

**Scheme 3**




**Reagents and conditions:** *i*. $All_3B$ (1.1 equiv. of **8**), $CH_2Cl_2$, ~20 °C, 2 h, the yield of **11** was >99%. *ii*. $All_3B$ (2.2 equiv. of **8**), toluene, 110 °C, 2 h, the yield of **12** was 80%. *iii*. $All_3B$ (3 equiv. of **8**), toluene, 110 °C, 5 h, the yield of **13** was 70%.

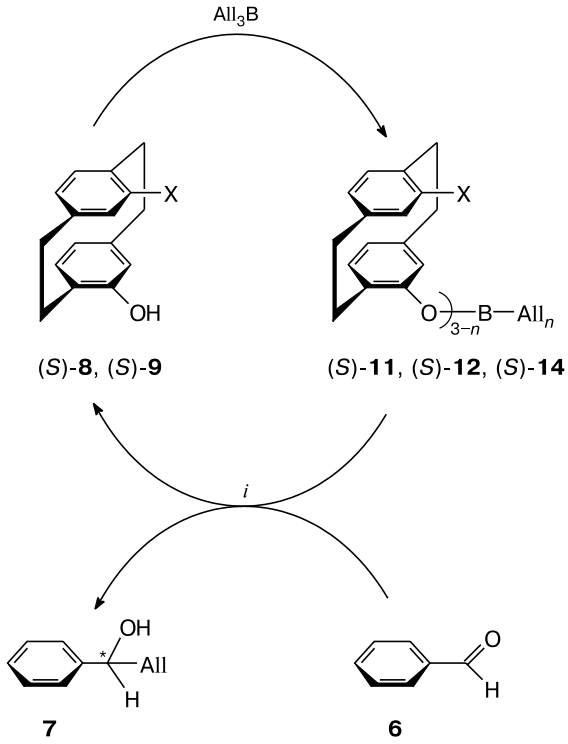
tained as the major product (according to the $^{11}B$ NMR spectrum, the yield was 70%).

Diallylborinate (*S*)-**11** and allylboronate (*S*)-**12** were tested in the asymmetric allylboration of benzaldehyde **6** (Scheme 4, Table 2, runs *1—4*).

The reactions were carried out with 1 equiv. of aldehyde **6** at −78 °C for 40 h in toluene or THF. The yield of product **7** was estimated from the intensity ratio of the signals for the protons of **7** and the protons of phenol **8** in the $^1H$ NMR spectra of the reaction mixtures. The enantioselectivity of the reaction with diallylborinate (*S*)-**11** was 23 (toluene) and 30% (THF) (see Table 2, runs *1* and *2*). In the reaction with allylboronate (*S*)-**12**, the enantiomeric excess of the reaction product substantially depends on the nature of the solvent. For example, the enantiomeric excess of alcohol (*R*)-**7** in the reaction in toluene was 24%, whereas it was as high as 60% in THF (see Table 2, runs *3* and *4*).

These experiments showed that phenols of the [2.2]paracyclophane series can be used as auxiliaries for the asymmetric allylboration. For example, the use of phenol (*S*)-**8** instead of the previously used alcohol ($S_p$,*S*)-**3** leads to an increase in the enantiomeric excess of the reaction product from 18 to 60%. A substantial advantage of phenol (*S*)-**8** as the reagent is that it is chemically

**Scheme 4**




X = H (**8**, **11**, **12**), Br (**9**, **14**); *n* = 2 (**11**), 1 (**12**, **14**)

**Reagents and conditions:** *i*. (*S*)-**11**, (*S*)-**12** or (*S*)-**14**, −78 °C, 40 h; then $NaBH_4$/EtOH and $NaOH/H_2O$.

stable. Thus, it is recovered from the reaction mixture in quantitative yield and the same enantiomeric purity, whereas homoallylic alcohol ($S_p$,*S*)-**3** (see Scheme 1) is unstable.

**Allylborating agents based on phenol 9.** The introduction of substituents at different positions of the three-dimensional paracyclophanyl moiety allows the design of related ligands by varying the chiral environment and

**Table 2.** Asymmetric allylboration of benzaldehyde **6**

| Run | Agent | Solvent | Yield of **7** | *ee* **7*** | Configuration of **7**** |
|---|---|---|---|---|---|
| | | | % | | |
| *1* | (*S*)-**11** | Toluene | 80 | 23 | *R* |
| *2* | (*S*)-**11** | THF | 75 | 30 | *R* |
| *3* | (*S*)-**12** | Toluene | 99 | 24 | *R* |
| *4* | (*S*)-**12** | THF | 24 | 60 | *R* |
| *5* | (*S*)-**14** | THF | 50 | 59 | *R* |

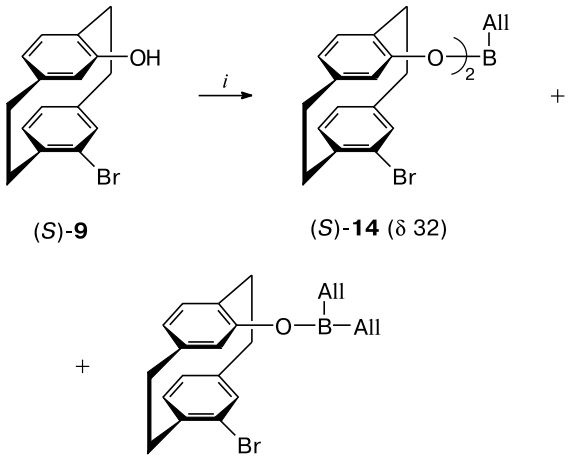
* The enantiomeric excess was determined by enantioselective HPLC.

** The configuration of the alcohol was determined by comparing the sign of the observed angle of rotation with the published data: $[\alpha]_D^{23}$ −44.92 (*c* 7.38, benzene) for (*S*)-**7** (*ee* 96%).[21]

steric crowding of the reaction center. Hence, we chose bromo-substituted phenol **9**,[17–19] which is an analog of phenol **8** and contains the bulky substituent in the *pseudo-ortho* position, as the model compound.

Since the best result in the allylboration reaction with the use of reagents based on phenol (*S*)-**8** was obtained for allylboronate (*S*)-**12**, we decided to synthesize the structurally similar allylborating agent based on bromophenol **9**. For this purpose, the reaction of bromophenol (*S*)-**9** with triallylborane was carried out under the conditions analogous to those used for the transformation (*S*)-**8** → (*S*)-**12** (the reagent ratio (*S*)-**9** : $All_3B$ = 2.2 : 1, toluene, 110 °C). However, after 2 h the $^{11}B$ NMR spectrum showed, along with a signal at δ 32 corresponding to allylboronate (*S*)-**14**, a signal at δ 53 belonging to diallylborinate (*S*)-**15** (Scheme 5). The ratio of products **14** to **15** was 4 : 1.

**Scheme 5**



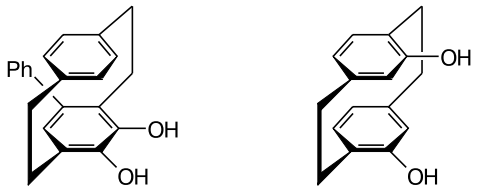

(*S*)-**9** (*S*)-**14** (δ 32) (*S*)-**15** (δ 53)

**Reagents and conditions:** *i*. $All_3B$, toluene, ~20 °C, 2 h, the yield of (*S*)-**14** was 95%; (*S*)-**15**, 5%.

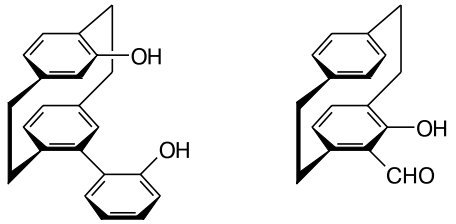
Product **14** was selectively synthesized by the reaction performed at room temperature. It appeared that the formation of almost pure allylboronate (*S*)-**14** was observed even in the reaction with the use of equimolar amounts of the reagents.

As demonstrated above, the highest enantioselectivity of the allylboration of benzaldehyde with allylboronate (*S*)-**12** was achieved at −78 °C in THF. Under the same conditions, the enantiomeric excess of the product in the reaction with reagent (*S*)-**14** remained unchanged (59%), whereas the yield of alcohol (*R*)-**7** increased from 24 to 50% (see Table 2, run *5*).

**Allylboration with the involvement of diols 16—19.** Chiral aliphatic diols are known[4,20] to be highly efficient as auxiliaries in the asymmetric allylboration. In addition, bifunctional paracyclophane derivatives with *ortho* and *pseudo-ortho* structures serve as efficient inductors of various reactions in the asymmetric synthesis and catalysis.[22–24] Hence, we examined the possibility of the use of bifunctional hydroxy derivatives of [2.2]paracyclophane in the allylboration reaction. In the test reactions with benzaldehyde, we used biphenols with the *ortho* and *pseudo-ortho* arrangement of the hydroxy groups ((*S*)-**16** (see Refs 18 and 19) and (*R*)-**17**,[25] respectively), dihydroxyarylparacyclophane (*S*)-**18**,[18,19] and hydroxyaldehyde (*R*)-**19** (see Ref. 26) as the auxiliaries.



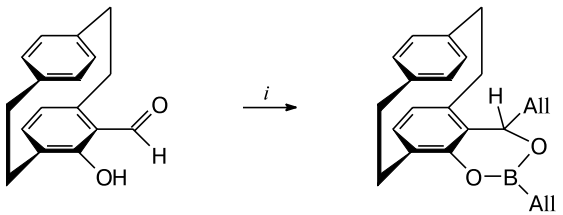

(*S*)-**16** (*R*)-**17**




(*S*)-**18** (*R*)-**19**

Allylboronic esters based on dihydroxy derivatives are cyclic compounds.[4,5,20] Hence, allylborating agents based on bifunctional [2.2]paracyclophane derivatives **16—19** were synthesized with the use of an equimolar amount of $All_3B$. The cyclic structures of esters were suggested based on the almost quantitative yield of the final allylboration product **7**. In the case of compound (*R*)-**19**, the formation of cyclic allylboronate ($R_p$,*S*)-**20** has been confirmed earlier[7] by $^{11}B$ NMR spectroscopic data (Scheme 6).

**Scheme 6**




(*R*)-**19** ($R_p$,*S*)-**20**
*de* 99% (δ 34)

**Reagents and conditions:** *i*. $All_3B$, $CH_2Cl_2$, ~20 °C, 0.5 h, >99%.

The allylboration of benzaldehyde was carried out in THF at −78 °C. Unexpectedly, the enantioselectivity in

the reactions with compounds **16—19** appeared to be low (*ee* of alcohol **7** was 9, 15, and 3% for (*S*)-**16**, (*R*)-**17**, and (*R*)-**19**, respectively) and depend only slightly on the mutual arrangement of the functional groups. In this series, the best result (*ee* of alcohol **7** was 23%) was achieved for aryl[2.2]paracyclophanyl biphenol (*S*)-**18**, which is conformationally labile with respect to the $C_{Ar}—C_{Ar}$ bond and in which one hydroxy group is present in the paracyclophanyl moiety and another hydroxy group is present in the aryl fragment.

To summarize, we characterized a new class of allylborating agents based on planar chiral phenols of the [2.2]paracyclophane series and their derivatives. The protolysis of triallylborane with 4-hydroxy- and 12-bromo-4-hydroxy[2.2]paracyclophanes was studied for the first time. The conditions for the preparation of individual diallylborinate **11**, allylboronates **12** and **14**, and borate **13** were found. Allylboronic esters based on enantiomerically pure compounds **8**, **9**, and **16—19** were tested in the asymmetric allylboration of benzaldehyde. The best results (*ee* of alcohol **7** was 60%) were achieved in the reactions with allylboronates ($S_p$,$S_p$)-**12** and ($S_p$,$S_p$)-**14** containing two paracyclophanyl fragments, which were synthesized from phenols (*S*)-**8** and (*S*)-**9**, respectively.

In the future, we plan to examine the possibility of performing the asymmetric allylboration with other reagents based on paracyclophane derivatives, in which the allylboron groups are attached directly to the paracyclophanyl moiety (diallylparacyclophanyl- and allyldiparacyclophanylboranes).

## Experimental

All reactions were carried out under argon in anhydrous solvents. The $^1H$ and $^{11}B$ NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 and 128.378 MHz, respectively) in $CDCl_3$, $CH_2Cl_2$, and toluene with the use of the residual signals for the protons of the solvents as the internal standard (δ 7.27 for $CDCl_3$ and 0 for $BF_3 \cdot Et_2O$). The TLC analysis was performed on Sorbfil PTSKh-AF-A-UF (Sorbpolimer, Russia) and Silufol UV-254 (Chemapol) plates. The enantioselective HPLC was carried out on a (*R*,*R*)-Whelk-01 column (25 cm × 4.6 mm) using a 100 : 1 heptane—$Pr^iOH$ mixture as the eluent (the elution rate was 1 mL $min^{-1}$) and an UV detector (254 nm). The enantioselective GLC was carried out on a Chiraldex-β-DM column (30 m × 0.25 mm), $T$ = 180 °C, helium as the carrier gas, 103.41 kPa, the split ratio was 75/1, a flame ionization detector.

**(*R*)-(+)-4-Hydroxy[2.2]paracyclophane ((*R*)-(+)-8).** Potassium hydroxide (0.764 g, 13.64 mmol) was added to a suspension of camphanic ester ($R_p$,*S*)-**10** (see Refs 15 and 16) (1.300 g, 3.22 mmol) in MeOH (120 mL). The reaction mixture was stirred at ~20 °C for 2 h. Then a saturated aqueous NaCl solution (120 mL) and benzene (60 mL) were added, and the mixture was vigorously stirred for 0.5 h. The organic layer was separated, and the aqueous layer was extracted with benzene (2×50 mL). The combined organic phases were dried with $Na_2SO_4$, and the solvent was removed under reduced pressure. The solid residue was passed through a layer of silica gel using benzene as the eluent. The yield of (*R*)-(+)-**8** was 0.713 g (99%), *ee* >99% (according to the GLC data, $t_s$ = 80.17, $t_r$ = 88.21), m.p. 229—230 °C (*cf.* lit. data[12]: m.p. 232—234 °C).

**(*S*)-(−)-4-Hydroxy[2.2]paracyclophane ((*S*)-(−)-8)** was synthesized analogously from camphanic ester ($S_p$,*S*)-**10** in 99% yield, *ee* >99%.

**(*S*)-([2.2]Paracyclophan-4-yl) diallylborinate ((*S*)-11).** A 0.3 *M* $All_3B$ solution in $CH_2Cl_2$ (1.8 mL, 0.515 mmol) was added with stirring to a solution of phenol (*S*)-**8** (*ee* >98%) (0.115 g, 0.513 mmol) in $CH_2Cl_2$ (5 mL). The reaction mixture was stirred for 2 h. Then excess $All_3B$ and the solvent were distilled off *in vacuo*. $^{11}B$ NMR (128.378 MHz, $CH_2Cl_2$), δ: 51. The yield was >99% (determined from the reaction of (*S*)-**11** with benzaldehyde).

**Bis-*O*,*O*´-{(*S*)-[2.2]paracyclophan-4-yl} allylboronate ((*S*)-12).** A 0.3 *M* $All_3B$ solution in toluene (1.1 mL, 0.314 mmol) was added with stirring to a solution of phenol (*S*)-**8** (0.155 g, 0.692 mmol) (*ee* >98%) in toluene (6 mL). The reaction mixture was refluxed for 2 h, and the solvent was distilled off *in vacuo*. $^{11}B$ NMR (128.378 MHz, $CH_2Cl_2$), δ: 27. The yield was 80% (determined from the reaction of (*S*)-**12** with benzaldehyde).

**Allylborating agents based on compounds 16—19** were synthesized analogously to compound (*S*)-**12** using $CH_2Cl_2$ as the solvent.

**Bis-*O*,*O*´-{(*S*)-12-bromo[2.2]paracyclophan-4-yl} allylboronate ((*S*)-14).** A 0.3 *M* $All_3B$ solution in toluene (0.8 mL, 0.233 mmol) was added with stirring to a solution of phenol (*S*)-**9** (*ee* >96%) (0.188 g, 0.513 mmol) in toluene (5 mL). The reaction mixture was stirred at ~20 °C for 2 h. $^{11}B$ NMR (128.378 MHz, toluene), δ: 32.

**Allylboration of benzaldehyde (general procedure).** Allylboronic ester, which was synthesized from compound **8** (**9** or **16—19**), was dissolved in THF (0.04 mol $L^{-1}$). The reaction mixture was cooled to −78 °C, and 1 mol-equiv. of freshly distilled benzaldehyde was added with stirring. After 40 h, the reaction mixture was treated with a 0.5 *M* $NaBH_4$ solution in EtOH, stirred for 1 h, and allowed to warm to ~20 °C. Then MeOH and a 0.5 *M* NaOH solution in $H_2O$ were successively added. The reaction mixture was stirred for 30 min and then concentrated. The residue was extracted with diethyl ether (3×15 mL), washed with $H_2O$, and dried with $Na_2SO_4$. Alcohol **7** was isolated by either vacuum distillation or extraction from the reaction mixture with pentane. The enantiomeric excess of **7** was determined by HPLC.

**X-ray diffraction study of compound (*R*)-8.** Colorless prismatic crystals of $C_{16}H_{16}O$ (*R*)-**8** (M = 224.29) are monoclinic, at 110 K $a$ = 26.327(3) Å, $b$ = 7.7134(8) Å, $c$ = 11.477(1) Å, β = 105.917(2)°, $V$ = 2241.2(4) $Å^3$, space group $C2$, $Z$ = 8, $d_{calc}$ = 1.329 g $cm^{-3}$. The intensities of 7267 reflections were measured on a Bruker SMART CCD Area Detector diffractometer at 110 K (Mo-Kα radiation, $2\theta_{max}$ = 54°) from a single crystal with dimensions 0.8×0.4×0.2 mm. After merging of the equivalent reflections, 4343 independent reflections were obtained ($R_{int}$ = 0.0177), which were used for the structure solution and refinement. Absorption (μ = 0.081 $mm^{-1}$) was ignored; the transmission coefficients $T_{max}$ and $T_{min}$ determined with the use of the SADABS program[27] were 0.985 and 0.945, respectively. The structure was solved by direct methods. All non-hydrogen atoms were located in difference electron density maps

and refined anisotropically based on $F^2_{hkl}$. All hydrogen atoms (except for the H atoms of the OH group, which were located in difference electron density maps) were positioned geometrically. All hydrogen atoms were refined using a riding model with $U(H) = 1.2U(C)$, where $U(C)$ are the equivalent thermal parameters of the parent atoms. The final $R$ factors were $R_1 = 0.0460$ (based on $F_{hkl}$ for 3937 reflections with $I > 2\sigma(I)$), $wR_2 = 0.1002$ (based on $F^2_{hkl}$ for all 4343 reflections), GOOF 0.996, 307 parameters were refined. All calculations were carried out using the SHELXTL PLUS 5 program package.[28]

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