waiting time (10 to 30 minutes) allowed the system to reach equilibrium. Steps of 2 mN m^{-1} were usually chosen. The subphase was water (Q grade, Millipore) with a resistivity higher than 18 MΩ cm. The dipping speed was generally set to 0.5 cm min^{-1}. Films were transferred onto optically polished calcium fluoride (precoated with three monolayers of behenic acid) for IR measurements, onto optically polished and silanized glass substrate for low-angle X-ray experiments, and onto a diamagnetic mylar sheet for magnetic SQUID measurements.

IR spectra were recorded on a FTIR 750 Nicolet spectrometer. To determine the orientation of the lipid molecules in the LB films, the linear dichroism in the IR region was used. In a first spectrum, the incident light was set perpendicular to the substrate normal; in a second, the incident IR beam formed an angle of 60° with the substrate normal. The out-of-plane dichroic ratio β for each band is then defined as the ratio of the IR absorption in both spectra. The angle between the substrate normal and the transition dipole moment can then be evaluated from β using a model already described.[15]

X-ray diffraction patterns were obtained using a conventional generator (Kristalloflex Siemens Ltd) delivering non-monochromatized line-focused $Cu_{K\alpha}$ radiation. This beam passes through the sample, which is mounted vertically and oscillated during exposure. The integrated intensities of the Bragg reflections were collected by an INEL CPS 120 curved position-sensitive detector (with a resolution of 0.1° in 2θ) associated with an IBM computer for peak assignments.

The magnetic measurements were performed with a Quantum Design MPMS-XL SQUID magnetometer between 2 and 300 K. For such experiments, about 300 layers were deposited on a diamagnetic mylar sheet ($0.075 \times 5 \times 15$ mm). The procedure followed for the magnetic susceptibility measurement is described elsewhere.[11] For the magnetization measurements the hysteresis loops were recorded in about 5 hours. Each loop contains 180 points. To stabilize each data point a time of about 2 minutes was required. The errors in the magnetization data are in the range of 1 – 5 %.

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Efficient Suzuki-Type Cross-Coupling of Enantiomerically Pure Cyclopropylboronic Acids**

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Transition metal catalyzed Suzuki-type cross-coupling reactions are versatile and powerful methods for the formation of carbon – carbon bonds, because most of these reactions are stereospecific and offer many other advantages.[1] The proposed mechanism of the palladium-catalyzed cross-coupling[1a] contains a transmetalation reaction between organoboron compounds and palladium halide complexes as well as subsequent reductive elimination steps. Undoubtedly, understanding the change in stereochemistry of the chiral carbon atom upon use of a chiral alkylboron compound as reagent is of interest for organic chemists. Bäckvall and Åkermark reported that the configuration of the chiral carbon atom of the alkyl group was retained upon transmetalation from mercury to palladium.[2] Stille found that the transmetalation reaction of a chiral benzyltin compound with a palladium complex in hexamethyl phosporamide (HMPA) proceeded with inversion.[3] Hiyama and co-workers investigated the palladium-catalyzed cross-coupling reaction of chiral alkylsilanes with aryl triflates (triflate = trifluoromethanesulfonate). They determined that the stereochemistry is affected by both the reaction temperature and the nature of the solvent and could be controlled from almost complete retention to inversion by tuning these factors.[4] Recently, we prepared racemic cyclopropylboronic acids and subjected them to Suzuki-type coupling reactions with bromoarenes[5] or bromoacrylates.[6] Herein we report the palladium-catalyzed cross-coupling of optically active cyclopropylboron compounds.

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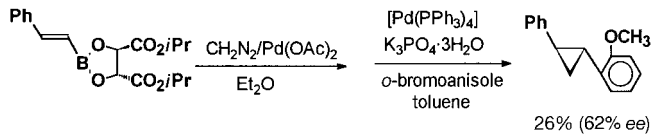
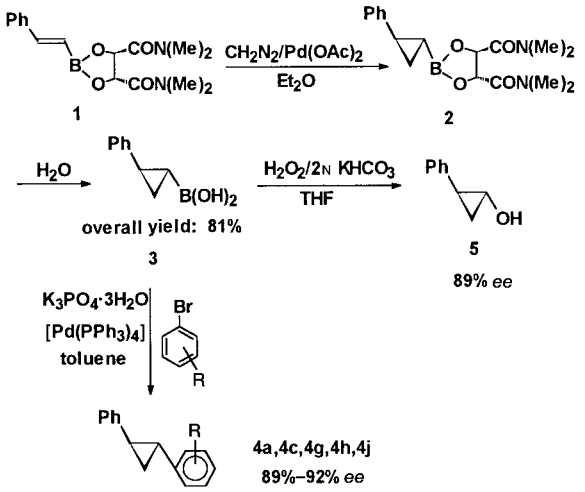
In the initial investigation, (*E*)-styrylboronic acid was esterified by (+)-diisopropyl tartrate (DIPT), and subsequent asymmetric cyclopropanation of the styrylboronic ester gave 2-phenylcyclopropylboronic ester. Afterwards, palladium-catalyzed cross-coupling with *o*-bromoanisole was conducted at 100 °C with toluene as solvent to afford optically active cyclopropyl-substituted anisol (62 % *ee*) in 26 % overall yield (Scheme 1).



Scheme 1. Synthesis of optically active cyclopropyl-substituted anisol by palladium-catalyzed cross-coupling.

The result was unsatisfactory, in particular the yield of coupling product was poor. Pietruszka et al. also investigated the cyclopropanation of alkenylboronic esters derived from (+)-DIPT and alkenyl boronic acids and the subsequent cross-coupling of the cyclopropanation product with iodobenzene; they obtained similar results.[7] The Suzuki-type cross-coupling of cyclopropylboronic esters with aryl halides was also reported by Marsden et al.,[8] but the yields of coupling products were lower. We recently showed that the yields of coupling products upon use of cyclopropylboronic acids[5, 6] as starting materials were higher than with cyclopropylboronic esters.[8] Therefore, we attempted to hydrolyze the cyclopropylboronic ester of DIPT with many reagents ($BF_3 \cdot Et_2O$, $TiCl_4$, $AlCl_3$, 2N HCl, 2N H_2SO_4, etc.) to afford the corresponding cyclopropylboronic acid, but the efforts failed. Fortunately, in numerous experiments on different derivatives of tartaric acid, it was found that in the asymmetrically induced cyclopropanation of (*E*)-1-alkenylboronic ester[9] (+)-*N*,*N*,*N*′*N*′-tetramethyltartaric acid diamide (TMTA)[10] is a better chiral auxiliary than (+)-DIPT. The optically active cyclopropylboronic ester of (+)-TMTA obtained in situ was readily hydrolyzed by water to give the corresponding optically active cyclopropylboronic acid in good yield (Scheme 2).

Under our previous conditions[5, 6] the optically active cyclopropylboronic acid could easily enter the cross-coupling reaction with bromobenzene to afford the optically active cyclopropyl-substituted benzene (Scheme 2). The absolute configuration of the product was determined by comparison of the specific rotation. For example, the (*E*)-styrylboronic ester of (+)-TMTA (**1**) was cyclopropanated to give, after hydrolysis, (1*R*,2*R*)-2-phenylcyclopropylboronic acid (**3**). This species underwent oxidation to (1*R*,2*S*)-(−)-2-phenyl-1-cyclopropanol (**5**), for which the sign of the specific rotation agreed with that reported[11] (Scheme 2). The sense of the specific rotation of product **4a** obtained by coupling of **3** with bromobenzene was also the same as that of (1*R*,2*R*)-(−)-1,2-diphenylcyclopropane[12] (Table 1), and the *ee* value of the oxidation product **5** was similar to that of **4a** (Scheme 2). In addition, the reactions of cyclopropylboronic acid of the same optical purity with different electrophiles gave the corresponding cross-coupling products with similar optical purities (Table 1). These results suggest that the absolute configuration of the center of chirality, on which the coupling reaction occurred, was retained in the coupling process.



Scheme 2. Synthetic route to optically active cyclopropyl-substituted benzene derivatives. See Table 1 for the substituent R.

Of course also *S*,*S* isomers (**4b, 4d**, **4e, 4f, 4i, 4k, 4m**) could be obtained by using (−)-TMTA as auxiliary. The results of the coupling reaction between optically active cyclopropylboronic acids and various electrophiles are shown in Table 1. The enantiomeric excesses of all products were determined by HPLC on appropriate chiral columns. Table 1 demonstrates that the chemical yields and optical purities of the coupling products thus obtained were higher than with previously reported methods.

We have presented the first detailed investigations of palladium-catalyzed Suzuki-type cross-coupling reactions with chiral organoboron coumpounds. The results indicate that the absolute configuration of the chiral carbon atom was retained in the cross-coupling process. The optical purities and yields of the coupling products are satisfactory. This method opens the door for the synthesis of other optical active cyclopropyl derivatives by the preparation and subsequent cross-coupling of optically active cyclopropylboronic acids with electrophiles.

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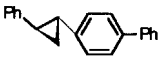
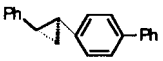
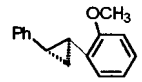
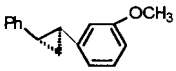
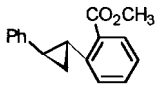
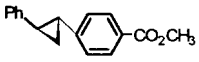
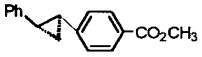
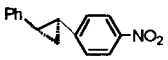
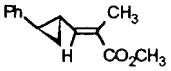
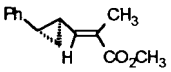
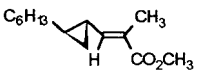
Table 1. Coupling reactions of various chiral cyclopropylboronic acids with electrophiles.[a]

Chiral auxiliary	Product		$[\alpha]_D^T$ [°] (c in $CHCl_3$)	Config.	Yield [%][b]	*ee* [%]
(+)-TMTA		**4a**	$[\alpha]_D^{17}$ −379.0 (0.496)[c]	(1*R*,2*R*)	77	91[d]
(−)-TMTA		**4b**	$[\alpha]_D^{16}$ 388.2 (1.003)[c]	(1*S*,2*S*)	81	91[d]
(+)-TMTA		**4c**	$[\alpha]_D^{16}$ −425.3 (1.123)	(1*R*,2*R*)	90	91[d]
(−)-TMTA		**4d**	$[\alpha]_D^{16}$ 421.8 (1.103)	(1*S*,2*S*)	88	90[d]
(−)-TMTA		**4e**	$[\alpha]_D^{16}$ 250.8 (1.250)	(1*S*,2*S*)	78	91[d]
(−)-TMTA		**4f**	$[\alpha]_D^{16}$ 343.6 (1.164)	(1*S*,2*S*)	73	90[e]
(+)-TMTA		**4g**	$[\alpha]_D^{16}$ −159.5 (0.981)	(1*R*,2*R*)	83	91[f]
(+)-TMTA		**4h**	$[\alpha]_D^{16}$ −450 (0.322)	(1*R*,2*R*)	79	92[d]
(−)-TMTA		**4i**	$[\alpha]_D^{12}$ 426.8 (0.963)	(1*S*,2*S*)-	84	90[d]
(+)-TMTA		**4j**	$[\alpha]_D^{16}$ −519.0 (0.973)	(1*R*,2*R*)	87	89[d]
(−)-TMTA		**4k**	$[\alpha_D^{12}$ 511.0 (1.000)	(1*S*,2*S*)	86	89[d]
(+)-TMTA		**4l**	$[\alpha]_D^{16}$ −377.3 (0.275)	(1*R*,2*R*)	80	92[d]
(−)-TMTA		**4m**	$[\alpha]_D^{17}$ 358.1 (0.296)	(1*S*,2*S*)	81	90[d]
(+)-TMTA		**4n**	$[\alpha]_D^{20}$ −40.1 (0.412)	(1*R*,2*R*)	76	82[d]

[a] Coupling reactions were conducted at 100 °C in toluene with the chiral cyclopropylboronic acids (1.1 equiv), the bromoarenes or bromoacrylates (1.0 equiv), $K_3PO_4 \cdot 3H_2O$ (3.3 equiv), and $[Pd(PPh_3)_4]$ (0.03 equiv). [b] Yields of isolated product based on the bromoarene or bromoacrylate. [c] (1*R*,2*R*)-1,2-Diphenylcyclopropane (**4a**): $[\alpha]_D^{20} = -418°$ ($c = 0.96$ in $CHCl_3$),[12b] 100 % *ee*; (1*S*,2*S*)-1,2-diphenylcyclopropane (**4b**): $[\alpha]_D^{22} = 362°$ ($c = 0.038$ in $CHCl_3$),[12a] 86 % *ee*. [d] Determined by HPLC (Chiralcel OD). [e] Determined by HPLC (Chiralcel OJ). [f] Determined by HPLC (Chiralcel AD).

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