Supporting Information (Part 1)

Catalytic Enantioselective Hydroboration of Cyclopropenes

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NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz) instrument. (+) and (-) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiments. In most cases, a broad signal was observed for the cyclopropyl CH next to boron atom in cyclopropyl boronates. Neither DEPT nor HMQC correlations were observed for such carbon atoms and these cases are indicated as broad . IR spectra were recorded on a Genesis II FT-IR Mattson spectrometer. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). HRMS analyses were performed in Mass Spectrometry Service Laboratory, University of Minnesota using a FINNIGAN MAT 95 instrument for HRCI (4% NH_3 in CH_4) or a VG 7070-HF instrument for HRFAB. Chiral GC analysis was performed on a Hewlett Packard Model 5890 Series II GC equipped with J&W Scientific capillary columns Cyclodex B and Cyclosil B (both 30 m x 0.25 mm x 0.25 m). Column chromatography was carried out employing Merck silica gel (Kieselgel 60, 63-200 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography.

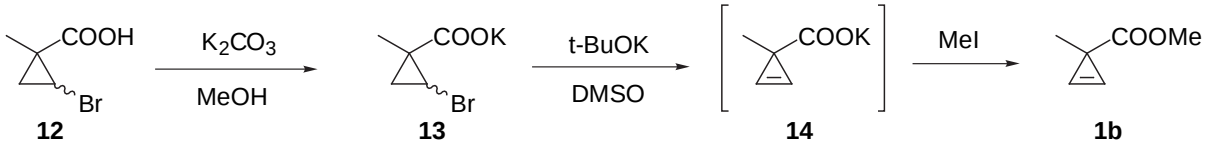
All manipulations with cyclopropenes, rhodium complexes, and chiral phosphine ligands were conducted under argon atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous dichloromethane, DMSO, and diethyl ether were purchased from Aldrich and stored over calcium hydride. THF was refluxed over sodium wire with benzophenone and distilled immediately before utilization. Cyclopropenes **1c**[1], **1a,f**[2], were prepared according to the known procedures. Procedures for preparation of other cyclopropenes as well as procedures for hydroboration and Suzuki cross-coupling reaction are provided below. Trimethylsilylacetylene in bulk was purchased from GFS Chemicals, transition metal catalysts and chiral phoshine ligands were bought from Strem. All other reagents and solvents used were commercially available and purchased from Aldrich, Acros Organics, or Avocado Research Chemicals.

Cyclopropenes.

1-Methylcycloprop-2-ene Carboxylic Acid Methyl Ester (1b). Cyclopropene **1b** was prepared according to the modified Baird-Bolesov method (Eq. 1).[3] 2-Bromo-1-methylcyclopropane carboxylic acid (**12**)[4] (43.7, 244 mmol) in methanol (100 mL) was added to a stirred suspension of

1. Arrowood, T. L.; Kaas, S. R. *Tetrahedron* **1999**, *55*, 6739.
2. See Supporting Inform.: Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2002**, *124*, 11566.
3. Kudrevich, S. V.; Rubin, M. A.; Tarabaeva, O. G.; Surmina, L. S.; Baird, M. S.; Bolesov, I. G. *Russ. J. Org. Chem. (Engl. Transl.)* **1994**, *30*, 1008; *Zh. Org. Khim.* **1994**, *30*, 945.
4. Latypova, M. M.; Katerinich, L. V.; Baranova, I. N.; Plemenkov, V. V.; Bolesov, I. G. *J. Org. Chem. USSR (Engl. Transl.)* **1982**, *18*, 2253.

K_2CO_3 (68 g, 488 mmol) in methanol (300 mL). The mixture was stirred overnight, filtered and evaporated dry. The residue was dried in high vacuum and the temperature was slowly raised to 100°C until no condensate was accumulating in a trap cooled with liquid nitrogen. The solid cake was ground in dry argon atmosphere to obtain **13** in quantitative yield as a hygroscopic powder, which can be stored in dry atmosphere at room temperature for a long period. The powder normally contains about 5% of K_2CO_3, which does not compromise further transformation.



12 **13** **14** **1b** (1)

t-BuOK (20.11 g, 180 mmol, 1.2 equiv.) was dissolved in anhydrous DMSO (30 mL) by heating to 60°C, then the mixture was cooled down to 30°C. Potassium salt **13** (32.64 g, 149.6 mmol) was dissolved in anhydrous DMSO (150 mL) and the solution was added rapidly via cannula to a stirred solution of t-BuOK. The mixture was stirred at 50°C, until a very viscous blend was formed (normally it takes ca. 2 hrs). Methyl iodide (37 mL, 0.6 mol, 4 equiv.) was added upon cooling and the mixture was stirred for 30 min, while completely liquefied and a crystalline precipitate of KI was formed. Then the mixture was quenched with water and extracted with ether. Combined organic solutions were washed (water, brine), dried ($MgSO_4$), filtered, and evaporated. The residue was distilled twice in vacuum to give pure material as a colorless liquid, bp 68-70°C (75 mm Hg). Yield 8.64 g (77.14 mmol, 52%). Spectral properties of the compound were identical to those reported in literature.[3]

1-Phenylcycloprop-2-ene carboxylic Acid Methyl Ester (1d). Methyl diazophenylacetate was prepared by modified literature procedure.[5] The modification allowed scaling up the synthesis and significantly improved the yield. n-BuLi (2.5M in hexanes) (80 mL, 200 mmol) was added dropwise at 0°C to a stirred solution of diisopropylamine (31 mL, 220 mmol) in anhydrous ether (150 mL). The mixture was cooled down to -78°C and HMPA (52 mL, 200 mmol) was added dropwise. The formed suspension was stirred for 30 min, then a solution of methyl phenylacetate (30 g, 200 mmol) in dry ether (50 mL) was added dropwise. The mixture was warmed up to -50°C for 20 min to form a clear solution, then cooled down to -78°C and solution of tosyl azide[6] (40 g, 233 mmol) in dry ether (60 mL) was added dropwise. The mixture was warmed up to room temperature and stirred overnight, then quenched by addition of ice-cold water (1200 mL) and extracted with pentane (3 x 300 mL). Combined organic phases were washed (water, brine), dried ($MgSO_4$), filtered and evaporated. The residue was purified by flash column chromatography on Silica gel (eluent - CH_2Cl_2) to obtain methyl diazophenylacetate as deep-orange oil identical to the material described in literature.[5] Yield 28.47 g (162 mmol, 81%) versus 55% as previously reported.[5]

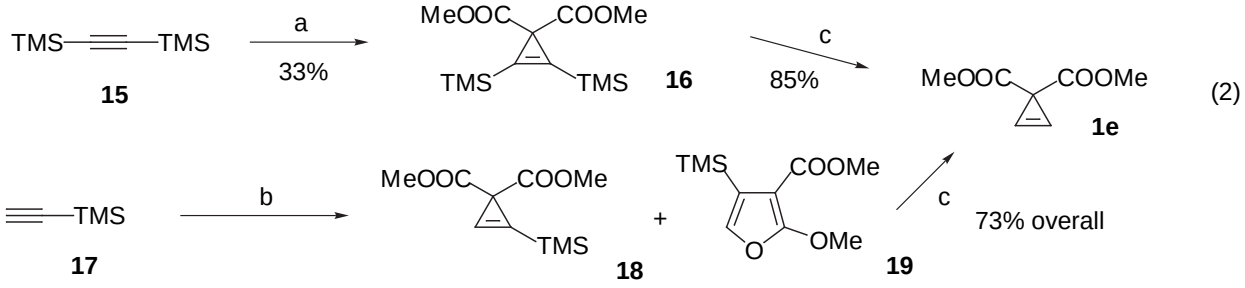
A solution of methyl diazophenylacetate (17.62 g, 100 mmol) in trimethylsilylacetylene (20 mL) was added via syringe pump over 18 hrs to a stirred at reflux suspension of $Rh_2(OAc)_4$ (20 mg, 0.045 mmol, 0.09 mol%) in trimethylsilylacetylene (200 mL). After the addition was complete, the reaction mixture was stirred at reflux for additional 2 hrs, until GC/MS analysis showed no starting material left. Then the reflux condenser was replaced with a distilling unit and

5. Muller, P.; Granicher, C. *Helv. Chim. Acta* **1993**, *76*, 521.
6. Von E. Doering, W.; De Puy, C. H. *J. Am. Chem. Soc*. **1953**, *75*, 5955.

most of the trimethylsilylacetylene was distilled from the mixture at ambient pressure. The residual solvent was removed in vacuum to obtain crude 2-phenyl-1-trimethylsilylcycloprop-2-ene carboxylic acid methyl ester as light-brown oil. According to GC/MS and NMR data, this material was pure enough for further transformation without an additional purification. ^{1}H NMR ($CDCl_3$, 500.13 MHz) 6.88 (s, 1H), 7.28 (m, 4H), 7.19 (m, 1H), 3.69 (s, 3H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 176.5, 142.9, 128.7 (+, 2C), 128.3 (+, 2C), 126.4 (+), 120.3, 116.3 (+), 52.3 (+), 31.8, -1.0 (+, 3C); GC/MS *m/z* 246 (M^+, 25), 203 (30), 142 (80), 114 (70), 73 (Me_3Si^+, 100).

Crude material obtained on the previous step was dissolved in THF (500 mL) and stirred at 0°C. 10% aqueous K_2CO_3 (200 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 1 hr, when GC/MS showed the reaction complete. Ether (300 mL) and brine (200 mL) were added to the mixture, aqueous phase was separated, organic phase was washed (brine, 2 x 150 mL), dried ($MgSO_4$), filtered, and evaporated. The residue was purified by preparative column chromatography on Silica gel (eluent hexane-EtOAc, 7:1). Yield 13.67 g (78.47 mmol, 78%). R_f 0.38 (eluent hexane-EtOAc, 5:1), yellow oil.
^{1}H°NMR ($CDCl_3$, 400.13 MHz) δ 7.36-7.25 (m, 5H), 7.23 (s, 2H), 3.72 (m, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 175.6, 141.5, 128.21 (+, 2C), 128.17 (+, 2C), 126.6 (+), 107.7 (+, 2C), 52.3 (+), 30.6; FT-IR (cm^{-1}, film) 3155, 3114, 3086, 3058, 2962, 2998, 2951, 1736, 1661, 1601, 1494, 1435, 1291, 1264, 1244, 1155, 1113, 1038, 1020, 1009, 998, 894, 790, 761, 738, 700, 666, 602, 548; GC/MS *m/z* 174 (M+, 20), 159 (M-Me, 20), 115 (M-COOMe, 100).

Cycloprop-2-ene-1,1-dicarboxylic Acid Dimethyl Ester (1e). Titled cyclopropene was obtained previously by Wheeller[7] in 28% overall yield via two-step procedure involving Cu-catalyzed cyclopropenation of bis-TMS-acetylene (**15**) with dimethyl diazomalonate followed by exhaustive desilylation (eq. 2). The authors also reported that employment of $Rh_2(OAc)_4$ as a catalyst for cyclopropenation reaction did not allow for the formation of desired compound **16**.[7]



a. dimethyl diazomalonate, $Cu(acac)_2$, 145°C, 36 h; b. dimethyl diazomalonate, $Rh_2(OAc)_4$, 60°C, 22 h
c. 10% aq. K_2CO_3/THF

Nonetheless, we found that $Rh_2(OAc)_4$ catalyzes cyclopropenation smoothly when TMS-acetylene (**17)** in a large excess was employed as a substrate. Cyclopropene **18** was formed as a major product in a 10:1 mixture with furan **19** (eq. 1). When this mixture was submitted to deprotection, cyclopropene **18** was desilylated smoothly to give desired compound **1e**, while silylfuran **19** stayed unchanged. Compounds **1e** and **19** were easily separable by short column chromatography. The updated procedure allowed for significant improvement of the yield.

7. Wheeler, T. N.; Ray, J. *J. Org. Chem*. **1987**, *52*, 4875.

A solution of dimethyl diazomalonate (15.8 g, 100 mmol) in trimethylsilylacetylene (15 mL) was added using syringe pump over 18 hrs to a refluxing stirred suspension of $Rh_2(OAc)_4$ (110 mg, 0.25 mmol, 0.5 mol%) in trimethylsilylacetylene (250 mL). After the addition was complete, the reaction mixture was stirred at reflux for additional 4 hrs, then reflux condenser was changed for a distillation unit and most of the trimethylsilylacetylene was distilled from reaction mixture under ambient pressure. Normally, it was possible to recycle about 200 mL of trimethylsilylacetylene, which was reused without additional purification. Still residue was filtered through a short column of Silica gel (eluent - EtOAc) and the eluate was concentrated and dissolved in THF (500 mL). The solution was stirred at 0°C and 10% aqueous K_2CO_3 (190 mL) was added dropwise. The mixture was allowed to reach room temperature and stirred for 1 hr, until GC/MS analysis showed the reaction complete. Aqueous layer was separated, organic phase was concentrated in vacuum to a volume of 150 mL and combined again with the aqueous phase. Ice-cold water (500 mL) was added, and the mixture was extracted with ether (3 x 300 mL). Combined etheral phases were washed (brine), dried ($MgSO_4$), filtered and concentrated in vacuum. Preparative short column chromatography on Silica gel (eluent hexane-EtOAc, 5:1→2:1) gave two fractions.

2-Methoxy-4-trimethylsilylfuran-3-carboxylic acid methyl ester (**19**), yield 1.74 g (7.62 mmol, 7.6%), R_f 0.44 (hexane-EtOAc, 4:1), light brown oil. ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 6.82 (s, 1H), 4.11 (s, 3H), 3.78 (s, 3H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 165.8, 164.0, 150.1, 122.4 (+), 91.5, 58.0 (+), 51.6 (+), -1.5 (+, 3C).

Cycloprop-2-ene-1,1-dicarboxylic acid dimethyl ester (**1e**), yield 11.48 g (73.5 mmol, 73.5%), Rf 0.13 (hexane-EtOAc, 4:1), light brown oil. ^{1}H NMR ($CDCl_3$, 500.13 MHz) 6.88 (s, 2H), 3.68 (s, 6H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 171.7, 102.7 (+, 2C), 52.8 (+, 2C), 30.2; FT-IR (cm^{-1}, film) 3166, 3122, 3003, 2956, 2907, 2846, 1755, 1672, 1437, 1377, 1306, 1256, 1192, 1143, 1076, 990, 950, 883, 817, 768, 720, 634.

2-Butylcycloprop-2-ene-1,1-dicarboxylic Acid Dimethyl Ester (1g). Preparation of this cyclopropene in a yield ~36% by photolytic decomposition of dimethyl diazomalonate in hexyne was reported.[8] On the other hand, Rh(II)-catalyzed reaction of diethyl diazomalonate was described to give corresponding diethyl ester in a yield 40%.[5] We employed a modification of the last procedure with dimethyl ester, which allowed for increased yield.

A solution of dimethyl diazomalonate (1.58 g, 10 mmol) in dry CH_2Cl_2 (5 mL) was added via syringe pump over 18 hrs to a stirred mixture of 1-hexyne (2.56 g, 31 mmol) and $Rh_2(OAc)_4$ (22 mg, 0.05 mmol, 1 mol%) in dry CH_2Cl_2 (10 mL). After the addition was complete, the mixture was stirred for additional 6 hrs, then filtered through short column of Silica gel (eluent — CH_2Cl_2) and evaporated. The residue was purified by preparative column chromatography on Silica gel (eluent hexane/EtOAc 7:1→5:1). Yield 1.57 g (7.4 mmol, 74%). Spectral properties of the compound were identical to those reported in literature.[9]

^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 6.32 (t, *J* = 1.3 Hz, 1H), 3.67 (s, 6H), 2.51 (td, *J* = 7.4 Hz, 1.3 Hz, 2H), 1.54 (m, 2H), 1.34 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 172.3 (2C), 114.9, 93.8 (+), 52.5 (+, 2C), 32.8, 28.9 (-), 24.0 (-), 22.5 (-), 14.0 (+).

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8. Hendrick, M. E. *J. Am. Chem. Soc*. **1971**, *93*, 6337.

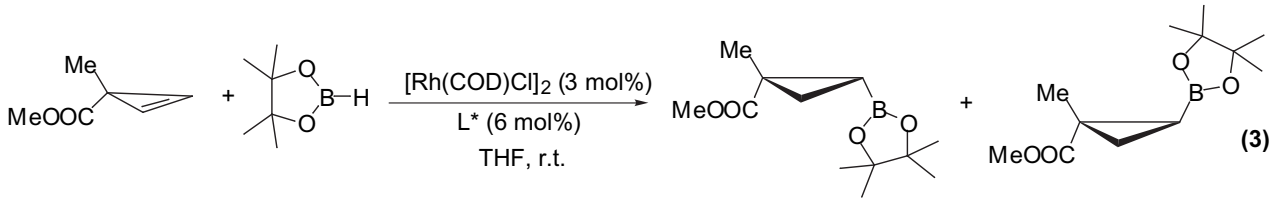
9. Dolgii, I. E.; Okonnishnikova, G. P.; Nefedov, O. M.; *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl.Transl.)* **1986**, *35*, 2571; *Izv. Akad. Nauk SSSR Ser. Khim*. **1986**, 2803.

Cyclopropylboronates.

Typical Procedure for Hydroboration of Cyclopropenes with Wilkinson's Catalyst.

An oven dried 3 mL Wheaton microreactor was loaded with $Rh(PPh_3)_3Cl$ (50 mg, 5 mol%). Anhydrous THF was added and the mixture was stirred for 1 min. 3-Methyl-3-phenylcyclopropene (**1a**) (130 mg, 1 mmol) was added, followed by PBH (4,4,5,5-tetramethyl[1,3,2]dioxaborolane (**2**), 150 µL, 1.03 equiv.). The mixture was stirred for 2 hrs at room temperature. Preparative column chromatography on Silica gel (eluent hexane-CH_2Cl_2 1:1) afforded 194 mg (0.75 mmol, 75%) of 10:1 mixture of ***trans*-3a** and ***cis*-3a**.

Table 1. Ligand Effect in the Asymmetric Hydroboration



1b **2** ***cis*-3b** ***trans*-3b**

#	Ligand	Time, h	Selectivity 3a/3b	Yield, %[a]	3a ee, %[b]	enantiomer
1	(*R*)-Pr^i-Dihydrooxazole	8	41/59	4	-	
2	(*S,S*)-DIOP	8	33/67	15	-	
3	(*R*)-QUINAP	8	17/83	9	~0	
4	(*R*)-PROPHOS	8	80/20	7	-	
5	(*R*)-MOP	8	-	traces	-	
6	TROST Ligand	8	-	traces	-	
7	TROST Ligand (Npht)	8	80/20	20	-	
8	(*R,R*)-Me-BPE	8	58/42	5	-	
9	(*R,R*)-Et-BPE	3	98/2	67	73	(+)-(*1R,2S*)
10	(*R*)-(*S*)-JOSIPHOS	8	50/50	47	64	(−)-(*1S,2R*)
11	(*S,S*)-BDPP	8	72/28	43	66	(+)-(*1R,2S*)
12	(*S,S*)-CHIRAPHOS	3	98/2	47	88	(+)-(*1R,2S*)
13	(*S,S*)-Et-FerroTANE	8	95/5	76	89	(−)-(*1S,2R*)
14	**(*S,S*)-NORPHOS**	**1**	**98/2**	**86**	**>99[c]**	**(+)-(*1R,2S*)**
15	**(*R*)-PHANEPHOS**	**3**	**>99/1**	**89**	**97**	**(+)-(*1R,2S*)**
16	(*R,R*)-Me-DUPHOS	3	>99/1	82	67	(+)-(*1R,2S*)
17	(*R,R*)-Pr^i-DUPHOS	3	98/2	92	11	(−)-(*1S,2R*)
18	**(*R*)-BINAP**	**0.3**	**>99/1**	**96**	**94**	**(–)-(*1S,2R*)**
19	**(S)-Tol-BINAP**	**0.3**	**>99/1**	**94**	**96**	**(+)-(*1R,2S*)**

[a] Combined GC yield. [b] Enantiomeric excess was determined by GC analysis using CYCLODEX B chiral column. [c] For another facial isomer (***trans*-3b**) ee was found to be 72%.

General Procedure for Chiral Phosphine Ligand Optimization (Table 1).
An oven-dried 1 mL Wheaton microreactor was loaded in glove-box with 3 mg (6 μmol, 3 mol%) of $[Rh(COD)Cl]_2$ and 12 μmol (6 mol%) of phosphine ligand. Anhydrous THF (200 μL) and n-pentadecane (internal standard, 29 μL) were added, and the mixture was stirred until homogeneous. PBH (**2**) (30 μL, 27 mg, 0.2 mmol, 1.0 eq.) was added, followed by cyclopropene **1b** (22.4 mg, 0.2 mmol). The mixture was stirred at room temperature for the time indicated in Table 1. Yields and diastereoselectivities were determined by GC/MS analysis, enantiomeric purity — by chiral capillary GC analysis (column CyclodexB).

Typical Procedure for Enantioselective Hydroboration of Cyclopropenes.

An oven-dried 1 mL Wheaton microreactor was loaded in glove-box with 7.5 mg (15 μmol, 3 mol%) of $[Rh(COD)Cl]_2$ and 19 mg (30 μmol, 6 mol%) of (R)-BINAP. Anhydrous THF (500 μL) was added, and the mixture was stirred until homogeneous. PBH (**2**) (75 μL, 54 mg, 0.5 mmol, 1.0 eq.) was added, followed by cyclopropene **1b** (56 mg, 0.5 mmol). The mixture was stirred for 20 min at room temperature, then loaded on short column of Silica gel. Flash chromatography (eluent hexane-EtOAc, 3:1) gave 113 mg (0.47 mmol, 94%) of **(-)-(*1S,2R*)-3b**.

***trans*-3a** ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.30 (m, 2H), 7.26 (m, 2H), 7.15 (m, 1H), 1.50 (s, 3H), 1.29 (s, 6H), 1.27 (s, 6H), 1.19 (dd, *J* = 9.7 Hz, 3.6 Hz, 1H), 1.02 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.37 (dd, *J* = 9.7 Hz, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 148.5, 128.5 (+, 2C), 127.4 (+, 2C), 126.0 (+), 83.6 (2C), 27.2, 25.6 (+, 2C), 25.0 (+, 2C), 23.3 (+), 20.7 (-), 11.2 (broad); ^{11}B NMR ($CDCl_3$, 160.46 MHz) δ 32.8; HRCI MS m/z 259.1870 $(M+H)^+$, Calcd for $C_{16}H_{24}BO_2$ 259.1869.

(-)-(*1S,2R*)-3b ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 3.64 (s, 3H), 1.34 (s, 3H), 1.32 (dd, *J* = 8.3 Hz, 3.4 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 0.85 (dd, *J* = 9.9 Hz, 3.4 Hz, 1H), 0.23 (dd, *J* = 9.9 Hz, 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 176.3, 83.7 (2C), 52.3 (+), 25.33 (+, 2C), 25.25 (+, 2C), 24.4, 21.5 (+), 20.1 (-), 12.63 (broad); ^{11}B NMR ($CDCl_3$, 160.46 MHz) δ 31.5; HRCI MS m/z 241.1605 $(M+H)^+$, Calcd for $C_{12}H_{22}BO_4$ 241.1611; $[\alpha]^{25}_D$ —32.9 (c = 1.01).

(-)-(*1R,2R*)-3c ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 4.09 (dq, *J* = 10.8 Hz, 7.2 Hz, 1H), 4.04 (dq, *J* = 10.8 Hz, 7.1 Hz, 1H), 1.27 (dd, *J* = 7.4 Hz, 3.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.220 (s, 6H), 1.217 (s, 6H), 0.87 (dd, *J* = 8.8 Hz, 3.2 Hz, 1H), 0.24 (dd, *J* = 8.8 Hz, 7.4 Hz, 1H), 0.02 (s, 9H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 175.5, 83.7 (2C), 60.8 (-), 25.22 (+, 2C), 25.20 (+, 2C), 19.3, 14.9 (-), 14.7 (+), 6.1 (broad), -2.3 (+, 3C); NOESY ($CDCl_3$, 500.13 MHz), selected cross peaks: δ_H/δ_H 0.87/0.02; ^{11}B NMR ($CDCl_3$, 160.46 MHz) δ 32.2; ^{29}Si NMR ($CDCl_3$, 99.36 MHz) δ 4.9; HRFAB MS m/z 313.2010 $(M+H)^+$, Calcd for $C_{15}H_{30}BO_4Si$ 313.2006; $[\alpha]^{25}_D$ —31.9 (c = 1.02).

(-)-(*1S,2R*)-3d ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.40 (m, 2H), 7.29 (m, 2H), 7.24 (m, 1H), 3.61 (s, 3H), 1.68 (dd, *J* = 8.4 Hz, 3.5 Hz, 1H), 1.35 (dd, *J* = 10.2 Hz, 3.5 Hz, 1H), 1.30 (s, 6H), 1.29 (s, 6H), 0.76 (dd, J = 10.2 Hz, 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 174.7, 140.7, 130.6 (+, 2C), 128.5 (+, 2C), 127.6 (+), 84.0 (2C), 52.8 (+), 34.8, 25.3 (+, 4C), 19.4 (-), 12.4 (broad); ^{1}H-^{13}C HMQC ($CDCl_3$, 500.13 MHz, 125.76 MHz) δ_H/δ_C 7.40/130.6, 7.29/128.5, 7.24/127.6,

3.61/52.8, (1.68/19.4 & 1.35/19.4), (1.30/25.3 & 1.29/25.3); ^{11}B NMR ($CDCl_3$, 160.46 MHz) δ 31.7; HRFAB MS m/z 303.1795 $(M+H)^+$; Calcd for $C_{17}H_{24}BO_4$ 303.1768; $[\alpha]^{25}_D$ —57.5 (c = 1.04).

(+)-(*2S*)-3e ^{1}H NMR ($CDCl_3$, 500.13 MHz) 3.72 (s, 3H), 3.70 (s, 3H), 1.53-1.50 (m, 2H), 1.22 (s, 6H), 1.21 (s, 6H), 1.08 (dd, *J* = 10.4 Hz, 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 171.2, 169.6, 84.3 (2C), 53.1 (+), 52.9 (+), 34.1, 25.19 (+, 2C), 25.17 (+, 2C), 19.4 (-), 11.9 (broad). ^{1}H-^{13}C HMQC ($CDCl_3$, 500.13 MHz, 125.76 MHz) δ_H/δ_C 3.72/52.9, 3.70/53.1, 1.52/19.4, (1.22&1.21)/(25.19&25.17); ^{11}B NMR ($CDCl_3$, 160.46 MHz) δ 31.3; HRCI MS m/z 285.1522 $(M+H)^+$, Calcd for $C_{13}H_{22}BO_6$ 285.1509; $[\alpha]^{25}_D$ +65.2 (c = 0.88).

(+)-(*1R,2S*)-3f ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 3.37 (d, *J* = 9.5 Hz, 1H), 3.31 (s, 3H), 3.29 (d, *J* = 9.5 Hz, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 1.18 (s, 3H), 0.70 (dd, *J* = 7.0 Hz, 3.5 Hz, 1H), 0.64 (dd, *J* = 9.2 Hz, 3.5 Hz, 1H), −0.16 (dd, J = 9.2 Hz, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 83.4 (2C), 78.2 (-), 58.8 (+), 25.4 (+, 2C), 24.9 (+, 2C), 23.9 (+), 23.6, 18.2 (-), 7.1 (broad); ^{1}H-^{13}C HMQC ($CDCl_3$, 500.13 MHz, 125.76 MHz) δ_H/δ_C (3.37/78.2 & 3.29/78.2), 3.31/58.8, 1.22/24.9, 1.21/25.4, 1.18/23.9, (0.70/18.2 & 0.64/18.2); NOESY ($CDCl_3$, 500.13 MHz), selected cross peaks: δ_H/δ_H 1.18/0.64, 1.18/−0.16; ^{11}B NMR ($CDCl_3$, 160.46 MHz) δ 32.7; HRCI MS m/z 227.1841 $(M+H)^+$, Calcd for $C_{12}H_{24}BO_3$ 227.1819; $[\alpha]^{25}_D$ +38.8 (c = 1.01)

Suzuki Cross-Coupling Reaction of Cyclopropylboronic Acid with Aryliodides.

Hydrolysis of Cyclopropyl Boronate (*1S,2R*)-3b. A slightly modified literature procedure[10] was applied. Cyclopropyl boronate **(-)-(*1S,2R*)-3b** (740 mg, 3.08 mmol) was dissolved in 25 mL of water/THF mixture (1:4). $NaIO_4$ (2.0 g, 3 equiv.) was added and the mixture was stirred for 5 min. An aqueous solution of HCl (2N, 1 mL) was added and the mixture was stirred for 1 hr at room temperature. The reaction mixture was extracted from water with EtOAc, combined organic phases were washed with brine, dried (Na_2SO_4), filtered, and evaporated to give cyclopropylboronic acid **(*1S,2R*)-4b**. Yield 485 mg (100%). In a similar manner cyclopropyl boronate **(+)-(*1R,2S*)-3f** was converted into cyclopropylboronic acid **(*1R,2S*)-4f.**

General Procedure of Suzuki Cross-Coupling Reaction. An oven-dried 3 mL Wheaton microreactor was loaded with $Pd(P^tBu_3)_2$ (26 mg, 0.05 mmol, 10 mol%) and anhydrous CsF (225 mg, 1.5 mmol, 3 equiv.). A solution of boronic acid **(*1S,2R*)-4b** (79 mg, 0.5 mmol) in dry benzene (0.5 mL) was added followed by 1.5-2 equiv. of aryl or vinyl iodide. The mixture was stirred at 80°C for the time, indicated in Table 3. Preparative column chromatography on Silica gel (eluent hexane/EtOAc 20:1 → 15:1) afforded coupling products **(*1S,2S*)-5-9**. Compound **(*1R,2R*)-10** was obtained in similar manner from boronic acid **(*1R,2S*)-4f**. 3N aqueous NaOH (3 equiv.) was employed as a base in this case.

(-)-(*1S,2S*)-5.[11] Yield 72 mg (0.38 mmol, 76%). ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.25-7.17 (m, 5H), 3.31 (s, 3H), 2.34 (dd, *J* = 8.7 Hz, 7.2 Hz, 1H), 1.95 (dd, *J* = 7.2 Hz, 4.9 Hz, 1H), 1.50 (s,

10. Falck, J. R.; Bondlela, M.; Venkataraman, S. K.; Srinivas, D. *J. Org. Chem*. **2001**, *66*, 7148.
11. Doyle, M. P.; Dorow, R. L.; Tamblyn, W. H. *J. Org. Chem*. **1982**, *47*, 4059.

3H), 1.14 (dd, J = 8.7 Hz, 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 173.4, 137.7, 129.4 (+, 2C), 128.2 (+, 2C), 126.9 (+), 51.8 (+), 34.2 (+), 28.2, 21.7 (+), 19.3 (-); GC/MS *m/z* 190 (30, M^+), 158 (45, M-MeOH), 131 (100, M-COOMe); $[\alpha]^{25}_D$ —36.2 (c = 1.01).

(-)-(*1S,2S*)-6. Yield 85 mg (0.39 mmol, 77%). ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.12 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 3.77 (s, 3H), 3.34 (s, 3H), 2.27 (1H, *J* = 8.7 Hz, 7.3 Hz, 1H), 1.89 (dd, *J* = 7.3 Hz, 4.9 Hz, 1H), 1.47 (s, 3H), 1.10 (dd, J = 8.7 Hz, 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 173.4, 158.6, 130.4 (+, 2C), 129.7, 113.6 (+, 2C), 55.6 (+), 51.8 (+), 33.6 (+), 28.0, 21.6 (+), 19.4 (-); GC/MS *m/z* 220 (25, M^+), 188 (30, M-MeOH), 161 (100, M-COOMe); $[\alpha]^{25}_D$ —49.6 (c = 1.03).

(-)-(*1S,2S*)-7. Yield 79 mg (0.32 mmol, 64%). ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 3.87 (s, 3H), 3.30 (s, 3H), 2.33 (dd, *J* = 8.6 Hz, 7.3 Hz, 1H), 1.97 (dd, *J* = 7.3 Hz, 5.1 Hz, 1H), 1.50 (s, 3H), 1.18 (dd, *J* = 8.6 Hz, 5.1 Hz); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 172.9, 167.4, 143.2, 129.6 (+, 2C), 129.4 (+, 2C), 128.7, 52.4 (+), 51.9 (+), 34.0 (+), 28.8, 21.7 (+), 19.6 (-); GC/MS *m/z* 248 (30, M^+), 217 (20, M-MeO), 189 (45, M-COOMe), 129 (100); $[\alpha]^{25}_D$ —44.9 (c = 0.88). Calculated for $C_{14}H_{16}O_4$ C 67.73, H 6.50, Found: C 67.64, H 6.59.

(+)-(*1S,2S*)-8. Yield 102 mg (0.43 mmol, 85%). ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.3 Hz, 1H), 7.53 (ps-t, 1H), 7.48 (ps-t, 1H), 7.44-7.40 (m, 2H), 3.08 (s, 3H), 2.66 (dd, J = 8.5 Hz, 7.4 Hz, 1H), 2.12 (dd, *J* = 7.4 Hz, 4.7 Hz, 1H), 1.73 (s, 3H), 1.34 (dd, J = 8.5 Hz, 4.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 173.4, 134.5, 133.8, 133.6, 128.9 (+), 127.7 (+), 127.0 (+), 126.3 (+), 125.9 (+), 125.7 (+), 124.5 (+), 51.7 (+), 32.8 (+), 27.5, 21.4 (+), 20.1 (-); GC/MS *m/z* 240 (17, M^+), 208 (20, M-MeOH), 181 (100, M-COOMe), 165 (95); $[\alpha]^{25}_D$ +188.3 (c = 1.05).

(*1S,2S*)-9. Yield 75 mg (0.33 mmol, 65%). ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.37-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.23-7.20 (m, 1H), 5.74 (dd, *J* = 8.7 Hz, 1.2 Hz, 1H), 2.14 (d, *J* = 1.2 Hz, 3H), 1.95 (ddd, *J* = 8.7 Hz, 8.5 Hz, 6.8 Hz, 1H), 1.60 (dd, *J* = 6.8 Hz, 4.5 Hz, 1H), 1.44 (s, 3H), 1.14 (dd, J = 8.5 Hz, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 174.3, 143.7, 137.1, 128.6 (+, 2C), 127.1 (+), 126.1 (+), 125.9 (+, 2C), 52.3 (+), 29.9 (+), 27.8, 23.4 (-), 21.5 (+), 16.6 (+). GC/MS *m/z* 230 (15, M^+), 171 (70, M-COOMe), 143 (100).

(*1R,2R*)-10. Yield 76 mg (0.43 mmol, 85%). ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.28-7.25 (m, 2H), 7.22-7.20 (m, 2H), 7.19-7.16 (m, 1H), 3.11 (s, 3H), 3.02 (dd, *J* = 10.0 Hz, 0.6 Hz, 1H), 2.93 (d, *J* = 10.0 Hz, 1H), 2.02 (dd, *J* = 8.2 Hz, 6.2 Hz, 1H), 1.30 (s, 3H), 1.02 (ps.-t, J = 6.2 Hz, 5.1 Hz, 1H), 0.86 (ddd, J = 8.2 Hz, 5.1 Hz, 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 139.5, 129.4 (+, 2C), 128.3 (+, 2C), 126.3 (+), 76.9 (-), 59.0 (+), 29.6 (+), 23.35, 23.30 (+), 16.5 (-); GC/MS *m/z* 176 (1, M^+), 131 (90, M-CH_2OMe), 121 (100), 72 (95, M-PhCH=CH_2).

Assignment of Absolute Configuration of Cyclopropyl Boronates.

Relative configuration of compound ***trans*-3a** was determined by stereospecific transformation into the known *trans*-2-methyl-2-phenylcyclopropanol by oxidation.[12] To a solution

of ***trans*-3a** (52 mg, 0.2 mmol) in THF (1 mL) aqueous solution of NaOH (3N, 100 μL) was added, followed by 30% hydrogen peroxide (100 μL). The mixture was stirred for 2 hrs at room temperature, then quenched with water and extracted with ether. Purification by short column chromatography afforded 18 mg (0.12 mmol, 60%) of cyclopropanol, identical to the material described in literature.[12] ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.20-7.60 (m, 5H), 3.63 (dd, *J* = 6.8 Hz, 3.5 Hz, 1H), 1.54 (s, 3H), 1.22 (dd, *J* = 6.8, 5.9 Hz, 1H), 0.84 (dd, J = 5.9 Hz, 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 145.9, 128.5 (+, 2C), 127.4 (+, 2C), 126.0 (+), 57.9 (+), 22.2 (-), 18.5 (+).

Relative and absolute configuration of 3b. Relative configuration of compound ***cis*-3b** was determined based on stereospecific transformation into known cis-1-methyl-2-phenylcyclopropene carboxylate **5** by Suzuki cross-coupling (see above). Spectral properties of the prepared compound were identical to the data reported in literature.[11] Absolute configuration of **(-)-(*1S,2S*)-5** (and **(-)-(*1S,2R*)-3b**) was assigned by reduction of compound **5** (Eq. 4). 52 mg (0.27 mmol) of (-)-**5** was stirred in 700 μL of dry THF at room temperature and 10 mg of $LiAlH_4$ was added in one portion. The mixture was quenched (sat. NH_4Cl), extracted (EtOAc), washed (diluted HCl, $NaHCO_3$, brine), dried (K_2CO_3), filtered, and concentrated. Flash column chromatography on Silica gel (eluent hexane-EtOAc 4:1) provided (-)-(1S,2S)-1-methyl-2-phenylcyclopropane methanol (**(-)-(*1S,2S*)-11**), which was assigned by comparison of its optical rotation with known (+)-(*1R,2R*)-enantiomer (Scheme 1).[13] Yield 37 mg (0.23 mmol, 84%). ^{1}H NMR ($CDCl_3$, 500.13 MHz) δ 7.30-7.26 (m, 2H), 7.24-7.22 (m, 2H), 7.21-7.18 (m, 1H), 3.36 (d, *J* = 11.6 Hz, 1H), 3.22 (d, *J* = 11.6 Hz, 1H), 2.07 (dd, *J* = 8.3 Hz, 6.0 Hz, 1H), 1.35 (s, 3H), 1.13 (br. s 1H), 1.05 (ps.-t, J = 6.0 Hz, 5.2 Hz), 0.83 (dd, J = 8.3 Hz, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125.76 MHz) δ 139.3, 129.0 (+, 2C), 128.8 (+, 2C), 126.5 (+), 67.3 (-), 29.6 (+), 25.9, 22.8 (+), 16.0 (-); $[\alpha]^{25}_D$ -12.8 (c = 3.05).

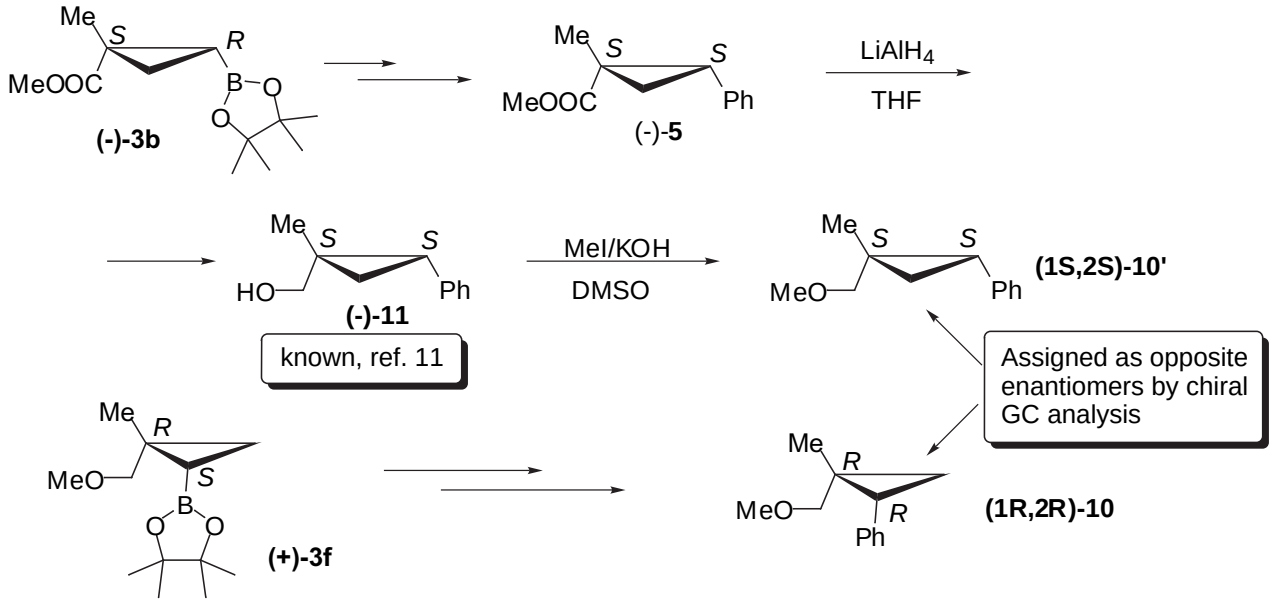
Relative and absolute configuration of 3f. Relative configurations of ***cis*-3f,** was independently confirmed by ^{1}H-^{1}H 2D NOESY spectra (see above). Absolute configuration of **(+)-(*1R,2S*)-3f** was determined based on stereospecific transformation into compound **10** by Suzuki coupling (see above). Authentic sample of **(*1S,2S*)-10** was prepared from **(-)-(*1S,2S*)-11** by methylation (Scheme 1). 22 mg (0.13 mmol) of **(-)-(1S,2S)-11** and powdered NaOH (20 mg, 0.5 mmol) were stirred in 500 μL of DMSO at room temperature and methyl iodide (50 μL) was added. The mixture was stirred at room temperature overnight, then quenched with water, and extracted with ether. Combined etheral phases were washed (5% aq. $Na_2S_2O_3$, water, brine), dried ($MgSO_4$), filtered, and evaporated. Column chromatography on Silica gel (eluent hexane-EtOAc 20:1). Yield of **(*1S,2S*)-10** 14 mg (0.08 mmol, 62%). Compound **(*1S,2S*)-10** showed ^{1}H and ^{13}C NMR and GC/MS properties identical to those described above for the compound **10**. Enantiomeric excess for **(*1S,2S*)-10** was found to be 94%, as determined by chiral GC analysis. Similar analysis for **10** indicated 87% ee. Control chiral GC analysis of about 2:1 mixture of **(*1S,2S*)-10** and **10** showed ~2:1 ratio of the same peaks with no other GC signals detected. Thus, we assigned configuration of **10** as (*1R,2R*).

Relative and absolute configuration of 3c-e. Relative configurations of ***cis*-3c,** was independently confirmed by ^{1}H-^{1}H 2D NOESY spectra (see above). Absolute configuration of compounds **3c-e** were assigned as follows. As discussed in the Text, the hydroboration of cyclopropenes **1b-e** is entirely facially controlled by the directing effect of an ester group and is

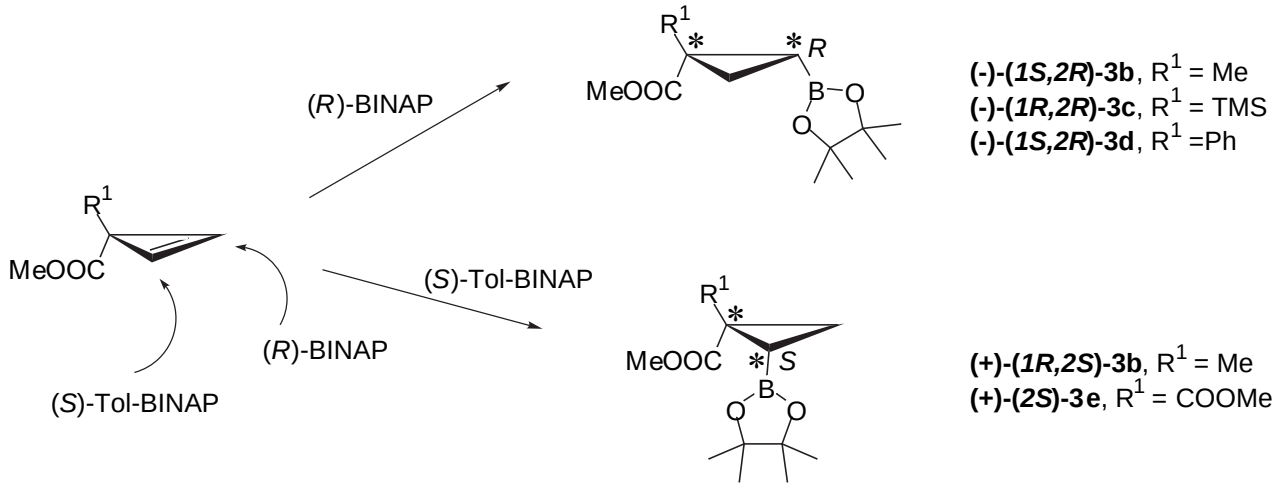
12. Rubin, M. A. PhD Thesis, Moscow State University, 1998.
13. Denmark S. E.; O Connor, S. P. *J. Org. Chem*. **1997**, *62*, 584.

not sensitive to the nature of the substituent R^1 at 3-position (R^1 = Me, Ph, TMS, COOMe). Hydroboration of **1b** in the presence of (*R*)-BINAP produces ***cis*-3b** with (*1S,2R*) configuration, whereas the use of a very similar ligand with opposite stereochemistry, (*S*)-Tol-BINAP, gives the opposite enantiomer (*1R,2S*) of ***cis*-3b** (SI, Table 1, entries 18, 19 and Scheme 2). Thus, we believe that absolute configuration of the resulting cyclopropyl boronates, obtained via hydroboration of ester-containing cyclopropenes **1b-e**, depends only upon configuration of chiral ligand used and is not affected by the nature of R^1 (Scheme 2). Consequently, we assigned the absolute configuration for the products of hydroboration of **1c** (R^1 = TMS), **1d** (R^1 = Ph), and **1e** (R^1 = COOMe) similar to that for **3b** (R^1 = Me), for which absolute configuration was assigned by transformation into the known compound (see above, Scheme 1).

Scheme 1.



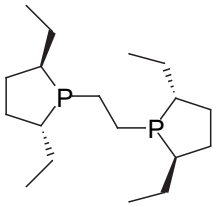
Scheme 2.



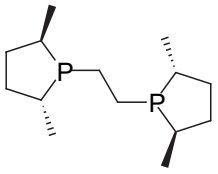
Absolute configuration of the Suzuki coupling products. For determination of absolute configuration of **5** and **10** see above (page SI9). Absolute configurations of compounds **6-9** were assigned as for **5** based on well established retentive stereochemistry of the Suzuki cross-coupling reaction of cyclopropyl boronates.[14]

14. (a) Yao, M.-L.; Deng, M.-Z. *Synthesis*, **2000**, 1095. (b) Yao, M.-L.; Deng, M.-Z. *J. Org. Chem.* **2000**, 65, 5034. (c) Yao, M.-L.; Deng, M.-Z. *New J. Chem*. **2000**, *24*, 425. (d) Chen, H.; Deng, M.-Z. *Org. Lett.* **2000**, *2*, 1649.

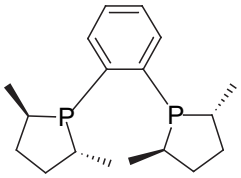
CHIRAL PHOSPHINE LIGANDS



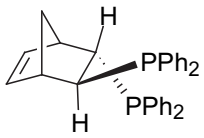
(R,R)-Et-BPE



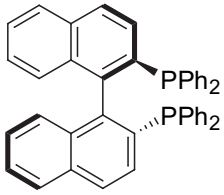
(R,R)-Me-BPE



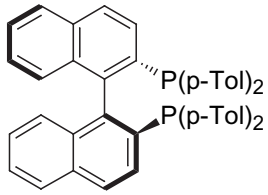
(R,R)-Me-DUPHOS



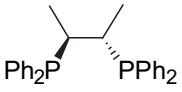
(S,S)-NORPHOS



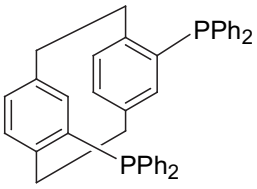
(R)-BINAP



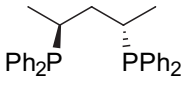
(S)-Tol-BINAP



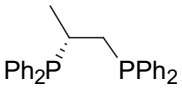
(S,S)-CHIRAPHOS



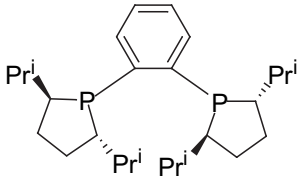
(R)-PHANEPHOS



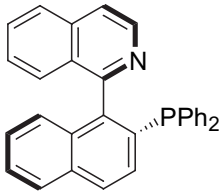
(S,S)-BDPP



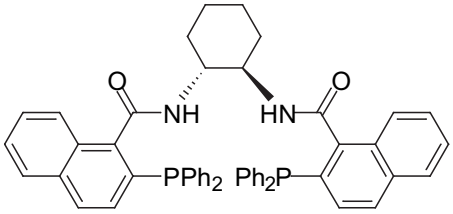
(R)-PROPHOS



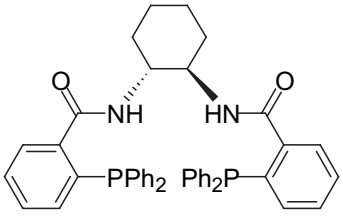
(R,R)-Pr^i-DUPHOS



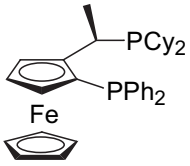
(R)-QUINAP



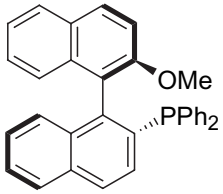
(R,R)-TROST LIGAND (NAPHTHYL)



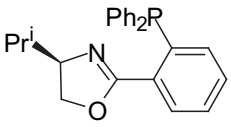
(R,R)-TROST LIGAND



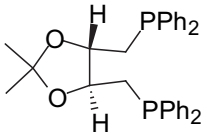
(R)-(S)-JOSIPHOS



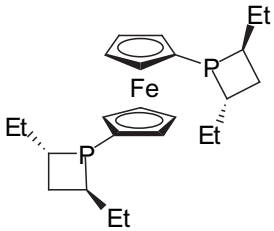
(R)-MOP



(R)-4-Pr^i-4,5-dihydrooxazole



(S,S)-DIOP



(S,S)-Et-FerroTANE