# Simple Large-Scale Preparation of 3,3-Disubstituted Cyclopropenes: Easy Access to Stereodefined Cyclopropylmetals via Transition Metal-Catalyzed Hydrometalation

Michael Rubin, Vladimir Gevorgyan*

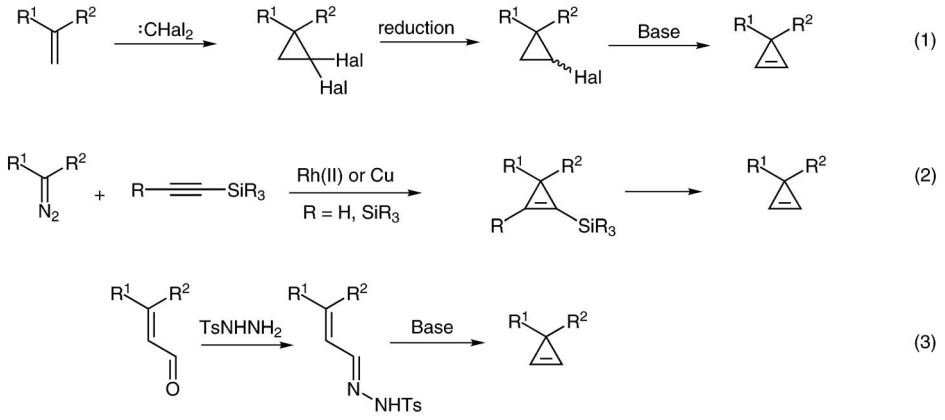
Department of Chemistry, University of Illinois at Chicago, 845 W. Taylor Street, Chicago, IL 60607-7061, USA
Fax +1(312)3550836; E-mail: vlad@uic.edu

*Received 15 November 2003*

PSP No 18

**Abstract:** 3,3-Disubstituted cyclopropenes have been readily prepared in a multigram scale via two different methods: (1) dehydrohalogenation of bromocyclopropanes, and (2) Rh-catalyzed addition of carbenoids to trimethylsilylacetylene followed by desilylation. Highly diastereoselective Pd-catalyzed hydrostannation and highly enantioselective Rh-catalyzed hydroboration of 3,3-disubstituted cyclopropenes afforded useful cyclopropylmetal building blocks in high yields.

**Key words:** cyclopropene, cyclopropane, hydrostannation, hydroboration, transition metal catalysis




**Scheme 1**

## Introduction

Due to the unusually high reactivity of the strained double bond, cyclopropenes continue to attract increasing attention of organic chemists.[1] Various types of addition and cycloaddition reactions with or without opening of the three-membered ring have been extensively studied.[2] Most recently great attention has been paid to transition metal-catalyzed reaction of cyclopropenes. Besides different types of rearrangements[3] and ring-opening reactions,[4] selective transition-metal catalyzed hydrometalation,[5] bimetalation[5a] and carbometalation[6] reactions have been found, which allowed access to highly substituted cyclopropyl units with defined configuration.

3,3-Disubstituted cyclopropenes represent one of the most attractive types of substrates for the investigation of transition metal-catalyzed reactions for the following reasons: (1) unsubstituted double bond often provides enhanced reactivity, however, it can be easily derivatized, if needed, via a variety of known methods; (2) substrates with two different substituents at C-3 position are the convenient reaction probes to investigate the facial selectivity with respect to steric and/or directing effects of substituents; (3) the presence of two enantiotopic carbon atoms allows for design of site-selective asymmetric reactions on cyclopropenes; (4) with minimal number of substituents, 3,3-disubstituted cyclopropenes, unlike their 1,2- and 1,3-analogs, have extended shelf-lives, and often are very easy to handle.

**SYNTHESIS** 2004, No. 5, pp 0796–0800
Advanced online publication: 09.12.2003
DOI: 10.1055/s-2003-44368; Art ID: Z16303SS

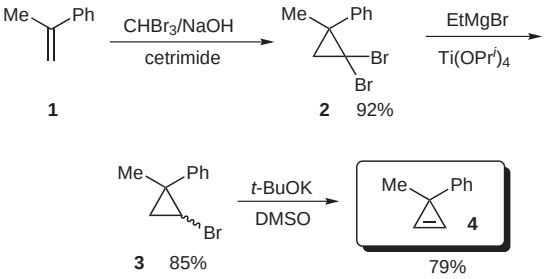
## Scope and Limitations

Interested in versatile access to 3,3-disubstituted cyclopropenes,[5] we were surprised to find that no convenient procedures for their large scale preparation have been reported in the literature. Accordingly, we analyzed the three most common methods for synthesis of cyclopropenes. The first method involves dehydrohalogenation of monohalocyclopropanes, which are in turn available via partial reduction of dihalocyclopropanes,[7] products of addition of dihalocarbenes to olefins[8] (Scheme 1, Procedure 1). Although all three steps of this sequence are long known, no reliable scaled-up procedures for synthesis of cyclopropenes via this method have ever been reported. It should be mentioned, that strong bases and nucleophilic reagents employed in these transformations, limit functional group tolerance of this approach. Another, perhaps more versatile method, Rh- or Cu-catalyzed decomposition of diazo compounds in the presence of alkynes provides good yields of cyclopropenes. However, as reported,[9] it is only moderately effective in reactions with deprotectable alkynes, such as silylalkynes, thus limiting access to 3,3-disubstituted cyclopropenes via this approach (Scheme 1, Procedure 2). A third potential method would involve the cyclization of vinylcarbenes, however, when applied to the synthesis of 3,3-disubstituted cyclopropenes, this procedure is plagued by low yields due to the formation of undesired isomerization products[10] (Scheme 1, Procedure 3). We have chosen first two methods for optimization, since, if proved successful, they would allow for the development of complementary preparative techniques to obtain a wide variety of 3,3-disubstituted cyclopropenes.

The optimized large-scale procedures reported herein are very simple, use inexpensive starting materials, and provide good yields of cyclopropenes. Further transformations of the prepared cyclopropenes, such as Pd-catalyzed diastereoselective hydrostannation and enantioselective hydroboration reactions, are also described. Pd-catalyzed hydrostannation was performed in a rather large scale, providing high yield of the corresponding cyclopropylstannanes, valuable multifunctionalized synthons for organic synthesis.[11] Rh-catalyzed asymmetric hydroboration of cyclopropenes allows for expeditious and efficient access to optically active cyclopropyl boronates, another class of extremely valuable stereodefined cyclopropyl building blocks[11] (Scheme 2). With easy availability, 3,3-disubstituted cyclopropenes could widely be used as versatile building blocks in organic synthesis.

## Procedures

3-Methyl-3-phenylcyclopropene (**4**) was prepared from α-methylstyrene (**1**) according to the modified three-step Bolesov's method.[12] Modifications made for all three steps allowed for scaling up the original procedure and significantly improving the yield of the cyclopropene **4** (Scheme 3). Purification of all intermediate materials and the final product are achieved by simple short-path vacuum distillation. Few points should be taken into consideration to obtain high yields: (a) To avoid thermal decomposition, distillation of all the compounds is to be done at temperatures not higher than 100–105 °C for compounds **2**, **3**, and not higher than 70 °C for compound **4**. (b) Short column chromatography of 1-methyl-1-phenyl-2-bromocyclopropane (**3**) is needed to remove the product of radical dimerization of diethyl ether. Although this impurity does not compromise the next step, it complicates the purification of the final compound. (c) During the synthesis, distillation and storage of cyclopropene, any contact with air should be excluded to prevent radical-initiated dimerization of **4**.



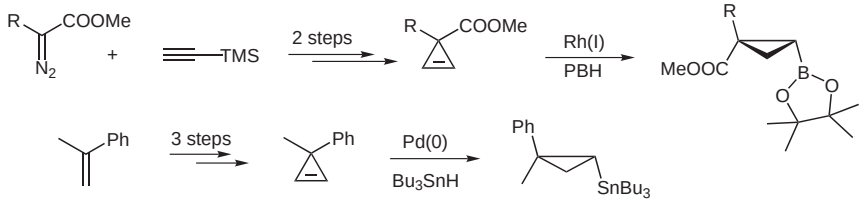

**Scheme 3**

**2,2-Dibromo-1-methyl-1-phenylcyclopropane (2)**

Preparation of dibromocyclopropane **2** was carried out under Makosza's PTC conditions.[13] To a vigorously stirred mixture of α-methylstyrene (**1**; 91 mL, 0.7 mol), $CHBr_3$ (135 mL) and cetrimide (1 g) was added 50% aq solution of NaOH (150 mL) dropwise. A cooling bath was used occasionally to keep the temperature of the reaction mixture at 35–40 °C. The reaction mixture was vigorously stirred for 30 h, and then $H_2O$ was added. The organic phase was separated and the aqueous phase was extracted with $CHCl_3$. The combined organic phases were washed with $H_2O$, 2% HCl and brine, and dried ($CaCl_2$), filtered, and concentrated. The residue was distilled in vacuum to obtain **2**; bp 100–102 °C/1 mm Hg); yield: 186.58 g (92%).

**2-Bromo-1-methyl-1-phenylcyclopropane (3)**

Dibromocyclopropane **2** was subjected to Ti-catalyzed selective reduction with EtMgBr.[14] Ti(*i*-PrO)$_4$ (2 mol%, 3.5 g) was added to the whole amount of dibromocyclopropane **2** obtained in the previous




**Scheme 2**

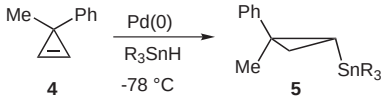
step dissolved in anhyd $Et_2O$ (800 mL). The mixture was stirred under argon at r.t. and 3 N etheral solution of EtMgBr (1.3 equiv, 280 mL) was added dropwise over 1 h. The reaction mixture was additionally stirred for 40 min at r.t. until GC analysis indicated the absence of starting material. The mixture was quenched with $H_2O$ (200 mL) and aq $H_2SO_4$ (1:5, 600 mL) and stirred until all the precipitate had dissolved. The etheral layer was separated and the aqueous layer was extracted with $Et_2O$. The combined organic phases were washed with $H_2O$ and brine, dried ($MgSO_4$), filtered, and concentrated. The residue was filtered through a short column of silica gel (hexane), the eluate was evaporated, and the residue was distilled in vacuum; bp 97–101 °C/10 mm Hg); yield: 115.13 g (85%).

**3-Methyl-3-phenylcyclopropene (4)**

*t*-BuOK (73.4 g, 0.654 mol) was stirred in anhyd DMSO (400 mL) at 60 °C under argon until the solution became homogenous, then the temperature was brought to 20 °C and bromocyclopropane **3** (114.0 g, 0.54 mol) was added dropwise over 1 h. Occasional cooling with an ice bath helped to keep the temperature at 20 °C. A deep bluish-green color was developed quickly in the reaction mixture and was retained through the course of the reaction. The mixture was stirred for 10 h at r.t., then poured into ice-cold $H_2O$ (1 L) and extracted with hexane (3 × 350 mL). The combined organic phases were washed with $H_2O$ (3 × 500 mL) and brine (400 mL), dried ($MgSO_4$) and concentrated. Fractional distillation of the residue in vacuum gave **4**; yield: 55.42 g (79%); bp 61–62 °C/10 mm Hg.

**Pd-Catalyzed Hydrostannation;[5a] Tributyl(2-methyl-2-phenylcyclopropyl)stannane (5a) ; Typical Procedure (Scheme 4)**

An oven-dried 50 mL two-neck round-bottom flask was loaded with $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) under argon. Anhyd THF (20 mL) was added and the mixture was stirred at r.t. until the catalyst had dissolved. The solution was cooled down to –78 °C, 3-methyl-3-phenylcyclopropene (**4**; 1.9 g, 14 mmol) was added and the mixture was stirred at –78 °C for 5 min. $Bu_3SnH$ (4 mL) was added via a syringe pump over 1.5 h. Then, the mixture was concentrated and the residue was purified by preparative column chromatography (hexane) to obtain 4.70 g (80%) of **5a**.




4 5

**5a**: R = Bu, 92%
(80% in 14 mmol scale)
**5b**: R = Me, 91%
**5c**: R = Ph, 92%

**Scheme 4**

**5a**

$^1$H NMR ($CDCl_3$, 500.13 MHz): δ = 7.27 (m, 4 H), 7.10 (m, 1 H), 1.55 (m, 6 H), 1.42 (s, 3 H), 1.35–1.30 (m, 7 H), 0.94–0.85 (m, 15 H), 0.77 (dd, *J* = 7.9, 4.7 Hz, 1 H), 0.35 (dd, *J* = 10.3, 7.9 Hz, 1 H).

$^{13}$C NMR ($CDCl_3$, 125.76 MHz): δ = 149.0, 128.1 (+, 2 C), 126.4 (+, 2 C), 125.2 (+), 29.2 (–, 3 C), 27.4 (–, 3 C), 26.8 (+), 23.3, 20.1 (–), 14.2 (+, $^1J_{Sn-C}$ = 373.7, 391.4 Hz), 13.7 (+, 3 C), 9.9 (–, 3 C).

$^1$H-$^{13}$C HMQC ($CDCl_3$, 500.13 MHz, 125.76 MHz): δH/δC = 7.27/128.1, 7.27/126.4, 7.10/125.2, 1.55/29.2, 1.42/26.8, 1.33/27.4, (1.30/20.1 and 0.77/20.1), 0.92/13.7, 0.88/9.9, 0.35/14.2.

$^{119}$Sn NMR ($CDCl_3$, 186.50 MHz): δ = –12.4.

HRMS (FAB): *m*/*z* calcd for $C_{18}H_{29}{}^{120}Sn$ $(M - Bu)^+$: 365.1291; found: 365.1285.

**5b**

$^1$H NMR ($CDCl_3$, 500.13 MHz): δ = 7.31–7.25 (m, 4 H), 7.16 (m, 1 H), 1.42 (s, 3 H), 1.32 (dd, *J* = 10.3, 3.9 Hz, 1 H), 0.79 (dd, *J* = 7.7, 3.9 Hz, 1 H), 0.39 (dd, *J* = 10.3, 7.7 Hz, 1 H), 0.17 (s, 9 H).

$^{13}$C NMR ($CDCl_3$, 125.76 MHz): δ = 149.1, 128.6 (+, 2 C), 126.6 (+, 2 C), 125.6 (+), 26.7 (+), 23.9, 20.8 (–), 15.9 (+, $^1J_{Sn-C}$ = 446.7, 467.9 Hz), –8.6 (+, 3 C).

$^1$H-$^{13}$C HMQC ($CDCl_3$, 500.13 MHz, 125.76 MHz): δH/δC = 7.29/128.6, 7.27/126.6, 7.16/125.6, 1.42/26.7, (1.32/20.8 and 0.79/20.8), 0.39/15.9, 0.17/–8.6.

$^{119}$Sn NMR ($CDCl_3$, 186.50 MHz): δ = 0.5.

MS (GC): *m*/*z* = 296 ($M^+$, <1%), 281 ($M^+$ – Me, 3%), 165 ($Me_3Sn^+$, 100%), 131 ($M^+ - Me_3Sn$, 90%).

**5c**

$^1$H NMR ($CDCl_3$, 500.13 MHz): δ = 8.04 (m, 6 H), 7.72 (m, 10 H), 7.64 (m, 3 H), 7.50 (m, 1 H), 1.92 (m, 1 H), 1.82 (s, 3 H), 1.41 (m, 2 H).

$^{13}$C NMR ($CDCl_3$, 125.76 MHz): δ = 148.7, 139.8 (3 C), 138.0 (+, 6 C), 129.8 (+, 2 C), 129.4 (+, 6 C), 129.2 (+, 3 C), 127.4 (+, 2 C), 126.5 (+), 28.0 (+), 24.5, 20.6 (–), 16.2 (+, $^1J_{Sn-C}$ = 504.4, 527.8 Hz).

$^1$H-$^{13}$C HMQC ($CDCl_3$, 500.13 MHz, 125.76 MHz): δH/δC = 8.04/138.0, 7.72/129.8, 7.72/129.4, 7.72/127.4, 7.64/129.2, 7.50/126.5, (1.92/20.6 and 1.41/20.6), 1.82/28.0, 1.41/16.2.

NOESY ($CDCl_3$, 500.13 MHz): δH/δH (selected cross peaks) = 1.82/7.72, 1.82/8.04.

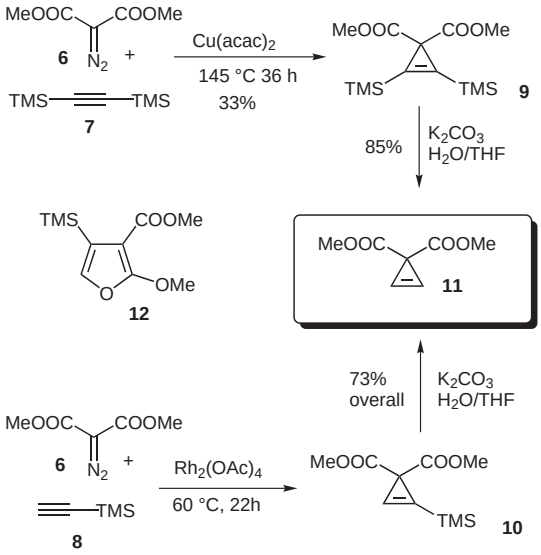
$^{119}$Sn NMR ($CDCl_3$, 186.50 MHz): δ = –101.75.

HRMS (FAB): *m*/*z* Calcd for $C_{28}H_{26}{}^{120}SnNa$: 505.0954; found: 505.0936.

**Dimethyl Cycloprop-2-ene-1,1-dicarboxylate (11) (Scheme 5)**

The titled cyclopropene was obtained previously by Wheeller in 28% overall yield via decomposition of dimethyl diazomalonate (**6**) in the presence of Cu-catalyst and bis(trimethylsilyl)acetylene (**7**), which was used as a solvent, followed by exhaustive desilylation of the formed bis(trimethylsilyl)cyclopropene **9**. The authors have also reported that employment of $Rh_2(OAc)_4$ as a catalyst for cyclopropenation reaction, however, no desired compound **9** was formed. Nonetheless, we found that $Rh_2(OAc)_4$ catalyzes smooth cyclopropenation[15] of terminal trimethylsilylacetylene (**8**), providing cyclopropene **10** as a major product in a 10:1 mixture with furan **12**.[16] When this mixture was submitted to deprotection, cyclopropene **10** was desilylated smoothly to give the desired compound **11**, while silylfuran **12** stayed unchanged. Compounds **11** and **12** were easily separable by short column chromatography. This modified procedure allowed for significant improvement of the yield of **11**.

A solution of dimethyl diazomalonate (**6**; 15.8 g, 100 mmol) in trimethylsilylacetylene (**8**; 15 mL) was added over 18 h to a refluxing stirred suspension of $Rh_2(OAc)_4$ (110 mg, 0.25 mmol, 0.5 mol%) in trimethylsilylacetylene (**8**; 250 mL) via a syringe pump. After the addition was complete, the reaction mixture was stirred at reflux for an additional 4 h, then the reflux condenser was changed for a distillation unit and most of the trimethylsilylacetylene (**8**) was distilled from reaction mixture under ambient pressure. Normally, it was possible to recycle about 200 mL of trimethylsilylacetylene (**8**), which was reused without additional purification. The residue was, filtered through a short column of silica gel (EtOAc) and the eluate was concentrated and dissolved in THF (500 mL). To a stirred solution of this at 0 °C was added 10% aq $K_2CO_3$ (190 mL) dropwise. The mixture was allowed to warm to r.t. and stirred for another 1 h, until GC analysis showed the completion of the reaction. The aqueous layer was separated, the organic phase was concentrated in vacuum to a volume of 150 mL and combined with the aqueous phase.




**Scheme 5**

Ice-cold $H_2O$ (500 mL) was added, and the mixture was extracted with $Et_2O$ (3 × 300 mL). The combined etheral phases were washed (brine), dried ($MgSO_4$), filtered and concentrated in vacuum. Preparative short column chromatography on silica gel (hexane–EtOAc, 5:1∅2:1) gave two fractions.

**Methyl 2-Methoxy-4-trimethylsilylfuran-3-carboxylate (12)**
Light brown oil; yield: 1.74 g (8%); $R_f$ 0.44 (hexane–EtOAc, 4:1).

$^1$H NMR ($CDCl_3$, 500.13 MHz): δ = 6.82 (s, 1 H), 4.11 (s, 3 H), 3.78 (s, 3 H), 0.23 (s, 9 H).

$^{13}$C NMR ($CDCl_3$, 125.76 MHz): δ = 165.8, 164.0, 150.1, 122.4 (+), 91.5, 58.0 (+), 51.6 (+), –1.5 (+, 3 C).

**Dimethyl Cycloprop-2-ene-1,1-dicarboxylate (11)**
Light brown oil; yield: 11.48 g (74%); $R_f$ 0.13 (hexane–EtOAc, 4:1).

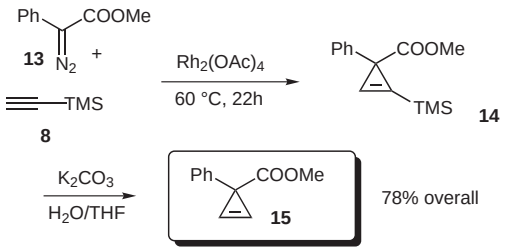
FT-IR (film): 3166, 3122, 3003, 2956, 2907, 2846, 1755, 1672, 1437, 1377, 1306, 1256, 1192, 1143, 1076, 990, 950, 883, 817, 768, 720, 634 cm$^{-1}$.

$^1$H NMR ($CDCl_3$, 500.13 MHz): δ = 6.88 (s, 2 H), 3.68 (s, 6 H).

$^{13}$C NMR ($CDCl_3$, 125.76 MHz): δ = 171.7, 102.7 (+, 2 C), 52.8 (+, 2 C), 30.2.

**Methyl 1-Phenylcycloprop-2-enecarboxylate (15) (Scheme 6)**
A solution of methyl diazophenylacetate (**13**; 17.62 g, 100 mmol) in trimethylsilylacetylene (**8**; 20 mL) was added via a syringe pump over 18 h to a stirred suspension of $Rh_2(OAc)_4$ (20 mg, 0.045 mmol, 0.09 mol%) in trimethylsilylacetylene (**8**; 200 mL) under reflux. After the addition was complete, the reaction mixture was refluxed for an additional 2 h until the GC analysis indicated the absence of starting material. Then the reflux condenser was replaced with a distilling unit and most of the trimethylsilylacetylene (**8**) was distilled from the mixture at ambient pressure. The residual solvent was removed in vacuum to obtain crude methyl 2-phenyl-1-trimethylsilylcycloprop-2-enecarboxylate (**14**) as a light-brown oil. According to GC/MS and NMR data, this material was pure enough for further transformation without additional purification.

**14**
$^1$H NMR ($CDCl_3$, 500.13 MHz): δ = 6.88 (s, 1 H), 7.28 (m, 4 H), 7.19 (m, 1 H), 3.69 (s, 3 H), 0.22 (s, 9 H).




**Scheme 6**

$^{13}$C NMR ($CDCl_3$, 125.76 MHz): δ = 176.5, 142.9, 128.7 (+, 2 C), 128.3 (+, 2 C), 126.4 (+), 120.3, 116.3 (+), 52.3 (+), 31.8, –1.0 (+, 3 C).

GC/MS : *m*/*z* = 246 ($M^+$, 25), 203 (30), 142 (80), 114 (70), 73 ($Me_3Si^+$, 100).

The crude material obtained on the previous step was dissolved in THF (500 mL) at 0 °C. 10% aq $K_2CO_3$ (200 mL) was added dropwise, and the mixture was stirred at r.t. for 1 h until GC showed completion of the reaction. $Et_2O$ (300 mL) and brine (200 mL) were added to the mixture, the aqueous phase was separated, and the organic phase was washed with brine (2 × 150 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by preparative column chromatography on silica gel (eluent: hexane–EtOAc, 7:1) to give **15** as a yellow oil; yield 13.67 g (78%); $R_f$ 0.38 (eluent: hexane–EtOAc, 5:1).

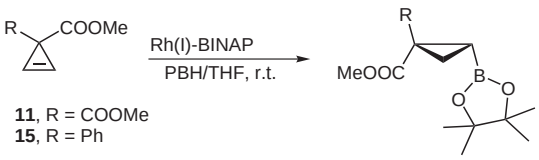
FT-IR (film): 3155, 3114, 3086, 3058, 2962, 2998, 2951, 1736, 1661, 1601, 1494, 1435, 1291, 1264, 1244, 1155, 1113, 1038, 1020, 1009, 998, 894, 790, 761, 738, 700, 666, 602, 548 cm$^{-1}$.

$^1$H NMR ($CDCl_3$, 400.13 MHz): δ = 7.36–7.25 (m, 5 H), 7.23 (s, 2 H), 3.72 (m, 3 H).

$^{13}$C NMR ($CDCl_3$, 100.61 MHz): δ = 175.6, 141.5, 128.21 (+, 2 C), 128.17 (+, 2 C), 126.6 (+), 107.7 (+, 2 C), 52.3 (+), 30.6.

GC/MS: *m*/*z* = 174 ($M^+$, 20), 159 ($M^+$ – Me, 20), 115 ($M^+ - CO_2Me$, 100).

**Enantioselective Hydroboration of Cyclopropenes;[5b] Methyl 1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropanecarboxylate [(–)-(1*S*,2*R*)-17]; Typical Procedure (Scheme 7)**
An oven-dried 1 mL Wheaton microreactor was loaded in a glovebox with $[Rh(COD)Cl]_2$ (7.5 mg, 15μmol, 3 mol%) and (*R*)-BINAP (19 mg, 30 μmol, 6 mol%). Anhyd THF (500 μL) was added, and the mixture was stirred until it became homogeneous. Pinacolborane (PBH, 75 μL, 54 mg, 0.50 mmol, 1.0 equiv) was added, followed by cyclopropene **15** (87 mg, 0.5 mmol). The mixture was stirred for 20 min at r.t., then loaded on a short column of silica gel. Flash chromatography (eluent: hexane–EtOAc, 3:1) gave 149 mg (99%) of (–)-(1*S*,2*R*)-**17**; $[\alpha]_D^{25}$ –57.5 (*c* = 1.04).




(+)-(2*S*)-**16**, R = COOMe, 99%, ee 98% [with (*S*)-TolBINAP]
(–)-(1*S*,2*R*)-**17**, R = Ph, 99%, ee 92% [with (*R*)-BINAP]

**Scheme 7**

$^1$H NMR ($CDCl_3$, 500.13 MHz): δ = 7.40 (m, 2 H), 7.29 (m, 2 H), 7.24 (m, 1 H), 3.61 (s, 3 H), 1.68 (dd, *J* = 8.4, 3.5 Hz, 1 H), 1.35 (dd, *J* = 10.2, 3.5 Hz, 1 H), 1.30 (s, 6 H), 1.29 (s, 6 H), 0.76 (dd, *J* = 10.2, 8.4 Hz, 1 H).

$^{13}$C NMR ($CDCl_3$, 125.76 MHz): δ = 174.7, 140.7, 130.6 (+, 2 C), 128.5 (+, 2 C), 127.6 (+), 84.0 (2 C), 52.8 (+), 34.8, 25.3 (+, 4 C), 19.4 (–), 12.4 (br).

$^1$H-$^{13}$C HMQC ($CDCl_3$, 500.13 MHz, 125.76 MHz): δH/δC = 7.40/130.6, 7.29/128.5, 7.24/127.6, 3.61/52.8, (1.68/19.4 and 1.35/19.4), (1.30/25.3 and 1.29/25.3).

$^{11}$B NMR ($CDCl_3$, 160.46 MHz): δ = 31.7.

HRMS (FAB): *m*/*z* calcd for $C_{17}H_{24}BO_4$ (M + H): 303.1768; found: 303.1795.

**(+)-(2*S*)-16**
$[\alpha]_D^{25}$ +65.2 (*c* = 0.88).

$^1$H NMR ($CDCl_3$, 500.13 MHz): δ = 3.72 (s, 3 H), 3.70 (s, 3 H), 1.53–1.50 (m, 2 H), 1.22 (s, 6 H), 1.21 (s, 6 H), 1.08 (dd, *J* = 10.4, 8.8 Hz, 1 H).

$^{13}$C NMR ($CDCl_3$, 125.76 MHz): δ = 171.2, 169.6, 84.3 (2 C), 53.1 (+), 52.9 (+), 34.1, 25.19 (+, 2 C), 25.17 (+, 2 C), 19.4 (–), 11.9 (br).

$^1$H-$^{13}$C HMQC ($CDCl_3$, 500.13 MHz, 125.76 MHz): δH/δC = 3.72/52.9, 3.70/53.1, 1.52/19.4, (1.22 and 1.21)/(25.19 and 25.17).

$^{11}$B NMR ($CDCl_3$, 160.46 MHz): δ = 31.3.

HRMS (CI): *m*/*z* calcd for $C_{13}H_{22}BO_6$ (M + H): 285.1509; found: 285.1522.

## Acknowledgment

The support of the National Science Foundation (CHE 0096889) is gratefully acknowledged.

## References

(1) For recent reviews, see: (a) Baird, M. S. *Chem. Rev.* **2003**, *103*, 1271. (b) Rademacher, P. *Chem. Rev.* **2003**, *103*, 933.
(2) (a) Padwa, A.; Fryxell, G. E. *Adv. Strain Org. Chem.* **1991**, *1*, 117. (b) Baird, M. S. *Top. Curr. Chem.* **1988**, *144*, 137. (c) Deem, M. L. *Synthesis* **1982**, 701. (d) Kartashov, V. R.; Skorobogatova, E. V.; Zefirov, N. S. *Russ. Chem. Rev. (Engl.)* **1993**, *62*, 935.
(3) (a) Padwa, A.; Blacklock, T. J.; Loza, R. *J. Am. Chem. Soc.* **1981**, *103*, 2404. (b) Cho, S. H.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1987**, *52*, 2631. (c) Muller, P.; Pautex, N.; Doyle, M. P.; Bagheri, V. *Helv. Chim. Acta* **1990**, *73*, 1233. (d) Ma, S.; Zhang, J.; Cai, Y.; Lu, L. *J. Am. Chem. Soc.* **2003**, *125*, 13954.
(4) Nakamura, I.; Bajracharya, G. B.; Yamamoto, Y. *J. Org. Chem.* **2003**, *68*, 2297.
(5) (a) Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2002**, *124*, 11566. (b) Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2003**, *125*, 7198.
(6) (a) Nakamura, M.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **2000**, *122*, 978. (b) Kubota, K.; Mori, S.; Nakamura, E. *J. Am. Chem. Soc.* **1998**, *120*, 13334. (c) Liao, L.; Fox, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 14322.
(7) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2002**, *102*, 4009.
(8) Fedorynski, M. *Chem. Rev.* **2003**, *103*, 1099.
(9) (a) Maier, G.; Wolf, B. *Synthesis* **1985**, 871. (b) Wheeler, T. N.; Ray, J. *J. Org. Chem.* **1987**, *52*, 4875. (c) O'Bannon, P. E.; Dailey, W. P. *J. Org. Chem.* **1991**, *56*, 2258.
(10) Wentrup, C.; Benedikt, J. *J. Org. Chem.* **1980**, *45*, 1407.
(11) See Refs.[5a,b] and references cited therein.
(12) Bolesov, I. G.; Ignatchenko, A. V.; Bovin, N. V.; Prudchenko, I. A.; Surmina, L. S.; Plemenkov, V. V.; Petrovskii, P. V.; Romanov, I. V.; Mel'nik, I. I. *Zh. Org. Khim.* **1990**, *26*, 102; *J. Org. Chem. USSR (Engl. Transl.)* **1990**, *26*, 89.
(13) (a) Makosza, M.; Wawrzyniewicz, M. *Tetrahedron Lett.* **1969**, 4659. (b) Makosza, M. *Pure Appl. Chem.* **1975**, *43*, 439.
(14) (a) Al Dulayymi, J. R.; Baird, M. S.; Bolesov, I. G.; Tveresovsky, V.; Rubin, M. *Tetrahedron Lett.* **1996**, *37*, 8933. (b) Al Dulayymi, J. R.; Baird, M. S.; Bolesov, I. G.; Nizovtsev, A. V.; Tverezovsky, V. V. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1603.
(15) This approach was employed for the preparation of ethyl 3-trimethylsilylcyclopropene-3-carboxylate, see: Arrowood, T. L.; Kaas, S. R. *Tetrahedron* **1999**, *55*, 6739.
(16) For transition metal-catalyzed 3-acyl- or 3-alkoxy-carbonylcyclopropene to furan isomerizations, see refs. 3c,d.