Intramolecular Asymmetric Cyclopropanation Using Air Stable Alkylboronic Esters

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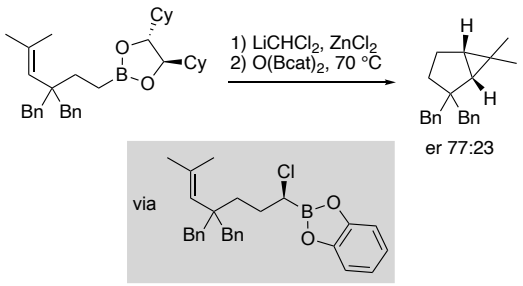
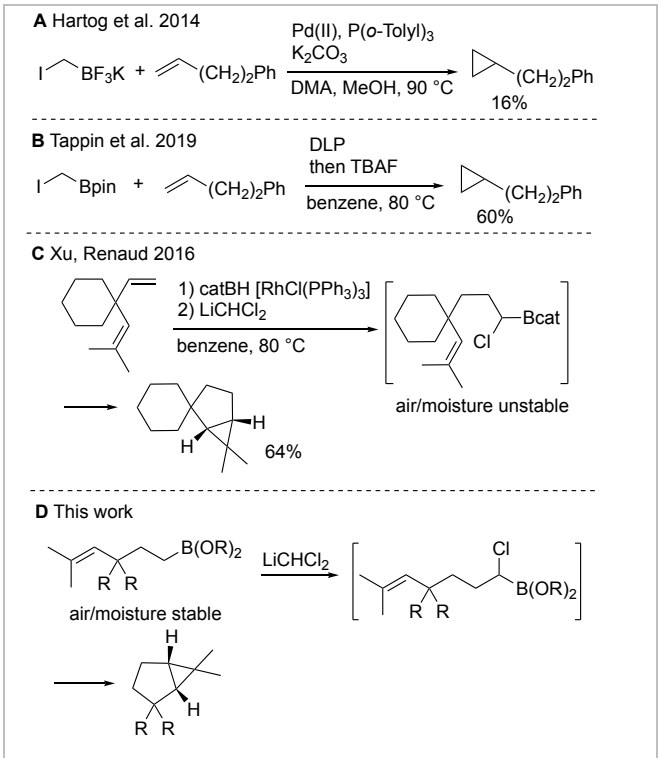


Received:
Accepted:
Published online:
DOI:

Abstract. The preparation of polysubstituted bicyclo[3.1.0]hexanes starting from air stable substituted pent-4-en-1-ylboronic esters has been investigated. The method involves a Matteson homologation with $LiCHCl_2$ leading to intermediates 1-chlorohex-5-en-1-yl boronic esters. The intramolecular cyclopropanation step was performed in a one-pot process. With pinacol boronic esters, the cyclopropanation step was either performed thermally at 140 °C or at 70 °C after in situ transesterification to a catechol boronic ester. This last approach is suitable for the preparation of enantioenriched bicyclo[3.1.0]hexanes using either chiral auxiliary control or by taking advantage of the sparteine controlled enantioselective boroalkylation of alcohols.

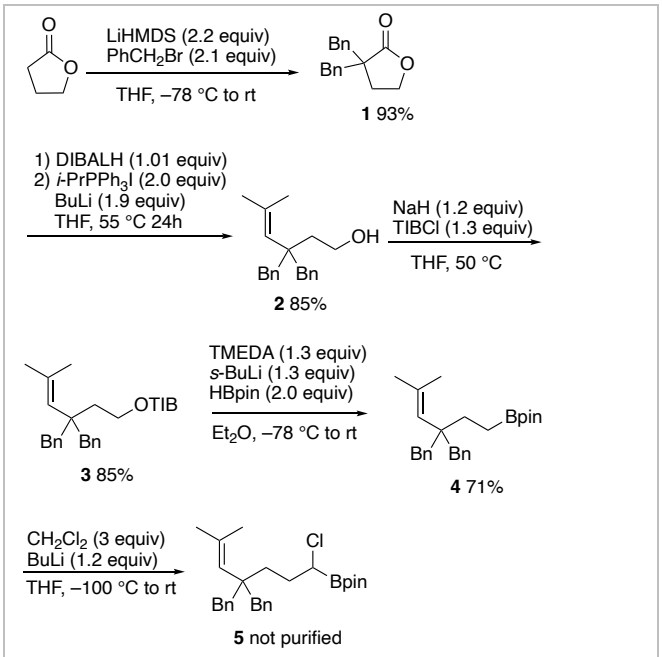
Key words cyclopropanation, boronic esters, Matteson homologation, α-chloroboronate, stereochemistry, fused cyclopropanes

Bicyclo[3.1.0]hexanes are found in a variety of natural and non-natural products, some of them possessing an interesting biological activities.[1–4] They are also valuable synthetic intermediates and are often involved in ring-opening processes as a result of the ring-strain contained in such bicyclic structures.[5–8] For decades, their synthesis has attracted a lot of attention.[9–11] Methods based on highly reactive species such as carbenes and metallocarbenes have been applied for their preparation.[12–14] Approaches based on metallation of unsaturated terminal epoxides[15,16] and aziridines,[17] intramolecular Simmons-Smith cyclopropanation,[18] and sulfur ylide chemistry[19,20] have also been reported. Takai and Charette used pinacol dichloro- and diodomethylboronic esters in intermolecular cyclopropanation of alkenes leading to borylated cyclopropanes.[21–24] Interestingly, 1-haloalkylboronates are potential precursors of carbenes and carbenoids but their use in cyclopropanation is limited to a palladium catalyzed intermolecular reaction (Scheme 1, A)[25] and to radical mediated process involving iodomethylboronic esters[26] (Scheme 1, B). Some years ago, we reported an uncatalyzed and spontaneous intramolecular cyclopropanation process involving *B*-(1-chloro-5-alken-1-yl)catecholborane intermediates that were prepared through selective hydroboration of dienes and their subsequent Matteson homologation (Scheme 1, C).[27] Despite its efficacy, the utility of this process is hampered by the instability of the *B*-alkylcatecholborane (alkyl–Bcat) derivatives which are notoriously air and moisture sensitive. Therefore, extending this reaction to air stable pinacol boronic esters (R–Bpin) and related esters is highly desirable for practical reasons and for the development of an asymmetric version of this reaction. Herein, we report the intramolecular cyclopropanation involving pinacol boronic esters (Scheme 1, D) as well as a study of the stereochemical outcome of the process leading to enantioenriched substituted bicyclo[3.1.0]hexanes.



Scheme 1 Cyclopropanation involving 1-haloboronic esters

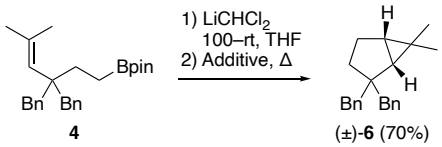
Synthesis of the acyclic precursor. In our initial work,[27] the *B*-(4-alken-1-yl)catecholboranes used for the Matteson homologation-cyclopropanation process were obtained by selective rhodium catalyzed hydroboration of 1,4-dienes which proved to be challenging. An improved and easily scalable synthesis was developed and is presented in Scheme 2. Bis-alkylation of γ-butyrolactone afforded **1** in 93% yield. Reduction of the lactone **1** with DIBALH and Wittig olefination provided the alcohol **2** in 85% yield. After esterification of **2** with 2,4,6-triisopropylbenzoyl chloride (TIB-Cl, 85% yield), the TIB-ester **3** was converted to the pinacol boronic ester in 71% yield according to Aggarwal's procedure via metalation of the ester and treatment with H-Bpin.[28] Homologation of the boronic ester **4** to the (1-chloro-5-alken-1-yl)boronic ester **5** was performed with lithiated dichloromethane according to the original work of Matteson.[29,30] The crude 1-chloroalkenylboronic ester **5** was formed in high yield and used without further purification for the cyclopropanation step. It is air stable but decomposes during flash-chromatography due to its instability on silica gel. It was characterized by ^{1}H- and ^{13}C-NMR spectroscopy.



Scheme 2 Scalable synthesis of pinacol 1-chloro-5-alken-1-ylboronic ester **5**

Thermal intramolecular cyclopropanation. The intramolecular cyclopropanation was investigated next starting from boronic ester **4** via in situ formation of the 1-chlorinated boronic ester **5**. The different reaction conditions tested for the cyclopropanation are summarized in Table 1. The reaction was first attempted in toluene at 100 °C and no reaction was observed (Table 1, entry 1). At 140 °C, the desired reaction took place and the bicyclo[3.1.0]hexane **6** was formed in 57% yield (determined by gas chromatography analysis of the reaction mixture) (Table 1, entry 2). However, isolation of analytically pure **6** was not possible due contamination by several olefinic side products. The influence of additives such as $AgBF_4$ and silica gel was tested but they were either ineffective or detrimental to the reaction (Table 1, entries 3 and 4). Interestingly, potassium benzoate at 140 °C was found to have a positive effect on the yield of the reaction and the product **6** was formed in 75% yield Table 1, entry 5). Neither the reaction time could be shortened, nor the temperature could be decreased indicating that the additive may simply slow down the competing decomposition of the bicyclic cyclopropane **6**.

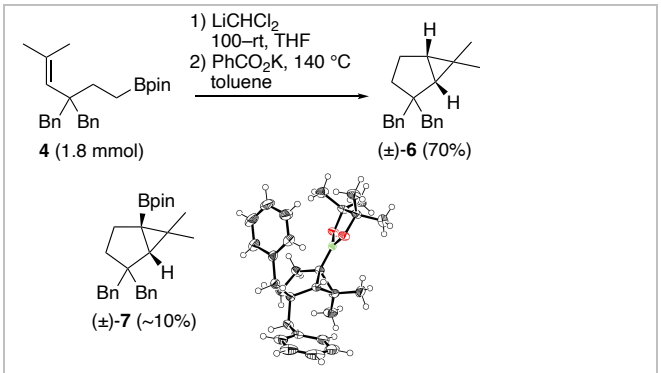
Table 1 Optimization of the cyclopropanation step in the presence of additives (yields determined by GC analysis)



Entry	Additive (equiv)	T	Yield
1	none	100 °C	–
2	none	140 °C	57%
3	$AgBF_4$ (1)	140 °C	51%
4	silica gel	140 °C	15%
5	$PhCO_2K$ (1)	140 °C	75%

The thermal reaction in presence of potassium benzoate was repeated on a preparative scale and it afforded bicycle **6** in 70%

isolated yield, together with a second product, the borylated bicycle **7**, whose structure was unambiguously assigned by single crystal X-ray crystallography but whose origin remains to be elucidated (Scheme 3).

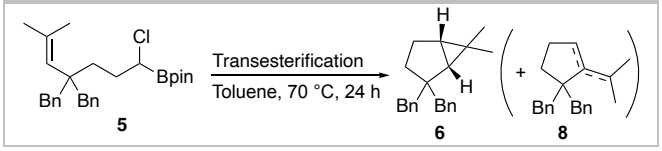


Scheme 3. Thermal intramolecular cyclopropanation in the presence of potassium benzoate. X-ray single crystal structure of side product **7** (CCDC 2264981, 50% probability ellipsoids)

Despite its efficiency, this approach suffers from the high reaction temperature required and the necessity to work in a closed reaction vessel. Moreover, it was later found that significantly lower yields (≤30 %) were obtained when α-chloroboronic esters derived from chiral diols were used.

Transesterification mediated intramolecular cyclopropanation. The higher temperature required for reaction with pinacol and related boronic esters relative to that required for catechol boronic esters was attributed to their reduced Lewis acidity. Therefore, we decided to investigate the in situ activation of the pinacol boronic esters via transesterification with more acidic diols such as catechol. Such an approach involving the in situ transesterification of R-Bpin to R–Bcat derivatives was recently reported to run radical reactions with air stable R-Bpin precursors.[31] Different transesterification procedures were tested, and results are summarized in Table 2. The reactions were run at 70 °C in toluene for 24 h. The use of catechol as transesterification agent was tested first. No reaction was observed at upon addition of catechol (2 equivalents) to the reaction mixture (Table 2, entry 1). Attempts to catalyze the transesterification with a Lewis acid led to decomposition of the starting chloride **5** without any formation of **6** (Table 2, entry 2). Interestingly, addition of naphthalene-1,2-diol (1.2 equivalents) provided the desired cyclopropanation product **6** in 26% yield together with the 2-propylidenecyclopentane **8** (Table 2, entry 3). In a separate experiment, it was shown that **8** was formed by reaction of **6** with HCl. Therefore, addition of a base to the reaction mixture was examined. No change was observed when solid K_2CO_3 was added (Table 2, entry 4). Addition of *sym*-collidine suppressed the formation of **8** but the yield of **6** remained very low (Table 2, entry 5). Propylene oxide, a good HCl trap led to a very similar result (Table 2, entry 6). To avoid formation of HCl, transesterification with naphthalene-1,2-diol boronic (MeBnap) and boric (MeOBnap and HOBnap) esters were examined but none of these reagents provided the desired product **6** (Table 2, entries 7–9). Interestingly, formation of **6** was observed with the catechol esters MeBcat, MeOBcat and CF_3CH_2OBcat (Table 2, entries 10–12). The best result was obtained when the catechol boric anhydride $O(Bcat)_2$ was used (Table 2, entry 13, 53% yield). Adding an acid to accelerate the transesterification led to full decomposition of the starting material (Table 2, entry 14) and decreasing the amount of $O(Bcat)_2$ gave a reduced yield (Table 2, entry 15). A rapid solvent screening showed that 1,1,1-trifluorotoluene (TFT) works equally well as toluene (Table 2, entries 16). More polar solvents such as THF, ethyl acetate and DMF gave either a reduced yield (Table 2, entries 17 and 18) or decomposition of the starting material (Table 2, entry 19).

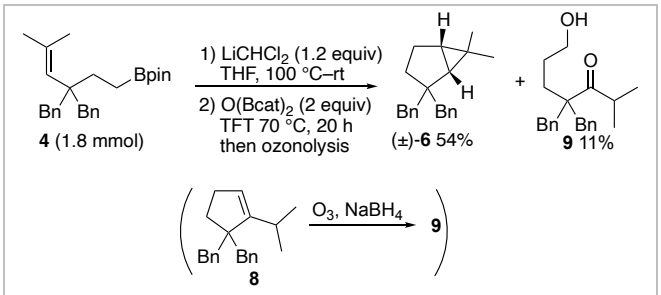
Table 2 Intramolecular cyclopropanation promoted by transesterification



Entry	Transesterification reagent (equiv)	Yield
1	catechol (2)	–
2	catechol (1.1), $BF_3{\cdot}OEt_2$ (2)	–[a]
3	naphthalene-1,8-diol (1.2)	26%[b]
4	naphthalene-1,8-diol (1.2), K_2CO_3 (2)	–[a,b]
5	naphthalene-1,8-diol (1.2), *sym*-collidine (2)	7%
6	naphthalene-1,8-diol (1.2), propylene oxide (2)	18%
7	MeBnap (2)	–
8	MeOBnap (2)	–
9	HOBnap (2)	–
10	MeBcat (2)	9%
11	MeOBcat (2)	27%
12	CF_3CH_2OBcat (2)	28%
13	$O(Bcat)_2$ (2)	53%
14	$O(Bcat)_2$ (2), TfOH (0.01)	–[a]
15	$O(Bcat)_2$ (1.1)	39%
16	$O(Bcat)_2$ (2)	52%[c]
17	$O(Bcat)_2$ (2)	42%[d]
18	$O(Bcat)_2$ (2)	32%[e]
19	$O(Bcat)_2$ (2)	–[a,f]

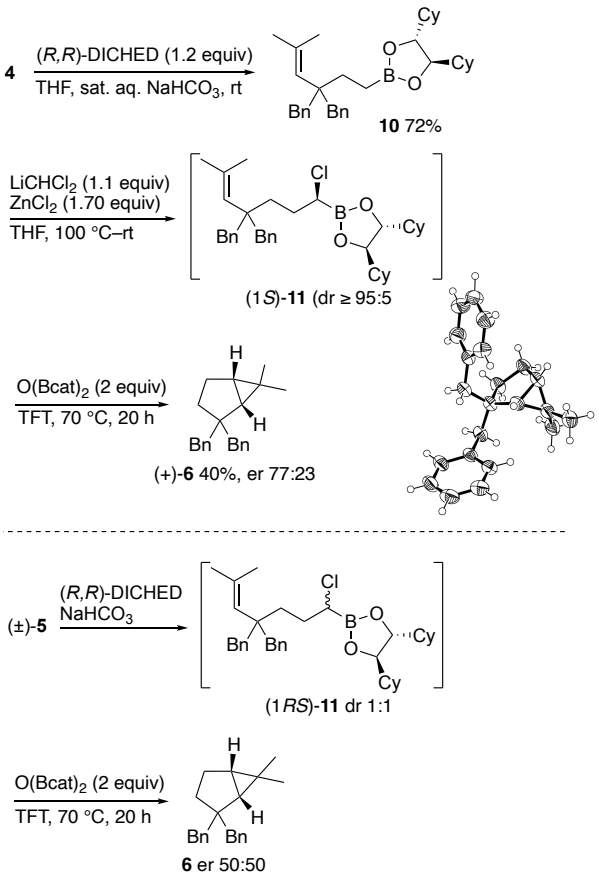
a) Decomposed starting material. b) Formation of alkene **8** was observed. c) In TFT. d) In THF. e) in EtOAc. f) In DMF

The reaction conditions described in Table 2, entry 16, i.e. using 2 equivalents of $O(Bcat)_2$ were adopted as standard reaction conditions for the cyclopropanation process. The conversion of the stable boronic ester **4** to **6** over a one-pot two-step process was examined next (Scheme 4). To facilitate purification of product **6**, the crude mixture of products was treated with ozone/$NaBH_4$ to convert all unsaturated side products into more polar compounds. The bicyclic product **6** was isolated in an overall yield of 54% together with the hydroxyketone **9**, presumably resulting from the ozonolysis of the cyclopentene side product **8**.



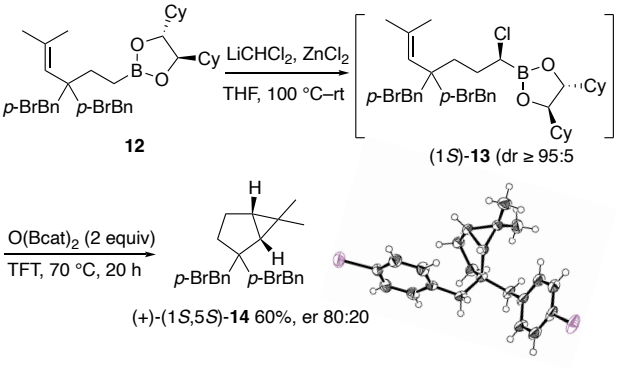
Scheme 4 Preparative formation of bicycle 6 from air stable 4 (one-pot two-step process)

Asymmetric intramolecular cyclopropanation: chiral auxiliary approach. The use of a chiral auxiliary to control the enantioselectivity of the intramolecular cyclopropanation process was investigated next. For this purpose, the (*R,R*)-DICHED boronic ester **10** was prepared by treatment of **4** with (*R,R*)-1,2-dicyclohexylethane-1,2-diol ((*R,R*)-DICHED) in presence of $NaHCO_3$.[32–34] The homologation was performed in THF in presence of $ZnCl_2$ according to the original procedure of Matteson.[35,36] After solvent switch to TFT, the intramolecular cyclopropanation was run according to our standard procedure. It afforded **6** as a 77:23 mixture of enantiomers (Scheme 5). The complete diastereoselectivity of the Matteson homologation process was confirmed by NMR analysis of **11** (see supporting information) and the erosion of enantioselectivity observed during product **6** formation can either results from epimerization of chloride **11** during the cyclopropanation process or from a non-stereospecific cyclopropanation process. Then, a 1:1 diastereomeric mixture of **11** was prepared by transesterification of **5** with (*R,R*)-DICHED. As anticipated, it afforded racemic **6** (Scheme 5) indicating that the stereochemical outcome of the process is controlled by the stereochemistry of the chlorinated α-center. In agreement with an early observation by Matteson,[37] epimerization of **11** could be discarded as the product enantiomeric ratio did not significantly decrease during the reaction (see supporting information). Consequently, the stereochemical outcome of the process is pointing towards a moderately stereoselective cyclization mechanism (vide supra). A single crystal X-ray analysis of optically pure (+)-**6** was performed confirming the structure of **6** but its absolute configuration could not be established due to low anomalous scattering.



Scheme 5 Asymmetric intramolecular cyclopropanantion based on chiral auxiliary control. X-ray single crystal structure of (+)-**6** (CCDC 2264984, 50% probability ellipsoids)

To determine the absolute configuration of the final bicyclic product, the whole reaction sequence was repeated with the brominated compound **12** prepared using and approach closely related to **4** (see supporting information). The (*R,R*)-DICHED boronic ester **12** was treated as previously described for **10** affording the bicycle **14** in 60% yield as a 80:20 mixture of enantiomers (Scheme 6). Recrystallization of a sample of **14** afforded optically pure material that was suitable for single crystal X-ray crystallography. The absolute configuration of the major isomer of **14** was established to be (1*S*,5*S*).



Scheme 6 Chiral auxiliary control: determination of the absolute configuration. X-ray single crystal structure of (+)-**14** (CCDC 2264985, 50% probability ellipsoids)

Based on these results, the stereochemical outcome of the process may be explained by the following mechanism (Figure 1).

Transesterification of (*R,R*)-**5/13** with O(Bcat)$_2$ affords the α-chlorinated catechol boronic ester **5'/13'**. Nucleophilic substitution of the chloride by the alkene, likely assisted by the neighboring acidic boron atom, takes place stereospecifically with inversion of the configuration at C(1). The process affords a *trans*/*cis* mixture of the zwitterionic intermediate **B**. The major isomer *trans*-**B** results from the transition state **A3** and/or **A4** that minimizes steric interactions between the alkene and the Bcat residue while the minor *cis*-**B** results from transition state **A1** and/or **A2** destabilized by steric interactions between the alkene and the Bcat residue. The second cyclization converting **B** to the bicyclic product **6/14** takes place with retention of the stereochemistry at the α-boron center for *cis*-**B** and with inversion for *trans*-**B**. Both retention[38] and inversion[39] of the configuration at the carbon bearing the boron atom have been observed in reaction of boron ate complexes with electrophiles including in cyclopropane formation.[40–44,27] Remarkably, the diastereoselectivity of the cyclization step of **5'/13'** leading to **B** is the major factor determining the enantiomeric purity of the final products **6/14**.

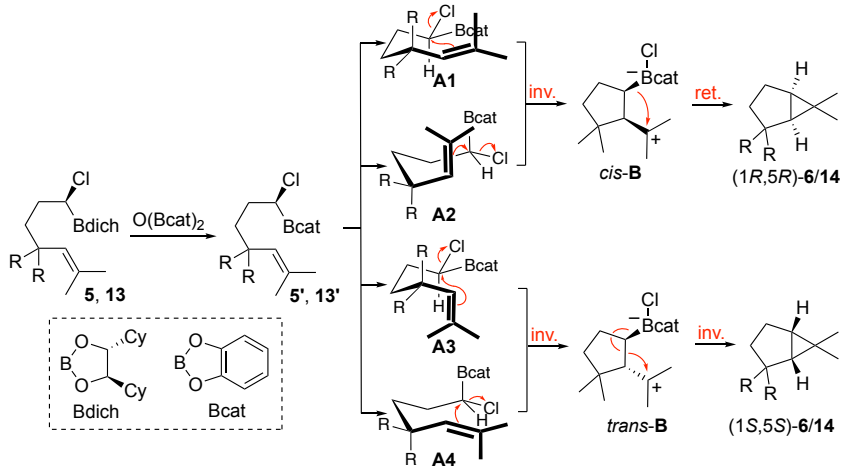
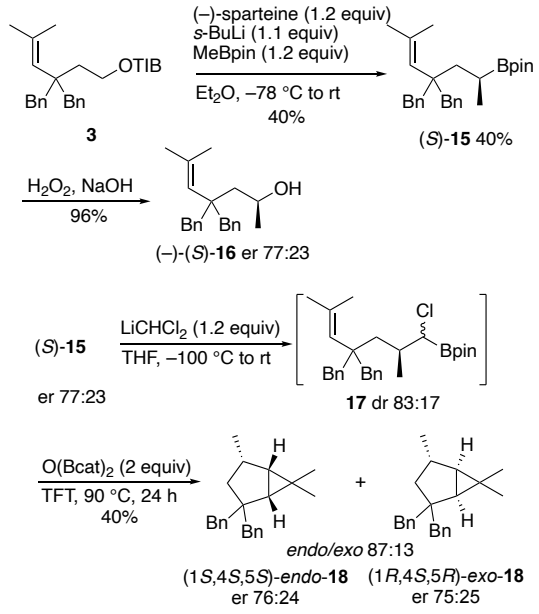


Figure 1 Stereochemical outcome of the chiral auxiliary controlled intramolecular cyclopropanation

Asymmetric intramolecular cyclopropanation: substrate control. Besides the chiral auxiliary approach depicted above, the boronic ester approach offers another easy way to prepare substituted enantioenriched bicyclo[3.1.0]hexanes using substrate control. Based on the work of Aggarwal,[45] TIB esters such as **3** are expected to be suitable substrates for the preparation of enantioenriched α-alkylated boronic esters that can be used in our homologation-intramolecular cyclopropanation reaction. Treatment of **3** with *s*-BuLi/(–)-sparteine followed by treatment with MeBpin afforded the chiral boronic ester **15** in 40% yield (Scheme 7). An enantiomeric ratio 77:23 was measured after conversion to the corresponding secondary alcohol **16**. The level of enantioselectivity was deceivingly low when compared to closely related examples reported by Aggarwal[45] and coll. but it was thought to be sufficient to provide of proof of concept for our approach. The enantioenriched **15** was undergoing the homologation-intramolecular cyclopropanation to provide the bicycle **18** in 40% yield as a satisfactory *endo/exo* 87:13 mixture of diastereomers (Scheme 7). As anticipated, the enantiomeric purity of the major *endo*-**18** (er 76:24) matches that of the starting boronic ester **15** (er 77:23).



Scheme 7 Asymmetric intramolecular cyclopropanation reaction using substrate control

A crude NMR analysis of the intermediate α-chloro boronic ester **17** indicated that the Matteson homologation process afforded a 83:17 mixture of diastereomer. This value was higher than expected and the relative configuration could not be attributed.[30] Both the *syn* and *anti* diastereomers of **17** may afford *endo*- and *exo*-**18**. The four most likely transition states **C1**–**C4** are depicted in Figure 2. The *syn* isomer of **17** presumably affords mainly *endo*-**18** via transition state **C1** preferred over **C2** due to minimization of A^{1,3}-strain.[46] The *anti* isomer of **17** is expected to afford preferentially *exo*-**18** via transition state **C4**. The high *endo*

diastereoselectivity observed suggests that the major diastereomer of **17** possesses the *syn* configuration, however this assumption was not experimentally confirmed.

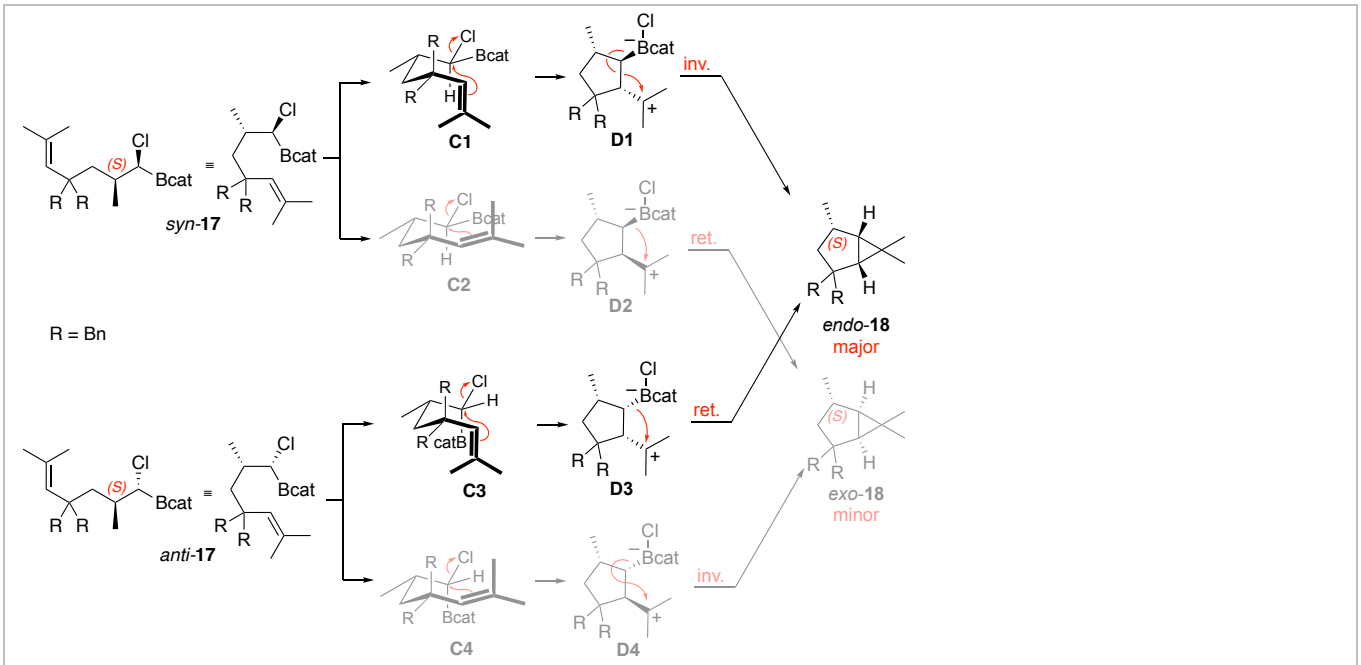


Figure 2 Proposed stereochemical outcome of the conversion of **17** to **18**

In conclusion, a method for the preparation of polysubstituted bicyclo[3.1.0]hexanes starting from air stable boronic esters has been developed. The method involves a Matteson homologation reaction affording an α-chloroboronic ester that undergoes an intramolecular cyclopropanation. With pinacol boronic esters, the cyclopropanation step can either be run at 140 °C or at 70 °C after in situ transesterification to a catechol boronic ester. This latter approach was found to be suitable for the preparation of enantioenriched bicyclo[3.1.0]hexanes by either using a chiral auxiliary control or by taking advantage of the sparteine controlled enantioselective boroalkylation of alcohols. The reaction presented here represents a proof of principle and is expected to open a broad range of applications for the synthesis of fused bicyclic cyclopropanes.

Funding Information

We thank the Swiss National Science Foundation for its financial support to the project 200020_201092.

Supporting Information

Yes

The X-ray crystallographic coordinates for structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 2264981 (**7**), CCDC 2264984 ((+)-**6**), and CCDC 2264985 ((+)-**14**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Primary Data

No.

Conflict of Interest

The authors declare no conflict of interest.

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