Synthesis of cyclopropyl pinacol boronic esters from dibromocyclopropanes

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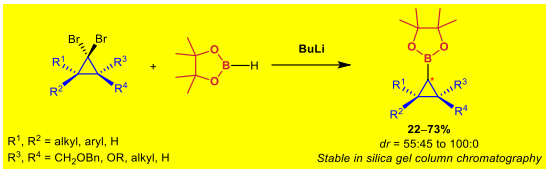

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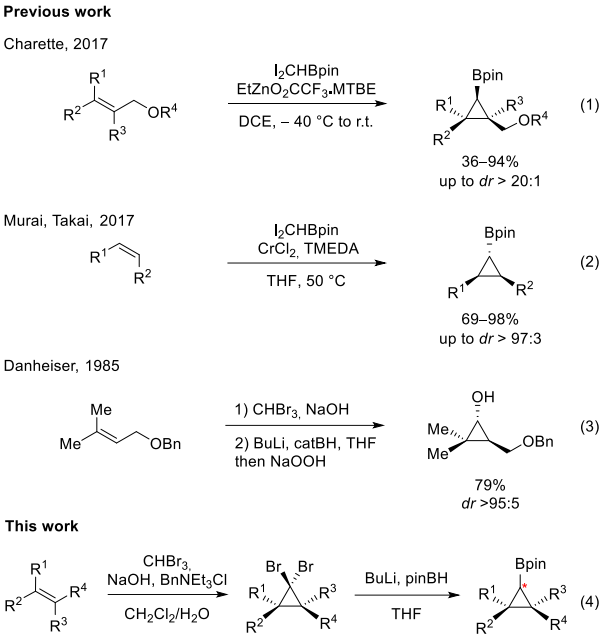
Abstract The synthesis of cyclopropyl pinacol boronic esters from dibromocyclopropanes *via* Matteson-Pasto rearrangement is reported. The method is readily scalable and shows limited levels of stereoinduction, with a selectivity that is in part complementary to that observed in existing stereoselective borylcyclopropanation strategies. The method can be used to rapidly access borylcyclopropanes as interesting building blocks for diversely functionalized cyclopropanes.

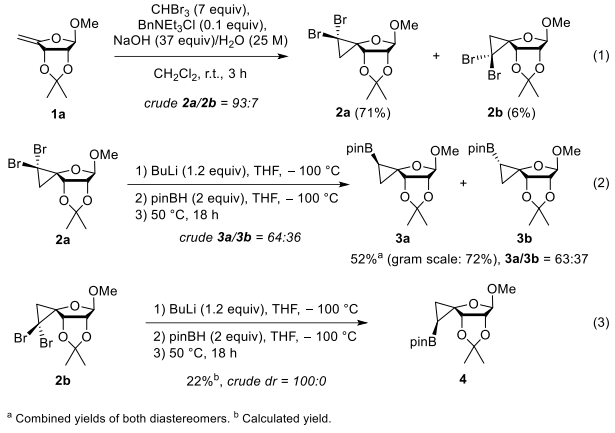
Key words olefins, dibromocyclopropanes, borylcyclopropanes, pinacolborane, Matteson-Pasto rearrangement

Organoboron derivatives are well known for their versatile chemical reactivity owing in particular to their use in Suzuki–Miyaura cross-couplings and in oxidations to hydroxylated compounds.[1] They can also have biological properties as they are found in natural products and drugs.[2] In the last decade, borylcyclopropanes have gained interest in organic synthesis as valuable building blocks for the functionalization of cyclopropanes.[3] In the course of ongoing synthetic investigations,[4] we developed an interest in the synthesis of cyclopropyl pinacol boronic esters. Generally, cyclopropyl pinacol boronic esters can be synthesized by borylation,[2a,5] borylcyclopropanation[6] as well as transformation of pinacol boron-containing molecules.[3d,7] Several recent reports on stereoselective borylcyclopropanations of olefins have drawn our attention in this regard (Scheme 1). Indeed, Charette and coworkers have synthesized diversely functionalized *trans*- and *cis*-cyclopropyl pinacol boronic esters respectively from (*E*)- and (*Z*)-protected allylic alcohols with high diastereoselectivity by using a Simmons-Smith-type reaction of a boromethylzinc carbenoid (Scheme 1, eq. 1).[6d] For sterically less biased allyl ethers, coordination of the zinc carbenoid to the oxygen of the allylic ether can already lead to high levels of diastereocontrol, although steric interactions between the substituents and the boron group readily override this effect. Similarly, Murai, Takai and coworkers have reported a more generally applicable, but less stereoselective borylcyclopropanation on non-activated olefins (Scheme 1, eq. 2).[6e] Here, high stereoselectivity can only be achieved in sterically biased (*Z*)-disubsituted olefins. The reaction is believed to involve a [2+2] cycloaddition of olefins with an *in situ*-generated chromocarbene, whose stereoselectivity is directed by the steric repulsion between the boryl group and the substituents of the olefins. Along with the direct borylcyclopropanation strategy, the borylation of cyclopropyl scaffolds is also a popular route, in particular starting from cyclopropyl halides.[5l-n,5p] The latter can be either commercially available or can be readily obtained from olefins by dihalocyclopropanation. In 1985, Danheiser reported the synthesis of a series of cyclopropanols from dibromocyclopropanes *via* the oxidation of an *in situ* formed cyclopropyl catechol boronic ester intermediate (Scheme 1, eq. 3).[5a] This method was complementary in terms of substrate scope and diastereocontrol to the works of Charette. In the present work, we decided to investigate the option to isolate the putative cyclopropylboronate intermediate by omitting the oxidative step and using pinacolborane instead of catecholborane. Indeed, due to the instability of the catechol analogues, choosing pinacolborane as an alternative would enable the isolation of the pinacol boronic esters *via* chromatography (Scheme 1, eq. 4).[5d]



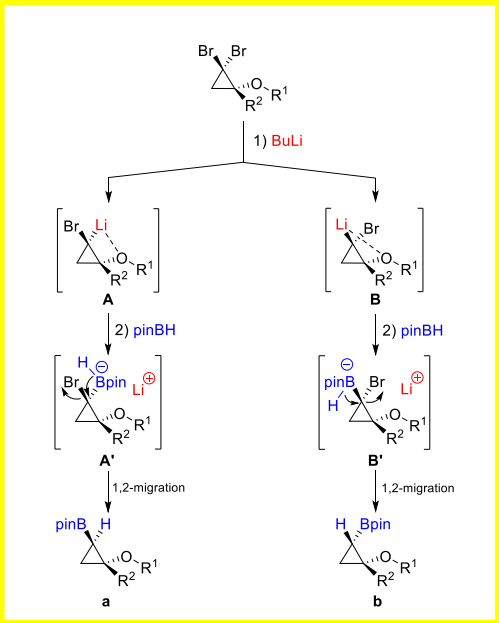
Scheme 1. Synthesis of cyclopropyl pinacol boronic esters from olefins

As part of our investigations towards 4'-spirocyclic nucleoside precursors,[4,8] the present study was initiated with the dibromocyclopropanation of 4-*exo*-methylene furanoside **1a** using a phase transfer catalysis procedure[9] and bromoform as a carbene precursor under basic conditions (Scheme 2, eq. 1). We were pleased to obtain the desired 4-spiro-dibromocyclopropane furanose derivative **2** with a high facial selectivity of **2a**/**2b** = 93:7 favoring the top-face approach of the dibromocarbene species on the most sterically accessible face of the double bond. Compounds **2a** and **2b** were separated successfully with a respective isolated yield of 71% and 6%. The transformation of **2a** and **2b** into the corresponding 4-spirocyclopropyl pinacol boronic esters was performed using butyl lithium and pinacol borane in THF at – 100 °C, followed by reaction at 50 °C overnight involving a Mattesson-Pasto rearrangement (Scheme 2, eq. 2 and 3)[5a]. When using substrate **2a**, furanose derivative **3** was obtained as a mixture of two isomers **3a** and **3b** in 52% yield with the *trans* **3a** product as the major isomer, indicating a moderate degree of stereoinduction (Scheme 2, eq. 2). This investigation was also spurred by the observation that the synthesis of **3** was readily scalable to one gram quantity, leading to a higher isolated yield of 72% without erosion of the stereoselectivity. Surprisingly, substrate **2b** afforded product **4** as a single diastereomer in a much lower isolated yield of 22% although by-products from unreacted reaction intermediates were observed (Scheme 2, eq. 3).



Scheme 2. Synthesis of 4-spirocyclopropyl pinacol boronic esters from 4-*exo*-methylene furanoside

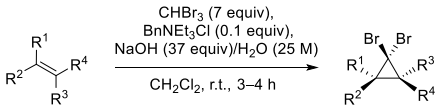
By considering the general mechanism simplifying the furanose scaffold as an ether-substituted dibromocyclopropane, the stereoselective outcome could be explained by the stereodirecting chelation of the lithium by the furanose's oxygen in the lithiated species (Scheme 3). Indeed, the reaction starts with a bromine/lithium exchange of one bromine by treating dibromocyclopropanes with butyl lithium to afford intermediates **A** and **B**. The Li–O chelation is more favored in **A** where the ether's oxygen and the lithium are in the same plane rather than in **B**. Then, the lithium/boron exchange occurs after adding pinacol borane which generates negatively charged boron ate complexes **A'** and **B'**. The 1,2-migration of a hydrogen atom from the boron to the carbon bearing the other bromine gives the corresponding diastereomers **a** and **b** of the cyclopropyl boronic ester. As the final two steps are believed to occur with stereoretention and stereoinversion, respectively, the observed stereocontrol in the formation of **3a** and **3b** is likely induced in the bromine-lithium exchange step. Similarly, the formation of one single isomer **4** from **2b** is highly favored but at the cost of the yield, probably due to a lower reactivity leading to several by-products.

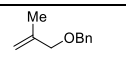
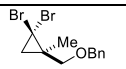
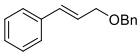
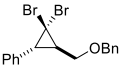
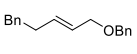
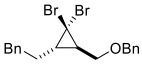
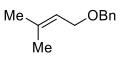
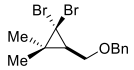
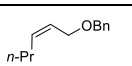
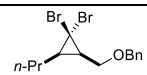


Scheme 3. Mechanism of cyclopropyl pinacol boronic esters formation from ether-substituted dibromocyclopropanes

As the diastereoselecivity might be influenced by a combination of steric hindrance and chelation of BuLi by ether oxygens in the case of furanose derivatives, we decided to investigate a range of simpler substrates such as allyl ethers. Starting with the dibromocyclopropanation using olefins **1b–h**, the desired dibromocyclopropanes **5, 6** and **8–10** were isolated in good yields although **7** and **11** were isolated in unexpectedly low yields of 28% and 16% respectively (Table 1). The reaction with cyclohexene **1h** required a modified procedure to be able to obtain the bicyclic compound **11**.

Table 1. Synthesis of dibromocyclopropanes

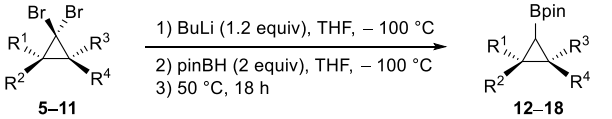


Olefins **1b–h**	Products **5**–**11**	Yield[a]
 **1b**	 **5**	78%
 **1c**	 **6**	74%
 **1d**	 **7**	28%
 **1e**	 **8**	80%
 **1f**	 **9**	72%
 **1g**	 **10**	69%
 **1h**	 **11**	16%[b]

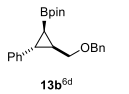
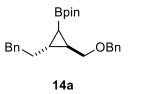
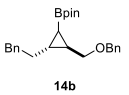
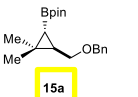
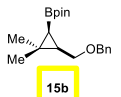
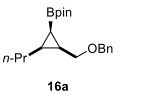
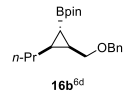
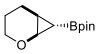
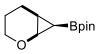
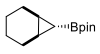
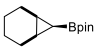
[a] Isolated yields. Dibromocyclopropanes **5**–**11** were obtained as racemic mixtures. All dibromocyclopropanes were stored under argon in the freezer. [b] Compound **11** was prepared using 1.25 equiv. of $CHBr_3$, 1.5 equiv. of NaOH 50% aq., 0.03 equiv. of $BnNEt_3Cl$ at 40 °C for 20 h.

Once prepared, dibromocyclopropanes **5–11** were transformed into cyclopropyl pinacol boronic esters **12**–**18** (Table 2). Using substrate **5**, compound **12** was obtained in a crude ratio **12a/12b** = 55:45 in 54% combined yield in a non-stereoselective manner. Next, *trans*-disubstituted dibromocyclopropanes **6** and **7** were tested. Although these substrates should have matched steric and chelation biases, cyclopropylboronates **13** and **14** were again formed without any obvious stereocontrol (as determined *via* analysis of crude proton NMR). The target compounds were isolated with 67% and 41% yield respectively, as mixtures of the two possible isomers with almost the same ratios. In the case of **14**, the stereochemistry of both isomers could not be determined unambiguously. We then focused on the *gem*-dimethyl substituted dibromocyclopropane **8**, as chelation-induced stereocontrol had been reported by Danheiser for this substrate (cf. Scheme 1, eq. 3). The cyclopropyl pinacol boronic ester **15** was isolated in 73% yield, again as a mixture of two diastereomers. Even by applying a slow addition of BuLi and then pinacolborane using a syringe pump, the result was a 68:32 ratio of **15a/15b**. This is surprisingly lower than the ratio reported by Danheiser,[5a] yet does show the same major *trans*-isomer, opposite to the selectivity found with Charette's borylcyclopropanation. The reaction using *cis*-disubstituted dibromocyclopropane **9** allowed to access the desired product with a crude ratio of 68:32 for **16a/16b** as a mixture of two isomers in isolated 48% yield. In the major isomer **16a**, the stereoconfiguration of the carbon bearing the pinacol boronic ester is reversed compared to **13a** which shows the influence of the *trans* and *cis* relation between the substituents of the dibromocyclopropanes. Interestingly, the stereoselectivity here is also reversed as compared to that previously observed in Murai and Takai's method (Scheme 1, eq. 2). Finally, higher levels of stereoinductions could only be observed for the cyclic substrates **10** and **11**, leading to products **17** and **18** respectively in 38% and 40 % yield with high diastereoselectivity. When comparing both crude ratios, the oxygen in substrate **10** does not seem to participate in the stereoinduction, which is likely to be controlled by the fused 6-membered ring. In these instances, the stereoselectivity does follow the observations by Murai and Takai.

Table 2. Synthesis of cyclopropyl pinacol boronic esters from dibromocyclopropanes



Substrate	Products **12–18**	Crude ratio **a/b**[a]	Yield
5	 **12a**[6d]  **12b**[6d]	55:45	54%[c]

6	 **13a**  **13b**[6d]	58:42	67%[c]
7	 **14a**  **14b**	57:43	41%
8	 **15a**  **15b**	68:32	73%[c,d]
9	 **16a**  **16b**[6d]	62:38	48%[c]
10	 **17a**[6e]  **17b**[6e]	91:9	38%
11	 **18a**[6e]  **18b**[6e]	93:7	40%[d]

[a] The ratio is determined from the ^{1}H NMR spectrum of the crude. Borylcyclopropanes **12**–**18** were obtained as racemic mixtures. [b] Isolated yields. [c] Combined isolated yields of both diastereomers. [d] Successive slow addition of BuLi and pinacolborane over 30 min using a syringe pump.

In conclusion, we have demonstrated a convenient two-step procedure for the elaboration of borylcyclopropanes from simple olefin substrates, *via* the robust synthesis of dibromocyclopropanes **2a–b** and **5–11**.[10] In our work, dibromocyclopropanes have been transformed into synthetically versatile cyclopropyl pinacol boronic esters **3a–b**, **4** and **12**–**18** in divergent yields and variable stereoselectivities *via* a Matteson-Pasto rearrangement.[12] This is an extension of Danheiser's previously developed synthetic method for cyclopropanols, allowing us to access cyclopropyl pinacol boronic esters that are stable upon isolation by column chromatography. Moreover, the procedure is readily amenable to the gram scale synthesis of this unique class of compounds as valuable building blocks towards substituted cyclopropanes.

Acknowledgment

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

References and Notes

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(10) **General dibromocyclopropanation procedure**: Substrate **1** (1 equiv) and benzyltriethylammonium chloride (0.1 equiv) were dissolved in a mixture of bromoform (7 equiv) and dichloromethane (c_1 = 0.75 M) and a solution of sodium hydroxide (25 M in H_2O, 37 equiv) was added dropwise at room temperature and under argon atmosphere. The mixture was stirred at room temperature for 3–4 h. The product was extracted with Et_2O (3 x) while discarding the polymeric tar. The combined organic phase was washed with brine, dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude was purified over silica gel column chromatography to afford the desired dibromocyclopropane. All dibromocyclopropanes were stored under argon in the freezer.

(3a'*S*,6'*R*,6a'*R*)-2,2-dibromo-6'-methoxy-2',2'-dimethyl-dihydro-6'*H*-spiro[cyclopropane-1,4'-furo[3,4d][1,3]-dioxole] (2)

Compound **2a** (13.65 g, 38.13 mmol, 71%, orange oil) and compound **2b** (1.10 g, 3.07 mmol, 6%, dark orange oil) were synthesized from methyl 2',3'-isopropylidene-4'-methylidene-D-erythro furanoside **1a** (10 g, 53.70 mmol, 1 equiv) according to the general procedure (3 h stirring at room temperature). The analysis of the 1H NMR spectrum of the crude mixture indicates a ratio **2a**/**2b** = 93:7. The crude was purified over silica gel column chromatography (elution with Petroleum Ether (PE) 100% then PE/EtOAc = 95:5 and 90:10) to afford the major isomer **2a** followed by the fraction containing the minor isomer **2b**.

2a: **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.13 (s, 1 H), 5.05 (d, J = 5.7 Hz, 1 H), 4.71 (d, J = 5.7 Hz, 1 H), 3.56 (s, 3 H), 2.00 (d, J = 9.5 Hz, 1 H), 1.96 (d, J = 9.5 Hz, 1 H), 1.46 (s, 3 H), 1.37 (s, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 113.4, 108.9, 85.5, 82.0, 73.6, 57.2, 33.4, 29.6, 26.7, 26.1 ppm. GCMS, LCMS and HRMS were not conclusive probably due to poor or no ionization.

2b: **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.08 (s, 1 H), 4.73 (d, J = 5.7 Hz, 1 H), 4.65 (d, J = 5.7 Hz, 1 H), 3.33 (s, 3 H), 1.98 (d, J = 8.7 Hz, 1 H), 1.83 (d, J = 8.7 Hz, 1 H), 1.58 (s, 3 H), 1.38 (s, 3 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 113.7, 109.0, 85.9, 84.9, 71.1, 55.4, 35.7, 26.6, 26.0, 22.9 ppm. **GCMS:** $[M]^{+\cdot}$ = 355, 19.85 min. HRMS was not conclusive probably due to poor or no ionization.

(±)-(((2,2-dibromo-1-methylcyclopropyl)methoxy)methyl)-benzene (5)

Compound **5** (288.5 mg, 0.86 mmol, 78%, orange oil) was synthesized from allyl ether **1b** (178.5 mg, 1.10 mmol, 1 equiv) according to the general procedure (3 h stirring at room temperature). The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 99:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39–7.27 (m, 5 H), 4.61–4.54 (m, 2 H), 3.63 (d, J = 10.1 Hz, 1 H), 3.59 (d, J = 10.1 Hz, 1 H), 1.57 (d, J = 7.6 Hz, 1 H), 1.49 (s, 3 H), 1.46 (d, J = 7.5 Hz, 1 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.2, 128.5 (2 C), 127.9 (3 C), 76.1, 73.1, 36.0, 32.9, 29.7, 21.3 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 352, 7.42 min. HRMS was not conclusive probably due to poor or no ionization.

(±)-((1*R*,3*R*)-3-((benzyloxy)methyl)-2,2-dibromo-cyclopropyl)benzene (6)

Compound **6** (321 mg, 0.81 mmol, 74%, orange oil) was synthesized from allyl ether **1c** (247 mg, 1.10 mmol, 1 equiv) according to the general procedure (4 h stirring at room temperature). The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 99:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42–7.25 (m, 10 H), 4.67 (d, J = 12.0 Hz, 1 H), 4.63 (d, J = 12.0 Hz, 1 H), 3.82–3.80 (m, 2 H), 2.66 (d, J = 8.4 Hz, 1 H), 2.27 (ddd, J = 8.4, 7.0, 6.0 Hz, 1 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.0, 135.7, 128.9 (2 C), 128.6 (2 C), 128.5 (2 C), 128.0 (3 C), 127.9, 73.2, 71.5, 39.7, 34.8, 34.7 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 414, 7.60 min. HRMS was not conclusive probably due to poor or no ionization.

(±)-(2-((1*S*,3*R*)-3-((benzyloxy)methyl)-2,2-dibromo-cyclopropyl)ethyl)benzene (7)

Compound **7** (133 mg, 0.31 mmol, 28%, yellow oil) was synthesized from allyl ether **1d** (277.6 mg, 1.10 mmol, 1 equiv) according to the general procedure (3.5 h stirring at room temperature). The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 99:1). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.36–7.20 (m, 10 H), 4.58 (d, J = 11.9 Hz, 1 H), 4.53 (d, J = 12.0 Hz, 1 H), 3.53 (d, J = 6.6 Hz, 2 H), 2.91–2.72 (m, 2 H), 1.96–1.80 (m, 2 H), 1.54–1.49 (m, 1 H), 1.30–1.23 (m, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 141.0, 138.0, 128.6 (2 C), 128.5 (2 C), 128.4 (2 C), 127.8 (2 C), 127.7, 126.1, 72.9, 71.5, 35.9, 32.3, 34.33, 34.31, 34.2 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 442, 7.77 min. HRMS was not conclusive probably due to poor or no ionization.

(±)-(*R*)-(((2,2-dibromo-3,3-dimethylcyclopropyl)methoxy)-methyl)benzene (8)

Compound **8** (307 mg, 0.88 mmol, 80%, yellow oil) was synthesized from allyl ether **1e** (194 mg, 1.10 mmol, 1 equiv) according to the general procedure (3 h stirring at room temperature). The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 99:1). The reaction was also performed on one gram scale of **1e** (5.68 mmol) to afford the desired product **8** (1.32 g, 3.79 mmol, 67%, yellow oil) and on three-gram scale of **1e** (17 mmol) to afford the desired product **8** (4.26 g, 12.23 mmol, 72%, yellow oil). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37–7.28 (m, 5 H), 4.60 (d, J = 11.9 Hz, 1 H), 4.53 (d, J = 11.9 Hz, 1 H), 3.67 (dd, J = 10.8, 6.7 Hz, 1 H), 3.51 (dd, J = 10.8, 6.8 Hz, 1 H), 1.62 (t, J = 6.7 Hz, 1 H), 1.42 (s, 3 H), 1.23 (s, 3 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 138.2, 128.6 (2 C), 127.9 (3 C), 73.1, 68.9, 44.8, 38.6, 28.6, 27.3, 19.7 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 366, 7.37 min. HRMS was not conclusive probably due to poor or no ionization.

(±)-((((1*R*,3*R*)-2,2-dibromo-3-propylcyclopropyl)methoxy)-methyl)benzene (9)

Compound **9** (320 mg, 0.79 mmol, 90% purity, 72%, orange oil) was synthesized from allyl ether **1f** (209.3 mg, 1.10 mmol, 1 equiv) according to the general procedure (3 h stirring at room temperature). The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 99:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37–7.29 (m, 5 H), 4.59 (d, J = 11.8 Hz, 1 H), 4.53 (d, J = 11.9 Hz, 1 H), 3.60 (dd, J = 10.6, 7.0 Hz, 1 H), 3.48 (dd, J = 10.6, 6.7 Hz, 1 H), 1.97 (dt, J = 11.2, 6.9 Hz, 1 H), 1.69 (dt, J = 11.2, 7.0 Hz, 1 H), 1.55–1.36 (m, 4 H), 0.97 (t, J = 7.2 Hz, 3 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 138.1, 128.6 (2 C), 127.9 (3 C), 73.2, 68.1, 34.6, 33.8, 32.6, 29.3, 21.8, 14.0 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 380, 7.64 min.

(±)-7,7-dibromo-2-oxabicyclo[4.1.0]heptane (10)

Compound **10** (194 mg, 0.76 mmol, 69%, orange oil) was synthesized from 3,4-dihydro-2*H*-pyran **1g** (0.1 mL, 1.10 mmol, 1

equiv) according to the general procedure (3 h stirring at room temperature). The crude was purified over silica gel column chromatography (elution with hexane/EtOAc = 95:5). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.89 (d, J = 8.1 Hz, 1 H), 3.78 (dt, J = 10.9, 3.7 Hz, 1 H), 3.35 (ddd, J = 11.8, 11.0, 2.4 Hz, 1 H), 2.09–1.98 (m, 1 H), 1.94–1.72 (m, 3 H), 1.38 (dddd, J = 13.7, 8.0, 5.4, 2.6 Hz, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 64.6, 59.9, 35.9, 27.6, 20.6, 17.4 ppm. **LCMS:** $[M]^{+\cdot}$ = 256, 1.21 min. HRMS was not conclusive probably due to poor or no ionization.

(±)-7,7-dibromobicyclo[4.1.0]heptane (11)

In a 250 mL 3-neck round-bottom flask, bromoform (0.22 mL, 12.5 mmol, 1.25 equiv) was added dropwise to stirred solution of cyclohexene **1h** (1.01 mL, 10 mmol, 1 equiv), benzyltriethylammonium chloride (68.3 mg, 0.30 mmol, 0.03 equiv) and a 50% aqueous solution of sodium hydroxide (0.79 mL, 15 mmol, 1.5 equiv) in dichloromethane (10 mL) at room temperature. The mixture was stirred at 40 °C for 20 h. The reaction mixture was then treated with water (20 mL) and the product was extracted with Et_2O (3 x 20 mL). The combined organic phase was dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude was purified over silica gel column chromatography (elution with hexane/EtOAc = 95:5) to afford the desired product **11** (401.5 mg, 1.58 mmol, 16%) as a yellowish oil. Data in accordance with the literature.[11] **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 2.05–1.95 (m, 2 H), 1.86–1.81 (m, 2 H), 1.60–1.55 (m, 2 H), 1.39–1.33 (m, 2 H), 1.25–1.14 (m, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 45.0, 27.2 (2 C), 20.8 (2 C), 20.3 (2 C) ppm.

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(12) **General procedure A**: In an oven dried two-neck round-bottom flask under argon atmosphere, dibromocyclopropane (1 equiv) was dissolved in anhydrous THF (c = 0.1 M). The solution was cooled to – 100 °C (ethanol/liquid nitrogen bath) and a solution of BuLi (2.5 M in hexane, 1.2 equiv) was added dropwise and the reaction was stirred for 45 min. Then, a solution of pinacolborane (1 M in THF, 2 equiv) was added dropwise and the resulting mixture was warmed to room temperature. Then, the reaction mixture was stirred for 18 h at 50 °C. The reaction was quenched by adding a saturated aqueous solution of $NaHCO_3$. The product was extracted with EtOAc (x 3). The combined organic phases were washed with water and brine. The combined organic phase was dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude was purified over silica gel column chromatography to afford the desired cyclopropyl pinacol boronic ester.

General procedure B: In an oven dried two-neck round-bottom flask under argon atmosphere, dibromocyclopropane (1 equiv) was dissolved in anhydrous THF (c = 0.1 M). The solution was cooled to – 100 °C (ethanol/liquid nitrogen bath) and a solution of BuLi (2.5 M in hexane, 1.2 equiv) was slowly added over 30 min using a syringe pump followed by a slow addition of a solution of pinacolborane (1 M in THF, 2 equiv) over 30 min using a syringe pump. The resulting mixture was stirred for 45 min at –100°C then warmed to room temperature. Then, the reaction mixture was stirred for 18 h at 50 °C. The reaction was quenched by adding a saturated aqueous solution of $NaHCO_3$. The product was extracted with EtOAc (x 3). The combined organic phases were washed with water and brine. The combined organic phase was dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude was purified over silica gel column chromatography to afford the desired cyclopropyl pinacol boronic ester.

2-((1*R*,3a'*S*,6'*R*,6a'*R*)-6'-methoxy-2',2'-dimethyldihydro-6'*H*-spiro [cyclopropane-1,4'-furo[3,4-d][1,3]dioxol]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)

Compound **3** (153.7 mg, 0.47 mmol, 52%, colorless oil, **3a**/**3b** = 63:37) was synthesized from dibromocyclopropane **2a** (322 mg, 0.90 mmol, 1 equiv) according to the general procedure **A**. The analysis of the ^{1}H NMR spectrum of the crude mixture indicates a ratio **3a**/**3b** = 66:34. The crude was purified over silica gel column chromatography (elution with PE/EtOAc = 95:5 to 90:10). The reaction was also performed on larger scale of **2a** (1 g, 2.79 mmol) to afford **3** (659.8 mg, 2.02 mmol, 72%, **3a**/**3b** = 66:34). For characterization purposes, both isomers were partially separated from each other over silica gel column chromatography (elution with PE/EtOAc = 95:5 to 90:10) to afford isomer **3b** as a pure fraction (colorless oil) followed by a mixture of both isomers and then isomer **3a** as a mixture containing 25% of minor isomer **3b** (colorless oil).

3a: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 4.97 (s, 1 H), 4.65 (d, J = 5.9 Hz, 1 H), 4.45 (d, J = 5.9 Hz, 1 H), 3.40 (s, 3 H), 1.49 (s, 3 H), 1.33 (s, 3 H), 1.25 (s, 6 H), 1.24 (s, 6 H), 1.22–1.21 (m, 1H), 1.17 (dd, J = 11.1, 5.5 Hz, 1 H), 0.31 (dd, J = 11.1, 8.5 Hz, 1 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 112.7, 109.4, 85.7, 85.4, 83.4 (2 C), 73.1, 56.1, 29.8, 26.7, 26.3, 25.5 (2 C), 24.5 (2 C), 10.8 ppm. **GCMS:** $[M]^{+\cdot}$ = 326, 15.24 min.

3b: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 4.91 (s, 1 H), 4.79 (d, J = 5.9 Hz, 1 H), 4.61 (d, J = 5.9 Hz, 1 H), 3.28 (s, 3 H), 1.51 (s, 3 H), 1.35 (s, 3 H), 1.28 (d, J = 11.3, 5.6 Hz, 1 H), 1.22 (s, 12 H), 1.04 (dd, J = 8.7, 5.6 Hz, 1 H), 0.35 (dd, J = 11.3, 8.7 Hz, 1 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 112.3, 108.2, 85.7, 83.4 (2 C), 82.0, 72.1, 55.0, 29.8, 26.6, 25.7, 25.0 (2 C), 24.7 (2 C), 10.1 ppm. **GCMS:** $[M]^{+\cdot}$ = 326, 14.39 min. HRMS was not recorded to confirm structural identity, but NMR and GCMS data are fully in line with the proposed structure.

2-((1*S*,3a'*S*,6'*R*,6a'*R*)-6'-methoxy-2',2'-dimethyldihydro-6'*H*-spiro [cyclopropane-1,4'-furo[3,4-d][1,3]dioxol]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

Compound **4** (66 mg, 0.20 mmol, 22% calculated, yellowish oil) was synthesized from dibromocyclopropane **2b** (321 mg, 0.90 mmol, 1 equiv) according to the general procedure **A**. The analysis of the ^{1}H NMR spectrum of the crude mixture indicates the presence of a single isomer of the product and several by-products. The crude was purified over silica gel column chromatography (elution with PE/EtOAc = 98:2, 95:5 and then 90:10) to afford a fraction of a by-product then a fraction containing product **4** contaminated with traces of inseparable impurities, followed by a ~1:1 mixture of the product **4** and another by-product and finally a fraction containing product **4** contaminated with traces of inseparable impurities.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.88 (s, 1 H), 4.60 (d, J = 5.9 Hz, 1 H), 4.52 (d, J = 5.9 Hz, 1 H), 3.28 (s, 3 H), 1.46 (s, 3 H), 1.27 (s, 3 H), 1.23 (s, 6 H), 1.21 (s, 6 H), 1.02–0.95 (m, 2 H), 0.54 (dd, J = 10.9, 8.2 Hz, 1 H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 112.0, 108.1, 85.5, 83.5 (2 C), 83.1, 72.2, 54.8, 26.6, 25.8, 24.92 (2 C), 24.86 (2 C), 17.9 (2 C) ppm. **GCMS:** $[M]^{+\cdot}$ = 326, 14.61 min. HRMS was not recorded to confirm structural identity, but NMR and GCMS data are fully in line with the proposed structure.

(±)-2-((1*R*,2*S*)-2-((benzyloxy)methyl)-2-methylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)

Compound **12** (49.4 mg, 0.16 mmol, 54% combined yield) was synthesized from dibromocyclopropane **5** (100 mg, 0.30 mmol, 1 equiv) according to the general procedure **A**. The analysis of the ^{1}H NMR spectrum of the crude mixture indicates a ratio **12a**/**12b** = 55:45. The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 99:1 to 95:5) to afford isomer **12a** (colorless oil), then a mixture of **12a**/**12b** and finally isomer **12b** (colorless oil). The individual isomers are described from pure analytical fractions. The NMR data of both isomers are in accordance with the literature.[6d]

12a: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.37–7.31 (m, 4 H), 7.28–7.24 (m, 1 H), 4.55 (d, J = 12.1 Hz, 1 H), 4.47 (d, J = 12.1 Hz, 1 H), 3.49 (d, J = 9.6 Hz, 1 H), 3.42 (d, J = 9.6 Hz, 1 H), 1.23 (s, 3 H), 1.20 (s, 6 H), 1.18 (s, 6 H), 0.72 (dd, J = 6.9, 3.6 Hz, 1 H), 0.68 (dd, J = 9.1, 3.5 Hz, 1 H), – 0.12 (dd, J = 9.1, 7.0 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: δ 139.1, 128.4 (2 C), 127.6 (2 C), 127.4, 83.1 (2 C), 75.6, 72.7, 25.1 (2 C), 24.7 (2 C), 23.7, 23.4, 18.0, 6.7 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 320, 7.65 min.

12b: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.37–7.24 (m, 5 H), 4.54 (d, *J* = 12.1 Hz, 1 H), 4.50 (d, *J* = 12.1 Hz, 1 H), 3.42 (dd, *J* = 9.9, 0.9 Hz, 1 H), 3.14 (d, *J* = 9.9 Hz, 1 H), 1.25 (s, 3 H), 1.24 (s, 6 H), 1.22 (s, 6 H), 0.73 (dd, *J* = 9.6, 3.6 Hz, 1 H), 0.66 (dd, *J* = 6.5, 3.2 Hz, 1 H), – 0.11 (dd, *J* = 9.6, 6.8 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: δ 138.9, 128.4 (2 C), 127.7 (2 C), 127.5, 83.2 (2 C), 79.4, 72.6, 25.3 (2 C), 24.7 (2 C), 22.5, 18.0, 17.2, 4.8 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 320, 7.63 min.

(±)-((1*R*,3*R*)-3-((benzyloxy)methyl)-2,2-dibromocyclopropyl)benzene (13)

Compound **13** (73 mg, 0.20 mmol, 67% combined yield) was synthesized from dibromocyclopropane **6** (118.8 mg, 0.30 mmol, 1 equiv) according to the general procedure **A**. The analysis of the ^{1}H NMR spectrum of the crude mixture indicates a ratio **13a**/**13b** = 58:42. The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 98:2 to 90:10) to afford isomer **13b** (colorless oil), then a mixture of **13a**/**13b** and finally isomer **13a** (yellowish oil). The individual isomers are described from pure analytical fractions. The NMR data of the minor isomer **13b** is in accordance with the literature.[6d] The stereochemistry of the major isomer **13a** was concluded from the stereochemistry of the minor isomer **13b**.

13a: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.36–7.10 (m, 10 H), 4.61 (d, *J* = 12.1 Hz, 1 H), 4.57 (d, *J* = 12.1 Hz, 1 H), 3.65 (dd, *J* = 10.5, 5.8 Hz, 1 H), 3.43 (dd, *J* = 10.5, 6.9 Hz, 1 H), 2.25 (dd, *J* = 10.5, 5.4 Hz, 1 H), 2.07-2.01 (m, 1 H), 1.02 (s, 6 H), 0.89 (s, 6 H), 0.41 (dd, *J* = 10.5, 6.6 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: δ 140.0, 138.8, 128.9 (2 C), 128.5 (2 C), 127.9 (2 C), 127.7 (2 C), 127.6, 126.0, 83.2 (2 C), 74.1, 72.4, 27.9, 24.9 (2 C), 24.5 (2 C), 22.2, 9.2 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 382, 7.77 min. **HRMS (ESI-TOF) m/z**: $[M+NH_4]^+$ Calcd for $C_{23}H_{33}BNO_3$ 382.2548; Found 382.2555.

13b: **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.37–7.07 (m, 10 H), 4.57 (d, *J* = 11.9 Hz, 1 H), 4.52 (d, *J* = 11.9 Hz, 1 H), 3.79 (dd, *J* = 10.2, 6.5 Hz, 1 H), 3.59 (dd, *J* = 10.2, 8.0 Hz, 1 H), 2.12 (dd, *J* = 6.0, 5.3 Hz, 1 H), 1.78 (dddd, *J* = 9.8, 7.9, 6.6, 5.0 Hz, 1 H), 1.24 (s, 6 H), 1.22 (s, 6 H), 0.58 (dd, *J* = 9.8, 6.4 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: δ 142.6, 138.8, 128.4 (4 C), 127.8 (2 C), 127.6, 125.9 (2 C), 125.8, 83.4 (2 C), 72.6, 71.1, 28.8, 27.8, 25.1 (2 C), 24.8 (2 C), 10.5 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 382, 7.78 min.

(±)-2-((2*R*,3*R*)-2-((benzyloxy)methyl)-3-phenethylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14)

Compound **14** (46.7 mg, 0.12 mmol, 41%, colorless oil, **14a**/**14b** = 55:45) was synthesized from dibromocyclopropane **7** (123 mg, 0.29 mmol, 1 equiv) according to the general procedure **A**. The analysis of the ^{1}H NMR spectrum of the crude mixture indicates a ratio **14a**/**14b** = 57:43. The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 98:2 to 95:5). The stereochemistry of isomers **14a** and **14b** could not be determined. Both isomers were described from the mixture and some NMR signals could be attributed to the corresponding isomer. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.35–7.14 (m, 20 H), 4.53–4.50 (m, 3 H), 4.47 (d, *J* = 11.9 Hz, 1 H_{14a}), 3.59 (dd, *J* = 10.1, 6.7 Hz, 1 H_{14a}), 3.47–3.39 (m, 2 H), 3.22 (dd, *J* = 10.5, 7.1 Hz, 1 H_{14b}), 2.75–2.63 (m, 4 H), 1.90–1.81 (m, 1 H_{14b}), 1.78–1.69 (m, 1 H_{14b}), 1.63 (d, *J* = 7.4 Hz, 1 H_{14a}), 1.59 (d, *J* = 7.5 Hz, 1 H_{14a}), 1.24–1.20 (m, 26 H), 1.01–0.84 (m, 2 H), 0.08–0.14 (m, 1 H_{14a}+1 H_{14b}) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: δ 142.6, 142.4, 139.0, 138.9, 128.7 (2 C), 128.6 (2 C), 128.5 (2 C), 128.40 (2 C), 128.36 (2 C), 128.3 (2 C), 127.8 (2 C), 127.7 (2 C), 127.6, 127.5, 125.8, 125.7, 83.2 (2 C_{14b}), 83.1 (2 C_{14a}), 74.7 (C_{14b}), 72.5 (C_{14a}), 72.3 (C_{14b}), 71.5 (C_{14a}), 36.8 (C_{14a}), 36.3(C_{14b}), 36.0(C_{14a}), 31.9 (C_{14b}), 29.8, 25.5, 25.2 (2 C_{14b}), 25.0 (2 C_{14a}), 24.84 (2 C_{14b}), 24.78 (2 C_{14a}), 24.6, 24.3, 23.9 ppm. The boron-bound carbons were not detected due to quadrupolar relaxation. **LCMS:** $[M_{14a}+NH_4]^{+\cdot}$ = 410, 8.06 min. **LCMS:** $[M_{14b}+NH_4]^{+\cdot}$ = 410, 8.12 min.

(±)-2-((3*R*)-3-((benzyloxy)methyl)-2,2-dimethylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15)

Compound **15** (70 mg, 0.22 mmol, 73% combined, **15a**/**15b** = 70:30) was synthesized from dibromocyclopropane **8** (104.4 mg, 0.30 mmol, 1 equiv) according to the general procedure **B**. The analysis of the ^{1}H NMR spectrum of the crude mixture indicates a ratio **15a**/**15b** = 68:32. The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 98:2 to 95:5) to afford isomer **15b** (colorless oil), then a mixture of **15a**/**15b** and finally isomer **15a** (colorless oil). The individual isomers are described from pure analytical fractions.

15a: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.34–7.26 (m, 5 H), 4.53 (d, *J* = 12.1 Hz, 1 H), 4.50 (d, *J* = 12.1 Hz, 1 H), 3.66 (dd, *J* = 10.6, 5.5 Hz, 1 H), 3.29 (dd, *J* = 10.6, 8.8 Hz, 1 H), 1.31–1.29 (m, 1 H), 1.24 (s, 6 H), 1.21 (s, 6 H), 1.18 (s, 3 H), 1.14 (s, 3 H), – 0.38 (d, *J* = 6.6 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: δ 139.0, 128.4 (2 C), 127.8 (2 C), 127.6, 83.1 (2 C), 72.4, 71.4, 29.9, 25.3 (2 C), 24.6 (2 C), 24.3, 23.5, 22.2, 13.5 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 334, 7.46 min. **HRMS (ESI-TOF) m/z**: $[M+NH_4]^+$ Calcd for $C_{19}H_{33}BNO_3$ 334.2548; Found 334.2547.

15b: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.37–7.27 (m, 5 H), 4.56 (d, *J* = 11.9 Hz, 1 H), 4.49 (d, *J* = 11.9 Hz, 1 H), 3.66 (d, *J* = 7.5 Hz, 2 H), 1.23 (d, *J* = 7.4 Hz, 1 H), 1.20 (s, 6 H), 1.19 (s, 6 H), 1.16 (s, 3 H), 1.15 (s, 3 H), – 0.04 (d, *J* = 9.6 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: δ 139.1, 128.4 (2 C), 127.9 (2 C), 127.5, 82.9 (2 C), 72.7, 68.9, 30.5, 29.9, 25.1 (2 C), 24.8 (2 C), 22.9, 17.5, 12.2 ppm. **LCMS:** $[M+NH_4]^{+\cdot}$ = 334, 7.47 min. HRMS was not conclusive probably due to poor or no ionization.

(±)-2-((1*S*,2*R*,3*S*)-2-((benzyloxy)methyl)-3-propylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)

Compound **16** (47.5 mg, 0.145 mmol, 48% combined yield) was synthesized from dibromocyclopropane **9** (119.5 mg, 0.30 mmol, 1 equiv) according to the general procedure **A**. The analysis of the ^{1}H NMR spectrum of the crude mixture indicates a ratio **16a**/**16b** = 62:38. The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 99:1 to 95:5) to afford isomer **16a** (yellowish oil), then a mixture of **16a**/**16b** and finally isomer **16b** (colorless oil). The individual isomers are described from pure analytical fractions. The NMR data of the minor isomer **16b** is in accordance with the literature.[6d] The stereochemistry of the major isomer **16a** was concluded from the stereochemistry of the minor isomer **16b**.

16a: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.38–7.27 (m, 5 H), 4.57 (d, *J* = 11.8 Hz, 1 H), 4.48 (d, *J* = 11.8 Hz, 1 H), 3.70 (dd, *J* = 10.1, 7.7 Hz, 1 H), 3.64 (dd, *J* = 10.1, 7.2 Hz, 1 H), 1.52–1.32 (m, 6 H), 1.21 (s, 6 H), 1.20 (s, 6 H), 0.91 (t, *J* = 7.2 Hz, 3 H), 0.15 (t, *J* = 9.4 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: δ 139.1, 128.4 (2 C), 127.9 (2 C), 127.5, 82.9 (2 C), 72.9, 68.3, 27.9, 25.1 (2 C), 24.9 (2 C), 23.6, 22.7, 21.9, 14.2 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. **LCMS:** $[M+NH_4]^{+\cdot}$ = 348, 7.97 min. **HRMS (ESI-TOF) m/z**: $[M+NH_4]^+$ Calcd for $C_{20}H_{35}BNO_3$ 348.2704; Found 348.2700.

16b: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.35–7.27 (m, 5 H), 4.55 (d, *J* = 12.0 Hz, 1 H), 4.49 (d, *J* = 12.0 Hz, 1 H), 3.59 (dd, *J* = 10.4, 5.9 Hz, 1 H), 3.37 (dd, *J* = 10.4, 8.3 Hz, 1 H), 1.48–1.36 (m, 6 H), 1.21 (s, 12 H), 0.90 (t, *J* = 7.2 Hz, 3 H), – 0.50 (t, *J* = 6.0 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: δ 138.9, 128.5 (2 C), 127.8 (2 C), 127.6, 83.0 (2 C), 72.6, 70.5, 31.2, 24.8 (4 C), 23.2, 22.8, 22.0, 14.1 ppm. The boron-bound carbon was not detected due to quadrupolar relaxation. **LCMS:** $[M+NH_4]^{+\cdot}$ = 348, 7.96 min.

(±)-2-((1*R*,6*S*,7*S*)-2-oxabicyclo[4.1.0]heptan-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17)

Compound **17** (34.4 mg, 0.153 mmol, 38%, colorless oil, **17a**/**17b** = 93:7) was synthesized from dibromocyclopropane **10** (102.4 mg, 0.40 mmol, 1 equiv) according to the general procedure **A**. The analysis of the ^{1}H NMR spectrum of the crude mixture indicates a ratio **17a**/**17b** = 91:9. The crude was purified over silica gel column chromatography (elution with hexane/EtOAc = 95:5 to 90:10). Only the major isomer **17a** from the mixture was described. The NMR data of the major isomer **17a** is in accordance with the literature.[6e] The stereochemistry of the minor isomer **17b** was concluded from the stereochemistry of the major isomer **17a**. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 3.65 (dd, *J* = 3.0, 6.7 Hz, 1 H),

3.58–3.54 (m, 1 H), 3.34 (td, *J* = 10.7, 2.8 Hz, 1 H), 1.97–1.93 (m, 2 H), 1.53–1.39 (m, 2 H), 1.25–1.22 (m, 1 H), 1.19 (m, 12 H), 0.07 (dd, *J* = 7.6, 3.0 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: *δ* 83.1 (2 C), 64.7, 57.2, 24.9 (2 C), 24.8 (2 C), 21.9, 20.5, 17.2, 8.3 ppm. **LCMS:** $[M+H]^{+\cdot}$ = 225, 6.34 min.

(±)-2-(bicyclo[4.1.0]heptan-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18)

Compound **18** (54 mg, 0.24 mmol, 40%, colorless oil, **18a**/**18b** = 93:7) was synthesized from dibromocyclopropane **11** (152.4 mg, 0.60 mmol, 1 equiv) according to the general procedure **B**. The analysis of the ^{1}H NMR spectrum of the crude mixture indicates a ratio **18a**/**18b** = 93:7. The crude was purified over silica gel column chromatography (elution with pentane/EtOAc = 98:2). Only the major isomer **18a** from the mixture was described. The NMR data of the major isomer **18a** is in accordance with the literature.[6e] The stereochemistry of the minor isomer **18b** was concluded from the stereochemistry of the major isomer **18a**. **^{1}H NMR (400 MHz, $CDCl_3$)**: *δ* 1.90–1.85 (m, 2 H), 1.68–1.62 (m, 2 H), 1.28–1.25 (m, 2 H), 1.21 (s, 12 H), 1.19–1.16 (m, 2 H), 1.14–1.11 (m, 2 H), – 0.38 (t, *J* = 5.8 Hz, 1 H) ppm. **^{13}C NMR (175 MHz, $CDCl_3$)**: *δ* 82.8 (2 C), 24.9 (4 C), 24.2 (2 C), 21.2 (2 C), 17.3 (2 C), 6.4 ppm.