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Enantiomerically Pure Vinylcyclopropylboronic Esters

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Dedicated to Professor Dr. Armin de Meijere on the occasion of his 70th birthday

Keywords: Boron / Cyclopropane / Asymmetric synthesis / Palladium / Natural products

Vinylcyclopropanes are versatile intermediates and products in organic synthesis. The corresponding enantiomerically pure boronic esters should lead to highly flexible building blocks with a variety of applications. A detailed study towards the selective synthesis of (*E*)- and (*Z*)-vinyl derivatives starting from the known diastereo- and enantiopure cyclopropylmethanols **3** and **4** is presented. The boronic esters were activated via their trifluoroboronates; the optimization of the reaction is discussed. The endeavour culminated in the synthesis of (–)-(1*S*,2*S*)-dictyopterene A (**38**).

Introduction

Vinylcyclopropanes are attractive synthetic intermediates for the synthesis of physiologically active components as well as natural products.[1] Especially noteworthy in this respect are oligocyclopropane-containing natural products such as the FR-900848 (**1**)[2] or ambruticin (**2**; Figure 1).[3] Vinylcyclopropanes are also important intermediates, for example, they have been used as intermediates in the synthesis of cyclopentanoid terpenes[4] using a [4+1] annulation strategy.[5] Consequently, a number of strategies have been devised for the enantioselective synthesis of the motif.[6]

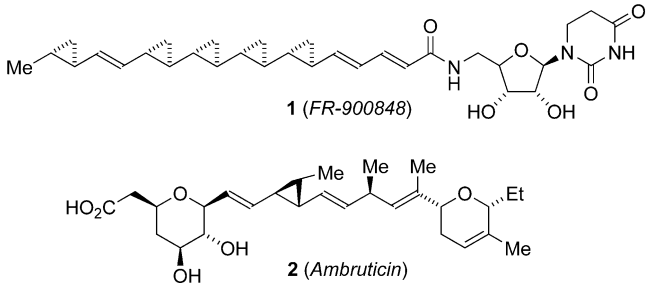

Figure 1. Naturally occurring vinylcyclopropanes.

A highly flexible approach was reported by Markó and coworkers.[7] The group synthesized vinylcyclopropylboronic esters by direct cyclopropanation of the corresponding diene with diazomethane, hence allowing further transformations of the boron moiety. The concept matched our own approach towards the corresponding enantiomerically pure intermediates. The key building blocks that stemmed from our search for highly stable boron intermediates[8] were the cyclopropylmethanols **3** and **4** (Figure 2).[9] We have previously demonstrated their use in a variety of transformations of both the side-chain,[10] for example, furnishing vinylcyclopropylboronates **5** and **6** by an oxidation/Horner–Wadsworth–Emmons chain elongation,[11] and the boron group.[9–12] Herein we describe the full details of our findings, focussing on the selective synthesis of substituted vinylcyclopropane derivatives and the activation of the robust boronic esters.

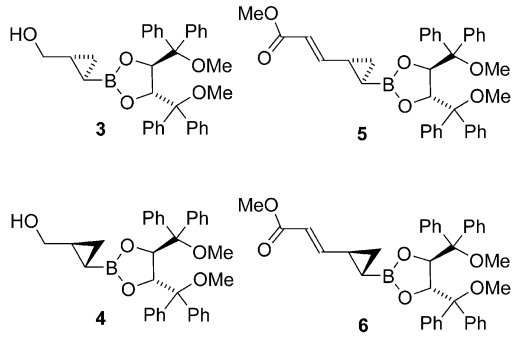

Figure 2. Key intermediates in the synthesis of vinylcyclopropylboronic esters.

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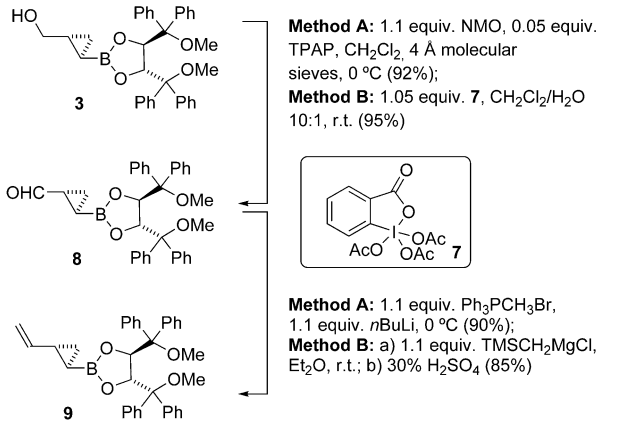
Results and Discussion

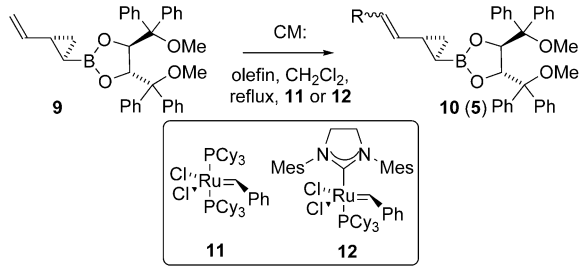
Synthesis by Cross-Metathesis

The starting point of our endeavour was the readily available alcohol **3**, which we used in a selective oxidation step, either performing the reaction under the conditions established by Ley et al. (92%; NMO: *N*-methylmorpholine *N*-oxide; TPAP: tetra-*n*-propylammonium perruthenate)[13] or by using the Dess–Martin periodinane **7** (95%).[14] The olefination of aldehyde **8** was achieved by a conventional Wittig reaction (90%) or a Peterson reaction (85%).[15] Both sequences were performed numerous times and proved to be equally reliable for providing vinylcyclopropane **9** in high yield (Scheme 1).

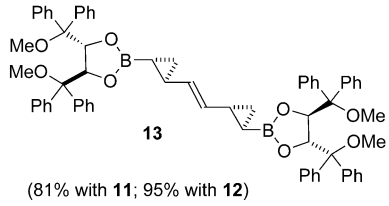


Scheme 1. Synthesis of vinylcyclopropane **9**.

Next we investigated the ability of vinylcyclopropane **9** to act as a coupling partner in a cross-metathesis to give vinylcyclopropanes **10** (and **5**) using the commercially available Grubbs catalysts **11** and **12** (Scheme 2).[16] The first results indicated that catalyst **11** would be of limited use:[10a] although styrene worked perfectly well to give compound **10a** in high yield and selectivity (95%, $E/Z > 98:2$), even methyl acrylate caused problems. The reaction was sluggish and gave the desired *E* product **5** in moderate yield (52%) only. "Dimer" **13** was obtained as a side-product in 14% yield; this derivative could actually be obtained in high yield (81–95%) when no other olefin was added to the reaction mixture. Catalyst **12** proved to be superior in all respects. The yield of product **10** or **5** was generally higher (70–96%) and there were hardly any limitations in the substrates that could be used: simple alkyl groups (**10b**,**c**) as well as silyl protecting groups (**10d**,**e**) were tolerated. Only allyl acetate (**10f**) or unprotected allyl alcohol (**10g**) did not form the desired vinylcyclopropanes. Although the *E*/*Z* selectivity was fair in most cases, a major drawback of the procedure was the difficulty of separating the diastereoisomers. Attempts to obtain pure isomers by chromatographic methods failed and in only two cases (products **10a**,**b**) did selective crystallization enable their purification, also providing proof of their configurations by X-ray structural analysis (Figure 3).[17] Therefore, we were looking for alternative methods to synthesize one isomer selectively.



		using **11**		using **12**	
Product	R	% Yield	(*E*)/(*Z*)	% Yield	(*E*)/(*Z*)
5	CO_2Me	52[a]	>95:5	91	>95:5
10a	Ph	95	>98:2	96	>98:2
10b	*n*Bu			83	85:15
10c	*n*Pe			81	85:15
10d	$TMSCH_2$			70	50:50
10e	CH_2OTES			90	85:15
10f	CH_2OAc			-	-
10g	CH_2OH			-	-



Scheme 2. Cross-metathesis of ester **9** with various terminal olefins $RCH=CH_2$. [a] +14% **13**. Abbreviations: Cy = cyclohexyl, TES = Et_3Si.

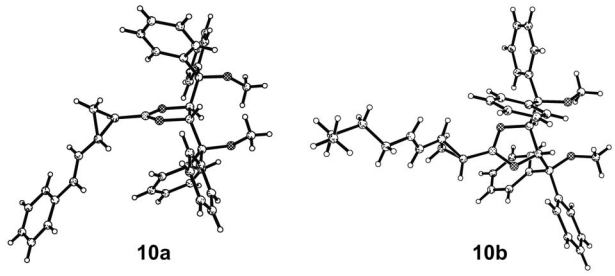
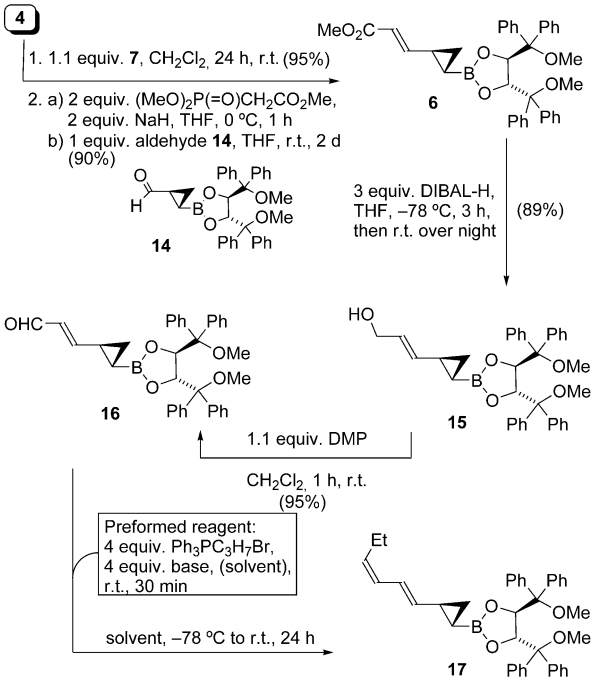


Figure 3. X-ray crystallographic structures of esters **10a** and **10b**.[17]

Synthesis by Wittig-Type Olefination

It has already been established that standard transformations, the oxidation of alcohol **4** to aldehyde **14** (95% yield) with the Dess–Martin reagent **7** followed by reaction with a stabilized ylide, led to the *E* product **6** exclusively (90%; Scheme 3).[11] We assumed that after a conventional reduction (to alcohol **15**; 89% yield)−oxidation sequence, the aldehyde **16** (95% yield) would be an ideal starting material for a selective synthesis of diene **17**, as required, for example, for the synthesis of dictyopterene B (see below).[18,19] As expected,[20] the consecutive Wittig reaction was highly *Z*-selective and could be influenced by the choice of solvent

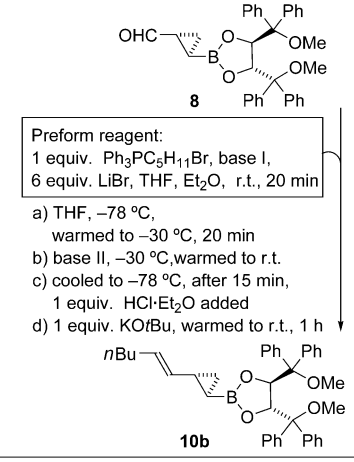
(THF, DME and dichloromethane were used) and counter-ion (lithium vs. sodium and potassium; entries 1–5, ratio determined from the crude product by a 600-MHz ^{1}H-NMR study). It proved to be most convenient to use THF as the solvent and potassium hexamethyldisilazide (KHMDS) as the base, which provided the highest yield of the desired diene **17** (entry 4: 96%, *E*/*Z* = 3:97). With the high selectivity observed, purification by selective crystallization of the *Z* isomer was readily achieved.



Entry[a]	Solvent	Base (4 equiv.)	Olefin **17** (*Z*):(*E*)	% Yield
1	THF	NaHMDS (1 M in THF)	91:9	76
2	CH_2Cl_2	NaHMDS (1 M in THF)	86:14	75
3	THF	LiHMDS (1 M in THF)	81:19	87
4	THF	KHMDS (neat)	97:3[b]	96
5	DME	KHMDS (neat)	97:3	89

Scheme 3. Wittig procedure: a) for all experiments only bases or solvents were modified; b) the minor diastereoisomer was removed by crystallization.

To gain access to the *E* isomers and, in view of our endeavour towards the synthesis of dictyopterene A (see below), in particular to the *n*-butyl derivative **10b**, we were looking for alternatives that were also compatible with the boronic ester moiety. First, we tested the Schlosser reaction[21] starting from aldehyde **8**; this procedure led to the olefin **10b**, albeit in poor yield and selectivity (Scheme 4). However, by altering the bases used for the two consecutive steps (from phenyllithium to *n*-butyllithium) as well as the equivalents used (from 2 to 1 equiv.), the efficiency could be increased and the desired *E* isomer **10b** was obtained in



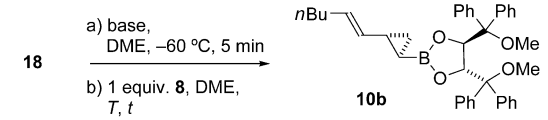
Entry[a]	Base I	Base II	Olefin **10b** (*E*):(*Z*)	% Yield
1	2 equiv. PhLi	2 equiv. PhLi	64 : 36	30
2	1 equiv. PhLi	1 equiv. PhLi	59 : 41	44
3	1 equiv. PhLi	1 equiv. *n*BuLi	70 : 30	53
4	1 equiv. *n*BuLi	1 equiv. *n*BuLi	80 : 20	70
5	1 equiv. *n*BuLi	2 equiv. *n*BuLi	67 : 33	23

Scheme 4. Schlosser procedure. The reaction conditions were same for all experiments, only the bases were modified.

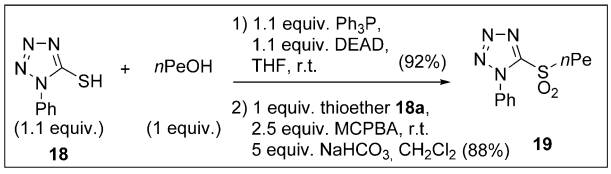
70% yield and in an 80:20 ratio (entry 4). Nevertheless, the approach was still not satisfactory for preparative purposes.

The Julia–Kocienski reaction proved to be the method of choice.[22] The required reagent was readily synthesized from thiol **18** and *n*-pentanol in two steps: Mitsunobu reaction (92%) followed by oxidation (88%) furnished the sulfone **19**. The observed *E* selectivity was high (>99:1) right from the start (Scheme 5, entry 1), but the yield needed to be increased (20%). Although increasing the amount of KHMDS did slightly improve the yield (36%, entry 2), changing the counter-ion to sodium (NaHMDS) led to a decrease in the selectivity (43% yield, *dr* 97:3; entry 3). Instead of using commercially available solutions of base in toluene, we next used neat KHMDS as the base, hence performing the transformation in DME as the only solvent (entries 4–8), thus further increasing the rate of the reaction. By optimizing the conditions (–60 °C, 10 min, 1.8 equiv. KHMDS and 1.5 equiv. **19**, entry 8) up to 93% yield of olefin **10b** was obtained; although the minor diastereoisomer was detectable in the crude product by NMR spectroscopy (not with a 300 MHz spectrometer), a single crystallization allowed the isolation of the *E* isomer.

Summing up, the Wittig-type olefinations investigated were compatible with the boronic ester moiety. Separation of the *E*/*Z* isomers was difficult if possible at all, hence an almost perfect selectivity was required. Despite the fact that the Julia–Kocienski reaction gave superb isomeric ratios, circumventing the optimization step for each substrate would be highly desirable. Cross-coupling reactions of substrates with a given configuration might be an alternative.

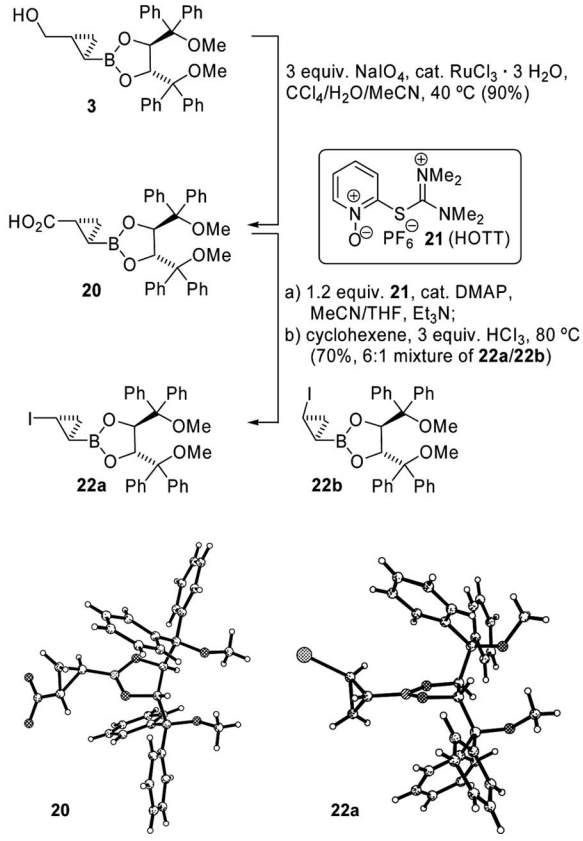


Entry	T [°C]	t[c]	Sulfone 19 (equiv.)	Base	Olefin 10b (E):(Z)	% Yield
1[a]	–78	15 h	1.2	1.2 equiv. KHMDS (0.5 M in toluene)	>99 : 1	20
2[a]	–78	15 h	1.2	3 equiv. KHMDS (0.5 M in toluene)	98 : 2	36
3[a]	–78	15 h	1.2	1.2 equiv. NaHMDS (1 M in toluene)	97 : 3	43
4[a]	–60	15 h	1.2	1.2 equiv. KHMDS (neat)	>99 : 1	46
5[b]	–60	15 h	1.2	1.4 equiv. KHMDS (neat)	>99 : 1	54
6[b]	–60	15 min	1.3	1.8 equiv. KHMDS (neat)	>99 : 1	73
7[b]	–78	1 min	1.3	1.8 equiv. KHMDS (neat)	>99 : 1	71
8[a]	–60	10 min	1.5	1.8 equiv. KHMDS (neat)	>99 : 1[d]	93[e]



Scheme 5. Julia–Kocienski procedure. a) Base was added over 5 min to sulfone **19**. The resulting solution was stirred for 1 h (entry 8: 5 min) and the aldehyde **8** was added over 5 min. b) Base was added over 20 min to sulfone **19** and aldehyde **8**. c) The reactions were in progress for the times shown, that is, after addition of all components to the reaction mixture, and then quenched with H_2O. d) The minor (*Z*)-olefin corresponding to **10b** was only detected by ^1H NMR (600 MHz); it was removed by recrystallization. e) The yield was slightly lower (91%) when performing the transformation on a larger scale (6.95 mmol).

investigation, we were pleased to find that the starting materials were obtained in high purity and in the case of the *trans* isomer **22a** even as a crystalline solid.



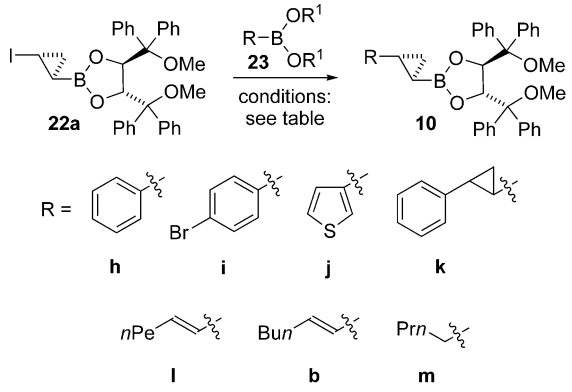
Scheme 6. Synthesis of the required iodide **22a**.

Synthesis by Cross-Coupling

We have previously reported the two-step sequence from alcohol **3** via the acid **20**, its "Barton ester" (preferentially generated with "HOTT reagent" **21**),[23] to the iodides **22a** and **22b** (Scheme 6).[10b] The ruthenium-catalysed oxidation of cyclopropylmethanol proceeded smoothly to furnish the corresponding crystalline acid **20** in high yield (90%), again not affecting the boron moiety. The following radical decarboxylation proved to be sensitive; it was essential that the required "Barton thiohydroxamic ester" was obtained in high purity. Although the approach via the acid chloride was feasible, the yield was poor (33%). The standard procedure using dicyclohexylcarbodiimide (DCC) for the direct esterification also furnished an inseparable side-product that interfered with the following radical step. As mentioned before, use of the "HOTT reagent" **21**[23] was the method of choice. The separable iodides **22a**,**b** were synthesized in 70% yield as a 6:1 mixture after the radical transformation in the presence of iodoform. Because the following Pd-catalysed coupling was a critical reaction for our

Prior to our investigation,[10b] only a few cross-coupling reactions[8c,24] of cyclopropyl iodides had been reported, despite the fact that the starting cyclopropanes are readily available.[25] To optimize the reaction we used different conditions, those reported in the literature essentially for cyclopropanes (conditions A–G, Scheme 7).[24b,26,9]

Although the product was detectable in some cases, in our hands the most reliable procedure was reported by Hildebrand and Marsden {conditions D: [$Pd(PPh_3)_4$], KO*t*Bu, DME, 80 °C}.[26a] With phenylboronic acid (**23h**), the first model substrate, product **10h** was obtained in high yield (87%).[27] Obvious limitations for the process are halides in the aromatic ring as the cyclopropyl iodide reacts relatively sluggishly; hence no product was obtained with boronic acid **10i**. On the other hand, a heterocyclic substituent, as in the thiophene derivative **23j**, represents no problem (yield of cyclopropane **10j**: 79%). Even cyclopropane/cyclopropane coupling was achieved in good yield (67% of dicyclopropane **10k**); instead of using the boronic acid, the corresponding dioxaborinane **23k**[28] was used. In all cases the boron derivative **23** was added in access (1.5 equiv.) as a dramatic decrease in yield was observed when only

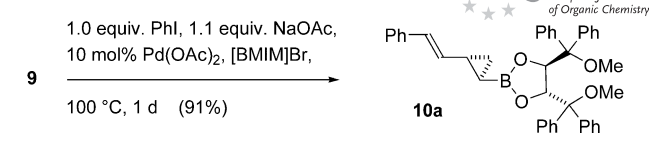


R	23 R^1	Conditions	% Yield (**10**)
h	H	**A**: $Pd(OAc)_2$, tBu_3P, KO*t*Bu, DME, 80 °C	–
h	H	**B**: $Pd(OAc)_2$, PPh_3, CsF, DME, 80 °C	–
h	H	**C**: $PdCl_2(dppf)$, KO*t*Bu, DME, 80 °C	–
h	H	**D**: $Pd(PPh_3)_4$, KO*t*Bu, DME, 80 °C	87
h	H	**E**: $Pd(PPh_3)_4$, K_3PO_4, toluene, 100 °C	–
h	H	**F**: $Pd(PPh_3)_4$, Na_2CO_3, [BMIM]BF_4/H_2O, 110 °C	–
i	H	**C**: $PdCl_2(dppf)$, KO*t*Bu, DME, 80 °C	–
i	H	**D**: $Pd(PPh_3)_4$, KO*t*Bu, DME, 80 °C	–
j	H	**B**: $Pd(OAc)_2$, PPh_3, CsF, DME, 80 °C	–
j	H	**D**: $Pd(PPh_3)_4$, KO*t*Bu, DME, 80 °C	79
k	$(CH_2)_3$	**D**: $Pd(PPh_3)_4$, KO*t*Bu, DME, 80 °C	67
k	$(CH_2)_3$	**E**: $Pd(PPh_3)_4$, K_3PO_4, toluene, 100 °C	–
l	H	**D**: $Pd(PPh_3)_4$, KO*t*Bu, DME, 80 °C	65
b	H	**C**: $PdCl_2(dppf)$, KO*t*Bu, DME, 80 °C	–
b	H	**D**: $Pd(PPh_3)_4$, KO*t*Bu, DME, 80 °C	62
b	H	**G**: $Pd(OAc)_2$, PPh_3, Cs_2CO_3, $n$$Bu_4NCl$, DMF/$H_2O$, 90 °C	–
m	H	**D**: $Pd(PPh_3)_4$, KO*t*Bu, DME, 80 °C	–

Scheme 7. Suzuki coupling of iodide **22a**.

1.0 equiv. was used. In view of the present vinylcyclopropane study we were especially pleased to find that substrates **23l**,**b**[28,29] do not represent any problem: the products **10l**,**b** were obtained in 65 and 62% yields, respectively. The protected boron moiety of the products remained intact and could be further elaborated in consecutive steps (see below). Although the formation of dicyclopropane **10k** was possible, simple alkylboronic acids (e.g., **23m**) could not, as expected, be successfully coupled.

We had previously shown that cyclopropyl iodides were not ideal reaction partners for the Stille or Heck reaction,[30] for example, iodide **22a** did not react under the recently reported[31] conditions with styrene, methyl acrylate or 1-heptene using ionic liquids. However, when reversing the reaction partners and exposing vinylcyclopropane **9** and iodobenzene to the reaction conditions (Scheme 8), the known product **10a** was selectively formed as a single isomer (91%). Thus, a new alternative protocol to the cross-metathesis reaction was established.

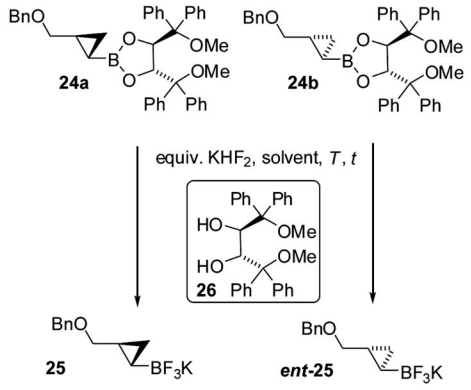


Scheme 8. Heck reaction of vinylcyclopropylboronic ester **9** ([BMIM]Br: 1-butyl-3-methylimidazolium bromide).

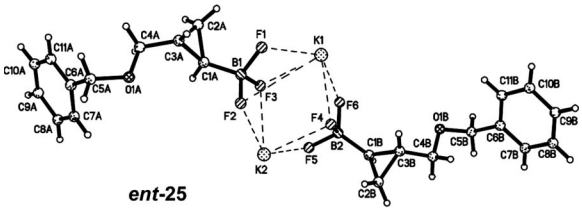
Activation of Boronic Esters

Before applying the synthesized vinylboronates, a convenient protocol to deprotect the boronic esters was required as the previously established procedure (activation with $LiAlH_4$ or MeLi)[8–11] is not compatible with many functional groups and especially not with the vinylcyclopropanes (e.g., starting from substrate **9** would yield the corresponding 1,3,2-dioxaborinane in 41% yield only[30,32]). A different approach was based on an alternative mode of activation, as shown by Genêt and Deng and their coworkers who used and modified the procedures of Vedejs et al. as well as Thierig and Umland for converting boronic acids and esters into the corresponding trifluoroborates with KHF_2.[33] As model substrates we chose the benzyl-protected cyclopropylmethanols **24a**,**b**, which are readily available in our group (Scheme 9).[12a,12b] When treating these substrates in methanol/water with 7 equiv. of KHF_2 at room temperature, no conversion was detected by TLC after 15 h. Increasing the reaction temperature and the equivalents of the reagents did initiate a slow conversion (25 h, 40 °C, 14 equiv. KHF_2). The optimum temperature was reached at 80 °C (ca. 90% conversion, ca. 70% yield of slightly impure **25**); complete conversion was not observed. However, increasing the amount of fluoride reagent to 50 equiv. did shift the equilibrium to furnish the product **25** after 2 d in 91% yield; no starting material was recovered. The work-up procedure towards pure product **25** needed some optimization. We found that the best results were obtained when the solvents were first evaporated under reduced pressure: the residue, the solids, were fractionally washed easily first with diethyl ether (extracting the diol) followed by acetonitrile (extracting the product **25**) leaving the inorganic salts on the filter. The work-up procedure was further simplified by omitting water as the solvent from the transformation; the products **25** and *ent*-**25** were obtained in 93% yield as pure crystalline solids, as determined by ^{19}F NMR spectroscopy, the structures of which could be solved by X-ray crystallography.

We were pleased to find that the isolated borates could be readily exposed to the coupling conditions, as reported by Deng and coworkers[33e], to furnish the desired enantiomerically pure cyclopropanes **27** and **28** in 66 and 85% yields, respectively (Scheme 10). However, for the envisaged use of the boron compounds in a Matteson homologation,[34] the reactivity of the intermediates **25** and *ent*-**25** would be too low. A number of protocols have been devised for the activation and hence the liberation of the corresponding acids. Kim and Matteson reported that $SiCl_4$ can

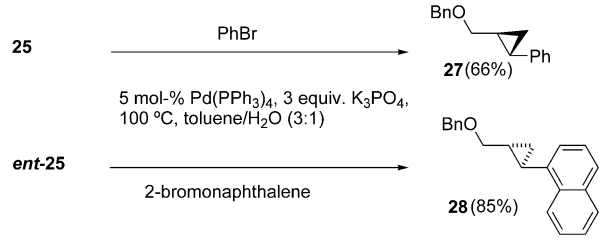


KHF_2 (equiv.)	Solvent	t [d]	T [°C]	Conversion	% Yield
7	MeOH-H_2O	4	r.t.	-	-
14	MeOH-H_2O	5	80	~ 90%	~70
50	MeOH-H_2O	2	80	quant.	91
50	MeOH	2	80	quant.	93

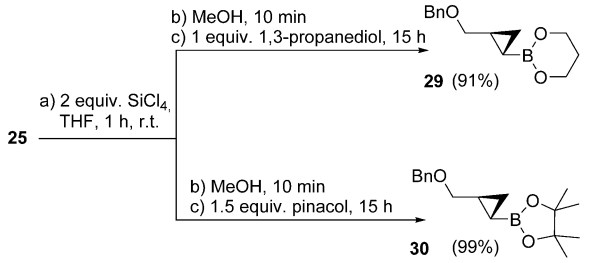


Scheme 9. Generation of borates **25** and ***ent*-25**.

activate trifluoroborates to form dichloroborane intermediates; these were directly converted into simple boronic esters.[35] The procedure was successfully applied to cyclopropane **25**: depending on the diol used either 1,3,2-dioxaborinane (**29**, 91%; Scheme 11) or 1,3,2-dioxaborolane **30** (quant.) was obtained, intermediates that were previously shown to be ideal reaction partners for the Suzuki–Miyaura coupling and the Matteson homologation. However, because the formation of HCl during the transformation cannot be prevented, sensitive substrates (including vinylcyclopropane **9**) are not compatible with these conditions. An alternative to the one-pot sequence was reported by Yuen and Hutton:[36] under basic conditions the boronic acid was first formed, which was subjected to esterification (conditions II: **29** was prepared in 75% yield over two steps), and under acidic conditions, using trimethylsilyl chloride in an aqueous environment, the acid was also formed and ultimately the ester **29** (conditions III: 94% over two steps). Slightly modifying the original protocol led in one-pot to the target compound: when forming the dichloroborane in the absence of water and adding 1,3-propanediol after 5 min, the desired product **29** was furnished in 95% yield (conditions IV). However, acidic conditions were not omitted. We solved the problem by adding triethylamine to quench the HCl formed without negatively influencing the transformation. Again, product **29** was isolated in good yield (conditions V: 92%). With these findings, transformation of the sensitive vinylcyclopropanes also seemed feasible.



Scheme 10. Suzuki coupling of borates **25** and ***ent*-25**.



Alternate conditions towards ester **29**:

II. (yield: 75%): 1. a) LiOH, MeCN/H_2O, 20 h; b) aq. NH_4Cl, 1 M HCl; 2. 0.95 equiv. 1,3-propanediol, 10 h.

III. (yield: 94%): 1. a) 3 equiv. Me_3SiCl, MeCN/H_2O, 20 h; b) aq. $NaHCO_3$; 2. 0.95 equiv. 1,3-propanediol, 10 h.

IV. (yield: 95%): a) 3 equiv. Me_3SiCl, MeCN, 5 min; b) 0.95 equiv. 1,3-propanediol, 30 min.

V. (yield: 92%): a) 3 equiv. Me_3SiCl, 3 equiv. Et_3N, MeCN, 5 min; b) 0.95 equiv. 1,3-propanediol, 30 min.

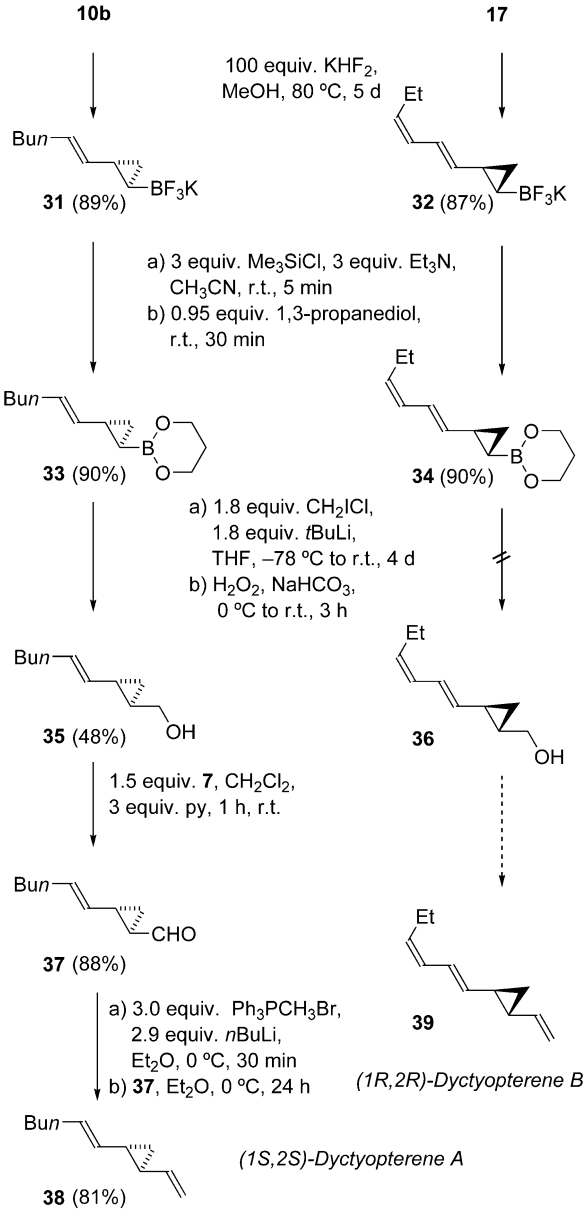
Scheme 11. Activation of borate **25**.

Synthetic Approach Towards the Dictyopterenes

Finally, we tried to apply the synthesized building blocks to a small natural product synthesis: dictyopterenes are unsaturated C_{11}-hydrocarbons bearing vinylcyclopropane subunits.[18,19] The natural compounds were first isolated by Moore et al. as major components from the odoriferous oil of the Hawaiian seaweeds, genus *Dictyopteris*;[19a] the 1*R*,2*R* configuration was established, although later (1*S*,2*S*)-dictyopterene B was discovered to be a minor component in female gametes and essential oils of the *Scytosiphonaceae*, *Chordariaceae* and *Dictyotacea* families.[19m] All compounds exhibit remarkable activity, including their sperm-attracting physiological ability. They are also responsible for the intense ocean smell. Although most synthetic approaches lead to mixtures of undesired isomers, few of the reported procedures afforded the optically pure dictyopterenes.[37]

Starting from the enantio- and diastereomerically pure boronic esters **10b** and **17**, we first needed to deprotect and activate the boron moiety. We applied the optimized conditions to form the borates **31** and **32** (Scheme 12; MeOH, KHF_2, 80 °C) in 89 and 87% yields, respectively, followed

by the transformation to the reactive boronic esters **33** and **34** (90% yields). The pure compounds were obtained after distillation of the crude products. The Matteson procedure, treatment with chloromethyllithium and subsequent oxidation with basic hydrogen peroxide, proved to be the bottle-neck in the sequence: Only with pure starting material could the transformation to alcohol **35** be successfully performed, albeit in moderate yield (48%); several attempts to convert the 1,3,2-dioxaborinane **34** into the desired product **36** failed. However, oxidation of the primary alcohol **35** with Dess–Martin periodinane **7**[14] proceeded smoothly to furnish aldehyde **37**. As expected, Wittig reaction[20] afforded in the last step (1*S*,2*S*)-dictyopterene A (**38**). The spectroscopic data were in full agreement with those previously reported.[19d]



Scheme 12. Synthetic route towards the dictyopterenes.

Conclusions

We have developed, optimized and evaluated a) various new approaches to enantio- and diastereomerically pure vinylcyclopropylboronic acids, including (for the first time) a Heck reaction in an ionic liquid, b) the deprotection of highly stable boronic esters to furnish borates and c) the activation of the borates forming 1,3,2-dioxaborinanes. The sequence was applied to the synthesis of dictyopterenes: although the Matteson homologation approach failed to yield (1*R*,2*R*)-dictyopterene B (**39**), it allowed the synthesis of (1*S*,2*S*)-dictyopterene A (**38**).

Experimental Section

General: Unless specified the reactions were carried out by using standard Schlenk techniques under dry N_2 with magnetic stirring. Glassware was oven-dried at 120 °C overnight. Solvents were dried and purified by conventional methods prior to use; tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Common solvents for chromatography (petroleum ether, EtOAc) were distilled prior to use; petroleum ether refers to the fraction with a boiling point in the range 40–60 °C. Column chromatography and flash column chromatography were performed on silica gel 60 (0.040–0.063 mm, 230–400 mesh). TLC (monitoring the course of the reactions) was performed on precoated plastic sheets (Polygram® SIL G/UV254, Macherey–Nagel) with detection by UV (254 nm) or by colouration with cerium molybdenum solution [phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), concd. H_2SO_4 (60 mL), H_2O (940 mL)]. Preparative medium-pressure liquid chromatography (MPLC) was performed with a Labomatic pump (MD-50/80/100), a packed column (25 × 300 mm or 40 × 475 mm), LiChroprep, Si 60 (15–25 μm) and UV detector (254 nm). ^1H and ^{13}C NMR spectra were recorded at room temp. in $CDCl_3$ (unless stated otherwise) with a Bruker ARX 300, ARX 500, DRX 600 or a Varian Inova 400 spectrometer. Chemical shifts are given in ppm relative to TMS as the internal standard [^1H, $Si(CH_3)_4$ δ = 0.00 ppm] or to the resonance of the solvent (^{13}C, $CDCl_3$ δ = 77.0 ppm); coupling constants J are given in Hz. Higher-order δ and J values are uncorrected. ^{13}C NMR signals were assigned on the basis of H–H COSY and HSQC or HMBC spectroscopy. Microanalyses were performed at the Institut für Organische Chemie, Stuttgart. Melting points or softening ranges (Büchi 510 and B-540, respectively) are uncorrected. Specific rotations were measured at 20 °C (Perkin–Elmer 241 MC or precisely 341). IR spectra were obtained with a Perkin–Elmer 283, Bruker IFS 28 or a Perkin–Elmer Spectrum One spectrometer. MS were recorded with a Finnigan MAT 95 [FAB (NBA: 3-nitrobenzyl alcohol), EI], a Varian MAT 711 (EI) or an Applied Biosystems/MDS SCIEX 4000 Q TRAP (ESI, LC–MS/MS) spectrometer.

Nomenclature: For convenience and easy data comparison the boron moieties were set to lowest substituent priority in contradiction to the IUPAC nomenclature guidelines.

Synthesis of Vinylcyclopropane 9

(4*R*,5*R*,1′*R*,2′*R*)-Aldehyde 8. Method A:[11] Cyclopropylmethanol **3** (1.10 g, 2.06 mmol, 1.00 equiv.), *N*-methylmorpholine *N*-oxide (390 mg, 2.88 mmol, 1.40 equiv.), 4 Å molecular sieves (1.5 g) and dry dichloromethane (10 mL) were placed in a Schlenk flask under dry nitrogen. The mixture was cooled to 0 °C, TPAP (40 mg, 0.10 mmol, 0.05 equiv.) was added and stirring was continued for 15 h at room temp. After filtration through a pad of Celite, the

residue was washed with dichloromethane and the organic solvent was removed under reduced pressure. Chromatography (silica gel, petroleum ether/ethyl acetate, 9:1) yielded the aldehyde **8** (1.01 g, 1.89 mmol, 92%).

Method B: Cyclopropylmethanol **3** (1.00 g, 1.87 mmol, 1.00 equiv.) was dissolved in dichloromethane (60 mL) and Dess–Martin periodinane (**7**; 0.83 g, 1.96 mmol, 1.05 equiv.) was added. The reaction mixture was stirred for 15 h at room temp., quenched with a 1 M aqueous solution of $Na_2S_2O_3$ (50 mL) and washed with aqueous saturated $NaHCO_3$ (50 mL); the aqueous layer was finally extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **8** was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 9:1) to afford aldehyde **8** (954 mg, 1.79 mmol, 95%) as colourless crystals; softening range 89–95 °C. $[a]_D^{20}$ = –96.7 (*c* = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3056, 3025, 2938, 2831, 2723, 1710, 1445, 1425, 1395, 1308, 1192, 1074, 1032, 1015, 966, 924, 896, 796, 698 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.27 (ddd, *J* = 10.2, *J* = 7.5, *J* = 4.8 Hz, 1 H, 1′-H), 0.94 (ddd, *J* = 7.6, *J* = 7.5, *J* = 3.9 Hz, 1 H, 3′-H_a), 1.06 (ddd, *J* = 10.2, *J* = 4.3, *J* = 3.9 Hz, 1 H, 3′-H_b), 1.28 (dddd, *J* = 7.6, *J* = 6.3, *J* = 4.8, *J* = 4.3 Hz, 1 H, 2′-H), 2.80 (s, 6 H, OC*H*$_3$), 5.12 (s, 2 H, 4-H, 5-H), 7.05–7.11 (m, 20 H, arom. H), 8.30 (d, *J* = 6.3 Hz, 1 H, C*H*O) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 3.0 (C-1′), 11.8 (C-2′), 28.6 (C-3′), 52.1 (CPh_2OCH_3), 78.2 (C-4, C-5), 83.6 (CPh_2OCH_3), 127.8, 127.9, 128.1, 128.3, 128.7, 130.1 (arom. CH), 141.3 (arom. C_{ipso}), 200.4 (C-4′) ppm. MS (EI, 70 eV): *m*/*z* (%) = 532 (<5) $[M]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{34}H_{33}BO_5$ (532.43): calcd. C 76.70, H 6.25; found C 75.72, H 6.26.

(4*R*,5*R*,1′*R*,2′*R*)-Vinylcyclopropane 9. Method A: Ph_3PMeBr (0.17 g, 0.48 mmol, 1.05 equiv.) was dissolved in dry THF (8 mL) and the mixture was cooled to 0 °C in a Schlenk flask. *n*BuLi (0.30 mL of a 1.6 M solution in hexane; 0.48 mmol, 1.05 equiv.) was added and stirring was continued for 1 h at 0 °C. The solution turned bright orange and aldehyde **8** (0.24 g, 0.46 mmol, 1 equiv.) in THF (1 mL) was added dropwise; the reaction mixture turned yellow. The cooling bath was removed and the mixture was stirred for 15 h at room temp. After the addition of saturated aqueous NH_4Cl solution (10 mL) the phases were separated and the aqueous phase extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product **9** was purified by column chromatography (petroleum ether/ethyl acetate, 95:5) to yield the vinylcyclopropane **9** as colourless crystals (0.22 g, 0.42 mmol, 90%).

Method B: Aldehyde **8** (700 mg, 1.31 mmol, 1.00 equiv.) was dissolved in dry Et_2O (2 mL) and cooled to 0 °C in a Schlenk flask. Me_3SiCH_2MgCl (1.71 mL of a 1 M solution in Et_2O; 1.71 mmol, 1.30 equiv.) was added and stirring was continued at 0 °C for 1 h. The reaction was quenched with sulfuric acid (1.3 mL of a 30% aqueous solution). After stirring at room temp. for 1 h, a 1 M aqueous NaOH solution was added to neutralize the reaction mixture. Separation of the phases was followed by the extraction of the aqueous layer with Et_2O (3 × 50 mL). The combined organic layers were dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 97:3) to yield olefin **9** (592 mg, 1.12 mmol, 85%) as a colourless solid; softening range 76–83 °C. $[a]_D^{20}$ = –92.2 (*c* = 0.45, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3040, 3010, 2980, 2940, 2919, 2815, 1481, 1450, 1435, 1423, 1399, 1355, 1305, 1230, 1199, 1061, 1017, 1003, 951, 920, 880, 819, 735, 678, 623, 613 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.44 (ddd, *J* = 9.9, *J* = 6.6, *J* = 5.2 Hz, 1 H, 1′-H), 0.29 (ddd, *J* = 10.2, *J* = 6.6, *J* = 3.5 Hz, 1 H, 3′-H_a), 0.41 (ddd, *J* = 9.9, *J* = 8.6, *J* = 3.5 Hz, 1 H, 3′-H_b), 1.35 (dddd, *J* = 10.2, *J* = 8.6, *J* = 8.6, *J* = 5.2 Hz, 1 H, 2′-H), 3.00 (s, 6 H, OC*H*$_3$), 4.75 (dd, *J* = 10.1, *J* = 1.8 Hz, 1 H, 5′-H_a), 4.97 (dd, *J* = 17.0, *J* = 1.8 Hz, 1 H, 5′-H_b), 5.11 (ddd, *J* = 17.0, *J* = 10.1, *J* = 8.6 Hz, 1 H, 4′-H), 5.26 (s, 2 H, 4-H, 5-H), 7.24–7.35 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 5.0 (C-1′), 12.7 (C-3′), 22.0 (C-2′), 51.7 (CPh_2OCH_3), 77.6 (C-4 and C-5), 83.2 (CPh_2OCH_3), 111.9 (C-5′), 127.1, 127.3, 127.5, 127.8, 128.4, 129.7 (arom. CH), 141.1, 141.3 (arom. C_{ipso}), 142.2 (C-4′) ppm. MS (EI, 70 eV): *m*/*z* (%) = 530 (<5) $[M]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{35}H_{35}BO_4$ (530.46): calcd. C 79.25, H 6.65; found C 79.13, H 6.67.

Synthesis by Cross-Metathesis

General Procedure for Cross-Metathesis (CM): Vinylcyclopropane **9** (1.0 equiv.), the terminal olefin $RCH{=}CH_2$ (5.0–15.0 equiv.) and the Grubbs catalyst **11** (A) or **12** (B; 0.01–0.05 equiv.) were dissolved in abs. dichloromethane (15 mL/mmol). The mixture was heated at reflux at 40 °C up to full conversion of the vinylcyclopropane **9** (check by TLC) and then filtered through Celite, rinsed with diethyl ether and the solvents were removed under reduced pressure. The crude product **5** or **10** were purified by column chromatography (silica gel, petroleum ether to petroleum ether/ethyl acetate, 98:2).

(1′*R*,2′*R*,4*R*,5*R*)-2-{2′-[(*E*)-2-Methoxycarbonylethenyl]cyclopropyl}-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (5):[11] A) Vinylcyclopropane **9** (75 mg, 0.14 mmol, 1.0 equiv.), methyl acrylate (20 mg, 0.28 mmol, 2.0 equiv.) and Grubbs catalyst **11** (10 mg, 10 μmol, 0.07 equiv.) in dichloromethane (4 mL) were allowed to react according to the general procedure for 5 d. The boronic ester **5** was isolated as colourless crystals (44 mg, 74 μmol, 52%); *E*/*Z* > 95:5. B) Vinylcyclopropane **9** (0.10 g, 0.19 mmol, 1.0 equiv.), methyl acrylate (0.16 g, 1.9 mmol, 10 equiv.) and the Grubbs catalyst **12** (10 g, 10 μmol, 0.05 equiv.) in dichloromethane (4 mL) were allowed to react according to the general procedure for 2 d. The boronic ester **5** was isolated as colourless crystals (0.10 g, 0.17 mmol, 91%); *E*/*Z* > 95:5; m.p. 157 °C. $[a]_D^{20}$ = –85.0 (*c* = 0.96, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3058, 3026, 2934, 1720, 1652, 1493, 1421, 1371, 1262, 1193, 1067, 1033, 1018, 969, 938, 856, 757, 738, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.19 (ddd, *J* = 10.2, *J* = 7.1, *J* = 5.1 Hz, 1 H, 1′-H), 0.39 (ddd, *J* = 7.5, *J* = 7.1, *J* = 3.7 Hz, 1 H, 3′-H_a), 0.52 (ddd, *J* = 10.2, *J* = 4.9, *J* = 3.7 Hz, 1 H, 3′-H_b), 1.46 (dddd, *J* = 10.1, *J* = 7.5, *J* = 5.1, *J* = 4.9 Hz, 1 H, 2′-H), 3.00 (s, 6 H, CPh_2OCH_3), 3.67 (s, 3 H, CO_2CH_3), 5.29 (s, 2 H, 4-H, 5-H), 5.78 (d, *J* = 15.4 Hz, 1 H, 5′-H), 6.19 (dd, *J* = 15.4, *J* = 10.1 Hz, 1 H, 4′-H), 7.25–7.33 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = –4.2 (C-1′), 14.1 (C-3′), 21.1 (C-2′), 51.3 (CPh_2OCH_3), 51.8 (CO_2CH_3), 77.4 (C-4 and C-5), 83.3 (CPh_2OCH_3), 117.7 (C-5′), 127.4, 127.5, 127.6, 127.8, 128.4, 129.7 (arom. CH), 141.0, 141.1 (arom. C_{ipso}), 153.9 (C-4′), 167.0 (CO_2CH_3) ppm. The spectroscopic data for boronic ester **5** were in full agreement with the previously reported data.[11]

(1′*R*,2′*R*,4*R*,5*R*)-4,5-Bis(methoxydiphenylmethyl)-2-[(*E*)-2′-styrylcyclopropyl]-1,3,2-dioxaborolane (10a). Method A: Vinylcyclopropane **9** (75 mg, 0.14 mmol, 1.0 equiv.), styrene (30 mg, 0.28 mmol, 2 equiv.) and Grubbs catalyst **11** (10 mg, 10 μmol, 0.07 equiv.) in dichloromethane (8 mL) were allowed to react according to the general procedure for 5 d. The boronic ester **10a** was isolated as colourless crystals (82 mg, 0.13 mmol, 95%); *E*/*Z* > 98:2.

Method B: Vinylcyclopropane **9** (0.20 g, 0.38 mmol, 1.0 equiv.), styrene (0.39 g, 3.8 mmol, 10 equiv.) and Grubbs catalyst **12**

(10 mg, 10 μmol, 0.03 equiv.) in dichloromethane (8 mL) were allowed to react according to the general procedure for 1 d. The boronic ester **10a** was isolated as colourless crystals (0.22 g, 0.36 mmol, 96%); *E*/*Z* > 98:2; m.p. 115 °C. $[\alpha]_D^{21}$ = –77.0 (*c* = 0.40, $CHCl_3$). IR (film): ṽ = 3058, 3024, 2934, 2850, 2833, 1493, 1446, 1421, 1365, 1240, 1215, 1193, 1067, 1033, 1019, 757, 701 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.32 (ddd, *J* = 9.9, *J* = 6.6, *J* = 5.2 Hz, 1 H, 1′-H), 0.39 (ddd, *J* = 7.7, *J* = 6.7, *J* = 3.5 Hz, 1 H, 3′-H_a), 0.52 (ddd, *J* = 9.9, *J* = 5.1, *J* = 3.5 Hz, 1 H, 3′-H_b), 1.47–1.52 (m, 1 H, 3′-H), 3.01 (s, 6 H, OCH_3), 5.29 (s, 2 H, 4-H, 5-H), 5.51 (dd, *J* = 15.7, *J* = 8.9 Hz, 1 H, 4′-H), 6.36 (d, *J* = 15.7 Hz, 1 H, 5′-H), 7.14–7.37 (m, 25 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 2.8 (C-1′), 13.2 (C-3′), 21.8 (C-2′), 51.7 (CPh_2OCH_3), 77.5 (C-4, C-5), 83.2 (CPh_2OCH_3), 125.5, 126.5, 127.2, 127.3, 127.5, 127.8, 128.3, 128.4 (arom. CH), 129.7 (C-4′), 134.6 (C-5′), 137.7, 141.1, 141.2 (arom. C_{ipso}) ppm. MS (FAB, NBA + NaI): *m*/*z* (%) = 629 (8) $[M + Na]^+$, 575 (<5) $[M – OCH_3]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{41}H_{39}BO_4$ (606.55): calcd. C 81.19, H 6.48; found C 81.17, H 6.73. The spectroscopic data for boronic ester **10a** were in full agreement with the literature.[10a]

(1′*R*,2′*R*,4*R*,5*R*)-2-{2′-[(*E*/*Z*)-Hex-1′′-enyl]cyclopropyl}-4,5-bis-(methoxydiphenylmethyl)-1,3,2-dioxaborolane (10b): Vinylcyclopropane **9** (0.10 g, 0.19 mmol, 1.0 equiv.), 1-hexene (0.32 g, 3.77 mmol, 20 equiv.) and Grubbs catalyst **12** (10 mg, 10 μmol, 0.05 equiv.) in dichloromethane (4 mL) were allowed to react according to the general procedure for 2 d. The boronic ester **10b** was isolated as colourless crystals (92 mg, 0.16 mmol, 83%), *E*/*Z* = 85:15. The pure *E* isomer was obtained by crystallization from *n*-pentane. (*E*)-Olefin **10b**: M.p. 113 °C. $[\alpha]_D^{20}$ = –79.7 (*c* = 1.0, $CHCl_3$). IR (film): ṽ = 3060, 3024, 2956, 2932, 2833, 1493, 1446, 1421, 1366, 1239, 1184, 1075, 1032, 1019, 965, 921, 857 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = –0.53 (ddd, *J* = 9.8, *J* = 6.5, *J* = 5.3 Hz, 1 H, 1′-H), 0.24 (ddd, *J* = 7.8, *J* = 6.4, *J* = 3.4 Hz, 1 H, 3′-H_a), 0.34 (ddd, *J* = 9.8, *J* = 6.5, *J* = 3.4 Hz, 1 H, 3′-H_b), 0.91 (t, *J* = 7.2 Hz, 3 H, 6′′-H), 1.17–1.27 (m, 1 H, 2′-H), 1.28–1.36 (m, 4 H, 4′′-H, 5′′-H), 1.95 (m, 2 H, 3′′-H), 2.99 (s, 6 H, OCH_3), 4.79 (dd, *J* = 15.1, *J* = 8.5 Hz, 1 H, 1′′-H), 5.25 (s, 2 H, 4-H, 5-H), 5.51 (dt, *J* = 15.1, *J* = 6.9 Hz, 1 H, 2′′-H), 7.27–7.34 (m, 20 H, arom. H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.8 (C-1′), 12.4 (C-6′′), 13.8 (C-3′), 21.0 (C-5′′), 22.1 (C-4′′), 27.2 (C-2′), 31.8 (C-3′′), 51.7 (CPh_2OCH_3), 77.7 (C-4, C-5), 83.3 (CPh_2OCH_3), 127.1, 127.2, 127.4, 127.7, 128.1, 128.3 (arom. CH), 129.6 (C-1′′), 133.5 (C-2′′), 141.1, 141.3 (arom. C_{ipso}) ppm. MS (FAB, NBA + NaI): *m*/*z* (%) = 609 (<5) $[M + Na]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{39}H_{43}BO_4$ (586.57): calcd. C 79.86, H 7.39; found C 79.91, H 7.31. (*Z*)-Olefin **10b** (determined from the mixture of diastereoisomers): ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.50 (ddd, *J* = 10.8, *J* = 6.5, *J* = 5.2 Hz, 1 H, 1′-H), 0.3 (overlaid with the *E* diastereoisomer, 1 H, 3′-H_a), 0.4 (overlaid with the *E* diastereoisomer, 1 H, 3′-H_b), 0.80 (t, *J* = 7.1 Hz, 3 H, 6′′-H), 1.11–1.22 (m, 7 H, 2′-H, 4′′-H, 5′′-H), 1.97 (ddt, *J* = 7.4, *J* = 2.7, *J* = 1.5 Hz, 2 H, 3′′-H), 2.99 (s, 6 H, OCH_3), 4.53 (ddt, *J* = 12.5, *J* = 11.7, *J* = 1.6 Hz,1 H, 1′′-H), 5.19 (ddt, *J* = 10.8, *J* = 7.4, *J* = 0.8 Hz,1 H, 2′′-H), 5.25 (s, 2 H, 4-H, 5-H), 7.25–7.35 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 2.2 (C-1′), 12.4 (C-3′), 16.7 (C-6′′), 21.0 (C-4′′/C-5′′), 22.4 (C-4′′/C-5′′), 29.5 (C-3′′), 31.5 (C-2′), 51.7 (CPh_2OCH_3), 77.7 (C-4, C-5), 83.4 (CPh_2OCH_3), 127.1, 127.2, 127.4, 127.7, 128.2, 128.4, 128.5, (arom. CH), 129.7 (C-1′′), 133.4 (C-2′′), 141.3, 141.4 (arom. C_{ipso}) ppm.

(1′*R*,2′*R*,4*R*,5*R*)-2-{2′-[(*E*/*Z*)-Hept-1′′-enyl]cyclopropyl}-4,5-bis-(methoxydiphenylmethyl)-1,3,2-dioxaborolane (10c): Vinylcyclopropane **9** (60 mg, 0.11 mmol, 1 equiv.), 1-heptene (110 mg, 1.10 mmol, 10 equiv.) and Grubbs catalyst **12** (6 mg, 0.05 mmol, 0.05 equiv.) in dichloromethane (4 mL) were allowed to react according to the general procedure for 1 d. The boronic ester **10c** was isolated as colourless crystals (55 mg, 90 μmol, 81%), *E*/*Z* = 85:15. The analytical data were determined from the mixture of diastereoisomers; softening range 98–107 °C. IR (film): ṽ = 3088, 3058, 3024, 2955, 2927, 2854, 2833, 1493, 1445, 1420, 1400, 1364, 1238, 1183, 1074, 1032, 1018, 1002, 963, 941, 920 cm^{-1}. (*E*)-Olefin **10c**: ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.47 (ddd, *J* = 9.8, *J* = 6.5, *J* = 5.3 Hz, 1 H, 1′-H), 0.29 (ddd, *J* = 7.8, *J* = 6.3, *J* = 3.4 Hz, 1 H, 3′-Ha), 0.39 (ddd, *J* = 9.8, *J* = 6.5, *J* = 3.4 Hz, 1 H, 3′-H_b), 0.91 (t, *J* = 7.2 Hz, 3 H, 7′′-H), 1.17–1.27 (m, 1 H, 2′-H), 1.28–1.36 (m, 6 H, 4′′-H, 5′′-H, 6′′-H), 1.95 (m, 2 H, 3′′-H), 2.99 (s, 6 H, OCH_3), 4.79 (dt, *J* = 15.1, *J* = 8.5 Hz, 1 H, 2′′-H), 5.25 (s, 2 H, 4-H, 5-H), 5.51 (dd, *J* = 15.1, *J* = 6.9 Hz, 1 H, 1′′-H), 7.27–7.34 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 1.8 (C-1′), 12.4 (C-7′′), 12.9 (C-3′), 16.7 (C-6′′), 21.0 (C-5′′), 22.1 (C-4′′), 27.2 (C-2′), 31.8 (C-3′′), 51.7 (CPh_2OCH_3), 77.4 (C-4, C-5), 83.2 (CPh_2OCH_3), 127.1, 127.2, 127.4, 127.7, 128.1, 128.3, (arom. CH), 129.6 (C-1′′), 133.4 (C-2′′), 141.1, 141.3 (arom. C_{ipso}) ppm. (*Z*)-Olefin **10c**: ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.50 (ddd, *J* = 10.8, *J* = 6.5, *J* = 5.2 Hz, 1 H, 1′-H), 0.29 (overlaid with the *E* diastereoisomer, 1 H, 3′-H_a), 0.39 (overlaid with the *E* diastereoisomer, 1 H, 3′-H_b), 0.80 (t, *J* = 7.1 Hz, 3 H, 7′′-H), 1.11–1.22 (m, 7 H, 2′-H, 4′′-H, 5′′-H, 6′′-H), 1.97 (ddt, *J* = 7.4, *J* = 2.7, *J* = 1.5 Hz, 2 H, 3′′-H), 2.99 (s, 6 H, OCH_3), 4.53 (ddt, *J* = 12.5, *J* = 11.7, *J* = 1.6 Hz, 1 H, 1′′-H), 5.19 (ddt, *J* = 10.8, *J* = 7.4, *J* = 0.8 Hz, 1 H, 2′′-H), 5.25 (s, 2 H, 4-H, 5-H), 7.25–7.35 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 2.2 (C-1′), 12.4 (C-3′), 16.7 (C-7′′), 21.0 (C-4′′, C-5′′, C-6′′), 22.4 (C-4′′, C-5′′, C-6′′), 29.5 (C-3′′), 31.5 (C-2′), 32.3 (C-4′′, C-5′′, C-6′′), 51.7 (CPh_2OCH_3), 77.7 (C-4, C-5), 83.4 (CPh_2OCH_3), 127.1, 127.2, 127.4, 127.7, 128.2, 128.4, 128.5, (arom. CH), 129.7 (C-2′′), 133.4 (C-2′′), 141.3, 141.4 (arom. C_{ipso}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 600 (<1) $[M]^+$, 568 (1) $[M – CH_3OH]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{40}H_{41}BO_4$ (600.59): calcd. C 79.99, H 7.55; found C 79.63, H 7.33.

(1′*R*,2′*R*,4*R*,5*R*)-4,5-Bis(methoxydiphenylmethyl)-2-{2′-[(*E*/*Z*)-3′′-(trimethylsilyl)prop-1′′-enyl]cyclopropyl}-1,3,2-dioxaborolane (10d): Vinylcyclopropane **9** (0.15 g, 0.28 mmol, 1.0 equiv.), allyltrimethylsilane (0.32 g, 2.8 mmol, 10 equiv.) and Grubbs catalyst **12** (10 g, 10 mmol, 0.04 equiv.) in dichloromethane (6 mL) were allowed to react according to the general procedure for 1 d. The boronic ester **10d** was isolated as colourless crystals (123 mg, 0.20 mmol, 70%); *E*/*Z* = 50:50. The analytical data were determined from the mixture of diastereoisomers; softening range 66–73 °C. IR (film): ṽ = 3058, 3025, 2999, 2853, 2904, 2898, 2832, 1493, 1446, 142, 1393, 1363, 1245, 1184, 1156, 1075, 1032, 1016, 964, 839, 774, 756, 698 cm^{-1}. (*E*)-Olefin **10d**: ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.43 (ddd, $^3J_{1'',3'b}$ = 9.8, *J* = 6.5, *J* = 5.1 Hz, 1 H, 1′-H), 0.05 [s, 9 H, Si(CH_3)$_3$], 0.31 (ddd, *J* = 9.7, *J* = 6.5, *J* = 3.4 Hz, 1 H, 3′-H_a), 0.42 (ddd, *J* = 9.8, *J* = 8.6, *J* = 3.4 Hz, 1 H, 3′-H_b), 1.39 (dddd, *J* = 9.7, *J* = 9.5, *J* = 8.6, *J* = 5.1 Hz, 1 H, 2′-H), 1.42 (dd, *J* = 7.9, *J* = 1.4 Hz, 1 H, 3′′-H), 3.10 (s, 6 H, OCH_3), 4.75 (ddt, *J* = 15.1, *J* = 9.5, *J* = 1.4 Hz, 1 H, 1′′-H), 5.36 (s, 2 H, 4-H, 5-H), 5.46 (ddt, *J* = 15.1, *J* = 7.9, *J* = 0.6 Hz, 1 H, 2′′-H), 7.35–7.46 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = –2.01 [Si(CH_3)$_3$], 11.4 (C-3′), 22.5 (C-2′), 51.7 (CPh_2OCH_3), 77.5 (C-4, C-5), 83.3 (CPh_2OCH_3), 123.9 (C-2′′), 127.1, 127.2, 127.4, 127.7, 128.4, (arom. CH), 132.1 (C-1′′), 141.1, 141.3 (arom. C_{ipso}) ppm. (*Z*)-Olefin **10d**: ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.39 (ddd, *J* = 9.9, *J* = 6.6, *J* = 5.3 Hz, 1 H, 1′-H), 0.05 [s, 9 H, Si(CH_3)$_3$], 0.38 (ddd, *J* = 9.8, *J* = 6.5, *J* = 3.5 Hz, 1 H, 3′-H_a), 0.52 (ddd, *J* = 9.9, *J* = 8.6, *J* = 3.5 Hz, 1 H, 3′-H_b), 1.49 (dddd, *J* = 10.8, *J* = 9.8, *J* = 8.6, *J* = 5.3 Hz, 1 H, 2′-H), 1.58 (dd, *J* = 9.6, *J* = 1.4 Hz, 1 H, 3′′-H), 3.11 (s, 6 H, OCH_3),

4.63 (ddt, J = 12.2, J = 10.8, J = 1.4 Hz, 1 H, 1′′-H), 5.33–5.40 (m, overlaid with the E diastereoisomer, 1 H, 2′′-H), 5.36 (s, 2 H, 4-H, 5-H), 7.35–7.46 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = –1.91 [Si(CH_3)$_3$], 12.4 (C-3′), 21.1 (C-2′), 53.3 (CPh_2OCH_3), 77.7 (C-4, C-5), 83.4 (CPh_2OCH_3), 124.0 (C-2′′), 127.1, 127.2, 127.4, 127.7, 128.4, (arom. CH), 132.1 (C-1′′), 141.2, 141.3 (arom. C_{ipso}) ppm; (C-1′) was not detectable in the spectrum. $C_{39}H_{45}BO_4Si$ (616.66): calcd. C 75.96, H 7.36; found C 75.83, H 7.31. MS (FAB, NBA + NaI): m/z (%) = 639 (10) $[M + Na]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{39}H_{54}BO_4Si$ (616.66): calcd. C 75.96, H 7.36; found C 75.83, H 7.31.

(1′*R*,2′*R*,4*R*,5*R*)-4,5-Bis(methoxydiphenylmethyl)-2-{2′-[(*E*/*Z*)-(2′′-triethylsilyloxymethyl)ethenyl]cyclopropyl}-1,3,2-dioxaborolane (10e): Vinylcyclopropane **9** (0.15 g, 0.28 mmol, 1.0 equiv.), triethylsilyl-protected allyl alcohol (0.73 g, 4.24 mmol, 15 equiv.) and Grubbs catalyst **12** (10 g, 10 μmol, 0.04 equiv.) in dichloromethane (6 mL) were allowed to react according to the general procedure for 1 d. The boronic ester **10e** was isolated as colourless crystals (173 mg, 0.26 mmol, 90%); *E*/*Z* = 85:15. The analytical data were determined from the mixture of diastereoisomers; softening range 56–61 °C. IR (film): $\tilde{\nu}$ = 3088, 3059, 3022, 2954, 2936, 2881, 2834, 1507, 1493, 1447, 1366, 1321, 1239, 1197, 1155, 1074, 1032, 967, 947, 924, 891, 844, 791, 757, 745, 732, 697, 667 cm^{-1}. (*E*)-Olefin **10e**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = –0.47 (ddd, J = 9.9, J = 6.6, J = 5.2 Hz, 1 H, 1′-H), 0.27 (ddd, J = 10.2, J = 6.6, J = 3.5 Hz, 1 H, 3′-H$_a$), 0.39 (ddd, J = 9.9, J = 8.6, J = 3.5 Hz, 1 H, 3′-H$_b$), 0.57 (q, J = 7.9 Hz, 6 H, 4′′-H), 0.93 (t, J = 7.9 Hz, 9 H, 5′′-H), 1.32 (dddd, J = 10.2, J = 8.7, J = 8.6, J = 5.2 Hz, 1 H, 2′-H), 2.99 (s, 6 H, OCH_3), 4.02 (dd, J = 5.5, J = 1.5 Hz, 2 H, 3′′-H), 4.97 (ddt, J = 15.2, J = 8.7, J = 1.5 Hz, 1 H, 1′′-H), 5.26 (s, 2 H, 4-H, 5-H), 5.51 (dt, J = 15.2, J = 5.7 Hz, 1 H, 2′′-H), 7.25–7.35 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 4.5 (C-4′′), 6.7 (C-5′′), 12.6 (C-3′), 20.5 (C-2′), 51.7 (CPh_2OCH_3), 63.4 (C-3′′), 77.6 (C-4, C-5), 83.3 (CPh_2OCH_3), 126.9 (C-2′′), 127.2, 127.3, 127.5, 127.8, 128.4, 129.7 (arom. CH), 135.0 (C-1′′), 141.1, 141.3 (arom. C_{ipso}) ppm; (C-1′) was not detectable in the spectrum. MS (EI, 70 eV): m/z (%) = 674 (<5) $[M]^+$, 643 (6) $[M - CH_3OH]^+$, 543 (8) $[M - (C_2H_5)_3SiO]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{42}H_{51}BO_5Si$ (674.74): calcd. C 74.76, H 7.62; found C 74.63, H 7.65.

(*E*)-1,2-Bis{(1*R*,2*R*)-2-[(4*R*,5*R*)-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolan-2-yl]cyclopropyl}ethene (13). Method A: Vinylcyclopropane **9** (0.10 g, 0.18 mmol, 1.0 equiv.) and Grubbs catalyst **11** (10 mg, 10 μmol, 0.015 equiv.) in dichloromethane (2 mL) were allowed to react according to the general procedure for 6 d. The boronic ester **13** was isolated as colourless crystals (79 mg, 76 μmol, 81%). B) Vinylcyclopropane **9** (280 mg, 0.57 mmol, 1 equiv.) and Grubbs catalyst **12** (10 mg, 10 μmol, 0.02 equiv.) in dichloromethane (8 mL) were allowed to react according to the general procedure for 1 d. The boronic ester **13** was isolated as colourless crystals (287 mg, 0.27 mmol, 95%); softening range 143–151 °C. $[a]_D^{21}$ = –119.5 (c = 0.63, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3023, 2993, 2904, 2897, 1445, 1421, 1361, 1319, 1248, 1236, 1183, 1157, 1032, 1018, 1001, 966, 950, 915, 870, 850, 795, 769 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = –0.56 (ddd, J = 9.8, J = 6.4, J = 5.3 Hz, 2 H, 2′-H), 0.17 (ddd, J = 7.8, J = 6.4, J = 3.4 Hz, 2 H, 3′-H$_a$), 0.26 (ddd, J = 9.8, J = 9.9, J = 5.3, J = 3.4 Hz, 2 H, 3′-H$_b$), 1.18 (dddd, J = 9.9, J = 9.8, J = 7.8, J = 5.2, J = 2.6 Hz, 2 H, 1′-H), 2.97 (s, 12 H, OCH_3), 4.74 (dd, J = 5.2, J = 2.6 Hz, 2 H, 1-H), 5.23 (s, 4 H, 4′′-H, 5′′-H), 7.23–7.31 (m, 40 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 1.8 (C-2′), 12.5 (C-1′), 20.8 (C-3′), 51.7 (CPh_2OCH_3), 77.5 (C-4′′, C-5′′), 83.2 (CPh_2OCH_3), 127.1, 127.2, 127.4, 127.7, 128.4, 129.6 (arom. CH), 131.4 (C-1), 141.1, 141.3 (arom. C_{ipso}) ppm. MS (FAB, NBA + NaI): m/z (%) = 1055 (10) $[M + Na]^+$, 1024 (<5) $[M + Na - OCH_3]^+$, 197 (100) $[Ph_2CO-CH_3]^+$. $C_{68}H_{66}B_2O_8$ (1032.87): calcd. C 79.07, H 6.45; found C 78.81, H 6.44.

Synthesis by Wittig-Type Olefination

(1′*S*,2′*S*,4*R*,5*R*)-2-(2′-Formylcyclopropyl)-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (14): Cyclopropylmethanol **4** (8.80 g, 16.5 mmol, 1 equiv.) was dissolved in dichloromethane (500 mL) and Dess–Martin periodinane **7** (7.7 g, 18.2 mmol, 1.1 equiv.) was added. The reaction mixture was stirred for 24 h at room temp., quenched with a 1 M aq. solution of $Na_2S_2O_3$ (250 mL) and aq. saturated $NaHCO_3$ (250 mL) and finally extracted with dichloromethane (3 × 300 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **14** was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 9:1) to afford the aldehyde **14** (8.33 g, 15.6 mmol, 95%) as colourless crystals; m.p. 79–85 °C. $[a]_D^{20}$ = –60.5 (c = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3060, 3025, 2940, 2833, 2729, 1709, 1446, 1426, 1396, 1309, 1190, 1074, 1033, 1015, 967, 924, 897, 758, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.23 (ddd, J = 10.1, J = 7.1, J = 4.9 Hz, 1 H, 1′-H), 0.91 (ddd, J = 10.1, J = 5.6, J = 4.0 Hz, 1 H, 3′-H$_a$), 1.05 (ddd, J = 8.1, J = 7.1, J = 4.0 Hz, 1 H, 3′-H$_b$), 1.23 (m, 1 H, 2′-H), 3.08 (s, 6 H, OCH_3), 5.32 (s, 2 H, 4-H, 5-H), 7.04–7.12 (m, 20 H, arom. H), 8.52 (d, J = 6.4 Hz, 1 H, 4′-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 2.0 (C-1′), 11.4 (C-2′), 28.3 (C-3′), 51.8 (CPh_2OCH_3), 77.8 (C-4, C-5), 83.2 (CPh_2OCH_3), 127.4, 127.6, 127.7, 127.9, 128.3, 129.7 (arom. CH), 140.9 (arom. C_{ipso}), 200.2 (CH=O) ppm. MS (EI, 70 eV): m/z (%) = 532 (<5) $[M]^+$, 501 (<5) $[M - OCH_3]^+$, 197 (100) $[Ph_2COCH_3]^+$. MS (+EMS): m/z (%) = 555 (24) $[M + Na]^+$, 197 (29) $[Ph_2COCH_3]^+$. $C_{34}H_{33}BO_5$ (532.43): calcd. C 76.70, H 6.25; found C 76.43, H 6.25.

(1′*S*,2′*S*,4*R*,5*R*)-2-{2-[(*E*)-2-Methoxycarbonylethenyl]cyclopropyl}-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (6): Trimethyl phosphonoacetate (2.58 g, 14.2 mmol, 2 equiv.) was added dropwise through a cannula to a stirred suspension of NaH (95%, 0.34 g, 14.2 mmol, 2 equiv.) in anhydrous THF (30 mL) at 0 °C under dry N_2. After 1 h aldehyde **14** (3.78 g, 7.10 mmol, 1 equiv.) in anhydrous THF (30 mL) was added dropwise. The resulting reaction mixture was stirred for 2 d at room temp., then quenched with aq. saturated NH_4Cl (40 mL) and extracted with Et_2O (3 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **6** was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 9:1) to furnish the ester **6** (6.81 g, 11.6 mmol, 90%) as colourless crystals; m.p. 90–95 °C. $[a]_D^{20}$ = +21.0 (c = 0.3, $CHCl_3$). IR (Film): $\tilde{\nu}$ = 3058, 3025, 2950, 2834, 1720, 1651, 1494, 1422, 1370, 1263, 1193, 1147, 1076, 1033, 1016, 969, 939, 856, 759, 738, 703 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = –0.22 (ddd, J = 9.8, J = 7.1, J = 5.1 Hz, 1 H, 1′-H), 0.61 (ddd, J = 9.8, J = 4.8, J = 3.7 Hz, 1 H, 3′-H$_a$), 0.78 (ddd, J = 7.6, J = 7.1, J = 3.7 Hz, 1 H, 3′-H$_b$), 1.01 (dddd, J = 10.1, J = 7.6, J = 5.1, J = 4.8 Hz, 1 H, 2′-H), 2.95 (s, 6 H, CPh_2OCH_3), 3.64 (s, 3 H, CO_2CH_3), 5.26 (s, 2 H, 4-H, 5-H), 5.78 (d, J = 15.4 Hz, 1 H, 2′′-H), 6.19 (dd, J = 15.4, J = 10.1 Hz, 1 H, 1′′-H), 7.25–7.32 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 2.0 (C-1′), 14.1 (C-3′), 21.0 (C-2′), 51.3 (CPh_2OCH_3), 51.7 (CO_2CH_3), 77.5 (C-4, C-5), 83.3 (CPh_2OCH_3), 117.9 (C-2′′), 127.2, 127.3, 127.6, 127.8, 128.4, 129.7 (arom. CH), 141.0, 141.1 (arom. C_{ipso}), 154.1 (C-1′′), 167.0 (CO_2CH_3) ppm. MS (FAB, NBA + NaI): m/z (%) = 611 (32) $[M + Na]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{37}H_{37}BO_6$ (588.50): calcd. C 75.51, H 6.34; found C 75.50, H 6.52.

(1′*S*,2′*S*,4*R*,5*R*)-2-{2-[(*E*)-2-Hydroxymethylethenyl]cyclopropyl}-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (15): DIBAL-

H (1 M in THF, 29.4 mL, 29.4 mmol, 3.0 equiv.) was added dropwise through a cannula to a stirred solution of ester **6** (5.76 g, 9.79 mmol, 1.0 equiv.) in anhydrous THF (150 mL) at –78 °C under N_2. After stirring for 3 h at –78 °C the reaction mixture was slowly warmed to room temp. and stirred overnight. It was then quenched with distilled H_2O (5 mL) and NaOH (8 mL of a 2 M aq. solution). After additional stirring for 30 min at room temp., a white precipitate was filtered off and washed thoroughly with Et_2O. The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **15** was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 8:2) to furnish alcohol **15** (4.89 g, 89%) as colourless crystals; m.p. 153–154 °C. $[\alpha]_D^{20}$ = –23.0 (*c* = 1.3, $CHCl_3$). IR (Film): $\tilde{\nu}$ = 3130, 3080, 3012, 2949, 2870, 1720, 1650, 1494, 1446, 1422, 1369, 1304, 1263, 1193, 1147, 1076, 1033, 1016, 969, 759, 736, 702, 650, 636 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.47 (ddd, *J* = 9.6, *J* = 6.8, *J* = 5.1 Hz, 1 H, 1′-H), 0.42 (ddd, *J* = 9.6, *J* = 5.1, *J* = 3.5 Hz, 1 H, 3′-H_a), 0.62 (ddd, *J* = 7.6, *J* = 6.8, *J* = 3.5 Hz, 1 H, 3′-H_b), 0.92 (dddd, *J* = 9.0, *J* = 7.6, *J* = 5.1, *J* = 5.1 Hz, 1 H, 2′-H), 1.13 (t, *J* = 5.9 Hz, 1 H, O*H*), 3.01 (s, 6 H, CPh_2OCH_3), 3.98–4.03 (m, 2 H, 1‴-H), 4.96 (dd, *J* = 15.2, *J* = 9.0 Hz, 1 H, 1″-H), 5.24 (s, 2 H, 4-H, 5-H), 5.61 (dt, *J* = 15.2, *J* = 5.9 Hz, 1 H, 2″-H), 7.25–7.32 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 2.0 (C-1′), 12.4 (C-3′), 20.4 (C-2′), 51.5 (CPh_2OCH_3), 63.4 (CH_2OH), 77.3 (C-4, C-5), 83.9 (CPh_2OCH_3), 126.5 (C-1″), 126.9, 127.3, 127.5, 127.6, 128.3, 129.5 (arom. CH), 137.2 (C-2″), 140.9, 141.0 (arom. C_{ipso}) ppm. MS (EI, 70 eV): *m*/*z* (%) = 560 (<0.1) $[M]^+$, 528 (1.5) $[M - CH_2OH]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{36}H_{37}BO_5$ (560.49): calcd. C 77.14, H 6.65; found C 76.80, H 6.73.

(*E*)-3-{(1*S*,2*S*)-2-[(4*R*,5*R*)-4,5-Bis(methoxydiphenylmethyl)-1,3,2-dioxaborolan-2-yl]cyclopropyl}acrylaldehyde (16): Alcohol **15** (4.50 g, 8.03 mmol, 1.0 equiv.) was dissolved in dichloromethane (270 mL) and Dess–Martin periodinane **7** (3.75 g, 8.83 mmol, 1.1 equiv.) was added. The reaction mixture was stirred for 1 h at room temp., quenched with aq. $Na_2S_2O_3$ (150 mL of a 1 M solution) and aq. saturated $NaHCO_3$ (150 mL) and finally extracted with dichloromethane (3 × 200 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **16** was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 9:1) to furnish aldehyde **16** (4.26 g, 7.63 mmol, 95%) as colourless crystals; m.p. 72–75 °C. $[\alpha]_D^{20}$ = +51.3 (*c* = 1.00, $CHCl_3$). IR (Film): $\tilde{\nu}$ = 3063, 3023, 2940, 2830, 1735, 1683, 1634, 1495, 1447, 1422, 1394, 1370, 1340, 1241, 1185, 1110, 1075, 1033, 1014, 968, 940, 926, 865, 758, 734 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = –0.07 (ddd, *J* = 9.4, *J* = 7.1, *J* = 5.3 Hz, 1 H, 1′-H), 0.76 (ddd, *J* = 9.4, *J* = 5.1, *J* = 4.3 Hz, 1 H, 3′-H_a), 0.96 (ddd, *J* = 7.6, *J* = 7.1, *J* = 4.3 Hz, 1 H, 3′-H_b), 1.18 (m, 1 H, 2′-H), 3.06 (s, 6 H, OCH_3), 5.32 (s, 2 H, 4-H, 5-H), 5.98 (dd, *J* = 9.8, *J* = 15.3 Hz, 1 H, 1″-H), 6.15 (dd, *J* = 7.7, *J* = 15.3 Hz, 1 H, 2″-H), 7.18–7.51 (m, 20 H, arom. H), 9.35 (d, *J* = 7.9 Hz, 1 H, 3″-H) ppm. ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 2.0 (C-1′), 15.1 (C-3′), 21.7 (C-2′), 51.7 (CPh_2OCH_3), 77.7 (C-4, C-5), 83.2 (CPh_2OCH_3), 127.3, 127.4, 127.7, 127.9, 128.4, 129.7 (arom. CH), 130.5 (C-2″), 140.9, 141.0 (arom. C_{ipso}), 163.6 (C-1″), 193.1 (*C*H=O) ppm. MS (+EMS): *m*/*z* (%) = 581 (100) $[M + Na]^+$. $C_{36}H_{35}BO_5 \cdot ½H_2O$ (567.26): calcd. C 76.21, H 6.39; found C 76.06, H 6.39.

(1′*S*,2′*S*,4*R*,5*R*)-{2′-[(1″*E*,3″*Z*)-Hexa-1″,3″-dienyl]cyclopropyl}-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (17): Representative procedure for Wittig olefination – Scheme 3, entry 4. A solution of *n*-propyltriphenylphosphonium bromide (10.2 g, 26.5 mmol, 4.0 equiv.) and KHMDS (5.29 g, 26.5 mmol, 4.0 equiv.) in anhydrous THF (300 mL) was stirred under dry N_2 at room temp. The orange solution of the formed ylide was stirred for 30 min and cooled to –78 °C. Then the aldehyde **16** (3.70 g, 6.63 mmol, 1.0 equiv.) in anhydrous THF (50 mL) was added dropwise through a cannula over 5 min. The reaction mixture was stirred for 1 h at –78 °C and then slowly warmed to room temp. and stirred overnight. The reaction mixture was quenched with aq. saturated $NaHCO_3$ (150 mL) and extracted with Et_2O (3 × 150 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **17** was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 95:5) to furnish the (*Z*)-olefin **17** (3.72 g, 6.36 mmol, 96%) as colourless crystals; *Z*/*E* = 97:3 (as judged by 600 MHz ^1H NMR spectroscopy). The minor *E* isomer **17** was removed by a single recrystallization from *n*-pentane. (*Z*)-Olefin **17**; m.p. 88–89 °C. $[\alpha]_D^{20}$ = +13.1 (*c* = 1.25, $CHCl_3$). IR (Film): $\tilde{\nu}$ = 3063, 3024, 2960, 2933, 2870, 2836, 1494, 1447, 1420, 1407, 1390, 1368, 1338, 1235, 1195, 1183, 1076, 1062, 1033, 1017, 1002, 985, 964, 949, 941, 920, 899, 870, 853, 794, 775, 759, 747, 732, 672, 663, 655 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = –0.39 (ddd, *J* = 9.0, *J* = 7.2, *J* = 5.1 Hz, 1 H, 1′-H), 0.49 (ddd, *J* = 9.0, *J* = 4.9, *J* = 3.6 Hz, 1 H, 3′-H_a), 0.69 (ddd, *J* = 10.9, *J* = 7.2, *J* = 3.6 Hz, 1 H, 3′-H_b), 0.95 (m, 1 H, 2′-H), 1.02 (t, *J* = 7.6 Hz, 3 H, 6″-H), 2.21 (m_c, 2 H, 5″-H), 3.01 (s, 6 H, OCH_3), 5.15 (dd, *J* = 9.2, *J* = 15.1 Hz, 1 H, 1″-H), 5.27 (dd, *J* = 10.9, *J* = 7.7 Hz, 1 H, 4″-H), 5.28 (s, 2 H, 4-H, 5-H), 5.82 (t, *J* = 10.9 Hz, 1 H, 3″-H), 6.31 (dd, *J* = 15.1, *J* = 10.9 Hz, 1 H, 2″-H), 7.21–7.56 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 3.0 (C-1′), 13.3 (C-3′), 14.4 (C-6″), 21.0 (C-5″), 21.6 (C-2′), 51.7 (CPh_2OCH_3), 77.5 (C-4, C-5), 83.3 (CPh_2OCH_3), 123.9 (C-2″), 127.1, 127.3, 127.5, 127.7, 129.1, 129.7 (arom. CH), 128.4 (C-3″), 130.9 (C-4″), 137.9 (C-1″), 141.2, 141.3 (arom. C_{ipso}) ppm. MS (+EPI): *m*/*z* (%) = 607 (33) $[M + Na]^+$, 413 (20), 381 (100), 249 (30), 218 (12), 197 (90) $[Ph_2COCH_3]^+$. $C_{39}H_{41}BO_4$ (584.55): calcd. C 80.13, H 7.07; found C 80.57, H 7.33.

5-(*n*-Pentylsulfonyl)-1-phenyl-1*H*-tetrazole (19): DEAD (40% solution in THF, 38 g, 87.4 mmol, 1.1 equiv.) was added dropwise to a stirred solution of *n*-pentanol (7.00 g, 79.4 mmol, 1.0 equiv.), triphenylphosphane (22.9 g, 87.4 mmol, 1.1 equiv.) and 1-phenyl-1*H*-tetrazole-5-thiol (**18**; 15.6 g, 87.4 mmol, 1.1 equiv.) in THF (250 mL) at room temp. The solution was stirred at room temp. overnight. After concentration under reduced pressure, the residue was treated with a mixture of petroleum ether/ethyl acetate (5:1). The precipitate was removed by filtration and the solid washed three times with the same mixture of solvents. The filtrate was concentrated and the residue purified by flash column chromatography (silica gel, dichloromethane) to furnish the thioether **18a** (19.9 g, 80.1 mmol, 92%) as an oil. IR (Film): $\tilde{\nu}$ = 2957, 2929, 2859, 1597, 1499, 1463, 1438, 1410, 1385, 1277, 1241, 1176, 1119, 1087, 1074, 1054, 1015, 978, 914, 759, 721, 693 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 0.89 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.42 (m, 4 H, 3′-H, 4′-H), 1.83 (tt, *J* = 7.3, *J* = 7.3 Hz, 2 H, 2′-H), 3.39 (t, *J* = 7.3 Hz, 2 H, 1′-H), 7.44–7.69 (m, 5 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.9 (CH_3), 22.1 (CH_2), 28.8 (CH_2), 30.7 (CH_2), 33.3 (CH_2), 123.8, 129.8, 130.1 (arom. CH), 133.7 (arom. C_{ipso}), 154.5 (*C*S) ppm. MS (+EPI): *m*/*z* (%) = 249 (100) $[M + 1]^+$.

$NaHCO_3$ (32.1 g, 382.5 mmol, 5 equiv.) followed by a solution of MCPBA (33.0 g, 191 mmol, 2.5 equiv.) in dichloromethane (300 mL) were added to a stirred solution of thioether **18a** (19.0 g, 76.5 mmol, 1.0 equiv.) in dichloromethane (300 mL). Stirring was continued at room temp. overnight. The mixture was poured into a solution of aq. saturated $NaHCO_3$ (200 mL) and $Na_2S_2O_3$ (200 mL), the organic layer was separated and the aqueous layer extracted with dichloromethane (3 × 300 mL). The combined or-

ganic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **19** was purified by flash column chromatography (silica gel, dichloromethane) to furnish sulfone **19** (18.9 g, 67.4 mmol, 88%) as orange crystals; m.p. 37–39 °C. IR (film): $\tilde{\nu}$ = 2954, 2932, 2871, 1728, 1594, 1497, 1459, 1426, 1399, 1348, 1301, 1255, 1229, 1153, 1107, 1077, 1058, 1015, 998, 926, 768, 729, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 600 MHz): δ = 0.92 (t, J = 7.2 Hz, 3 H, CH_3), 1.42 (m_c, 4 H, 2 CH_2), 1.95 (m_c, 2 H, CH_2), 3.73 (m_c, 2 H, 1′-H), 7.57–7.72 (m, 5 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.1 (CH_3), 22.0 (CH_2), 22.4 (CH_2), 30.6 (CH_2), 56.4 (CH_2), 125.5, 130.1, 131.9 (arom. CH), 133.5 (arom. C_{ipso}), 153.9 (*C*S) ppm. MS (+EMS): *m*/*z* (%) = 303 (65) [M + Na]$^+$, 281 (100) [M + 1]$^+$. The spectroscopic data for sulfone **19** were in full agreement with those reported in the literature.[22a]

Synthesis of Boronic Ester 10b

Representative Procedure for the Wittig–Schlosser Olefination (Scheme 4, Entry 4): *n*BuLi (1.6 M in hexane, 0.12 mL, 0.19 mmol, 1 equiv.) was added dropwise through a cannula to a stirred solution of *n*-pentyltriphenylphosphonium bromide (0.08 g, 0.19 mmol, 1.0 equiv.) and LiBr (0.10 g, 1.13 mmol, 6.0 equiv.) in anhydrous THF (2 mL) and diethyl ether (1.5 mL) at room temp. under dry N_2. After 20 min of vigorous stirring at room temp., the red solution was cooled to –78 °C and aldehyde **8** (0.10 g, 0.19 mmol, 1.0 equiv.) in THF (1 mL) was added. Stirring was continued for 20 min at –30 °C before *n*BuLi (1.4 M in hexane, 0.13 mL, 0.19 mmol, 1.0 equiv.) was added. The resulting dark-red betaine ylide solution was kept for 30 min at room temp. and for 15 min at –78 °C. Then a 2 M solution of HCl in diethyl ether (0.09 mL, 0.19 mmol, 1.0 equiv.) was added causing immediate decolourization. The cooling bath was removed and the reaction was stirred for 10 min at room temp. KO*t*Bu (0.02 g, 0.19 mmol, 1.0 equiv.) was added and the reaction mixture was stirred for an additional 1 h and then quenched with H_2O (1 mL), diluted with Et_2O (4 mL) and H_2O (4 mL) and extracted with Et_2O (3 × 4 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **10b** was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 95:5) to furnish olefin **10b** (0.08 g, 0.14 mmol, 70%) as colourless crystals; *E*/*Z* = 80:20 (as judged by 300 MHz ^1H NMR spectroscopy).

Representative Procedure for the Julia–Kocienski Olefination (Scheme 5, Entry 8). Method A: A solution of KHMDS (0.07 g, 0.34 mmol, 1.8 equiv.) in anhydrous DME (2 mL) was added dropwise through a cannula to a stirred solution of the sulfone **19** (0.08 g, 0.28 mmol, 1.5 equiv.) in anhydrous DME (4 mL) over 5 min at –60 °C under dry N_2. The yellow-orange solution was stirred for 5 min and the aldehyde **8** (0.10 g, 0.19 mmol, 1.0 equiv.) in anhydrous DME (2 mL) was added dropwise through a cannula over 5 min. Stirring was continued for 10 min at –60 °C. The reaction was then quenched with H_2O (1 mL) and the mixture vigorously stirred whilst warming to room temp. It was then diluted with Et_2O (4 mL) and H_2O (4 mL) and extracted with Et_2O (3 × 4 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **10b** was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 95:5) to afford the (*E*)-olefin **10b** (0.10 g, 0.17 mmol, 93%) as colourless crystals; *E*/*Z* > 99:1 (as judged by 300 MHz ^1H NMR spectroscopy). The minor *Z* isomer **6** was only detected by 600 MHz ^1H NMR spectroscopy (*E*/*Z* = 98:2) and was removed by a single recrystallization from *n*-pentane.

Representative Procedure on a Larger Scale According to Scheme 5, Entry 8. Method A: Sulfone **19** (2.92 g, 10.4 mmol, 1.5 equiv.) in anhydrous DME (60 mL), a solution of KHMDS (2.5 g, 12.5 mmol, 1.8 equiv.) in anhydrous DME (45 mL) and aldehyde **8** (3.7 g, 6.95 mmol, 1 equiv.) in anhydrous DME (45 mL) were used. Yield of ester **10b**: 3.98 g (6.77 mmol, 91%).

Representative Procedure for the Julia–Kocienski Olefination (Scheme 5, Entry 6). Method B: A solution of KHMDS (0.07 g, 0.34 mmol, 1.8 equiv.) in anhydrous DME (4 mL) was added dropwise through a cannula to a stirred solution of the aldehyde **8** (0.10 g, 0.19 mmol, 1.0 equiv.) and sulfone **19** (0.07 g, 0.24 mmol, 1.3 equiv.) in anhydrous DME (4 mL) over 20 min at –60 °C under dry N_2. Stirring was continued for 15 min at –60 °C and then quenched with H_2O (0.3 mL). The mixture was stirred vigorously whilst warming to room temp. and then diluted with Et_2O (4 mL) and H_2O (4 mL) and extracted with Et_2O (3 × 4 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product **10b** was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate, 95:5) to furnish olefin **10b** (*E*/*Z* > 99:1 as judged by 300 MHz NMR spectroscopy; 0.08 g, 0.14 mmol, 73%) as colourless crystals.

The analytical data for boronic ester **10b** were presented in the cross-metathesis section (see above).

Synthesis by Cross-Coupling

(1′*R*,2′*R*,4*R*,5*R*)- and (1′*S*,2′*S*,4*R*,5*R*)-2-(2′-Iodocyclopropyl)-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (22a and 22b): [$RuCl_3$·3H_2O] (0.06 g, 0.24 mmol, 0.05 equiv.) was added to a vigorously stirred solution of cyclopropylmethanol **3** (2.61 g, 4.88 mmol, 1.0 equiv.) and $NaIO_4$ (3.13 g, 14.65 mmol, 3.0 equiv.) in a mixture of CCl_4/H_2O/CH_3CN (6 mL/8 mL/6 mL) at room temp. The reaction was heated at reflux for 2–3 h at 40 °C and then aq. saturated NH_4Cl (60 mL) was added. The reaction mixture was filtered through a pad of Celite and washed with ethyl acetate. The aqueous layer was extracted with ethyl acetate (3 × 80 mL) and the combined organic layers were dried ($MgSO_4$) and the solvent removed under reduce pressure. The crude product **20** was purified by column chromatography (petroleum ether/ethyl acetate, 8:2 + 1% AcOH) to furnish the carboxylic acid **20** as colourless crystals (2.41 g, 4.40 mmol, 90%); m.p. 188–189 °C. $[\alpha]_D^{21}$ = –111.9 (*c* = 1.00, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3027, 2950, 2902, 2834, 1690, 1487, 1446, 1402, 1334, 1295, 1243, 1192, 1077, 1026, 959, 923, 699, 653, 601 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.21 (ddd, J = 10.4, J = 7.6, J = 5.0 Hz, 1 H, 1′-H), 0.39 (ddd, J = 10.5, J = 7.6, J = 3.1 Hz, 1 H, 3′-H_a), 0.98 (ddd, J = 10.4, J = 7.5, J = 3.1 Hz, 1 H, 3′-H_b), 1.45 (ddd, J = 10.5, J = 7.5, J = 5.0 Hz, 1 H, 2′-H), 3.01 (s, 6 H, O*CH*$_3$), 5.31 (s, 2 H, 4-H, 5-H), 7.24–7.35 (m, 20 H, arom. H), 11.5 (br. s, COO*H*) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = –0.9 (C-1′), 13.6 (C-3′), 18.6 (C-2′), 51.7 (CPh_2OCH_3), 77.7 (C-4, C-5), 83.3 (CPh_2OCH_3), 127.3, 127.4, 127.6, 127.8, 128.3, 129.6 (arom. CH), 140.8, 140.9 (arom. C_{ipso}), 180.2 (*C*OOH) ppm. MS (FAB, NBA + NaI): *m*/*z* (%) = 593 (65) [M + 2 Na]$^+$, 571 (2) [M + Na]$^+$, 197 (100) [Ph_2COCH_3]$^+$.

In a Schlenk flask covered with aluminium foil, carboxylic acid **20** (0.29 g, 0.50 mmol, 1.0 equiv.), "HOTT" reagent **21** (0.24 g, 0.60 mmol, 1.2 equiv.) and DMAP (0.03 g, 0.30 mmol, 0.6 equiv.) were dissolved in abs. CH_3CN (1 mL). THF (3 mL) and Et_3N (0.22 mL, 1.6 mmol, 3.2 equiv.) were added and the mixture was stirred for 1 h at room temp (TLC control: petroleum ether/ethyl acetate, 7:3). Half of the solvent was removed under reduced pressure and abs. cyclohexene (1 mL) and iodoform (0.63 g, 1.59 mmol, 3.2 equiv.) were added. The mixture was heated at 80 °C (reflux) for 15 h. The solvents and volatile compound were then removed under reduced pressure. The remaining dark oil was diluted with diethyl ether (20 mL) and the insoluble precipitates were removed

by filtration through a pad of Celite and rinsed thoroughly with diethyl ether. The organic layer was washed with a 1 M solution of $Na_2S_2O_3$ (10 mL) and brine (10 mL) and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product **22** was purified by column chromatography (petroleum ether to petroleum ether/ethyl acetate, 99:1) to furnish a mixture of the *trans* isomer **22a** and the *cis* isomer **22b** (6:1); yield 0.23 g (0.37 mmol, 70%). The diastereoisomers were separated by MPLC (petroleum ether/ethyl acetate, 99.3:0.7). Both iodocyclopropanes **22** were obtained as colourless crystals. Isomer **22a**: Softening range 125–130 °C. $[\alpha]_D^{21}$ = –105.2 (*c* = 0.48, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3057, 3025, 2925, 2848, 2832, 1493, 1445, 1404, 1369, 1248, 1228, 1182, 1074, 1032, 1016, 967, 955, 916, 899, 879 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.08 (ddd, *J* = 10.6, *J* = 7.1, *J* = 4.9 Hz, 1 H, 1′-H), 0.50 (ddd, *J* = 7.1, *J* = 7.1, *J* = 4.9 Hz, 1 H, 3′-H_a), 0.76 (ddd, *J* = 10.6, *J* = 4.7, *J* = 4.7 Hz, 1 H, 3′-H_b), 2.14 (ddd, *J* = 7.1, *J* = 4.8, *J* = 4.7 Hz, 1 H, 2′-H), 3.01 (s, 6 H, OCH_3), 5.30 (s, 2 H, 4-H, 5-H), 7.22–7.37 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = –15.9 (C-2′), 6.0 (C-1′), 15.6 (C-3′), 51.7 (CPh_2OCH_3), 77.6 (C-4, C-5), 83.2 (CPh_2OCH_3), 127.1, 127.2, 127.4, 127.6, 127.7, 127.8, 128.3, 128.4, 129.6 (arom. C), 140.9 (arom. C_{ipso}) ppm. MS (FAB, NBA + NaI): *m*/*z* (%) = 653 (20) $[M + Na]^+$, 527 (2) $[M + Na – I]^+$, 197 (100) $[Ph_2COCH_3]^+$. HRMS (FAB, NBA + NaI): calcd. for $[M + Na]^+$ 653.1336; found 653.1331. $C_{33}H_{32}BIO_4$ (630.32): C 62.88, H 5.12; found C 63.80, H 5.95. Isomer **22b**: Softening range 85–92 °C. $[\alpha]_D^{21}$ = –153.3 (*c* = 0.40, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3055, 3026, 2930, 2847, 2831, 1493, 1445, 1411, 1375, 1320, 1252, 1193, 1074, 1032, 1016, 968, 923, 896, 858 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.20 (ddd, *J* = 10.9, *J* = 8.0, *J* = 8.0 Hz, 1 H, 1′-H), 0.23 (ddd, *J* = 7.9, *J* = 5.1, *J* = 5.0 Hz, 1 H, 3′-H_a), 1.09 (ddd, *J* = 10.9, *J* = 7.4, *J* = 5.0 Hz, 1 H, 3′-H_b), 2.50 (ddd, *J* = 7.6, *J* = 7.6, *J* = 5.3 Hz, 1 H, 2′-H), 3.02 (s, 6 H, OCH_3), 5.29 (s, 2 H, 4-H, 5-H), 7.21–7.48 (m, 20 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = –13.9 (C-2′), 3.0 (C-1′), 15.5 (C-3′), 51.7 (CPh_2OCH_3), 77.6 (C-4, C-5), 83.3 (CPh_2OCH_3), 127.2, 127.3, 127.4, 127.7, 128.7, 129.8 (arom. CH), 141.3 (arom. C_{ipso}) ppm. MS (FAB, NBA + NaI): *m*/*z* (%) = 653 (15) $[M + Na]^+$, 197 (100) $[Ph_2COCH_3]^+$. $C_{33}H_{32}BIO_4$ (630.32): calcd. C 62.88, H 5.12; found C 62.86, H 5.19.

General Procedure for the Suzuki Coupling Reaction of Iodocyclopropane 22a (Scheme 7, Condition D): Iodocyclopropane **22a** (1.0 equiv.) was dissolved in 1,2-dimethoxyethane (10 mL/mmol). After addition of the boron derivative **23** (1.5 equiv.), $[Pd(PPh_3)_4]$ (5 mol-%) and KO*t*Bu (2 mL/mmol **22a** of a 1 M solution in *t*BuOH) the mixture was carefully deoxygenated by the freeze technique. After 15–24 h at 80 °C the mixture was diluted with diethyl ether, filtered through a pad of Celite, rinsed with diethyl ether and the solvents were removed under reduced pressure. The crude product **10** was purified by flash column chromatography (silica gel, petroleum ether/diethyl ether, 99:1).

(1′*R*,2′*R*,4*R*,5*R*)-{2′-[(*E*)-Hex-1′′-enyl]cyclopropyl}-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (10b): Iodocyclopropane **22a** (150 mg, 0.24 mmol, 1.0 equiv.), (*E*)-hex-1-enylboronic acid (**23b**; 40 mg, 0.31 mmol, 1.3 equiv.), the catalyst $[Pd(PPh_3)_4]$ (25 mg, 0.02 mmol, 0.07 equiv.) and KO*t*Bu (1 M in *n*-butanol, 0.72 mL, 0.72 mmol, 3.0 equiv.) in abs. DME (3 mL) were allowed to react according to the general procedure for 24 h. The product **10b** was isolated as colourless crystals (87 mg, 0.15 mmol, 62%). The analytical data for the boronic ester **10b** were presented in the cross-metathesis section (see above).

(1′*R*,2′*R*,4*R*,5*R*)-4,5-Bis(methoxydiphenylmethyl)-2-(2′-phenylcyclopropyl)-1,3,2-dioxaborolane (10h): Iodocyclopropane **22a** (90 mg, 0.14 mmol, 1.0 equiv.), phenylboronic acid (**23h**; 30 mg, 0.21 mmol, 1.5 equiv.), the catalyst $[Pd(PPh_3)_4]$ (13 mg, 0.01 mmol, 0.07 equiv.) and KO*t*Bu (1 M in *n*-butanol, 0.29 mL, 0.29 mmol, 2.0 equiv.) in abs. DME (1.5 mL) were allowed to react according to the general procedure for 20 h. The product **10h** was isolated as colourless crystals (72 mg, 0.12 mmol, 87%). All the spectroscopic data for boronic ester **10h** were in full agreement with those reported previously.[8a]

(1′*R*,2′*R*,4*R*,5*R*)-4,5-Bis(methoxydiphenylmethyl)-2-[2′-(thiophen-3′′-yl)cyclopropyl]-1,3,2-dioxaborolane (10j): Iodocyclopropane **22a** (80 mg, 0.13 mmol, 1.0 equiv.), thiophene-3-boronic acid (**23j**; 20 mg, 0.19 mmol, 1.5 equiv.), the catalyst $[Pd(PPh_3)_4]$ (12 mg, 0.01 mmol, 0.07 equiv.) and KO*t*Bu (1 M in *n*-butanol, 0.28 mL, 0.28 mmol, 2.0 equiv.) in abs. DME (1.5 mL) were allowed to react according to the general procedure for 20 h. The product **10j** was isolated as colourless crystals (58 mg, 0.10 mmol, 79%). All the spectroscopic data for boronic ester **10j** were in full agreement with those reported previously.[10b]

(1′*R*,2′*R*,4*R*,5*R*)-4,5-Bis(methoxydiphenylmethyl)-2-[2′-(2′′-phenylcyclopropyl)cyclopropyl]-1,3,2-dioxaborolane (10k): Iodocyclopropane **22a** (80 mg, 0.13 mmol, 1 equiv.), the *rac*-phenylcyclopropylboronic ester **23k**[28] (0.4 g, 0.19 mmol, 1.5 equiv.), the catalyst $[Pd(PPh_3)_4]$ (12 g, 0.01 mmol, 0.07 equiv.) and KO*t*Bu (1 M in *n*-butanol, 0.28 mL, 0.28 mmol, 2.0 equiv.) in abs. DME (1.5 mL) were allowed to react according to the general procedure for 25 h. The product **10k** was isolated as colourless crystals (53 mg, 0.09 mmol, 67%). All the spectroscopic data for boronic ester **10k** were in full agreement with those reported previously.[10b]

(1′*R*,2′*R*,4*R*,5*R*)-{2′-[(*E*)-Hept-1′′-enyl]cyclopropyl}-4,5-bis(methoxydiphenylmethyl)-1,3,2-dioxaborolane (10l): Iodocyclopropane **22a** (150 mg, 0.24 mmol, 1.0 equiv.), (*E*)-hept-1-enylboronic acid (**23b**; 44 mg, 0.31 mmol, 1.3 equiv.), the catalyst $[Pd(PPh_3)_4]$ (25 mg, 0.02 mmol, 0.07 equiv.) and KO*t*Bu (1 M in *n*-butanol, 0.72 mL, 0.72 mmol, 3.0 equiv.) in abs. DME (3 mL) were allowed to react according to the general procedure for 24 h. The product **10l** was isolated as colourless crystals (94 mg, 0.16 mmol, 65%). All the spectroscopic data for boronic ester **10l** were in full agreement with those reported previously.[10b]

Procedure for the Heck Coupling Reaction

(1′*R*,2′*R*,4*R*,5*R*)-4,5-Bis(methoxydiphenylmethyl)-2-[(*E*)-2′-styrylcyclopropyl]-1,3,2-dioxaborolane (10a): Vinylcyclopropane **9** (40 mg, 0.08 mmol, 1 equiv.), $Pd(OAc)_2$ (3.0 mg, 0.03 mmol, 0.1 equiv.) and NaOAc (10 mg, 0.08 mmol, 1.1 equiv.) were dissolved in the ionic liquid [BMIM]Br (20 mL) by vigorously stirring at 75 °C. The solution was carefully deoxygenated by the freeze technique. After the addition of PhI (30 mg, 0.15 mmol, 2.0 equiv.), the mixture was heated for 1 d at 100 °C. After the addition of water (80 mL), the mixture was transferred into a separation funnel. The layer was extracted with diethyl ether (3 × 40 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **10a** was purified by flash column chromatography (petroleum ether/diethyl ether, 99:1) to furnish boronic ester **10a** (42 mg, 69 μmol, 91%) as colourless crystals. The analytical data for boronic ester **10a** were presented in the cross-metathesis section (see above).

By extracting the remaining aqueous layer with dichloromethane, drying the organic layer with $MgSO_4$ and removing the dichloromethane, about 50% of the ionic liquid could be recovered.

Activation of the Boronic Esters

Synthesis of Cyclopropyltrifluoroborates 25 and *ent*-25: KHF_2 (50 equiv.) was placed in a round-bottomed Teflon® flask and dis-

solved in MeOH (80–100 mL/mmol boronic ester). The boronic ester (1 equiv.), dissolved in a minimum amount of dichloromethane, was added and the mixture heated at 80 °C for 1–3 d. The solvents were removed under reduced pressure and the remaining colourless solids transferred to a Büchner funnel and washed with diethyl ether (or *n*-pentane) to elute the diol **26**. The product (alkyltrifluoroborate) was dissolved in acetonitrile, the solvent was removed under reduced pressure and the remaining solid, if required, recrystallized from acetonitrile.

Potassium (1*S*,2*S*)-[2-(Benzyloxymethyl)cyclopropyl]trifluoroborate (25): KHF_2 (18.1 g, 232 mmol, 50 equiv.) and cyclopropylboronic ester **24a**[12a,12b] (2.90 g, 4.64 mmol, 1.0 equiv.) in MeOH (460 mL) were heated at reflux at 80 °C for 2 d according to the representative procedure. The residue was washed in a Büchner funnel with diethyl ether to elute the diol **26**. The borate **25** was dissolved in acetonitrile. The product **25** was isolated as colourless crystals (0.97 g, 3.62 mmol, 78%[38]); m.p. 198 °C. $[\alpha]_D^{20}$ = +16.4 (*c* = 0.50, DMSO). IR (film): $\tilde{\nu}$ = 3063, 3030, 3000, 2945, 2888, 2864, 1496, 1470, 1454, 1417, 1374, 1358, 1305, 1246, 1205, 1169, 1130, 1101, 1090, 1076, 1065, 1038, 942, 888, 820, 805, 743, 698 cm^{-1}. ^1H NMR ([D_6]DMSO, 400 MHz): δ = –0.87 (ddd, *J* = 9.6, *J* = 6.5, *J* = 3.4 Hz, 1 H, 1-H), –0.17 (ddd, *J* = 9.6, *J* = 3.7, *J* = 2.9 Hz, 1 H, 3-H_a), 0.09 (ddd, *J* = 6.8, *J* = 6.5, *J* = 2.9 Hz, 1 H, 3-H_b), 0.58–0.66 (m, 1 H, 2-H), 3.06 (dd, *J* = 10.2, *J* = 7.5 Hz, 1 H, 4-H_a), 3.31 (dd, *J* = 10.2, *J* = 6.1 Hz, 1 H, 4-H_b), 4.43 (d, *J* = 12.2 Hz, 1 H, 5-H_a), 4.49 (d, *J* = 12.2 Hz, 1 H, 5-H_b), 7.22–7.36 (m, 5 H, arom. H) ppm. ^{13}C NMR ([D_6]DMSO, 100 MHz): δ = 7.0 (C-3), 13.6 (C-2), 70.6 (C-5), 76.5 (C-4), 127.0, 127.3, 128.1 (arom. C), 139.2 (arom. C_{ipso}) ppm. ^{19}F NMR ([D_6]DMSO, 400 MHz): δ = –140.07 (s, 3 F, BF_3K) ppm. MS (ES): *m*/*z* (%) = 285 (40) $[M + NH_3]^+$, 307 (100) $[M + K]^+$.

Potassium (1*R*,2*R*)-[2-(Benzyloxymethyl)cyclopropyl]trifluoroborate (*ent*-25): KHF_2 (5.50 g, 70.5 mmol, 50 equiv.) and cyclopropylboronic ester **24b** (0.88 g, 1.41 mmol, 1.0 equiv.) in MeOH (150 mL) were heated at reflux at 80 °C for 2 d according to the representative procedure. The product ***ent*-25** was isolated as colourless crystals (0.345 g, 1.29 mmol, 93%); m.p. 197 °C. $[\alpha]_D^{20}$ = –16.4 (*c* = 0.50, DMSO). All the spectroscopic data for borate ***ent*-25** were in full agreement with those reported previously.[10b]

Suzuki Coupling of the Borates: A suspension of the cyclopropyltrifluoroborate **25**/***ent*-25** (1 equiv.), 5–10 mol-% [$Pd(PPh_3)_4$] and K_3PO_4 (3.0 equiv.) in toluene/H_2O (3:1; 8 mL/mmol borate) was deoxygenated by the freeze technique. The aryl bromide (1.2 equiv.) was added at room temp. The mixture was stirred at 100 °C until complete conversion was detected (as judged by TLC). After filtration through a pad of Celite and $MgSO_4$ and extensive rinsing with diethyl ether, the solvent was removed under reduce pressure. The crude product **27**/**28** was purified by column chromatography.

(1*S*,2*S*)-[2-(Benzyloxymethyl)cyclopropyl]benzene (27): Borate **25** (79 mg, 0.30 mmol, 1.0 equiv.), phenyl bromide (40 μL, 0.36 mmol, 1.2 equiv.), [$Pd(PPh_3)_4$] (30 mg, 30 μmol, 0.05 equiv.) and K_3PO_4 (0.21 g, 0.99 mmol, 3.0 equiv.) in toluene/H_2O (3:1; 2.4 mL) were allowed to react according to the general procedure for 2 d at 100 °C. The crude product **27** was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 98:2) to furnish cyclopropylbenzene **27** (48 g, 0.2 mmol, 66%) as a colourless oil. $[\alpha]_D^{20}$ = +101.2 (*c* = 0.41, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.91 (ddd, *J* = 8.8, *J* = 5.3, *J* = 5.2 Hz, 1 H, 3′-H_a), 0.96 (ddd, *J* = 8.4, *J* = 5.2, *J* = 5.1 Hz, 1 H, 3′-H_b), 1.43 (ddddd, *J* = 8.4, *J* = 6.8, *J* = 6.4, *J* = 5.3, *J* = 5.3 Hz, 1 H, 1′-H), 1.78 (ddd, *J* = 8.8, *J* = 5.1, *J* = 5.3 Hz, 1 H, 2′-H), 3.42 (dd, *J* = 10.3, *J* = 6.8 Hz, 1 H, 1-H_a), 3.51 (dd, *J* = 10.3, *J* = 6.4 Hz, 1 H, 1-H_b), 4.53 (s, 2 H, CH_2Ph), 6.98 –7.43 (m, 10 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.2 (C-3′), 21.4 (C-2′), 22.6 (C-1′), 72.5 (CH_2Ph), 73.5 (C-1), 125.0, 125.8, 127.5, 127.6, 128.2, 128.4 (arom. CH), 138.4, 142.6 (arom. C_{ipso}) ppm. The spectroscopic data for cyclopropylbenzene **27** were in full agreement with those reported in the literature.[39]

(1*R*,2*R*)-[2-(Benzyloxymethyl)cyclopropyl]naphthalene (28): Borate ***ent*-25** (79 mg, 0.30 mmol, 1.0 equiv.), 1-bromonaphthalene (70 mg, 0.36 mmol, 1.2 equiv.), [$Pd(PPh_3)_4$] (6.0 mg, 5.0 μmol, 0.05 equiv.) and K_3PO_4 (0.21 g, 0.98 mmol, 3.0 equiv.) in toluene/H_2O (3:1;0.6 mL) were allowed to react according to the general procedure for 15 h at 100 °C. The crude product **28** was purified by flash column chromatography (SiO_2, *n*-pentane, then petroleum ether/ethyl acetate, 98:2) to furnish cyclopropylnaphthalene **28** (73 mg, 0.25 mmol, 85%) as a colourless oil. $[\alpha]_D^{20}$ = –13.1 (*c* = 0.65, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3061, 3043, 3003, 2926, 2853, 1594, 1508, 1495, 1453, 1392, 1357, 1260, 1203, 1166, 1091, 1072, 1027, 963, 797, 775, 732, 695 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.00 (ddd, *J* = 10.0, *J* = 5.1, *J* = 4.7 Hz, 1 H, 4-H_a), 1.13 (ddd, *J* = 8.4, *J* = 5.4, *J* = 4.7 Hz, 1 H, 4-H_b), 1.48 (dddd, *J* = 10.0, *J* = 7.2, *J* = 6.2, *J* = 5.4, *J* = 5.2 Hz, 1 H, 2-H), 2.28 (ddd, *J* = 8.4, *J* = 5.1, *J* = 5.2 Hz, 1 H, 3-H), 3.61 (dd, *J* = 10.2, *J* = 7.2 Hz, 1 H, 1-H_a), 3.72 (dd, *J* = 10.2, *J* = 6.2 Hz, 1 H, 1-H_b), 4.61 (d, *J* = 12.0 Hz, 1 H, 1′-H_a), 4.65 (d, *J* = 12.0 Hz, 1 H, 1′-H_b), 7.25–7.28 (m, 1 H, arom. 2′′′-H), 7.28–7.32 (m, 1 H, arom. 3′′′-H), 7.34–7.39 (m, 3 H, arom. 2′′,4′′,6′′-H), 7.40–7.43 (m, 2 H, arom. 3′′,5′′-H), 7.45–7.51 (m, 2 H, arom. 7′′′, 8′′′-H), 7.68–7.71 (m, 1 H, arom. 4′′′-H), 7.81–7.85 (m, 1 H, arom. 6′′′-H), 8.48–8.50 (m, 1 H, arom. 9′′′-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 11.1 (C-4), 19.6 (C-3), 20.3 (C-2), 72.6 (C-1′), 74.1 (C-1), 124.0 (C-2′′′), 124.6 (C-9′′′), 125.4, 125.6 (C-2′′ or C-4′′ or C-6′′), 125.8 (C-7′′′, C-8′′′), 126.8 (C-4′′′), 127.5 (C-3′′′), 127.6 (C-3′′, C-5′′), 128.3 (C-2′′ or C-4′′ or C-6′′), 128.4 (C-6′′′), 133.4 (C-10′′′), 133.5 (C-5′′′), 137.9 (C-1′′), 138.6 (C-1′′′) ppm. MS (EI, 70 eV): *m*/*z* (%) = 288 (100) $[M]^+$, 197 (30) $[M - C_7H_7]^+$, 181 (50) $[M - C_7H_7O]^+$, 167 (100) $[M - C_8H_9O]^+$. $C_{21}H_{20}O$ (288.38): calcd. C 87.27, H 6.99; found C 86.81, H 6.99.

Synthesis of Boronic Esters from Borate 25

(1′*S*,2′*S*)-2-[2′-(Benzyloxymethyl)cyclopropyl]-1,3,2-dioxaborinane (29). Method I: Borate **25** (0.20 g, 0.75 mmol, 1.0 equiv.) was suspended in abs. THF (1.0 mL). $SiCl_4$ (1.49 mL, 1.49 mmol, 1 M solution in dichloromethane, 2.0 equiv.) was added dropwise at room temp. A clear solution formed and stirring was continued for 1 h. The mixture was cooled to 0 °C and methanol (0.30 mL, 7.45 mmol) was added followed after 10 min by 1,3-propanediol (0.04 mL, 0.74 mmol, 1.0 equiv.). The volatiles were removed under reduced pressure after 15 h at room temp. The residue was diluted with *n*-pentane and neutralized by adding Et_3N dropwise. The precipitates were filtered off and washed with *n*-pentane. The mother liquor was concentrated under reduced pressure and the remaining oil containing the crude product **29** was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 98:2 to 92:8) to furnish boronic ester **29** as a colourless oil (167 mg, 0.68 mmol, 91%).

Method II: Borate **25** (0.13 g, 0.48 mmol, 1.0 equiv.) was suspended in acetonitrile (5.0 mL) and water (24 μL) under argon. LiOH (40 mg, 1.7 mmol, 3.5 equiv.) was added and a clear solution formed. Stirring was continued for 20 h at room temp. The solution was treated with an aqueous saturated NH_4Cl solution (4 mL) and 1 M aqueous hydrochloric acid (1 mL). The aqueous layer was repeatedly extracted with ethyl acetate and the combined organic layers were dried with Na_2SO_4. The solvent was removed under re-

duced pressure and the boronic acid obtained was dissolved in a minimum amount of dichloromethane and treated with pentane (2.5 mL). 1,3-Propanediol (30 μL, 0.41 mmol) was added and the mixture was stirred for 10 h at room temp., dried with Na_2SO_4, filtered and concentrated under reduced pressure to furnish the product **29** as a colourless oil (76 mg, 0.30 mmol, 75%).

Method III: Borate **25** (0.13 g, 0.48 mmol, 1.0 equiv.) was suspended in acetonitrile (5.0 mL) and water (24 μL) under argon. Chlorotrimethylsilane (0.18 mL, 1.45 mmol, 3.0 equiv.) was added and stirring was continued for 24 h at room temp. The mixture was treated with an aqueous saturated $NaHCO_3$ solution (0.75 mL), dried with Na_2SO_4, filtered and thoroughly washed with ethyl acetate. The solvent was removed under reduced pressure and the boronic acid obtained was dissolved in a minimum amount dichloromethane and treated with pentane (2.5 mL). 1,3-Propanediol (30 μL, 0.41 mmol) was added and the mixture was stirred for 10 h at room temp., dried with Na_2SO_4, filtered and concentrated under reduced pressure to furnish the product **29** as a colourless oil (107 mg, 0.43 mmol, 94%).

Method IV: Borate **25** (0.10 g, 0.37 mmol, 1.0 equiv.) was suspended in acetonitrile (4.0 mL) under argon. The mixture was treated with chlorotrimethylsilane (0.14 mL, 1.12 mmol, 3.0 equiv.) and stirring was continued for 5 min at room temp. before 1,3-propanediol (25 μL, 0.35 mmol) was added. After 30 min at room temp., the mixture was dried with Na_2SO_4, filtered and concentrated under reduced pressure to furnish the product **29** as a colourless oil (83 mg, 0.33 mmol, 95%).

Method V: Borate **25** (50 mg, 0.19 mmol, 1.0 equiv.) was suspended in acetonitrile (2.0 mL) and Et_3N (78 μL, 0.56 mmol) under argon. The mixture was treated with chlorotrimethylsilane (70 μL, 0.56 mmol, 3.0 equiv.) and stirring was continued for 5 min at room temp. before 1,3-propanediol (10 μL, 0.18 mmol) was added. After 30 min at room temp., the mixture was directly concentrated under reduced pressure to furnish the crude product **29**. Filtration through a pad of Celite (eluent: *n*-pentane/ethyl acetate, 9:1) yielded the boronic ester **29** as a colourless oil (40 mg, 0.16 mmol, 92%). The spectroscopically pure products were used for further transformations as obtained. $[\alpha]_D^{20}$ = –47.0 (*c* = 0.93, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3065, 3033, 2999, 2945, 2889, 2855, 1481, 1453, 1420, 1397, 1356, 1324, 1291, 1274, 1225, 1203, 1137, 1091, 1073, 1027, 990, 963, 935, 916, 847, 736, 697, 665 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = –0.38 (ddd, *J* = 9.6, *J* = 6.3, *J* = 5.1 Hz, 1 H, 1′-H), 0.43 (ddd, *J* = 8.4, *J* = 5.1, *J* = 3.4 Hz, 1 H, 3′-H_a), 0.67 (ddd, *J* = 7.7, *J* = 6.3, *J* = 3.4 Hz, 1 H, 3′-H_b), 1.24 (ddddd, *J* = 9.6, *J* = 8.4, *J* = 7.7, *J* = 6.9, *J* = 6.6 Hz, 1 H, 2′-H), 1.88 (q, *J* = 5.5 Hz, 2 H, 5-H), 3.28 (dd, *J* = 10.2, *J* = 6.9 Hz, 1 H, 4′-H_a), 3.33 (dd, *J* = 10.2, *J* = 6.6 Hz, 1 H, 4′-H_b), 3.91 (t, *J* = 5.5 Hz, 4 H, 4/6-H), 4.51 (d, *J* = 12.1 Hz, 1 H, 5′-H_a), 4.68 (d, *J* = 12.1 Hz, 1 H, 5′-H_b), 7.23–7.34 (m, 5 H, arom. H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = ≈1.9 (C-1′), 9.1 (C-3′), 16.8 (C-2′), 27.3 (C-5), 61.5 (C-4/6), 72.3 (C-5′), 75.1 (C-4′), 127.2, 128.3, 129.6 (arom. CH), 138.7 (arom. C_{ipso}) ppm.

(1′*S*,2′*S*)-2-[2′-(Benzyloxymethyl)cyclopropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30): Borate **25** (0.20 g, 0.75 mmol, 1.0 equiv.) was suspended in abs. THF (1.0 mL). $SiCl_4$ (1.49 mL, 1.49 mmol, 1 M solution in dichloromethane, 2.0 equiv.) was added dropwise at room temp. A clear solution formed and stirring was continued for 1 h. The mixture was cooled to 0 °C and methanol (0.30 mL, 7.45 mmol) was added followed after 10 min by pinacol (0.18 g, 1.50 mmol, 2.0 equiv.). The volatiles were removed under reduced pressure after 10 h at room temp. The residue was diluted with *n*-pentane and neutralized by adding Et_3N dropwise. The precipitates were filtered off and washed with *n*-pentane. The mother liquor was concentrated under reduced pressure and the remaining oil containing the crude product **30** was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate, 98:2 to 92:8) to furnish boronic ester **30** as a colourless oil (0.21 g, 0.74 mmol, 99%). The spectroscopically pure product was used for further transformations as obtained. $[\alpha]_D^{20}$ = –7.4 (*c* = 0.73, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3066, 3027, 2977, 2931, 2856, 1496, 1469, 1454, 1425, 1388, 1378, 1364, 1336, 1316, 1260, 1215, 1165, 1143, 1087, 1027, 1008, 967, 932, 903, 838, 800, 734, 696, 673 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = –0.23 (ddd, *J* = 9.6, *J* = 6.2, *J* = 5.8 Hz, 1 H, 1′-H), 0.55 (ddd, *J* = 9.6, *J* = 5.1, *J* = 3.5 Hz, 1 H, 3′-H_a), 0.77 (ddd, *J* = 8.1, *J* = 6.5, *J* = 3.5 Hz, 1 H, 3′-H_b), 1.21 (s, 12 H, CH_3), 1.34–1.38 (m, 1 H, 2′-H), 3.25 (dd, *J* = 10.4, *J* = 7.1 Hz, 1 H, 4′-H_a), 3.45 (dd, *J* = 10.4, *J* = 6.1 Hz, 1 H, 4′-H_b), 4.53 (s, 2 H, 5′-H), 7.23–7.35 (m, 5 H, arom. H) ppm. ^{13}C NMR ([D_6]DMSO, 100 MHz): δ = –1.6 (C-1′), 9.6 (C-3′), 17.2 (C-2′), 24.6, 24.7 (*C*H_3), 72.3 (C-4′), 74.8 (C-5′), 82.9 (C-4, C-5), 127.4, 127.6, 128.3 (arom. CH), 138.6 (arom. C_{ipso}) ppm.

Synthetic Approach Towards the Dictypterenes

Potassium (1*R*,2*R*)-2-[(*E*)-Hex-1′-enyl]cyclopropyltrifluoroborate (31): KHF_2 (13.3 g, 171 mmol, 100 equiv.) was suspended in methanol (400 mL) and cyclopropylboronic ester **10b** (1.00 g, 1.71 mmol, 1.00 equiv.) was added. The mixture was heated at 80 °C (reflux) for 5 d. The solvent was removed completely under reduced pressure and the residue was washed in a Büchner funnel first with *n*-pentane, eluting the diol **26**, followed by acetonitrile, eluting the product **31**. The solvent was removed under reduced pressure to furnish borate **31** as a colourless solid (0.35 g, 1.52 mmol, 89%). Decomp. at 210 °C. $[\alpha]_D^{20}$ = –8.5 (*c* = 0.40, acetone). IR (film): $\tilde{\nu}$ = 3060, 2999, 2958, 2926, 2873, 2859, 1610, 1456, 1391, 1358, 1313, 1231, 1074, 1023, 930, 892, 852, 729, 695 cm^{-1}. ^1H NMR ([D_6]acetone, 400 MHz): δ = –0.52 (ddd, *J* = 9.7, *J* = 7.2, *J* = 3.5 Hz, 1 H, 1-H), 0.05 (ddd, *J* = 9.7, *J* = 3.5, *J* = 2.7 Hz, 1 H, 3-H_a), 0.41 (ddd, *J* = 7.2, *J* = 7.2, *J* = 2.7 Hz, 1 H, 3-H_b), 0.85 (m, 3 H, 6′-H), 1.10 (dddd, *J* = 9.0, *J* = 7.2, *J* = 3.5, *J* = 3.5 Hz, 1 H, 2-H), 1.26 (m, 4 H, 4′-H, 5′-H), 1.91 (ddt, *J* = 7.3, *J* = 6.7, *J* = 1.3 Hz, 2 H, 3′-H), 4.86 (ddt, *J* = 15.2, *J* = 9.0, *J* = 1.3 Hz, 1 H, 1′-H), 5.30 (dt, *J* = 15.2, *J* = 6.7 Hz, 1 H, 2′-H) ppm. ^{13}C NMR ([D_6]acetone, 100 MHz): δ = 11.7 (C-3), 15.2 (C-6′), 18.9 (C-2), 23.8 (C-4, C-5′), 34.0 (C-3′), 125.8 (C-2′), 140.2 (C-1′) ppm; no signal for C-1 observed. ^{19}F NMR ([D_6]acetone, 400 MHz): δ = –144.35 (s, 3 F, BF_3K) ppm. MS (ESI): *m*/*z* (%) = 253 (50) [M + Na]$^+$.

Potassium {(1*S*,2*S*)-2-[(1′*E*,3′*Z*)-Hexa-1′,3′-dienyl]cyclopropyl}-trifluoroborate (32): KHF_2 (20.0 g, 256 mmol, 100 equiv.) was suspended in methanol (500 mL) and cyclopropylboronic ester **17** (1.50 g, 2.56 mmol, 1 equiv.) was added. The mixture was heated at 80 °C (reflux) for 5 d. The solvent was removed completely under reduced pressure and the residue was washed in a Büchner funnel first with *n*-pentane, eluting the diol **26**, followed by acetonitrile, eluting the product **32**. The solvent was removed under reduced pressure to furnish the borate **32** as a colourless solid (0.51 g, 2.24 mmol, 87%). Decomp. at 208 °C. $[\alpha]_D^{20}$ = +4.05 (*c* = 0.37, DMSO). IR (film): $\tilde{\nu}$ = 2965, 2927, 2876, 1666, 1645, 1618, 1459, 1373, 1306, 1203, 1071, 1019, 897, 870, 742, 697 cm^{-1}. ^1H NMR ([D_6]acetone, 600 MHz): δ = –0.40 (m_c, 1 H, 1-H), 0.15 (m_c, 1 H, 3-H_a), 0.55 (ddd, *J* = 9.5, *J* = 7.1, *J* = 2.4 Hz, 1 H, 3-H_b), 0.95 (t, *J* = 7.5 Hz, 3 H, 6′-H), 1.21 (m_c, 1 H, 2-H), 2.15 (m_c, 2 H, 5′-H), 5.08 (dd, *J* = 10.8, *J* = 7.5 Hz, 1 H, 4′-H), 5.13 (dd, *J* = 9.6, *J* = 14.9 Hz, 1 H, 1′-H), 5.83 (t, *J* = 11.1 Hz, 1 H, 3′-H), 6.27 (dd, *J* = 14.9, *J* = 11.1 Hz, 1 H, 2′-H) ppm. ^{13}C NMR ([D_6]acetone,

151 MHz): δ = 12.1 (C-1, C-3), 14.8 (C-6′), 19.0 (C-2), 21.5 (C-5′), 121.2 (C-2′), 128.5 (C-4′), 129.9 (C-3′), 144.8 (C-1′) ppm. ^{19}F NMR ([D$_6$]DMSO, 565 MHz): δ = –148.12 (s, 3 F, BF_3K) ppm. MS (–EMS): *m*/*z* (%) = 251 (4) [M + Na]$^+$, 223 (31) [M + Na – C_2H_4]$^+$, 189 (100) [$C_9H_{13}BF_3$]$^+$.

(1′*R*,2′*R*)-2-{2′-[(*E*)-Hex-1′′-enyl]cyclopropyl}-1,3,2-dioxaborinane (33): Borate **31** (800 mg, 3.48 mmol, 1.0 equiv.) was suspended in CH_3CN (32 mL) and Et_3N (1.5 mL, 10.4 mmol, 3.0 equiv.) and trimethylsilyl chloride (1.3 mL, 10.4 mmol, 3.0 equiv.) was added. The suspension became coarse-grained/milky. The mixture was kept for 5 min at room temp. before 1,3-propanediol (0.25 mL, 3.30 mmol, 0.95 equiv.) was added. Stirring was continued for 30 min, followed by removal of the volatiles under reduced pressure. The crude product **33** was filtered through a pad of Celite (*n*-pentane/ethyl acetate, 9:1) to remove the precipitates and was further purified by distillation (b.p. 120–125 °C/7 Torr) to furnish dioxaborinane **33** (0.65 g, 3.13 mmol, 90%) as a colourless oil. $[\alpha]_D^{20}$ = –94 (*c* = 0.60, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2977, 2957, 2926, 2856, 1481, 1438, 1417, 1389, 1370, 1318, 1276, 1215, 1165, 1142, 1112, 1087, 959, 912, 855, 697, 672 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = –0.26 (m_c, 1 H, 1′-H), 0.53 (m_c, 1 H, 3′-H_a), 0.78 (m_c, 1 H, 3′-H_b), 0.88 (t, *J* = 6.8 Hz, 3 H, 6′′-H), 1.26–1.32 (m, 4 H, 4′′-H, 5′′-H), 1.44–1.51 (m, 1 H, 2′-H), 1.91 (q, *J* = 5.5 Hz, 2 H, 5-H), 1.95 (dt, *J* = 7.0, *J* = 6.8 Hz, 1 H, 3′′-H), 3.94 (t, *J* = 5.5 Hz, 4 H, 4-H, 6-H), 4.91 (ddt, *J* = 15.2, *J* = 8.7, *J* = 1.4 Hz, 1 H, 1′′-H), 5.52 (dt, *J* = 15.2, *J* = 6.8 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.1 (C-3′), 13.9 (C-6′′), 20.1 (C-2′), 22.2 (C-5′′), 24.7 (C-5), 31.8 (C-4′′), 32.2 (C-3′′), 61.7 (C-4, C-6), 128.3 (C-2′′), 133.9 (C-1′′) ppm; no signal for C-1′ observed. GC–MS (EI, 70 eV): *m*/*z* (%) = 208 (30) [M]$^+$, 179 (30) [M – C_2H_5]$^+$, 165 (100) [M – C_3H_7]$^+$, 151 (25) [M – C_4H_9]$^+$, 137 (18) [M – C_5H_{11}]$^+$.

(1′*S*,2′*S*)-2-{2′-[(1′′*E*,3′′*Z*)-Hexa-1′′,3′′-dienyl]cyclopropyl}-1,3,2-dioxaborinane (34): Borate **32** (1.00 g, 4.38 mmol, 1.0 equiv.) was suspended in CH_3CN (44 mL) and Et_3N (1.8 mL, 13.2 mmol, 3.0 equiv.) and trimethylsilyl chloride (1.7 mL, 13.2 mmol, 3.0 equiv.) was added. The suspension became coarse-grained/milky. The mixture was kept for 5 min at room temp. before 1,3-propanediol (0.30 mL, 4.38 mmol, 0.95 equiv.) was added. Stirring was continued for 30 min, followed by removal of the volatiles under reduced pressure. The crude product **34** was filtered through a pad of Celite (*n*-pentane/ethyl acetate, 9:1) to remove the precipitates and was further purified by distillation (b.p. 140–145 °C/11 Torr) to furnish dioxaborinane **34** (0.81 g, 3.93 mmol, 90%) as a colourless oil. $[\alpha]_D^{20}$ = +37.2 (*c* = 0.60, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2948, 2891, 1712, 1601, 1484, 1420, 1329, 1280, 1226, 1202, 1164, 1130, 1056, 983, 922, 866, 843, 789, 744, 691, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = –0.16 (ddd, *J* = 9.7, *J* = 6.7, *J* = 5.2 Hz, 1 H, 1′-H), 0.62 (ddd, *J* = 9.7, *J* = 4.8, *J* = 3.5 Hz, 1 H, 3′-H_a), 0.88 (ddd, *J* = 7.4, *J* = 6.7, *J* = 3.5 Hz, 1 H, 3′-H_b), 0.99 (t, *J* = 7.7 Hz, 3 H, 6′′-H), 1.59 (dddd, *J* = 9.3, *J* = 7.4, *J* = 5.2, *J* = 4.8 Hz, 1 H, 2′-H), 1.91 (q, *J* = 5.4 Hz, 2 H, 5-H), 2.17 (m_c, 2 H, 5′′-H), 3.94 (t, *J* = 5.4 Hz, 4 H, 4-H, 6-H), 5.01 (dd, *J* = 9.3, *J* = 15.0 Hz, 1 H, 1′′-H), 5.11 (dd, *J* = 10.8, *J* = 7.4 Hz, 1 H, 4′′-H), 5.74 (t, *J* = 11.1, *J* = 10.8 Hz, 1 H, 3′′-H), 6.28 (dd, *J* = 15.0, *J* = 11.1 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 8.6 (C-1′), 12.9 (C-3′), 14.4 (C-6′′), 20.9 (C-2′), 21.0 (C-5′′), 27.4 (C-5), 61.7 (C-4, C-6), 123.5 (C-1′′), 127.8 (C-4′′), 130.9 (C-3′′), 136.5 (C-2′′) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 206 (29) [M]$^+$, 177 (32) [M – C_2H_5]$^+$, 163 (7) [M – C_3H_7]$^+$.

(1′*R*,2′*R*)-{2′-[(*E*)-Hex-1′′-enyl]cyclopropyl}methanol (35): Dioxaborinane **33** (0.70 g, 3.36 mmol, 1.0 equiv.) was dissolved in anhydrous THF (5 mL) at room temp. and chloroiodomethane (0.45 mL, 6.06 mmol, 1.8 equiv.) was added. The reaction mixture was cooled to –78 °C before *t*BuLi (3.6 mL of a 1.7 M solution in *n*-pentane, 6.06 mmol, 1.8 equiv.) was slowly added. After 30 min the cooling bath was removed and the mixture stirred for 4 d at room temp. The mixture was carefully quenched with aqueous saturated $NaHCO_3$ (4.2 mL) and 30% H_2O_2 (8.4 mL) at 0 °C. After 10 min the cooling bath was removed and the mixture was stirred for 3 h at room temp. The layers were separated and the aqueous layer extracted with Et_2O (3 × 8 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product **35** was purified by column chromatography (silica gel, *n*-pentane/diethyl ether, 2:1) to furnish cyclopropylmethanol **35** (0.25 g, 1.62 mmol, 48%) as a colourless liquid. $[\alpha]_D^{20}$ = –13.5 (*c* = 0.40, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3332, 3001, 2956, 2925, 2872, 1456, 1408, 1378, 1318, 1266, 1238, 1149, 1039, 1017, 958, 868, 789, 727 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 0.48–0.55 (m, 2 H, 3′-H), 0.81 (t, *J* = 7.2 Hz, 3 H, 6′′-H), 0.99–1.04 (m, 1 H, 1′-H), 1.18–1.26 (m, 4 H, 4′′-H, 5′′-H), 1.26–1.31 (m, 1 H, 2′-H), 1.89 (ddt, *J* = 7.2, *J* = 6.8, *J* = 1.4 Hz, 2 H, 3′′-H), 1.99 (s, 1 H, O*H*), 3.41 (dd, *J* = 11.2, *J* = 7.0 Hz, 1 H, 1-H_a), 3.44 (dd, *J* = 11.2, *J* = 6.8 Hz, 1 H, 1-H_b), 4.95 (ddt, *J* = 15.2, *J* = 8.2, *J* = 1.4 Hz, 1 H, 1′′-H), 5.42 (ddt, *J* = 15.2, *J* = 6.8, *J* = 0.7 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 11.3 (C-3′), 13.9 (C-6′′), 19.4 (C-1′), 22.2 (C-5′′), 22.6 (C-2′), 31.7 (C-4′′), 32.1 (C-3′′), 66.4 (C-1), 129.1 (C-2′′), 131.8 (C-2′) ppm. The spectroscopic data for alcohol **35** were in full agreement with those reported in the literature.[37f]

(1*R*,2*R*)-2′-[(*E*)-Hex-1′′-enyl]cyclopropane-1′-carbaldehyde (37): Cyclopropylmethanol **35** (198 mg, 1.28 mmol, 1.0 equiv.) was dissolved in dichloromethane (10 mL). Dess–Martin periodinane **7** (825 mg, 1.95 mmol, 1.5 equiv.) and pyridine (0.30 mL, 3.89 mmol, 3.0 equiv.) were added and the mixture stirred for 1 h at room temp. The reaction mixture was diluted with *n*-pentane (5 mL), directly filtered through a short pad of silica gel and concentrated under reduced pressure. The crude product **37** was purified by flash column chromatography (silica gel, *n*-pentane/dichloromethane, 1:1) to furnish aldehyde **37** (173 g, 1.14 mmol, 88%) as a colourless liquid. $[\alpha]_D^{20}$ = –97.5 (*c* = 0.20, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2953, 2921, 2853, 1737, 1711, 1457, 1377, 1314, 1260, 1145, 1088, 1019, 968, 859, 801, 721, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.88 (t, *J* = 7.1 Hz, 3 H, 6′′-H), 1.14 (ddd, *J* = 8.6, *J* = 6.4, *J* = 5.0 Hz, 1 H, 3′-H_a), 1.22–1.36 (m, 4 H, 4′′-H, 5′′-H), 1.47 (ddd, *J* = 8.6, *J* = 5.0, *J* = 5.0 Hz, 1 H, 3′-H_b), 1.85 (dddd, *J* = 8.6, *J* = 5.0, *J* = 5.0, *J* = 3.7 Hz, 1 H, 1′-H), 1.98 (ddt, *J* = 7.2, *J* = 6.8, *J* = 1.4 Hz, 2 H, 3′′-H), 2.07 (dddd, *J* = 8.6, *J* = 8.2, *J* = 6.4, *J* = 3.7 Hz, 1 H, 1′-H), 5.03 (ddt, *J* = 15.2, *J* = 8.2, *J* = 1.5 Hz, 1 H, 1′′-H), 5.63 (ddt, *J* = 15.2, *J* = 6.8, *J* = 0.6 Hz, 1 H, 2′′-H), 9.13 (d, *J* = 5.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR ($CDCl_3$, 76 MHz): δ = 13.9 (C-6′′), 15.1 (C-3′), 22.2 (C-5′′), 25.2 (C-2′), 31.4 (C-1′), 31.7 (C-4′′), 32.1 (C-3′′), 128.4 (C-2′′), 132.4 (C-2′), 199.9 (C-1) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 152 (15) [M]$^+$, 134 (18) [M – H_2O]$^+$, 123 (19) [M – C_2H_5]$^+$, 95 (52) [M – C_4H_9]$^+$, 81 (100) [M – C_5H_{11}]$^+$. The spectroscopic data for aldehyde **37** were in full agreement with those reported in the literature.[37f]

(–)-(1*S*,2*S*)-Dictyopterene A (38): *n*BuLi (1.78 mL of 1.6 M solution in hexane, 2.86 mmol, 2.9 equiv.) was added dropwise through a cannula to a stirred solution of methyltriphenylphosphonium bromide (1.06 g, 2.96 mmol, 3.0 equiv.) in anhydrous diethyl ether (10 mL) at 0 °C under N_2. The yellow-orange solution was stirred for 30 min before aldehyde **37** (0.15 g, 0.99 mmol, 1.0 equiv.) in anhydrous diethyl ether (2 mL) was added dropwise through a cannula over a period of 5 min. The reaction mixture was stirred overnight. The mixture was then diluted with *n*-pentane (5 mL), directly

filtered through a short pad of silica gel and concentrated under reduced pressure. The crude product **38** was purified by flash column chromatography (silica gel, *n*-pentane) to furnish dictyopterene A (**38**; 0.12 g, 0.80 mmol, 81%) as a colourless liquid. $[\alpha]_D^{20}$ = –69.3 (*c* = 0.40, $CHCl_3$) [ref.[19d] $[\alpha]_D^{22}$ = +72.0 (*c* = 6.74, $CHCl_3$) for the (1*R*,2*R*) enantiomer]. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.75–0.84 (m, 2 H, 3′-H), 0.87 (t, *J* = 7.0 Hz, 3 H, 6′′-H), 1.25–1.35 (m, 4 H, 4′′-H, 5′′-H), 1.36–1.41 (m, 2 H, 1′-H, 2′-H), 1.95–2.05 (m, 2 H, 3′′-H), 4.84 (dd, *J* = 10.2, *J* = 2.3 Hz, 1 H, 2-H_a), 4.98 (dd, *J* = 17.2, *J* = 2.3 Hz, 1 H, 2-H_b), 5.03 (dd, *J* = 15.1, *J* = 6.1 Hz, 1 H, 1′′-H), 5.36 (ddd, *J* = 10.2, *J* = 17.2, *J* = 6.7 Hz, 1 H, 1-H), 5.46 (dt, *J* = 15.1, *J* = 6.9 Hz, 1 H, 2′′-H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.1 (C-6′′), 14.8 (C-3′), 22.3 (C-5′′), 23.6 (C-2′), 24.3 (C-1′), 31.8 (C-4′′), 32.2 (C-3′′), 111.8 (C-2), 129.2 (C-2′′), 131.6 (C-1′′), 140.9 (C-1) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 150 (100) $[M]^+$, 135 (15) $[M - CH_3]^+$, 122 (24) $[M - CH_2{=}CH_2]^+$, 121 (60) $[M - C_2H_5]^+$. The spectroscopic data for dictyopterene **38** were in full agreement with those reported in the literature.[37]

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