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RADICAL REACTIONS IN ORGANOBORON CHEMISTRY II [1] - INTER- AND INTRAMOLECULAR ADDITION OF CARBON CENTERED RADICALS TO ALKENYLBORANES .

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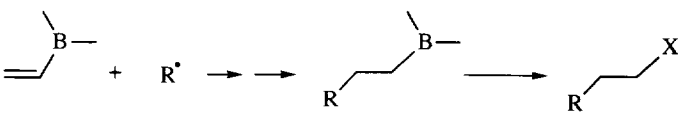
Abstract - The intermolecular addition of carbon centered radicals to alkenylboranes has been studied. The influence of the olefin and boron substituents on the reactivity and the regioselectivity was determined. Competitive experiments were carried out to estimate the relative reactivity of a series of vinylboranes and other electron deficient alkenes. Intramolecular versions of these additions were also described as well as some further transformations of selected adducts.

INTRODUCTION

The synthetic utility of radical additions to multiple bonds has been amply demonstrated mainly in regard to the creation of new carbon-carbon bonds.[2] In intermolecular additions, simple alkyl substituted carbon radicals, which may be considered to be essentially nucleophilic, react efficiently only with electron deficient alkenes.[2] Unlike acrylic esters, acrylamides, acrylonitrile or vinylsulfones, alkenylboranes have been scarcely used in radical reactions.[1, 3] We report herein our preliminary results related to the reactivity of these alkenes toward carbon centered radicals (Scheme 1). The main benefits of using **1** were expected in the activation of the carbon-carbon double bond and the further transformations of the adducts in various other useful intermediates by exploiting the rich organoboron chemistry.[4] Of additional interest was the possible control of the reactivity and stereoselectivity *via* the variation of the boron subtituents. Intramolecular versions of these reactions were also examined in the second part of this work.

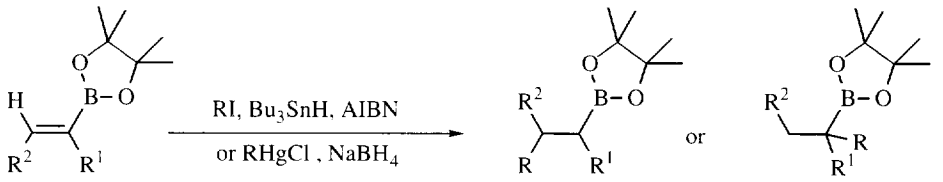


Scheme 1

RESULTS AND DISCUSSION

Intermolecular additions

We first examined the intermolecular addition to alkenylboronic esters **1** derived from pinacol (Scheme 1, Table I). They were readily accessible by known procedures [4] (hydroboration of alkynes or borylation of alkenyl metals) and were handled without special precaution. Two commonly used methods for conducting radical reactions were applied [2] : the tin hydride method from a iodo derivative and the decomposition of an organomercurial.



1 **2** **2'**

Scheme 2

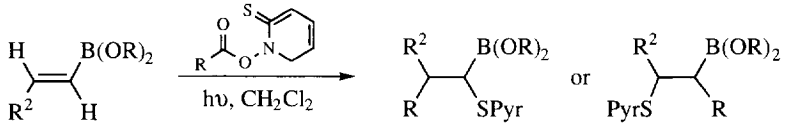
Table I : Addition of alkyl radicals to alkenylboronic esters **1**.

Entry	alkene	adduct	R^1	R^2	R	Method	Yield (%)[a]
1	**1a**	**2a**	H	H	*t*-Bu	A[b]	75
2	**1a**	**2a**	H	H	*t*-Bu	B[c]	83
3	**1a**	**2a'**	H	H	*c*-Hex	A[b]	15(35[d])
4	**1b**	**2b**	Me	H	*t*-Bu	A[b]	55
5	**1c**	-	H	nBu	*t*-Bu	A[b]	-
6	**1d**	**2'd**	H	CO_2Me	*c*-Hex	A[b]	46

a - Isolated yields. b - alkene (1 equiv), RI (7 equiv), Bu_3SnH(2.2 equiv). c - alkene (1 equiv), RHgCl (3 equiv), $NaBH_4$ (3 equiv)
d - alkene (6 equiv), RI (1 equiv), Bu_3SnH (1.1 equiv)

The reaction of the parent derivative **1a** with the *t*-butyl radical yielded the corresponding boronic ester **2a** with good yields (entries 1 and 2). In contrast, a poor result was obtained with the cyclohexyl radical. It was only slightly improved by using a sixfold excess of starting alkene (entry 3). The rate reducing effect of an α-methyl substituent was not surprising (entry 4) and the absence of adduct when R^1 = *n*-Bu as well (entry 5). The addition proceeded highly regioselectively with **1a** and **1b** giving only attack on the less substituted carbon atom. An ester group at C-2 ($R^1 = CO_2Me$) exerted both accelerating and high directing effects since the regioisomer **2'** was only formed in a 46 % yield (entry 6).

The photolysis of O-acyl derivatives of N-hydroxypyridine-2-thione [5] was also tested with boronic esters **1a** and **1d**. Unlike the tin hydride or the organomercurial methods, the addition reaction was not terminated by hydrogen atom transfer, but by the abstraction of thiopyridyl fragment. It then opened an interesting route to new α-functionalized boronic esters (Scheme 3, Table II).



1 3 4

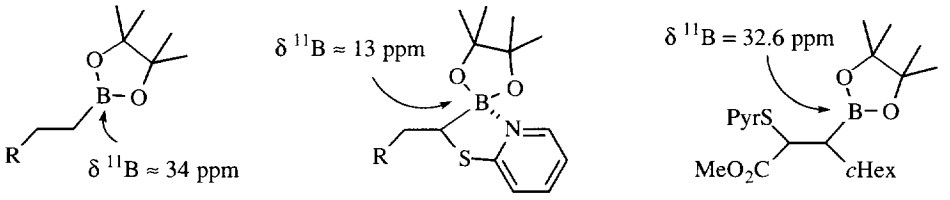
Scheme 3

Table II : Reaction of O-acyl derivatives of N-hydroxypyridine-2-thione with **1**.

Entry	Alkene	Adduct	R^2	R	Yield (%)[a,b]
1	**1a**	**3a**	H	*t*-Bu	58
2	**1a**	**3b**	H	*c*-Hex	36[c]
3	**1a**	**3c**	H	$PhCH_2CH_2$	32
4	**1d**	**4**	CO_2Me	*c*-Hex	34

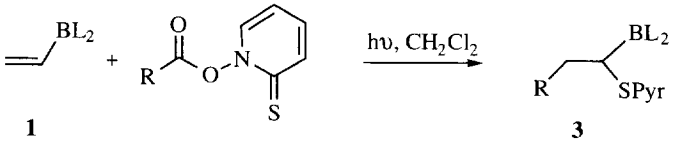
a - Isolated yields. b - alkene (5equiv), O-acyl derivatives of N-hydroxypyridine-2-thione (1 equiv).
c - mixture of two diastereoisomers 75/25

Single regioisomers were obtained from **1a** and **1d** as previously observed. Yields are quite similar to those obtained with the tin hydride method. It is worthy to note the presence of an intramolecular chelation between boron and nitrogen of **3** that was confirmed by a high field ^{11}B chemical shift. Such a shielding was not observed for the ester **4**.



2 3 4

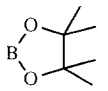
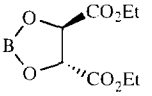
Barton radical chain procedure furnished very stable adducts easily identified in ^1H NMR and appeared to be the most convenient to evaluate the reactivity of alkenylboranes. We first modified the substituents at boron (Scheme 4, Table III). Vinyl-9-BBN [6] **1f** displayed significantly improved reactivity compared with the corresponding boronic ester (entry 3 and 4). Radical additions to alkenes are subject to frontier molecular orbital theory.[2] Not surpringly, the presence of the 9-BBN substituent that lowered the LUMO energy [6] promoted the nucleophilic radical addition.



1 3

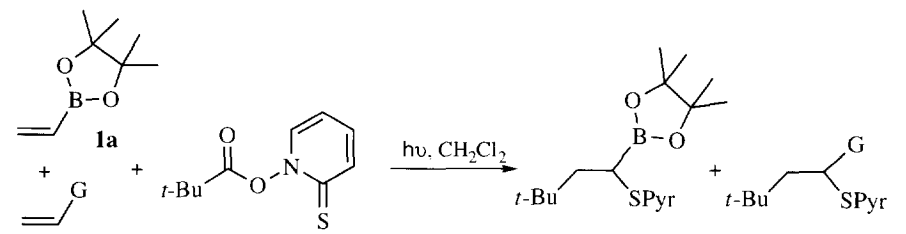
Scheme 4

Table III - Modification of boron substituents.

Entry	Vinylborane	BL_2	R	Adduct	Yield (%)[a,b]
1	**1a**		*t*-Bu	**3a**	58
2	**1e**		*t*-Bu	**3e**	63 [c]
3	**1f**		*t*-Bu	**3f**	78
4	**1f**		*c*-Hex	**3g**	68

a - Isolated yields. b - alkene (5equiv), N-hydroxypyridine-2-thione derivative (1 equiv). c - two diastereoisomers (60/40).

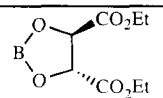
We also conducted a series of competitive experiments to compare alkenylboranes with other electron deficient olefins (Scheme 5, Table IV). Authentic samples of each possible adduct were first prepared. Their ratio in crude mixtures were determined by examination of the ^1H NMR spectra. As it can be seen from these data, diethyltartrate vinylboronic ester **1e** and acrylamide **6** showed quite similar reactivities and a carboxylic ester group was clearly a better activating group than a boronic ester derived from pinacol. Unfortunately, vinyl-9-BBN, the most reactive of the tested alkenylboranes, showed a limited stability under these conditions and could not be included in this study.



x = 1e, 5, 6 or 7 **3a** **y = 3e, 8, 9 or 10**

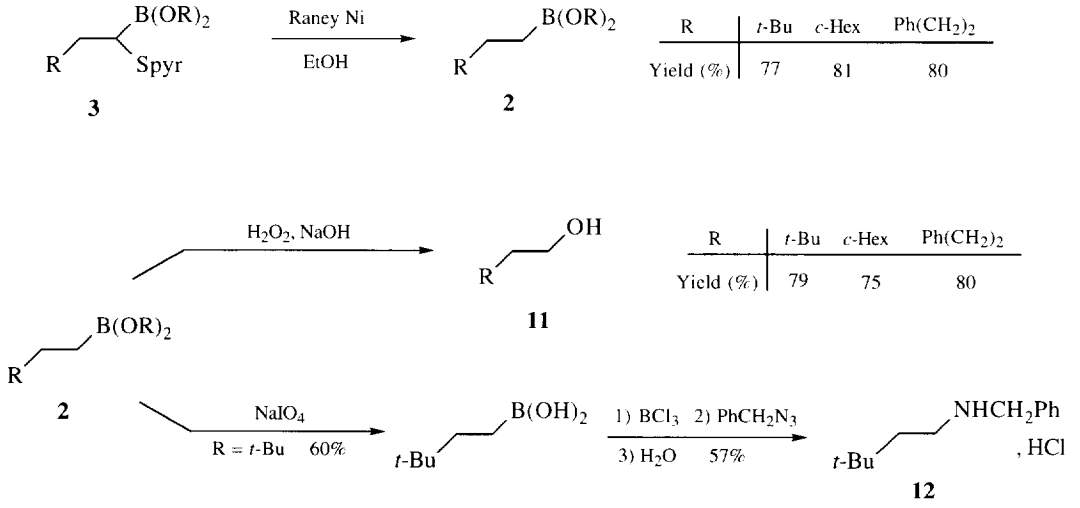
Scheme 5

Table IV - Competitive addition of *t*-Bu$^{\bullet}$ to alkenes.

Entry	G	Alkene	y	3a/y
1		**1e**	**3e**	28/72
2	CO_2CH_3	**5**	**8**	4/96
3	$CONMe_2$	**6**	**9**	20/80
4	C_6H_5	**7**	**10**	100/0

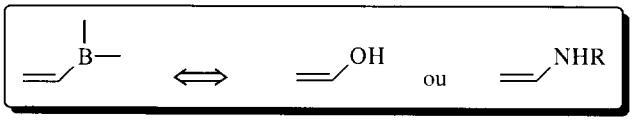
a - **1a** (1 equiv), **x** (1 equiv), N-hydroxypyridine-2-thione O-pivaloate (1 equiv).

After having established the scope and limitations of intramolecular carbon centered radical additions to alkenylboranes, we illustrated the synthetic potential of the adducts by achieving some transformations of selected compounds (Scheme 6). Reductive elimination of the thiopyridyl group of **3a-3c** with Raney Nickel [7] gave compounds of type **2** with good yields. Oxidation of **2** with hydrogen peroxide in the presence of sodium hydroxide [8] yielded the alcohols **11**. Conversion of the boronic ester **2** to the corresponding dichloroborane *via* the boronic acid [9, 10] and further reductive alkylation of benzylazide [11] gave the amine hydrochloride **12**.



Scheme 6

Vinylboranes may be therefore regarded as synthetic equivalents of enols and enamines in these intermolecular radical additions.[12] That was all the more interesting because of the absence of reactivity of these electron rich alkenes towards nucleophilic alkyl radicals.

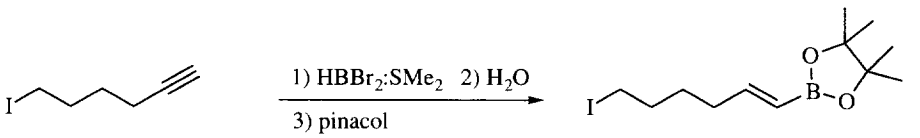


Intramolecular additions

Radical intramolecular addition are the central steps in the synthesis of many cyclic organic compounds and, among them, the cyclization of variously substituted hex-5-enyl radicals constitutes a particularly efficient method for the preparation of five membered rings. [2] The factors affecting these reactions are now well understood (competition between *endo* and *exo* mode, stereochemistry of the products)[13] and we selected this class of radical cyclizations to determine the practibility of such approaches in the case of unsaturated boronic esters.[14]

Starting compounds were prepared using classical organoboron chemistry including :

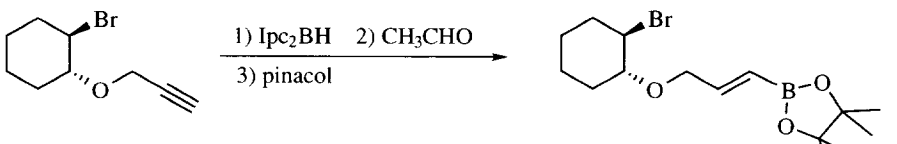
- Hydroboration of 6-iodohex-1-yne with dibromoborane-dimethylsulfide complex followed by hydrolysis and treatment with pinacol (Scheme 7).[15]



13 (70%)

Scheme 7

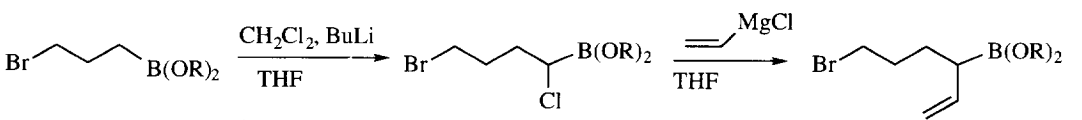
- Hydroboration of a propargyl ether [16] with diisopinocampheylborane followed by treatment with excess of acetaldehyde and pinacol (Scheme 8).[17]

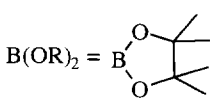


14 (73%)

Scheme 8

- Homologation of the 3-bromopropylboronic ester derived from pinacol followed by addition of vinylmagnesium bromide (Scheme 9).[18]



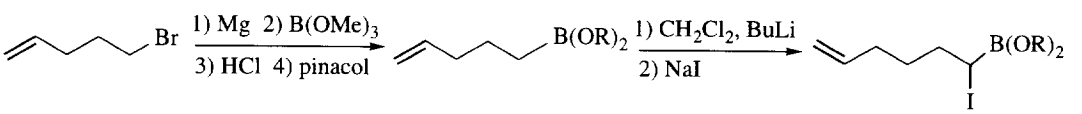
$B(OR)_2$ = 

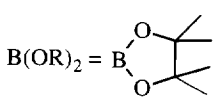
15 (85%)

16 (95%)

Scheme 9

- Borylation of 5-pentenylmagnesium bromide with trimethylborate followed by treatment with hydrochloric acid and pinacol.[19] The boronic ester **17** was then homologated with dichloromethyllithium.[18] Exchange chloride/iodide in acetone led to **18** (Scheme 10)



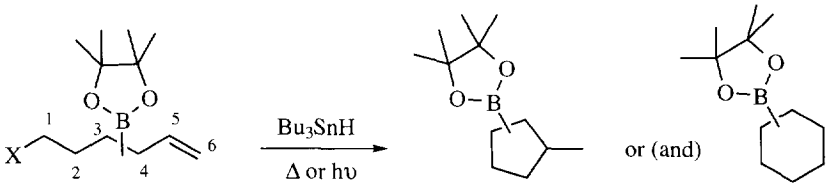
$B(OR)_2$ = 

17 (55%)

18 (72%)

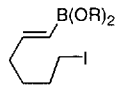
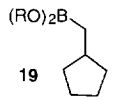
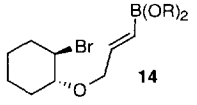
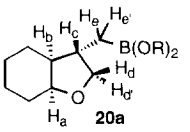
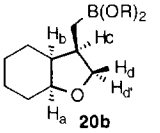
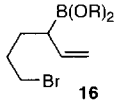
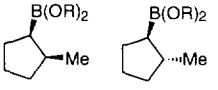
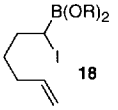
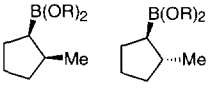
Scheme 10

The required alkyl radicals were generated photochemically or thermally by reaction of the halides **13**, **14**, **16** and **18** and Bu_3SnH (Scheme 11, Table V). Ring closures occurred with good yields and products were fully characterized by ^1H, ^{13}C NMR, elemental analysis or high resolution mass spectra. Cyclopentylmethyl boronic ester **19**, (E)-2-methylcyclopentylboronic ester **21a** and cyclohexylboronic ester **22** were prepared independently by hydroboration of methylenecyclopentane, 1-methylcyclopentene and cyclohexene [15] that allowed to determine the relative ratio of each isomer in the crude mixtures by ^1H NMR and capillary gas chromatography. The *cis* junction of **20a** and **20b** was ascertained by examination of the ^1H NMR (J_{HaHb} = 2.8 and 4.5 Hz) and the relationship between H_b and H_c (see table V, entry 2) by NOESY experiments (presence of NOE effects between H_a,H_b ; H_c,H_d ; H_a,H_e for **20a** and between H_a,H_b ; H_a,H_c ; H_b,H_c ; H_c,$H_{d'}$ for **20b**).



Scheme 11

Table V - Cyclization of unsaturated boronic esters

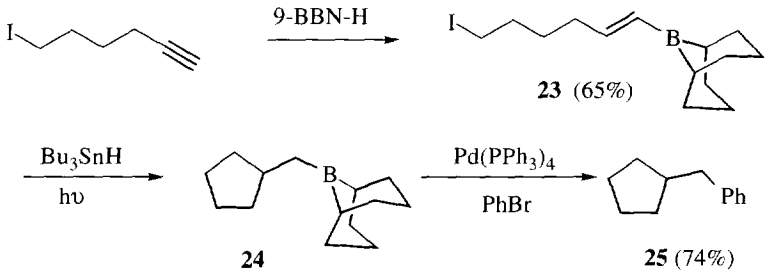
Entry	substrate	products	initiation	yield (%)[a]
1	 **13**	 **19**	Δ, AIBN	**19** (93)
			hυ	**19** (87)
2	 **14**	 **20a**  **20b**	Δ, AIBN	**20a** (52), **20b** (28)
3	 **16**	 **21a** **21b** **22**	Δ, AIBN	**21a** (13), **21b** (68), **22**(2)
			hυ	**21a** (8), **21b** (72), **22**(1)
4	 **18**	 **21a** **21b** **22**	Δ, AIBN	**21a** (36), **21b** (38), **22**(11)
			hυ	**21a** (43), **21b** (34), **22**(8)

a - Isolated yields

As expected, the presence of a boronic ester on C-6 accelerated 5-*exo* cyclizations (entries 1 and 2) due to favorable FMO interactions and no 6 membered ring was detected. The introduction of the same group

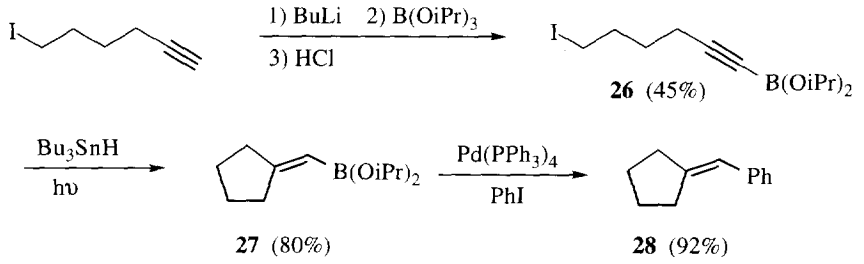
on C-4 or C-5 sufficiently retarded attack of the radical at C-5 to enable the *endo* mode to be observed (entries 3 and 4). Concerning the stereochemistry of these cyclisations, 4-substituted hex-5-enyl radical led mostly to *trans* product (entry 3) that follows the guidelines proposed by A.L. Beckwith.[13] 1-Substituted hex-5-enyl radical generated from **18** gave a mixture of *cis* and *trans* cyclopentanes in quite similar amounts (entry 3) as it was observed in a similar situation by D.P. Curran *et al.*[20] *Cis* ring junction was only present in the case of **15** with a *trans* relationship between Ha and Hc for the major isomer **20a** (entry 2).

Adducts **19-22** were potential precursors of the corresponding alcohols and amines as previously shown. We prefered to study other reactions of these cyclic products in order to point out the importance of the boron substituents in further transformations. For example, the 9-BBN derivative **23**, which was prepared by hydroboration of 6-iodohex-1-yne with 9-BBN-H [21], afforded the benzylcyclopentane **25** after irradiation with Bu_3SnH and reaction with bromobenzene in the presence of tetrakis(triphenylphosphine)palladium(0) (Schema 12).[22]



Schema 12

6-Iodohexyn-1-yldiisopropoxyborane **26** was prepared from the corresponding 1-lithiohex-1-yne.[23] After cyclisation and palladium catalysed cross-coupling with iodobenzene, the alkene **28** was obtained in a 73% yield (Schema 13).



Schema 13

In conclusion, alkenylboranes have been proved to be useful traps for nucleophilic alkyl radicals, thus opening attractive routes to diversely substituted alkyl- and alkenylboronic esters and, therefore, to a large variety of synthetic intermediates. Further investigations are underway to explore the synthetic potential of radical additions to other unsaturated organoboranes including the possiblity of employing esters of opticaly active diols as chiral directors.

EXPERIMENTAL SECTION

Light sensitive compounds (alkyl iodides and O-acyl derivatives of N-hydroxypyridine-2-thione) were handled in the dark. The reactions requiring a nitrogen atmosphere were performed in flame dried glassware and were stirred magnetically. Toluene,THF and dichloromethane were dried immediately prior to use by distillation under nitrogen from sodium benzophenone ketyl and P_2O_5, respectively. Melting points were determined on a Kofler apparatus and were uncorrected. IR spectra were recorded on a Perkin Elmer 1420 model and samples examined as liquid film or nujol suspension. Frequencies ν are expressed in cm^{-1}. Unless otherwise noted, NMR spectra were measured in $CDCl_3$ solutions on a Bruker AC 300 (300 MHz for ^1H and 75.5 MHz for ^{13}C). Chemical shifts are reported in parts per million (δ) downfield relative to tetramethylsilane as an internal standard and apparent coupling constants (J) are in hertz (Hz). The following abbreviations are used : s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra were obtained on a Varian MAT 311 (Centre Régional de Mesures Physiques, Université de Rennes I). Microanalysis were performed at the Central Laboratory for Analysis, CNRS, Lyon (France). Thin layer chromatography was performed on aluminum plates coated with a 0.02 mm layer of silica gel 60F-254 purchased from Merck wheras column chromatography purifications were performed on silica gel (70-230 mesh). Analytical gas chromatography was performed on a Fisons-8000 instrument equiped with a (50 % phenyl)methylpolysiloxane DB-17 Megabore, 30M, 1 μm, 0.53 mm ID column and a flame ionization detector (FID) using azote as a carrier gas. Starting vinylboronic esters were prepared according reported procedures : **1a**[19] **1b**[19], **1c**[15], **1d**[17], **1e**[24], **1f**[6].

INTERMOLECULAR ADDITIONS

- from an alkyl halide

In a typical procedure, a solution of vinylboronic ester **1** (1 mmol) and alkyl iodide (7 mmol) in 5 mL of degeased toluene was irradiated at 20-25°C with a 500 W halogen lamp. A solution of tributyltinhydride (2.2 mmol) in 5 mL of toluene was then added *via* a syringe pump over a period of 2 h. After the end of addition, the reaction was continued for one hour. Most of the solvent was evaporated, technical diethylether (20 mL) was added followed by 2.2 mmol of DBU [20] and the solution was titrated with 0.1 M iodine in ether After the iodine colour just persists, the mixture was filtered through a plug of silica gel and anhydrous magnesium sulfate. Concentration under vacuum gave an oil which was purified by bulb to bulb distillation or by column chromatography on silica gel.

- from an organomercury halide

To a solution of *t*-butylmercury chloride [25] (1 mmol) and of vinylboronic ester **1** (3 mmol) in 15 mL of CH_2Cl_2 was added at 0°C in two portions a solution of sodium borohydride (3 mmol) in 5 mL of cold water. Filtration of precipitated mercury through celite followed by concentration gave an oil which was purified by bulb to bulb distillation.

- from an O-acyl derivative of N-hydroxypyridine-2-thione.

In a typical procedure, to the acylchloride (1 mmol) in anhydrous CH_2Cl_2 (10 mL) was added under argon the sodium salt of N-hydroxypyridine-2-thione and a small amount of DMAP (10 mg) with exclusion of light (aluminium foil).[5] The reaction mixture was stirred at room temperature for 1 hour. 5 mmol

of **1** was then added and the yellow solution was irradiated with a 500 W halogen lamp for 30 minutes. The mixture was washed with water, saturated NaCl and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was subjected to flash chromatography on silica gel to give compounds **3**.

***3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane* 2a**. 75 %. $bp_{0.02}$ = 45-50°C. ^1H NMR ($CDCl_3$) δ : 0.62-0.73 (m, CH_2-B, 2H), 0.85 (s, $C(CH_3)_3$, 9H), 1.25 (s, $C(CH_3)_2$, 12H), 1.19-1.30 (m, $C\underline{H}_2$-CH_2-B, 2H). ^{13}C NMR ($CDCl_3$) δ : 5.8 (CH_2B, broad), 24.8 ($C(\underline{C}H_3)_3$), 28.8 ($C(\underline{C}H_3)_2$), 30.7 ($\underline{C}(CH_3)_3$), 37.7 ($\underline{C}H_2$-CH_2-B), 82.7 ($\underline{C}(CH_3)_2$). ^{11}B NMR (C_6D_6) δ : 34.2. Anal. Calc. for $C_{12}H_{25}BO_2$: C, 67.94 ; H 11.88 , Found : C, 67.7 ; H, 11.9.

***2-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane* 2a'**. 15 % (35% when **1a** (6 equiv), iodocyclohexane (1 equiv), Bu_3SnH (1.1 equiv)). Rf (diethylether/heptane : 19/1) = 0.45. $bp_{0.05}$ = 55-60°C. ^1H NMR ($CDCl_3$) δ : 0.71-0.81 (m, CH_2-B, 2H), 0.81-0.97 (m, 2H), 1.00-1.25 (m, 4H), 1.24 (s, $C(CH_3)_2$, 12H), 1.24-1.37 (m, $C\underline{H}_2$-CH_2-B, 2H), 1.55-1.80 (m, 5H). ^{13}C NMR ($CDCl_3$) δ : 8.5 ($\underline{C}H_2$-B, broad), 24.8 ($C(\underline{C}H_3)_2$), 26.4 (CH_2), 26.7 (CH_2), 31.4 ($\underline{C}H_2$-CH_2-B), 33.0 (CH_2), 39.9 (CH), 82.8 ($\underline{C}(CH_3)_2$).^{11}B NMR (C_6D_6) δ : 34.2. Anal. Calc. for $C_{14}H_{27}BO_2$: C, 70.60 ; H 11.43 , Found : C, 70.7 ; H, 11.4.

***4,4-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentane* 2b.** 55 %. $bp_{0.01}$ = 35-40°C. ^1H NMR ($CDCl_3$) δ : 0.87 (s, $C(CH_3)_3$, 9H), 0.90-1.12 (m, 4H), 1.23 (s, $C(CH_3)_3$, 12 H), 1.59 (dd, J = 10.1 et 13.8, H). ^{13}C NMR ($CDCl_3$) δ : 12.9 (CH-B,broad), 18.2 ($\underline{C}H_3$-CH), 24.6 ($C(\underline{C}H_3)_2$), 29.7 ($C(\underline{C}H_3)_3$), 31.0 ($\underline{C}(CH_3)_3$), 48.1 (CH_2), 82.7 ($\underline{C}(CH_3)_2$). HRMS m/z calc. for $C_{12}H_{24}O_2{}^{11}B$ $[M - {}^{\bullet}CH_3]^+$: 211,1829 . Found : 211,186.

***Methyl 3-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate* 2'd**. 46%. Rf (diethylether) = 0.3. $bp_{0.05}$ = 80-85°C. ^1H NMR ($CDCl_3$) δ : 0.84-1.40 (m, 7H), 1.16 (s, $C(CH_3)_2$, 6H), 1.18 (s, $C(CH_3)_2$, 6H), 1.46-1.70 (m, 5H), 2.29 (dd, J = 5.6 et 16.4, 1H), 2.40 (dd, J = 10.5 et 16.4, H), 3.56 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$) δ : 24.6 ($C(\underline{C}H_3)_2$), 24.9 ($C(\underline{C}H_3)_2$), 26.5 (CH_2), 26.6 (CH_2), 26.65 (CH_2), 32.1 (CH_2), 32.4 (CH_2), 33.3 (CH_2), 39.1 (CH), 51.2 (OCH_3), 83.0 ($\underline{C}(CH_3)_2$), 174.6 (C=O). The carbon α to boron was not found. ^{11}B NMR (C_6D_6) δ : 33.7.

***3,3-dimethyl-1-(pyridylthio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) butane* 3a**. 58%. Rf (diethylether/heptane : 3/1) = 0.4. mp = 122 °C. ^1H NMR ($CDCl_3$) δ : 0.93 (s, $C(CH_3)_3$, 9H), 1.20 (s, $C(CH_3)_2$, 6H), 1.22 (dd, J = 11.7 et 15.0, 1H), 1.28 (s, $C(CH_3)_2$, 6H), 2.13 (dd, J = 0.9 and 15.0, 1H), 2.42 (dd, J = 0.9 and 11.7, 1H), 7.12 (ddd J = 1.1, 5,9 and 7.2, 1H), 7.33 (ddd, J = 0.9, 1.1 and 8.4, 1H), 7.69 (ddd, J = 1.3, 7.2 and 8.4, 1H), 8.43 (ddd, J = 0.9, 1.3 and 5.9, 1H). ^{13}C NMR ($CDCl_3$) δ : 26.2 ($C(\underline{C}H_3)_2$), 26.4 ($C(\underline{C}H_3)_2$), 29.8 ($C(\underline{C}H_3)_3$), 31.5 ($\underline{C}(CH_3)_3$), 33.3 (BCH, broad), 47.1 (CH_2), 80.2 ($\underline{C}(CH_3)_2$), 118.7 (CH), 122.8 (CH), 140.2 (CH), 141.9 (CH), 164.4 (S-$\underline{C}$=N). ^{11}B NMR δ : 13.0. Anal. Calc. for $C_{17}H_{28}BNOS$: C, 63.55 ; H, 8.78 ; N, 4.36. Found : C, 63.3 ; H, 8.6 ; N, 4.2.

***2-cyclohexyl-1-(pyridylthio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane* 3b**. 36%. Rf (diethylether) = 0.3. mp = 120 °C. ^1H NMR ($CDCl_3$) δ : 0.72-1.05 (m, 2H), 1.05-1.32 (m, 4H) ; 1.20 (s, $C(CH_3)_2$, 6H), 1.27 (s, $C(CH_3)_2$, 6H), 1.32-1.50 (m, 1H,), 1.50-1.78 (m, 5H), 1.90 (d , J = 12.8, 1H), 2.57 (dd, J = 2.9 and 13.0, 1H), 7.13 (ddd, J = 1.0, 5.7 and 7.3, 1H), 7.34 (ddd, J = 0.9, 1.0 and 8.2, 1H), 7.69 (ddd, J = 1.5, 7.3 and 8.2, 1H), 8.44 (ddd, J = 0.9, 1.5 and 5.7, 1H). ^{13}C NMR ($CDCl_3$) δ : 26.1 ($C(\underline{C}H_3)_2$), 26.3 ($C(\underline{C}H_3)_2$), 26.8 (CH_2); 31.6 (CH_2), 34.6 (CH_2), 37.0 (CH), 37.3 (BCH), 40.4 (BCH$\underline{C}H_2$), 80.0 ($\underline{C}(CH_3)_2$), 118.9 (CH), 123.1 (CH), 140.2 (CH), 142.3 (CH), 164.0 (S-

C=N). ^{11}B NMR ($CDCl_3$) δ: 12.9. Anal. Calc. for $C_{19}H_{30}BNO_2S$: C, 65.70 ; H, 8.71 ; N, 4.03. Found : C, 65.3 ; H, 8.5 ; N, 3.9.

4-phenyl-1-(pyridylthio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane **3c.** 32%. Rf (diethylether) = 0.3. ^1H NMR ($CDCl_3$) δ : 1.19 (s, $C(CH_3)_2$, 6H), 1.17-1.45 (m, 1H), 1.27 (s, $C(CH_3)_2$, 6H), 1.57-1.90 (m, $PhCH_2\underline{C}H_2$, 2H), 1.90-2.05 (m, 1H), 2.44 (dd, J = 3.2 and 11.9, 1H), 2.48-2.72 (m, $PhC\underline{H}_2$, 2H), 7.11 (ddd, J = 0.9, 5.9 and 7.2, 1H), 7.12-7.29 (m, 5H), 7.32 (ddd, J = 0.8, 0.9 and 8.2, 1H), 7.66 (ddd, J = 1.5, 7.2 and 8.2, 1H), 8.43 (ddd, J = 0.9, 1.5 and 5.9, 1H).^{13}C NMR ($CDCl_3$) δ : 26.1 ($C(\underline{C}H_3)_2$), 26.4 ($C(\underline{C}H_3)_2$), 31.8 ($PhCH_2\underline{C}H_2$), 32.6 ($BCH\underline{C}H_2$), 35.7 ($Ph\underline{C}H_2$), 40.8 (BCH, broad), 80.1 ($\underline{C}(CH_3)_2$), 119.0 (CH), 123.0 (CH), 125.5 (CH), 128.2 (CH), 128.4 (CH), 140.3 (CH), 142.2 (CH), 142.6 (C), 163.8 (S-$\underline{C}$=N).^{11}B NMR ($CDCl_3$) δ : 12.9. HRMS m/z calc. for $C_{21}H_{28}NO_2S^{11}B$ $[M]^{+\cdot}$: 369,1933. Found : 369,191.

3,3-dimethyl-1-(pyridylthio)-1-(diethyl 4,5-dicarboxylate-1,3,2-dioxaborolan-2-yl) butane **3e** 63 %. Rf(diethylether /heptane : 2/1) = 0.2. Mixture of two diastereoisomers (60/40). A 90/10 mixture of the diastereoisomers sponteanously cristallized. ^1H and ^{13}C NMR data of each isomer were deduced from the spectra of the two mixtures. Major diastereoisomer : ^1H NMR($CDCl_3$) δ : 0.94 (s, $C(CH_3)_3$, 9H), 1.31 (t, J = 7.1, 6H), 1.46 (dd, J = 11.0 and 15.0, 1H), 1.92 (dd, J = 1.9 and 15.0, 1H), 2,79 (dd, J = 1.9 and 11.0, 1H), 4.20-4.32 (m, 4H), 4.68 (d, J = 6.1, 1H), 4.73 (d, J = 6.1, 1H), 7.17 (t, J = 7.1, 1H), 7.33 (d, J = 8.2,1H), 7.73 (dt, J = 1.5 and 7.7, 1H), 8.63 (d, J = 5.0, 1H). RMN ^{13}C ($CDCl_3$, 75 MHz) δ : 14.1 ($\underline{C}H_3$-CH_2), 29.7 ($C(\underline{C}H_3)_3$), 31.45 ($\underline{C}(CH_3)_3$), 32.7 (C-B, broad), 46.0 (CH_2), 61.3 ($\underline{C}H_2$-CH_3), 78.0 (CH), 119.2 (CH), 122.0 (CH), 140.7 (CH), 142.5 (CH), 164.6 (S-C=N), 172.1 (C=O). Minor diastereoisomer : ^1H NMR($CDCl_3$) δ : 0.96 (s, $C(CH_3)_3$, 9H), 1.32 (t, J = 7.1, 6H), 1.57 (dd, J = 11,0 and 15.2, 1H), 2.05 (dd, J = 1.9 and 15,2, 1H), 2.79 (dd, J = 1.9 and 11.0, 1H). 4.20-4.32 (m, 4H), 4.67 (d, J = 7.0, 1H), 4.70 (d, J = 7.0, 1H), 7.17 (t, J = 7.1, 1H), 7.33 (d, J = 8.2,1H), 7.73 (dt, J = 1.5 and 7.7, 1H), 8.68 (d, J = 5.8, 1H). ^{13}C NMR ($CDCl_3$), δ : 14.2 ($\underline{C}H_3$-CH_2), 29.7 ($C(\underline{C}H_3)_3$), 31.4 ($\underline{C}(CH_3)_3$), 32.7 (C-B, broad), 44.8 (CH_2), 61.2 ($\underline{C}H_2$-CH_3), 77.9 (CH), 119.4 (CH), 122.1 (CH), 140.6 (CH), 142.7 (CH), 164.5 (S-C=N), 171.5 (C=O). ^{11}B ($CDCl_3$) δ : 14.9 (for the two diastereoisomers). HRMS m/z calc. for $C_{21}H_{28}NO_2S^{11}B$ $[M]^{+\cdot}$: 369,1933. Found : 369,191.

3,3-dimethyl-1-(pyridylthio)-1-(9-borabicyclo[3.3.1.]non-9-yl)butane **3f**. 78% Rf (diethylether/heptane : 1/4).= 0.5 mp = 110-112 °C. ^1H NMR ($CDCl_3$) δ : 0.67-1.21 (m, 4H), 0.92 (s, $C(CH_3)_3$, 9H), 1.11 (dd, J = 11.3 and 15.1, 1H), 1.41-2.09 (m, 10H), 1.92 (d, J = 15.1, 1H), 2.17-2.32 (m, 1H), 2.83 (d, J = 11.3, 1H), 7.02 (ddd, J = 0.9, 6.0 and 7.1, 1H), 7.33 (ddd, J = 0.8, 0.9 and 8.4, 1H), 7.56 (ddd, J = 1.5, 7.1 and 8.4, 1H), 8.64 (d, J = 0.9, 1.5 and 6.0, 1H). ^{13}C NMR($CDCl_3$) δ : 22.0 (BCH of 9BBN, broad), 23.7 (CH_2), 24.4 (CH_2), 29.6 (CH_2), 30.0 ($C(\underline{C}H_3)_3$), 30,6 (CH_2), 31.6 ($\underline{C}(CH_3)_3$), 32.8 (CH_2), 34.7 (CH_2), 39.5 (BCHS, broad), 45.1 ($\underline{C}H_2C(CH_3)_3$), 117.7 (CH), 122.4 (CH), 137.6 (CH), 144.8 (CH), 165.3 (SC=N). ^{11}B NMR, δ : 5.2. Anal. Calc. for $C_{19}H_{30}BNS$: C, 72.37 ; H, 9.59. Found : C, 72.4 ; H, 9.4.

2-cyclohexyl-1-(pyridylthio)-1-(9-borabicyclo[3.3.1.]non-9-yl)ethane **3g**. 68%. mp = 115-116°C. Rf (diethylether/heptane : 1/5) = 0.5. ^1H NMR ($CDCl_3$) δ : 0.70-2.42 (m, 28H), 2.93 (dd, J = 2.0 and 12.7, 1H), 7.03 (ddd, J = 0.9, 5.9 and 7.3, 1H), 7.34 (ddd, J = 0.8, 0.9 and 8.4, 1H), 7.56 (ddd, J = 1.2, 7.3 and 8.4, 1H), 8.44 (ddd, J = 0.9, 1.2 and 5.9, 1H). ^{13}C NMR ($CDCl_3$) δ : 22.0 (BCH, broad), 23.8 (CH_2), 24.5 (CH_2), 26.3 (CH_2), 26.6 (CH_2), 26.9 (CH_2), 29.6 (CH_2), 30,4 (CH_2), 31.6 (CH_2), 32.8 (CH_2), 35.0 (CH_2), 35.4 (CH_2), 36.6 (CH), 39.0 ($BCH\underline{C}H_2$), 41.7 (BCHS, broad), 117.9 (CH), 122.7

(C), 137.7 (CH), 145.1 (CH), 165.1 (SC=N). ^{11}B NMR ($CDCl_3$) δ : 5.4. Anal. Calc. for $C_{21}H_{32}BNS$: C, 65.70 ; H, 8.71 ; N, 4.03. Found : C, 65.3 ; H, 8.5 ; N, 4.0

***Methyl 3-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(pyridylthio)propanoate* 4**. 34%. Rf(diethylether/heptane : 20/80) = 0.3. Mixture of two diastereoisomers (75/25). The major diastereoisomer cristallized spontaneously from the mixture, mp = 95-96°C : ^{1}H NMR ($CDCl_3$) δ : 0.80-1,32 (m, 5H) , 1.23 (s, 6H) , 1.26 (s, 6H) , 1.40-1.90 (m, 6H) , 1.55 (dd, J = 3.6 and 11.9, 1H), 3.66 (s, OCH_3, 3H), 4.84 (d, J = 11.9, 1H), 6.99 (ddd, J = 0.9, 4.9 and 7.4, 1H), 7.24 (dt, J = 0.9 and 8.0, 1H), 7.47 (dt, J = 1.8, 7.4 and 8.0, 1H), 8.42 (dt, J = 0.9 and 4.9, 1H). ^{13}C NMR ($CDCl_3$) δ : 24.7 (CH_2), 25.1 ($C(\underline{C}H_3)_2$), 26.5 (CH_2), 26.7 (CH_2), 32.7 (C-B, broad), 33.5 (CH_2), 36.8 (CH), 46.1 (CH), 52.1 (OCH_3), 83.4 ($\underline{C}(CH_3)_2$), 119.9 (CH), 122.6 (CH), 136.0 (CH), 149.3 (CH), 157.8 (C=O), 174.0 (S-C=N). Minor diastereoisomer (signals deduced from the mixture of the two diastereoisomers) : ^{1}H NMR ($CDCl_3$) δ : 0.80-1.32 (m, 5H) , 1.19 (s, 6H) , 1.25 (s, 6H), 1.40-1.90 (m, 7H), 3.70 (s, OCH_3, 3H), 4.84 (d, J = 8.6, 1H), 6.93 (ddd, J = 1.0, 5.0 and 7.4, 1H), 7.20 (dt, J = 1.0 and 8.0, 1H), 7.44 (dt, J = 1.9, 8.0 and 8.4, 1H), 8.42 (dt, J = 0.9, 1.0 and 5.9, 1H). ^{13}C NMR ($CDCl_3$) δ : 24.8 (CH_2), 25.0 ($C(\underline{C}H_3)_2$), 26.6 (CH_2), 26.9 (CH_2), 32.7 (C-B, broad), 33.1 (CH_2), 38.0 (CH), 45.9 (CH), 52.2 (OCH_3), 83.6 ($\underline{C}(CH_3)_2$), 119.6 (CH), 121.9 (CH), 135.9 (CH), 149.4 (CH), 157.9 (C=O), 173.9 (S-C=N). ^{11}B NMR ($CDCl_3$) δ : 32.6 (for the two diastereoisomers). Anal. Calc. for $C_{21}H_{32}BNO_4S$: C, 62.22 ; H, 7.96 ; N, 3.46. Found : C, 61.9 ; H, 7.8 ; N, 3.4

Competitions experiments

Adducts derived from methyl acrylate and dimethyl acrylamide were first prepared according to the literature.[5]

***Methyl 4,4-dimethyl-2-(pyridylthio)pentanoate* 8**. 60%. $bp_{0.02}$ = 80-85°C. ^{1}H NMR ($CDCl_3$) δ : 0.97 (s, $C(CH_3)_3$, 9H), 1.72 (dd, J = 4.3 and 14.2, 1H), 2.13 (dd, J = 9.1 and 14,2, 1H), 3,70 (s, OCH_3, 3H), 4.65 (dd, J = 4.3 and 9,1, 1H), 7.00 (ddd, J = 1.2, 5.0 and 7.3, 1H), 7.19 (dt, J = 1.2 and 8.2, 1H), 7.49 (ddd, J = 0.9, 7.2 and 8.2, 1H), 8.43 (ddd, J = 0.9, 1.2 and 5.0, 1H). ^{13}C NMR ($CDCl_3$) δ : 29.3 ($C(\underline{C}H_3)_3$), 31.5 ($\underline{C}(CH_3)_3$), 42.8 (CH), 46.1 (CH_2), 52.4 (OCH_3), 120.0 (CH), 122.3 (CH), 136.2 (CH), 149.5 (CH), 157.2 (C=N), 174.0 (C=O).Anal. Calc. for $C_{13}H_{19}NO_2S$: C, 61.63 ; H, 7.56 ; N, 5.53. Found : C, 61.4 ; H, 7.6 ; N, 5.5.

***N,N-dimethyl 4,4-dimethyl-2-(pyridylthio)pentanamide* 9**. 41%. mp = 79°C. ^{1}H NMR ($CDCl_3$) δ : 0.93 (s, $C(CH_3)_3$, 9H), 1.63 (dd, J = 3.3 and 13.9, 1H), 2.43 (dd, J = 9.7 and 13.9, 1H), 2.97 (s, NCH_3, 3H), 3.20 (s, NCH_3, 3H), 5.18 (dd, J = 3.3 and 9.7, 1H), 6.99 (ddd, J = 1.0, 4.9 and 7.4, 1H), 7.15 (ddd, J = 0.9, 1.0 and 7.2, 1H), 7.48 (ddd, J = 1.8, 7.2 and 7.9, 1H), 8.41 (ddd, J = 0.9, 1.8 and 4.9, 1H). ^{13}C NMR ($CDCl_3$) δ : 29.6 ($C(\underline{C}H_3)_3$), 31.3 ($\underline{C}(CH_3)_3$), 36.2 (N-CH_3), 37.5 (N-CH_3), 39.0 (CH), 47.2 (CH_2), 119.8 (CH), 122.4 (CH), 136.1 (CH), 149.2 (CH), 157.2 (SC=N), 172.4 (C=O). Anal. Calc. for $C_{14}H_{22}N_2OS$: C, 63.12 ; H, 8.32 ; N, 10.51. Found : C, 63.3 ; H, 8.0 ; N, 10.5

In a standard procedure for competition experiments, the Barton ester derived from pivaloylchloride was first prepared in the dark in CH_2Cl_2 as described previously. To this solution, a mixture of the two alkenes (1 equiv.-1 equiv.) was then added and irradiation with a 500 W halogen lamp was kept for 30 mn. PRESAT ^{1}H NMR spectra (irradiation of CH_2Cl_2) of the crude mixtures were recorded. Integration of the appropriate signals gave the product ratios (Table VI, see also Table IV).

Table VI : Integrated signals for the determination of the products ratio in competitive experiments.

Alkenes	H in **3a**	X	H in **x**	**3a/x**
1a/1e	2.42 (dd)	**3e**	2.79 (dd)	28/72
1a/5	2.42 (d)	**8**	1.72 (dd)	4/96
1a/6	2.03 (dd)	**9**	2.43 (dd)	20/80
1a/7	a	**10**	a	100/0

[a] **3a** was the only detected adduct.

Reductive elimination of the thiopyridyl group

To a solution of the addition product **3** (1 mmol) in absolute ethanol (5 mL) was added Raney Nickel (1 g) and the mixture was refluxed for 2 h. The suspension was filtered through celite and the solvent removed under reduced pressure. The residue was then purified by bulb to bulb distillation.

***3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane* 2a.** 77%. $bp_{0.05}$ = 40-45°C.

***2-cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane* 2b'**. 81%. $bp_{0.05}$ = 60-65°C.

***4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane* 2c**. 80%. $bp_{0.05}$ = 80-85°C. ^{1}H NMR ($CDCl_3$) δ : 0.81 (t, J =7.9, BCH_2, 2H), 1.23 (s, $C(CH_3)_2$, 12H), 1.36-1.72 (m, $BCH_2C\underline{H}_2C\underline{H}_2$, 4H), 2.60 (t, J = 7.9, $PhCH_2$, 2H), 7.10-7.31 (m, 5H). ^{13}C NMR ($CDCl_3$) δ : 10.9 (BCH_2, broad), 23.7 ($PhC\underline{H}_2$), 24.8 ($C(\underline{C}H_3)_2$), 34.2 (CH_2), 35.7 (CH_2), 82.9 ($\underline{C}(CH_3)_2$), 125.5 (CH), 128.2 (CH), 128.4 (CH), 142.9 (C). Anal. Calc. for $C_{15}H_{23}BO_2$: C, 73.19 ; H, 9.42 . Found : C, 73.4 ; H, 9.7.

Oxidation

The organoborane **2** (2.5 mmol) in 5 mL of THF was oxidized by adding 3.3 mL of 3N NaOH (10 mmol), followed by 1 mL of 30 % H_2O_2 at such rate that a temperature of 25-30°C was maintained. The reaction mixture was kept at 55°C for 3 h. An equal volume of diethylether was then added and the organic phase separated. The aqueous phase was extracted with 2 x 10 mL of diethylether. The combined organic phases were dried over $MgSO_4$. Removal of the solvent yielded a residue which was purified by column chromatography on silica gel or (and) bulb to bulb distillation.

***3,3-dimethylbutanol* 11a**. 78%. bp_{15} = 50-55°C (lit [26] : bp = 140-142°C). ^{1}H NMR ($CDCl_3$) δ : 0.92 (s, $C(C\underline{H}_3)_3$, 9H) ; 1.51 (t, J = 7.8, $C\underline{H}_2CH_2OH$, 2H) ; 2.90 (broad s, $CH_2O\underline{H}$, 1H) ; 3.57 (t, J = 7.8, $C\underline{H}_2OH$, 2H). ^{13}C NMR ($CDCl_3$) δ : 29.5 ($\underline{C}(CH_3)_3$) ; 29.7 ($C(\underline{C}H_3)_3$) ; 46.3 ($\underline{C}H_2CH_2OH$) ; 59.7 ($\underline{C}H_2OH$).

***2-cyclohexylethanol* 11b**. 75 %. bp_{15} = 100-105°C. (lit [27] : bp_{12} = 101-102°C). Rf (heptane/diethylether = 60/40) = 0.4. ^{1}H NMR ($CDCl_3$) δ : 0.82-1.91 (m, 14H), 3.67 (t, J = 6.6, $C\underline{H}_2OH$, 2H). ^{13}C NMR ($CDCl_3$) δ : 26.3 (CH_2), 26.6 (CH_2), 33.4 (CH_2), 34.2 (CH), 40.4 (CH_2), 60.8 (CH_2OH).

***4-phenylbutanol* 11c**. 80%. bp_{15} = 135-140°C. (lit [28]: bp_{12} = 134-135°C). Rf (heptane/diethylether = 60/40) = 0.1. ^{1}H NMR ($CDCl_3$) δ : 1.52-1.71 (m, 4H), 2.19 (broad s , OH , 1H), 2.61 (t, J = 7.3, $PhC\underline{H}_2$, 2H), 3.59 (t, J = 6.2, $C\underline{H}_2OH$, 2H), 7.03-7.30 (m, 5H). ^{13}C NMR ($CDCl_3$) δ : 27.5 (CH_2), 32.2 (CH_2), 35.6 (CH_2), 62.6 (CH_2OH), 125.7 (CH), 128.3 (CH), 128.4 (CH), 142.3 (C).

Amination

To a solution of 1 mmol of boronic ester **2a** in 20 mL of acetone/water (50/50) was added 2 mmol of $NaIO_4$. After 15 h at room temperature, the acetone was removed by distillation and the aqueous phase was extracted with 3 x 10 mL of diethylether. The combined organic phases were dried over $MgSO_4$ and concentrated to give a white solid which was used in the next step without purification. To this boronic acid in 2 mL of anhydrous CH_2Cl_2 was added at -78°C 0.5 mL of a 3M solution of BCl_3 in hexane. After stirring 15 mn, the cooling bath was removed and the mixture was allowed to reach room temperature. Solvent and excess of BCl_3 were removed under reduced pressure (15 mm Hg). 5 mL of anhydrous CH_2Cl_2 were then added, followed by 0.8 mmol of $PhCH_2N_3$. After stirring 15 h at room temperature, 5 mL of a saturated aqueous NH_4Cl solution. Extraction with 3 x 5 mL of CH_2Cl_2, drying over $MgSO_4$ and concentration furnished a white solid which was purified by filtration on silica gel. Elution with heptane/diethylether (50-50) gave excess of $PhCH_2N_3$. Methanol-diethylether (10-90) yielded the hydrochloride **12**.

***N-benzyl 3,3-dimethylbutanamine hydrochloride* 12**. 57%. mp = 224-226°C. ^{1}H NMR ($CDCl_3$) δ : 0.89 (s, $C(C\underline{H}_3)_3$, 9H), 1.53-1.61 (m, $C\underline{H}_2C(CH_3)_3$, 2H), 2.68-2.76 (m, $NHC\underline{H}_2CH_2C(CH_3)_2$, 2H), 3.90 (s, $PhC\underline{H}_2NH$, 2H), 5.96 (broad s, NH), 7.20-7.47 (m, 5H). ^{13}C NMR ($CDCl_3$) : δ : 29.4 ($C(\underline{C}H_3)_3$), 29.8 ($\underline{C}(CH_3)_3$), 41.7 ($\underline{C}H_2t$-Bu), 44.4 ($NH\underline{C}H_2CH_2t$-Bu), 52.5 ($Ph\underline{C}H_2NH$), 127.5 (CH), 128.7 (CH), 129.0 (CH), 136.0 (C). HRMS m/z calc. for $C_{13}H_{21}N$: $[M]^+$: 191.16943. Found : 191.167.

INTRAMOLECULAR ADDITIONS

Syntheses of the starting compounds

6-iodohex-1-yne

To a stirred suspension of 19 g of NaI (128 mmol) in 150 mL of acetone was added 2.5 g (21.4 mmol) of 6-chlorohex-1-yne . The mixture was heated 16 h at reflux. The acetone was distillated and 20 mL of water was added. The aqueous phase was extracted with 3 x 30 ml of diethylether. Combined organic phases were washed with brine, dried on $MgSO_4$ and concentrated. Distillation of the residue furnished a colorless liquid.

75%. bp_{15} = 70-75°C. ^{1}H NMR ($CDCl_3$) δ : 1.58–1.71 (m, 2H), 1.88-2.02 (m, 2H), 1.98 (t, J = 2,0, C≡C$\underline{H}$, 1H), 2.18-2.28 (m, 2H), 3.21 (t, J = 6.8, $C\underline{H}_2I$, 2H). ^{13}C NMR ($CDCl_3$) δ : 6.2 ($\underline{C}H_2I$), 17.4 (CH_2), 29.1 (CH_2), 32.2 (CH_2), 69.0 ($H\underline{C}{\equiv}CCH_2$), 83.6 ($HC{\equiv}\underline{C}CH_2$).

2-[(E)-6-iodohex-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **13.**

To a solution of 6-iodohex-1-yne (xx mmol) in 10 mL of anhydrous CH_2Cl_2 was added 50 mL of a 1M solution of $HBBr_2$: SMe_2 in CH_2Cl_2.[15] After 15 h at room temperature, the solution was transfered via a canula to an ice-water mixture. The aqueous phase was extracted with 2 x 50 mL of ether. Addition of 4.95 g of 2,3-dimethyl-2,3-butanediol to the combined organic phases was followed by stirring 12 h at room temperature. After concentration, flash chromatography of the residue furnished 9.6 g of a colorless oil which slowly cristallized.

70%. $bp_{0.05}$ = 75-80°C. mp = 35°C. ^{1}H NMR ($CDCl_3$) δ : 1.26 (s, $C(C\underline{H}_3)_2$, 12H), 1.42-1.57 (m, 2H), 1.74-1.86 (m, 2H), 2.18 (qd, J = 1.4 and 7.4, CH_2C=C, 2H), 3.18 (t, J = 6.9, CH_2I, 2H), 5.44 (dt, J = 1.4 and 17.9, BC$\underline{H}$=CH, 1H), 6.60 (dt, J = 6.4 and 17.9, BCH=C$\underline{H}$, 1H). ^{13}C NMR ($CDCl_3$) δ : 6.7 (CH_2I), 24.8 ($C(\underline{C}H_3)_2$), 29.1 ($\underline{C}H_2CH$=CHB), 32.8 (CH_2), 34.5 (CH_2), 83.0 ($\underline{C}(CH_3)_2$), 119.0

(B<u>C</u>H=CH, broad), 153.4 (BCH=<u>C</u>H). Anal. Calc. for $C_{12}H_2BIO_2$: C, 42.89 ; H, 6.60. Found : C, 42.8 ; H, 6.8.

***3-(E)-[(trans-2-bromocyclohexyloxy)-1-propen-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* 14.**

Borane-methyl sulfide complex (1.0 mL, 10 mmol) was added dropwise to a solution of (-)-α-pinene (3.6 mL, 23 mmol) in 10 mL freshly distilled THF, at 0°C, under a nitrogen atmosphere. The mixture was kept at 0°C for 1 h and allowed to reach room temperature by removing the cold bath. Two hours later, the resulting suspension of diisopinocampheylborane was cooled to -40°C when a THF solution of *trans*-1-propargyloxy-2-bromocyclohexane (2.66 g, 2.9 mmmol)[16] was slowly added. The reaction mixture was kept at -40°C for 1.5 h and then allowed to warm slowly to room temperature. After 5 h, the mixture was cooled to 0°C and freshly distilled acetaldehyde (8.0 mL) was added. After heating at 40°C for 12 h, the excess acetaldehyde was removed under vacuum. The crude yellowish oil thus obtained was directly transesterified by 2,3-dimethylbutane-2,3-diol (pinacol) as previously described for **13** and, then, purified by column chromatography on silica gel.

77%. Rf (heptane/diethylether = 90/10) = 0.5. ^{1}H NMR ($CDCl_3$) δ: 1.15-1.50 (m, 3H), 1.26 (s, $C(CH_3)_2$, 12H), 1.60-1,85 (m, 3H), 2.04-2.20 (m, 1H), 2.23-2.37 (m, 1H), 3.39 (sext, J = 8.1, 1H), 4.02 (oct, J = 8.1, 1H), 4.18 (dd, J = 1.8 and 4.8, 2H), 5.75 (dt, J = 1.8 and 18.4, 1H), 6.67 (dt, J = 4.8 and 18.4, 1H). ^{13}C NMR ($CDCl_3$) δ: 22.9 (CH_2), 24.8 ($C(\underline{C}H_3)_2$), 24.9 (CH_2), 30.3 (CH_2), 35.0 (CH_2), 55.2 (CHBr), 71.3 (CH_2O), 81.2 (CHO), 83.2 ($\underline{C}(CH_3)_2$), 119.1 (CB, broad), 149.4 (CH). ^{11}B NMR ($CDCl_3$) δ : 30.0.

***2-(1-chloro-4-bromobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* 15**

A solution of 2 mL (31.2 mmol) of anhydrous CH_2Cl_2 in 40 mL of anhydrous THF was cooled at -100°C. (Dichloromethyl)lithium was prepared by adding 13.8 mL (22.1 mmol) of 1.6 M solution of n-BuLi in hexane dropwise down the side of the flask keeping the temperature rigourously < -100°C. The reaction mixture was stirred for an additionnal 0.5 h and 5 g (20 mmol) of 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [29] in 10 mL of anhydrous THF was injected. 1.9 g (14 mmol) of rigourously anhydrous powdered zinc chloride was added to the cold mixture. The mixture was allowed to warm slowly to room temperature and stirred overnight. The reaction mixture was diluted in 30 mL of diethylether and stirred with 10 mL of saturated aqueous ammonium chloride. The aqueous phase was separated, extracted with 2 x 10 mL of diethylether. After drying over $MgSO_4$ concentration yielded a residue which was purified by bulb to bulb distillation.

85%. $bp_{0.05}$ = 60°C. ^{1}H NMR ($CDCl_3$) δ: 1.30 (s, $C(CH_3)_2$, 12H), 1.90-2.20 (m, 4H), 3.41-3.44 (m, 3H). ^{13}C NMR ($CDCl_3$) δ : 24.6 ($C(\underline{C}H_3)_2$), 30.4 (CH_2), 32.4 (BCHCl$\underline{C}H_2$), 33.0 ($\underline{C}H_2$Br), 42.5 (B<u>C</u>HCl, broad), 84.5 ($\underline{C}(CH_3)_2$). Anal. Calc. for $C_{10}H_{19}BBrClO_2$: C, 40.38 ; H, 6.44. Found : C, 40.5 ; H, 6.6.

***2-(1-vinyl-4-bromobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* 16**

To a solution of 3 g (10 mmol) of **15** in 20 mL of anhydrous THF was added at -78°C 8.41 mL (11 mmol) of a 1.2 M solution of vinylmagnesium in THF. After stirring overnight, the mixture was quenched with 5 mL of saturated aqueous NH_4Cl. Extraction with 2 x 10 mL of diethylether and concentration of the organic phases yielded a residue which was distillated under reduced pressure.

95%. $bp_{0.05}$ = 65-70°C. ^{1}H NMR ($CDCl_3$) δ : 1.24 (s, $C(C\underline{H}_3)_2$, 12H), 1.50-2.00 (m, 5H), 3.40 (t, J = 6.9, $C\underline{H}_2Br$, 2H), 4.94-5.03 (m, $C\underline{H}_2$=CH, 2H), 5.70-5.82 (m, CH_2=C$\underline{H}$, 1H). ^{13}C NMR ($CDCl_3$) δ : 24.7 ($C(\underline{C}H_3)_2$), 28.6 (CH_2Br), 29.5 (BCH, broad), 32.2 (CH_2), 33.7 (CH_2), 83.3 ($\underline{C}(CH_3)_2$), 114.2 ($\underline{C}H_2$=CH), 138.8 (CH_2=$\underline{C}$H).

***2-(pent-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* 17**

A solution of 2.85 g (22 mmol) of $B(OMe)_3$ in 10 mL of THF was cooled at 78°C. To this was added 21 mL (20 mmol) of a 0.95 M solution of (pent-4-en-1-yl) magnesium bromide in THF. The reaction mixture was stirred overnight at room temperature. Workup with saturated aqueous NH_4Cl and diethylether as the usual manner followed by distillation yielded 2.2 g of colorless oil.

55%. $bp_{0.01}$ = 40-45°C. ^{1}H NMR ($CDCl_3$) δ : 0.80 (t, J = 7.9, $BC\underline{H}_2$, 2H), 1.24 (s, $C(C\underline{H}_3)_2$, 12H), 1.44-1.57 (m, $BCH_2C\underline{H}_2$, 2H), 2.00-2.10 (m, CH_2=$CHC\underline{H}_2$, 2H), 4.99-5.03 (m, 2H), 5.80 (ddt, J = 6.5, 10.2 et 17.3, 1H). ^{13}C NMR ($CDCl_3$) δ : 10.0 (BCH_2, broad), 23.4 ($BCH_2\underline{C}H_2$), 24.8 ($C(\underline{C}H_3)_2$), 36.4 ($\underline{C}H_2CH$=CH_2), 82.9 ($\underline{C}(CH_3)_2$), 114.4 (CH=$\underline{C}H_2$), 138.9 ($\underline{C}$H=CH_2).

***2-(2-iodohex-5-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* 18**

(Dichloromethyl) lithium was generated from 8.5 mmol of n-BuLi and 0.8 mL (12.8 mmol of CH_2Cl_2 in 20 mL of anhydrous THF as previously described for **15**, then treated with 1.56 g (8 mmol) of **17** followed by 1.5 g (11 mmol) powdered anhydrous zinc chloride. After warming to 20°C and keeping 12 h at this temperature, the mixture was concentrated keeping the bath below 30°C. 30 mL of diethylether were added followed by 10 mL of saturated aqueous NH_4Cl. Extraction with 2 x 10 mL of diethylether followed by drying over $MgSO_4$ and concentration yielded 1.45 g of a residue which was purified by bulb to bulb distillation. Exchange chloride/iodide was realized in the usual manner described previously for 6-iodohex-1-yne. Bulb to bulb distillation of the crude pruct yielded a colorless oil.

90%. $bp_{0.01}$ = 55-60°C. ^{1}H NMR ($CDCl_3$) δ : 1.27 (s, $C(C\underline{H}_3)_2$, 12H), 1.30-1.60 (m, $BCHIC\underline{H}_2$, 2H), 1.85 (m, $BCHICH_2C\underline{H}_2$, 2H), 2.07 (m, $C\underline{H}_2CH$=CH_2, 2H), 3.21 (t, J = 8.1, $BC\underline{H}I$, 1H), 4.99-5.05 (m, 2H), 5.80 (ddt, J = 6.5, 10.3 and 17.0, $C\underline{H}$=CH_2, 1H). ^{13}C NMR ($CDCl_3$) δ : 9.5 (BCHI, broad), 24.4 ($C(\underline{C}H_3)_2$), 30.4 ($BCHI\underline{C}H_2$), 32.9 (CH_2), 34.2 (CH_2), 83.9 ($\underline{C}(CH_3)_2$), 114.8 (CH=$\underline{C}H_2$), 138.2 ($\underline{C}$H=CH_2).

Intramolecular additions

General procedure for the cyclization of alkenylboronic esters

A solution of the bromide (or iodide) precursor (3 mmol) in 10 mL of toluene was desoxygenated with argon for 15 mn. The reaction mixture was irradiated or heated at 90°C. To this, a solution of tributyltinhydride (3.3 mmol) and AIBN (0.05 equiv.) was slowly added *via* a syringue pump over 2 h. Reaction was continued for an additionnal period of 1 h after addition. The solvent was evaporated and the residue diluted with 20 mL of diethylether. DBU (1 equiv.) was added and the solution was filtered through a plug of celite. Concentration gave an oil which was purified by column chromatography on silica gel. The ratio of isomers was determined by ^{1}H NMR or (and) capillary gas chromatography prior to the purification step (Table VII, see also Table V).

Table VII - Cyclization of unsaturated boronic esters

boronic ester	products	initiation	isolated yield (%)[a]
13	**19**	Δ, AIBN	93
		hυ	87
14	**20a** (65), **20b** (35)	Δ, AIBN	80
16	**21a** (15), **21b** (82), **22**(3)	Δ, AIBN	83
	21a (10), **21b** (89), **22**(1)	hυ	81
18	**21a** (42), **21b** (45), **22**(13)	Δ, AIBN	85
	21a (51), **21b** (39), **22**(10)	hυ	85

***2-(cyclopentylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* 19**

It was prepared independently by hydroboration of methylenecyclopentane with $HBBr_2$:SMe_2 followed by treatment with pinacol as reported in the literature [15].

90%. $bp_{0.01}$ = 40-45°C . ^1H NMR ($CDCl_3$) δ : 0.83 (d, J = 7.4, BCH_2, 2H), 0.98-1.13 (m, 2H), 1.24 (s, $C(C\underline{H}_3)_2$, 12H), 1.42-1.67 (m, 4H), 1.72-1.84 (m, 2H), 1.96 (hept, J = 7.4, $BCH_2C\underline{H}$, 1H). ^{13}C NMR ($CDCl_3$) δ : 19.0 (BCH_2, broad), 24.8 ($C(\underline{C}H_3)_2$), 25.1 (CH_2); 35.0 (CH_2), 36.1 ($BCH_2\underline{C}H$), 82.8 ($\underline{C}(CH_3)_2$).^{11}B NMR ($CDCl_3$) δ : 33,7. Anal. Calc. for $C_{12}H_{23}BO_2$: C, 68.59 ; H, 11.03. Found : C, 68.5 ; H, 10.9.

***8-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-7-oxabicyclo[3.3.1] nonane* 20a** and **20b**

80 %. Rf (heptane-diethylether = 4/1). Mixture of two diastereoisomers (65/35). Chemical shifts, coupling constants and stereochemistry of the major isomer were assigned by using ^1H-^1H ; ^1H-^{13}C correlation spectra, irradiation and NOESY experiments. (Ha, Hb, Hc, Hd and He were defined in table IV). Major isomer : ^1H NMR ($CDCl_3$) δ : 0.70 - 1.59 (m, 10H), 1.24 (s, 12H), 1.54 (m, JHaHb = 4.5 and JHaHc = 7.5, Hb), 2.16 (m, JHcHb = 7.5, Hc), 3.34 (dd, JHd'Hc = 5.8 and JHdHd' = 8.5, Hd'), 3.93 (t, J = 4.5, Ha), 4.17 (dd, JHdHd' = 8.5 and JHdHc = 7.7). ^{13}C NMR ($CDCl_3$) δ : 15.9 (broad, CH_2B), 21.5 (CH_2), 23.3 (CH_2), 24.6 (CH_2), 24.7 ($C(\underline{C}H_3)_2$), 26.6 (CH_2), 39.3 (CHc), 45.9 (CHb), 74.3 (CHd), 76.2 (CHa), 83.1 ($\underline{C}(CH_3)_2$). Minor isomer : ^1H NMR ($CDCl_3$) δ : 0.70 - 1.59 (m, 10H), 1.24 s (12H), 1.82 (m, JHaHb = 2.8 and JHbHc = 5.6, Hb), 2.53 (m, JHbHc = 5.6, Hc), 3.43 (dd, JHdHa' = 8.0 and JHd'Hc = 10.3, Hd'), 3.96 (t, JHaHb = 2.8, Ha), 3.97 (dd, JHdHd' = 8.0 and JHdHc = 8.3, Hd). ^{13}C NMR ($CDCl_3$) δ : 8.7 (CH_2B, broad), 20.5 (CH_2), 22.0 (CH_2), 24.8 ($C(\underline{C}H_3)_2$), 26.9 (CH_2), 29.7 (CH_2), 39.5 (CHc), 41.1 (CHb), 72.6 (CHd), 78.1 (CHa), 83.1 ($\underline{C}(CH_3)_2$).

***2-(cis-2-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* 21a**

21a was not isolated, but only characterized by its NMR data which were deduced from the ^1H and ^{13}C NMR spectra of the mixtures obtained by cyclization of **16** and **18**.

^{1}H NMR ($CDCl_3$) δ : 0.92 (d, J = 7.0, C$\underline{H}_3$CH, 3H), 1.24 (s, C(C$\underline{H}_3$)$_2$, 12H), 1.45-2.00 (m, 8H). ^{13}C NMR ($CDCl_3$) δ : 24.9 (CH$\underline{C}$H$_3$), 26.6 (C($\underline{C}$H$_3$)$_2$), 28.6 (CH_2), 28.6 (CH_2), 31.4 (B$\underline{C}$H), 35.3 (CH_2), 38.3 ($\underline{C}$HCH$_3$), 82.7 ($\underline{C}$(CH$_3$)$_2$).

***2-(trans-2-methylcyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* 21b**

It was prepared independently by hydroboration of 1-methylcyclopentene with $HBBr_2$:SMe_2 followed by treatment with pinacol as reported in the literature [15]

65%. $bp_{0.01}$ = 50-55°C . ^{1}H NMR ($CDCl_3$) δ : 1.01 (d, J = 6.3, C$\underline{H}_3$CH, 3H), 1.24 (s, C(C$\underline{H}_3$)$_2$, 12H), 1.45-2.00 (m, 8H). ^{13}C NMR ($CDCl_3$) δ : 20.6 (CH$\underline{C}$H$_3$), 24.7 (C($\underline{C}$H$_3$)$_2$), 25.6 (CH_2), 28.6 (CH_2), 31.4 (B$\underline{C}$H), 36.1 (CH_2), 38.3 ($\underline{C}$HCH$_3$), 82.7 ($\underline{C}$(CH$_3$)$_2$).

***2-(cyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* 22**

It was prepared independently by hydroboration of cyclohexene with $HBBr_2$:SMe_2 followed by treatment with pinacol as reported in the literature [15]

70%. $bp_{0.01}$ = 55-65°C ^{1}H NMR ($CDCl_3$) δ : 0.90-1.00 (m, BCH), 1.23 (s, C(C$\underline{H}_3$)$_2$, 12H), 1.20-1.40 (m, 4H), 1.53-1.70 (m, 6H). ^{13}C NMR ($CDCl_3$) δ : 22.0 (B$\underline{C}$H), 24.7 (C($\underline{C}$H$_3$)$_2$), 26.7 (CH_2), 27.1 (CH_2), 27.9 (CH_2), 82.6 ($\underline{C}$(CH$_3$)$_2$).

Cyclization of a B-alkenyl-9-BBN 23

***trans-6-iodo-1-(9-borabicyclo[3.3.1.]non-9-yl)hex-1-ene* 23**

To a solution of 26 mmol (5.4 g) of 6-iodohex-1-yne in 20 mL of anhydrous THF [21] was added at 0°C 1.46 g (12 mmol) of 9-BBN-H in 20 mL of anhydrous THF. After stirring overnight à 5-10°C, the reaction mixture was kept at 25°C for 2 h. Distillation of THF and excess of alkyne yielded a residue which was purified by bulb to bulb distillation.

65%. $bp_{0.05}$ = 100-105°C. ^{1}H NMR($CDCl_3$) δ : 1.05-2.03 (m, 18 H), 2.30 (qd, J = 1.0 and 7.3, BCH=CHC$\underline{H}_2$, 2H), 3.20 (t, J = 6.9, CH_2I, 2H), 6.24 (dt, J = 1.0 and 17.3, BC$\underline{H}$=CH, 1H), 6.80 (dt, J = 6.4 and 17.3, BCH=C$\underline{H}$, 1H). ^{13}C NMR ($CDCl_3$) δ : 6.6 (CH_2I), 23.4 (CH_2), 29.2 (BCH=CHC$\underline{H}_2$), 30.0 (CH, broad), 33.0 (CH_2), 33.4 (CH_2), 33.7 (CH_2), 134.8 (B$\underline{C}$H=CH, broad), 154.6 (BCH=$\underline{C}$H).

***cyclopentylmethylbenzene* 25**

23 was cyclized photochemically as previously described to give after distillation **24** ($bp_{0.05}$ = 85-95°C) as a colorless oil which was used without supplementary purification in the cross-coupling step. A solution of 0.86 g (4.2 mmol) of **24**, 0.1 g de $Pd(Ph_3)_4$, 1.25 g (8 mmol) of bromobenzene in 20 mL of THF and 5 mL (15 mmol) of a 3N NaOH was heated at reflux for 36 h. After cooling, the reaction mixture was diluted with 20 mL of diethylether. The aqueous phase was separated and extracted with 2 x 10 mL of ether. The combined organic phases were dried over $MgSO_4$. Concentration of the solvent yielded a residue which was purified by bulb to bulb distillation.

74%. $bp_{0.05}$ = 40-45°C (lit.[30].bp = 233°C) ^{1}H NMR ($CDCl_3$) δ : 0.80-1.90 (m, 8H) ; 2.06 (hept, J = 7.4, PhC$\underline{H}_2$C$\underline{H}$, 1H), 2.58 (d, J = 7.4, PhC$\underline{H}_2$CH, 2H), 7.05-7.30 (m, 5H). ^{13}C NMR ($CDCl_3$) δ : 25.2 (CH_2), 32.5 (CH_2), 41.9 (PhC$\underline{H}_2$CH), 42.0 (PhC$\underline{H}_2$), 125.5 (CH), 128.1 (CH), 128.8 (CH), 142.3 (C).

Cyclization of an alkynylboronic ester 26

***Diisopropyl 6-iodohex-1-ynylboronate* 26**

A solution of 6-iodohex-1-yne (3.15 g, 15 mmol) in 15 mL of anhydrous diethylether was cooled at -78°C and n-BuLi (9.4 ml (15 mmol) of 1.6 M solution in hexane) was slowly added.[23] After 0.5 h, the lithium acetylide was added dropwise to a solution of 2.8 g (15 mmol) of $B(OiPr)_3$ precooled at -78°C. The reaction was maintained at this temperature for two hours after which anhydrous HCl in diethylether (15.5 mmol in 15.5 mL) was added. After removal of LiCl by filtration over a short column of celite, distillation of the solvent yielded a residue which was purified by bulb to bulb distillation.

45%. $bp_{0.05}$ = 100-105°C. ^1H NMR ($CDCl_3$) δ : 1.20 (d, J = 6.2, $CH(C\underline{H}_3)_2$, 12H), 1.61-1.73 (m, $C\underline{H}_2CH_2CH_2I$, 2H), 1.92-2.02 (m, $C\underline{H}_2CH_2I$, 2H), 2.32 (t, J = 6.9, $BC{\equiv}CC\underline{H}_2$, 2H), 3.21 (t, J = 6.9, $C\underline{H}_2I$, 2H), 4.54 (hept, J = 6.2, $OC\underline{H}(CH_3)_2$, 2H). ^{13}C NMR ($CDCl_3$) δ : 5.8 (CH_2I), 18.5 ($BC{\equiv}C\underline{C}H_2$), 24.3 ($CH(\underline{C}H_3)_2$), 28.9 ($CH_2$), 32.3 ($CH_2$), 67.4 ($\underline{C}H(CH_3)_2$), 103.0 (B-C≡$\underline{C}$). The carbon B-$\underline{C}$≡C was not found.

***Diisopropyl cyclopentylidenemethyl boronate* 27**

A solution of 1 g (2.9 mmol) of alcynylboronic ester **26** in 10 mL of toluene was irradiated with a high pressure Hg lamp. To this solution was slowly added *via* a syringe pump for 2 h 0.92 g (3.2 mmol) of Bu_3SnH in 10 mL of toluene. Irradiation was maintained for an additionnal hour. Concentration yielded a residue which was distillated under reduced pressure. This product was used in the next step without supplementary purification. However, if pinacol (1 equiv.) was added before the distillation of toluene, the pinacol ester thus obtained was stable and was purified by column chromatography on silica gel.

27. 80%. $bp_{0,05}$ = 50-55°C. ^1H NMR ($CDCl_3$) δ : 1.16 (d, J = 6.1, $CH(C\underline{H}_3)_2$, 12H), 1.55-1.73 (m, 4H), 2.36-2.39 (m, 2H), 2.43-2.53 (m, 2H), 4.43 (hept, J = 6.1, $C\underline{H}(CH_3)_2$), 5.37 (quint, J = 2.2, $BC\underline{H}$=C, 1H). ^{13}C NMR ($CDCl_3$) δ : 24.7 (s, $CH(C\underline{H}_3)_2$), 25.9 (CH_2), 27.0 (CH_2), 33.2 (CH_2), 32.8 (CH_2), 37.2 (CH_2), 65.1 ($\underline{C}H(CH_3)_2$), 110.0 (B$\underline{C}$H=C, broad), 167.6 (BCH=$\underline{C}$). ^{11}B NMR ($CDCl_3$) δ : 28.8.

27 as its pinacol ester. 82%. Rf (heptane/diethylether: 95/5) = 0.4.$bp_{0,05}$ = 40-45°C. ^1H NMR ($CDCl_3$) δ : 1.25 (s, $C(C\underline{H}_3)_2$, 12H), 1.56-1.74 (m, CH_2, 4H), 2.36 (m, $BCH{=}CC\underline{H}_2$, 2H), 2.52 (m, $BCH{=}CC\underline{H}_2$, 2H), 5.27 (quint, J = 2.1, $BC\underline{H}$=C, 1H). ^{13}C NMR ($CDCl_3$) δ : 24.9 (s, $C(C\underline{H}_3)_2$), 25.9 (CH_2), 26.8 (CH_2), 33.2 (CH_2), 37.0 (CH_2), 82.5 ($\underline{C}(CH_3)_2$), 108.0 (B$\underline{C}$H=C, broad), 171.9 (BCH=$\underline{C}$). ^{11}B NMR ($CDCl_3$) δ : 29.5. Anal. Calc. for $C_{12}H_{21}BO_2$: C, 69.26 ; H, 10.17. Found : C, 69.2 ; H, 10.1.

***Cyclopentylidenemethyl benzene* 28**

A solution of 0.50 g (2.3 mmol) of **27**, 0.3 g (0,26 mmol) of $Pd(Ph_3)_4$, 0.42 g (2.1 mmol) of iodobenzene in 5 mL of benzene was heated at reflux for 2 h. After cooling, the reaction mixture was diluted with 20 mL of diethylether. The aqueous phase was separated and extracted with 2 x 10 mL of ether. The combined organic phases were dried over $MgSO_4$. Concentration of the solvent yielded a residue which was purified by bulb to bulb distillation.

28. 92%. $bp_{0,05}$ = 60-70°C.(litt [31] : bp_{17} = 123-124°C) ^1H NMR ($CDCl_3$) δ : 1.58-1.70 (m, 2H), 1.72-1.81 (m, 2H), 2.42-2.56 (m, 4H), 6.34 (quint, J = 2.3, C=C$\underline{H}$Ph, 1H), 7.09-7.18 (m, 2H), 7.26-7.31 (m, 3H). ^{13}C NMR ($CDCl_3$) δ : 25.6 (CH_2), 27.2 (CH_2), 31.2 (CH_2), 35.9 (CH_2), 120.8 (CH), 126.4 (CH), 127.9 (CH), 128.0 (CH), 138.9 (C), 147.1 (CH).

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