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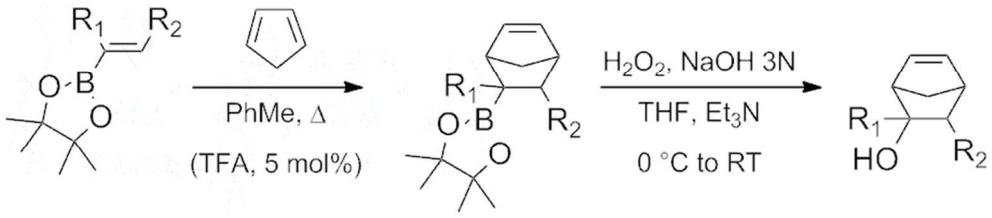

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ARTICLE TYPE

Diels-Alder Reactions of Pinacol Alkenylboronates: An experimental and theoretical study

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We have studied the Diels-Alder reactions of pinacol alkenylboronates with cyclopentadiene under two different conditions: thermal heating at 170 °C in a pressure tube and with catalytic TFA (5 mol%) at 80 °C. Yields varied significantly from system to system and also for the uncatalyzed and catalyzed methodologies. Moderate to excellent *exo*-stereoselectivities were obtained in all cases. The theoretical study of the thermal reactions shed some light into the intriguing substituent effects observed experimentally. A variety of substituted 5-norbornen-2-ols were easily generated by subsequent *in-situ* oxidation of the cycloadducts with alkaline hydrogen peroxide.

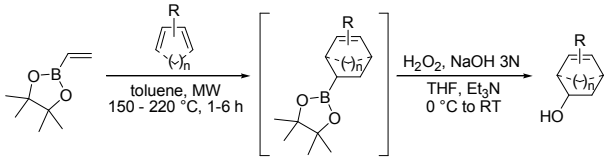
Introduction

The Diels-Alder (DA) reactions of boron-activated dienophiles were first described more than five decades ago. In the last years, a renewed interest in such processes arouse, both from the experimental and theoretical viewpoints.[1-32] We have recently shown that the Diels-Alder reactions of vinylboronates can be easily performed using microwave irradiation giving excellent yields of the cycloadducts. Vinylboronic acid pinacol ester showed good stability towards hydrolysis, operational simplicity and yields of Diels-Alder products. The [4+2] cycloadditions of pinacol vinylboronate with a variety of cyclic and acyclic dienes under microwave irradiation generated the boronate cycloadducts in excellent yields in short reaction times (1-6 h) (Scheme 1).[32] For example, the reaction with cyclopentadiene was complete in 1 h at 150 ºC, affording the products in quantitative yield with a 38:62 *endo*/*exo* ratio. Subsequent *in-situ* oxidation of the cycloadducts with alkaline hydrogen peroxide yielded the alcohols efficiently, demonstrating the utility of these intermediates for direct C-O bond-forming reactions.

As part of our continuing work in the field, we have now studied the Diels-Alder reactions of cyclopentadiene with pinacol alkenylboronates with different substitution patterns under different reaction conditions with the aims of developing new methodologies, gaining additional knowledge about the reactivity of boron-substituted dienophiles and analyzing their possible use as synthetic equivalents of substituted enols.

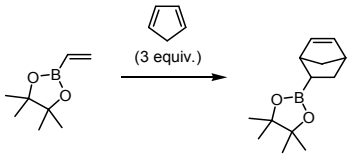
Results and discussion

To carry out this study we have used cyclopentadiene, which was chosen for being a reactive cyclic 1,3-diene and also for the interesting structural and synthetic properties of the bicyclo[2.2.1]heptane products.[33] To investigate the substituent



Scheme 1

Table 1 Diels-Alder reaction of pinacol vinylboronate (**1a**) with cyclopentadiene



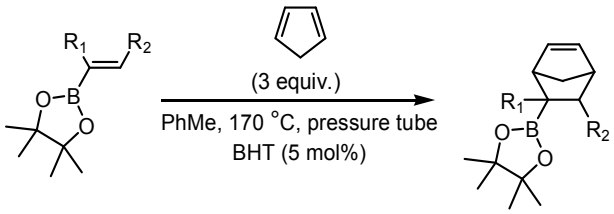
Entry	Conditions	Yield (%) *endo*/*exo*[a]
1	Toluene, 150 ºC, MW, 1 h[32]	100 38:62
2	Xylenes, reflux, 1 h	54 35:65
3	Toluene, reflux, 5 h	96 35:65
4	Toluene, 150 ºC, 1 h, pressure tube	79 32:68
5	Toluene, 150 ºC, 2 h, pressure tube	86 37:63
6	Toluene, 170 ºC, 5 h, pressure tube, BHT (5 mol%)	92 40:60
7	Toluene, 170 ºC, 1 h, pressure tube, BHT (5 mol%)	96 35:65

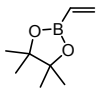
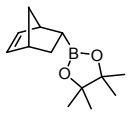
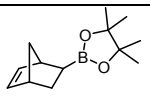
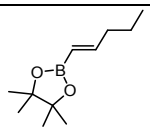
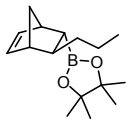
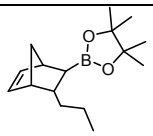
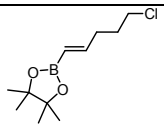
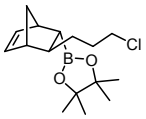
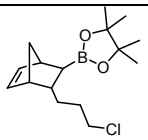
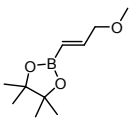
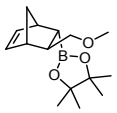
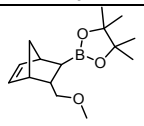
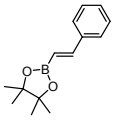
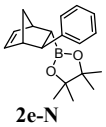
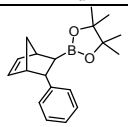
[a] Determined by ^{1}H NMR.

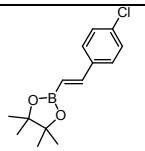
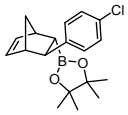
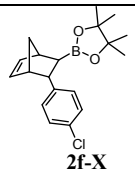
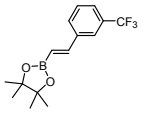
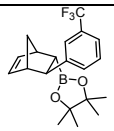
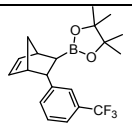
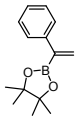
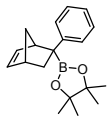
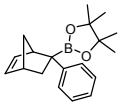
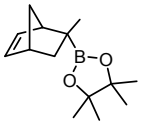
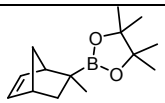
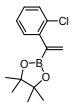
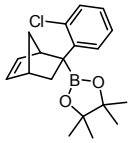
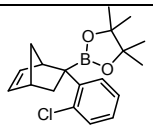
effect on the outcome of the thermal Diels-Alder reaction, we tested a range of commercially available alkenylboronates with alkyl or aryl groups with different substitution patterns in the 1- and 2-positions of the carbon-carbon double bond. Initial screening reactions under microwave heating with the pinacol esters of *trans*-1-penten-1-ylboronic acid and *trans*-2-phenylvinylboronic acid suggested that the presence of substituents in the double bond of the substrates retarded the cycloaddition process considerably. Therefore, the use of microwave irradiation proved impractical. We then re-investigated the Diels-Alder reaction of pinacol vinylboronate with cyclopentadiene under a large number of thermal conditions using conventional heating. Table 1 summarizes the outcome of some descriptive experiments. Entry 1 shows the result previously obtained in our laboratories at 150 °C under microwave irradiation for 1 h.[32] When the reaction was performed in refluxing xylenes under conventional heating, a 54% yield was obtained (Entry 2). We managed to get a 96% yield in refluxing toluene with a longer reaction time (Entry 3). As an alternative, use of a pressure tube at 150 °C in 1 h gave the cycloadduct in 79% yield (Entry 4), while increasing the time to 2 h raised the yield to 86% (Entry 5). If the bath temperature was set to 170 °C, a 92% yield was generated in 5 h, and a nearly quantitative yield was obtained in 1 h (Entries 6 and 7). BHT (5 mol%) was added to prevent undesired radical side reactions. The *endo*/*exo* ratios varied slightly around 38:62 for all reactions.

Having optimized the conditions for the thermal reaction of pinacol vinylboronate under conventional heating, we next turned our attention to the [4+2] cycloadditions of the substituted substrates (Table 2). All the reactions were optimized to yield the greatest amount of products. Lower temperatures or shorter reaction times afforded poorer yields while higher temperatures or longer reaction times either did not increase the yield or led to some decomposition.

Table 2 Thermal Diels-Alder reaction of alkenylboronates with cyclopentadiene



Entry	Dienophile	Time (h)	Yield (%)[a] *endo*/*exo*[b]	Products
1	 **1a**	1	96 35:65	 **2a-N**  **2a-X**
2	 **1b**	24	78 (100) 17:83	 **2b-N**  **2b-X**
3	 **1c**	24	89 20:80	 **2c-N**  **2c-X**
4	 **1d**	24	88 (100) 15:85	 **2d-N**  **2d-X**
5	 **1e**	24	29 (90) 35:65	 **2e-N**  **2e-X**

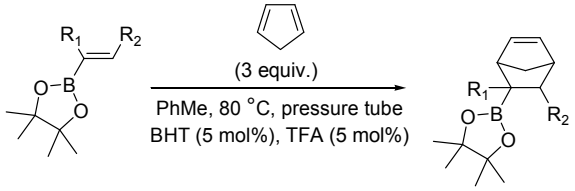
6	 **1f**	24	20 (70) 40:60	 **2f-N**  **2f-X**
7	 **1g**	24	19 (48) 37:63	 **2g-N**  **2g-X**
8	 **1h**	1	25 (91) 10:90	 **2h-N**  **2h-X**
9	 **1i**	24	72 (80) 9:91	 **2i-N**  **2i-X**
10	 **1j**	12	Traces[c]	 **2j-N**  **2j-X**

[a]Yields based on recovered starting materials (BRSM) in parenthesis. [b]Relative to the pinacol boronate moiety, determined by ^{1}H NMR. [c]The starting material was recovered.

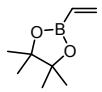
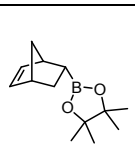
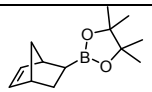
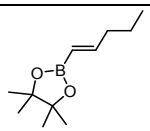
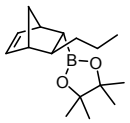
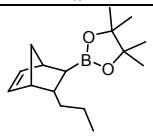
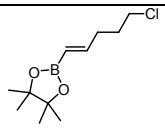
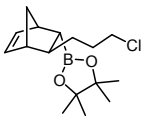
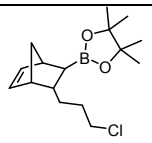
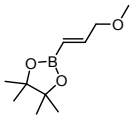
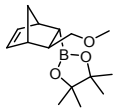
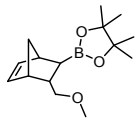
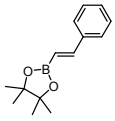
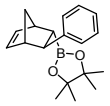
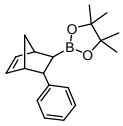
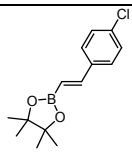
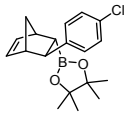
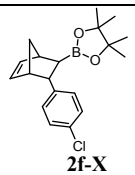
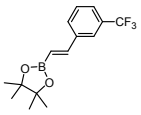
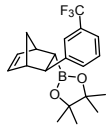
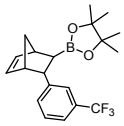
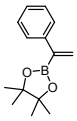
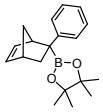
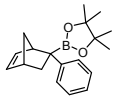
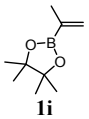
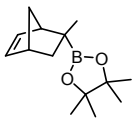
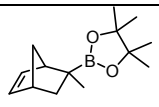
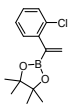
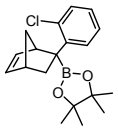
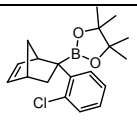
As found in our initial experiments with microwave heating, longer reactions times than for the parent dienophile (**1a**) were needed in all cases, excluding **1h** (Entry 8). However, for the latter the yield was very low and did not increase by extending the reaction time (25% in 1 h *endo*/*exo* 10:90, 21% in 12 h *endo*/*exo* 41:59). Alkyl-substituted substrates performed much better than the aromatic analogues, giving yields in the range 72-89% (Entries 2-4 and 9). We reasoned that the conjugated aromatic ring donated electron density to the carbon-carbon double bond. However, the introduction of electron-withdrawing substituents on the phenyl ring did not improve the reactivity of such systems (Entries 5-8 and 10). Regarding the stereoselectivities, the *exo* cycloadduct predominated in all reactions. The highest *exo*-stereoselectivity was observed for isopropenylboronic acid pinacol ester (**1i**) (*endo*/*exo* 9:91, Entry 9), while alkenylboronates with alkyl groups in the 2-position exhibited *endo*/*exo* ratios higher than 20:80 (Entries 2-4). The aromatic compounds showed moderate *exo*-selectivities, similar to the one obtained with the unsubstituted system (*endo*/*exo* ~ 40:60).

In the next stage, we aimed to determine whether milder conditions could be used so we embarked in the development of the acid-catalyzed version of the reaction under study (Table 3).[34-37] Many experiments were run for the Diels-Alder reactions of pinacol esters of vinylboronic acid (**1a**), *trans*-1-penten-1-ylboronic acid (**1b**) and *trans*-2-phenylvinylboronic acid (**1e**) to determine the optimal conditions. Brønsted acids gave better results than Lewis acids, due to the greater polymerization of the diene in the presence of the latter. Among the Brønsted acids, we tried acetic acid, trifluoroacetic acid (TFA) and triflic acid. We tested up to 2 equivalents of Brønsted acids and 10 equivalents of cyclopentadiene, solvents like toluene, dichloromethane and water, and temperatures ranging from room temperature to

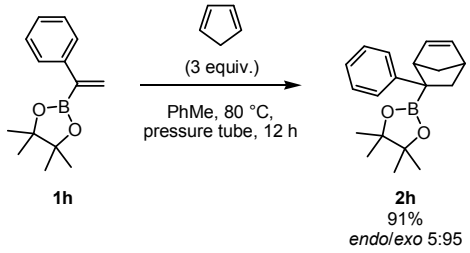
Table 3 TFA-catalyzed Diels-Alder reaction of alkenylboronates with cyclopentadiene



Entry	Dienophile	Time (h)	Yield (%)[a] *endo*/*exo*[b]	Products

1	 **1a**	5	88 36:64	 **2a-N**	 **2a-X**
2	 **1b**	24	traces[c]	 **2b-N**	 **2b-X**
3	 1c	24	traces[c]	 **2c-N**	 **2c-X**
4	 **1d**	24 72	17 (75) 14:86 26 (68) 10:90	 **2d-N**	 **2d-X**
5	 **1e**	24 72	32 (92) 17:83 38 (98) 17:83	 **2e-N**	 **2e-X**
6	 **1f**	24 72	20 (70) 36:64 31 (70) 29:71	 **2f-N**	 **2f-X**
7	 **1g**	24 72	24 (78) 10:90 45 (73) 10:90	 **2g-N**	 **2g-X**
8	 **1h**	12	83 6:94	 **2h-N**	 **2h-X**
9	 **1i**	24	15 (24) 9:91	 **2i-N**	 **2i-X**
10	 **1j**	12	Traces[c]	 **2j-N**	 **2j-X**

[a]Yields based on recovered starting materials (BRSM) in parenthesis. [b] Relative to the pinacol boronate moiety, determined by ^{1}H NMR. [c]The starting material was recovered.



Scheme 2

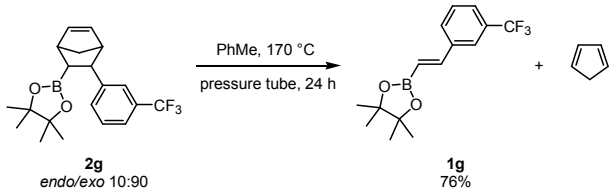
150 °C. For the reaction of **1a**, we determined that best yields of the cycloadducts were obtained in 5 h at 80 °C with 5 mol % of TFA (Entry 1, 88%, *endo*/*exo* 36:64). When we run the reaction in the absence of TFA, a 20% yield was generated, with the same *endo*/*exo* ratio. Use of a pressure tube, though not necessary in toluene at 80 °C, was preferred to avoid evaporation of the small loading of the catalyst (Bp 72.4 °C). Quite unexpectedly, under catalyzed conditions only 1-phenylvinylboronic acid pinacol ester (**1h**) performed well (Entry 8, 83%, *endo*/*exo* 6:94). The other dienophiles gave yields below 45%. However, it is interesting to note that in this case aromatic alkenylboronates afforded better yields than the aliphatic compounds. Also, considerably higher *exo*-selectivities than for the uncatalyzed reactions were observed. Possibly, the acid catalyst interacts with the π electrons of the aromatic ring and therefore withdraws electron density from the conjugated unsaturated system leading to the activation of the double bond. Within the aliphatic alkenylboronates, **1d**, having a possible site for protonation (oxygen atom) gave better results than **1b** and **1c**.

We were surprised to note that the background reaction of dienophile **1h** afforded a very high yield of the corresponding boronate cycloadduct (91%) with excellent *exo*-selectivity (*endo*/*exo* 5:95) (Scheme 2). Under the same conditions, vinylboronic acid pinacol ester (**1a**) gave a lower yield (45%), which was a bit unexpected since previous experiments at higher temperatures suggested that the parent compound was more reactive than **1h** (Table 2).

We tested whether we could perform the catalyzed reaction of alkenylboronate **1h** at room temperature using the same amount of diene, catalyst, and BHT, but we only obtained a 17% yield with a 3:97 *endo*/*exo* ratio (96% BRSM) after 12 h.

Since, as commented above, prolonged exposure to the reaction conditions did not increase the yields of the products we figured that thermodynamic equilibria had been reached. Also, dienophile **1h** gave a 25% (91% BRSM) in 1 h at 170 °C (Entry 8, Table 2), while the yield was much better after 12 h at 80 °C (91%, Scheme 2), so we suspected that under the initial thermal conditions the energy barrier of the Diels-Alder reaction has been surpassed and that some retro Diels-Alder might have taken place. For that reason, we submitted cycloadduct **2g** (*endo*/*exo* 10:90) to the conditions of the uncatalyzed thermal reaction (Scheme 3). Indeed, the retro Diels-Alder reaction occurred, giving 76% of alkenylboronate **1g** and 15% of recovered cycloadduct **2g** (a mixture with a very similar composition to the one obtained when submitting the direct reaction).

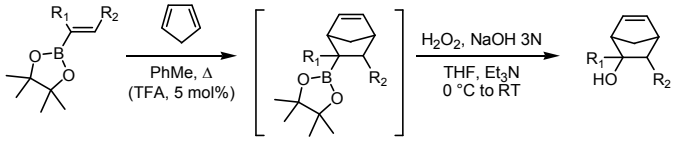
Finally, we studied the tandem Diels-Alder reaction of



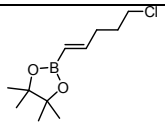
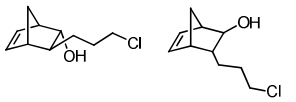
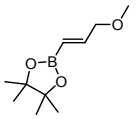
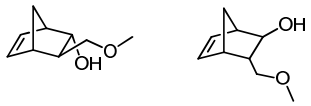
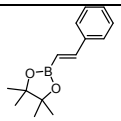
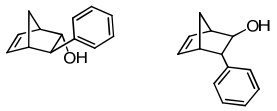
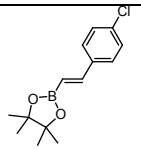
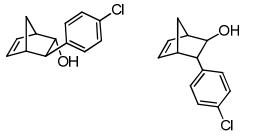
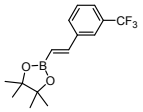
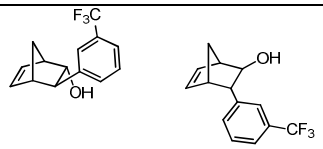
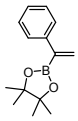
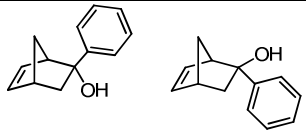
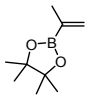
Scheme 3

alkenylboronates with cyclopentadiene-oxidation (Table 4).

Table4 Tandem Diels-Alder reaction of alkenylboronates with cyclopentadiene-oxidation



Entry	Dienophile	Overall yield (%) *endo*/*exo*[a]	Products DA + [O]
1	**1a**	93[b] 39:61	**3a-N** **3a-X**
2	**1b**	79[b] 15:85	**3b-N** **3b-X**

3	 **1c**	82[b] 14:86	 **3c-N** **3c-X**
4	 **1d**	82[b] 12:88	 **3d-N** **3d-X**
5	 **1e**	37[c] 13:87	 **3e-N** **3e-X**
6	 **1f**	28[c] 13:87	 **3f-N** **3f-X**
7	 **1g**	44[c] 9:91	 **3g-N** **3g-X**
8	 **1h**	88[d] 3:97	 **3h-N** **3h-X**
9	 1i	66[b] 9:91	 3i-N 3i-X

[a]Determined by NMR integration. [b]Non TFA-catalyzed thermal conditions were used. [c]TFA-catalyzed conditions were used. [d]Conditions shown in Scheme 2 were used..

Except for the compounds with aryl groups at the 2-position (Entries 5-7), we coupled the non-catalyzed thermal conditions shown in Table 2 for the cycloaddition step with the final oxidation with alkaline hydrogen peroxide in one-pot. Overall yields for the two-step sequence were very similar to the ones obtained in the Diels-Alder reactions, which suggests that *in situ* transformation of the boronate cycloadducts to the corresponding alcohols occurs very efficiently. In general, the substituted 5-norbornen-2-ols were obtained with acceptable to very good yields, which demonstrated that alkenylboronic esters can be used as synthetic equivalents of substituted enols. Due to their high functionalization, the alcohol products can be foreseen as valuable synthetic intermediates towards a variety of chemical structures. We anticipate that other transformations of the cycloadduct intermediates could be developed for further elaboration of C-C, C-O and C-N bonds.

Computational study

To gain a deeper insight into the mechanism of the Diels-Alder reactions of the dienophiles under study we performed a theoretical study. In particular, we intended to examine the reversibility of such processes and whether the starting material/products distribution was determined by thermodynamic or kinetic control. Therefore, we optimized the geometries in toluene of the reactants, the transition structures and the products to compute the activation and reaction energies at 170 ºC. In addition, we analyzed the geometries and the properties of the dienophiles and the transition structures with the aim of rationalizing the reactivity and selectivity trends.

Computational methods. All calculations were performed with the Gaussian 09 package.[38] We carried out thorough conformational analyses to locate the lowest energy geometry for all the structures under study. Final geometry optimizations were carried out using MPWB1K global-hybrid meta-GGA functional[39] together with 6-311G* basis. Solvent effects of toluene were taken into account through full optimizations using the polarizable continuum model (PCM) as developed by Tomasi's group[40] in the framework of self-consistent reaction field (SCRF).[41-43] The vibrational frequencies were calculated to determine the nature of the stationary points and to evaluate zero-

point vibrational energy (ZPVE) and thermal corrections at 443 K (170 ºC). The frontier molecular orbitals (FMOs) were computed

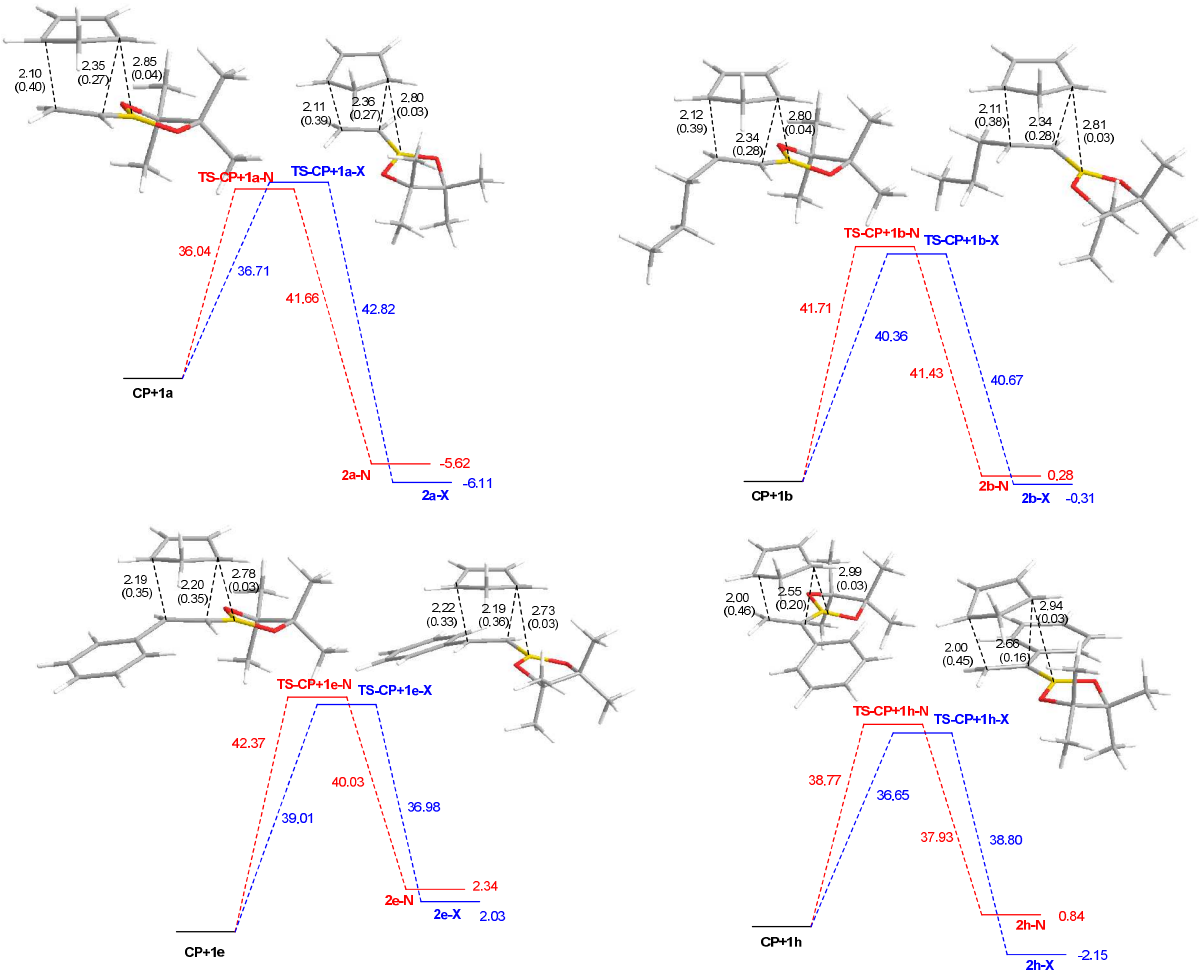


Fig.1 MPWB1K/6-311G* free energy profiles for the Diels-Alder reactions of pinacol alkenylboronates **1a** (top left), **1b** (top right), **1e** (bottom left) and **1h** (bottom right) with cyclopentadiene (free activation energies in toluene at 170 ºC for the direct and reverse reaction, in kcal/mol). The optimized geometries in toluene for the transition structures with selected distances in Å and Wiberg bond indexes in parentheses are also shown.

with the same method. Intrinsic Reaction Coordinate (IRC) calculations were run to verify if the transition structures were directly connected to the reactants and the products.

Fig.1 shows the free energy profiles for the Diels-Alder reactions of selected dienophiles with cyclopentadiene as a means to compare the reaction channels (for all the energy profiles see the ESI). Also, the optimized geometries for the corresponding transition structures with selected distances and Wiberg bond indexes are shown. Table 5 gathers the computed free energies of activation, reaction free energies and *endo*/*exo* selectivities at 170 ºC in toluene for all the Diels-Alder reactions under study. All transition structures exhibit classical [4+2] geometries and are asynchronic. However, the ones corresponding to the dienophiles with aromatic substituents in C-2 (**1e-1g**) are less asynchronic and the asynchronicity is reversed, i.e. the carbon atom directly attached to boron (C-1) is closer to the diene carbon than C-2. Carbon-carbon distances for the other systems are in line with previous results: the presence of the boron atom makes C-2 more electron deficient, so it becomes closer to the corresponding carbon atom in the diene than C-1.[44] Analysis of FMOs indicates that the reactions under study are normal electron-demand Diels-Alder reactions. From the atomic coefficients for the LUMOs of the dienophiles, it appears that the computed reversal of asynchonicity is caused by electronic effects since compounds **1e-1g** have larger coefficients at C-1 than at C-2, in contrast to the rest of the dienophiles. However, we do not discard the contribution of steric effects. In addition, the transition structures of alkenylboronates with aromatic susbtituents in C-1 (**1h** and **1j**) are extremely asynchronic, with asynchronicities as high as 0.66 Å. Nonetheless, IRC calculations connected the transition structures with the reactants and the products, therefore all reactions were computed to be concerted. In this case, comparison of the atomic coefficients corresponding to the LUMOs of the dienophiles suggests that the higher asynchronicity is determined by steric effects rather than electronic effects. The non-classical [4+3] carbon-boron interactions are weak (C-B distances 2.70-3.15 Å, WBI 0.04-002) and very similar for the *endo* and *exo* approaches. Consequently, the observed moderate to high *exo*-selectivities seems to be a consequence of unfavorable van der Waals interactions in the *endo* transition structures.

Also, the short distance (*ca.* 2.4 Å) between one of the methylene hydrogens of the cyclopentadiene moiety and one of the oxygens of the pinacol boronate in the *exo* transition structures suggests

the possibility that hydrogen bond interactions contribute to

Table 5 MPWB1K/6-311G* free energies of activation, reaction energies and *endo*/*exo* selectivities at 170 ºC in toluene for the Diels-Alder reactions of pinacol alkenylboronates **1a-1j** with cyclopentadiene[a]

Dienophile	TS	$\Delta G^{\#}_{Tol}$	*endo*/*exo*	ΔG_{Tol}	*endo*/*exo*
1a	*endo*	36.04	68:32	-5.62	37:63
	exo	36.71		-6.11	
1b	*endo*	41.71	18:82	0.28	34:66
	exo	40.36		-0.31	
1c	*endo*	41.25	17:83	-1.09	61:39
	exo	39.81		-0.70	
1d	*endo*	39.44	10:90	-3.99	46:54
	exo	37.53		-4.15	
1e	*endo*	42.37	2:98	2.34	41:59
	exo	39.01		2.03	
1f	*endo*	40.75	29:71	1.36	79:21
	exo	39.97		2.53	
1g	*endo*	40.72	22:78	2.16	51:49
	exo	39.59		2.19	
1h	*endo*	38.77	8:92	0.84	3:97
	exo	36.65		-2.15	
1i	*endo*	40.25	8:92	-1.30	51:49
	Exo	38.13		-1.24	
1j	*endo*	41.92	24:76	1.47	79:21
	exo	40.91		2.65	

[a]Energies in kcal/mol.

determine the diastereoselectivity. NBO calculations indicate that this accounts for a stabilization of 0.30-0.75 kcal/mol of the *exo* transition structures relative to their *endo* counterparts.

The lowest energy barriers correspond to the reactions of substrates **1a** and **1h**, while the one for analogue **1j** is the highest one, in accordance with the experimental reactivities. However, the free energies of activation for the other reactions do not match the reactivity trend accurately. For that reason, we optimized the geometries of the products and computed the reaction energies. By analyzing the barriers for the direct reactions (Diels-Alder reaction) and the reverse reaction (retro Diels-Alder reaction) we propose that the low product yields for the reactions of dienophiles **1e** - **1g** at 170 ºC, might be related to the higher reversibility of the reactions as a result of the higher energies of the products and the resulting lower energy barriers for the retro Diels-Alder reactions. The higher energies of the products corresponding to the reactions of aromatic alkenylboronates **1e** - **1g** appear to be originated from steric clashes between the aromatic ring and the [2.2.1] backbone.

For **1b**-**1d** and **1i**, the *endo*/*exo* selectivities calculated from activation free energies are in agreement with the experimental values. For the more reactive dienophiles **1a** and **1h** the calculated *endo*/*exo* selectivities from the reaction energies are in excellent accordance with the experimental outcome, indicating the dominio of the termodinamical control in these reactions. The *endo*/*exo* ratios for **1e** - **1g** are closer to the figures obtained from reaction energies, which supports that in these cases the starting material/products distribution is a consequence of thermodynamic equilibration. On the other hand, free reaction energies of the products predict that the reactions with the **1a**-**1d** and **1h**-**1i** should be exergonic and therefore, the boronate cycloadducts should predominate while that the reactions with **1e**-**1g** and **1j** should be endergonic and the starting alkenylboronates should be the major components of the reaction mixtures. Therefore, free energy trends, gave us a hint to better understand the reaction mechanism.

Another point that deserves to be remarked is the high reactivity of substrate **1h**. Inspection of the geometry of the corresponding transition structures reveals that a non-classical hydrogen bond (NCHB) between an aromatic proton at the ortho position and one of the oxygens of the pinacol boronate might be responsible for the peculiar reactivity. Such interaction is much stronger in the *exo* transition structure than in its *endo* counterpart (*exo*: 2.17 Å, 1.25 kcal/mol, *endo*: 2.38 Å, 0.28 kcal/mol), and also than in the starting dienophile (2.55 Å, 0.15 kcal/mol). The unexpected lack of reactivity of structurally related analogue **1j** is reflected in a higher free energy barrier obtained from the calculations, which might result from geometric constraints imposed by the bulky chlorine atom. The dihedral angle between the aromatic ring and the double bond in the optimized geometry of the reactant is 54 degrees, making the approach of the diene more difficult. The aforementioned dihedral angle is reduced to roughly 26 degrees in the transition structures, in contrast to the planar geometries corresponding to 1-phenylvinylboronic acid pinacol ester (**1h**).

Conclusions

We have investigated the Diels-Alder reactions of pinacol alkenylboronates with cyclopentadiene. The outcome of the studied transformation was shown to be very sensitive to the substitution of the dienophile both under thermal and TFA-catalyzed conditions. Theoretical calculations disclosed some interesting substituent effects for these [4+2] cycloadditions. We have found that the thermal Diels-Alder reactions of alkenylboronates with aryl groups in the 2-position give low yields because they are highly reversible. The high reactivity of 1-phenylvinylboronic acid pinacol ester (**1h**) was explained in terms of a stabilizing non-classical hydrogen bond between an aromatic proton and the boronate moiety. We have also synthesized a range of substituted 5-norbornen-2-ols in one-pot by performing the tandem Diels-Alder reactions - alkaline hydrogen peroxide oxidation, demonstrating the versatility of alkenylboronic esters as synthetic equivalents of substituted enols.

Experimental section

General experimental procedures. All reagents and solvents were used directly as purchased or purified according to standard procedures. Analytical thin layer chromatography was carried out using commercial silica gel plates (Merck, Silica Gel 60 F254) and visualization was effected with short wavelength UV light (254 nm) and a *p*-anisaldehyde solution (2.5 mL of *p*-anisaldehyde + 2.5 mL of H_2SO_4 + 0.25 mL of AcOH + 95 mL of EtOH). Column chromatography was performed with silica gel 60 H (Merck), slurry packed, run under low pressure of nitrogen. The Diels-Alder reactions were monitored using TLC and ^{11}B NMR analysis in $CDCl_3$. NMR spectra were recorded at 300 MHz for ^1H, 75 MHz for ^{13}C, 96 MHz for ^{11}B and 282 MHz for ^{19}F NMR on a Bruker Avance-300 DPX spectrometer with $CDCl_3$ as solvent and $(CH_3)_4Si$ (^1H) and $CDCl_3$ (^{13}C, 76.9 ppm) as internal standards. ^{11}B and ^{19}F NMR spectra were externally

referenced to BF_3-Et_2O and $CFCl_3$, respectively. Chemical shifts are reported in delta (δ) units in parts per million (ppm) and splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad. Coupling constants are recorded in Hertz (Hz). Isomeric ratios were determined by ^{1}H NMR integration. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrometer using sodium chloride plates or potassium bromide pellets. Absorbance frequencies are recorded in reciprocal centimeters (cm^{-1}). The high resolution mass spectra (HRMS) were obtained with a Bruker MicroTOF-Q II instrument (Bruker Daltonics, Billerica, MA). Detection of the ions was performed with electrospray ionization (ESI), positive ion mode and Atmospheric Pressure Chemical Ionization (APCI). The structure of the products were determined by a combination of spectroscopic methods such as IR, 1D and 2D NMR (including NOE, DEPT, COSY, HSQC and HMBC experiments) and HRMS. In some cases, NMR calculations were also performed to corroborate the stereochemistry and the assignment. In addition, we confirmed the structure of the Diels-Alder products by oxidation of the boronates to the alcohols, some of which were described in the literature.

Diels-Alder reactions of alkenylboronates: synthesis of boronates 2a-2i

General procedure A: To a pressure tube equipped with a stirring bar were added dry toluene (1.5 mL), vinylboronate **1** (typically 0.25 mmol), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 5 mol %) and cyclopentadiene (0.75 mmol) under nitrogen atmosphere. The resulting reaction mixture was stirred at 170 ºC for the reported time (1-24 h). The solvent was removed under reduced pressure, and the crude was purified by column chromatography (hexane/AcOEt) to afford the corresponding boronate.

General procedure B: To a pressure tube equipped with a stirring bar were added dry toluene (1.5 mL), vinylboronate **1** (typically 0.28 mmol), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 5 mol %), cyclopentadiene (0.84 mmol) and trifluoroacetic acid (TFA, 5 mol %) under nitrogen atmosphere. The resulting reaction mixture was stirred at 80 ºC for the reported time (5-72 h). The solvent was removed under reduced pressure, and the crude was purified by column chromatography (hexane/AcOEt) to afford the corresponding boronate.

2-Bicyclo[2.2.1]hept-5-en-2-yl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2a).[32] Boronate 2a was obtained as a mixture of diastereomers according to the general procedures A and B using vinylboronate 1a (0.28 mmol) and cyclopentadiene (0.84 mmol). A small fraction of each diastereomer could be separated and characterized.

a) Procedure A: Reaction time: 1 h. Yield: 96% (59.1 mg), *endo*/*exo* 36:65.

b) Procedure B: Reaction time: 5 h. Yield: 88% (54.2 mg), *endo*/*exo* 36:64.

4,4,5,5-Tetramethyl-2-(3-propyl-bicyclo[2.2.1]hept-5-en-2-yl)-[1,3,2]dioxaborolane (2b). Boronate **2b** was obtained as a mixture of diastereomers according to the general procedure A, using alkenylboronate **1b** (0.22 mmol) and cyclopentadiene (0.66 mmol). A small fraction of the *exo* diastereomer could be separated and characterized. Reaction time: 24 h. Yield: 78% (45.0 mg), *endo*/*exo* 17:83. **Boronate 2b-X** (major compound, yellowish oil) IR (film) ν_{max} 2956, 2926, 2870, 2359, 2344, 1371, 1312, 1146, 978, 853, 698 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.17 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 2.9 Hz, 1H, H-6), 5.87 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 2.9 Hz, 1H, H-5), 2.77 (br s, 1H, H-4), 2.74 (br s, 1H, H-1), 2.15-2.04 (m, 1H, H-3), 1.36-1.26 (m, 4H, H-7 and H-11), 1.24 (br s, 12H, H-9), 1.10-0.92 (m, 2H, H-10), 0.85 (t, $J_{11,12}$= 7.3 Hz, 3H, H-12), 0.16 (dd, $J_{2,3}$= 5.3, $J_{1,2}$= 1.6 Hz, 1H, H-2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3 (CH, C-6), 131.5 (CH, C-5), 82.8 (2C, C-8), 48.5 (CH_2, C-7), 46.1 (CH, C-4), 45.0 (CH, C-1), 42.2 (CH, C-3), 37.6 (CH_2, C-10), 24.7 ($2CH_3$, C-9), 24.6 ($2CH_3$, C-9), 21.8 (CH_2, C-11), 14.4 (CH_3, C-12), C-2 signal missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 34.2. **Boronates 2b-X and 2b-N** (yellowish oil) IR (film) ν_{max} 2957, 2926, 2870, 2359, 2342, 1371, 1312, 1244, 1146, 968, 853, 692 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.17 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 2.9 Hz, 1H, H-6X), 6.10 (dd, $J_{5,6}$= 5.5, $J_{4,5}$= 3.1 Hz, 1H, H-5N), 5.98 (dd, $J_{5,6}$= 5.5, $J_{4,5}$= 2.8 Hz, 1H, H-6N), 5.87 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 2.9 Hz, 1H, H-5X), 2.92 (br s, 1H, H-1N), 2.77 (br s, 1H, H-4X), 2.74 (br s, 1H, H-1X), 2.50 (br s, 1H, H-4N), 2.15-2.04 (m, 1H, H-3X), 1.40-1.26 (m, 11H, H-7X, H-11X, H-3N, H-7N, H-10N and H-11N), 1.24 (s, 12H, H-9X), 1.18 (s, 12H, H-9N), 1.10-0.92 (m, 2H, H-10X), 0.92-0.78 (m, 4H, H-2N and H-12N), 0.85 (t, $J_{11,12}$= 7.3 Hz, 3H, H-12X), 0.16 (dd, $J_{2,3}$= 5.3, $J_{1,2}$= 1.6 Hz, 1H, H-2X). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3 (CH, C-6X), 137.2 (CH, C-5N), 135.1 (CH, C-6N), 131.5 (CH, C-5X), 82.7 (2C, C-8N), 82.2 (2C, C-8X), 48.5 (CH_2, C-7X), 47.2 (CH_2, C-7N), 47.1 (CH, C-4N), 46.1 (CH, C-4X), 45.0 (CH, C-1X), 44.7 (CH, C-1N), 42.2 (CH, C-3X), 42.0 (CH, C-3N), 39.6 (CH_2, C-10N), 37.6 (CH_2, C-10X), 24.8 ($2CH_3$, C-9N), 24.7 ($2CH_3$, C-9X), 24.6 ($2CH_3$, C-9X), 24.5 ($2CH_3$, C-9N), 21.9 (CH_2, C-11N), 21.8 (CH_2, C-11X), 14.4 ($2CH_3$, C-12X and C-12N), C-2 signals missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 34.1. HRMS (APCI) calcd for $C_{16}H_{28}BO_2$ $(M+H)^+$ 263.2177, found 263.2178. **2-[3-(3-Chloro-propyl)-bicyclo[2.2.1]hept-5-en-2-yl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2c)**. Boronate **2c** was obtained as a mixture of diastereomers according to the general procedure A, using alkenylboronate **1c** (0.21 mmol) and cyclopentadiene (0.63 mmol). A small fraction of *exo* diastereomer could be separated and characterized. Reaction time: 24 h. Yield: 89% (55.5 mg), *endo*/*exo* 20:80. **Boronate 2c-X** (major compound, yellowish oil) IR (film) ν_{max} 2965, 2926, 2358, 2341, 1373, 1314, 1144, 852, 669, 430, 411 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20 (dd, $J_{5,6}$= 5.3, $J_{1,6}$= 3.2 Hz, 1H, H-6), 5.88 (dd, $J_{5,6}$= 5.3, $J_{4,5}$= 2.9 Hz, 1H, H-5), 3.51 (t, $J_{11,12}$= 6.9 Hz, 2H, H-12), 2.78 (br s, 2H, H-1 and H-4), 2.14-2.04 (m, 1H, H-3), 1.75 (quintet, $J_{10,11}$= $J_{11,12}$= 7.2 Hz, 2H, H-11), 1.34-1.27 (m, 2H, H-7), 1.24 (s, 12H, H-9), 1.16-1.02 (m, 2H, H-10), 0.18 (br d, $J_{2,3}$ = 5.2 Hz, 1H, H-2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6 (CH, C-6), 131.2 (CH, C-5), 83.0 (2C, C-8), 48.6 (CH_2, C-7), 46.2 (CH, C-1), 45.3 (CH_2, C-12), 45.0 (CH, C-4), 41.6 (CH, C-3), 32.5 (CH_2, C-10), 31.8 (CH, C-11), 24.7 ($4CH_3$, C-9), C-2 signal missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 33.8. **Boronates 2c-X and 2c-N** (yellowish oil) IR (film) ν_{max} 2965, 2930, 2358, 2342, 1373, 1144, 852, 717, 546, 411, 401 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20 (dd, $J_{5,6}$= 5.3, $J_{1,6}$= 3.2 Hz, 1H, H-6X), 6.17 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 3.2 Hz, 1H, H-5N), 6.00 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 2.8 Hz, 1H, H-6N), 5.88 (dd, $J_{5,6}$= 5.3, $J_{4,5}$= 2.9 Hz, 1H, H-5X), 3.58 (t, $J_{11,12}$= 6.8, 1H, H-12N), 3.57 (t, $J_{11,12}$= 6.9, 1H, H-12N), 3.51

(t, $J_{11,12}$= 6.9 Hz, 2H, H-12X), 2.95 (br s, 1H, H-1N), 2.78 (br s, 2H, H-1X and H-4X), 2.51 (br s, 1H, H-4N), 2.14-2.04 (m, 1H, H-3X), 1.84 (quintet, $J_{10,11}$= $J_{11,12}$= 7.0 Hz, 2H, H-11N), 1.75 (quintet, $J_{10,11}$= $J_{11,12}$= 7.2 Hz, 2H, H-11X), 1.44-1.41 (m, 1H, H-3N), 1.38-1.32 (m, 2H, H-7N), 1.34-1.27 (m, 2H, H-7X), 1.24 (s, 12H, H-9X), 1.18 (br s, 12H, H-9N), 1.16-1.02 (m, 4H, H-10X and H-10N), 0.84-0.79 (m, 1H, H-2N), 0.18 (br d, $J_{2,3}$= 5.2 Hz, 1H, H-2X). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7 (CH, C-6X), 137.1 (CH, C-5N), 135.4 (CH, C-6N), 131.2 (CH, C-5X), 83.0 (2C, C-8X), 82.8 (2C, C-8N), 48.6 (CH_2, C-7X), 47.2 (CH_2, C-7N and CH, C-4N), 46.2 (CH, C-4X), 45.3 ($2CH_2$, C-12X and C-12N), 45.0 (CH, C-1X), 44.6 (CH, C-1N) 41.6 (CH, C-3X), 41.0 (CH, C-3N), 32.5 ($2CH_2$, C-10X and C-10N), 31.8 ($2CH_2$, C-11X and C-11N), 24.8 ($2CH_3$, C-9N), 24.7 ($4CH_3$, C-9X), 24.5 ($2CH_3$, C-9N), C-2 signals missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 34,0. HRMS (APCI) calcd for $C_{16}H_{27}BClO_2$ $(M+H)^+$ 297.1787, found 297.1822.**2-(3-Methoxymethylbicyclo[2.2.1]hept-5-en-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2d)**. Boronate **2d** was obtained as a mixture of diastereomers according to the general procedures A and B, using alkenylboronate **1d** (0.22 mmol) and cyclopentadiene (0.66 mmol). A small fraction of *exo* diastereomer could be separated and characterized.

a) Procedure A: Reaction time: 24 h. Yield: 88% (51.1 mg), *endo*/*exo* 15:85.

b) Procedure B: Reaction time: 72 h. Yield: 26% (15.1 mg), *endo*/*exo* 10:90.

Boronate 2d-X (major compound, yellowish oil) IR (film) ν_{max} 3055, 2976, 2926, 2868, 1406, 1369, 1313, 1145, 1109, 852, 723 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 3.0 Hz, 1H, H-6), 5.90 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 3.0 Hz, 1H, H-5), 3.29 (s, 3H, H-11), 3.14 (dd, $J_{10a,10b}$= 9.5, $J_{3,10a}$= 5.7 Hz, 1H, H-10a), 2.93 (br s, 1H, H-4), 2.84 (t, $J_{10a,10b}$= $J_{3,10b}$ = 9.5 Hz, 1H, H-10b), 2.79 (br s, 1H, H-1), 2.42 (m, 1H, H-3), 1.33 (br s, 2H, H-7), 1.23 (s, 12H, H-9), 0.08 (br d, $J_{2,3}$ = 5.9 Hz, 1H, H-2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4 (CH, C-6), 131.5 (CH, C-5), 83.0 (2C, C-8), 76.5 (CH_2, C-10), 58.6 (CH_3, C-11), 48.4 (CH_2, C-7), 44.4 (CH, C-1), 44.2 (CH, C-4), 41.9 (CH, C-3), 24.7 ($4CH_3$, C-9), C-2 signal missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 34.0. HRMS (APCI) calcd for $C_{15}H_{26}BO_3$ $(M+H)^+$ 265.1970, found 265.1967.

Boronates 2d-X and 2d-N (yellowish oil) IR (film) ν_{max} 3055, 2976, 2927, 2889, 2868, 1371, 1313, 1145, 1107, 974, 852, 723 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.18 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 3.0 Hz, 1H, H-6X), 6.10 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 3.1 Hz, 1H, H-5N), 6.04 (dd, $J_{5,6}$= 5.5, $J_{1,6}$= 2.8 Hz, 1H, H-6N), 5.90 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 3.0 Hz, 1H, H-5X), 3.49 (dd, $J_{10a,10b}$= 9.4, $J_{3,10a}$= 5.4 Hz, 1H, H-10aN), 3.34 (s, 3H, H-11N), 3.29 (s, 3H, H-11X), 3.22 (t, $J_{3,10b}$= $J_{10a,10b}$= 9.4 Hz, 1H, H-10bN), 3.14 (dd, $J_{10a,10b}$= 9.5, $J_{3,10a}$= 5.7 Hz, 1H, H-10aX), 2.93 (br s, 2H, H-4X and H-1N), 2.84 (t, $J_{3,10b}$ = $J_{10a,10b}$= 9.5 Hz, 1H, H-10bX), 2.79 (br s, 1H, H-1X), 2.75 (br s, 1H, H-4N), 2.42 (m, 1H, H-3X), 1.81 (dt, $J_{3,10b}$= 9.4, $J_{3,10a}$= $J_{2,3}$= 5.3 Hz, 1H, H-3N), 1.33 (br s, 4H, H-7X and H-7N), 1.23 (s, 12H, H-9X), 1.17 (s, 12H, H-9N), 0.78 (dd, $J_{2,3}$= 5.2, $J_{1,2}$= 3.3 Hz, 1H, H-2N), 0.08 (br d, $J_{2,3}$ = 5.9 Hz, 1H, H-2X). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4 (CH, C-6X), 136.9 (CH, C-5N), 135.9 (CH, C-6N), 131.5 (CH, C-5X), 83.0 (2C, C-8X), 82.9 (2C, C-8N), 77.5 (CH_2, C-10N), 76.5 (CH_2, C-10X), 58.6 ($2CH_3$, C-11X and C-11N), 48.4 (CH_2, C-7X), 46.7 (CH_2, C-7N), 44.4 (CH, C-1X), 44.2 (CH, C-4X), 44.1 (CH, C-4N), 44.0 (CH, C-1N), 42.3 (CH, C-3N), 41.9 (CH, C-3X), 24.7 ($4CH_3$, C-9X), 24.6 ($4CH_3$, C-9N), C-2 signals missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 33,8.

4,4,5,5-Tetramethyl-2-(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)-[1,3,2]-dioxaborolane (2e). Boronate **2e** was obtained as a mixture of diastereomers according to the general procedures A and B, using alkenylboronate **1e** (0.20 mmol) and cyclopentadiene (0.60 mmol).

a) Procedure A: Reaction time: 24 h. Yield: 29% (17.3 mg), *endo*/*exo* 35:65.

b) Procedure B: Reaction time: 24 h. Yield: 32% (19 mg), *endo*/*exo* 17:83. Reaction time: 72 h. Yield: 38% (22.5 mg), *endo*/*exo* 17:83.

Boronates 2e-X and 2e-N (yellowish oil) IR (film) ν_{max} 2957, 2928, 2870, 1468, 1454, 1404, 1371, 1146, 853, 679 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.08 (m, 10H, ArH-X and ArH-N), 6.30 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 3.2 Hz, 1H, H-6X), 6.26 (dd, $J_{5,6}$=5.6, $J_{4,5}$= 3.3 Hz, 1H, H-5N), 6.15 (dd, $J_{5,6}$= 5.6, $J_{1,2}$= 2.9 Hz, 1H, H-6N), 5.79 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 2.7 Hz, 1H, H-5X), 3.51 (dd, $J_{2,3}$= 5.8, J = 3.2 Hz, 1H, H-3X), 3.16 (br s, 1H, H-4X), 3.11 (br s, 1H, H-1N), 2.95 (br s, 2H, H-1X and H-4N), 2.86 (br d, $J_{2,3}$= 5.9 Hz, 1H, H-3N), 1.63 (br d, $J_{7a,7b}$= 8.6, 1H, H-7aN), 1.56 (br d, $J_{7a,7b}$= 8.3 Hz, 1H, H-7aX), 1.49-1.41 (m, 1H, H-7bN), 1.42-1.36 (m, 2H, H-7bX and H-2N), 1.25 (s, 12H, H-9X), 1.22 (s, 12H, H-9N), 1.02 (dd, $J_{2,3}$= 5.9, J= 1.8, 1H, H-2X). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7 (C, Ar-N), 145.1 (C, Ar-X), 138.6 (CH, C-6X), 137.6 (CH, C-5N), 136.5 (CH, C-6N), 132.1 (CH, C-5X), 128.2 (2CH, Ar-N), 128.1 (2CH, Ar-X), 127.7 (2CH, Ar-X), 127.5 (2CH, Ar-N), 125.5 (CH, Ar-X), 125.3 (CH, Ar-N), 83.2 (2C, C-8X), 83.1 (2C, C-8N), 49.0 (CH_2, C-7X), 48.9 (CH, C-4X), 48.0 (CH_2,C-7N), 47.9 (CH, C-4N), 46.5 (2CH, C-3X and C-3N), 45.9 (CH, C-1X), 45.2 (CH, C-1N), 24.9 ($2CH_3$, C-9N), 24.8 ($2CH_3$, C-9X), 24.7 ($2CH_3$, C-9X), 24.6 ($2CH_3$, C-9N), C-2 signals missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 33.3. HRMS (APCI) calcd for $C_{19}H_{26}BO_2$ $(M+H)^+$ 297.2020, found 297.2033.

4,4,5,5-tetramethyl-2-[3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl]-[1,3,2]-dioxaborolane (2f). Boronate **2f** was obtained as a mixture of diastereomers according to the general procedures A and B, using alkenylboronate **1f** (0.17 mmol) and cyclopentadiene (0.51 mmol).

a) Procedure A: Reaction time: 24 h. Yield: 20% (11.2 mg), *endo*/*exo* 40:60.

b) Procedure B: Reaction time: 24 h. Yield: 20% (11.2 mg), *endo*/*exo* 36:64. Reaction time: 72 h. Yield: 31% (17.4 mg), *endo*/*exo* 29:71.

Boronates 2f-X and 2f-N (yellowish oil) IR (film) ν_{max} 3059, 2974, 2931, 2870, 1492, 1371, 1315, 1143, 1091, 1014, 972, 848, 798, 729 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 4H, H-11N and H-12N), 7.17 (br d, $J_{11,12}$= 8.5 Hz, 2H, H-11X), 7.07 (br d, $J_{12,11}$= 8.5 Hz, 2H, H-12X), 6.31 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 3.1 Hz, 1H, H-6X), 6.25 (dd, $J_{5,6}$= 5.7, $J_{4,5}$= 3.1 Hz, 1H, H-5N), 6.15 (dd, $J_{5,6}$= 5.7, $J_{1,6}$ = 2.9 Hz, 1H, H-6N), 5.76 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 2.8 Hz, 1H, H-5X), 3.45 (dd, $J_{2,3}$= 6.0, $J_{3,4}$= 3.8 Hz, 1H, H-3X), 3.11 (br s, 2H, H-4X and H-1N), 2.94 (br s, 2H, H-1X and H-4N), 2.80 (br d, $J_{2,3}$= 5.6 Hz, 1H, H-3N), 1.58-1.51 (m, 2H, H-7X and H-7N), 1.47 (br d, $J_{7a,7b}$= 8.3, 1H, H-7N), 1.40 (m, 1H, H-7X), 1.33 (m, 1H, H-2N), 1.25 (s, 12H, H-9X), 1.22 (s, 12H, H-9N), 0.95 (dd, $J_{2,3}$ = 6.0, $J_{1,2}$= 2.0 Hz, 1H, H-2X). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2 (C, C-10N), 143.6 (C, C-10X), 138.9 (CH, C-

6X), 137.4 (CH, C-5N), 136.7 (CH, C-6N), 131.8 (CH, C-5X), 131.2 (C, C-13X), 129.4 (2CH, C-11X), 128.8 (2CH, C-11N), 128.2 (2CH, C-12N), 127.8 (2CH, C-12X), 83.3 (2C, C-8X), 83.2 (2C, C-8N), 49.1 (CH_2, C-7X), 48.9 (CH, C-4X), 47.9 (CH, C-4N and CH_2, C-7N), 46.1 (2CH, C-3N and C-3X), 45.8 (CH, C-1X), 45.1 (CH, C-1N), 24.9 ($2CH_3$, C-9N), 24.8 ($2CH_3$, C-9X), 24.7 ($2CH_3$, C-9X), 24.6 ($2CH_3$, C-9N), C-2 and C-13N signals missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 33.3. HRMS (APCI) calcd for $C_{19}H_{25}BClO_2$ $(M+H)^+$ 331.1631, found 331.1628.

4,4,5,5-Tetramethyl-2-[3-(3-trifluoromethylphenyl)bicyclo[2.2.1]hept-5-en-2-yl]-[1,3,2]dioxaborolane (2g) Boronate **2g** was obtained as a mixture of diastereomers according to the general procedures A and B, using alkenylboronate **1g** (0.27mmol) and cyclopentadiene (0.81 mmol).

a) Procedure A: Reaction time: 24 h. Yield: 19% (18.7 mg), *endo*/*exo* 37:63.

b) Procedure B: Reaction time: 24 h. Yield: 24% (23.6 mg), *endo*/*exo* 10:90. Reaction time: 72 h. Yield: 45% (44.3 mg), *endo*/*exo* 10:90.

Boronates 2g-X and 2g-N (yellowish oil) IR (film) ν_{max} 3045, 2926, 1715, 1445, 1354, 1265, 1080, 737, 664, 600 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.78-7.26 (m, 8H, ArH-X and ArH-N) 6.34 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 2.9 Hz, 1H, H-6X), 6.27 (dd, $J_{5,6}$= 5.5, $J_{4,5}$= 3.0Hz, 1H, H-5N), 6.17 (dd, $J_{5,6}$= 5.5, $J_{1.6}$= 2.8 Hz, 1H, H-6N), 5.76 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 2.9 Hz, 1H, H-5X), 3.53 (dd, $J_{2,3}$=5.8, $J_{3,4}$= 3.3 Hz, 1H, H-3X), 3.15 (br s, 2H, H-4X and H-1N), 2.98 (br s, 2H, H-1X and H-4N), 2.89 (br d, $J_{2,3}$= 5.7 Hz, 1H, H-3N), 1.60-1.45 (m, 3H, H-7aX, and H-7N), 1.44-1.34 (m, 2H, H-7bX and H-2N), 1.26 (s, 12H, H-9X), 1.23 (s, 12H, H-9N), 1.02 (dd, $J_{2,3}$= 5.8, $J_{1,2}$ =2.1 Hz, 1H, H-2X). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7 (C, Ar-N), 146.1 (C, Ar-X), 139.1 (CH, C-6X), 137.4 (CH, C-5N), 136.7 (CH, C-6N), 131.7 (CH, C-5X), 131.4 (CH, Ar-X), 130.6 (CH, Ar-N), 130.4 (C, $J_{C,F}$= 29.5 Hz, Ar-X), 128.6 (CH, Ar-N), 128.1 (CH, Ar-X), 125.0 (CH, Ar-N), 124.8 (CH, $J_{C,F}$= 3.7 Hz, Ar-X), 122.6 (CH, Ar-N), 122.5 (CH, Ar-N), 122.4 (CH, $J_{C,F}$= 3.7 Hz, Ar-X), 83.3 (2C, C-8X), 83.2 (2C, C-8N), 49.2 (CH_2, C-7X), 48.9 (CH, C-4X), 48.0 (CH_2, C-7N), 47.5 (CH, C-4N), 46.5 (2CH, C-3X and C-3N), 45.9 (CH, C-1X), 45.2 (CH, C-1N), 24.9 ($2CH_3$, C-9N), 24.8 ($2CH_3$, C-9X), 24.7 ($2CH_3$, C-9X), 24.6 ($2CH_3$, C-9N), C-12N, C-2 and CF_3 signals missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 33.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5. HRMS (APCI) calcd for $C_{20}H_{25}BF_3O_2$ $(M+H)^+$ 365.1894, found 365.1879.

4,4,5,5-Tetramethyl-2-(2-phenylbicyclo[2.2.1]hept-5-en-2-yl)-[1,3,2]-dioxaborolane (**2h**). Boronate **2h** was obtained as a mixture of diastereomers according to the general procedures A and B, using alkenylboronate **1h** (0.17 mmol) and cyclopentadiene (0.51 mmol).

a) Procedure A: Reaction conditions: 12 h at 170 ºC. Yield: 21% (10.6 mg), *endo*/*exo* 41:59. Reaction conditions: 12 h at 80 ºC. Yield: 91% (45.8 mg), *endo*/*exo* 5:95.

b) Procedure B: Reaction time: 12 h. Yield: 83% (41.8 mg), *endo*/*exo* 6:94.

Boronates 2h-X and 2h-N (white solid, mp 81.5-83.3 ºC) IR (KBr) ν_{max} 3065, 2976, 2864, 1371, 1327, 1314, 1215, 1138, 1051,856, 698, 611 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.39-7.00 (m, 10H, ArH-X and ArH-N), 6.25 (dd, $J_{5,6}$= 5.4, $J_{1,6}$= 2.9 Hz, 1H, H-6N), 6.21 (dd, $J_{5,6}$= 5.4, $J_{4,5}$= 3.0 Hz, 1H, H-5N), 6.03 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 2.9 Hz, 1H, H-5X), 5.90 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 2.6 Hz, 1H, H-6X), 3.58 (br s, 1H, H-1X), 3.48 (br s, 1H, H-1N), 2.88 (br s, 2 H, H-4X and H-4N), 2.48 (dd, $J_{3n,3x}$= 11.5, $J_{3x,4}$= 3.9 Hz, 1H, H-3_xX), 2.05 (br d, $J_{3n,3x}$= 11.2 Hz, 1H, H-3_nN), 1.93 (dd, $J_{3n,3x}$= 11.2, $J_{3x,4}$= 3.4 Hz, 1H, H-3_xN), 1.51-1.39 (m, 4H, H-3_nX, H-7aX, and H-7N), 1.31 (br d, $J_{7a,7b}$= 8.3 Hz, 1H, H-7bX), 1.11 (s, 6H, H-9X), 1.10 (s, 12H, H-9X and H-9N), 1.08 (s, 6H, H-9N). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.4 (C, Ar-X), 138.8 (CH, C-5N), 136.4 (CH, C-6X), 136.0 (CH, C-6N), 134.9 (CH, C-5X), 128.1 (2CH, Ar-X), 127.8 (2CH, Ar-X), 127.6 (2CH, Ar-N), 125.2 (2CH, Ar-N), 124.5 (CH, Ar-X), 83.3 (2C, C-8X), 83.2 (2C, C-8N), 49.0 (CH_2, C-7X), 47.8 (CH, C-1X), 47.3 (CH, C-1N), 47.2 (CH_2, C-7N), 43.4 (CH, C-4N), 42.4 (CH, C-4X), 39.0 (CH_2, C-3N) 35.6 (CH_2, C-3X), 24.5 ($2CH_3$, C-9N) 24.3 ($2CH_3$, C-9X), 24.2 ($4CH_3$, C-9X and C-9X), C-2, C-10N and C-13N signals missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 33.3. HRMS (APCI) calcd for $C_{19}H_{26}BO_2$ $(M+H)^+$ 297.1010, found 297.2016.

4,4,5,5-Tetramethyl-2-(2-methylbicyclo[2.2.1]hept-5-en-2-yl)-[1,3,2]-dioxaborolane (2i). Boronate **2i** was obtained as a mixture of diastereomers according to the general procedures A and B, using alkenylboronate **1i** (0.5 mmol) and cyclopentadiene (1.5 mmol). A small fraction of *exo* diastereomer could be separated and characterized.

a) Procedure A: Reaction time: 24 h. Yield: 72% (84.3 mg), *endo*/*exo* 9:91.

b) Procedure B: Reaction time: 24 h. Yield: 15% (17.6 mg), *endo*/*exo* 9:91.

Boronate 2i-X (major compound, yellowish liquid) IR (film) ν_{max} 3055, 2958, 2927, 2866, 1456, 1371, 1354, 1303, 1145, 719 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.12 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 3.1 Hz, 1H, H-6), 6.00 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 2.9 Hz, 1H, H-5), 2.75 (br s, 2H, H-1 and H-4), 2.03 (dd, $J_{3n,3x}$= 11.3, J= 3.8 Hz, 1H, H-3_x), 1.28-1.12 (m, 2H, H-7), 1.24 (s, 12H, H-9), 0.81 (s, 3H, H-10), 0.53 (dd, $J_{3n,3x}$= 11.3, J= 2.5 Hz, 1H, H-3_n). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3 (CH, C-6), 133.8 (CH, C-5), 83.0 (2C, C-8), 49.7 (CH_2, C-7), 48.9 (CH, C-4), 43.4 (CH, C-1), 36.6 (CH_2, C-3), 24.6 ($4CH_3$, C-9), 22.1 (CH_3, C-10), C-2 signal missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 35.0. **Boronates 2i-X and 2i-N** (yellow liquid) IR (film) ν_{max} 2954, 2924, 2852, 1604, 1463, 1446, 1435, 1359, 1303, 1145, 1022, 746 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.14 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 3.1 Hz, 1H, H-6N), 6.12 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 3.1 Hz, 1H, H-6X), 6.00 (dd, $J_{5,6}$= 5.6, $J_{4,5}$=2.9 Hz, 2H, H-5X and H-5N), 2.76 (br s, 3H, H-1X, H-4X and H-4N), 2.53 (br s, 1H, H-1N), 2.03 (dd, $J_{3n,3x}$= 11.3, J= 3.8 Hz, 1H, H-3_xX), 1.52-1.12 (m, 6H, H-7X, H-3N and H-7N), 1.24 (s, 12H, H-9X), 1.19 (s, 12H, H-9N), 1.13 (s, 3H, H-10N), 0.81 (s, 3H, H-10X), 0.53 (dd, $J_{3n,3x}$= 11.3, J= 2.5 Hz, 1H, H-3_nX). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0 (CH, C-6N), 136.6 (CH, C-5N), 136.3 (CH, C-6X), 133.8 (CH, C-5X), 83.0 (2C, C-8X), 82.8 (2C, C-8N), 50.0 (CH, C-1N), 49.7 (CH_2, C-7X), 48.9 (CH, C-4X), 45.6 (CH_2, C-3N), 43.4 (CH, C-1X), 42.9 (CH, C-4N), 37.9 (CH_2, C-7N), 36.6 (CH_2, C-3X), 24.6 ($8CH_3$, C-9X and C-9N), 24.2 (CH_3, C-10N), 22.1 (CH_3, C-10X), C-2 signals missing. ^{11}B NMR (96 MHz, $CDCl_3$) δ 34.3. HRMS (APCI) calcd for $C_{14}H_{24}BO_2$ $(M+H)^+$ 235.1864, found 235.1770.

Tandem Diels-Alder reaction of alkenylboronates - oxidation: synthesis of alcohols

General procedure C: To a pressure tube equipped with a stirring bar were added dry toluene (1.5 mL), vinylboronate **1** (typically 0.27 mmol), cyclopentadiene (0.81 mmol) and BHT (5 mol%) under nitrogen atmosphere. Trifluoroacetic acid (5 mol%) was also added to the reactions of alkenylboronates **1e**, **1f** and **1g**. The resulting reaction mixture was stirred at the reported temperature (170/80 ºC) for the reported time (5-72 h), then diluted with THF (3 mL) and transferred to a 25 mL round-bottom flask. After the addition of Et_3N (1 mL) the solution was cooled to 0 ºC, treated alternately with 3N NaOH (3 mL) and 30% H_2O_2 (3 mL) under nitrogen atmosphere, and then allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with water (10 mL) and extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with NH_4Cl (15 mL) and brine (15 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure at 0 ºC, and the crude was purified by column chromatography (pentane/Et_2O for alcohols **3a** and **3i** and hexane/AcOEt for alcohols **3b-3h**) to afford the corresponding alcohol (**3a-i**).

Bicyclo[2.2.1]hept-5-en-2-ol (3a). Alcohol **3a** was obtained as a mixture of diastereomers according to the general procedure C, using vinylboronate **1a** (0.28 mmol) and cyclopentadiene (0.84 mmol). Diels-Alder reaction step conditions: 1 h at 170 ºC. Overall l yield: 93% (28.6 mg), *endo*/*exo* 39:61.

3-Propyl-bicyclo[2.2.1]hept-5-en-2-ol (3b). Alcohol **3b** was obtained as a mixture of diastereomers according to the general procedure C, using alkenylboronate **1b** (0.22 mmol) and cyclopentadiene (0.66 mmol). Diels-Alder reaction step conditions: 24 h at 170 ºC. Overall yield: 79% (26.1 mg), *endo*/*exo* 15:85. **Alcohols 3b-X and 3b-N** (yellowish oil) IR (film) ν_{max} 3404, 2957, 2922, 2851, 2358, 1717, 1024, 849, 667 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.48 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 3.1 Hz, 1H, H-5N), 6.11 (dd, $J_{5,6}$= 5.7, $J_{4,5}$= 2.6 Hz, 1H, H-5X), 6.09 (m, 1H, H-6N), 6.02 (dd, $J_{5,6}$= 5.7, $J_{1,6}$= 3.1 Hz, 1H, H-6X), 3.91 (br s, 1H, H-2N), 3.33 (br s, 1H, H-2X), 2.89 (br s, 1H, H-1N), 2.67 (br s, 1H, H-1X), 2.65 (br s, 1H, H-4X), 2.50 (br s, 1H, H-4N), 1.79 (d, $J_{7a,7b}$= 8.5, 1H, H-7aX), 1.66-1.56 (m, 2H, H-3X and H-7bX), 1.54-1.07 (m, 10H, H-8X, H-9X, H-7N, H-8N and H-9N), 1.02-0.98 (m, 1H, H-3N), 0.93 (t, $J_{9,10}$= 7.2 Hz, 3H, H-10N), 0.90 (t, $J_{9,10}$= 6.9 Hz, 3H, H-10X). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2 (CH, C-5N), 137.3 (CH, C-5X), 133.8 (CH, C-6X), 131.6 (CH, C-6N), 79.9 (CH, C-2N), 79.0 (CH, C-2X), 50.9 (CH, C-4X), 50.8 (CH, C-3N), 50.5 (CH, C-3X), 48.3 (CH, C-1N), 47.3 (CH, C-4N), 46.6 (CH_2, C-7X), 45.2 (CH_2, C-7N), 44.5 (CH, C-1X), 36.9 (CH_2, C-8N), 35.8 (CH_2, C-8X), 21.7 (CH_2, C-9N), 21.6 (CH_2, C-9X), 14.2 ($2CH_3$, C-10X and C-10N). HRMS (APCI) calcd for $C_{10}H_{17}O$ $(M+H)^+$ 153.1274, found 153.1277. **3-(3-Chloro-propyl)-bicyclo[2.2.1]hept-5-en-2-ol (3c)**. Alcohol **3c** was obtained as a mixture of diastereomers according to the general procedure C, using alkenylboronate **1c** (0.21 mmol) and cyclopentadiene (0.63 mmol). A small fraction of *exo* diastereomer could be separated and characterized. Diels-Alder reaction step conditions: 24 h at 170 ºC. Overall yield: 82% (32.1 mg), *endo*/*exo* 14:86. **Alcohol 3c-X** (major compound, yellowish oil) IR (film) ν_{max} 3362, 2963, 2868, 2359, 2344, 2322, 1558, 1541, 1489, 1456, 1373, 1339, 1214, 995, 849, 718 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.13 (dd, $J_{5,6}$= 5.7, $J_{1,6}$= 2.7 Hz, 1H, H-5), 6.05 (dd, $J_{5,6}$= 5.7, $J_{4,5}$= 3.1 Hz, 1H, H-6), 3.54 (t, $J_{9,10}$= 6.3 Hz, 2H, H-10), 3.36 (br s, 1H, H-2), 2.68 (br s, 1H, H-1), 2.66 (br s, 1H, H-4), 1.89-1.77 (m, 3H, H-7a and H-9), 1.68-1.59 (m, 2H, H-3 and H-7b), 1.52 (br s, 1H, OH), 1.47-1.28 (m, 2H, H-8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0 (CH, C-5), 134.2 (CH, C-6), 78.8 (CH, C-2), 51.0 (CH, C-4), 49.8 (CH, C-3), 46.6 (CH_2, C-7), 45.1 (CH_2, C-10), 44.5 (CH, C-1), 31.5 (CH_2, C-9), 30.7 (CH_2, C-8). **Alcohols 3c-X and 3c-N** (yellowish oil) IR (film) ν_{max} 3345, 3327, 3059, 2964, 2935, 2870, 1456, 1339, 1028, 849, 717, 648 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.49 (dd, $J_{5,6}$= 5.8, $J_{4,5}$= 3.0 Hz, 1H, H-5N), 6.13 (dd, $J_{5,6}$= 5.7, $J_{4,5}$= 2.7 Hz, 1H, H-5X), 6.11 (m, 1H, H-6N), 6.05 (dd, $J_{5,6}$= 5.7, $J_{1,6}$= 3.1 Hz, 1H, H-6X), 3.93 (br s, 1H, H-2N), 3.58 (t, $J_{9,10}$= 6.5 Hz, 2H, H-10N), 3.54 (t, $J_{9,10}$= 6.3 Hz, 2H, H-10X), 3.36 (br s, 1H, H-2X), 2.91 (br s, 1H, H-1N), 2.68 (br s, 1H, H-1X), 2.66 (br s, 1H, H-4X), 2.51 (br s, 1H, H-4N), 1.98-1.77 (m, 7H, H-7aX, H-9X, H-8N and H-9N), 1.68-1.49 (m, 5H, H-3X, H-7bX, OH-X and H-7N), 1.47-1.28 (m, 2H, H-8X), 1.04-0.96 (m, 1H, H-3N). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1 (CH, C-5N), 137.0 (CH, C-5X), 134.2 (CH, C-6X), 131.8 (CH, C-6N); 79.6 (CH, C-2N), 78.8 (CH, C-2X), 51.0 (CH, C-4X), 50.2 (CH, C-3N), 49.8 (CH, C-3X), 48.3 (CH,C-1N), 47.4 (CH, C-4N), 46.6 (CH_2, C-7X), 45.2 (CH_2, C-7N), 45.1 ($2CH_2$, C-10X and C-10N), 44.5 (CH, C-1X), 31.8 (CH_2, C-8N), 31.5 ($2CH_2$, C-9X and C-9N), 30.7 (CH_2, C-8X). HRMS (APCI) calcd for $C_{10}H_{15}ClO$ $(M+H-H_2O)^+$ 169.0779, found 169.0810. **Methoxymethyl-bicyclo[2.2.1]hept-5-en-2-ol (3d)**. Alcohol **3d** was obtained as a mixture of diastereomers according to the general procedure C, using alkenylboronate **1d** (0.22 mmol) and cyclopentadiene (0.66 mmol). A small fraction of *exo* diastereomer could be separated and characterized. Diels-Alder reaction step conditions: 24 h at 170 ºC. Overall yield: 82% (27.8 mg), *endo*/*exo* 12:88. **Alcohol 3d-X** (major compound, yellowish oil) IR (film) ν_{max} 3400, 2970, 2920, 2891, 2872, 2850, 1109, 1033, 717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.11 (dd, $J_{5,6}$= 5.7, $J_{1,6}$= 2.7 Hz, 1H, H-5), 6.06 (dd, $J_{5,6}$= 5.5, $J_{4,5}$= 3.3 Hz, 1H, H-6), 3.43 (br s, 1H, H-2), 3.33 (s, 3H, H-9), 3.22 (dd, J_{gem}= 14.4, $J_{3,8}$= 8.0 Hz, 1H, H-8), 3.19 (dd, J_{gem}= 14.4, $J_{3,8}$= 7.9 Hz, 1H, H-8), 2.78 (br s, 1H, H-4), 2.71 (br s, 1H, H-1), 1.90 (m, 1H, H-3), 1.85 (br d, $J_{7a,7b}$= 8.5 Hz, 1H, H-7b), 1.75 (br s, 1H, OH), 1.66 (dd, $J_{7a,7b}$= 8.5, $J_{2,7a}$= 1.6 Hz, 1H, H-7a). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1 (CH, C-5), 134.4 (CH, C-6), 76.2 (CH, C-2), 75.8 (CH_2, C-8), 58.8 (CH_3, C-9), 50.7 (CH, C-3), 50.5 (CH, C-1), 46.7 (CH_2, C-7), 43.1 (CH, C-4). **Alcohols 3d-X and 3d-N** (yellowish oil) IR (film) ν_{max} 3415, 3059, 2970, 2922, 2872, 2827, 1134, 1111, 1083, 1035, 985, 918, 717 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.47 (dd, $J_{5,6}$= 5.7, $J_{1,6}$= 3.3 Hz, 1H, H-5N), 6.13 (dd, $J_{5,6}$= 5.7, $J_{4,5}$= 2.9 Hz, 1H, H-6N), 6.11 (dd, $J_{5,6}$= 5.7, $J_{1,6}$= 2.7 Hz, 1H, H-5X), 6.06 (dd, $J_{5,6}$= 5.5, $J_{4,5}$= 3.3 Hz, 1H, H-6X), 4.00 (br s, 1H, H-2N), 3.56-3.49 (m, 1H, H-8N), 3.43 (br s, 1H, H-2X), 3.36 (s, 3H, H-9N), 3.40-3.33 (m, 1H, H-8N), 3.33 (s, 3H, H-9X), 3.21 (dd, J_{gem}= 17.0, $J_{3,8}$= 8.0 Hz, 1H, H-8X), 3.18 (dd, J_{gem}= 17.1, $J_{3,8}$= 7.9 Hz, 1H, H-8X), 2.93 (br s, 1H, H-1N), 2.78 (br s, 1H, H-4X), 2.71 (br s, 1H, H-1X), 2.65 (br s, 1H, H-4N), 1.9 (m, 1H, H-3X), 1.85 (br d, $J_{7a,7b}$= 8.5 Hz, 1H, H-7X), 1.76 (br s, 1H, OH-X), 1.66 (dd, $J_{7a,7b}$= 8.5, $J_{3,7a}$= 1.6 Hz, 1H, H-7X), 1.48 (m, 2H, H-7N), 1.43-1.29 (m, 1H, H-3N). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5 (CH, C-5N), 137.1 (CH, C-5X), 134.4 (CH, C-6X), 132.4 (CH, C-6N), 76.7 (CH, C-2N), 76.2 (CH, C-2X), 75.8 (CH_2, C-8X), 75.7 (CH_2, C-8N), 58.9 (CH_3, C-9N),

58.8 (CH_3, C-9X), 50.8 (CH, C-3N), 50.7 (CH, C-3X), 50.5 (CH, C-1X), 48.0 (CH, C-1N), 46.7 (CH_2, C-7X), 45.2 (CH_2, C-7N), 44.9 (CH, C-4N), 43.1 (CH, C-4X). HRMS (APCI) calcd for $C_9H_{13}O$ $(M+H-H_2O)^+$ 137.0961, found 137.0938.

3-Phenylbicyclo[2.2.1]hept-5-en-2-ol (3e). Alcohol **3e** was obtained as a mixture of diastereomers according to the general procedure C, using alkenylboronate **1e** (0.20 mmol) and cyclopentadiene (0.60 mmol). Diels-Alder reaction step conditions: TFA (5 mol %), 72 h at 80 ºC. Overall l yield: 37% (13.8 mg), *endo*/*exo* 13:87. **Alcohols 3e-X and 3e-N** (yellowish oil) IR (film) ν_{max} 3061, 3323, 2968, 2939, 2922, 1033, 746, 717, 698 cm^{-1}. ^1H NMR (300 MHz) δ 7.39-7.14 (m, 10H, ArH-X and ArH-N), 6.64 (dd, $J_{5,6}$= 5.7, $J_{4,5}$= 3.2 Hz, 1H, H-5N), 6.25 (dd, $J_{5,6}$= 5.7, $J_{1,6}$= 2.9 Hz, H-6N), 6.20 (dd, $J_{5,6}$= 5.7, $J_{5,4}$= 3.3 Hz, 1H, H-5X), 6.07 (br d, $J_{5,6}$= 5.7 Hz, 1H, H-6X), 4.42 (br s, 1H, H-2N), 4.04 (br s, 1H, H-2X), 3.02 (br s, 4H, H-3X, H-4X, H-1N and H-4N), 2.83 (br s, 1H, H-1X), 2.36 (t, $J_{2,3}$= $J_{3,4}$= 3.0 Hz, 1H, H-3N), 2.05 (br d, $J_{7a,7b}$= 8.3 Hz, 1H, H-7aX), 1.79 (br d, $J_{7a,7b}$= 8.5 Hz, 1H, H-7aN), 1.76 (br d, $J_{7a,7b}$= 8.3 Hz, 1H, H-7bX), 1.67-1.61 (m, 1H, H-7bN). ^{13}C NMR (75 MHz) δ 143.8 (C, Ar-N), 143.3 (C, Ar-X), 141.3 (CH, C-5N), 137.6 (CH, C-6X), 134.0 (CH, C-5X), 132.9 (CH, C-6N), 128.5 (2CH, Ar-N), 128.0 (2CH, Ar-X), 127.8 (2CH, Ar-X), 127.2 (2CH, Ar-N), 126.0 (2CH, Ar-X and Ar-N), 80.7 (CH, C-2N), 79.4 (CH, C-2X), 55.4 (CH, C-3X), 55.3 (CH, C-3N), 51.3 (CH, C-1X), 48.6 (CH, C-1N), 48.1 (CH, C-4N), 47.3 (CH_2, C-7X), 47.1 (CH, C-4X), 45.7 (CH_2, C-7N). HRMS (APCI) calcd for $C_{13}H_{13}$ $(M+H-H_2O)^+$ 169.1012, found 169.1041.

3-(4-Chlorophenyl)bicyclo[2.2.1]hept-5-en-2-ol (3f). Alcohol **3f** was obtained as a mixture of diastereomers according to the general procedure C, using alkenylboronate **1f** (0.17 mmol) and cyclopentadiene (0.51 mmol). Diels-Alder reaction conditions: TFA (5 mol %), 72 h at 80 ºC. Overall yield: 28% (10.5 mg), *endo*/*exo*13:87. **Alcohols 3f-X and 3f-N** (yellowish oil) IR (film) ν_{max} 3361, 3340, 2964, 2916, 2848, 1490, 1091, 1033, 1012, 798, 727 cm^{-1}. ^1H NMR (300 MHz) δ 7.31-7.19 (m, 6H, ArH-X and ArH-N), 7.14-7.09 (m, 2H, ArH-X), 6.63 (dd, 1H, $J_{5,6}$= 5.9, $J_{4,5}$= 3.3 Hz, H-5N), 6.25 (dd, 1H, $J_{5,6}$= 5.8, $J_{1,6}$= 3.0 Hz, H-6N), 6.16 (dd, 1H, $J_{5,6}$= 5.7, $J_{4,5}$= 3.3 Hz, H-5X), 6.04 (br d, 1H, $J_{5,6}$= 5.70 Hz, H-6X), 4.35 (br s, 1H, H-2N), 3.98 (br s, 1H, H-2X), 3.03 (br s, 1H, H-4*N*), 2.99 (br s, 3H, H-3X, H-4X and H-1N,), 2.83 (br s, 1H, H-1X), 2.32 (t, 1H, $J_{2,3}$= $J_{3,4}$= 3.0 Hz, H-3N), 2.04 (br d, 1H, $J_{7a,7b}$= 8.6 Hz, H-7aX), 1.76 (br d, $J_{7a,7b}$ = 8.6 Hz, 1H, H-7bX), 1.76-1.60 (m, 2H, H-7N). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8 (2C, Ar-X and Ar-N), 141.2 (CH, C-5N), 137.3 (CH, C-6X), 134.2 (CH, C-5X), 132.9 (CH, C-6N), 131.8 (C, Ar-X), 129.1 (2CH, Ar-X), 128.5 (4CH, Ar-N), 128.1 (2CH, Ar-X), 80.9 (C, C-2N), 79.5 (C, C-2X), 54.8 (CH, C-3N), 54.6 (CH, C-3X), 51.3 (CH, C-1X), 48.6 (CH, C-4N), 47.9 (CH, C-1N), 47.3 (CH_2, C-7X), 47.0 (CH, C-4X), 45.7 (CH_2, C-7N), C-8N not detected. HRMS (APCI) calcd for $C_{13}H_{12}Cl$ $(M+H-H_2O)^+$ 203.0628, found 203.0586.

3-(3-(Trifluoromethyl)phenyl)bicyclo[2.2.1]hept-5-en-2-ol (3g) Alcohol **3g** was obtained as a mixture of diastereomers according to the general procedure C, using alkenylboronate **1g** (0.27 mmol) and cyclopentadiene (0.81 mmol). Diels-Alder reaction step conditions: TFA (5 mol %), 72 h at 80 ºC. Overall yield: 97% (30.0 mg), *endo*/*exo* 9:91. **Alcohols 3g-X and 3g-N** (yellowish oil) IR (film) ν_{max} 3343, 3308, 2970, 2916, 2359, 2344, 1331, 1165, 1124, 1074, 1034, 795, 721, 669 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.71-7.31 (m, 8H, ArH-X and ArH-N), 6.65 (dd, $J_{5,6}$= 5.4, $J_{4,5}$= 3.1 Hz, 1H, H-5N), 6.27 (dd, $J_{5,6}$= 5.4, $J_{1,6}$= 2.8 Hz, 1H, H-6N), 6.20 (dd, $J_{5,6}$= 5.7, $J_{1,6}$= 3.3 Hz, 1H, H-6X), 6.05 (dd, $J_{5,6}$= 5.7, $J_{4,5}$= 2.7 Hz, 1H, H-5X), 4.39 (m, 1H, H-2N), 4.03 (br s, 1H, H-2X), 3.07 (m, 2H, H-3X and H1-N), 3.04 (br s, 2H, H-4X and H-4N), 2.85 (br s, 1H, H-1X), 2.10 (m, 1H, H-3N), 2.06 (br d, $J_{7a,7b}$= 8.8 Hz, 1H, H-7aX), 1.90 (br s 1H, OH-X), 1.82-1.76 (m, 1H, H-7bX), 1.76-1.63 (m, 2H, H-7N). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5 (C, Ar-N), 144.3 (C, Ar-X), 141.0 (CH, C-5N), 137.2 (CH, C-5X), 134.4 (CH, C-6X), 133.1 (CH, C-6N), 131.2 (CH, Ar-X), 130.3 (C, $J_{C,F}$= 32.0 Hz, Ar-X), 129.7 (CH, Ar-N), 128.9 (CH, Ar-N), 128.4 (CH, Ar-X), 126.1 (CH, Ar-N), 124.6 (CH, Ar-N), 124.5 (CH, $J_{C,F}$= 3.5 Hz, Ar-X), 122.9 (CH, $J_{C,F}$= 3.9 Hz, ArX), 122.4 (CH, Ar-N), 80.8 (CH, C-2N), 79.4 (CH, C-2X), 55.1 (CH, C-3N), 55.0 (CH, C-3X), 51.4 (CH, C-1X), 48.6 (CH, C-4N), 47.3 (CH_2, C-7X), 47.8 (CH, C-1N), 47.0 (CH, C-4X), 45.7 (CH, C-7N). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.6. HRMS (APCI) calcd for $C_{14}H_{12}F_3$ $(M+H-H_2O)^+$ 237.0886, found 237.0902. **2-Phenylbicyclo[2.2.1]hept-5-en-2-ol (3h)**. Alcohol **3h** was obtained as a mixture of diastereomers according to the general procedure C using alkenylboronate **1h** (0.17 mmol) and cyclopentadiene (0.51 mmol). A small fraction of *exo* diastereomer could be separated and characterized. Diels-Alder reaction step conditions: 12 h at 80 ºC. Overall yield: 100 % (28.8 mg), *endo/exo* 6:94. **Alcohol 3h-X** (major compound, white solid, mp 62.5-63.0 ºC) IR (KBr) ν_{max} 3364, 2986, 2970, 2945, 1493, 1447, 1274, 1061, 1028, 989, 894, 758, 721, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 -7.19 (m, 5H, ArH), 6.17 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 3.0 Hz, 1H, H-5), 5.78 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 3.1 Hz, 1H, H-6), 3.08-3.03 (m, 1H, H-1), 2.98 (br s, 1H, H-4), 2.16 (br d, $J_{7a,7b}$= 8.6 Hz, 1H, H-7b), 2.13 (dd, $J_{3n,3x}$= 12.2, $J_{3n,4}$= 2.3 Hz, 1H, H-3_n), 2.03 (dd, $J_{3n,3x}$= 12.2, $J_{3x,4}$= 3.5 Hz, 1H, H-3_x), 1.95 (br s, 1H, OH), 1.75-1.68 (m, 1H, H-7a). ^{13}C NMR (75 MHz, $CDCl_3$) δ146.6 (C, Ar), 138.9 (CH, C-5), 134.5 (CH, C-6), 128.1 (2CH, Ar), 127.0 (3CH, Ar), 82.7 (C, C-2), 54.3 (CH, C-1), 48.2 (CH_2, C-7), 43.1 (CH_2, C-3), 41.9 (CH, C-4). **Alcohols 3h-X and 3h-N** (white solid) IR (KBr) ν_{max} 3366, 2970, 2945, 1491, 1447, 1274, 1061, 1028, 989, 895, 758, 721, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.63-7.19 (m, 10H, ArH-X and ArH-N), 6.58 (dd, $J_{5,6}$= 5.7, $J_{1,6}$= 3.0 Hz, 1H, H-6N), 6.33 (dd, $J_{5,6}$= 5.7, $J_{4,5}$= 3.0 Hz, 1H, H-5N), 6.17 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 3.0 Hz, 1H, H-5X), 5.78 (dd, $J_{5,6}$= 5.6, $J_{1,6}$= 3.1 Hz, 1H, H-6X), 3.24-3.20 (m, 1H, H-4N), 3.08-3.03 (m, 1H, H-1X), 2.98 (br s, 2H, H-4X and H-1N), 2.49 (dd, $J_{3x,3n}$= 12.6, $J_{3x,4}$= 3.7 Hz, 1H, H-3xN), 2.16 (br d, $J_{7a,7b}$= 8.6 Hz, 1H, H-7bX), 2.13 (dd, $J_{3n,3x}$= 12.2, $J_{3n,4}$= 2.3 Hz, 1H, H-3_nX), 2.03 (dd, $J_{3n,3x}$= 12.2, $J_{3x,4}$= 3.5 Hz, 1H, H-3_xX), 1.95 (br s, 1H, OH-X), 1.83 (br s, 1H, OH-N), 1.75-1.68 (m, 1H, H-7aX), 1.63-1.60 (m, 2H, H-7N), 1.52-1.44 (m, 1H, H-3_nN). ^{13}C NMR (75 MHz, $CDCl_3$) δ146.6 (2C, Ar-X and Ar-8N), 141.3 (C, C-6N), 138.9 (CH, C-5X), 134.5 (CH, C-6X), 133.6 (C, C-5N), 129.2 (CH, Ar-N), 128.1 (4CH, Ar-X and Ar-N), 127.0 (3CH, Ar-X), 82.7 (C, C-2X), 54.3 (CH, C-1X), 53.2 (CH, C-4N), 49.3 (CH_2, C-7N), 48.2 (CH_2, C-7X), 44.8 (CH_2, C-3N), 43.3 (CH_2, C-1N), 43.1 (CH_2, C-3X), 41.9 (CH, C-4X). C-2N signal missing. HRMS (ESI) calcd for $C_{13}H_{14}ONa$ $(M+Na)^+$ 209.1250, found 209.0937.

2-Methyl-bicyclo[2.2.1]hept-5-en-2-ol (3i).[45-48] Alcohol **3i** was obtained as a mixture of diastereomers according to the general procedure C using alkenylboronate **1i** (0.5 mmol) and cyclopentadiene (1.5 mmol). Diels-Alder reaction step conditions: 24 h at 170 ºC. Overall yield: 66% (40.9 mg), *endo*/*exo* 9:91. **Alcohols 3i-X and 3i-N** (yellowish liquid) IR (film) ν_{max} 3381, 3061, 2956, 2924, 2868, 2852, 1446, 1330, 1251, 1109, 939, 887, 729, 705 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.42 (dd, $J_{5,6}$= 5.63, $J_{1,6}$= 3.1 Hz, 1H, H-6N), 6.19 (dd, $J_{5,6}$= 5.6, $J_{4,5}$= 3.0 Hz, 1H, H-5N), 6.12 (dd, $J_{5,6}$= 5.5, $J_{4,5}$= 2.9 Hz, 1H, H-5X), 6.06 (dd, $J_{5,6}$ = 5.5, $J_{1,6}$= 3.2 Hz, 1H, H-6X), 2.82 (br s, 2H, H-4X and H-4N), 2.65 (br s, 1H, H-1N), 2.48 (br s, 1H, H-1X), 1.92 (br d, $J_{7a,7b}$= 8.5 Hz, 1H, H-7X), 1.80 (dd, $J_{3n,3x}$= 12.2, J= 3.6 Hz, 1H, H-3_xN), 1.68 (dd, $J_{3n,3x}$= 12.1, J= 3.8 Hz, 1H, H-3_xX), 1.59-1.48 (m, 2H, H-7N), 1.56 (br d, $J_{7a,7b}$= 8.5 Hz, 1H, H-7X), 1.49 (s, 3H, H-8N), 1.28-1.21 (m, 1H, H-3_nX), 1.22 (s, 3H, H-8X), 1.16 (dd, $J_{3n,3x}$= 12.3, J=3.3 Hz, 1H, H-3_nN). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0 (CH, C-6N), 138.4 (CH, C-5X), 134.5 (CH, C-6X), 133.5 (CH, C-5N), 79.1 (C, C-2X), 78.5 (C, C-2N), 54.9 (CH, C-1X), 53.8 (CH, C-1N), 49.5 (CH_2, C-7N), 48.4 (CH_2, C-7X), 44.9 (CH_2, C-3N), 43.5 (CH_2, C-3X), 43.0 (CH, C-4N), 42.3 (CH, C-4X), 28.2 (CH_3, C-8N), 27.7 (CH_3, C-8X). HRMS (APCI) calcd for $C_8H_{13}O$ $(M+H)^+$ 125.0966, found 125.0961.

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Notes and references

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