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Imino Diels–Alder reaction of boronates. Preparation and characterization of new 3,4-dihydroquinoline and 1,2,3,6-tetrahydropyridine derivatives

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Abstract

The preparation of 3,4-dihydroquinolines (**2a**–**d** and **3a**,**b**,**d**), as well as 1,2,3,6-tetrahydropyridines (**4a**–**e**) by imino Diels–Alder reaction of boronates (**1a**–**e**) with 2,3-dimethylbutadiene is reported. Boronates (**1a**–**d**) containing substituents *meta* and *para* relative to the imino fragment lead to diastereomeric mixtures of 4-methyl-4-ethenyl-3,4-dihydroquinolines (**2**, **3**) and tetrahydropyridines (**4**). In contrast, the presence of an electron withdrawing substituent at the para position (**1e**), favors the iminodienophile behavior giving 4,5-dimethyl-1,2,3,6-tetrahydropyridine (**4e**) as the main product. The results show that boronates derived from Schiff bases are electron deficient species which can act either as dienophiles or dienes in the reaction with 2,3-dimethylbutadiene to give 3,4-dihydroquinolines and 1,2,3,6-tetrahydropyridines. All products were characterized by NMR and X-ray diffraction analysis of **2b**, **2d**, **3d** and **4c** allowed to assign the relative configuration of the newly formed stereogenic centers.

Keywords: Imino Diels–Alder; Boronates; NMR; X-ray

1. Introduction

The imino Diels–Alder (IDA) reaction [1–7] is a powerful method for the preparation of six-membered ring heterocycles containing nitrogen with high regio- and stereoselectivity, as a consequence, it has been widely studied in the last decade and applied to the synthesis of a great number of natural products and biologically interesting heterocycles [8–10].

The 1- [4] and 2-aza-1,3-butadiene [5] systems have been used in IDA [6] reactions both as dienes and dienophiles. In particular, 2-azabutadienes are useful reagents for the synthesis of quinoline derivatives, wherein the reactivity of the π-system can be controlled by appropriate substituents. Moreover, several methods have been developed to activate the system present in arylimines which include the use of Lewis [11–13] or Brönsted acids [14], lanthanides [15–17], I_2 [18] polar solvents [17,19,20], cationic species [21,22], as well as a polymer-supported scandium catalyst [23]. More recently, acid catalysis [24] and activation of the dienophile employing the nitrosonium ion (NO^+) [25] have been reported.

The aza Diels–Alder reaction of iminium salts with 2,3-dimethylbutadiene has been reported to yield tetrahydropyridines under mild conditions where the iminium salt behaves as the dienophile (Scheme 1). Grieco [26] described that these reactions can be carried out in aqueous solution under relatively mild conditions using iminium salts

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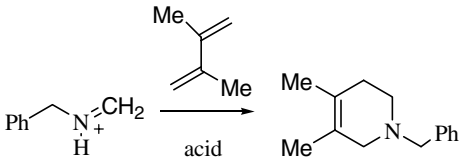


Scheme 1. Synthesis of 1,2,3,6-tetrahydropyridine.

generated *in situ* under Mannich-like conditions. In turn, Bailey [27–30] carried out a study of the reaction employing trifluoroacetic acid as the catalyst to obtain pipecolic acid derivatives with high regio- and diastereoselectivity. Stella [31] reported the diastereoselective synthesis of tetrahydropyridines using the CF_3–COOH–BF_3 complex as catalyst.

Moreover, in the reaction between arylimines (PhCH=NAr) and 2,3-dimethylbutadiene, both behaviors have been found, leading to tetrahydroquinoline derivatives when the π-system acts as 2-azabutadiene, and tetrahydropyridines when it behaves as iminodienophile (Scheme 2). For instance Kobayashi [32] reported that IDA reaction of arylimines with dienes or alkenes catalyzed by lanthanide triflates produces pyridine and quinoline derivatives when R = OMe and X = Ph. Lucchini [33] observed that changes in the substituents (R = NO_2 and X = COPh) at the arylimine and the presence of BF_3, leads to exclusive formation of the tetrahydropyridine derivative which transforms into the pyrido[1,2-α]indole upon reflux in toluene.

In previous studies it has been reported that the C=N bond in dioxaboracines is polarized by coordination of the nitrogen atom to boron through a N→B dative bond, as evidenced by formation of acetolysis products [34] (Scheme 3). Thus the coordination bond between the nitrogen and boron atoms polarizes the imine bond increasing the reactivity of dioxaborocines towards the imino-Diels Alder reaction by taking advantage of boron adducts. The results showed that boron adducts derived from Schiff bases are electron deficient species that react with sulfolene providing a new route to 3,4-dihydroquinolines [35] (Scheme 3).

Continuing our studies on the reactivity of type **1** boronates in the imino Diels–Alder reaction, we decided to study the stereochemistry and electronic effects in the reaction of a series of boron adducts (**1a**–**e**) with 2,3-dimethylbutadiene.

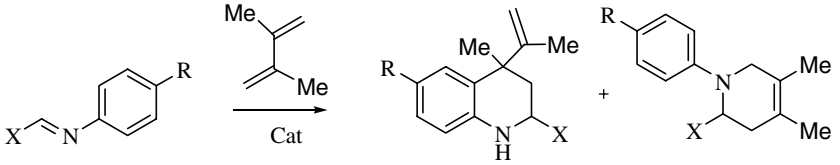
2. Results and discussion

The IDA reaction of boronates **1a**–**e** was carried out in a sealed ampule using 3 equiv. of 2,3-dimethylbutadiene and stirring 12–72 h at 120 °C in toluene under a N_2 atmosphere and in the dark. Boronates **1a**–**1d** afforded a mixture of the diastereomeric 3,4-tetrahydroquinolines **2a**–**d**, and **3a**,**b**,**d**, as well as tetrahydropyridine derivatives **4a**–**d**; in contrast, boronate **1e** gave tetrahydropyridine **4e** as the main product, along with a complex mixture of hydrolyzed products. The selectivity in the formation of **4e** can be attributed to the electronic effect due to the presence of the nitro group at the *para* position with respect to the aza-dienophile fragment (CH=N) which increases the electron deficient character and promotes a normal demand IDA reaction with 2,3-dimethylbutadiene while boronates **1a**–**d** behave as aza-butadienes in an inverse demand IDA reaction (Scheme 4).

The ^{1}H NMR analyses of the crude reaction mixture for derivatives **1a**–**1d** evidenced the formation of three different products; the ratios were determined by signal integration of H-3 as summarized in Table 1. The products were purified by column chromatography on silica gel for complete spectroscopic characterization and elemental analysis; however, they undergo extensive decomposition during purification by chromatographic procedures, as has been previously noted [24]. It is important to mention that in the reaction of boronate **1e**, the tetrahydropyridine derivative **4e** precipitates from the reaction mixture and was separated by filtration, increasing the yield of the product. The ^{1}H NMR spectra of the filtrate showed the presence of hydrolyzed products which decomposed upon purification.

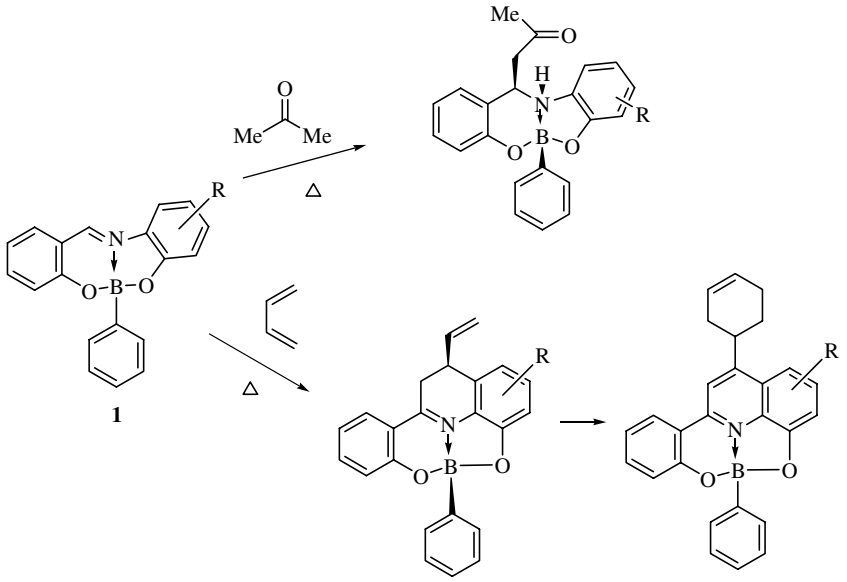
As mentioned above, the mixture of diastereomeric 3,4-dihydroquinolines (**2a**–**2d** and **3a**, **b**, **d**) is obtained owing to the azabutadiene behavior of the iminoboronates **1a**–**1d**. In the case of derivatives **1a** and **1c**, the main products are those where the allylic substituent is on the same side as the B-phenyl group (**2a** and **2c**); for **1b**, the diastereoisomer **3b** was predominant and for **1d** the same ratio of **2d** and **3d** was obtained while only traces of **3c** were obtained from **1c**.

Since it has been reported that dihydroquinolines can be formed by imino-Claisen rearrangement of tetrahydropyridine derivatives [36,37], compounds **2a**–**2d**, **3a**, **b**, **d**, and **4a**–**e** were submitted to prolonged heating, however no observable change in product ratio was detected. Thus,

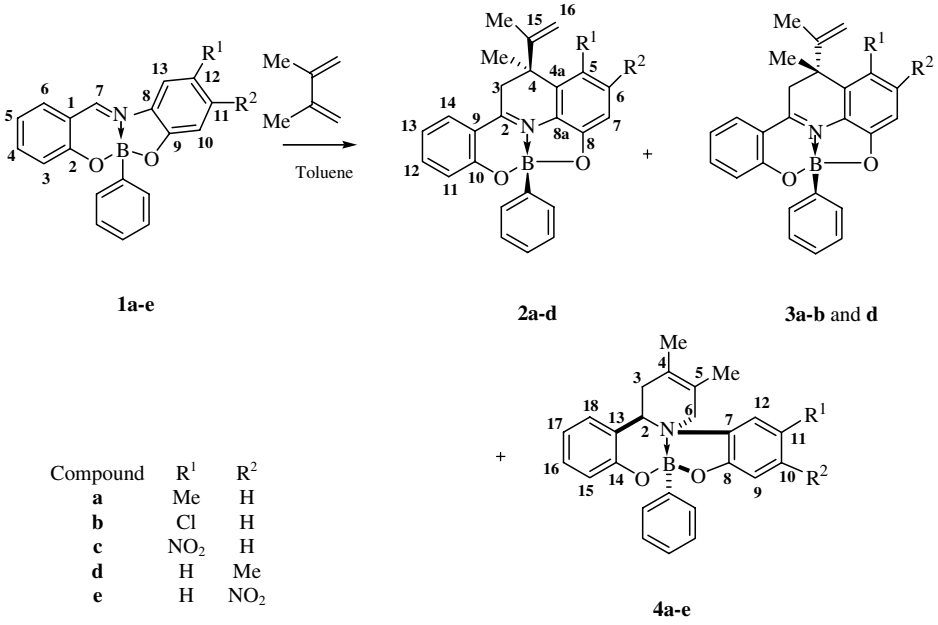


	Catalyst	Products
R=OMe, X=Ph	Lanthanide triflates	Tetrahydroquinoline and tetrahydropyridine
R=NO_2, X=COPh	BF_3	Tetrahydropyridine

Scheme 2. Products from the reaction of arylimines with 2,3-dimethylbutadiene.



Scheme 3. Products from the acetolysis and the IDA reaction of boronates.



Compound	R^1	R^2
a	Me	H
b	Cl	H
c	NO_2	H
d	H	Me
e	H	NO_2

Scheme 4. Preparation of dihydroquinolines (**2**, **3**) and tetrahydropyridine (**4**).

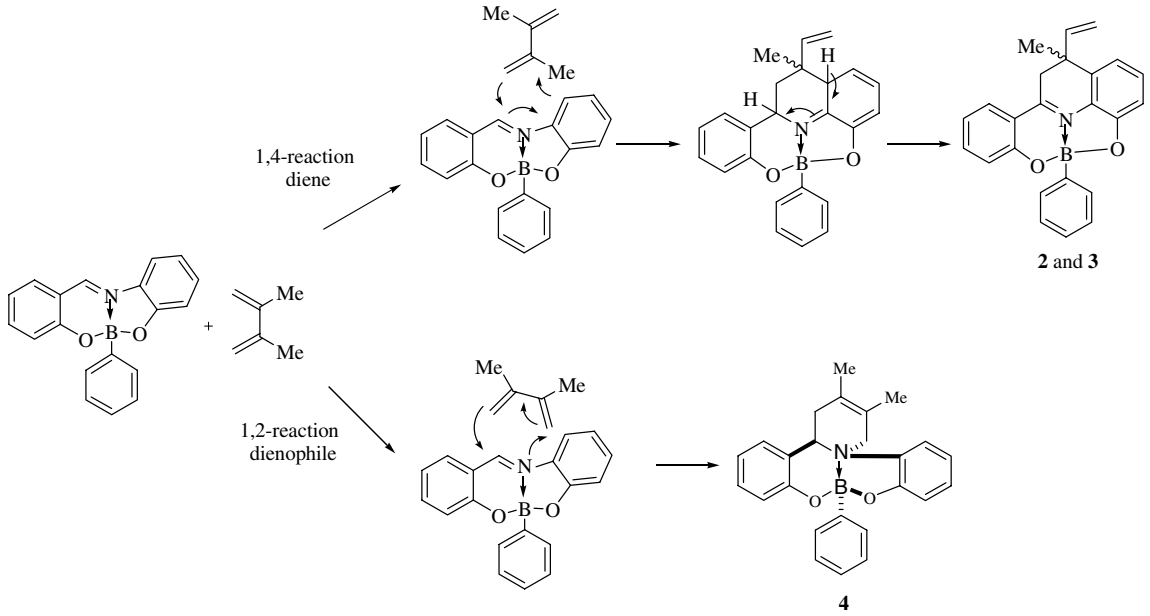
Table 1
Products from the IDA reaction of boronates **1a**–**1e**

Entry	Combined yield[a] (%)	Product ratio[b]			Time (h)
		2	**3**	**4**	
1a	75	50	30	20	12
1b	89	15	50	35	12
1c	89	73	7	20	12
1d	75	40	40	20	72
1e	57			100	12

[a] Yields were calculated based on the conversion of starting material.
[b] Ratio obtained by integration of the H-3 signal in the proton NMR spectra.

the thermal IDA reaction of boronates **1a**–**1d** with 2,3-dimethylbutadiene may be rationalized by initial cycloaddition of the 2-azabutadiene system, followed by rearomatization to give the corresponding dihydroquinolines **2** and **3** while the formation of derivates **4a**–**e** involves a normal demand IDA reaction between the butadiene system and the imino fragment (C=N) contained in the boronate which acts as dienophile, this behavior is promoted by electron-withdrawing groups, as observed for derivate **1e** which has a nitro group (Scheme 5).

It is well known that the imino Diels–Alder reaction depends on the HOMO–LUMO energy separation of the



Scheme 5. Mechanism proposed for the formation of dihydroquinolines and tetrahydropyridines.

components. In turn, the energy separation is controlled by susbtituent effects in the diene or dienophile, so that electron-withdrawing substituents lower the energy of both HOMO and LUMO, while electron-donating groups increase their energies. For the reaction of boronates **1a**–**e**, the corresponding tetrahydropyridines **4a**–**e**, are obtained as a result of the dienophile character of the imine group reacting in a normal demand IDA $HOMO_{Diene}$–$LUMO_{Dienophile}$ controlled reaction with 2,3-dimethylbutadiene. The dual behavior of the aza-π system, present in arylimines containing electron-donating groups, has been observed in reactions with different activated dienes [38], moreover the preference for a particular behavior depends on electronic effects, as reported by Kobayashi [32]. In the case of boronate **1e**, the increase in the yield of **4e** is attributed to an electron-withdrawing group at the *para* position with respect to the imine fragment moiety that increases the electron-deficient character of the aza-π system (HOMO and LUMO) and favors an imino-dienophile behavior in a normal demand IDA reaction with dimethylbutadiene (diene). In contrast the tetrahydropyridine derivative is the minor product in the case of **1a** and **1d**, which contain a methyl group at the *para* and *meta* position to the imine group and these groups favors formation of the corresponding dihydroquinoline.

Unambiguous assignment of the ^{13}C and ^{1}H spectra for all compounds was based on one and two dimensional techniques (COSY, HETCOR and HMBC). The ^{1}H NMR spectrum of the new dihydroquinolines **2a**–**d** showed the disappearance of the signal for the imine proton (8.54–8.31 ppm) present in boronates **1a**–**d**. Evidence for the formation of products **2a**–**d** is the presence of an AB system for the H-3a and H-3b diastereotopic protons and the corresponding signal for the vinyl protons. The individual assignment of H-16a (4.85–5.03 ppm) and H-16b (4.67–4.87 ppm) was based on the coupling constant values displayed by the methyl group (Me-15, $^{4}J_{trans} = 1.2$–0.7 Hz) [39] and comparison with the chemical shifts found for analogous dihydroquinolines prepared by reaction of boronates with sulfolene [35]. The distinction between the diastereomeric dihydroquinolines **2** and **3** was based on the ^{1}H NMR spectrum, since the signal for H-3 appears as an AB system in **2a**–**d** ($J_{gem} = 20.1$–19.6 Hz) with a $\Delta\delta = 1$, while the same protons exhibits very close chemical shifts in type **3** derivatives. This allowed to establish the relative configuration of the epimeric dihydroquinolines. The difference in the $\Delta\delta$ can be explained by observation of the relative disposition of the methyl and vinyl fragment, as shown in Fig. 1. For type **2** compounds, Ha is shielded by the vinyl fragment, while this fragment is located between both hydrogens in type **3**, as depicted in the Newman projections obtained from the X-ray structures of **2d** and **3d**.

The ^{1}H NMR spectra of tetrahydropyridines (**4a**–**e**) show an ABX system for H-3 and an AB system for the H-6 aliphatic protons that confirm ring formation. The assignment of the individual signals for H-3a (3.04–3.15 ppm) and H-3b (2.45–2.50 ppm) was based on observation of the coupling constant with H-2 which

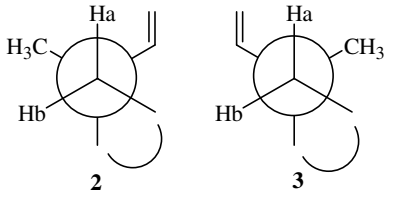


Fig. 1. Newman projections for derivates **2** and **3**.

showed values of $^{3}J_{anti} = 10.0–10.4$ Hz and $^{3}J_{gauche} = 4.2–5.9$ Hz.

The ^{13}C NMR spectra of the dihydroquinoline derivatives **2a–d** showed the presence of six new signals; two vinyl carbons, two aliphatic C-3 (38.6–42.8 ppm) and C-4 (41.6–44.1 ppm) and two methyl signals, evidencing the formation of a new heterocyclic ring; the signals for the vinyl system were observed at 146.2–147.4 ppm (C-15) and 111.7–113.6 ppm (C-16) and heterocyclic ring closure leads to a 10 ppm deshielding for the alpha carbon (C-4a, 128.1–131.2 ppm). For the diastereomeric dihydroquinolines **3a–b** and **3d**, the ^{13}C NMR shows C-3 and C-4 in the regions between 38.4–40.4 ppm and 42.7–43.5 ppm, respectively; the vinylic carbons appear in the range from 145.8 to 147.8 ppm for C-15 and 114.2–115.4 ppm for C-16, very similar to type **2** derivatives. In general, the distinction between the C-2 and C-10 signals which had very similar chemical shifts in derivates **2** and **3**, was achieved based on the HMBC (heteronuclear multiple bond correlation) spectra which showed three bond couplings between C-2 and H-3, as well as H-11 with C-10; in turn C-4a and C-8a were assigned based on the observed couplings between Me-4, H-3 with C-4a and Me-15 with the H-16 vinylic protons. The ^{11}B NMR spectra showed chemical shifts in the range from 7.5 to 7.7 ppm for derivates **2a–d** and from 7.7 to 7.9 ppm for **3a–b,d**, these shifts are characteristic for tetracoordinated boron atoms [40] and have values similar to the precursor boronates.

The ^{13}C NMR spectra of tetrahydropyridines (**4a–e**) showed the presence of two olefinic signals for C-4 and C-5 in 125.3 and 121.3 ppm, respectively, as well as the appearance of two new aliphatic carbons (C-6 and C-3) in the range from 62.0 to 61.4 ppm and 37.0 to 36.6 ppm, respectively. The signal for C-2 is shifted 90 ppm to low frequency with regard to the corresponding boronate (**1**) which is indicative of a change in the hybridization from sp^2 to sp^3. The ^{11}B NMR signals present chemical shifts between 10 and 11 ppm characteristic for tetracoordinated boron atoms [40].

The X-ray diffraction analysis of the new dihydroquinolines **2b**, **2d** and **3d** (Fig. 2) allowed to establish their structure and relative configuration. Selected bond distances, angles, torsion angles and values for the *T*etra*H*edral *C*haracter (THC) are listed in Table 2, while Table 3 summarizes crystallographic data for all compounds.

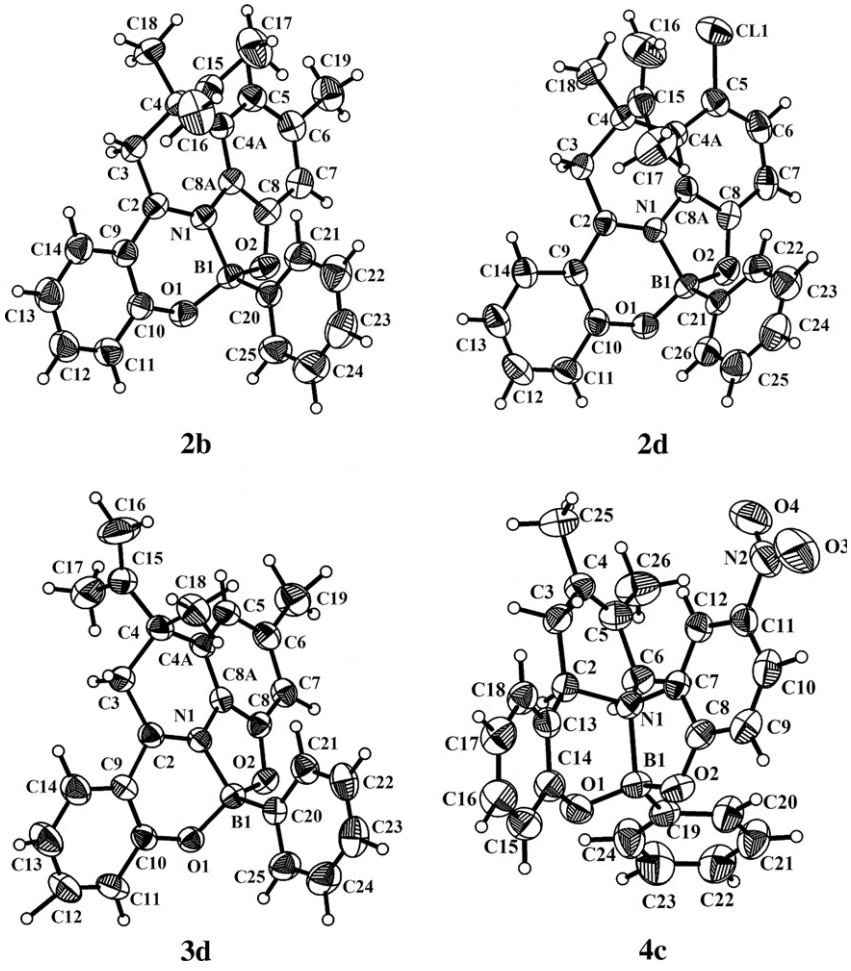


Fig. 2. Perspective view of the molecular structures for compounds **2b**, **2d**, **3d** and **4c.** Ellipsoids are shown at the 50% probability level.

Table 2
Selected bond lengths, bond angles torsion angles and THC values for **2b**, **2d**, **3d** and **4c**

Compound	**2b**	**2d**	**3d**	**4c**[a]
Bond length (Å)				
N(1)–B(1)	1.5756(18)	1.575(2)	1.570(3)	1.764(3)
N(1)–C(8a)	1.3882(17)	1.395(2)	1.390(3)	1.464(2)
N(1)–C(2)	1.2947(18)	1.292(2)	1.290(3)	1.531(2)
O(1)–B(1)	1.4655(18)	1.463(2)	1.461(3)	1.441(3)
O(1)–C(10)	1.3562(18)	1.363(2)	1.352(3)	1.375(2)
O(2)–B(1)	1.5133(18)	1.516(2)	1.511(3)	1.481(2)
O(2)–C(8)	1.3563(17)	1.361(2)	1.369(3)	1.330(2)
B(1)–C_{Ph}	1.601(2)	1.601(3)	1.613(3)	1.587(3)
Bond angles (°)				
O(1)–B(1)–N(1)	104.42(11)	104.51(14)	105.68(19)	107.79(14)
O(1)–B(1)–O(2)	113.75(11)	114.14(15)	113.13(19)	111.53(16)
O(1)–B(1)–C_{Ph}	113.19(11)	113.49(16)	112.67(19)	112.53(16)
O(2)–B(1)–N(1)	99.48(11)	98.69(14)	100.37(18)	98.81(14)
O(2)–B(1)–C_{Ph}	110.75(11)	111.50(15)	111.05(19)	113.37(16)
N(1)–B(1)–C_{Ph}	114.39(11)	113.43(15)	113.24(19)	111.91(14)
C(10)–O(1)–B(1)	115.32(10)	115.13(13)	116.99(19)	115.01(15)
B(1)–O(2)–C(8)	108.75(10)	108.23(13)	108.76(18)	112.92(14)
C(2)–N(1)–C(8a)	122.41(11)	123.42(15)	122.7(2)	112.58(13)
C(2)–N(1)–B(1)	126.82(11)	126.91(15)	126.6(2)	108.19(13)
C(2)–N(1)–C(6)	–	–	–	107.11(13)
C(8a)–N(1)–B(1)	108.34(11)	108.83(13)	107.98(19)	101.51(12)
Torsion angles (°)				
O(1)–B(1)–N(1)–C(2)	31.47(17)	33.9(2)	32.7(3)	7.95(18)
O(2)–B(1)–N(1)–C(8a)	−13.31(12)	−18.03(2)	−11.0(2)	10.51(16)
C(20)–B(1)–N(1)–C(8a)[b]	100.02(17)°	104.73(12)°	107.4(2)°	13.1(2)
C(8a)–C(4a)–C(4)–C(15)	96.14(19)°	84.98(14)°	−153.7(2)°	–
THC (%)	68	66	72	74

[a] For **4c:** C(8a) = C(7) and C(10) = C(14).
[b] For **4c:** the torsion angle is C(6)–N(1)–B(1)–C(19).

The N→B bond distance for the 3,4-dihydroquinolines **2b**, **2d** and **3d** showed values from 1.570(3) to 1.5756(18) Å, in agreement with values reported for analogous systems [35]. The angles around the boron atom have values close to a tetrahedron (Table 2). The *T*etra-*H*edral *C*haracter was evaluated using the method described by Höpfl [41] showing an average value of 68% (Table 2) which is close to the value shown by similar derivates [35] but are smaller than those observed in reported boronates [42] due to an increase in the annular tension of the dihydroquinoline ring. The angles around the O(2)–B(1)–N(1) fragment, which are part of the five membered-ring are smaller than the other angles around the boron atom. In compounds **2b** and **2d** the vinyl substituent and the phenyl group attached to the boron atom are in a *syn* disposition with a perpendicular relationship to the plane of the quinoline ring, showing torsion angle values of 100.02(17)°, 104.73(12)° and 96.14(19)°, 84.98(14)° for the C(20)–B(1)–N(1)–C(8a) and C(8a)–C(4a)–C(4)–C(15) fragments, respectively. In compound **3d**, the vinyl substituent and phenyl group have an *anti* disposition, showing torsion angle values of 107.4(2)° and −153.7(2)° for the C(20)–B(1)–N(1)–C(8a) and C(8a)–C(4a)–C(4)–C(15) fragments, respectively (Fig. 1).

The X-ray analysis of **4c** allowed to confirm the structure of the tetrahydropyridine derivative (Fig. 2), the *trans* stereochemistry for the N1 and C-2 stereogenic centers can be attributed to the dynamic behavior of the weak N→B coordination bond leading to a *trans* fusion for the two six-member rings which is more stable. Table 2 contains selected bond distances, angles, torsion angles and values for the THC of **2b**, **2d**, **3d** and **4c**, Table 3 summarizes the crystallographic data. The N→B bond length for compound **4c** is 1.764(3) Å, which is larger than those reported for type **1** boronates and 3,4-dihydroquinoline derivates **2** and **3**, but is close to those reported for the N(sp^3)→B of dioxaborocines 1.677(3) Å obtained by acetolysis [34]. The difference is attributed to the hybridization change from of the nitrogen atom from sp^2 to sp^3, as reported in the literature [43].

For **4c** the six membered-ring shows a twist-boat conformation with torsion angles of 42.5(18)° and 51.1(2)° for the C(13)–C(2)–N(1)–B(1) and C(13)–C(14)–O(1)–B(1) fragments, respectively; the same conformation was found in dioxaborocines [34] and boronates prepared by reaction of diphenylboronic acid with 2-(2-pyridyl)-ethanol [42]. The different conformation observed for the six member ring is related to the change in hybridization of the atoms in the C=N fragment (sp^2) to C–N (sp^3). The tetrahydro-

Table 3
Crystallographic data for compounds **2b**, **2d**, **3d** and **4c**

Compound[a]	**2b**	**2d**	**3d**	**4c**
Crystal data				
Formula	$C_{25}H_{21}BClNO_2$	$C_{26}H_{24}BNO_2$	$C_{26}H_{24}BNO_2$	$C_{25}H_{23}BN_2O_4$
Crystal size	$0.35 \times 0.30 \times 0.20$	$0.25 \times 0.30 \times 0.25$	$0.30 \times 0.50 \times 0.37$	$0.50 \times 0.20 \times 0.25$
FW (g/mol)	413.71	393.27	393.29	426.3
Space group	$P2_1/c$	$P\bar{1}$	$P2$	$P2_1$
Cell parameters				
a (Å)	10.8458(2)	9.171(5)	8.2626(2)	7.7229(2)
b (Å)	11.1373(2)	10.750(5)	12.9791(4)	11.8444(4)
c (Å)	16.9467(4)	11.911(5)	10.3246(3)	12.0220(5)
α (°)	90	67.669(5)	90	90
β (°)	97.8870(10)	73.709(5)	107.6220	100.8280(10)
γ (°)	90	88.089(5)	90	90
V (Å^{-3})	2027.68(7)	1039.1(9)	1055.26(5)	1080.11(2)
Z	4	2	2	2
D (g/cm^3)	1.355	1.26	1.238	1.31
Data collection[b]				
Limit of θ	4–27	3.4–27.5	3.76–27.49	3.4–27.5
Total reflections	8315	7830	4334	4798
Unique reflections	4565	4644	4334	4798
Refinement				
$R/R_w(F)$[c]	0.0457/0.1056	0.0462/0.1165	0.0506/0.1347	0.0411/0.0878
$R/R_w(F^2)$ (all data)	0.0831/0.1229	0.0618/0.1279	0.0581/0.1409	0.0589/0.0971
Goodness-of-fit	0.974	1.025	1.071	1.06
Number of variables	356	368	356	382
$\Delta\rho_{min}$ (e Å^{-3})	−0.318	−0.155	−0.162	−0.114
$\Delta\rho_{max}$ (e Å^{-3})	0.183	0.219	0.187	0.118

[a] SHELXS 1997, versión 1.8.
[b] $T = 295$ K, $\lambda_{Mo\,K\alpha} = 0.7173$ radiation.
[c] $R = \sum(\|F_o| - |F_c\|)/\sum|F_o\|$, $R_o w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

pyridine ring obtained by IDA reaction showed a half-chair conformation.

3. Conclusions

Boronates react with dimethylbutadiene both by an inverse electron demand IDA ($LUMO_{diene}$–$HOMO_{dienophile}$ controlled) reaction to produce dihydroquinolines derivates **2a–d**, **3a–b** and **3d** which is attributed to an aza-butadiene behavior, while tetrahydropyridines are obtained by normal IDA reaction where the (C=N) group acts as azadienophile. It was found that when an electron withdrawing substituent is located at the *para* position with respect to the imine group, an azadienophile behavior is favored (normal demand IDA reaction), while methyl group substituents favor an azadiene character (inverse demand IDA reaction). As far as we know this dual behavior has not been observed in butadiene reactions, nonetheless previous reports by Kobayashi [32] have shown that tetrahydroquinolines are the main products of the reaction between 2,3-dimethylbutadiene and arylimines when electrondonating groups are present at the *para* position of the nitrogen system. The reaction of the boronate **1e** containing an electron-withdrawing group *para* to the nitrogen system, with 2,3-dimethylbutadiene is diastereoselective and gives the *trans* fused tetrahydropyridines as the main product.

4. Experimental

4.1. Instruments

NMR studies were obtained on Bruker 300 Avance DPX and JEOL 270 and JEOL eclipse +400 spectrometers. Standards were $BF_3 \cdot OEt_2$(^{11}B). Chemical shifts are stated in parts per million. IR spectra were recorded on a Perkin Elmer 16F-PC FT-IR spectrophotometer. Mass spectra were determined on a HP 5989 A equipment, all experiments were obtained by electronic impact at 20 eV. Elemental analyses were realized on a Thermofinnigan Flash 1112 C, H, N, S, O instrument. Melting points were obtained on Electrothermal 9200 equipment and are uncorrected.

4.2. X-ray crystallography

X-ray diffraction studies of single crystal were realized on a KAPPA CCD diffractometer ($\lambda_{Mo\,K\alpha} = 0.71073$ Å) at room temperature (298 K) over crystals obtained by slow evaporation of hexane–ethyl acetate solutions (95:5).

Solution and refinement: direct method SHELXS-92 for structure solution and the SHELXL-97 [44] software package for refinement and data output.

4.3. Materials

Starting materials and solvents were commercially available. Compounds **1a**–**e** were obtained by the method described in the literature [34,35].

4.4. General procedure for the imino Diels–Alder reaction of boron adducts

Boron adducts **1a**–**d** (1 equiv.), 3,4-dimethylbutadiene (3 equiv.), 2 ml of toluene and traces of hydroquinone were placed in a sealed ampule and heated for 12 h at 120 °C under nitrogen atmosphere and protected from light. For compound **1d**, an excess of the diene (6 equiv.) and three days under heating were employed. The solvent was removed under vacuum and the products were purified on silica gel (70–230 mesh) using a hexane–ethyl acetate solvent mixture (95:5).

4.4.1. Phenyl[2(2′-hydroxyphenyl-O)-4α-methyl-4β-(2-propenyl)-5-methyl-8-(3,4-dihydroquinolate) O′,N]boron (**2a**)

The title compound was prepared from **1a** (1.00 g, 3.19 mmol) and 3,4-dimethylbutadiene (0.79 g, 9.58 mmol), to give **2a** with mp: 168–169 °C. IR ν_{max} (KBr) 3445, 2927, 1647 (C=N), 1611, 1459, 1264, 1187, 988, 929, 902, 756, 702 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 393 (M^+, 1), 316 ($M^+-C_6H_5$, 100), 300 (10), 286 (15), 274 (14), 260 (12), 236 (18), 77 (17). ^1H NMR (270 MHz, $CDCl_3$) δ: 7.50 (1H, t, $J = 7.5$ Hz, H-12), 7.46 (1H, d, $J = 7.6$ Hz, H-14), 7.32 (2H, dd, $J = 6.4$, 3.0 Hz, H-*o*), 7.22 (1H, d, $J = 7.5$ Hz, H-11), 7.13–7.10 (3H, m, H-*m*,*p*), 7.04 (1H, d, $J = 8.2$ Hz, H-6), 6.90 (1H, dd, $J = 7.5$, 7.6 Hz, H-13), 6.80 (1H, d, $J = 8.2$ Hz, H-7), 4.85 (1H, s, H-16a), 4.67 (1H, s, H-16b), 3.55 (1H, d, $J = 19.6$ Hz, H-3a), 2.58 (1H, d, $J = 19.6$ Hz, H-3b), 2.38 (3H, s, Me-5), 1.80 (3H, s, Me-15), 1.73 (3H, s, Me-4) ppm. ^{13}C NMR (68 MHz, $CDCl_3$) δ: 158.2 (C-2), 157.2 (C-10), 154.2 (C-8), 146.5 (C-15), 137.0 (C-12), 135.1 (C-6), 131.1 (C-*o*), 129.4 (C-5), 129.1 (C-4a), 127.5 (C-*p*), 127.3 (C-*m*), 127.1 (C-14), 126.1 (C-8a), 121.2 (C-11), 119.8 (C-13), 118.5 (C-9), 112.4 (C-16), 112.2 (C-7), 43.7 (C-4), 39.8 (C-3), 26.4 (Me-4), 21.3 (Me-5), 19.2 (Me-15) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 7.5 ppm ($h_{1/2} = 152.7$ Hz). Anal. Calc. for $C_{26}H_{24}NBO_2$: C, 79.40; H, 6.15; N, 3.56. Found: C, 79.53; H, 6.48; N, 3.48%.

4.4.2. Phenyl[2(2′-hydroxyphenyl-O)-4α-methyl-4β-(2-propenyl)-5-chloro-8-(3,4-dihydroquinolate) O′,N]boron (**2b**)

The title compound was prepared from **1b** (1.00 g, 3.09 mmol) and 3,4-dimethylbutadiene (0.76 g, 9.27 mmol) to give **2b** with mp: 217–219 °C. IR ν_{max} (KBr) 3449, 1655 (C=N), 1610, 1552, 1458, 1381, 1263, 1183, 1001, 916, 900, 759, 705 cm^{-1}. MS (70 eV) *m/z* (%) 413 (M^+, 1), 336 ($M^+-C_6H_5$, 100), 321 (13), 306 (15), 294 (18), 280 (15), 259 (7) 77 (30) ^1H NMR (270 MHz, $CDCl_3$) δ: 7.53 (1H, td, $J = 8.6$, 1.6 Hz, H-12); 7.50 (1H, dd, $J = 7.6$, 1.6 Hz, H-14), 7.30 (2H, dd, $J = 6.6$, 2.8 Hz, H-*o*), 7.22 (2H, d, $J = 8.6$ Hz, H-6, 11), 7.15–7.11 (3H, m, H-*m*, p), 6.93 (1H, td, $J = 8.6$, 7.6 Hz, H-13), 6.83 (1H, d, $J = 8.6$ Hz, H-7), 4.88 (1H, d, $J = 1.2$ Hz, H-16a), 4.72 (1H, s, H-16b), 3.63 (1H, d, $J = 19.6$ Hz, H-3a), 2.64 (1H, d, $J = 19.6$ Hz, H-3b), 1.88 (3H, d, $J = 0.6$ Hz, Me-4), 1.84 (3H, s, Me-15) ppm. ^{13}C NMR (67 MHz, $CDCl_3$) δ: 159.7 (C-2), 157.2 (C-10), 154.6 (C-8), 146.2 (C-15), 137.7 (C-12), 133.8 (C-6), 130.9 (C-*o*), 130.4 (C-8a), 128.2 (C-4a), 127.7 (C-*p*), 127.4 (C-*m*), 127.3 (C-14), 121.6 (C-5), 121.3 (C-11), 120.1 (C-13), 118.2 (C-9), 113.7 (C-7), 112.1 (C-16), 44.1 (C-4), 39.9 (C-3), 25.8 (Me-4), 19.3 (Me-15) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 7.7 ppm ($h_{1/2} = 183.5$ Hz). Anal. Calc. for $C_{25}H_{21}NBO_2Cl$: C, 72.58; H, 5.11; N, 3.38. Found: C, 72.14; H, 5.08; N, 3.29%.

4.4.3. Phenyl[2(2′-hydroxyphenyl-O)-4α-methyl-4β-(2-propenyl)-5-nitro-8(3,4-dihydroquinolate) O′,N]boron (**2c**)

The title compound was prepared from **1c** (1.00 g, 2.90 mmol) and 3,4-dimethylbutadiene (0.72 g, 8.70 mmol) to give **2c** with mp: 209–210 °C. IR ν_{max} (KBr) 2972, 1725, 1634 (C=N), 1523, 1458, 1351, 1280, 1194, 994, 921, 757 cm^{-1}. MS (70 eV) *m/z* (%) 424 (M^+, 1), 347 ($M^+-C_6H_5$, 100), 317 (7), 286 (21), 274 (28), 260 (36), 246 (19), 77 (21). ^1H NMR (270 MHz, $CDCl_3$) δ: 7.87 (1H, d, $J = 8.7$ Hz, H-6), 7.61 (1H, td, $J = 7.2$, 1.5 Hz, H-12), 7.49 (1H, dd, $J = 8.1$, 1.5 Hz, H-14), 7.37–7.34 (2H, m, H-*o*), 7.29 (1H, d, $J = 8.3$ Hz, H-11), 7.21–7.16 (3H, m, H-*m*,*p*), 6.97 (1H, td, $J = 7.2$, 1.0 Hz, H-13), 6.88 (1H, d, $J = 8.6$ Hz, H-7), 5.03 (1H, d, $J = 1.0$ Hz, H-16a), 4.87 (1H, s, H-16b), 3.38 (1H, d, $J = 20.1$ Hz, H-3a), 2.83 (1H, d, $J = 20.1$ Hz, H-3b), 1.84 (3H, s, 15-Me), 1.78 (3H, s, 4-Me) ppm. ^{13}C NMR (67 MHz, $CDCl_3$) δ: 161.1 (C-2), 159.5 (C-8), 157.5 (C-10), 147.4 (C-15), 139.7 (C-5), 138.6 (C-12), 130.9 (C-*o*), 129.4 (C-8a), 129.2 (C-6), 128.2 (C-*p*), 128.1 (C-4a), 127.9 (C-14), 127.8 (C-*m*), 121.3 (C-11), 120.6 (C-13), 117.9 (C-9), 113.6 (C-16), 111.6 (C-7), 43.0 (C-4), 42.8 (C-3), 24.4 (Me-4), 21.0 (Me-15) ppm. ^{11}B NMR (86 MHz, $CDCl_3$) δ: 7.7 ppm ($h_{1/2} = 206.4$ Hz). Anal. Calc. for $C_{25}H_{21}N_2BO_4$: C, 70.77; H, 4.98; N, 6.60. Found: C, 70.45; H, 4.99; N, 6.35%.

4.4.4. Phenyl[2(2′-hydroxyphenyl-O)-4α-methyl-4β-(2-propenyl)-6-methyl-8-(3,4-dihydroquinolate) O′,N]boron (**2d**)

The title compound was prepared from **1d** (1.00 g, 3.19 mmol) and 3,4-dimethylbutadiene (1.57 g, 19.14 mmol) to **2d** with mp: 199–201 °C. IR ν_{max} (KBr) 2956, 2920, 1640 (C=N), 1606, 1552, 1454, 1370, 1330, 1251, 1187, 1037, 992, 893, 846, 758 cm^{-1}. MS (70 eV) *m/z* (%) 393 (M^+, 1), 316 ($M^+-C_6H_5$, 100), 300 (15), 274 (14), 286 (14), 274 (13), 258 (3), 77(30). ^1H NMR (300 MHz,

$CDCl_3$) δ: 7.53 (1H, d, $J = 7.5$ Hz, H-14); 7.51 (1H, t, $J = 8.9$ Hz, H-12), 7.40–7.36 (2H, m, H-*o*), 7.24 (1H, dd, $J = 8.9$, 1.0 Hz, H-11), 7.19–7.16 (3H, m, H-*m*,*p*), 6.94 (1H, dd, $J = 7.9$, 7.5 Hz, H-13), 6.75 (1H, s, H-7), 6.67 (1H, s, H-5), 4.85 (1H, d, $J = 1.0$ Hz, H-16a), 4.72 (1H, s, H-16b), 3.70 (1H, d, $J = 19.6$ Hz, H-3a), 2.46 (1H, d, $J = 19.6$ Hz, H-3b), 2.43 (3H, s, Me-6), 1.82 (3H, d, $J = 1.0$ Hz, Me-15), 1.63 (3H, s, Me-4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.6 (C-2), 156.9 (C-10), 155.7 (C-8), 147.0 (C-15), 142.8 (C-6), 136.9 (C-12), 131.2 (C-4a), 131.1 (C-*o*), 127.6 (C-*p*), 127.5 (C-*m*), 127.1 (C-14), 127.0 (C-8a), 121.2 (C-11), 120.0 (C-13), 118.8 (C-9), 115.8 (C-5), 112.9 (C-7), 111.7 (C-16), 41.6 (C-4), 38.6 (C-3), 23.9 (Me-4), 23.0 (Me-6), 19.4 (Me-15) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 7.7 ppm ($h_{1/2} = 202.4$ Hz). Anal. Calc. for $C_{26}H_{24}NBO_2$: C, 79.40; H, 6.15; N, 3.56. Found: C, 79.27; H, 6.27; N, 3.50%.

4.4.5. Phenyl[2(2′-hydroxyphenyl-O)-4β-methyl-4α-(2-propenyl)-5-methyl-8-(3,4-dihydroquinolate) O′,N]boron (**3a**)

The compound was purified by chromatography using hexane:ethyl acetate (95:5) which yield yellow crystals. Mp: 185–186 °C. IR ν_{max} (KBr) 3441, 2927, 1648 (C=N), 1613, 1458, 1377, 1269, 1184, 989, 753 cm^{-1}. MS (70 eV) *m*/*z* (%) 393 (M^+, 1), 316 ($M^+-C_6H_5$, 100), 286 (16), 274 (14), 260 (11), 259 (9), 77 (11). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (1H, dt, $J = 7.6$, 1.5 Hz, H-12); 7.43 (1H, d, $J = 7.6$ Hz, H-14), 7.39 (2H, dd, $J = 6.2$, 2.9 Hz, H-*o*), 7.29 (1H, d, $J = 7.6$ Hz, H-11), 7.18–7.16 (3H, m, H-*m*,*p*), 7.01 (1H, d, $J = 8.2$ Hz, H-6), 6.93 (1H, t, $J = 7.6$ Hz, H-13), 6.82 (1H, d, $J = 8.2$ Hz, H-7), 5.28 (1H, s, H-16a), 5.18 (1H, s, H-16b), 2.97 (2H, s, H-3), 2.23 (3H, s, Me-5), 1.78 (3H, s, Me-15), 1.57 (3H, s, Me-4) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.3 (C-10, C-2), 154.8 (C-8), 147.8 (C-15), 137.0 (C-12), 134.8 (C-6), 131.2 (C-*o*), 128.8 (C-4a), 128.3 (C-8a), 127.7 (C-*p*), 127.5 (C-*m*), 127.2 (C-14), 125.5 (C-5), 121.2 (C-11), 119.9 (C-13), 118.8 (C-9), 114.0 (C-16), 112.0 (C-7), 43.0 (C-4), 40.0 (C-3), 25.5 (Me-4), 21.0 (Me-15), 18.5 (Me-5) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 7.7 ppm ($h_{1/2} = 193$ Hz). Anal. Calc. for $C_{26}H_{24}NBO_2$: C, 79.40; H, 6.15; N, 3.56. Found: C, 79.25; H, 6.49; N, 3.53%.

4.4.6. Phenyl[2(2′-hydroxyphenyl-O)-4β-methyl-4α-(2-propenyl)-5-chloro-8-(3,4-dihydroquinolate) O′,N]boron (**3b**)

The compound was purified by chromatography using hexane:ethyl acetate (95:5). Mp: 209–210 °C. IR ν_{max} (KBr) 2964, 1647 (C=N), 1612, 1459, 1379, 1264, 1185, 1045, 990, 923, 823, 756, 705 cm^{-1}. MS (70 eV) *m*/*z* (%) 413 (M^+, 1), 336 ($M^+-C_6H_5$, 100), 321 (14), 306 (15), 294 (20), 280 (15), 259 (8), 105 (17), 77(20). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.59 (1H, ddd, $J = 8.0$, 7.5, 1.3 Hz, H-12); 7.45 (1H, dd, $J = 7.5$, 1.3 Hz, H-14), 7.39–7.36 (2H, m, H-*o*), 7.31 (1H, d, $J = 8.0$ Hz, H-11), 7.21–7.19 (4H, m, H-6, *p*,*m*), 6.96 (1H, t, $J = 7.5$ Hz, H-13), 6.88 (1H, d, $J = 8.6$ Hz, H-7), 5.26 (1H, s, H-16a), 5.17 (1H, s, H-16b), 3.03 and 3.00 (2H, AB, $J = 1.4$ Hz, H-3), 1.82 (3H, s, Me-15), 1.65 (3H, s, Me-4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.1 (C-2), 157.8 (C-10), 155.6 (C-8), 146.8 (C-15), 138.0 (C-12), 133.6(C-6), 131.4 (C-*o*), 129.6 (C-8a), 128.6 (C-4a), 128.2 (C-*p*), 128.0 (C-*m*), 127.8 (C-14), 121.6 (C-11), 121.3 (C-5), 120.5 (C-13), 118.8 (C-9), 114.2 (C-16), 113.7 (C-7), 43.5 (C-4), 40.4 (C-3), 25.5 (Me-4), 21.4 (Me-15) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 7.9 ppm. Anal. Calc. for $C_{26}H_{21}NBO_2Cl$: C, 72.58; H, 5.11; N, 3.38. Found: C, 72.52; H, 5.14; N, 3.41%.

4.4.7. Phenyl[2(2′-hydroxyphenyl-O)-4β-methyl-4α-(2-propenyl)-6-methyl-8-(3,4-dihydroquinolate) O′,N]boron (**3d**)

The compound was purified by chromatography using hexane:ethyl acetate (95:5), mp: 247–248 °C. IR ν_{max} (KBr) 2928, 1622 (C=N), 1455, 1373, 1329, 1194, 990, 897, 752, 702 cm^{-1}. MS (70 eV) *m*/*z* (%) 393 (M^+, 1), 316 ($M^+-C_6H_5$, 100), 300 (16), 274 (15), 259 (9), 77(19). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.55 (1H, ddd, $J = 8.3$, 7.2, 1.3 Hz, H-12); 7.46–7.43 (3H, m, H-*o*, 14), 7.31 (1H, d, $J = 8.3$ Hz, H-11), 7.22–7.19 (3H, m, H-*m*,*p*), 6.94 (1H, td, $J = 7.2$, 1.0 Hz, H-13), 6.74 (1H, s, H-7), 6.40 (1H, s, H-5), 5.30 (2H, s, H-16), 3.09 (1H, d, $J = 19.9$ Hz, H-3a), 2.94 (1H, d, $J = 19.9$ Hz, H-3b), 2.38 (3H, s, Me-6), 1.80 (3H, s, Me-15), 1.54 (3H, s, Me-4) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 157.9 (C-2), 157.4 (C-10), 156.6 (C-8), 145.8 (C-15), 143.3 (C-6), 137.2 (C-12), 131.8 (C-4a), 129.5 (C-*o*), 128.0 (C-*p*), 127.9 (C-*m*), 127.5 (C-14), 126.5 (C-8a), 121.5 (C-11), 120.3 (C-13), 119.4 (C-9), 116.0 (C-5), 115.4 (C-16), 112.9 (C-7), 42.7 (C-4), 38.4 (C-3), 27.2 (Me-4), 23.2 (Me-6), 21.1 (Me-15) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 7.8 ppm ($h_{1/2} = 206.4$ Hz). Anal. Calc. for $C_{26}H_{24}NBO_2$: C, 79.40; H, 6.15; N, 3.56. Found: C, 79.53; H, 6.21; N, 3.53%.

4.4.8. Phenyl[4,5-dimethyl-1[2′-hydroxyphenyl-O-(5′-methyl)]-(1,2,3,6-tetrahydropyridinate)-O′,N-2(2″-hydroxyphenyl-O)] boron (**4a**)

The compound was purified by chromatography using hexane:ethyl acetate (95:5). Mp: 264–265 °C, IR ν_{max} (KBr): 2909, 1613 (C=C), 1504, 1281, 1210, 1022, 973, 736 cm^{-1}. MS (70 eV) *m*/*z* (%) 395 (M^+, 8), 380 (5), 318 ($M^+-C_6H_5$, 7), 290 (4), 236 (100), 171 (6), 77 (8). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (2H, dd, $J = 6.4$, 2.7 Hz, H-*o*); 7.25 (3H, dd, $J = 6.0$, 2.7 Hz, H-*m*,*p*), 7.14 (1H, ddd, $J = 8.0$, 7.3, 1.5 Hz, H-16), 7.02 (1H, d, $J = 8.0$ Hz, H-15), 6.86–6.84 (3H, m, H-10, 12, 18), 6.75 (1H, d, $J = 8.8$ Hz, H-9), 6.74 (1H, t, $J = 7.3$ Hz, H-17), 4.46 (1H, dd, $J = 10.2$, 5.7 Hz, H-2), 3.44 (1H, d, $J = 15.8$ Hz, H-6a), 3.30 (1H, d, $J = 15.7$ Hz, H-6b), 3.02 (1H, dd, $J = 17.6$, 10.2 Hz, H-3a), 2.42 (1H, dd, $J = 17.6$, 4.6 Hz, H-3b), 2.22 (3H, s, Me-11), 1.51 (3H, s, Me-4), 0.87 (3H, s, Me-5) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.9 and 155.8 (C-8, C-14), 135.2 (C-7), 133.2 (C-*o*),

130.5 (C-10), 129.8 (C-16), 128.1 (C-11), 127.9 (C-*p*), 127.1 (C-18), 126.7 (C-*m*), 126.3 (C-13), 125.0 (C-4), 121.5 (C-5), 120.2 (C-17), 120.0 (C-15), 119.2 (C-12), 113.5 (C-9), 63.2 (C-2), 61.4 (C-6), 36.7 (C-3), 21.0 (Me-11), 17.7 (Me-4), 15.3 (Me-5) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 10.5 ppm. Anal. Calc. for $C_{26}H_{26}NBO_2$: C, 78.99; H, 6.62; N, 3.54. Found: C, 78.95; H, 6.55; N, 3.41%.

4.4.9. Phenyl[4,5-dimethyl-1[2′-hydroxyphenyl-O-(5′-chloro)]-(1,2,3,6-tetrahydropyridinate)-O′,N-2(2″-hydroxyphenyl-O)] boron (**4b**)

The compound was purified by chromatography using hexane:ethyl acetate (95:5). Mp: 259–260 °C, IR ν_{max} (KBr) 3050, 2903, 1608 (C=C), 1488, 1277, 1214, 1092, 1040, 968, 736, 584. MS (70 eV) *m*/*z* (%) 415 (M^+, 19), 400 (11), 338 ($M^+-C_6H_5$, 9), 296 (4), 256 (100), 221 (6), 171 (12), 77 (13), 41 (11). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (2H, dd, $J = 6.4$, 3.1 Hz, H-*o*); 7.27–7.25 (3H, m, H-*m*,*p*), 7.17 (1H, td, $J = 7.8$, 1.5 Hz, H-16), 7.05–7.01 (3H, m, H-10, 12, 15), 6.88 (1H, dd, $J = 7.3$, 1.5 Hz, H-18), 6.79 (1H, d, $J = 8.8$ Hz, H-9), 6.78 (1H, dd, $J = 7.8$, 7.3 Hz, H-17), 4.41 (1H, dd, $J = 10.0$, 5.9 Hz, H-2), 3.42 (1H, d, $J = 16.0$ Hz, H-6a), 3.30 (1H, d, $J = 16.0$ Hz, H-6b), 3.04 (1H, dd, $J = 18.0$, 10.0 Hz, H-3a), 2.45 (1H, dd, $J = 18.0$, 5.9 Hz H-3b), 1.53 (3H, s, Me-4), 0.87 (3H, s, Me-5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9 (C-8), 155.5 (C-14), 136.3 (C-7), 133.1 (C-*o*), 130.1 (C-10), 130.0 (C-16), 128.2 (C-*p*), 127.2 (C-18), 126.8 (C-*m*), 125.9 (C-11), 125.2 (C-4), 123.0 (C-13), 121.2 (C-5), 120.7 (C-17), 120.2 (C-12), 119.5 (C-15), 114.8 (C-9), 63.6 (C-2), 61.5 (C-6), 36.6 (C-3), 17.7 (Me-4), 15.3 (Me-5) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 10.9 ppm, ($h_{1/2} = 278.3$ Hz). Anal. Calc. for $C_{25}H_{23}NBO_2Cl$: C, 72.22; H, 5.57; N, 3.37. Found: C, 72.25; H, 5.77; N, 3.34%.

4.4.10. Phenyl[4,5-dimethyl-1[2′-hydroxyphenyl-O-(5′-nitro)]-(1,2,3,6-tetrahydropyridinate)-O′,N-2(2″-hydroxyphenyl-O)]boron (**4c**)

The compound was purified by chromatography using hexane:ethyl acetate (95:5). Mp: 268–269 °C, IR ν_{max} (KBr) 3050, 2918, 2856, 2341, 1604 (C=C), 1520, 1492, 1460, 1341, 1308, 1218, 1044, 949, 738 cm^{-1}. MS (70 eV) *m*/*z* (%) 426 (M^+, 12), 411 (6), 348 ($M^+-C_6H_5$, 5), 267 (100), 221 (41), 171 (18), 91 (8), 77 (14). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (1H, s, H-12); 8.06 (1H, dd, $J = 9.2$, 2.6 Hz, H-10), 7.62 (2H, dd, $J = 6.6$, 2.9 Hz, H-*o*), 7.30–7.29 (3H, m, H-*m*,*p*), 7.18 (1H, ddd, $J = 7.8$, 7.3, 1.8 Hz, H-16), 7.04 (1H, d, $J = 7.8$ Hz, H-15), 6.90 (1H, d, $J = 9.2$ Hz, H-9), 6.88 (1H, dd, $J = 7.5$, 1.8 Hz, H-18), 6.78 (1H, td, $J = 7.4$, 7.5, 1.1 Hz, H-17), 4.51 (1H, dd, $J = 10.4$, 5.7 Hz, H-2), 3.56 (1H, d, $J = 15.8$ Hz, H-6a), 3.34 (1H, d, $J = 15.8$ Hz, H-6b), 3.09 (1H, dd, $J = 18.5$, 10.4 Hz, H-3a), 2.50 (1H, dd, $J = 18.5$, 4.2 Hz, H-3b), 1.56 (3H, s, Me-4), 0.86 (3H, s, Me-5) ppm. ^{13}C NMR (67 MHz, $CDCl_3$) δ: 163.9 (C-8), 154.9 (C-14), 139.8 (C-11), 136.0 (C-7), 133.0 (C-*o*), 130.3 (C-16), 128.5 (C-*p*), 127.3 (C-18), 127.2 (C-10), 127.0 (C-*m*), 125.9 (C-13), 125.5 (C-4), 121.3 (C-17), 121.0 (C-5), 120.5 (C-15), 116.5 (C-12), 113.6 (C-9), 64.4 (C-2), 62.0 (C-6), 36.9 (C-3), 17.7 (Me-4), 15.2 (Me-5) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 11.8 ppm ($h_{1/2} = 280$ Hz). Anal. Calc. for $C_{25}H_{23}N_2BO_4$: C, 70.44; H, 5.43; N, 6.57. Found: C, 70.57; H, 5.67; N, 6.41%.

4.4.11. Phenyl[4,5-dimethyl-1[2′-hydroxyphenyl-O-(4′-methyl)]-(1,2,3,6-tetrahydropyridinate)-O′,N-2(2″-hydroxyphenyl-O)]boron (**4d**)

The compound was purified by chromatography using hexane:ethyl acetate (95:5). Mp: 248–249 °C, IR ν_{max} (KBr) 3046, 2910, 1607 (C=C), 1495, 1443, 1294, 1213, 1016, 968, 734, 708, 602 cm^{-1}. MS (70 eV) *m*/*z* (%) 395 (M^+, 4), 380 (3), 318 ($M^+-C_6H_5$, 5), 236 (100), 209 (11), 171 (7), 91 (5), 77 (9). ^{1}H NMR (270 MHz, $CDCl_3$) δ: 7.64–7.60 (2H, m, H-*o*); 7.24–7.21 (3H, m, H-*m*,*p*), 7.13 (1H, td, $J = 7.4$, 1.7 Hz, H-16), 7.10 (1H, d, $J = 7.4$ Hz, H-15), 6.90 (1H, d, $J = 8.0$ Hz, H-12), 6.83 (1H, dd, $J = 7.4$, 1.7 Hz H-18), 6.72 (1H, td, $J = 7.4$, 1.2 Hz, H-17), 6.66 (1H, s, H-9), 6.49 (1H, d, $J = 8.0$ Hz, H-11), 4.42 (1H, dd, $J = 9.9$, 5.7 Hz, H-2), 3.39 (1H, d, $J = 16.3$ Hz, H-6a), 3.26 (1H, d, $J = 15.8$ Hz, H-6b), 3.05–2.95 (1H, m, H-3a), 2.45–2.36 (1H, m, H-3b), 2.19 (3H, s, Me-10), 1.50 (3H, s, Me-4), 0.86 (3H, s, Me-5) ppm. ^{13}C NMR (67 MHz, $CDCl_3$) δ: 158.1 (C-8), 155.9 (C-14), 140.2 (C-10), 133.1 (C-*o*), 133.0 (C-7), 129.7 (C-16), 127.8 (C-*p*), 127.0 (C-18), 126.7 (C-*m*), 126.4 (C-13), 125.0 (C-4), 121.5 (C-5), 120.2 (C-17), 120.0 (C-15), 119.5 (C-11), 118.4 (C-12), 114.4 (C-9), 63.3 (C-2), 61.4 (C-6), 36.6 (C-3), 21.6 (Me-10), 17.6 (Me-4), 12.2 (Me-5) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 10.7 ppm ($h_{1/2} = 261.8$ Hz). Anal. Calc. for $C_{26}H_{26}NBO_2$: C, 78.98; H, 6.58; N, 3.54. Found: C, 78.96; H, 6.30; N, 3.64%.

4.4.12. Phenyl[4,5-dimethyl-1[2′-hydroxyphenyl-O-(4′-nitro)]-(1,2,3,6-tetrahydropyridinate)-O′,N-2(2″-hydroxyphenyl-O)]boron (**4e**)

The title compound was prepared from **1e** (1.00 g, 2.90 mmol) and 3,4-dimethylbutadiene (0.79 g, 9.58 mmol), to give **4e** as a yellow solid with mp: 274–275 °C, IR ν_{max} (KBr) 3048, 2909, 1607 (C=C), 1532, 1487, 1346, 1215, 967, 738. MS (70 eV) *m*/*z* (%) 426 (M^+, 17), 411 (8), 348 ($M^+-C_6H_5$, 6), 267 (100), 221 (37), 171 (15), 128 (7), 91 (5), 77 (11). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68–7.64 (4H, m, H-*o*, 11, 9); 7.32–7.30 (3H, m, H-*m*,*p*), 7.22 (1H, d, $J = 8.6$ Hz, H-12), 7.19 (1H, td, $J = 7.4$, 1.7 Hz, H-16), 7.06 (1H, d, $J = 7.4$ Hz, H-15), 6.85 (1H, dd, $J = 6.6$, 1.5 Hz, H-18), 6.78 (1H, ddd, $J = 7.4$, 6.5, 1.0 Hz, H-17), 4.51 (1H, dd, $J = 10.2$, 5.9 Hz, H-2), 3.50 (1H, d, $J = 16.0$ Hz, H-6a), 3.35 (1H, d, $J = 16.0$ Hz, H-6b), 3.15–3.06 (1H, m, H-3a), 2.51–2.47 (1H, m, H-3b), 1.56 (3H, s, Me-4), 0.89 (3H, s, Me-5) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3 (C-8), 155.6 (C-14), 149.3 (C-10), 141.6 (C-7), 133.4 (C-*o*), 130.7 (C-16), 128.8 (C-*p*), 127.4 (C-18), 127.3 (C-*m*), 126.0 (C-13), 125.8 (C-4), 121.5 (C-17), 121.3 (C-5), 120.8 (C-15), 119.9 (C-12),

114.6 (C-11), 109.5 (C-9), 64.3 (C-2), 61.8 (C-6), 37.0 (C-3), 18.1 (Me-4), 15.6 (Me-5) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 11.65 ppm, ($h_{1/2} = 256$ Hz). Anal. Calc. for $C_{25}H_{23}N_2BO_4$: C, 70.44; H, 5.43; N, 6.57. Found: C, 70.14; H, 5.42; N, 6.57%.

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Appendix A. Supplementary material

CCDC numbers 625106, 625107, 625108 and 625109 contain the supplementary crystallographic data for **2b**, **2d**, **3d** and **4c**. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.02.012.

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