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Imino Diels–Alder reaction of boronates: A new route to 3,4-dihydroquinolines

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Abstract

The synthesis of a series of 3,4-dihydroquinolines (**3b–e**, **3h** and **3i)** by Imino Diels–Alder reactions involving sulfolene and boronates **2a–j** derived from Schiff bases is described. The reactions are regioselective leading to 4-substituted dihydroquinolines with a *cis* relative stereochemistry between the phenyl group on the boron atom and the vinyl substituent at position 4, as established by X-ray diffraction analyses of **3b**, **3e**, **3h** and **3i**.

Boronates **2** containing substituents *meta* to the imino fragment lead to 4-ethenyl-dihydroquinolines while *para* substituted derivatives are more reactive and lead to 4-cyclohexenylquinolines **4** formed by a second Diels–Alder reaction with excess of butadiene. The results show that boronates derived from Schiff bases are electron deficient species that react with sulfolene providing a new route to 3,4-dihydroquinolines. Moreover, polarization of the imine bond activates these system toward cycloaddition.

Keywords: Dihydroquinoline; Quinoline; Boronate; X-ray; NMR; Imino–Diels–Alder

1. Introduction

Hetero Diels–Alder reactions constitute a powerful method for the preparation of biologically interesting heterocycles [1]. For instance, the Imino Diels–Alder reaction (IDA) provides a rapid means for the construction of functionalized rings containing nitrogen. In recent years the potential of this reaction has been explored and increasing efforts have been directed to activate imine systems toward cycloaddition by increasing its electron-deficient character.

Concerning the reaction of arylimines with activated dienophiles, the use of Lewis acid catalysts such as $InCl_3$ [2], $SmI_2(THF)_2$ [3], BF_3–Et_2O or $Yb(OTf)_3$ [4,5] provides access to tetrahydroquinolines. Similarly, acids like HBF_4, CF_3CO_2H and TsOH [6] have been employed for the reaction with Danishefsky's diene whereby the first one provides the best results. In other cases, the use of Lewis acids has been combined with the presence of electron withdrawing substituents in the imine fragment providing a substantial increase in the yield of quinolines [4]. More recently, the use of polar solvents such as fluorinated alcohols has been reported for the preparation of tetrahydroquinolines [7].

A main drawback in the catalyzed IDA reaction is that although the reaction is promoted by Lewis acids, more than stoichiometric amounts are required. Moreover, the acids may be trapped by the nitrogen atoms present in the reactants or products which, in some cases, are sensitive to acid conditions [8].

It has been reported that arylimines can act as iminodienophile as well as azabutadiene systems, for this

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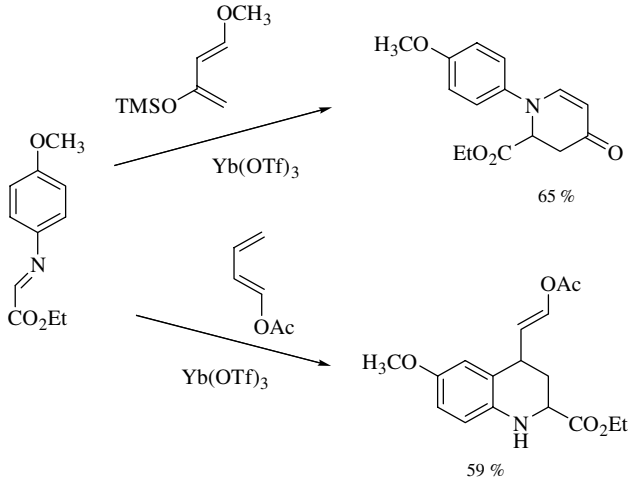
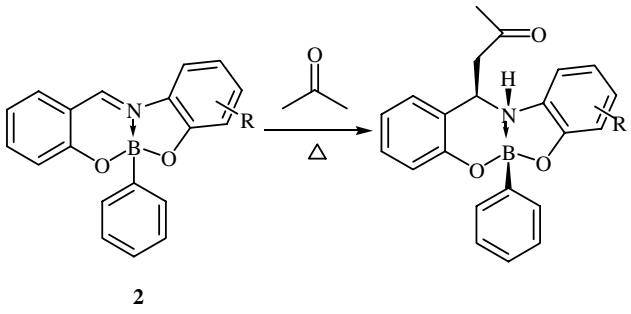
reason, they can undergo intramolecular Diels–Alder reactions [9]. Lucchini [10] described the reaction of β-ketoarylimines with 1,3-butadiene under BF_3 catalysis showing that, in this case, the imine behaves both, as imino-dienophile and azabutadiene, thus leading to two types of derivatives: tetrahydroquinolines and tetrahydropyridines. Hermitage [11] reported that these arylimines react readily as dienophiles with a wide range of activated dienes, and as dienes with a range of deactivated dienophiles, employing $Yb(OTf)_3$, as the Lewis acid (Scheme 1). The same author reported that, under Lewis-acid catalyzed conditions, this reaction proceeds by a non-concerted mechanism [12]. There are also a few reports on the use of cationic aza Diels–Alder reactions for the preparation of tetrahydroquinolines from arylimines and α-methylstyrene in the presence of tris(4-bromophenylaminium)hexachloroantimonate [13].

Owing to their electron-deficient character, simple aza-dienes are less reactive toward common electron deficient dienophiles. The basic concept of activation in an IDA reaction is to utilize the lone pair of electrons of the nitrogen atom in the coordination with the Lewis acid. This coordination changes the FMO's (frontier molecular orbitals) of the imino-dienophile and the energy difference between the $HOMO_{diene}$ and the $LUMO_{iminodienophile}$ is thus reduced [1b]. As a consequence, these molecules tend to undergo inverse electron demand Diels–Alder reactions.

Continuing our studies on the reactivity of boronate derivatives, we decided to explore the IDA reaction of a series of boron adducts (**2a**–**j**). In previous studies it had been reported that the C=N bond in these adducts is polarized by coordination of nitrogen to the boron atom through a N → B dative bond, as evidenced by formation of acetolysis products [14] (Scheme 2). Thus the aim of this study is to investigate alternatives that would increase the reactivity of arylimines towards the IDA taking advantage of boron adducts. The results show that boron adducts derived from Schiff bases are electron deficient species that react with sulfolene providing a new route to 3,4-dihydroquinolines.



Scheme 1. Products from the reaction of an arylimine with two dienes.



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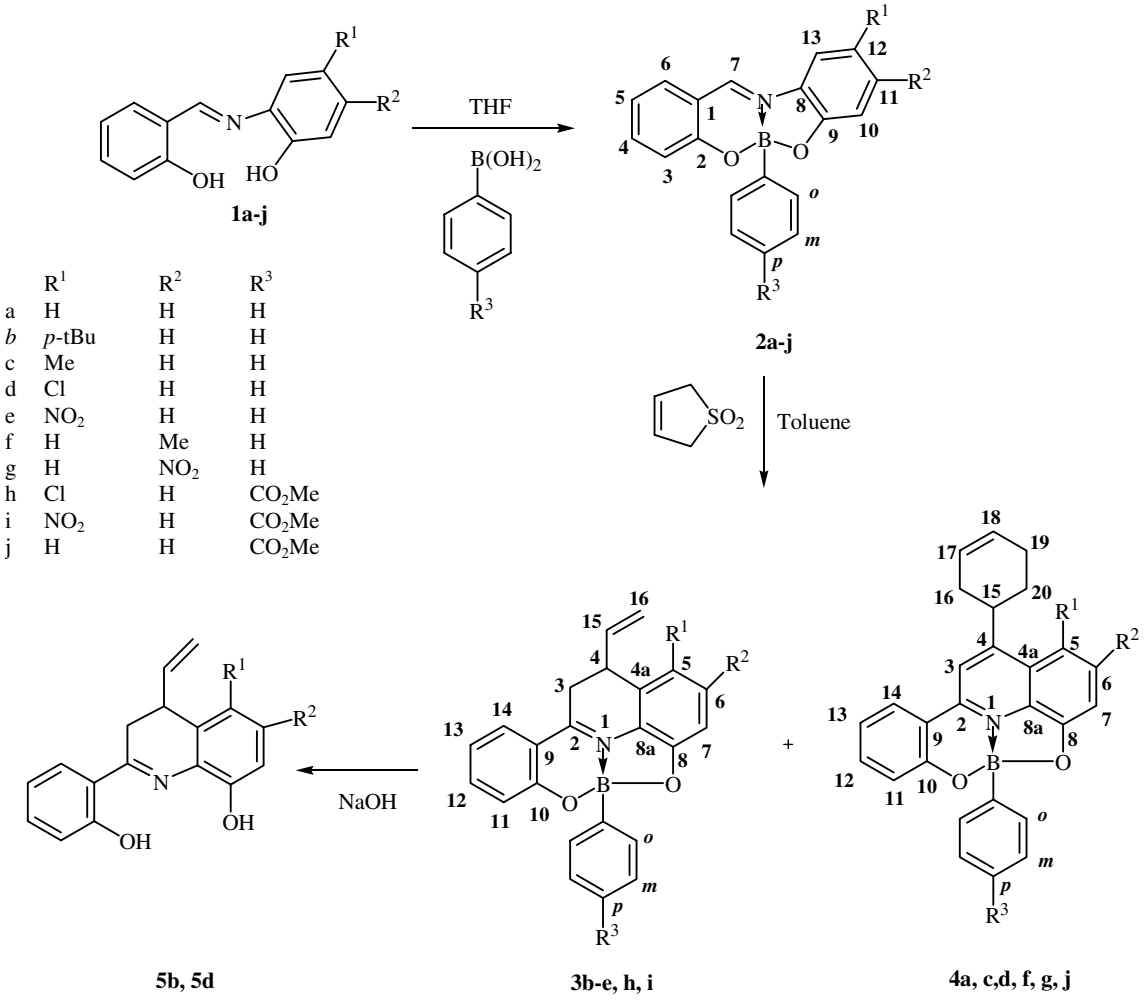
Scheme 2. Acetolysis of type **2** boronates to give dioxaborocines.

2. Results and discussion

Boronates (**2a**–**j**) were prepared according to the procedure reported in the literature by reaction of Schiff bases (**1a**–**j**) with the corresponding phenylboronic acid under reflux of THF. Compounds **2b**, **2g**, **2h** and **2i** are new and were characterized by spectroscopic techniques; the remaining derivatives (**2a**, **2c**, **2d**, **2e**, **2f** and **2j**) have been previously described in the literature [14] (Scheme 3).

In a first approximation, the formation of type **2** products was established by the observation of the C=N stretching band in the IR spectra. For example, boronates **2b** and **2g** show bands in 1663 and 1626 cm^{-1}, which are shifted to higher wavenumber compared to the ligands (1629 and 1621 cm^{-1}), owing to the formation of the N–B coordinative bond. As additional evidence, the ^1H NMR data show that the signal corresponding to the azomethine group is shifted to lower frequency in the boronate compared to the free ligands ($\Delta\delta = 0.34$ in **2b** and 0.47 ppm in **2g**). The same effect is observed in the ^{13}C NMR spectra which show that, upon complexation, the signals for C-7 are shifted upfield (147.8 (**2b**) and 152.7 ppm (**2g**)) compared to the signals in the corresponding ligands which appear at 163.8 and 164.9 ppm, respectively. The small differences between **2b** and **2g**, are attributed to the substituents at the aminophenol moiety, and are in agreement with the shifts expected based on substituent chemical shift effects (SCS) and the data previously reported for **2c**, **2d** and **2e** [14]. The ^{11}B NMR chemical shifts are in the range between 7.9 and 8.7 ppm characteristic for tetracoordinated species [15]. In general, the mass spectra of boronates (**2b**, **2g**–**i**) show the peak for the molecular ion and the base peak corresponds to loss of the arylboronic fragment.



	R^1	R^2	R^3
a	H	H	H
b	*p*-tBu	H	H
c	Me	H	H
d	Cl	H	H
e	NO_2	H	H
f	H	Me	H
g	H	NO_2	H
h	Cl	H	CO_2Me
i	NO_2	H	CO_2Me
j	H	H	CO_2Me

Scheme 3. Synthesis of 2,3-dihydroquinolines **3** and quinolines **4** from boron adducts (**2**).

The X-ray diffraction analysis of **2b** confirmed the heterocyclic structure (Fig. 1). Selected bond distances and angles, torsion angles and TetraHedral Character (THC) are listed in Table 1, while Table 2 summarizes the crystallographic data. The distance for the N → B dative bond is 1.569 (13) Å being smaller than that reported for boronate **2a** and similar to **2d** [14]. The bond distances for this type of compounds are in the range from 1.586(2) to 1.681(5) Å [14,16] and [17].

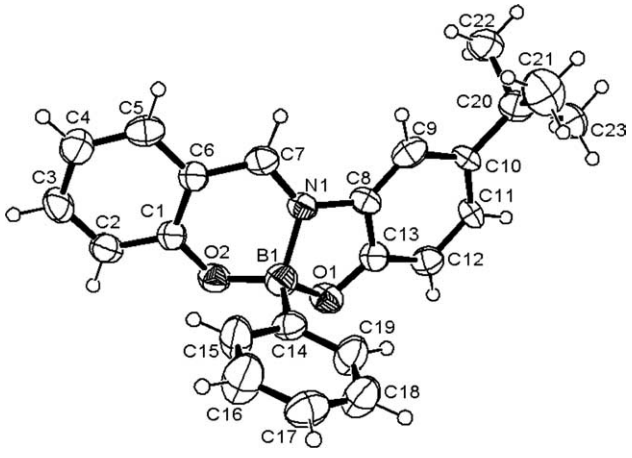


Fig. 1. Perspective view for the molecular structure of boronate **2b.** Ellipsoids are shown at the 50% probability level.

The IDA reaction of boronates **2a**–**j** was carried out in a sealed ampule using 6 equivalents of sulfolene, toluene as solvent and stirring 12–22 h at 120 °C under N_2 atmosphere in the dark. Boronates **2b**, **2e**, **2h** and **2i** afforded the 3,4-dihydroquinolines **3b**, **3e**, **3h** and **3i**; compounds **2c** and **2d** afforded a mixture of the corresponding dihydroquinolines **3c**–**d** and traces of quinolines **4c** and **4d** while boronates **2a**, **2f**, **2g** and **2j** yielded the 4-substituted quinolines **4a**, **4f**, **4g** and **4j** (Scheme 3) in low yields.

It is important to mention that NMR analyses of the crude reaction mixture showed that the products are formed in good yields; however, the presence of an allylic system, as well as the boronate moiety lead to extensive decomposition upon purification by chromatographic

Table 1
Selected bond lengths, bond angles, torsion angles and THC value for **2b**, **3b, 3e**, **3h**, **3i**, **4c** and **4d**

Compound	**2b**[a]	**3b**	**3e**	**3h**	**3i**	**4c**	**4d**
Bond lengths (Å)							
N(1)–B(1)	1.569(13)	1.577(5)	1.566(4)	1.575(3)	1.576(3)	1.578(5)	1.590(3)
N(1)–C(8a)	1.411(8)	1.382(5)	1.391(4)	1.391(3)	1.392(3)	1.359(4)	1.387(2)
N(1)–C(2)	1.292(6)	1.298(5)	1.298(3)	1.308(3)	1.297(3)	1.321(4)	1.367(2)
O(1)–B(1)	1.496(6)	1.475(5)	1.463(4)	1.466(3)	1.462(3)	1.472(5)	1.470(3)
O(1)–C(10)	1.364(5)	1.353(5)	1.363(4)	1.345(3)	1.362(3)	1.361(4)	1.433(3)
O(2)–B(1)	1.496(6)	1.479(6)	1.530(4)	1.516(3)	1.508(3)	1.509(5)	1.608(3)
O(2)–C(8)	1.333(7)	1.365(5)	1.349(3)	1.347(3)	1.354(2)	1.358(4)	1.356(3)
B(1)–C_{Ph}	1.595(7)	1.590(6)	1.593(5)	1.603(4)	1.608(3)	1.596(5)	1.620(3)
Bond angles (°)							
O(1)–B(1)–N(1)	106.6(5)	104.9(3)	105.6(2)	106.2(2)	106.02(17)	103.2(3)	103.11(16)
O(1)–B(1)–O(2)	110.5(6)	113.6(4)	113.5(2)	113.0(3)	113.96(18)	115.1(3)	113.79(17)
O(1)–B(1)–C_{Ph}	113.3(7)	113.5(4)	113.9(3)	112.8(2)	113.13(18)	112.3(3)	112.32(17)
O(2)–B(1)–N(1)	100.3(7)	100.0(4)	98.4(2)	99.03(19)	99.53(16)	98.3(3)	100.15(15)
O(2)–B(1)–C_{Ph}	112.3(4)	113.0(4)	109.9(2)	111.3(2)	110.96(17)	110.2(3)	112.22(17)
N(1)–B(1)–C_{Ph}	112.8(7)	110.7(3)	114.5(3)	113.7(2)	112.37(18)	116.9(3)	114.38(17)
C(10)–O(1)–B(1)	115.9(4)	117.3(3)	115.2(2)	119.42(19)	117.26(17)	115.9(3)	115.28(15)
B(1)–O(2)–C(8)	107.4(6)	109.8(3)	108.0(2)	109.69(18)	108.85(15)	108.7(3)	108.32 (15)
C(2)–N(1)–C(8a)	129.5(6)	122.9(3)	122.6(3)	122.2(2)	122.96(18)	122.0(3)	124.21(15)
C(2)–N(1)–B(1)	122.9(7)	126.1(4)	127.1(2)	126.3(2)	126.99(18)	127.2(3)	127.47(16)
C(8a)–N(1)–B(1)	107.0(5)	108.3(3)	108.7(2)	108.50(19)	107.75(15)	109.8(3)	107.21(16)
Torsion angles (°)							
O(1)–B(1)–N(1)–C(2)	36.3(7)	31.7(6)	30.5(3)	28.1(3)	29.4(3)	−35.7(5)	−37.3(3)
O(2)–B(1)–N(1)–C(8a)	−20.5(7)	−12.3(4)	−17.8(3)	−13.2(2)	−15.1(2)	14.7(4)	13.4(2)
C(4a)–C(4)–C(15)C(16)		0.5(7)	−1.5(6)	124.5(4)	−128.8(4)	−91.7(5)	−83.7(3)
N(1)–C(8a)–C(8)–O(2)	−2.3(6)	−3.7(5)	−1.9(3)	−1.7(2)	−41(3)	−3.4(4)	−2.6(3)
THC (%)	74.4	70.1	68.0	70.5	71.3	62.2	66.16

[a] For compound **2b** the numbering scheme is different: C(2) = C(7), C(8a) = C(8), C(8) = C(13), C(10) = C(1), O(1) = O(2), O(2) = O(1).

procedures, this has been observed previously in the literature [4]. Nonetheless, for type **3** derivatives the yields were improved by extraction with a saturated NH_4Cl solution and successive washings with hexane.

Formation of 4-cyclohexenyl substituted quinolines **4** can be explained by a second Diels–Alder reaction of the vinylic substituent in type 3 compounds with excess of butadiene present in the reaction medium under pressure, since butadiene is not an active diene and therefore requires strong reaction conditions [18], even when the second IDA reaction is followed by aromatization.

The results show that boronates substituted at position 11 (R^2) favor formation of quinolines (**4**), while substituents *meta* to the imino fragment (R^1) lead to dihydroquinolines as the major products.

The ^1H NMR spectra of 3,4-dihydroquinolines **3b**–**e**, **3h**, **3i** show the disappearance of the signal for the imine proton (H-7). Evidence for the formation of the IDA adduct was obtained from the ABX systems assigned to the allylic system (H-16a, H-16b and H-15), and the AMX system from the aliphatic protons (H-3a, H-3b and H-4). Individual assignment of the vinylic H-16a (5.09–5.19 ppm) and H-16b (4.99–5.14 ppm) signals was performed based on coupling constants with H-15 ($^3J_{cis}$ = 10 Hz, $^3J_{trans}$ = 17 Hz), H-4 (^4J = 1.3 Hz), and comparison with values reported in the literature [19]. The same procedure was used for the assignment of the aliphatic protons: H-3a ($^2J_{gauche}$ = 1.2 Hz) and H-3b ($^2J_{anti}$ = 7.4 ppm) based on observed couplings with H-4 [19].

Unambiguous assignment of the ^{13}C and ^1H spectra for all compounds was based on one and two dimensional techniques (COSY, HETCOR and HMBC). The ^{13}C NMR spectra of 3,4-dihydroquinoline derivatives (**3b**–**3e**, **3h** and **3i**) showed the presence of two new aliphatic signals corresponding to C-3 and C-4, in the range between 31.8 and 36.4 ppm, as well as vinylic carbons in the range from 135.2 to 137.9 (C-15) and 116.0 to 117.3 (C-16). The signal corresponding to C-4a appears in the range from 123.8 to 124.7 ppm which was shifted 10 ppm upfield with regard to the corresponding signal (C-13) in the boronate. Also the signal ascribed to C-5 in 3,4-dihydroquinolines was shifted around 17 ppm upfield with regard to the boronate (C-12). The ^{11}B NMR spectra of 3,4-dihydroquinolines showed signals between 7.8 and 8.6 ppm, characteristic for tetracoordinated boron atoms [15].

The X-ray diffraction analysis of **3b**, **3e**, **3h** and **3i** (Fig. 2) established the structure for the 3,4-dihydroquinolines derivatives. Selected bond distances, angles,

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

Compound[a]	**2b**	**3b**	**3e**	**3h**	**3i**	**4c**	**4d**
Crystal data							
Formula	$C_{23}H_{22}BNO_2$	$C_{27}H_{26}BNO_2$	$C_{23}H_{17}BN_2O_4$	$C_{25}H_{19}BNClO_3$	$C_{50}H_{38}B_2N_4O_{10}$	$C_{28}H_{24}BN\ O_2$	$C_{27}H_{21}BNClO_2$
Crystal size	$0.24\times0.24\times0.18$	$0.24\times0.24\times0.18$	$0.2\times0.2\times0.3$	$0.25\times0.25\times0.3$	$0.4\times0.4\times0.5$	$0.4\times0.4\times0.3$	$0.15\times0.35\times0.45$
FW (g/mol)	355.23	407.3	396.20	427.70	876.46	417.29	437.71
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Cell parameters							
a (Å)	8.219(5)	8.8579(8)	10.922(2)	12.4738(3)	12.350(5)	12.447(3)	12.4926(2)
b (Å)	17.731(5)	19.661(3)	13.491(2)	13.7940(4)	12.596(5)	14.893(2)	14.9250(3)
c (Å)	12.880(5)	12.5186(10)	12.901(3)	12.6889(4)	13.987(5)	13.056(3)	13.9250(3)
α (°C)	90.0	90.0	90.0	90.0	83.080 (5)	90.0	90.0
β (°C)	92.335 (5)	93.459(7)	90.929 (16)	93.4600 (10)	89.246 (5)	93.459(7)	117.2410(10)
γ (°C)	90.0	90.0	90.0	90.0	84.590 (5)	90.0	90.0
V (Å^{-3})	1875.5 (15)	2176.2 (5)	1900.6 (6)	2179.32 (11)	2150.4 (14)	2147.6 (7)	2308.38 (8)
Z	4	4	4	4	2	4	4
δ_{calcd} (g/cm^3)	1.258	1.243	1.385	1.304	1.354	1.291	1.259
Data collection[b]							
Limit of θ	2–26	2–26	2–27	3–28	3–28	2–26	2–27
Total reflections	3934	4541	4047	9094	16085	4547	9161
Unique reflections	2002	4261	3844	4920	9562	4356	4922
Refinement							
R/R_w (F)[c]	0.041/0.221	0.044/0.274	0.054/0.179	0.052/0.103	0.060/0.129	0.0564/0.2251	0.0520/0.0821
R/R_w (F^2) (all data)	0.065/0.102	0.102/0.172	0.120/0.166	0.129/0.155	0.152/0.190	0.1230/0.1756	0.1220/0.1403
Goodness-of-Fit	1.05	0.92	0.98	1.02	1.02	0.907	1.022
Number of variables	234	384	328	357	736	386	374
$\Delta\rho_{min}$ (e Å^{-3})	−0.10	−0.20	−0.31	−0.26	−0.42	−0.198	−0.359
$\Delta\rho_{max}$ (e Å^{-3})	0.10	0.17	0.56	0.26	0.40	0.229	0.304

[a] SHELXS-1993, versión 1.8.
[b] T = 295 K, $\lambda_{Mo\ K\alpha}$ = 0.71073 radiation.
[c] $R = \sum(\|F_o\|F_c\|)/\sum|F_o|, R_o w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

torsion angles and values for the THC are listed in Table 1, while Table 2 summarizes crystallographic data for all compounds. The distance for the N → B bond in 3,4-dihydroquinolines **3b**, **3e**, **3h** and **3i** showed values from 1.566(4) to 1.577(5) Å, in agreement with values reported for boronates [14]. The angles around the boron atom have values close to a tetrahedron (Table 2). The THC character was evaluated using the method described by Höpfl [17] showing an average value of 70% (Table 1) which is smaller than that observed in previously reported boronates [14] 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-rings, are smaller that other angles around the boron atom. The vinyl substituent and the phenyl group attached to boron are *cis*, and in turn these groups are perpendicular to the plane of the quinoline ring (Fig. 2). This allows to conclude that the IDA reaction on boron adducts provides the *endo* product.

As mentioned above, in the case of boronates **2a**, **2c**, **2d**, **2f**, **2g**, and **2j**, excess of sulfolene led to formation of quinolines **4a**, **4c**, **4d**, **4f**, **4g** and **4j**, which are obtained by a second Diels–Alder reaction with butadiene.

The ^{1}H NMR spectra of quinolines **4a**, **4c**, **4d**, **4f**, **4g** and **4j** showed signals corresponding to aliphatic protons which were assigned to the cyclohexenyl fragment as well as olefinic protons around 5.90 ppm for H-17 and H-18. The aromatic region shows signals characteristic for the quinoline system, a singlet for H-3 in the range between 7.59 and 7.79 ppm. The ^{13}C NMR spectra show two sets of signals for several carbon atoms in the quinoline fragment, indicative of the existence of two diastereoisomers.

The X-ray analysis of **4c** and **4d** established the structure of the quinoline derivatives. Table 2 summarizes crystallographic data for the two compounds and Table 1 contains selected bond distances, angles, torsion angles and values for the THC.

The N → B bond lengths for compounds **4c** and **4d** are 1.578(5) and 1.590(3) Å, respectively, which are significantly shorter than those reported for boronates derived from 8-hydroxyquinoline and diphenylboronic 1.61(1), 9-BBN 1.637(3) [20] or diethylboronic acid 1.636(5) Å [21].

The torsion angle for the NCCO fragment in the five-membered boroxazolidine ring of **4c** (−3.4°) and **4d** (−2.6°) showed a value closer to that of boronate **2b** −2.3(6) than to those reported for derivatives prepared from 8-hydroxyquinoline and diphenylboronic acid (−0.7) [20]. The five-membered ring in **4c** and **4d** is

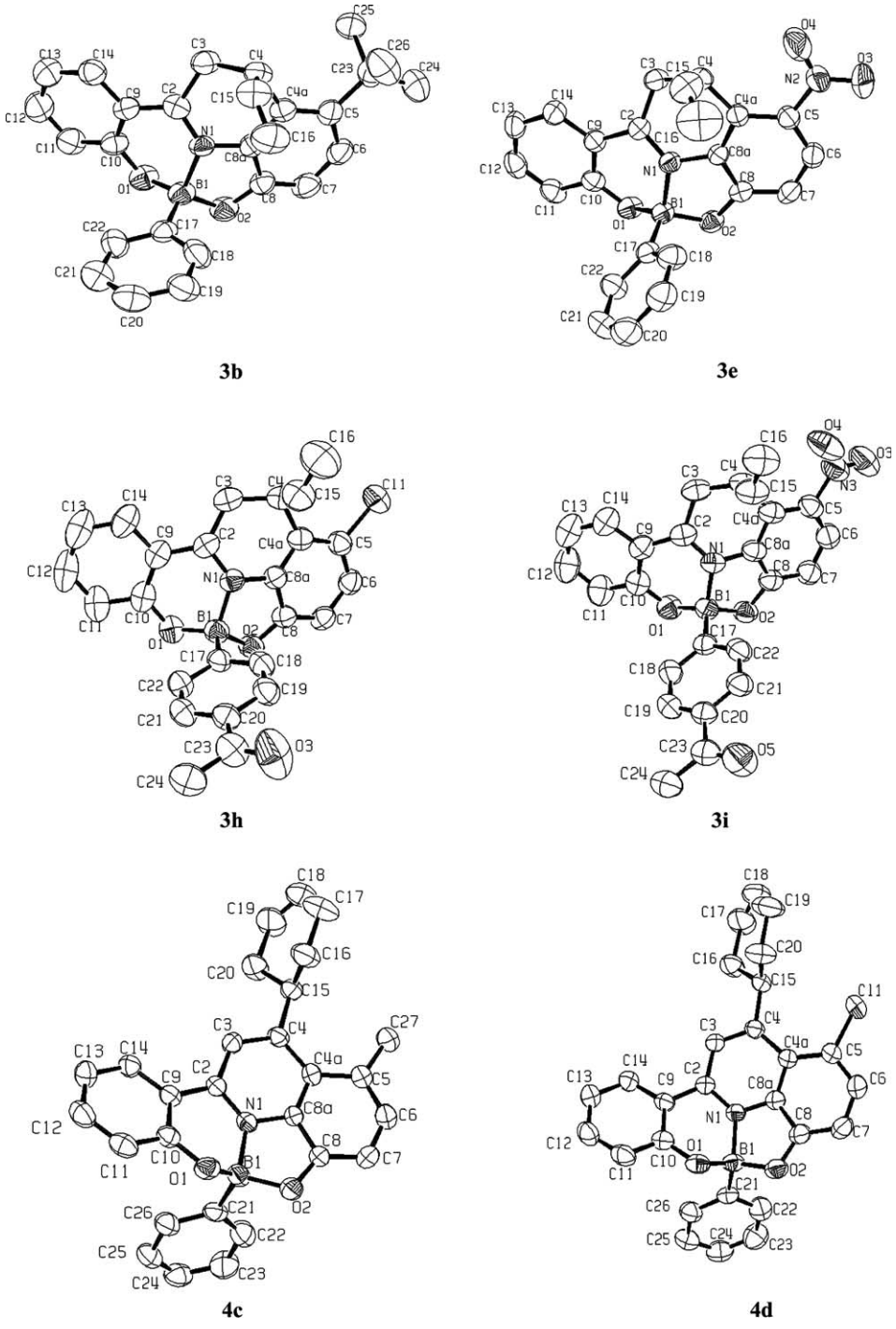
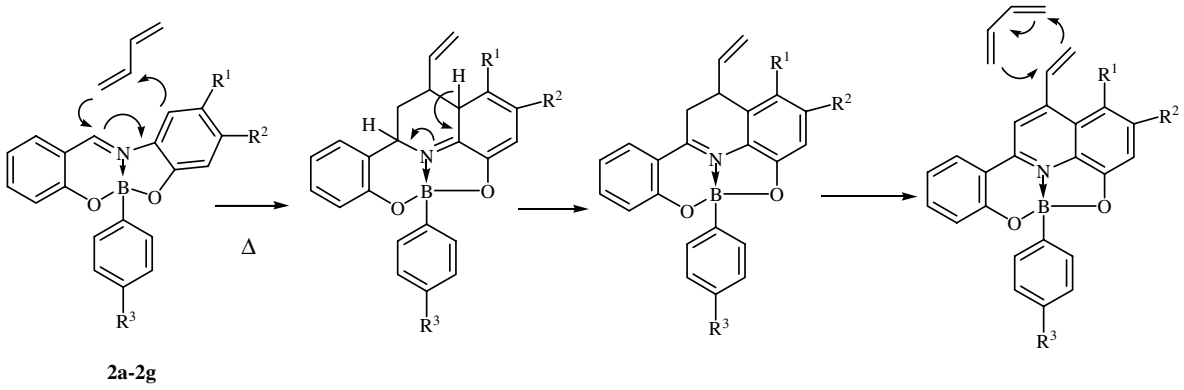


Fig. 2. Perspective view of the molecular structures for compounds **3b**, **3e**, **3h**, **3i**, **4c** and **4d**.

nearly planar with a deviation of the boron atom from the plane of −0.094 and 0.088 Å, respectively. Also, for the six-membered ring, the deviation of the oxygen atom is 0.235 and −0.257 Å for **4c** and **4d**.

The cyclohexenyl substituent shows a half-chair conformation with a torsion angle of 5.2° for the C17–C18–C19–C20 fragment and 54.56° for C–16–C15–C20–C19, with C-15 out of the plane of the six-membered ring (Fig. 2). The cyclohexenyl group is perpendicular to the plane of the hydroxyquinoline ring with torsion angles of C(4a)–C(4)–C(15)–C(16) −91.7° (5) and −83.7° (3) in **4c** and **4d**, respectively.

The 3,4-dihydroquinolines adducts **3b** and **3d**, were hydrolyzed under basic conditions to give dihydroquinolines **5b** and **5d** in quantitative yields (Scheme 3). The products were analyzed by NMR, which shows that the hydrogens at position 3 undergo deuterium exchange upon standing in methanol-d_6. The ^{13}C NMR



2a-2g

Scheme 4. Mechanism proposed for the formation of dihydroquinolines and quinolines from boronates and sulfolene.

spectra showed that C-10 is shifted 6.0 ppm upfield compared to the IDA adducts, while the chemical shifts for the remaining signals are fairly constant.

Concerning the reaction mechanism, it has been reported that IDA reaction of arylimines with some dienophiles, employing a Lewis acid as catalyst, are non-concerted processes [12]. An $HOMO_{dienophile}$–$LUMO_{2\text{-azabutadiene}}$ controlled asynchronous process (inverse electron demand) has been proposed, although a stepwise zwitterionic mechanism is possible for polar dienophiles or for catalyzed processes [11,12,22,23], since experimental evidence indicates that the concerted pathway is 2.7 kcal mol^{-1} below the stepwise alternative [24].

In the case of the boronates studies herein, the thermal IDA reaction of boronates **2a**–**2g** with sulfolene may be rationalized by initial cycloaddition of sulfolene to the 2-azabutadiene system, followed by aromatization to give dihydroquinolines **3b**–**e**, **3h** and **3i** (Scheme 4). In turn, compounds **4c** and **4d** are formed by Diels–Alder reaction of the vinyl fragment with excess sulfolene followed by aromatization to give the corresponding quinoline.

3. Conclusions

Boron adducts derived from Schiff bases provide a new route for the synthesis of 3,4-dihydroquinolines and quinolines. The reaction proceeds by inverse electron demand because the 2-azabutadiene system present in the boronates is electron deficient and it reacts with butadiene, an electron-activated dienophile. The reaction is regioselective, as expected for hetero Diels–Alder reactions yielding the 4-substituted derivatives. Furthermore, only one stereoisomer was isolated showing a *cis* disposition between the vinyl substituent and the phenyl group. Additionally, the reaction is sensitive to stereoelectronic effects and substituents *para* to the imine bond, in the fragment derived from the aminophenol, increase the reactivity and lead to further Diels–Alder reaction of the vinylic fragment; while *meta* substituted derivatives lead to dihydroquinolines. Moreover, polarization of the imine bond in boronates activates these systems toward cycloaddition, providing a new route to dihydroquinoline synthesis. Further studies using other electron rich dienophiles are in progress.

4. Experimental

4.1. Instrumentals

NMR studies were obtained on Bruker 300 Avance DPX 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. 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. Solution and refinement: direct method SHELXS-92 for structure solution and the SHELXL-97 [25] software package for refinement and data output.

4.2.1. Materials

Starting materials and solvents were commercially available. [2-(2-Hydroxybenzyliden)amino]-phenol (**1a**), [2-(2-hydroxybenzyliden)amino]-4-methylphenol (**1c**), [2-(2-hydroxybenzyliden)amino]-4-chlorophenol (**1d**), [2-(2-hydroxybenzyliden)amino]-4-nitrophenol (**1e**), [2-(2-hydroxybenzyliden)amino]-5-methylphenol (**1f**), 2-phenyl-4′-methylbenzo[d]benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-ene (**2c**), 2-phenyl-4′-chlorobenzo[d]-benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-ene (**2d**),

2-phenyl-4′-nitrobenzo[d]benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-ene (**2e**), 2-phenyl-3′-methylbenzo[d]benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-ene (**2f**) and 2-[(4-acetyl)phenyl]-benzo[d]-benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-eno (**2j**) were prepared as described in the literature [14].

4.2.2. General procedure for the preparation of Schiff bases *1b* and *1g*

Equimolar quantities of the corresponding *o*-aminophenol and salicylaldehyde were heated under reflux in methanol for 30 min. The solvent and water formed during the reaction were removed with a Dean-Stark trap to yield a solid, which was washed with a hexane/ethyl acetate mixture (9:1) and used without further purification.

*4.2.2.1. [2-(2-Hydroxybenzyliden)amino]-4-tert-butylphenol (**1b**).* The title compound was prepared from 1.00 g (6.05 mmol) of 2-amino-4-*tert*-butyl-phenol and 0.73 g (6.05 mmol) of salicylaldehyde to give 1.46 g (90% yield) of **1b** as a brown solid. M.p.: 139–139 °C. IR $\bar{\nu}_{max}$ (KBr) 3453, 2960, 1629 (C=N), 1527, 1486, 1486, 1285, 1220, 1147 cm^{-1}. MS (70 eV) *m/z* (%) 269 (M^+, 61), 254 (100), 212 (2), 176 (6), 160 (12), 148 (4), 132 (15), 120 (7), 77 (6), 51 (3).^{1}H NMR (300 MHz, $CDCl_3$) δ:12.47 (1H, br, OH), 8.69 (1H, s, H-7); 7.46 (1H, dd, J = 7.6, 1.6 Hz, H-6), 7.41 (1H, ddd, J = 8.2, 7.5, 1.6 Hz, H-4), 7.26 (1H, dd, J = 8.5, 2.3 Hz, H-11), 7.13 (1H, d, J = 2.3 Hz, H-13), 7.04 (1H, d, J = 8.2 Hz, H-3), 6.99 (1H, td, J = 7.5, 1.3 Hz, H-5), 6.97 (1H, d, J = 8.5 Hz, H-10), 5.79 (1H, br, OH), 1.35 (9H, s, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ:163.8 (C-7), 160.7 (C-2), 147.8 (C-12), 144.3 (C-9), 135.3 (C-8), 133.8 (C-4), 132.8 (C-6), 125.9 (C-11), 119.7 (C-5), 119.5 (C-1), 117.4 (C-3), 115.6 (C-10), 115.5 (C-13), 34.6 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$). Anal. Calc. for $C_{17}H_{19}NO_2$: C, 75.83; H, 7.06; N, 5.20. Found: C, 75.83; H, 7.42; N, 5.26%.

*4.2.2.2. [2-(2-Hydroxybenzyliden)amino]-5-nitrophenol (**1g**).* The title compound was prepared from 3.00 g (19.58 mmol) of 2-amino-5-nitrophenol and 2.39 g (19.60 mmol) of salicylaldehyde, to give 3.60 g (90% yield) of 1 g as a red solid. M.p.: 220 °C. IR $\bar{\nu}_{max}$ (KBr) 3453, 2924, 2344, 1621 (C=N), 1523, 1344, 1215, 763 cm^{-1} MS (70 eV) *m/z* (%) 258 (M^+, 100), 241 (9), 211 (32), 183 (10), 165 (31), 120 (8), 107 (5), 94 (15), 78 (10). ^{1}H NMR (300 MHz, $CDCl_3$) δ:13.04 (1H, s, OH), 10.72 (1H, s, OH), 9.01 (1H, s, H-7), 7.79 (1H, dd, J = 9.4, 2.4 Hz, H-12), 7.77 (1H, d, J = 2.4 Hz, H-10), 7.68 (1H, dd, J = 7.8, 1.3 Hz, H-6), 7.52 (1H, d, J = 9.4 Hz, H-13), 7.44 (1H, td, J = 7.8, 1.3 Hz, H-4), 7.01 (1H, td, J = 7.8, 1.3 Hz, H-5), 6.97 (1H, d, J = 7.8, H-3). ^{13}C NMR (75 MHz, $CDCl_3$) δ:164.9 (C-7), 160.7 (C-2), 151.2 (C-9), 145.9 (C-11), 142.0 (C-8), 134.0 (C-4), 132.7 (C-6), 120.6 (C-13), 119.4 (C-1), 119.2 (C-5), 116.8 (C-3), 115.1 (C-12), 110.8 (C-10). Anal. Calc. for $C_{13}H_{10}N_2O_4$: C, 60.46; H, 3.87; N, 10.85. Found: C, 60.42; H, 3.98; N, 10.81%.

4.2.3. General procedure for the preparation of boron adducts *2b, 2g, 2h, 2i*

An equimolar amount of phenylboronic acid (or 4-acetylphenylboronic) was added to a solution of the tridentate ligand in THF (usually about 15 ml for 2–3 mmol). The mixture was refluxed for 1 h (for **2b** and **2g**) or 8 h (for **2h** and **2i**), the solvent and the water formed during the reaction were removed with a Dean-Stark trap. The solid was collected by filtration and washed with small amounts of an ethyl acetate/hexane mixture (1:9).

*4.2.3.1. [2-Phenyl-4′-tert-butylbenzo[d]benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-ene (**2b**).* The title compound was prepared from 1.00 g (2.81 mmol) of **1b** and phenylboronic acid (0.34 g 2.81 mmol), to give 1.05 g (80% yield) of **2b** as an orange solid. M.p.: 203–205 °C. IR $\bar{\nu}_{max}$ (KBr) 2962, 1623 (C=N), 1455, 1176, 961, 752 cm^{-1}. MS (70 eV) *m/z* (%) 355 (M^+, 10), 340 (3), 278 (M^+–C_6H_5, 100), 262 (40), 248 (9), 222 (3), 117 (7), 77 (3), 51 (2). ^{1}H NMR (400 MHz, $CDCl_3$): 8.35 (1H, s, H-7), 7.53 (1H, dd, J = 8.3, 7.5 Hz, H-4), 7.46 (1H, d, J = 1.3 Hz, H-13), 7.40 (1H, d, J = 8.8 Hz, H-11), 7.26–7.39 (3H, m, H-*o*, 6), 7.21 (1H, d, J = 8.3 Hz, H-3), 7.13–7.19 (3H, m, H-*m*, *p*), 7.04 (1H, d, J = 8.8 Hz, H-10), 6.93 (1H, t, J = 7.5 Hz, H-5), 1.34 (9H, s, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ:157.4 (C-2), 156.6 (C-9), 147.8 (C-7), 142.9 (C-12), 137.6 (C-4), 131.3 (C-*o*), 131.3 (C-6), 130.0 (C-8), 129.9 (C-11), 127.8 (C-*p*), 127.4 (C-*m*), 120.3 and 120.2 (C-3 and C-5), 119.3 (C-1), 114.5 (C-10), 111.7 (C-13), 34.6 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$). ^{11}B NMR (96 MHz, $CDCl_3$) δ: 7.9 ppm ($h_{1/2}$ = 288 Hz). Anal. Calc. for $C_{23}H_{22}NO_2B$: C, 77.74; H, 6.19; N, 3.94. Found: C, 77.34; H, 6.30; N, 3.99%.

*4.2.3.2. 2-Phenyl-5′-nitrobenzo[d]benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-ene (**2g**).* The title compound was prepared from 3.00 g (11.62 mmol) of **1g** and phenylboronic acid (1.42 g, 11.61 mmol), to give 1.05 g (92% yield) of **2g** as an orange solid. M.p.: 227–228 °C. IR $\bar{\nu}_{max}$ (KBr) 3443, 2924, 2853, 1626 (C=N), 1526, 1339, 1181, 956, 758 cm^{-1}. MS (70 eV) *m/z* (%) 344 (M^+, 14), 268 (17), 267 (M^+–C_6H_5, 100), 221 (46), 193 (1). ^{1}H NMR (300 MHz, $CDCl_3$) δ:8.54 (1H, s, H-7), 7.93 (1H, d, J = 2.2 Hz, H-10), 7.87 (1H, dd, J = 8.6, 2.2 Hz, H-12), 7.69 (1H, ddd, J = 8.6, 7.1, 1.5 Hz, H-4), 7.58 (1H, d, J = 8.6 Hz, H-13), 7.50 (1H, dd, J = 7.8, 1.6 Hz, H-6), 7.32–7.26 (3H, m, H-*o*, H-3), 7.22–7.15 (3H, m H-*m*, *p*), 7.04 (1H, ddd, J = 1.1, 7.2, 7.8 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.0 (C-9), 158.7 (C-2), 152.7 (C-7), 150.4 (C-11), 140.4 (C-4),

136.2 (C-8), 132.6 (C-6), 131.4 (C-*o*), 128.8 (C-*p*), 128.0 (C-*m*), 121.4 and 121.1 (C-5, C-3), 119.3 (C-1), 115.5 and 115.3 (C-12, C-13), 110.8 (C-10). ^{11}B NMR (96 MHz, $CDCl_3$) δ: 8.7 ppm ($h_{1/2}$ = 152 Hz). Anal. Calc. for $C_{19}H_{13}N_2O_4B$: C, 66.27; H, 3.77; N, 8.13. Found: C, 65.98; H, 3.84; N, 7.96%.

*4.2.3.3. 2-(4-Acetylphenyl)-4′-chlorobenzo[d]benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-ene (**2h**).* The title compound was prepared from 1d (2.50 g, 10.09 mmol) and 4-acetylphenylboronic acid (1.82 g, 11.0 mmol) to give 3.21 g (85% yield) as a yellow solid. M.p.: 213–215 °C. IR $\bar{\nu}_{max}$ (KBr) 3339, 3035, 1672 (C=O), 1619 (C=N), 1548, 1469, 1268, 1182, 957, 824, 759 cm^{-1}. MS (70 eV) *m/z* (%); 375 (M^+, 1), 258 (37), 257 (24), 256 (M^+-$C_6H_4COCH_3$, 100), 221(11), 77(10), 42(8). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.42 (1H, s, H-7), 7.72 (2H, d, *J* = 8.2 Hz, H-*m*), 7.61 (1H, ddd, *J* = 8.5, 7.5, 1.6 Hz, H-4), 7.49 (1H, d, *J* = 2.2 Hz, H-13), 7.44 (1H, dd, *J* = 7.8, 1.6 Hz, H-6), 7.39 (2H, d, *J* = 8.2 Hz, H-*o*), 7.32 (1H, dd, *J* = 8.7, 2.2 Hz, H-11), 7.24 (1H, d, *J* = 8.5 Hz, H-3), 7.04 (1H, d, *J* = 8.7 Hz, H-10), 7.00 (1H, td, *J* = 7.5, 1.0 Hz, H-5), 2.50 (3H, s, Me). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 198.7 (C=O), 157.6 (C-2), 157.3 (C-9), 150.1 (C-7), 139.1 (C-4), 136.8 (C-8), 132.6 (C-11), 131.9 (C-6), 131.5 (C-*o*), 131.2 (C-*p*), 127.5 (C-*m*), 124.6 (C-12), 121.1 (C-5), 120.6 (C-3), 119.1 (C-10), 116.3 (C-1), 115.6 (C-13), 26.8 (Me).^{11}B NMR ($CDCl_3$, 96.3 MHz) δ: 8.0 ppm.($h_{1/2}$ = 219 Hz). Anal. Calc. for $C_{21}H_{15}BNO_3Cl$: H, 3.99; C, 67.11; N, 3.72. Found: H, 4.00; C, 67.15; N, 3.66%.

*4.2.3.4. 2-(4-Acetylphenyl)-4′-nitrobenzo-[d]benzo[h]-6-aza-1,3-dioxa-2-boracyclonon-6-ene (**2i**).* The title compound was prepared from **1e** (3.00 g, 11.6 mmol) and 4-acetylphenylboronic acid (2.10 g, 12.80 mmol) to give 2.62 g (58% yield). M.p.: 218–220 °C. IR $\bar{\nu}_{max}$ (KBr) 3089, 3043, 2984, 1676 (C=O), 1631(C=N), 1512, 1465, 1333, 1273, 1182, 920 cm^{-1}. MS (70 eV) *m/z* 386 (M^+, 2), 267 (M^+-$C_6H_4COCH_3$, 100), 268 (16), 222 (10), 221(68), 220 (25), 76 (10), 43 (12). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.67 (1H, s, H-7), 8.47 (1H, s, H-13), 8.33 (1H, dd, *J* = 9.0, 1.5 Hz, H-11), 7.74 (2H, d, *J* = 8.2 Hz, H-*m*), 7.69 (1H, dd, *J* = 8.1, 7.5 Hz, H-4), 7.54 (1H, d, *J* = 7.5 Hz, H-6), 7.39 (2H, d, *J* = 8.2 Hz, H-*o*), 7.27 (1H, d, *J* = 8.1 Hz, H-3), 7.17 (1H, d, *J* = 9.0 Hz, H-10), 7.07 (1H, t, *J* = 7.5 Hz, H-5), 2.52 (3H, s, Me). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ: 198.6 (CO), 163.5 (C-12), 158.0 (C-2), 152.6 (C-7), 140.4 (C-9), 140.1 (C-4), 137.1 (C-*p*), 132.5 (C-6), 131.3 (C-*o*), 130.8 (C-8), 128.7 (C-11), 127.6 (C- *m*), 121.6 (C-5), 120.8 (C-3), 119.0 (C-1), 114.9 (C-10), 112.0 (C-13), 26.8 (Me). ^{11}B NMR ($CDCl_3$, 86.68 MHz) δ: 8.2 ppm ($h_{1/2}$ = 385 Hz). Anal. Calc. for $C_{21}H_{15}N_2BO_5$: C, 65.32; H, 3.92; N, 7.25. Found: C, 65.37; H, 3.84; N, 7.20%.

4.2.4. General procedure for the Imino Diels–Alder reaction of boron adducts

Boron adducts **2a**–**2j** (1 equiv), sulfolene (3 equiv), 2 ml of toluene and traces of hydroquinone were placed in a sealed ampule and heated for 12–22 h at 120 °C under nitrogen atmosphere and protected from light. The solvent was removed under vacuum and the product extracted with a CH_2Cl_2-saturated NH_4Cl solution. The organic phase was dried over Na_2SO_4, and evaporated under vacuum. Samples for elemental analysis were obtained by purification on silica gel (70–230 mesh) using hexane–ethylacetate (95:5).

*4.2.4.1. Phenyl[2(2′-hydroxyphenyl-O)-4-ethenyl-5-tert-buthyl-8-(3,4-dihydroquinolate)O′,N))]boron (**3b**).* The title compound was prepared from ***2b*** (1.00 g, 2.80 mmol) and sulfolene (1.00 g, 8.40 mmol), heating for 12 h, to give 1.00 g (87% yield) of ***3b***. M.p.: 363–364 °C. IR $\bar{\nu}_{max}$ (KBr) 3047, 2920, 1629 (C=N), 1551, 1463, 1325, 1186, 1015, 956, 755 cm^{-1}. MS (70 eV) *m/z* (%) 407 (M^+, 1), 330 (100), 300 (7), 283 (5), 129 (9), 97 (7), 57 (16). ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.52 (1H, ddd, *J* = 8.5, 7.1, 1.5 Hz, H-12); 7.49 (1H, dd, *J* = 7.9, 1.5 Hz, H-14), 7.38–7.42 (2H, m, H-*o*), 7.35 (1H, d, *J* = 8.7 Hz, H-6), 7.24 (3H, dd, *J* = 8.5, 1.0 Hz, H-11), 7.16-7.19 (3H, m, H-*m*, *p*), 6.92 (1H, ddd, *J* = 7.9, 7.1, 1.0 Hz, H-13), 6.88 (1H, d, *J* = 8.7 Hz, H-7), 5.95 (1H, ddd, *J* = 17.1, 10.3, 5.2 Hz, H-15), 5.16 (1H, ddd, *J* = 10.3, 1.7, 0.8 Hz, H-16a), 4.99 (1H, ddd, *J* = 17.1, 1.7, 0.8 Hz, H-16b), 4.43–4.38 (1H, m, H-4), 3.51 (1H, dd, *J* = 19.5, 1.7 Hz, H- 3a), 2.76 (1H, dd, *J* = 19.5, 6.4 Hz, H-3b), 1.40 (9H, s, Me). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ:158.7 (C-2), 156.9 (C-10), 153.9 (C-8), 138.0 (C-5), 137.9 (C-15), 137.2 (C-12), 131.1 (C-*o*), 130.1 (C-8a), 129.3 (C-6), 127.5 (C-*p*), 127.3 (C-*m*, 14), 124.7 (C-4a), 120.9 (C-11), 119.8 (C-13), 118.5 (C-9), 117.3 (C-16), 111.8 (C-7), 36.4 (C-4), 35.4 (*C*-Me), 33.1 (C-3), 31.9 (C-*Me*). ^{11}B NMR (96 MHz, $CDCl_3$) δ: 7.9 ppm ($h_{1/2}$ = 77 Hz). Anal. Calc. for $C_{27}H_{26}NO_2B$: C, 79.61; H, 6.39; N, 3.43. Found: C, 80.01; H, 6.71; N, 3.57%.

*4.2.4.2. Phenyl[2(2′-hydroxyphenyl-O)-4-ethenyl-5-methyl-8-(3,4-dihydroquinolate) O′, N))] boron (**3c**).* The title compound was prepared from ***2c*** (1.00 g, 3.19 mmol) and sulfolene (1.13 g, 9.60 mmol), heating for 22 h, to give 0.90 g (77% yield) of ***3c***. M.p.: 164–165 °C and ***4c*** in traces. IR $\bar{\nu}_{max}$ (KBr) 2920, 1623 (C=N), 1462, 1265, 1188, 920, 760 cm^{-1}. MS (70 eV) *m/z* (%) 365 (M^+, 0.2), 288 (100), 273 (22), 260 (16), 77 (10), 51(2). ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.52 (1H, ddd, *J* = 8.4, 7.6, 1.3 Hz, H-12); 7.47 (1H, dd, *J* = 7.6, 1.3 Hz, H-14), 7.40–7.38 (2H, m, H-*o*), 7.26 (1H, d, *J* = 8.4 Hz, H-11), 7.17–7.15 (3H, m, H-*m*, *p*), 7.10 (1H, d, *J* = 8.2 Hz, H-6), 6.92 (1H, td, *J* = 7.6, 1.0 Hz, H-13), 6.84 (1H, d, *J* = 8.2 Hz, H-7), 5.93 (1H, ddd, *J* = 17.0,

10.0, 6.8 Hz, H-15), 5.09 (1H, dd, J = 9.8, 1.2 Hz, H-16a), 5.06 (1H, dd, J = 17.0, 1.2 Hz, H-16b), 3.92 (1H, dt, J = 7.2, 1.2 Hz, H-4), 3.48 (1H, d, J = 19.8 Hz, H-3a), 2.80 (1H, dd, J = 19.8, 7.7 Hz, H-3b), 2.23 (3H, s, Me). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 158.5 (C-2), 157.0 (C-10), 154.1 (C-8), 137.0 (C-12), 137.0 (C-15), 133.0 (C-6), 131.0 (C-*o*), 128.5 (C-8a), 127.6 (C-*p*), 127.4 (C-*m*), 127.2 (C-14), 125.3 (C-5), 124.2 (C-4a), 121.1 (C-11), 119.9 (C-13), 118.8 (C-9), 116.0 (C-16), 112.1 (C-7), 35.0 (C-4), 32.6 (C-3), 16.4 (Me). ^{11}B NMR (96 MHz, $CDCl_3$) δ: 7.9 ppm ($h_{1/2}$ = 58 Hz). Anal. Calc. for $C_{24}H_{20}NO_2B$: C, 78.90; H, 5.47; N, 3.80. Found: C, 78.85; H, 5.60; N, 3.80%.

*4.2.4.3. Phenyl[2(2′-hydroxyphenyl-O)-4-ethenyl-5-chloro-8-(3,4-dihydroquinolate)O′, N))] boron (**3d**).* The title compound was prepared from ***2d*** (1.00 g, 2.99 mmol) and sulfolene (1.10 g, 9.00 mmol), heating for 12 h, to give 0.90 g (83% yield) of ***3d***. M.p.: 184–185 °C and ***4d*** in traces. IR $\bar{\nu}_{max}$ (KBr) 3078, 2921, 1601 (C═N), 1534, 1469, 1289, 1142, 917, 814, 743 cm^{-1}. MS (70 eV) *m*/*z* (%) 385 (M^+, 1), 362 (3), 308 (100), 293 (20), 272 (11), 245 (7), 77 (7), 51 (7). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (1H, ddd, J = 8.4, 7.1, 1.5 Hz H-12), 7.51 (1H, dd, J = 8.0, 1.7 Hz, H-14), 7.38 (2H, dd, J = 6.5, 3.0 Hz, H-*o*), 7.28 (1H, d, J = 8.4 Hz, H-11), 7.27 (1H, d, J = 8.7 Hz, H-6), 7.20–7.18 (3H, m, H-*m*, *p*), 6.96 (1H, ddd, J = 7.8, 7.1, 1.1 Hz, H-13), 6.88 (1H, d, J = 8.7 Hz, H-7), 5.95 (1H, ddd, J = 17.0, 10.2, 6.4 Hz, H-15), 5.17 (1H, dd, J = 10.2, 1.2 Hz, H-16a), 5.15 (1H, dd, J = 17.0, 1.2 Hz, H-16b), 4.12 (1H, ddd, J = 7.6, 6.3, 1.2 Hz, H-4), 3.35 (1H, dd, J = 20.0, 1.2 Hz, H-3a), 2.86 (1H, dd, J = 20.0, 7.6 Hz, H-3b). ^{13}C NMR (75 MHz, $CDCl_3$) δ:160.2 (C-2), 157.2 (C-10), 154.7 (C-8), 138.0 (C-12), 136.0 (C-15), 131.8 (C-6), 131.1 (C-o), 129.8 (C-8a), 128.0 (C-*p*), 127.7 (C-*m*), 127.6 (C-14), 124.2 (C-4a), 121.4 (C-11), 121.3 (C-5), 120.4 (C-13), 118.7 (C-9), 116.8 (C-16), 113.7 (C-7), 35.1 (C-4), 32.4 (C-3). ^{11}B NMR (96 MHz, $CDCl_3$) δ:8.2 ppm ($h_{1/2}$ = 48 Hz). Anal. Calc. for $C_{23}H_{17}NO_2BCl$: C, 71.68; H, 4.41; N, 3.63. Found: C, 71.66; H, 4.48; N, 3.98%.

*4.2.4.4. Phenyl[2(2′-hydroxyphenyl-O)-4-ethenyl-5-nitro-8-(3,4-dihydroquinolate)O′, N))] boron (**3e**).* The title compound was prepared from ***2e*** (1.00 g, 2.90 mmol) and sulfolene (1.00 g, 8.70 mmol), heating for 12 h, to give 0.80 g (70% yield) of ***3e***. M.p.: 215–217 °C. IR $\bar{\nu}_{max}$ (KBr) 3071, 3045, 3007, 1639 (C═N), 1511, 1464, 1331, 1289, 1189, 907, 750 cm^{-1}. MS (70 eV) *m*/*z* (%) 396 (M^+, 1), 319 (100), 272 (23), 246 (31), 77 (11), 51 (7). ^{1}H NMR (400 MHz, $CDCl_3$) δ:8.30 (1H, d, J = 9.0 Hz, H-6); 7.62 (1H, ddd, J = 8.4, 7.2, 1.5 Hz, H-12), 7.56 (1H, dd, J = 7.2, 1.2 Hz, H-14), 7.32–7.29 (3H, m, H-11 y-*o*), 7.19–7.16 (3H, m, H-*m*, *p*), 7.00 (1H, td, J = 7.2, 1.2 Hz, H-13), 6.96 (1H, d, J = 9.0 Hz, H-7), 6.05 (1H, ddd, J = 17.0, 10.4, 6.1 Hz, H-15), 5.18 (1H, dd, J = 10.4, 1.4 Hz, H-16a), 5.14 (1H, dd, J = 17.1, 1.4 Hz, H-16b), 4.93 (1H, td, J = 6.1, 1.5 Hz, H-4), 3.65 (1H, d, J = 20.2 Hz, H-3a), 2.80 (1H, dd, J = 20.2, 7.5 Hz, H-3b). ^{13}C NMR (75 MHz, $CDCl_3$) δ:162.7 (C-2), 160.6 (C-8), 157.3 (C-10), 138.7 (C-12), 137.2 (C-5), 135.3 (C-15), 130.8 (C-*o*), 129.9 (C-6), 129.7 (C-8a), 128.2 (C-*p*), 127.9 (C-14), 127.7 (C-*m*), 123.8 (C-4a), 121.3 (C-11), 120.7 (C-13), 118.1 (C-9), 117.0 (C-16), 112.3 (C-7), 35.0 (C-4), 31.8 (C-3). ^{11}B NMR (96 MHz, $CDCl_3$) δ:8.6 ppm ($h_{1/2}$ = 58 Hz). Anal. Calc. for $C_{23}H_{17}N_2O_4B$: C, 69.69; H, 4.29; N, 7.07. Found: C, 70.05; H, 4.35; N, 7.27%.

*4.2.4.5. p-Acetylphenyl[2(2′-hydroxyphenyl-O)-4-ethenyl-5-chloro-8-(3,4-dihydroquinolate) O′, N))]boron (**3h**).* The title compound was prepared from **2h** (1.00 g, 2.70 mmol) and sulfolene (0.94 g, 8.0 mmol), heating for 20 h, to give 0.81 g (71% yield) of **3h**. M.p.: 197–198°C. IR $\bar{\nu}_{max}$ (KBr) 2997, 1682 (C═N), 1549, 1461, 1359, 1267, 1183, 1127, 1076, 1043, 993, 912, 821, 760, 727, 596 cm^{-1}. MS (70 eV) *m*/*z* 427 (M^+, 4), 308 (100), 257 (24), 293 (18), 280(15), 76(10), 43(14). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.76 (2H, d, J = 8.2 Hz, H-*m*), 7.60 (1H, td, J = 8.0, 1.4 Hz, H-12), 7.54 (1H, dd, J = 8.0, 1.4 Hz, H-14), 7.45 (2H, d, J = 8.3 Hz, H-*o*), 7.29 (1H, d, J = 8.4 Hz, H-6), 7.27 (1H, d, J = 8.0 Hz, H-11), 6.99 (1H, t, J = 8.5 Hz, H-13), 6.89 (1H, d, J = 8.4 Hz, H-7), 5.95 (1H, ddd, J = 16.7, 10.4, 6.2 Hz, H-15), 5.18 (1H, dd, J = 10.2, 1.0 Hz, H-16a), 5.12 (1H, dd, J = 16.8, 1.3 Hz, H-16b), 4.14 (1H, ddd, J = 7.5, 6.2, 1.3 Hz, H-4), 3.60 (1H, d, J = 20.1 Hz, H-3a), 2.90 (1H, dd, J = 20.1, 7.7 Hz, H-3b), 2.51 (3H, s, Me). ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ: 198.6 (CO), 160.5 (C-2), 156.9 (C-10), 154.4 (C-8), 138.1 (C-12), 136.6 (C-*p*), 135.7 (C-15), 131.9 (C-6), 131.1 (C-*o*), 129.4 (C-8a), 127.6 (C-14), 127.5 (C-*m*), 124.2 (C-4a), 121.5 (C-5), 121.2 (C-11), 120.5 (C-13), 118.4 (C-9), 116.6 (C-16), 113.7 (C-7), 34.9 (C-4), 32.3 (C-3), 26.6 (Me). ^{11}B NMR ($CDCl_3$, 96.3 MHz) δ: 7.8 ppm ($h_{1/2}$ = 96 Hz). Anal. Calc. for $C_{25}H_{19}NO_3B$: C, 70.17; H, 4.44 N, 3.27. Found: C, 70.34; H, 4.54; N, 3.18%.

*4.2.4.6. p-Acetylphenyl[2(2′-hydroxyphenyl-O)-4-ethenyl-5-nitro-8-(3,4-dihydroquinolate) O′, N))]boron (**3i**).* The title compound was prepared from **2i** (1.00 g, 2.59 mmol) and sulfolene (0.92 g, 7.77 mmol), heating for 12 h, to give 0.85 g (75% yield) of **3i**. M.p.: 158–160 °C. IR $\bar{\nu}_{max}$ (KBr) 3083, 2920, 1680 (C═O), 1626 (C═N), 1515, 1462, 1332, 1270, 1187, 909, 817, 760 cm^{-1}. MS (70 eV) *m*/*z* 438 (M^+, 0.2), 320 (20), 319 (100), 273 (11), 272 (27), 271 (11), 246 (43), 245 (23). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.31 (1H, d, J = 9.2 Hz H-6), 7.76 (2H, d, J = 8.2 Hz, H-*m*), 7.64 (1H, ddd, J = 8.3, 7.3, 1.6 Hz, H-12), 7.60 (1H, dd,

J = 7.3, 1.6 Hz, H-14), 7.41 (2H, d, J = 8.2 Hz, H-*o*), 7.29 (1H, d, J = 8.3 Hz, H-11), 7.03 (1H, td, J = 7.3, 1.1 H-13), 6.99 (1H, d, J = 9.2 Hz, H-7), 6.07 (1H, ddd, J = 17.0, 10.3, 6.0 Hz, H-15), 5.19 (1H, dd, J = 10.3, 1.4 Hz, H-16a), 5.12 (1H, dd, J = 17.0, 1.4 Hz, H-16b) 4.96 (1H, t, J = 6.0 Hz, H-4) 3.71 (1H, d, J = 20.1 Hz, H-3a), 2.92 (1H, dd, J = 20.1, 7.3 Hz, H-3b), 2.50 (3H, s, Me). ^{13}C NMR ($CDCl_3$, 100.5 MHz) δ: 198.5 (CO), 163.0 (C-2), 160.3 (C-8), 157.0 (C-10), 138.9 (C-12), 137.3 (C-5), 136.8 (C-*p*), 135.2 (C-15), 130.9 (C*o*), 129.9 (C-6), 129.5 (C-8a), 127.9 (C-14), 127.5 (C-*m*), 123.8 (C-4a), 121.3 (C-11),120.9 (C-13), 118.0 (C-9), 116.8 (C-16), 112.4 (C-7), 34.8 (C-4),31.7 (C-3), 26.6 (Me). ^{11}B NMR ($CDCl_3$, 128.26 MHz) δ: 8.1 ppm ($h_{1/2}$ = 64 Hz). Anal. Calc. for $C_{25}H_{19}N_2O_5B$: C, 68.49; H, 4.33; N, 6.39. Found: C, 68.87; H, 4.37; N, 6.31%.

*4.2.4.7. Phenyl[2(2′-hydroxyphenyl-O)-4-(3′-cyclohexenyl)-8-quinolate)-O′, N]boron (**4a**).* The compound was prepared as described previously heating for 22 h in 67% yield determined by NMR, and purified by chromatography using hexane:ethyl acetate (95:5). M.p.: 198–200 °C. IR $\bar{\nu}_{max}$ (KBr) 3026, 2914, 1610, 1552, 1498, 1260, 1186, 1037, 907, 874, 755 cm^{-1}. MS (70 eV) *m/z* 430 (M^+–CH_3, 0.1), 327 (25), 326 (100), 325 (26), 273(18), 272 (90), 271(25). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (1H, d, J = 7.5 Hz, H-14), 7.63 (1H, s, H-3), 7.62 (1H, s, H-3′), 7.56 (1H, t, J = 8.1 Hz, H-6), 7.53 (1H, t, J = 7.3 Hz, H-12), 7.39 (1H, d, J = 8.3 Hz, H-7), 7.35–7.33 (3H, m, H-11, *o*), 7.15-7.13 (3H, m, H-*m*, *p*), 7.01 (1H, dt, J = 7.5, 1.0 Hz, H-13), 5.88 (2H, s, H-17, 18) 3.67-3.66 (1H, m, H-15), 2.58–1.99 (6H, m, H-16, H-19, H-20). ^{13}C NMR (100.53 MHz, $CDCl_3$) δ: 160.5 (C-4) 160.3 (C-4′), 157.6 (C-8), 156.7 (C-10), 145.5 (C-2), 136.9 (C-8a), 135.5 (C-12), 131.7 (C-*o*), 131.2 (C-6), 127.7 (C-*p*), 127.5 (C-*m* and C-17, C-17′), 125.9 (C-18), 125.7 (C-18′), 125.8 (C-4a), 125.7 (C-4a′), 125.3 (C1-14), 121.8 (C-11), 120.2 (C-13), 119.1 (C-9), 114.4 (C-3), 114.2 (C-3′), 111.0 (C-7), 110.0 (C-5), 36.2 (C-15), 32.5 (C-16), 31.8 (C-16′), 28.9 (C-19), 28.3 (C-19′), 25.4 (20), 25.3 (C-20′). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ: 9.2 ppm ($h_{1/2}$ = 96 Hz). Anal. Calc. for $C_{27}H_{22}NBO_2$: C, 80.39; H, 5.46; N, 3.47. Found: C, 80.14; H, 5.64; N, 3.38%.

*4.2.4.8. Phenyl[2(2′-hydroxyphenyl-O)-4-(3′-cyclohexenyl)-5-methyl-8- quinolate) O′, N))] boron (**4c**).* M.p.: 215–216 °C. IR $\bar{\nu}_{max}$ (KBr) 3025, 2921, 1611, 1554, 1505, 1453, 1374, 1241,1181, 933, 751, 698 cm^{-1}. MS (70 eV) *m/z* (%) 417 (M^+, 0.3), 394 (3), 340 (100), 286 (54), 270 (19), 77(19), 43(15). ^{1}H NMR (270 MHz, $CDCl_3$) δ:7.78 (1H, dd, J = 7.9, 1.7 Hz, H-14), 7.77 (1H, dd, J = 7.9, 1.8 Hz, H-14′), 7.68 (1H, s, H-3), 7.67 (1H, s, H-3′), 7.51 (1H, ddd, J = 8.4, 7.7, 1.7 Hz, H-12), 7.52 (1H, dt, J = 7.7, 1.8 Hz, H-12′), 7.35–7.29 (4H, m, H-6, 11, *o*), 7.14–7.10 (3H, m, H-*m*, *p*), 7.00 (1H, d, J = 7.7 Hz, H-7), 6.99 (1H, dt, J = 7.7, 1.0 Hz, H-13), 6.98 (1H, dt, J = 7.7, 1.1 Hz, H-13′), 5.88 (2H, s, H-17, H-18), 5.87 (2H, s, H-17′, H-18′), 4.12–4.03 (1H, m, H-15), 2.80 (3H, s, Me), 2.54–1.91 (6H, m, H-16, 19, 20). ^{13}C NMR (68 MHz, $CDCl_3$) δ:162.4 (C-4), 162.3 (C-4′), 156.8 (C-10), 156.0 (C-8), 144.6 (C-2), 137.0 (C-8a), 135.4 (C-12), 133.8 (C-6), 131.6 (C-*o*), 127.5 and 127.4 (C-17, C-*p* and C-*m*), 125.9 and 125.8 (C-18), 125.3 (C-14), 125.3 (C-4a), 122.0 (C-5), 121.7 (C-11), 120.1 (C-13), 118.7 (C-9), 115.1 (C-3), 109.8 (C-7), 37.0 (C-15), 33.7 (C-19), 33.2 (C-19′), 30.3 (C-20), 29.9 (C-20′), 25.1 (C-16), 25.5 (C-16′), 22.9 (Me). ^{11}B NMR (96 MHz, $CDCl_3$) δ:8.8 ppm ($h_{1/2}$ = 78 Hz). Anal. Calc. for $C_{28}H_{24}NO_2B$: C, 80.57; H, 5.75; N, 3.35. Found: C, 80.56; H, 5.81; N, 3.81%.

*4.2.4.9. Phenyl[2(2′-hydroxyphenyl-O)-4-(3′-cyclohexenyl)-5-chloro-8- quinolate-O′, N)]boron (**4d**).* M.p.: 232–233 °C. MS (70 eV) *m/z* (%) 437 (M^+, 0.2), 380 (2), 360 (100), 306 (77), 270 (36), 245 (5), 77 (14), 51 (11). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (1H, d, J = 8.5 Hz, H-14), 7.74 (1H, s, H-3), 7.72 (1H, s, H-3′), 7.56 (1H, d, J = 8.1, H-6), 7.55 (1H, dd, J = 8.1, 7.7 Hz, H-12), 7.34 (1H, d, J = 8.1, H-11), 7.30–7.28 (2H, m, H-*o*), 7.15–7.11 (3H, m, H-*m*, *p*), 7.02 (1H, d, J = 8.4 Hz, H-7), 7.02 (1H, t, J = 7.7 Hz, H-13), 5.87 (2H, s, H-17, 18), 4.64–4.55 (1H, m, H-15), 2.63–1.85 (6H, m, H-16, 19, 20). ^{13}C NMR (75 MHz, $CDCl_3$) δ:161.8 (C-4), 161.7 (C-4′), 156.9 (C-10), 156.8 (C-8), 145.8 (C-2), 137.2 (C-8a), 136.2 (C-12), 133.5 (C-6), 133.5 (C-6′), 131.7 (C-*o*), 127.9 (C-*p*), 127.8 and 127.6 (C-17 and C-*m*), 126.0 and 125.8 (C-18), 125.7 (C-14), 123.2 (C-4a), 123.1 (C-4a), 121.9 (C-11), 120.5 (C-13), 118.5 (C-9), 116.1 (C-3), 116.0 (C-3′), 110.6 (C-7), 36.4 (C-15), 36.3 (C-15′), 33.3 (C-19), 32.7 (C-19′), 30.4 (C-20), 29.7 (C-20′), 25.6 (C-16, C-16′). ^{11}B NMR (96 MHz, $CDCl_3$) δ: 9.5 ppm ($h_{1/2}$ = 77 Hz). Anal. Calc. for $C_{27}H_{21}NO_2BCl$: C, 74.05; H, 4.80; N, 3.20. Found: C, 73.60; H, 5.00; N, 3.40%.

*4.2.4.10. Phenyl[2(2′-hydroxyphenyl-O)-4-(3′-cyclohexenyl)-6-methyl-8- quinolate-O′, N)]boron (**4f**).* Prepared from **2f** (0.80 g, 2.55 mmol) and sulfolene (0.90 g, 7.66 mmol) after heating for 12 h. The little compound decomposes extensively during chromatographic purification. M.p.: 249–250 °C, IR $\bar{\nu}_{max}$ (KBr) 3023, 2919, 1614, 1553, 1497, 1460, 1380, 1187, 1035, 974, 906, 751, 701 cm^{-1}. MS (70 eV) *m/z* (%) 417 (M^+, 0.2), 340 (100), 286 (73), 270 (9), 77 (9), 51 (7). ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.76 (1H, d, J = 7.7 Hz, H-14), 7.59 (1H, s, H-3), 7.51 (1H, t, J = 7.8 Hz, H-12), 7.36–7.33 (3H, m, H-11, *o*), 7.17 (1H, s, H-5), 7.15–7.11 (3H, m, H-*m*, *p*), 6.99 (1H, t, J = 7.7 Hz, H-13),

6.96 (1H, s, H-7), 5.88 (2H, s, H-17, 18), 3.66–3.59 (1H, m, H-15), 2.58 (3H, s, Me), 2.58–1.95 (6H, m, H-16, 19, 20). ^{13}C NMR (75 MHz, $CDCl_3$) δ:159.5 (C-4), 159.3 (C-4′), 157.3 (C-8), 156.5 (C-10), 144.4 (C-2), 142.3 (C-6), 135.1 (C-12), 134.6 (C-8a), 131.6 (C-*o*), 127.5 (C-*p*), 127.4 (C-*m*), 127.3, 125.9 and 125.7 (C-17, C-18), 125.1 (C-14, 4a), 121.7 (C-11), 120.1 (C-13), 119.1 (C-9), 114.4 (C-3), 114.2 (C-3′), 111.8 (C-7), 110.1 (C-5), 36.0 (C-15), 32.5 (C-19), 31.7 (C-19′), 28.8 (C-20), 28.2 (C-20′), 25.3 (C-16, C-16′), 23.6 (Me). ^{11}B NMR (96 MHz, $CDCl_3$) δ: 9.1 ppm ($h_{1/2}$ = 64 Hz). Anal. Calc. for $C_{28}H_{24}NO_2B$: C, 80.57; H, 5.75; N, 3.35. Found: C, 80.46; H, 5.91; N, 3.23%.

*4.2.4.11. Phenyl[2(2′-hydroxyphenyl-O)-4-(3′-cyclohexenyl)-6-nitro-8-quinolate-O′, N)]boron (**4g**).* Prepared from **2g** (1.00 g, 2.90 mmol) and sulfolene (1.03 g, 8.72 mmol) after heating for 12 h. The little compound decomposes extensively upon chromatographic purification. M.p.: 221–223 °C. IR $\bar{\nu}_{max}$ (KBr) 3021, 2919, 1608, 1553, 1498, 1338, 1314, 1251, 1192, 904, 863, 740 cm^{-1}. MS (70 eV) *m/z* (%) 448 (M^+, 0.2), 371 (100), 341 (21), 317 (49), 271 (56), 245 (7), 77 (3), 44 (16). ^{1}H NMR (300 MHz, $CDCl_3$) δ:8.45 (1H, d, J = 1.5 Hz, H-7), 7.89 (1H, d, J = 0.7 Hz, H-5), 7.88 (1H, d, J = 0.7 Hz, H-5′), 7.84 (1H, dt, J = 7.5, 1.8 Hz, H-14), 7.79 (1H, s, H-3), 7.78 (1H, s, H-3′), 7.64 (1H, dd, J = 7.5, 8.3 Hz, H-12), 7.39 (1H, d, J = 8.3 Hz, H-11), 7.35–7.33 (2H, m, H-*o*), 7.24–7.14 (3H, m, H-*m*, *p*), 7.09 (1H, t, J = 7.5 Hz, H-13), 5.93 (2H, s, H-17, 18), 3.77–3.65 (1H, m, H-15), 2.62–1.99 (6H, m, H-16, 19, 20). ^{13}C NMR (75 MHz, $CDCl_3$): 162.9 (C-4), 162.8 (C-4′), 158.2 (C-8), 157.1 (C-10), 150.4 (C-6), 148.8 (C-2), 138.7 (C-8a), 137.3 (C-12), 131.7 (C-*o*), 128.3 (C-*p*), 127.8 (C-*m*), 127.6 (C-17), 125.9 (C-14), 125.5 and 125.3 (C-18, 18′), 123.5 (C-4a), 123.4 (C-4a′), 122.1 (C-11), 120.9 (C-13), 118.6 (C-9), 116.4 (C-3), 116.2 (C-3′), 109.0 (C-7), 104.7 (C-5), 36.5 (C-15), 32.8 (C-19), 32.1 (C-19′), 29.0 (C-20), 28.5 (C-20′), 25.2 (C-16), 25.1 (16′). ^{11}B NMR (96 MHz, $CDCl_3$) δ:9.9 ppm ($h_{1/2}$ = 48 Hz). Anal. Calc.. for $C_{27}H_{21}$-N_2O_4B: C, 71.56; H, 4.81; N, 6.42. Found: C, 71.76; H, 4.89; N, 6.51%.

*4.2.4.12. p-Acetylphenyl[2(2′-hydroxyphenyl-O)-4-(3′-cyclohexenyl)-8-quinolate)-O′, N]boron (**4j**).* The compound was prepared as described previously heating for 26 h, and purified by column chromatography using hexane:ethyl acetate (95:5), it decomposes upon purification. M.p.: 230–231 °C. IR $\bar{\nu}_{max}$ (KBr) 1682, 1610, 1502, 1386,1254, 1180, 1037, 909, 820, 755, 703 cm^{-1}. MS (70 eV) *m/z* 430 (M^+–CH_3, 0.1), 327 (25), 326 (100), 325 (26), 273(18), 272 (90), 271(25). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (1H, dd, J = 8.0, 1.7 Hz, H-14), 7.78 (1H, dd, J = 8.0, 1.7 Hz, H-14′), 7.71 (1H, d, J = 8.4 Hz, H-*m*), 7.66 (1H, s, H-3), 7.65 (1H, s, H-3′), 7.58 (1H, t, J = 7.8 Hz, H-6), 7.53 (1H, dd, J = 8.4, 7.3 Hz, H-12), 7.42 (1H, d, J = 8.4 Hz, H-*o*), 7.41 (1H, d, J = 6.6 Hz, H-5), 7.33 (1H, d, J = 8.4 Hz, H-11), 7.12 (1H, d, J = 7.8 Hz, H-7), 7.02 (1H, dt, J = 7.3, 1.1 Hz, H-13), 5.88 (2H, s, H-17, 18) 3.68-3.60 (1H, m, H-15), 2.55-2.00 (6H, m H-16, H-19, H-20), 2.48 (3H, s, Me). ^{13}C NMR (100.53 MHz, $CDCl_3$) δ:198.8 (CO), 160.8 (C-4) 160.7 (C-4′), 157.2 (C-8), 156.2 (C-10), 145.5 (C-2), 136.3 (C-8a), 135.7 (C-12), 131.7 (C-*o*), 131.3 (C-6), 127.4 (C-17), 127.3 (C-*m*), 125.7 and 125.5 (C-18, C-18′), 125.3 (C-14 and C-4a), 121.7 (C-13), 120.4 (C-11), 118.9 (C-9), 114.4 (C-3), 114.2 (C-3), 111.1 (C-7), 110.3 (C-5), 36.2 (C-15), 32.3 (C-16), 31.8 (C-16′), 28.8 (C-19), 28.3 (C-19′), 26.6 (Me). 25.2 (C-20). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ: 8.0 ppm ($h_{1/2}$ = 64 Hz). Anal. Calc. for $C_{29}H_{24}NBO_3$: H, 5.43; C, 78.22; N, 3.15. Found: H, 5.57; C, 77.02; N, 3.06%.

4.2.4.13. Hydrolysis of 3,4-dihydroquinolines adducts. Equimolar quantities of the 3,4-dihydroquinoline adduct and NaOH were stirred 10 min in CH_2Cl_2. The yield was quantitative.

*4.2.4.14. [2(2′-Hydroxyphenyl]-4-ethenyl-5-tert-butyl-8-hydroxy-3,4-dihydroquinoline (**5b**).* The title compound was prepared from **3b** (0.20 g, 0.49 mmol) and NaOH (0.02 g, 0.49 mmol) to give 157 mg (99.5% yield) of **5b**. M.p.: 220–221 °C. IR $\bar{\nu}_{max}$ (KBr) 3443, 2963, 1601, 1529, 1495, 1257, 1142, 918, 823, 745, 559 cm^{-1}. MS (70 eV) *m/z* (%) 321 (M^+, 30) 306 (14), 294 (100), 276 (11), 228 (4), 91 (3), 77 (2). ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.56 (1H, d, J = 7.7 Hz, H-14); 7.29–7.18 (2H, m, H-12, 6), 6.90–6.79 (3H, m, H-11, 7, 13), 5.71 (1H, ddd, J = 16.8, 10.9, 5.2 Hz, H-15), 4.95 (1H, d, J = 10.3 Hz, H-16a), 4.68 (1H, d, J = 16.8 Hz, H-16b), 4.20 (1H, br, H-4), 3.35 (1H, d, J = 16.5 Hz, H-3a), 2.70 (1H, d, J = 6.2 Hz, H-3b), 1.38 (9H, s, C (CH_3)$_3$). Anal. Calc. for $C_{21}H_{23}NO_2$: C, 78.50; H, 7.16; N, 4.36. Found: C, 78.05; H, 7.43; N, 4.23%.

*4.2.4.15. [2(2′-Hydroxyphenyl]-4-ethenyl-5-tert-butyl-8-hydroxy-3,4-dihydroquinoline-**d**$_2$ (**5b-d**$_2$).* The sample undergoes deuterium exchange upon standing in deuterated methanol. MS (70 eV) *m/z* (%) 323 (M^+, 46), 308 (24), 296 (100), 278 (17), 264 (7), 229 (5), 115 (10), 83 (16), 57 (28), 41 (45). ^{1}H NMR (300 MHz, methanol-d_4) δ:7.67 (1H, dd, J = 8.5, 1.6 Hz, H-14); 7.28 (1H, ddd, J = 8.5, 7.3, 1.6 Hz, H-12), 7.16 (1H, d, J = 8.9 Hz, H-6), 6.78 (1H, d, J = 8.5 Hz, H-11), 6.72 (1H, d, J = 8.9 Hz, H-7), 6.63 (1H, t, J = 7.3 Hz, H-13), 5.85 (1H, ddd, J = 16.0, 10.8, 4.4 Hz, H-15), 4.96 (1H, dd, J = 10.1, 1.5 Hz, H-16a), 4.71 (1H, dd, J = 16.0, 1.4 Hz, H-16b), 4.33 (1H, dd, J = 2.2, 4.4 Hz, H-4), 1.39 (9H, s, C

(CH_3)$_3$). ^{13}C NMR (75 MHz, methanol-d_4) δ: 171.7 (C-2), 163.9 (C-10), 154.1 (C-8), 138.4 (C-15), 134.2 (C-12), 133.8 (C-5), 128.3 (C-14), 127.5 (C-4a), 126.8 (C-8a), 126.2 (C-6), 121.3 (C-11), 116.2 (C-9), 116.1 (C-7), 115.3 (C-16), 114.5 (C-13), 34.9 (C-4), 34.4 (C-3), 31.7 $C(CH_3)_3$), 31.3 $C(CH_3)_3$).

*4.2.4.16. [2(2′-Hydroxyphenyl]-4-ethenyl-5-chloro-8-hydroxy-3,4-dihydroquinoline (**5d**).* The title compound was prepared from **3d** (0.20 g, 0.52 mmol) and NaOH (0.02 g, 0.49 mmol) to give 152 mg (98% yield) of **5d**. M.p.: 209–210 °C. IR $\bar{\nu}_{max}$ (KBr) 3443, 3077, 1601, 1535, 1478, 1288, 1141, 916, 813, 741, 561 cm^{-1}. MS (70 eV) *m*/*z* (%) 299 (M^+, 20), 272 (100), 244 (5), 237 (3), 91 (5). ^{1}H NMR (400 MHz, methanol-d_4) δ: 7.80 (1H, dd, J = 8.1, 1.5 Hz, H-14); 7.35 (1H, ddd, J = 8.4, 7.6, 1.5 Hz, H-12), 7.13 (1H, d, J = 8.8 Hz, H-6), 6.90 (1H, d, J = 8.4 Hz, H-11), 6.88 (1H, dd, J = 8.1, 7.6, 1.0 Hz, H-13), 6.84 (1H, d, J = 8.8 Hz, H-7), 5.77 (1H, ddd, J = 17.1, 10.5, 5.7 Hz, H-15), 4.96 (1H, dt, J = 10.5, 1.3 Hz, H-16a), 4.82 (1H, dt, J = 17.1, 1.3 Hz, H-16b), 4.03 (1H, d, J = 5.7, 7.4, 1.3 Hz, H-4), 3.63 (1H, dd, J = 1.3, 17.2 Hz, H-3a), 2.74 (1H, dd, J = 7.4, 17.2 Hz, H-3b), ^{13}C NMR (75 MHz, methanol-d_4) δ:166.9 (C-2), 163.4 (C-10), 150.3 (C-8), 135.7 (C-15), 133.1 (C-12), 129.5 (C-8a), 128.1 (C-14), 127.9 (C-6), 127.1 (C-4a), 122.8 (C-5), 118.8 (C-9), 118.1 (C-11), 117.9 (C-13), 115.3 (C-7), 114.4 (C-16), 34.7 (C-4), 27.2 (C-3). Anal. Calc. for $C_{17}H_{14}NO_2Cl$: C, 68.11; H, 4.70; N, 4.67. Found: C, 67.98; H, 5.01; N, 4.56%.

*4.2.4.17. [2(2′-Hydroxyphenyl]-4-ethenyl-5-chloro-8-hydroxy-3,4-dihydroquinoline-d_2 (**5d-d_2**).* The sample undergoes deuterium exchange upon standing in deuterated methanol. ^{1}H NMR (400 MHz, methanol-d_4) δ:7.78 (1H, dd, J = 8.0, 1.5 Hz, H-14); 7.34 (1H, ddd, J = 8.6, 7.7, 1.5 Hz, H-12), 7.12 (1H, d, J = 8.7 Hz, H-6), 6.90 (1H, d, J = 8.6 Hz, H-11), 6.87 (1H, dd, J = 8.0, 7.7 Hz, H-13), 6.82 (1H, d, J = 8.7 Hz, H-7), 5.76 (1H, ddd, J = 17.2, 10.4, 5.5 Hz, H-15), 4.95 (1H, dt, J = 10.4, 1.4 Hz, H-16a), 4.81 (1H, dt, J = 17.2, 1.4 Hz, H-16b), 4.01 (1H, d, J = 5.5 Hz, H-4).

5. Supplementary material

For compounds **2b**, **3b**, **3d**, **3e**, **3h**, **3i**, and **4c** full crystallographic data were submitted as CIF files with the Cambridge Crystallographic Data Center, CCDC Nos. for **2b**, 257175 for **3b**, 257176 for **3c**, 257177 for **3h**, 257178 for **3i**, 257179 for **4c** 257180 and for **4d**, 257181 CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: www:http://www.ccdc.cam.ac.uk).

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References

[1] (a) A. Kumar, Chem. Rev. 101 (2001) 1;
(b) K.A. Jörgensen, Angew. Chem. Int. 39 (2000) 3558;
(c) J. Sauer, R. Sustmann, Angew. Chem. Int. 19 (1980) 779;
(d) S. Danishefsky, N. Kato, D. Askin, J.F. Kerwin, J. Am. Chem. Soc. 104 (1982) 360.
[2] G. Babu, P.T. Perumal, Tetrahedron Lett. 39 (1998) 3225.
[3] J. Collin, N. Jaber, M.I. Lannou, Tetrahedron Lett. 42 (2001) 7405.
[4] B. Crousse, J.P. Bégué, D. Bonnet-Delpon, J. Org. Chem. 65 (2000) 5009.
[5] Kobayashi, H. Isthiani, S. Nagayama, Synthesis (1995) 1195.
[6] T. Akiyama, J. Takaya, H. Kagoshima, Tetrahedron Lett. 40 (1999) 7831.
[7] M.V. Spanedda, V.D. Hoang, B. Crousse, D. Bonnet-Delpon, J.-P. Bégué, Tetrahedron Lett. 44 (2003) 217.
[8] (a) D.L. Boger, S.M. Weinreb, Hetero Diels–Alder Methodology in Organic Synthesis, Academic Press, San Diego, 1987 (Chapters 2 and 9);
(b) P. Buonora, J.-C. Olsen, T. Oh, Tetrahedron 57 (2001) 6099.
[9] (a) J. Hamer, 1–4 Cycloaddition Reactions: the Diels–Alder Reaction in Heterocyclic Synthesis, Academic Press, New York, 1967 (Chapter 5);
(b) M. Behforouz, M. Ahmadian, Tetrahedron 56 (2000) 5259, and reference [7] (chapter 9).
[10] V. Lucchini, M. Prato, G. Scorrano, P. Tecilla, J. Org. Chem. 53 (1988) 2251.
[11] S. Hermitage, D.A. Jay, A. Whiting, Tetrahedron Lett. 43 (2002) 9633.
[12] S. Hermitage, J.A.K. Howard, D. Jay, R.G. Pritchard, M.R. Probert, A. Whiting, Org. Biomol. Chem. 2 (2004) 2451.
[13] (a) O. Wiest, E. Steckhan, Angew. Chem. Int. Ed. Engl. 32 (1993) 901;
(b) C.F. Gürtler, S. Blechert, E. Steckhan, Angew. Chem. Int. Ed. Engl. 34 (1995) 1900;
(c) J. Xiandong, L. Hechun, H. Congde, Z. Wei, L. Jianming, Y. Li, Z. Guangyu, L. Zhong-Li, Synlett. (2003) 1707.
[14] V. Barba, D. Cuahutle, R. Santillan, N. Farfán, Can. J. Chem. 79 (2001) 1229.
[15] H. Nöth, B. Wrackmeyer, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, Springer Verlag, Berlin, New York, 1978.
[16] N. Farfán, H. Höpfl, R. Santillan, Main Group Chem. New 7 (1999) 3.
[17] H. Höpfl, J. Organomet. Chem. 581 (1999) 129.
[18] T. Lomberget, I. Chataigner, D. Bouyssi, J. Maddaluno, G. Balme, Tetrahedron Lett. 45 (2004) 3437.
[19] H. Günther, NMR Spectroscopy, Basic Principies, Concept and Applications in Chemistry, second ed., Wiley, New York, 1995, pp. 519 and 521.

[20] H. Höpfl, V. Barba, G. Vargas, N. Farfán, R. Santillan, D. Castillo, Chem. Heterocycl. Compd. 35 (1999) 912–1999.
[21] Q. Wu, M. Esteghamatian, N.-X. Hu, Z. Popovic, G. Enrigh, Y. Tao, M. D'Iorio, S. Wang, Chem. Mater. 12 (2000) 79.
[22] M.A. McCarrick, Y.-D. Wu, K.N. Houk, J. Org. Chem. 58 (1993) 3330.
[23] F. Linkert, S. Laschat, S. Kotila, T. Fox, Tetrahedron 52 (1996) 955.
[24] P.B. Karadakov, D.L. Cooper, J. Gerratt, J. Am. Chem. Soc. 120 (1998) 3975.
[25] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.