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Synthesis, NMR and X-Ray Diffraction Analysis of Boron Complexes Derived from Hydroxychalcones

Horacio Reyes,[1] Ma. Concepción García,[1] Blanca M. Flores,[1] Héctor López-Rebolledo,[1]
Rosa Santillán,[1] Norberto Farfán*[2]

[1] Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional,
Apdo. Postal 14-740, 07000 México D.F., México
[2] Departamento de Química Orgánica, Facultad de Química, Universidad Nacional Autónoma de México, Circuito Escolar,
Ciudad Universitaria, México 04510, D. F.

Dedicated to Prof. Pedro Joseph-Nathan on the occasion of his 65th birthday.

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Abstract. The synthesis of a series of "push-pull" boron complexes obtained by reaction of hydroxychalcones with borontrifluoride etherate and diphenylboronic acid is described. These derivatives have potential application in non-linear optics, since they present a conjugated π system, a boron atom which can act as acceptor and a donor substituent at the *para* position.

Keywords: Boron complexes, hydroxychalcones, diphenylboronic acid

Resumen. El presente trabajo describe la síntesis de una serie de complejos de boro "push-pull" preparados por reacción de hidroxichalconas con trifluoroboro eterato y ácido difenilborónico. Estos complejos podrían tener buenas propiedades de óptica no lineal, ya que presentan un sistema π, un átomo de boro que puede actuar como el grupo aceptor y el sustituyente en la posición *para* que actúa como el grupo donador

Palabras clave: Complejos de Boro, hidroxichalconas, ácido difenilborónico

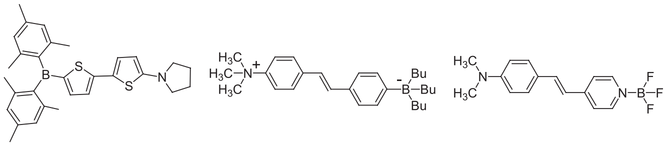
At present there is great interest in materials with high nonlinear optical (NLO) responses both from the scientific and technological points of view [1]. Although inorganic solids such as $LiNbO_3$ and KH_2PO_4 have traditionally attracted the widest attention [2], it has recognized that molecular materials possess superior NLO characteristics such as faster response times, lower dielectric constants, and enhanced NLO responses [3]. Along this line, chalcones which are naturally occurring substances with fungicidal [4], antibacterial [5] and carcinogenic [6] activities, as well as potent antiplatelet agents [7] have been recently used as NLO materials [8] due to the fact that they exhibit fluorescent properties as sensors [9].

The 2'-hydroxychalcones, in particular, have been widely used in coordination chemistry with different metals such as Co(II), Ni(II), Cu(II) [10], Sn(IV) [11] and Te(IV) [12]. Moreover, the efficiency of the 2'-hydroxychalcones to form complexes has been used to identify different metal cations like U(VI) [13], Ge(IV) [14], Al(III) [15], Eu(III) [16] and Be(II) [17].

Although organoboron compounds have received considerable attention for their interesting applications in medicinal chemistry, as anticancer agents, in Boron Neutron Capture Terapy (BNCT) [18], in organic synthesis and [19] as materials with fluorescence [20], the literature concerning organoboron complexes with NLO properties is scarce. In this respect the boron atom has been used in three different forms due to the fact that it shows excellent properties as electronaceptor (**1**) [21, 22], as zwiterionic complex (**2**) [23] and as acid base adduct with BF_3 (**3**) and $B(C_6F_5)_3$ [24, 25] (Scheme 1).

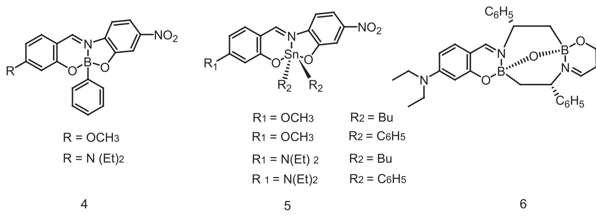
In a previous paper, we reported a series of "pull-pull" boronates, in which the possibility of switching NLO properties taking advantage of the rotation of the phenyl ring attached to the boron atom was studied using a semiempirical approach [26] (**4**). This study showed that the NLO skeleton of the boron derivatives was invariably bent, leading to chromophores with reduced NLO response. In order to overpass this difficulty we extended our studies to the synthesis of a series of tin compounds [27] (**5**), which exhibited, in average, 50 % better NLO response than the boron analogues giving values in the range of metal organic NLO materials. Also, we reported the NLO properties of a chiral oxobridged borate [28] (**6**), that possesses two chromophores and shows twice the NLO response (Scheme 2).

Continuing our investigations on boronates we describe herein the formation of "push-pull" boron complexes derived from chalcones. These derivatives present a π system, a boron atom which can act as acceptor and a substituent at the *para* position acting as the donor atom with potential NLO properties.

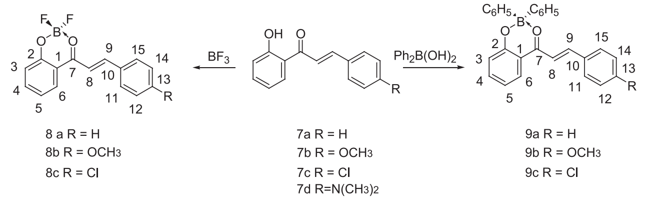


1 2 3

Scheme 1



Scheme 2



Scheme 3

Preparation of 2'-hydroxychalcones **7a**-**7d** **[**29**],** and the corresponding boron complexes **8a** **[**30a] and **8b** **[**30b] was carried out as described in the literature.

The difluoro- **8a**-**8c** and diphenylboronates **9a**-**9c** were synthesized by reaction of hydroxychalcones **7a**-**7c** with boron triflouride diethyl etherate in anhydrous ethyl ether and diphenylboronic acid in benzene, respectively (Scheme 3). The latter was obtained by HCl treatment from the corresponding 2-aminoethyl complex. In the case of the *N*,*N*-dimethyl substituted hydroxychalcone, the reaction provided a complex mixture of compounds due to the fact that the amine group reacted with the boron Lewis acid. Also the use of a 2:1 ratio of BF_3 to the chalcone led to a very unstable product.

The existence of the oxygen boron coordination bond in compounds **8a**-**8c** and **9a**-**9c** was established by ^{11}B NMR (Table 1), which shows the characteristic signal in the range, from 0.2 to 0.4 ppm for the difluoro derivatives (**8a**-**8c**) and between 8.7 - 9.5 ppm for **9a**-**9c**. In the case of compounds **8a**-**8c** the ^{19}F NMR chemical shifts were in the range of 141.8 to -145.3 ppm.

The mass spectra show the molecular ion, and the fragments corresponding to the loss of fluorine and phenyl groups for compounds **8a**-**8c** and **9a**-**9c,** respectively.

The IR data (Table 1) show a 15-20 cm^{-1} shift of the carbonyl band in the boron complexes (1620-1625 cm^{-1}) with respect to the 2'-hydroxychalcones (1640 cm^{-1}), due to the coordination of the boron atom to oxygen.

Formation of the complexes increases delocalization as evidenced by the fact that the hydroxychalcones are yellow crystals while the complexes are red. The UV spectra confirm this fact and provides insight into the NLO properties. Table 1 summarizes these data for compounds **7a**-**7c**, **8a**-**8c** and **9a**-**9c** in chloroform. Comparison of the values for the hydroxychalcones (**7a**-**7c**) with those of the boron complexes shows a red shift and an increase in intensity which evidences their potential as NLO materials. It is important to mention that the red-colored solution turns yellow within 24 h due to the formation of the starting hydroxylchalcones. The UV spectra confirmed the complete hydrolysis of the boron complex within 40 to 80 min.

Table 2 summarizes the ^{1}H NMR data for hydroxychalcones **7a**-**7c** and the boron complexes **8a**-**8c** and **9a**-**9c**. Comparison of the chemical shifts of the two derivatives shows that upon complexation the signals are slightly shifted to higher frequencies ($\Delta\delta$ = 0.15), the H-9 vinyl proton shifts an average of 0.60 ppm and 0.45 ppm in **8a**-**8c** and **9a**-**9c,** respectively, indicating an important contribution from the resonance structure that has delocalization of the positive charge in the π system [figure 1 (C)]. These results show that fluorine compounds have a larger effect than the diphenyl derivatives, due to the electronegativity of the fluorine atom. Unambiguous assignment of the ^{1}H NMR spectra was based on COSY spectra.

As shown by the UV experiments, the boron derivatives decompose in solution; moreover, they are only slightly solu-

Table 1. ^{11}B NMR , IR, UV data, IR for compounds **7a**-**7c,** **8a**-**8c** and **9a**-**9c**

Compound	^{11}B NMR δ (ppm)	IR (cm^{-1}) C=O	IR (cm^{-1}) C=C	UV λ_{max} (nm)	UV $\varepsilon(dm^3mol^{-1}cm^{-1})$
7a	—-	1640	1574	317	18664
7b	—-	1640	1565	366	24229
7c	—-	1640	1564	323	22596
8a	0.3	1621	1561	375	19491^a
8b	0.2	1620	1555	455	34802^a
8c	0.4	1621	1556	381	18677^a
9a	9.0	1623	1557	365	27913^a
9b	9.5	1625	1554	410	27354^a
9c	8.7	1625	1553	410	29491^a

a) decomposes in solution

Table 2. ^{1}H NMR data for compounds **7a**-**7c**, **8a**-**8c**, and **9a**-**9c** (δ, $CDCl_3$)

	H-3	H-4	H-5	H-6	H-8	H-9	H-11,15	H-12,14	OH
7a	7.04	7.50	6.95	7.94	7.66	7.94	7.67	7.43-7.45	13.00
7b	7.01	7.46	6.90	7.90	7.53	7.89	7.61	6.94	12.94
7c	7.04	7.51	6.96	7.91	7.63	7.87	7.60	7.41	12.76
8a	7.17	7.59	7.07	7.97	7.66	8.51	7.79	7.54	—
8b	7.14	7.70	6.94	7.92	7.47	8.49	7.76	7.01	—
8c	7.20	7.81	6.97	7.96	7.89	8.47	7.74	7.52	—
9a	7.16	7.59-7.62	6.80	7.59-7.62	7.52	8.38	7.70-7.77	7.48-7.57	—
9b	7.12	7.45-7.72	6.78	7.45-7.72	7.39	8.35	7.45-7.72	7.00	—
9c	7.15	7.50-7.56	6.81	7.67	7.53	8.31	7.58	7.47	—

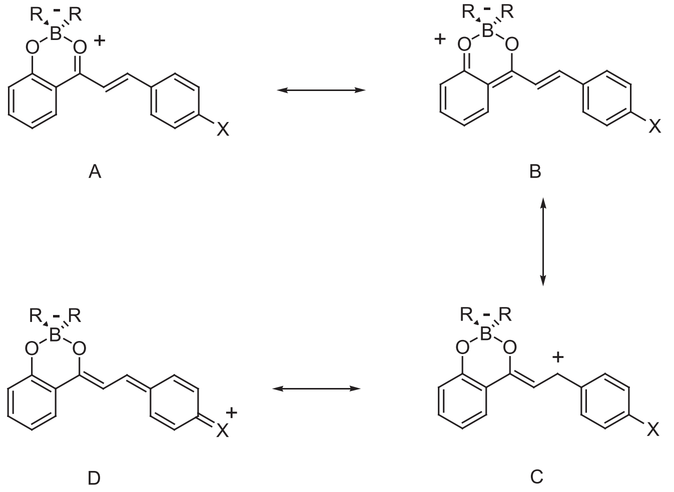


Fig. 1. Resonance structures for BR_2 complexes.

ble in $CDCl_3$ and the determination of the ^{13}C NMR spectra in DMSO-d_6 led to decomposition within a few minutes. For this reason, only the ^{13}C NMR spectra of two diphenyl derivatives (**9a** and **9b**) were obtained (Table 3).

The X-ray structures (Figures 2 and 3) confirmed that the boron atom is coordinated to the oxygen of the carbonyl group to form a six-membered ring. The newly formed ring has a half-chair conformation, the O1-C2-C1-C7-O2 fragment is planar and the boron atom is deviated out of the plane. The differences in the C2-O1 and C7-O2 bond lengths range from 0.038-0.0018 Å (Table 5). The crystallographic data of **8b**, **8c**, **9a** and **9c,** as well as the hydroxychalcone **7b** is given in Table 4. Selected bond length and angles are shown in Tables 5 and 6, respectively.

The values for the tetrahedral character (THC) [31] of the boron atoms are 88 %, and 89 % for fluorine derivatives (**8b**, **8c**) and 76 % and 82% for **9a** and **9c,** respectively. These values indicate a larger distortion for the boron atom in the derivative containing two phenyl groups in the six-membered ring diphenyl derivatives (C-B-C 118.13° and 115.20°) compared to the fluorine derivatives F-B-F bond angles (111.06° and 110.9°) and can be attributed to ring strain.

It is important to note the electronic influence of the substituent at C-13, as evidenced upon comparison of the C7-C8 and C9-C10 bond lengths which is 0.1 Å in average shorter than the normal C-C bond (1.54 Å). These results confirm ð delocalization in these complexes.

At present, the synthesis of a chalcone containing an asymmetric carbon to induce crystallization in a noncentrosymmetric group, as well as more stable metal complexes similar to those described in the literature [10-17, 32] is underway in order to improve the NLO properties.

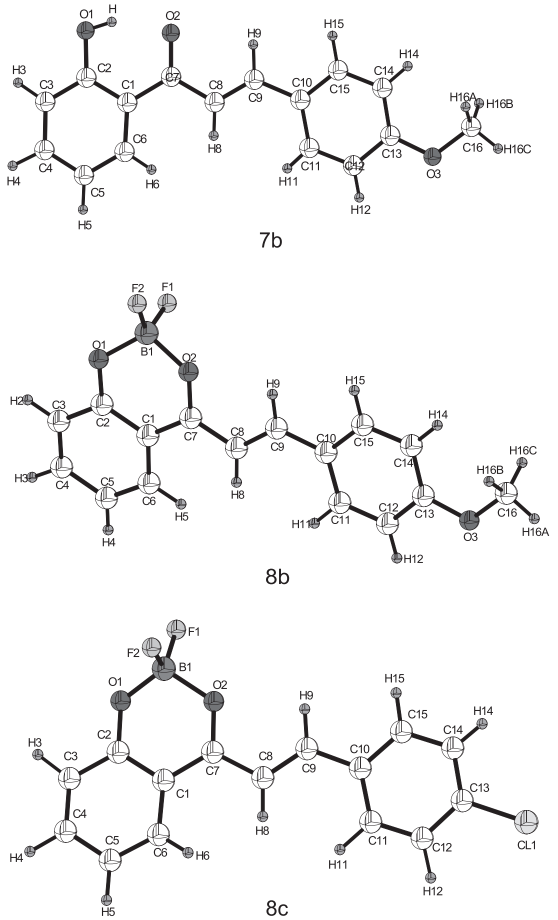
Conclusions

The spectroscopic data show that boron complexes of chalcones (**8a-8c** and **9a-9c**) are good candidates for NLO properties, since they exhibit a delocalized "push-pull" system.

Table 3 ^{13}C NMR data for compounds **9a** and **9b** in $CDCl_3$

	C-1	C-2	C-3	C-4	C5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13
7a	119.9	163.5	118.7	136.2	119.9	129.6	193.5	118.4	145.2	134.4	128.9	128.5	130.8
7b	120.2	163.6	118.7	136.1	117.6	129.5	193.7	118.6	145.4	127.4	130.5	114.4	162.1
9a[a]	120.2	167.0	122.0	141.9	119.2	129.9	187.6	117.0	151.2	134.8	129.9	129.5	132.9
9b[b]	119.0	166.5	121.9	141.2	118.9	128.4	187.1	114.2	151.3	128.0	129.6	115.0	163.8

a) C_{ortho}= δ 132.1, C_{meta}= δ 127.3, C_{para}= δ 126.6. *b*), C_{ortho} = δ 132.1, C_{meta} = δ 127.2, C_{para} = δ 126.5.

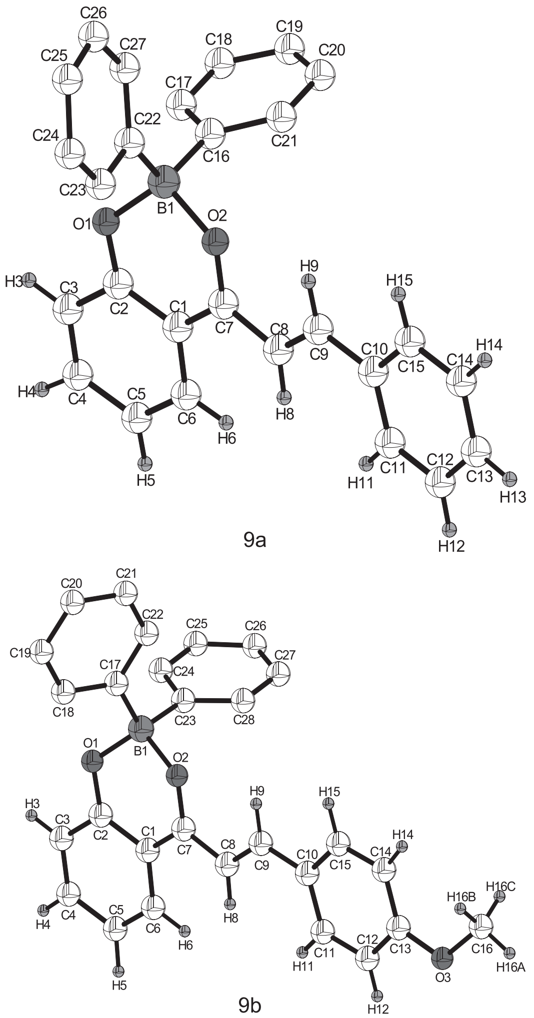


7b

8b

8c

Fig. 2. Crystal structures of compounds **7b, 8b** and **8c**



9a

9b

Fig. 3. Crystal structures of compounds **9a** and **9b**

Table 4. Crystal data for compounds **7b, 8b, 8c, 9a** and **9b**.

	7b	**8b**	**8c**	**9a**	**9b**
Chemical formula	$C_{16}H_{14}O_3$	$C_{16}H_{13}BF_2O_3$	$C_{15}H_{10}BClF_2O_2$	$C_{27}H_{21}BO_2$	$C_{31}H_{26}BO_3$
Formula weight	254.27	302.07	304.47	388.25	457.33
Crystal system	Ortorhombic	Monoclínic	Monoclínic	Monoclínic	Monoclínic
Space group	P c a 2	P 21/c	P 21/c	C 2/c	P 21/n
A (Å)	25.271(5)	8.050 (2)	8.146 (2)	30.805 (6)	12.5308 (4)
B (Å)	4.0516(8)	12.570 (3)	13.099 (3)	6.8120 (10)	8.5465 (3)
C (Å)	12.659(3)	14.200 (3)	13.195 (3)	20.515 (4)	23.5386 (8)
α (°)	90	90	90	90	90
Â (°)	90	104.28 (3)	104.76 (3)	92.12 (3)	103.2950 (10)
γ (°)	90	90	90	90	90
V (A3)	1296.1(4)	1392.5 (6)	1361.5 (6)	4302.0 (13)	2453.29 (14)
Temperature (K)	293(2)	293 (2)	293 (2)	293 (2)	293 (2)
Z	4	4	4	8	4
No. of collected reflections	2648	5379	5224	12585	9604
No.of Independent reflections	2648	3128	3025	4070	5505
R	0.0406	0.0457	0.0467	0.0458	0.0571
Rw	0.0846	0.0720	0.0838	0.0880	0.1419
No. of parameters	229	252	231	356	409

Tabla 5. Selected bond length (Å) for compounds **7b**, **8b**, **8c**, **9a** and **9b**.

	7b	**8b**	**8c**	**9a**	**9b**
O(1)-C(2)	1.347 (3)	1.340 (2)	1.332 (3)	1.3243 (19)	1.329 (2)
C(2)-C(1)	1.402 (3)	1.409 (2)	1.417 (3)	1.410 (2)	1.409 (3)
C(1)-C(7)	1.473 (3)	1.436 (2)	1.428 (3)	1.434 (2)	1.433 (3)
C(7)–O(2)	1.246 (3)	1.294 (18)	1.285 (2)	1.2761 (18)	1.291 (3)
C(7)–C(8)		1.434 (2)	1.445 (3)	1.452 (2)	1.440 (3)
C(8)-C(9)	1.327 (3)	1.350 (2)	1.338 (3)	1.330 (2)	1.331 (4)
C(9)-C(10)	1.425 (3)	1.444 (2)	1.455 (3)	1.454 (2)	1.446 (3)
C(10)-C(11)	1.400 (3)				
C(11)-C(12)	1.367 (3)				
B(1)–O(1)	—-	1.445 (2)	1.444 (3)	1.495 (2)	1.493 (3)
B(1)–O(2)	—-	1.504 (2)	1.506 (3)	1.570 (2)	1.561 (3)

Table 6. Selected bond angles (°) for compounds **7b, 8b**, **8c**, **9a** and **9b**

	8b	**8c**		**9a**	**9b**
F(1)-B(1)-F(2)	111.06 (15)	110.9 (2)	C(22)-(B1)-C(16)	118.13 (14)	115.20 (19)
F(1)-B(1)-O(1)	111.19 (14)	110.03 (18)	O(1)-B(1)-C(22)	107.95 (13)	109.10 (2)
F(2)-B(1)-O(1)	110.14 (15)	111.0 (2)	O(1)-B(1)-C(16)	111.30 (14)	111.58 (19)
F(1) –B(1)-O(2)	106.75 (14)	107.03 (19)	O(2)-B(1)-C(22)	105.57 (14)	106.50 (18)
F(2)-B(1)-O(2)	106.83 (13)	106.95 (17)	O(2)-B(1)-C(16)	106.36 (13)	106.88 (19)
O(1)-B(1)-O(2)	110.73 (14)	110.77(18)	O(1)-B(1)-O(2)	106.83 (12)	107.13 (18)
B(1)-O(1)-C(2)	119.98 (16)	119.33 (13)	B(1)-O(1)-C(2)	121.12 (13)	119.30 (18)
B(1)-O(2)-C(7)	123.09 (16)	122.63 (13)	B(1)-O(2)-C(7)	123.14 (13)	121.43 (18)
	7b			**7b**	
O(1)-C(2)-C(1)	122.01(19)		C(2)-C(1)-C(7)	119.74(18)	
C(1)-C(7)-O(2)	119.69(18)		O(2)-C(7)-C(8)	119.72(19)	
C(8)-C(9)-C(10)	127.90(2)		C(10)-C(11)-C(12)	121.8(2)	

Unfortunately, the complexes studied herein decomposed in solution, and in the solid state they crystallized in centrosymmetric space groups, therefore the NLO properties are canceled.

Experimental Section

Starting Materials and Equipment

All starting materials were purchased from Aldrich Chemical Co. Solvents were used without further purification. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected. Infrared spectra were measured on a Perkin-Elmer 16F-PC FT-IR spectrometer. ^{1}H and ^{13}C-NMR spectra were recorded on Jeol GX 270 and Jeol Eclipse + 400 spectrometers. Chemical shifts (δ, ppm) are relative to $(CH_3)_4Si$ for ^{1}H and ^{13}C and to $BF_3(OEt_2)$, for ^{11}B. Mass spectra were obtained on a HP 5989A spectrometer. UV spectra were recorded on a Perkin-Elmer Lambda 12 UV/VIS spectrophotometer. Elemental analyses were carried out on a Thermo Finnigan Flash 1112 elemental analyzer.

Structure Analysis and Refinement

In all cases, the single crystals suitable for X-ray structural studies were obtained by slow evaporation from mixtures of CH_2Cl_2 and hexane. The crystal data were recorded on an Enraf Nonius Kappa-CCD ($l_{MoK}a$=0.71073 Å, graphite monochromator, T=293 K, CCD rotating images scan mode). The crystals were mounted on a Lindeman tube. Absorption corrections were performed within the SHELX [32] program or by the semiempirical correction through MULTISCAN procedure (PLATON) [34]. All reflection data set were corrected for Lorentz and polarization effects. The first structure solution was obtained using the SHELXS-97 program and then SHELXL-97 ver. 34 program was applied for refinement and output data [33]. All software manipulations were done under the WIN-GX [35] environment program set. Molecular perspectives were drawn under ORTEP 3 [36] drawing application. All heavier atoms were found by Fourier map difference and refined anisotropically. Some hydrogen atoms were found by Fourier maps differences and refined isotropically. The remaining hydrogen atoms were geometrically modeled and not refined.

The preparation of the 2'-hydroxychalcone (**7a**), 4-methoxy-2'-hydroxychalcone (**7b**), 4-chloro-2'-hydroxychalcone (**7c**), 4-dimethylamino-2'-hydroxychalcone (**7d**) were performed as described in the literature [29]. Boron, difluoro[1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-oato-O,O'] (**8a**) and boron, difluoro[1-(2-hydroxyphenyl)-3-(4-methoxyphenyl-2-propen-1-oato-O,O'] (**8b**) have been described in the literature [30].

General method for the preparation of 2,2-difluorodioxaborinates 8a-8c

Equimolecular quantities of the 2'-hydroxychalcone (**7a-7c)** and boron trifluoride were added slowly in anhydrous ethyl ether and the solution was allowed to stand overnight to give a solid which was filtered and washed with ethyl ether.

Boron, difluoro[1-(2-hydroxyphenyl)-3-phenyl-2-propeno-1-ato-O,O'] (8a). Compound **8a** was prepared from 0.220 g (1.00 mmol) of 2'-hydroxychalcone and 0.12 mL (1.00 mmol of boron trifluoride to give yellow crystals in 78 %, yield (0.206 g), mp 247-251 °C (Lit. [30a] 247-251 °C). The IR and some NMR data is given in reference 30a .^{1}H NMR (400 MHz, $CDCl_3$), [δ, ppm]: 7.07 (1H, t, *J* = 8.1 Hz, H-5), 7.17 (1H, d, *J* = 8.1 Hz, H-3), 7.51 (1H, s, H-13), 7.54 (2H, d, *J* = 8.12 Hz, H-12, H-14), 7.59 (1H, d, *J* = 7.26 Hz, H-4), 7.66 (1H, d, *J* = 15.4 Hz, H-8), 7.79 (2H, d, *J* = 8.12 Hz, H-11, H-15), 7.97 (1H, dd, *J* = 7.26 Hz, H-6), 8.51 (1H, d, *J* = 15.4 Hz, H-9). ^{11}B NMR (128.26 MHz, $CDCl_3$), [δ, ppm]: 0.3 ($h_{1/2}$ = 36.2 Hz). MS *m/z* (%): 272 (M^+, 8.1), 271 (100), 253 (9), 207 (2.8), 195 (5.4), 178 (1.0), 169 (1.9), 141 (7), 131 (1.9), 103 (2.7), 77 (6). Anal calcd for $C_{15}H_{11}BF_2O_2$, C 66.32%, H 4.15%. Found C 66.22 %, H 4.08 %

Boron, difluoro[1-(2-hydroxyphenyl)-3-(4-methoxyphenyl-2-propenoato-O,O'] (8b). Compound **8b** was prepared from 0.250 g (1.00 mmol) of 2'-hydroxy-4-methoxychalcone and 0.12 ml (1.00 mmol) boron trifluoride, the product was obtained as red crystals (0.218 g) in 74 % yield, mp 227-230 °C. IR ν_{max} (KBr) 3061, 1620 (C=O), 1555 (C=C), 1500, 1432, 1407, 1301, 1245, 1034, 933, 890, 830, 759, 703, 658, 553,513 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$), [δ, ppm]: 3.91 (3H, s, OCH_3), 6.94 (1H, d, *J* = 8.4 Hz, H-5), 7.00 (2H, d, *J* = 8.6 Hz, H-12, H-14), 7.14 (1H, d, *J* = 8.4 Hz, H-3), 7.47 (1H, d, *J* =15.1 Hz, H-8), 7.70 (1H, t, *J* = 7.4 Hz, H-4), 7.76 (2H, d, *J* = 8.6 Hz, H-11, H-15), 7.92 (1H, d, *J* = 7.4 Hz, H-6), 8.49 (1H, d, *J* = 15.1 Hz, H-9). ^{11}B NMR (86.68 MHz, $CDCl_3$), [δ, ppm]: 0.2 ($h_{1/2}$ = 28.9 Hz). MS *m/z* (%): 302 (M^+, 100), 271 (26.3), 254 (10.1), 237 (33.7), 195 (15.4), 161 (29.1), 133 (21.8), 108 (11.5). Anal calc for $C_{16}H_{13}BF_2O_3$, C 63.72%, H 4.15 %. Found C 63.62 %, H 4.34 %,

Boron, difluoro[1-(2-hydroxyphenyl)-3-(4-chlorophenyl)-2-propenoato-O,O'] (8c). Compound **8c** was prepared from 0.250 g (1.00 mmol) of 4-chloro-2'-hydroxychalcone and 0.12 ml (1.00 mmol) of boron trifluoride, the product was obtained as orange crystals, 0.190 g in 74 % yield mp: 262-264 °C. IR õ$_{max}$ (KBr) 3088, 1621 (C=O), 1556 (C=C), 1511, 1478, 1415, 1391, 1319, 1261, 1245, 1154, 1087, 1038, 984, 923, 889, 868, 825, 758, 705, 644, 565, 493 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$), [δ, ppm]: 6.97 (1H, t, *J* = 7.9 Hz, H-5), 7.20 (2H, d, *J* = 8.8 Hz, H-3), 7.52 (3H, m, H-8, H12, H14), 7.74 (2H, d, *J* = 8.4 Hz, H-11, H-15), 7.81 (1H, t, *J* = 8.8 Hz, H-4), 7.96 (1H, m, H-6), 8.47 (1H, d, *J* = 15.4 Hz, H-9). ^{11}B NMR (128.26 MHz, $CDCl_3$), [δ, ppm]: 0.4 ($h_{1/2}$= 64.1 Hz). MS *m/z* (%): 306 (M^+,100), 271 (38.3), 241 (46.7), 205 (6.6), 195 (72.7), 169 (33.9), 137 (21.5), 102 (14.3). Anal calcd for $C_{15}H_{10}BClF_2O_2$, C 58.92 %, H 3.25%. Found C 58.78 %, H 3.29%.

General method for the preparation of 2,2-diphenyldioxaborinanes 9a-9c.

Equimolecular quantities of the 2'-hydroxychalcone (**7a-7c**) and diphenylborinic acid were added slowly in ethyl benzene. The reaction mixture was refluxed for 2 h using a Dean-Stark trap and crystallized.

Boron, diphenyl[1-(2-hydroxyphenyl)-3-phenyl-2-propenato-O,O'] (9a). Compound **9a** was prepared from 0.220 g (1.0 mmol) the 2'-hydroxychalcone and 0.180 g (1.0 mmol) of diphenyl borinic acid, the product was obtained as red crystals, 0.134 g in 78 % yield, mp: 217-219 °C. IR ν_{max} (KBr) 3008, 1623 (C=O), 1557 (C=C), 1516, 1471, 1390, 1310, 1255, 1232, 1208, 1148, 1053, 1026, 948, 886, 745, 700, 657, 512 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$), [δ, ppm]: 6.68 (1H, t, *J* = 7.6 Hz, H-5), 7.16 (1H, d, *J* = 8.6 Hz, H-3), 7.05 (6H, m, H-*meta* H-*para* BPh_2), 7.48-7.57 (3H, m, H-12, H-14, H-13), 7.52 (1H, d, *J* = 15.2 Hz, H-8), 7.59-7.62 (2H, m, H-4, H-6), 7.65-7.68 (4H, m, H-*ortho* BPh_2), 7.70-7.77 (2H, m, H-11, H-15), 8.38 (1H, d, *J* = 15.2 Hz, H-9). ^{11}B NMR (86.68 MHz, $CDCl_3$), [δ, ppm]: 9.0 ($h_{1/2}$= 780.1 Hz). MS *m/z* (%): 388 (M^+,7), 311 (100), 233 (1.3), 147(3), 78(3). Anal calcd. for $C_{27}H_{21}BO_2$, C 83.70, H 5.45. Found C 83.52, H 5.45

Boron, diphenyl[1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)-2-propenato-O,O'] (9b). Compound **9b** was prepared from 0.220 g (1.00 mmol) of 2'-hydroxy-4-methoxychalcone and 0.180 g (1.00 mmol) of diphenyl borinic acid, the product was obtained as red crystals, (0.170 g) in 80 %, yield, mp 194-196 °C. IR ν_{max} (KBr) 1625 (C=O), 1554 (C=C), 1515, 1480, 1398, 1323, 1269, 1244, 1130, 1039, 932, 895, 837, 760, 667, 547, 510 cm,$^{-1}$. ^{1}H NMR (270 MHz, $CDCl_3$), [δ, ppm]: 3.88 (3H, s, OCH_3), 6.78 (1H, ddd, *J* = 8.2, 7.1, 1.0 Hz, H–5), 7.00 (2H, d, *J* = 8.9 Hz, H-12, H-14), 7.12 (1H, d, *J* = 8.0 Hz, H-3), 7.18-7.28 (6H, m, H-*meta*, H-*para* BPh_2), 7.39 (1H, d, *J* = 15.2 Hz, H-8), 7.45-7.72 (6H, m, H-4, H-6, H-*ortho* BPh_2), 7.45-7.72 (2H, d, *J* = 8.9 Hz, H11, H15), 8.35 (1H, d, *J* = 15.2 Hz, H-9). ^{11}B NMR (86.68 MHz, $CDCl_3$), [δ, ppm]: 9.5 ($h_{1/2}$ = 346.7 Hz). MS *m/z* (%): 418 (M^+,23.9), 387 (2.4), 341 (100), 311 (6.9), 297 (9.0), 263 (3.2), 233 (7.7), 209 (21.3), 181 (4.2), 165 (2.6), 121 (2.5). Anal calcd. for $C_{28}H_{23}BO_3$ C 80.55 %, H 5.58%. Found C 80.40%, H 5.54%

Boron, diphenyl[1-(2-hydroxyphenyl)-3-(4-chlorophenyl)-2-propenato-O,O'] (**9c**)

Compound **9c** was prepared from 0.250 g (1.00 mmol) of 4-chloro-2'-hydroxychalcone and 0.180 g (1.00 mmol) of diphenyl borinic acid. The product was obtained as red crystals (0.310 g in 78 % yield, mp 217-219 °C. IR õ$_{max}$ (KBr) 3042, 1625 (C=O), 1553 (C=C), 1514, 1411, 1391, 1344, 1317, 1237, 1201, 1148, 1085, 1051, 950, 917, 887, 822, 729, 703, 648, 618, 493 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$), [δ, ppm]: 6.81 (1H, ddd, *J* = 7.7, 7.03, 1.3 Hz, H-5), 7.15 (1H, dd, *J* = 7.9, 0.9 Hz, H-3), 7.21-7.28 (6H, m, H-*meta*, H-*para* BPh_2), 7.47 (1H, d, *J* = 7.0, H-12, H-14), 7.50-7.56 (1H, m, H-4), 7.53 (1H, d, *J* = 15.4 Hz, H-8), 7.58 (2H, d, *J* = 8.4 Hz, H-11, H-15), 7.61-7.65 (4H, m, H-*ortho* BPh_2), 7.67 (1H, d, *J* = 6.6 Hz, H-6), 8.31 (1H, d, *J* = 15.4 Hz, H-9). ^{11}B NMR (399.78 MHz), [δ, ppm]: 8.74 ($h_{1/2}$= 999.4 Hz). MS *m/z* (%): 422 (M^+,69), 387 (29), 345 (100), 309 (49), 267 (43), 233 (65), 209 (70), 178 (59), 147 (24), 78 (26). Anal calcd for $C_{27}H_{21}BO_2$ C 83.75%, H 5.48%. *Found* C 83.52%, H 5.45%

Tables of crystallographic parameters, atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, as well as a listing of structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 297174, 297175, 297176, 297177 and 297178 for **7d, 8b, 8c, 9a,** and **9b**). Copy of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: *deposit@ccdc.cam.ac.uk* or http://www.ccdc.cam.ac.uk).

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